First Enantioselective Total Synthesis of Amphidinolide F

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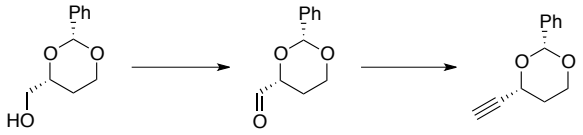
Electronic Supplementary Information: Experimental

General. Infrared spectra were recorded neat unless otherwise indicated and are reported in cm^{-1}. ^1H NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent. ^{13}C NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent.

Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at 120°C or by flame, then cooled under argon. Dry THF and CH_2Cl_2 were obtained via a solvent purification system. All other solvents and commercially available reagents were either purified via literature procedures or used without further purification.

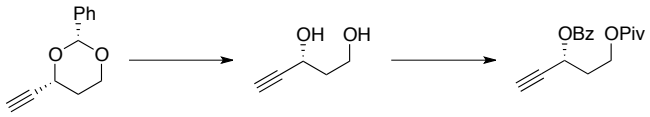


8 **44** **10**

Alkyne 10: To a stirred solution of oxalyl chloride (8.88 g, 6.1 mL, 70.0 mmol) in CH_2Cl_2 (154.0 mL) at -78 ºC was cannulated a solution of DMSO (11.43 g, 10.4 mL, 146.3 mmol) in CH_2Cl_2 (77.0 mL). After 15 min, a solution of alcohol **8**[1] (12.36 g, 63.6 mmol) in CH_2Cl_2 (77.0 mL) was cannulated to it. After 45 min, Et_3N (32.20 g, 44.7 mL, 318.2 mmol) was added. After 10 min, the cooling bath was removed and the reaction was quenched with H_2O (150 mL). The aqueous layer was extracted with CH_2Cl_2 (3 X 300 mL) and the dried ($MgSO_4$) extract was concentrated *in vacuo* to give the crude aldehyde **44**.

To a stirred solution of Ohira-Bestmann reagent **9**[2] (18.30 g, 95.4 mmol) in THF (320.0 mL) at -78 ºC was added NaOMe (191.0 mL, 95.5 mmol, 0.5 M in THF) over 30 min. A solution of crude aldehyde in THF (160.0 mL) was cannulated to it and was slowly warmed to 0 ºC over 2.5 h. The reaction was quenched with sat. aq. NH_4Cl (150 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 X 300 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give alkyne **10** (8.02 g, 42.6 mmol, 67%) as colorless oil: $[\alpha]_D^{23}$ = +29.0 (*c* = 1.02, $CHCl_3$); IR: (neat) 3287, 2967, 2931, 2857, 1455, 1399, 1303, 1119, 1097, 1007, 760 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.52-7.54 (m, 2H), 7.35-7.40 (m, 3H), 5.54 (s, 1H), 4.69 (dt, *J* = 11.5, 2.4 Hz, 1H), 4.30 (ddd, *J* = 11.7, 4.9, 1.3 Hz, 1H), 3.99 (td, *J* = 12.1, 2.5 Hz, 1H), 2.57 (d, *J* = 2.1 Hz, 1H),

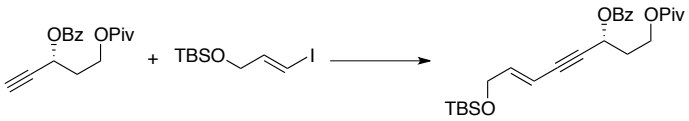
2.27-2.33 (m, 1H), 1.80-1.83 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 137.8, 129.1, 128.3, 126.2, 101.6, 81.6, 73.8, 67.2, 66.6, 31.9; HRMS (EI+) calcd. for $C_{12}H_{12}O_2$ (M+) 188.08373, found 188.08406.



10 **45** **11**

Benzoate Ester 11: To a stirred solution of benzylidine acetal **10** (5.34 g, 28.3 mmol) in MeOH (108.0 mL) at rt was added *p*-TSA•H_2O (54.0 mg, 0.283 mmol). After 3 h, the reaction was quenched with Et_3N (425 mg, 0.60 mL, 4.20 mmol) and the solvent was removed *in vacuo* to give the crude diol **45**.

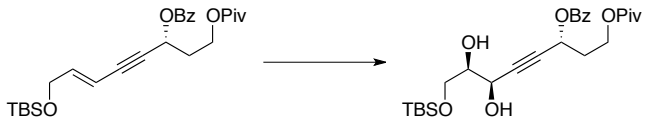
To a stirred solution of the crude diol **45** in CH_2Cl_2 / pyridine (81.0 mL, 2.5:1) at 0 ºC was added pivaloyl chloride (3.76 g, 3.9 mL, 31.2 mmol). After 1.5 h, DMAP (343 mg, 2.83 mmol) followed by benzoyl chloride (4.98 g, 4.1 mL, 35.4 mmol) were added and the reaction was warmed to rt. After 2.5 h, the reaction was quenched with sat. aq. $NaHCO_3$ (75 mL) and the aqueous layer was extracted with Et_2O (3 X 200 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give benzoate ester **11** (4.99 g, 17.3 mmol, 61%) as colorless oil: $[\alpha]_D^{23}$ = +35.3 (*c* = 1.02, $CHCl_3$); IR: (neat) 3291, 3264, 2972, 2933, 2898, 2871, 1727, 1481, 1450, 1271, 1155, 1092, 1065, 1026, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.09 (m, 2H), 7.59 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.44-7.48 (m, 2H), 5.74 (td, *J* = 6.7, 2.1 Hz, 1H), 4.30 (td, *J* = 6.3, 2.0 Hz, 2H), 2.55 (d, *J* = 2.1 Hz, 1H), 2.23-2.38 (m, 2H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 165.2, 133.3, 129.8, 129.5, 128.4, 80.3, 74.4, 61.3, 60.0, 38.7, 33.9, 27.1; HRMS (CI+) calcd. for $C_{17}H_{21}O_4$ (M+H) 289.1440, found 289.1434.



11 **12** **13**

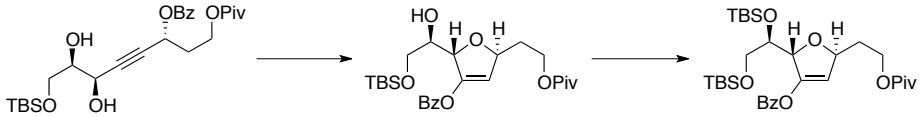
Enyne 13: To a stirred solution of $PdCl_2(PPh_3)_2$ (995 mg, 1.41 mmol) in THF (163.0 mL) at rt was added CuI (810 mg, 4.25 mmol). A solution of alkyne **11** (8.17 g, 28.3 mmol) and vinyl iodide **12**[3] (9.30 g, 31.1 mmol) in THF (163.0 mL) was cannulated to it. Et_3N (43.0 g, 60 mL, 424.9 mmol) was added dropwise over 15 min. After 2.5 h, the reaction was quenched with sat. aq. NH_4Cl (150 mL) and the aqueous layer was extracted with Et_2O (3 X 300 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-15% EtOAc / hexanes, to give enyne **13** (10.11 g, 22.0 mmol, 78%) as colorless oil: $[\alpha]_D^{23}$ = +6.3 (*c* = 1.02, $CHCl_3$); IR: (neat) 2949, 2929, 2851, 1731, 1466, 1267, 1155, 1104, 952, 832, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.10 (m, 2H), 7.59 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.44-7.48 (m, 2H), 6.27 (dt, *J* = 15.7, 4.0 Hz, 1H), 5.88 (dt, *J* = 1.5, 6.6 Hz, 1H), 5.80 (ddt, *J* = 15.7, 2.1, 1.9 Hz, 1H), 4.29 (t, *J* = 6.3 Hz, 2H), 4.23 (dd, *J* = 4.0, 2.1 Hz, 1H),

2.23-2.37 (m, 2H), 1.21 (s, 9H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 165.3, 143.9, 133.2, 129.8, 129.7, 128.4, 107.5, 85.4, 84.4, 62.7, 62.2, 60.3, 38.7, 34.2, 27.1, 25.8, 18.3, -5.4; HRMS (ES+) calcd. for $C_{26}H_{38}O_5SiNa$ (M+Na) 481.2386, found 481.2398.



13 **14**

Diol 14: To a stirred solution of AD-mix-β (30.53 g) in t-BuOH / H_2O (660.0 mL, 1:1) at rt was added $MeSO_2NH_2$ (2.10 g, 22.0 mmol). After 15 min, the mixture was cooled down to 0 ºC and transferred to a flask containing the enyne **13** (10.11 g, 22.0 mmol) at 0 ºC. After 40 h, the reaction was quenched with solid Na_2SO_3 (35.0 g, 277.5 mmol) and the aqueous layer was extracted with EtOAc (4 X 400 mL). The combined organic layer was washed with brine (250 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-40% EtOAc / hexanes, to give diol **14** (9.44 g, 19.2 mmol, 87%) as colorless oil: $[\alpha]_D^{23}$ = +17.0 (*c* = 1.00, $CHCl_3$); IR: (neat) 3460, 2954, 2927, 2856, 1723, 1478, 1265, 1146, 1097, 841, 786, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.08 (m, 2H), 7.61 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.78 (td, *J* = 6.7, 1.3 Hz, 1H), 4.48 (td, *J* = 5.3, 1.4 Hz, 1H), 4.24-4.38 (m, 2H), 3.71-3.85 (m, 3H), 2.81-2.83 (m, 1H), 2.71 (d, *J* = 6.0 Hz, 1H), 2.23-2.38 (m, 1H), 1.22 (s, 9H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 165.2, 133.3, 129.8, 129.5, 128.4, 84.3, 82.7, 73.9, 63.6, 63.4, 61.5, 60.1, 38.7, 34.0, 27.1, 25.8, 18.2, -5.50, -5.54; HRMS (ES+) calcd. for $C_{26}H_{40}O_7SiNa$ (M+Na) 515.2441, found 515.2419.

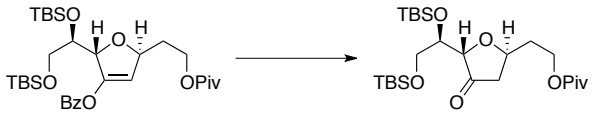


14 **16** **17**

Dihydrofuran 17: To a stirred solution of diol **14** (5.30 g, 10.7 mmol) in dry C_6H_6 (105.0 mL) was added $AgBF_4$ (210 mg, 1.07 mmol) and heated to 80 ºC in dark. After 1.45 h, the reaction was cooled down to rt and the solvent was reduced to 15 mL *in vacuo*. The residue was quickly passed through a plug of silica gel, eluting with 15-20% EtOAc / hexanes, to give the unstable dihydrofuran **16** (3.70 g, 7.51 mmol, 70%) as colorless oil.

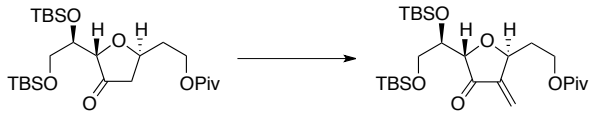
To a stirred solution of alcohol **16** (3.70 mg, 7.51 mmol) in CH_2Cl_2 (83.0 mL) at -78 ºC were added 2,6-lutidine (3.21 g, 3.5 mL, 30.0 mmol) followed by TBSOTf (3.97 g, 3.5 mL, 15.0 mmol). After 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (50 mL) and the aqueous layer was extracted with Et_2O (3 X 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give bis TBS ether **17** (3.87 g, 6.38 mmol, 85%) as colorless oil: $[\alpha]_D^{23}$ = +17.0 (*c* =

1.00, $CHCl_3$); IR: (neat) 2956, 2925, 2886, 2855, 1750, 1731, 1466, 1260, 1155, 1088, 839, 777 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.08-8.09 (m, 2H), 7.63-7.66 (m, 1H), 7.50-7.52 (m, 2H), 6.11 (t, *J* = 1.5 Hz, 1H), 5.07-5.09 (m, 1H), 4.98 (dt, *J* = 5.7, 1.5 Hz, 1H), 4.20-4.27 (m, 2H), 3.85 (td, *J* = 6.6, 1.2 Hz, 1H), 3.78 (dd, *J* = 9.8, 7.5 Hz, 1H), 3.65 (dd, *J* = 9.7, 5.8 Hz, 1H), 1.97-2.04 (m, 2H), 1.22 (s, 9H), 0.94 (s, 9H), 0.84 (s, 9H), 0.114 (s, 3H), 0.112 (s, 3H), 0.05 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.6, 163.1, 144.9, 133.7, 129.9, 129.0, 128.6, 111.8, 81.8, 81.4, 72.9, 64.2, 61.1, 38.7, 35.5, 27.2, 26.0, 25.7, 18.4, 18.0, -4.1, -5.21, -5.24, -5.3; HRMS (ES+) calcd. for $C_{32}H_{55}O_7Si_2$ (M+H) 607.3486, found 607.3475.



17 **7**

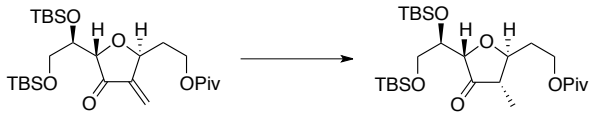
Ketone 7: To a stirred solution of enol benzoate **17** (4.93 g, 8.12 mmol) in Et_2O (86.0 mL) at -78 ºC was added MeLi•LiBr (7.4 mL, 16.2 mmol, 2.2 M in Et_2O) dropwise. After 1.5 h, the reaction was quenched with sat. aq. NH_4Cl (50 mL) and the aqueous layer was extracted with Et_2O (3 X 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give ketone **7** (3.30 g, 6.57 mmol, 81%) as colorless oil: $[\alpha]_D^{23}$ = -56.3 (*c* = 1.03, $CHCl_3$); IR: (neat) 2954, 2927, 2883, 2856, 1761, 1734, 1472, 1358, 1287, 1255, 1157, 1091, 835, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.64-4.71 (m, 1H), 4.25 (t, *J* = 6.3 Hz, 2H), 4.15 (bs, 1H), 4.03 (ddd, *J* = 8.9, 5.3, 1.7 Hz, 1H), 3.74 (t, *J* = 9.2 Hz, 1H), 3.55 (dd, *J* = 9.6, 5.3 Hz, 1H), 2.56 (dd, *J* = 18.0, 6.3 Hz, 1H), 2.25 (ddd, *J* = 18.0, 9.0, 1.0 Hz, 1H), 1.99-2.06 (m, 2H), 1.22 (s, 9H), 0.90 (s, 9H), 0.85 (s, 9H), 0.086 (s, 3H), 0.084 (s, 3H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.8, 178.4, 80.1, 74.9, 74.7, 63.0, 61.0, 43.6, 38.7, 35.5, 27.2, 25.9, 25.7, 18.3, 17.8, -4.4, -5.2, -5.3, -5.4; HRMS (ES+) calcd. for $C_{25}H_{51}O_6Si_2$ (M+H) 503.3224, found 503.3199.



7 **19**

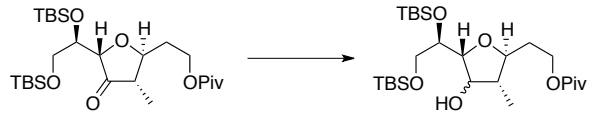
Enone 19: To a stirred solution of ketone **7** (1.91 g, 3.79 mmol) in THF (40.0 mL) at -78 ºC was added LDA[4] (7.6 mL, 7.60 mmol, 1 M in THF / hexanes) and warmed to -50 ºC over 15 min. After 35 min, DMPU (4.86 g, 4.6 mL, 37.9 mmol) was added followed by a solution of Eschenmoser's salt **18** (3.51 g, 18.9 mmol) in THF (40.0 mL). The reaction was slowly warmed to -10 ºC over 50 min and quenched with sat. aq. $NaHCO_3$ (30 mL) and the aqueous layer was extracted with Et_2O (3 X 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 4-10% EtOAc / hexanes, to give enone **19** (1.38 g, 2.68 mmol, 71%) as colorless oil:

$[\alpha]_D^{23}$ = -117.6 (*c* = 1.00, $CHCl_3$); IR: (neat) 2953, 2929, 2883, 2855, 1731, 1645, 1474, 1256, 1158, 1112, 1084, 835, 781 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 6.12 (d, *J* = 2.8 Hz, 1H), 5.34 (d, *J* = 2.4 Hz, 1H), 5.08 (ddd, *J* = 8.6, 5.9, 2.8 Hz, 1H), 4.30-4.33 (m, 2H), 4.29 (d, *J* = 1.3 Hz, 2H), 4.06 (ddd, *J* = 9.0, 5.3, 1.5 Hz, 1H), 3.75 (dd, *J* = 9.4, 9.1 Hz, 1H), 3.54 (dd, *J* = 9.5, 5.2 Hz, 1H), 2.16-2.21 (m, 1H), 1.93-1.98 (m, 1H), 1.22 (s, 9H), 0.91 (s, 9H), 0.78 (s, 9H), 0.093 (s, 3H), 0.090 (s, 3H), 0.04 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 205.6, 178.5, 145.1, 116.8, 80.3, 74.9, 74.7, 63.0, 60.5, 38.7, 34.8, 27.2, 25.9, 25.6, 18.3, 17.8, -4.4, -5.3, -5.4, -5.5; HRMS (ES+) calcd. for $C_{26}H_{50}O_6Si_2Na$ (M+Na) 537.3044, found 537.3033.



19 **20**

Ketone 20: To a stirred solution of enone **19** (1.28 g, 2.48 mmol) in toluene (45.0 mL) was added $(Ph_3P)_3RhCl$ (230 mg, 0.248 mmol) at rt and a hydrogen balloon was fitted to it. After 30 h, the reaction was directly loaded onto column and purified by flash chromatography over silica gel, eluting with 6-10% EtOAc / hexanes, to give ketone **20** (1.14 g, 2.20 mmol, 89%) as colorless oil: $[\alpha]_D^{23}$ = -31.0 (*c* = 1.00, $CHCl_3$); IR: (neat) 2959, 2932, 2878, 2856, 1761, 1728, 1462, 1287, 1255, 1151, 1118, 1069, 841, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.26-4.39 (m, 3H), 4.16 (ddd, *J* = 10.4, 8.6, 3.4 Hz, 1H), 4.07 (ddd, *J* = 9.4, 5.1, 1.6 Hz, 1H), 3.74 (t, *J* = 9.4 Hz, 1H), 3.54 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.08-2.21(m, 2H), 1.93-2.02 (m, 1H), 1.22 (s, 9H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.85 (s, 9H), 0.089 (s, 3H), 0.086 (s, 3H), 0.07 (s, 3H), 0.009 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.0, 178.4, 81.3, 80.0, 74.3, 62.8, 60.9, 48.1, 38.7, 34.2, 27.2, 25.9, 25.8, 18.3, 17.7, 9.6, -4.5, -4.8, -5.3, -5.4; HRMS (ES+) calcd. for $C_{26}H_{53}O_6Si_2$ (M+H) 517.3381, found 517.3359.

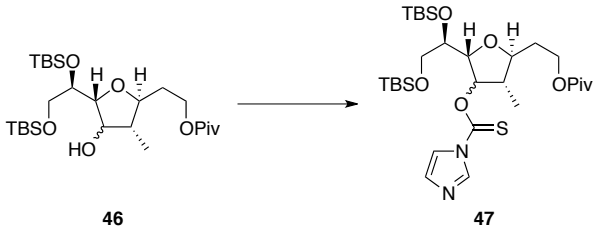


20 **46**

Alcohol 46: To a stirred solution of ketone **20** (1.10 g, 2.12 mmol) in MeOH (40.0 mL) at 40 ºC was added $NaBH_4$ (81.0 mg, 2.12 mmol). After 1 h, another portion of $NaBH_4$ (40.5 g, 1.06 mmol) was added. After additional 30 min, the reaction was quenched with sat. aq. NH_4Cl (20 mL) and the aqueous layer was extracted with EtOAc (4 X 40 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give diastereomeric alcohol **46** (1.01 g, 1.95 mmol, 92%) as colorless oil. Analytically pure samples of the individual diastereomers could be obtained via chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give sequentially the major diastereomer followed by the minor diastereomer. **46** Major isomer: $[\alpha]_D^{23}$ = -44.2 (*c* = 1.03, $CHCl_3$); IR:

(neat) 3493, 2948, 2921, 2856, 1728, 1472, 1391, 1363, 1287, 1282, 1255, 1157, 1097, 841, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.31 (ddd, *J* = 10.8, 7.2, 4.8 Hz, 1H), 4.17 (ddd, *J* = 10.8, 8.2, 6.4 Hz, 1H), 4.12-4.14 (m, 1H), 3.98 (ddd, *J* = 8.2, 8.1, 3.8 Hz, 1H), 3.88 (td, *J* = 9.7, 2.5 Hz, 1H), 3.73 (dd, *J* = 8.0, 2.9 Hz, 1H), 3.56-3.65 (m, 3H), 1.88-1.97 (m, 2H), 1.64-1.72 (m, 1H), 1.21 (s, 9H), 1.06 (d, *J* = 6.8 Hz, 1H), 0.93 (s, 9H), 0.90 (s, 9H), 0.137 (s, 3H), 0.134 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 86.9, 78.9, 74.5, 72.9, 65.9, 62.0, 44.9, 38.7, 33.6, 27.2, 25.8, 18.3, 9.7, -4.4, -4.9, -5.6; HRMS (ES+) calcd. for $C_{26}H_{55}O_6Si_2S$ (M+H) 519.3537, found 519.3512.

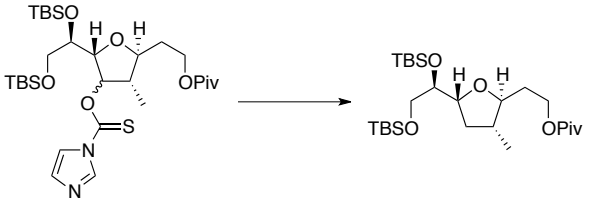
46 Minor Isomer: $[\alpha]_D^{23}$ = -28.9 (*c* = 1.05, $CHCl_3$); IR: (neat) 3504, 2954, 2921, 2883, 2856, 1734, 1712, 1456, 1282, 1255, 1167, 1075, 835, 781 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 4.26 (ddd, *J* = 10.8, 7.0, 4.8 Hz, 1H), 4.15 (ddd, *J* = 10.9, 8.4, 6.2 Hz, 1H), 3.68-3.74 (m, 3H), 3.60-3.66 (m, 4H), 1.87-1.96 (m, 2H), 1.76-1.81 (m, 1H), 1.21 (s, 9H), 1.09 (d, *J* = 6.6 Hz, 1H), 0.92 (s, 9H), 0.90 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.4, 85.4, 79.4, 78.6, 75.0, 65.8, 61.5, 46.1, 38.7, 33.6, 27.2, 25.87, 25.83, 18.29, 18.27, 13.9, -4.5, -4.7, -5.3, -5.4; HRMS (ES+) calcd. for $C_{26}H_{55}O_6Si_2S$ (M+H) 519.3537, found 519.3511.



46 **47**

Thioate 47: To a stirred solution of diastereomeric alcohol **46** (1.01 g, 1.95 mmol) in toluene (24.0 mL) was added thiocarbonyldiimidazole (497 mg, 2.78 mmol) at rt and heated to 100 ºC. After 24 h, the reaction cooled down to rt and the solvent was removed *in vacuo*. The residue was directly loaded onto column and purified by flash chromatography over silica gel, eluting with 10-20% EtOAc / hexanes, to give diastereomeric thioate **47** (1.12 g, 1.78 mmol, 91%) as colorless oil. Analytically pure samples of the individual diastereomers could be obtained via chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give sequentially the major diastereomer followed by the minor diastereomer. **47** Major Isomer: $[\alpha]_D^{23}$ = -18.5 (*c* = 1.00, $CHCl_3$); IR: (neat) 2954, 2927, 2883, 2856, 1761, 1734, 1472, 1358, 1287, 1255, 1157, 1091, 835, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.60 (s. 1H), 7.09 (s, 1H), 6.31 (dd, *J* = 3.4, 3.3 Hz, 1H), 4.29-4.35 (m, 1H), 4.19-4.25 (m, 2H), 3.79-3.88 (m, 2H), 3.59 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.48 (dd, *J* = 10.7, 4.5 Hz, 1H), 2.29-2.38 (m, 1H), 1.93-2.01 (m, 1H), 1.74-1.83 (m, 1H), 1.22 (s, 9H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.84 (s, 9H), 0.11 (s, 3H), 0.07 (s, 3H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.4, 178.3, 136.7, 131.2, 117.6, 85.8, 82.2, 79.9, 73.3, 65.9, 61.4, 45.5, 38.7, 33.3, 27.2, 25.9, 25.8, 18.4, 18.3, 10.5, -4.4, -4.6, -5.4; HRMS (ES+) calcd. for $C_{30}H_{57}O_6N_2Si_2S$ (M+H) 629.3476, found 629.3481.

47 Minor Isomer: $[\alpha]_D^{23}$ = -25.7 (*c* = 1.05, $CHCl_3$); IR: (neat) 2954, 2927, 2879, 2856, 1724, 1472, 1461, 1394, 1331, 1280, 1241, 1225, 1150, 1095, 989, 836, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.63 (s. 1H), 7.06 (t, *J* = 0.8 Hz, 1H), 5.96 (dd, *J* = 5.5, 3.9 Hz, 1H), 4.30 (dd, *J* = 11.3, 5.7 Hz, 1H), 4.26 (t, *J* = 3.3 Hz, 1H), 4.14-4.20 (m, 1H), 3.99-4.03 (m, 1H), 3.91 (td, *J* = 8.6, 3.3 Hz, 1H), 3.70 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.61 (dd, *J* = 9.8, 5.0 Hz, 1H), 2.21-2.30 (m, 1H), 1.92-2.00 (m, 1H), 1.81-1.90 (m, 1H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.21 (s, 9H), 0.91 (s, 9H), 0.87 (s, 9H), 0.17 (s, 3H), 0.13 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.9, 178.4, 136.9, 130.9, 117.9, 90.7, 82.1, 81.9, 74.5, 63.9, 61.4, 46.7, 38.7, 33.2, 27.2, 25.9, 18.3, 18.0, 14.4, -4.1, -4.3, -5.33, -5.34; HRMS (ES+) calcd. for $C_{30}H_{57}O_6N_2Si_2S$ (M+H) 629.3476, found 629.3475.



47 **21**

Tetrahydrofuran 21: To a stirred solution of diastereomeric thioate **47** (1.12 g, 1.78 mmol) in deoxygenated toluene (96.0 mL) at rt was added AIBN (29.3 mg, 0.178 mmol) and heated to 95 ºC. Bu_3SnH (1.04 g, 0.96 mL, 3.56 mmol) was added dropwise over 45 min. After another 45 min, the reaction was cooled down to rt and the solvent was removed *in vacuo*. The residue was directly loaded onto the column and purified by flash chromatography over silica gel, eluting with 3-6% EtOAc / hexanes, to give tetrahydrofuran **21** (859 mg, 1.71 mmol, 96%) as colorless oil: $[\alpha]_D^{23}$ = -35.0 (*c* = 1.03, $CHCl_3$); IR: (neat) 2958, 2926, 2886, 2854, 1733, 1473, 1457, 1361, 1282, 1250, 1154, 1106, 1074, 938, 835, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.26 (ddd, *J* = 10.8, 7.1, 5.1 Hz, 1H), 4.14 (ddd, *J* = 10.8, 7.7, 6.6 Hz, 1H), 4.00-4.05 (m, 1H), 3.63-3.68 (m, 1H), 3.53-3.59 (m, 2H), 3.44 (td, *J* = 8.9, 2.9 Hz, 1H), 2.04 (dt, *J* = 12.0, 6.6 Hz, 1H), 1.80-1.94 (m, 2H), 1.64-1.73 (m, 1H), 1.52 (td, *J* = 11.6, 9.7 Hz, 1H), 1.20 (s, 9H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.908 (s, 9H), 0.904 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.068 (s, 3H), 0.063 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 81.6, 78.5, 75.7, 65.1, 62.1, 40.1, 38.6, 36.7, 33.1, 27.2, 25.9, 18.4, 18.2, 15.9, -4.3, -4.6, -5.3; HRMS (ES+) calcd. for $C_{26}H_{55}O_5Si_2$ (M+H) 503.3588, found 503.3586.

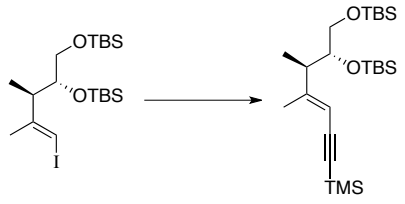
21 **48**

Alcohol 48: To a stirred solution of bis-TBS ether **21** (501 mg, 0.997 mmol) in THF (10.0 mL) at 0 ºC was added a stock solution of HF•pyr[5] (5.5 mL) over 1 h. After 24 h, the reaction quenched with sat. aq. $NaHCO_3$ (30 mL) and the aqueous layer was extracted with EtOAc / Et_2O (2:1, 3 X 60 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography

over silica gel, eluting with 10-30% EtOAc / hexanes, to give alcohol **48** (322 mg, 0.828 mmol, 83%) as colorless oil: $[\alpha]_D^{23}$ = -31.3 (*c* = 1.04, $CHCl_3$); IR: (neat) 3494, 2957, 2930, 2882, 2855, 1730, 1477, 1461, 1284, 1252, 1153, 1102, 1055, 940, 838, 778 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 4.27 (ddd, *J* = 10.9, 7.1, 4.9 Hz, 1H), 4.14 (ddd, *J* = 10.9, 8.2, 6.3 Hz, 1H), 4.06 (dt, *J* = 9.7, 6.0 Hz, 1H), 3.65-3.69 (m, 2H), 3.53-3.57 (m, 1H), 3.48 (td, *J* = 6.3, 2.8 Hz, 1H), 2.37-2.39 (m, 1H), 2.09 (dt, *J* = 12.1, 6.5 Hz, 1H), 1.91-1.96 (m, 1H), 1.86-1.91 (m, 1H), 1.68-1.72 (m, 1H), 1.43 (td, *J* = 11.5, 10.1 Hz, 1H), 1.21 (s, 9H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 81.8, 79.8, 74.7, 64.2, 61.8, 39.9, 38.6, 36.8, 33.0, 27.1, 25.9, 18.2, 15.9, -4.4, -4.8; HRMS (ES+) calcd. for $C_{20}H_{40}O_5Si_2Na$ (M+Na) 411.2543, found 411.2542.

48 **22**

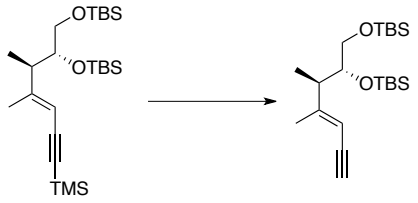
Aldehyde 22: To a stirred solution of alcohol **48** (322 mg, 0.828 mmol) in CH_2Cl_2 (11.0 mL) at 0 ºC was added pyridine (786 mg, 0.81 mL, 9.94 mmol) followed by Dess-Martin periodinane (1.40 g, 3.31 mmol) in one portion. After 30 min, the reaction was warmed to rt. After another 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (25 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-15% EtOAc / hexanes, to give aldehyde **22** (279 mg, 0.721 mmol, 87%) as colorless oil: $[\alpha]_D^{23}$ = -72.6 (*c* = 1.04, $CHCl_3$); IR: (neat) 2953, 2925, 2859, 1731, 1478, 1454, 1283, 1252, 1155, 1112, 940, 839, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 1.4 Hz, 1H), 4.29 (ddd, *J* = 9.2, 6.6, 4.0 Hz, 1H), 4.23 (ddd, *J* = 10.9, 7.1, 5.2 Hz, 1H), 4.13 (ddd, *J* = 10.9, 7.8, 6.5 Hz, 1H), 3.95 (dd, *J* = 4.0, 1.4 Hz, 1H), 3.53 (td, *J* = 9.0, 3.0 Hz, 1H), 2.13 (dt, *J* = 12.1, 6.8 Hz, 1H), 1.83-1.96 (m, 2H), 1.59-1.73 (m, 2H), 1.20 (s, 9H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.95 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 203.8, 178.5, 82.6, 80.0, 78.5, 61.8, 39.7, 38.7, 36.1, 32.8, 27.2, 25.8, 18.3, 15.7, -4.6, -4.9; HRMS (CI+) calcd. for $C_{20}H_{39}O_5Si$ (M+H) 387.2567, found 387.2560.



24 **49**

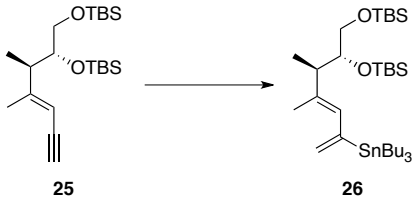
TMS Enyne 49: To a stirred solution of $PdCl_2(PPh_3)_2$ (71.0 mg, 0.101 mmol) in THF (13.0 mL) at rt was added CuI (57.8 mg, 0.303 mmol) followed by a solution of TMS acetylene (993 mg, 1.45 mL, 10.1 mmol) and vinyl iodide **24**[6] (980 mg, 2.02 mmol) in THF (13.0 mL). Et_3N (3.07 g, 4.2 mL, 30.3 mmol) was added dropwise over 15 min. After 1 h, the reaction was quenched with sat. aq.

NH_4Cl (30 mL) and the aqueous layer was extracted with Et_2O (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-2% EtOAc / hexanes, to give TMS enyne **49** (718 mg, 1.57 mmol, 78%) as colorless oil: $[\alpha]_D^{23}$ = +27.5 (*c* = 1.04, $CHCl_3$); IR: (neat) 2956, 2925, 2898, 2851, 2135, 1478, 1260, 1088, 832, 777 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 5.40 (br s, 1H), 3.64 (ddd, *J* = 6.7, 5.2, 4.2 Hz, 1H), 3.46 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.42 (dd, *J* = 10.0, 6.8 Hz, 1H), 2.50 (qd, *J* = 7.0, 4.2 Hz, 1H), 1.94 (d, *J* = 1.1 Hz, 3H), 1.07 (d, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.90 (S, 9H), 0.21 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.4, 106.7, 103.8, 96.7, 76.3, 65.2, 44.0, 26.0, 25.9, 18.3, 18.2, 18.1, 15.8, 0.19, -4.1, -4.9, -5.3, -5.4.



49 **25**

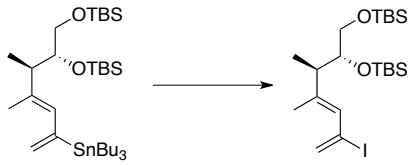
Enyne 25: To a stirred solution of TMS enyne **49** (718 mg, 1.57 mmol) in MeOH (8.0 mL) at rt was added finely powdered K_2CO_3 (165 mg, 1.19 mmol). After 2 h, the solvent was removed *in vacuo* and the residue was dissolved in Et_2O / H_2O (3:1, 100 mL). The aqueous layer was extracted with Et_2O (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-2% EtOAc / hexanes, to give enyne **25** (574 mg, 1.49 mmol, 95%) as colorless oil: $[\alpha]_D^{23}$ = +11.4 (*c* = 1.01, $CHCl_3$); IR: (neat) 3312, 2952, 2925, 2885, 2857, 1474, 1466, 1387, 1356, 1253, 1119, 1099, 1063, 1012, 834, 810, 779 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (bs, 1H), 3.64 (dt, *J* = 6.5, 4.5 Hz, 1H), 3.48 (dd, *J* = 10.0, 5.1 Hz, 1H), 3.41 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.05 (d, *J* = 2.0 Hz, 1H), 2.50-2.56 (m, 1H), 1.94 (d, *J* = 0.6 Hz, 3H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.90 (s, 9H), 0.077 (s, 3H), 0.070 (s, 3H), 0.059 (s, 3H), 0.056 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 105.5, 82.0, 79.7, 76.2, 65.2, 43.9, 25.9, 25.8, 18.2, 18.0, 15.8, -4.2, -4.9, -5.3, -5.4; HRMS (ES+) calcd. for $C_{21}H_{43}O_2Si_2$ (M+H) 383.2802, found 383.2819.



25 **26**

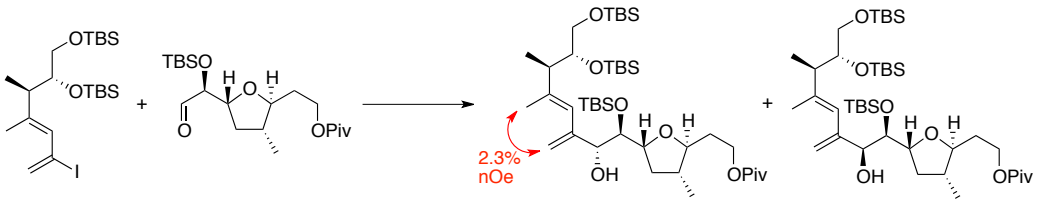
Dienyl Stannane 26: To a stirred solution of enyne **25** (697 mg, 1.82 mmol) in degassed THF (88.0 mL) at 0 ºC was added $PdCl_2(PPh_3)_2$ (63.9 mg, 0.091 mmol) followed by Bu_3SnH (1.06 g, 0.98 mL, 3.64 mmol) over 2 min. After 20 min, the reaction was passed through a plug of silica gel eluting with hexanes (200 mL) buffered with 1% Et_3N. The solvent was removed *in vacuo* and the

residue was purified by flash chromatography over silica gel, eluting with pentane buffered with 1% Et_3N, to give dienyl stannane **26** (884 mg, 1.31 mmol, 72%) as colorless oil: $[\alpha]_D^{23}$ = +11.8 (*c* = 1.00, $CHCl_3$); IR: (neat) 2954, 2923, 2885, 2855, 1472, 1466, 1365, 1254, 1119, 1095, 1063, 1003, 956, 833, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (s, 1H), 5.65 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.32 (dd, *J* = 3.5, 1.2 Hz, 1H), 3.69 (td, *J* = 5.8, 3.8 Hz, 1H), 3.53 (dd, *J* = 10.0, 5.8 Hz, 1H), 3.47 (dd, *J* = 10.0, 5.8 Hz, 1H), 2.42 (qd, *J* = 7.2, 3.8 Hz, 1H), 1.71 (d, *J* = 1.1 Hz, 3H), 1.46-1.56 (m, 6H), 1.29-1.38 (m, 6H), 1.09 (d, *J* = 7.2 Hz, 3H), 0.90-0.95 (m, 33H), 0.098 (s, 3H), 0.094 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 135.2, 131.8, 126.6, 76.8, 65.6, 45.0, 29.0, 27.3, 26.0, 25.9, 18.3, 18.1, 16.0, 15.9, 13.6, 9.9, -4.1, -4.8, -5.3; HRMS (ES+) calcd. for $C_{33}H_{70}O_2Si_2SnNa$ (M+Na) 697.3834, found 697.3802.



26 **27**

Dienyl Iodide 27: To a stirred solution of dienyl stannane **26** (884 mg, 1.31 mmol) in CH_2Cl_2 (100.0 mL) at 0 ºC was cannulated a solution of I_2 (665 mg, 2.62 mmol) in CH_2Cl_2 (50.0 mL). After 15 min, the reaction was quenched with 10% aq. $Na_2S_2O_3$ (50 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with pentane with 1% Et_3N, to give dienyl iodide **27** (469 mg, 0.918 mmol, 70%) as colorless oil: $[\alpha]_D^{23}$ = +7.5 (*c* = 1.01, $CHCl_3$); IR: (neat) 2954, 2927, 2883, 2855, 1603, 1472, 1254, 1123, 1095, 1063, 833, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 5.93 (s, 1H), 5.92 (t, *J* = 1.3 Hz, 1H), 3.68 (td, *J* = 5.8, 4.3 Hz, 1H), 3.42-3.49 (m, 2H), 2.43 (qd, *J* = 7.1, 4.3 Hz, 1H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.90 (s, 9H), 0.08 (s, 3H), 0.079 (s, 3H), 0.071 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 131.1, 127.4, 104.0, 76.5, 65.2, 44.1, 26.0, 25.9, 18.3, 18.1, 16.2, 15.7, -4.1, -4.8, -5.2, -5.3; HRMS (ES+) calcd. for $C_{21}H_{44}IO_2Si_2$ (M+H) 511.1925, found 511.1914.



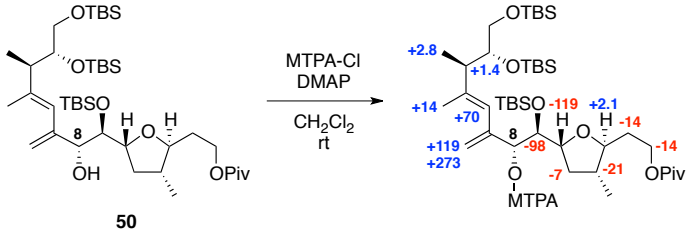
27 **22** **50** **51**

Alcohols 50 and 51: To a stirred solution of dienyl iodide **27** (442 mg, 0.865 mmol) in THF (7.5 mL) at -78 ºC was added n-BuLi (0.90 mL, 1.44 mmol, 2.5 M in hexane). After 45 min, a solution of aldehyde **22** (279 mg, 0.721 mmol) in THF (7.5 mL, pre-cooled to -78 ºC) was cannulated to it. After 1 h, the reaction

was quenched with sat. aq. NH_4Cl (25 mL) and the aqueous layer was extracted with Et_2O (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 4-10% EtOAc / hexanes, to give the diastereomeric alcohols **50** and **51** (345 mg, 0.447 mmol, 62%) as colorless oils. Analytically pure samples of the individual diastereomers could be obtained via chromatography over silica gel, eluting with 4-10% EtOAc / hexanes, to give sequentially the major diastereomer **50** followed by the minor diastereomer **51**. Major Isomer (**50**): $[\alpha]_D^{23}$ = +28.3 (*c* = 1.03, $CHCl_3$); IR: (neat) 3478, 2956, 2925, 2883, 2859, 1727, 1474, 1462, 1287, 1158, 1092, 835, 773 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 5.66 (s, 1H), 5.52 (s, 1H), 5.04 (s, 1H), 4.25-4.29 (m, 1H), 4.22 (bd, *J* = 5.88 Hz, 1H), 4.13-4.17 (m, 2H), 4.09 (d, *J* = 7.0 Hz, 1H), 3.67 (td, *J* = 6.0, 4.0 Hz, 1H), 3.61 (t, *J* = 2.8 Hz, 1H), 3.58 (td, *J* = 9.1, 2.8 Hz, 1H), 3.45-3.49 (m, 2H), 2.49 (qd, *J* = 7.1, 4.0 Hz, 1H), 1.98 (dt, *J* = 11.8, 6.8 Hz, 1H), 1.90-1.95 (m, 1H), 1.78 (s, 3H), 1.66-1.72 (m, 1H), 1.64 (td, *J* = 11.4, 9.5 Hz, 1H), 1.22 (s, 9H), 1.08 (d, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.95 (s, 9H), 0.914 (s, 9H), 0.910 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.5, 145.4, 141.5, 124.8, 113.8, 82.7, 78.1, 78.0, 76.6, 74.1, 65.4, 61.8, 45.3, 39.4, 38.7, 37.0, 32.8, 27.2, 26.0, 25.98, 25.94, 18.3, 18.2, 18.1, 16.3, 16.1, 15.6, -4.1, -4.3, 4.5, -4.8, -5.31, -5.37; HRMS (ES+) calcd. for $C_{41}H_{82}O_7Si_3Na$ (M+Na) 793.5266, found 793.5294.

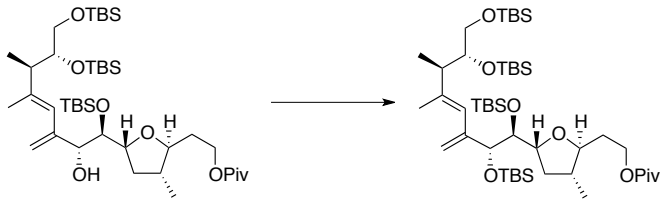
Minor isomer (**51**): ^1H NMR (400 MHz, $CDCl_3$) δ 5.65 (s, 1H), 5.34 (t, *J* = 1.6 Hz, 1H), 5.02 (s, 1H), 4.27(ddd, *J* = 10.8, 7.2, 4.9 Hz, 1H), 4.13 (ddd, *J* = 10.8, 8.0, 6.5 Hz, 1H), 4.04 (ddd, *J* = 9.8, 7.3, 6.0 Hz, 1H), 3.91 (d, *J* = 9.3 Hz, 1H), 3.69 (td, *J* = 5.7, 4.1 Hz, 1H), 3.57 (dd, *J* = 7.4, 1.3 Hz, 1H), 3.44-3.53 (m, 3H), 2.91 (d, *J* = 9.3 Hz, 1H), 2.46 (qd, *J* = 7.1, 4.0 Hz, 1H), 2.15 (dt, *J* = 11.9, 6.2 Hz, 1H), 1.87-1.96 (m, 2H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.66-1.75 (m, 1H), 1.27-1.37 (m, 1H), 1.21 (s, 9H), 1.10 (d, *J* = 7.1 Hz, 3H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 18H), 0.89 (s, 9H), 0.12 (s, 3H), 0.08 (s, 6H), 0.05 (s, 6H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 145.8, 142.2, 123.7, 112.9, 81.6, 80.2, 76.0, 73.2, 65.5, 61.8, 45.3, 39.9, 38.6, 37.9, 33.2, 27.2, 26.06, 26.01, 25.9, 18.4, 18.3, 18.1, 17.6, 16.1, 16.0, -3.9, -4.1, -4.7, -4.8, -5.2, -5.3.

Mosher ester determination of stereochemistry in compound 50[7]



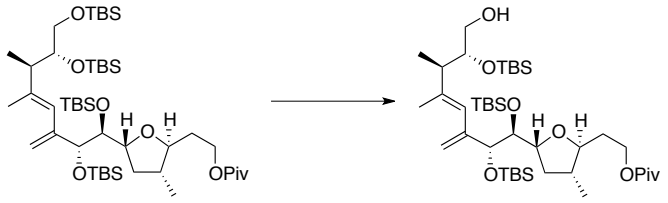
50

^1H NMR shift differences [(S)-MTPA-(R)-MTPA] reported in Hertz ($CDCl_3$, 700 MHz)



50 **23**

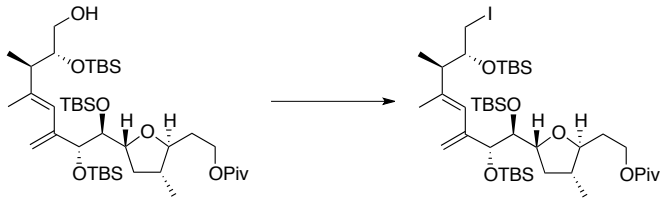
TBS Ether 23: To a stirred solution of alcohol **50** (195 mg, 0.252 mmol) in CH_2Cl_2 (6.5 mL) at -78 ºC were added 2,6-lutidine (103 mg, 118 µL, 1.01 mmol) followed by TBSOTf (133 mg, 117 µL, 0.505 mmol). After 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (15 mL) and the aqueous layer was extracted with Et_2O (3 X 40 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 2-5% EtOAc / hexanes, to give the TBS ether **23** (195 mg, 0.220 mmol, 87%) as colorless oil: $[\alpha]_D^{23}$ = +34.6 (*c* = 1.04, $CHCl_3$); IR: (neat) 2956, 2925, 2883, 2859, 1731, 1470, 1462, 1256, 1158, 1100, 1081, 832, 773 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 5.66 (s, 1H), 5.33 (t, *J* = 2.0 Hz, 1H), 4.96 (s, 1H), 4.27 (ddd, *J* = 10.8, 7.2, 4.8 Hz, 1H), 4.11-4.15 (m, 2H), 3.97 (ddd, *J* = 9.8, 7.2, 6.2 Hz, 1H), 3.65-3.67 (m, 1H), 3.54 (dd, *J* = 7.3, 2.3 Hz, 1H), 3.43-3.47 (m, 2H), 3.31 (td, *J* = 9.2, 2.6 Hz, 1H), 2.51 (qd, *J* = 7.1, 4.0 Hz, 1H), 2.07 (dt, *J* = 12.3, 6.4 Hz, 1H), 1.87-1.92 (m, 1H), 1.76-1.83 (m, 1H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.64-1.69 (m, 1H), 1.21-1.27 (m, 1H), 1.20 (s, 9H), 1.09 (d, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.917 (s, 9H), 0.915 (s, 9H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.085 (s, 3H), 0.081 (s, 3H), 0.05 (s, 3H), 0.04 (s, 6H), 0.02 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.4, 145.2, 140.9, 125.7, 114.3, 80.2, 79.5, 79.0, 78.5, 65.4, 62.1, 45.6, 40.3, 38.7, 37.9, 33.0, 27.2, 26.1, 26.0, 25.9, 18.43, 18.40, 18.3, 18.1, 16.06, 16.00, 15.9, -4.1, -4.2, -4.3, -4.7, -4.83, -4.85, -5.3, -5.4; HRMS (TOF+) calcd. for $C_{47}H_{96}O_7Si_4Na$ (M+Na) 907.6125, found 907.6106.



23 **52**

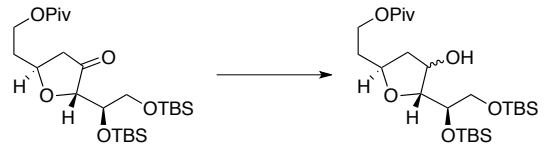
Alcohol 52: To a stirred solution of TBS ether **23** (264 mg, 0.298 mmol) in THF (3.3 mL) at 0 ºC was added a stock solution of HF•pyr (1.2 mL).[5] After 32 h, the reaction was quenched with sat. aq. $NaHCO_3$ (3.0 mL) and the aqueous layer was extracted with EtOAc / Et_2O (1:1, 4 X 30 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 6-12% EtOAc / hexanes, to give alcohol **52** (186 mg, 0.241 mmol, 81%) as colorless oil: $[\alpha]_D^{23}$ = +22.5 (*c* = 1.01, $CHCl_3$); IR: (neat) 3420, 2956, 2925, 2879, 2855, 1727, 1470, 1454, 1283, 1248, 1162, 1069, 839, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1H), 5.31 (t, *J* = 1.7 Hz, 1H), 4.97 (s, 1H), 4.26 (ddd, *J* = 10.8, 7.2, 4.8 Hz, 1H), 4.10-4.16 (m, 2H), 3.95 (ddd, *J* = 9.9, 7.0, 6.1

Hz, 1H), 3.78 (dt, *J* = 5.5, 4.8 Hz, 1H), 3.53-3.57 (m, 3H), 3.35 (td, *J* = 9.0, 2.8 Hz, 1H), 2.46-2.53 (m, 1H), 2.06 (dt, *J* = 12.1, 6.3 Hz, 1H), 1.85-1.93 (m, 1H), 1.80 (d, *J* = 1.1 Hz, 3H), 1.62-1.75 (m, 2H), 1.21-1.30 (m, 1H), 1.20 (s, 9H), 1.07 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.918 (s, 9H), 0.915 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 145.1, 140.6, 125.4, 114.8, 80.5, 79.4, 78.9, 78.6, 75.2, 64.4, 62.0, 46.4, 40.3, 38.6, 38.1, 33.1, 27.2, 26.1, 25.9, 25.8, 18.4, 18.3, 18.1, 16.0, 14.7, -4.2, -4.3, -4.6, -4.7; HRMS (ES+) calcd. for $C_{41}H_{82}O_7Si_3Na$ (M+Na) 793.5266, found 793.5232.



52 **6**

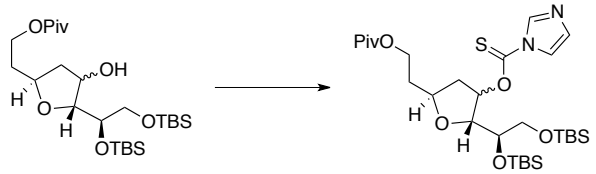
Iodide 6: To a stirred solution of alcohol **52** (186 mg, 0.241 mmol) in benzene (6.0 mL) at 5 ºC were sequentially added imidazole (82.1 mg, 1.20 mmol), PPh_3 (190 mg, 0.723 mmol) and I_2 (153 mg, 0.602 mmol). After 10 min, the reaction was warmed to rt and wrapped with aluminum foil. After 1 h, the reaction was quenched with sat. aq. $Na_2S_2O_3$ (20 mL) and the aqueous layer was extracted with Et_2O (3 X 40 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 2-5% EtOAc / hexanes, to give iodide **6** (191 mg, 0.216 mmol, 90%) as colorless oil: $[\alpha]_D^{23}$ = +27.6 (*c* = 1.02, $CHCl_3$); IR: (neat) 2955, 2923, 2853, 1730, 1472, 1460, 1253, 1159, 1073, 1037, 834, 775 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.82 (s, 1H), 5.34 (dd, *J* = 2.1, 1.4 Hz, 1H), 4.99 (s, 1H), 4.27 (ddd, *J* = 10.8, 7.2, 4.8 Hz, 1H), 4.12-4.16 (m, 2H), 3.98 (ddd, *J* = 9.9, 6.8, 6.1 Hz, 1H), 3.69 (dt, *J* = 6.7, 4.4 Hz, 1H), 3.56 (dd, *J* = 6.9, 3.1 Hz, 1H), 3.37 (td, *J* = 9.1, 2.8 Hz, 1H), 3.18 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.15 (dd, *J* = 10.0, 6.8 Hz, 1H), 2.67 (qd, *J* = 6.9, 4.7 Hz, 1H), 2.06 (dt, *J* = 12.2, 6.2 Hz, 1H), 1.88-1.92 (m, 1H), 1.80-1.85 (m, 1H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.65-1.70 (m, 1H), 1.27-1.32 (m, 1H), 1.21 (s, 9H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.93 (s, 9H), 0.92 (s, 18H), 0.14 (s, 3H), 0.108 (s, 3H), 0.106 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.4, 145.0, 139.5, 126.3, 115.2, 80.5, 79.2, 78.6, 78.5, 74.9, 62.1, 47.1, 40.3, 38.7, 38.1, 33.2, 27.2, 26.2, 26.0, 25.8, 18.4, 18.3, 18.0, 16.1, 16.0, 15.0, 11.4, -4.0, -4.1, -4.2, -4.73, -4.75; HRMS (ES+) calcd. for $C_{41}H_{81}O_6Si_3INa$ (M+Na) 903.4283, found 903.4263.



7 53

Alcohol 53: To a stirred solution of ketone **7** (3.30 g, 6.57 mmol) in MeOH (83.0 mL) at rt was added $NaBH_4$ (249 mg, 6.57 mmol). After 1 h, the reaction was quenched with sat. aq. NH_4Cl (50 mL) and the MeOH was removed *in vacuo*. EtOAc (150 mL) was added to the residue and the aqueous layer was extracted with EtOAc (3 X 150 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-20% EtOAc / hexanes, to give diastereomeric alcohol **53** (3.17 g, 6.27 mmol, 95%) as colorless oil. Analytically pure samples of the individual diastereomers could be obtained via chromatography over silica gel, eluting with 10-20% EtOAc / hexanes, to give sequentially the major diastereomer followed by the minor diastereomer. **53** Major Isomer: $[\alpha]_D^{23}$ = -30.8 (*c* = 1.00, $CHCl_3$); IR: (neat) 3490, 2960, 2929, 2855, 1731, 1470, 1287, 1260, 1158, 1092, 835, 781 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 4.40 (bs, 1H), 4.34-4.38 (m, 1H), 4.24 (ddd, *J* = 10.9, 6.2, 5.4 Hz, 1H), 4.16 (ddd, *J* = 10.9, 8.3, 6.1 Hz, 1H), 3.97 (ddd, *J* = 8.8, 8.3, 3.8 Hz, 1H), 3.70 (dd, *J* = 8.0, 3.1 Hz, 1H), 3.58-3.65 (m, 2H), 2.15 (dd, *J* = 12.9, 5.2 Hz, 1H), 1.81-1.90 (m, 2H), 1.70 (ddt, *J* = 1.9, 4.6, 11.6 Hz, 1H), 1.21 (s, 9H), 0.93 (s, 9H), 0.90 (s, 9H), 0.139 (s, 6H), 0.133 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.5, 87.2, 74.0, 72.7, 65.8, 61.9, 41.2, 38.7, 35.0, 27.2, 25.8, 18.3, 18.2, -4.4, -4.9, -5.68, -5.69; HRMS (ES+) calcd. for $C_{25}H_{53}O_6Si_2$ (M+H) 505.3381, found 505.3394.

53 Minor Isomer: $[\alpha]_D^{23}$ = -28.7 (*c* = 1.01, $CHCl_3$); IR: (neat) 3490, 2960, 2925, 2859, 1734, 1715, 1474, 1256, 1155, 1092, 839, 777 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 4.24-4.28 (m, 1H), 4.19-4.22 (m, 1H), 4.10-4.17 (m, 2H), 3.68-3.70 (m, 3H), 3.64 (dd, *J* = 12.0, 5.9 Hz, 1H), 3.39 (m, 1H) 2.42 (ddd, *J* = 12.0, 7.0, 6.2 Hz, 1H), 1.93-1.97 (m, 1H), 1.87-1.92 (m, 1H), 1.72 (dt, *J* = 8.8, 12.1 Hz, 1H), 1.21 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.127 (s, 3H), 0.124 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.5, 86.1, 74.7, 74.1, 72.9, 65.5, 61.6, 40.4, 38.7, 35.4, 27.2, 25.8, 18.28, 18.24, -4.5, -4.7, -5.3, -5.4; HRMS (ES+) calcd. for $C_{25}H_{35}O_6Si_2$ (M+H) 505.3381, found 505.3394.

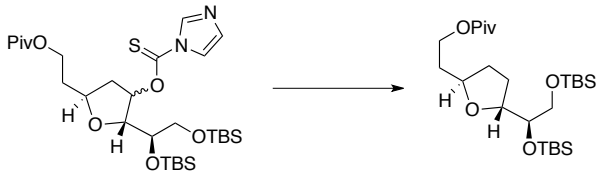


53 54

Thioate 54: To a stirred solution of diastereomeric alcohol **53** (3.17 g, 6.27 mmol) in deoxygenated toluene (75.0 mL) at rt was added thiocarbonyl-diimidazole (3.36 g, 18.8 mmol) heated to 100 ºC. After 20 h, the solvent was removed *in vacuo*. The residue was directly loaded onto column and purified by

flash chromatography over silica gel, eluting with 15-30% EtOAc / hexanes, to give diastereomeric thioate **54** (3.82 g, 6.21 mmol, 99%) as colorless oil. Analytically pure samples of the individual diastereomers could be obtained via chromatography over silica gel, eluting with 15-30% EtOAc / hexanes, to give sequentially the major diastereomer followed by the minor diastereomer. **54** Major Isomer: $[\alpha]_D^{23}$ = -14.5 (*c* = 1.02, $CHCl_3$); IR: (neat) 2953, 2929, 2894, 2855, 1727, 1474, 1392, 1283, 1244, 1151, 1104, 832, 781 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.60 (s, 1H), 7.09 (dd, *J* = 1.6, 0.8 Hz, 1H), 5.97 (t, *J* = 3.3 Hz, 1H), 4.30-4.34 (m, 1H), 4.25 (ddd, *J* = 11.0, 6.3, 5.3 Hz, 1H), 4.19 (ddd, *J* = 11.0, 8.1, 6.2 Hz, 1H), 4.13 (dd, *J* = 7.8, 3.1 Hz, 1H), 3.95 (dt, *J* = 7.8, 4.5 Hz, 1H), 3.57-3.61 (m, 2H), 2.52 (ddd, *J* = 14.3, 6.2, 0.9 Hz, 1H), 2.06 (ddd, *J* = 14.3, 9.1, 4.6 Hz, 1H), 1.87-1.94 (m, 2H), 1.21 (s, 9H), 0.92 (s, 9H), 0.83 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H), -0.02 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 182.6, 178.4, 136.6, 131.0, 117.7, 84.4, 82.2, 73.8, 72.6, 66.0, 61.5, 39.3, 38.7, 35.0, 27.2, 25.9, 25.8, 18.5, 18.3, -4.4, -4.6, -5.4, -5.5; HRMS (ES+) calcd. for $C_{29}H_{55}O_6N_2Si_2S$ (M+H) 615.3319, found 615.3309.

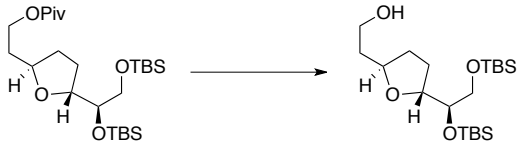
54 Minor Isomer: $[\alpha]_D^{23}$ = -21.4 (*c* = 1.04, $CHCl_3$); IR: (neat) 2956, 2929, 2883, 2855, 1727, 1470, 1396, 1337, 1287, 1244, 1228, 1158, 1088, 835, 773 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.64 (t, *J* = 1.4 Hz, 1H), 7.09 (dd, *J* = 1.6, 0.8 Hz, 1H), 6.00 (ddd, *J* = 7.3, 2.8, 2.1 Hz, 1H), 4.44 (t, *J* = 2.1 Hz, 1H), 4.38-4.42 (m, 1H), 4.23 (ddd, *J* = 11.1, 6.1, 5.6 Hz, 1H), 4.19 (ddd, J = 11.1, 8.1, 5.8 Hz, 1H), 3.93 (ddd, *J* = 7.7, 4.8, 2.8 Hz, 1H), 3.71 (dd, *J* = 9.8, 7.8 Hz, 1H), 3.58 (dd, *J* = 9.8, 4.9 Hz, 1H), 2.75 (dt, *J* = 14.0, 7.4 Hz, 1H), 1.96-2.01 (m, 1H), 1.89-1.94 (m, 2H), 1.21 (s, 9H), 0.90 (s, 18H), 0.15 (s, 3H), 0.13 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 183.5, 178.5, 136.9, 130.9, 117.8, 86.9, 83.2, 74.3, 63.5, 61.6, 38.7, 38.5, 35.4, 27.2, 25.9, 18.3, 17.9, -4.2, -4.7, -5.32, -5.35; HRMS (ES+) calcd. for $C_{29}H_{55}O_6N_2Si_2S$ (M+H) 615.3319, found 615.3298.



54 **28**

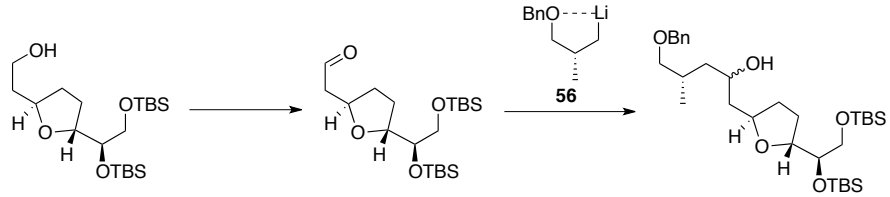
Tetrahydrofuran 28: To a stirred solution of thioate **54** (3.82 g, 6.21 mmol) in deoxygenated toluene (340.0 mL) at rt was added AIBN (102 mg, 0.621 mmol) and heated to 95 ºC. Bu_3SnH (3.61 g, 3.4 mL, 12.4 mmol) was added dropwise over 45 min. After additional 1.5 h, the reaction was cooled down to rt and the solvent was removed *in vacuo*. The residue was directly loaded onto the column and purified by flash chromatography over silica gel, eluting with 3-6% EtOAc / hexanes, to give tetrahydrofuran **28** (2.76 g, 5.65 mmol, 91%) as colorless oil: $[\alpha]_D^{23}$ = -21.6 (*c* = 1.02, $CHCl_3$); IR: (neat) 2958, 2931, 2859, 1734, 1474, 1288, 1255, 1156, 1097, 836, 779 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.12-4.22 (m, 2H), 3.98-4.10 (m, 2H), 3.67(dd, *J* = 11.6, 7.8 Hz, 1H), 3.55-3.59 (m,

2H), 2.02-2.09 (m, 1H), 1.74-1.98 (m, 4H), 1.51 (ddd, *J* = 18.2, 11.7, 8.6 Hz, 1H), 1.20 (s, 9H), 0.909 (s, 9H), 0.905 (s, 9H), 0.091 (s, 3H), 0.089 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.6, 78.9, 76.2, 75.8, 65.0, 62.1, 38.7, 34.8, 32.5, 27.5, 27.2, 26.0, 25.9, 18.4, 18.2, -4.2, -4.7, -5.3; HRMS (ES+) calcd. for $C_{25}H_{53}O_5Si_2$ (M+H) 489.3432, found 489.3418.



28 **55**

Alcohol 55: To a stirred solution of pivaloyl ester **28** (1.51 g, 3.08 mmol) in Et_2O (58.0 mL) at 0 ºC was added $LiAlH_4$ (235 mg, 6.17 mmol) in one portion. After 30 min, the reaction was quenched with dropwise addition of H_2O (3.0 mL) and the organic layer was decanted. The solid formed was washed with Et_2O (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 15-20% EtOAc/ hexanes, to give alcohol **55** (1.20 g, 2.96 mmol, 96%) as colorless oil: $[\alpha]_D^{23}$ = -20.8 (*c* = 1.01, $CHCl_3$); IR: (neat) 3443, 2953, 2921, 2879, 2851, 1470, 1458, 1260, 1081, 1003, 835, 777cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.12-4.19 (m, 2H), 3.78-3.82 (m, 2H), 3.65 (dd, *J* = 11.2, 8.1 Hz, 1H), 3.54-3.59 (m, 2H), 3.01-3.04 (m, 1H), 2.02-2.09 (m, 1H), 1.92-2.00 (m, 1H), 1.68-1.87 (m, 3H), 1.58 (ddd, *J* = 18.2, 11.8, 8.6 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.91 (s, 9H), 0.90 (s, 9H), 0.09 (s, 6H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 80.2, 79.3, 75.5, 64.8, 62.0, 37.0, 32.6, 27.2, 25.99, 25.90, 18.3, 18.1, -4.2, -4.7, -5.4; HRMS (ES+) calcd. for $C_{20}H_{45}O_4Si_2$ (M+H) 405.2856, found 405.2871.



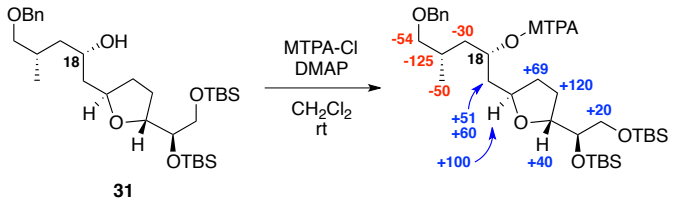
55 **29** **31/32**

Alcohols 31 and 32: To a stirred solution of oxalyl chloride (377 mg, 0.26 mL, 2.97 mmol) in CH_2Cl_2 (18.0 mL) at -78 ºC was cannulated a solution of DMSO (483 mg, 0.44 mL, 6.19 mmol) in CH_2Cl_2 (2.9 mL). After 10 min, a solution of alcohol **55** (1.00 g, 2.47 mmol) in CH_2Cl_2 (5.0 mL) was cannulated to it. After 40 min, Et_3N (1.25 g, 1.8 mL, 12.37 mmol) was added and the cooling bath was removed. After 15 min, the reaction was quenched with H_2O (30 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 X 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and was quickly passed through a short plug of silica gel to give the crude aldehyde **29**.

To a solution of Iodide **30**[8] (860 mg, 2.96 mmol) in Et_2O (50.0 mL) at -78 ºC was added t-BuLi (3.5 mL, 5.93 mmol, 1.7 M in pentane). After 10 min, the reaction was warmed to rt for 25 min and then cooled back down to -78 ºC. A

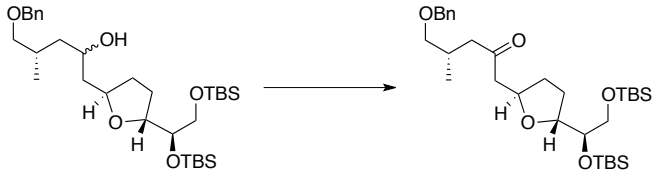
solution of the crude aldehyde **29** in Et_2O (35.0 mL and 2 X 2.5 mL wash) was cannulated to it. After 30 min, the reaction was quenched with sat. aq. NH_4Cl (35 mL) and the aqueous layer was extracted with Et_2O (3 X 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give diastereomeric alcohols **31** and **32** (1.00 g, 1.78 mmol, 72%, 1.5:1 dr) as colorless oil: Major alcohol **31**: $[\alpha]_D^{23}$ = -14.4 (*c* = 1.01, $CHCl_3$); IR: (neat) 3490, 2957, 2929, 2872, 2858, 1458, 1253, 1095, 835, 776, cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.35-7.36 (m, 4H), 7.28-7.30 (m, 1H), 4.53 (s, 2H), 4.13-4.17 (m, 2H), 3.93 (t, *J* = 9.0 Hz, 2H), 3.88 (s, 1H), 3.66 (dd, *J* = 11.7, 8.1 Hz, 1H), 3.56-3.58 (m, 2H), 3.39 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.31 (dd, *J* = 9.1, 6.5 Hz, 1H), 2.05-2.09 (m, 2H), 1.92-1.96 (m, 1H), 1.79-1.85 (m, 1H), 1.63-1.65 (m, 1H), 1.59 (ddd, *J* = 13.7, 9.0, 5.2 Hz, 1H), 1.48-1.56 (m, 2H), 1.25 (ddd, *J* = 13.7, 8.2, 3.7 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.914 (s, 9H), 0.910 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.073 (s, 3H), 0.070 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 138.7, 128.2, 127.5, 127.3, 80.0, 79.4, 76.4, 75.7, 72.8, 69.4, 65.0, 43.3, 42.1, 33.0, 30.2, 26.9, 25.98, 25.90, 18.3, 18.1, 17.3, -4.2, -4.7, -5.3, -5.4; HRMS (ES+) calcd. for $C_{31}H_{59}O_5Si_2$ (M+H) 567.3901, found 567.3882.

Mosher ester determination of stereochemistry in compound 31[7]



31

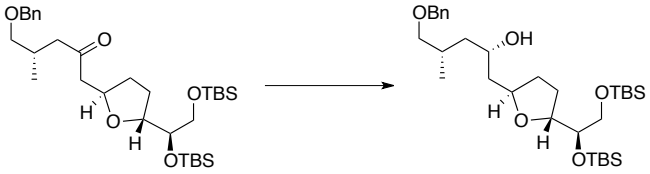
^1H NMR shift differences [(S)-MTPA-(R)-MTPA] reported in Hertz ($CDCl_3$, 700 MHz)



31/32 **57**

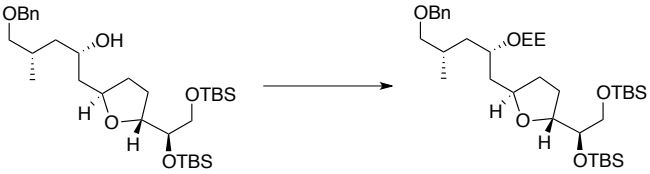
Ketone 57: To a stirred solution of diastereomeric alcohols **31/32** (747 mg, 1.31 mmol) in CH_2Cl_2 (26.0 mL) with 4 Å mol. sieves (500 mg) were added NMO (463 mg, 3.95 mmol) followed by TPAP (46.3 mg, 0.131 mmol). After 30 min, the reaction was directly loaded onto column and purified by flash chromatography over silica gel, eluting with 10-15% EtOAc / hexanes, to give ketone **57** (708 mg, 1.25 mmol, 95%) as colorless oil: $[\alpha]_D^{23}$ = -12.6 (*c* = 1.03, $CHCl_3$); IR: (neat) 2954, 2929, 2856, 1713, 1471, 1361, 1253, 1096, 835, 777, 735 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.33-7.37 (m, 4H), 7.28-7.31 (m, 1H), 4.49 (s, 2H), 4.32 (ddd, *J* = 12.3, 8.6, 6.2 Hz, 1H), 4.08 (td, *J* = 7.4, 3.4 Hz, 1H), 3.66 (dd, *J* = 11.7, 7.9 Hz, 1H), 3.55-3.57 (m, 2H), 3.35 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.28 (dd, *J* = 9.2, 6.8 Hz, 1H), 2.72 (dd, *J* = 15.5, 6.8 Hz, 1H), 2.62 (dd, *J* = 16.3,

5.4 Hz, 1H), 2.51 (dd, *J* = 15.5, 6.1 Hz, 1H), 2.38-2.42 (m, 1H), 2.34 (dd, *J* = 16.3, 7.6 Hz, 1H), 2.10-2.14 (m, 1H), 1.91-1.95 (m , 1H), 1.81-1.87 (m, 1H), 1.44-1.49 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 18H), 0.09 (s, 3H), 0.08 (s, 3H), 0.068 (s, 3H), 0.065 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 209.0, 138.5, 128.3, 127.59, 127.53, 78.9, 75.7, 75.5, 75.0, 72.9, 65.0, 49.3, 47.5, 32.5, 29.5, 27.4, 26.0, 25.9, 18.4, 18.2, 17.2, -4.2, -4.7, -5.32, -5.34; HRMS (ES+) calcd. for $C_{31}H_{56}O_5Si_2Na$ (M+Na) 587.3564, found 587.3553.



57 **31**

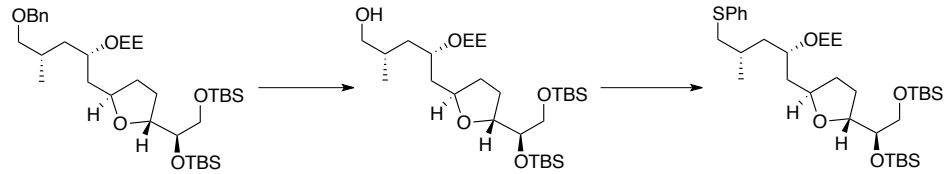
Alcohol 31: To a stirred solution of ketone **57** (708 mg, 1.25 mmol) in THF (100.0 mL) was added L-Selectride (3.8 mL, 3.80 mmol, 1 M in THF) and warmed to -30 ºC over 1 h. After 5 h, the reaction was quenched with sat. aq. NH_4Cl (30 mL) and the aqueous layer was extracted with Et_2O (3 X 60 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give pure alcohol **31** (638 mg, 1.12 mmol, 90%, 15:1 dr) as colorless oil.



31 **58**

EE ether 58: To a stirred solution of alcohol **31** (946 mg, 1.67 mmol) in CH_2Cl_2 (26.0 mL) were added ethyl vinyl ether (3.00 g, 4.0 mL, 41.7 mmol) followed by PPTS (1.5 mg, 41.7 µmol). After 14 h, the reaction was quenched with Et_3N (1.44 g, 2.0 mL, 14.2 mmol) and was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 3-6% EtOAc / hexanes, to give EE ether **58** (1.00 g, 1.57 mmol, 94%) as colorless oil: $[\alpha]_D^{23}$ = -21.0 (*c* = 1.00, C_6H_6); IR: (neat) 2954, 2929, 2857, 1471, 1361, 1253, 1091, 960, 835, 777 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35-7.36 (m, 4H (2 diastereomers)), 7.29-7.30 (m, 1H (1 diastereomer)), 4.72 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.68 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.52 (s, 2H (2 diastereomers)), 4.06-4.10 (m, 1H (2 diastereomers)), 3.94-4.01 (m, 1H (2 diastereomers)), 3.87 (ddd, *J* = 13.0, 8.1, 4.0 Hz, 1H (1 diastereomer)), 3.78 (ddd, *J* = 12.6, 8.4, 4.4 Hz, 1H (1 diastereomer)), 3.61-3.69 (m, 2H (2 diastereomers)), 3.54-3.58 (m , 2H (2 diastereomers)), 3.45-3.53 (m, 1H (2 diastereomers)), 3.35-3.38 (m, 1H (2 diastereomers)), 3.23-3.28 (m, 1H (2 diastereomers)), 2.08-2.13 (m, 1H (1 diastereomer)), 1.98-2.04 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.90-1.96 (m, 2H (2 diastereomers)), 1.77-1.85 (m, 1H (2 diastereomers)), 1.54-1.63 (m, 2H (2 diastereomers)), 1.42-

1.48 (m, 1H (2 diastereomers)), 1.31-1.37 (m, 1H (2 diastereomers)), 1.30 (d, *J* = 5.2 Hz, 3H (2 diastereomers)), 1.21 (t, *J* = 7.0 Hz, 3H (2 diastereomers)), 1.01 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 1.00 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 0.91 (s, 9H (2 diastereomers)), 0.90 (s, 9H (2 diastereomers)), 0.094 (s, 3H), 0.090 (s, 3H), 0.08 (s, 3H)), 0.07 (s, 3H)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 138.8, 138.7, 128.3, 128.2, 127.5, 127.4, 127.3, 99.6, 98.3, 78.6, 78.5, 76.4, 76.3, 76.2, 76.0, 72.9, 72.87, 72.84, 71.9, 65.1, 60.7, 60.5, 41.8, 41.2, 39.0, 38.6, 33.2, 32.9, 29.8, 29.7, 27.39, 27.36, 26.0, 25.9, 20.9, 20.7, 18.4, 18.1, 17.3, 17.0, 15.4, 15.3, -4.1, -4.2, -4.6, -4.7; HRMS (ES+) calcd. for $C_{35}H_{66}O_6Si_2Na$ (M+Na) 661.4296, found 661.4295.

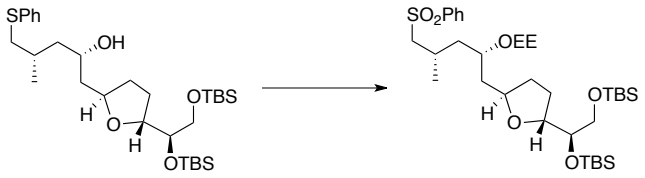


58 **33** **59**

Sulfide 59: To a stirred solution of benzyl ether **58** (756 mg, 1.18 mmol) in i-PrOH (49.0 mL) was added Pd/C (510 mg, 10 mol% by weight). The flask was fitted with a H_2 balloon and purged with H_2. After 18 h, the reaction was passed through a plug of celite and the celite plug was washed with EtOAc (100 mL). The solvent was removed *in vacuo* to give the crude alcohol **33**.

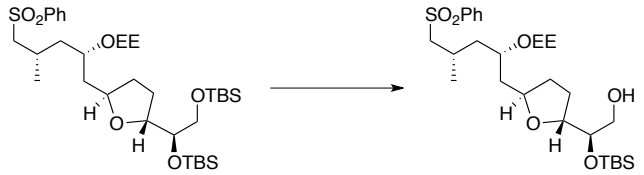
To a stirred solution of crude alcohol **33** in THF (7.0 mL) at 0 ºC were added Ph_2S_2 (426 mg, 1.95 mmol) followed by n-Bu_3P (413 mg, 0.52 mL, 2.04 mmol) and the reaction was warmed to rt. After 15 h, the solvent was removed *in vacuo* and the residue was purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give sulfide **59** (592 mg, 0.923 mmol, 78%) as colorless oil: $[\alpha]_D^{23}$ = -36.9 (*c* = 1.03, C_6H_6); IR: (neat) 2955, 2929, 2857, 1472, 1376, 1253, 1091, 959, 835, 776, 736, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.36 (m, 2H (2 diastereomers)), 7.25-7.29 (m, 2H (2 diastereomers)), 7.13-7.18 (m, 1H (2 diastereomers)), 4.70 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.64 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.05-4.11 (m, 1H (2 diastereomers)), 3.92-4.01 (m, 1H (2 diastereomers)), 3.82-3.88 (m, 1H (1 diastereomer)), 3.72-3.79 (m, 1H (1 diastereomer)), 3.64-3.71 (m, 1H (2 diastereomers)), 3.50-3.62 (m, 3H (2 diastereomers)), 3.37-3.47 (m, 1H (1 diastereomer)), 2.93-2.99 (m, 1H (2 diastereomers)), 2.74-2.81 (m, 1H (2 diastereomers)), 1.87-2.10 (m, 3H (2 diastereomers)), 1.68-1.85 (m, 3H (2 diastereomers)), 1.51-1.58 (m, 1H (2 diastereomers)), 1.39-1.48 (m, 2H (2 diastereomers)), 1.27 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.23 (d, *J* = 5.2 Hz (1 diastereomer)), 1.19 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.14 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.08 (d, *J* = 6.5 Hz, 3H (1 diastereomer)), 1.07 (d, *J* = 6.5 Hz, 3H (1 diastereomer)), 0.91 (s, 18H (2 diastereomers)), 0.09 (s, 6H (2 diastereomers)), 0.073 (s, 3H (2 diastereomers)), 0,070 (s, 3H (2 diastereomers)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 129.1, 129.0, 128.79, 128.73, 125.6, 125.5, 99.8, 98.1, 78.6, 78.5, 77.2, 76.24, 76.20, 76.1, 73.1, 71.8,

65.0, 60.7, 60.3, 41.99, 41.91, 41.6, 41.3, 41.1, 33.2, 33.0, 29.3, 27.3, 26.0, 25.9, 20.8, 20.6, 19.3, 19.1, 18.4, 18.1, 15.3, -4.1, -4.2, -4.7, -5.3; HRMS (ES+) calcd. for $C_{34}H_{64}O_5SSi_2Na$ (M+Na) 663.3911, found 663.3882.



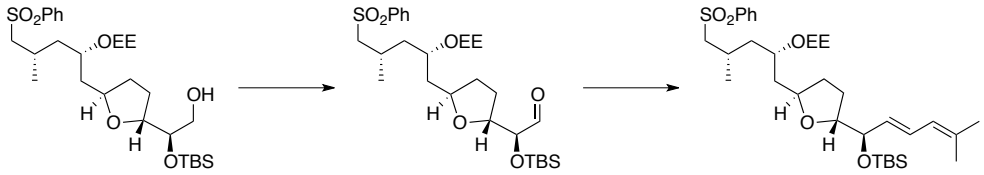
59 **34**

Sulfone 34: To a stirred solution of sulfide **59** (592 mg, 0.923 mmol) in CH_3CN (16.0 mL) at rt were added NMO (325 mg, 2.77 mmol) followed by TPAP (163 mg, 0.461 mmol). After 12 h, the reaction was directly loaded onto column and purified by flash chromatography over silica gel, eluting with 10-30% EtOAc / hexanes, to give sulfone **34** (574 mg, 0.852 mmol, 92%) as colorless oil: $[\alpha]_D^{23}$ = -27.8 (*c* = 1.00, C_6H_6); IR: (neat) 2955, 2929, 2856, 1471, 1446, 1377, 1307, 1253, 1147, 1086, 835, 776, 689 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.93-7.96 (m, 2H (2 diastereomers)), 7.64-7.67 (m, 1H (2 diastereomers)), 7.56-7.59 (m, 2H (2 diastereomers)), 4.67 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.62 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.05-4.09 (m, 1H (2 diastereomers)), 3.88-3.94 (m, 1H (2 diastereomers)), 3.81-3.85 (m, 1H (1 diastereomer)), 3.69-3.72 (m, 1H (1 diastereomer)), 3.63-3.66 (m, 1H (2 diastereomers)), 3.59-3.63 (m, 1H (1 diastereomer)), 3.50-3.56 (m, 3H (1H of 1 diastereomer and 2H of 2 diastereomers)), 3.40-3.47 (m, 1H (2 diastereomers)), 3.23 (dd, *J* = 14.2, 4.7 Hz, 1H (1 diastereomer)), 3.17 (dd, *J* = 14.2, 4.3 Hz, 1H (1 diastereomer)), 2.97 (dd, *J* = 8.2, 5.5 Hz, 1H (1 diastereomer)), 2.95 (dd, *J* = 8.3, 5.7 Hz, 1H (1 diastereomer)), 2.32-2.37 (m, 1H (1 diastereomer)), 2.21-2.26 (m, 1H (1 diastereomer)), 1.96-2.01 (m, 1H (2 diastereomers)), 1.86-1.94 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.78-1.84 (m, 1H (2 diastereomers)), 1.72-1.76 (m, 1H (1 diastereomer)), 1.39-1.62 (m, 4H (2 diastereomers)), 1.23 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.21 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.19 (t, *J* = 7.1 Hz, 3H (1 diastereomer)), 1.17 (t, *J* = 7.1 Hz, 3H (1 diastereomer)), 1.148 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 1.145 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 0.909 (s, 9H (1 diastereomer)), 0.907 (s, 9H (1 diastereomer)), 0.89 (s, 9H (2 diastereomers)), 0.06-0.08 (m, 12H (2 diastereomers)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 141.2, 141.0, 133.5, 133.3, 129.2, 129.1, 128.04, 128.0, 99.9, 97.9, 78.6, 78.5, 76.0, 75.9, 72.9, 71.1, 65.0, 63.26, 63.20, 60.7, 60.6, 41.8, 41.7, 41.5, 40.7, 33.2, 33.0, 27.3, 27.2, 26.0, 25.9, 25.86, 25.83, 20.7, 20.6, 19.8, 19.7, 18.4, 18.1, 15.4, 15.3, -4.20, -4.22, -4.6, -4.7, -5.3; HRMS (ES+) calcd. for $C_{34}H_{64}O_7SSi_2Na$ (M+Na) 695.3809, found 695.3818.



34 **60**

Alcohol 60: To a stirred solution of bis-TBS ether **34** (574 mg, 0.852 mmol) in THF (8.0 mL) at 0 ºC was added a stock solution of HF•pyr[5] (4.8 mL) over 30 min. After 24 h, the reaction quenched with sat. aq. $NaHCO_3$ (50 mL) and the aqueous layer was extracted with EtOAc / Et_2O (2:1, 3 X 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 20-60% EtOAc / hexanes, to give alcohol **60** (380 mg, 0.679 mmol, 80%) as colorless oil: $[\alpha]_D^{23}$ = -30.2 (*c* = 1.01, C_6H_6); IR: (neat) 3468, 2957, 2930, 2857, 1462, 1447, 1377, 1306, 1253, 1145, 1086, 1056, 836, 777, 689 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.93-7.95 (m, 2H (2 diastereomers)), 7.64-7.67 (m, 1H (2 diastereomers)), 7.56-7.59 (m, 2H (2 diastereomers)), 4.67 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.63 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.06-4.10 (m, 1H (2 diastereomers)), 3.94-4.01 (m, 1H (2 diastereomers)), 3.80-3.83 (m, 1H (1 diastereomer)), 3.65-3.71 (m, 3H (1H of 1 diastereomer and 2H of 2 diastereomers)), 3.56-3.61 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 3.52 (ddd, *J* = 14.0, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.46 (ddd, *J* = 14.0, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.42 (ddd, *J* = 14.0, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.22 (dd, *J* = 14.2, 5.0 Hz, 1H (1 diastereomer)), 3.16 (dd, *J* = 14.2, 4.6 Hz, 1H (1 diastereomer)), 2.95-2.99 (m, 1H (2 diastereomers)), 2,45-2.47 (m, 1H (2 diastereomers)), 2.32-2.38 (m, 1H (1 diastereomer)), 2.21-2.28 (m, 1H (1 diastereomer)), 2.01-2.06 (m, 1H (2 diastereomers)), 1.88-1.97 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.72-1.79 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.61-1.69 (m, 1H (2 diastereomers)), 1.49-1.57 (m, 1H (2 diastereomers)), 1.42-1.48 (m, 2H (2 diastereomers)), 1.24 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.23 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.19 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.17 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.13 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 1.12 (d, *J* = 6.7 Hz, 3H (1 diastereomer)), 0.92 (s, 9H (2 diastereomers)), 0.112-0.117 (m, 6H (2 diastereomers)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 140.1, 140.0, 133.5, 133.4, 129.2, 129.1, 128.0, 127.9, 99.9, 97.7, 80.4, 80.3, 76.3, 76.2, 74.47, 74.42, 72.8, 70.7, 64.6, 63.13, 63.10, 60.5, 60.3, 41.7, 41.5, 40.6, 32.9, 32.7, 27.5, 25.88, 25.81, 25.78, 20.59, 20.50, 20.0, 19.7, 18.1, 15.4, 15.3, -4.5, -4.6; HRMS (ES+) calcd. for $C_{28}H_{50}O_7SSiNa$ (M+Na) 581.2944, found 581.2930.

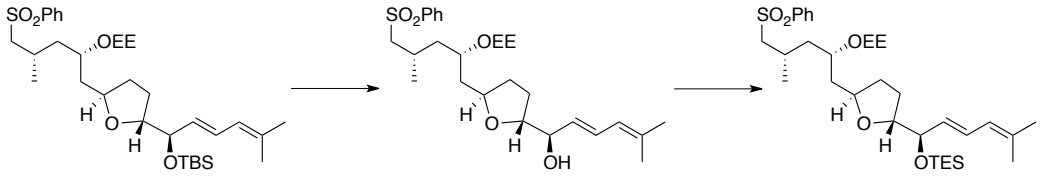


60 **35** **37**

Diene 37: To a stirred solution of oxalyl chloride (103 mg, 72 µL, 0.814 mmol) in CH_2Cl_2 (4.2 mL) at -78 ºC was cannulated a solution of DMSO (133 mg, 0.12 mL, 1.70 mmol) in CH_2Cl_2 (1.2 mL). After 15 min, a solution of alcohol **60** (380 mg, 0.679 mmol) in CH_2Cl_2 (2.0 mL and 2 X 0.5 mL wash) was cannulated to it. After 45 min, Et_3N (346 mg, 0.48 mL, 3.39 mmol) was added. After 10 min, the cooling bath was removed and the reaction was quenched with H_2O (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 X 50 mL) and the dried ($MgSO_4$) extract was concentrated *in vacuo* and was quickly passed through a short plug of silica gel to give the crude aldehyde **35**.

To a stirred solution of tributyl phosphonium salt **36** (341 mg, 0.970 mmol) in THF (7.6 mL) at -45 ºC was added n-BuLi (0.40 mL, 1.00 mmol, 2.5 M in hexane) and was warmed to rt over 45 min. After 2 h, the reaction was cooled back down to -78 ºC and a solution of the crude aldehyde **35** in THF (7.6 mL) was cannulated to it. The reaction was slowly warmed to rt over 2.5 h. After another 3 h, the reaction was quenched with H_2O (15 drops) and the solvent was removed *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10-30% EtOAc / hexanes, to give diene **37** (401 mg, 0.658 mmol, 97%, 11:1 *E:Z* inseparable mixture) as colorless oil: $[\alpha]_D^{23}$ = +12.7 (*c* = 1.02, C_6H_6); IR: (neat) 2956, 2928, 2856, 1446, 1378, 1308, 1253, 1148, 1086, 959, 836, 776, 689 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.93-796 (m, 2H (2 diastereomers)), 7.64-7.67 (m, 1H (2 diastereomers)), 7.56-7.59 (m, 2H (2 diastereomers)), 6.43-6.47 (m, 1H (2 diastereomers of E isomer)), 6.21 (t, *J* = 11.2 Hz, 1H of Z isomer), 6.06-6.09 (m, 1H of Z isomer)), 5.83 (d, *J* = 11.0 Hz, 1H (2 diastereomers of E isomer)), 5.53 (ddd, *J* = 14.1, 5.7, 3.1 Hz, 1H (2 diastereomers of E isomer)), 5.29 (q, *J* = 10.1 Hz, 1H of Z isomer), 4.67 (q, J = 5.2 Hz, 1H (1 diastereomer)), 4.63 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.46 (dd, *J* = 9.0, 5.2 Hz, 1H of Z isomer), 4.16 (t, *J* = 5.6 Hz, 1H (2 diastereomers)), 3.86-3.94 (m, 2H (2 diastereomers)), 3.79-3.83 (m, 1H (1 diastereomer)), 3.67-3.71 (m, 1H (1 diastereomer)), 3.60 (ddd, *J* = 14.1, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.53 (ddd, *J* = 14.1, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.41-3.47 (m, 1H (2 diastereomers)), 3.25 (dd, *J* = 14.2, 4.7 Hz, 1H (1 diastereomer)), 3.18 (dd, *J* = 14.2, 4.4 Hz, 1H (1 diastereomer)), 2.95-2.99 (m, 1H (2 diastereomers)), 2.32-2.37 (m, 1H (1 diastereomer)), 2.21-2.26 (m, 1H (1 diastereomer)), 1.92-1.98 (m, 1H (2 diastereomers)), 1.84-1.91 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.79 (s, 3H (2 diastereomers)), 1.77 (s, 3H (2 diastereomers)), 1.67-1.75 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.57-1.66 (m, 1H (2 diastereomers)), 1.39-1.54 (m, 3H (2 diastereomers)), 1.24 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.22 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.19 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.18 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.154 (d,

J = 6.6 Hz, 3H (1 diastereomer)), 1.152 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 0.921 (s, 9H (1 diastereomer)), 0.920 (s, 9H (1 diastereomer)), 0.05-0.08 (m, 6H (2 diastereomers)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 140.2, 140.0, 135.04, 135.02, 133.5, 133.3, 129.97, 129.95, 129.2, 129.1, 128.0, 127.9, 127.45, 127.43, 124.7, 99.9, 98.0, 82.1, 82.0, 76.0, 75.7, 75.6, 72.8, 71.1, 63.19, 63.12, 60.6, 60.5, 41.8, 41.7, 41.6, 40.7, 32.9, 32.7, 27.24, 27.21, 25.9, 25.8, 20.7, 20.5, 20.0, 19.7, 18.2, 15.4, 15.3, -4.4, -4.6; HRMS (ES+) calcd. for $C_{33}H_{56}O_6SSiNa$ (M+Na) 631.3465, found 631.3459.

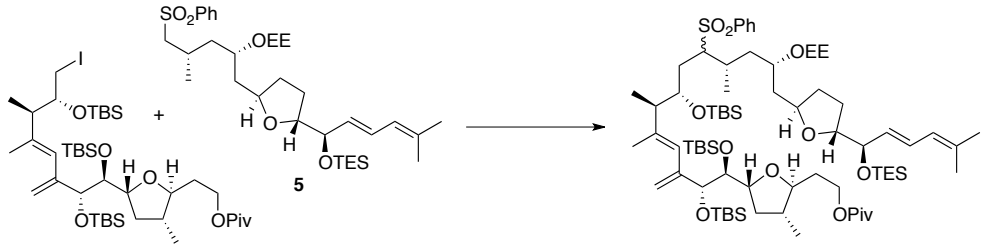


37 **61** **5**

Dienyl Sulfone 5: To a stirred solution of TBS ether **37** (401 mg, 0.658 mmol) in THF (6.7 mL) at rt was added TBAF (2.0 mL, 2.00 mmol, 1 M in THF). After 12 h, the reaction quenched with H_2O (25 mL) and the aqueous layer was extracted with EtOAc / Et_2O (1:1, 3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give the crude alcohol **61**.

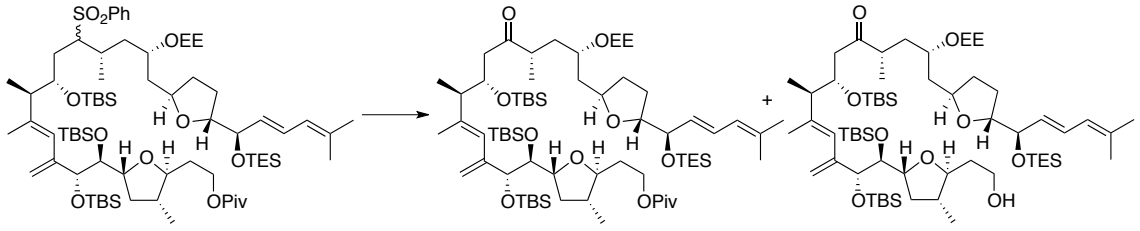
To a stirred solution of crude alcohol **61** in CH_2Cl_2 (8.7 mL) at 0 ºC were sequentially added Et_3N (523 mg, 0.73 mL, 5.17 mmol), DMAP (39.1 mg, 0.323 mmol) and TESCl (341 mg, 0.38 mL, 2.26 mmol). The reaction was slowly warmed to rt over 2 h. After another 3 h, the reaction was quenched with sat. aq. NH_4Cl (25 mL) and the aqueous layer was extracted with Et_2O (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-30% EtOAc / hexanes, to give dienyl sulfone **5** (379 mg, 0.622 mmol, 95%) as colorless oil: $[\alpha]_D^{23}$ = +18.0 (*c* = 1.00, C_6H_6); IR: (neat) 2957, 2913, 2876, 1446, 1377, 1308, 1148, 1086, 1018, 959, 841, 741, 689 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.93-796 (m, 2H (2 diastereomers)), 7.64-7.67 (m, 1H (2 diastereomers)), 7.56-7.59 (m, 2H (2 diastereomers)), 6.42-6.46 (m, 1H (2 diastereomers of E isomer)), 6.21 (t, *J* = 11.3 Hz, 1H of Z isomer), 6.07-6.09 (m, 1H of Z isomer)), 5.82 (d, *J* = 11.0 Hz, 1H (2 diastereomers of E isomer)), 5.52 (ddd, *J* = 15.0, 6.1, 3.0 Hz, 1H (2 diastereomers of E isomer)), 5.29 (q, *J* = 10.2 Hz, 1H of Z isomer), 4.66 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.63 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.46-4.48 (m, 1H of Z isomer), 4.15 (t, *J* = 5.6 Hz, 1H (2 diastereomers)), 3.86-3.94 (m, 2H (2 diastereomers)), 3.78-3.82 (m, 1H (1 diastereomer)), 3.67-3.70 (m, 1H (1 diastereomer)), 3.60 (ddd, *J* = 14.1, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.53 (ddd, *J* = 14.1, 9.2, 7.0 Hz, 1H (1 diastereomer)), 3.41-3.47 (m, 1H (2 diastereomers)), 3.25 (dd, *J* = 14.2, 4.7 Hz, 1H (1 diastereomer)), 3.17 (dd, *J* = 14.2, 4.4 Hz, 1H (1 diastereomer)), 2.94-2.98 (m, 1H (2 diastereomers)), 2.31-2.36 (m, 1H (1 diastereomer)), 2.20-2.26 (m, 1H (1 diastereomer)), 1.92-1.98 (m, 1H (2 diastereomers)), 1.84-1.91 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.79 (s, 3H (2 diastereomers)), 1.77 (s, 3H (2 diastereomers)),

1.68-1.75 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.57-1.65 (m, 1H (2 diastereomers)), 1.38-1.53 (m, 3H (2 diastereomers)), 1.24 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.22 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.19 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.17 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.148 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 1.147 (d, *J* = 6.6 Hz, 3H (1 diastereomer)), 0.96 (t, *J* = 8.0 Hz, 9H (2 diastereomers)), 0.61 (q, *J* = 7.9 Hz, 6H (2 diastereomers)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 140.2, 140.0, 135.13, 135.11, 133.5, 133.3, 129.96, 129.95, 129.2, 129.1, 128.0, 127.9, 127.54, 127.53, 124.6, 99.8, 98.0, 82.1, 82.0, 76.0, 75.68, 75.63, 72.8, 71.1, 63.17, 63.10, 60.6, 60.5, 41.9, 41.7, 41.6, 40.7, 32.9, 32.7, 27.32, 27.30, 25.9, 25.8, 20.6, 20.5, 19.9, 19.7, 18.2, 15.4, 15.3, 6.8, 5.0; HRMS (ES+) calcd. for $C_{33}H_{56}O_6SSiNa$ (M+Na) 631.3465, found 631.3466.



Coupled sulfone 38: To a stirred solution of sulfone **5** (325 mg, 0.533 mmol) in THF (2.2 mL) at -60 ºC was added LHMDS (0.54 mL, 0.540 mmol, 1 M in THF) and warmed to -10 ºC over 1 h. HMPA (515 mg, 0.50 mL, 2.87 mmol) was added and the reaction was warmed to 0 ºC over 15 min. The reaction was cooled back down to -10 ºC and a solution of iodide **6** (188 mg, 0.213 mmol) in THF (2.0 mL and 2 X 0.35 mL wash) was cannulated to it and warmed to 0 ºC. After 1.5 h, the cooling bath was removed. After another 1 h, the reaction was quenched with sat. aq. NH_4Cl (20 mL) and the aqueous layer was extracted with Et_2O (3 X 30 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-20% EtOAc / hexanes, to give diastereomeric coupled sulfone **38** (215 mg, 0.157 mmol, 74%) as colorless oil along with recovered sulfone **5** (191 mg, 0.313 mmol). Coupled sulfone **38**: $[\alpha]_D^{23}$ = -10.0 (*c* = 1.00, C_6H_6); IR (neat): 2956, 2935, 2886, 2862, 1730, 1467, 1382, 1304, 1252, 1148, 1081, 1007, 835, 776 cm^{-1} ; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.89-7.94 (m, 2H (4 diastereomers)), 7.60-7.65 (m, 1H (4 diastereomers)), 7.52-7.57 (m, 2H (4 diastereomers)), 6.43-6.48 (m, 1H (4 diastereomers)), 5.79 (m, 2H (1H of 2 diastereomers and 1H of 4 diastereomers)), 5.69 (s, 1H (1 diastereomer)), 5.68 (s, 1H (1 diastereomer)), 5.52 (dt, *J* = 15.1, 6.4 Hz, 1H (4 diastereomers)), 5.30-5.33 (m, 1H (4 diastereomers)), 5.05 (s, 1H (1 diastereomer)), 5.01 (s, 1H (1 diastereomer)), 4.88 (s, 1H (1 diastereomer)), 4.86 (s, 1H (2 diastereomers)), 4.66 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.61 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.59 (q, *J* = 5.1 Hz, 1H (1 diastereomer)), 4.49 (q, *J* = 5.1 Hz, 1H (1 diastereomer)), 4.36-4.39 (m, 1H (2 diastereomers)), 4.25-4.29 (m, 1H (4 diastereomers)), 4.07-4.16 (m, 4H (1H of 2 diastereomers and 3H of 4 diastereomers)), 3.96-4.00 (m, 1H (2

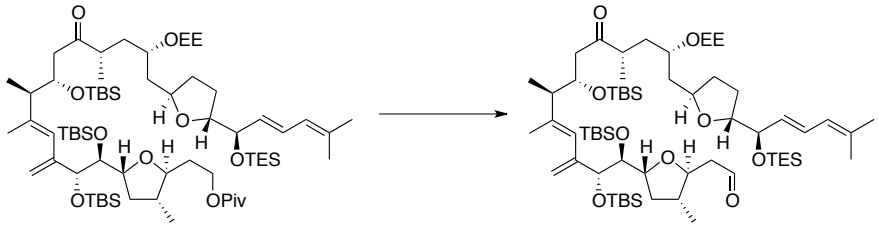
diastereomers)), 8.84-3.94 (m, 3H (1H of 2 diastereomers and 2H of 4 diastereomers)), 3.71-3.76 (m, 1H (1 diastereomer)), 3.65-3.69 (m, 1H (1 diastereomer)), 3.52-3.62 (m, 2H (1H of 2 diastereomers + 2H of 4 diastereomers)), 3.43-3.48 (m, 1H (2 diastereomers)), 3.36-3.42 (m, 2H (1H of 2 diastereomers and 1H of 4 diastereomers)), 3.27-3.35 (m, 1H of 2 diastereomers)), 3.10-3.21 (m, 1H (2 diastereomers)), 2.40-2.44 (m, 1H (2 diastereomers)), 2.31-2.34 (m, 1H (2 diastereomers)), 2.14-2.30 (m, 1H (4 diastereomers)), 2.00-2.12 (m, 2H (4 diastereomers)), 1.76-1.99 (m, 6H (4 diastereomers)), 1.90 (s, 3H (2 diastereomers)), 1.88 (s, 3H (2 diastereomers)), 1.79 (s, 3H (4 diastereomers)), 1.777 (s, 3H (2 diastereomers)), 1.771 (s, 3H (2 diastereomers)), 1.62-1.71 (m, 3H (4 diastereomers)), 1.36-1.46 (m, 2H (4 diastereomers)), 1.26-1.33 (m, 4H (4 diastereomers)), 1.19-1.23 (m, 13H (4 diastereomers)), 1.13-1.18 (m, 4H (4 diastereomers)), 1.06-1.10 (m, 3H (4 diastereomers)), 0.98-1.01 (m, 3H), 0.95-0.98 (m, 9H (4 diastereomers)), 0.85-0.93 (m, 27H (4 diastereomers)), 0.59-0.63 (m, 6H (4 diastereomers)), 0.03-0.18 (m, 18H (4 diastereomers)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 178.4, 145.56, 145.50, 145.4, 140.5, 140.2, 140.1, 139.8, 139.6, 139.0, 138.8, 135.1, 135.0, 133.3, 133.2, 133.1, 129.99, 129.97, 129.92, 129.91, 129.2, 129.1, 129.09, 129.06, 128.98, 128.94, 128.3, 125.8, 125.7, 124.79, 124.74, 124.6, 115.33, 115.30, 114.6, 114.5, 100.0, 99.5, 97.8, 97.7, 82.2, 82.19, 82.11, 80.54, 80.50, 80.3, 79.6, 79.53, 79.51, 79.2, 78.8, 78.7, 78.6, 76.28, 76.23, 76.18, 76.10, 75.8, 75.79, 75.75, 75.6, 72.4, 72.3, 72.0, 71.4, 71.1, 70.8, 70.6, 66.3, 65.6, 65.5, 62.15, 62.10, 61.1, 60.78, 60.75, 48.5, 48.4, 47.3, 47.0, 42.4, 42.1, 41.7, 41.4, 40.35, 40.32, 39.6, 39.2, 38.6, 38.1, 38.0, 35.8, 35.2, 33.1, 33.0, 32.8, 32.68, 32.63, 31.9, 29.7, 29.4, 29.3, 29.2, 28.8, 28.78, 28.71, 28.6, 27.6, 27.59, 27.54, 27.4, 27.2, 26.1, 26.0, 25.97, 25.91, 20.9, 20.7, 20.6, 20.5, 18.4, 18.3, 18.2, 18.1, 18.0, 17.9, 17.5, 17.2, 16.0, 15.9, 15.5, 15.4, 15.2, 11.7, 11.3, 6.93, 6.91, 4.9, -3.8, -4.15, -4.18, -4.2, -4.3, -4.4, -4.5, -4.6, -4.7; HRMS (ES+) calcd. for $C_{74}H_{136}O_{12}SSi_4Na$ (M+Na) 1383.8727, found 1383.8776.



38 **4** **39**

Ketone 4 and Alcohol 39: To a stirred solution of sulfone **38** (173.4 mg, 0.127 mmol) in THF (2.2 mL) at -50 ºC was added LDA[4] (0.32 mL, 0.32 mmol, 1 M in THF / hexanes). After 5 min, DMPU (1.27 g, 1.2 mL, 9.88 mmol) was added and was slowly warmed to -25 ºC over 20 min. The reaction was cooled back down to -50 ºC and a solution of Davis oxaziridine[9] (91.4 mg, 0.350 mmol) in THF (1.0 mL) was cannulated to it. The reaction was warmed to -35 ºC over 20 min and then quenched with sat. aq. NH_4Cl (20 mL) and the aqueous layer was extracted with Et_2O (3 X 50 mL). The dried ($MgSO_4$) extract was concentrated *in*

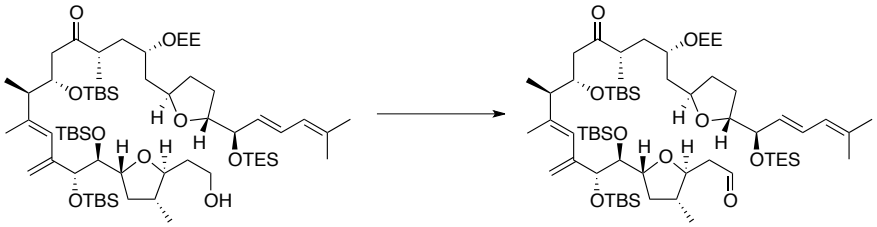
vacuo and purified by flash chromatography over silica gel, eluting with 6-20% EtOAc / hexanes, to give the ketone **4** (66.0 mg, 53.4 µmol, 42%) and alcohol **39** (33.6 mg, 29.2 µmol, 23%) as colorless oil along with the recovered sulfone **38** (49.9 mg, 36.6 µmol, 29%). Ketone **4**: $[\alpha]_D^{23}$ = +30.0 (*c* = 1.03, C_6H_6); IR (neat): 2956, 2932, 2859, 1731, 1719, 1461, 1377, 1251, 1078, 835, 776 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 6.43-6.48 (m, 1H (2 diastereomers)), 5.83 (d, *J* = 11.0 Hz, 1H (2 diastereomers)), 5.59 (s, 1H (2 diastereomers)), 5.53 (ddd, *J* = 15.1, 6.0, 3.2 Hz, 1H (2 diastereomers)), 5.32 (s, 1H (2 diastereomers)), 4.96 (s, 1H (2 diastereomers)), 4.65-4.68 (m, 1H (2 diastereomers)), 4.35-4.37 (m, 1H (2 diastereomers)), 4.24-4.28 (m, 1H (2 diastereomers)), 4.10-4.16 (m, 2H (2 diastereomers)), 4.08 (s, 1H (2 diastereomers)), 3.89-3.97 (m, 3H (2 diastereomers)), 3.74-3.78 (m, 1H (1 diastereomer)), 3.57-3.67 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 3.45-3.53 (m, 2H (2 diastereomers)), 3.33 (dt, *J* = 9.2, 2.7 Hz, 1H (2 diastereomers)), 2.77 (qd, *J* = 7.4, 4.3 Hz , 1H (1 diastereomer)), 2.57-2.66 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 2.54 (dd, *J* = 5.6, 3.5 Hz, 1H (1 diastereomer)), 2.51 (dd, *J* = 5.6, 3.5 Hz, 1H (1 diastereomer)), 2.36-2.41 (m, 1H (2 diastereomers)), 2.03-2.07 (m, 1H (2 diastereomers)), 1.94-2.01 (m, 2H (2 diastereomers)), 1.80-1.91 (m, 3H (2 diastereomers)), 1.81 (s, 3H (2 diastereomers)), 1.79 (s, 3H (2 diastereomers)), 1.77 (s, 3H (2 diastereomers)), 1.63-1.71 (m, 2H (2 diastereomers)), 1.48-1.52 (m, 1H (2 diastereomers)), 1.37-1.46 (m, 2H (2 diastereomers)), 1.26-1.30 (m, 4H (2 diastereomers)), 1.19-1.22 (m, 12H (2 diastereomers)), 1.08 (d, *J* = 7.0 Hz, 3H (2 diastereomers)), 1.05 (d, *J* = 6.9 Hz, 3H (1 diastereomer)), 1.04 (d, *J* = 6.9 Hz, 3H (1 diastereomer)), 0.98 (d, *J* = 6.4 Hz, 3H (2 diastereomers)), 0.97 (t, *J* = 7.9 Hz, 3H (2 diastereomers)), 0.907 (s, 9H (2 diastereomers)), 0.905 (s, 9H (1 diastereomer)), 0.904 (s, 9H (1 diastereomer)), 0.892 (s, 9H (1 diastereomer)), 0.890 (s, 9H (1 diastereomer)), 0.61 (q, *J* = 7.9 Hz, 6H (2 diastereomers)), 0.113 (s, 3H (1 diastereomer)), 0.111 (s, 3H (1 diastereomer)), 0.08 (s, 3H (2 diastereomers)), 0.06 (s, 3H (2 diastereomers)), 0.04 (s, 3H (1 diastereomer)), 0.03 (s, 3H (1 diastereomer)), 0.02 (s, 3H (2 diastereomers)), 0.007 (s, 3H (1 diastereomer)), 0.004 (s, 3H (1 diastereomer)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 213.1, 212.7, 178.4, 145.1, 140.93, 140.91, 135.16, 135.13, 129.87, 129.83, 127.4, 125.4, 124.6, 115.04, 115.00, 99.8, 98.8, 98.4, 82.19, 82.14, 80.45, 80.43, 79.4, 78.8, 78.5, 76.1, 76.0, 75.6, 72.5, 71.3, 70.47, 70.40, 62.1, 61.3, 61.1, 47.9, 47.8, 45.5, 45.4, 43.0, 42.8, 41.8, 41.2, 40.3, 38.6, 38.0, 37.0, 36.9, 33.1, 32.9, 32.7, 29.7, 27.4, 27.2, 26.1, 26.0, 25.97, 25.90, 20.8, 20.7, 18.4, 18.36, 18.30, 17.9, 17.1, 17.0, 16.1, 16.0, 15.7, 15.4, 15.3, 14.1, 14.0, 6.9, 4.9, -4.23, -4.26, -4.44, -4.46, -4.7, 4.8; HRMS (ES+) calcd. for $C_{68}H_{130}O_{11}Si_4Na$ (M+Na) 1257.8588, found 1257.8564.



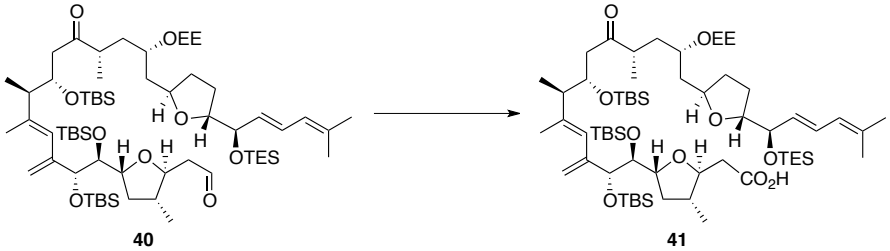
Aldehyde 40: To a stirred solution of pivaloyl ester **4** (46.2 mg, 37.3 µmol) in Et_2O (2.7 mL) at -20 ºC was added $LiAlH_4$ (3.6 mg, 93.4 µmol) in one portion. After 25 min, the reaction was quenched with H_2O (10 drops) and the organic layer was decanted. The solid formed was washed with Et_2O (3 X 20 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give the crude diol.

To a stirred solution of oxalyl chloride (23.7 mg, 16.5 µL, 0.187 mmol) in CH_2Cl_2 (1.0 mL) at -78 ºC was cannulated a solution of DMSO (29.2 mg, 27 µL, 0.374 mmol) in CH_2Cl_2 (0.50 mL). After 20 min, a solution of the crude diol in CH_2Cl_2 (1.2 mL + 2 X 0.25 mL wash) was cannulated to it. After 45 min, Et_3N (37.8 mg, 53 µL, 0.374 mmol) was added. After 10 min, the reaction was quenched with H_2O (10 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 X 20 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give aldehyde **40** (35.6 mg, 30.9 µmol, 83%) as colorless oil: $[\alpha]_D^{23}$ = +14.9 (*c* = 0.35, C_6H_6); IR: (neat) 2959, 2927, 2857, 1732, 1710, 1662, 1635, 1465, 1380, 1078, 835, 781 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 9.82 (dd, *J* = 2.9, 2.3 Hz, 1H (2 diastereomers)), 6.44-6.48 (m, 1H (2 diastereomers)), 5.83 (d, *J* = 11.0 Hz, 1H (2 diastereomers)), 5.60 (s, 1H (2 diastereomers)), 5.53 (ddd, *J* = 15.1, 6.0, 3.2 Hz, 1H (2 diastereomers)), 5.32 (t, *J* = 1.7 Hz, 1H (2 diastereomers)), 4.97 (s, 1H (2 diastereomers)), 4.68 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.66 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.37-4.39 (m, 1H (2 diastereomers)), 4.16 (t, *J* = 5.9 Hz, 1H (2 diastereomers)), 4.08 (s, 1H (2 diastereomers)), 3.99-4.02 (m, 1H (2 diastereomers)), 3.89-3.97 (m, 1H (2 diastereomers)), 3.75-3.78 (m, 1H (1 diastereomer)), 3.73 (td, *J* = 3.5 Hz, 1H (2 diastereomers)), 3.58-3.67 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 3.54 (dt, *J* = 7.1, 2.5 Hz, 1H (2 diastereomers)), 3.45-3.52 (m, 1H (2 diastereomers)), 2.76-2.81 (m, 1H (1 diastereomer)), 2.59-2.68 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 2.57 (dd, *J* = 3.4, 2.3 Hz, 1H (1 diastereomer)), 2.55 (dd, *J* = 3.4, 2.3 Hz, 1H (1 diastereomer)), 2.47-2.52 (m, 2H (2 diastereomers)), 2.38-2.42 (m, 1H (2 diastereomers)), 2.06-2.10 (m, 1H (2 diastereomers)), 1.95-2.01 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.84-1.90 (m, 3H (1H of 1 diastereomer and 2H of 2 diastereomers)), 1.83 (s, 3H (2 diastereomers)), 1.79 (s, 3H (2 diastereomers)), 1.77 (s, 3H (2 diastereomers)), 1.65-1.72 (m, 1H (2 diastereomers)), 1.48-1.53 (m, 1H (2 diastereomers)), 1.38-1.46 (m, 2H (2 diastereomers)), 1.296 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.291 (d, *J* = 5.2 Hz, 3H (1 diastereomer)), 1.22 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.21 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.09 (d, *J* = 7.0 Hz, 3H (2 diastereomers)), 1.06 (d, *J* = 6.9 Hz, 3H (1 diastereomer)), 1.05 (d, *J* = 6.9 Hz, 3H (1 diastereomer)), 1.02 (d, *J*

= 6.5 Hz, 3H (2 diastereomers)), 0.97 (t, *J* = 7.9 Hz, 3H (2 diastereomers)), 0.913 (s, 9H (1 diastereomer)), 0.912 (s, 9H (1 diastereomer)), 0.897 (s, 9H (2 diastereomers)), 0.896 (s, 9H (2 diastereomers)), 0.62 (q, *J* = 7.9 Hz, 6H (2 diastereomers)), 0.12 (s, 3H (1 diastereomer)), 0.11 (s, 3H (1 diastereomer)), 0.08 (s, 3H (2 diastereomers)), 0.04 (s, 6H (2 diastereomers)), 0.028 (s, 3H (2 diastereomers)), 0.025 (s, 3H (2 diastereomers)), 0.01 (s, 3H (1 diastereomer)), 0.007 (s, 3H (1 diastereomer)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 213.0, 212.6, 202.1, 145.0, 141.1, 141.0, 135.1, 135.0, 129.9, 129.8, 127.5, 127.4, 125.2, 124.6, 115.1, 115.0, 99.8, 98.4, 82.2, 82.1, 79.9, 79.8, 79.3, 78.66, 78.60, 76.1, 76.0, 75.6, 72.6, 71.3, 70.4, 70.3, 61.3, 61.1, 48.0, 47.9, 47.6, 45.4, 45.3, 43.1, 42.8, 41.8, 41.2, 40.6, 37.5, 37.1, 36.9, 32.9, 32.7, 29.7, 27.4, 26.1, 26.0, 25.95, 25.91, 25.89, 20.8, 20.7, 18.4, 18.3, 18.2, 17.9, 17.26, 17.24, 16.1, 15.7, 15.6, 15.4, 15.3, 14.0, 13.9, 6.9, 4.9, -4.1, -4.2, -4.45, -4.46, -4.7, -4.8; HRMS (ES+) calcd. for $C_{63}H_{120}O_{10}Si_4Na$ (M+Na) 1171.7856, found 1171.7769.

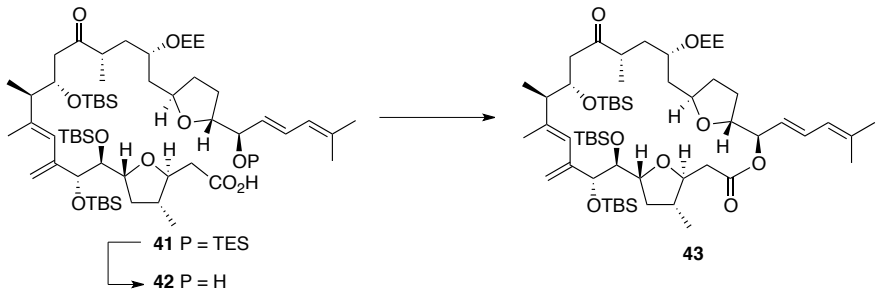


Aldehyde 40: To a stirred solution of oxalyl chloride (10.4 mg, 7.2 µL, 82.4 µmol) in CH_2Cl_2 (0.50 mL) at -78 ºC was cannulated a solution of DMSO (12.9 mg, 11.8 µL, 0.165 mmol) in CH_2Cl_2 (0.25 mL). After 15 min, a solution of alcohol **39** (19.0 mg, 16.5 µmol) in CH_2Cl_2 (0.50 mL + 2 X 0.10 mL wash) was cannulated to it. After 45 min, Et_3N (16.7 mg, 24 µL, 0.165 mmol) was added. After 10 min, the reaction was quenched with H_2O (5 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 X 15 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give aldehyde **40** (15.8 mg, 13.7 µmol, 83%) as colorless oil.



Carboxylic Acid 41: To a stirred solution of aldehyde **40** (35.6 mg, 30.9 µmol) in t-BuOH / H_2O (1:1, 3.0 mL) at 0 ºC were sequentially added 2-methyl-2-butene (108 mg, 0.16 mL, 1.54 mmol), $NaH_2PO_4 \cdot H_2O$ (42.7 mg, 0.309 mmol) and $NaClO_2$ (14.1 mg, 0.154 mmol). After 15 min, the reaction was warmed to rt. After another 1.5 h, the reaction was diluted with H_2O (7.5 mL) and the aqueous layer

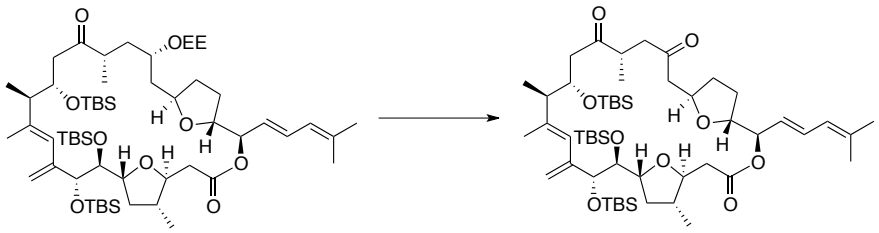
was extracted with EtOAc / Et_2O (1:1, 3 X 20 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-30 % EtOAc / hexanes, to give carboxylic acid **41** (30.7 mg, 26.3 µmol, 85%) as light yellow oil: $[\alpha]_D^{23}$ = +23.4 (*c* = 0.87, C_6H_6); IR (neat): 3385, 2959, 2930, 2886, 2862, 1713, 1465, 1382, 1252, 1084, 1005, 835, 776 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 10.00 (bs, 1H (2 diastereomers)), 6.43-6.48 (m, 1H (2 diastereomers)), 5.83 (d, *J* = 10.9 Hz, 1H (2 diastereomers)), 5.60 (s, 1H (1 diastereomer)), 5.59 (s, 1H (1 diastereomer)), 5.53 (ddd, *J* = 15.1, 6.0, 2.8 Hz, 1H (2 diastereomers)), 5.36 (t, *J* = 1.8 Hz, 1H (1 diastereomer)), 5.35 (t, *J* = 1.7 Hz, 1H (1 diastereomer)), 5.00 (s, 1H (2 diastereomers)), 4.68 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.66 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.41-4.44 (m, 1H (1 diastereomer)), 4.36-4.38 (m, 1H (1 diastereomer)), 4.17 (t, *J* = 5.4 Hz, 1H (1 diastereomer)), 4.16 (t, *J* = 5.3 Hz, 1H (1 diastereomer)), 4.10-4.13 (m, 2H (2 diastereomers)), 3.89-3.98 (m, 2H (2 diastereomers)), 3.76-3.80 (m, 1H (1 diastereomer)), 3.61-3.68 (m, 2H (2 diastereomers)), 3.52-3.60 (m, 2H (2 diastereomers)), 3.46-3.50 (m, 1H (1 diastereomer)), 2.78-2.83 (m, 1H (1 diastereomer)), 2.58-2.70 (m, 3H (1H of 1 diastereomer and 2H of 2 diastereomers)), 2.39-2.54 (m, 3H (2 diastereomers)), 2.10-2.14 (m, 1H (2 diastereomers)), 1.94-2.01 (m, 2H (2 diastereomers)), 1.81-1.93 (m, 3H (2 diastereomers)), 1.83 (d, *J* = 1.0 Hz, 3H (1 diastereomer)), 1.82 (d, *J* = 1.0 Hz, 3H (1 diastereomer)), 1.79 (s, 3H (2 diastereomers)), 1.77 (s, 3H (2 diastereomers)), 1.66-1.73 (m, 1H (2 diastereomers)), 1.48-1.53 (m, 1H (2 diastereomers)), 1.36-1.47 (m, 2H (2 diastereomers)), 1.27-1.34 (m, 4H (2 diastereomers)), 1.22 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.21 (t, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.104 (d, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.102 (d, *J* = 7.0 Hz, 3H (1 diastereomer)), 1.05 (d, *J* = 6.9 Hz, 3H (2 diastereomers)), 1.03 (d, *J* = 6.5 Hz, 3H (1 diastereomer)), 1.01 (d, *J* = 6.5 Hz, 3H (1 diastereomer)), 0.97 (t, *J* = 7.9 Hz, 3H (2 diastereomers)), 0.89-0.92 (m, 27H (4 diastereomers)), 0.62 (q, *J* = 7.9 Hz, 6H (2 diastereomers)), 0.01-0.12 (m, 18H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 213.0, 212.6, 172.0, 144.9, 141.5, 141.4, 135.16, 135.10, 129.88, 129.82, 127.5, 125.1, 124.8, 124.6, 115.1, 114.7, 99.7, 98.5, 82.2, 82.1, 80.2, 80.16, 80.11, 78.9, 78.7, 78.0, 76.17, 76.12, 75.6, 75.5, 72.5, 71.2, 70.4, 70.2, 61.7, 61.1, 47.8, 47.7, 45.4, 45.1, 43.1, 42.7, 41.8, 41.2, 39.8, 37.9, 37.7, 37.58, 37.55, 37.1, 36.9, 32.9, 32.6, 29.7, 27.4, 26.09, 26.01, 25.9, 25.8, 20.8, 20.7, 18.3, 18.2, 17.9, 17.2, 17.1, 16.1, 15.69, 15.65, 15.5, 15.39, 15.34, 14.1, 13.8, 6.9, 4.9, -3.9, -4.40, -4.43, -4.47, -4.71, -4.74, -4.78; HRMS (ES+) calcd. for $C_{63}H_{120}O_{11}Si_4Na$ (M+Na) 1187.7805, found 1187.7740.



Macrolactone 43: To a stirred solution of carboxylic acid **41** (30.7 mg, 26.3 µmol) in dry MeOH (2.5 mL) at 0 ºC was added methanolic PPTS solution (50 µL).[10] After 15 min, the reaction was warmed to rt. After another 35 min, the reaction was quenched with sat. aq. $NaHCO_3$ (8 mL) and the aqueous layer was extracted with EtOAc (3 X 20 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give the intermediate crude seco acid **42**.

To a stirred solution of crude seco acid **42** in THF (1.0 mL) at 0 ºC were added Et_3N (4.7 mg, 6.6 µL, 46.7 µmol) followed by 2,4,6-trichlorobenzoyl chloride (7.6 mg, 4.9 µL, 31.1 µmol). After 45 min, the reaction was diluted with toluene (1.8 mL). In a separate flask, a solution of DMAP (5.7 mg, 46.7 µmol) in toluene (7.0 mL) was warmed to 70 ºC and the solution of mixed acid anhydride was added dropwise over 6 h to it. After another 30 min, the reaction was cooled down to rt and was directly loaded onto column and purified by flash chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give macrolactone **43** (17.7 mg, 17.1 µmol, 65%) as colorless oil: $[\alpha]_D^{23}$ = +2.0 (*c* = 1.00, $CHCl_3$); IR: (neat) 2959, 2930, 2859, 1745, 1708, 1465, 1384, 1255, 1090, 837, 778 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 6.52-6.56 (m, 1H (2 diastereomers)), 6.17 (s, 1H (1 diastereomer)), 6.16 (s, 1H (1 diastereomer)), 5.78 (d, *J* = 11.0 Hz, 1H (2 diastereomers)), 5.35-5.38 (m, 1H (2 diastereomers)), 5.00 (s, 1H (1 diastereomer)), 4.98 (s, 1H (1 diastereomer)), 4.95 (t, *J* = 8.3 Hz, 1H (2 diastereomers)), 4.91 (s, 1H (1 diastereomer)), 4.70 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.67 (q, *J* = 5.2 Hz, 1H (1 diastereomer)), 4.20 (s, 1H (1 diastereomer)), 4.19 (s, 1H (1 diastereomer)), 3.96-4.05 (m, 2H (2 diastereomers)), 3.89-3.94 (m, 2H (2 diastereomers)), 3.54-3.76 (m, 4H (2 diastereomers)), 2.95-3.05 (m, 1H (2 diastereomers)), 2.71-2.75 (m, 1H (1 diastereomer)), 2.59-2.63 (m, 1H (1 diastereomer)), 2.45-2.51 (m, 2H (2 diastereomers)), 2.27-2.38 (m, 2H (2 diastereomers)), 2.11 (br s, 1H (2 diastereomers)), 2.04-2.07 (m, 2H (1H of 1 diastereomer and 1H of 2 diastereomers)), 1.91-1.99 (m, 2H (2 diastereomers)), 1.85-1.89 (m, 1H (1 diastereomer)), 1.70-1.81 (m, 10H (2 diastereomers)), 1.49-1.60 (m, 4H (2 diastereomers)), 1.28-1.34 (m, 5H (2 diastereomers)), 1.23 (t, *J* = 7.0 Hz, 3H (2 diastereomers)), 1.08-1.13 (m, 6H (2 diastereomers)), 1.03-1.05 (m, 3H (2 diastereomers)), 0.91 (s, 18H (2 diastereomers)), 0.85 (s, 9H (2 diastereomers)), 0.02-0.11 (m, 18H (2 diastereomers)); ^{13}C NMR (176 MHz, $CDCl_3$) δ 212.0, 211.6, 170.49, 170.45, 146.4, 146.3, 140.83, 140.80, 137.6, 137.5, 131.26, 131.22, 129.0, 125.05, 125.01, 124.2, 114.36, 114.33, 99.7, 97.8, 81.8, 80.0, 79.2, 79.1, 78.8, 78.20, 78.17, 77.7, 77.6, 75.5, 75.2, 71.7, 71.6, 70.2, 62.2, 61.7,

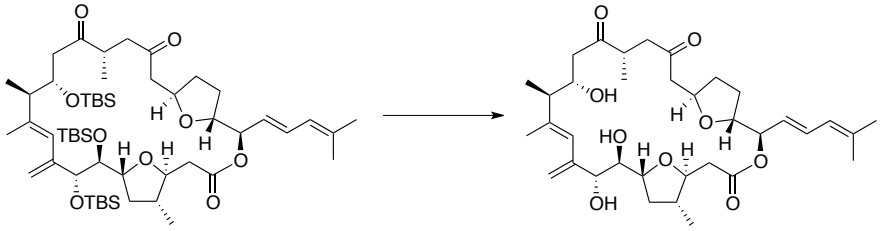
56.0, 47.2, 47.1, 46.2, 42.5, 41.8, 41.7, 40.78, 40.74, 39.88, 39.80, 38.79, 38.73, 34.7, 34.5, 32.7, 31.9, 30.3, 30.2, 29.4, 29.2, 29.0, 26.5, 26.1, 25.9, 25.8, 22.7, 21.2, 21.0, 18.7, 18.58, 18.52, 17.9, 16.6, 16.4, 16.3, 16.2, 16.0, 15.6, 15.2, 14.1, -3.9, -4.0, -4.4, -4.5, -4.6, -4.7, -4.8, -5.4, -5.5; HRMS (ES+) calcd. for $C_{57}H_{104}O_{10}Si_3Na$ (M+Na) 1055.6835, found 1055.6757.



43 62

Diketone 62: The macrolactone **43** (6.8 mg, 6.57 µmol) in THF / AcOH / H_2O (0.78 mL, 4:4:1) was stirred at rt. After 20 h, the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and the aqueous layer was extracted with EtOAc / Et_2O (2:1, 3 X 15 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give the crude alcohol.

To a stirred solution of crude alcohol in CH_2Cl_2 (1.0 mL) at 0 ºC were added pyridine (10.4 mg, 10.7 µL, 0.131 mmol) followed by Dess-Martin periodinane (16.7 mg, 39.5 µmol). After 15 min, the reaction was warmed to rt. After another 2.45 h, the reaction was quenched with sat. aq. $NaHCO_3$ (mL) and the aqueous layer was extracted with Et_2O (3 X 15 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-15% EtOAc / hexanes, to give diketone **62** (3.9 mg, 4.06 µmol, 62%) as colorless oil: $[\alpha]_D^{23}$ = +0.92 (*c* = 0.55, $CHCl_3$); IR: (neat) 2959, 2929, 2860, 1740, 1708, 1662, 1632, 1467, 1387, 1258, 1098, 1045, 838, 781 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$, ***Note:*** *NMR analysis indicated that compound* ***62*** *exists as a mixture of comformational isomers*) δ 6.54 (dd, *J* = 15.2, 11.0 Hz, 1H), 6.01 (br s, 0.5H), 5.77 (br d, *J* = 11.0 Hz, 1H), 5.57-5.68 (br m, 0.2H), 5.36-5.47 (br m, 1.3H), 5.12 (br s, 1H), 5.05 (br s, 1H), 4.95 (br s, 1H), 4.42-4.61 (br m, 1H), 4.25 (br s, 1H), 3.91-4.06 (br m, 3H), 3.71 (br s, 0.7H), 3.55 (br s, 1.3H), 2.98 (br s 1H), 2.84-2.87 (br m, 1H), 2.73 (br s, 1H), 2.60 (dd, *J* = 14.3, 3.3 Hz, 1H), 2.43 (br s, 4H), 2.17 (br s, 1H), 2.00 (br s, 2H), 1.86-1.94 (m, 2H), 1.79 (br s, 3H), 1.78 (s, 3H), 1.77 (s, 3H)1.62-1.65 (m, 1H), 1.52-1.58 (m, 2H), 1.22-1.27 (m, 1H), 1.14 (br s, 3H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.03 (br s, 3H), 0.90 (s, 27H), 0.03-0.09 (m, 18H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 211.0, 207.5, 170.5, 146.3, 140.7, 140.3, 137.87, 137.80, 131.6, 128.6, 124.7, 124.2, 114.7, 113.7, 81.4, 80.0, 79.5, 78.7, 75.2, 71.6, 50.4, 46.7, 46.3, 42.8, 41.1, 40.6, 39.8, 38.3, 36.6, 32.2, 28.5, 26.4, 26.06, 26.01, 25.8, 18.5, 18.4, 17.7, 16.5, 15.9, 15.6, -4.1, -4.6, -4.8; HRMS (ES+) calcd. for $C_{53}H_{94}O_9Si_3Na$ (M+Na) 981.6103, found 981.6069.



62 amphidinolide F (**3**)

Amphidinolide F (**3**)**:** To a solution of tri-TBS ether **62** (3.9 mg, 4.06 µmol) in CH_3CN (0.60 mL) at rt was added $Et_3N•3HF$ (0.48 mL) followed by Et_3N (0.41 mL). After 7 d, the reaction was diluted with EtOAc (15 mL) and poured into sat. aq. solution of $NaHCO_3$ (7 mL) and the aqueous layer was extracted with EtOAc (3 X 15 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 1-5% MeOH / EtOAc, to give amphidinolide F (**3**) (1.4 mg, 2.27 µmol, 56%) as pale yellow amorphous solid: $[\alpha]_D^{23}$ = -49.0 (*c* = 0.10, $CHCl_3$), {lit.[11] $[\alpha]_D^{30}$ = -57 (*c* = 0.10, $CHCl_3$)}; ^{1}H NMR (700 MHz, $CDCl_3$, ***Note:*** *NMR data is concentration dependent, data reported below is for 1.4 mg of* ***3*** *in 0.18 mL of* $CDCl_3$) δ 6.55 (dd, *J* = 14.9, 11.0 Hz, 1H), 6.02 (br s, 1H), 5.79 (br d, *J* = 11.0 Hz, 1H), 5.37 (dd, *J* = 15.0, 8.4 Hz, 1H), 5.22 (t, *J* = 8.2 Hz, 1H), 5.20 (d, *J* = 1.3 Hz, 1H), 4.98 (br s, 1H), 4.35-4.39 (m, 1H), 4.15 (br s, 1H), 4.11 (dd, *J* = 14.9, 7.3 Hz, 1H), 4.01 (br s, 1H), 3.97 (br t, *J* = 9.0 Hz, 1H), 3.85-3.88 (m, 1H), 3.84 (dt, *J* = 9.5, 2.6 Hz, 1H), 3.80 (br t, *J* = 7.8 Hz, 1H), 3.56 (br s, 2H), 3.13-3.18 (m, 1H), 3.08 (dd, *J* = 17.5, 8.9 Hz, 1H), 2.77 (dd, *J* = 15.2, 9.1 Hz, 1H), 2.74 (dd, *J* = 15.8, 8.4 Hz, 1H), 2.49-2.58 (m, 4H), 2.34-2.38 (m, 1H), 2.28-2.32 (m, 1H), 2.09-2.14 (m, 2H), 1.94-1.98 (m, 1H), 1.81-1.86 (m, 1H), 1.79 (s, 3H), 1.78 (s, 3H), 1.74 (d, *J* = 1.1 Hz, 3H), 1.47-1.54 (m, 2H), 1.36-1.40 (m, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 213.77, 207.77, 171.22, 144.45, 140.04, 138.29, 132.06, 124.52, 124.19, 124.04, 116.11, 81.45, 79.90, 78.94, 77.84, 76.51(2C), 75.01, 70.62, 49.38, 48.57, 46.03, 45.55, 42.79, 39.79, 38.70, 36.77, 31.98, 28.43, 26.08, 18.51, 16.24, 15.53, 15.40, 13.77; HRMS (ES+) calcd. for $C_{35}H_{53}O_9$ (M+H) 617.3690, found 617.3685.

References

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4. **Preparation of LDA Solution:** To a solution of diisopropylamine (1 equiv.) in THF (0.46 mL per mmol) at -78°C was added n-BuLi (1 equiv., 2.5 M in hexanes). After 5 min, the white slurry was warmed to -10°C and stirred for an additional 15 min.

5. **Preparation of HF•pyr Solution:** The stock solution was prepared by mixing HF•pyr (1.0 mL, 70% HF in pyridine), pyridine (2.0 mL) and THF (5.0 mL).

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10. **Preparation of PPTS Solution:** The stock solution was prepared by mixing PPTS (20.0 mg) in MeOH (3.0 mL).

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First Enantioselective Total Synthesis of Amphidinolide F

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Electronic Supplementary Information: NMR Spectra

First Enantioselective Total Synthesis of Amphidinolide F

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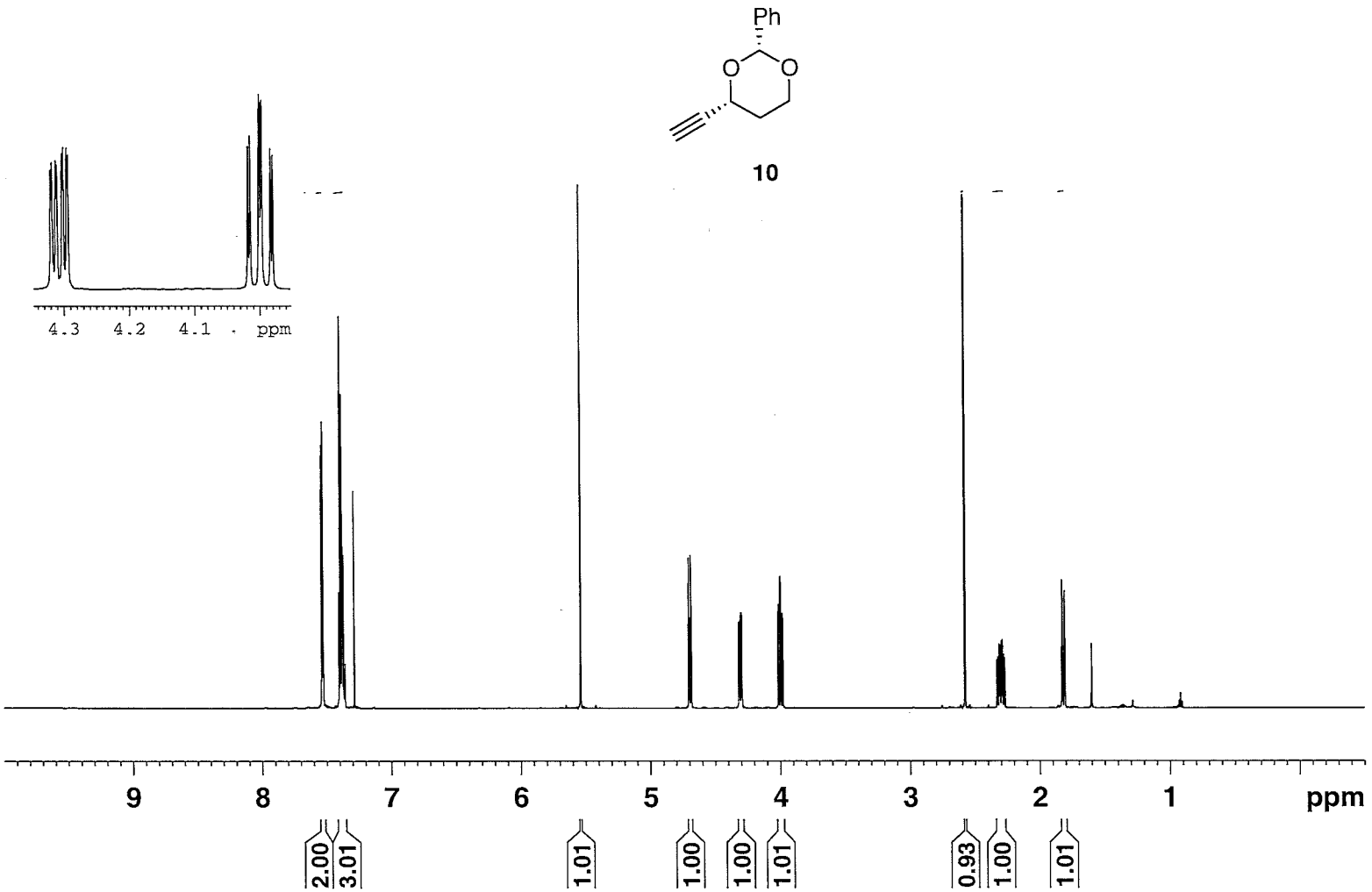
Alkyne

7.541 7.541 7.538 7.529 7.529 7.528 7.408 7.405 7.395 7.393 7.387 7.385 7.382 7.380 7.377 7.370 7.288 5.540 4.707 4.704 4.701 4.691 4.688 4.684 4.319 4.317 4.312 4.310 4.303 4.301 4.296 4.294 4.018 4.014 4.000 3.997 3.996 3.983 3.979 2.579 2.576 1.828 1.826 1.825 1.809 1.807



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FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	22.6
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DE	6.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
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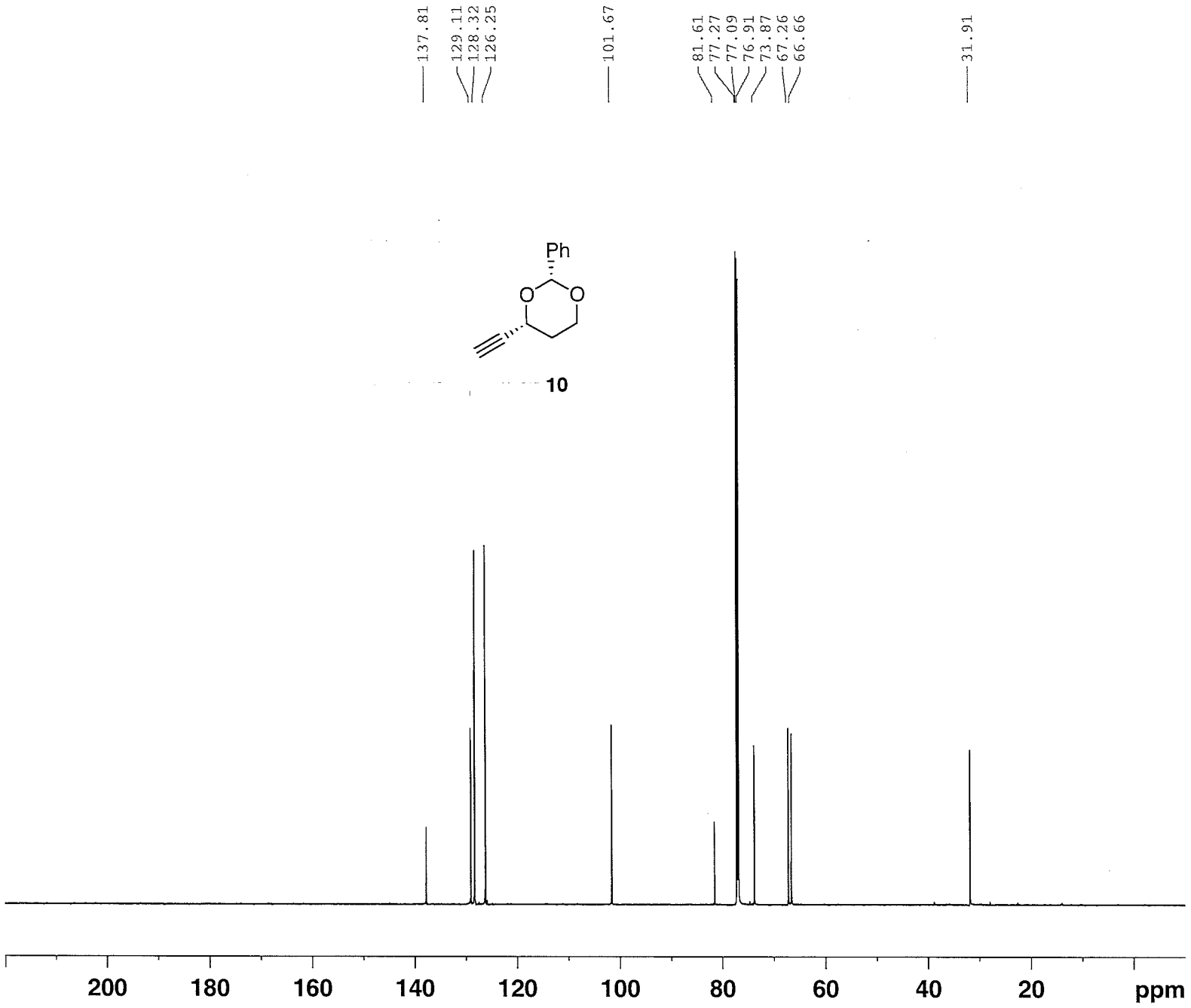
PC	1.00

Alkyne



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SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
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TD0	1
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PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MH
======== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Benzoate Ester

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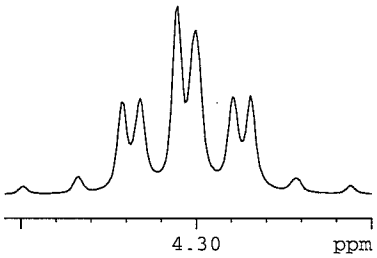

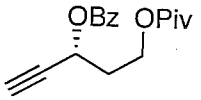

11

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PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6793.478 Hz
FIDRES	0.207320 Hz
AQ	2.4117749 sec
RG	35.9
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DE	6.50 usec
TE	299.4 K
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TD0	1
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P1	14.00 usec
PL1	0.00 dB
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SI	32768
SF	400.1400000 MHz
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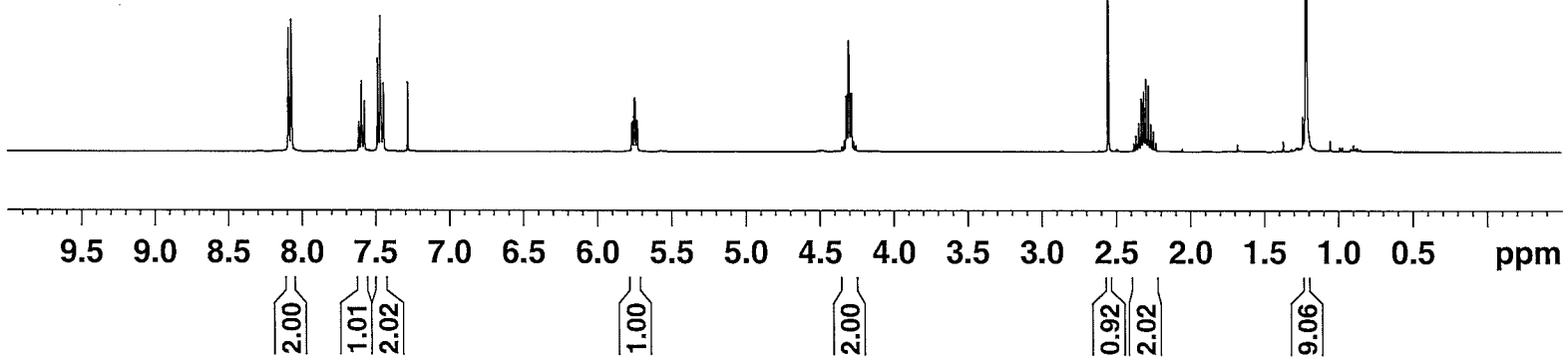
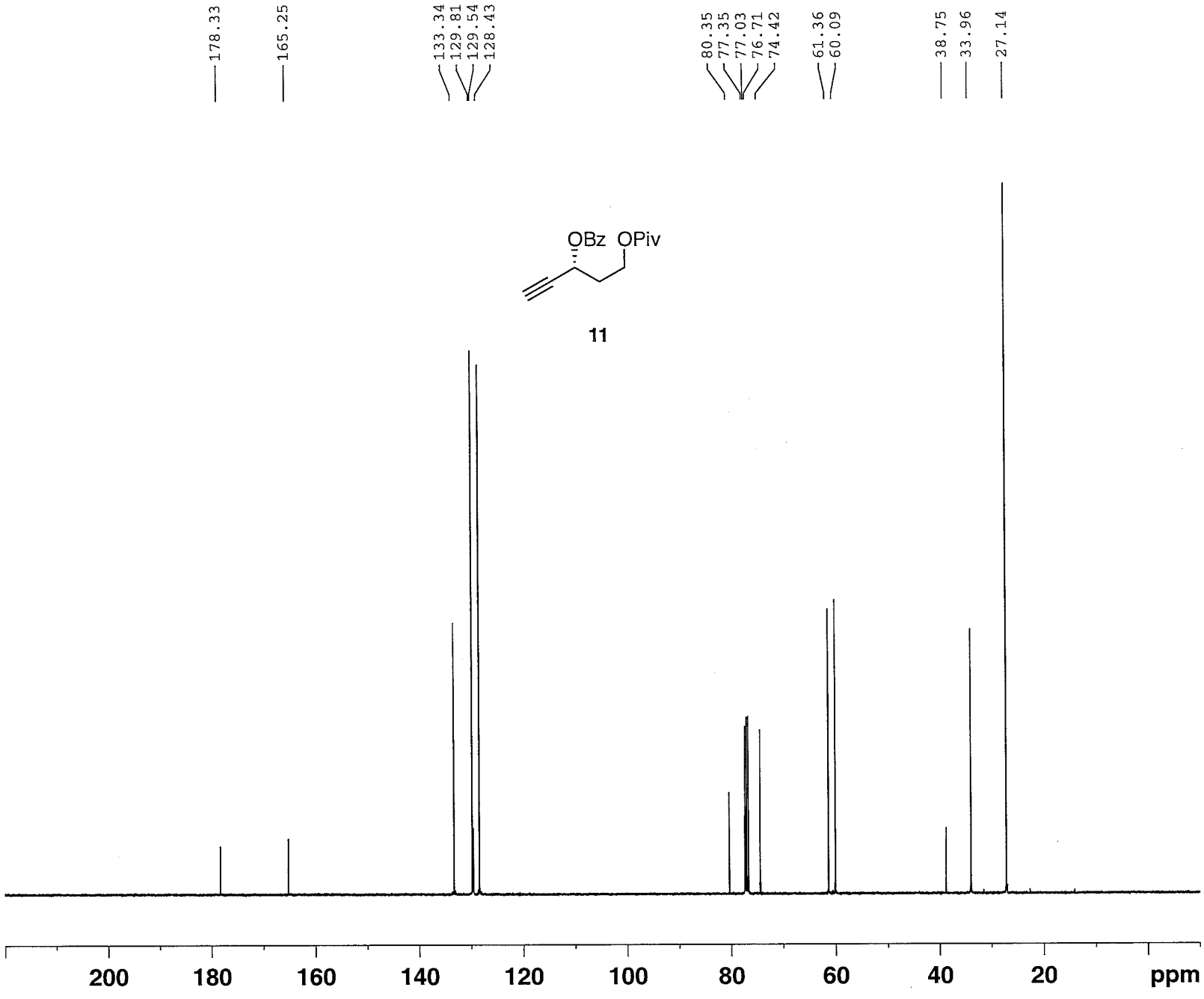
PC	1.00



Benzoate Ester



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TD	65536
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SWH	23980.814 Hz
FIDRES	0.365918 Hz
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RG	18390.4
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DE	6.50 usec
TE	301.7 K
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D11	0.03000000 sec
TD0	1
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P1	9.00 usec
PL1	-2.00 dB
SFO1	100.6258476 MHz
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NUC2	1H
PCPD2	90.00 usec
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PL12	16.16 dB
PL13	17.00 dB
SFO2	400.1416006 MHz
SI	32768
SF	100.6152830 MHz
WDW	EM
SSB	0
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PC	1.40

Eneyne

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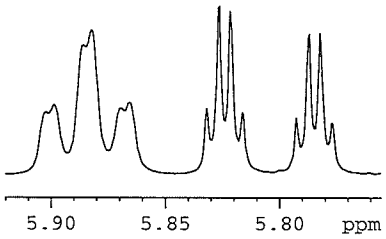

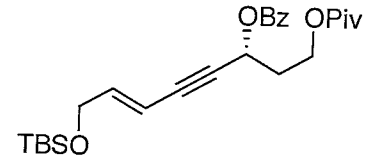

13

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FIDRES	0.207320 Hz
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SI	32768
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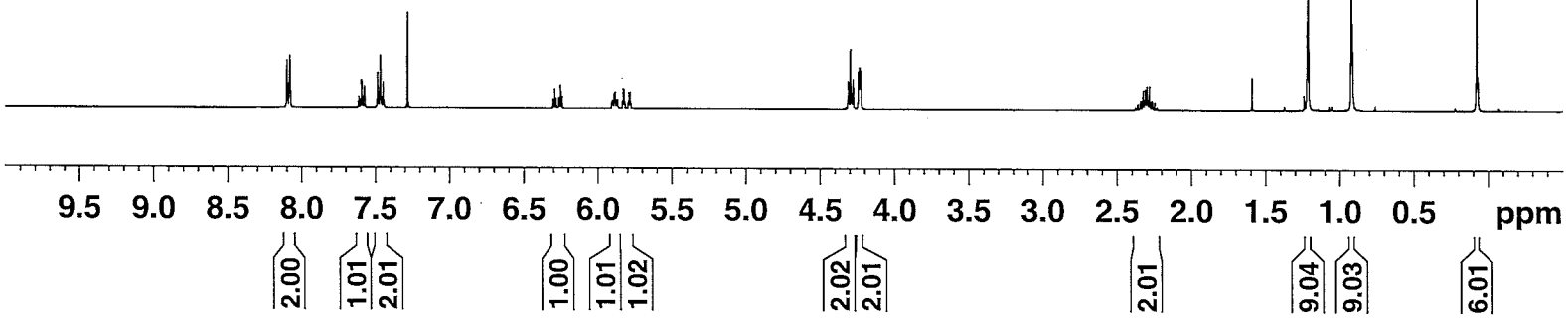

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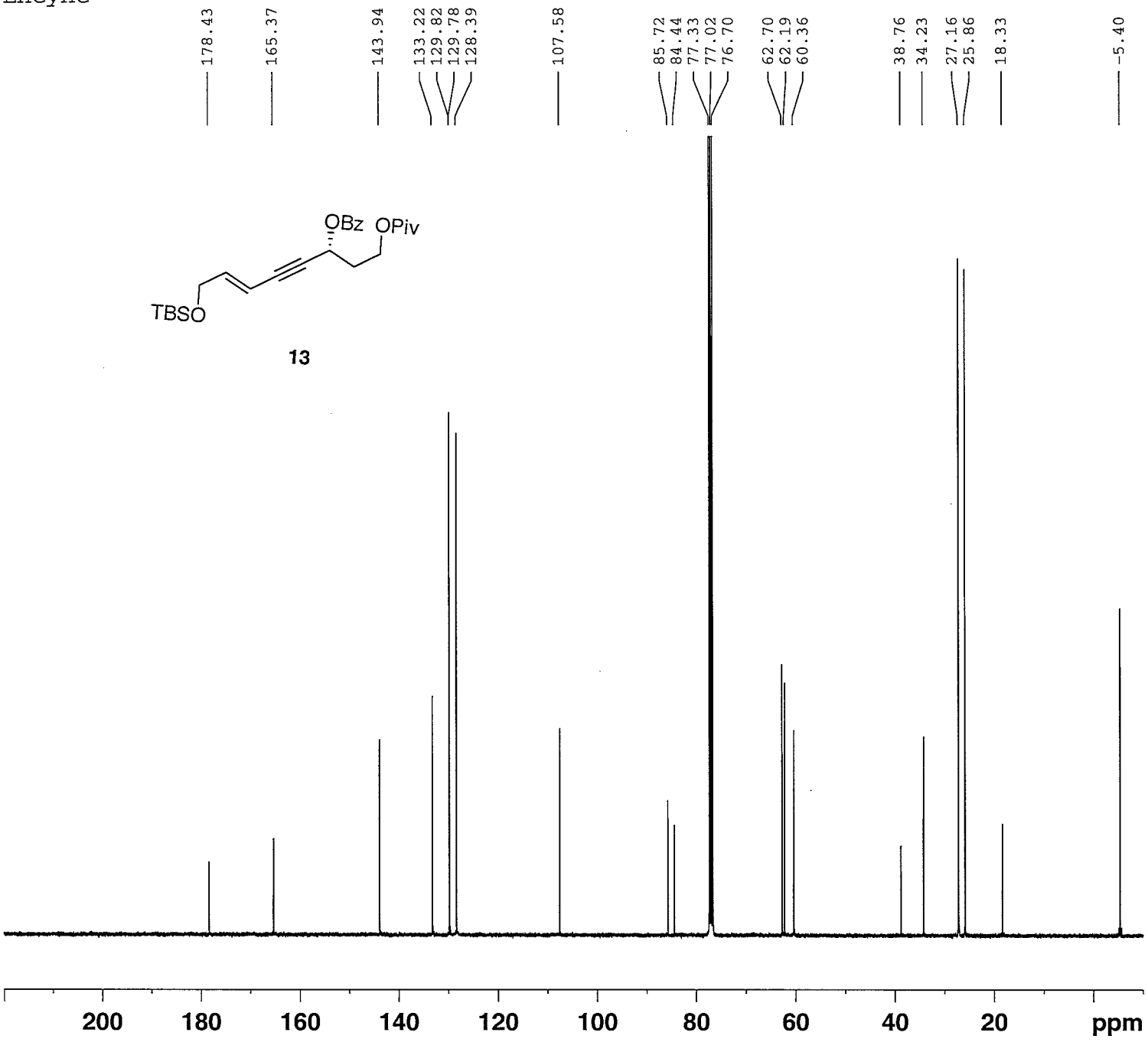


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FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                    16384
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DE                   6.50 usec
TE                  299.3 K
D1              0.20000000 sec
D11             0.03000000 sec
TD0                       1

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PL13                 17.00 dB
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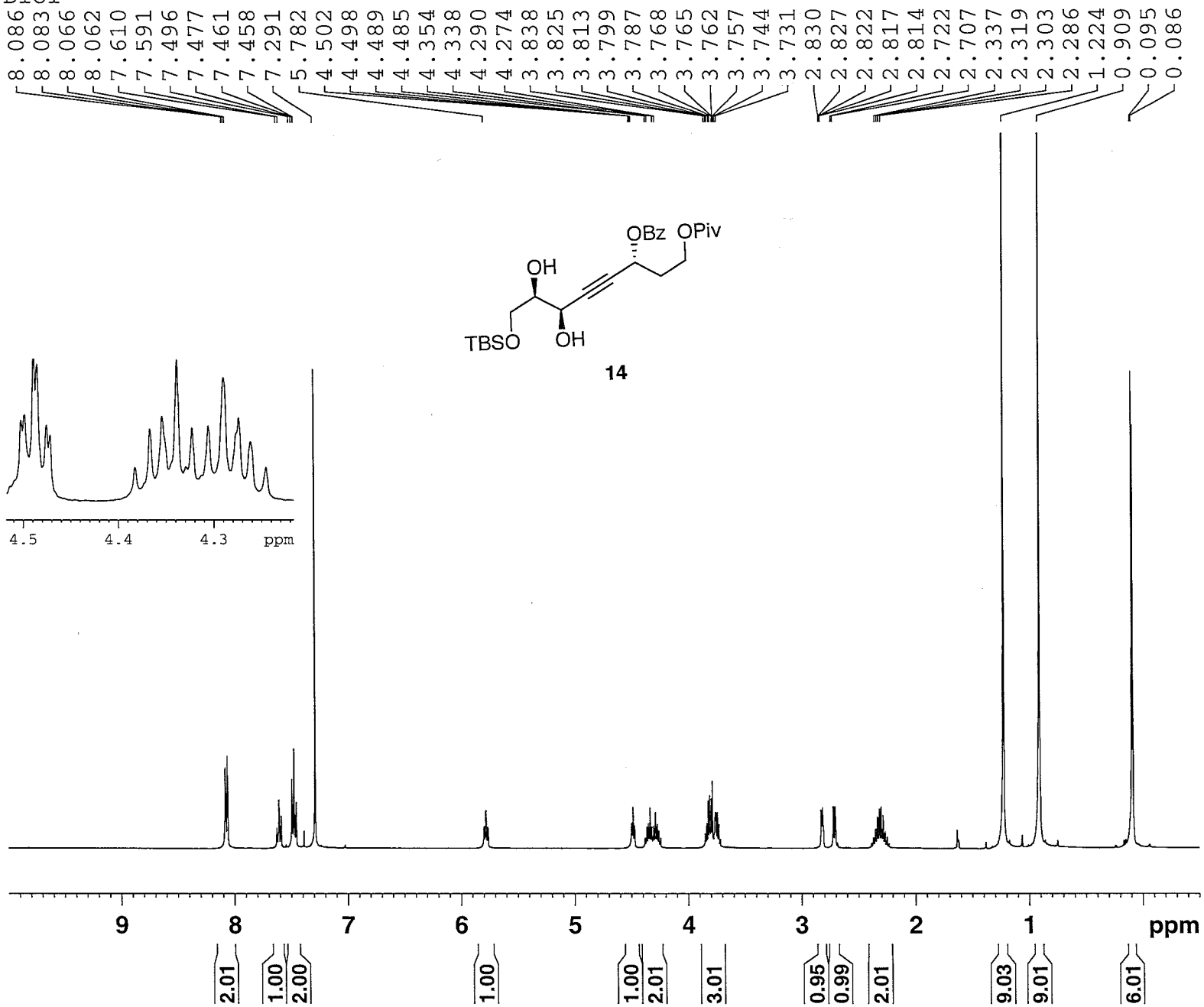
Diol



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PULPROG	zg30
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NS	32
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TE	300.1 K
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SSB	0
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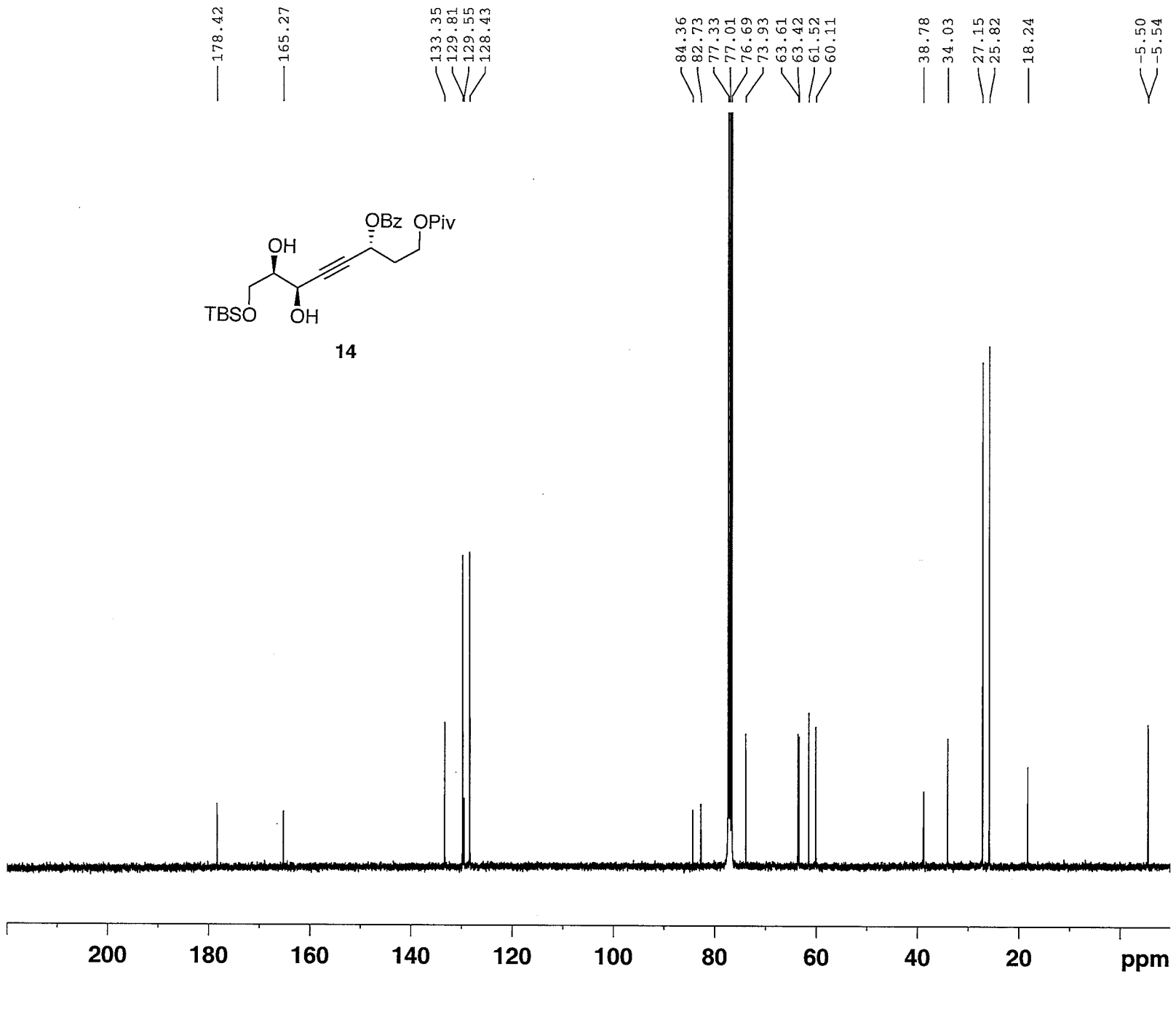
PC	1.00

Diol



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NS	9810
DS	4
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FIDRES	0.383387 H
AQ	1.3042164 s
RG	16384
DW	19.900 u
DE	6.50 u
TE	301.3 K
D1	2.00000000 s
D11	0.03000000 s
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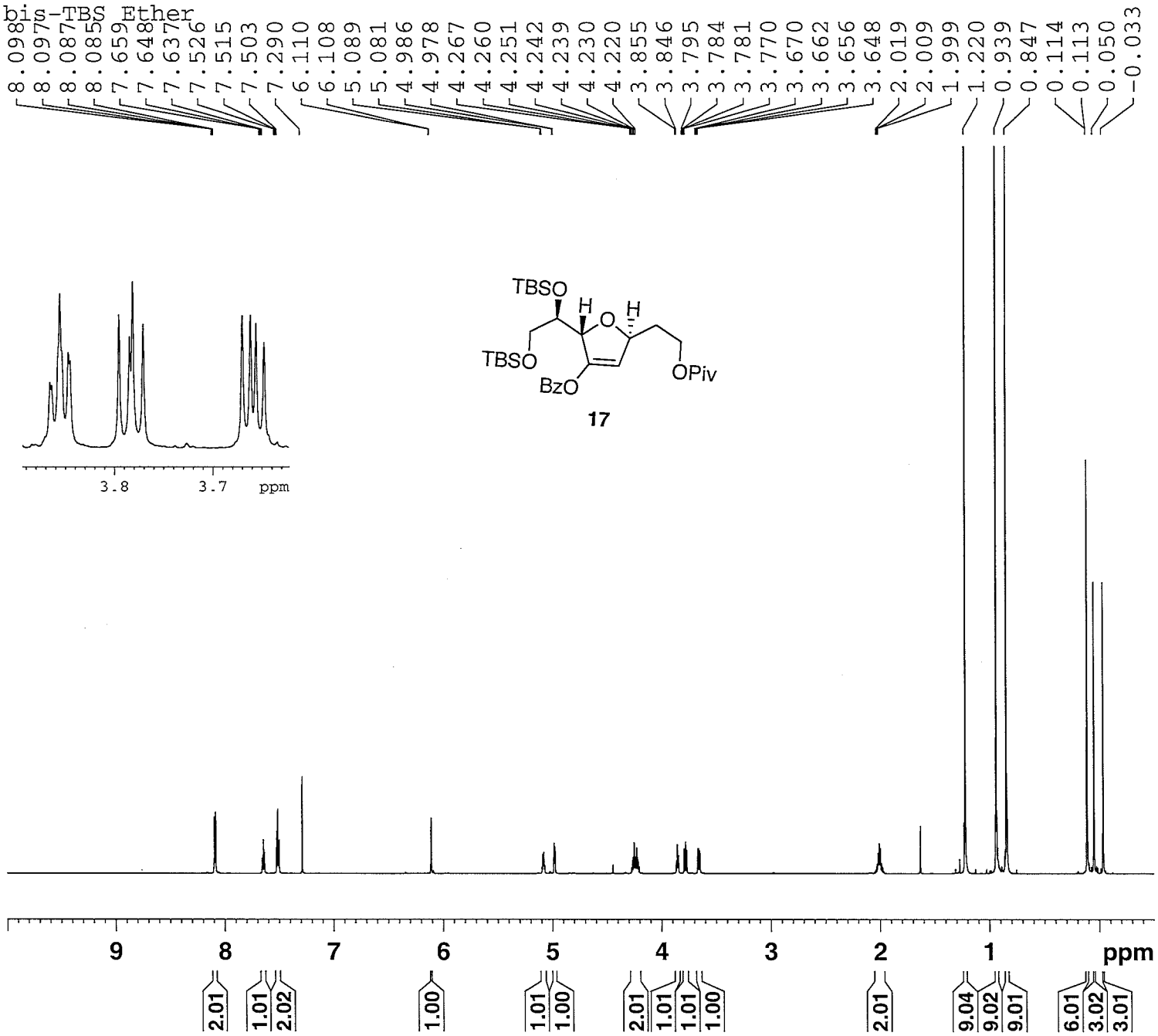
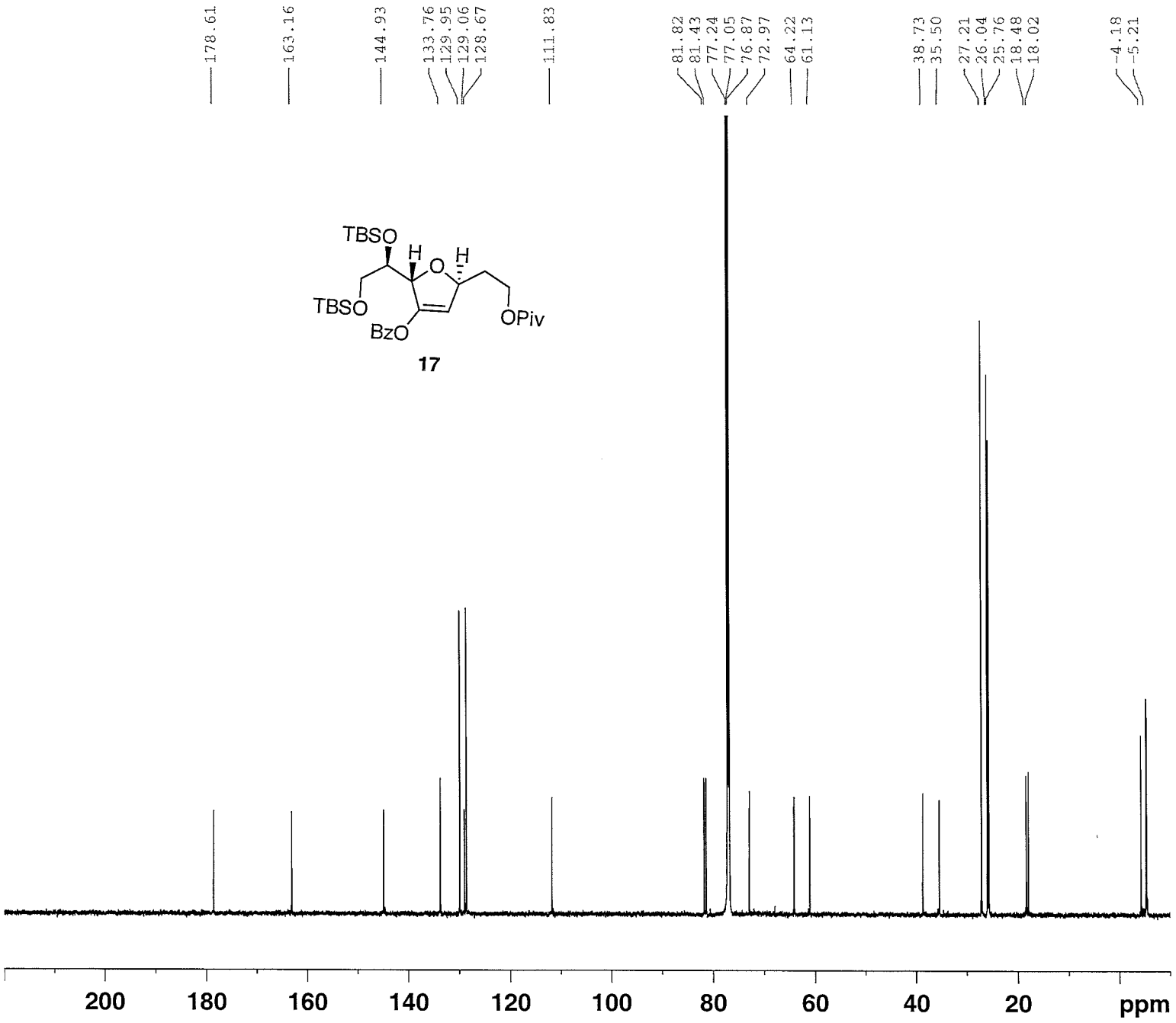
PL1	-2.00 d
PL1W	46.89702606 W
SFO1	100.6255966 M
========	CHANNEL f2 =====
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 u
PL2	0.00 d
PL12	16.16 d
PL13	17.00 d
PL2W	10.27361584 W
PL12W	0.24872722 W
PL13W	0.20498557 W
SFO2	400.1366005 M
SI	32768
SF	100.6140260 M
WDW	EM
SSB	0
LB	1.00 H
GB	0
PC	1.40

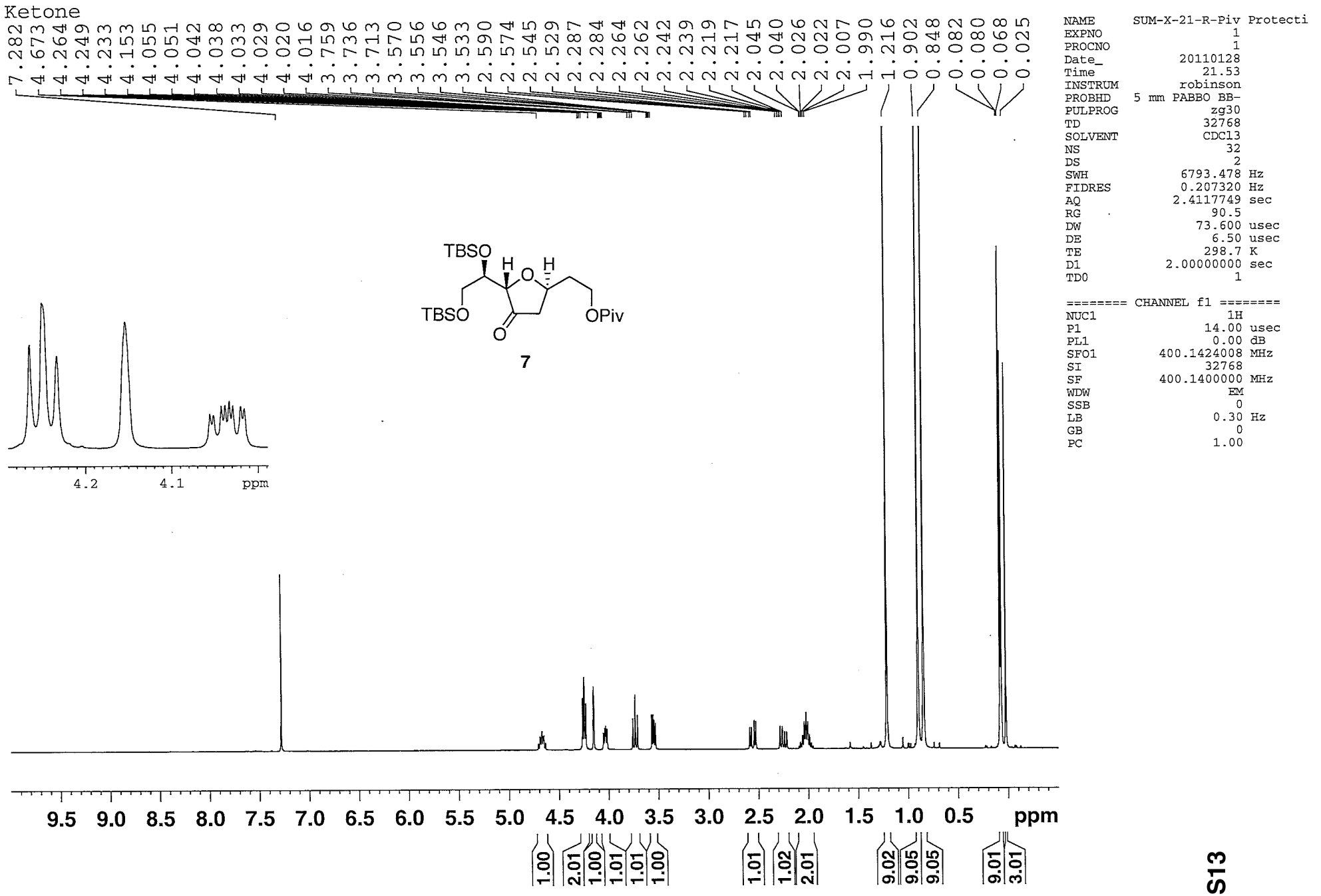


NAME	SUM-XI-77-bis-TBS Eth
EXPNO	1
PROCNO	1
Date_	20110609
Time	22.08
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.181652 Hz
AQ	2.7525620 sec
RG	45.2
DW	42.000 usec
DE	16.50 usec
TE	298.2 K
D1	2.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MHz
SI	65536
SF	700.1200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

bis-TBS Ether



NAME	SUM-XI-77-bis-TBS Eth
EXPNO	2
PROCNO	1
Date_	20110609
Time	22.20
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	133
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	203
DW	12.000 usec
DE	15.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MHz
SI	131072
SF	176.0453140 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40


Ketone
7.282
4.673
4.264
4.249
4.233
4.153
4.055
4.051
4.042
4.038
4.033
4.029
4.020
4.016
3.759
3.736
3.713
3.570
3.556
3.546
3.533
2.590
2.574
2.545
2.529
2.287
2.284
2.264
2.262
2.242
2.239
2.219
2.217
2.045
2.040
2.026
2.022
2.007
1.990
1.216
0.902
0.848
0.082
0.080
0.068
0.025
TBSO
H
O
H
TBSO
OPiv
O
7
4.2
4.1
ppm
NAME SUM-X-21-R-Piv Protecti
EXPNO 1
PROCNO 1
Date_ 20110128
Time 21.53
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 90.5
DW 73.600 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.01
1.00
1.01
1.01
1.00
1.01
1.02
2.01
9.02
9.05
9.05
9.01
3.01

Ketone

216.83
178.43
80.13
77.33
77.01
76.69
74.94
74.70
63.00
61.04
43.64
38.71
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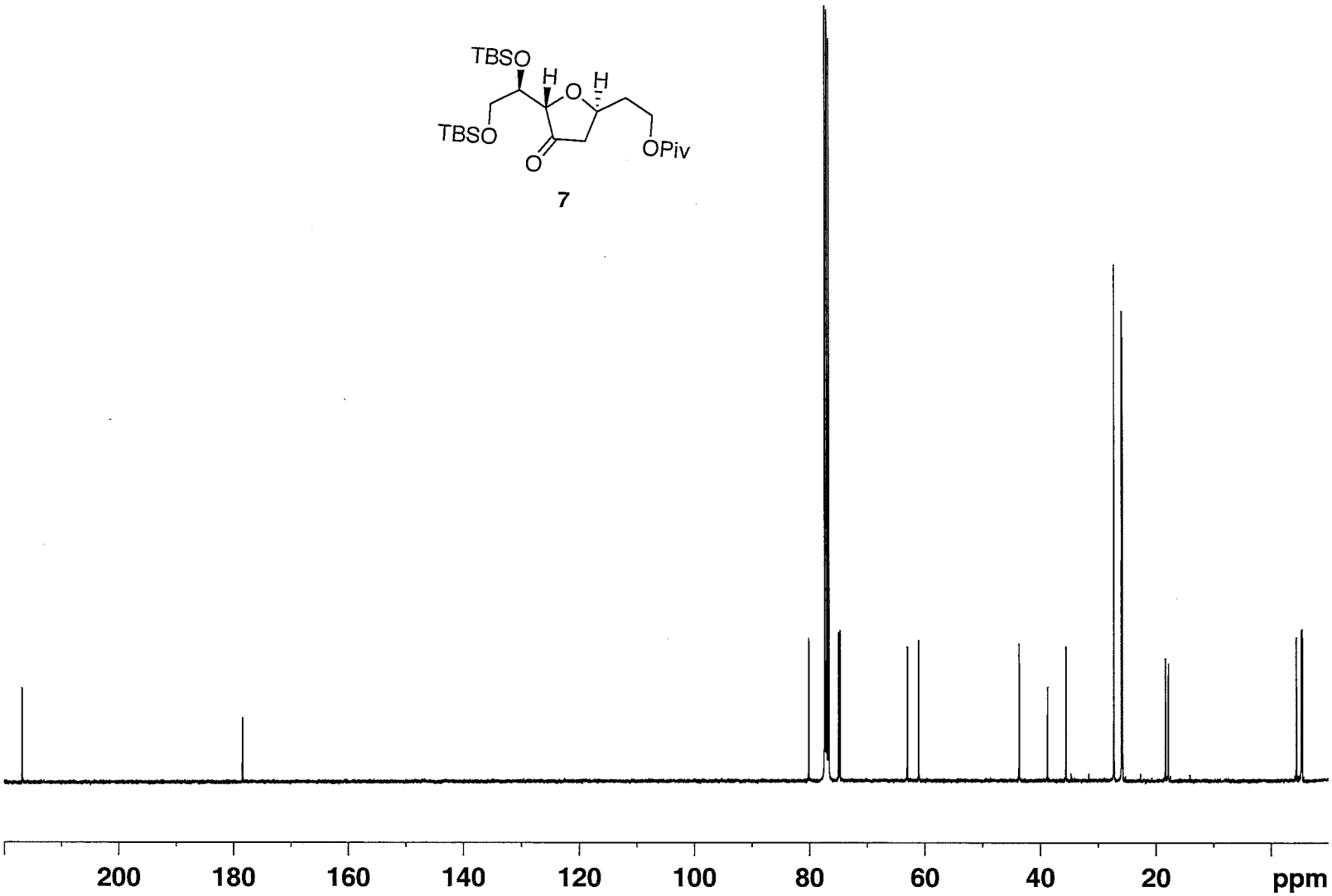
25.90
25.74
18.30
17.83
-4.42
-5.27

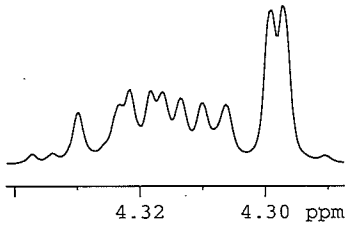
7

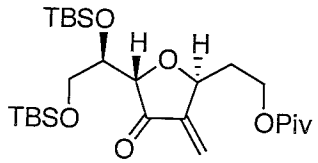


NAME	SM-IV-97-R-Ketor
EXPNO	3
PROCNO	1
Date_	20100423
Time	23.43
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10240
DS	4
SWH	25125.629 H
FIDRES	0.383387 H
AQ	1.3042164 s
RG	18390.4
DW	19.900 u
DE	6.50 u
TE	301.0 K
D1	2.00000000 s
D11	0.03000000 s
TD0	1
========	CHANNEL f1 =====
NUC1	13C
P1	9.00 u
PL1	-2.00 d
PL1W	46.89702606 W
SFO1	100.6255966 M
========	CHANNEL f2 =====
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 u
PL2	0.00 d
PL12	16.16 d
PL13	17.00 d
PL2W	10.27361584 W
PL12W	0.24872722 W
PL13W	0.20498557 W
SFO2	400.1366005 M
SI	32768
SF	100.6140260 M
WDW	EM
SSB	0
LB	1.00 H
GB	0
PC	1.40

Enone

7.290 6.131 6.127 5.347 5.343 5.088 5.083 5.079 5.075 5.071 4.330 4.322 4.318 4.316 4.313 4.310 4.306 4.299 4.297 4.079 4.077 4.072 4.070 4.067 4.064 4.059 4.057 3.772 3.759 3.745 3.558 3.550 3.544 3.536 2.176 1.978 1.965 1.957 1.224 0.911 0.787 0.093 0.090 0.041 -0.038





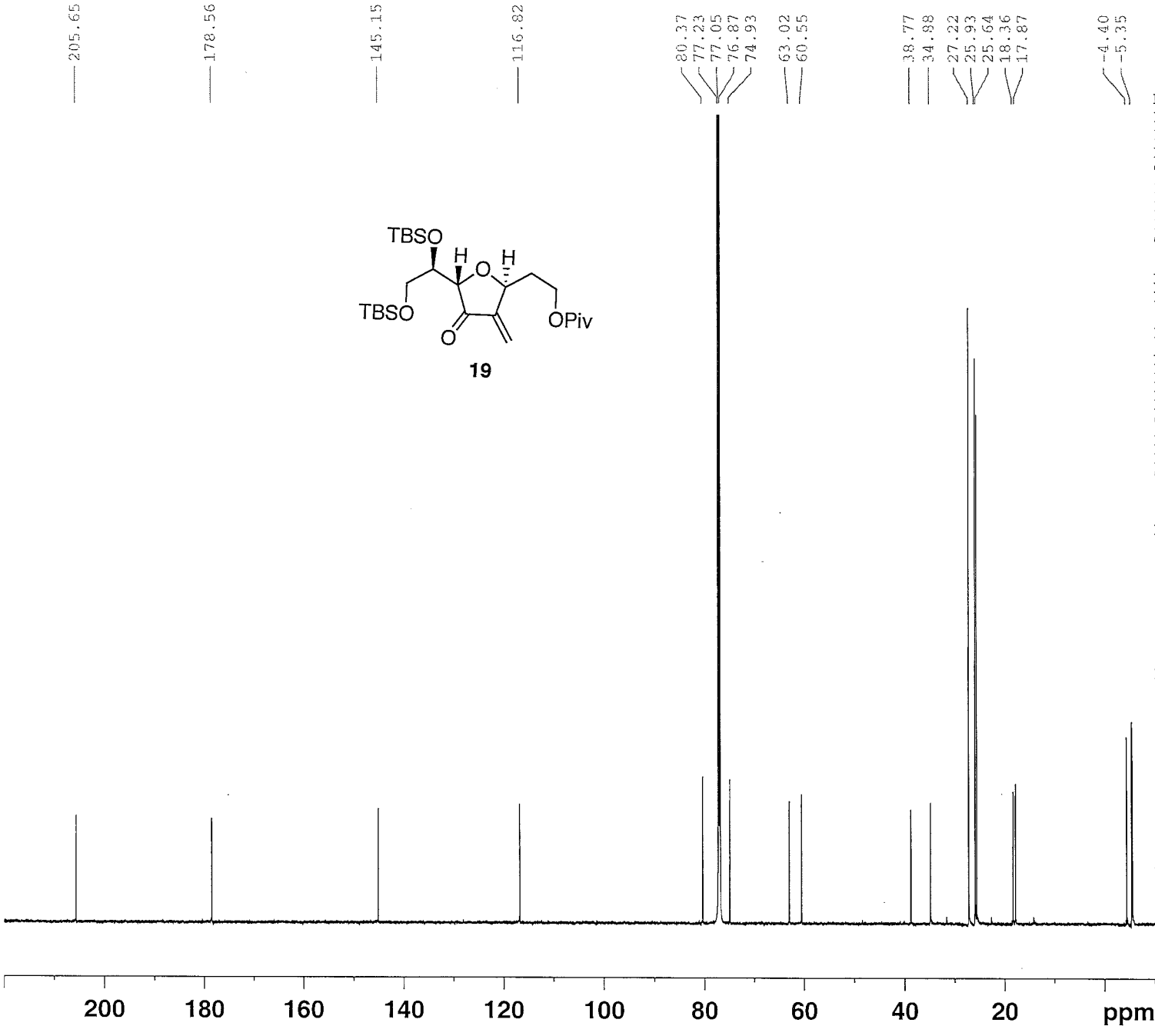
19

NAME	SUM-X-18-Enone
EXPNO	1
PROCNO	1
Date_	20110131
Time	16.51
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	65536
SOLVENT	CDC13
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.181652 Hz
AQ	2.7525620 se
RG	45.2
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	65536
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

9 8 7 6 5 4 3 2 1 ppm

1.00 1.00 1.00 3.01 1.00 1.01 1.01 1.00 1.00 9.02 9.05 9.01 6.02 3.03 3.03

Enone



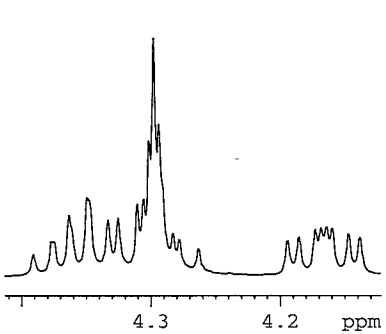
19

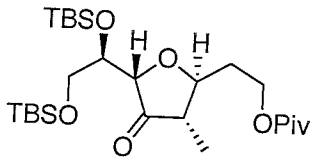
NAME	SUM-X-18-Enone
EXPNO	2
PROCNO	1
Date_	20110131
Time	16.58
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	269
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	203
DW	12.000 usec
DE	15.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MHz
SI	131072
SF	176.0453140 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alpha-Me-Ketone

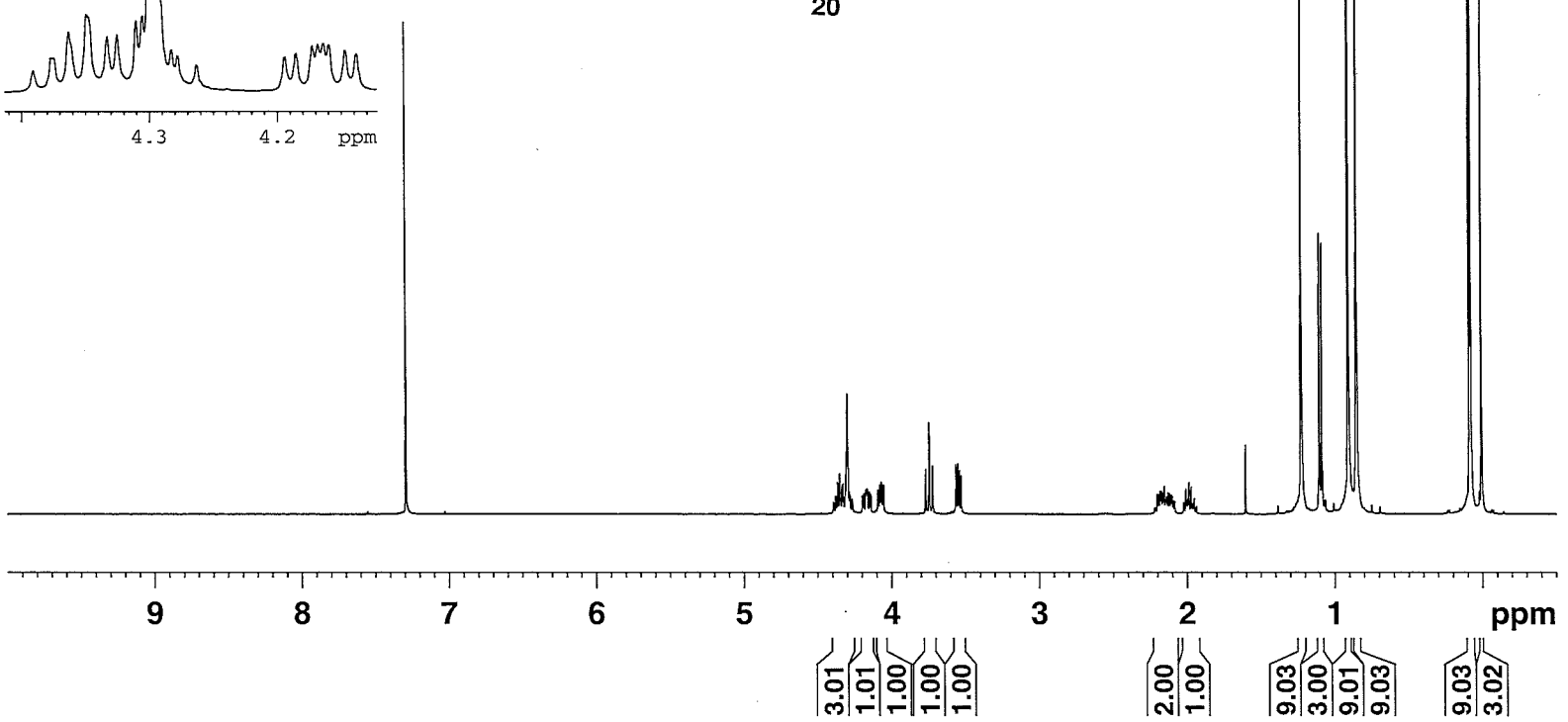
7.292 4.363 4.349 4.347 4.333 4.325 4.310 4.305 4.301 4.297 4.293 4.173 4.168 4.164 4.160 4.091 4.087 4.078 4.074 4.067 4.063 4.055 4.051 3.766 3.742 3.719 3.562 3.550 3.539 3.526 2.179 2.156 2.153 2.126 2.007 1.985 1.971 1.228 1.106 1.088 0.909 0.854 0.090 0.087 0.079 0.009

NAME	SM-VII-10-R-Hydrogenati
EXPNO	4
PROCNO	1
Date_	20100512
Time	22.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	90.5
DW	78.000 usec
DE	6.50 usec
TE	299.4 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.00 usec
PL1	0.00 dB
PL1W	10.27361584 W
SFO1	400.1378009 MHz
SI	32768
SF	400.1350000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

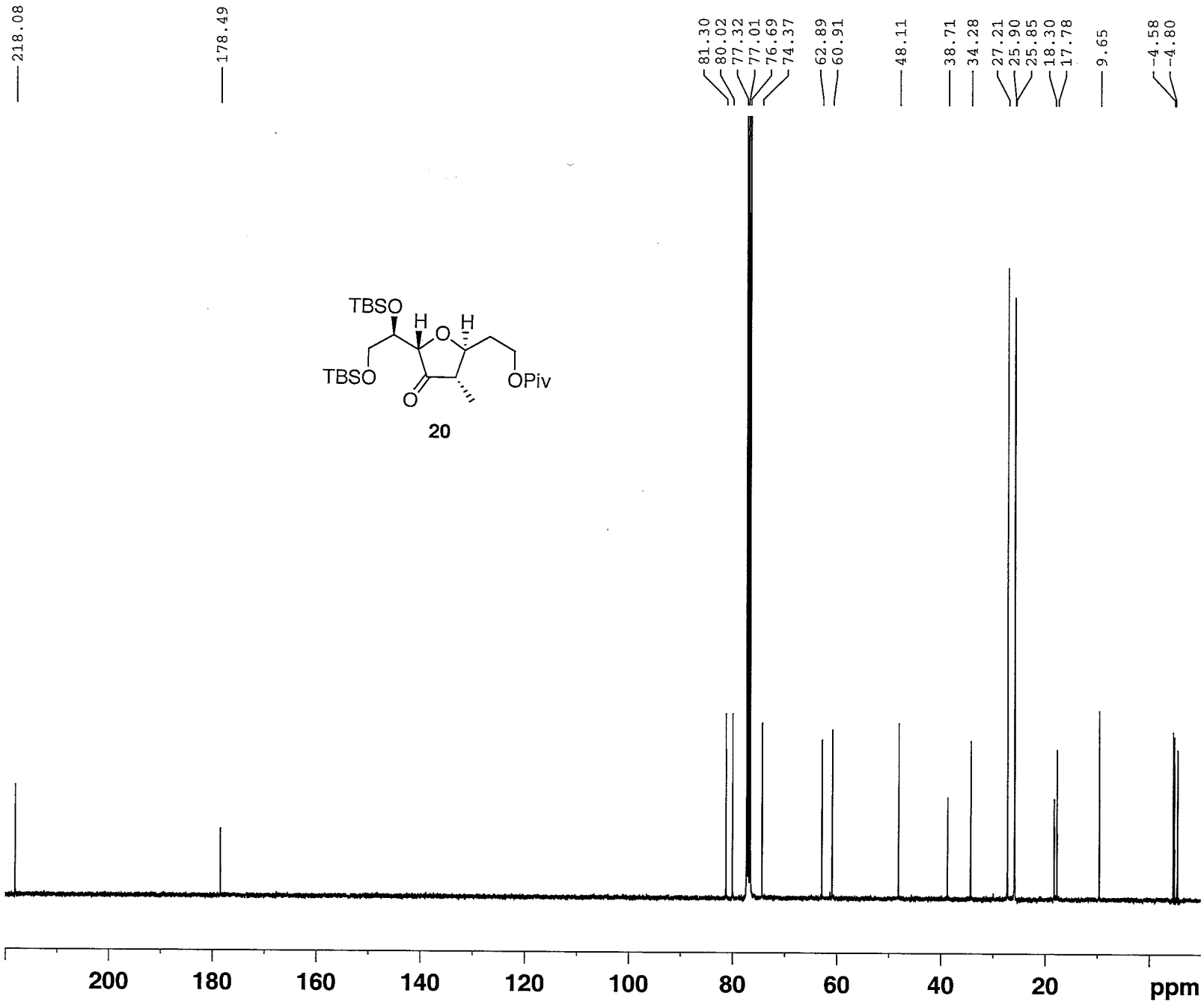




20



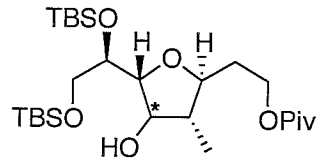
Alpha-Me-Ketone



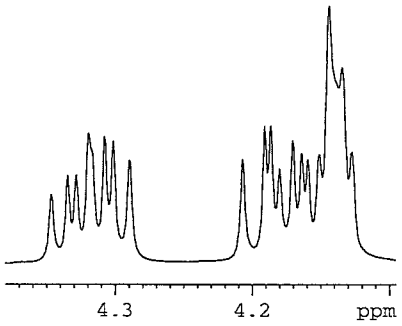
NAME	SM-VII-10-R-Hydrogena
EXPNO	5
PROCNO	1
Date_	20100512
Time	22.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10240
DS	4
SWH	25125.629 Hz
FIDRES	0.383387 Hz
AQ	1.3042164 sec
RG	20642.5
DW	19.900 usec
DE	6.50 usec
TE	300.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.00 usec
PL1	-2.00 dB
PL1W	46.89702606 W
SFO1	100.6255966 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	0.00 dB
PL12	16.16 dB
PL13	17.00 dB
PL2W	10.27361584 W
PL12W	0.24872722 W
PL13W	0.20498557 W
SFO2	400.1366005 MHz
SI	32768
SF	100.6140260 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Alcohol (Major Isomer)

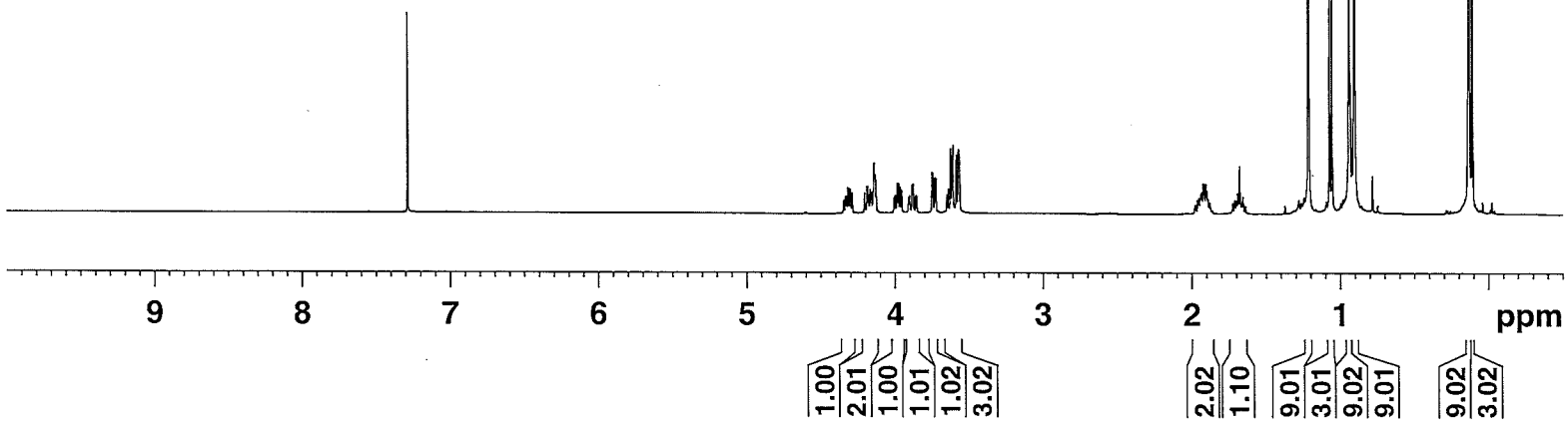
7.291 4.319 4.307 4.301 4.191 4.186 4.170 4.159 4.151 4.143 4.134 4.127 3.985 3.977 3.965 3.955 3.884 3.878 3.751 3.744 3.731 3.724 3.641 3.626 3.616 3.609 3.587 3.572 3.569 3.562 1.934 1.924 1.918 1.906 1.899 1.680 1.675 1.216 1.074 1.057 0.940 0.906 0.137 0.134 0.130 0.110



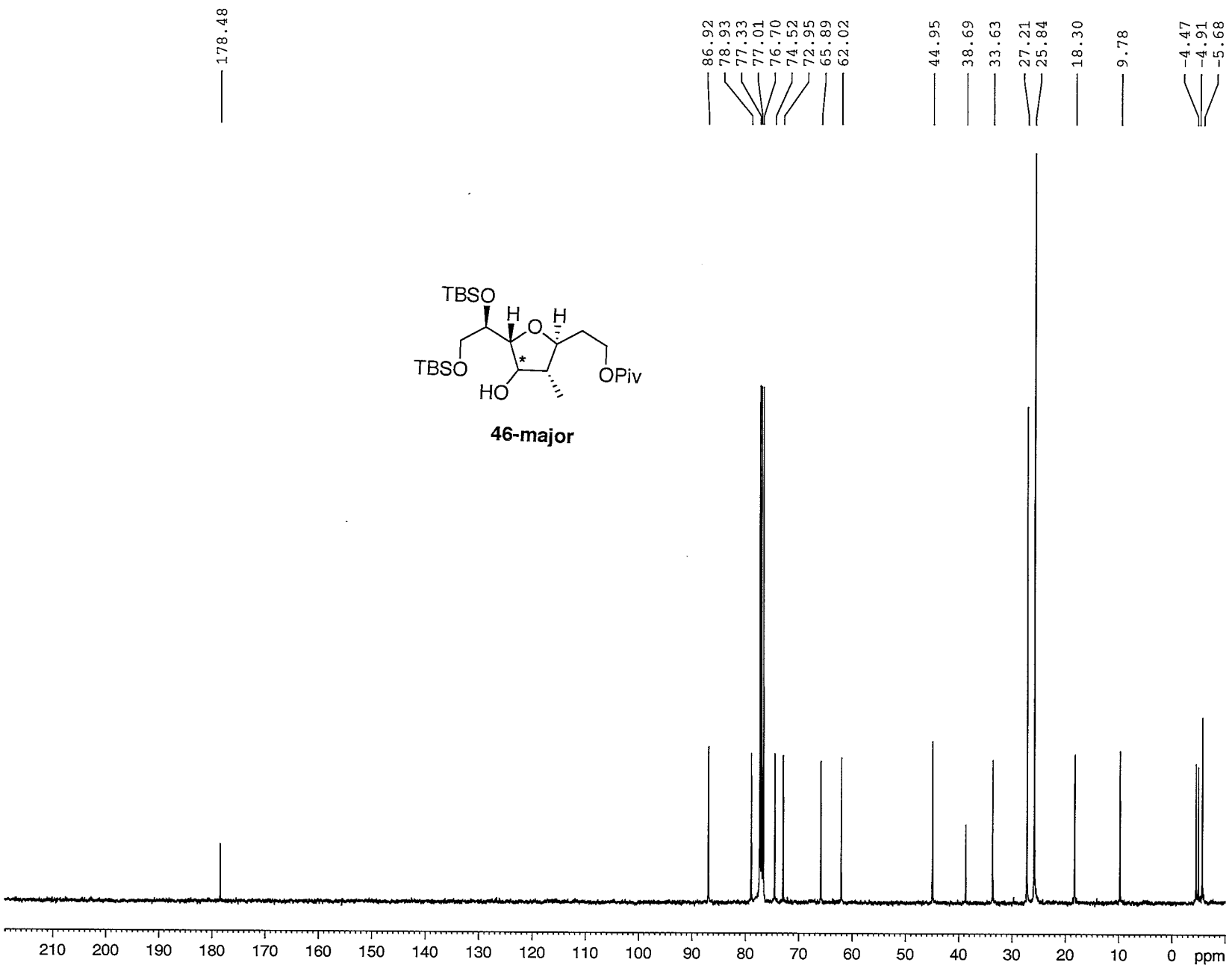
46-major



NAME	SM-VII-12-R-Alcoh
EXPNO	2
PROCNO	1
Date_	20100518
Time	10.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 se
RG	35.9
DW	78.000 us
DE	6.50 us
TE	299.0 K
D1	2.00000000 se
TD0	1
======== CHANNEL f1 =======	
NUC1	1H
P1	14.00 us
PL1	0.00 dB
PL1W	10.27361584 W
SFO1	400.1378009 MH:
SI	32768
SF	400.1350000 MH:
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

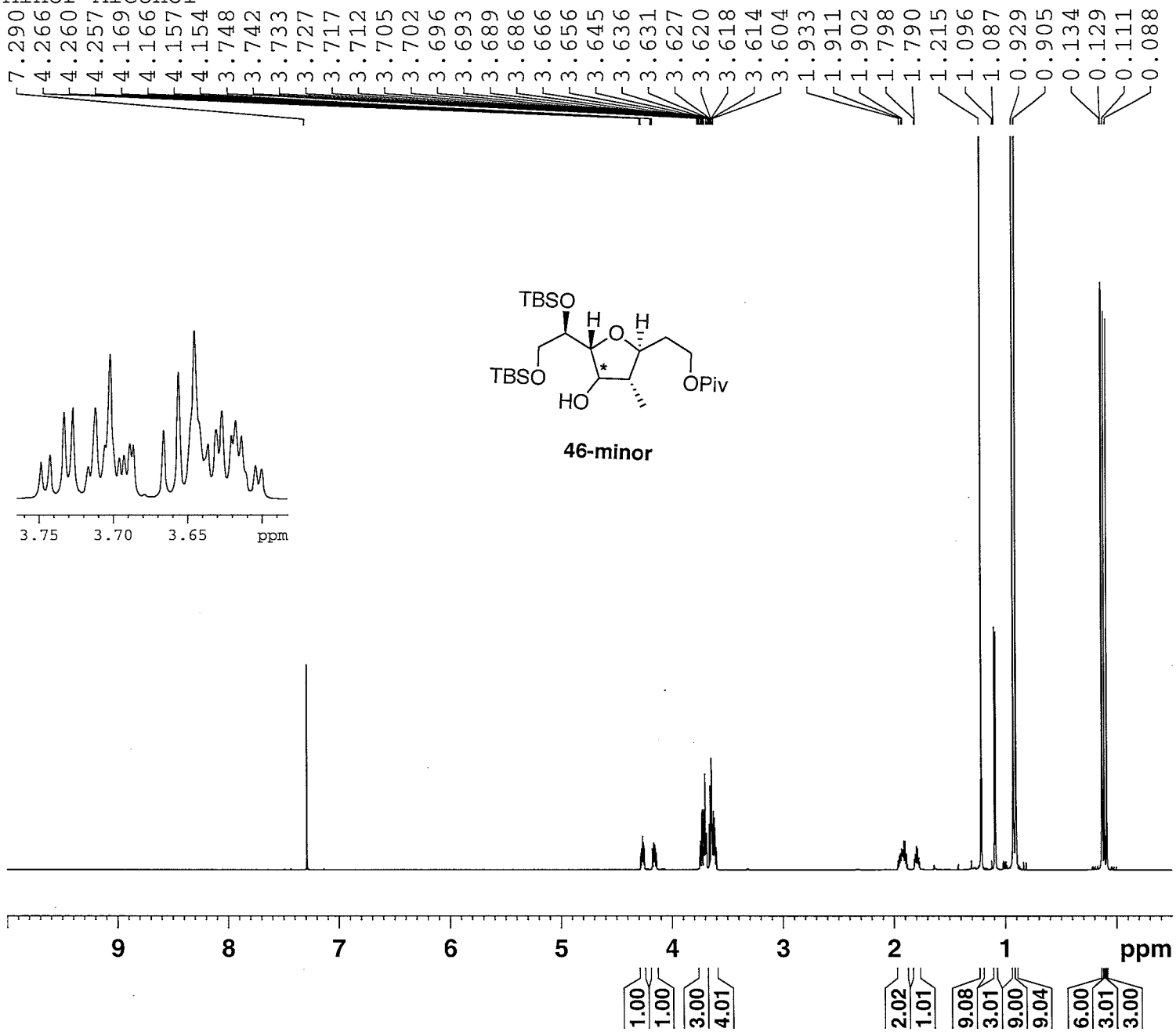


Alcohol (Major Isomer)



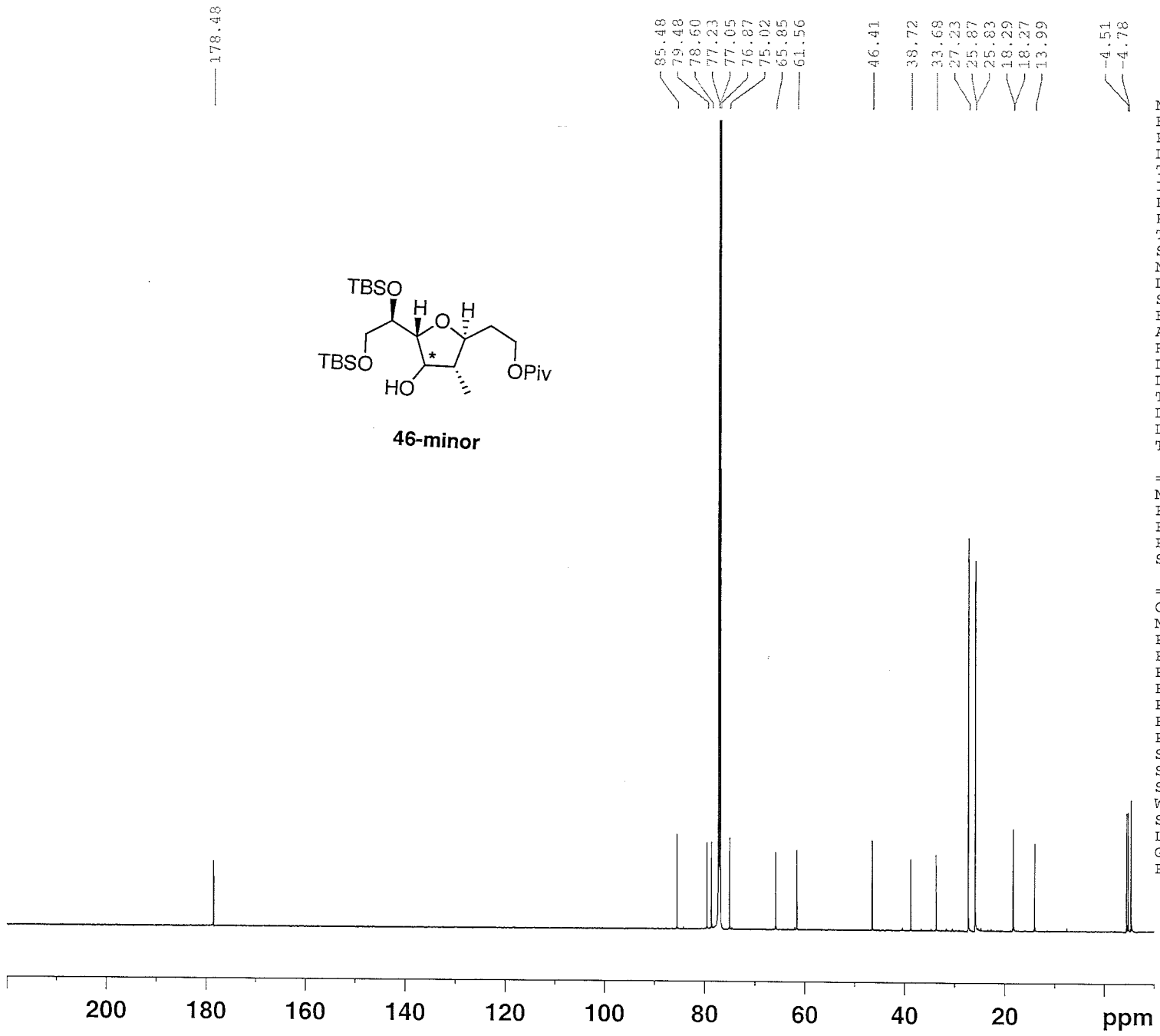

```
Current Data Parameters
NAME      SUM-VII-12-Alcoh
EXPNO                    5
PROCNO                   1
DU                      /m
USER                Subham

F2 - Acquisition Parameter
Date_              20100517
Time                 20.24
INSTRUM             DPX400
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2314
DS                       4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 se
RG                 3649.1
DW                20.850 us
DE                 6.00 us
TE                300.2 K
D1           2.00000000 se
d11          0.03000000 se
DELTA        1.89999998 se
TD0                      1

======== CHANNEL f1 ======
NUC1                   13C
P1                  8.30 us
PL1                -3.00 dB
SFO1        100.6517495 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                   1H
PCPD2              90.00 us
PL2                -3.00 dB
PL12               15.00 dB
PL13               15.00 dB
SFO2        400.2466010 MH

F2 - Processing parameters
SI                   32768
SF          100.6416850 MH
WDW                     EM
SSB                      0
LB                  3.00 Hz
GB                       0
PC                    1.40
```

Minor Alcohol

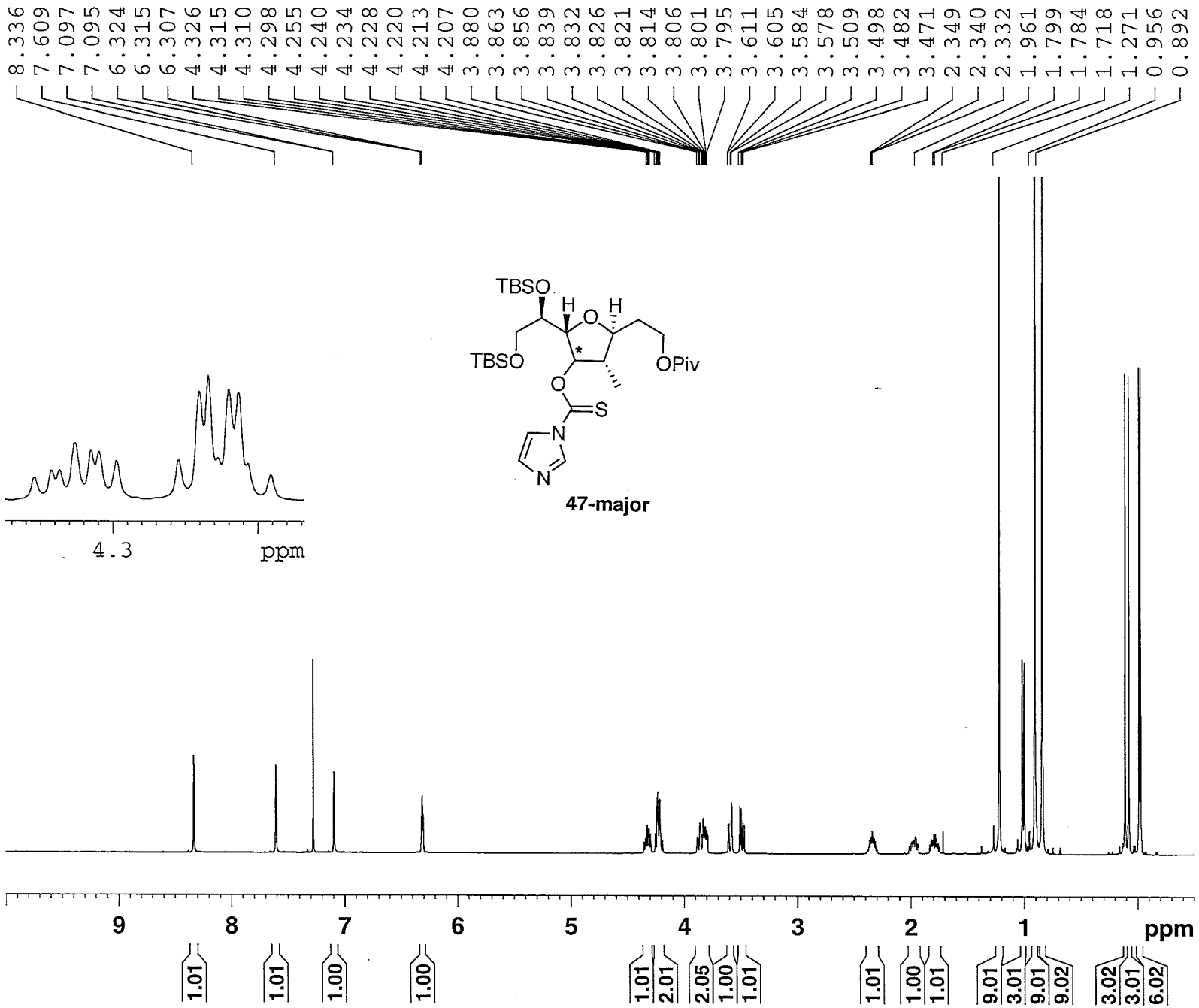


NAME	SUM-X-25-Minor Alcoh
EXPNO	1
PROCNO	1
Date_	20110202
Time	13.38
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.181652 Hz
AQ	2.7525620 sec
RG	50.8
DW	42.000 usec
DE	16.50 usec
TE	298.2 K
D1	2.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MHz
SI	65536
SF	700.1200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Minor Alcohol

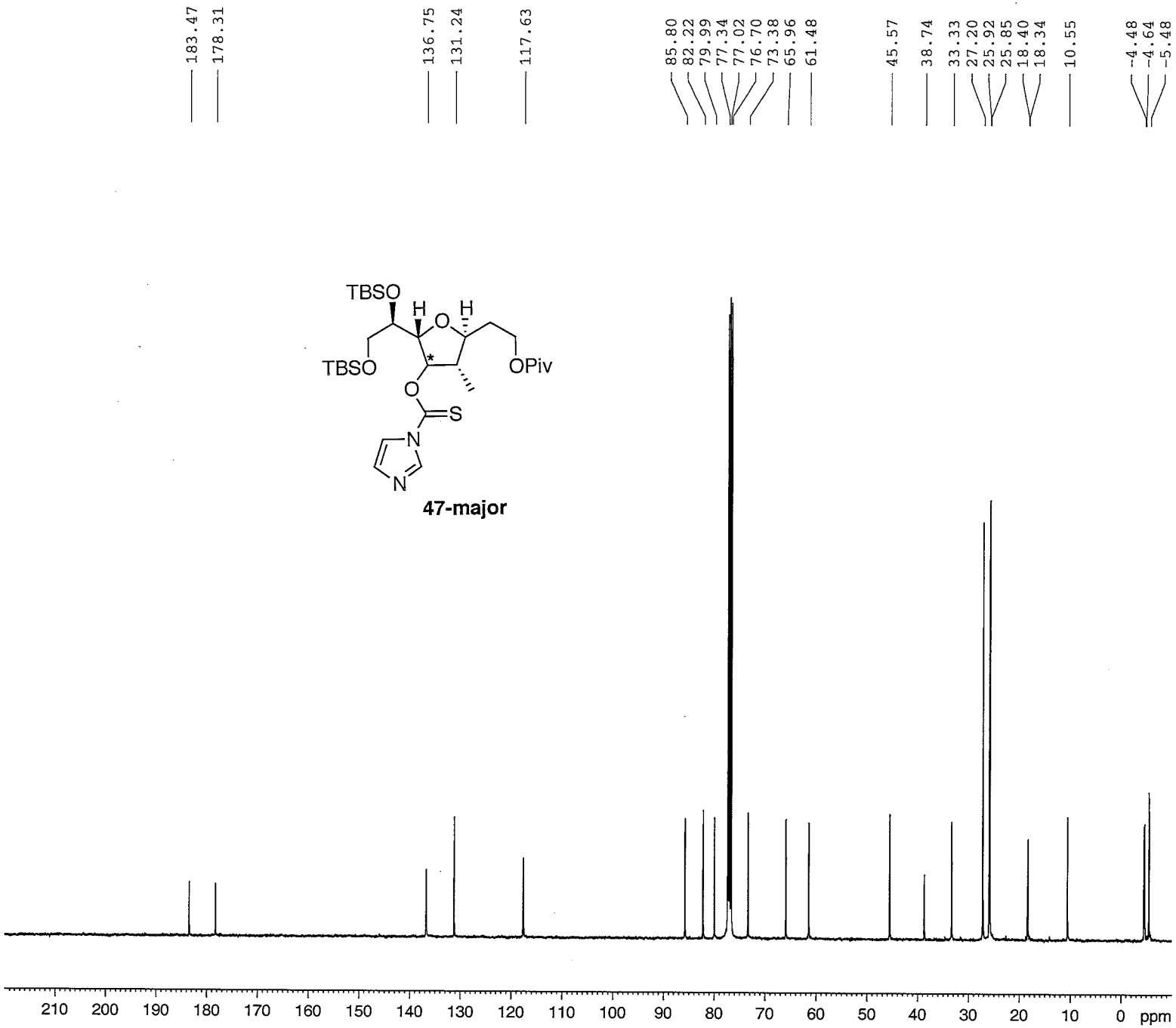


NAME	SUM-X-25-Minor Alcohol
EXPNO	2
PROCNO	1
Date_	20110202
Time	13.54
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	1253
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	203
DW	12.000 usec
DE	15.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MHz
SI	131072
SF	176.0453140 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

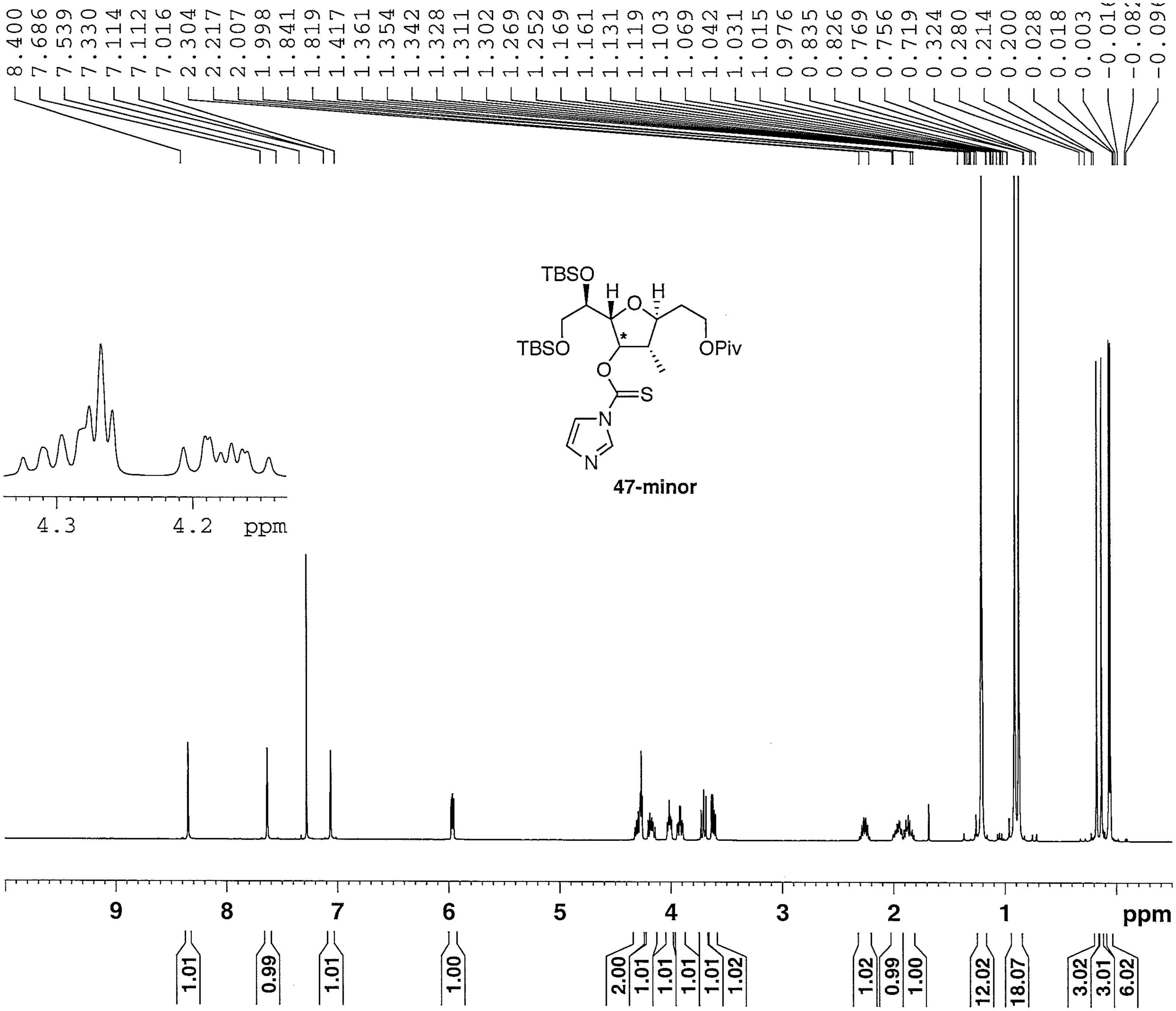



```
Current Data Parameters
NAME      SUM-VII-13-Thioa
EXPNO                    3
PROCNO                   1

F2 - Acquisition Paramete
Date_             20100515
Time                 22.17
INSTRUM            DPX400
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               6410.256 H
FIDRES            0.195625 H
AQ                2.5559540 s
RG                     114
DW                  78.000 u
DE                   6.00 u
TE                  299.2 K
D1             1.00000000 s
TD0                      1

======== CHANNEL f1 =====
NUC1                    1H
P1                  13.50 u
PL1                 -3.00 d
SFO1          400.2478017 M

F2 - Processing parameter
SI                   32768
SF            400.2450000 M
WDW                     EM
SSB                      0
LB                    0.30 H
GB                       0
PC                    1.00
```

Thioate (Major Isomer)



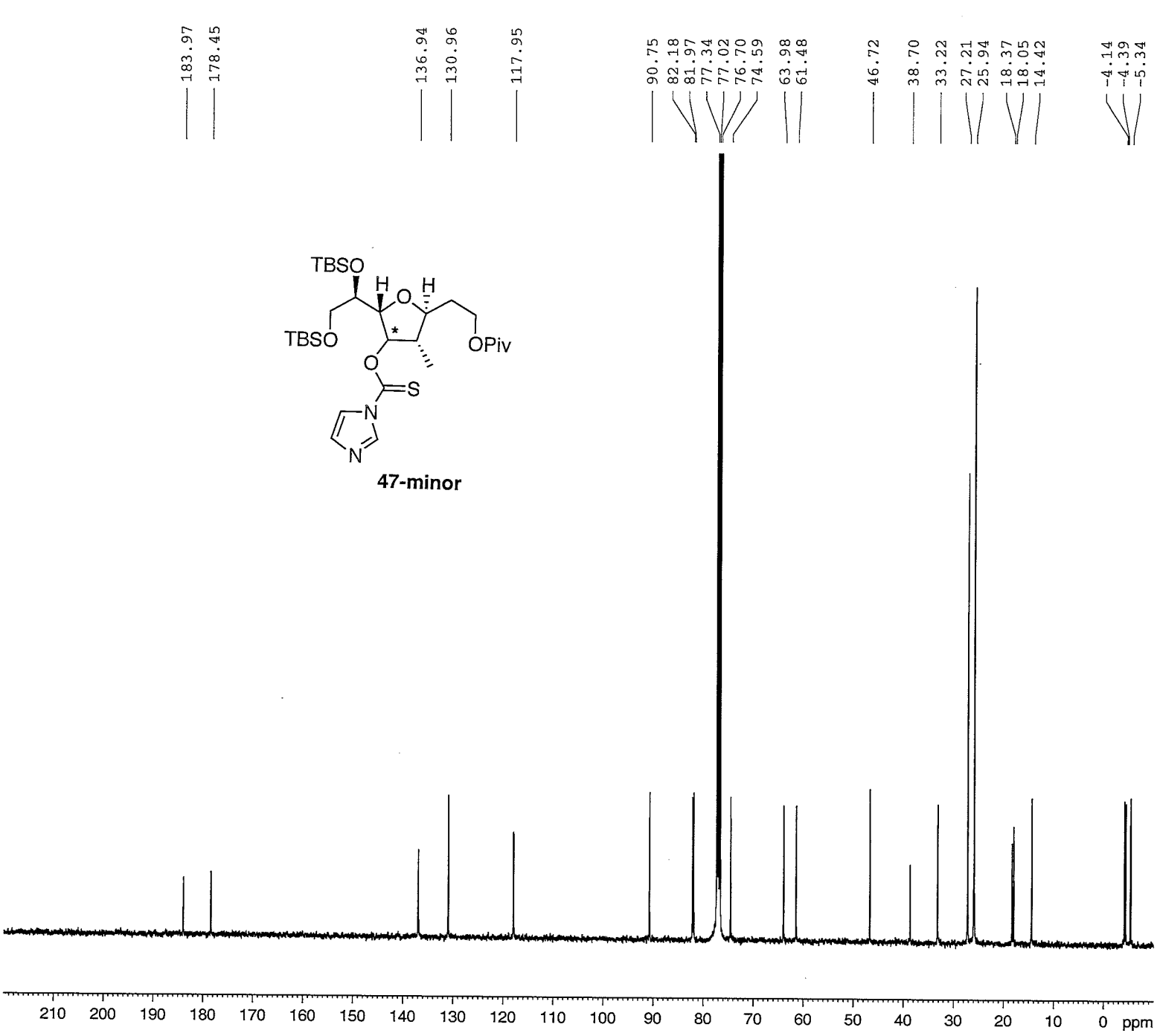

```
Current Data Parameters
NAME      SUM-VII-13-Thioate
EXPNO                      5
PROCNO                     1
DU                        /m
USER                  Subham

F2 - Acquisition Parameters
Date_              20100515
Time                  22.34
INSTRUM             DPX400
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                  10240
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               20642.5
DW               20.850 usec
DE                6.00 usec
TE                299.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.30 usec
PL1                -3.00 dB
SFO1         100.6521517 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               15.00 dB
PL13               15.00 dB
SFO2         400.2466010 MHz

F2 - Processing parameters
SI                  32768
SF           100.6416850 MHz
WDW                    EM
SSB                     0
LB                 3.00 Hz
GB                      0
PC                   1.40
```



47-minor

Current Data Parameters	
NAME	SUM-VII-13-Thioa
EXPNO	1
PROCNO	1
F2 - Acquisition Paramete	
Date_	20100515
Time	16.50
INSTRUM	DPX400
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 H
FIDRES	0.195625 H
AQ	2.5559540 s
RG	143.7
DW	78.000 u
DE	6.00 u
TE	298.2 K
D1	1.00000000 s
TD0	1
======== CHANNEL f1 =====	
NUC1	1H
P1	13.50 u
PL1	-3.00 d
SFO1	400.2478017 M
F2 - Processing parameter	
SI	32768
SF	400.2450000 M
WDW	EM
SSB	0
LB	0.30 H
GB	0
PC	1.00

Thioate (Minor Isomer)



Current Data Parameters

NAME	SUM-VII-13-Thioate
EXPNO	2
PROCNO	1
DU	/m
USER	Subham

F2 - Acquisition Parameters

Date_	20100515
Time	17.04
INSTRUM	DPX400
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	5000
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	9195.2
DW	20.850 usec
DE	6.00 usec
TE	299.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

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

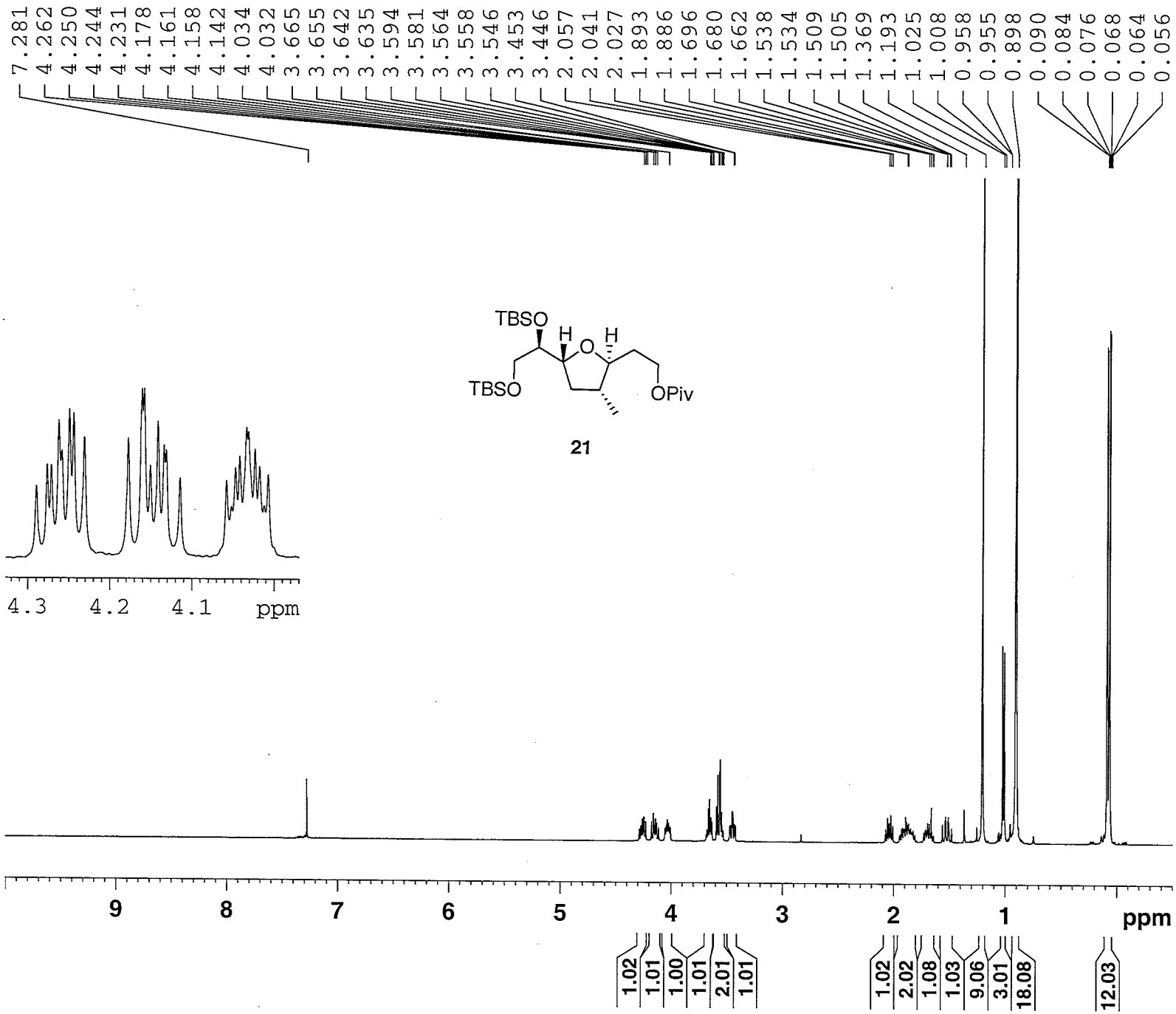
NUC1	13C
P1	8.30 usec
PL1	-3.00 dB
SFO1	100.6521517 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.00 dB
PL12	15.00 dB
PL13	15.00 dB
SFO2	400.2466010 MHz

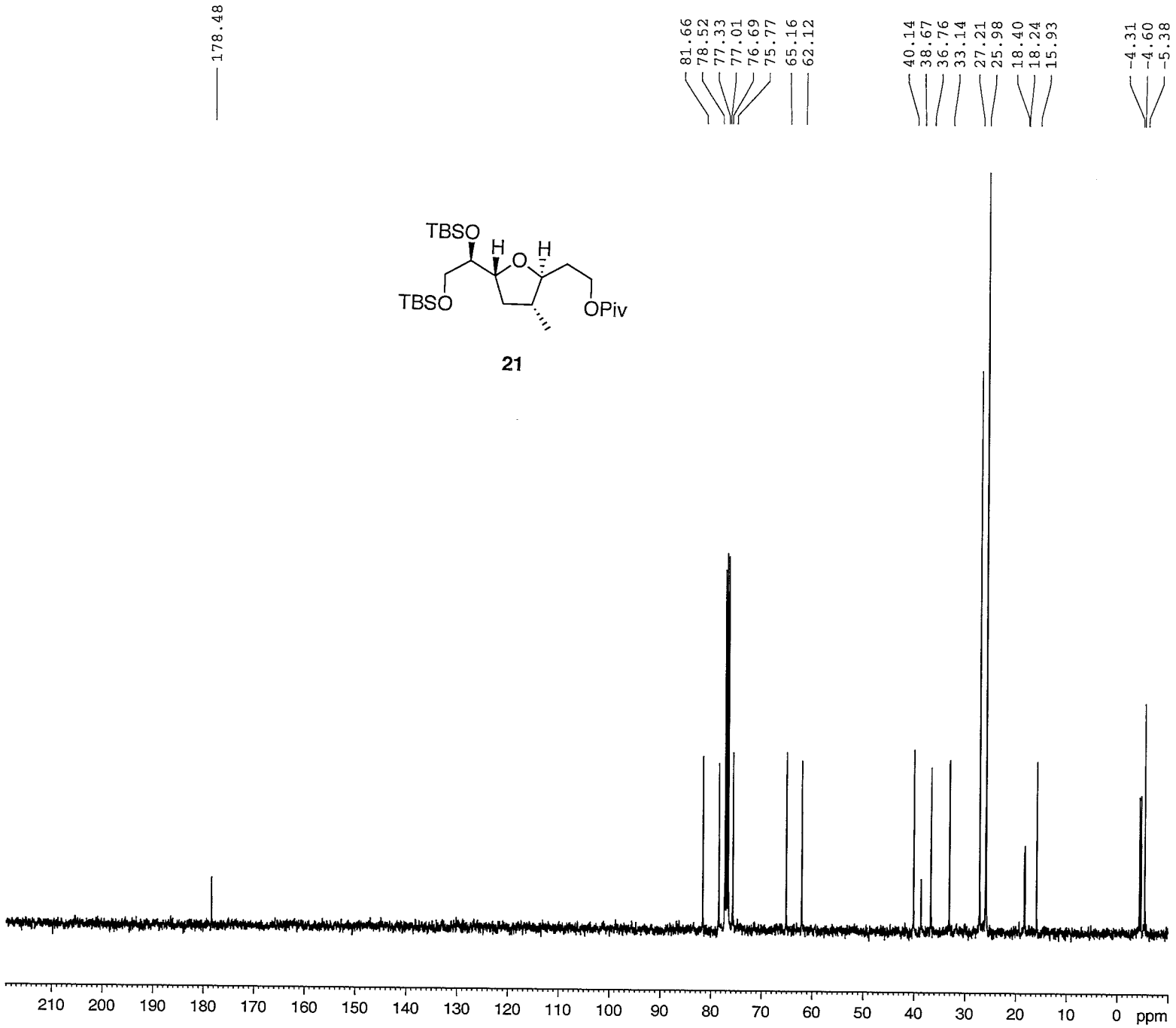
F2 - Processing parameters

SI	32768
SF	100.6416850 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40




```
Current Data Parameters
NAME      SUM-VII-17-THF R
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameter
Date_            20100520
Time                17.26
INSTRUM           DPX400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH           6410.256 H
FIDRES        0.195625 H
AQ            2.5559540 s
RG                 71.8
DW              78.000 u
DE               6.00 u
TE              299.2 K
D1          2.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                13.50 u
PL1               -3.00 d
SFO1       400.2478017 M

F2 - Processing parameter
SI                 32768
SF       400.2450000 M
WDW                   EM
SSB                    0
LB                0.30 H
GB                     0
PC                1.00
```

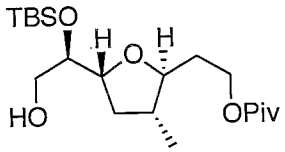
Tetrahydrofuran




```
Current Data Parameters
NAME      SUM-VII-17-THF Ring
EXPNO                    3
PROCNO                   1
DU                      /m
USER                Subham

F2 - Acquisition Parameters
Date_            20100520
Time                17.39
INSTRUM           DPX400
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   494
DS                     4
SWH          23980.814 Hz
FIDRES         0.365918 Hz
AQ           1.3664756 sec
RG             18390.4
DW              20.850 usec
DE               6.00 usec
TE              299.2 K
D1          0.20000000 sec
d11         0.03000000 sec
DELTA       0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                8.30 usec
PL1              -3.00 dB
SFO1       100.6517495 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            90.00 usec
PL2              -3.00 dB
PL12             15.00 dB
PL13             15.00 dB
SFO2       400.2466010 MHz

F2 - Processing parameters
SI                 32768
SF         100.6416850 MHz
WDW                   EM
SSB                    0
LB                3.00 Hz
GB                     0
PC                  1.40
```

Primary alcohol

7.290 4.274 4.272 4.267 4.263 4.167 4.158 4.155 4.146 4.142 4.074 4.060 3.675 3.673 3.667 3.567 3.558 3.548 3.500 3.497 3.488 3.484 3.475 3.471 2.395 2.387 2.379 2.101 2.092 2.084 2.075 1.709 1.707 1.700 1.457 1.442 1.440 1.426 1.423 1.409 1.216 1.046 1.037 0.929 0.138 0.120



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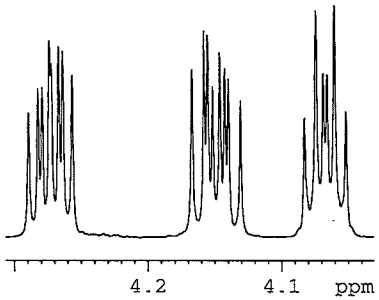
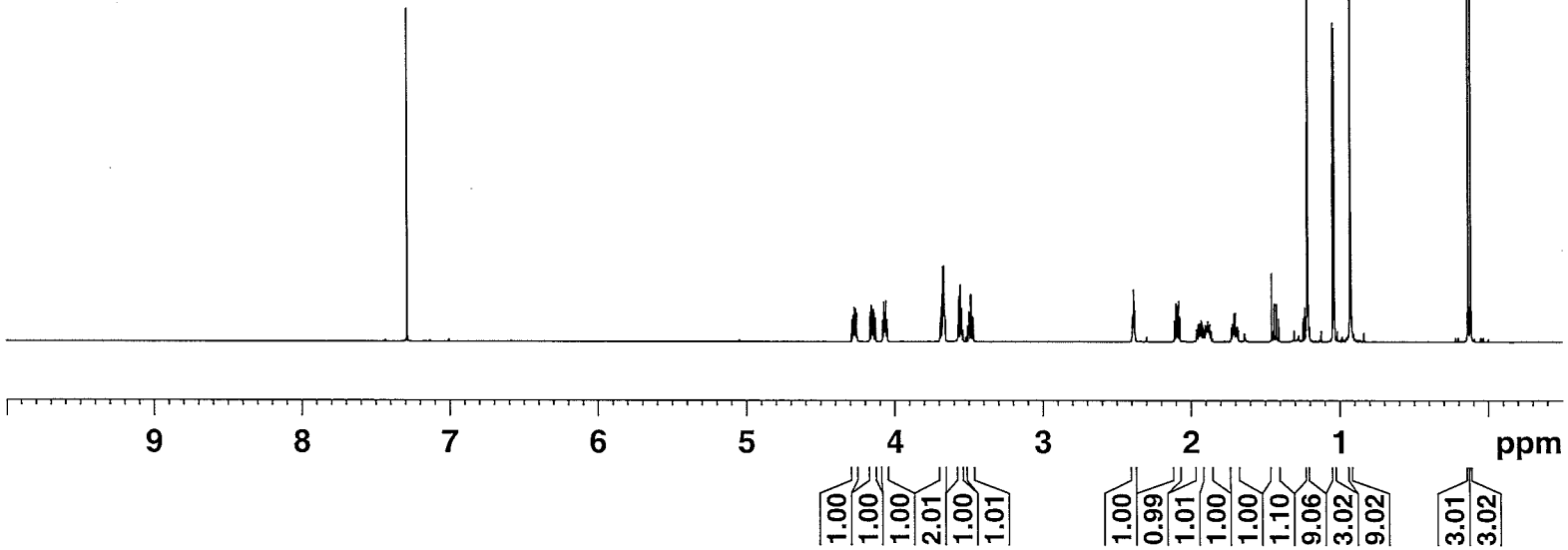
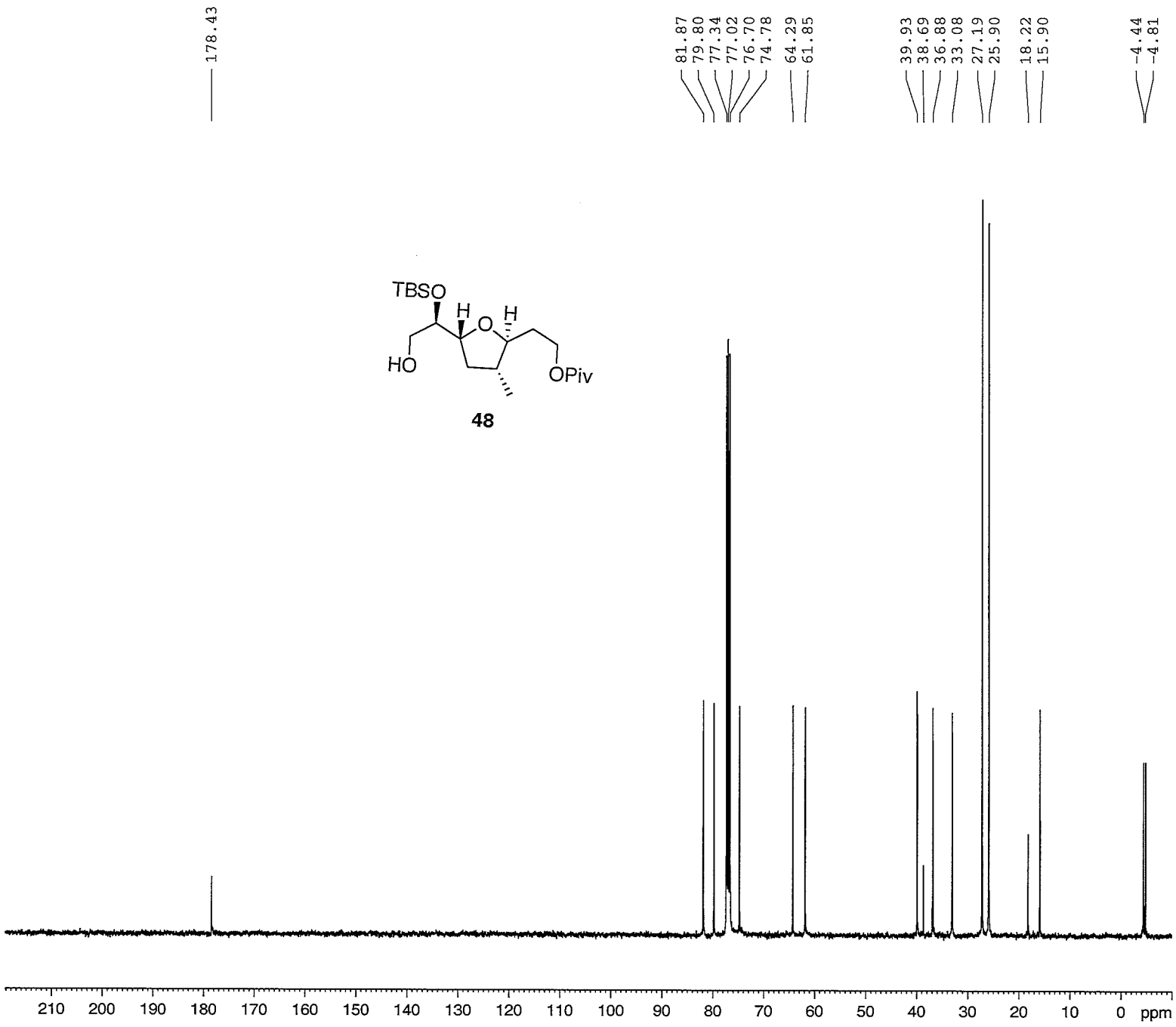


NAME	SUM-IX-18-Primary Alcoh
EXPNO	1
PROCNO	1
Date_	20110225
Time	23.57
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.181652 Hz
AQ	2.7525620 sec
RG	57
DW	42.000 usec
DE	16.50 usec
TE	298.2 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MHz
SI	65536
SF	700.1200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



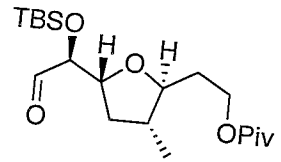
Alcohol



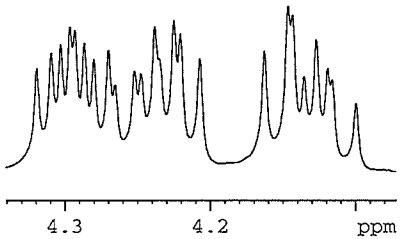

```
Current Data Parameters
NAME      SUM-VII-28-Alcohol
EXPNO                      2
PROCNO                     1
DU                        /m
USER                  Subham

F2 - Acquisition Parameters
Date_              20100531
Time                  22.18
INSTRUM             DPX400
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    5513
DS                       4
SWH             23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                 9195.2
DW                20.850 usec
DE                 6.00 usec
TE                299.2 K
D1           0.20000000 sec
d11          0.03000000 sec
DELTA        0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.30 usec
PL1                -3.00 dB
SFO1         100.6517495 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               15.00 dB
PL13               15.00 dB
SFO2         400.2466010 MHz

F2 - Processing parameters
SI                   32768
SF          100.6416850 MHz
WDW                     EM
SSB                      0
LB                  3.00 Hz
GB                       0
PC                    1.40
```

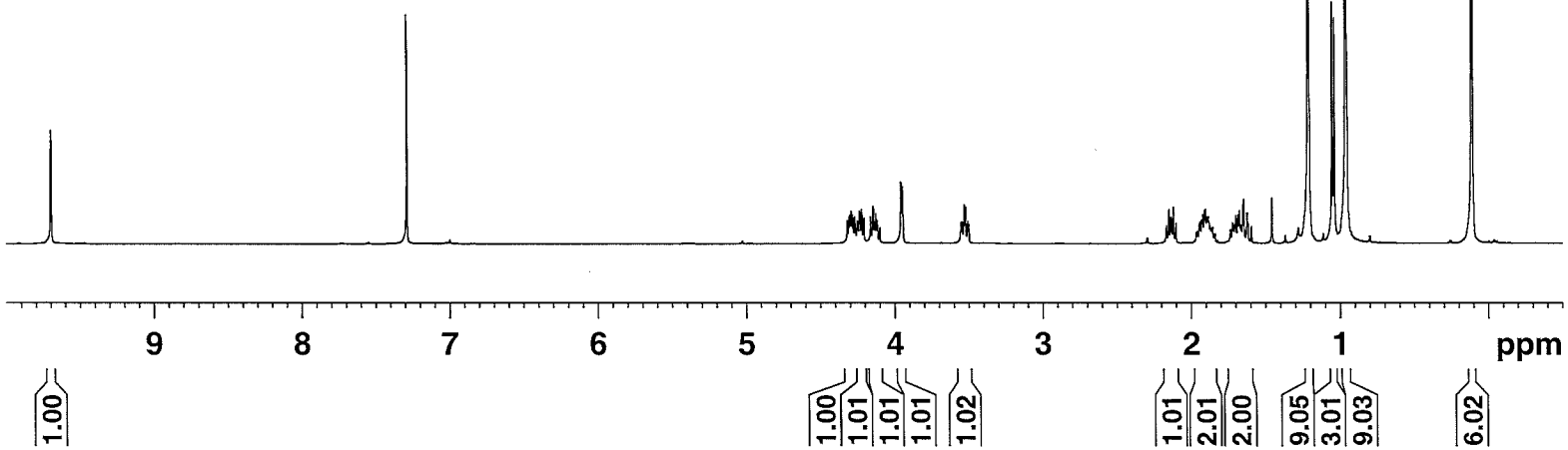
Aldehyde

9.698 9.695 7.291 4.309 4.302 4.296 4.293 4.286 4.279 4.269 4.237 4.224 4.220 4.207 4.162 4.146 4.143 4.126 4.119 3.958 3.955 3.948 3.945 3.531 3.524 2.148 2.135 2.118 1.928 1.922 1.910 1.904 1.892 1.884 1.700 1.684 1.675 1.651 1.645 1.622 1.210 1.053 1.037 0.958 0.112 0.106



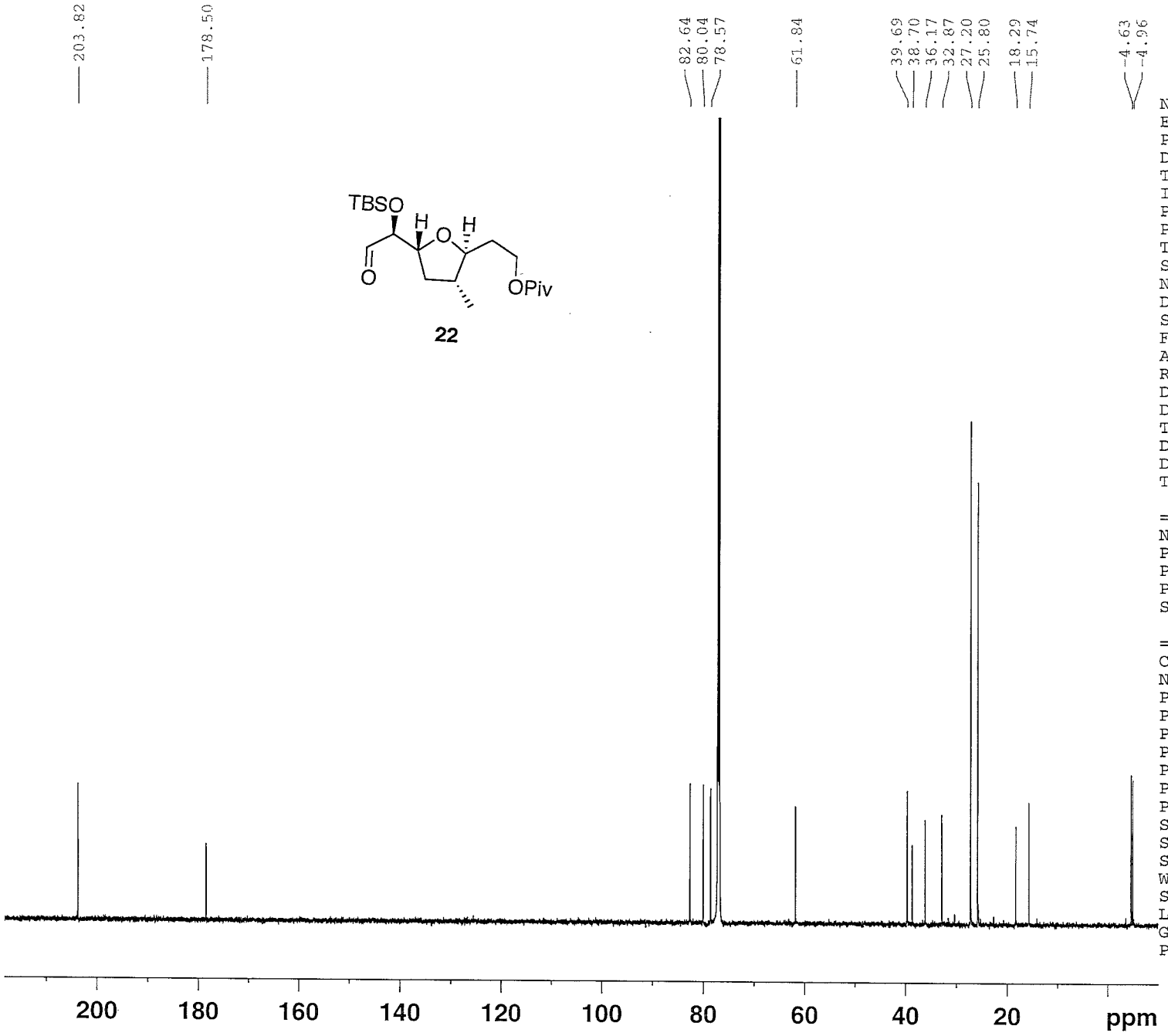
22





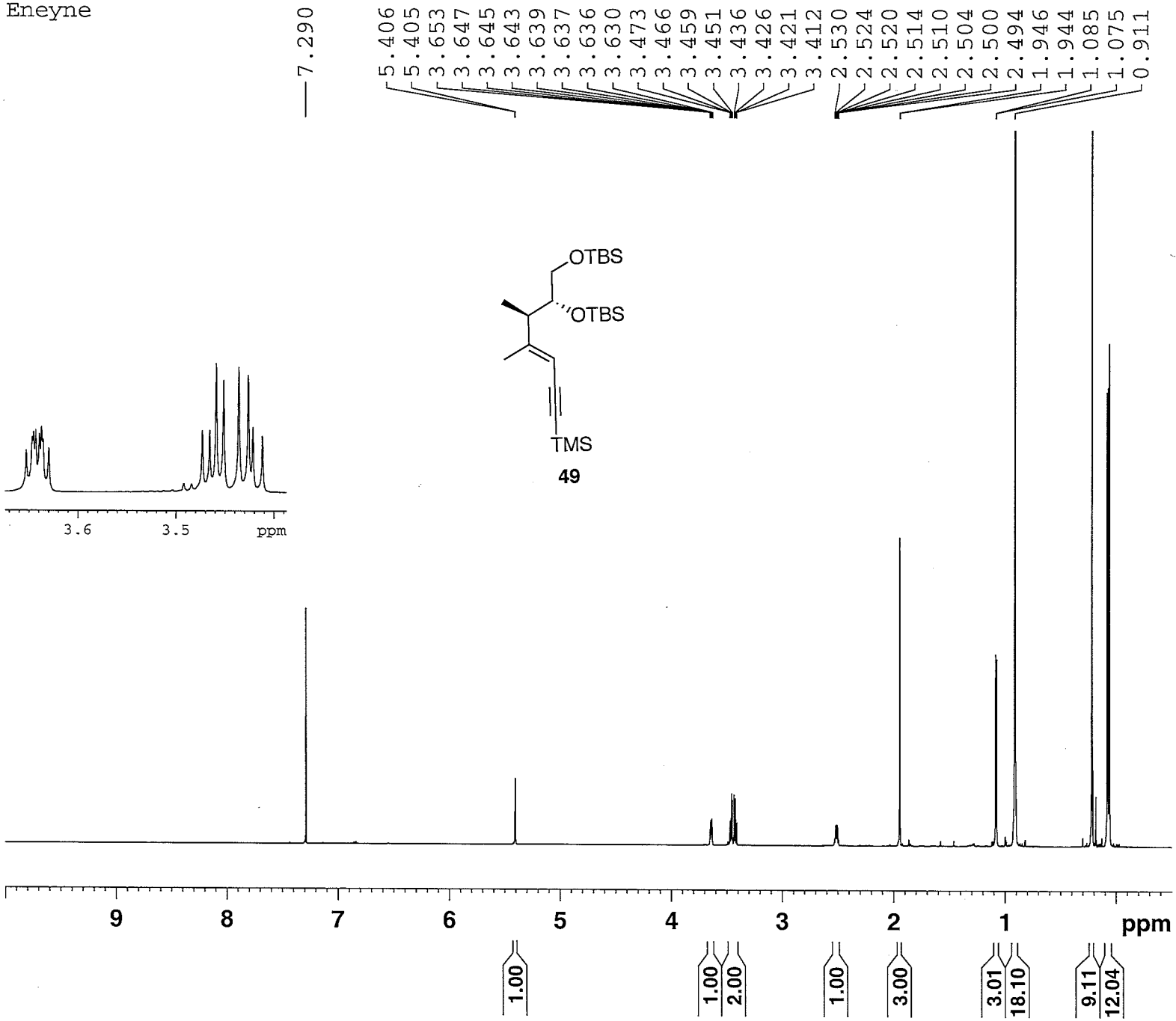
NAME	SM-V-79-R-Aldehyd
EXPNO	1
PROCNO	1
Date_	20100108
Time	15.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 se
RG	64
DW	78.000 us
DE	6.50 us
TE	299.7 K
D1	1.00000000 se
TD0	1
======== CHANNEL f1 ======	
NUC1	1H
P1	14.00 us
PL1	0.00 dB
PL1W	10.27361584 W
SFO1	400.1378009 MH:
SI	32768
SF	400.1350000 MH:
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Aldehyde



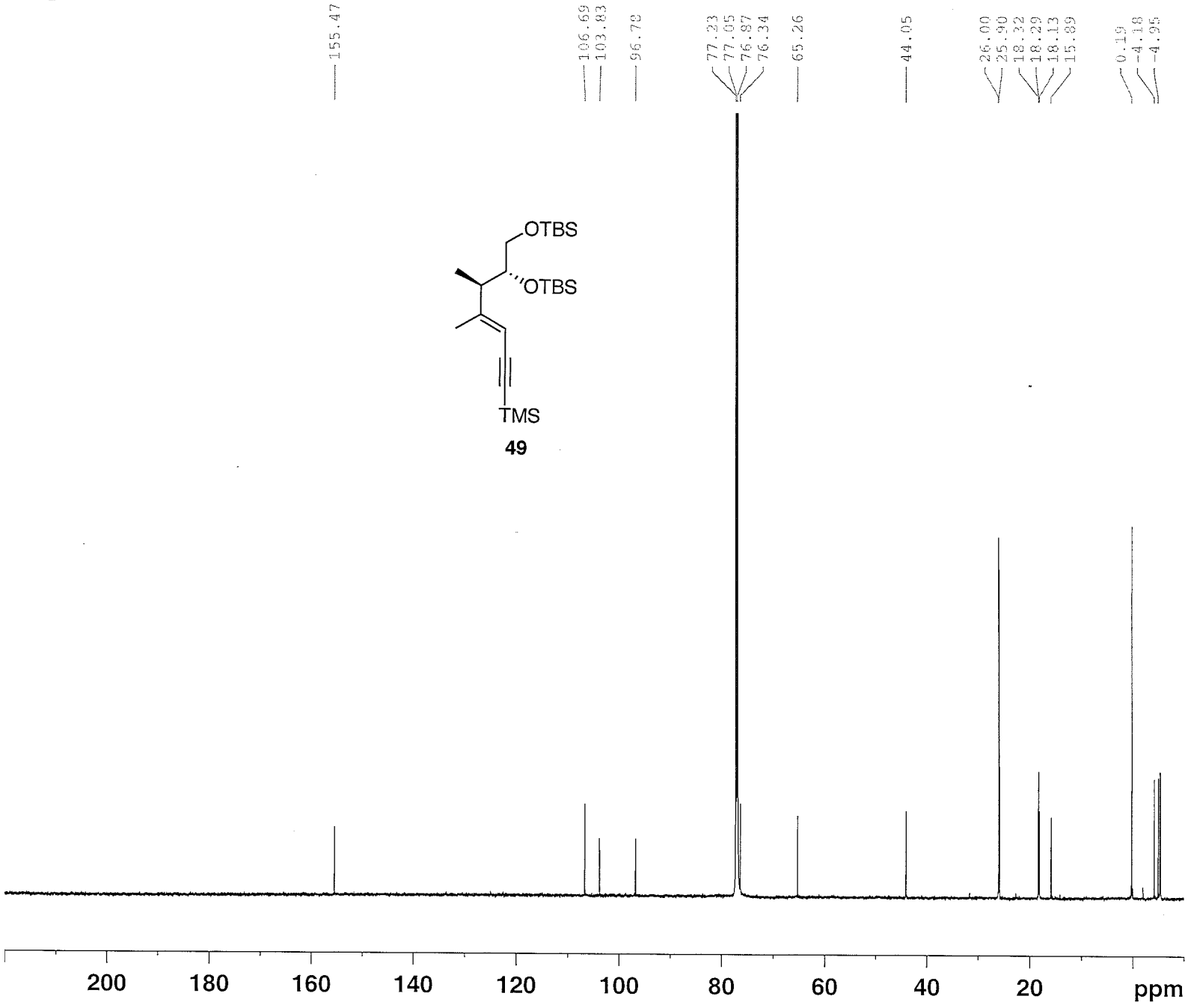
NAME	SUM-IX-37-Aldehyde
EXPNO	2
PROCNO	1
Date_	20100930
Time	16.28
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	235
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	203
DW	12.000 usec
DE	15.00 usec
TE	297.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0629186 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MHz
SI	131072
SF	176.0453140 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Eneyne



NAME	SUM-X-56-Eneyne
EXPNO	1
PROCNO	1
Date_	20110225
Time	15.54
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.181652 Hz
AQ	2.7525620 se
RG	50.8
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH:
SI	65536
SF	700.1200000 MH:
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Eneyne



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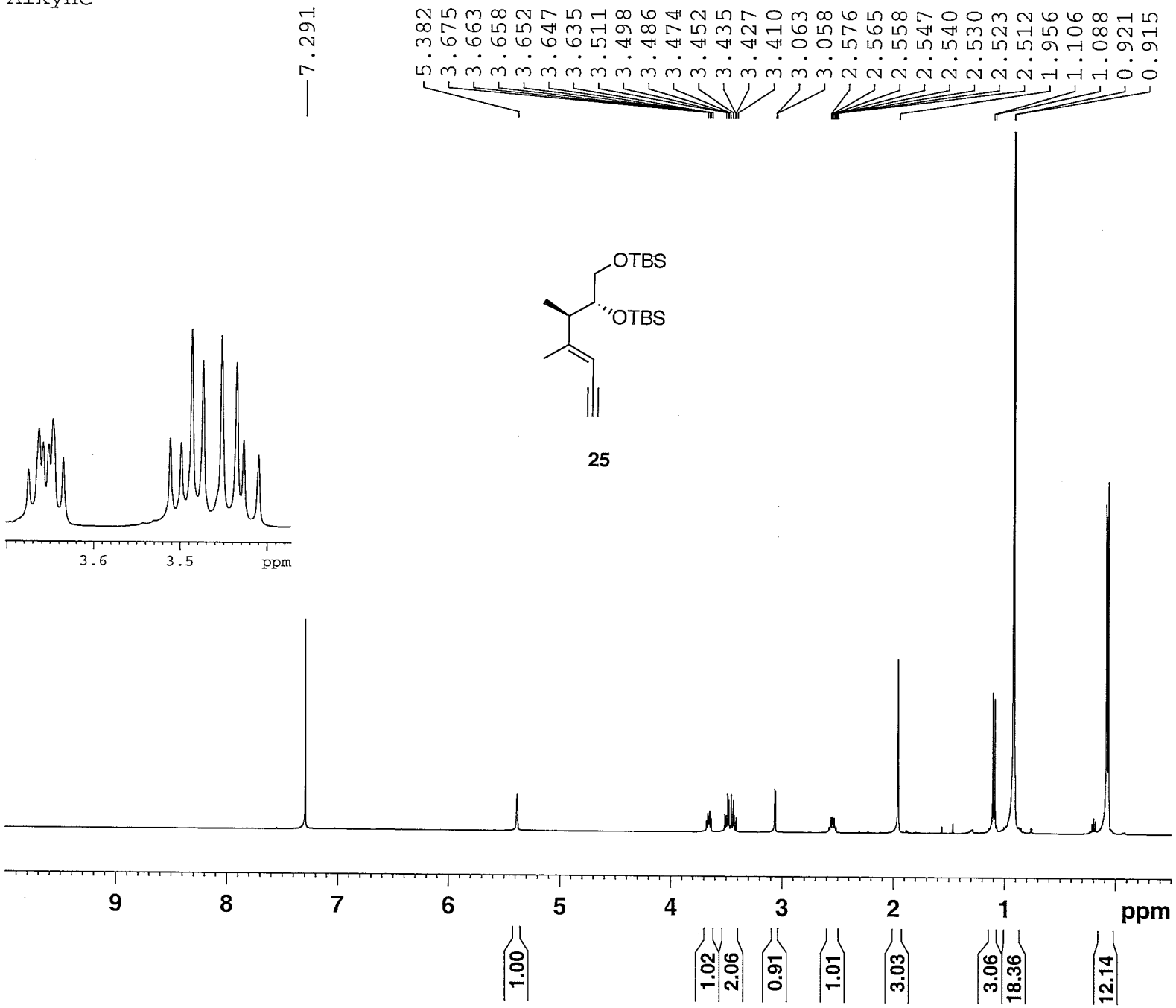
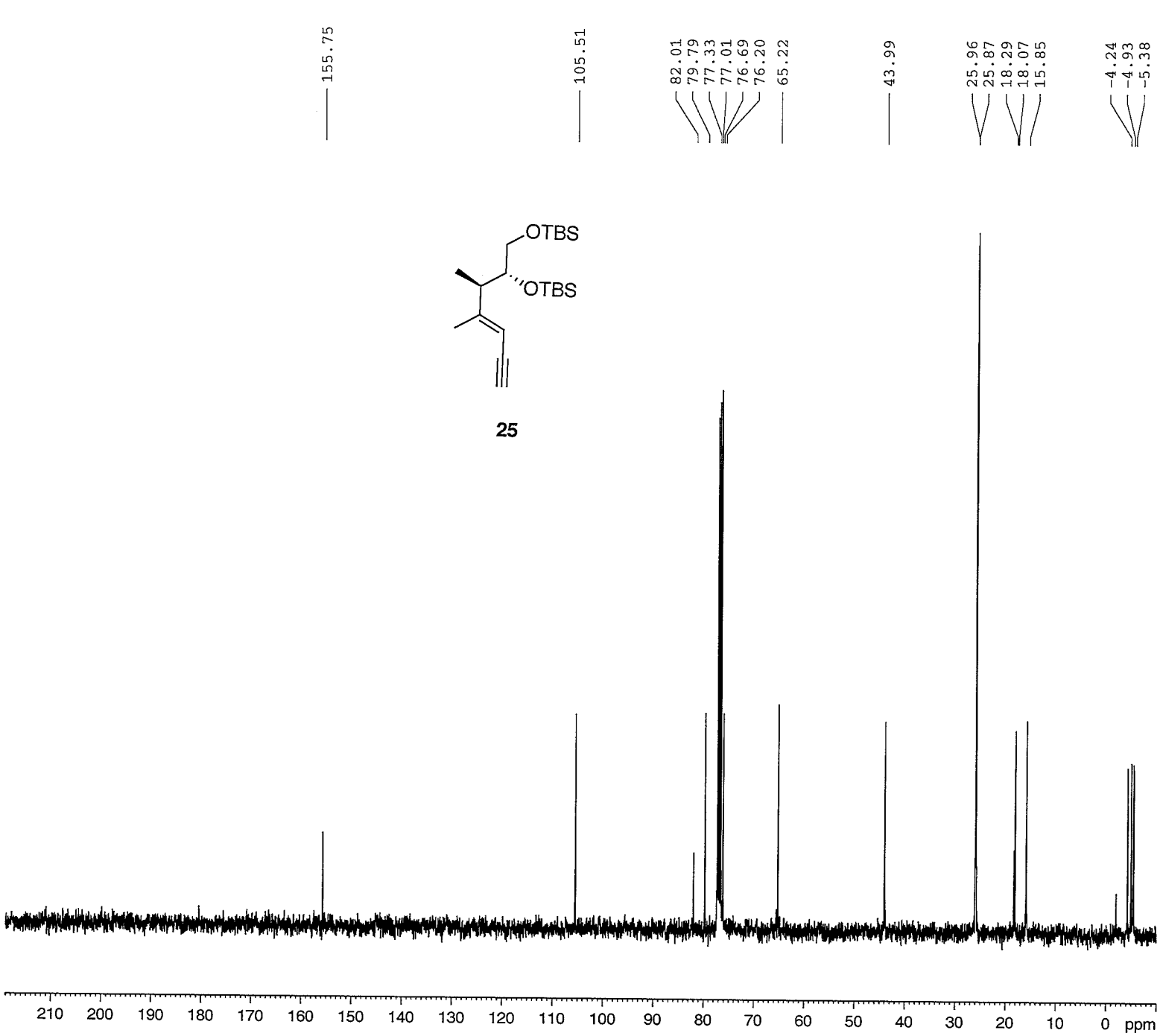
NAME	SUM-X-56-Eneyne
EXPNO	2
PROCNO	1
Date_	20110225
Time	16.02
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	181
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alkyne



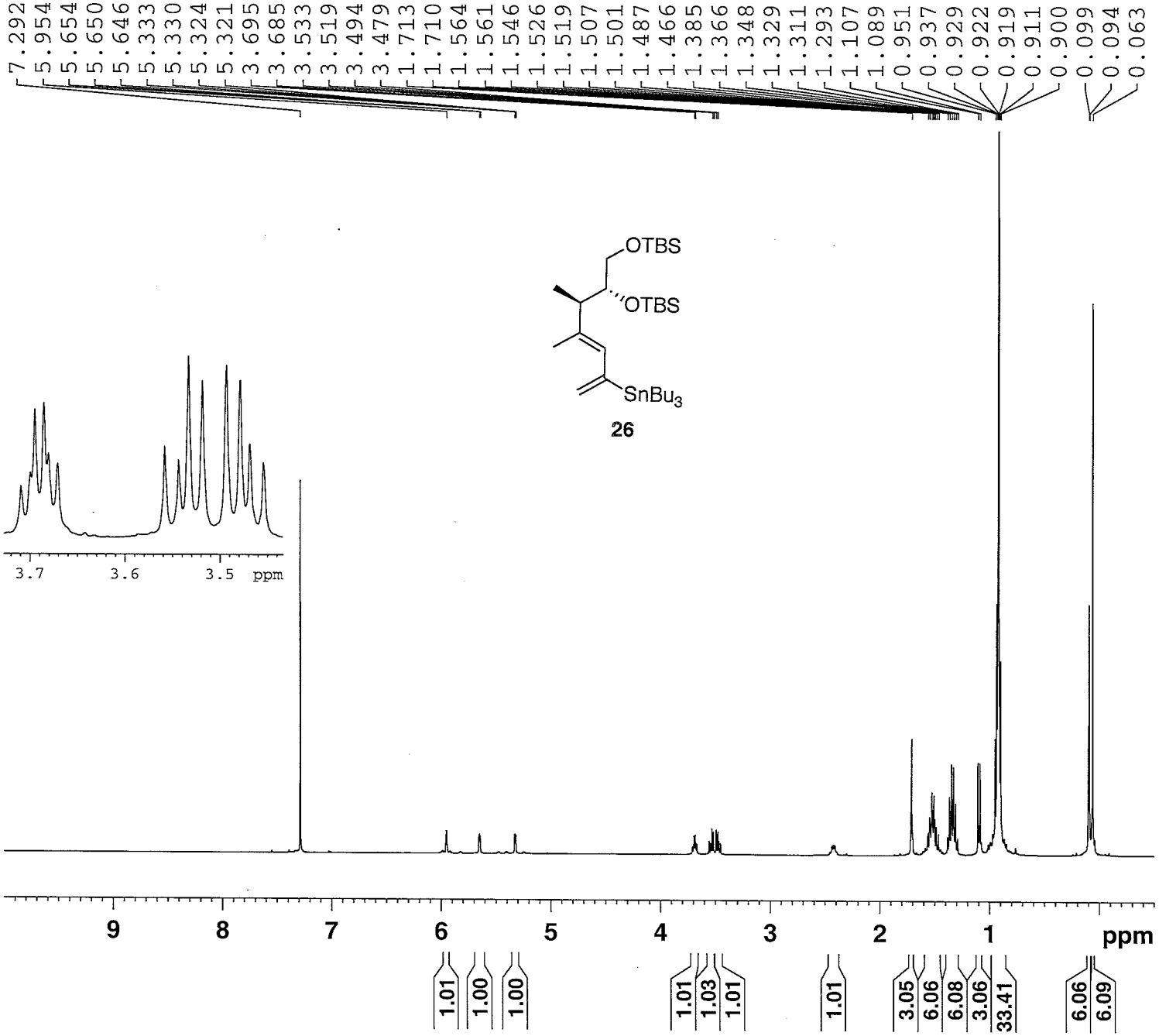
NAME	SM-VI-92-R-Alkyne
EXPNO	1
PROCNO	1
Date_	20100502
Time	0.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 se
RG	128
DW	78.000 us
DE	6.50 us
TE	299.4 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	14.00 us
PL1	0.00 dB
PL1W	10.27361584 W
SFO1	400.1378009 MH
SI	32768
SF	400.1350000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Ene-yne



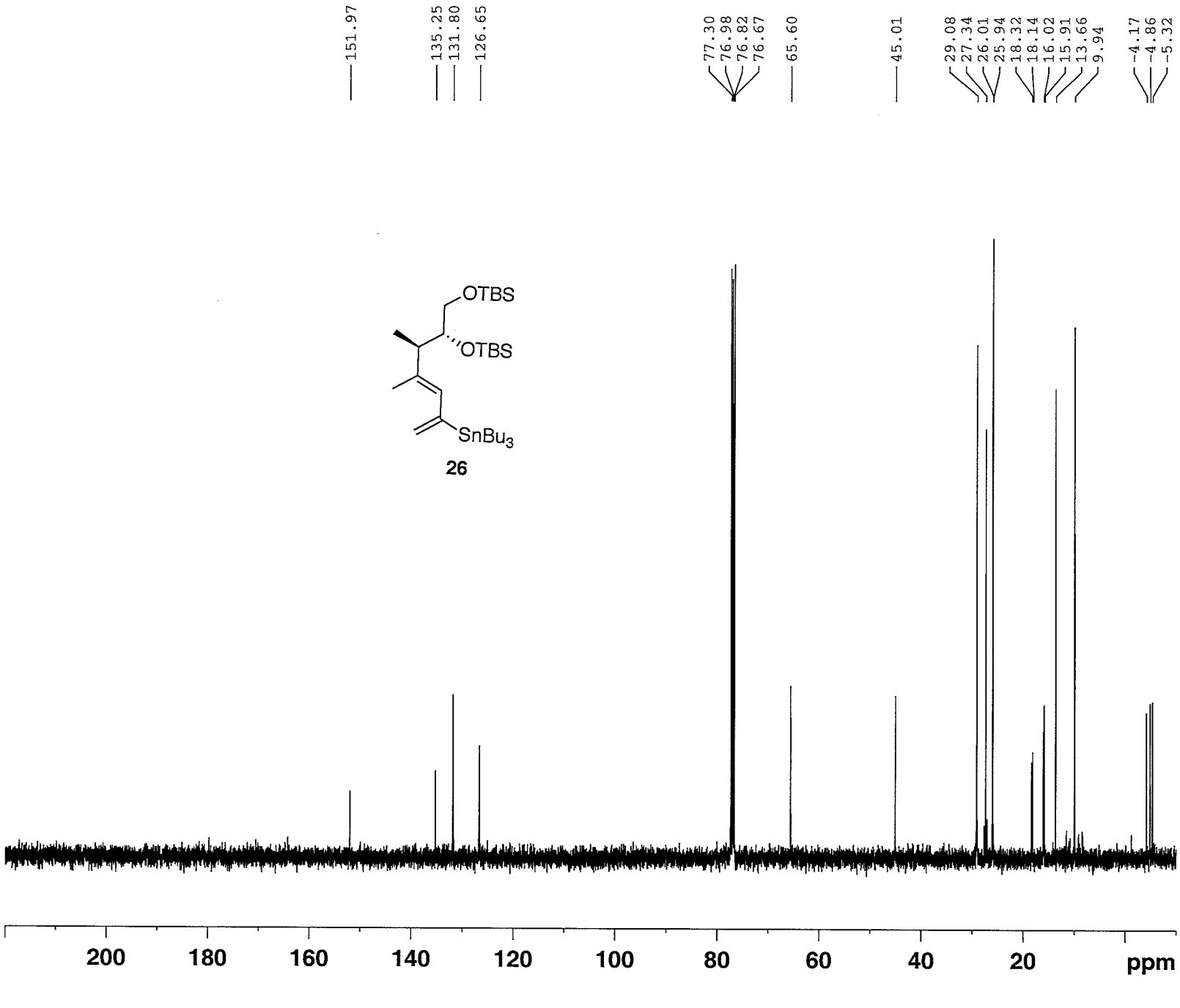

```
Current Data Parameters
NAME      SUM-VII-31-Eneyne
EXPNO                    2
PROCNO                   1
DU                      /m
USER                Subham

F2 - Acquisition Parameters
Date_             20100601
Time                 1.32
INSTRUM            DPX400
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    322
DS                      4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                9195.2
DW               20.850 usec
DE                6.00 usec
TE                300.2 K
D1           0.20000000 sec
d11          0.03000000 sec
DELTA        0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.30 usec
PL1               -3.00 dB
SFO1        100.6517495 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              15.00 dB
PL13              15.00 dB
SFO2        400.2466010 MHz

F2 - Processing parameters
SI                 32768
SF          100.6416850 MHz
WDW                   EM
SSB                    0
LB                 3.00 Hz
GB                     0
PC                  1.40
```

Dienyl Vinyl Stannane

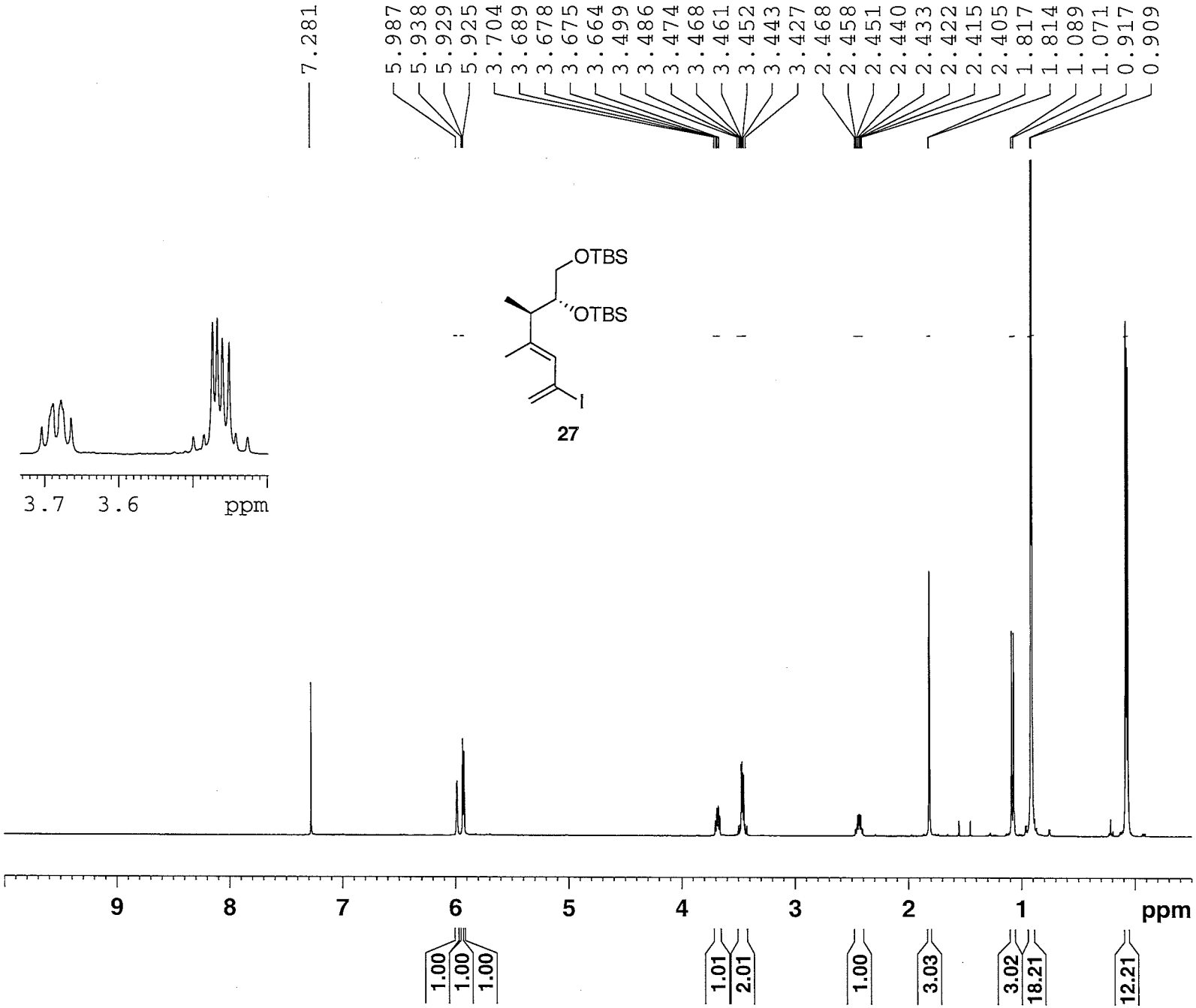


NAME	SM-VII-18-R-Vinyl Stanna
EXPNO	1
PROCNO	1
Date_	20100518
Time	18.11
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	128
DW	78.000 usec
DE	6.50 usec
TE	299.0 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.00 usec
PL1	0.00 dB
PL1W	10.27361584 W
SFO1	400.1378009 MHz
SI	32768
SF	400.1350000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Dienyl Vinyl Stannane



NAME	SM-VII-76-R-Vinyl Stan
EXPNO	3
PROCNO	1
Date_	20100801
Time	18.13
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	436
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	9195.2
DW	20.850 usec
DE	6.50 usec
TE	301.6 K
D1	0.20000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	-2.00 dB
SFO1	100.6258476 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	0.00 dB
PL12	16.16 dB
PL13	17.00 dB
SFO2	400.1416006 MHz
SI	32768
SF	100.6152830 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



Current Data Parameters

NAME	SUM-VII-19-Vinyl Iod
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20100609
Time	21.57
INSTRUM	DPX400
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	161.3
DW	78.000 usec
DE	6.00 usec
TE	299.2 K
D1	2.00000000 sec
TD0	1

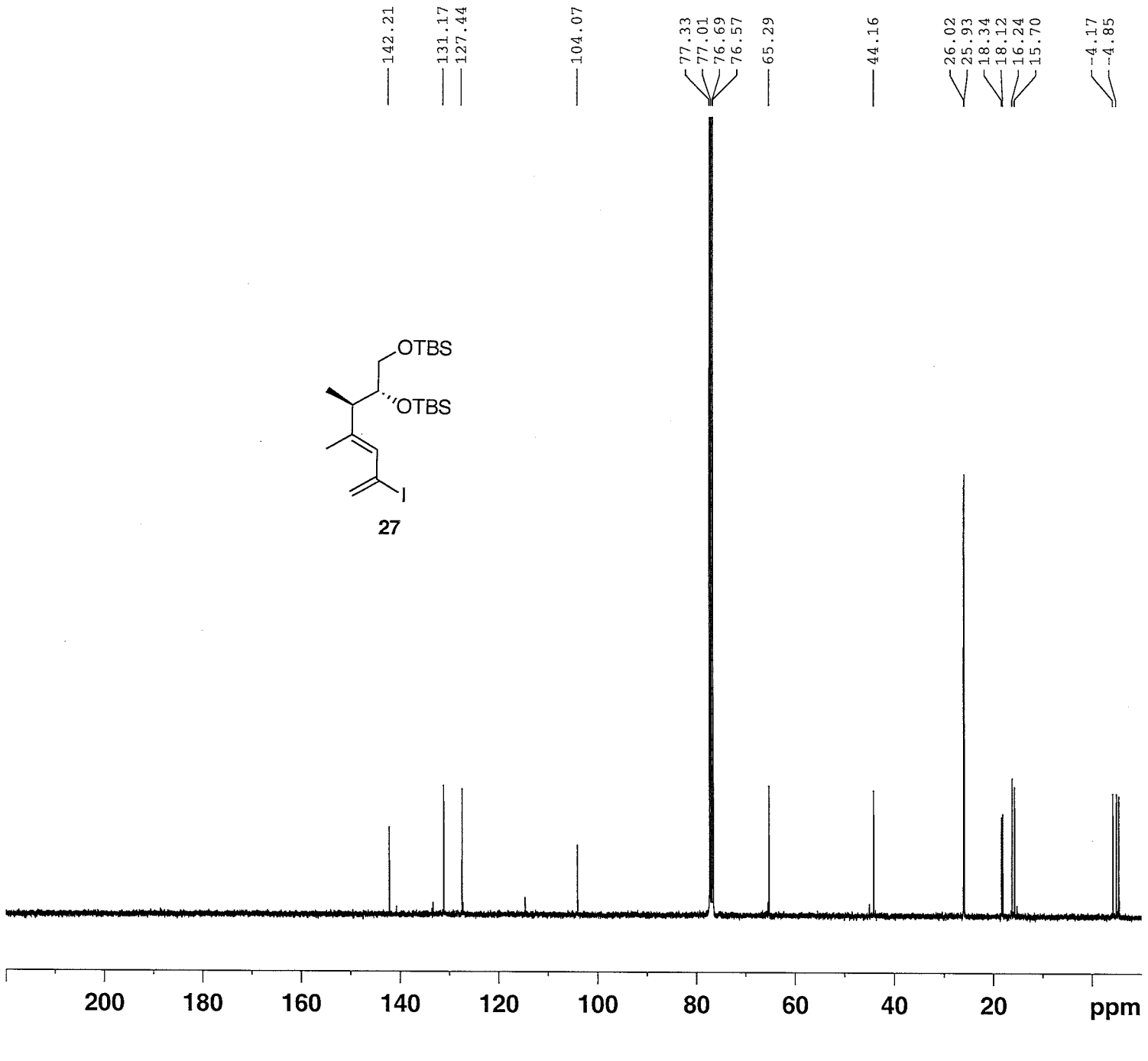
======== CHANNEL f1 ========

NUC1	1H
P1	13.50 usec
PL1	-3.00 dB
SFO1	400.2478017 MHz

F2 - Processing parameters

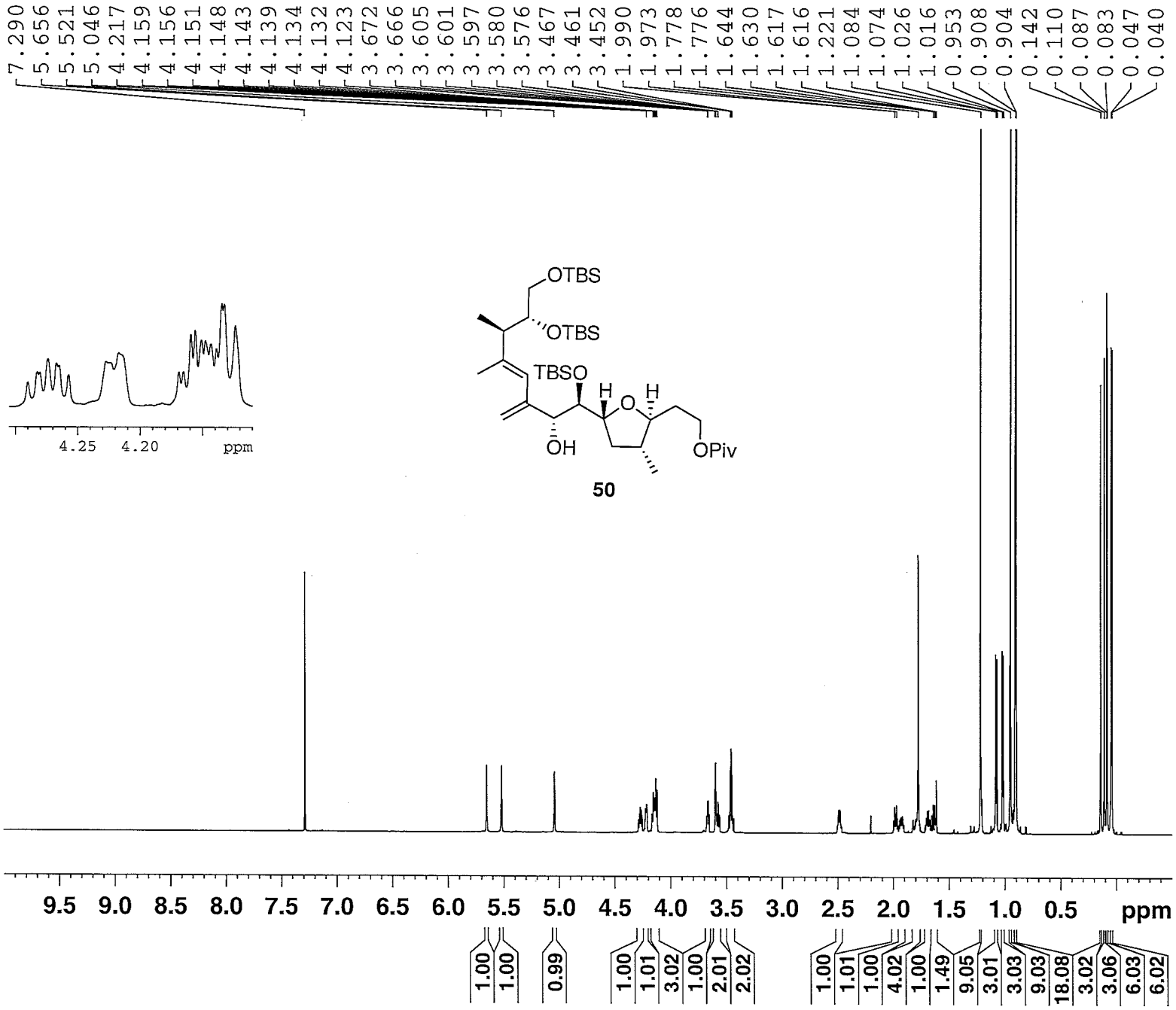
SI	32768
SF	400.2450000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Dienyl Vinyl Iodide




```
NAME        SM-VI-95-R-Dienyl Vinyl Iodi
EXPNO                  3
PROCNO                 1
Date_           20100502
Time              23.02
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3000
DS                    4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG               18390.4
DW                19.900 usec
DE                 6.50 usec
TE                300.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                -2.00 dB
PL1W         46.89702606 W
SFO1        100.6255966 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               16.16 dB
PL13               17.00 dB
PL2W         10.27361584 W
PL12W         0.24872722 W
PL13W         0.20498557 W
SFO2        400.1366005 MHz
SI                 32768
SF          100.6140260 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

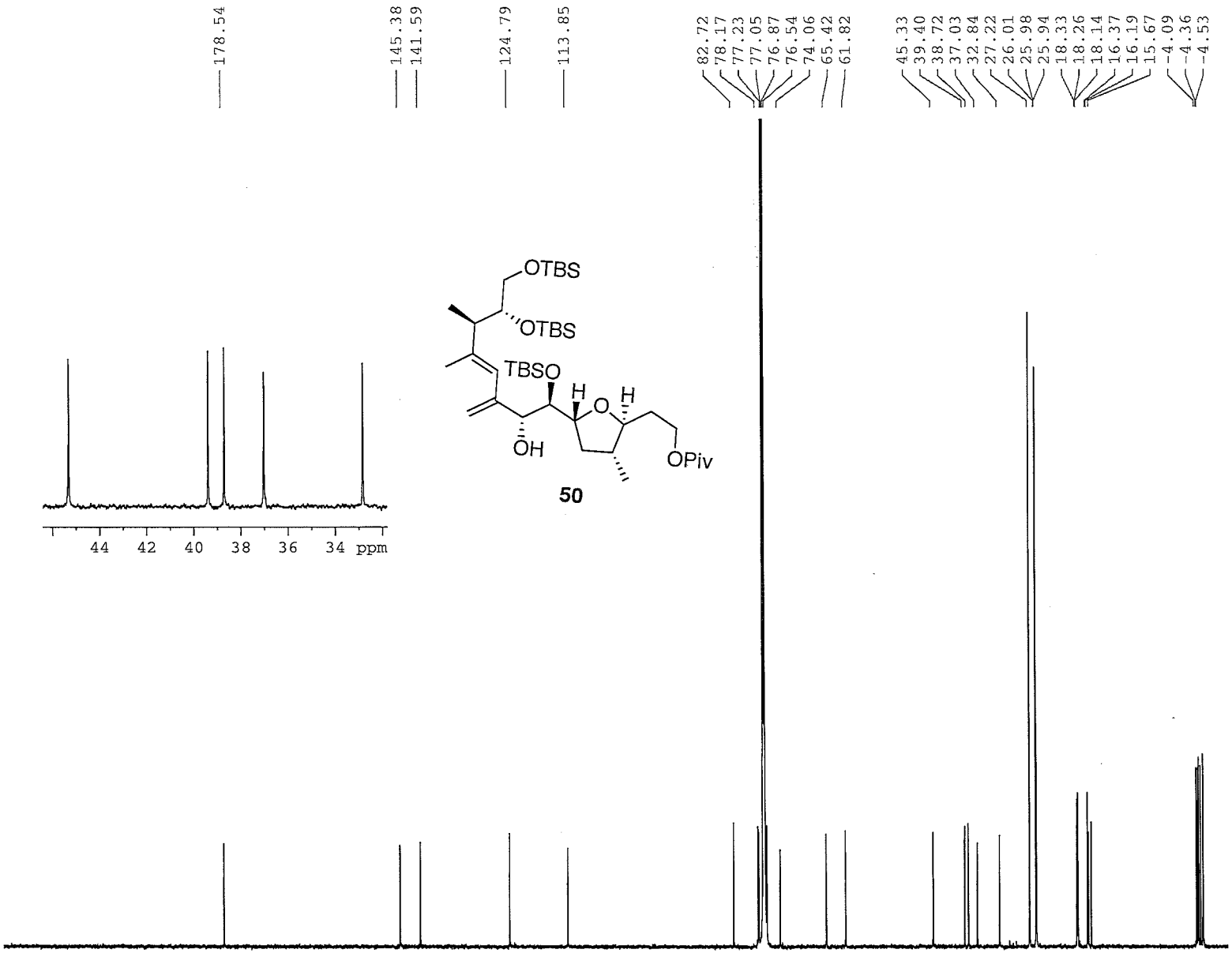
Alcohol



50

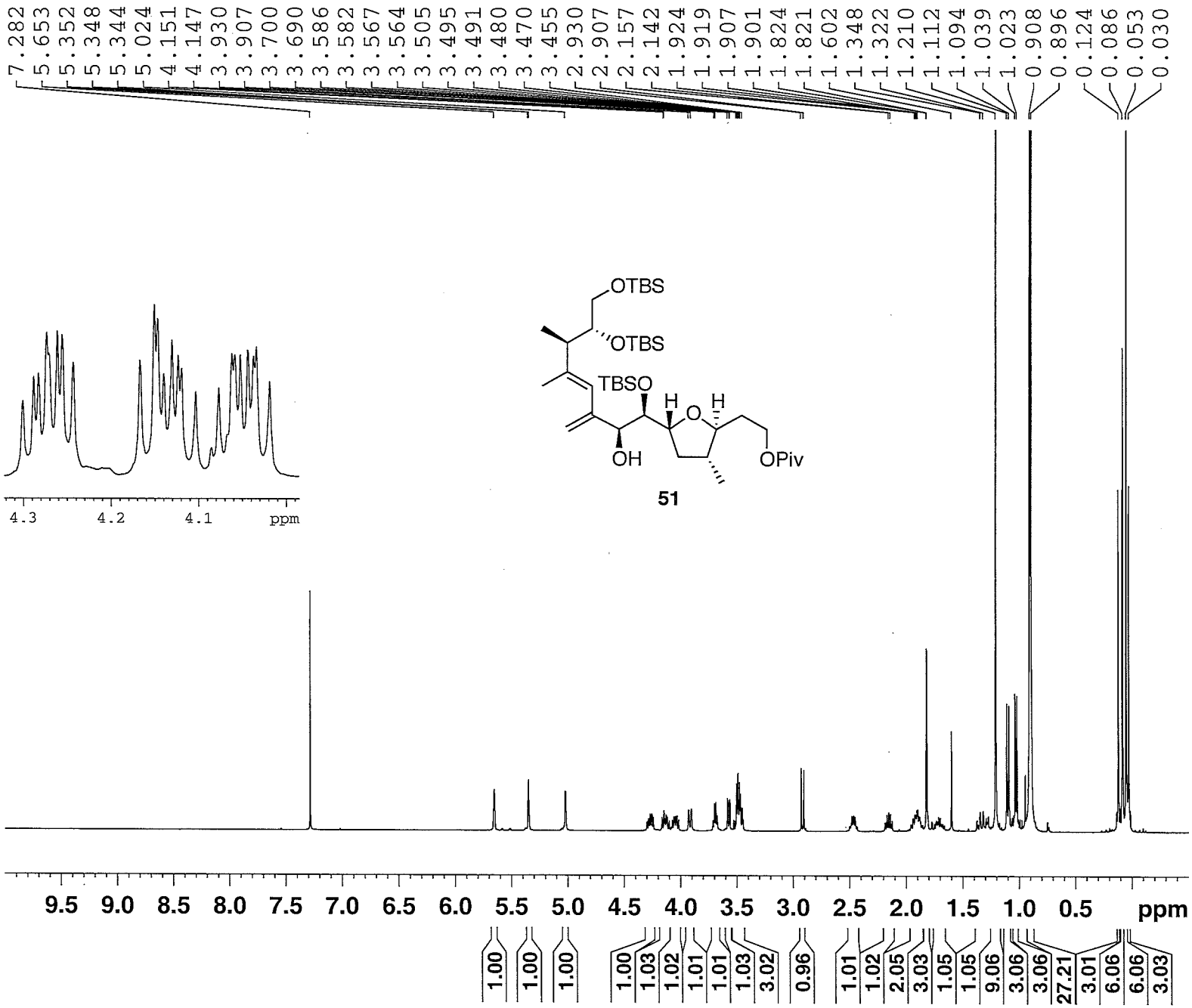
NAME	SUM-XII-39-Alcohol
EXPNO	2
PROCNO	1
Date_	20110717
Time	19.00
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	57
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	131072
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Alcohol



NAME	SUM-XII-39-Alcoho
EXPNO	3
PROCNO	1
Date_	20110717
Time	19.09
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	997
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

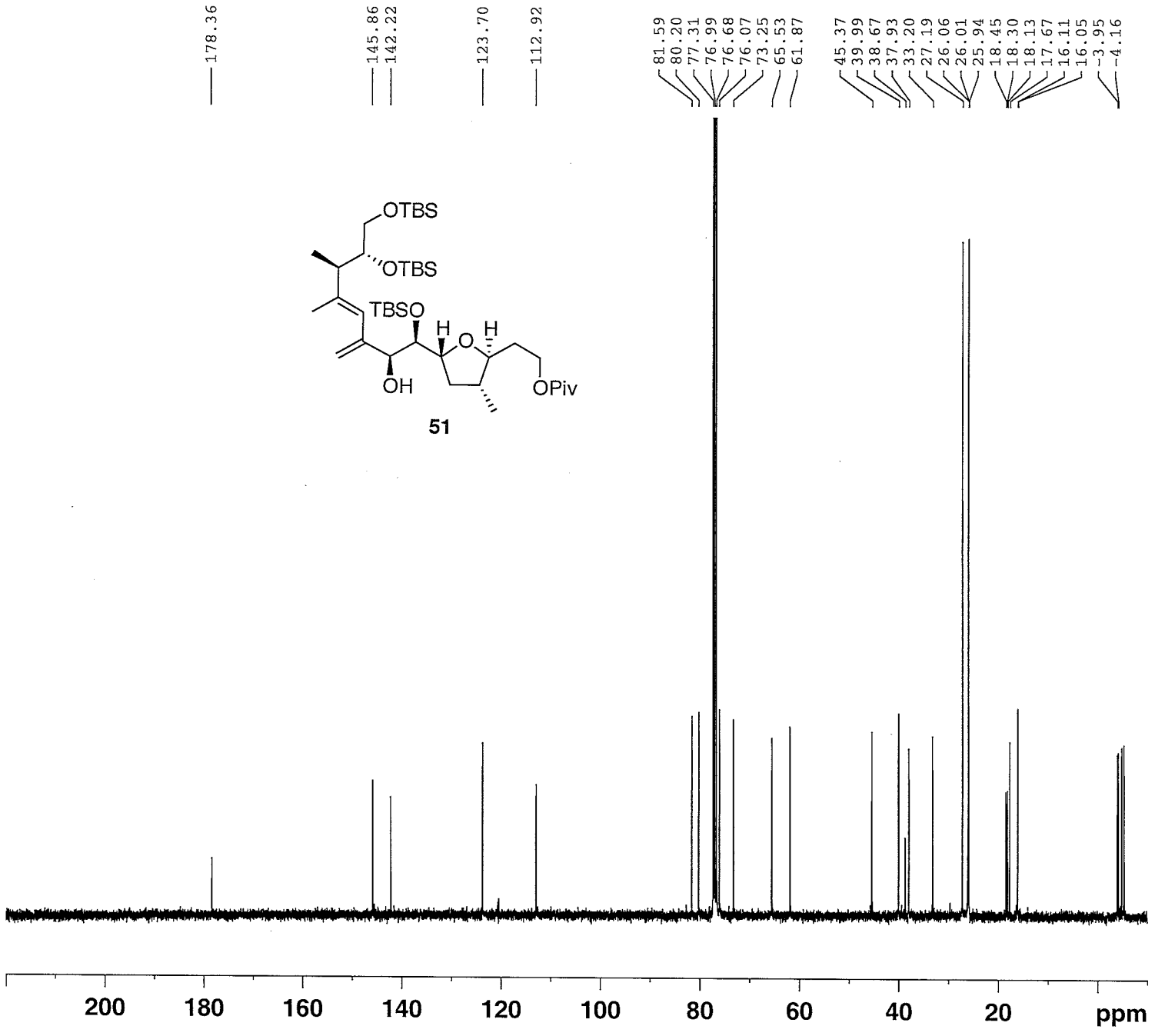
Diene (Bottom Minor Spot)



51

NAME	SUM-IX-06-R-Diene
EXPNO	3
PROCNO	1
Date_	20100831
Time	0.35
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6793.478 Hz
FIDRES	0.207320 Hz
AQ	2.4117749 se
RG	57
DW	73.600 us
DE	6.50 us
TE	299.4 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	14.00 us
PL1	0.00 dB
SFO1	400.1424008 MH
SI	32768
SF	400.1400000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

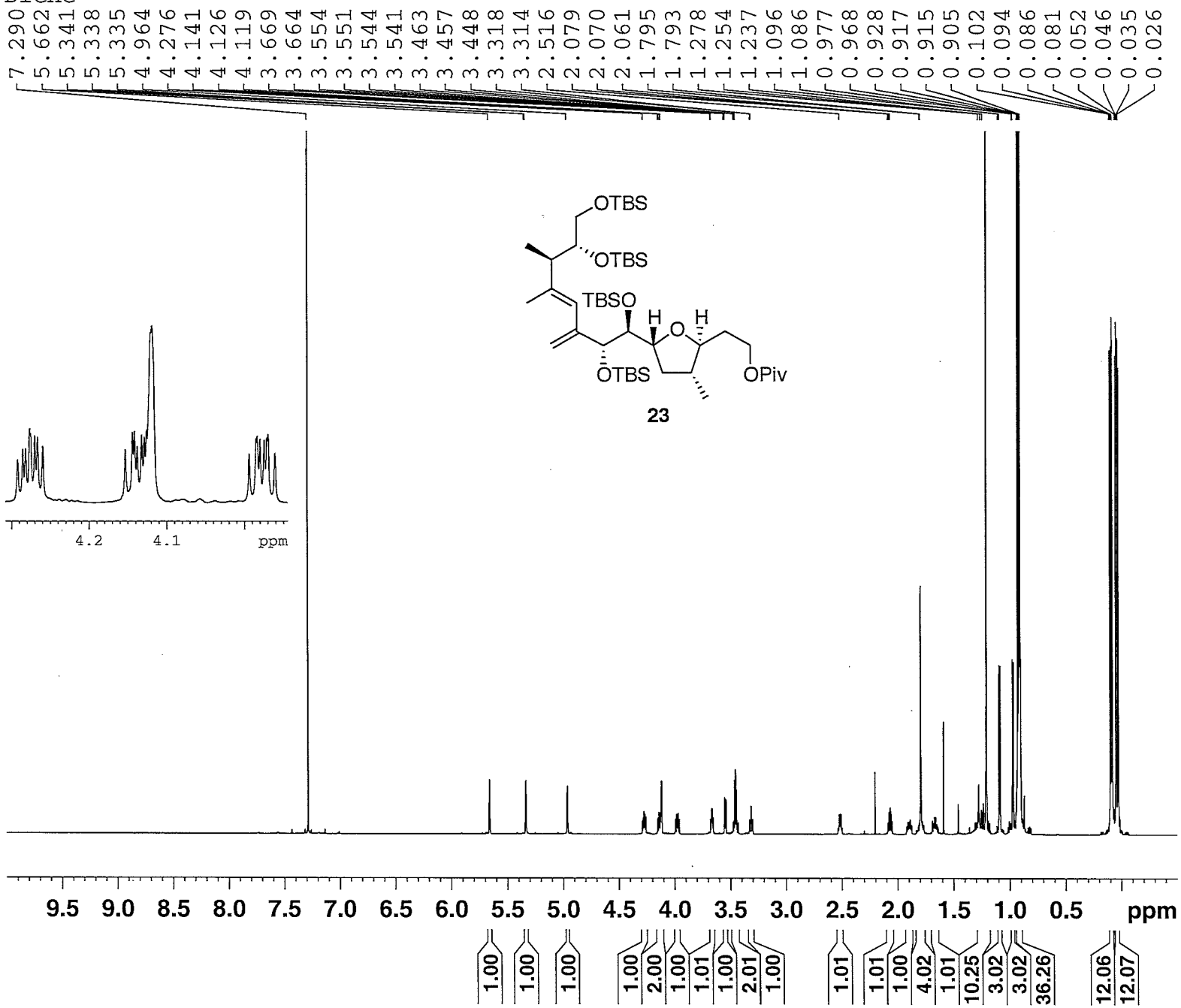
Diene (Bottom Minor Spot)



51

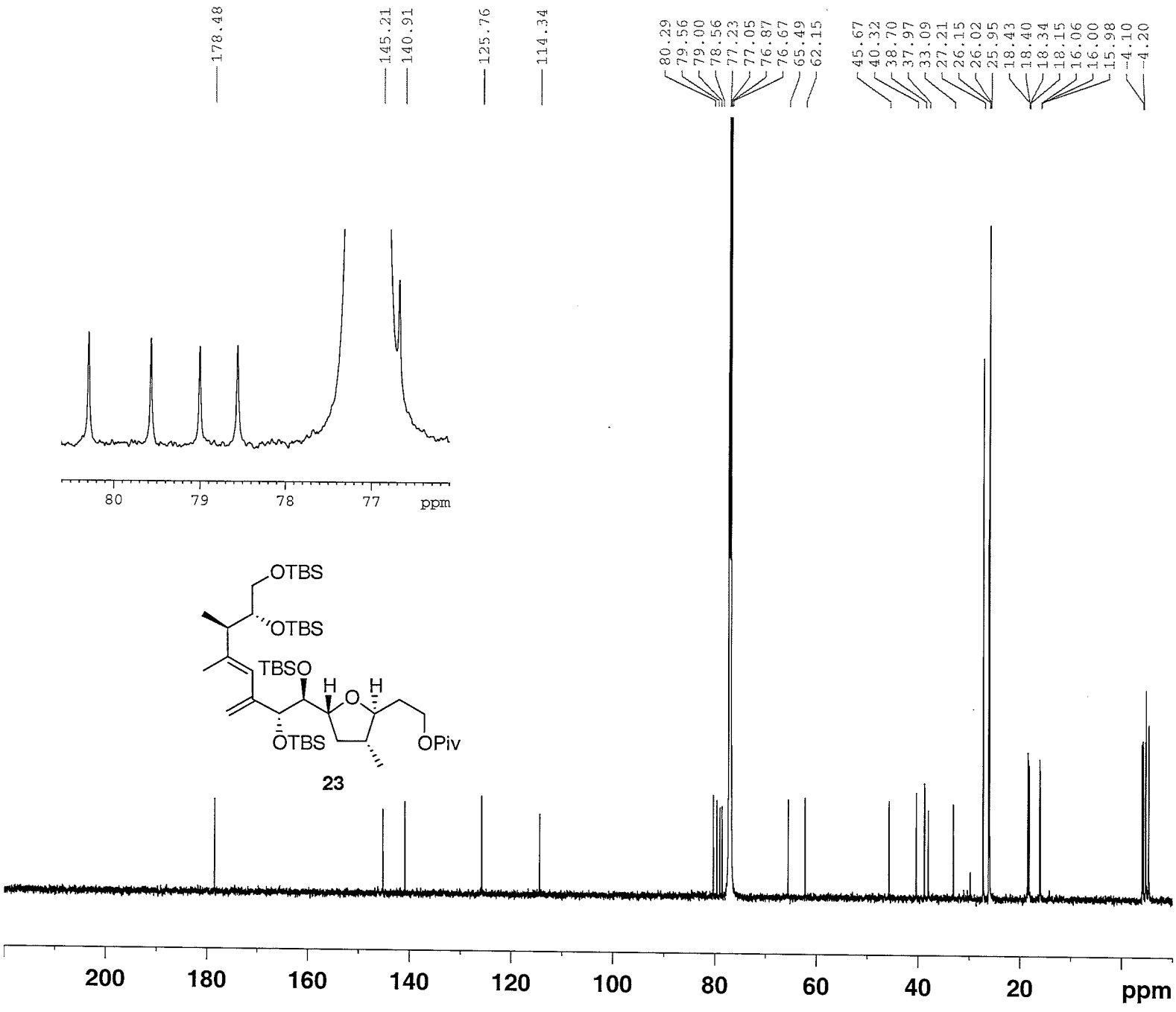
NAME	SUM-IX-06-R-Diene
EXPNO	5
PROCNO	1
Date_	20100831
Time	1.02
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	4000
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	18390.4
DW	20.850 use
DE	6.50 use
TE	301.1 K
D1	0.20000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 =======	
NUC1	13C
P1	9.00 use
PL1	-2.00 dB
SFO1	100.6258476 MHz
======== CHANNEL f2 =======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 use
PL2	0.00 dB
PL12	16.16 dB
PL13	17.00 dB
SFO2	400.1416006 MHz
SI	32768
SF	100.6152830 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Diene



NAME	SUM-XII-15-Diene
EXPNO	1
PROCNO	1
Date_	20110701
Time	16.57
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	57
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	131072
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

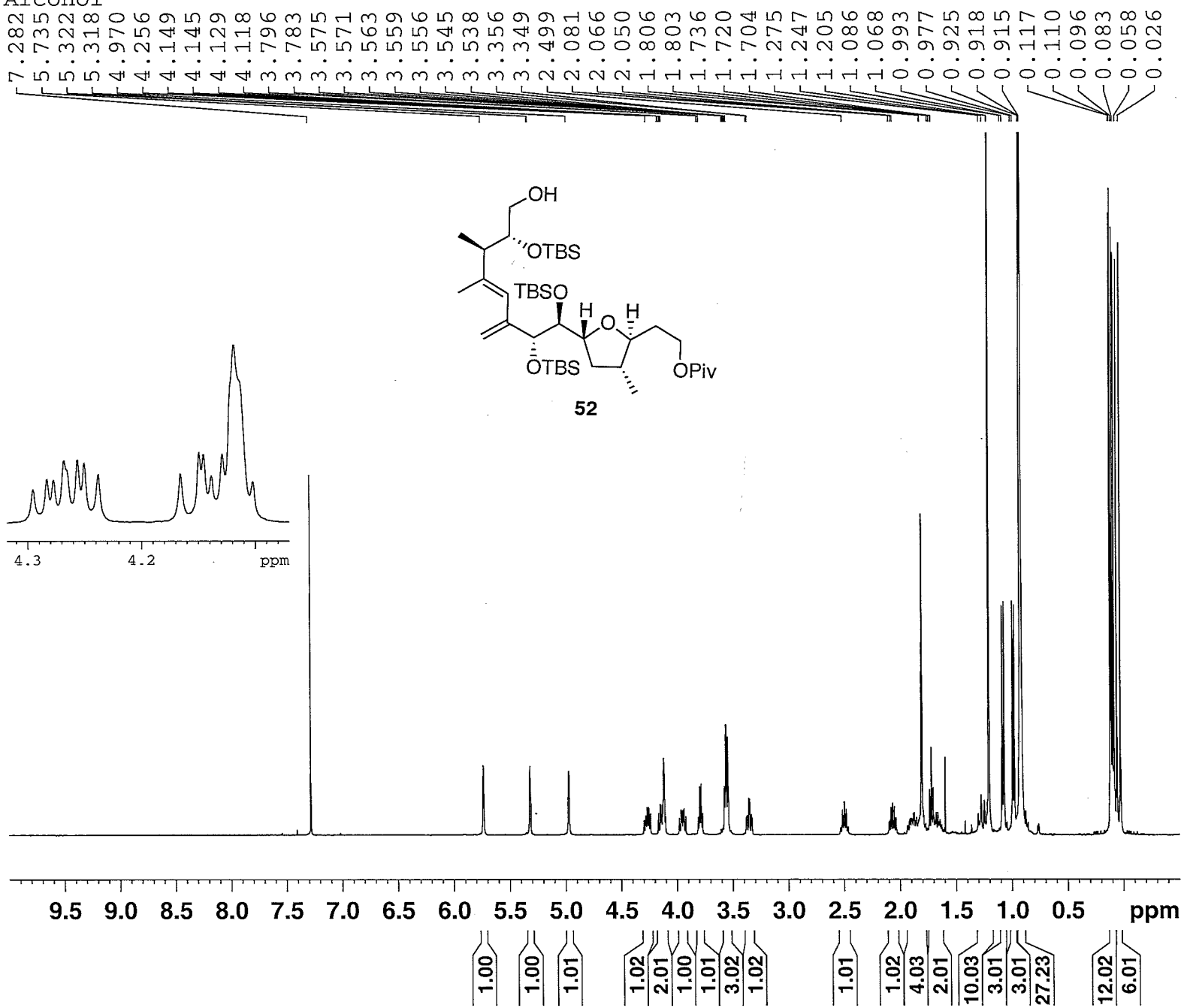
Diene



23

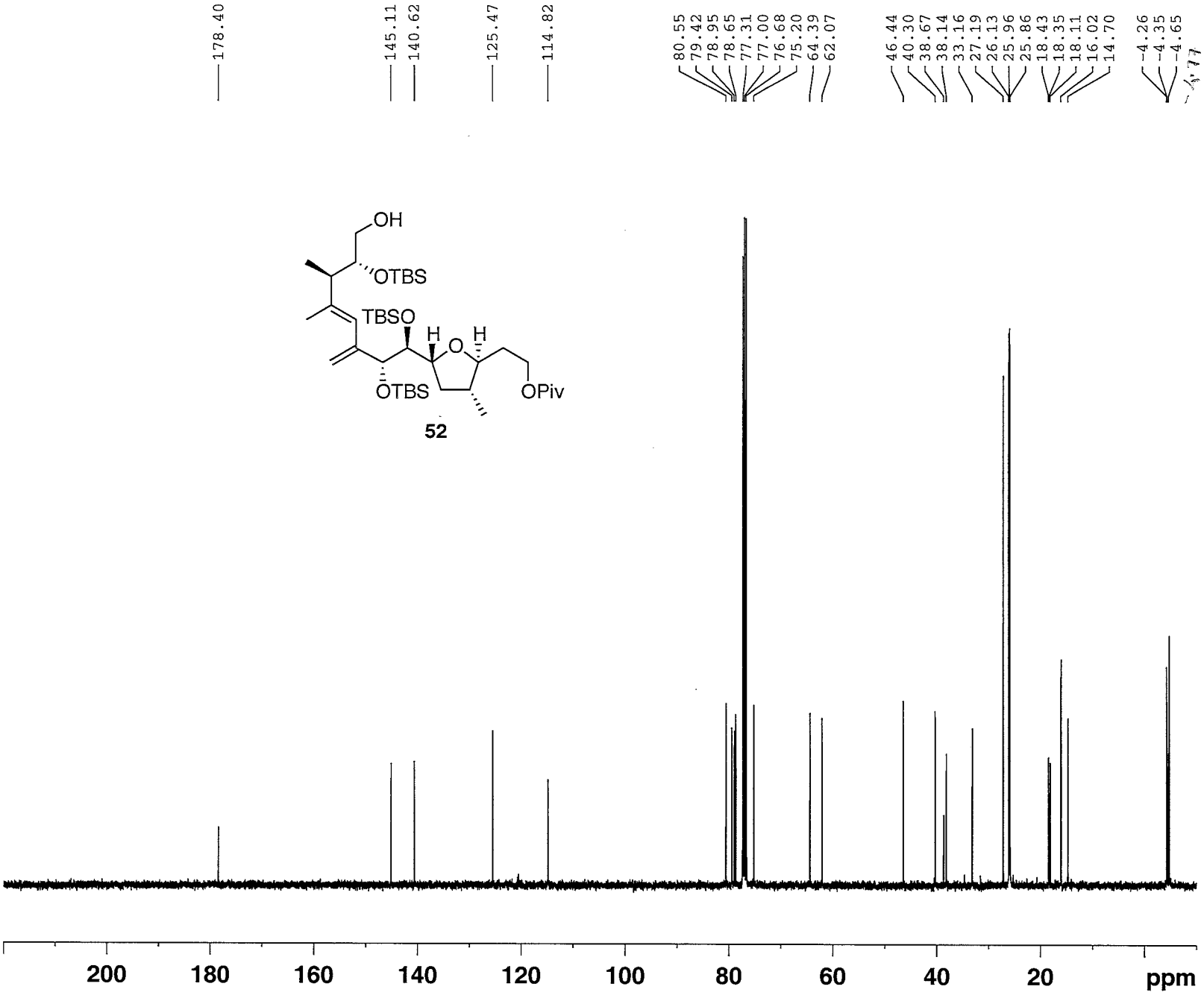
NAME	SUM-XII-15-Diene
EXPNO	2
PROCNO	1
Date_	20110701
Time	17.21
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	528
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alcohol

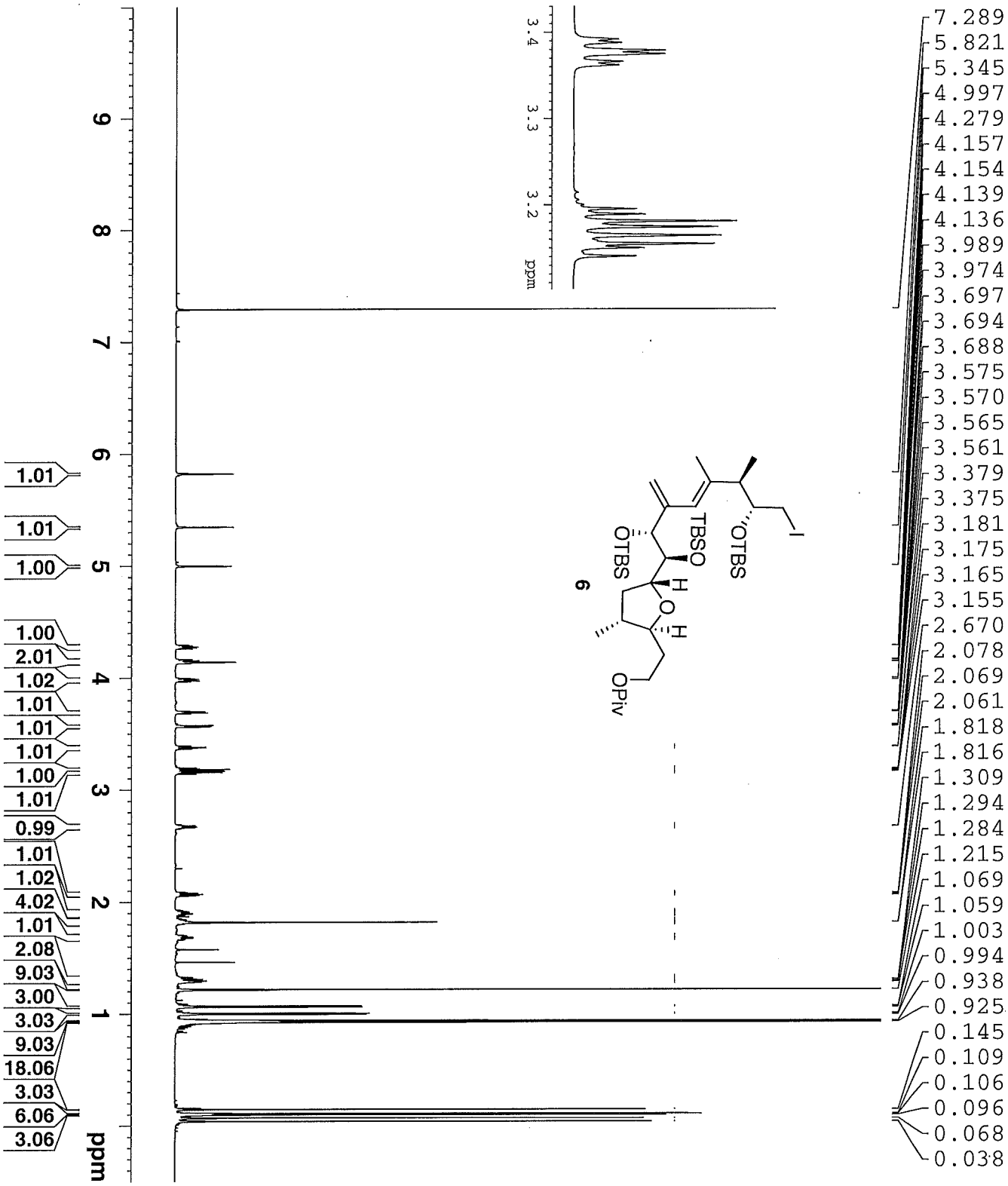


NAME	SM-VII-25-R-Alcoh
EXPNO	2
PROCNO	1
Date_	20100830
Time	22.11
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6793.478 Hz
FIDRES	0.207320 Hz
AQ	2.4117749 se
RG	4
DW	73.600 us
DE	6.50 us
TE	299.2 K
D1	2.00000000 se
TD0	1
======== CHANNEL f1 ======	
NUC1	1H
P1	14.00 us
PL1	0.00 dB
SFO1	400.1424008 MH
SI	32768
SF	400.1400000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Alcohol

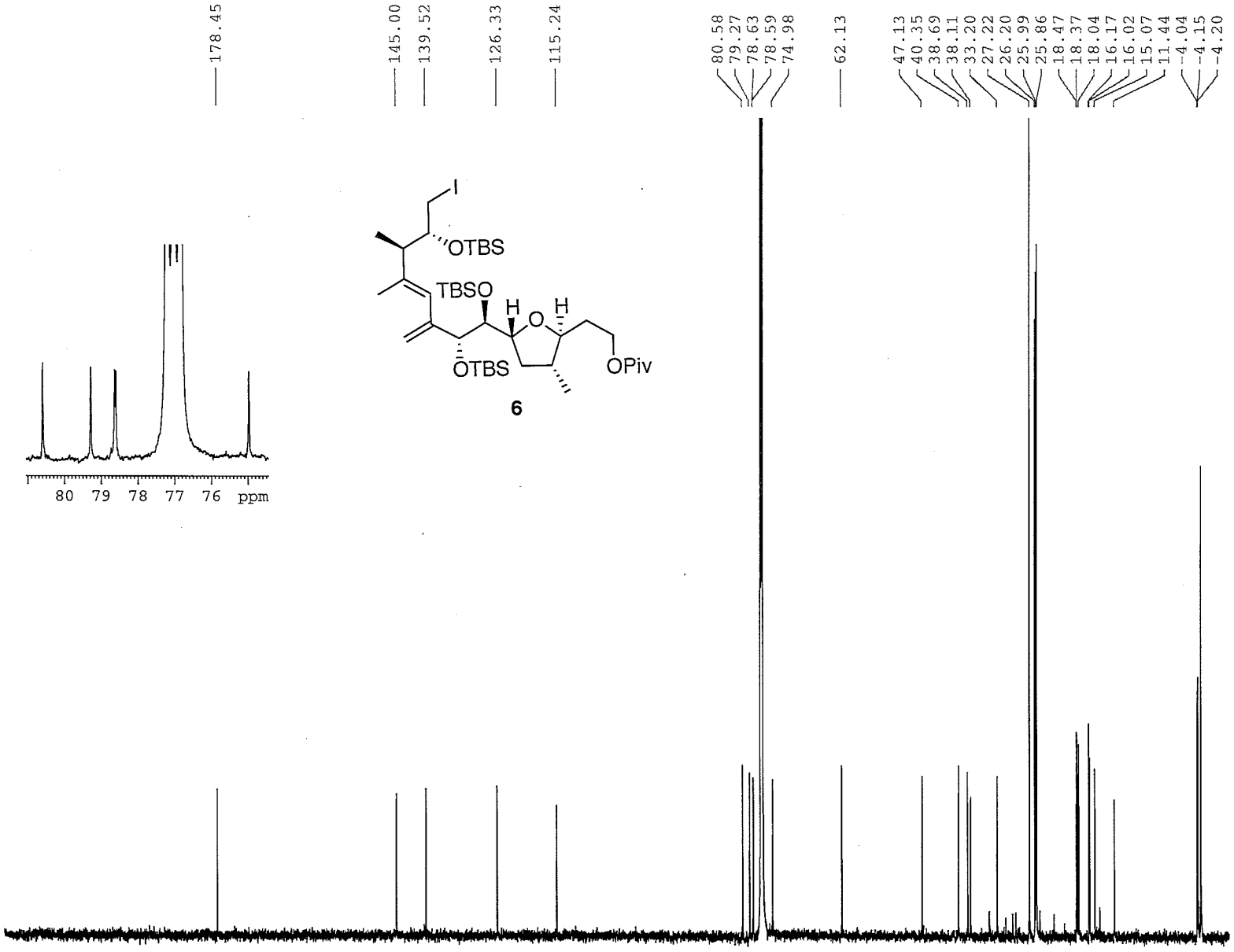


NAME	SM-VII-25-R-Alcc
EXPNO	4
PROCNO	1
Date_	20100830
Time	22.27
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	4455
DS	4
SWH	23980.814 H
FIDRES	0.365918 H
AQ	1.3664756 s
RG	14596.5
DW	20.850 u
DE	6.50 u
TE	299.4 K
D1	0.20000000 s
D11	0.03000000 s
TD0	1
========	CHANNEL f1 =====
NUC1	13C
P1	9.00 u
PL1	-2.00 d
SFO1	100.6258476 M
========	CHANNEL f2 =====
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 u
PL2	0.00 d
PL12	16.16 d
PL13	17.00 d
SFO2	400.1416006 M
SI	32768
SF	100.6152830 M
WDW	EM
SSB	0
LB	1.00 H
GB	0
PC	1.40



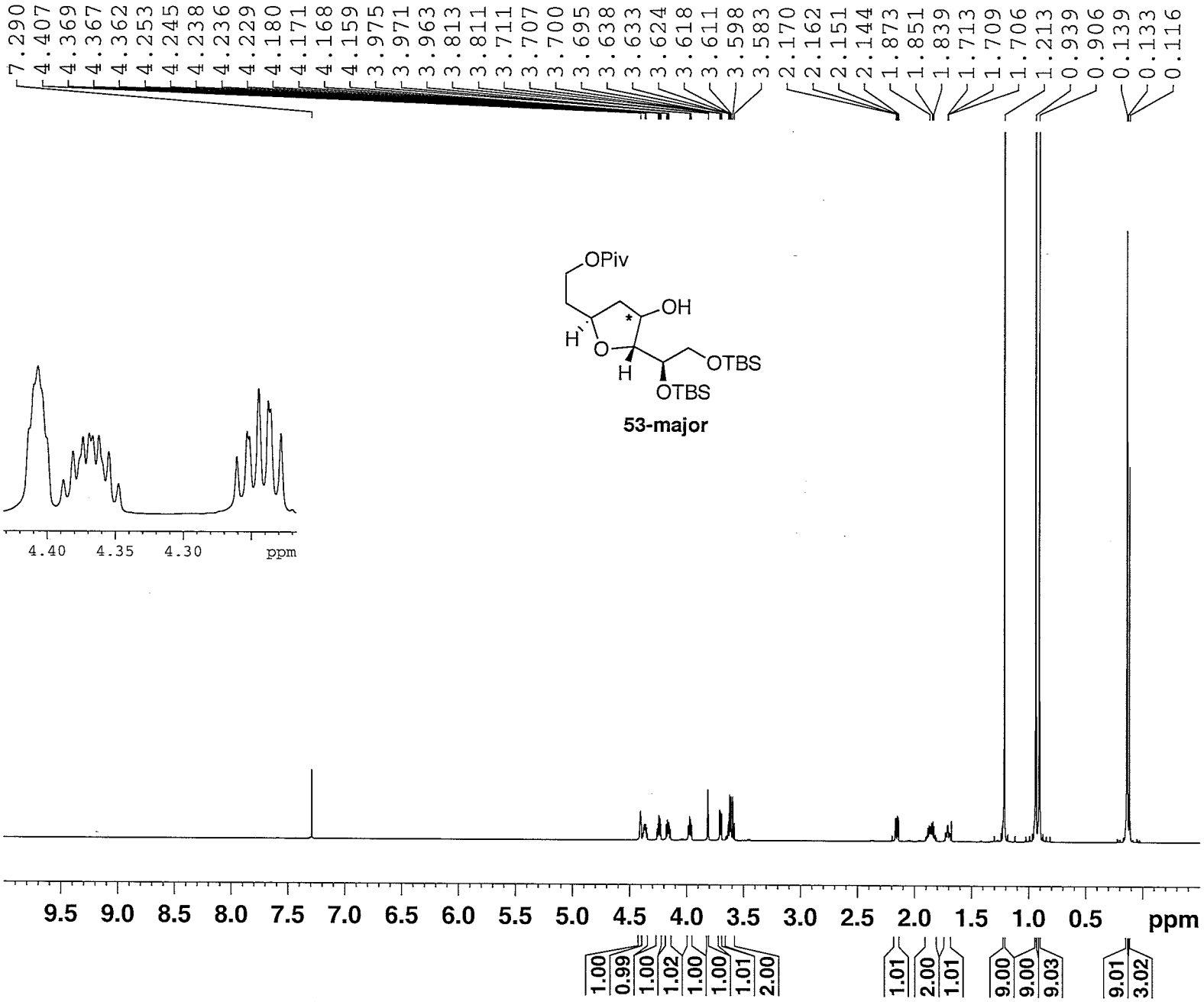

```
NAME                    SM-VII-44
EXPNO                           1
PROCNO                          1
Date_                20100618
Time                    15.46
INSTRUM                  spect
PROBHD     5 mm CPDCH 13C
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                11904.762 Hz
FIDRES             0.181652 Hz
AQ                 2.75255620 se
RG                      45.2
DW                     42.000 us
DE                     16.50 us
TE                     297.9 K
D1                  2.00000000 se
TD0                         1

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.40 us
PL1                    -3.20 dB
PL1W               33.59817505 W
SFO1               700.1245508 MH
SI                     65536
SF                 700.1200000 MH
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

Iodide



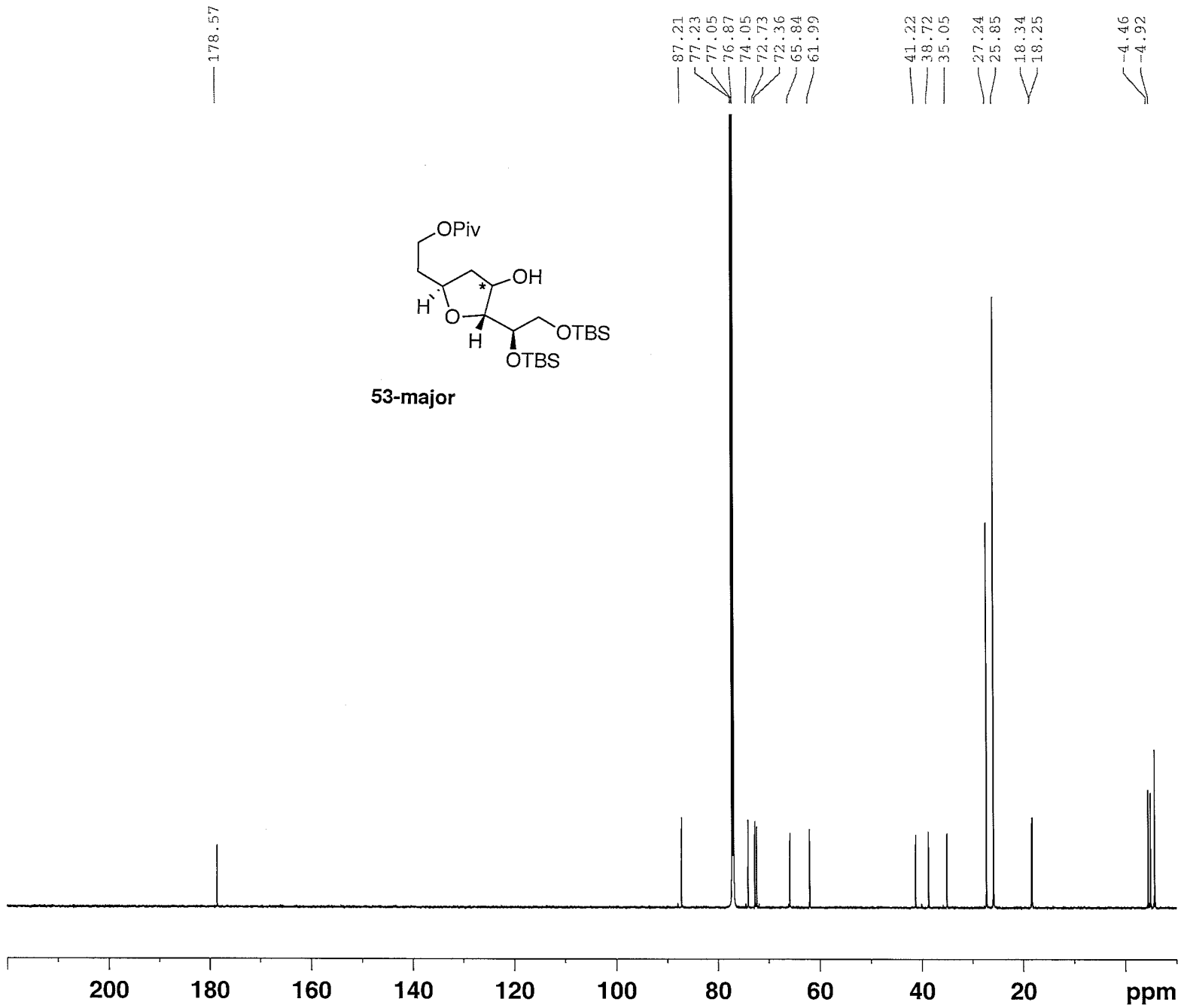
NAME	SM-VII-44
EXPNO	2
PROCNO	1
Date_	20100618
Time	16.01
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	296
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.0 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
======== CHANNEL f1 ======	
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0629186 MH
======== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alcohol (Major Iosmer)



NAME	SUM-XII-23-Alcoho
EXPNO	2
PROCNO	1
Date_	20110705
Time	21.30
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	57
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	131072
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

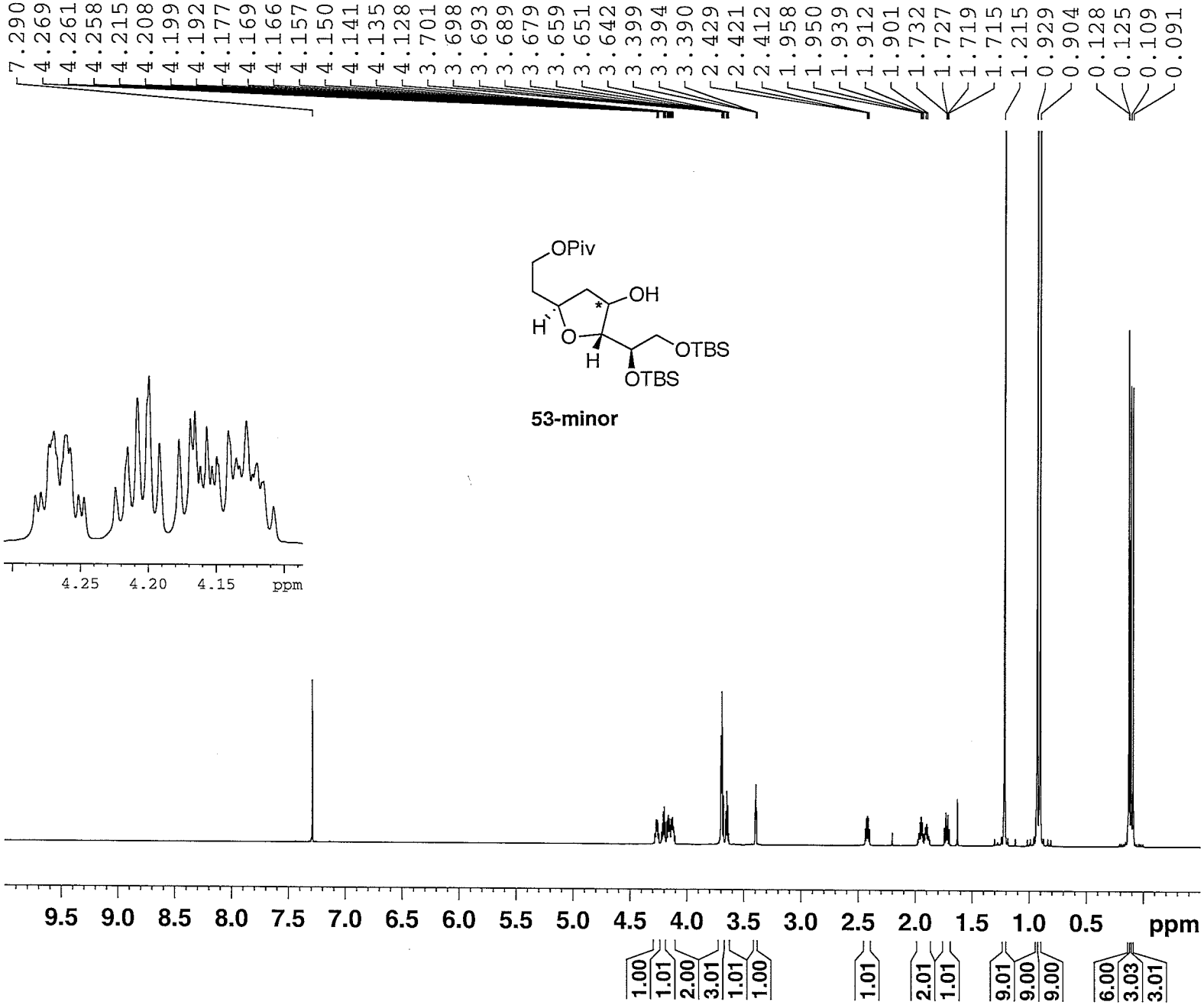
Alcohol (Major Iosmer)



F

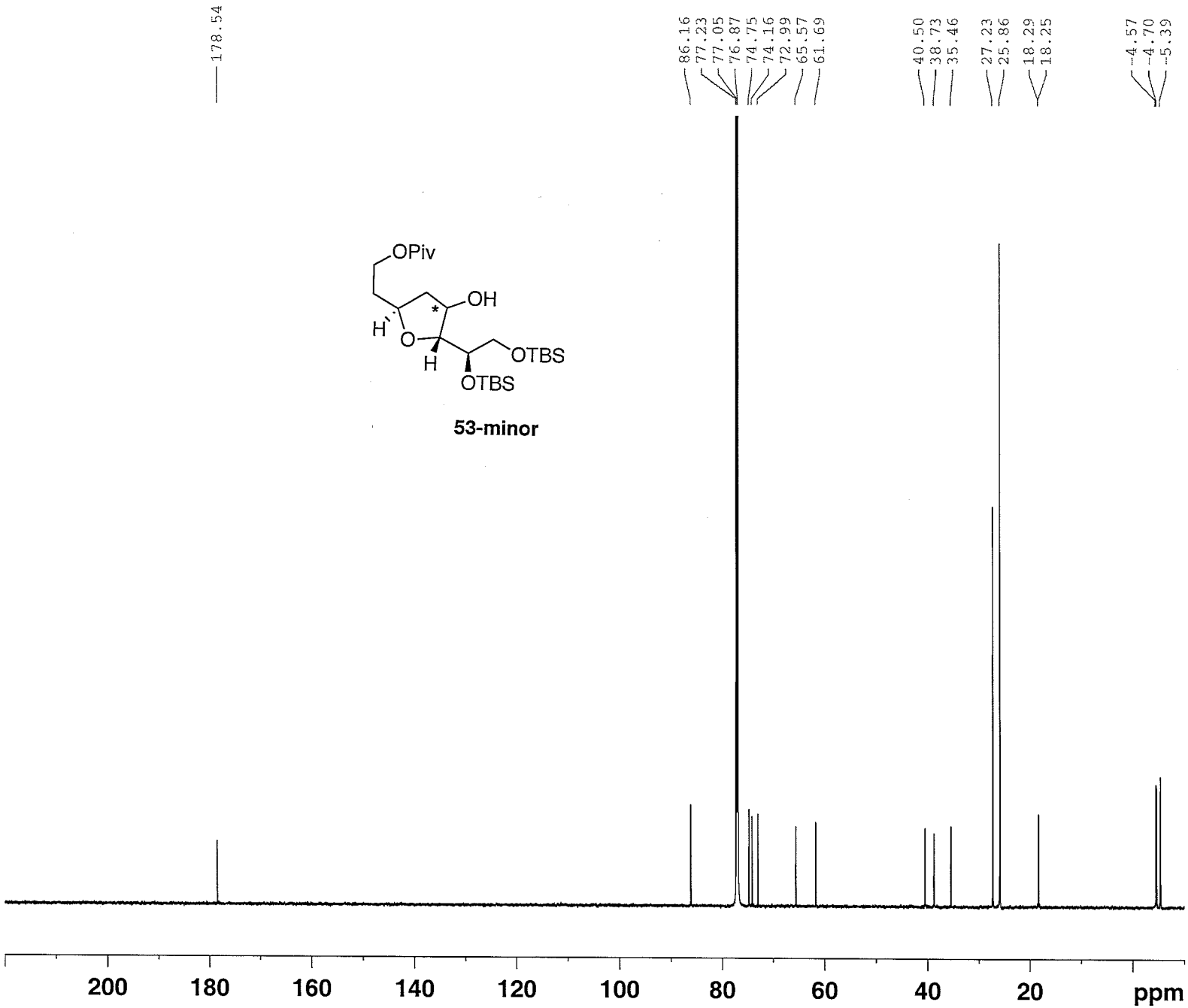
NAME	SUM-XII-23-Alcoho
EXPNO	3
PROCNO	1
Date_	20110705
Time	21.40
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	126
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
======== CHANNEL f1 ======	
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
======== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alcohol (Minor Iosmer)



NAME	SUM-XII-23-Alcoho
EXPNO	7
PROCNO	1
Date_	20110705
Time	23.51
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	18
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	57
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	131072
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

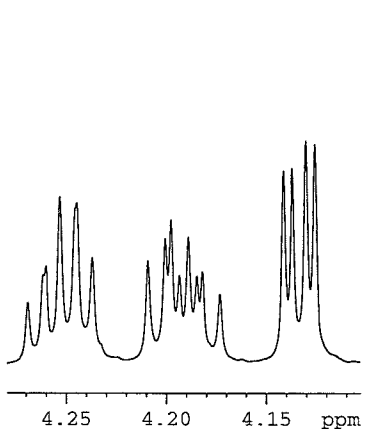
Alcohol (Minor Iosmer)

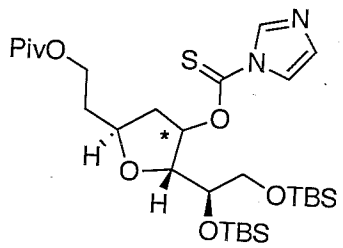


NAME	SUM-XII-23-Alcoho
EXPNO	8
PROCNO	1
Date_	20110706
Time	17.38
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	201
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
======== CHANNEL f1 ======	
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
======== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Major Thioate

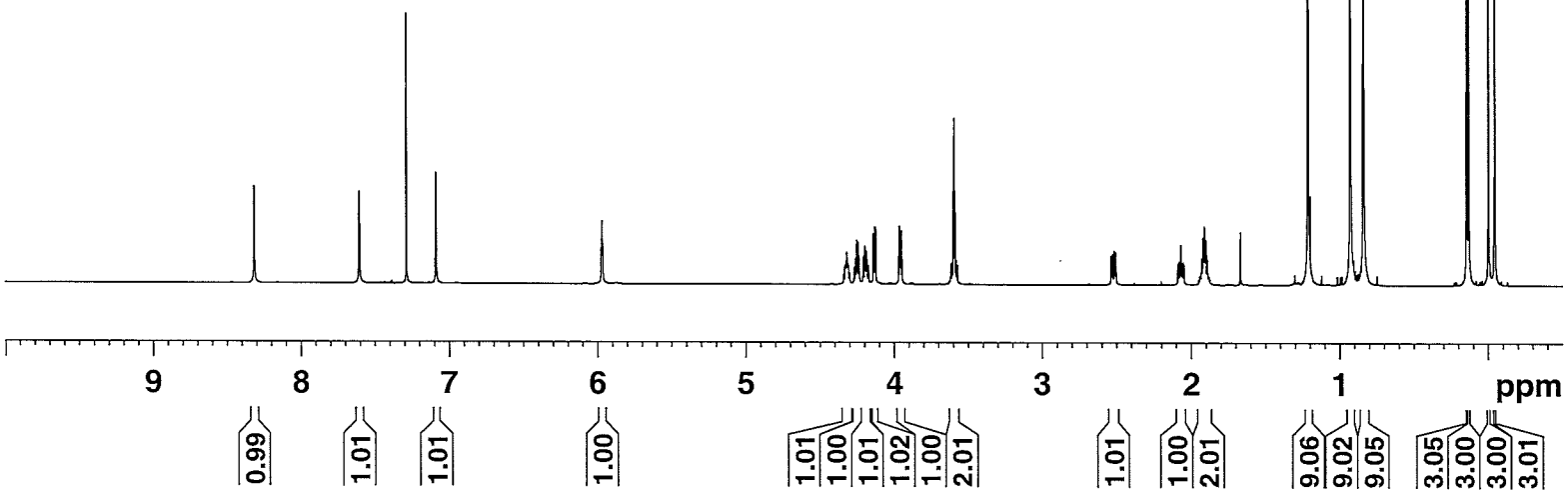
8.318 7.608 7.290 7.092 7.091 7.090 5.976 5.971 5.966 4.321 4.253 4.245 4.237 4.209 4.200 4.197 4.189 4.141 4.137 4.130 4.125 3.971 3.965 3.960 3.958 3.954 3.947 3.602 3.595 3.589 2.536 2.527 2.515 2.506 2.067 1.929 1.920 1.910 1.901 1.213 0.927 0.839 0.143 0.131 -0.002 -0.044



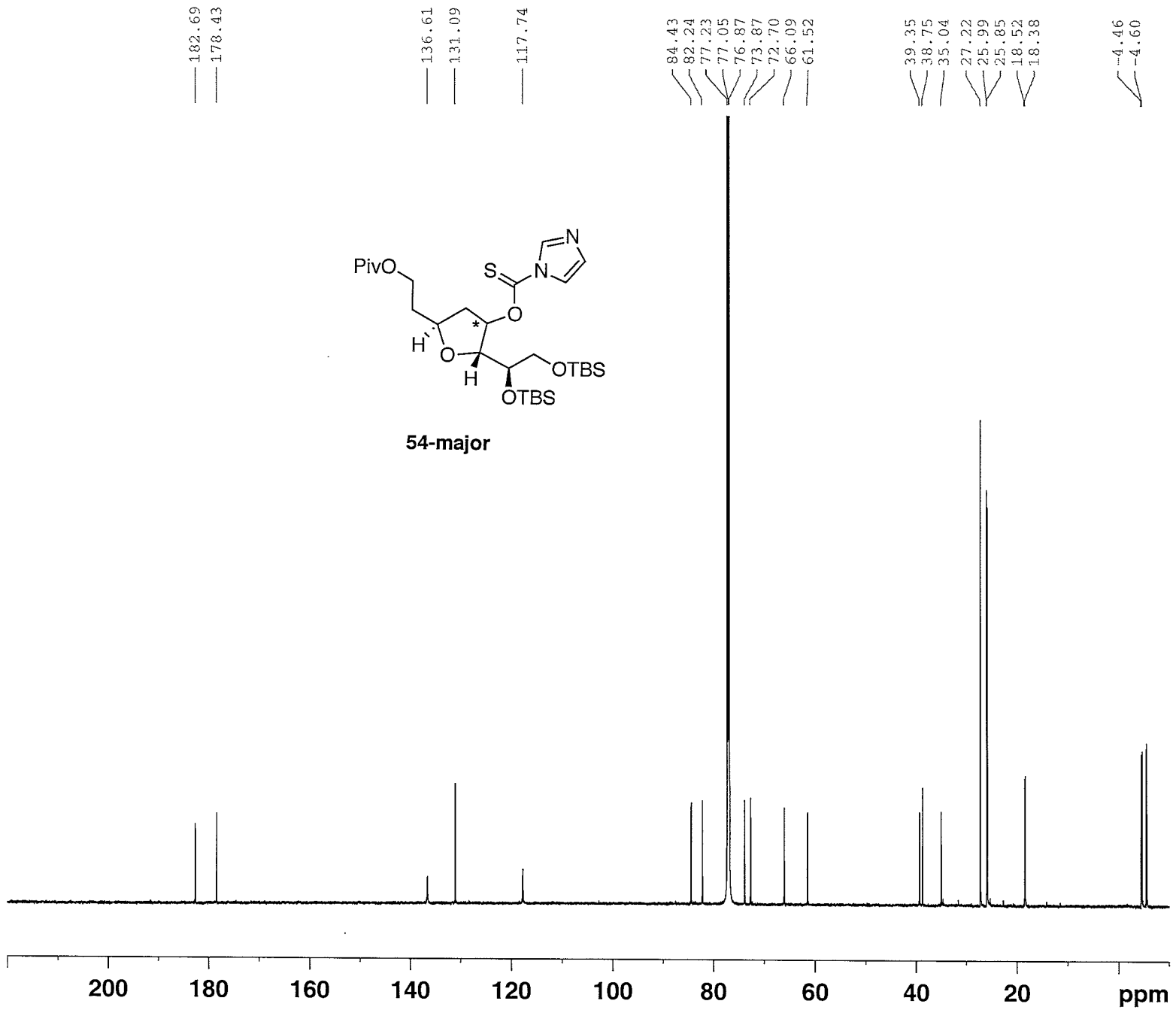


54-major

NAME	SUM-XI-81-Thioate
EXPNO	1
PROCNO	1
Date_	20110612
Time	19.22
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.181652 Hz
AQ	2.7525620 se
RG	57
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	65536
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



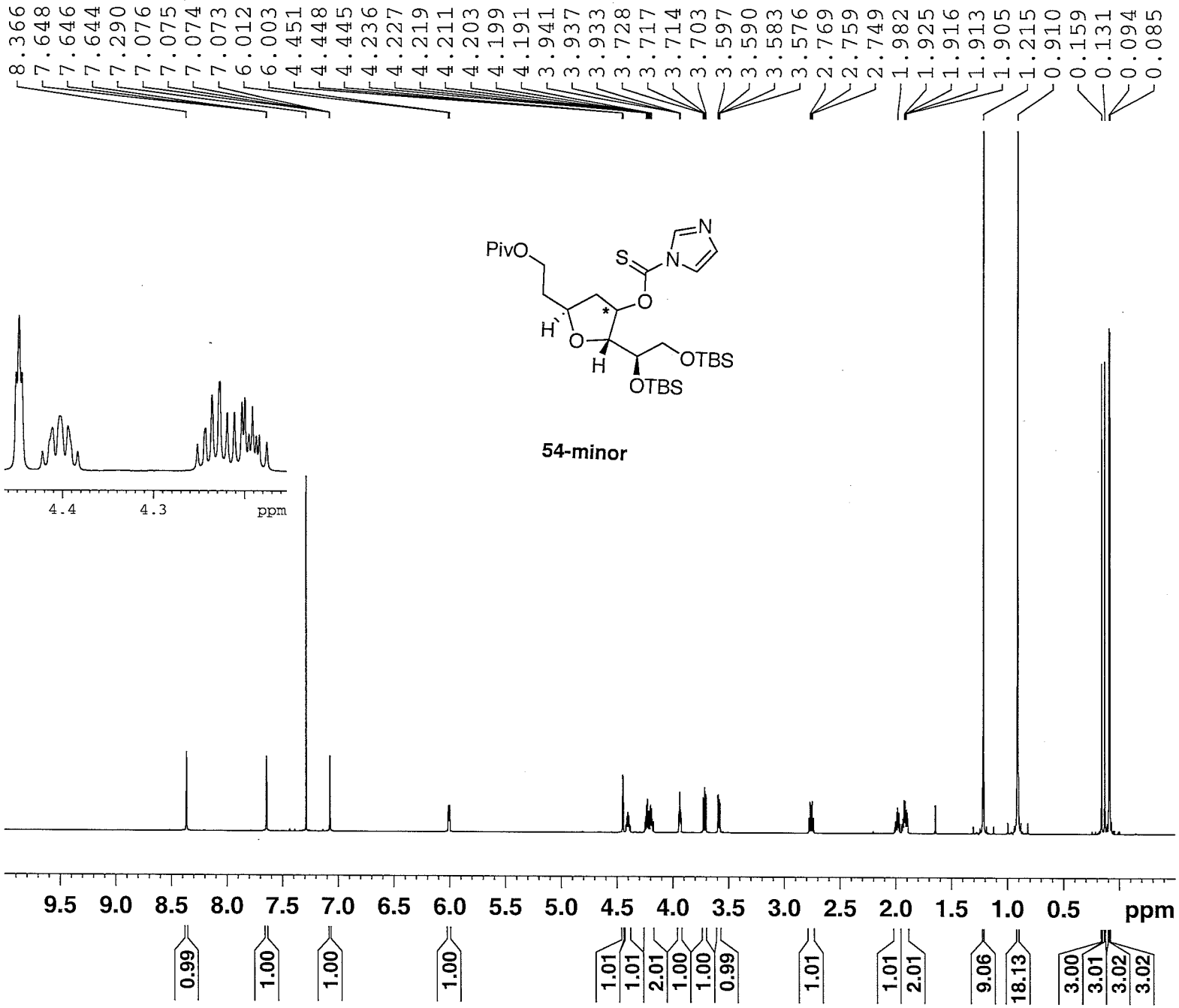
Major Thioate



54-major

NAME	SUM-XI-81-Thioate
EXPNO	2
PROCNO	1
Date_	20110612
Time	19.31
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	1009
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

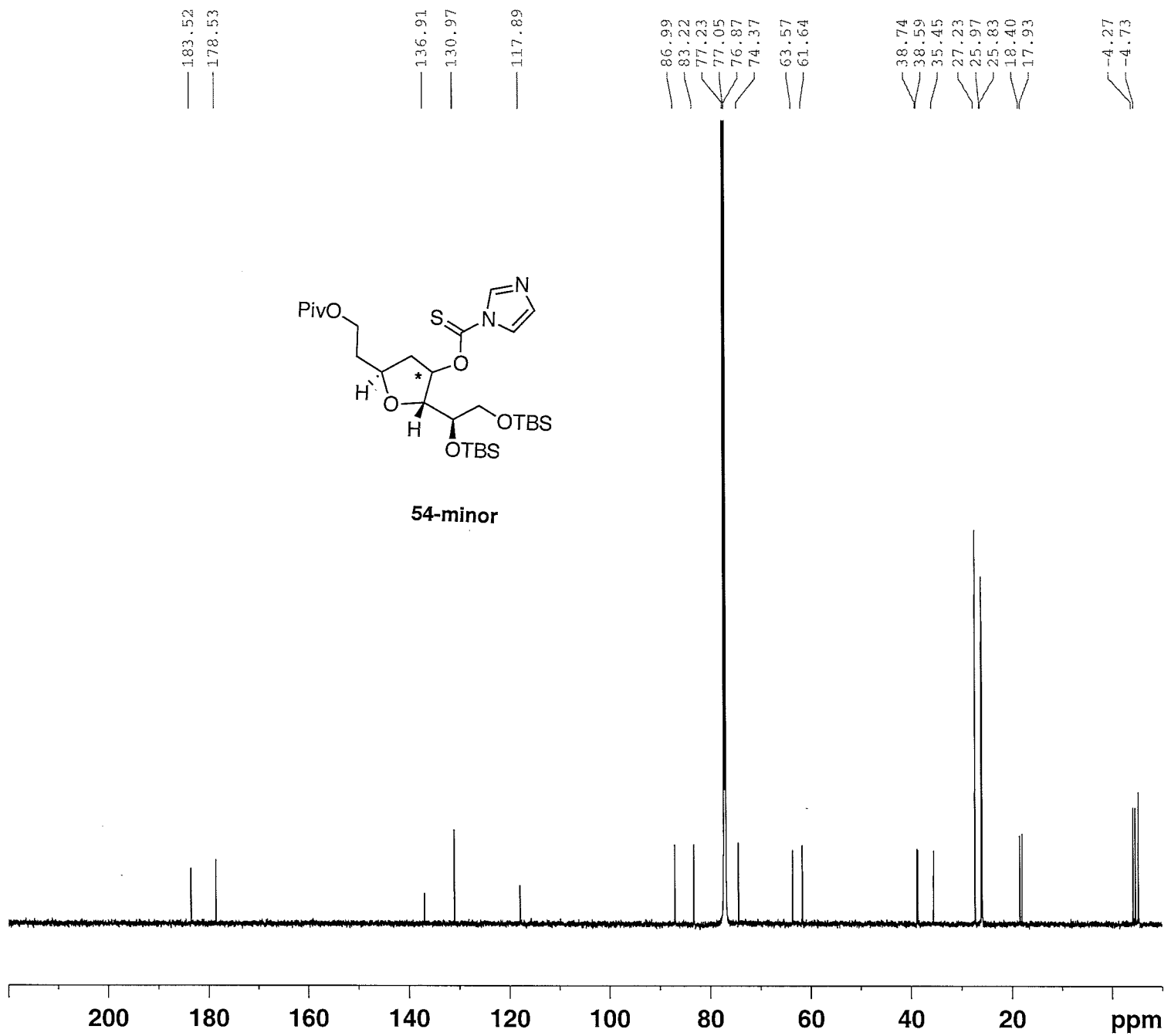
Minor Thioate



54-minor

NAME	SUM-XI-80-Thioate
EXPNO	3
PROCNO	1
Date_	20110615
Time	22.43
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	24
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	101
DW	42.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1245508 MH
SI	131072
SF	700.1200000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Minor Thioate

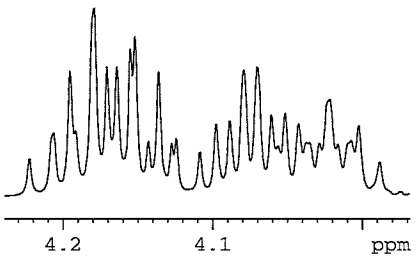


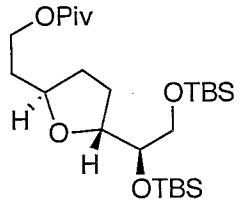
54-minor

NAME	SUM-XI-80-Thioate
EXPNO	4
PROCNO	1
Date_	20110615
Time	22.49
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	129
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Tetrahydrofuran

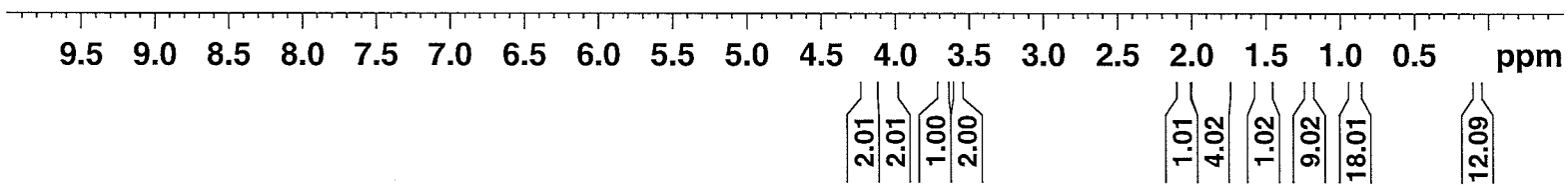
7.282 4.195 4.179 4.170 4.164 4.154 4.152 4.136 4.079 4.070 4.060 4.051 4.021 3.703 3.683 3.674 3.654 3.595 3.582 3.574 3.572 3.566 3.553 1.935 1.918 1.884 1.867 1.853 1.849 1.842 1.835 1.831 1.813 1.799 1.796 1.783 1.544 1.520 1.514 1.207 0.909 0.905 0.091 0.089 0.074 0.069



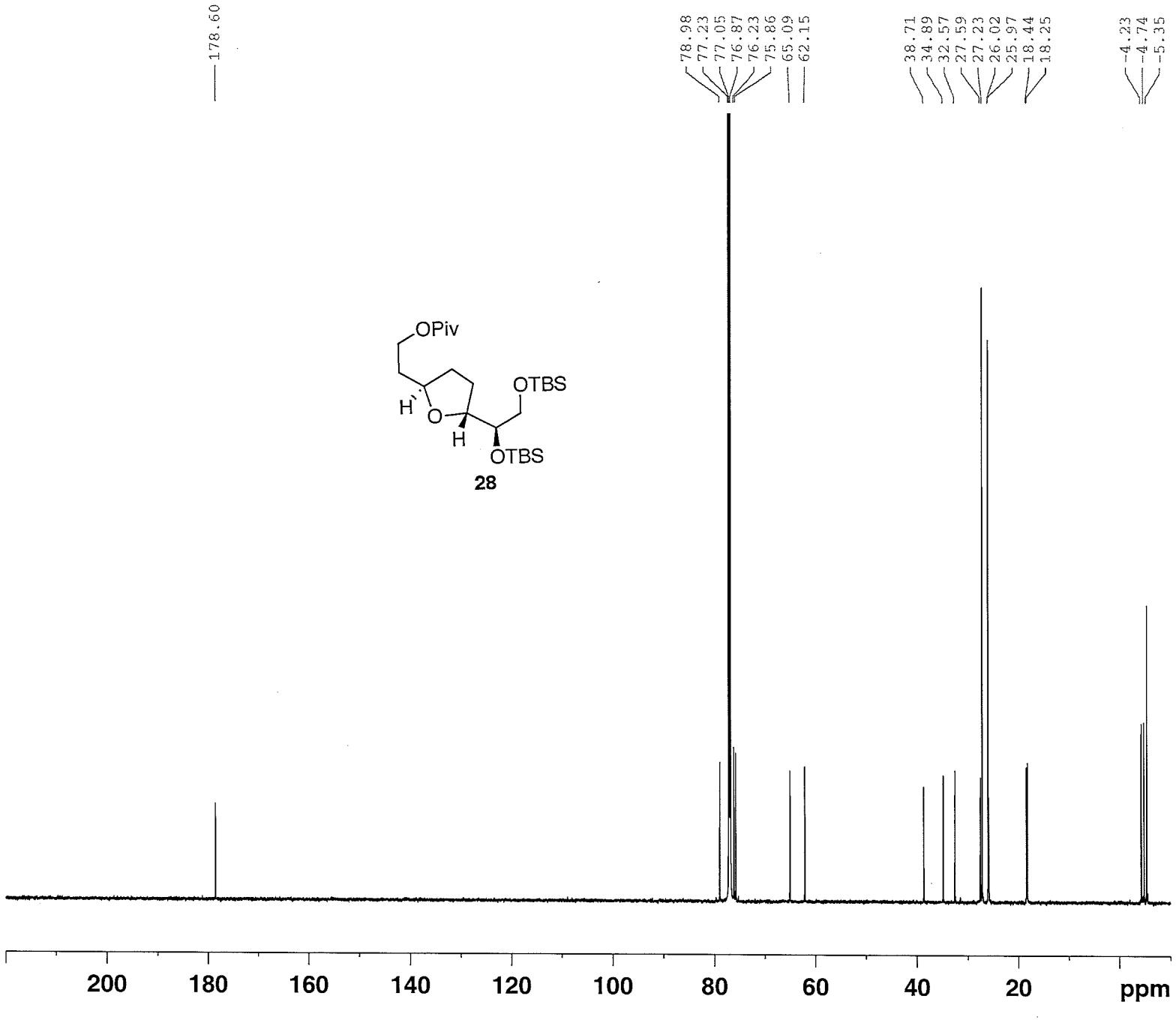


28

NAME	SUM-XI-82-R-THF
EXPNO	2
PROCNO	1
Date_	20110614
Time	0.08
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6793.478 Hz
FIDRES	0.207320 Hz
AQ	2.4117749 se
RG	45.3
DW	73.600 us
DE	6.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	14.00 us
PL1	0.00 dB
SFO1	400.1424008 MH
SI	32768
SF	400.1400000 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

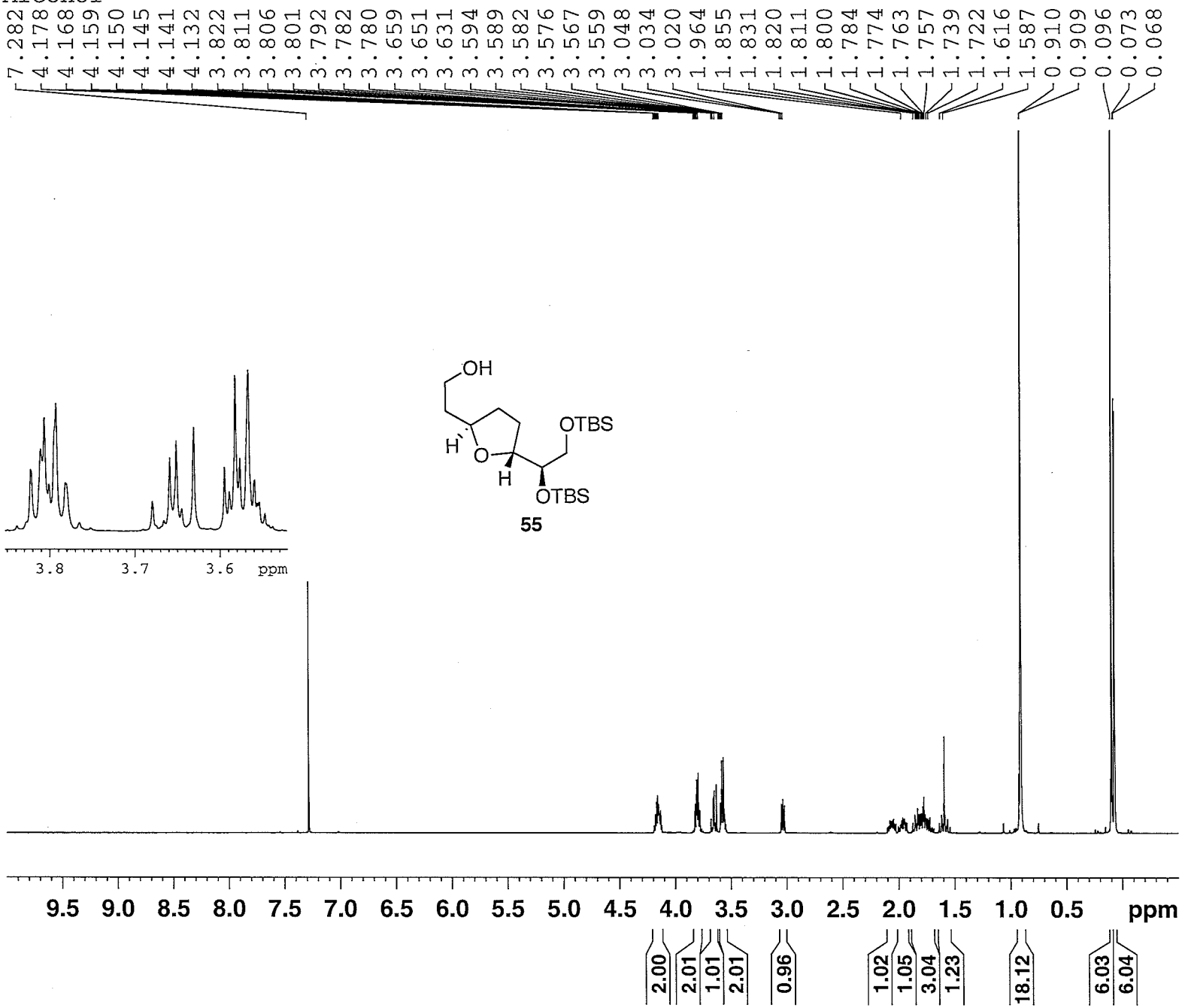


Tetrahydrofuran



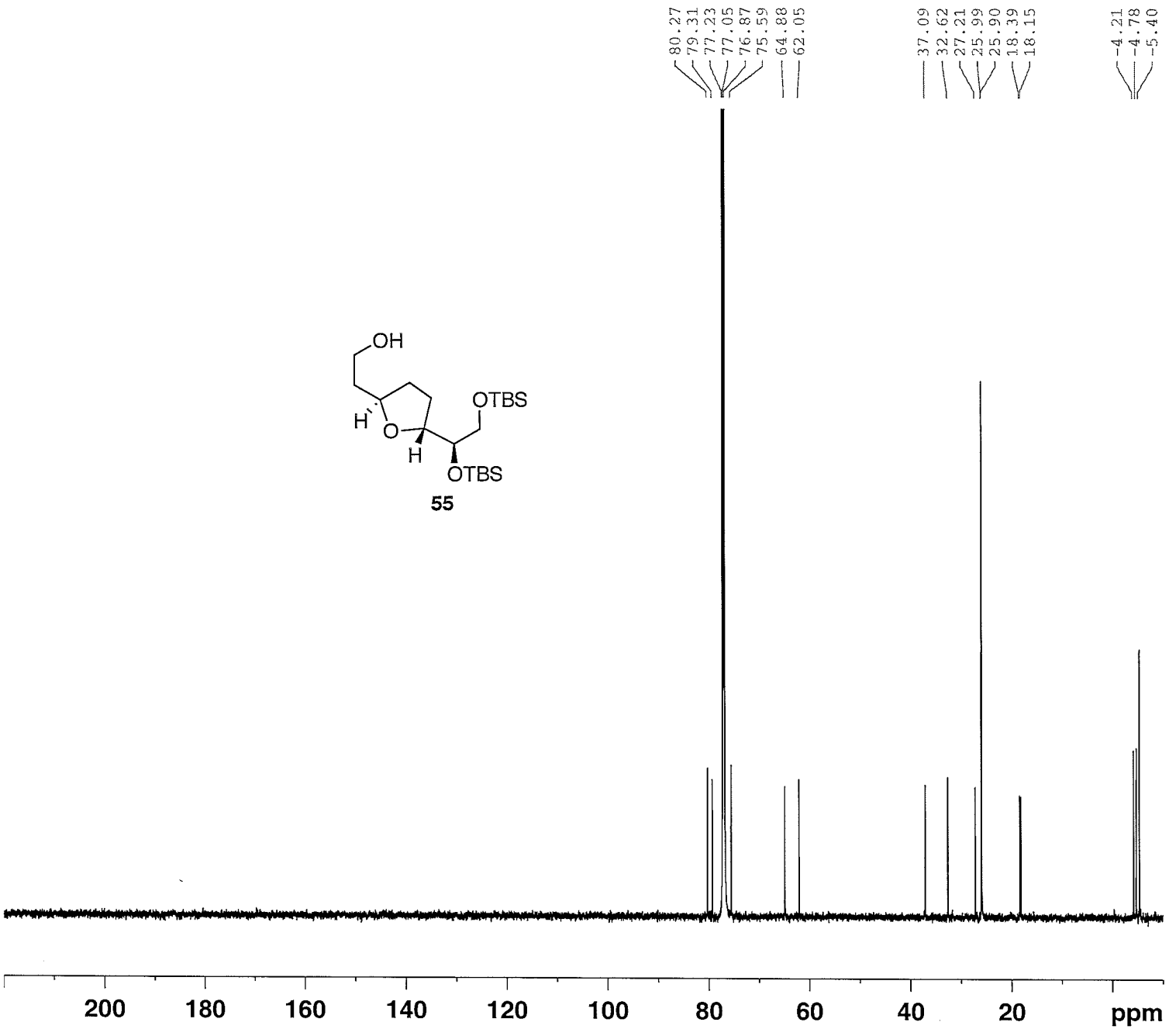
NAME	SUM-XI-82-top THF
EXPNO	4
PROCNO	1
Date_	20110614
Time	17.56
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	101
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alcohol



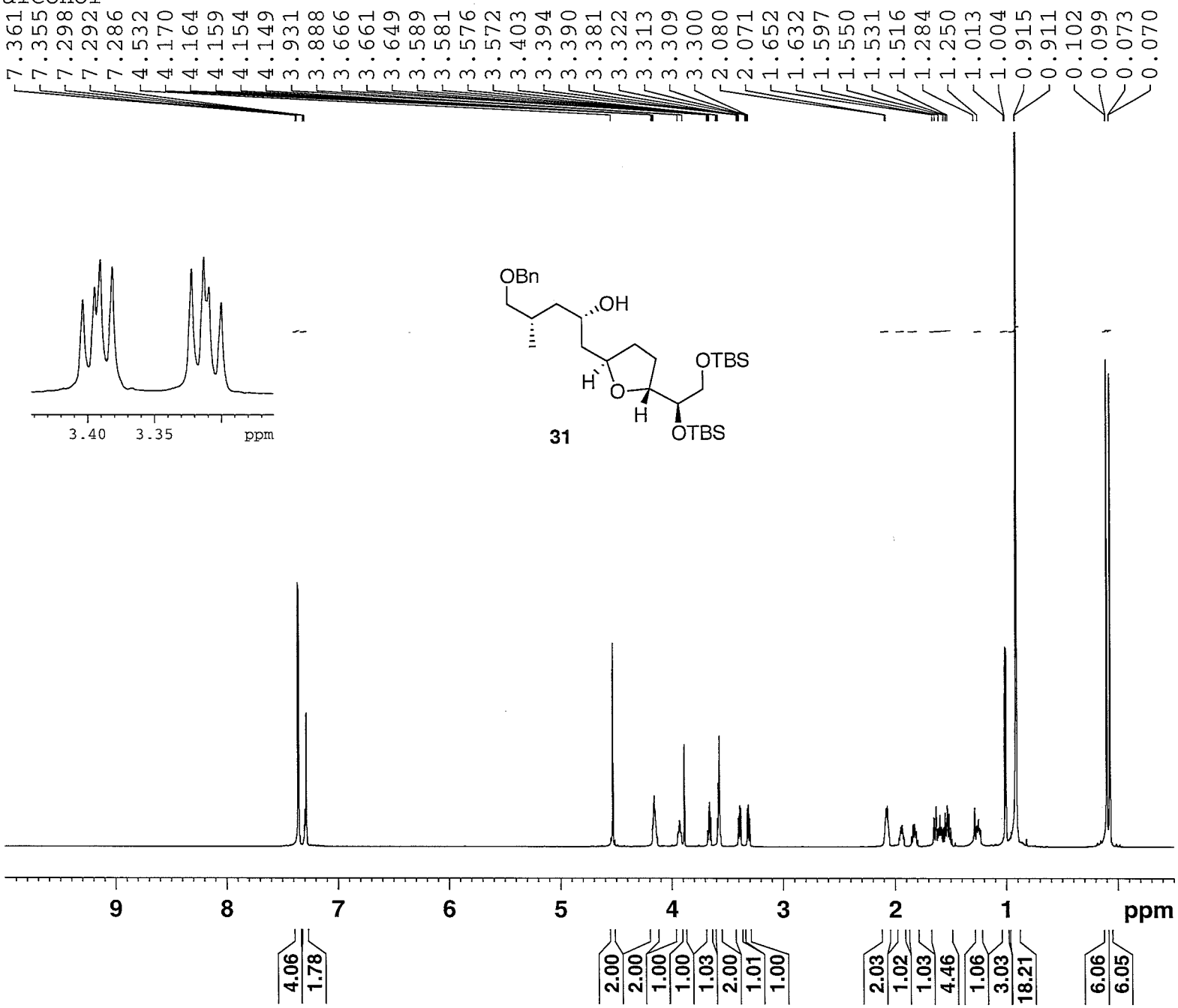
NAME	SUM-XI-83-R-Alcoh
EXPNO	1
PROCNO	1
Date_	20110614
Time	19.58
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6793.478 Hz
FIDRES	0.207320 Hz
AQ	2.4117749 se
RG	128
DW	73.600 us
DE	6.50 us
TE	298.3 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	14.00 us
PL1	0.00 dB
SFO1	400.1424008 MH:
SI	32768
SF	400.1400000 MH:
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Alcohol



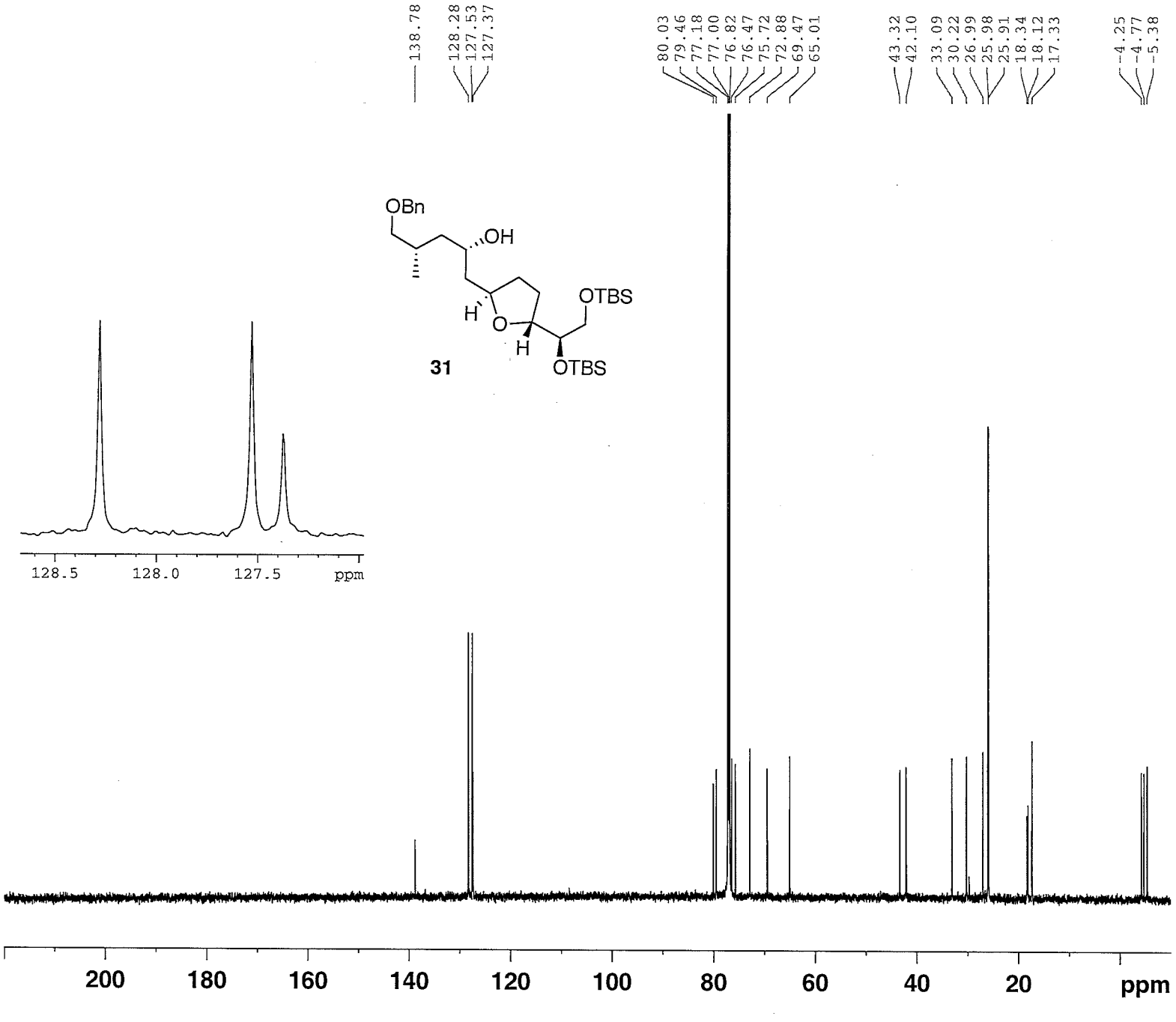
NAME	SUM-XI-83-Alcohol
EXPNO	2
PROCNO	1
Date_	20110614
Time	19.34
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	161
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 se
RG	203
DW	12.000 us
DE	15.00 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0637988 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MH
SI	131072
SF	176.0453140 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

alcohol



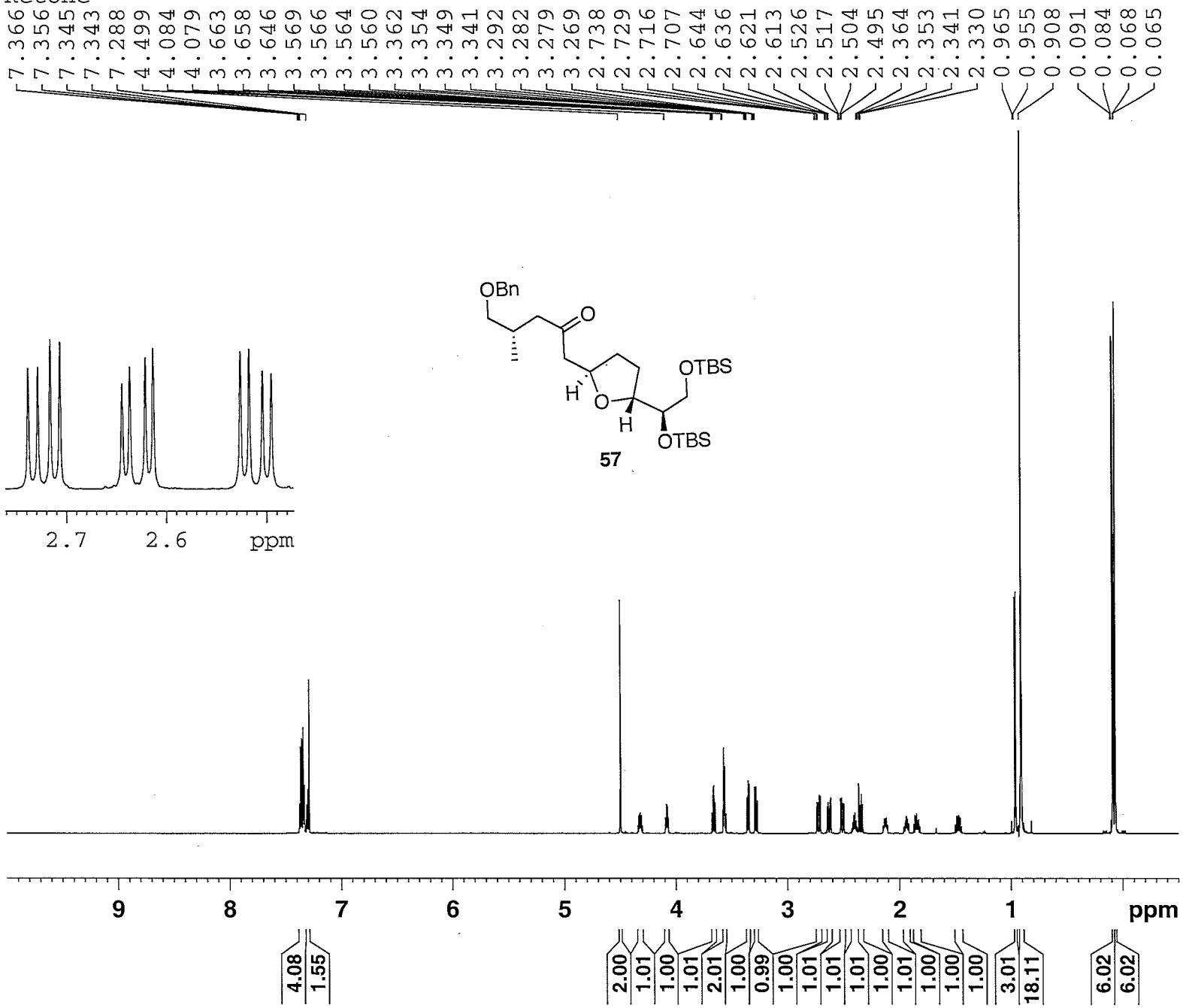
NAME	SUM-XIV-22-Alcoho
EXPNO	1
PROCNO	1
Date_	20111023
Time	22.28
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	128
DW	42.000 us
DE	6.50 us
TE	299.0 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	13.75 us
PL1	-3.00 dB
PL1W	32.08600616 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

alcohol



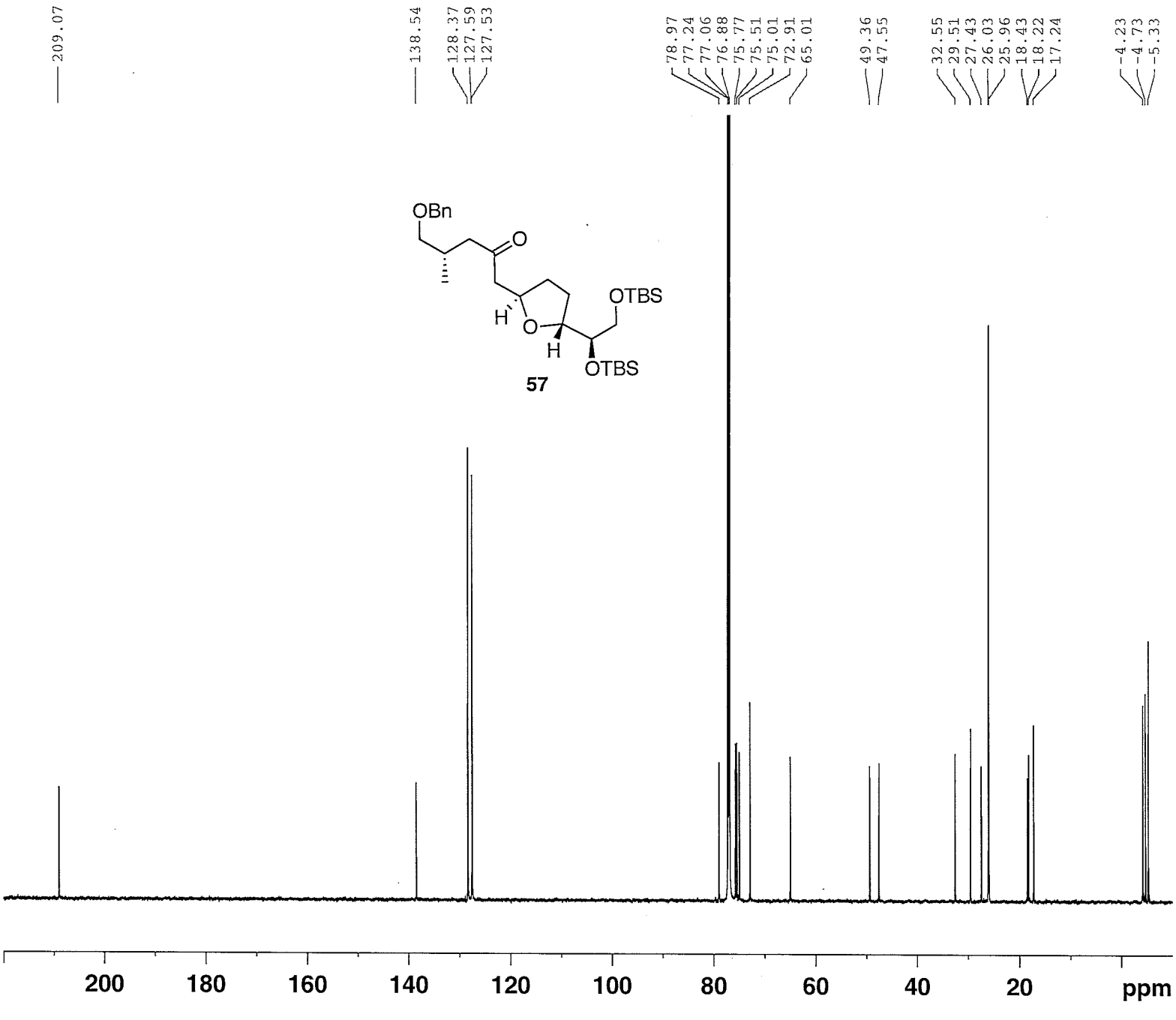
NAME	SUM-XIV-22-Alcoho
EXPNO	2
PROCNO	1
Date_	20111023
Time	23.20
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	6.50 us
TE	300.4 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.30 us
PL1	2.00 dB
PL1W	67.83342743 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 us
PL2	-3.00 dB
PL12	12.30 dB
PL13	12.30 dB
PL2W	32.08600616 W
PL12W	0.94692516 W
PL13W	0.94692516 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Ketone



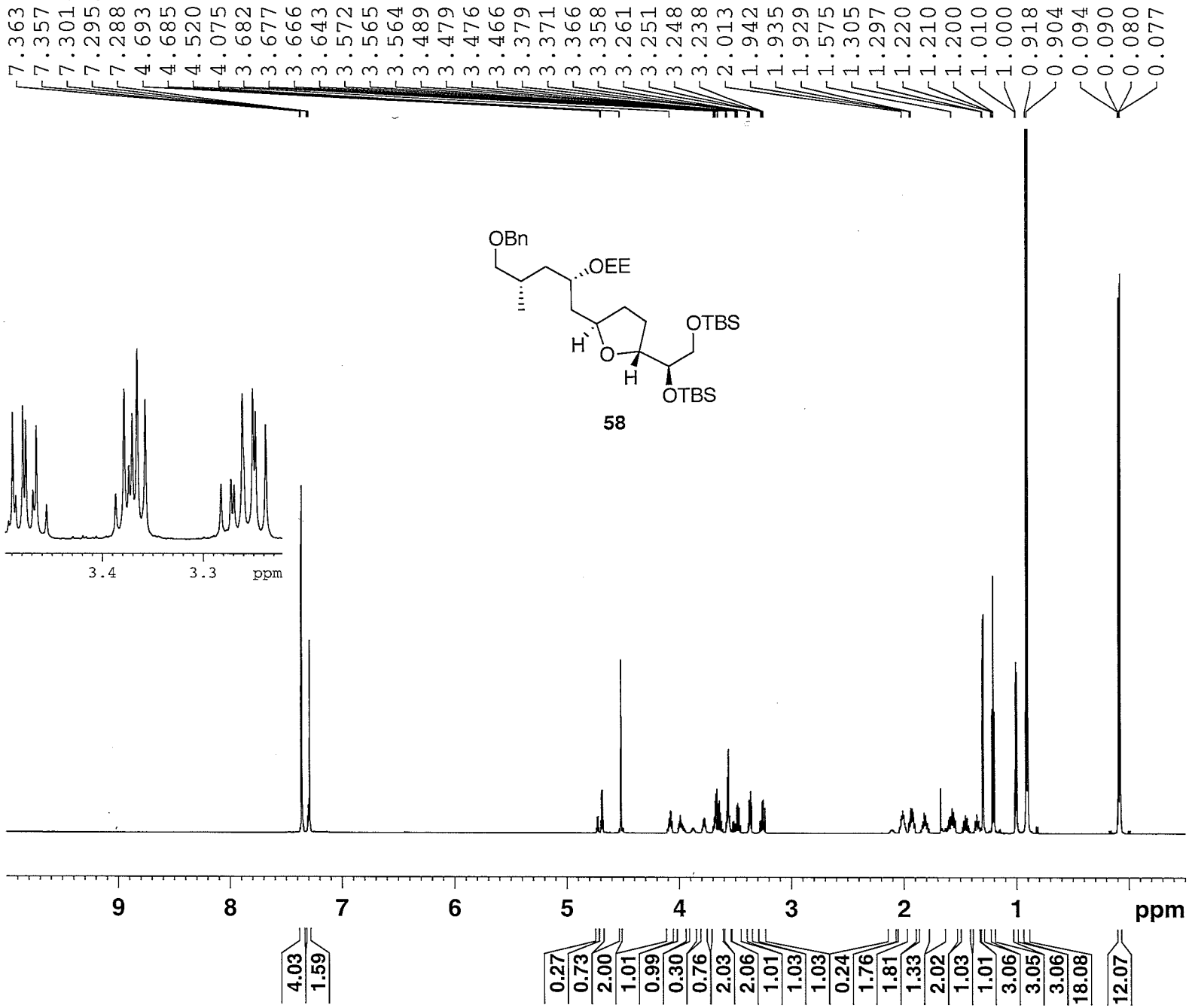
NAME	SUM-XV-16-Ketone
EXPNO	1
PROCNO	1
Date_	20120402
Time	0.27
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	40.3
DW	42.000 us
DE	6.50 us
TE	298.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Ketone



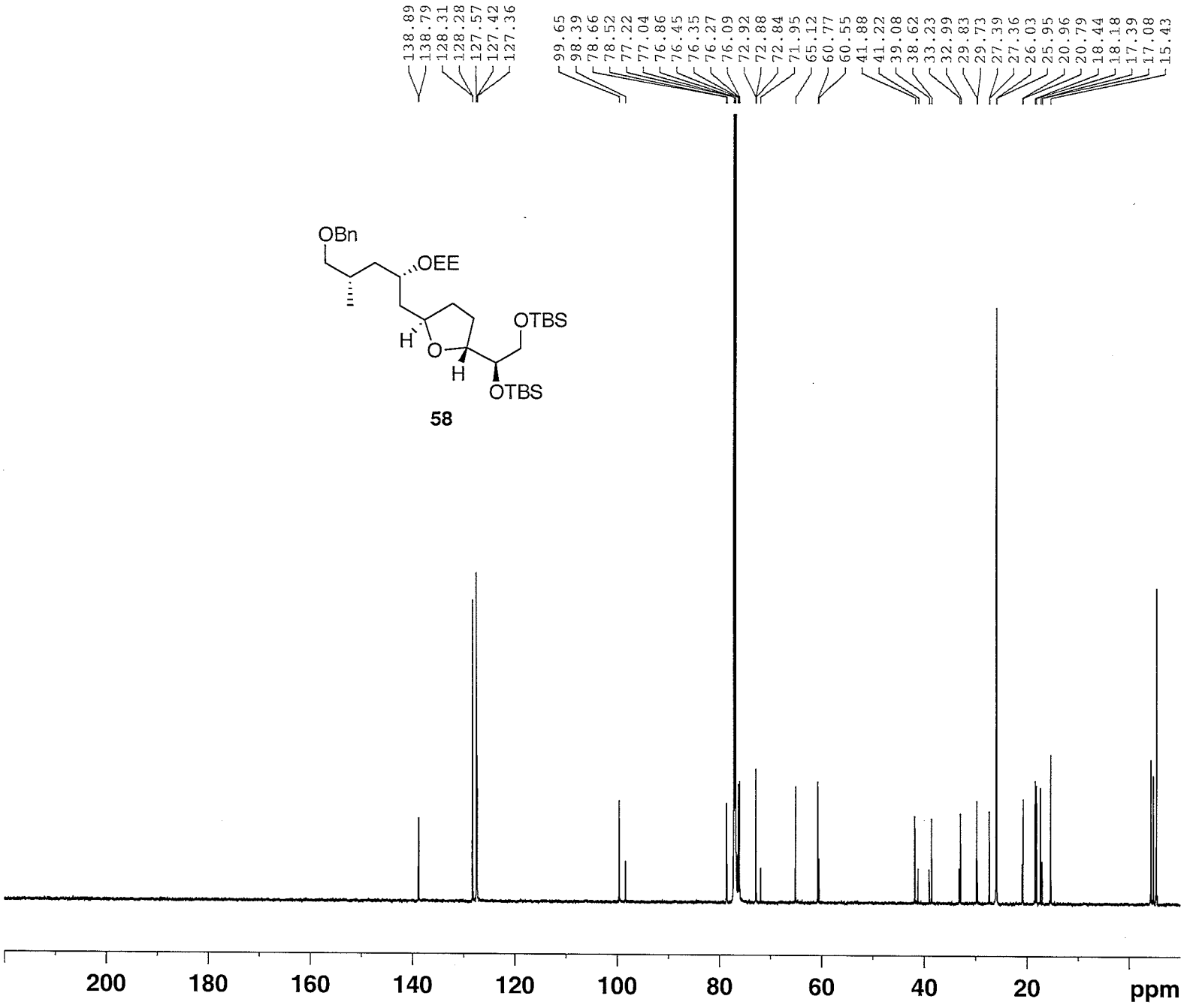
NAME	SUM-XV-16-Ketone
EXPNO	2
PROCNO	1
Date_	20120402
Time	0.36
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	206
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

EE Ether



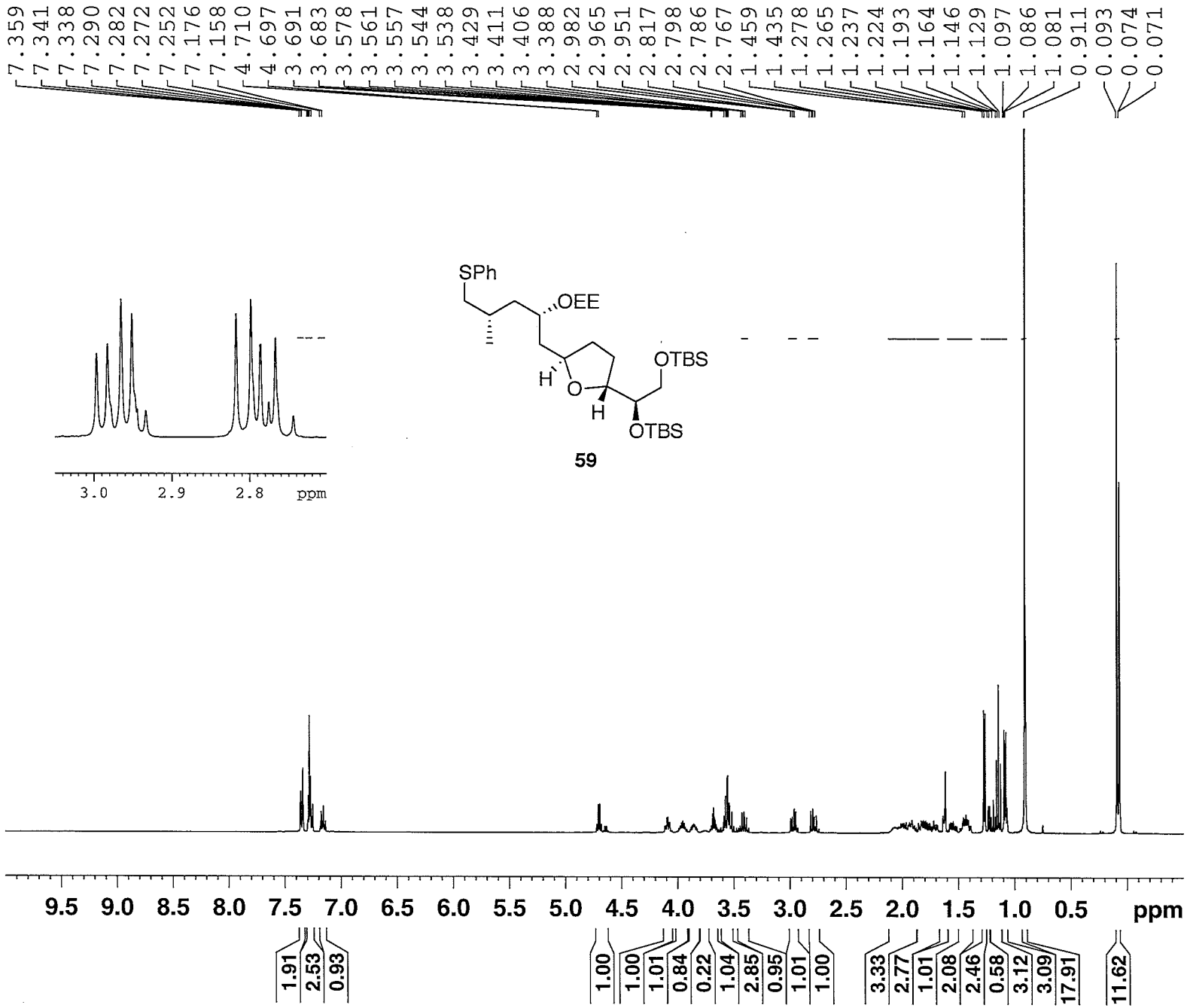
NAME	SUM-XV-19-EE Protecti
EXPNO	1
PROCNO	1
Date_	20120404
Time	13.22
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 sec
RG	22.6
DW	42.000 usec
DE	6.50 usec
TE	303.2 K
D1	2.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MHz
SI	131072
SF	700.1471400 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

EE Ether



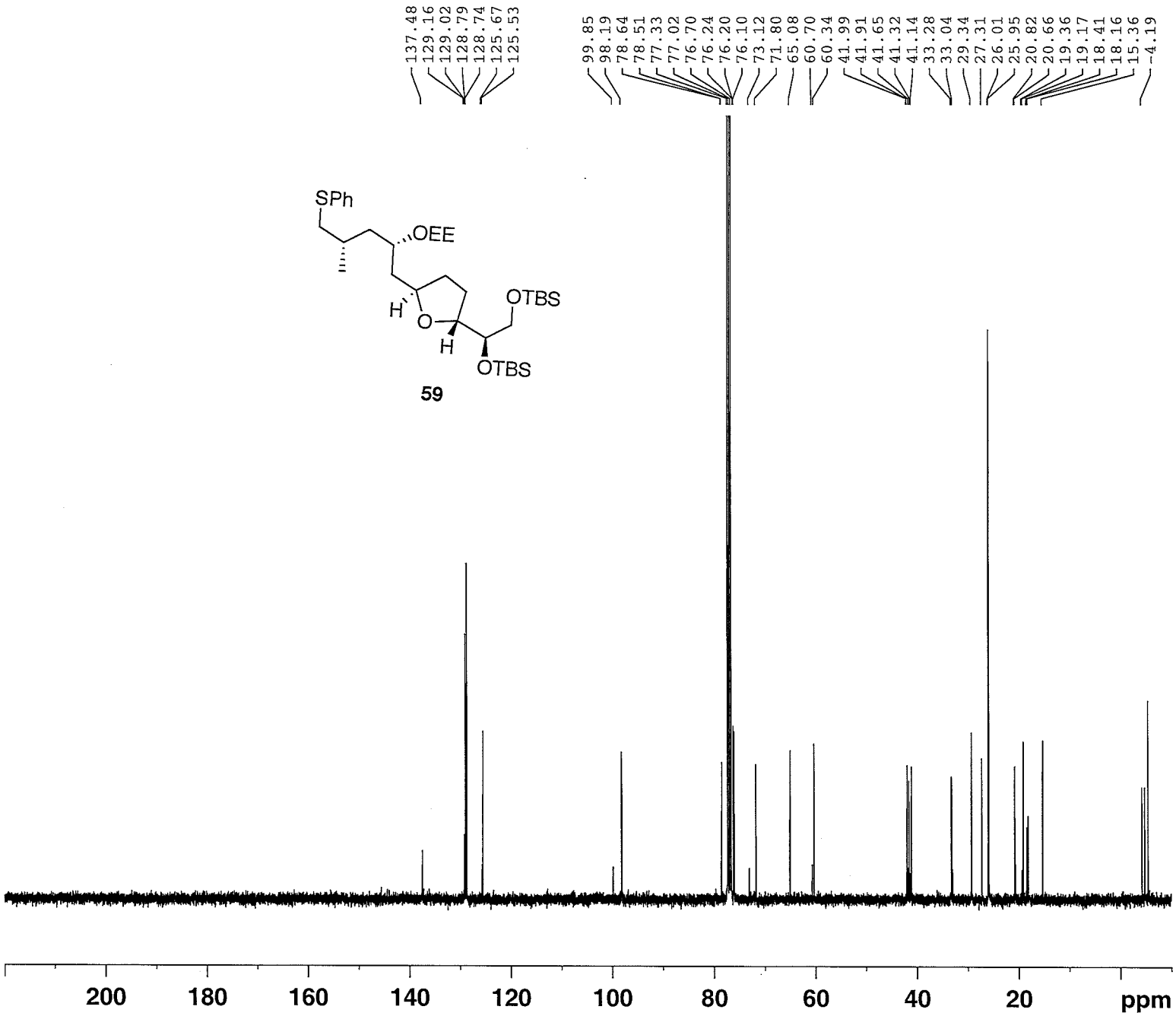
NAME	SUM-XV-19-EE Protecti
EXPNO	2
PROCNO	1
Date_	20120404
Time	13.36
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	301
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	303.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Sulfide



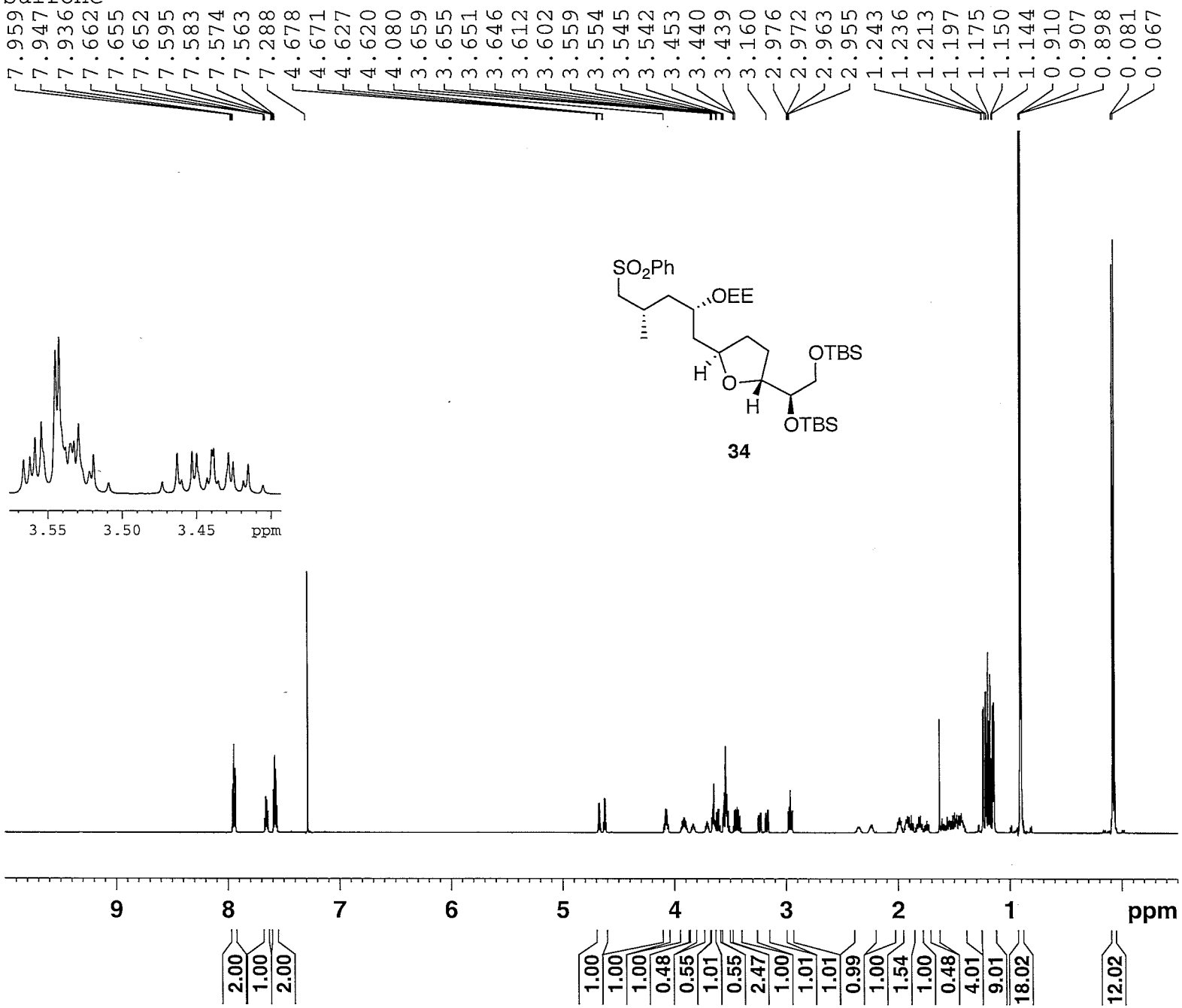
NAME	SUM-XIV-56-R-Sulfi
EXPNO	1
PROCNO	1
Date_	20111127
Time	18.19
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6793.478 Hz
FIDRES	0.207320 Hz
AQ	2.4117749 sec
RG	71.8
DW	73.600 use
DE	6.50 use
TE	298.2 K
D1	2.00000000 sec
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	14.00 use
PL1	0.00 dB
SFO1	400.1424008 MHz
SI	32768
SF	400.1400000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Sulfide



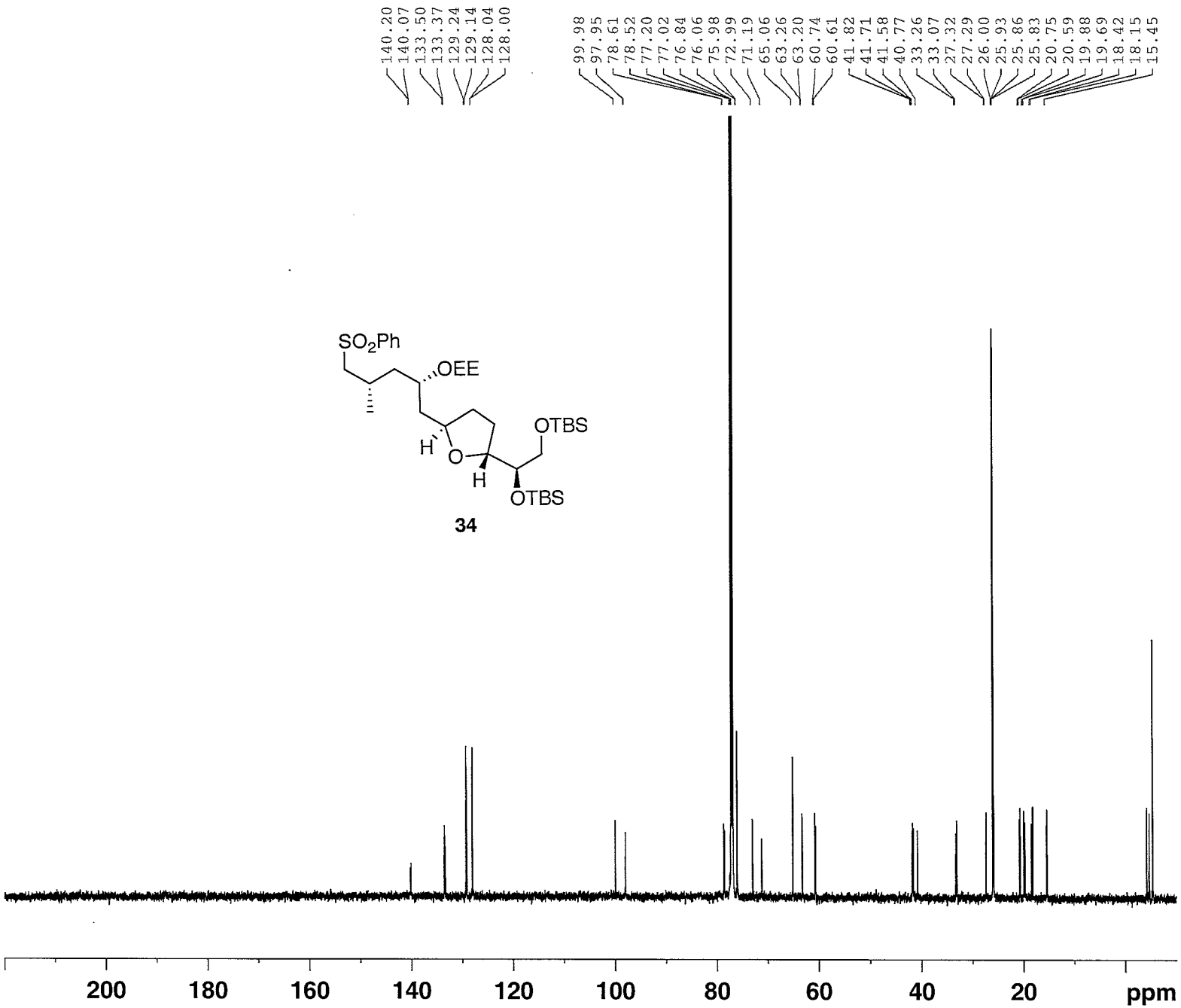
NAME	SUM-XIV-56-R-Sulfic
EXPNO	2
PROCNO	1
Date_	20111127
Time	18.26
INSTRUM	robinson
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2134
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	23170.5
DW	20.850 usec
DE	6.50 usec
TE	298.6 K
D1	0.20000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.00 usec
PL1	-2.00 dB
SFO1	100.6258476 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	0.00 dB
PL12	16.16 dB
PL13	17.00 dB
SFO2	400.1416006 MHz
SI	32768
SF	100.6152830 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Sulfone



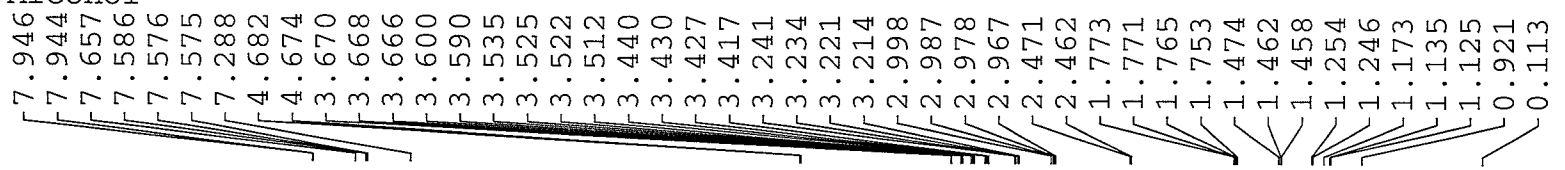
NAME	SUM-XIV-57-Sulfon
EXPNO	3
PROCNO	1
Date_	20111202
Time	14.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	128
DW	42.000 us
DE	6.50 us
TE	298.0 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	13.75 us
PL1	-3.00 dB
PL1W	32.08600616 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

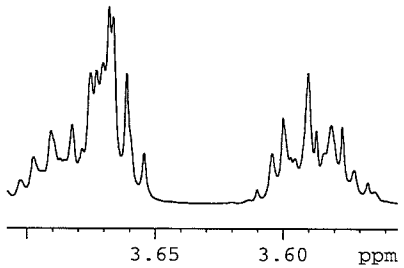
Sulfone

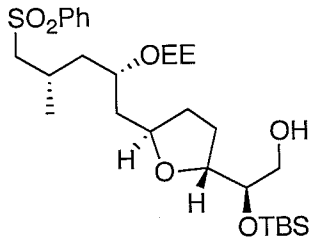


NAME	SUM-XIV-57-Sulfon
EXPNO	4
PROCNO	1
Date_	20111202
Time	14.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	928
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	6.50 us
TE	298.4 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.30 us
PL1	2.00 dB
PL1W	67.83342743 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 us
PL2	-3.00 dB
PL12	12.30 dB
PL13	12.30 dB
PL2W	32.08600616 W
PL12W	0.94692516 W
PL13W	0.94692516 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Alcohol







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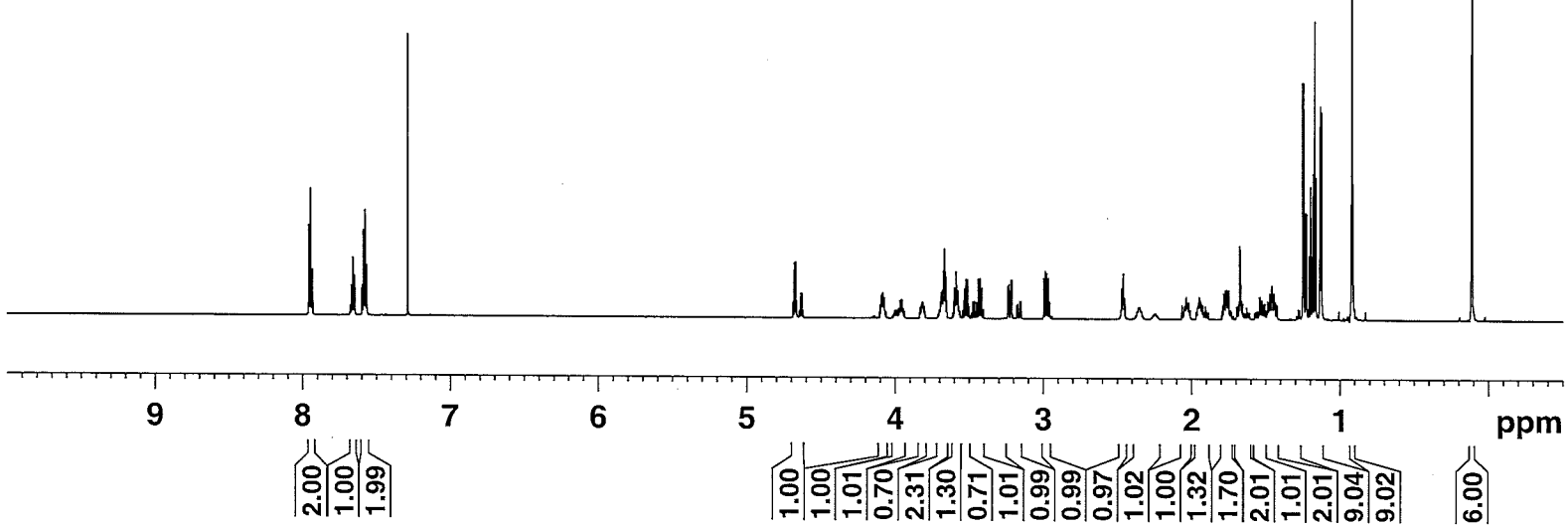
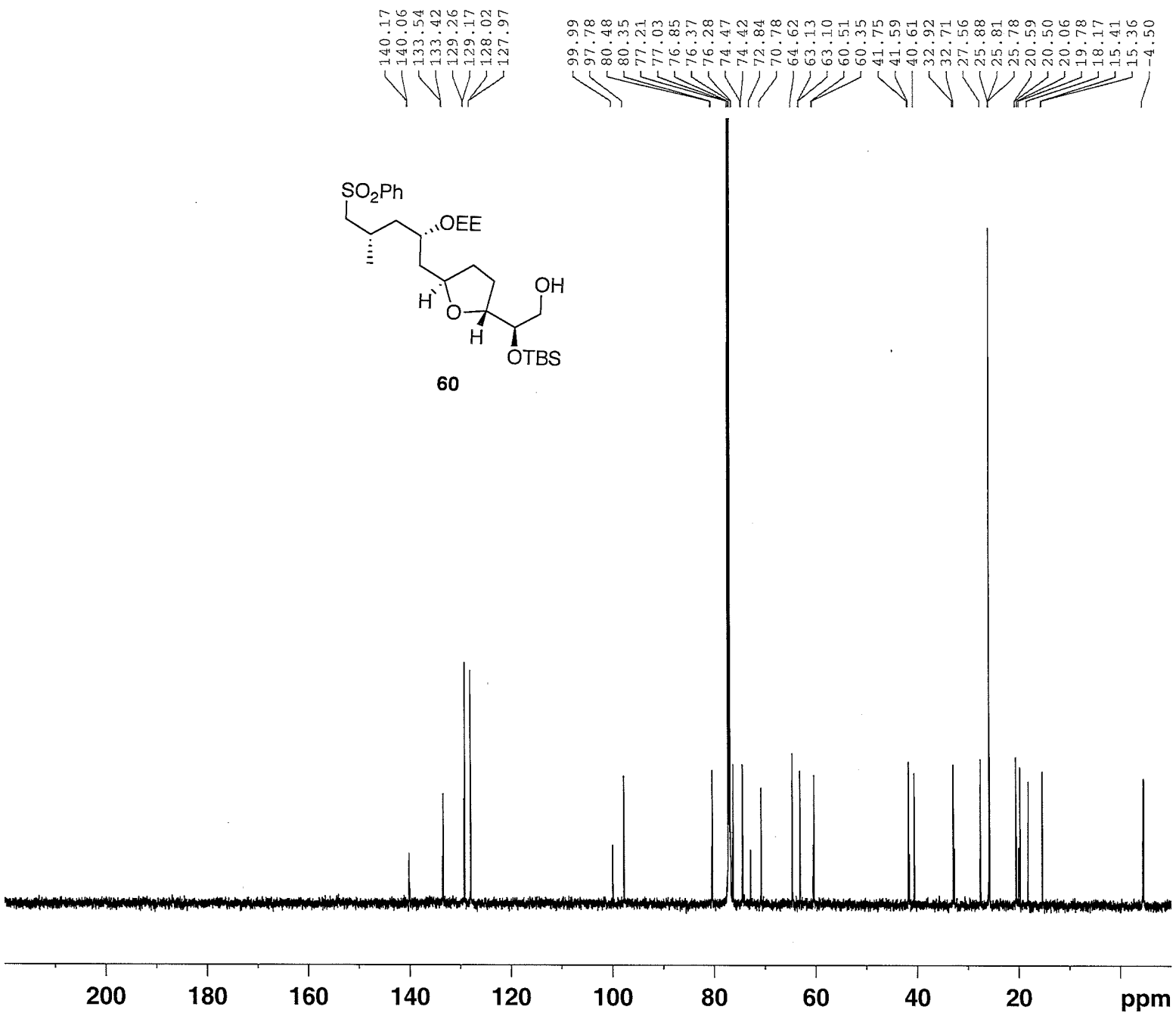
NAME	SUM-XIV-59-Alcoho
EXPNO	3
PROCNO	1
Date_	20120105
Time	9.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	144
DW	42.000 us
DE	6.50 us
TE	298.9 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	13.75 us
PL1	-3.00 dB
PL1W	32.08600616 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

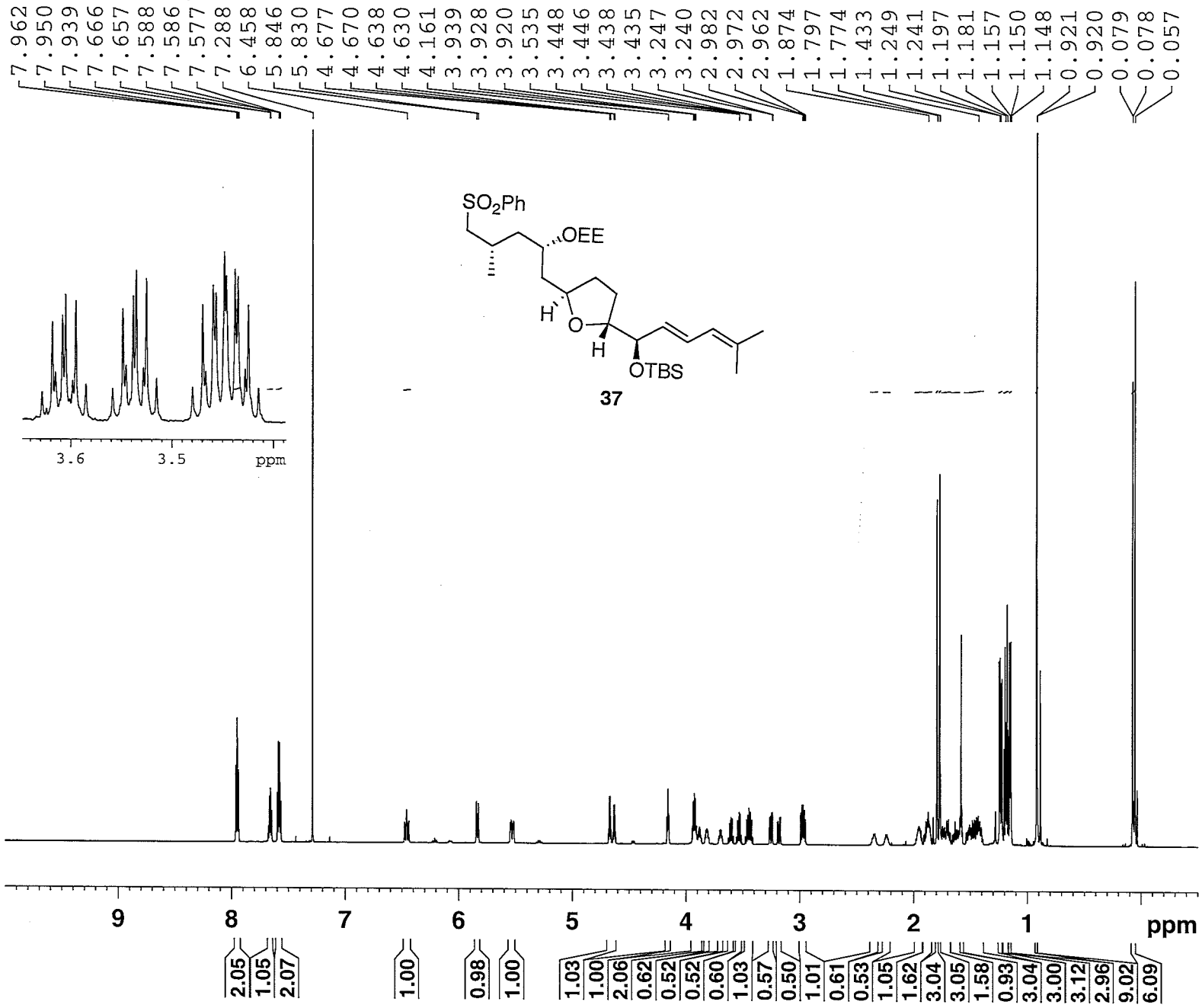


Alcohol



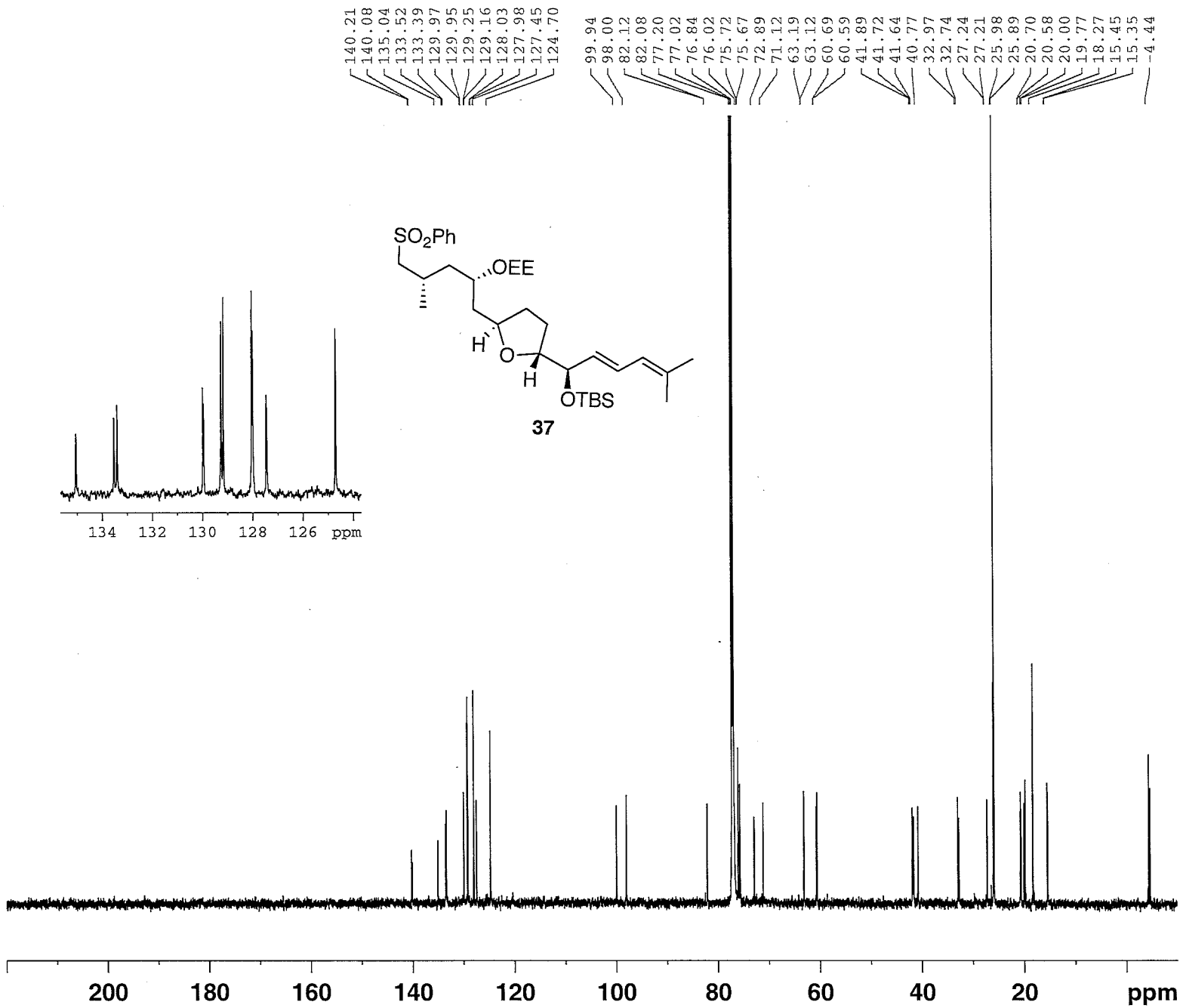
NAME	SUM-XIV-59-Alcoho
EXPNO	4
PROCNO	1
Date_	20120105
Time	10.11
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	696
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	6.50 us
TE	298.7 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
======== CHANNEL f1 =======	
NUC1	13C
P1	9.30 us
PL1	2.00 dB
PL1W	67.83342743 W
SFO1	176.0706235 MH
======== CHANNEL f2 =======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 us
PL2	-3.00 dB
PL12	12.30 dB
PL13	12.30 dB
PL2W	32.08600616 W
PL12W	0.94692516 W
PL13W	0.94692516 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Sidearm Diene



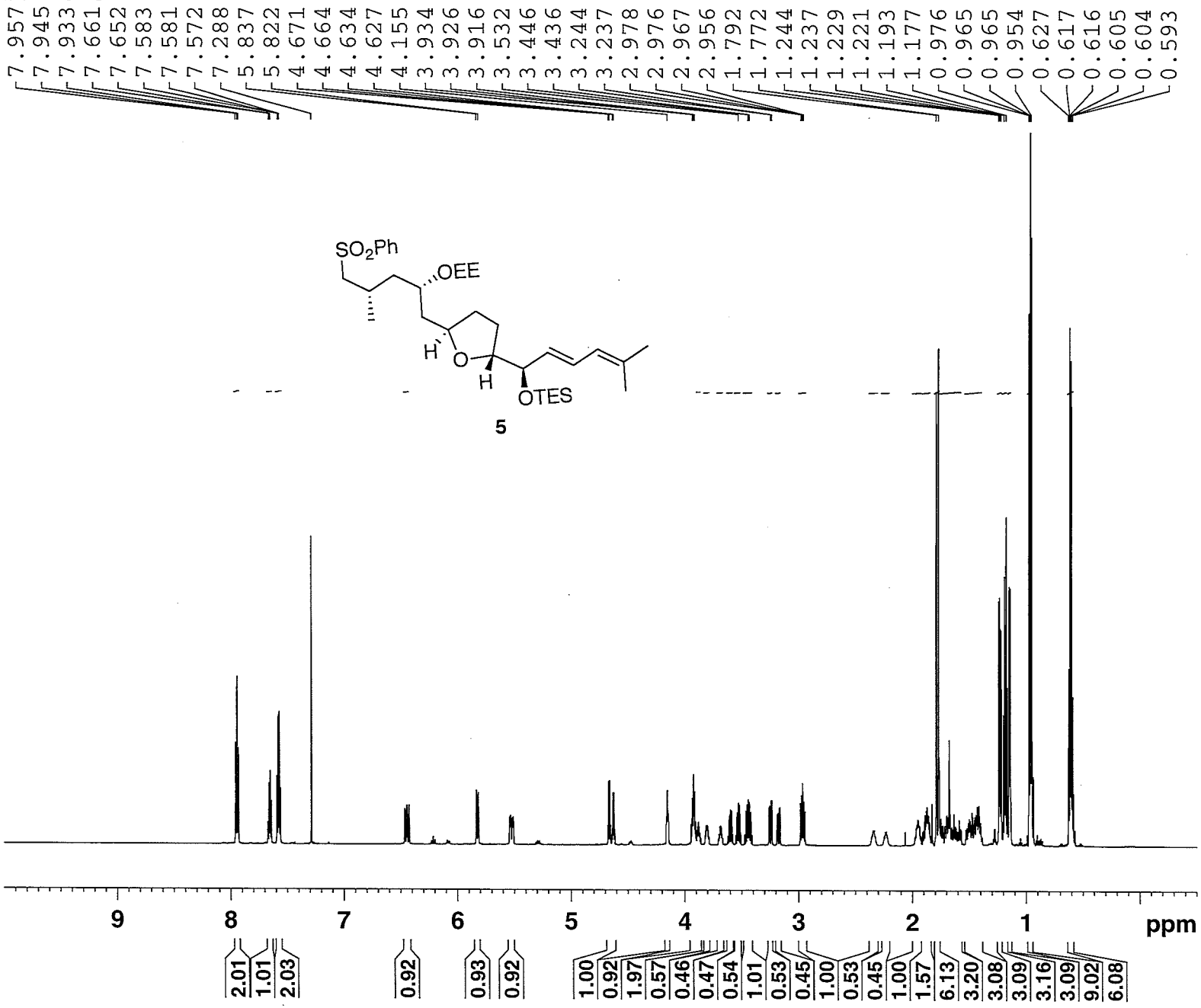
NAME	SUM-XIV-61-Diene
EXPNO	1
PROCNO	1
Date_	20120107
Time	14.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	95236
SOLVENT	CDC13
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	203
DW	42.000 us
DE	6.50 us
TE	298.9 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 =======
NUC1	1H
P1	13.75 us
PL1	-3.00 dB
PL1W	32.08600616 W
SFO1	700.1516910 MH:
SI	131072
SF	700.1471400 MH:
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Sidearm Diene



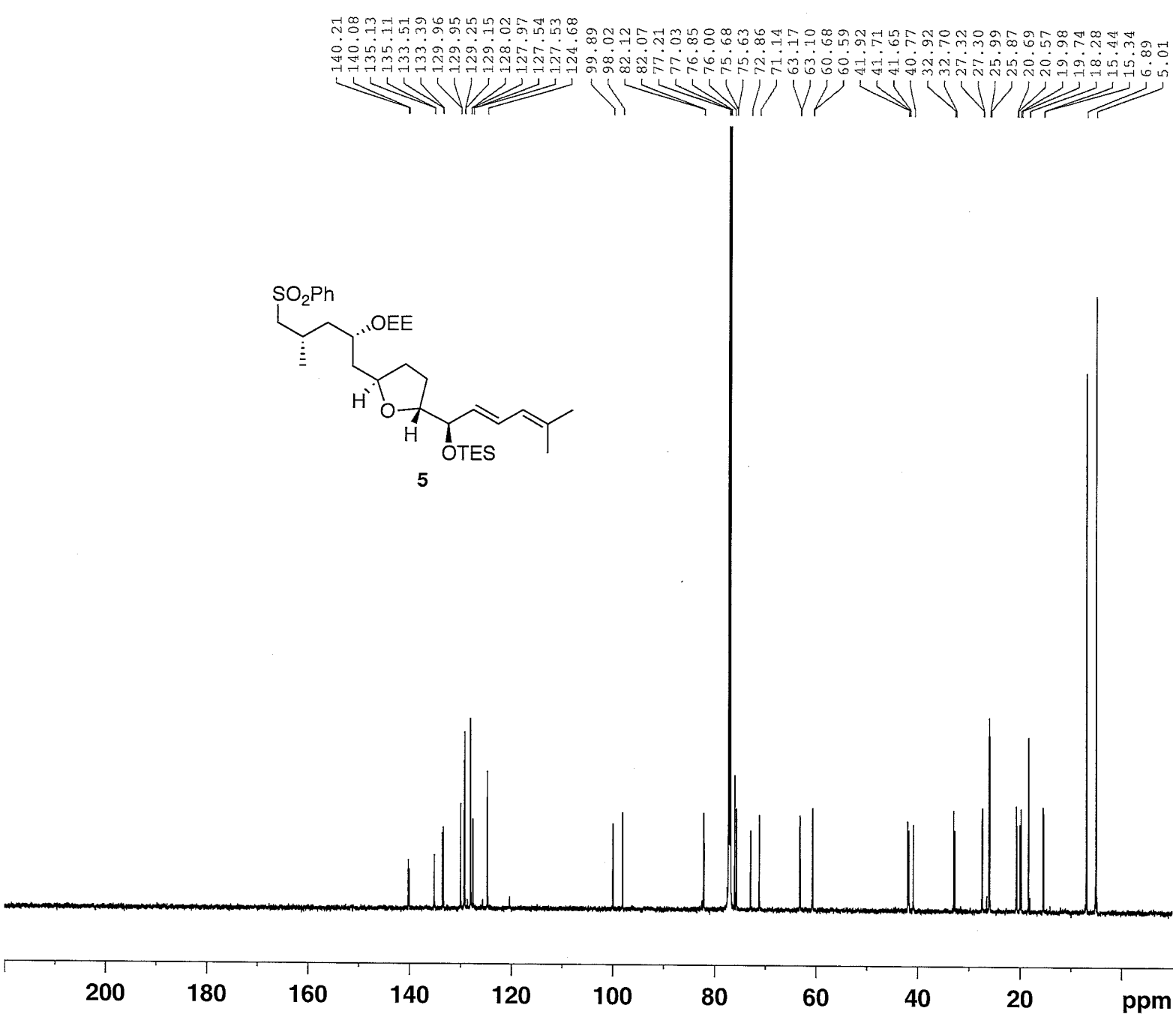
NAME	SUM-XIV-61-Diene
EXPNO	5
PROCNO	1
Date_	20120107
Time	15.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	5000
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	6.50 us
TE	299.0 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.30 us
PL1	2.00 dB
PL1W	67.83342743 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 us
PL2	-3.00 dB
PL12	12.30 dB
PL13	12.30 dB
PL2W	32.08600616 W
PL12W	0.94692516 W
PL13W	0.94692516 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Sulfone



NAME	SUM-XIV-63-Diene
EXPNO	1
PROCNO	1
Date_	20120109
Time	18.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	101
DW	42.000 us
DE	6.50 us
TE	298.7 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	13.75 us
PL1	-3.00 dB
PL1W	32.08600616 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

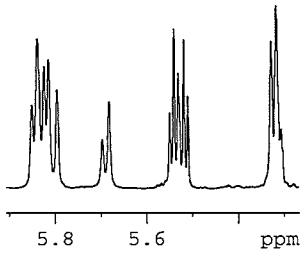
Sulfone

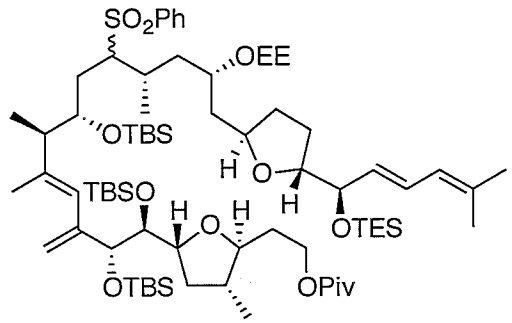


NAME	SUM-XIV-63-Diene
EXPNO	2
PROCNO	1
Date_	20120109
Time	18.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2449
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	6.50 us
TE	299.1 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.30 us
PL1	2.00 dB
PL1W	67.83342743 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 us
PL2	-3.00 dB
PL12	12.30 dB
PL13	12.30 dB
PL2W	32.08600616 W
PL12W	0.94692516 W
PL13W	0.94692516 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Coupled Sulfone

7.941 7.929 7.895 7.631 7.566 7.554 7.288 6.458 5.839 5.540 5.519 5.317 5.315 5.145 4.100 3.899 3.888 3.571 1.901 1.887 1.849 1.794 1.791 1.772 1.682 1.671 1.435 1.268 1.261 1.214 1.213 1.210 1.170 1.160 1.138 1.131 1.090 0.976 0.967 0.966 0.937 0.914 0.873 0.621 0.090 0.066





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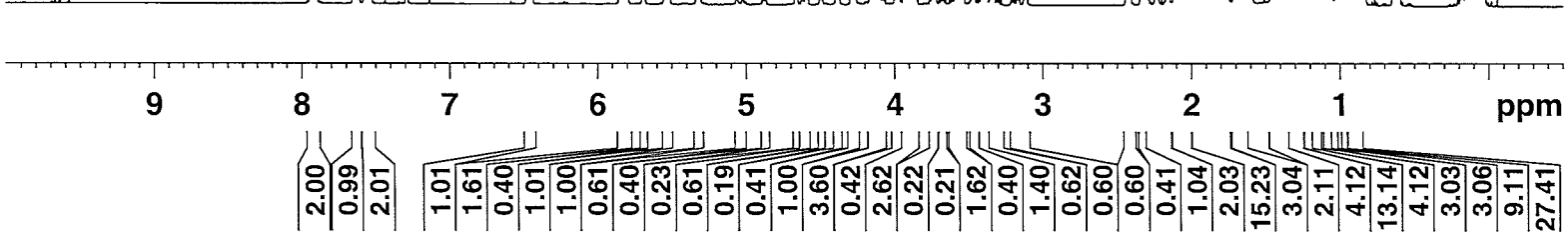
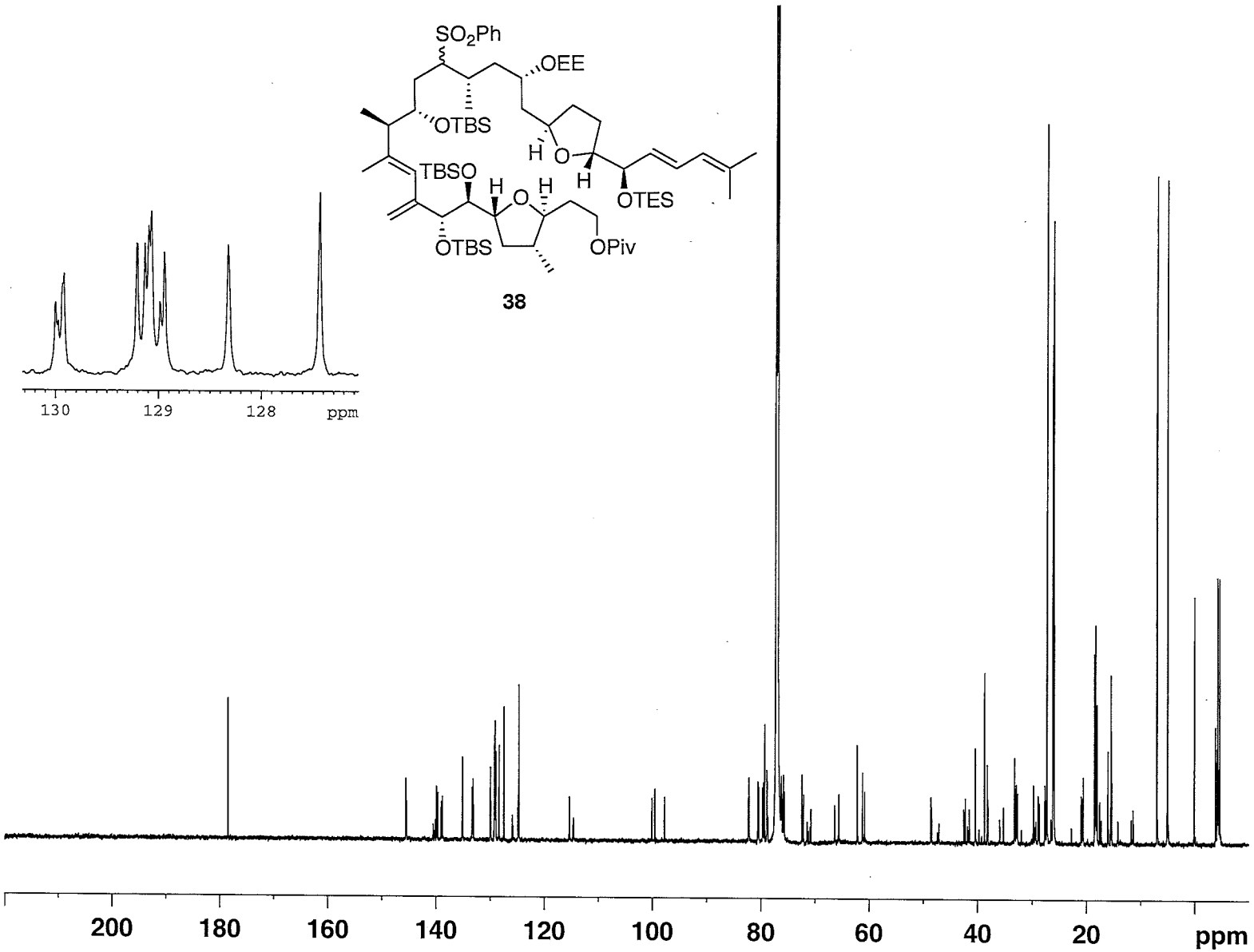
NAME	SUM-XV-34-Coupled Sulfo
EXPNO	1
PROCNO	1
Date_	20120412
Time	22.43
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	63
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 sec
RG	22.6
DW	42.000 usec
DE	6.50 usec
TE	303.2 K
D1	2.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MHz
SI	131072
SF	700.1471400 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



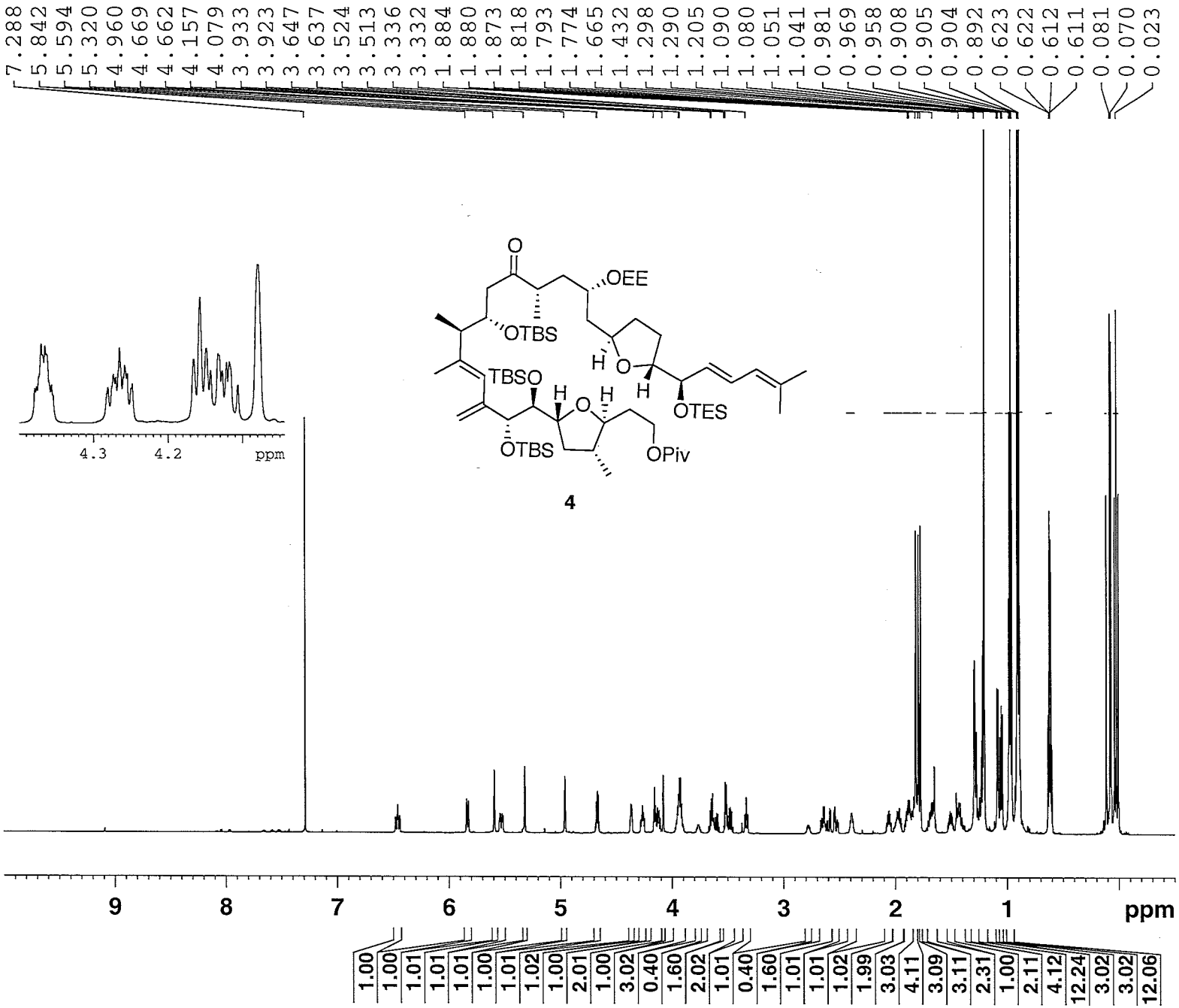
Coupled Sulfone

178.44 145.51 135.09 133.12 129.92 129.21 129.13 129.09 129.07 128.94 128.32 127.43 124.67 82.20 79.67 79.52 79.29 78.86 77.21 77.03 76.85 76.29 76.19 76.11 75.86 75.80 75.70 72.41 62.16 62.10 61.17 40.36 40.33 38.69 38.18 33.19 33.09 32.88 32.64 29.72 27.59 27.21 26.16 26.02 25.97 25.91 20.55 18.46 18.37 18.28 18.18 18.07 17.99 16.02 15.98 15.43 15.29 6.93 6.92 5.00 -3.87 -4.16 -4.18 -4.28 -4.35 -4.43 -4.58 -4.65 -4.70



NAME	SUM-XV-34-Coupled Sulfo
EXPNO	2
PROCNO	1
Date_	20120412
Time	22.54
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	5120
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	303.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	13
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

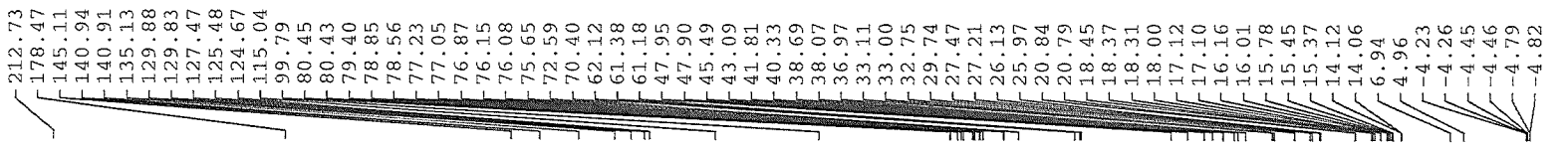
Ketone



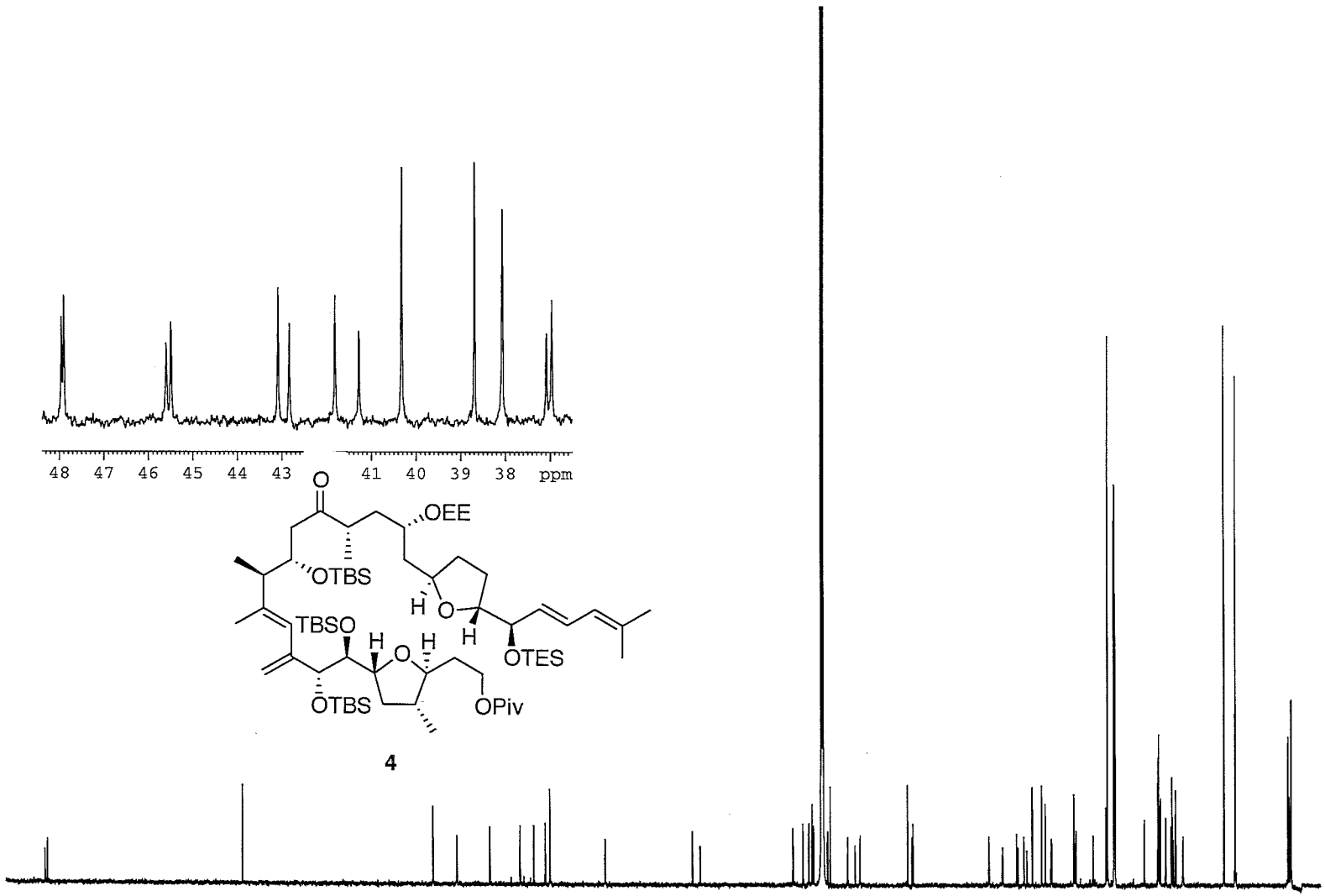
NAME	SUM-XIV-66-Ketone
EXPNO	1
PROCNO	1
Date_	20120223
Time	16.05
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	32
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	22.6
DW	42.000 us
DE	6.50 us
TE	298.3 K
D1	2.00000000 se
TD0	1
======== CHANNEL f1 ======	
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

F

Ketone

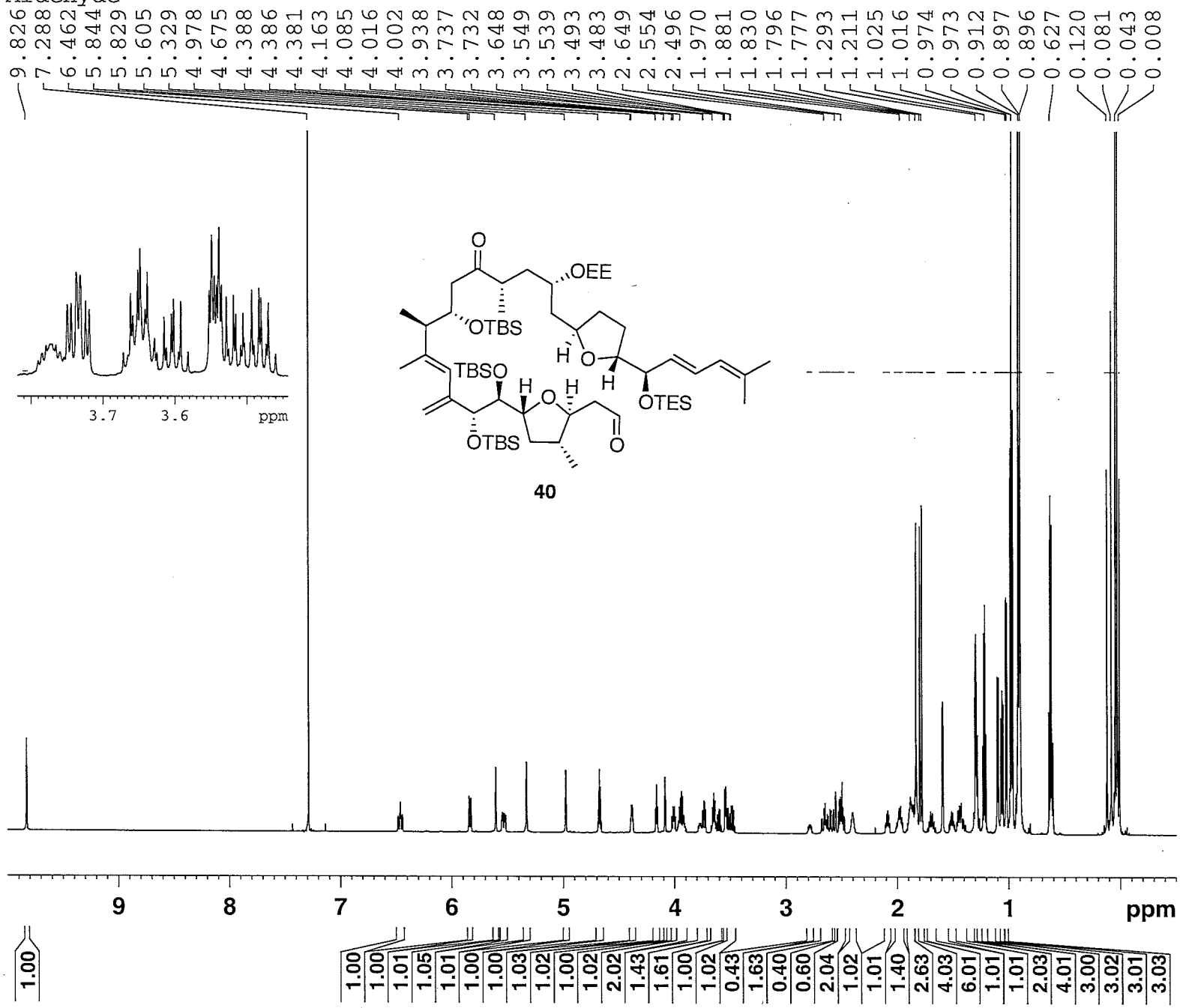


4



NAME	SUM-XIV-66-Ketone
EXPNO	2
PROCNO	1
Date_	20120223
Time	16.21
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	386
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	6.50 us
TE	298.3 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Aldehyde

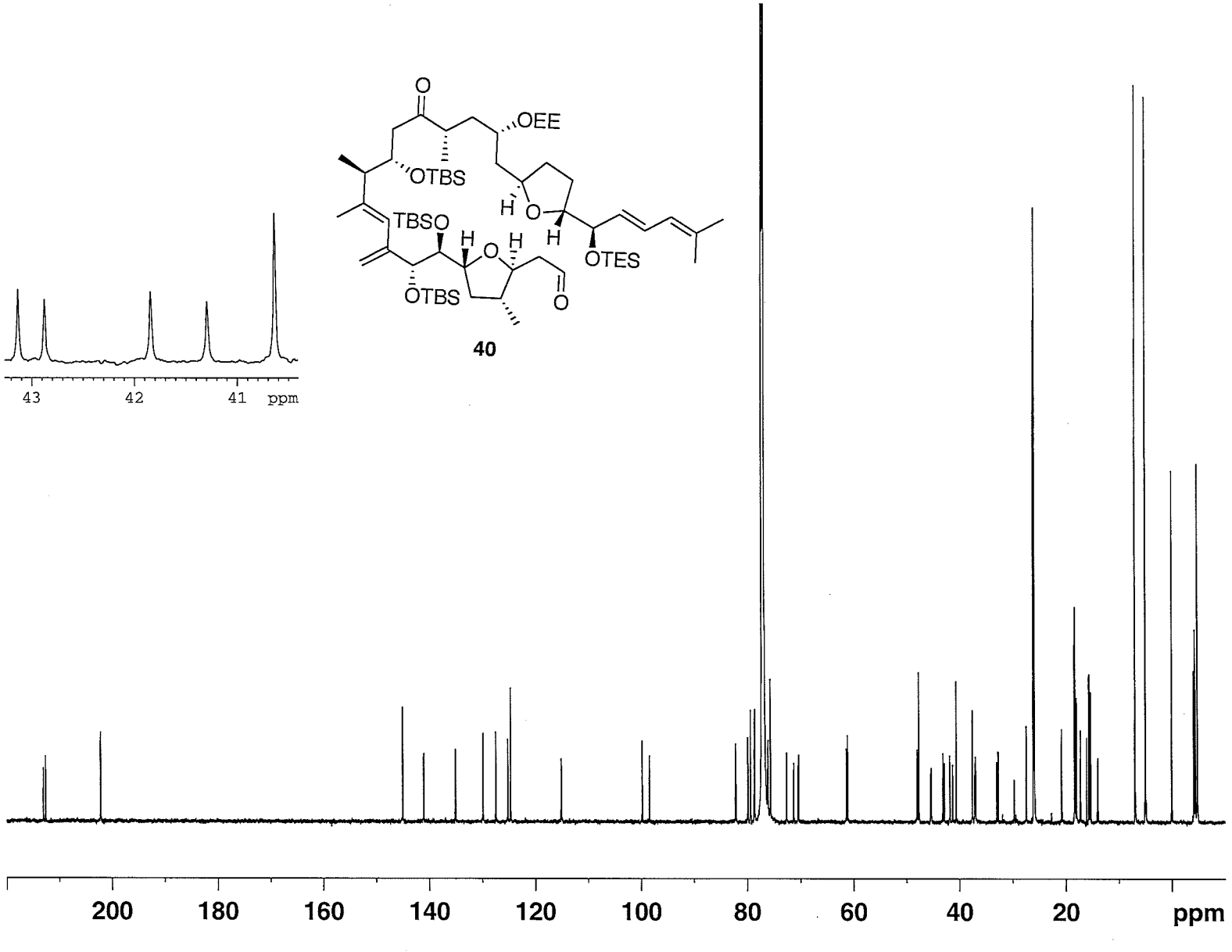


NAME	SUM-XV-36-Aldehyd
EXPNO	1
PROCNO	1
Date_	20120414
Time	2.16
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	56
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	22.6
DW	42.000 us
DE	6.50 us
TE	303.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MH:
SI	131072
SF	700.1471400 MH:
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Aldehyde

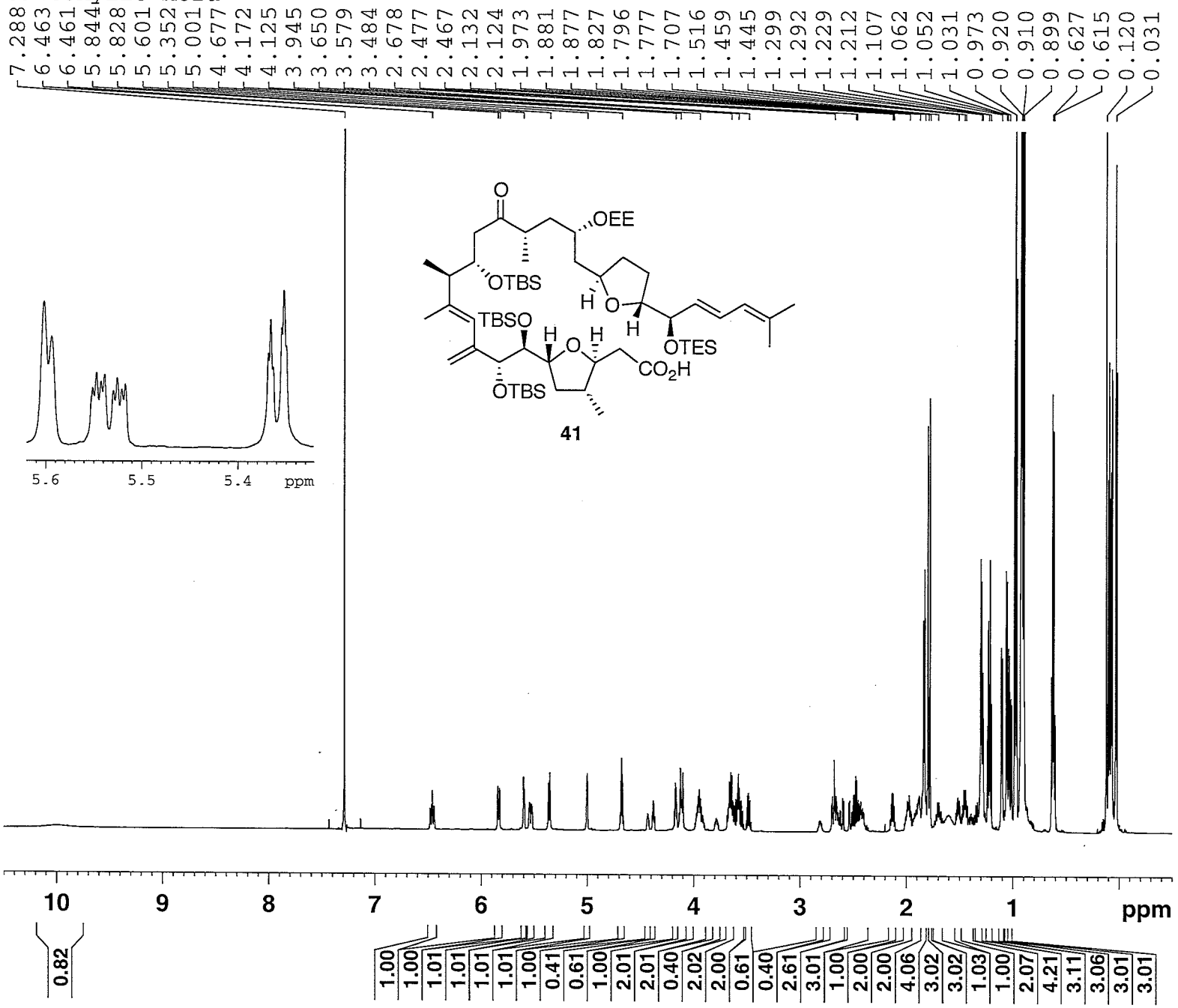
212.66 202.18 145.04 141.10 135.12 135.08 129.91 129.86 127.48 125.20 124.68 99.82 98.45 82.20 82.15 79.89 79.39 78.66 78.60 77.21 77.03 76.85 76.16 76.09 75.64 72.62 71.30 70.37 61.39 61.15 48.02 47.97 47.68 45.33 43.13 42.87 41.84 41.29 40.64 37.59 37.12 36.98 32.98 32.73 27.45 26.11 26.01 25.95 25.90 20.84 20.77 18.42 18.35 18.28 17.99 17.24 16.10 15.72 15.63 15.45 15.36 14.00 13.95 6.91 4.99 -4.10 -4.29 -4.47 -4.79

40



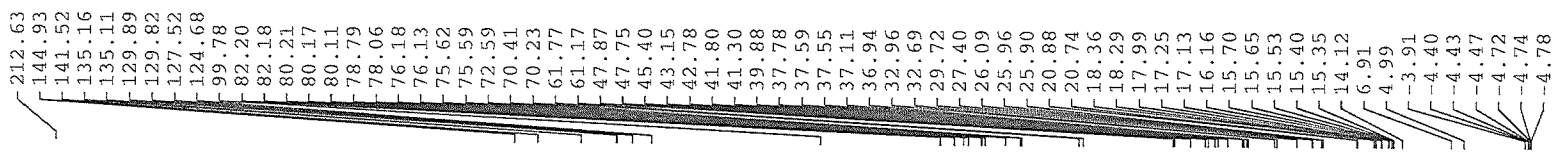
NAME	SUM-XV-36-Aldehyd
EXPNO	2
PROCNO	1
Date_	20120414
Time	2.29
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10120
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	16.50 us
TE	303.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	15
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Carboxylic Acid



NAME	SUM-XV-37-Acid
EXPNO	1
PROCNO	1
Date_	20120415
Time	4.16
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	72
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	22.6
DW	42.000 us
DE	6.50 us
TE	303.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Carboxylic Acid



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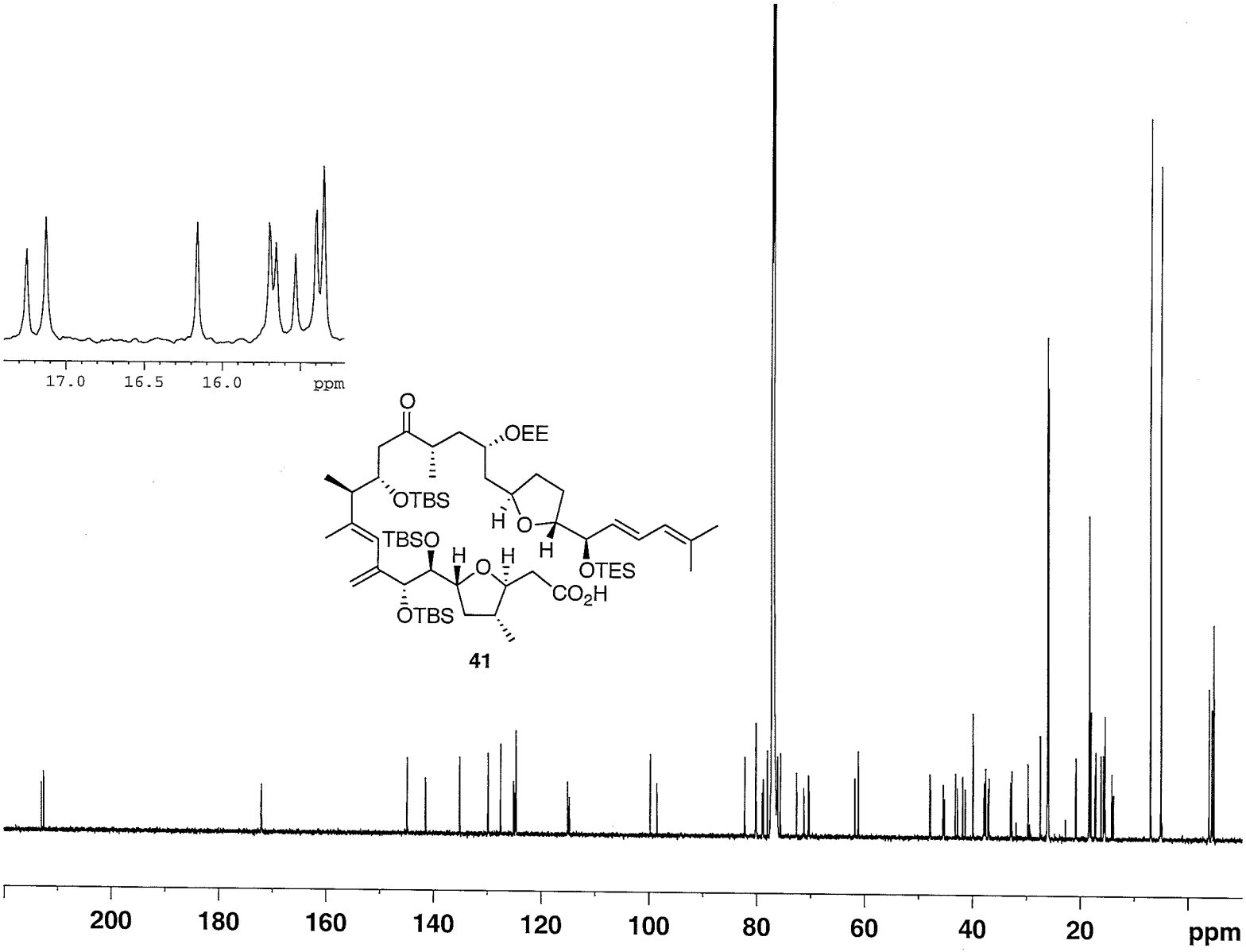
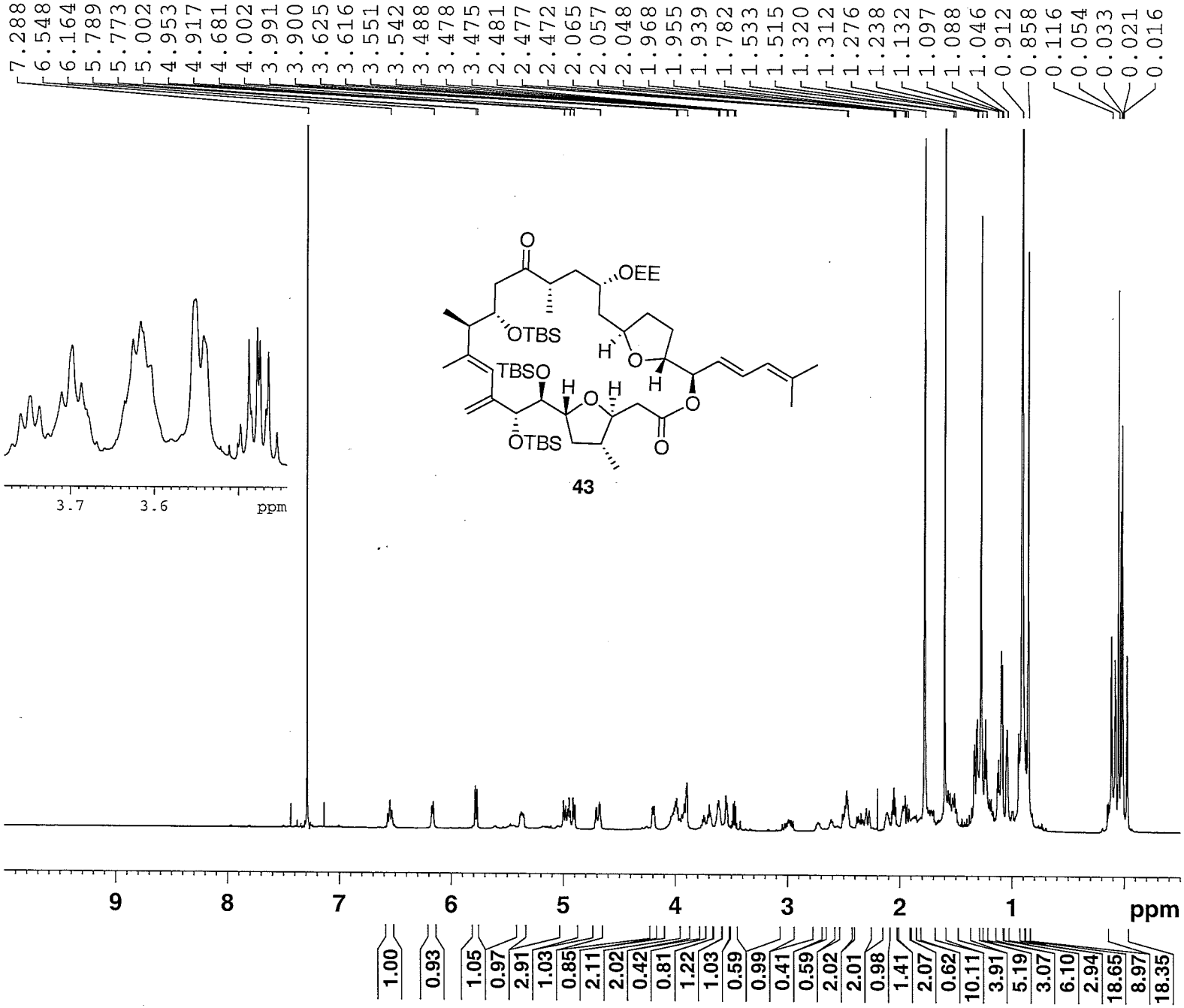


NAME	SUM-XV-37-Acid
EXPNO	2
PROCNO	1
Date_	20120415
Time	4.30
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	5720
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	16.50 us
TE	303.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	15
======== CHANNEL f1 ======	
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MH:
======== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MH:
SI	32768
SF	176.0521380 MH:
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Macrolactone



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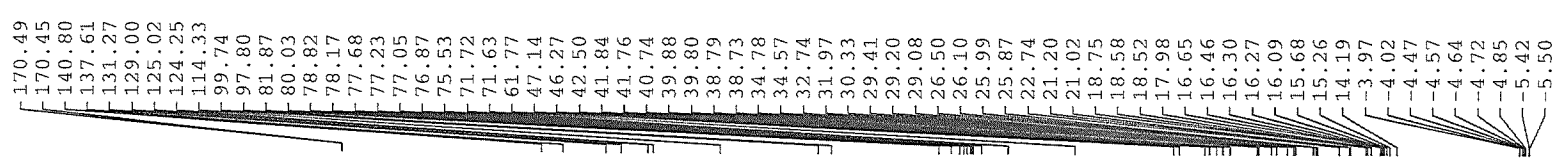
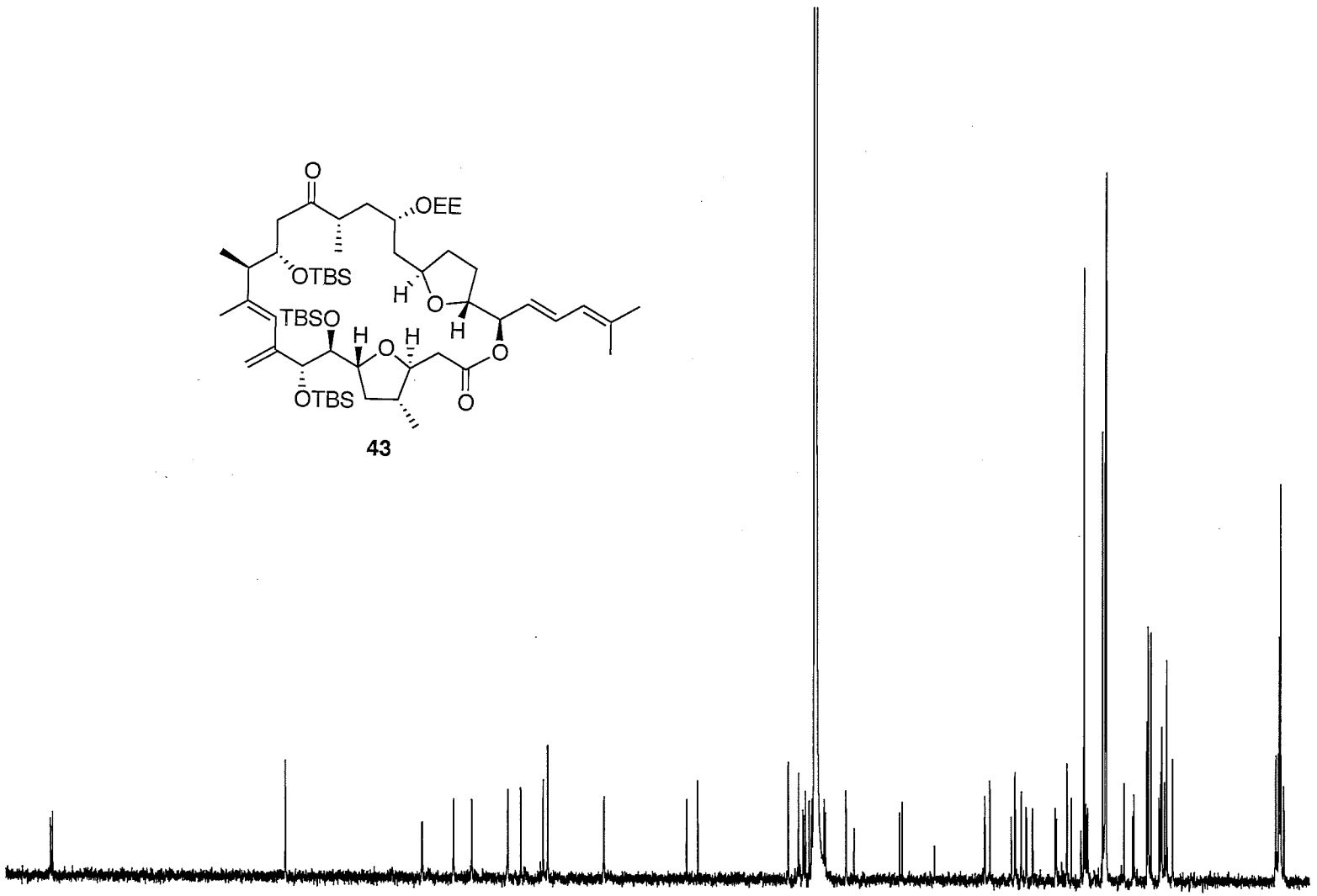
NAME	SUM-XIV-81-Macrolactonizati
EXPNO	1
PROCNO	1
Date_	20120218
Time	1.50
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	100
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 sec
RG	32
DW	42.000 usec
DE	6.50 usec
TE	298.5 K
D1	2.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MHz
SI	131072
SF	700.1471400 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Macrolactone

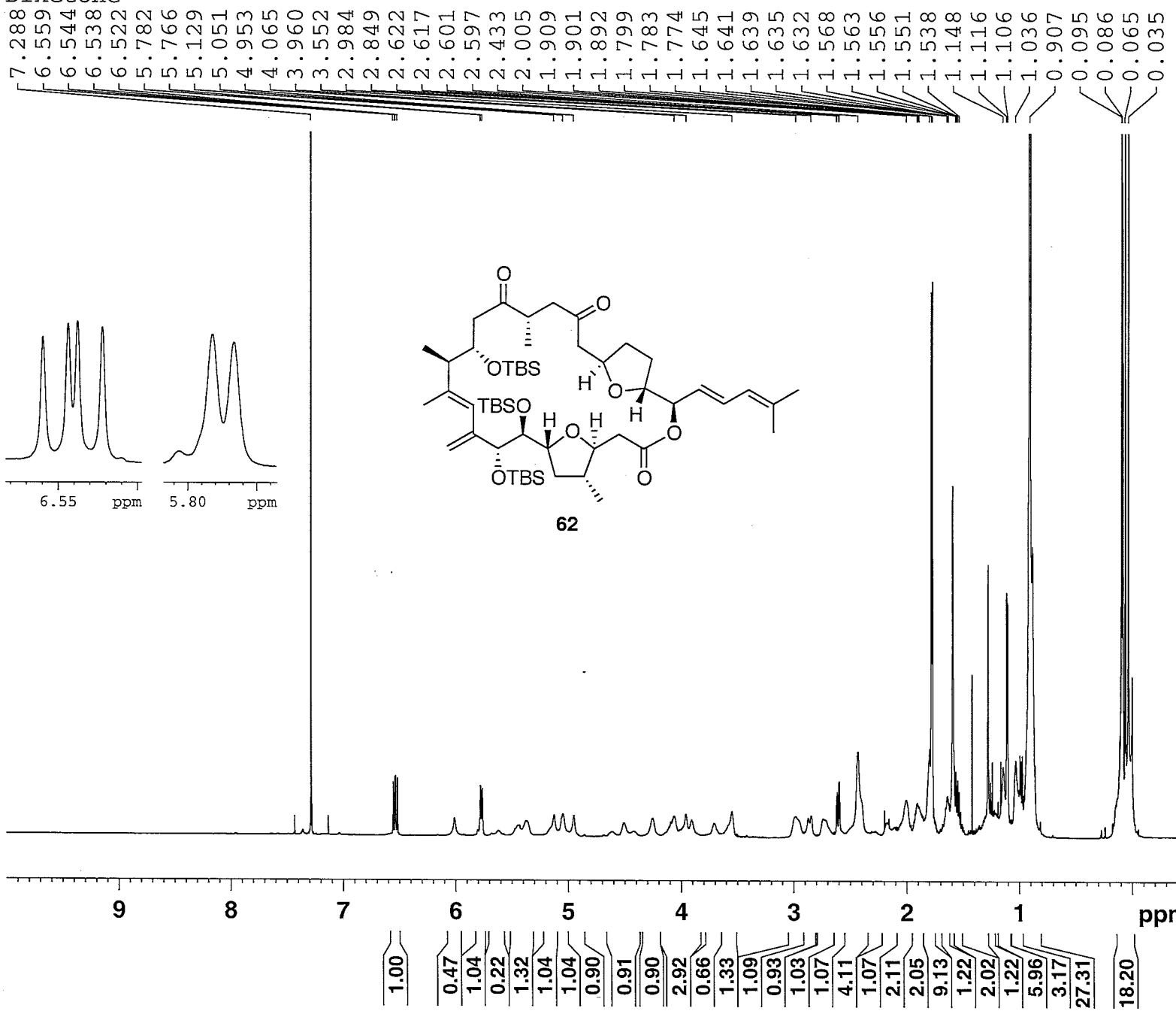


43

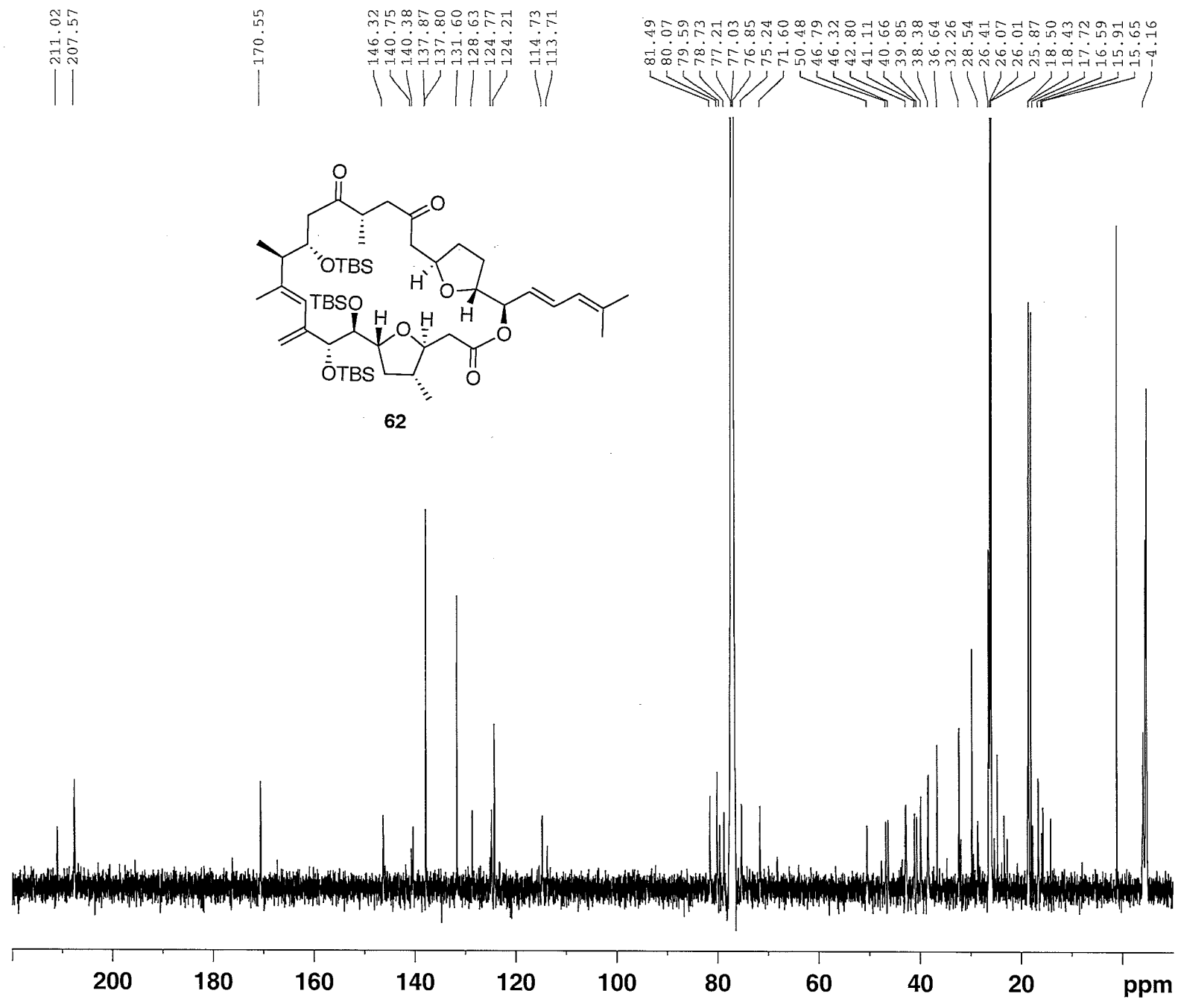


NAME	SUM-XV-09-Macrolacto
EXPNO	2
PROCNO	1
Date_	20120328
Time	23.01
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2955
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

Diketone



NAME	SUM-XV-27-Diketon
EXPNO	1
PROCNO	1
Date_	20120408
Time	1.41
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDCl3
NS	320
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 se
RG	25.4
DW	42.000 us
DE	6.50 us
TE	303.2 K
D1	2.00000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	1H
P1	9.40 us
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MH
SI	131072
SF	700.1471400 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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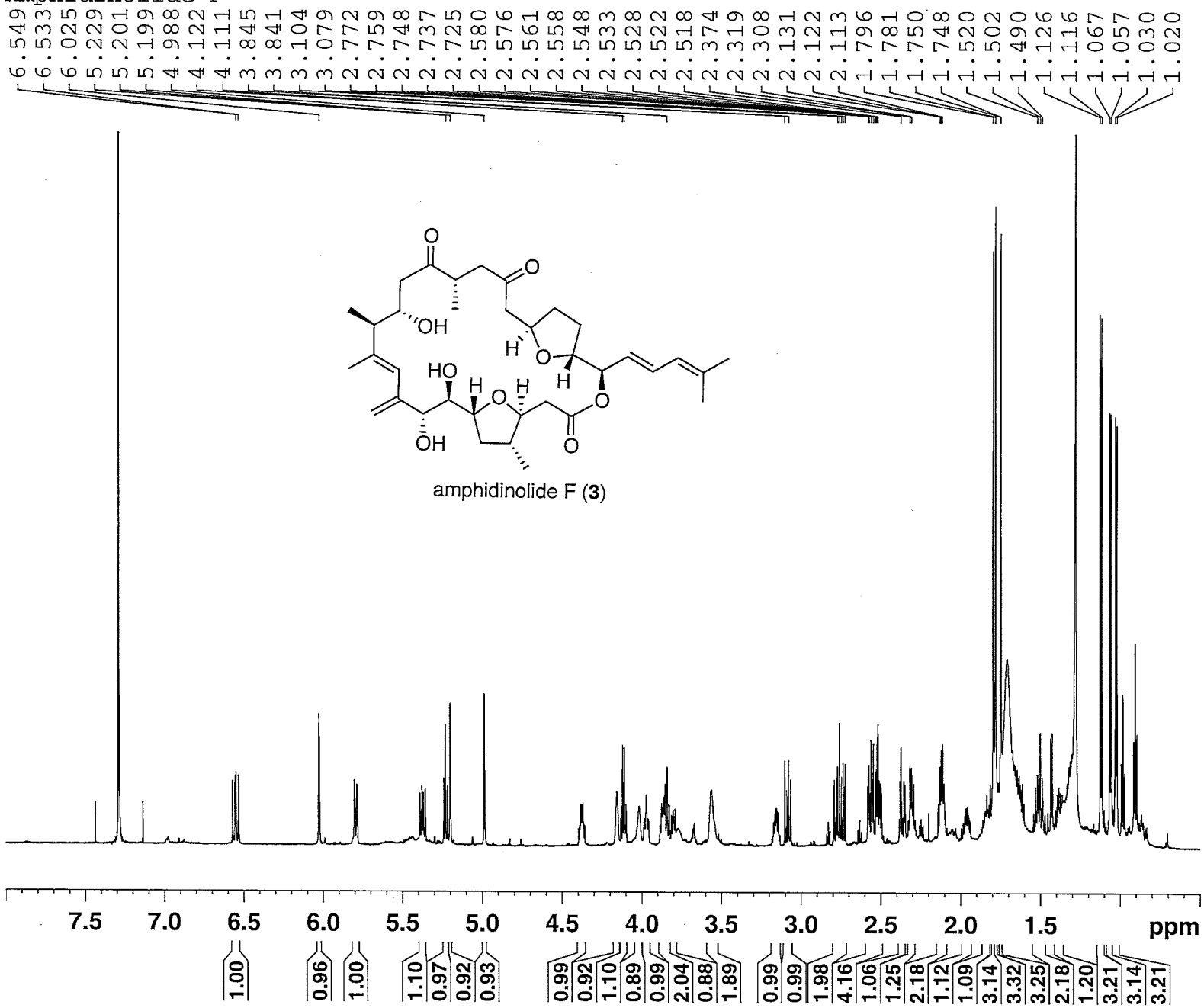
NAME	SUM-XV-15-Diketon
EXPNO	5
PROCNO	999
Date_	20120330
Time	1.44
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	11000
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 se
RG	203
DW	12.000 us
DE	16.50 us
TE	298.2 K
D1	2.00000000 se
D11	0.03000000 se
TD0	1
========	CHANNEL f1 ======
NUC1	13C
P1	9.00 us
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MH
========	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 us
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MH
SI	32768
SF	176.0521380 MH
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

F 1.4m

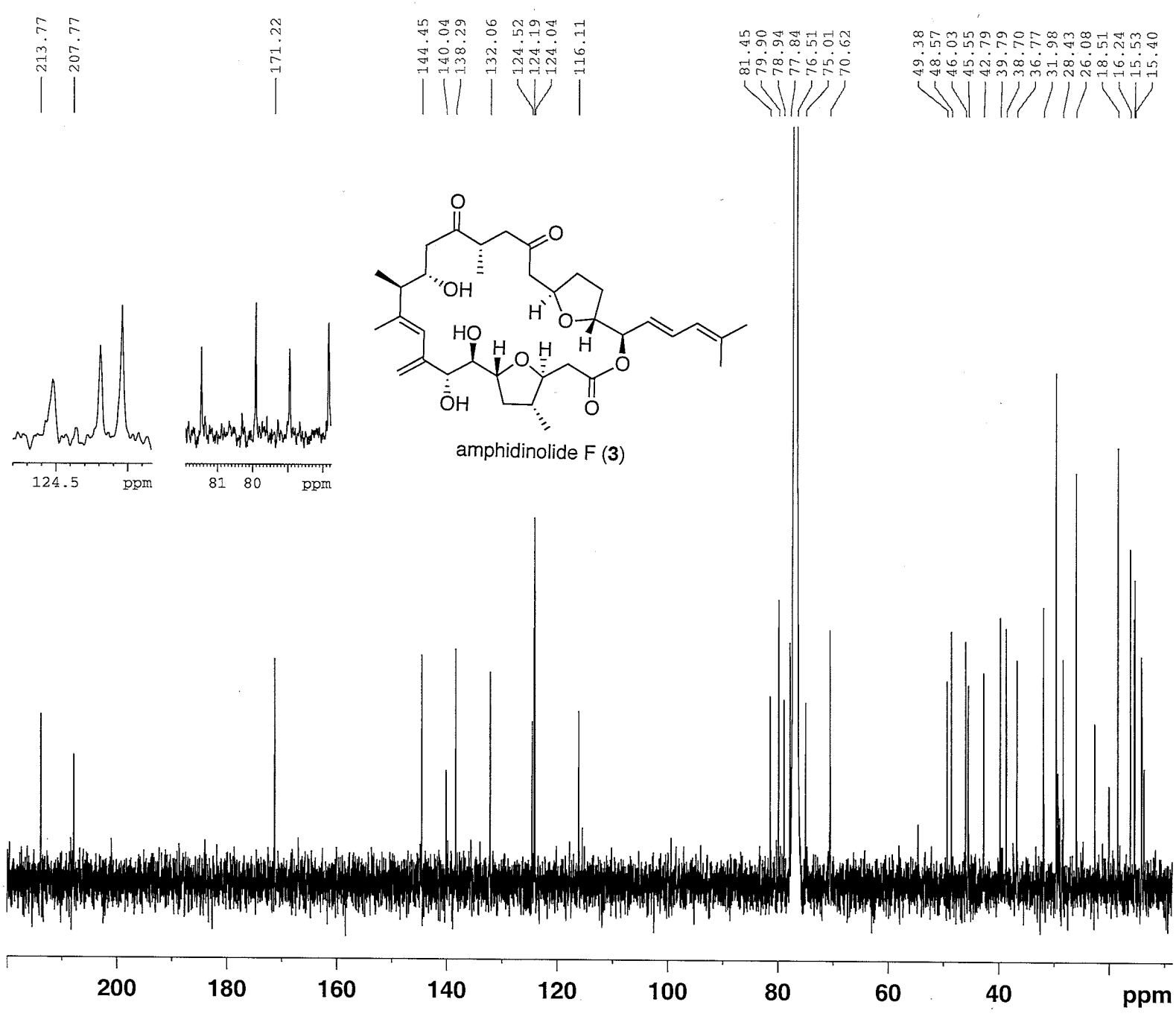
Amphidinolide F



amphidinolide F (**3**)

NAME	SUM-XV-40-Amphidinolide
EXPNO	1
PROCNO	1
Date_	20120417
Time	23.44
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zg30
TD	95236
SOLVENT	CDC13
NS	320
DS	2
SWH	11904.762 Hz
FIDRES	0.125003 Hz
AQ	3.9999621 sec
RG	25.4
DW	42.000 usec
DE	6.50 usec
TE	303.2 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1516910 MHz
SI	131072
SF	700.1471400 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Amphidinolide F

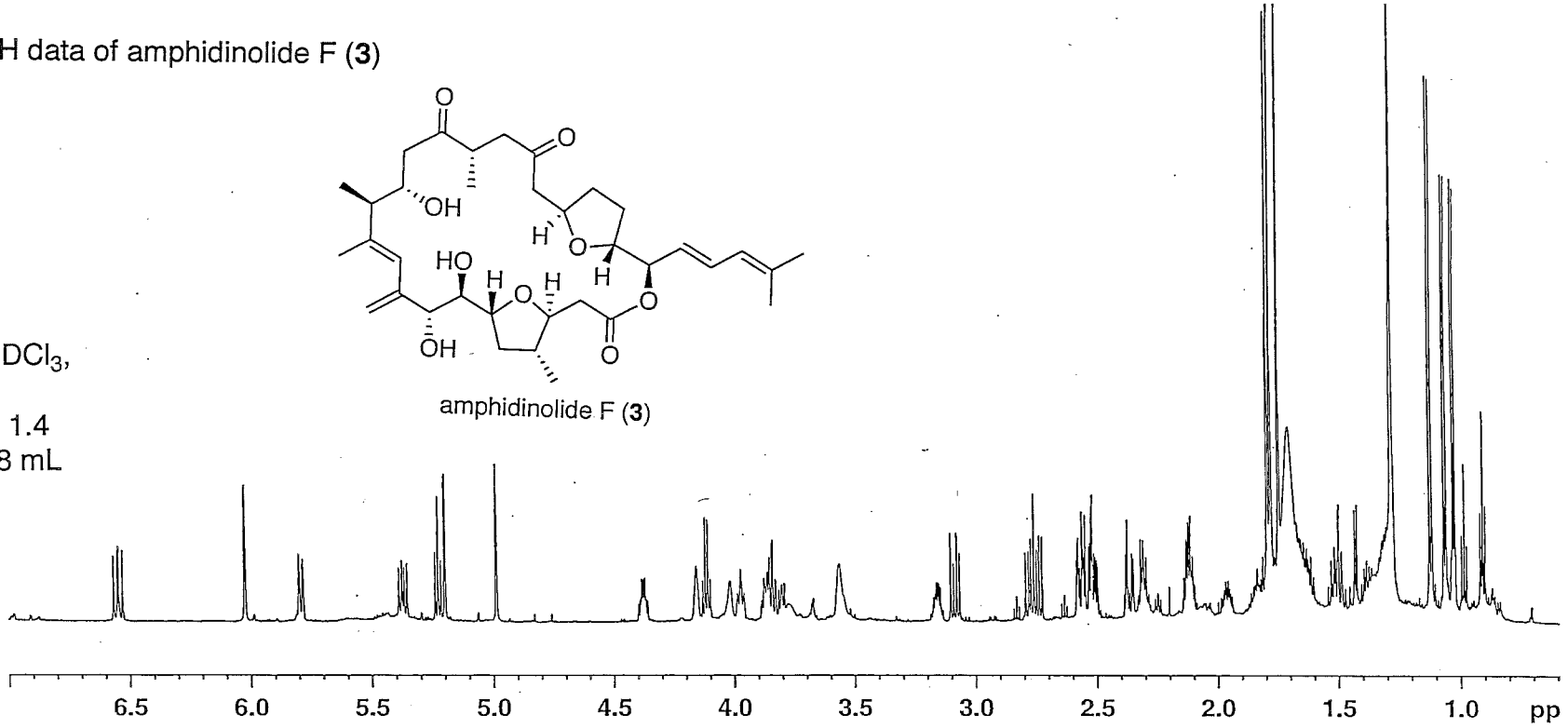


NAME	SUM-XV-40-Amphidinolide
EXPNO	3
PROCNO	1
Date_	20120418
Time	1.39
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	15028
DS	4
SWH	41666.668 Hz
FIDRES	0.635783 Hz
AQ	0.7864820 sec
RG	203
DW	12.000 usec
DE	16.50 usec
TE	303.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	75
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0706238 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 MHz
SI	32768
SF	176.0521380 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

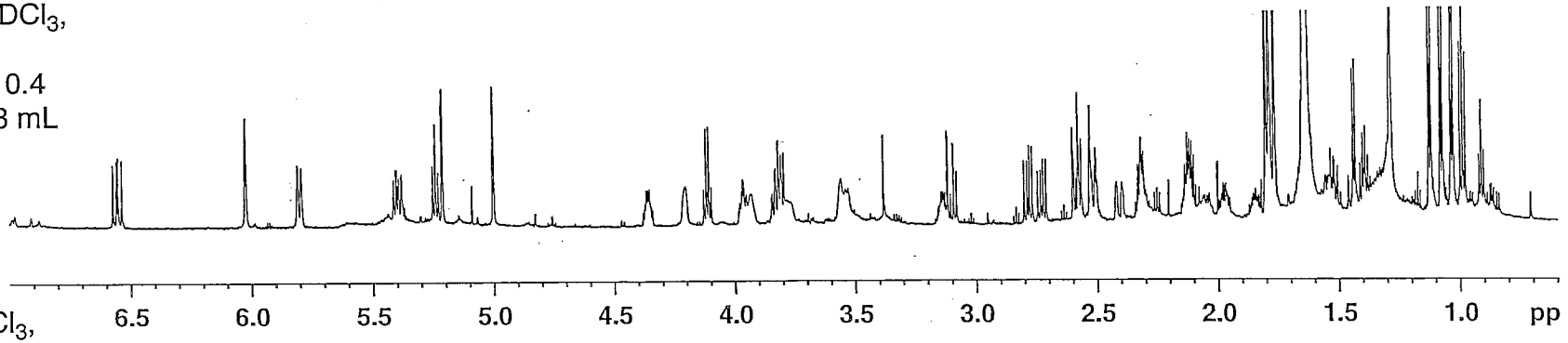
Comparison of ^{1}H data of amphidinolide F (**3**)

amphidinolide F (**3**)

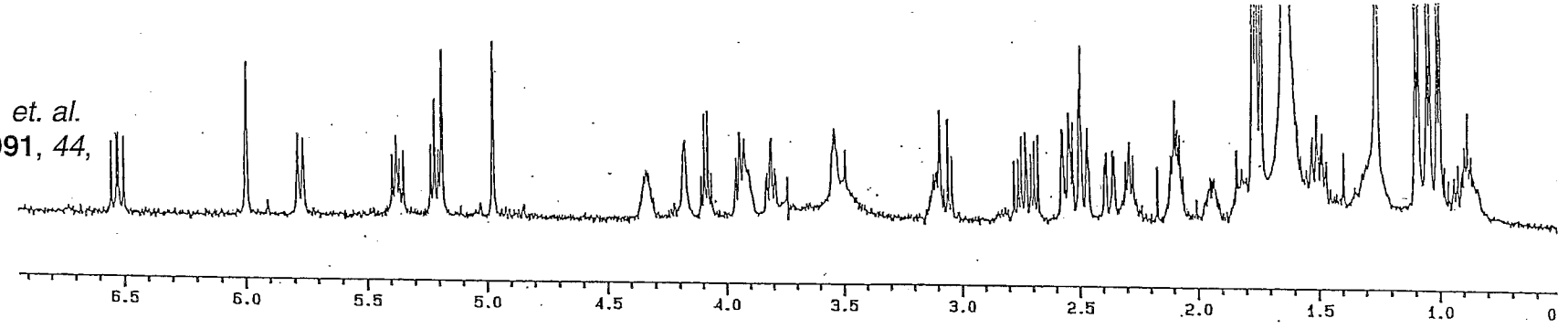
Synthetic **3** ($CDCl_3$, 700 MHz, Concentration 1.4 mg of **3** in 0.18 mL $CDCl_3$).



Synthetic **3** ($CDCl_3$, 700 MHz; Concentration 0.4 mg of **3** in 0.18 mL $CDCl_3$).



Natural **3** ($CDCl_3$, 500 MHz, concentration unknown) Kobayashi, J. *et. al.* *J. Antibiot.* **1991**, *44*, 1259-1261.



Comparison of ^{13}C data of amphidinolide F (**3**)

No.	Synthetic **3** (176 MHz, $CDCl_3$[a])	Natural **3**[b] (125 MHz, $CDCl_3$)
1	171.22	171.16
2	38.70	38.65
3	81.45	81.26
4	39.79	39.67
5	36.77	36.81
6	78.94	79.08
7	76.51	76.71
8	76.51	76.71
9	144.45	144.37
10	124.52	124.62
11	140.04	140.00
12	49.38	49.46
13	70.62	70.50
14	45.55	45.65
15	213.77	213.58
16	42.79	42.93
17	46.03	45.81
18	207.77	207.47
19	48.57	48.45
20	75.01	74.82
21	31.98	31.84
22	28.43	28.46
23	79.90	79.87
24	77.84	77.93
25	124.04	123.97
26	132.06	132.09
27	124.19	124.06
28	138.29	138.25
29	26.08	26.00
30	18.51	18.43
31	15.53	15.39
32	116.11	116.16
33	13.77	13.94
34	15.40	15.29
35	16.24	16.20

[a] Concentration 1.4 mg of **3** in 0.18 mL $CDCl_3$. [b] J. Kobayashi, M. Tsuda, M. Ishibashi, H. Shigemori, T. Yamasu, H. Hirota, T. Sasaki, *J. Antibiot.* **1991**, *44*, 1259-1261.