Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

12-Membered to strained 11-membered ring: First stereoselective total synthesis of (–)-asteriscunolide C

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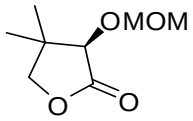
Contents

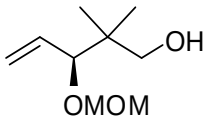
General: Flasks were oven or flame dried and cooled in a desiccator. Dry reactions were carried out under an atmosphere of Ar or N_2. Solvents and reagents were purified by standard methods. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by either staining with $KMnO_4$ or under UV lamp. ^{1}H NMR and ^{13}C NMR were recorded on Bruker, AVANCE III 400 spectrometer and the chemical shifts are based on TMS peak at δ = 0.00 ppm for ^{1}H NMR and $CDCl_3$ peak at δ = 77.00 ppm (t) in ^{13}C NMR. IR spectra were obtained on Perkin Elmer FT-IR spectrometer. Optical rotations were measured with Jasco P-2000 digital polarimeter. HRMS was recorded with Micromass: Q-Tof micro (YA-105) spectrometer using positive electrospray ionization by TOF method.

(*R*)-3-(Methoxymethoxy)-4,4-dimethyldihydrofuran-2(3*H*)-one (13)[1]



To a solution of D-(−)-pantolactone **12** (1.0 g, 7.68 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) at 0 °C were added DIPEA (3.32 mL, 19.21 mmol, 2.5 equiv) and MOMCl (9.60 mL, 19.21 mmol, 2 M solution in toluene, 2.5 equiv). The resulting solution was warmed to room temperature and refluxed for 24 h. It was then quenched with sat. aq. $NaHCO_3$ (10 mL) and the solution extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **13** (1.27 g, 95%) as colorless oil. **$[\alpha]_D^{25}$** +123.15 (*c* 0.68, $CHCl_3$); **IR** ($CHCl_3$): 2966, 2936, 2903, 2828, 1786, 1631, 1467, 1400, 1376, 1298, 1202, 1149, 1121, 1062, 1028, 1013, 995, 921, 944, 921, 892, 815, 710, 669, 643 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.00 (d, J = 6.8 Hz, 1H), 4.73 (d, J = 6.8 Hz, 1H), 4.07 (s, 1H), 4.00 (d, J = 8.8 Hz, 1H), 3.93 (d, J = 8.8 Hz, 1H), 3.45 (s, 3H), 1.21 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 96.1, 78.3, 76.1, 55.9, 40.2, 23.1, 19.4.

(*S*)-3-(Methoxymethoxy)-2,2-dimethylpent-4-en-1-ol (14)[1]

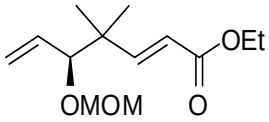


To a solution of **13** (0.5 g, 2.87 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) at −78 ^{o}C was added DIBAL-H (1.97 mL, 3.44 mmol, 1.75 M solution in toluene, 1.2 equiv) dropwise over 10 min. The resulting solution was stirred at same temperature for 2 h. It was then quenched with sat. aq. Rochelle salt (5 mL) and the solution extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give the lactol (0.505 g) as colorless oil.

To a white suspension of methyltriphenylphosphonium bromide (2.05 g, 5.74 mmol, 2.0 equiv) in dry THF (20 mL) at 0 °C was added *n*-BuLi (3.60 mL, 5.74 mmol, 1.6 M in hexane, 2.0 equiv). The resulting solution was stirred at 0 °C for 30 min and then the solution of above

lactol (0.505 g, 2.87 mmol, 1.0 equiv) in THF (5 mL) was added dropwise and stirred at 0 °C to room temperature for 16 h. It was then quenched with sat. aq. NH_4Cl (10 mL) and the solution extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **14** (0.425 g, 85%) as colorless oil. **$[\alpha]_D^{25}$** +138.62 (*c* 0.32, $CHCl_3$); **IR** ($CHCl_3$): 3460, 3079, 2962, 2886, 2825, 2780, 2066, 1642, 1473, 1423, 1365, 1274, 1149, 1099, 1041, 920, 969, 877, 668 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.78−5.68 (m, 1H), 5.31 (ddd, *J* = 10.0, 1.7, 0.6 Hz, 1H), 5.23 (ddd, *J* = 17.2, 1.8, 0.8 Hz, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 4.52 (d, *J* = 6.6 Hz, 1H), 3.88 (d, *J* = 8.1 Hz, 1H), 3.60 (d, *J* = 11.0 Hz, 1H), 3.40 (s, 3H), 3.33 (d, *J* = 11.0 Hz, 1H), 0.94 (s, 3H), 0.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.3, 119.6, 94.1, 84.2, 70.5, 55.9, 38.5, 22.3, 19.6.

(*S*,*E*)-Ethyl 5-(methoxymethoxy)-4,4-dimethylhepta-2,6-dienoate (15)

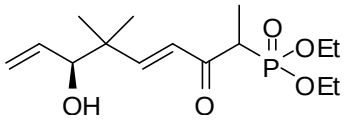


To a solution of DMSO (0.370 mL, 5.16 mmol, 3.0 equiv) in CH_2Cl_2 (25 mL) at −78 °C was added oxalyl chloride (0.220 mL, 2.58 mmol, 1.5 equiv). The resulting solution was stirred for 15 min, and then the solution of alcohol **14** (0.3 g, 1.72 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added and stirring continued for 45 min. It was then quenched with Et_3N (1.01 mL, 7.74 mmol, 4.5 equiv) and sat. aq. $NaHCO_3$ (20 mL) and the solution extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The crude aldehyde (0.296 g) was used without purification for next step.

To a solution of triethyl phosphonoacetate (0.578 g, 2.58 mmol, 1.5 equiv) in dry THF (15 mL) at 0 °C was added NaH (0.103 g, 2.58 mmol, 60% in mineral oil, 1.5 equiv) portionwise. The resulting mixture was stirred at 0 °C for 30 min, and then a solution of above aldehyde (0.296 g) in dry THF (5 mL) was added and stirred at 0 °C to room temperature for 16 h. It was then quenched with sat. aq. NH_4Cl (10 mL) and the solution extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **15** (0.362 g, 87%) as colorless oil. **$[\alpha]_D^{25}$** +85.6 (*c* 0.5, $CHCl_3$); **IR** ($CHCl_3$): 3079, 2981, 2890, 2825, 1721, 1652, 1468, 1424, 1386, 1367, 1311, 1272, 1181, 1162, 1149, 1098, 1037, 996, 920, 894, 864, 668 cm^{-1}; **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.08 (d, J = 16.0 Hz, 1H), 5.79 (d, J = 16.0 Hz, 1H), 5.61−5.56 (m, 1H), 5.31 (dd, J = 10.4, 1.5 Hz, 1H), 5.22 (dd, J = 17.6, 0.9 Hz, 1H), 4.67 (d, J = 6.9 Hz, 1H), 4.48 (d, J = 6.9 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.76 (d, J = 8.3 Hz, 1H), 3.36 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H), 1.09 (s, 3H), 1.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 155.3, 134.2, 120.3, 119.1, 93.6, 83.6, 60.2, 55.8, 40.5, 23.9, 22.3, 14.3; **HRMS** *m/z* calcd for $[C_{13}H_{22}O_4 + H]^+$ 243.1596, found 243.1597.

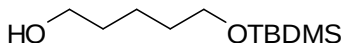
Diethyl (7*S*,*E*)-7-hydroxy-6,6-dimethyl-3-oxonona-4,8-dien-2-ylphosphonate (11)



To a solution of diethyl ethylphosphonate (1.44 g, 8.67 mmol, 3.0 equiv) in dry THF (30 mL) at −78 °C was added *n*-BuLi (5.42 mL, 8.67 mmol, 1.6 M in hexane, 3.0 equiv). The resulting solution was stirred at −78 °C to 0 °C for 1 h, then cooled back to −78 °C and a solution of ester **15** (0.7 g, 2.89 mmol, 1.0 equiv) in THF (10 mL) was added. The resulting mixture was stirred at −78 °C for 2 h. It was then quenched with sat. aq. NH_4Cl (10 mL) and the solution extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The crude ketophosphonate was used without purification for the next step.

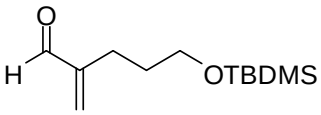
To a solution of above crude ketophosphonate in THF (20 mL) was added 4 N HCl (10 mL). The resulting mixture was refluxed for 2 h. It was then quenched with sat. aq. $NaHCO_3$ (20 mL) and the solution extracted with EtOAc (3× 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **11** (0.809 g, 88%) as colorless oil. **IR** ($CHCl_3$): 3401, 2983, 2940, 2876, 1694, 1669, 1623, 1456, 1392, 1317, 1240, 1164, 1098, 1024, 970, 993, 869, 797, 667 cm^{-1}; NMR data for one diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (d, J = 16.2 Hz, 1H), 6.27 (d, J = 16.3 Hz, 1H), 5.92−5.80 (m, 1H), 5.33−5.19 (m, 2H), 4.20−4.03 (m, 4H), 3.93 (dd, J = 0.9, 7.1 Hz, 1H), 3.62−3.45 (m, 1H), 1.42−1.26 (m, 9H), 1.11 (s, 3H), 1.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.2, 155.6, 136.4, 128.2, 117.3, 79.4, 62.8 (d), 62.5 (d) 44.3 (d), 41.7, 23.1, 21.6, 16.35, 16.31, 10.8 (d); **HRMS** *m/z* calcd for $[C_{15}H_{27}O_5P + H]^+$ 319.1675, found 319.1671.

5-(*tert*-Butyldimethylsilyloxy)-pentan-1-ol (17)



To a stirred solution of 1,5-pentane diol **16** (1.0 g, 9.60 mmol) in dry THF (40 mL) at 0 ^{o}C was added NaH (0.384 g, 9.60 mmol, 1.0 equiv) in portions over 15 min. The reaction mixture was stirred at room temperature for 30 min, then cooled to 0 °C and TBDMSCl (1.45 g, 9.60 mmol, 1.0 equiv) was added. The reaction mixture was stirred at room temperature for 12 h. It was then quenched with ice cold water (10 mL) and the solution extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1 to 4:1) as eluent to give **17** (1.78 g, 85%) as colorless oil. **IR** ($CHCl_3$): 3370, 2933, 2859, 1472, 1389, 1362, 1256, 1100, 1040, 1006, 939, 919, 837, 666 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.65−3.59 (m, 4H), 1.60−1.41 (m, 4H), 1.39−1.37 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 63.1, 62.9, 32.4, 25.9, 22.0, 18.3, −5.3.

5-(*tert*-Butyldimethylsilyloxy)-2-methylenepentanal (18)

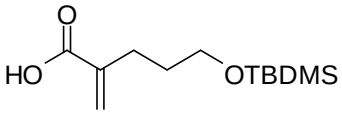


To a solution of DMSO (0.314 mL, 4.42 mmol, 3.0 equiv) in CH_2Cl_2 (25 mL) at −78 °C was added oxalyl chloride (0.190 mL, 2.20 mmol, 1.5 equiv). The resulting mixture was stirred for 15 min, then a solution of alcohol **17** (0.322 g, 1.47 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added and stirring continued for 45 min. It was then quenched with Et_3N (2.87 mL, 6.61 mmol, 4.5 equiv) and sat. aq. $NaHCO_3$ (5 mL). The solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The crude aldehyde (0.319 g) was used without purification for next step.

To a solution of above aldehyde (0.319 g) and formalin (0.110 mL, 1.47 mmol, 37% formaldehyde in water, 1.0 equiv) in *i*-PrOH (0.2 mL) were added propionic acid (0.011 mL, 0.147 mmol, 10 mol%) and pyrolidine (0.012 mL, 0.147 mmol, 10 mol%). The resulting mixture was stirred at 45 °C for 24 h. It was then quenched with sat. aq. $NaHCO_3$ (2 mL) and the solution extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1 to 4:1) as eluent to give **18** (0.316

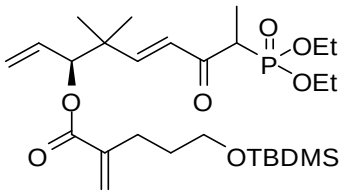
g, 94%, over two steps) as colorless oil. **IR** ($CHCl_3$): 2955, 2930, 2886, 1697, 1628, 1463, 1389, 1361, 1256, 1104, 1006, 958, 837, 814, 776, 713, 667 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 6.26 (d, J = 0.8 Hz, 1H), 5.99 (d, J = 0.5 Hz, 1H), 3.60 (t, J = 6.3 Hz, 2H), 2.29 (t, J = 7.7 Hz, 2H), 1.67−1.63 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.7, 149.9, 134.1, 62.3, 30.7, 25.9, 24.2, 18.3, −5.4; **HRMS** *m/z* calcd for $[C_{12}H_{24}O_2Si]^+$ 228.1546, found 228.1539.

5-(*tert*-Butyldimethylsilyloxy)-2-methylenepentanoic acid (10)



To a solution of aldehyde **18** (0.1 g, 0.438 mmol, 1.0 equiv) and cyclohexene (0.108 g, 1.31 mmol, 3.0 equiv) in *t*-BuOH (3 mL) at 5 °C was added a solution of $NaH_2PO_4.2H_2O$ (0.137 g, 0.876 mmol, 2.0 equiv) and $NaClO_2$ (0.091 g, 1.01 mmol, 2.3 equiv) in water (1.5 mL) dropwise over 10 min. The resulting yellow mixture was stirred at room temperature for 1 h. It was then quenched with sat. aq. NH_4Cl (5 mL) and the solution extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give **10** (0.094 g, 88%) as colorless oil. **IR** ($CHCl_3$): 3439, 3019, 2956, 2931, 2900, 2858, 1714, 1628, 1472, 1464, 1448, 1300, 1257, 1158, 1074, 1021, 952, 911, 837, 668 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.29 (d, J = 0.9 Hz, 1H), 5.67 (d, J = 1.4 Hz, 1H), 3.63 (t, J = 6.3 Hz, 2H), 2.36 (t, J = 7.7 Hz, 2H), 1.74−1.67 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 139.7, 127.2, 62.3, 31.3, 27.9, 25.9, 18.3, −5.3; **HRMS** *m/z* calcd for $[C_{12}H_{24}O_3Si + H]^+$ 245.1573, found 245.1565.

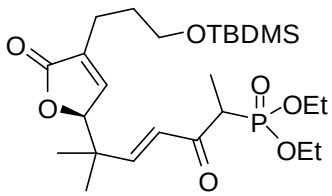
(3*S*,*E*)-8-(Diethoxyphosphoryl)-4,4-dimethyl-7-oxonona-1,5-dien-3-yl 5-(tert-butyldimethyl silyloxy)-2-methylenepentanoate (9)



To a solution of acid **10** (0.170 g, 0.695 mmol, 1.5 equiv) in toluene (5 mL) was added Et_3N (0.194 mL, 1.39 mmol, 3.0 equiv) and stirred at same temperature for 30 min. Then 2,4,6-trichlorobenzoyl chloride (0.145 mL, 0.93 mmol, 2.0 equiv) was added and the reaction

mixture was stirred at room temperature for 45 min. After complete conversion of acid (judged by TLC) were added alcohol **11** (0.147 g, 0.461 mmol, 1.0 equiv) in toluene (5 mL) and DMAP (0.170 g, 1.39 mmol, 3.0 equiv). The resulting mixture was stirred at room temperature for 2 h and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **9** (0.237 g, 94%) as colorless oil. **IR** ($CHCl_3$): 2983, 2956, 2932, 2859, 1720, 1693, 1673, 1627, 1472, 1390, 1368, 1318, 1251, 1195, 1161, 1100, 1055, 1025, 969, 946, 837, 814, 667 cm^{-1}; NMR data for one diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (d, J = 15.8 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H), 6.16 (s, 1H), 5.77−5.68 (m, 1H), 5.56 (s, 1H), 5.27−5.22 (m, 2H), 5.17 (d, J = 6.4 Hz, 1H), 4.15−4.05 (m, 4H), 3.61 (t, J = 6.4 Hz, 2H), 3.45–3.31 (m, 1H), 2.35 (t, J = 7.5 Hz, 2H), 1.70−1.63 (m, 2H), 1.38 (dd, J = 18.0, 7.1 Hz, 3H), 1.30 (dt, J = 7.0, 4.4 Hz, 6H), 1.11 (s, 6H), 0.88 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8, 166.0, 152.2, 140.2, 132.6, 127.1, 125.0, 119.2, 80.2, 62.6 (d), 62.5 (d), 62.3, 45.4 (d), 40.7, 31.4, 28.2, 25.9, 23.0, 22.8, 18.3, 16.4, 16.3, 11.1 (d), −5.4; **HRMS** *m/z* calcd for $[C_{27}H_{49}O_7PSi + H]^+$ 545.3063, found 545.3066.

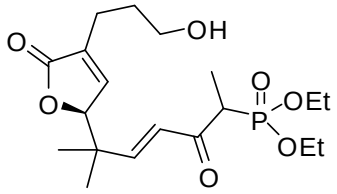
Diethyl (*E*)-6-[(*S*)-4-(3-*tert*-butyldimethylsilyloxypropyl)-5-oxo-2,5-dihydrofuran-2-yl]-6-methyl-3-oxohept-4-en-2-ylphosphonate (19)



To a solution of **9** (0.1 g, 0.183 mmol, 1.0 equiv) in dry and degassed toluene (20 mL) was added Grubb's II-generation catalyst (15.6 mg, 10 mol%). The resulting solution was refluxed for 36 h. The reaction mixture was concentrated and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **19** (87 mg, 92%) as colorless oil. **IR** ($CHCl_3$): 2945, 2858, 1760, 1697, 1673, 1629, 1472, 1391, 1366, 1317, 1252, 1188, 1104, 1064, 1025, 166, 872, 838, 777, 665 cm^{-1}; NMR data for one diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (dd, J = 3.9, 1.6 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 4.70 (dd, J = 9.8, 1.6 Hz, 1H), 4.15−4.05 (m, 4H), 3.61 (dt, J = 6.1, 1.2 Hz, 2H), 3.41–3.31 (m, 1H), 2.36−2.32 (m, 2H), 1.75−1.71 (m, 2H), 1.40−1.27 (m, 9H), 1.15 (d, J = 5.7 Hz, 3H), 1.09 (s, 3H), 0.87 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.5, 173.2, 150.3, 144.9, 136.2, 127.9, 86.2, 62.7 (d), 62.6 (d), 62.1, 45.6 (d), 40.7, 30.5,

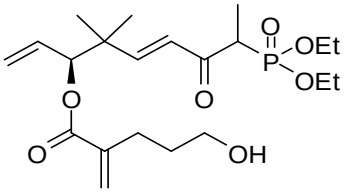
25.9, 23.2, 22.8, 21.9, 18.3, 16.4, 16.3, 10.9 (d), −5.4; **HRMS** *m/z* calcd for $[C_{25}H_{45}O_7PSi + H]^+$ 517.2751, found 517.2746.

Diethyl (*E*)-6-[(*S*)-4-(3-hydroxypropyl)-5-oxo-2,5-dihydrofuran-2-yl]-6-methyl-3-oxohept-4-en-2-ylphosphonate (20)



To a solution of **19** (80 mg, 0.155 mmol, 1.0 equiv) in MeOH (10 mL) was added 4 N HCl (1 mL). The resulting solution was stirred at room temperature for 4 h. It was then quenched with sat. aq. $NaHCO_3$ (5 mL) and MeOH was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **20** (53 mg, 85%) as colorless oil. **IR** ($CHCl_3$): 3433, 2979, 2938, 2874, 1753, 1671, 1696, 1628, 1458, 1391, 1363, 1319, 1239, 1160, 1097, 1062, 1022, 969, 912, 875, 795, 733, 669 cm^{-1}; NMR data for one diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11−7.09 (m, 1H), 7.80 (d, J = 15.9 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 4.74 (dd, J = 8.8, 1.6 Hz, 1H), 4.17−4.06 (m, 4H), 3.65−3.56 (m, 2H), 3.55−3.32 (m, 1H), 2.41 (dt, J = 7.1, 1.3 Hz, 1H), 1.88−1.67 (m, 4H), 1.41−1.29 (m, 9H), 1.23 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.5, 173.7, 149.9, 146.0, 135.6, 128.2, 86.4, 62.9 (d), 62.6 (d), 60.9, 45.7 (d), 40.7, 30.1, 23.6, 22.1, 21.4, 16.4, 16.3, 10.9 (d); **HRMS** *m/z* calcd for $[C_{19}H_{31}O_7P + H]^+$ 403.1886, found 403.1900.

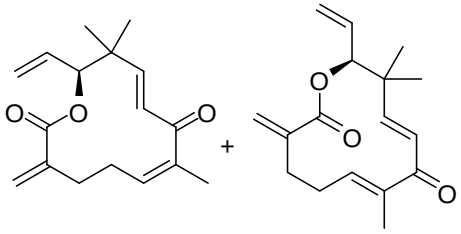
(3*S*,*E*)-8-(Diethoxyphosphoryl)-4,4-dimethyl-7-oxonona-1,5-dien-3-yl 5-hydroxy-2-methylenepentanoate (21)



To a solution of **9** (0.1 g, 0.183 mmol, 1.0 equiv) in MeOH (10 mL) was added 4 N HCl (1 mL). The resulting solution was stirred at room temperature for 4 h. It was then quenched with sat. aq. $NaHCO_3$ (5 mL) and MeOH was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with

brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **21** (73 mg, 92%) as colorless oil. **IR** ($CHCl_3$): 3422, 2984, 2939, 2874, 1718, 1627, 1455, 1388, 1366, 1318, 1240, 1184, 1160, 1140, 1048, 1024, 971, 668, cm^{-1}; NMR data for one diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (d, J = 16.0 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H), 6.18 (s, 1H), 5.77−5.68 (m, 1H), 5.56 (d, J = 1.4 Hz, 1H), 5.28−5.23 (m, 2H), 5.17−5.14 (m, 1H), 4.15−4.04 (m, 4H), 3.61 (t, J = 6.3 Hz, 2H), 3.43−3.31 (m, 1H), 2.38 (t, J = 7.8 Hz, 2H), 1.73−1.66 (m, 2H), 1.40−1.21 (m, 12H), 1.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.0, 166.2, 152.3, 140.3, 132.4, 127.2, 125.6, 119.6, 80.5, 62.7 (d), 62.6 (d), 61.7, 45.2 (d), 40.6, 31.9, 28.2, 23.8, 22.7, 16.34, 16.3, 11.1 (d); **HRMS** *m/z* calcd for $[C_{21}H_{35}O_7P + H]^+$ 431.2199, found 431.2192.

(*S*,6*Z*,9*E*)-7,11,11-Trimethyl-3-methylene-12-vinyloxacyclododeca-6,9-diene-2,8-dione (22) (1:1) mixture with (*S*,6*E*,9*E*)-7,11,11-Trimethyl-3-methylene-12-vinyloxacyclododeca-6,9-diene-2,8-dione (23)



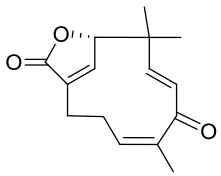
22 (1:1) **23**

To a solution of alcohol **21** (45 mg, 0.104 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) was added Dess-Martin periodinate (98 mg, 0.23 mmol, 2.2 equiv). The resulting mixture was stirred at room temperature for 1 h. It was then quenched with a solution of 10% aq. $Na_2S_2O_3$ and sat. aq. $NaHCO_3$ (1:1, 2 mL) and the solution extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was passed through a short pad of silica gel and washed with petroleum ether/EtOAc (1:1) to give the aldehyde which was used for next step.

To a solution of K_2CO_3 (86.2 mg, 0.624 mmol, 6.0 equiv) and 18-crown-6 (0.330 g, 1.25 mmol, 12.0 equiv) in toluene (40 mL) at 60 ^oC was added a solution of above aldehyde (45 mg) in toluene (12 mL) over a period of 4 h. The resulting solution was stirred at 60 °C for 12 h. It was then quenched with sat. aq. NH_4Cl (5 mL) and the solution extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give a mixture of **22:23** (1:1, by ^{1}H-NMR, 19 mg, 66%) as

colorless oil. Data of mixture: **IR** ($CHCl_3$): 3016, 2926, 2854, 1720, 1646, 1464, 1369, 1300, 1283, 1182, 1146, 1100, 1021, 989, 938, 668 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.67 (d, J = 16.2 Hz, 1H), 6.28−6.21 (m, 3H), 6.03−5.99 (m, 3H), 5.96−5.77 (m, 2H), 5.62 (s, 1H), 5.51−5.47 (m, 2H), 5.43 (d, J = 6.8 Hz, 1H), 5.37−5.30 (m, 4H), 5.03 (d, J = 6.8 Hz, 1H), 2.91−2.85 (m, 1H), 2.62−2.10 (m, 7H), 1.86 (s, 3H), 1.78 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 200.3, 168.3, 166.0, 153.7, 153.6, 143.6, 141.8, 140.4, 138.0, 137.8, 131.8, 131.75, 130.6, 129.6, 127.3, 125.0, 123.7, 119.5, 119.0, 81.7, 81.0, 41.3, 40.6, 33.0, 30.0, 29.8, 29.0, 23.5, 23.0, 20.9, 20.4, 19.7. 12.0; **HRMS** *m/z* calcd for $[C_{17}H_{22}O_3 + H]^+$ 275.1647, found 275.1655.

(−)-Asteriscunolide C (3)



To a stirred mixture of **22** and **23** (12 mg, 0.044 mmol, 1.0 equiv) in dry and degassed toluene (10 mL) was added Grubb's IInd generation catalyst (3.7 mg, 10 mol%). The resulting solution was refluxed for 24 h and more Grubb's IInd generation catalyst (1.9 mg, 5 mol%) was added and stirred for another 48 h. The reaction mixture was concentrated and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give (−)-**3** (4.85 mg, 90% based on the proportion of **22** in substrate mixture) as white solid. **mp** 159−160 ^{o}C, (lit.[2] 164 ^{o}C); **$[\alpha]_D^{25}$** −252.9 (*c* 0.4, $CHCl_3$), [lit.[2] $[\alpha]_D^{24}$ = −260 (*c* 0.90)]; **IR** ($CHCl_3$): 3020, 2928, 2855, 1760, 1652, 1462, 1453, 1369, 1317, 1180, 1067, 1053, 894, 856, 668 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.28 (d, J = 16.6 Hz, 1H), 5.91 (d, J = 16.6 Hz, 1H), 5.48 (bd, J = 11.8 Hz, 1H), 4.72 (s, 1H), 2.52−1.76 (m, 4H), 1.86 (s. 3H), 1.36 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.6, 173.7, 156.4, 149.7, 138.6, 135.6, 129.5, 128.5, 85.6, 40.7, 33.8, 24.6, 22.8, 21.1, 21.0; **HRMS** *m/z* calcd for $[C_{15}H_{18}O_3 + H]^+$ 247.1334, found 247.1326.

References

1 A. K. Hajare, L. S. Datrange, Y. L. N. Murthy, D. Bhuniya, D. S. Reddy, *Synthesis*, 2011, 1067.

2 A. San Feliciano, A. F. Barrero, M. Medarde, J. M. Miguel del Corral, A. Aramburu Aizpiri, F. Sanchez-Ferrando, *Tetrahedron*, 1984, **40**, 873.

RAF-VPC-4-150-1H

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D1                           1.00000000 sec
TD0                                 1

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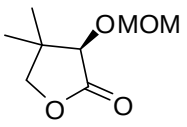

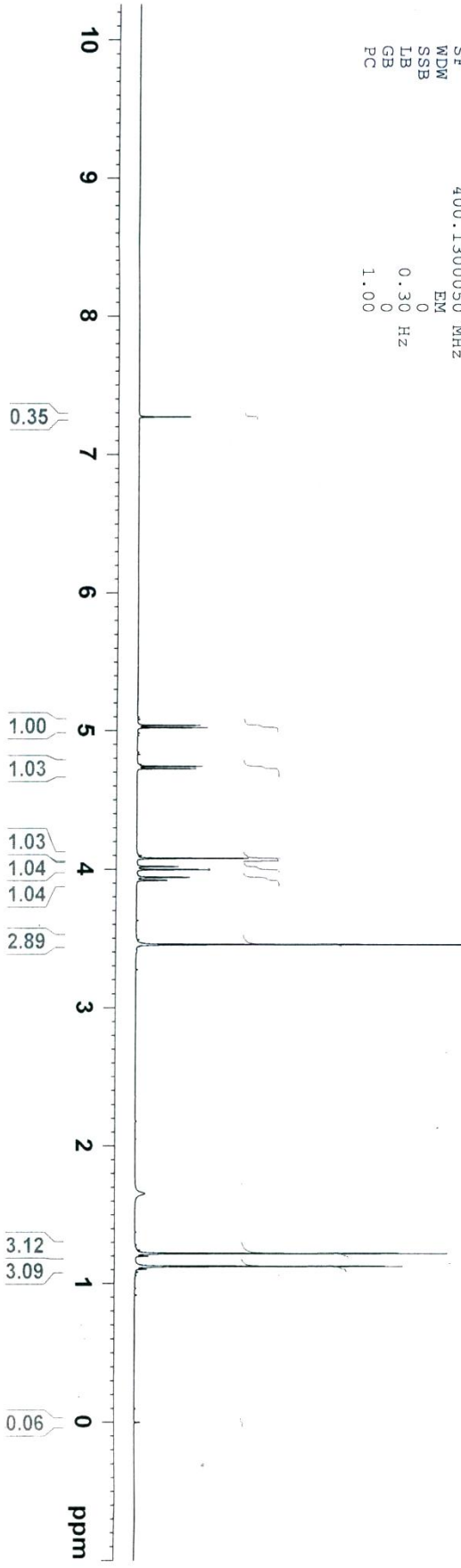

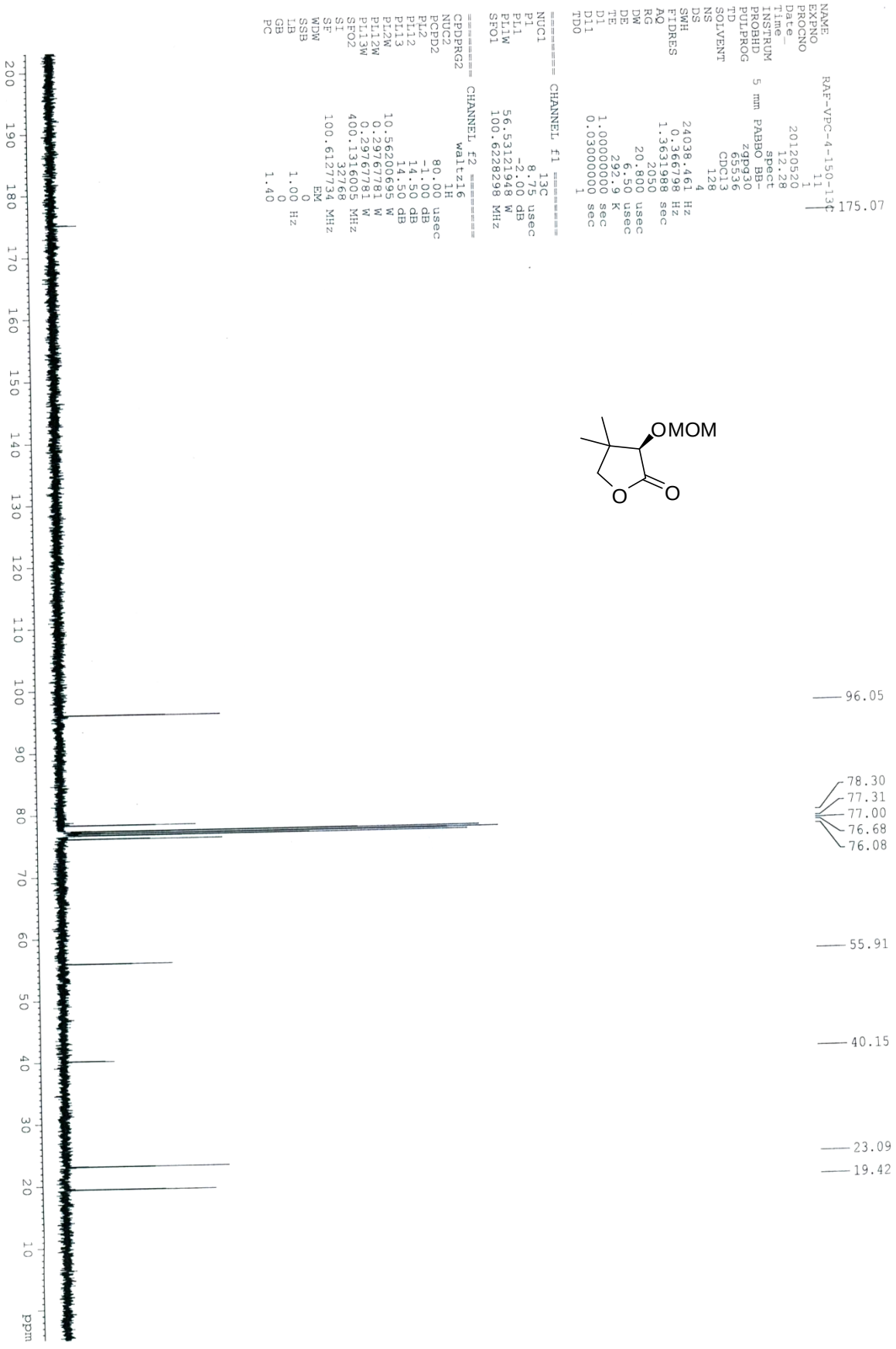
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PL13W 0.29767781 W
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SI 32768
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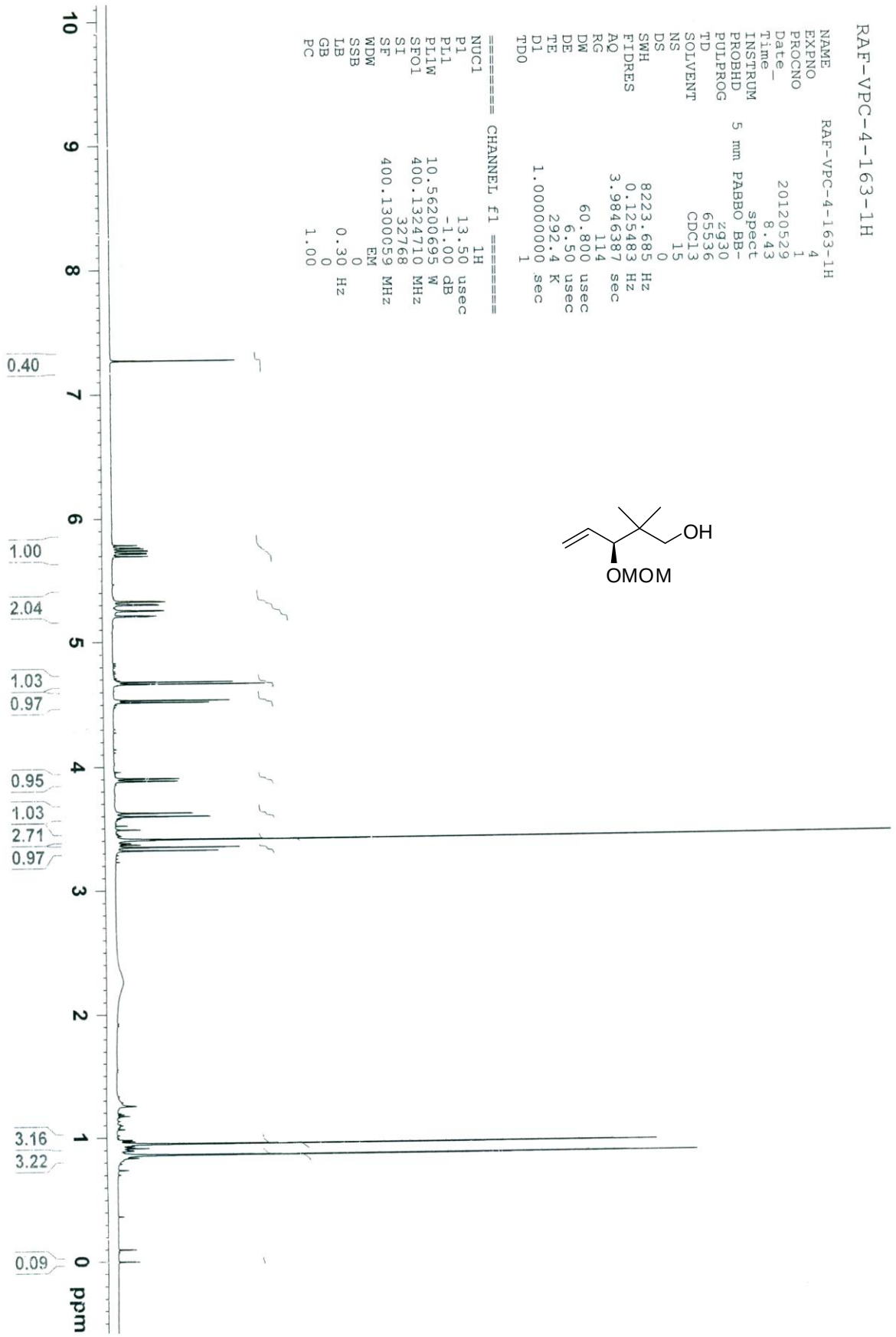
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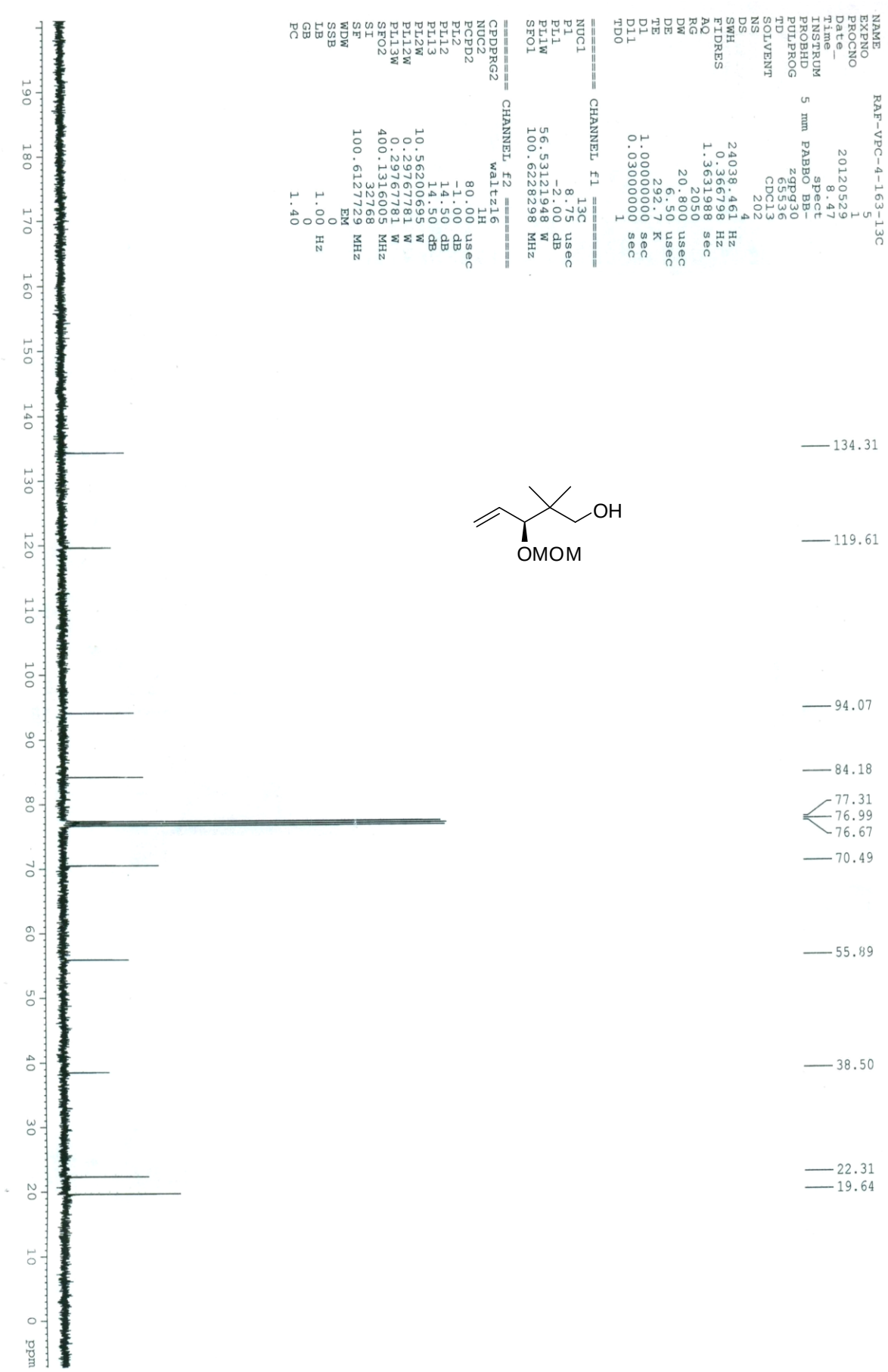
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SSB 0
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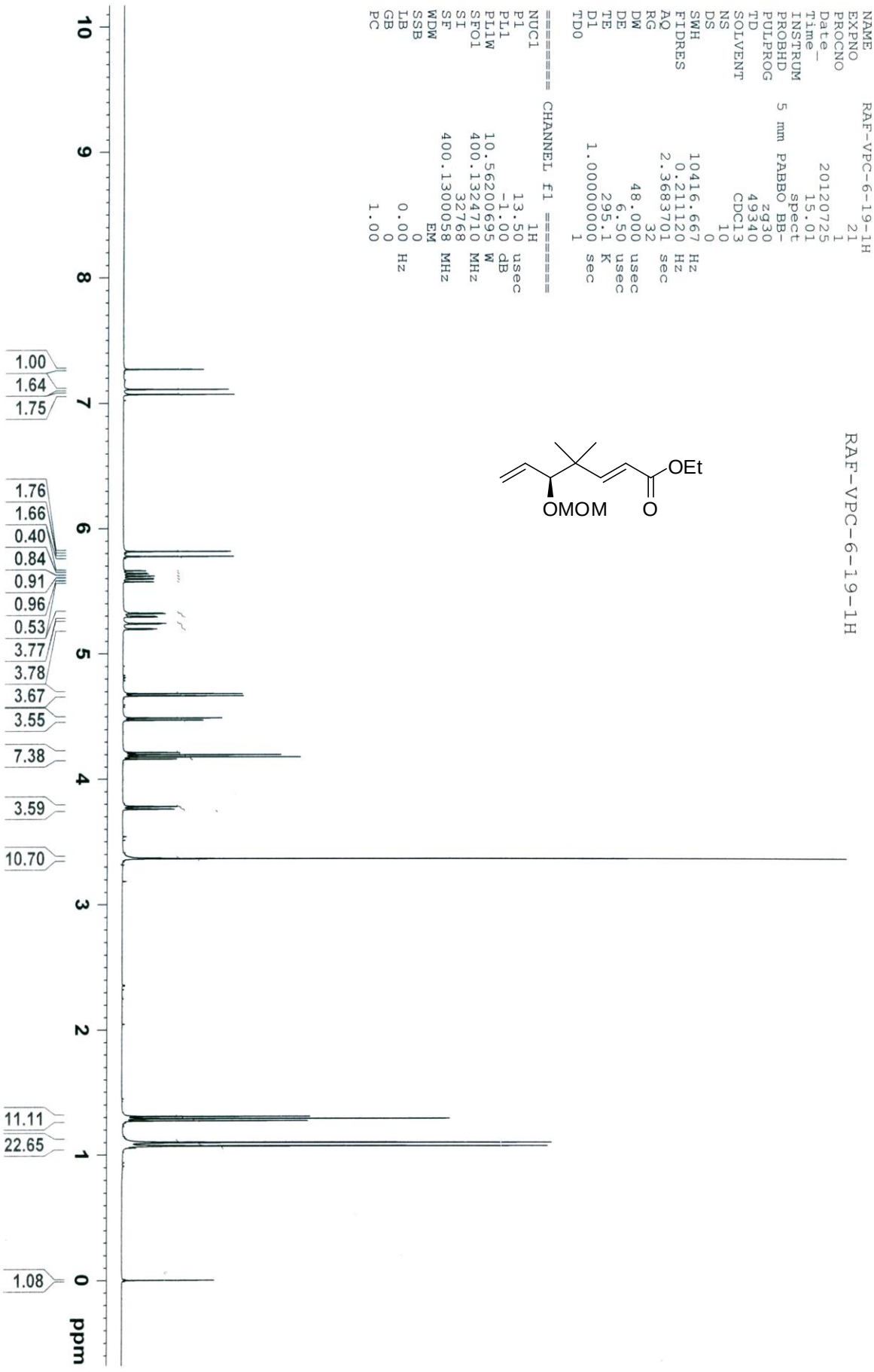
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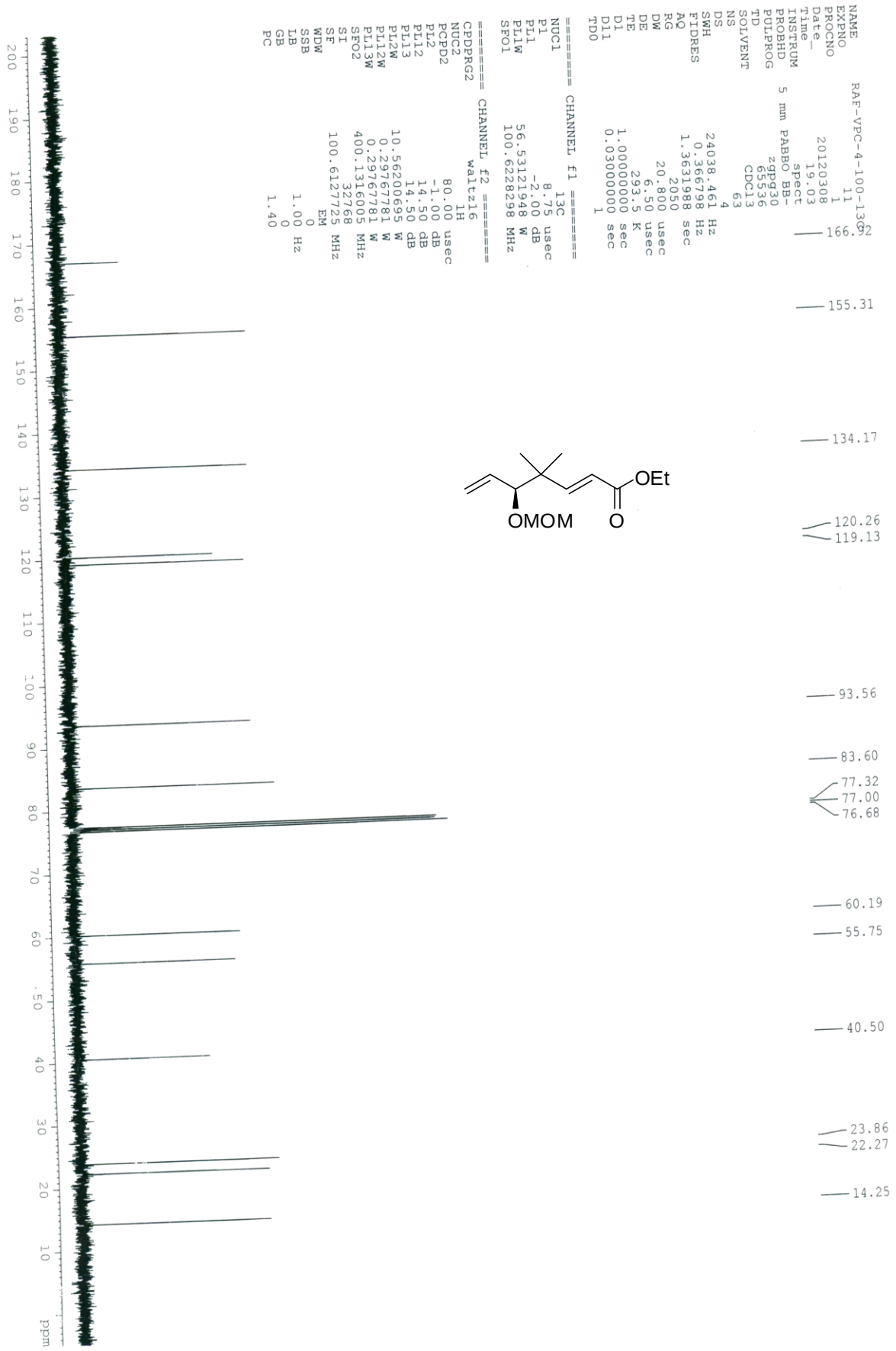
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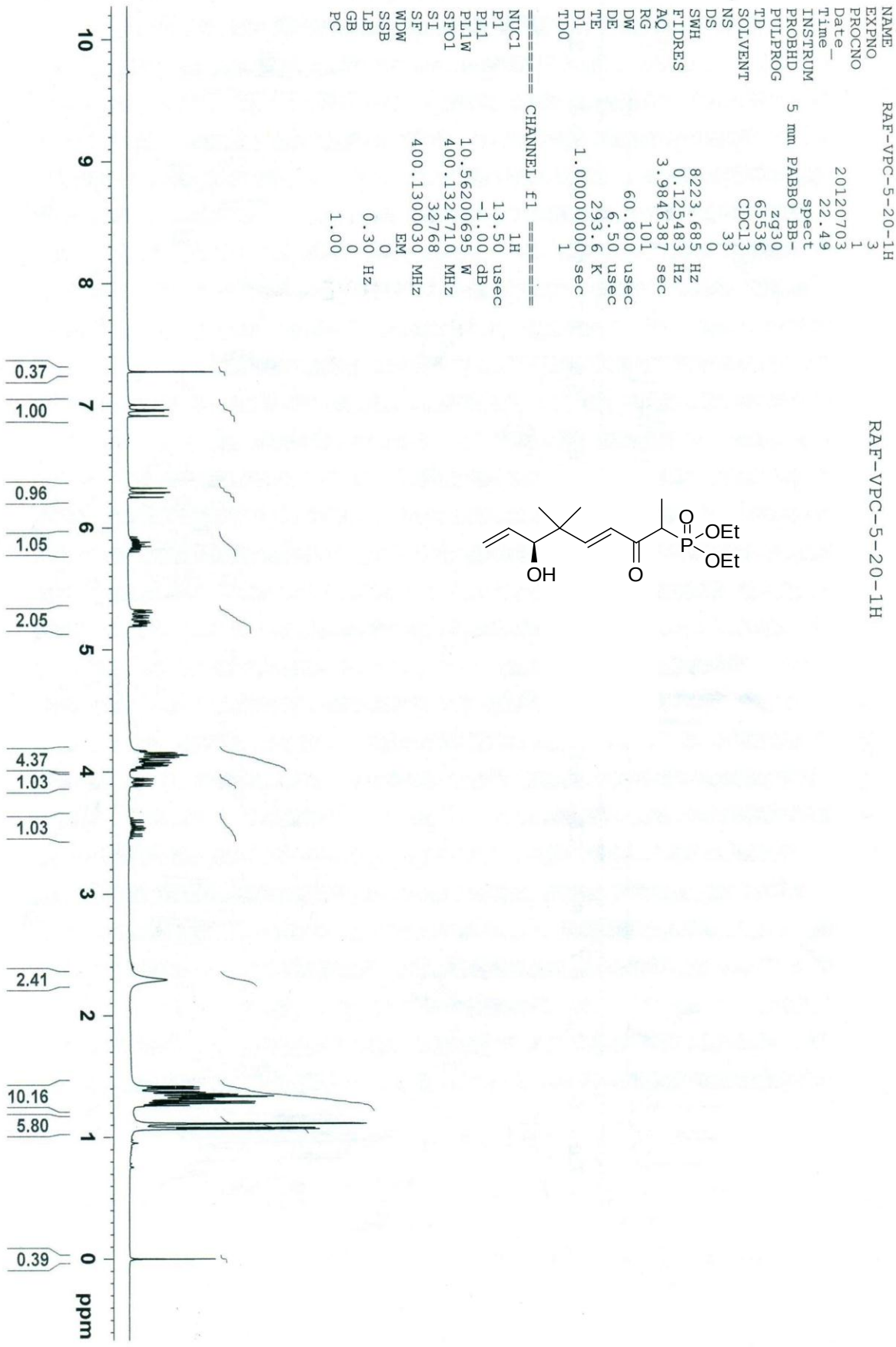
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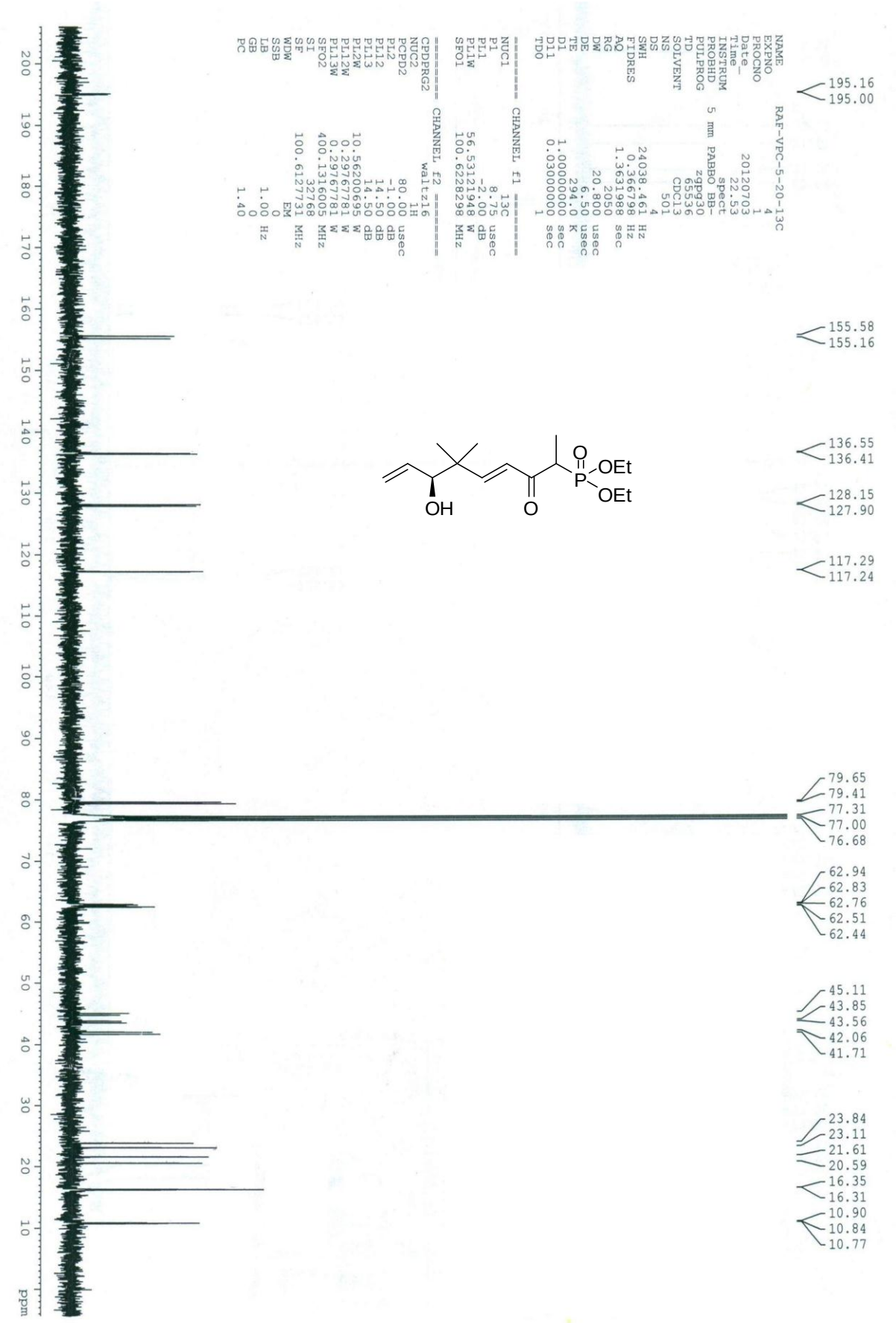
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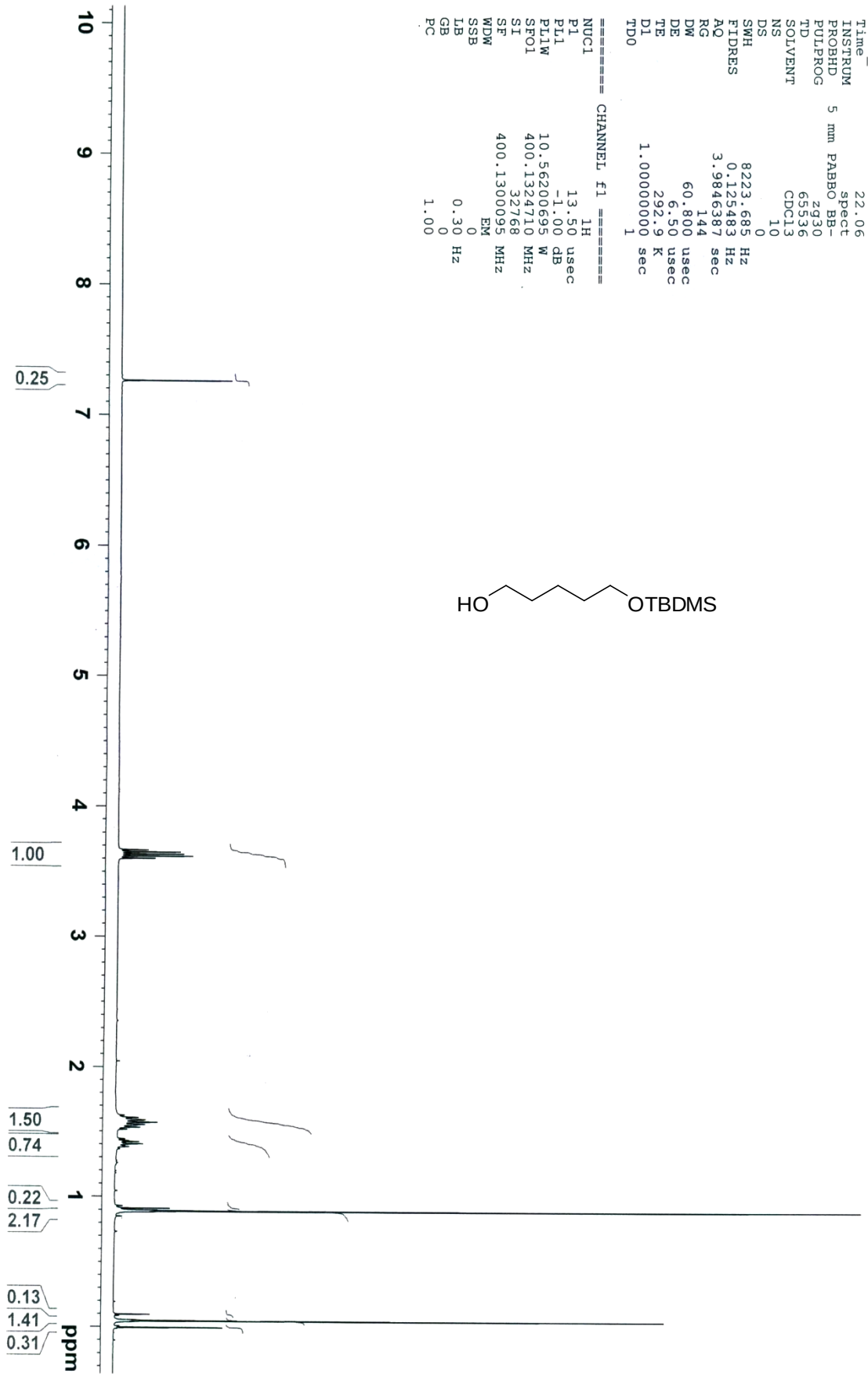
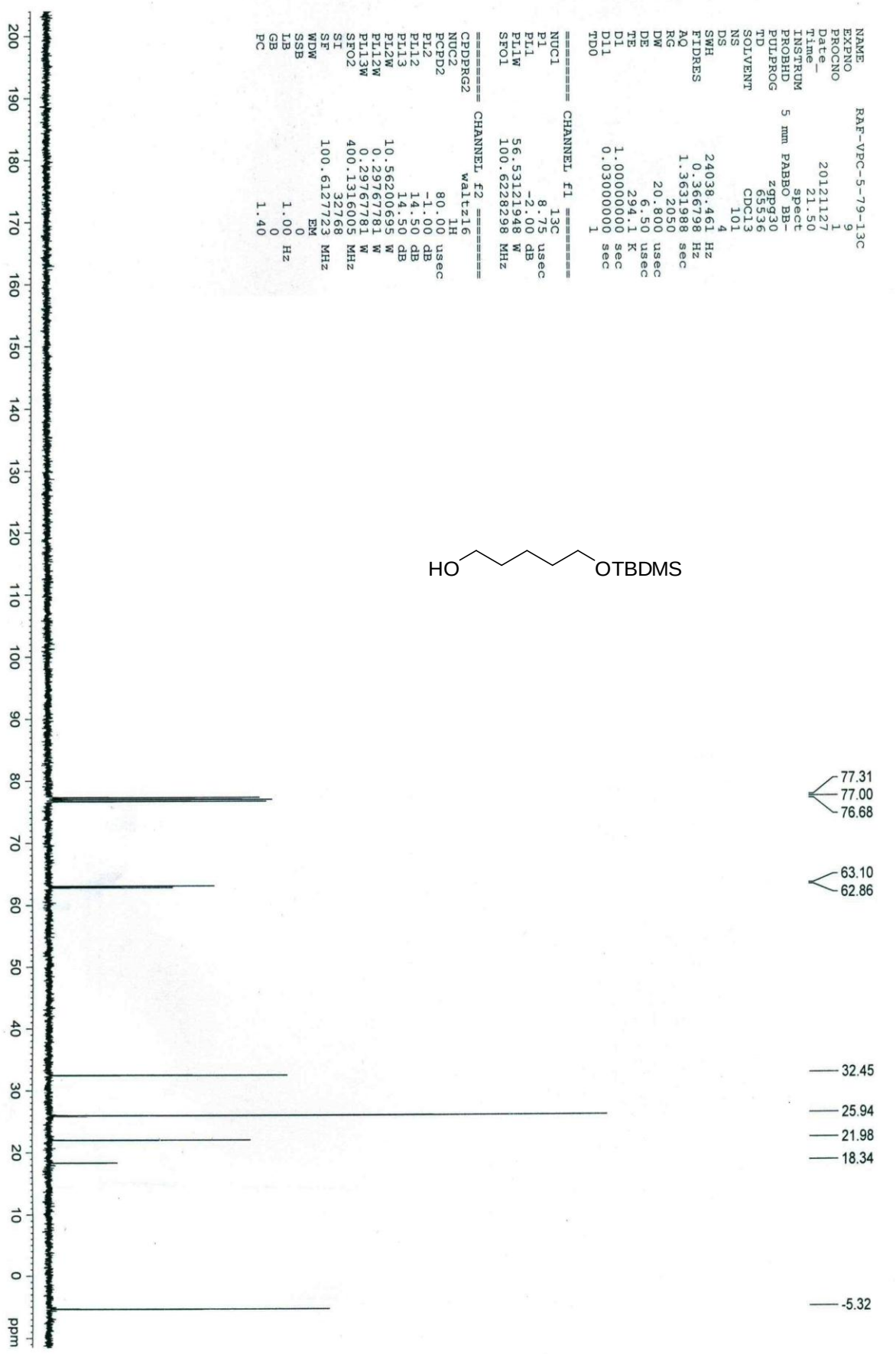
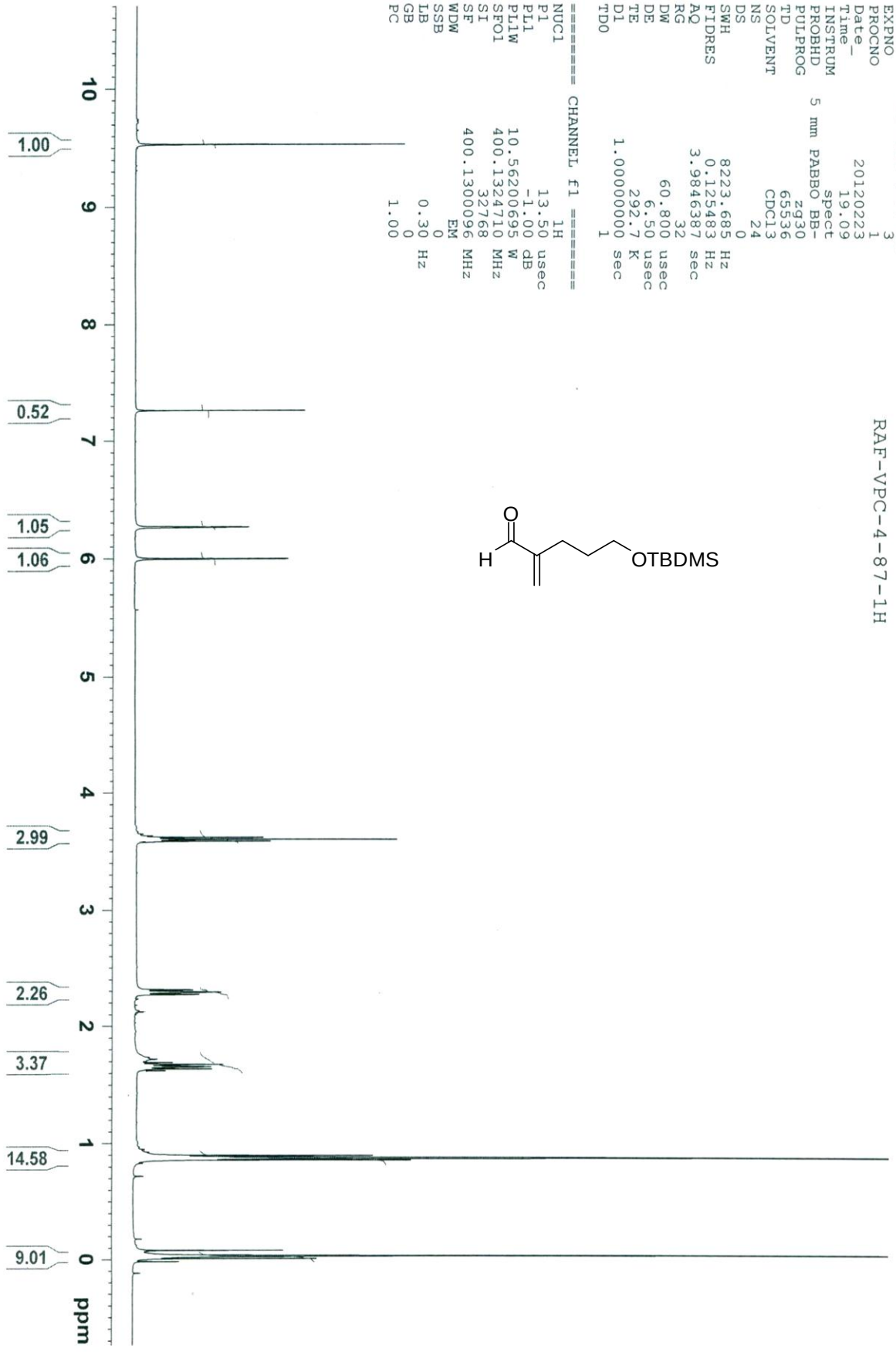
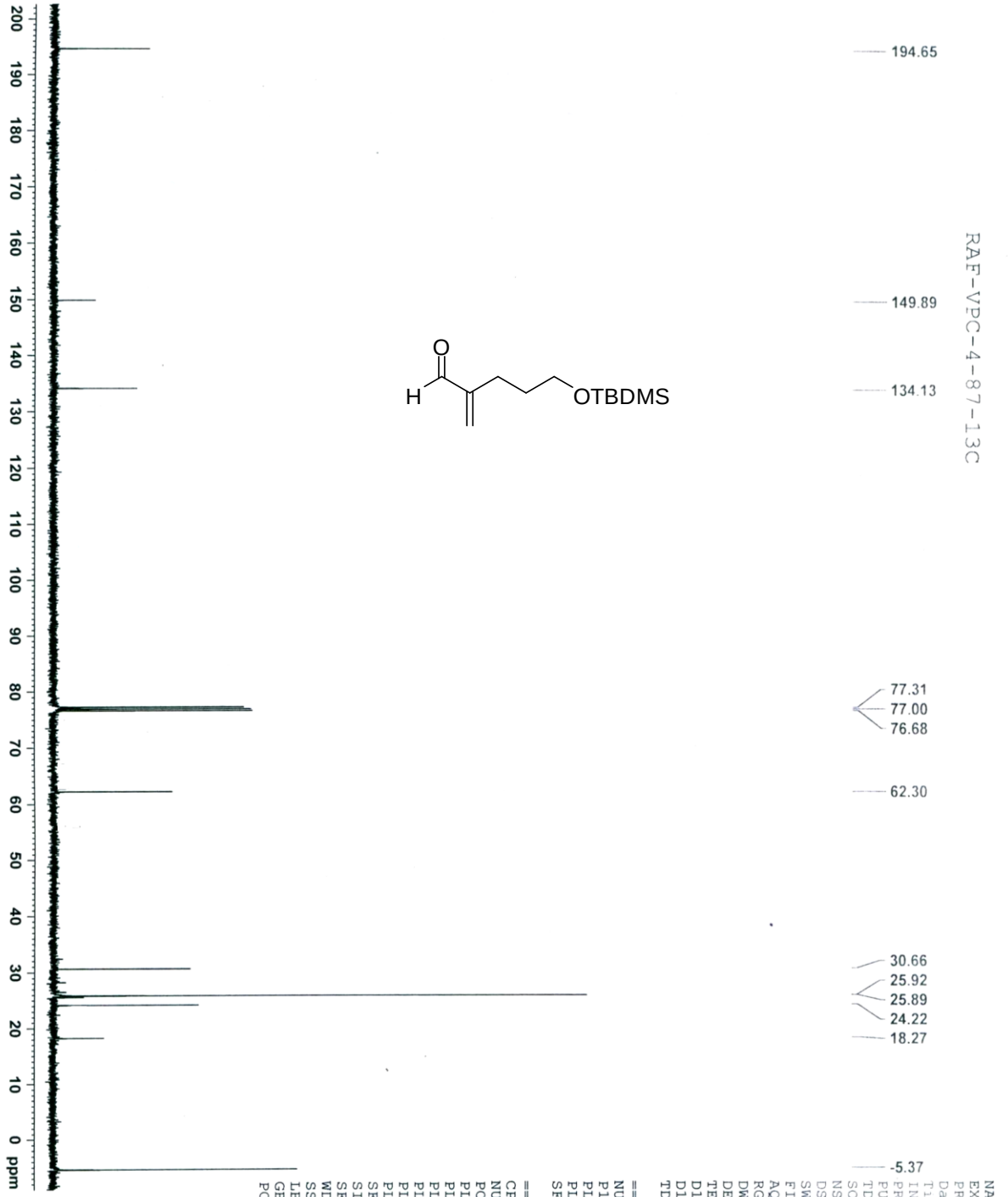
10
ppm


NAME RAF-VPC-5-79-1H
EXPNO 5
PROCNO 1
Date_ 20121215
Time_ 22.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 292.9 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
OTBDMS
RAF-VPC-5-79-1H
0.25
1.00
1.50
0.74
0.22
2.17
0.13
1.41
0.31
ppm


NAME RAF-VPC-5-79-13C
EXPNO 9
PROCNO 1
Date_ 20121127
Time_ 21.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 101
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HO
OTBDMS
77.31
77.00
76.68
63.10
62.86
32.45
25.94
21.98
18.34
-5.32
ppm

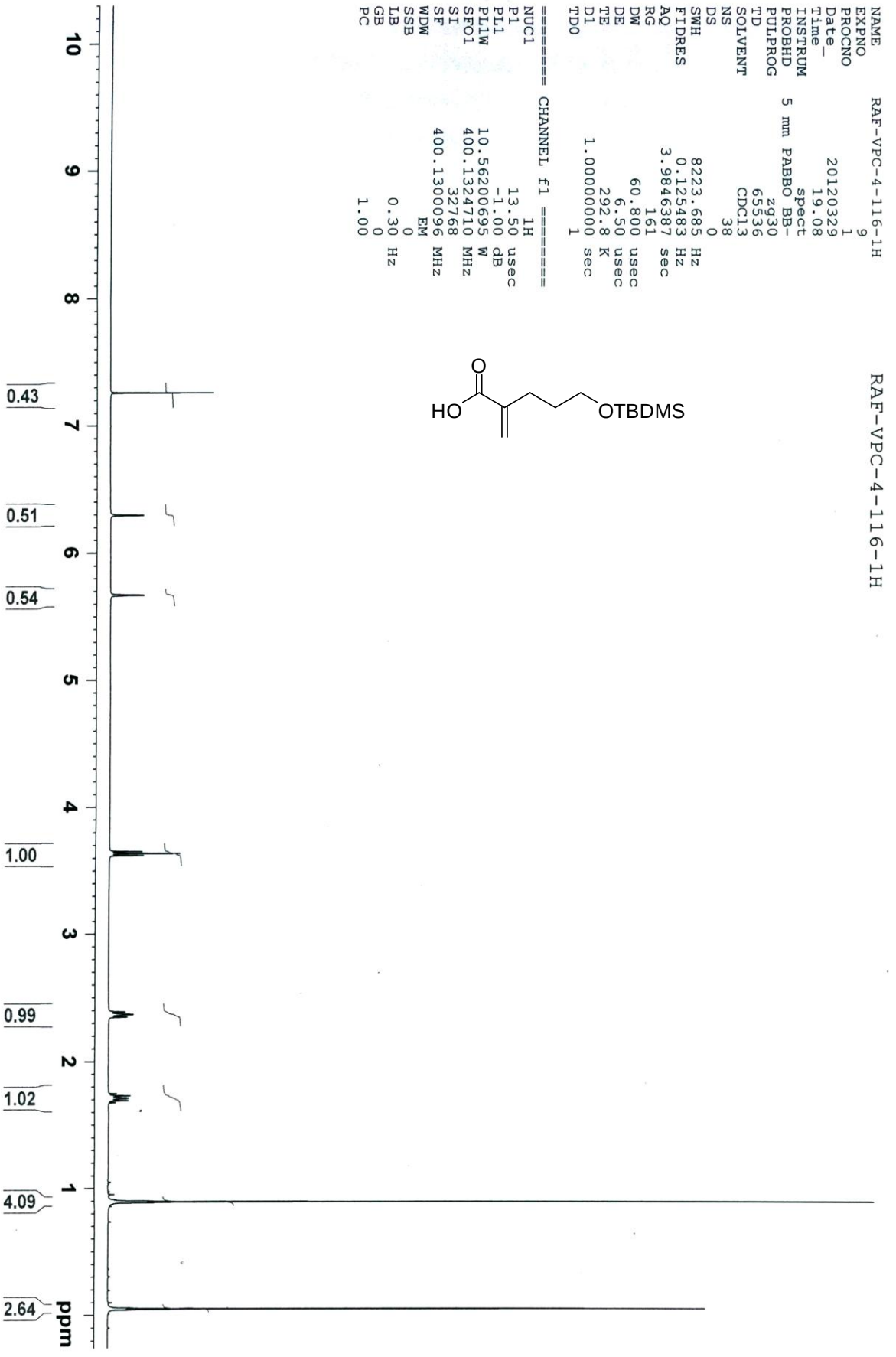

NAME RAF-VPC-4-87-1H
EXPNO 3
PROCNO 1
Date_ 20120223
Time_ 19.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 292.7 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
RAF-VPC-4-87-1H
O
H
OTBDMS
1.00
0.52
1.05
1.06
2.99
2.26
3.37
14.58
9.01
10
9
8
7
6
5
4
3
2
1
0
ppm

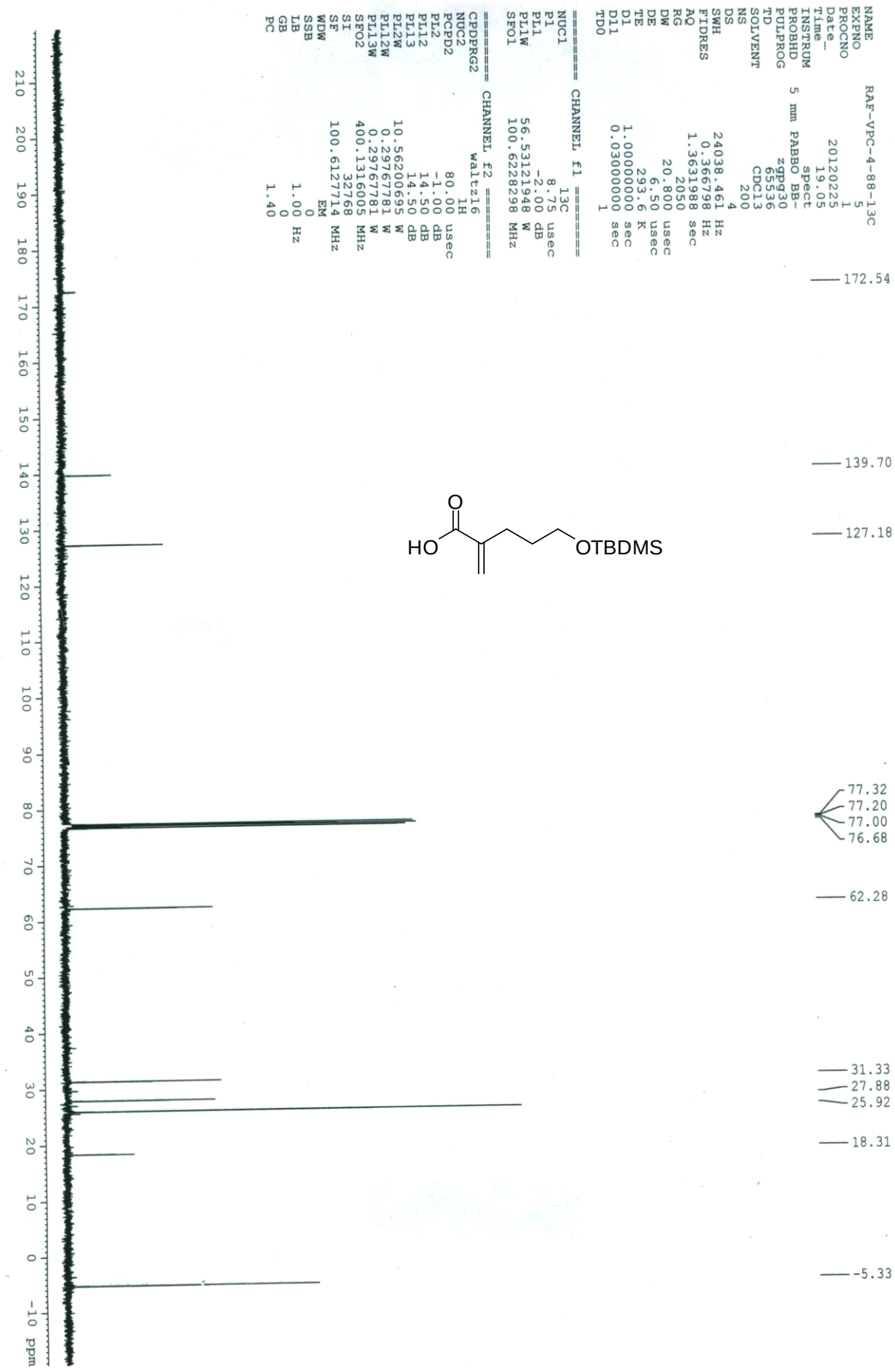


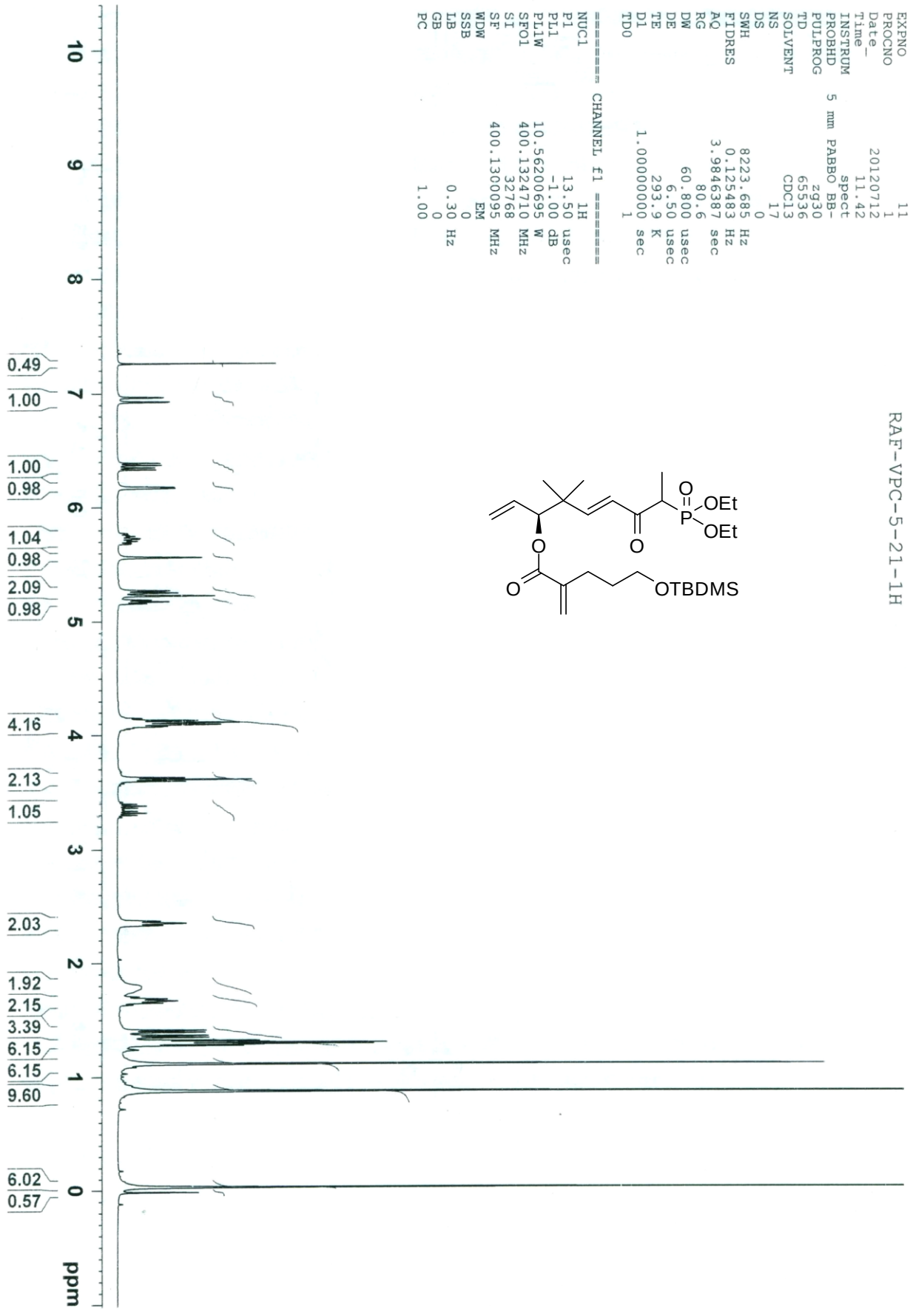

```
NAME                                RAF-VPC-4-87-13C
EXPNO                                            20
PROCNO                                            1
Date_                                      20120225
Time                                          21.04
INSTRUM                                        spect
PROBHD                     5 mm PABBO BB-
PULPROG                                    zgpg30
TD                                          65536
SOLVENT                                     CDCl3
NS                                             80
DS                                              4
SWH                                     24038.461 Hz
FIDRES                                   0.366798 Hz
AQ                                       1.3631988 sec
RG                                            2050
DW                                       20.800 usec
DE                                        6.50 usec
TE                                           293.1 K
D1                                      1.00000000 sec
D11                                     0.03000000 sec
TD0                                              1

========== CHANNEL f1 ========
NUC1                                           13C
P1                                        8.75 usec
PL1                                      -2.00 dB
PL1W                          56.53121948 W
SFO1                          100.6228298 MHz

========== CHANNEL f2 ========
CPDPRG2                                    waltz16
NUC2                                           1H
PCPD2                                     80.00 usec
PL2                                      -1.00 dB
PL12                                     14.50 dB
PL13                                     14.50 dB
PL2W                          10.56200695 W
PL12W                          0.29767781 W
PL13W                          0.29767781 W
SFO2                          400.1316005 MHz
SI                                         32768
SF                            100.6127737 MHz
WDW                                           EM
SSB                                            0
LB                                      1.00 Hz
GB                                             0
PC                                          1.40
```

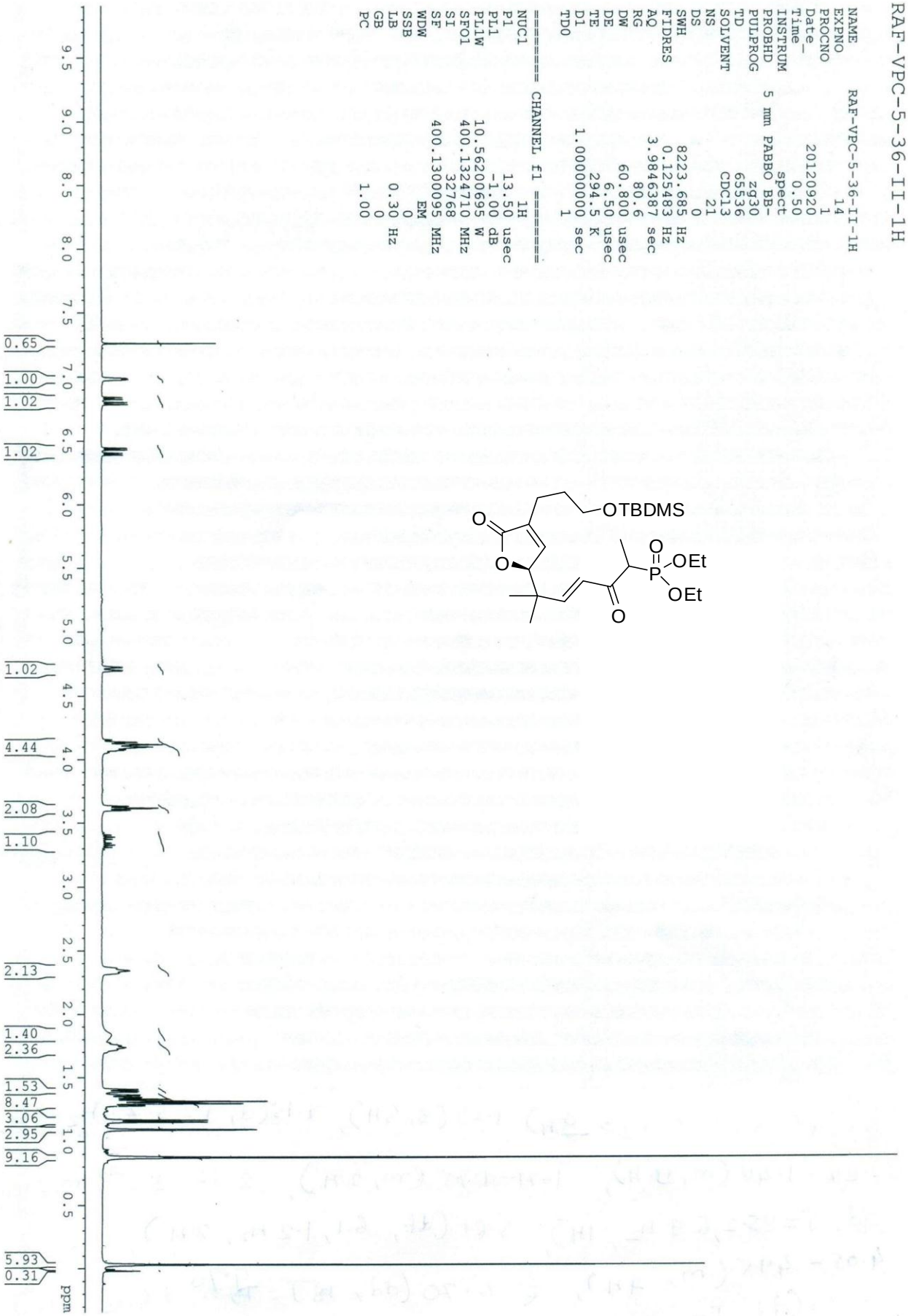

NAME RAF-VPC-4-116-1H
EXPNO 9
PROCNO 1
Date_ 20120329
Time_ 19.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 38
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
DW 60.800 usec
DE 6.50 usec
TE 292.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
O
OTBDMS
RAF-VPC-4-116-1H
10
9
8
7
6
5
4
3
2
1
ppm
0.43
0.51
0.54
1.00
0.99
1.02
4.09
2.64

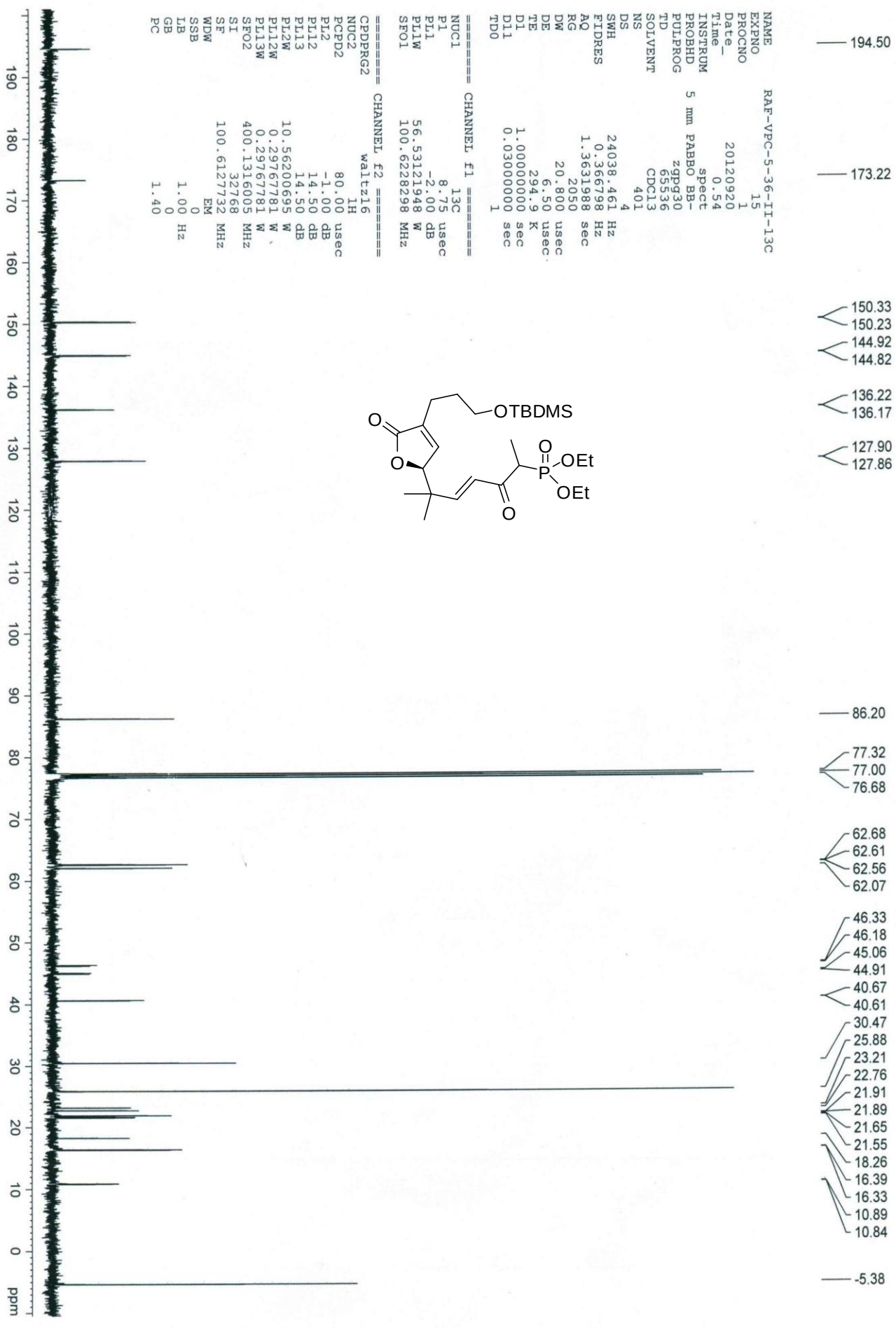

NAME RAF-VPC-4-88-13C
EXPNO 5
PROCNO 1
Date_ 20120225
Time_ 19.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HO
O
OTBDMS
172.54
139.70
127.18
77.32
77.20
77.00
76.68
62.28
31.33
27.88
25.92
18.31
-5.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

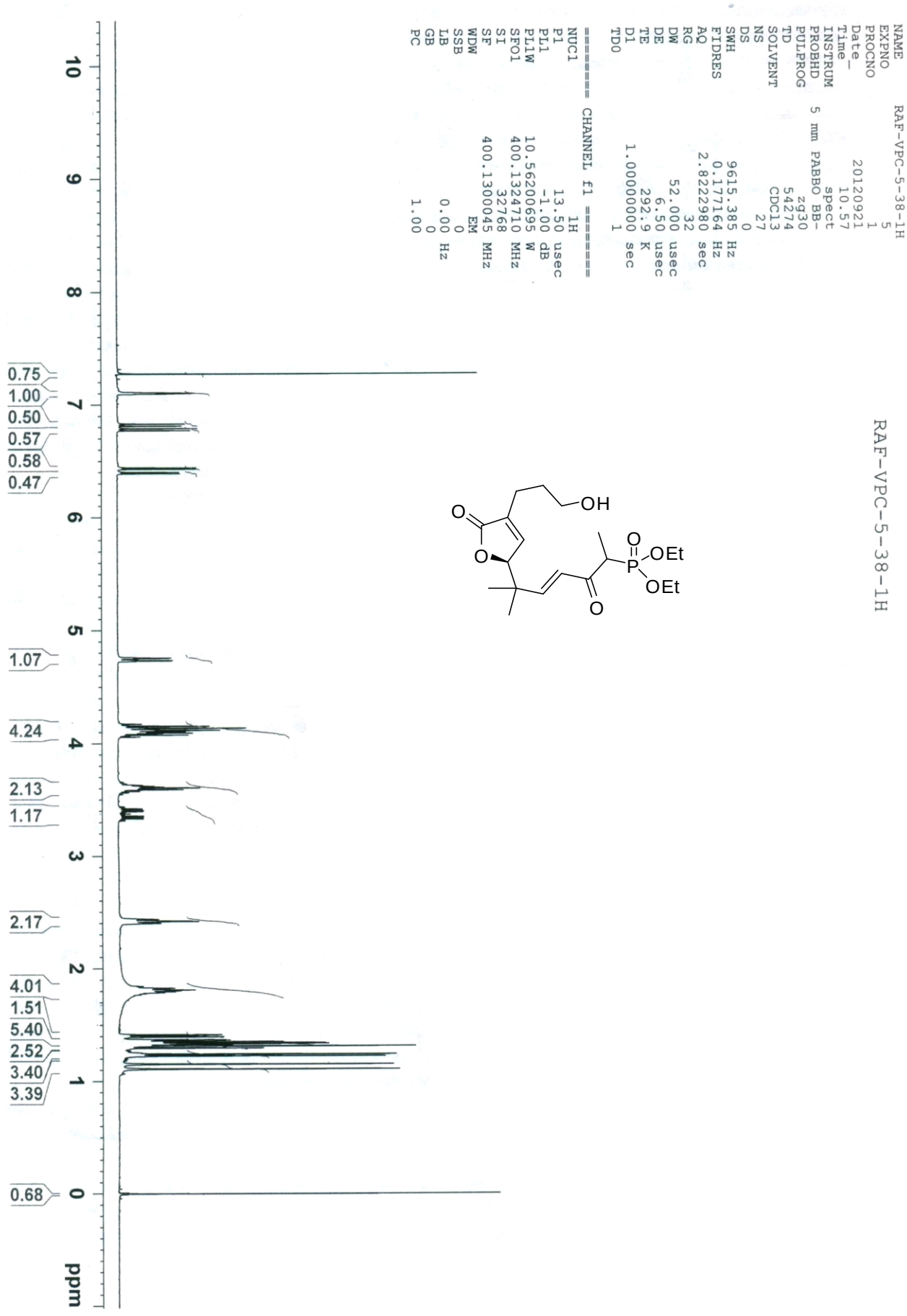

NAME RAF-VPC-5-21-1H
EXPNO 11
PROCNO 1
Date_ 20120712
Time_ 11.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 17
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
RAF-VPC-5-21-1H
O
P
OEt
OEt
O
O
O
OTBDMS
0.49
1.00
1.00
0.98
1.04
0.98
2.09
0.98
4.16
2.13
1.05
2.03
1.92
2.15
3.39
6.15
6.15
9.60
6.02
0.57
10
9
8
7
6
5
4
3
2
1
0
ppm

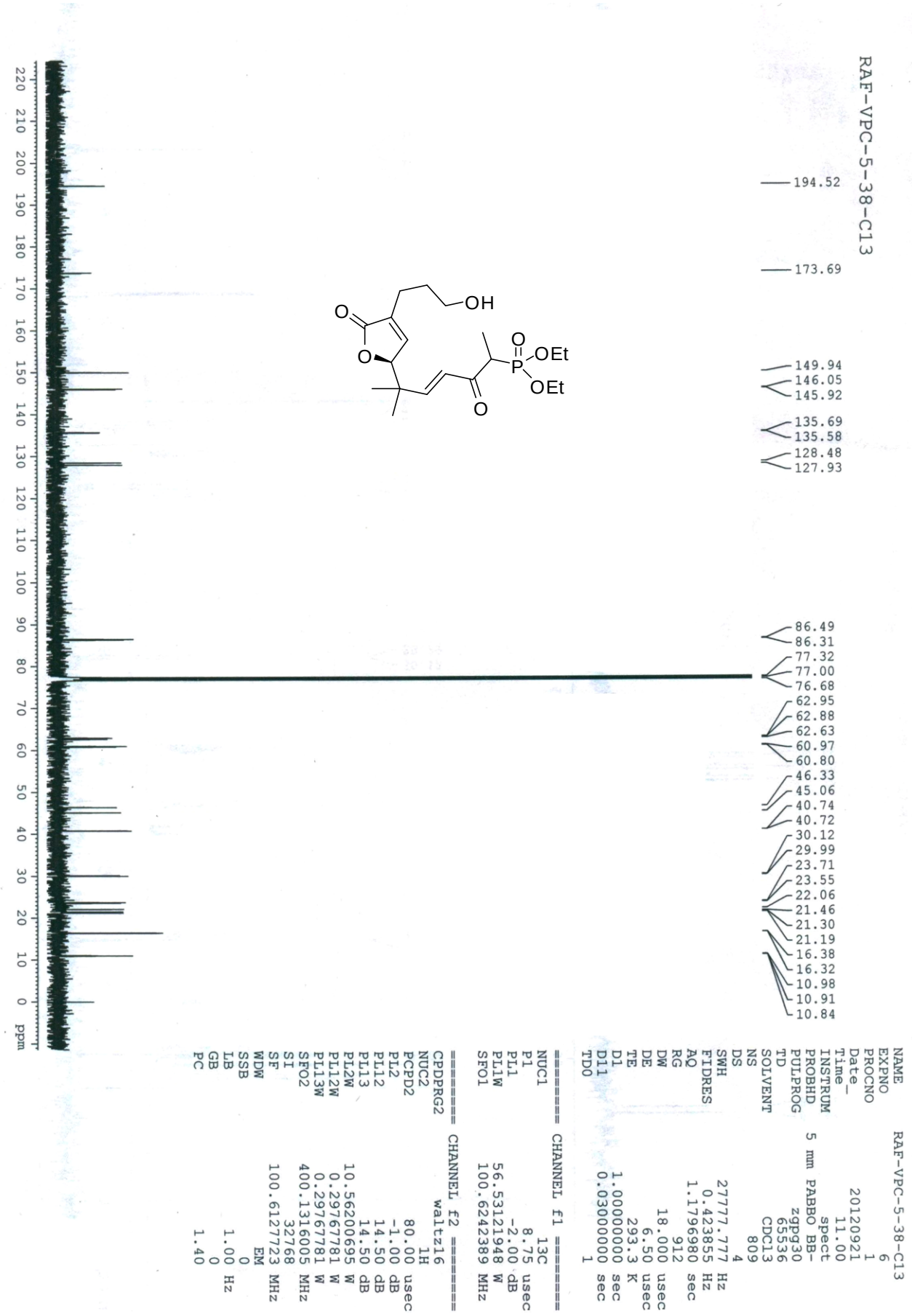

NAME RAF-VPC-5-21-13C
EXPNO 12
PROCNO 1
Date_ 20120712
Time_ 11.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 351
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
OEt
P
OEt
O
O
O
OTBDMS
194.75
166.01
152.35
152.16
140.23
132.58
132.54
127.15
127.10
125.04
119.24
80.16
77.31
76.99
76.68
62.59
62.55
62.48
62.26
46.13
45.92
44.86
44.65
40.74
40.69
31.36
28.18
25.90
23.12
23.02
23.00
22.82
18.28
16.38
16.33
11.08
11.03
10.97
-5.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

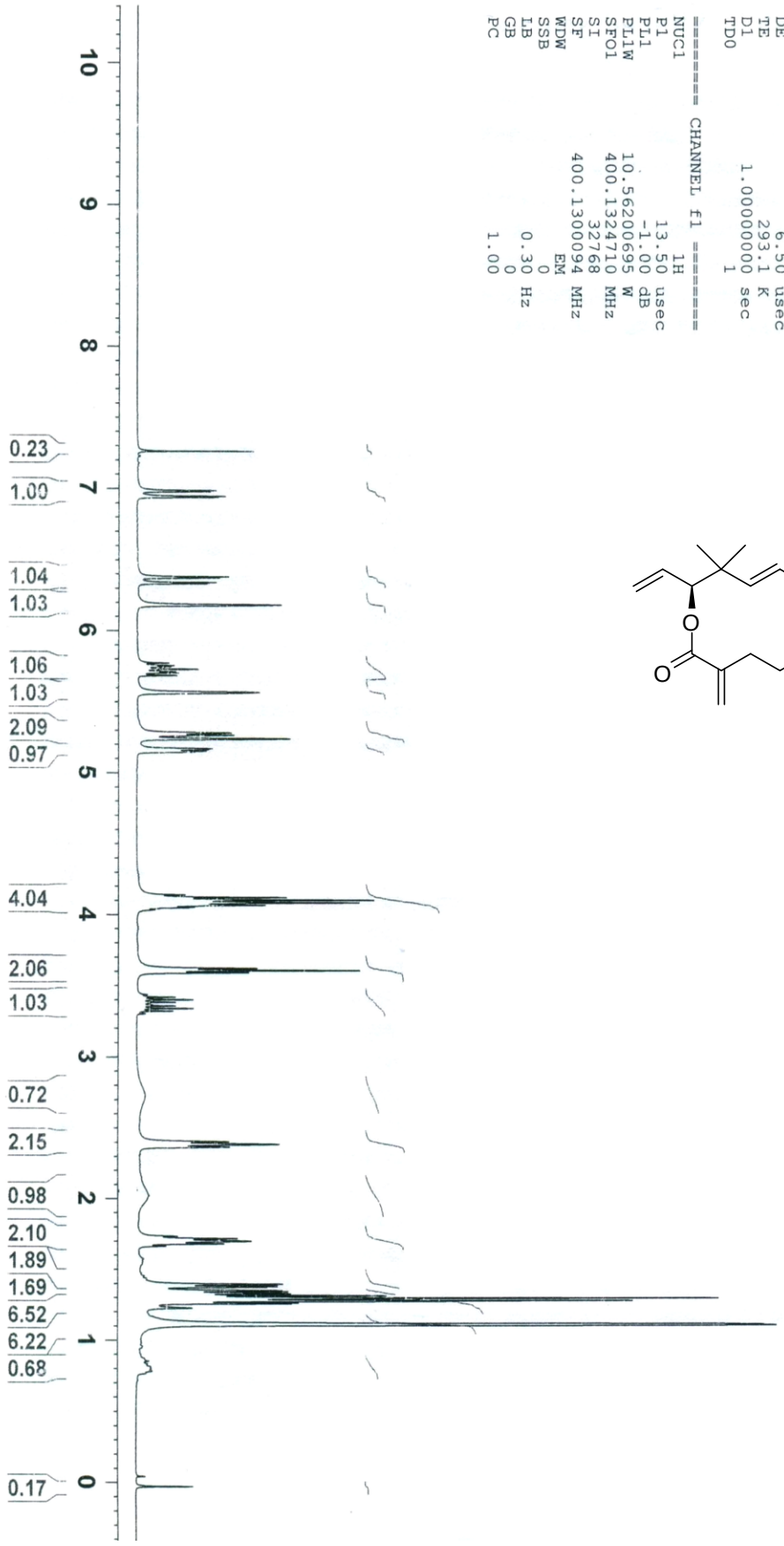
RAF-VPC-5-36-II-1H

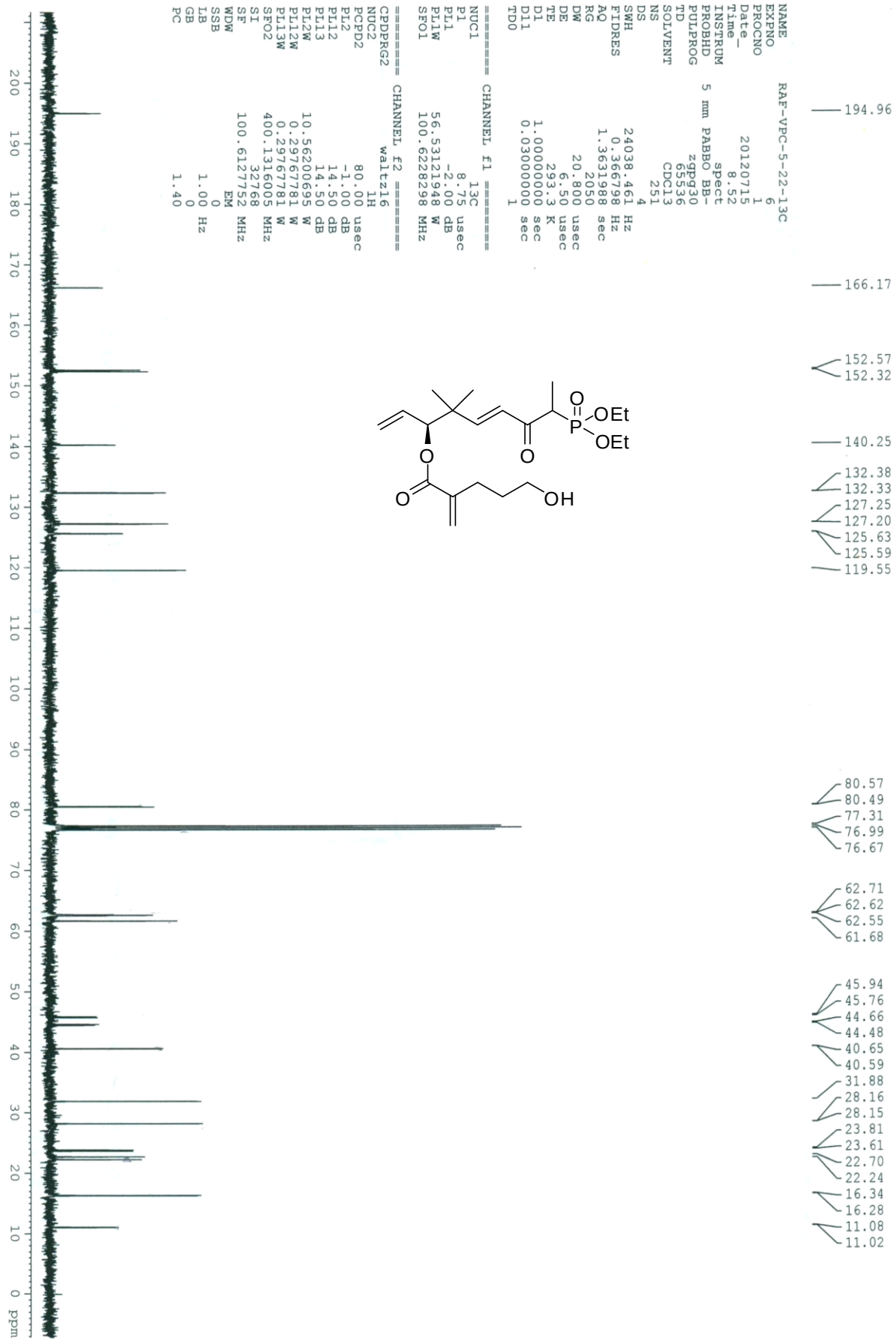


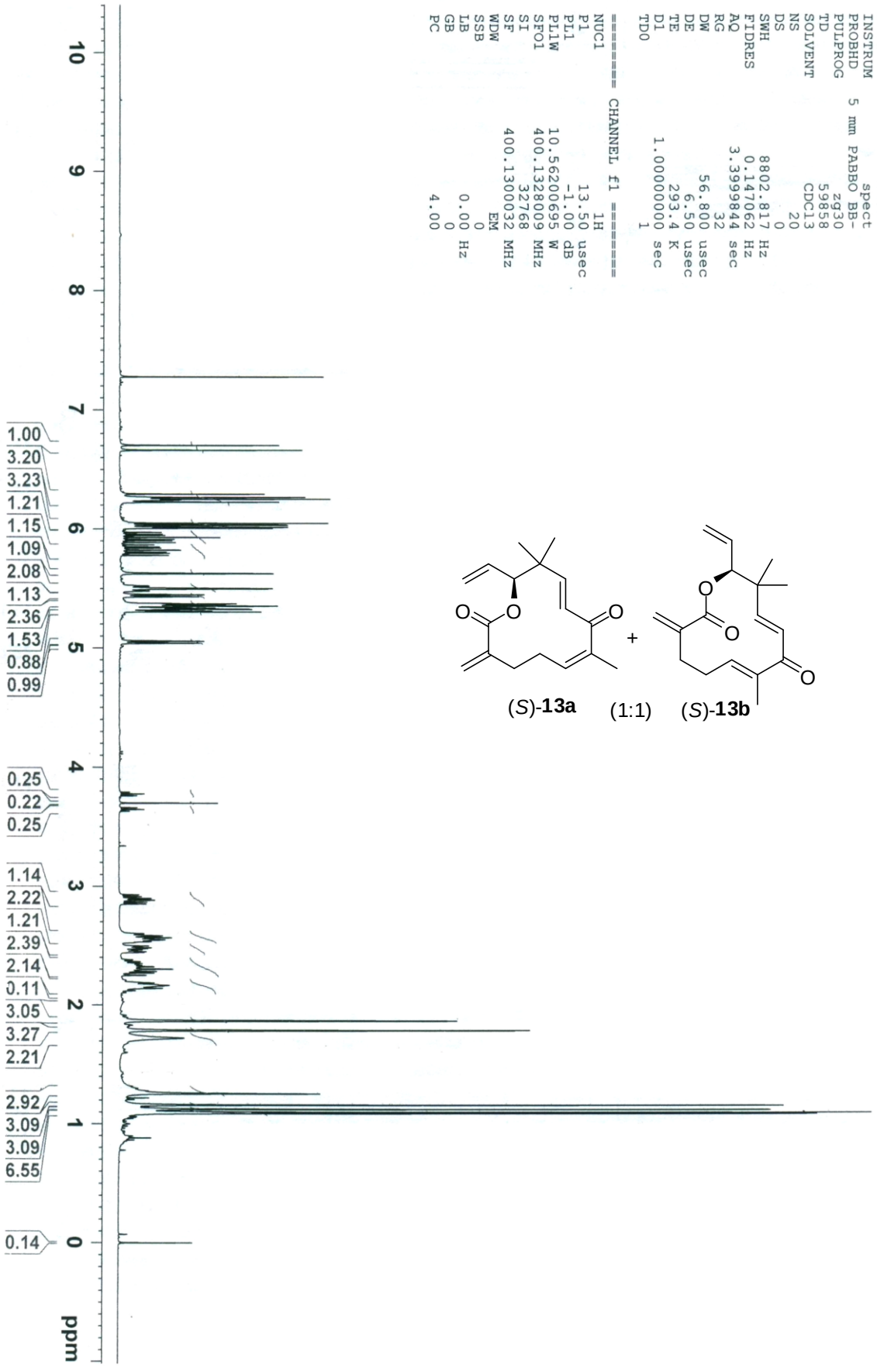



NAME RAF-VPC-5-38-1H
EXPNO 5
PROCNO 1
Date_ 20120921
Time_ 10.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDC13
NS 27
DS 0
SWH 9615.385 Hz
FIDRES 0.177164 Hz
AQ 2.8222980 sec
RG 32
DW 52.000 usec
DE 6.50 usec
TE 292.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300045 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
RAF-VPC-5-38-1H
OH
O
O
O
O
OEt
P
OEt
0.75
1.00
0.50
0.57
0.58
0.47
1.07
4.24
2.13
1.17
2.17
4.01
1.51
5.40
2.52
3.40
3.39
0.68
10
9
8
7
6
5
4
3
2
1
0
ppm

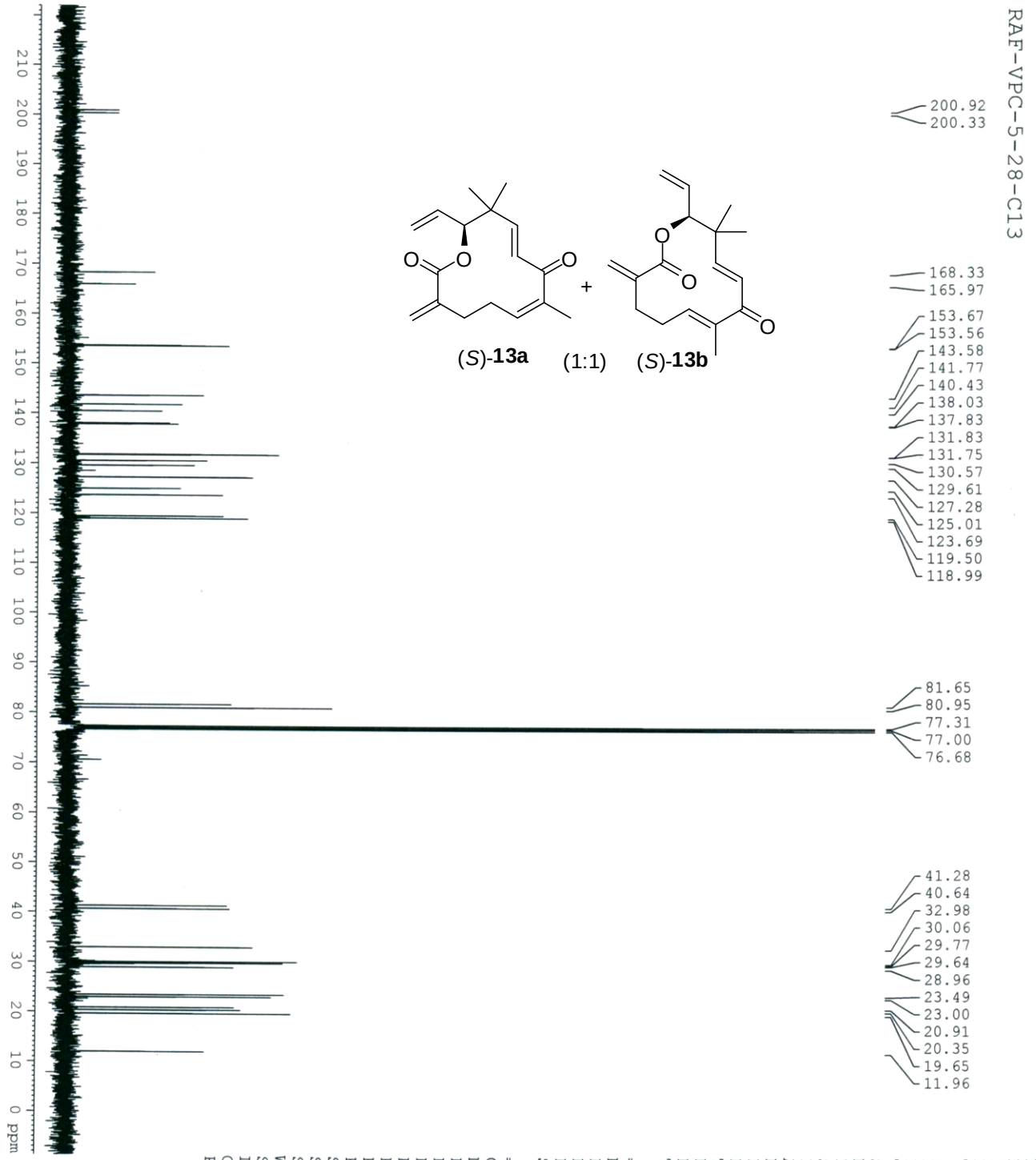

RAF-VPC-5-38-C13
194.52
173.69
149.94
146.05
145.92
135.69
135.58
128.48
127.93
86.49
86.31
77.32
77.00
76.68
62.95
62.88
62.63
60.97
60.80
46.33
45.06
40.74
40.72
30.12
29.99
23.71
23.55
22.06
21.46
21.30
21.19
16.38
16.32
10.98
10.91
10.84
OH
O
O
O
P
OEt
OEt
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
NAME RAF-VPC-5-38-C13
EXPNO 6
PROCNO 1
Date_ 20120921
Time_ 11.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 809
DS 4
SWH 27777.777 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 912
DW 18.000 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6242389 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127723 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


NAME RAF-VPC-5-22-1H
EXPNO 5
PROCNO 1
Date_ 20120715
Time_ 8.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 19
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 57
DW 60.800 usec
DE 6.50 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.23
1.00
1.04
1.03
1.06
1.03
2.09
0.97
4.04
2.06
1.03
0.72
2.15
0.98
2.10
1.89
1.69
6.52
6.22
0.68
0.17
10
9
8
7
6
5
4
3
2
1
0
O
OEt
P
OEt
O
O
O
OH


NAME RAF-VPC-5-22-13C
EXPNO 6
PROCNO 1
Date_ 20120715
Time_ 8.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 251
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127752 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
P
OEt
OEt
O
O
O
OH
194.96
166.17
152.57
152.32
140.25
132.38
132.33
127.25
127.20
125.63
125.59
119.55
80.57
80.49
77.31
76.99
76.67
62.71
62.62
62.55
61.68
45.94
45.76
44.66
44.48
40.65
40.59
31.88
28.16
28.15
23.81
23.61
22.70
22.24
16.34
16.28
11.08
11.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



(*S*)-**13a** (1:1) (*S*)-**13b**

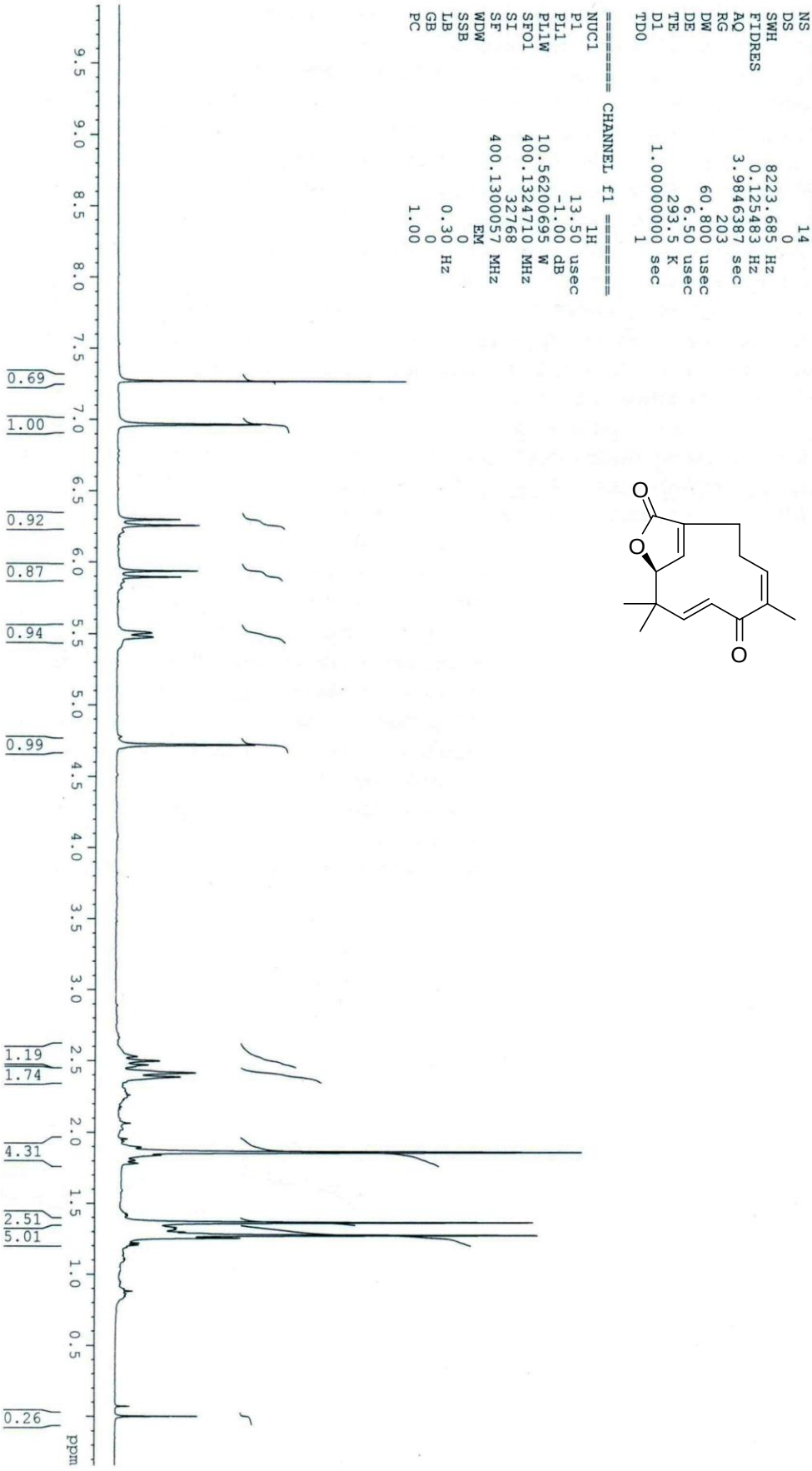


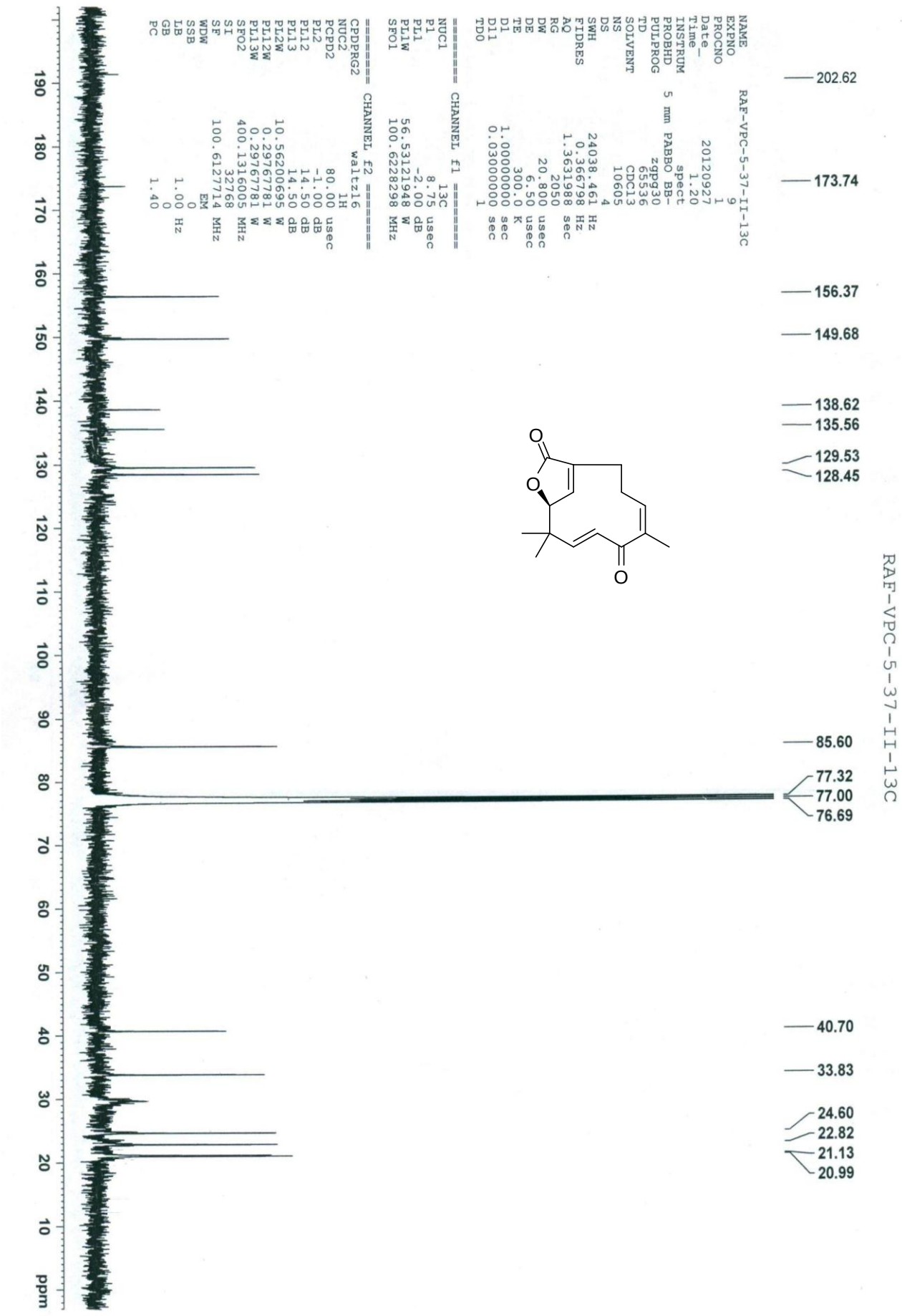

```
NAME                                    RAF-VPC-5-28-C13
EXPNO                                                13
PROCNO                                                1
Date_                                          20120214
Time_                                          11.36
INSTRUM                                          spect
PROBHD                      5 mm PABBO BB-
PULPROG                                       zgpg30
TD                                             65536
SOLVENT                                      CDCl3
NS                                               200
DS                                                 2
SWH                                        27573.529 Hz
FIDRES                                         0.420739 Hz
AQ                                         1.1884362 sec
RG                                               912
DW                                          18.133 usec
DE                                           6.50 usec
TE                                            294.1 K
D1                                         1.00000000 sec
D11                                        0.03000000 sec
TD0                                                1

========== CHANNEL f1 ==========
NUC1                                            13C
P1                                           8.75 usec
PL1                                           -2.00 dB
PL1W                                    56.53121948 W
SFO1                                    100.6248425 MHz

========== CHANNEL f2 ==========
CPDPRG2                                      waltz16
NUC2                                            1H
PCPD2                                        80.00 usec
PL2                                           -1.00 dB
PL12                                          14.50 dB
PL13                                          14.50 dB
PL2W                                    10.56200695 W
PL12W                                    0.29767781 W
PL13W                                    0.29767781 W
SFO2                                    400.1316005 MHz
SI                                              32768
SF                                      100.6127741 MHz
WDW                                             EM
SSB                                              0
LB                                            1.00 Hz
GB                                               0
PC                                            1.40
```

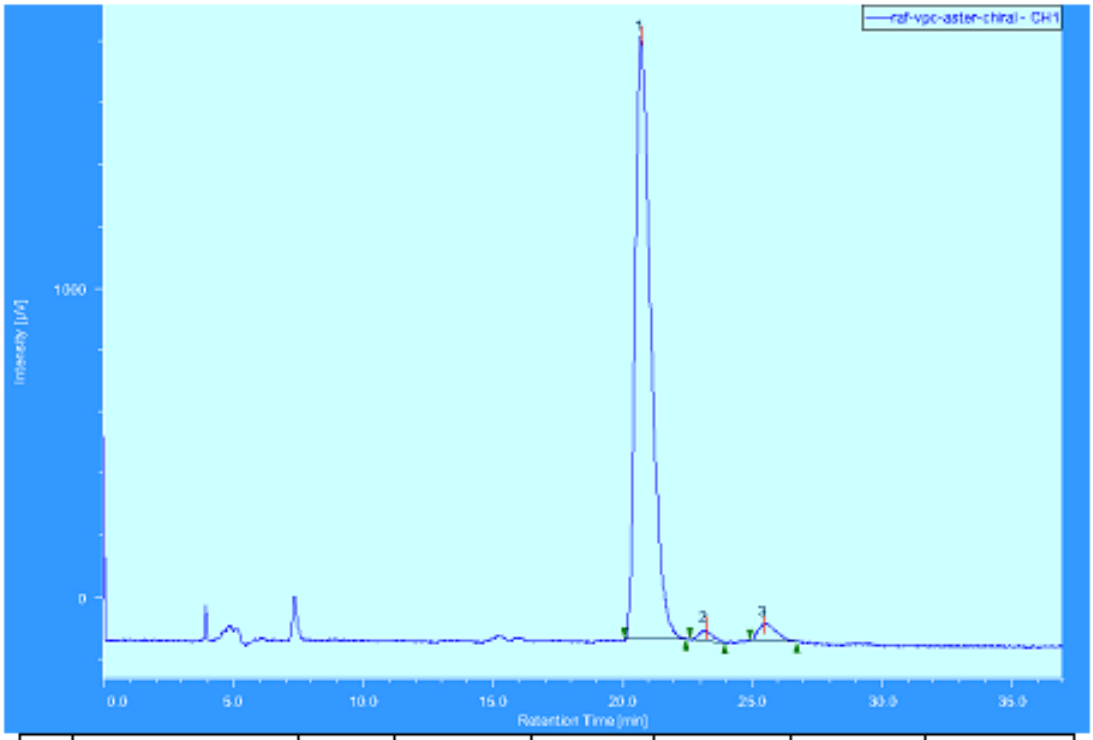
RAF-VPC-5-37-1H




NAME RAF-VPC-5-37-II-13C
EXPNO 9
PROCNO 1
Date_ 20120927
Time_ 1.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10605
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
202.62
173.74
156.37
149.68
138.62
135.56
129.53
128.45
85.60
77.32
77.00
76.69
40.70
33.83
24.60
22.82
21.13
20.99
RAF-VPC-5-37-II-13C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

HPLC Chromatogram of (-)-asteriscunolide C **3**

CHIRALCEL OD-H column,
Sample Name: raf-vpc-aster-chiral 20/02/2013
Solvent Composition: *n*-Hexane:IPA (88:12)
Flow rate: 0.8ml/min
t_R = 20.692 min, chemical purity ~96%



#	Peak Name	CH	tR	Area	Height	Area%	Height%
1	Unknown	1	20.692	82874	1951	95.751	95.590
2	Unknown	1	23.158	1064	34	1.229	1.666
3	Unknown	1	25.442	2614	56	3.020	2.744