Total Synthesis of Methymycin

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Supplementary Information

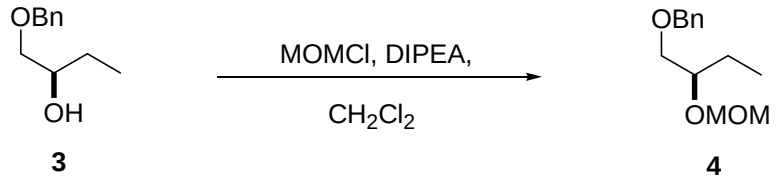
Table of contents

General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 and Brucker Avance 500 NMR Spectrometer. The chemical shifts are reported in ppm on scale downfield from TMS, and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad peak. IR specta were recorded on JASCO FT/IR-300E. Optical rotations were measured by JASCO DIP-1000 digital polarometer in solution in a 1-dm cell. High resolution mass spectra were recorded on a Jeol JMS700 by using FAB method. All reagent and solvents were reagent grade and used without further purification unless specified otherwise. Technical grade ethyl acetate, hexane, and pentane used for column chromatography were distilled prior to use. Tetrahydrofuran (THF) and diethyl ether, when used as solvents for reactions, were freshly distilled from sodium-benzophenone ketyl. Dimethylformamide (DMF) was stored over 4-Å molecular sieves, and diethylamide was distilled before use. Flash chromatography was carried out on Woelm 32-64 μm silica packed in glass columns.

Experimental Section

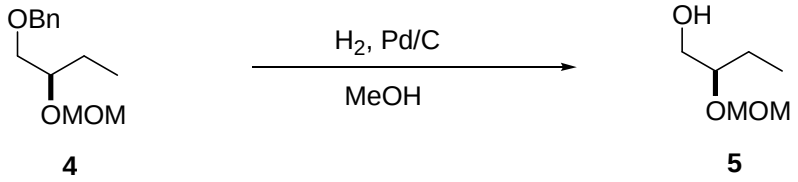
(2*R*)-1-Benzyloxy-2-(methoxymethoxy)butane (**4**)



3 **4**

To a solution of (2*R*)-1-benzyloxybutan-2-ol (**3**) (1.70 g, 9.43 mmol) obtained as described in the previous procedure in CH_2Cl_2 (20 mL) was added *N*,*N*-diisopropylethylamine (10.1 mL, 56.6 mmol) at 0 °C. The resulting solution was stirred for 30 min at 0 °C, and to this solution was added the chloromethylmethyl ether (2.14 mL, 28.3 mmol). After stirred for 10 min at 0 °C and the solution was warmed to room temperature, stirred for 16 h. After the reaction was completed, saturated aqueous NH_4Cl solution (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 30 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (hexane:EtOAc=7:1) afforded (2*R*)-1-Benzyloxy-2-(methoxymethoxy)butane (**4**) (1.69 g, 80%) as a colorless oil: $[\alpha]_D^{25.5}$ 19.6 (*c* 1.62, $CHCl_3$); IR (film): 2932.2, 1723.1, 1455.0, 1365.4, 1273.8, 1210.1, 1103.1, 1040.4, 918.9, 846.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.99 (t, *J* = 7.5 Hz, 3H), 1.72~1.55 (m, 2H), 3.42 (s, 3H), 3.55 (d, *J* = 5.0 Hz, 2H), 3.76 (m, 1H), 4.58 (s, 2H), 4.72 (d, *J* = 6.8 Hz, 1H), 4.81(d, *J* = 6.8 Hz, 1H), 7.38~7.27 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 128.2, 127.5, 127.4, 95.9, 77.4, 73.2, 72.3, 55.3, 24.8, 9.7; HRMS: *m/z* calcd for $C_{13}H_{21}O_3(M+H)^+$, 225.1491, found: 225.1486.

(2*R*)-2-(Methoxymethoxy)butan-1-ol (**5**)

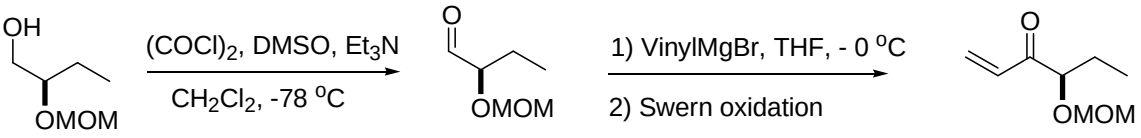


4 **5**

A solution of (2*R*)-1-benzyloxy-2-(methoxymethoxy)butane (**4**) (1.69 g, 7.53 mmol) in MeOH (30 mL) was stirred under hydrogen (1 atm, balloon) at room temperature in the presence of 5% palladium on charcoal (3.4 g). The resulting mixture was stirred at room temperature for 18 h. After filtration through a pad of Celite with ether (3 × 30 mL), the solution was concentrated.

Purification by flash chromatography (pentane:ether = 1:1) afforded the alcohol **5** (1.01 g, 92%) as a colorless oil: $[\alpha]_D^{26.6}$ 66.1 (*c* 1.36, $CHCl_3$); IR (film): 3419.2, 2936.1, 1648.8, 1463.7, 1214.0, 1038.5, 918.0, 836.0, 419.4cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$,): δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.52~1.40 (m, 2H), 3.16 (s, 1H), 3.33 (s, 1H), 3.45 (m, 2H), 3.53 (m, 1H), 4.67 (dd, *J* = 17.0, 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 96.5, 82.5, 64.8, 55.3, 24.3, 9.7; HRMS: m/z calcd for $C_6H_{15}O_3(M+H)^+$, 135.1021, found:135.1025

(4*R*)-4-(Methoxymethoxy)hex-1-en-3-one (**7**)



5 **6** **7**

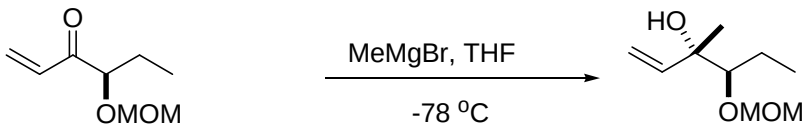
A flame-dried round-bottomed flask was charged with a solution of oxalyl chloride (4.20 mL, 48.1 mmol) in CH_2Cl_2 (30 mL) at -78 °C. The mixture was added dimethyl sulfoxide (3.94 mL, 55.5 mmol) at -78 °C. This mixture was stirred for 30 min before alcohol **5** (1.66 g 12.3 mmol) in CH_2Cl_2 (6 mL) was added. After 10 min, the reaction mixture was added triethylamine (25.8 mL, 185 mmol) and stirred for 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with ether (40 mL) and saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 40 mL), and washed with saturated aqueous NaCl (50 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated to provide the desired (2*R*)-2-(methoxymethoxy)butanal (**6**) (1.63 g, 100%) which was used for the next step without further purification.

To a stirred solution of the aldehyde **6** (1.63 g, 12.3 mmol) prepared as described in the previous procedure and THF (30 mL) was added vinylmagnesium bromide (1.00 M, 24.7 mL, 24.7 mmol) at 0 °C. After stirred for 1 h, the reaction mixture was diluted with ether (10 mL) and saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 30 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired vinyl alcohol (791 mg, 40%, 2 steps) as a colorless oil.

A flame-dried round-bottomed flask was charged with a solution of oxalyl chloride (1.03 mL, 11.9 mmol) in CH_2Cl_2 (20 mL) at -78 °C. The mixture was added dimethyl sulfoxide (0.95 mL,

13.3 mmol) at -78 °C. This mixture was stirred for 30 min before the vinyl alcohol (791 mg, 4.95 mmol), which was prepared as described in the previous procedure, in CH_2Cl_2 (3 mL) was added. After 10 min, the reaction mixture was added *N*,*N*-disopropyl ethylamine (4.41 mL, 24.7 mmol) and stirred for 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with ether (40 mL) and saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 30 mL), and washed with saturated aqueous NaCl (50 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired vinyl ketone **7** (578 mg, 74%) as a colorless oil: $[\alpha]_D^{24.4}$ 66.1 (*c* 1.36, $CHCl_3$); IR (film): 2938.0, 1700.9, 1614.1, 1462.7, 1403.0, 1159.0, 1103.1, 919.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.76 (m, 2H), 3.34 (s, 3H), 3.33 (s, 1H), 4.13 (*J* = 6.5 Hz, 1H), 4.66~4.59 (dd, *J* = 14.0, 6.9 Hz, 2H), 6.40~5.7 (ddd, *J* = 17.4, 10.5, 1.6 Hz, 2H), 6.71~6.62 (dd, *J* = 17.4, 10.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.0, 131.9, 129.3, 96.2, 82.4, 56.0, 25.4, 9.5.

(3*S*, 4*R*)-4-(Methoxymethoxy)-3-methylhex-1-en-3-ol (**8**)



7 **8**

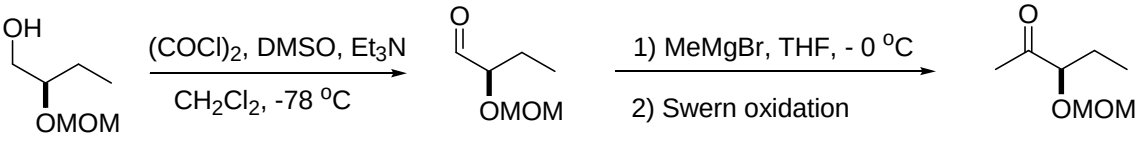
To a stirred solution of vinyl ketone **7** (578 mg, 3.65 mmol) in THF (15 mL) was added methylmagnesium bromide (3 M, 1.83 mL, 5.49 mmol) at -78 °C. After stirred for 1 h, the reaction mixture was diluted with Et_2O (10 mL) and saturated aqueous NH_4Cl solution (10 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired alcohol **8** (625 mg, 98%) as a colorless oil: $[\alpha]_D^{24.9}$ -23.4 (*c* 1.50, $CHCl_3$); IR (film): 3449.1, 2967.9, 1716.3, 1641.1, 1462.7, 1367.3, 1103.1, 1034.6, 920.8 (film): cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.20 (s, 3H), 1.66~1.34 (m, 2H), 3.23~3.19 (dd, *J* = 9.9, 2.7 Hz, 1H), 3.40 (s, 3H), 3.72 (s, 1H), 4.64 (d, *J* = 6.8 Hz, 1H), 4.76 (d, *J* = 6.8 Hz, 1H), 5.32~5.11 (ddd, *J* = 17.3, 10.7, 1.6 Hz, 2H), 6.00~5.90 (dd, *J* = 17.3, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.1, 113.5, 99.0, 91.9, 74.5, 56.0, 24.5, 24.2, 11.0; HRMS: m/z calcd for $C_9H_{17}O_2(M+H-H_2O)^+$, 157.1229, found:157.1235.

(3*S*, 4*R*)-3-Methylhex-1-en-3,4-diol (**9**)

8 **9**

To a stirred solution of alcohol **8** (625 mg, 3.59 mmol) in dry THF (3 mL) at room temperature was added 6 N HCl (3 mL). After stirred for 2 h, the reaction mixture was diluted with ether (10 mL) and aqueous saturated $NaHCO_3$ (10 mL). The layers were then separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), and dried ($MgSO_4$). After being concentrated, purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired diol **9** (322 mg, 69%) as a colorless oil: $[\alpha]_D^{24.3}$ 18.5 (*c* 1.28, $CHCl_3$); IR (film): 3427.9, 2974.7, 2878.2, 1644.0, 1456.0, 1414.5, 1099.2, 976.8, 922.8, 883.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.21 (s, 3H), 1.57~1.11 (m, 2H), 2.93 (s, 2H), 3.26 (dd, *J* = 10.5, 2.2 Hz, 1H), 5.26~5.08 (ddd, *J* = 10.8, 10.0, 1.3 Hz, 2H), 5.91~5.81 (dd, *J* = 17.4, 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.7, 114.3, 79.7, 75.5, 24.5, 24.1, 11.1, 10.8; HRMS: m/z calcd for $C_7H_{13}O(M+H-H_2O)^+$, 113.0966, found:113.0965.

(3*R*)-3-(Methoxymethyloxy)-pentan-2-one (**10**)



5 **6** **10**

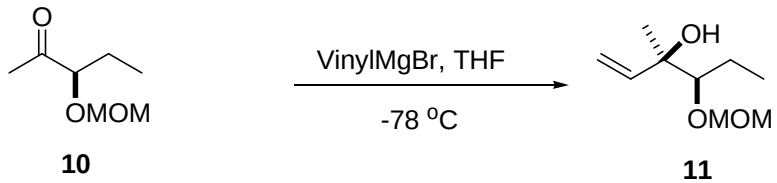
A flame-dried round-bottomed flask was charged with a solution of oxalyl chloride (2.54 mL, 29.1 mmol) in CH_2Cl_2 (20 mL) at -78 °C. To the mixture was added dimethyl sulfoxide (2.38 mL, 33.5 mmol) at -78 °C. This mixture was stirred for 30 min before alcohol **5** (1.00 g 7.45 mmol) in CH_2Cl_2 (5 mL) was added. After stirred for 10 min, triethylamine (15.6 mL, 111.8 mmol) was added to the reaction mixture and the resulting mixture was stirred for 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with ether (30 mL) and saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 30 mL), and washed with saturated aqueous NaCl (40 mL). The organic solutions were combined, dried ($MgSO_4$), and

concentrated to provide the desired aldehyde **6** which was used for the next step without further purification.

To a stirred solution of the aldehyde **6,** which was prepared as described in the previous procedure, in THF (20 mL) was added methylmagnesium bromide (3 M, 7.45 mL, 22.4 mmol) at 0 °C. The reaction mixture was stirred for 1 h before it was diluted with ether (10 mL). To this, then, was added a saturated aqueous NH_4Cl solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 30 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired alcohol (376 mg, 34%, 2 steps) as a colorless oil.

A flame-dried round-bottomed flask was charged with a solution of oxalyl chloride (0.861 mL, 9.87 mmol) in CH_2Cl_2 (10 mL) at -78 °C. To the mixture was added dimethyl sulfoxide (0.808 mL, 11.4 mmol) at -78 °C. This mixture was stirred for 30 min before the alcohol (376 mg, 2.53 mmol), which was prepared in the previous step, in CH_2Cl_2 (3 mL) was added. After 10 min, the reaction mixture was added triethylamine (5.29 mL, 38.0 mmol) and stirred for 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with ether (10 mL) and saturated aqueous NH_4Cl solution (10 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL), and washed with saturated aqueous NaCl (30 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired methyl ketone **10** (296 mg, 80%) as a colorless oil: $[\alpha]_D^{24.4}$ 45.2 (*c* 1.13, $CHCl_3$); IR (film): 2938.0, 1716.3, 1463.7, 1354.8, 1215.9, 1155.2, 1122.4, 1035.6, 918.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.75~1.65 (m, 2H), 2.15 (s, 3H), 3.37 (s, 3H), 3.93 (t, *J* = 6.2 Hz, 1H), 4.67 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.9, 96.3, 83.8, 55.9, 26.0, 25.0, 9.5.

(3*R*, 4*R*)-4-(Methoxymethoxy)-3-methylhex-1-en-3-ol (**11**)

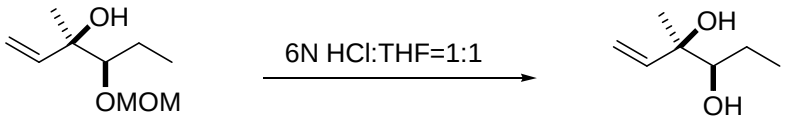


10 **11**

To a stirred solution of methyl ketone **10** (296 mg, 2.02 mmol), prepared as described in the

previous procedure, in THF (10 ml) was added vinylmagnesium bromide (1.00 M, 3.03 mL, 3.03 mmol) at -78 °C. After stirred for 1 h, the reaction mixture was diluted with Et_2O (10 mL) and saturated aqueous NH_4Cl solution (10 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired alcohol **11** (218 mg, 62%) as a colorless oil: $[\alpha]_D^{26.2}$ -19.3 (*c* 1.18, $CHCl_3$); IR (film): 3449.1, 2967.9, 1641.1, 1462.7, 1367.3, 1103.1, 1034.6, 920.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.18 (s, 3H), 1.63~1.27 (m, 2H), 3.17~3.13 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.40 (s, 3H), 3.45 (s, 1H), 4.62 (d, *J* = 6.7 Hz, 1H), 4.75 (d, *J* = 6.7 Hz, 1H) 5.34~5.06 (ddd, *J* = 17.3, 10.7, 1.5 Hz, 2H), 5.87~5.78 (dd, *J* = 17.3, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 113.8, 98.8, 90.1, 74.5, 55.9, 24.0, 21.8, 11.0; HRMS: m/z calcd for $C_9H_{17}O_2(M+H-H_2O)^+$, 157.1229, found:157.1231.

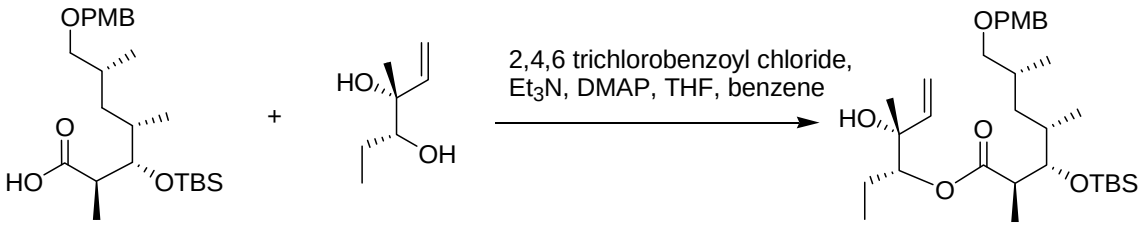
(3*R*, 4*R*)-3-Methylhex-1-ene-3,4-diol (**12**)



11 **12**

To a stirred solution of alcohol **11** (218 mg, 1.25 mmol) in dry THF (2 mL) at room temperature was added 6 N HCl (2 mL). After 2 h, the reaction mixture was diluted with ether (10 mL), then to this mixture was added aqueous saturated $NaHCO_3$ (5 mL). The layers were then separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), and dried ($MgSO_4$). After being concentrated, purification of the residue by flash chromatography (pentane:ether = 1:1) afforded the desired diol **12** (86 mg, 53%) as a colorless oil: $[\alpha]_D^{24.7}$ 15.7 (*c* 0.61, $CHCl_3$); IR (film): 3406.6, 2975.6, 2878.2, 1643.1, 1458.9, 1414.5, 1094.4, 975.8, 923.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.23 (s, 3H), 1.63~1.28 (m, 2H), 2.22 (s, 2H), 3.34 (d, *J* = 10.0 Hz, 1H), 5.36~5.15 (ddd, *J* = 17.4, 10.8, 1.2 Hz, 2H), 5.96~5.86 (dd, *J* = 17.4, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.7, 114.2, 78.7, 75.5, 23.7, 21.4, 11.1; HRMS: m/z calcd for $C_7H_{13}O(M+H-H_2O)^+$, 113.0966, found:113.0968.

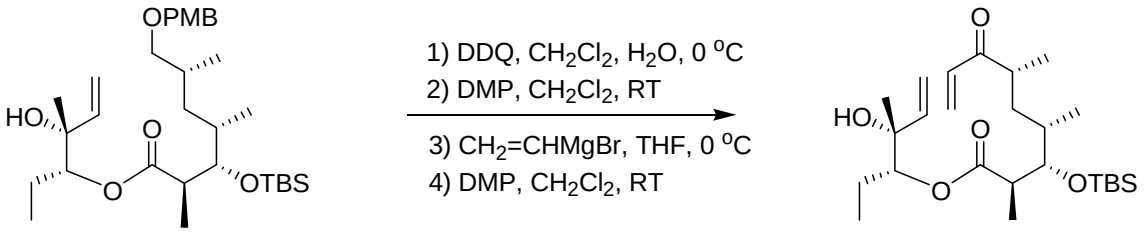
(1*R*,2*R*)-1-Ethyl-2-hydroxy-2-methylbut-3-enyl-(2*R*,3*S*,4*S*,6*R*)-3-(*tert*butyldimethylsilanyloxy)-7-(4-methoxybenzyloxy)-2,4,6-trimethylheptanoate (**14b)**



13 **12** **14b**

To a solution of carboxylic acid **13** (56 mg, 0.13 mmol) in THF (2 mL) at room temperature were added triethylamine (27 µL, 0.19 mmol) and 2,4,6-trichlorobenzoyl chloride (25 µL, 0.16 mmol). The mixture was stirred for 3 h at room temperature, and the solids were filtered off and washed with hexane (5 mL). The combined solution was concentrated under reduced pressure. The residue was dissolved in benzene (2 mL), and to this solution a solution of alcohol **12** (20 mg, 0.15 mmol) and DMAP (22 mg, 0.18 mmol) in benzene (2 mL) was added. After being stirred for 16 h, the reaction mixture was diluted with ether (10 ml), and washed with saturated $NaHCO_3$ (5 mL) and saturated NaCl (5 mL), dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (hexane/EtOAc = 4:1) afforded the desired ester **14b** (57 mg, 81%) as a colorless oil: $[\alpha]_D^{22.3}$ 16.8 (*c* 1.17, $CHCl_3$); IR (film): 3449.1, 2956.3, 1731.8, 1613.2, 1513.9, 1461.8, 1248.7, 1172.5, 1058.7, 836.0, 774.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.05 (s, 6H), 0.89 (m, 21H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.21 (m, 3H), 1.40 (m, 2H), 1.70 (m, 2H), 1.81 (dddd, *J* = 13.1, 6.6, 6.6, 6.6 Hz, 1H), 2.29 (s, 1H), 2.62 (dddd, *J* = 13.8, 6.9, 6.9, 6.9 Hz, 1H), 3.21 (ddd, *J* = 32.0, 9.0, 5.6 Hz, 2H), 3.80 (s, 3H), 3.89 (dd, *J* = 5.6, 3.1 Hz, 1H), 4.42 (d, *J* = 12.5 Hz, 2H), 4.78 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.10 (d, *J* = 10.7 Hz, 1H), 5.32 (d, J = 17.3 Hz, 1H), 5.89 (dd, *J* = 17.2, 10.7 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1, 159.0, 142.8, 130.7, 129.1, 113.6, 113.5, 79.8, 75.4, 75.3, 75.0, 72.6, 55.2, 42.1, 36.9, 36.3, 31.0, 26.0, 23.3, 22.3, 18.5, 16.6, 14.6, 10.6, -4,1, -4,2; HRMS: m/z calcd for $C_{31}H_{55}O_6Si(M+H)^+$, 551.3768, found: 551.3766.

(1*R*,2*R*)-1-Ethyl-2-hydroxy-2-methyl-but-3-enyl (2*R*,3*S*,4*S*,6*R*)-3-(*tert*butyldimethylsilanyloxy)-2,4,6-trimethyl-7-oxonon-8-enoate (**15b**)



14b **15b**

To a stirred solution of ester **14b** (54 mg, 0.098 mmol) in H_2O (0.3 mL) and CH_2Cl_2 (3 mL) was added the DDQ (45 mg, 0.196 mmol) at 0 °C. After 2.5 h, the reaction mixture was diluted with CH_2Cl_2 (5 mL), then to this mixture was added aqueous saturated $NaHCO_3$ (5 mL). The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (5 mL), water (5 mL), and dried ($MgSO_4$). After being concentrated, purification of the residue by flash chromatography (hexane:EtOAc = 3:1) afforded the desired primary alcohol (39 mg, 93%) as a colorless oil: $[\alpha]_D^{26.6}$ 21.4 (*c* 1.09, $CHCl_3$); IR (film): 3374.8, 2929.3, 1731.8, 1461.8, 1375.0, 1253.5, 1176.4, 1057.8, 836.0, 774.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.08 (s, 6H), 0.90 (m, 21H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.24 (s, 3H), 1.61 (m, 6H), 2.22 (dddd, *J* = 14.3, 7.1, 7.1, 7.1 Hz, 1H), 3.42 (ddd, *J* = 45.6, 10.8, 10.8 Hz, 2H), 3.86 (dd, *J* = 7.3, 2.2 Hz, 1H), 4.79 (dd, *J* = 10.2, 2.5 Hz, 1H), 5.13 (d, *J* = 10.7 Hz, 1H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.91 (dd, *J* = 17.3, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.8, 142.4, 113.9, 80.1, 75.9, 75.0, 66.9, 42.8, 35.9, 34.6, 32.6, 29.7, 26.0, 22.7, 22.3, 18.4, 18.0, 17.1, 15.7, 10.7, -4.0, -4.0; HRMS: m/z calcd for $C_{23}H_{47}O_5Si$ $(M+H)^+$: 431.3193, found: 431.3197 .

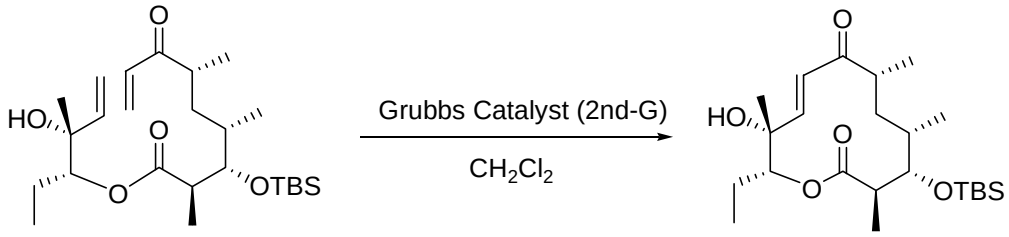
To a solution of the primary alcohol (35.0 mg, 0.081 mmol) obtained as described in the previous procedure and CH_2Cl_2 (4 mL) was added Dess-Martin periodinane (68.9 mg, 0.162 mmol) at 0 °C. The resulting solution was stirred for 1.5 h and was diluted with CH_2Cl_2 (10 mL). After the reaction was completed, aqueous saturated $NaHCO_3$ (10 mL) and aqueous saturated $Na_2S_2O_3$ (5 mL) were added. The resulting mixture was stirred and the organic layer was extracted and washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL), dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (hexane:EtOAc = 5:1) afforded the desired aldehyde (27 mg, 79%): ^1H NMR (300 MHz, $CDCl_3$,): δ 0.07 (s, 6H), 0.88 (m, 3H), 0.90 (s, 9H), 0.93 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 7.1 Hz, 3H), 1.25 (s, 3H), 1.63 (m, 3H), 1.86 (ddd, *J* = 13.8, 9.5, 3.7 Hz, 1H), 2.43 (m, 2H), 2.72 (dddd, *J* = 14.5, 7.3, 7.3, 7.3 Hz, 1H), 3.85 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.80 (dd, *J* = 10.1, 2.8 Hz, 1H), 5.11 (d, *J* = 11.4 Hz, 1H), 5.32 (dd, *J* = 17.3 Hz, 1H), 5.90 (dd, *J* = 17.3, 10.8 Hz, 1H), 9.56 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.8, 176.0, 142.5, 113.7, 80.1, 76.4, 75.0, 44.1, 43.4, 36.2, 32.3, 26.1, 22.8, 22.5, 18.4, 17.2, 15.5, 14.8, 10.6, -3.9, -3.9.

To a stirred solution of the aldehyde (27 mg, 0.063 mmol) prepared as described in the previous procedure and THF (5 ml) was added vinylmagnesium bromide (1 M, 94 μL, 0.094 mmol) at 0 °C. After stirred for 1 h, the reaction mixture was diluted with Et_2O (5 mL) and saturated aqueous NH_4Cl solution (5 mL). The organic layer was separated, and the aqueous layer was

extracted with ether (3 × 5 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (hexane:EtOAc = 3:1) afforded the desired vinyl alcohol (22.7 mg, 79%) as a colorless oil.

To a stirred solution of the alcohol (22.7 mg, 0.050 mmol), which was prepared as described in the previous procedure, in CH_2Cl_2 (3 ml) was added Dess-Martin periodinane (42 mg, 0.099 mmol) at 0 °C. The resulting solution was stirred for 2 h and diluted with CH_2Cl_2 (5 mL). After the reaction was completed, aqueous saturated $NaHCO_3$ (10 mL) and aqueous saturated $Na_2S_2O_3$ (5 mL) were added. The resulting mixture was stirred and the organic layer was separated and washed with saturated aqueous $NaHCO_3$ (5 mL), water (5 mL), and finally dried ($MgSO_4$). Concentration followed by purification of the residue by flash chromatography (hexane:EtOAc = 10:1) afforded the desired vinylketone **15b** as a colorless oil (22 mg, 97%): $[\alpha]_D^{26.8}$ 16.5 (c 1.79, $CHCl_3$); IR (film) : 3486.7, 2928.4, 2856.1, 1730.8, 1612.2, 1461.8, 1377.9, 1255.4, 1174.4, 1055.8, 837.0, 775.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 0.06 (s, 6H), 0.88 (m, 3H), 0.90 (s, 9H), 1.12 (d, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 7.2 Hz, 3H), 1.25 (m, 3H), 1.29 (s, 3H), 1.38 (m, 2H), 1.63 (m, 3H), 1.93 (m, 3H), 2.84 (m, 1H), 2.94 (m, 1H), 3.18 (s, 1H), 3.81 (d, *J* = 8.2 Hz, 1H), 4.81 (dd, *J* = 9.8, 2.7 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 5.27 (d, *J* = 17.3 Hz, 1H), 5.87 (m, 2H), 6.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.1, 176.3, 142.7, 135.3, 128.9, 113.6, 80.2, 76.7, 74.7, 43.3, 40.8, 36.2, 33.8, 29.7, 26.1, 22.6, 18.8, 18.4, 17.6, 15.8, 10.7, -3.8, -3.8.; HRMS: m/z calcd for $C_{25}H_{47}O_5Si(M+H)^+$, 455.3193, found: 455.3196.

(*E*)-(3*R*,4*S*,5*S*,7*R*,11*R*,12*R*)-4-(*tert*-Butyldimethylsilanyloxy)-12-ethyl-3,5,7,11-tetramethyloxacyclododec-9-ene-2,8-dione (**16b**)

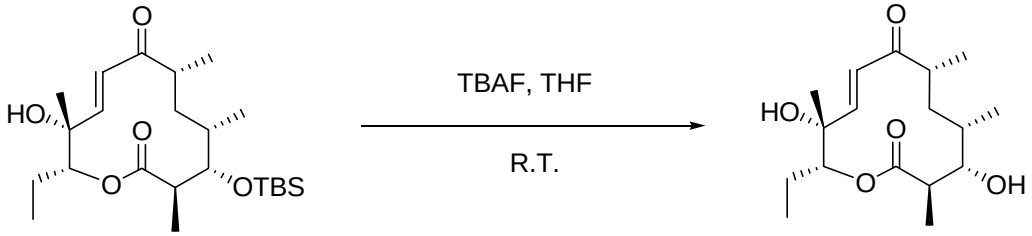


15b **16b**

A flame-dried round-bottomed flask was charged with a solution of vinylketone **15b** (4.7 mg, 0.0097 mol) in CH_2Cl_2 (3 mL). Grubbs Catalyst (2nd-Generation) (0.4 mg, 0..48 μmol) was subsequently added as a solid, producing a light brown solution, which was stirred for 12 h at room temperature. The mixture was then concentrated to give a dark brown oil. Purification of this residue by flash chromatography (hexane:EtOAc = 5:1) afforded the lactone **16b** (3.5 mg, 85%) as a white solid: mp 194.0~196.0 °C; $[\alpha]_D^{26.4}$ 73.8 (*c* 1.45, $CHCl_3$); IR (film): 3397.0,

2969.8, 1727.9, 1681.6, 1630.5, 1461.8, 1251.6, 1088.6, 1-56.8, 973.9, 836.0, 774.3cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (d, *J* = 3.1 Hz, 6H), 0.89 (m, 3H), 0.90 (s, 9H) 0.94 (d, *J* = 7.0 Hz, 3H), 1.23 (m, 6H), 1.34 (s, 3H), 1.65 (m, 1H), 1.78 (m, 2H), 1.98 (s, 1H), 2.53 (m, 1H), 2.70 (m, 1H), 3.57 (d, *J* = 10.0 Hz, 1H), 4.83 (dd, *J* = 8.7, 5.1 Hz, 1H), 6.46 (d, *J* = 15.4 Hz, 1H), 6.67 (d, *J* = 15.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.2, 176.0, 147.9, 124.7, 79.0, 76.7, 75.4, 45.1, 44.3, 34.2, 33.5, 26.2, 23.3, 20.5, 18.5, 18.4, 17.5, 17.4, 10.0, -3.1, -3.4; HRMS: m/z calcd for $C_{23}H_{43}O_5Si(M+H)^+$, 427.2880, found: 427.2882.

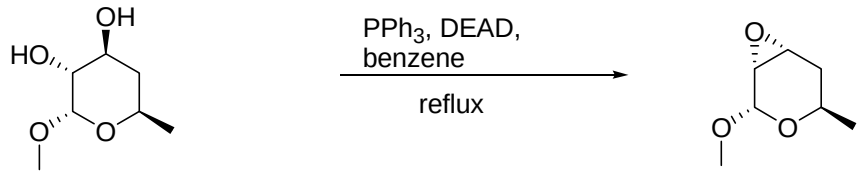
epi-Methynolide (**2b**)



16b **2b**

To a stirred solution of lactone **16b** (3.5 mg, 0.0082 mmol) in dry THF(1 mL) at room temperature was added 1.0 M TBAF (80 μL, 0.082 mmol) via a syringe. After 2.5 h, the reaction mixture was concentrated. Purification by flash chromatography (hexane:EtOAc = 1:2) afforded *epi*-methynolide (**2b**) (2.0 mg, 78%) as a white solid: mp 163.5~166.0 °C; $[\alpha]_D^{26.4}$ 74.7 (*c* 0.20, $CHCl_3$); IR (film): 3446.2, 2969.8, 2936.1, 1707.7, 1686.4, 1632.5, 1458.9, 1375.0, 1312.3, 1153.2, 1080.9, 994.1cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.4 Hz, 3H), 1.01 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.37 (s, 3H), 1.32-1.52 (m, 2H), 1.48-1.68 (m, 2H), 1.74-1.84(m, 2H), 1.95 (s, 1H), 2.56 (ddq, *J* = 7.1, 6.9, 3.6 Hz, 1H)), 2.67(dq, *J* = 10.4, 6.8 Hz, 1H), 3.57(dd, *J* = 10.4, 5.6 Hz, 1H)), 4.85(dd, *J* = 8.3, 5.7 Hz, 1H)), 6.46(d, *J* = 15.4 Hz, 1H), 6.67 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.9, 174.4, 148.0, 124.6, 77.9, 76.6, 75.4, 45.2, 43.4, 33.2, 33.1, 20.4, 19.3, 17.4, 6.3, 16.6, 10.0; HRMS: m/z calcd for $C_{17}H_{28}O_5$: 312.1937, found: 312.1945.

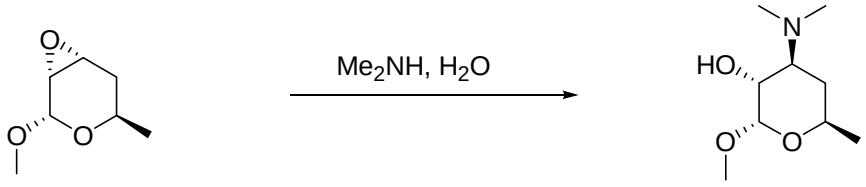
Methyl 2,3-anhydro-4,6-dideoxy-α-D-ribo-hexopyranoside (**18**)



17 **18**

To a solution of diol **17** (1.79 mg, 11.04 mmol) in benzene (30 mL) at room temperature were added PPh_3 (4.34 g, 16.56 mmol) and DEAD (40% in toluene, 7.2 mL, 16.56 mmol). The resulting solution was stirred for 30 min at room temperature before it was warmed to 100 °C. After additional stirring for 16 h at 100 °C, the solution was cooled to room temperature. After 30 min, the reaction mixture benzene was evaporated and concentrated. Purification of the residue by flash chromatography (pentane:Et_2O=1:1) afforded the epoxide **18** (1.41 mg, 89 %) as a colorless oil: $[\alpha]_D^{25.5}$ 74.2 (*c* 0.80, $CHCl_3$); IR (film): 2974.6, 1445.4, 1394.3, 1258.3, 1192.8, 1160.9, 1132.0, 1069.3, 1029.8, 981.6, 945.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 1.03 (d, *J* = 8.9 Hz, 3H), 1.48 (dd, *J* = 14.5, 11.1 Hz, 1H), 1.93 (d, *J* = 14.6 Hz, 1H), 3.22 (t, *J* = 3.6 Hz, 1H), 3.26 (s, 1H), 3.34 (s, 3H), 3.78 (m, 1H), 4.81 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 95.3, 60.0, 55.0, 50.8, 50.5, 32.1, 20.4; HRMS: m/z calcd for $C_7H_{12}O_3$, 144.0786, found: 144.0788.

Methyl α-D-desosaminide (**19**)

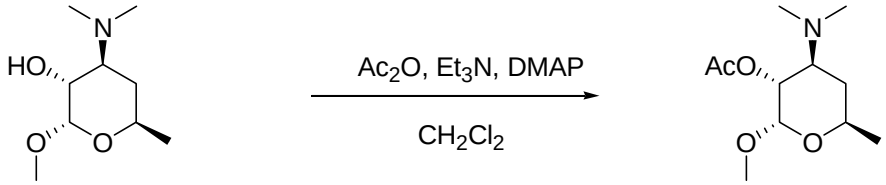


18 **19**

Epoxide **18** (1.41 mg, 9.78 mmol) was added to a solution of 40 % aqueous dimethylamine (30 mL) and the resulting mixture was stirred for 60 h at room temperature. After the mixture was concentrated under reduced pressure, purification of the residue by flash chromatography (CH_2Cl_2:MeOH=7:1) afforded the methyl α-D-desosaminide **19** (1.21 g, 65 %) as a colorless oil: $[\alpha]_D^{25.7}$ 160.6 (*c* 1.47, $CHCl_3$); IR (film): 3463.5, 2935.1, 1456.0, 1382.7, 1277.6, 1202.4, 1099.2, 1052.9, 981.6, 940.1, 837.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 1.20 (d, *J* = 6.3 Hz, 3H), 1.25 (m, 1H), 1.72 (ddd, *J* = 5.8, 3.0, 3.0 Hz, 1H), 2.28 (s, 6H), 2.92 (ddd, *J* = 12.0, 3.8 Hz, 1H), 3.43 (s, 3H), 3.54 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.90 (dddd, *J* = 6.2, 6.2, 6.2, 2.0 Hz, 1H), 4.85 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 99.5, 68.5, 60.3, 54.9, 39.8, 29.0, 21.2;

HRMS: m/z calcd for $C_9H_{19}NO_3$, 189.1365, found: 189.1363.

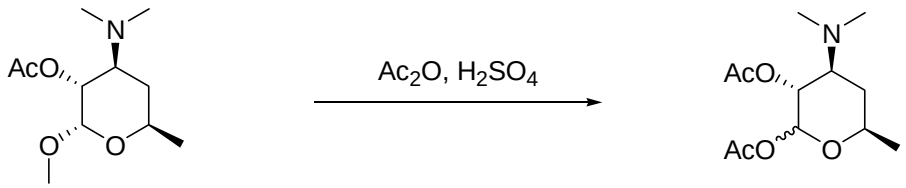
Methyl 2-*O*-acetyl-3-dimethylamino-3,4,6-trideoxy-α-D-xylohexopyranoside (**20**)



19 **20**

To a solution of Methyl a-D-desosaminide **19** (1.00 mg, 5.28 mmol) CH_2Cl_2 (10 mL) at 0 °C were added DMAP (322 mg, 2.64 mmol), triethylamine (2.2 mL, 15.8 mmol) and acetic anhydride (1.5 mL, 15.8 mmol). The resulting solution was stirred for 10 min at 0 °C before it was warmed to room temperature. After additional stirring for 1 h at room temperature and then to this was added a saturated aqueous $NaHCO_3$ solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 10 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (EtOAc:MeOH = 10:1) afforded **20** (990 mg, 72%) as a colorless oil: : $[\alpha]_D^{25.2}$ 152.5 (*c* 1.97, $CHCl_3$); IR (film): 2940.9, 2782.8, 2133.9, 1744.3, 1455.0, 1372.1, 1246.8, 1128.2, 1042.3, 945.0, 923.7, 903.5, 870.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 1.02 (d, *J* = 6.3 Hz, 3H), 1.19 (ddd, *J* = 12.2, 12.2, 12.2 Hz, 1H), 1.61 (ddd, *J* = 13.0, 4.0, 2.2 Hz, 1H), 1.93 (s, 3H), 2.10 (s, 6H), 2.95 (ddd, *J* = 12.0, 12.0, 4.2 Hz, 1H), 3.20 (s, 3H), 3.74 (ddddd, *J* = 12.5, 6.2, 6.2, 6.2, 2.0 Hz, 1H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.71 (dd, *J* = 11.0, 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 97.4, 70.3, 63.8, 57.3, 54.5, 40.1, 32.1, 20.7, 20.4; HRMS: m/z calcd for $C_{11}H_{21}NO_4$, 231.1471, found: 231.1470.

1, 2-Di-*O*-acetyl-D-desosamine (**21**)

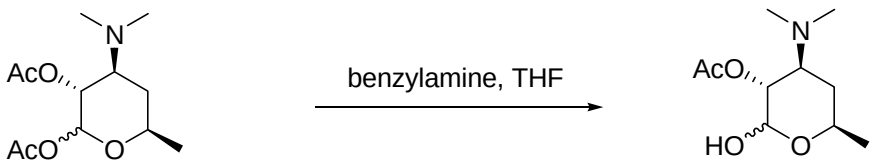


20 **21**

To a stirred solution of **20** (990 mg, 4.28 mmol) in acetic anhydride (6 mL) was added the

H_2SO_4 solution [H_2SO_4 (8 drops) in acetic anhydride (1 mL)] (0.5 mL) at 0 °C. The resulting solution was stirred for 10 min at 0 °C before it was warmed to room temperature. After additional stirring for 1 h at room temperature $NaHCO_3$ (300 mg) was added to the mixture. After 30 min, Et_2O (20 mL) and a saturated aqueous $NaHCO_3$ solution (20 mL) were added to the mixture. The resulting mixture was stirred for 2 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with ether (5 × 15 mL). The organic solutions were combined, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (EtOAc:MeOH = 10:1) afforded the desired product **21** (α:ß=5:1, 810 mg, 74 %) as a colorless oil. IR (film): 2975.6, 1748.2, 1373.1, 1243.9, 1139.7, 1058.7, 1012.5, 925.7, 843.7 cm^{-1}; major (α) ^{1}H NMR (300 MHz, $CDCl_3$,): δ 1.17 (d, *J* = 6.2 Hz, 3H), 1.37 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.83 (ddd, *J* = 13.1, 3.7, 2.4 Hz, 1H), 2.00 (s, 3H), 2.09 (s, 3H), 2.26 (s, 6H), 3.12 (ddd, *J* = 11.5, 11.5, 4.0 Hz, 1H), 4.00 (m, 1H), 4.99 (dd, *J* = 11.1, 3.6 Hz, 1H), 6.18 (dd, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 169.5, 90.6, 68.7, 67.1, 57.5, 40.1, 31.4, 21.0, 20.9; minor (ß) ^{1}H NMR (300 MHz, $CDCl_3$,): δ 1.47 (d, *J* = 6.1 Hz, 3H), 1.35 (m, 1H), 1.75 (m, 1H), 1.95 (s, 3H), 2.04 (s, 3H), 2.24 (s, 6H), 2.79 (ddd, *J* = 10.8, 10.8, 4.3 Hz, 1H), 3.68 (m, 1H), 4.89 (dd, *J* = 10.5, 8.0 Hz, 1H), 5.55 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 169.4, 93.5, 70.4, 69.6, 62.9, 40.4, 30.3, 21.4, 20.9; HRMS: m/z calcd for $C_{12}H_{21}NO_5$, 259.1420, found: 259.1423.

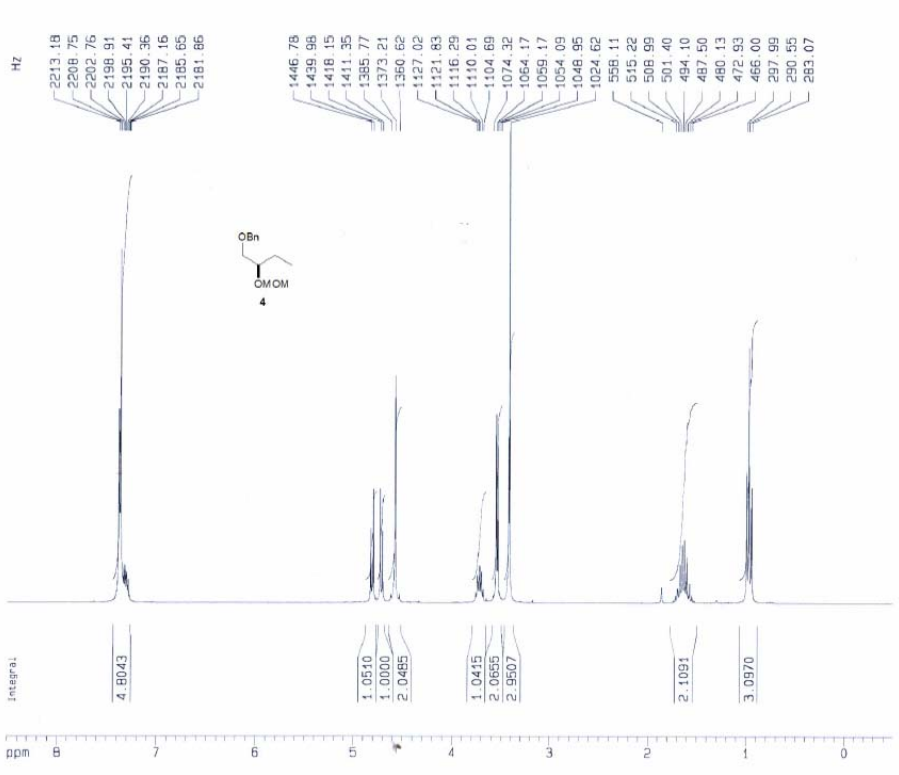
2-*O*-acetyl-D-desosamine (**22**)



21 **22**

To a stirred solution of **21** (810 mg, 3.12 mmol) in dry THF (10 mL) at room temperature was added benzylamine (683 µL, 6.24 mmol) via a syringe. After 18 h, the reaction mixture was concentrated. Purification by flash chromatography (CH_2Cl_2:MeOH= 7:1) afforded 2-*O*-acetyl-D-desosamine (**22**) (α:ß = 0.7:1, 480 mg, 71%) as a colorless oil: major (ß) ^{1}H NMR (300 MHz, $CDCl_3$,): δ 1.28 (d, *J* = 6.2 Hz, 3H), 1.39 (m, 1H), 1.80 (m, 1H), 2.13 (s, 3H), 2.29 (s, 6H), 2.82 (ddd, *J* = 12.1, 10.5, 4.3 Hz, 1H), 3.62 (ddddd, *J* = 12.2, 6.2, 6.2, 6.2, 2.0 Hz, 1H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.71 (dd, *J* = 10.4, 7.7 Hz, 1H); minor (ß) ^{1}H NMR (300 MHz, $CDCl_3$,): δ 1.20 (d, *J* = 6.2 Hz, 3H), 1.39 (m, 1H), 1.80 (m, 1H), 2.13 (s, 3H), 2.30 (s, 6H), 3.20 (ddd, *J* = 12.1, 12.1, 4.1 Hz, 1H), 4.18 (ddddd, *J* = 12.7, 6.5, 6.5, 6.5, 2.4 Hz, 1H), 4.91 (dd, *J* = 11.1, 3.6 Hz, 1H),

5.32 (d, J = 3.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 170.6, 96.8, 91.0, 73.2, 70.8, 69.5, 64.4, 62.4, 57.1, 40.6, 40.5, 32.2, 31.5, 21.4, 21.1.

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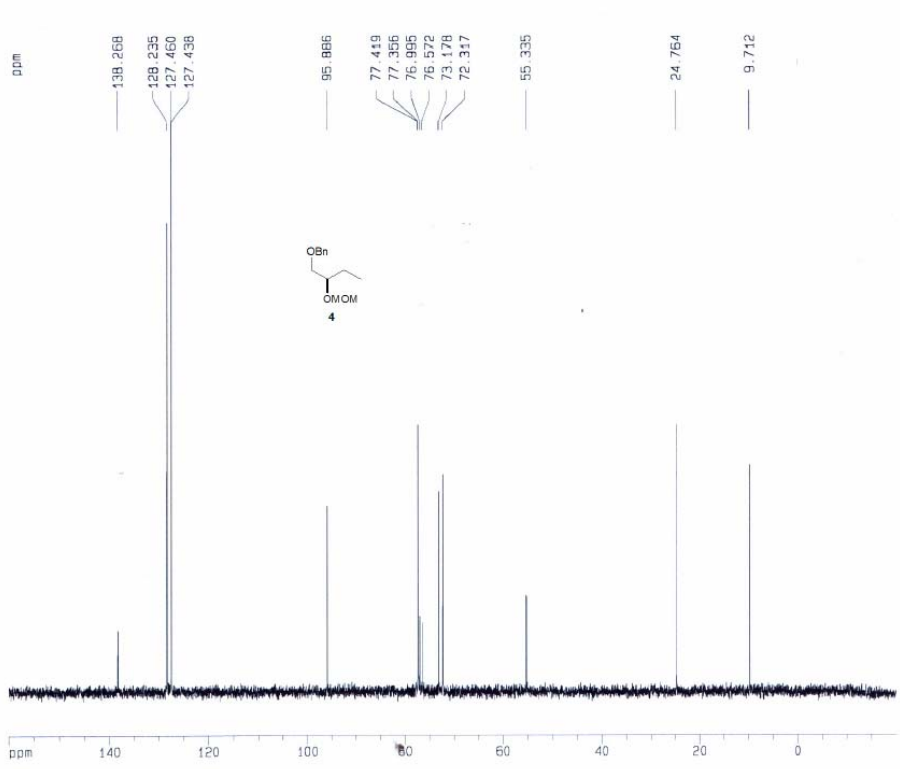
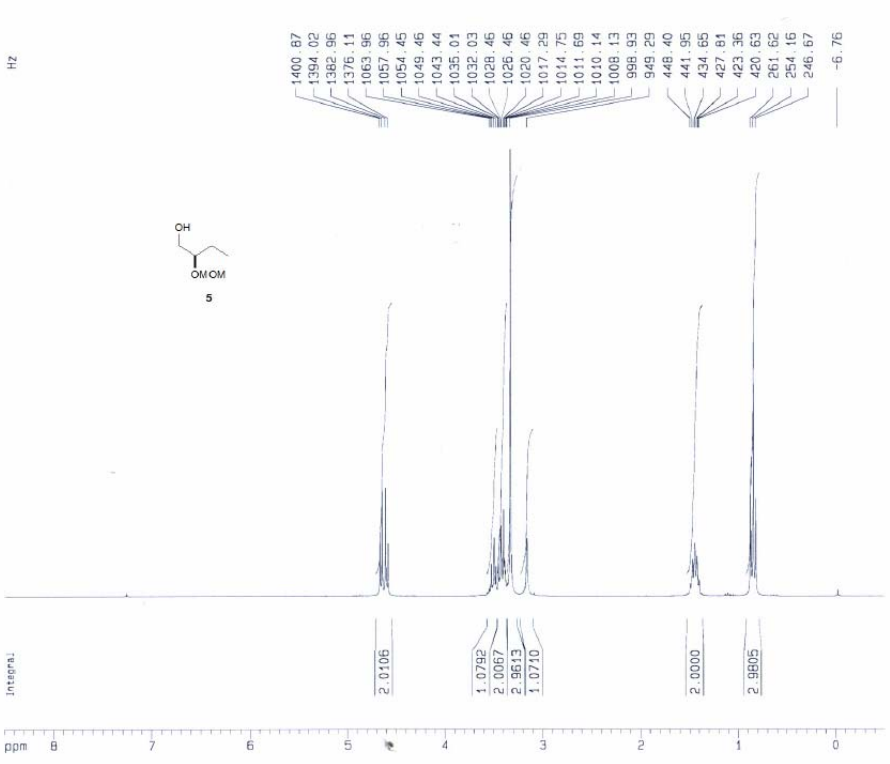



```
Current Data Parameters
NAME                  ryk
EXPNO                 117
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050816
Time                 21.29
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              19607.844 Hz
FIDRES               0.299192 Hz
AQ                1.6712180 sec
RG                  13004
DW                  25.500 usec
DE                   6.00 usec
TE                  300.0 K
D12               0.00002000 sec
PL13                20.00 dB
D1                2.00000000 sec
CPDPRG2            waltz16
PCPD2               100.00 usec
SFO2            300.1312005 MHz
NUC2                   1H
PL2                  0.00 dB
PL12                18.00 dB
P1                  21.00 usec
SFO1             75.4760204 MHz
NUC1                   13C
PL1                  0.00 dB
D11               0.03000000 sec

F2 - Processing parameters
SI                  32768
SF              75.4677568 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P                160.000 ppm
F1                12074.84 Hz
F2P                -20.000 ppm
F2                -1509.36 Hz
PPMCM               9.00000 ppm/cm
HZCM              679.20984 Hz/cm
```

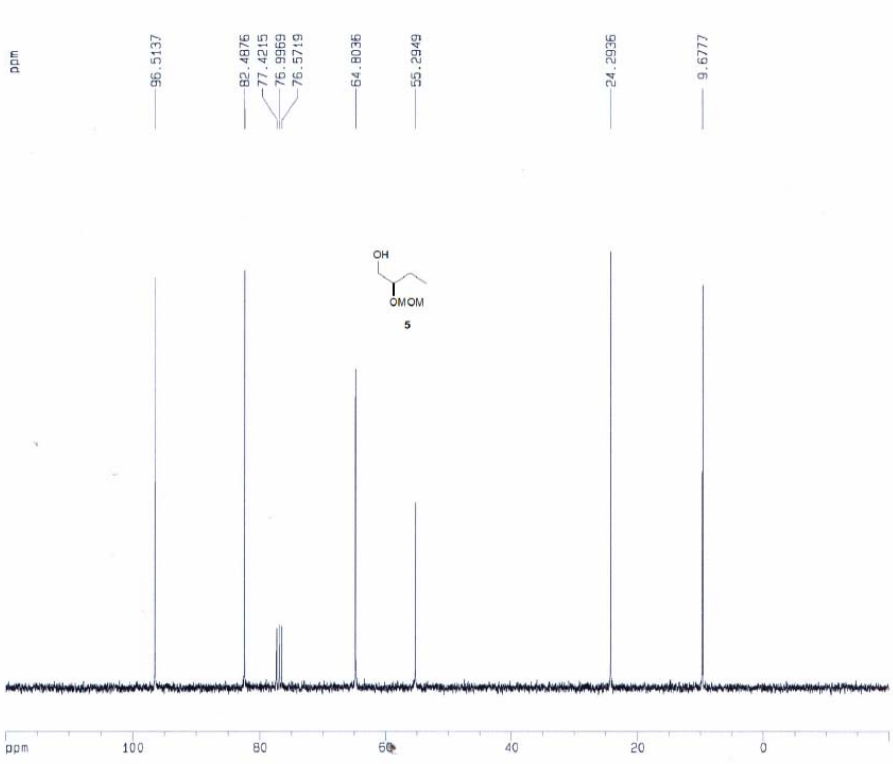



```
Current Data Parameters
NAME                  nyk
EXPNO                 212
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050902
Time                  22.59
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                     40.3
DW                 81.000 usec
DE                  6.00 usec
TE                  300.0 K
D1                 1.00000000 sec
P1                   19.50 usec
SFO1             300.1318534 MHz
NUC1                    1H
PL1                  0.00 dB

F2 - Processing parameters
SI                   16384
SF               300.1300068 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  8.500 ppm
F1                 2551.10 Hz
F2P                 -0.500 ppm
F2                 -150.07 Hz
PPMCM              0.45000 ppm/cm
HZCM             135.05850 Hz/cm
```

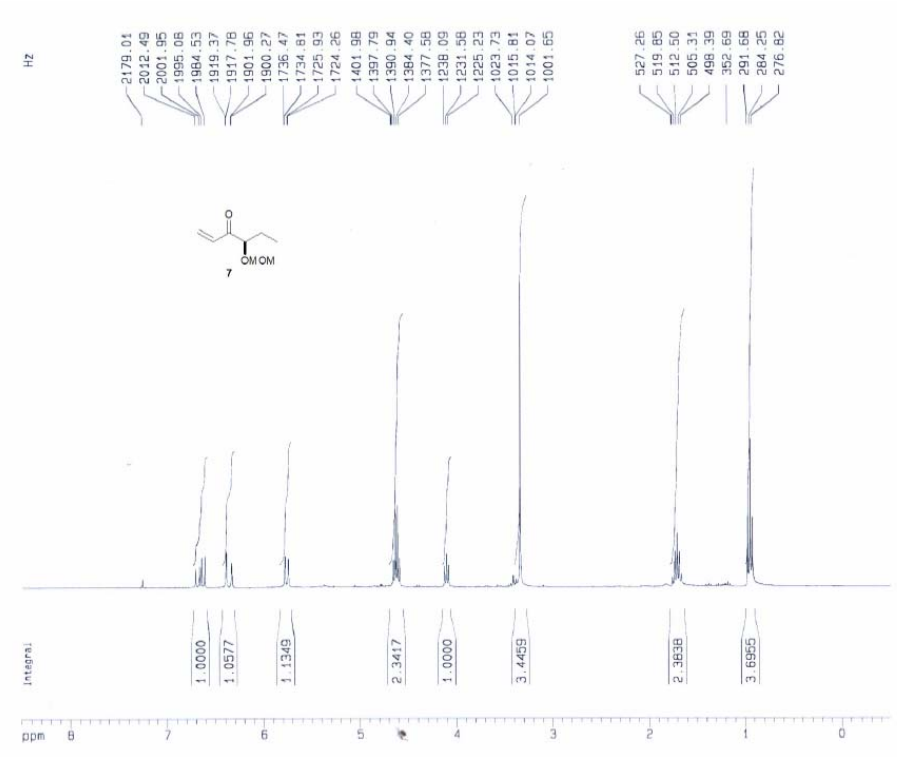



```
Current Data Parameters
NAME                  nyk
EXPNO                 213
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050902
Time                  23.03
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      19
DS                       2
SWH                19607.844 Hz
FIDRES             0.299192 Hz
AQ                 1.6712180 sec
RG                     8192
DW                 25.500 usec
DE                  6.00 usec
TE                  300.0 K
D12                0.00002000 sec
PL13                 20.00 dB
D1                 2.00000000 sec
CPDPRG2             waltz16
PCPD2              100.00 usec
SFO2             300.1312005 MHz
NUC2                    1H
PL2                  0.00 dB
PL12                 18.00 dB
P1                   21.00 usec
SFO1              75.4760204 MHz
NUC1                   13C
PL1                  0.00 dB
D11                0.03000000 sec

F2 - Processing parameters
SI                   32768
SF               75.4677574 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                120.000 ppm
F1                 9056.13 Hz
F2P                -20.000 ppm
F2                 -1509.36 Hz
PPMCM              7.00000 ppm/cm
HZCM             528.27429 Hz/cm
```

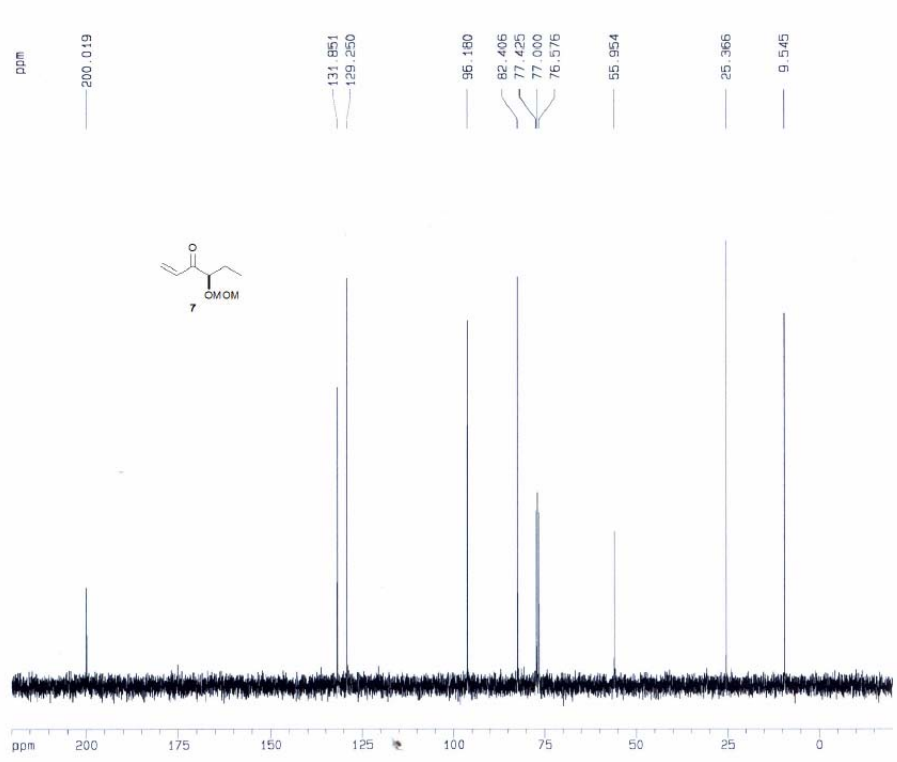



```
Current Data Parameters
NAME                  ryk
EXPNO                  87
PROCNO                  1

F2 - Acquisition Parameters
Date_           20050923
Time                22.24
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.188388 Hz
AQ               2.6542580 sec
RG                   90.5
DW                 81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec
P1                 19.50 usec
SFO1          300.1318534 MHz
NUC1                   1H
PL1                 0.00 dB

F2 - Processing parameters
SI                 16384
SF            300.1300098 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1               2551.10 Hz
F2P               -0.500 ppm
F2                -150.07 Hz
PPMCM             0.45000 ppm/cm
HZCM            135.05850 Hz/cm
```

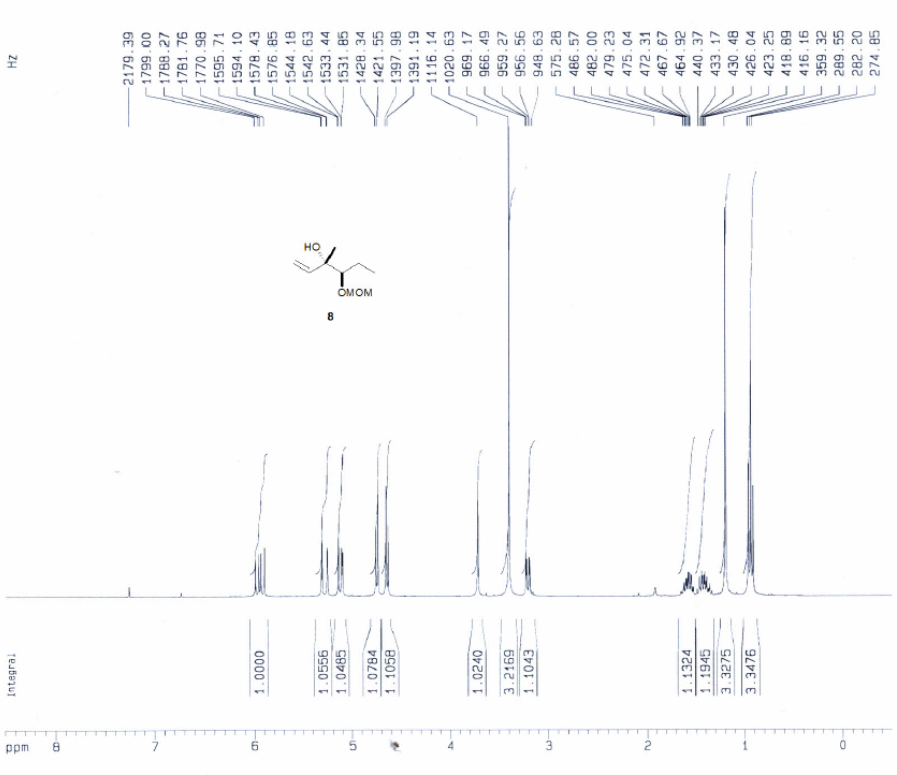



```
Current Data Parameters
NAME                  ryk
EXPNO                  88
PROCNO                  1

F2 - Acquisition Parameters
Date_           20050923
Time                22.30
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                     46
DS                      2
SWH              19607.844 Hz
FIDRES           0.299192 Hz
AQ               1.6712180 sec
RG                   8192
DW                 25.500 usec
DE                  6.00 usec
TE                 300.0 K
D12             0.00002000 sec
PL13               20.00 dB
D1              2.00000000 sec
CPDPRG2            waltz16
PCPD2             100.00 usec
SFO2          300.1312005 MHz
NUC2                   1H
PL2                 0.00 dB
PL12               18.00 dB
P1                 21.00 usec
SFO1          75.4750204 MHz
NUC1                   13C
PL1                 0.00 dB
D11             0.03000000 sec

F2 - Processing parameters
SI                 32768
SF            75.4677514 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              220.000 ppm
F1              16602.90 Hz
F2P               -20.000 ppm
F2              -1509.35 Hz
PPMCM             12.00000 ppm/cm
HZCM            905.61304 Hz/cm
```

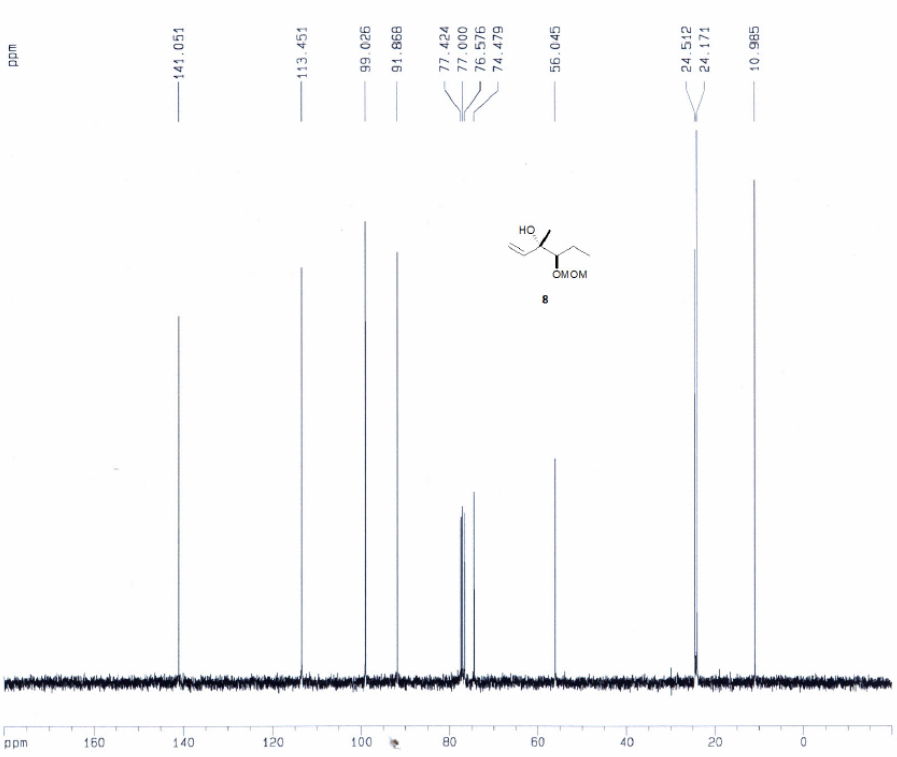



```
Current Data Parameters
NAME                  ryk
EXPNO                  45
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050912
Time                  22.50
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES            0.188360 Hz
AQ                2.6542580 sec
RG                     71.8
DW                81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1                1.00000000 sec
P1                   19.50 usec
SFO1           300.1318534 MHz
NUC1                    1H
PL1                   0.00 dB

F2 - Processing parameters
SI                    16384
SF             300.1300063 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  8.500 ppm
F1                2551.10 Hz
F2P                 -0.500 ppm
F2                 -150.07 Hz
PPMCM             0.45000 ppm/cm
HZCM            135.05850 Hz/cm
```

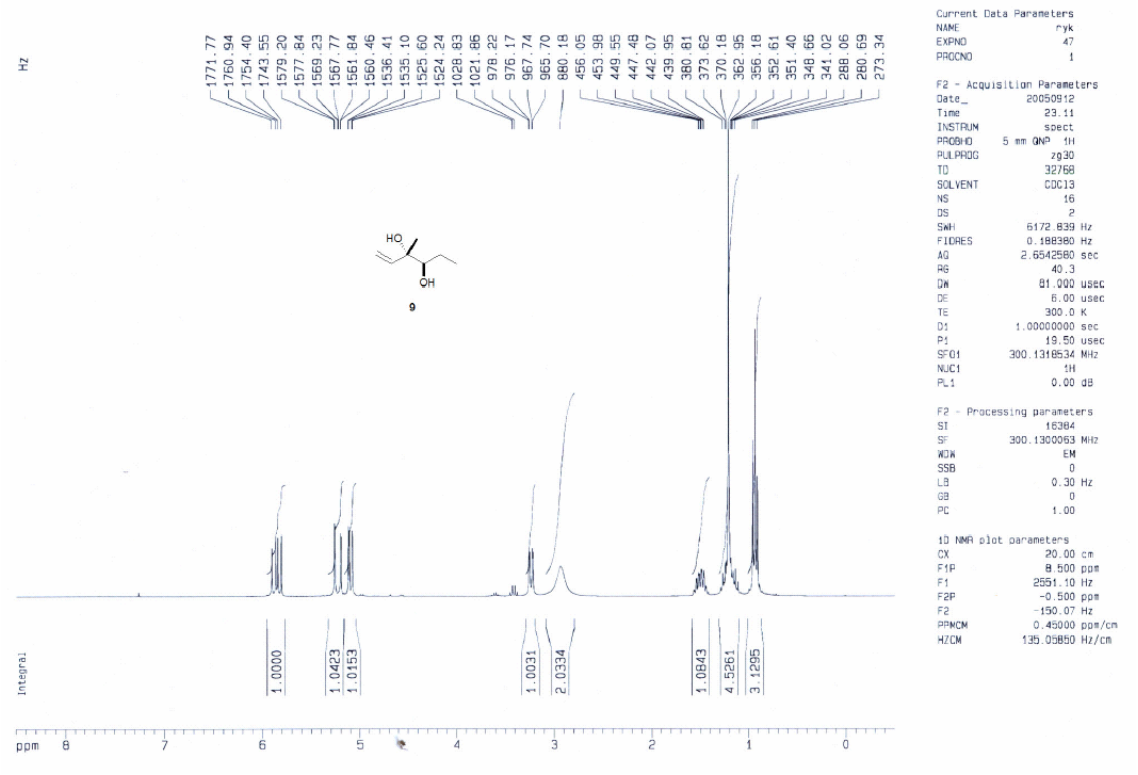



```
Current Data Parameters
NAME                  ryk
EXPNO                  46
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050912
Time                  23.02
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      100
DS                        2
SWH               19607.844 Hz
FIDRES            0.299192 Hz
AQ                1.6712180 sec
RG                     8192
DW                25.500 usec
DE                 6.00 usec
TE                 300.0 K
D12              0.00002000 sec
PL13                  20.00 dB
D1                2.00000000 sec
CPDPRG2             waltz16
PCPD2               100.00 usec
SFO2           300.1312005 MHz
NUC2                    1H
PL2                   0.00 dB
PL12                 18.00 dB
P1                   21.00 usec
SFO1            75.4760204 MHz
NUC1                    13C
PL1                   0.00 dB
D11              0.03000000 sec

F2 - Processing parameters
SI                    32768
SF             75.4677537 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                180.000 ppm
F1              13564.20 Hz
F2P                -20.000 ppm
F2              -1509.35 Hz
PPMCM            10.00000 ppm/cm
HZCM            754.67749 Hz/cm
```

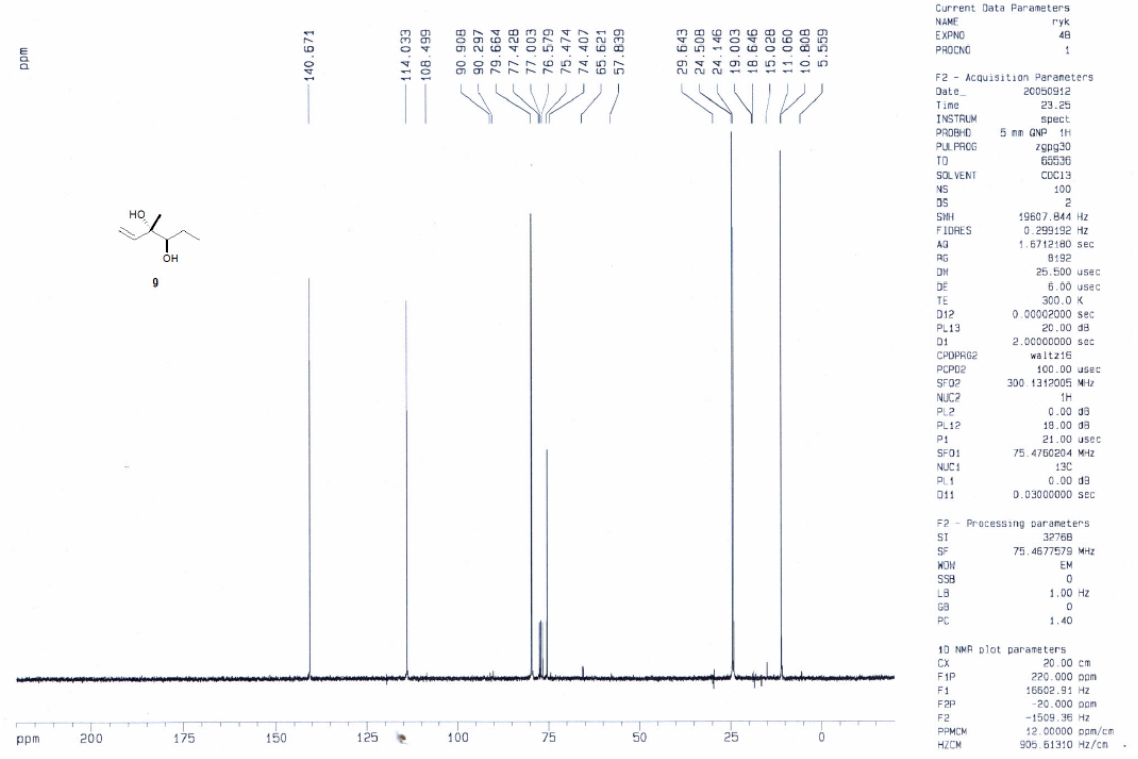



```
Current Data Parameters
NAME                  ryk
EXPNO                  47
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050912
Time                 23.11
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                    40.3
DW                  81.000 usec
DE                   6.00 usec
TE                  300.0 K
D1                1.00000000 sec
P1                   19.50 usec
SFO1            300.1318534 MHz
NUC1                    1H
PL1                   0.00 dB

F2 - Processing parameters
SI                      16384
SF                300.1300063 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  8.500 ppm
F1                 2551.10 Hz
F2P                 -0.500 ppm
F2                 -150.07 Hz
PPMCM              0.45000 ppm/cm
HZCM             135.05850 Hz/cm
```

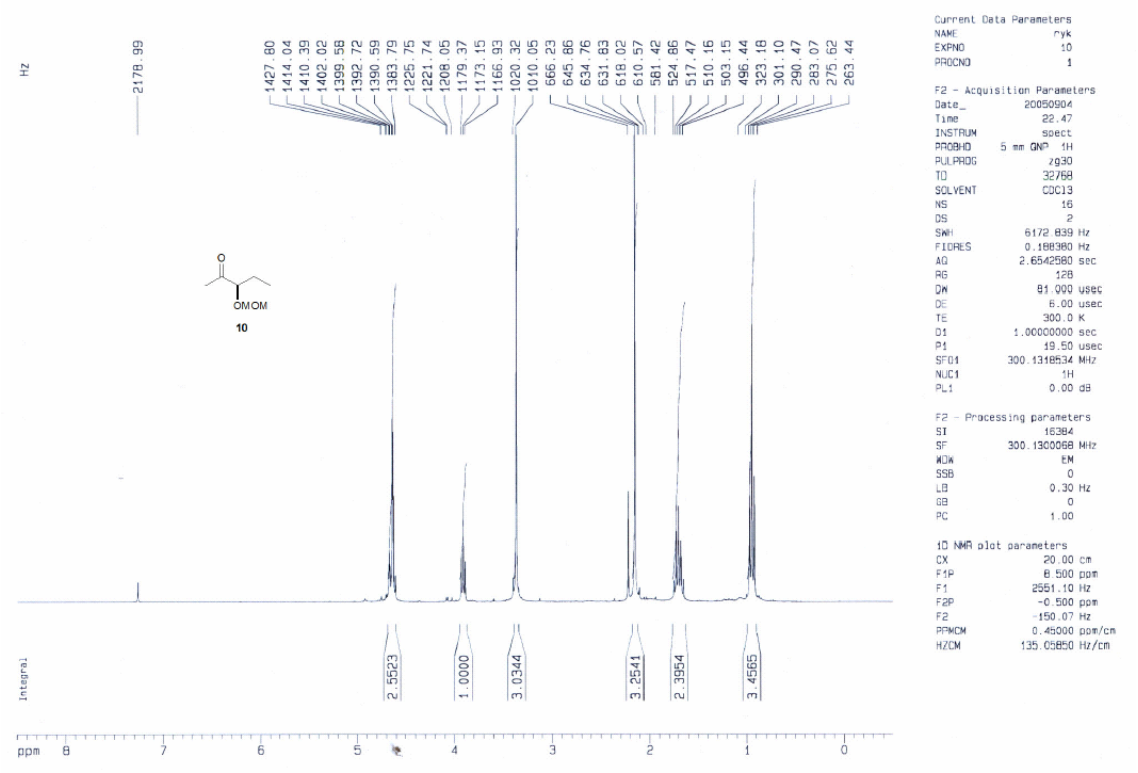



```
Current Data Parameters
NAME                  ryk
EXPNO                  48
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050912
Time                 23.25
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     100
DS                       2
SWH              19607.844 Hz
FIDRES            0.299192 Hz
AQ                1.6712180 sec
RG                    8192
DW                  25.500 usec
DE                   6.00 usec
TE                  300.0 K
D12               0.00002000 sec
PL13                 20.00 dB
D1                2.00000000 sec
CPDPRG2              waltz16
PCPD2               100.00 usec
SFO2            300.1312005 MHz
NUC2                    1H
PL2                   0.00 dB
PL12                 18.00 dB
P1                   21.00 usec
SFO1             75.4760204 MHz
NUC1                    13C
PL1                   0.00 dB
D11               0.03000000 sec

F2 - Processing parameters
SI                      32768
SF                75.4677579 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                220.000 ppm
F1                16602.91 Hz
F2P                -20.000 ppm
F2                -1509.36 Hz
PPMCM             12.00000 ppm/cm
HZCM             905.61310 Hz/cm
```

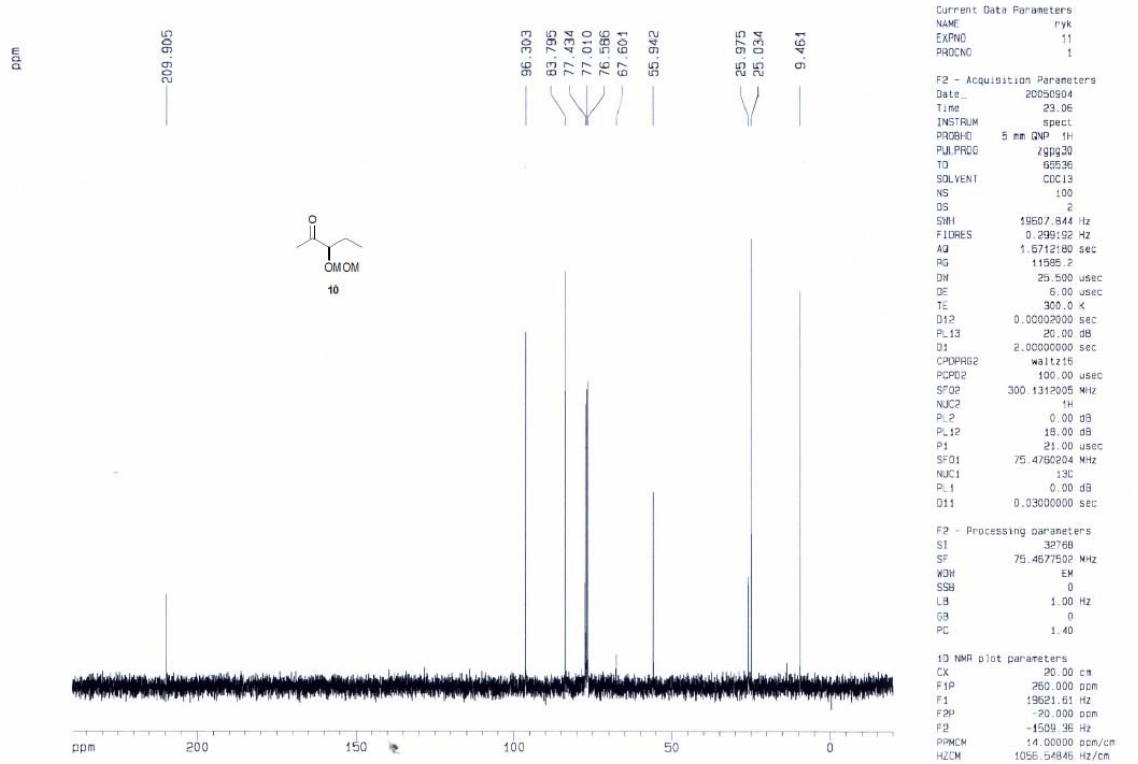



```
Current Data Parameters
NAME                  ryk
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20050904
Time                22.47
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.188380 Hz
AQ               2.6542580 sec
RG                    128
DW                91.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
P1                19.50 usec
SFO1           300.1318534 MHz
NUC1                   1H
PL1                 0.00 dB

F2 - Processing parameters
SI                 16384
SF            300.1300068 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1               2551.10 Hz
F2P               -0.500 ppm
F2               -150.07 Hz
PPMCM             0.45000 ppm/cm
HZCM            135.05850 Hz/cm
```

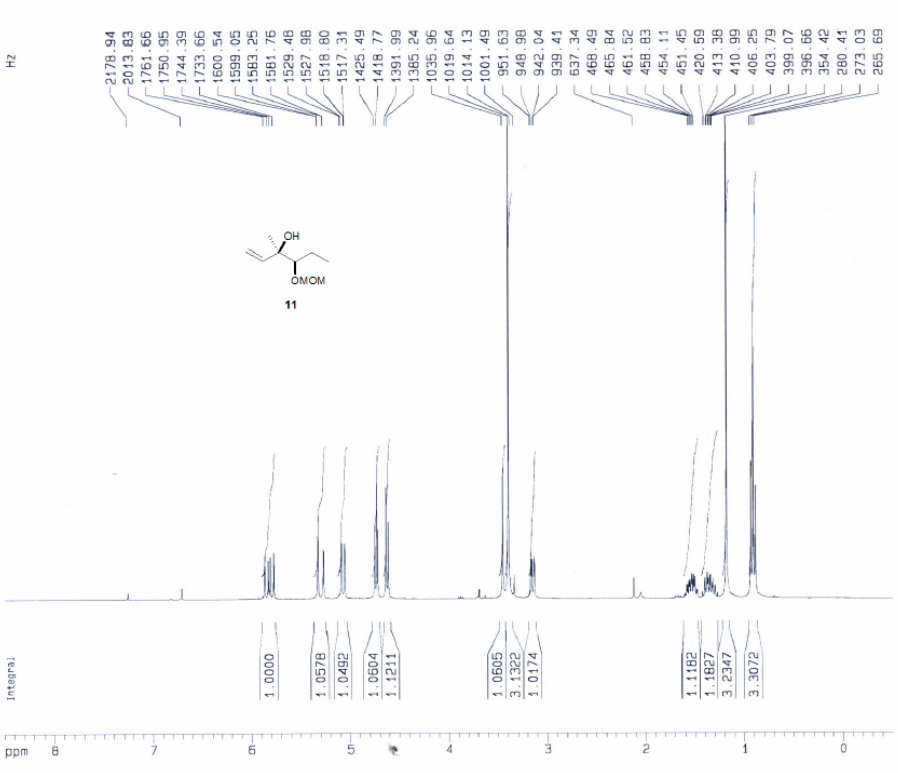



```
Current Data Parameters
NAME                  ryk
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20050904
Time                23.06
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG          zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    100
DS                      2
SWH             19607.844 Hz
FIDRES           0.299192 Hz
AQ               1.6712180 sec
RG                 11585.2
DW                25.500 usec
DE                 6.00 usec
TE                300.0 K
D12            0.00002000 sec
PL13                20.00 dB
D1             2.00000000 sec
CPDPRG2           waltz16
PCPD2             100.00 usec
SFO2           300.1312005 MHz
NUC2                   1H
PL2                 0.00 dB
PL12                18.00 dB
P1                 21.00 usec
SFO1            75.4760204 MHz
NUC1                   13C
PL1                 0.00 dB
D11            0.03000000 sec

F2 - Processing parameters
SI                 32768
SF            75.4677502 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              260.000 ppm
F1             19621.61 Hz
F2P              -20.000 ppm
F2             -1509.96 Hz
PPMCM            14.00000 ppm/cm
HZCM           1056.54846 Hz/cm
```

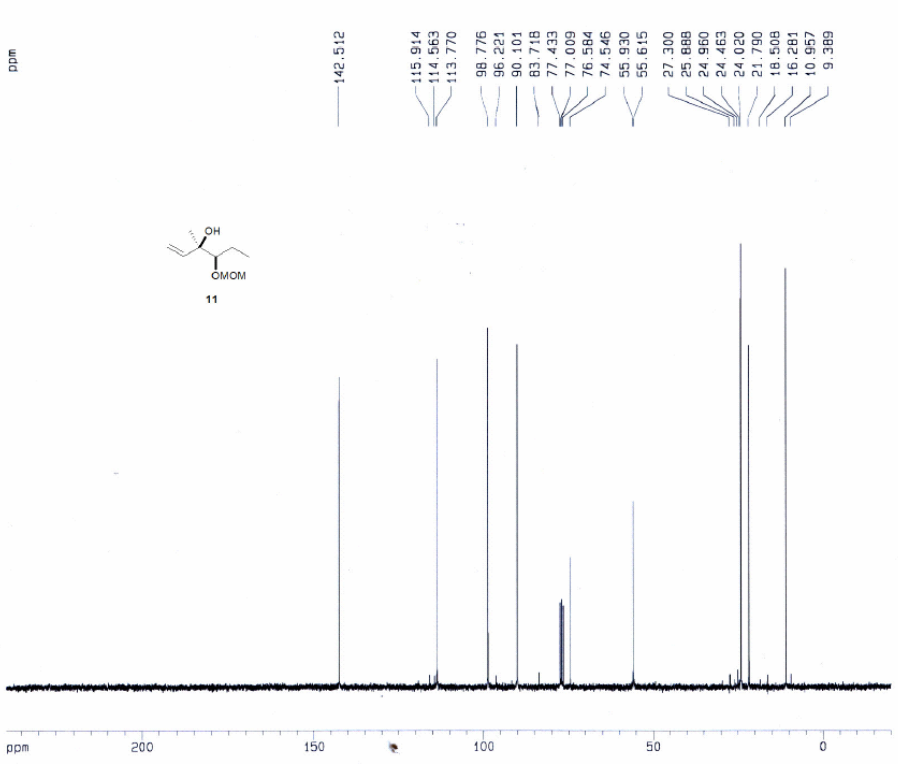



```
Current Data Parameters
NAME                  ryk
EXPNO                  20
PROCNO                  1

F2 - Acquisition Parameters
Date_           20050905
Time                22.59
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              6172.839 Hz
FIDRES           0.188380 Hz
AQ               2.6542560 sec
RG                  40.3
DW                 81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec
P1                 19.50 usec
SFO1            300.1318534 MHz
NUC1                  1H
PL1                 0.00 dB

F2 - Processing parameters
SI                 16384
SF              300.1300068 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1                2551.10 Hz
F2P               -0.500 ppm
F2                -150.07 Hz
PPMCM             0.45000 ppm/cm
HZCM            135.05850 Hz/cm
```

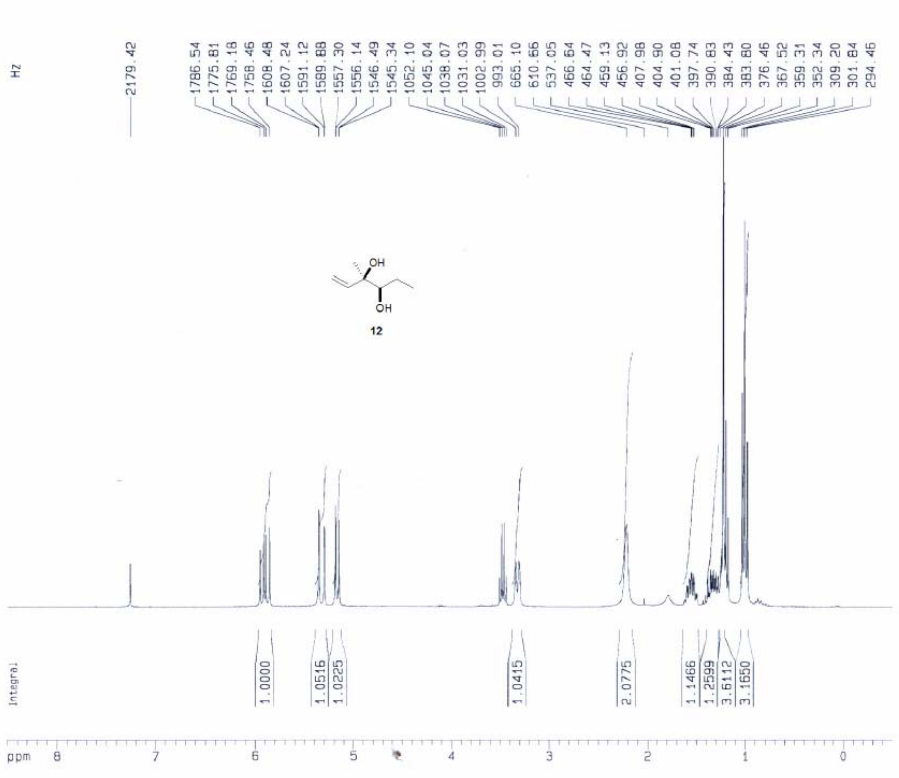



```
Current Data Parameters
NAME                  ryk
EXPNO                  21
PROCNO                  1

F2 - Acquisition Parameters
Date_           20050905
Time                23.15
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     2
SWH             19607.844 Hz
FIDRES           0.299192 Hz
AQ               1.6712180 sec
RG                 11585.2
DW                 25.500 usec
DE                  6.00 usec
TE                 300.0 K
D12             0.00002000 sec
PL13               20.00 dB
D1              2.00000000 sec
CPDPRG2          waltz16
PCPD2             100.00 usec
SFO2            300.1312005 MHz
NUC2                  1H
PL2                 0.00 dB
PL12               18.00 dB
P1                 21.00 usec
SFO1             75.4760204 MHz
NUC1                  13C
PL1                 0.00 dB
D11             0.03000000 sec

F2 - Processing parameters
SI                 32768
SF              75.4677543 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               240.000 ppm
F1              18112.26 Hz
F2P               -20.000 ppm
F2              -1509.36 Hz
PPMCM             13.00000 ppm/cm
HZCM            981.08075 Hz/cm
```

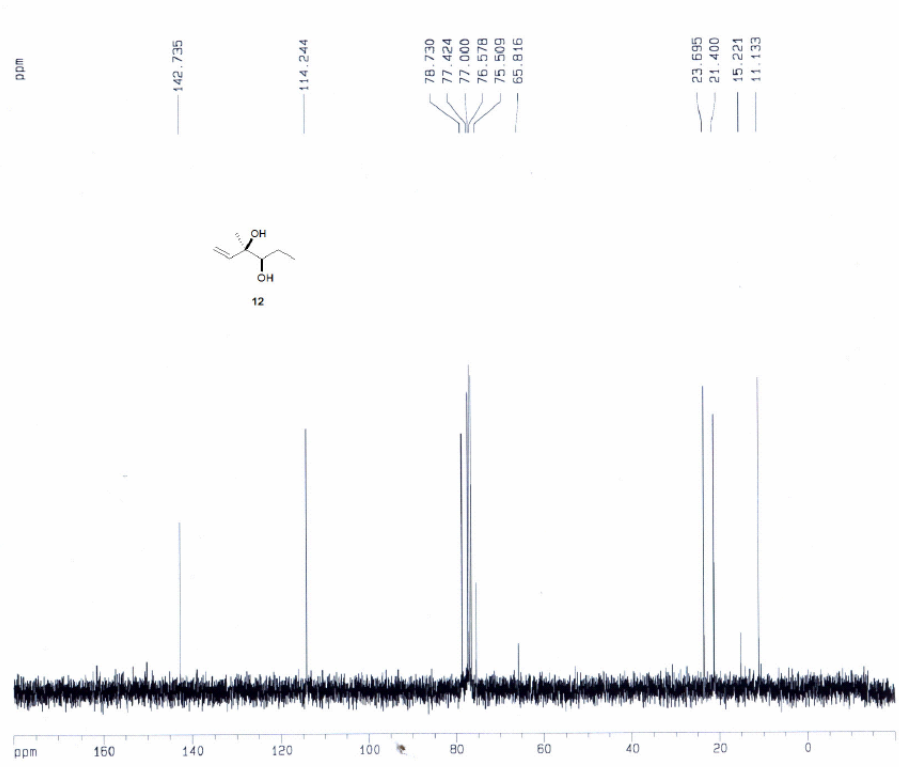


Current Data Parameters
NAME ryk
EXPNO 89
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050923
Time 22.39
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542560 sec
RG 161
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 19.50 usec
SFO1 300.1318534 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

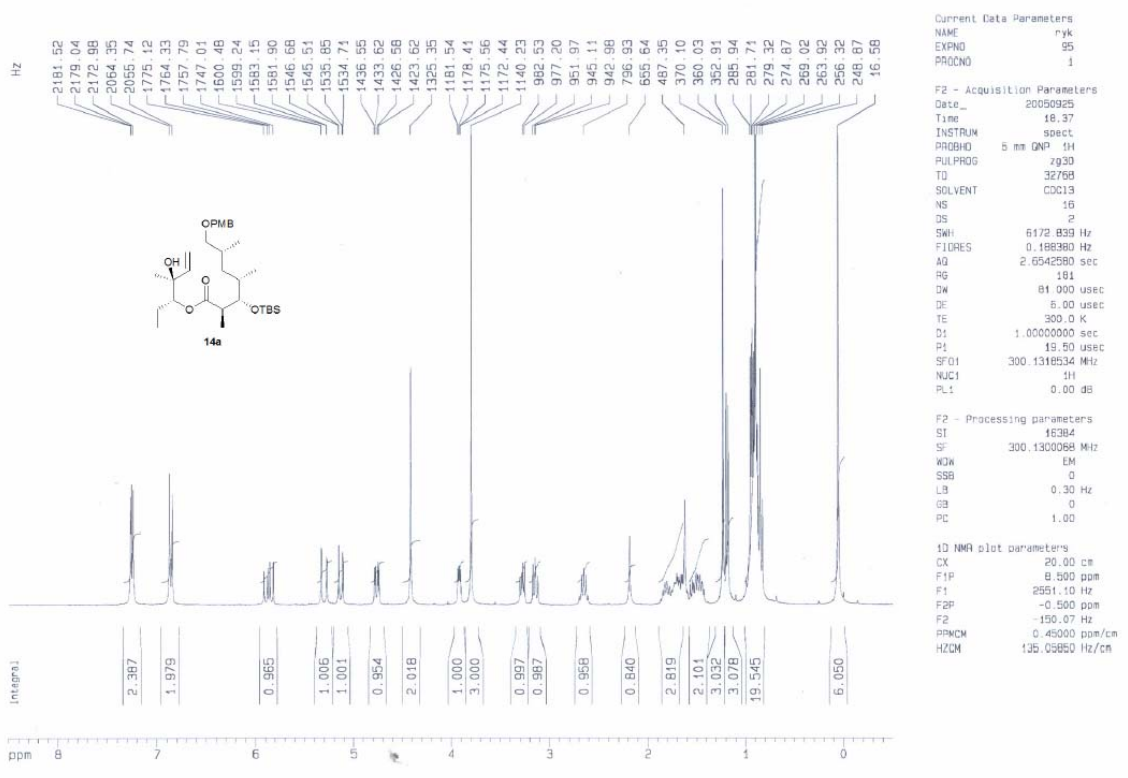


Current Data Parameters
NAME ryk
EXPNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050923
Time 22.47
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 69
DS 2
SWH 19607.844 Hz
FIDRES 0.299192 Hz
AQ 1.6712180 sec
RG 9192
DW 25.500 usec
DE 6.00 usec
TE 300.0 K
D12 0.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1312005 MHz
NUC2 1H
PL2 0.00 dB
PL12 18.00 dB
P4 21.00 usec
SFO1 75.4760204 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 75.4677502 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 180.000 ppm
F1 13584.20 Hz
F2P -20.000 ppm
F2 -1509.35 Hz
PPMCM 10.00000 ppm/cm
HZCM 754.67749 Hz/cm

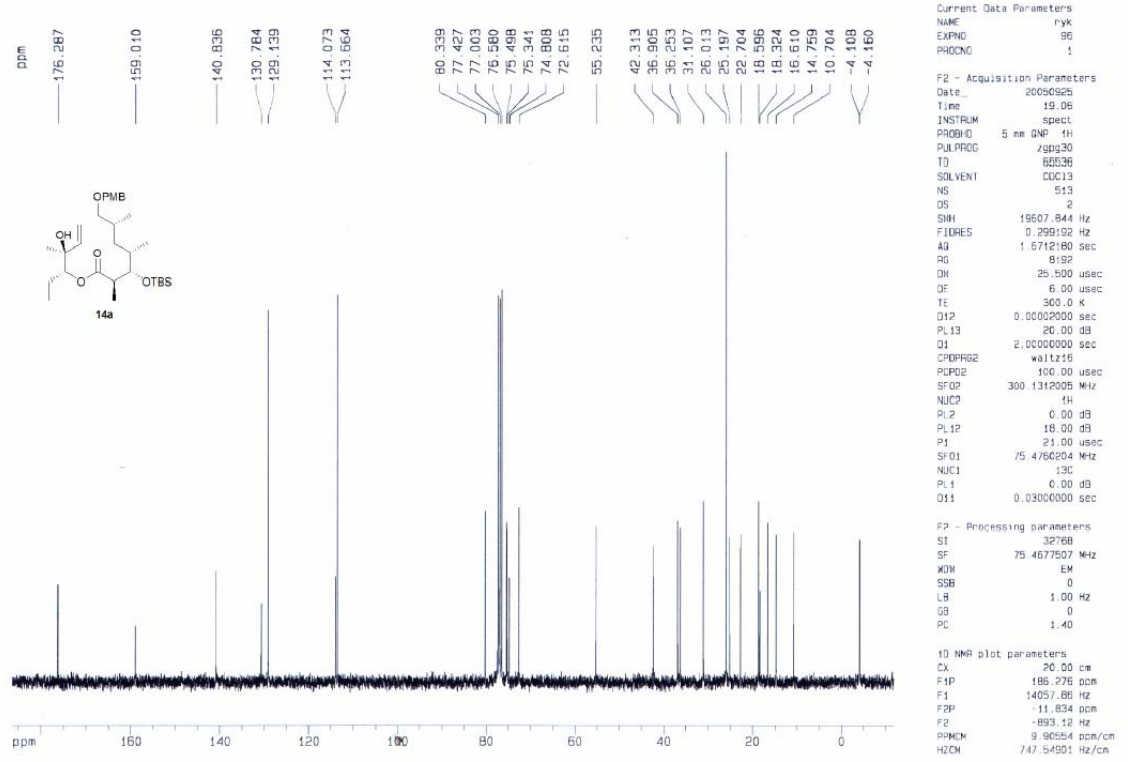


Current Data Parameters
NAME ryk
EXPNO 95
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050925
Time 18.37
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 19.50 usec
SFO1 300.1316534 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

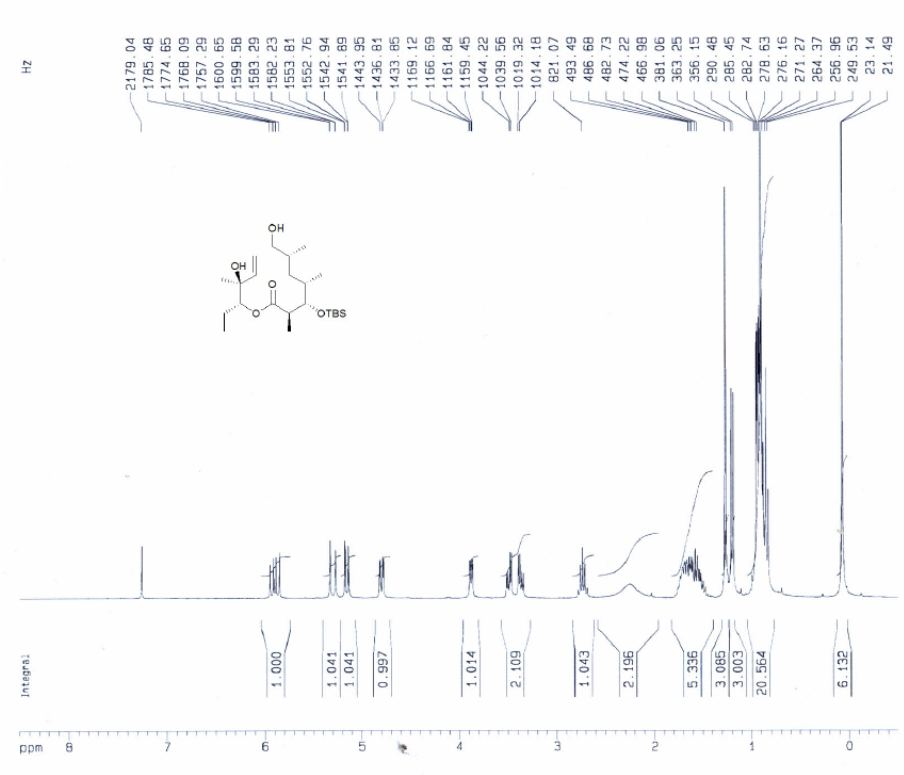


Current Data Parameters
NAME ryk
EXPNO 96
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050925
Time 19.06
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 513
DS 2
SWH 19607.844 Hz
FIDRES 0.299192 Hz
AQ 1.6712180 sec
RG 8192
DW 25.500 usec
DE 6.00 usec
TE 300.0 K
D12 0.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1312005 MHz
NUC2 1H
PL2 0.00 dB
PL12 18.00 dB
P1 21.00 usec
SFO1 75.4760204 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 75.4677507 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 186.276 ppm
F1 14057.86 Hz
F2P -11.834 ppm
F2 -893.12 Hz
PPMCM 9.90554 ppm/cm
HZCM 747.54901 Hz/cm

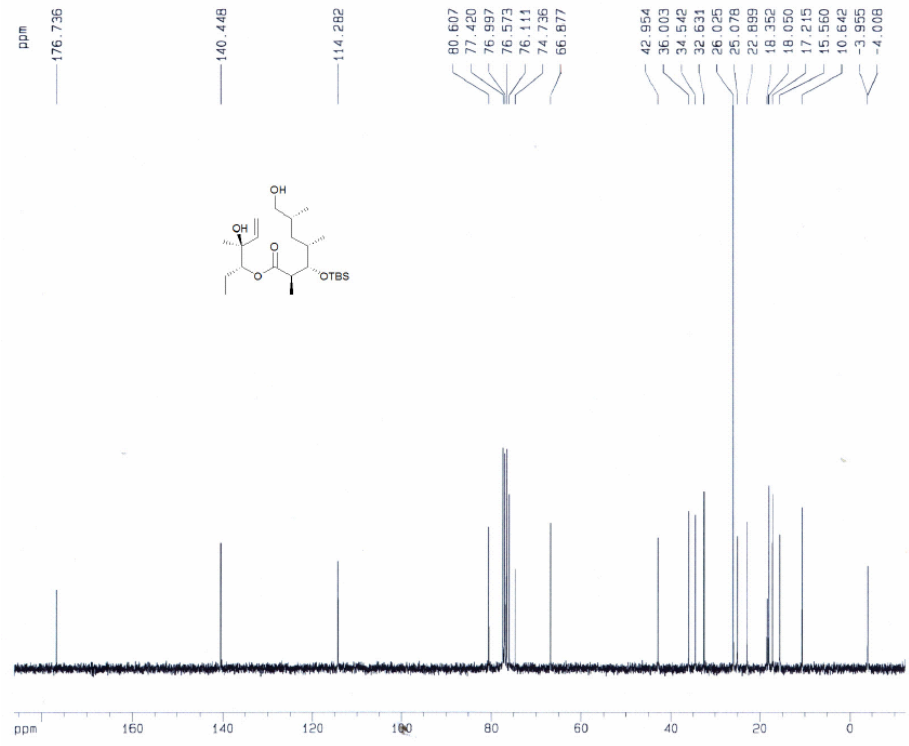



```
Current Data Parameters
NAME                  nyk
EXPNO                  55
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050914
Time                  1.46
INSTRUM              spect
PROBHD     5 mm GNP  1H
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                    90.5
DW                  81.000 usec
DE                   6.00 usec
TE                  300.0 K
D1                 1.00000000 sec
P1                   19.50 usec
SFO1              300.1318534 MHz
NUC1                    1H
PL1                  0.00 dB

F2 - Processing parameters
SI                      16384
SF                300.1300068 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  8.500 ppm
F1                 2551.10 Hz
F2P                 -0.500 ppm
F2                 -150.07 Hz
PPMCM                0.46000 ppm/cm
HZCM               135.08860 Hz/cm
```

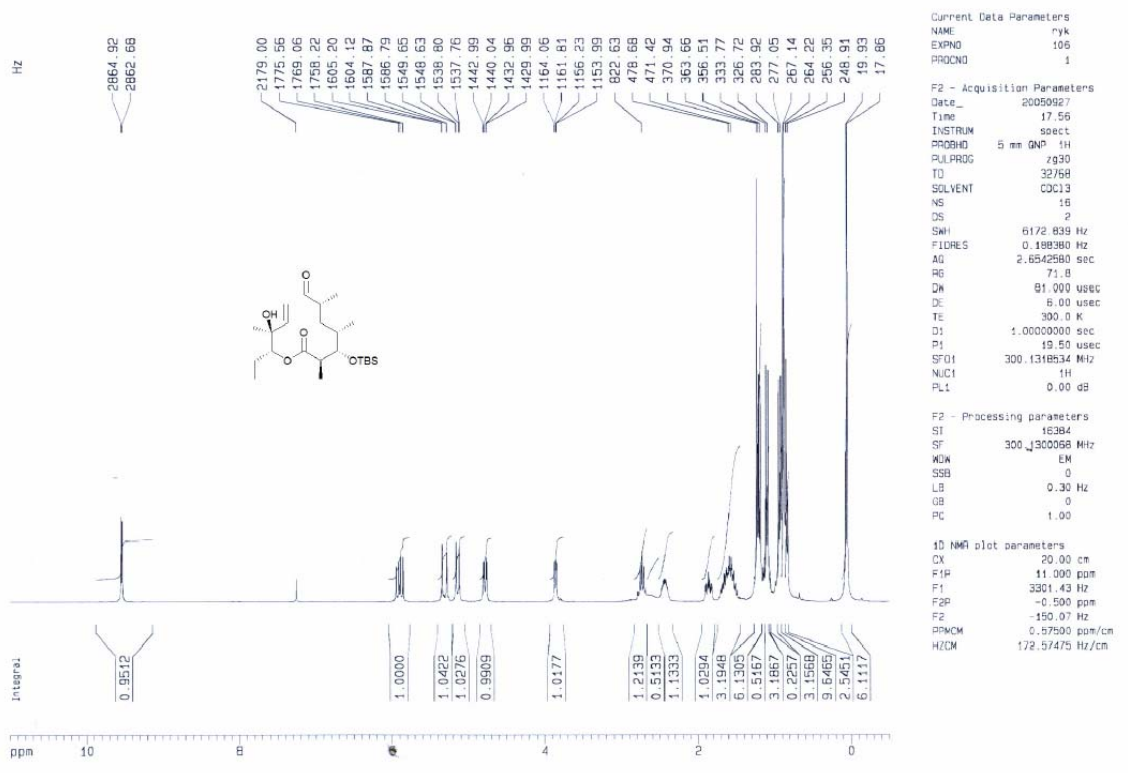



```
Current Data Parameters
NAME                  nyk
EXPNO                 101
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050926
Time                 18.55
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG              zgpg30
TD                  65536
SOLVENT              CDCl3
NS                     251
DS                       2
SWH                19607.844 Hz
FIDRES             0.299192 Hz
AQ                 1.6712180 sec
RG                    8192
DW                  25.500 usec
DE                   6.00 usec
TE                  300.0 K
D12                0.00002000 sec
PL13                 20.00 dB
D1                 2.00000000 sec
CPDPRG2              waltz16
PCPD2              100.00 usec
SFO2              300.1312005 MHz
NUC2                    1H
PL2                  0.00 dB
PL12                 18.00 dB
P1                   21.00 usec
SFO1               75.4760204 MHz
NUC1                    13C
PL1                  0.00 dB
D11                0.03000000 sec

F2 - Processing parameters
SI                      32768
SF                75.4677513 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                186.019 ppm
F1                 14038.41 Hz
F2P                -12.342 ppm
F2                 -931.42 Hz
PPMCM                9.91803 ppm/cm
HZCM               748.49176 Hz/cm
```

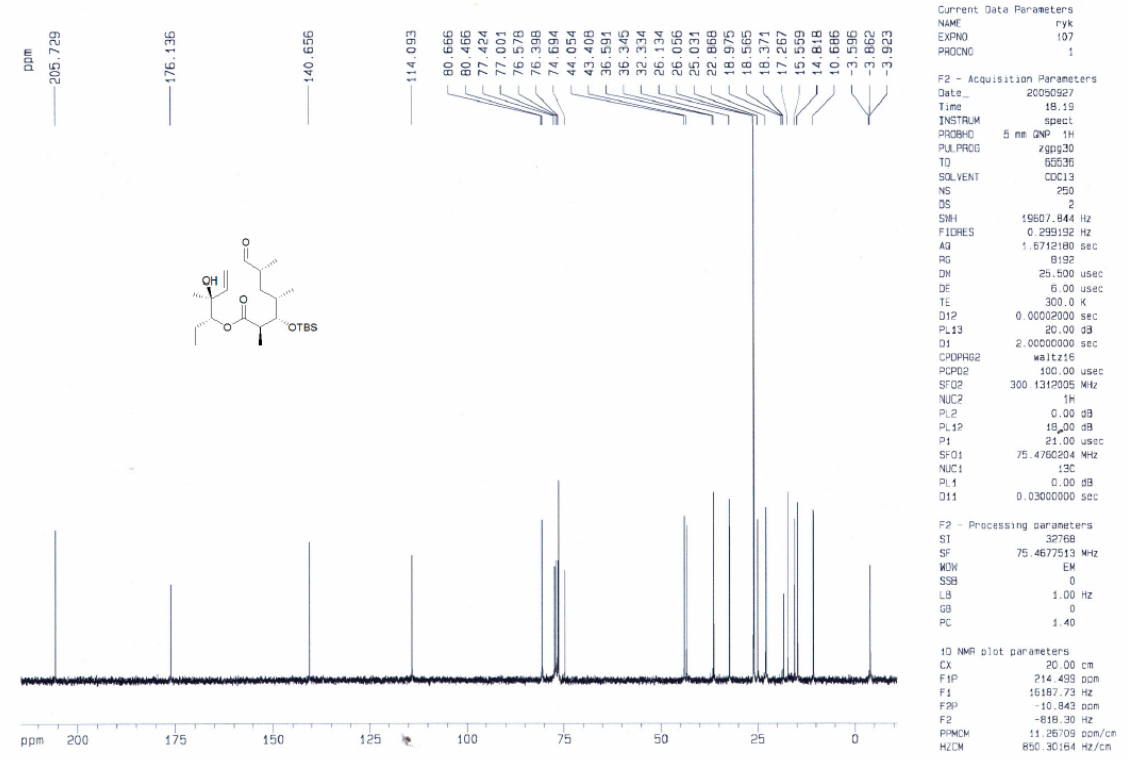



```
Current Data Parameters
NAME                  ryk
EXPNO                 106
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050927
Time                 17.56
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                    71.8
DW                91.000 usec
DE                 6.00 usec
TE                 300.0 K
D1                1.00000000 sec
P1                   9.50 usec
SFO1            300.1318534 MHz
NUC1                   1H
PL1                 0.00 dB

F2 - Processing parameters
SI                    16384
SF              300.1300068 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                11.000 ppm
F1                3301.43 Hz
F2P                -0.500 ppm
F2                -150.07 Hz
PPMCM             0.57500 ppm/cm
HZCM            172.57475 Hz/cm
```

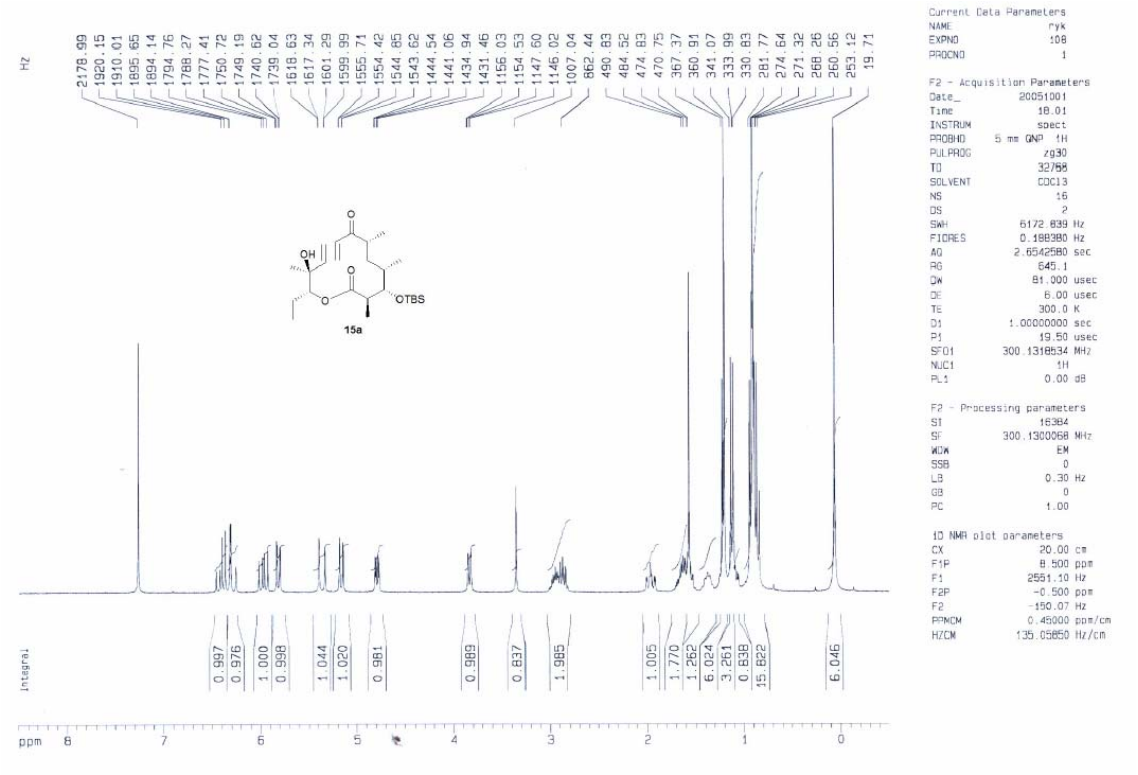



```
Current Data Parameters
NAME                  ryk
EXPNO                 107
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050927
Time                 18.19
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      250
DS                       2
SWH              19607.844 Hz
FIDRES            0.299192 Hz
AQ                1.6712180 sec
RG                    8192
DW                25.500 usec
DE                 6.00 usec
TE                 300.0 K
D12               0.00002000 sec
PL13                20.00 dB
D1                2.00000000 sec
CPDPRG2             waltz16
PCPD2              100.00 usec
SFO2            300.1312005 MHz
NUC2                   1H
PL2                 0.00 dB
PL12               18.00 dB
P1                  21.00 usec
SFO1             75.4760204 MHz
NUC1                   13C
PL1                 0.00 dB
D11               0.03000000 sec

F2 - Processing parameters
SI                    32768
SF               75.4677513 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P                214.499 ppm
F1               16187.73 Hz
F2P                -10.843 ppm
F2                -818.30 Hz
PPMCM             11.26709 ppm/cm
HZCM             850.30164 Hz/cm
```

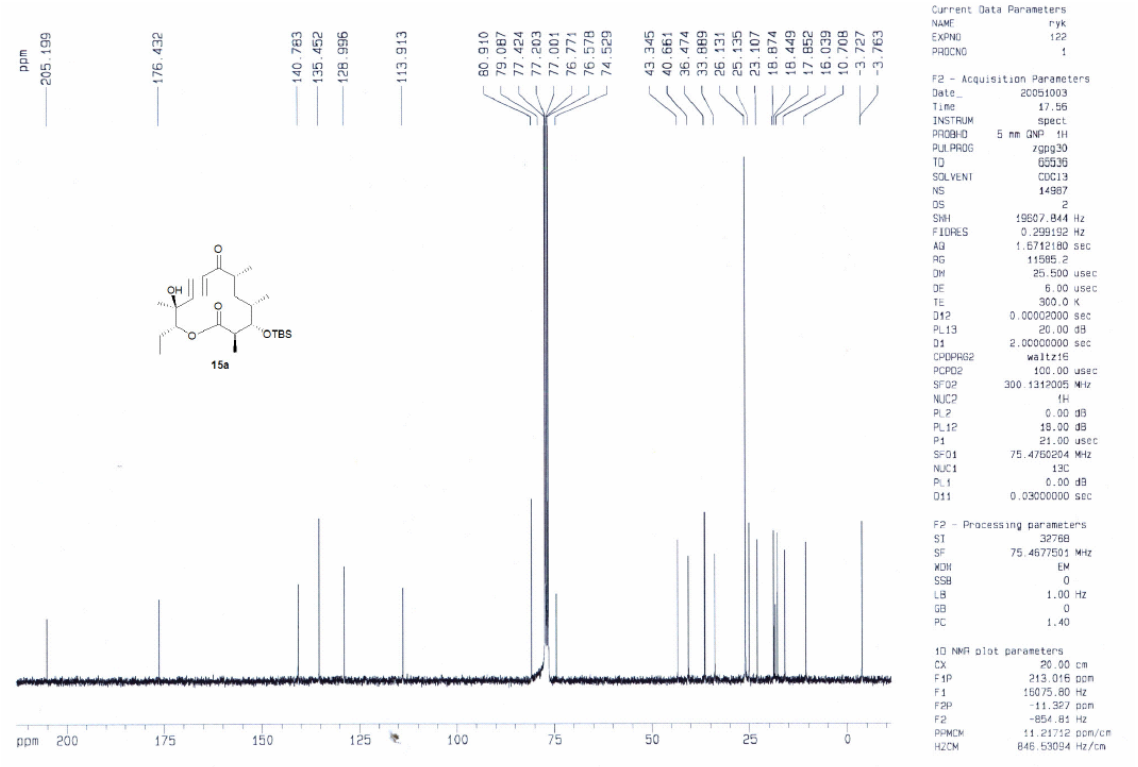


Current Data Parameters
NAME ryk
EXPNO 108
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051001
Time 18.01
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 19.50 usec
SFO1 300.1318534 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

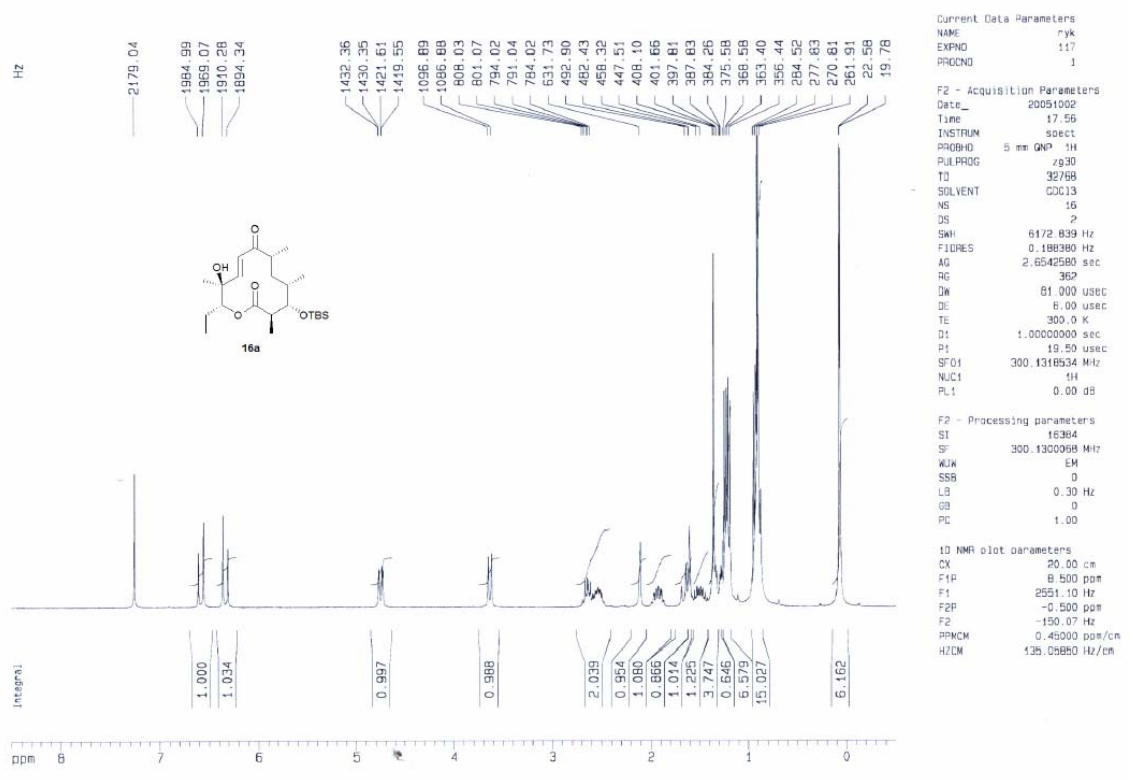


Current Data Parameters
NAME ryk
EXPNO 122
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051003
Time 17.56
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 14987
DS 2
SWH 19607.844 Hz
FIDRES 0.299192 Hz
AQ 1.6712180 sec
RG 11585.2
DW 25.500 usec
DE 6.00 usec
TE 300.0 K
D12 0.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1312005 MHz
NUC2 1H
PL2 0.00 dB
PL12 18.00 dB
P1 21.00 usec
SFO1 75.4760204 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 75.4677501 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 213.016 ppm
F1 16075.80 Hz
F2P -11.327 ppm
F2 -854.81 Hz
PPMCM 11.21712 ppm/cm
HZCM 846.59094 Hz/cm

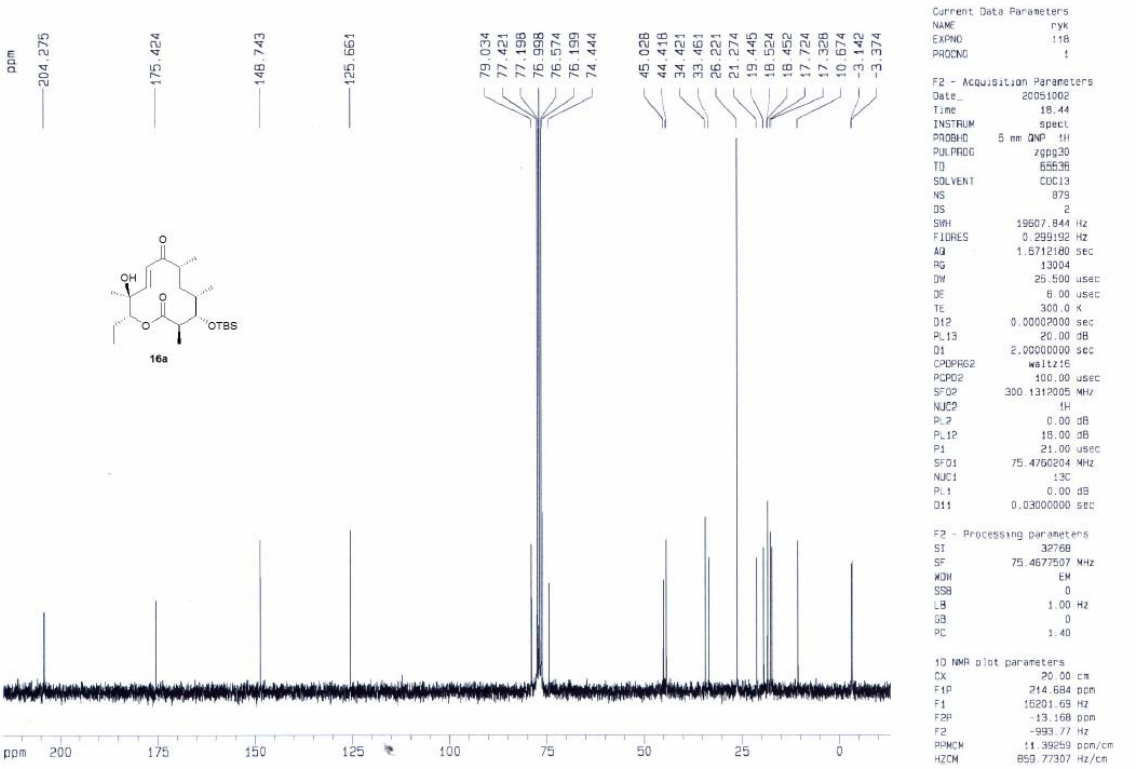



```
Current Data Parameters
NAME                  ryk
EXPNO                 117
PROCNO                  1

F2 - Acquisition Parameters
Date_              20051002
Time                 17.56
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                     362
DW                81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1                1.00000000 sec
P1                  19.50 usec
SFO1             300.1318534 MHz
NUC1                   1H
PL1                 0.00 dB

F2 - Processing parameters
SI                    16384
SF               300.1300068 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 8.500 ppm
F1                2551.10 Hz
F2P                -0.500 ppm
F2                -150.07 Hz
PPMCM             0.45000 ppm/cm
HZCM              135.05850 Hz/cm
```

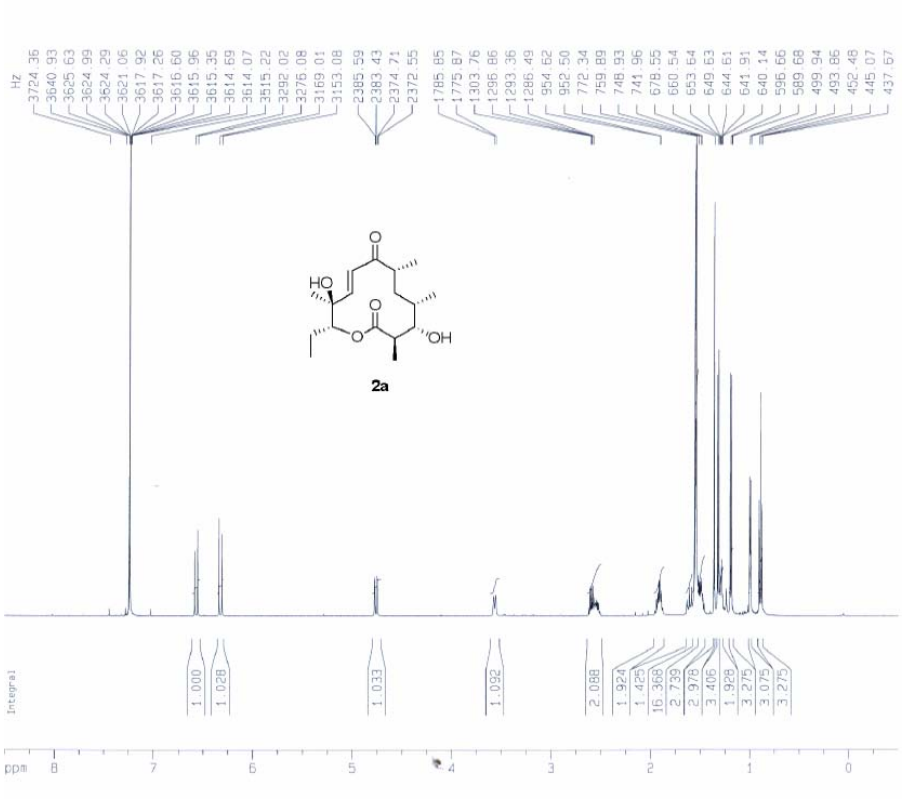



```
Current Data Parameters
NAME                  ryk
EXPNO                 118
PROCNO                  1

F2 - Acquisition Parameters
Date_              20051002
Time                 18.44
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     879
DS                       2
SWH              19607.844 Hz
FIDRES            0.299192 Hz
AQ                1.6712180 sec
RG                   13004
DW                25.500 usec
DE                 6.00 usec
TE                 300.0 K
D12               0.00002000 sec
PL13                20.00 dB
D1                2.00000000 sec
CPDPRG2            waltz16
PCPD2              100.00 usec
SFO2             300.1312005 MHz
NUC2                   1H
PL2                 0.00 dB
PL12                18.00 dB
P1                  21.00 usec
SFO1              75.4760204 MHz
NUC1                   13C
PL1                 0.00 dB
D11               0.03000000 sec

F2 - Processing parameters
SI                    32768
SF               75.4677507 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                214.684 ppm
F1                16201.69 Hz
F2P                -13.168 ppm
F2                 -993.77 Hz
PPMCM             11.39259 ppm/cm
HZCM              859.77307 Hz/cm
```



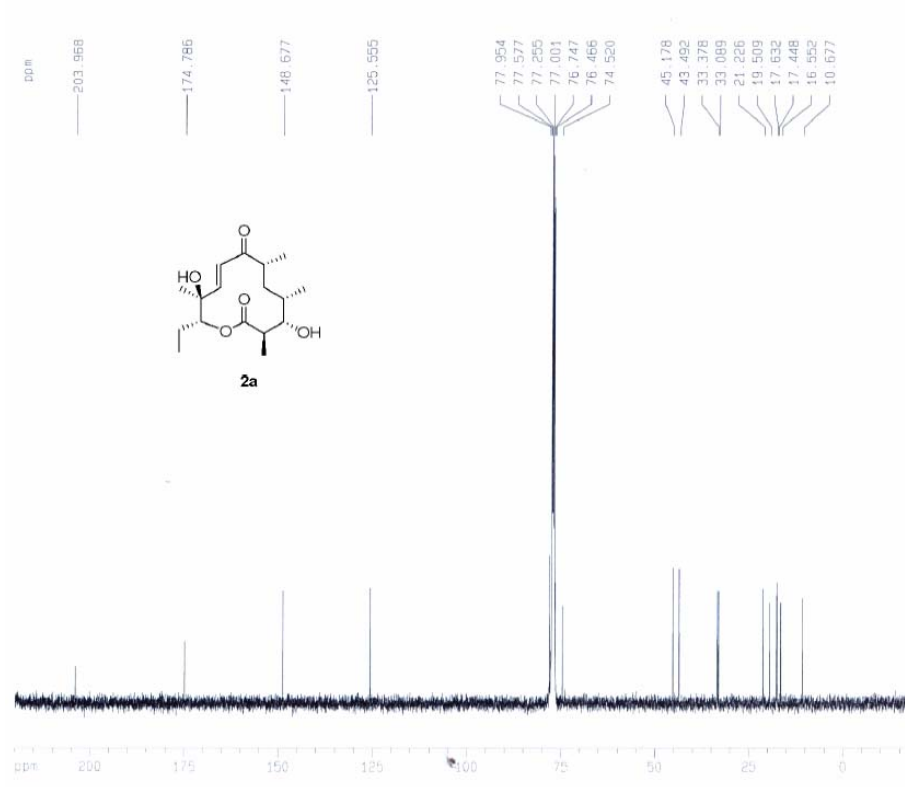
Current Data Parameters
NAME 20050921
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050922
Time 18.21
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 256
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 812.7
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.80 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300231 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 30.00 cm
F1P 8.500 ppm
F1 4251.11 Hz
F2P -0.500 ppm
F2 -250.06 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05850 Hz/cm



Current Data Parameters
NAME 20050921
EXPNO 5
PROCNO 1

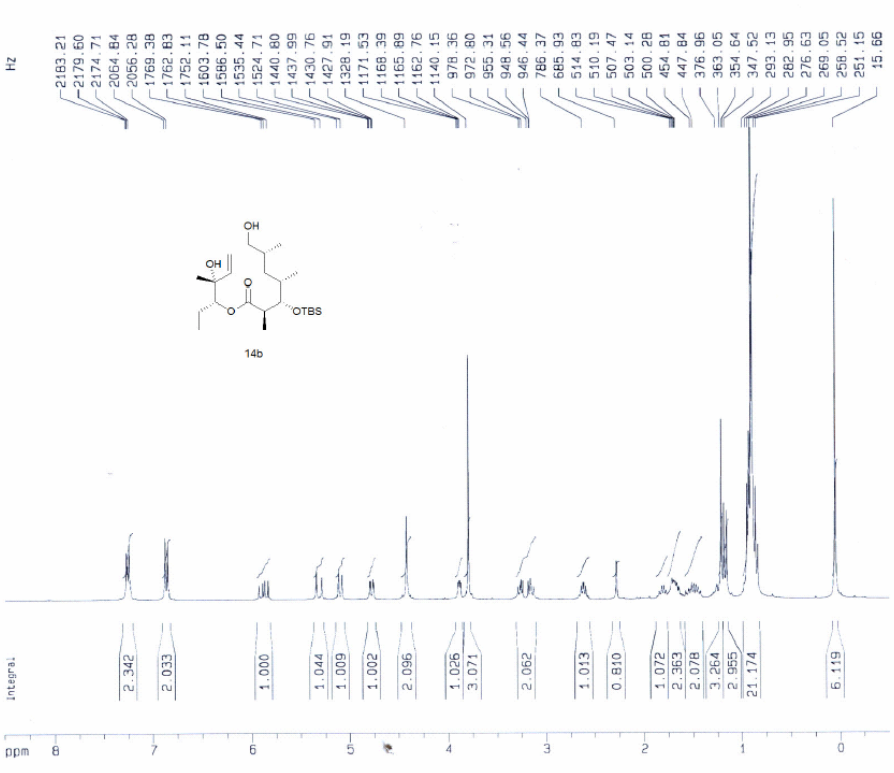
F2 - Acquisition Parameters
Date_ 20050923
Time 8.46
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 19946
DS 4
SWH 31446.541 Hz
FIDRES 0.479836 Hz
AQ 1.0420883 sec
RG 512
DW 15.900 usec
DE 6.00 usec
TE 298.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 2.60 dB
SFO1 125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.80 dB
PL12 21.72 dB
PL13 23.00 dB
SFO2 500.1325006 MHz

F2 - Processing parameters
SI 32768
SF 125.7577909 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 3.00 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -20.000 ppm
F2 -2515.15 Hz
PPMCM 12.00000 ppm/cm
HZCM 1509.09338 Hz/cm

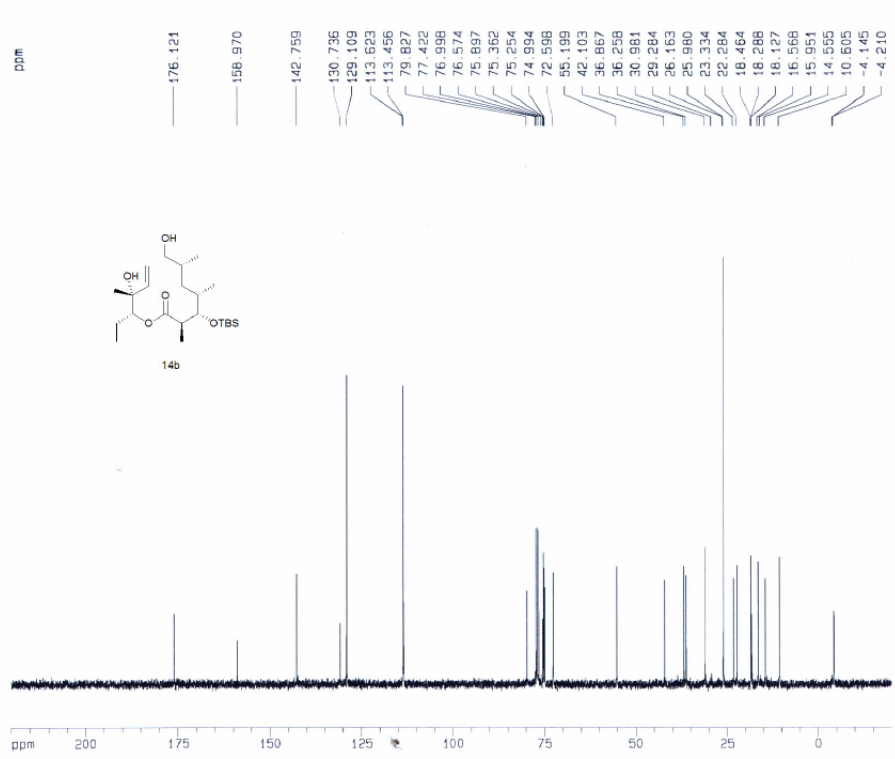



```
Current Data Parameters
NAME                  ryk
EXPNO                  55
PROCNO                  1

F2 - Acquisition Parameters
Date_              20070219
Time                   8.36
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG               zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.824 Hz
FIDRES             0.188380 Hz
AQ                 2.6542649 sec
RG                      90.5
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                 1.00000000 sec
P1                   18.00 usec
SFO1             300.1310765 MHz
NUC1                    1H
PL1                   0.00 dB

F2 - Processing parameters
SI                      16384
SF               300.1300048 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  8.500 ppm
F1                 2551.10 Hz
F2P                 -0.500 ppm
F2                  -150.07 Hz
PPMCM              0.45000 ppm/cm
HZCM             135.05850 Hz/cm
```

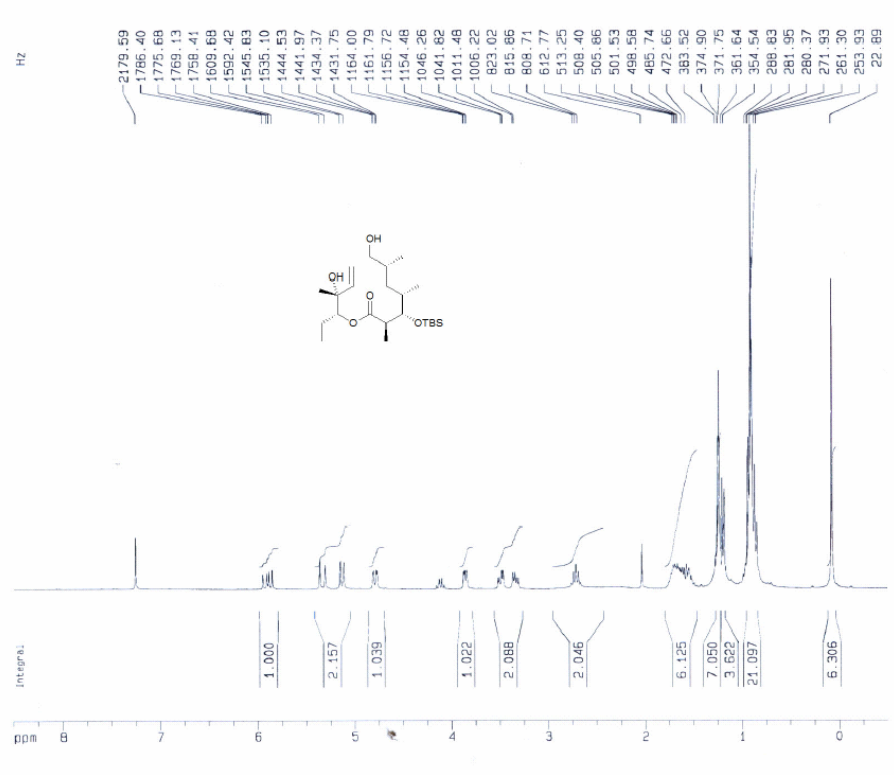



```
Current Data Parameters
NAME                  ryk
EXPNO                  56
PROCNO                  1

F2 - Acquisition Parameters
Date_              20070219
Time                   8.46
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      165
DS                        2
SWH               19607.844 Hz
FIDRES             0.299192 Hz
AQ                 1.6712180 sec
RG                    9195.2
DW                   25.500 usec
DE                    6.00 usec
TE                   300.0 K
D12                0.00002000 sec
PL13                 20.00 dB
D1                 2.00000000 sec
CPDPRG2             waltz16
PCPD2                100.00 usec
SFO2             300.1312005 MHz
NUC2                    1H
PL2                   0.00 dB
PL12                 18.00 dB
P1                   21.00 usec
SFO1              75.4760204 MHz
NUC1                    13C
PL1                   0.00 dB
D11                0.03000000 sec

F2 - Processing parameters
SI                       32768
SF                75.4677525 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                220.000 ppm
F1                 16602.90 Hz
F2P                -20.000 ppm
F2                 -1509.35 Hz
PPMCM             12.00000 ppm/cm
HZCM              905.61304 Hz/cm
```

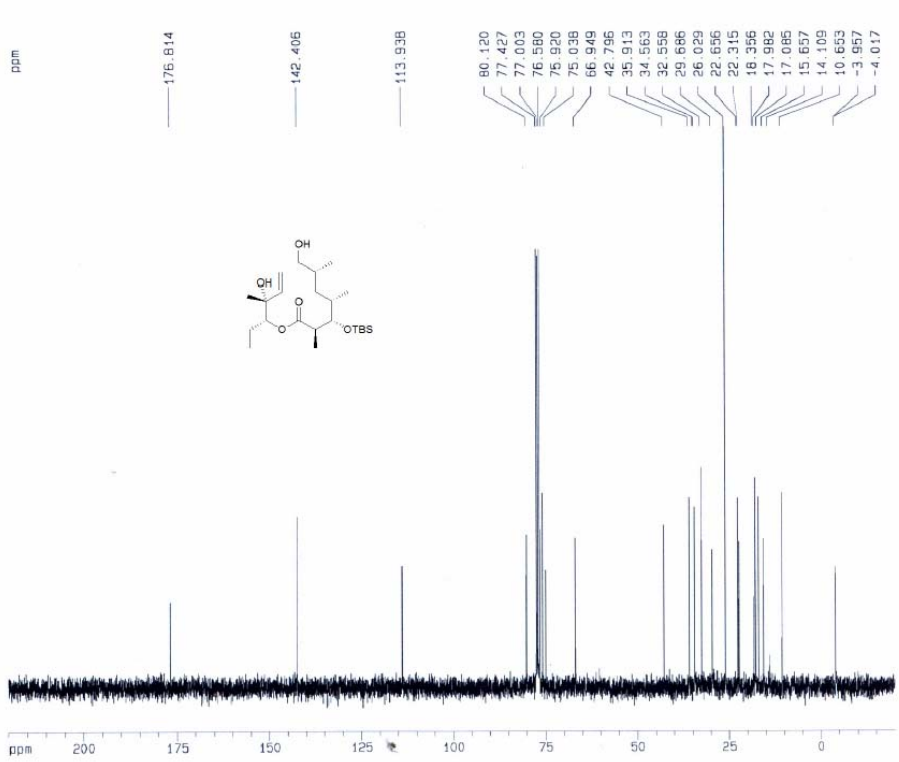


Current Data Parameters
NAME ryk
EXPNO 60
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070220
Time 10.02
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.824 Hz
FIDRES 0.188380 Hz
AQ 2.6542649 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 18.00 usec
SFO1 300.1310765 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300048 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

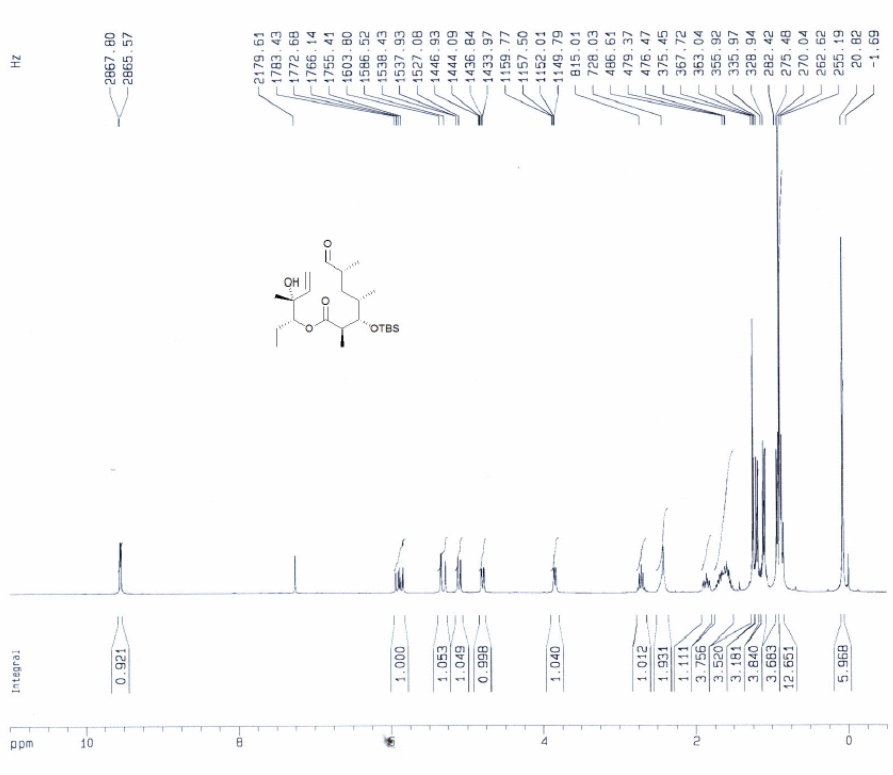


Current Data Parameters
NAME ryk
EXPNO 61
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070220
Time 10.09
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 176
DS 2
SWH 19607.844 Hz
FIDRES 0.299192 Hz
AQ 1.6712180 sec
RG 9195.2
DW 25.500 usec
DE 6.00 usec
TE 300.0 K
D12 0.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1312005 MHz
NUC2 1H
PL2 0.00 dB
PL12 18.00 dB
P1 21.00 usec
SFO1 75.4760204 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 75.4677507 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -20.000 ppm
F2 -1509.35 Hz
PPMCM 12.00000 ppm/cm
HZCM 905.61304 Hz/cm

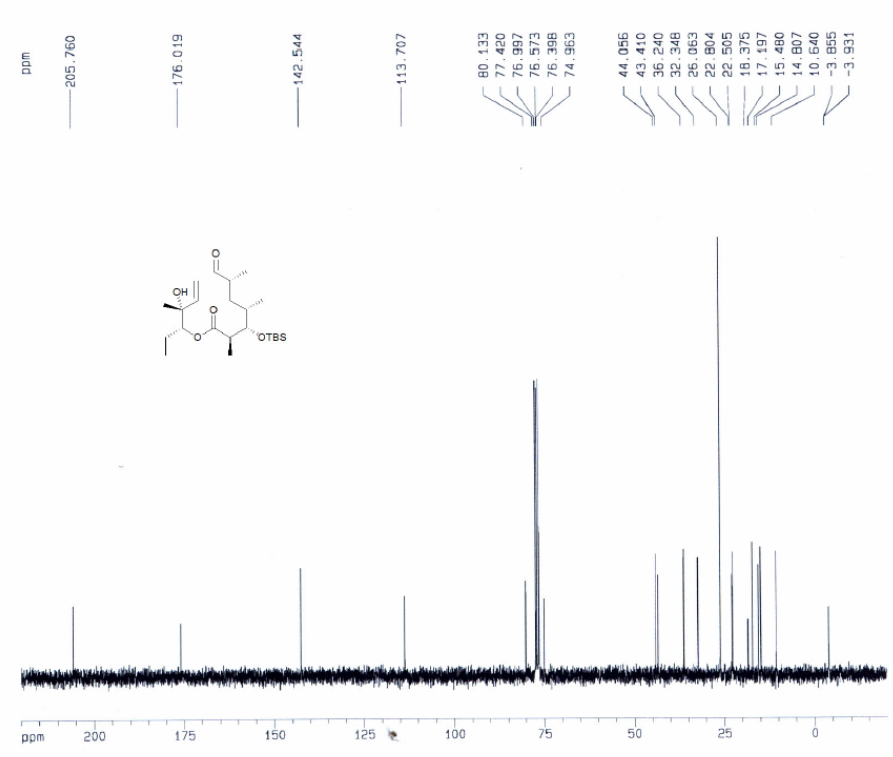


Current Data Parameters
NAME ryk
EXPNO 67
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070224
Time 5.29
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6172.824 Hz
FIDRES 0.188380 Hz
AQ 2.6542649 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 18.00 usec
SFO1 300.1310765 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300048 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 3301.43 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.57500 ppm/cm
HZCM 172.57475 Hz/cm

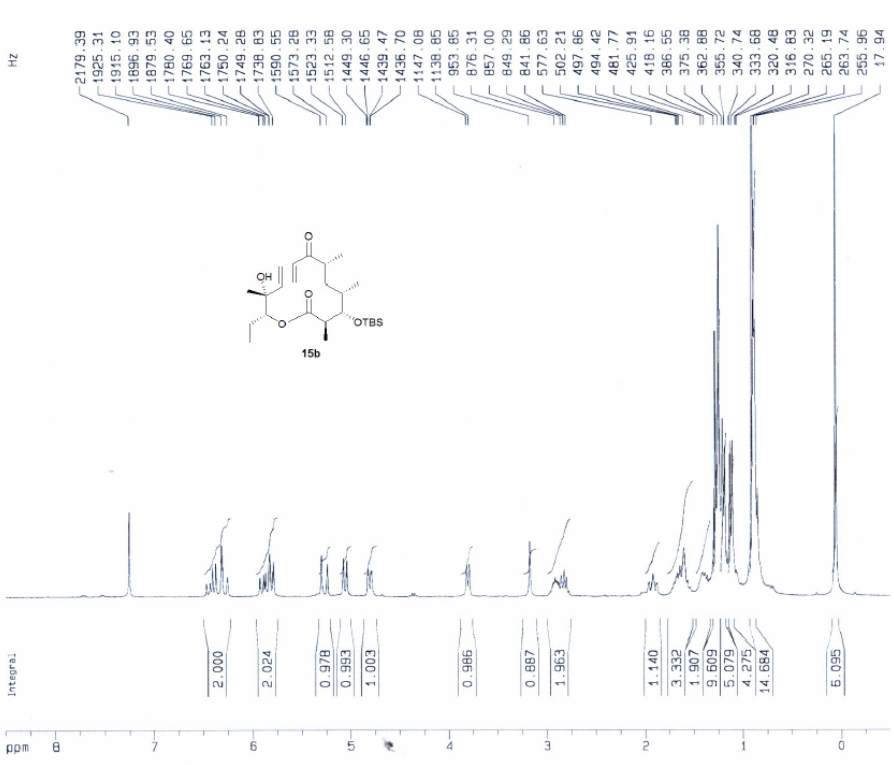


Current Data Parameters
NAME ryk
EXPNO 68
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070224
Time 5.39
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 19607.844 Hz
FIDRES 0.299192 Hz
AQ 1.6712180 sec
RG 9195.2
DW 25.500 usec
DE 6.00 usec
TE 300.0 K
D12 0.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1312005 MHz
NUC2 1H
PL2 0.00 dB
PL12 18.00 dB
P1 21.00 usec
SFO1 75.4760204 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 75.4677513 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -20.000 ppm
F2 -1509.35 Hz
PPMCM 12.00000 ppm/cm
HZCM 905.61304 Hz/cm

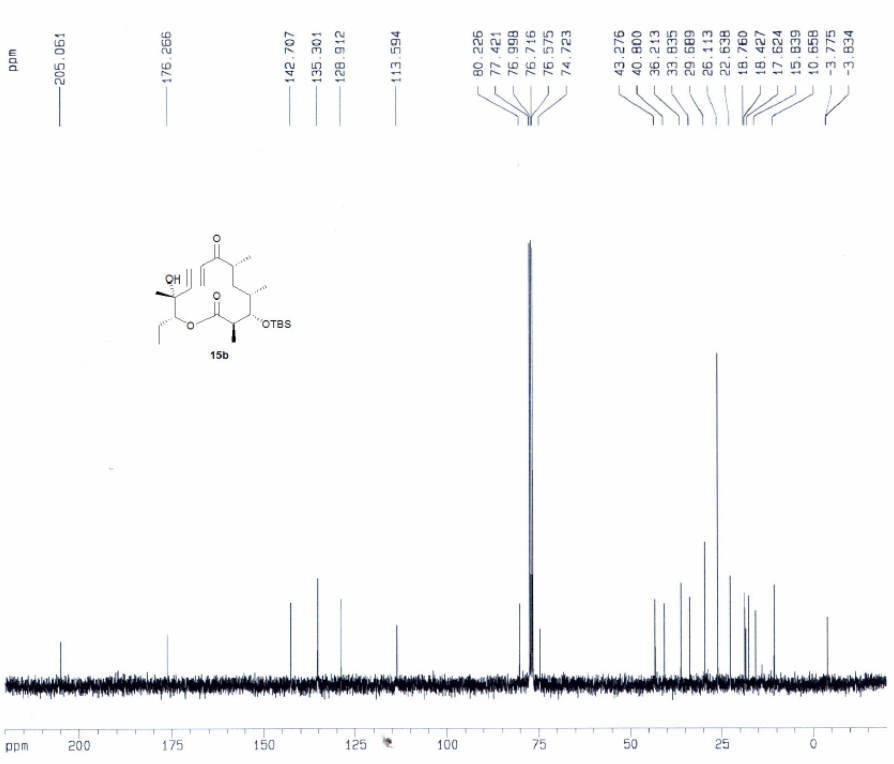



```
Current Data Parameters
NAME                  ryk
EXPNO                  72
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070225
Time                6.46
INSTRUM            spect
PROBHD     5 mm GNP  1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6172.824 Hz
FIDRES          0.188380 Hz
AQ              2.6542649 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1              1.00000000 sec
P1                18.00 usec
SFO1          300.1310765 MHz
NUC1                  1H
PL1                0.00 dB

F2 - Processing parameters
SI                 16384
SF            300.1300051 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1                2551.10 Hz
F2P               -0.500 ppm
F2                -150.07 Hz
PPMCM          0.45000 ppm/cm
HZCM          135.05850 Hz/cm
```

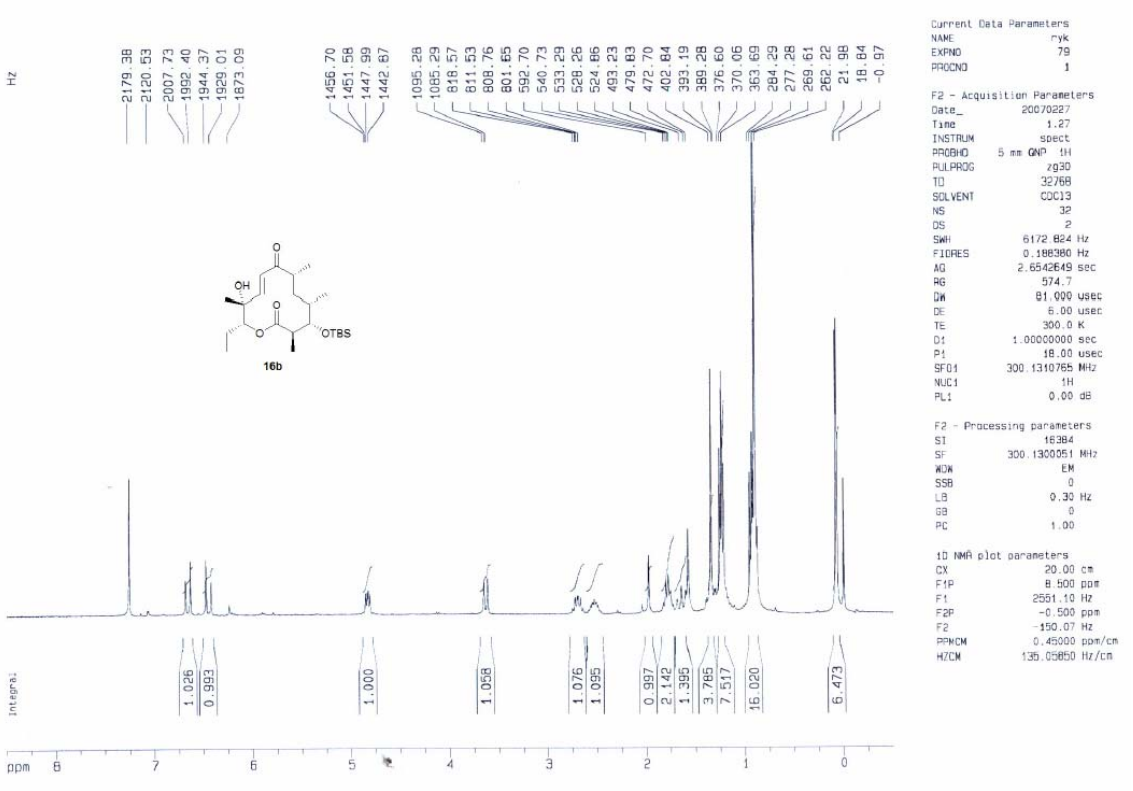



```
Current Data Parameters
NAME                  ryk
EXPNO                  73
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070225
Time                6.52
INSTRUM            spect
PROBHD     5 mm GNP  1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   264
DS                     2
SWH            19607.844 Hz
FIDRES          0.299192 Hz
AQ              1.6712180 sec
RG                  9195.2
DW                25.500 usec
DE                 6.00 usec
TE                300.0 K
D12             0.00002000 sec
PL13               20.00 dB
D1              2.00000000 sec
CPDPRG2           waltz16
PCPD2             100.00 usec
SFO2          300.1312005 MHz
NUC2                  1H
PL2                0.00 dB
PL12              18.00 dB
P1                21.00 usec
SFO1           75.4760204 MHz
NUC1                  13C
PL1                0.00 dB
D11             0.03000000 sec

F2 - Processing parameters
SI                 32768
SF            75.4677507 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              220.000 ppm
F1              16602.90 Hz
F2P              -20.000 ppm
F2              -1509.35 Hz
PPMCM          12.00000 ppm/cm
HZCM          905.61304 Hz/cm
```

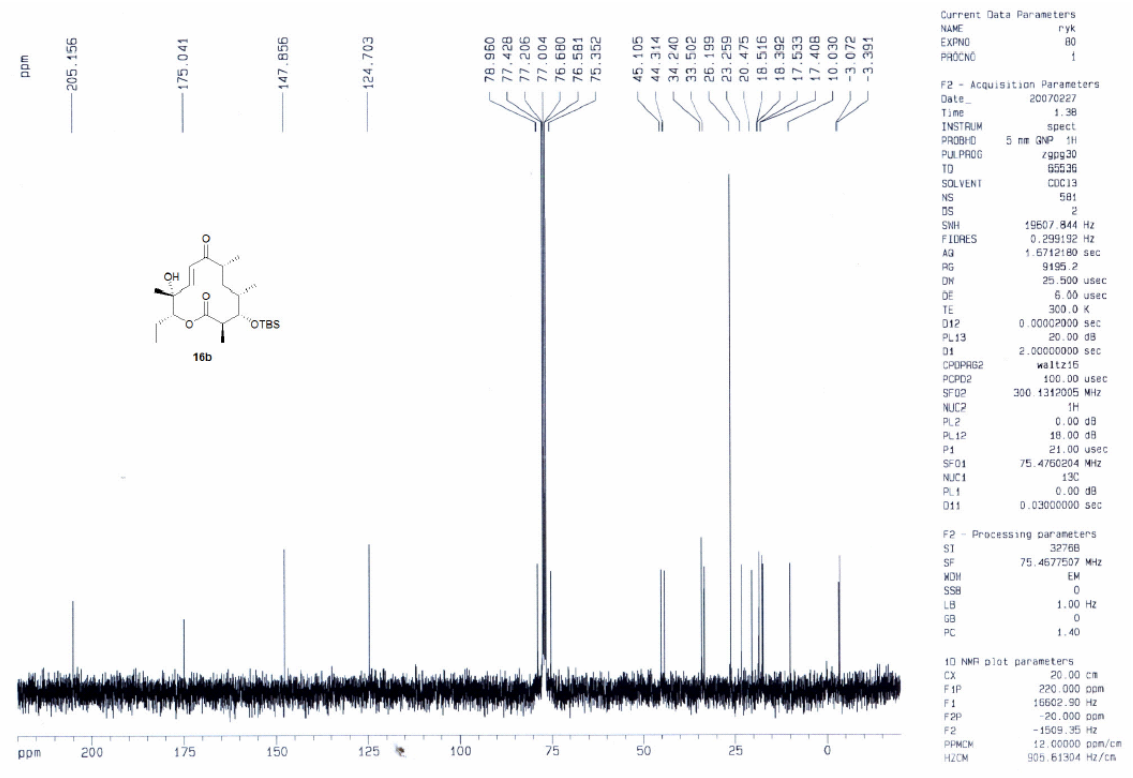



```
Current Data Parameters
NAME                  ryk
EXPNO                  79
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070227
Time                1.27
INSTRUM            spect
PROBHD     5 mm GNP 1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH              6172.824 Hz
FIDRES           0.188380 Hz
AQ               2.6542649 sec
RG                 574.7
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1              1.00000000 sec
P1                18.00 usec
SFO1           300.1310765 MHz
NUC1                  1H
PL1                0.00 dB

F2 - Processing parameters
SI                 16384
SF            300.1300051 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1              2551.10 Hz
F2P               -0.500 ppm
F2              -150.07 Hz
PPMCM           0.45000 ppm/cm
HZCM          135.05850 Hz/cm
```

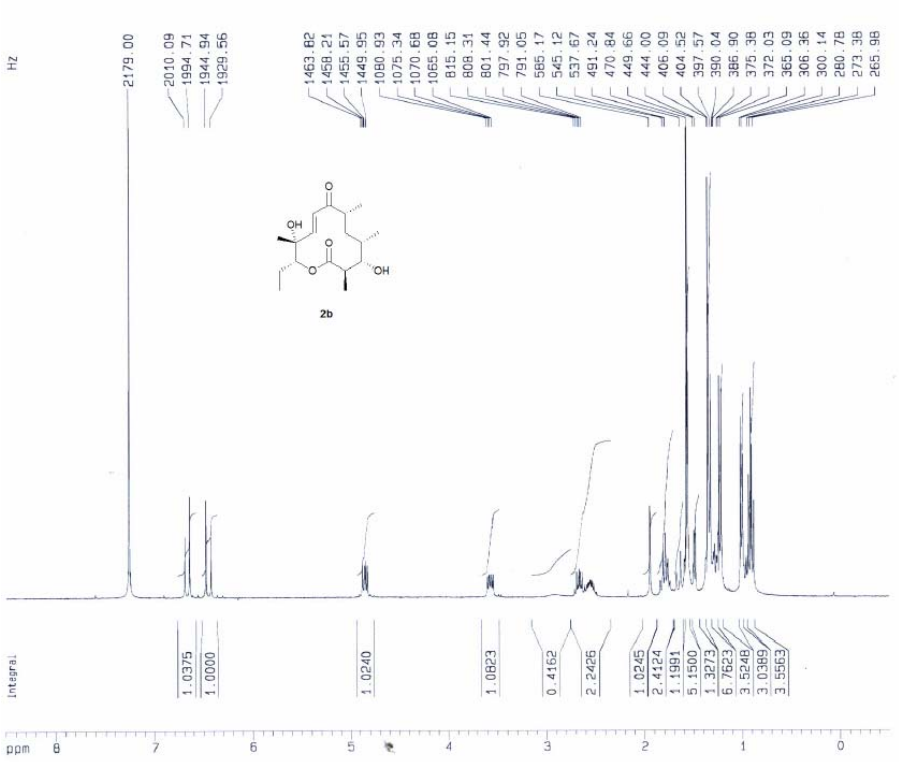



```
Current Data Parameters
NAME                  ryk
EXPNO                  80
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070227
Time                1.38
INSTRUM            spect
PROBHD     5 mm GNP 1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   581
DS                     2
SWH             19607.844 Hz
FIDRES           0.299192 Hz
AQ               1.6712180 sec
RG                 9195.2
DW                25.500 usec
DE                 6.00 usec
TE                300.0 K
D12             0.00002000 sec
PL13               20.00 dB
D1              2.00000000 sec
CPDPRG2          waltz16
PCPD2             100.00 usec
SFO2           300.1312005 MHz
NUC2                  1H
PL2                0.00 dB
PL12               18.00 dB
P1                21.00 usec
SFO1           75.4760204 MHz
NUC1                  13C
PL1                0.00 dB
D11             0.03000000 sec

F2 - Processing parameters
SI                 32768
SF            75.4677507 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              220.000 ppm
F1              16602.90 Hz
F2P              -20.000 ppm
F2              -1509.35 Hz
PPMCM           12.00000 ppm/cm
HZCM          905.61304 Hz/cm
```

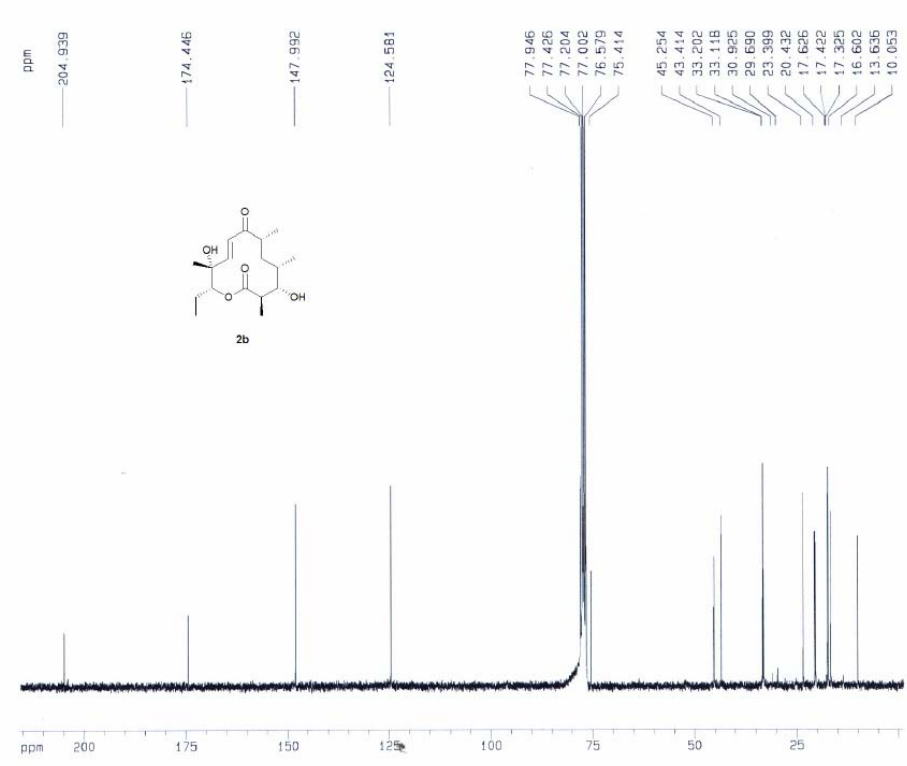



```
Current Data Parameters
NAME                  ryk
EXPNO                  23
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050906
Time                  3.17
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      64
DS                       2
SWH                6172.839 Hz
FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                   1290.2
DW                  81.000 usec
DE                   6.00 usec
TE                   300.0 K
D1                1.00000000 sec
P1                   19.50 usec
SFO1             300.1318534 MHz
NUC1                    1H
PL1                   0.00 dB

F2 - Processing parameters
SI                      16384
SF                300.1300068 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  8.500 ppm
F1                 2551.10 Hz
F2P                 -0.500 ppm
F2                 -150.07 Hz
PPMCM              0.45000 ppm/cm
HZCM             135.05850 Hz/cm
```

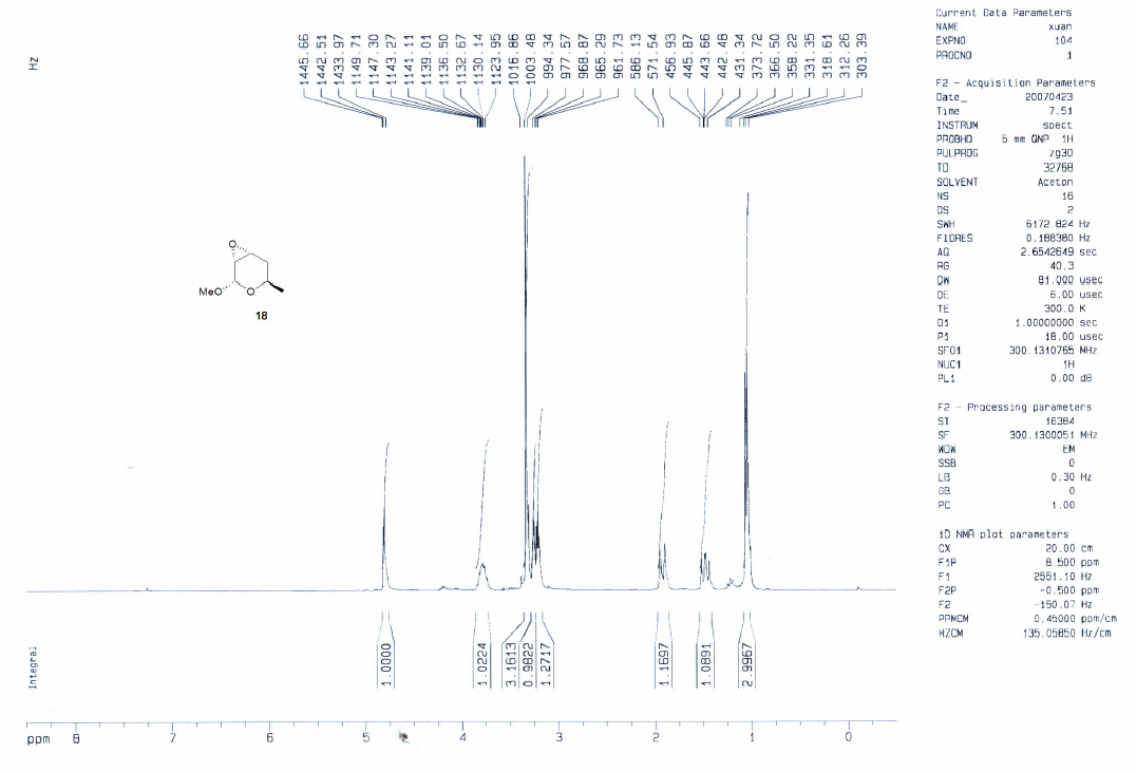



```
Current Data Parameters
NAME                  ryk
EXPNO                  30
PROCNO                  1

F2 - Acquisition Parameters
Date_              20050909
Time                 18.48
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG           zgpg30
TD                  65536
SOLVENT              CDCl3
NS                    6247G
DS                       2
SWH               19607.844 Hz
FIDRES            0.299192 Hz
AQ                1.6712180 sec
RG                    8192
DW                  25.500 usec
DE                   6.00 usec
TE                   300.0 K
D12               0.00002000 sec
PL13                 20.00 dB
D1                2.00000000 sec
CPDPRG2           waltz16
PCPD2               100.00 usec
SFO2             300.1312005 MHz
NUC2                    1H
PL2                   0.00 dB
PL12                 18.00 dB
P1                   21.00 usec
SFO1              75.4760204 MHz
NUC1                    13C
PL1                   0.00 dB
D11               0.03000000 sec

F2 - Processing parameters
SI                      32768
SF                75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                215.566 ppm
F1                 16268.31 Hz
F2P                 -1.274 ppm
F2                 -96.13 Hz
PPMCM             10.64201 ppm/cm
HZCM             818.22198 Hz/cm
```

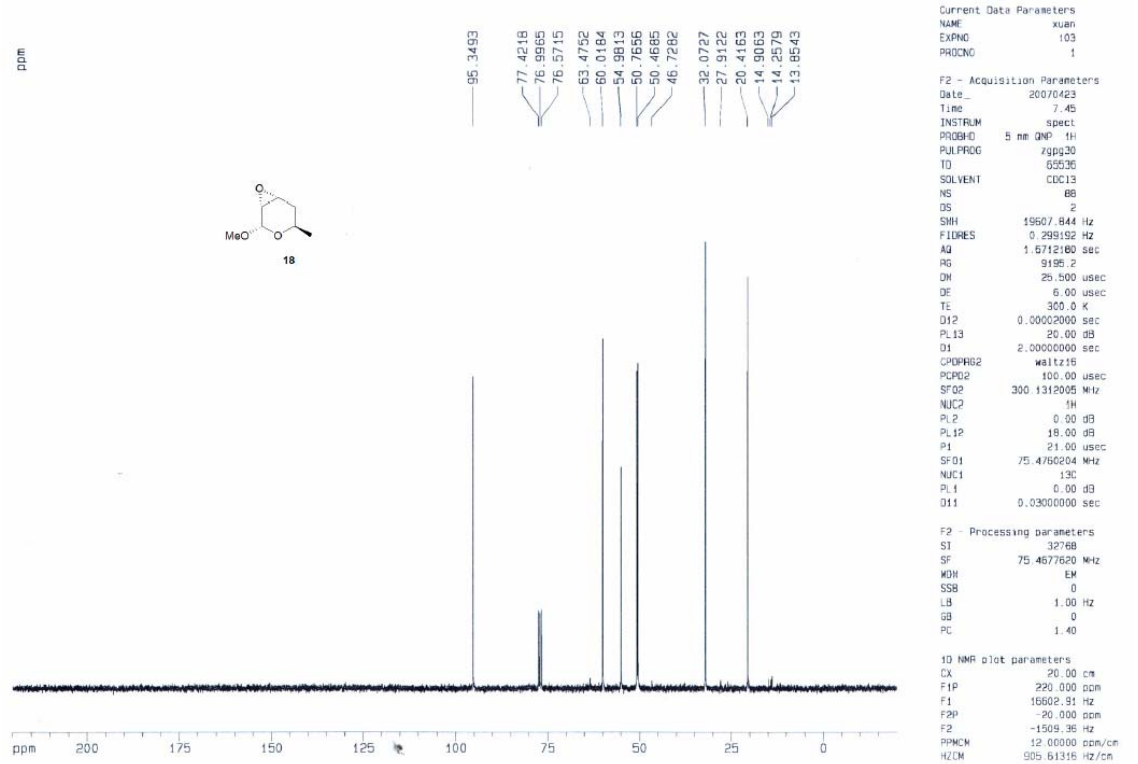


Current Data Parameters
NAME xuan
EXPNO 104
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070423
Time 7.51
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT Aceton
NS 16
DS 2
SWH 6172.824 Hz
FIDRES 0.188380 Hz
AQ 2.6542649 sec
RG 40.3
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 18.00 usec
SF01 300.1310765 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300051 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45000 ppm/cm
HZCM 135.05850 Hz/cm

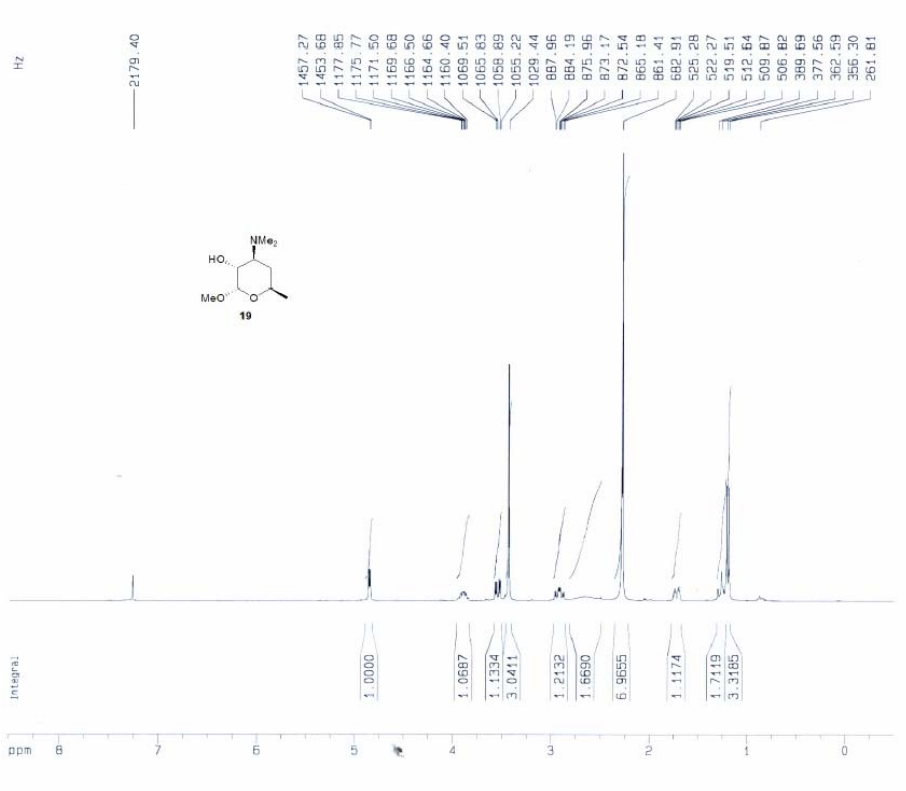


Current Data Parameters
NAME xuan
EXPNO 103
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070423
Time 7.45
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 88
DS 2
SWH 19607.844 Hz
FIDRES 0.299192 Hz
AQ 1.6712180 sec
RG 9195.2
DW 25.500 usec
DE 6.00 usec
TE 300.0 K
D12 0.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SF02 300.1312005 MHz
NUC2 1H
PL2 0.00 dB
PL12 18.00 dB
P1 21.00 usec
SF01 75.4760204 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 75.4677620 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 16602.91 Hz
F2P -20.000 ppm
F2 -1509.36 Hz
PPMCM 12.00000 ppm/cm
HZCM 905.61316 Hz/cm

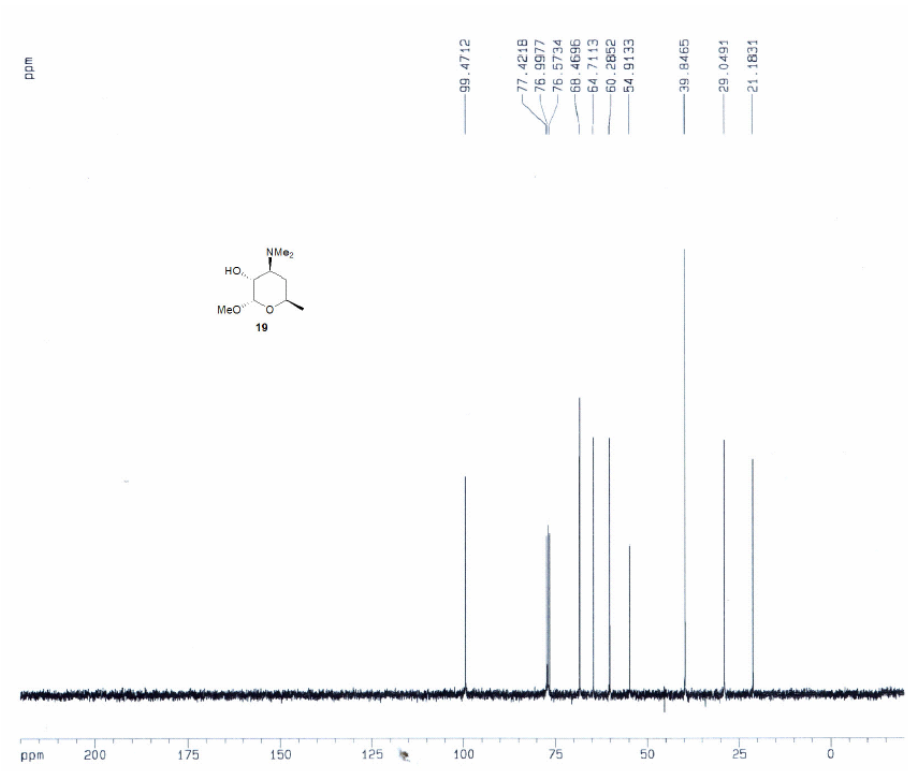



```
Current Data Parameters
NAME                  phs
EXPNO                 160
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070804
Time                 0.18
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.824 Hz
FIDRES           0.188380 Hz
AQ               2.6542649 sec
RG                    362
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1              1.00000000 sec
P1                 18.00 usec
SFO1          300.1310765 MHz
NUC1                   1H
PL1                 0.00 dB

F2 - Processing parameters
SI                 16384
SF            300.1300051 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1              2551.10 Hz
F2P               -0.500 ppm
F2              -150.07 Hz
PPMCM           0.46000 ppm/cm
HZCM          138.09850 Hz/cm
```

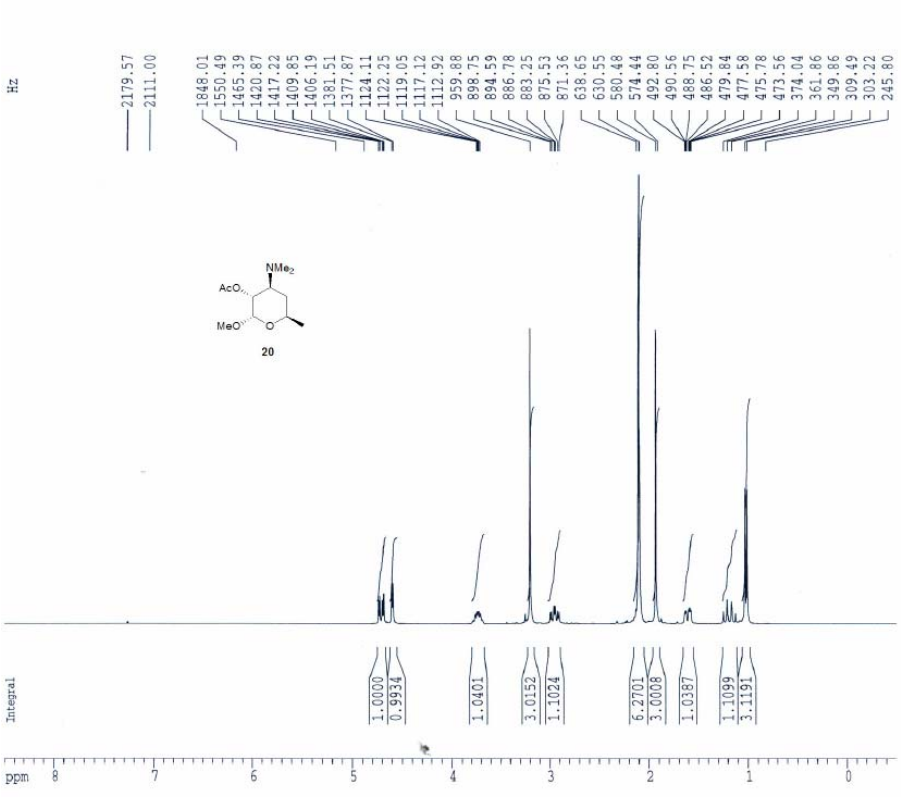



```
Current Data Parameters
NAME                  xuan
EXPNO                  108
PROCNO                   1

F2 - Acquisition Parameters
Date_           20070427
Time                 7.51
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    113
DS                      2
SWH             19607.844 Hz
FIDRES           0.299192 Hz
AQ               1.6712180 sec
RG                 9195.2
DW                25.500 usec
DE                 6.00 usec
TE                300.0 K
D12             0.00002000 sec
PL13               20.00 dB
D1              2.00000000 sec
CPDPRG2           waltz16
PCPD2             100.00 usec
SFO2          300.1312005 MHz
NUC2                   1H
PL2                 0.00 dB
PL12               18.00 dB
P1                 21.00 usec
SFO1           75.4760204 MHz
NUC1                  13C
PL1                 0.00 dB
D11             0.03000000 sec

F2 - Processing parameters
SI                  32768
SF             75.4677543 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              220.000 ppm
F1              16602.90 Hz
F2P              -20.000 ppm
F2              -1509.35 Hz
PPMCM           12.00000 ppm/cm
HZCM          905.61304 Hz/cm
```



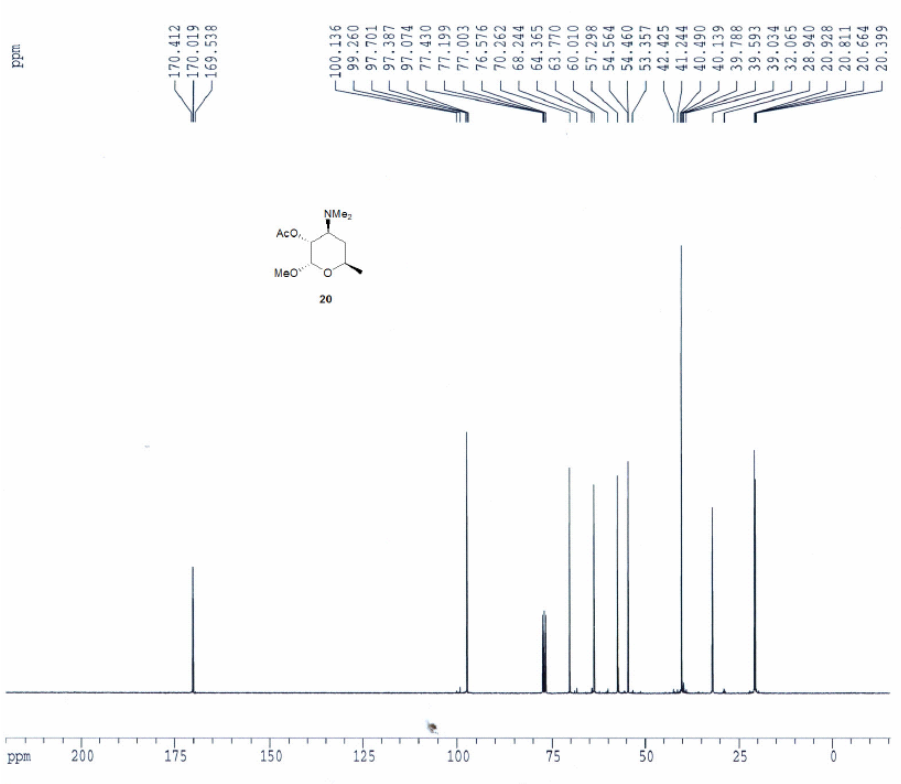

```
Current Data Parameters
NAME                  40-249
EXPNO                    462
PROCNO                     1

F2 - Acquisition Parameters
Date_              20080826
Time                   4.11
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES                0.188380 Hz
AQ                 2.6542580 sec
RG                       20.2
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                 2.00000000 sec

============ CHANNEL f1 =========
NUC1                      1H
P1                     11.80 usec
PL1                    -4.00 dB
SFO1              300.1318534 MHz

F2 - Processing parameters
SI                        32768
SF                300.1300053 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                     8.500 ppm
F1                   2551.10 Hz
F2P                    -0.500 ppm
F2                   -150.07 Hz
PPMCM                 0.45000 ppm/cm
HZCM                135.05850 Hz/cm
```




```
Current Data Parameters
NAME                  40-249
EXPNO                    463
PROCNO                     1

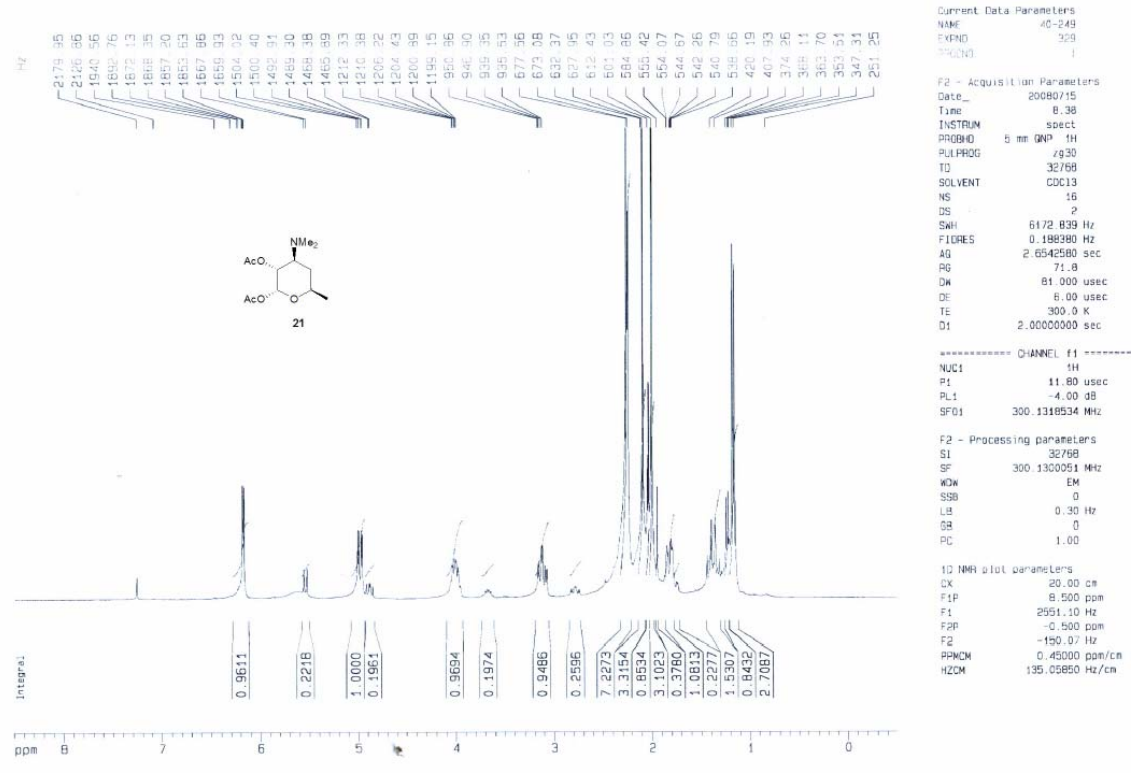
F2 - Acquisition Parameters
Date_              20080826
Time                   4.18
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      997
DS                        4
SWH               18832.393 Hz
FIDRES                0.287360 Hz
AQ                 1.7400308 sec
RG                       8192
DW                   26.550 usec
DE                    6.00 usec
TE                   300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec

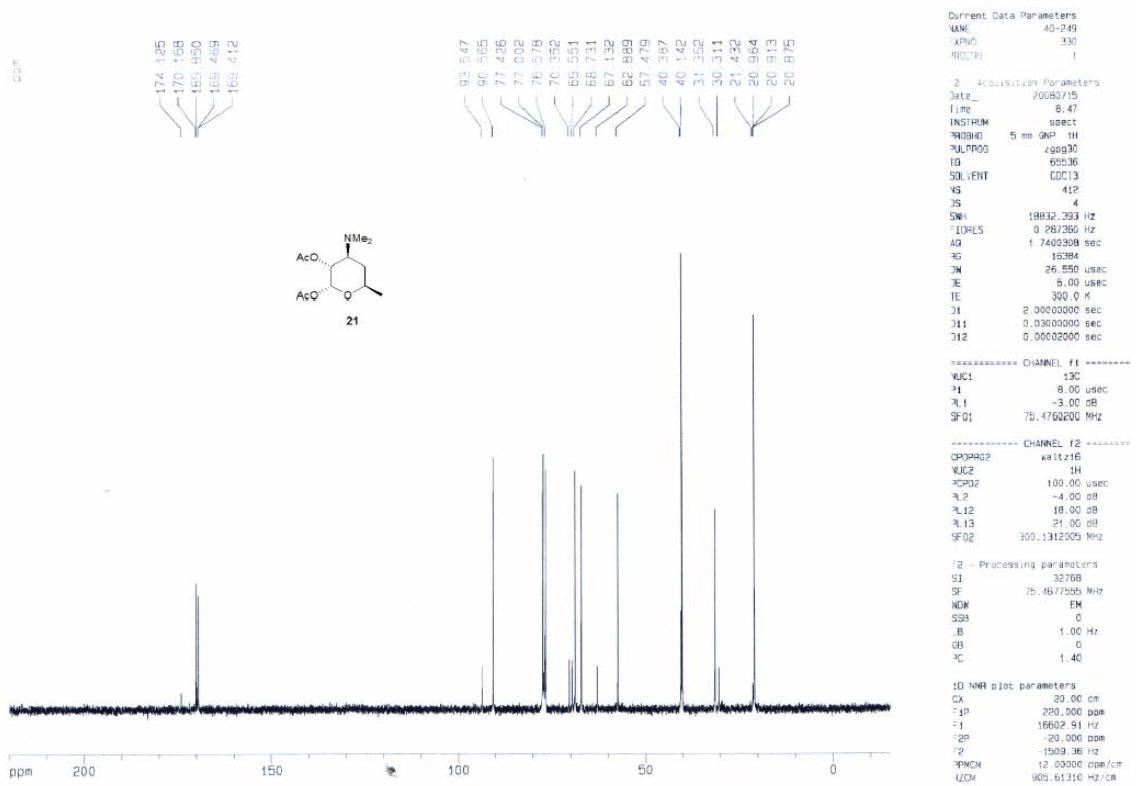
============ CHANNEL f1 =========
NUC1                      13C
P1                      8.00 usec
PL1                    -3.00 dB
SFO1              75.4760200 MHz

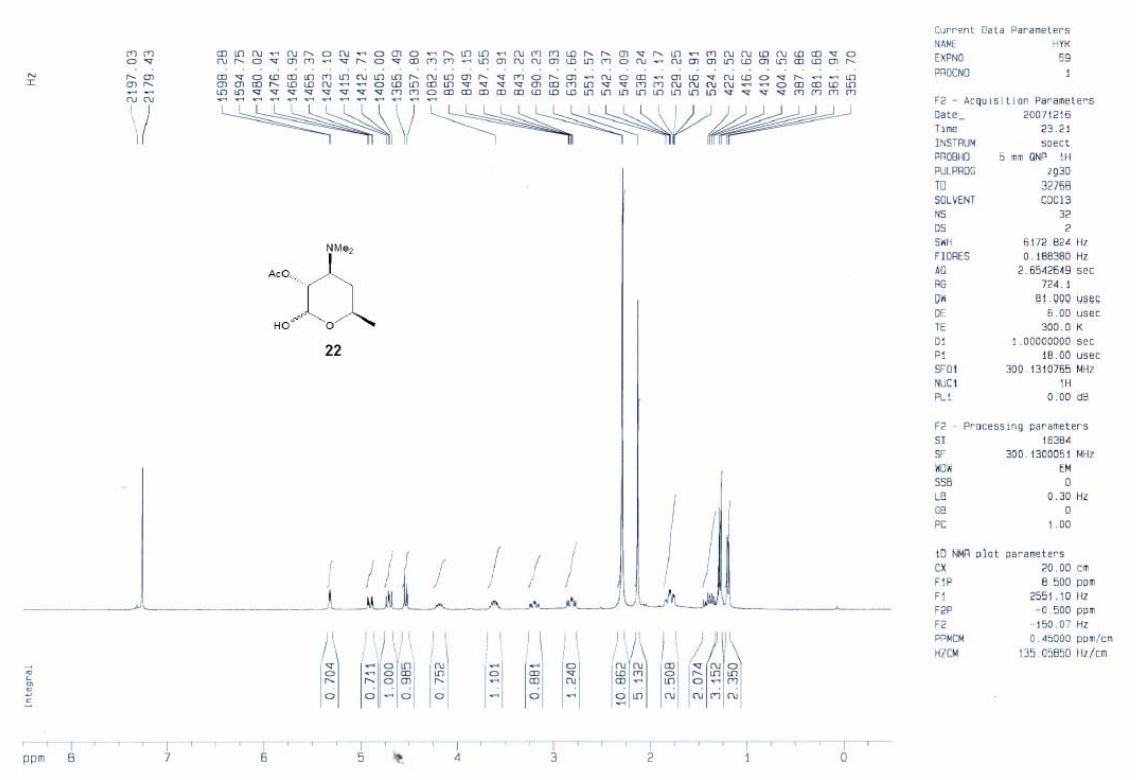
============ CHANNEL f2 =========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   18.00 dB
PL13                   21.00 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                75.4677635 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
F1P                   220.000 ppm
F1                   16602.91 Hz
F2P                   -20.000 ppm
F2                   -1509.36 Hz
PPMCM                12.00000 ppm/cm
HZCM                905.61316 Hz/cm
```


NMe2
AcO
AcO
O
21
Integral
0.9611
0.2218
1.0000
0.1961
0.9694
0.1974
0.9486
0.2596
7.2273
3.3154
0.8534
3.1023
0.3780
1.0813
0.2277
1.5307
0.8432
2.7087
ppm


NMe2
AcO
AcO
O
21
ppm
200
150
100
50
0

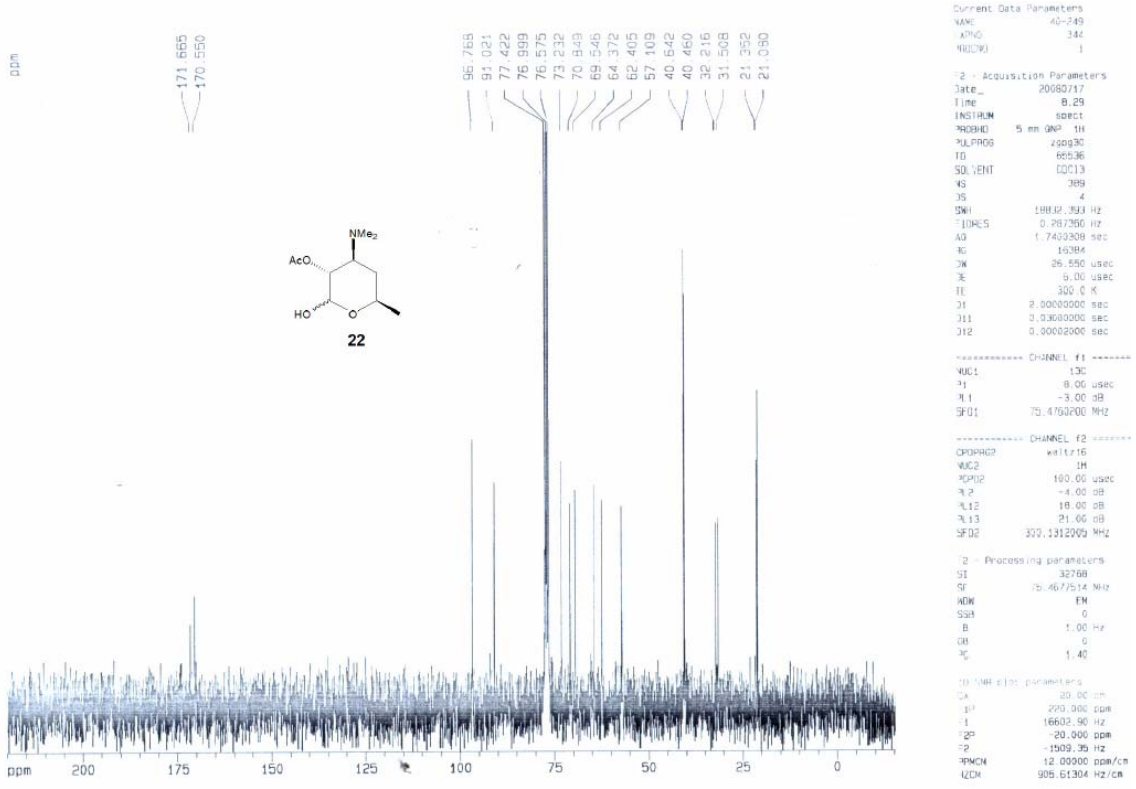



```
Current Data Parameters
NAME                  HYK
EXPNO                  59
PROCNO                  1

F2 - Acquisition Parameters
Date_           20071216
Time                23.21
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              6172.824 Hz
FIDRES           0.188380 Hz
AQ               2.6542649 sec
RG                  724.1
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
P1                18.00 usec
SFO1          300.1310765 MHz
NUC1                   1H
PL1                0.00 dB

F2 - Processing parameters
SI                 16384
SF           300.1300051 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                8.500 ppm
F1                2551.10 Hz
F2P               -0.500 ppm
F2                -150.07 Hz
PPMCM             0.45000 ppm/cm
HZCM            135.05850 Hz/cm
```




```
Current Data Parameters
NAME                 40-249
EXPNO                   344
PROCNO                    1

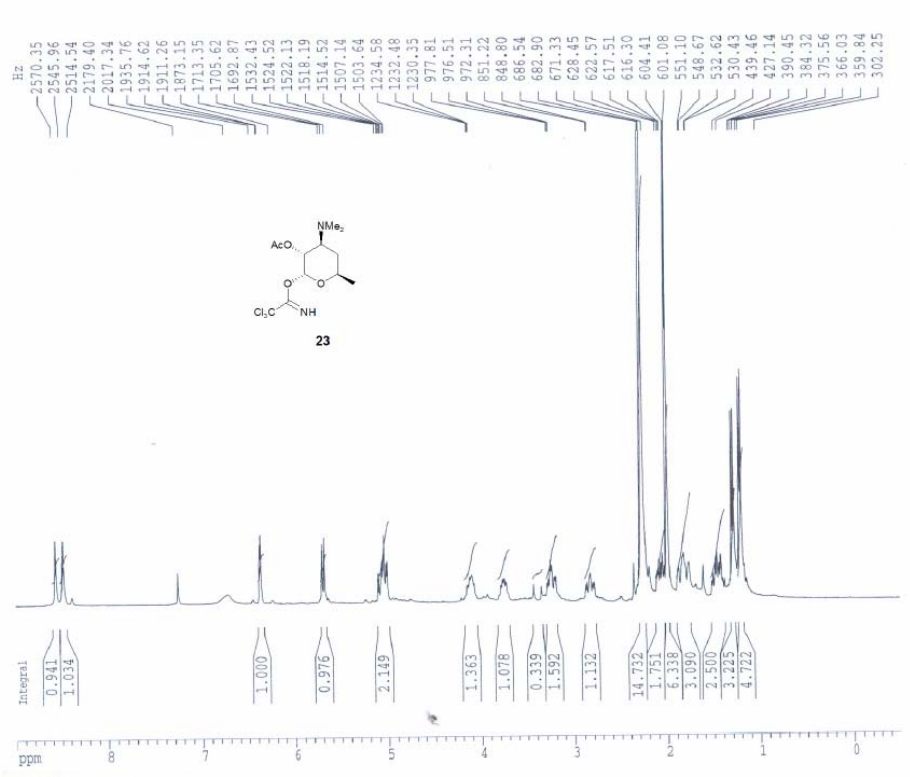
F2 - Acquisition Parameters
Date_           20080717
Time                 8.29
INSTRUM             spect
PROBHD     5 mm QNP  1H
PULPROG          zgpg30
TD                 65536
SOLVENT             CDCl3
NS                   389
DS                     4
SWH              19802.793 Hz
FIDRES           0.287350 Hz
AQ               1.7403309 sec
RG                 16384
DW                26.550 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.00 usec
PL1                -3.00 dB
SFO1          75.4760200 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -4.00 dB
PL12               18.00 dB
PL13               21.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677514 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              229.900 ppm
F1              16602.90 Hz
F2P              -20.000 ppm
F2              -1509.35 Hz
PPMCM            12.00000 ppm/cm
HZCM           905.61304 Hz/cm
```




```
Current Data Parameters
NAME                  40-249
EXPNO                    709
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081105
Time                   7.43
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                     101.6
DW                  81.000 usec
DE                   6.00 usec
TE                   300.0 K
D1                 2.00000000 sec

============ CHANNEL f1 =========
NUC1                      1H
P1                     11.80 usec
PL1                    -4.00 dB
SFO1             300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF               300.1300066 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
F1P                    9.000 ppm
F1                  2701.17 Hz
F2P                   -0.500 ppm
F2                  -150.07 Hz
PPMCM                 0.47500 ppm/cm
HZCM                142.56175 Hz/cm
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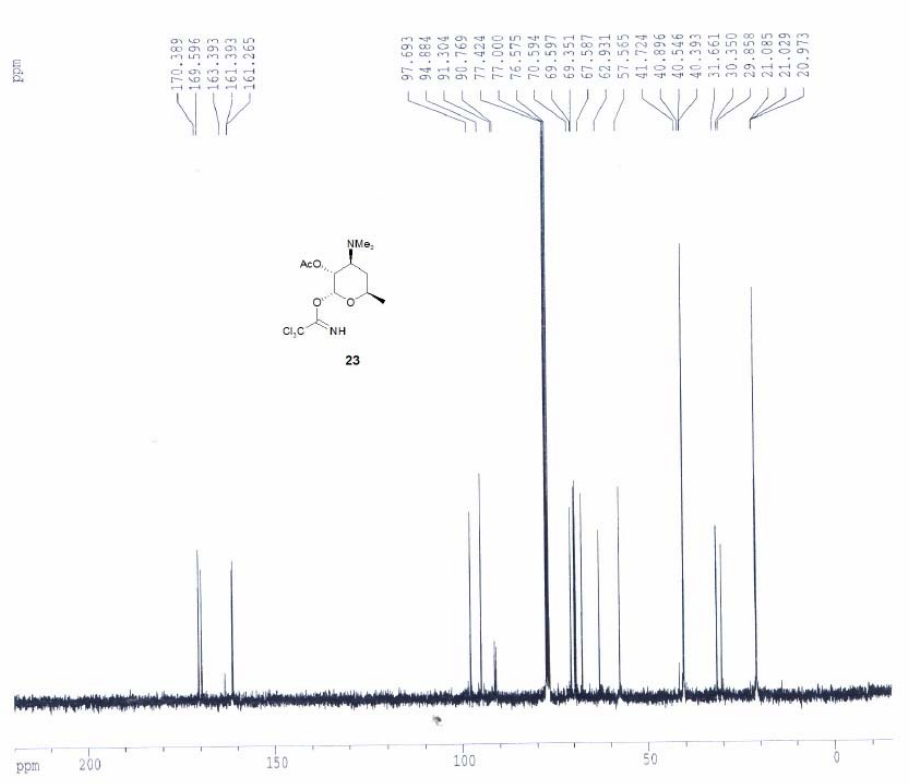



```
Current Data Parameters
NAME                  40-249
EXPNO                    710
PROCNO                     1

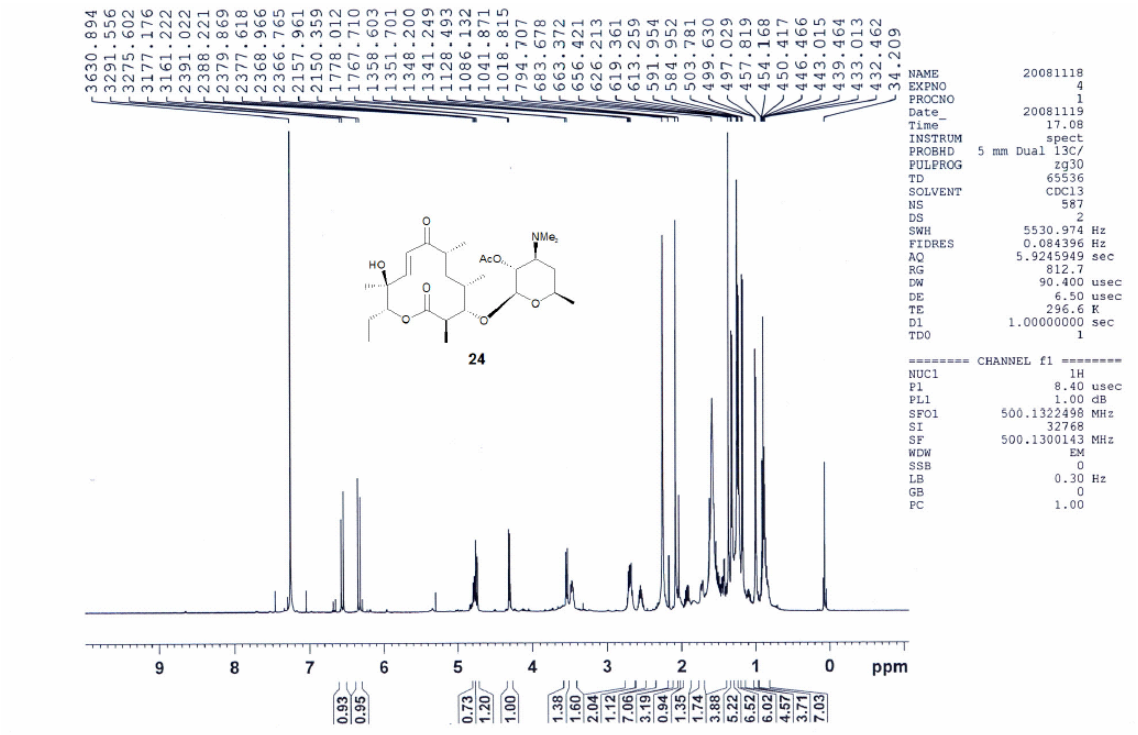
F2 - Acquisition Parameters
Date_              20081105
Time                   7.50
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      529
DS                        4
SWH                18832.393 Hz
FIDRES             0.287360 Hz
AQ                 1.7400308 sec
RG                     16384
DW                  26.550 usec
DE                   6.00 usec
TE                   300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec

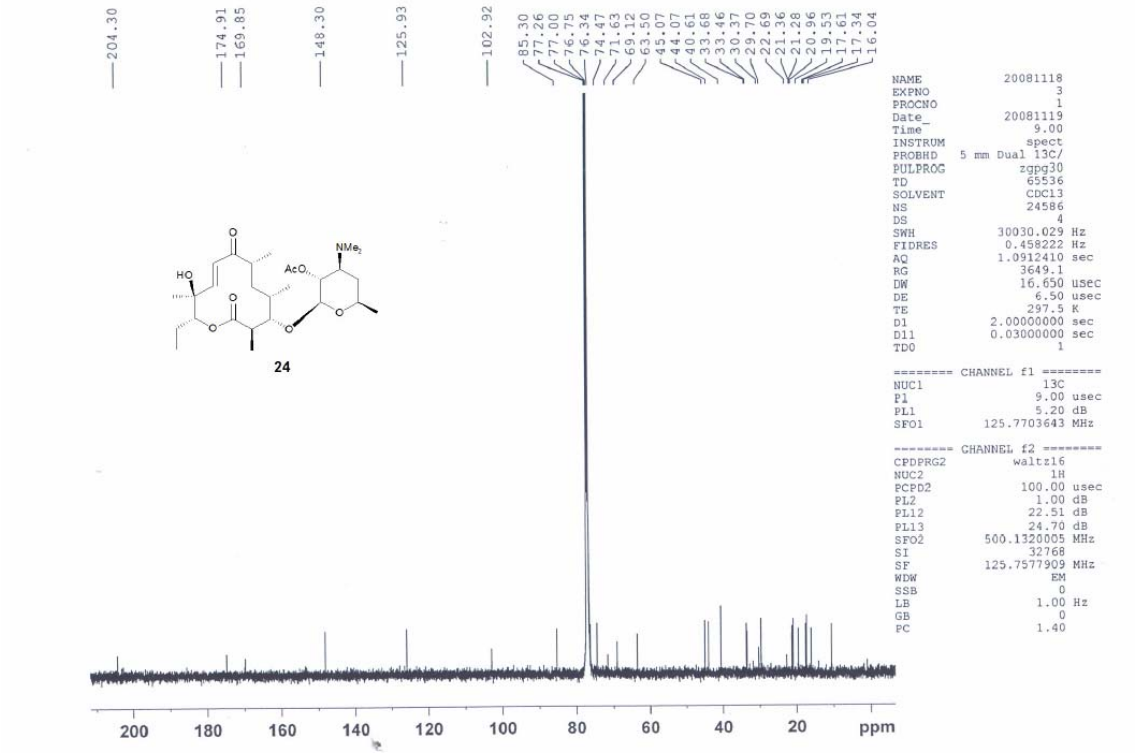
============ CHANNEL f1 =========
NUC1                      13C
P1                     8.00 usec
PL1                    -3.00 dB
SFO1             75.4760200 MHz

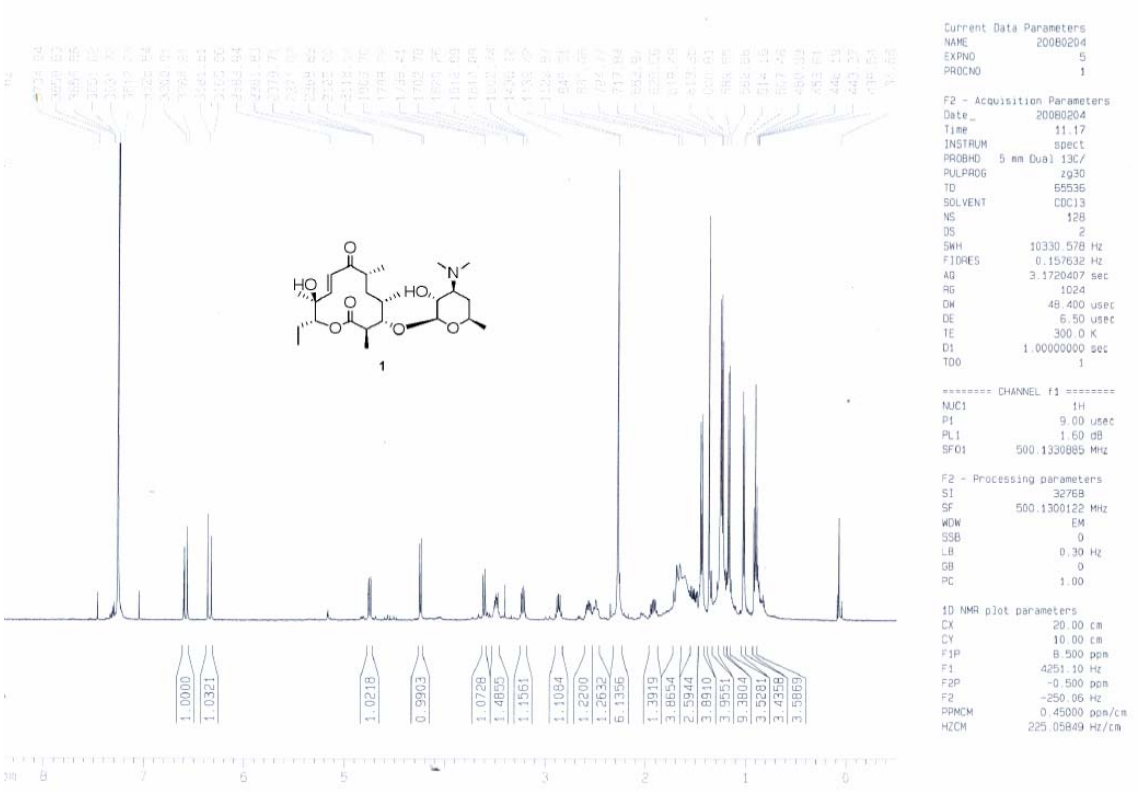
============ CHANNEL f2 =========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                    -4.00 dB
PL12                   18.00 dB
PL13                   21.00 dB
SFO2             300.1312005 MHz

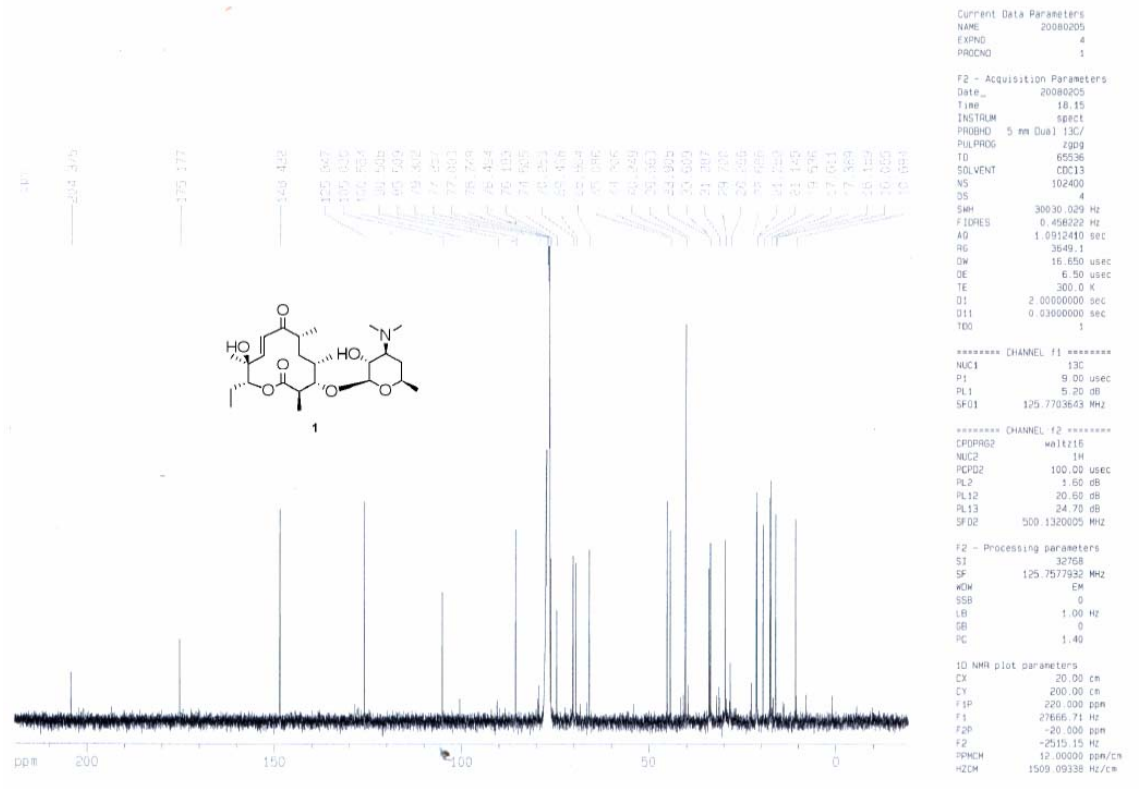
F2 - Processing parameters
SI                    32768
SF               75.4677555 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40

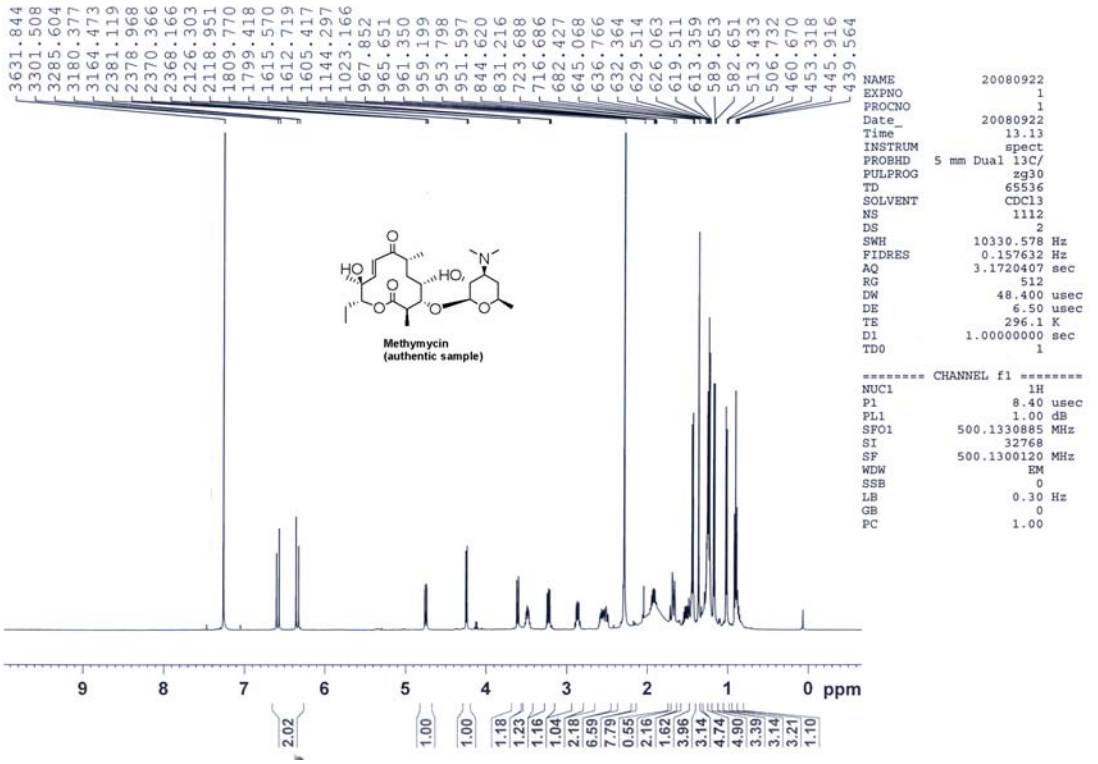
1D NMR plot parameters
CX                    20.00 cm
F1P                  220.000 ppm
F1                  16602.91 Hz
F2P                  -20.000 ppm
F2                  -1509.36 Hz
PPMCM                12.00000 ppm/cm
HZCM                905.61310 Hz/cm
```

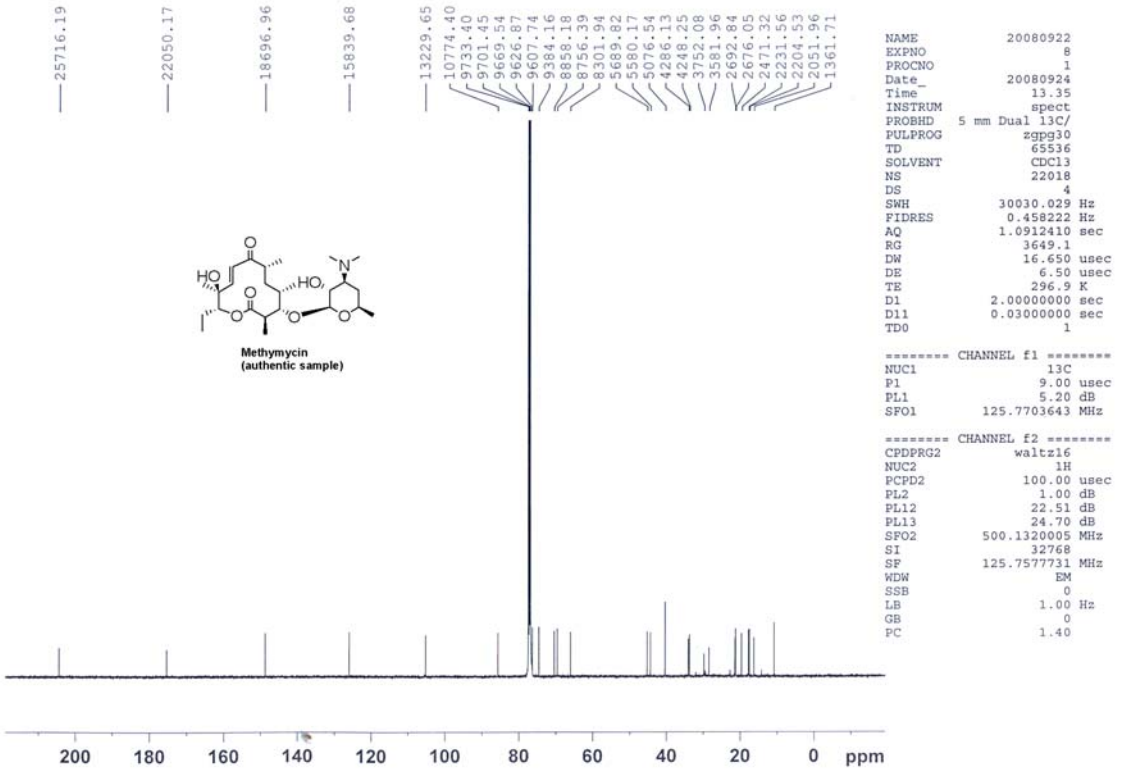

3630.894
3291.556
3275.602
3177.176
3161.222
2391.022
2388.221
2379.869
2377.618
2368.966
2366.765
2157.961
2150.359
1778.012
1767.710
1358.603
1351.701
1348.200
1341.249
1128.493
1086.132
1041.871
1018.815
794.707
683.678
663.372
656.421
626.213
619.361
613.259
591.954
584.952
503.781
499.630
497.029
457.819
454.168
450.417
446.466
443.015
439.464
433.013
432.462
34.209
NAME 20081118
EXPNO 4
PROCNO 1
Date_ 20081119
Time 17.08
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 587
DS 2
SWH 5530.974 Hz
FIDRES 0.084396 Hz
AQ 5.9245949 sec
RG 812.7
DW 90.400 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.40 usec
PL1 1.00 dB
SFO1 500.1322498 MHz
SI 32768
SF 500.1300143 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
AcO
NMe2
24
9 8 7 6 5 4 3 2 1 0 ppm
0.93 0.95 0.73 1.20 1.00 1.38 1.60 2.04 1.12 7.06 3.19 0.94 1.35 1.74 3.88 5.22 6.52 6.02 4.57 3.71 7.03


204.30
174.91
169.85
148.30
125.93
102.92
85.30
77.26
77.00
76.75
76.34
74.47
71.63
69.12
63.50
45.07
44.07
40.61
33.68
33.46
30.37
29.70
22.69
21.36
21.28
20.96
19.53
17.61
17.34
16.04
NAME 20081118
EXPNO 3
PROCNO 1
Date_ 20081119
Time 9.00
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 24586
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 3649.1
DW 16.650 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 5.20 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 22.51 dB
PL13 24.70 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577909 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HO
AcO
NMe2
24
200 180 160 140 120 100 80 60 40 20 ppm


1
1.0000
1.0321
1.0218
0.9903
1.0728
1.4855
1.1561
1.1084
1.2200
1.2632
6.1356
1.3919
3.8654
2.5944
3.8910
3.9551
3.3804
3.5281
3.4358
3.5869
Current Data Parameters
NAME 20080204
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080204
Time 11.17
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 1024
DW 48.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.60 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 8.500 ppm
F1 4251.10 Hz
F2P -0.500 ppm
F2 -250.06 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm


1
Current Data Parameters
NAME 20080205
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080205
Time 18.15
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 102400
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 3649.1
DW 16.650 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 5.20 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 20.60 dB
PL13 24.70 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577932 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 200.00 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -20.000 ppm
F2 -2515.15 Hz
PPMCM 12.00000 ppm/cm
HZCM 1509.09338 Hz/cm


Methymycin
(authentic sample)
ppm


Methymycin
(authentic sample)
ppm