



Supporting Information

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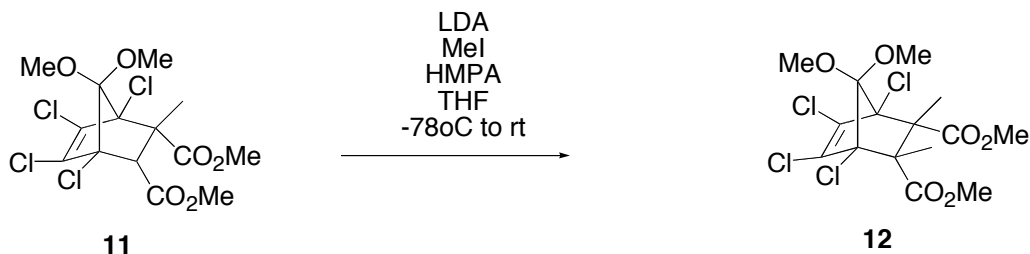
A Synthetic Pathway to Either Enantiomer of Merrilactone A

Zhaoyang Meng and Samuel J. Danishefsky

General. All reactions were carried out under an argon atmosphere. Tetrahydrofuran, diethyl ether, and dichloromethane were purified by passing through solvent columns.* Other solvents were obtained commercially and were used as received. All other reagents were reagent grade and purified where necessary. Reactions were monitored by thin layer chromatography (TLC) using EM Science 60F silica gel plates (0.25 mm). Compounds were visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution, followed by heating. Flash column chromatography was performed over Scientific Adsorbents Inc. silica gel (32-63 mm). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-Spectrospin spectrometers. The chemical shifts are reported as δ values (ppm) relative to TMS. Coupling constants (J) are reported in hertz. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR Spectrophotometer (NaCl plates, film). Low-Resolution mass spectra were performed on a JEOL LC/MS system using chemical ionization. High-resolution mass

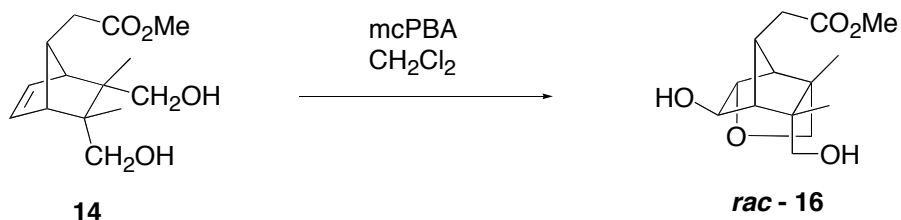
spectra were recorded on a JEOL-DX-303 HF mass spectrometer.

*Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518



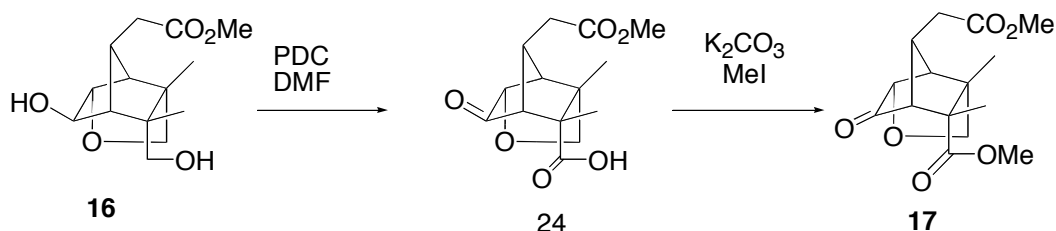
To a magnetically stirred solution of diisopropylamine (3.022 ml, 21.56 mmol) in anhydrous THF (80mL) cooled to -78°C was added dropwise $n\text{-BuLi}$ (13.5 ml, 21.56 mmol) by syringe. After complete addition, the reaction mixture was warmed to 0°C and stirred for 15min. The reaction mixture was cooled to -78°C , to it was added dropwise a solution of the diester **11** (7.0 g, 16.59 mmol) in THF (40 mL), and stirring was continued at -78°C for 1 hr and at -30°C for another 1 hr. The mixture was again cooled to -78°C , and HMPA (4.996 mL, 28.72 mmol) was added followed by MeI (1.497 mL, 24.05 mmol). The reaction mixture was stirred at -78°C for 1 hr and then slowly warmed up to rt and finally left at room temperature overnight. The reaction mixture, after quenched with saturated NH_4Cl , was extracted with CH_2Cl_2 . The CH_2Cl_2 extract was dried over Na_2SO_4 ,

filtered and concentrated *in vacuo*. Chromatography (0 to 10% EtOAc in Hexane) afforded **12** (6.83 g, 95%). ¹H NMR (CDCl₃, 400 MHz): δ 1.68 (s, 6H), 3.51 (s, 3H), 3.56 (s, 3H), 3.60 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): 18.8, 52.0, 52.5, 52.8, 61.1, 79.8, 113.2, 131.2, 171.5; IR (NaCl, cm⁻¹): 1750.3, 1727.2, 1254.0; HRMS Found: 434.9925 (M+H), Calc. for C₁₅H₁₉Cl₄O₆ 434.9857;



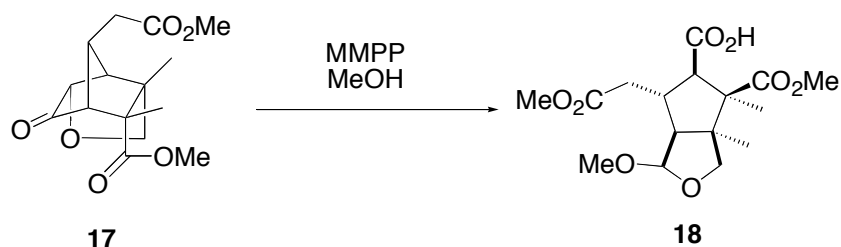
To a solution of diol **14** (980.3 mg, 3.85 mmol) in CH₂Cl₂ (25 mL) was added at 0°C mCPBA (1722 mg, 7.71 mmol) in one portion. The reaction was slowly warmed up to room temperature and stirred overnight. The mixture was concentrated to reduce the volume to approximately 10 mL and then applied to SiO₂ column. Flash chromatography (50 to 100% EtOAc in hexanes) gave cyclic ether **rac-16** (938.8 mg, 90%). ¹H NMR (CDCl₃, 400 MHz): δ 1.18 (s, 3H), 1.27 (s, 3H), 1.95 (s, 1H), 2.33 (d, J = 5.1, 1H), 2.75 – 2.89 (m, 3H), 3.44 (d, J = 9.0, 1H), 3.63 (d, J = 9.2, 1H), 3.70 (s, 3H), 3.80 (d, J = 9.0, 1H), 3.91 (s, 1H), 4.08 (d, J = 5.3,

1H); ^{13}C NMR (CDCl_3 , 100 MHz): 18.8, 21.9, 34.4, 39.3, 44.5, 48.8, 51.8, 54.3, 55.4, 66.2, 76.7, 77.3, 88.4, 173.2; IR (NaCl, cm^{-1}): 3406.3, 2951.9, 2877.7, 1733.8, 1034.8; HRMS Found: 271.1538 (M+H), Calc. for $\text{C}_{14}\text{H}_{23}\text{O}_5$ 271.1467;



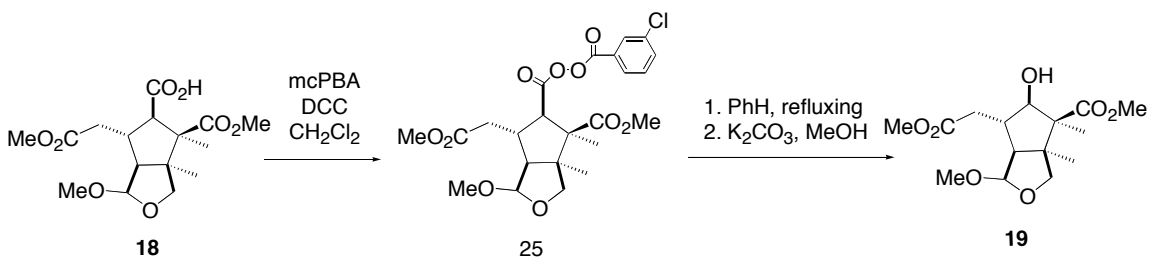
A solution of cyclic ether **16** (917.3 mg, 3.39 mmol) in DMF (18mL) was treated with PDC (10.2 g, 27.15 mmol) at room temperature and stirred for 1 day. The reaction was worked up by poured into water (100 mL) and thoroughly extracted with ether. The ether extraction was washed with brine, dried with MgSO_4 , and concentrated *in vacuo*. The crude keto-acid **24** was dissolved in dry acetone (25 mL). Methyl iodide (2.1mL, 33.9 mmol) and anhydrous potassium carbonate (4.7 g, 33.9 mmol) were added. After 10 hrs at reflux, the mixture was cooled, diluted with CH_2Cl_2 , filtered and evaporated. The residue was dissolved in CH_2Cl_2 and purified by flash chromatography (20 to 50% EtOAc in Hexane) to afford keto-ester **17**. ^1H NMR (C_6D_6 , 400 MHz): δ 0.82 (s, 3H), 1.11 (s, 3H), 1.92 (t, $J = 8.0$, 1H), 2.05 (d, $J = 5.6$, 1H), 2.24 (d, $J = 8.0$, 1H), 2.50 (s, 1H), 3.28 (s, 3H), 3.30 (s,

3H), 3.32 (d, $J = 8.9$, 1H), 3.89 (d, $J = 5.6$, 1H), 4.20 (d, $J = 8.9$, 1H); ^{13}C NMR (C_6D_6 , 100 MHz): 17.7, 23.7, 34.2, 38.3, 51.6, 51.7, 51.8, 53.0, 54.9, 59.6, 79.6, 84.1, 171.1, 174.9, 203.2; IR (NaCl, cm^{-1}): 1772.0, 1734.0; LRMS Found: 297.04 (M+H), Calc. $\text{C}_{15}\text{H}_{21}\text{O}_6$ 297.12.



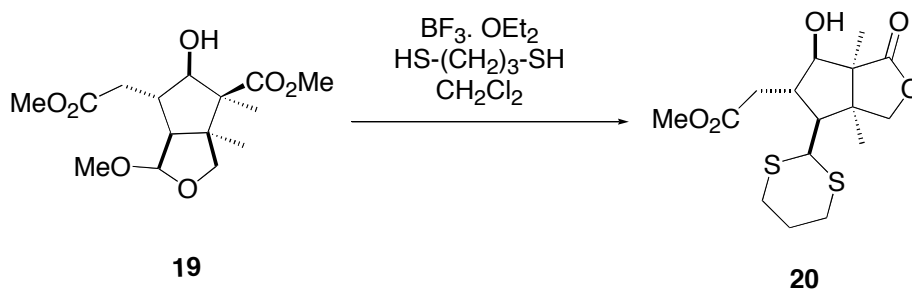
To a solution of keto-ester **17** (696.3 mg, 2.34 mmol) in MeOH (30 mL) was added MMPP (magnesium monoperoxyphthalate hexahydrate, tech 80%, 4.4 g, 7.02 mmol) in one portion at 0°C. After stirring at room temperature for 10hrs, the white suspension was diluted with water, acidified with 1 M HCl to pH 2-3, and extracted 3 times with CH_2Cl_2 . The organic extract was washed with brine, dried over Na_2SO_4 , and rotary evaporated. Column chromatography (30 to 70% EtOAc in hexanes) gave carboxylic acid **18** (706.1 mg, 88%). ^1H NMR (CDCl_3 , 400 MHz): δ 1.15 (s, 3H), 1.40 (s, 3H), 1.98 (dd, $J = 5.6$, $J = 1.5$, 1H), 2.44 (dd, $J = 15.8$, $J = 9.7$, 1H), 2.69 (d, $J = 10.3$, 1H), 2.98 (dd, $J = 15.8$, $J = 4.1$, 1H), 3.17 (m, 1H), 3.30 (s, 3H), 3.48 (d, $J = 9.4$, 1H),

3.67 (s, 3H), 3.68 (s, 3H), 4.04 (d, $J = 9.4$, 1H), 4.73 (d, $J = 1.5$, 1H); **HRMS** Found: 343.1383 (M-H), Calc. for $C_{16}H_{23}O_8$ 343.1471;



To a solution of carboxylic acid **17** (309.2 mg, 0.90 mmol) and mCPBA (401 mg, 1.80 mmol) in CH_2Cl_2 (10 mL) was added DCC (369.9 mg, 1.80 mmol) at $0^\circ C$ with stirring. After 2hr, the precipitate was filtered off. The filtrate was concentrated and subjected to flash chromatography (10 to 30% EtOAc in Hexanes) to give mixed peroxide **25** (369.2 mg, 83%). The mixed peroxide **25** (238.1 mg, 0.48 mmol) in benzene (15 mL) was refluxing for 10hrs with stirring. The solvent was removed *in vacuo*. The residue was redissolved in dry MeOH (10 mL) and treated with anhydrous K_2CO_3 (263 mg, 1.91 mmol). After stirring for 5hrs at room temperature, the solution was diluted with CH_2Cl_2 , filtered and evaporated. The residue was dissolved in CH_2Cl_2 and purified by flash chromatography (0 to 30% EtOAc in Hexanes) to afford **19** (105.5 mg, 70%). 1H NMR ($CDCl_3$, 400

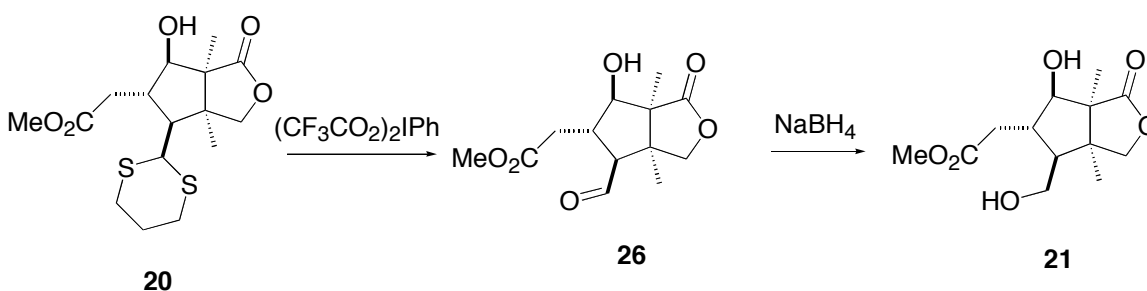
MHz): δ 1.14 (s, 3H), 1.26 (s, 3H), 1.85 (d, J = 6.8, 1H), 2.39 (dd, J = 15.6, J = 9.4, 1H), 2.64 (m, 1H), 2.79 (dd, J = 15.6, J = 5.2, 1H), 3.06 (d, 11.1, 1H), 3.30 (s, 3H), 3.48 (d, J = 9.4, 1H), 3.54 (dd, J = 11.1, J = 9.4, 1H), 3.69 (s, 3H), 3.72 (s, 3H), 4.12 (d, J = 9.4, 1H), 4.78 (s, 1H); **^{13}C NMR (CDCl₃, 75 MHz):** 19.1, 21.5, 38.9, 45.1, 51.6, 52.0, 54.0, 54.8, 56.2, 61.4, 73.7, 84.6, 111.9, 172.9, 176.1; **IR (NaCl, cm⁻¹):** 3525.8, 2952.3, 1732.6, 1436.6; **HRMS Found:** 317.1597 (M+H), Calc. for C₁₅H₂₅O₇ 317.1522;



Boron trifluoride etherate (169 mL, 1.33 mmol) was added dropwise to a solution of ketal **19** (105.5 mg, 0.33 mmol) and 1, 3-propanedithiol (201 mL, 2.00 mmol) in CH₂Cl₂ (10 mL) at 0°C. The reaction was stirred at room temperature for 12hrs, then poured into saturated NaHCO₃ and extracted 3 times with CH₂Cl₂. The CH₂Cl₂ extract was dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography to afford dithiane-lactone **20** (61.4 mg, 51%). **^1H NMR (CDCl₃, 400 MHz):** δ 1.20 (s, 3H),

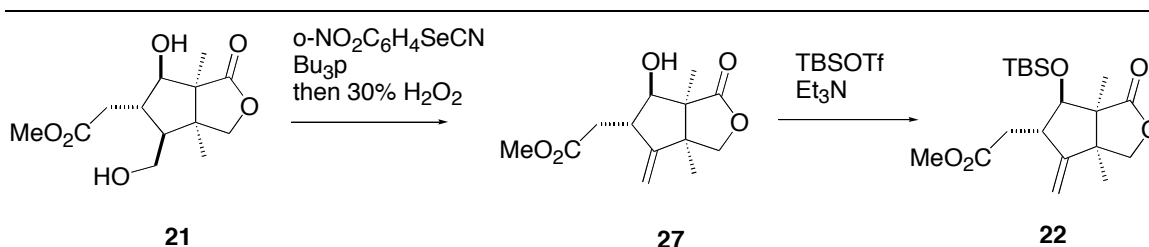
1.25 (s, 3H), 1.80 – 2.28 (m, 4H), 2.53 (dd, $J = 16.2$, $J = 7.5$, 1H), 2.82 – 2.95 (m, 5H), 3.43 (d, $J = 8.4$, 1H), 3.66 (dd, $J = 17.3$, $J = 8.7$, 1H), 3.69 (s, 3H), 3.89 (d, $J = 10.0$, 1H), 4.30 (d, $J = 4.4$, 1H), 5.03 (d, $J = 10.0$, 1H);

HRMS Found: 361.1160 (M+H), Calc. For $C_{16}H_{25}O_5S_2$ 361.1065;



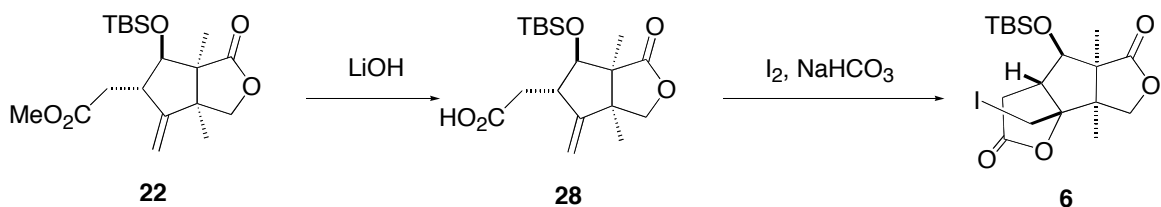
Bis(trifluoroacetoxy)iodobenzene (120 mg, 0.27 mmol) was added at 0°C to a stirred solution of dithiane-lactone **20** (61.0 mg, 0.17 mmol), water (1 mL) and CH_3CN (9 mL). After it was stirred at room temperature for 10 min, the reaction was quenched with saturated sodium bicarbonate solution, and extracted 3 times with CH_2Cl_2 . Drying ($MgSO_4$) and removal of solvents gave a residue which was purified by flash chromatography (30 to 60% EtOAc in Hexanes) to give aldehyde **26** (23.0 mg, 50%). To a solution aldehyde **26** (23.0 mg, 0.085 mmol) in MeOH (2 mL) was added at 0°C $NaBH_4$ (6.5 mg, 0.17 mmol). After the mixture was stirred at 0°C for 1h, HOAc (0.2 mL) was added. The mixture was then

concentrated and the resulting residue was purified by flash chromatography (40 to 70% EtOAc in Hexanes) to yield diol **21** (23.4mg, 100%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 1.11 (s, 3H), 1.29 (s, 3H), 1.44 (m, 1H), 1.93 (m, 1H), 2.34 (dd, $J = 16.9$, $J = 8.0$, 1H), 2.47 (dd, $J = 7.3$, $J = 4.7$, 1H), 2.81 (dd, $J = 16.9$, $J = 4.1$, 1H), 3.44 – 3.80 (m, 4H), 3.70 (s, 3H), 3.82 (d, $J = 9.8$, 1H), 4.80 (d, $J = 9.8$, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz): 15.6, 22.2, 29.7, 35.8, 42.5, 47.5, 52.1, 52.8, 59.9, 73.8, 77.2, 81.7, 174.3, 181.9; IR (NaCl, cm^{-1}): 3467.9, 2920.0, 1736.4; HRMS Found: 273.1337 (M+H), Calc. For $\text{C}_{13}\text{H}_{21}\text{O}_6$ 273.1260;



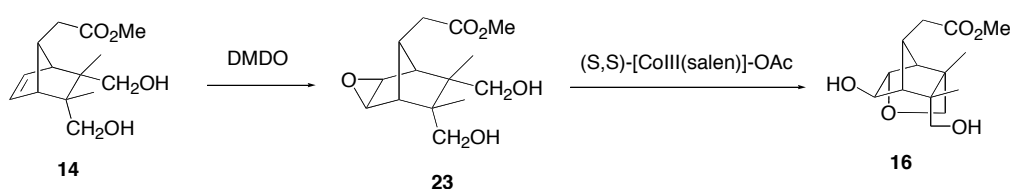
n-Tributylphosphine (46 mL, 0.18 mmol) was added dropwise to a solution of diol **21** (10.1 mg, 0.037 mmol) and *o*-nitrophenylselenocyanate (42 mg, 0.18 mmol) in THF (2 mL). The whole solution quickly turned to red color. After stirring at room temperature for 2hrs, the solution was concentrated and chromatographed (10 to 50% EtOAc in

Hexanes) to give crude *o*-nitrophenyl selenide. Hydrogen peroxide (30%, 1mL) was added to a solution of selenide in THF (2 mL) at 0°C. After stirring at room temperature overnight, the reaction mixture was poured into saturated Na₂S₂O₃ and extracted 3 times with CH₂Cl₂. The organic layers were combined and dried over Na₂SO₄, filtered and concentrated *in vacuo*. Residue was purified by column chromatography (0 to 30% EtOAc in Hexane) to give alcohol **27** (8.0 mg, 86%). To a solution of alcohol **27** (5.0 mg, 0.020 mmol) in CH₂Cl₂ (1 mL) was added Et₃N (8.2 mL, 0.060 mmol) then TBSOTf (9.0 mL, 0.040 mmol) at 0°C. The mixture was stirred at room temperature for 12hrs. The reaction mixture, after quenched with 0.1N HCl, was extracted 3 times with CH₂Cl₂. The CH₂Cl₂ extract was dried over Na₂SO₄, filtered and concentrated *in vacuo*. Chromatography (0 to 10% EtOAc in Hexane) afforded **22** (5.6 mg, 76%). ¹H NMR (CDCl₃, 300 MHz): δ 0.07 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 1.18 (s, 3H), 1.19 (s, 3H), 2.48 (dd, J = 15.8, J = 7.3, 1H), 2.59 (dd, J = 15.8, J = 6.7, 1H), 3.05 (m, 1H), 3.71 (s, 3H), 3.89 (d, J = 8.6, 1H), 3.90 (d, J = 3.6, 1H), 4.19 (d, J = 8.6, 1H), 4.99 (d, J = 2.2, 1H), 5.04 (d, J = 2.2, 1H); LRMS Found: 369.0 (M+1), Calc. 368.20.



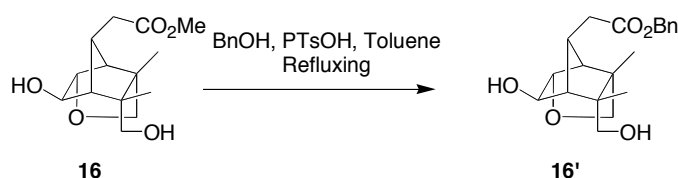
The ester **22** (4.0 mg, 0.011 mmol) was stirred with a solution of LiOH (1.4 mg, 0.033 mmol) in a mixture of MeOH (1.5 mL) and water (0.5 mL) at room temperature for 12 hrs, diluted with water, acidified with 1 M HCl to pH 2-3, and extracted 3 times with CH₂Cl₂. The organic extract was washed with brine, dried over Na₂SO₄, and rotary evaporated. To a solution of crude carboxylic acid **28** in THF (0.5 mL), was added 1 mL of saturated aqueous NaHCO₃. The mixture was cooled in an ice bath, treated with a solution of I₂ (8.2 mg, 0.033 mmol) in THF (1.5 mL), protected from light, and stirred at room temperature for 12 hrs. Excess I₂ was quenched by addition of saturated Na₂S₂O₃, the mixture was diluted with water and extracted 3 times with CH₂Cl₂. The organic extract was washed with brine, dried over Na₂SO₄, and rotary evaporated. Column chromatography (10 to 30% EtOAc in hexanes) gave iodolactone **6** (4.0 mg, 75%). ¹H NMR (CDCl₃, 400 MHz): δ 0.074 (s, 3H), 0.077 (s, 3H), 0.88 (s, 9H), 1.16 (s, 3H), 1.23 (s, 3H), 2.45 (dd, J = 19.1, J = 2.3, 1H), 2.79 (dd, J = 11.5, J = 2.3, 1H), 3.34 (d, J = 11.1, 1H), 3.35 (dd, , J = 19.1, J = 11.5, 1H), 3.56 (d, J

= 11.1, 1H), 3.82 (s, 1H), 3.88 (d, J = 8.4, 1H), 4.30 (d, J = 8.4, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): -5.0, -4.6, 8.0, 16.0, 16.4, 17.9, 25.7, 37.5, 56.1, 57.2, 61.3, 72.4, 87.9, 95.5, 173.7, 175.9; HRMS Found: 481.0907 (M+H), Calc. For $\text{C}_{18}\text{H}_{30}\text{O}_5\text{SiI}$ 481.0829;

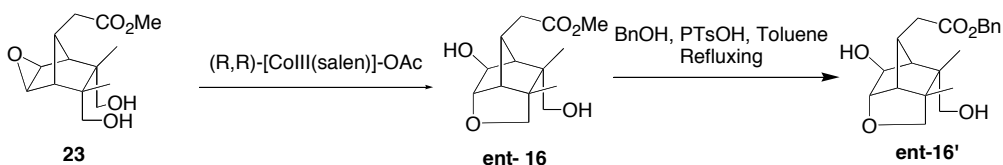


To a solution of diol **14** (21mg, 0.083 mmol) in CH_2Cl_2 (1mL) was added a solution of DMDO in acetone (~0.07 M, 3.5 mL) at room temperature. The reaction mixture was then stirred for 20min. The solvent was removed to afford the crude epoxide **23**. ^1H NMR (CDCl_3 , 300 MHz): δ 1.30 (s, 6H), 2.22 (s, 2H), 2.38 (t, J = 8.8, 1H), 2.83 (d, J = 8.8, 2H), 3.08 (br, 2H), 3.37 (s, 2H), 3.50 (d, J = 10.9, 2H), 3.69 (s, 3H), 4.21, (d, J = 10.9, 2H). The crude epoxide was dissolved in THF (0.5mL) and cooled to -78°C . To this solution was added (*S*, *S*)-[Co^{III}(salen)]-OAc (16 mg, 0.025 mmol, 0.3 eq.). The mixture was stirred at -78°C for 48hr and kept in -25°C freezer for 48hr. The reaction mixture was loaded directly onto a SiO_2 column and purified by flash chromatography (50 to 100% EtOAc in Hexane) to afford of

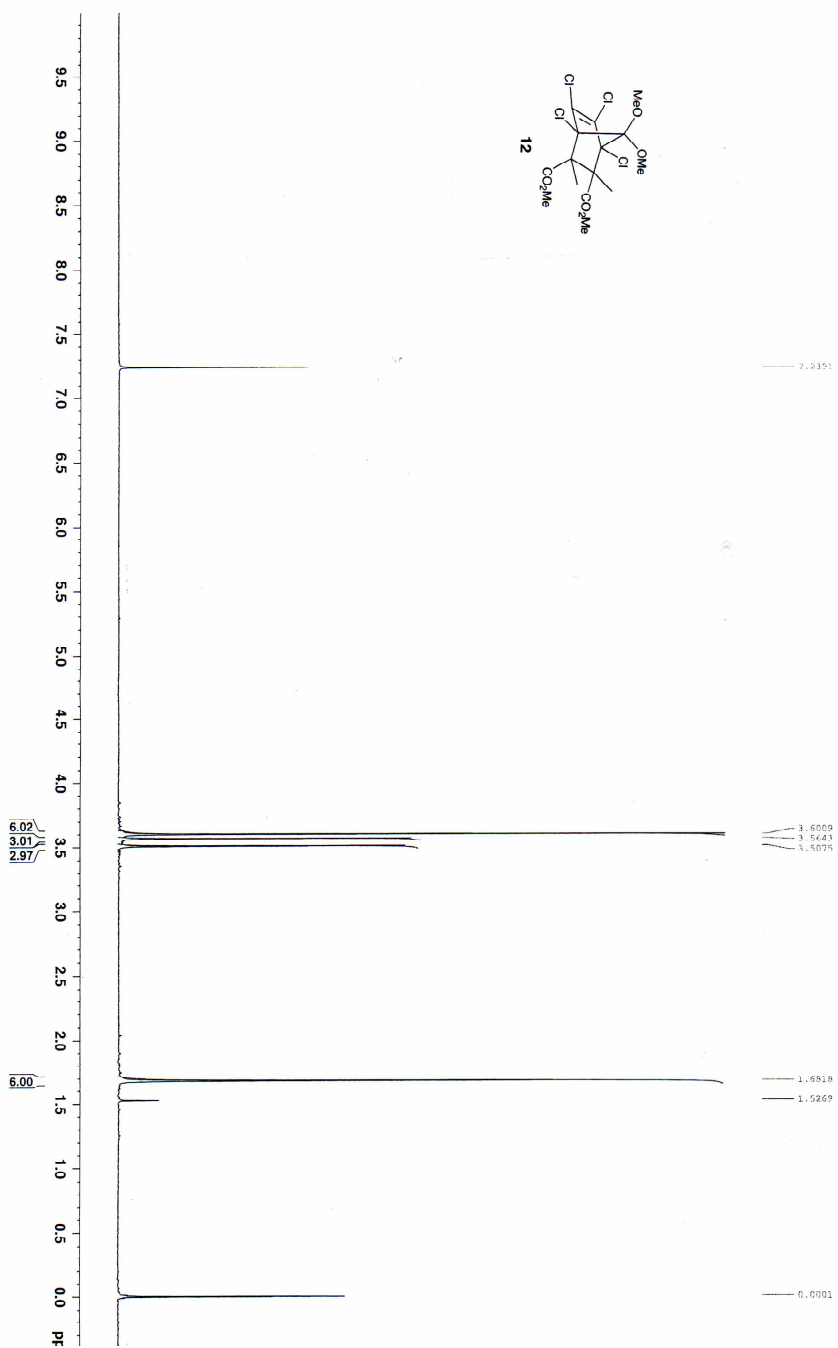
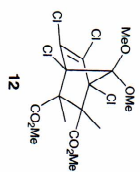
asymmetric **16** (19mg, 86%). For the purposes of determining the enantiomeric ratio, **16** was converted to the benzyl ester **16'**. The enantiomers were analyzed by chiral HPLC as benzyl ester using a Chiracel AD column (15% IPA in hexanes, 1ml/min, t_R = 15.41, 18.33 min). **^1H NMR (CDCl_3 , 400 MHz):** δ 1.16 (s, 3H), 1.26 (s, 3H), 1.93 (s, 1H), 2.31 (d, J = 5.2, 1H), 2.85 (m, 3H), 3.43 (d, J = 9.0, 1H), 3.61 (dd, J = 25.3, J = 10.3, 2H), 3.78 (d, J = 9.0, 1H), 3.90 (s, 1H), 4.06 (dd, J = 5.2, J = 1.6, 1H), 5.15 (s, 2H), 7.36 (m, 5H); **^{13}C NMR (CDCl_3 , 100 MHz):** 19.0, 21.9, 34.7, 39.5, 44.7, 48.9, 54.7, 55.6, 66.4, 66.8, 76.0, 77.7, 88.5, 128.0, 128.1, 128.4, 135.7, 172.3; **IR (NaCl, cm^{-1}):** 1732S (C=O); **MS** Found: 347.63 (M+H), Calc. For $\text{C}_{20}\text{H}_{26}\text{O}_5$ 346.18; $[\alpha]_D^{23}$ -10.9 (c 0.19, CHCl_3) for **16'**.



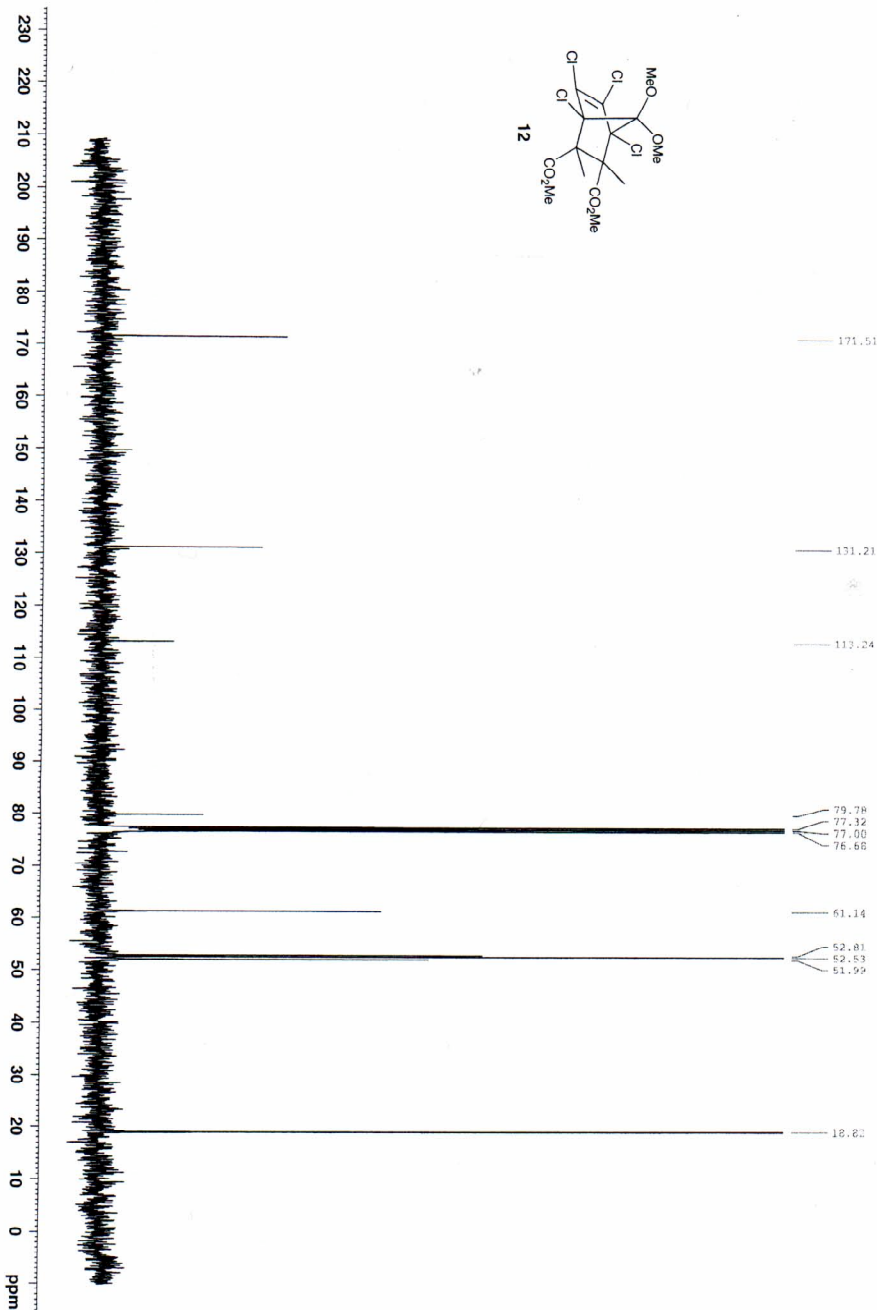
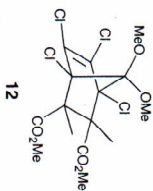
The procedure described above was repeated with (R, R)-[Co^{III}(salen)]-OAc catalyst, to afford **ent-16**, which was converted to benzyl ester **ent-16'**. $[\alpha]_D^{23}$ 7.9 (c 0.34, CHCl_3) for **ent-16'**.



proton standard



2Me-Dimethyl ester-Cl4 13Cproton 400Mhz



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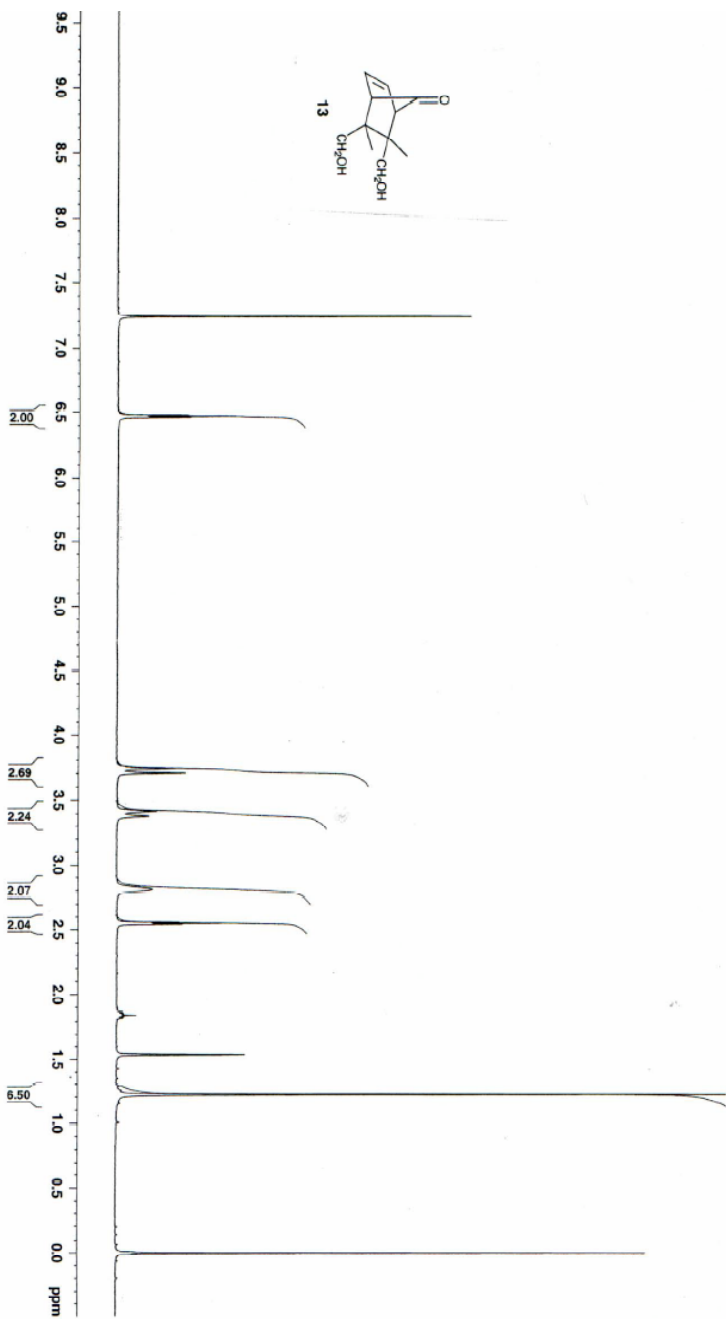
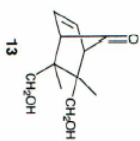
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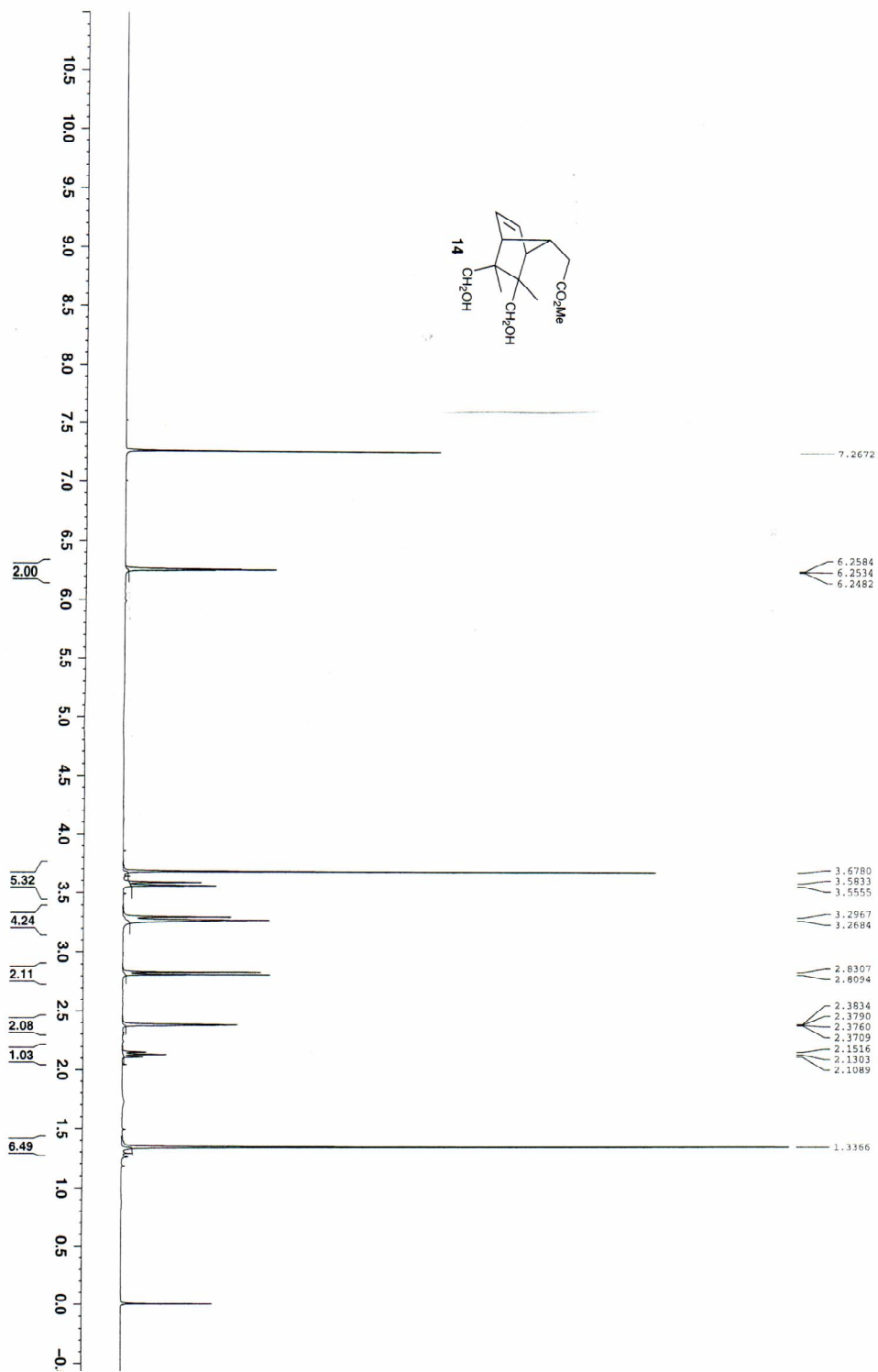
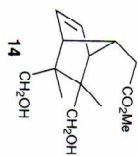
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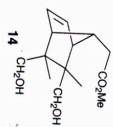
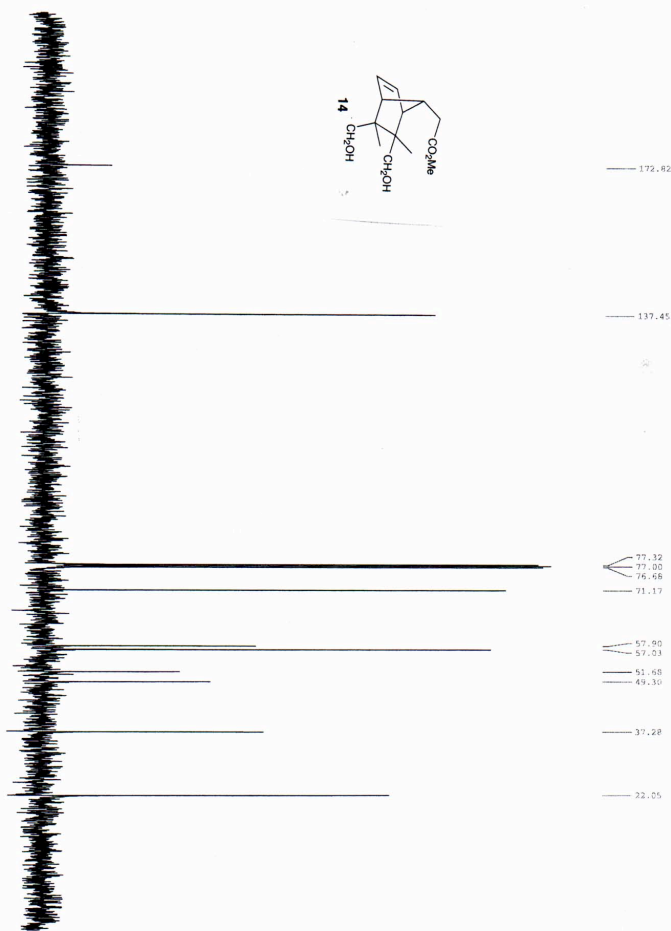


Proton 400MHz
400MHz kg/MeOH then IN HCl/THF Column 1st10.21.03



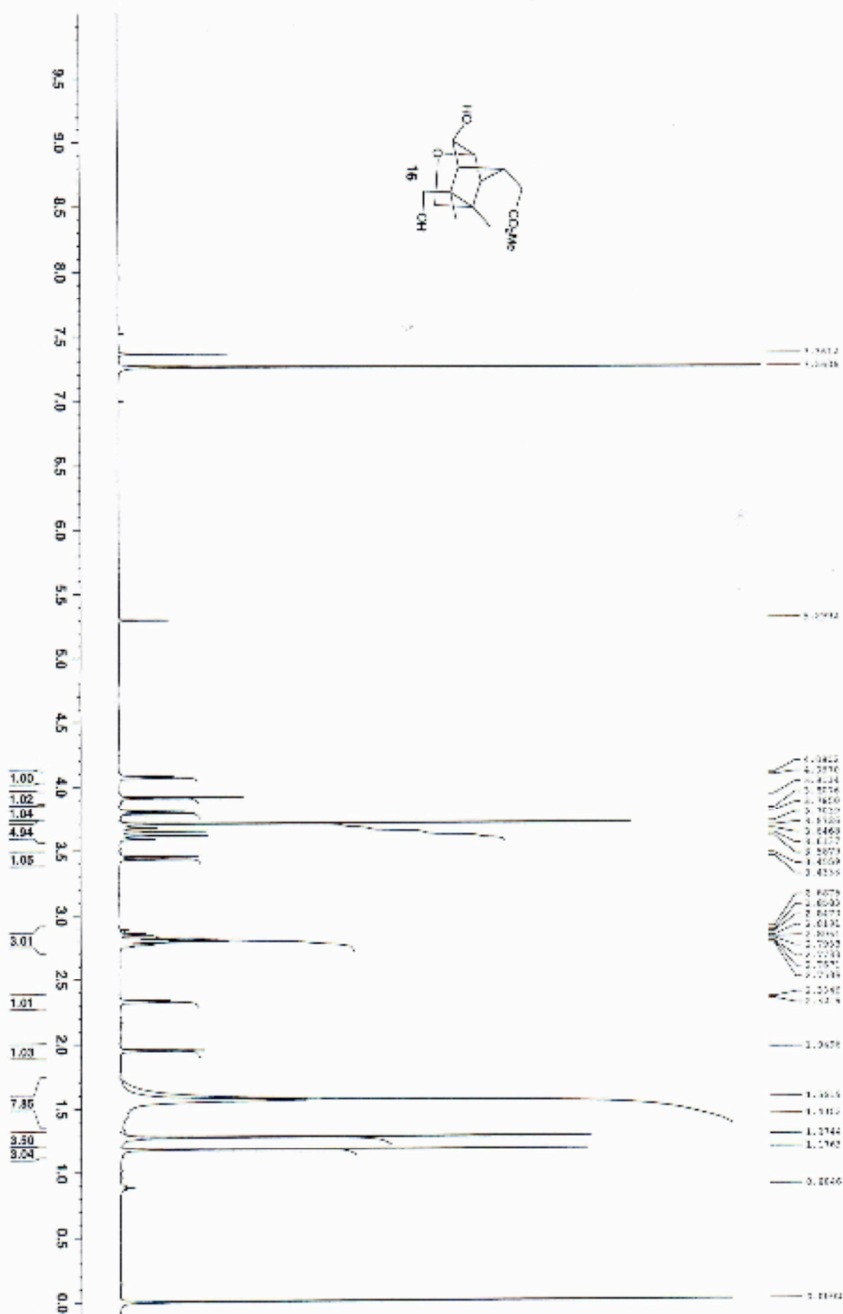
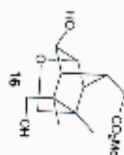
13C mg/MeOH then IN HCl/THF Column 1st spot 10.21.03proton 400MHz

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

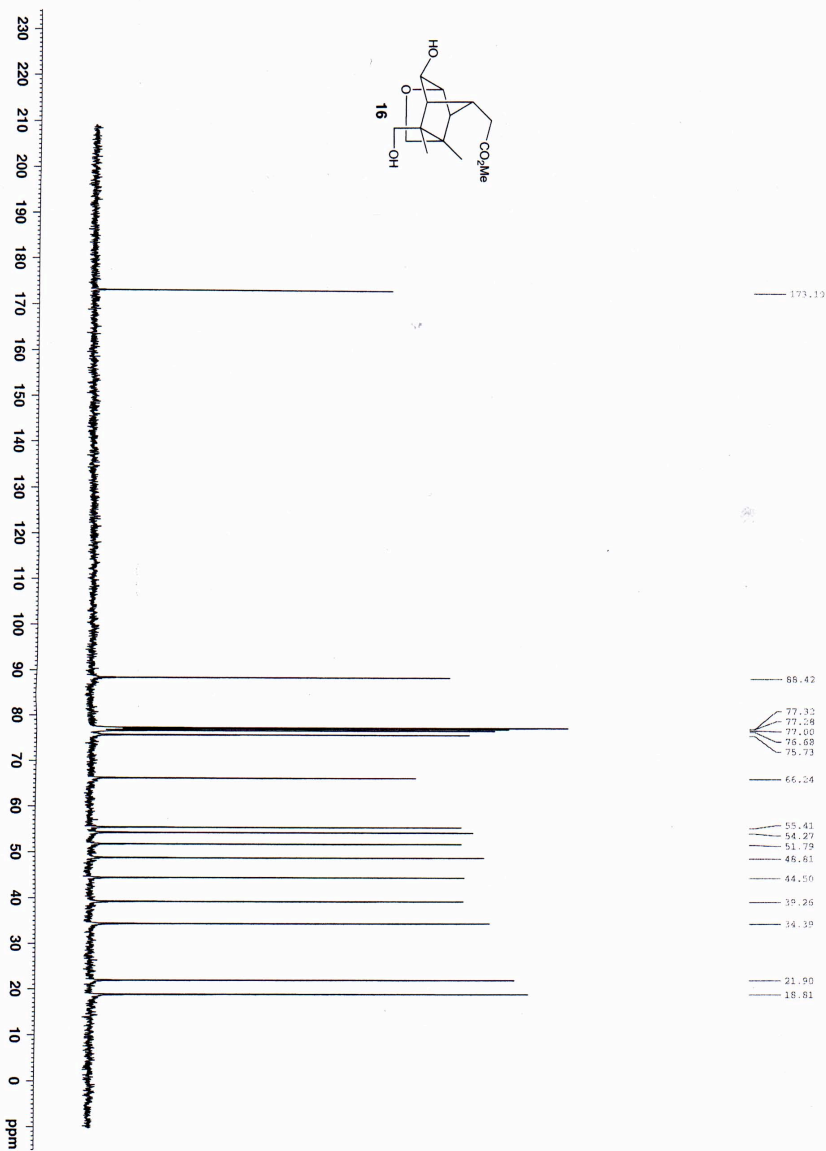
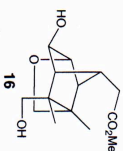


Current Data Parameters
 Name: 10.21.03-04
 PROTON
 F2 - Acquisition Parameters
 Date_: 200210
 Time: 11:11
 Instrument: 5 mm NMR spect
 PULPROG: zgpg30
 TO: 327
 SFO: 400
 NS: 4
 DS: 4
 SWH: 22075.0
 FIDRES: 0.4736
 AQ: 0.04244
 RG: 163
 INE: 22.6
 LRE: 4.4
 TE: 300
 DE: 0.552000
 D1: 0.030000
 d12: 0.000020
 ===== CHANNEL f1 =====
 NU1: 1
 PC1: 17.1
 SFO1: 100.55938
 ===== CHANNEL f2 =====
 CH2: 42.8
 CH3: 96.1
 CH4: 0.1
 CH5: 23.1
 CH6: 399.92159
 SFO2: 100.55937
 F2 - Processing parameters
 SI: 655
 SF: 100.55937
 WBW: 3.
 GB: 1.
 PC: 1.

SP06000 400MHz

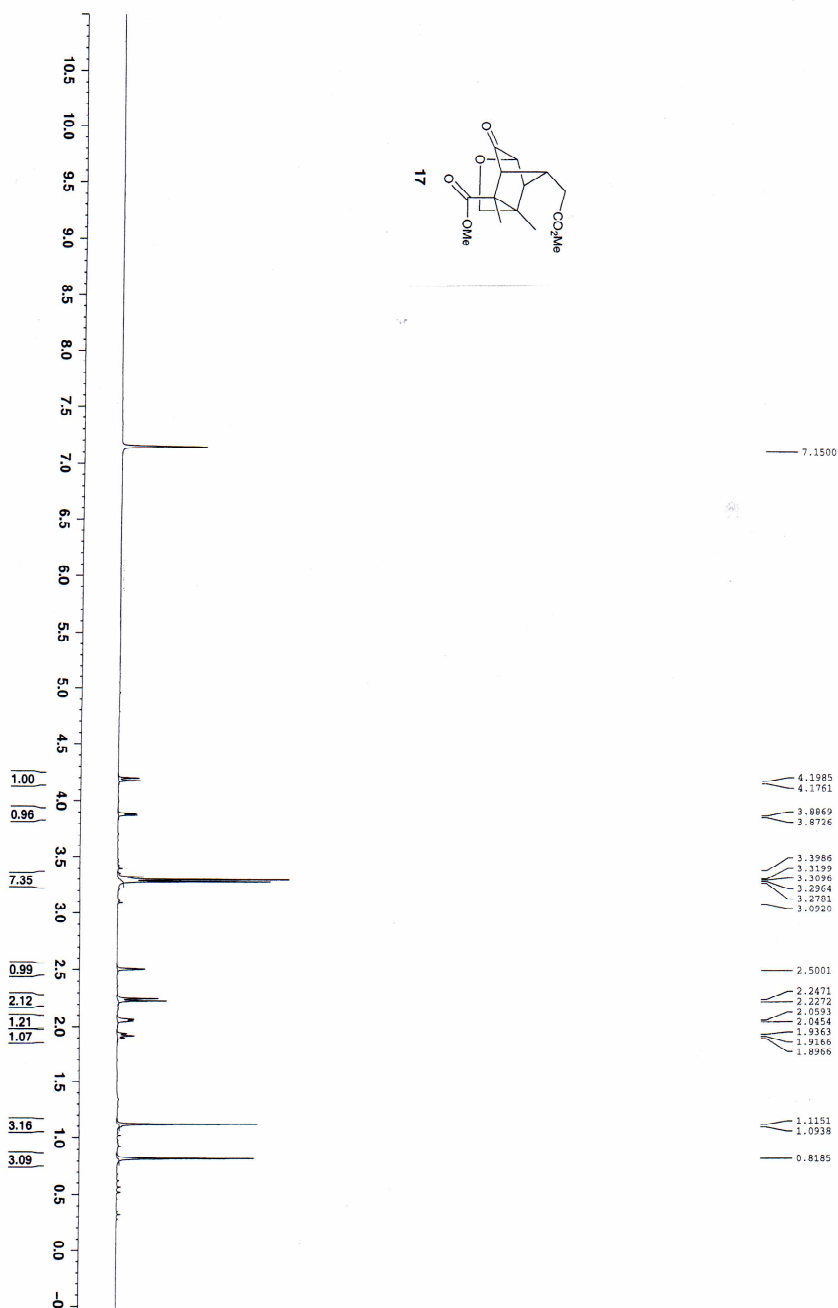
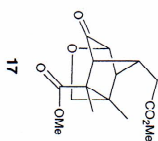


MCEBA-Epo-Diol 400MHz 13Cproton 400Mhz

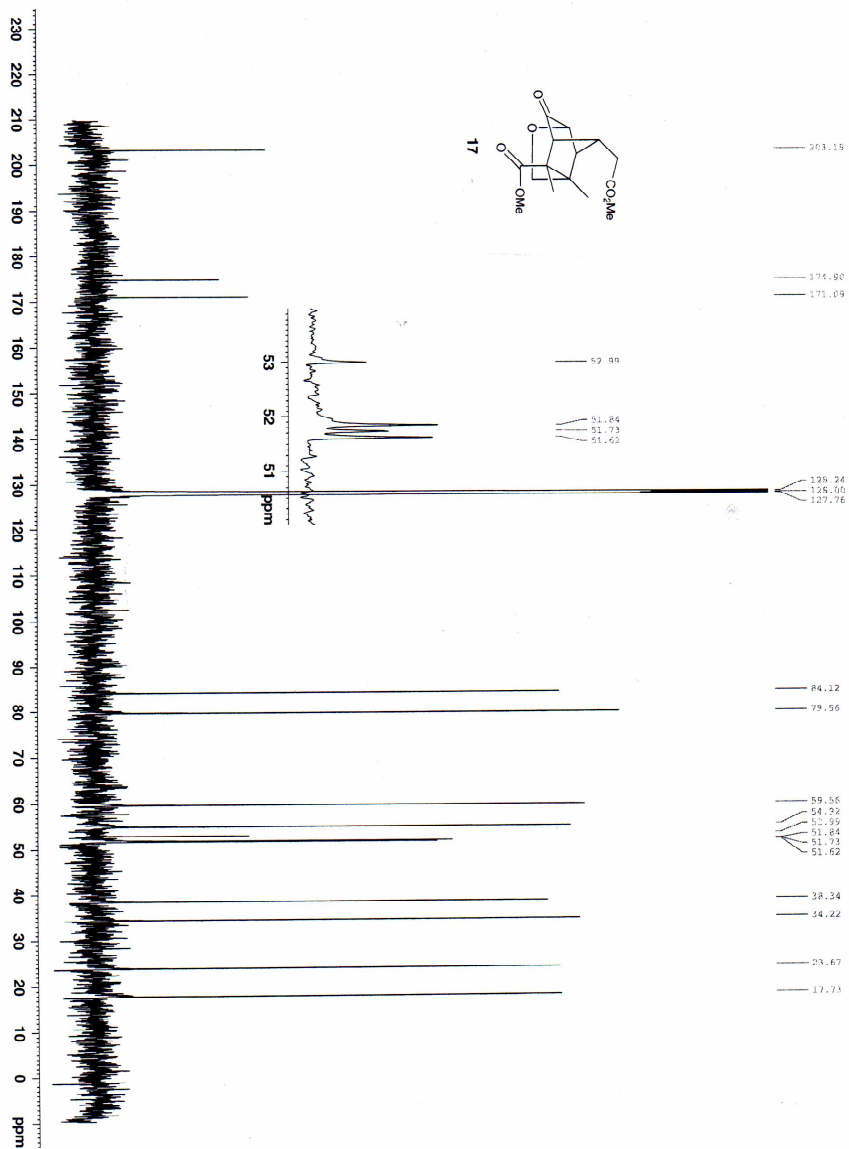


Current Data Parameters
NAME 11.03.05-epo-
EXPNO 11.03.05-epo-
PROCNO 1
F2 - Acquisition Param
Date_ 20031110
Time 14.40
INSTRUM 5 mm Multisc
PROBHD 1H/13C
PULPROG zgpg30
TD 3276
SOLVENT AcetC
NS 256
DS 4
SWH 22075.05
FIDRES 0.161313
AQ 0.742245
RG 1638
RW 22.65
AQ 0.742245
DE 6.6
TE 300.
D1 0.2500000
d11 0.0300000
d12 0.0002000
===== CHANNEL f1 =====
NUC1 13
P1 17.0
PL1 -1.0
SFO1 100.569980
===== CHANNEL f2 =====
CHRGPG2 waltz16
NUC2 13
P2 17.0
PL2 -1.0
SFO2 100.569980
PCPD2 96.2
RG2 1638
RW 22.65
AQ 0.742245
DE 6.6
TE 300.
D1 0.2500000
d11 0.0300000
d12 0.0002000
F2 - Processing Param
SI 6553
SF 100.559981
WDW 100.559981
SSB 3.0
GB 1.0
PC 1.4

PPC-NEI-06D6-01/16/04 400MHzproton 400MHz



FDC-MeI-CeD6-400MHzproton 400Mhz



Current Data Parameters
 NAME 0116 04-FDC-M
 EXPTNO 2
 PROCNO 1
 P2 - Acquisition Param
 F2 2049414
 Time 9.02
 INSTRUM 5 mm BBO spect
 PULPROG zgpg30
 FIDRES 31768
 AQC 325
 DS 32015.0545
 AO 0.742482
 FIDRES 0.673677
 DE 6.00
 DW 22.656
 DI 0.25600001
 D11 0.03600001
 D12 0.000200
 ===== CHANNEL f1 =====
 NU1 17.50
 P1 1.00
 P2 1.00
 SFO1 100.565980
 ===== CHANNEL f2 =====
 CH2 11
 WAIT 11
 F2 56.2
 P1 23.0
 P13 23.0
 SFO2 359.921599
 P2 - Processing param
 S2 180.553926
 WNM E
 LSR 3.0
 GB 1.4
 PC

proton 400Mhz

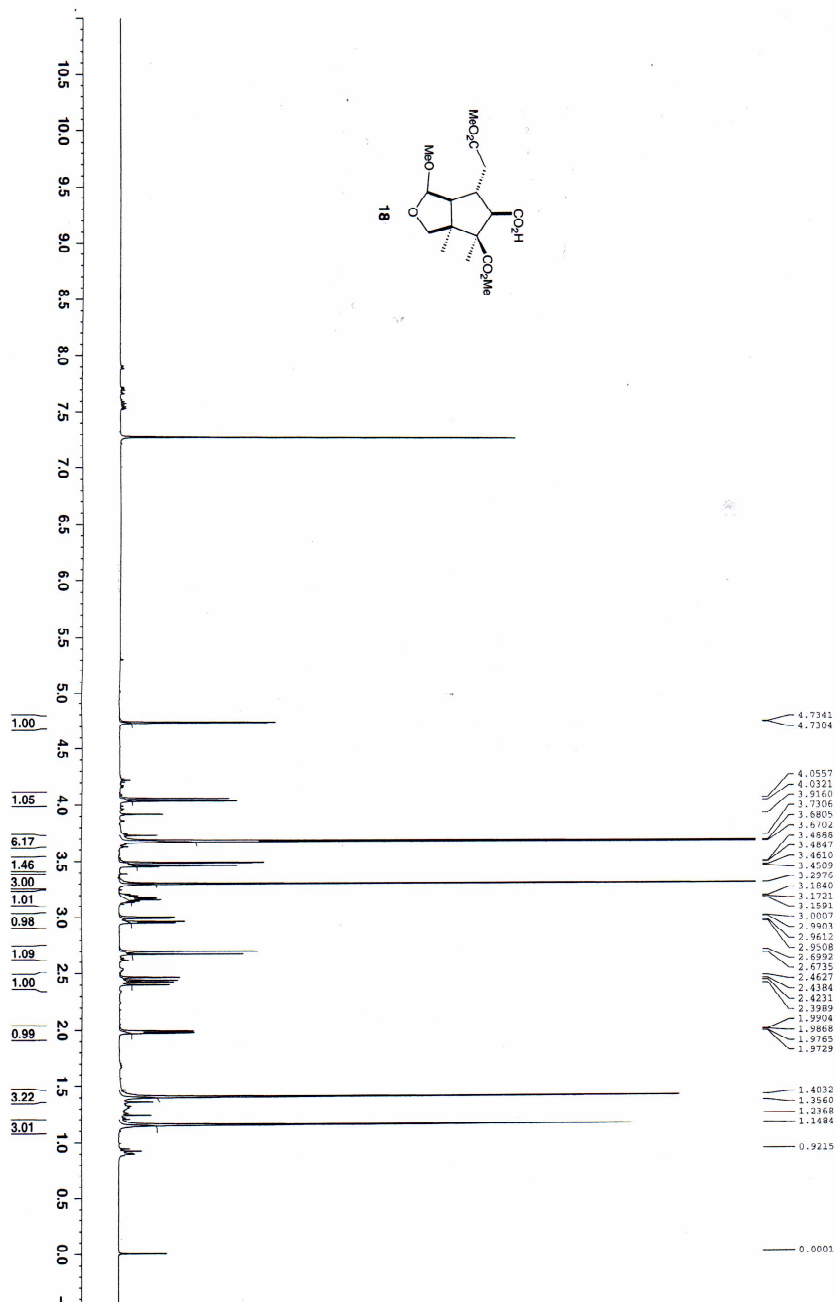
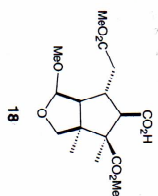
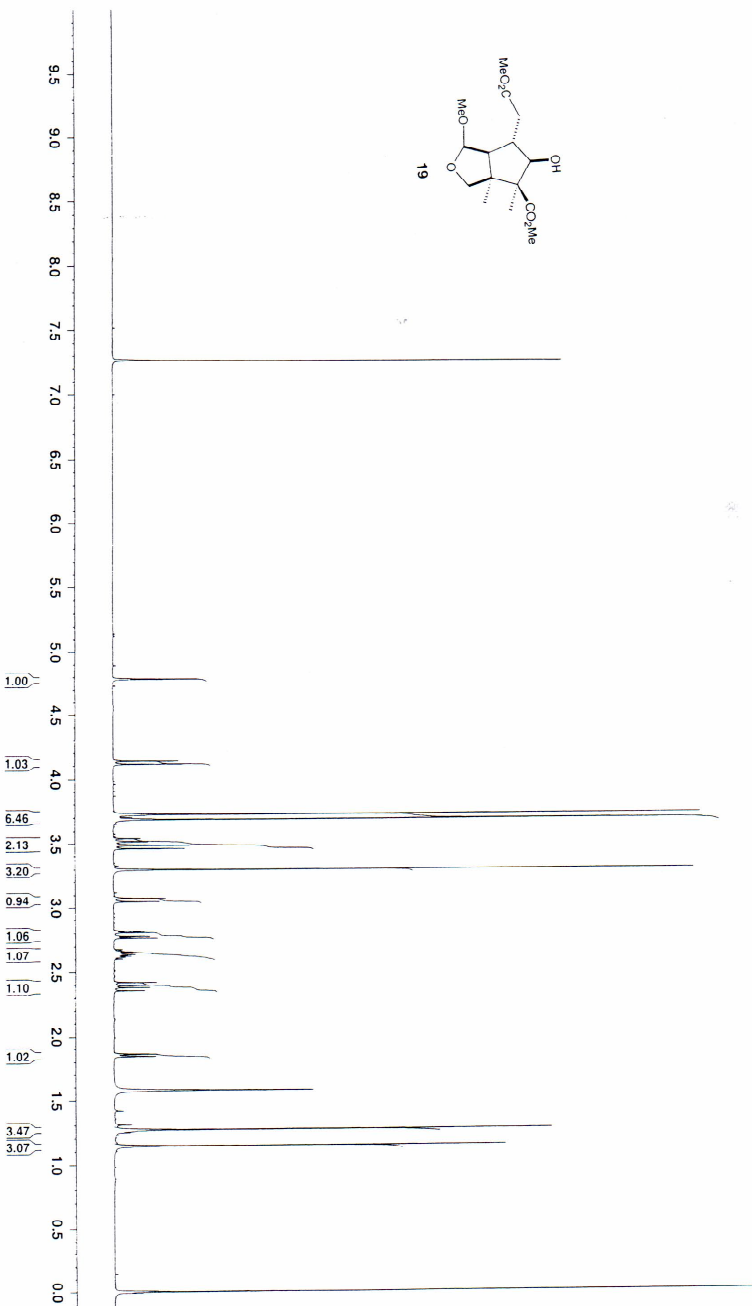


Figure 1 is a dendrogram illustrating the hierarchical clustering of 15 samples based on their genetic similarity. The samples are numbered 1 through 15. The dendrogram shows a primary split between sample 1 and a large cluster of samples 2-15. Within the 2-15 cluster, there are several sub-clusters, including a group of samples 2-10 and a group of samples 11-15. The scale on the right indicates genetic distance from 0 to 0.25.



CHEMICAL NAME

174.076
172.992

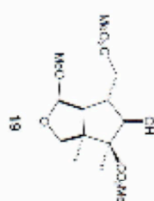
111.892

84.168
77.426
77.002
76.579
73.703

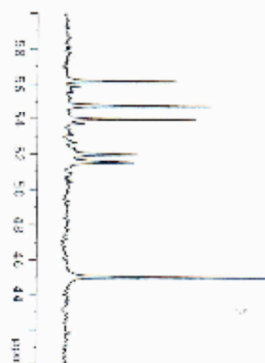
55.184
54.802
53.983
52.038
51.563
48.954
36.930

21.523
18.303

300 MHz

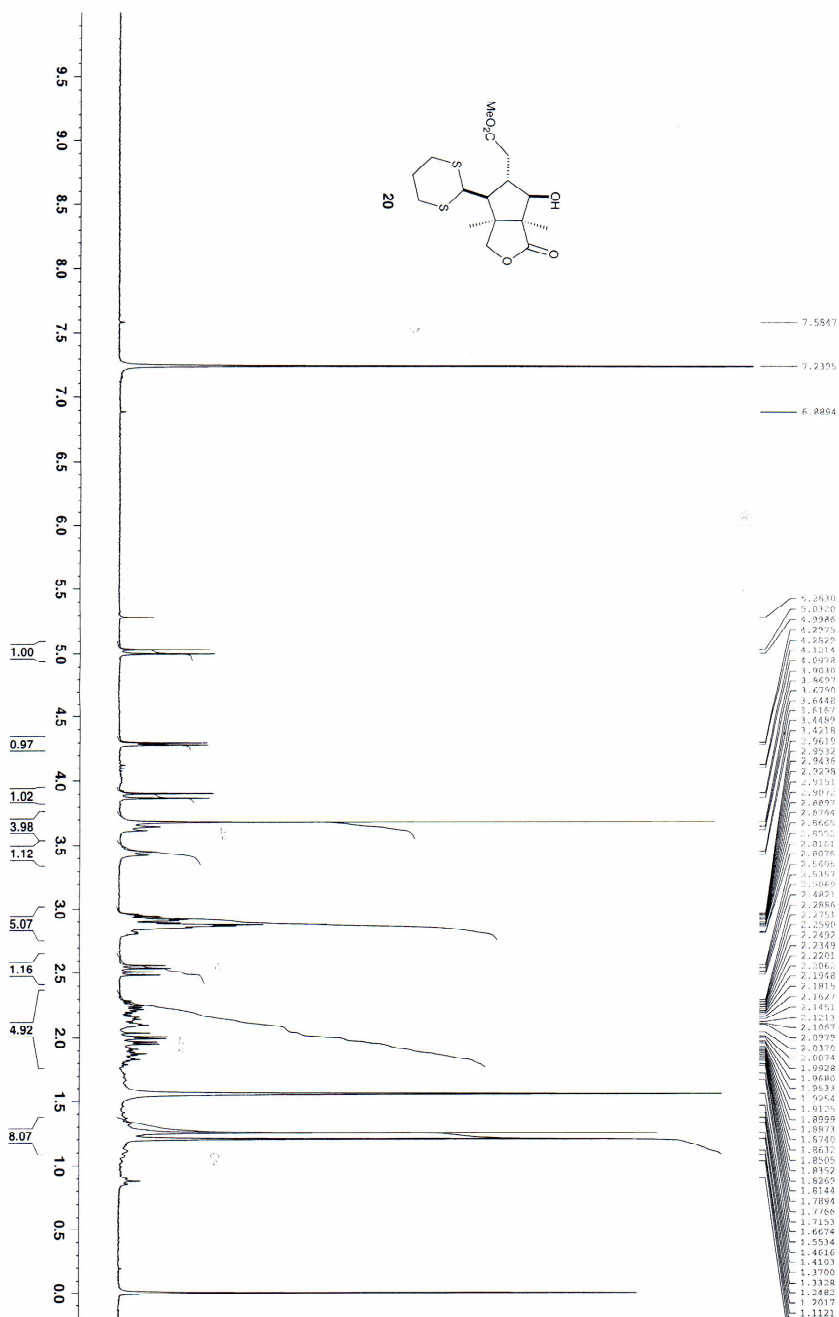


55.184
54.802
53.983
52.038
51.563
48.954

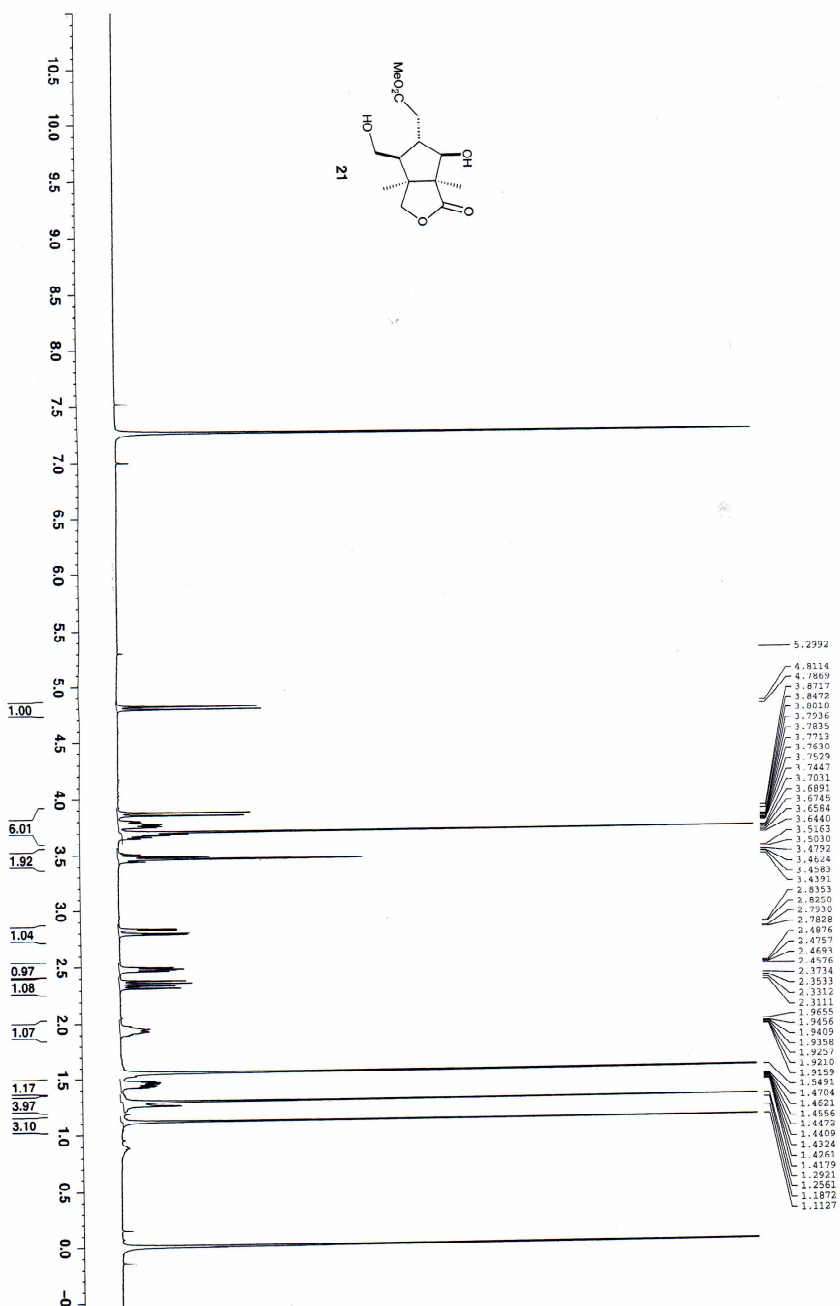
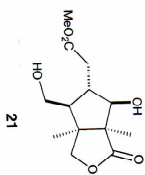


260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30

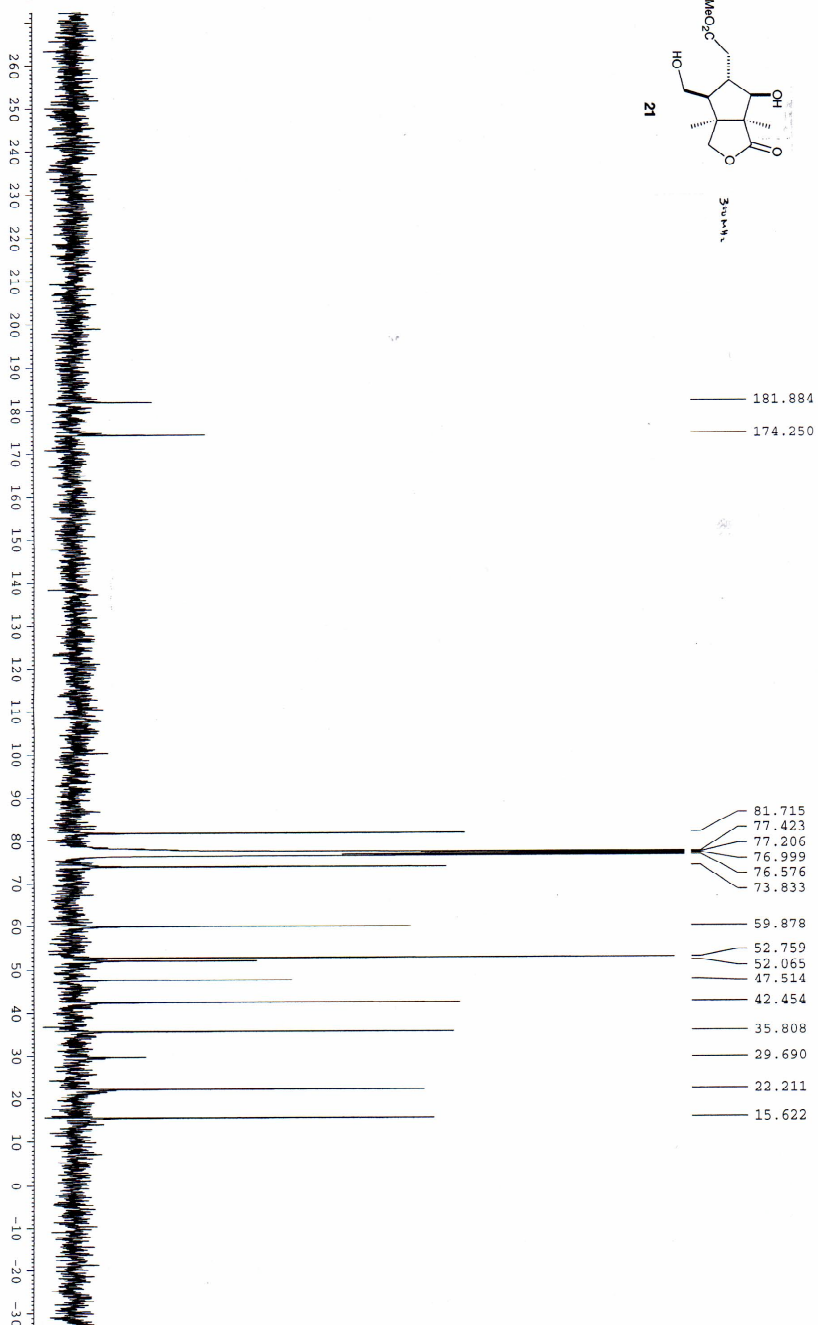
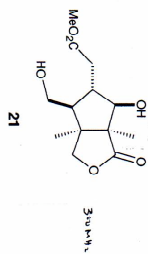
proton standard

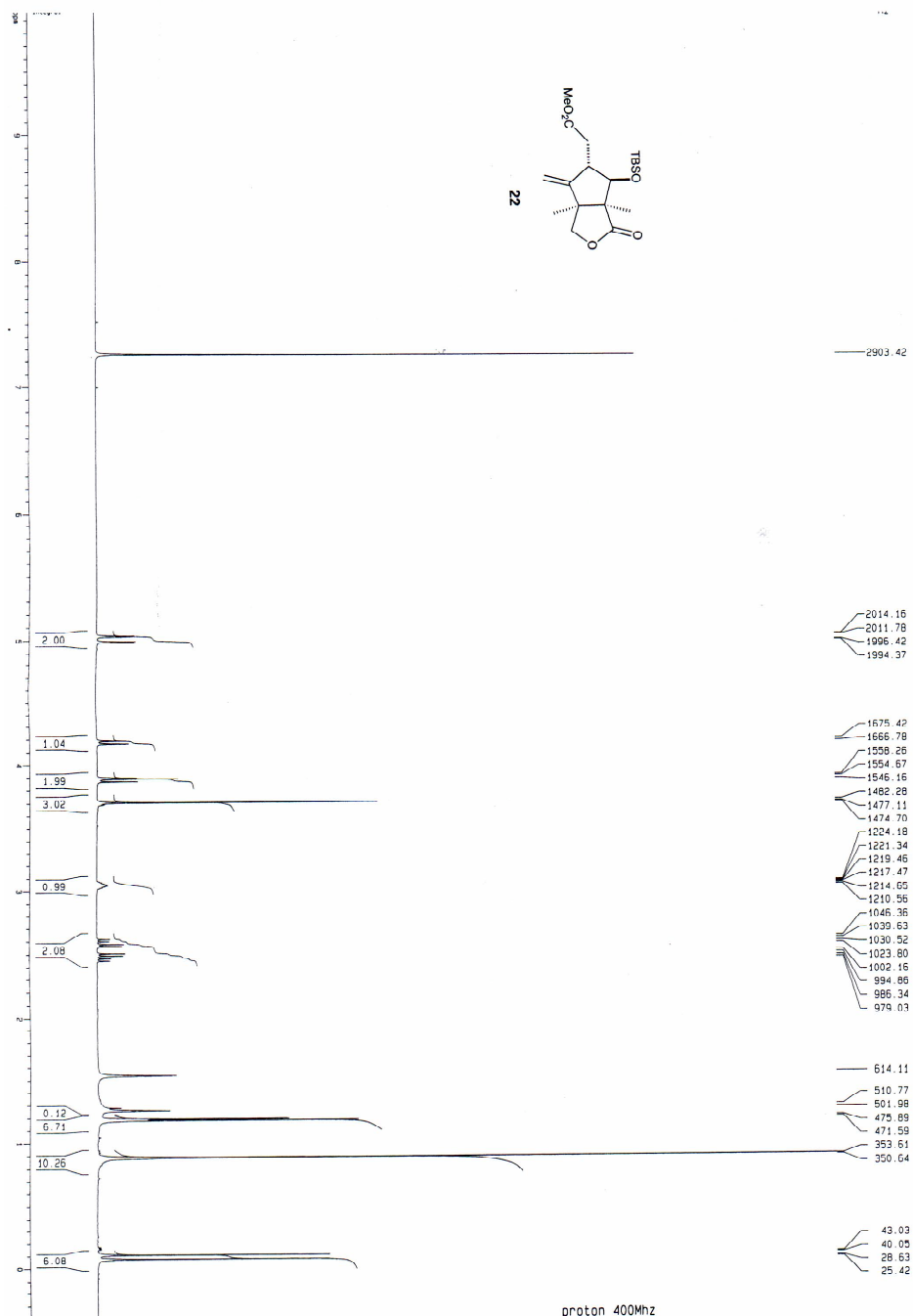


NABH4 - Dial 400 MHz/Proton 400MHz

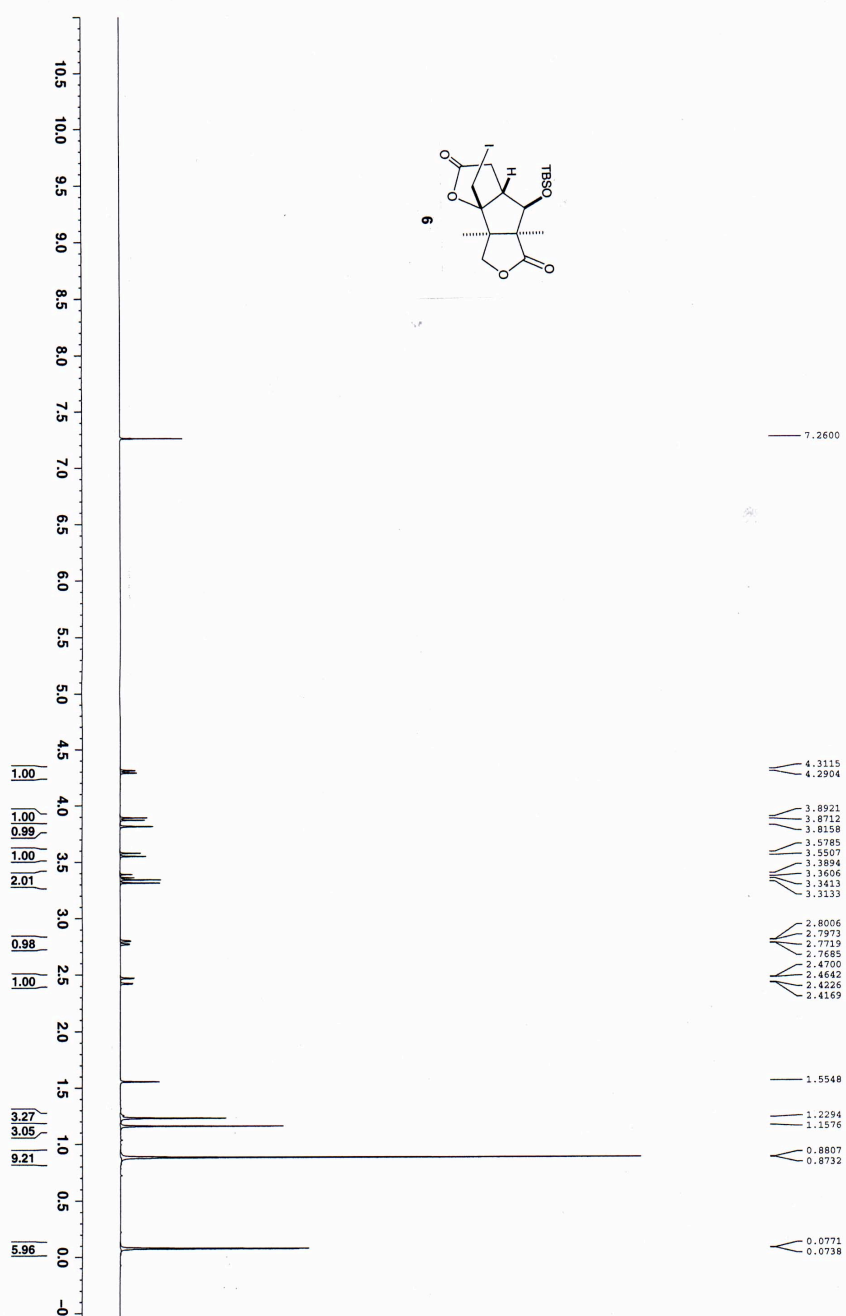
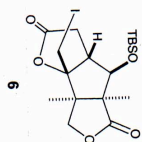


NAME4 CHO to Diol 10.23.03 300MHzcarbon NMR



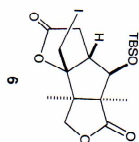


Iodo-400MHzproton 400Mhz



proton 400mhz

175.93
173.69



95.45
87.90
77.32
77.00
76.88
76.41
61.28
57.23
56.96
37.40
25.74
17.92
16.41
16.05
7.95
-4.59
-4.98

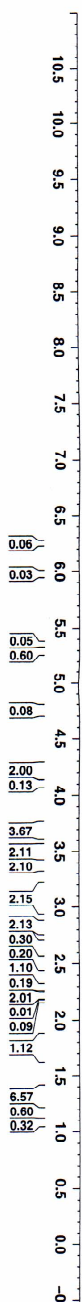
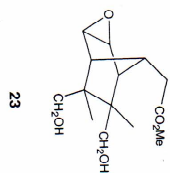
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Current Data Parameters
NAME
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Time 20.21
INSTRUM 5 mm Nal-K25
PULPROG zgpg30
TD 327
SOLVENT DMSO
NS 144
DS 23016
AQ 0.74224
RG 256
IN 22.5
DE 6.1
DI 0.250000
D1 0.030001
d12 0.000021
===== CHANNEL f1 :
NUC1 1H
P1 17
PL1 -1
SFO1 400.56591
===== CHANNEL f2 :
NUC2 13C
P2 17
PL2 -1
SFO2 100.56591
===== CHANNEL f3 :
NAME waitc
NUC3 13C
P3 96
PL3 0
SFO3 100.56591
===== CHANNEL f4 :
NAME waitc
NUC4 13C
P4 96
PL4 0
SFO4 100.56591
SI - Processing parameters
SI 100.56591
WDW 3
SSB 3
GB 1
PC 1

Diol-DMDO-dry over Na2SO4-9.16.04proton standard

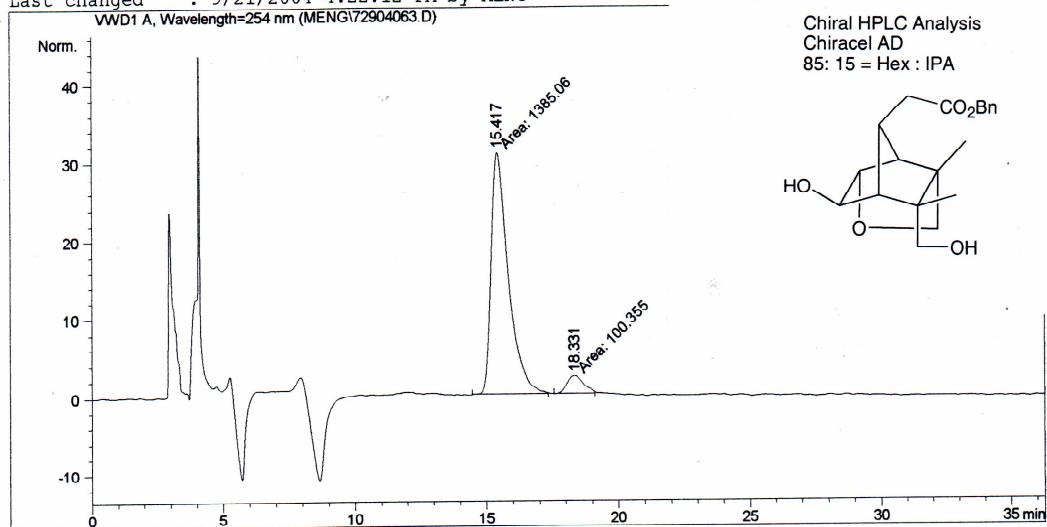
7.2600

6.2565
6.2458
6.2431
5.9837
5.1548
5.1019
4.7479
4.4373
4.3954
4.2107
4.1741
4.1309
4.0961
4.0743
4.0642
4.0328
3.9270
3.8942
3.8572
3.8440
3.8186
3.7997
3.7693
3.7014
3.6854
3.6769
3.6449
3.6054
3.5963
3.5796
3.5204
3.4940
3.4539
3.4390
3.4210
3.3725
3.3123
3.2757
3.2534
3.2301
3.0942
2.9517
2.8477
2.8184
2.7979
2.7822
2.7618
2.6943
2.6648
2.6309
2.6051
2.5126
2.4798
2.4395
2.4060
2.3770
2.3475
2.3073
2.2181
2.1808
2.1376
2.0554
1.9751
1.9498
1.7530
1.5084
1.4885
1.4273
1.3647
1.3446
1.3058
1.2725
1.2451
1.2278
1.1972
1.1769
1.1084
1.0899
0.0814



CHIRACEL AD
85:15

=====
Injection Date : 9/20/2004 4:40:57 PM
Sample Name : CO2Bn-(S,S)--78C Location : Vial 1
Acq. Operator : MENG
Acq. Method : C:\HPCHEM\1\METHODS\FURUUCHI.M
Last changed : 8/24/2004 3:19:17 PM by MENG
Analysis Method : C:\HPCHEM\1\METHODS\FURUUCHI.M
Last changed : 9/21/2004 4:22:12 PM by MENG
=====

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	15.417	MM	0.7468	1385.05530	30.90910	93.2440
2	18.331	MM	0.7435	100.35492	2.24952	6.7560

Totals : 1485.41022 33.15862

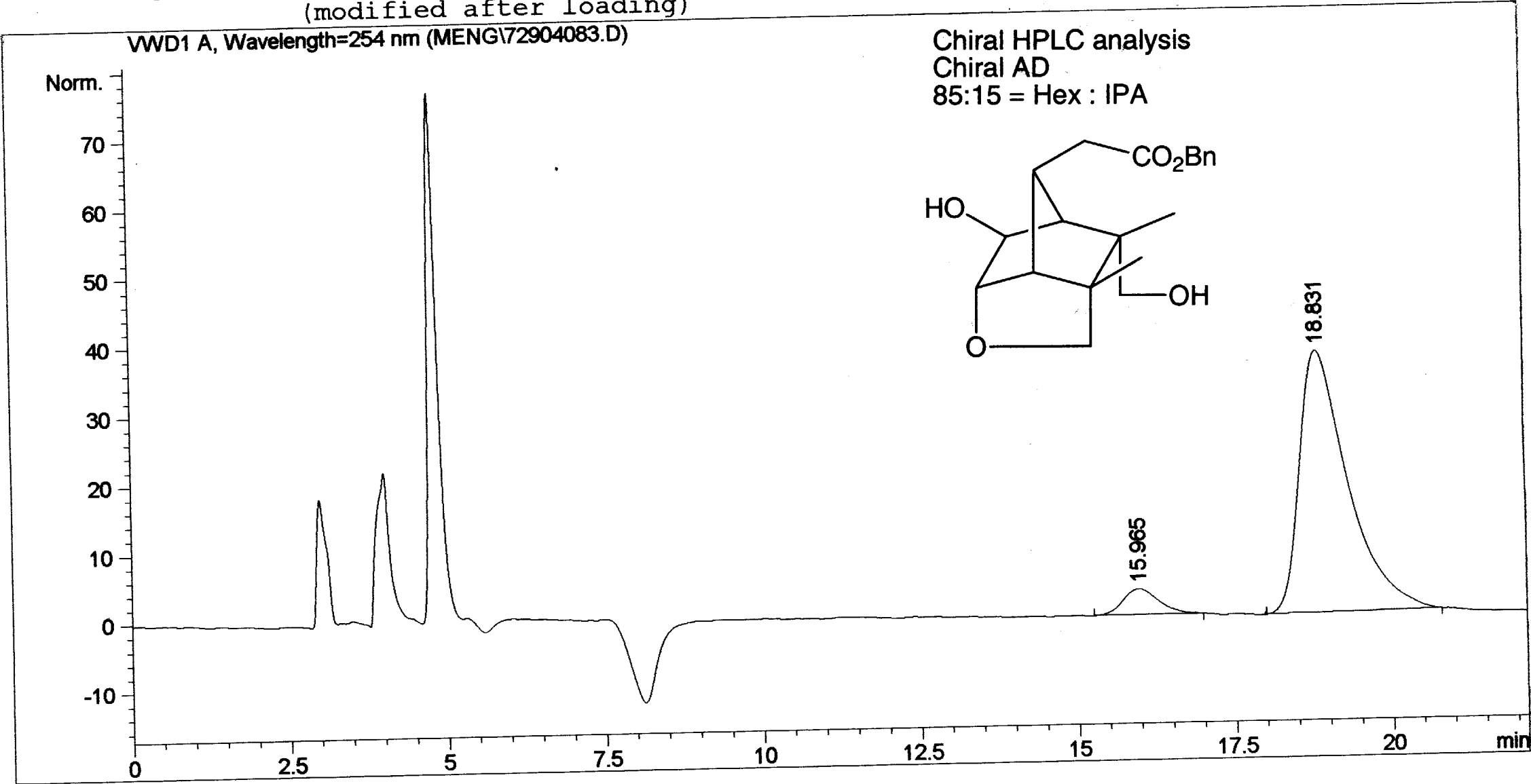
Results obtained with enhanced integrator!

=====
*** End of Report ***
=====

CHIRACEL AD
85:15

=====
Injection Date : 11/10/2004 2:36:53 PM
Sample Name : Bn-R,R--78C
Acq. Operator : MENG
Method : C:\HPCHEM\1\METHODS\FURUUCHI.M
Last changed : 10/23/2004 5:15:40 PM by MENG
(modified after loading)

Location : Vial 1



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	15.965	BB	0.6113	151.64317	3.77508	6.9402
2	18.831	PB	0.7906	2033.35901	37.97851	93.0598

Totals : 2185.00218 41.75358

Results obtained with enhanced integrator!

=====
*** End of Report ***