Supporting information for:

Enantioselective Total Synthesis of All of the Known Chiral Cleroindicins, (C-F): Clarification Among Optical Rotations and Assignments

Todd A. Wenderski, Shenlin Huang, and Thomas R. R. Pettus.*

Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara CA 93106.

pettus@chem.ucsb.edu

Table of Contents

I. General Techniques, page S1-S2
II. Experimental Procedures and spectral data, pages S2 – S10
III. Revised Biosynthetic Pathway, page S11
IV. HPLC traces, ^{1}H NMR spectra, ^{13}C NMR spectra, IR spectra
A. HPLC traces, pages S12 – S17
B. NMR and IR spectra, pages S18 – S59
V. References, page S59

I. General Techniques – In reactions, where water was *not* present as solvent, reagent, or by-product, vessels were flame-dried under a slow nitrogen flow. A slight positive pressure of dry nitrogen was maintained via rubber septum seal during the course of the reaction. The nitrogen stream originated from a regulated high pressure 55 L N_2 *(l)* tank and was further dried by passage through a tube filled with $CaSO_4$. Reagents were purified according to the procedures described in *Purification of Laboratory Chemicals* (W.L. F. Armarego and C. L. L. Chai).

Reactions were monitored by analytical thin-layer chromatography on hard layer silica gel-60$^{F\text{-}250}$ plates cut into 1x2.5cm pieces. Visualization was effected by ultraviolet light (254 nm), followed by staining (Seebach, permanganate, or I_2 followed by PMA) the plate, followed by drying with a heat gun or on a micro-hot plate. The Seebach stain was made with 25 g of phosphomolybdic acid, 10 g of cerium sulfate, 60 mL H_2SO_4, and 940 mL of H_2O. The potassium permanganate stain was made with 200 mL H_2O, 1.33 g $KMnO_4$, 13.33 g of K_2CO_3, and 4 mL of 5% NaOH. I_2 stain consisted of a chamber containing I_2 impregnated silica gel. PMA (phosphomolybdic acid) stain was made by dissolving 10 g of phosphomolybdic acid in 100 mL of absolute ethanol.

All reactions were stirred with PTFE coated magnetic stir bars and magnetic stirrers. Removal of solvents was typically accomplished using a rotary evaporator connected to a vacuum pump. The condenser was cooled to 0 °C by a chiller circulator bath. If the product was non-volatile, trace solvents were removed using a freeze dryer system at a pressure of approximately 0.01 mmHg.

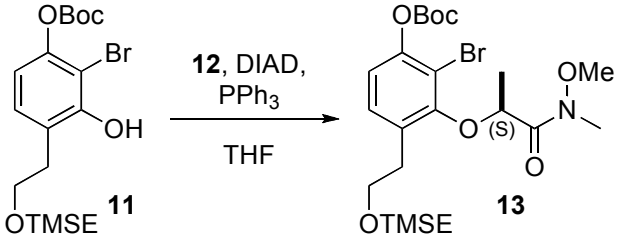
For distillation, a specific low pressure (760 – 1 mm Hg) was obtained and monitored with a vacuum controller in combination with a direct drive pump. Bulb-to-bulb distillation was performed using a glass oven. Chromatography was performed following the method used by W. C. Still (*J. Org. Chem.* **1977**, *42*, 1258-1259).

Deuterated chloroform was filtered through basic alumina prior to use. Solvents were distilled before use, under a slight positive pressure of nitrogen. Diethyl ether, tetrahydrofuran, benzene, and toluene were distilled from sodium and benzophenone. Dichloromethane and nitromethane were distilled from CaH_2. Atmosphere (1 atm) hydrogenations were carried out using a balloon.

^{1}H-NMR spectra were recorded using a 400 MHz or 500 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance of $CDCl_3$ (7.27 ppm). ^{13}C NMR spectra were recorded at 100 MHz or 125 MHz with a solvent resonance of $CDCl_3$ (77.23 ppm). Infrared spectra were recorded on a Fourier transform infrared spectrometer with 2 cm resolution as a neat sample on a NaCl plate. Infrared frequencies are reported in reciprocal centimeters (cm^{-1}). Silica columns for HPLC, were 25 cm long in length and contained 5 μm spherisorb. Mass spectra were recorded at an ionizing voltage of either 70 or 20 eV.

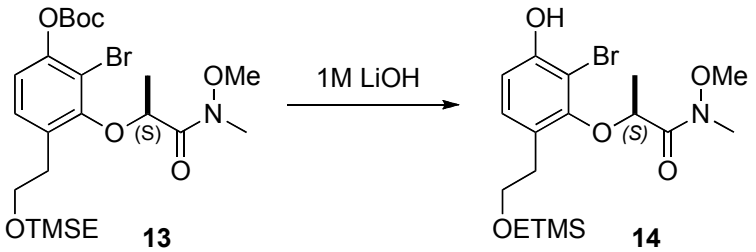
II. Additional Experimental Procedures

(*S*)-2-Bromo-3-(1-(methoxy(methyl)amino)-1-oxopropan-2-yloxy)-4-(2-(2-(trimethylsilyl)ethoxy)ethyl)phenyl *tert*-butyl carbonate (13).



Diisopropyl azodicarboxylate (DIAD) (0.86 mL, 4.39 mmol) was added dropwise to a stirring solution of triphenylphosphine (PPh_3) (1.151 g, 4.39 mmol) in THF (14 mL) at 0 ˚C. The resulting suspension was stirred at 0 ˚C to rt for 1 h. The mixture was cooled to 0 ˚C and a solution of phenol **11** (1.267 g, 2.92 mmol) in THF (9 mL) was added via cannula followed by a solution of (*R*)-2-hydroxy-*N*-methoxy-*N*-methylpropanamide 12 (0.430 g, 3.22 mmol) in THF (6 mL). The reaction was stirred at 0 ˚C to rt for 24 h. Afterwards, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography with 15% EtOAc/hexanes (R_f = 0.2) to afford colorless oil **13** (1.39 g, 2.54 mmol, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 5.32 (q, J = 6.4 Hz, 1H), 3.58 (t, J = 6.8 Hz, 2H), 3.52 (s, 3H), 3.50 (t, J = 8 Hz, 2H), 3.17 (s, 3H), 3.10 (m, 1H), 2.97 (m, 1H), 1.55 (s, 9H), 1.54 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 8 Hz, 2H), –0.02 (s, 9H); ^{13}C NMR (100 MHz. $CDCl_3$) δ 172.0, 154.4, 151.0, 147.9, 133.3, 129.9, 118.7, 112.1, 84.2, 75.0, 70.0, 68.1, 61.7, 32.4, 30.8, 27.8, 18.3, 18.0, –1.2; IR (thin film) 2980, 2951, 2939, 2895, 2858, 1765, 1678, 1153 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{38}BrNO_7SiNa$: 570.1499. Found 570.1504.

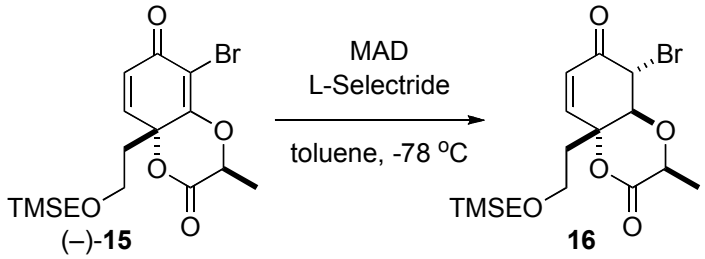
(*S*)-2-(2-Bromo-3-hydroxy-6-(2-(2-(trimethylsilyl)ethoxy)ethyl)phenoxy)-*N*-methoxy-*N*-methylpropanamide (14).



To a stirring solution of *tert*-butyl carbonate **13** (2.156 g, 3.93 mmol) in THF/MeOH (60 mL/40 mL) at 0 ˚C, 1M aq LiOH (22 mL, 22 mmol) was added in one portion. The reaction was stirred at 0 ˚C to room temperature for 8 hours. The reaction was then quenched with 1M HCl and extracted with EtOAc four times. The combined

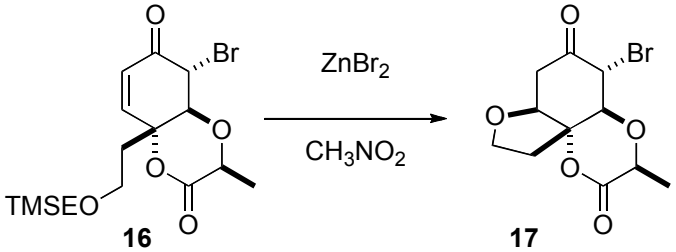
organic layer was washed with water, brine, and dried with Na_2SO_4. The filtered solution was concentrated and the crude residue was purified by chromatography with 25% EtOAc/hexanes (R_f = 0.2) to afford colorless oil **14** (1.67 g, 3.73 mmol, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.57 (s, 1H), 5.19 (q, J = 6 Hz, 1H), 3.55 (s, 3H), 3.55 (t, 2H), 3.50 (t, J = 9.6 Hz, 2H), 3.19 (s, 3H), 2.97 (m, 2H), 1.51 (d, J = 6.4 Hz, 3H), 0.92 (t, J = 8.4 Hz, 2H), –0.03 (s, 9H); ^{13}C NMR (100 MHz. $CDCl_3$) δ 172.3, 153.6, 152.6, 130.1, 126.3, 111.9, 105.9, 75.2, 70.3, 68.1, 61.6, 32.5, 30.5, 18.3, 18.0, –1.3; IR (thin film) 2951, 2893, 2862, 1651, 1431, 1076 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{30}BrNO_5SiNa$: 470.0974. Found 470.0986.

(3*S*,4a*S*,5*R*,8a*R*)-5-Bromo-3-methyl-8a-(2-(2-(trimethylsilyl)ethoxy)ethyl)-4a,5-dihydrobenzo[*b*][1,4]dioxine-2,6(3*H*,8a*H*)-dione (16).



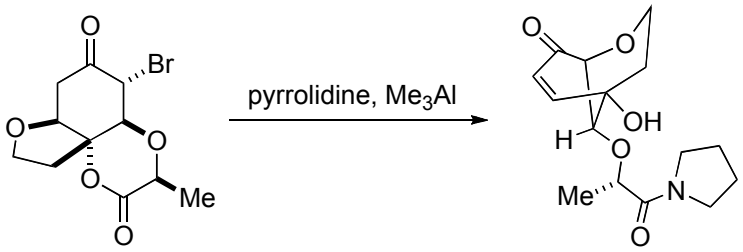
To a flame dried flask equipped with a stir bar, was charged with 2,6-di-*tert*-butyl-4-methylphenol (BHT) (0.534 g, 2.43 mmol), and toluene (5 mL). The solution was cooled to 0 ˚C and $AlMe_3$ (1.4 M in hexanes, 0.87 mL, 1.21 mmol) was added. The resulting mixture of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) was stirred at 0 ˚C to room temperature for 1 h, then cooled to –78 ˚C. In a separate flask, dienone **15** (0.196 g, 0.485 mmol) was dissolved in toluene (1.2 mL), and the solution was added via cannula to the MAD at –78 ˚C, immediately turning deep purple. The reaction was stirred for 5 min, then L-Selectride (1M in THF, 0.5 mL, 0.5 mmol) was added, and the solution was stirred for another 5 min at –78 ˚C. The reaction mixture was quenched with 1M aq Rochelle's salt, diluted with EtOAc, and quickly warmed by hand to rt. It was stirred vigorously for 1 h. The aqueous layer was extracted with EtOAc and the combined organics were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash chromatography with 15% EtOAc/hexanes (R_f = 0.2) to give **16** as colorless oil (0.163 g, 0.403 mmol, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 10 Hz, 1H), 6.13 (d, J = 10.4 Hz, 1H), 4.62 (q, J = 7.2 Hz, 1H), 4.62 (d, J = 12 Hz, 1H), 4.13 (d, J = 12 Hz, 1H), 3.65 (m, 2H), 3.47 (m, 2H), 2.41 (m, 1H), 2.10 (m, 1H), 1.67 (d, J = 7.2 Hz, 3H), 0.89 (t, J = 6.8 Hz, 2H), 0.04 (s, 9H); ^{13}C NMR (100 MHz. $CDCl_3$) δ 188.8, 169.0, 149.9, 126.9, 82.0, 80.5, 74.6, 68.7, 64.0, 50.0, 37.2, 18.3, -1.2; IR (thin film) 2951, 2870, 1755, 1686, 1246, 1099 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{25}BrO_5SiNa$: 427.0552. Found 427.0550.

(2*S*,41*R*,7a*S*,10*R*,10a*S*)-10-Bromo-2-methyltetrahydro-2H-benzofuro[4-*b*][1,4]dioxine-3,9(10*H*,10a*H*)-dione (17).



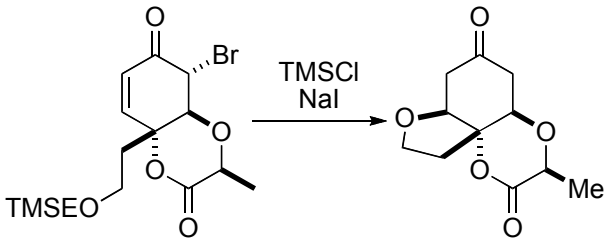
$ZnBr_2$ (89 mg, 0.40 mmol) was added to a stirring solution of **16** (41 mg, 0.1 mmol) in CH_3NO_2 (1.3 mL). The reaction was stirred for 24 h at room temperature. The reaction was quenched with 1 M HCl and extracted with EtOAc four times. The combined organic layer was washed with $NaHCO_3$ (aq), brine, dried (Na_2SO_4), and filtered. The solution was concentrated and the crude residue was purified by chromatography with 15% EtOAc/hexanes to afford colorless oil **17** (25 mg, 0.080 mmol, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (q, J = 7.2 Hz, 1H), 4.34 (dd, J = 2 Hz, J = 4.8 Hz, 1H), 4.30 (d, J = 10.4 Hz, 1H), 4.12 (d, J = 10.4 Hz, 1H), 4.06 (m, 1H), 3.88 (m, 1H), 2.96 (dd, J = 4.8 Hz, J = 15.2 Hz, 1H), 2.84 (dd, J = 0.8 Hz, J = 16.4 Hz, 1H), 2.13 (m, 2H), 1.66 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz. $CDCl_3$) δ 198.4, 168.6, 89.1, 79.8, 78.3, 74.3, 66.3, 45.4, 42.0, 36.4, 18.5; IR (thin film) 2986, 2922, 2953, 2872, 2854, 1736, 1244, 1203, 1122 cm^{-1}; $[\alpha]_D^{25}$ = –78.5 ($CHCl_3$, c = 1.2). HRMS (EI) calcd for $C_{11}H_{13}BrO_5$: 303.9946. Found 303.9953.

5-hydroxy-9-((*S*)-1-oxo-1-(pyrrolidin-1-yl)propan-2-yloxy)-2-oxabicyclo[3.3.1]non-6-en-8-one (19).



A solution of pyrrolidine (8.3 μL, 0.098 mmol) in CH_2Cl_2 (1.0 mL) was cooled to 0 ˚C and $AlMe_3$ (25% wt/wt in hexanes, 43 μL, 0.098 mmol) was added dropwise. The solution was stirred for 1 h, and allowed to slowly warm to room temperature. It was cooled to 0 ˚C and the dione **17** (10 mg, 0.033 mmol) as a solution in CH_2Cl_2 (0.5 mL) was added to the aluminum amide via cannula. The reaction was stirred from 0 ˚C to rt for 24 h. It was quenched with 1M Rochelle's salt (2 mL), diluted in EtOAc (3mL) and stirred vigorously for 1 h. The aqueous layer was extracted with EtOAc (4 x 3 mL), and the combined organics were washed with brine (2 mL), dried (Na_2SO_4), and concentrated. Flash chromatography of the residue (20% EtOAc/hexanes, R_f = 0.3) yielded colorless oil **19** (5.4 mg, 0.018 mmol, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, J = 10.5 Hz, 1H), 6.37 (s, 1H), 6.26 (d, J = 10 Hz, 1H), 4.30 (q, J = 6.5 Hz, 1H), 4.13 (s, 1H), 3.94 (dd, J = 5.5 Hz, J = 12 Hz, 2H), 3.58 (m, 2H), 3.47 (m, 2H), 3.38 (s, 1H), 3.33 (m, 1H), 2.57 (dt, J = 6 Hz, J = 13 Hz, 1H), 2.01 (m, 3H), 1.91 (m, 2H), 1.49 (d, J = 6.5 Hz, 3H); HRMS (ESI) calcd for $C_{15}H_{21}NO_5Na$: 318.1317. Found 318.1310.

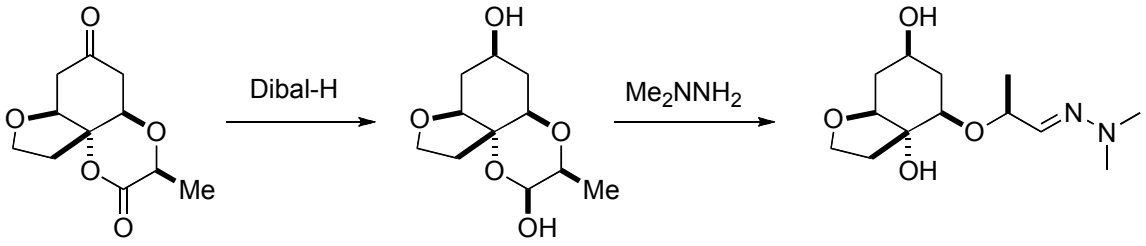
(2*S*,41*R*,7a*S*,10a*R*)-2-Methyltetrahydro-2*H*-benzofuro[4-*b*][1,4]dioxine-3,9(10*H*,10a*H*)-dione (20).



16 (–)-**20**

To a solution of **16** (0.142 g, 0.35 mmol) in CH_3CN (5.8 mL) was added NaI (0.633 g, 4.2 mmol), followed by TMSCl (0.36 mL, 2.8 mmol). The resulting orange solution was stirred at room temperature for 24 hours then quenched with saturated aq $Na_2S_2O_3$. The colorless solution was diluted with EtOAc, separated and the aqueous layer was extracted with EtOAc four times. The combined organics were washed with brine, dried (Na_2SO_4), and concentrated. The crude material was purified by flash chromatography with 35% EtOAc/hexanes (R_f = 0.25) to afford **20** as a colorless oil (77 mg, 0.34 mmol, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.58 (q, J =7 Hz, 1H), 4.28 (dd, J = 6 Hz, J = 12.5 Hz, 1H), 4.27 (d, J = 2 Hz, 1H), 4.05 (t, J= 8 Hz, 1H), 3.87 (m, 1H), 2.84 (dd, J = 6 Hz, J = 19 Hz, 1H), 2.74 (dd, J = 2 Hz, J = 16 Hz, 1H), 2.68 (dd, J = 4.5 Hz, J = 16.5 Hz, 1H), 2.36 (dd, J = 12.5 Hz, J = 19Hz, 1H), 2.33 (m, 1H), 2.05 (dd, J = 4.5 Hz, J = 14 Hz, 1H), 1.60 (d, J = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.0, 169.6, 89.6, 80.2, 73.9, 72.1, 66.2, 43.9, 40.0, 36.0, 18.6; IR (neat): 2986, 2889, 1728 cm^{-1}; HRMS (EI): m/z calcd for $C_{11}H_{14}O_5$: 226.0841. found 226.0837. $[\alpha]_D^{25}$ = –123.9 ($CHCl_3$, c = 1.0).

(3a*R*,4*R*,6*R*,7a*S*)-4-((*S*,*E*)-1-(2,2-dimethylhydrazono)propan-2-yloxy)octahydrobenzofuran-3a,6-diol ([22]).

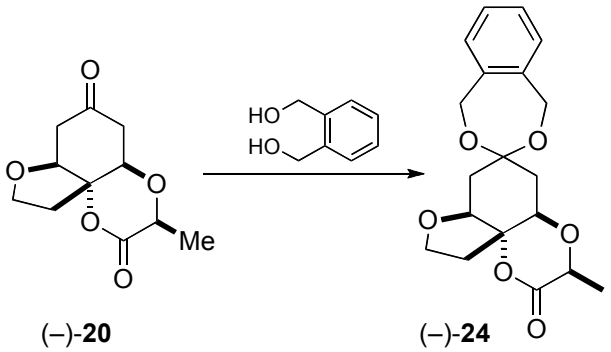


20 [**21**] [**22**]

To a solution of **20** (5.0 mg, 0.022 mmol) in CH_2Cl_2 (0.3 mL) cooled to –78 ˚C was added DIBAL-H (1M in hexanes, 0.09 mL, 0.09 mmol) and the solution was stirred for 1 h. The reaction mixture was quenched with 1M aq Rochelle's salt, diluted with CH_2Cl_2, quickly warmed to room temperature and stirred vigorously for 45 min. The aqueous layer was extracted with CH_2Cl_2. The combined organics were washed with brine, dried with Na_2SO_4, and concentrated.

To a solution of the crude **21** (5.0 mg) in CH_2Cl_2 (0.3 mL) was added H_2NNMe_2 (4 μL, 0.09 mmol). The reaction was stirred at room temperature for 4 h, then concentrated under reduced pressure to afford the hydrazone **22**, which was taken on crude in following manipulations.

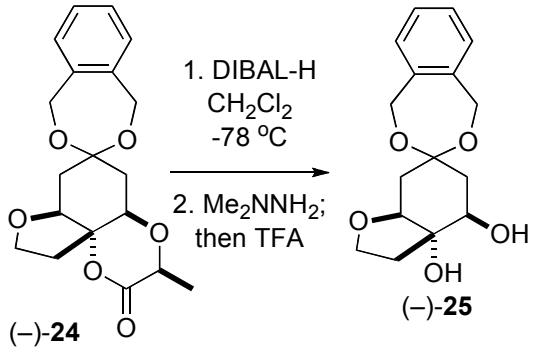
(2'*S*,41'*R*,7a'*S*,10a'*R*)-2'-Methyl-1,5,5',6',7a',8',10',10a'-octahydrospiro[benzo[*e*][1,3]dioxepine-3,9'-benzofuro[4-*b*][1,4]dioxin]-3'(2'*H*)-one (24).



(–)-**20** (–)-**24**

To a solution of 1,2-benzenedimethanol (32 mg, 0.23 mmol, 1.1 equiv) and ketone **20** (48 mg, 0.212 mmol, 1 equiv) in benzene (2 mL) was added catalytic *p*-toluene sulfonic acid hydrate. The resulting mixture was heated at reflux for 24 h with azeotropic removal of water by a Dean-Stark trap. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, quenched with $NaHCO_3$ (saturated), and extracted with CH_2Cl_2 (4x). The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash chromatography (35% EtOAc/hexanes, $R_f = 0.3$) to provide the ketal-lactone **24** as a colorless oil (62.4 mg, 0.18 mmol, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 2H), 7.10 (m, 2H), 4.90 (m, 4H), 4.60 (q, $J = 7.2$ Hz, 1H), 4.18 (m, 4H), 2.58 (m, 2H), 2.06 (m, 1H), 1.75 (m, 1H), 1.60 (d, $J = 6.8$ Hz, 3H), 1.50 (m, 2H); ^{13}C NMR (100 MHz. $CDCl_3$) δ 170.2, 137.5, 137.3, 127.3, 126.4, 101.8, 91.3, 78.4, 74.5, 72.6, 65.5, 65.3, 65.0, 36.1, 33.9, 32.9, 18.7; IR (thin film) 2955, 2920, 2897, 2851, 1744, 1091 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{22}O_6Na$: 369.1314. Found 369.1308. $[\alpha]_D^{25} = +13.5$ ($CHCl_3$, c = 0.5).

(3a'*S*,4'*R*,7a'*S*)-1,3',3a',4',5,5',7',7a'-Octahydro-2'*H*-spiro[benzo[*e*][1,3]dioxepine-3,6'-benzofuran]-3a',4'-diol (25).



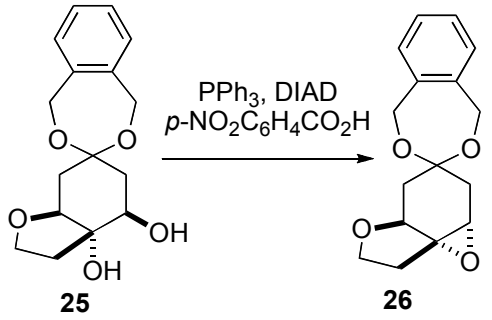
(–)-**24** (–)-**25**

To a solution of **24** (0.011 g, 0.033 mmol) in CH_2Cl_2 (0.4 mL) cooled to –78 ˚C was added DIBAL-H (1M in hexanes, 0.07 mL, 0.07 mmol) and the solution was stirred for 1 h. The reaction mixture was quenched with 1M Rochelle's salt, dilute with CH_2Cl_2, quickly warmed to room temperature and stirred vigorously for 45 minutes. The aqueous layer was extracted with CH_2Cl_2. The combined organics were washed with brine, dried with Na_2SO_4, and concentrated.

To a solution of the crude reaction material in CH_2Cl_2 (0.4 mL) was added H_2NNMe_2 (4 μL, 0.09 mmol). The reaction was stirred at room temperature for 4 h, and then TFA (cat.) was added to the solution. After 3 h, the reaction mixture was concentrated and the residue was purified by flash chromatography with EtOAc (R_f = 0.25) to yield **25** (7.2 mg, 0.025 mmol, 75% yield, > 99% ee). Enantiomeric ratio was measured by HPLC (Chiralcel OD-H, 15% IPA/Hexanes, $t_{R1} = 15.47$ min, $t_{R2} = 19.00$ min). ^{1}H NMR (400 MHz, C_5D_5N) δ 7.09 (m, 1H), 7.03 (m, 1H), 7.00 (m, 1H), 6.80 (m, 1H), 4.96 (m, 2H), 4.82 (m, 3H), 4.53 (dd, $J = 6.8$ Hz, $J = 10.4$ Hz, 1H), 4.41 (dd, $J = 8.4$ Hz, $J = 16.8$ Hz, 1H), 4.20 (m, 1H), 2.88 (m, 1H), 2.66 (m, 2H), 2.43 (m, 1H), 2.10 (t, J =

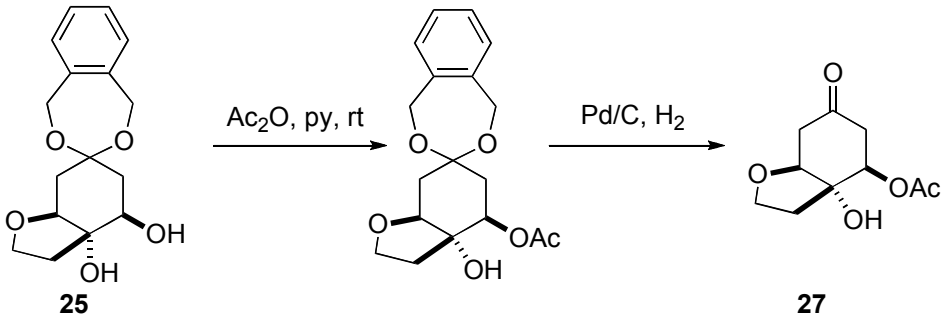
12.8 Hz, 1H), 1.77 (m, 1H); ^{13}C NMR (100 MHz, C_5D_5N) δ 139.2, 138.9, 127.4, 126.9, 126.8, 102.9, 84.6, 82.7, 72.5, 66.4, 65.1, 65.0, 38.2, 37.3, 33.1; IR (thin film) 3429, 2951, 2920, 2851, 1076 cm^{-1}; HRMS (ESI) calcd for C16H20O5Na: 315.1208. Found 315.1211. $[\alpha]_D^{25} = -17.5$ ($CHCl_3$, c = 0.75).

Epoxide 26.



To a solution of 4-nitrobenzoic acid (14.9 mg, 0.089 mmol) and diol **25** (6.5 mg, 0.022 mmol) in anhydrous THF (0.5 mL) at 0 ˚C, was added triphenylphosphine (23.3 mg, 0.089 mmol), DIAD (0.017 mL, 0.089 mmol). The reaction was stirred at rt for 16 h and then the reaction mixture was diluted with diethyl ether. The solution was washed with saturated aq $NaHCO_3$, then brine. The organic layer was dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to afford epoxide **26** as colorless oil (4.9 mg, 0.018 mmol, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (m, 2H), 7.06 (m, 2H), 4.88 (m, 4H), 4.08 (dt, J = 4.5 Hz, J = 8 Hz, 1H), 3.98 (m, 2H), 3.45 (d, J = 3 Hz, 1H), 2.66 (d, J = 15.5 Hz, 1H), 2.59 (ddd, J = 1.5 Hz, J = 5.5 Hz, J = 13 Hz, 1H), 2.29 (dt, J = 8 Hz, J = 13.8 Hz, 1H), 2.14 (ddd, J = 4 Hz, J = 7 Hz, J = 13.5 Hz, 1H), 2.09 (dd, J = 3 Hz, J = 15.5 Hz, 1H), 1.62 (dd, J = 10 Hz, J = 13 Hz, 1H); ^{13}C NMR (100 MHz. $CDCl_3$) δ 138.0, 137.8, 127.1, 127.0, 126.3, 102.3, 74.1, 67.0, 65.8, 65.1, 65.0, 58.4, 34.2, 33.4, 31.4; IR (thin film) 2954, 2920, 2851, 1458, 1076 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}O_4Na$: 297.1103. Found 297.1109.

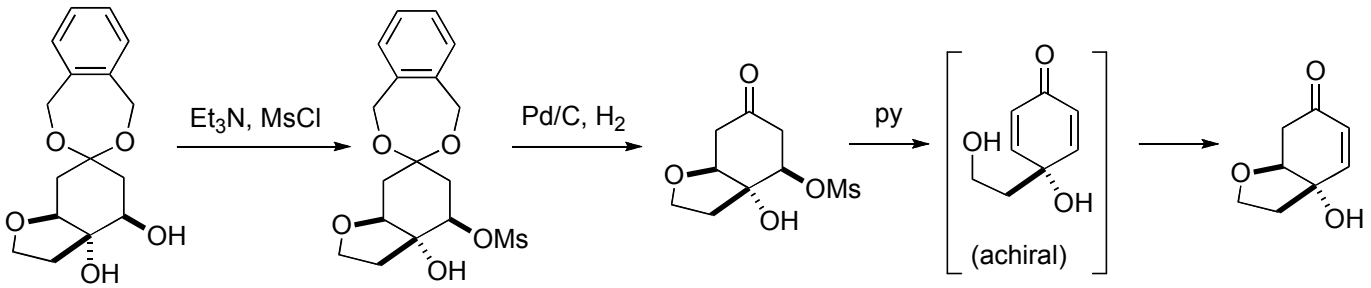
Acetate (27).



To a solution of diol **25** (5 mg, 0.017 mmol) in pyridine (0.2 mL) was added Ac_2O (2 μL, 0.019 mmol). After 24 h of stirring, the reaction mixture was diluted with CH_2Cl_2, washed with $CuSO_4$ (aq), extracted with CH_2Cl_2 (4x), washed with water and brine. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The resulting mono-acetate was carried forward without purification.

A solution of the above mono-acetate in MeOH (0.2 mL) containing 5% Pd/C catalyst (3 mg) was stirred under 1 atm of hydrogen at room temperature for 12 hours. The reaction mixture was filtered through a pad of Celite, and concentrated under reduced pressure to afford the crude product.

Cleroindicin F (7): Patially racemized method.



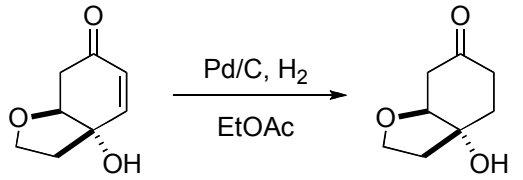
25 >99% ee **28** **7** ≤90% ee

To a solution of diol **25** (17 mg, 0.058 mmol) in CH_2Cl_2 (6.8 mL) at 0 ˚C was added Et_3N (0.09 mL, 0.7 mmol). After 15 min, MsCl (0.018 mL, 0.233 mmol) was added to the reaction mixture. Five minutes later, the reaction mixture was diluted with CH_2Cl_2, quenched with aq NH_4Cl (saturated), and extracted with CH_2Cl_2 (4x). The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The resulting mono-mesylate was carried forward without purification.

A solution of the above mono-mesylate in THF/MeOH (0.4 mL/0.4 mL) containing 5% Pd/C catalyst (10 mg) was stirred under 1 atm of hydrogen at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and concentrated under reduced pressure.

A solution of the crude product in CH_2Cl_2 (0.6 mL) was added pyridine (0.047 mL, 0.58 mmol). After 18 h of stirring, the reaction mixture was diluted with CH_2Cl_2, washed with $CuSO_4$ (aq.), extracted with CH_2Cl_2 (4x), washed with water and brine. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash chromatography (70% EtOAc/hexanes) to provide cleroindicin F (**7**) as colorless oil (81% yield over 3 steps, 90% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, J = 10 Hz, 1H), 6.04 (d, J = 10 Hz, 1H), 4.25 (t, J = 6.0 Hz, 1H), 4.08 (dd, J = 8.5 Hz, J = 15 Hz, 1H), 3.96 (dd, J = 8.5 Hz, J = 15 Hz, 1H), 3.50 (bs, 1H), 2.80 (dd, J = 4.5 Hz, J = 17 Hz, 1H), 2.63 (dd, J = 6 Hz, J = 17 Hz, 1H), 2.32 (m, 1H), 2.24 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 147.8, 129.2, 81.9, 76.0, 66.5, 40.5, 39.8; IR (thin film) 3418, 2920, 2851, 1666 cm^{-1}; HRMS (ESI) calcd for $C_8H_{10}O_3$: 154.0630. Found 154.0625. ^{1}H and ^{13}C NMR, IR, and HRMS data were consistent with that reported in the literature.[i]

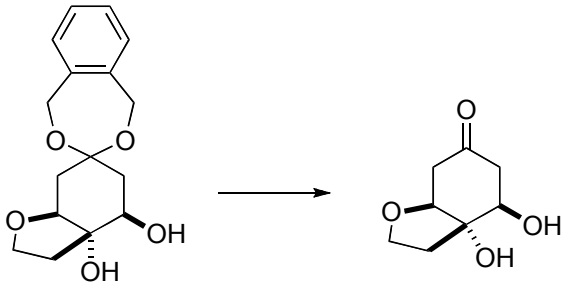
Cleroindicin C (3).



(+)-cleroindicin F (**7**) (–)-cleroindicin C (**3**)

A solution of cleroindicin F (**7**) (20 mg, 0.13 mmol) in EtOAc (1 mL) containing 5% Pd/C catalyst (50 mg) was stirred under 1 atm of hydrogen at room temperature for 1 hour. The reaction mixture was filtered through a pad of Celite, and concentrated under reduced pressure. The crude product was purified by flash chromatography (75% EtOAc/hexanes, R_f = 0.3) to provide cleroindicin C (**3**) as colorless oil (17 mg, 0.11 mmol, 80 % yield). ^{1}H NMR (400 MHz, C_5D_5N) δ 4.29 (t, J = 4.0 Hz, 1H), 3.94 (m, 2H), 2.98 (dd, J = 4.8 Hz, J = 15.6 Hz, 1H), 2.80 (dd, J = 4.0 Hz, J = 16.0 Hz, 1H), 2.68 (ddd, J = 4.8 Hz, J = 8.4 Hz, J = 16.8 Hz, 1H), 2.35 (m, 1H), 2.24 (m, 1H), 2.20 (m, 2H), 2.07 (dt, J = 8.4 Hz, J = 12.4 Hz, 1H); IR (thin film) 3305, 2943, 2860, 1705, 1059 cm^{-1}. $[\alpha]_D^{25}$ = –79.0 (MeOH, c = 0.1). HRMS (ESI) calcd for $C_8H_{12}O_3Na$: 179.0684. Found 179.0678. ^{1}H and ^{13}C NMR, IR, and HRMS data were consistent with that reported in the literature.[i]

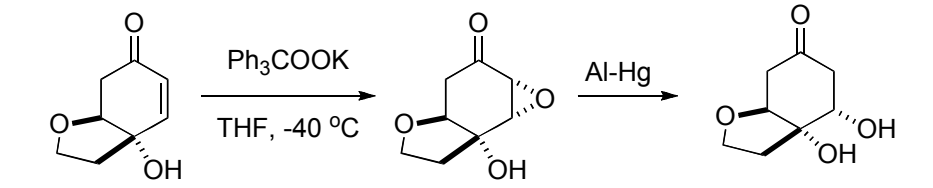
Epi-cleorindicin D (4).



(–)-**25** (–)-**4**

A solution of **25** (29.0 mg, 0.1 mmol) in THF/MeOH (0.5 mL/0.5 mL) containing 5% Pd/C catalyst (10 mg) was stirred under 1 atm of hydrogen at room temperature for 3 h. The reaction mixture was filtered through a pad of Celite, and concentrated under reduced pressure. The crude product was purified by flash chromatography with EtOAc (R_f = 0.2) to provide the previously assigned structure for cleroindicin D (**4**) as colorless oil (15.2 mg, 0.09 mmol, 88% yield). ^{1}H NMR (400 MHz, C_5D_5N) δ 4.74 (dd, J = 4.8 Hz, J = 10.8 Hz, 1H), 4.42 (t, J = 4.4 Hz, 1H), 4.05 (m, 2H), 3.02 (dd, J = 4.8 Hz, J = 18 Hz, 1H), 2.97 (d, J = 4.4 Hz, 2H), 2.80 (m, 1H), 2.79 (dd, J = 10.4 Hz, J = 18 Hz, 1H), 2.27 (ddd, J = 2 Hz, J = 5.6 Hz, J = 13.2 Hz, 1H); ^{13}C NMR (125 MHz. $CDCl_3$) δ 206.9, 82.9, 82.6, 72.1, 66.5, 43.1, 42.9, 35.8; IR (thin film) 3387, 2955, 2924, 2854, 1724 cm^{-1}; HRMS (ESI) calcd for $C_8H_{12}O_4Na$: 195.0633. Found 195.0630. $[\alpha]_D^{25}$ = –35.5 ($CHCl_3$, c = 0.4).

Cleroindicin D (5).



(+)-cleroindicin F (**7**)
>99% ee

30
>99% ee

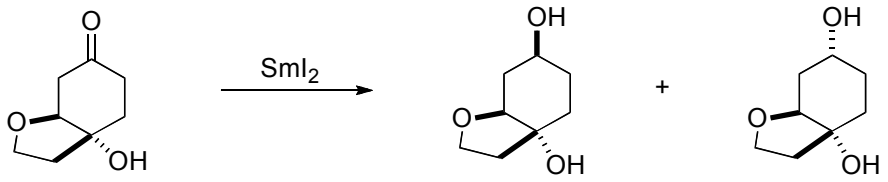
(–)-cleroindicin D (**5**)

To a suspension of KH (8.2 mg, 0.20 mmol) in THF (0.4 mL) at –78 ˚C was added Ph_3COOH (113 mg, 0.41 mmol). After 10 min, enone **7** (13.2 mg, 0.086 mmol) in THF (0.86 mL) was added to the Ph_3COOK solution. The reaction mixture was then warmed up to –40 ˚C. Once the starting material was consumed (about 40 min), the reaction mixture was diluted with CH_2Cl_2, quenched with Na_2SO_3 (sat.), and extracted with CH_2Cl_2 (4x). The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash chromatography with EtOAc to provide epoxide **30**. The spectroscopic data matched that reported in the literature.[ii] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (m, 3H), 3.64 (dd, J = 2.4 Hz, J = 4.4 Hz, 1H), 3.46 (dd, J = 0.8 Hz, J = 4.4 Hz, 1H), 3.06 (dd, J = 4.0 Hz, J = 14.8 Hz, 1H), 2.67 (bs, 1H), 2.40 (dd, J = 3.2 Hz, J = 14.8 Hz, 1H), 2.28 (ddd, J = 4.4 Hz, J = 7.6 Hz, J = 13.2 Hz, 1H), 2.17 (dt, J = 8.4 Hz, J = 13.6 Hz, 1H).

To a solution of the above epoxide **30** (22 mg, 0.13 mmol) in a mixture of THF (5.2 mL), EtOH (2.6 mL), H_2O (2.6 mL) and saturated aqueous $NaHCO_3$ (0.5 mL) at 0 ˚C, aluminum amalgam (freshly prepared from 0.500 g of aluminum foil) was added. The reaction mixture was vigorously stirred at 0 ˚C for 40 min, then

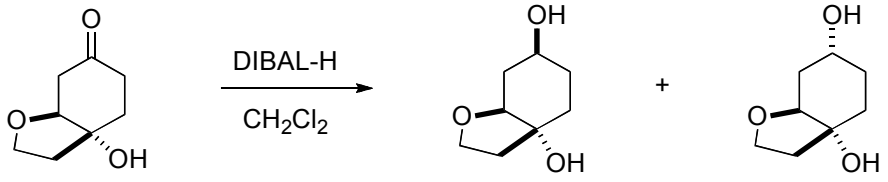
filtered through Celite. The filtrate was diluted with EtOAc, washed with brine and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc, R_f = 0.2) to provide cleroindicin D (**5**) as colorless oil (6.0 mg, 0.035 mmol, 40% yield over 2 steps). ^{1}H NMR (400 MHz, C_5D_5N) δ 4.36 (m, 1H), 4.35 (t, J = 4.4 Hz, 1H), 4.00 (m, 2H), 3.24 (dd, J = 4.8 Hz, J = 16.8 Hz, 1H), 3.02 (dd, J = 6.8 Hz, J = 16.8 Hz, 1H), 2.85 (dd, J = 3.2 Hz, J = 15.6 Hz, 1H), 2.81 (dd, J = 3.6 Hz, J = 15.6 Hz, 1H), 2.28 (m, 2H); HRMS (ESI) calcd for $C_8H_{12}O_4Na$: 195.0633. Found 195.0637. $[\alpha]_D^{25}$ = –38.0 (MeOH, c = 0.5). ^{1}H and ^{13}C NMR, IR, and HRMS data were consistent with that reported in the literature.[ib, ii]

Cleroindicin E (6).



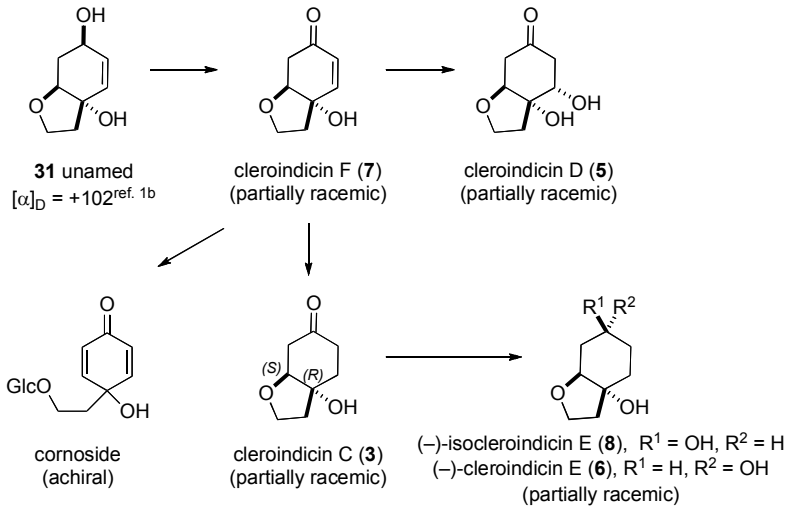
To a solution of cleroindicin C (**3**) (6 mg, 0.038 mmol) in THF/H_2O (0.5 mL/0.1 mL) at 0 ˚C was added SmI_2 (0.1M in THF, 0.76 ml, 0.076 mmol), and the mixture was stirred at this same temperature for 10 min. The reaction mixture was quenched with $NaHCO_3$(sat.), and extracted with CH_2Cl_2. The combined organics were washed with brine, dried with Na_2SO_4, and concentrated to afford an inseparable mixture of isocleroindicin E (**8**) and cleroindicin E (**6**) (1:2) (5 mg, 0.032 mmol, 85% yield) which was spectroscopically identical to that reported in the literature.[i] $C_8H_{14}O_3Na$: 181.0841. Found 181.0835.

Isocleroindicin E (8).



To a solution of cleroindicin C (**3**) (10 mg, 0.064 mmol) in CH_2Cl_2 (0.7 mL) at –78 ˚C was added DIBAL-H (1M in hexanes, 0.07 ml, 0.07 mmol), and the mixture was stirred at this same temperature for 1 h. The reaction mixture was quenched with 1M Rochelle's salt, diluted with CH_2Cl_2, quickly warmed to room temperature and stirred vigorously for 45 minutes. The aqueous layer was extracted with CH_2Cl_2. The combined organics were washed with brine, dried with Na_2SO_4, and concentrated. The crude product was purified by flash chromatography (10% MeOH/EtOAc, R_f = 0.3) to provide isocleroindicin E (**8**) as colorless oil (8.5 mg, 0.054 mmol, 84 % yield). ^{1}H NMR (400 MHz, C_5D_5N) δ 4.26 (dd, J = 8.0 Hz, J = 16.4 Hz, 1H), 4.22 (dd, J = 5.6 Hz, J = 9.2 Hz, 1H), 4.08 (m, 1H), 4.02 (m, 1H), 2.45 (m, 1H), 2.30 (ddd, J = 4.0 Hz, J = 8.4 Hz, J = 14.4 Hz, 1H), 2.20 (m, 1H), 2.15 (m, 1H), 2.02 (m, 1H), 1.98 (m, 1H), 1.83 (m, 1H), 1.74 (m, 1H). HRMS (ESI) calcd for $C_8H_{14}O_3Na$: 181.0841. Found 181.0835. $[\alpha]_D^{25}$ = –22.0 (MeOH, c = 0.4). ^{1}H NMR and HRMS data were consistent with that reported in the literature.[ib] Our rotation is slightly less than that reported by Hase ($[\alpha]_D^{25}$ = –23.0),[1b] most likely because of the small amount of inseparable **6** present in our sample.

III. Revised Biosynthetic Pathway



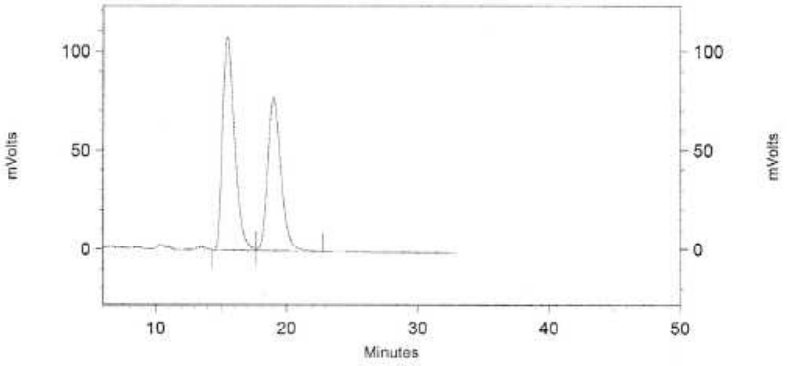
We have found that cleroindicins **3**, **5**–**7**, are at least partially racemic in nature. However the unnamed cleroindicin **31**, isolated by Hase, appears to be unracemized because their hydrogenation of **31** to isocleroindicin E (**8**) resulted in a more optically active material ($[\alpha]_D^{25} = -23.0$) than the natural isocleroindicin E (**8**) ($[\alpha]_D^{25} = -6.00$). [ib] Therefore, it appears that **31** is the biosynthetic precursor to chiral cleroindicins, as well as achiral cornoside.

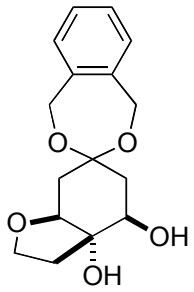
IV. Scanned HPLC traces, NMR, and IR spectra

HPLC data for racemic **25**:

HPLC Report

SH13-11_15%IPA_1ml-min-OD-H-02
Acquired: 10/15/2008 5:41:27 PM
Method Name: C:\EZStart\Projects\Default\Methods\untitled.met
Data: C:\Shuang\SH13-11_15%IPA_1ml-min-OD-H-02214.dat





(±)-**25**

SPD-10Avp

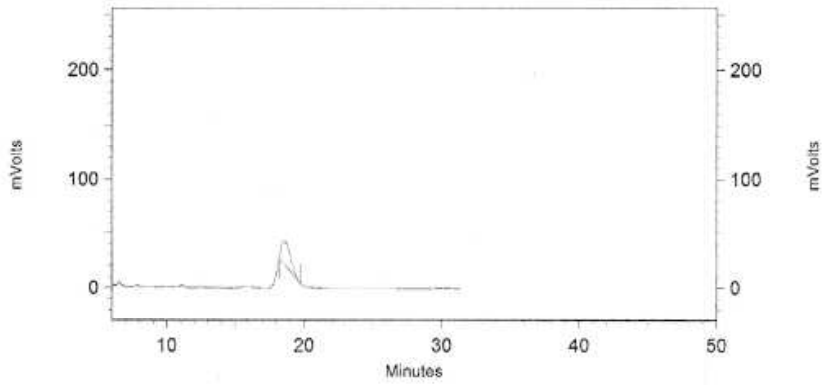
Ch1-220nm
Results

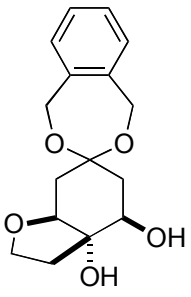
Pk #	Name	Retention Time	Area	Area Percent	Height	Height Percent
1		15.473	6788904	55.314	107819	58.227
2		18.997	5484508	44.686	77351	41.773
Totals			12273412	100.000	185170	100.000

HPLC data for enantioenriched **25**:

HPLC Report

SH13-11_15%IPA_1ml-min-OD-H-04-enantio
Acquired: 10/15/2008 10:43:32 PM
Method Name: C:\EZStart\Projects\Default\Methods\untitled.met
Data: C:\Shuang\SH13-11_15%IPA_1ml-min-OD-H-04-enantio218.dat





(–)-**25**

SPD-10Avp

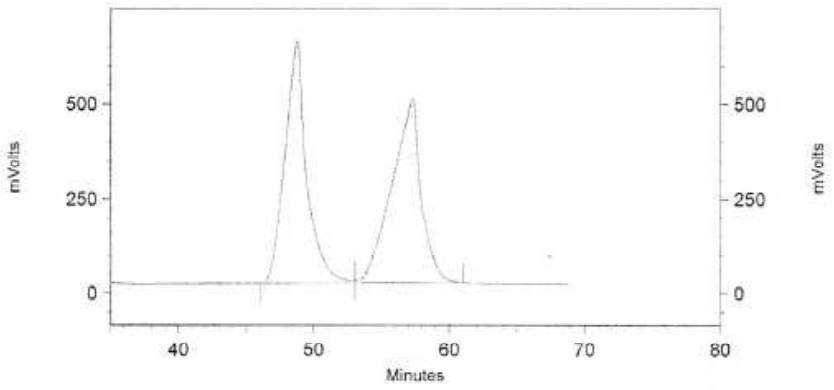
Ch1-220nm
Results

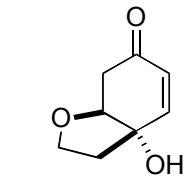
Pk #	Name	Retention Time	Area	Area Percent	Height	Height Percent
1		18.567	978474	100.000	21490	100.000
Totals			978474	100.000	21490	100.000

HPLC data for racemic cleroindicin F (**7**):

HPLC Report

SH7-enone-12-enone-5IPA-Hex-AD-H
Acquired: 8/5/2008 5:00:46 PM
Method Name: C:\EZStart\Projects\Default\Methods\untitled.met
Data: C:\Shuang\SH7-enone-12-enone-5IPA-Hex-AD-H133.dat





(±)-cleroindicin F (**7**)

SPD-10Avp

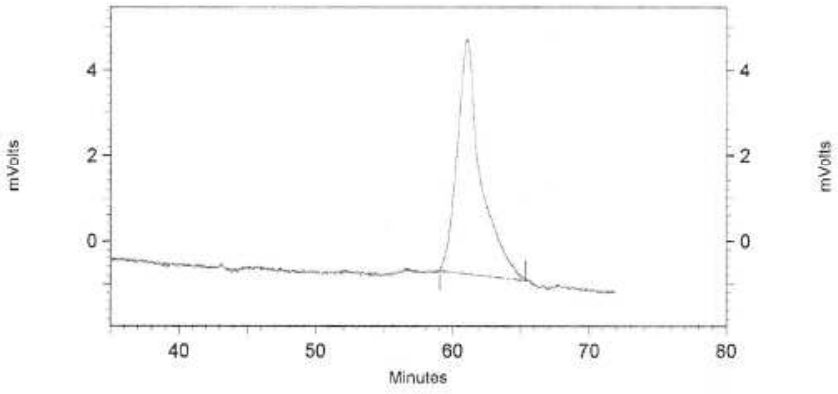
Ch1-210nm
Results

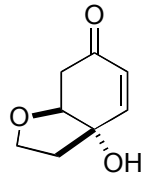
Pk #	Name	Retention Time	Area	Area Percent	Height	Height Percent
1		48.783	71681283	49.516	639420	56.752
2		57.305	73081867	50.484	487272	43.248
Totals			144763150	100.000	1126692	100.000

HPLC data for enantioenriched (+)-cleroindicin F (**7**):

HPLC Report

SH13-27-enone02_4%IPA_1mL_AD-H
Acquired: 10/31/2008 1:33:19 AM
Method Name: C:\EZStart\Projects\Default\Methods\untitled.met
Data: C:\Shuang\SH13-27-enone02_4%IPA_1mL_AD-H230.dat





(+)-cleroindicin F (**7**)

SPD-10Avp

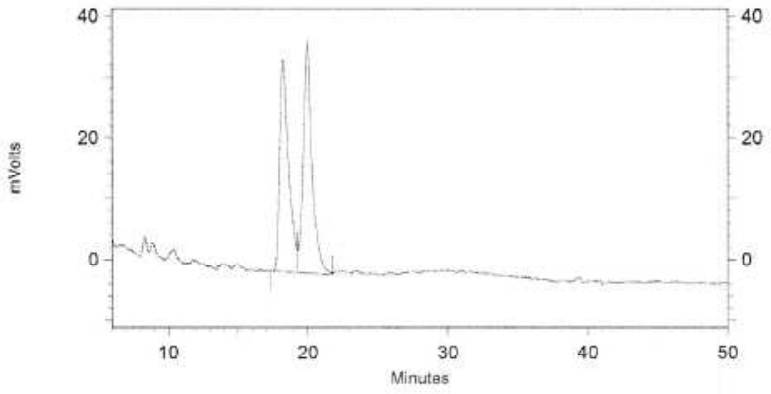
Ch1-210nm
Results

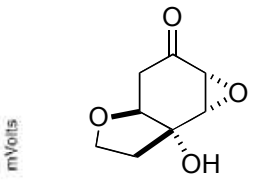
Pk #	Name	Retention Time	Area	Area Percent	Height	Height Percent
1		61.047	651441	100.000	5490	100.000
Totals			651441	100.000	5490	100.000

HPLC data for racemic epoxide **30**:

HPLC Report

SH7-expoxide-racemic-10%IPA_1mL_AD-H
Acquired: 11/13/2008 11:52:39 AM
Method Name: C:\EZStart\Projects\Default\Methods\untitled.met
Data: C:\Shuang\SH7-expoxide-racemic-10%IPA_1mL_AD-H232.dat





(±)-**30**

SPD-10Avp

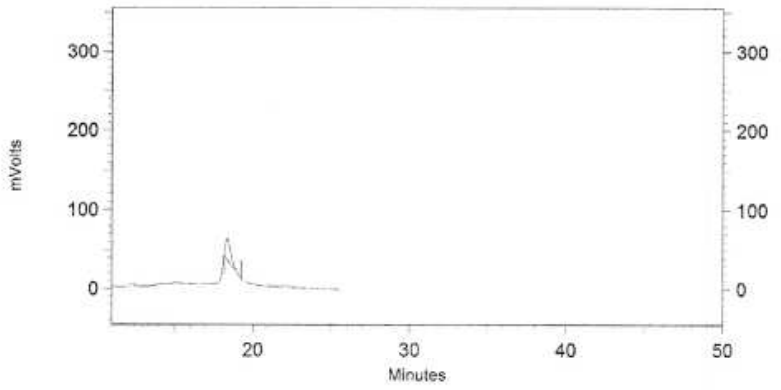
Ch1-210nm
Results

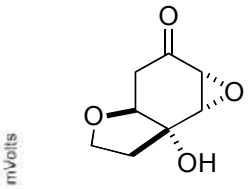
Pk #	Name	Retention Time	Area	Area Percent	Height	Height Percent
1		18.223	1559009	48.514	34936	47.771
2		19.967	1654540	51.486	38196	52.229
Totals			3213549	100.000	73132	100.000

HPLC data for enantioenriched epoxide **30**:

HPLC Report

SH13-47-expoxide-enantiopure-10%IPA_1mL_AD-H
Acquired: 11/13/2008 1:05:05 PM
Method Name: C:\EZStart\Projects\Default\Methods\untitled.met
Data: C:\Shuang\SH13-47-expoxide-enantiopure-10%IPA_1mL_AD-H233.dat





(–)-**30**

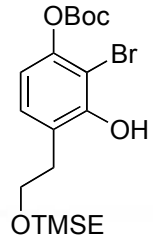
SPD-10Avp

Ch1-210nm
Results

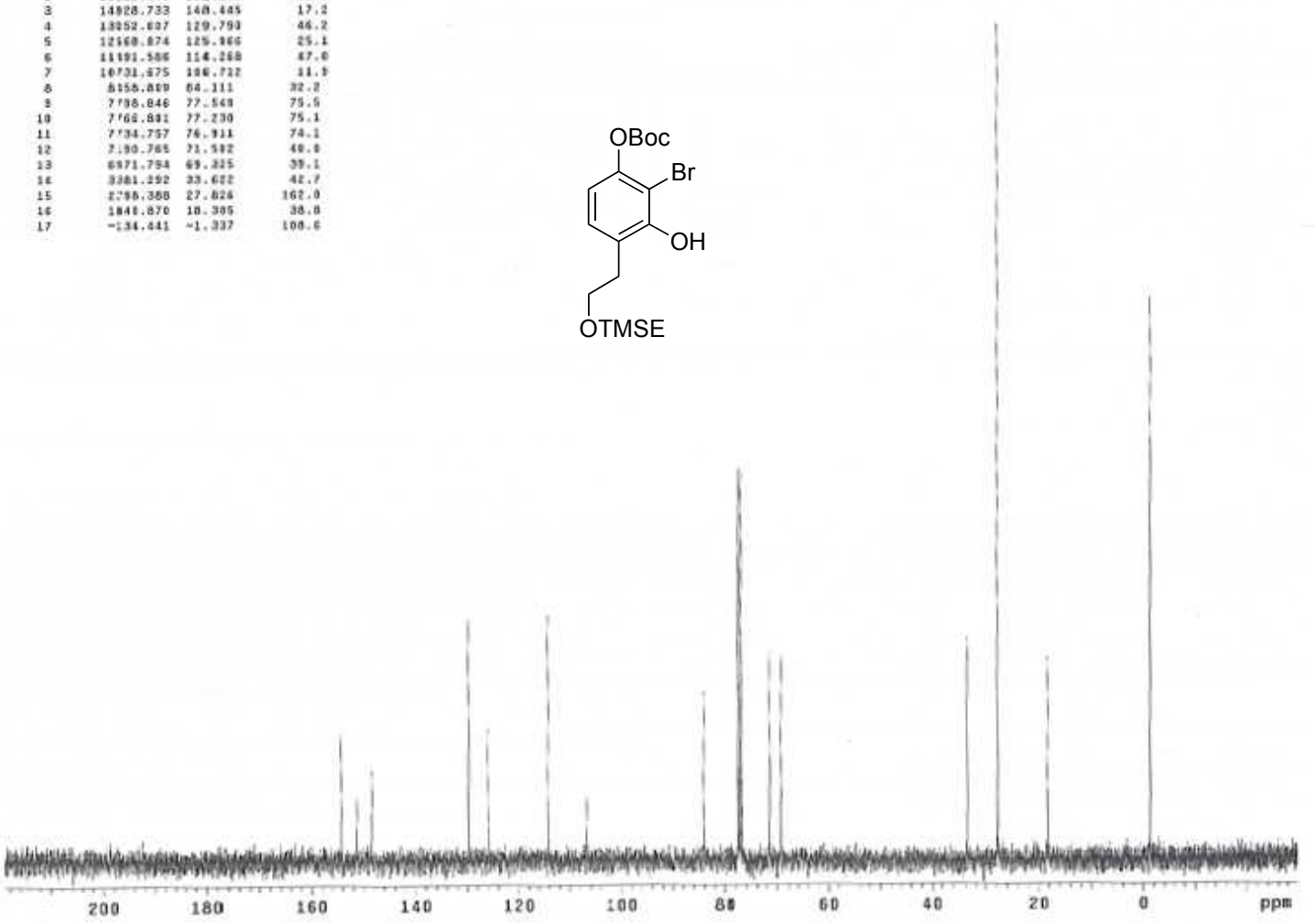
Pk #	Name	Retention Time	Area	Area Percent	Height	Height Percent
1		18.380	643383	100.000	26197	100.000
Totals			643383	100.000	26197	100.000

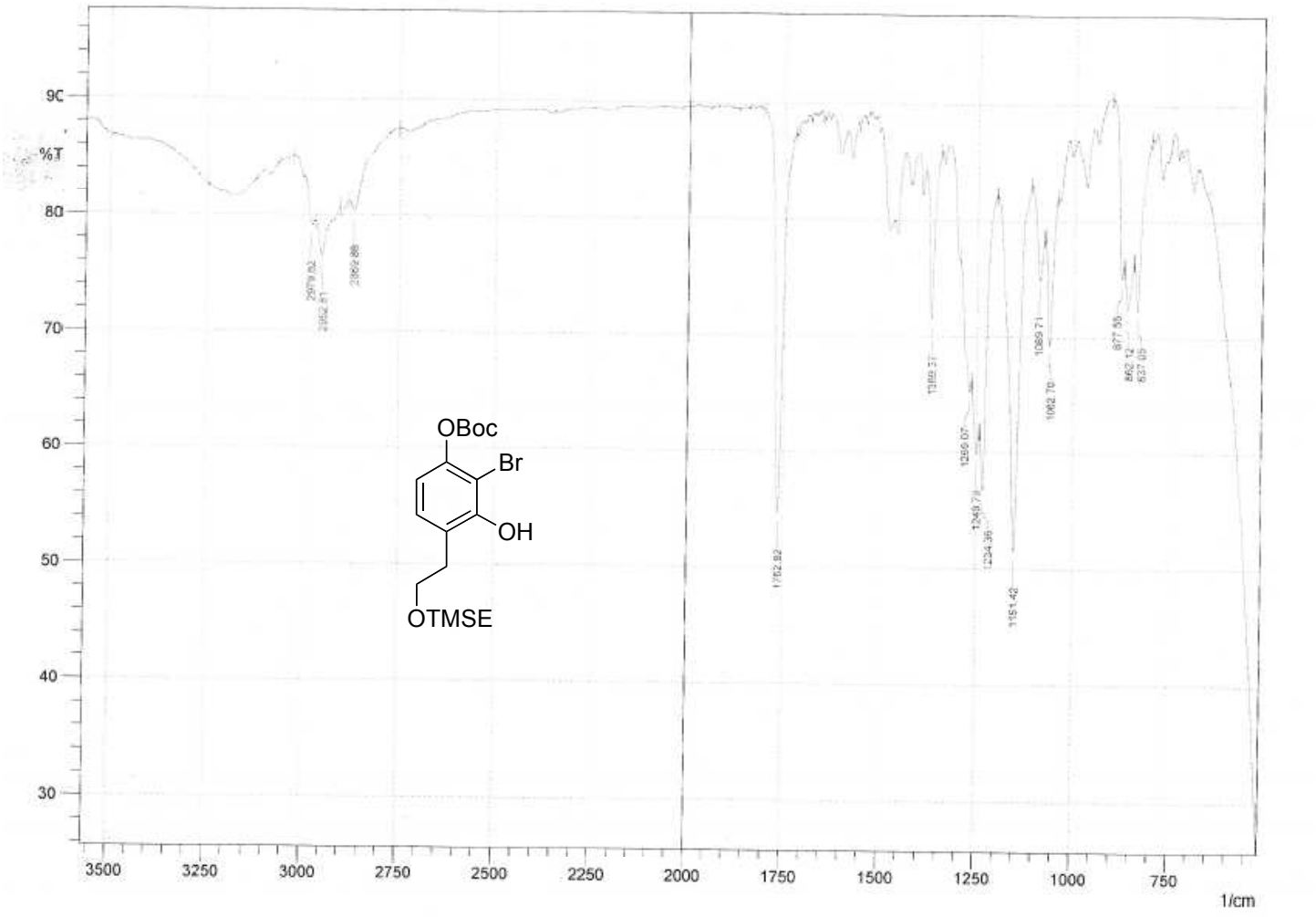
Compound **11**:

INDEX	FREQUENCY	PPM	HEIGHT
1	3667.557	9.170	18.4
2	2907.627	7.270	2.9
3	2881.522	7.205	7.7
4	2793.384	6.984	8.8
5	2684.822	6.713	9.6
6	2676.684	6.693	8.5
7	1485.119	3.713	7.6
8	1480.052	3.701	11.2
9	1474.831	3.688	8.3
10	1441.971	3.605	8.8
11	1433.525	3.584	8.2
12	1431.375	3.579	6.3
13	1424.619	3.562	9.1
14	1171.412	2.929	7.4
15	1165.344	2.916	10.6
16	1161.277	2.904	7.2
17	654.248	1.636	3.4
18	647.031	1.618	5.4
19	628.684	1.572	148.3
20	613.863	1.535	4.3
21	604.650	1.512	3.1
22	597.894	1.495	2.7
23	506.223	1.266	2.6
24	419.927	1.050	8.7
25	417.316	1.043	3.8
26	411.328	1.028	7.7
27	402.575	1.007	8.3
28	354.053	0.885	3.3
29	35.738	0.089	2.7
30	33.436	0.084	3.1
31	30.518	0.076	2.7
32	27.601	0.069	3.3
33	23.898	0.059	5.9
34	18.234	0.046	5.6
35	11.617	0.029	15.1
36	7.946	0.020	151.2
37	-8.484	-0.021	3.2
38	-16.808	-0.040	2.8



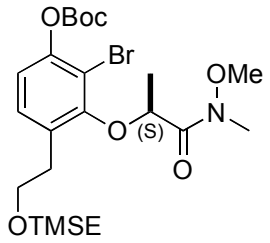
INDEX	FREQUENCY	PPM	HEIGHT
1	15515.451	154.289	24.6
2	15212.555	151.265	11.9
3	14928.733	148.445	17.2
4	13052.637	129.793	46.2
5	12568.874	125.966	25.1
6	11491.586	114.268	47.0
7	10731.675	106.712	11.9
8	8156.889	84.111	32.2
9	7798.848	77.548	75.5
10	7766.881	77.230	75.1
11	7734.757	76.911	74.1
12	7190.765	71.502	40.8
13	6971.794	69.325	39.1
14	3381.292	33.622	42.7
15	2796.388	27.804	162.0
16	1848.870	18.385	38.8
17	-134.441	-1.337	106.6

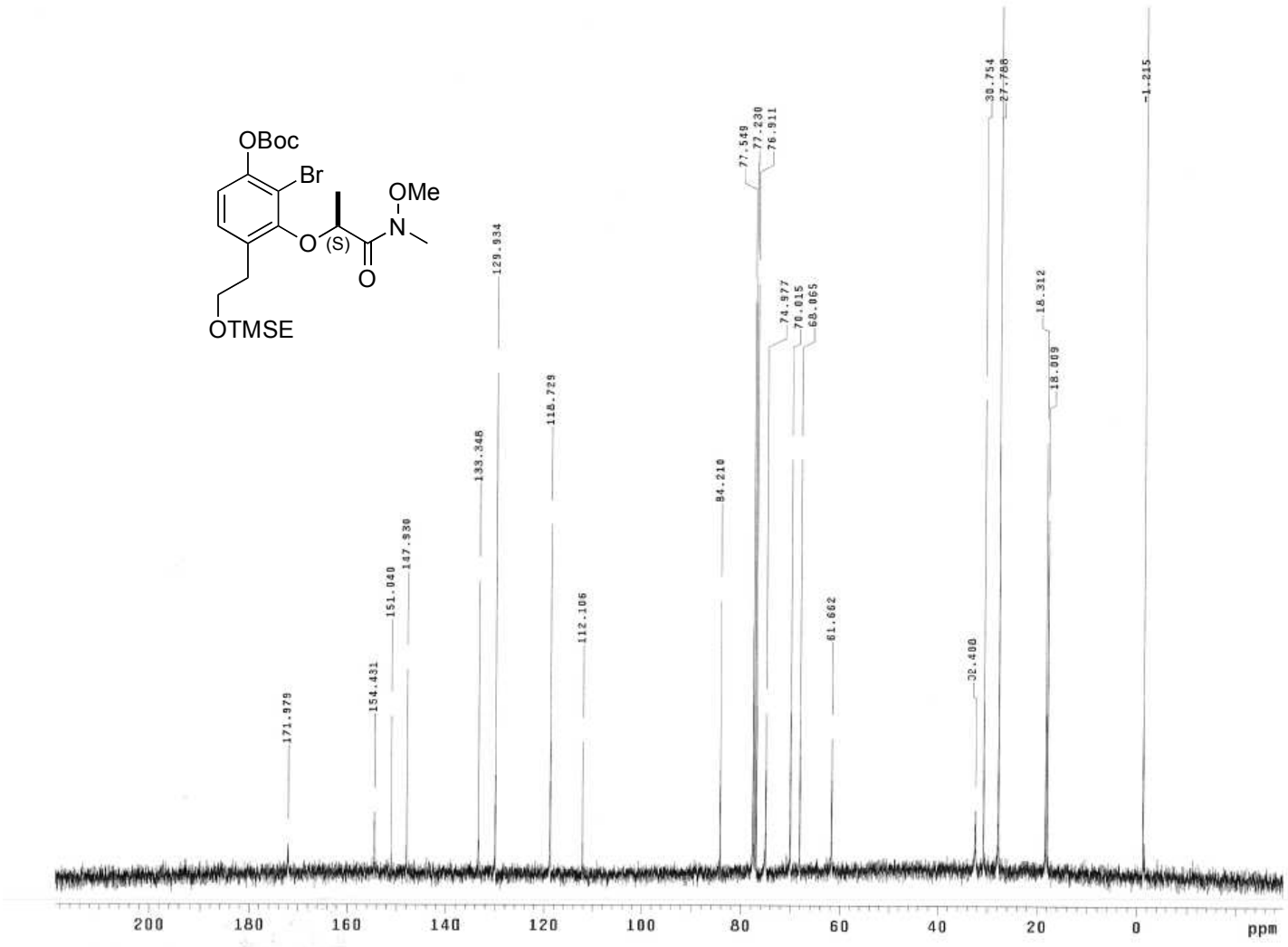


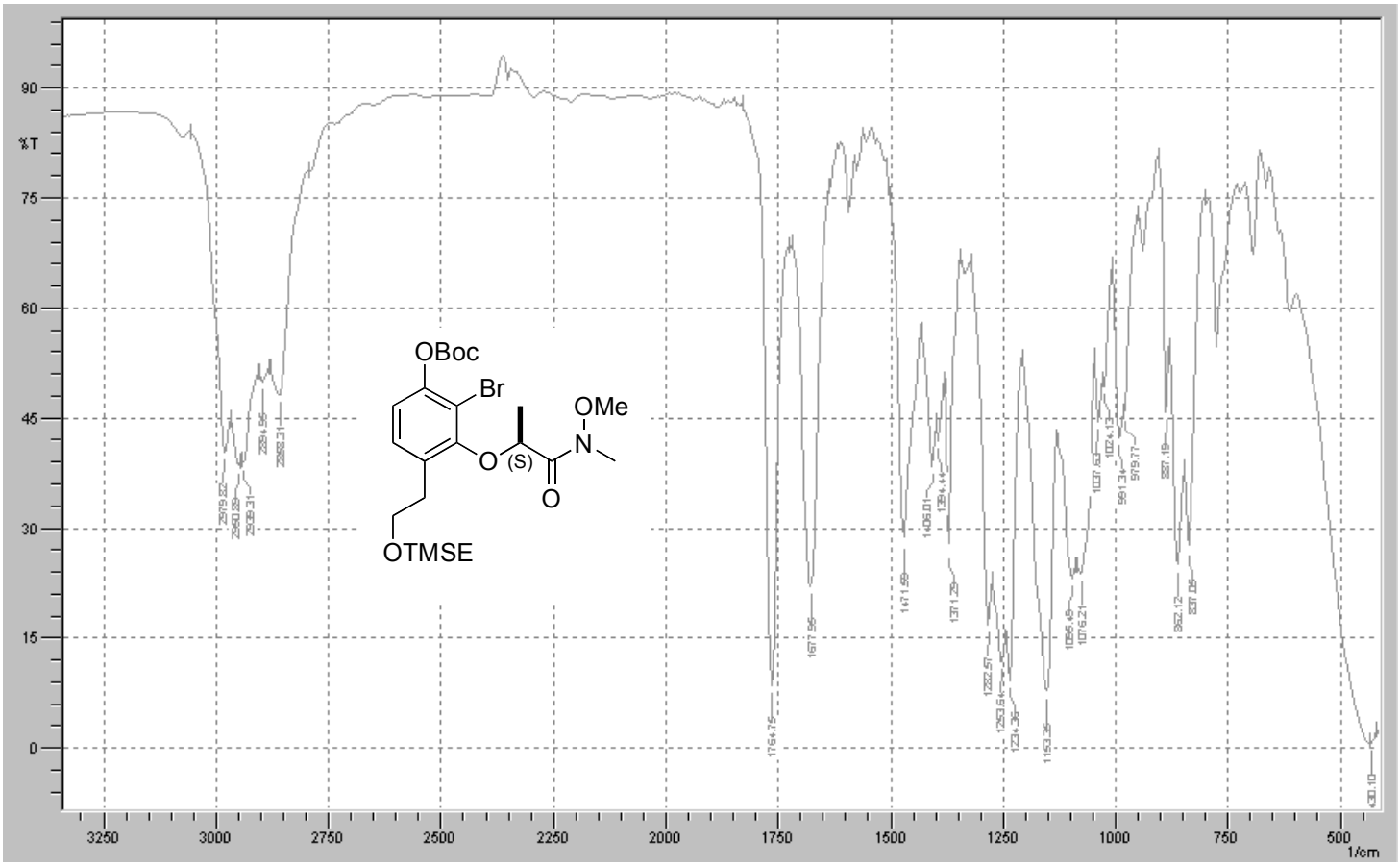

%T
90
80
70
60
50
40
30
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
1/cm
OBoc
Br
OH
OTMSE

Compound **13**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2908.855	7.273	8.4	40	3.186	0.008	2.0
2	2900.717	7.253	7.8	41	-2.803	-0.007	13.8
3	2773.576	6.935	8.6	42	-6.027	-0.015	151.2
4	2765.284	6.914	7.6	43	-9.252	-0.023	4.9
5	2129.731	5.325	1.7				
6	2123.435	5.309	1.7				
7	1439.053	3.598	5.8				
8	1432.297	3.581	13.3				
9	1425.540	3.564	6.7				
10	1408.957	3.523	16.8				
11	1404.811	3.512	10.0				
12	1402.201	3.506	2.6				
13	1396.366	3.491	7.6				
14	1390.838	3.478	1.9				
15	1388.227	3.471	7.8				
16	1269.378	3.174	29.2				
17	1247.727	3.120	1.9				
18	1240.510	3.102	2.2				
19	1233.600	3.084	2.9				
20	1226.997	3.068	1.3				
21	1193.677	2.985	1.7				
22	1186.920	2.968	3.3				
23	1180.010	2.950	2.4				
24	1172.793	2.932	2.2				
25	753.442	1.884	3.6				
26	634.593	1.587	1.3				
27	620.312	1.551	135.7				
28	616.627	1.542	23.3				
29	612.942	1.533	5.4				
30	610.024	1.525	20.5				
31	371.558	0.929	7.2				
32	368.947	0.922	1.6				
33	363.112	0.908	6.4				
34	357.738	0.894	1.7				
35	354.974	0.888	6.6				
36	18.541	0.046	1.4				
37	17.773	0.044	1.6				
38	16.699	0.042	2.8				
39	5.182	0.013	1.2				

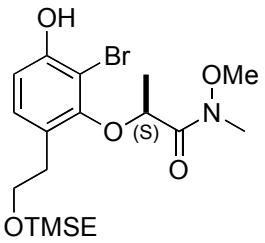


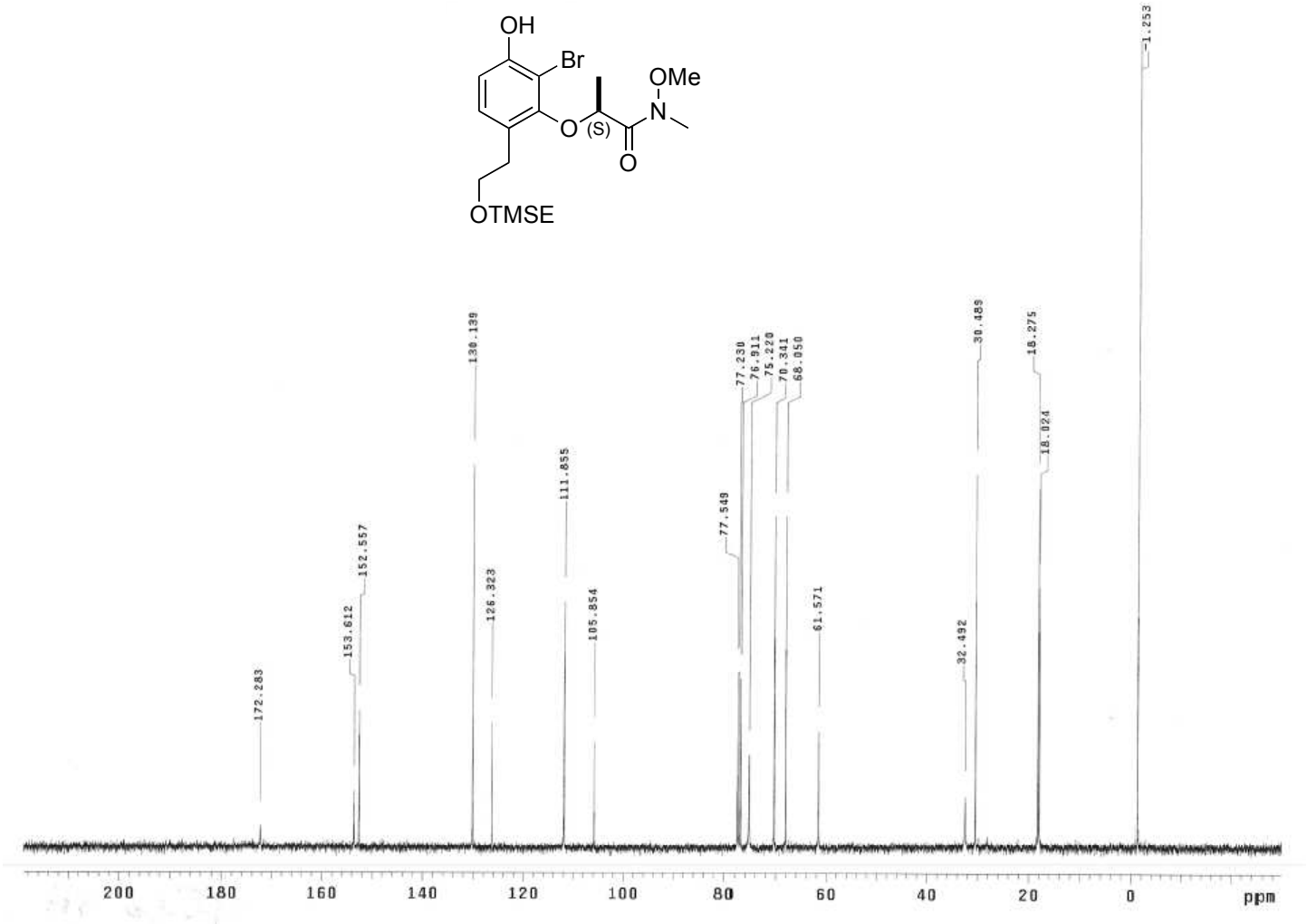

OBoc
Br
OMe
N
O
(S)
O
OTMSE
171.979
154.431
151.040
147.930
133.348
129.934
118.729
112.106
84.210
77.549
77.230
76.911
74.977
70.015
68.065
61.662
32.400
30.754
27.788
18.312
18.009
-1.215
200
180
160
140
120
100
80
60
40
20
0
ppm

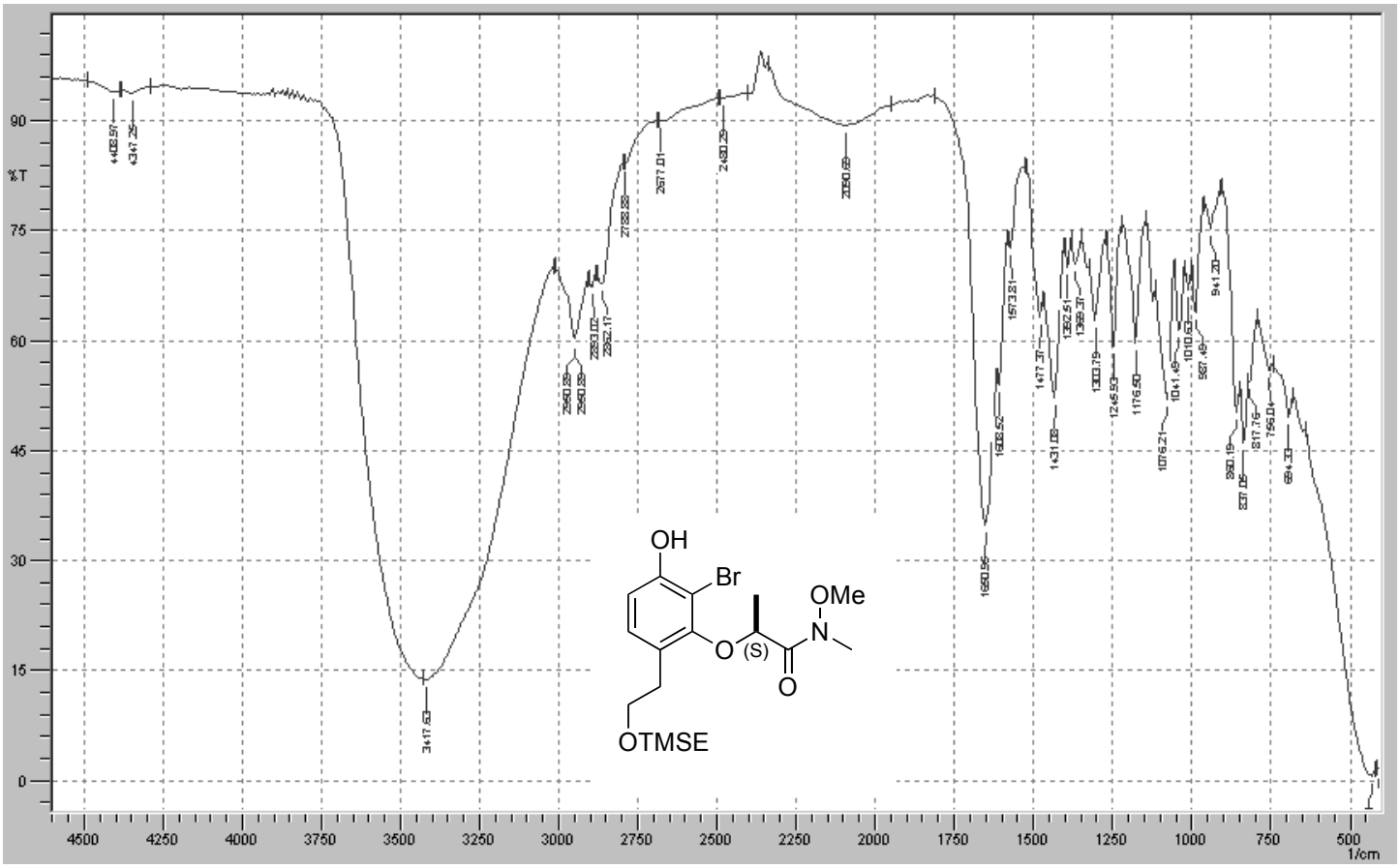

%T
90
75
60
45
30
15
0
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
OBoc
Br
OMe
N
O
(S)
O
OTMSE

Compound **14**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2907.627	7.270	3.7	40	-22.457	-0.056	4.9
2	2830.697	7.078	19.9	41	-24.607	-0.062	3.2
3	2822.252	7.057	21.1	42	-60.845	-0.152	2.9
4	2692.807	6.733	24.3				
5	2684.362	6.712	21.0				
6	2625.551	6.565	9.4				
7	2079.059	5.198	6.9				
8	2072.817	5.183	6.5				
9	1430.301	3.576	18.9				
10	1419.859	3.550	64.9				
11	1412.028	3.531	15.2				
12	1404.197	3.511	24.0				
13	1396.826	3.493	24.9				
14	1387.613	3.469	21.4				
15	1276.902	3.193	67.2				
16	1196.441	2.991	3.6				
17	1189.684	2.975	5.6				
18	1182.467	2.957	10.0				
19	1175.557	2.939	13.9				
20	1171.872	2.930	10.0				
21	1168.494	2.922	9.6				
22	1164.962	2.913	12.6				
23	1157.899	2.895	7.9				
24	1150.836	2.877	4.2				
25	1025.998	2.565	3.0				
26	606.646	1.517	58.8				
27	600.197	1.501	54.7				
28	500.388	1.251	3.3				
29	494.553	1.237	3.7				
30	369.869	0.925	21.4				
31	366.951	0.917	8.2				
32	361.731	0.904	21.8				
33	353.285	0.883	18.7				
34	11.324	0.028	4.6				
35	4.568	0.011	11.6				
36	2.572	0.006	10.6				
37	-2.342	-0.006	16.4				
38	-13.091	-0.033	373.6				
39	-16.315	-0.041	19.2				

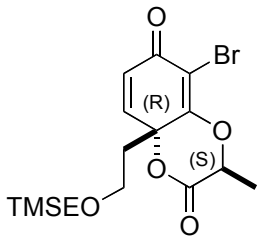


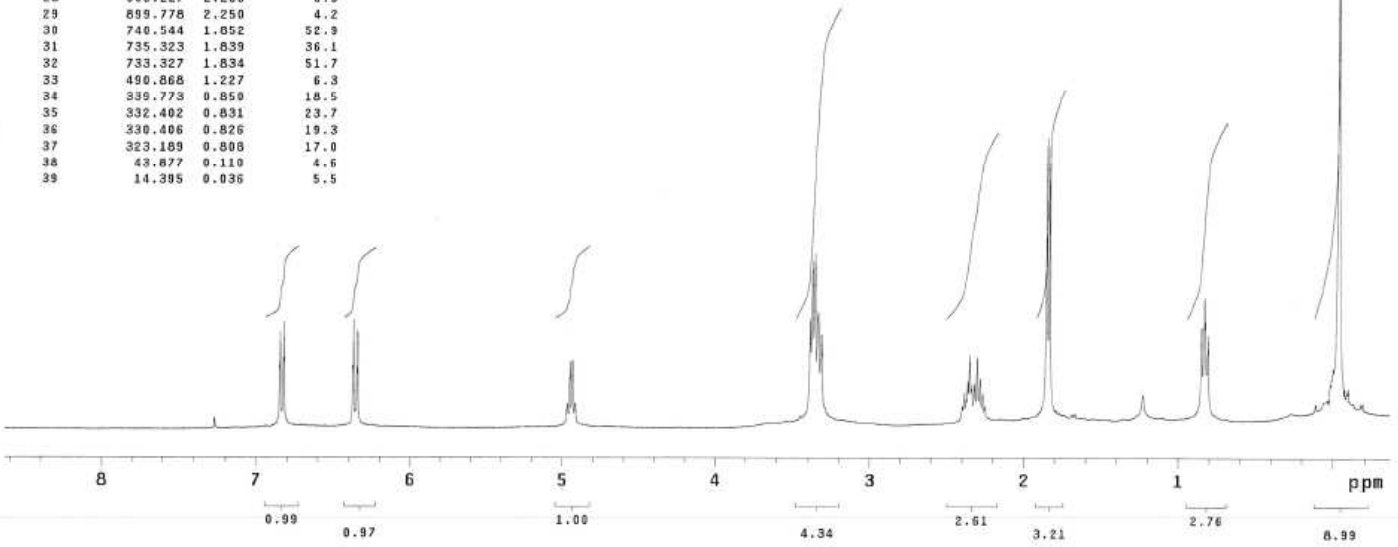

OH
Br
OMe
N
O
(S)
O
OTMSE
172.283
153.612
152.557
130.139
126.323
111.855
105.854
77.549
77.230
76.911
75.220
70.341
68.050
61.571
32.492
30.488
18.275
18.024
1.253
200
180
160
140
120
100
80
60
40
20
0
ppm

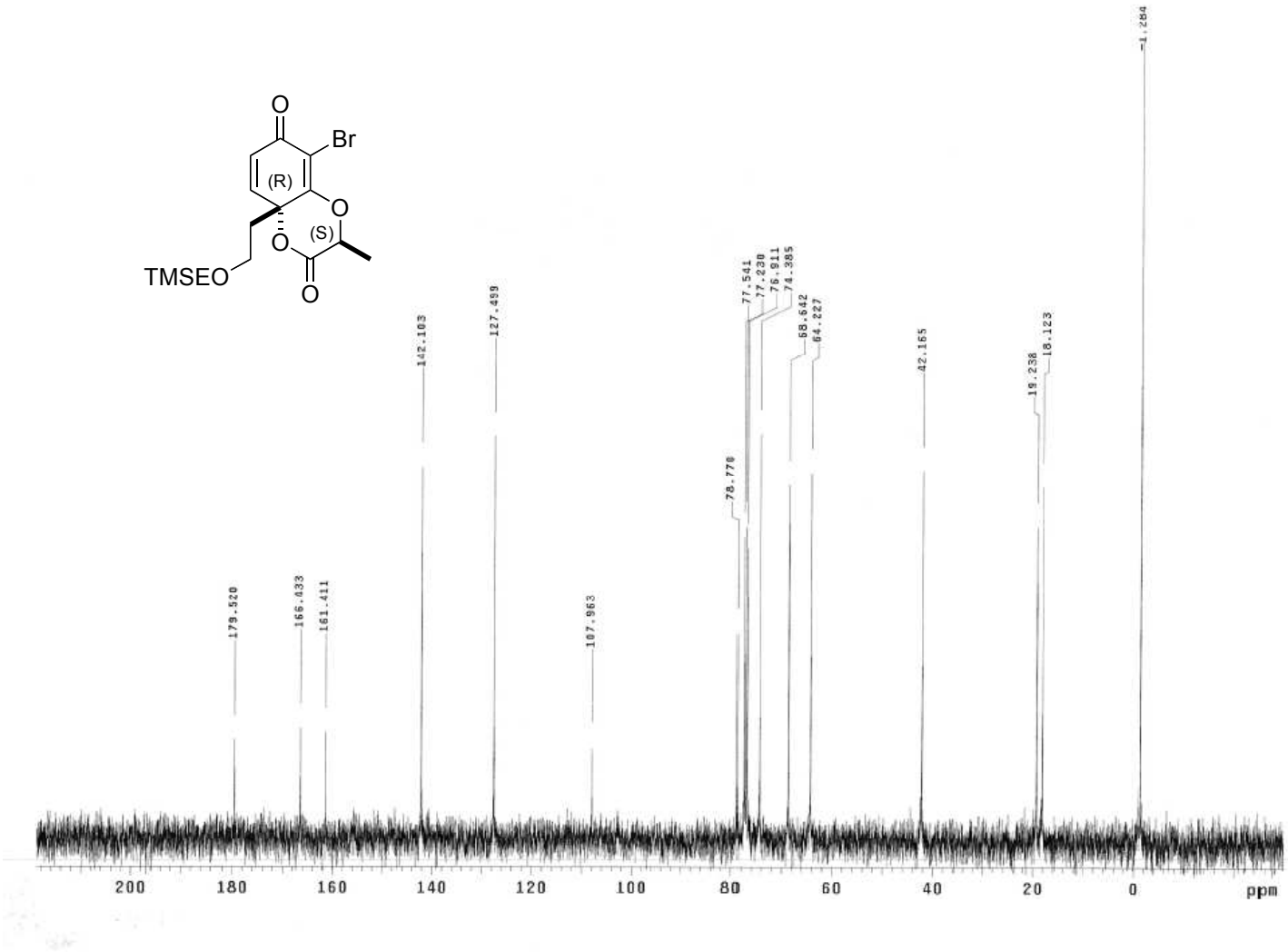

%T
90
75
60
45
30
15
0
4500
4250
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
OH
Br
OMe
N
O
(S)
O
OTMSE

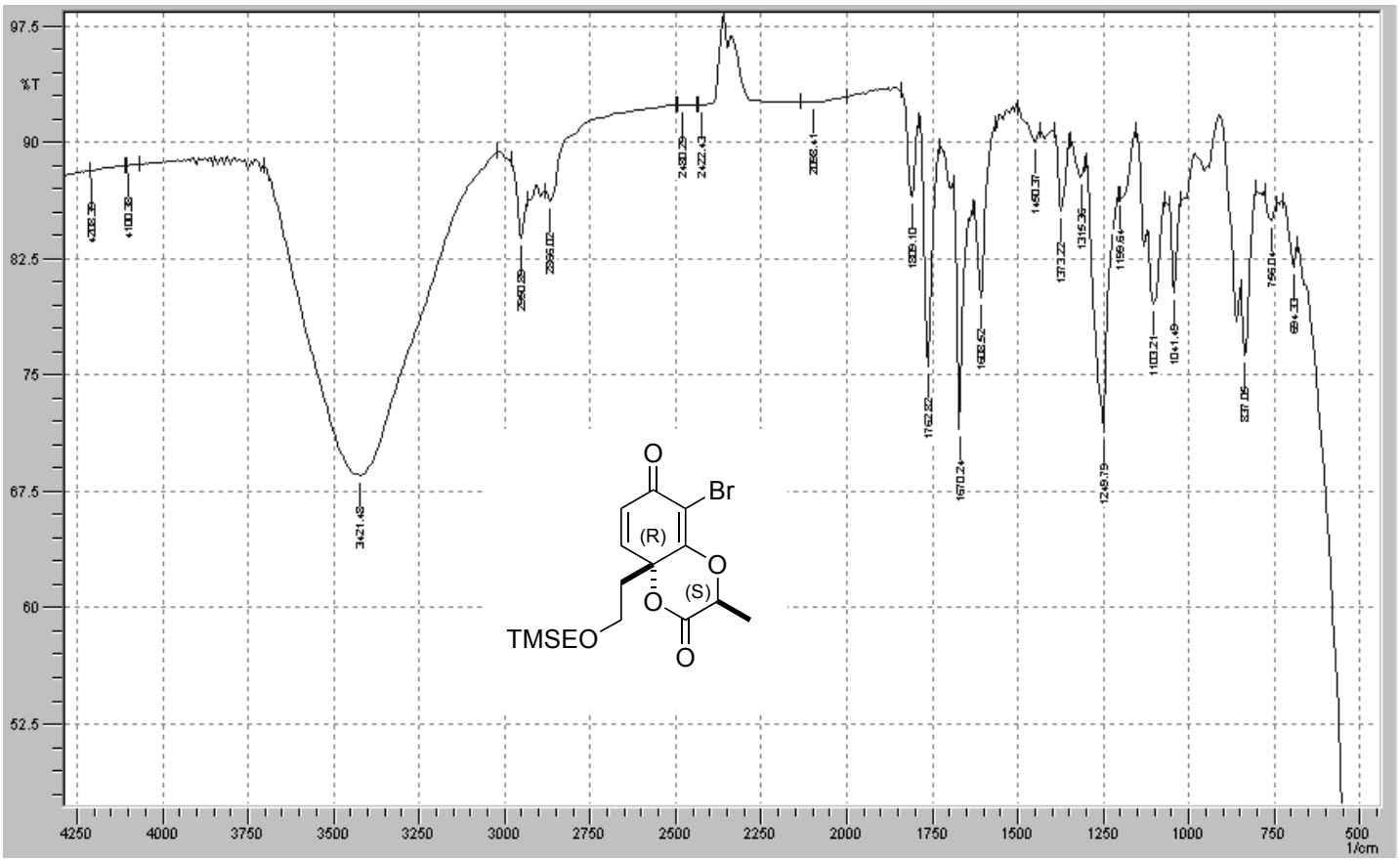
Compound **15**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2739.794	6.850	11.4	40	11.324	0.028	5.5
2	2738.105	6.846	17.5	41	-0.499	-0.001	11.0
3	2729.660	6.825	12.9	42	-12.783	-0.032	173.6
4	2727.971	6.821	19.2	43	-14.780	-0.037	275.9
5	2549.543	6.375	11.3	44	-30.595	-0.076	7.3
6	2547.393	6.369	19.5	45	-37.659	-0.094	6.8
7	2539.562	6.350	10.6	46	-39.809	-0.100	7.3
8	2537.412	6.344	17.6	47	-74.665	-0.187	4.7
9	1986.928	4.968	4.7				
10	1979.711	4.950	12.2				
11	1972.647	4.932	12.5				
12	1965.430	4.914	4.8				
13	1354.599	3.387	19.8				
14	1349.532	3.374	30.4				
15	1342.929	3.358	31.9				
16	1334.177	3.336	21.2				
17	1326.039	3.316	17.1				
18	1324.196	3.311	13.8				
19	958.742	2.397	4.3				
20	953.828	2.385	6.7				
21	948.607	2.372	5.5				
22	944.461	2.361	8.7				
23	939.548	2.349	13.5				
24	934.634	2.337	7.9				
25	927.263	2.318	8.2				
26	920.507	2.302	13.0				
27	913.904	2.285	9.1				
28	906.227	2.266	6.6				
29	899.778	2.250	4.2				
30	740.544	1.852	52.9				
31	735.323	1.839	36.1				
32	733.327	1.834	51.7				
33	490.868	1.227	6.3				
34	339.773	0.850	18.5				
35	332.402	0.831	23.7				
36	330.406	0.826	19.3				
37	323.189	0.808	17.0				
38	43.877	0.110	4.6				
39	14.395	0.036	5.5				



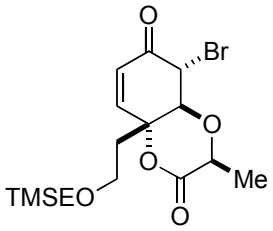


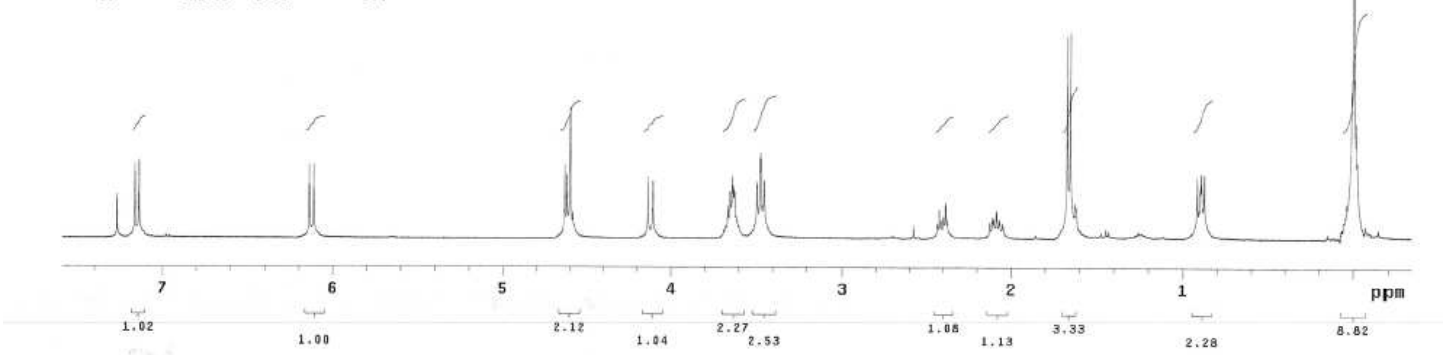

O
Br
(R)
O
(S)
O
TMSEO
O
179.520
166.433
161.411
142.103
127.499
107.963
78.770
77.541
77.230
76.911
74.385
68.642
64.227
42.165
19.238
18.123
-1.284
200
180
160
140
120
100
80
60
40
20
0
ppm

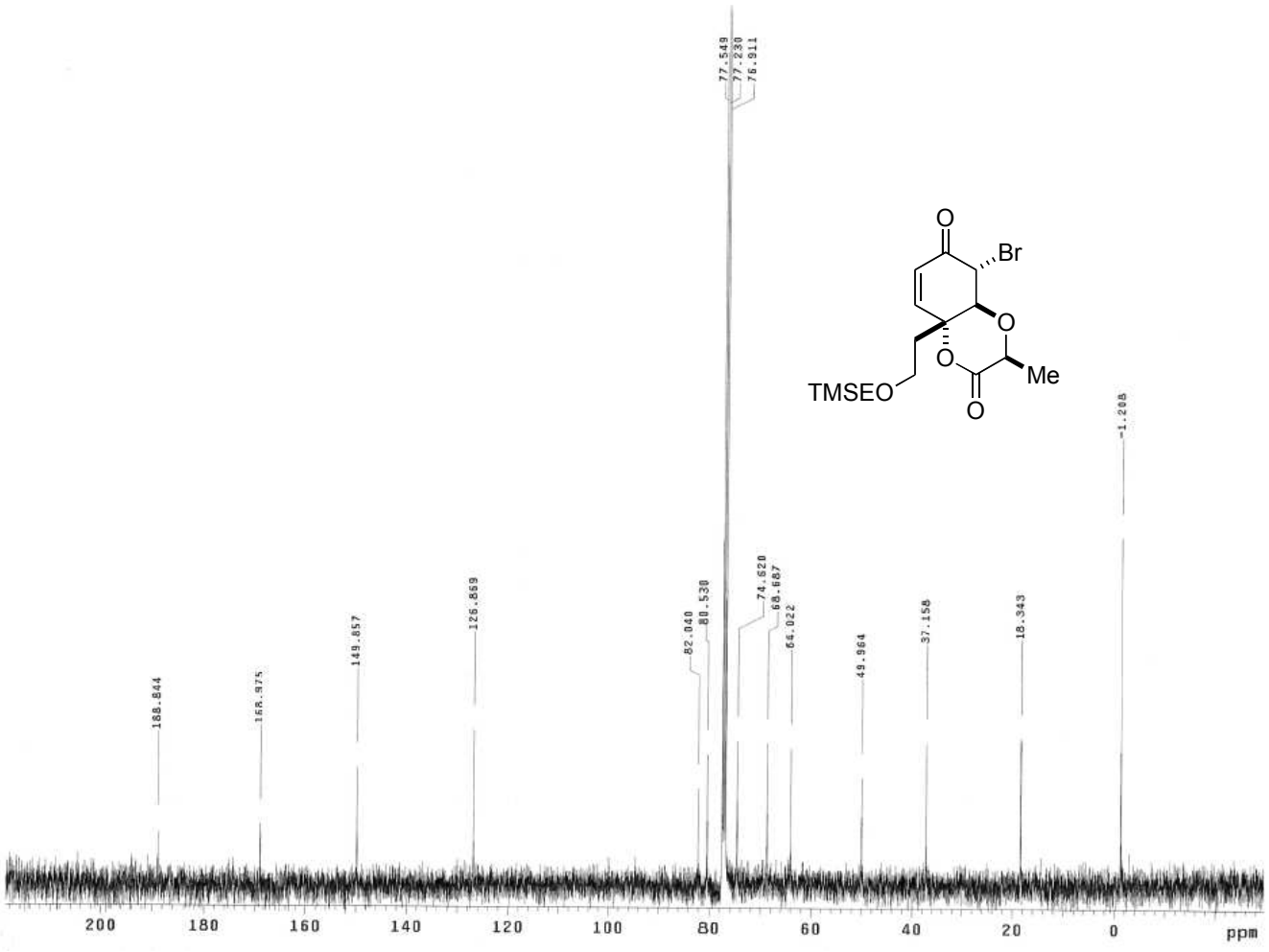

%T
97.5
90
82.5
75
67.5
60
52.5
4250
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
3421.48
2940.28
2895.02
2430.29
2422.43
2068.41
1829.10
1762.82
1670.24
1628.52
1460.37
1373.22
1315.36
1249.79
1199.64
1103.21
1041.49
837.06
756.04
694.33
O
Br
(R)
O
(S)
O
TMSEO
O

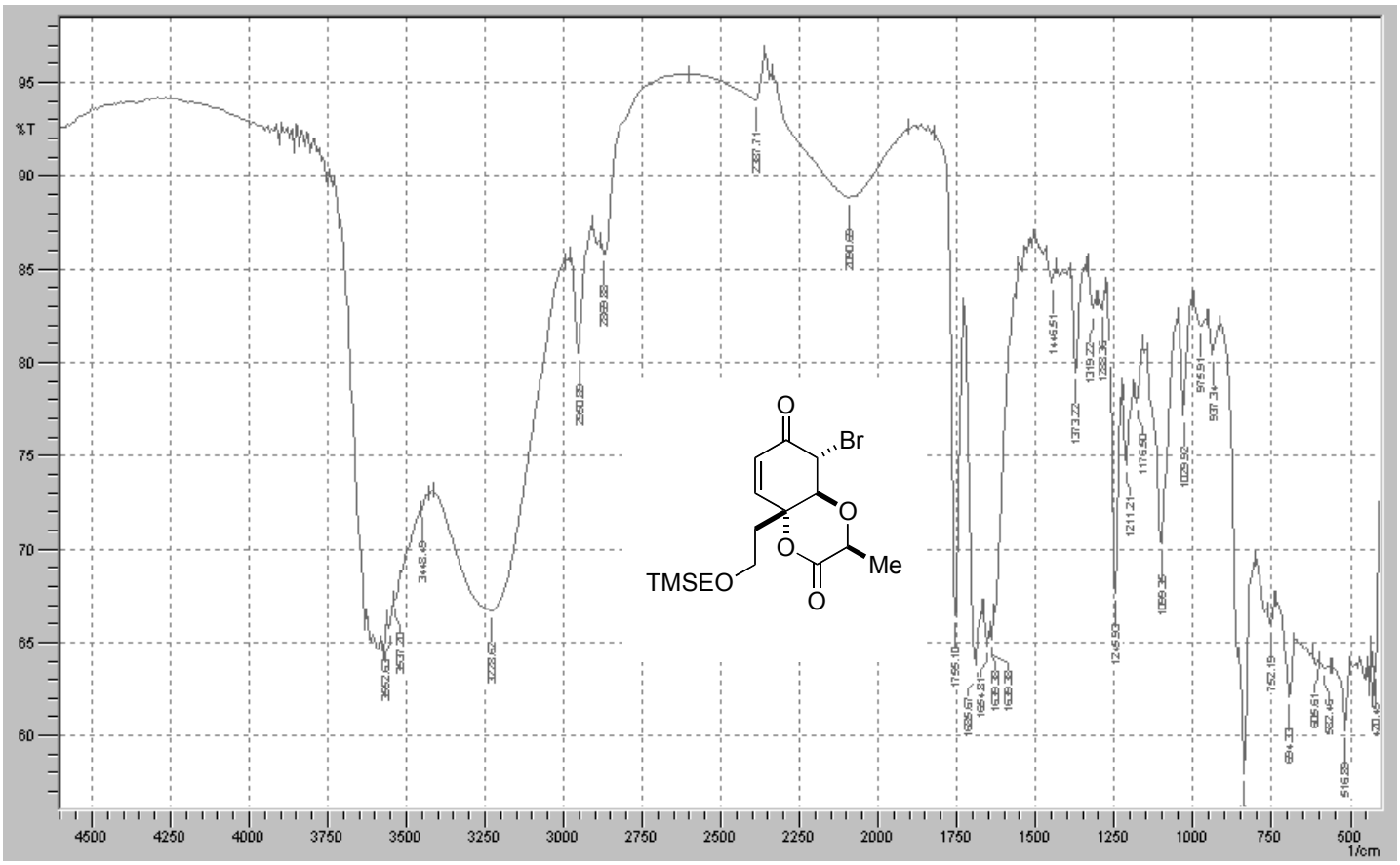
Compound **16**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2907.627	7.270	8.2	40	820.545	2.052	3.0
2	2865.767	7.165	13.7	41	818.395	2.046	2.2
3	2855.573	7.140	14.5	42	668.989	1.673	37.7
4	2455.106	6.139	13.6	43	662.079	1.655	38.4
5	2444.974	6.113	13.6	44	649.487	1.624	6.8
6	1854.412	4.637	5.3	45	647.491	1.619	5.9
7	1852.569	4.632	13.7	46	367.105	0.918	11.5
8	1847.502	4.619	12.0	47	363.266	0.908	5.5
9	1840.439	4.602	24.3	48	360.502	0.901	5.5
10	1833.529	4.584	5.1	49	358.506	0.896	12.2
11	1654.948	4.138	11.5	50	356.970	0.893	10.2
12	1642.970	4.108	10.6	51	354.053	0.885	6.8
13	1470.685	3.677	2.4	52	350.214	0.876	12.0
14	1465.311	3.664	6.2	53	21.305	0.053	3.4
15	1460.397	3.651	8.8	54	15.163	0.038	6.7
16	1456.097	3.641	11.6	55	4.722	0.012	27.2
17	1453.948	3.635	9.8	56	1.497	0.004	267.0
18	1451.951	3.630	9.2	57	-1.881	-0.005	29.8
19	1449.802	3.625	8.9	58	-5.259	-0.013	21.5
20	1396.980	3.493	10.6	59	-8.637	-0.022	14.3
21	1394.830	3.488	6.0	60	-26.757	-0.067	2.2
22	1389.609	3.474	15.2	61	-28.446	-0.071	2.4
23	1388.381	3.471	16.2				
24	1383.160	3.458	6.4				
25	1381.010	3.453	10.6				
26	1380.243	3.451	10.9				
27	1030.604	2.577	2.5				
28	973.636	2.434	3.0				
29	969.490	2.424	5.5				
30	965.037	2.413	3.6				
31	959.202	2.398	4.3				
32	954.749	2.387	6.8				
33	950.450	2.376	3.9				
34	850.334	2.126	3.2				
35	844.038	2.110	4.1				
36	841.274	2.103	4.0				
37	835.286	2.088	5.3				
38	829.604	2.074	3.9				
39	826.687	2.067	3.4				



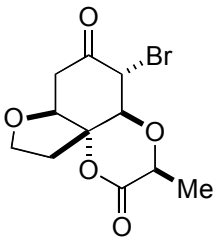


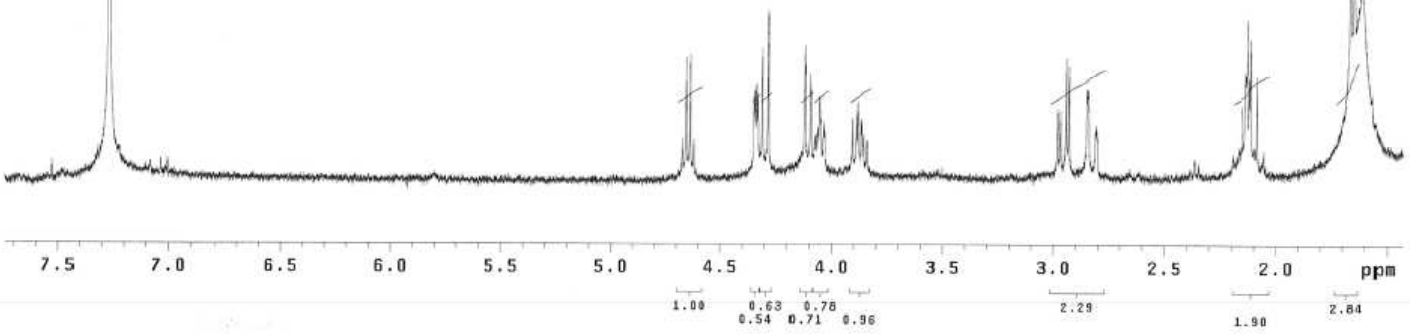

O
Br
O
O
Me
TMSEO
O
77.549
77.230
76.911
188.844
168.375
149.857
126.869
82.040
80.530
74.620
68.687
64.022
49.864
37.158
18.343
-1.208
200
180
160
140
120
100
80
60
40
20
0
ppm

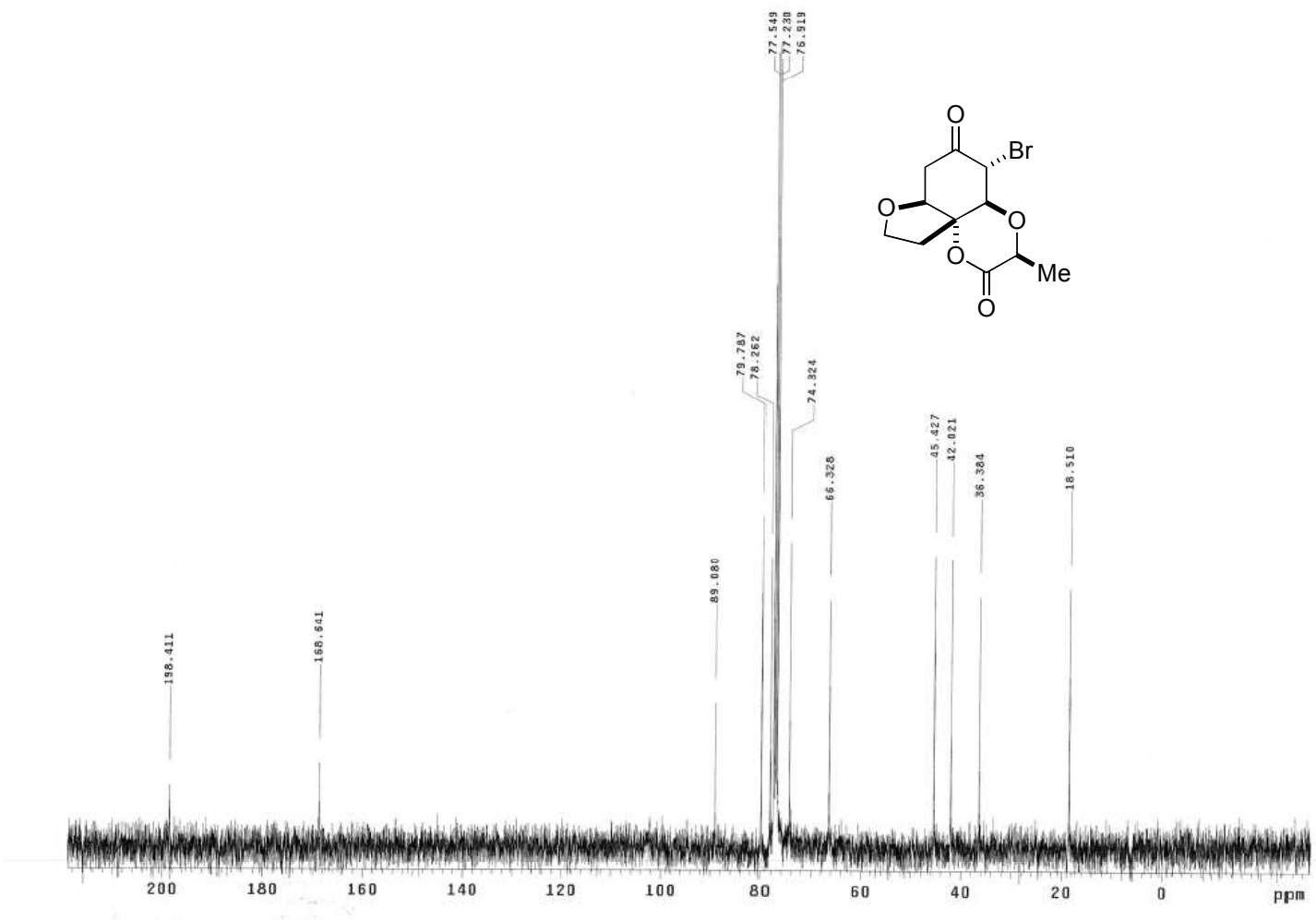

%T
95
90
85
80
75
70
65
60
4500
4250
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
2357.71
2050.69
2940.89
2898.88
3448.49
3228.62
1755.10
1446.51
1373.22
1319.22
1288.36
1211.21
1176.50
1029.52
975.91
937.34
1245.53
1089.35
752.19
O
Br
O
O
Me
TMSEO
O

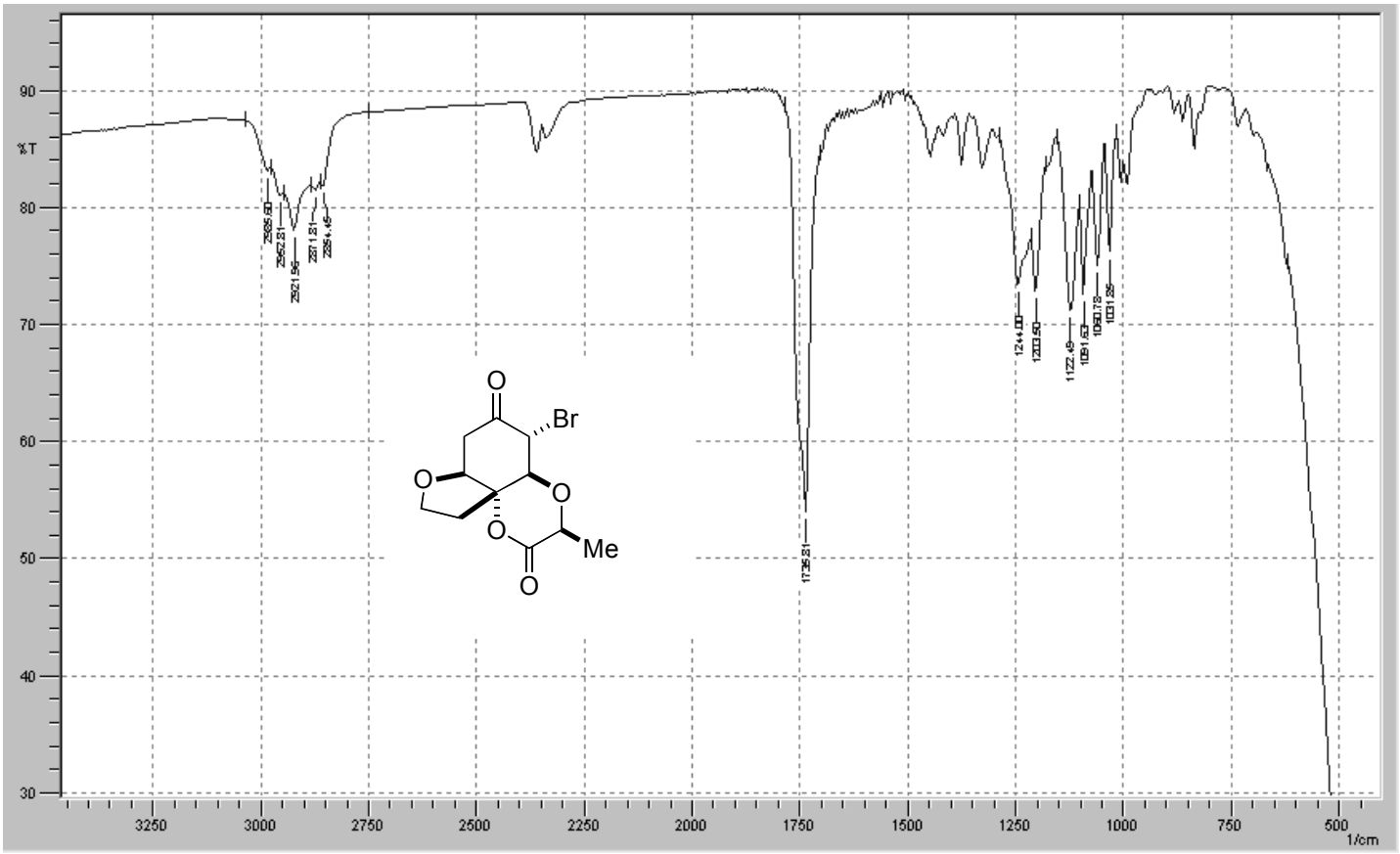
Compound **17**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2927.589	7.320	12.3	40	659.622	1.649	110.4
2	2907.627	7.270	506.9	41	645.495	1.614	40.2
3	1869.460	4.674	13.7				
4	1862.397	4.657	28.0				
5	1855.333	4.639	28.6				
6	1848.270	4.621	13.5				
7	1738.634	4.347	21.1				
8	1736.484	4.342	22.2				
9	1733.873	4.335	23.2				
10	1731.724	4.330	21.6				
11	1723.432	4.309	29.9				
12	1712.990	4.283	36.5				
13	1649.573	4.124	30.2				
14	1639.132	4.098	25.2				
15	1628.537	4.072	14.6				
16	1625.312	4.064	15.8				
17	1622.394	4.057	21.1				
18	1615.792	4.040	16.6				
19	1562.356	3.906	17.3				
20	1555.599	3.889	18.4				
21	1553.450	3.884	20.1				
22	1547.461	3.869	16.8				
23	1545.925	3.865	17.2				
24	1542.854	3.858	14.4				
25	1536.866	3.843	13.4				
26	1192.295	2.981	19.0				
27	1187.535	2.969	18.6				
28	1176.939	2.943	28.0				
29	1172.026	2.930	26.6				
30	1139.933	2.850	22.5				
31	1138.858	2.848	22.5				
32	1123.350	2.809	16.1				
33	863.079	2.158	19.8				
34	855.862	2.140	25.6				
35	852.484	2.131	35.1				
36	848.645	2.122	24.5				
37	846.188	2.116	31.5				
38	834.825	2.087	24.9				
39	666.685	1.667	108.5				



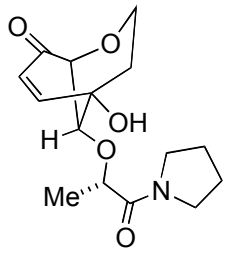


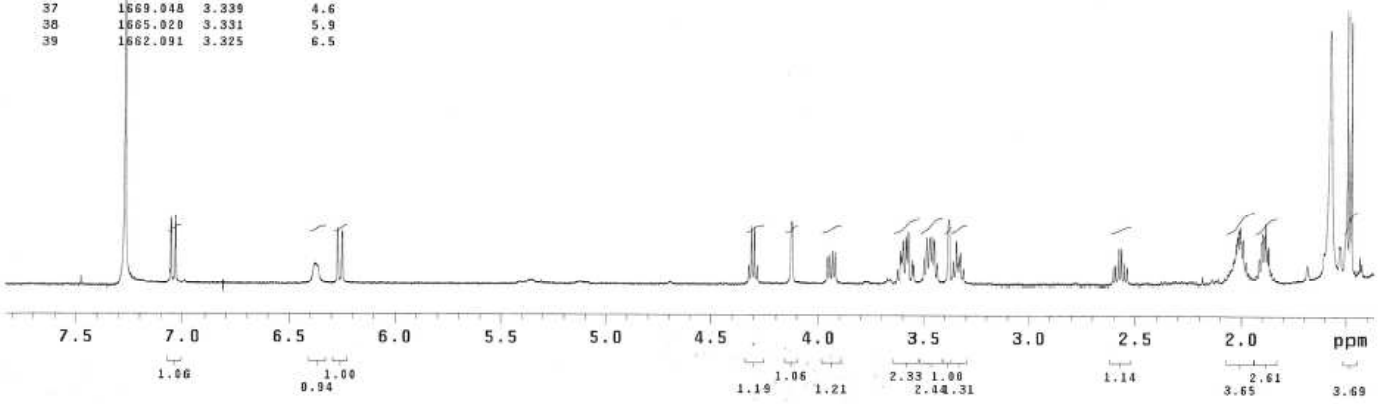

77.549
77.230
76.919
79.787
78.262
74.324
66.328
89.080
45.427
42.021
36.384
18.510
198.411
168.641
200
180
160
140
120
100
80
60
40
20
0
ppm
O
Br
O
O
O
Me
O


%T
90
80
70
60
50
40
30
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
2365.90
2362.31
2321.96
2271.31
2254.45
1735.81
1244.03
1203.50
1122.49
1091.63
1060.78
1031.26
O
Br
O
O
O
Me
O

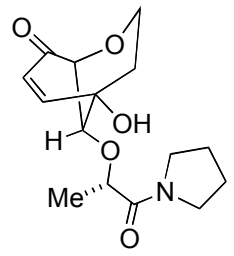
Compound **19**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3633.956	7.270	319.7	40	1654.860	3.311	3.5
2	3527.957	7.058	3.0	41	1300.616	2.602	3.8
3	3524.753	7.052	12.5	42	1294.666	2.590	4.2
4	3514.501	7.031	13.0	43	1287.709	2.576	7.3
5	3186.986	6.376	4.2	44	1281.851	2.564	7.3
6	3134.811	6.271	10.1	45	1274.711	2.550	4.6
7	3133.621	6.269	10.7	46	1268.578	2.538	3.8
8	3124.559	6.251	9.7	47	1012.644	2.026	8.4
9	3123.552	6.249	10.2	48	1009.257	2.019	9.4
10	2160.137	4.322	4.1	49	1006.328	2.013	10.9
11	2153.638	4.309	11.3	50	1002.301	2.005	11.3
12	2146.956	4.295	11.0	51	1000.104	2.001	8.7
13	2140.457	4.282	3.9	52	995.802	1.992	9.0
14	2062.103	4.125	12.1	53	988.753	1.978	4.9
15	1977.615	3.956	5.7	54	983.261	1.967	2.9
16	1971.940	3.945	6.0	55	963.581	1.928	2.6
17	1965.532	3.932	6.6	56	956.991	1.915	5.5
18	1959.582	3.920	6.4	57	949.393	1.899	10.2
19	1811.752	3.625	3.3	58	944.725	1.890	9.8
20	1804.429	3.610	6.6	59	942.162	1.885	11.9
21	1801.775	3.605	5.7	60	938.409	1.877	7.2
22	1798.754	3.599	8.7	61	934.930	1.870	7.7
23	1792.255	3.586	9.4	62	927.882	1.856	3.0
24	1789.234	3.579	8.7	63	841.930	1.684	4.2
25	1785.756	3.573	10.3	64	788.107	1.577	47.8
26	1776.785	3.555	5.1	65	764.582	1.530	7.9
27	1773.490	3.548	4.3	66	746.824	1.494	51.5
28	1749.233	3.499	5.4	67	740.142	1.481	49.3
29	1742.002	3.485	9.2	68	724.764	1.450	3.4
30	1735.411	3.472	9.2	69	719.547	1.440	5.9
31	1730.651	3.462	9.4	70	714.787	1.430	4.6
32	1723.786	3.449	8.8				
33	1717.836	3.437	4.5				
34	1690.467	3.382	12.5				
35	1679.208	3.359	4.9				
36	1671.977	3.345	8.7				
37	1669.048	3.339	4.6				
38	1665.020	3.331	5.9				
39	1662.091	3.325	6.5				



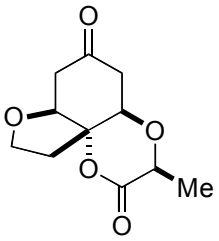


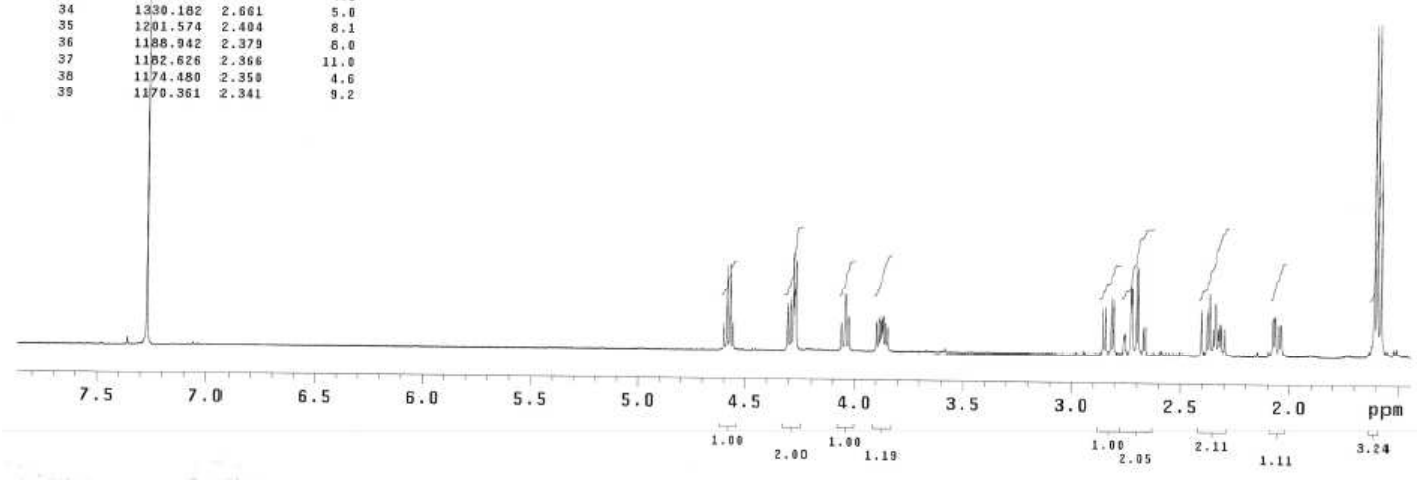
INDEX	FREQUENCY	PPM	HEIGHT
1	21660.200	172.332	6.4
2	19607.697	156.002	8.7
3	16335.766	129.970	19.5
4	12813.740	101.948	6.4
5	9972.145	79.340	10.0
6	9738.867	77.484	516.5
7	9706.958	77.230	541.8
8	9675.049	76.976	539.8
9	9189.520	73.113	18.2
10	8664.752	68.938	9.9
11	7797.182	62.036	13.3
12	5880.506	46.786	10.9
13	5817.983	46.289	12.2
14	3858.619	30.700	11.6
15	3760.737	29.921	39.4
16	3322.639	26.435	17.4
17	3003.984	23.900	16.1
18	2331.746	18.552	20.3

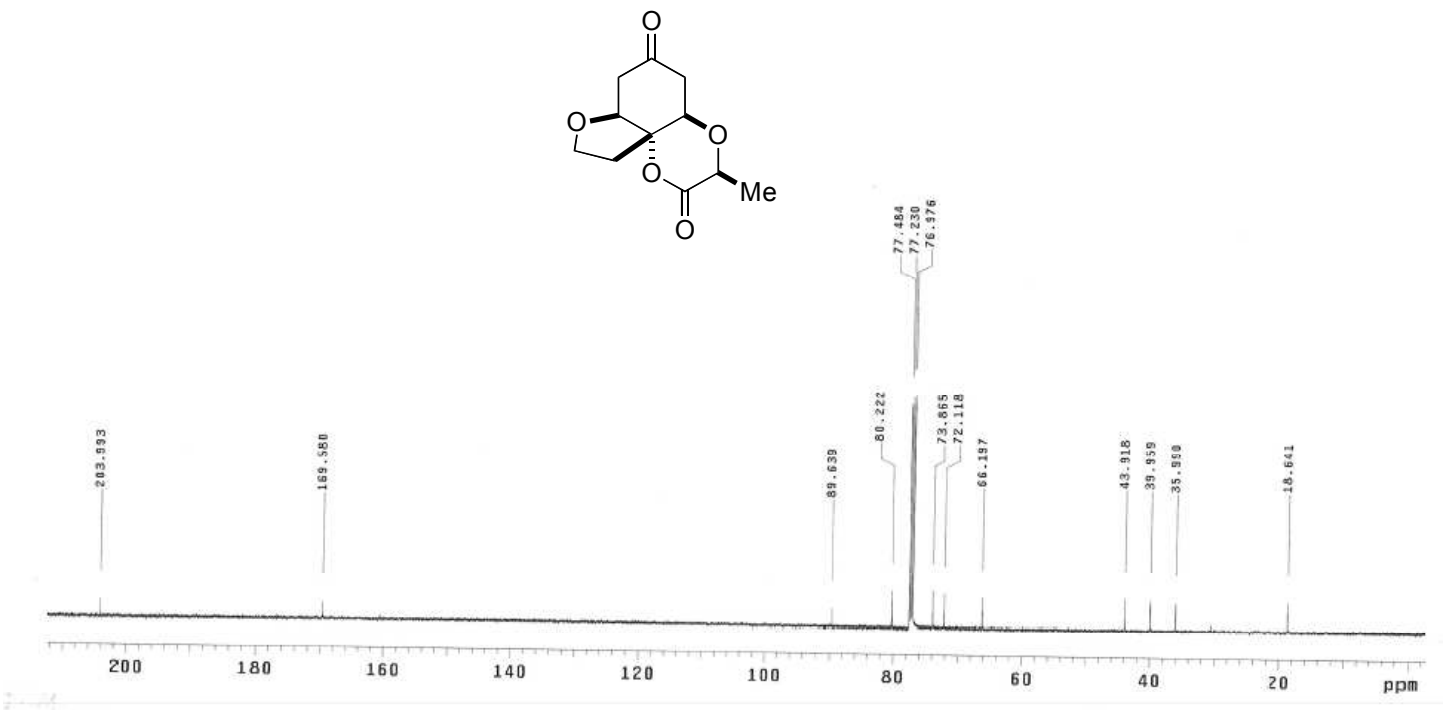


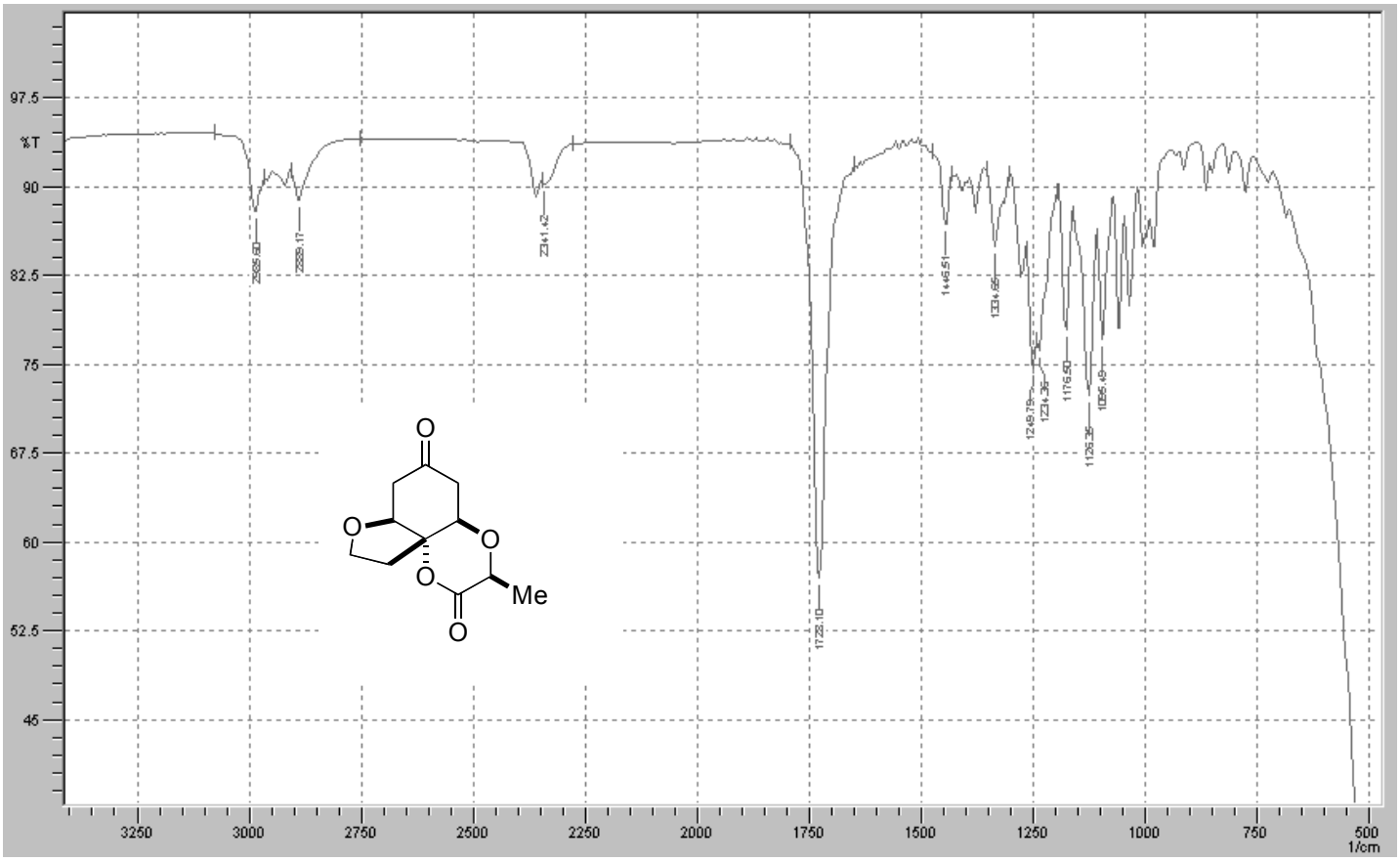
Compound **20**:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3633.956	7.278	65.7	40	1162.946	2.327	4.7
2	2298.448	4.598	4.8	41	1160.475	2.322	5.6
3	2291.308	4.584	15.2	42	1156.996	2.315	5.4
4	2284.260	4.570	15.4	43	1148.941	2.299	4.7
5	2277.303	4.556	5.0	44	1037.542	2.076	6.8
6	2151.075	4.303	8.5	45	1033.423	2.067	7.1
7	2145.034	4.291	9.1	46	1023.629	2.048	5.4
8	2138.626	4.278	17.5	47	1019.326	2.039	5.6
9	2136.521	4.274	10.7	48	803.760	1.608	53.7
10	2134.141	4.270	11.3	49	796.711	1.594	53.9
11	2132.219	4.266	16.0	50	788.198	1.577	35.2
12	2029.424	4.060	4.9				
13	2021.186	4.044	10.3				
14	2012.673	4.027	6.2				
15	1948.690	3.898	5.5				
16	1943.747	3.889	6.1				
17	1939.902	3.881	5.7				
18	1937.156	3.875	6.4				
19	1934.776	3.871	5.8				
20	1932.122	3.865	6.4				
21	1928.186	3.857	5.9				
22	1923.243	3.848	4.4				
23	1427.668	2.856	8.4				
24	1421.626	2.844	8.5				
25	1408.720	2.818	10.1				
26	1402.678	2.806	9.8				
27	1379.337	2.759	3.3				
28	1376.957	2.755	3.7				
29	1363.043	2.727	12.1				
30	1360.847	2.722	12.0				
31	1350.961	2.703	15.9				
32	1346.384	2.694	15.7				
33	1334.759	2.670	4.8				
34	1330.182	2.661	5.0				
35	1201.574	2.404	8.1				
36	1188.942	2.379	8.0				
37	1182.626	2.366	11.0				
38	1174.480	2.350	4.6				
39	1170.361	2.341	9.2				



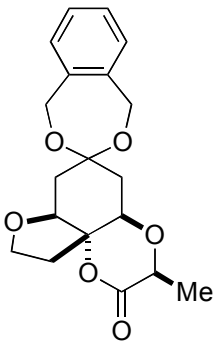


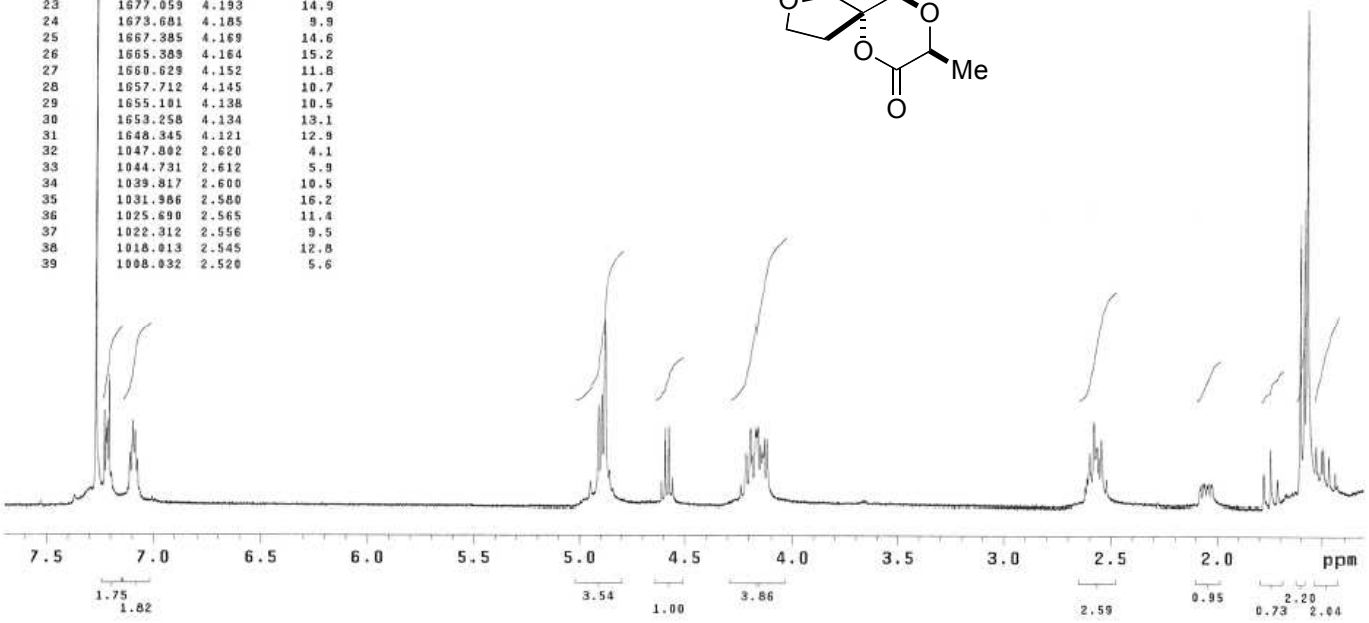

O
O
O
O
O
Me
203.993
169.580
89.639
80.222
77.484
77.230
76.976
73.865
72.118
66.187
43.918
39.959
35.950
18.641
200
180
160
140
120
100
80
60
40
20
ppm


97.5
%T
90
82.5
75
67.5
60
52.5
45
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
2985.60
2888.17
2341.42
1723.10
1446.51
1334.66
1249.79
1234.36
1176.50
1138.35
1056.49
O
O
O
O
Me
O

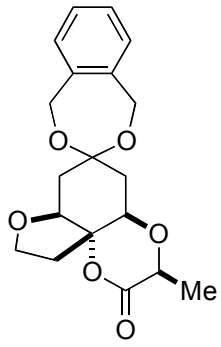
Compound **24**:

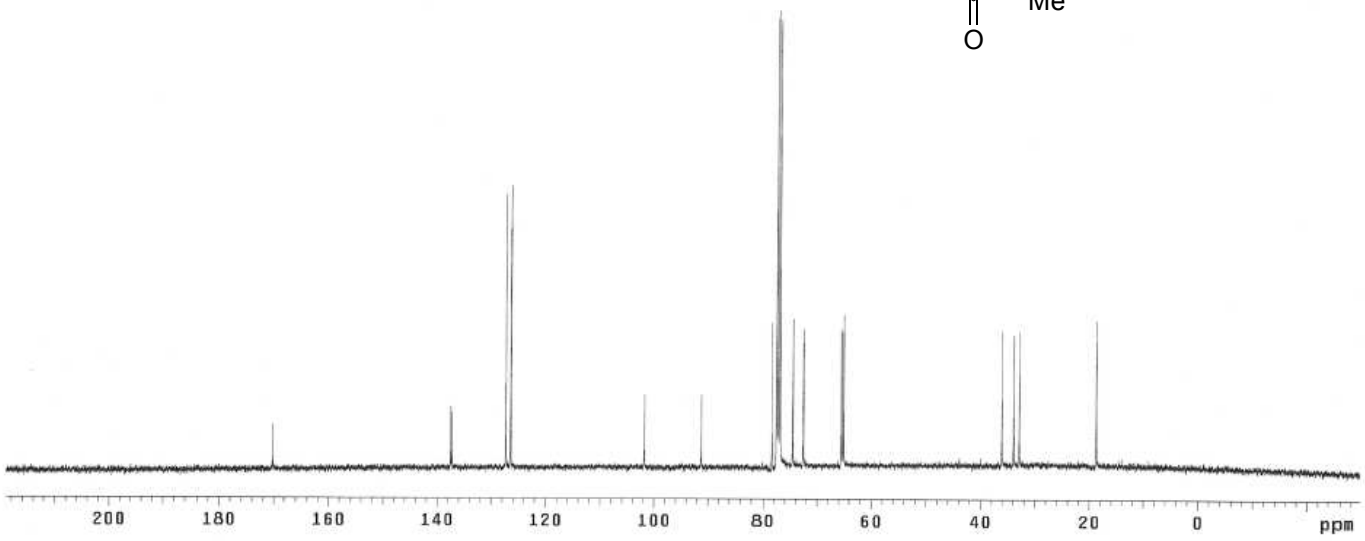
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2907.627	7.270	152.4	40	831.293	2.078	4.5
2	2891.350	7.229	18.1	41	825.919	2.065	4.9
3	2887.972	7.221	14.8	42	823.462	2.059	4.8
4	2885.976	7.216	16.5	43	817.320	2.044	4.8
5	2882.598	7.207	24.6	44	809.950	2.025	4.7
6	2876.605	7.197	6.6	45	711.676	1.779	6.8
7	2843.442	7.110	10.2	46	698.931	1.748	11.1
8	2838.528	7.097	16.1	47	685.879	1.715	5.7
9	2834.689	7.088	14.3	48	642.731	1.607	52.9
10	2829.929	7.076	9.1	49	635.821	1.590	55.7
11	2123.896	5.310	11.7	50	629.986	1.575	92.7
12	1979.711	4.950	5.1	51	612.021	1.530	11.9
13	1964.662	4.912	19.2	52	601.886	1.505	11.0
14	1958.213	4.896	21.0	53	598.201	1.496	11.5
15	1952.532	4.882	35.1	54	587.913	1.470	9.8
16	1943.319	4.859	7.1	55	575.782	1.440	6.9
17	1844.277	4.611	5.0				
18	1837.214	4.594	14.9				
19	1830.151	4.576	15.2				
20	1823.087	4.558	5.7				
21	1694.871	4.238	4.5				
22	1684.737	4.212	10.3				
23	1677.059	4.193	14.9				
24	1673.681	4.185	9.9				
25	1667.385	4.169	14.6				
26	1665.389	4.164	15.2				
27	1660.629	4.152	11.8				
28	1657.712	4.145	10.7				
29	1655.101	4.138	10.5				
30	1653.258	4.134	13.1				
31	1648.345	4.121	12.9				
32	1047.802	2.620	4.1				
33	1044.731	2.612	5.9				
34	1039.817	2.600	10.5				
35	1031.986	2.580	16.2				
36	1025.690	2.565	11.4				
37	1022.312	2.556	9.5				
38	1018.013	2.545	12.8				
39	1008.032	2.520	5.6				

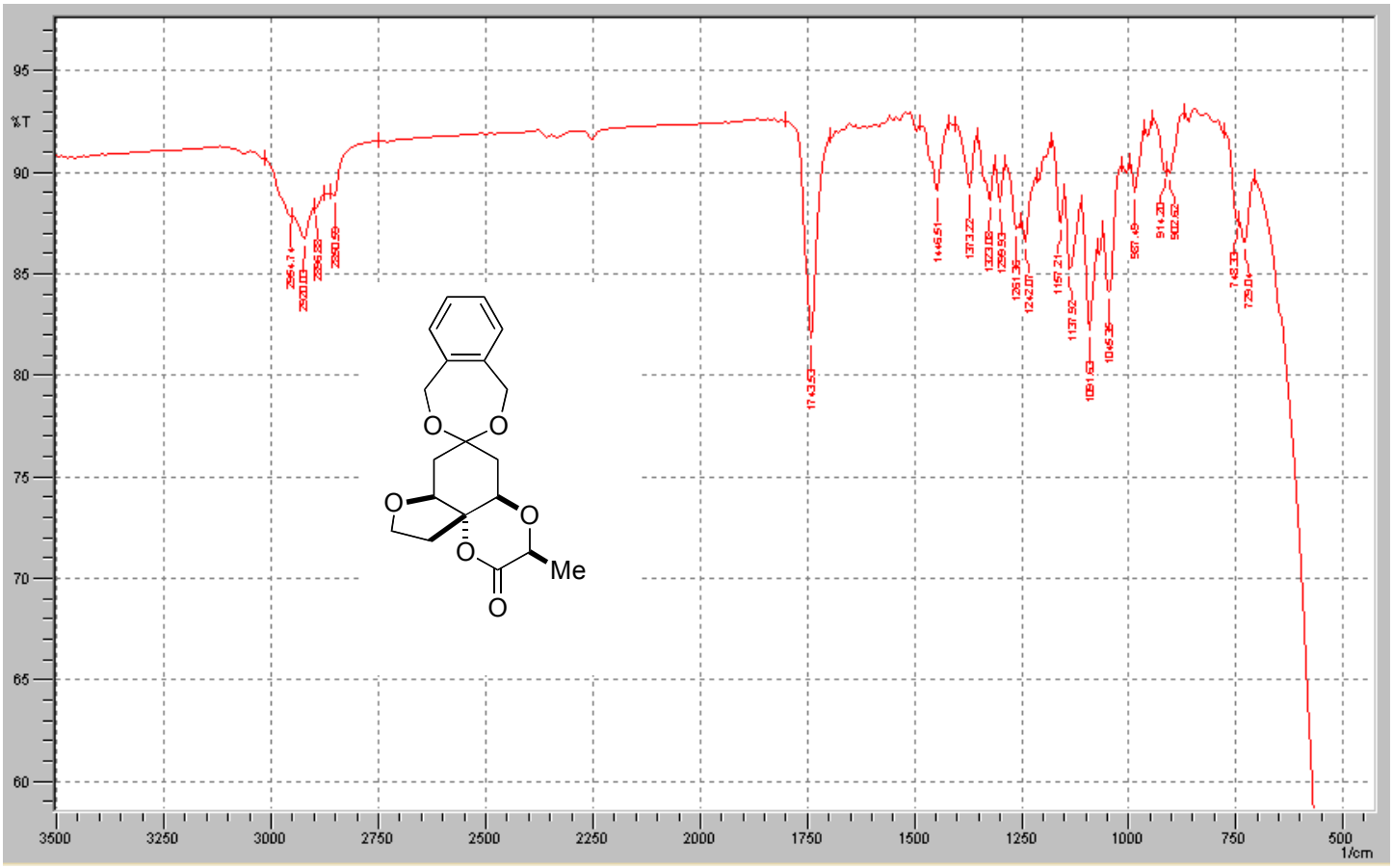




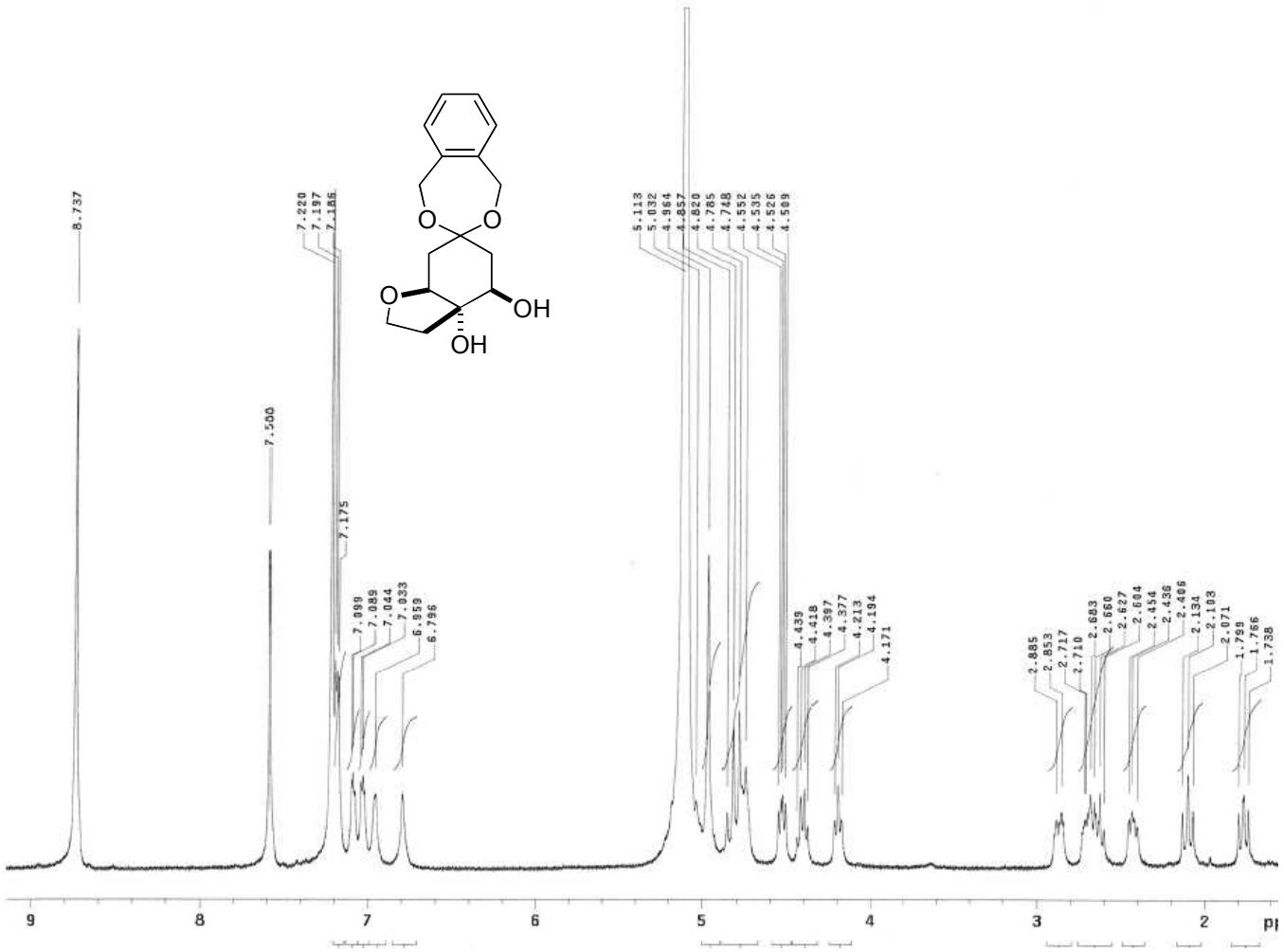
INDEX	FREQUENCY	PPM	HEIGHT
1	17119.961	170.234	8.8
2	13824.725	137.468	11.9
3	13804.125	137.263	11.1
4	12801.592	127.294	51.5
5	12713.089	126.414	53.2
6	10233.460	101.757	14.2
7	9177.519	91.258	14.2
8	7887.349	78.429	27.8
9	7798.846	77.549	84.7
10	7787.401	77.435	9.2
11	7766.801	77.230	86.1
12	7735.520	76.919	84.3
13	7494.423	74.522	28.4
14	7299.868	72.587	26.6
15	6591.076	65.539	26.6
16	6567.424	65.304	26.1
17	6540.720	65.038	29.2
18	3633.069	36.126	26.2
19	3410.284	33.911	25.6
20	3310.336	32.917	26.1
21	1882.070	18.715	28.3

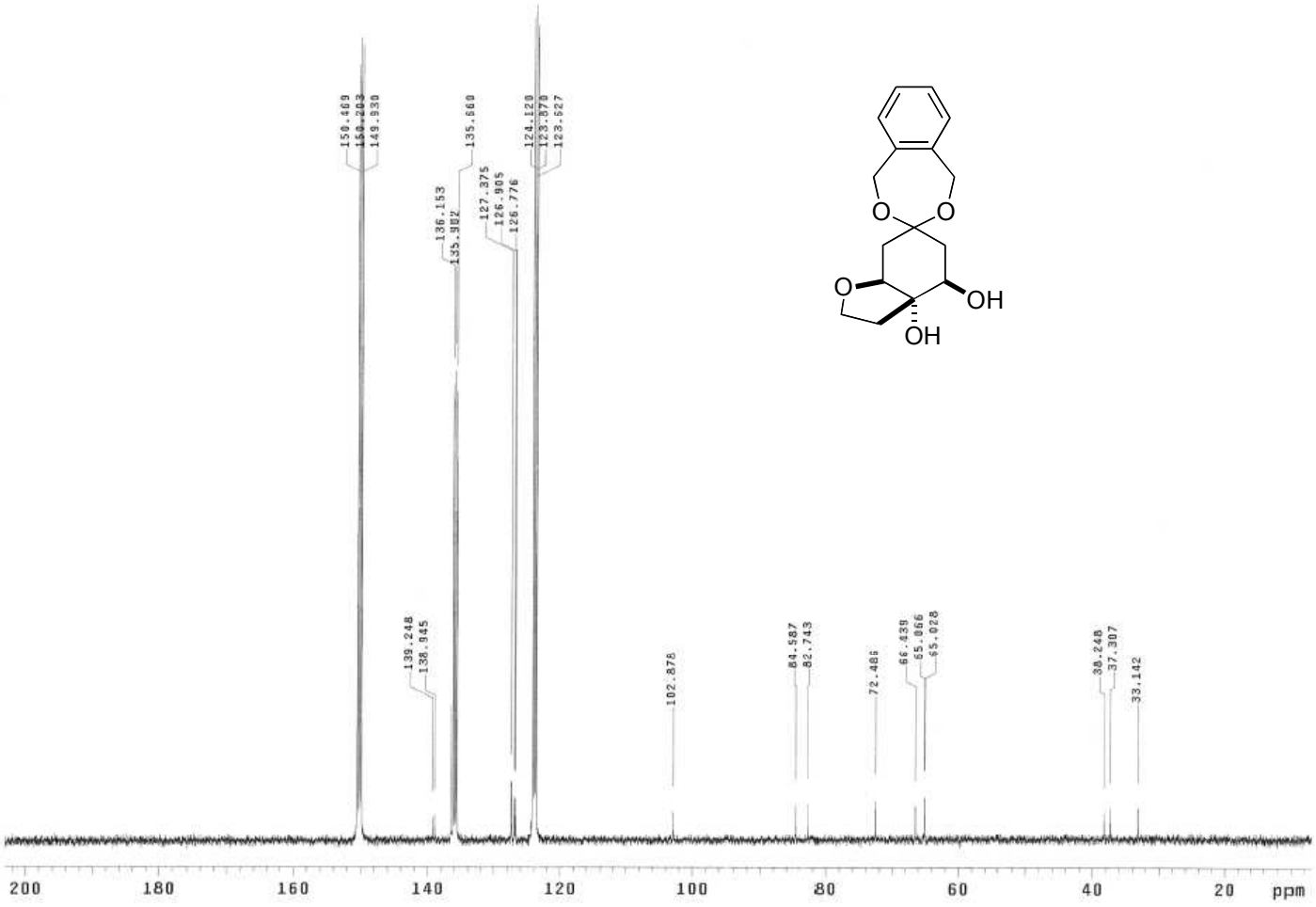


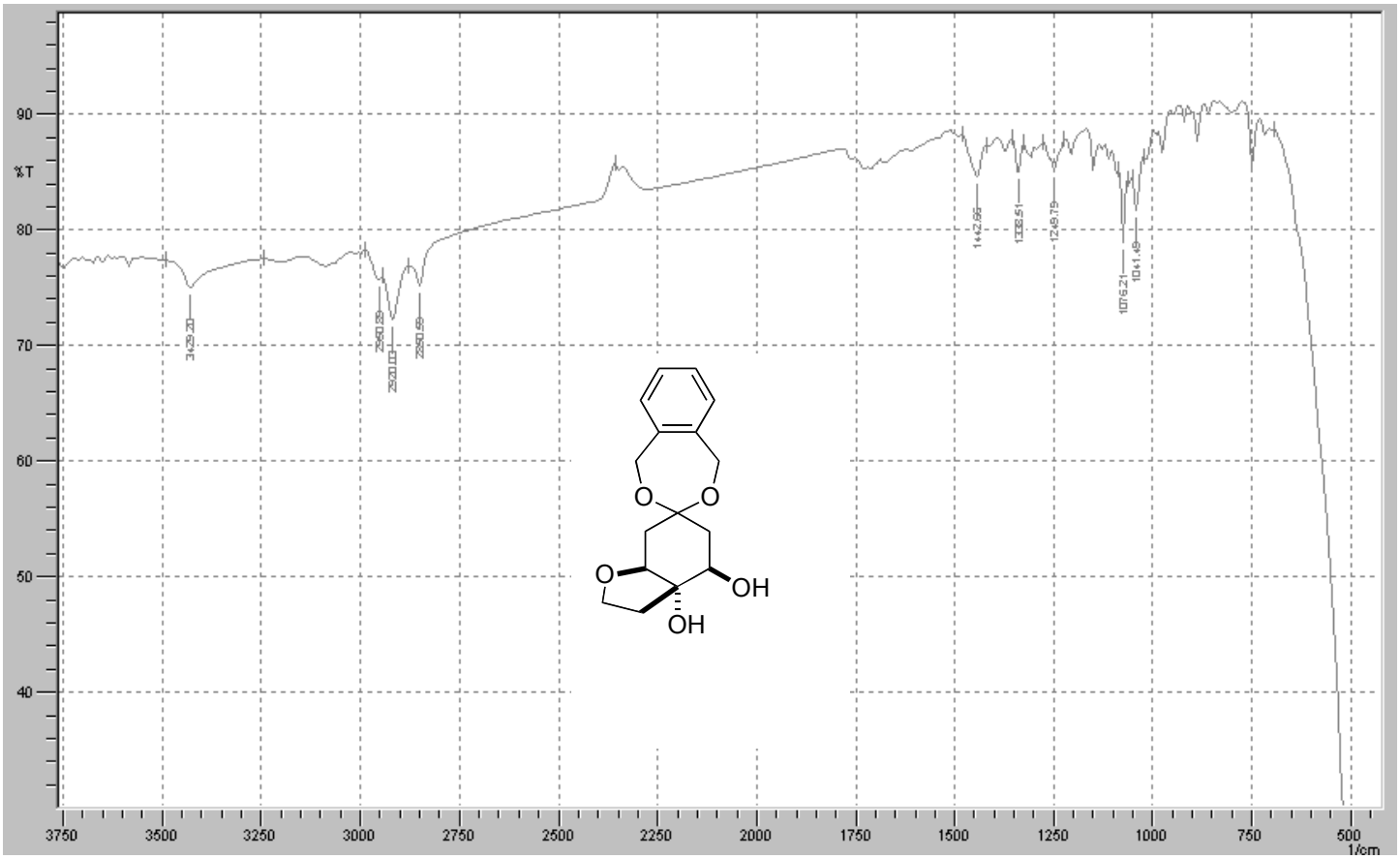



%T
95
90
85
80
75
70
65
60
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
Me
O

Compound **25**:

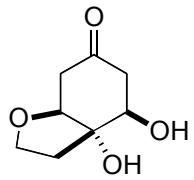

8.737
7.500
7.220
7.197
7.186
7.175
7.099
7.089
7.044
7.033
6.959
6.796
5.113
5.032
4.964
4.857
4.820
4.785
4.748
4.552
4.535
4.526
4.509
4.439
4.418
4.397
4.377
4.213
4.194
4.171
2.885
2.853
2.717
2.710
2.683
2.660
2.627
2.604
2.454
2.438
2.406
2.134
2.103
2.071
1.799
1.766
1.738
O
O
O
OH
OH
9
8
7
6
5
4
3
2
pp

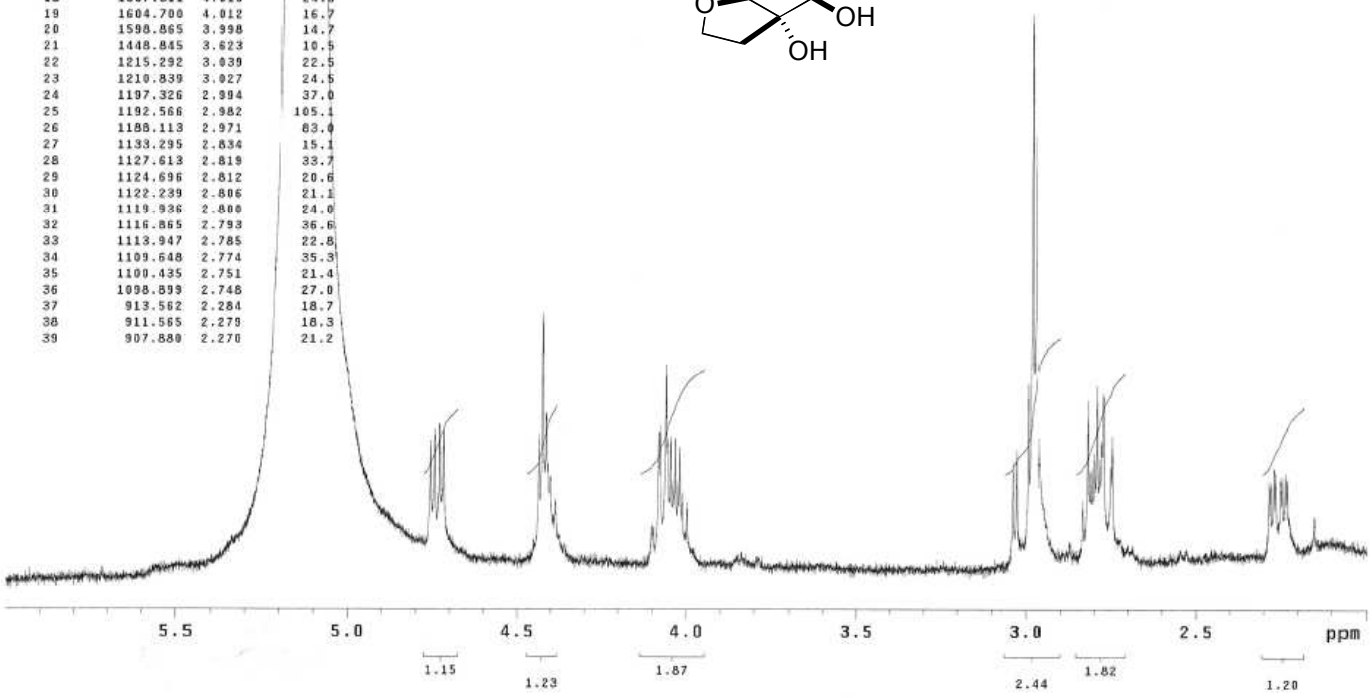

150.469
150.203
149.930
139.248
138.945
136.153
135.982
135.660
127.375
126.905
126.776
124.128
123.878
123.627
102.878
84.587
82.743
72.486
66.438
65.066
65.028
38.248
37.307
33.142
O
O
O
OH
OH
200
180
160
140
120
100
80
60
40
20
ppm

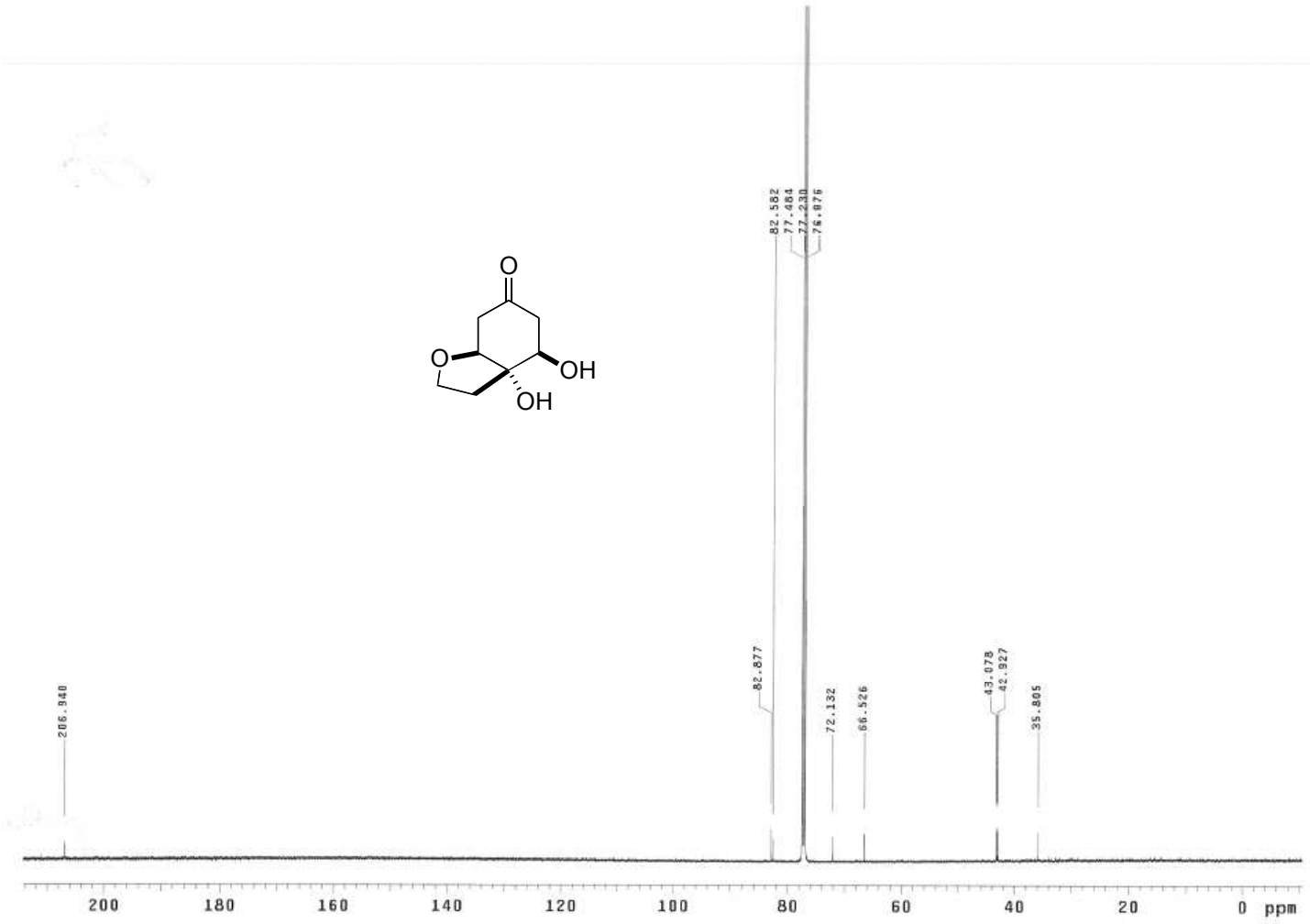

%T
90
80
70
60
50
40
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
O
O
O
OH
OH

Epi-cleroindicin D (**4**):

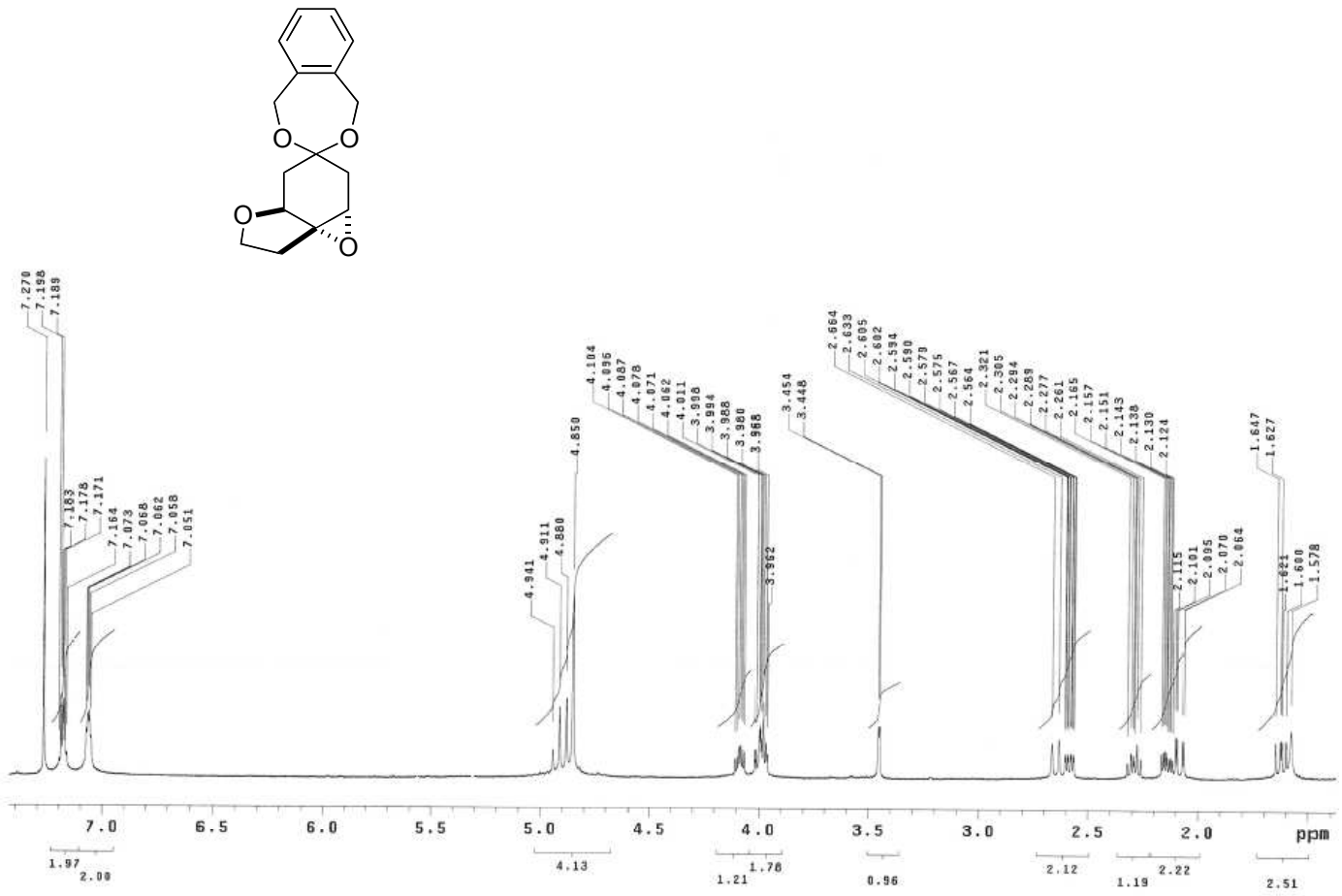
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2053.534	5.134	1623.8	40	905.884	2.265	20.3
2	1902.131	4.756	26.3	41	900.203	2.251	19.2
3	1897.524	4.744	28.3	42	898.053	2.245	19.5
4	1891.382	4.729	29.5	43	894.368	2.236	20.3
5	1886.929	4.718	28.4	44	892.371	2.231	19.0
6	1773.915	4.435	27.4	45	860.279	2.151	12.3
7	1769.462	4.424	49.9				
8	1765.162	4.413	31.5				
9	1754.721	4.387	15.3				
10	1640.632	4.102	10.7				
11	1632.340	4.081	27.9				
12	1630.344	4.076	29.1				
13	1623.894	4.060	40.4				
14	1618.213	4.046	26.9				
15	1615.449	4.039	18.7				
16	1612.992	4.033	26.7				
17	1609.768	4.025	19.0				
18	1607.311	4.019	24.9				
19	1604.700	4.012	16.7				
20	1598.865	3.998	14.7				
21	1448.845	3.623	10.5				
22	1215.292	3.039	22.5				
23	1210.839	3.027	24.5				
24	1197.326	2.994	37.0				
25	1192.566	2.982	105.1				
26	1188.113	2.971	83.0				
27	1133.295	2.834	15.1				
28	1127.613	2.819	33.7				
29	1124.696	2.812	20.6				
30	1122.239	2.806	21.1				
31	1119.936	2.800	24.0				
32	1116.865	2.793	36.6				
33	1113.947	2.785	22.8				
34	1109.648	2.774	35.3				
35	1100.435	2.751	21.4				
36	1098.899	2.748	27.0				
37	913.562	2.284	18.7				
38	911.565	2.279	18.3				
39	907.880	2.270	21.2				

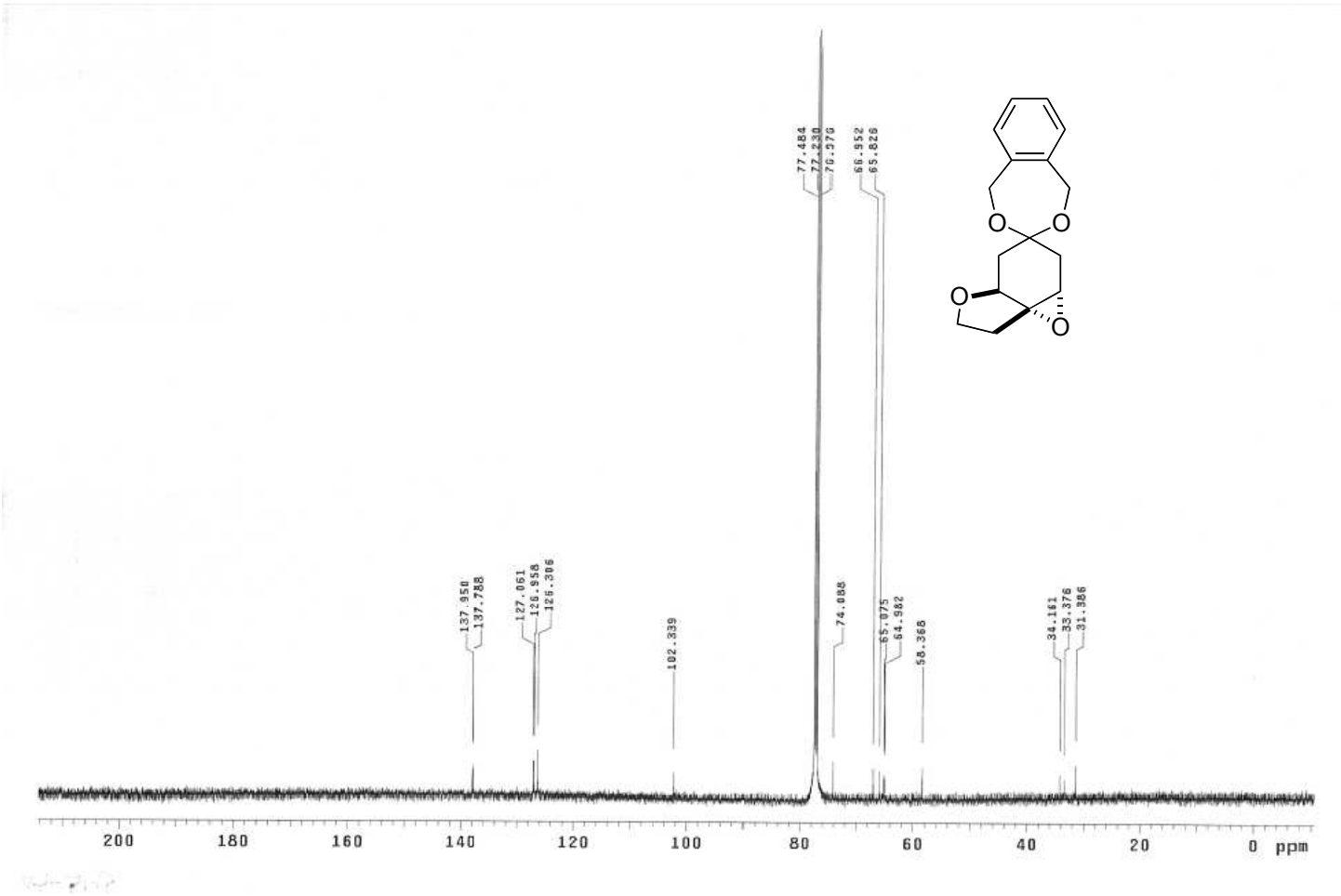





O
O
OH
OH
206.940
82.877
82.582
77.484
77.230
76.976
72.132
66.526
43.078
42.927
35.805
200
180
160
140
120
100
80
60
40
20
0 ppm

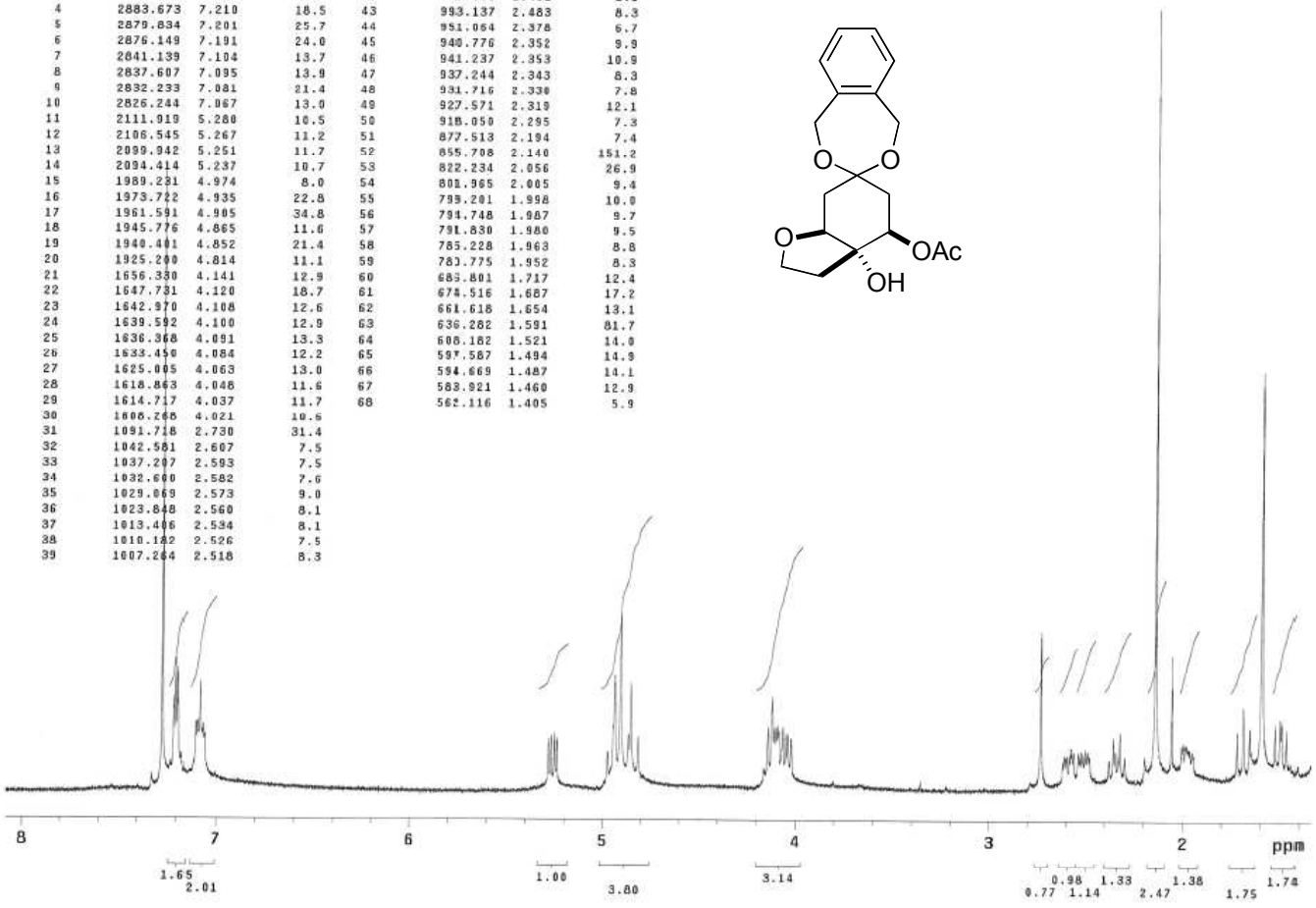
Compound **26**:


7.270
7.198
7.189
7.183
7.178
7.171
7.164
7.073
7.068
7.062
7.058
7.051
4.941
4.911
4.880
4.859
4.104
4.096
4.087
4.078
4.071
4.062
4.011
3.998
3.994
3.988
3.980
3.968
3.962
3.454
3.448
2.664
2.633
2.605
2.602
2.594
2.590
2.579
2.575
2.567
2.564
2.321
2.305
2.294
2.269
2.277
2.261
2.165
2.157
2.151
2.143
2.138
2.130
2.124
2.115
2.101
2.095
2.070
2.064
1.647
1.627
1.621
1.600
1.578
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
1.97
2.00
4.13
1.21
1.76
0.96
2.12
1.19
2.22
2.51


77.484
77.230
76.976
66.952
65.826
137.950
137.788
127.061
126.958
126.306
102.339
74.088
65.075
64.982
58.368
34.161
33.376
31.386
200
180
160
140
120
100
80
60
40
20
0 ppm

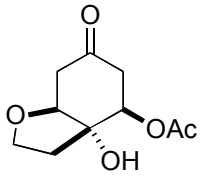
Acetate (crude):

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2908.702	7.273	45.0	40	1003.732	2.510	7.8
2	2907.627	7.270	119.2	41	999.433	2.499	8.8
3	2890.122	7.226	6.1	42	996.669	2.492	8.1
4	2883.673	7.210	18.5	43	993.137	2.483	8.3
5	2879.834	7.201	25.7	44	951.064	2.378	6.7
6	2876.149	7.191	24.0	45	940.776	2.352	9.9
7	2841.139	7.104	13.7	46	941.237	2.353	10.9
8	2837.607	7.095	13.9	47	937.244	2.343	8.3
9	2832.233	7.081	21.4	48	931.716	2.330	7.8
10	2826.244	7.067	13.0	49	927.571	2.319	12.1
11	2111.919	5.280	10.5	50	918.050	2.295	7.3
12	2106.545	5.267	11.2	51	877.513	2.194	7.4
13	2099.942	5.251	11.7	52	855.708	2.140	151.2
14	2094.414	5.237	10.7	53	822.234	2.056	26.9
15	1989.231	4.974	8.0	54	801.965	2.005	9.4
16	1973.722	4.935	22.8	55	799.201	1.998	10.0
17	1961.591	4.905	34.8	56	794.748	1.987	9.7
18	1945.776	4.865	11.6	57	791.830	1.980	9.5
19	1940.401	4.852	21.4	58	785.228	1.963	8.8
20	1925.200	4.814	11.1	59	780.775	1.952	8.3
21	1656.330	4.141	12.9	60	686.801	1.717	12.4
22	1647.731	4.120	18.7	61	674.516	1.687	17.2
23	1642.970	4.108	12.6	62	661.618	1.654	13.1
24	1639.592	4.100	12.9	63	636.282	1.591	81.7
25	1636.368	4.091	13.3	64	606.182	1.521	14.0
26	1633.450	4.084	12.2	65	597.587	1.494	14.9
27	1625.005	4.063	13.0	66	594.669	1.487	14.1
28	1618.863	4.048	11.6	67	583.921	1.460	12.9
29	1614.717	4.037	11.7	68	562.116	1.405	5.9
30	1606.266	4.021	10.6				
31	1091.718	2.730	31.4				
32	1042.581	2.607	7.5				
33	1037.207	2.593	7.5				
34	1032.600	2.582	7.6				
35	1029.069	2.573	9.0				
36	1023.848	2.560	8.1				
37	1013.406	2.534	8.1				
38	1010.182	2.526	7.5				
39	1007.264	2.518	8.3				

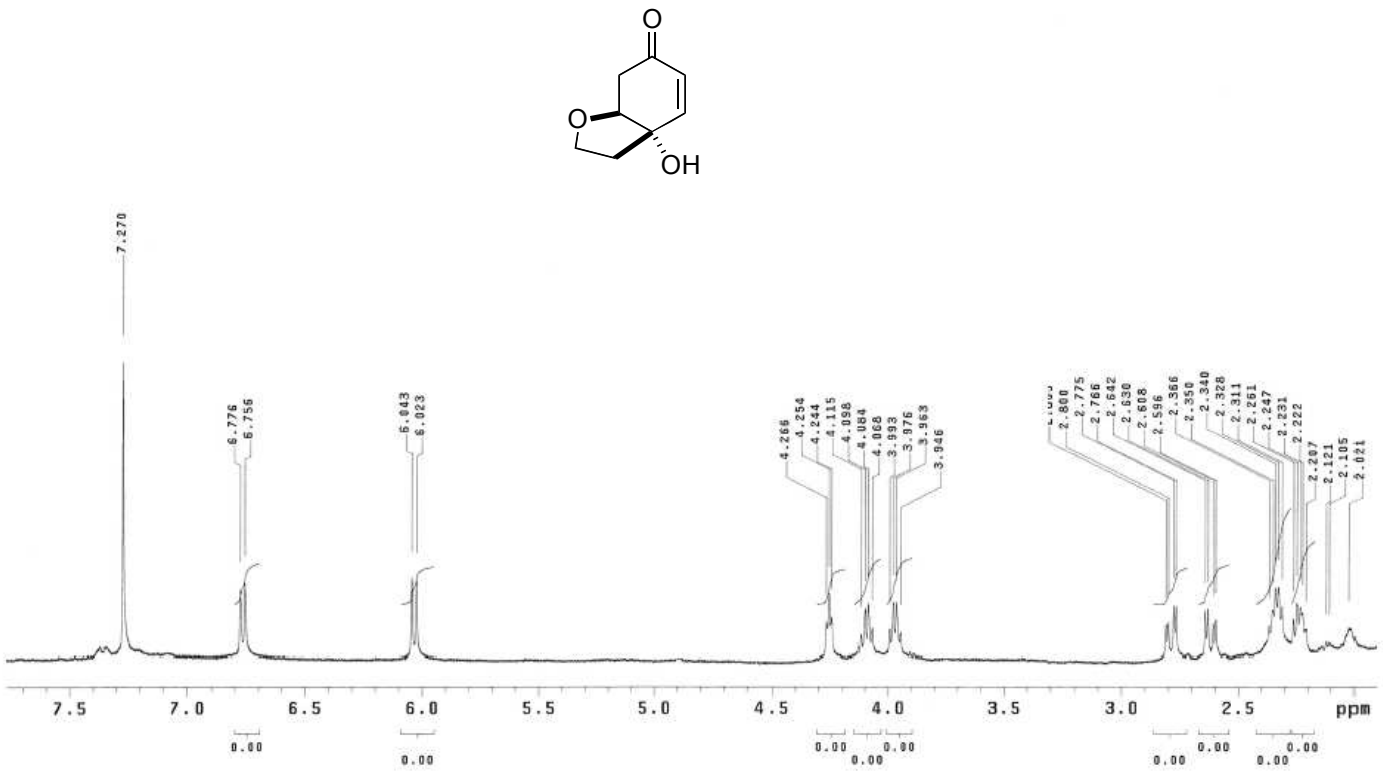


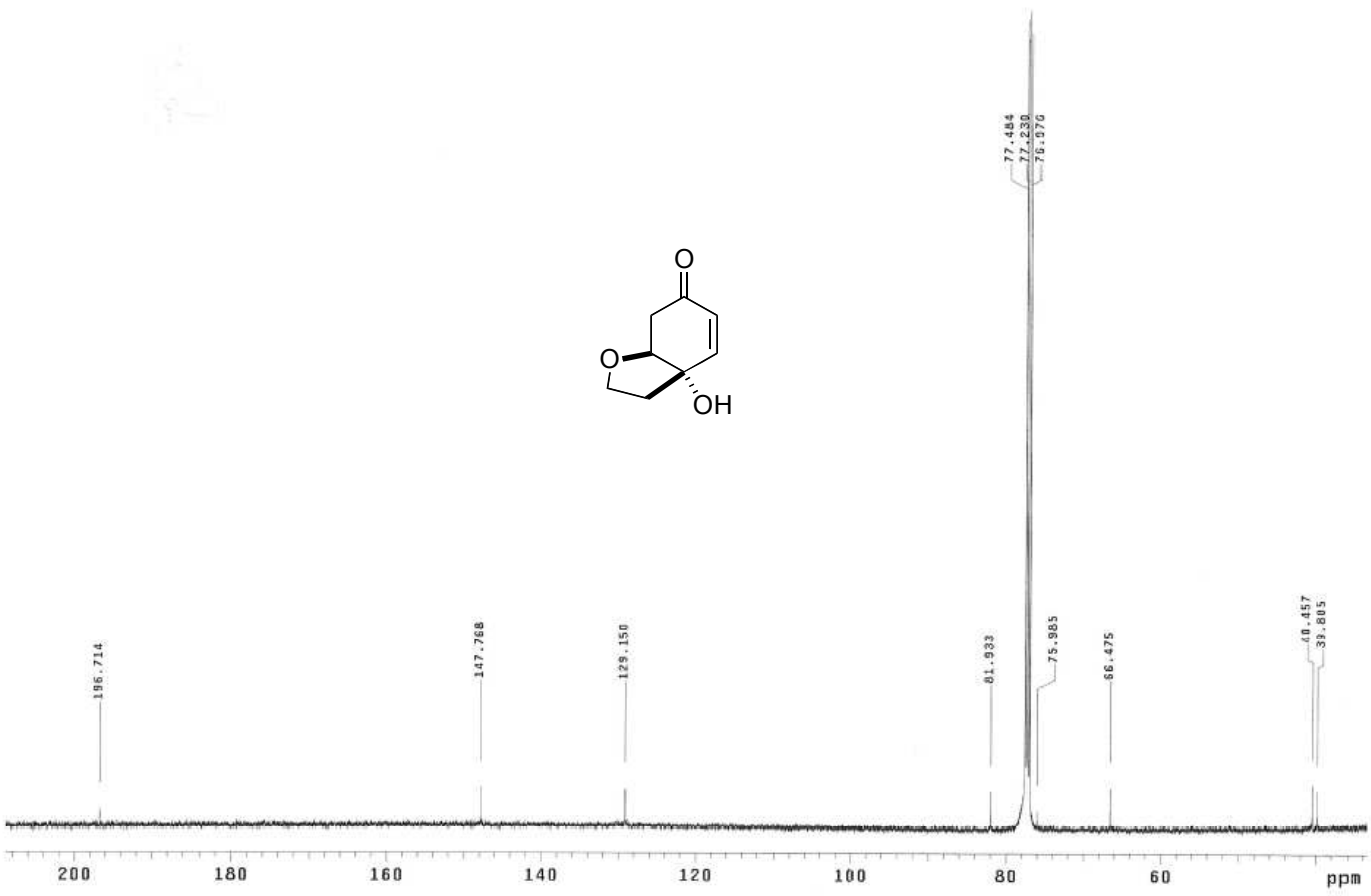
Compound **27** (crude):

INDEX	FREQUENCY	PPM	HEIGHT
1	2907.627	7.270	199.7
2	2786.321	6.967	26.7
3	2069.539	5.175	11.4
4	2064.318	5.161	10.8
5	2057.408	5.144	11.7
6	2051.880	5.130	10.2
7	1648.652	4.122	9.7
8	1640.514	4.102	11.8
9	1632.375	4.081	13.4
10	1622.241	4.056	12.6
11	1601.204	4.004	11.0
12	1591.684	3.980	10.3
13	1581.396	3.954	11.4
14	1575.100	3.938	10.3
15	1553.450	3.884	17.3
16	1291.029	3.228	93.1
17	1283.198	3.208	104.7
18	1098.781	2.747	6.9
19	1072.217	2.681	9.5
20	1054.865	2.638	9.0
21	987.917	2.470	6.9
22	967.955	2.420	11.4
23	954.903	2.388	12.4
24	917.590	2.294	17.5
25	903.924	2.260	54.7
26	870.449	2.176	33.1
27	849.873	2.125	93.2
28	778.932	1.948	15.1
29	647.798	1.620	12.2
30	617.241	1.543	17.3
31	604.650	1.512	21.7
32	591.905	1.480	17.9
33	575.322	1.438	22.1
34	554.285	1.386	133.6
35	536.780	1.342	28.1
36	523.728	1.309	35.4
37	513.133	1.283	48.8
38	503.306	1.258	108.6



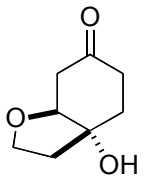
Cleroindicin F (**7**):

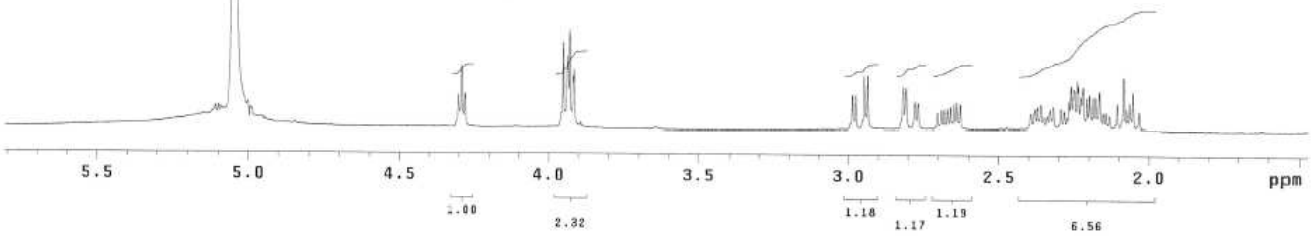



O
O
OH
77.484
77.230
76.976
196.714
147.768
129.150
81.933
75.985
66.475
40.457
39.805
200
180
160
140
120
100
80
60
ppm

Cleroindicin C (**3**):

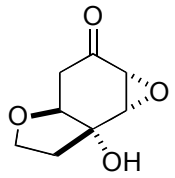
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2059.183	5.149	2.4	40	927.490	2.319	4.4
2	2043.676	5.110	3.9	41	917.465	2.294	3.9
3	2039.760	5.100	3.8	42	912.923	2.283	3.5
4	2036.784	5.093	3.7	43	909.007	2.273	2.3
5	2033.182	5.084	3.4	44	906.658	2.267	5.4
6	2018.771	5.048	408.5	45	903.995	2.260	8.3
7	2001.071	5.003	4.7	46	901.645	2.254	6.1
8	1997.625	4.995	3.6	47	899.766	2.250	7.5
9	1721.867	4.303	6.1	48	895.360	2.239	9.2
10	1716.621	4.292	11.8	49	894.127	2.236	8.1
11	1712.392	4.282	6.4	50	890.681	2.227	6.2
12	1580.504	3.952	16.3	51	888.801	2.222	7.2
13	1574.396	3.936	13.7	52	888.018	2.220	8.1
14	1572.203	3.931	18.7	53	882.692	2.207	6.0
15	1567.190	3.918	9.7	54	879.403	2.199	6.6
16	1565.937	3.915	11.0	55	874.861	2.187	6.2
17	1194.554	2.987	6.4	56	871.258	2.178	6.1
18	1190.012	2.975	6.4	57	866.402	2.166	7.2
19	1178.690	2.948	10.2	58	861.390	2.154	3.2
20	1174.191	2.936	10.0	59	857.474	2.144	3.3
21	1126.731	2.817	7.9	60	852.775	2.132	2.6
22	1122.502	2.807	7.7	61	842.437	2.106	5.0
23	1110.911	2.778	5.2	62	834.135	2.086	9.9
24	1106.838	2.767	4.9	63	829.986	2.075	3.9
25	1081.150	2.703	3.2	64	825.677	2.064	5.1
26	1076.294	2.691	3.6	65	821.448	2.054	7.0
27	1072.535	2.682	3.7	66	813.146	2.033	3.4
28	1067.992	2.670	3.9				
29	1064.233	2.661	4.3				
30	1059.377	2.649	4.8				
31	1055.775	2.640	5.0				
32	1051.232	2.628	4.7				
33	957.251	2.393	3.0				
34	952.552	2.382	3.8				
35	948.793	2.372	4.2				
36	944.094	2.361	4.8				
37	940.334	2.351	2.3				
38	935.792	2.340	2.5				
39	931.876	2.330	3.8				

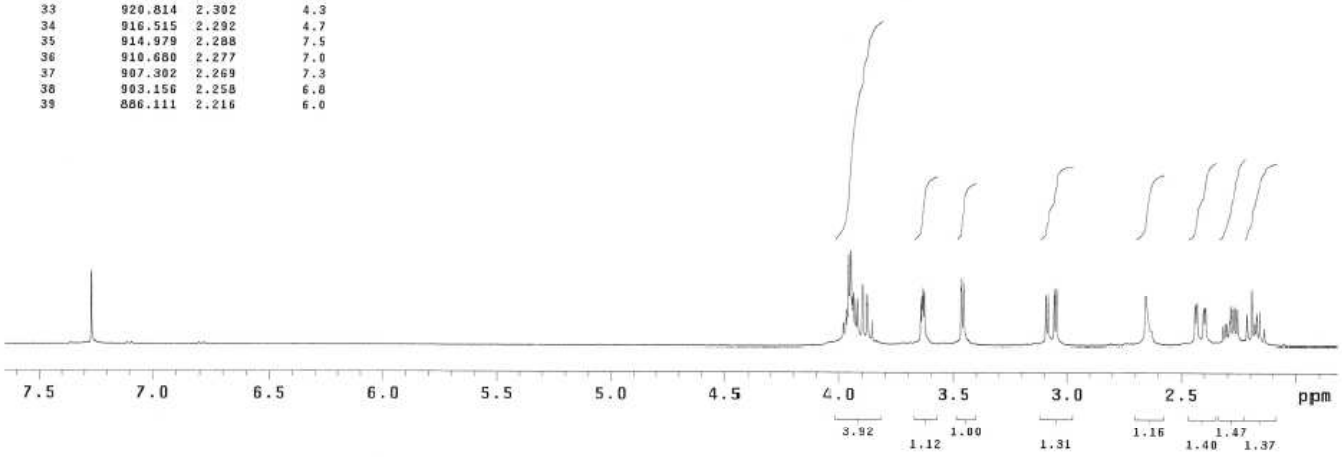




Epoxide **30**:

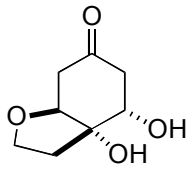
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2987.627	7.270	13.8	40	877.820	2.195	10.8
2	1592.298	3.981	4.2	41	872.752	2.182	4.2
3	1588.152	3.971	5.3	42	869.374	2.174	6.1
4	1586.003	3.966	6.8	43	864.307	2.161	6.4
5	1583.239	3.959	17.1	44	855.862	2.140	3.3
6	1579.400	3.949	17.8				
7	1576.943	3.943	9.1				
8	1574.947	3.938	10.1				
9	1570.801	3.928	8.6				
10	1567.423	3.919	8.8				
11	1558.824	3.898	11.7				
12	1551.146	3.878	9.8				
13	1542.240	3.856	4.6				
14	1457.326	3.644	8.8				
15	1455.023	3.638	9.5				
16	1453.180	3.633	11.0				
17	1451.030	3.628	10.5				
18	1386.845	3.466	10.9				
19	1386.078	3.466	12.6				
20	1382.699	3.457	10.5				
21	1381.932	3.455	11.8				
22	1237.746	3.095	9.5				
23	1233.907	3.085	9.9				
24	1222.852	3.058	10.8				
25	1219.013	3.048	10.8				
26	1062.236	2.656	9.3				
27	976.093	2.441	7.7				
28	973.176	2.433	8.1				
29	961.352	2.404	7.0				
30	958.281	2.396	7.2				
31	928.338	2.321	3.8				
32	924.039	2.310	4.1				
33	920.814	2.302	4.3				
34	916.515	2.292	4.7				
35	914.979	2.288	7.5				
36	910.680	2.277	7.0				
37	907.302	2.269	7.3				
38	903.156	2.258	6.8				
39	886.111	2.216	6.0				

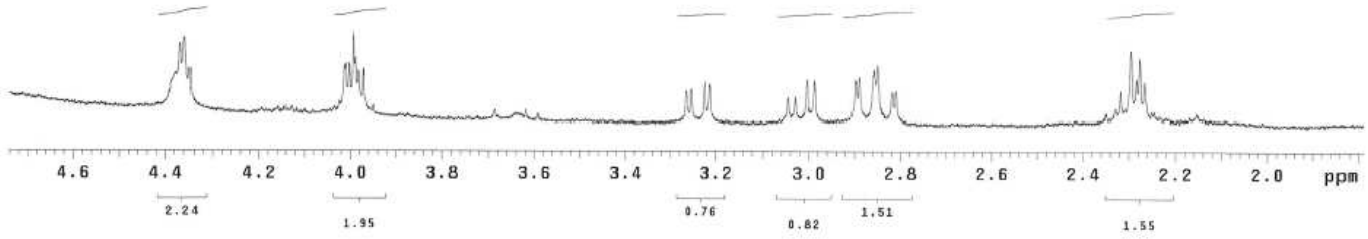




Cleroindicin D (**5**):

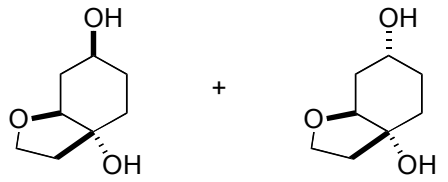
INDEX	FREQUENCY	PPM	HEIGHT
1	1895.221	4.739	5.8
2	1747.504	4.369	14.9
3	1743.665	4.360	15.9
4	1739.519	4.349	10.2
5	1657.215	4.144	3.9
6	1605.315	4.014	11.0
7	1604.086	4.011	11.2
8	1601.015	4.003	11.3
9	1597.176	3.993	16.9
10	1595.487	3.989	12.3
11	1592.877	3.983	9.9
12	1588.424	3.972	10.2
13	1306.041	3.266	6.3
14	1301.435	3.254	6.6
15	1289.611	3.224	8.1
16	1285.158	3.213	7.5
17	1218.056	3.046	5.1
18	1211.453	3.029	5.1
19	1201.472	3.004	8.3
20	1195.023	2.988	8.3
21	1158.785	2.897	8.2
22	1155.560	2.889	8.9
23	1142.969	2.858	10.2
24	1139.744	2.850	11.1
25	1127.306	2.819	6.0
26	1123.928	2.810	6.2
27	927.074	2.318	6.4
28	918.168	2.296	13.9
29	913.255	2.283	8.5
30	910.644	2.277	12.4
31	906.345	2.266	7.9



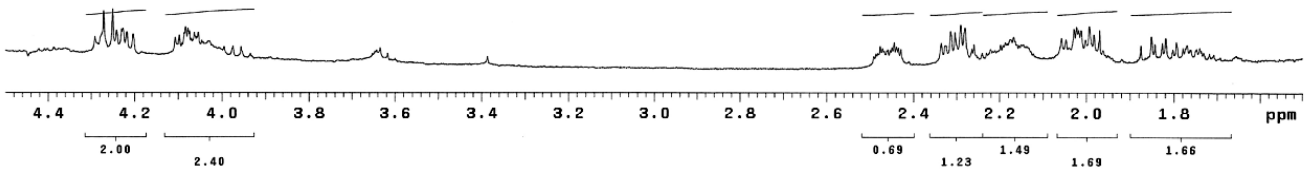


Compound **8/6** = 10/1

INDEX	FREQUENCY	PPM	HEIGHT
1	1716.464	4.292	5.9
2	1708.476	4.272	10.8
3	1700.174	4.251	11.1
4	1696.415	4.242	7.1
5	1690.619	4.227	7.4
6	1687.017	4.218	6.8
7	1681.221	4.204	6.3
8	1642.845	4.108	5.8
9	1639.086	4.098	6.2
10	1633.447	4.084	7.7
11	1631.098	4.078	7.5
12	1625.459	4.064	6.7
13	1621.700	4.055	6.7
14	977.770	2.445	4.8
15	934.069	2.335	4.6
16	925.454	2.314	6.9
17	921.381	2.304	6.7
18	916.056	2.290	8.1
19	912.140	2.281	7.6
20	903.838	2.260	4.4
21	867.029	2.168	5.8
22	822.701	2.057	5.5
23	818.472	2.046	5.3
24	811.110	2.028	7.4
25	808.917	2.023	7.8
26	807.037	2.018	7.1
27	804.688	2.012	7.1
28	800.772	2.002	5.2
29	797.169	1.993	7.9
30	792.940	1.983	6.3
31	787.771	1.970	7.1
32	740.467	1.851	5.9
33	737.178	1.843	4.5
34	730.756	1.827	4.7
35	727.623	1.819	5.6
36	717.755	1.795	4.9

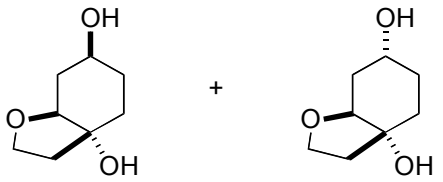


8 10:1 **6**

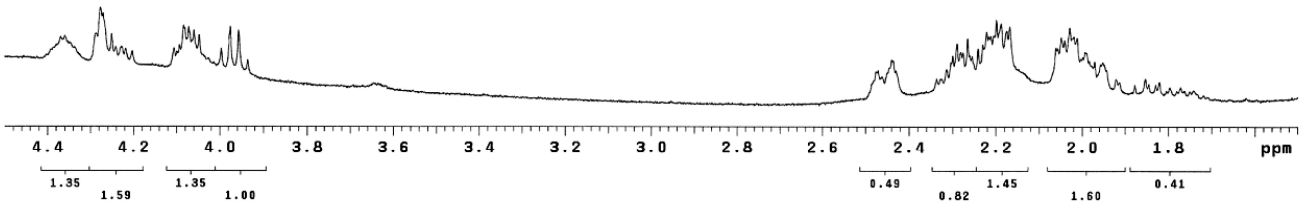


Compound **6**/**8** = 2/1:

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	1743.875	4.360	12.7	40	807.664	2.019	12.5
2	1710.669	4.277	18.3	41	804.688	2.012	12.3
3	1700.331	4.251	13.0	42	797.326	1.994	9.6
4	1696.728	4.242	10.5	43	788.241	1.971	7.7
5	1691.089	4.228	10.6	44	780.879	1.952	7.6
6	1687.330	4.219	10.2				
7	1681.065	4.203	9.7				
8	1642.219	4.106	10.3				
9	1637.363	4.094	10.9				
10	1633.291	4.084	14.6				
11	1628.592	4.072	14.4				
12	1623.736	4.060	13.8				
13	1619.037	4.048	12.8				
14	1598.674	3.997	10.2				
15	1590.372	3.976	14.4				
16	1582.854	3.958	13.8				
17	1574.396	3.936	8.1				
18	988.265	2.471	6.0				
19	975.891	2.440	8.1				
20	930.153	2.326	4.4				
21	925.611	2.314	6.2				
22	919.815	2.300	8.8				
23	915.899	2.290	11.2				
24	912.453	2.281	9.5				
25	910.260	2.276	9.4				
26	906.031	2.265	12.2				
27	901.802	2.255	8.8				
28	896.320	2.241	10.3				
29	892.090	2.231	11.0				
30	888.488	2.222	13.5				
31	884.415	2.211	12.6				
32	879.246	2.198	15.8				
33	875.017	2.188	15.0				
34	869.692	2.175	13.6				
35	867.185	2.168	14.5				
36	824.424	2.061	10.4				
37	819.568	2.049	12.4				
38	816.435	2.041	11.8				
39	811.266	2.028	14.3				



8 1:2 **6**



V. References

(i) (a) Tian, J.; Zhao, Q.-S; Zhang, H.-J.; Lin, Z.W.; Sun, H.-D. *J. Nat. Prod.* **1997**, *60*, 766-769. (b) Hase,T.; Kawamoto, Y.; Kasai, R.; Yamasaki, K.; Picheansoonthon, C. *Phytochemistry* **1995,** *39*, 235-241.

(ii) Barradas, S.; Carreño, González-López, M.; Latorre, A.; Urbano, A. *Org. Lett.* **2007**, *9*, 5019-5022.