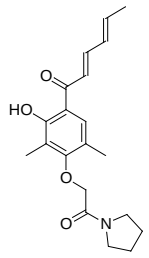
Supporting Information: Pettus, T. R. R. *et al*

Selected physical properties and spectra of compounds **9**, **12**, **13**, **14**, **16** and **17** and synthetic **1** and **2** are provided.

General information: The following section provides general information. Immediately following this information are general and/or specific reaction conditions and spectral data for compounds along with a representative ^{1}H NMR spectrum.

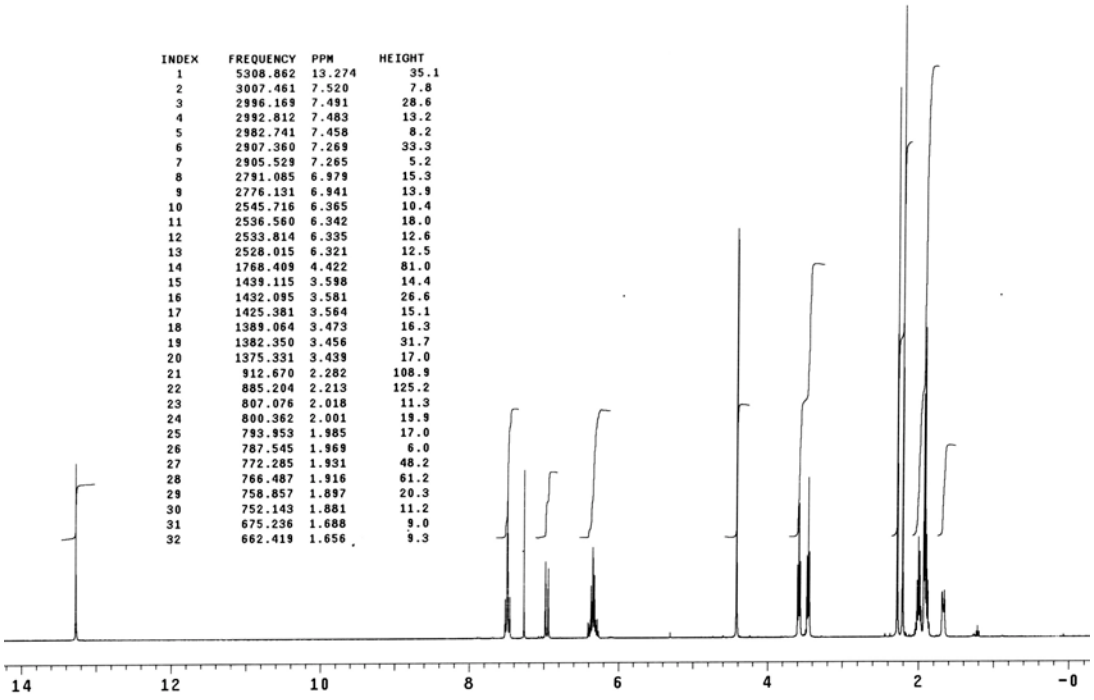
Reactions were monitored by analytical thin-layer chromatography on EM-Science hard layer silica gel-60$^{F\text{-}250}$ plates cut into 1x2.5^{cm} sections. Visualization was effected by ultraviolet light (254 nm), followed by dipping the plate into the appropriate stain and charring on a *Fisher*® micro-hot plate. The primary stain was made with [25 g of phosphoromolybdic acid and 10 g of cerium sulfate and 60 mL H_2SO_4 and 940 mL of H_2O]. Distillations were accomplished with a short-path condenser configured with multiple receiving flasks. A specific low pressure (760-1 mm Hg) was obtained and monitored with a *Buchi*®-vacuum controller model number B-721 in combination with a *Welch*® direct drive pump model number 8915A. Lower pressures were achieved using a vacuum manifold connected to an oil-diffusion pump and backed by a *Welch*® direct drive vacuum pump model number 8910A. Chromatography was performed following the method prescribed by W. C. Still.[1] In reactions, where water was <u>*not*</u> present as a 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 septa seal during the course of the reaction. The nitrogen stream originated from a high pressure 55 L *(l)* N_2 tank and was further dried by passing through a Drierite® tube. Reagents were purified according to the procedures describe in the *Perrin & Perrin* laboratory manual. All reactions were stirred with Teflon-coated magnetic stir bars via *Thomas*® magnetic stirrers. Removal of solvents was normally accomplished using a *Buchi*® rotary evaporator model number R-114 connected to a KNF®-vacuum pump model number UN820-3. The condenser was cooled to 0 °C by a Fisher® circulator bath model number 1013S. Trace solvents were removed by a *Labconco*® freeze dryer system at a pressure of approximately 0.01 mm Hg. The following solvents were distilled before use, under a slight positive pressure of nitrogen. Diethyl ether was distilled from sodium benzophenone ketyl. Methylene chloride, di-*n*-butyl ether and acetone were distilled from calcium hydride. The chloroform, isopropyl alcohol and hexanes used for infrared spectra and HPLC analyses. Acetonitrile was distilled over CaH_2 for circular dichroism spectra. Melting points were determined on a *Fisher-Johns*® melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded at 400 MHz or 500 MHz on a *Varian*® spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance of $CDCl_3$ (7.27 ppm) as the internal standard. Chemical ^{13}C NMR spectra were recorded at (100 MHz) with a solvent resonance of $CDCl_3$ (77.23 ppm) as the internal standard. Infrared spectra were recorded on a *Shimadzu*® FT infrared spectrometer with 2 cm resolution in a solution cell (CH_2Cl_2). Infrared frequencies are reported in reciprocal centimeters (cm^{-1}). HPLC analyses for *enantiomeric excess* were performed isochratically using a *Shimadzu*® system (a 10 mL/min pump and dual channel UV detector) with a Chiracel columns. Non-enantiomeric separations of materials by HPLC used 5 μ 25 cm long spherisorb columns supplied by *Jones*® Chromatography. Circular dichroism spectra were recorded on an Aviv CD spectrophotometer model 202 at 25 °C. Optical rotations were recorded on a Perkin Elmer Polarimeter model 341 at 25 °C. Mass spectra were recorded on a VG-7035 mass spectrometer at an ionizing voltage of either 70 or 20 eV.

[1] Still, W. C.; Kahn, K.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2924.

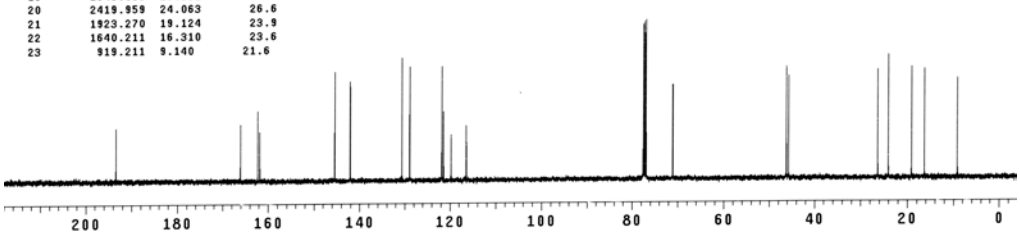


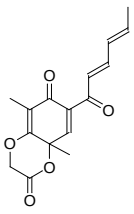
Amide 12: yellow oil Rf=0.44 CH_2Cl_2/acetone (12/1); ^{1}H NMR ($CDCl_3$,400 MHz) δ 13.3 (s, OH), 7.50 (m, 2H), 6.96 (d, 1H, J = 15.1 Hz), 6.35 (m, 2H), 4.43 (s, 2H), 3.59 (t, 2H, J = 7.1 Hz), 3.46 (t, 2H, J = 7.1 Hz), 2.29 (s, 3H), 2.22 (s, 3H), 2.01 (m, 2H), 1.92 (d, 3H, J = 6.2 Hz), 1.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 193.4, 166.1, 162.3, 161.8, 145.5, 142.1, 130.7, 128.9, 121.8, 121.5, 119.8, 116.5, 71.1, 46.3, 45.8, 26.4, 24.1, 19.2, 16.3, 9.2; IR ($CHCl_3$, λ-max cm^{-1}) 3688, 3009, 1644, 1500, 1361, 768; HRMS(EI) calcd for $C_{20}H_{25}NO_4$ 343.1784, found: 343.1783.

INDEX	FREQUENCY	PPM	HEIGHT
1	5308.862	13.274	35.1
2	3007.461	7.520	7.8
3	2996.169	7.491	28.6
4	2992.812	7.483	13.2
5	2982.741	7.458	8.2
6	2907.360	7.269	33.3
7	2905.529	7.265	5.2
8	2791.085	6.979	15.3
9	2776.131	6.941	13.9
10	2545.716	6.365	10.4
11	2536.560	6.342	18.0
12	2533.814	6.335	12.6
13	2528.015	6.321	12.5
14	1768.409	4.422	81.0
15	1439.115	3.598	14.4
16	1432.095	3.581	26.6
17	1425.381	3.564	15.1
18	1389.064	3.473	16.3
19	1382.350	3.456	31.7
20	1375.331	3.439	17.0
21	912.670	2.282	108.9
22	885.204	2.213	125.2
23	807.076	2.018	11.3
24	800.362	2.001	19.9
25	793.953	1.985	17.0
26	787.545	1.969	6.0
27	772.285	1.931	48.2
28	766.487	1.916	61.2
29	758.857	1.897	20.3
30	752.143	1.881	11.2
31	675.236	1.688	9.0
32	662.419	1.656	9.3

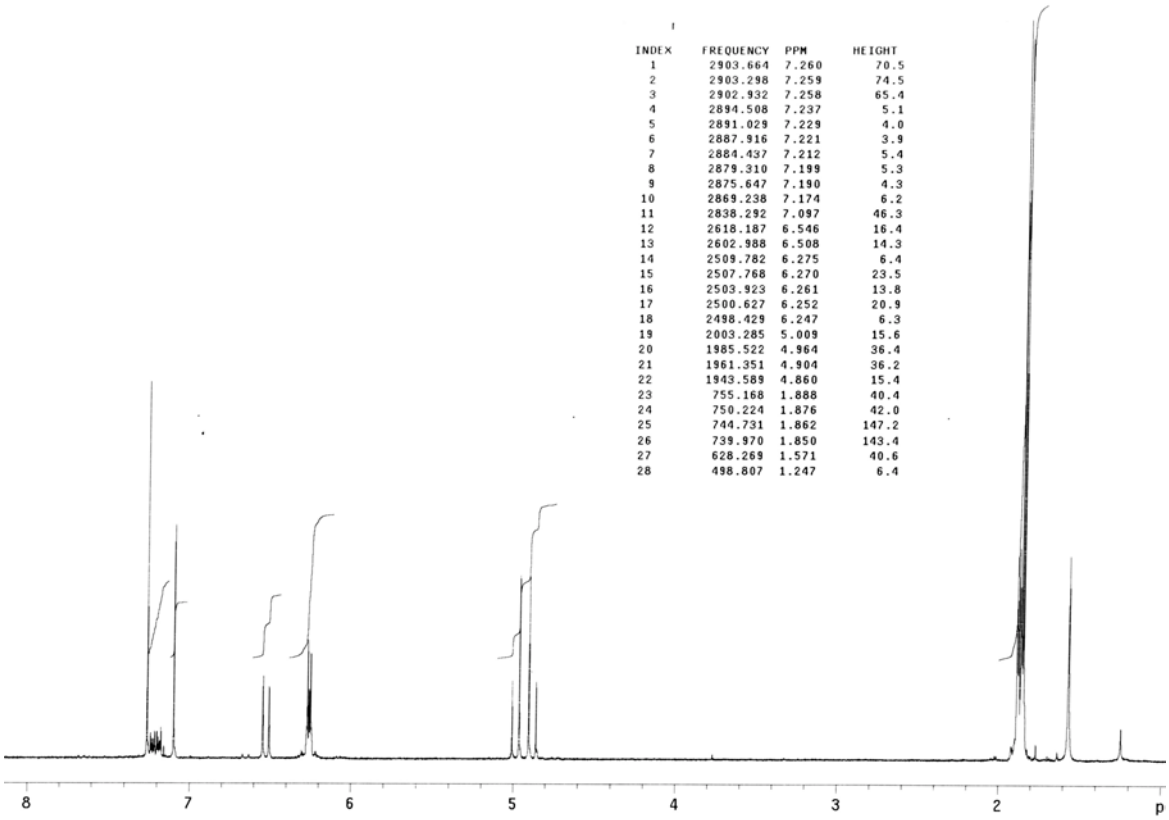


INDEX	FREQUENCY	PPM	HEIGHT
1	19447.761	193.381	11.6
2	16701.095	166.069	12.3
3	16317.325	162.253	15.1
4	16270.784	161.790	10.7
5	14624.311	145.418	23.5
6	14286.318	142.057	21.4
7	13137.296	130.632	26.4
8	12962.578	128.895	24.6
9	12249.971	121.809	24.5
10	12210.297	121.414	14.9
11	12043.208	119.753	9.9
12	11709.030	116.430	11.9
13	7798.846	77.549	33.4
14	7766.802	77.230	33.9
15	7734.757	76.911	34.3
16	7148.039	71.077	20.4
17	4647.810	46.216	24.2
18	4599.743	45.738	22.2
19	2648.085	26.332	23.5
20	2419.959	24.063	26.6
21	1923.270	19.124	23.9
22	1640.211	16.310	23.6
23	919.211	9.140	21.6

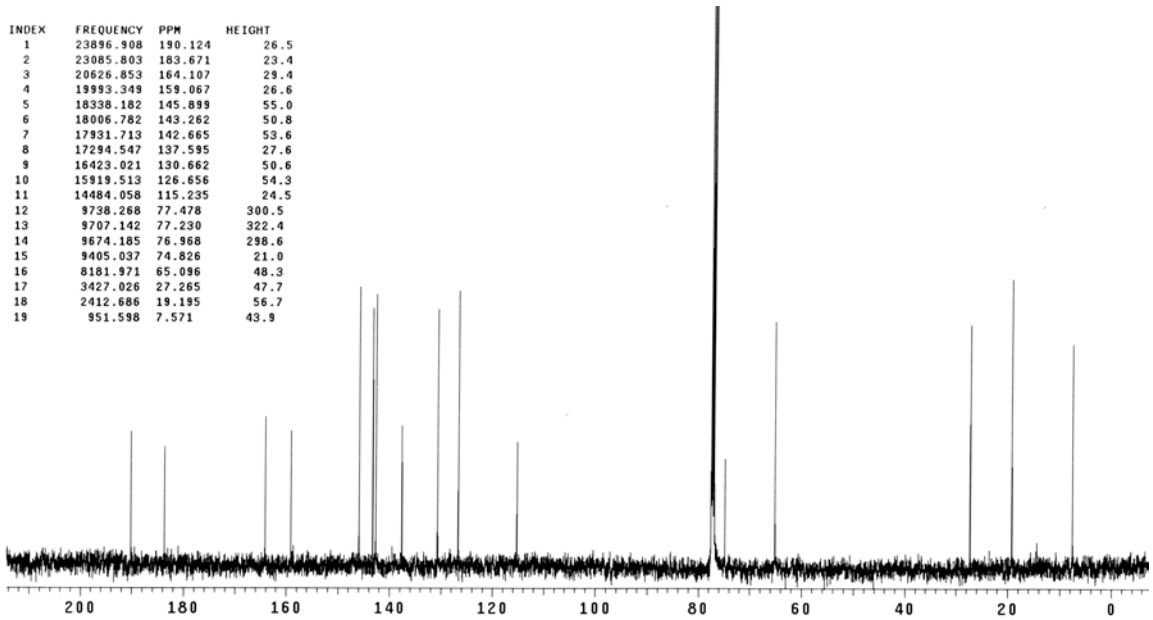




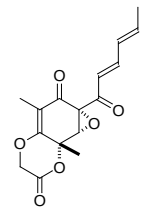
Dienone 9: pale yellow oil Rf=0.32 Hexanes/EtOAc (2/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (m, 1H), 7.09 (s, 1H), 6.52 (d, 1H, J = 15.2 Hz),6.25 (m, 2H), 4.92 (AB, 2H, J = 17.8 Hz), 1.88 (d, 3H, J = 5.2 Hz), 1.86 (s, 3H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 190.1, 183.7, 164.1, 159.1, 145.9, 143.3, 142.7, 137.6, 130.7, 126.7, 115.2, 74.8, 65.1, 27.3, 19.2, 7.8; IR ($CHCl_3$, λ-max cm^{-1}) 3022, 1769, 1621, 1293, 1190; HRMS(CI) calcd for $(M+H)^+$ $C_{16}H_{17}O_5$ 289.0998, found: 289.1070.



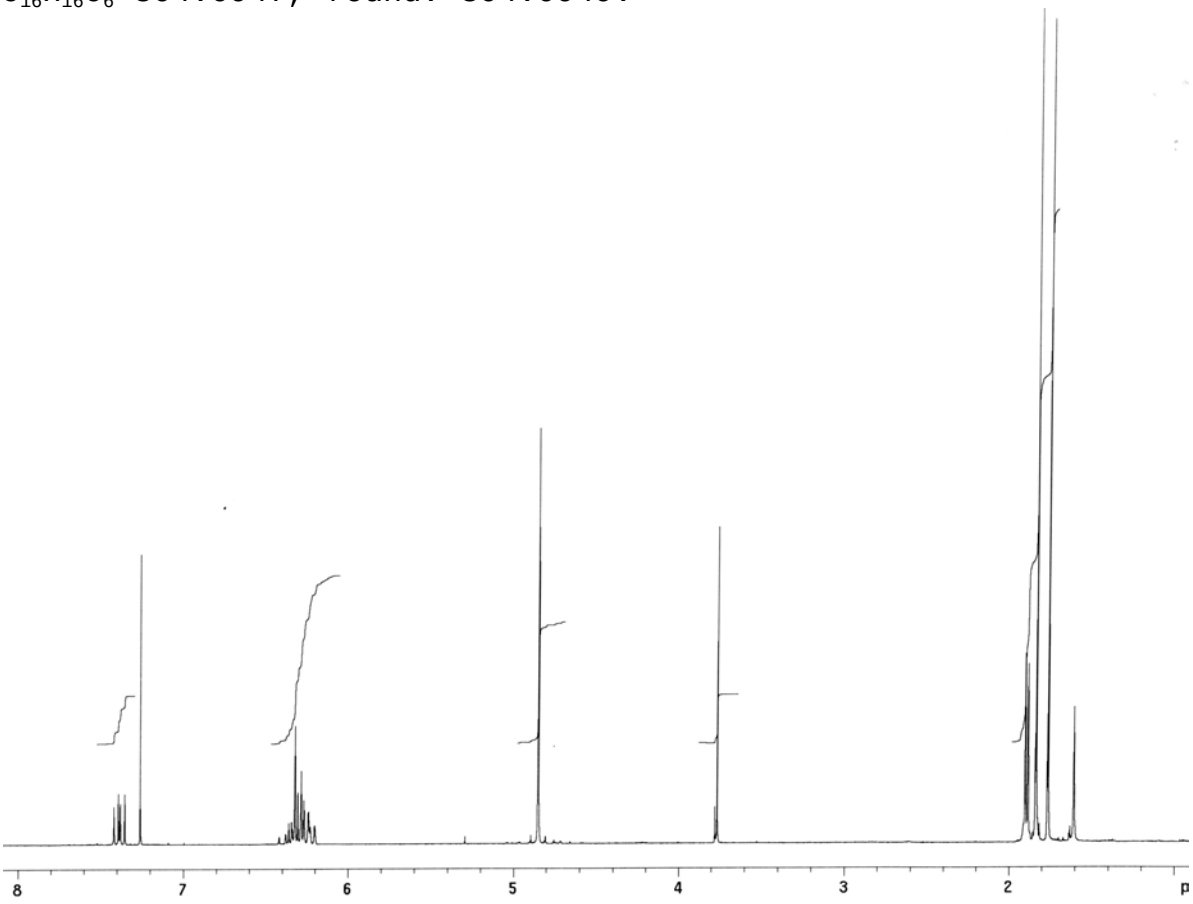
INDEX	FREQUENCY	PPM	HEIGHT
1	2903.664	7.260	70.5
2	2903.298	7.259	74.5
3	2902.932	7.258	65.4
4	2894.508	7.237	5.1
5	2891.029	7.229	4.0
6	2887.916	7.221	3.9
7	2884.437	7.212	5.4
8	2879.310	7.199	5.3
9	2875.647	7.190	4.3
10	2869.238	7.174	6.2
11	2838.292	7.097	46.3
12	2618.187	6.546	16.4
13	2602.988	6.508	14.3
14	2509.782	6.275	6.4
15	2507.768	6.270	23.5
16	2503.923	6.261	13.8
17	2500.627	6.252	20.9
18	2498.429	6.247	6.3
19	2003.285	5.009	15.6
20	1985.522	4.964	36.4
21	1961.351	4.904	36.2
22	1943.589	4.860	15.4
23	755.168	1.888	40.4
24	750.224	1.876	42.0
25	744.731	1.862	147.2
26	739.970	1.850	143.4
27	628.269	1.571	40.6
28	498.807	1.247	6.4



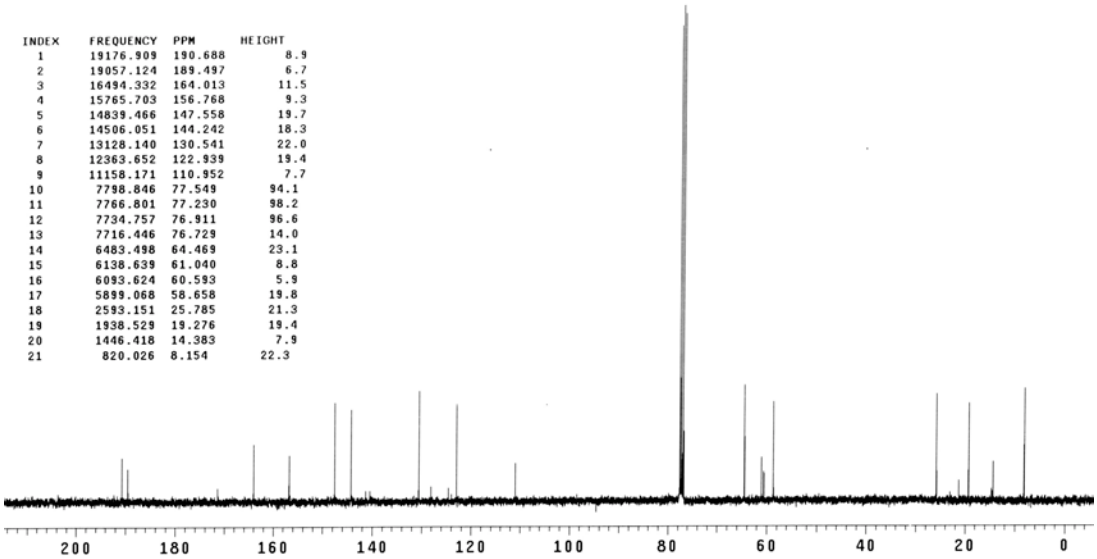
INDEX	FREQUENCY	PPM	HEIGHT
1	23896.908	190.124	26.5
2	23085.803	183.671	23.4
3	20626.853	164.107	29.4
4	19993.349	159.067	26.6
5	18338.182	145.899	55.0
6	18006.782	143.262	50.8
7	17931.713	142.665	53.6
8	17294.547	137.595	27.6
9	16423.021	130.662	50.6
10	15919.513	126.656	54.3
11	14484.058	115.235	24.5
12	9738.268	77.478	300.5
13	9707.142	77.230	322.4
14	9674.185	76.968	298.6
15	9405.037	74.826	21.0
16	8181.971	65.096	48.3
17	3427.026	27.265	47.7
18	2412.686	19.195	56.7
19	951.598	7.571	43.9

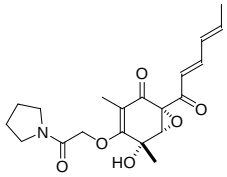


Epoxide 13: pale yellow oil Rf=0.24 Hexanes/EtOAc (2/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (dd, 1H, J1 = 15.6 Hz, J2 = 10.7 Hz), 6.40-6.24 (m, 3H), 4.85 (s, 2H), 3.76 (s, 1H), 1.89 (d, 3H, J = 6.77 Hz), 1.83 (s, 3H), 1.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 190.7, 189.5, 164.0, 156.8, 147.5, 144.2, 130.5, 122.9, 110.9, 70.7, 64.5, 61.0, 58.6, 25.8, 19.3, 8.2; IR ($CHCl_3$, λ-max cm^{-1}) 3022, 1775, 1687, 1645, 1593, 1292; HRMS(EI) calcd for $C_{16}H_{16}O_6$ 304.0947, found: 304.0949.

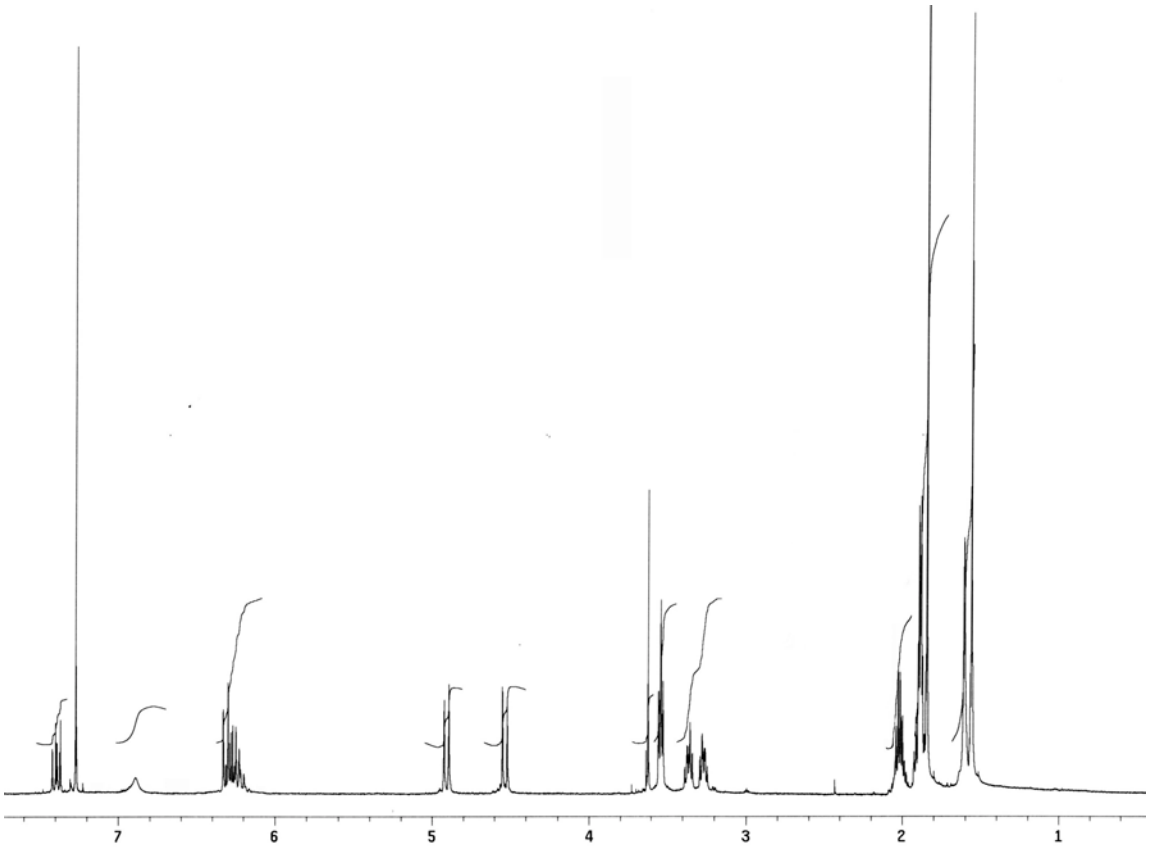


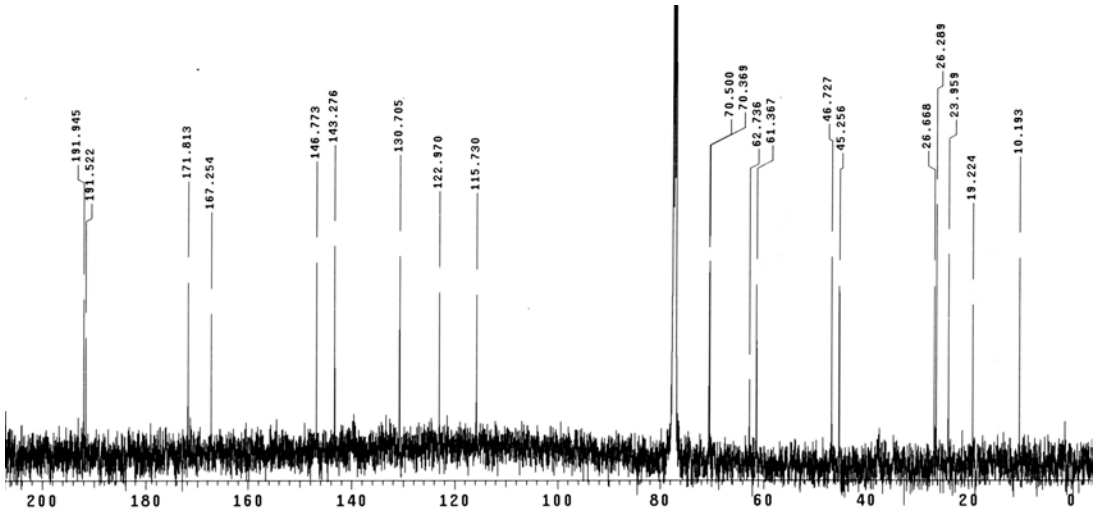
INDEX	FREQUENCY	PPM	HEIGHT
1	19176.909	190.688	8.9
2	19057.124	189.497	6.7
3	16494.332	164.013	11.5
4	15765.703	156.768	9.3
5	14839.466	147.558	19.7
6	14506.051	144.242	18.3
7	13128.140	130.541	22.0
8	12363.652	122.939	19.4
9	11158.171	110.952	7.7
10	7798.846	77.549	94.1
11	7766.801	77.230	98.2
12	7734.757	76.911	96.6
13	7716.446	76.729	14.0
14	6483.498	64.469	23.1
15	6138.639	61.040	8.8
16	6093.624	60.593	5.9
17	5899.068	58.658	19.8
18	2593.151	25.785	21.3
19	1938.529	19.276	19.4
20	1446.418	14.383	7.9
21	820.026	8.154	22.3

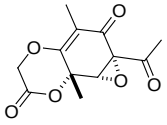




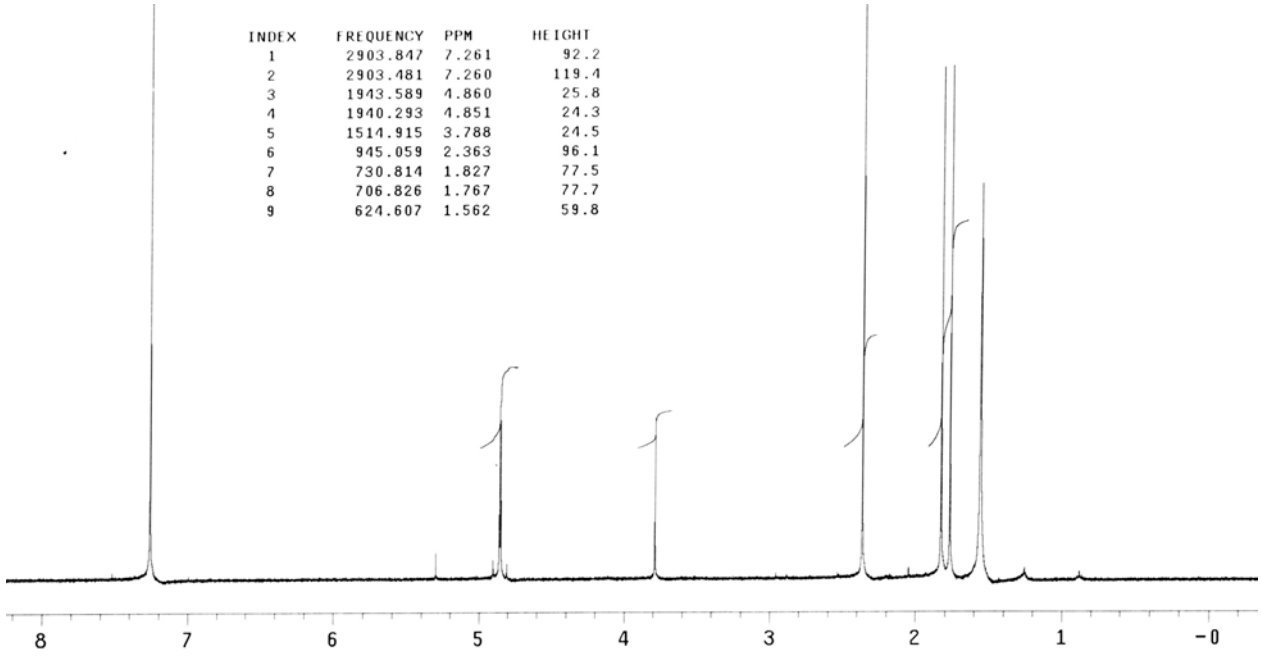
Amide 14: pale yellow oil Rf=0.50 EtOAc (100%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (m, 1H), 6.90 (br s, OH), 6.31 (d, 1H, J = 15.0 Hz), 6.31-6.20 (m, 2H), 4.91 (d, 1H, J = 15.0 Hz), 4.52 (d, 1H, J = 15.0 Hz), 3.62 (s, 1H), 3.54 (t, 2H, J = 7.0 Hz), 3.35 (m, 1H), 3.27 (m, 1H), 2.05 (m, 2H), 1.89-1.85 (m, 2H), 1.88 (d, 3H, J = 6.2 Hz), 1.84 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 191.9, 191.5, 171.8, 167.3, 146.8, 143.3, 130.7, 123.0, 115.7, 70.5, 70.4, 62.7, 61.4, 46.7, 45.3, 26.7, 26.3, 24.0, 19.2, 10.2; IR ($CHCl_3$, λ-max cm^{-1}) 3280, 3020, 1645, 1217; HRMS(EI) calcd for $C_{20}H_{25}NO_6$ 375.1682, found: 375.1692.



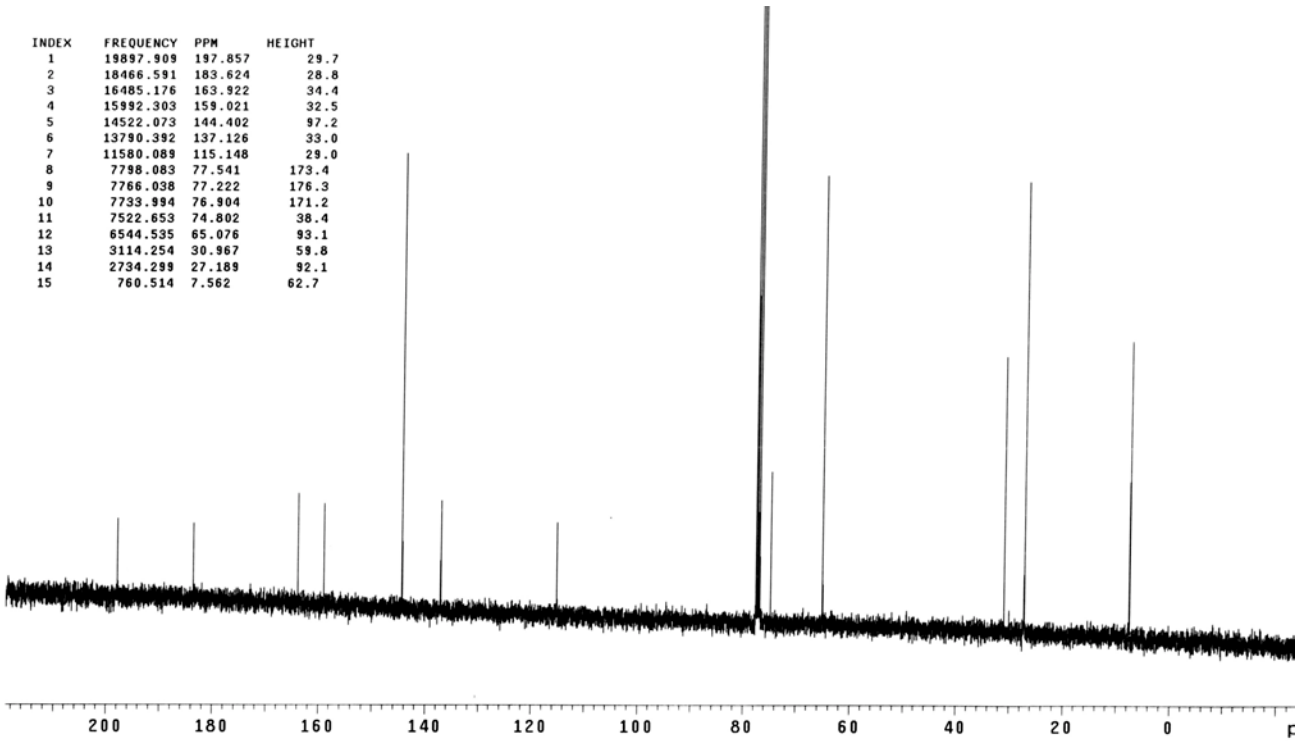




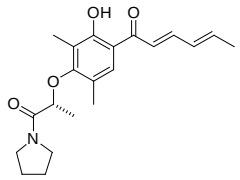
epoxide 16 colorless solid: m.p. 165-167 °C; Rf=0.47 Hexanes/EtOAc (1/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.85 (s, 2H), 3.79(s, 1H), 2.34 (s, 3H), 1.81 (d, 3H, J = 5.2 Hz), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.0, 189.2, 163.9, 157.0, 110.8, 76.6, 64.5, 61.2, 58.6, 28.2, 25.7, 8.1; IR ($CHCl_3$, λ-max cm^{-1}) 3022, 1776, 1730, 1642, 1294; HRMS(EI) calcd for $C_{12}H_{12}O_6$ 252.0634, found: 252.0636.



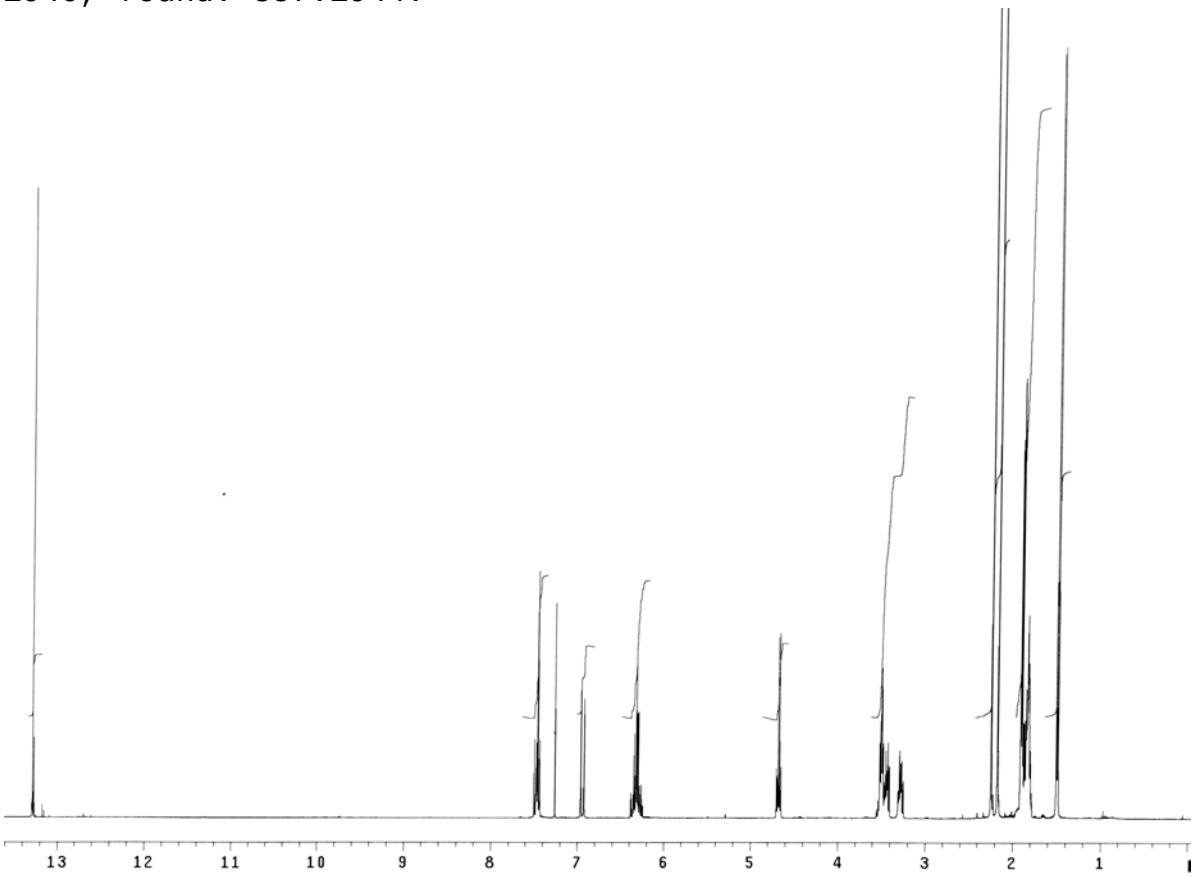
INDEX	FREQUENCY	PPM	HEIGHT
1	2903.847	7.261	92.2
2	2903.481	7.260	119.4
3	1943.589	4.860	25.8
4	1940.293	4.851	24.3
5	1514.915	3.788	24.5
6	945.059	2.363	96.1
7	730.814	1.827	77.5
8	706.826	1.767	77.7
9	624.607	1.562	59.8



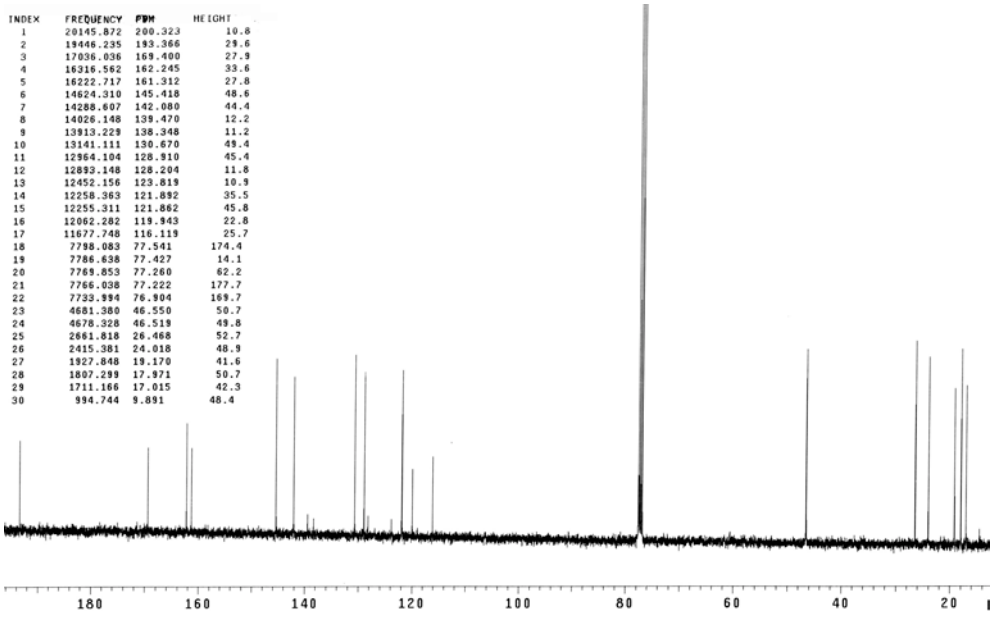
INDEX	FREQUENCY	PPM	HEIGHT
1	19897.909	197.857	29.7
2	18466.591	183.624	28.8
3	16485.176	163.922	34.4
4	15992.303	159.021	32.5
5	14522.073	144.402	97.2
6	13790.392	137.126	33.0
7	11580.089	115.148	29.0
8	7798.083	77.541	173.4
9	7766.038	77.222	176.3
10	7733.994	76.904	171.2
11	7522.653	74.802	38.4
12	6544.535	65.076	93.1
13	3114.254	30.967	59.8
14	2734.299	27.189	92.1
15	760.514	7.562	62.7

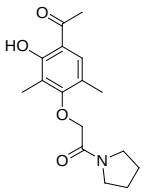


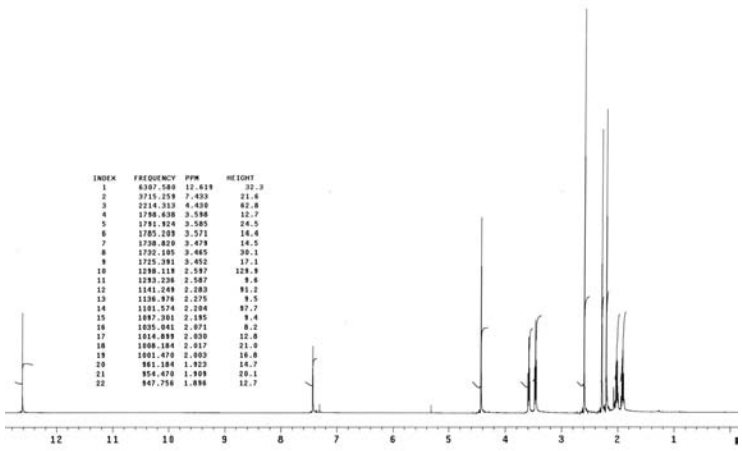
Lactic Acid Derivative 17 yellow oil Rf=0.55 CH_2Cl_2/acetone (12/1); $[\alpha]_D$ = +35.1° (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 13.30 (s, OH), 7.46 (m, 2H), 6.95 (d, 1H, J = 15.0 Hz), 6.32 (m, 2H), 4.66 (q, 1H, J = 6.8 Hz), 3.50 (m, 2H), 3.42 (m, 1H), 3.29 (m, 1H), 2.24 (s, 3H), 2.17 (s, 3H), 1.90 (d, 3H, J = 5.8 Hz), 1.88-1.59 (m, 4H), 1.49 (d, 3H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 193.4, 169.4, 162.2, 161.3, 145.4, 142.1, 130.7, 128.9, 121.9, 121.8, 119.9, 116.1, 77.3, 46.6, 46.5, 26.5, 24.0, 19.2, 18.0, 17.0, 9.9; IR ($CHCl_3$, λ-max cm^{-1}) 3685, 3027, 2983, 1644, 1622, 1360; HRMS(EI) calcd for $C_{21}H_{27}NO_4$ 357.1940, found: 357.1944.



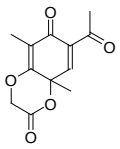
INDEX	FREQUENCY	PPM	HEIGHT
1	20145.872	200.323	10.8
2	19446.235	193.366	29.6
3	17036.036	169.400	27.9
4	16316.562	162.245	33.6
5	16222.717	161.312	27.8
6	14624.310	145.418	48.6
7	14288.607	142.080	44.4
8	14026.148	139.470	12.2
9	13913.229	138.348	11.2
10	13141.111	130.670	49.4
11	12964.104	128.910	45.4
12	12893.148	128.204	11.8
13	12452.156	123.819	10.9
14	12258.363	121.892	35.5
15	12255.311	121.862	45.8
16	12062.282	119.943	22.8
17	11677.748	116.119	25.7
18	7798.083	77.541	174.4
19	7786.638	77.427	14.1
20	7769.853	77.260	62.2
21	7766.038	77.222	177.7
22	7733.994	76.904	169.7
23	4681.380	46.550	50.7
24	4678.328	46.519	49.8
25	2661.818	26.468	52.7
26	2415.381	24.018	48.9
27	1927.848	19.170	41.6
28	1807.299	17.971	50.7
29	1711.166	17.015	42.3
30	994.744	9.891	48.4

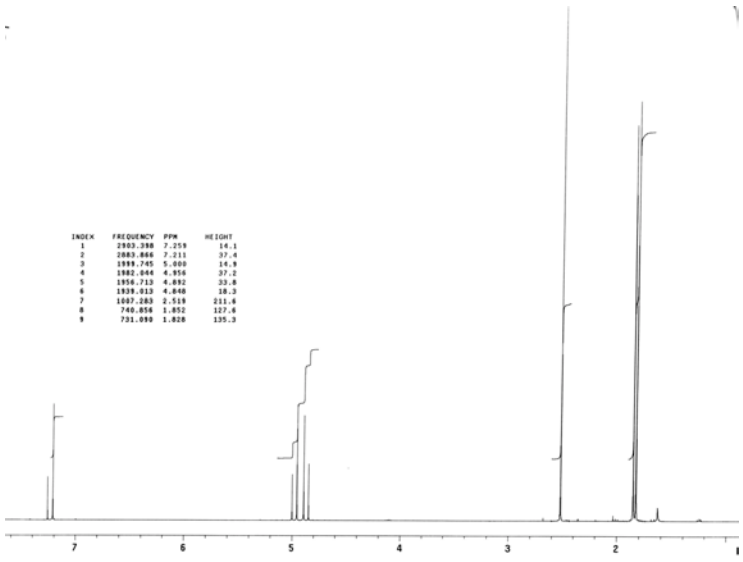




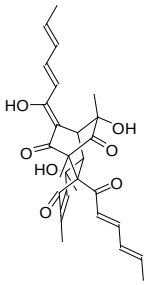


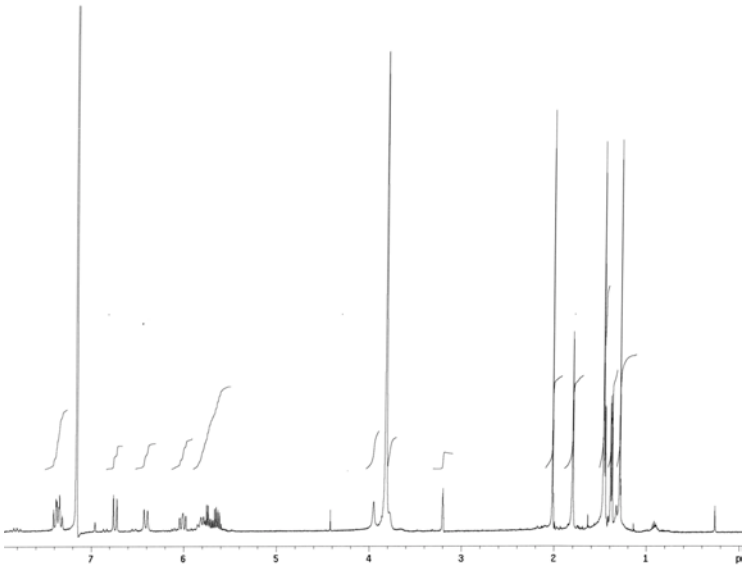
INDEX	FREQUENCY	PPM	HEIGHT
1	6307.580	12.619	32.3
2	3715.259	7.433	21.6
3	2214.313	4.430	62.8
4	1798.638	3.598	12.7
5	1791.924	3.585	24.5
6	1785.208	3.571	16.6
7	1730.820	3.479	14.5
8	1732.105	3.465	30.1
9	1725.391	3.452	17.1
10	1298.119	2.597	129.8
11	1293.236	2.587	9.6
12	1141.249	2.283	91.2
13	1136.976	2.275	9.5
14	1101.574	2.204	97.7
15	1097.301	2.195	9.4
16	1035.041	2.071	8.2
17	1014.899	2.030	12.8
18	1008.184	2.017	21.0
19	1001.470	2.003	16.8
20	961.184	1.923	14.7
21	954.470	1.909	20.1
22	947.756	1.896	12.7

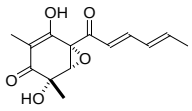




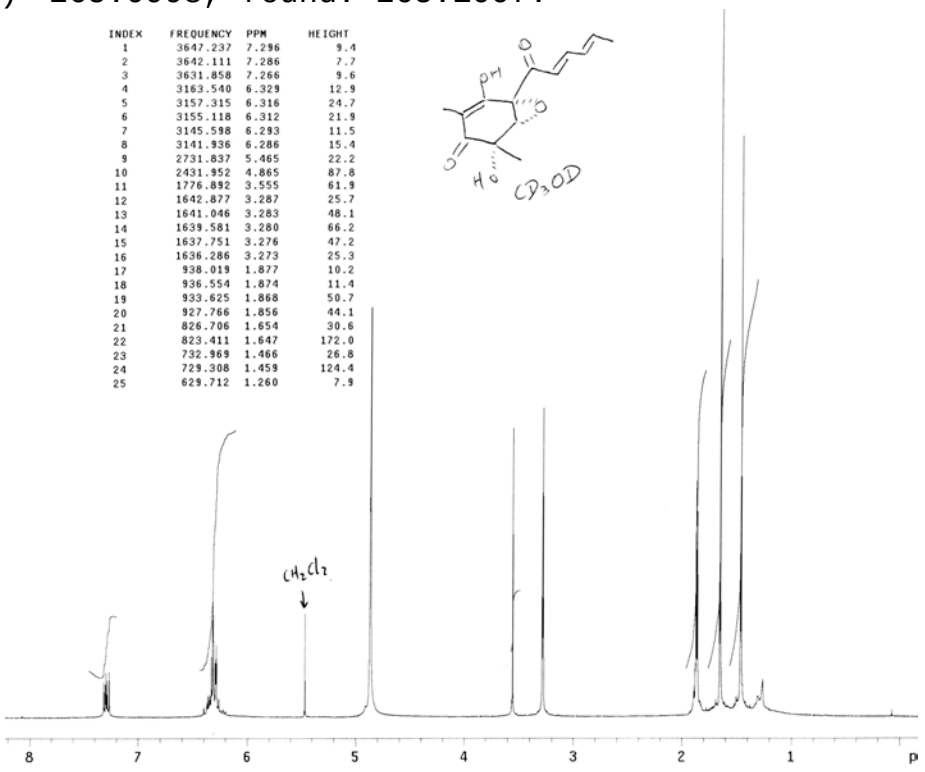
INDEX	FREQUENCY	PPM	HEIGHT
1	2903.398	7.259	14.1
2	2883.866	7.211	37.4
3	1999.745	5.000	14.9
4	1982.044	4.956	37.2
5	1956.713	4.892	33.8
6	1939.013	4.848	18.3
7	1007.283	2.519	211.6
8	740.856	1.852	127.6
9	731.099	1.828	135.3



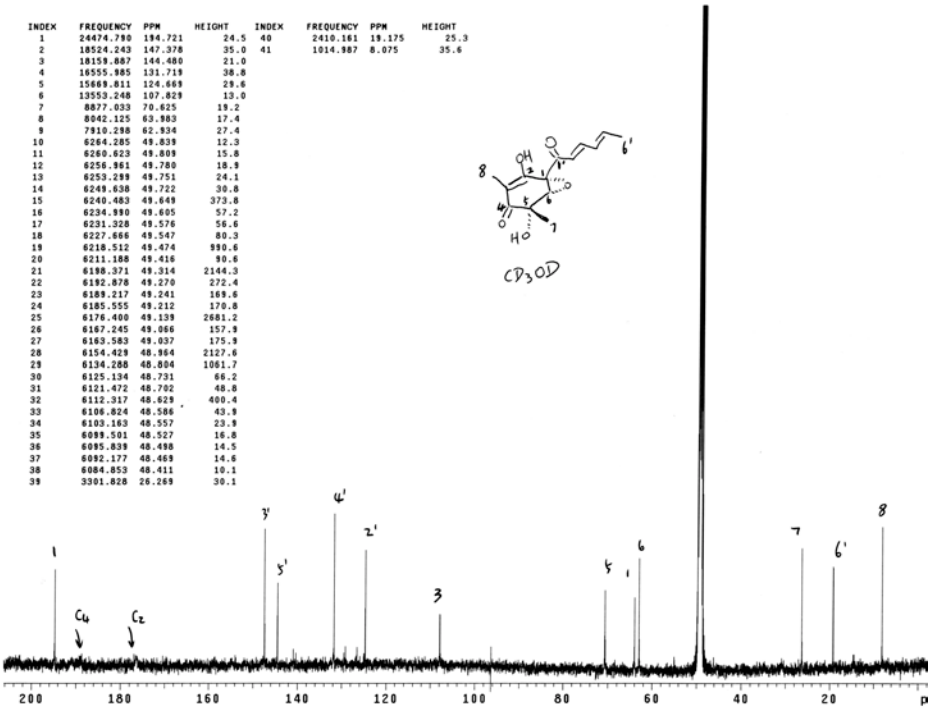




synthetic epoxysorbicillinol (**1**) yellow amorphous powder Rf=0.16 CH_2Cl_2/methanol (7/1); ^{1}H NMR ($CDCl_3$,400 MHz) δ 10.16 (s,enolic OH), 7.58 (m, 1H), 6.45 (m, 1H), 6.30 (m, 2H), 3.98 (s, H6 and OH), 1.95 (d, 3H, J = 6.8 Hz), 1.81(s, 3H), 1.35 (s, 3H); ^{1}H NMR (CD_3OD,400 MHz) δ 7.29 (m, 1H), 6.66-6.27 (m, 3H), 3.56 (s, 1H), 1.86 (d, 3H, J = 5.9 Hz), 1.64(s, 3H), 1.46 (s, 3H); ^{13}C NMR (CD_3OD,100.6 MHz) δ 194.7, 189 (evasive)[1d], 173(evasive)[1d], 147.4, 144.5, 131.7, 124.7, 107.8, 70.6, 64.0, 62.9, 26.3, 19.2, 8.1; IR ($CHCl_3$, ν_{max} cm^{-1}) 3420, 3009, 1675, 1390, 800; HRMS(CI) calcd for $C_{14}H_{16}O_5$ $(M+H)^+$ 265.0998, found: 265.1007.



INDEX	FREQUENCY	PPM	HEIGHT
1	3647.237	7.296	9.4
2	3642.111	7.286	7.7
3	3631.858	7.266	9.6
4	3163.540	6.329	12.9
5	3157.315	6.316	24.7
6	3155.118	6.312	21.9
7	3145.598	6.293	11.5
8	3141.936	6.286	15.4
9	2731.837	5.465	22.2
10	2431.952	4.865	87.8
11	1776.892	3.555	61.9
12	1642.877	3.287	25.7
13	1641.046	3.283	48.1
14	1639.581	3.280	66.2
15	1637.751	3.276	47.2
16	1636.286	3.273	25.3
17	938.019	1.877	10.2
18	936.554	1.874	11.4
19	933.625	1.868	50.7
20	927.766	1.856	44.1
21	826.706	1.654	30.6
22	823.411	1.647	172.0
23	732.969	1.466	26.8
24	729.308	1.459	124.4
25	629.712	1.260	7.9



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	24474.790	194.721	24.5	40	2410.161	19.175	25.3
2	18524.243	147.378	35.0	41	1014.987	8.075	35.6
3	18159.887	144.480	21.0				
4	16555.985	131.719	38.8				
5	15669.811	124.669	29.6				
6	13553.248	107.829	13.0				
7	8877.033	70.625	19.2				
8	8042.125	63.983	17.4				
9	7910.298	62.934	27.4				
10	6264.285	49.839	12.3				
11	6260.623	49.809	15.8				
12	6256.961	49.780	18.9				
13	6253.299	49.751	24.1				
14	6249.638	49.722	30.8				
15	6240.483	49.649	373.8				
16	6234.990	49.605	57.2				
17	6231.328	49.576	56.6				
18	6227.666	49.547	80.3				
19	6218.512	49.474	990.6				
20	6211.188	49.416	90.6				
21	6198.371	49.314	2144.3				
22	6192.878	49.270	272.4				
23	6189.217	49.241	169.6				
24	6185.555	49.212	170.8				
25	6176.400	49.139	2681.2				
26	6167.245	49.066	157.9				
27	6163.583	49.037	175.9				
28	6154.429	48.964	2127.6				
29	6134.288	48.804	1061.7				
30	6125.134	48.731	66.2				
31	6121.472	48.702	48.8				
32	6112.317	48.629	400.4				
33	6106.824	48.586	43.9				
34	6103.163	48.557	23.9				
35	6098.501	48.527	16.8				
36	6095.839	48.498	14.5				
37	6092.177	48.469	14.6				
38	6084.853	48.411	10.1				
39	3301.828	26.269	30.1				