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Sequential 1,2-Addition-Electrocyclic Ring Closures Involving Acyclic α,β-Unsaturated Iminiums: A Formal [3+3] Cycloaddition Strategy to Unique Pyranyl Spirocycles.

authored by

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General Procedure for the Cyclization with 4-Hydroxy-α–pyrones with Unstaurated Iminiums.

The appropriate starting enal (1-2 mmol) (filtered through silica gel if it is from commercial sources) was dissolved in anhydrous EtOAc (dried over CaH_2 quickly, filtered through celite, and stored over molecular seives), and 2.0 eq piperidine was added dropwise via syringe. The solution was cooled to -10 °C (ice in acetone), and 2.0 eq of acetic anhydride was added carefully dropwise. After stirring for an additional 5 minutes at -10 °C, the iminium mixture was sealed under a blanket of dry nitrogen and heated at 85 °C (sand bath) for 30 - 60 min. The warm iminium solution was then transferred quickly via a cannula to a solution of 4-hydroxy-2–pyrones (0.4 to 0.5 mole% to the starting enal) in anhydrous EtOAc. The reaction mixture was again sealed under a blanket of nitrogen and heated at 85 °C in a sand bath for 24-96 h. The reaction progress was monitored by using TLC analysis (mostly 50% ethyl acetate in hexane, but the following solvent system allowed the observation of disappearance of the starting pyrone: 5 : 45 : 50 of methanol : ethyl acetate : ether). When the reaction was completed, the mixture was concentrated under reduced pressure, and the desired cyclized product was isolated using silica gel column chromatography (gradient eluent: ethyl acetate in hexane, 5-50%).

Characterizations for Cyclized Products: 2, 6, 8, 10, 12, 14, 16, 18, 20, 21, 23, 24, 26, 27, 29, 30, 32, and 33.

For Compound **2**.
R_f = 0.49 (30% EtOAc in hexane);
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 6H), 3.89 (s, 3H), 5.44 (d, 1H, J = 9.9 Hz), 6.36 (d, 1H, J = 0.6 Hz), 6.48 (dd, 1H, J = 0.6, 9.9 Hz), 6.97 (m, 2H), 7.78 (m, 2H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 28.6, 29.7, 55.5, 80.1, 96.2, 101.1, 105.1, 114.3, 116.6, 123.8, 125.1, 127.3, 160.3, 161.9, 164.3;
IR (neat) cm^{-1} 2980m, 1734s, 1654s, 1608s, 1559m, 1518m, 1466m, 1394m, 1374m, 1325m, 1270s, 1182s, 1114m, 1061m, 1030m, 868w, 833m, 737m;
mass spectrum (EI): m/e (%relative intensity) 284 (45) M^+, 269 (100), 256 (5), 198 (5), 177 (8), 135 (100), 77 (38);
m/e calcd for $C_{17}H_{16}O_4$ 284.1049, measd 284.1045.

For Compound **6**.
R_f = 0.30 (25% EtOAc in hexane);
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 6H), 3.90 (s, 3H), 5.39 (d, 1H, J = 9.8 Hz), 6.44 (d, 1H, J = 9.8 Hz), 6.91 (s, 1H), 6.94 (d, 1H, J = 8.5 Hz), 6.99 (t, 1H, J =7.8 Hz), 7.35 (m, 1H), 7.93 (dd, 1H, J = 2.0, 7.5 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 28.6, 55.6, 80.0, 99.2, 102.9, 111.4, 116.4, 119.8, 120.8, 125.4, 128.9, 131.8, 156.8, 157.5, 162.0, 164.3;
IR (neat) cm^{-1} 2975m, 1714s, 1636m, 1614m, 1551s, 1494m, 1456m, 1421m, 1375m, 1250m, 1152m, 1126m, 1100m, 1024m, 858w, 736m;
mass spectrum (EI): m/e (%relative intensity) 284 (33) M^+, 269 (90), 256 (12), 189 (13), 135 (43), 77 (11), 32 (100);
m/e calcd for $C_{17}H_{16}O_4$ 284.1048, measd 284.1036.

For Compound **8**.
R_f = 0.82 (methanol : ethyl acetate : ether 5 : 45 : 50)
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 6H), 3.84 (s, 3H), 5.43 (d, 1H, J = 9.9 Hz), 6.42 (s, 1H), 6.45 (d, 1H, J = 9.9 Hz), 6.98 (m, 1H), 7.33 (m, 3H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 29.7, 55.5, 61.9, 80.3, 98.1, 99.4, 110.5, 116.4, 117.2, 118.0, 125.6, 130.0, 132.6, 160.0, 161.7, 164.0;
IR (neat) cm^{-1} 2971w, 2878w, 1710s, 1636m, 1625m, 1601s, 1490m, 1457w, 1442w, 1266m, 1210m, 1040w, 988w, 850m;
mass spectrum (EI): m/e (%relative intensity) 284 (32) M^+, 270 (16), 269 (100), 135 (20);
m/e calcd for $C_{17}H_{16}O_4$ 284.1049, measd 284.1046.

For Compound **10**.
R_f = 0.44 (30% EtOAc in hexane);
^{1}H NMR (200 MHz, $CDCl_3$) δ 1.38 (s, 6H), 3.81 (s, 3H), 3.83 (s, 3H), 5.32 (d, 1H, J = 9.8 Hz), 6.26 (s, 1H), 6.34 (d, 1H, J = 9.8 Hz), 6.79 (d, 1H, J = 8.6 Hz), 7.18 (d, 1H, J = 2.1 Hz), 7.29 (dd, 1H, J = 2.1, 8.6 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 28.5, 55.9, 56.0, 80.1, 96.5, 98.0, 108.0, 110.9, 116.3, 119.0, 123.8, 125.1, 148.2, 151.2, 160.0, 161.9, 164.0;
IR (neat) cm^{-1} 2936m, 1713s, 1636s, 1615s, 1582m, 1548s, 1516s, 1464m, 1426m, 1378m, 1326w, 1270s, 1204m, 1170m, 1144m, 1100m, 1024m, 988w, 810w, 769w, 726m;
mass spectrum (EI): m/e (%relative intensity) 314 (42) M^+, 299 (100), 165 (31), 149 (12), 31 (44);
m/e calcd for $C_{18}H_{18}O_5$ 314.1154, measd 314.1153.

For Compound **12**.
R_f = 0.45 (30% EtOAc in hexane);
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 6H), 3.84 (s, 6H), 5.44 (d, 1H, J = 10.5 Hz), 6.41(s, 1H), 6.45 (d, 1H, J = 10.5 Hz), 6.55 (brs, 1H), 6.94 (brs, 2H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 28.6, 55.6, 80.3, 98.3, 99.5, 103.5, 118.1, 116.4, 125.6, 133.2, 160.0, 161.1, 161.7, 163.9;
IR (neat) cm^{-1} 2936m, 1713s, 1636s, 1615s, 1582m, 1548s, 1516s, 1464m, 1426m, 1378m, 1326w, 1270s, 1204m, 1170m, 1144m, 1100m, 1024m, 988w, 810w;
mass spectrum (EI): m/e (%relative intensity) 314 (80) M^+, 299 (100), 165 (12), 149 (12), 31 (30);
m/e calcd for $C_{18}H_{18}O_5$ 314.1154, measd 314.1156.

For Compound **14**.
R_f = 0.29 (25% EtOAc in hexane);
^{1}H NMR (200 MHz, $CDCl_3$) δ 1.44 (s, 6H), 2.03 (s, 3H), 5.35 (d, 1H, J = 10.0 Hz), 5.76 (s, 1H), 6.73 (d, 1H, J = 10.0 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 27.6, 80.1, 97.8, 100.4, 116.2, 124.9, 162.4, 162.5, 164.2;
IR (neat) cm^{-1} 2974m, 2926s, 1718s, 1647s, 1560s, 1448m, 1420m, 1364m, 1327m, 1253m, 1210m, 1144m, 1099m, 994m, 721m;
mass spectrum (EI): m/e (%relative intensity) 192 (20) M^+, 177 (100), 135 (15), 43 (22);
m/e calcd for $C_{11}H_{12}O_3$ 192.0786, measd 192.0787.

For Compound **16** (known compound).
R_f = 0.27 (25% EtOAc in hexane);
^{1}H NMR (200 MHz, $CDCl_3$) δ 1.44 (d, 3H, J = 9.0 Hz), 2.03 (s, 3H), 5.11 (dq, 1H, J = 1.6, 9.0 Hz), 5.40 (dt, 1H, J = 1.6, 9.9 Hz), 5.77 (s, 1H), 6.42 (d, 1H, J = 9.9 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 29.7, 31.3, 79.3, 98.7, 100.3, 117.1, 122.5, 162.6, 162.8, 164.8;
IR (neat) cm^{-1} 2924m, 1705m, 1649m, 1582m, 1540m, 1456m, 1216w, 911w, 859w, 814w, 732m;
mass spectrum (EI): m/e (%relative intensity) 178 (37) M^+, 163 (100), 121 (10), 66 (14), 42 (22);
m/e calcd for $C_{10}H_{10}O_3$ 178.0630, measd 178.0630.

For Compound **18**.
R_f = 0.30 (25% EtOAc in hexane);
^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, 3H, J = 7.2 Hz), 1.40 (m, 2H), 1.65 (m, 2H), 2.17 (s, 3H), 4.98 (m, 1H), 5.38 (dd, 1H, J = 3.2, 10.0 Hz), 5.75 (s, 1H), 6.39 (dd, 1H, J = 5.6, 10.0 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 18.2, 21.2, 37.9, 77.5, 98.5, 100.1, 118.0, 120.0, 162.4, 162.6, 165.0;
IR (neat) cm^{-1} 3090w, 2962s, 2934s, 2874s, 1695s, 1650s, 1565s, 1556s, 1453s, 1427s, 1382m, 1346m, 1310s, 1219s, 1146s, 1034m, 1005s, 967m, 916m, 820m, 732s;
mass spectrum (EI): m/e (%relative intensity) 206 (15) M^+, 189 (31), 163 (97), 151 (26), 139 (100), 122 (38), 110 (31), 94 (38), 83 (68);
m/e calcd for $C_{12}H_{14}O_3$ 206.0943, measd 206.0942.

For Compound **20** and **21**.
R_f = 0.68 (50% EtOAc in hexane);
^{1}H NMR (500 MHz, $CDCl_3$) for **20**: δ 2.20 (s, 3H), 5.58 (dd, 1H, J = 3.4, 10.2 Hz), 5.76 (s, 1H), 5.99 (dd, 1H, J = 1.6, 3.4 Hz), 6.65 (dd, 1H, J =1.6, 10.2 Hz), 7.34-7.71 (m, 5H);
for **21**: δ 2.21 (s, 3H), 3.59 (brs, 1H), 3.67 (brs, 1H), 5.82 (s, 1H), 6.91 (d, 1H, J = 15.0 Hz), 7.69-8.78 (m, 5H);
^{13}C NMR (75 MHz, $CDCl_3$) it was difficult to assign the mixture.
IR (neat) cm^{-1} 3054s, 2986s, 2927s, 2853m, 1731m, 1612m, 1573m, 1456m, 1379m, 1265s, 1097m, 1016m, 896m, 738s, 704s.
mass spectrum (EI): m/e (%relative intensity) 240 (100) M^+, 197 (13), 163 (20), 141 (6), 128 (35), 115 (7), 102 (7), 77 (6).
m/e calcd for $C_{15}H_{12}O_3$ 240.0786, measd 240.0779.

For Compound **23**.
R_f = 0.52 (20% EtOAc in hexane) ;
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (m, 8H), 1.99 (m, 2H), 3.96 (s, 3H), 5.46 (d, 1H, J = 9.9 Hz), 6.47 (d, 1H, J = 9.9 Hz), 6.89 (s, 1H), 6.98 (d, 1H, J = 8.4 Hz), 7.04 (m, 1H), 7.39 (m, 1H), 7.95 (dd, 1H, J=1.8, 7.8 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 25.1, 36.6, 55.7, 81.0, 103.1, 111.4, 116.9, 120.9, 124.0, 124.9, 128.9, 129.1, 131.5, 131.7, 157.5, 162.0, 164.4;
IR (neat) cm^{-1} 2927s, 2854s, 1716m, 1540m, 1457m, 1264s, 896m, 870m, 746s, 707m;
mass spectrum (EI): m/e (%relative intensity) 324 (66) M^+, 281 (100), 135 (47), 77 (10);

m/e calcd for $C_{20}H_{20}O_4$ 324.1362, measd 324.1358.

For Compound **24**.

R_f = 0.72 (60% EtOAc in hexane) ;

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (m, 8H), 1.95 (m, 2H), 2.21 (s, 3H), 5.40 (d, 1H, J = 11.2 Hz), 5.82 (s, 1H), 6.20 (d, 1H, J = 11.2 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 21.0, 25.0, 36.5, 81.0, 98.6, 100.4, 116.8, 124.3, 162.4, 162.5 164.3;

IR (neat) cm^{-1} 3053s, 2934s, 1707s, 1646m, 1560s, 1448m, 1265s, 1227m, 1144m, 996m, 739s;

mass spectrum (EI): m/e (%relative intensity) 232 (37) M^+, 190 (15), 189 (100), 176 (10);

m/e calcd for $C_{14}H_{16}O_3$ 232.1099, measd 232.1090.

For Compound **26**.

R_f = 0.41 (30% EtOAc in hexane);

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (m, 4H), 1.90 (m, 2H), 2.20 (m, 2H), 3.92 (s, 3H), 3.94 (s, 3H), 5.42 (d, 1H, J = 9.8 Hz), 6.37 (s, 1H), 6.45 (d, 1H, J = 9.8 Hz), 6.91 (d, 1H, J = 8.6 Hz), 7.30 (d, 1H, J = 2.1 Hz), 7.39 (dd, 1H, J = 2.1, 8.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 40.7, 56.1, 56.2, 71.1, 96.7, 98.9, 108.2, 111.0, 117.1, 118.2, 119.1, 124.1, 152.1, 153.2, 161.8, 162.0, 168.1;

IR (neat) cm^{-1} 3060m, 2958s, 1717m, 1685s, 1635s, 1545s, 1517s, 1456m, 1386m, 1328m, 1273m, 1170m, 1144m, 1025m, 859w, 806m, 768m, 734m, 701m;

mass spectrum (EI): m/e (%relative intensity) 341 (24) M^++1, 340 (100) M^+, 312 (17), 311 (52), 201 (10), 165 (92), 149 (18), 77 (10),

m/e calcd for $C_{20}H_{20}O_5$ 340.1311, measd 340.1301.

For Compound **27**.

R_f = 0.58 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (m, 4H), 1.80 (m, 2H), 2.11 (m, 2H), 2.19 (s, 3H), 5.36 (d,1H, J = 10.5 Hz), 5.74 (s, 1H), 6.38 (d, 1H, J = 10.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 25.0, 36.5, 81.0, 98.6, 100.4, 116.8, 124.3, 162.4, 162.5, 164.3;

IR (neat) cm^{-1} 3054m, 2967m, 2876, 1706s, 1647s, 1627m, 1560s, 1508w, 1448m, 1425m, 1388m, 1338m, 1266s, 1236m, 1194m, 1149m, 1033w, 998m, 971w, 818w, 740s, 705s;

mass spectrum (EI): m/e (%relative intensity) 218 (46), 190 (22), 189 (100), 91 (7), 43 (16);

m/e calcd for $C_{13}H_{14}O_3$ 218.0943, measd 218.0945.

For Compound **29**.

R_f = 0.54 (50% EtOAc in hexane);

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (m, 2H), 1.90 (m, 2H), 2.24 (s, 3H), 3.76 (m, 2H), 3.84 (m, 2H), 5.40 (d, 1H, J = 10.0 Hz), 5.87 (s, 1H), 6.47 (d, 1H, J = 10.0 Hz);

^{13}C NMR (125 MHz, $CDCl_3$): δ 20.2, 36.5, 62.9, 78.0, 98.7, 100.2, 117.7, 123.1, 162.2, 162.9, 163.8;

IR (neat) cm^{-1} 3090m, 2949m, 2865s, 1716s, 1645s, 1561s, 1468m, 1448s, 1434s, 1391m, 1330s, 1267m, 1228s, 1159s, 1123m, 1100s, 1040s, 1079m, 1020m, 1010m, 996s, 965s, 838m, 7942, 726s;

mass spectrum (EI): m/e (%relative intensity) 234 (34) M^+, 205 (41), 190 (29), 189 (33), 176 (100), 91 (19), 43 (29), 31 (15);

m/e calcd for $C_{13}H_{14}O_4$ 234.0892, measd 234.0888.

For Compound **30**.

R_f = 0.22 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84 (m, 2H), 1.99 (m, 2H), 3.75 (m, 2H), 3.80 (m, 2H), 3.94 (s, 3H), 3.96 (s, 3H), 5.44 (d, 1H, J = 9.9 Hz), 6.41 (d, 1H, J = 0.6 Hz), 6.53 (d, 1H, J = 9.9 Hz), 6.91 (d, 1H, J = 8.6 Hz), 7.31 (d, 1H, J = 1.8 Hz), 7.43 (dd, 1H, J = 1.8, 8.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$): δ 36.6, 56.1, 56.2, 63.0, 78.0, 96.4, 99.2, 108.3, 111.1, 117.9, 119.2, 123.4, 123.9, 149.3, 151.7, 160.7, 161.7, 163.9;

IR (neat) cm^{-1} 3086w, 2948s, 2919m, 2880m, 2840m, 1702s, 1678s, 1624s, 1545s, 1516s, 1462m, 1437m, 1388m, 1270s, 1220s, 1171m, 1142s, 1093w, 1024s, 985w, 911w, 843m, 808w;

mass spectrum (EI): m/e (%relative intensity) 356 (60) M^+, 298 (55), 217 (37), 165 (100), 125 (50);

m/e calcd for $C_{20}H_{20}O_6$ 356.1260, measd 356.1261.

For Compound **32** (major isomer only).

R_f = 0.61 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 3H), 0.87 (s, 3H), 1.20 (s, 3H), 1.58 (m, 2H), 1.81 (m, 1H), 1.99 (m, 1H), 2.40 (m, 2H), 2.90 (m, 1H), 3.92 (s, 3H), 5.33 (d, 1H, J = 10.4 Hz), 6.55 (d, 1H, J = 10.4 Hz), 6.83 (s, 1H), 6.96 (d, 1H, J = 8.5 Hz), 7.03 (t, 1H, J = 7.7 Hz), 7.38 (dt, 1H, J = 1.7, 8.5 Hz), 7.92 (dd, 1H, J = 1.7, 7.7 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 11.0, 18.9, 20.9, 27.3, 30.0, 34.4, 45.1, 48.9, 49.8, 55.7, 80.1, 98.6, 102.3, 111.6, 117.4, 120.7, 120.9, 123.5, 129.1, 131.7, 155.0, 157.3, 162.0, 165.2;

IR (neat) cm^{-1} 2948s, 2929s, 2870m, 2840m, 1712s, 1634s, 1614m, 1550s, 1991m, 1427w, 1373m, 1285w, 1250m, 1181w, 1039w;

mass spectrum (EI): m/e (%relative intensity) 378 (30) M^+, 335 (8), 268 (100), 231 (10), 218 (5), 135 (60), 77 (15);

m/e calcd for $C_{24}H_{26}O_4$ 378.1831, measd 378.1827.

For Compound **33**.

R_f = 0.48 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (s, 3H), 0.86 (s, 3H), 0.90 (m, 1H), 0.95 (s, 3H), 1.05 (m, 1H), 1.24 (m, 1H), 1.61 (m, 1H), 1.63 (m, 1H), 1.76 (m, 1H), 2.21 (m, 1H), 3.90 (s, 3H), 5.04 (d, 1H, J = 5.9 Hz), 5.97 (d, 1H, J = 5.9 Hz), 6.99 (d, 1H, J = 8.5 Hz), 7.05 (t, 1H, J = 7.7 Hz), 7.12 (brs, 1H), 7.38 (dt, 1H, J = 1.7, 8.5 Hz), 7.92 (dd, 1H, J = 1.7, 7.7 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 12.8, 18.9, 19.7, 27.9, 30.8, 34.8, 44.8, 47.9, 51.8, 55.6, 105.8, 111.4, 111.5, 117.8, 119.4, 120.9, 128.9, 131.9, 136.2, 154.5, 155.9, 157.6, 168.3, 168.4;

IR (neat) cm^{-1} 2948s, 2870m, 2840w, 1663s, 1609m, 1560s, 1491m, 1462w, 1344w, 1280m, 1250s, 1123w, 1024m;

mass spectrum (EI): m/e (%relative intensity) 378 (25) M^+, 335 (5), 268 (100), 231 (8), 218 (13), 135 (35), 77 (5);

m/e calcd for $C_{24}H_{26}O_4$ 378.1831, measd 378.1828.

Characterizations for Pyrones: 1, 5, 7, 9, and 11.

For Compound **1**: (59 %)
R_f = 0.52 (methanol : ethyl acetate : hexane: 5 : 45 : 50);
^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6) δ 3.85 (s, 3H), 5.53 (d, 1H, J = 1.8 Hz), 6.36 (d, 1H, J = 1.8 Hz), 6.94 (d, 2H, J = 9.0 Hz), 7.76 (d, 2H, J = 9.0 Hz);
^{13}C NMR (75 MHz, methanol-d_4) δ 54.6, 88.4, 96.7, 114.1, 123.4, 127.1, 161.5, 162.3, 166.6, 172.4;
IR (neat) cm^{-1} 3056s, 2997m, 2978s, 2957m, 2938m, 1702s, 1653m, 1633s, 1594s, 1565s, 1461m, 1422m, 1358w, 1274w, 1255w, 1206m, 1156s;
mass spectrum (EI): m/e (%relative intensity) 218 (5) M^+ , 192 (85), 135 (60), 77 (20), 69 (100);
m/e calcd for $C_{12}H_{10}O_4$ 218.0579, measd 218.0583.

For Compound **5**: (52 %)
R_f = 0.48 (methanol : ethyl acetate : hexane: 5 : 45 : 50);
^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6) δ 3.90 (d, 3H, J = 1.8 Hz), 5.55 (dd, 1H, J = 2.1, 3.3 Hz), 6.92 (d, 1H, J = 2.1 Hz), 6.96 (d, 1H, J = 10.2 Hz), 7.02 (t, 1H, J = 8.4 Hz), 7.37 (dt, 1H, J = 1.5, 10.2 Hz), 7.92 (dd, 1H, J = 1.5, 8.4 Hz);
^{13}C NMR (75 MHz, $CDCl_3$/DMSO-d_6) δ 55.5, 90.4, 103.3, 111.5, 119.6, 120.6, 128.8, 131.5, 157.3, 160.4, 164.9, 170.8;
IR (neat) cm^{-1} 3583b, 1780w, 1718s, 1625w, 1558s, 1493m, 1457m, 1372m, 1251s, 1186m, 1155m, 1060w, 1017w, 932w, 860m, 760w;
mass spectrum (EI): m/e (%relative intensity) 218 (83) M^+ , 187 (38), 135 (100), 77 (25);
m/e calcd for $C_{12}H_{10}O_4$ 218.0579, measd 218.0579.

For Compound **7**: (35 %)
R_f = 0.44 (methanol : ethyl acetate : hexane: 5 : 45 : 50);
^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6): δ 3.84 (s, 3H), 5.59 (d, 1H, J = 1.9 Hz), 6.45 (d, 1H, J = 1.9 Hz), 6.96 (m, 1H), 7.32 (m, 3H);
IR (neat) cm^{-1} 3452b, 1654s, 1540m, 1458m, 863m;
^{13}C NMR (75 MHz, $CDCl_3$/DMSO-d_6) δ 55.2, 90.4, 98.6, 110.7, 116.4, 117.8, 129.7, 132.5, 159.7, 160.2, 160.6, 170.6;
mass spectrum (EI): m/e (%relative intensity) 218 (100) M^+, 190 (65), 176 (18), 135 (91), 107 (17), 92 (15), 77 (17), 32 (10);
m/e calcd for $C_{12}H_{10}O_4$ 218.0579, measd 218.0577.

For Compound **9**: (45 %)
R_f = 0.39 (methanol : ethyl acetate : hexane: 5 : 45 : 50);
^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6): δ 3.90 (s, 3H), 3.92 (s, 3H), 5.53 (d, 1H, J = 2.1 Hz), 6.35 (d, 1H, J = 2.1 Hz), 6.88 (d, 1H, J = 8.7 Hz), 7.30 (d, 1H, J = 2.1 Hz), 7.38 (dd, J = 2.1, 8.7 Hz);
^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6) δ 55.7, 55.8, 89.3, 97.0, 108.2, 110.9, 118.8, 123.9, 148.7, 150.9, 160.4, 164.4, 170.7;
IR (neat) cm^{-1} 3043s, 2986s, 1648m, 1606m, 1540m, 1421s, 1218m, 1157m, 896s, 751s;
mass spectrum (EI): m/e (%relative intensity) 248 (100) M^+, 220 (18), 206 (46), 165 (91), 124 (6), 92 (5), 77 (6), 32 (13), 28 (46);
m/e calcd for $C_{13}O_5H_{12}$ 248.0684, measd 248.0680.

For Compound **11**.
R_f = 0.48 (methanol : ethyl acetate : hexane: 5 : 45 : 50);
^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6) δ 3.80 (s, 6H), 5.57 (d, 1H, J = 2.1 Hz), 6.41 (d, 1H, J = 2.1 Hz), 6.51 (t, 1H, J = 2.1 Hz), 6.91 (d, 2H, J = 2.1 Hz);
^{13}C NMR (125 MHz, $CDCl_3$/DMSO-d_6) δ 55.7, 90.9, 98.9, 103.6, 104.9, 133.4, 160.5, 161.0, 165.0, 170.6;
IR (neat) cm^{-1} 2997m, 2957m, 2938m, 1702s, 1633s, 1594s, 1565s, 1461m, 1422m, 1358w, 1274w, 1255w, 1206m, 1156s;
mass spectrum (EI): m/e (%relative intensity) 248 (89) M^+, 220 (18), 206 (46), 165 (100), 124 (6), 92 (5), 77 (6), 32 (13), 28 (46);
m/e calcd for $C_{13}O_5H_{12}$ 248.0684, measd 248.0682.

^{1}H NMR and FTIR Characterizations For Known Enals: 22, 25, 28, and 31.

For Compound **22**.

R_f = 0.43 (CH_2Cl_2);

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.75 (m, 10H), 5.81 (d, J = 8.2 Hz), 10.01 (d, J = 8.2 Hz).

IR (neat) cm^{-1} 3055s, 2937s, 2861s, 2685w, 1704s, 1644s, 1540w, 1449s, 1421s, 1264s, 1220s, 1184s, 1128m, 1037m, 997w, 941m, 896s, 855m, 746s, 706s;

For Compound **25**.

R_f = 0.82 (50% EtOAc in hexane);

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58-1.86 (m, 4H), 2.56 (m, 2H), 2.82 (m, 2H), 6.01 (m, 1H), 9.85 (d, 1H, J = 9.0 Hz);

IR (neat) cm^{-1} 2955s, 2364m, 1699s, 1540m, 1416m, 1196s, 870m, 858m, 740m;

For Compound **28**.

R_f = 0.33 (50% EtOAc in hexane);

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.51 (m, 1H), 2.86 (m, 2H), 3.98 (m, 1H), 3.83 (m, 3H), 5.91 (d, 1H, J = 6.5 Hz), 10.02 (d, 1H, J = 7.0 Hz);

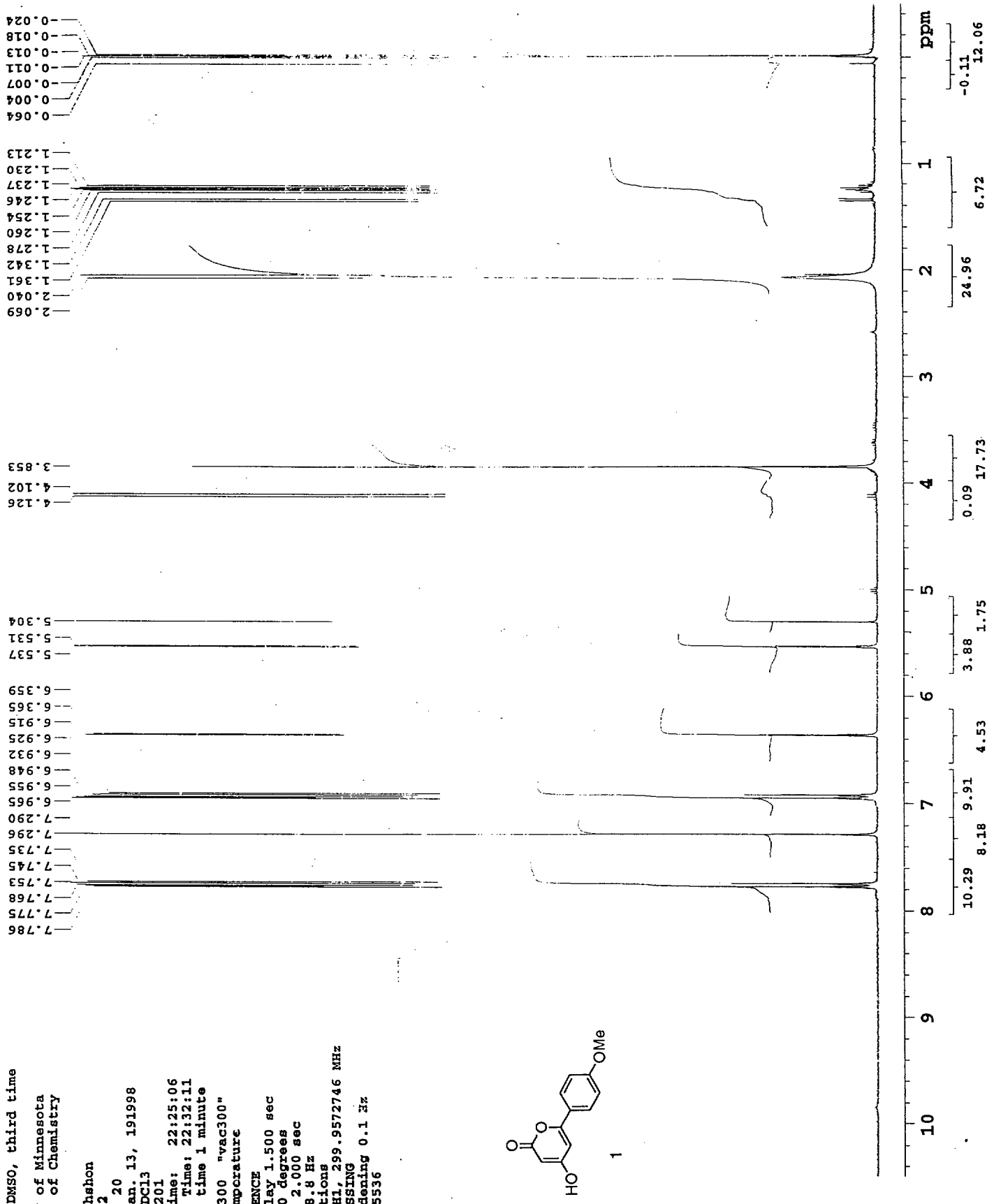
IR (neat) cm^{-1} 3060s, 2931s, 2858s, 1717s, 1648m, 1540m, 1421m, 1266s, 1179m, 1154m, 1095m, 1003m, 848m, 738s, 702s;

For Compound **31**.

R_f = 0.75 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (s, 3H), 0.95 (s, 3H), 0.98 (s, 3H), 1.23 (m, 2H), 1.81 (m, 2H), 1.90 (m, 1H), 2.45 (dd, 1H, J = 2.1, 18.0 Hz), 2.88 (d, 1H, J = 18.0 Hz), 5.80 (brd, 1H, j = 8.1 Hz), 9.84 (d, 1H, J = 8.1 Hz);

IR (neat) cm^{-1} 2934s, 2854m, 1669s, 1560m, 1541m, 1458m, 961m;



pyrone in DMSO, third time

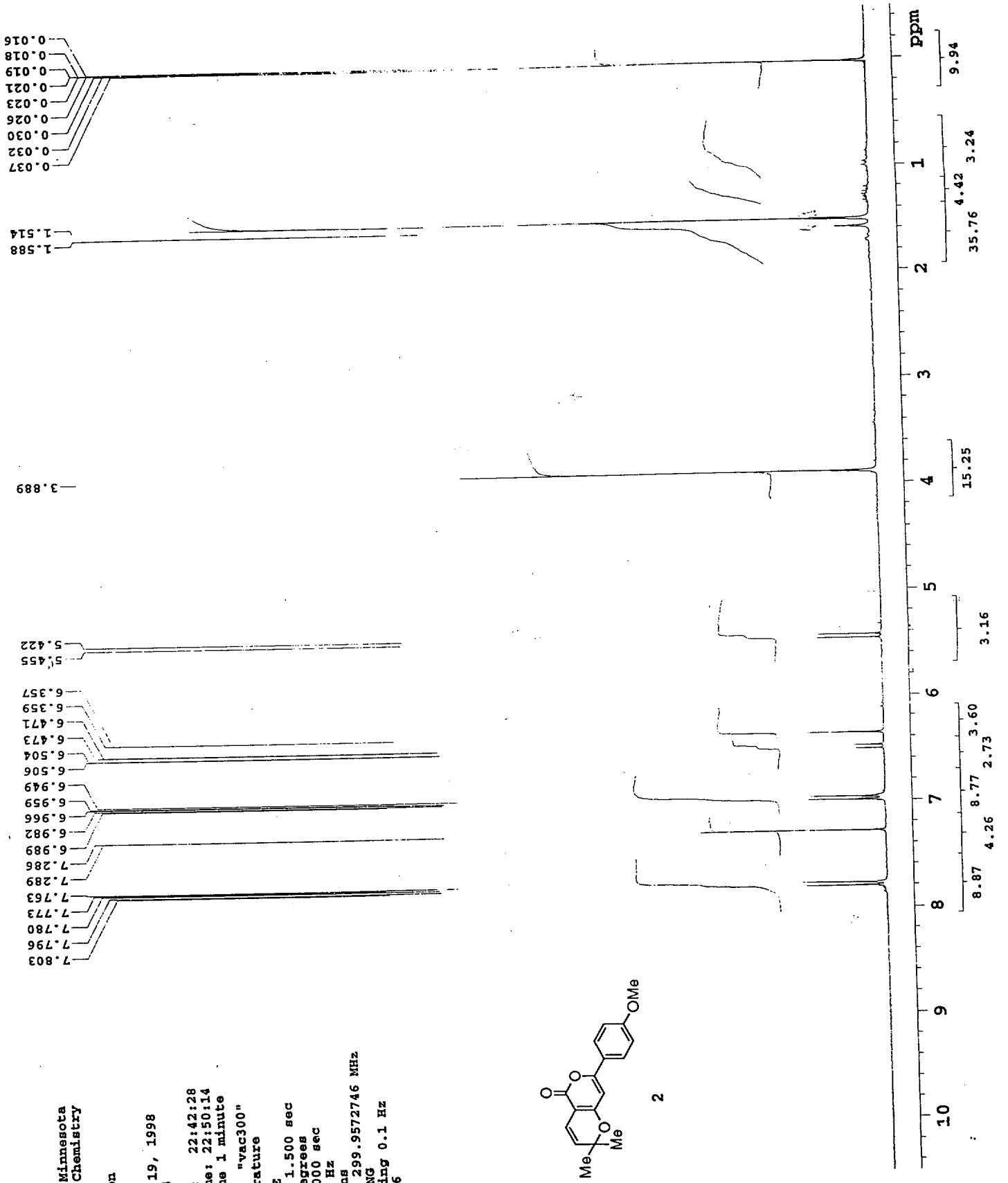
University of Minnesota
Department of Chemistry
VAC-300

User: rhahon
Sample: 32
Spin rate: 20
Date: Jan. 13, 191998
Solvent: CDCl3
File: 3201
Starting Time: 22:25:06
Completion Time: 22:32:11
Total acq. time 1 minute

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572746 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536

1



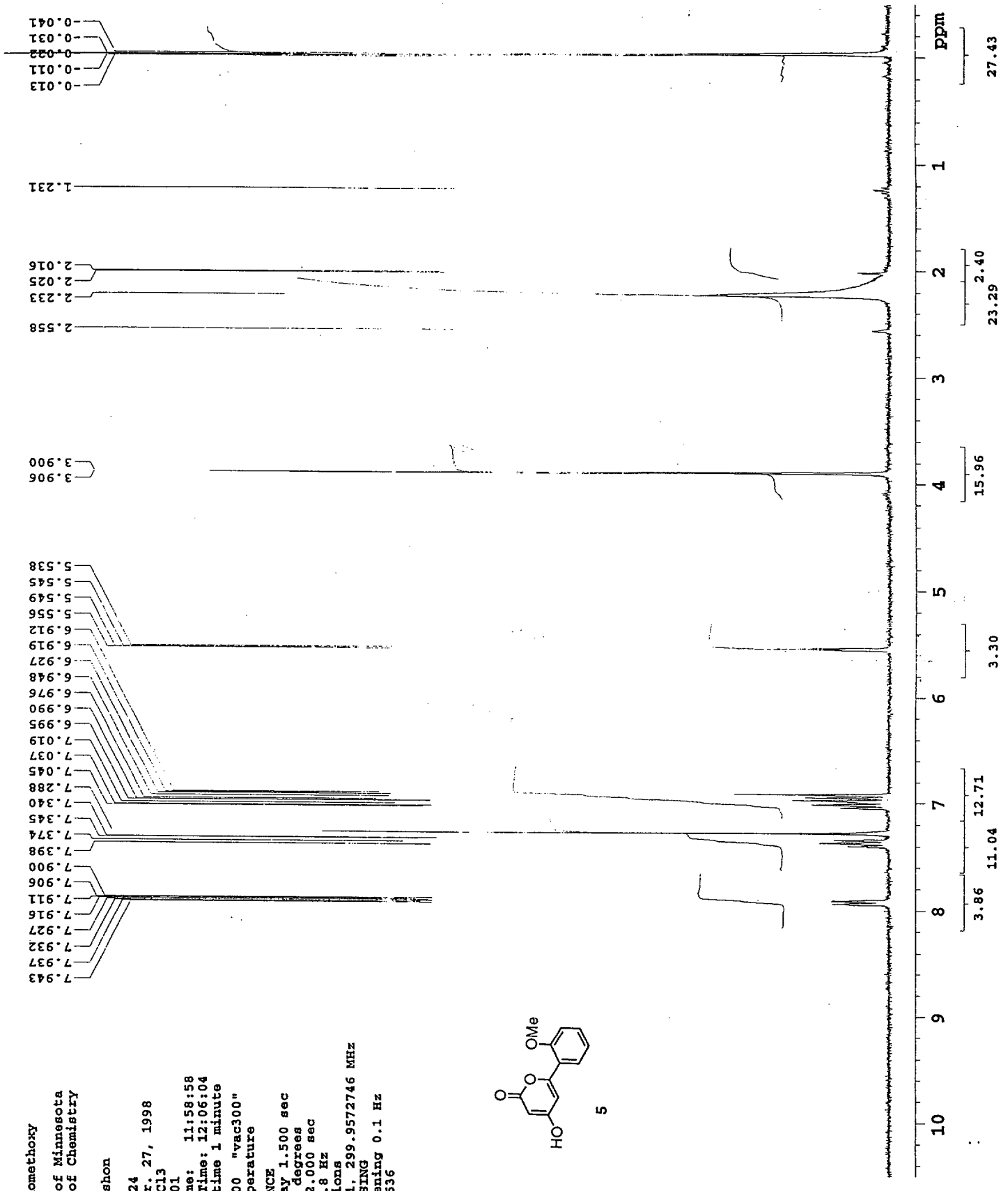
fra 4

University of Minnesota
Department of Chemistry
VAC-300

User: rhshon
Sample: 48
Spin rate: 24
Date: Feb. 19, 1998
Solvent: CDCl3
File: 4801
Starting Time: 22:42:28
Completion Time: 22:50:14
Total acq. time 1 minute

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572746 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536



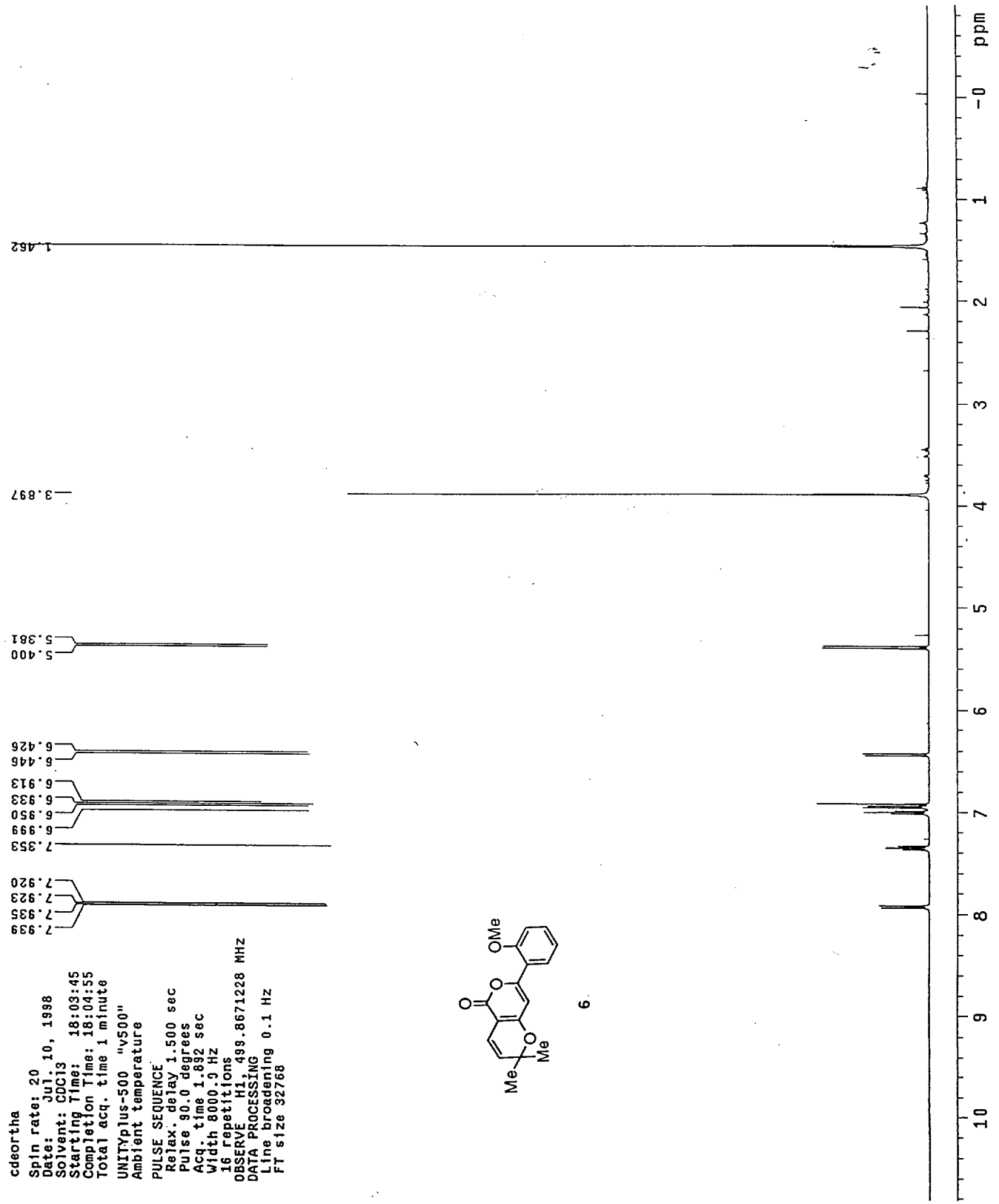
pyrone orthomethoxy

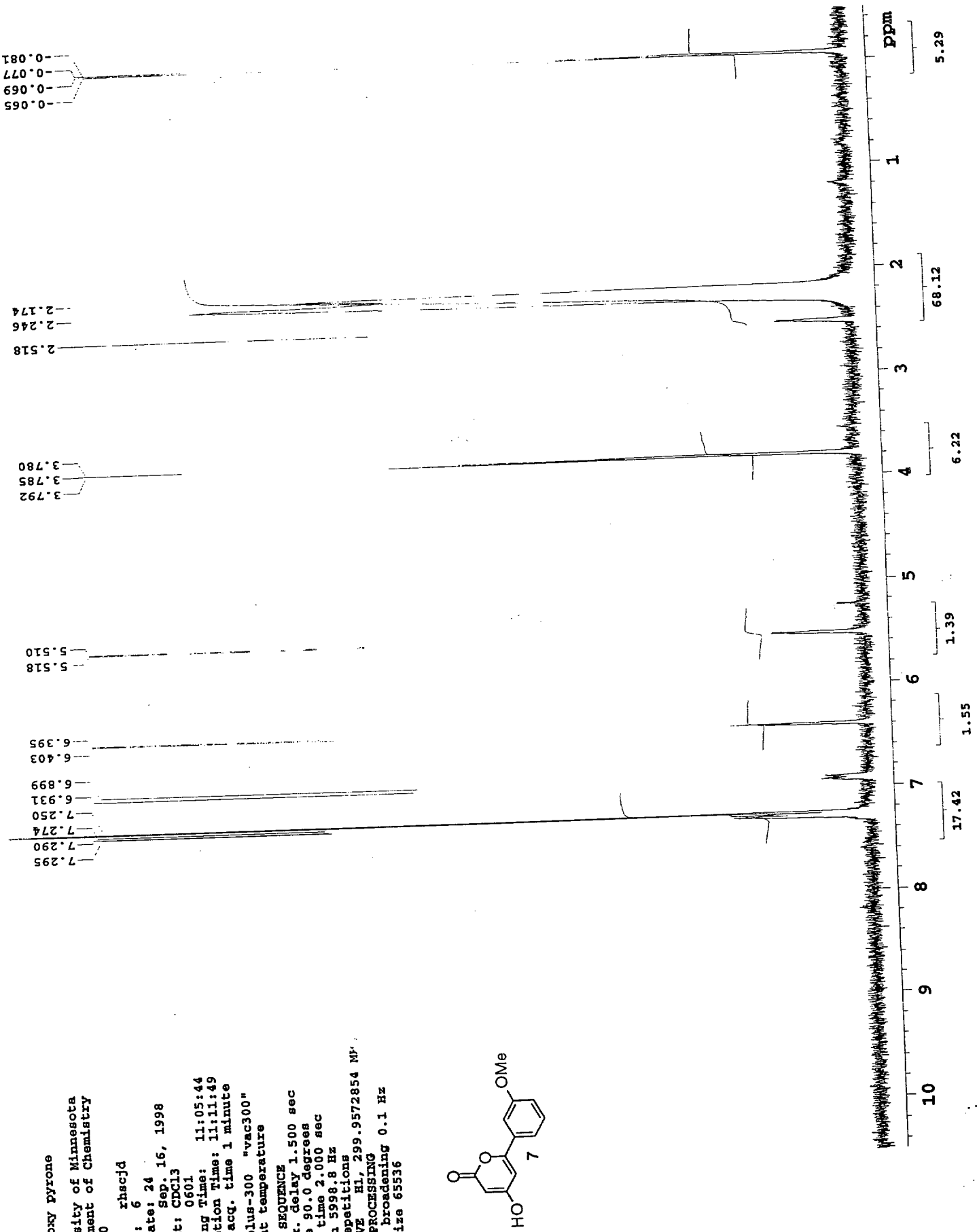
University of Minnesota
Department of Chemistry
VAC-300

User: rhshon
Sample: 10
Spin rate: 24
Date: Apr. 27, 1998
Solvent: CDCl3
File: 1001
Starting Time: 11:58:58
Completion Time: 12:06:04
Total acq. time 1 minute

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572746 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536




m-methoxy pyrone
University of Minnesota
Department of Chemistry
VAC-300
User: rhscjd
Sample: 6
Spin rate: 24
Date: Sep. 16, 1998
Solvent: CDCl3
File: 0601
Starting Time: 11:05:44
Completion Time: 11:11:49
Total acq. time 1 minute
UNITYplus-300 "vac300"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572854 M
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
OMe
HO
7
ppm
0.081
0.077
0.069
0.065
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2.246
2.518
3.780
3.785
3.792
5.510
5.518
6.395
6.403
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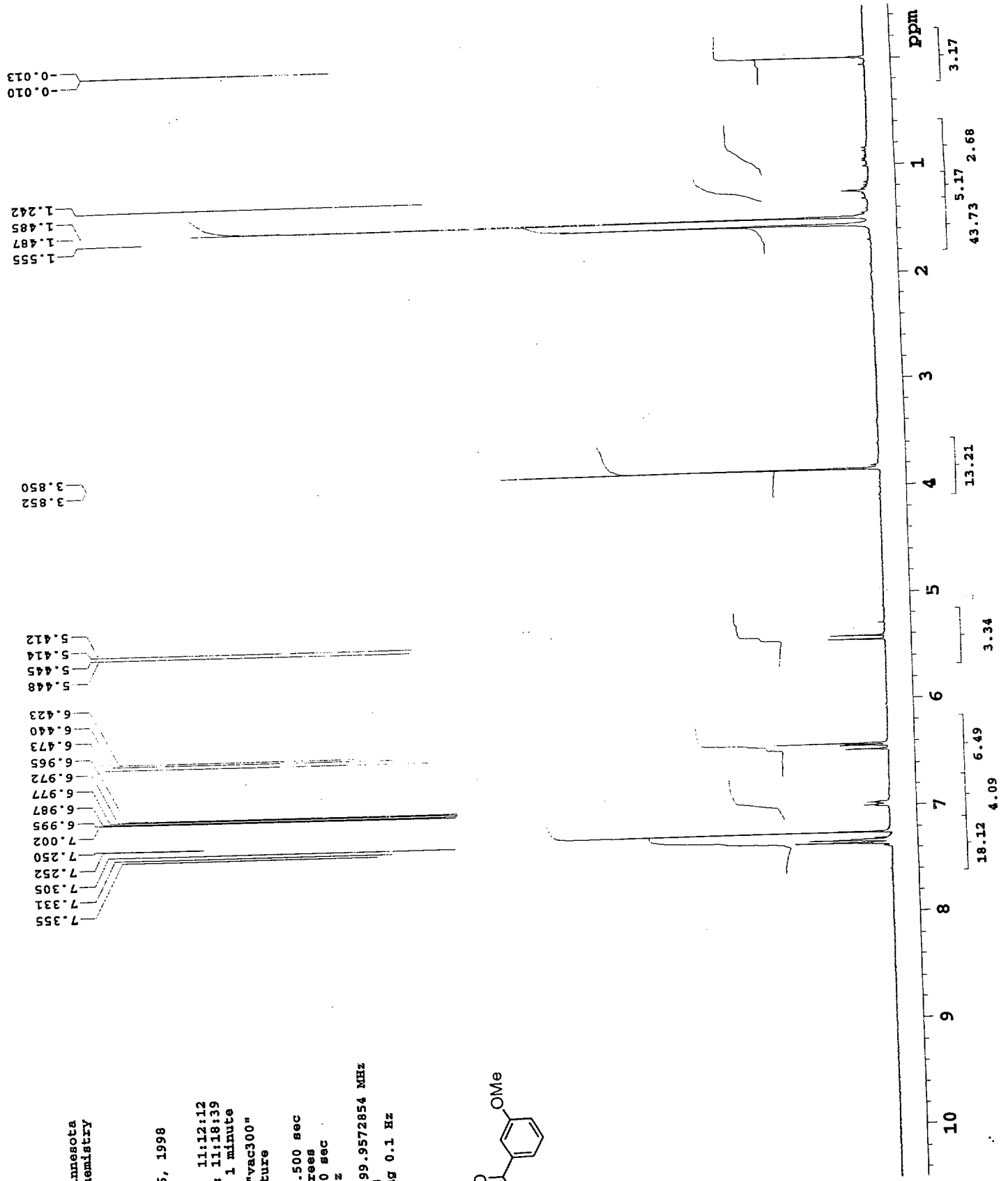
5.29
68.12
6.22
1.39
1.55
17.42



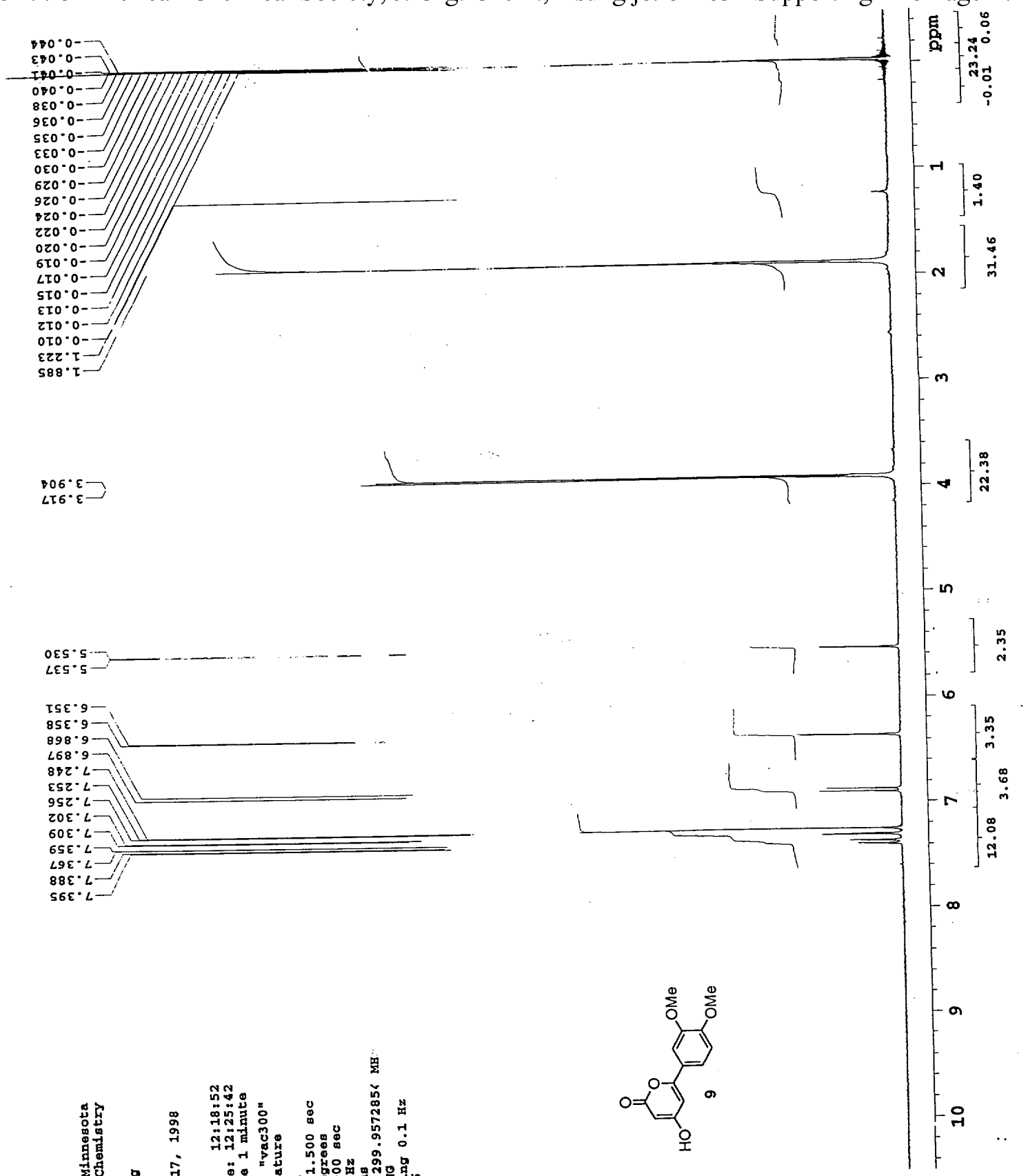
m-methoxy CDE

University of Minnesota
Department of Chemistry
VAC-300

User: rhscjd
Sample: 7
Spin rate: 24
Date: Sep. 16, 1998
Solvent: CDCl3
File: 0701
Starting Time: 11:12:12
Completion Time: 11:18:39
Total acq. time 1 minute

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572854 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536



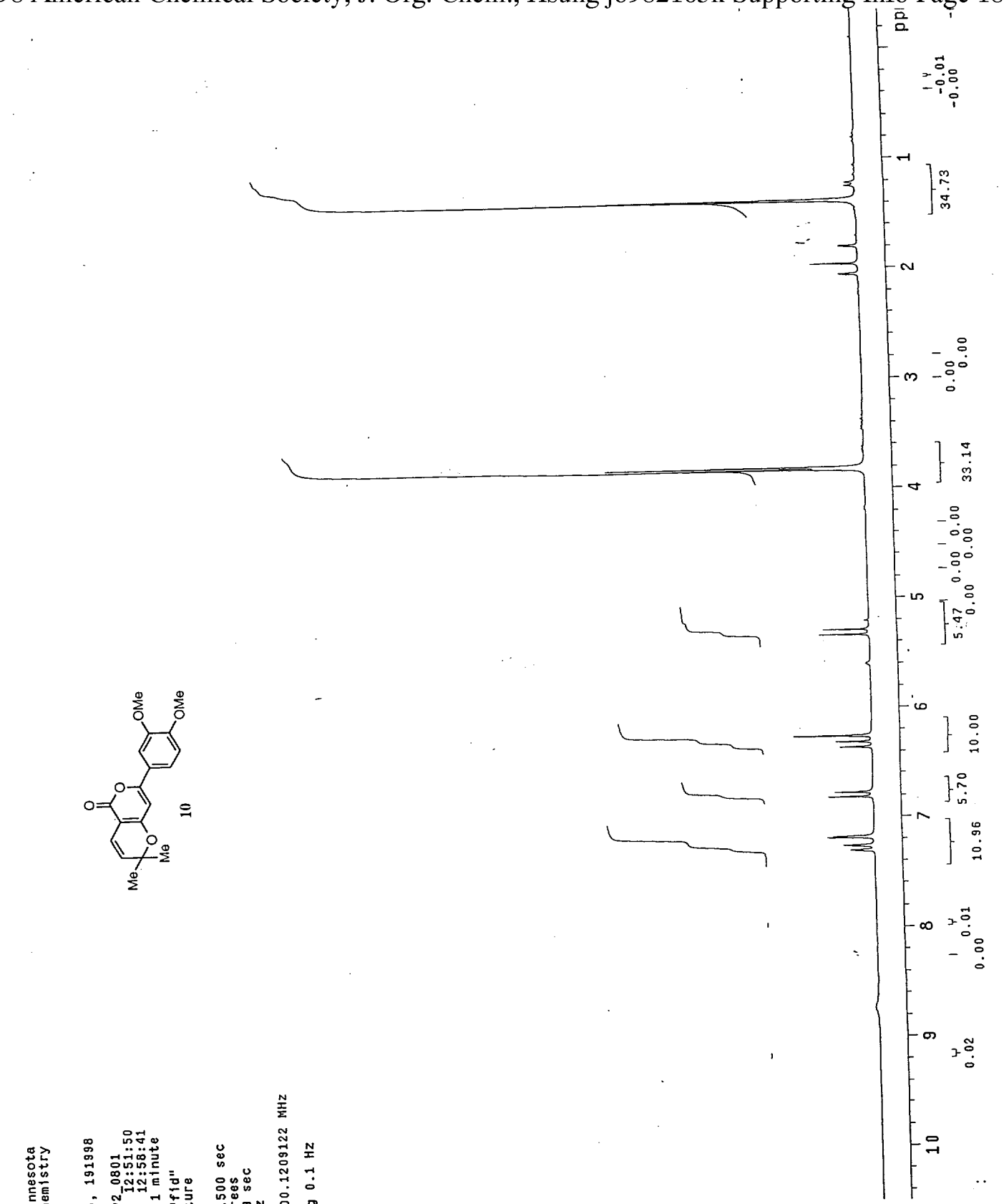
Hong

University of Minnesota
Department of Chemistry
VAC-300

User: rhsgmg
Sample: 20
Spin rate: 24
Date: Jun. 17, 1998
Solvent: CDCl3
File: 2001 12:18:52
Starting Time: 12:25:42
Completion Time: 1 minute
Total acq. time

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572854 MH
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536




ppm
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8
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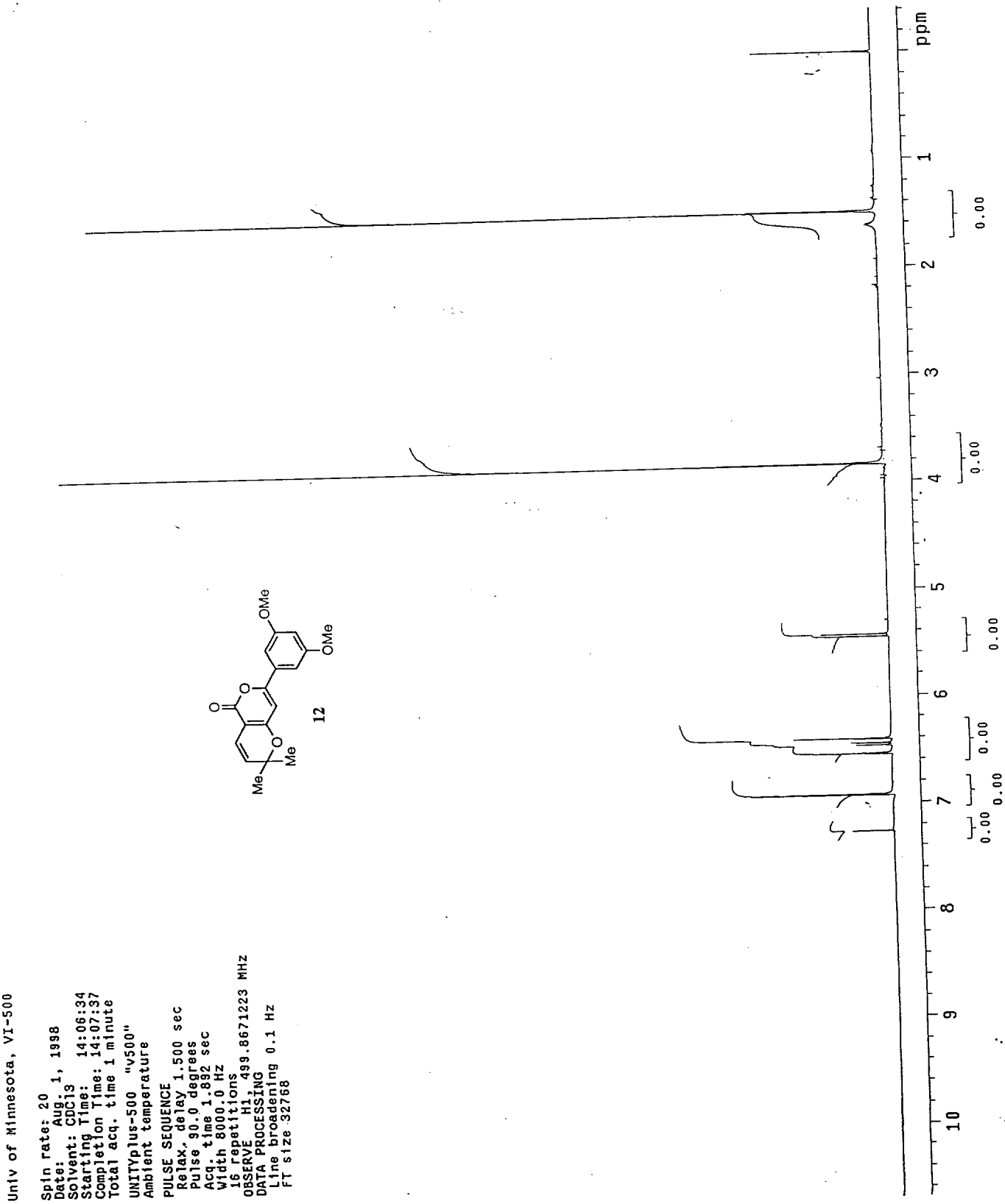
10
OMe
OMe
11
O
O
HO



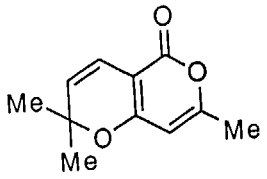
fra2

University of Minnesota
Department of Chemistry
VAC-200

User: rhshon
Date: Apr. 21, 191998
Solvent: CDCl3
File: 980421v2_0201
Starting Time: 11:31:04
Completion Time: 11:38:28
Total acq. time 1 minute

UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 4002.4 Hz
16 repetitions
OBSERVE H1, 200.1209122 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



14

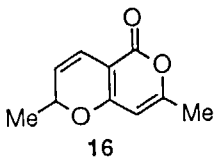
fraction 1

University of Minnesota
Department of Chemistry
VAC-200

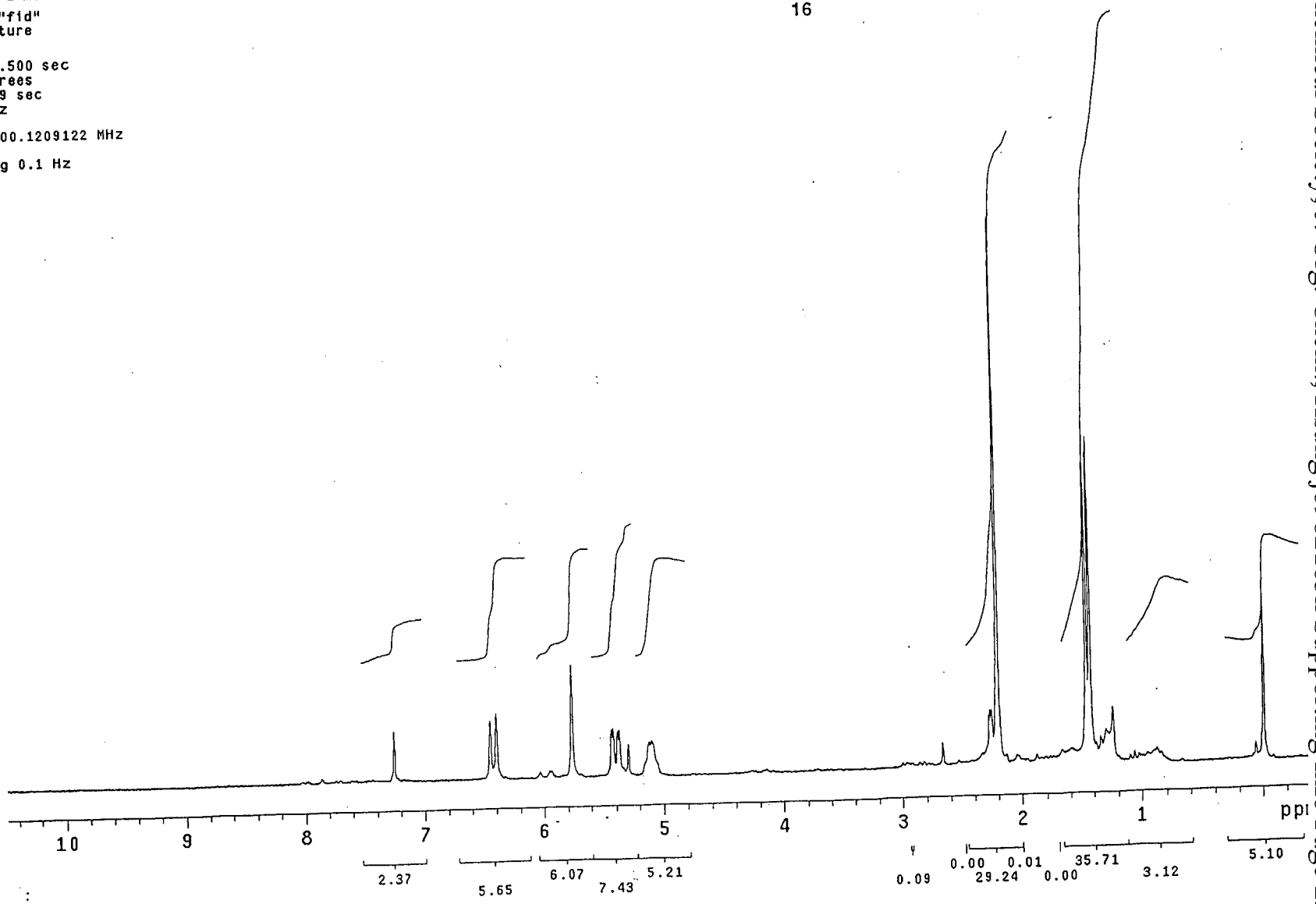
User: rhshon
Date: Apr. 22, 191998
Solvent: CDCl3
File: 980422v2_1101
Starting Time: 19:04:22
Completion Time: 19:26:27
Total acq. time 1 minute

UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 4002.4 Hz
16 repetitions
OBSERVE H1, 200.1209122 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



16



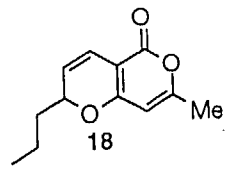
transhexenalcde

University of Minnesota
Department of Chemistry
VAC-300

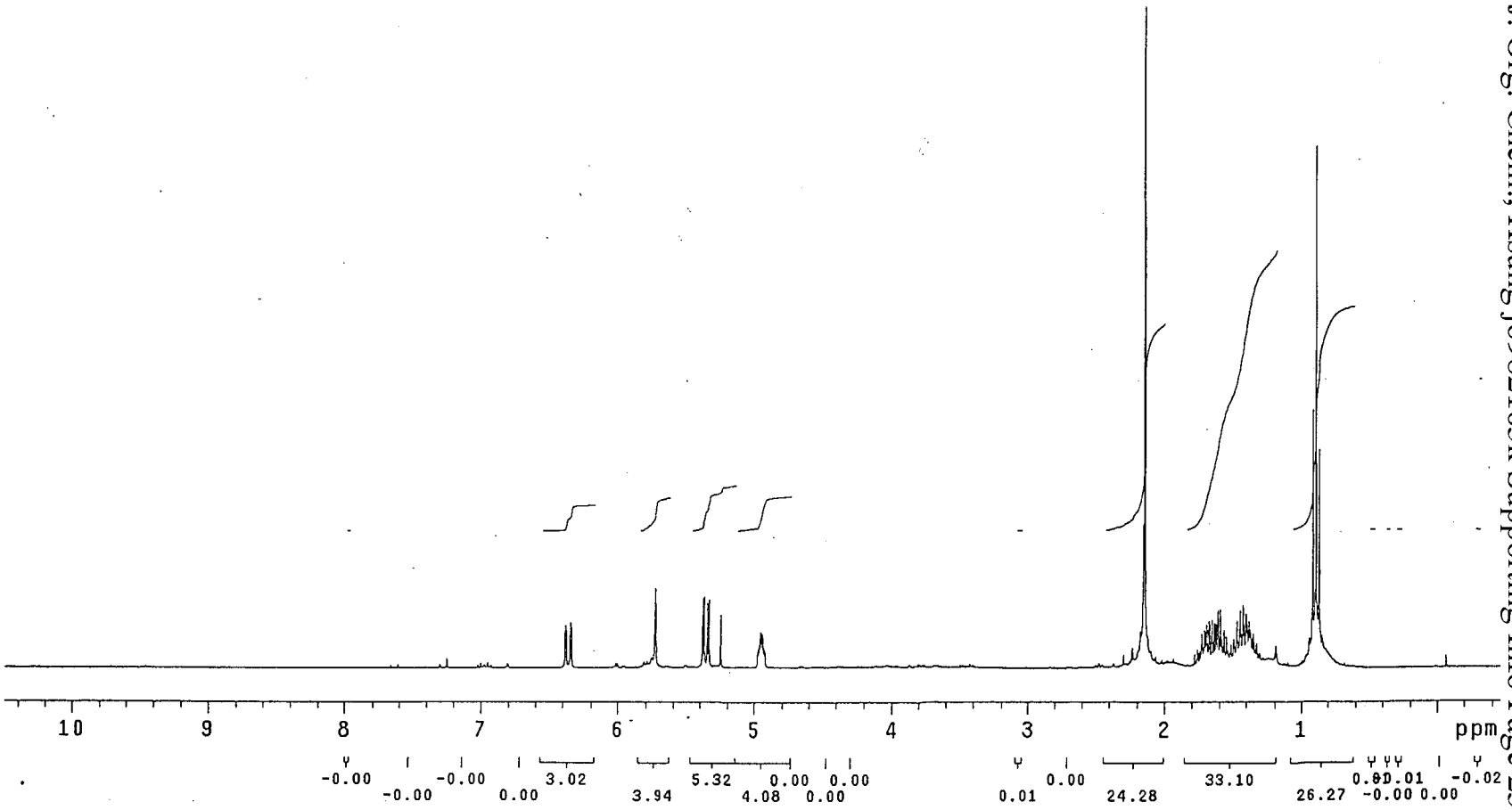
User: rhshon
Date: Jul. 2, 191998
Solvent: CDCl3
File: 980701v3_4301
Starting Time: 00:06:53
Completion Time: 00:13:57
Total acq. time 1 minute

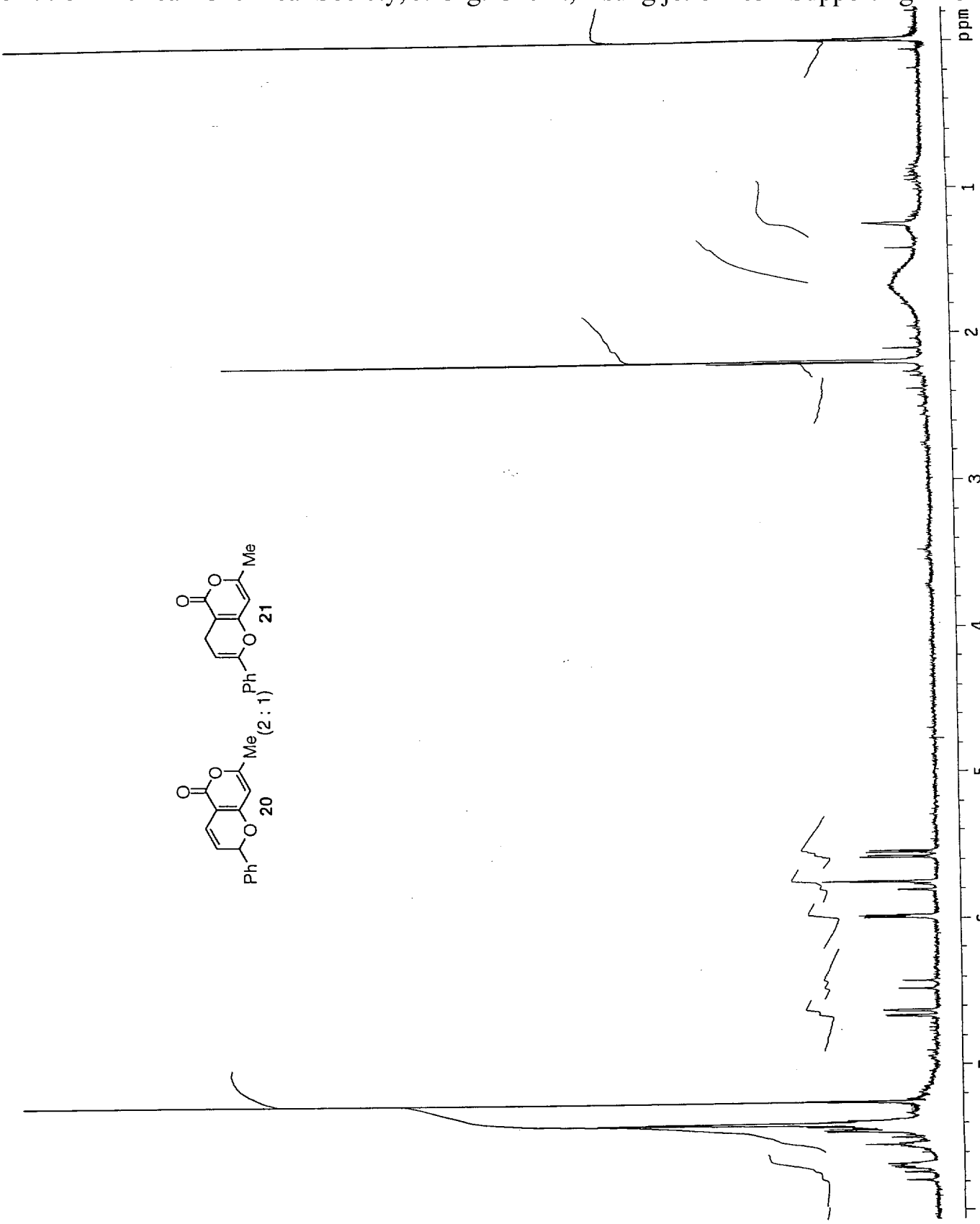
UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9572854 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536



18

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Ph
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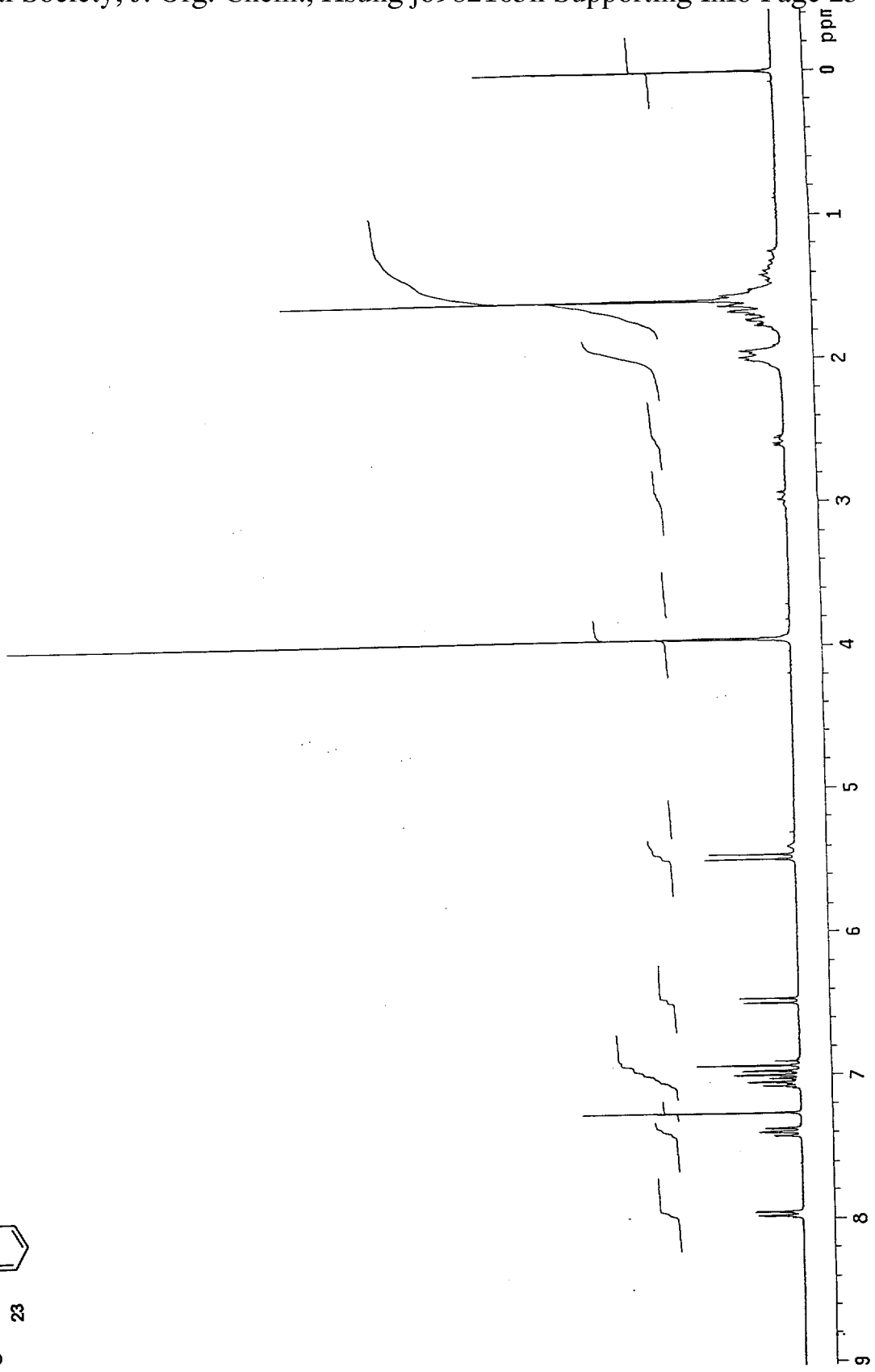
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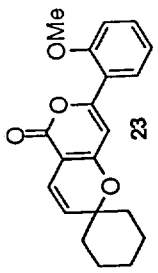
9


OMe
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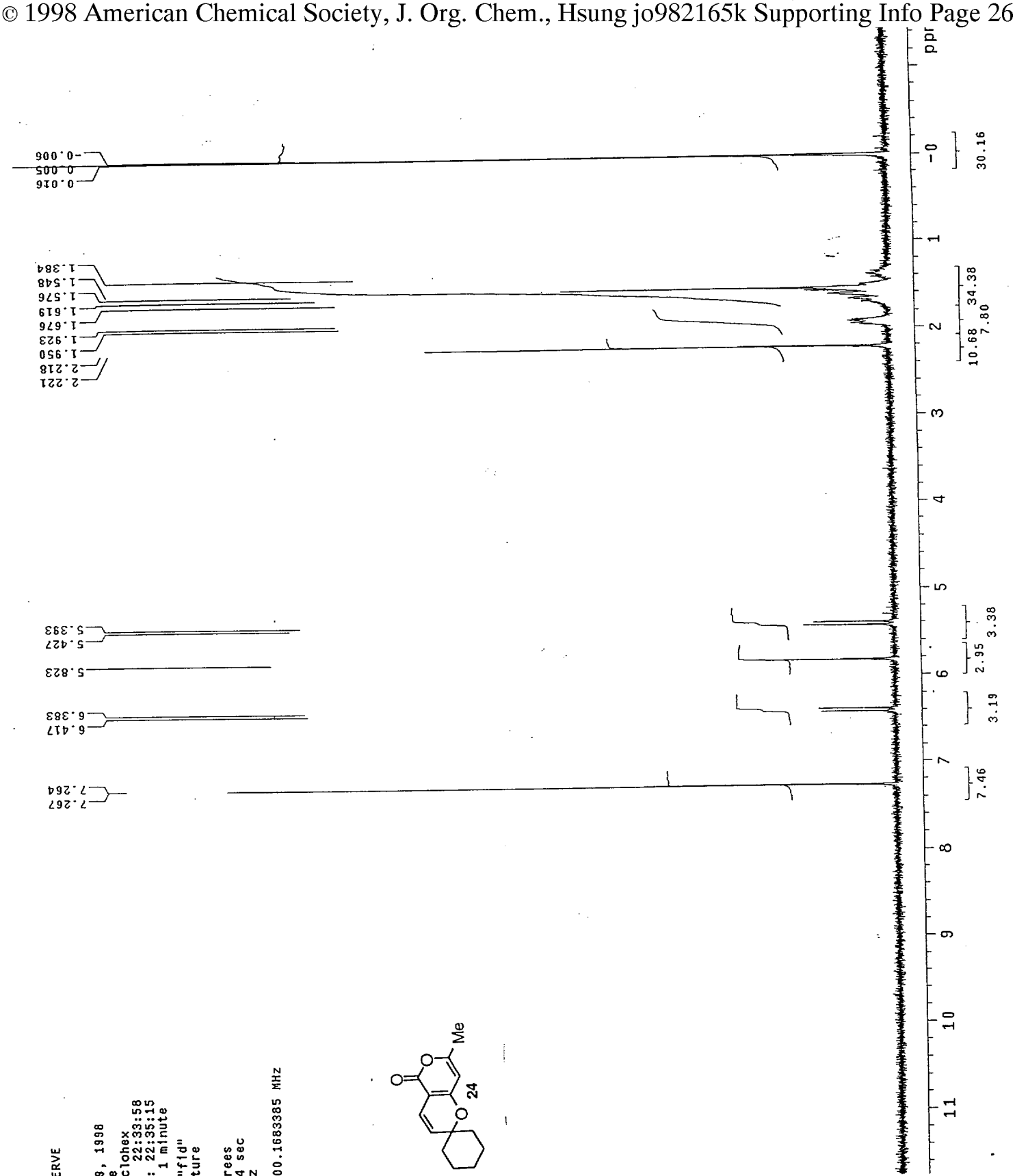
O
O
23



STANDARD 1H OBSERVE

User: rhshon
Date: May. 29, 1998
Solvent: Benzene
File: enalcyclohex
Starting Time: 22:33:58
Completion Time: 22:35:15
Total acq. time 1 minute

UNITYplus-500 "fld"
Ambient temperature

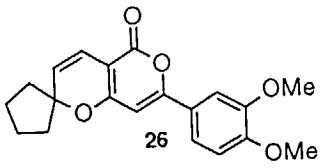
PULSE SEQUENCE
Pulse 31.5 degrees
Acq. time 3.744 sec
Width 4000.0 Hz
16 repetitions
OBSERVE H1, 300.1683385 MHz
DATA PROCESSING
FT size 32768

cdecyclopen34methoxy

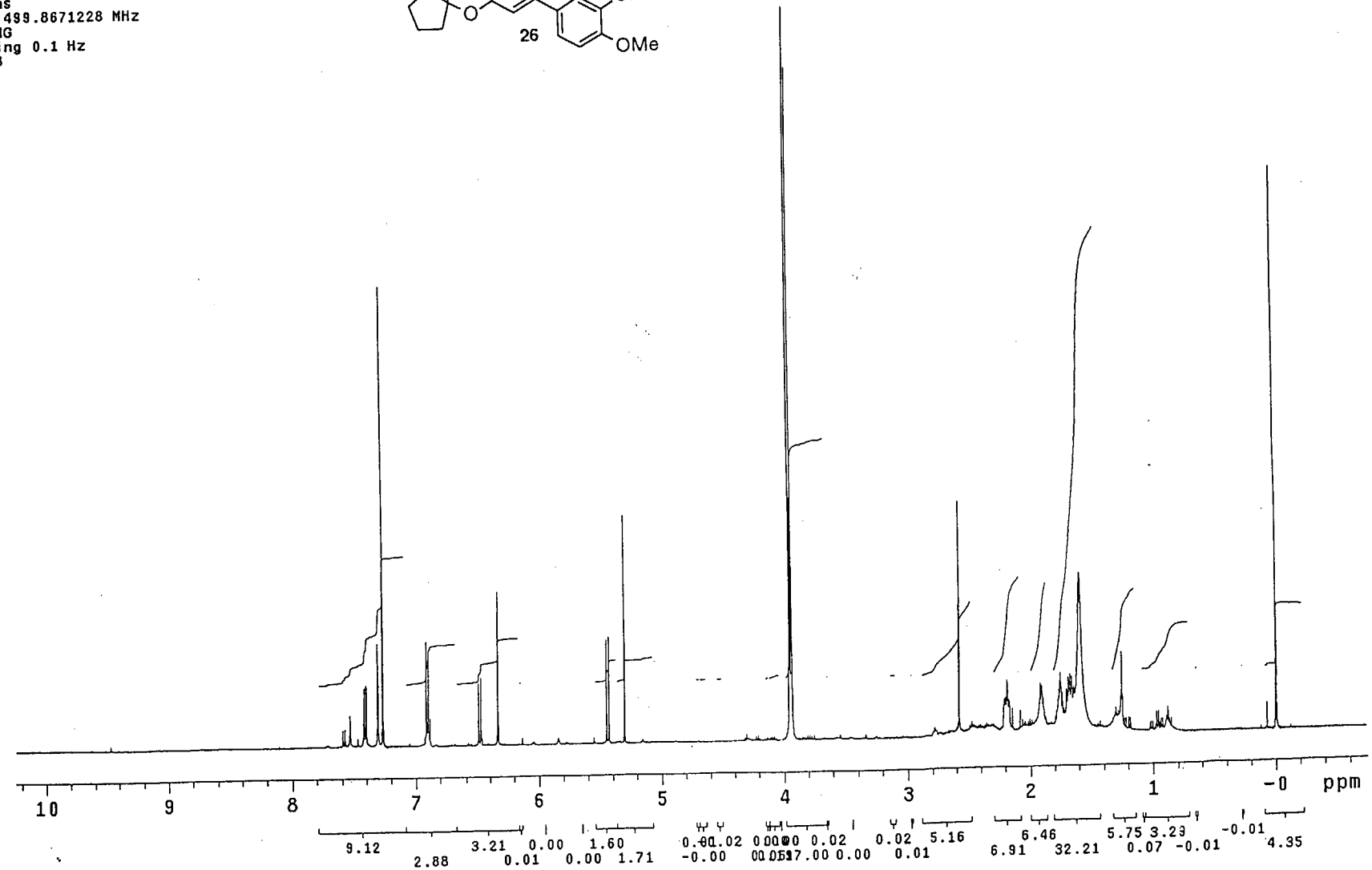
User: rhshon
Date: Jul. 10, 191998
Solvent: CDCl3
File: cdecyclopen3,4methoxy
Starting Time: 19:49:31
Completion Time: 19:50:30
Total acq. time 1 minute

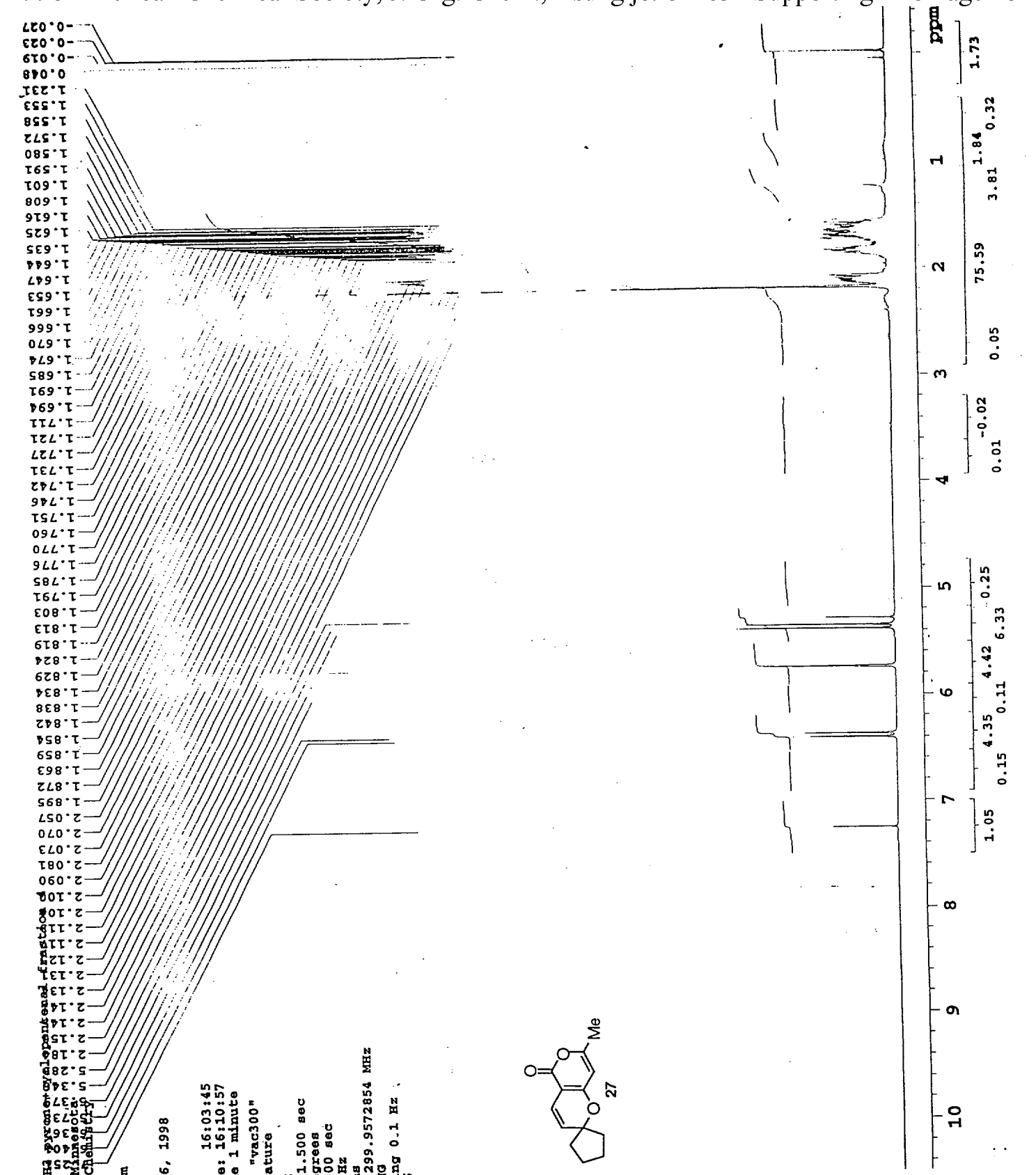
UNITYplus-500 "fid"
Ambient temperature

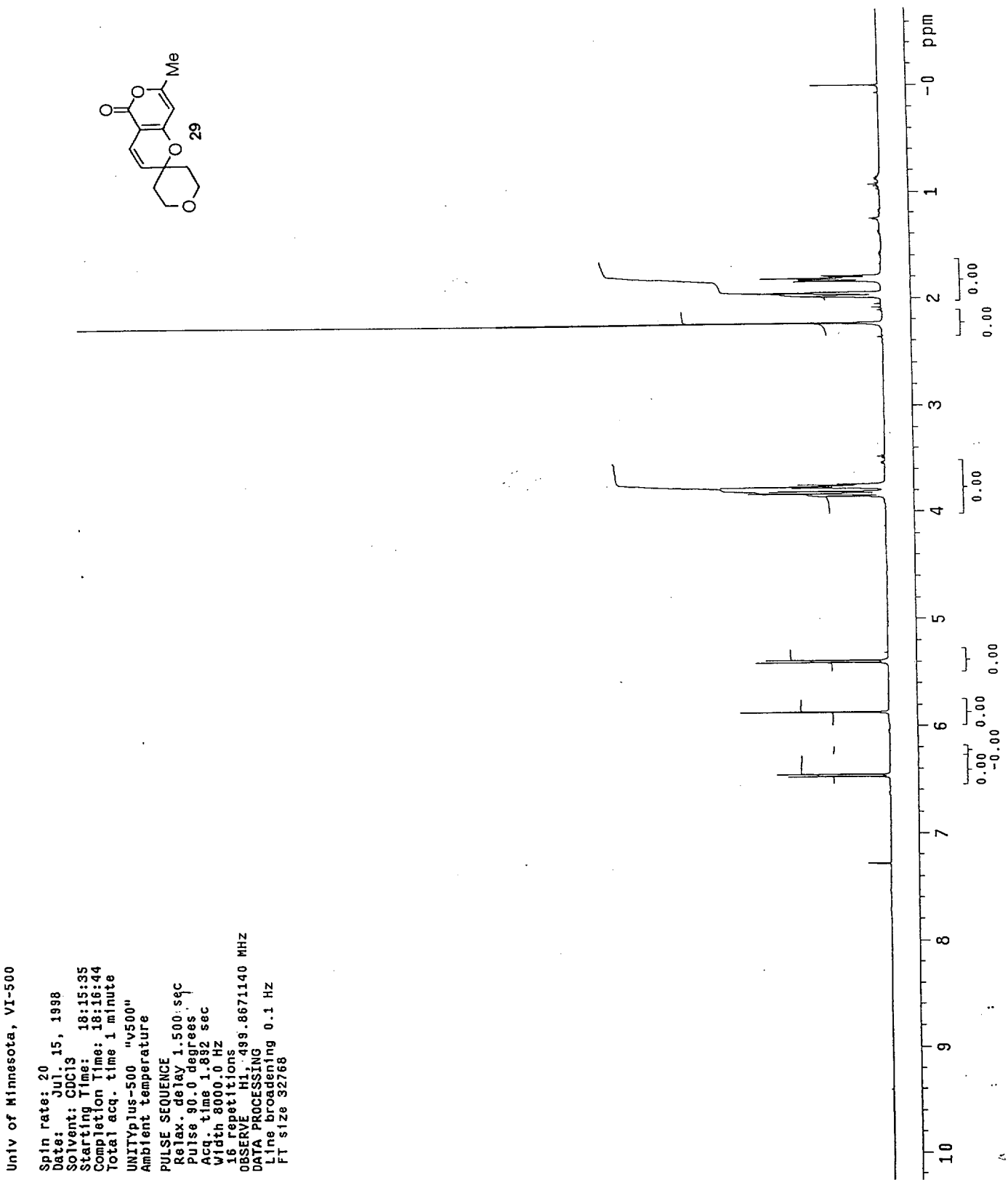
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8671228 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768

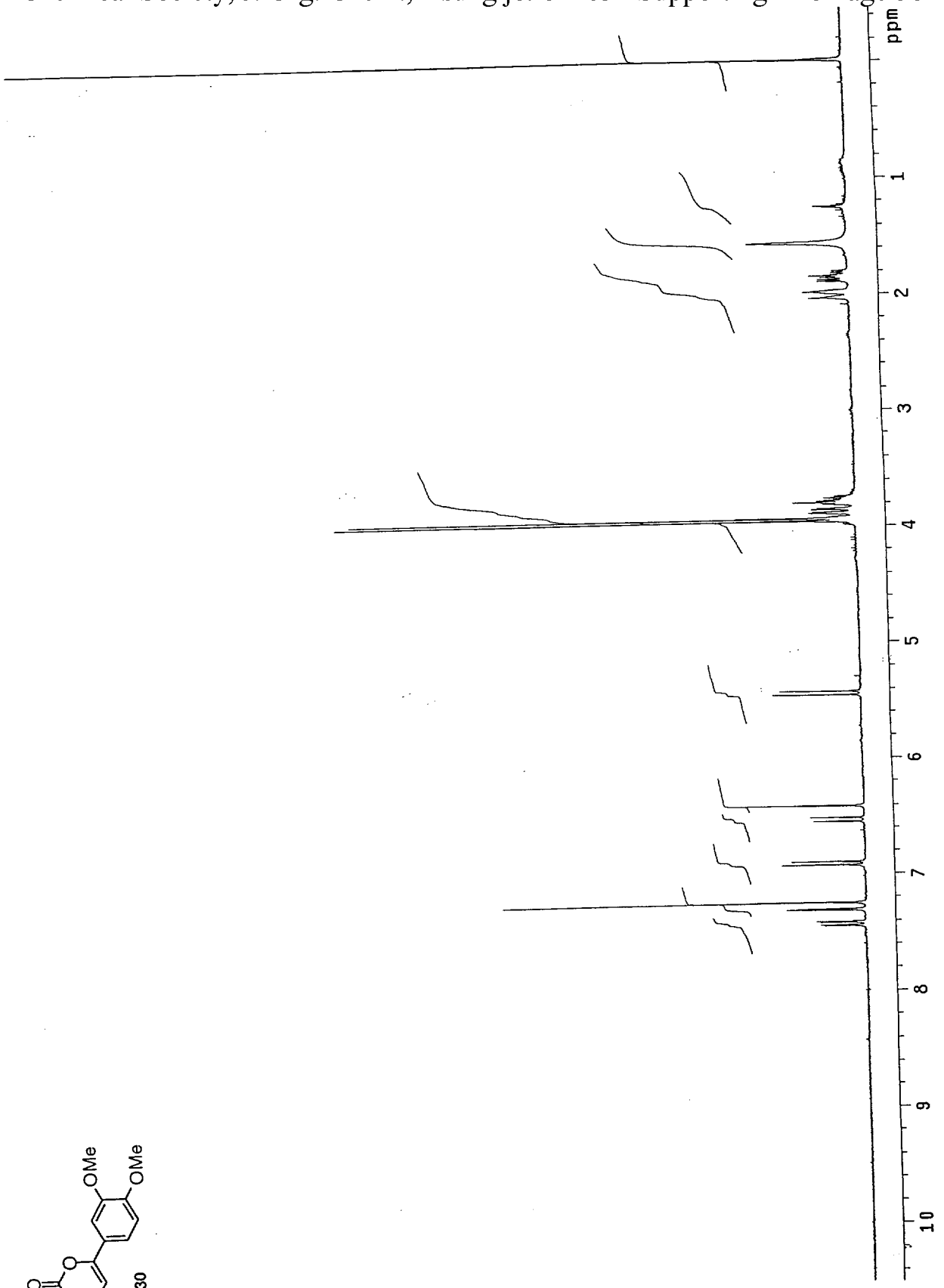


26









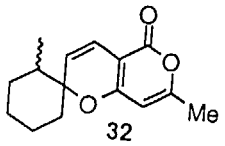
30

Univ of Minnesota, VI-500

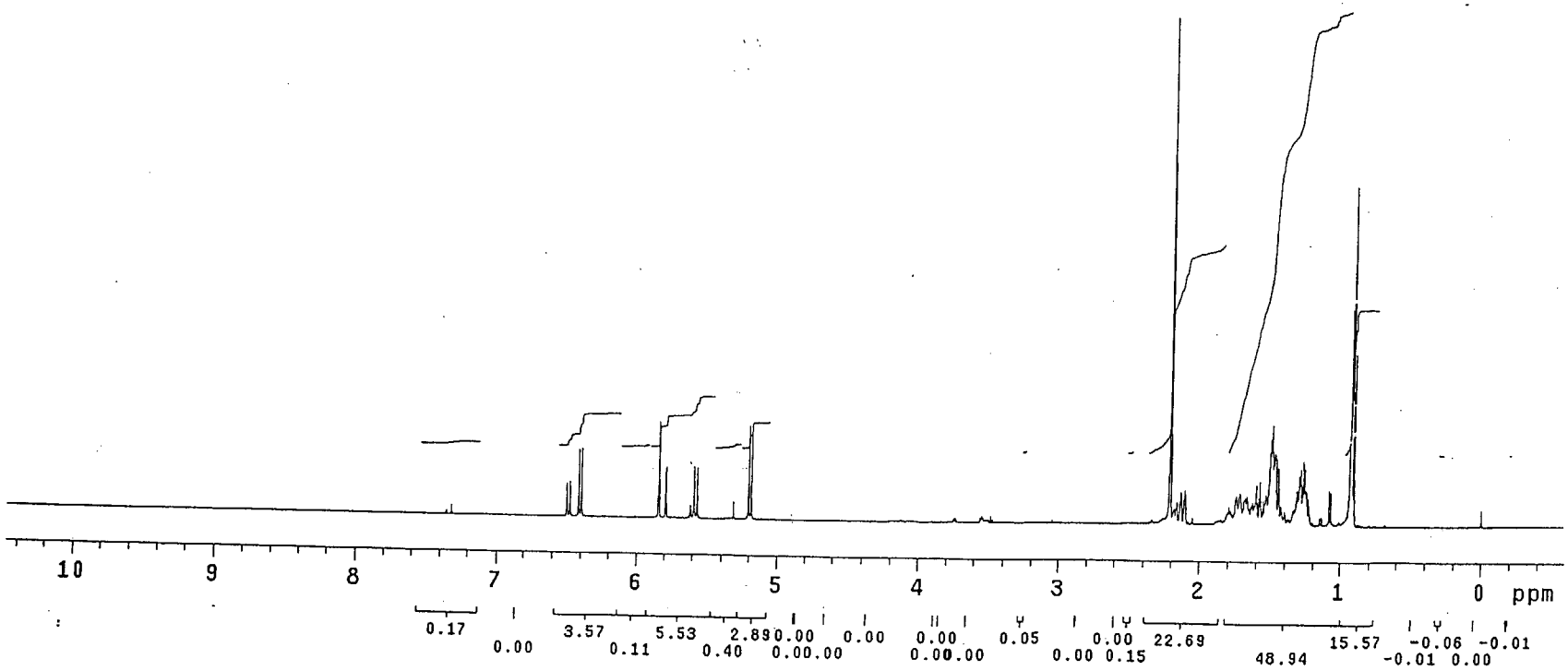
User: rhshon
Date: Jul. 28, 191998
Solvent: CDCl3
File: hexmethylenalf2
Starting Time: 21:30:42
Total acq. time 1 minute

UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8670954 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



32

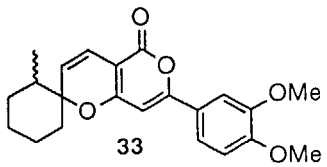


STANDARD 1H OBSERVE

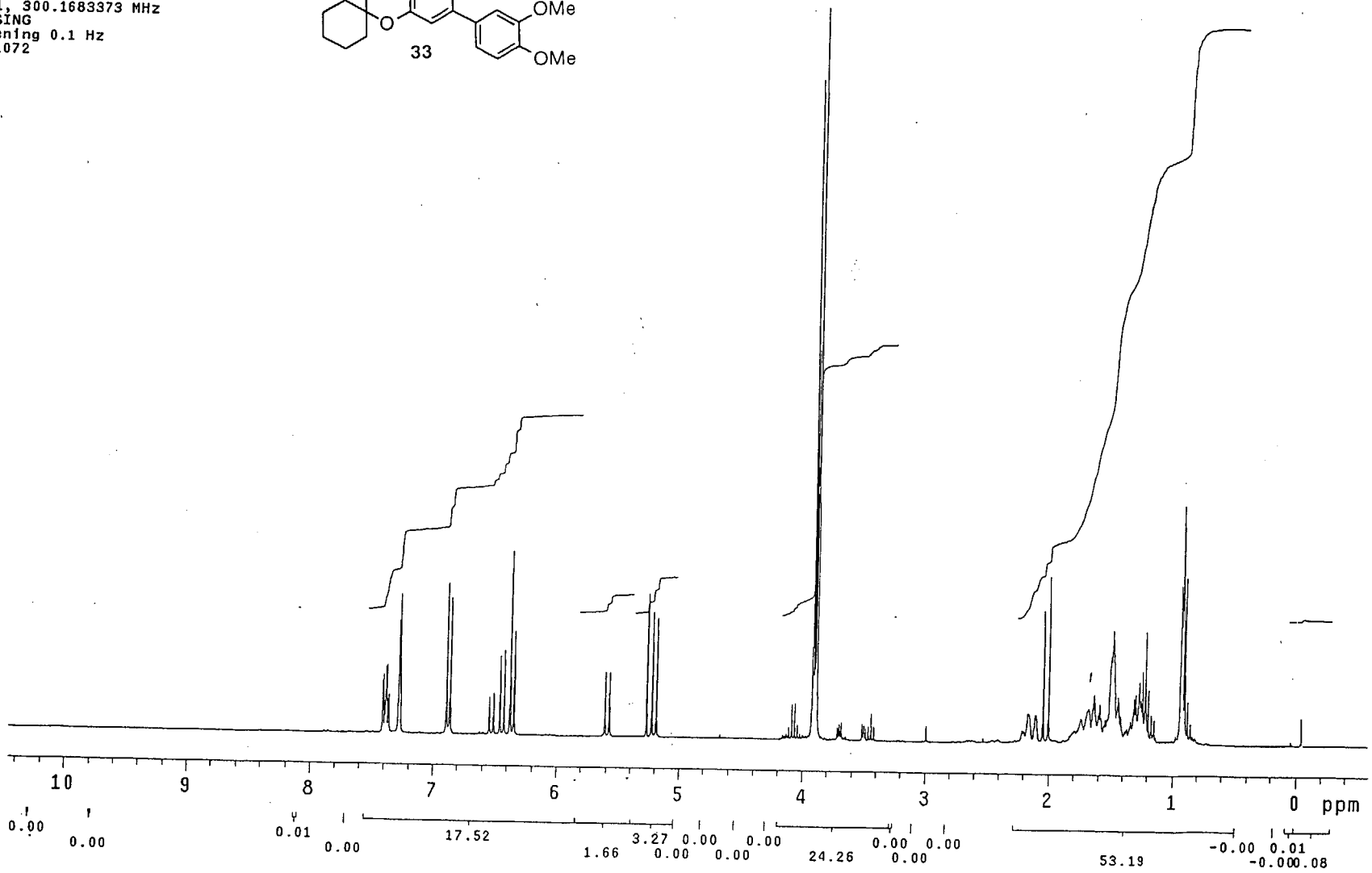
User: rhshon
Date: Jul. 29, 1998
Solvent: CDCl3
File: phenylmethycyclohexylenal
Starting Time: 16:58:58
Completion Time: 17:00:11
Total acq. time 1 minute

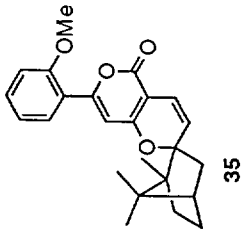
UNITYplus-500 "fid"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 6003.3 Hz
16 repetitions
OBSERVE H1, 300.1683373 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072



33





35