Studies directed toward the synthesis of the massileunicellins. 2.

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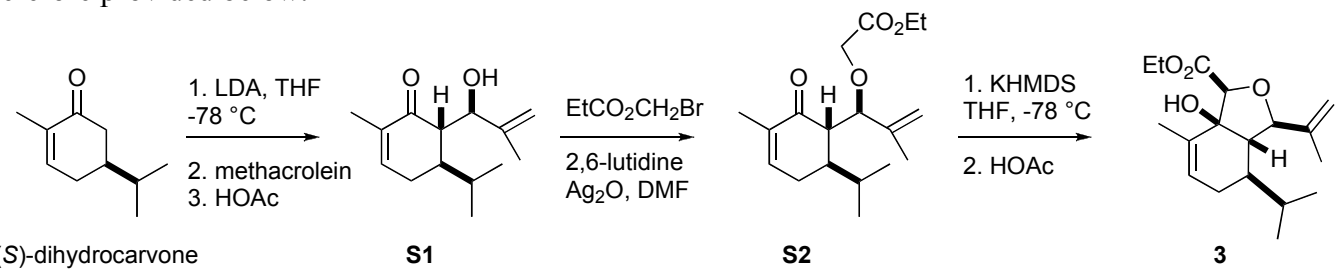
Supplementary data

Our previous report (ref 7, main text) was published prior to *Tetrahedron Letters'* providing supplementary data online. The experimental procedures and data for compounds **S1**, **S2** and **3** are therefore provided below.



(*S*)-dihydrocarvone **S1** **S2** **3**

Hydroxyketone S1. To a solution of diisopropylamine (8.77 g, 86.7 mmol) in THF (100 mL) was added dropwise n-BuLi (30.2 mL, 2.87 M in hexane, 86.7 mmol) at -78 °C. After 15 min, (*S*)-dihydrocarvone (9.63 g, 62.0 mmol) was added dropwise. The mixture was allowed to stir for 15 min, after which methacrolein (8.l g, 115.6 mmol) was added dropwise. After 4 h at -78 °C, AcOH (5.21 g, 86.7 mmol) was added. After 20 min, the reaction mixture was allowed to warm to rt, then was diluted with ether (200 mL) and washed with water (150 mL). The aqueous layer was extracted with ether (3 x 100 mL) and the combined organic layers were washed with brine (150 mL) and dried over anhydrous $MgSO_4$. The organic solvent was removed in vacuo. Purification of the residue by flash chromatography over silica gel (1/10 v/v, EtOAc/hexanes) afforded hydroxyketone **S1** as a colorless oil (13.1 g, 95%).

IR (film) 3454, 1662 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$+ D_2O) δ 6.61 (m, 1H), 4.98 (m, 1H), 4.93 (m, 1H), 4.22 (d, J=9.5 Hz, 1H), 2.53 (dd, J=2.7, 9.4 Hz + m, 3H), 2.26-2.52 (app dhept, J=20.4, 2.8 Hz, 1H), 2.16-2.23 (app dd, J=19.9, 5.54 Hz, 1H), 1.76 (s, 3H), 1.75 (s, 3H), 1.55-1.65 (m, 2H), 0.85 (m, 6H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 202.03, 145.14, 143.76, 134.85, 114.45, 75.83, 52.91, 42.24, 29.38, 25.42, 20.80, 15.98, 15.87. Anal Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.42; H, 10.03.

Glycolate S2. To a solution of alcohol **S1** (9.3 g, 41.0 mmol) in anhydrous DMF (26 mL) was added Ag_2O (38.5 g, 166.0 mmol), ethyl bromoacetate (27.9 g, 166.0 mmol) and 2,6-lutidine (17.8 g, 166.0 mmol). The reaction mixture was allowed to stir at 4 °C for 7 days, then was filtered through a short silica gel column with ether (200 mL). The filtrate was washed with cold 3N HC1 (200 mL). The aqueous layer was extracted with ether (3 x 100 mL) and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (200 mL), brine (200 mL) and then dried over anhydrous $MgSO_4$. After removal of solvent in vacuo, the dark brown oil was purified twice via flash chromatography over silica gel (1/7 v/v, EtOAc/hexanes) to afford glycolate **S2** as a pale yellow oil (8.2 g, 65%).

IR (film) 1754, 1683 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.4 (m, 1H), 5.1 (s, 1H), 5.0 (s, 1H), 4.17 (d, J=l0.19 Hz, 1H), 4.1 (m, 2H), 3.9 (d, J=16.63 Hz, 1H), 3.8 (d, J=16.63 Hz, 1H), 2.7 (dd, J=10.19, 1.78 Hz, 1H), 2.42 (app dsept, J=20.0, 2.6 Hz, 1H), 2.2 (dd, J=5.2, 19.90 Hz, lH), 1.81 (s, 3H), 1.63 (s, 3H), 1.4-1.6 (m, 2H), 1.20 (t, J=7.13 Hz, 3H), 0.86 (m, 6H). ^{13}C-NMR (67 MHz, $CDC1_3$) δ 200.06, 170.15, 141.66, 140.38, 135.07, 117.84, 84.11, 64.33, 60.42, 51.68, 42.67, 29.06, 25.43, 21.37, 20.52, 16.05, 15.73, 14.15. HRMS calcd for $C_{18}H_{29}O_4$ (MH^+), 308.1988, found 309.2082.

Isobenzofuran 3. KHMDS (58.2 mL, 0.5 M in toluene, 29.1 mmol) was added over 5 min to a solution of glycolate **S2** (7.8 g, 25.5 mmol) in THF (100 mL) at -78 °C. After addition of KHMDS, AcOH (1.84 g, 30.7 mmol) was added at -78 °C immediately in one portion. After 10 min at -78 °C, the reaction mixture was warmed to rt, diluted with ether (150 mL) and washed with water (100 mL). The aqueous layer was extracted with ether (3 x 80 mL) and the combined organic layers were washed with brine (150 mL) and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo. Purification of the residue by flash chromatography over silica gel (1/10 v/v, EtOAc/hexanes) afforded isobenzofuran **3** as a colorless oil (6.2 g, 85%).

IR (film) 3511, 1737 cm^{-1}. ^{1}H-NMR (270 MHz, $CDC1_3$) δ 5.56 (m, 1H), 5.19 (s, 1H), 4.94 (s, 1H), 4.15-4.28 (m, 4H), 3.18 (s, 1H), 2.26 (t, J=7.92 Hz, 1H), 1.9 (m, 2H), 1.75-1.9 (m, 4H), 1.7 (s, 3H), 1.3 (m, 1H), 1.21 (t, J=7.1 Hz, 3H), 0.90 (d, J=6.73 Hz, 3H), 0.76 (d, J=6.73 Hz, 3H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 170.77, 144.63, 133.11, 113.83, 86.17, 83.46, 81.88, 61.42, 51.42, 40.52, 27.22, 23.42, 21.49, 17.97, 17.61, 14.11.

Epoxyketone 7. At -78 °C, dry pyridine (21.0 mL, 260 mmol) was added to a suspension of dry silica gel (13.0 g) and CrO_3 (13.0 g, 130 mmol) in anhydrous CH_2Cl_2 (200 mL). After 15 min, a solution of alcohol **3** (4.78 g, 15.5 mmol) in CH_2Cl_2 (50 mL) was added at -78 °C. The resultant mixture was allowed to warm to rt. After 4 h, the mixture was filtered through a short silica gel column with ether (200 mL). The filtrate was concentrated in vacuo and the residue purified via flash chromatography over silica gel (1/7 v/v, EtOAc/hexanes) to afford epoxyketone **7** as a white solid, mp 94-96 °C, (4.5 g, 90%).

IR (film) 1749, 1720 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.08 (s, 1H), 5.02 (s, 1H), 4.36 (s, 1H), 4.1-4.3 (m, 3H), 2.64 (d, J=9.5 Hz, 1H), 2.59 (m, 1H), 2.52 (d, J=11.5 Hz, 1H), 2.00 (dd, J=2.5, 13.0 Hz, 1H), 1.92 (s, 3H), 1.67-1.82 (m, 2H), 1.44 (s, 3H), 1.26 (t, J=7.12 Hz, 3H), 0.79 (d, J=6.73 Hz, 3H), 0.75 (d, J=6.73 Hz, 3H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 207.46, 168.61, 143.34, 117.43, 89.34, 78.81, 74.50, 63.34, 61.56, 45.41, 41.37, 32.52, 28.05, 20.84, 16.07, 15.47, 14.23, 11.45. Anal Calcd for $C_{18}H_{26}O_5$ C, 67.06; H, 8.13. Found: C, 66.99; H, 8.07.

Alcohol 9. KHMDS (119.5 mL, 0.5 M in toluene, 59.8 mmol) was added dropwise to a solution of epoxyketone **7** (6.43 g, 19.93 mmol) in ether (250 mL) at -78 °C, followed after 15 min by TMSC1 (9.59 mL, 79.72 mmol). The reaction mixture was allowed to warm to rt. After 3 h, it was poured into cold saturated aqueous $NaHCO_3$ solution (300 mL) and extracted with cold hexanes (3 x 150 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford enol ether **8** as a pale yellow oil (11.0 g, 100%), which was used without further purification.

To a solution of enol ether **8** (11.0 g, 19.93 mmol) and acetone (14.8 mL, 199.3 mmol) in CH_3CN (290 mL) was added an aqueous Na_2EDTA solution (199.3 mL, 4 x 10^{-4} M) at rt. A mixture of Oxone (16.7 g, 26.63 mmol) and $NaHCO_3$ (6.0 g, 69.2 mmol) was added to the above mixture in portions over 10 h. The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 200 mL). The combined extracts were washed with brine (300 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to yield a pale yellow oil, 11.8 g.

The oil was dissolved in anhydrous THF (100 mL) and TBAF (43 mL, 1 M in THF, 43 mmol) was added slowly into the solution at 0 °C. After 30 min, water (100 mL) was added into the reaction mixture.

The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 60 mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Purification of the residue via flash chromatography over silica gel (1/6 to 1/3 v/v, EtOAc/hexanes) afforded alcohol **9** as a pale yellow oil (5.6 g, 83%).

IR (film) 3480, 1730, 1676 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.02 (s, 1H), 4.97 (s, 1H), 4.75 (d, J=6.93 Hz, 1H), 4.66 (dd, J=4.75, 10.98 Hz, 1H), 4.2 (m, 2H), 3.3 (m, 2H), 3.16 (s, 1H), 1.95 (m, 1H), 1.79 (s, 3H), 1.68 (t, J=10.98 Hz, 1H), 1.58 (s, 3H), 1.30 (t, J=7.12 Hz, 3H), 1.07 (d, J=6.93 Hz, 3H), 0.97 (d, J=6.93 Hz, 3H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 208.93, 161.59, 143.29, 142.88, 120.59, 114.75, 88.89, 73.37, 72.42, 62.29, 56.27, 46.13, 27.54, 22.58, 21.67, 16.66, 16.37, 14.04. HRMS: Calcd for $C_{18}H_{26}O_6Na$, 361.1627; found 361.1628.

Triol 10. Anhydrous AcOH (58 mL) was added slowly into a suspension of $NMe_4BH(OAc)_3$ (22.6 g, 85.5 mmol) in anhydrous CH_3CN (58 mL). After 40 min, the mixture was cooled to -43 °C and a solution of ketone **9** (3.69 g, 10.88 mmol) in CH_3CN (58 mL) was added slowly. The reaction mixture was allowed to warm to -20 °C. After 24 h, the mixture was warmed to 0 °C and water (100 mL) was added. A mixture of CH_2Cl_2 (100 mL) and water (100 mL) was added and the mixture neutralized to pH 7 by addition of $NaHCO_3$ at 0 °C. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined extracts were washed with brine (150 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Purification of the residue through a short pad of silica gel (1/1, v/v, EtOAc/hexanes) afforded triol **10** as a white foam (3.52 g, 95%).

IR (film) 3435, 1732 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.14 (s, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 4.56 (d, J=11.48 Hz, 1H), 4.28 (m, 2H), 4.05 (s, 1H), 3.95 (t, J=5.34 Hz, 1H), 3.62 (s, 1H), 3.08 (t, J=12.47 Hz, 1H), 3.00 (s, 1H), 1.62-1.89 (m, 5H), 1.49 (s, 3H), 1.29 (t, J=7.12 Hz, 3H), 0.97 (d, J=6.93 Hz, 3H), 0.63 (d, J=6.73 Hz, 3H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 162.49, 142.10, 140.68, 134.81, 117.14, 91.63, 74.03, 70.50, 67.29, 62.21, 50.74, 43.75, 26.51, 23.34, 21.39, 16.62, 15.95, 14.17.

Diacetate 11. Triethylamine (5.8 mL, 40.6 mmol) was added to a solution of triol **10** (2.71 g, 7.97 mmol) and DMAP (101 mg, 0.797 mmol) in anhydrous CH_2Cl_2 (60 mL), followed by dropwise addition of Ac_2O (2.27 mL, 23.9 mmol) at -10 °C. The reaction mixture was stirred at -10 °C for 16 h. Water (100 mL) was added and the aqueous layer extracted with CH_2Cl_2 (3 x 50 mL). The combined extracts were washed with brine (100 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was purified via flash chromatography over silica gel (1/2, v/v, EtOAc/hexanes) to afford diacetate **11** as a white foam (2.71 g, 80%).

IR (film) 3460, 2965,1742 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.31 (dd, J=4.35, 7.62 Hz, 1H), 5.00 (m, 2H), 4.97 (s, 1H), 4.65 (d, J=9.90 Hz, 1H), 4.25 (m, 2H), 3.18 (dd, J=9.90, 12.27 Hz, 1H), 2.01 (s, 3H), 1.96 (s, 3H), 1.76-1.91 (m, 2H), 1.74 (s, 3H), 1.48 (s, 3H), 1.29 (t, J=7.13 Hz, 3H), 0.84 (d, J=7.13 Hz, 3H), 0.74 (d, J=6.73 Hz, 3H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 170.20, 169.89, 162.05, 142.57, 141.10, 116.06, 90.50, 74.19, 69.23, 68.18, 62.08, 48.43, 45.17, 26.61, 23.87, 21.33, 21.09, 20.85, 16.51, 15.76, 14.11.

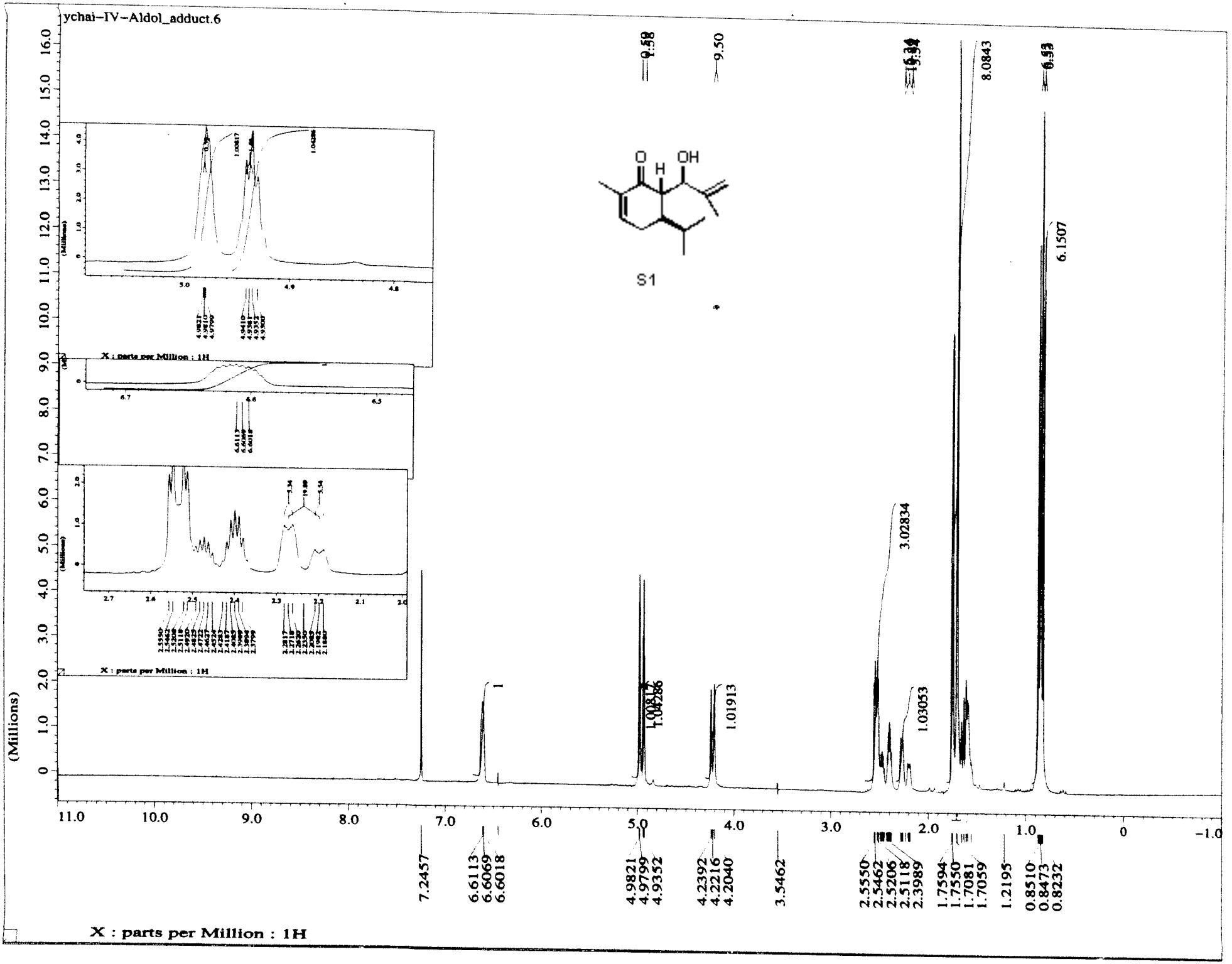
Ketone 12. A solution of OsO_4 (0.72 mL, 4 % by wt solution in water) was added dropwise to a mixture of methanesulfonamide (0.34 g, 3.53 mmol), K_2CO_3 (1.5 g, 10.51 mmol), $K_3Fe(CN)_6$ (3.45 g, 10.5 mmol), $(DHQD)_2PHAL$ (136 mg, 0.176 mmol) and diacetate **11** (1.5 g, 3.53 mmol) in t-BuOH (35 mL) and water (35 mL) at 4 °C. After 3 h at 4 °C, cold saturated $Na_2S_2O_3$ was added. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x 40 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was purified via flash chromatography over silica gel (3/1, v/v, EtOAc/hexanes) to afford the intermediate triol as a white foam (1.5 g, 95%).

To a solution of the triol (3.9 g, 8.49 mmol) in THF (80 mL) was added $NaIO_4$ (3.63 g, 16.98 mmol), followed by water (80 mL). The reaction mixture was stirred at rt for 5 h and then filtered. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine (80 mL), dried over anhydrous $MgSO_4$,filtered and concentrated in vacuo. The residue was purified via flash chromatography through a short silica gel column (1/1, v/v EtOAc/hexanes) to afford ketone **12** as a white foam (3.26 g, 90%).

IR (film) 3474, 1742 cm^{-1}. ^{1}H-NMR (270 MHz, $CDC1_3$) δ 5.36 (dd, J=3.56, 9.7 Hz, rew1H), 5.27 (s, 1H), 5.06 (d, J=3.56 Hz, 1H), 4.3 (m, 2H), 3.36 (dd, J=7.52, 12.07 Hz, 1H), 2.27 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.72-1.83 (m, 2H), 1.40 (s, 3H), 1.28 (t, J=7.12 Hz, 3H), 0.93 (d, J=6.93 Hz, 3H), 0.82 (d, J=6.73 Hz, 1H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 207.53, 170.17, 170.02, 161.34, 140.67, 75.09, 69.65, 62.07, 47.03, 46.69, 27.20, 25.93, 24.00, 21.90, 21.07, 20.85, 16.07, 14.06.

Hydroisobenzofuran 13. Crabtree's catalyst (1.24 g, 1.52 mmol) was added to a solution of ketone **12** (3.3 g, 7.62 mmol) in CH_2Cl_2 (160 mL). The reaction mixture was shaken under 80 psi of H_2 for 20 h. The mixture was concentrated in vacuo and the residue purified via flash chromatography over silica gel (1/3, v/v, EtOAc/hexanes) to afford isobenzofuran **13** as a white foam (3.3 g, 100%).

IR (film) 3474, 1740 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.37 (dd, J=3.17, 6.14 Hz, 1H), 5.00 (d, J=3.17 Hz, 1H), 4.75 (d, J=6.43 Hz, 1H), 4.58 (d, J=8.11 Hz, 1H), 4.3 (m, 2H), 2.77 (t, J=6.93 Hz, 1H), 2.52 (s, 1H), 2.45 (app q, J=7.52 Hz, 1H), 2.23 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.0 (m, 1H), 1.8 (m, 1H), 1.46 (s, 3H), 1.34 (t, J=7.32 Hz, 3H), 0.99 (d, J=6.93 Hz, 3H), 0.96 (t, J=6.93 Hz, 3H). ^{13}C-NMR (67 MHz, $CDC1_3$) δ 209.33, 171.36, 170.49, 169.85, 87.29, 80.26, 74.28, 71.66, 71.02, 61.62, 51.97, 43.33, 41.98, 29.90, 25.89, 22.70, 22.50, 21.25, 21.00, 18.39, 14.22.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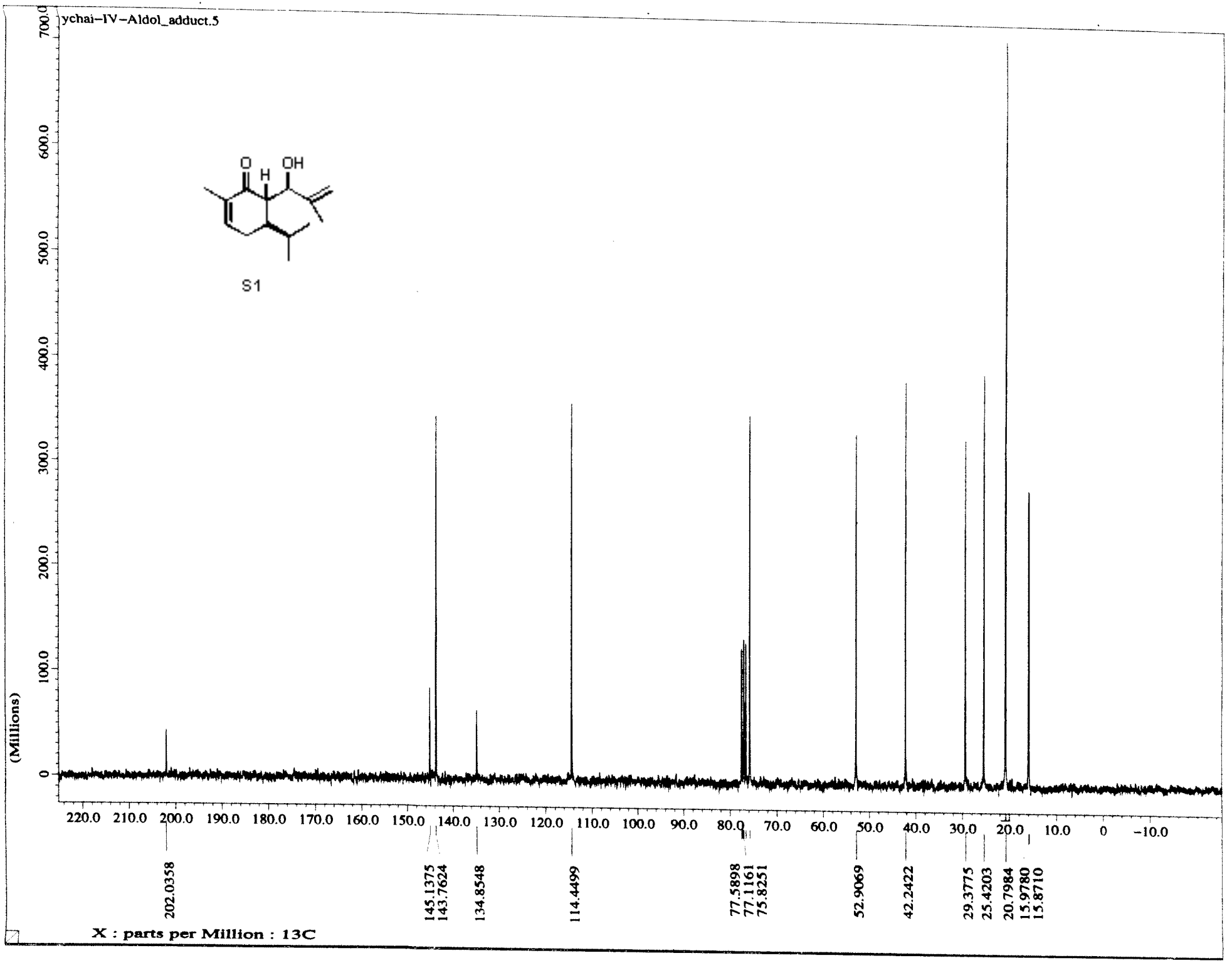
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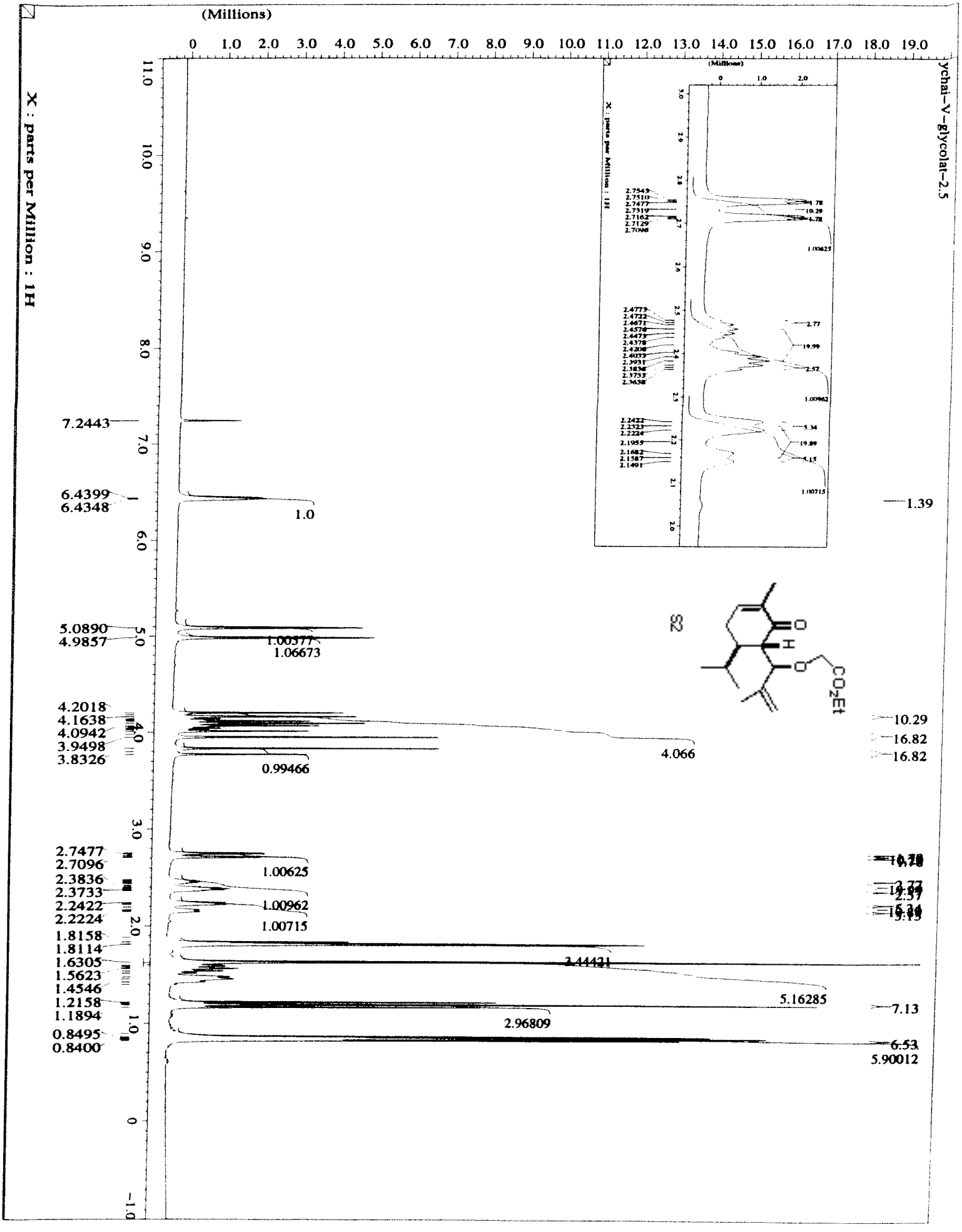
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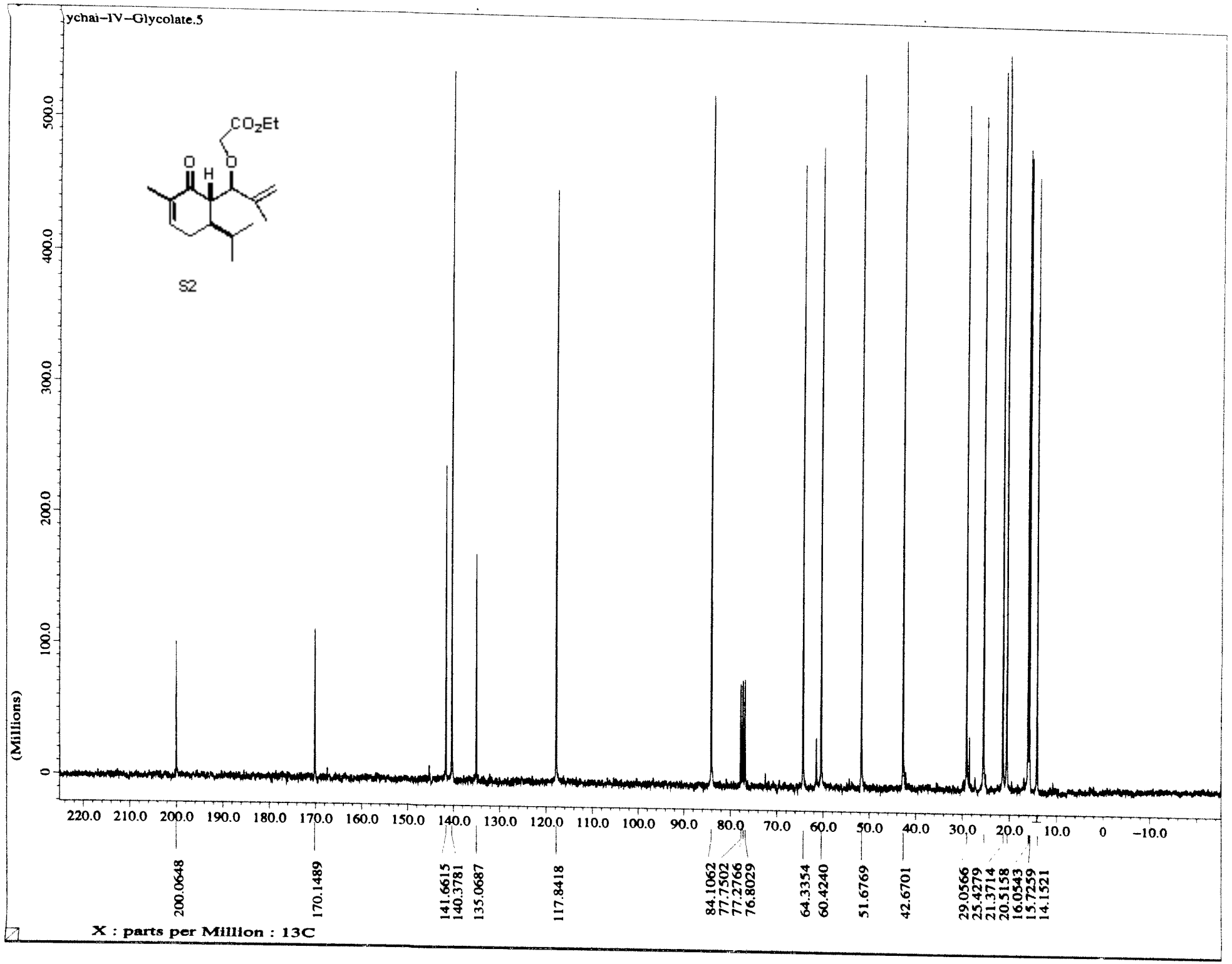
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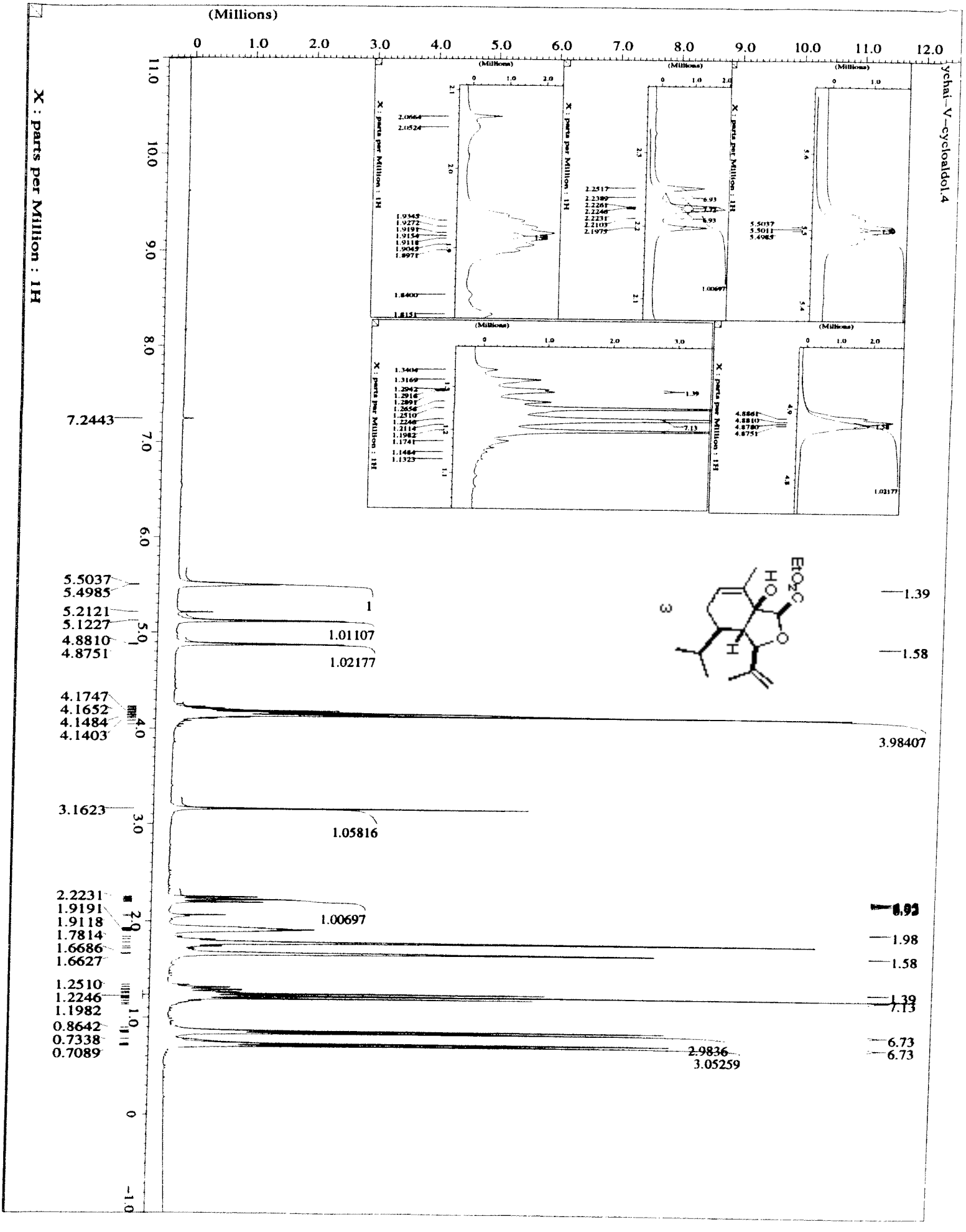
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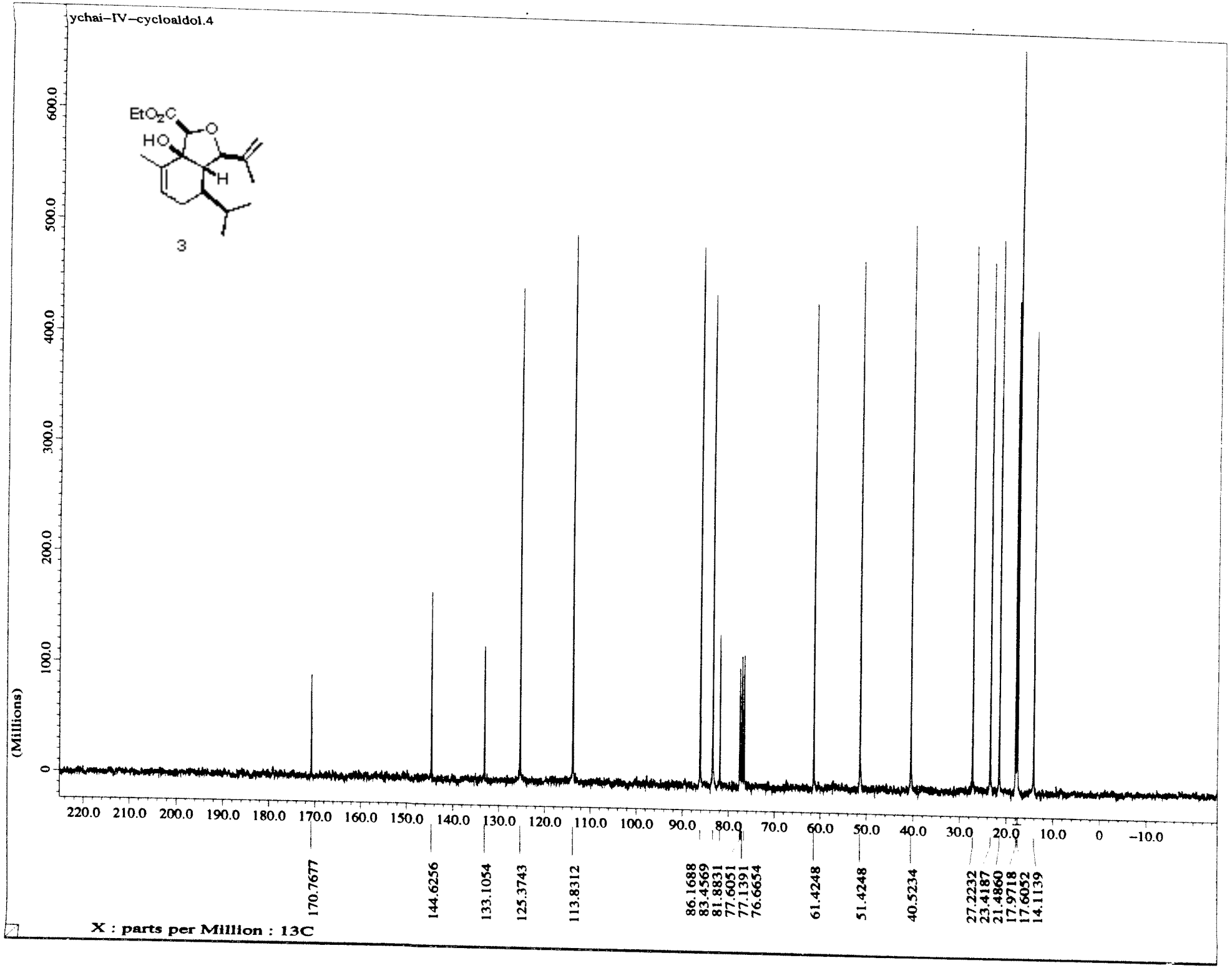
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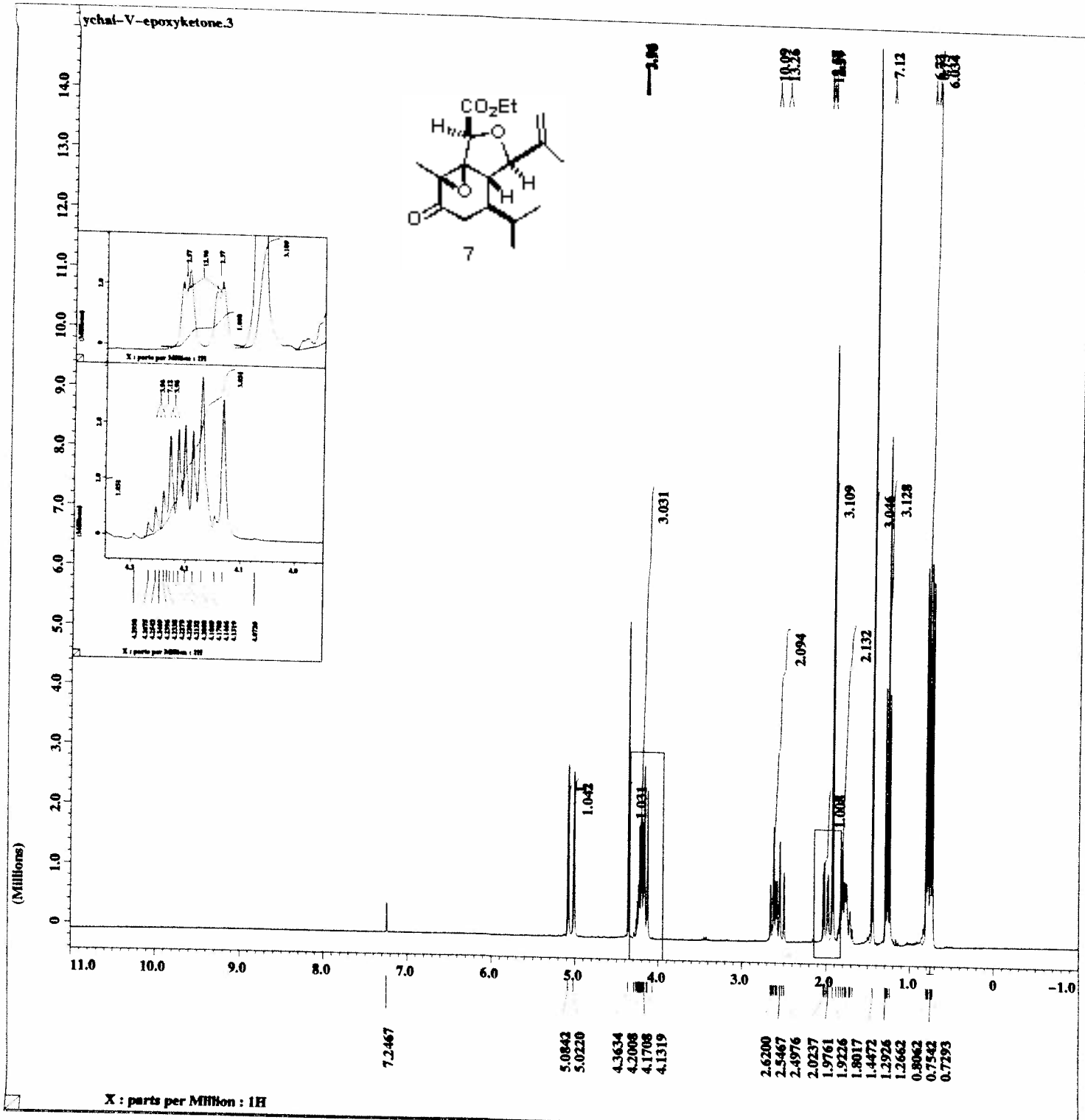
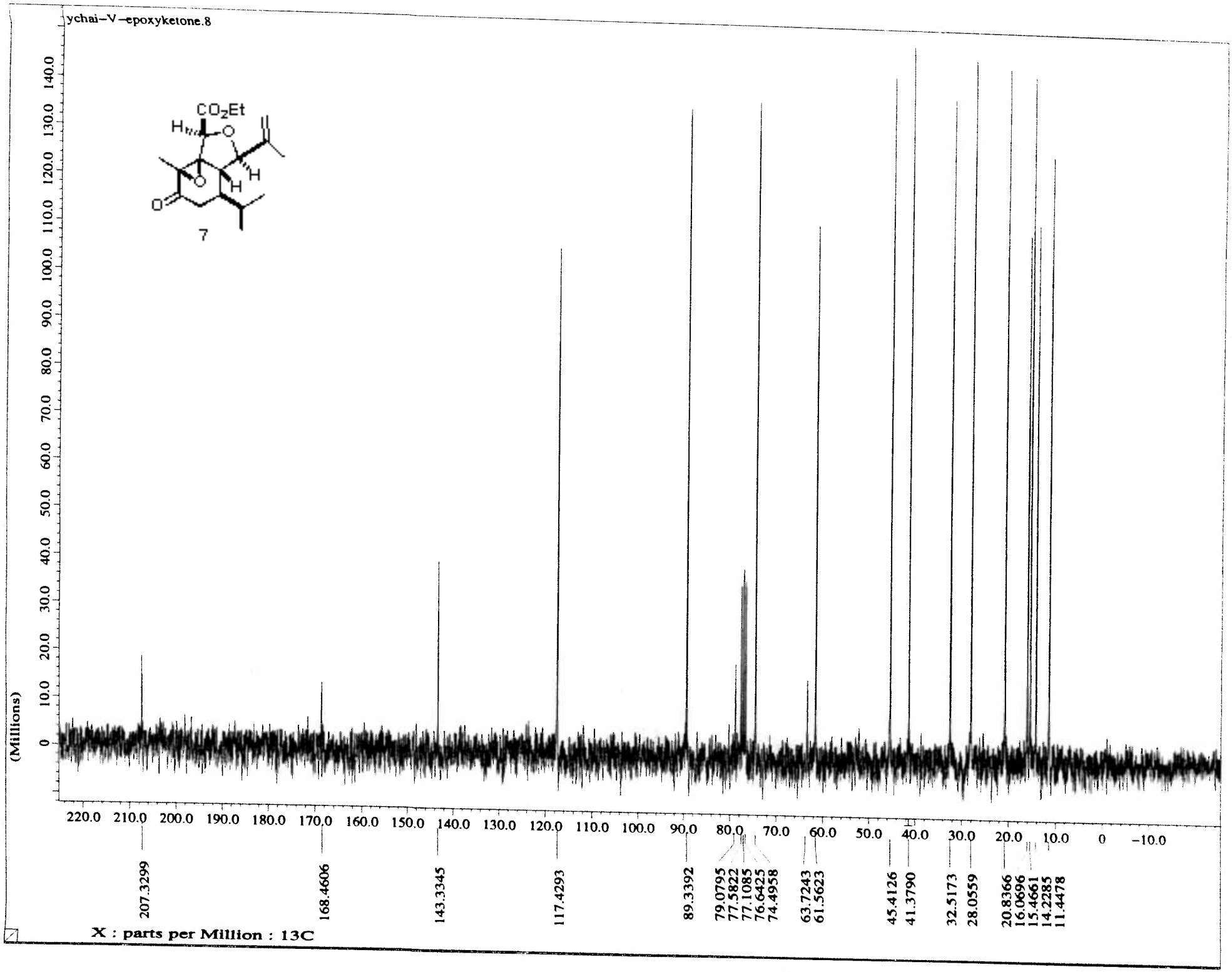
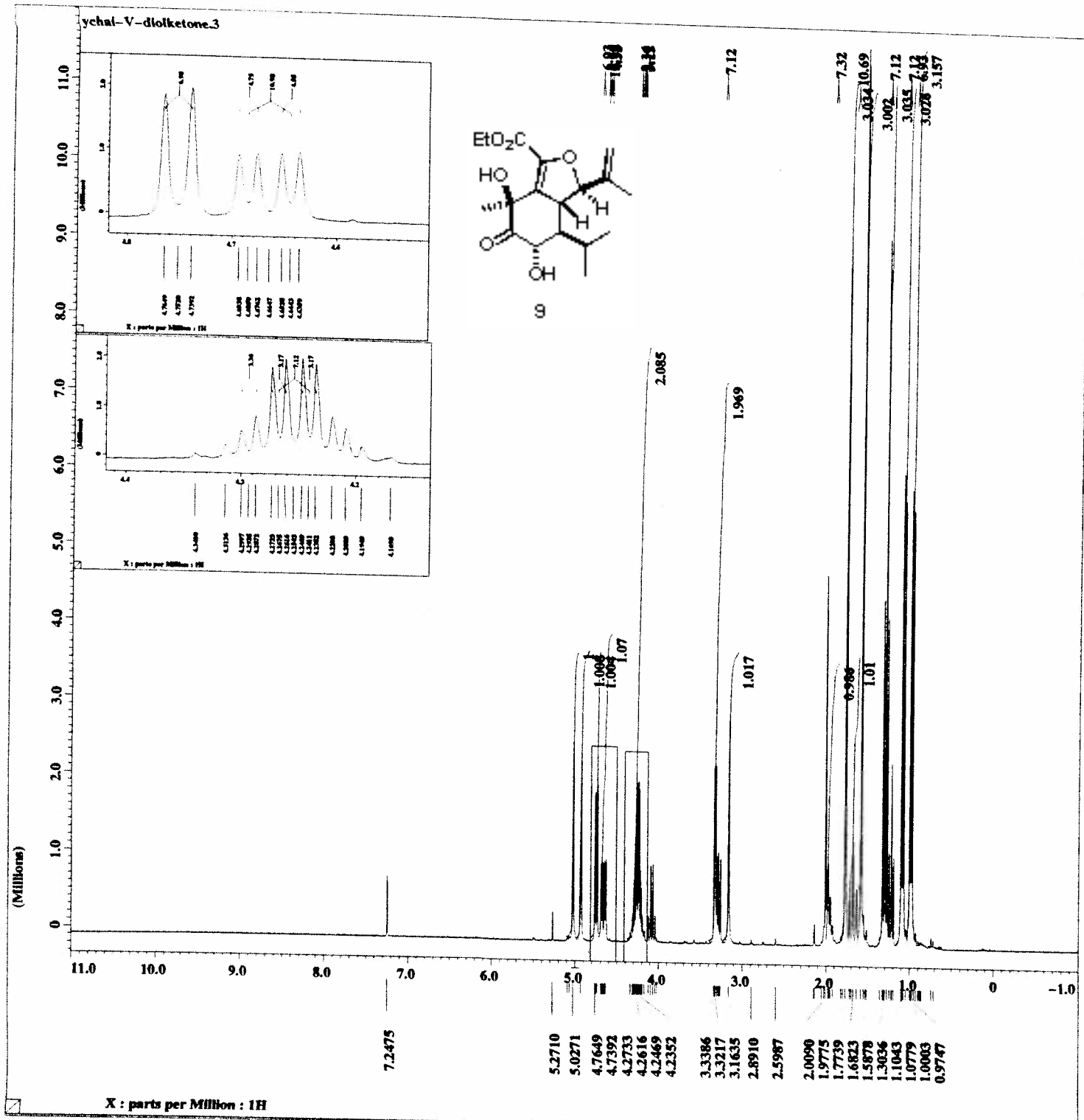


JEOL

---- ACQUISITION PARAMETERS ----

Derived from:	ychai-V-epoxyketone.1
File Name	= ychai-V-epoxyketone.4
Author	= mcintoshgroup
Sample ID	= S#401722
Content	= Single Pulse Experime
Creation Date	= 13-DEC-2004 11:59:36
Revision Date	= 13-DEC-2004 11:20:58
Spec Site	= Delta NMR
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Field_strength	= 6.345446[T] (270[MHz]
X_acq_duration	= 5.0528256[s]
X_domain	= 1H
X_freq	= 270.16608844[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.19790907[Hz]
X_sweep	= 3.24254215[kHz]
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 10.4[us]
X_acq_time	= 5.0528256[s]
X_angle	= 45[deg]
X_pulse	= 5.2[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Relaxation_delay	= 4[s]
Unblank_time	= 2[us]


ychai-V-epoxyketone.8
CO2Et
H
O
H
H
O
7
(Millions)
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
207.3299
168.4606
143.3345
117.4293
89.3392
79.0795
77.5822
77.1085
76.6425
74.4958
63.7243
61.5623
45.4126
41.3790
32.5173
28.0559
20.8366
16.0696
15.4661
14.2285
11.4478
X : parts per Million : 13C



JEOL

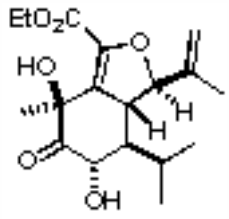
```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-diolketone.1
File Name          = ychai-V-diolketone.3
Author             = mcintosbgroup
Sample ID          = S#391090
Content            = Single Pulse Experime
Creation Date      = 13-DEC-2004 11:41:52

Revision Date      = 13-DEC-2004 10:55:46
Spec Site          = Delta NMR

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Field_strength     = 6.345446[T] (270[MHz]
X_acq_duration     = 5.0528256[s]
X_domain           = 1H
X_freq             = 270.16608844[MHz]
X_offset           = 5[ppm]
X_points           = 16384
X_prescans         = 0
X_resolution       = 0.19790907[Hz]
X_sweep            = 3.24254215[kHz]
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 10.4[us]
X_acq_time         = 5.0528256[s]
X_angle            = 45[deg]
X_pulse            = 5.2[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 4[s]
Unblank_time       = 2[us]
```

ychai-V-diolketone.5



9

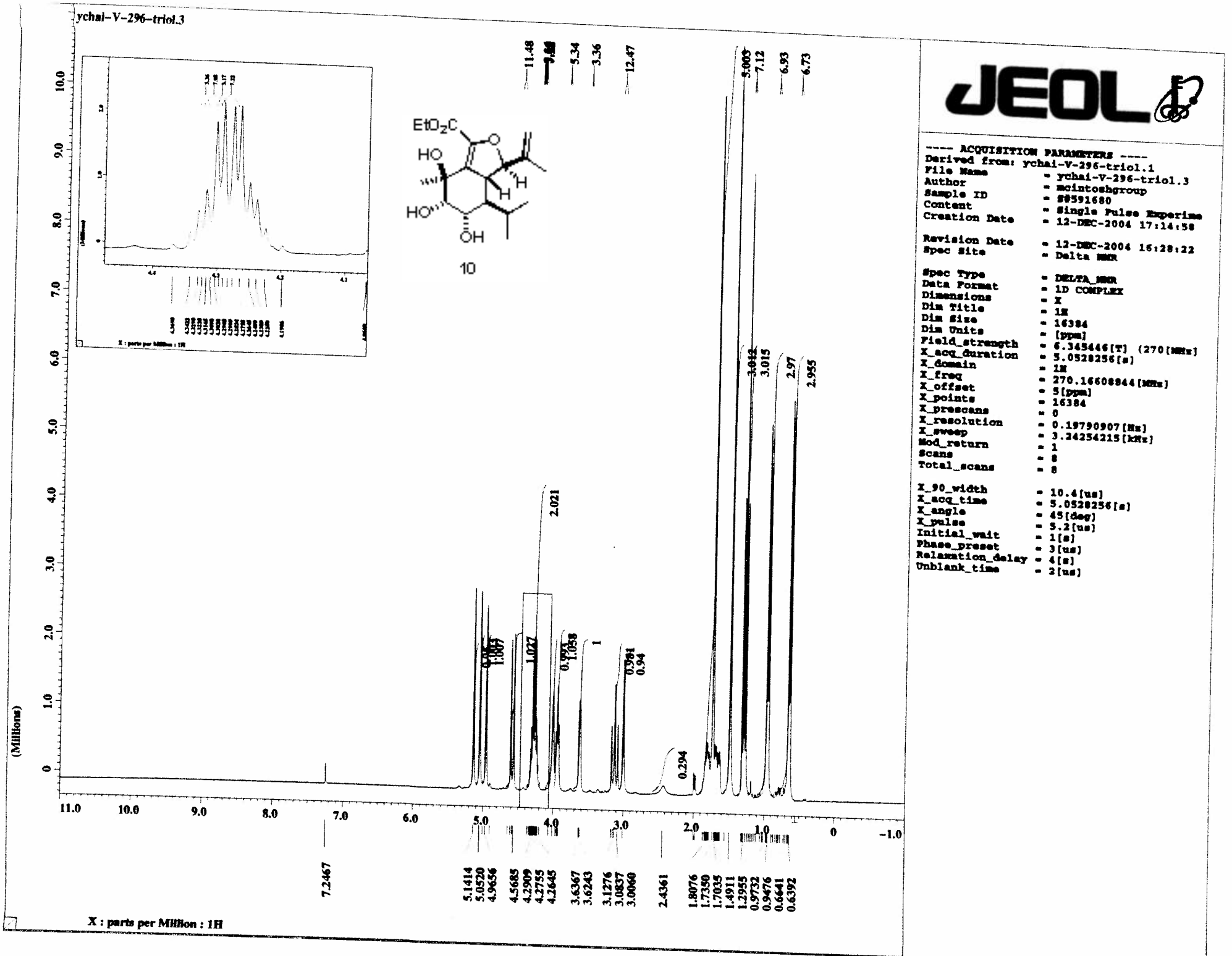
JEOL

```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-diolketone.2
File Name          = ychai-V-diolketone.5
Author             = mcintoshgroup
Sample ID          = S0391583
Content            = Single Pulse with Bro
Creation Date      = 13-DEC-2004 11:54:21

Revision Date      = 13-DEC-2004 11:11:01
Spec Site          = Delta NMR

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Field_strength     = 6.345446[T] (270[MHz]
X_acq_duration     = 1.9267584[s]
X_domain           = 13C
X_freq             = 67.93330993[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.51900643[Hz]
X_sweep            = 17.00680272[kHz]
Irr_domain         = 1H
Irr_freq           = 270.16608844[MHz]
Irr_offset         = 5[ppm]
Mod_return         = 1
Scans              = 119
Total_scans        = 119

X_90_width         = 8.3[us]
X_acq_time         = 1.9267584[s]
X_angle            = 90[deg]
X_pulse            = 8.3[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 4[s]
Unblank_time       = 2[us]
```



JEOL

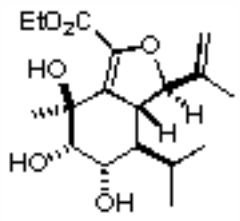
```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-296-triol.1
File Name          = ychai-V-296-triol.3
Author             = mcintoshgroup
Sample ID          = #9591680
Content            = Single Pulse Experime
Creation Date      = 12-DEC-2004 17:14:58

Revision Date      = 12-DEC-2004 16:28:22
Spec Site          = Delta NMR

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Field_strength     = 6.345446[T] (270[MHz]
X_acq_duration     = 5.0528256[s]
X_domain           = 1H
X_freq             = 270.16608844[MHz]
X_offset           = 5[ppm]
X_points           = 16384
X_prescans         = 0
X_resolution       = 0.19790907[Hz]
X_sweep            = 3.24254215[kHz]
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 10.4[us]
X_acq_time         = 5.0528256[s]
X_angle            = 45[deg]
X_pulse            = 5.2[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 4[s]
Unblank_time       = 2[us]
```

ychai-V-296-triol_copy.3



10

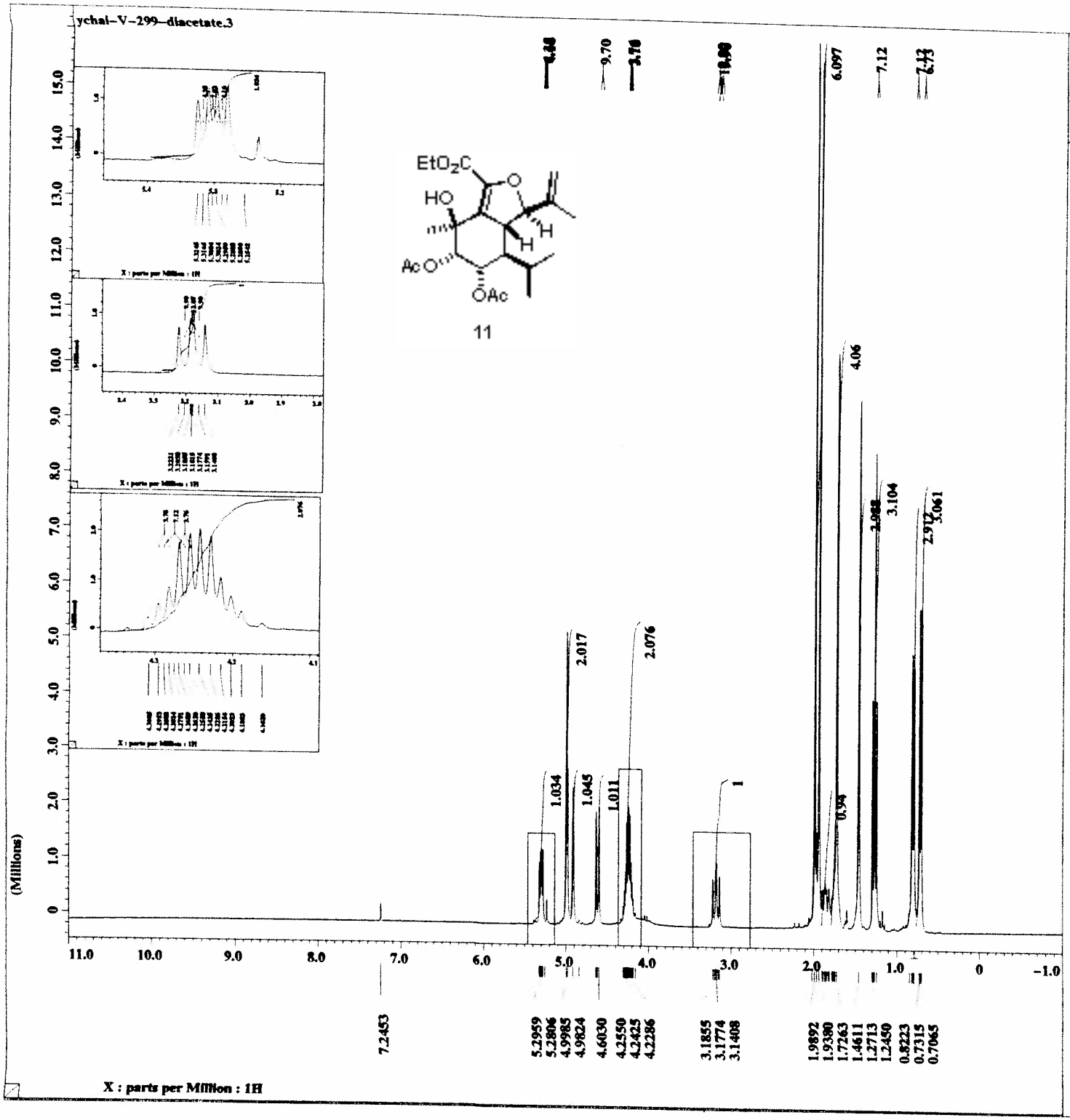
JEOL

```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-296-triol_copy.1
File Name          = ychai-V-296-triol_cop
Author             = mcintoshgroup
Sample ID          = #8592067
Content            = Single Pulse with Bro
Creation Date      = 12-DEC-2004 17:25:32

Revision Date      = 12-DEC-2004 16:40:35
Spec Site          = Delta NMR

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Field_strength     = 6.345446[T] (270[MHz]
X_acq_duration     = 1.9267584[s]
X_domain           = 13C
X_freq             = 67.93330993[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.51900643[Hz]
X_sweep            = 17.00680272[kHz]
Irr_domain         = 1H
Irr_freq           = 270.16608844[MHz]
Irr_offset         = 5[ppm]
Mod_return         = 1
Scans              = 100
Total_scans        = 100

X_90_width         = 8.3[us]
X_acq_time         = 1.9267584[s]
X_angle            = 90[deg]
X_pulse            = 8.3[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 4[s]
Unblank_time       = 2[us]
```



JEOL

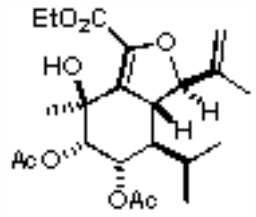
```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-299-diacetate.1
File Name           = ychai-V-299-diacetate
Author              = mcintoshgroup
Sample ID           = S0601520
Content             = Single Pulse Experime
Creation Date       = 12-DEC-2004 17:32:16

Revision Date       = 12-DEC-2004 16:55:53
Spec Site           = Delta NMR

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Field_strength      = 6.345446[T] (270[MHz]
X_acq_duration      = 5.0528256[s]
X_domain            = 1H
X_freq              = 270.16608844[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 0
X_resolution        = 0.19790907[Hz]
X_sweep             = 3.24254215[kHz]
Mod_return          = 1
Scans               = 8
Total_scans         = 8

X_90_width          = 10.4[us]
X_acq_time          = 5.0528256[s]
X_angle             = 45[deg]
X_pulse             = 5.2[us]
Initial_wait        = 1[s]
Phase_preset        = 3[us]
Relaxation_delay    = 4[s]
Unblank_time        = 2[us]
```

ychai-V-299-diacetate_copy.4



11

(Millions)

600.0
500.0
400.0
300.0
200.0
100.0
0

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

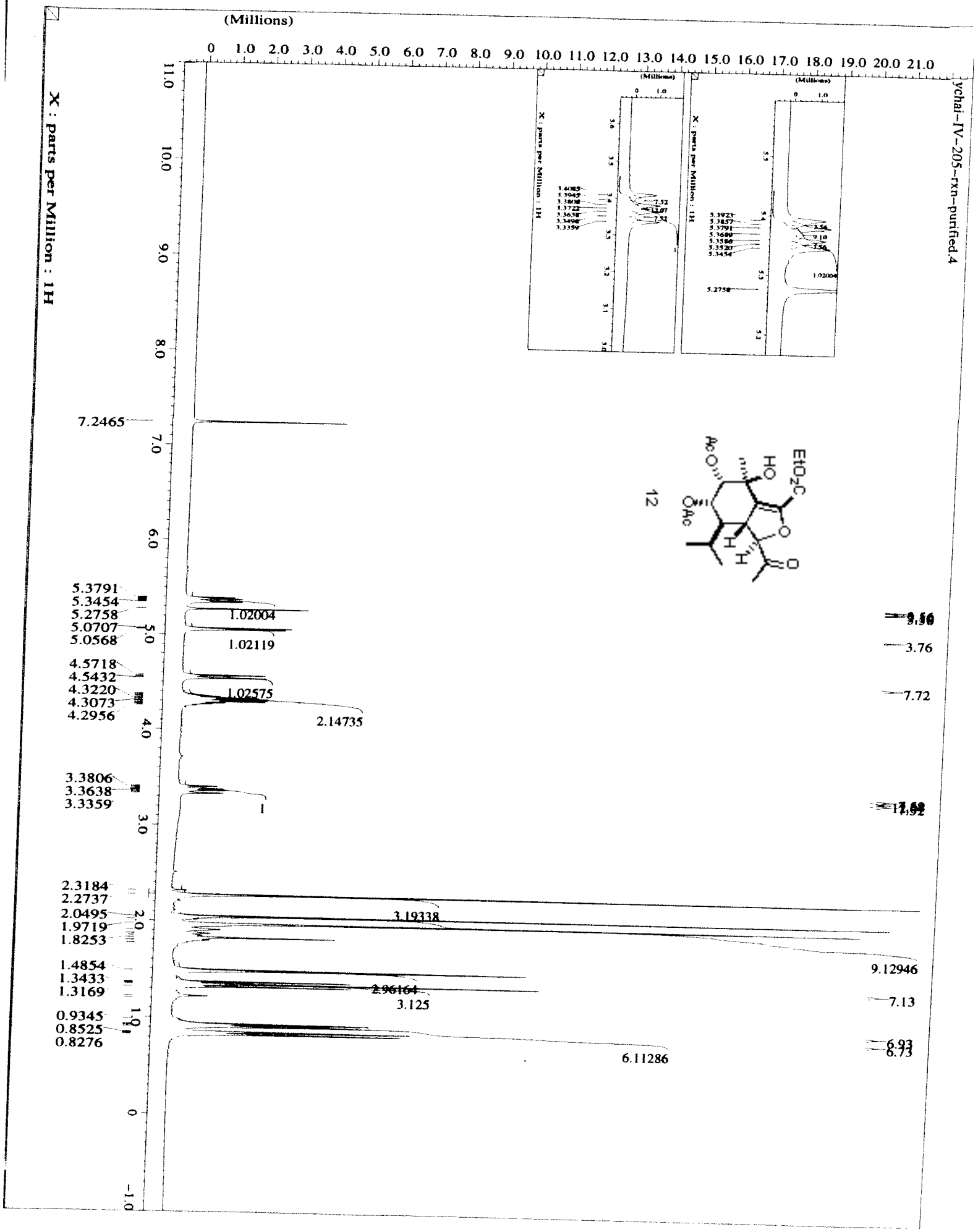
170.2110
169.8978
162.0592
142.5850
141.1029
116.0668
90.5036
77.6761
77.2101
76.7364
74.2076
69.2340
68.2178
62.0677
48.4151
45.1911
26.6107
21.0871
20.8502
16.5107
15.7620
14.1042

X : parts per Million : 13C

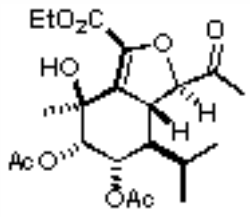
JEOL

---- ACQUISITION PARAMETERS ----

Derived from:	ychai-V-299-diacetate_copy
File Name	= ychai-V-299-diacetate
Author	= mcintoshgroup
Sample ID	= S#729127
Content	= Single Pulse with Bro
Creation Date	= 12-DEC-2004 21:29:49
Revision Date	= 12-DEC-2004 20:43:32
Spec Site	= Delta NMR
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Field_strength	= 6.345446[T] (270[MHz]
X_acq_duration	= 1.9267584[s]
X_domain	= 13C
X_freq	= 67.93330993[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 0.51900643[Hz]
X_sweep	= 17.00680272[kHz]
Irr_domain	= 1H
Irr_freq	= 270.16608844[MHz]
Irr_offset	= 5[ppm]
Mod_return	= 1
Scans	= 272
Total_scans	= 272
X_90_width	= 8.3[us]
X_acq_time	= 1.9267584[s]
X_angle	= 135[deg]
X_pulse	= 12.45[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Relaxation_delay	= 4[s]
Unblank_time	= 2[us]


(Millions)
X : parts per Million : 1H
ychai-IV-205-rxn-purified.4
7.2465
5.3791
5.3454
5.2758
5.0707
5.0568
1.02004
1.02119
4.5718
4.5432
4.3220
4.3073
4.2956
1.02575
2.14735
3.3806
3.3638
3.3359
1
2.3184
2.2737
2.0495
1.9719
1.8253
3.19338
1.4854
1.3433
1.3169
2.96164
3.125
0.9345
0.8525
0.8276
6.11286
12
AcO
OAc
HO
EtO2C
O
H
H
O
9.56
3.76
7.72
9.12946
7.13
6.93
6.73

ychai-V-303-ketone_copy.3



12

JEOL

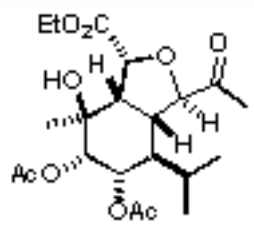
```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-303-ketone_copy.1
File Name          = ychai-V-303-ketone_co
Author             = mcintoshgroup
Sample ID          = S0613300
Content            = Single Pulse with Bro
Creation Date      = 12-DEC-2004 18:04:42

Revision Date      = 12-DEC-2004 17:20:02
Spec Site          = Delta NMR

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Field_strength     = 6.345446[T] (270[MHz]
X_acq_duration     = 1.9267584[s]
X_domain           = 13C
X_freq             = 67.93330993[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.51900643[Hz]
X_sweep            = 17.00680272[kHz]
Irr_domain         = 1H
Irr_freq           = 270.16608844[MHz]
Irr_offset         = 5[ppm]
Mod_return         = 1
Scans              = 130
Total_scans        = 130

X_90_width         = 8.3[us]
X_acq_time         = 1.9267584[s]
X_angle            = 90[deg]
X_pulse            = 8.3[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 4[s]
Unblank_time       = 2[us]
```

ychai-V-crabtree reduction.5



13

JEOL

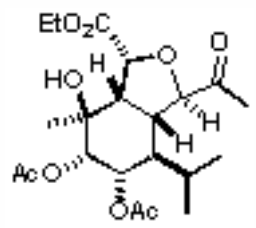
```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-V-crabtree reduction
File Name          = ychai-V-crabtree redu
Author             = mcintoshgroup
Sample ID          = S#471079
Content            = Single Pulse Experime
Creation Date      = 14-OCT-2004 13:55:02

Revision Date      = 14-OCT-2004 13:09:08
Spec Site          = Delta NMR

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Field_strength     = 6.345446[T] (270[MHz]
X_acq_duration     = 5.0528256[s]
X_domain           = 1H
X_freq             = 270.16608844[MHz]
X_offset           = 5[ppm]
X_points           = 16384
X_prescans         = 0
X_resolution       = 0.19790907[Hz]
X_sweep            = 3.24254215[kHz]
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 10.4[us]
X_acq_time         = 5.0528256[s]
X_angle            = 45[deg]
X_pulse            = 5.2[us]
Initial_wait       = 1[s]
Phase_preset       = 3[us]
Relaxation_delay   = 4[s]
Unblank_time       = 2[us]
```

ychai-VI-ketone-reduction.4



13

JEOL

```
---- ACQUISITION PARAMETERS ----
Derived from: ychai-VI-ketone-reduction.
File Name           = ychai-VI-ketone-reduc
Author              = mcintoshgroup
Sample ID           = S#778872
Content             = Single Pulse with Bro
Creation Date       = 28-JUL-2005 00:35:01

Revision Date       = 27-JUL-2005 23:46:40
Spec Site           = Delta NMR

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Field_strength      = 6.345446[T] (270[MHz]
X_acq_duration      = 1.9267584[s]
X_domain            = 13C
X_freq              = 67.93330993[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0.51900643[Hz]
X_sweep             = 17.00680272[kHz]
Irr_domain          = 1H
Irr_freq            = 270.16608844[MHz]
Irr_offset          = 5[ppm]
Mod_return          = 1
Scans               = 1383
Total_scans         = 1383

X_90_width          = 8.3[us]
X_acq_time          = 1.9267584[s]
X_angle             = 90[deg]
X_pulse             = 8.3[us]
Initial_wait        = 1[s]
Phase_preset        = 3[us]
Relaxation_delay    = 3[s]
Unblank_time        = 2[us]
```