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## Supplementary Material

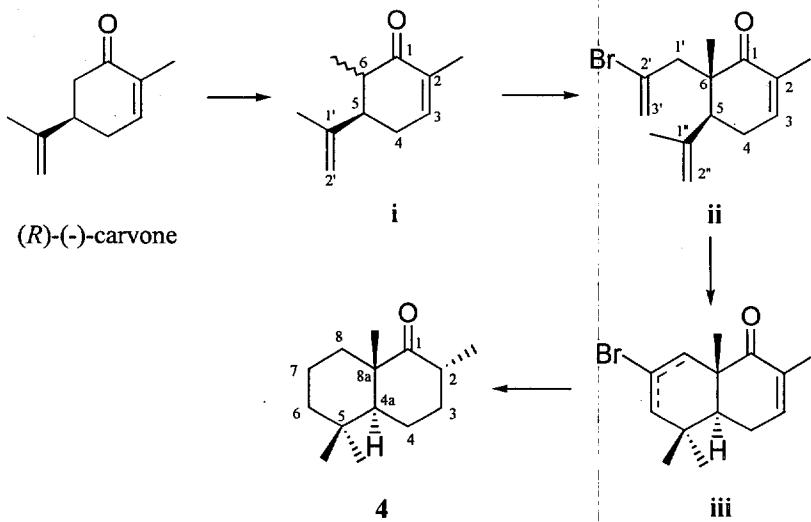
# Synthesis of Terpenoid Unsaturated 1,4-Dialdehydes. $\pi$ -Facial Selectivity in the Diels-Alder Reaction of the 1-Vinyl-2-methylcyclohexene Moiety of Polycyclic Systems with DMAD

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## Supplementary Experimental Section

## Preparation of decalone 4 from (*R*)-(−)-Carvone.



**(5*R*,6*S*)- and (5*R*,6*R*)-5-Isopropenyl-2,6-dimethyl-2-cyclohexen-1-one (i).** To a solution of LDA (generated from 8.13 mL of a 1.6 M solution of BuLi in hexanes and 1.82 mL of diisopropylamine ; 13 mmol) in THF (16 mL) at -10 °C under argon was slowly added during 2 h a solution of (*R*)-(–)-carvone (1.50 g, 10 mmol) in THF (5 mL).

After the reaction mixture had been allowed to warm to 0 °C and then stirred at this temperature for 30 min, it was cooled at -20 °C and treated with MeI (0.49 mL, 40 mmol). The reaction mixture was then slowly allowed to warm to 0 °C during 1 h, poured into cooled NH<sub>4</sub>Cl saturated aqueous solution, and extracted with hexane. Workup as usual afforded an oily residue, which was purified by column chromatography using hexane-ether 9 : 1 as eluent, to give a mixture of epimeric methyl ketones **i** (1.42 g, 87%) as a colorless oil. This mixture was used directly in the next step, but a small sample was rechromatographed by MPLC, using hexane-ether 95:5 as eluent, in order to obtain the spectroscopic data of each epimeric methyl ketone.

**(5*R*,6*S*)-i** (less polar isomer) : <sup>1</sup>H NMR (199.95 MHz, CDCl<sub>3</sub>) δ 6.65 (1H, m, H-3), 4.77 (2H, m, H-2''), 2.5-2.1 (4H, m, H-4α, H-4β, H-5, H-6), 1.74 (3H, br s, Me-1'), 1.67 (3H, br s, Me-2), 1.02 (3H, d, *J* 6.3, Me-6); <sup>13</sup>C NMR (50.32 MHz, CDCl<sub>3</sub>) δ 12.50 (Me-6), 16.10 (Me-2), 18.21 (Me-1'), 31.18 (C-4), 44.23 (C-5), 50.58 (C-6), 113.12 (C-2'), 134.78 (C-2), 143.25 (C-3), 145.65 (C-1'), 201.66 (C-1).

**(5*R*,6*R*)-i** (more polar isomer) : <sup>1</sup>H NMR (199.95 MHz, CDCl<sub>3</sub>) δ 6.70 (1H, m, H-3), 4.89 (1H, br s, H-2''α), 4.71 (1H, br s, H-2''β), 2.8-2.2 (4H, m, H-4α, H-4β, H-5, H-6), 1.76 (3H, br s, Me-1'), 1.68 (3H, br s, Me-2), 0.90 (3H, d, *J* 7.1, Me-6); <sup>13</sup>C NMR (50.32 MHz, CDCl<sub>3</sub>) δ 10.48 (Me-6), 15.95 (Me-2), 21.89 (Me-1'), 26.31 (C-4), 44.79 (C-5), 43.00 (C-6), 111.46 (C-2'), 133.70 (C-2), 143.94 (C-3), 144.95 (C-1'), 203.48 (C-1).

**(5*S*,6*S*)-6-(2-Bromoallyl)-5-isopropenyl-2,6-dimethyl-2-cyclohexen-1-one**

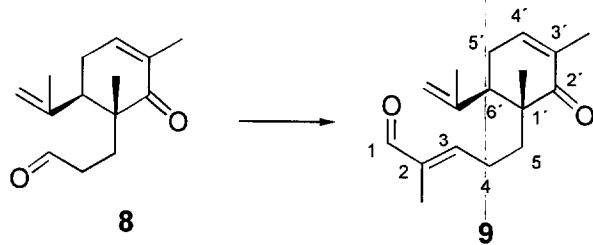
(ii). To THF solution of LDA [prepared from 1.6 M BuLi in hexanes (4.94 mL, 7.9 mmol), diisopropylamine (1.1 mL, 7.9 mmol), and THF (16 mL)] was added dropwise, over a period of 1 h at -78 °C a solution of the epimeric ketones **i** (1.0 g, 6.09 mmol) in THF (7.5 mL) and HMPA (1.7 mL). The solution was stirred at -78 °C for 1 h and then slowly allowed to warm to -10 °C during 2 h. After the solution was again cooled to -50 °C, 2,3-dibromopropene (1.15 mL, 9.76 mmol) was added. The reaction mixture was then slowly allowed to warm to -10 °C during 2 h, poured into a cooled saturated

aqueous NH<sub>4</sub>Cl solution, and extracted with ether. Workup of the extract afforded a residue, which was purified by chromatography, using hexane-ether 98:2 as eluent, to give the enone **ii** (1.272 mg, 73%) as a yellowish oil : <sup>1</sup>H NMR (299.95 MHz, CDCl<sub>3</sub>) δ 6.58 (1H, m, H-3), 5.57 (1H, br s, H-3'α), 5.45 (1H, br s, H-3'β), 4.75 (1H, br s, H-2''α), 4.72 (1H, br s, H-2''β), 2.90 (1H, dd, *J* 6, 4 Hz), 2.84 and 2.71 (2H, AB system, *J* 15 Hz), 2.71 (1H, m, H-4), 2.19 (1H, m, H-4), 1.78 (3H, br s, Me-2), 1.58 (3H, br s, Me-1'), 1.08 (3H, s, Me-6); <sup>13</sup>C NMR (75.43 MHz, CDCl<sub>3</sub>) δ 16.48 (Me-2), 19.52 (Me-6), 21.97 (Me-1'), 28.48 (C-4), 48.10 (C-6), 48.82 (C-1'), 49.34 (C-5), 114.44 (C-2''), 121.12 (C-3'), 128.45 (C-2'), 134.51 (C-2), 141.40 (C-3), 145.78 (C-1''), 202.64 (C-1).

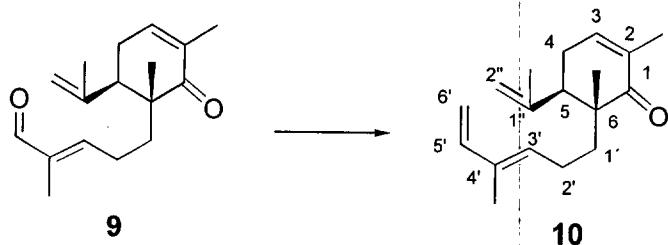
**(4aS,8aS,2R)-2,5,5,8a-Tetramethylperhydro-1-naphthalenone (4).** A solution of the enone **ii** (1.0 g, 3.53 mmol) in a mixture of trifluoroacetic acid (25 mL) and trifluoroacetic anhydride (0.25 mL) was stirred at rt under argon for 24 h. After this time most of the trifluoroacetic acid was eliminated under vacuum and the residue was neutralized with a 10% aqueous solution of NaHCO<sub>3</sub> and extracted with hexane. The organic extracts were washed with H<sub>2</sub>O and brine, dried, and concentrated to give the crude product, which was purified by chromatography, using hexane-ether from 98:2 to 95:5 as eluent, to give the decalone **iii** (699 mg, 70%) as a mixture of regioisomers of the A ring double bond.

A solution of this mixture (699 mg), Et<sub>3</sub>N (0.70 mL, 5 mmol) and 10% palladium on carbon (176 g) in EtOH (10 mL) was stirred at rt under an atmosphere of hydrogen for 4 h. After filtration, the mixture was poured into H<sub>2</sub>O and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were washed with diluted hydrochloric acid, aqueous NaHCO<sub>3</sub> and brine. Drying and evaporation of the solvent gave a solid residue (512 mg ; a 7:3 mixture of epimeric methyl ketones) that was treated at rt with methanolic sodium methoxide (10 mL of a 0.25 M solution of sodium methoxide in anhydrous methanol). After 2 h the reaction mixture was poured into water and extracted with hexane. The extracts were washed with brine, dried and concentrated. The residue was chromatographed, using hexane-ether 97:3 as eluent, to afford the ketone **4** (510 mg, 98% from **iii**) as a white solid : mp 53-55 °C (from pentane) [lit.<sup>7</sup> 46-

49];  $[\alpha]^{22}_D -25$  (*c* 6.2,  $\text{CHCl}_3$ ) [lit.<sup>7</sup> -38]; IR (KBr) 1700, 1450, 1375, 980,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (299.95 MHz,  $\text{CDCl}_3$ )  $\delta$  2.66 (1H, m, H-2), 2.07 (1H, H-3 $\beta$ ), 1.11 (3H, s, Me-8a), 0.94 (3H, d, *J* 6.6, Me-2), 0.90 (3H, s, Me-5 $\beta$ ), 0.85 (3H, s, Me-5 $\alpha$ ); MS (EI) *m/z* 208 ( $M^+$ , 41), 193 (35), 175 (38), 165 (24), 69 (100).

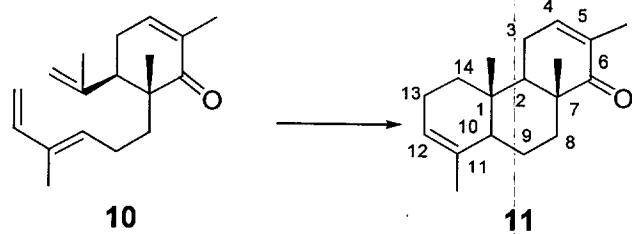


**(E)-5-[(1*R*,6*R*)-6-Isopropenyl-1,3-dimethyl-2-oxo-3-cyclohexenyl]-2-methyl-2-pentenal (9).** A solution of aldehyde **8** (538 mg, 2.44 mmol) and commercial ( $\alpha$ -formylethylidene)triphenylphosphorane (895 mg, 2.81 mmol) in benzene (15 mL) was warmed at 80 °C for 24 h. The mixture was allowed to cool to rt and treated with a solution of saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The aqueous phase was separated and extracted with ethyl ether. The combined organic extracts were washed with water and brine and dried. The oily residue obtained after evaporation of the solvent was purified by flash chromatography, using hexane-ethyl acetate 9:1 as eluent, to afford  $\alpha,\beta$ -unsaturated aldehyde **9** (565 g, 89%) as an oil:  $[\alpha]^{25}_D +42$  (*c* 1.2,  $\text{CHCl}_3$ ); IR (film) 3080, 1680, 1665, 1435, 1370, 900  $\text{cm}^{-1}$   $^1\text{H}$  NMR (299.95 MHz,  $\text{CDCl}_3$ )  $\delta$  9.35 (1H, s, H-1), 6.60 (1H, m, H-4 $'$ ), 6.40 (1H, ddd, *J* 7.5, 7.5, 1.5, H-3), 4.83 and 4.76 (each 1H, two s, H<sub>2</sub>-2 $''$ ), 2.75 (1H, dd, *J* 7.0, 7.0, H-6 $'$ ), 2.52 and 2.38 (each 1H, two m, H<sub>2</sub>-5), 1.77 (3H, m, Me-3 $'$ ), 1.69 (3H, s, Me-2), 1.67 (3H, s, Me-1 $''$ ), 1.06 (3H, s, Me-1 $'$ ); MS (EI) *m/z* 260 ( $M^+$ , 12), 164 (100), 149 (46), 123 (80), 95 (27), 82 (55), 55 (25); HRMS calcd for  $C_{17}\text{H}_{24}\text{O}_2$  260.1776, found 260.1771.



**(5*R*,6*R*)-5-Isopropenyl-2,6-dimethyl-6-[(3*E*)-4-methyl-3,5-hexadienyl]-2-cyclohexen-1-one (10).**

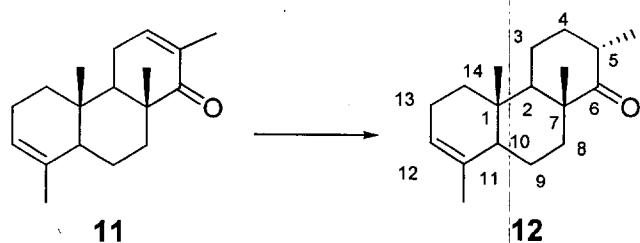
Methyltriphenylphosphonium bromide (1.58 g, 4.06 mmol) was suspended in THF (10 mL) and the mixture was cooled to -20 °C. A solution of BuLi in hexanes (1.6 M, 2.44 mL, 3.9 mmol) was dropwise added and the solution was allowed to warm to rt and stirred for 15 min. After cooling to -20 °C, compound 9 (352 mg, 1.36 mmol) in THF (9 mL) was added slowly and the mixture stirred for 1 h. After this time, the mixture was treated with saturated aqueous NH<sub>4</sub>Cl, poured into water and extracted with ethyl acetate. The combined organic layer were washed sequentially with diluted hydrochloric acid, 5% aqueous NaHCO<sub>3</sub>, and brine and dried. Evaporation of the solvent and flash chromatography, using hexane-ethyl acetate 9:1 as eluent, provided compound 10 (318 mg, 91%) as an oil: IR (film) 3095, 1680, 1665, 1445, 985, 900 cm<sup>-1</sup>; <sup>1</sup>H NMR (299.95 MHz, CDCl<sub>3</sub>) δ 6.55 (1H, m, H-3), 6.32 (1H, dd, *J* 17.0, 10.5, H-5'), 5.40 (1 H, dd, *J* 7.5, 7.5, H-3'), 5.05 and 4.90 (each 1H, two m, H<sub>2</sub>-6'), 4.78 and 4.72 (each 1H, two br s, H<sub>2</sub>-2''), 2.72 (1 H, dd, *J* 5.5, 5.5, H-5), 2.59 and 2.28 (each 1H, m, H<sub>2</sub>-11), 1.77 (3 H, m, Me-2), 1.69 (3 H, s, Me-4'), 1.63 (3 H, s, Me-1''), 1.03 (3 H, s, Me-6).



**(1*S*,10*S*,2*R*,7*R*)-1,5,7,11-Tetramethyltricyclo[8.4.0.0<sup>2,7</sup>]tetradeca-4,11-dien-6-one (11).**

A toluene solution (10 mL) of 10 (264 mg, 1.03 mmol) and one drop of propylene oxide was sealed under argon in a tube and heated at 185 °C for 6 days. After

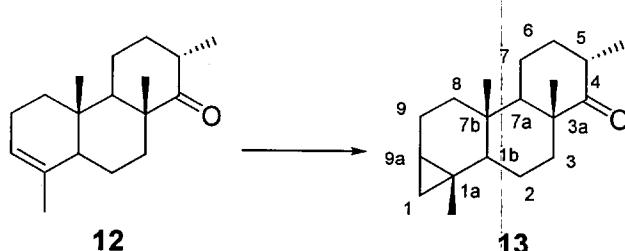
cooling, the tube was opened and the solvent removed *in vacuo* to give an oily residue, which was purified by flash chromatography, using hexane-ethyl acetate 9:1 as eluent, to afford *ketone 11* (228 mg, 86%) as a white solid : mp. 95-97 °C (from ethyl ether);  $[\alpha]^{25}_D +74$  (*c* 9.8, CHCl<sub>3</sub>); IR (KBr) 3009, 1670, 916 cm<sup>-1</sup>; <sup>1</sup>H NMR (299.95 MHz, CDCl<sub>3</sub>) 6.65 (1 H, m, H-4), 5.27 (1 H, br s, H-12), 1.73 (3 H, m, Me-5), 1.62 (3 H, s, Me-11), 1.06 (3 H, s, Me-7), 0.87 (3 H, s, Me-1); MS (EI) *m/z* 258 (M<sup>+</sup>, 54), 243 (17), 229 (12), 161 (25), 147 (17), 136 (54), 124 (32), 123 (100), 107 (52), 93 (27); HRMS calcd for C<sub>18</sub>H<sub>26</sub>O 258.1984, found 258.1988.



**(1*S*,5*R*,10*S*,2*R*,7*R*)-1,5,7,11-Tetramethyltricyclo[8.4.0.0<sup>2,7</sup>]tetradec-11-en-6-one**

**(12).** A mixture of powdered tellurium (250 mg, 1.96 mmol), NaBH<sub>4</sub> (176 mg, 4.66 mmol) and anhydrous ethanol (6.5 mL), was heated and stirred under argon at 80 °C. After 45 min the mixture was cooled to rt and a solution of the enone **11** (127 mg, 0.49 mmol) in a 3:1 mixture of ethanol-pentane (5.5 mL) was added. After refluxing for about 1.5 h, the mixture was cooled and filtered through a short pad of silica gel, eluting with hexane-ether 9:1. Evaporation of the solvent afforded a mixture of C-5 epimeric methyl ketones. A solution of this mixture in THF (2.5 mL) was treated with 5% NaOMe in MeOH (7 mL). The reaction mixture was stirred for 1 h and poured into water. Extraction with ether and work up as usual afforded a residue, which was purified by chromatography, using hexane-ether 9:1 as eluent, to give the ketone **12** (101 mg, 80% from enone **11**) as a white solid : mp 87.1-87.9 °C (from methanol);  $[\alpha]^{22}_D +36$  (*c* 3.2, CHCl<sub>3</sub>); IR (KBr) 2930, 2856, 1707, 1454, 1378, 1223, 1136, 772; <sup>1</sup>H NMR (299.95 MHz, CDCl<sub>3</sub>) δ 5.24 (1 H, bs, H-12), 2.66 (1H, ddq, *J* 13.0, 6.5, 6.4, H-5), 2.1 (1H, dddd, *J* 13.0, 6.5, 2.8, 3.8, H-4α), 2.0 (2H, m, H-13), 1.62 (3H, s, Me-11), 1.17 (3H, s, Me-7), 0.82 (3H, s, Me-1), 0.96 (3 H, d, *J* 6.4, Me-5); MS (EI) *m/z* 260 (M<sup>+</sup>,

100), 245 (26), 231 (23), 217 (13), 175 (67); HRMS calcd for  $C_{18}H_{28}O$  260.2140, found 260.2135.



**(1b*S*,5*S*,7b*S*,9a*S*,1a*R*,3a*R*,7a*R*)-1a,3a,5,7b-Tetramethylperhydrocyclopropano**

**[a]phenanthren-4-one (13).** A solution of compound **12** (132 mg, 0.51 mmol) in dry toluene (8 mL) was treated with diethylzinc (3.2 mL of a 1 M solution in hexane, 3.2 mmol). Diiodomethane (0.50 mL, 6.24 mmol) was introduced dropwise during 10 min, and the mixture was stirred for 6 h, poured into saturated aqueous  $NH_4Cl$  solution, and extracted with ether. Work up as usual gave a residue, which was purified by chromatography, using hexane-ethyl acetate 9:1 as eluent, to afford cyclopropane **13** (138 mg, 97%) as a white solid: mp 135.2–135.8 °C (from methanol );  $[\alpha]^{25}_D +79$  (*c* 2.1,  $CHCl_3$ ); IR (KBr) 2922, 2859, 1704, 1447, 1377, 1013, 907, 733  $cm^{-1}$ ;  $^1H$  NMR (299.95 MHz,  $CDCl_3$ )  $\delta$  2.64 (1H, ddq, *J* 13.0, 6.5, 6.4, H-5), 2.09 (1H, dddd, *J* 13.0, 6.5, 3.7, 2.7, H-6 $\alpha$ ), 1.65 (3H, m, H-2, H-8 $\beta$ ), 1.6 (2H, m, H-3), 1.5–2 (4H, m, H-11, H-2), 1.12 (3 H, s, Me-3a), 1.1 (1H, m, H-6 $\beta$ ), 0.9 (2H, m, H-9, H-1b), 0.95 (3 H, s, Me-1a), 0.96 (3 H, s, Me-7b), 0.90 (3 H, d, *J* 6.5, Me-5), 0.52 (1H, m, H-9a), 0.5 (1H, m, H-8 $\alpha$ ), 0.4 (1H, dd, *J* 9.2, 3.7, H-1 $\beta$ ), 0.05 (1H, dd, *J* 5.6, 3.7, H-1 $\alpha$ ); MS (EI) *m/z* 275 ( $M^++1$ , 30), 274 ( $M^+$ , 100), 259 (40 ), 232 (43), 205 (13), 189 (40), 135 (88), 121 (62), 107 ( 50 ), 95 (47 ); HRMS calcd for  $C_{19}H_{30}O$  274.2296, found 274.2302.

**Table I.**  $^{13}\text{C}$  Chemical Shifts ( $\delta$ ) in ppm from TMS of compounds 4-7.<sup>1,2</sup>

Compound	4	5	(1 <i>S</i> )-5 <sup>3</sup>	6	7
C-1	216.16	76.36	80.82	142.02	39.31
C-2	39.87	33.97	35.82	126.79	126.65
C-3	35.73	30.80 <sup>a</sup>	31.80 <sup>a</sup>	38.11	115.46
C-4	21.33	21.58	21.69	19.03 <sup>a</sup>	27.50
C-4a	54.20	45.47	48.47	51.28	-
C-5	34.18	33.30	33.32	33.33	152.42 <sup>a</sup>
C-6	41.60	41.80	41.96	41.80	155.32 <sup>a</sup>
C-7	18.15	18.50	18.58	18.88 <sup>a</sup>	38.95
C-8	33.21	32.31 <sup>a</sup>	32.71 <sup>a</sup>	33.50	26.72
C-8a	48.78	41.52	42.36	37.64	-
C-9	-	-	-	-	17.30
C-10	-	-	-	-	43.98
C-11	-	-	-	-	33.82
C-12	-	-	-	-	42.08
C-13	-	-	-	-	19.18
C-14	-	-	-	-	40.24
C-1'	-	141.98	138.33	135.19	-
C-2'	-	113.74	115.22	118.22	-
Me-1	-	-	-	-	25.44
Me-2	14.99	16.12 <sup>b</sup>	15.78	21.05	-
Me-5 $\alpha$	33.04	33.69	33.78	33.22	-
Me-5 $\beta$	21.99	22.03	21.84	21.58	-
Me-7	-	-	-	-	26.00
Me-8a	18.75	16.86 <sup>b</sup>	14.52	19.98	-
Me-11 $\alpha$	-	-	-	-	32.74
Me-11 $\beta$	-	-	-	-	21.18
CO <sub>2</sub> Me-5	-	-	-	-	166.20 <sup>b</sup>
CO <sub>2</sub> Me-6	-	-	-	-	169.62 <sup>b</sup>
CO <sub>2</sub> Me-5	-	-	-	-	51.82 <sup>c</sup>
CO <sub>2</sub> Me-6	-	-	-	-	52.04 <sup>c</sup>

(1) At 75.4 MHz in CDCl<sub>3</sub>. Assignment of the resonance signals are based on DEPT and, in most cases, HMQC experiments.

(2) The signals with the same superscript may be interchanged within the same column. (3) Epimer of alcohol 5 at the carbinol center.

**Table II.**  $^{13}\text{C}$  Chemical Shifts ( $\delta$ ) in ppm from TMS of compounds 8-10.<sup>1,2</sup>

Compound			
	<b>8</b>	<b>9</b>	<b>10</b>
C-1	201.83	195.21	203.38
C-2	39.18	139.26	134.23
C-3	28.80 <sup>a</sup>	154.27	141.51
C-4	-	24.11	28.82
C-5	-	35.68	50.08
C-6	-	-	47.58
C-1'	46.92	47.69	37.40
C-2'	203.31	203.38	23.20
C-3'	134.01	134.16	141.43
C-4'	142.26	142.21	132.57
C-5'	28.29 <sup>a</sup>	28.85	132.57
C-6'	49.87	49.57	110.64
C-1''	145.61	146.75	146.39
C-2''	114.55	114.56	114.05
Me-2	-	9.12	16.41
Me-6	-	-	22.20
Me-1'	22.11	22.23	-
Me-3'	16.27	16.37	-
Me-4'	-	-	11.58
Me-1''	19.11	19.36	19.26

(1) At 75.4 MHz in  $\text{CDCl}_3$ . Assignment of the resonance signals are based on DEPT and, in most cases, HMQC experiments. (2) The signals with the same superscript may be interchanged within the same column

Table III.  $^{13}\text{C}$  Chemical Shifts ( $\delta$ ) in ppm from TMS of compounds 11-16.<sup>1,2</sup>

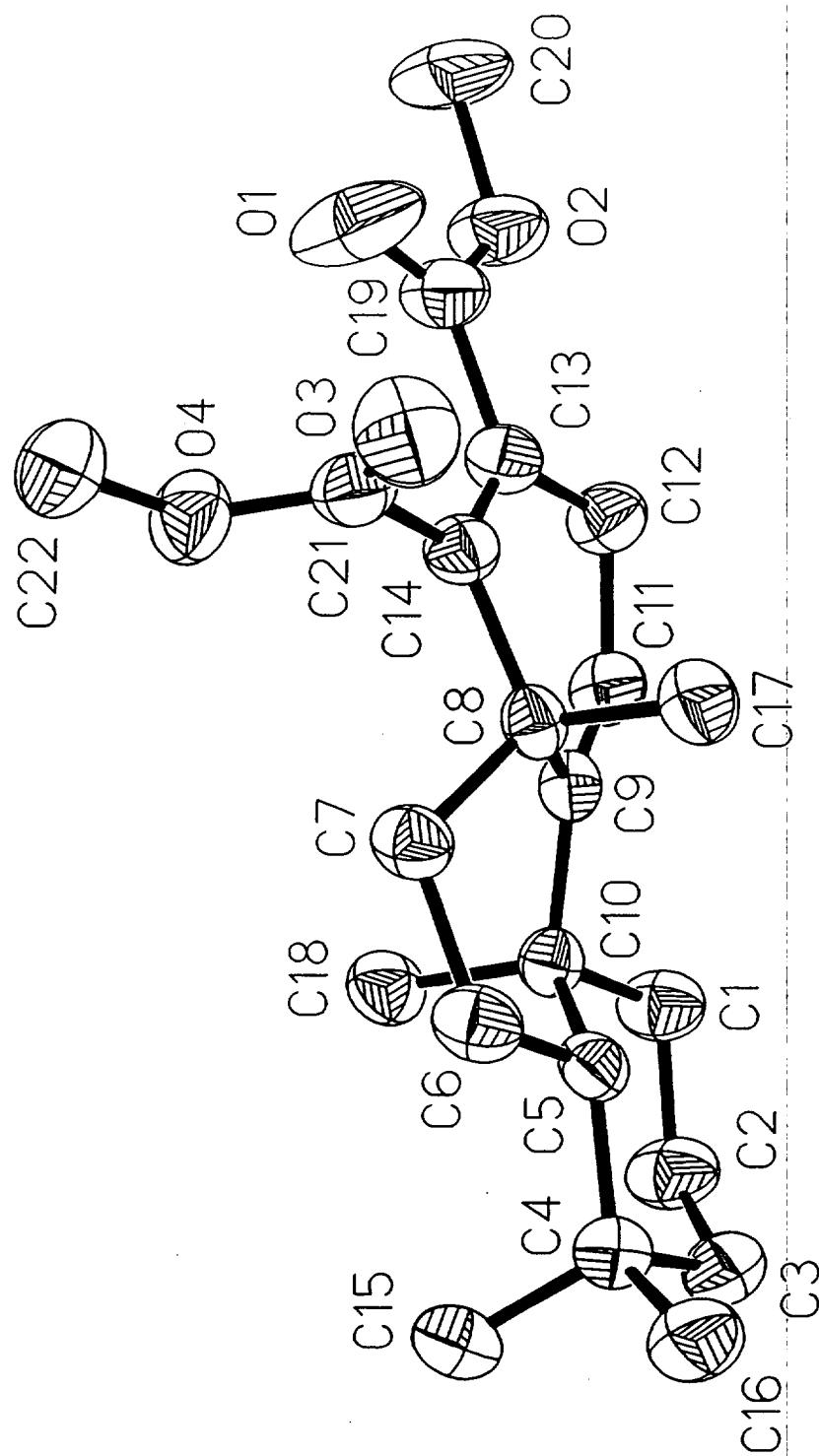
Compound						
C-1	36.14	37.02	22.47	22.46	22.63 <sup>a</sup>	44.83
C-1a	-	-	16.29	16.36	16.39	-
C-1b	-	-	51.70	51.64	51.99	-
C-2	50.60	55.65	21.53	21.11 <sup>a</sup>	22.32 <sup>a</sup>	36.27
C-3	23.92	20.74 <sup>a</sup>	33.68	38.99	32.65	34.21
C-3a	-	-	48.67	41.54	37.61	-
C-4	143.37	35.96	216.76	79.47	142.06	18.87
C-5	133.15	40.02	39.78	33.82	126.72	18.42
C-6	204.12	216.76	35.75	32.87	38.58	22.50
C-7	44.63	48.94	20.93	21.77 <sup>a</sup>	18.49	16.11
C-7a	-	-	54.82	46.14	52.08	-
C-7b	-	-	36.84	35.76	35.84	-
C-8	34.91	34.13	34.81	35.08	34.77	51.85
C-9	20.07	20.28 <sup>a</sup>	19.19	19.36	19.28	22.31
C-9a	-	-	18.30	18.37	18.30	-
C-10	48.49	48.84	-	-	-	40.73
C-11	-135.05	-134.85	-	-	-	-39.14 <sup>a</sup>
C-12	120.22	120.51	-	-	-	126.75
C-13	22.59	23.02	-	-	-	115.32
C-14	34.02	35.65	-	-	-	26.70
C-15	-	-	-	-	-	152.46 <sup>b</sup>
C-16	-	-	-	-	-	155.82 <sup>b</sup>
C-17	-	-	-	-	-	38.92 <sup>a</sup>
C-18	-	-	-	-	-	27.56
C-19	-	-	-	-	-	16.95
Me	13.28 (Me-1)	13.28 (Me-1)	23.46 (Me-1a)	23.46 (Me-1a)	23.73 (Me-1a)	12.45 (Me-2)
Me	16.37(Me-5)	15.23 (Me-5)	19.66 (Me-3a)	17.72 (Me-3a)	20.79 <sup>b</sup> (Me-3a)	23.56 (Me-7)
Me	18.61 (Me-7)	20.46 (Me-7)	14.99 (Me-5)	16.00 (Me-5)	20.94 <sup>b</sup> (Me-5)	26.59 (Me-11)
Me	21.31 (Me-11)	21.55 (Me-11)	13.37 (Me-7b)	13.13 (Me-7b)	12.74 (Me-7b)	25.88 (Me-17)

(1) At 75.4 MHz in  $\text{CDCl}_3$ . Assignment of the resonance signals are based on DEPT and, in most cases, HMQC experiments. (2) The signals with the same superscript may be interchanged within the same column. (3) C-1' at  $\delta$  141.95 ppm; C-2' at  $\delta$  113.87 ppm. (4) C-1' at  $\delta$  135.03 ppm; C-2' at  $\delta$  118.35 ppm. (5)  $\text{CO}_2\text{CH}_3$  at C-15 and C-16 at 51.85 and 52.04 ppm, respectively;  $\text{CO}_2\text{CH}_3$  at C-15 and C-16 at 169.59 and 166.17 ppm, respectively;

### Crystallographic Section

**Table IV. Crystal data and structure refinement for compound 7.**

Identification code	acr01	
Empirical formula	C <sub>22</sub> H <sub>32</sub> O <sub>4</sub>	
Formula weight	360.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.2476(8) Å b = 12.9442(17) Å c = 12.3694(9) Å	α = 90°. β = 97.895(8)°. γ = 90°.
Volume	990.8(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.208 Mg/m <sup>3</sup>	
Absorption coefficient	0.081 mm <sup>-1</sup>	
F(000)	392	
Crystal size	0.53 x 0.48 x 0.18 mm <sup>3</sup>	
Theta range for data collection	2.29 to 26.95°	
Index ranges	-7<=h<=1, -16<=k<=16, -15<=l<=15	
Reflections collected	4685	
Independent reflections	4256 [R(int) = 0.0416]	
Completeness to theta = 26.95°	100.0 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4256 / 242 / 236	
Goodness-of-fit on F <sup>2</sup>	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1147	
R indices (all data)	R1 = 0.1240, wR2 = 0.1493	
Absolute structure parameter	1.3(19)	
Extinction coefficient	0.018(3)	
Largest diff. peak and hole	0.183 and -0.184 e.Å <sup>-3</sup>	



**Figure 1.** The structure of 7 giving the crystallographic numbering scheme. Hydrogen atoms have been omitted for clarity.

**Table V.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound 7. U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
C(1)	7781(7)	4278(3)	1912(3)	50(1)
C(2)	8764(8)	4165(3)	3102(3)	58(1)
C(3)	8929(7)	3032(3)	3432(3)	55(1)
C(4)	10267(6)	2391(3)	2737(3)	44(1)
C(5)	9327(6)	2551(3)	1516(3)	37(1)
C(6)	10502(6)	1904(3)	725(3)	44(1)
C(7)	10120(6)	2256(3)	-463(3)	40(1)
C(8)	7911(5)	2756(3)	-791(3)	34(1)
C(9)	7659(6)	3675(3)	-39(3)	35(1)
C(10)	9009(6)	3687(3)	1106(3)	36(1)
C(11)	6370(6)	4449(3)	-402(3)	42(1)
C(12)	5269(7)	4536(3)	-1554(3)	48(1)
C(13)	6383(6)	3901(3)	-2327(3)	40(1)
C(14)	7653(6)	3120(3)	-1983(3)	37(1)
C(15)	12666(6)	2643(4)	3029(3)	55(1)
C(16)	9978(8)	1252(3)	3014(4)	59(1)
C(17)	6095(6)	1955(3)	-726(3)	49(1)
C(18)	11164(6)	4257(3)	1024(3)	48(1)
C(19)	6011(7)	4163(3)	-3513(3)	50(1)
C(20)	4193(9)	5279(4)	-4849(3)	84(2)
C(21)	8687(6)	2431(3)	-2727(3)	44(1)
C(22)	11843(7)	2138(4)	-3543(3)	66(1)
O(1)	6764(7)	3716(3)	-4208(2)	89(1)
O(2)	4695(5)	4967(2)	-3713(2)	62(1)
O(3)	7942(5)	1632(2)	-3080(2)	64(1)
O(4)	10643(4)	2778(2)	-2875(2)	53(1)

**Table VI.** Bond lengths [Å] and angles [°] for compound 7.

C(1)-C(2)	1.523(5)	C(6)-C(5)-C(4)	113.2(3)
C(1)-C(10)	1.543(5)	C(6)-C(5)-C(10)	110.8(3)
C(2)-C(3)	1.522(6)	C(4)-C(5)-C(10)	117.1(3)
C(3)-C(4)	1.524(5)	C(7)-C(6)-C(5)	115.0(3)
C(4)-C(15)	1.528(5)	C(6)-C(7)-C(8)	113.4(3)
C(4)-C(16)	1.530(5)	C(7)-C(8)-C(9)	109.4(3)
C(4)-C(5)	1.557(5)	C(7)-C(8)-C(14)	110.9(3)
C(5)-C(6)	1.547(5)	C(9)-C(8)-C(14)	109.8(3)
C(5)-C(10)	1.559(5)	C(7)-C(8)-C(17)	110.2(3)
C(6)-C(7)	1.526(5)	C(9)-C(8)-C(17)	110.6(3)
C(7)-C(8)	1.527(4)	C(14)-C(8)-C(17)	105.9(3)
C(8)-C(9)	1.531(4)	C(11)-C(9)-C(8)	119.4(3)
C(8)-C(14)	1.536(5)	C(11)-C(9)-C(10)	122.2(3)
C(8)-C(17)	1.547(5)	C(8)-C(9)-C(10)	118.3(3)
C(9)-C(11)	1.324(5)	C(1)-C(10)-C(9)	109.8(3)
C(9)-C(10)	1.546(5)	C(1)-C(10)-C(18)	108.6(3)
C(10)-C(18)	1.551(5)	C(9)-C(10)-C(18)	108.3(3)
C(11)-C(12)	1.499(5)	C(1)-C(10)-C(5)	108.1(3)
C(12)-C(13)	1.502(5)	C(9)-C(10)-C(5)	108.6(3)
C(13)-C(14)	1.319(5)	C(18)-C(10)-C(5)	113.4(3)
C(13)-C(19)	1.493(5)	C(9)-C(11)-C(12)	123.9(3)
C(14)-C(21)	1.491(5)	C(11)-C(12)-C(13)	111.8(3)
C(19)-O(1)	1.186(5)	C(14)-C(13)-C(19)	119.8(3)
C(19)-O(2)	1.328(5)	C(14)-C(13)-C(12)	121.6(3)
C(20)-O(2)	1.455(5)	C(19)-C(13)-C(12)	118.6(3)
C(21)-O(3)	1.191(5)	C(13)-C(14)-C(21)	123.5(3)
C(21)-O(4)	1.338(4)	C(13)-C(14)-C(8)	121.6(3)
C(22)-O(4)	1.450(5)	C(21)-C(14)-C(8)	114.3(3)
C(2)-C(1)-C(10)	114.0(3)	O(1)-C(19)-O(2)	123.0(4)
C(3)-C(2)-C(1)	110.8(3)	O(1)-C(19)-C(13)	125.3(4)
C(2)-C(3)-C(4)	113.3(3)	O(2)-C(19)-C(13)	111.7(3)
C(3)-C(4)-C(15)	110.3(3)	O(3)-C(21)-O(4)	124.0(4)
C(3)-C(4)-C(16)	107.9(3)	O(3)-C(21)-C(14)	124.4(4)
C(15)-C(4)-C(16)	107.1(3)	O(4)-C(21)-C(14)	111.4(3)
C(3)-C(4)-C(5)	108.2(3)	C(19)-O(2)-C(20)	116.3(3)
C(15)-C(4)-C(5)	115.4(3)	C(21)-O(4)-C(22)	116.1(3)
C(16)-C(4)-C(5)	107.8(3)		

**Table VII. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound 7.**  
**The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^*{}^2 U_{11} + \dots + 2 h k a^* b^* U_{12} ]$**

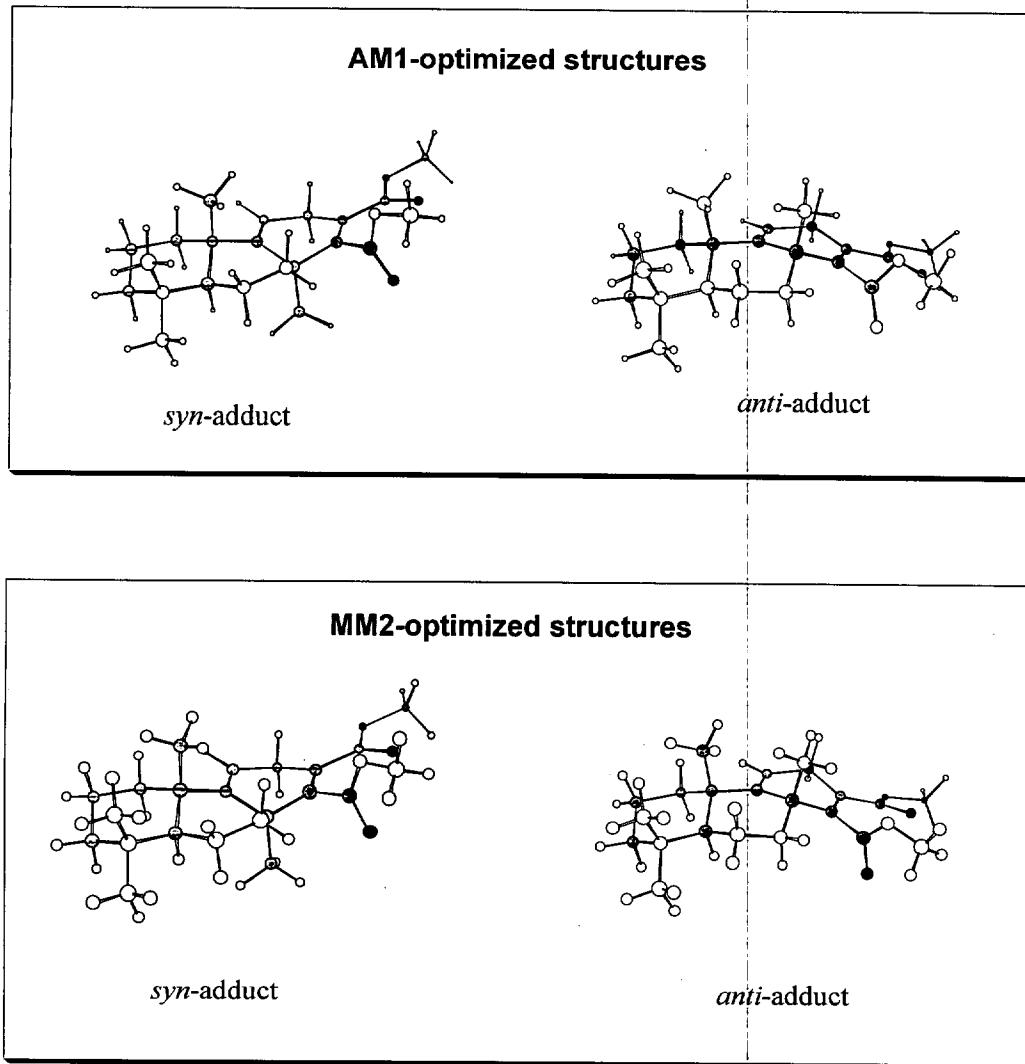
	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C(1)	60(3)	51(2)	39(2)	-6(2)	3(2)	12(2)
C(2)	70(3)	66(3)	37(2)	-5(2)	7(2)	19(2)
C(3)	57(2)	70(3)	38(2)	4(2)	8(2)	2(2)
C(4)	43(2)	48(2)	41(2)	4(2)	3(2)	2(2)
C(5)	31(2)	39(2)	39(2)	2(2)	-1(2)	-3(2)
C(6)	46(2)	38(2)	45(2)	-1(2)	0(2)	11(2)
C(7)	39(2)	40(2)	39(2)	-2(2)	2(2)	9(2)
C(8)	29(2)	32(2)	41(2)	1(2)	6(1)	2(2)
C(9)	32(2)	36(2)	38(2)	-1(2)	7(2)	-2(2)
C(10)	35(2)	36(2)	36(2)	-1(2)	7(2)	1(2)
C(11)	48(2)	40(2)	40(2)	-5(2)	10(2)	12(2)
C(12)	51(2)	50(2)	42(2)	3(2)	8(2)	12(2)
C(13)	42(2)	40(2)	37(2)	-3(2)	1(2)	0(2)
C(14)	39(2)	39(2)	33(2)	-5(2)	3(2)	-1(2)
C(15)	47(2)	64(3)	49(2)	3(2)	-6(2)	3(2)
C(16)	63(3)	56(3)	56(3)	16(2)	3(2)	-2(2)
C(17)	43(2)	52(2)	52(2)	2(2)	3(2)	-7(2)
C(18)	45(2)	46(2)	51(2)	3(2)	-2(2)	-8(2)
C(19)	54(2)	57(3)	39(2)	-1(2)	0(2)	12(2)
C(20)	111(4)	97(4)	38(3)	18(3)	-10(3)	25(3)
C(21)	46(2)	50(2)	35(2)	-1(2)	3(2)	5(2)
C(22)	60(3)	89(4)	51(3)	-8(2)	18(2)	10(3)
O(1)	130(3)	99(3)	39(2)	4(2)	14(2)	53(2)
O(2)	70(2)	73(2)	42(2)	9(1)	-1(1)	25(2)
O(3)	66(2)	59(2)	67(2)	-29(2)	10(2)	-6(2)
O(4)	53(2)	60(2)	51(2)	-11(1)	17(1)	-4(1)

**Table VIII. Hydrogen coordinates (x 10<sup>4</sup>) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for compound 7.**

	x	y	z	U(eq)
H(1A)	7745	5006	1721	60
H(1B)	6300	4033	1830	60
H(2A)	10192	4474	3209	69
H(2B)	7875	4528	3563	69
H(3A)	7485	2743	3373	66
H(3B)	9572	2984	4190	66
H(5)	7865	2262	1447	45
H(6A)	12041	1925	977	53
H(6B)	10039	1191	759	53
H(7A)	10251	1665	-931	48
H(7B)	11235	2748	-584	48
H(11)	6135	4969	86	51
H(12A)	5253	5254	-1779	57
H(12B)	3783	4307	-1588	57
H(15A)	13488	2243	2578	65
H(15B)	13122	2478	3783	65
H(15C)	12894	3365	2911	65
H(16A)	8485	1064	2835	71
H(16B)	10427	1145	3780	71
H(16C)	10842	833	2602	71
H(17A)	4716	2275	-942	59
H(17B)	6171	1706	9	59
H(17C)	6272	1388	-1206	59
H(18A)	12034	4263	1728	58
H(18B)	10865	4955	786	58
H(18C)	11928	3907	510	58
H(20A)	3240	5864	-4901	101
H(20B)	3504	4717	-5269	101
H(20C)	5503	5461	-5127	101
H(22A)	13213	2455	-3599	79
H(22B)	11038	2067	-4258	79
H(22C)	12073	1468	-3215	79

**Table IX.** Torsion angles [°] for compound 7.

C(10)-C(1)-C(2)-C(3)	-56.5(5)	C(4)-C(5)-C(10)-C(9)	-168.8(3)
C(1)-C(2)-C(3)-C(4)	58.1(5)	C(6)-C(5)-C(10)-C(18)	-61.0(4)
C(2)-C(3)-C(4)-C(15)	73.1(4)	C(4)-C(5)-C(10)-C(18)	70.7(4)
C(2)-C(3)-C(4)-C(16)	-170.3(3)	C(8)-C(9)-C(11)-C(12)	-5.8(5)
C(2)-C(3)-C(4)-C(5)	-53.9(4)	C(10)-C(9)-C(11)-C(12)	171.4(3)
C(3)-C(4)-C(5)-C(6)	-177.9(3)	C(9)-C(11)-C(12)-C(13)	-21.3(5)
C(15)-C(4)-C(5)-C(6)	58.2(4)	C(11)-C(12)-C(13)-C(14)	21.3(5)
C(16)-C(4)-C(5)-C(6)	-61.4(4)	C(11)-C(12)-C(13)-C(19)	-159.3(3)
C(3)-C(4)-C(5)-C(10)	51.5(4)	C(19)-C(13)-C(14)-C(21)	-3.1(6)
C(15)-C(4)-C(5)-C(10)	-72.5(4)	C(12)-C(13)-C(14)-C(21)	176.3(4)
C(16)-C(4)-C(5)-C(10)	167.9(3)	C(19)-C(13)-C(14)-C(8)	-174.0(3)
C(4)-C(5)-C(6)-C(7)	-162.8(3)	C(12)-C(13)-C(14)-C(8)	5.4(5)
C(10)-C(5)-C(6)-C(7)	-29.0(4)	C(7)-C(8)-C(14)-C(13)	-152.3(3)
C(5)-C(6)-C(7)-C(8)	-30.1(4)	C(9)-C(8)-C(14)-C(13)	-31.3(4)
C(6)-C(7)-C(8)-C(9)	57.1(4)	C(17)-C(8)-C(14)-C(13)	88.2(4)
C(6)-C(7)-C(8)-C(14)	178.4(3)	C(7)-C(8)-C(14)-C(21)	36.0(4)
C(6)-C(7)-C(8)-C(17)	-64.7(4)	C(9)-C(8)-C(14)-C(21)	157.1(3)
C(7)-C(8)-C(9)-C(11)	153.0(3)	C(17)-C(8)-C(14)-C(21)	-83.5(4)
C(14)-C(8)-C(9)-C(11)	31.0(4)	C(14)-C(13)-C(19)-O(1)	0.6(7)
C(17)-C(8)-C(9)-C(11)	-85.5(4)	C(12)-C(13)-C(19)-O(1)	-178.8(5)
C(7)-C(8)-C(9)-C(10)	-24.3(4)	C(14)-C(13)-C(19)-O(2)	180.0(4)
C(14)-C(8)-C(9)-C(10)	-146.2(3)	C(12)-C(13)-C(19)-O(2)	0.6(5)
C(17)-C(8)-C(9)-C(10)	97.2(3)	C(13)-C(14)-C(21)-O(3)	-94.0(5)
C(2)-C(1)-C(10)-C(9)	169.1(3)	C(8)-C(14)-C(21)-O(3)	77.5(5)
C(2)-C(1)-C(10)-C(18)	-72.6(4)	C(13)-C(14)-C(21)-O(4)	91.3(4)
C(2)-C(1)-C(10)-C(5)	50.9(4)	C(8)-C(14)-C(21)-O(4)	-97.2(4)
C(11)-C(9)-C(10)-C(1)	32.6(5)	O(1)-C(19)-O(2)-C(20)	0.4(7)
C(8)-C(9)-C(10)-C(1)	-150.3(3)	C(13)-C(19)-O(2)-C(20)	-179.0(4)
C(11)-C(9)-C(10)-C(18)	-85.9(4)	O(3)-C(21)-O(4)-C(22)	2.4(5)
C(8)-C(9)-C(10)-C(18)	91.3(4)	C(14)-C(21)-O(4)-C(22)	177.1(3)
C(11)-C(9)-C(10)-C(5)	150.5(3)		
C(8)-C(9)-C(10)-C(5)	-32.3(4)		
C(6)-C(5)-C(10)-C(1)	178.5(3)		
C(4)-C(5)-C(10)-C(1)	-49.7(4)		
C(6)-C(5)-C(10)-C(9)	59.4(4)		



Method	<i>anti</i> -adduct	<i>syn</i> -adduct	$\Delta E_{\text{syn}-\text{anti}}$ (kcal/mol)
AM1(atomic units)	-0.2789264	-0.2767965	1.3
PM3 (atomic units)	-0.2847138	-0.283822	0.6
MM2 (kcal/mol)	56.8	57.7	0.9

**Figure 2.** Optimized structures and energies of the Diels-Alder adducts formed in the reaction of diene 6 with DMAD.

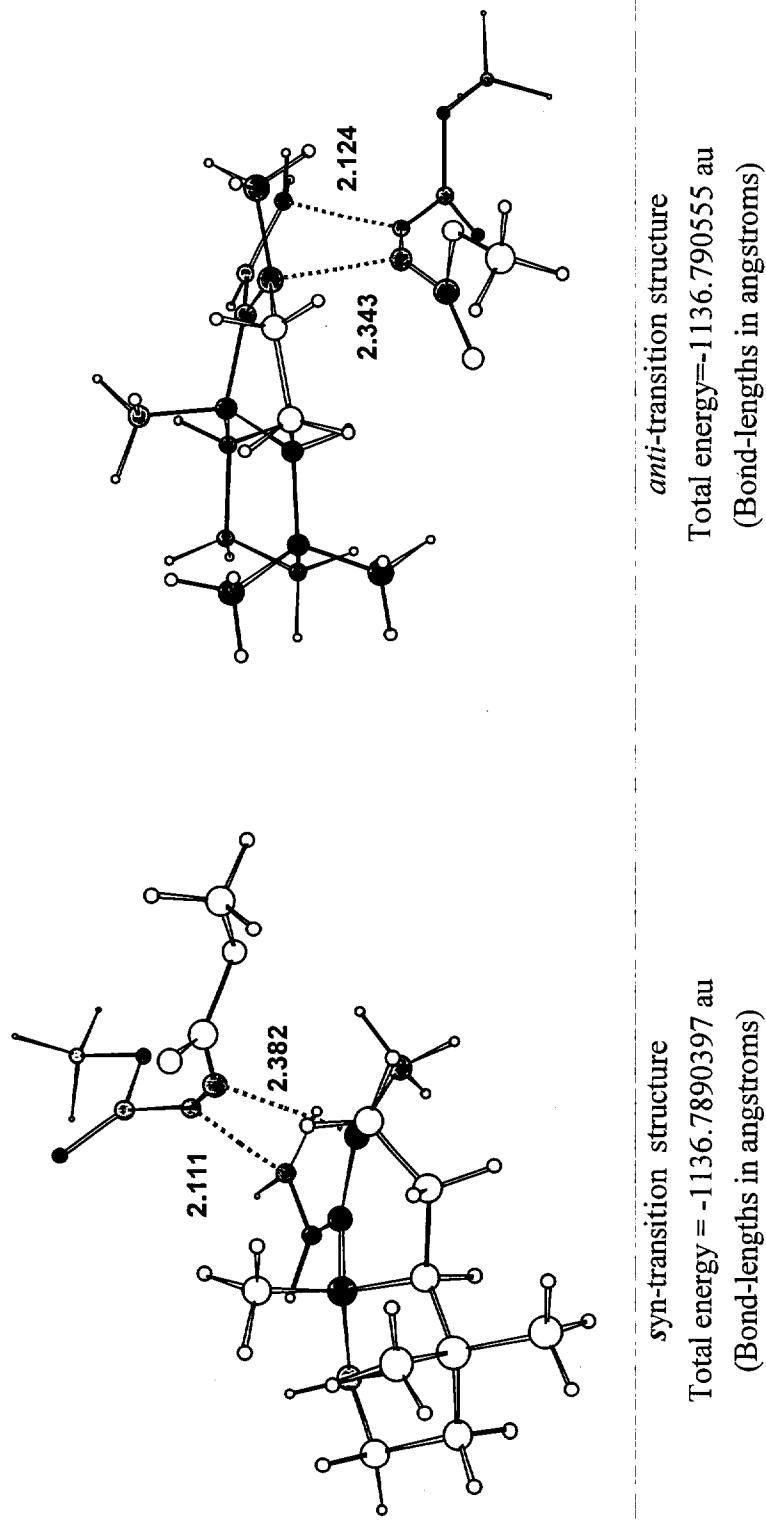
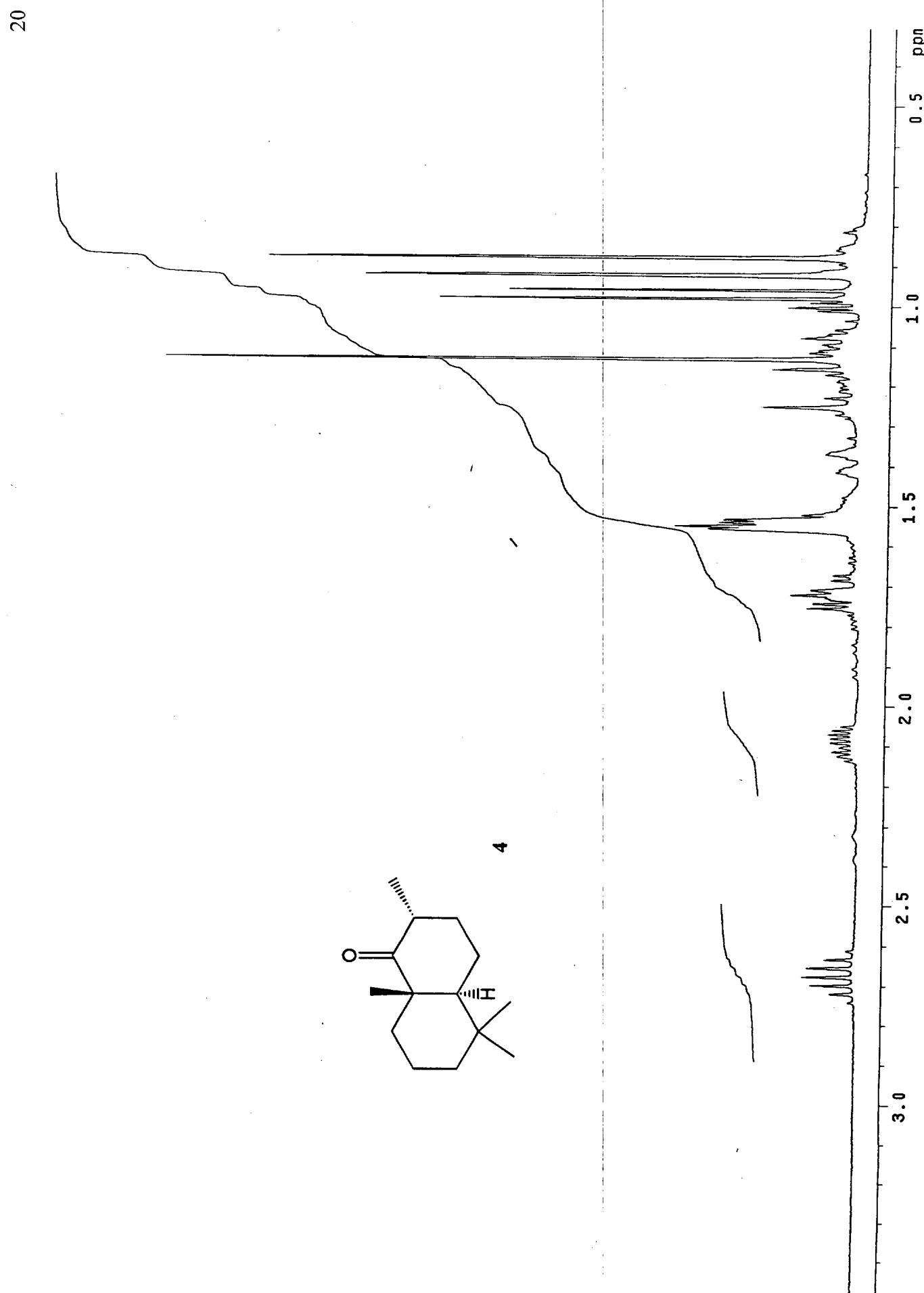
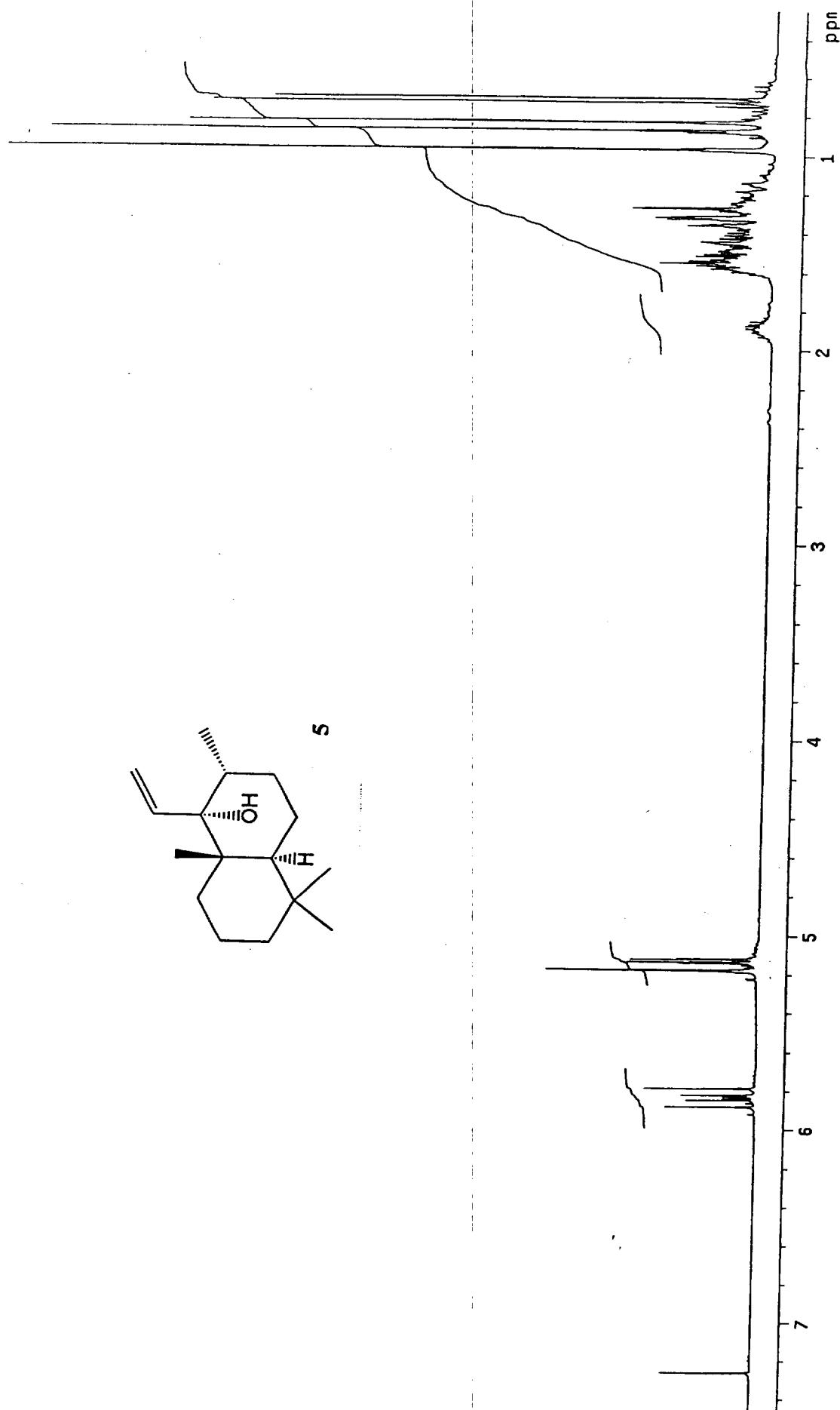


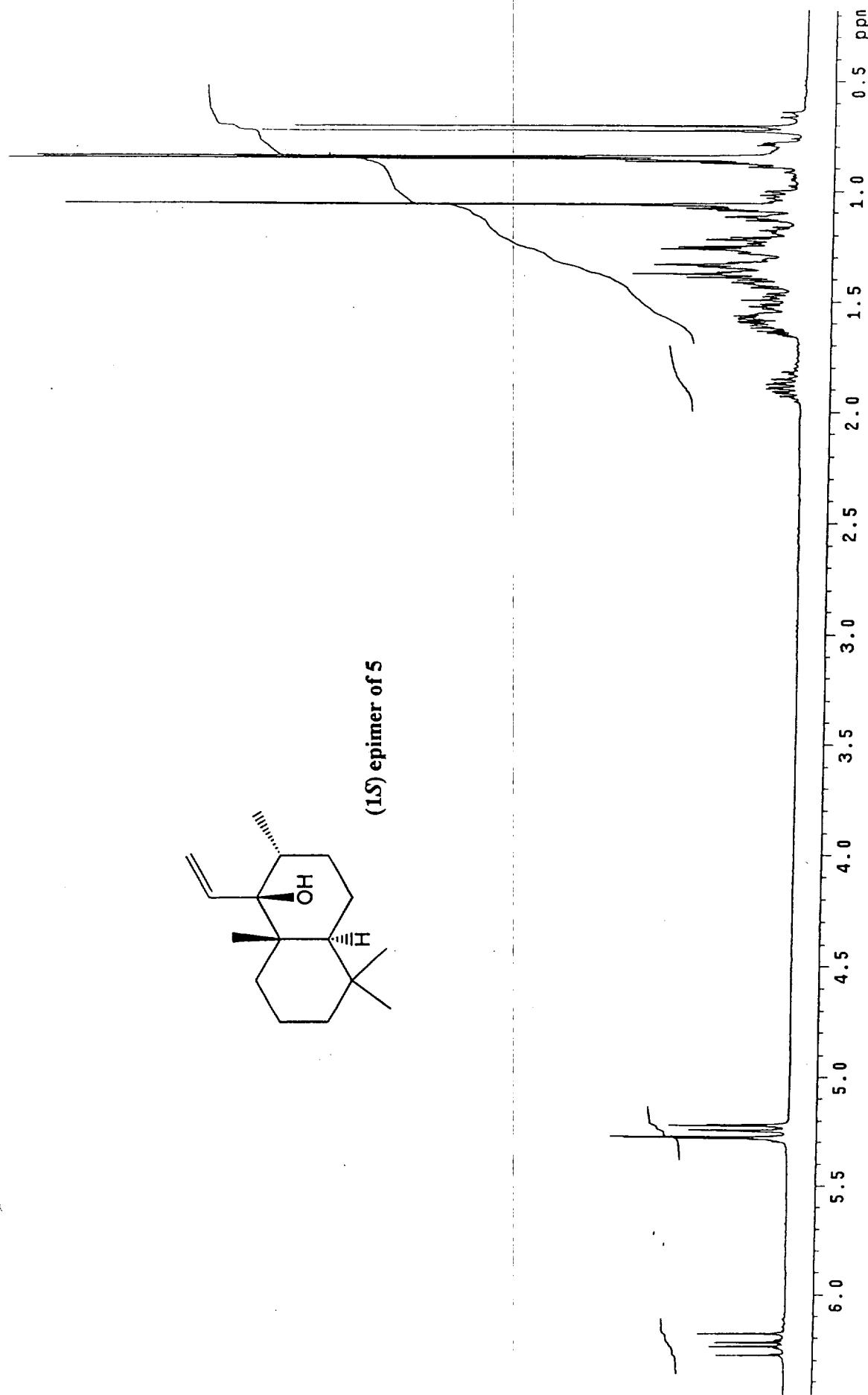
Figure 3. Transition optimized structures of the Diels-Alder reaction of diene 6 with DMAD at HF/STO-3G.



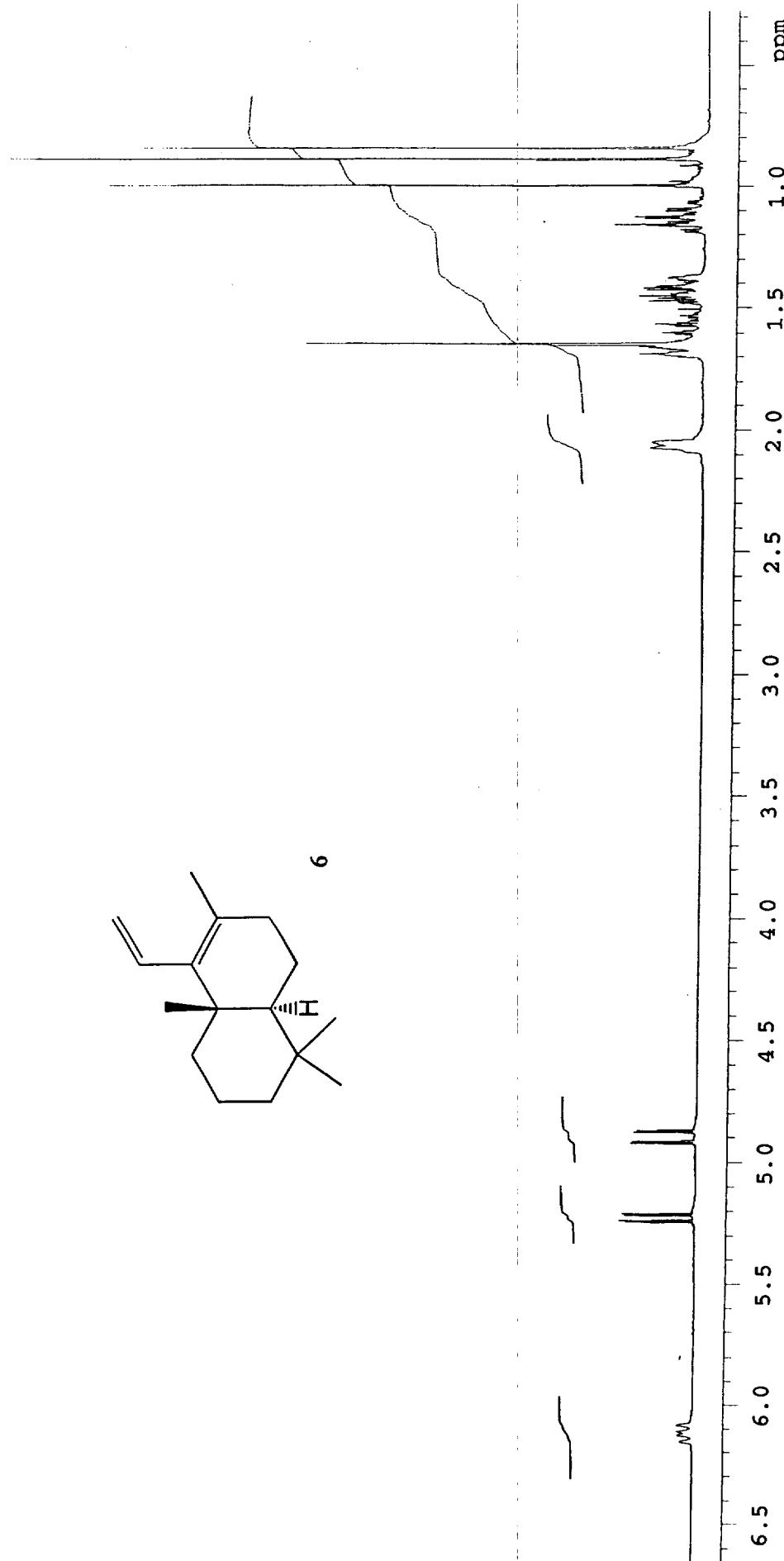
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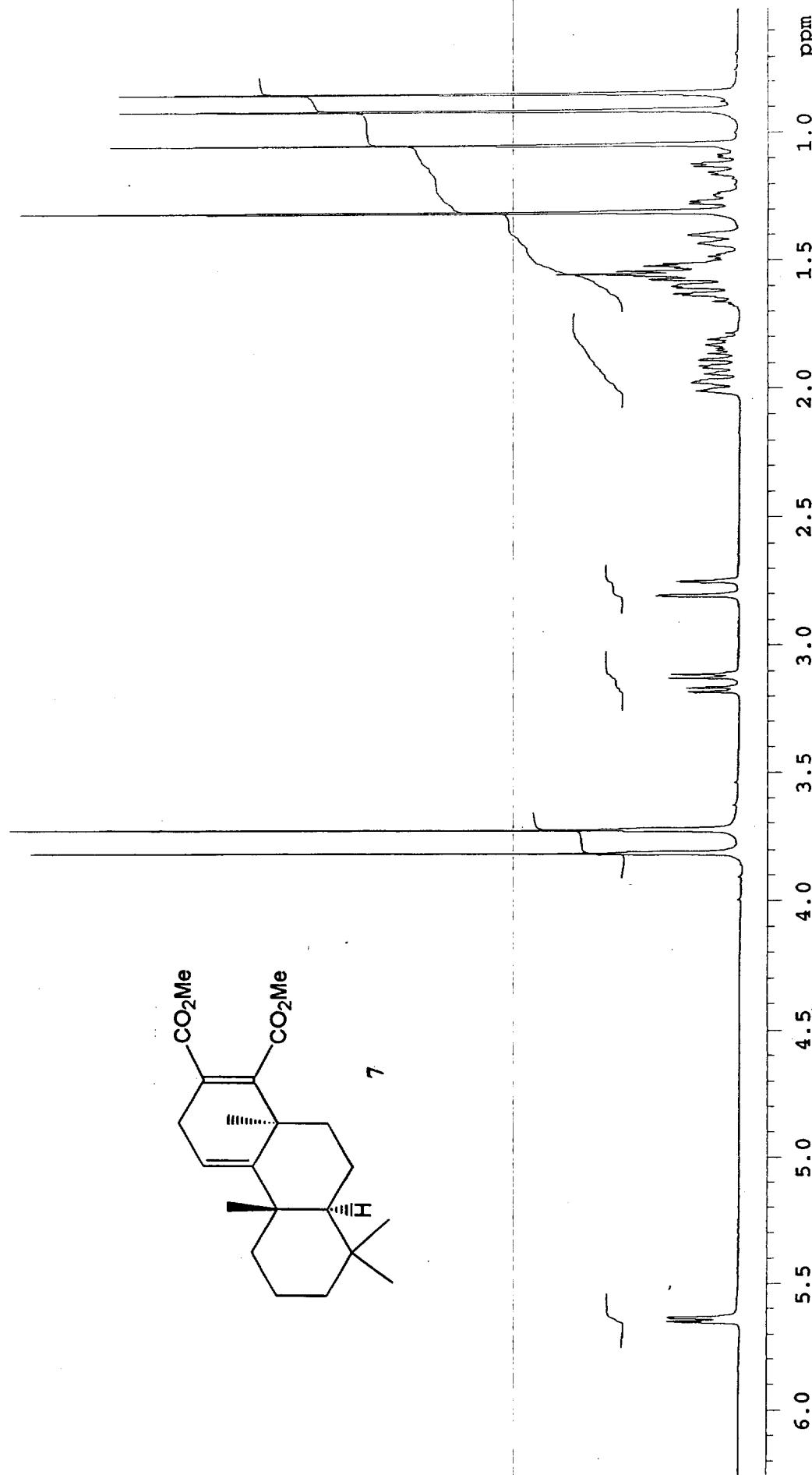
22

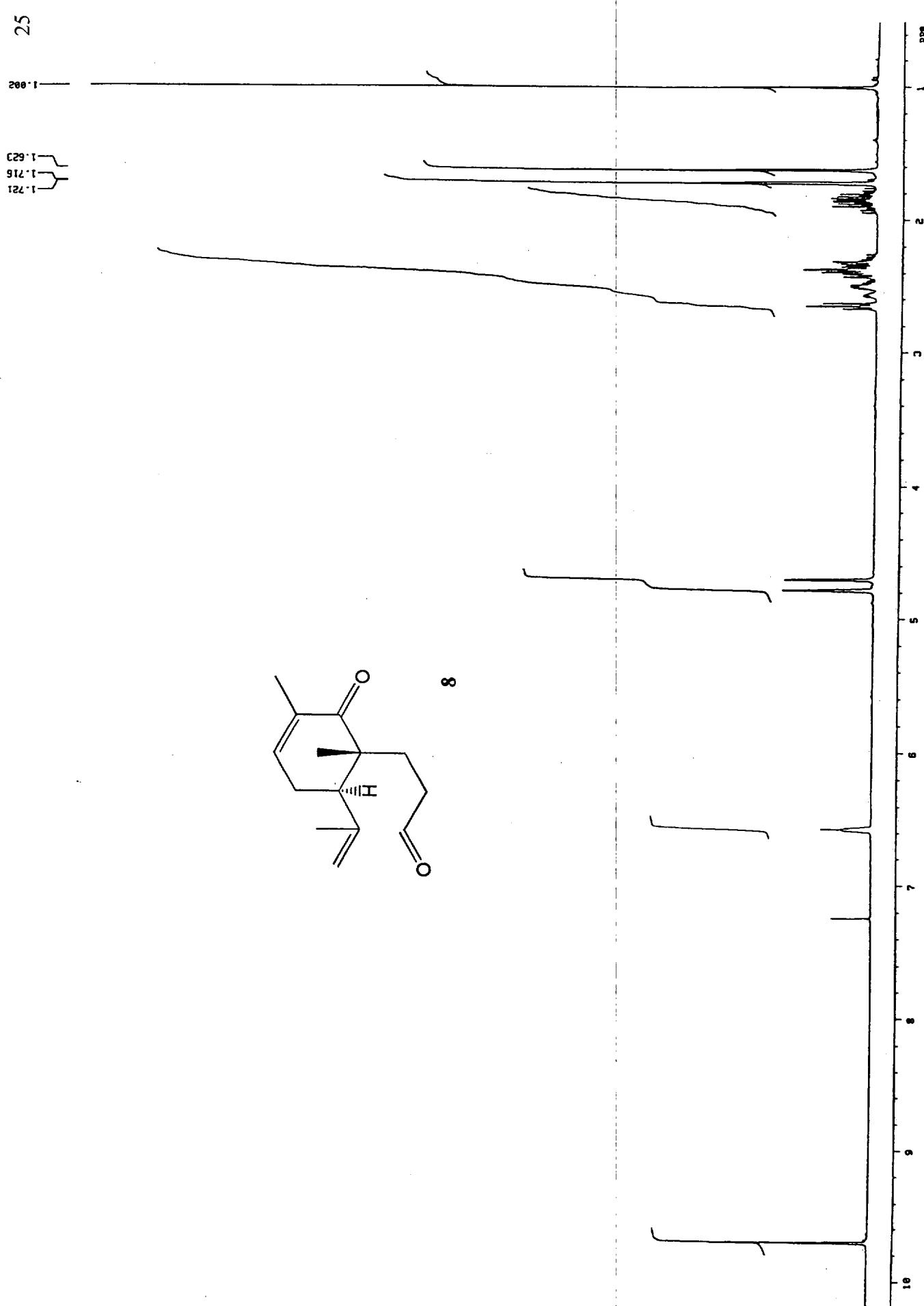


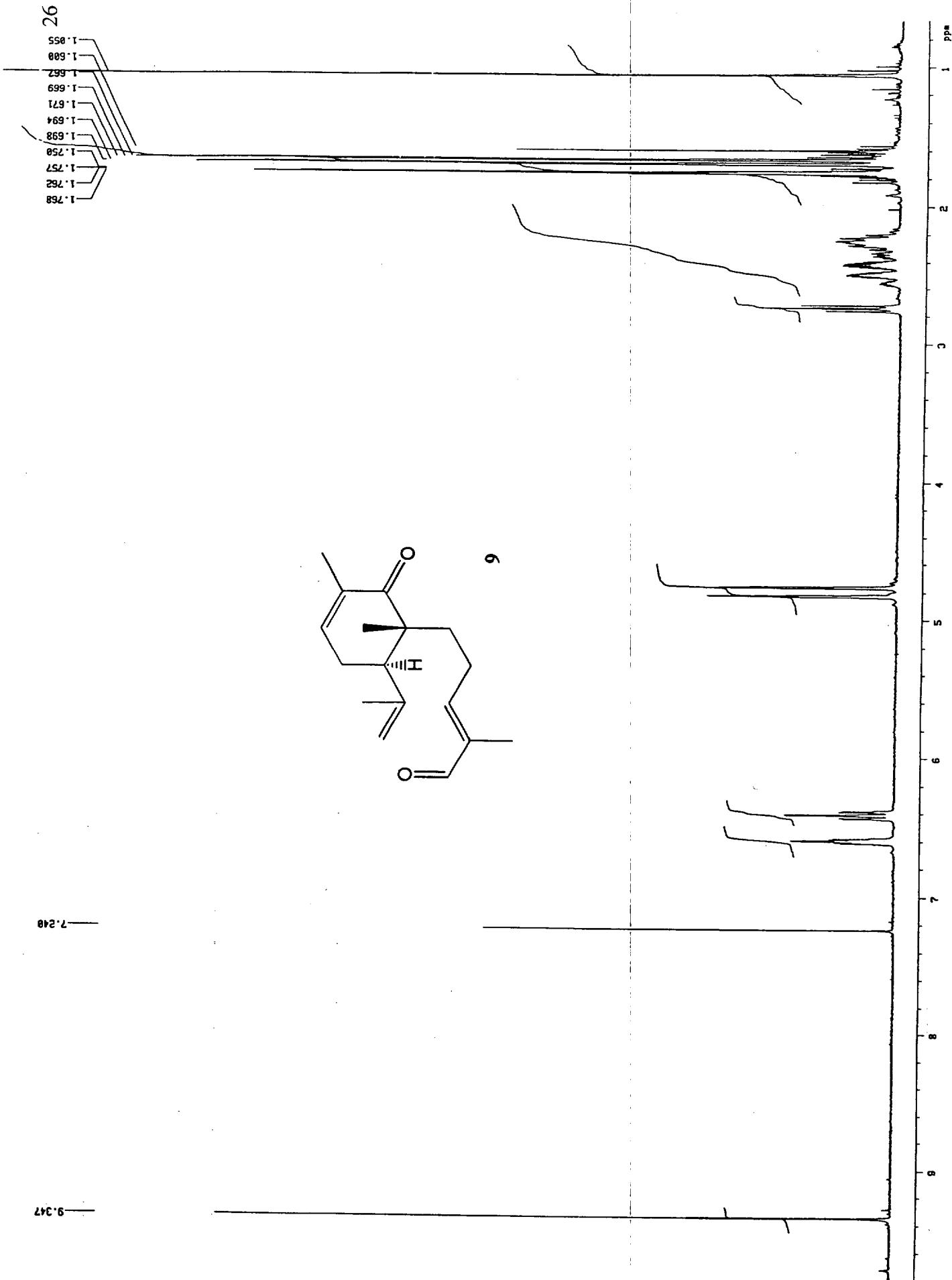
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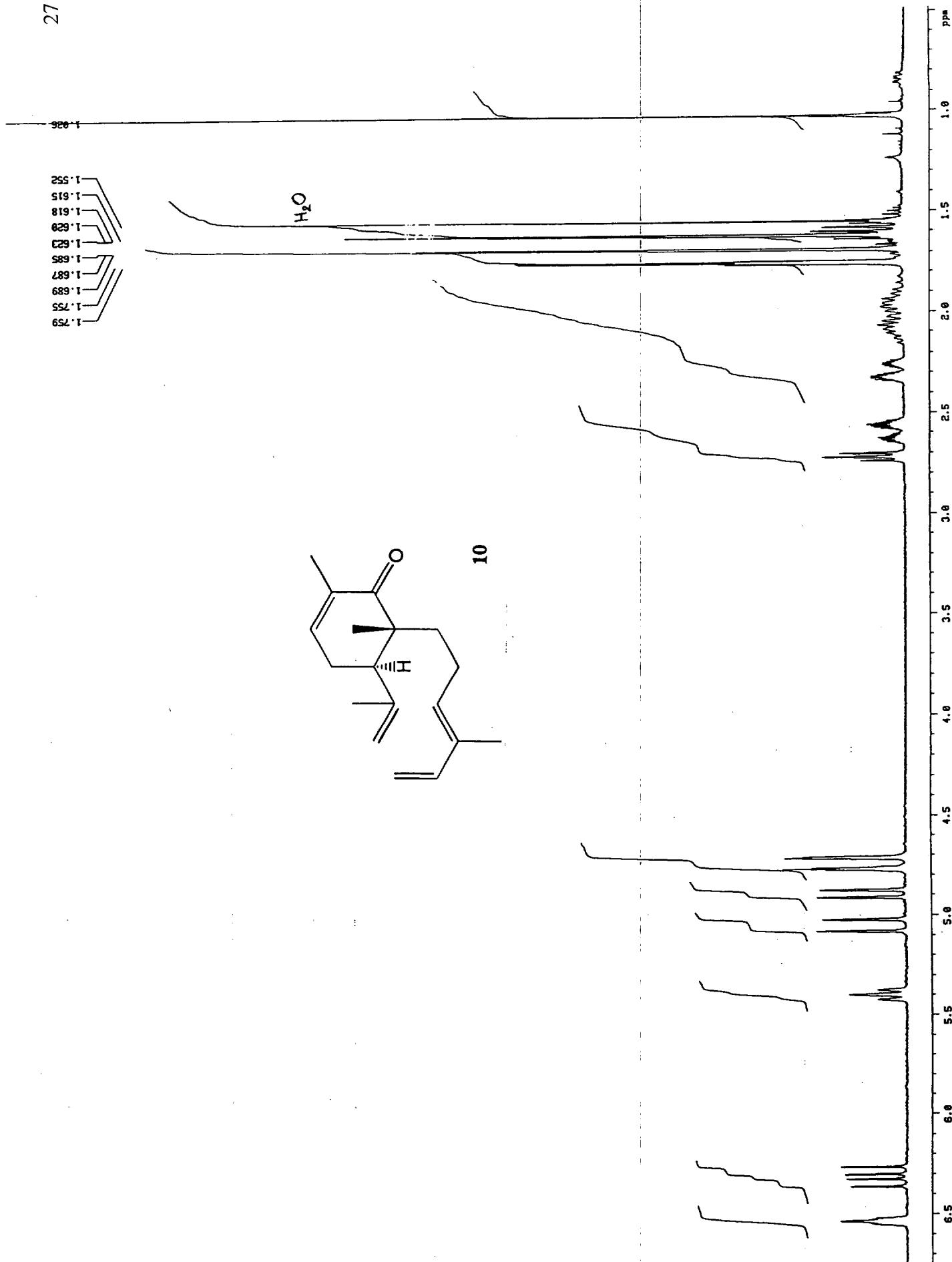
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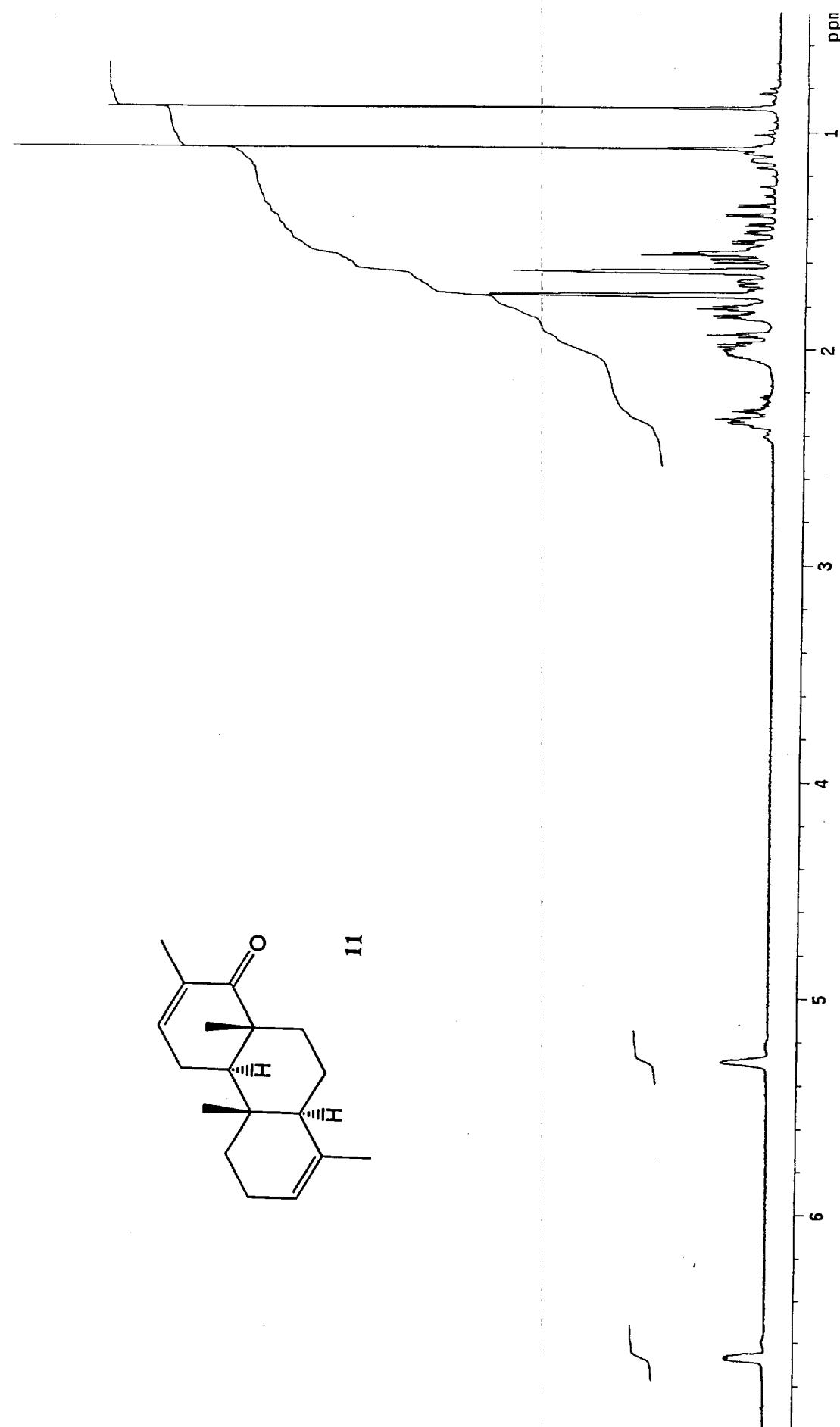




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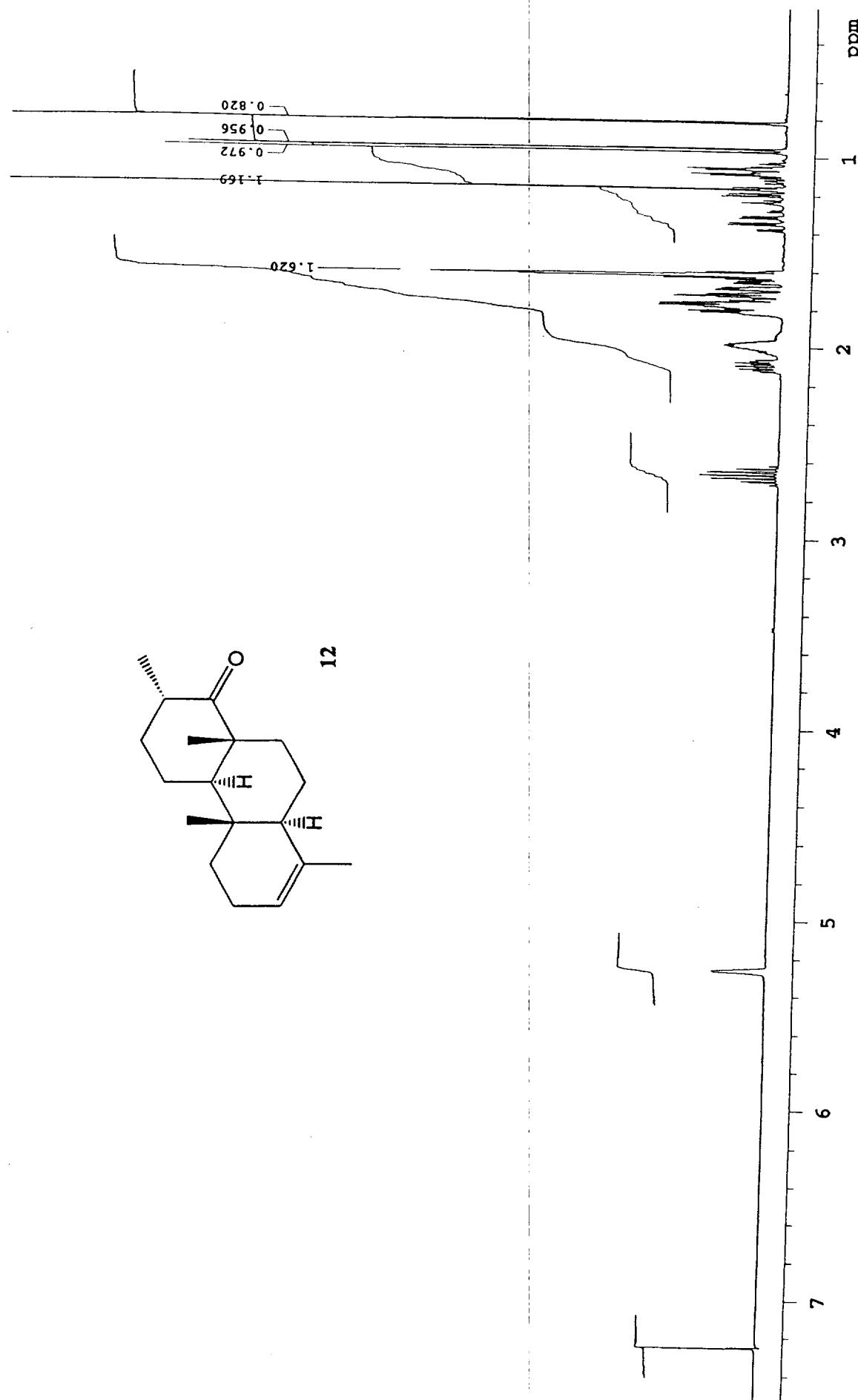


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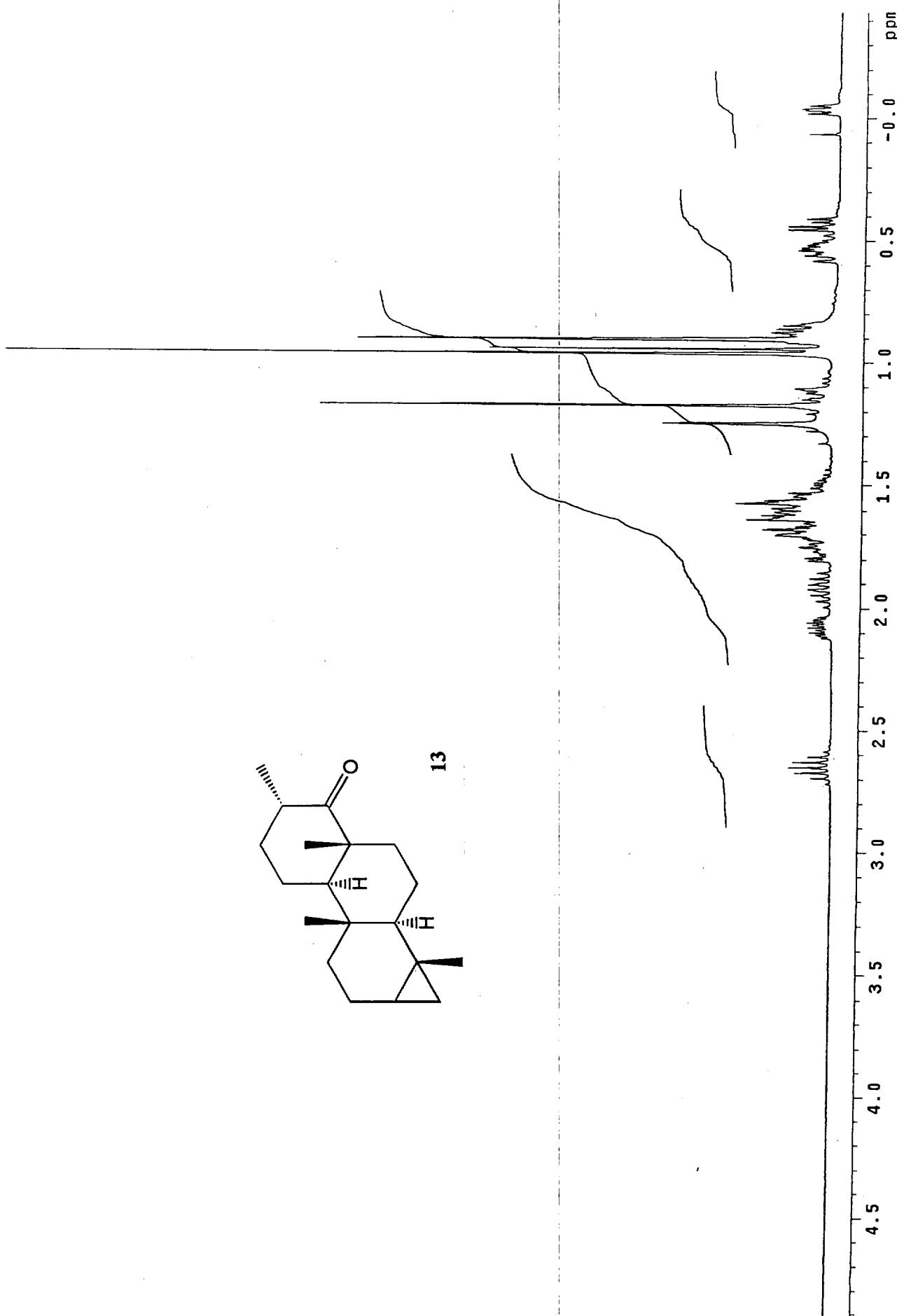
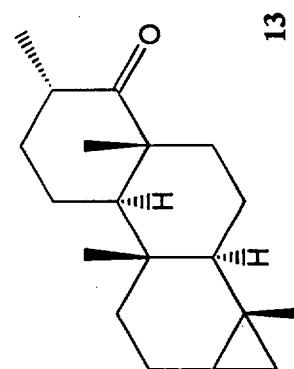


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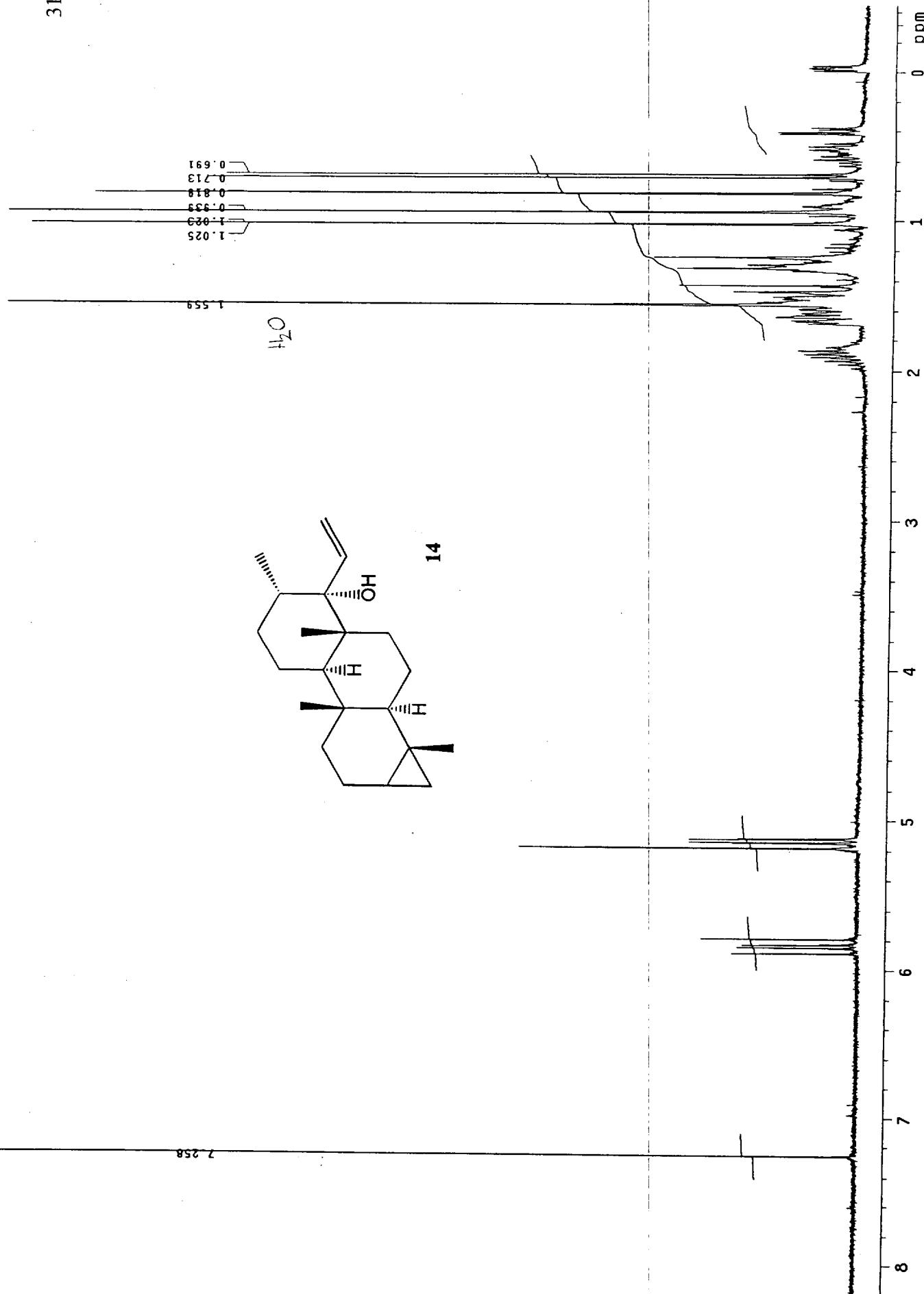
29



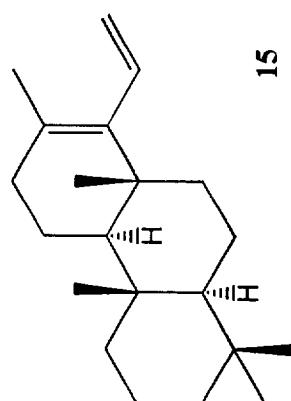
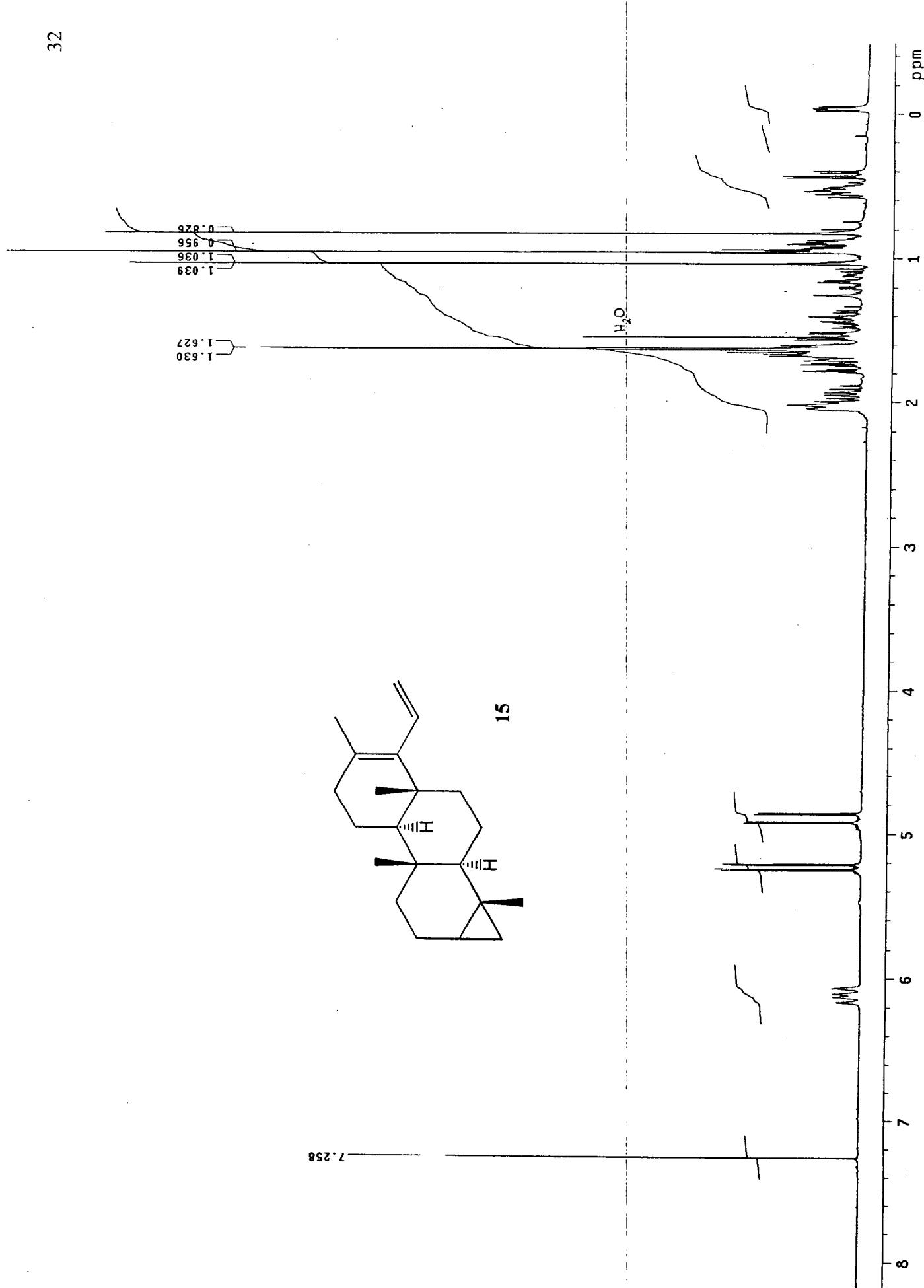
30



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