Synthesis of CDE and BCDE Molecular Fragments of the Limonoids Havanensin and Azadiradione

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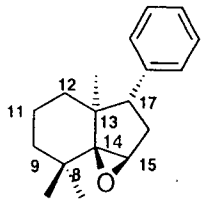
Supporting information. ^{1}H and ^{13}C spectra for compounds **1**, **2a**, **3a**, **4**, **5**, **7**, **8**, **9a**, **11a,b**, **12**, **13**, **14a,b**, **15a,b**, **16a,b**, **17**, **18**, **19**, **20**, **21** and **22**. H-C correlations for compounds **9a,b**, **14a,b**, **18**, **19**, **21**, **22**. X-ray crystallographic data for compounds **13** and **22**.

3a,7,7-Trimethyl-3-phenyloctahydroinden-1-one 13

Crystal data: $C_{18}H_{24}O$; Mr= 256.37; monoclinic; space group P21/c; unit cell dimensions a= 8.0447 (5) Å, b= 23.464 (3) Å; c= 8.0809 (5) Å, $\alpha = 90°$, $\beta = 99.41°$, $\gamma = 90$ °; volume 1504.8 (2) $Å^3$; Z=4, Dx=1.132 mg/m^3; absorption coefficient 0.515 mm^{-1}; crystal size 0.54 x 0.36 x 0.30 mm; θ range for data collection 3.77° to 65.00 °; limiting indices $-9 \leq h \leq 9$, $0 \leq k \leq 27$, $0 \leq l \leq 9$; R = 0.0586; Rw = 0.1152.

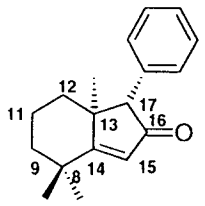
3a,6,6,9a-Tetramethyl-3-phenyl-3,3a,4,5,5a,6,7,8,9,9a-decahydrocyclopenta[a]naphthalen-2-on 22.

Crystal data: $C_{23}H_{30}O$; Mr= 322.47; Orthorhombic; space group P21 21 21; unit cell dimensions a= 8.8289 (7) Å, b= 7.9556 (5) Å; c= 26.849 (2) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90$ °; volume 1885.9 (2) $Å^3$; Z=4, Dx=1.136 mg/m^3; absorption coefficient 0.507 mm^{-1}; crystal size 0.48 x 0.24 x 0.18 mm; θ range for data collection 3.29° to 64.99 °; limiting indices $-10 \leq h \leq 10$, $0 \leq k \leq 9$, $0 \leq l \leq 31$; R = 0.0483; Rw = 0.0795.



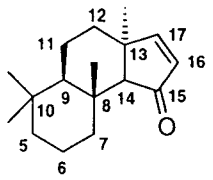
18

C	δ C (ppm)	δ H (ppm)	HMBC
8	33.7	--	Me (C8)
9	38.2	1.40, 1.50	Me (C8)
11	19.1	1.60	
12	34.2	1.60	Me (C13)
13	43.0	--	H-12, H-16, Me (C13)
14	73.3	--	Me (C8), Me (C13)
15	57.5	3.58	H-16
16	29.4	2.00	
17	49.1	2.87	H (Ph), H-15, Me (C13)
Me (C8)	25.6	1.17	H-9, Me (C8)
Me (C8)	27.7	0.85	H-9, Me (C8)
Me (C13)	17.5	0.65	H-17, H-12



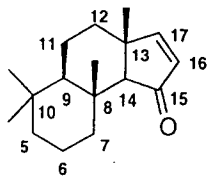
19

C	δ C (ppm)	δ H (ppm)	HMBC
8	36.1	--	Me (C8)
9	40.9	1.50, 1.70	Me (C8)
11	18.6		H-12
12	39.7	1.60, 2.00	H-17, Me (C13)
13	48.8	--	H-15, H-17, Me (C13)
14	191.9	--	H-15, Me (C8), Me (C13)
15	125.7	6.02	
16	207.1	--	H-15, H-17
17	68.7	3.55	H (Ph), Me (C13)
Me (C8)	27.2	1.27	Me (C8)
Me (C8)	31.2	1.26	Me (C8)
Me (C13)	24.9	0.88	H-17, H-12



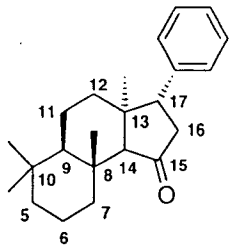
9a

C	δ C (ppm)	δ H (ppm)	HMBC
5	42.3	1.20, 1.40	H-7, Me (C10) α, Me (C10) β
6	18.3		
7	43.2	1.20, 2.43	H-14, Me (C8)
8	38.3	--	H-14, Me (C8)
9	47.8	1.22	Me (C8), Me (C10) α, Me (C10) β
10	33.7	--	Me (C10) α, Me (C10) β
11	18.3		
12	29.8	1.50, 1.60	Me (C13)
13	44.3	--	Me (C13)
14	67.1	1.66	Me (C8), Me (C13)
15	211.6	--	H-14
16	131.8	5.96	
17	173.0	7.37	Me (C13)
Me (C8)	17.1	0.81	H-9, H-14
Me (C10) α	32.8	0.85	Me (C10) β
Me (C10) β	21.2	0.89	Me (C10) α
Me (C13)	28.0	1.17	H-14



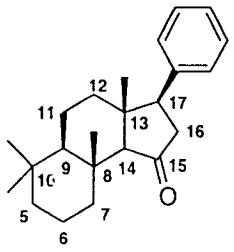
9b

C	δ C (ppm)	δ H (ppm)	HMBC
5	41.9	1.12, 1.35	Me (C10) α, Me (C10) β
6	18.1		
7	35.8	1.35, 2.40	Me (C8)
8	39.3	--	Me (C8)
9	45.9	1.03	H-14, Me (C8), Me (C10) α, Me (C10) β
10	33.8	--	Me (C10) α
11	19.2	1.40, 1.60	
12	34.8		Me (C13)
13	45.7	--	Me (C13)
14	66.6	1.75	H-16, H-17, Me (C8), Me (C13)
15	211.0	--	H-14, H-16, H-17
16	131.6	5.92	
17	172.5	7.29	Me (C13)
Me (C8)	24.4	1.15	H-7, H-14
Me (C10) α	32.5	0.75	Me (C10) β
Me (C10) β	21.4	0.84	Me (C10) α
Me (C13)	28.6	1.24	



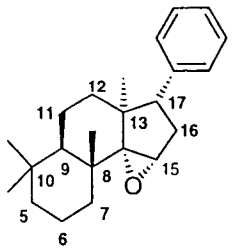
14a

C	δ C (ppm)	δ H (ppm)	HMBC
5	41.7	1.20, 1.45	H-7, Me (C10) α, Me (C10) β
6	18.1		
7	41.4	1.10, 2.10	H-5, H-14, Me (C8)
8	37.5	--	H-14, Me (C8)
9	53.8	0.88	Me (C8), Me (C10) α, Me (C10) β
10	33.3	--	Me (C10) α, Me (C10) β
11	18.2		
12	34.6	1.10, 1.90	Me (C13)
13	42.9	--	H-16
14	71.7	1.78	Me (C8), Me (C13)
15	220.7	--	H-14
16	42.6	2.48, 2.74	
17	46.1	3.68	H (Ph), H-14, Me (C13)
Me (C8)	17.0	1.09	H-14
Me (C10) α	33.5	0.82	Me (C10) β
Me (C10) β	22.0	0.90	Me (C10) α
Me (C13)	27.3	1.68	H-14



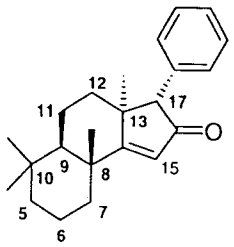
14b

C	δ C (ppm)	δ H (ppm)	HMBC
5	42.0	1.20, 1.4.0	Me (C10) α, Me (C10) β
6	18.1	1.40, 1.70	H-7
7	34.5	1.25, 2.93	H-5, Me (C8)
8	38.0	--	Me (C8)
9	49.6	1.07	Me (C10) α, Me (C10) β
10	33.2	--	Me (C10) α, Me (C10) β
11	19.6	1.50, 1.70	
12	39.2	1.50, 1.75	H-14, Me (C13)
13	44.7	--	H-14, Me (C13)
14	64.1	1.94	H-17, Me (C8), Me (C13)
15	220.2	--	H-14, H-16, H-17
16	45.2	2.48, 2.95	
17	50.0	2.81	H (Ph), Me (C13)
Me (C8)	23.2	1.01	H-14
Me (C10) α	32.9	0.86	Me (C10) β
Me (C10) β	21.6	0.80	Me (C10) α
Me (C13)	26.8	0.92	H-14



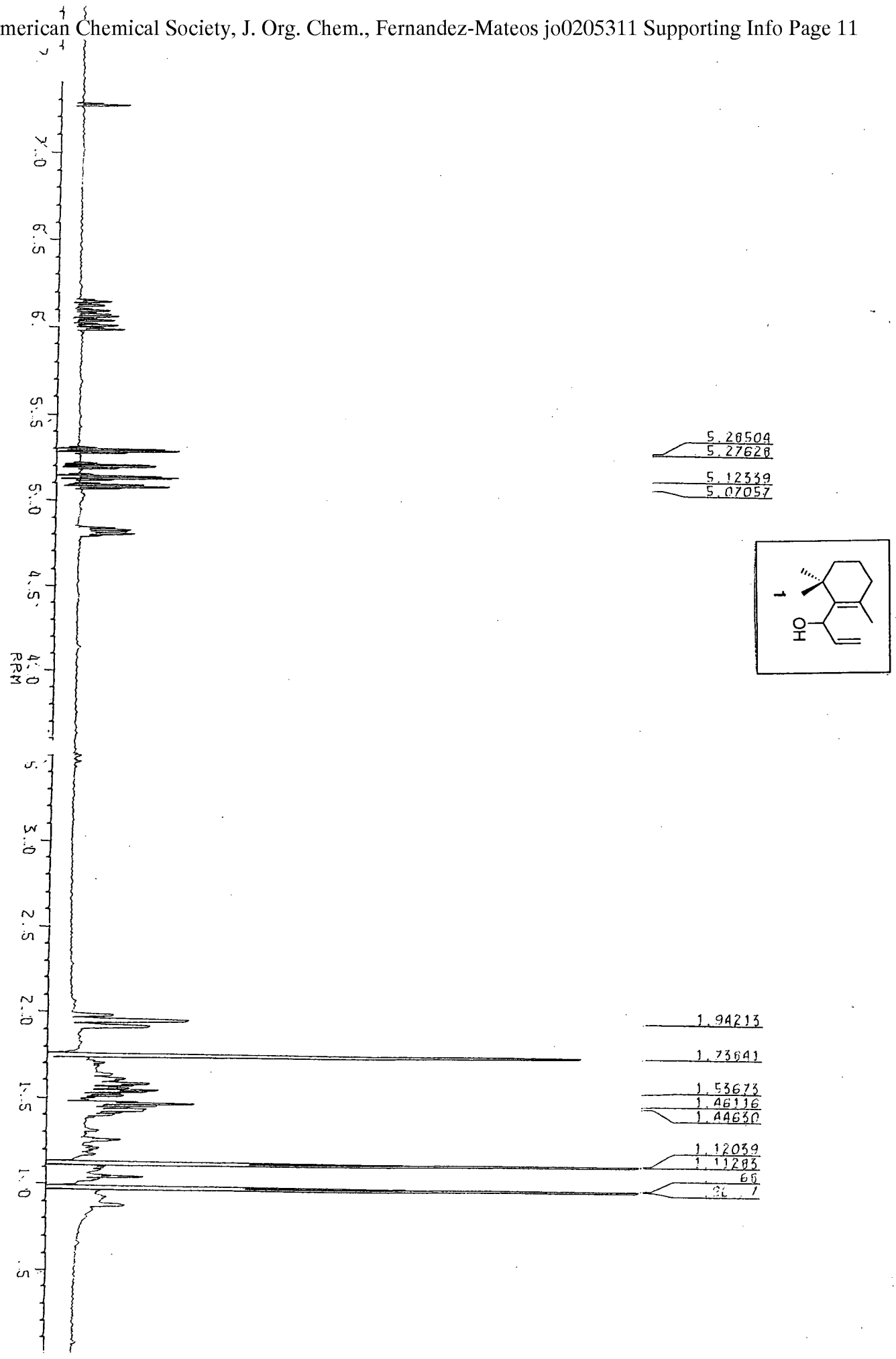
21

C	δ C (ppm)	δ H (ppm)	HMBC
5	42.0	1.20, 1.40	Me (C10) α, Me (C10) β
6	17.8	0.80	
7	33.8	0.90, 1.30	H-9, Me (C8)
8	36.2	--	Me (C8)
9	44.4	1.55	H-11, H-12, Me (C8)
10	33.7	--	Me (C10) α, Me (C10) β
11	17.8	0.80	
12	32.8	1.70	H-17, Me (C13)
13	44.3	--	H-15, H-17
14	81.3	--	Me (C8), Me (C13)
15	61.0	3.36	H-16
16	32.3	2.13	H-15, H-17
17	63.7	3.27	H (Ph), H-15, Me (C13)
Me (C8)	22.7	1.19	H-7
Me (C10) α	32.3	0.83	Me (C10) β
Me (C10) β	21.4	0.94	Me (C10) α
Me (C13)	18.5	0.61	H-17



22

C	δ C (ppm)	δ H (ppm)	HMBC
5	41.9	1.20, 1.50	H-7, Me (C10) α, Me (C10) β
6	18.8	1.55, 1.80	
7	38.3	1.40, 2.00	H-6, Me (C8)
8		--	Me (C8)
9	43.8	1.85	Me (C8), Me (C10) α, Me (C10) β
10	33.6	--	Me (C10) α, Me (C10) β
11	17.0	1.80, 1.90	
12	30.2	1.85, 2.00	Me (C13)
13	49.1	--	H-15, H-17, Me (C13)
14	197.9	--	H-15, Me (C8), Me (C13)
15	123.6	5.98	
16	206.9	--	H-15, H-17
17	69.6	3.56	H (Ph),H-15, Me (C13)
Me (C8)	25.2	1.24	H-7, H-9
Me (C10) α	33.0	0.88	Me (C10) β
Me (C10) β	21.2	0.97	Me (C10) α
Me (C13)	26.8	0.94	H-17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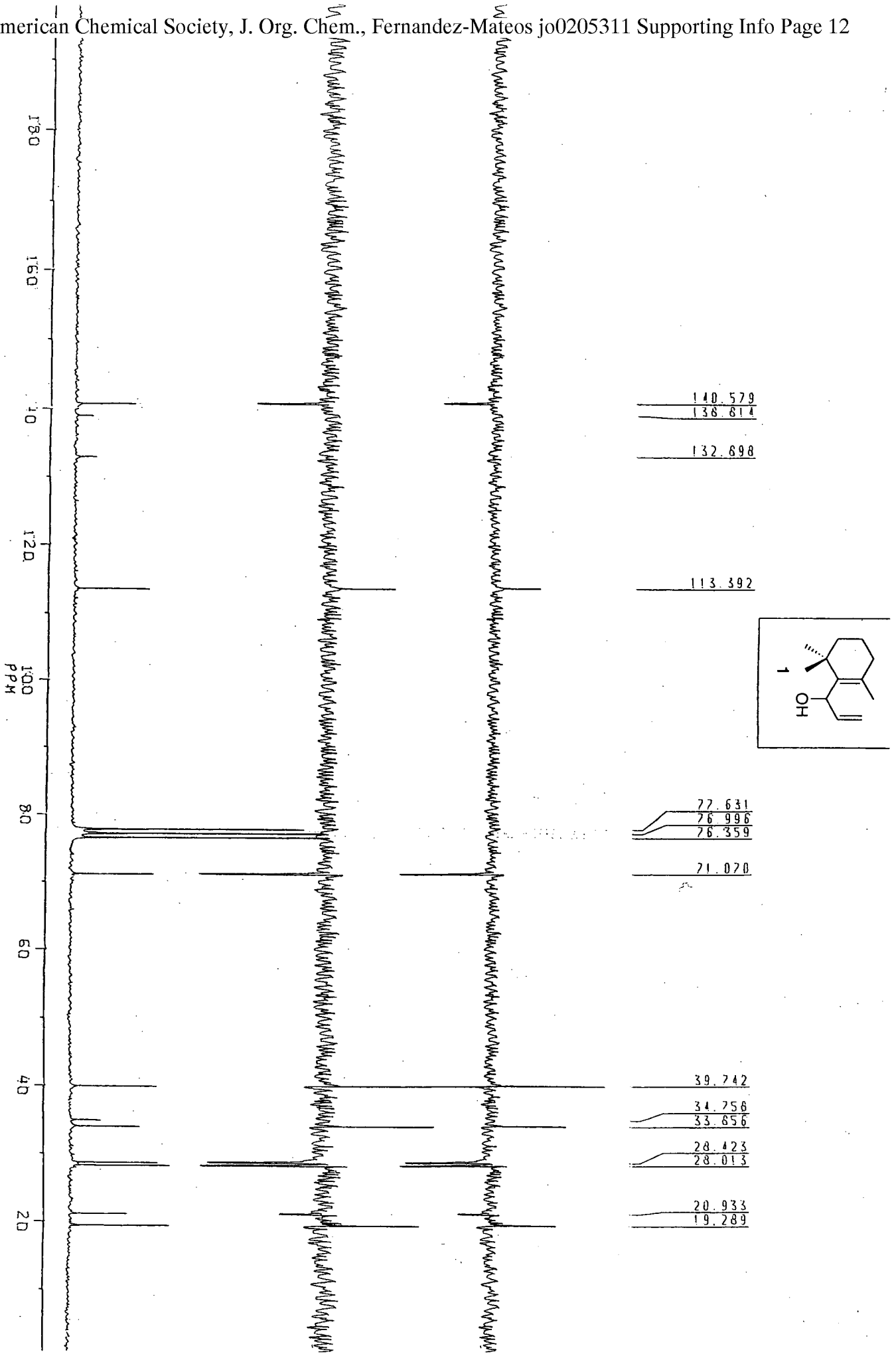

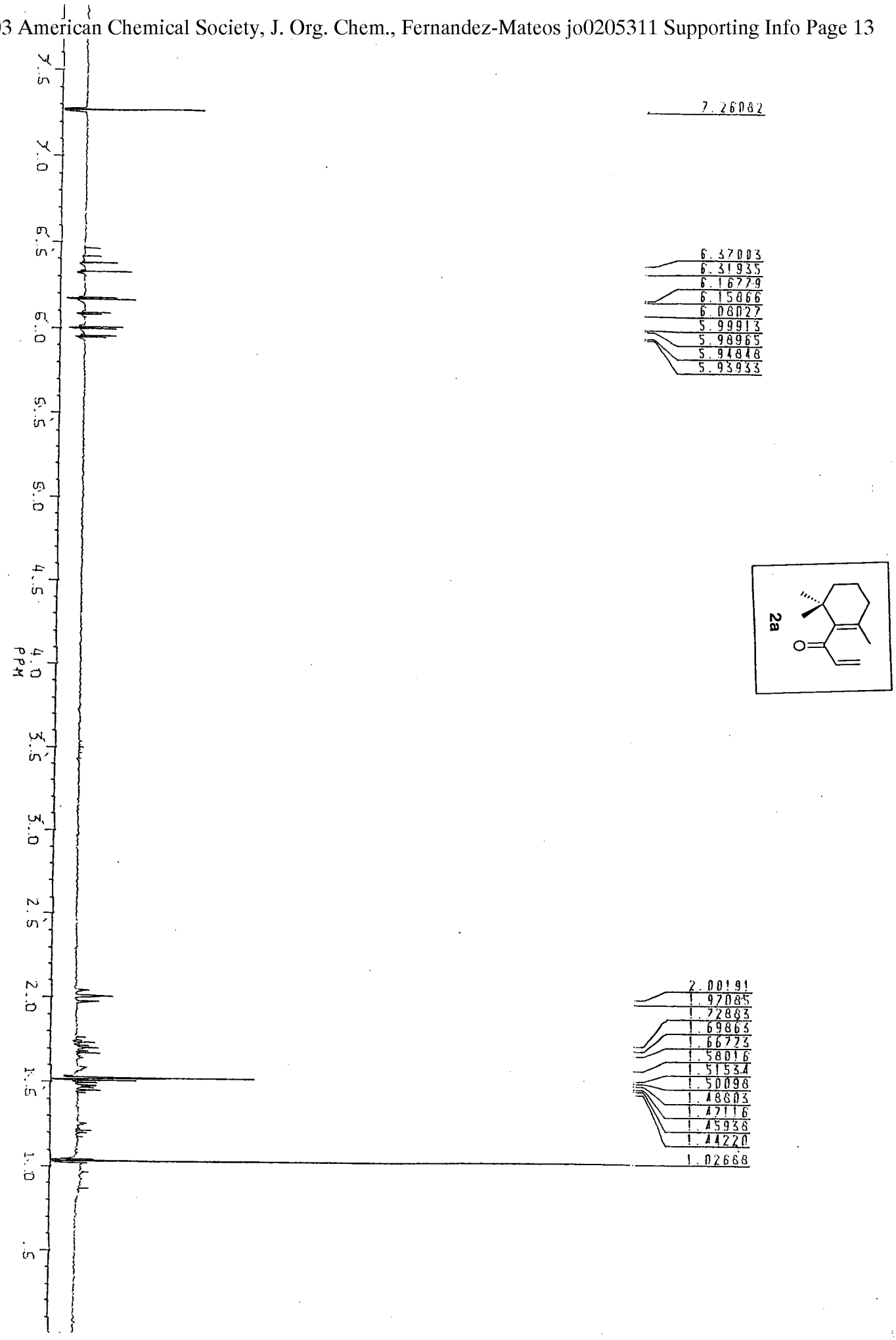

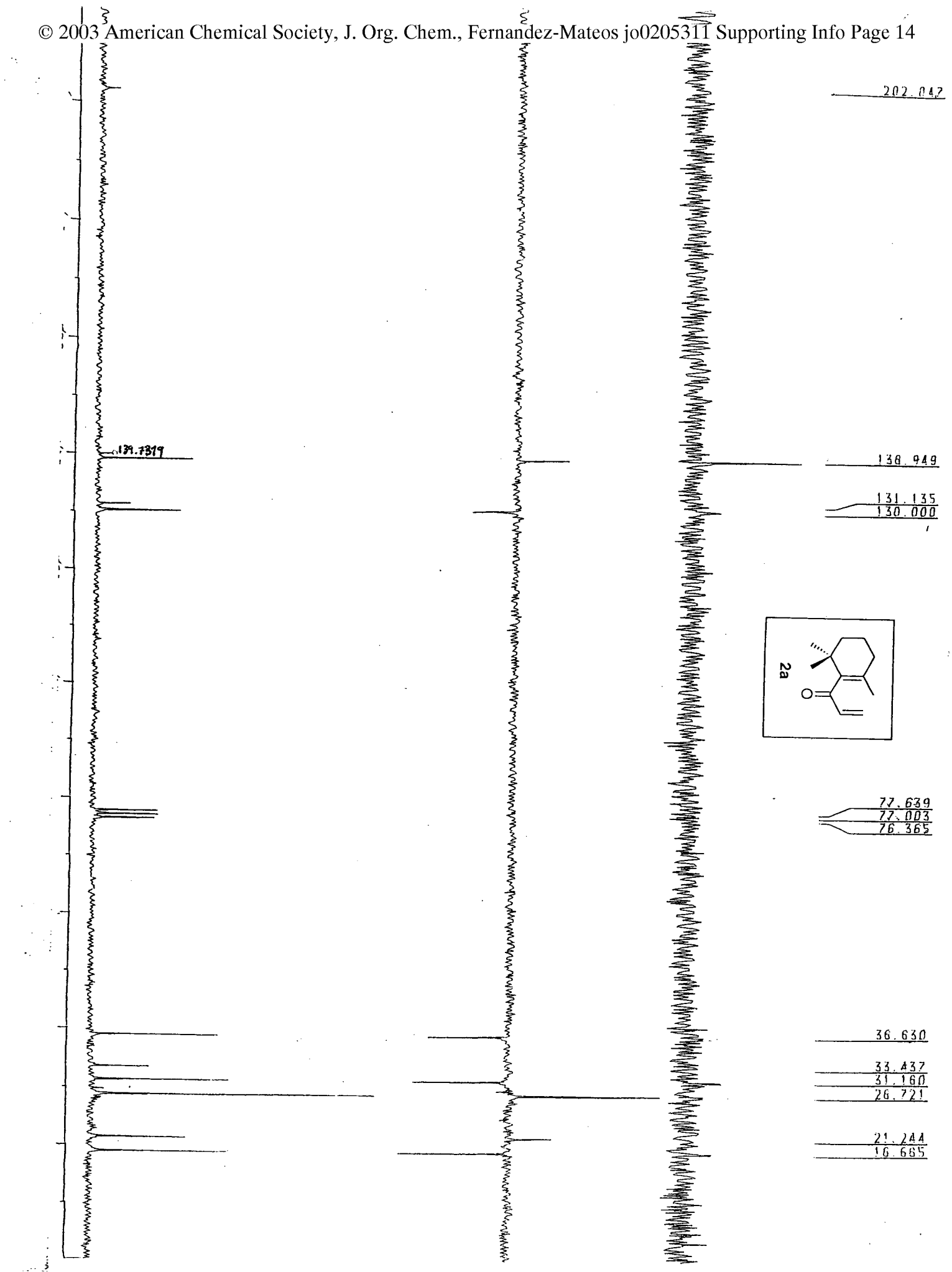

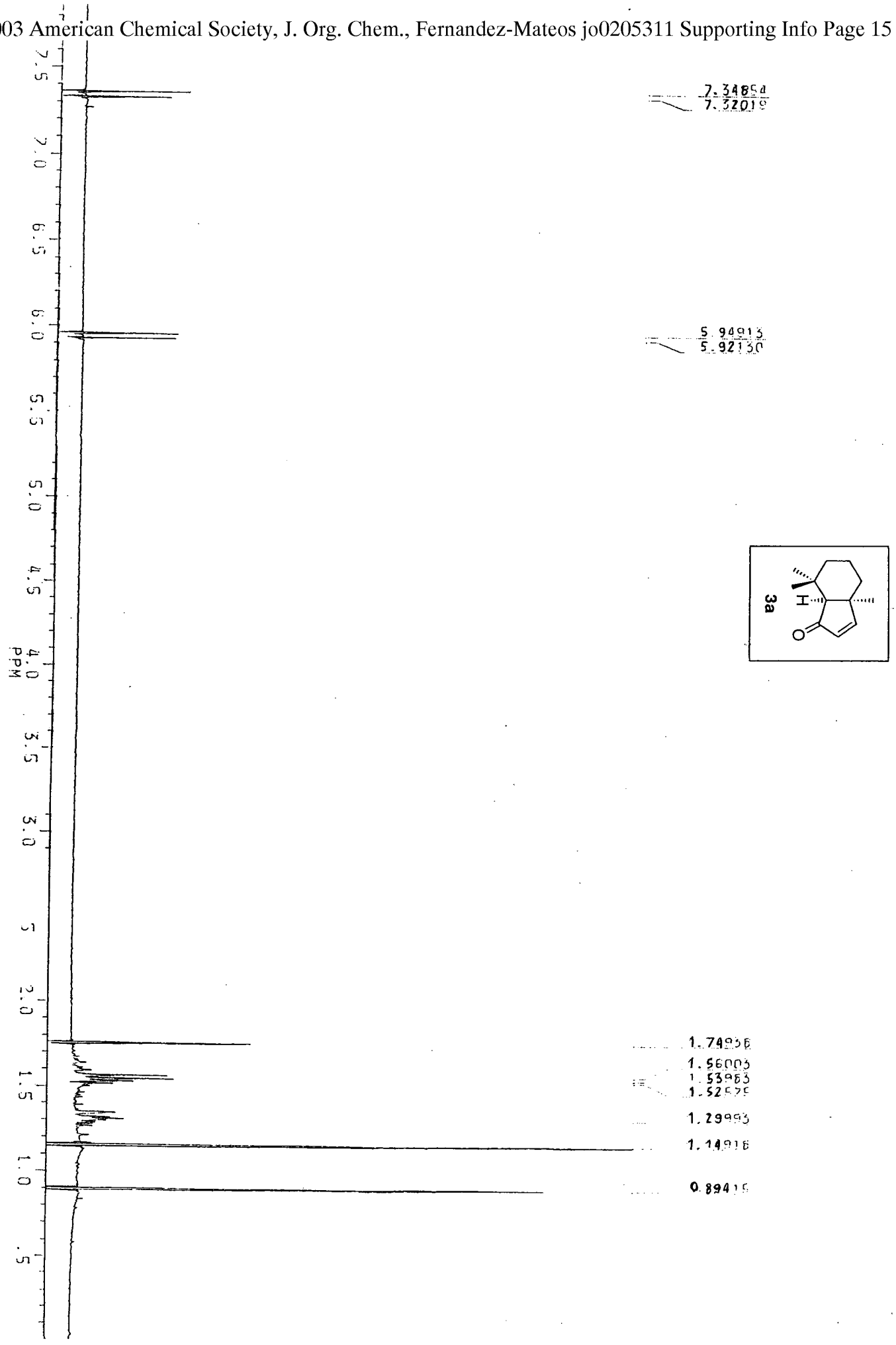

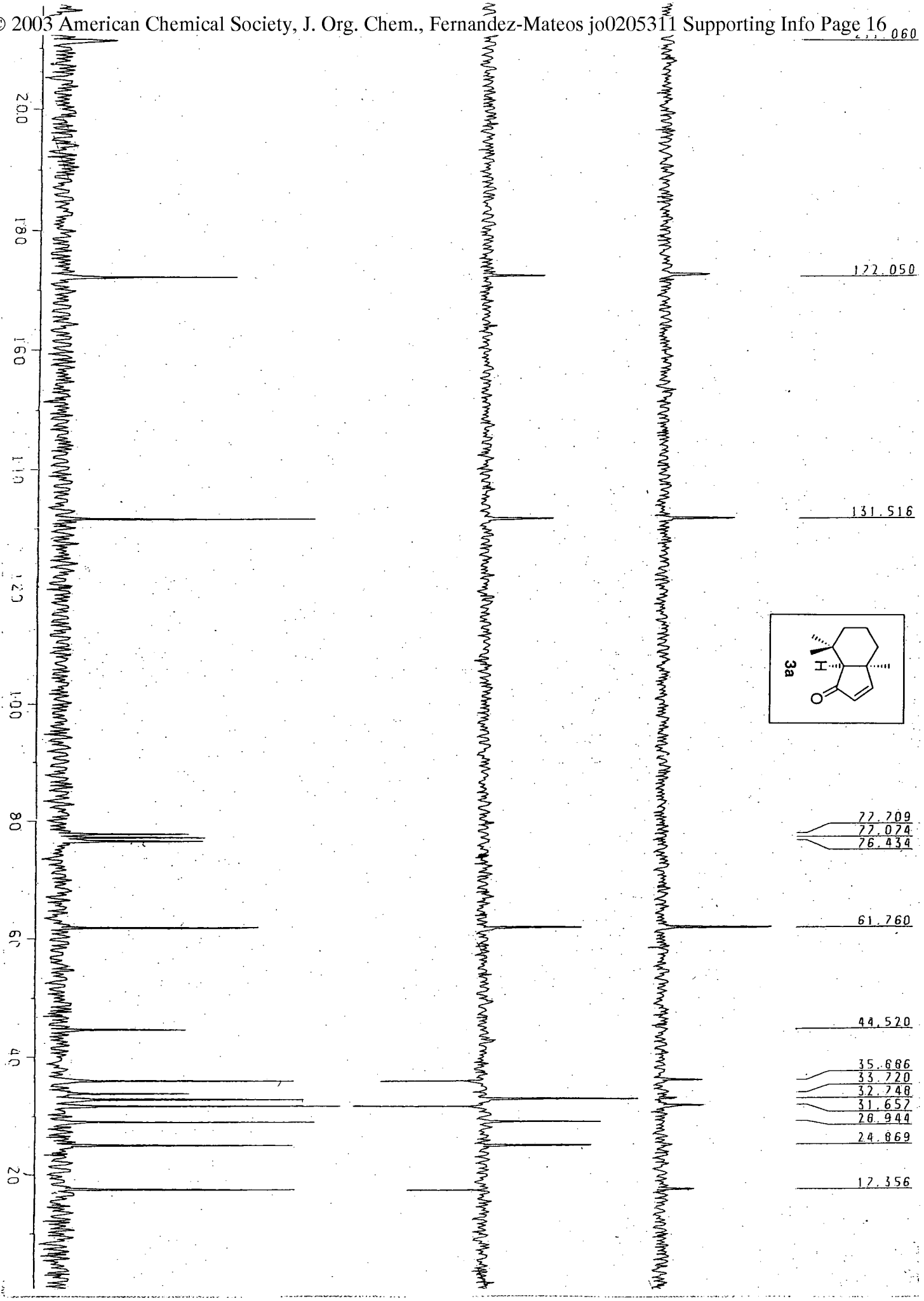

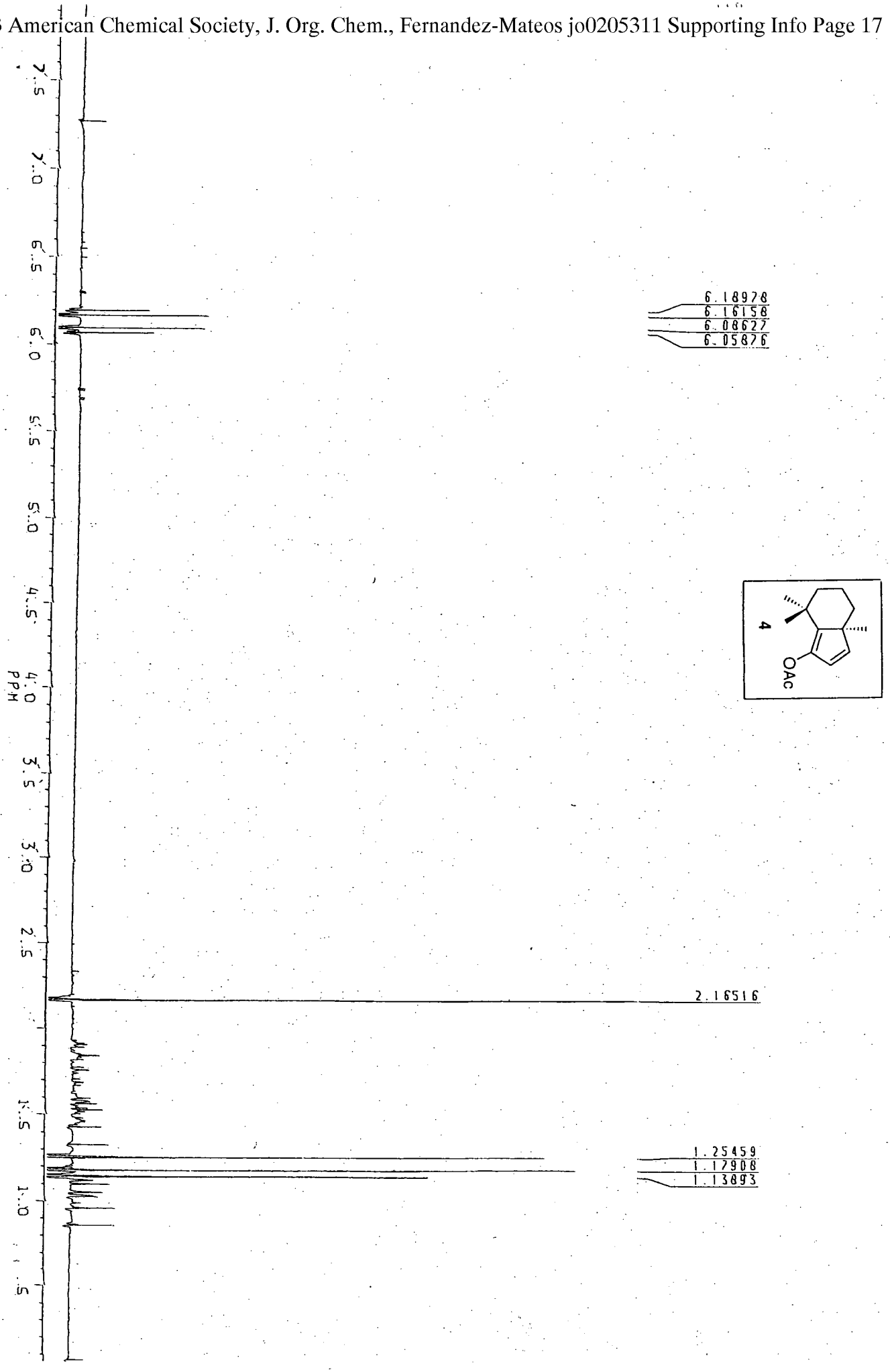

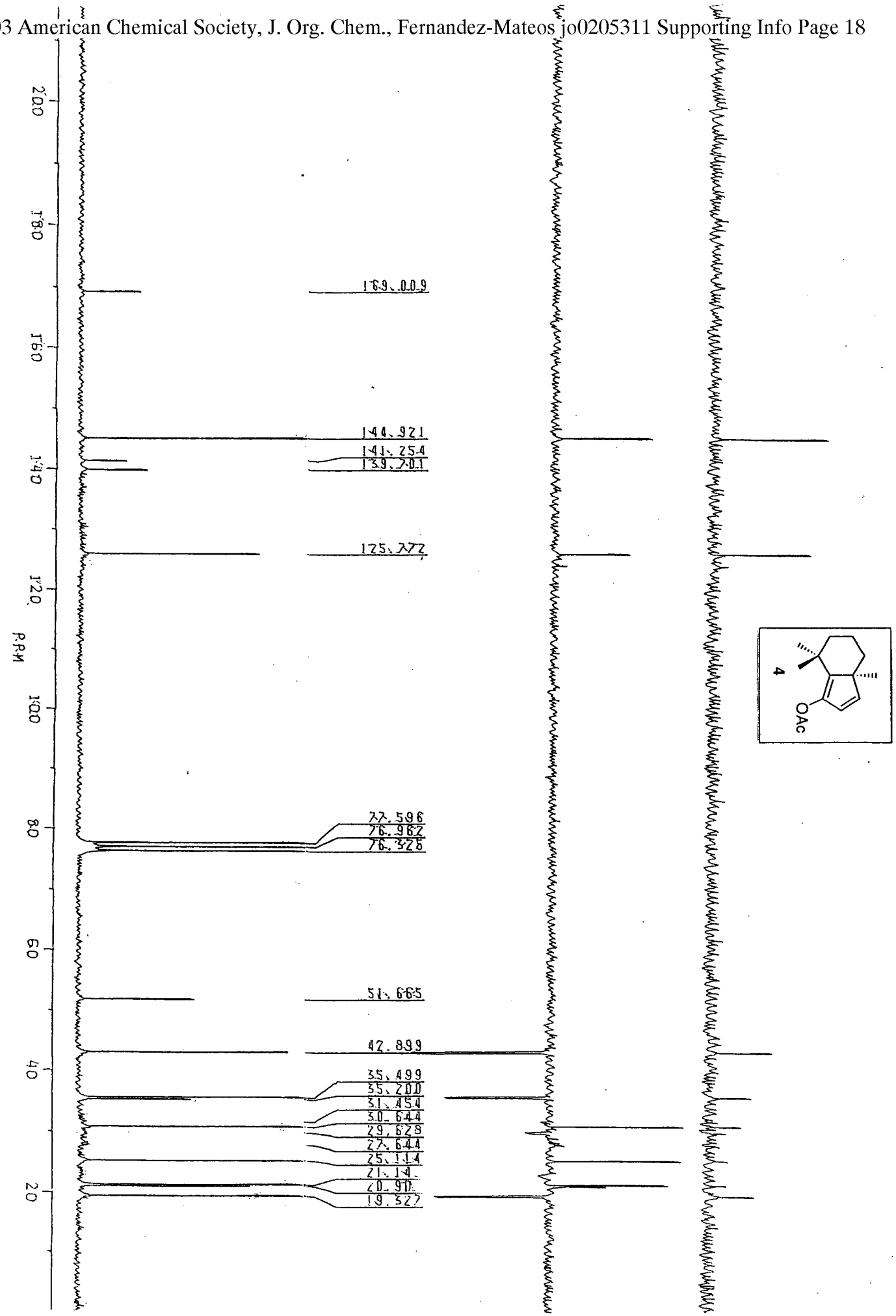

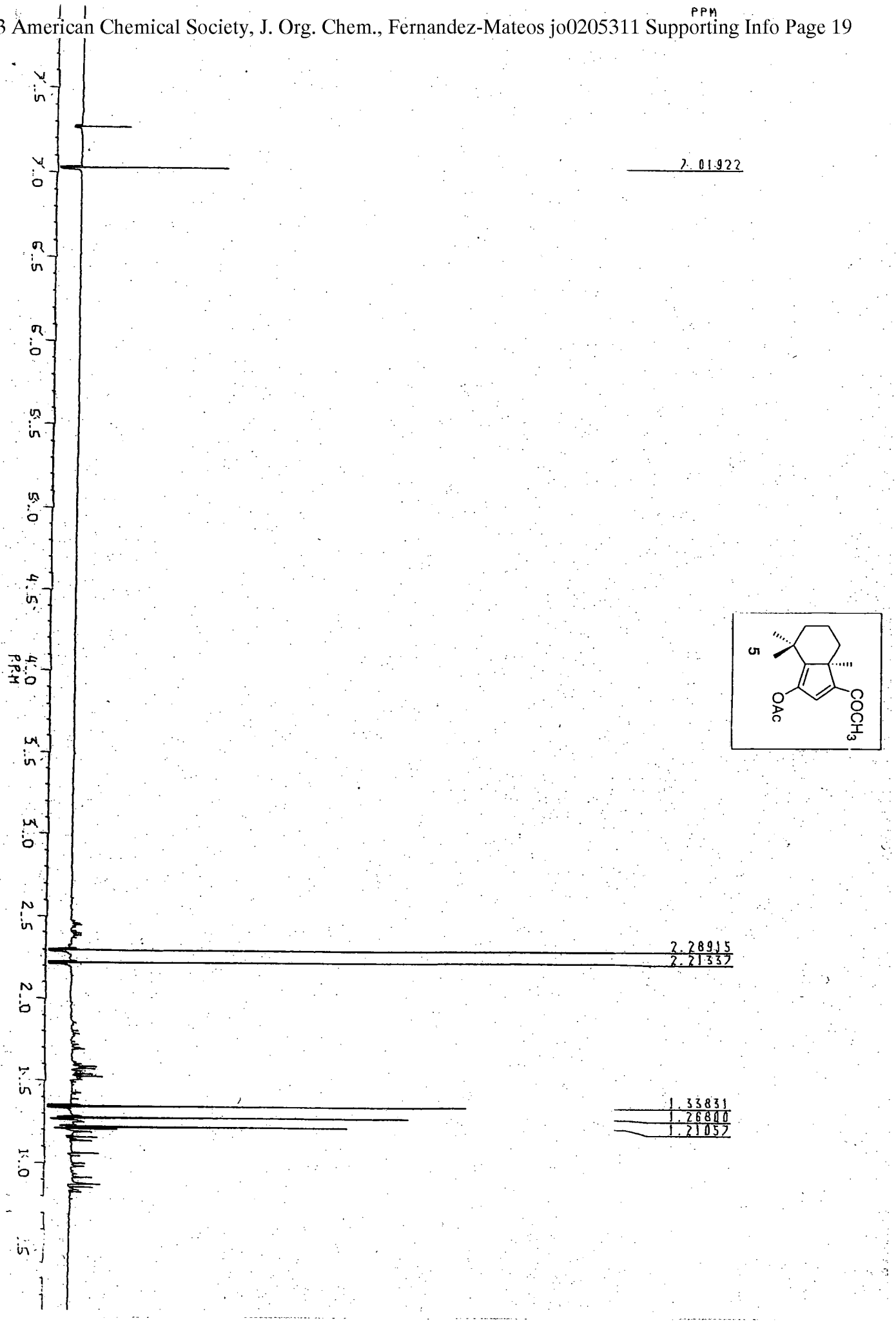

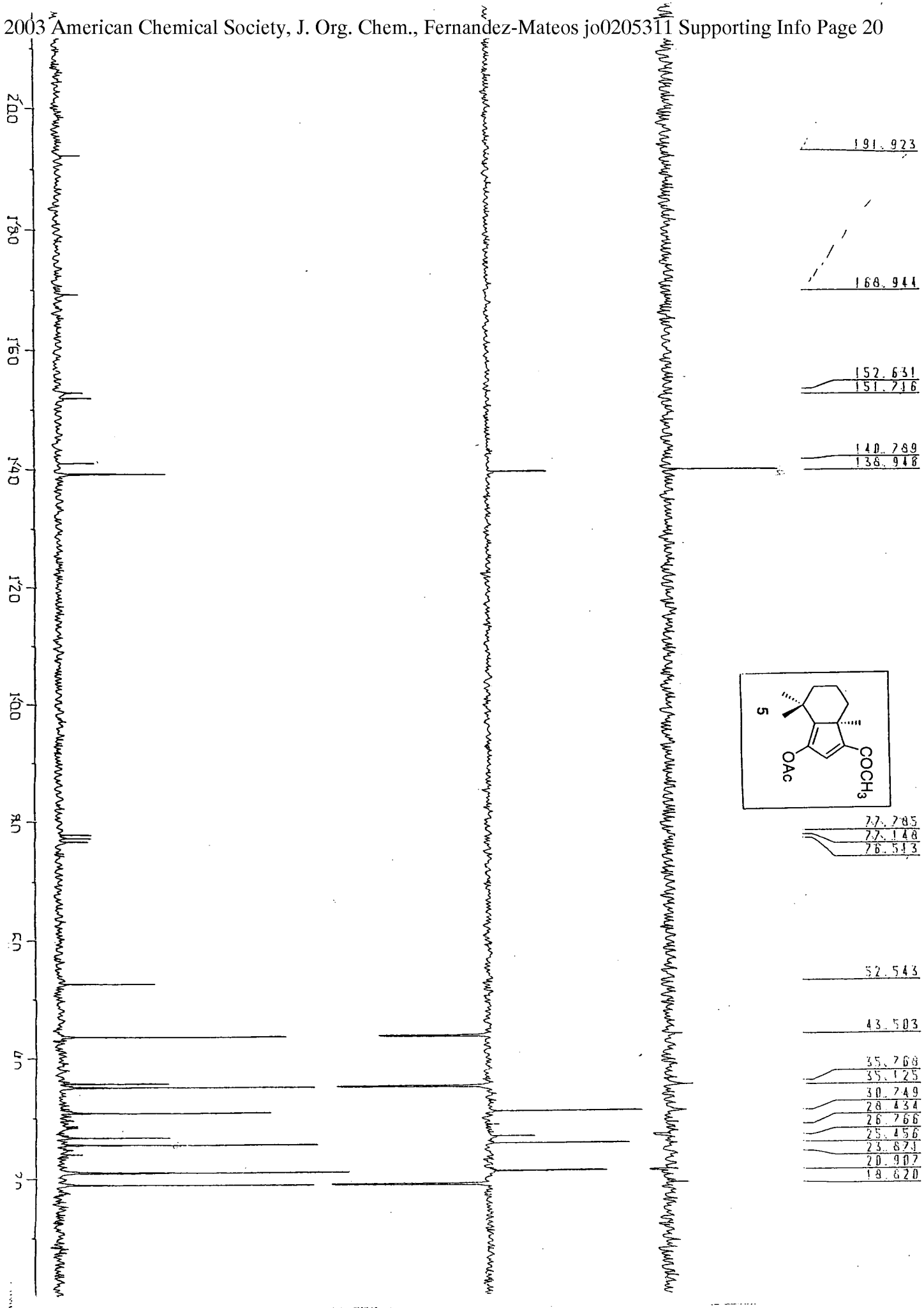

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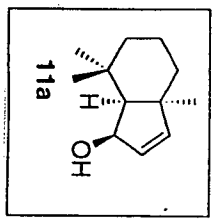

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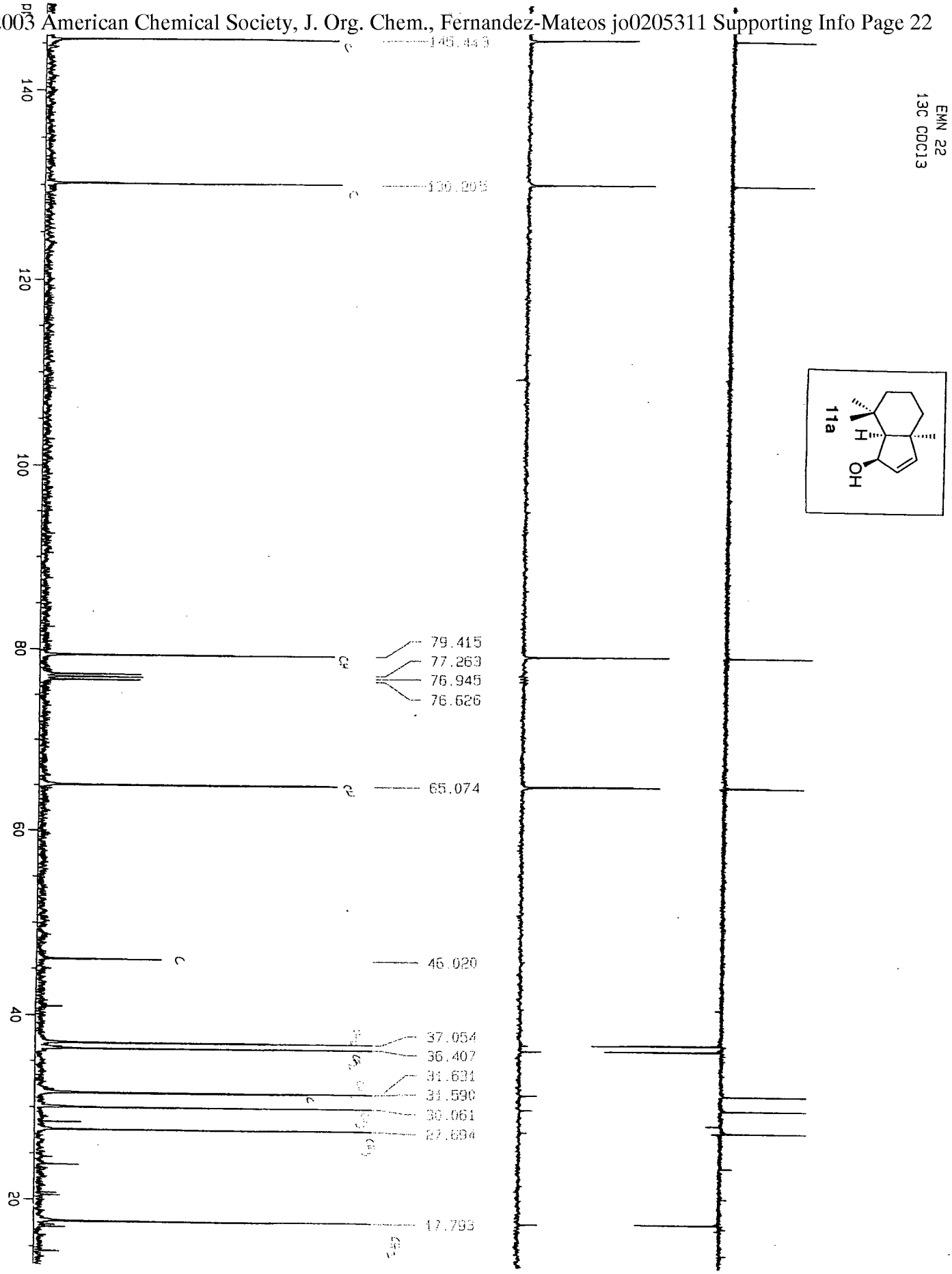

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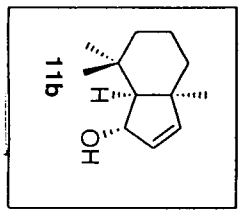

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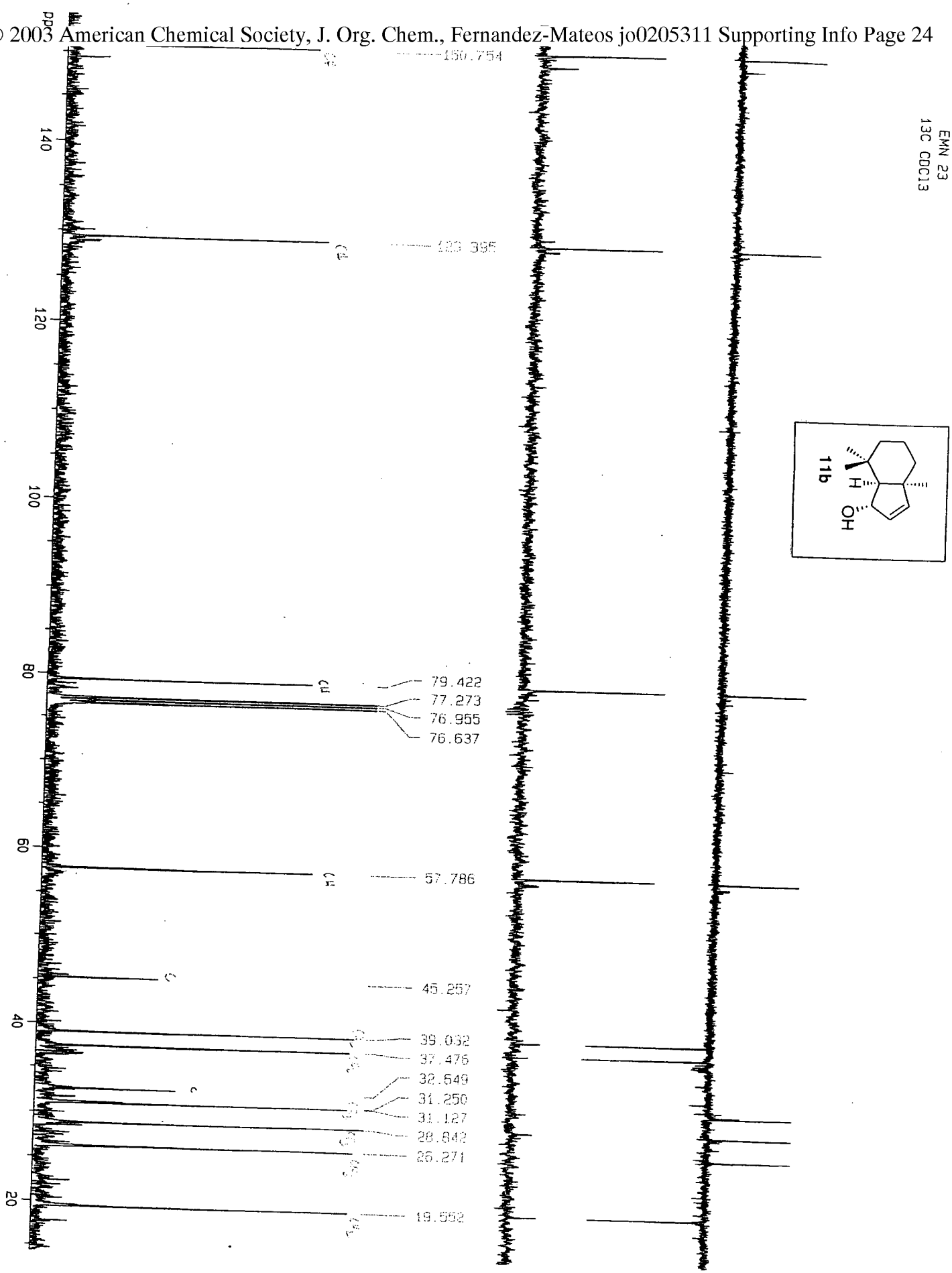

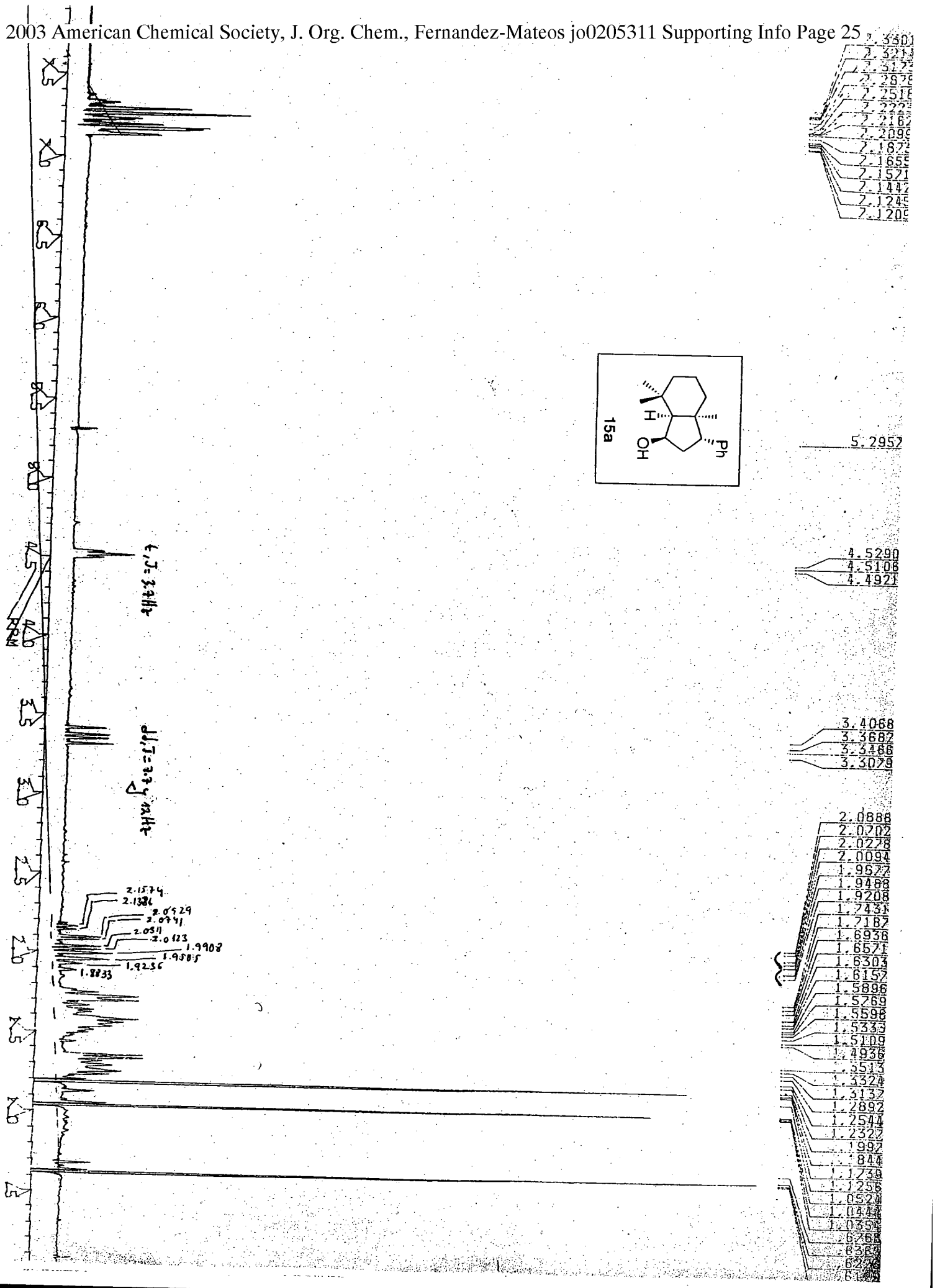

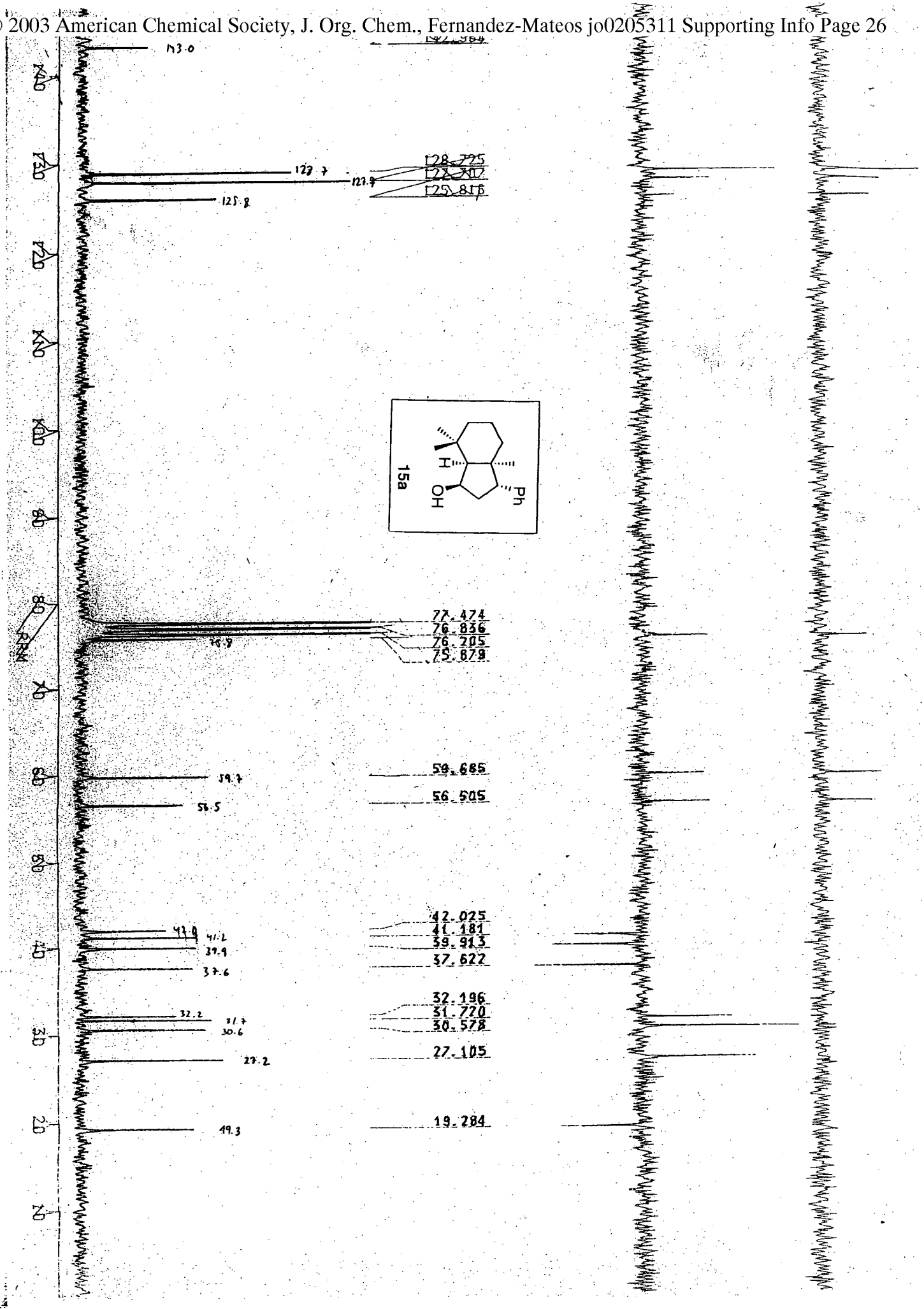

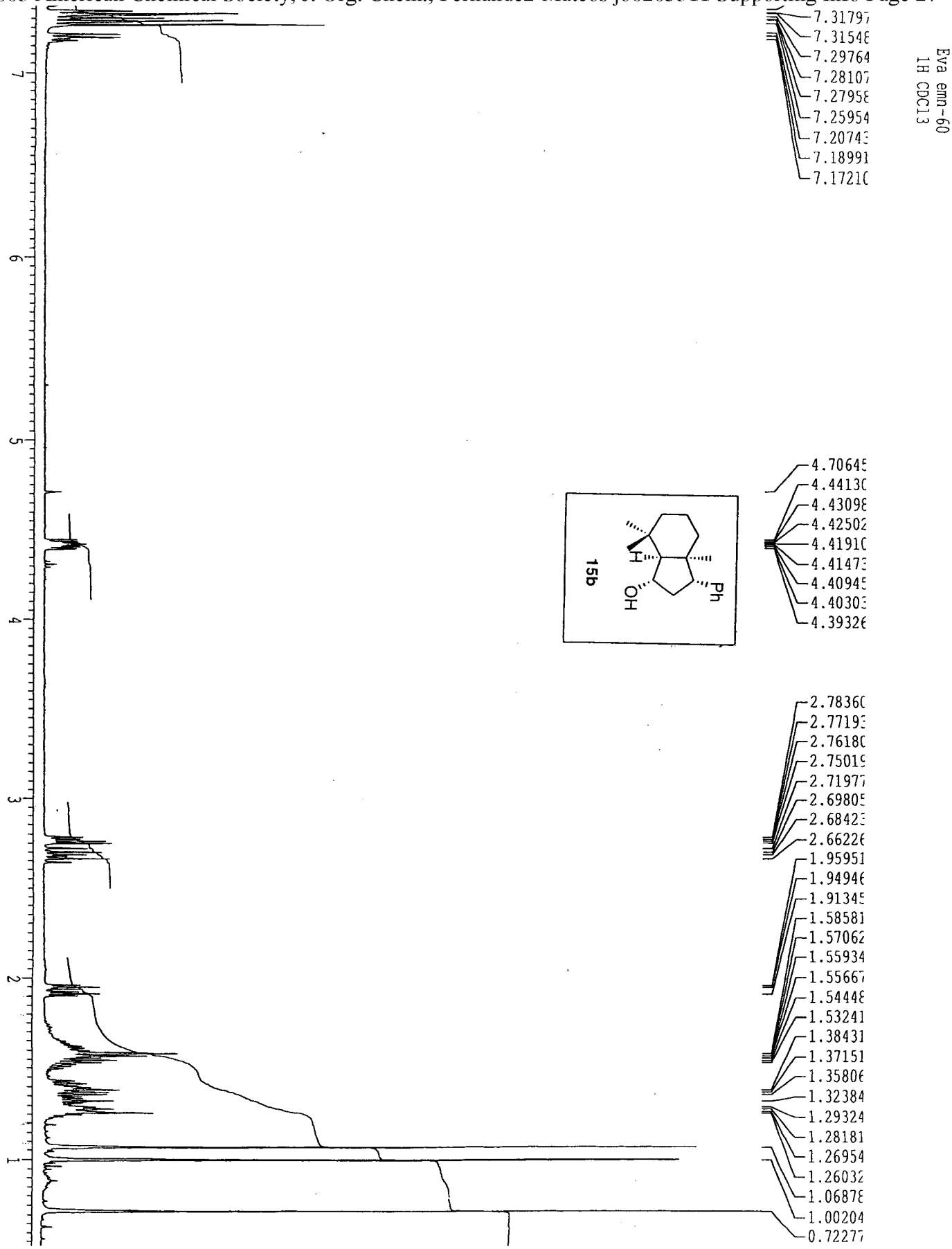

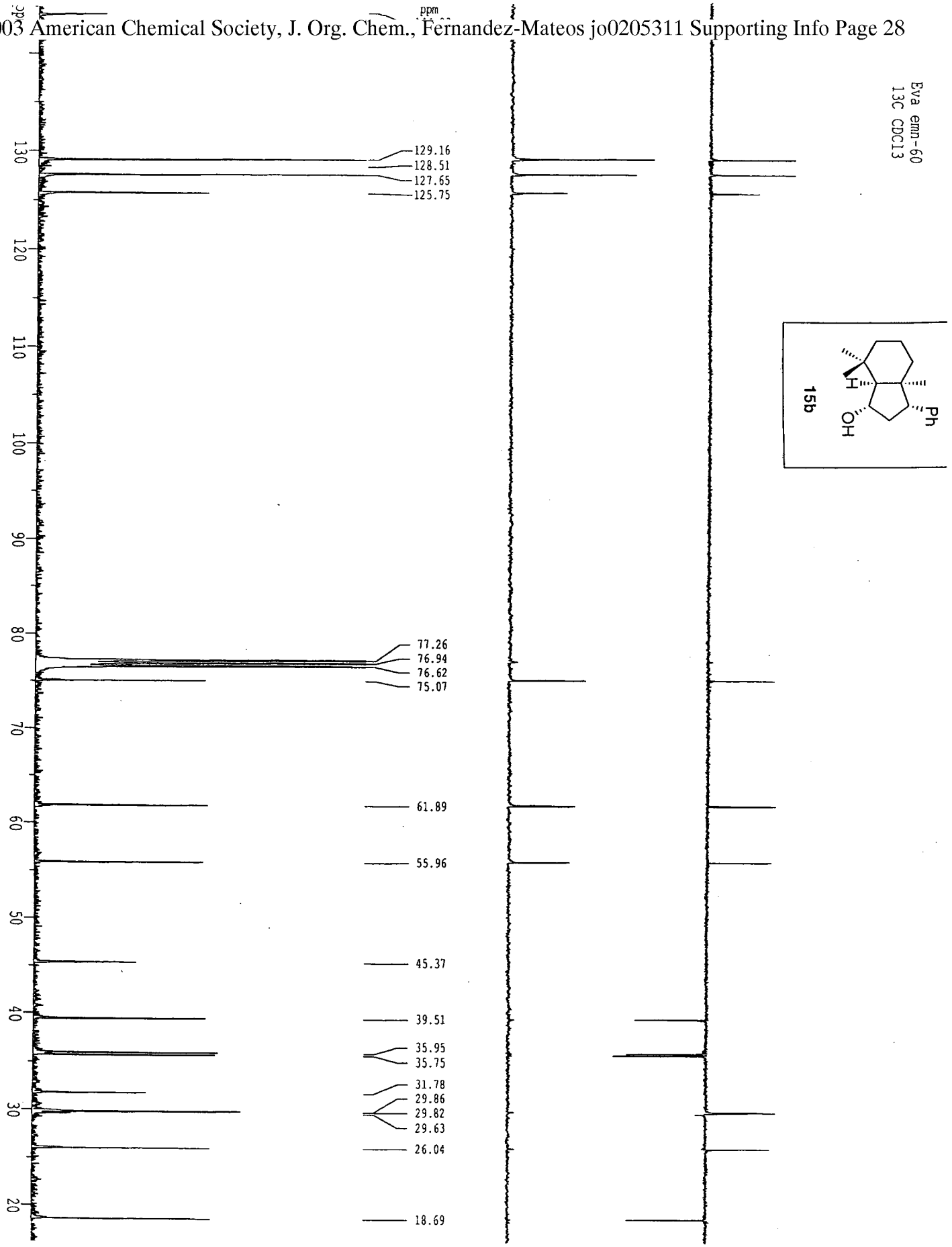

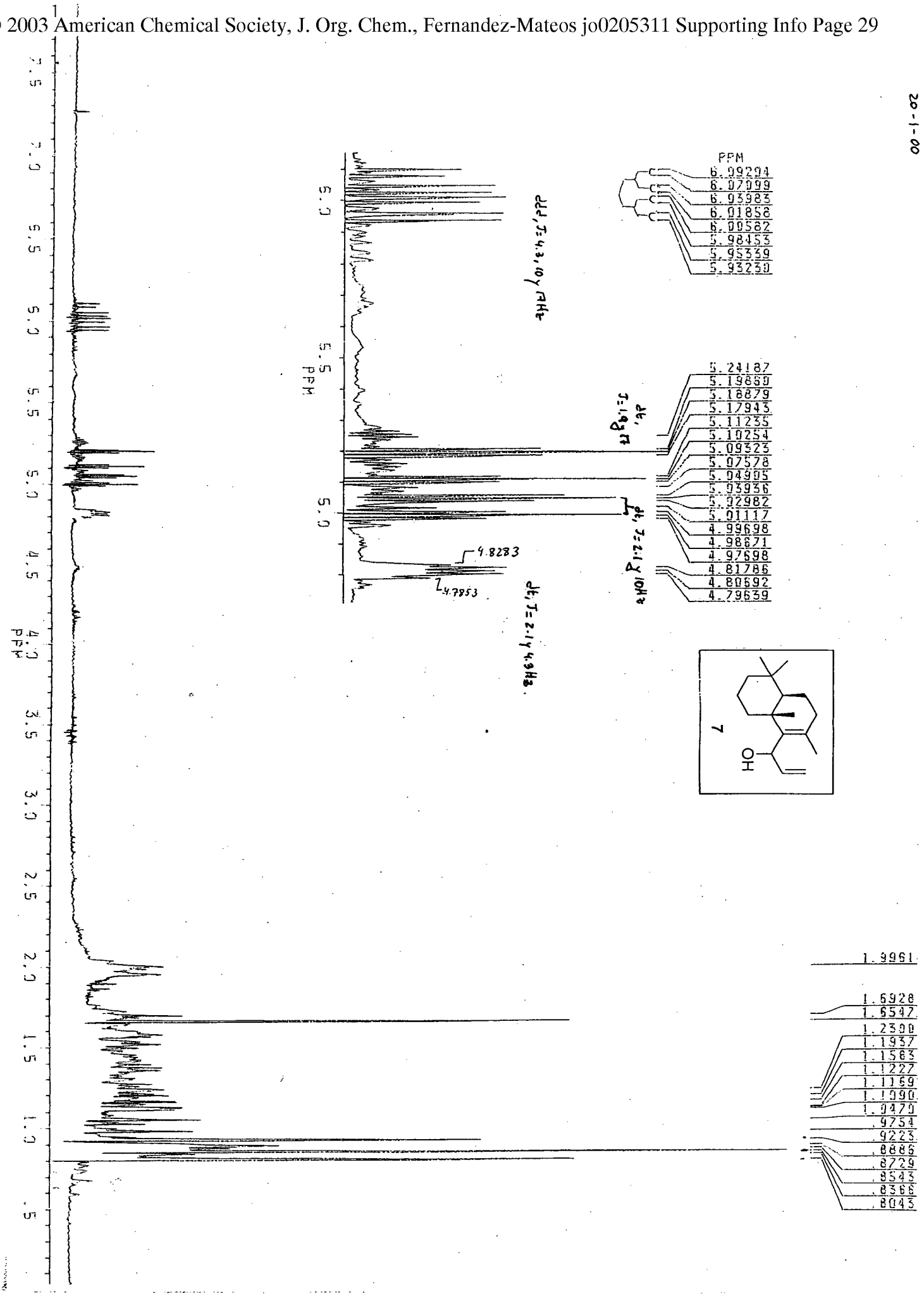

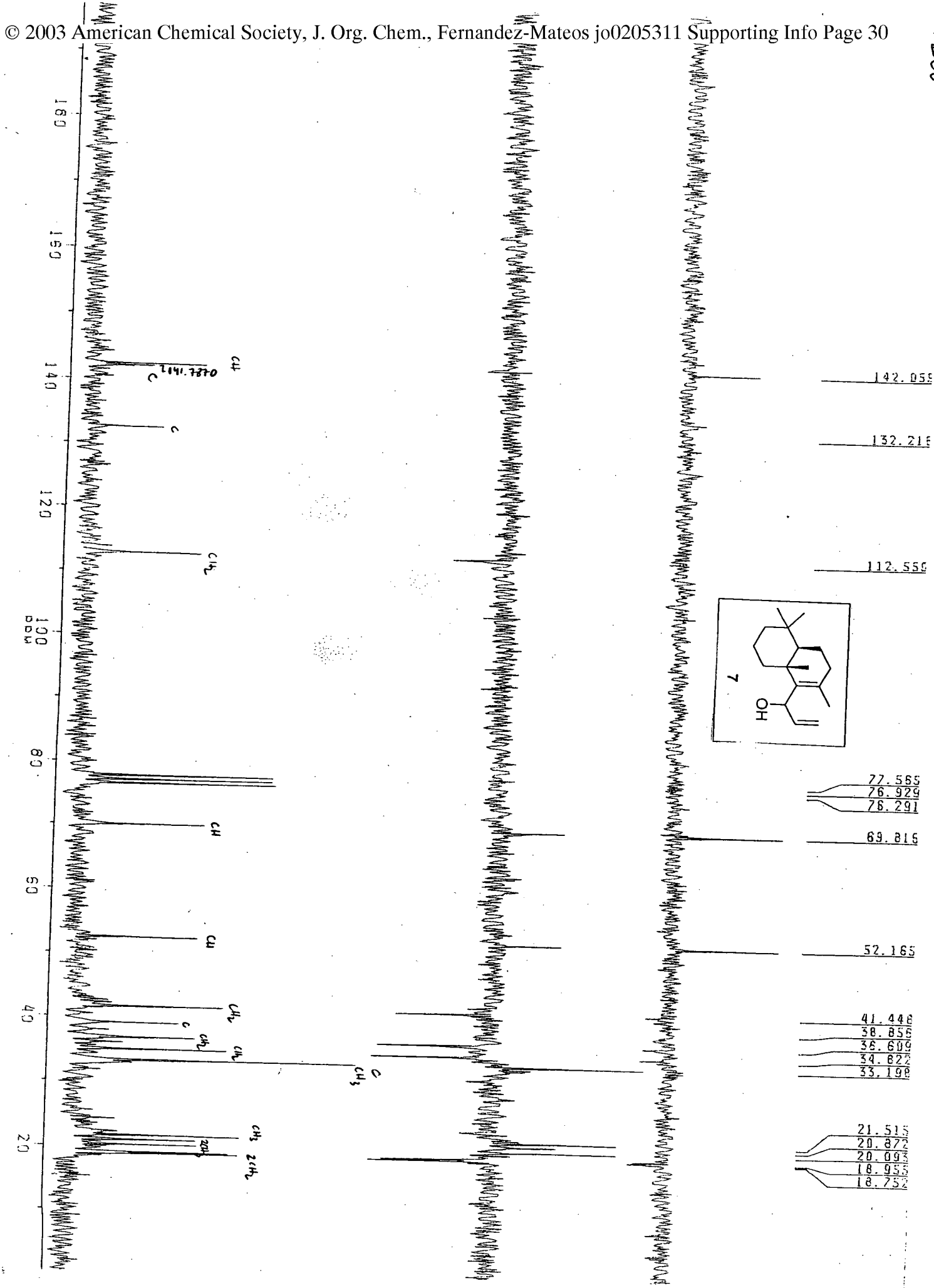

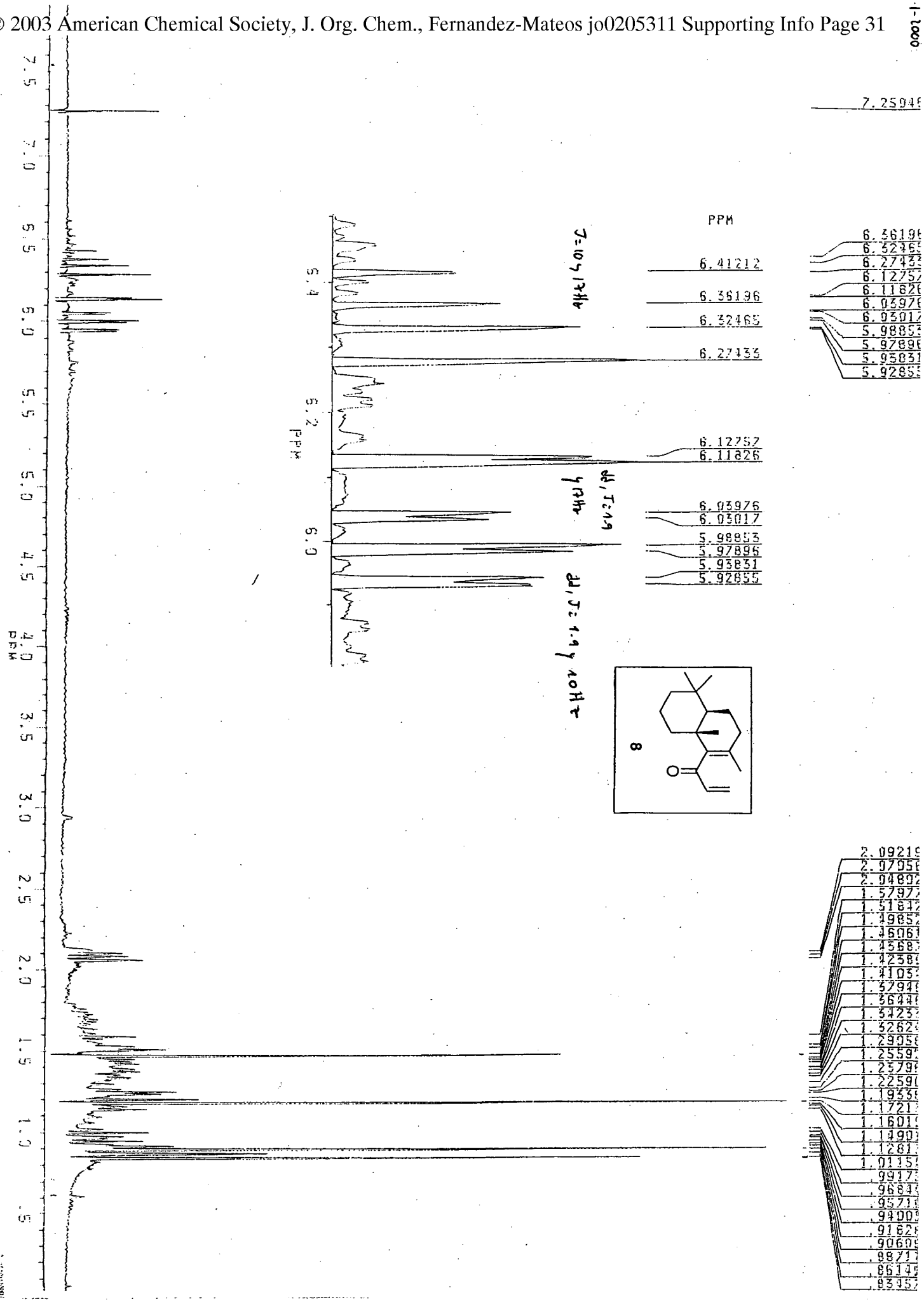

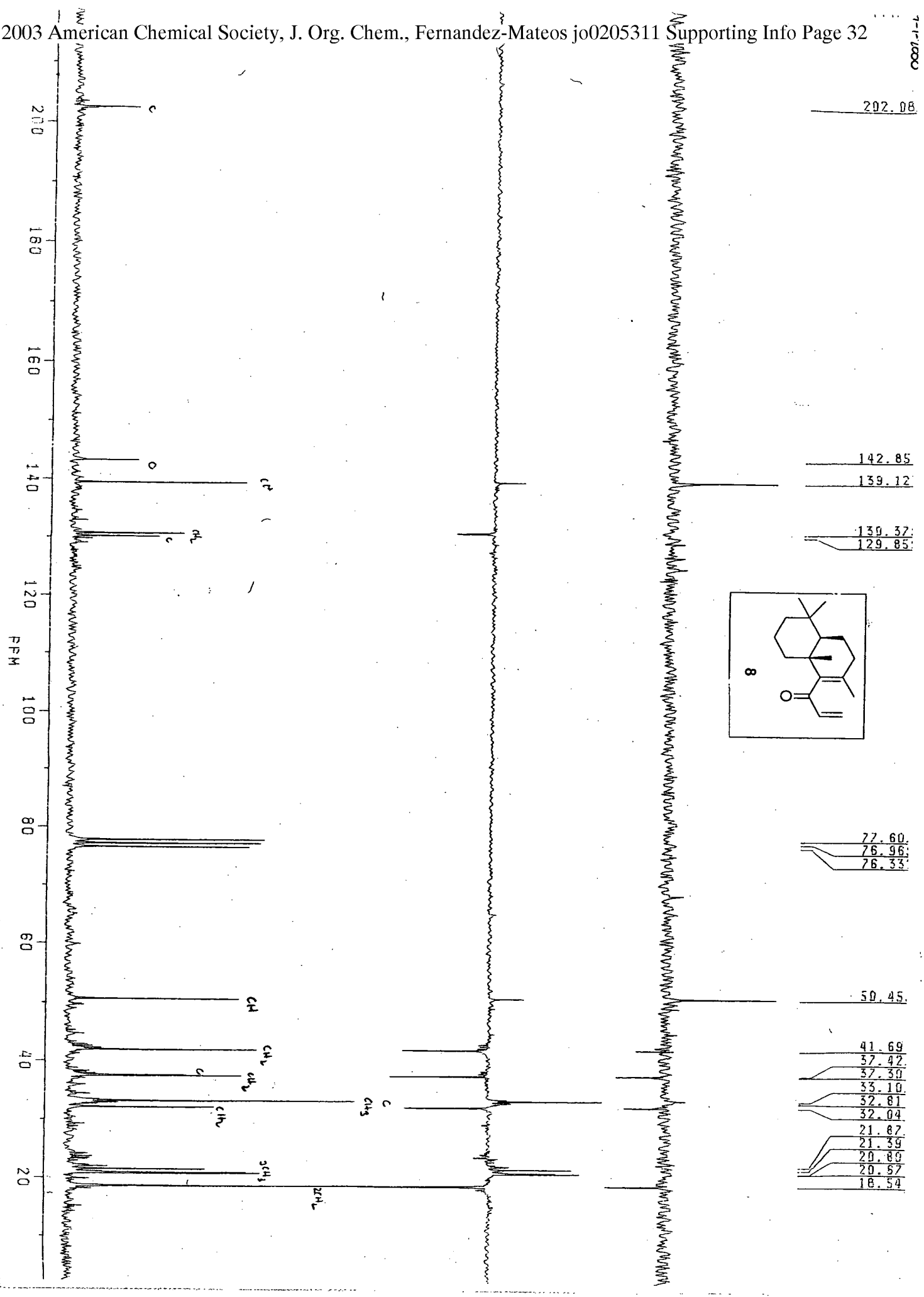

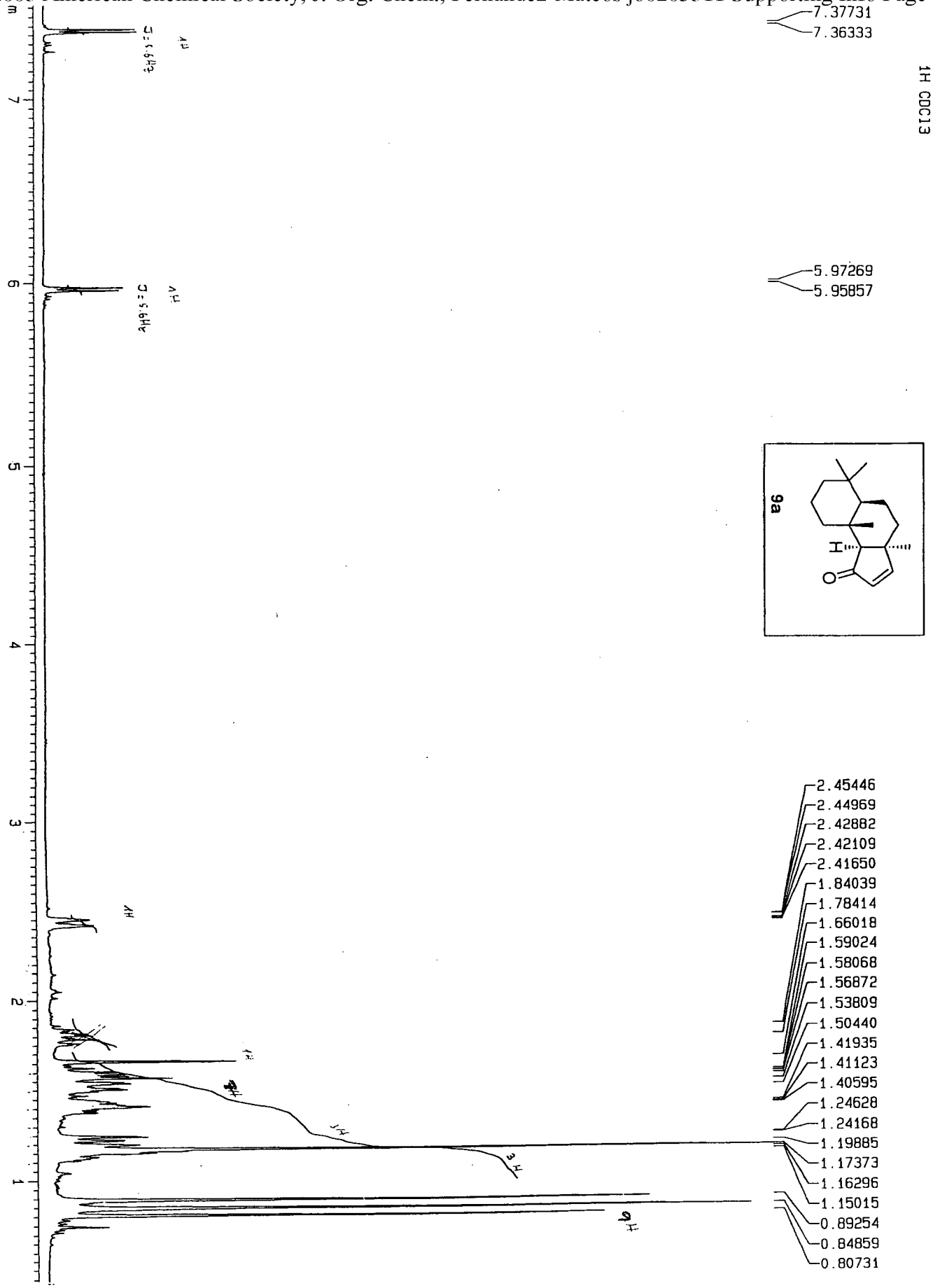

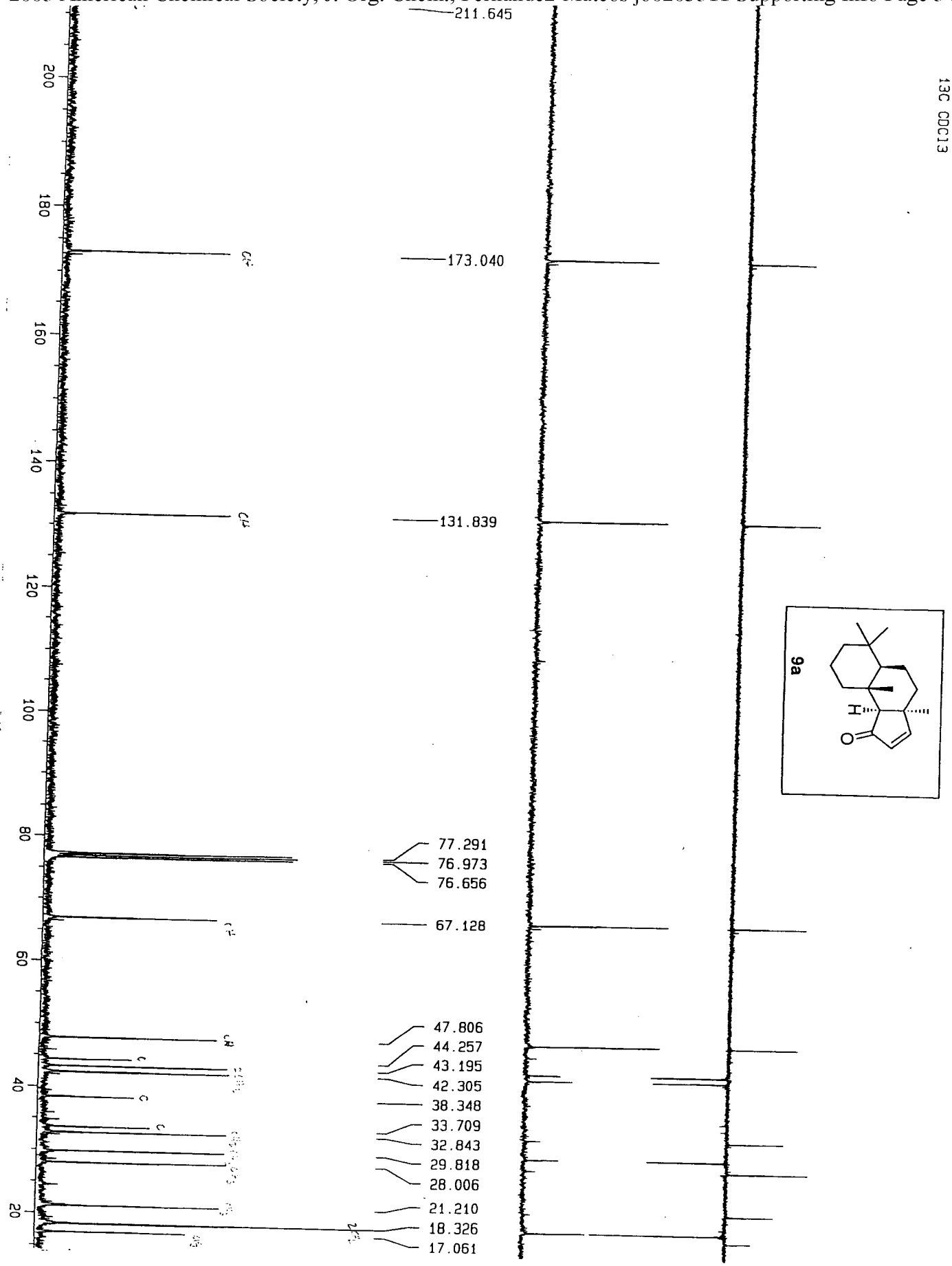

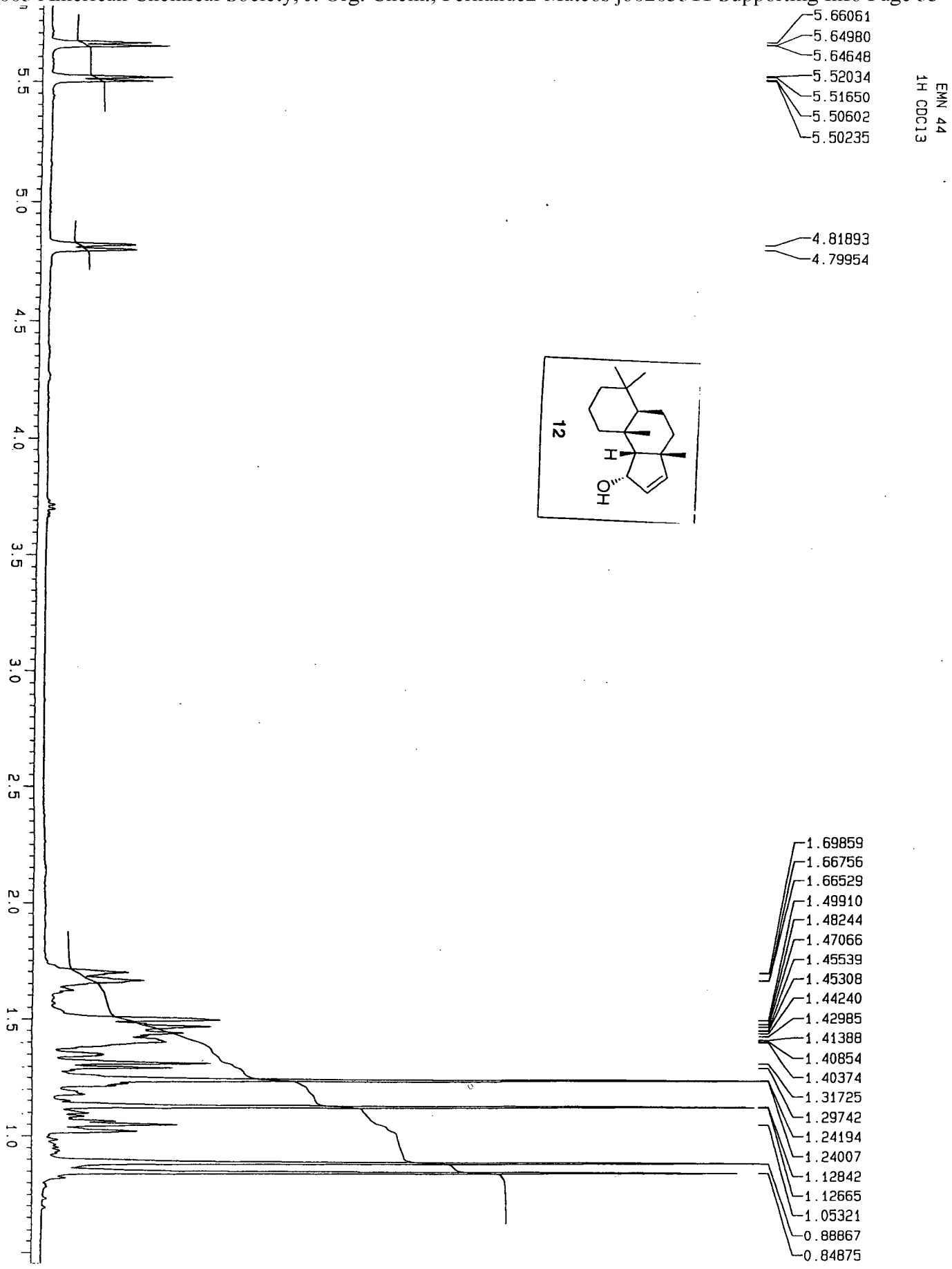
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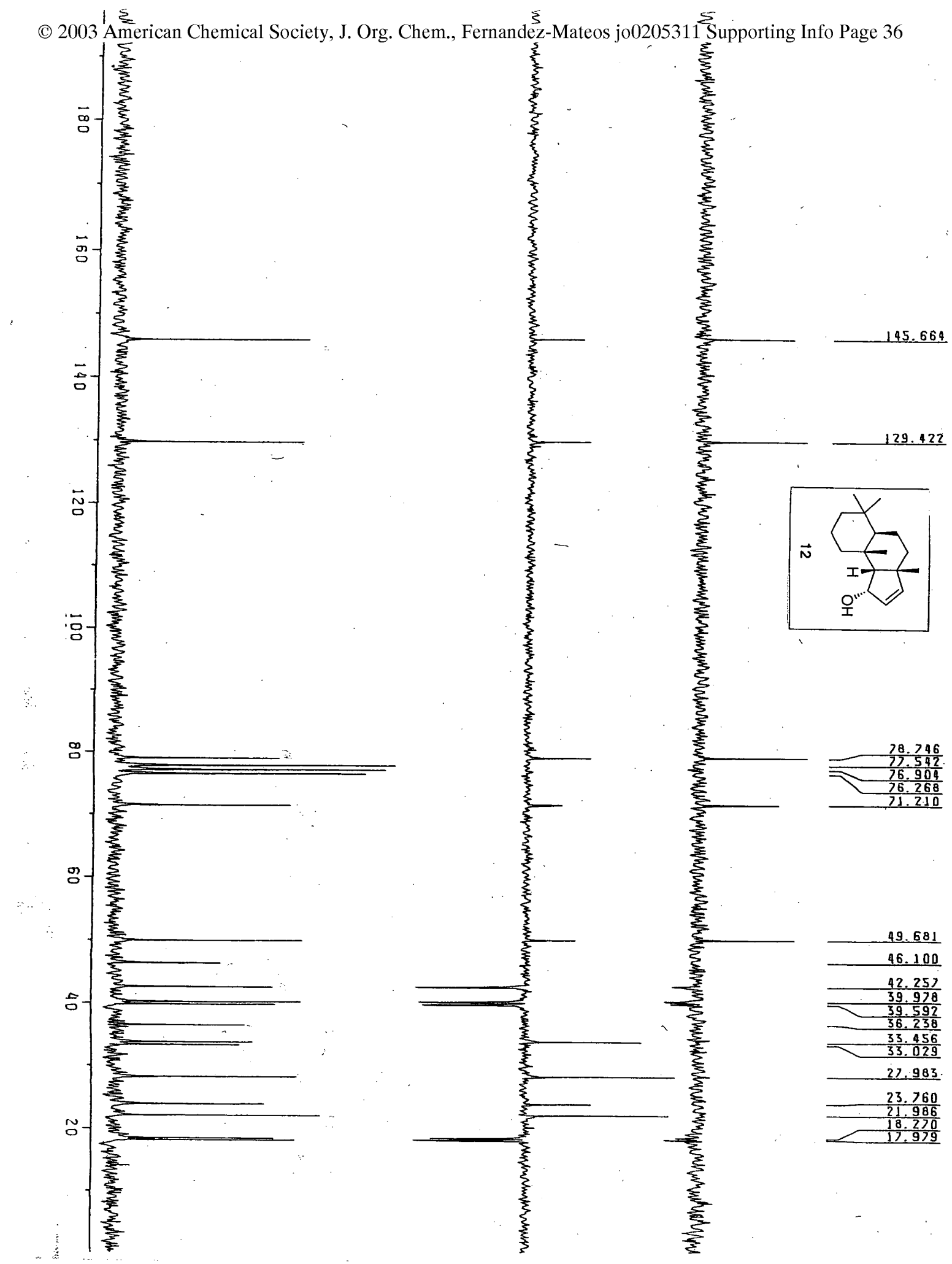

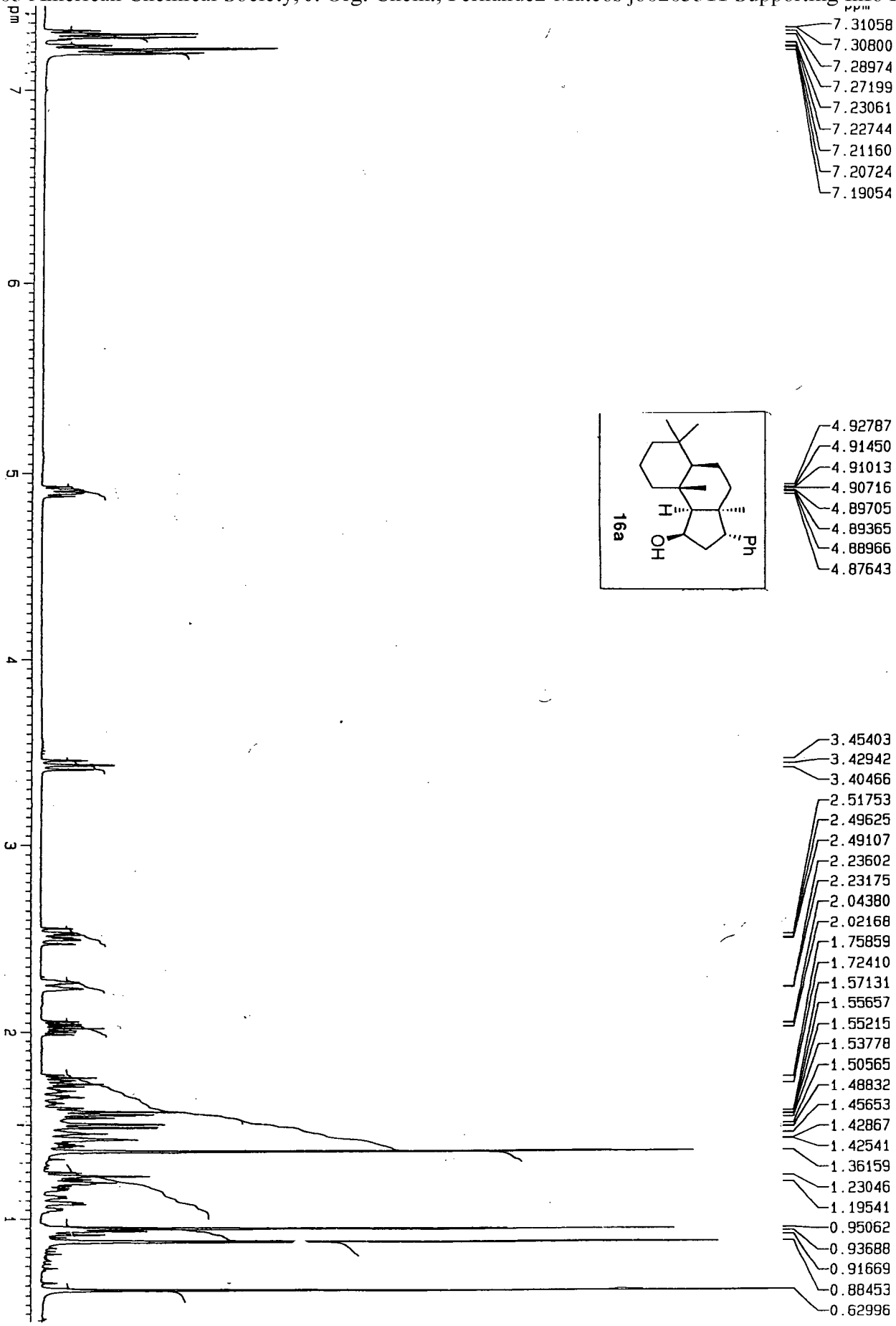
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