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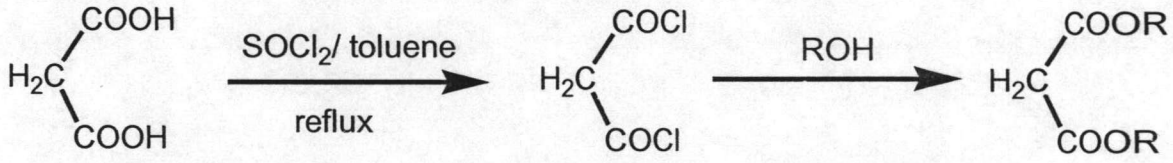
APPENDICES

APPENDIX A

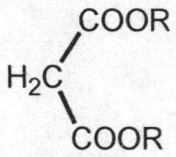
A. Synthesis of malonate Esters

General Procedure[24]

A mixture of 0.01 mol of malonic acid and 0.02 mol of thionyl chloride were refluxed in toluene at 110 °C. To the top of the condenser is attached an exit tube leading to a gas-absorption trap (K_2CO_3). A mixture was heated until no further evolution of hydrogen chloride was observed (45-60 minutes). An aspirator vacuum was then applied to the top of the condenser to remove any remaining thionyl chloride before 0.01 mol of alcohol was added. The mixture was again refluxed on water bath at 80 °C for 1 hour. It was then placed on a sand bath and refluxed at 110 °C in order to complete the reaction (1.5 hours, checked by TLC). The reaction mixture was cooled and washed with 100 ml of 2% sodium bicarbonate solution. The general equation is shown below:



Two malonate esters were synthesized and their structures are displayed in Fig A.1.



Cpds	Substance	R
M1	Di-(2-ethylhexyl)-malonate	C_8H_{17} (iso)
M2	Dihexyl malonate	C_6H_{13}

Figure A.1 Structure of the synthesized malonate esters

Malonate esters

Di-(2-ethylhexyl)-malonate (**M1**): pale yellow oil (58%), IR (neat, cm^{-1}): 2959, 2865, 1748, 1465, 1382, 1324, 1269, 1145 and 1013; ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.02-3.99 (d, *J*=5.8 Hz, 4H), 3.30 (s, 2H) and 1.59-0.79 (m, 30H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 166.4 (COOR), 67.5, 41.4, 38.5, 30.1, 28.7, 23.4, 22.7, 13.7 and 10.7 (alkyl carbons).

Dihexylmalonate (**M2**): pale yellow oil (71%), IR (neat, cm^{-1}): 2931, 2865, 1743, 1465, 1382, 1324, 1273, 1145 and 1005; ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.13-4.04 (t, 4H), 3.32 (s, 2H) and 1.66-0.77 (m, 22H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 166.3 (COOR), 65.2, 41.3, 31.1, 28.2, 25.2, 22.2 and 13.6 (alkyl carbons).

APPENDIX B

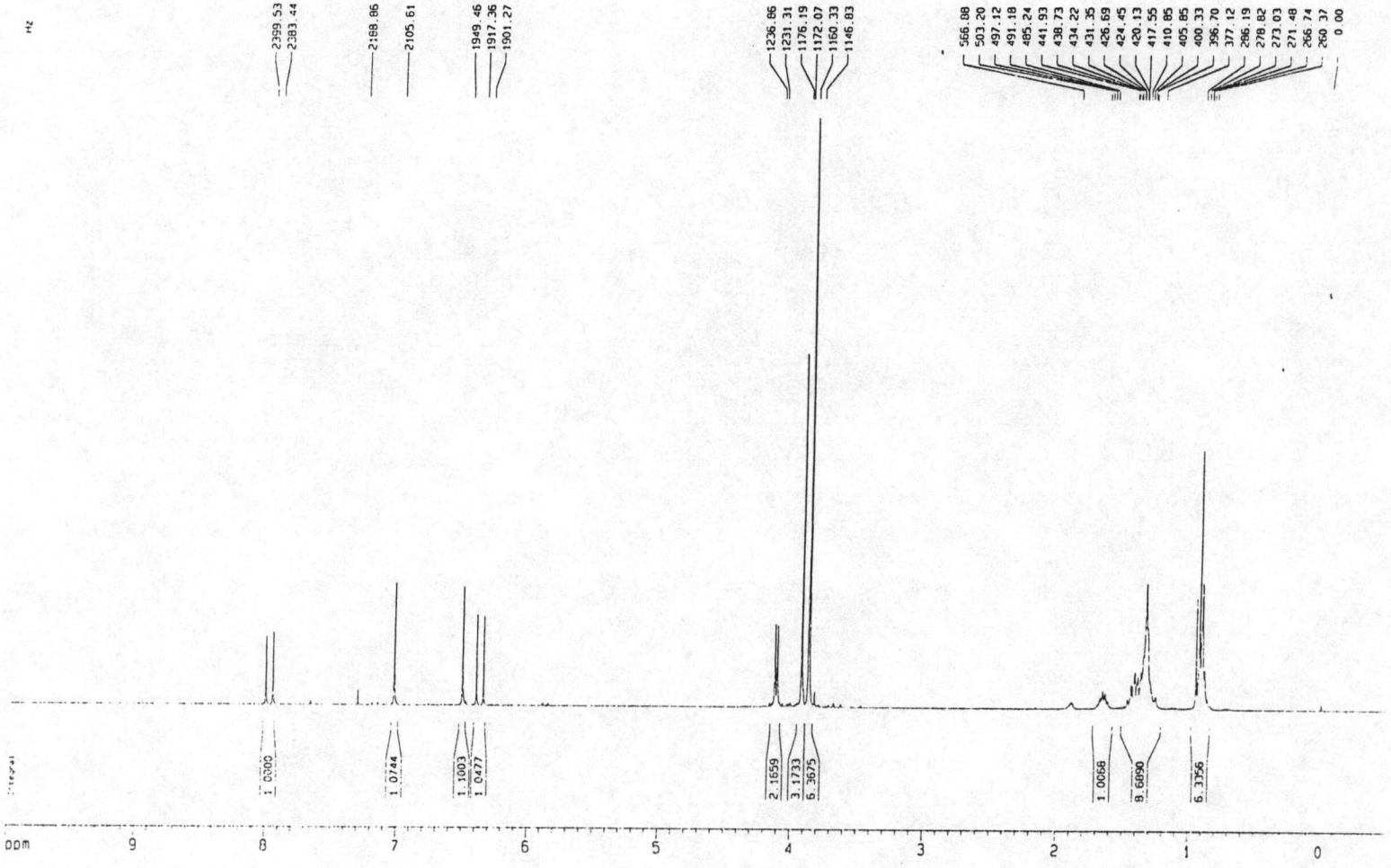


Figure B.1 ^{1}H-NMR spectrum of 2-ethylhexyl-2,4,5-trimethoxycinnamate (**E8**)

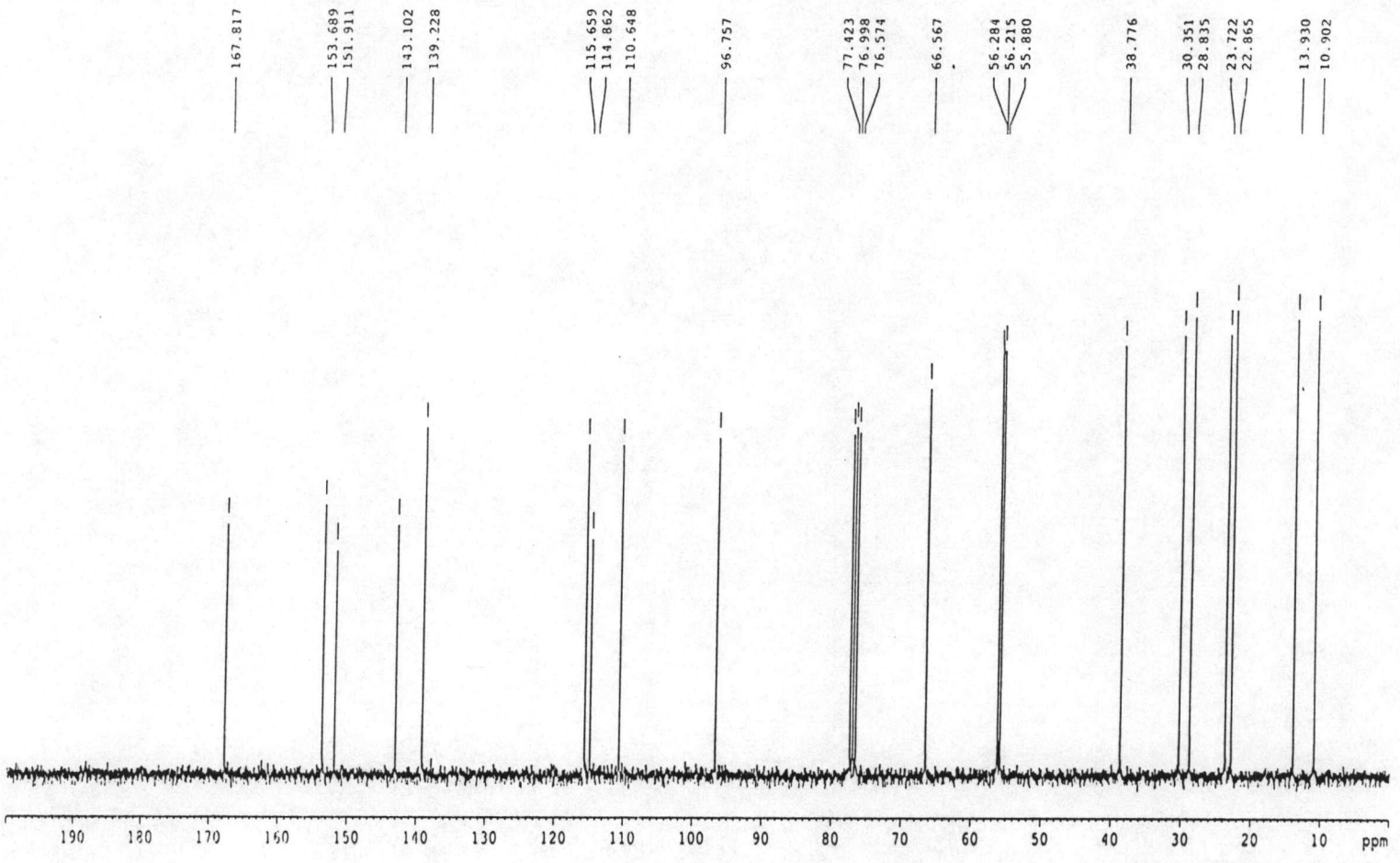


Figure B.2 ^{13}C-NMR spectrum of 2-ethylhexyl-2,4,5-trimethoxycinnamate (**E8**)

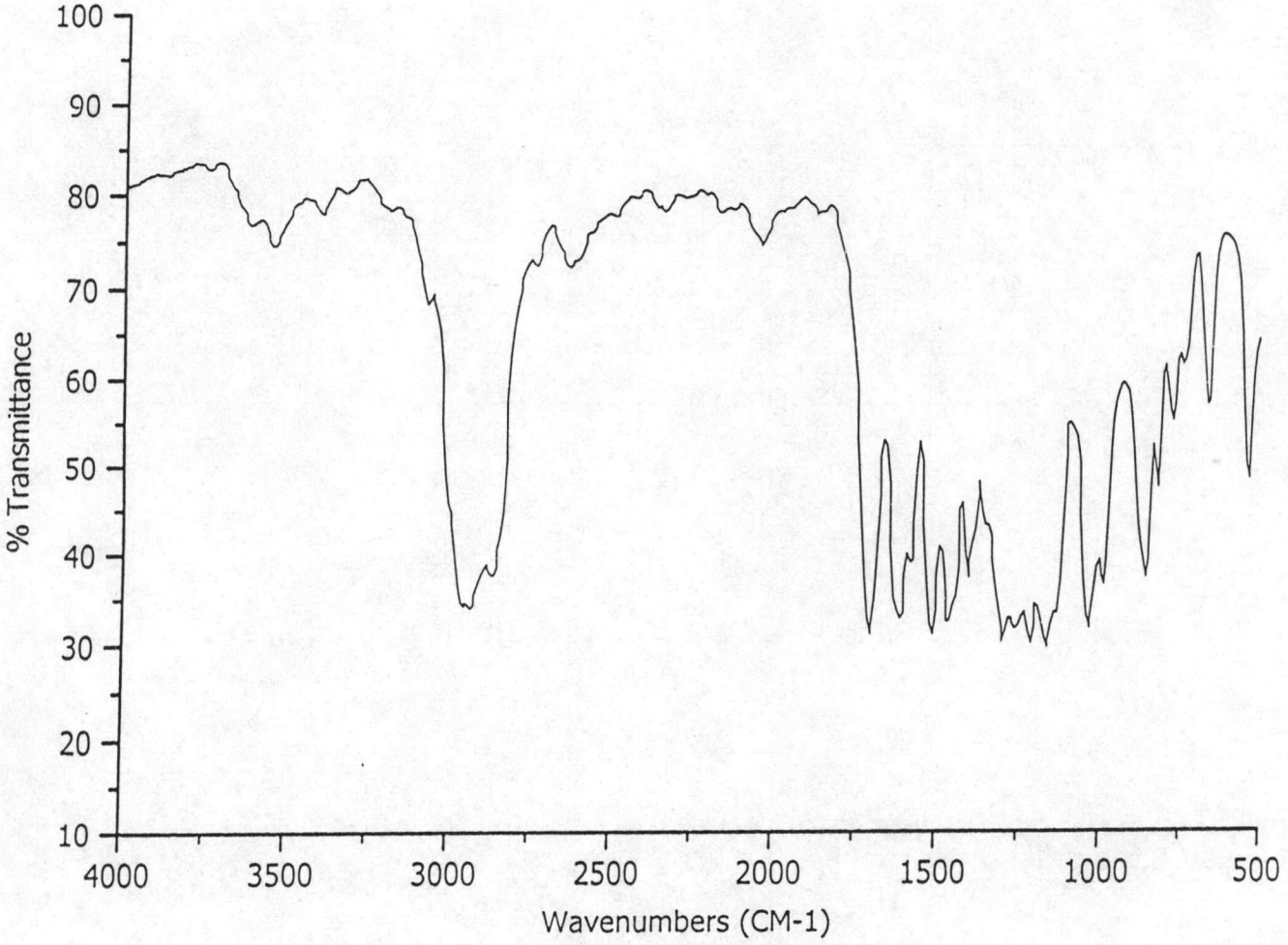


Figure B.3 IR spectrum of 2-ethylhexyl-2,4,5-trimethoxycinnamate (**E8**)

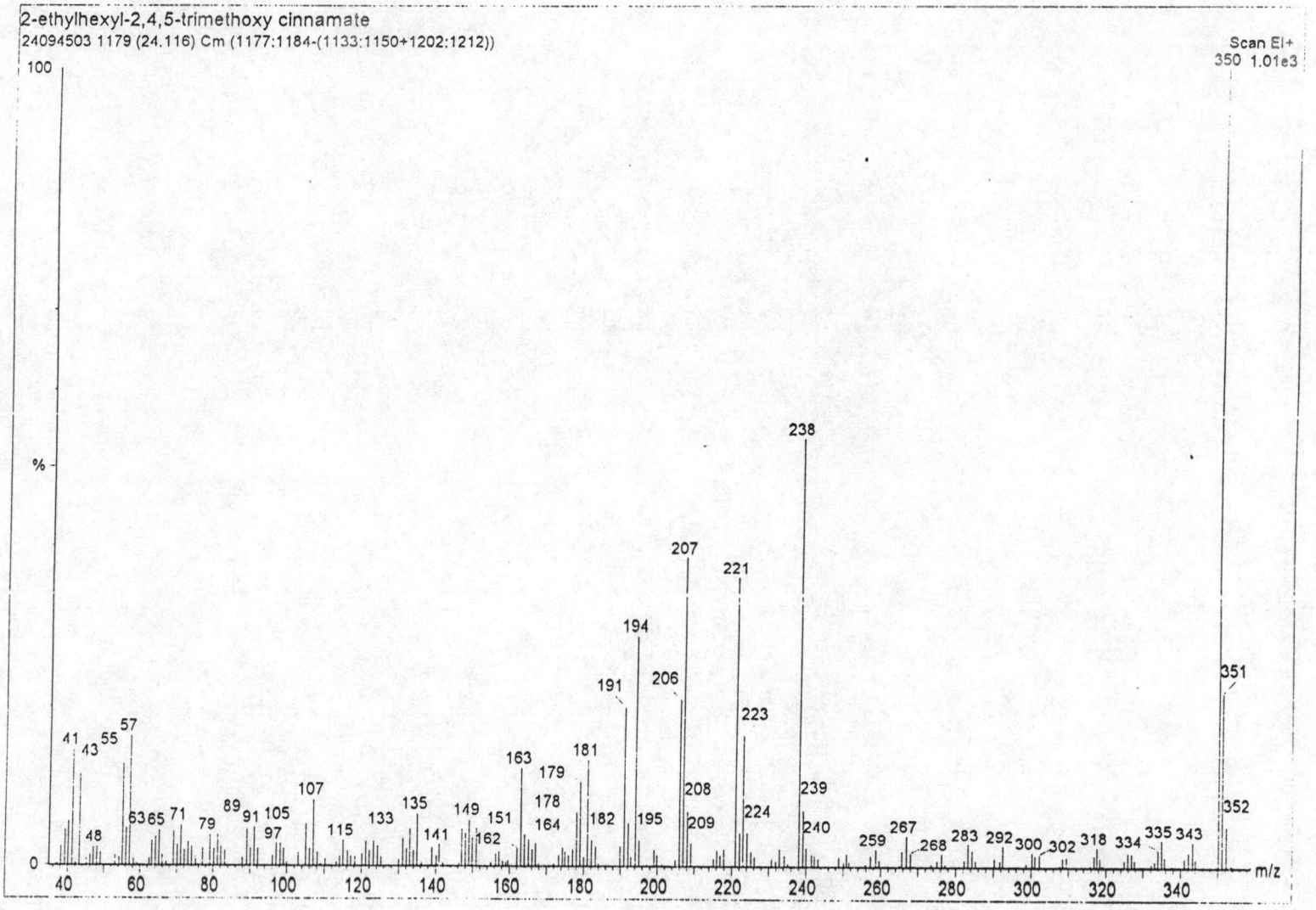


Figure B.4 Mass spectrum of 2-ethylhexyl-2,4,5-trimethoxycinnamate (**E8**)

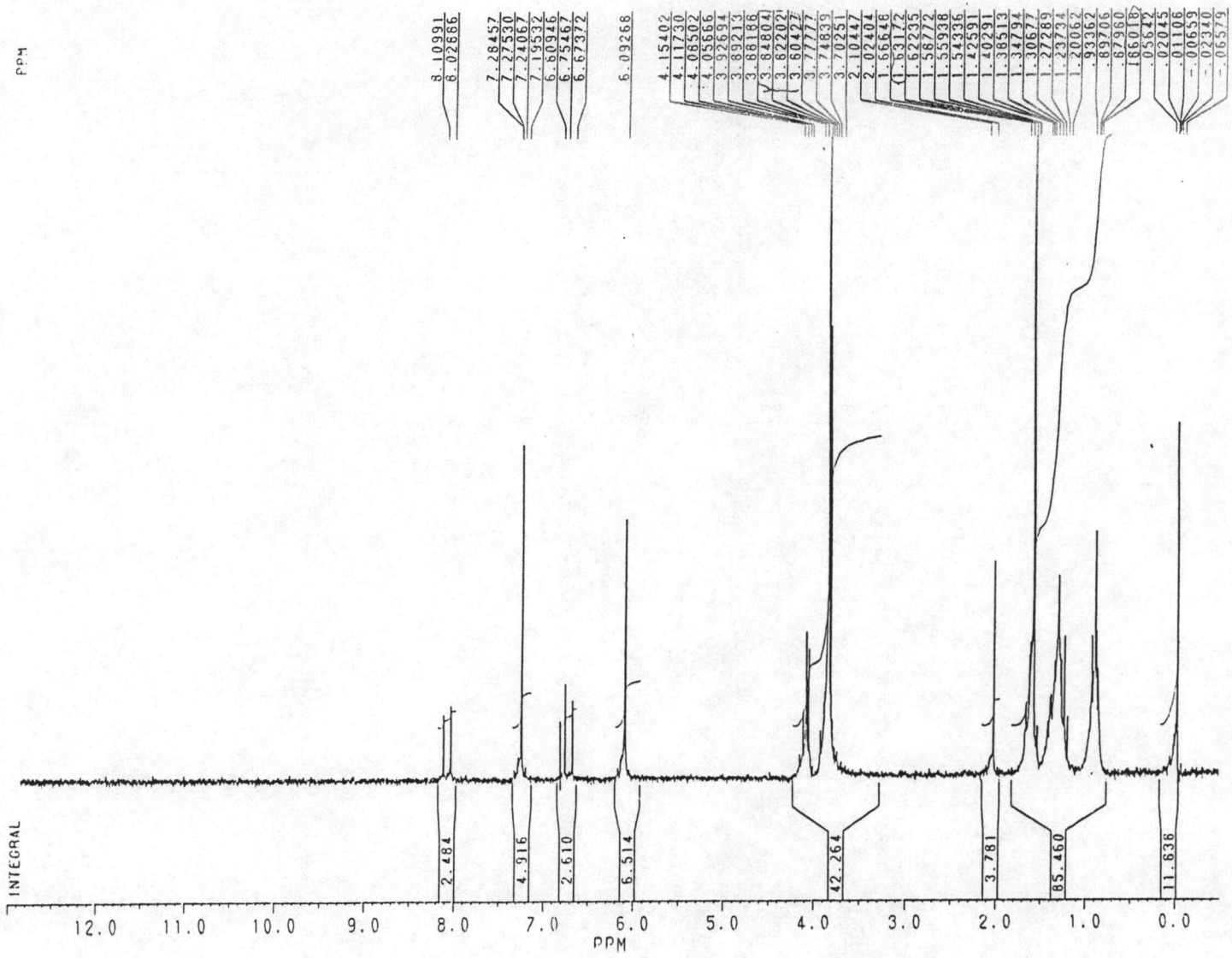


Figure B.5 ^{1}H-NMR spectrum of 2-ethylhexyl-2,4,6-trimethoxycinnamate (**E10**)

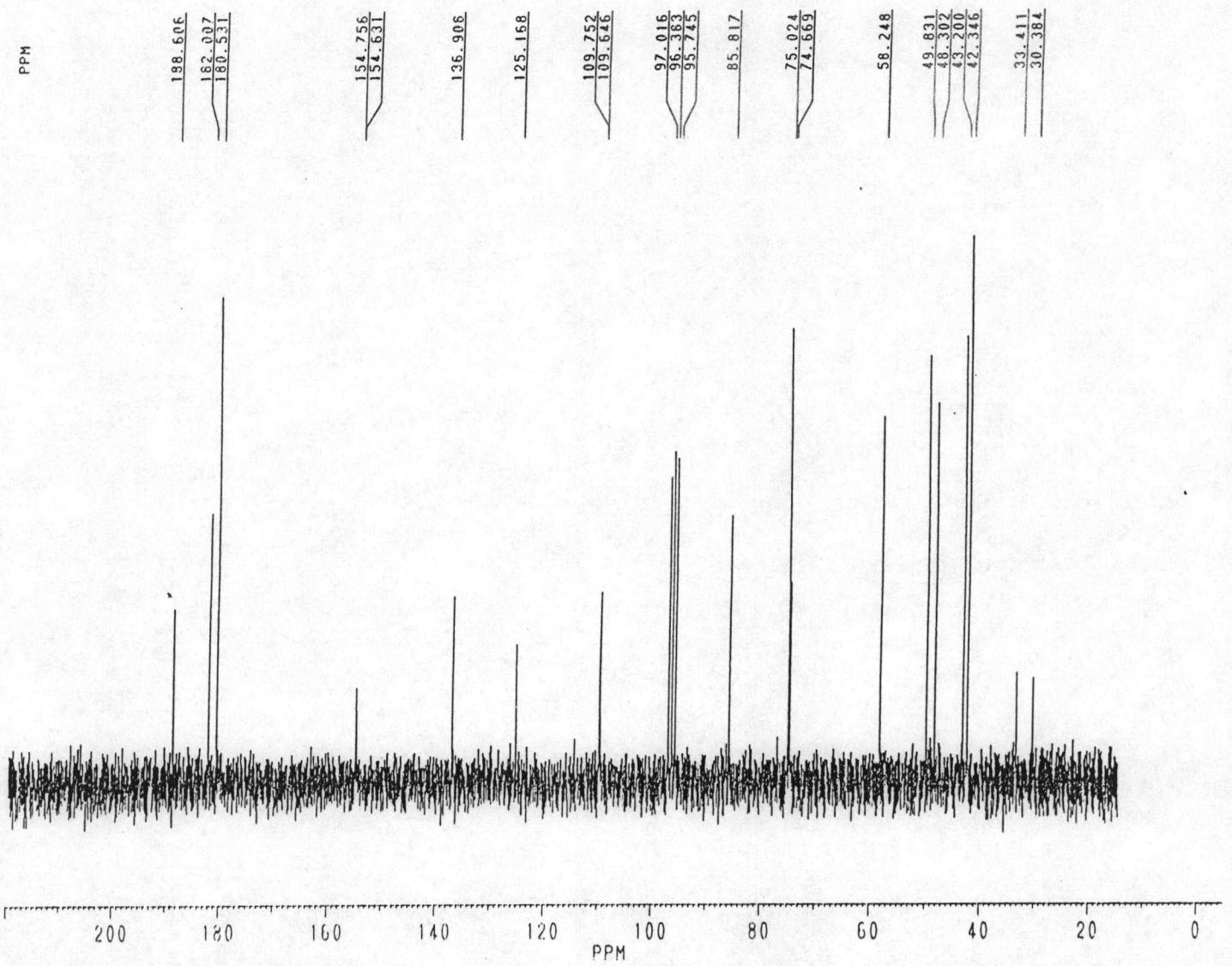


Figure B.6 ^{13}C-NMR spectrum of 2-ethylhexyl-2,4,6-trimethoxycinnamate (**E10**)

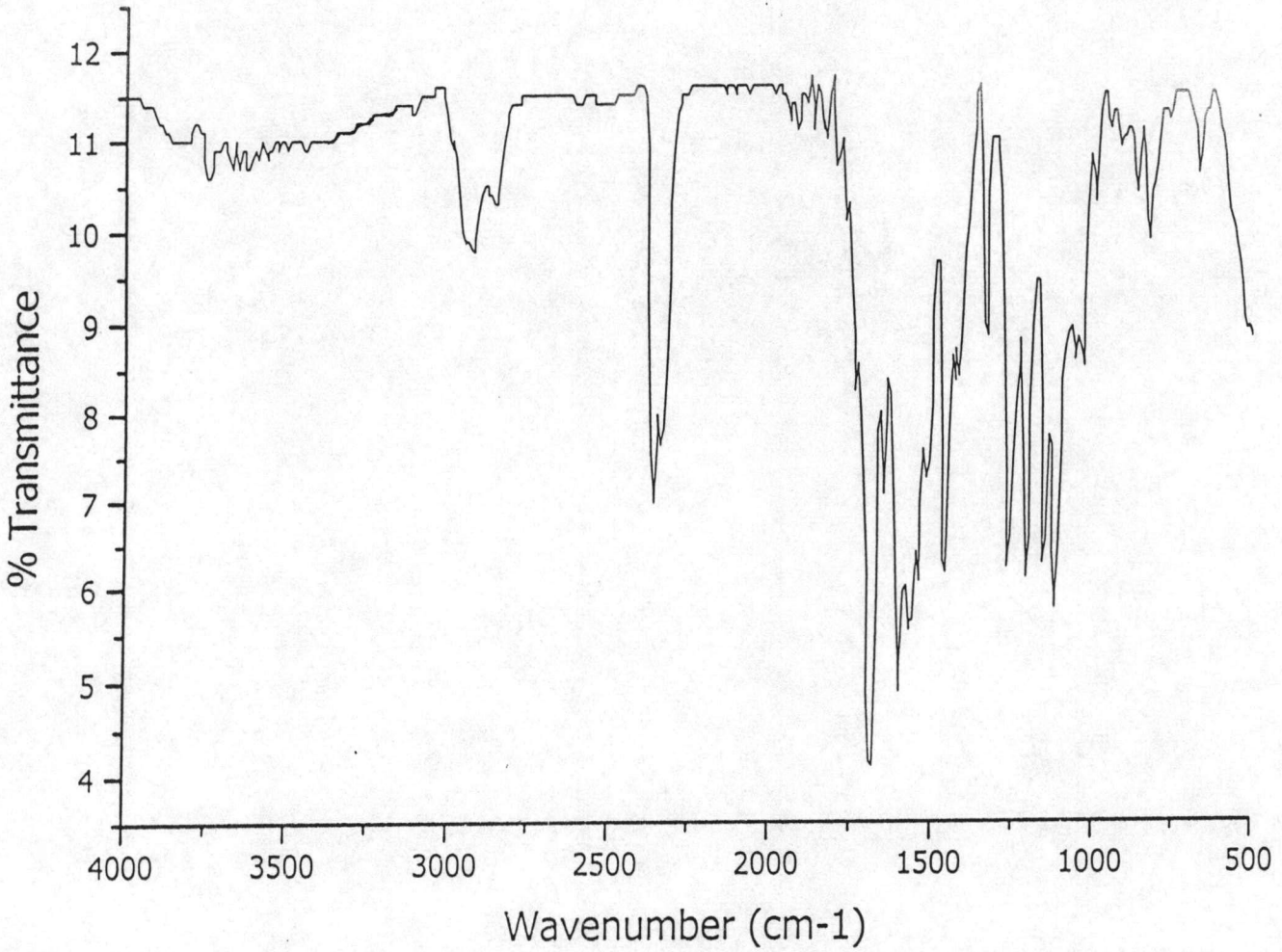


Figure B.7 IR spectrum of 2-ethylhexyl-2,4,6-trimethoxycinnamate (**E10**)

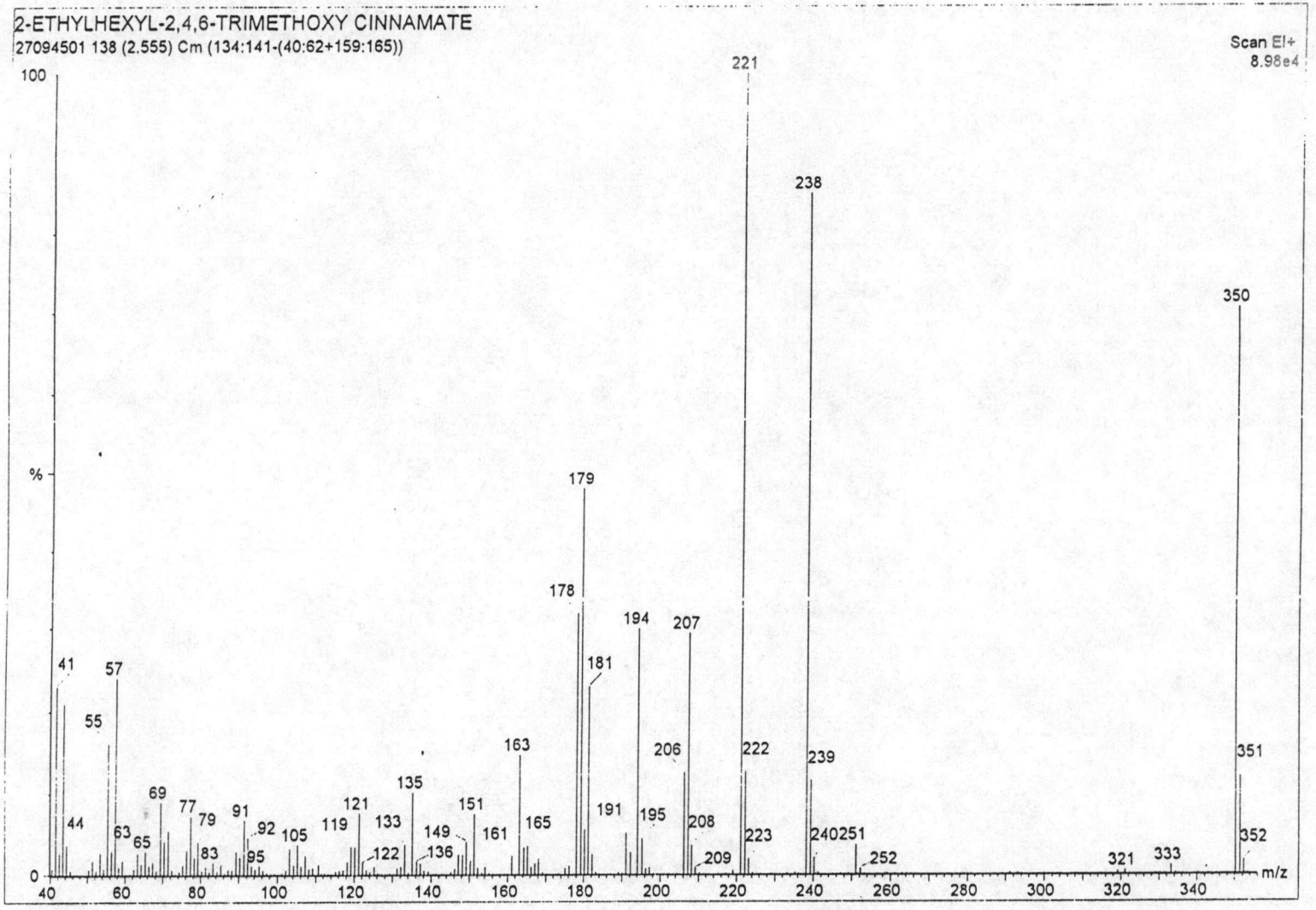


Figure B.8 Mass spectrum of 2-ethylhexyl-2,4,6-trimethoxycinnamate (**E10**)

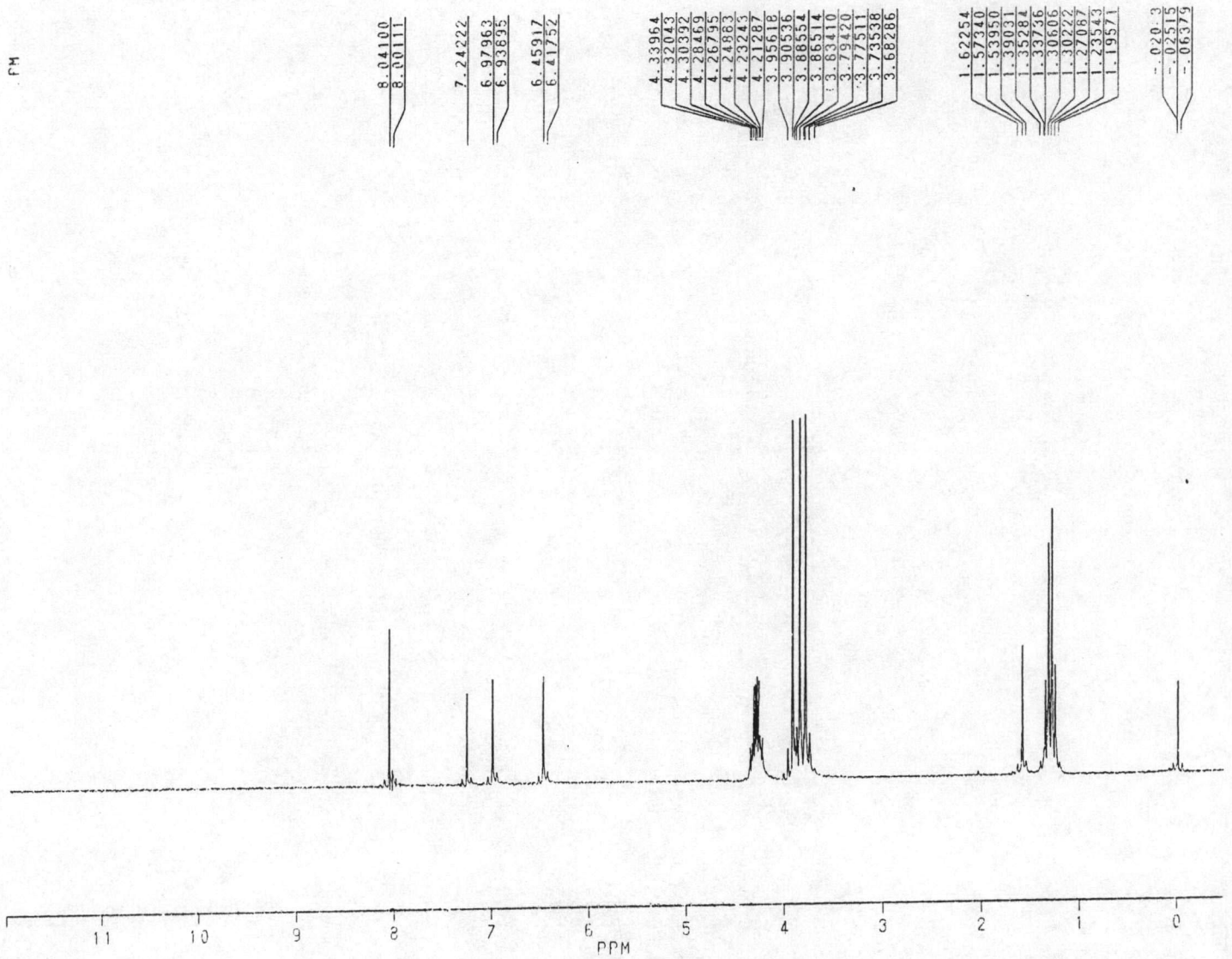


Figure B.9 ^{1}H-NMR spectrum of diethyl-2,4,5-trimethoxybenzalmalonate (**BM8-1**)

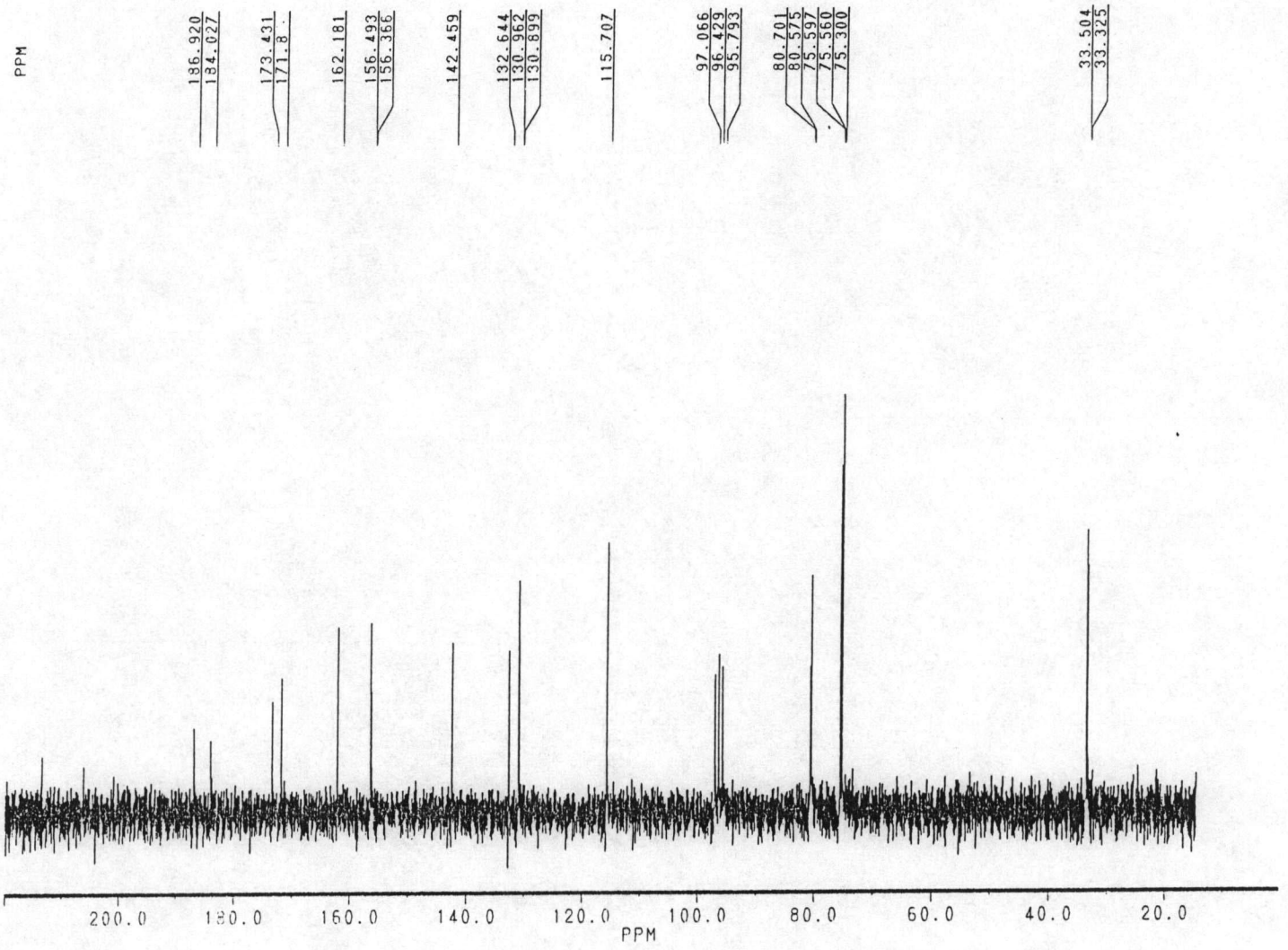


Figure B.10 ^{13}C-NMR spectrum of diethyl-2,4,5-trimethoxybenzalmalonate (**BM8-1**)

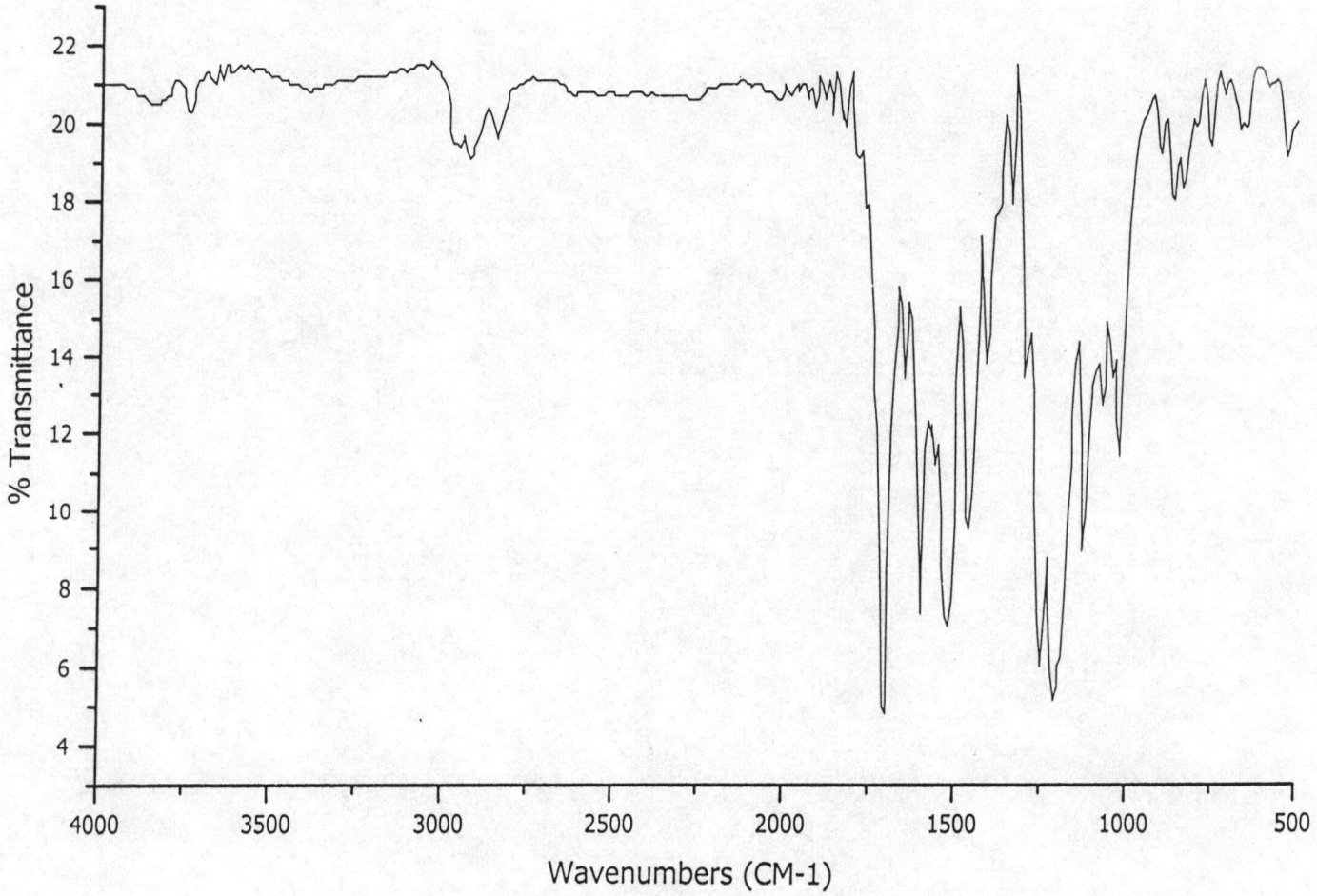


Figure B.11 IR spectrum of diethyl-2,4,5-trimethoxybenzalmalonate (**BM8-1**)

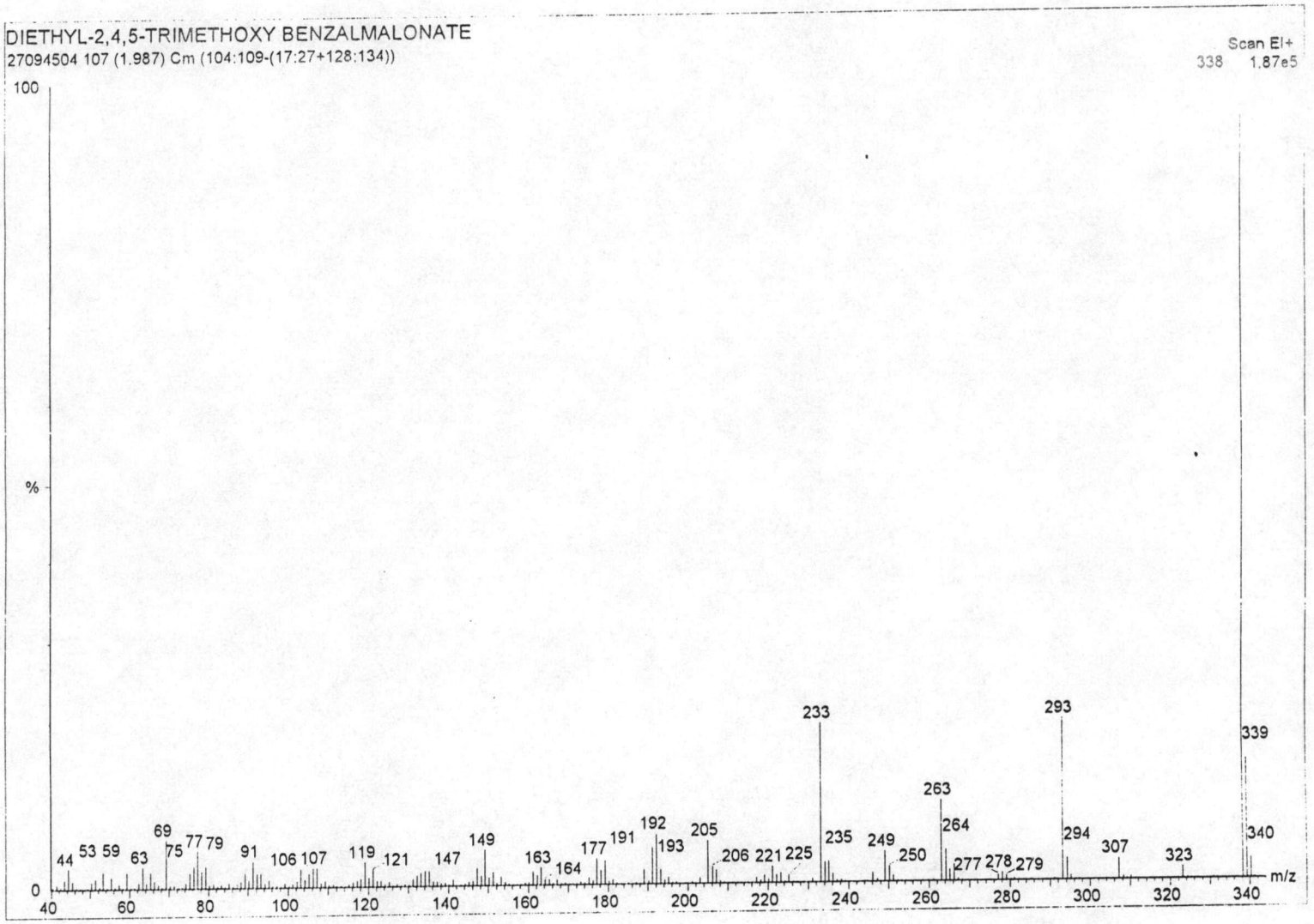


Figure B.12 Mass spectrum of diethyl-2,4,5-trimethoxybenzalmalonate (**BM8-1**)

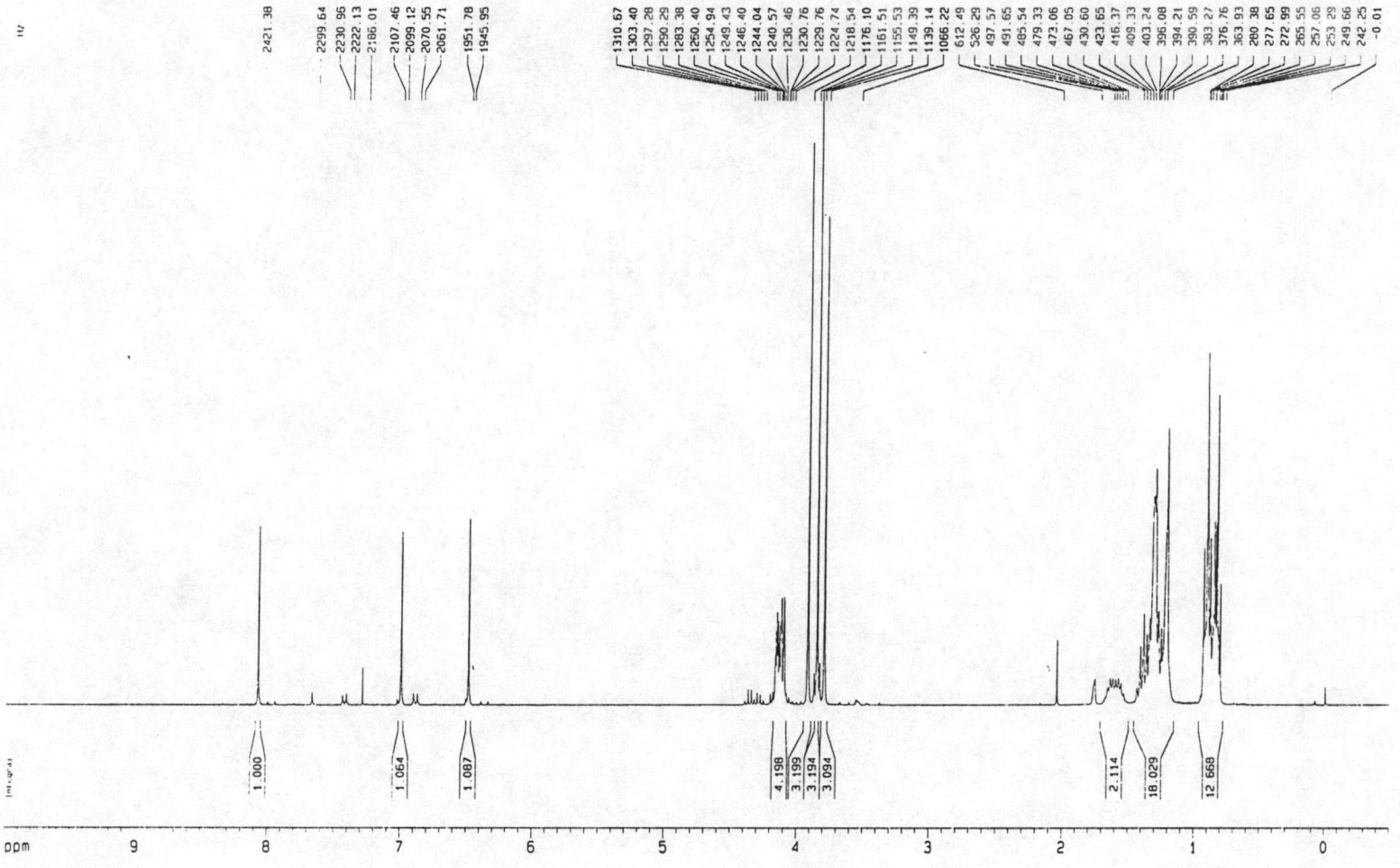


Figure B.13 ^{1}H-NMR spectrum of di-(2-ethylhexyl)-2,4,5-trimethoxybenzalmalonate (**BM8-2**)

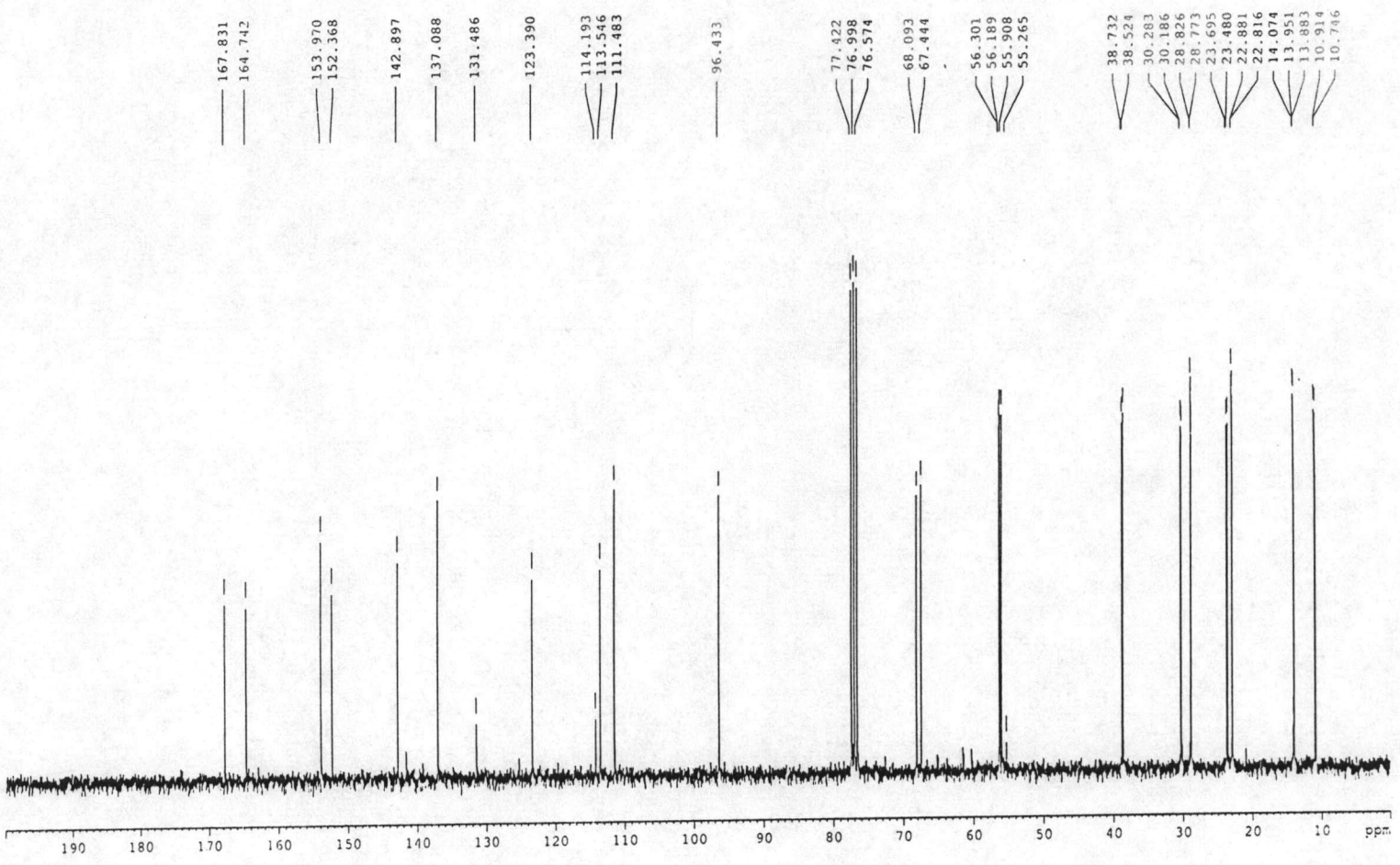


Figure B.14 ^{13}C-NMR spectrum of di-(2-ethylhexyl)-2,4,5-trimethoxybenzalmalonate (**BM8-2**)

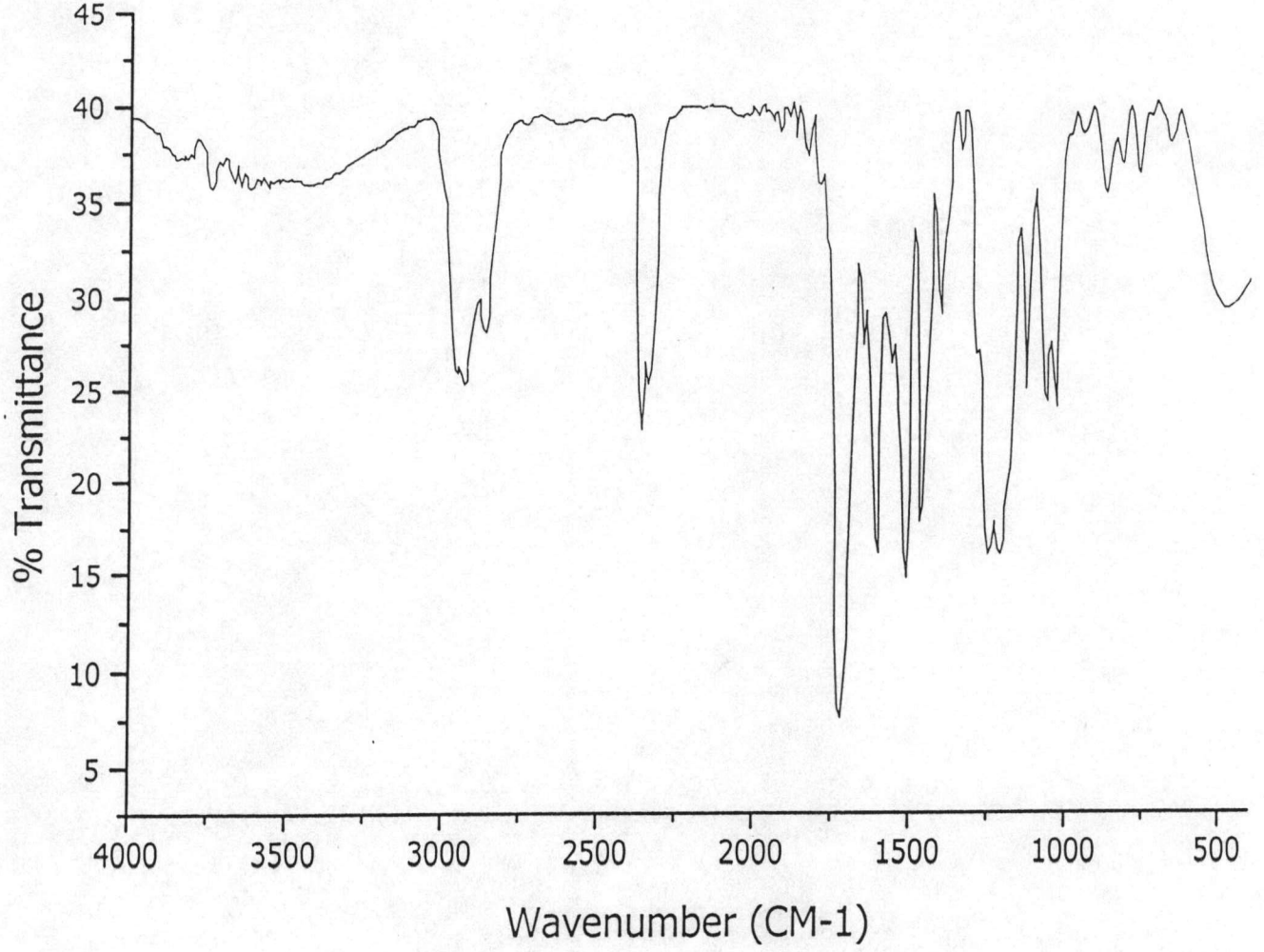


Figure B.15 IR spectrum of di-(2-ethylhexyl)-2,4,5-trimethoxybenzalmalonate (**BM8-2**)

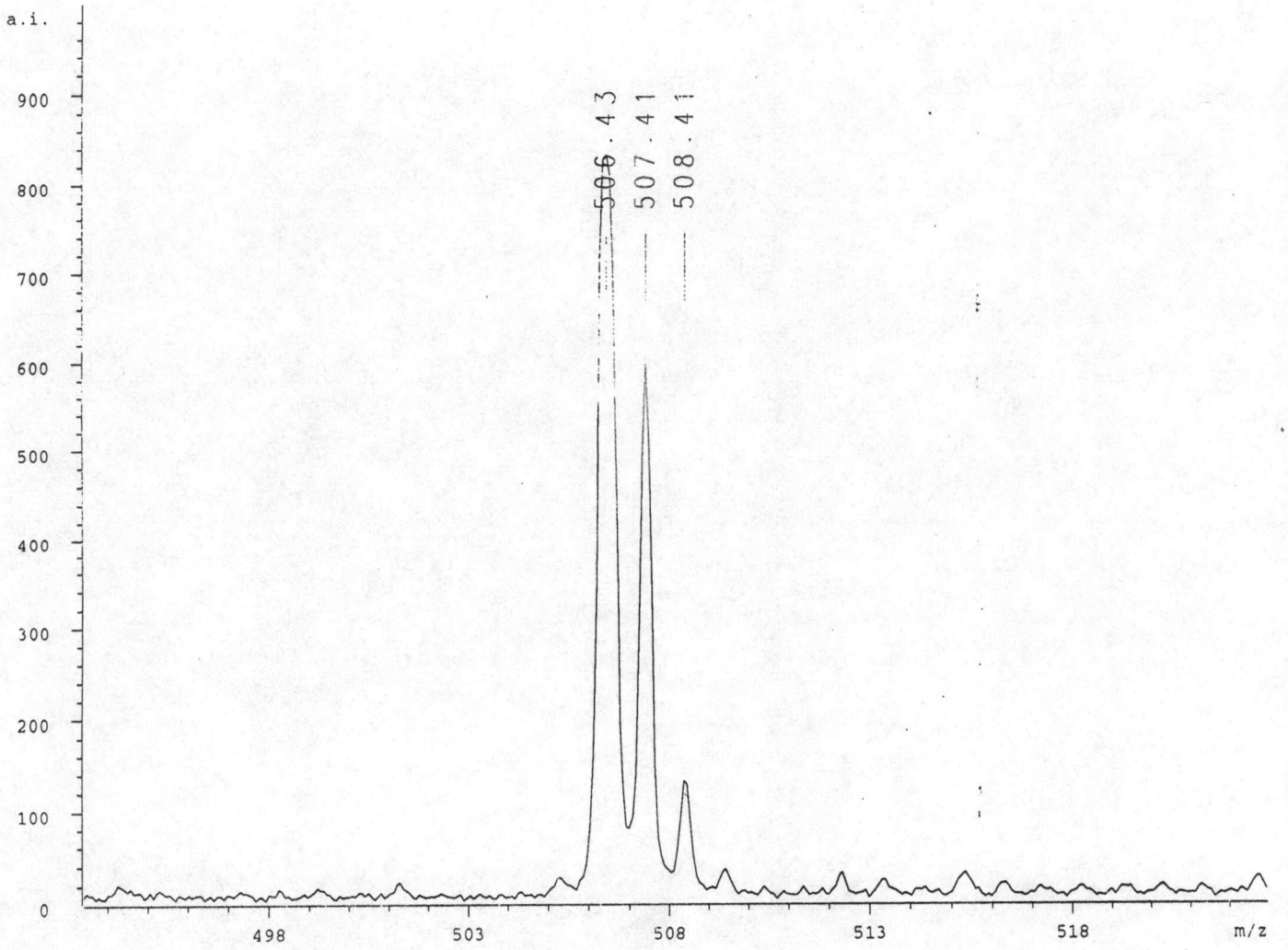


Figure B.16 Mass spectrum (MALDI-TOF) of di-(2-ethylhexyl)-2,4,5-trimethoxybenzalmalonate (BM8-2)

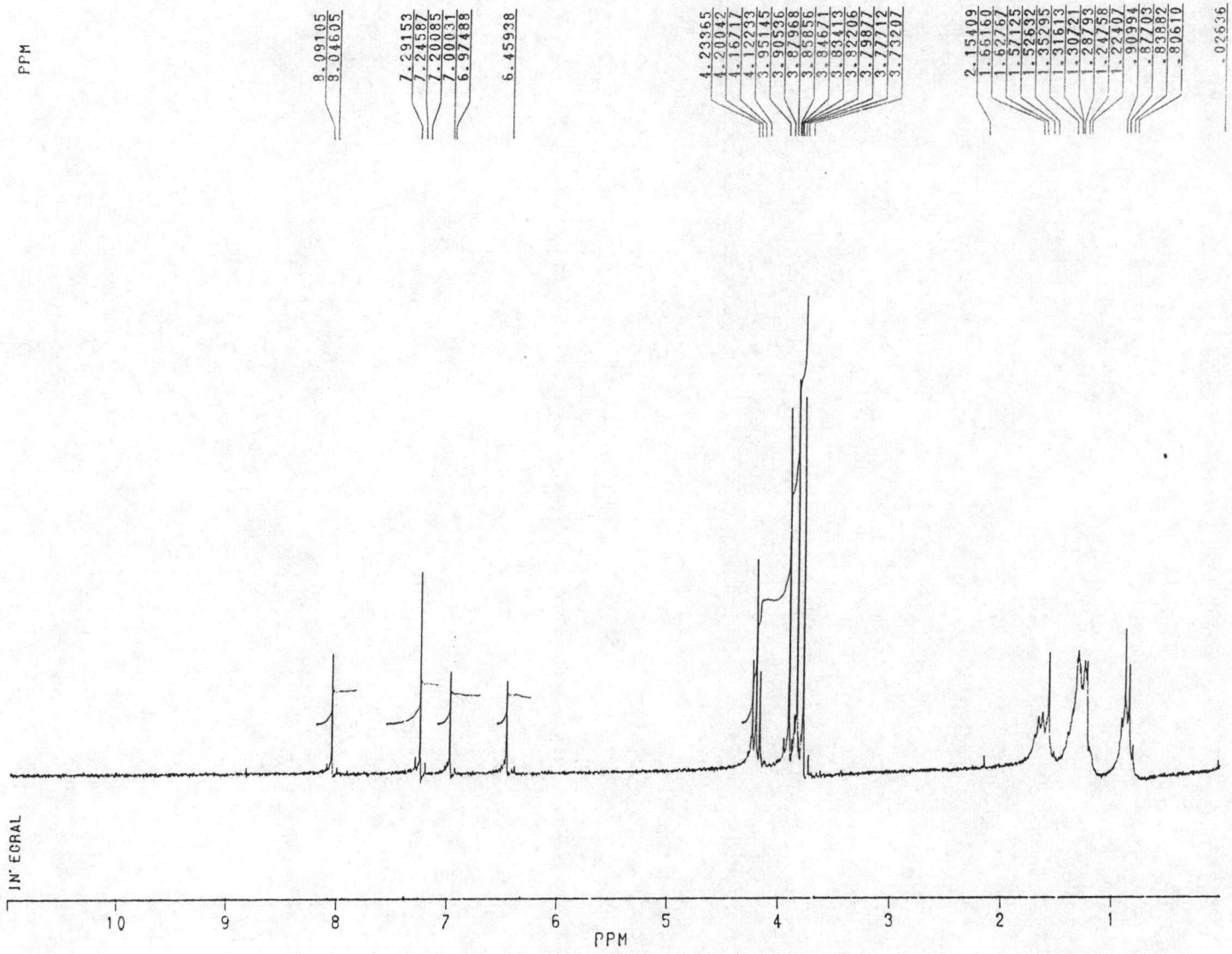


Figure B.17 ^{1}H-NMR spectrum of dihexyl-2,4,5-trimethoxybenzalmalonate (**BM8-3**)

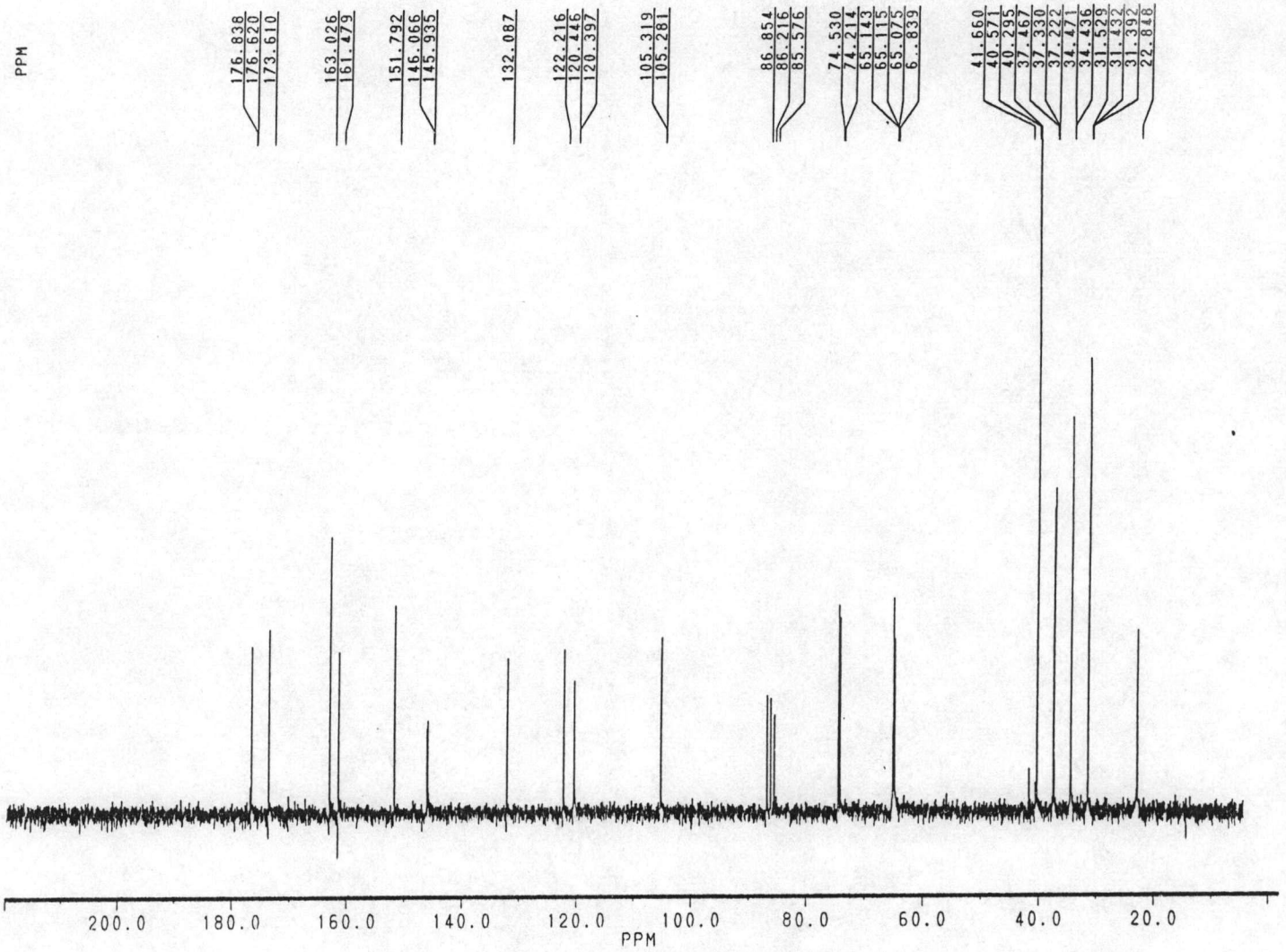


Figure B.18 ^{13}C-NMR spectrum of dihexyl-2,4,5-trimethoxybenzalmalonate (**BM8-3**)

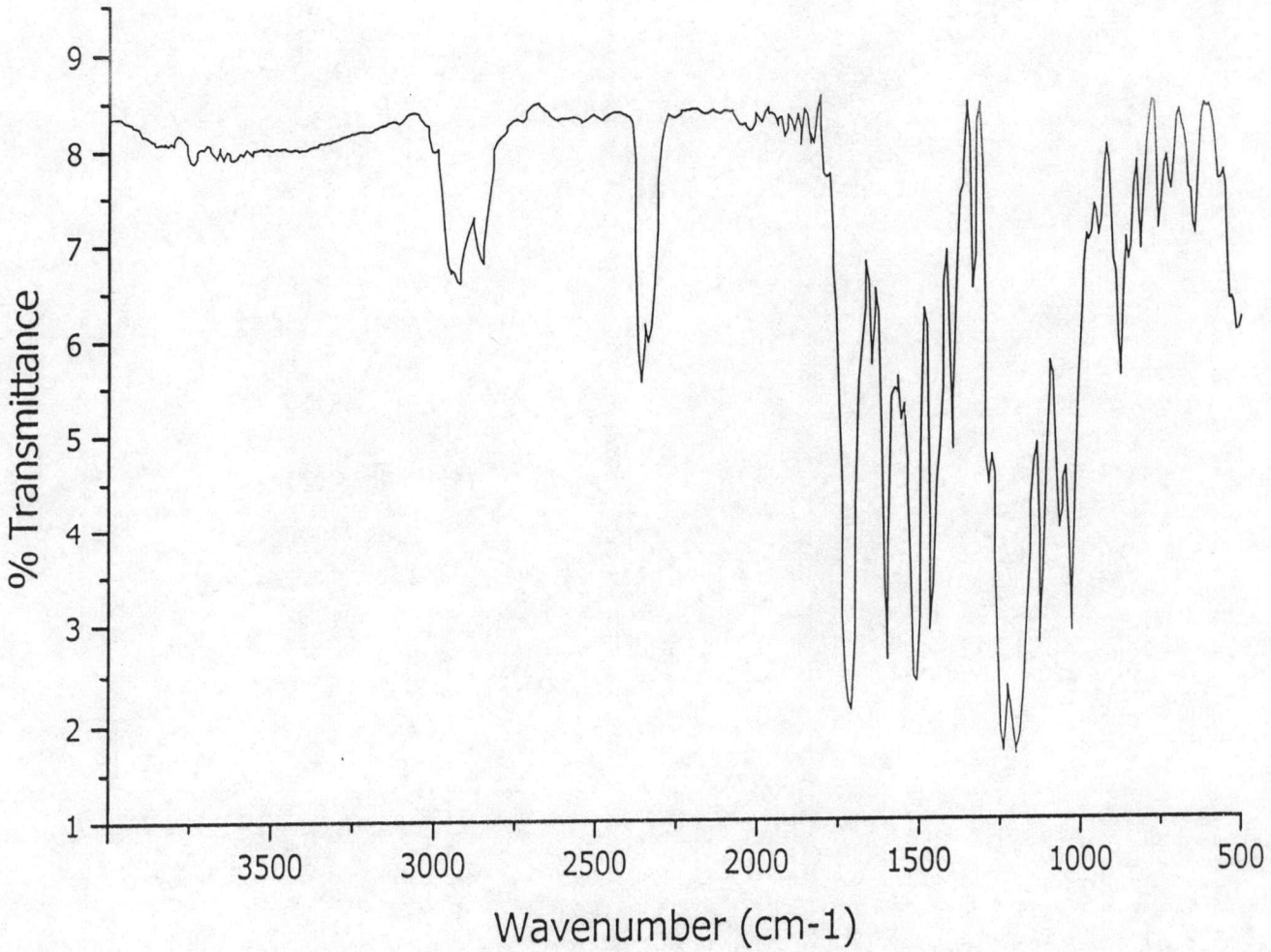


Figure B.19 IR spectrum of dihexyl-2,4,5-trimethoxybenzalmalonate (**BM8-3**)

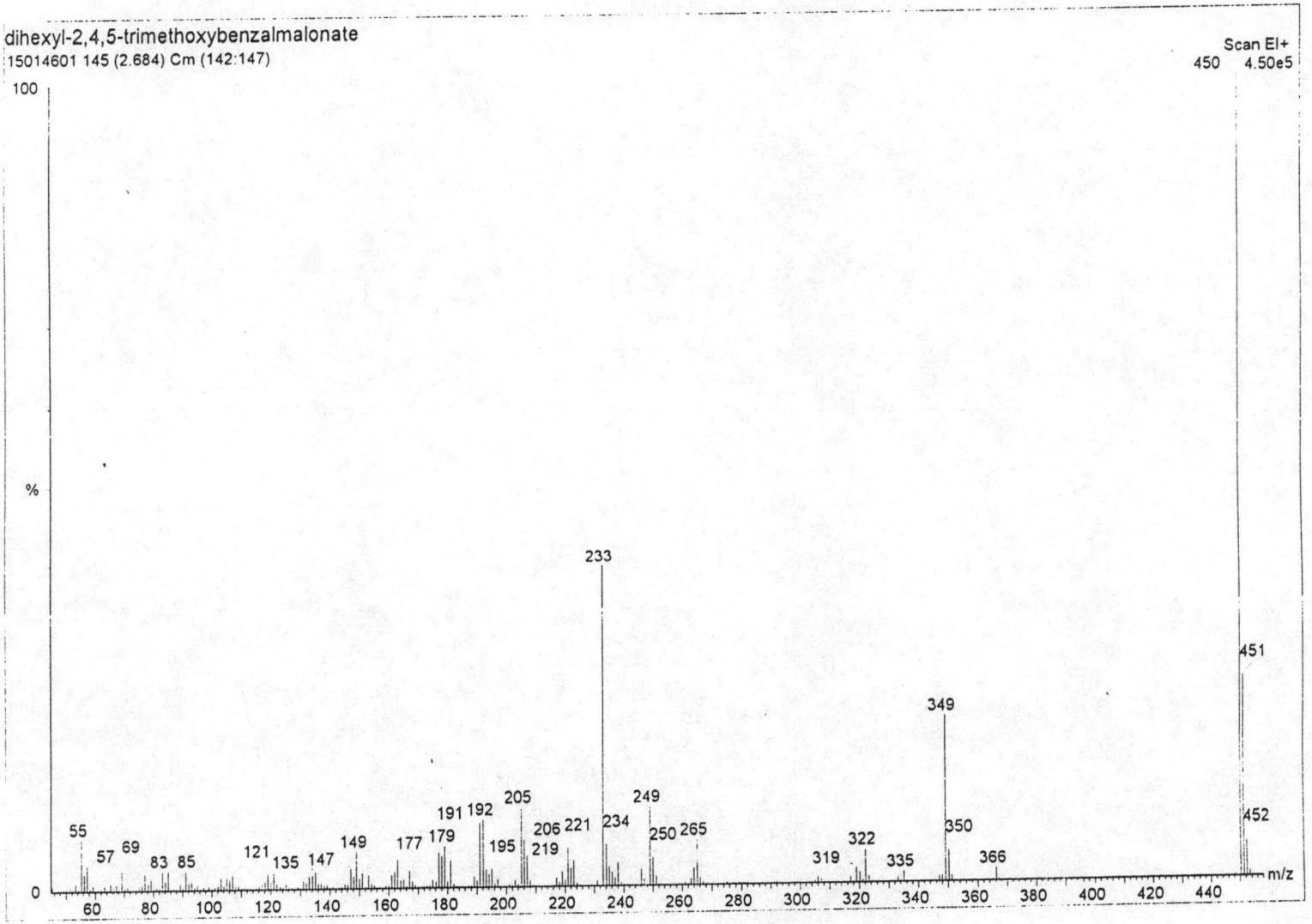


Figure B.20 Mass spectrum of dihethyl-2,4,5-trimethoxybenzalmalonate (**BM8-3**)

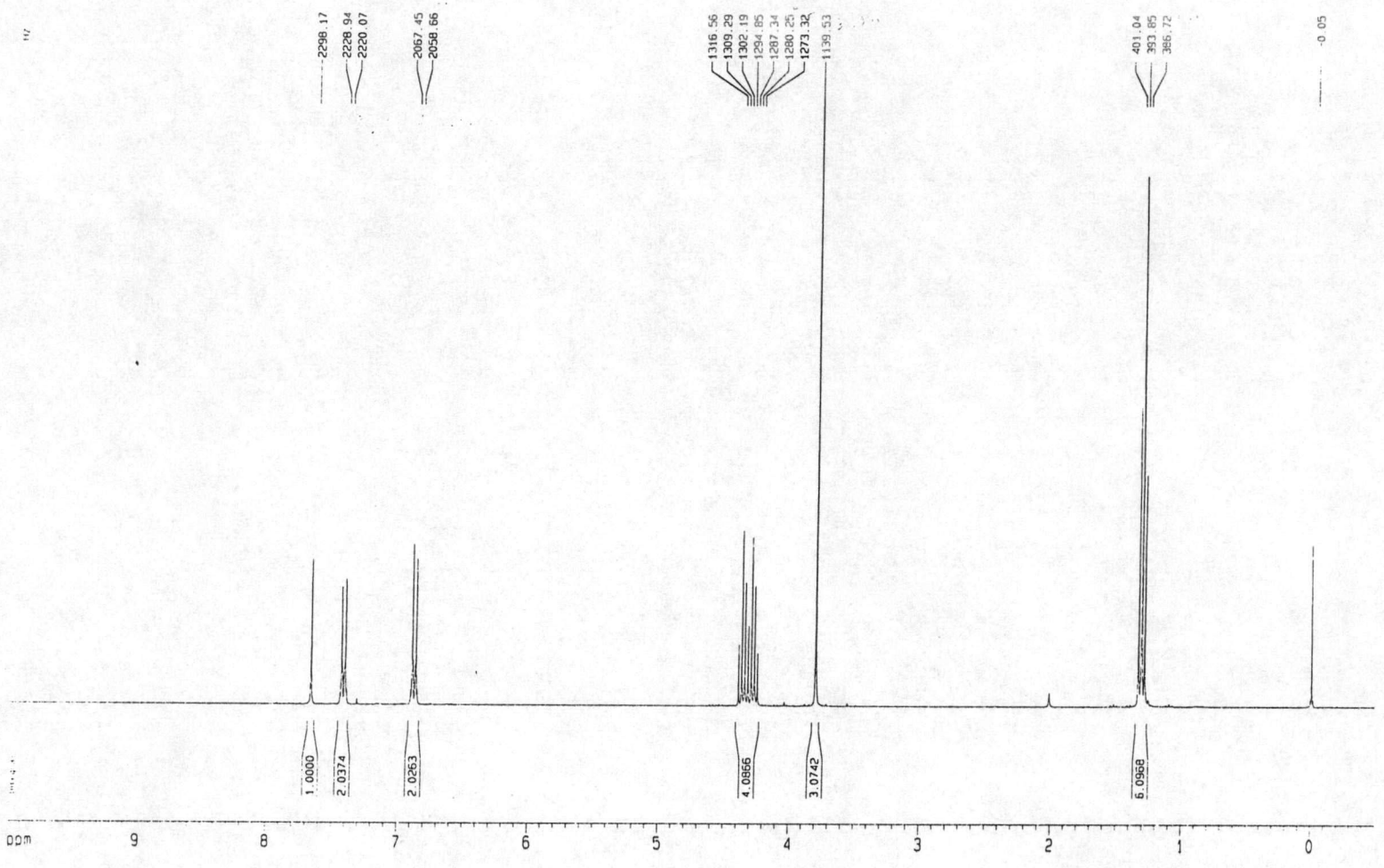


Figure B.21 ^{1}H-NMR spectrum of diethyl-4-methoxybenzalmalonate (**BM1-1**)

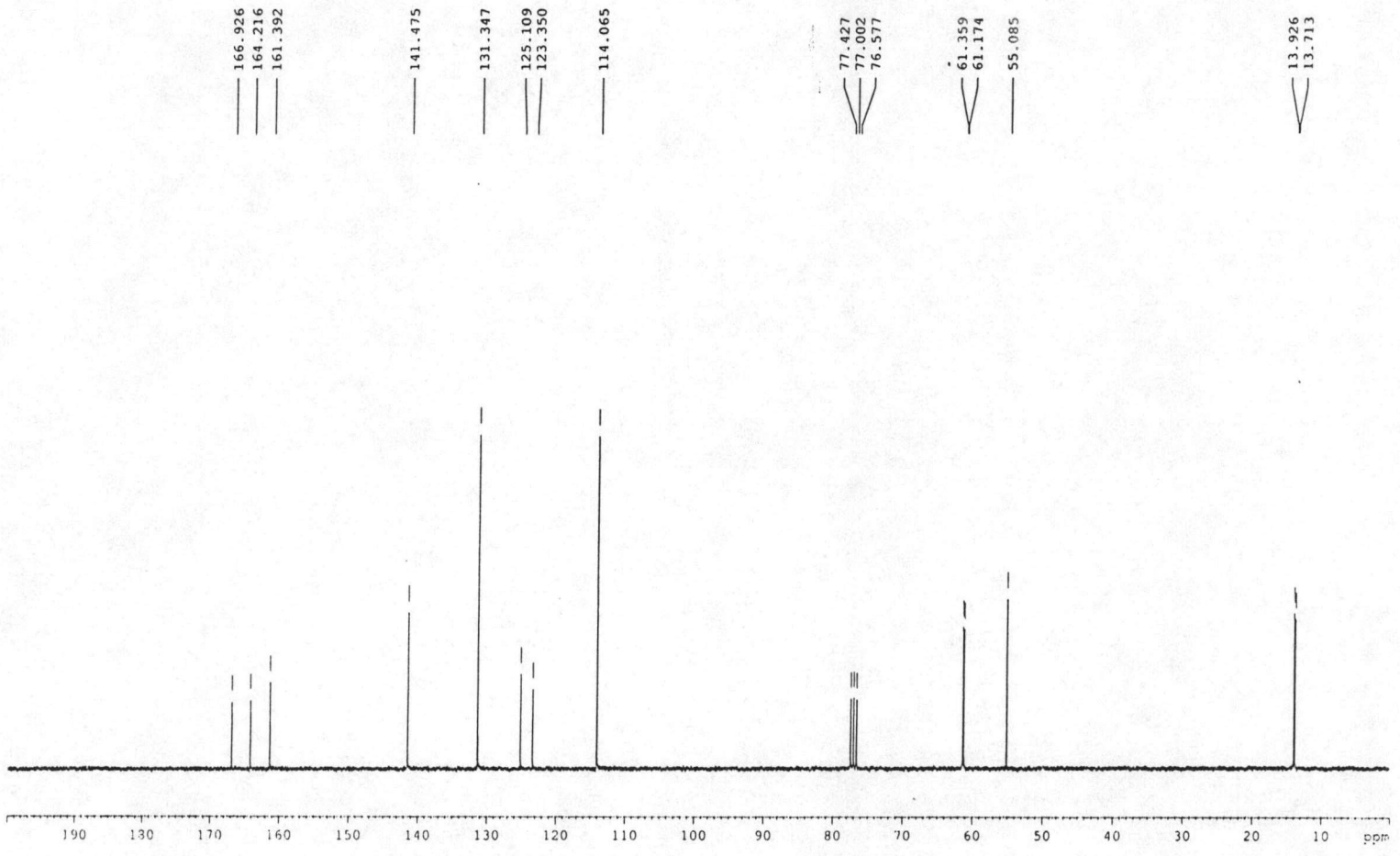


Figure B.22 ^{13}C-NMR spectrum of diethyl-4-methoxybenzalmalonate (**BM1-1**)

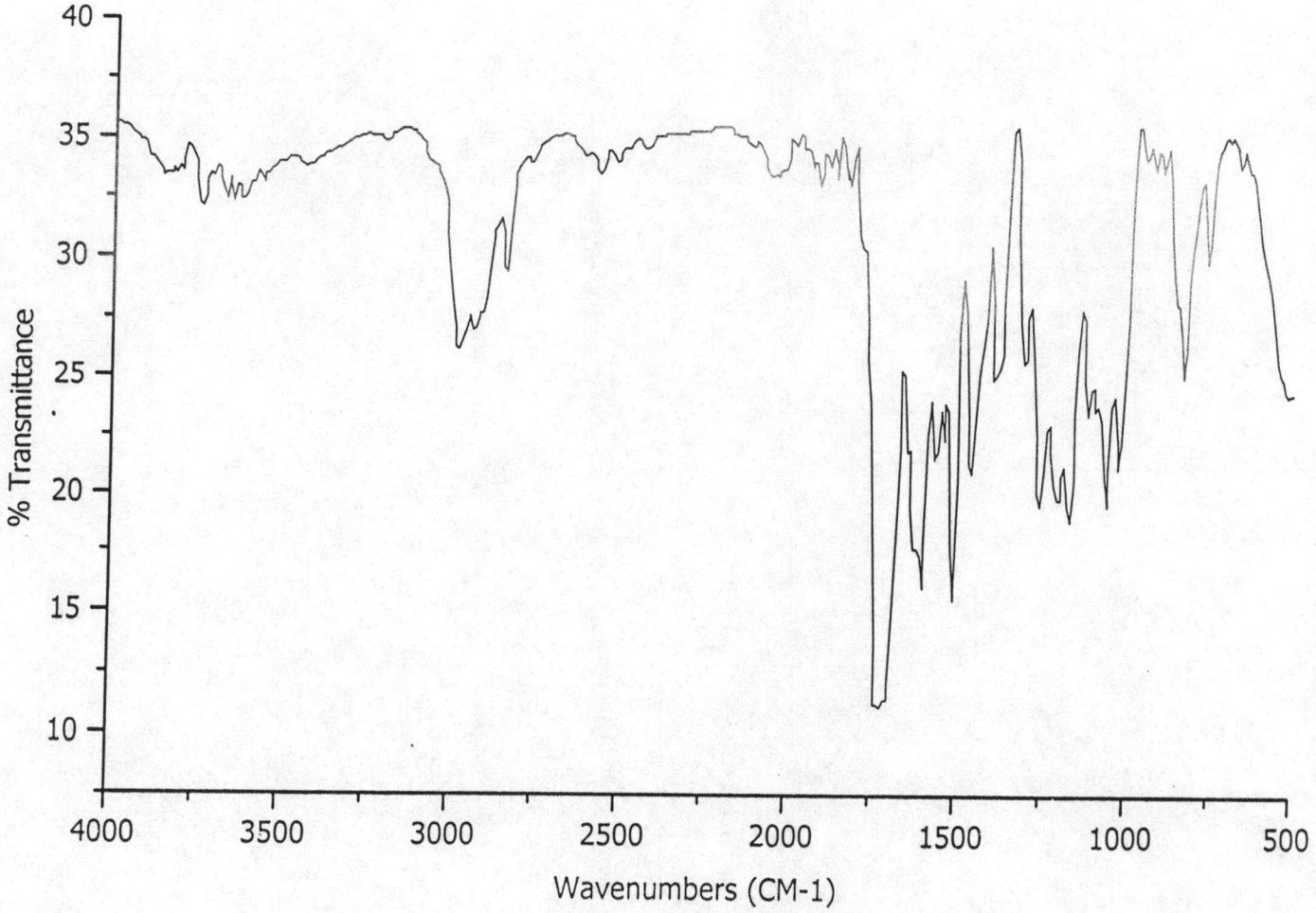


Figure B.23 IR spectrum of diethyl-4-methoxybenzalmalonate (**BM1-1**)

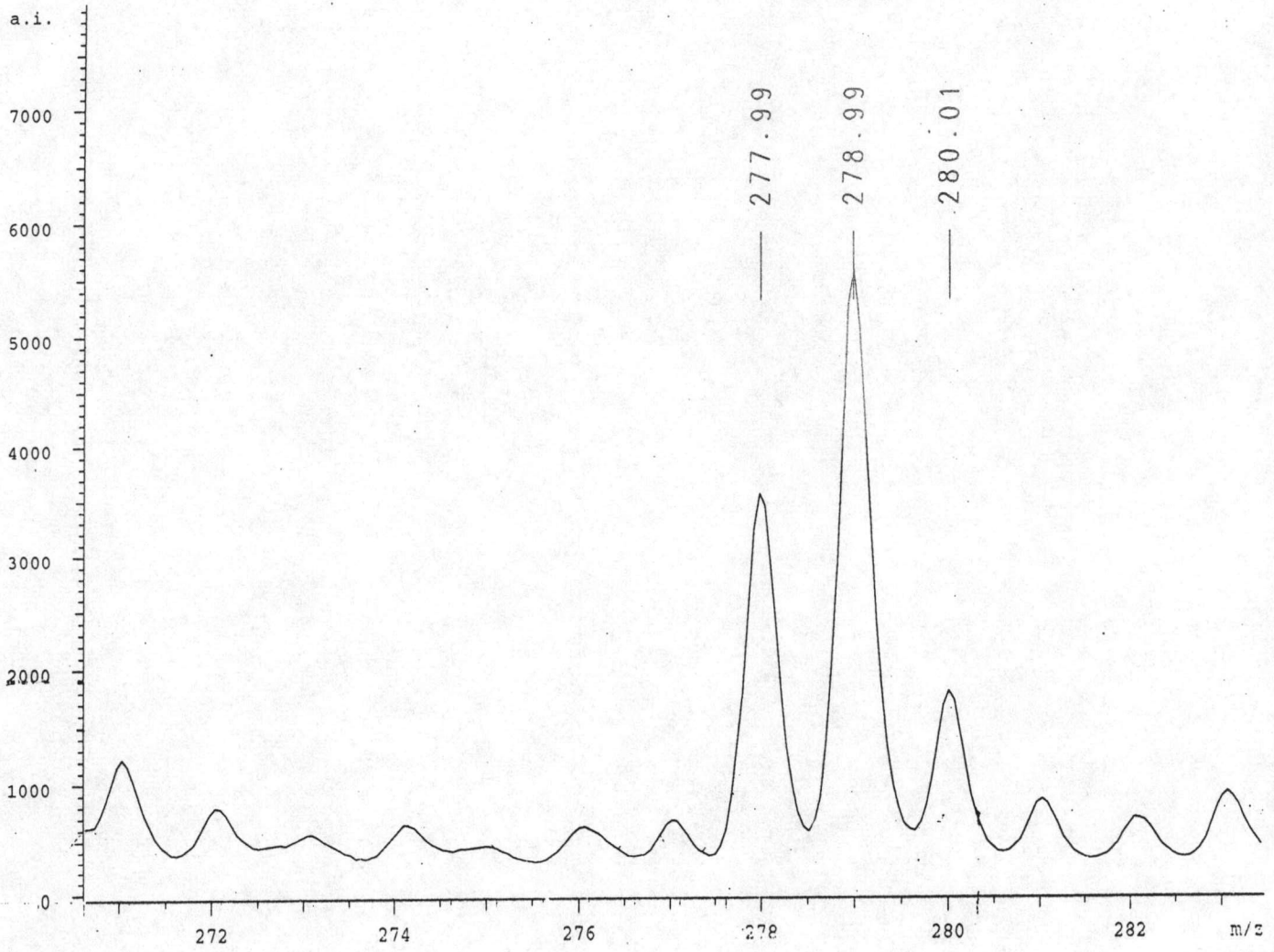


Figure B.24 Mass spectrum (MALDI-TOF) of diethyl-4-methoxybenzalmalonate (**BM1-1**)

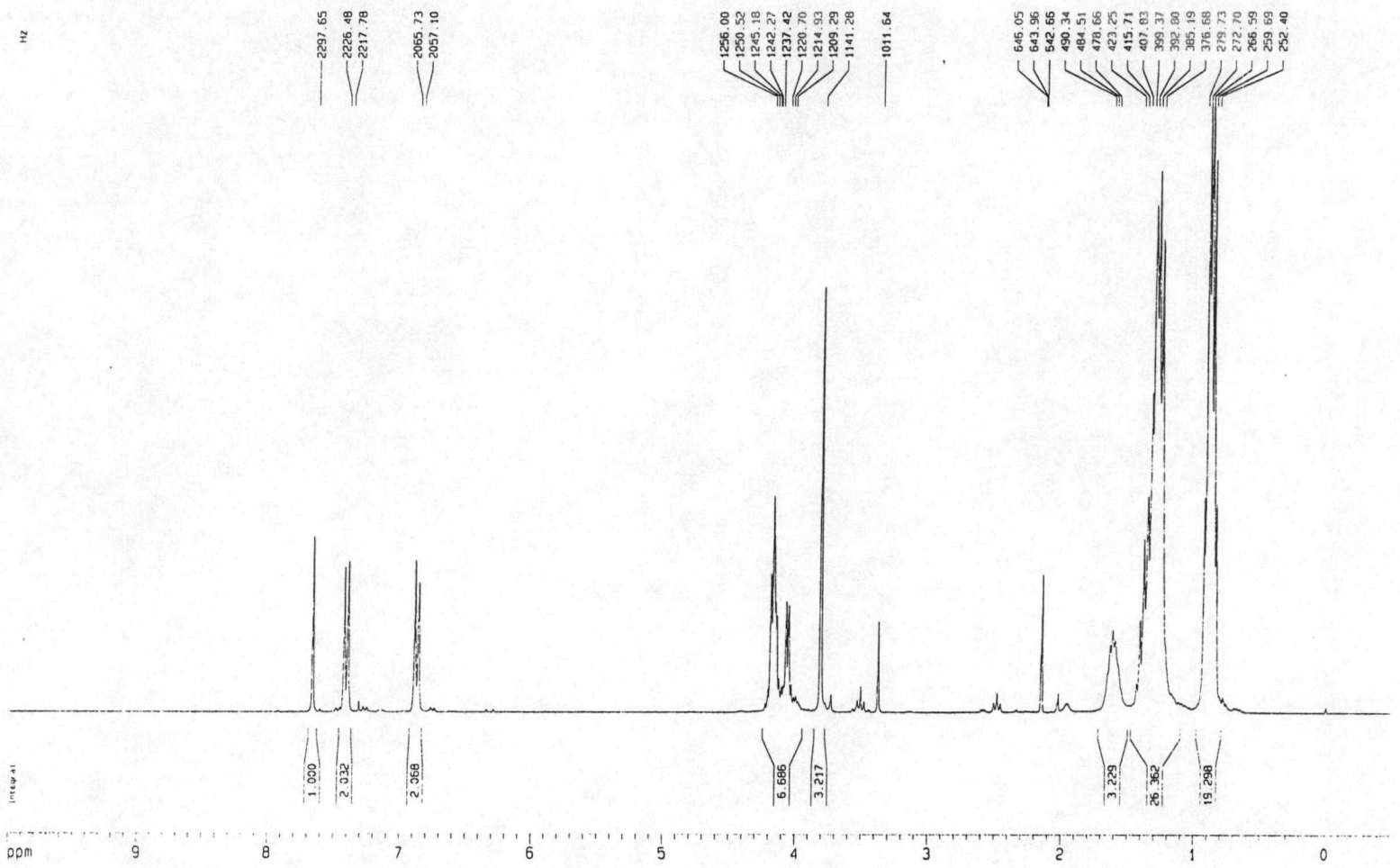


Figure B.25 ^{1}H-NMR spectrum of di-(2-ethylhexyl)-4-methoxybenzalmalonate (**BM1-2**)

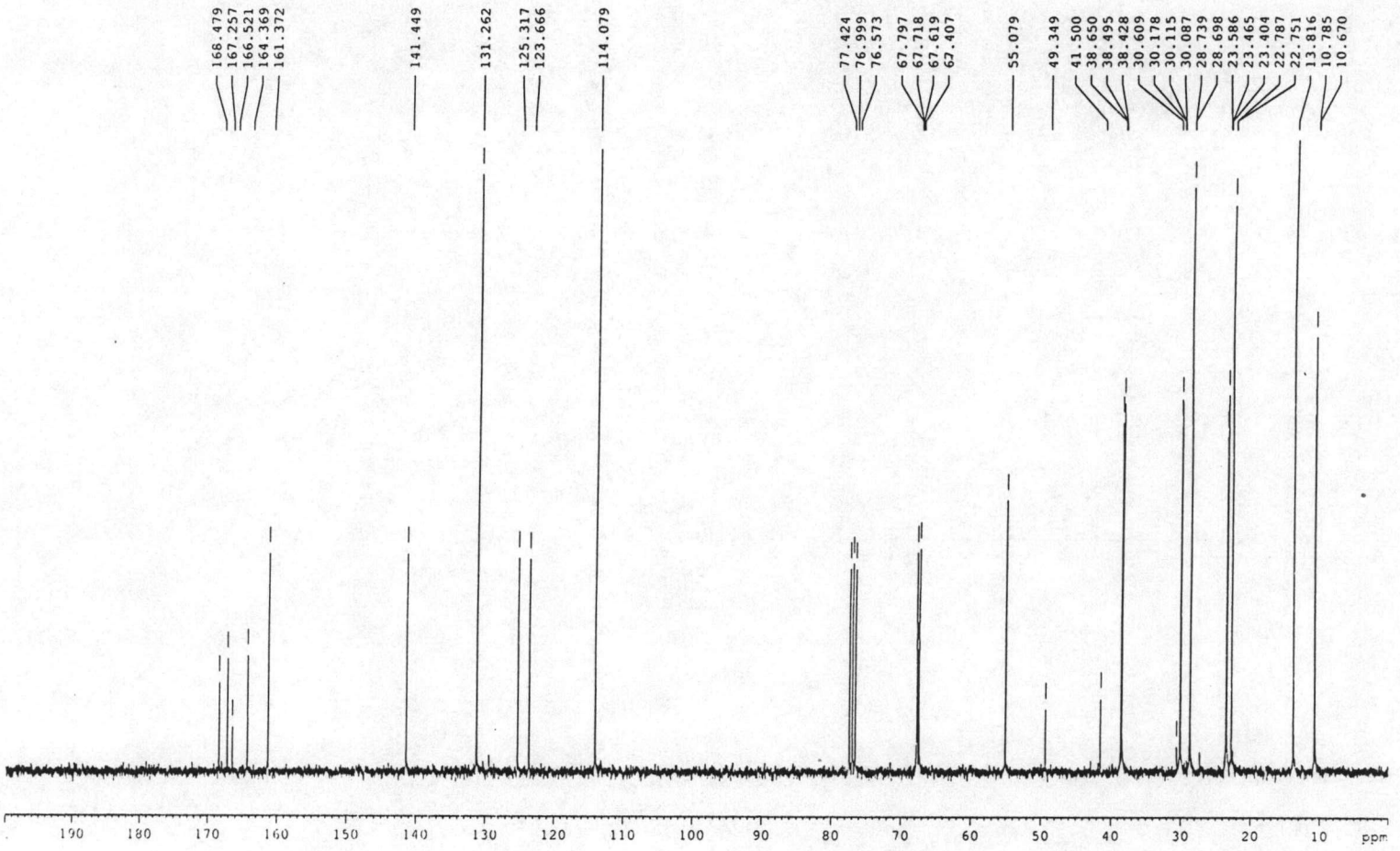


Figure B.26 ^{13}C-NMR spectrum of di-(2-ethylhexyl)- 4-methoxybenzalmalonate (**BM1-2**)

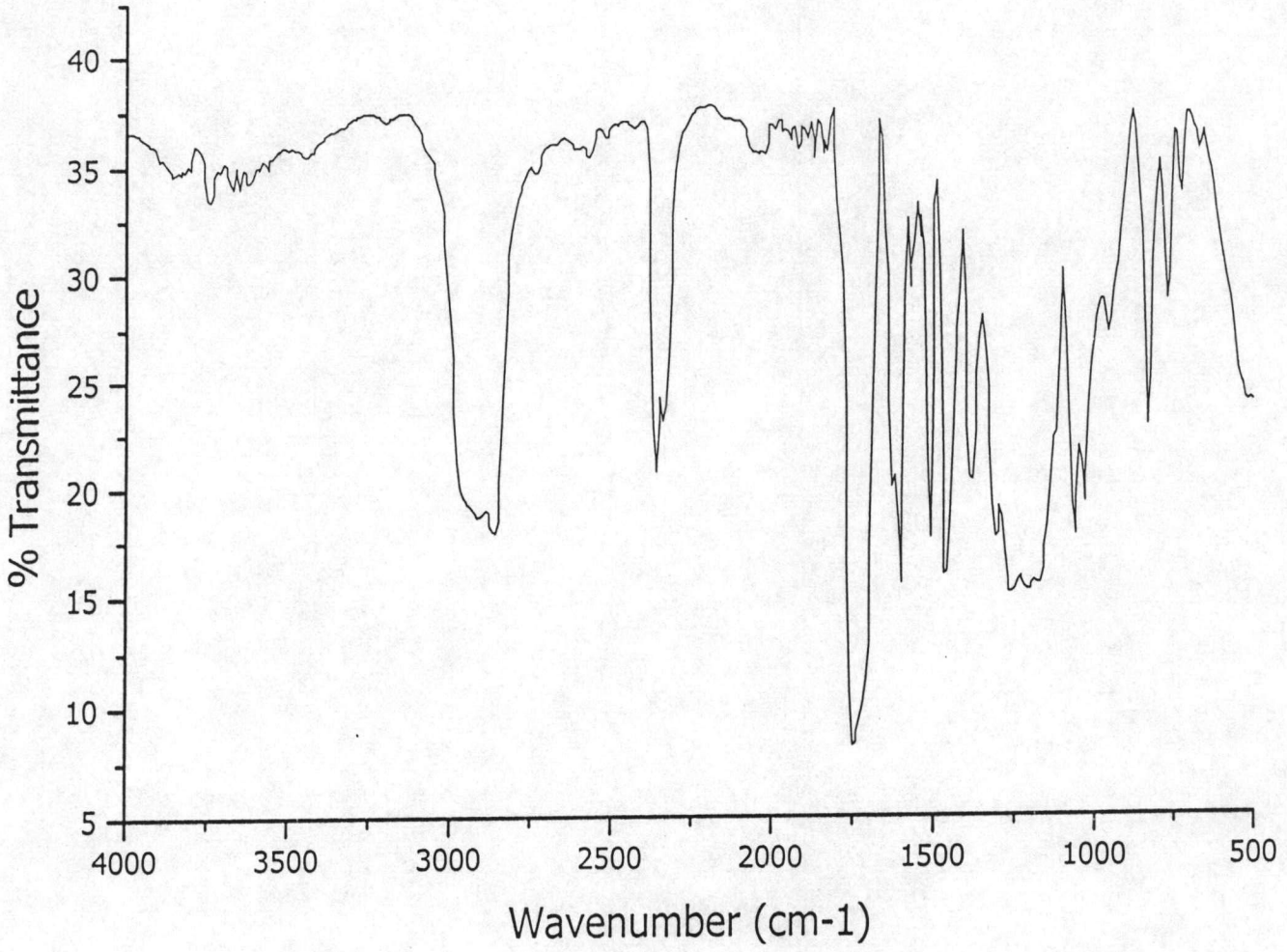


Figure B.27 IR spectrum of di-(2-ethylhexyl)- 4-methoxybenzalmalonate (**BM1-2**)

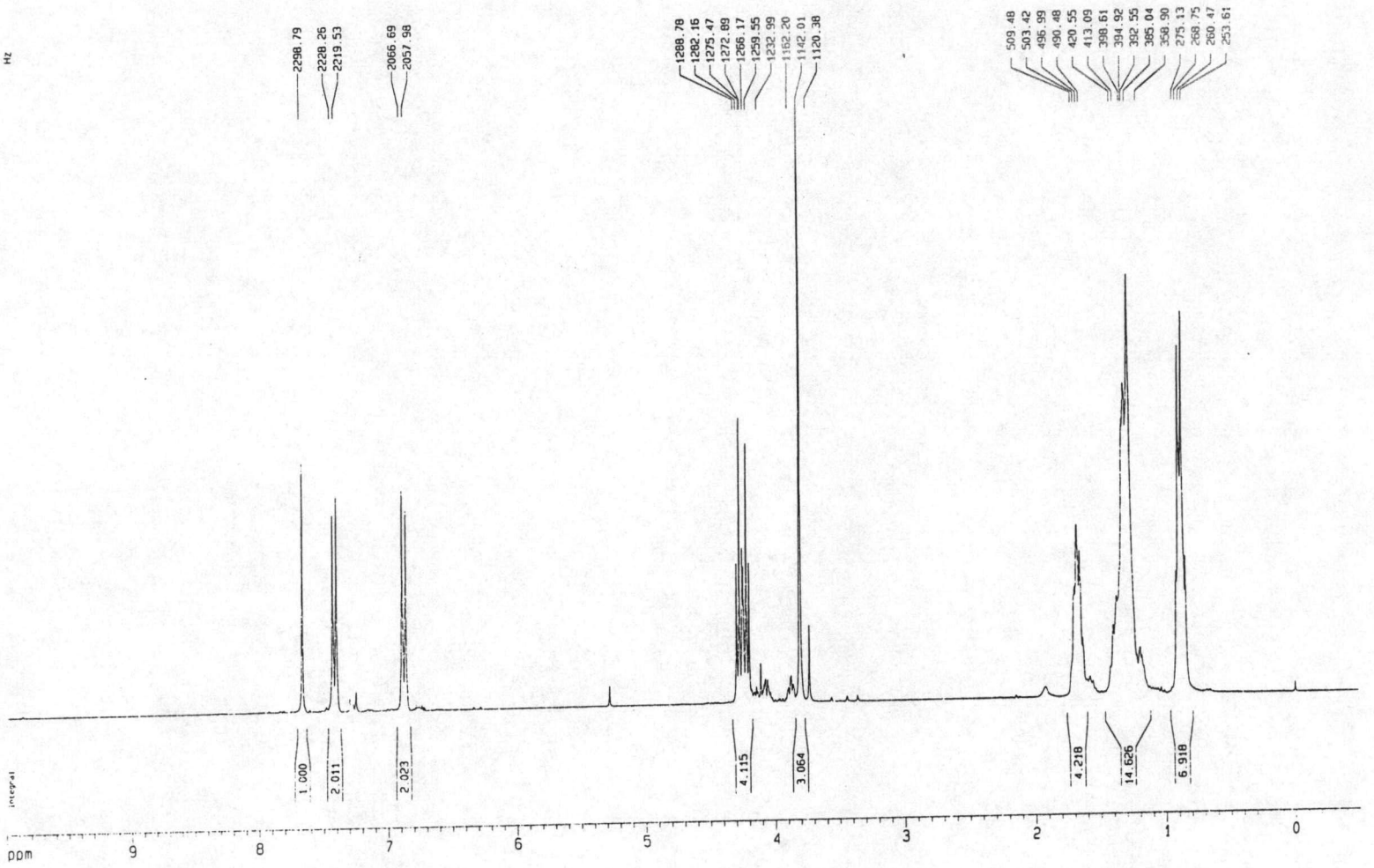


Figure B.28 ^{1}H-NMR spectrum of dihexyl-4-methoxybenzalmalonate (**BM1-3**)

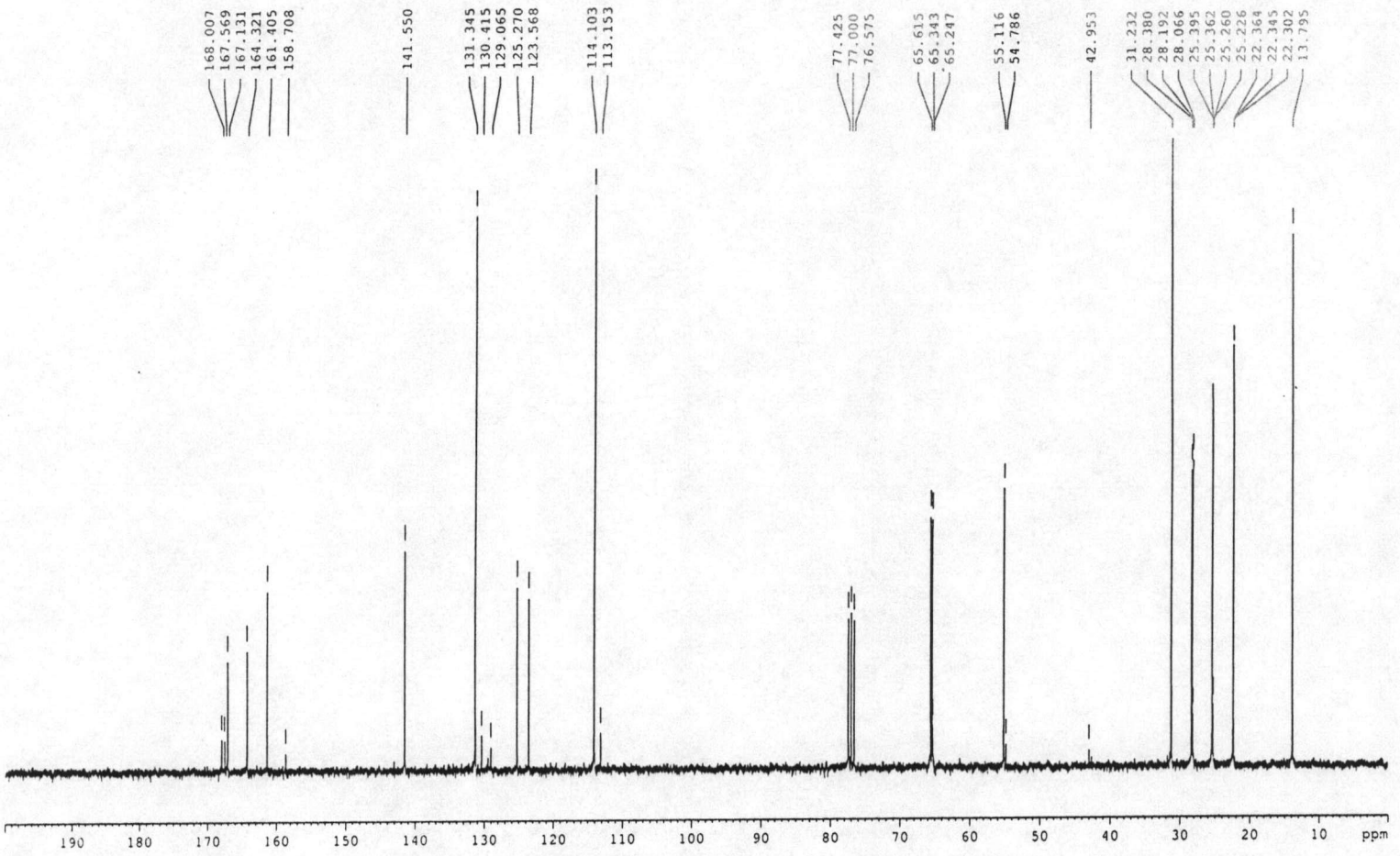


Figure B.29 ^{13}C-NMR spectrum of dihexyl-4-methoxybenzalmalonate (**BM1-3**)

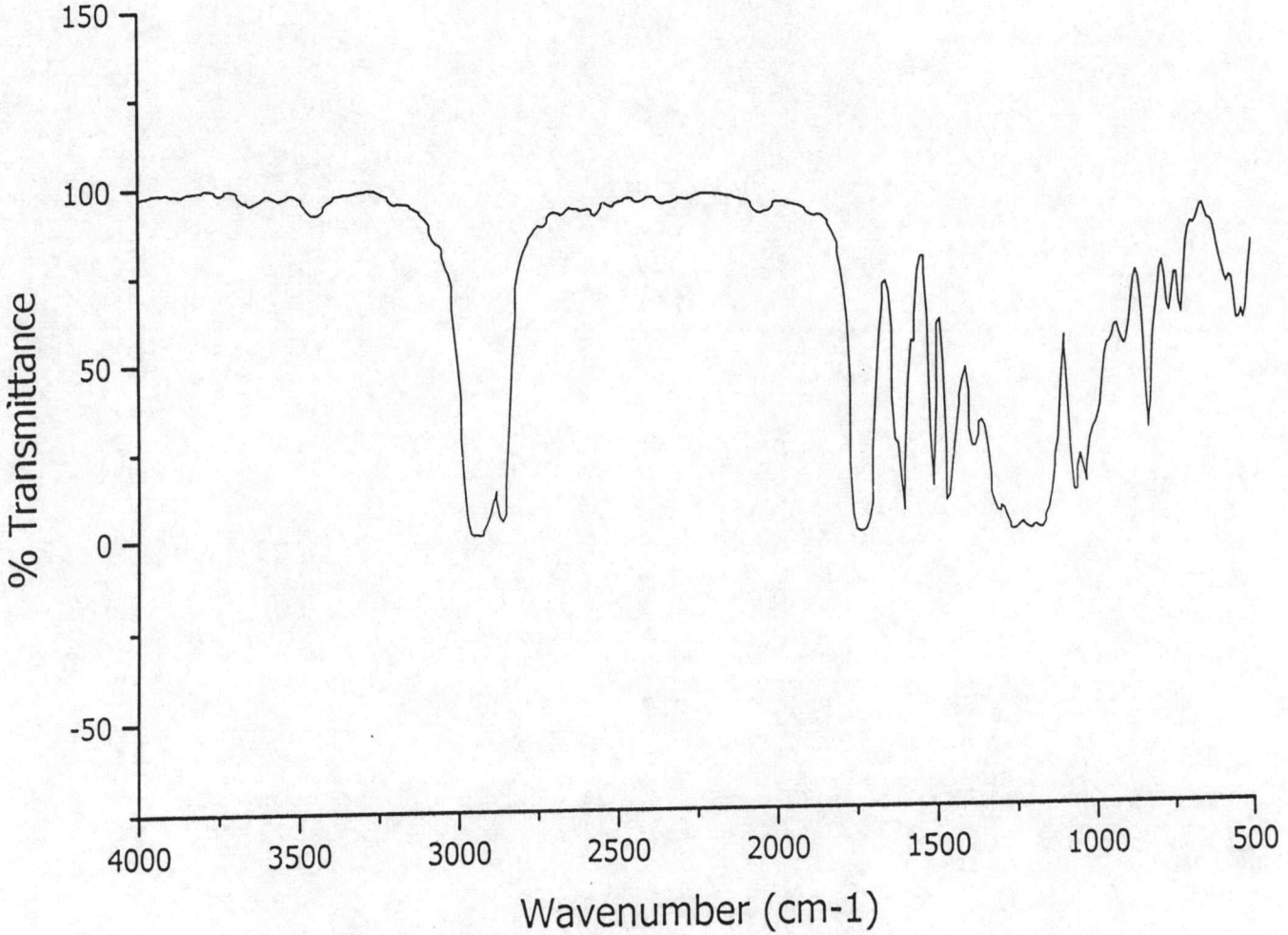


Figure B.30 IR spectrum of dihexyl-4-methoxybenzalmalonate (BM1-3)

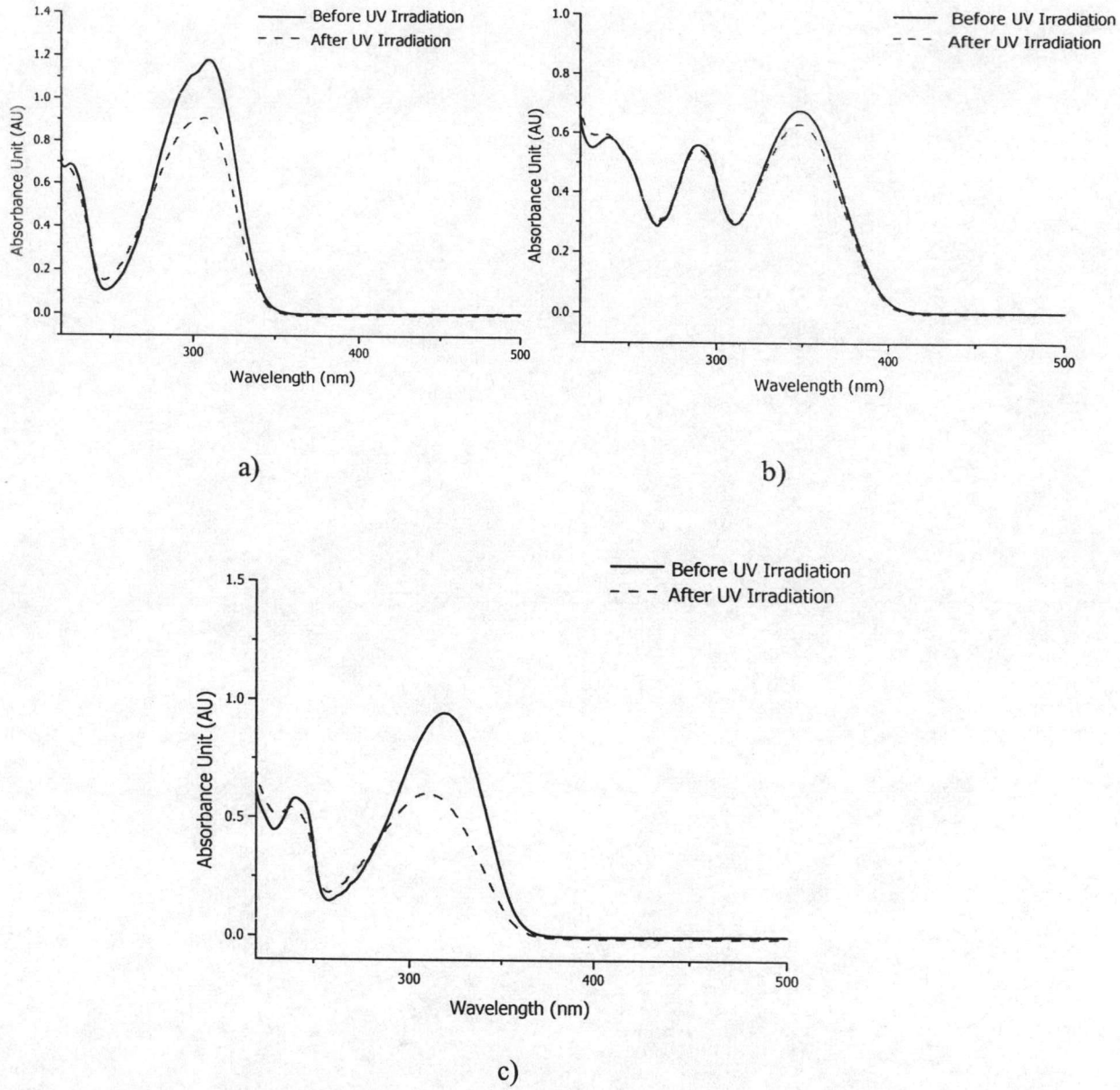


Figure B.31 UV spectra of a) OMC, b) **E8** and c) **E10** before and after UV irradiation for 2 hours

APPENDIX C

C.1 Photostability Test

Table C.1 Percent relative absorbance of synthesized UV-filters in UVA region in methanol

Time (h)	Percent Relative Absorbance			
	E2	**BM8-1**	**BM8-2**	**BM8-3**
0	100	100	100	100
1	-	100	98.25	98.36
1.25	79.98	-	-	-
2	78.74	100	99.07	98.52
3	-	100	99.95	98.57
4	-	100	100	97.81
5.5	78.33	-	-	-
7	-	100	99.11	93.45
10	75.76	-	-	-
11	-	99.4	99.61	97.26
16	76.97	-	-	-
18	-	100	100	96.83
26.5	75.82	-	-	-
28	-	100	96.33	100
34.5	75.12	-	-	-
36	-	100	95.15	100

Table C.2 Percent relative absorbance of synthesized UV-filters in UVB region in methanol

Time (h)	Percent Relative Absorbance								
	E1[a]	**E8**	**E10**	**BM8-1**	**BM8-2**	**BM8-3**	**BM1-1**	**BM1-2**	**BM1-3**
0	100	100	100	100	100	100	100	100	100
1	66.71	-	48.38	100	98.54	97.88	100	99.75	98.72
1.25	-	78.36	-	-	-	-	-	-	-
2	68.66	79.19	47.78	98.72	98.44	98.76	-	-	-
2.5	-	79.93	-	-	-	-	-	-	-
3	69.38	-	50.23	99.75	99.16	99.6	100	99.21	99.68
4	68.47	-	48.56	99.16	99.42	98.81	-	-	-
5	-	-	-	-	-	-	100	99.59	99.87
5.5	-	77.96	-	-	-	-	-	-	-
7	70.46	-	48.35	97.86	98.26	97.96	-	-	-
8	-	-	-	-	-	-	100	98	99.62
10	-	77.72	-	-	-	-	-	-	-
11	69	-	50.78	95.92	98.55	98.13	-	-	-
16	-	77.48	-	-	-	-	100	96.83	99.27
18	69.81	-	52.15	96.24	99.95	97.97	-	-	-
21.5	-	-	-	-	-	-	100	99.74	98.81
26.5	-	76.76	-	-	-	-	-	-	-
28	69.76	-	52.57	99.11	97.28	97.27	-	-	-
34.5	-	76.73	-	-	-	-	-	-	-
36	64.83	-	44.8	99	97.12	100	-	-	-

[a] Standard OMC (**E1**)

Table C.3 Percent relative absorbance of synthesized UV-filters in UVA region in hexanes

Time (h)	Percent Relative Absorbance			
	E8	**BM8-1**	**BM8-2**	**BM8-3**
0	100	100	100	100
1	90.79	100	98	99.5
3	89.9	100	99.42	100
7.25	90.07	100	99.57	99.88
12.25	95.19	101.74	100	100
18	96.1	100.73	100	103.9
22.5	95.01	104.3	100	105.1
27.58	94.69	100	105	105.3

Table C.4 Percent relative absorbance of synthesized UV-filters in UVB region in hexanes

Time (h)	Percent Relative Absorbance								
	E1[a]	**E8**	**E10**	**BM8-1**	**BM8-2**	**BM8-3**	**BM1-1**	**BM1-2**	**BM1-3**
0	100	100	100	100	100	100	100	100	100
1	82.37	87.09	55.82	97.67	96.15	97.62	100	100	99.91
3	81.87	85.94	55.43	96.94	98.42	96.51	100	99.35	97.98
5	-	-	-	-	-	-	98.26	98.82	96.27
7.25	81.29	84.75	55.14	95.43	97.67	94.45	-	-	-
8	-	-	-	-	-	-	98	100	95.4
12.25	83.49	85.52	56.21	93.32	100	95.26	-	-	-
16	-	-	-	-	-	-	98.78	100	96.27
18	83.6	85.05	54.82	92.88	100	93.94	-	-	-
21.5	-	-	-	-	-	-	96.77	100	97.88
22.5	84.29	83.76	55.06	91.34	100	93.22	-	-	-
27.5	84.29	84.15	55.04	91.74	91.73	100	-	-	-

[a] Standard OMC (**E1**)

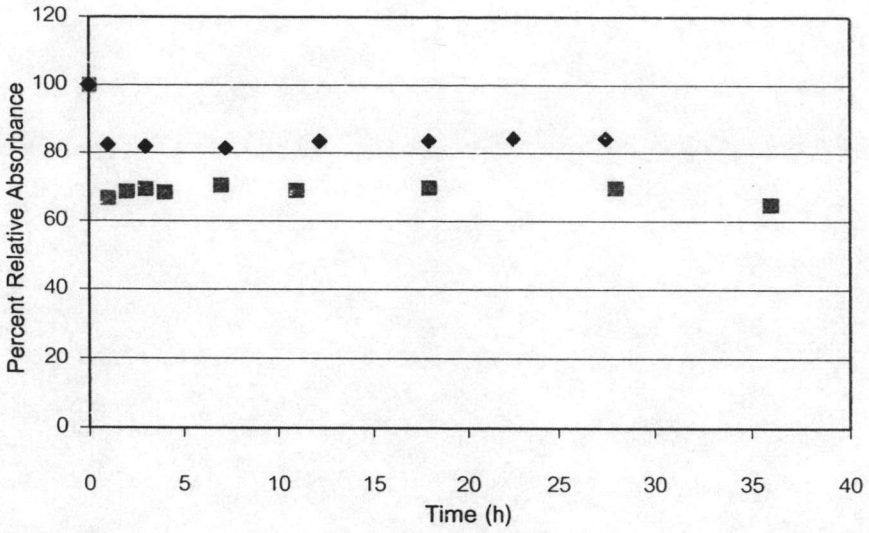
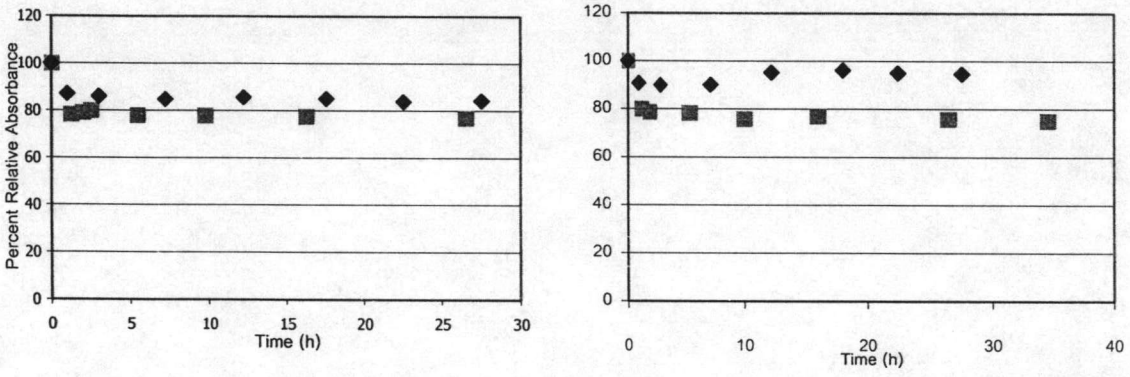


Figure C.1 Photo-equilibrium of OMC (**E1**); ■ in methanol and ◆ in hexanes



a) b)

Figure C.2 Photo-equilibrium of 2-ethylhexyl-2,4,5-trimethoxycinnamate (**E8**); ■ in methanol and ◆ in hexanes; a) absorbed in UVB region and b) absorbed in UVA region

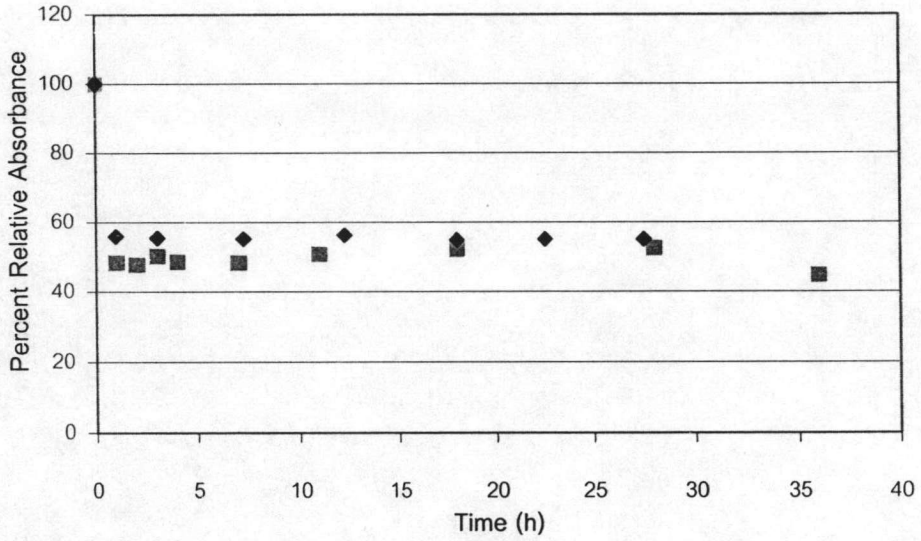
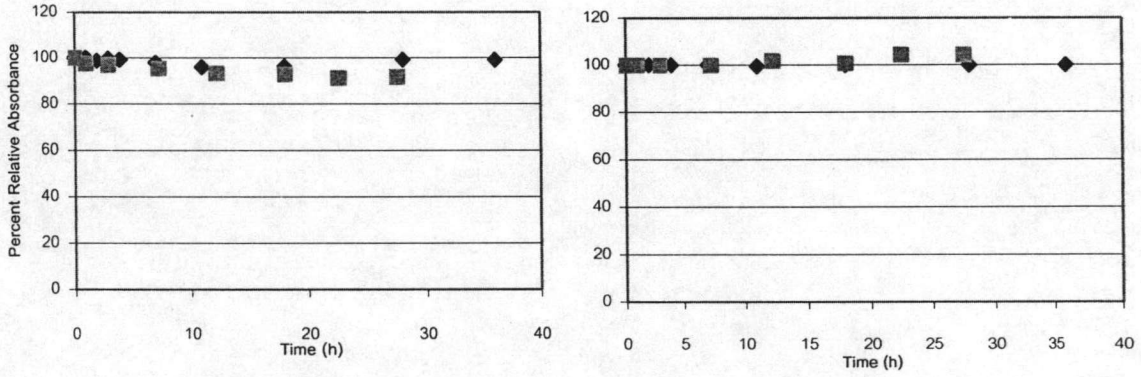
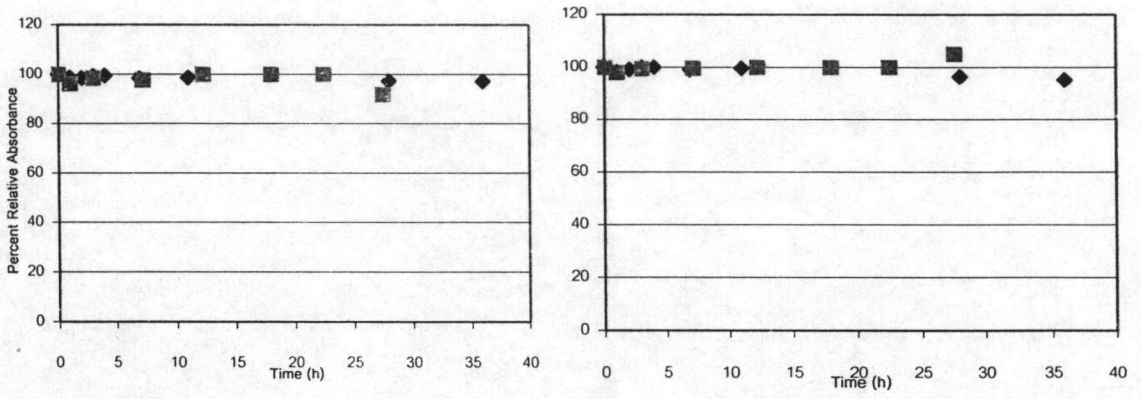


Figure C.3 Photo-equilibrium of 2-ethylhexyl-2,4,6-trimethoxycinnamate (**E10**); ■ in methanol and ◆ in hexanes



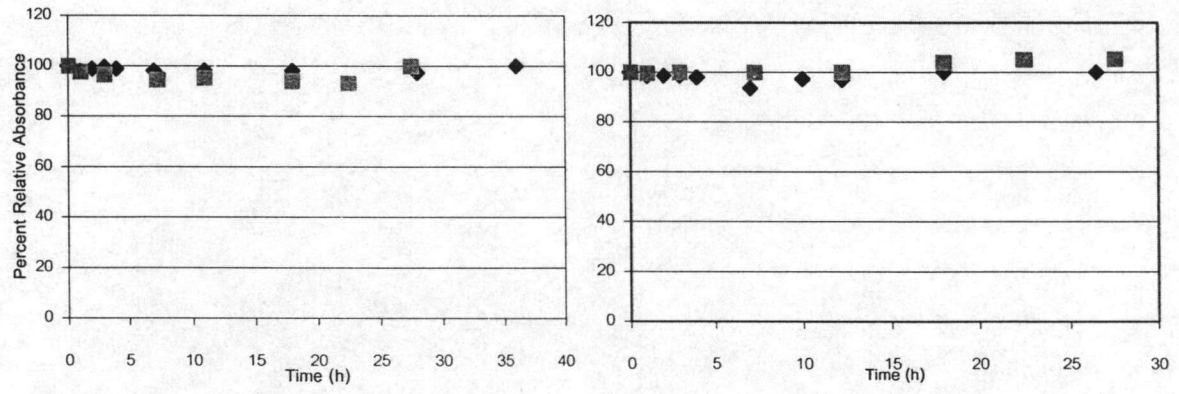
a) b)

Figure C.4 Photo-equilibrium of diethyl-2,4,5-trimethoxybenzalmalonate (**BM8-1**); ■ in methanol and ◆ in hexanes; a) absorbed in UVB region and b) absorbed in UVA region



a) b)

Figure C.5 Photo-equilibrium of di-(2-ethylhexyl)-2,4,5-trimethoxybenzalmalonate (**BM8-2**); ■ in methanol and ◆ in hexanes; a) in UVB region and b) in UVA region



a) b)

Figure C.6 Photo-equilibrium of dihexyl-2,4,5-trimethoxybenzalmalonate (**BM8-3**); ■ in methanol and ◆ in hexanes; a) in UVB region and b) in UVA region

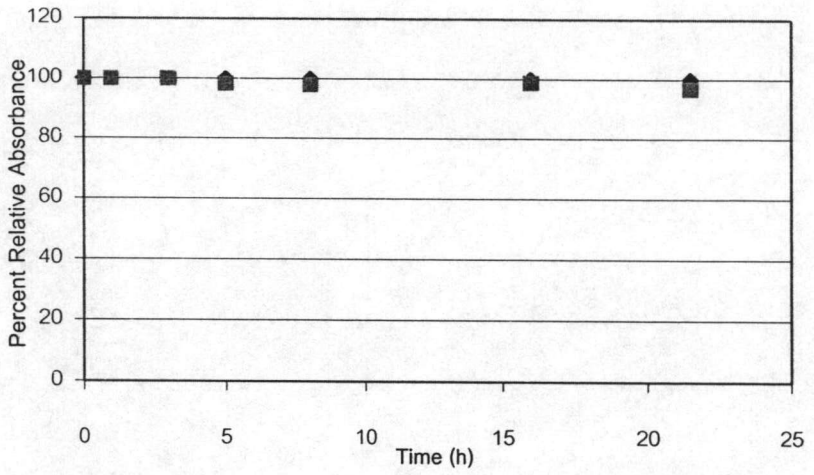


Figure C.7 Photo-equilibrium of diethyl-4-trimethoxybenzalmalonate (**BM1-1**); ■ in methanol and ◆ in hexanes

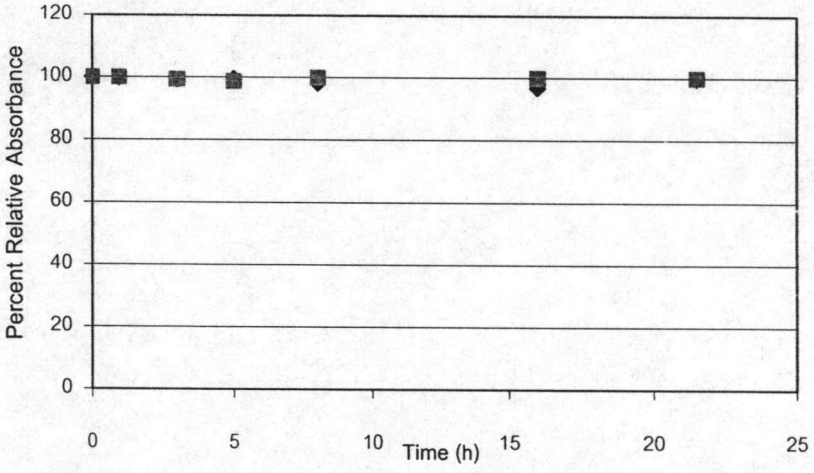


Figure C.8 Photo-equilibrium of di-(2-ethylhexyl)-4-trimethoxybenzalmalonate (**BM1-2**); ■ in methanol and ◆ in hexanes

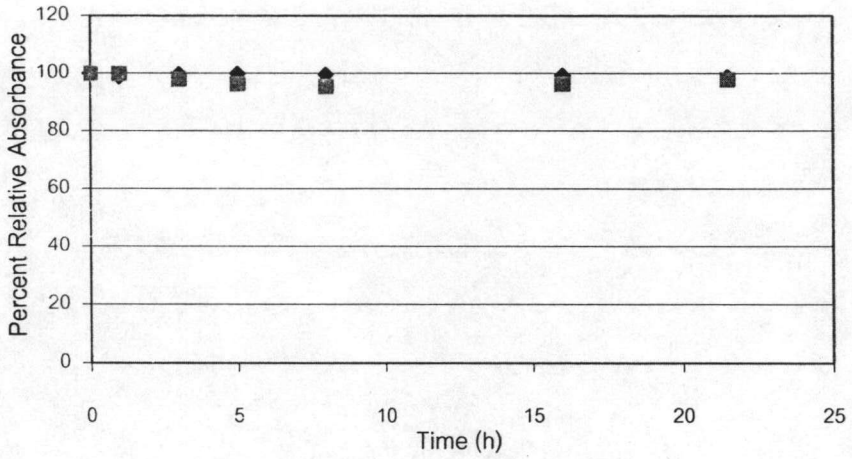


Figure C.9 Photo-equilibrium of dihexyl-4-trimethoxybenzalmalonate (**BM1-3**); ■ in methanol and ◆ in hexanes

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