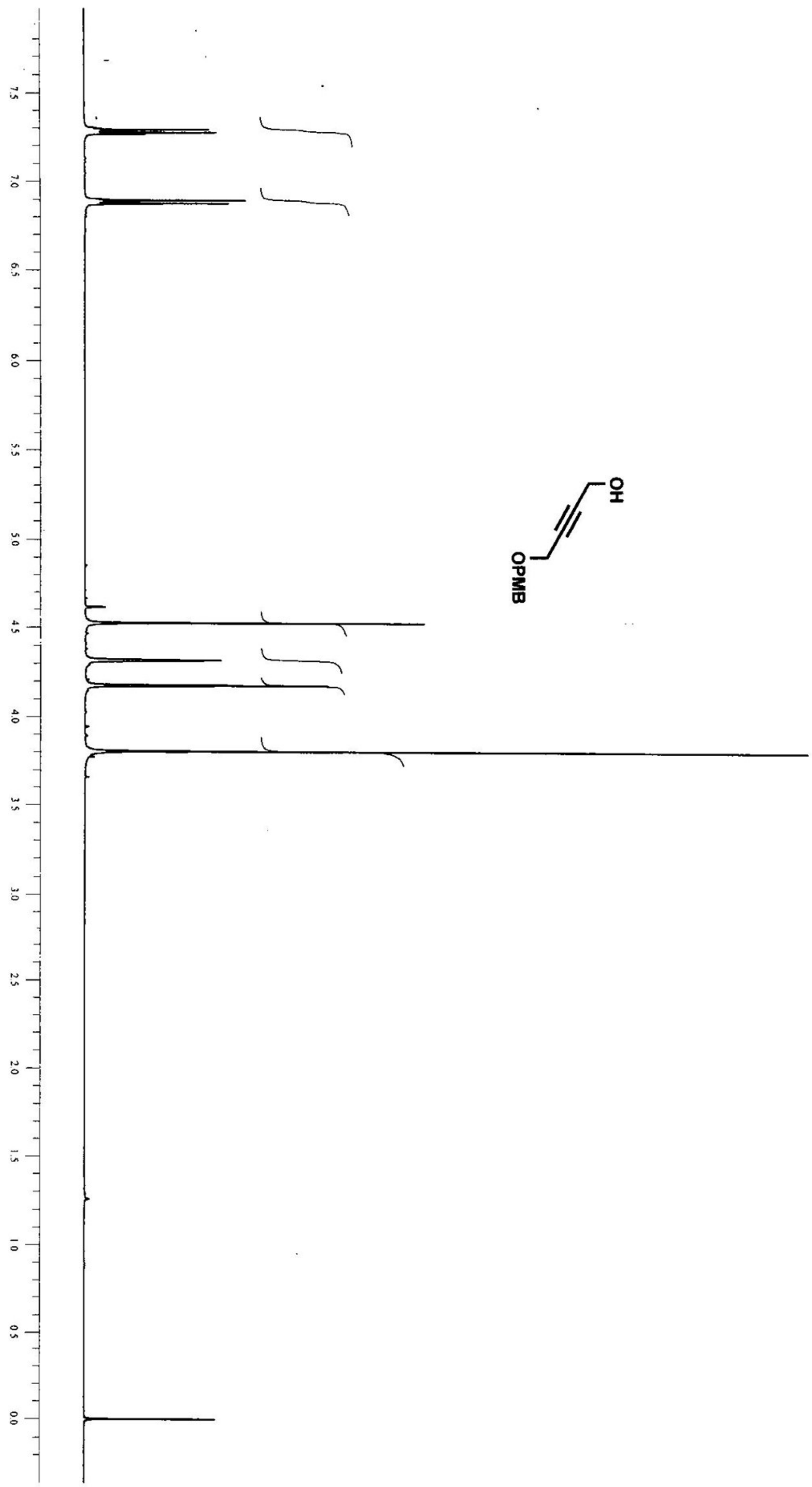
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

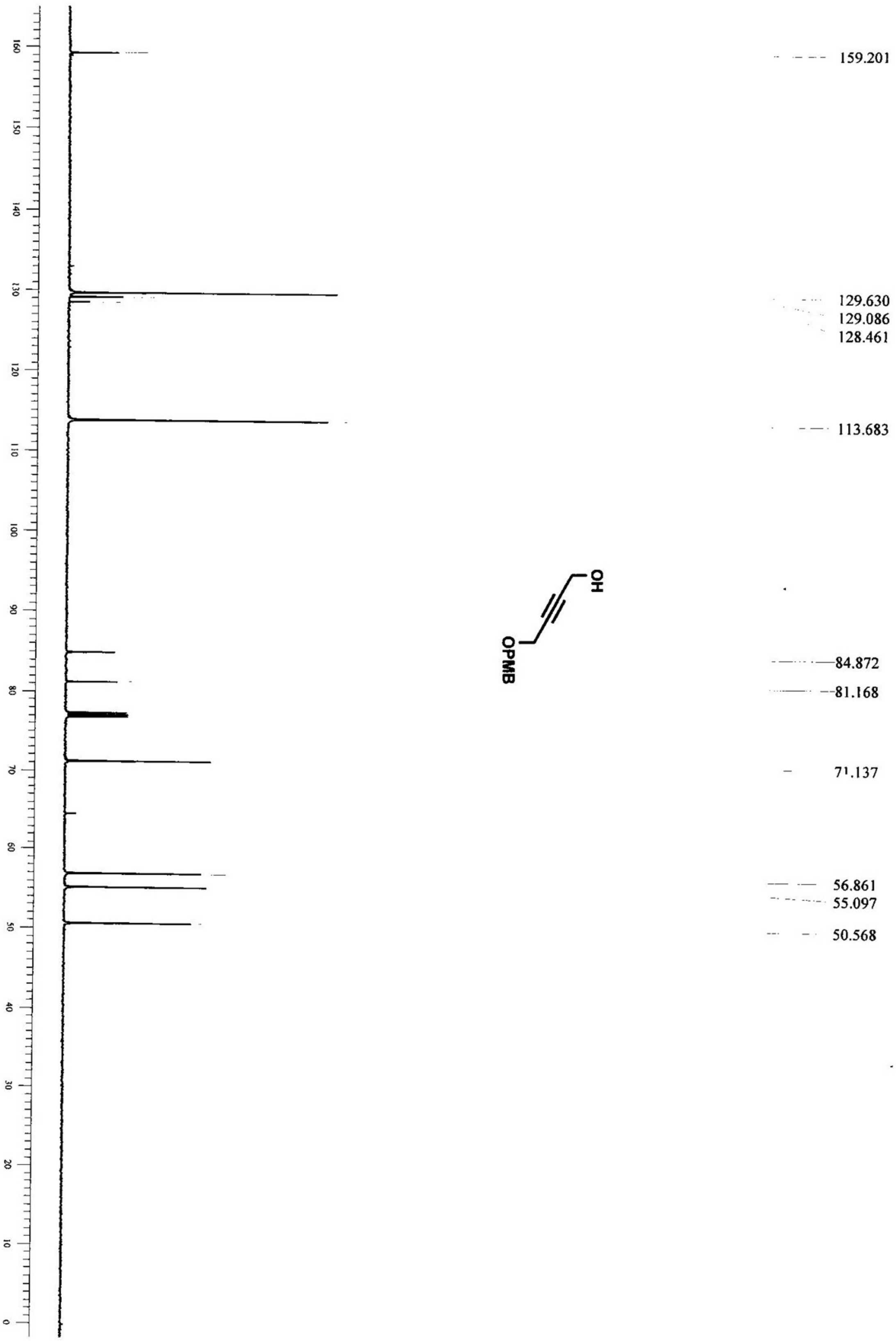
Supporting Information for

Gold-Catalyzed Hosomi-Sakurai Type Reaction for the Total Synthesis of Herboxidiene

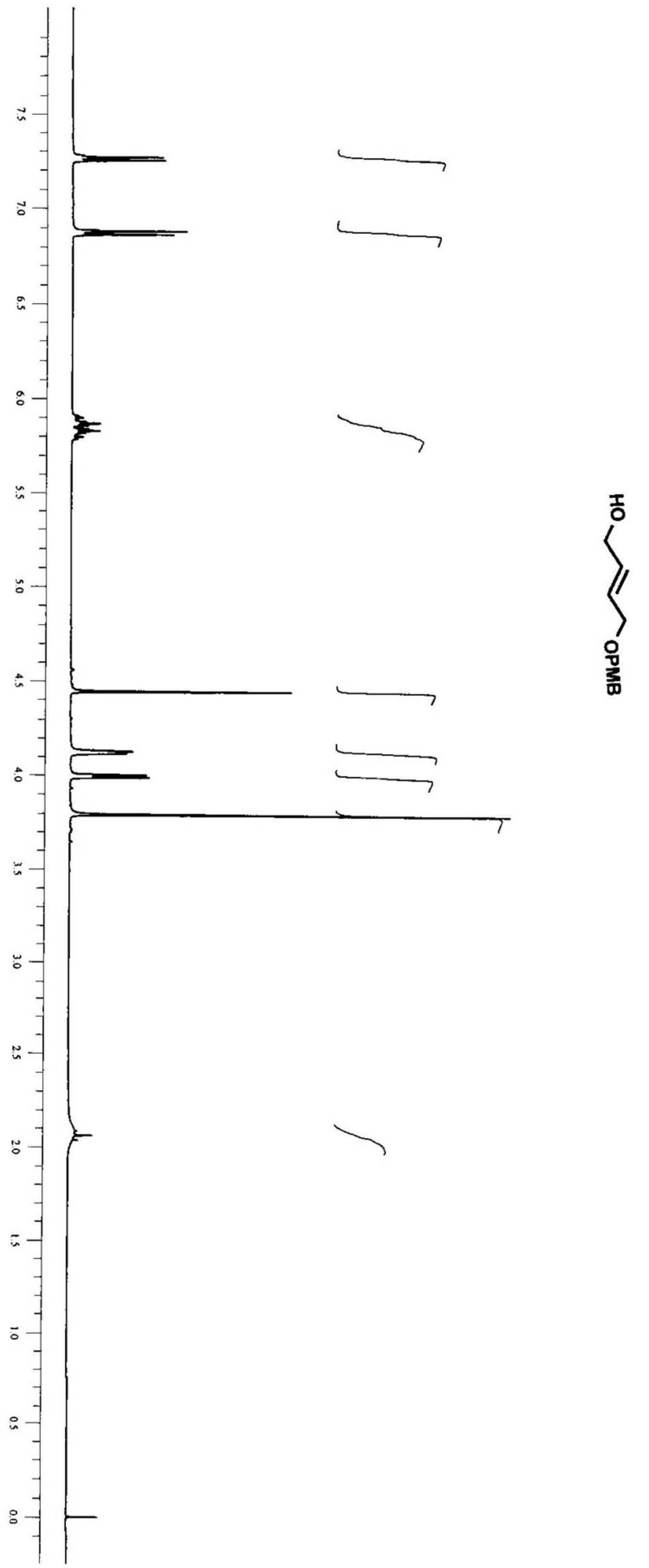
Barla Thirupathi and Debendra K. Mohapatra*



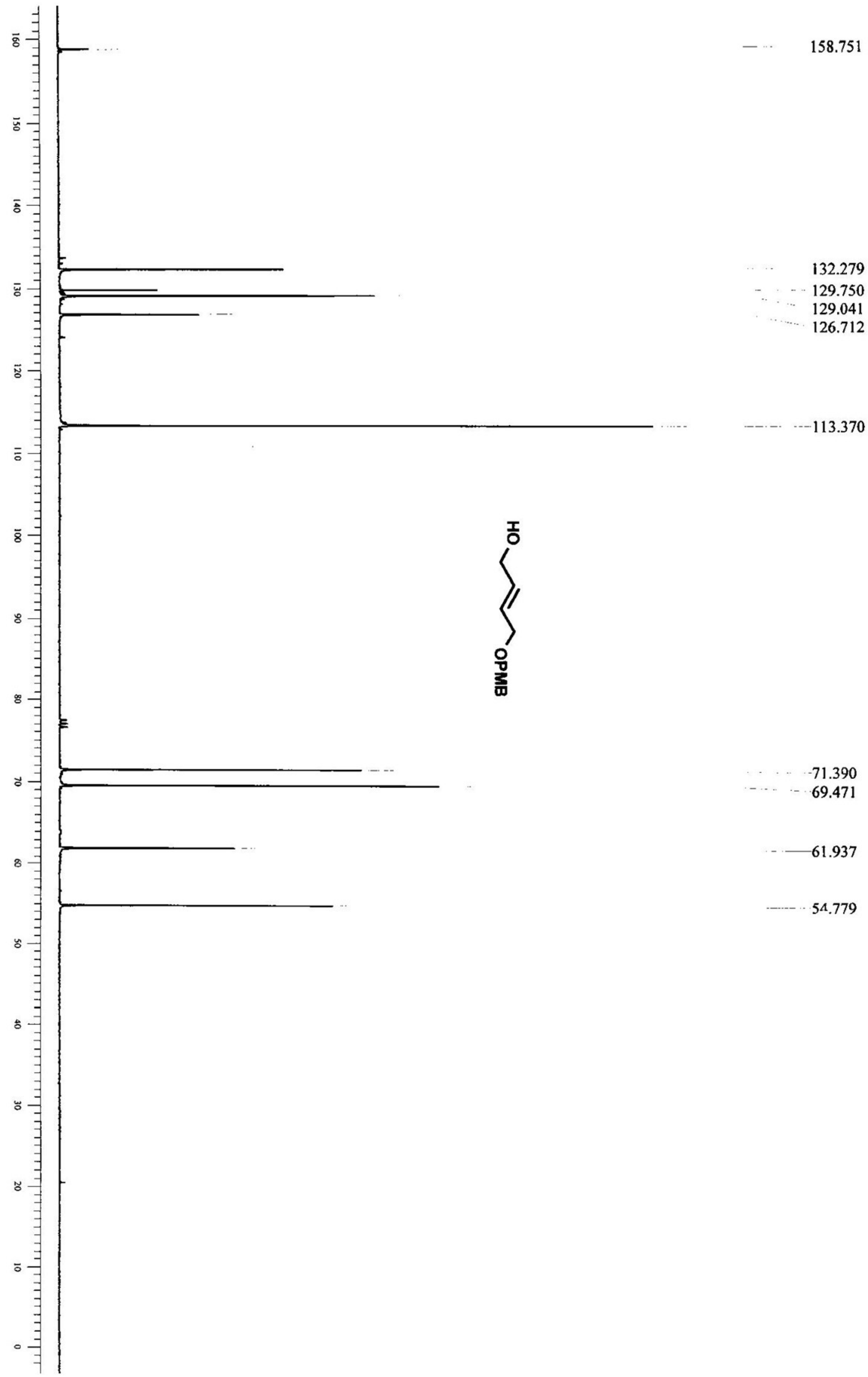
^{1}H NMR of 9 ($CDCl_3$, 300 MHz)



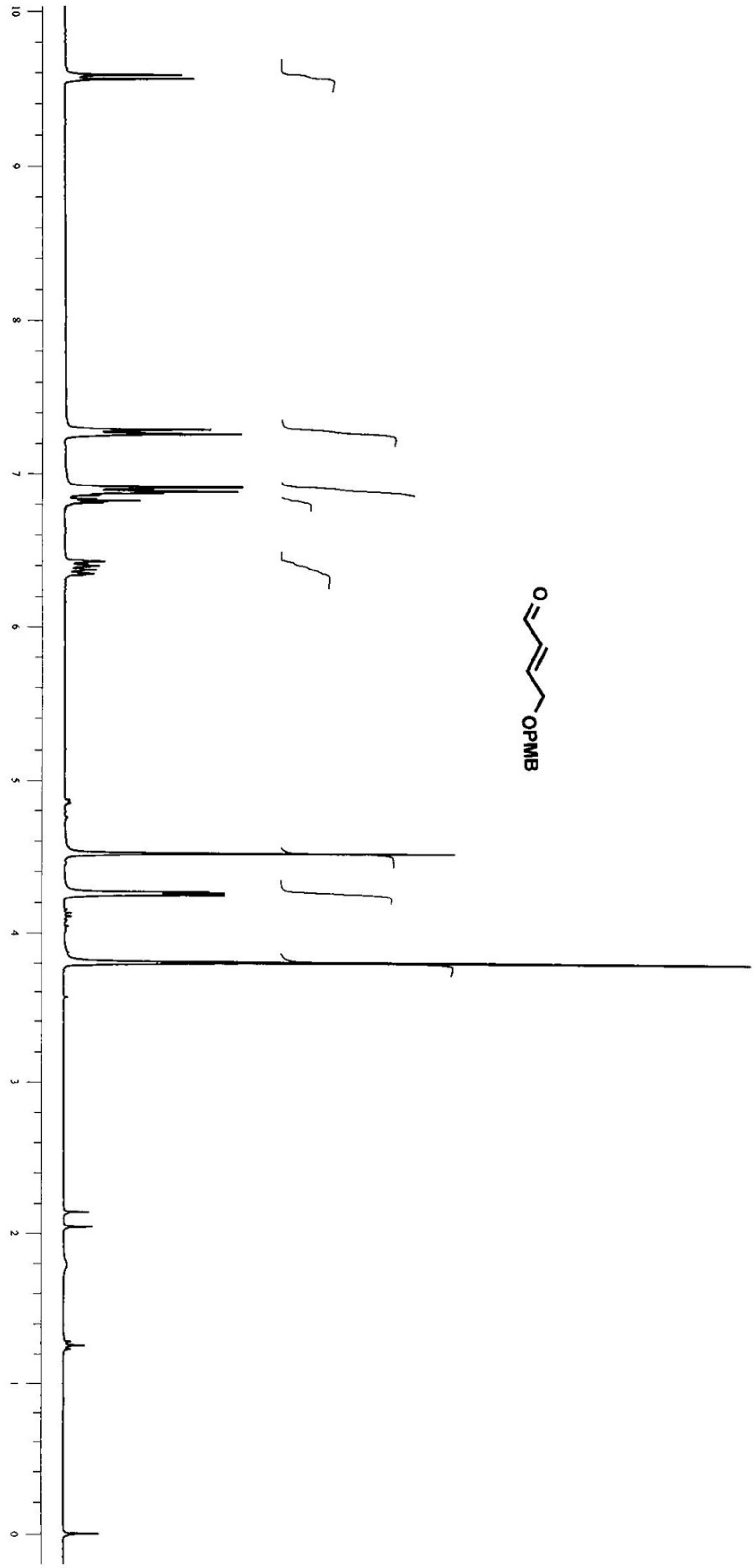
^{13}C NMR of 9 ($CDCl_3$, 75 MHz)



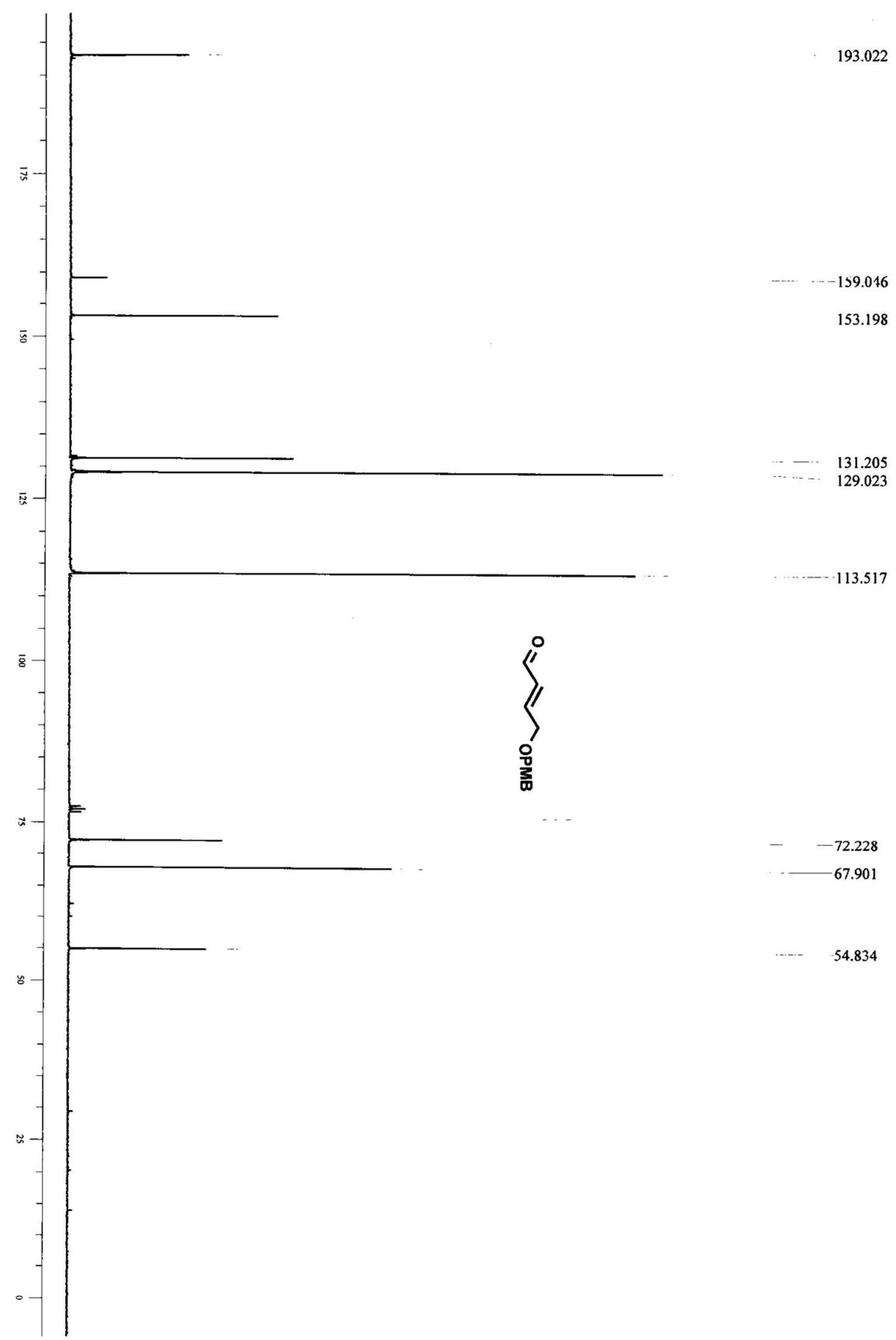
^{1}H NMR of 10 ($CDCl_3$, 300 MHz)



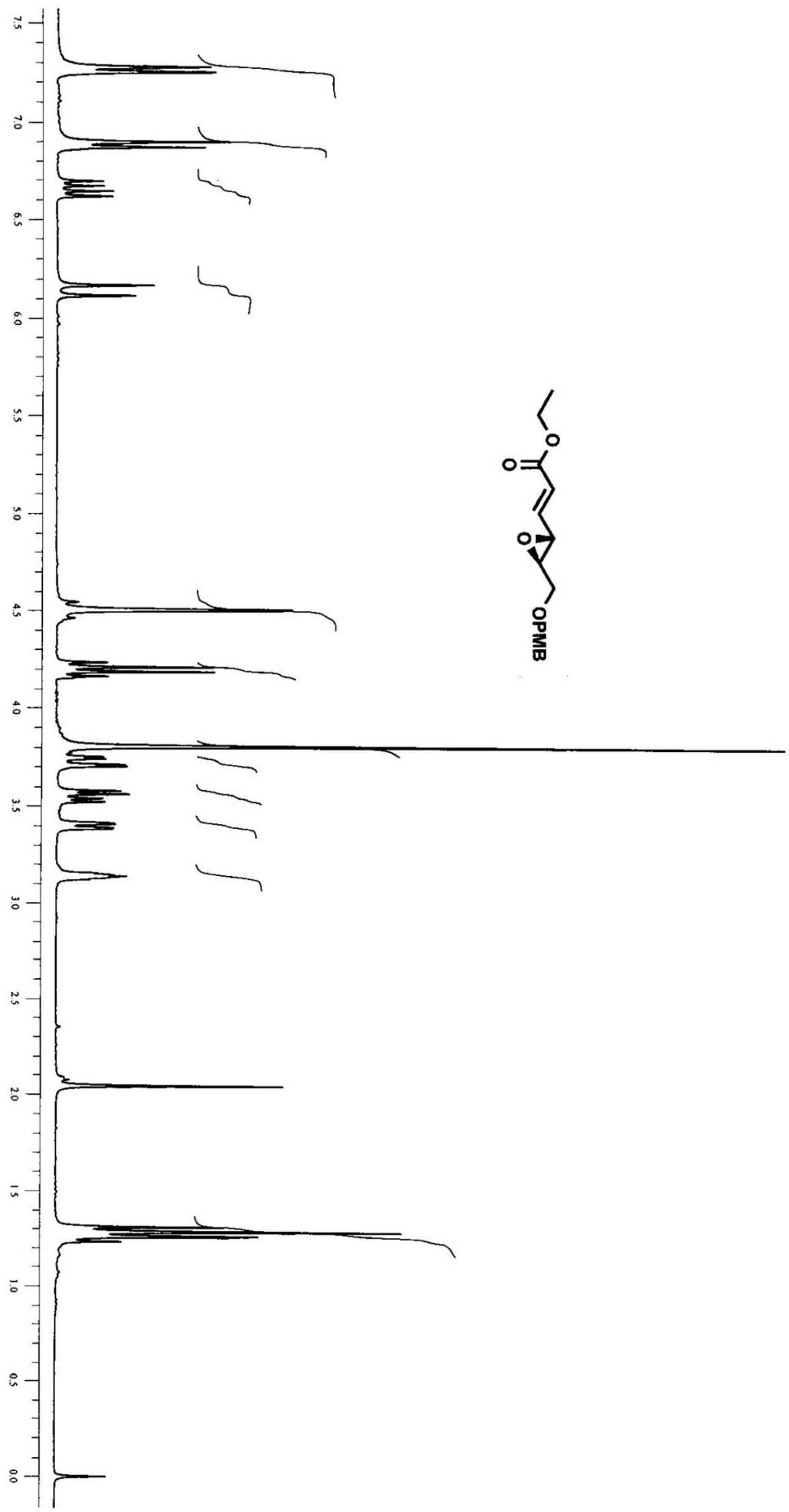
^{13}C NMR of 10 ($CDCl_3$, 75 MHz)



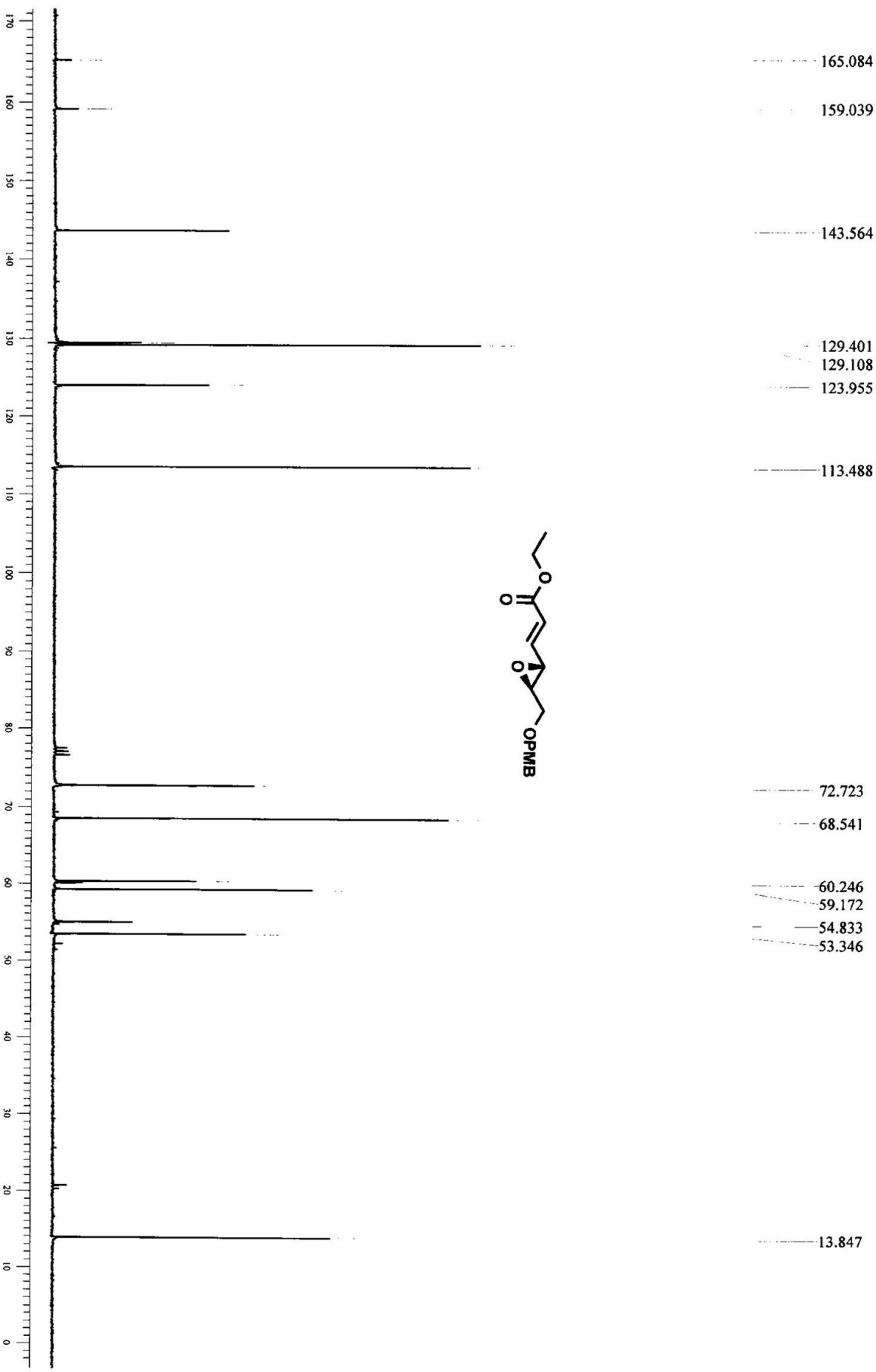
^{1}H NMR of 11 ($CDCl_3$, 300 MHz)



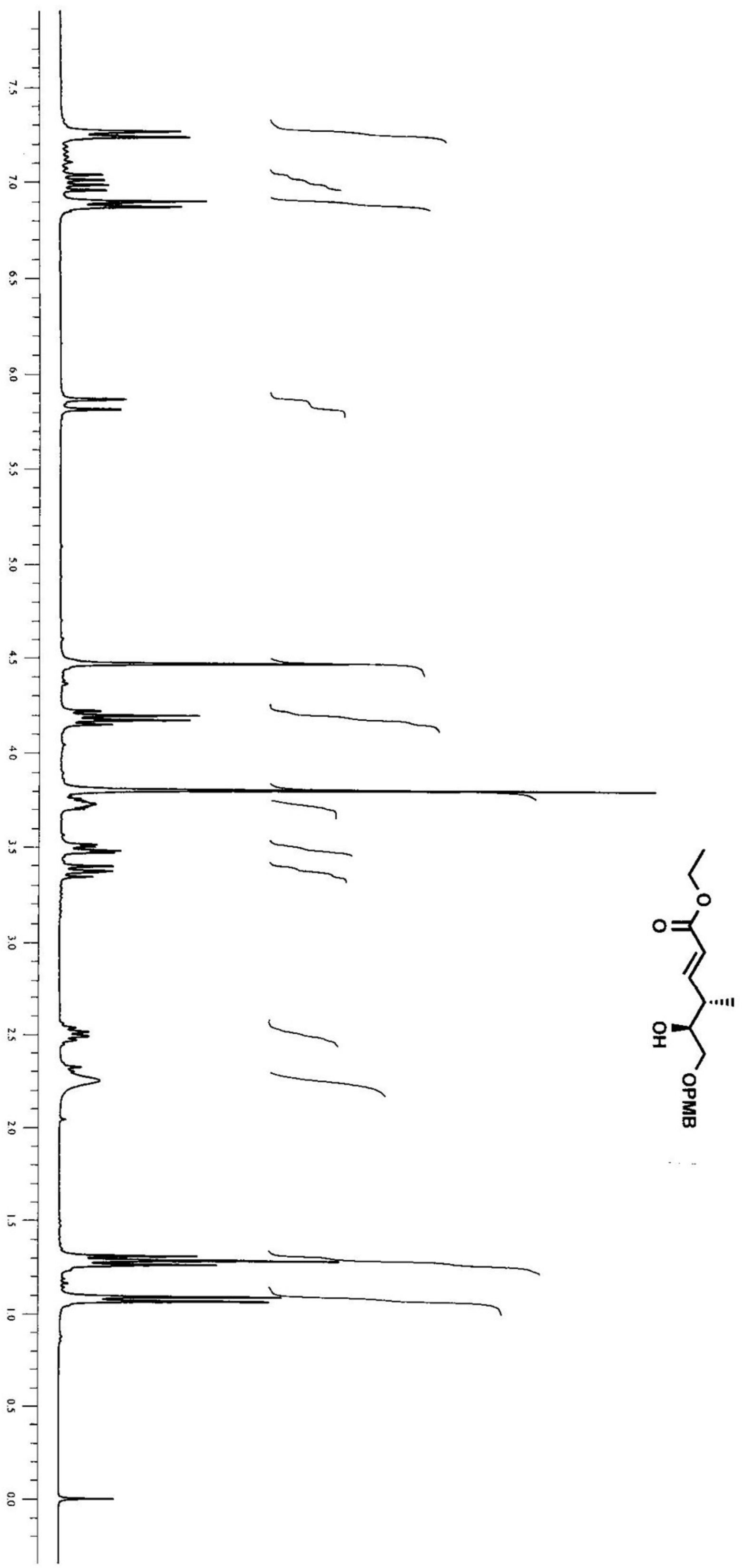
^{13}C NMR of 11 ($CDCl_3$, 75 MHz)



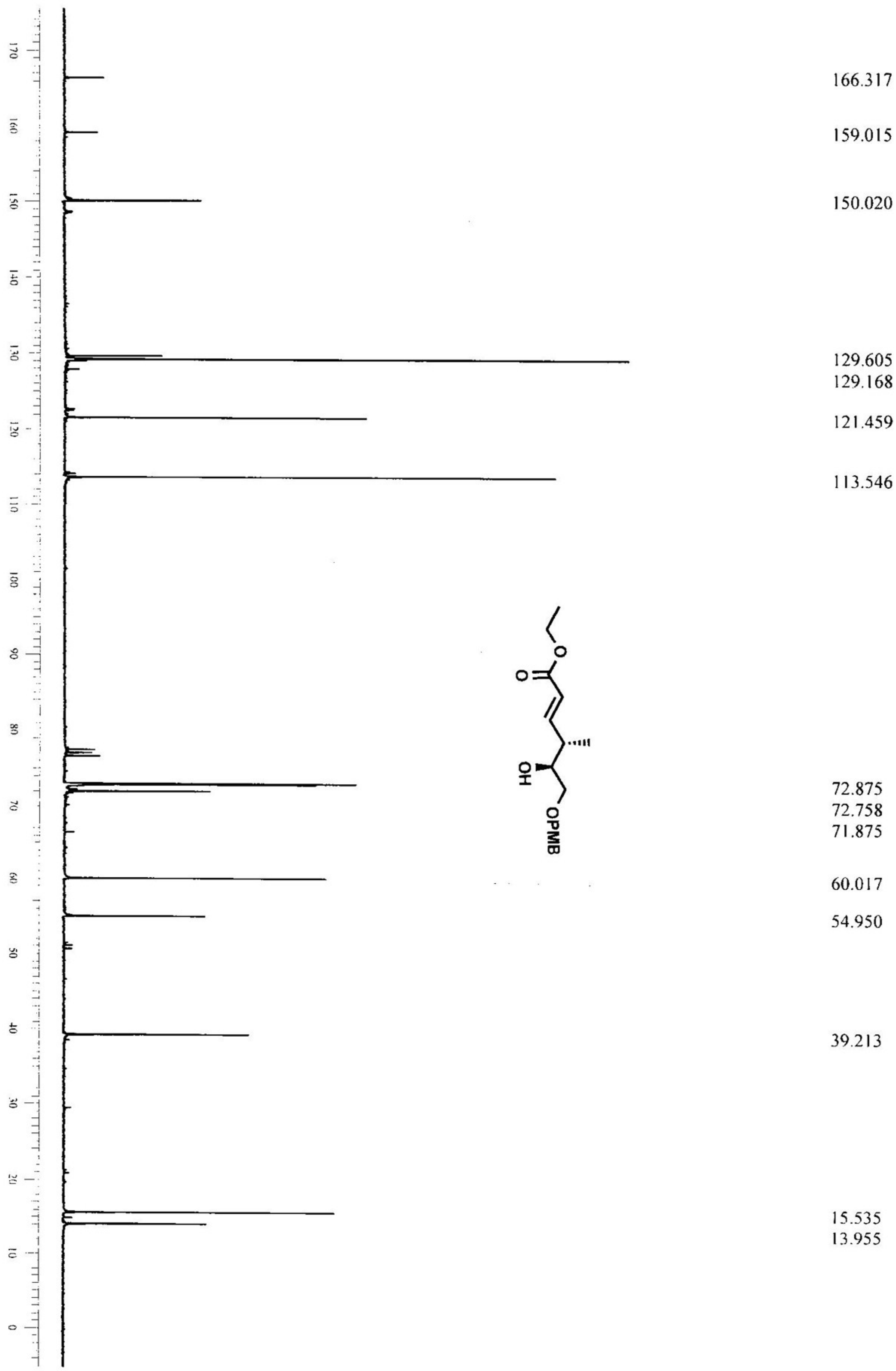
^{1}H NMR of 12 ($CDCl_3$, 300 MHz)



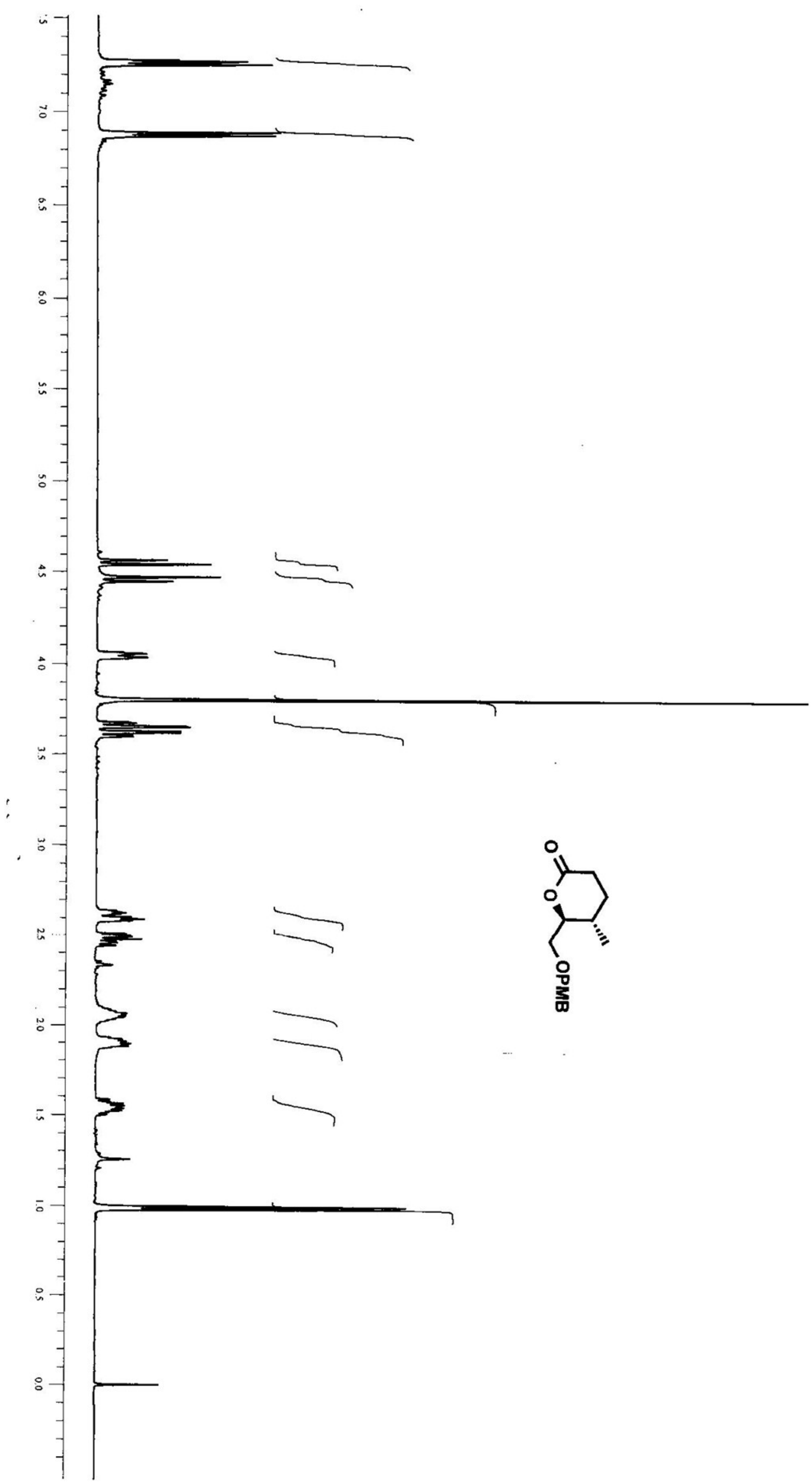
^{13}C NMR of 12 ($CDCl_3$, 75 MHz)



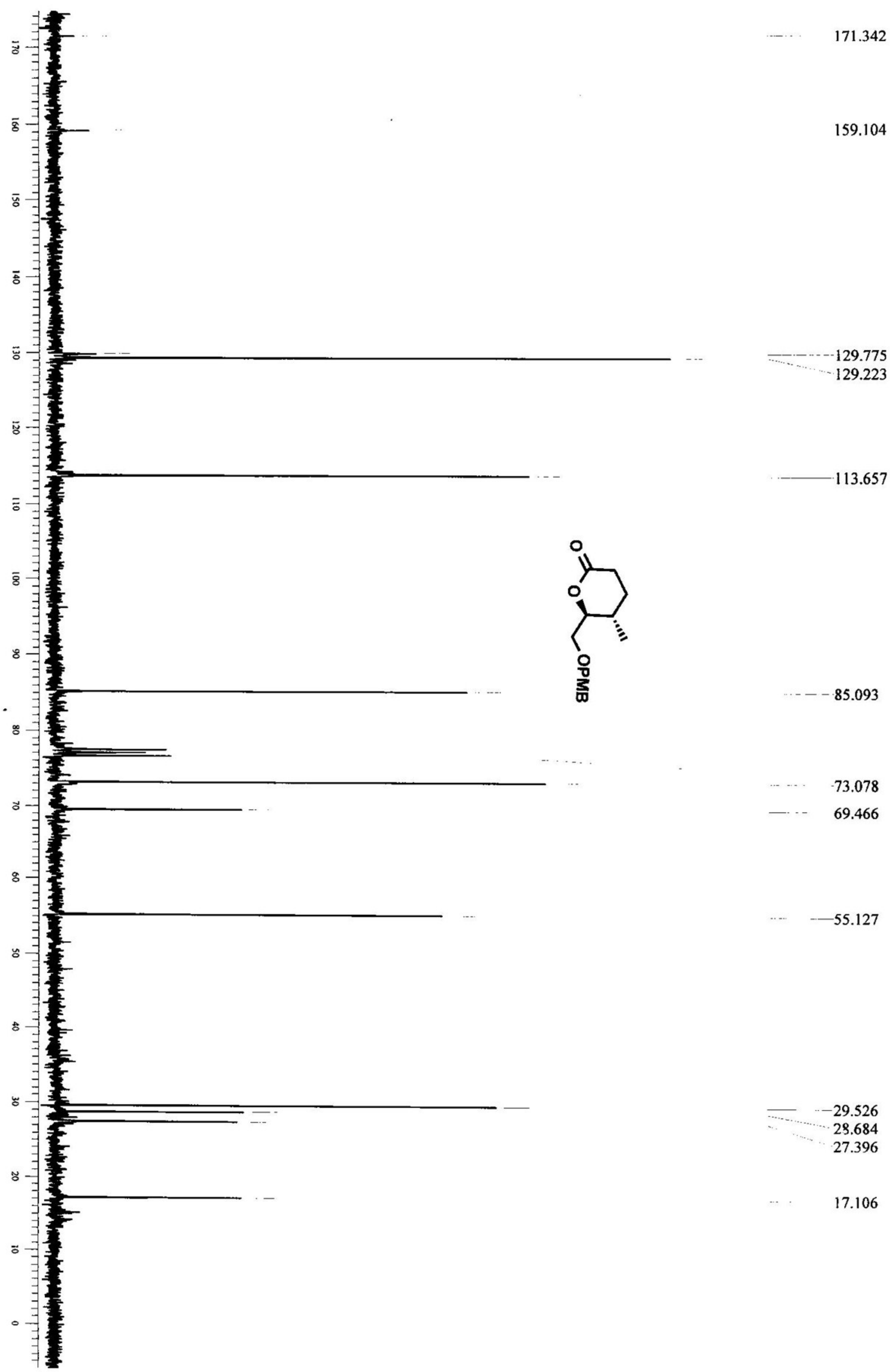
^{1}H NMR of 13 ($CDCl_3$, 300 MHz)



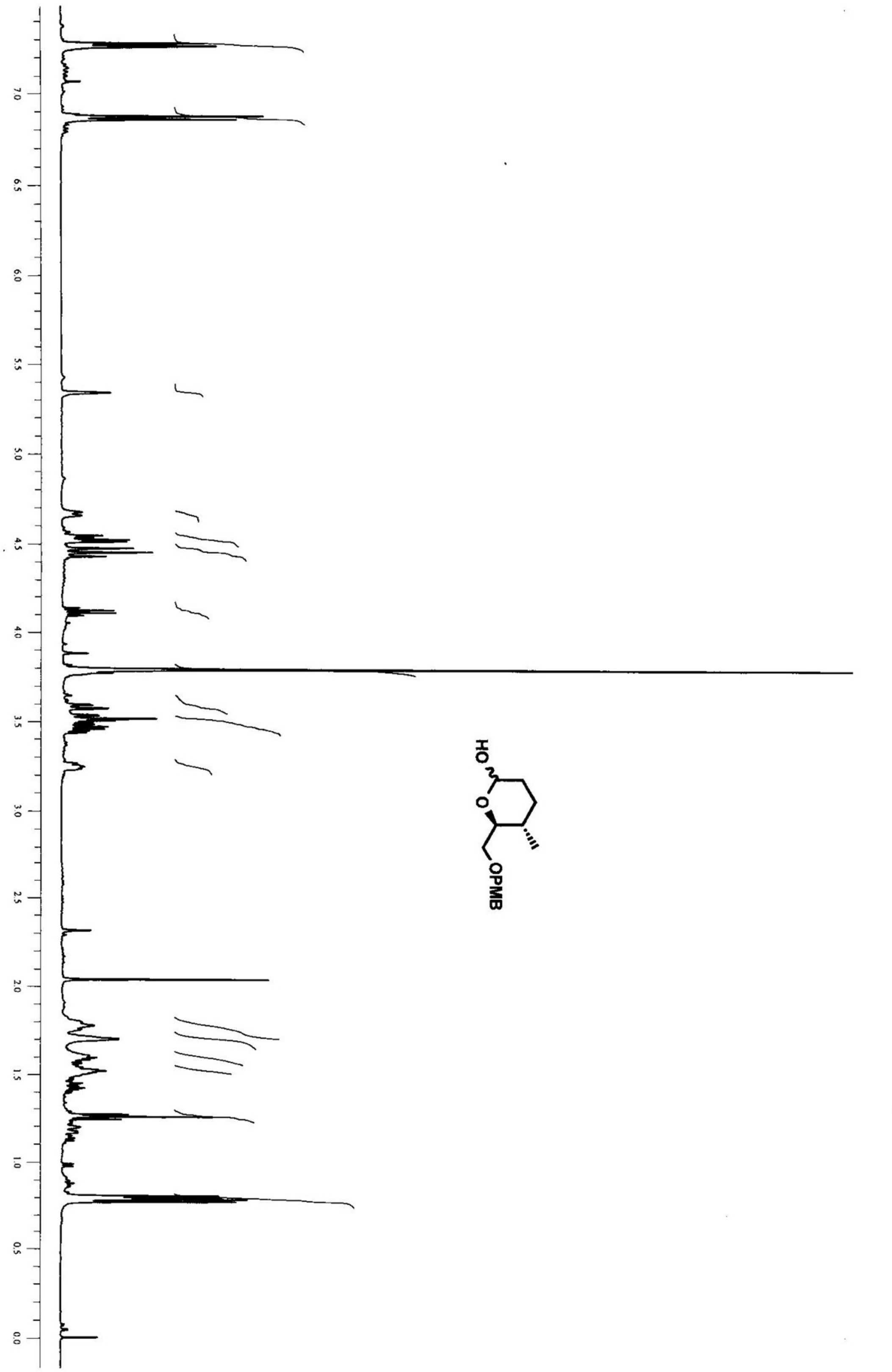
^{13}C NMR of 13 ($CDCl_3$, 75 MHz)



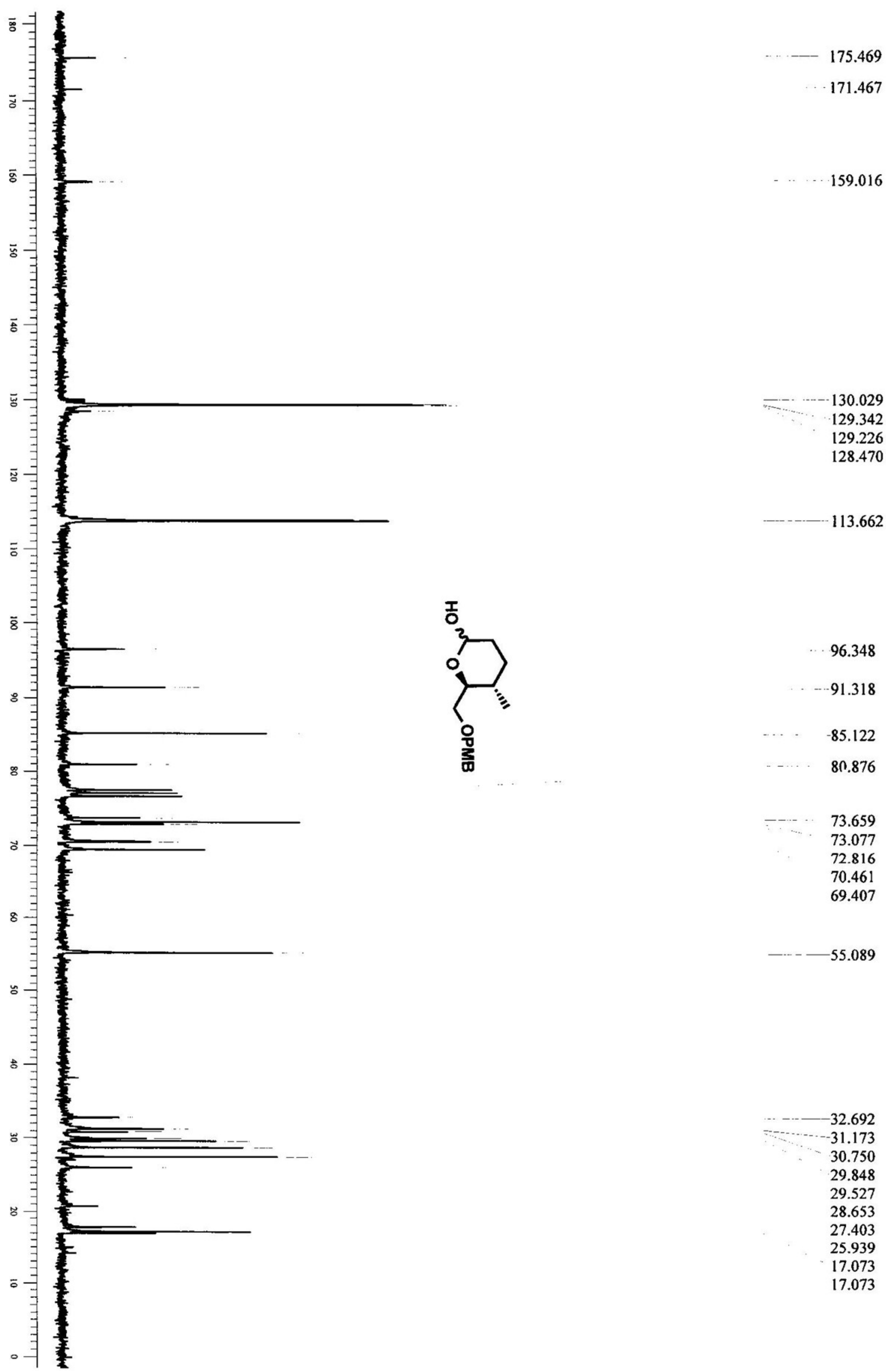
[1]H NMR of 14 ($CDCl_3$, 300 MHz)



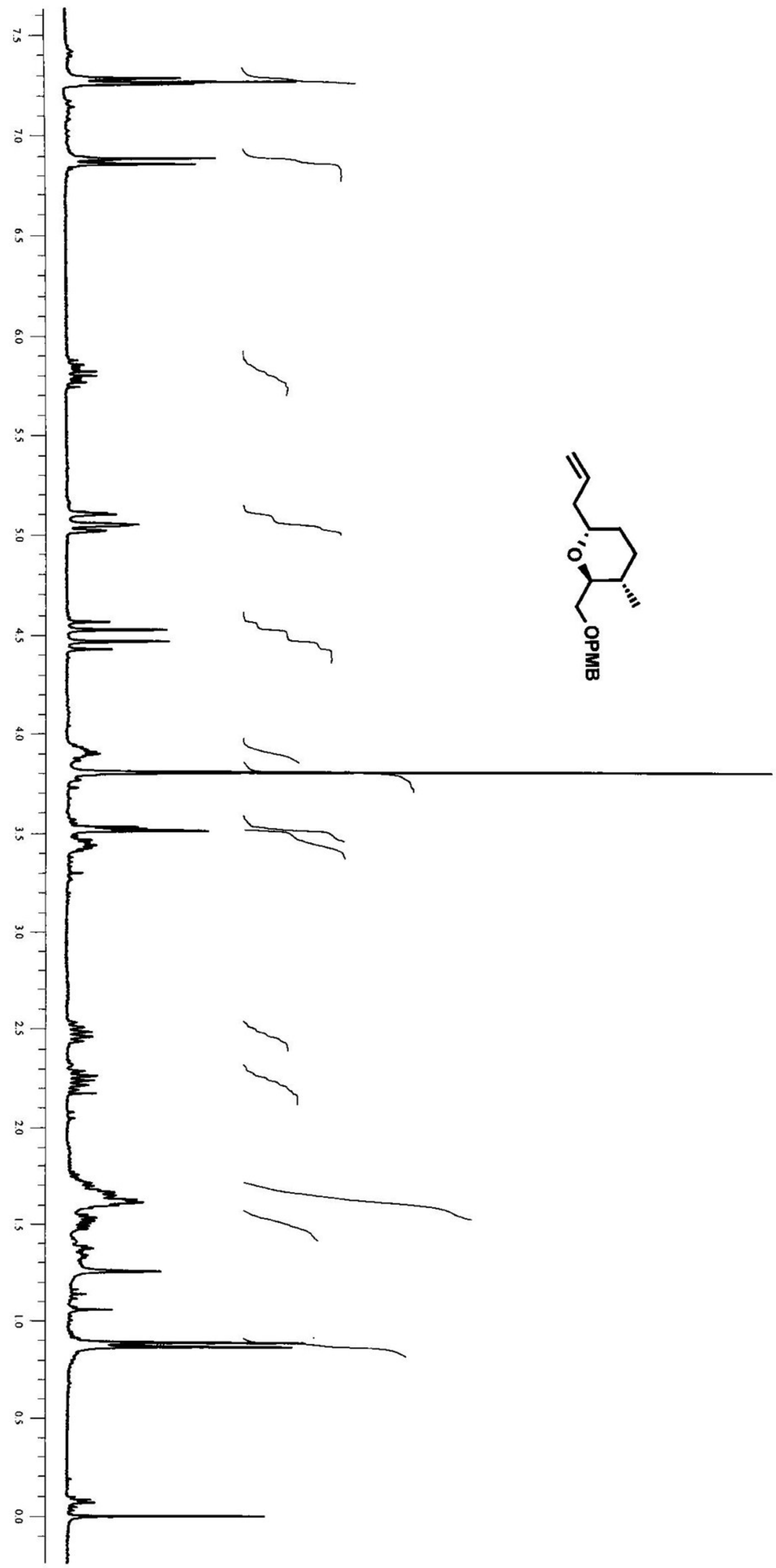
^{13}C NMR of 14 ($CDCl_3$, 75 MHz)



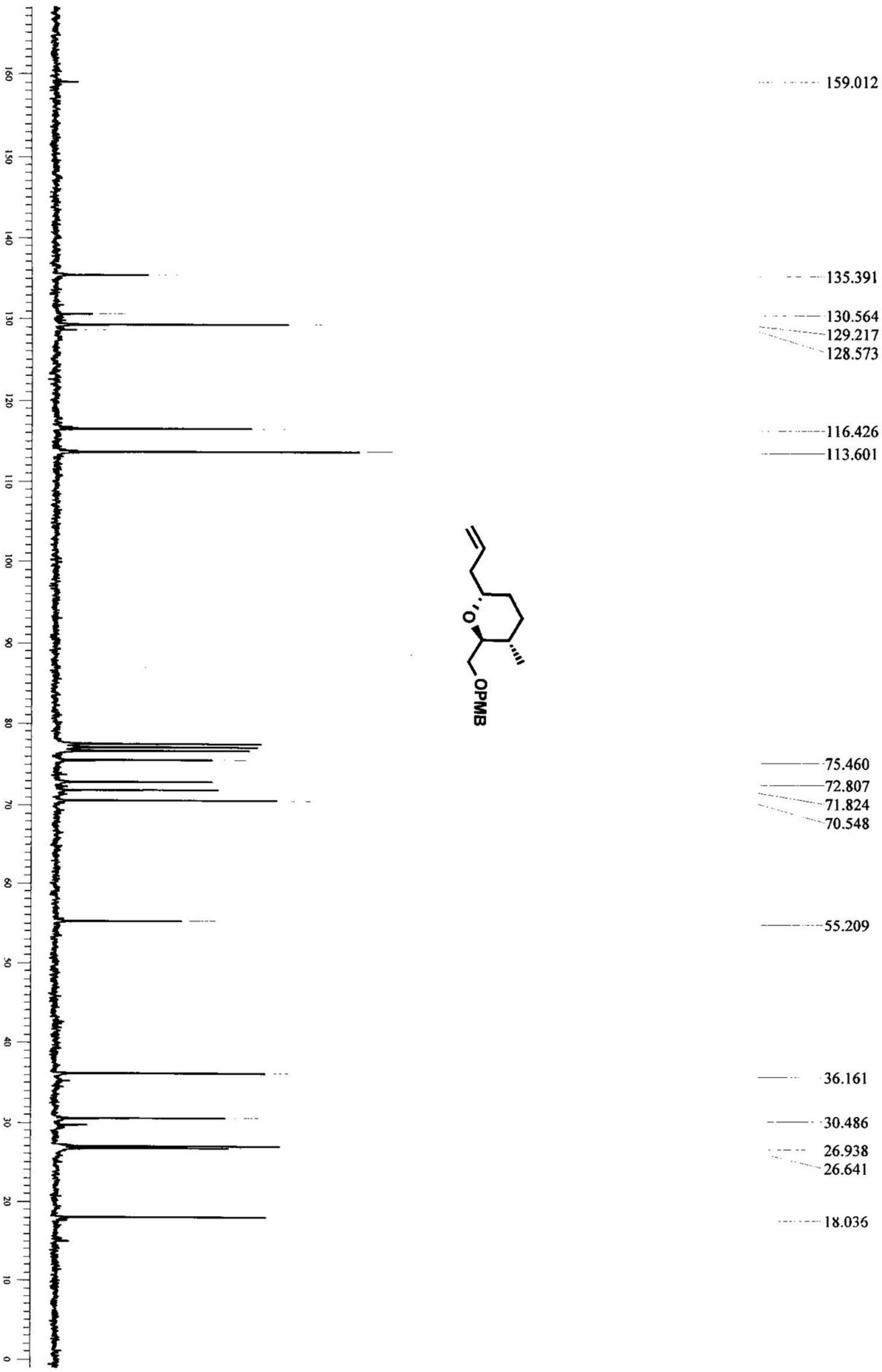
^{1}H NMR of 5 ($CDCl_3$, 300 MHz)



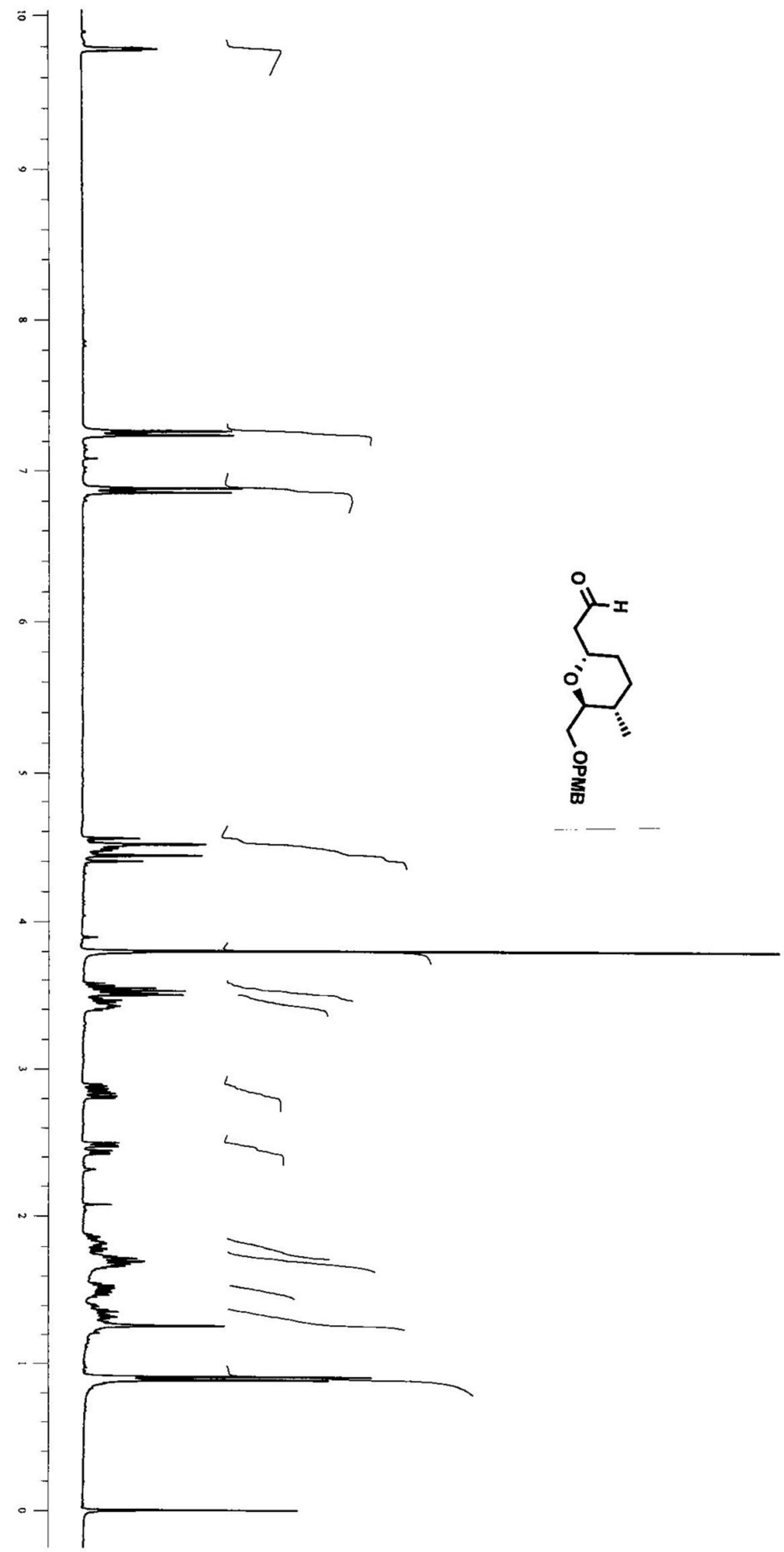
^{13}C NMR of 5 (CDCl$_3$, 125 MHz)



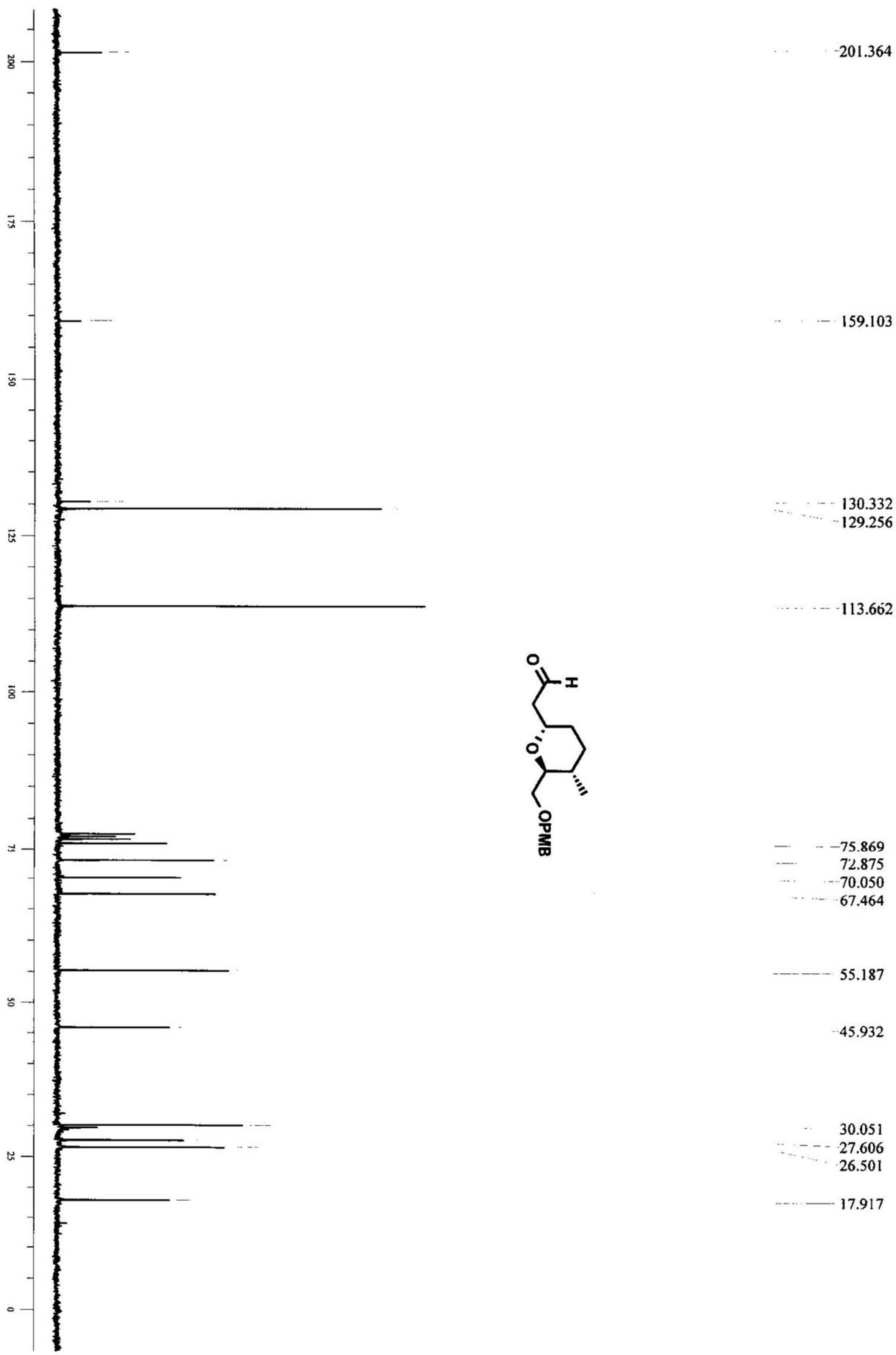
^{1}H NMR of 15 ($CDCl_3$, 300 MHz)



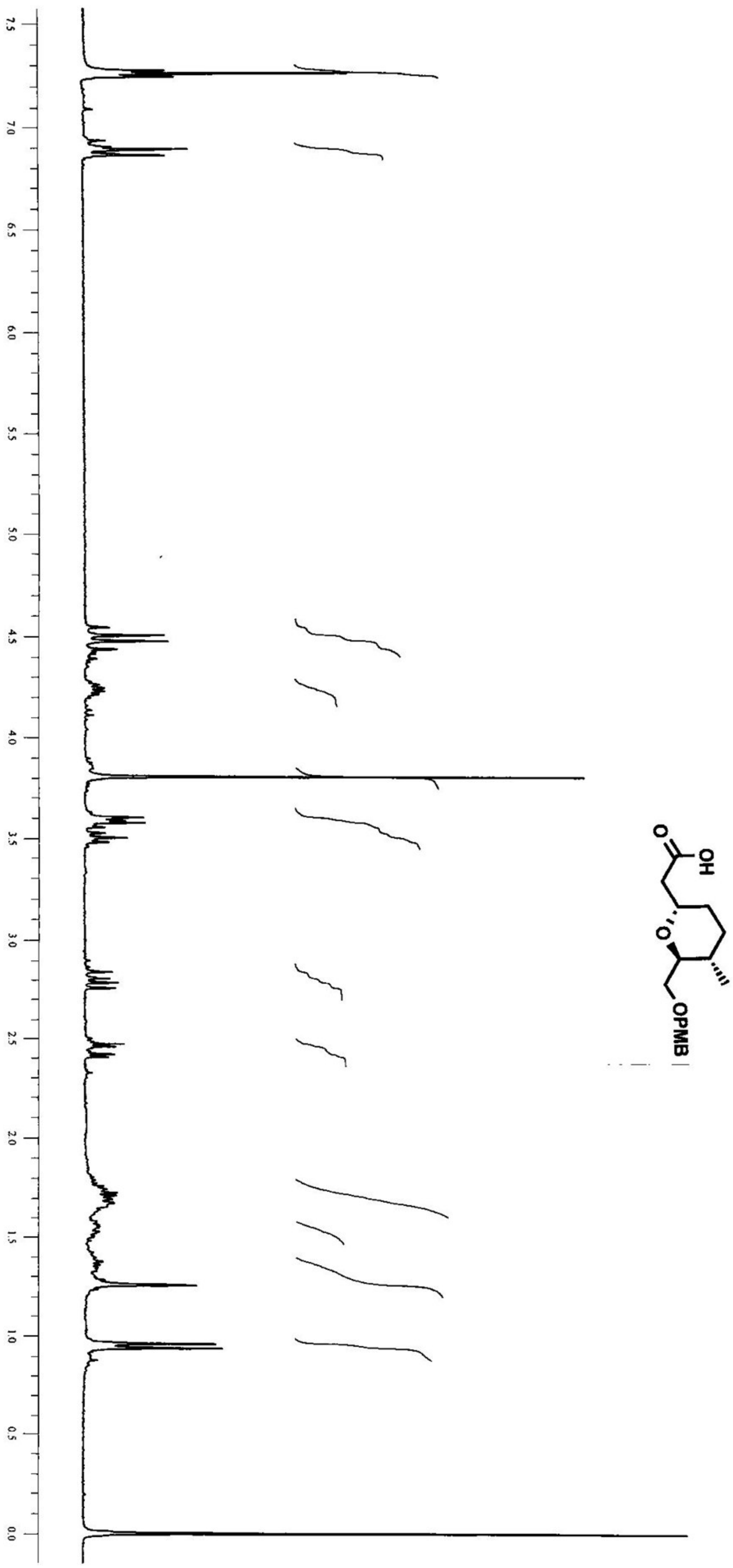
^{13}C NMR of 15 ($CDCl_3$, 75 MHz)



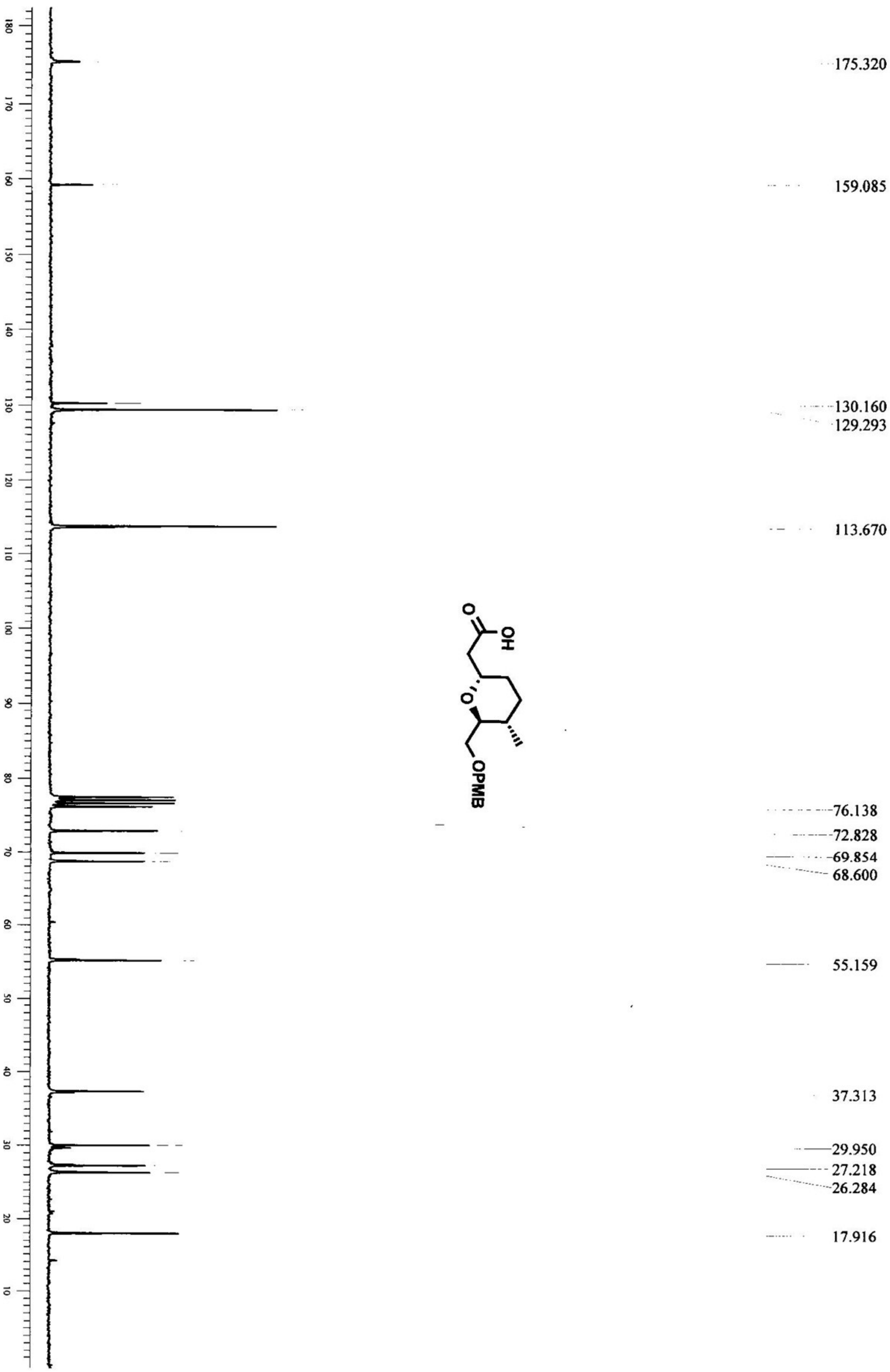
^{1}H NMR of Aldehyde ($CDCl_3$, 300 MHz)



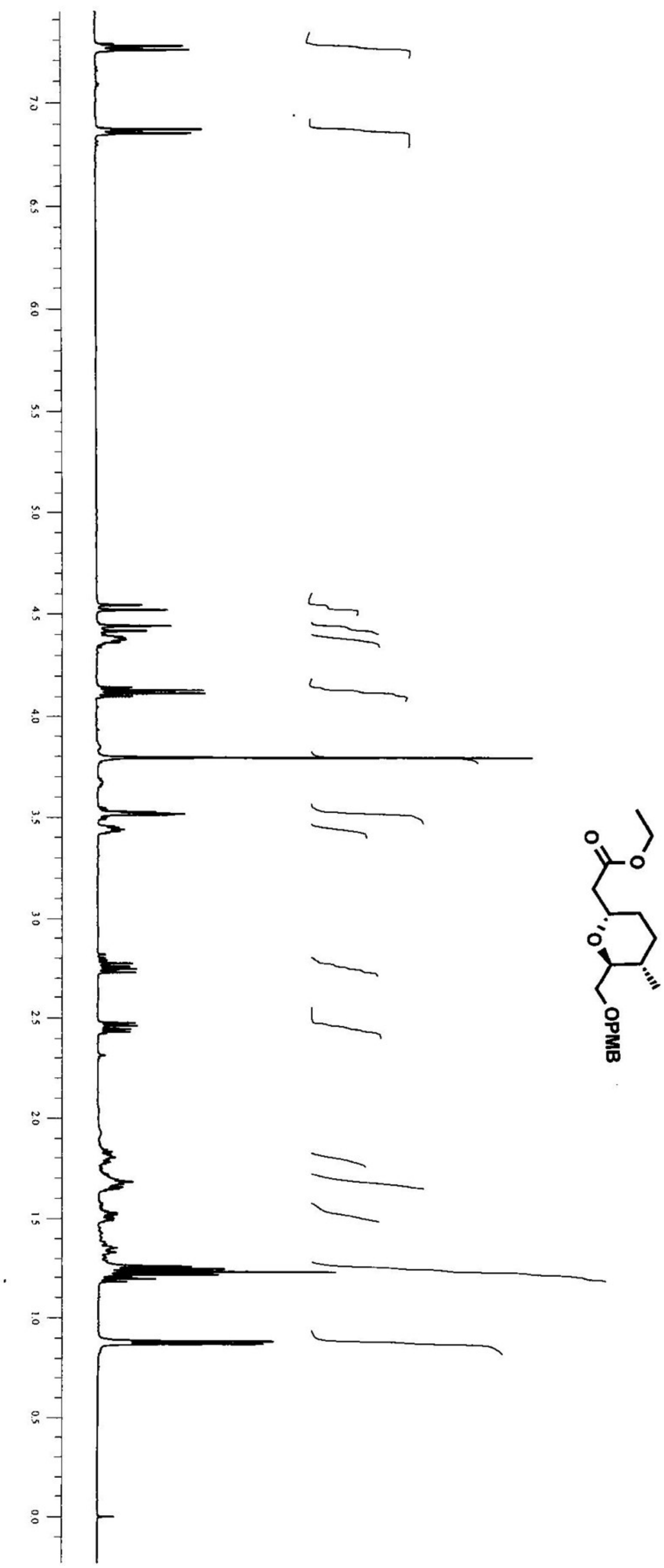
^{13}C NMR of Aldehyde ($CDCl_3$, 75 MHz)



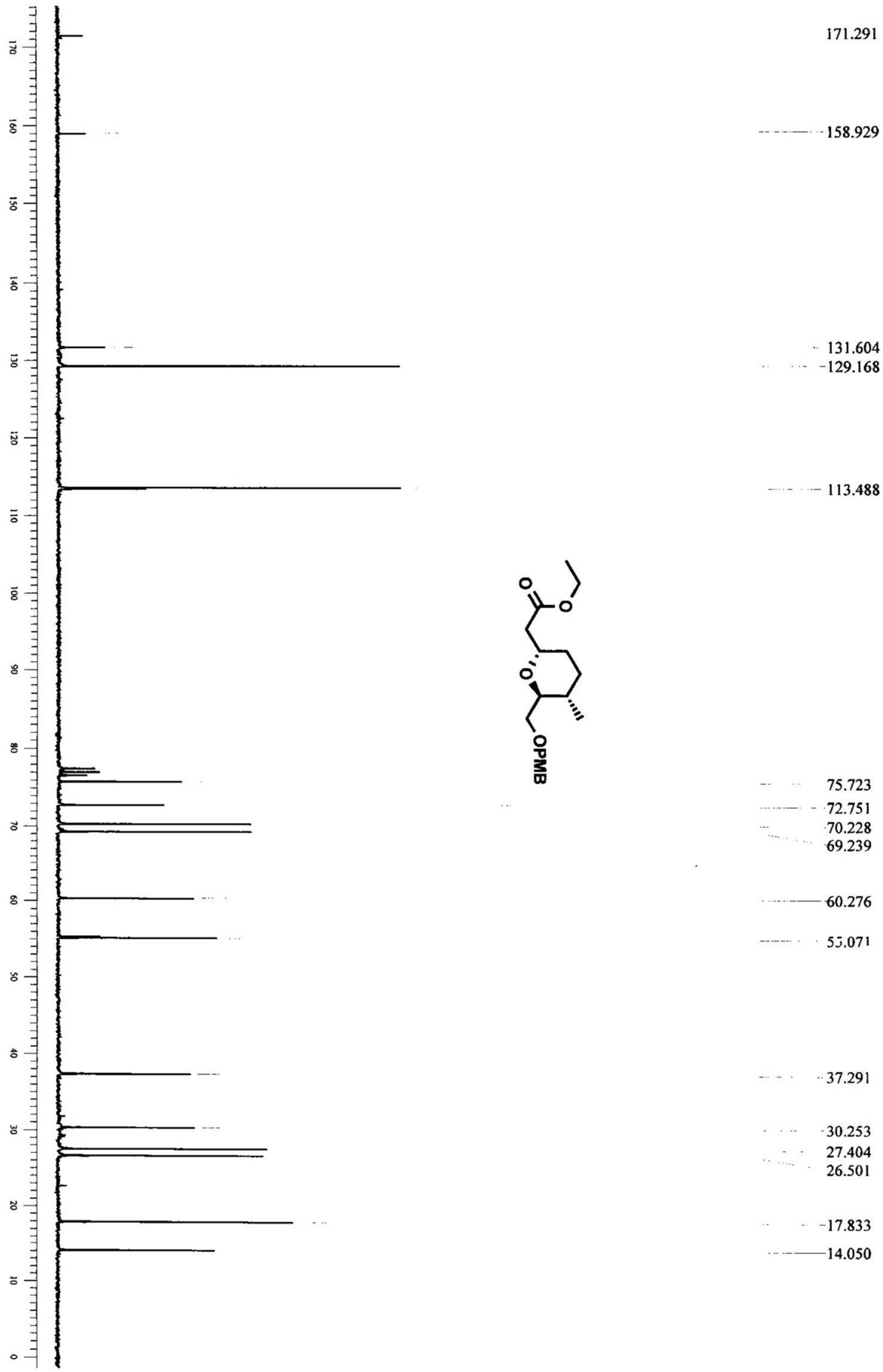
^{1}H NMR of 16 ($CDCl_3$, 300 MHz)



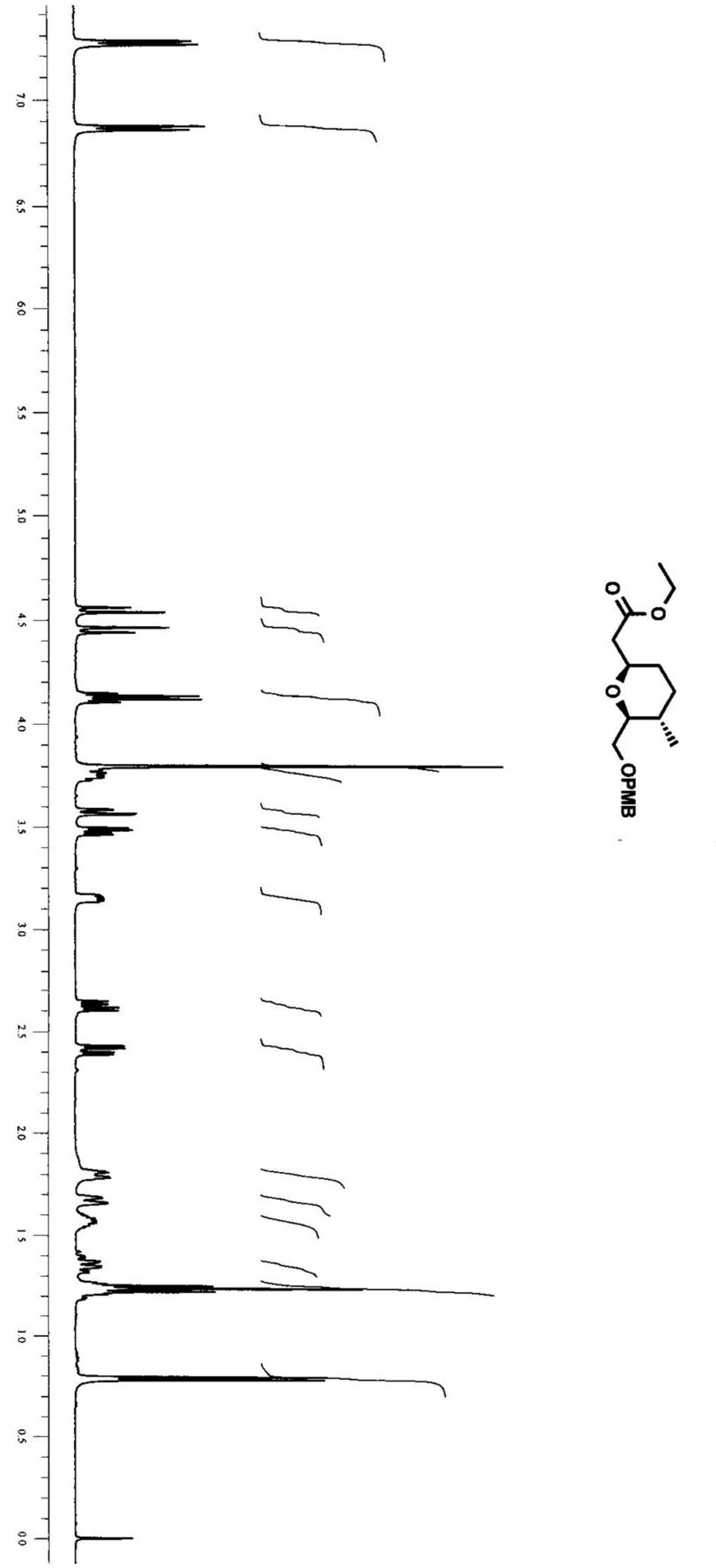
^{13}C NMR of 16 ($CDCl_3$, 125 MHz)



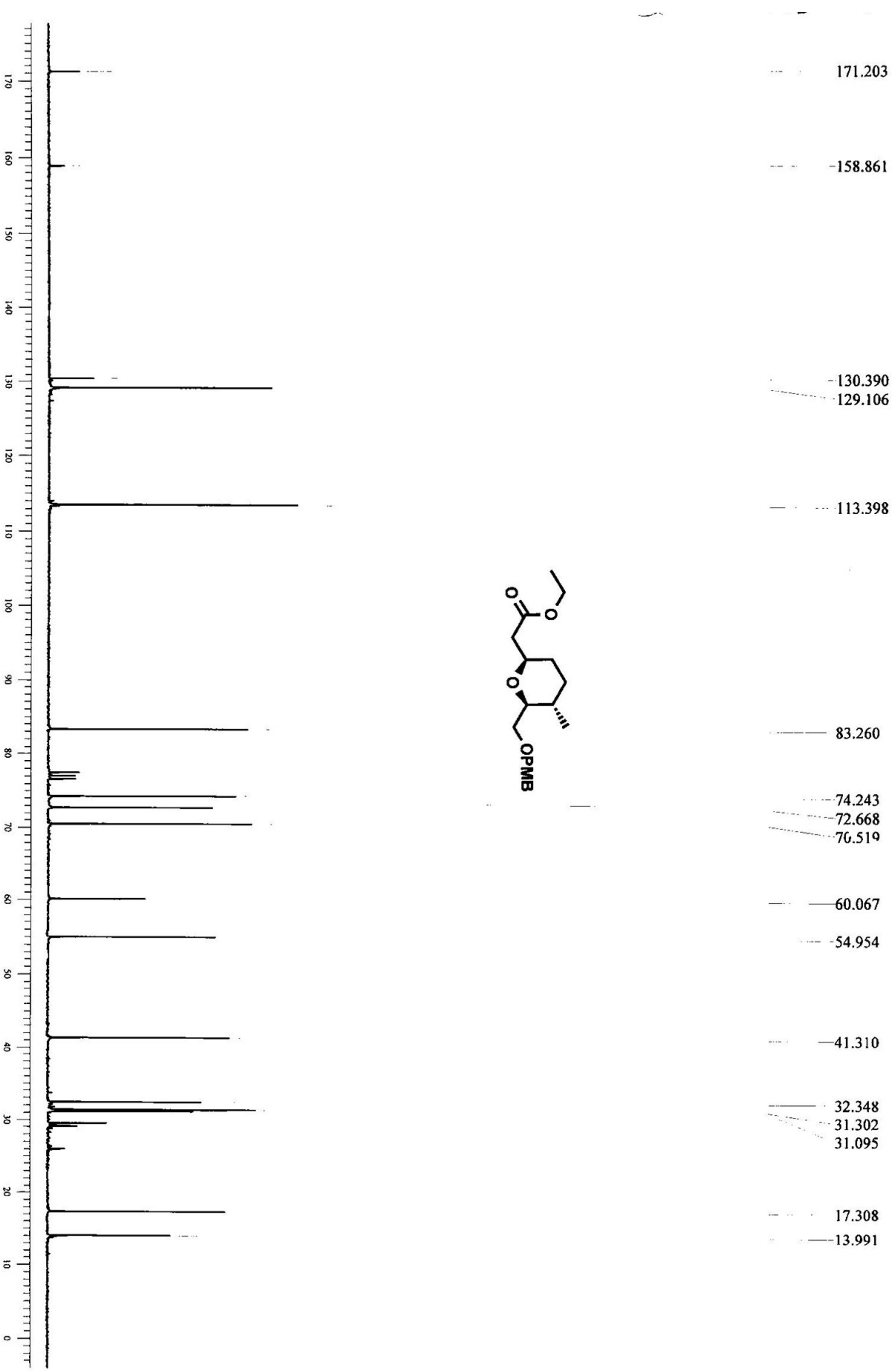
^{1}H NMR of 17 ($CDCl_3$, 300 MHz)



^{13}C NMR of 17 ($CDCl_3$, 75 MHz)

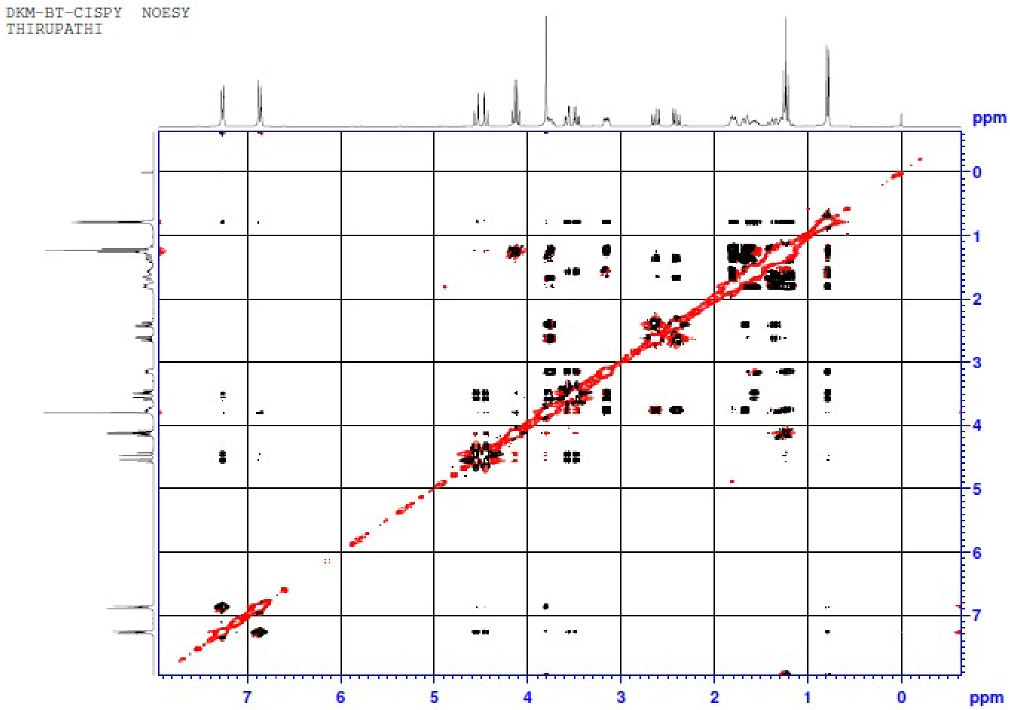


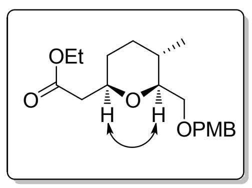
[1]H NMR of 4 ($CDCl_3$, 300 MHz)

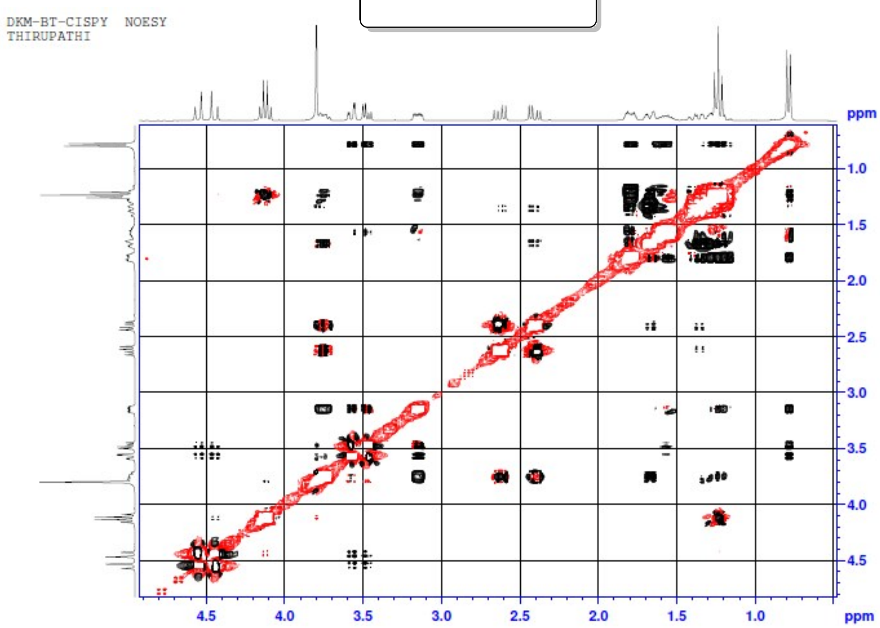


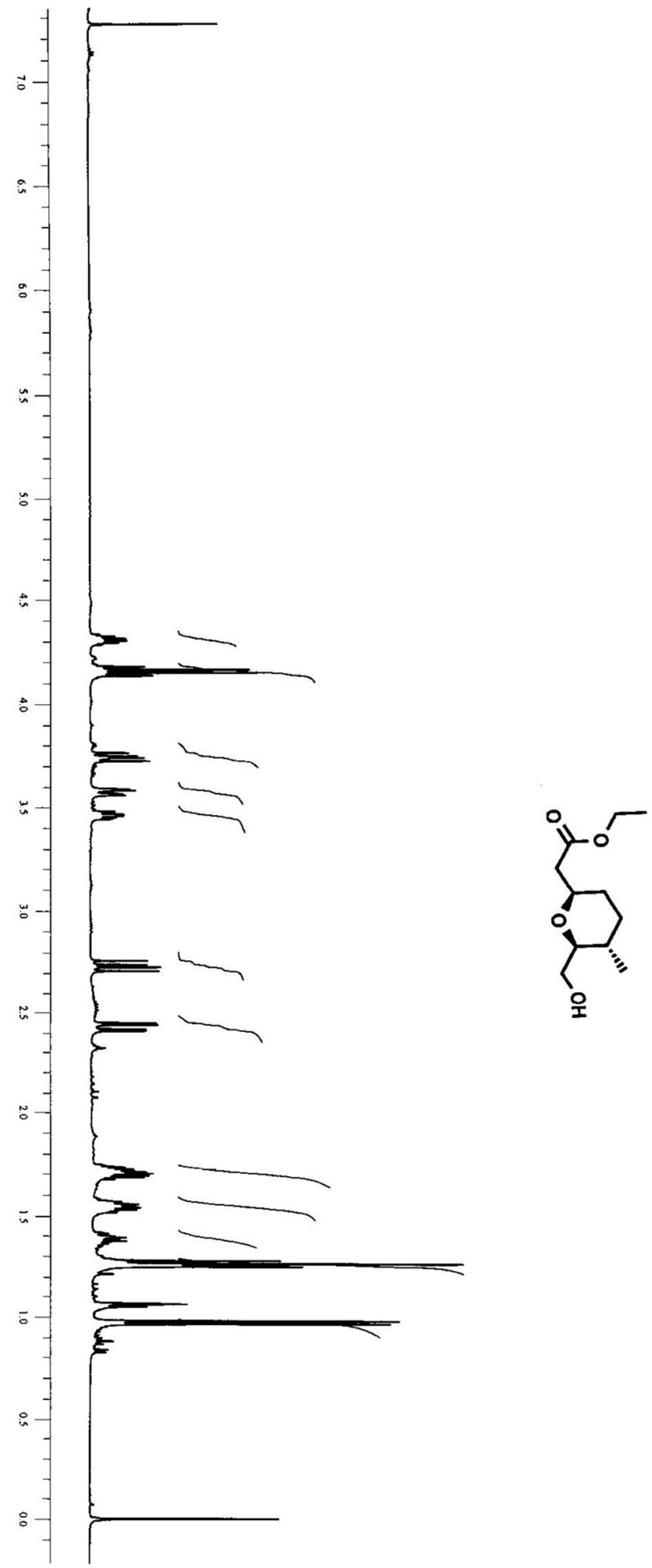
^{13}C NMR of 4 ($CDCl_3$, 75 MHz)

The key NOE correlations of compound 4 are shown below:

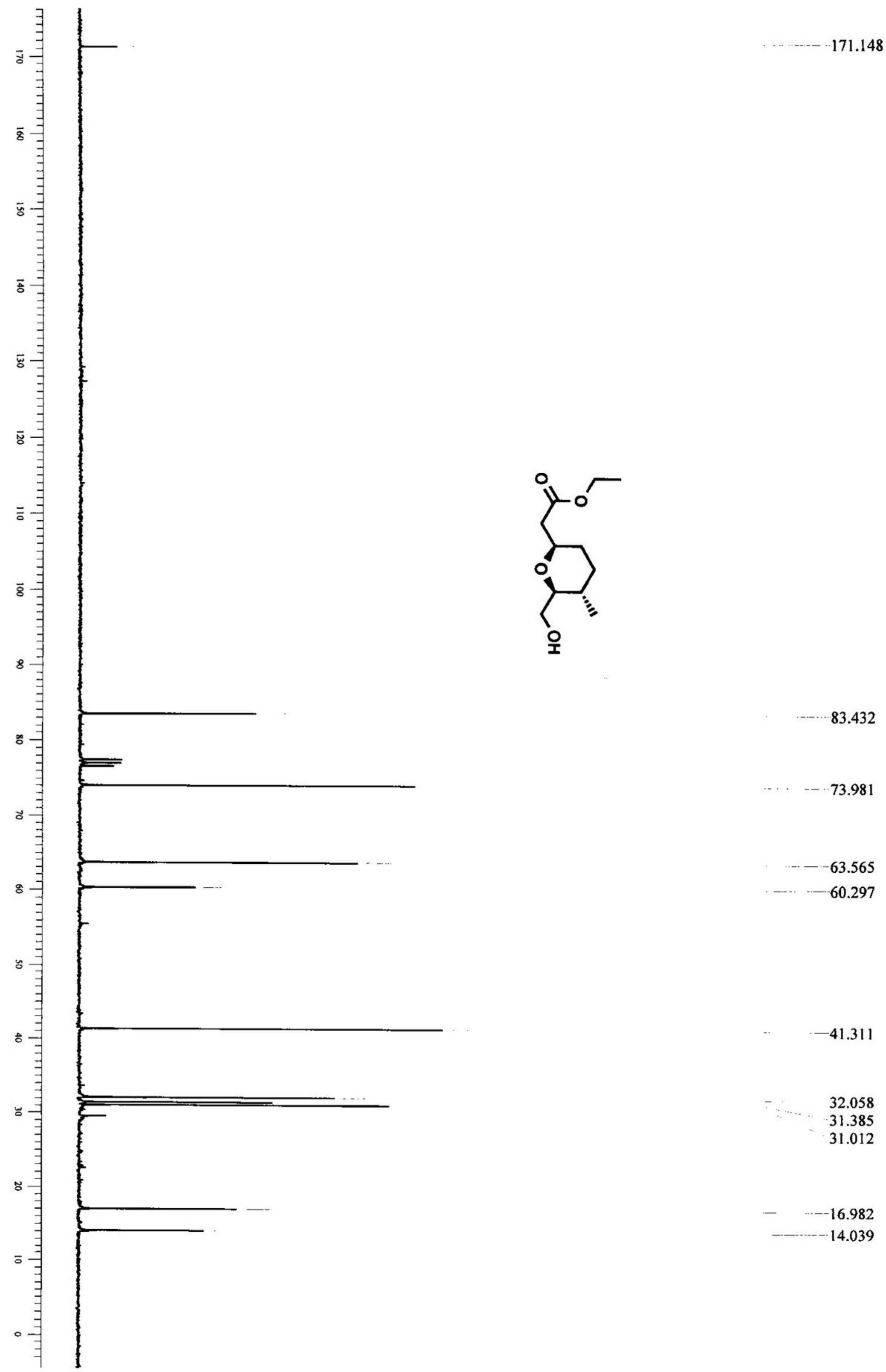




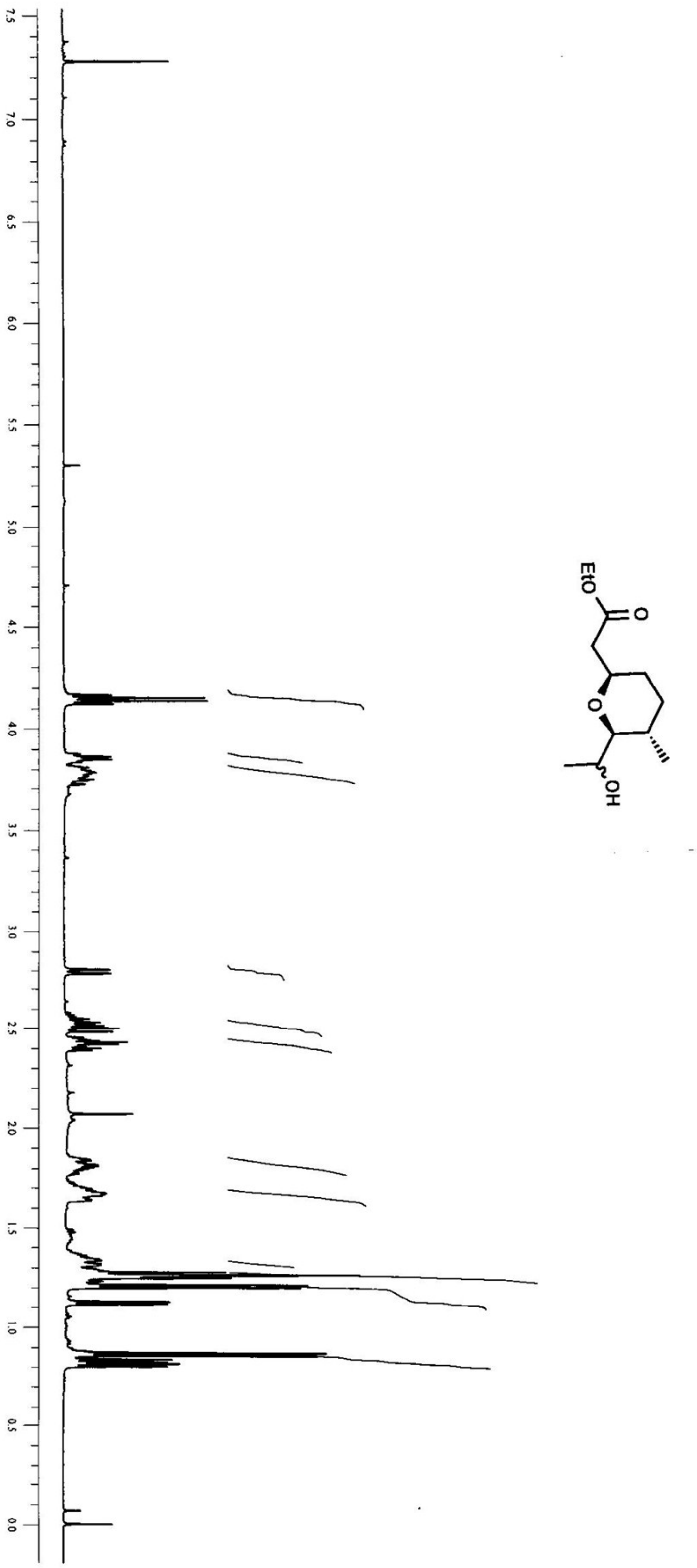




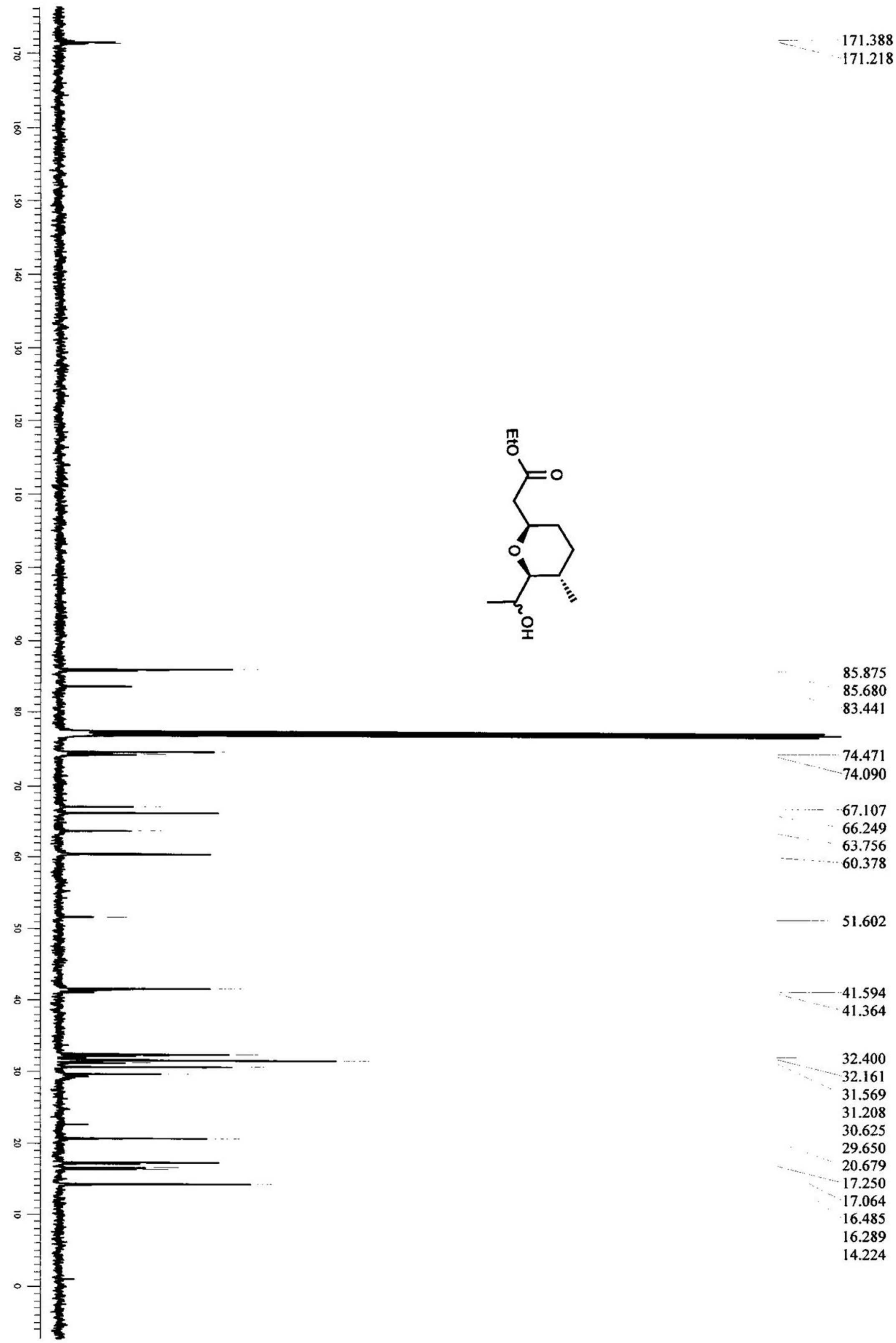
^{1}H NMR of 18 ($CDCl_3$, 300 MHz)



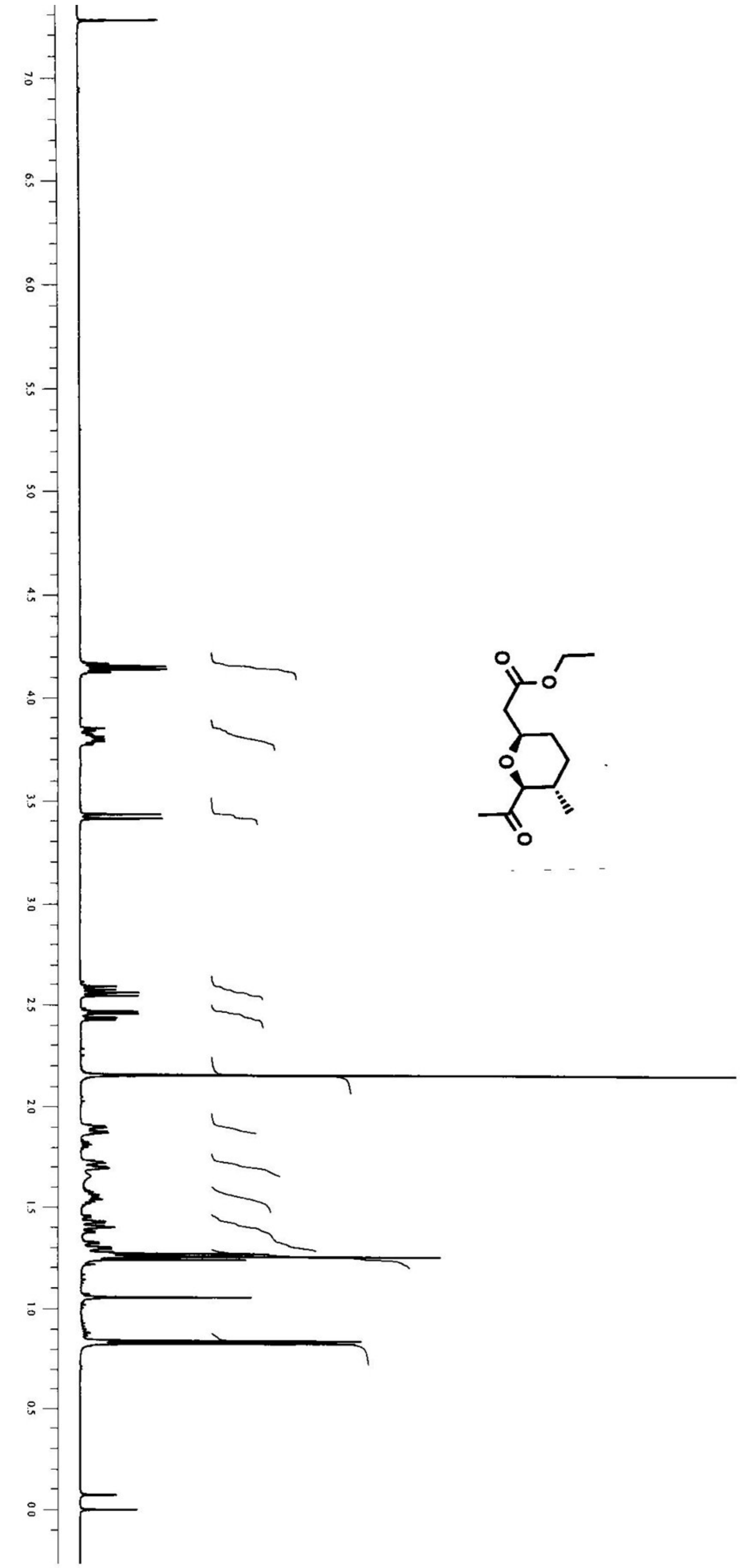
^{13}C NMR of 18 ($CDCl_3$, 75 MHz)



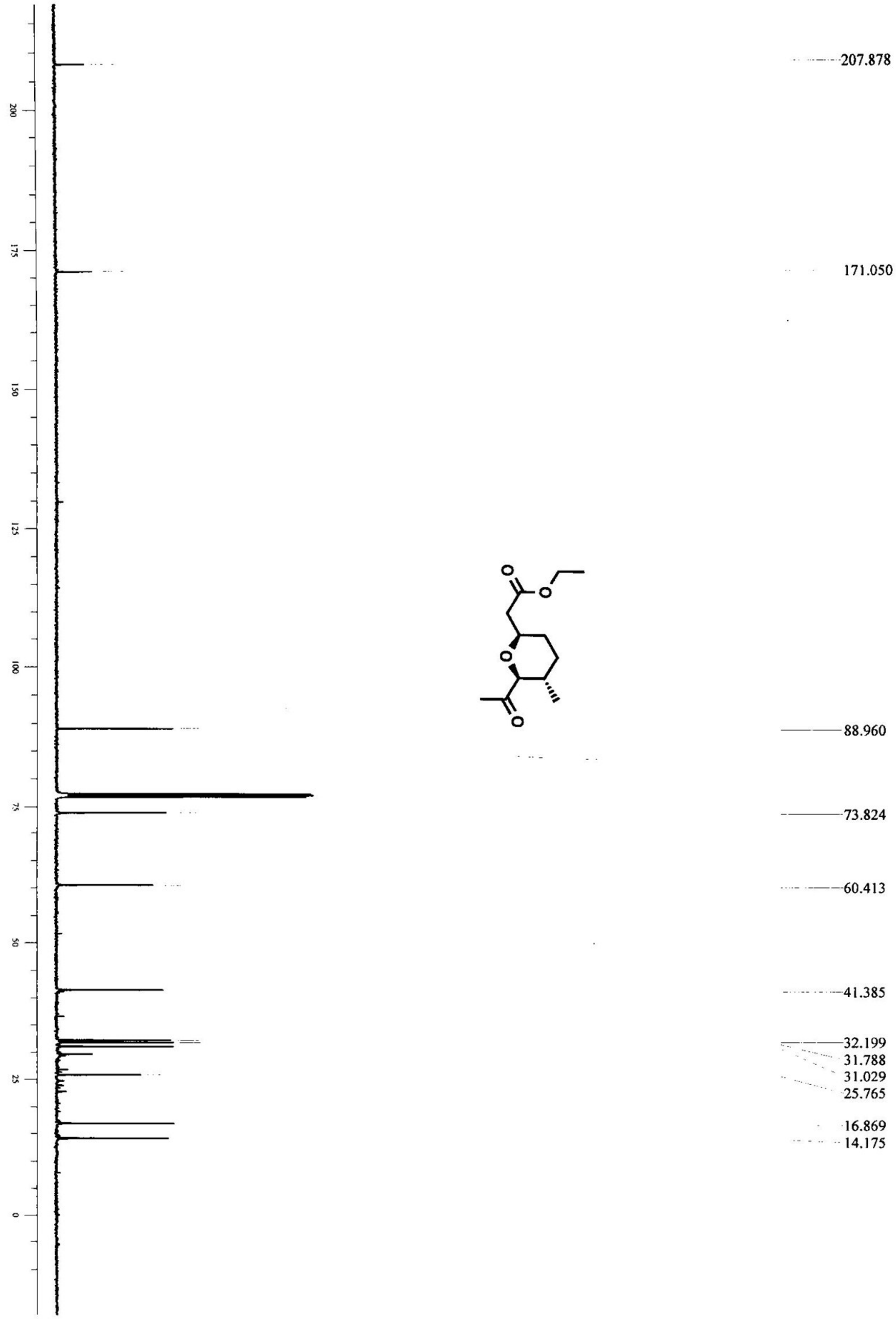
[1]H NMR of 19 ($CDCl_3$, 300 MHz)



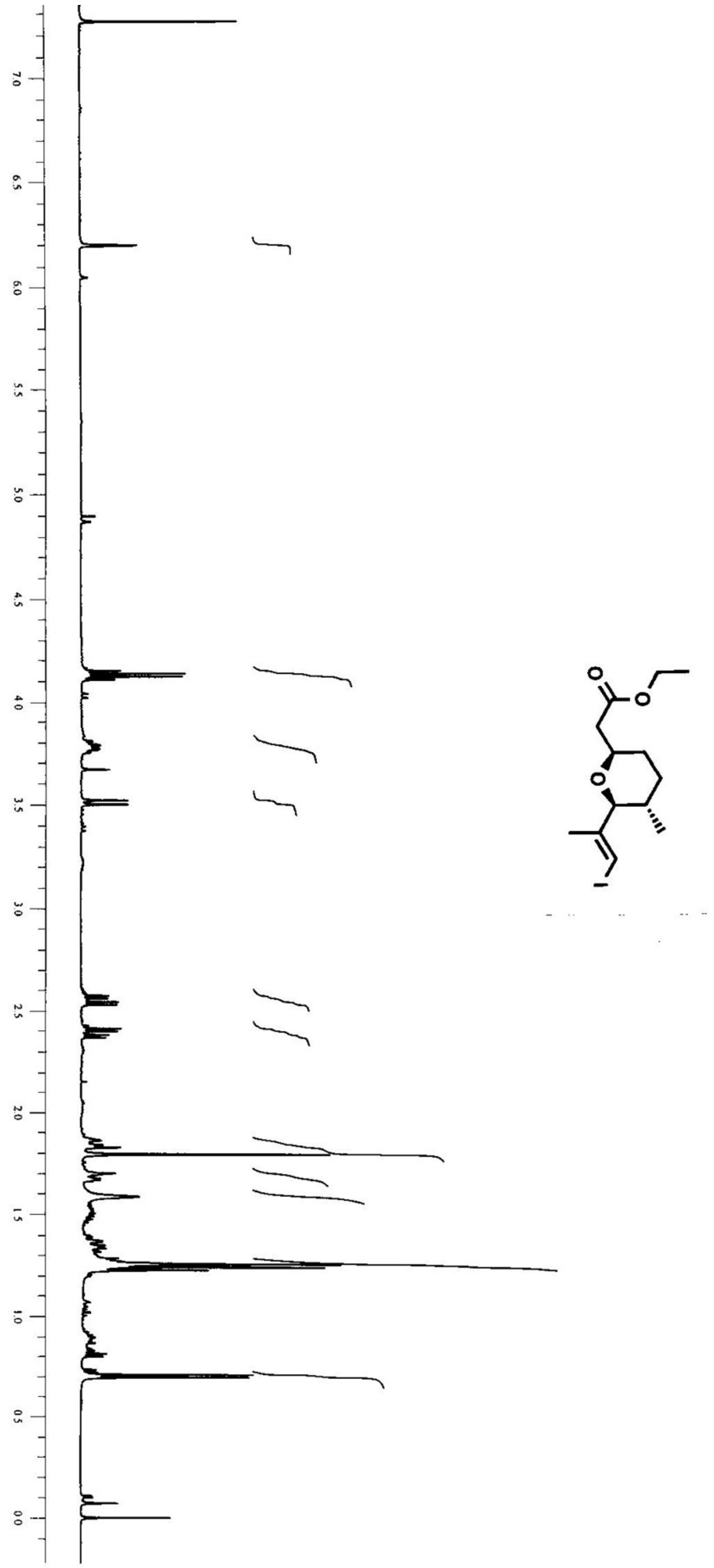
^{13}C NMR of 19 ($CDCl_3$, 75 MHz)



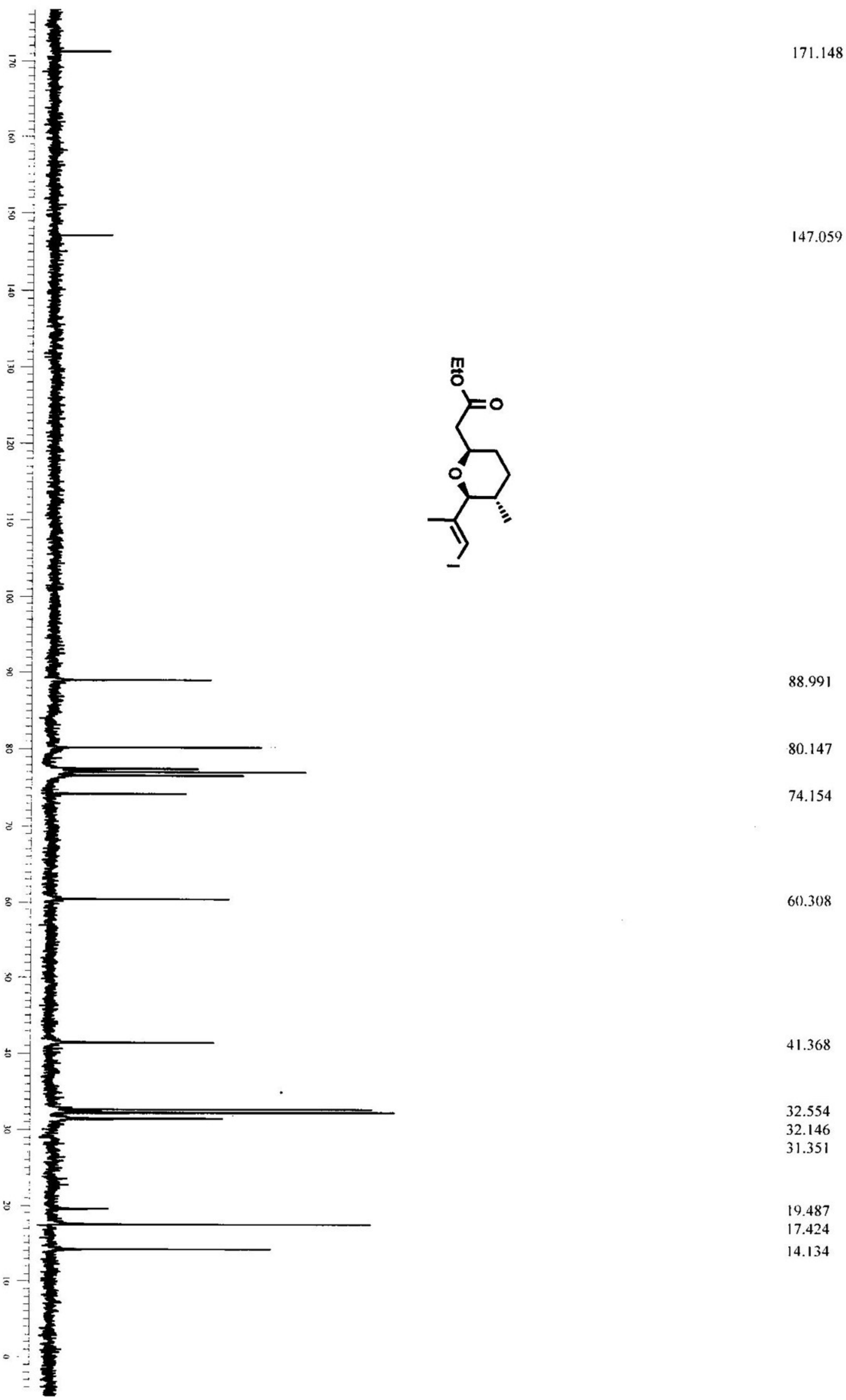
^{1}H NMR of 20 ($CDCl_3$, 300 MHz)



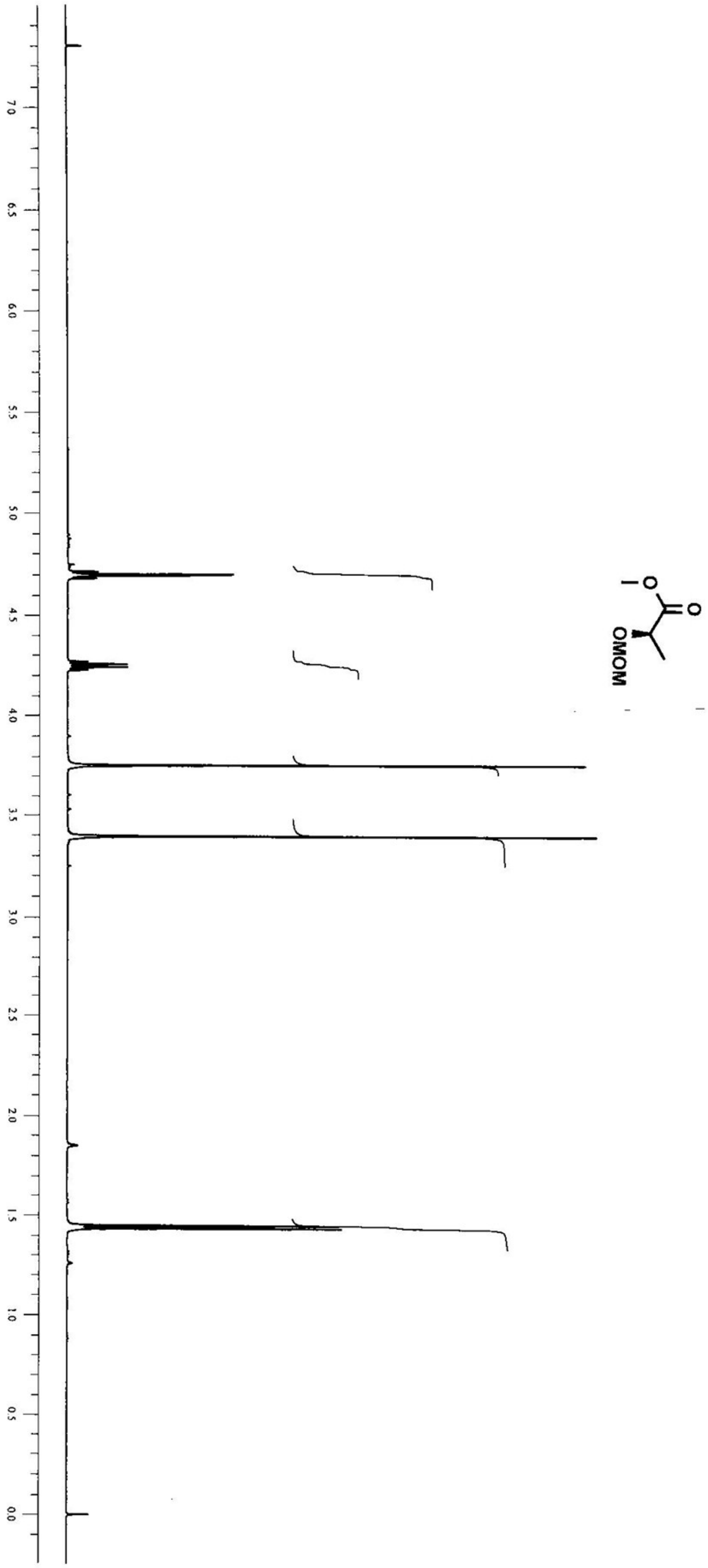
^{13}C NMR of 20 ($CDCl_3$, 75 MHz)



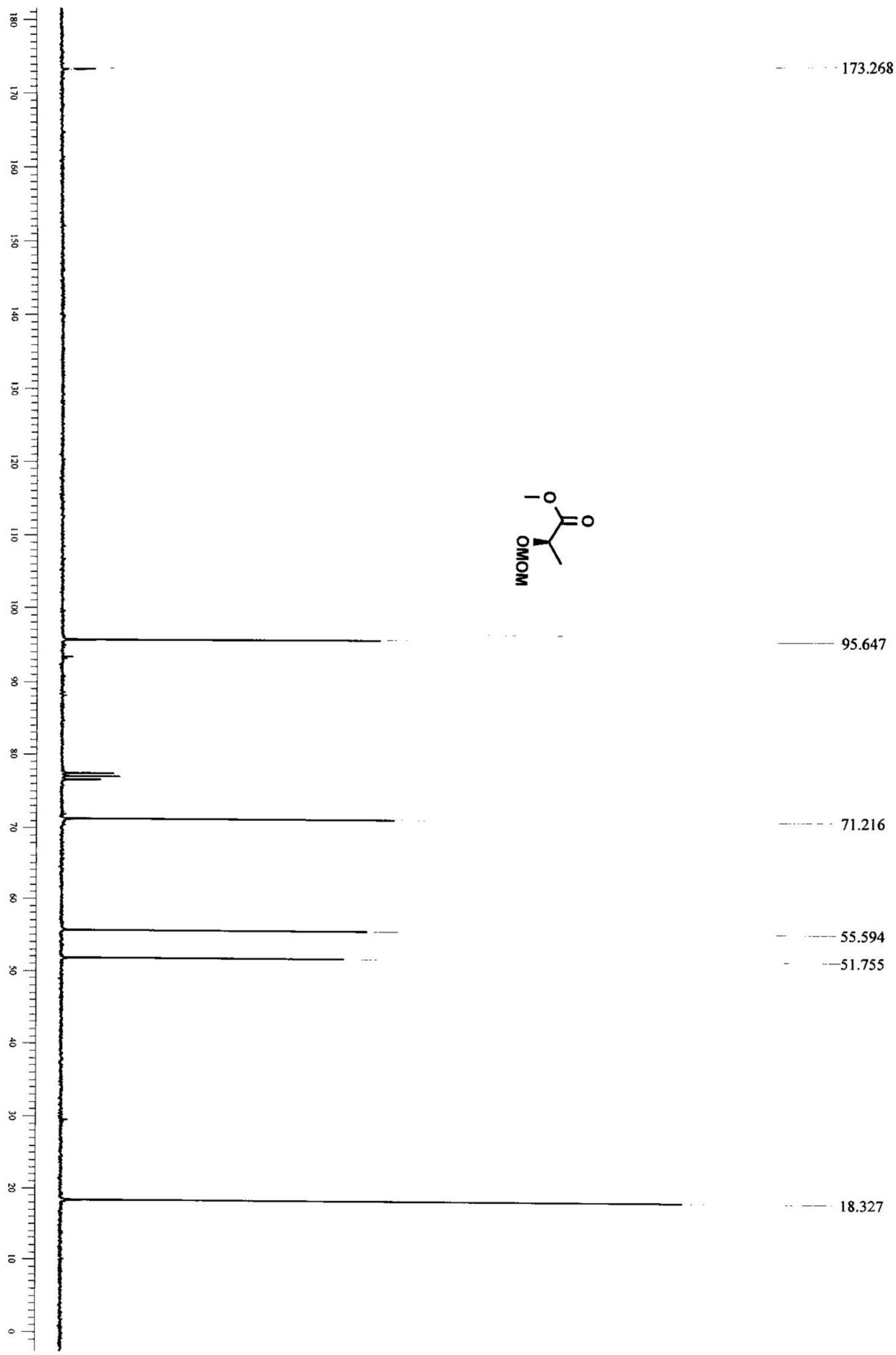
[1]H NMR of 2 ($CDCl_3$, 300 MHz)



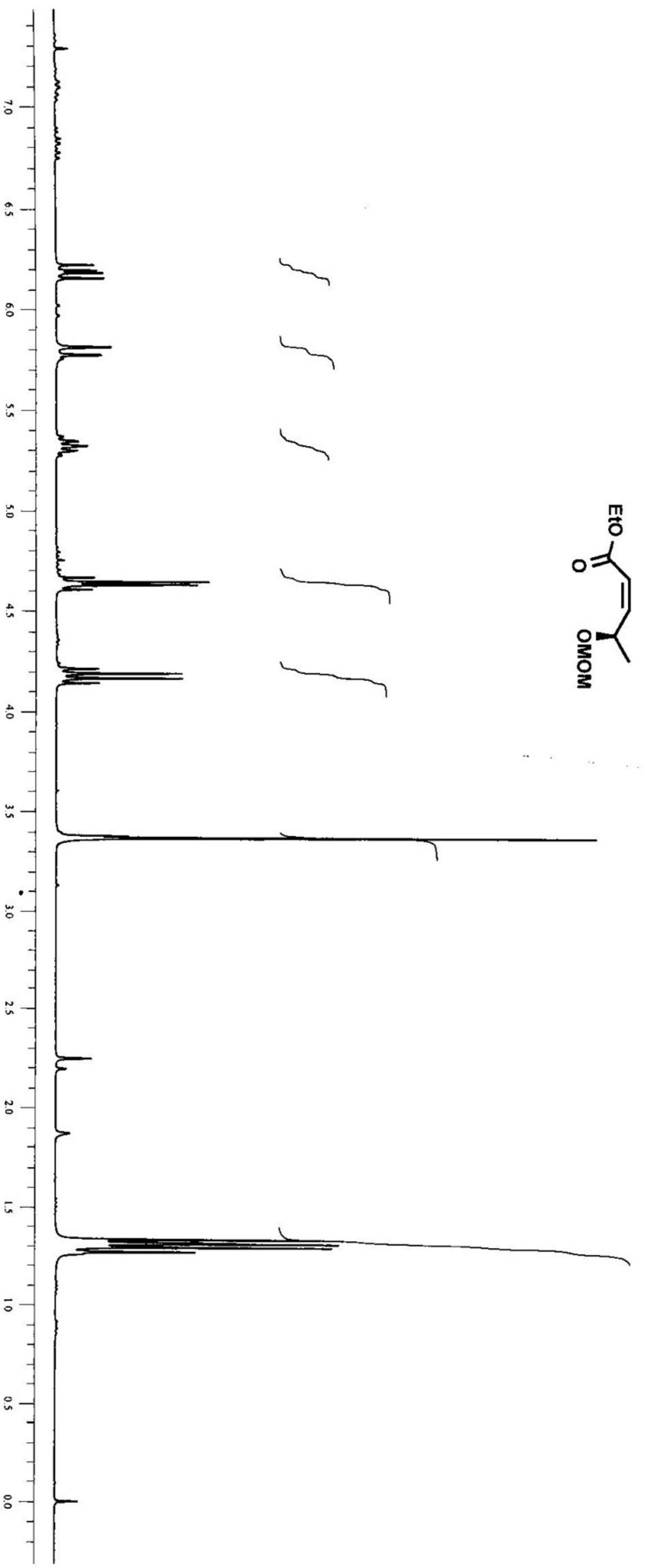
^{13}C NMR of 2 (CDCl$_3$, 75 MHz)



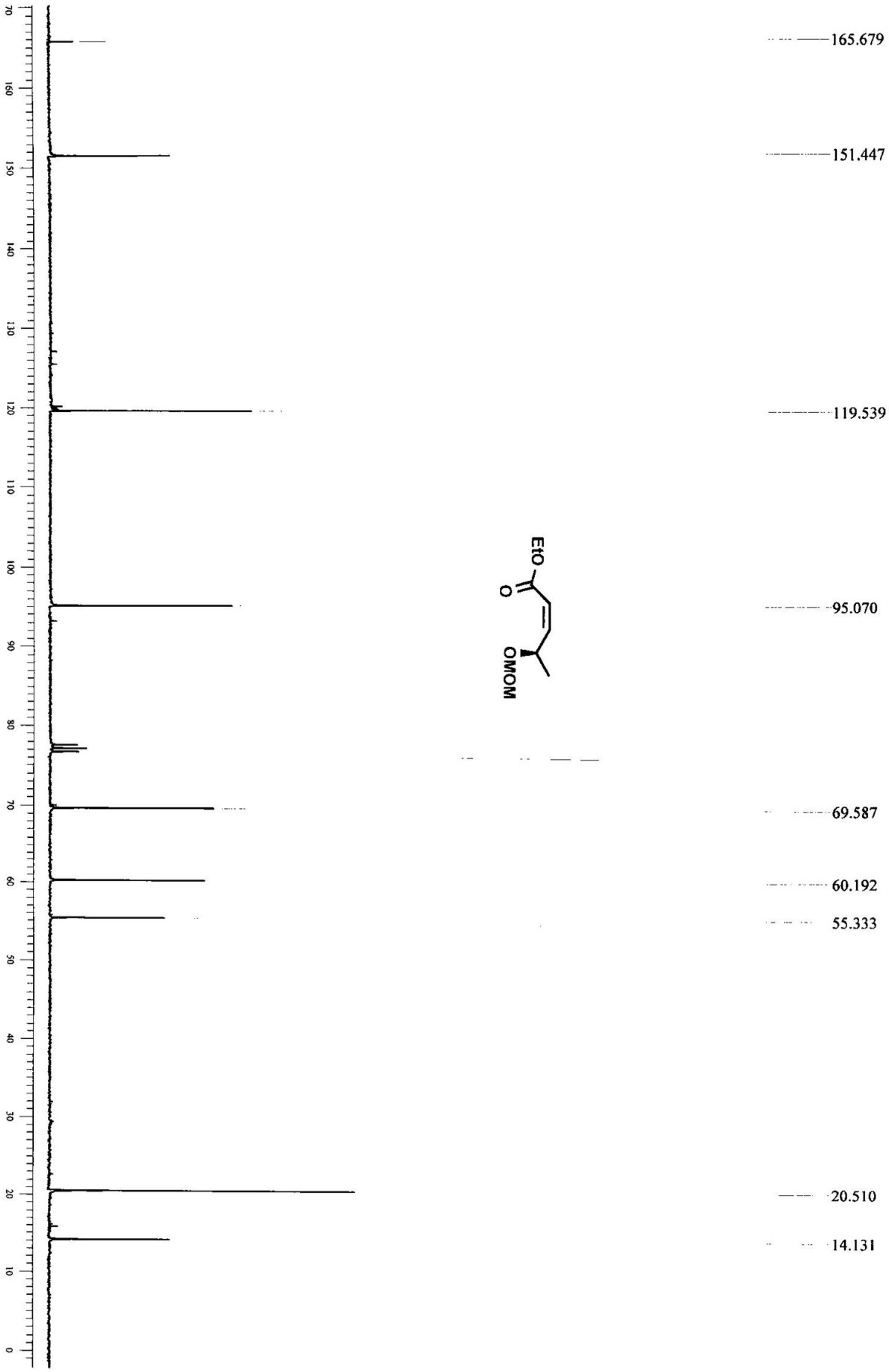
^{1}H NMR of 21 ($CDCl_3$, 300 MHz)



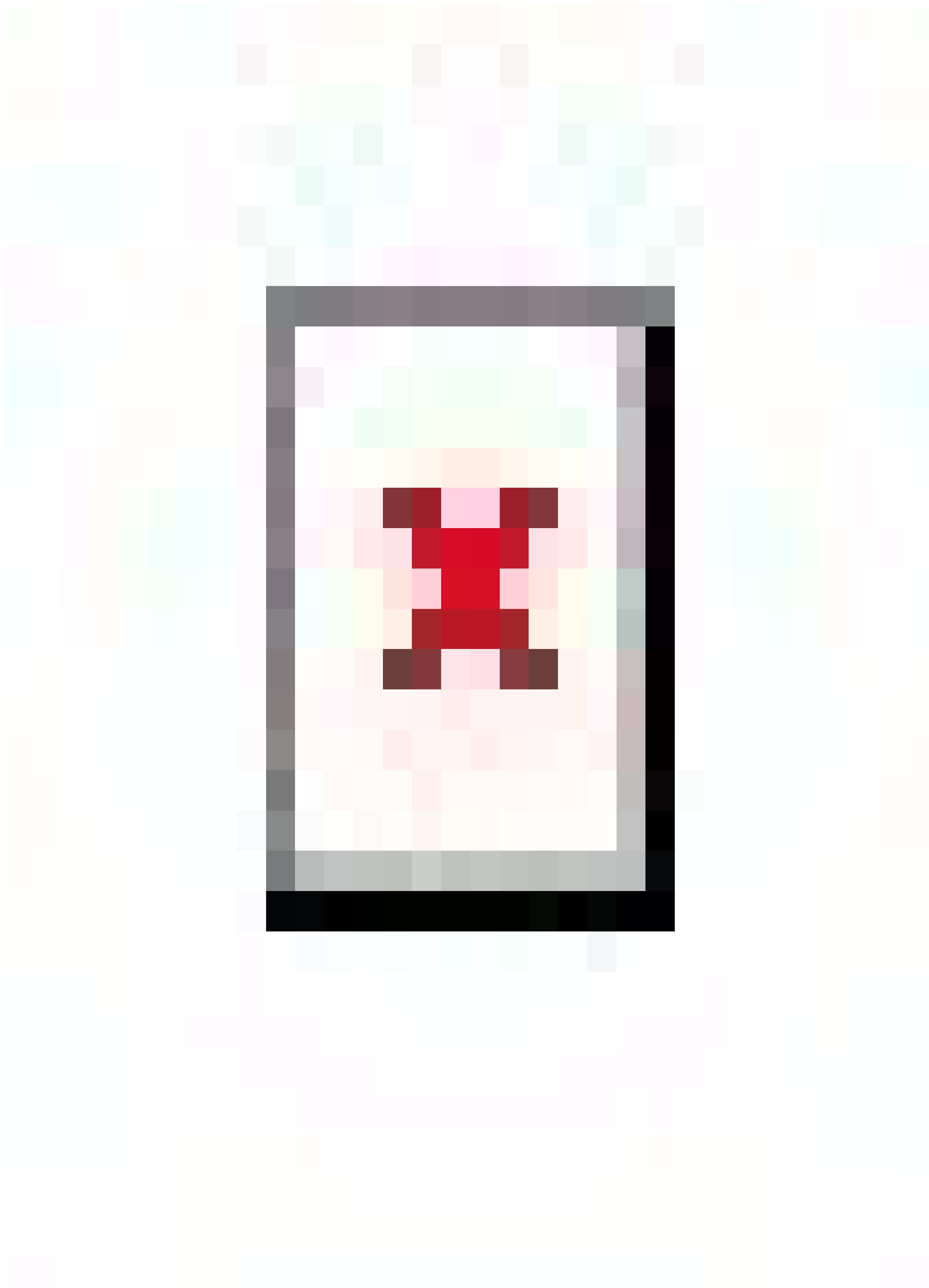
^{13}C NMR of 21 ($CDCl_3$, 75 MHz)



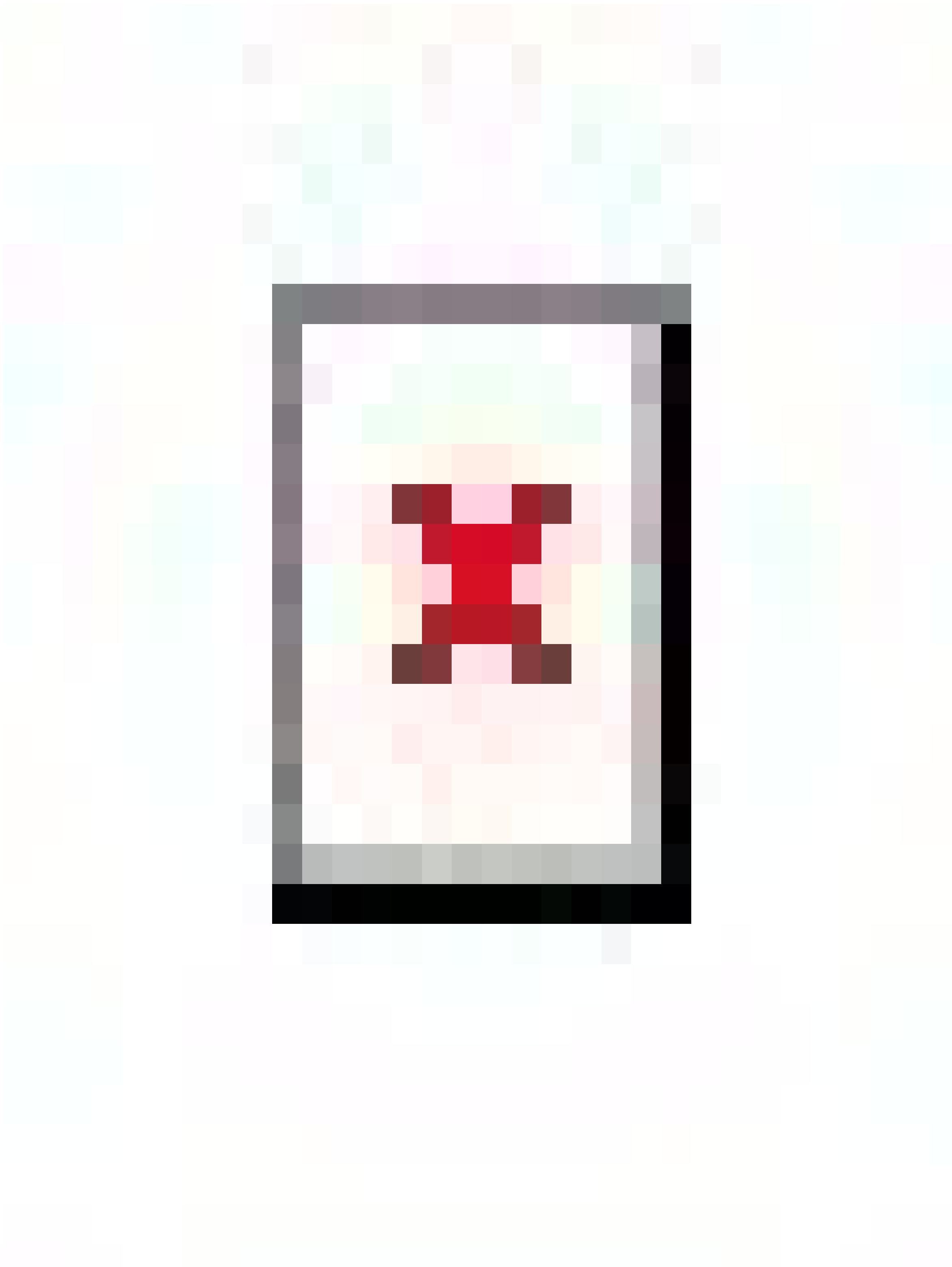
^{1}H NMR of 23 ($CDCl_3$, 300 MHz)



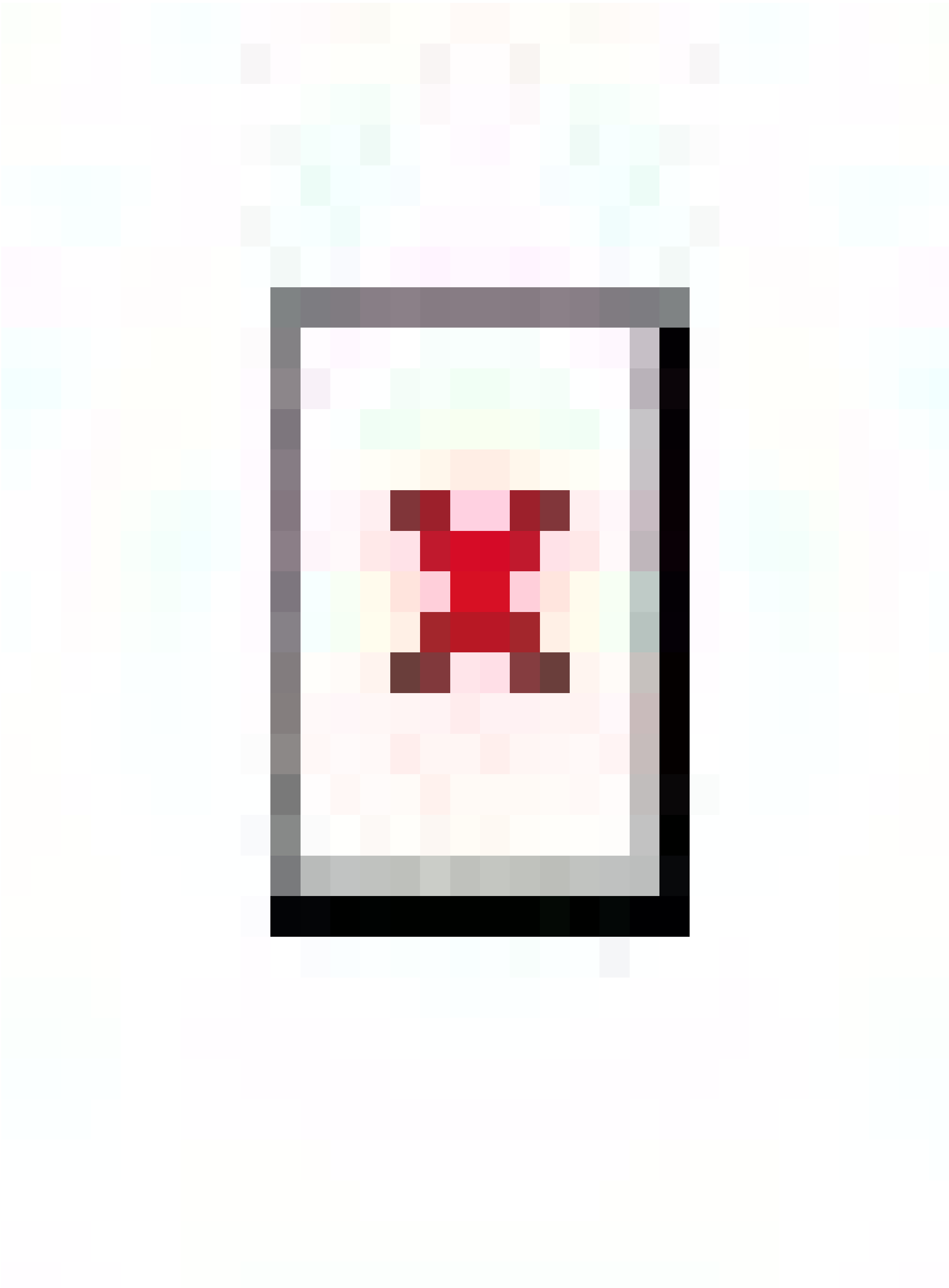
^{13}C NMR of 23 ($CDCl_3$, 75 MHz)



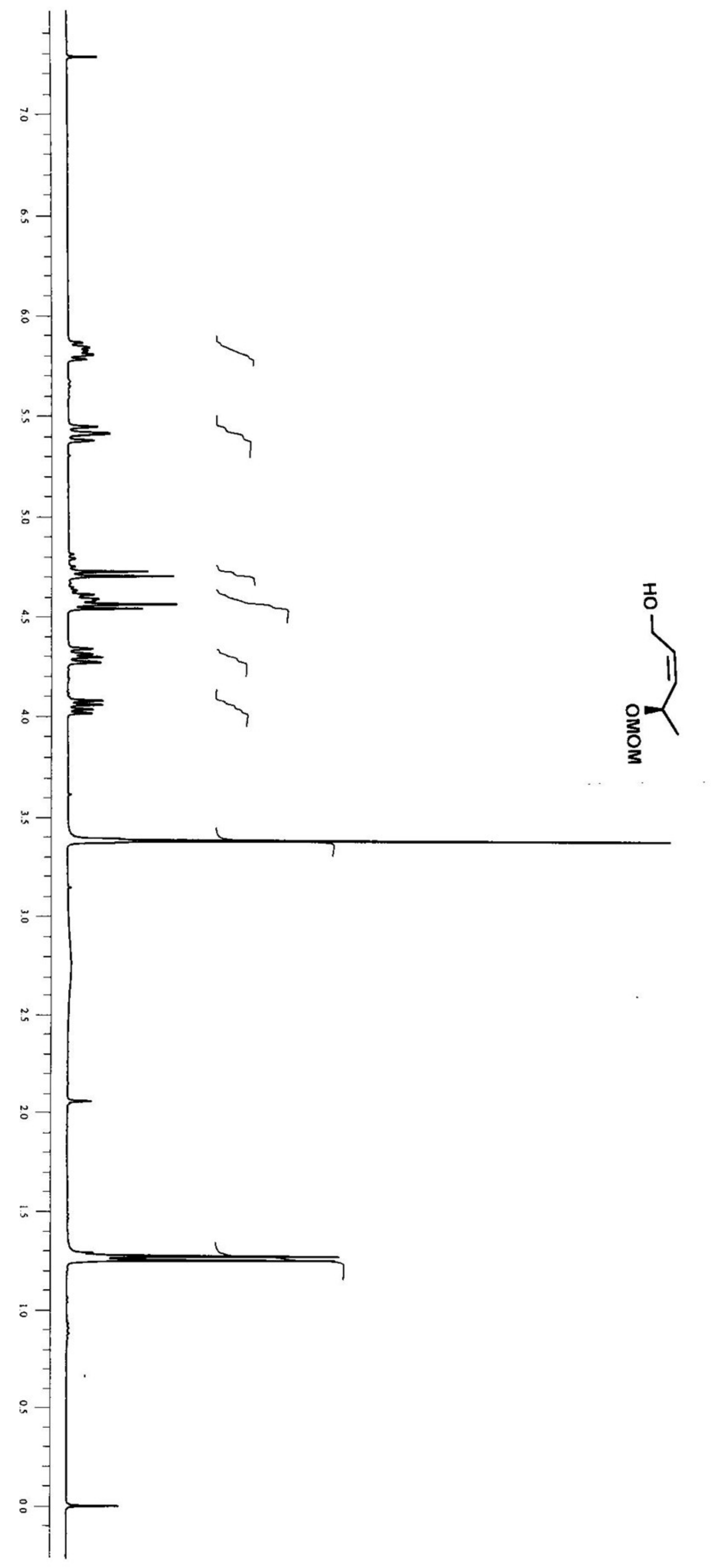
HPLC Chromatogram of 23



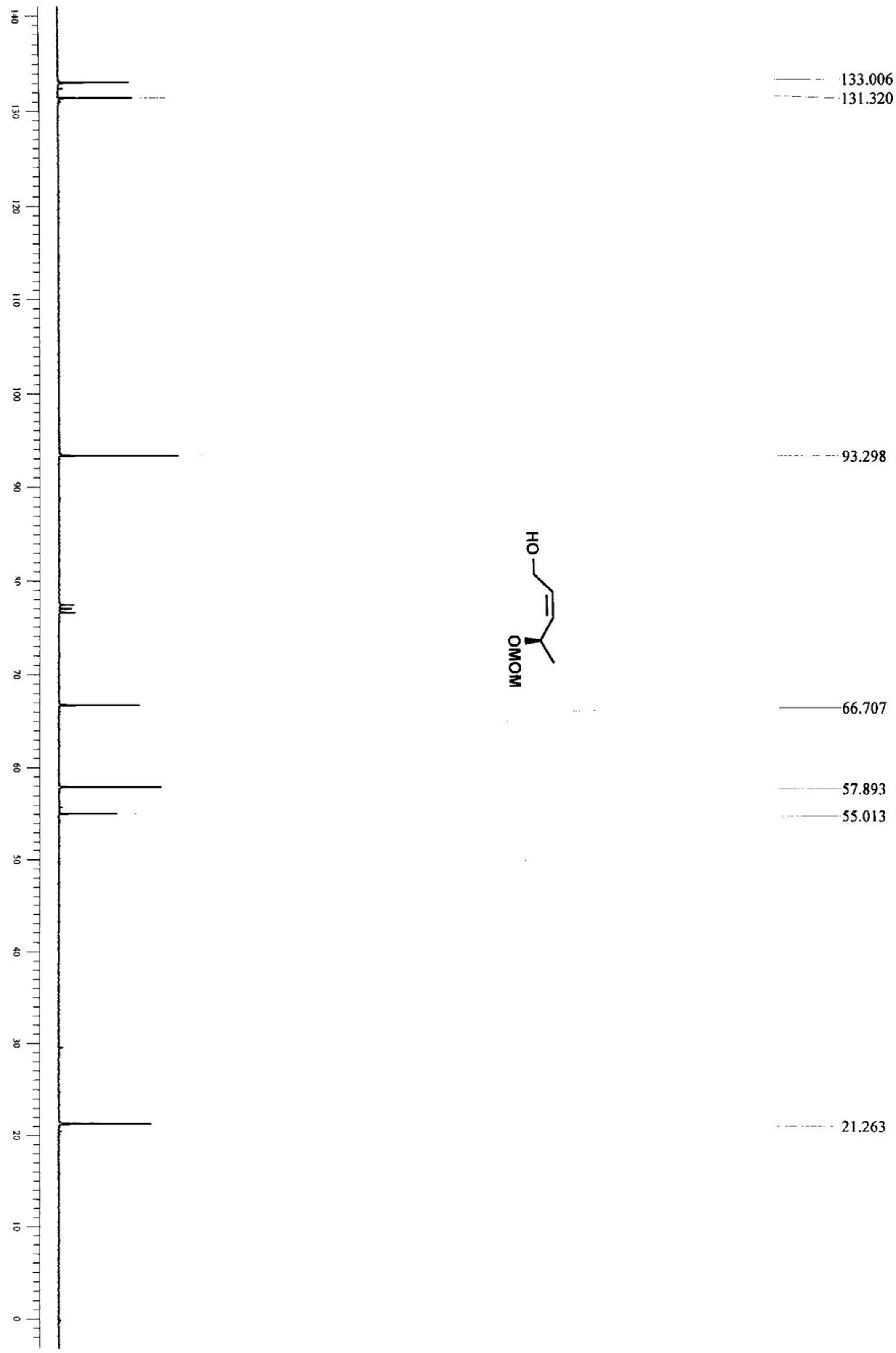
HPLC Chromatogram of 23



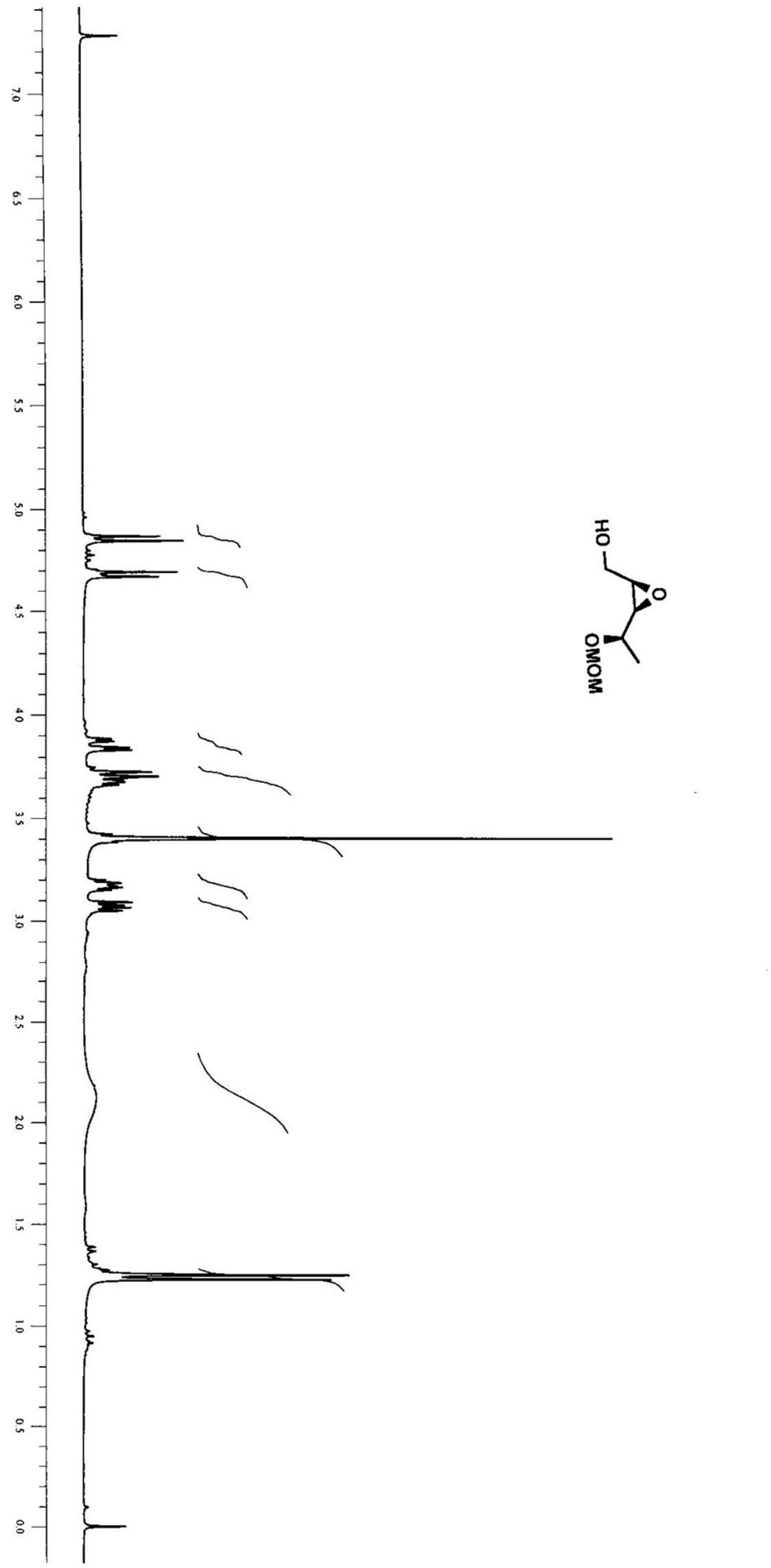
LCMS Chromatogram of 23



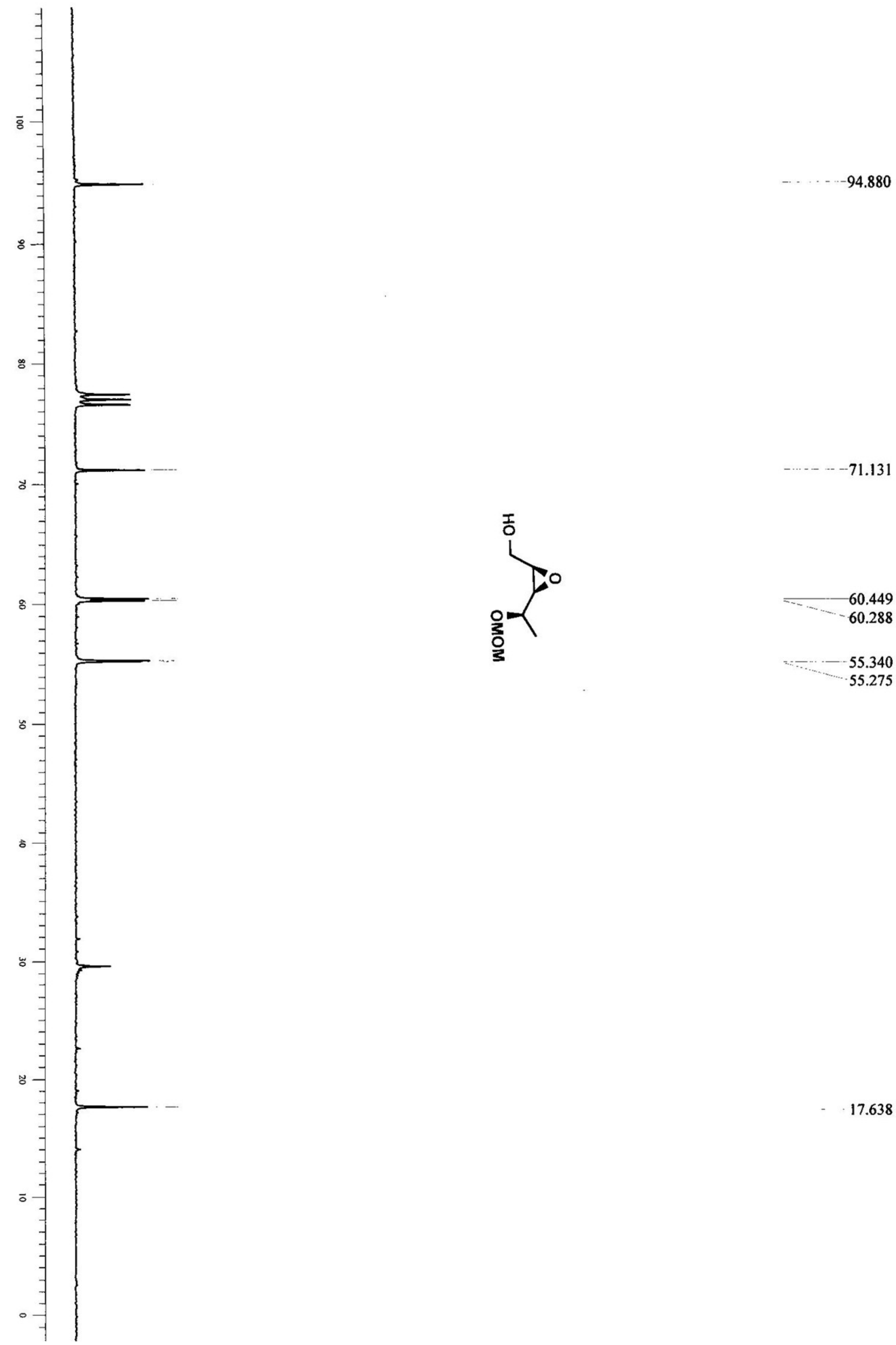
^{1}H NMR of 24 ($CDCl_3$, 300 MHz)



^{13}C NMR of 24 ($CDCl_3$, 75 MHz)



^{1}H NMR of 25 ($CDCl_3$, 300 MHz)



^{13}C NMR of 25 ($CDCl_3$, 75 MHz)

Data File D:\DATA\SCS2014\17042014000002.D
Sample Name: DKM-BT-EPOXIDE-400

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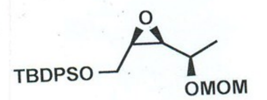
Acq. Operator   : V.RAJESH
Acq. Instrument : Instrument 1                 Location : Vial 31
Injection Date  : 4/17/2014 4:04:08 PM
                                             Inj Volume : 10 µl
Acq. Method     : D:\METHODS\LCM.m
Last changed    : 4/17/2014 4:22:33 PM by V.RAJESH
Analysis Method : D:\METHODS\MASS L.M
Last changed    : 5/7/2014 12:22:32 PM by V.RAJESH
Method Info     : COLUMN:ATLANTIS C18,250 X 4.6MM,5U
                  MOBILEPHASE:60% ACN IN WATER(0.1% F.A)
                  FLOWRATE:1ML/MIN
                  DECTION:210NM

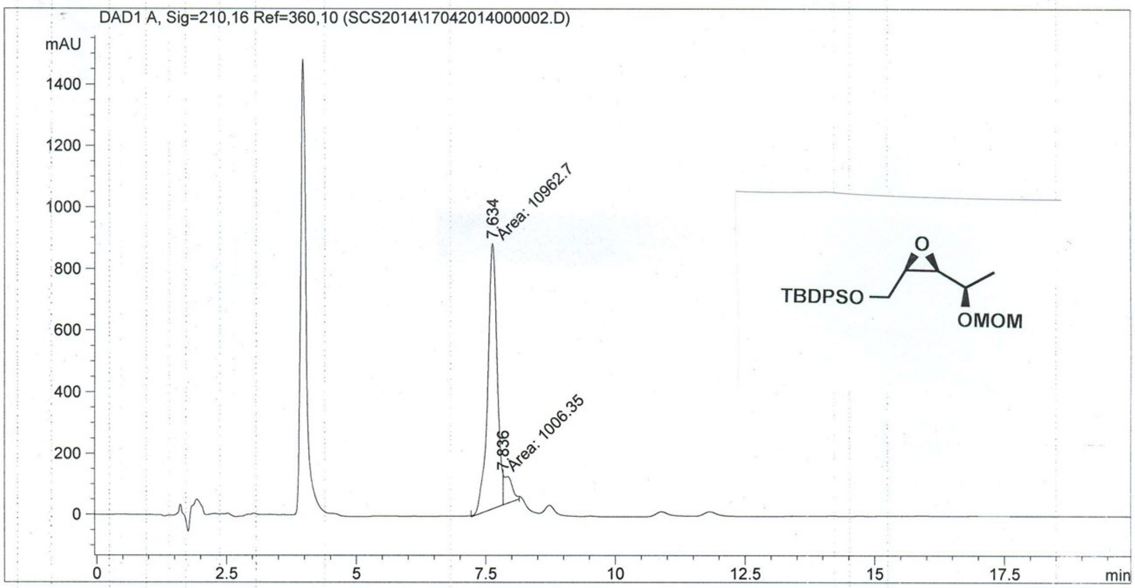
Sample Info     : ATLANTIS dC18, 80% H2O IN ACN
```



Instrument 1 5/7/2014 12:22:39 PM V.RAJESH   Page 1 of 2

HPLC Chromatogram of TBDPS ether of 25

Data File D:\DATA\SCS2014\17042014000002.D
Sample Name: DKM-BT-EPOXIDE-400



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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,16 Ref=360,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.634	MF	0.2114	1.09627e4	864.13080	91.5921
2	7.836	FM	0.1517	1006.35382	99.38139	8.4079
Totals :				1.19691e4	963.51218	

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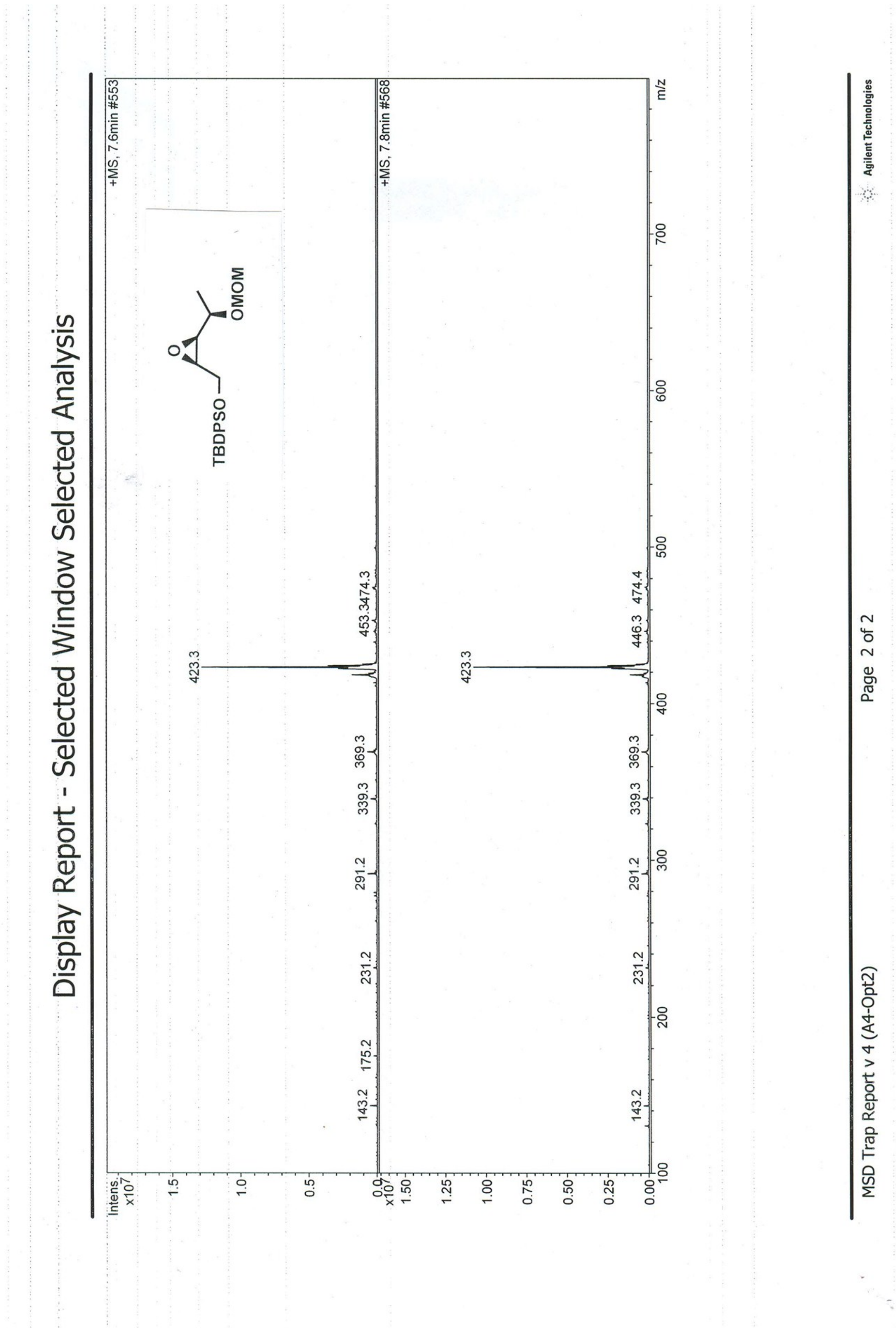
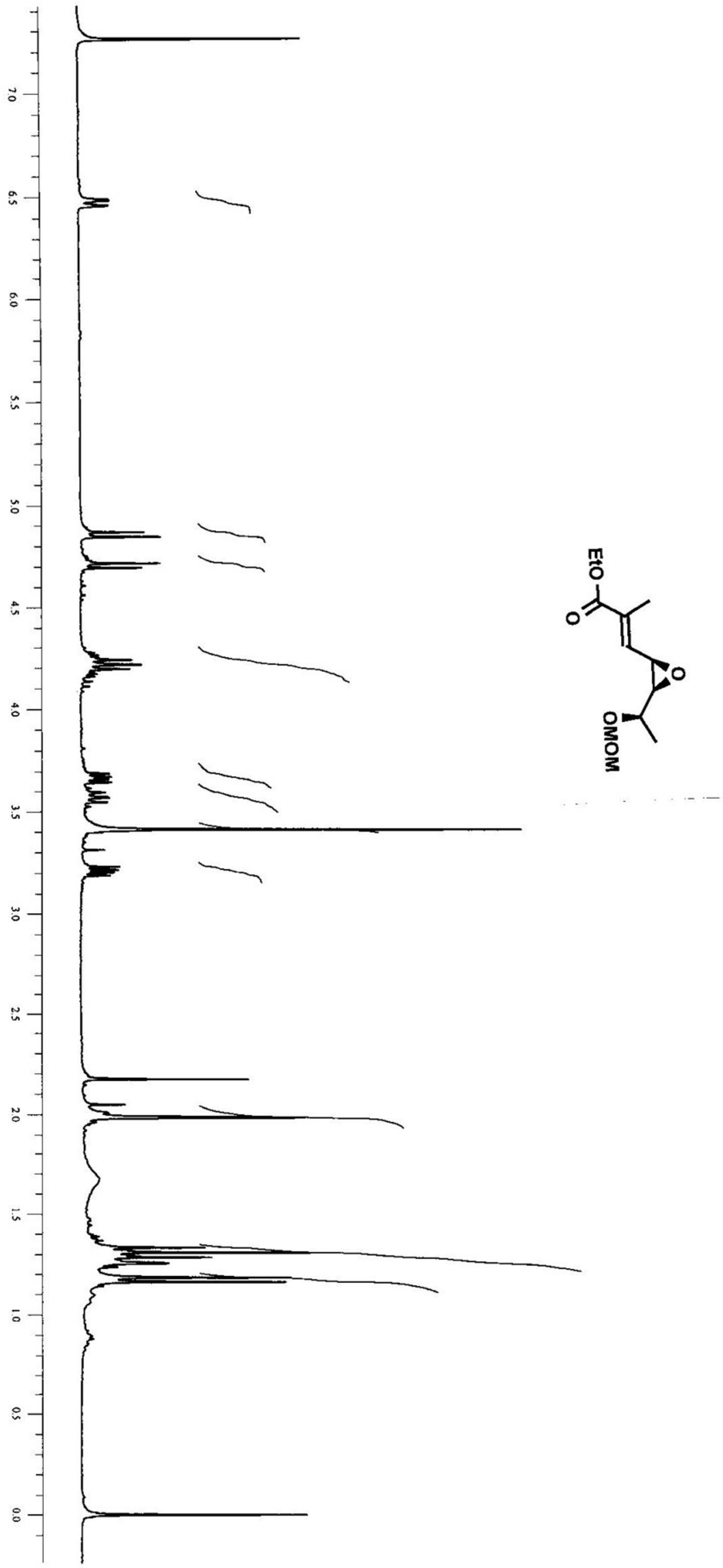
*** End of Report ***

Instrument 1 5/7/2014 12:22:39 PM V.RAJESH Page 2 of 2

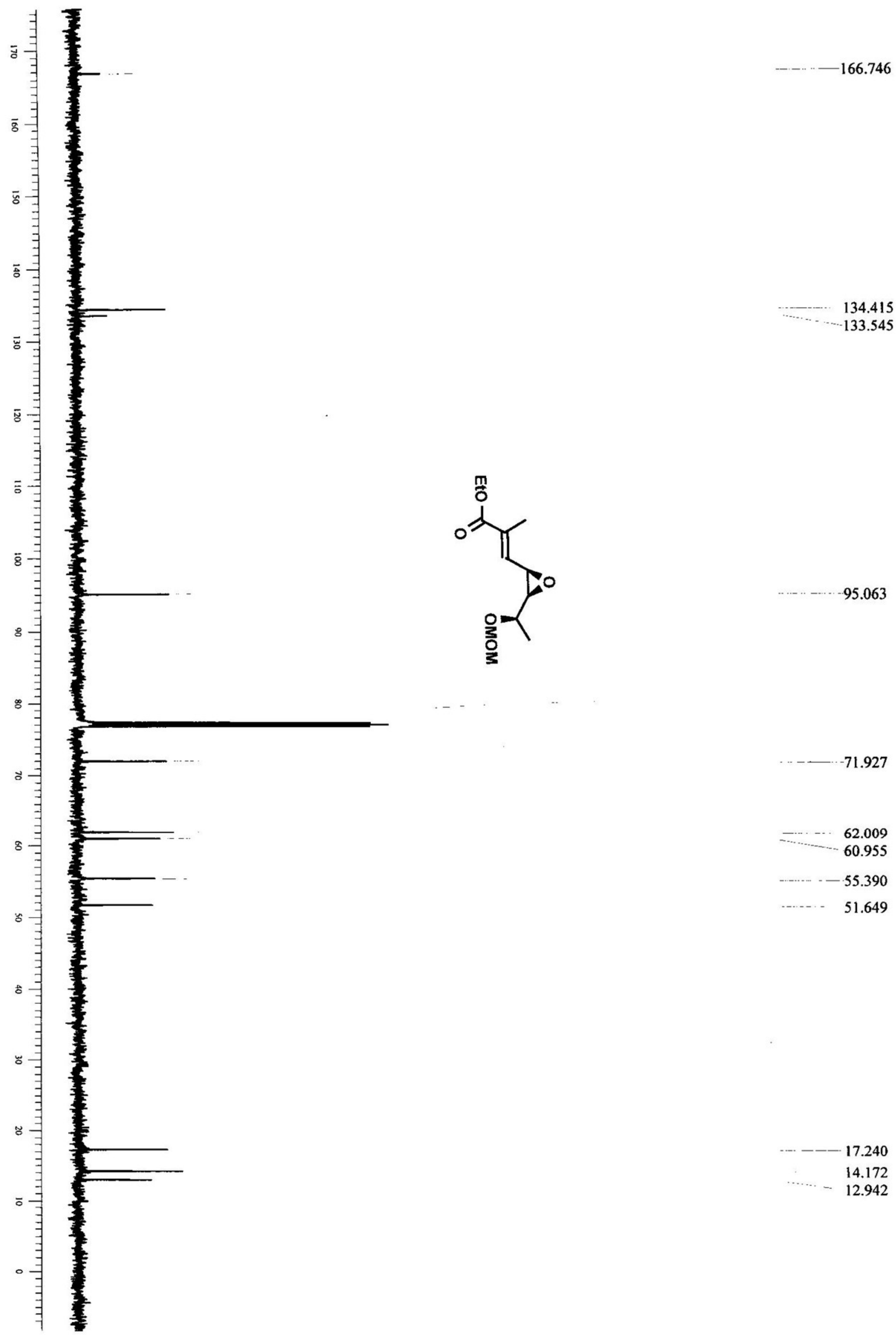
HPLC Chromatogram of TBDPS ether of 25



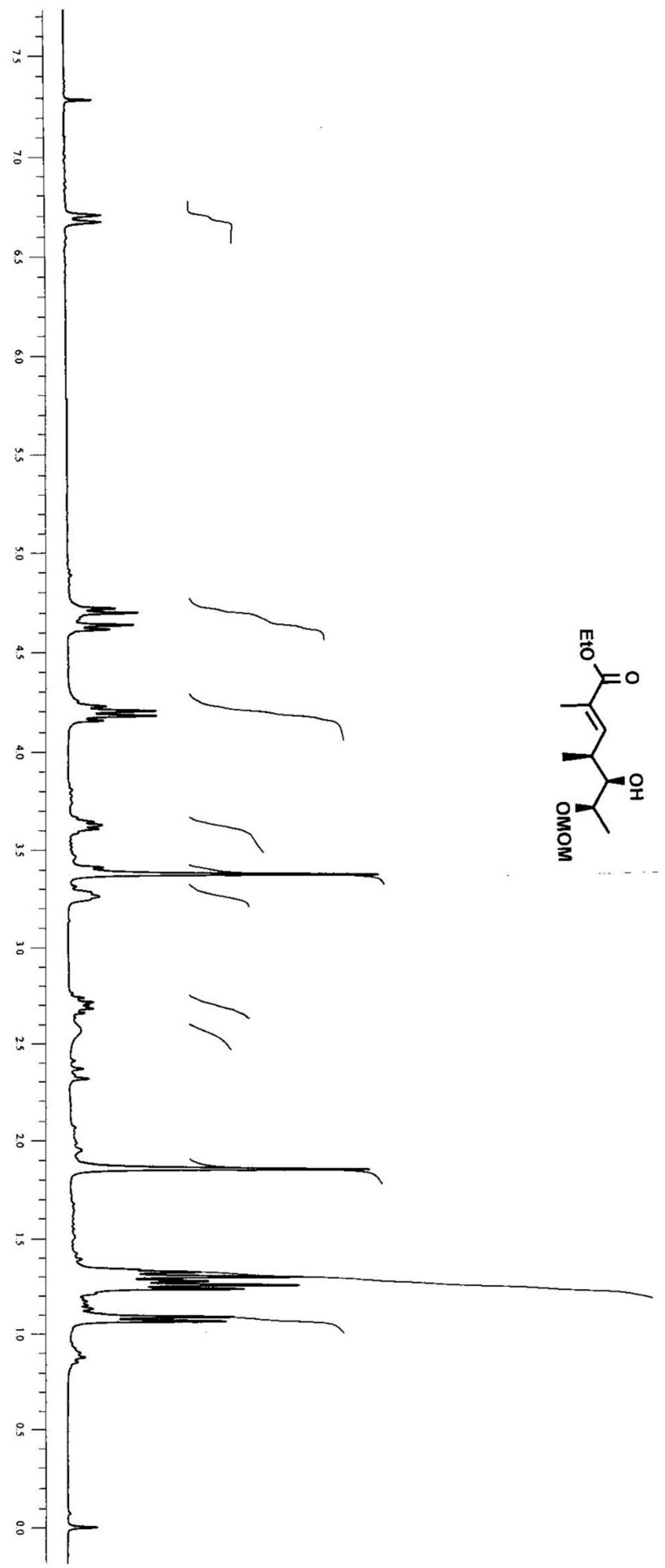
LCMS Chromatogram of TBDPS ether of 25



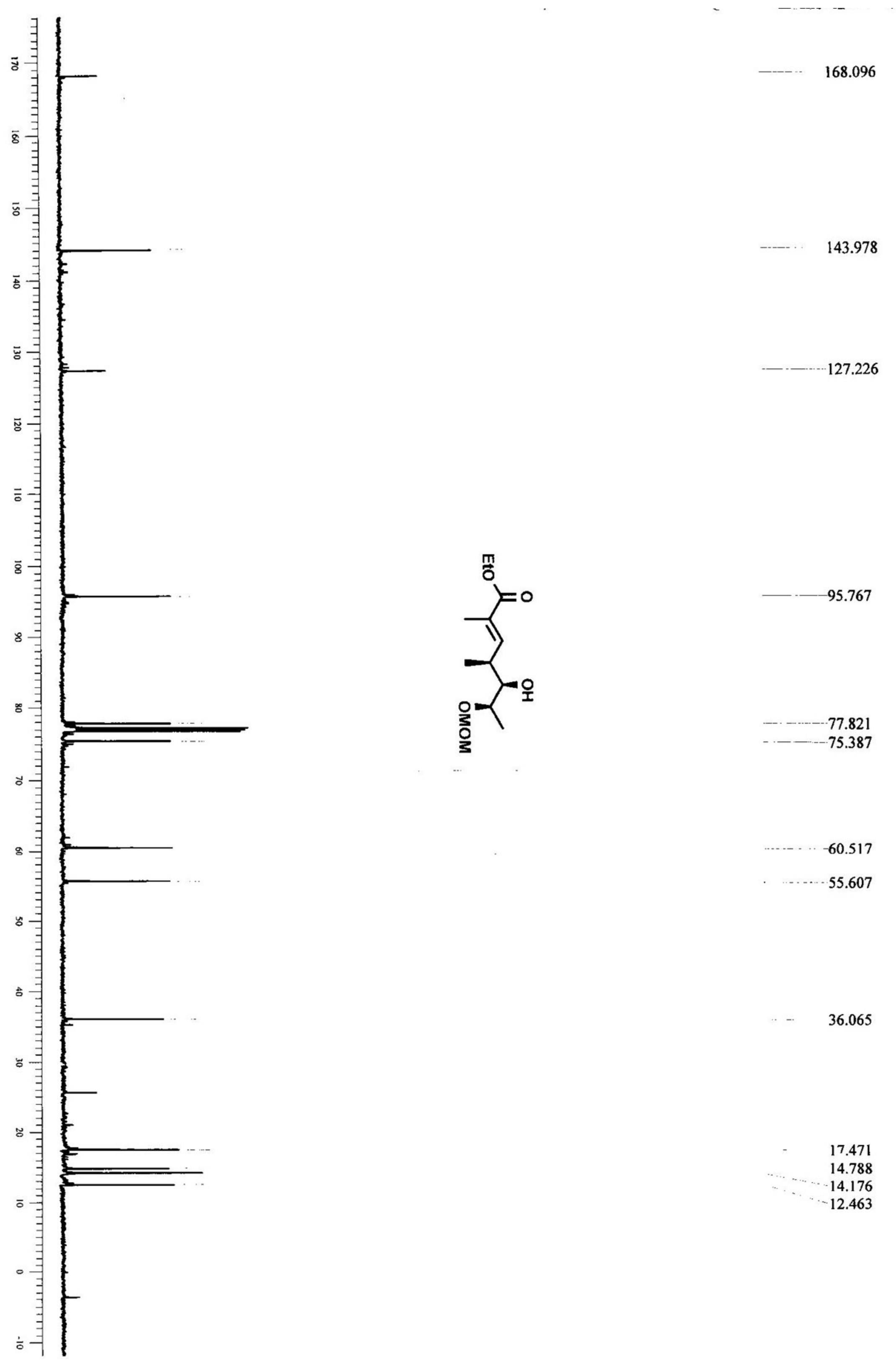
^{1}H NMR of 26 ($CDCl_3$, 300 MHz)



^{13}C NMR of 26 ($CDCl_3$, 75 MHz)



^{1}H NMR of 27 ($CDCl_3$, 300 MHz)



^{13}C NMR of 27 ($CDCl_3$, 75 MHz)

Data File D:\DATA\DKM2014\04042014000054.D
Sample Name: DKM-BT-C3 260

TMAL

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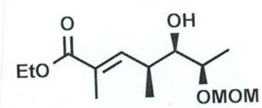
Acq. Operator : V.RAJESH
Acq. Instrument : Instrument 1 Location : Vial 11
Injection Date : 4/4/2014 5:21:06 PM
Inj Volume : 10 µl
Acq. Method : D:\METHODS\LCM.m
Last changed : 4/4/2014 5:19:29 PM by V.RAJESH
Analysis Method : D:\METHODS\LCM.m
Last changed : 4/5/2014 11:43:32 AM by V.RAJESH
Method Info : COLUMN: XDBC18, 4.6 X 150MM,5U
MOBILE PHASE: 55% ACN IN WATER (0.1% F.A)
FLOW RATE: 1ML/MIN
DETECTION: 210 NM

Sample Info :



Instrument 1 4/5/2014 11:43:46 AM V.RAJESH Page 1 of 2

HPLC Chromatogram of 27

Data File D:\DATA\DKM2014\04042014000054.D
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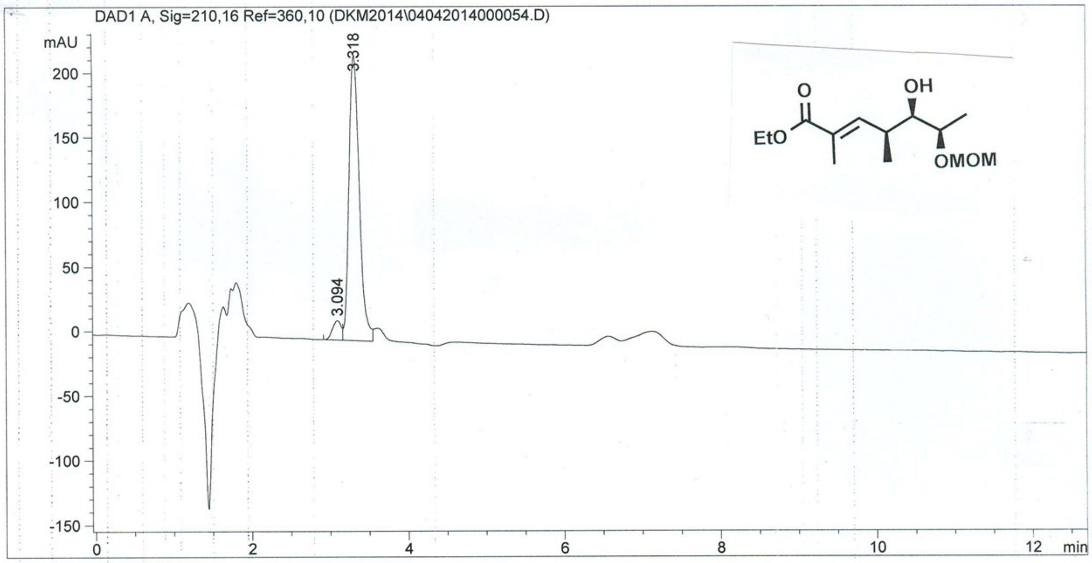

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Area Percent Report
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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,16 Ref=360,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.094	BV	0.1232	114.64812	14.99150	5.3594
2	3.318	VV	0.1469	2024.55969	220.91406	94.6406
Totals :				2139.20782	235.90556	

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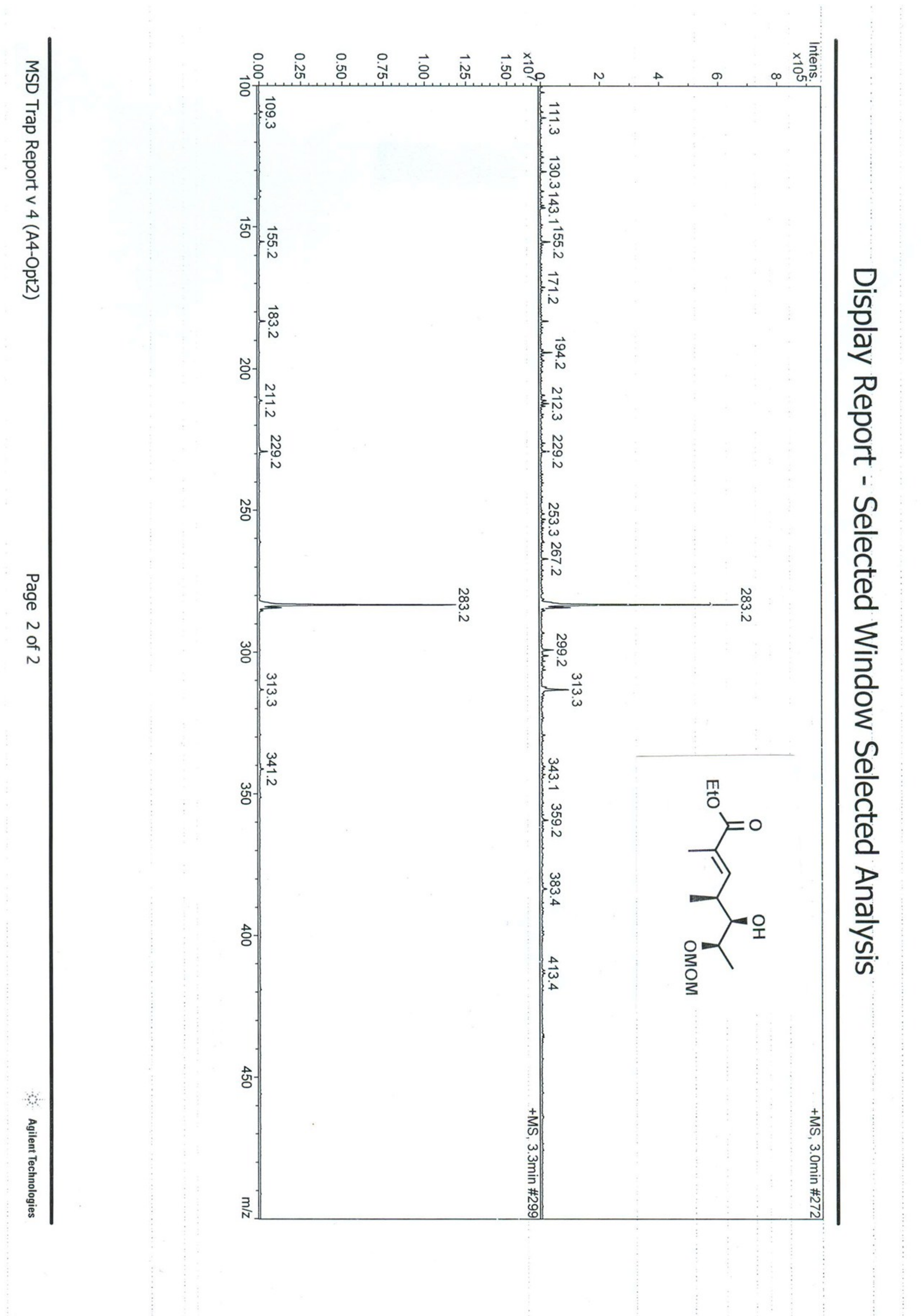
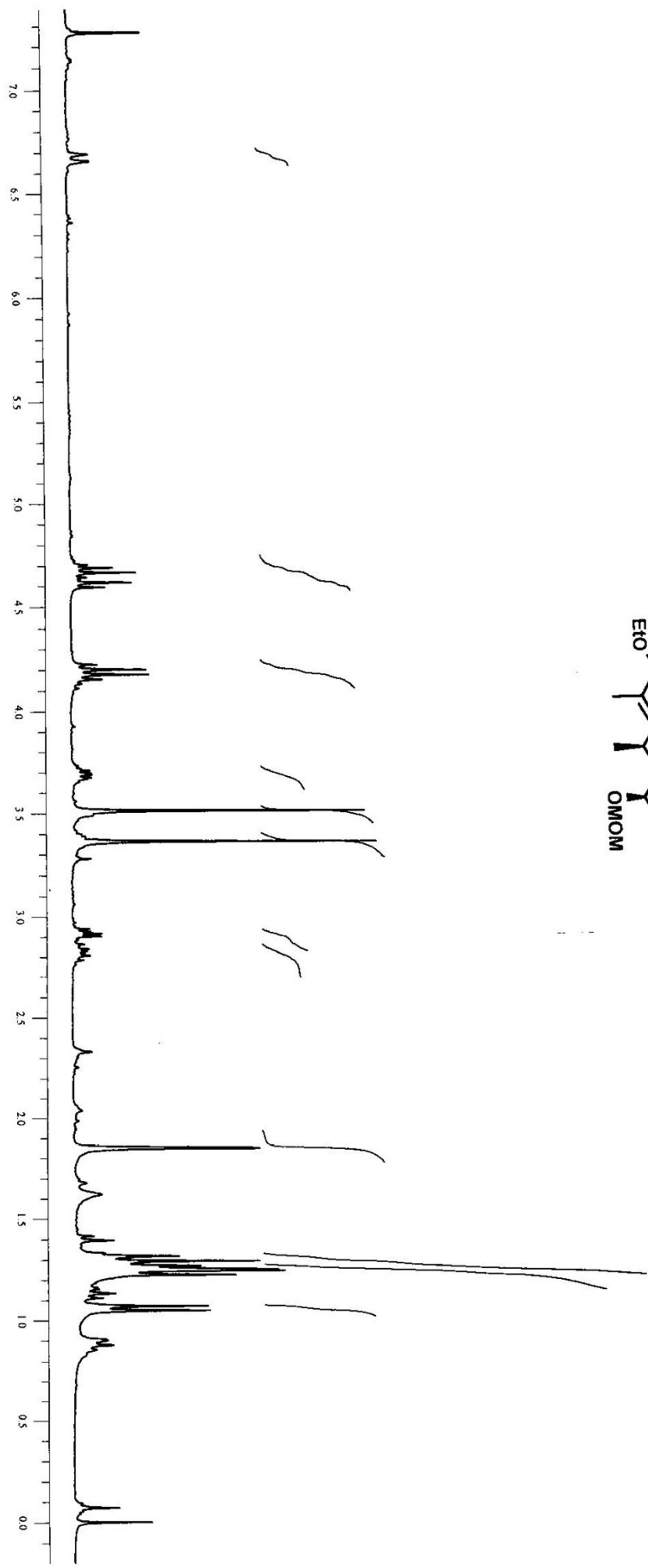
*** End of Report ***

Instrument 1 4/5/2014 11:43:46 AM V.RAJESH Page 2 of 2

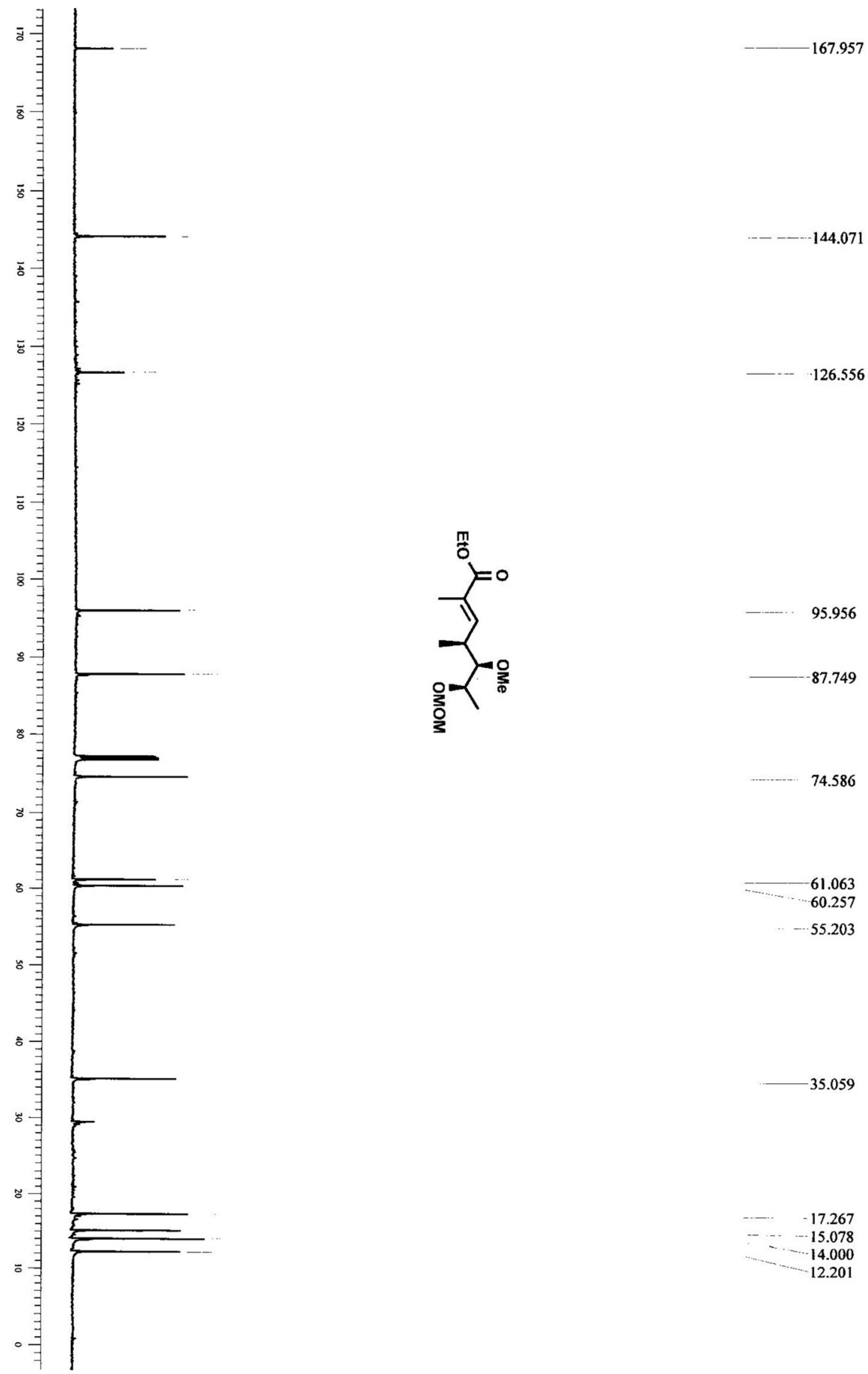
HPLC Chromatogram of 27



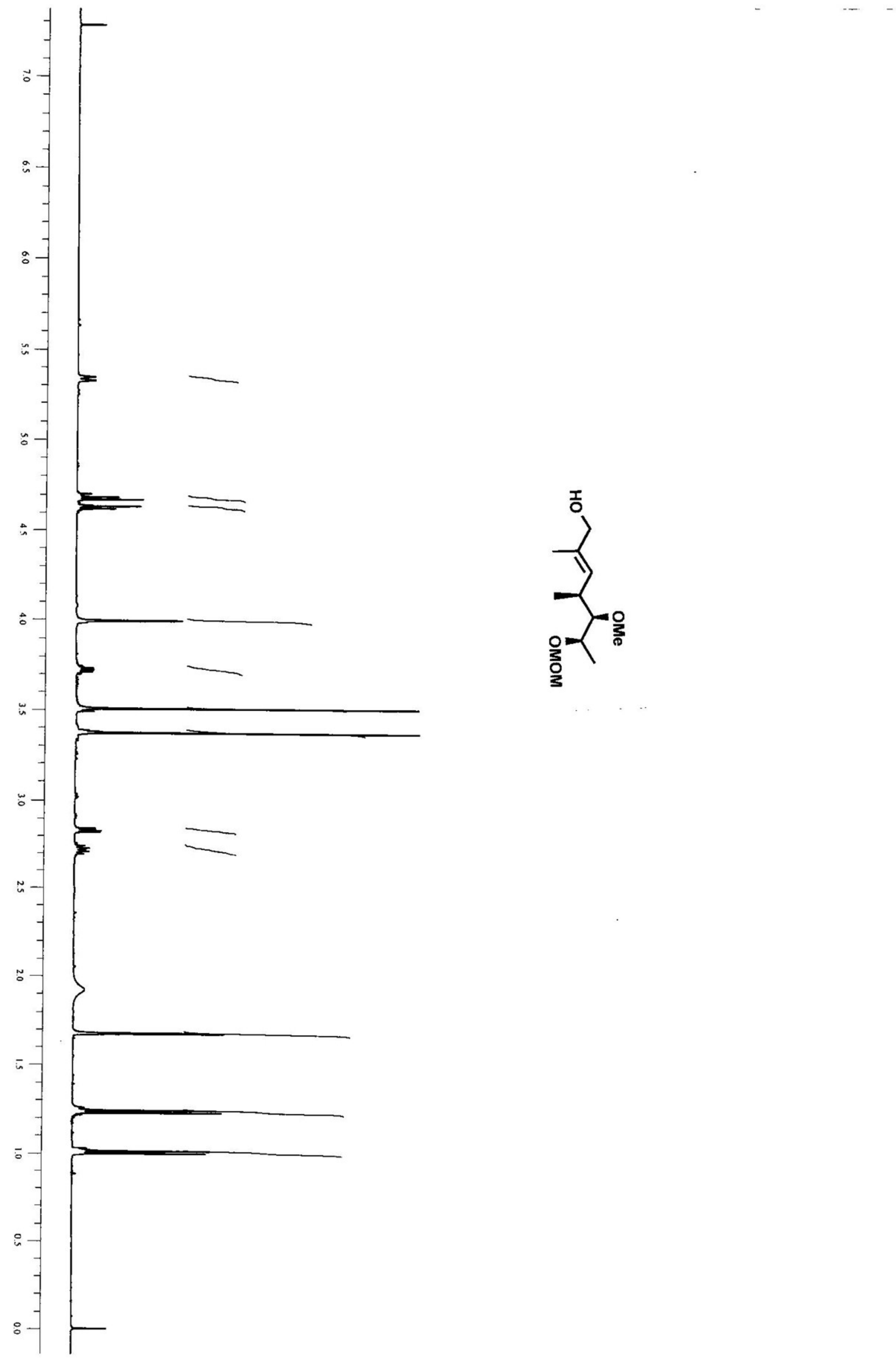
LCMS Chromatogram of 27



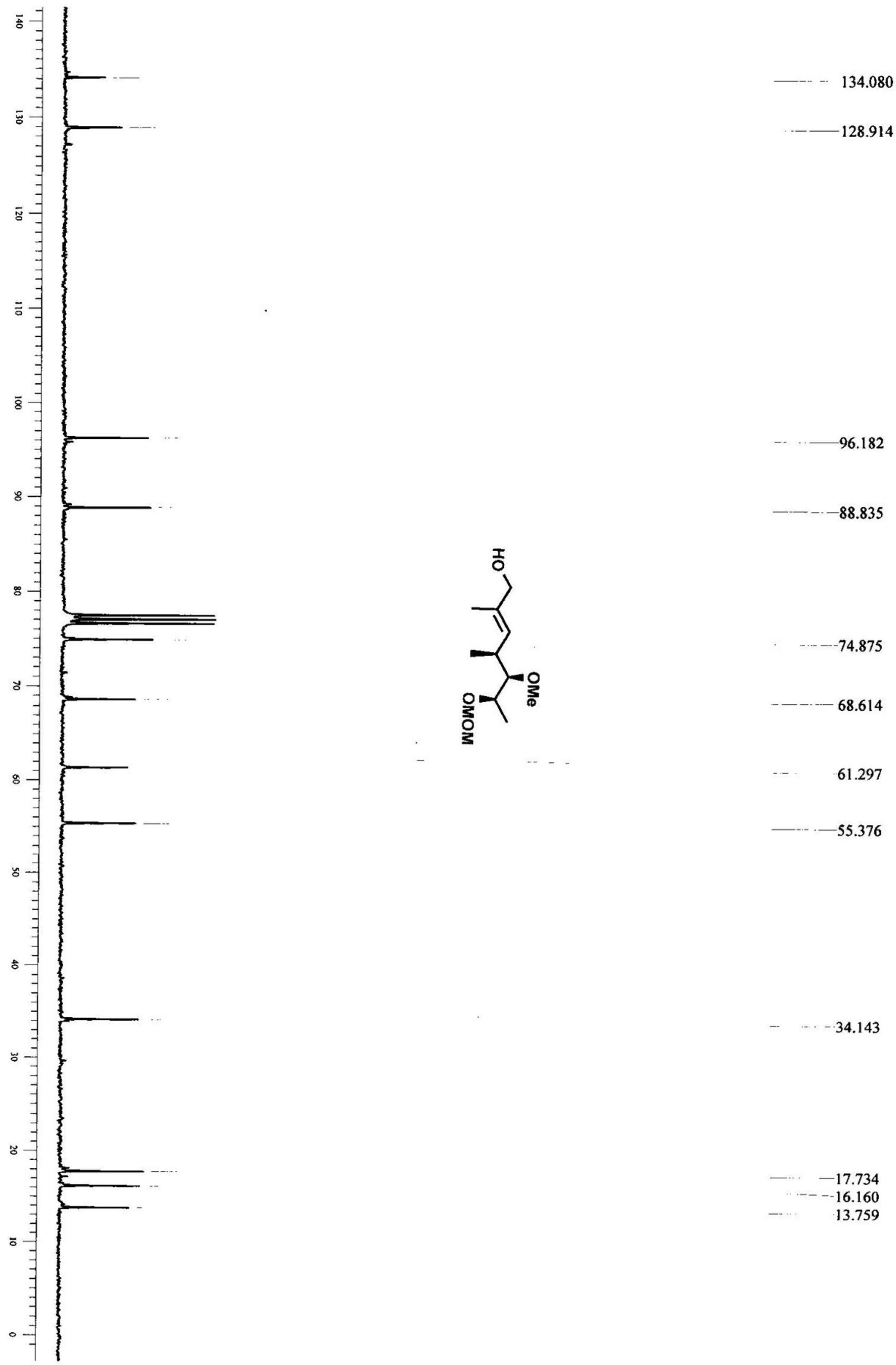
^{1}H NMR of 7 ($CDCl_3$, 300 MHz)



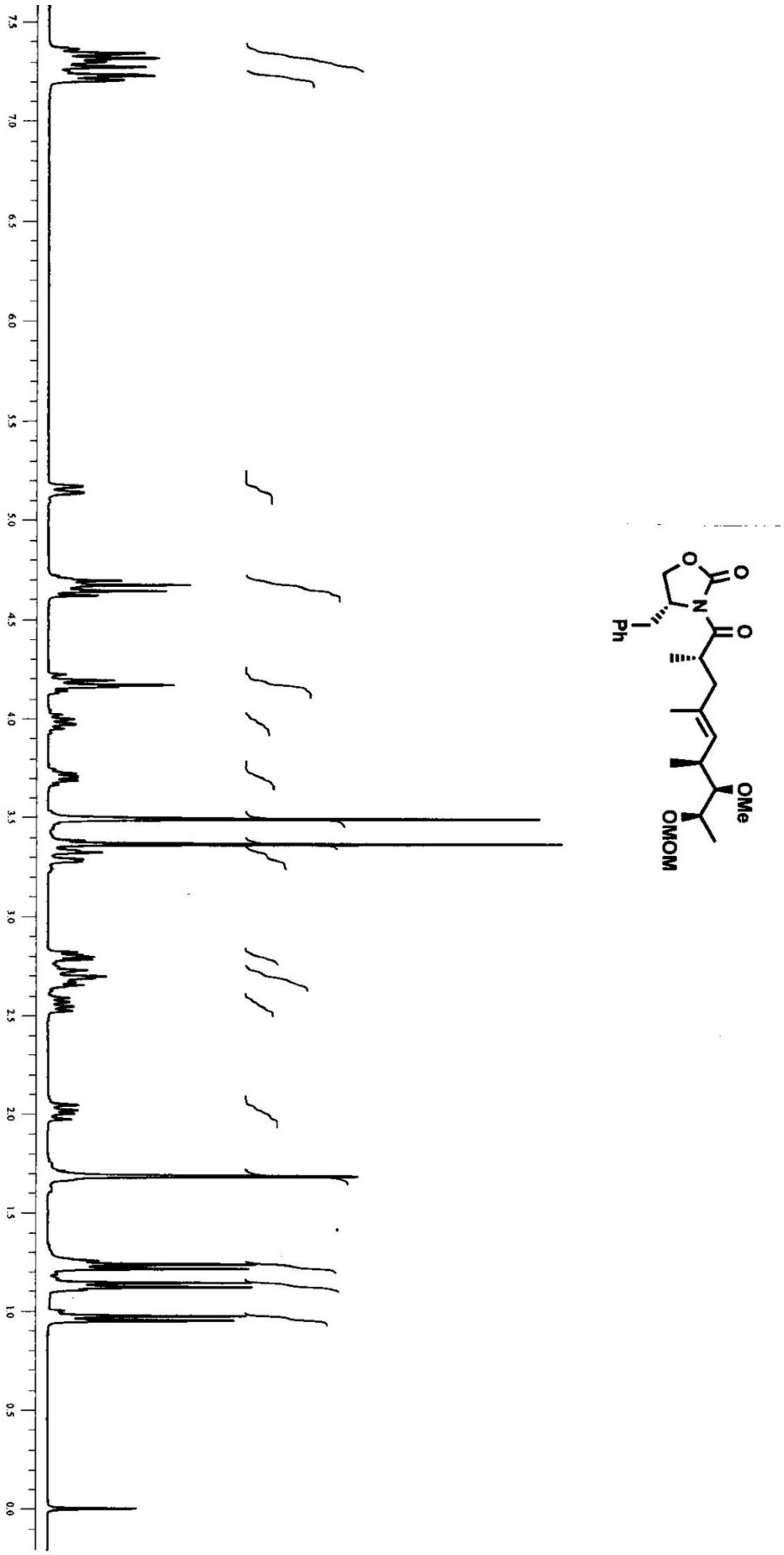
^{13}C NMR of 7 ($CDCl_3$, 75 MHz)



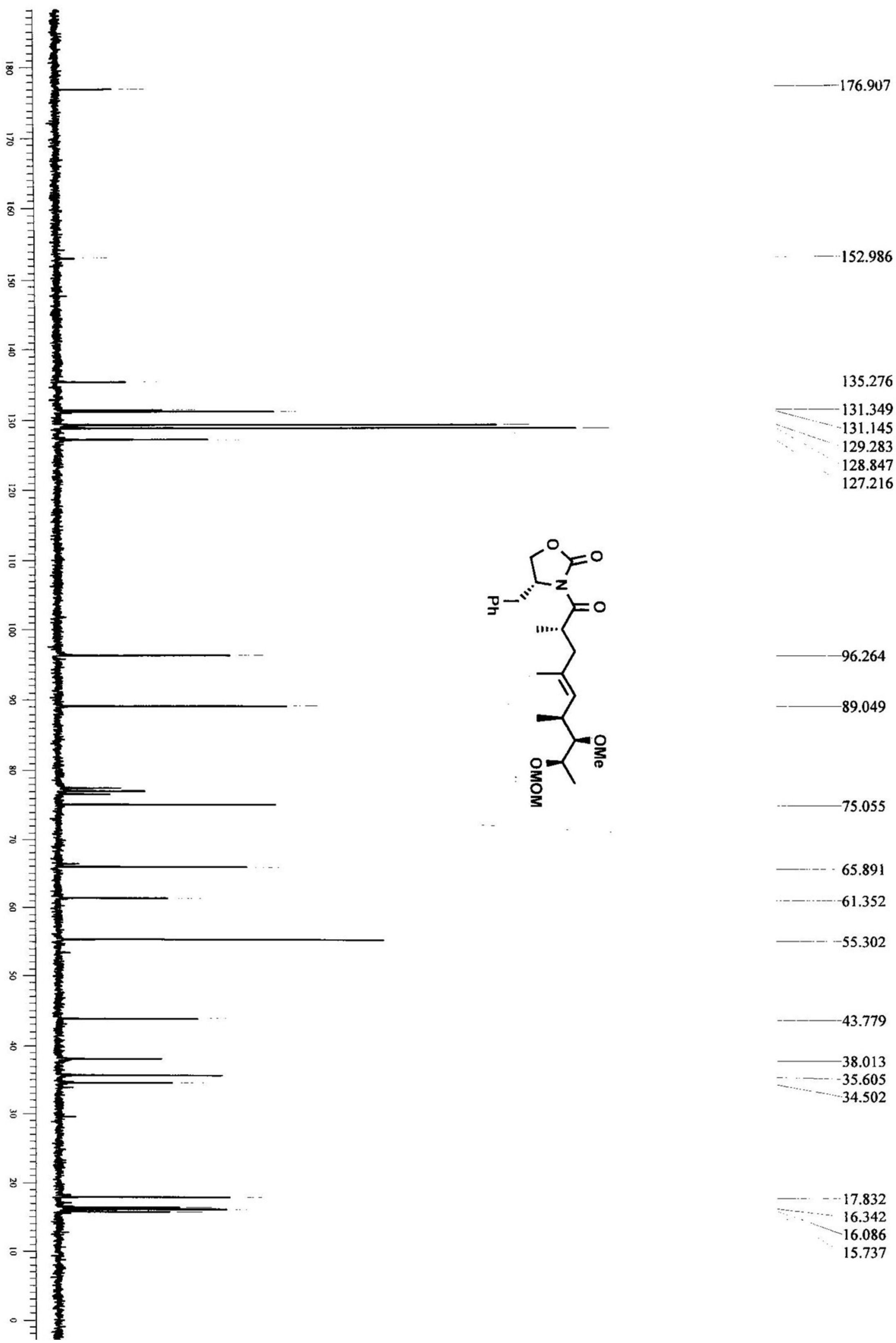
^{1}H NMR of 28 ($CDCl_3$, 300 MHz)



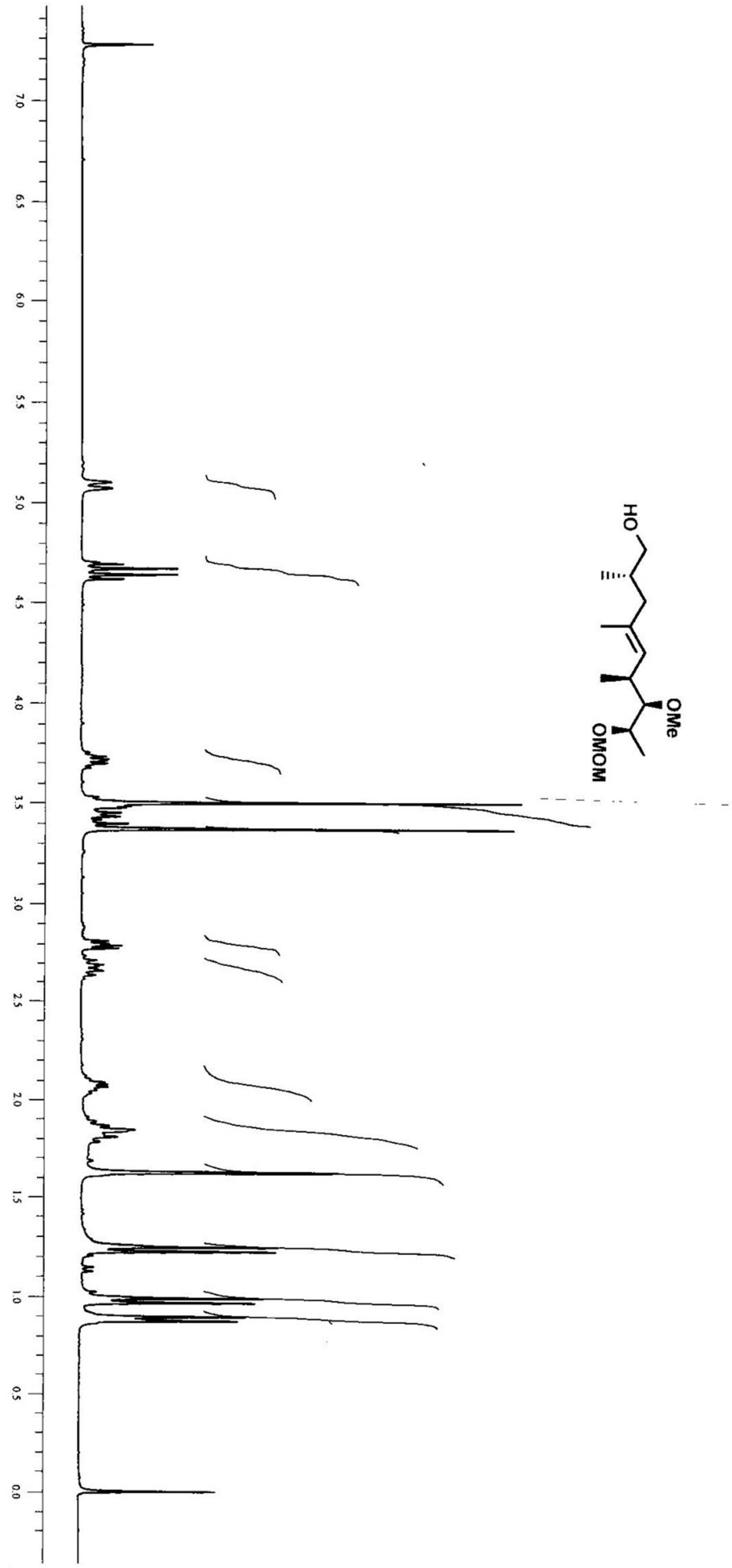
^{13}C NMR of 28 ($CDCl_3$, 75 MHz)



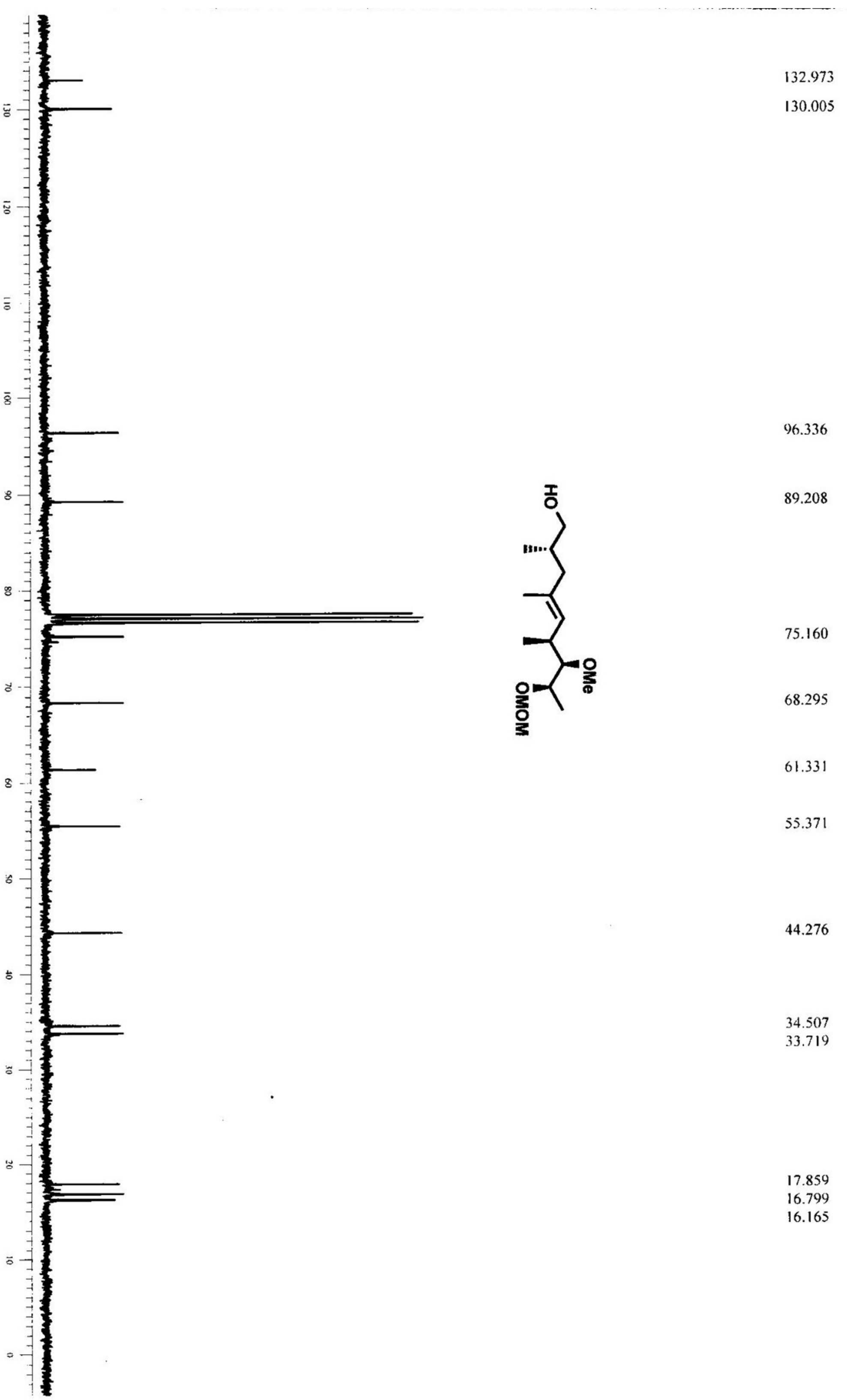
^{1}H NMR of 30 ($CDCl_3$, 300 MHz)



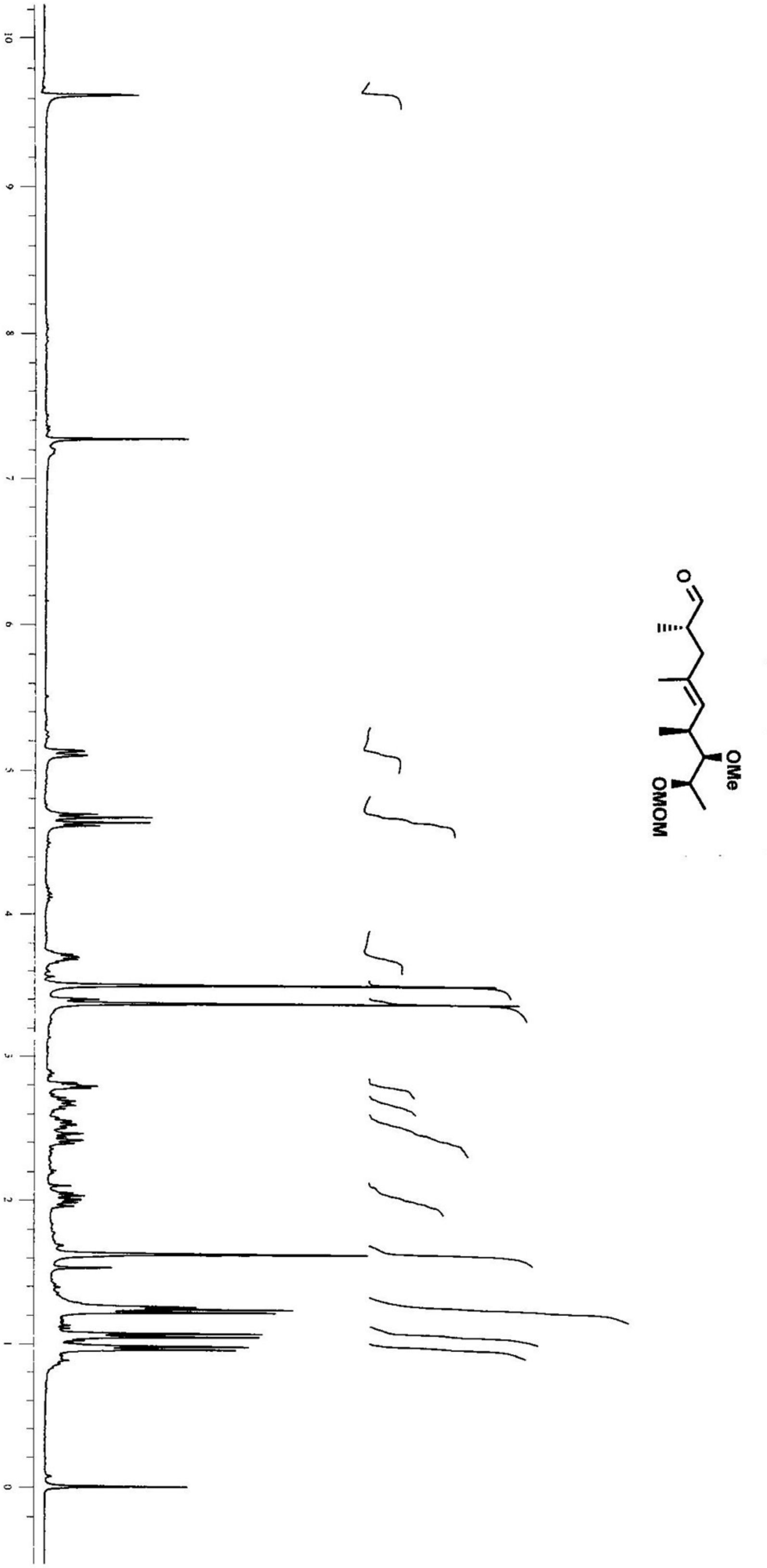
^{13}C NMR of 30 ($CDCl_3$, 75 MHz)



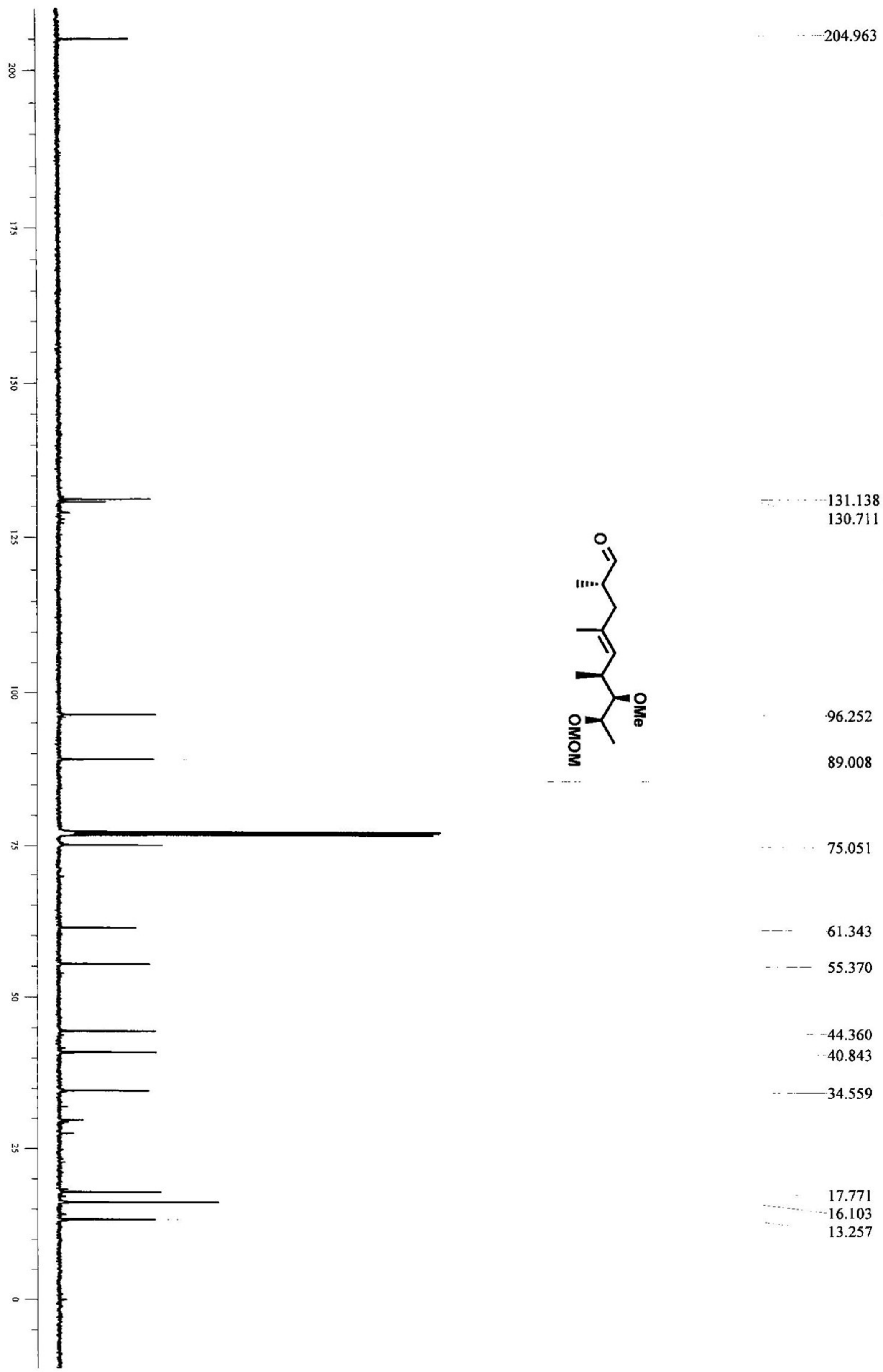
[1]H NMR of 31 ($CDCl_3$, 300 MHz)



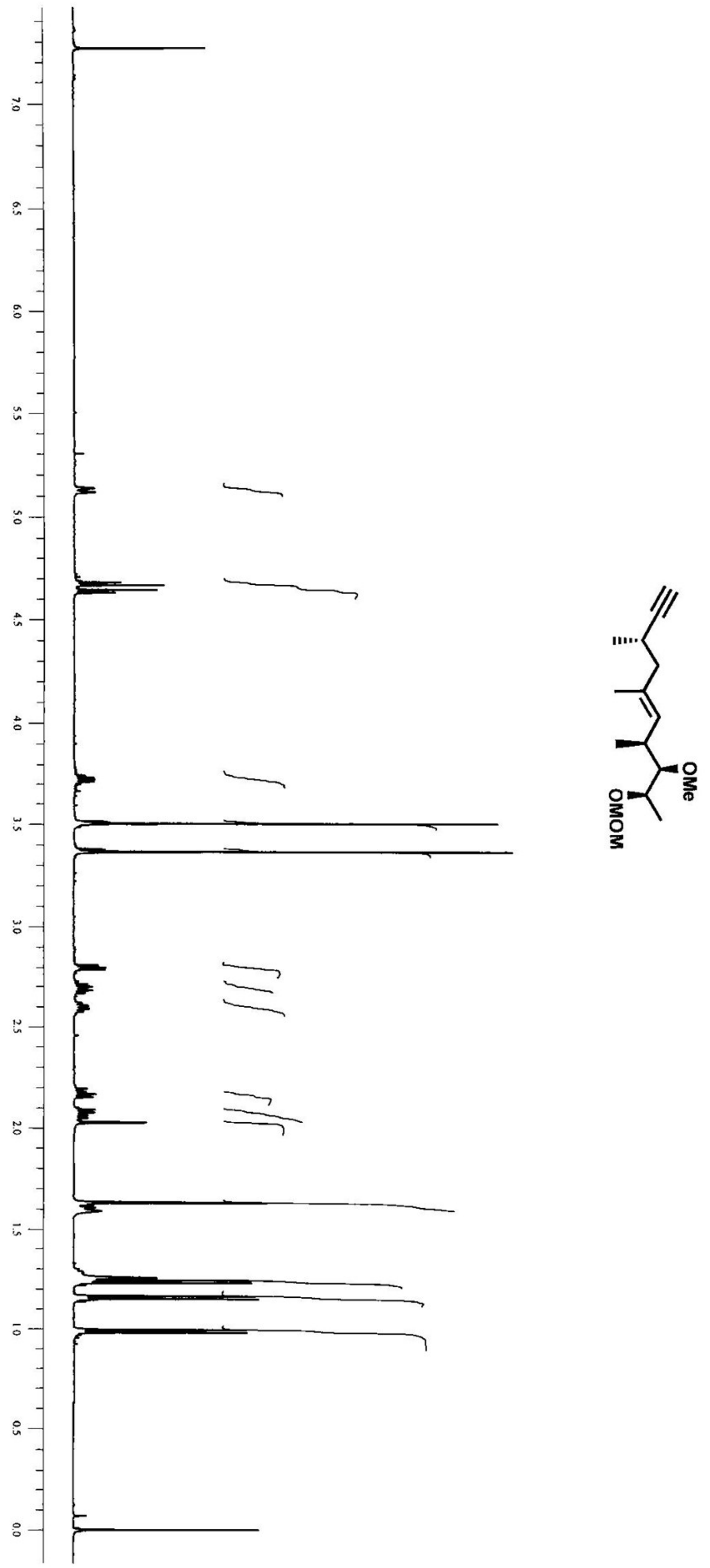
^{13}C NMR of 31 ($CDCl_3$, 75 MHz)



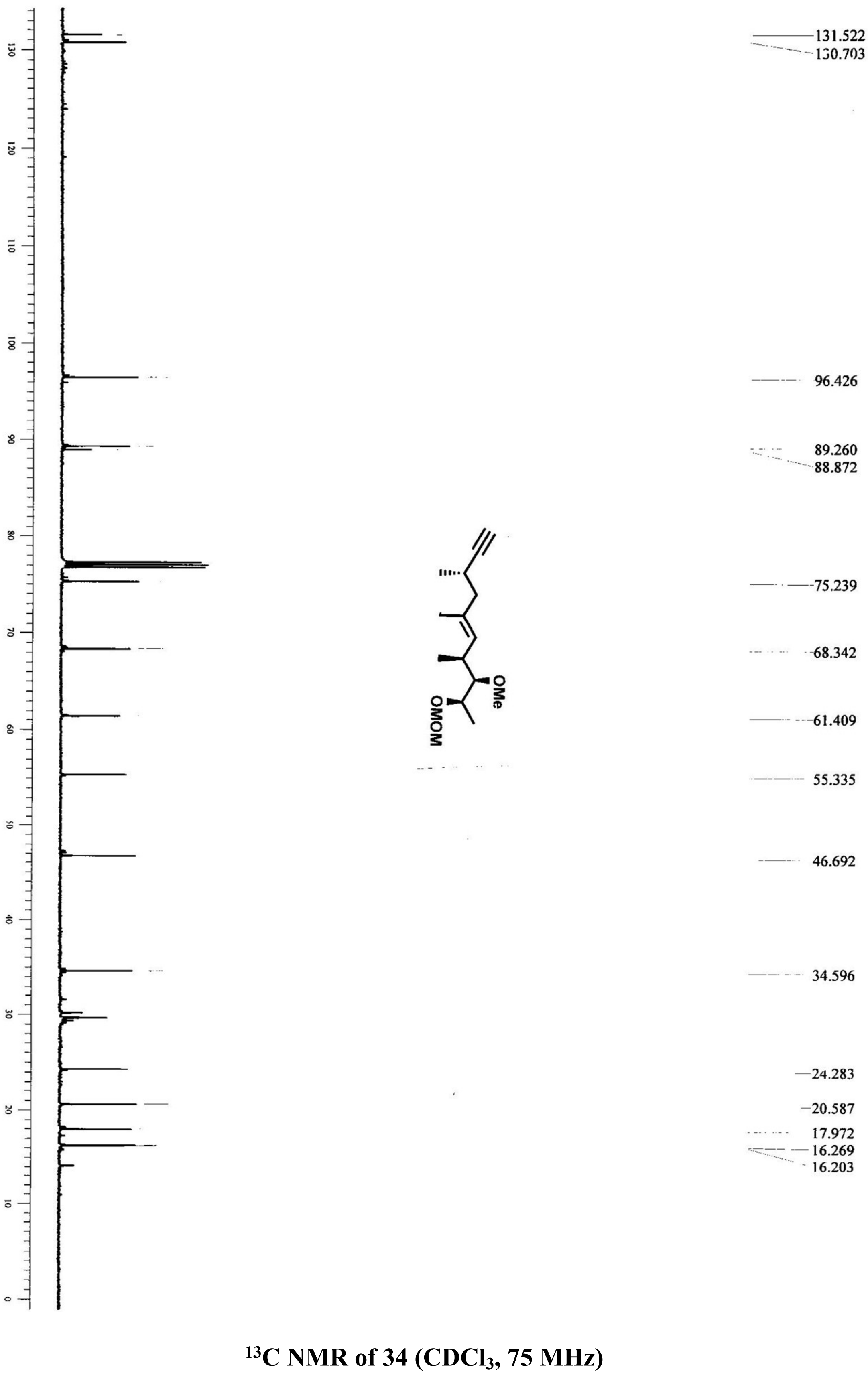
^{1}H NMR of 32 ($CDCl_3$, 300 MHz)



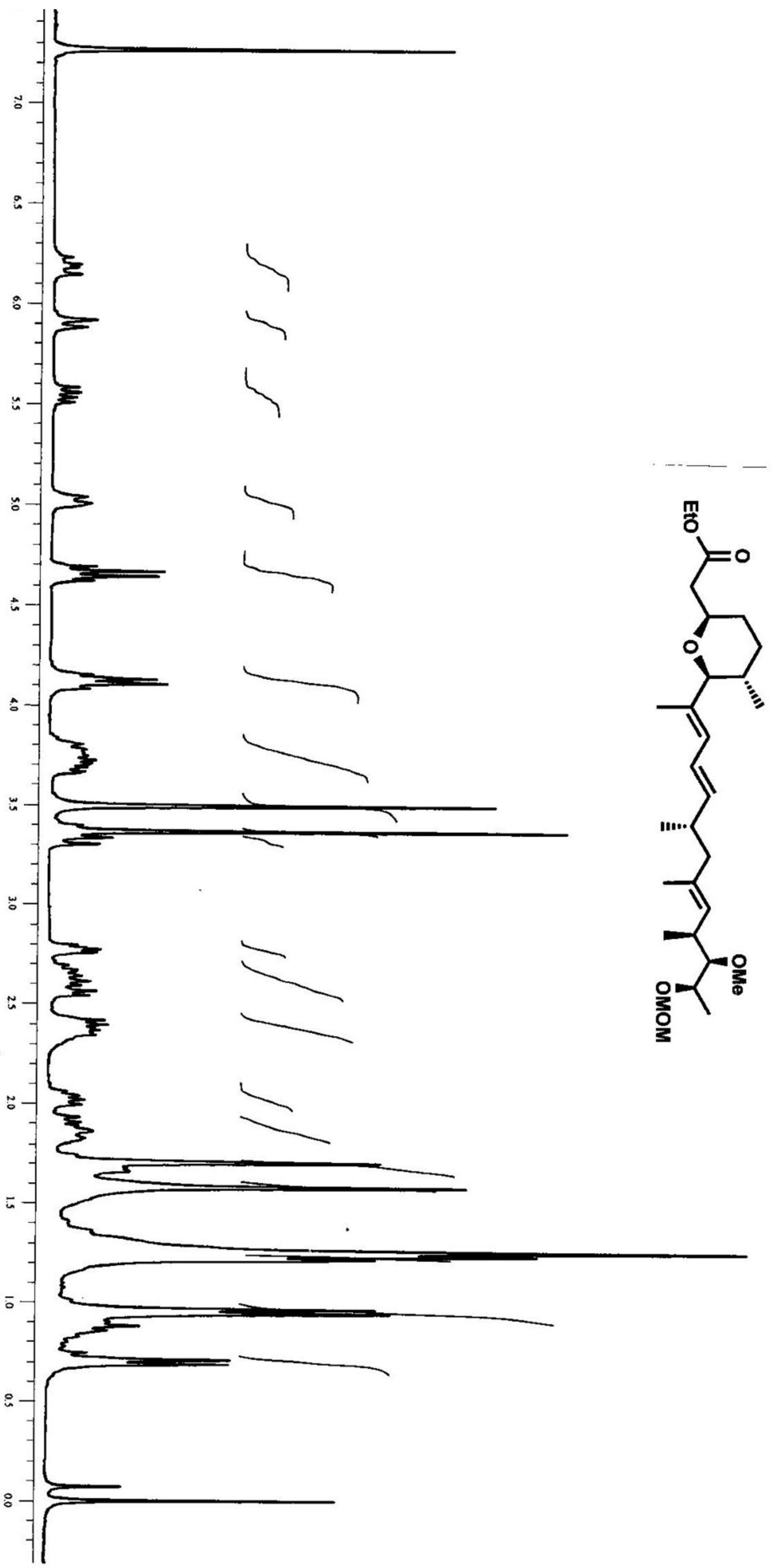
^{13}C NMR of 32 ($CDCl_3$, 75 MHz)



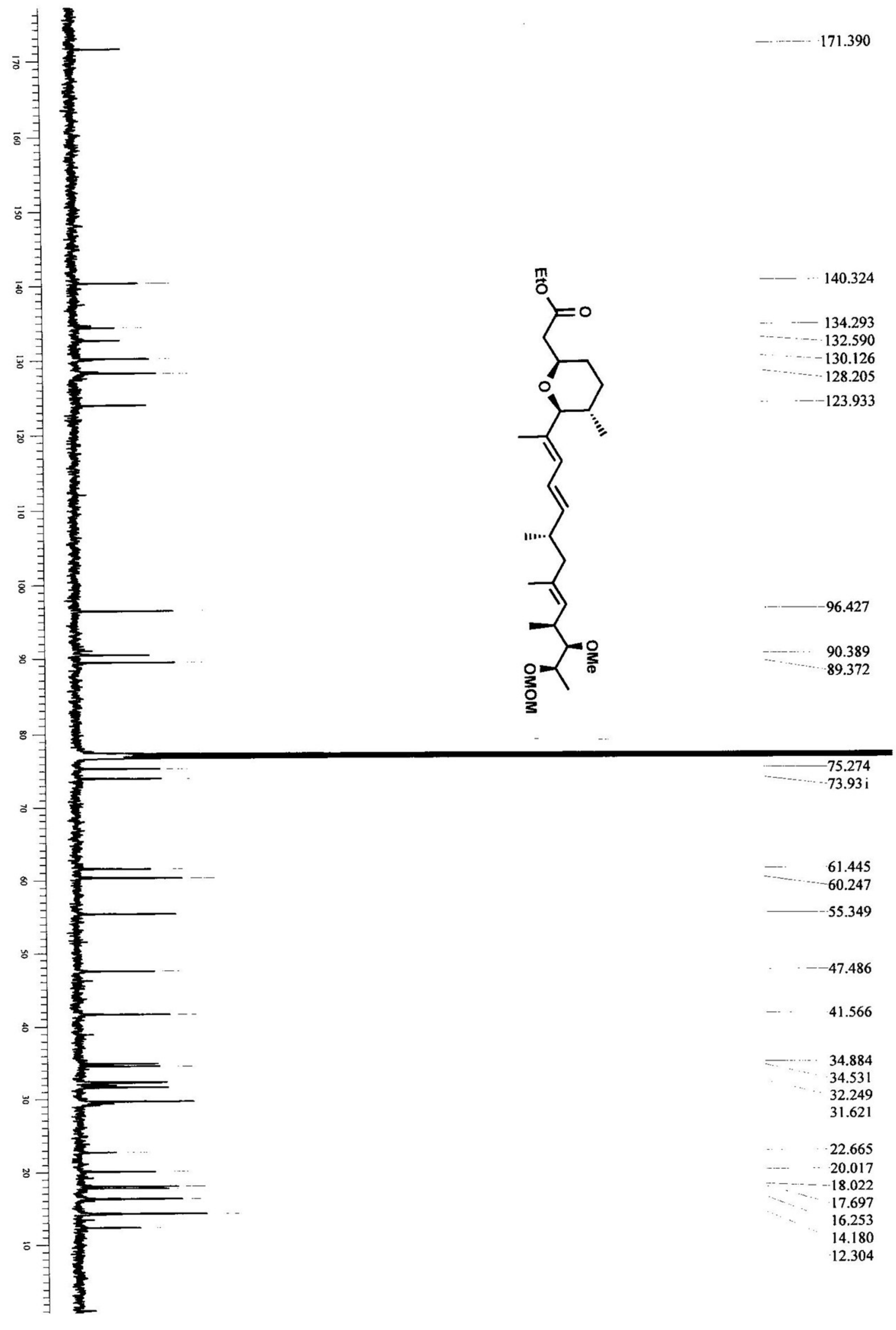
^{1}H NMR of 34 ($CDCl_3$, 300 MHz)



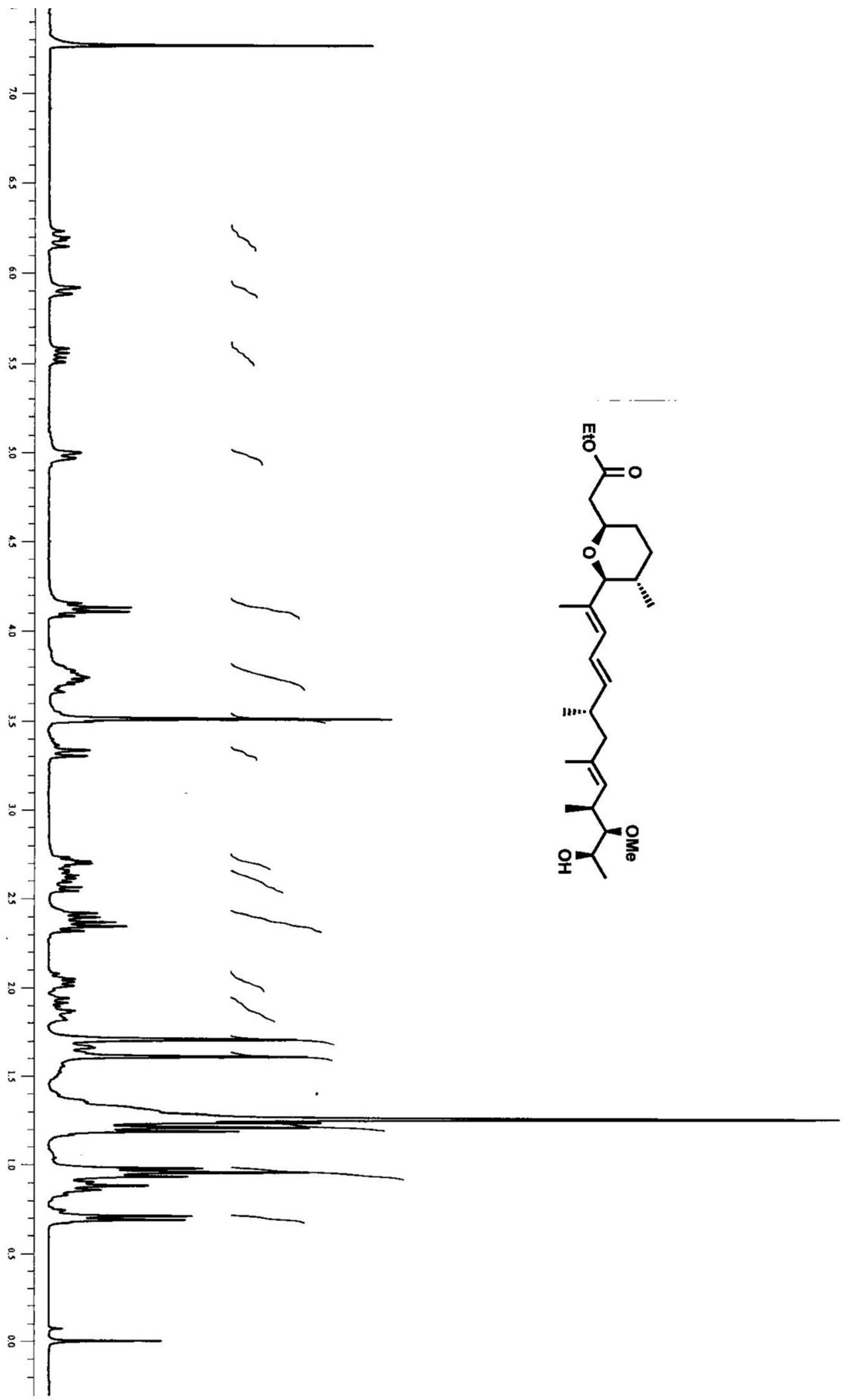
^{13}C NMR of 34 ($CDCl_3$, 75 MHz)



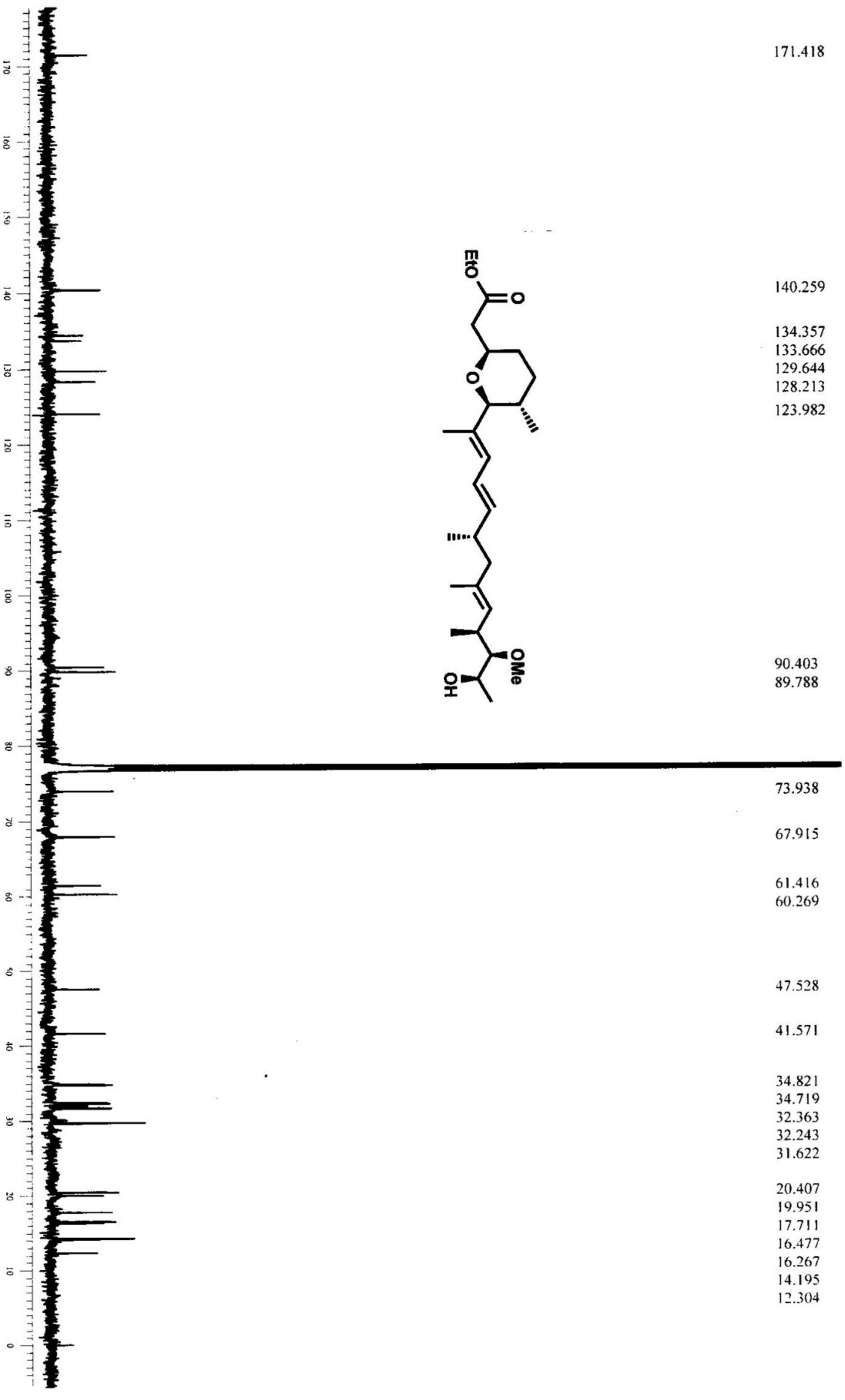
^{1}H NMR of 35a ($CDCl_3$, 300 MHz)



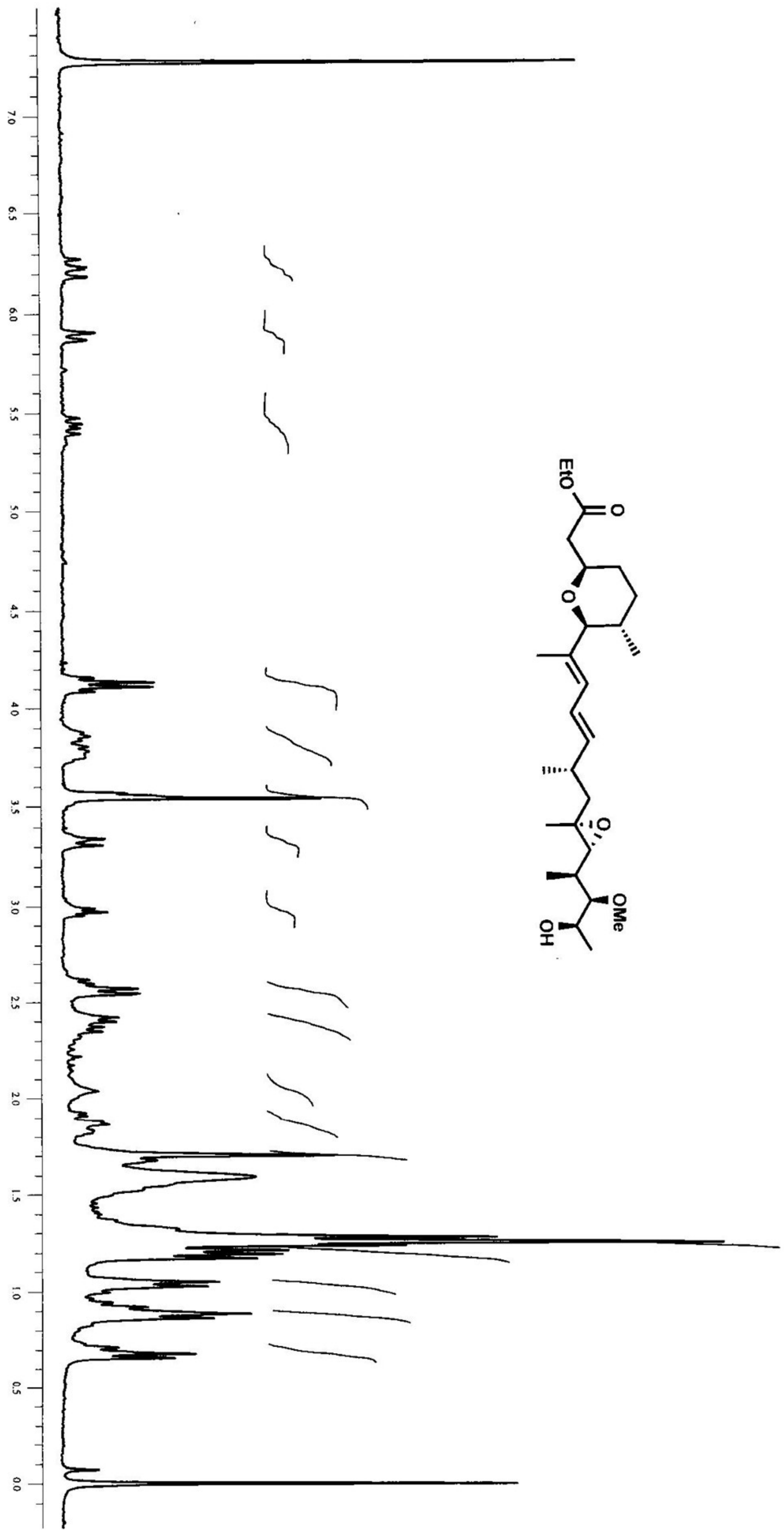
^{13}C NMR of 35a ($CDCl_3$, 75 MHz)



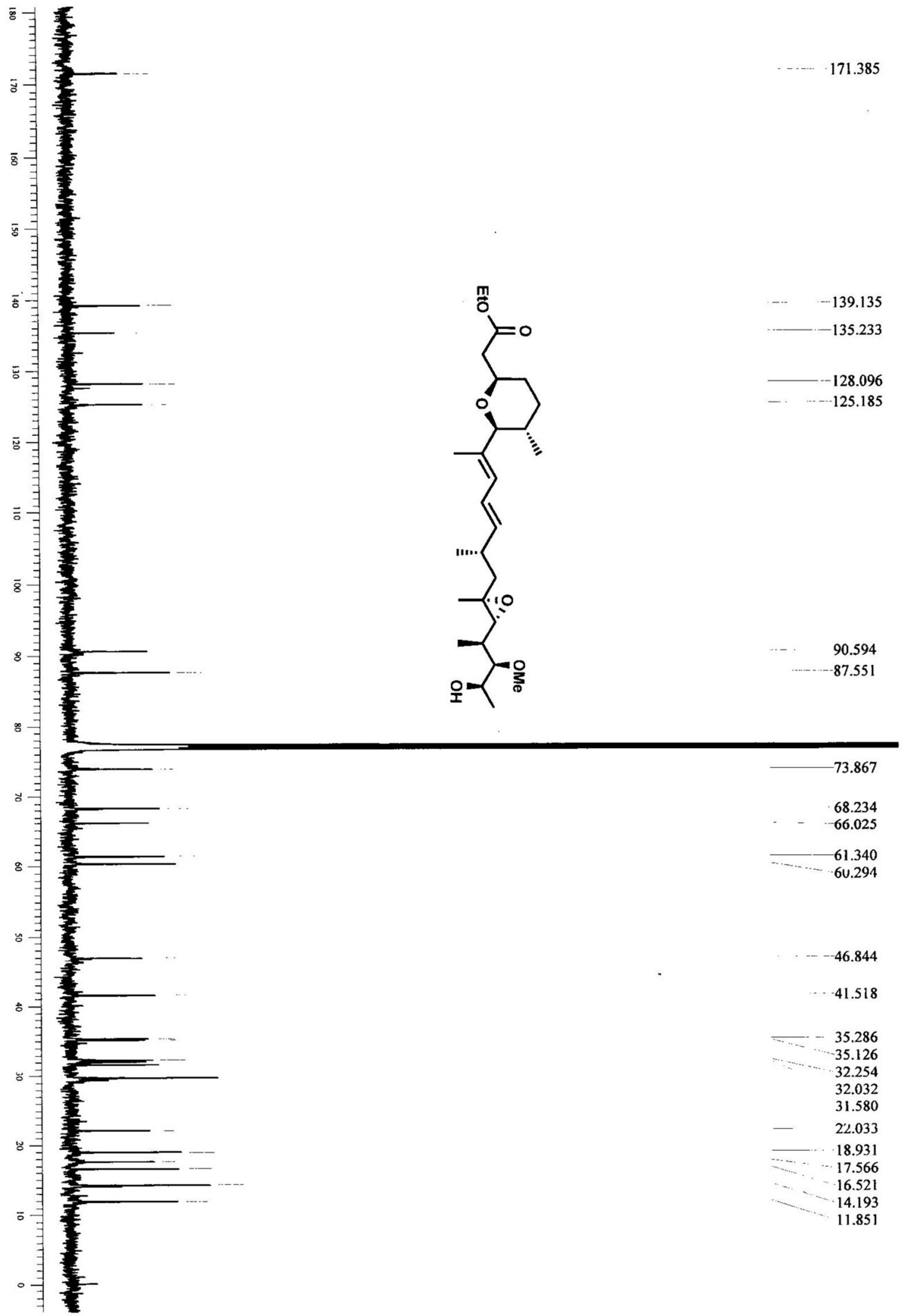
¹H NMR of 35 ($CDCl_3$, 300 MHz)



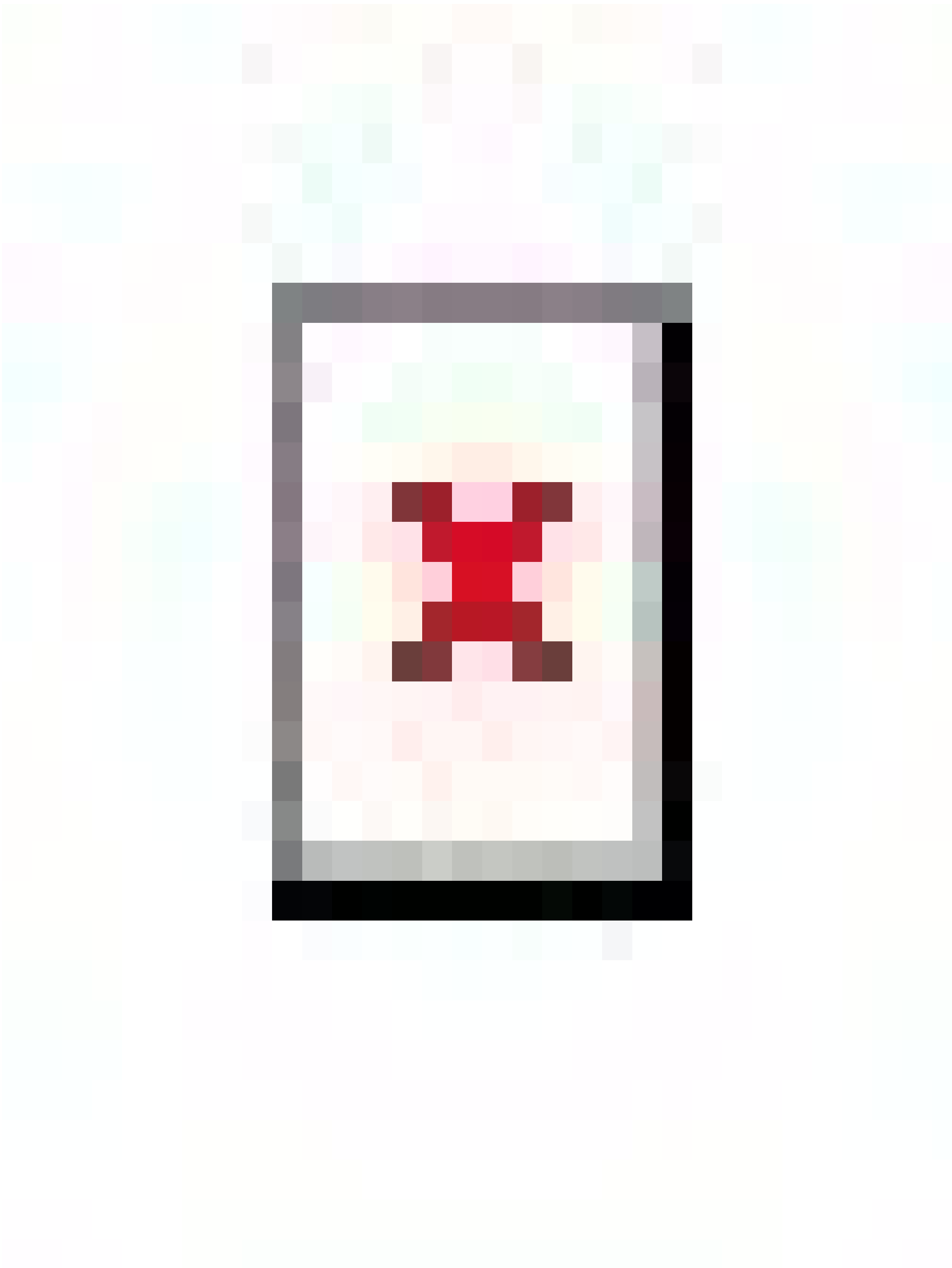
[13]C NMR of 35 ($CDCl_3$, 75 MHz)



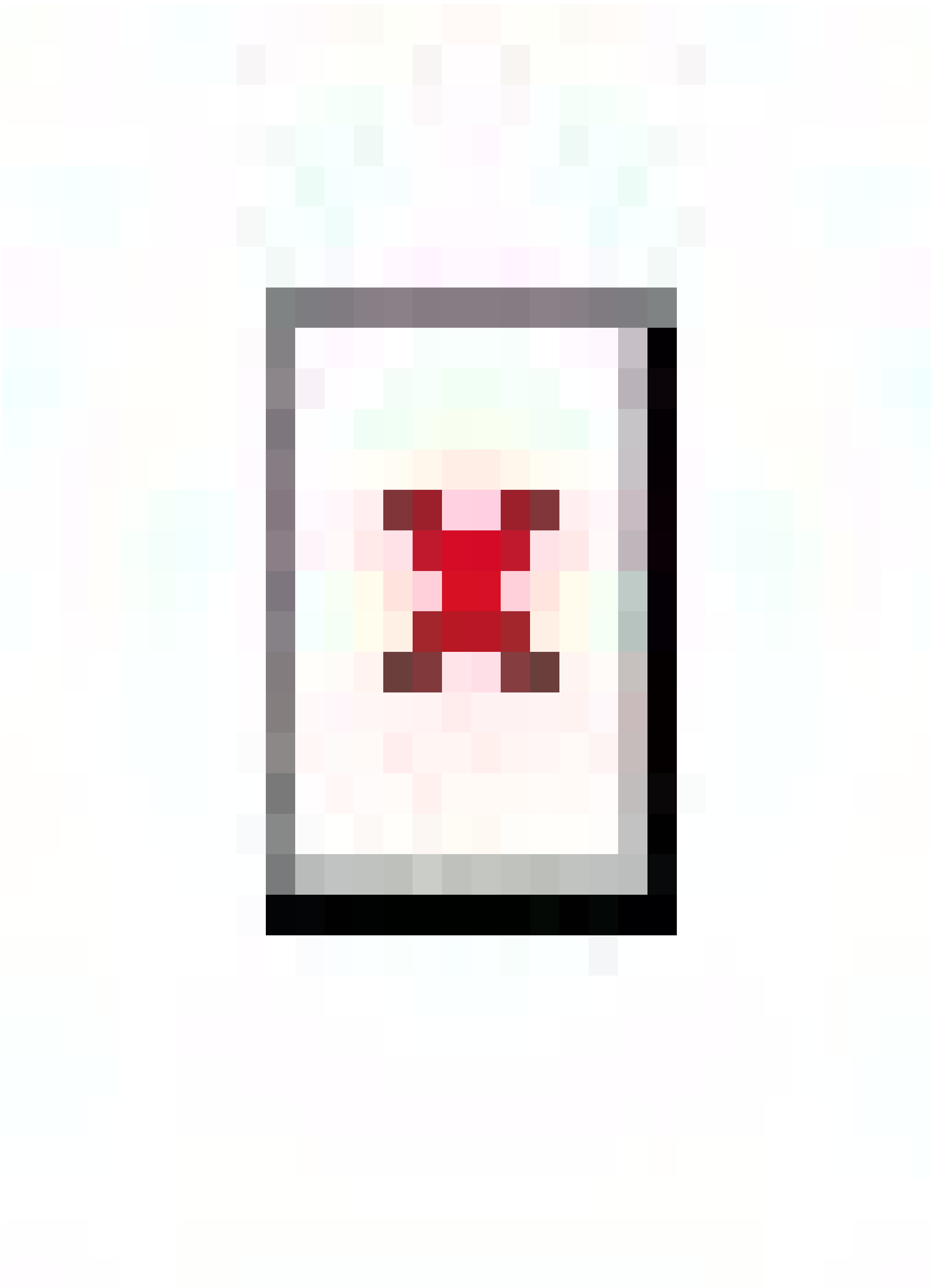
^{1}H NMR of 36 ($CDCl_3$, 300 MHz)



^{13}C NMR of 36 ($CDCl_3$, 125 MHz)



[1]H NMR of 1 ($CDCl_3$, 300 MHz)



^{13}C NMR of 1 ($CDCl_3$, 75 MHz)

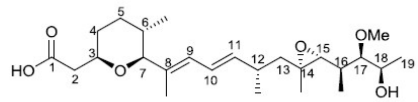


Table 1: ^{1}H NMR data of our synthesis, natural product and Kocienski total synthesis

Position	Natural[1]			Kocienski[10]			Our Synthesis		
	δ	multiplicity	*J* (Hz)	δ	multiplicity	*J* (Hz)	δ	multiplicity	*J* (Hz)
2A	2.45	dd	14.1, 6.6	2.46	dd	15.6, 7.2	2.46	m	-
2B	2.25	dd	14.1, 7.5	2.38	dd	15.3, 5.7	2.39	dd	15.4, 5.3
3	3.76	m	-	3.80-3.70	m	-	3.81-3.75	m	-
4A	1.86–1.68	m	-	1.90-1.82	m	-	1.89-1.84	m	-
4B	1.30	m	-	1.40-1.22	m	-	1.39-1.32	m	-
5A	1.86-1.68	m	-	1.74-1.65	m	-	1.74-1.72	m	-
5B	1.26-1.12	m	-	1.40-1.22	m	-	1.39-1.32	m	-
6	1.55	m	-	1.60-1.43	m	-	1.62-1.47	m	-
6-Me	0.66	d	6.6	0.68	d	6.6	0.69	d	6.5
7	3.34	d	9.9	3.34	d	9.9	3.35	d	9.8
8-Me	1.68	s	-	1.69	s		1.70	s	-
9	5.90	d	11.1	5.92	d	10.8	5.92	d	10.8
10	6.29	dd	15.0, 10.8	6.30	dd	15.0, 10.8	6.30	dd	15.1, 10.8
11	5.45	dd	15.0, 9.0	5.47	dd	15.0, 9.1	5.48	dd	15.1, 9.1
12	2.44	m	-	2.50-2.38	m	-	2.48-2.43	m	-
12-Me	1.03	d	6.6	1.04	d	6.7	1.05	d	6.5
13A	1.91	dd	13.1, 4.3	1.92	dd	13.4, 4.3	1.93	dd	13.4, 4.3
13B	1.26-1.12	m	-	1.18	dd	13.0, 11.2	1.27-1.15	m	-
14-Me	1.27	s	-	1.28	s	-	1.28	s	-
15	2.65	d	9.6	2.65	d	9.4	2.66	d	9.5
16	1.45	m	-	1.60-1.43	m	-	1.62-1.47	m	-
16-Me	0.83	d	6.9	0.83	d	6.9	0.83	d	7.0
17	2.96	dd	6.0, 4.5	2.97	dd	6.1, 4.3	2.98	dd	6.2, 4.3
18	3.78	dq	6.6,6.3	3.78	q	6.4	3.79	q	6.5
19	1.11	d	6.6	1.10	d	6.4	1.11	d	6.5
O-Me	3.52	s	-	3.52	s	-	3.53	s	-

Table 2: ^{13}C NMR data of our synthesis, natural product and Kocienski total synthesis:

Position	Natural δ^{1}	Kocienski δ^{10}	Our Synthesis δ	$\Delta\delta$ with natural	$\Delta\delta$ with Kocienski
C1	179.8	175.3	175.4	-4.4	+0.1
C2	46.4	42.3	42.3	-4.1	0.0
C3	77.0	75.5	75.6	-1.4	+0.1
C4	33.1	32.8	32.8	-0.3	0.0
C5	33.7	33.4	33.5	-0.2	+0.1
C6	33.5	33.4	33.4	-0.1	0.0
C6-Me	18.2	18.1	18.1	-0.1	0.0
C7	92.2	92.2	92.2	0.0	0.0
C8	136.5	136.2	136.2	-0.3	0.0
C8-Me	12.1	12.1	12.1	0.0	0.0
C9	129.5	129.6	129.7	+0.2	+0.1
C10	126.6	126.5	126.6	0.0	+0.1
C11	140.5	140.7	140.7	+0.2	0.0
C12	36.5	36.6	36.6	+0.1	0.0
C12-Me	22.7	22.7	22.7	0.0	0.0
C13	48.1	48.1	48.1	0.0	0.0
C14	62.6	62.6	62.7	+0.1	+0.1
C14-Me	16.8	16.8	16.8	0.0	0.0
C15	67.8	67.9	67.9	+0.1	0.0
C16	36.4	36.4	36.6	+0.2	+0.2
C16-Me	11.7	11.5	11.6	-0.1	+0.1
C17	88.6	88.5	88.6	0.0	+0.1
C18	69.8	69.9	69.9	+0.1	0.0
C19	19.9	19.8	19.9	0.0	+0.1
OMe	61.9	61.9	61.9	0.0	0.0

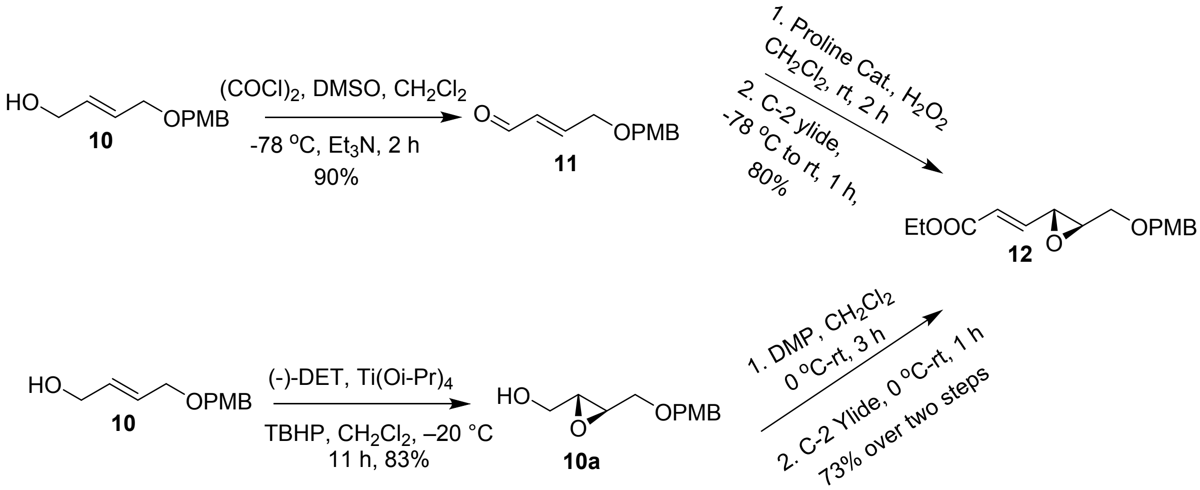
Table 3: ^{1}H NMR data of our synthesis, natural product and literature syntheses:

Position	Natural δ^{1} (mulitiplicity, J Hz)	Kocienski δ^{10} (mulitiplicity, J Hz)	J. S. Panek δ^{13} (mulitiplicity, J Hz)	C. J. Forsyth δ^{14} (mulitiplicity, J Hz)	A. K. Ghosh δ^{15} (mulitiplicity, J Hz)	P. Romea, F. Urpí δ^{16} (mulitiplicity, J Hz)	Our Synthesis δ (mulitiplicity, J Hz)
2A	2.45 (dd, 14.1, 6.6)	2.46 (dd,15.6, 7.2)	2.46 (dd, 15.6, 7.2)	2.47 (dd, 15.3, 7.2)	2.46 (dd, 15.3, 7.3)	2.47 (dd, 15.3, 7.3)	2.46 (m, -)
2B	2.25 (dd, 14.1, 7.5)	2.38 (dd, 15.3, 5.7)	2.38 (dd, 15.6, 7.0)	2.38 (dd, 15.3, 5.7)	2.38 (dd, 15.3, 5.7)	2.39 (dd, 15.3, 5.7)	2.39 (dd, 15.4, 5.3)
3	3.76 (m, -)	3.80-3.70 (m, -)	3.80-3.70 (m, -)	3.83-3.74 (m, -)	3.79-3.74 (m, -)	3.80-3.74 (m, -)	3.81-3.75 (m, -)
4A	1.86–1.68 (m, -)	1.90-1.82 (m, -)	1.90-1.82 (m, -)	1.93 (dd, 13.5, 4.2)	1.93 (dd, 13.3, 4.3)	1.93 (dd, 13.4, 4.3)	1.89-1.84 (m, -)
4B	1.30 (m, -)	1.40-1.22 (m, -)	1.40-1.22 (m, -)	1.36-1.28 (m, -)	1.39-1.21	1.39-1.28 (m, -)	1.39-1.32 (m, -)
5A	1.86-1.68 (m, -)	1.74-1.65 (m, -)	1.74-1.65 (m, -)	1.88-1.78 (m, -)	1.88-1.84 (m, -)	1.74-1.68 (m,-)	1.74-1.72 (m, -)
5B	1.26-1.12 (m, -)	1.40-1.22 (m, -)	1.40-1.22 (m, -)	1.60-1.45 (m, -)	1.52-1.47 (m, -)	1.61-1.46 (m, -)	1.39-1.32 (m, -)
6	1.55 (m, -)	1.60-1.43 (m, -)	1.60-1.43 (m ,-)	1.60-1.45 (m, -)	1.58-1.53 (m, -)	1.61-1.46 (m, -)	1.62-1.47 (m, -)
6-Me	0.66 (d, 6.6)	0.68 (d, 6.6)	0.70 (d, 6.8)	0.68 (d, 6.6)	0.69 (d, 6.6)	0.69 (d, 6.6)	0.69 (d, 6.5)
7	3.34 (d, 9.9)	3.34(d, 9.9)	3.34(d, 10.0)	3.35(d, 9.9)	3.35(d, 9.9)	3.35 (d, 9.8)	3.35(d, 9.8)
8-Me	1.68 (s, -)	1.69 (s, -)	1.70 (s, -)	1.69 (s, -)	1.69 (s, -)	1.70 (d, 1.2)	1.70 (s, -)
9	5.90 (d, 11.1)	5.92 (d, 10.8)	5.92 (d, 10.8)	5.92 (d, 10.8)	5.92 (d, 10.8)	5.92 (brd, 10.8)	5.92 (d, 10.8)
10	6.29 (dd, 15.0, 10.8)	6.30 (dd, 15.0, 10.8)	6.30 (dd, 14.8, 10.8)	6.31(dd, 15.0, 10.8)	6.30 (dd, 15.0, 10.7)	6.30 (ddd, 15.0, 10.8, 0.5)	6.30 (dd,15.1, 10.8)
11	5.45 (dd, 15.0, 9.0)	5.47 (dd, 15.0, 9.1)	5.50 (dd, 14.8, 8.8)	5.48 (dd, 15.0, 9.0)	5.47 (dd, 14.9, 9.1)	5.48 (dd, 15.0, 9.1)	5.48 (dd, 15.1, 9.1)
12	2.44 (m, -)	2.50-2.38 (m,-)	2.50-2.38 (m, -)	2.50-2.30 (m, -)	2.45-2.42 (m,-)	2.48-2.42 (m, -)	2.48-2.43 (m,-)
12-Me	1.03 (d, 6.6)	1.04 (d, 6.7)	1.05 (d, 6.4)	1.04 (d, 6.6)	1.05 (d, 6.7)	1.05 (d, 6.7)	1.05 (d, 6.5)
13A	1.91(dd, 13.1, 4.3)	1.92 (dd, 13.4, 4.3)	1.92 (dd,13.2, 4.4)	1.93 (dd,13.5, 4.2)	1.93 (dd, 13.4, 4.3)	1.93 (dd, 13.4, 4.3)	1.93 (dd, 13.4, 4.3
13B	1.26-1.12 (m, -)	1.18 (dd,13.0, 11.2)	1.26-1.18 (m, -)	1.24-1.15 (m, -)	1.22-1.15 (m, -)	1.27-1.15 (m, -)	1.27-1.15 (m, -)
14-Me	1.27 (s,)	1.28 (s, -)	1.29 (s, -)	1.28 (s, -)	1.28 (s, -)	1.28 (s, -)	1.28 (s, -)
15	2.65 (d, 9.6)	2.65 (d, 9.4)	2.65 (d, 9.2)	2.65 (d, 9.3)	2.66 (d, 9.4)	2.66 (d, 9.4)	2.66 (d, 9.5)
16	1.45 (m,-)	1.60-1.43 (m, -)	1.60-1.43 (m, -)	1.60-1.45 (m, -)	1.58-1.53 (m, -)	1.61-1.43 (m, -)	1.62-1.47 (m, -)
16-Me	0.83 (d, 6.9)	0.83 (d, 6.9)	0.83 (d, 7.0)	0.82 (d, 6.9)	0.83 (d, 7.0)	0.83 (d, 7.0)	0.83 (d, 7.0)
17	2.96 (dd, 6.0, 4.5)	2.97 (dd, 6.1, 4.3)	2.98 (dd, 6.4, 4.4)	2.97(dd, 6.3, 4.2)	2.97 (dd, 6.3, 4.2)	2.98 (dd, 6.4, 4.2)	2.98 (dd, 6.2, 4.3)
18	3.78 (dq, 6.6,6.3)	3.78 (q, 6.4)	3.81(q, 6.4)	3.83-3.74 (m, -)	3.81 (q, 6.4)	3.79 (p, 6.4)	3.79 (q, 6.5)
19	1.11 (d, 6.6)	1.10 (d, 6.4)	1.11 (d, 6.4)	1.11 (d, 6.6)	1.11 (d, 6.5)	1.11 (d, 6.4)	1.11 (d, 6.5)
OMe	3.52 (s,-)	3.52 (s, -)	3.52 (s, -)	3.52 (s, -)	3.53 (s, -)	3.53 (s, -)	3.53 (s, -)

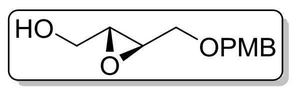
Table 4: ^{13}C NMR data of our synthesis, natural product and literature syntheses

Position	Natural δ[1]	Kocienski δ[10]	J. S. Panek δ[13]	C. J. Forsyth δ[14]	A. K. Ghosh δ[15]	P. Romeo, Urpí δ[16]	Our Synthesis δ
C1	179.8	175.3	175.1	175.5	175.4	175.2	175.4
C2	46.4	42.3	42.3	42.5	42.4	42.3	42.3
C3	77.0	75.5	75.5	75.7	75.5	75.5	75.6
C4	33.1	32.8	32.8	32.9	32.8	32.8	32.8
C5	33.7	33.4	33.7	33.6	33.5	33.5	33.5
C6	33.5	33.4	33.5	33.5	33.4	33.4	33.4
C6-Me	18.2	18.1	18.0	18.2	18.1	18.1	18.1
C7	92.2	92.2	91.9	92.3	92.2	92.2	92.2
C8	136.5	136.2	136.2	136.3	136.2	136.2	136.2
C8-Me	12.1	12.1	12.6	12.2	12.1	12.1	12.1
C9	129.5	129.6	129.2	129.8	129.6	129.6	129.7
C10	126.6	126.5	126.4	126.7	126.6	126.5	126.6
C11	140.5	140.7	140.5	140.9	140.7	140.7	140.7
C12	36.5	36.6	36.4	36.7	36.6	36.5	36.6
C12-Me	22.7	22.7	22.4	22.9	22.7	22.7	22.7
C13	48.1	48.1	48.0	48.3	48.3	48.1	48.1
C14	62.6	62.6	62.7	62.8	62.6	62.6	62.7
C14-Me	16.8	16.8	16.9	16.8	16.8	16.8	16.8
C15	67.8	67.9	67.8	68.0	67.9	67.9	67.9
C16	36.4	36.4	36.2	36.6	36.6	36.4	36.6
C16-Me	11.7	11.5	11.5	11.7	11.5	11.6	11.6
C17	88.6	88.5	88.6	88.7	88.5	88.6	88.6
C18	69.8	69.9	69.9	70.1	69.9	69.9	69.9
C19	19.9	19.8	19.9	20.0	19.8	19.8	19.9
OMe	61.9	61.9	61.9	62.0	61.9	61.9	61.9

Alternative scheme for the synthesis of compound 12:

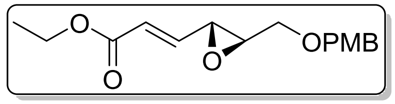


((2*R*,3*R*)-3-(((4-methoxybenzyl)oxy)methyl)oxiran-2-yl)methanol (10a):



To a suspension of flame dried 4Å molecular sieves CH_2Cl_2 (40 mL) at −30 °C, was added D-(−)- diethyl tartarate (0.69 mL, 4.03 mmol) followd by $Ti(OiPr)_4$ (0.59 mL, 2.02 mmol) and tertbutylhydroperoxide (6.7 mL, 6 M solution in toluene, 40.4 mmol) The reaction mixture was stirred at −30 °C for 1 h before addition of allylic alcohol **10** (4.2 g, 20.2 mmol) in anhydrous CH_2Cl_2 (20 mL). The reaction mixture was stirred at −20 °C for 10 h. After completion of the reaction (monitored by TLC), it was quenched with 20% NaOH solution (50 mL). The reaction mass was allowed to stir for 1 h before filtration through a small bed of Celite and washed with CH_2Cl_2 (50 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layer was washed with water (2 x 100 mL) and dried solvent removed under reduced pressure. The crude mass was purified by silica gel chromatography (ethyl acetate/ hexane = 1:3) to afford **10a** (4.0 g, 88%) as a light yellow liquid. $[\alpha]_D^{25}$ +14.4 (96% ee)[1]; IR (Neat): 3494, 3018, 1612, 1245, 1216, 1038 cm ^{1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.50 (ABq, J = 21.5, 11.6 Hz, 2H), 3.90 (dd, J = 12.8, 1.3 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, J = 11.6, 3.0 Hz, 1H), 3.62 (dd, J = 12.6, 4.1 Hz, 1H), 3.49 (dd, J = 12.3, 5.9 Hz, 1H), 3.21 (m, 1H), 3.07 (m, 1H), 2.20 (br s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 129.9, 129.4, 113.8, 72.8, 69.5, 61.4, 55.9, 55.2, 54.4 ppm. HRMS (ESI): m/z calcd. for $C_{12}H_{14}O_3Na$ $[M + Na]^+$: 229.0835; found: 229.0847.

(*E*)-Ethyl3-((2R,3S)-3-((R)-1-(methoxymethoxy)ethyl)oxiran-2-yl)-2-methylacrylate(12):



To a stirred solution of epoxy alcohol **10a** (1.0 g, 4.46 mmol) in dry CH_2Cl_2 (15 mL), was added Dess-Martin periodinane (2.2 g, 5.35 mmol) at 0 °C under nitrogen atmosphere and stirred for 3 h. After completion of the reaction (monitored by TLC), it was quenched with water (10 mL) and filtered through a small bed of Celite. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layer was washed with saturated aqueous sodium thiosulphate solution (2 × 25 mL), saturated aqueous $NaHCO_3$ solution (2 × 20) and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the crude product was used for the next reaction without further purification.

To a stirred solution of crude aldehyde (1.2 g, 5.35 mmol) in benzene (10 mL), was added C-2 Wittig ylide (5.80 g, 16.0 mmol) at room temperature. The reaction mixture was stirred at 40 ^{o}C for 4 h. After completion of the reaction (monitored by TLC), solvent was removed under reduced pressure. The crude mass was purified by silica gel chromatography (ethyl acetate/hexane = 1:10) to furnish **12** (0.91g,70% over two steps) spectral and analytical data of this compound is identical with above compound **12.**

*First method is better than the second because of the good overall yield.

Reference for epoxide

1. A. Takemura, K. Fujiwara, K. Shimawaki, A. Murai, H. Kawai, T. Suzuki, *Tetrahedron*. 2005, **61**, 7392