

Organic-inorganic hybrid porous sulfonated zinc phosphonate material: efficient catalyst for biodiesel synthesis at room temperature

Malay Pramanik, Mahasweta Nandi, Hiroshi Uyama and Asim Bhaumik*

Supporting Information

Table 1S. Indexing of orthorhombic structure of HZnP-1.

<i>h</i>	<i>k</i>	<i>l</i>	2 theta [°]	d
1	0	0	8.015	10.999
2	0	0	16.174	5.494
2	0	1	17.445	5.130
0	0	3	18.697	4.747
2	1	1	20.003	4.424
1	2	0	22.010	4.060
3	0	0	24.395	3.666
0	1	4	27.016	3.297
3	0	2	27.459	3.266
3	1	2	29.182	3.054
3	0	3	30.780	2.902
0	3	1	31.289	2.853
1	3	0	31.727	2.815
1	3	1	32.375	2.762
4	1	1	34.618	2.579
2	0	5	35.481	2.529
3	1	4	36.692	2.451
0	2	5	37.510	2.386
0	0	6	37.808	2.373
4	2	0	38.673	2.327
4	1	3	39.241	2.296
2	2	5	41.164	2.189
1	4	0	42.214	2.142
1	4	1	42.691	2.119
2	4	0	44.616	2.030
4	3	1	45.778	1.980
2	0	7	47.667	1.908
6	0	0	49.651	1.833

Unit cell parameters

Parameters	Deviations
$a = 11.00153$	0.00955
$b = 8.74173$	0.00740
$c = 14.62239$	0.01371
$V = 1371.48 \text{ \AA}^3$	ESD = 2.122

Table 2S. Indexing of orthorhombic structure of HZnPS-1.

<i>h</i>	<i>k</i>	<i>l</i>	2 theta [°]	d
1	1	0	10.600	8.358
0	0	2	11.660	7.653
1	2	0	15.566	5.705
1	2	1	16.304	5.346
0	1	3	18.581	4.774
2	1	1	18.895	4.708
1	3	0	21.394	4.150
2	2	1	22.078	4.032
1	3	1	22.370	4.005
0	3	2	22.846	3.884
1	2	3	23.379	3.803
2	2	2	24.286	3.668
3	0	1	25.719	3.453
0	4	0	26.385	3.380
2	3	1	26.563	3.354
0	4	1	26.916	3.301
0	0	5	29.190	3.061
0	1	5	29.983	2.986
3	3	1	32.687	2.741
2	3	4	35.006	2.557
4	0	2	35.600	2.511
2	5	0	37.367	2.410
4	0	3	37.967	2.358
4	2	2	38.403	2.354
0	0	7	41.214	2.187
1	0	7	42.222	2.142
1	1	7	42.840	2.116
2	6	1	44.037	2.056
0	3	7	46.124	1.967
2	4	6	47.782	1.902

Unit cell parameters

Parameters	Deviations
<i>a</i> = 10.64963	0.01560
<i>b</i> = 13.51797	0.01882
<i>c</i> = 15.30462	0.01518
V = 2203.273	ESD = 4.960

Calculation of acid strength of HZnPS-1: 100 mg sulphonated material (HZnPS-1) was stirred in 50 ml water for 8 h at 313 K. After cooling at room temperature, 10 ml sodium hydroxide solution with strength 0.03125 (N) was added to 10 ml aqueous mixture of HZnPS-1 and stirred overnight. Then after filtration, the excess NaOH solution was titrated with 0.1 (N) oxalic acid solutions. 2.2 ml oxalic acid was required to reach the neutral point.

$$V_{\text{NaOH}} \times S_{\text{NaOH}} \equiv V_{\text{OX}} \times S_{\text{OX}}$$

$$V_{\text{NaOH}} \times 0.03125 \equiv 2.2 \times 0.1$$

$$V_{\text{NaOH}} = 7.02 \text{ ml}$$

So the NaOH required to neutralized the acidic site of the HZnPS-1 = (10-7.02) ml = 2.96 ml.

$$V_{\text{NaOH}} \times S_{\text{NaOH}} \equiv V_{\text{HZnPS-1}} \times S_{\text{HZnPS-1}}$$

$$2.96 \times 0.03125 \equiv 10 \times S_{\text{HZnPS-1}}$$

$$S_{\text{HZnPS-1}} = 0.0093 \text{ (N)}$$

The equivalent weight of sulphonic acid group (-SO₃H) is 81.

So, 50 ml 0.0093 (N) HZnPS-1 mixture solution contains 0.0379 gm free sulphonic acid side.

Calculation: 1000 ml 1 (N) HZnPS-1 \equiv 81 gm free sulphonic acid in the solid matrix (HZnPS-1)

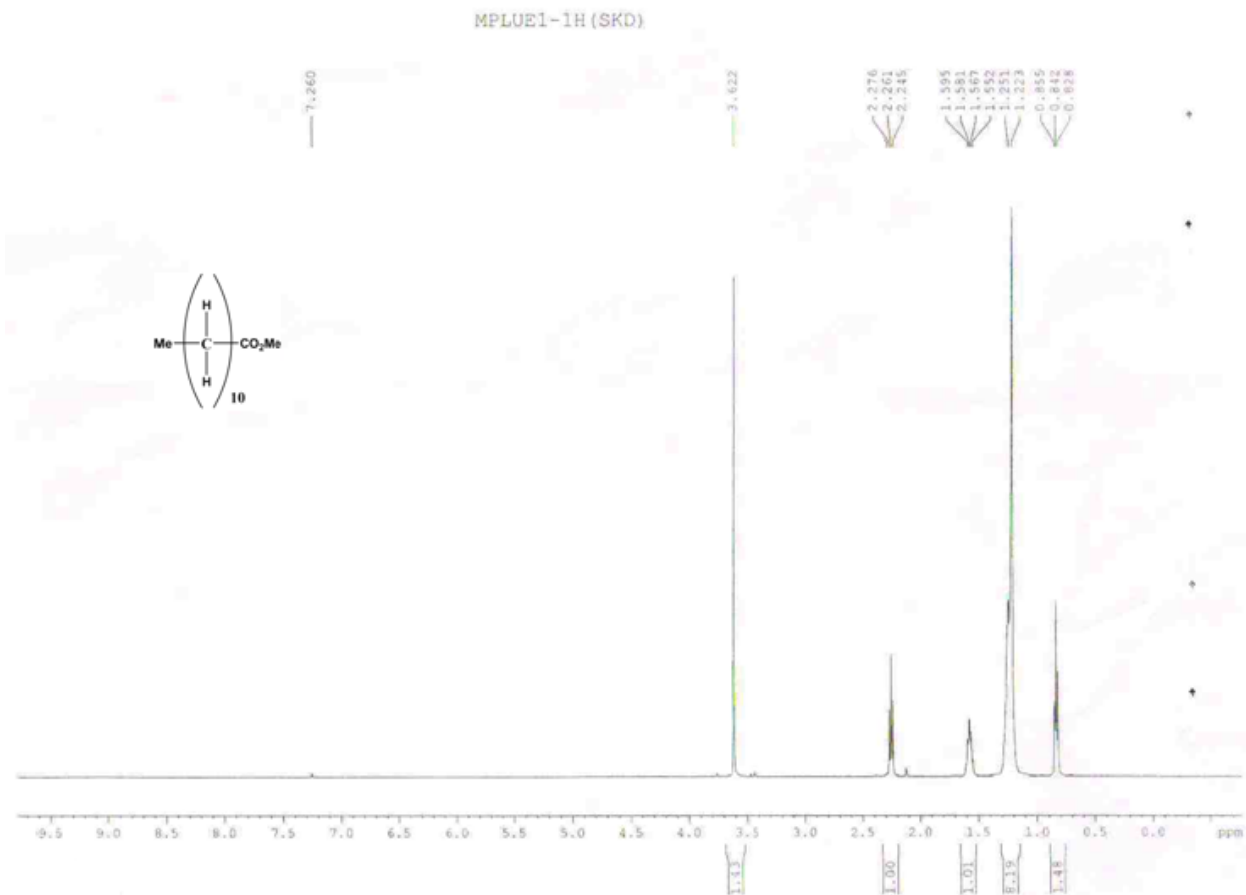
$$50 \text{ ml } 0.0093 \text{ (N) HZnPS-1} \equiv 0.0379 \text{ gm free sulphonic acid.}$$

$$= 0.467 \text{ mmol free sulphonic acid.}$$

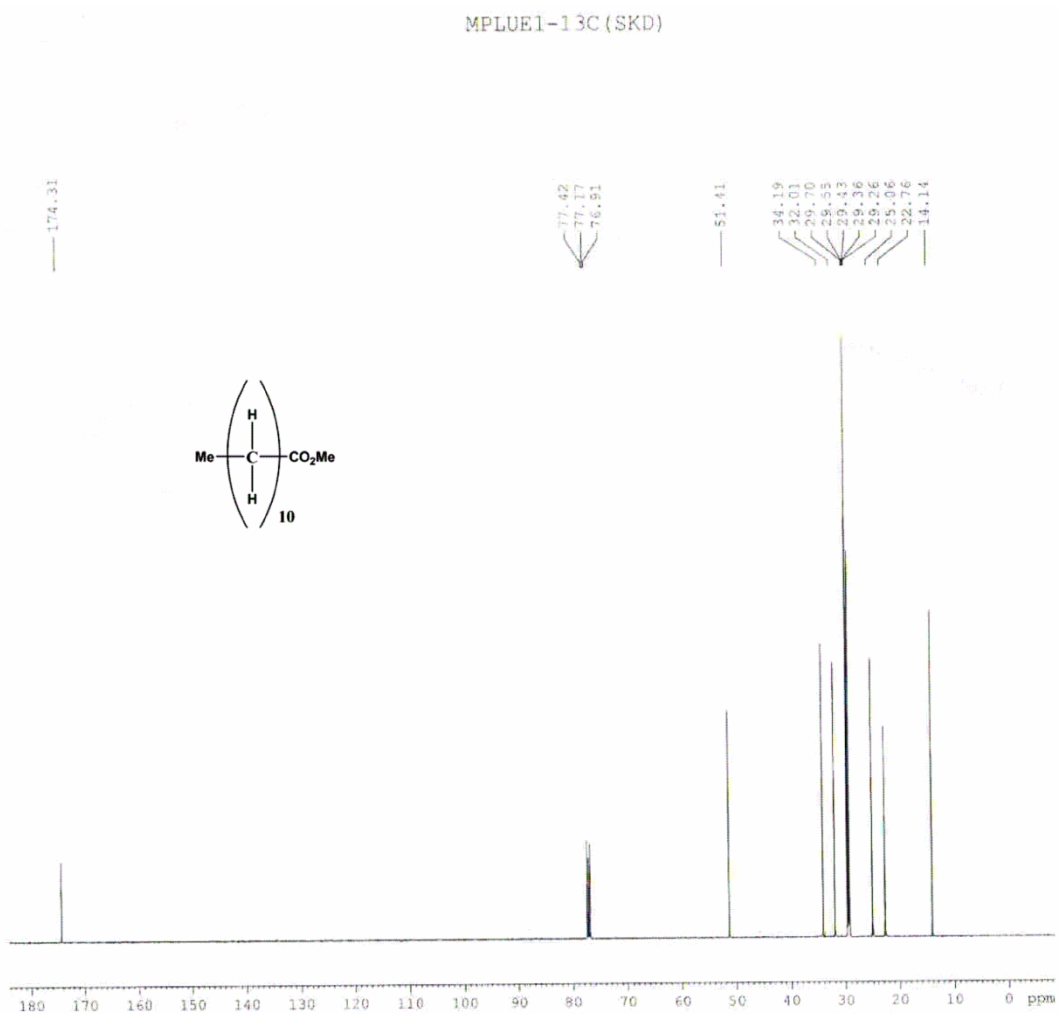
100 mg sample (HZnPS-1) contains 0.467 mmol free sulphonic acid.

1000 mg sample (HZnPS-1) contains 4.67 mmol free sulphonic acid.

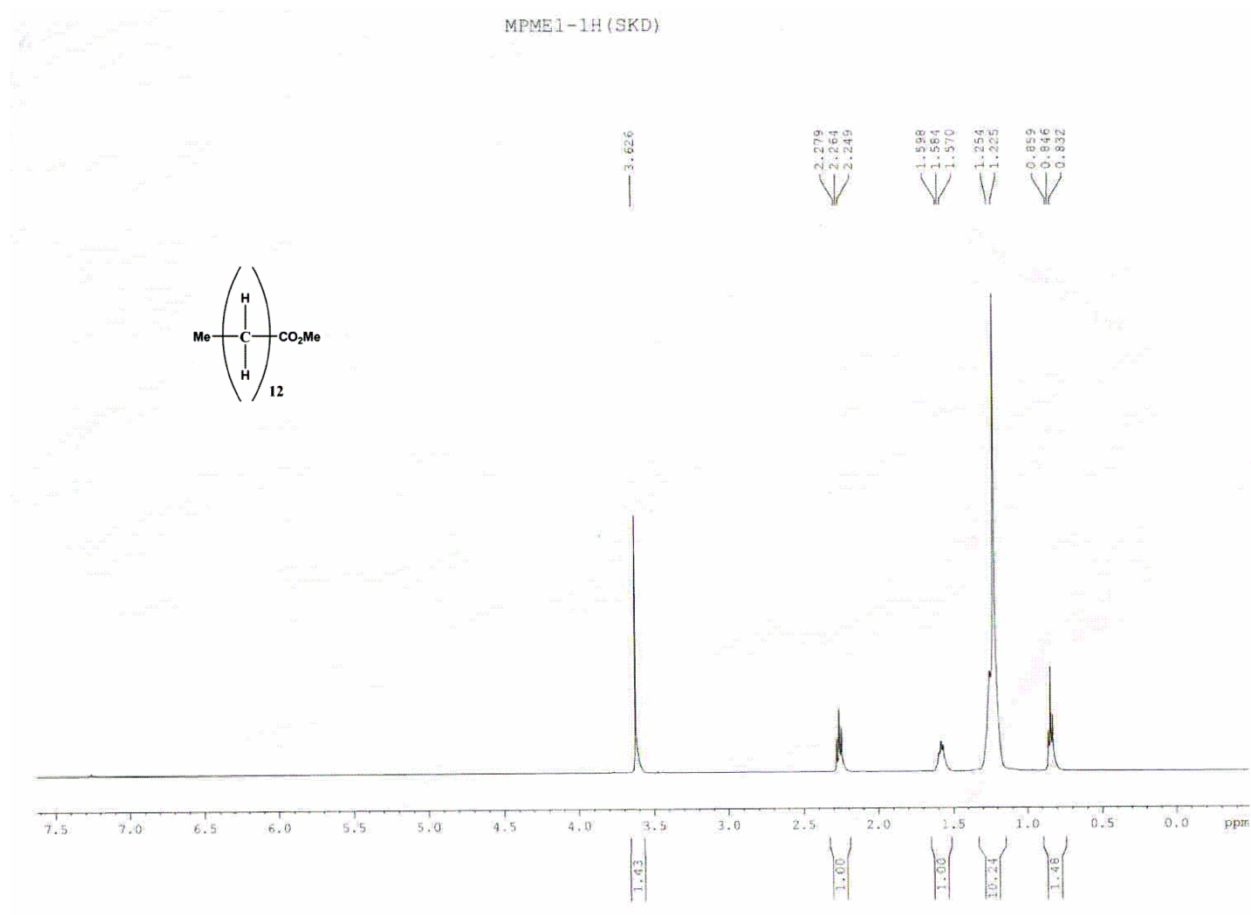
^1H NMR of Entry 1



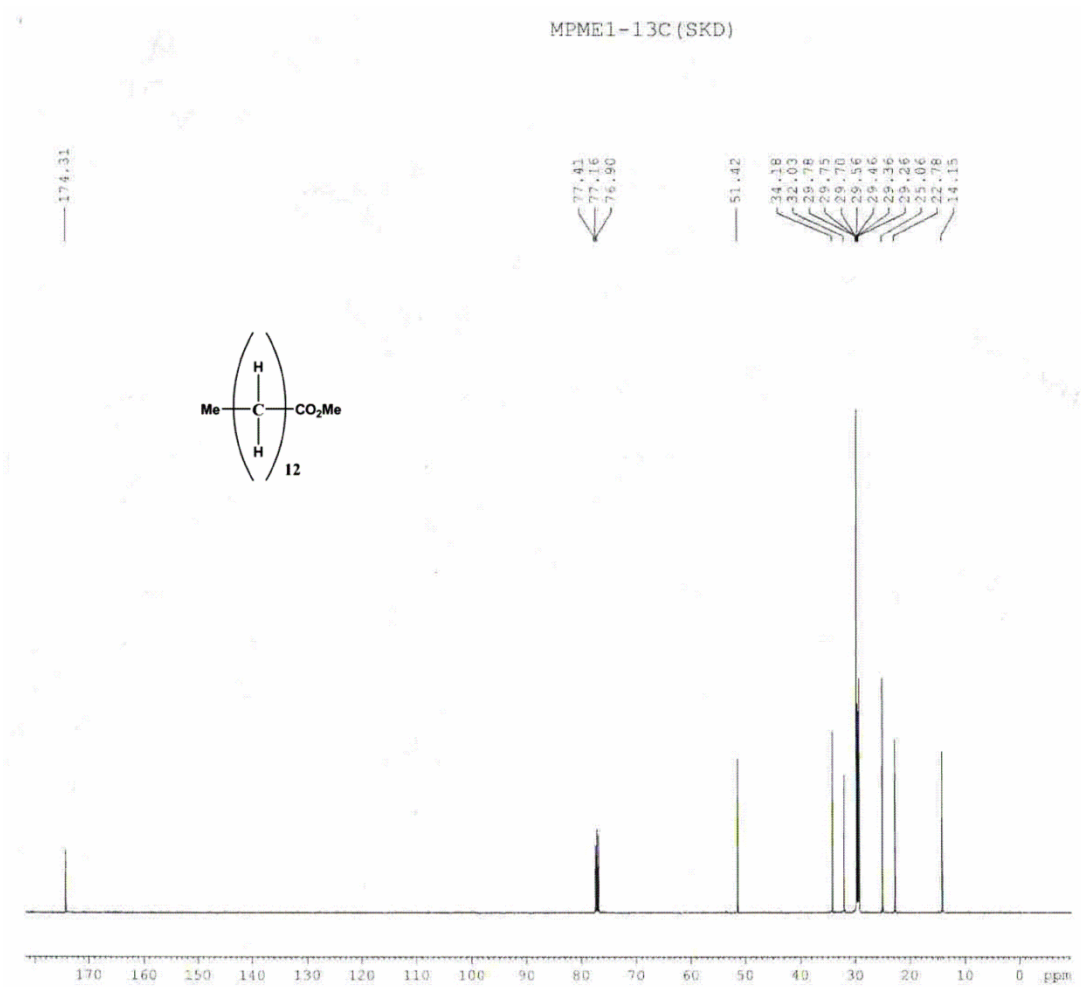
¹³C NMR of Entry 1



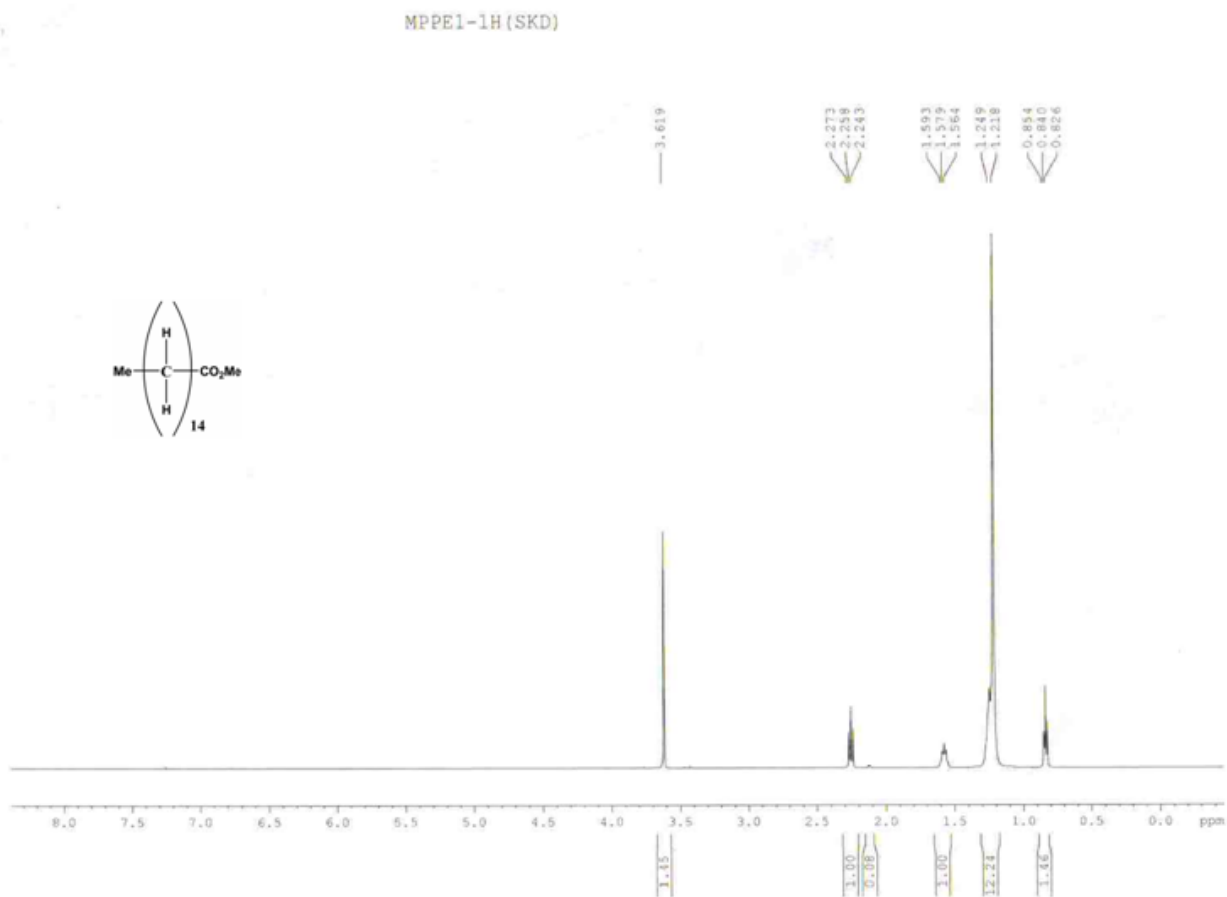
^1H NMR of Entry 2



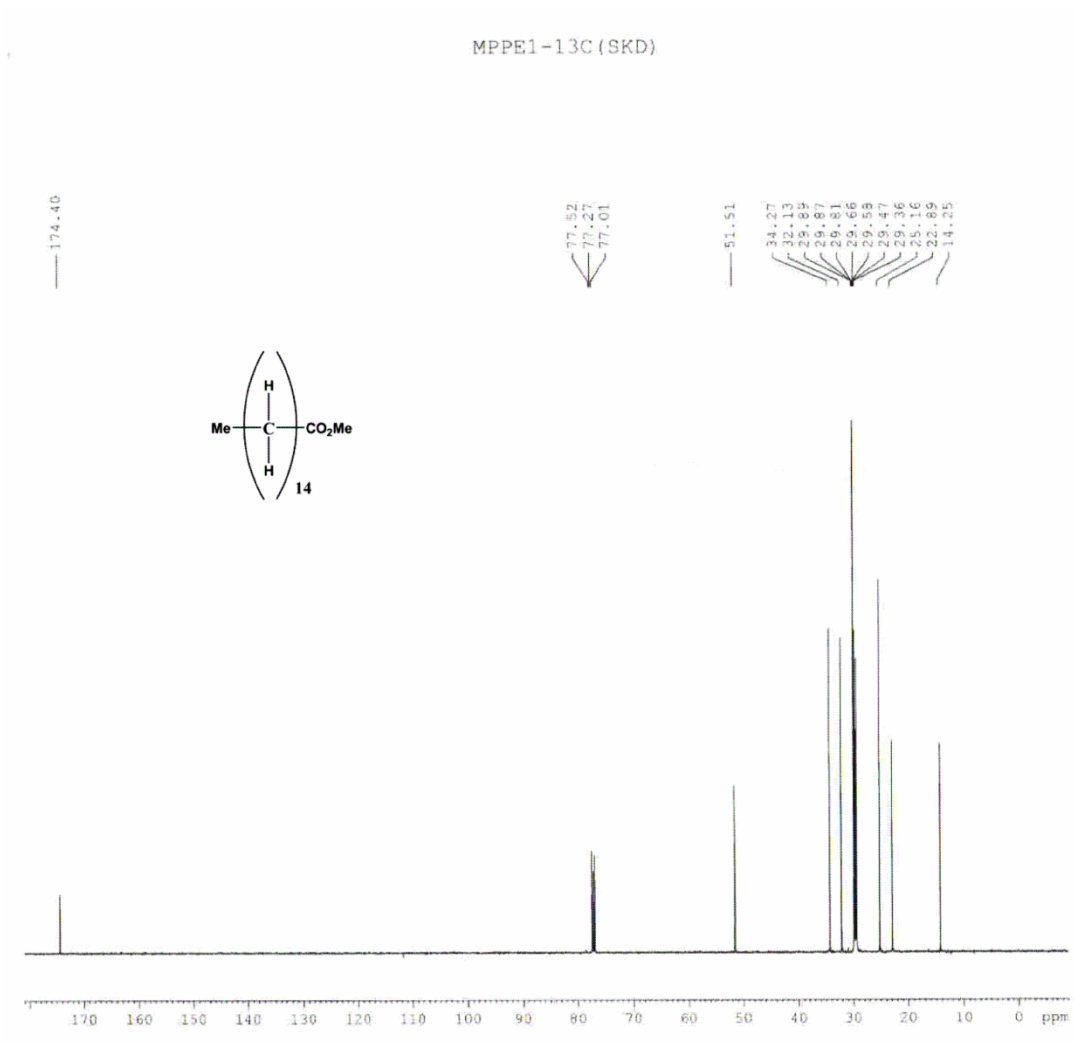
¹³C NMR of Entry 2



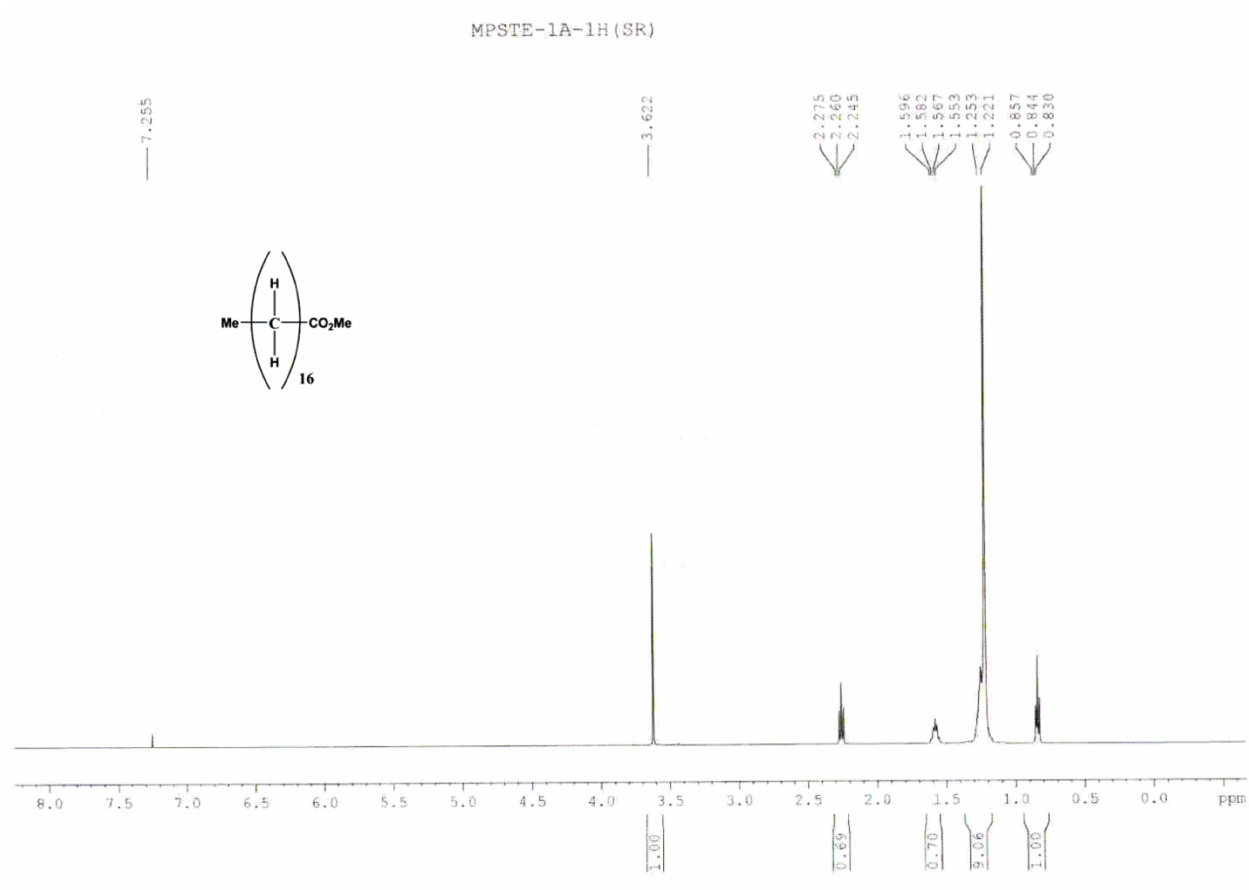
¹H NMR of Entry 3



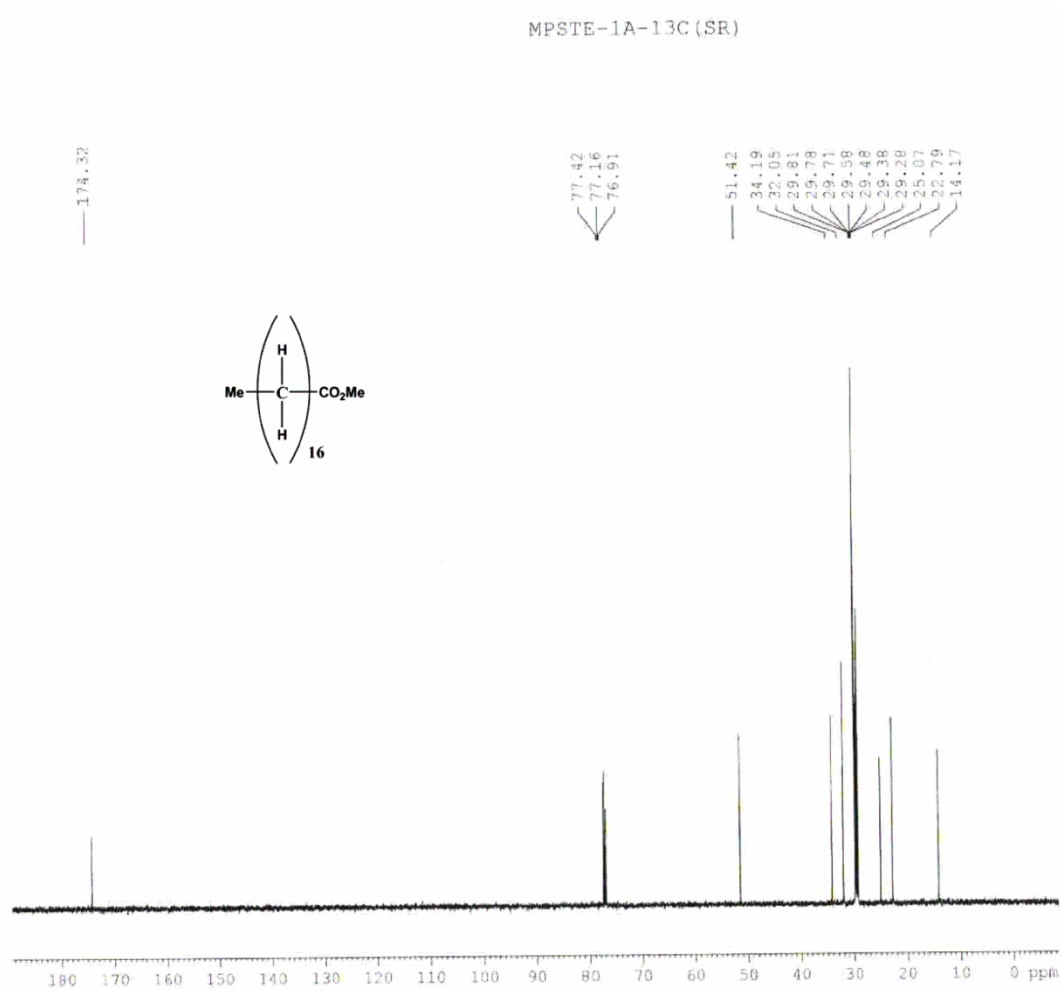
^{13}C NMR of Entry 3



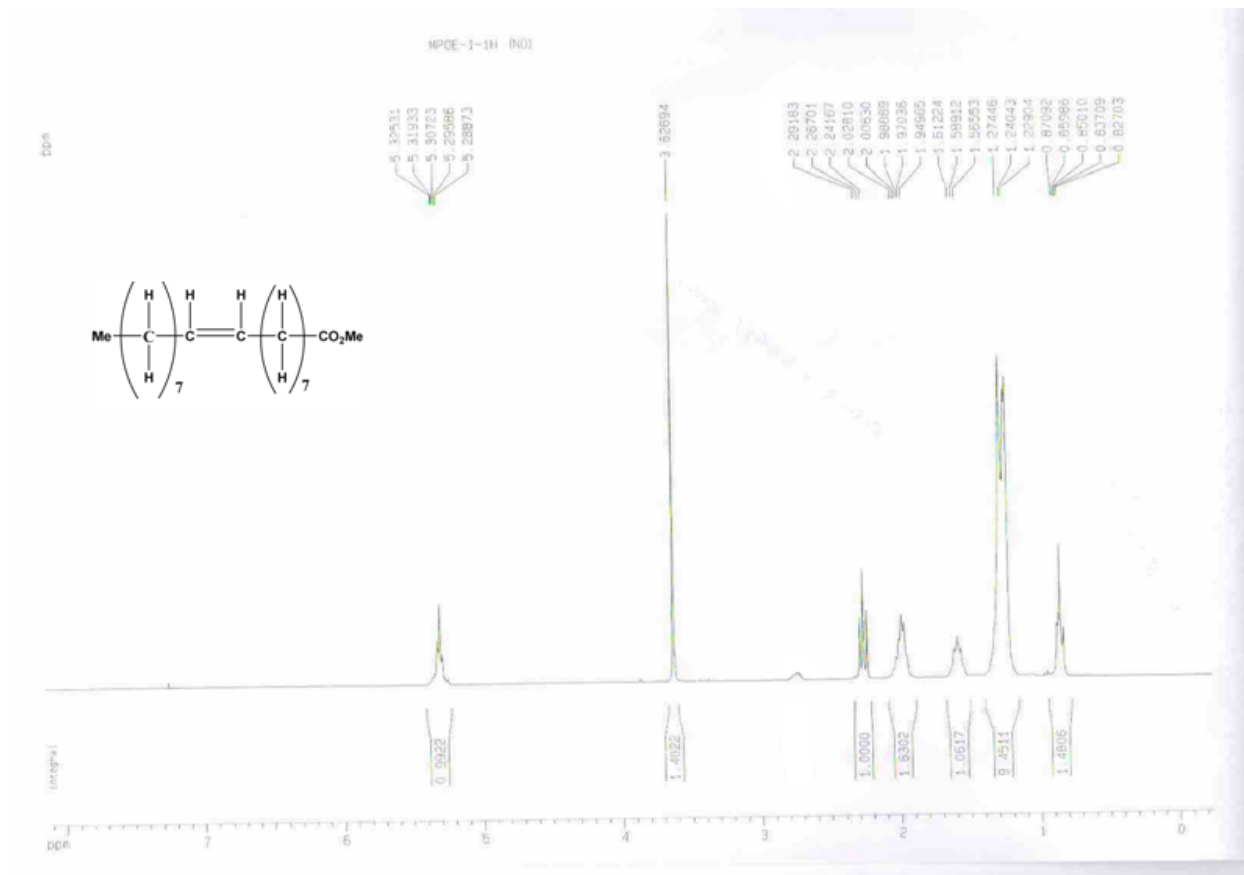
¹H NMR of Entry 4



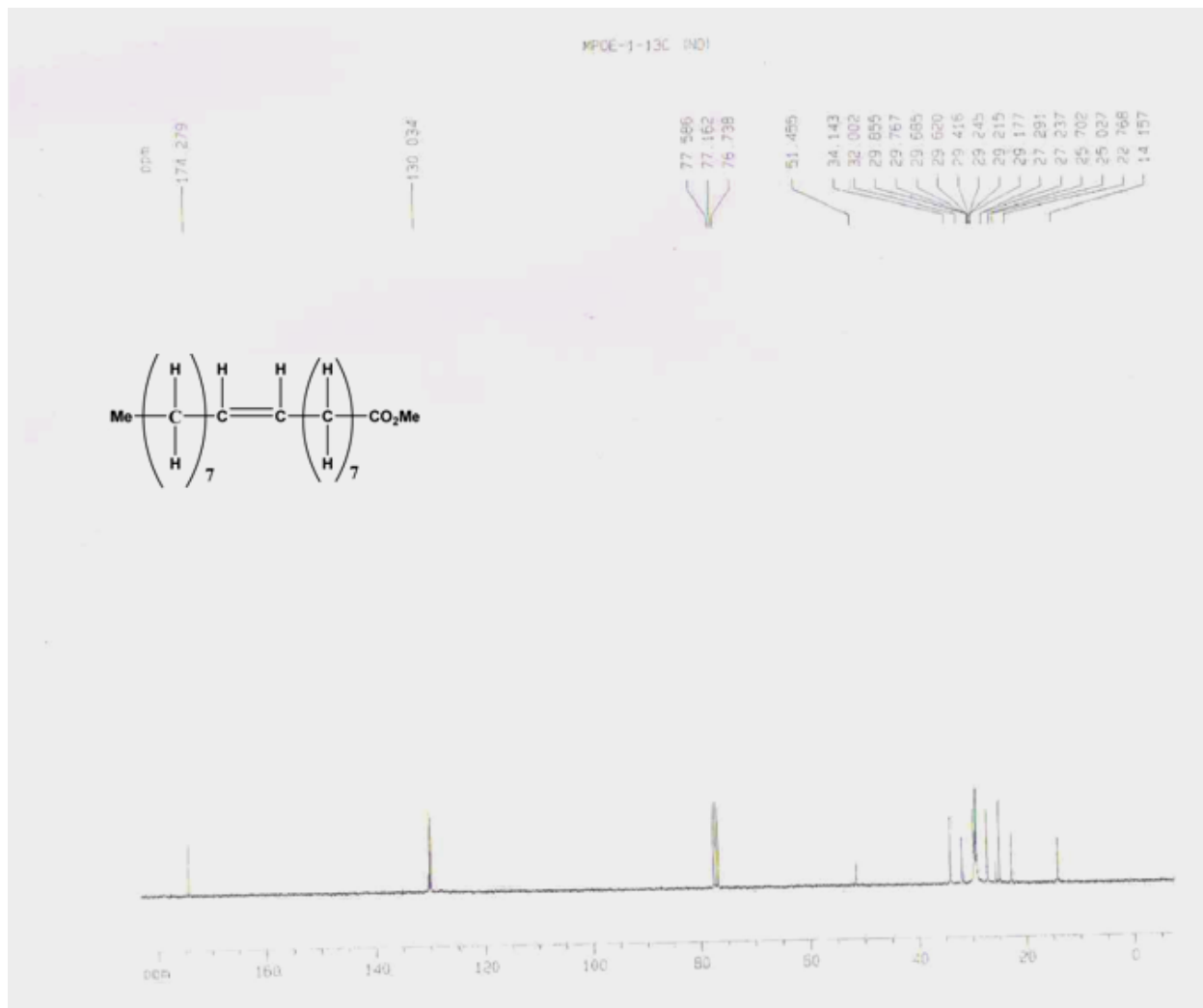
^{13}C NMR of Entry 4



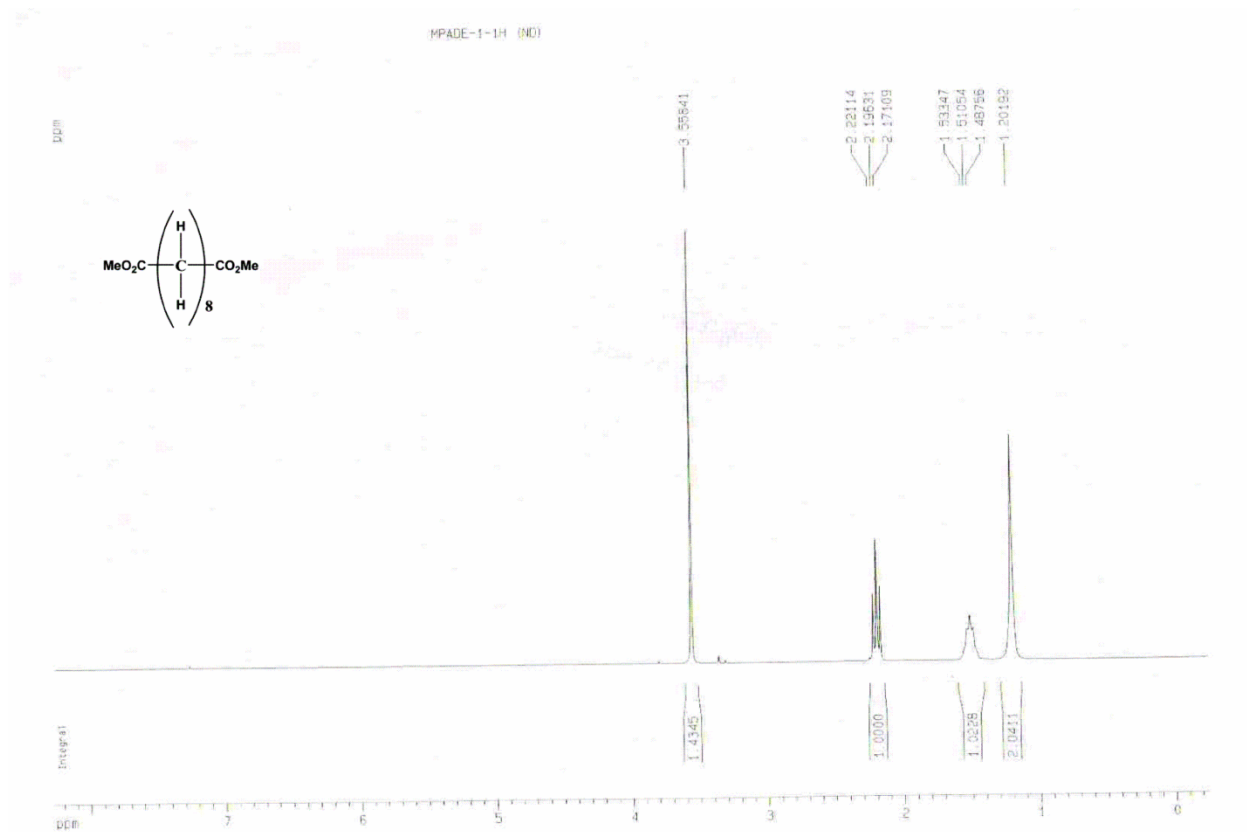
^1H NMR of Entry 5



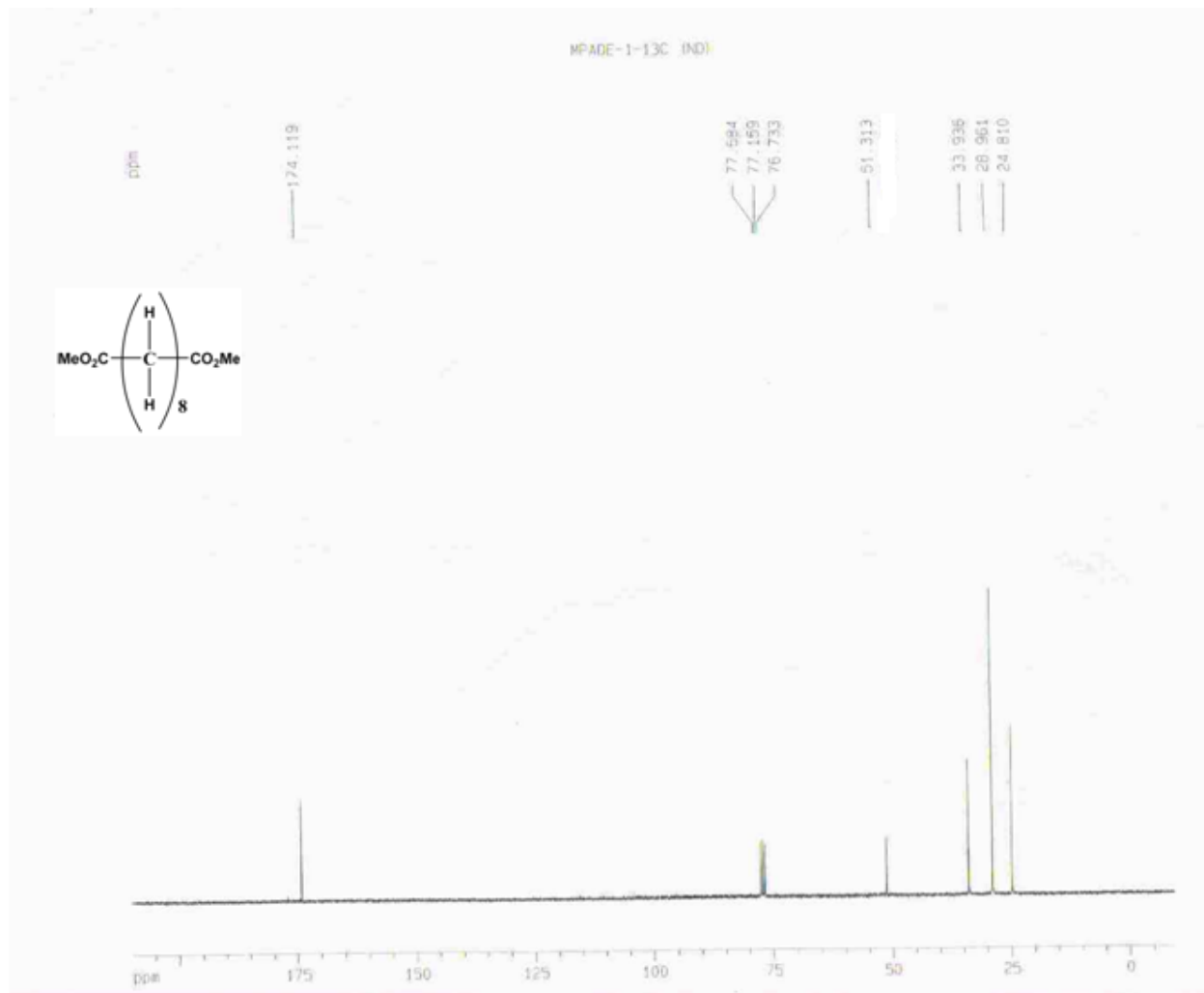
^{13}C NMR of Entry 5



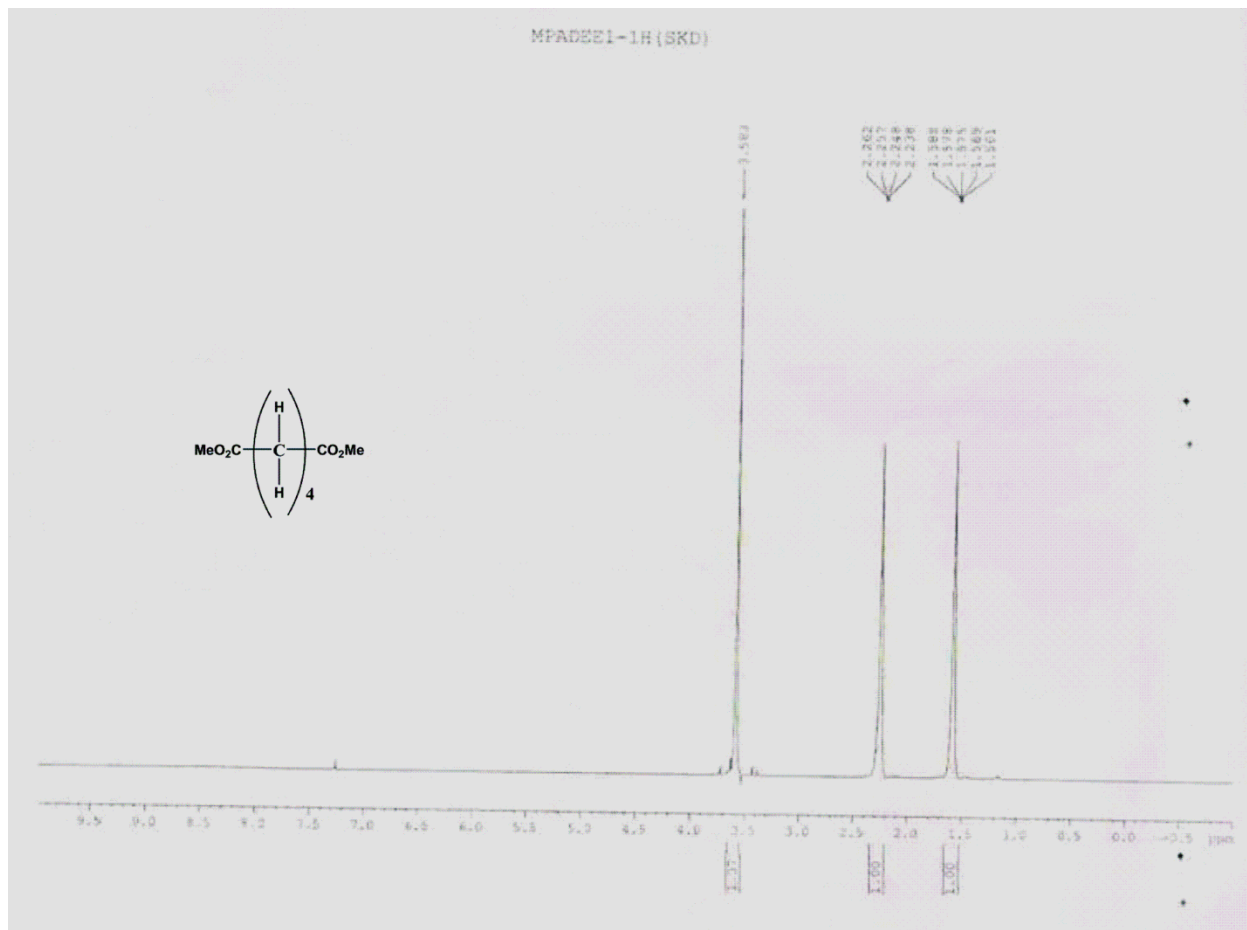
^1H NMR of Entry 6



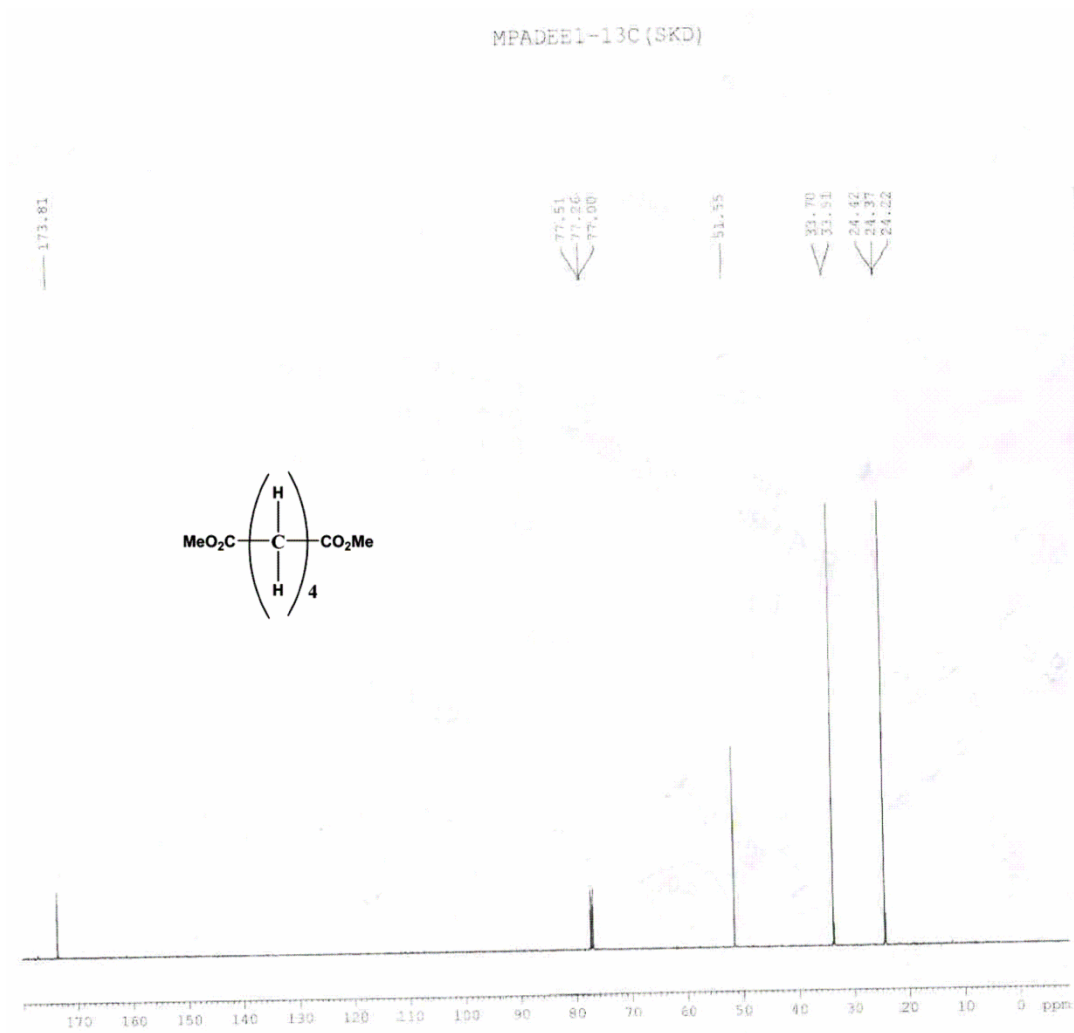
^{13}C NMR of Entry 6



^1H NMR of Entry 7

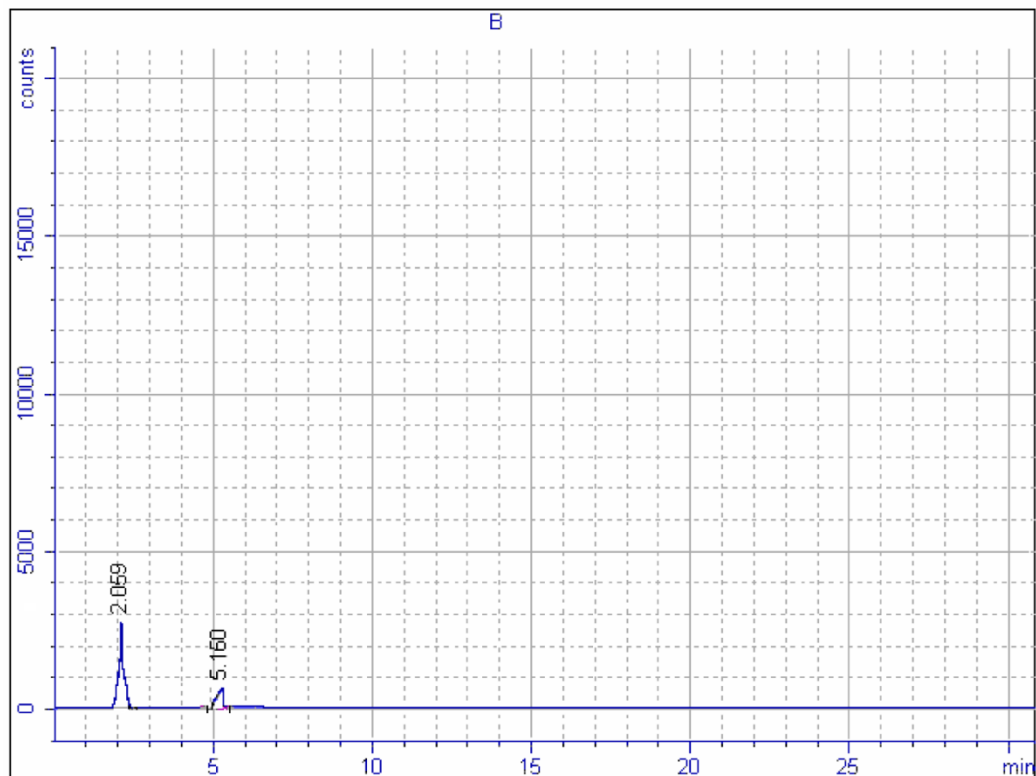


^{13}C NMR of Entry 7



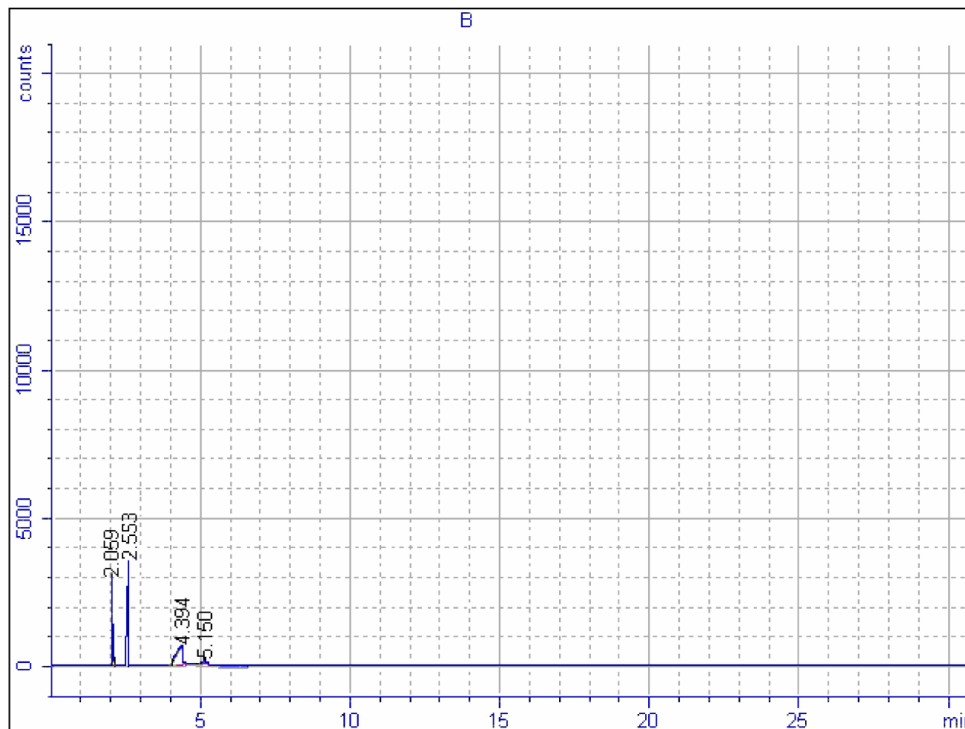
GC Analysis of Table 3 reaction mixtures

Sample name:	TE-ECNA- blank
Sample note:	TE-ECNA- blank
Submission time:	Friday, April 20, 2012 11:23:27 AM
Injection date:	Friday, April 20, 2012 12:05:31 PM
GC Description:	Gas Chromatograph
Signal description:	OOS1 A, B
Method:	75-1-7-270-2



Calibration last saved:					
Multiplier:		1.0000			
Dilution:		1.0000			
Sample amount:		0.0000 Microlitres			
Sample type:		Sample			
Sampling source:		Manual			
Signal	Retention Time [min]	Type	Width [min]	Area [counts*s]	Area %
1	2.059	BV	0.047	11251.69996	78.23320
1	5.160	PB	0.133	3130.87761	21.76311

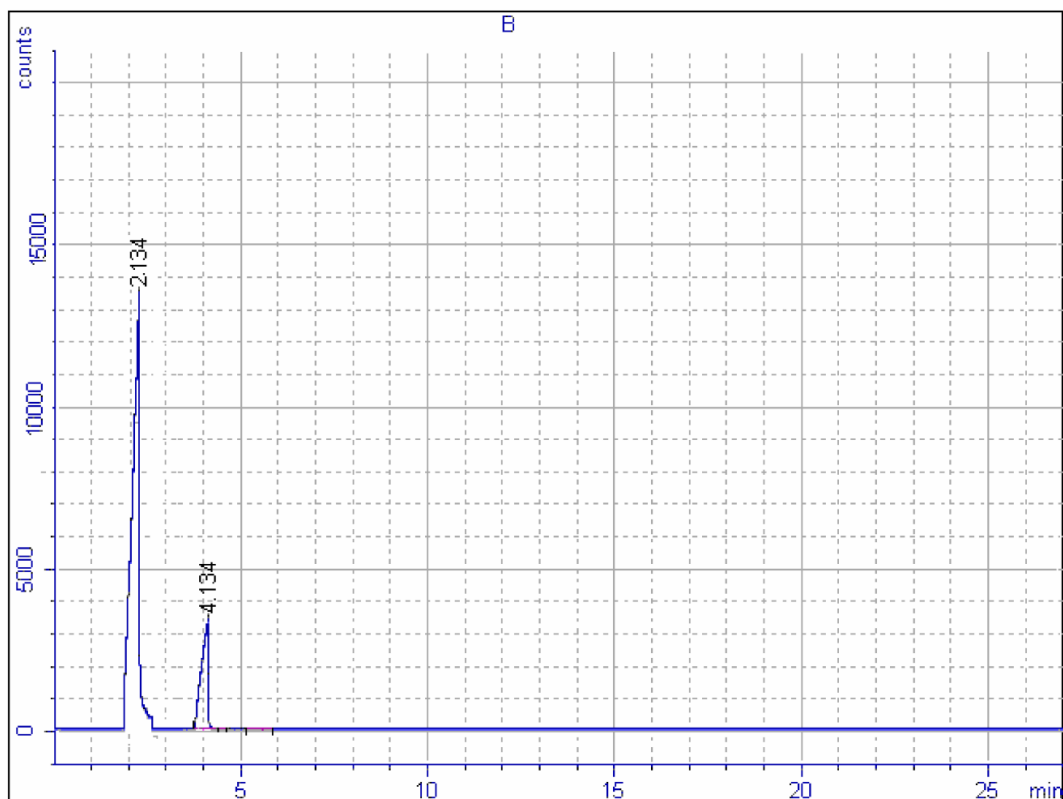
Sample name:	TE-ECA- HZnPS-1
Sample note:	TE-ECA- HZnPS-1
Submission time:	Friday, April 20, 2012 11:23:27 AM
Injection date:	Friday, April 20, 2012 12:53:21 PM
GC Description:	Gas Chromatograph
Signal description:	OOS1 A, B
Method:	75-1-7-270-2



Calibration last saved:	
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Dilution:	1.0000
Sample amount:	0.0000 Microlitres
Sample type:	Sample
Sampling source:	Manual

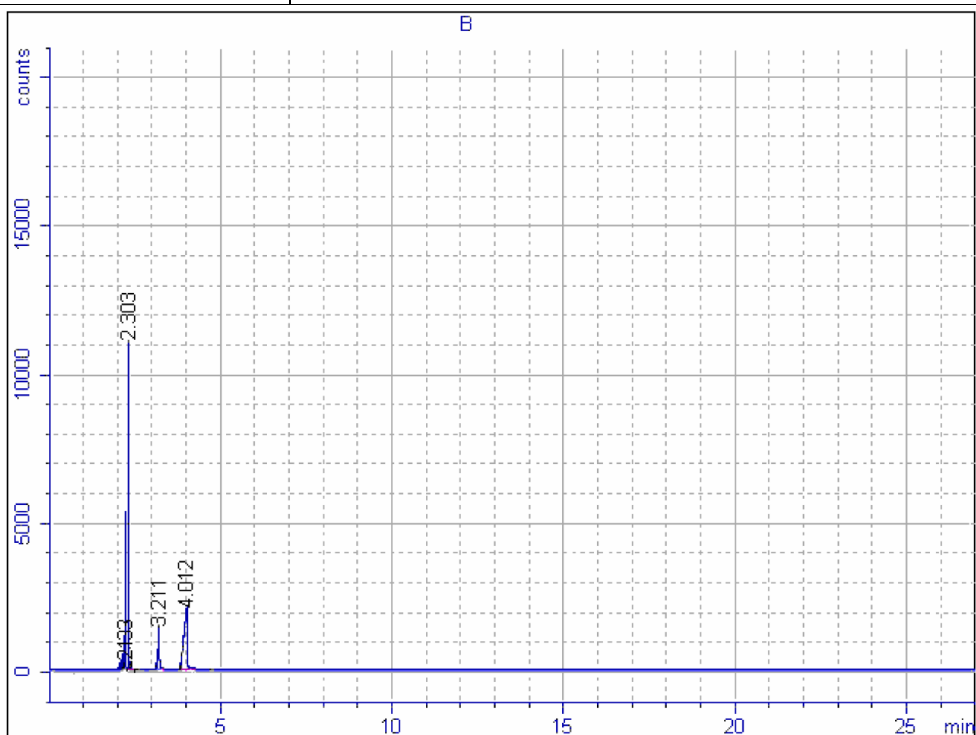
Signal	Retention Time [min]	Type	Width [min]	Area [counts*s]	Area %
1	2.059	PV	0.038	1746.75420	12.19689
1	2.533	VB	0.054	4216.27250	29.4320
1	4.394	PB	0.175	6796.96231	47.44555
1	5.150	PV	0.133	1541.87761	10.76311

Instrument run log:	TE- ECA- blank
Sample name:	TE- ECA- blank
Sample note:	TE -ECA- blank
Submission time:	Tuesday, April 17, 2012 1:30:27 PM
Injection date:	Tuesday, April 17, 2012 2:45:01 PM
GC Description:	Gas Chromatograph - SN: @COM1:
Signal description:	OOS1 A, B
Method:	80-2-5-200



Calibration last saved:					
Multiplier:	1.0000				
Dilution:	1.0000				
Sample amount:	0.0000 Microlitres				
Sample type:	Sample				
Sampling source:	Manual				
Signal	Retention Time [min]	Type	Width [min]	Area [counts*s]	Area %
1	2.458	BP	0.206	37982.10640	81.6735
1	4.134	PV	0.150	8440.46801	18.3245

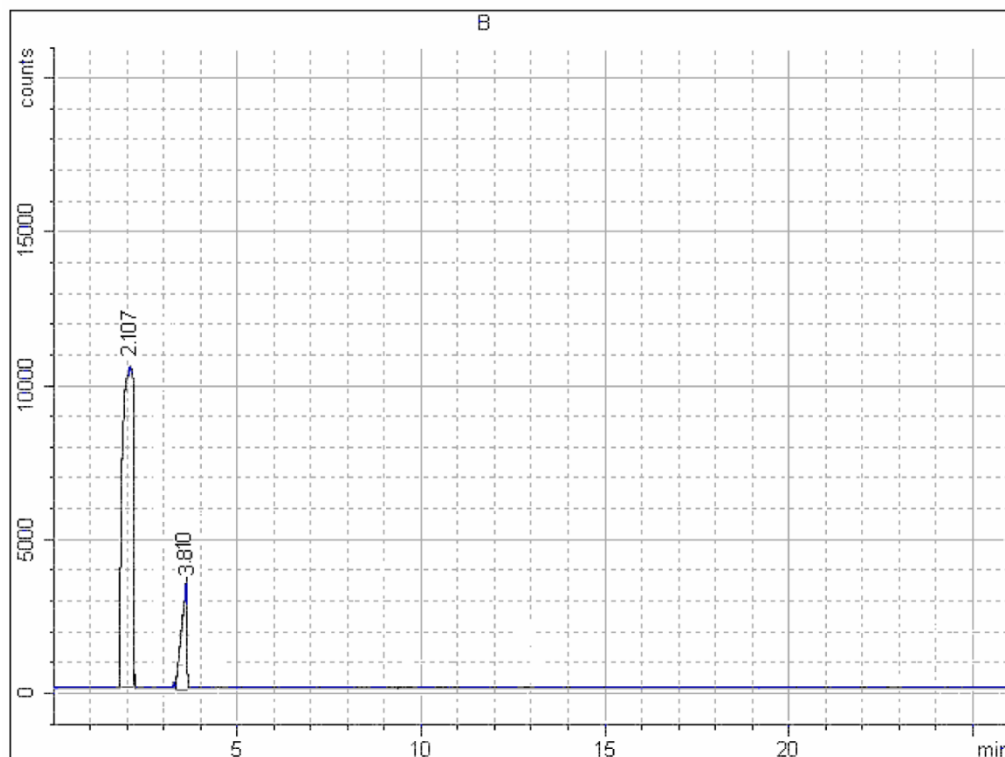
Sample name:	TE-ECA- HZnPS-1
Sample note:	TE-ECA- HZnPS-1
Submission time:	Tuesday, April 17, 2012 1:30:46 PM
Injection date:	Tuesday, April 17, 2012 3:16:10 PM
GC Description:	Gas Chromatograph - SN: @COM1:
Signal description:	OOS1 A, B
Method:	80-2-5-200



Calibration last saved:	
Multiplier:	1.0000
Dilution:	1.0000
Sample amount:	0.0000 Microlitres
Sample type:	Sample
Sampling source:	Manual

Signal	Retention Time [min]	Type	Width [min]	Area [counts*s]	Area %
1	2.133	PV	0.038	6120.75420	37.27689
1	2.303	VB	0.014	10778.27250	17.25800
1	3.211	PB	0.047	3826.21132	18.75882
1	4.012	PV	0.081	7366.31637	26.73700

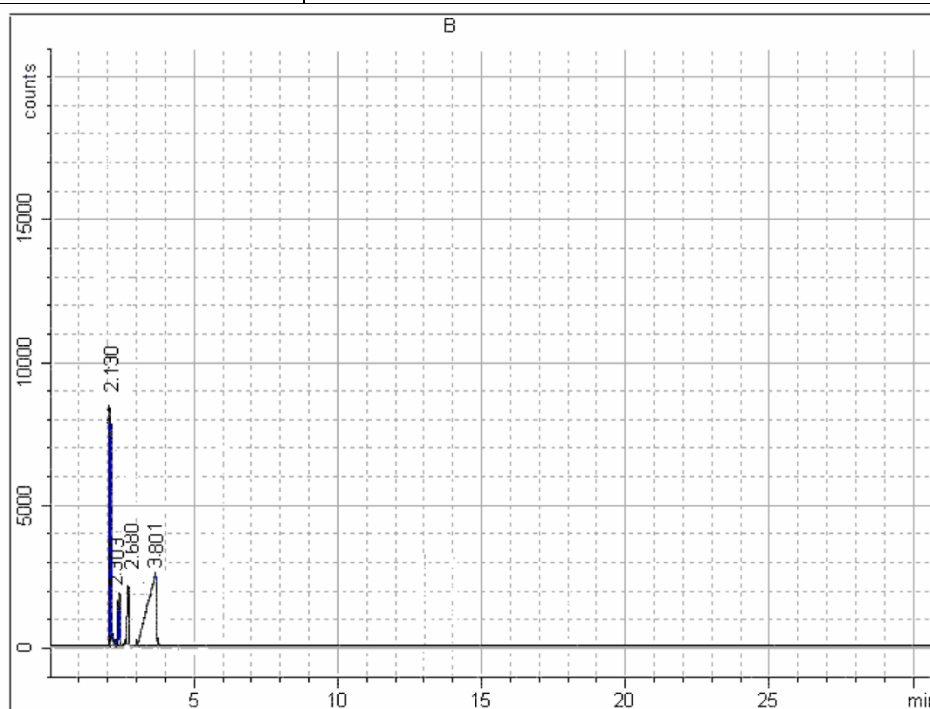
Instrument run log:	TE- EA- blank
Sample name:	TE- EA- blank
Sample note:	TE -EA- blank
Submission time:	Friday, April 20, 2012 11:23:27 AM
Injection date:	Friday, April 20, 2012 01:23:27 PM
GC Description:	Gas Chromatograph - SN: @COM1:
Signal description:	OOS1 A, B
Method:	75-1-7-270-2



Calibration last saved:	
Multiplier:	1.0000
Dilution:	1.0000
Sample amount:	0.0000 Microlitres
Sample type:	Sample
Sampling source:	Manual

Signal	Retention Time [min]	Type	Width [min]	Area [counts*s]	Area %
1	2.107	BV	0.230	10962.69996	76.23320
1	3.810	PB	0.133	3418.87761	23.76311

Instrument run log:	TE- EA- HZnPS-1
Sample name:	TE- EA- HZnPS-1
Sample note:	TE -EA- HZnPS-1
Submission time:	Friday, April 20, 2012 11:23:27 AM
Injection date:	Friday, April 20, 2012 02:11:25 PM
GC Description:	Gas Chromatograph - SN: @COM1:
Signal description:	OOS1 A, B
Method:	75-1-7-270-2
Method last saved:	Monday, October 04, 2010 7:34:50 PM



Calibration last saved:					
Multiplier:	1.0000				
Dilution:	1.0000				
Sample amount:	0.0000 Microlitres				
Sample type:	Sample				
Sampling source:	Manual				
Signal	Retention Time [min]	Type	Width [min]	Area [counts*s]	Area %
1	2.130	PV	0.038	6499.75420	45.37689
1	2.303	VB	0.034	1924.27250	13.4320
1	2.680	PB	0.045	2068.96231	14.44555
1	3.801	PV	0.204	3833.87761	26.76311