Supporting Information

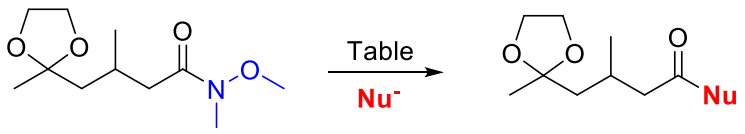
Improved synthesis of 2,4,6-trialkylpyridines from 1,5-diketoalkanes: total synthesis of Anibamine

Takeru Miyakoshi, Hiroyuki Konno

Department of Biochemical Engineering, Graduate School of Science and Technology, Yamagata University, Yonezawa, Yamagata 992-8510, Japan
e-mail: konno@yz.yamagata-u.ac.jp

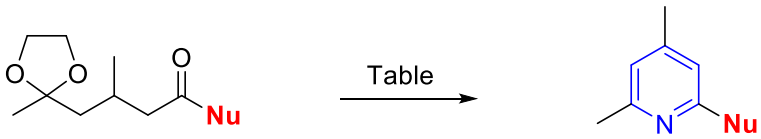
Contents

Synthetic procedures for 4a, b, d, e, f and 3a-g



9 **4a, b, d, e,f**

condition	product	yield (%)
Allylmagnesiumbromide, THF, -78 °C, 3h	**4a**	85
n-BuLi, ether, -78 °C, 3h	**4b**	80
Phenylmagnesiumbromide, THF, r.t., 1h	**4d**	53
p-Tolylmagnesiumbromide, THF, 0 °C to r.t., 3h	**4e**	79
1-Decyne, *n*-BuLi, THF, -78 °C to r.t., 12h	**4f**	93



4a-g **3a-g**

substrate	condition	product	yield (%)[a,b]
4a	1) NH_2OH•HCl, AcONa, EtOH, H_2O 2) AcOH, reflux	**3a**	37
4c		**3c**	61[c]
4b		**3b**	86
4d		**3d**	88
4e		**3e**	78
4f		**3f**	35[d]
4g		**3g**	65
4b		**3b**	31[e,f]

[a]Isolated yield. [b]2 steps yield. [c]Reaction was conducted at 110 °C. [d]Methoxyamine was employed. [e]Oxime's hydroxy group was mesylated. [f]3 steps yield.

6-Methyl-8-(2,2-dimethyldioxolane)-nonen-4-one (4a) To a solution of **9** (303 mg, 1.31 mmol) in THF (4.5 mL) at -78 ^{o}C under nitrogen atmosphere was added allylmagnesiumbromide (0.7 M in Et_2O, 2.70 mL, 1.89 mmol) with dropwise manner and stirred at -78 ^{o}C for 3 h. The reaction mixture was quenched by sat. NH_4Cl aq. at 0 ^{o}C and the aqueous phase was extracted by AcOEt, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:5 v/v) to give **4a** (237 mg, 85% yield) as a colorless oil.

4,6-Dimethyl-2-(propen-1-ny)-pyridine (3a) To a solution of **4a** (109 mg, 5.14 mmol) in EtOH (1.6 mL) and H_2O (1.6 mL) were added NaOAc (77.3 mg, 10.3 mmol) and hydroxylamine hydrochloride (65.5 mg, 10.3 mmol). The reaction mixture was stirred at room temperature overnight. The reaction mixture was added to H_2O. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the oxime intermediate. A stirring solution of the oxime intermediate in AcOH (5.8 mL) was refluxed for 24 h. The reaction mixture was cooled to room temperature and the solvent was carefully removed under reduced pressure. The residue was added to sat. $NaHCO_3$ aq. and the aqueous layer was extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:4 v/v) to give **3a** (28.3 mg, 37% yield over 2 steps) as a yellow oil.

4,6-Dimethyl-2-(propanyl)-pyridine (3c) To a solution of **4c** (91.9 mg, 0.439 mmol) in EtOH (1.4 mL) and H_2O (1.4 mL) was added AcONa (360 mg, 4.39 mmol), hydroxylamine hydrochloride (153 mg, 2.20 mmol). The reaction mixture was stirred overnight. The reaction mixture was added to H_2O and separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the oxime intermediate. A stirring solution of the oxime intermediate in AcOH (5.5 mL) was heated at 110 ^{o}C for 1 h. The reaction mixture was cooled to room temperature and the solvent was carefully removed under reduced pressure. The residue was added to sat. $NaHCO_3$ aq. and the aqueous layer was extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$,

filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:5 v/v) to give **3c** (38.9 mg, 61% yield over 2 steps) as a yellow oil.

3-Methyl-5-(2,2-dimethyldioxolane)-1-phenylhexanone (4d) To a solution of THF (4.3 mL) was added Mg (110 mg, mmol), iodide (catalytic amount) and bromobenzene (0.20 mL) under nitrogen atmosphere. After color of the reaction mixture changed into colorless, the reaction mixture was added bromobenzene (0.25 mL) dropwise. To this solution was added **9** (105 mg, 0.454 mmol) in THF (1.5 mL) dropwise at room temperature and stirred for 1 h. The reaction mixture was quenched with sat. NH_4Cl aq. at 0 ^oC. The aqueous phase was extracted by Et_2O, washed with 1M NaOH, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:6 v/v) to give **4d** (60.2 mg, 53% yield) as a colorless oil.

4,6-Dimethyl-2-phenylpyridine (3d) To a solution of **4d** (14.4 mg, 0.05 mmol) in EtOH (0.2 mL) and H_2O (0.2 mL) were added AcONa (41 mg, 0.5 mmol) and hydroxylamine hydrochloride (18 mg, 0.25 mmol). The reaction mixture was stirred at 45 ^oC overnight. The reaction mixture was added to H_2O and separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the oxime intermediate. A stirring solution of the oxime intermediate in AcOH (1.2 mL) was refluxed for 16 h. The reaction mixture was cooled to room temperature and the solvent was carefully removed under reduced pressure. The residue was added to sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of column chromatography (AcOEt-hexane, 1:6 v/v) gave **3d** (8.0 mg, 88% yield over 2 steps) as a pale orange oil.

***p*-Methylphenyl-3-methyl-5-(2,2-dimethyldioxolane)-hexanone (4e)** To a solution of **9** (31.6 mg, 0.137 mmol) in THF (0.4 mL) was added *p*-tolylmagnesium bromide (0.1 M in THF, 4 mL, 0.39 mmol) at 0 ^oC, then warmed to room temperature and stirred for 3 h. The reaction mixture was quenched with sat. NH_4Cl aq. at 0 ^oC. The aqueous phase was extracted by Et_2O, washed with 1M NaOH, dried over $MgSO_4$, filtered and

concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:4 v/v) to give **4e** (32.6 mg, 79% yield) as a colorless oil.

2-*p*-Methylphenyl-4,6-dimethylpyridine (3e) To a solution of **4e** (32.6 mg, 0.11 mmol) in EtOH (0.4 mL) and H_2O (0.4 mL) were added AcONa (90.2 mg, 1.1 mmol) and hydroxylamine hydrochloride (38.2 mg, 0.55 mmol). The reaction mixture was stirred at 45 ^oC overnight. The reaction mixture was added to H_2O and separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the oxime intermediate. A stirring solution of the oxime intermediate in AcOH (2.5 mL) was refluxed for 23 h. The reaction mixture was cooled to room temperature and the solvent was carefully removed under reduced pressure. The residue was added to sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:6 v/v) to give **3e** (16.4 mg, 78% yield over 2 steps) as a pink oil.

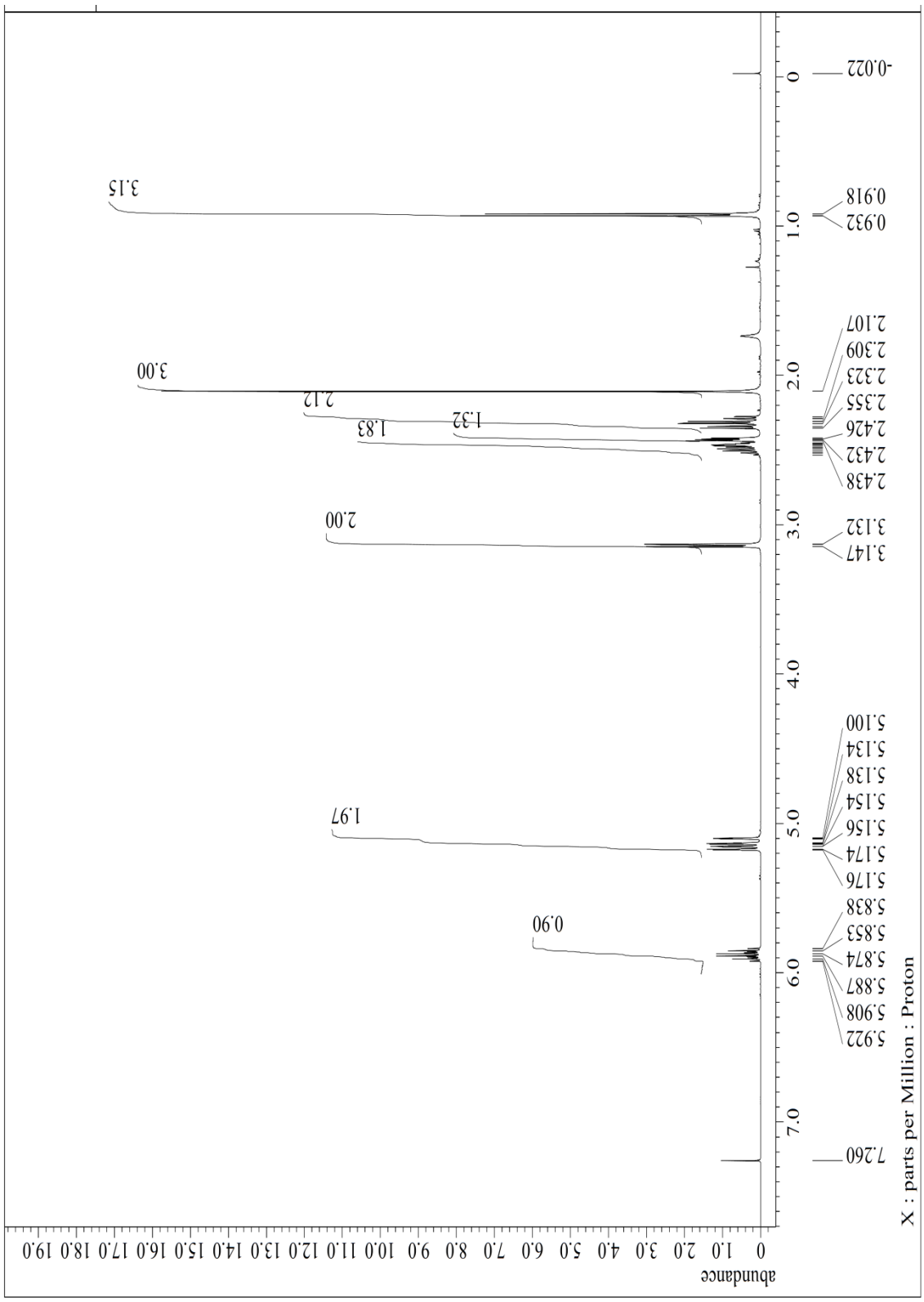
4-Methyl-2-(2,2-dimethyldioxolane)-7-hexadecyn-6-one (4f) To a solution of 1-Decyne (295 μL, 1.43 mmol) in THF (1.4 mL) at -78 ^oC under nitrogen atmosphere was added *n*-BuLi (2.5 M in hexane, 0.6 mL, 1.30 mmol) at -78 ^oC. After the stirring for 30 min at 0 ^oC, **9** (101 mg, 0.437 mmol) was added to the mixture at -78 ^oC and the reaction mixture was allowed to warm to room temperature. After the stirring for 12 h, the reaction was quenched with sat. NH_4Cl aq. at 0 ^oC. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:8 v/v) to give **4f** (125 mg, 93% yield) as a colorless oil.

2-Decynyl-4,6-dimethylpyridine (3f) To a solution of **4f** (51.1 mg, 0.166 mmol) in EtOH (0.5 mL) and H_2O (0.5 mL) was added AcONa (136 mg, 1.66 mmol), methoxyamine hydrochloride (0.15 mL, 0.83 mmol) and stirred at room temperature overnight. The reaction mixture was added to H_2O. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the methoxyamine intermediate. A stirring solution of the methoxyamine intermediate in AcOH (2.1 mL) was refluxed for 6 h. The reaction

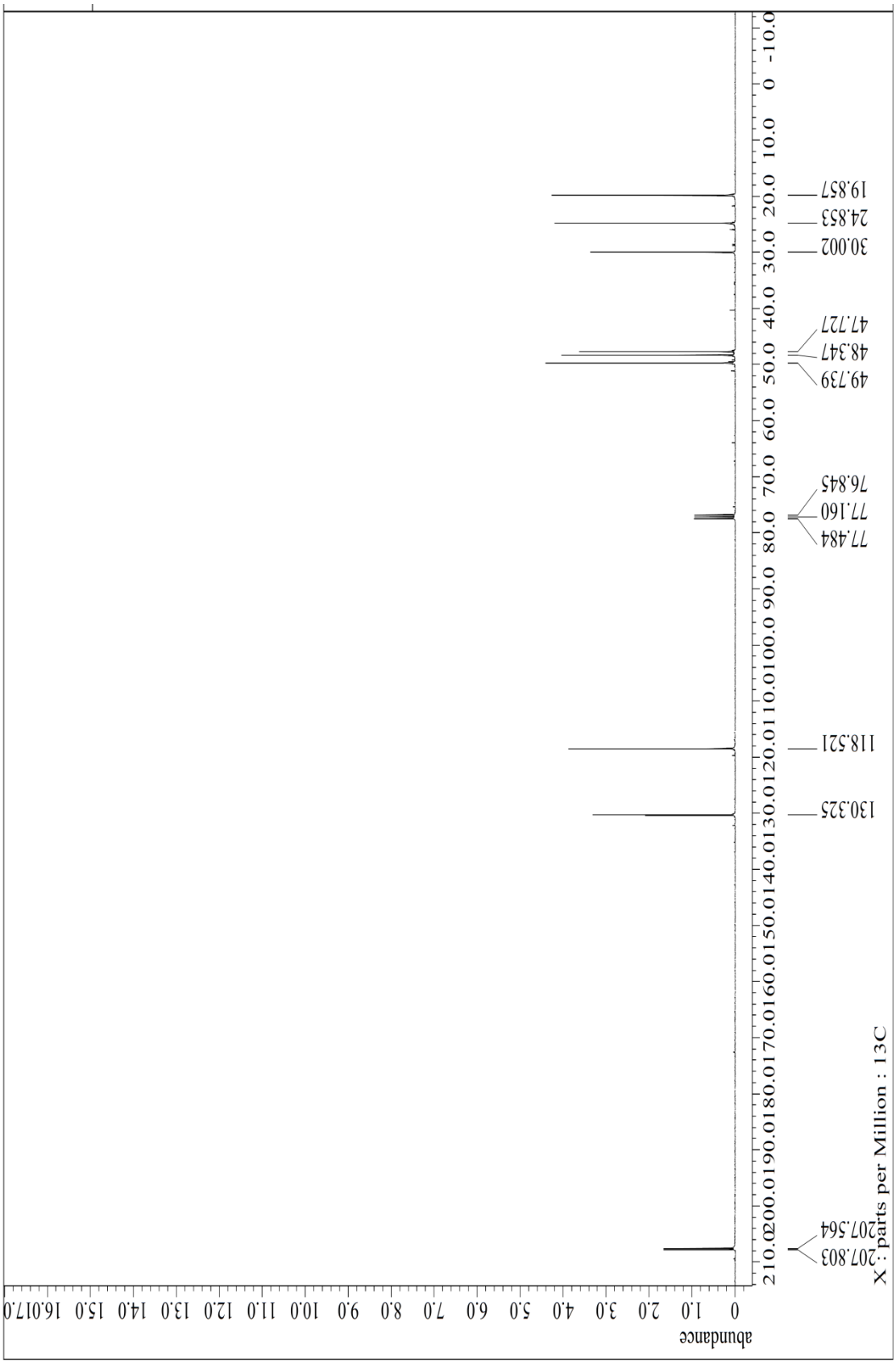
mixture was cooled to room temperature and the solvent was carefully removed under reduced pressure. The residue was added to sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:8 v/v) to give **3f** (14.4 mg, 36% yield over 2 steps) as a yellow oil.

2-Decanyl-4,6-dimethylpyridine (3g) To a solution of **4g** (72.3 mg, 0.231 mmol) in EtOH (0.8 mL) and H_2O (0.8 mL) were added AcONa (189 mg, 2.31 mmol) and hydroxylamine hydrochloride (80.3 mg, 1.16 mmol). After the stirring overnight, the reaction mixture was added to H_2O. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the oxime intermediate. A stirring solution of the oxime intermediate in AcOH (2.9 mL) was refluxed for 1 h. The reaction mixture was cooled to room temperature and the solvent was carefully removed under reduced pressure. The residue was added to sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic fractions were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified with column chromatography (AcOEt-hexane, 1:10 v/v) gave **3g** (37.3 mg, 65% yield over 2 steps) as a yellow oil.

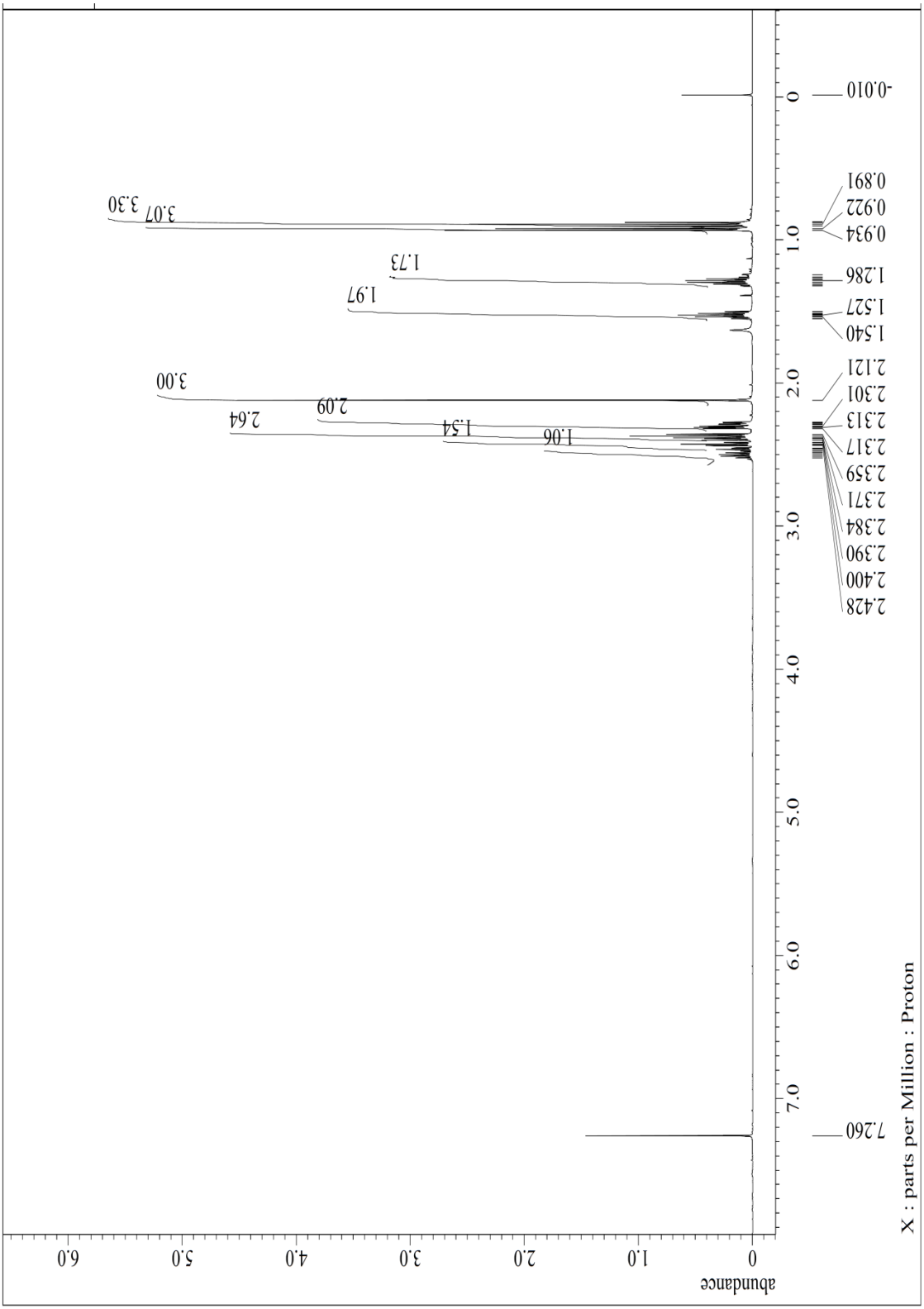
^{1}H NMR of **2a**


X : parts per Million : Proton
abundance
7.260
5.922
5.908
5.887
5.874
5.853
5.838
5.176
5.174
5.156
5.154
5.138
5.134
5.100
3.147
3.132
2.438
2.432
2.426
2.355
2.323
2.309
2.107
0.932
0.918
-0.022
0.90
1.97
2.00
1.32
1.83
2.12
3.00
3.15

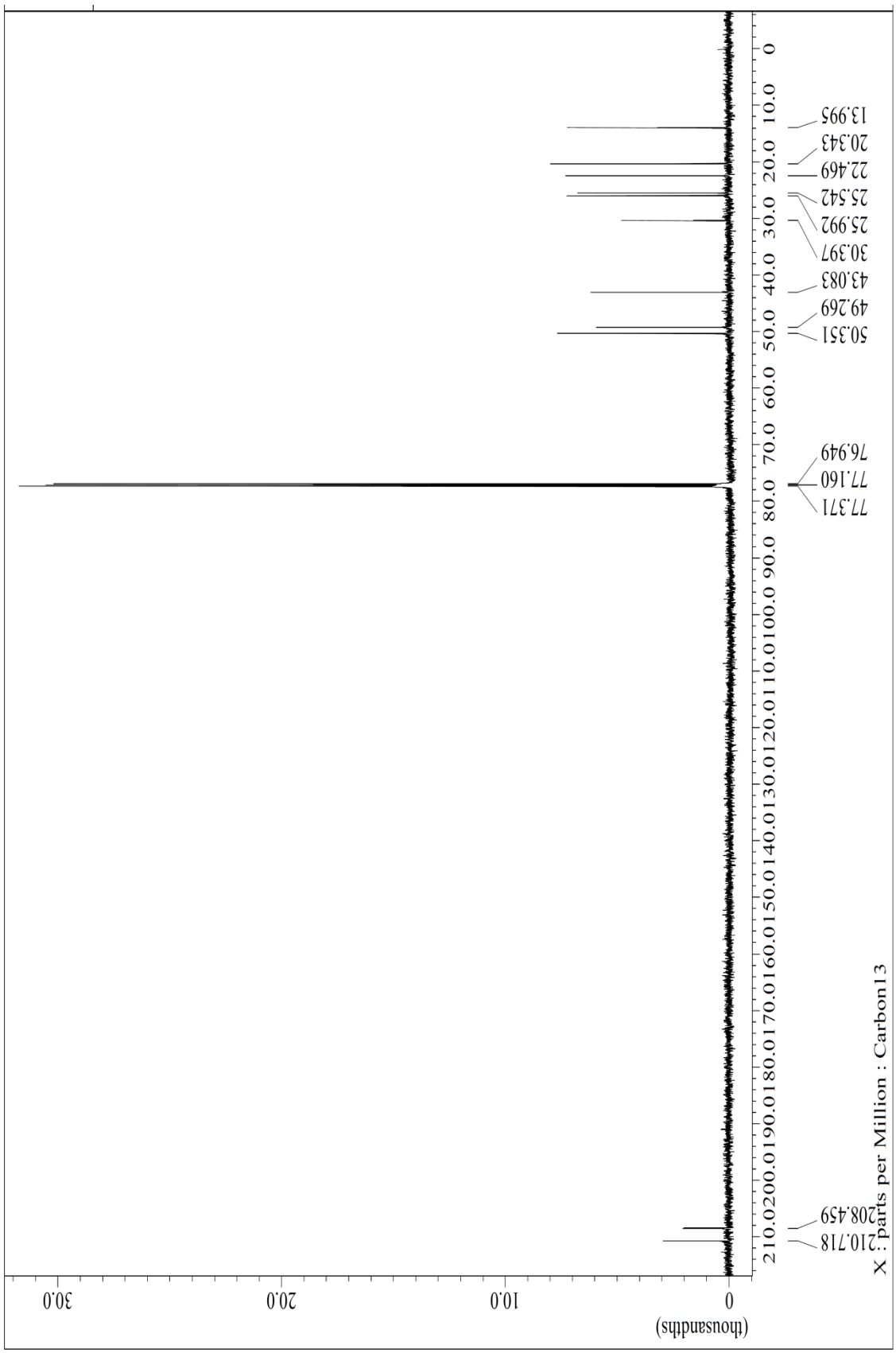
^{13}C NMR of **2a**


X : parts per Million : 13C
abundance
207.803
207.564
130.325
118.521
77.484
77.160
76.845
49.739
48.347
47.727
30.002
24.853
19.857

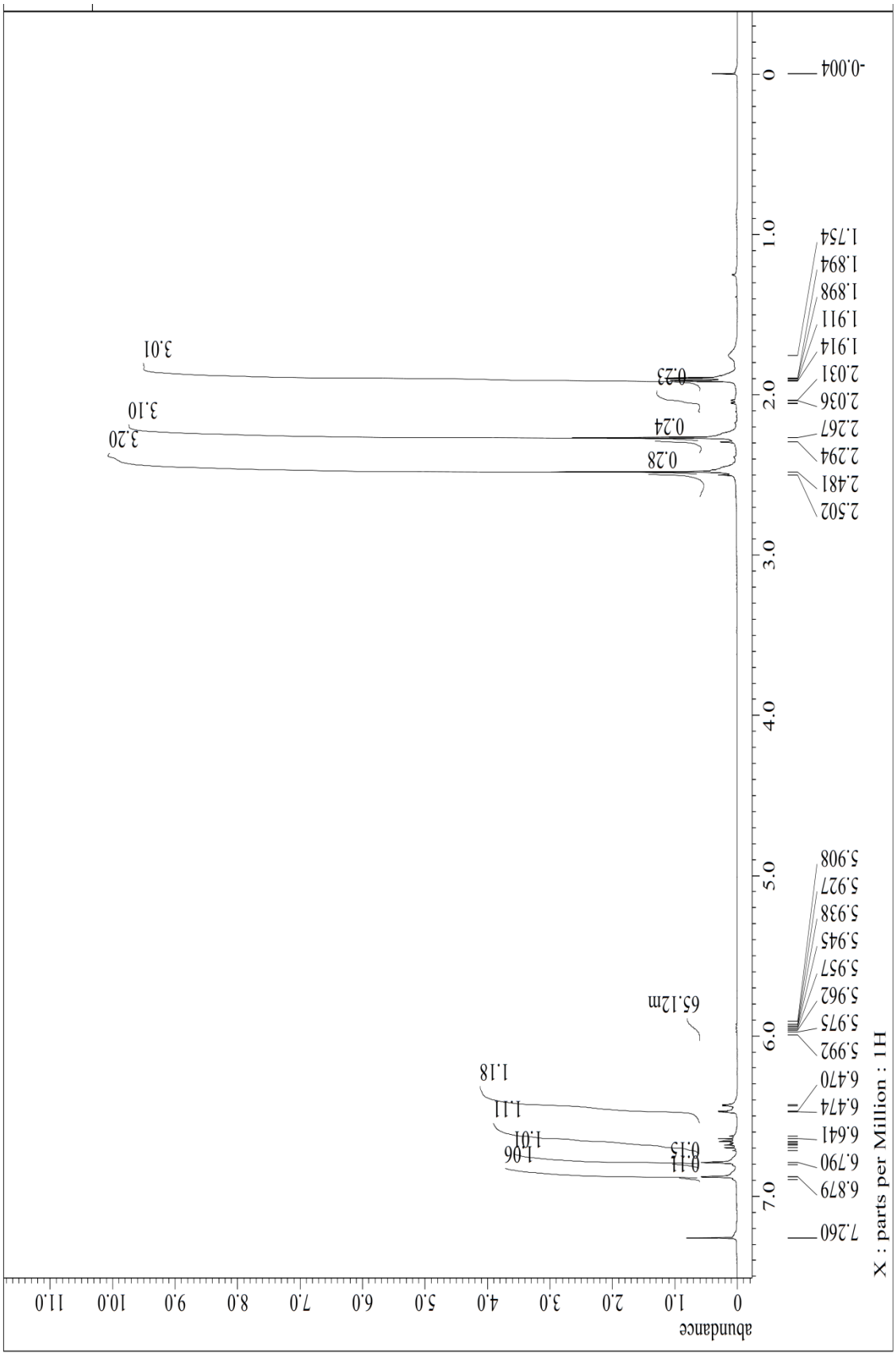
^{1}H NMR of **2b**


X : parts per Million : Proton
abundance
7.260
-0.010
0.891
0.922
0.934
1.286
1.527
1.540
2.121
2.301
2.313
2.317
2.359
2.371
2.384
2.390
2.400
2.428
3.00
2.64
2.09
1.54
1.06
1.97
1.73
3.07
3.30

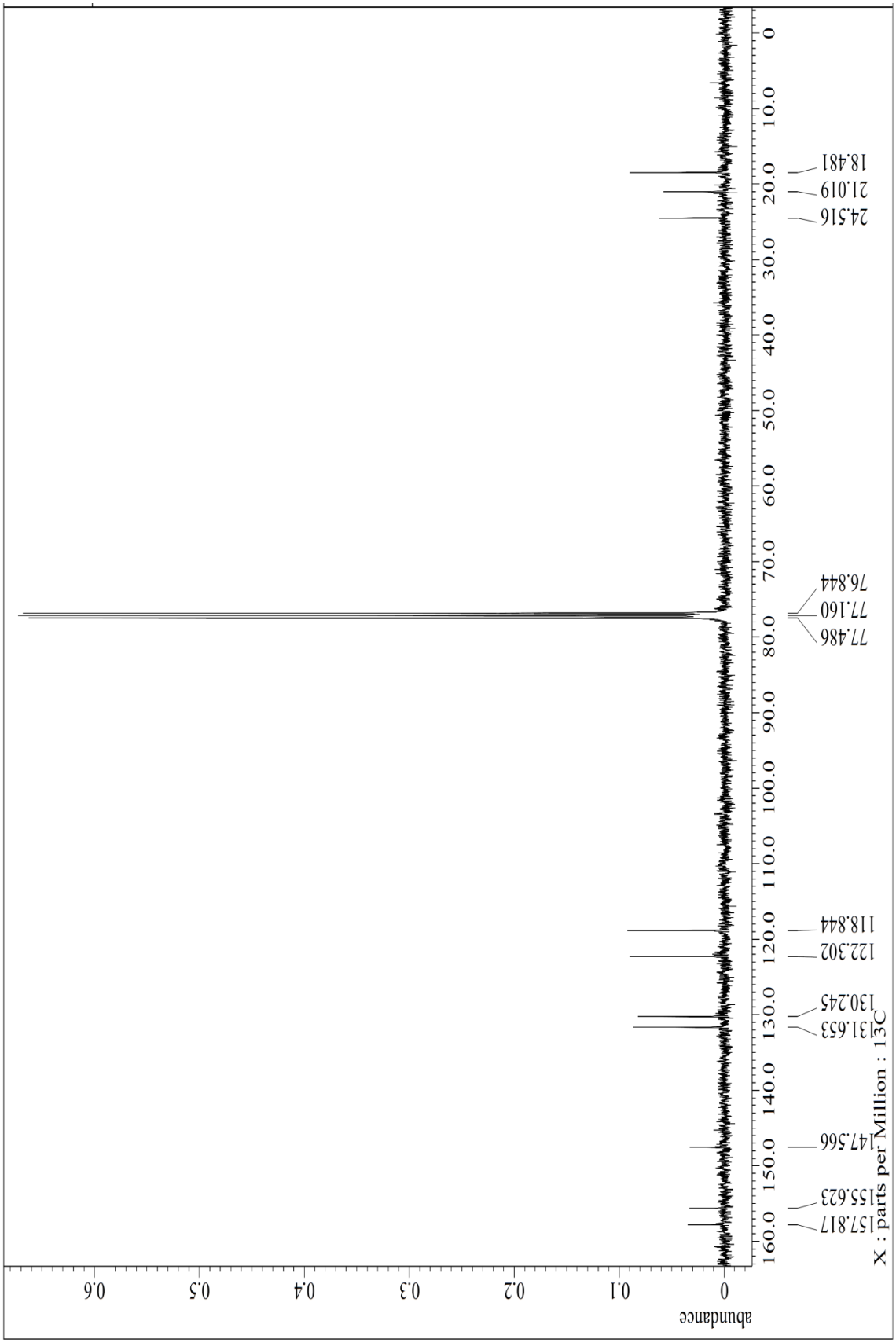
^{13}C NMR of **2b**


X : parts per Million : Carbon13
(thousandths)
0
10.0
20.0
30.0
210.718
208.459
77.371
77.160
76.949
50.351
49.269
43.083
30.397
25.992
25.542
22.469
20.343
13.995

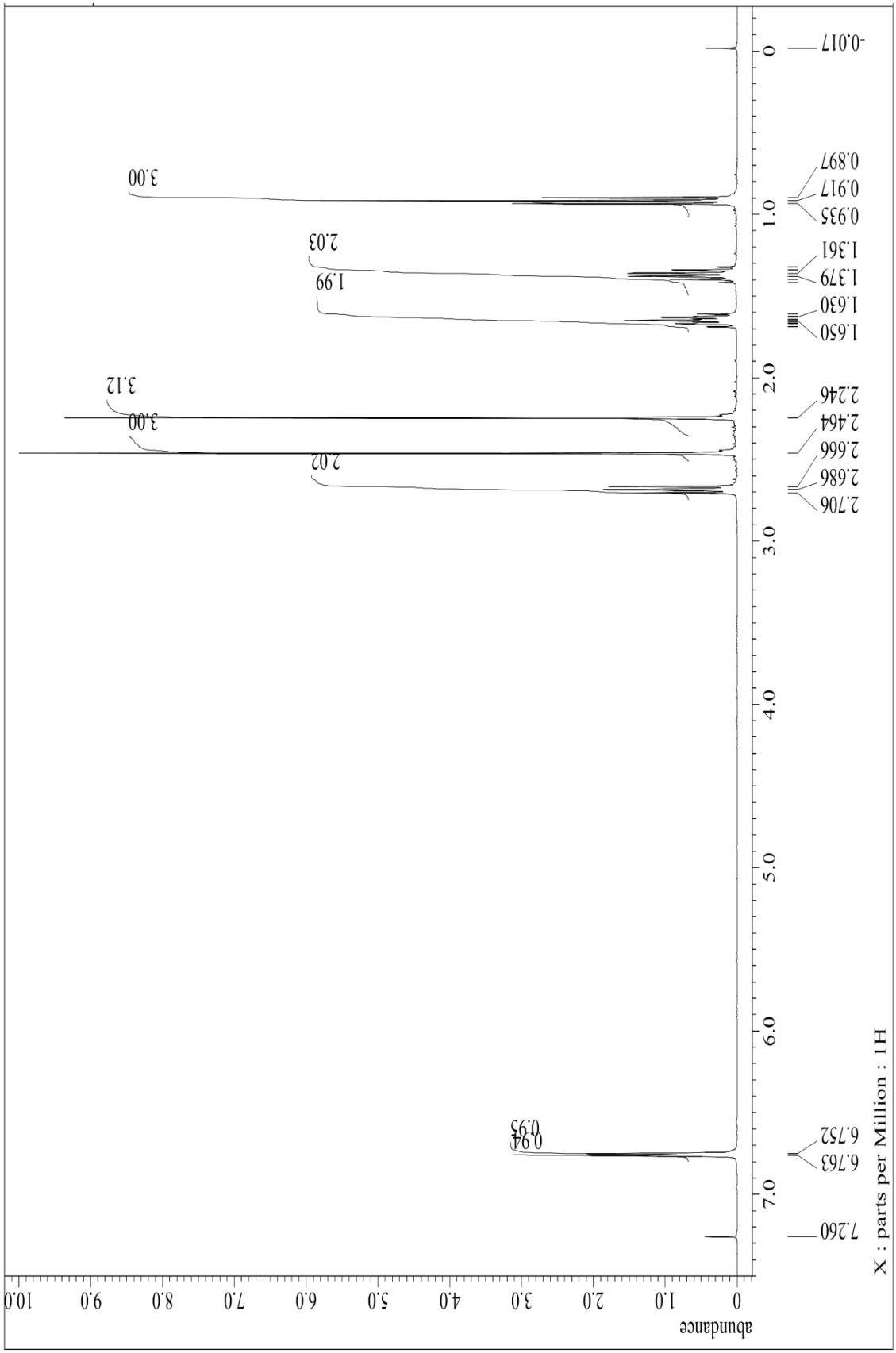
^{1}H NMR of **3a**


X : parts per Million : 1H
abundance
7.260
6.879
6.790
6.641
6.474
6.470
5.992
5.975
5.962
5.957
5.945
5.938
5.927
5.908
65.12m
2.502
2.481
2.294
2.267
2.036
2.031
1.914
1.911
1.898
1.894
1.754
1.18
1.11
1.06
1.01
0.15
0.11
3.20
3.10
3.01
0.28
0.24
0.23
-0.004

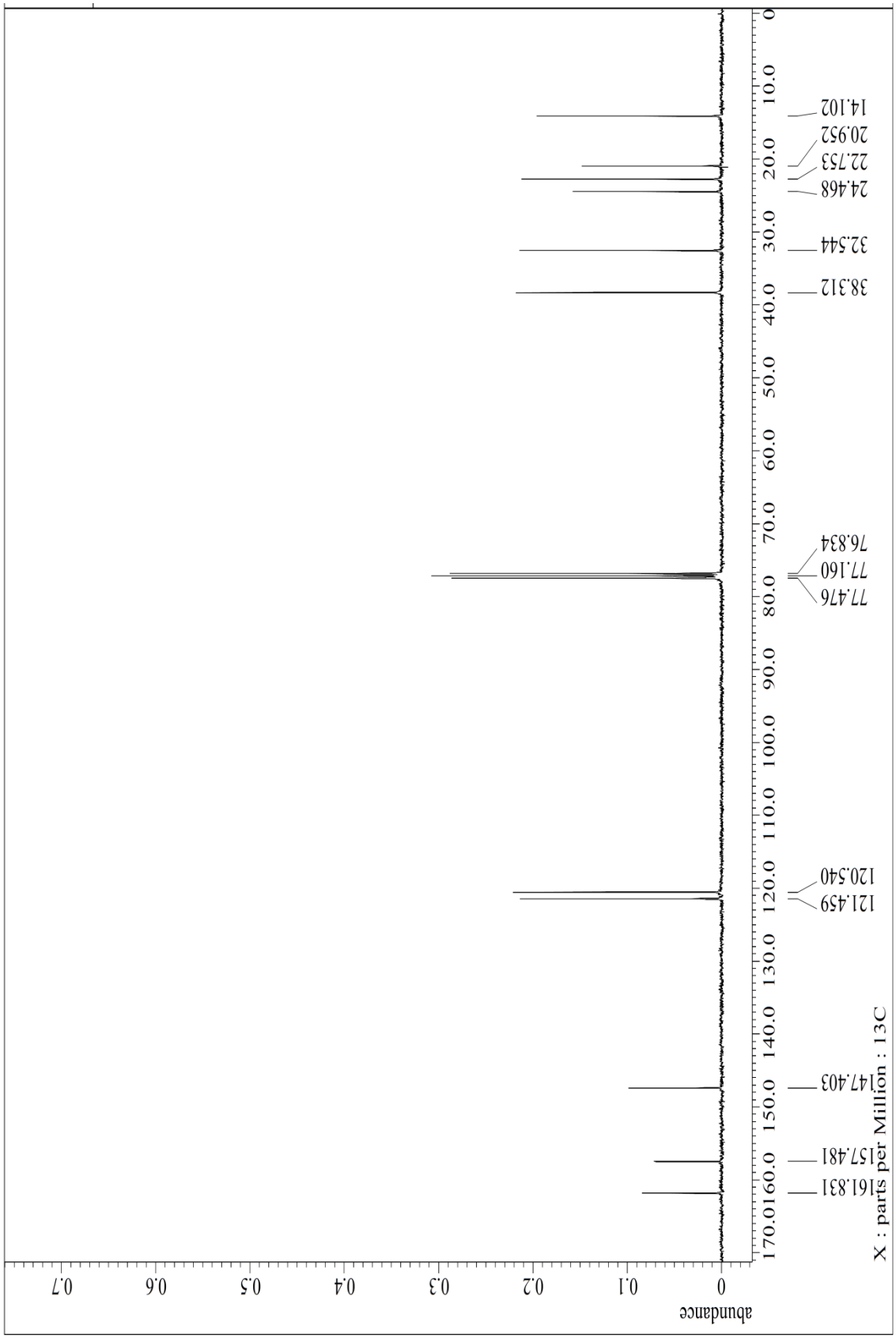
^{13}C NMR of **3a**


X : parts per Million : 13C
abundance
157.817
155.623
147.566
131.653
130.245
122.302
118.844
77.486
77.160
76.844
24.516
21.019
18.481

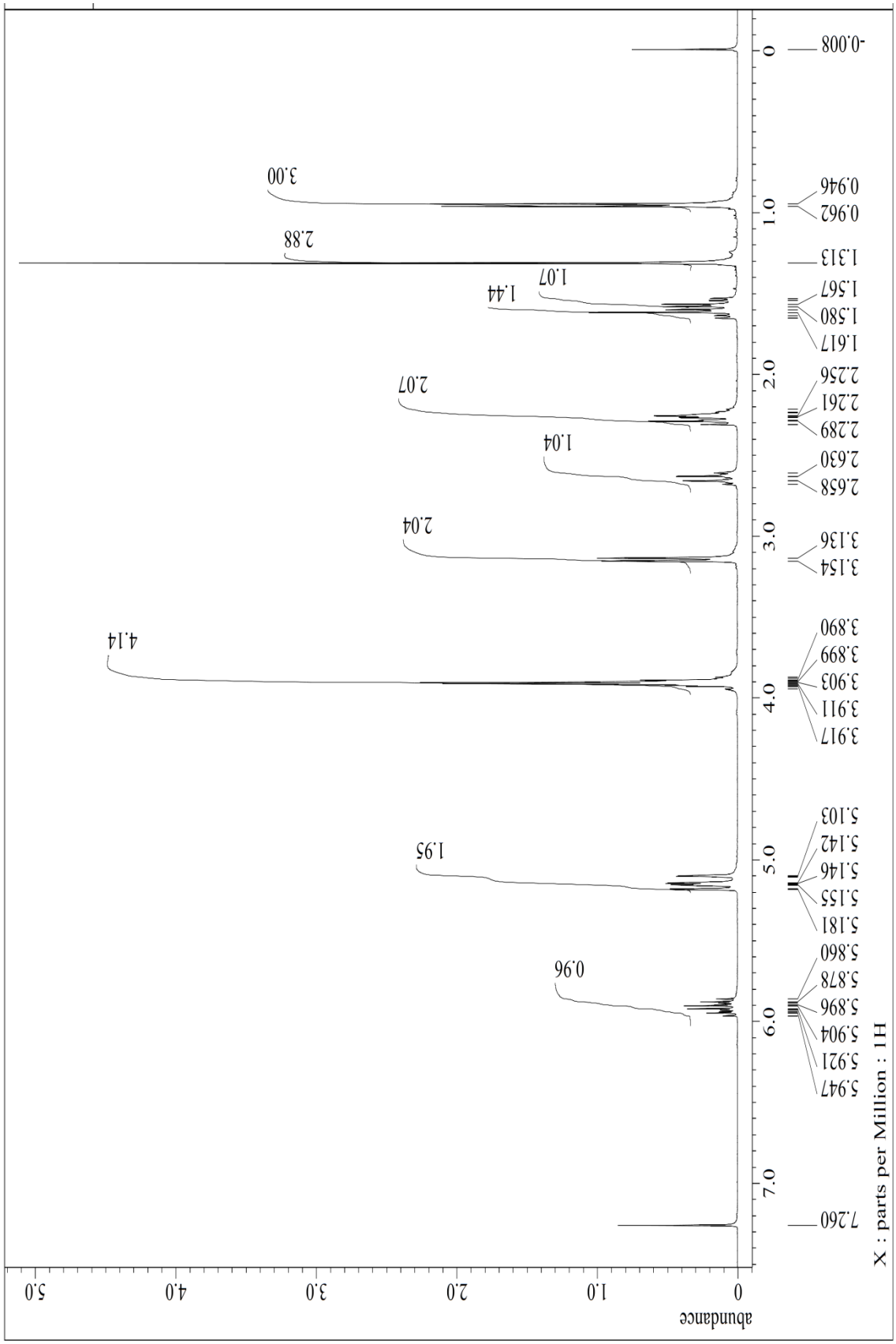
^{1}H NMR of **3b**


-0.017
0.897
0.917
0.935
1.361
1.379
1.630
1.650
2.246
2.464
2.666
2.686
2.706
3.00
2.02
3.12
3.00
1.99
2.03
3.00
0.94
0.95
6.752
6.763
7.260
X : parts per Million : 1H
abundance

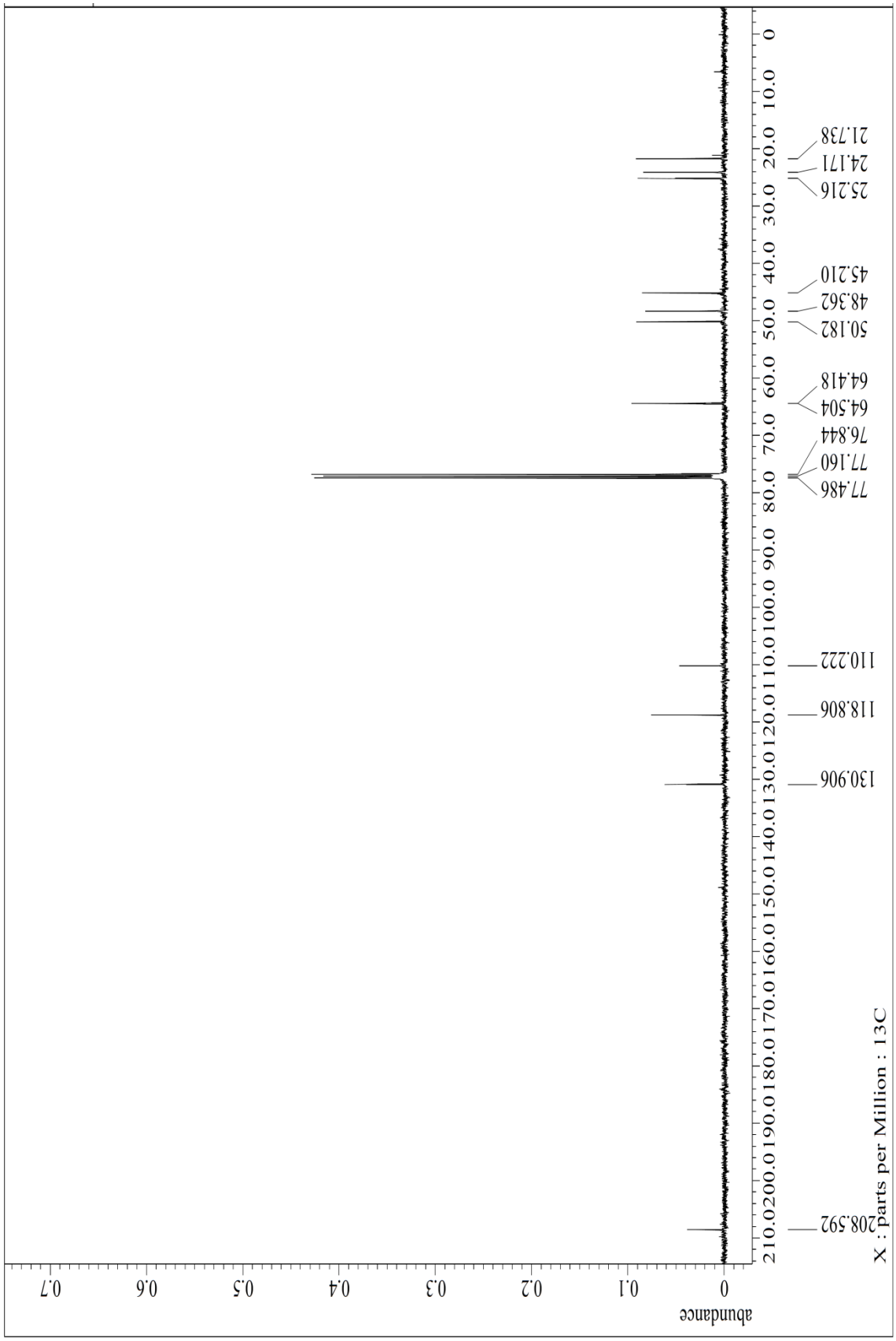
^{13}C NMR of **3b**


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
X : parts per Million : 13C
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.831
157.481
147.403
121.459
120.540
77.476
77.160
76.834
38.312
32.544
24.468
22.753
20.952
14.102

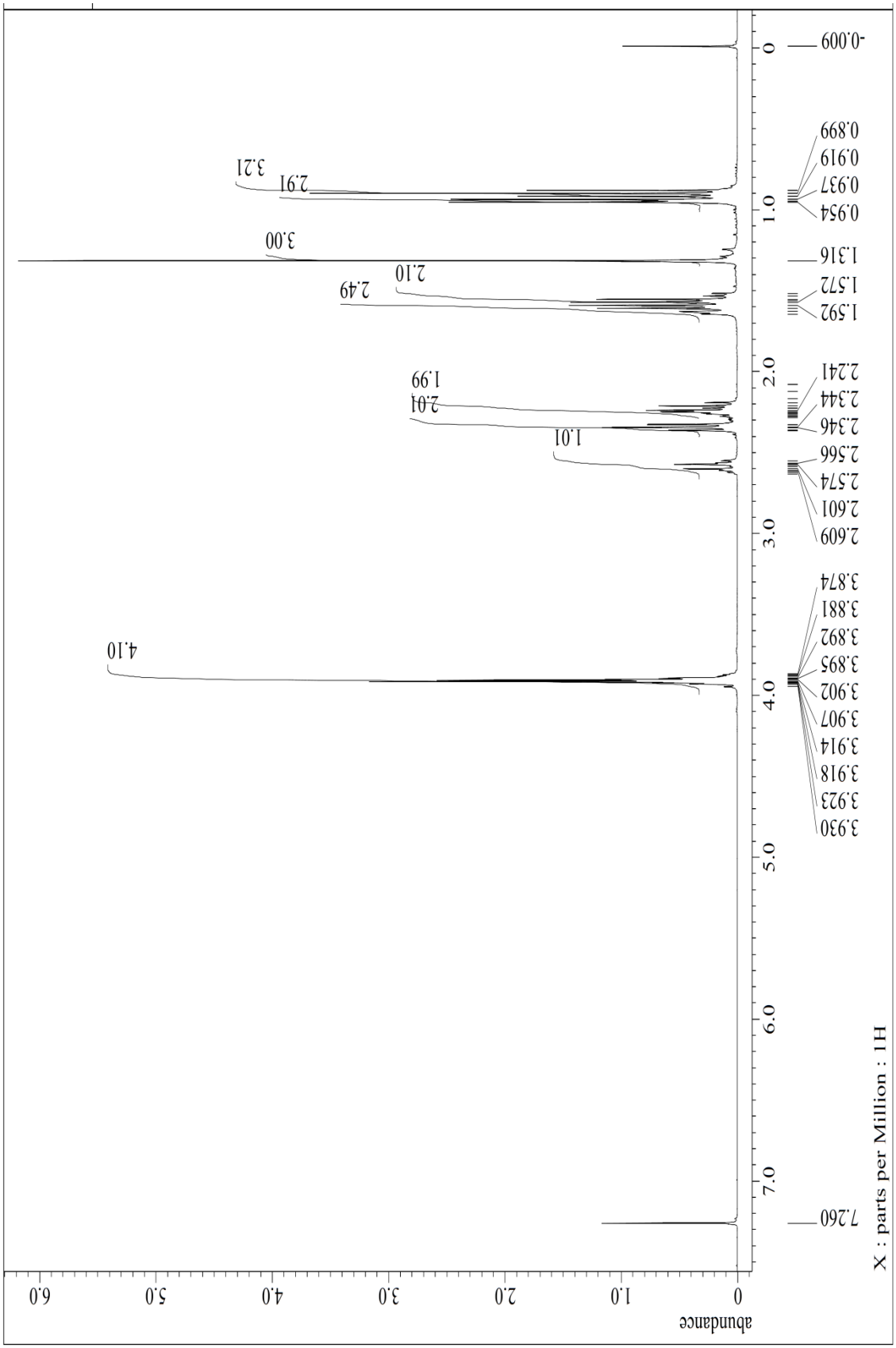
^{1}H NMR of **4a**


X : parts per Million : 1H
abundance
-0.008
0
0.946
0.962
1.313
1.567
1.580
1.617
2.256
2.261
2.289
2.630
2.658
3.136
3.154
3.890
3.899
3.903
3.911
3.917
5.103
5.142
5.146
5.155
5.181
5.860
5.878
5.896
5.904
5.921
5.947
7.260
3.00
2.88
1.07
1.44
2.07
1.04
2.04
4.14
1.95
0.96

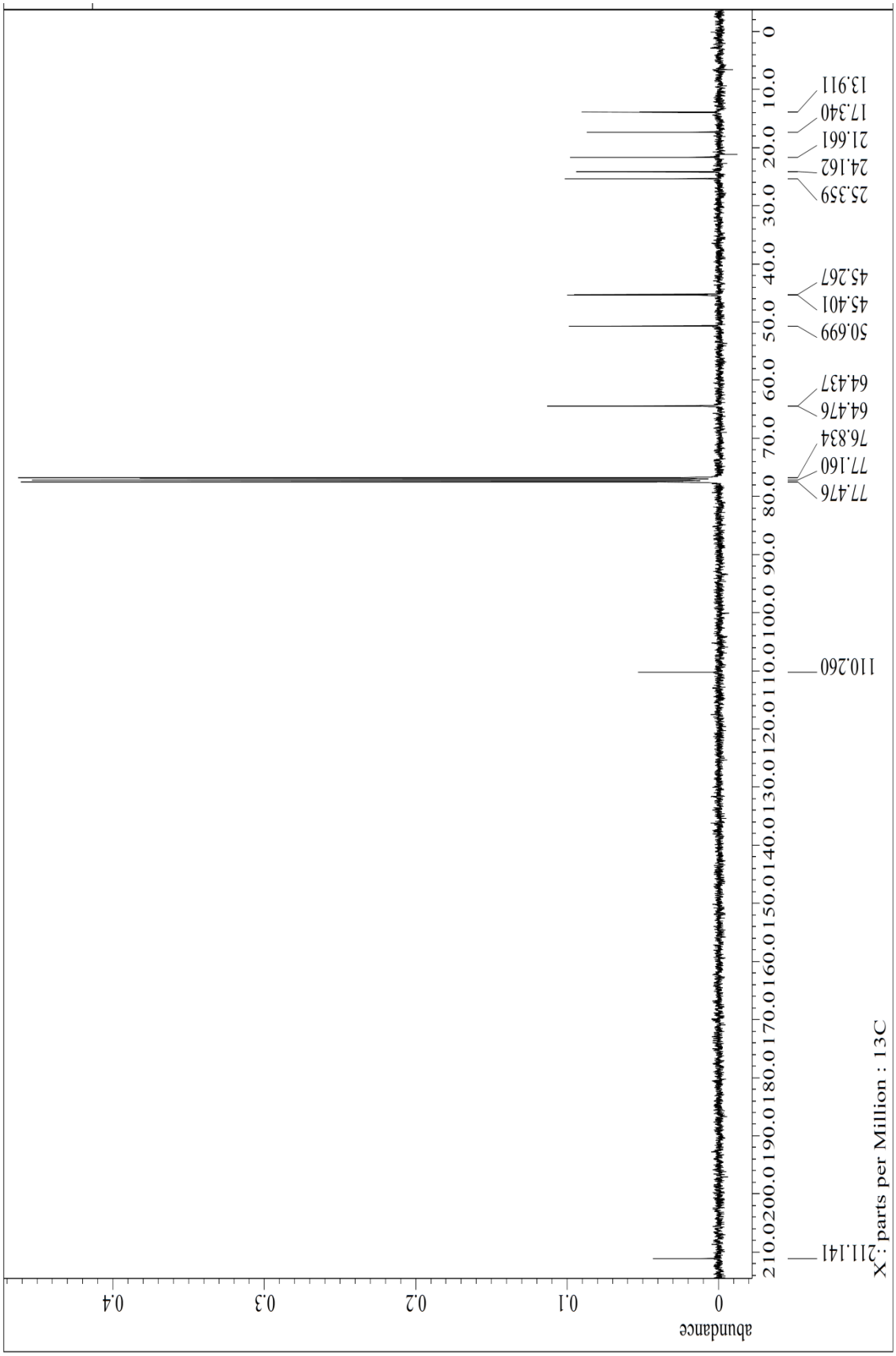
^{13}C NMR of **4a**


X : parts per Million : 13C
abundance
208.592
130.906
118.806
110.222
77.486
77.160
76.844
64.504
64.418
50.182
48.362
45.210
25.216
24.171
21.738

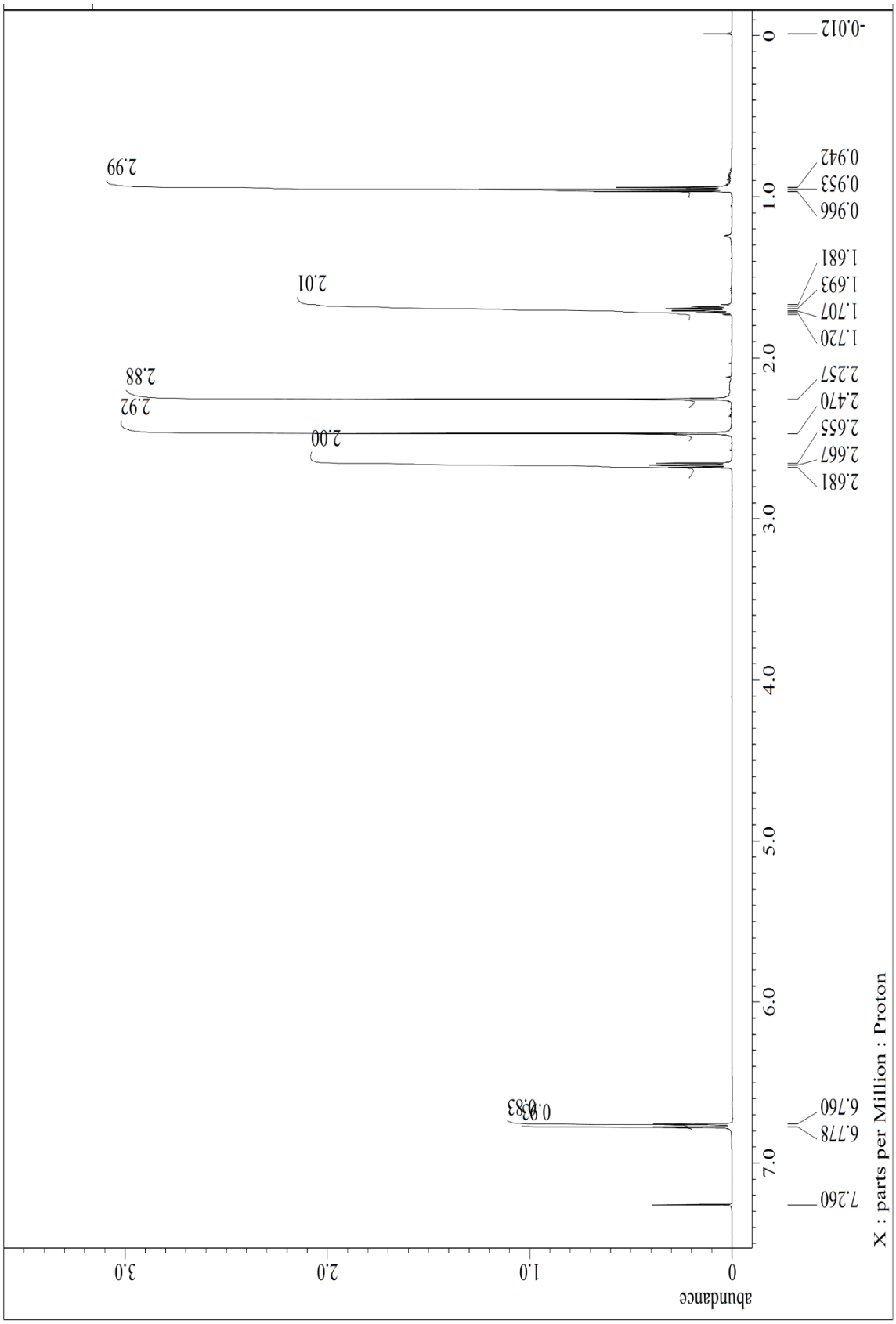
^{1}H NMR of **4c**


X : parts per Million : 1H
abundance
7.260
-0.009
0.954
0.937
0.919
0.899
1.316
1.592
1.572
2.241
2.344
2.346
2.566
2.574
2.601
2.609
3.874
3.881
3.892
3.895
3.902
3.907
3.914
3.918
3.923
3.930
4.10
1.01
1.99
2.01
2.10
2.49
3.00
2.91
3.21

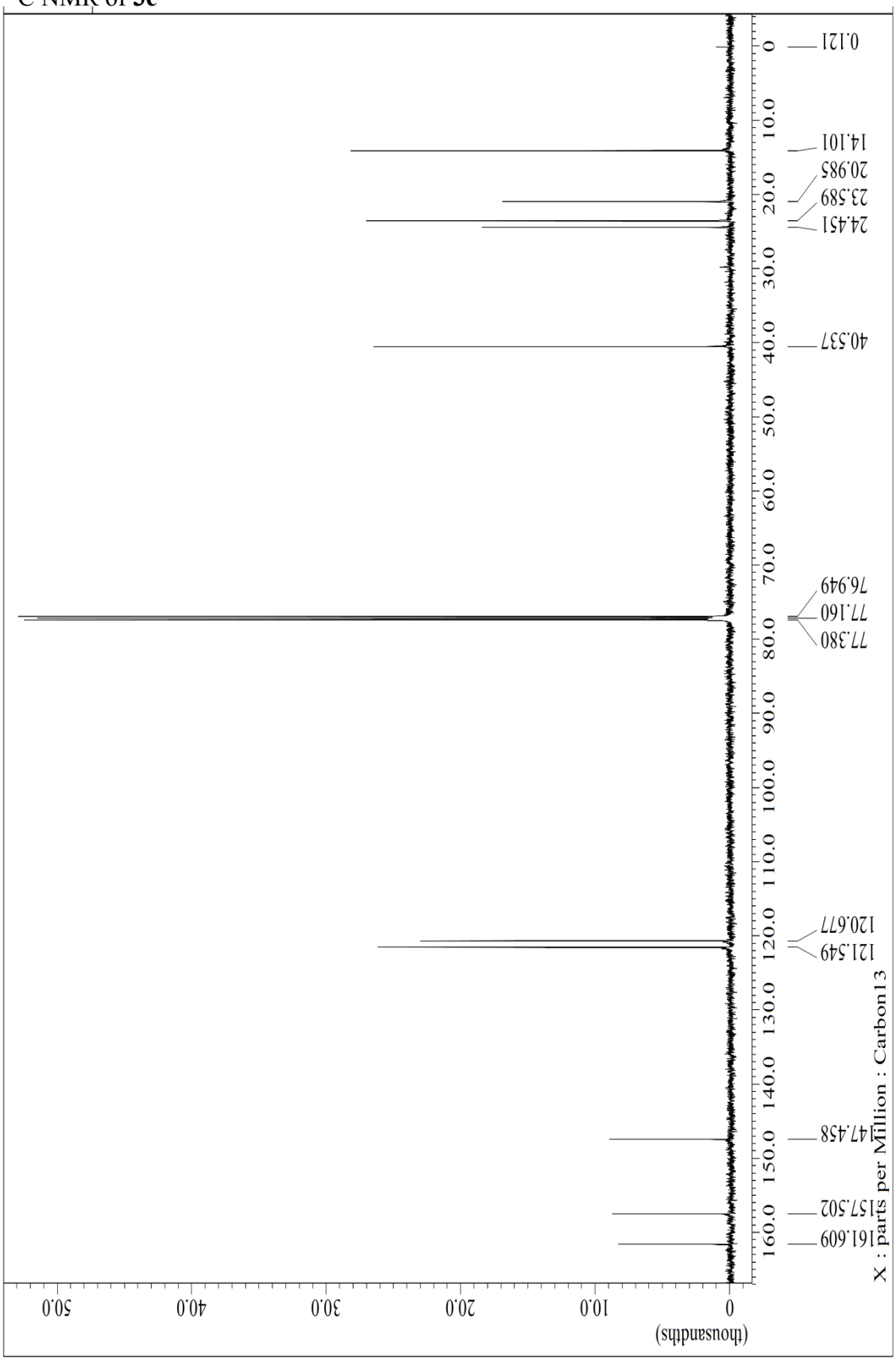
^{13}C NMR of **4c**


X : parts per Million : 13C
abundance
211.141
110.260
77.476
77.160
76.834
64.476
64.437
50.699
45.401
45.267
25.359
24.162
21.661
17.340
13.911

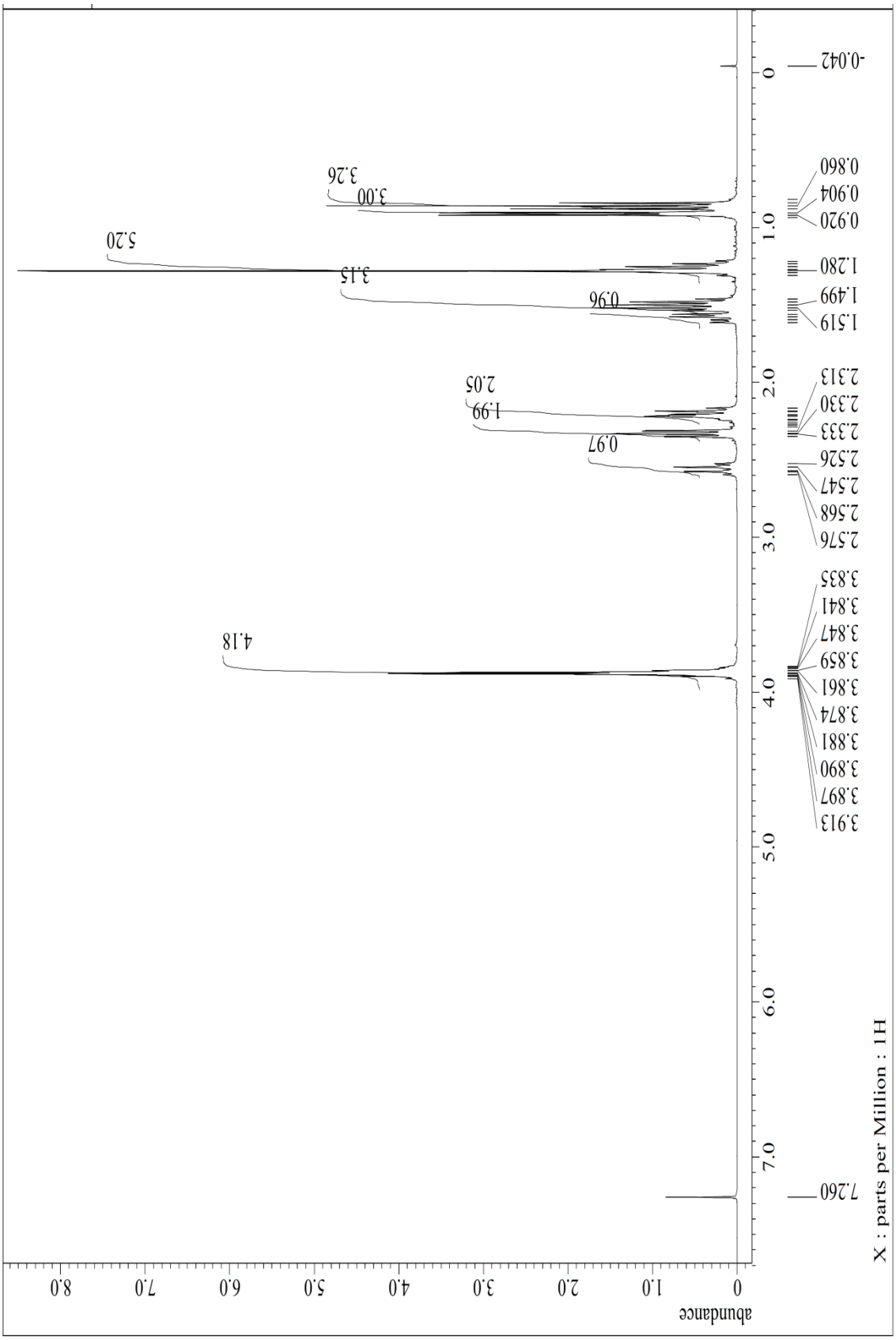
^{1}H NMR of **3c**


-0.012
0.942
0.953
0.966
1.681
1.693
1.707
1.720
2.257
2.470
2.655
2.667
2.681
2.99
2.01
2.88
2.92
2.00
0.83
6.760
6.778
7.260
X : parts per Million : Proton
abundance

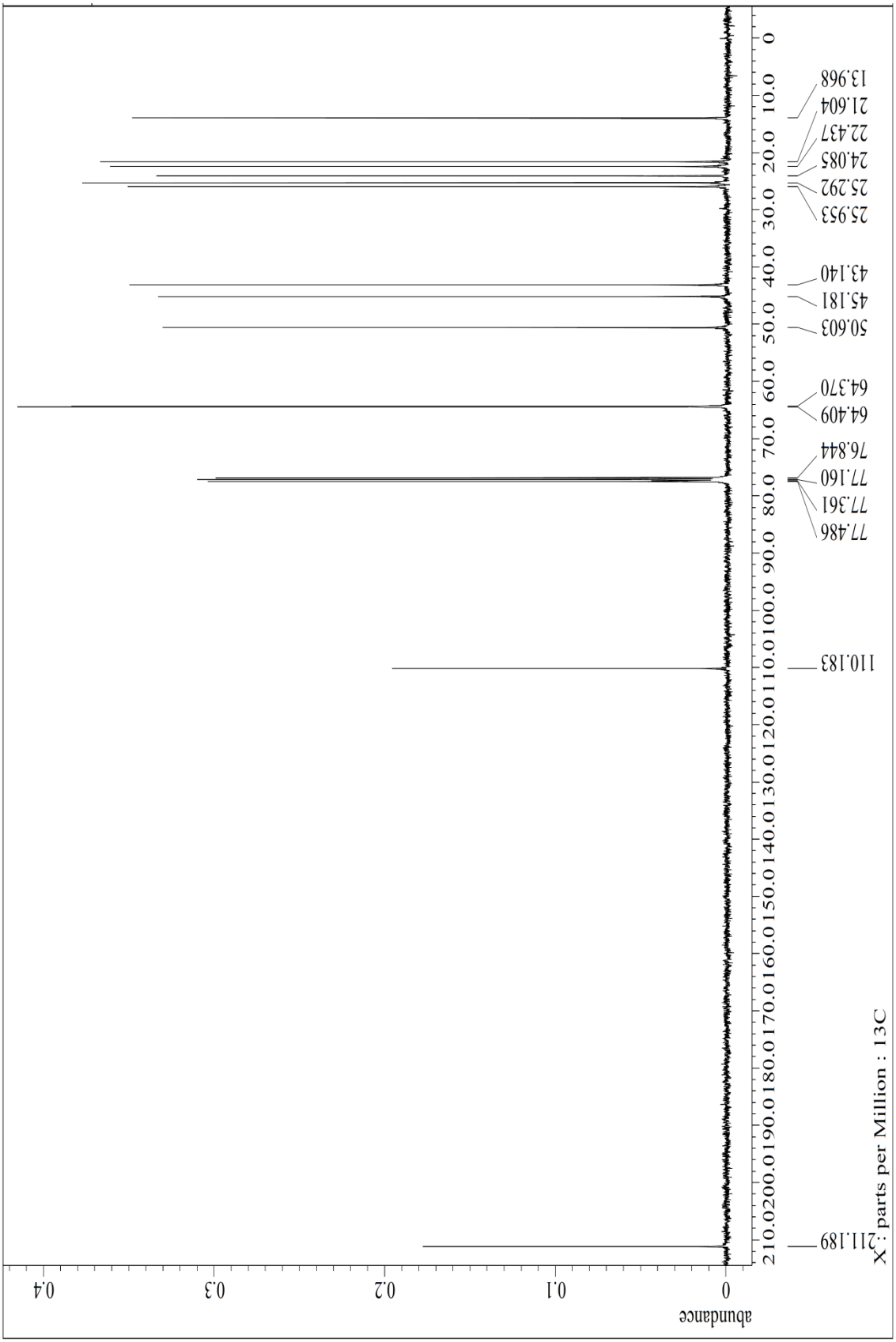
^{13}C NMR of **3c**


0.121
14.101
20.985
23.589
24.451
40.537
76.949
77.160
77.380
120.677
121.549
147.458
157.502
161.609
X : parts per Million : Carbon13
(thousandths)

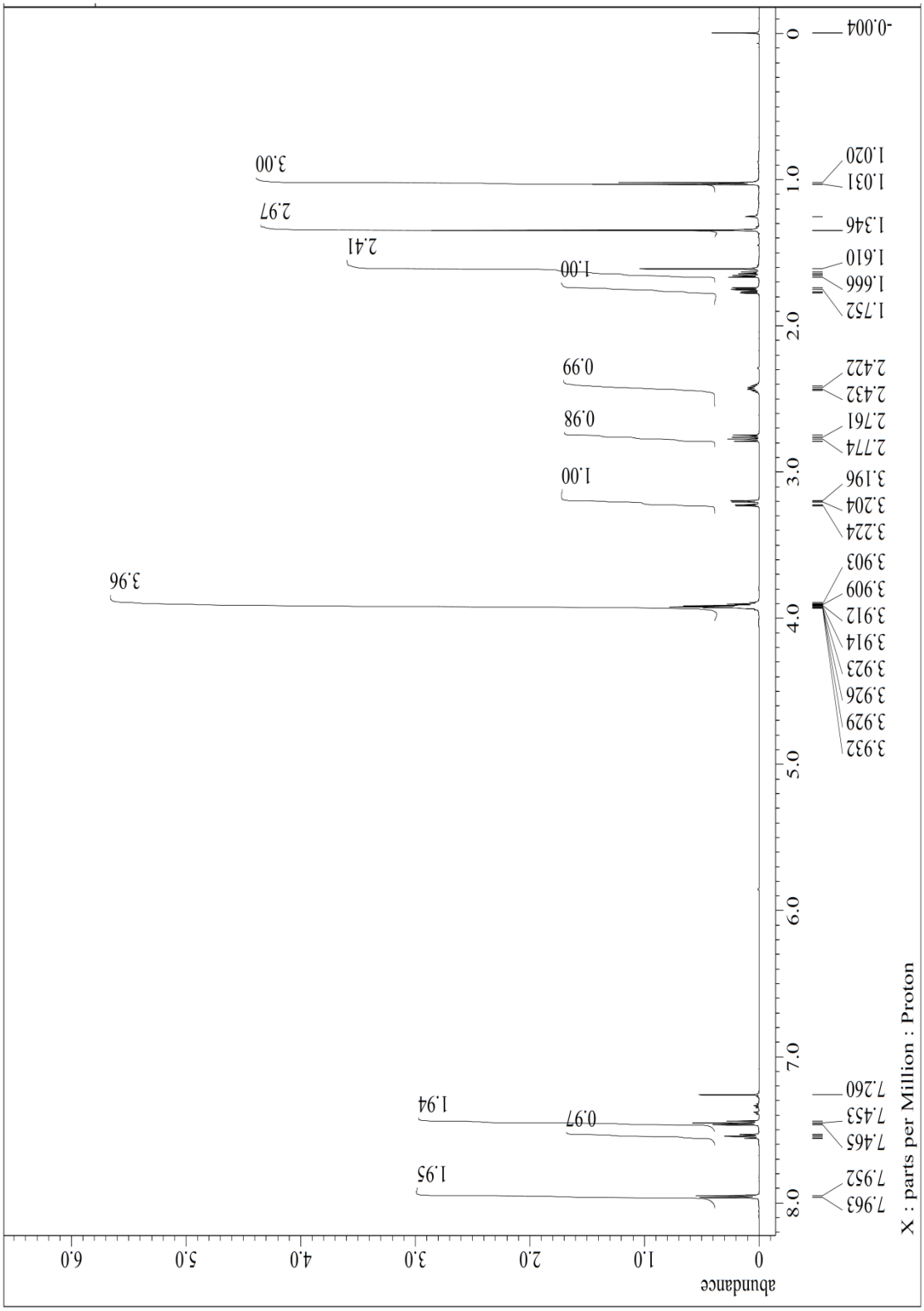
^{1}H NMR of **4b**


-0.042
0
0.860
0.904
0.920
1.280
1.499
1.519
2.313
2.330
2.333
2.526
2.547
2.568
2.576
3.835
3.841
3.847
3.859
3.861
3.874
3.881
3.890
3.897
3.913
7.260
4.18
0.96
3.15
5.20
0.97
1.99
2.05
3.00
3.26
abundance
X : parts per Million : 1H

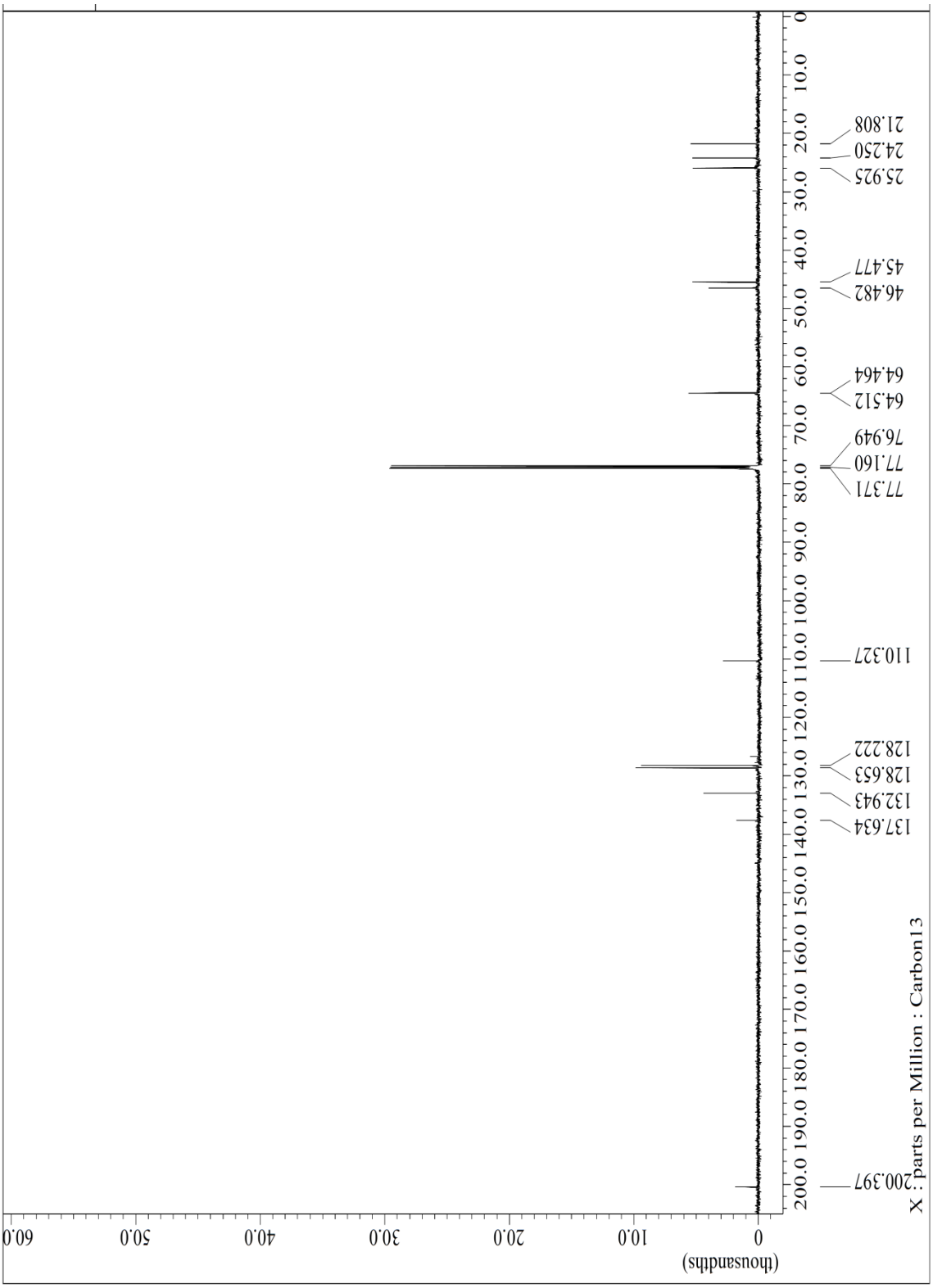
^{13}C NMR of **4b**


X : parts per Million : 13C
abundance
211.189
110.183
77.486
77.361
77.160
76.844
64.409
64.370
50.603
45.181
43.140
25.953
25.292
24.085
22.437
21.604
13.968

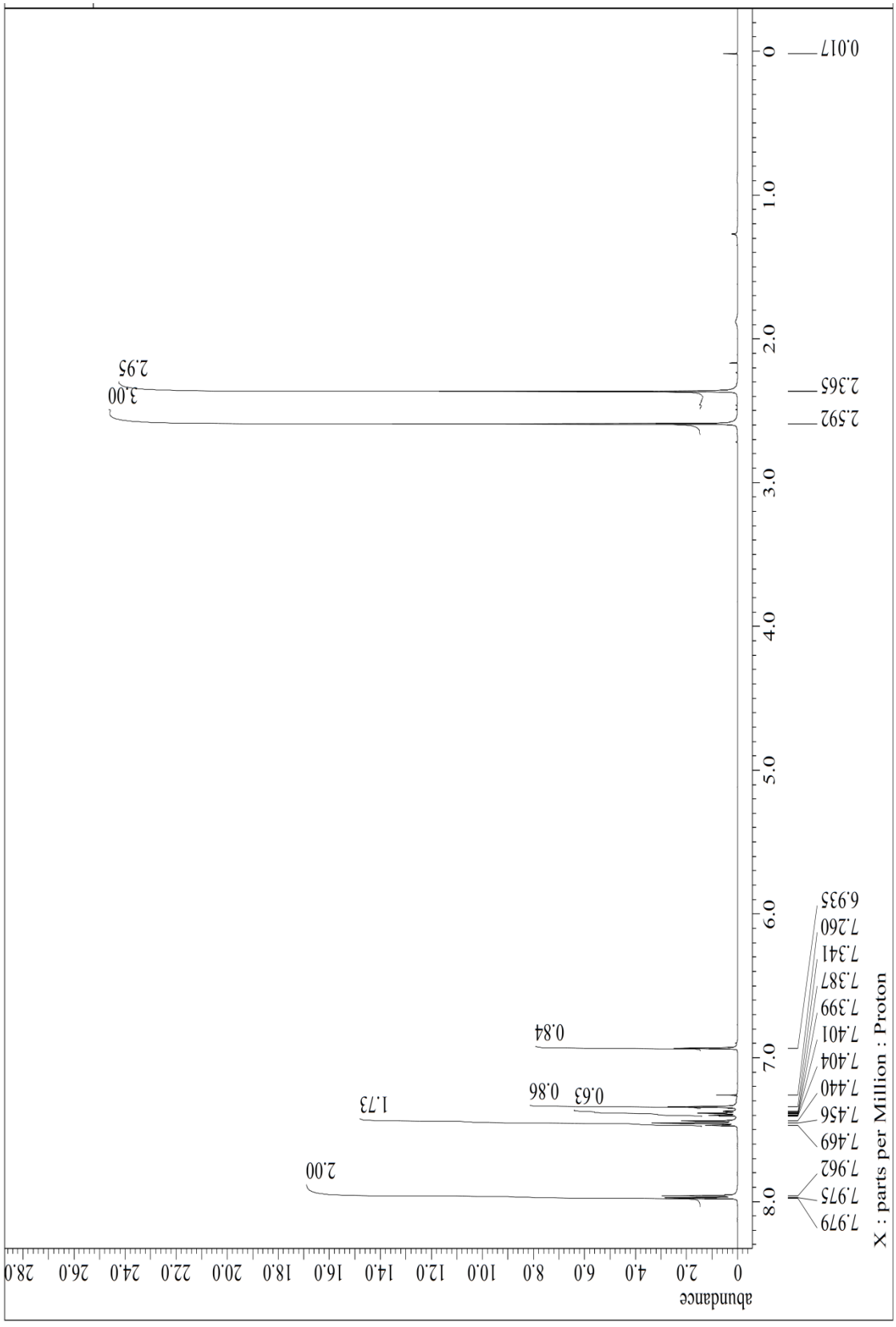
^{1}H NMR of **4d**


-0.004
1.020
1.031
1.346
1.610
1.666
1.752
2.422
2.432
2.761
2.774
3.196
3.204
3.224
3.903
3.909
3.912
3.914
3.923
3.926
3.929
3.932
7.260
7.453
7.465
7.952
7.963
1.95
0.97
1.94
3.96
1.00
0.98
0.99
1.00
2.41
2.97
3.00
X : parts per Million : Proton
abundance

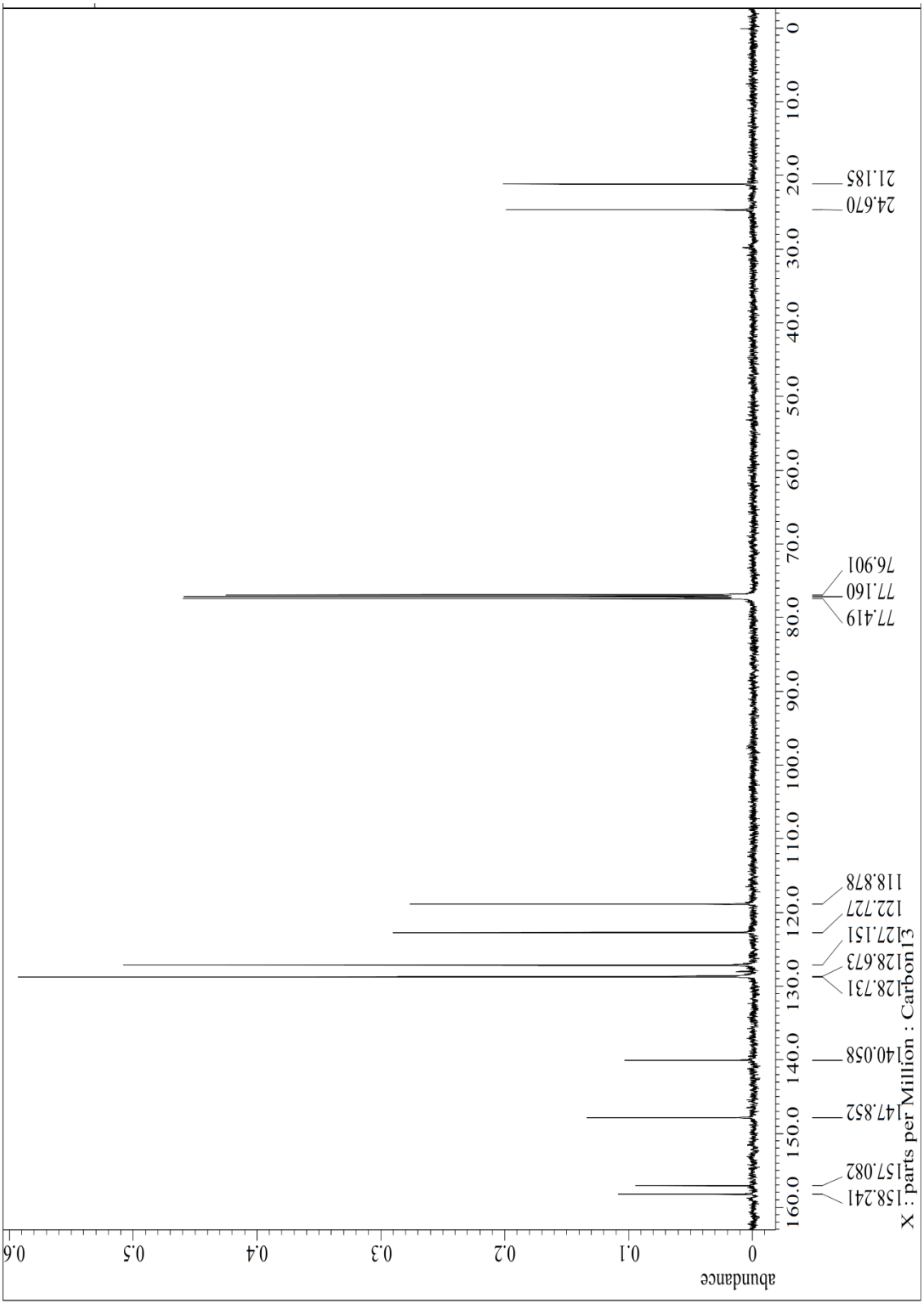
^{13}C NMR of 4**d**


X : parts per Million : Carbon13
200.397
137.634
132.943
128.653
128.222
110.327
77.371
77.160
76.949
64.512
64.464
46.482
45.477
25.925
24.250
21.808
(thousandths)

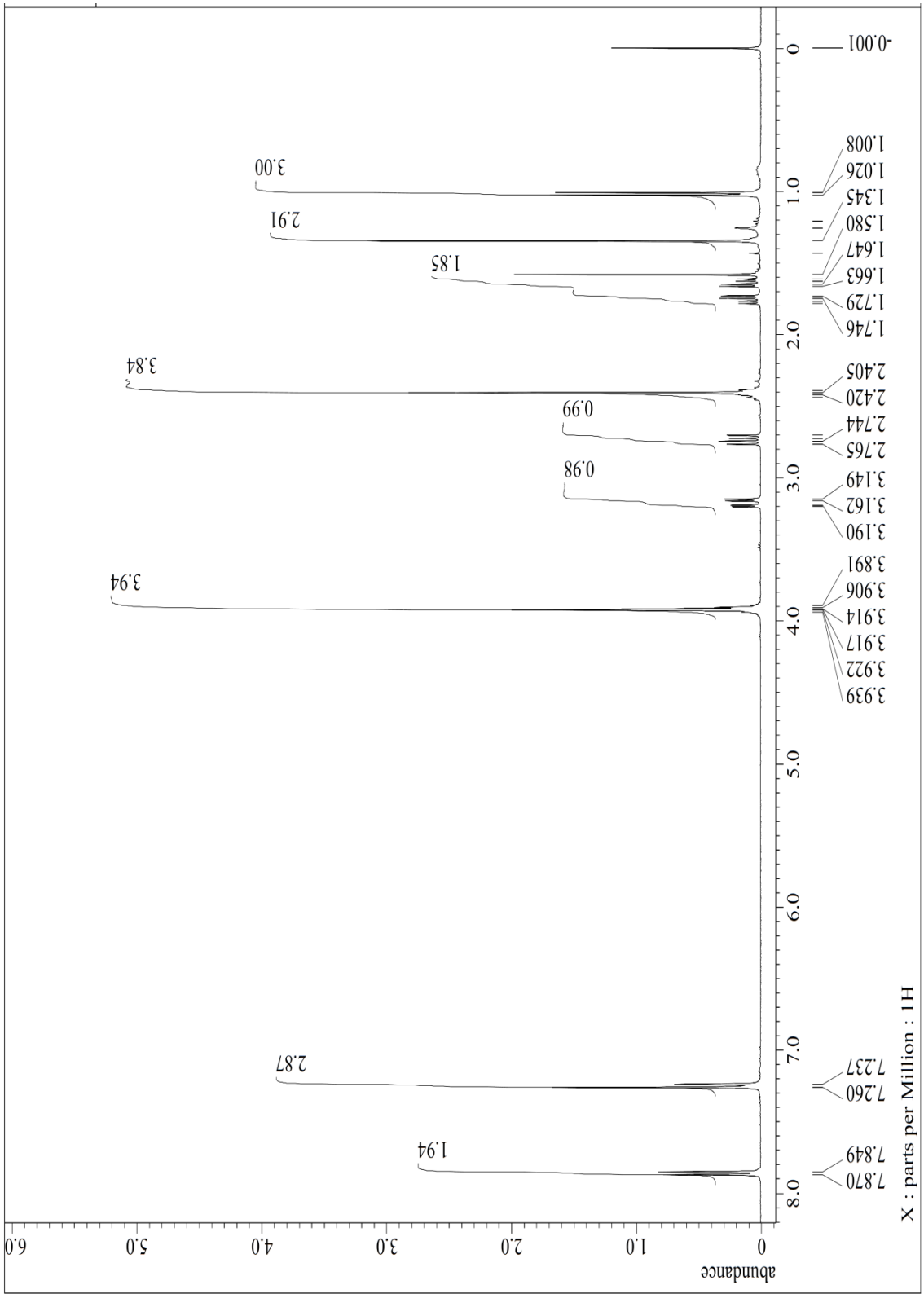
^{1}H NMR of **3d**


0.017
2.365
2.592
2.95
3.00
0.84
0.63
0.86
1.73
2.00
7.979
7.975
7.962
7.469
7.456
7.440
7.404
7.401
7.399
7.387
7.341
7.260
6.935
X : parts per Million : Proton
abundance

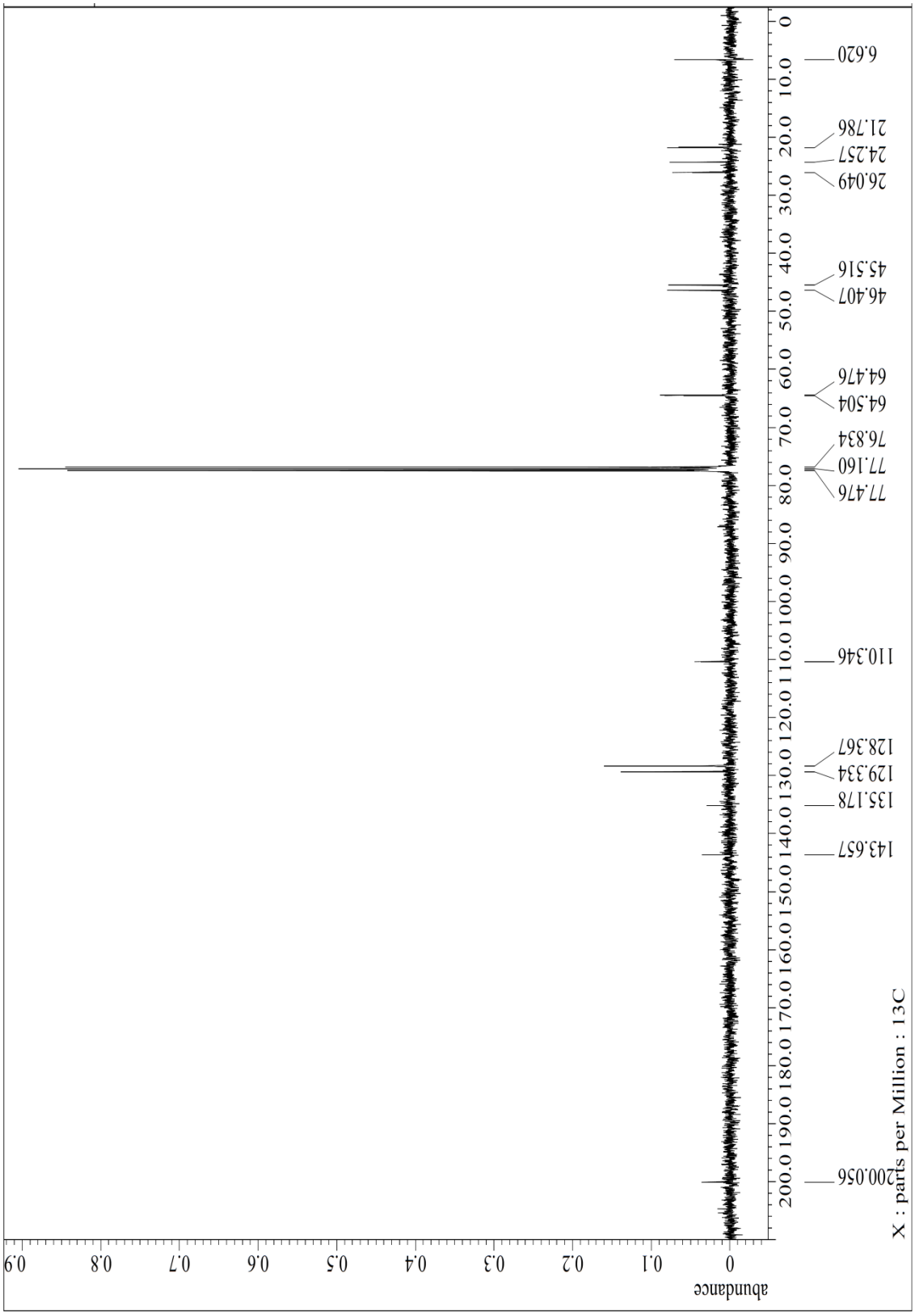
^{13}C NMR of **3d**


X : parts per Million : Carbon13
158.241
157.082
147.852
140.058
128.731
128.673
127.151
122.727
118.878
77.419
77.160
76.901
24.670
21.185
abundance

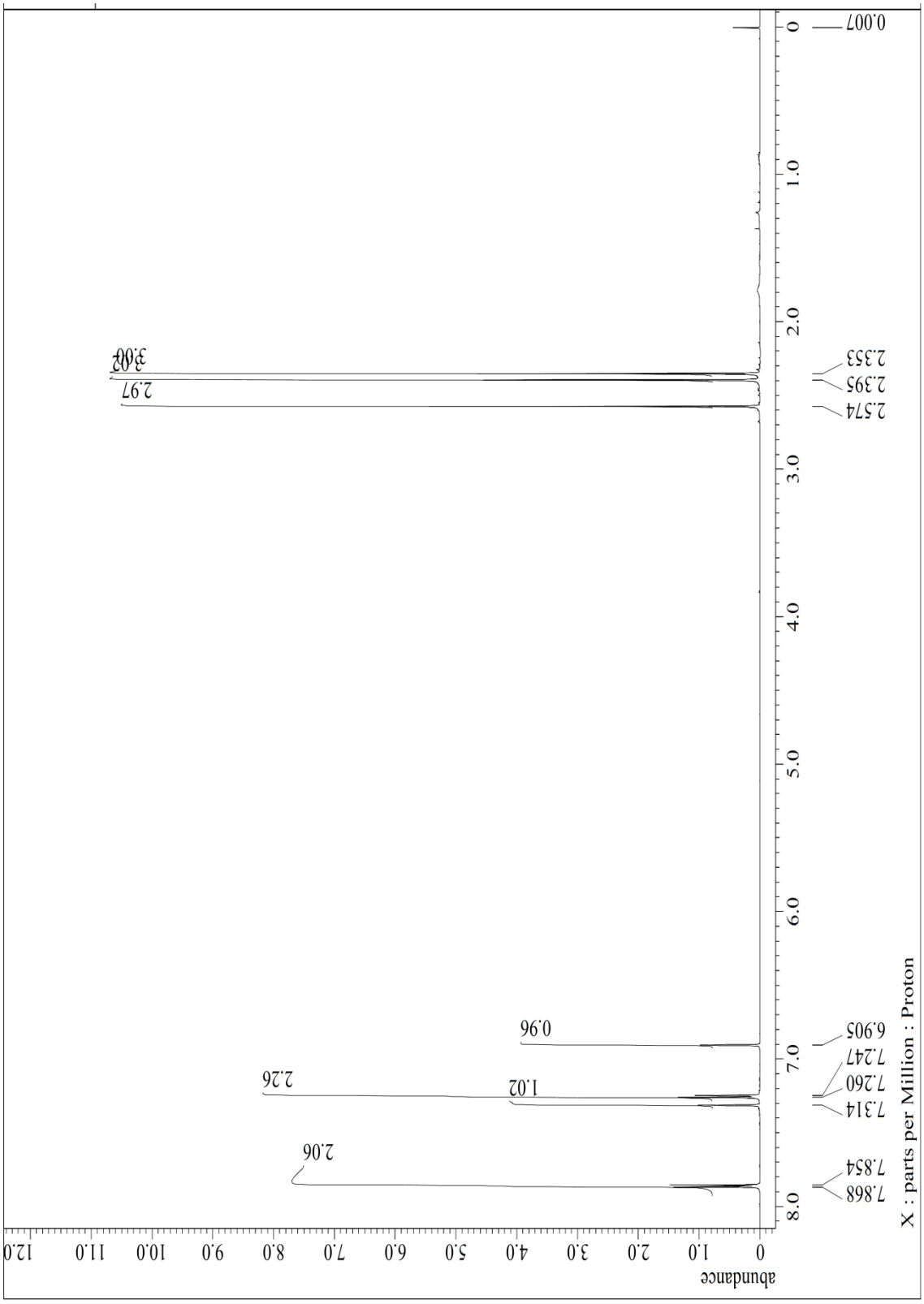
^{1}H NMR of **4e**


-0.001
1.008
1.026
1.345
1.580
1.647
1.663
1.729
1.746
2.405
2.420
2.744
2.765
3.149
3.162
3.190
3.891
3.906
3.914
3.917
3.922
3.939
7.237
7.260
7.849
7.870
3.00
2.91
1.85
3.84
0.99
0.98
3.94
2.87
1.94
abundance
X : parts per Million : 1H

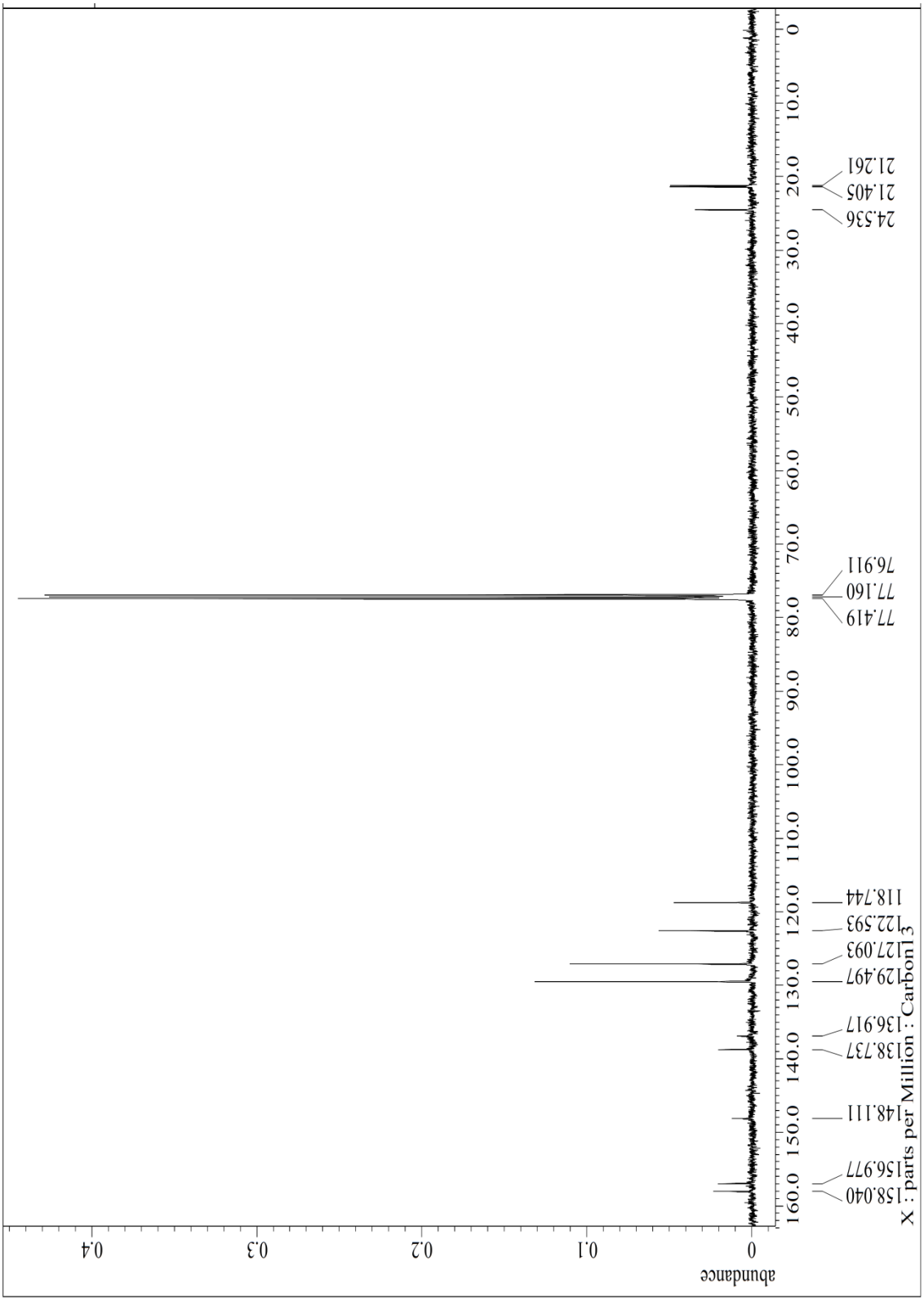
^{13}C NMR of **4e**


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
200.056
143.657
135.178
129.334
128.367
110.346
77.476
77.160
76.834
64.504
64.476
46.407
45.516
26.049
24.257
21.786
6.620

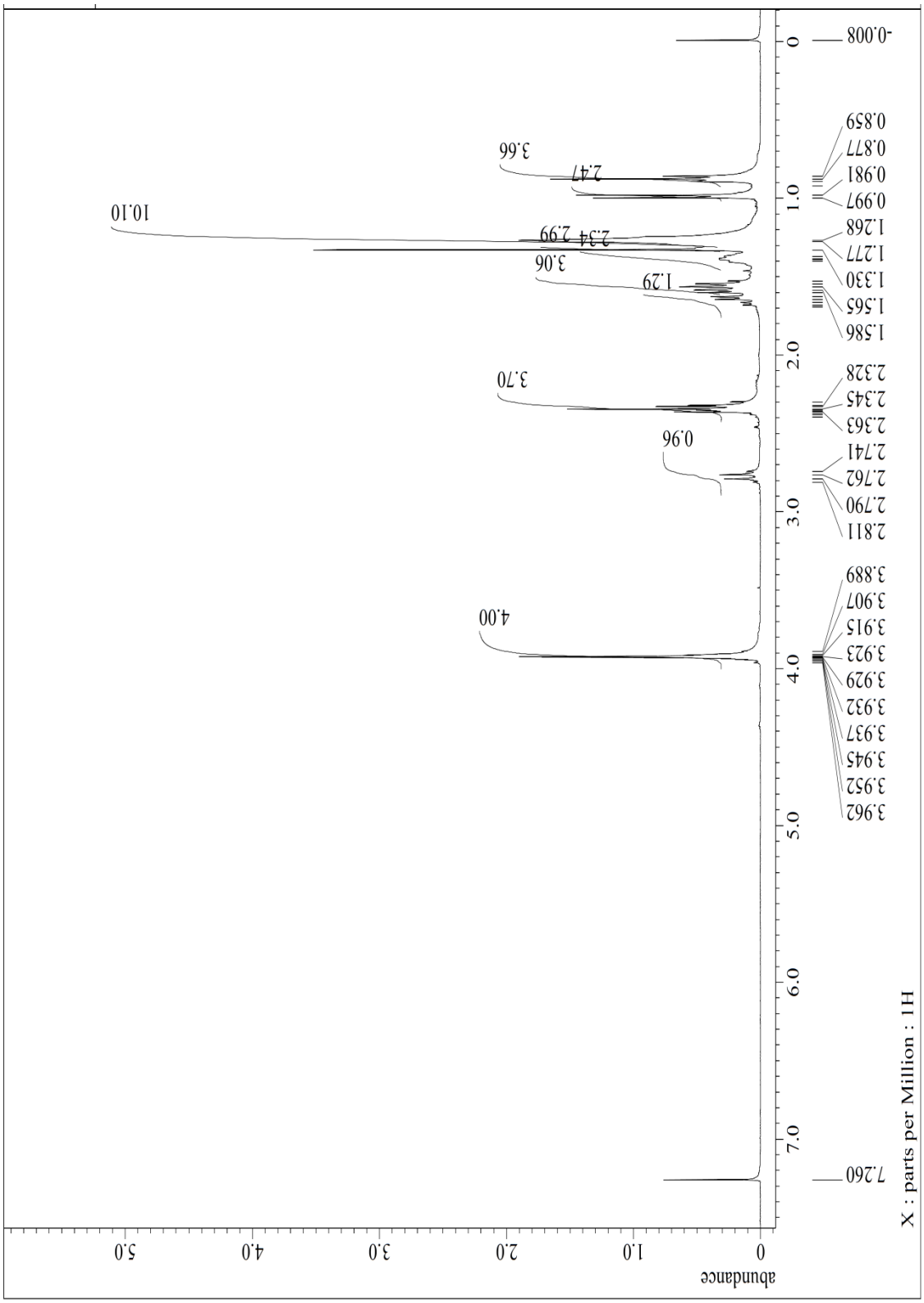
^{1}H NMR of **3e**


0.007
2.353
2.395
2.574
2.97
3.00
6.905
7.247
7.260
7.314
7.854
7.868
0.96
1.02
2.06
2.26
X : parts per Million : Proton
abundance

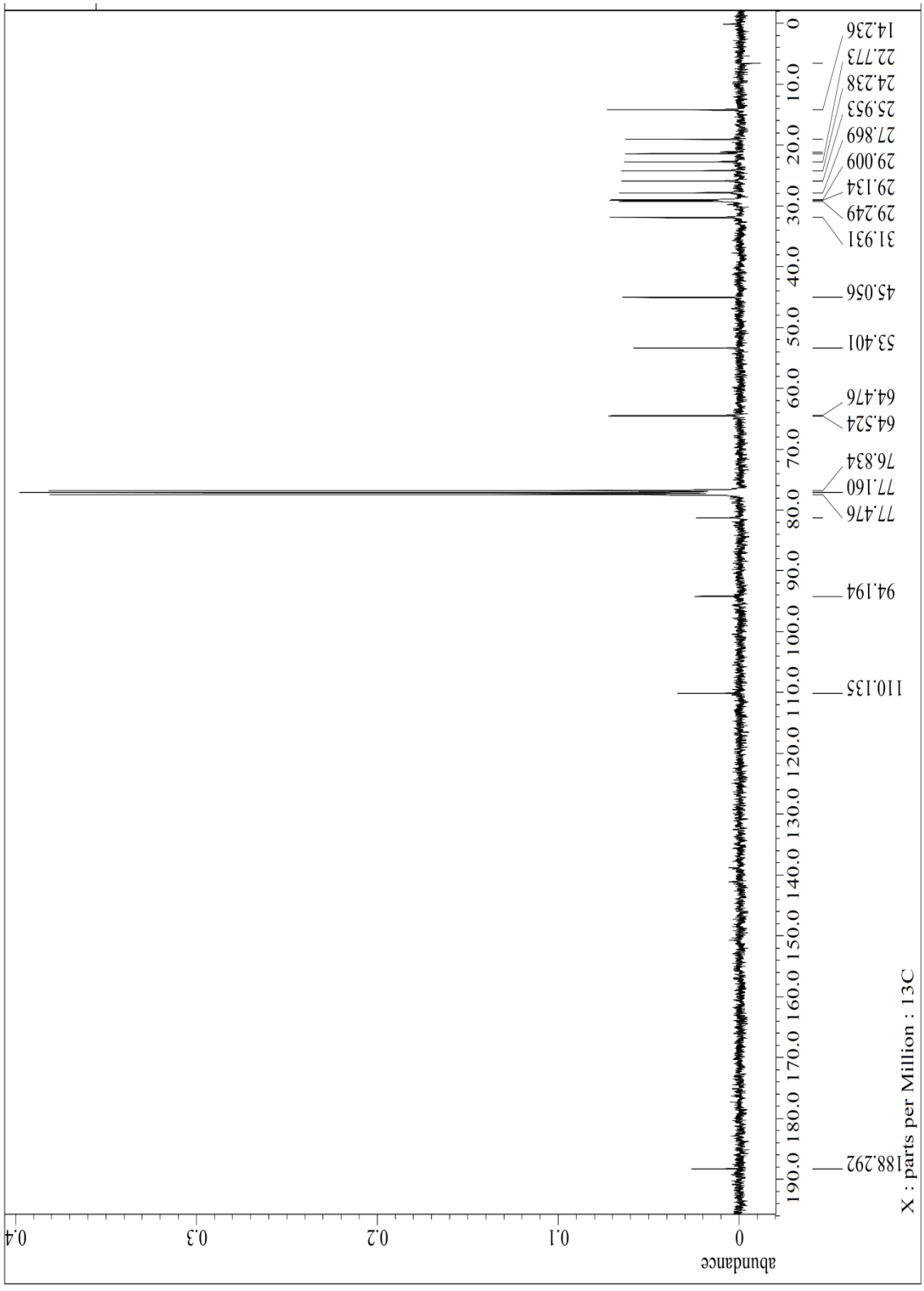
^{13}C NMR of **3e**


158.040
156.977
148.111
138.737
136.917
129.497
127.093
122.593
118.744
77.419
77.160
76.911
24.536
21.405
21.261
X : parts per Million : Carbon13
abundance

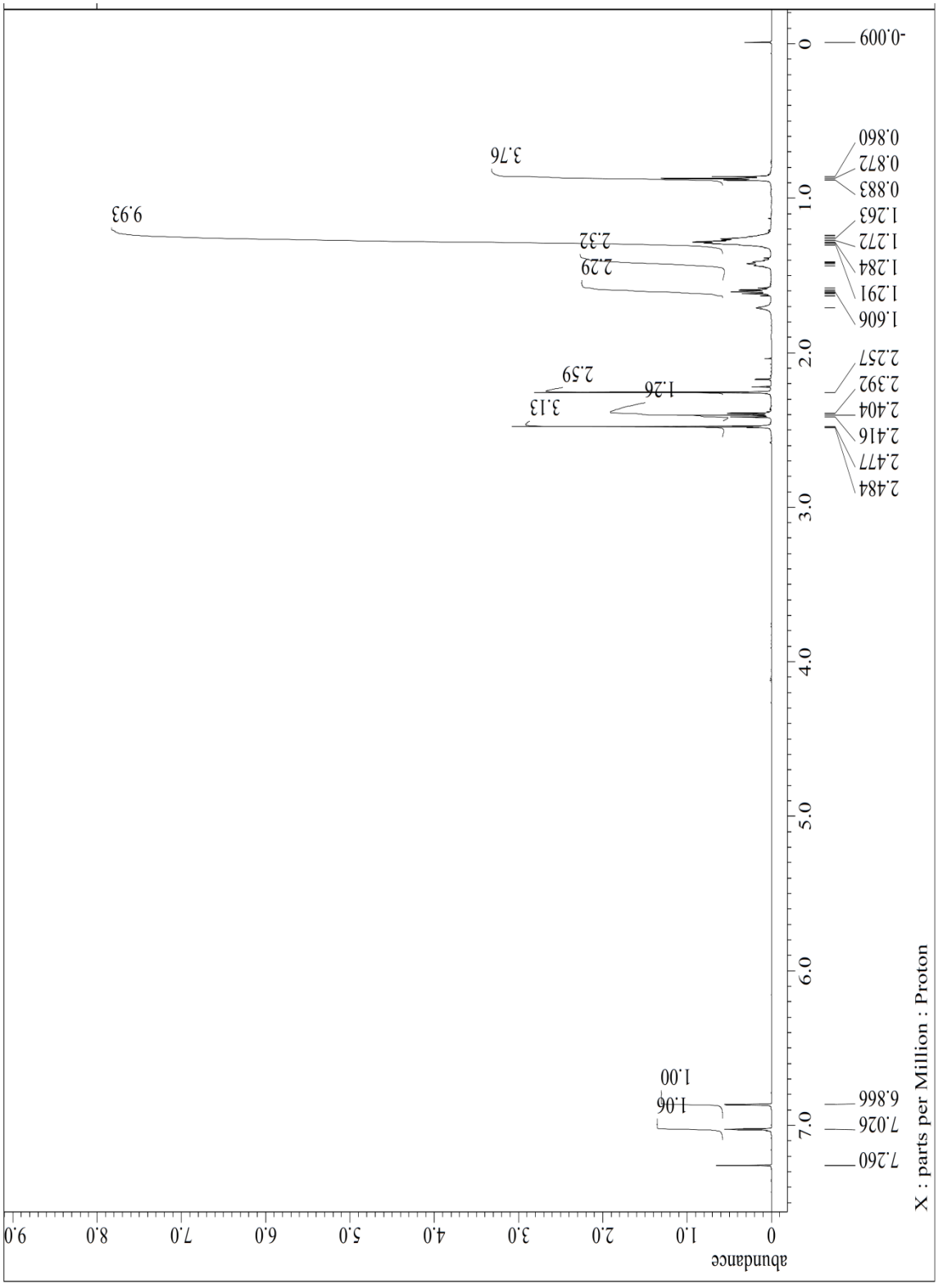
^{1}H NMR of **4f**


-0.008
0.859
0.877
0.981
0.997
1.268
1.277
1.330
1.565
1.586
2.328
2.345
2.363
2.741
2.762
2.790
2.811
3.889
3.907
3.915
3.923
3.929
3.932
3.937
3.945
3.952
3.962
7.260
4.00
0.96
3.70
1.29
3.06
2.34
2.99
10.10
2.47
3.66
X : parts per Million : 1H
abundance

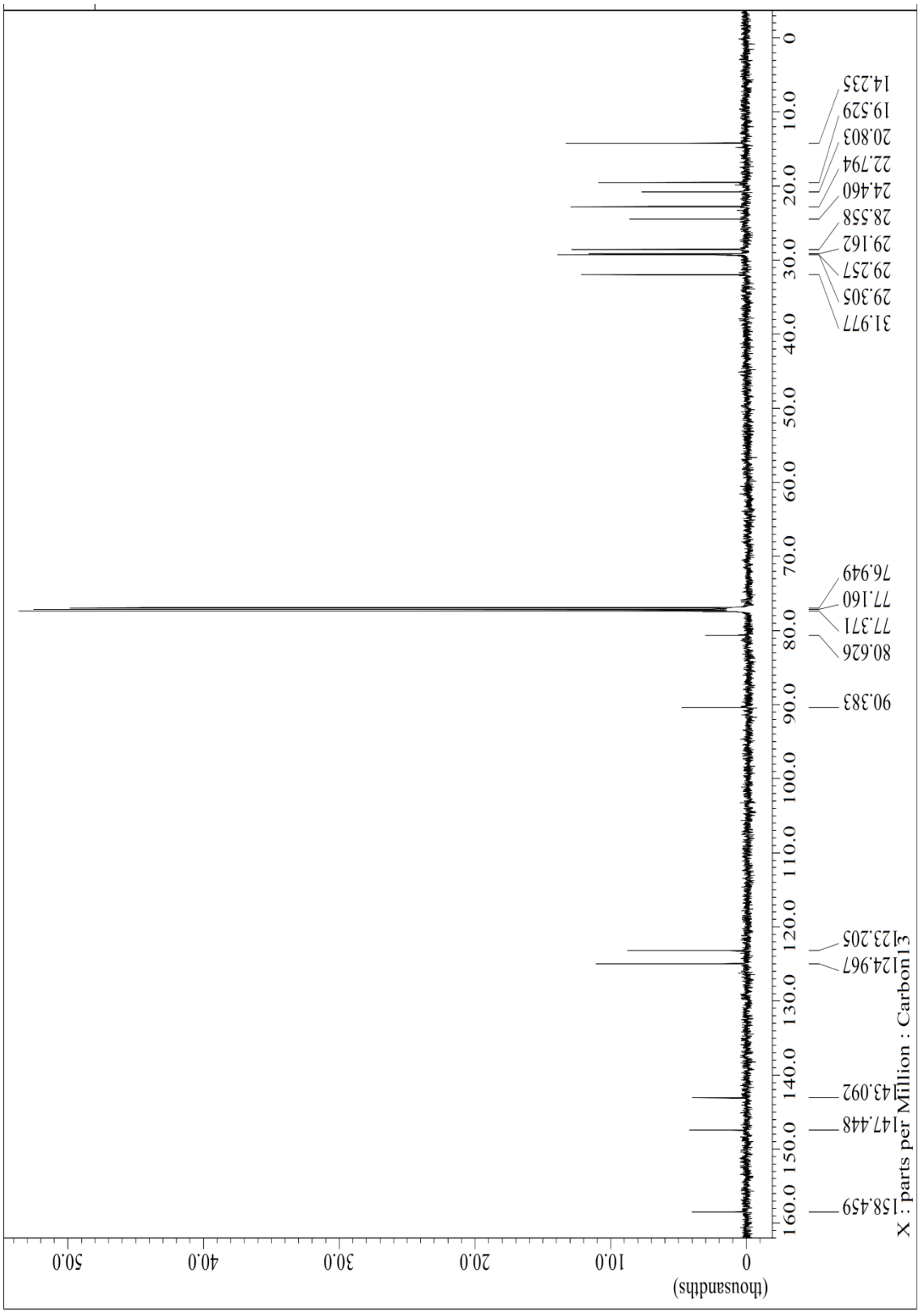
^{13}C NMR of **4f**


abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
188.292
110.135
94.194
77.476
77.160
76.834
64.524
64.476
53.401
45.056
31.931
29.249
29.134
29.009
27.869
25.953
24.238
22.773
14.236

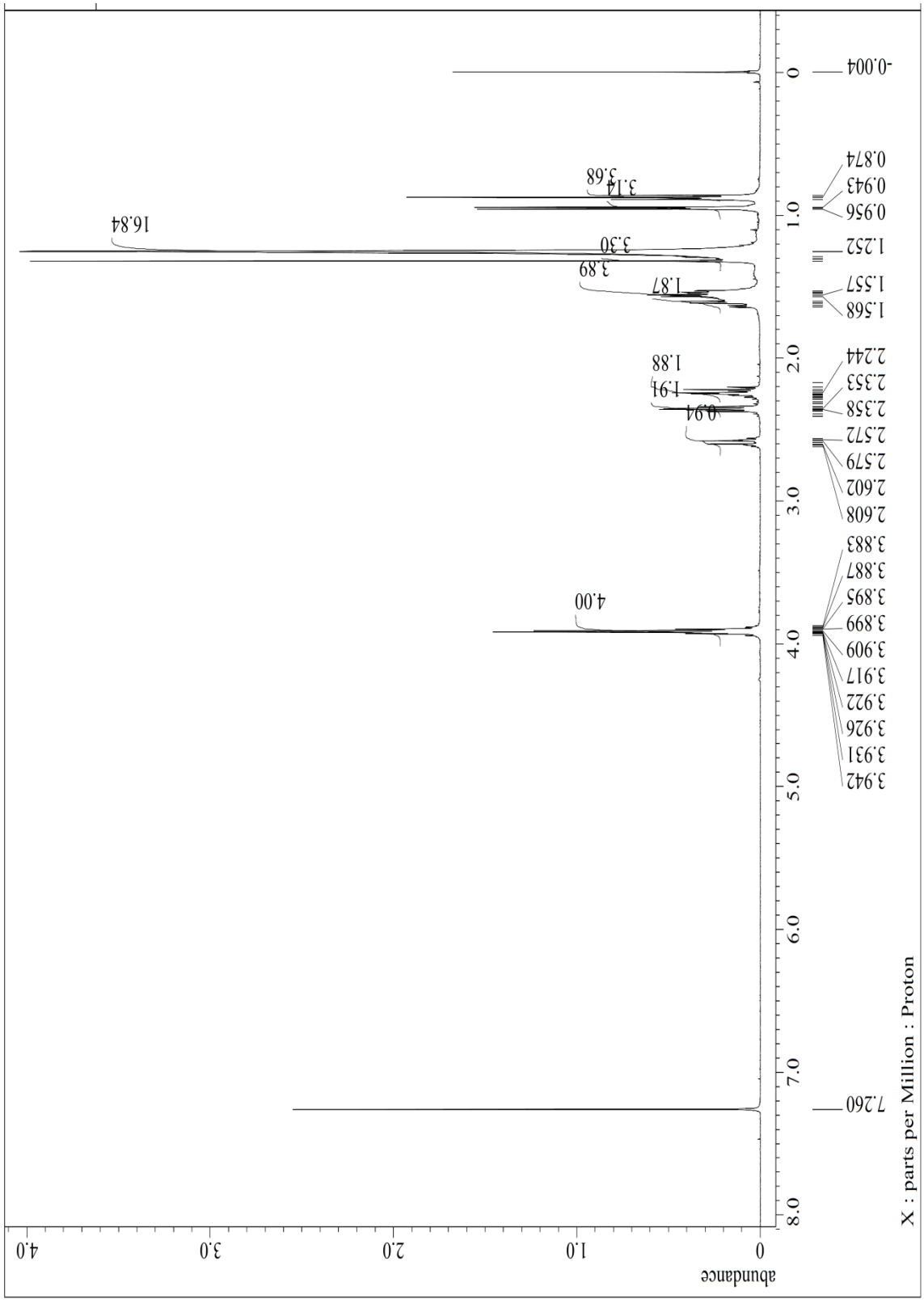
^{1}H NMR of **3f**


X : parts per Million : Proton
abundance
7.260
7.026
6.866
1.06
1.00
3.76
9.93
2.32
2.29
2.59
1.26
3.13
2.484
2.477
2.416
2.404
2.392
2.257
1.606
1.291
1.284
1.272
1.263
0.883
0.872
0.860
-0.009

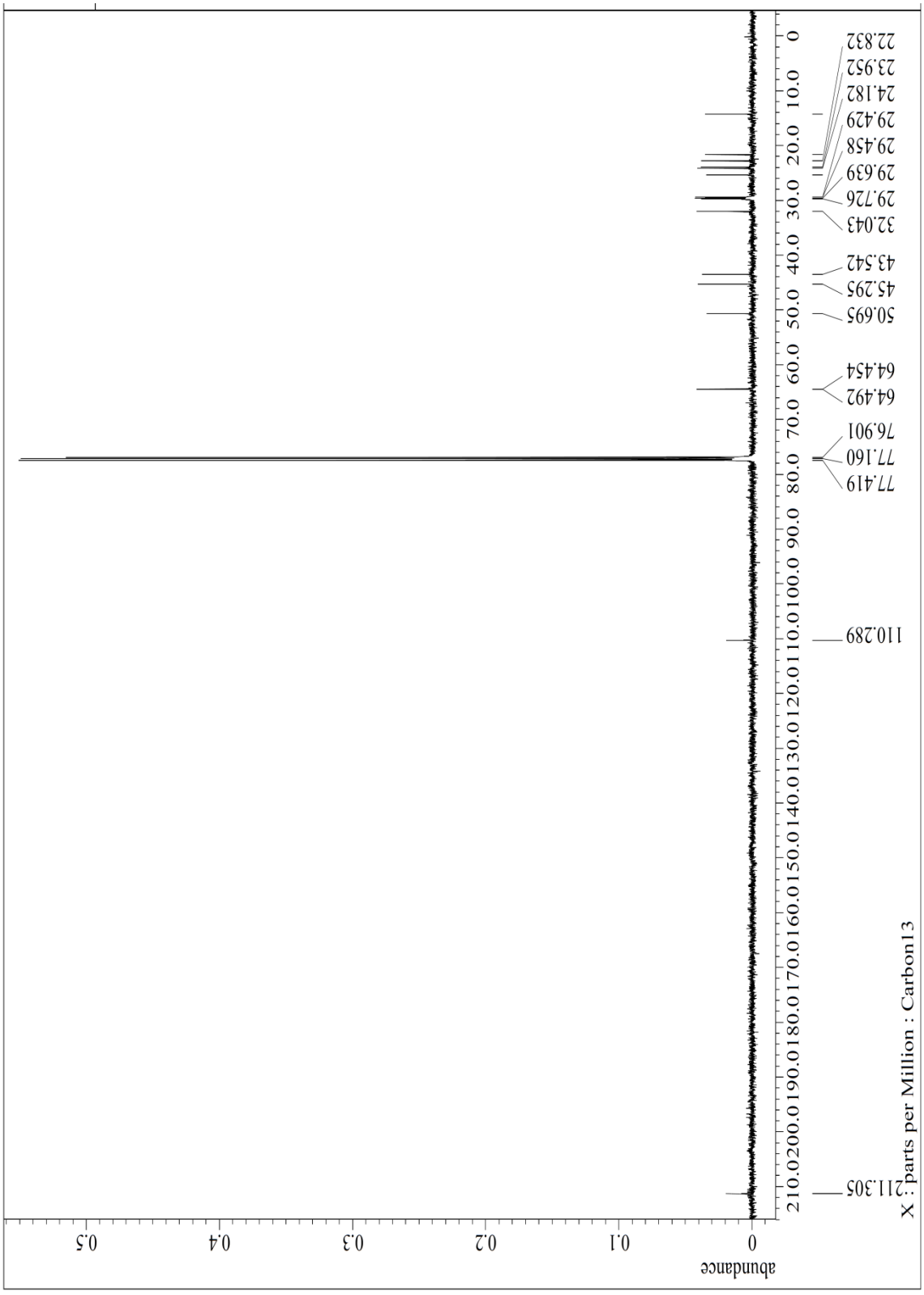
^{13}C NMR of **3f**


158.459
147.448
143.092
124.967
123.205
90.383
80.626
77.371
77.160
76.949
31.977
29.305
29.257
29.162
28.558
24.460
22.794
20.803
19.529
14.235
X : parts per Million : Carbon13
(thousandths)

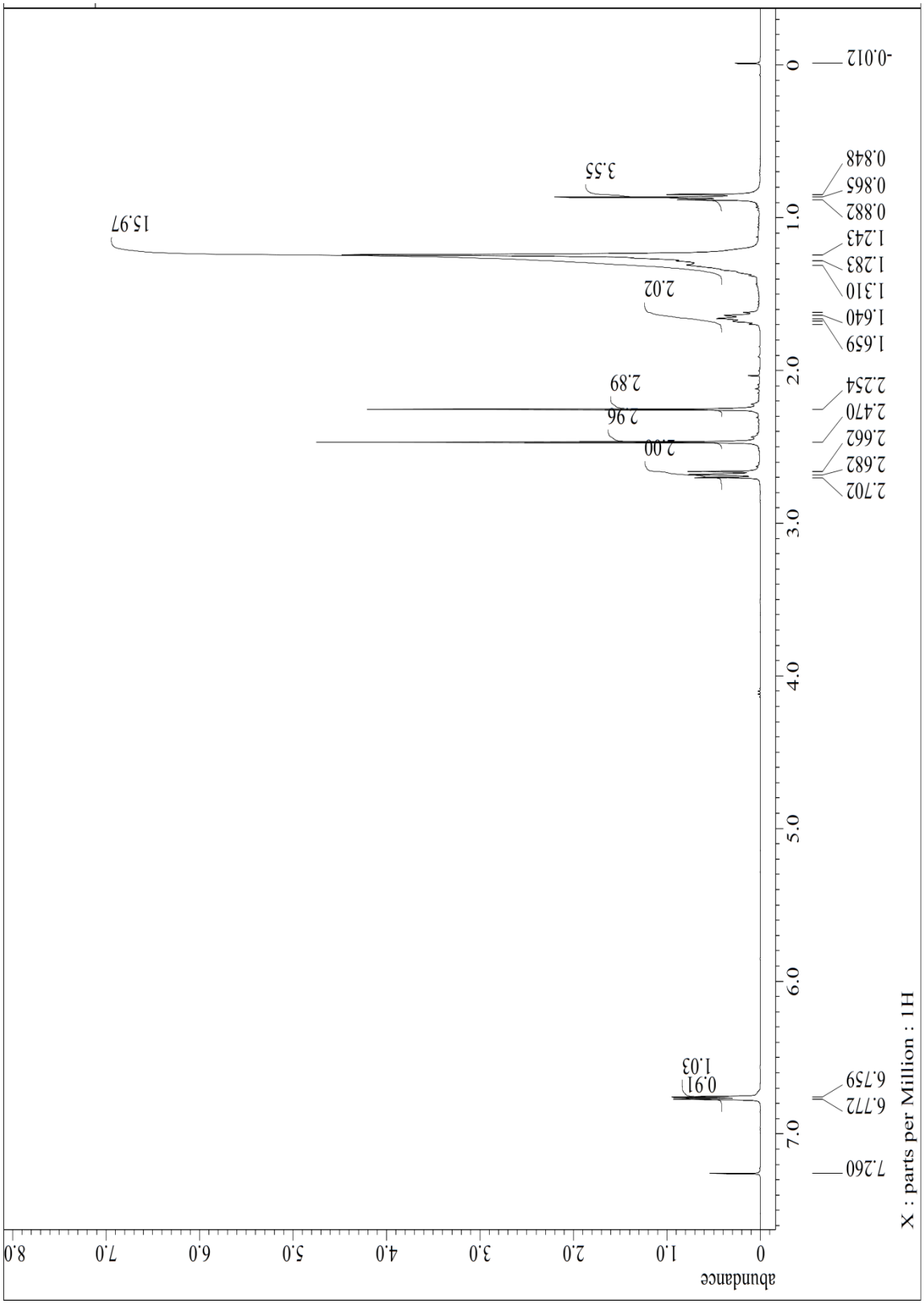
^{1}H NMR of **4g**


-0.004
0.874
0.943
0.956
1.252
1.557
1.568
2.244
2.353
2.358
2.572
2.579
2.602
2.608
3.883
3.887
3.895
3.899
3.909
3.917
3.922
3.926
3.931
3.942
7.260
4.00
0.94
1.88
1.91
1.87
3.89
3.30
16.84
3.14
3.68
abundance
X : parts per Million : Proton

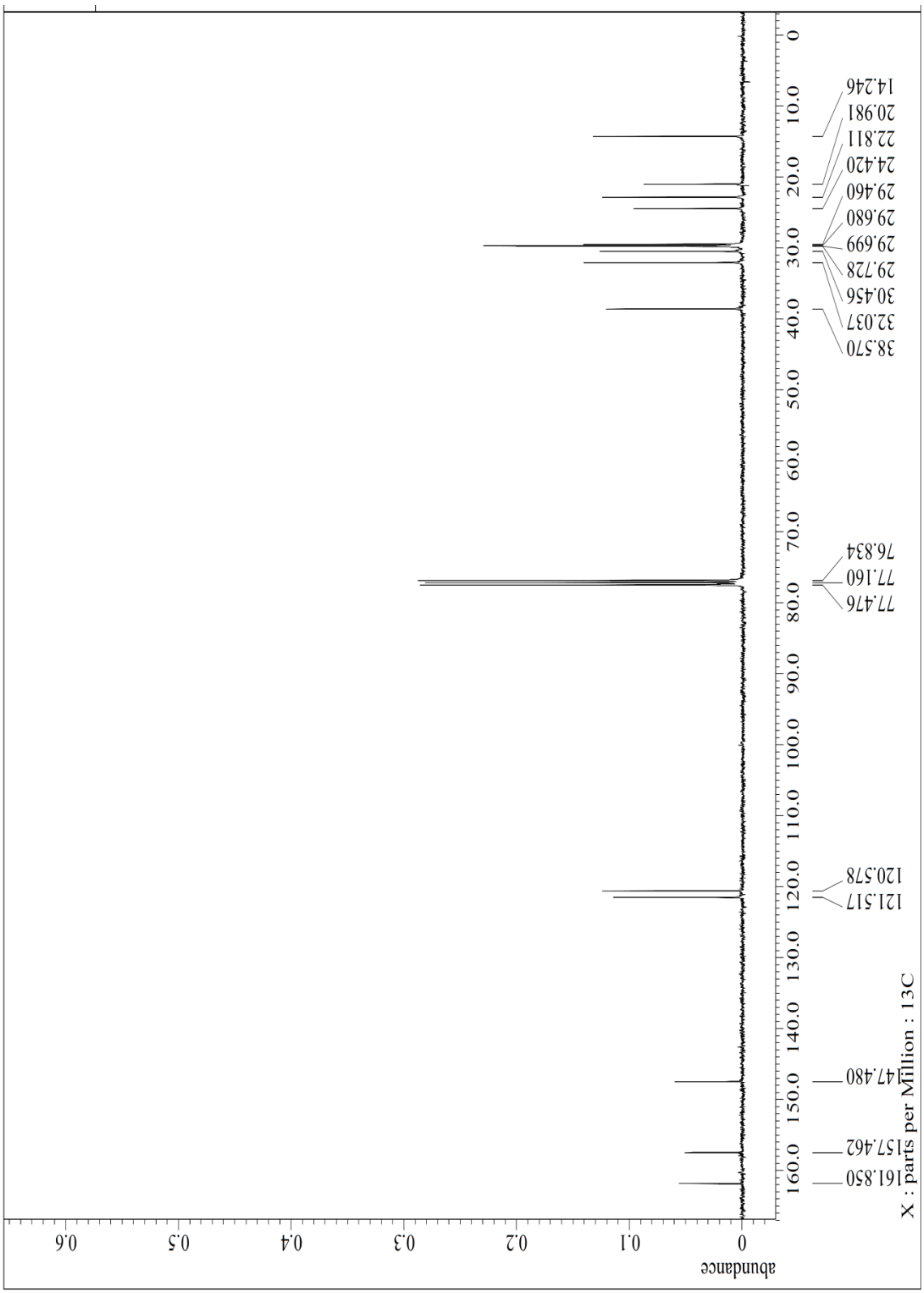
^{13}C NMR of **4g**


X : parts per Million : Carbon13
abundance
211.305
110.289
77.419
77.160
76.901
64.492
64.454
50.695
45.295
43.542
32.043
29.726
29.639
29.458
29.429
24.182
23.952
22.832

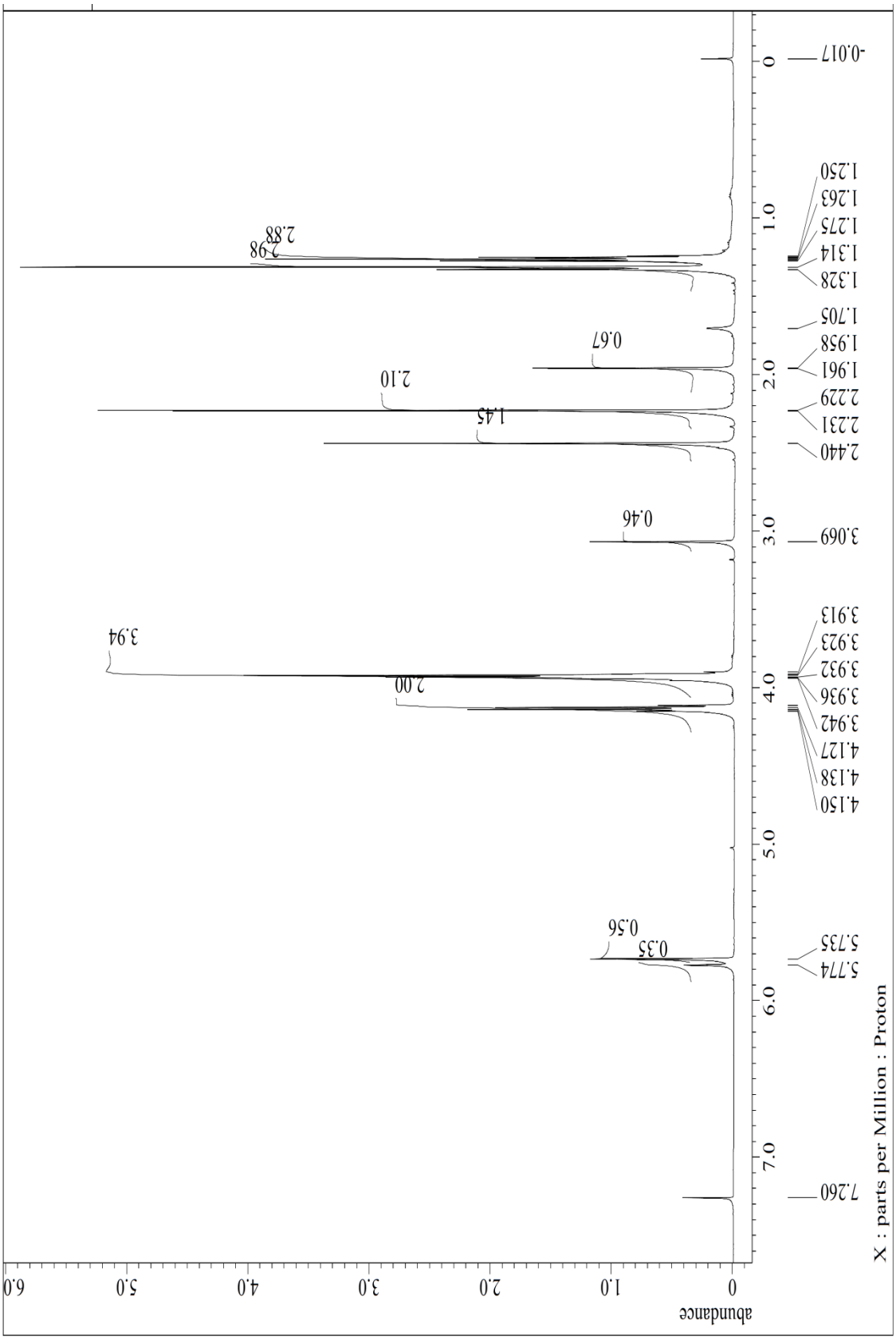
^{1}H NMR of **3g**


abundance
X : parts per Million : 1H
7.260
6.772
6.759
0.91
1.03
15.97
3.55
2.02
2.89
2.96
2.00
2.702
2.682
2.662
2.470
2.254
1.659
1.640
1.310
1.283
1.243
0.882
0.865
0.848
-0.012

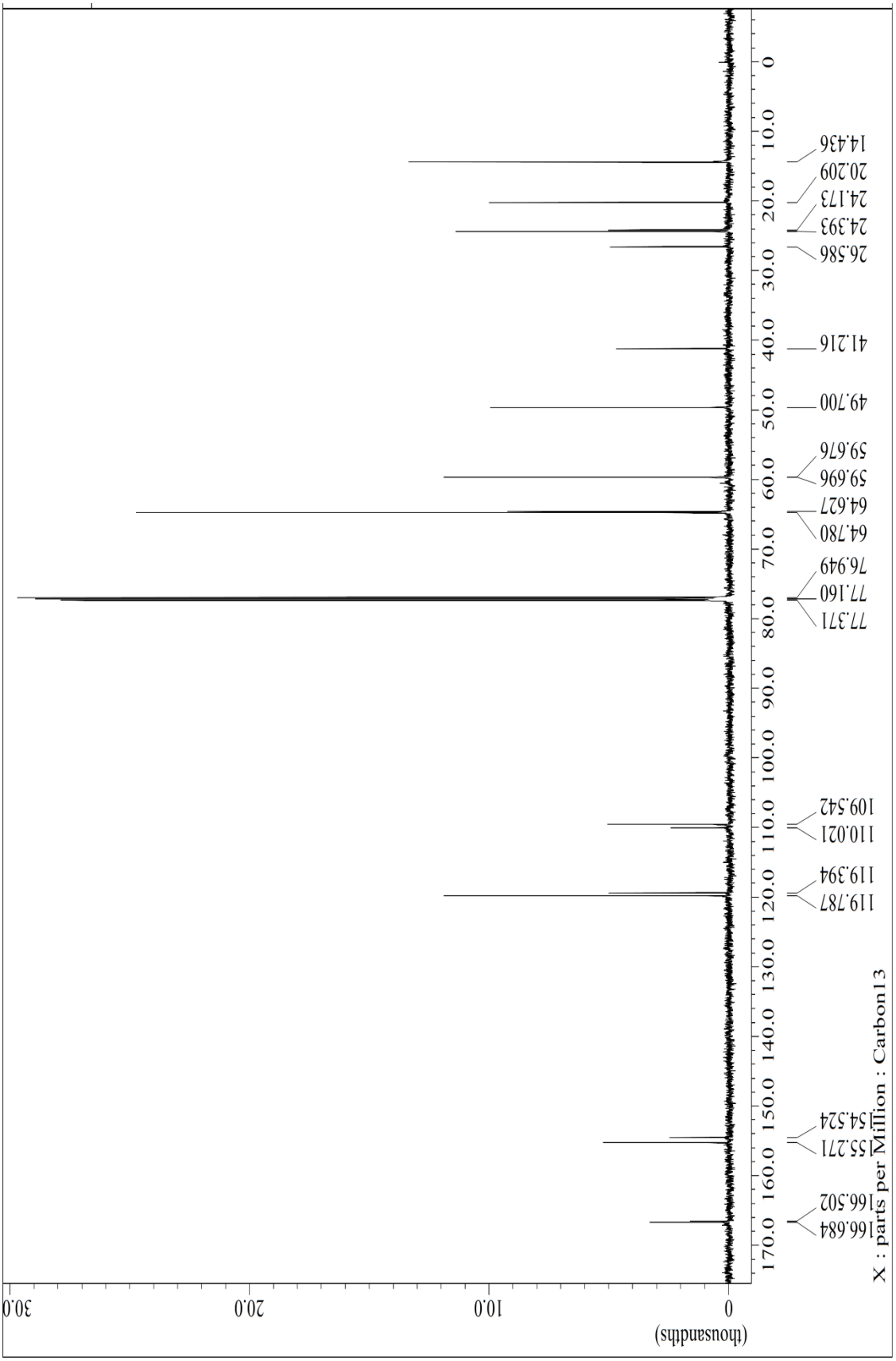
^{13}C NMR of **3g**


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
X : parts per Million : 13C
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
161.850
157.462
147.480
121.517
120.578
77.476
77.160
76.834
38.570
32.037
30.456
29.728
29.699
29.680
29.460
24.420
22.811
20.981
14.246

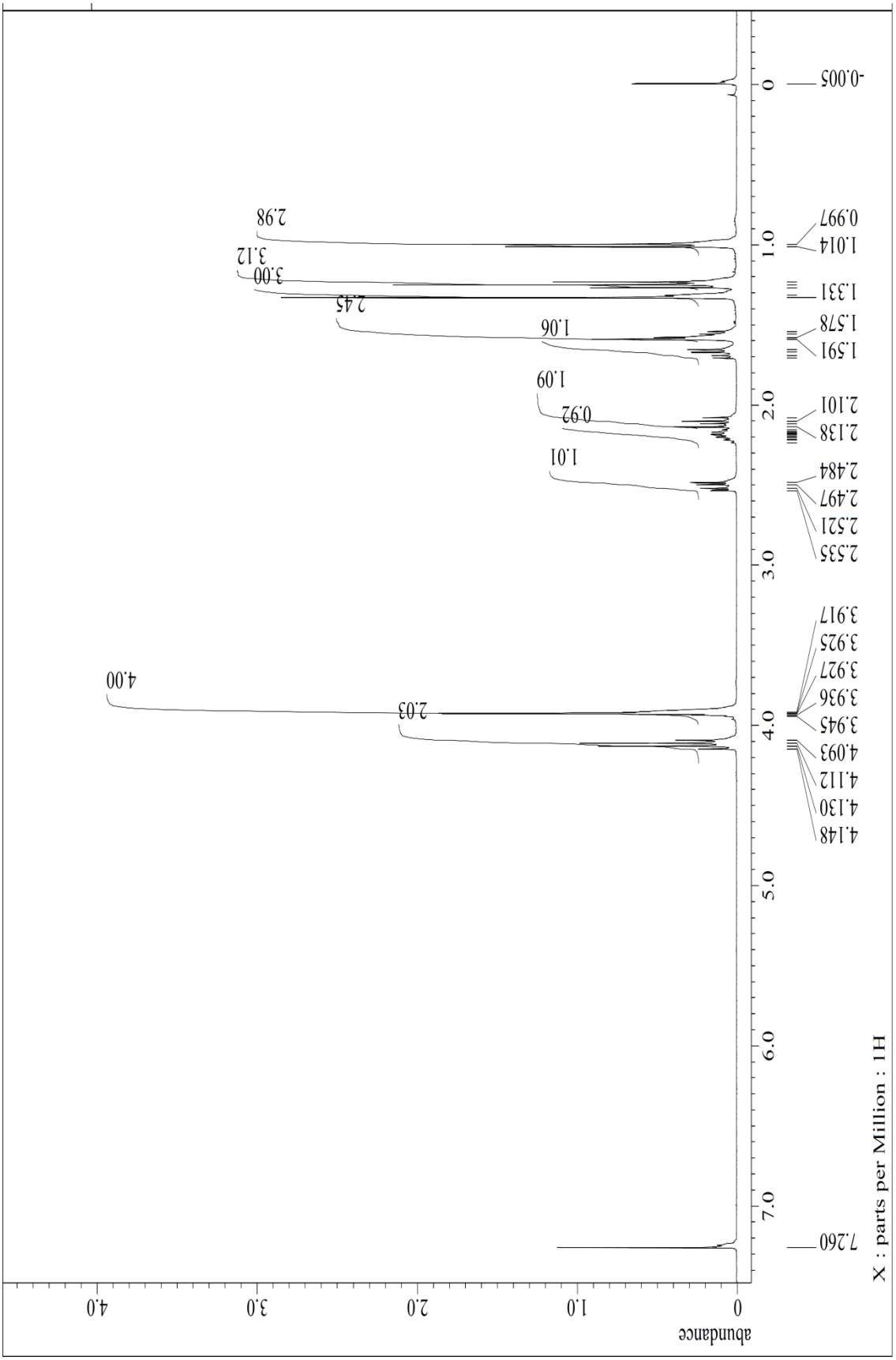
^{1}H NMR of **6**


X : parts per Million : Proton
abundance
-0.017
7.260
5.774
5.735
4.150
4.138
4.127
3.942
3.936
3.932
3.923
3.913
3.069
2.440
2.231
2.229
1.961
1.958
1.705
1.328
1.314
1.275
1.263
1.250
0.35
0.56
0.46
2.00
3.94
1.45
2.10
0.67
2.98
2.88

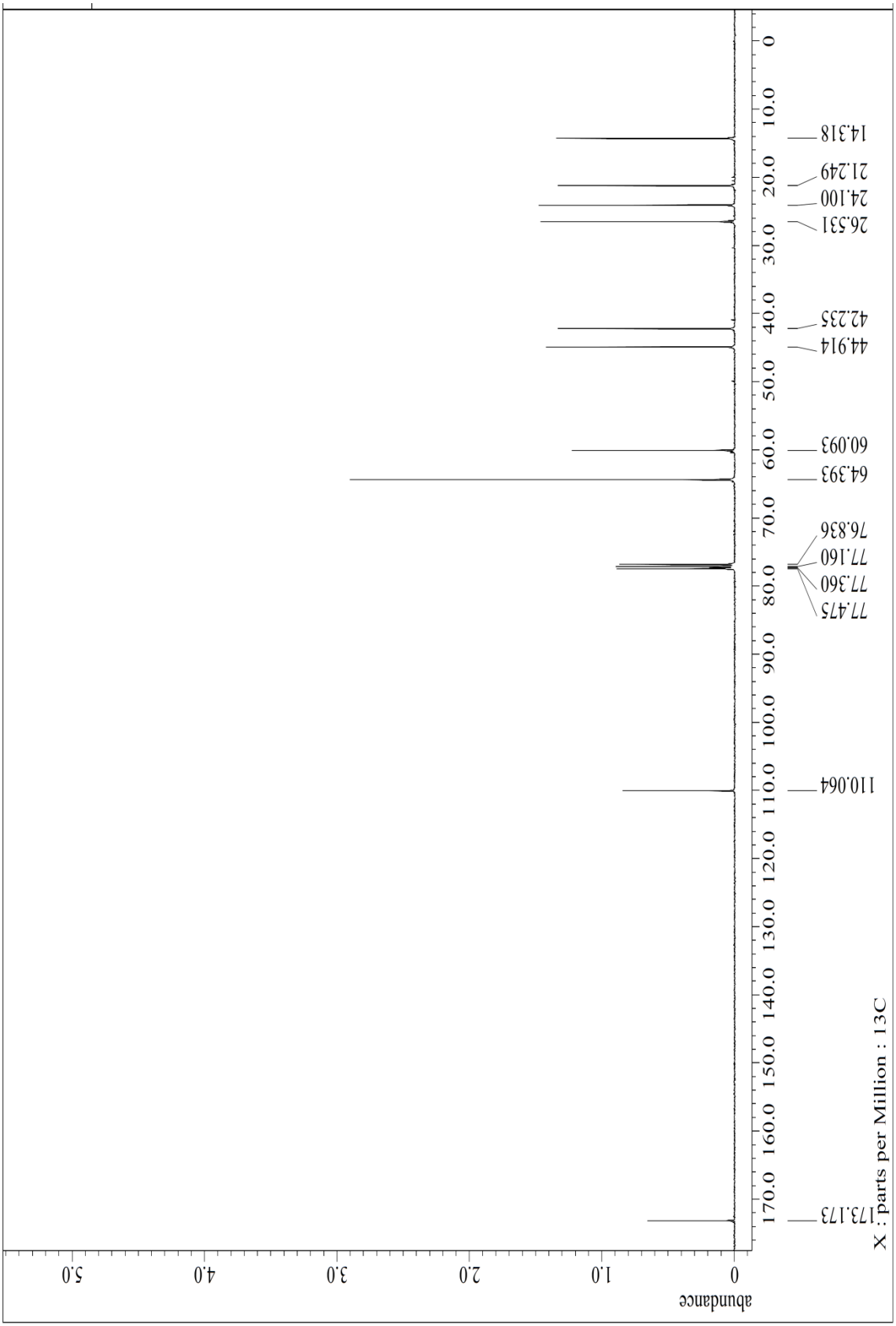
^{13}C NMR of **6**


166.684
166.502
155.271
154.524
119.787
119.394
110.021
109.542
77.371
77.160
76.949
64.780
64.627
59.696
59.676
49.700
41.216
26.586
24.393
24.173
20.209
14.436
X : parts per Million : Carbon13
(thousandths)

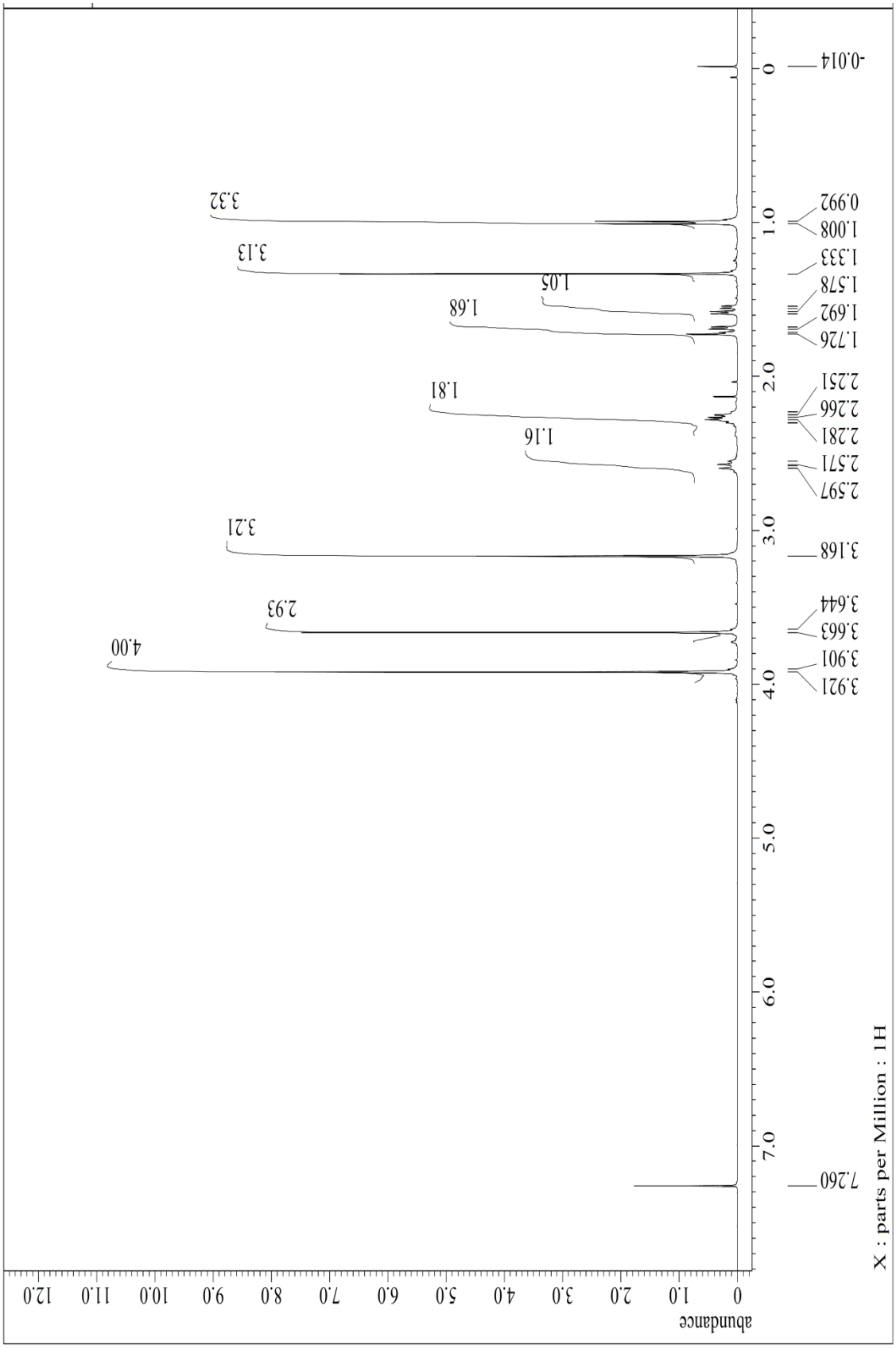
^{1}H NMR of **7**


X : parts per Million : 1H
abundance
7.260
-0.005
0.997
1.014
1.331
1.578
1.591
2.101
2.138
2.484
2.497
2.521
2.535
3.917
3.925
3.927
3.936
3.945
4.093
4.112
4.130
4.148
4.00
2.03
1.01
0.92
1.09
1.06
2.45
3.00
3.12
2.98

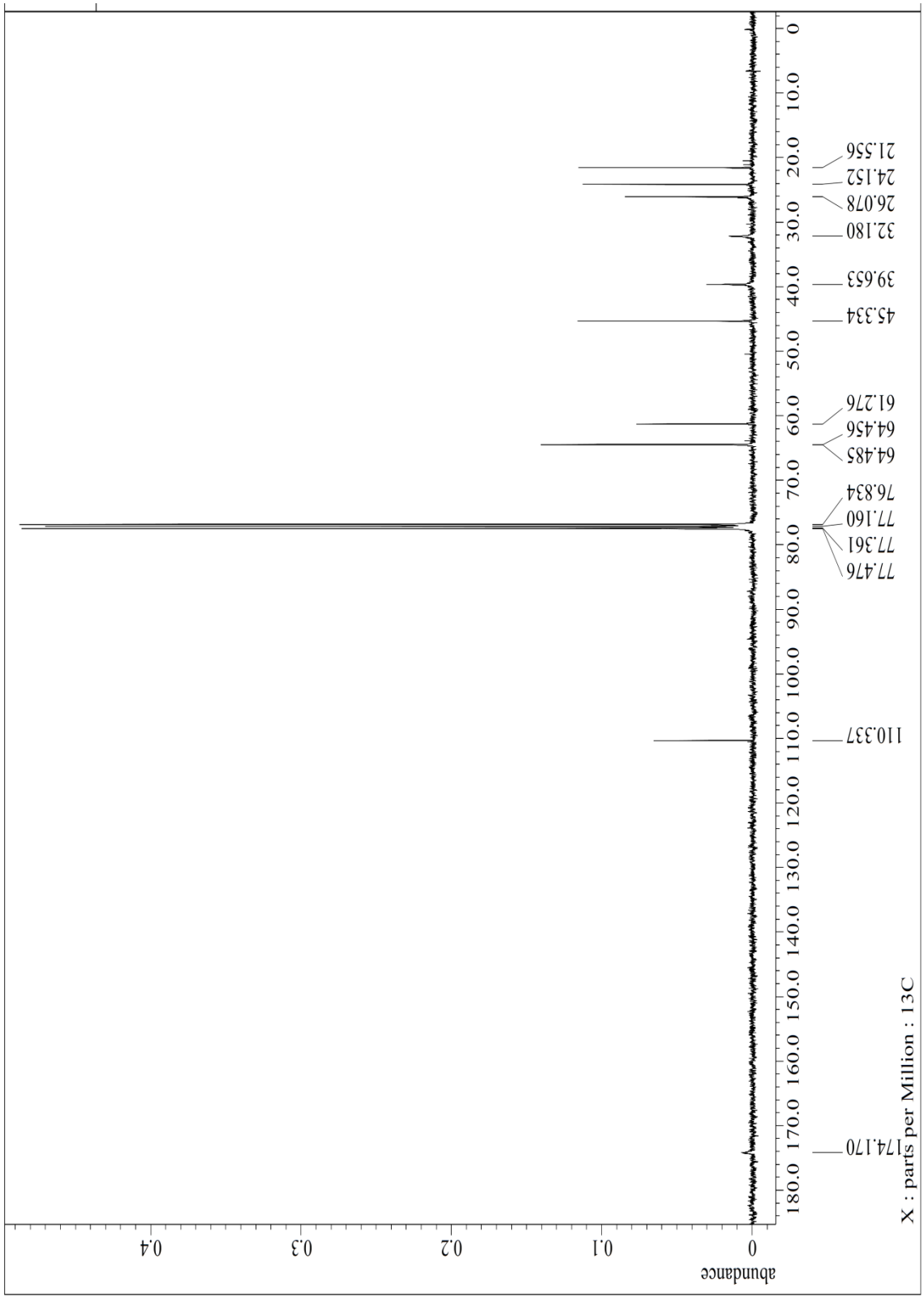
^{13}C NMR of **7**


X : parts per Million : 13C
abundance
173.173
110.064
77.475
77.360
77.160
76.836
64.393
60.093
44.914
42.235
26.531
24.100
21.249
14.318

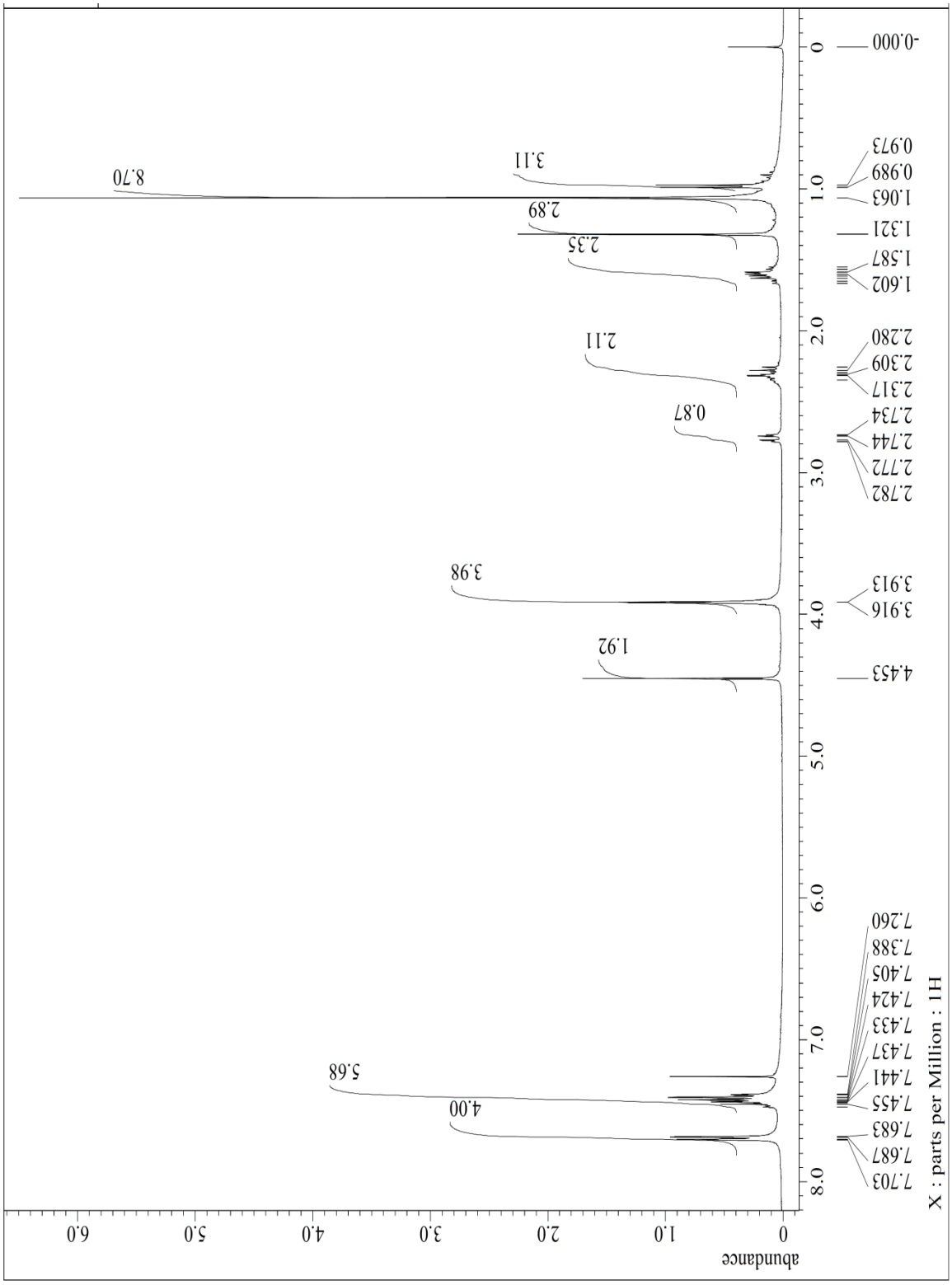
^{1}H NMR of **9**


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
X : parts per Million : 1H
7.260
3.921
3.901
3.663
3.644
3.168
2.597
2.571
2.281
2.266
2.251
1.726
1.692
1.578
1.333
1.008
0.992
-0.014
4.00
2.93
3.21
1.16
1.81
1.68
1.05
3.13
3.32

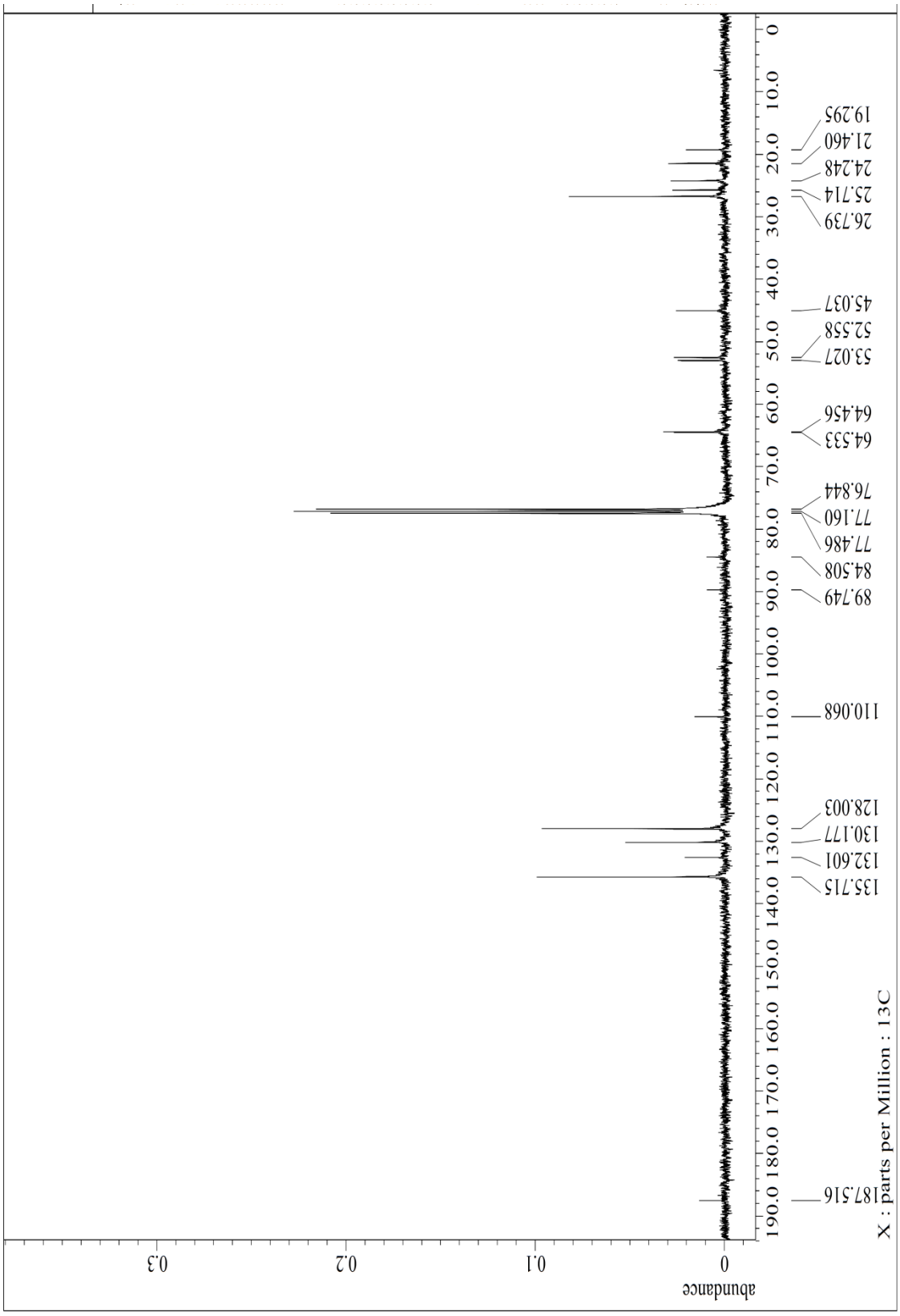
^{13}C NMR of **9**


174.170
110.337
77.476
77.361
77.160
76.834
64.485
64.456
61.276
45.334
39.653
32.180
26.078
24.152
21.556
X : parts per Million : 13C
abundance

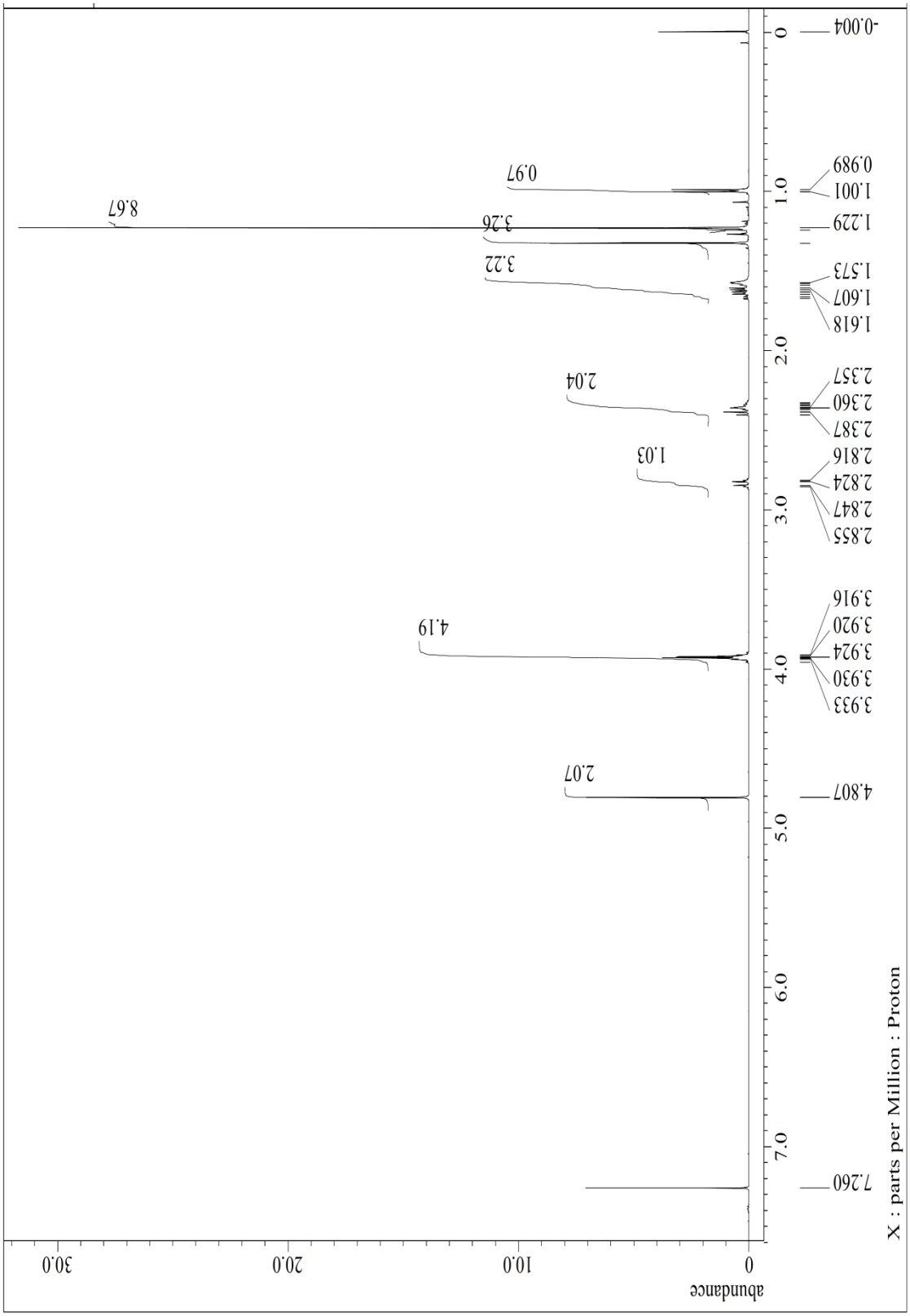
^{1}H NMR of **10**


-0.000
0.973
0.989
1.063
1.321
1.587
1.602
2.280
2.309
2.317
2.734
2.744
2.772
2.782
3.913
3.916
4.453
7.260
7.388
7.405
7.424
7.433
7.437
7.441
7.455
7.683
7.687
7.703
8.70
3.11
2.89
2.35
2.11
0.87
3.98
1.92
4.00
5.68
X : parts per Million : 1H
abundance

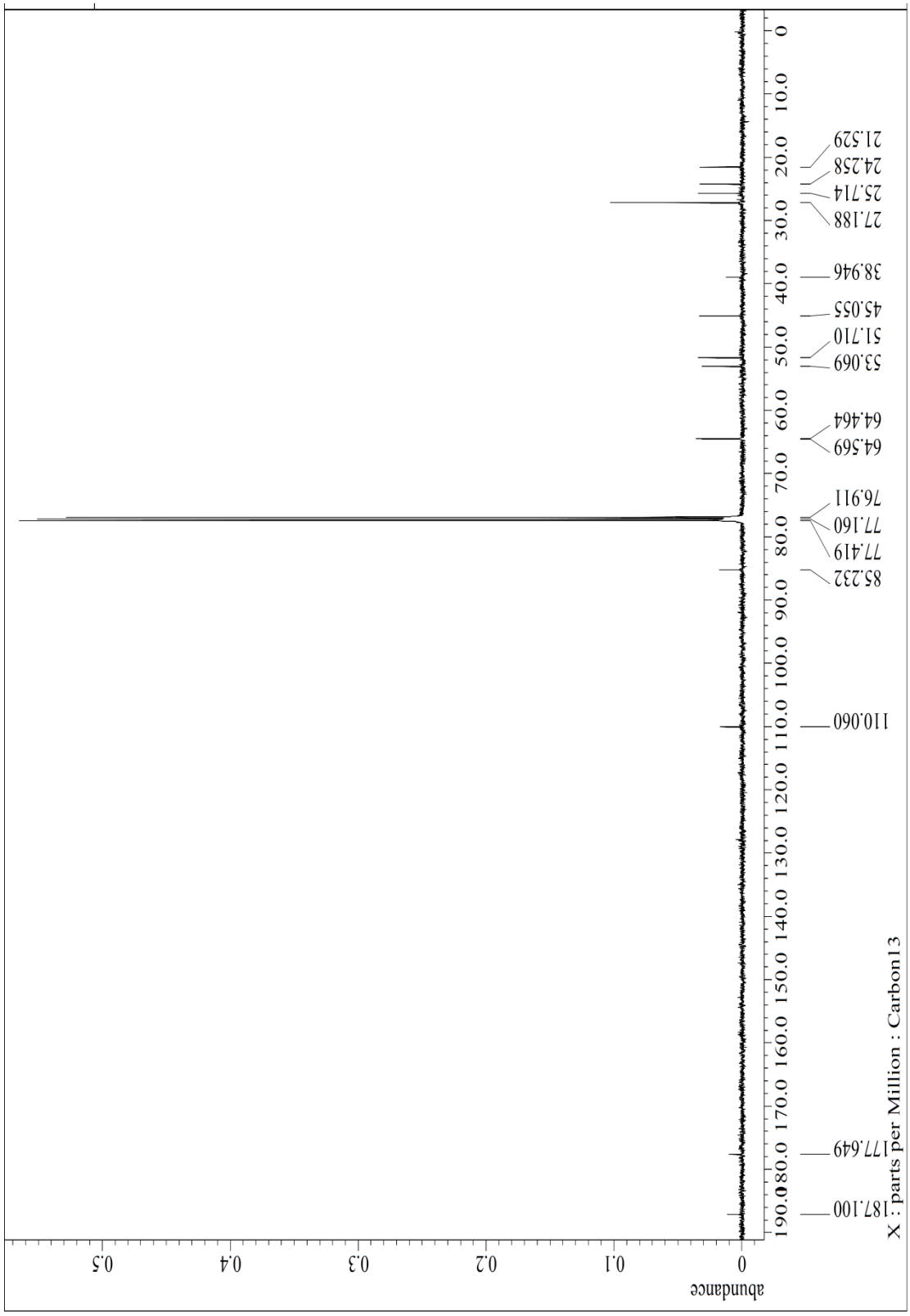
^{13}C NMR of **10**


abundance
0
0.1
0.2
0.3
X : parts per Million : 13C
187.516
135.715
132.601
130.177
128.003
110.068
89.749
84.508
77.486
77.160
76.844
64.533
64.456
53.027
52.558
45.037
26.739
25.714
24.248
21.460
19.295

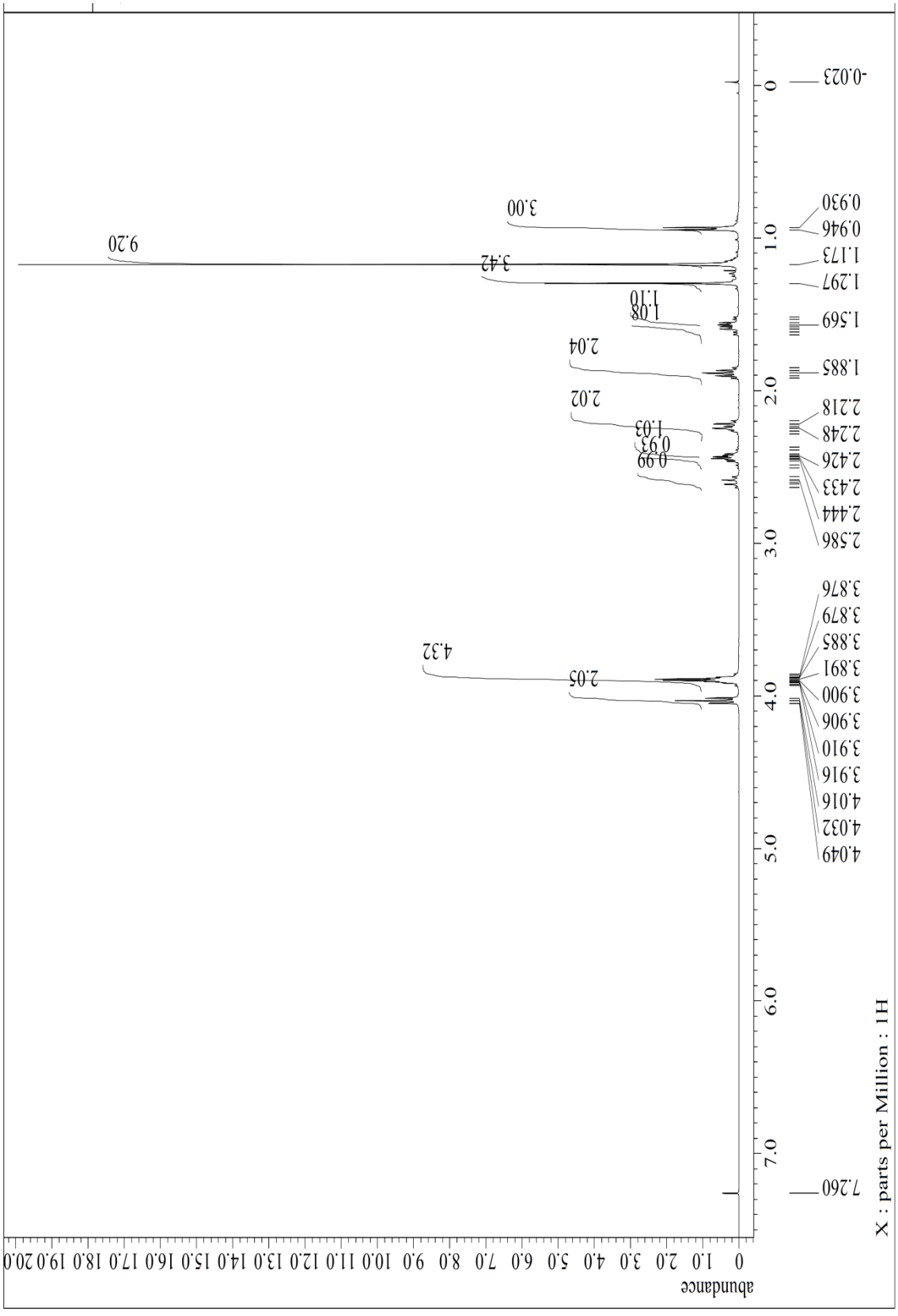
^{1}H NMR of **11**


-0.004
0.97
8.67
3.26
3.22
2.04
1.03
4.19
2.07
4.807
7.260
0.989
1.001
1.229
1.573
1.607
1.618
2.357
2.360
2.387
2.816
2.824
2.847
2.855
3.916
3.920
3.924
3.930
3.933
abundance
X : parts per Million : Proton

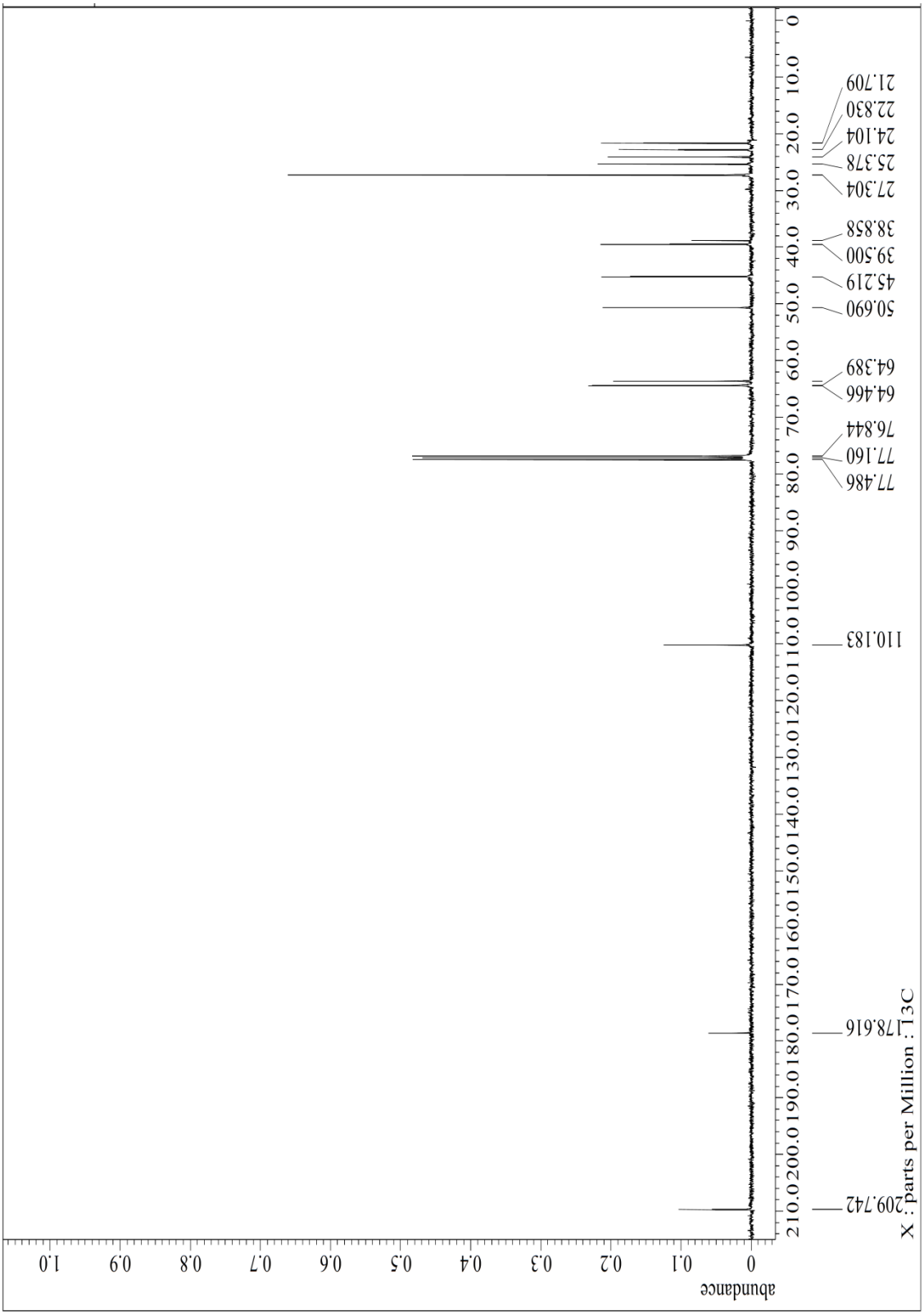
^{13}C NMR of **11**


abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : Carbon13
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
187.100
177.649
110.060
85.232
77.419
77.160
76.911
64.569
64.464
53.069
51.710
45.055
38.946
27.188
25.714
24.258
21.529

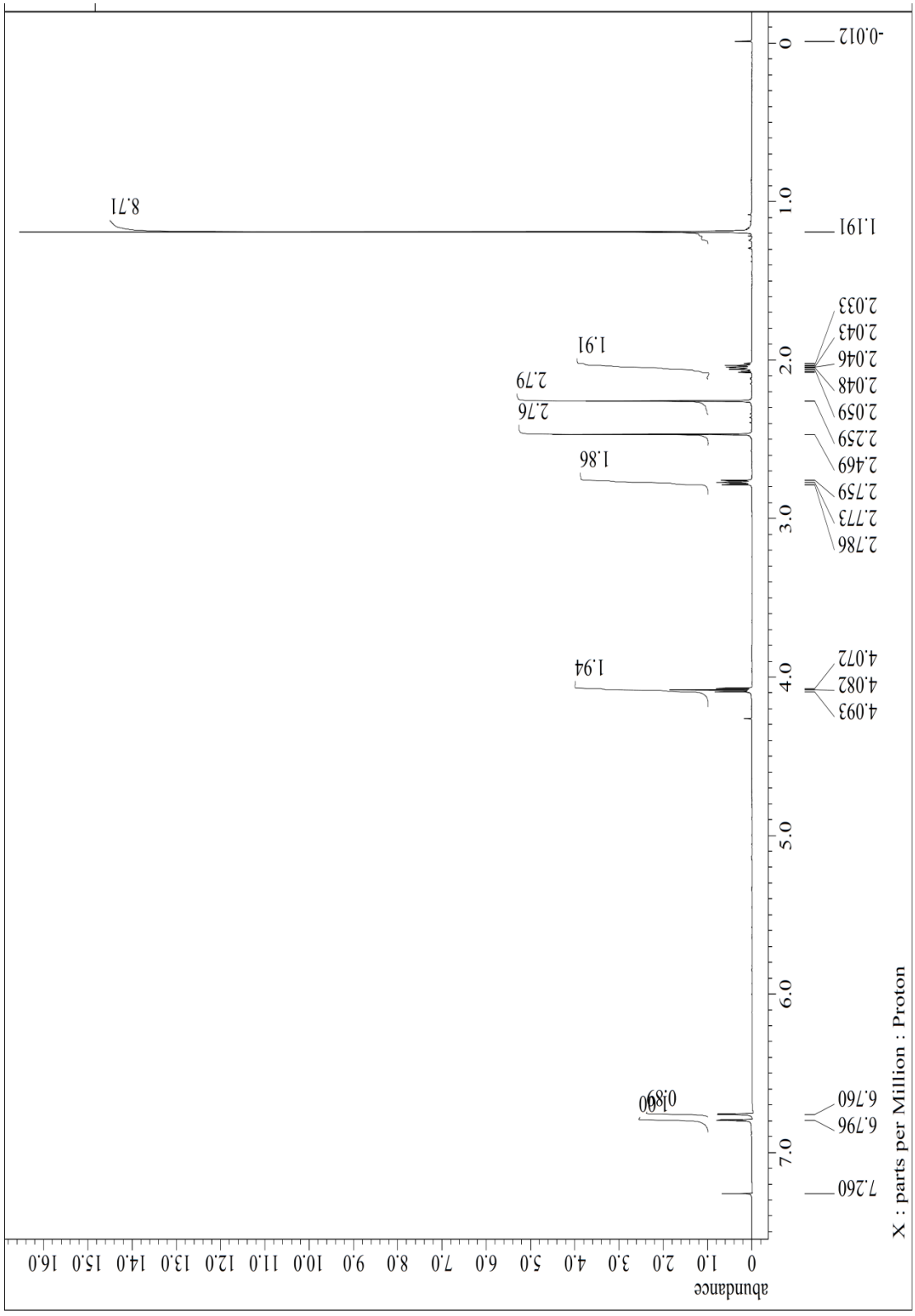
^{1}H NMR of **12**


X : parts per Million : 1H
abundance
-0.023
7.260
9.20
4.32
3.42
3.00
2.05
2.04
2.02
1.08
1.10
1.03
0.99
0.93
1.569
1.885
2.218
2.248
2.426
2.433
2.444
2.586
3.876
3.879
3.885
3.891
3.900
3.906
3.910
3.916
4.016
4.032
4.049
1.297
1.173
0.946
0.930

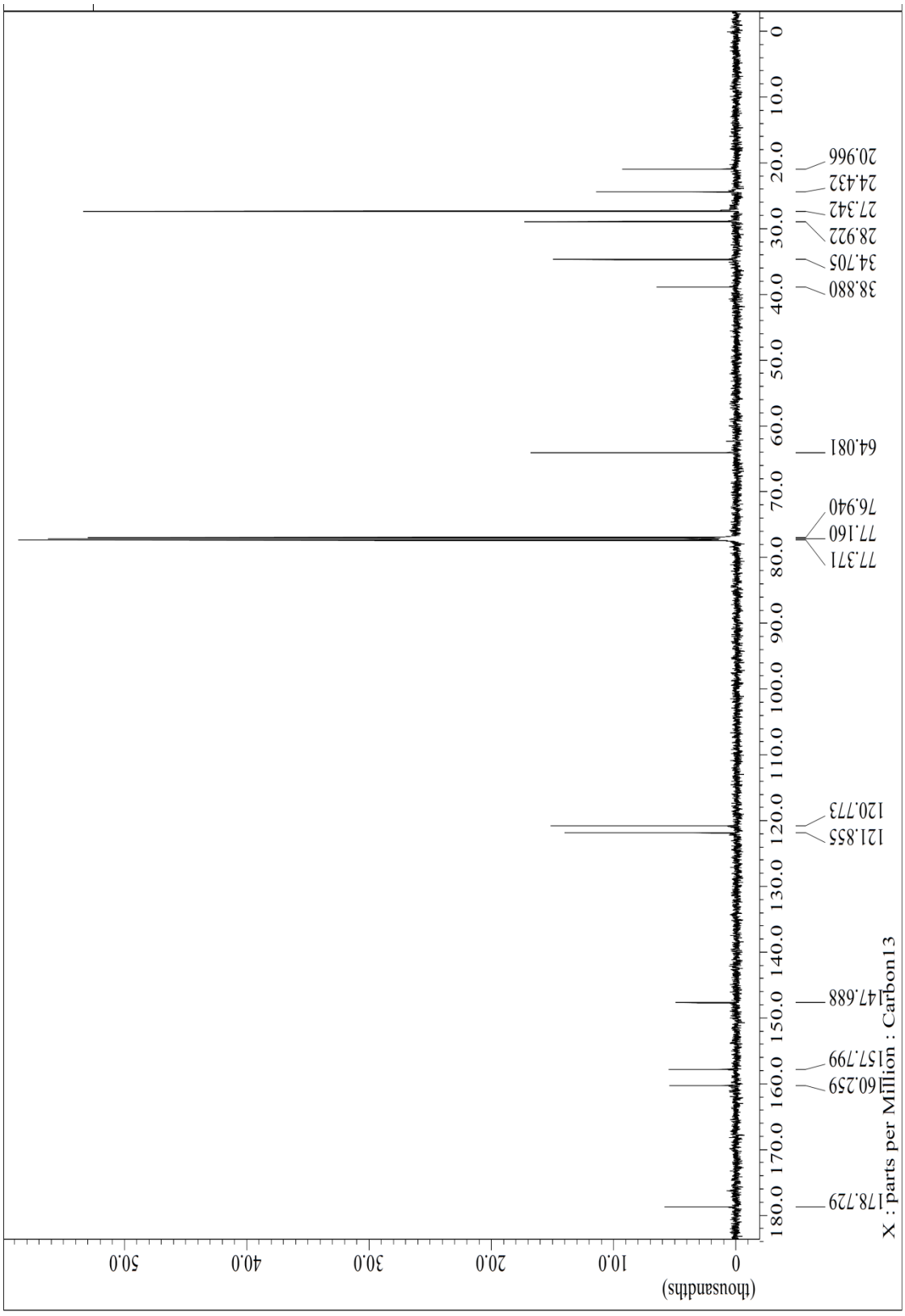
^{13}C NMR of **12**


X : parts per Million : 13C
209.742
178.616
110.183
77.486
77.160
76.844
64.466
64.389
50.690
45.219
39.500
38.858
27.304
25.378
24.104
22.830
21.709
abundance

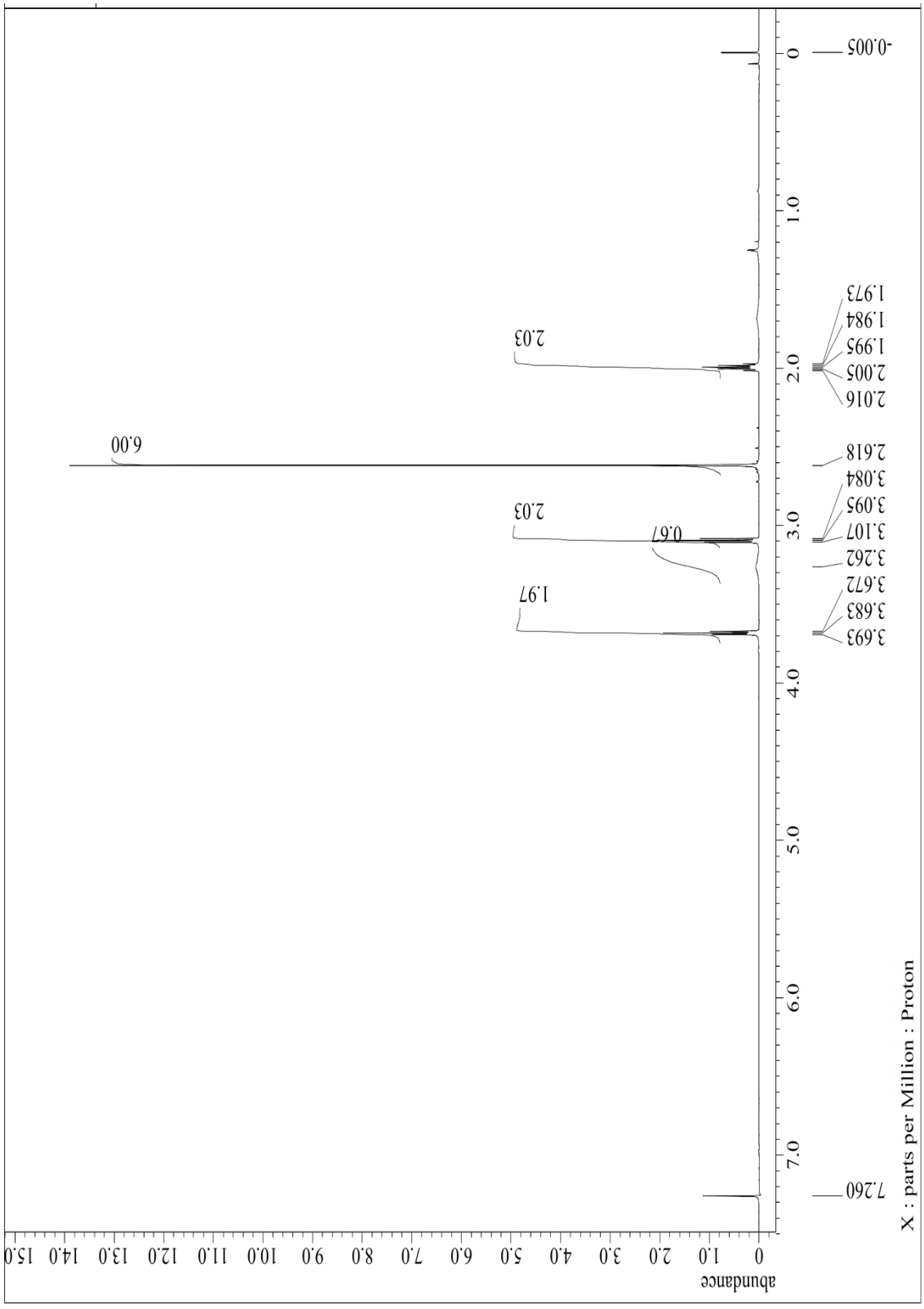
^{1}H NMR of **13**


-0.012
0
1.191
1.0
8.71
2.033
2.043
2.046
2.048
2.059
2.259
2.469
2.759
2.773
2.786
1.91
2.79
2.76
1.86
2.0
1.94
4.072
4.082
4.093
3.0
4.0
5.0
6.760
6.796
1.000
0.890
6.0
7.0
7.260
X : parts per Million : Proton
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0

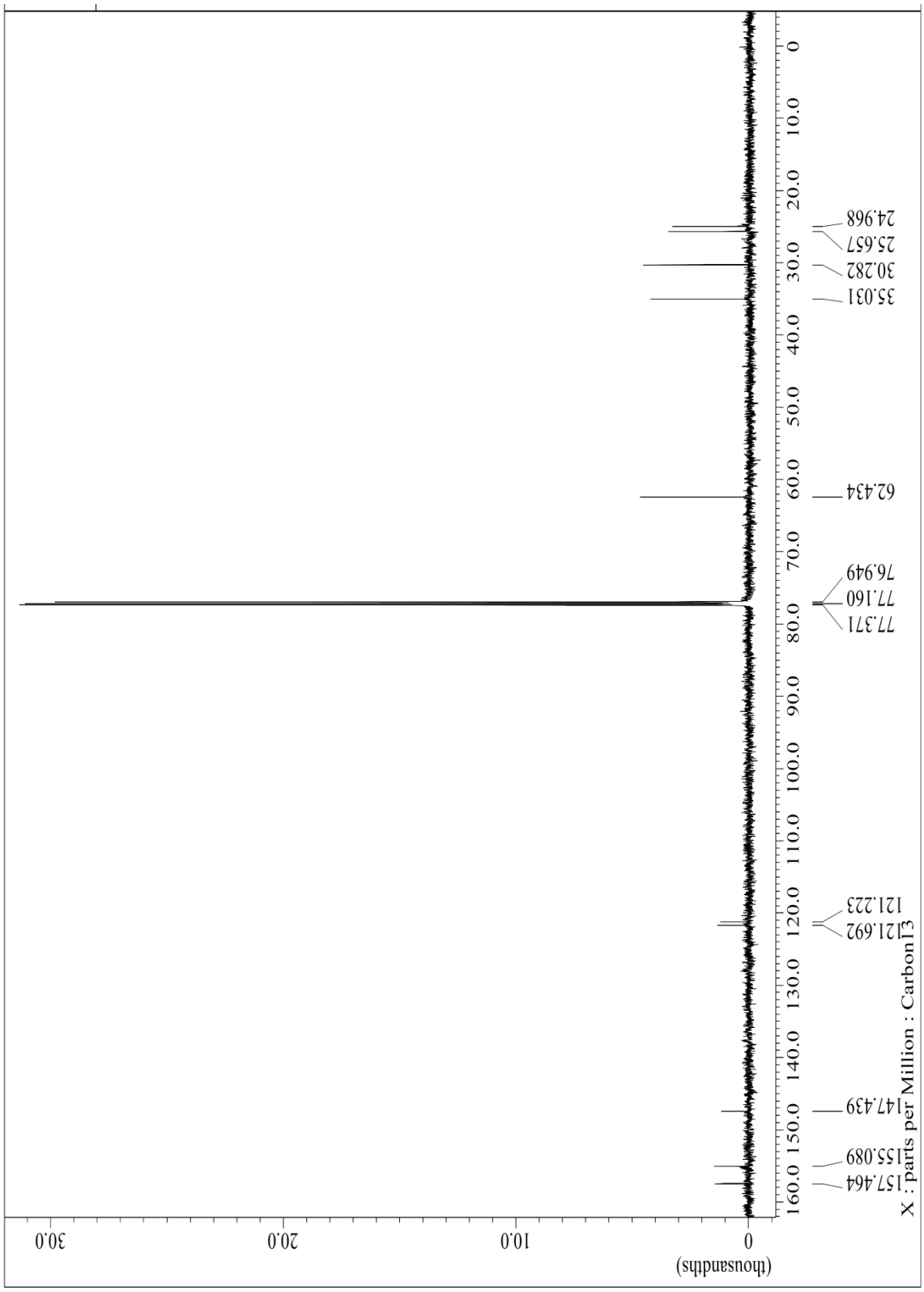
^{13}C NMR of **13**


X : parts per Million : Carbon13
(thousandths)
178.729
160.259
157.799
147.688
121.855
120.773
77.371
77.160
76.940
64.081
38.880
34.705
28.922
27.342
24.432
20.966

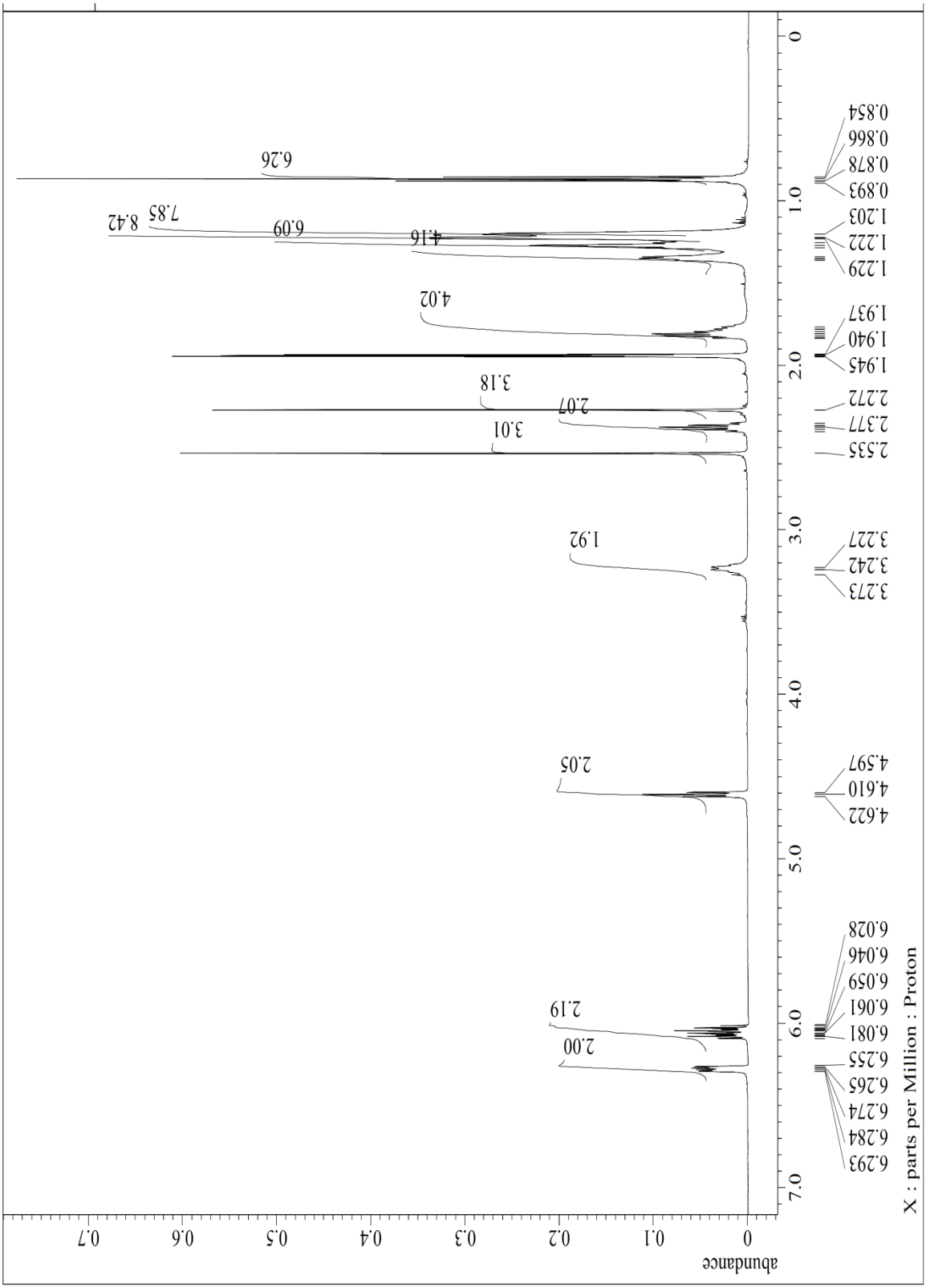
^{1}H NMR of **14**


-0.005
7.260
6.00
2.03
2.03
1.97
0.67
2.618
3.084
3.095
3.107
3.262
3.672
3.683
3.693
2.016
2.005
1.995
1.984
1.973
X : parts per Million : Proton
abundance

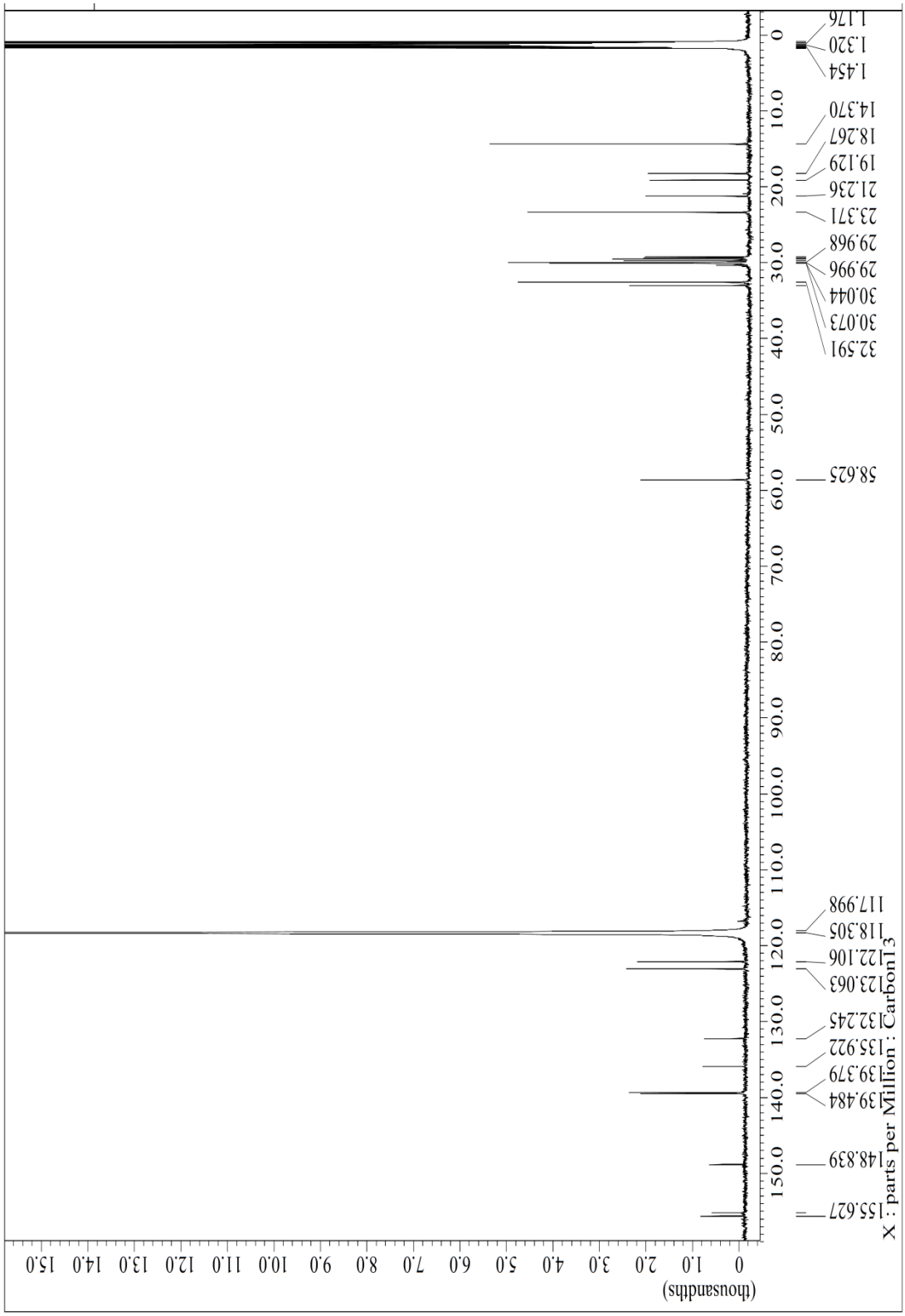
^{13}C NMR of **14**


24.968
25.657
30.282
35.031
62.434
76.949
77.160
77.371
121.223
121.692
147.439
155.089
157.464
X : parts per Million : Carbon13
(thousandths)

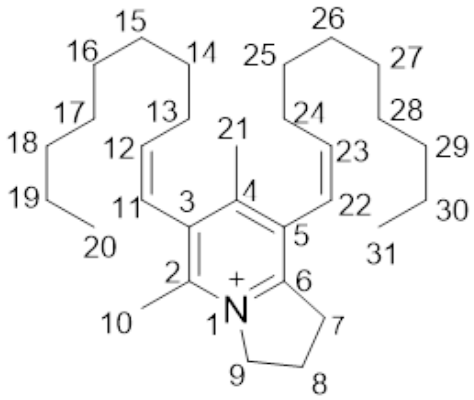
^{1}H NMR of Anibamine (**1**)



^{13}C NMR of Anibamine (**1**)



Spectral comparison with natural anibamine (1)[7] and synthetic one



	Natural Anibamine (^{1}H: 400MHz, ^{13}C: 100MHz)		Synthetic Anibamine (^{1}H: 600MHz, ^{13}C: 150MHz)			
position	δ_C	δ_H	δ_C	δ_H	$\Delta\delta_C$	$\Delta\delta_H$
2	149.0		148.8		0.2	
3	135.9		135.9		0	
4	155.6		155.6		0	
5	132.2		132.2		0	
6	155.2		155.2		0	
7	33.0	3.24	33.0	3.23	0	0.01
8	21.3	2.30	21.2	2.38	0.1	0.08
9	58.6	4.6	58.6	4.61	0	0.01
10	18.3	2.50	18.3	2.54	0	0.04
11, 22	123.0, 122.1	6.3	123.1, 122.1	6.28, 6.27	0.1, 0	0.02, 0.03
12, 23	139.5, 139.4	6.0	139.5, 139.4	6.07, 6.04	0, 0	0.07, 0.04
13, 24	29.7, 29.5	1.78	29.7, 29.5	1.80	0, 0	0.02
14, 25	29.3, 29.2	1.40	29.4, 29.3	1.35	0.1, 0.1	0.05
15, 26	29.95, 29.95	1.21	29.97, 29.97	1.27, 1.23, 1.20	0.02, 0.02	0.06, 0.02, 0.01
16, 27	30.03, 29.99	1.21	30.04, 30.00	1.27, 1.23, 1.20	0.01, 0.01	0.06, 0.02, 0.01
17, 28	30.06, 30.06	1.21	30.07, 30.07	1.27, 1.23, 1.20	0.01, 0.01	0.06, 0.02, 0.01
18, 29	32,6	1.21	32.6	1.27, 1.23, 1.20	0	0.06, 0.02, 0.01
19, 30	23.3	1.25	23.4	1.27	0.1	0.02
20, 31	14.4	0.83	14.4	0.87	0	0.04
21	19.1	2.26	19.1	2.27	0	0.01