Supporting Information

Efficient *ipso*-nitration of arylboronic acids with iron nitrate as the nitro source

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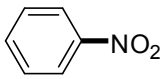
General experimental procedures

All reagents and solvents were obtained from commercial suppliers and used without further purification. $Fe(NO_3)_3 \cdot 9H_2O$ was purchased from Sigma-Aldrich, and other reagents were purchased from Beijing Ouhe Technology Ltd. Co.. All reagents were weighed and handled in air at room temperature. Flash chromatography was performed on silica gel (200 ～ 300 mesh). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.24ppm, ^{13}C NMR: $CDCl_3$ at 77.0ppm) or using tetramethylsilane (TMS) in the solvent of DMSO-d_6 as the internal standard (^{1}H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0ppm).

General procedure for synthesis of nitroarenes (2a-v)

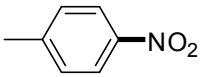
A 10 mL schlenk tube equipped with a magnetic stirrer, $Fe(NO_3)_3 \cdot 9H_2O$ (0.5 mmol, 202 mg), aromatic boronic acid (1 mmol), toluene (1.5 mL) were added to the tube, and the tube with an N_2 ballon (1 atm) was sealed and put into a pre-heated oil bath at 80℃ for 18 h. After the resulting solution was cooled to room temperature, toluene was removed by a vacuum, and the residue was purified by a column chromatography on silica gel to provide the desire product.

The characterization data of compounds 2a-v



2a

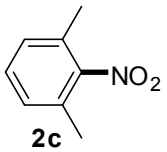
Nitrobenzene (2a).[1] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow oil. Yield 92% (113 mg). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.16 (d, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.52 (t, 2H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 147.7, 134.3, 128.9, 122.9. GC-MS 123.1.



2b

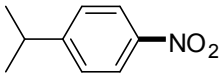
4-Nitrotoluene (2b).[1] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 92% (126.1 mg), mp 51℃. 1H NMR ($CDCl_3$, 600 MHz) δ 8.08 (d, 2H, J = 8.7 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.52 (t, 2H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 147.7, 134.3, 128.9, 122.9.

GC-MS m/z 137.1.



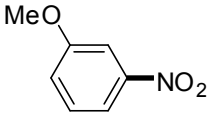
2c

2, 6-Dimethyl-1-Nitrobenzene (2c).[2] Eluent: Ethyl acetate/petroleum ether (1:100). Colorless oil. Yield 60% (90.6 mg). 1H NMR ($CDCl_3$, 600 MHz) δ 7.23 (t, 1H, J = 7.33 Hz), 7.09 (d, 2H, J = 7.33 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 152.03, 130.04, 129.52, 128.9, 17.46. GC-MS m/z 151.2.



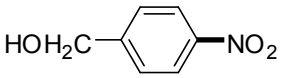
2d

1-Isopropyl-4-Nitrobenzene (2d).[3] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow oil. Yield 88% (145.4 mg). 1H NMR ($CDCl_3$, 600 MHz) δ 8.06 (d, 2H, J = 8.7 Hz), 7.29 (d, 2H, J = 8.7 Hz), 2.94 (m, 1H), 1.2 (d, 2H, J = 6.87 Hz) . ^{13}C NMR ($CDCl_3$, 100 MHz) 155.7, 145.4, 126.4, 122.8, 33.4, 22.7. GC-MS m/z 165.2.



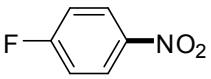
2e

3-Nitroanisole (2e).[1] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 87% (133.2mg), mp 34℃. 1H NMR ($CDCl_3$, 600 MHz) δ 7.83 (dd, 1H, J = 2.1, 8.3 Hz), 7.74 (dd, 2H, J = 2.8, 8.3 Hz), 7.43 (t, 1H, J = 8.3 Hz), 7.23 (dd, 1H, J = 2.8, 8.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 160.2, 149.3, 130.0, 121.3, 115.8, 108.2, 55.9. GC-MS m/z 153.1.



2f

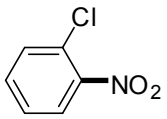
4-Nitrobenaylalchol (2f).[1] Eluent: Ethyl acetate/petroleum ether (1:10). Yellow solid. Yield 78% (119.3 mg), mp 90℃. 1H NMR ($CDCl_3$, 600 MHz) δ 8.16 (d, 2H, J =8.7 Hz), 7.5 (d, 2H, J = 8.7 Hz), 4.81 (s, 2H), 2.09 (s,1H). ^{13}C NMR ($CDCl_3$, 100 MHz) 148.3, 147.3, 127.1, 123.8, 64.0. GC-MS m/z 153.1.



2g

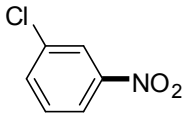
4-Fluoronitrobenzene (2g).[1] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow oil. Yield

85% (119.1 mg). 1H NMR ($CDCl_3$, 600MHz) δ 8.28 (m, 2H), 7.22 (m, 2H,). ^{13}C NMR ($CDCl_3$, 100 MHz) 167.6, 165.0, 144.3, 126.4, 126.3, 116.6, 116.3. 19F NMR ($CDCl_3$，400MHz) 101.87. GC-MS m/z 141.1.



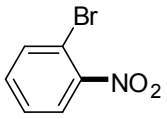
2h

2-Nitrochlorobenzene (2h).[4] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 68% (106.8mg), mp 30℃. 1H NMR ($CDCl_3$, 600 MHz) δ 7.85 (d, 1H, J = 8.24 Hz), 7.52 (m, 2H), 7.40 (t, 1H, J = 8.24 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 148.0, 133.3, 131.9, 127.7, 127.1, 125.7. GC-MS m/z 157.5.



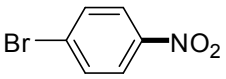
2i

3-Nitrochlorobenzen (2i).[1] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 88% (138.7mg), mp 42℃. 1H NMR ($CDCl_3$, 600MHz) δ 8.24 (s, 1H), 8.14 (d, 1H, J = 8.3 Hz), 7.69 (d, 1H, J = 8.3 Hz),8.14 (t, 1H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 148.7, 135.5, 134.8, 130.5, 123.9, 121.8. GC-MS m/z 157.5.



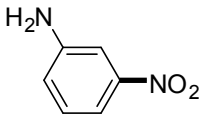
2j

1-Bromo-2-nitrobenzene (2j).[1] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 72% (145.5 mg), mp 38℃. 1H NMR ($CDCl_3$, 600 MHz) δ 7.84 (d, 1H, J = 7.6 Hz), 7.75 (d, 1H, J = 8.3 Hz), 7.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) 149.8, 135.1, 133.3, 128.3, 125.7, 114.5. GC-MS m/z 202.0.



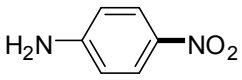
2k

1-Bromo-4-nitrobenzene (2k).[5] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 89% (179.2mg), mp 120℃. 1H NMR ($CDCl_3$, 600MHz) δ 8.09 (d, 2H, J = 8.25 Hz), 7.68 (d, 2H, J = 8.25 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) GC-MS m/z=202.0



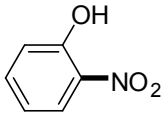
2l

2-Nitroaniline (2l).[1] Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 60% (82.8 mg), mp 110℃. 1H NMR ($CDCl_3$, 600 MHz) δ 7.57 (d, 1H, *J* = 8.2 Hz), 7.49 (s, 1H), 7.27 (t, 1H, *J* = 8.2 Hz), 6.95 (d, 2H, *J* = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 149.3, 147.5, 130.0, 120.7, 113.2, 109.1. GC-MS m/z 138.1.



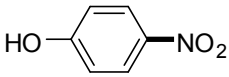
2m

4-Nitroaniline (2m).[6] Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 60% (82.8mg), mp 145℃. 1H NMR ($CDCl_3$, 600 MHz) δ 8.06 (d, 2H, *J* = 8.94 Hz), 6.61 (d, 2H, *J* = 8.94 Hz), 4.28 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) 152.6, 152.5, 126.4, 113.4. GC-MS m/z 138.1.



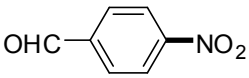
2n

3-Notrophenol (2n).[7] Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 70% (97.4mg), mp 40℃. 1H NMR ($CDCl_3$, 600 MHz) δ 10.57 (s, 1H), 8.09 (d, 1H, *J* = 8.24 Hz), 7.57 (t, 1H, *J* = 7.79 Hz), 7.14 (t, 1H, *J* = 8.7 Hz), 6.98 (t, 1H, *J* = 7.79 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 155.2, 137.6, 133.7, 125.2, 120.3, 120.0. GC-MS m/z 139.1.



2o

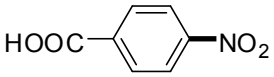
4-Nitrophenol (2o).[8] Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 90% (125.2mg), mp 111℃. 1H NMR ($CDCl_3$, 600MHz) δ 8.16 (d, 2H, *J* = 9.16 Hz), 6.92 (d, 2H, *J* = 9.16 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 161.6, 141.6, 126.4, 115.8. GC-MS m/z 139.1.



2p

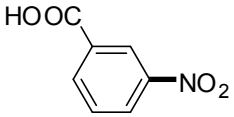
4-Nitrobenzaldelyde (2p).[1] Eluent: Ethyl acetate/petroleum ether (1:80). Yellow solid. Yield 74% (111.7mg), mp 101℃. 1H NMR ($CDCl_3$, 600 MHz) δ 10.17 (s, 1H), 8.40 (d, 2H, *J* = 8.3 Hz), 8.08 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 190.4, 151.1, 140.1, 130.5, 124.4.

GC-MS m/z 151.1.



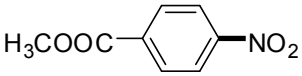
2q

4-Nitrobenzonic acid (2q).[1] Eluent: Ethyl acetate/petroleum ether (1:2.5). Yellow solid. Yield 82% (137.0mg), mp 236℃. 1H NMR ($CDCl_3$, 600 MHz) δ 13.72 (s, 1H), 8.33 (d, 2H, J = 8.7 Hz), 8.18 (d, 2H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 166.3, 150.5, 136.9, 131.2, 124.2. GC-MS m/z 167.1.



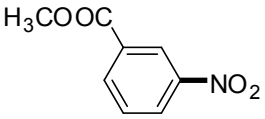
2r

3-Nitrobenzonic acid (2r).[1] Eluent: Ethyl acetate/petroleum ether (1:2.5). Yellow solid. Yield 75% (125.30mg), mp 138℃. 1H NMR ($CDCl_3$, 600MHz) δ 13.76 (s, 1H), 8.62 (d, 2H, J = 1.4 Hz), 8.47 (dd, 1H, J = 1.4, 8.3 Hz), 8.35 (d, 1H, J = 7.6Hz), 7.82 (dd, 1H, J = 8.3, 7.6 Hz) ^{13}C NMR ($CDCl_3$, 100 MHz) 166.0, 148.4, 135.8, 132.9, 131.0, 127.8, 124.2. GC-MS m/z 167.1.



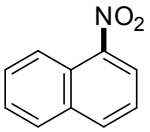
2s

Methyl-4-Nitrobenzoate (2s).[2] Eluent: Ethyl acetate/petroleum ether (1:5). Yellow solid. Yield 86% (155.7mg), 95℃. 1H NMR ($CDCl_3$, 600MHz) δ 8.30 (d, 2H, J = 8.7 Hz), 8.22 (d, 2H, J = 8.7 Hz), 3.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) 165.2, 150.5, 135.5, 130.8, 123.6, 52.9. GC-MS m/z 181.2.



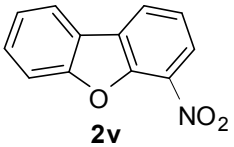
2t

Methyl-3-Nitrobenzoate (2t).[9] Eluent: Ethyl acetate/petroleum ether (1:5). Yellow solid. Yield 78% (141.2mg), mp 79℃. 1H NMR ($CDCl_3$, 600 MHz) δ 8.87 (s, 1H), 8.40 (m, 2H), 7.66 (t, 1H, J = 7.79 Hz), 3.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) 165.0, 148.3, 135.4, 131.9, 129.7, 127.4, 124.7, 52.9. GC-MS m/z 181.2.



2u

1-Nitronophthalene (2u).[5] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 82% (141.9mg), mp 55℃. 1H NMR ($CDCl_3$, 600 MHz) δ 8.55 (d, 1H, *J* = 8.24 Hz), 8.21 (d, 1H, *J* = 7.79 Hz), 8.10 (d, 1H, *J* = 8.24 Hz), 7.94 (d, 1H, *J* = 8.24 Hz), 7.70 (m, 1H), 7.61 (m, 1H), 7.52 (d, 1H, *J* = 7.79 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 146.6, 134.8, 134.4, 129.5, 128.7, 127.4, 125.2, 124.2, 124.1, 123.2. GC-MS m/z 173.2.



2v

Dibenzo[*b,d*]furan (2v).[7] Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 78% (166.1mg), mp 96℃ 1H NMR ($CDCl_3$, 600 MHz) δ 8.27 (d, 1H, *J* = 8.25 Hz), 8.23(d, 1H, *J* = 7.56 Hz), 7.98 (d, 1H, *J* = 7.56 Hz), 7.94 (d, 1H, *J* = 8.24 Hz), 7.73 (m, 1H, *J* = 8.25 Hz), 7.56 (t, 1H, *J* = 7.22 Hz), 7.45 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) 156.8, 148.5, 133.9, 128.8, 128.3, 126.9, 124.0, 122.9, 122.6, 122.2, 120.8, 112.4. GC-MS m/z 213.0.

EPR measurement

The EPR measurement was performed on a X-band EPR (10.0 GHz) instrument JES FA200 (JEOL). The mixture of 4-methylphenyl boronic acid (0.1 mmol) and $Fe(NO_3)_3$ (0.05 mmol) in 0.5mL of toluene was added into an EPR tube. Conditions of EPR measurements were as follows: microwave power (1 mW), central field (250 mT), magnetic width (500 mT), modulation width (0.2 mT), time constant (0.3 s), measure time (4 min) in Figure 1 in text. Conditions of EPR measurements were as follows: microwave power (10mW), central field (323 mT), magnetic width (4 mT), modulation (0.03 mT), time constant (0.3 s), measurement time (8 min) in Figure 2 in text. The simulation of the hyperfine structure on the free radical was taken by the ISO-SIMU software from JEOL company. Based on the measurement spectrum and references[10], the simulation parameters are as follows: A_N = 1.001 mT, $A^{11}{}_B$ = 0.190 mT, $A^{10}{}_B$ = 0.064 mT, $A^{orth}{}_H$ = 0.185 mT, $A^{meta}{}_H$ = 0.81 mT, $A^{methyl}{}_H$ = 0.205mT.

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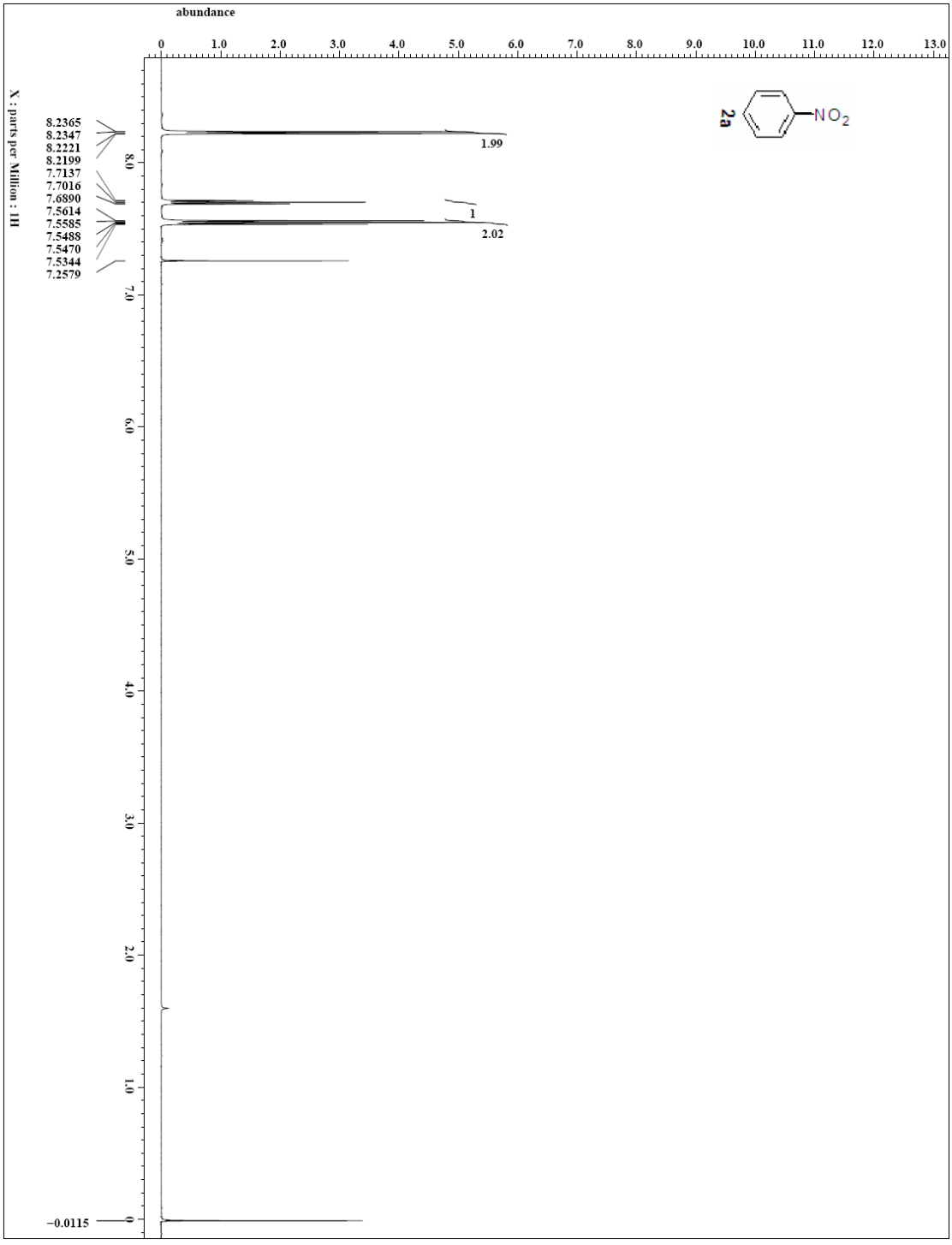
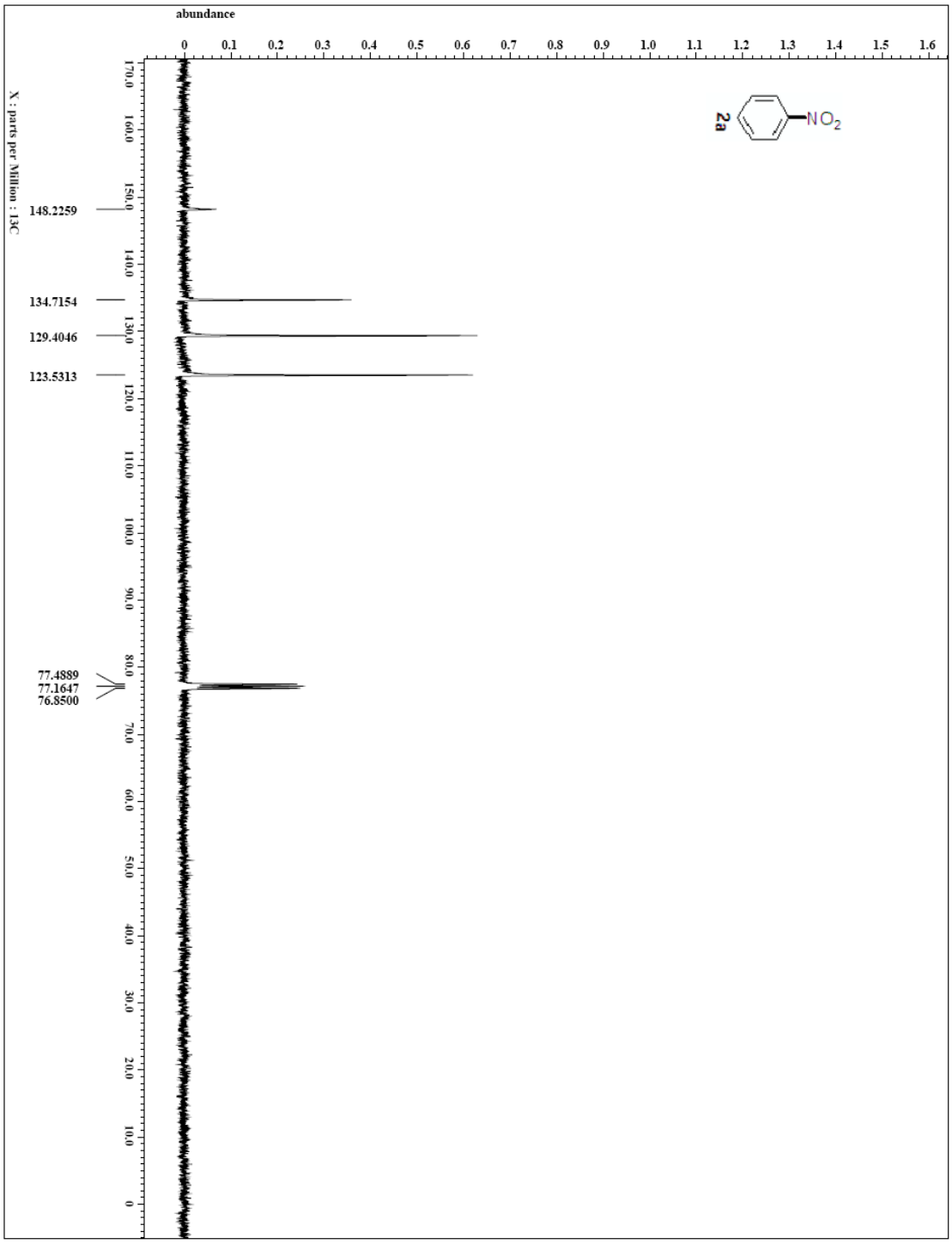
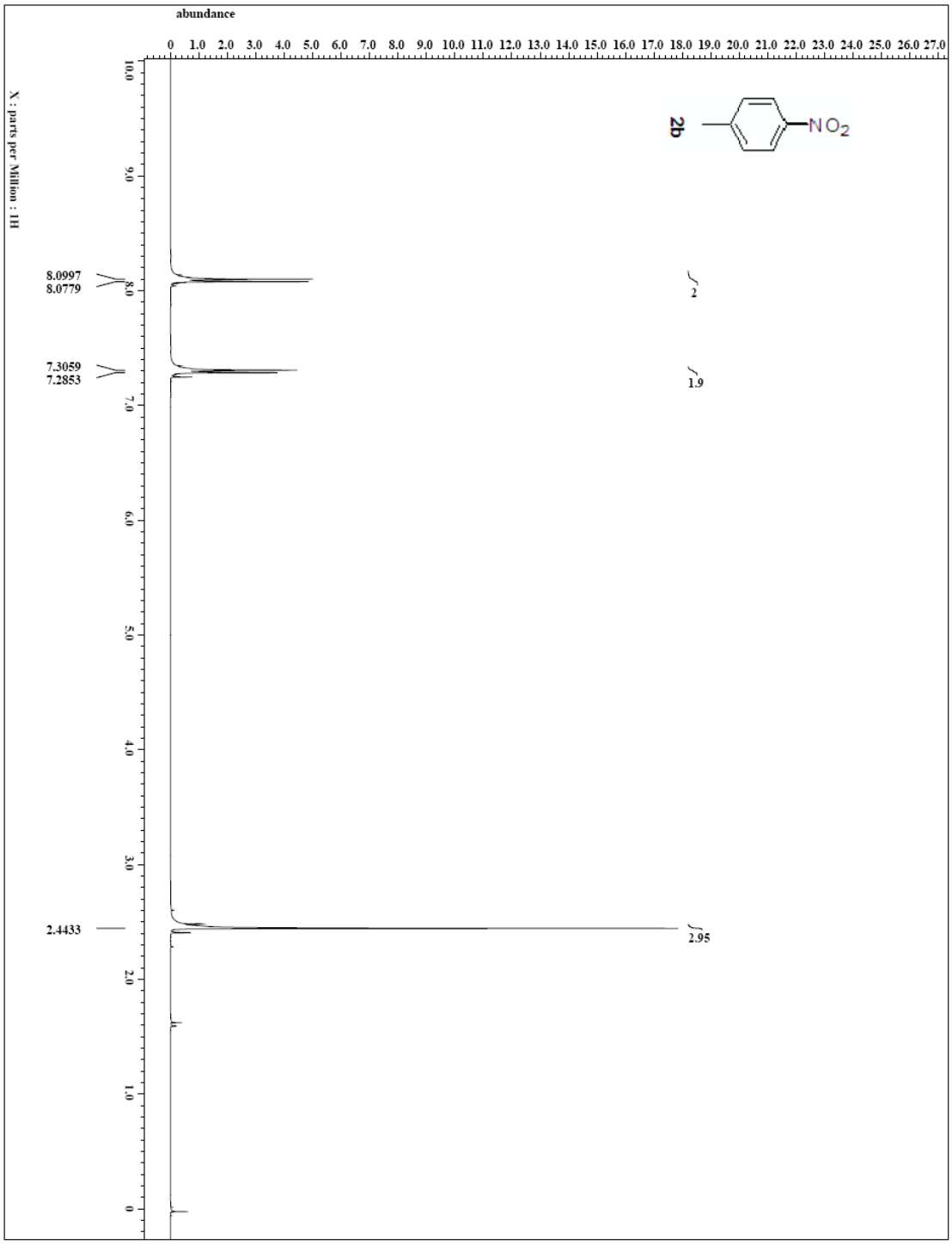
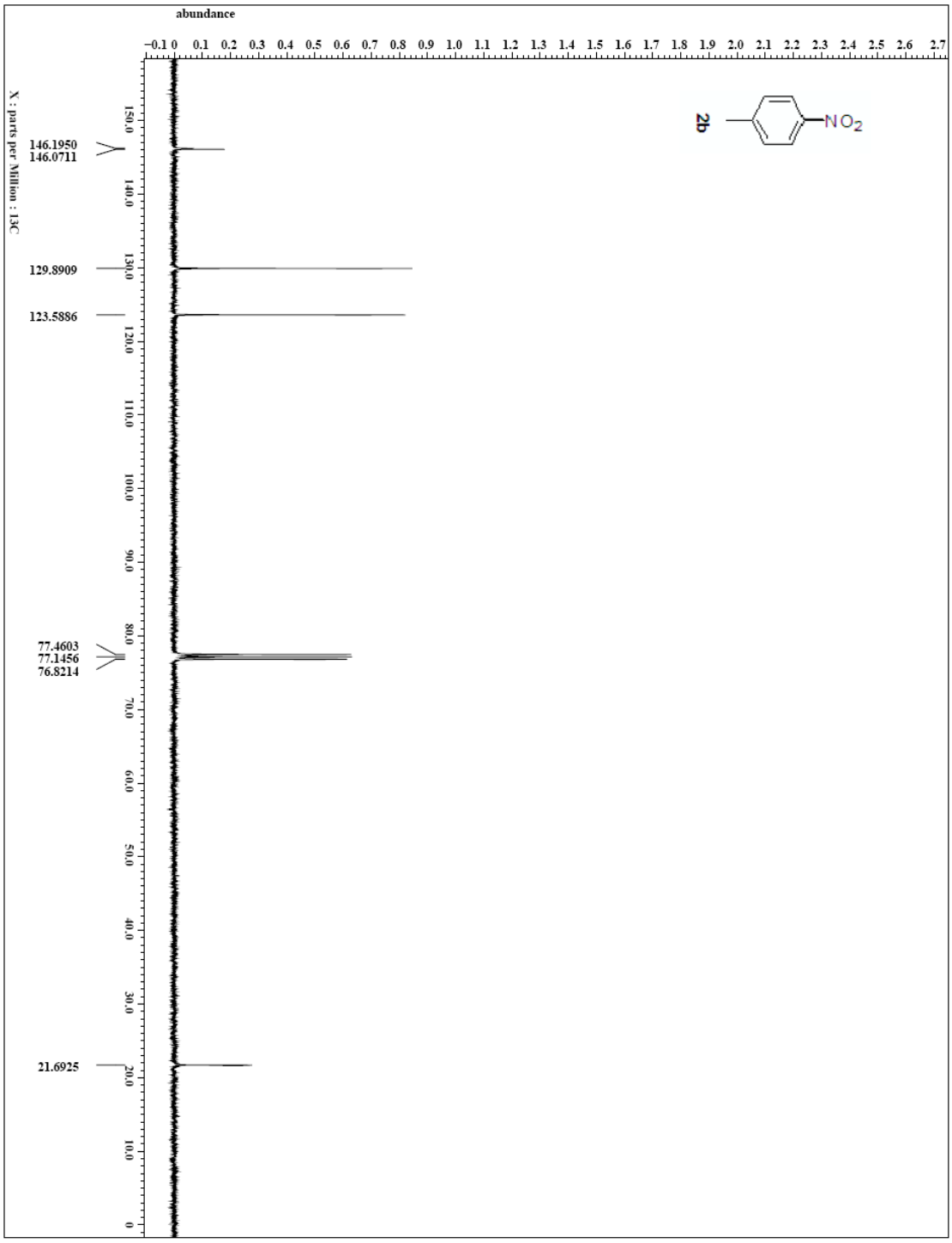
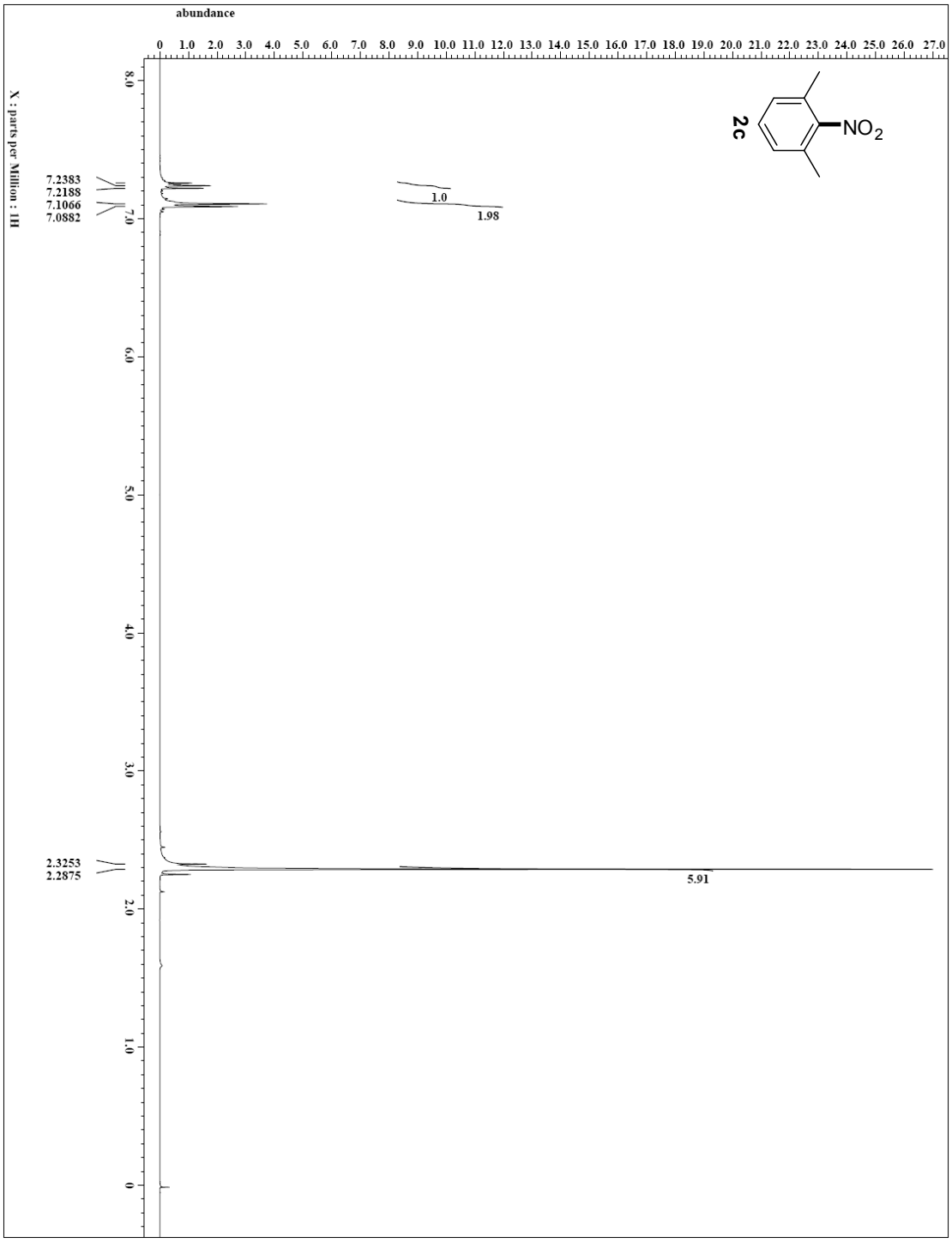
10 (a) J. R. Morton, K. F. Preston and S. J. Strach, *J. Phys. Chem.* 1979, **83**, 533-536. (b) S. Hahne and U. Schindewolf. *J. Phys. Chem.* 1975, **79**, 2922-2928. (c) J. C. A. Boeyens, *J. Phys. Chem.* 1967, **71**, 2969-2974.

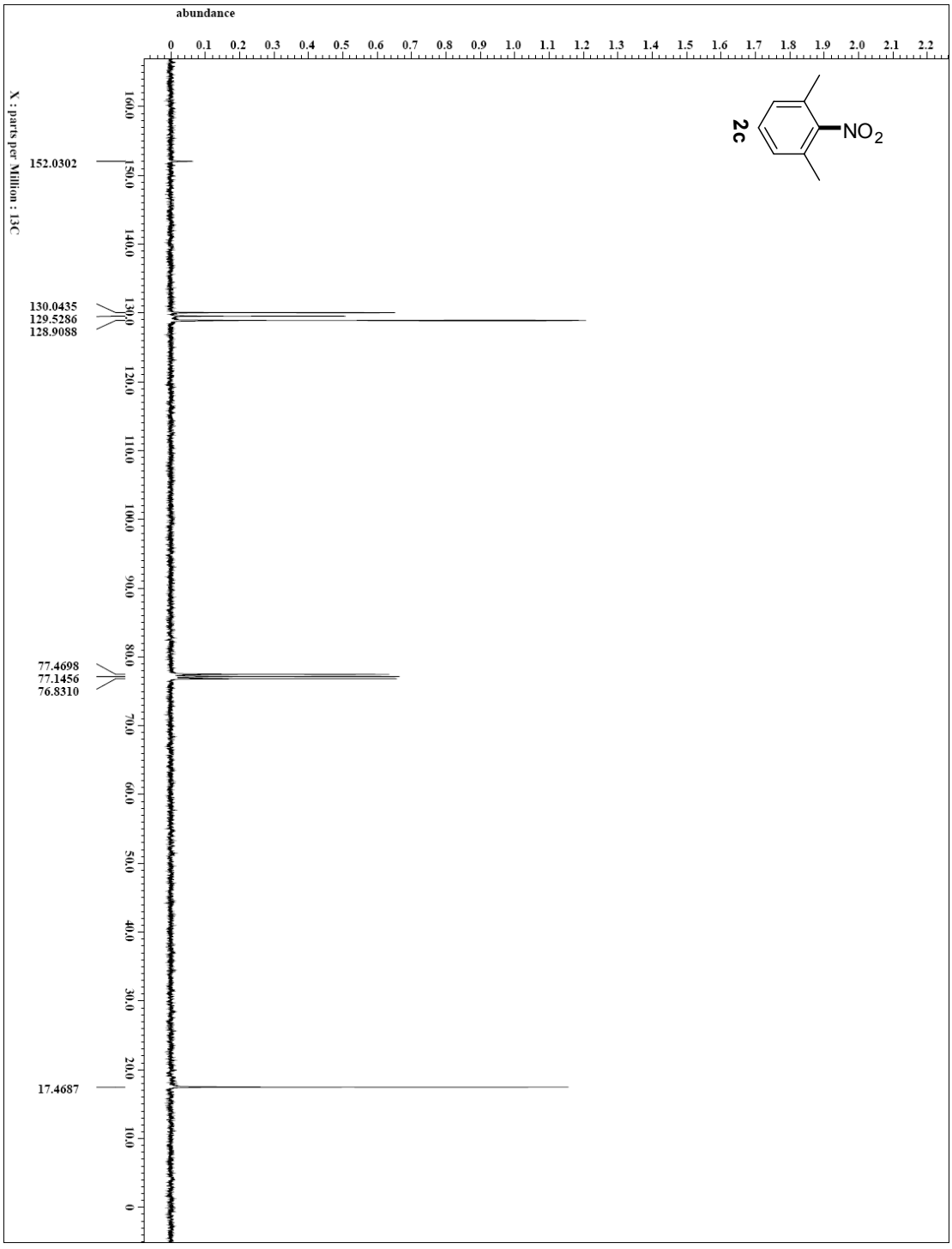


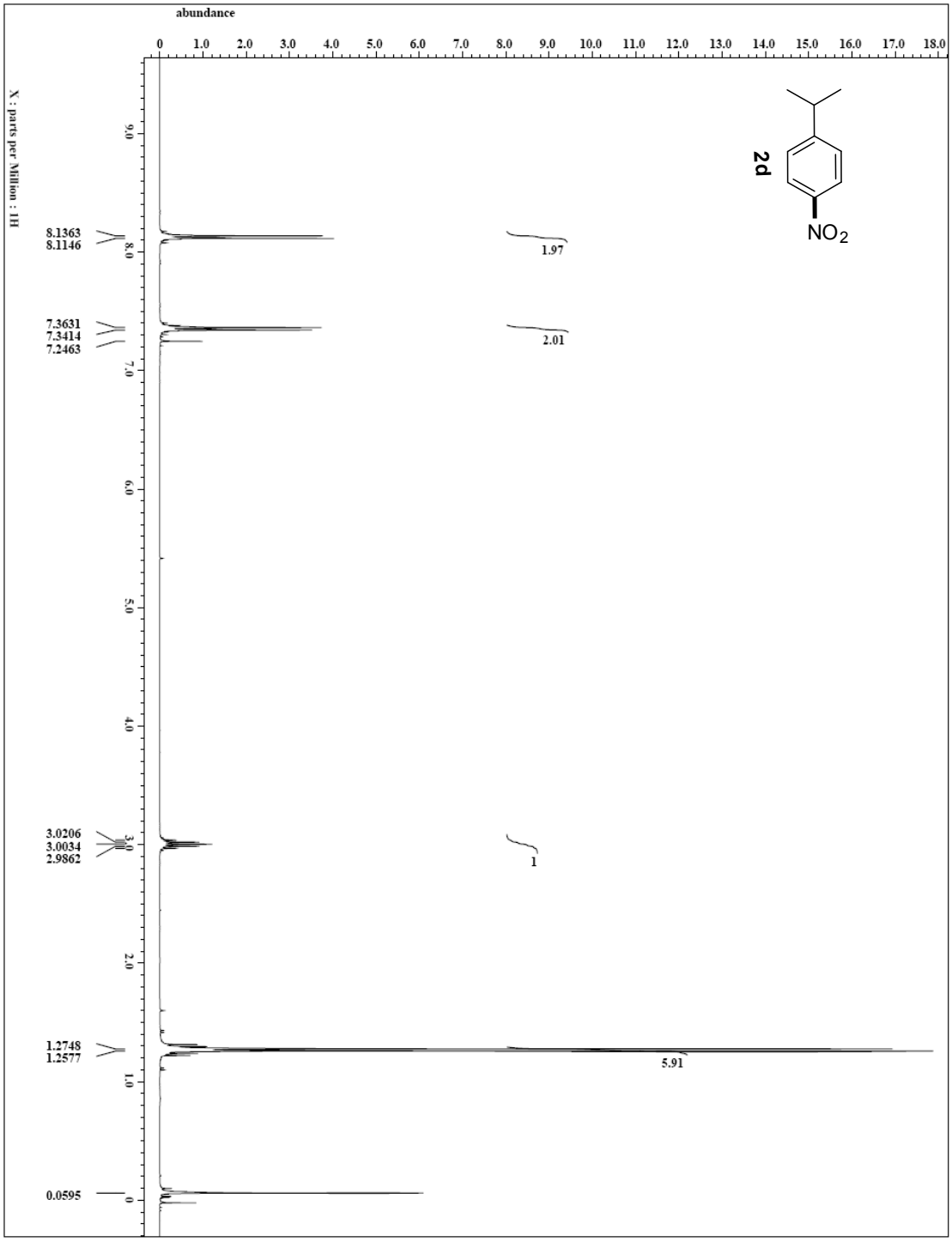


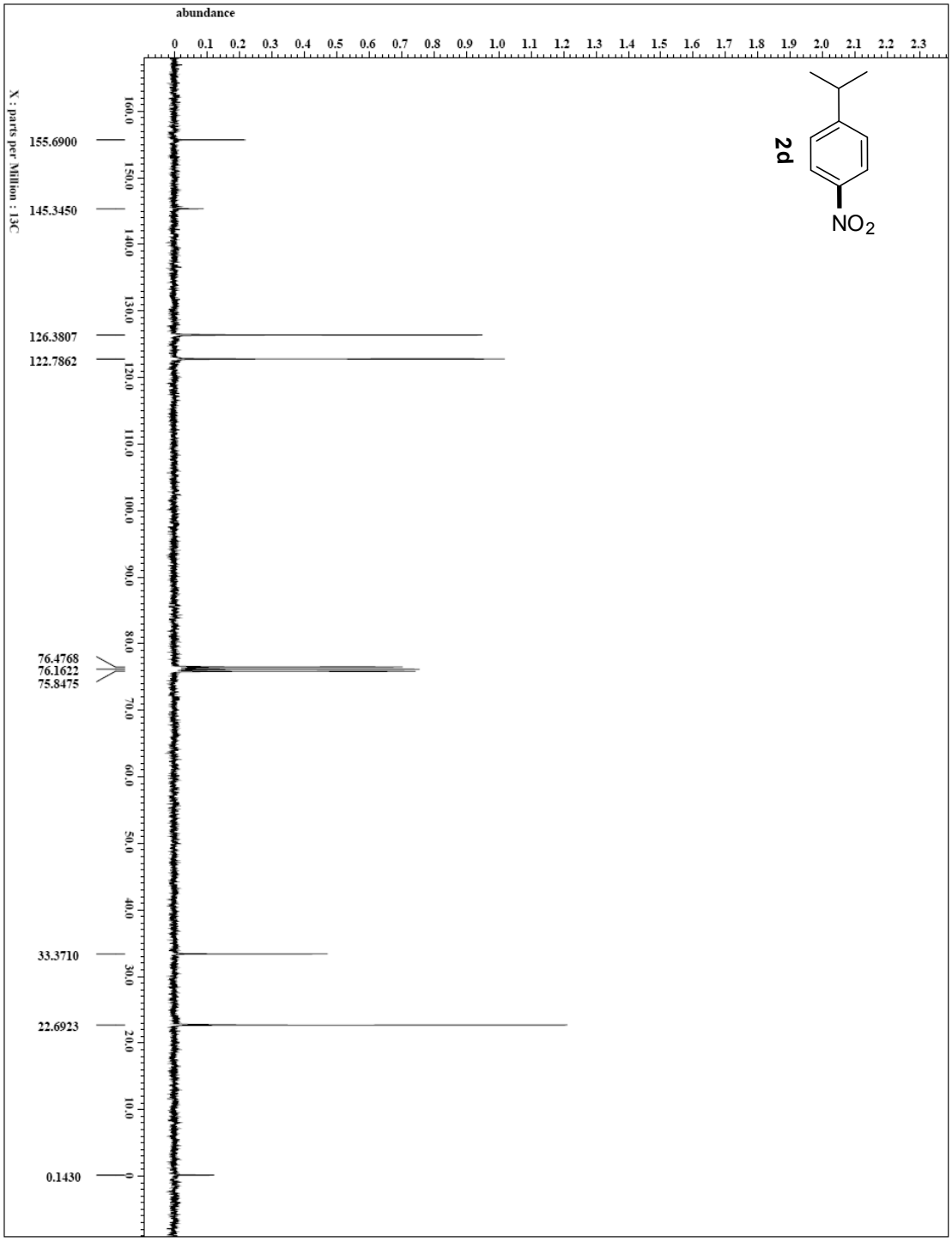


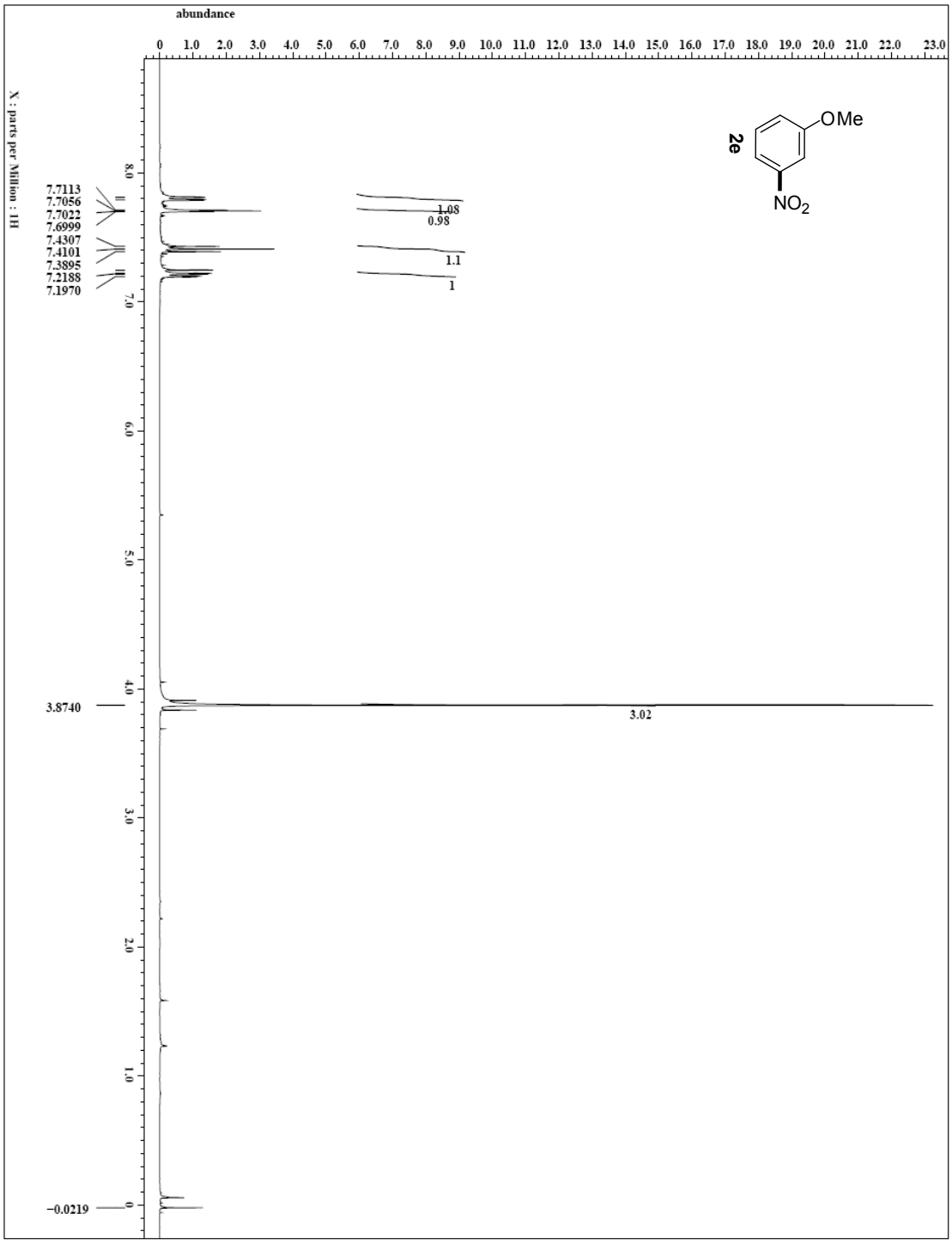

abundance
X : parts per Million : 13C
146.1950
146.0711
129.8909
123.5886
77.4603
77.1456
76.8214
21.6925
2b
NO2

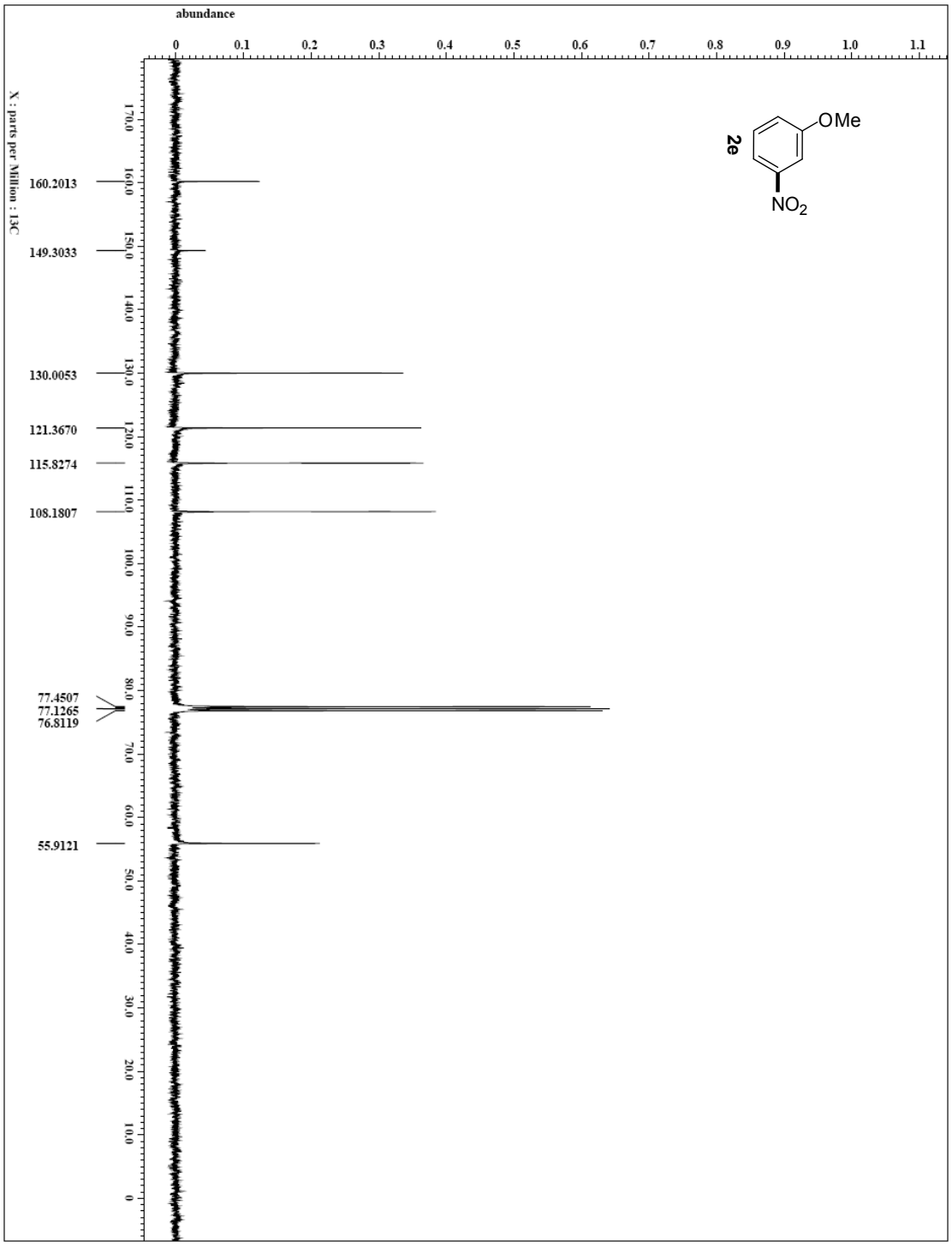


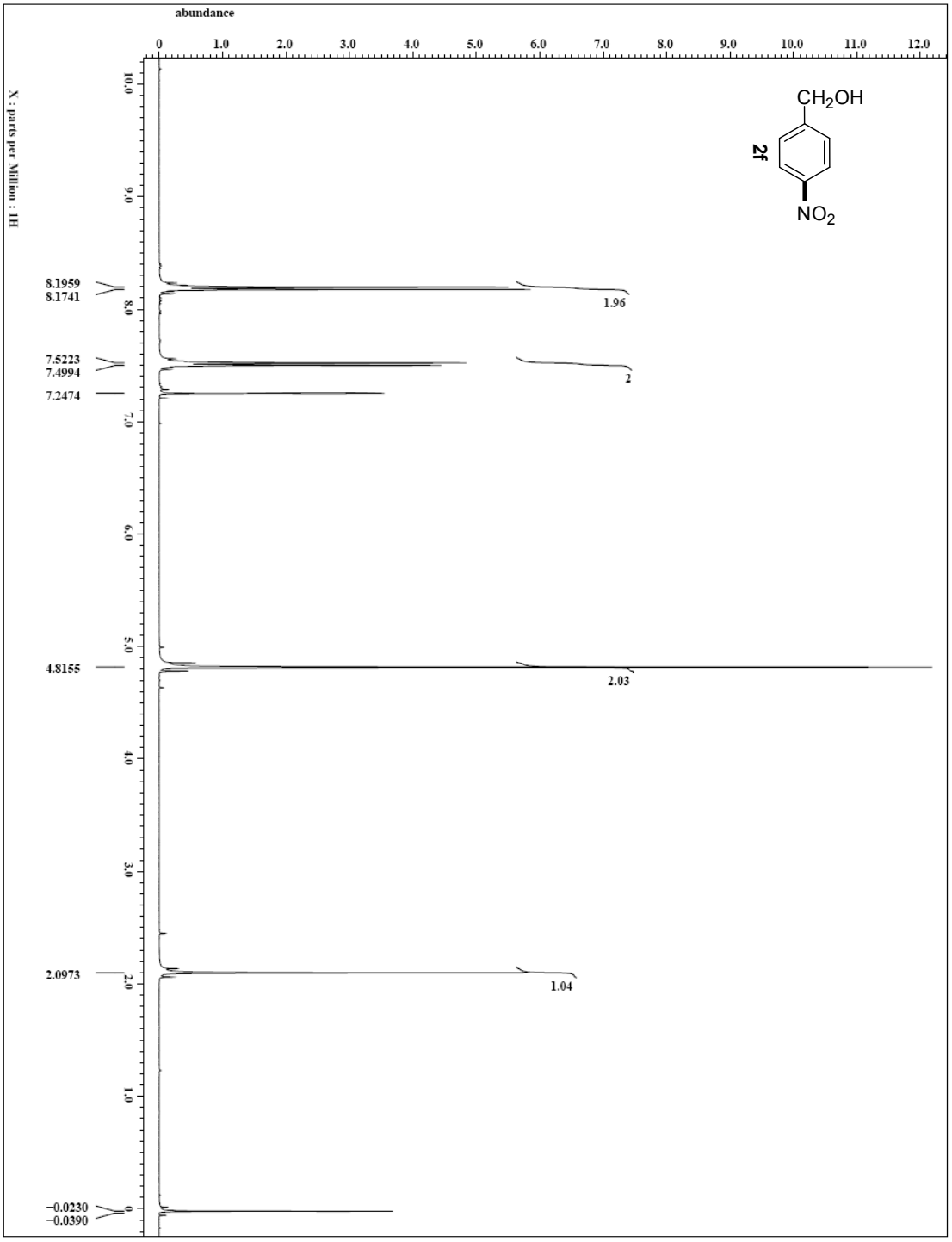


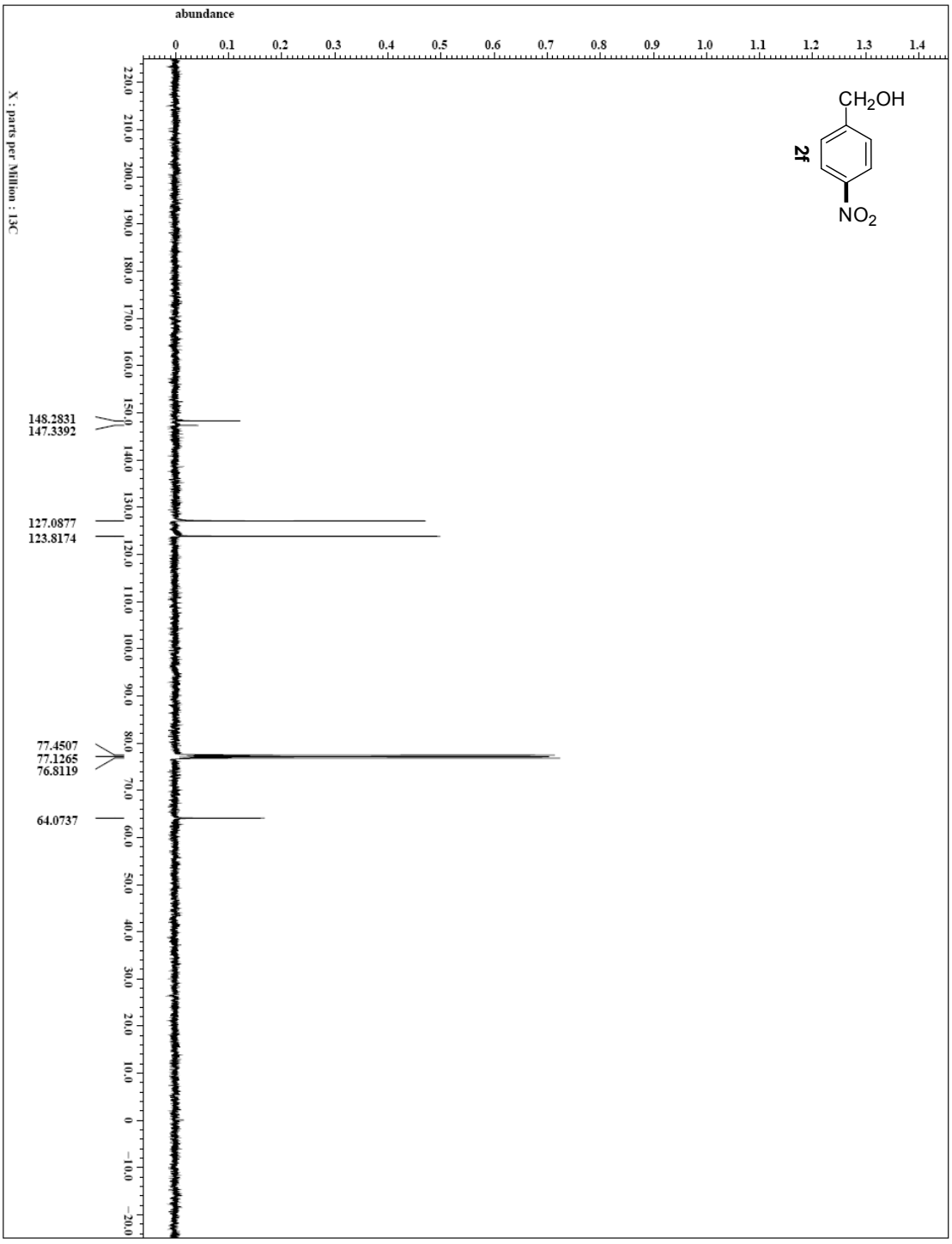


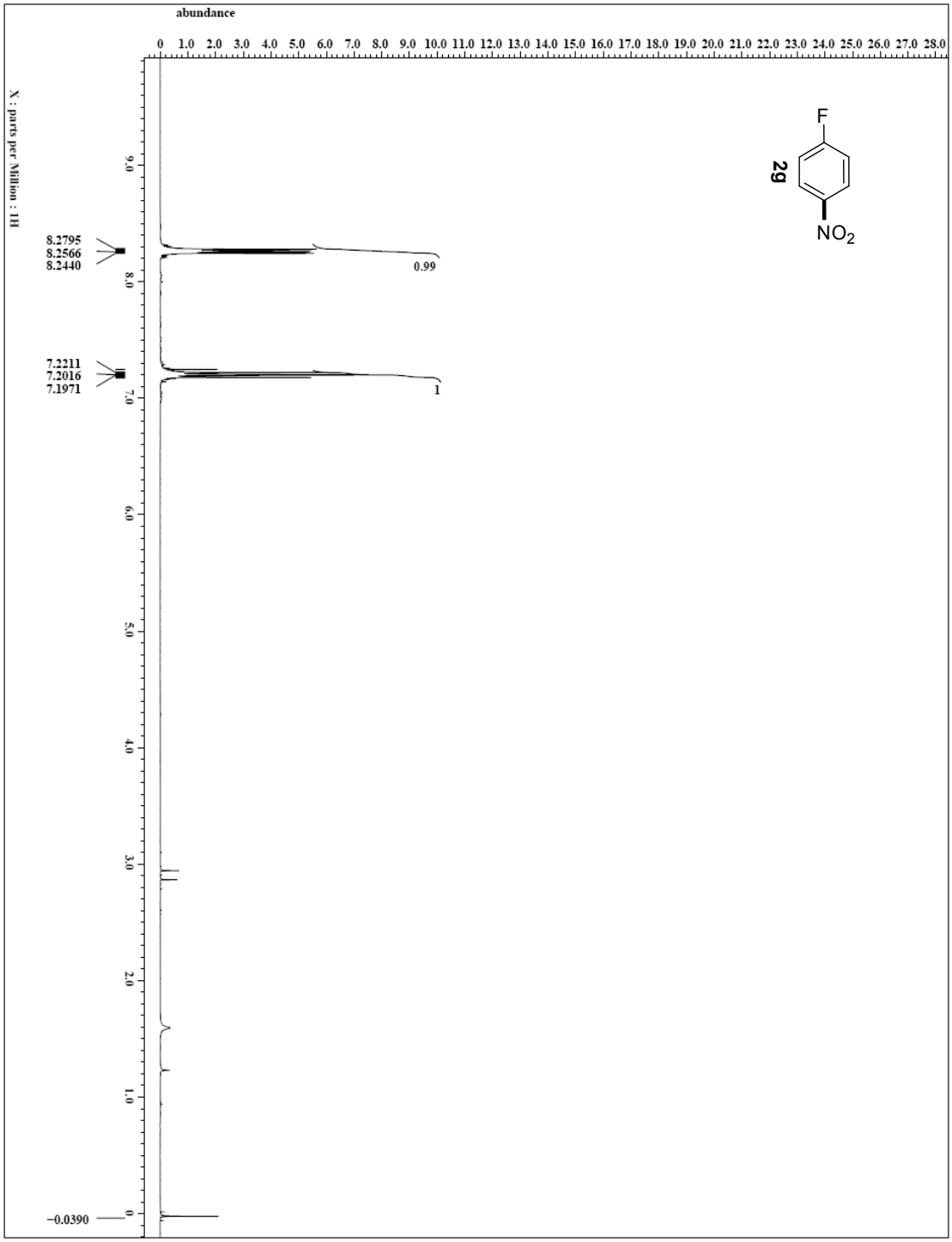

abundance
X : parts per Million : 13C
155.6900
145.3450
126.3807
122.7862
76.4768
76.1622
75.8475
33.3710
22.6923
0.1430
2d
NO2

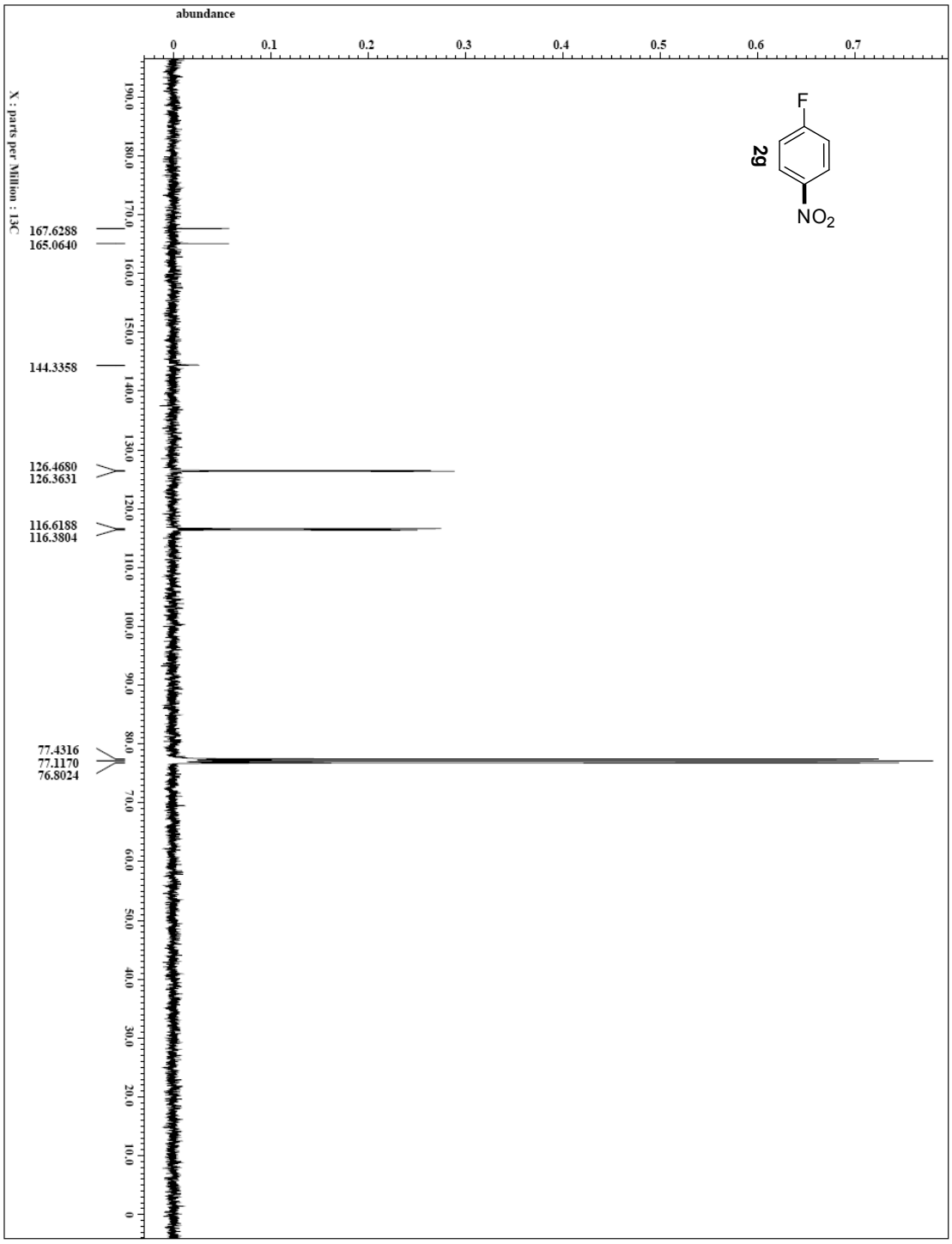


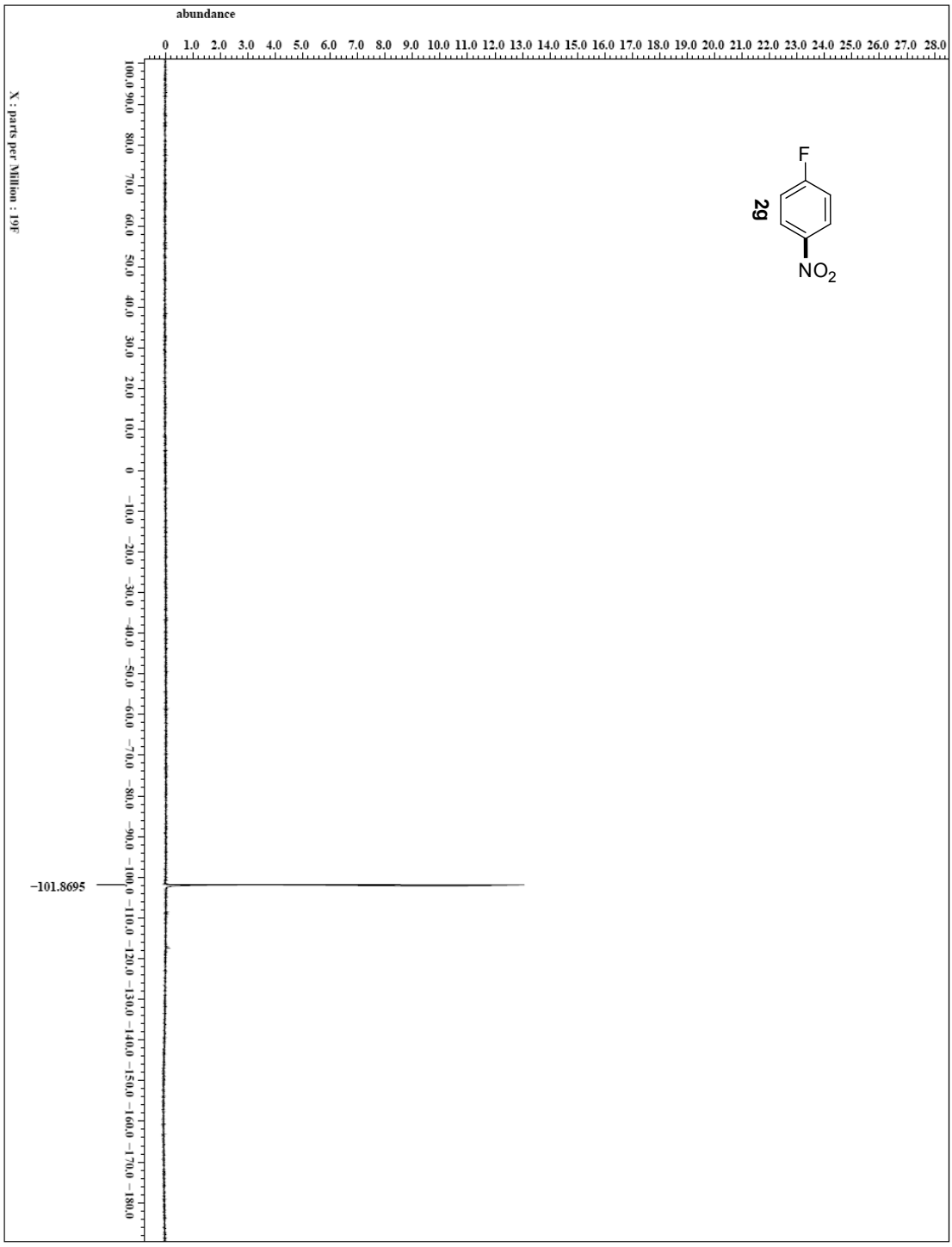


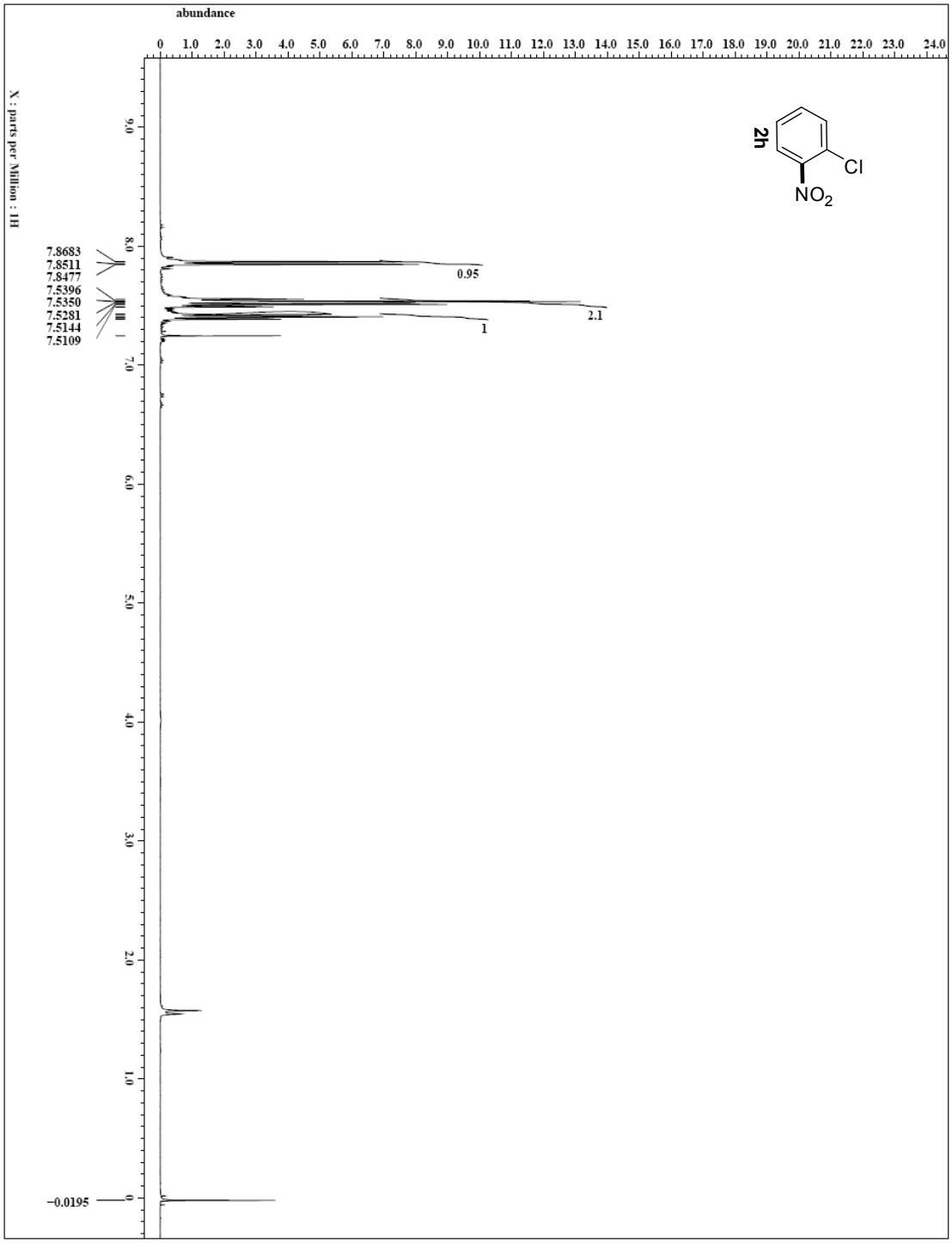


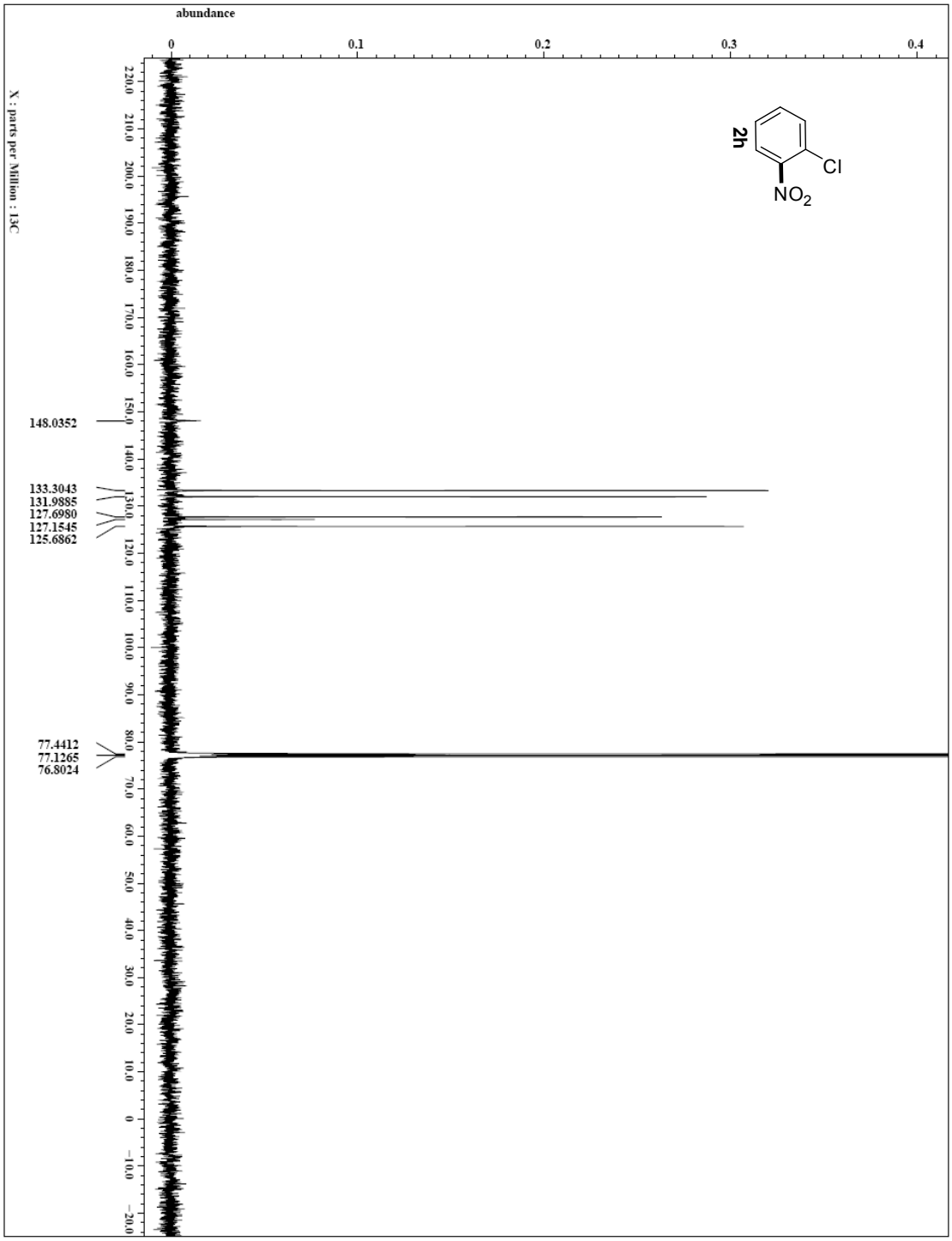


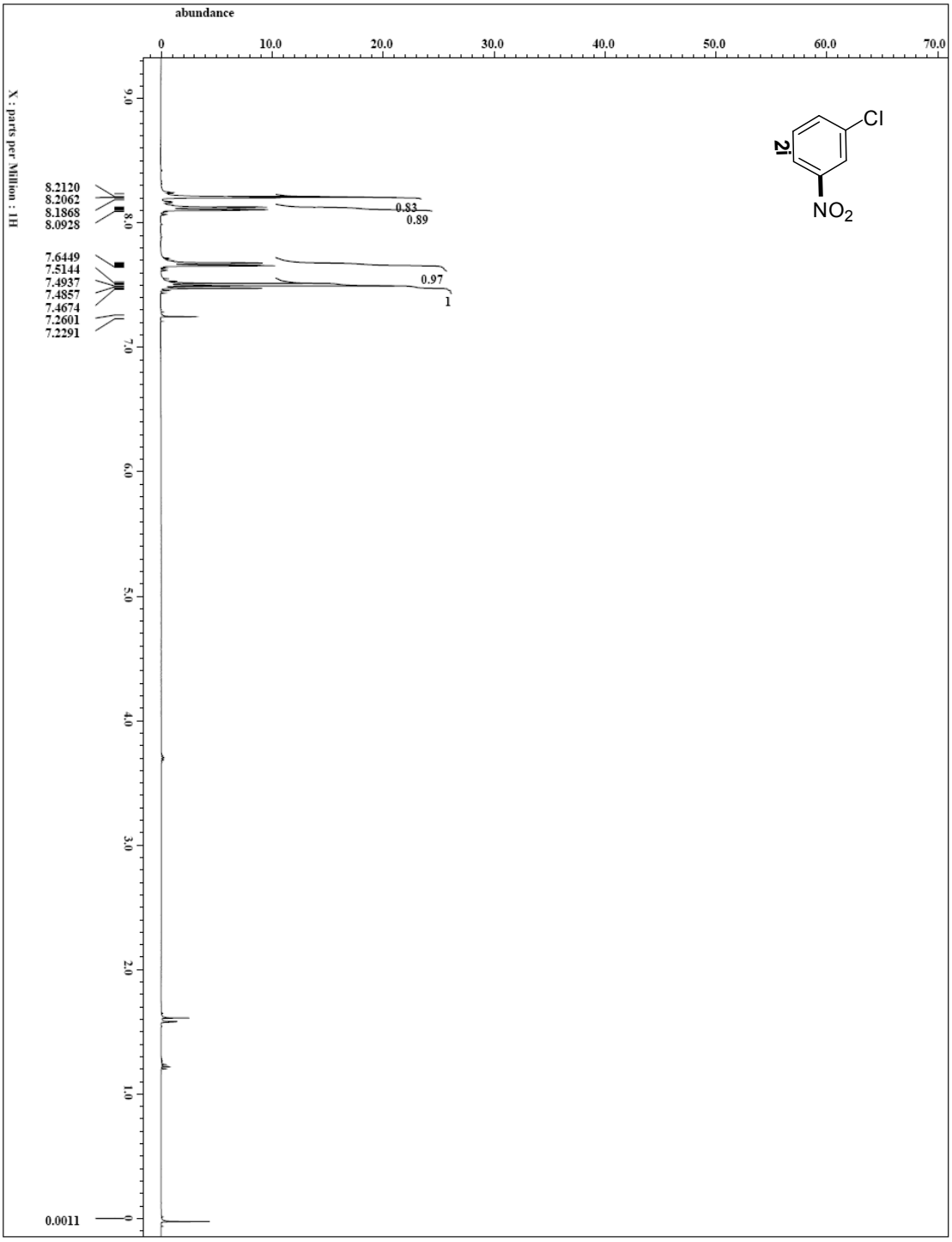


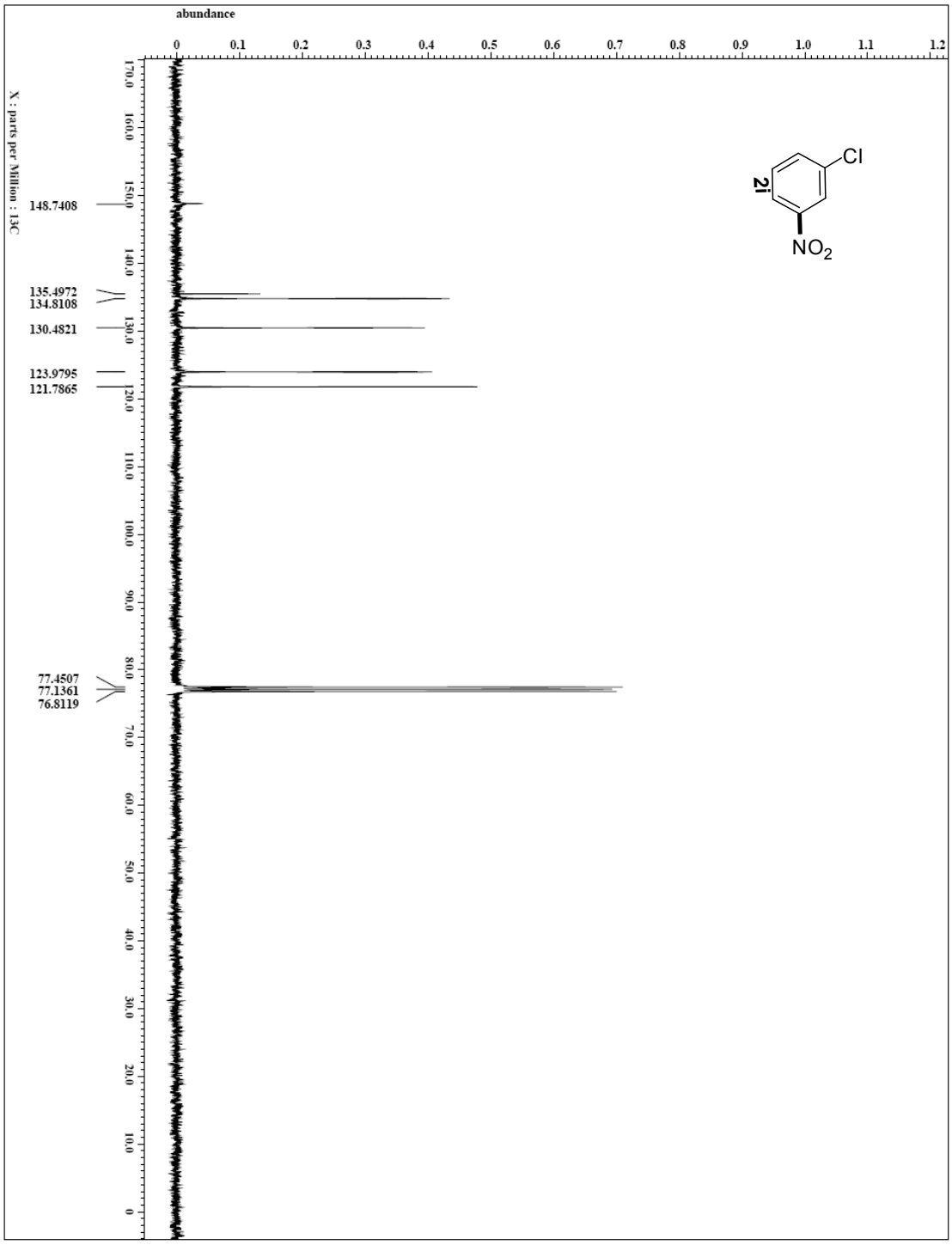


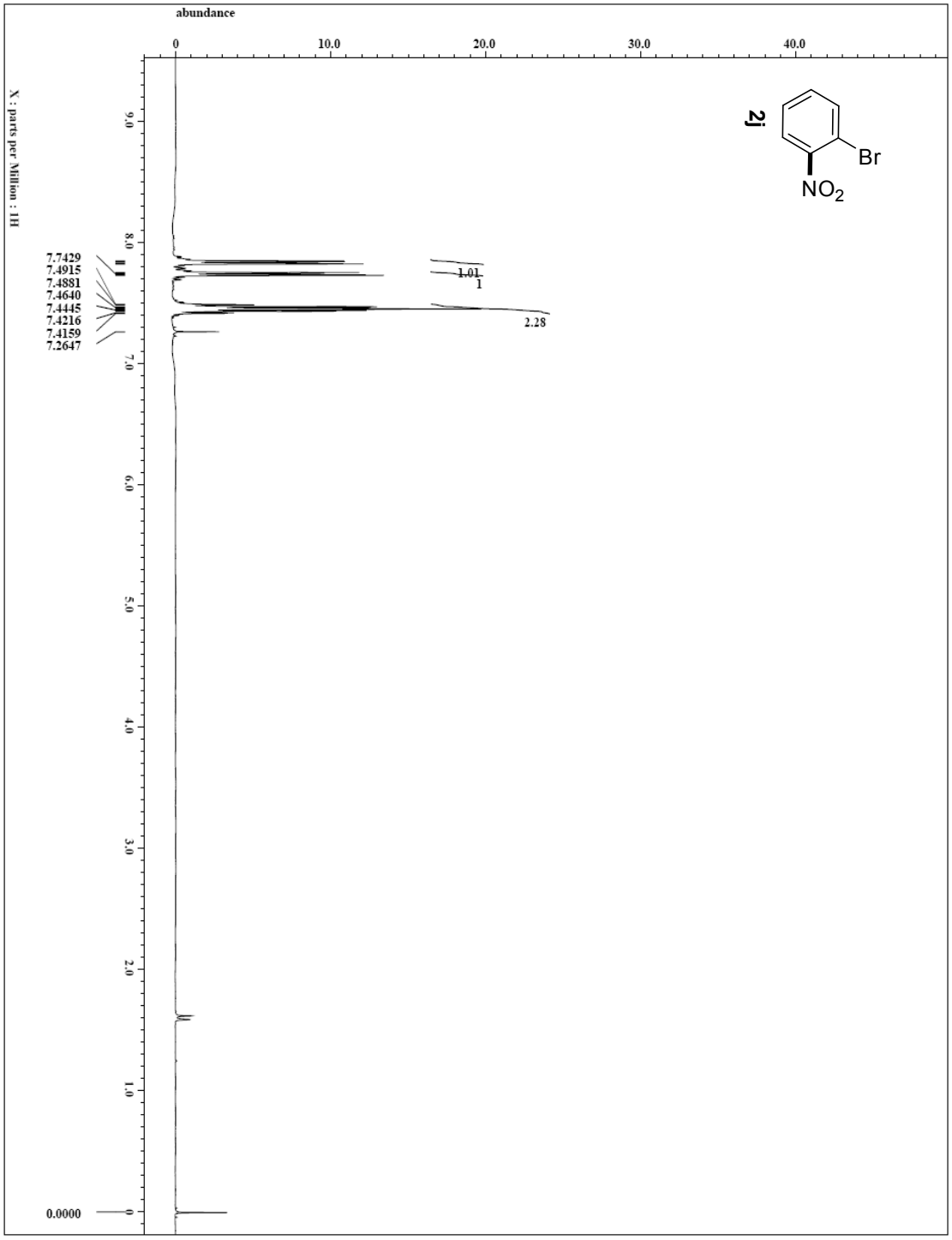


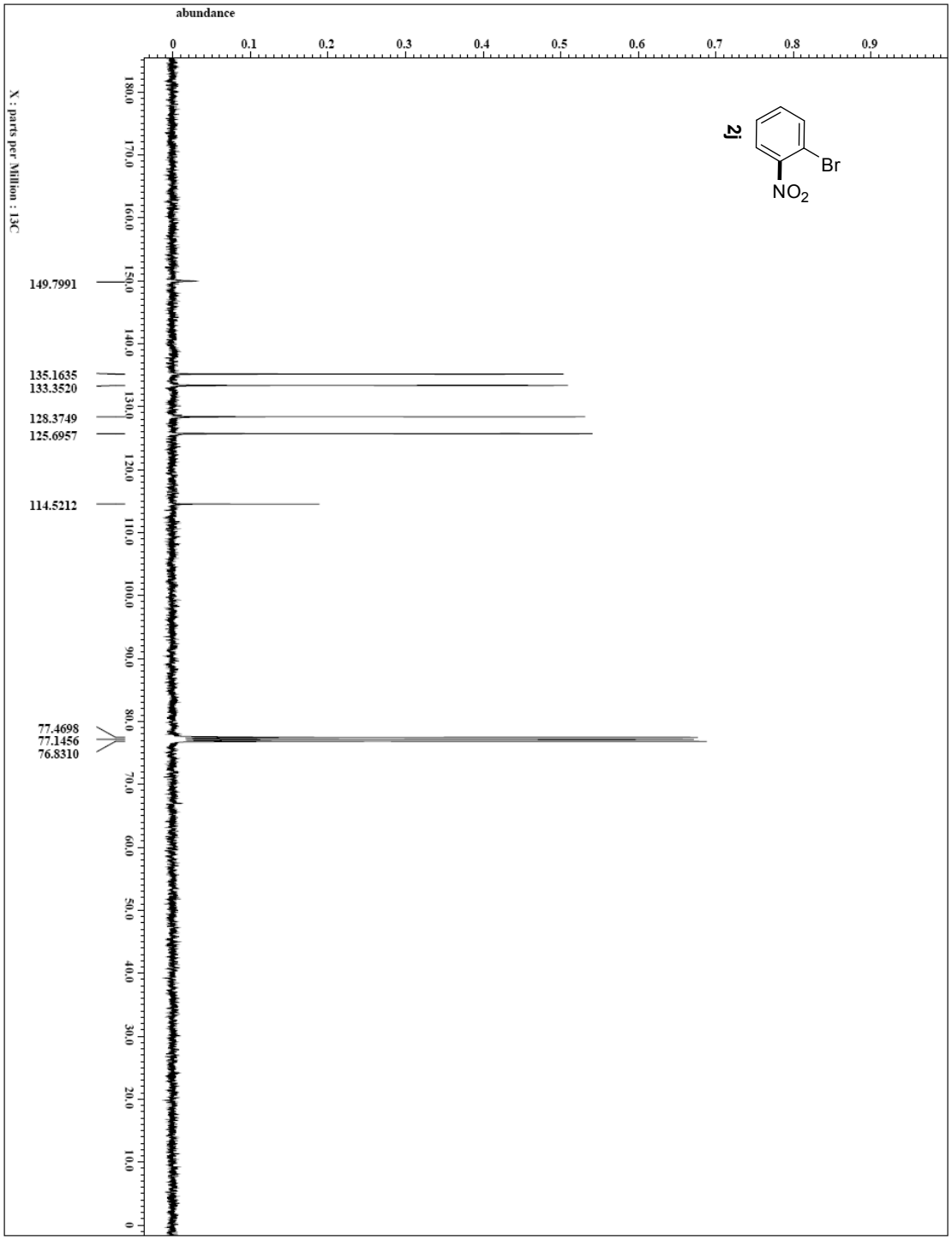


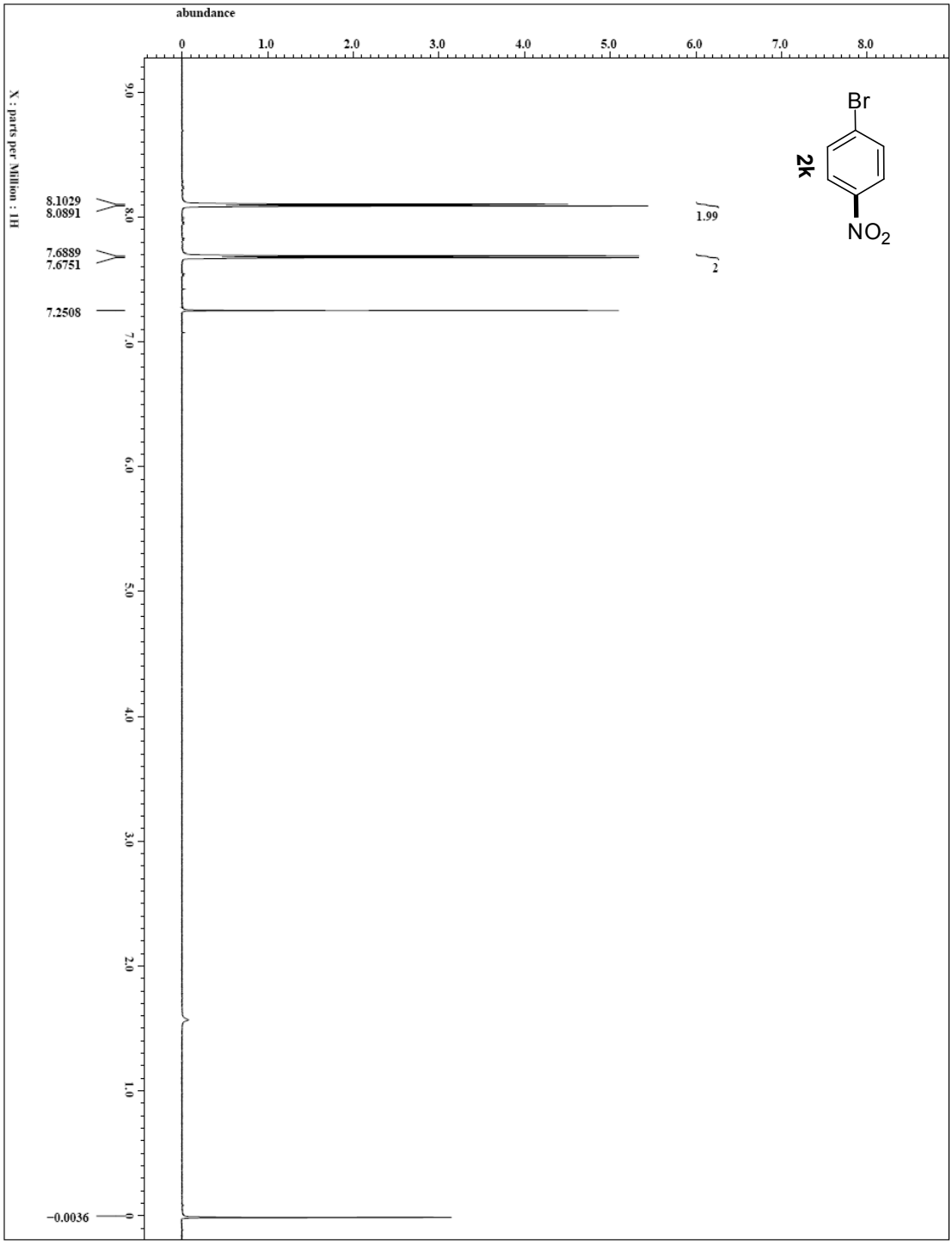

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
148.0352
133.3043
131.9885
127.6980
127.1545
125.6862
77.4412
77.1265
76.8024
2h
Cl
NO2

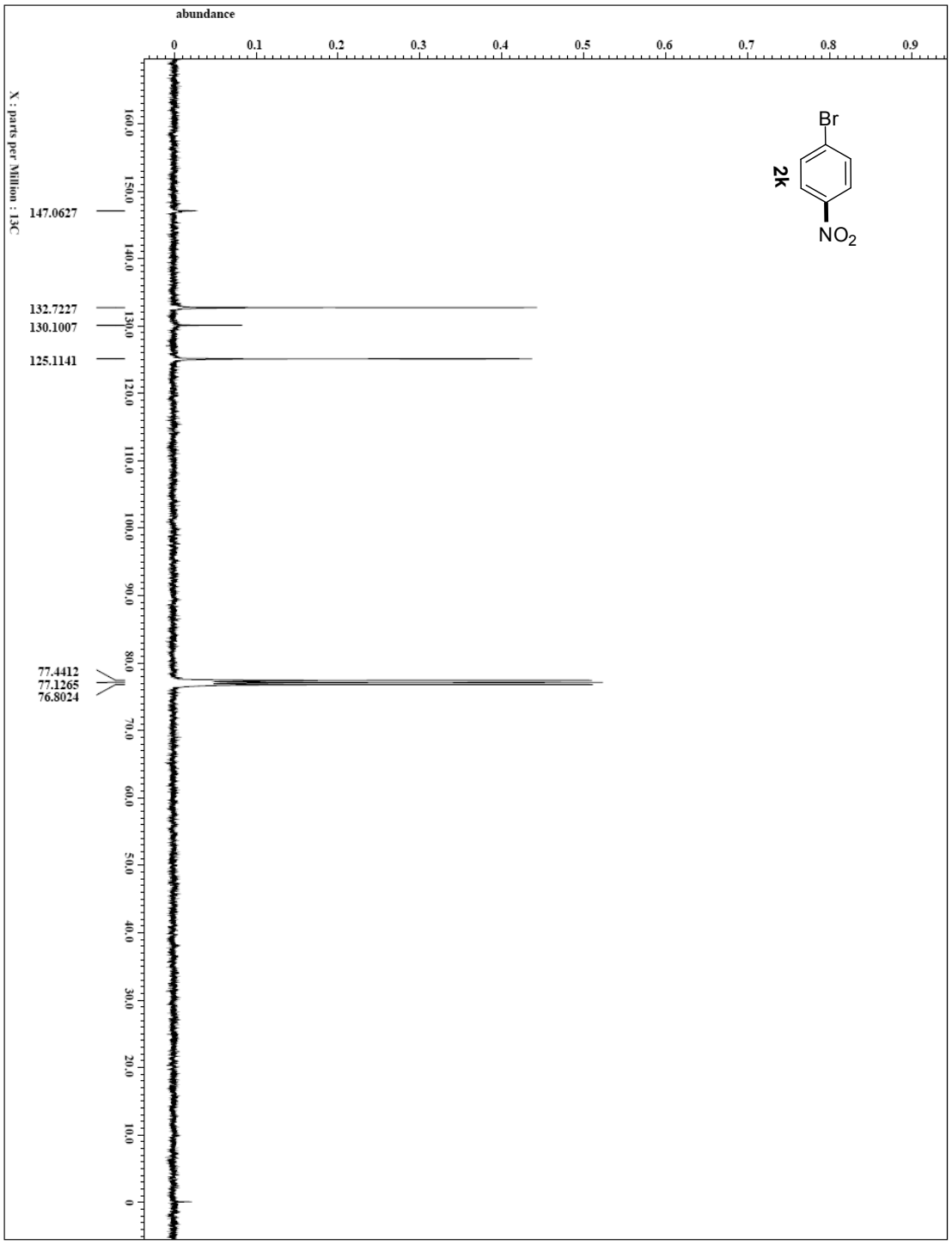

abundance
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.2120
8.2062
8.1868
8.0928
7.6449
7.5144
7.4937
7.4857
7.4674
7.2601
7.2291
0.0011
0.83
0.89
0.97
1
Cl
NO2

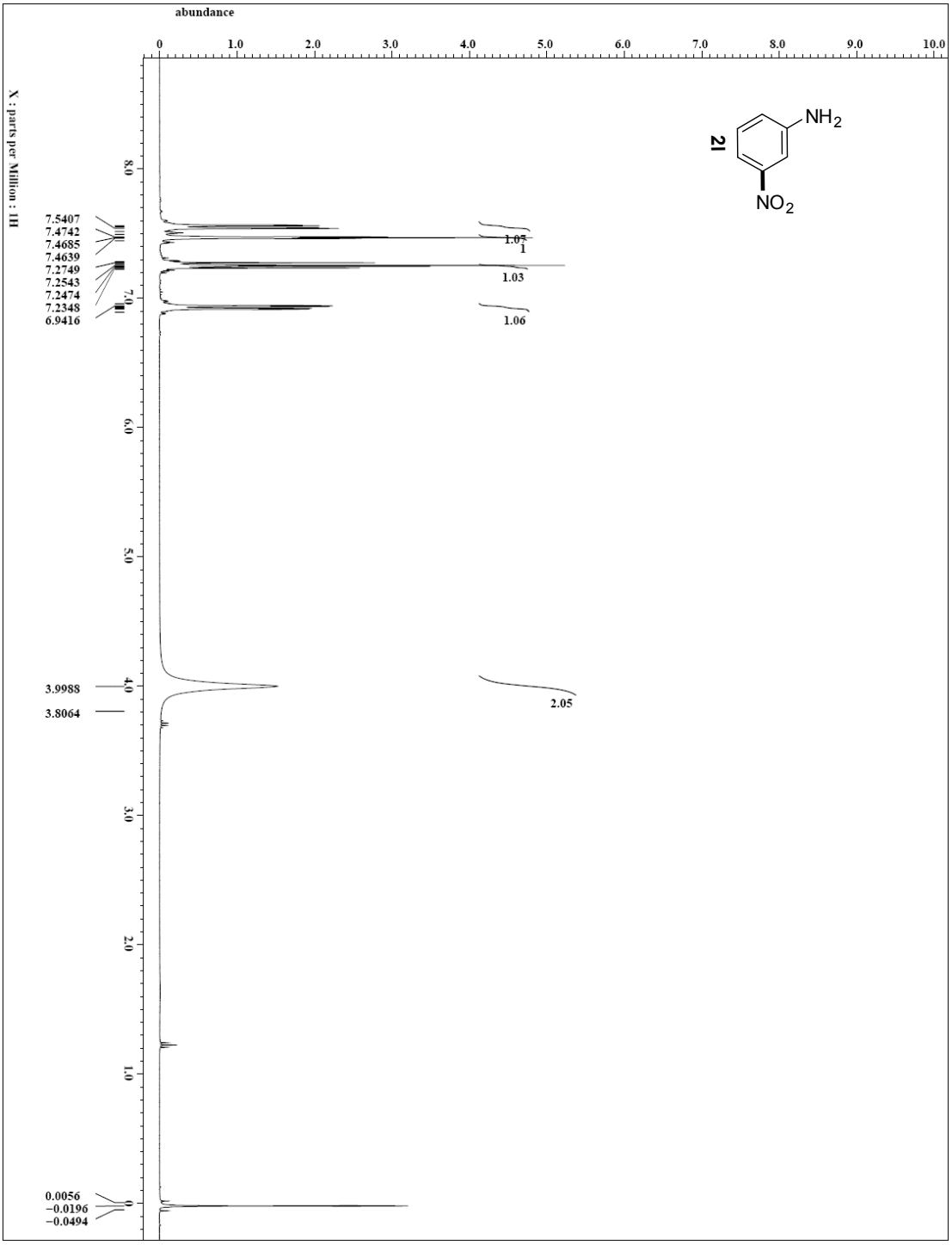


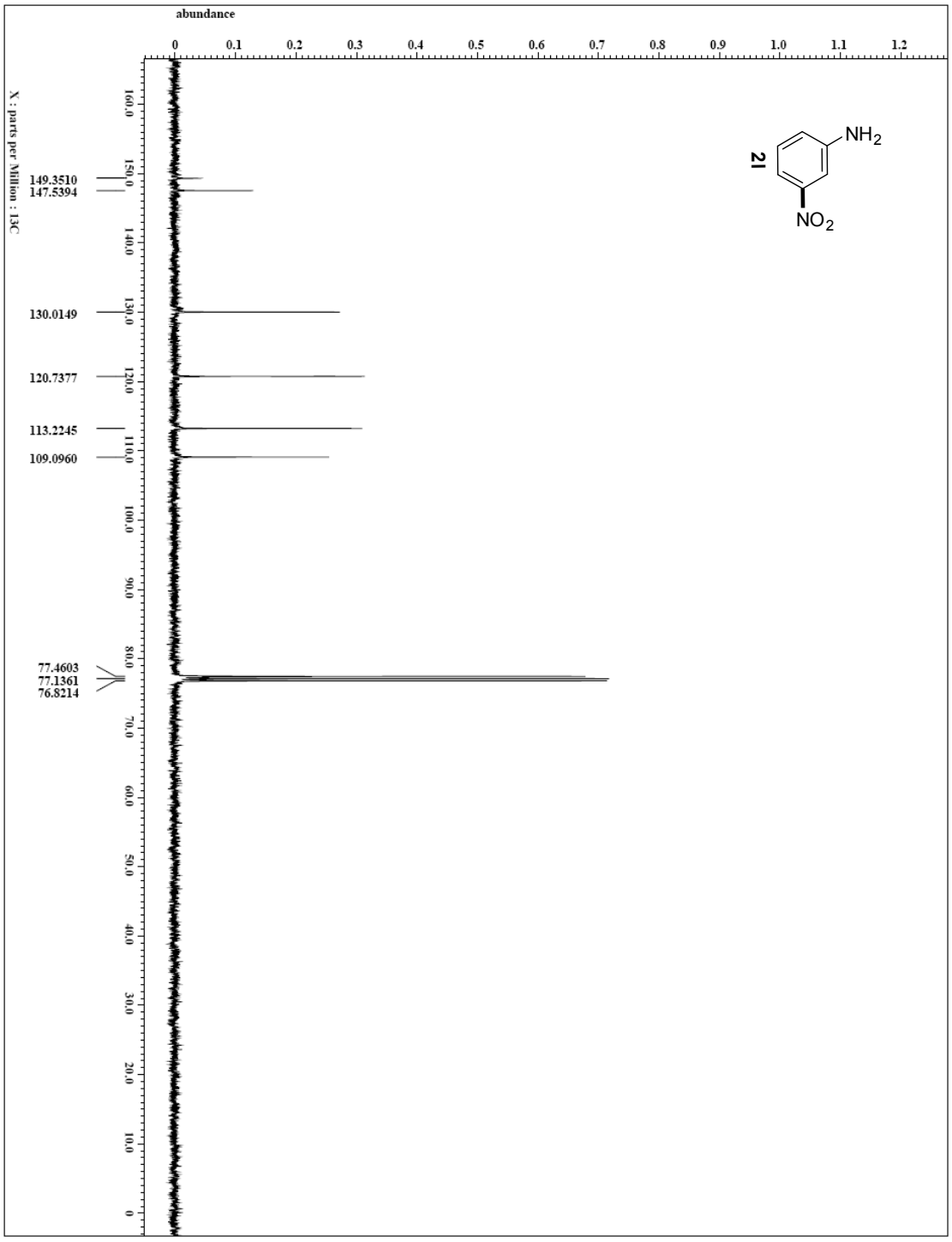


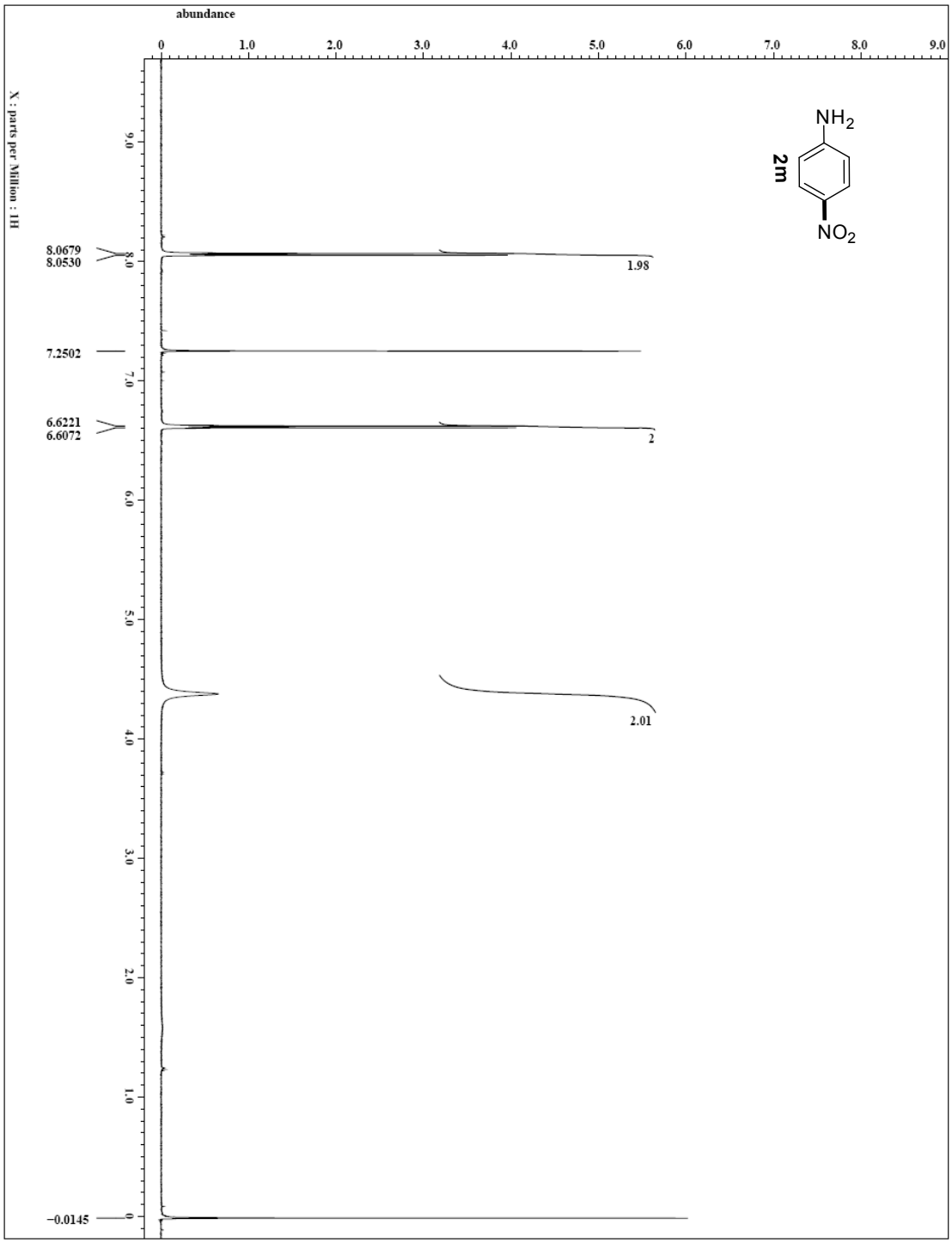


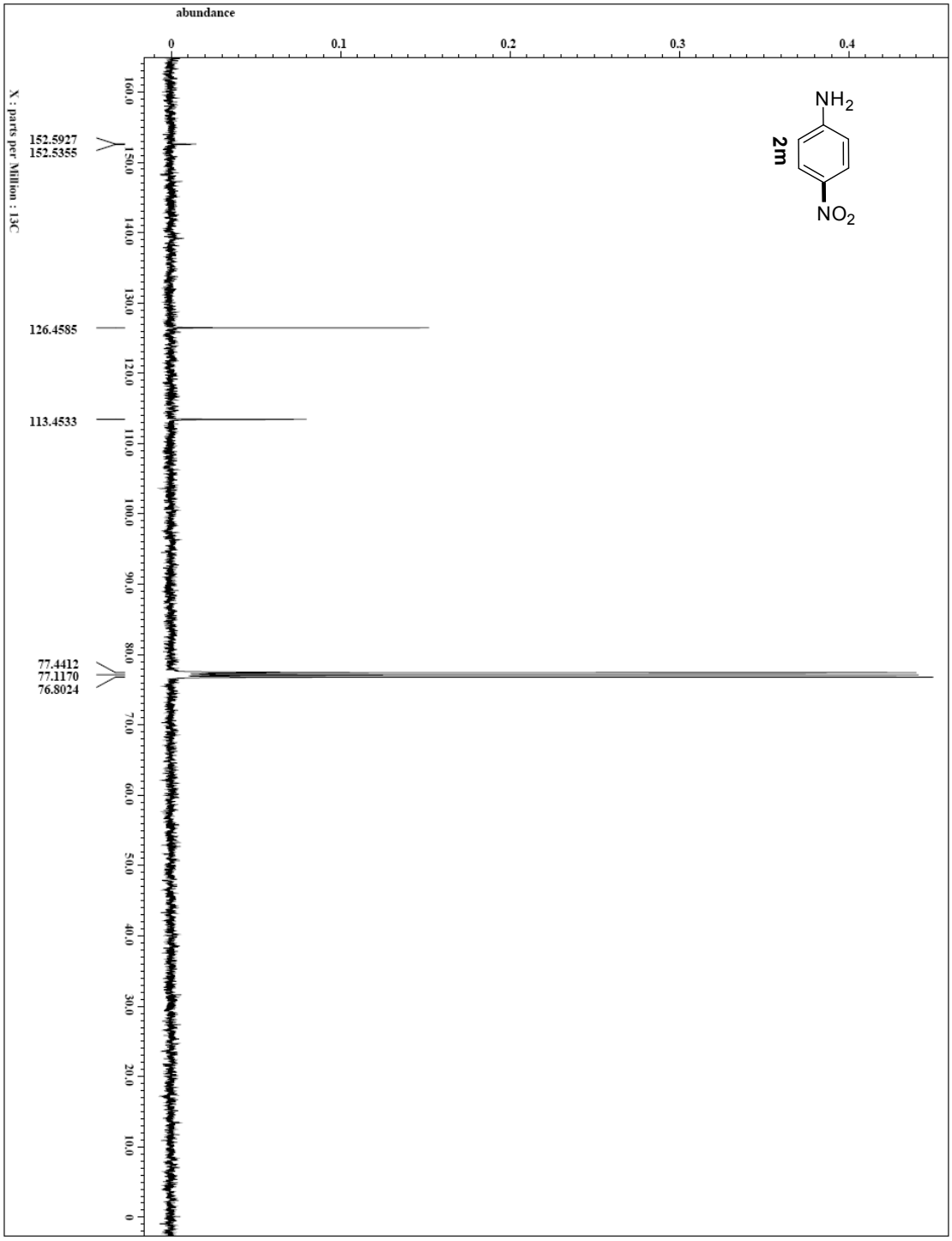


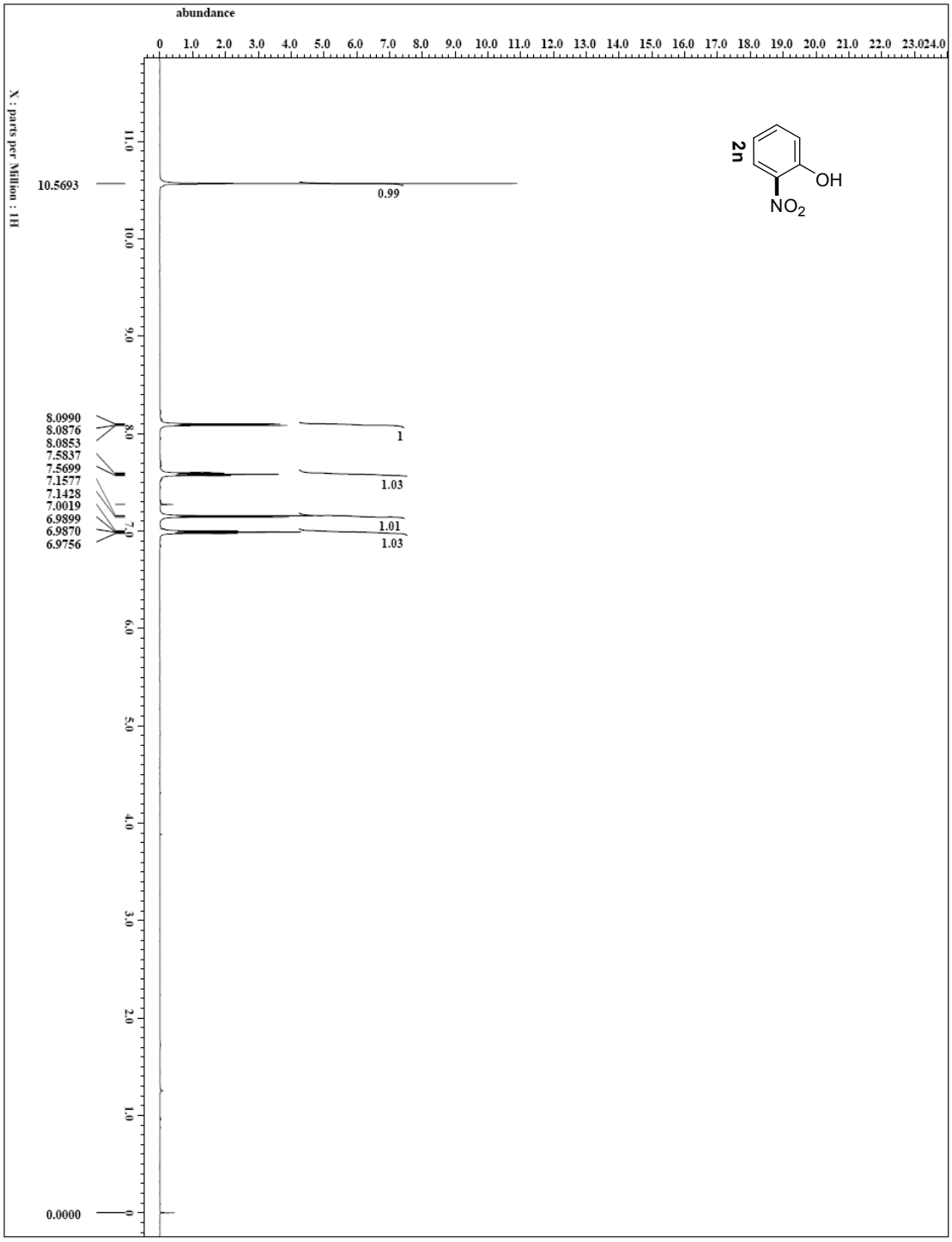


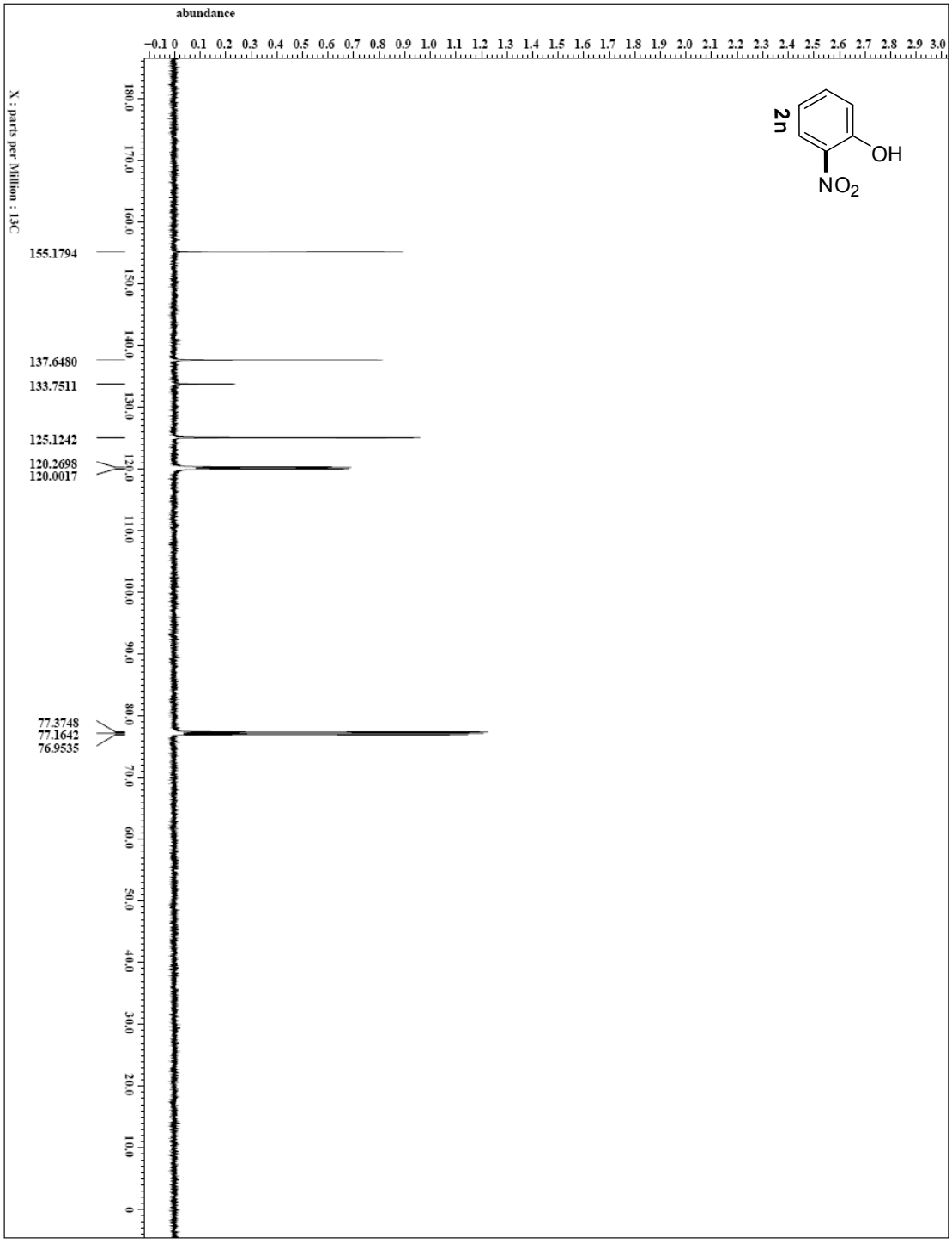


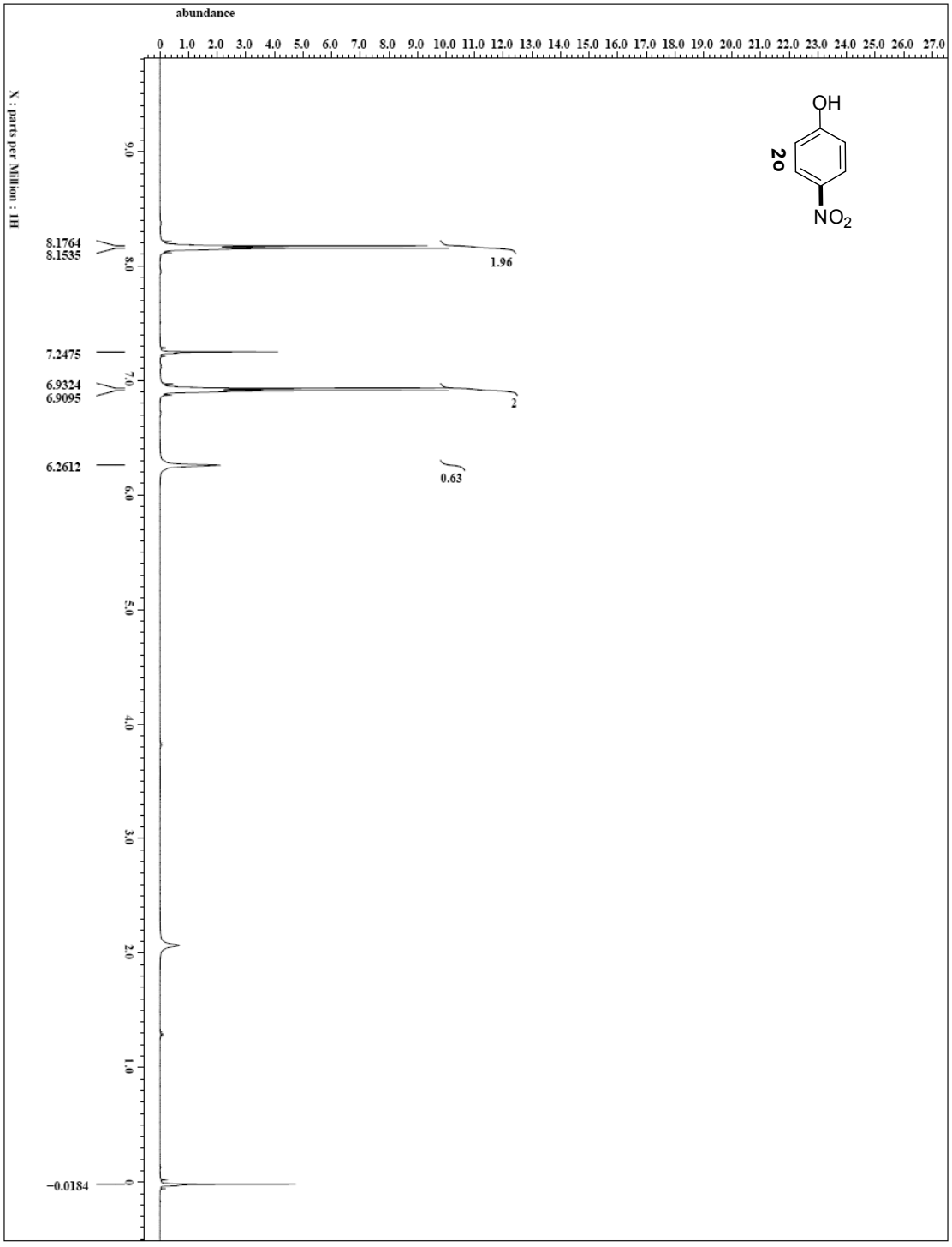

abundance
X : parts per Million : 13C
149.3510
147.5394
130.0149
120.7377
113.2245
109.0960
77.4603
77.1361
76.8214
21
NH2
NO2

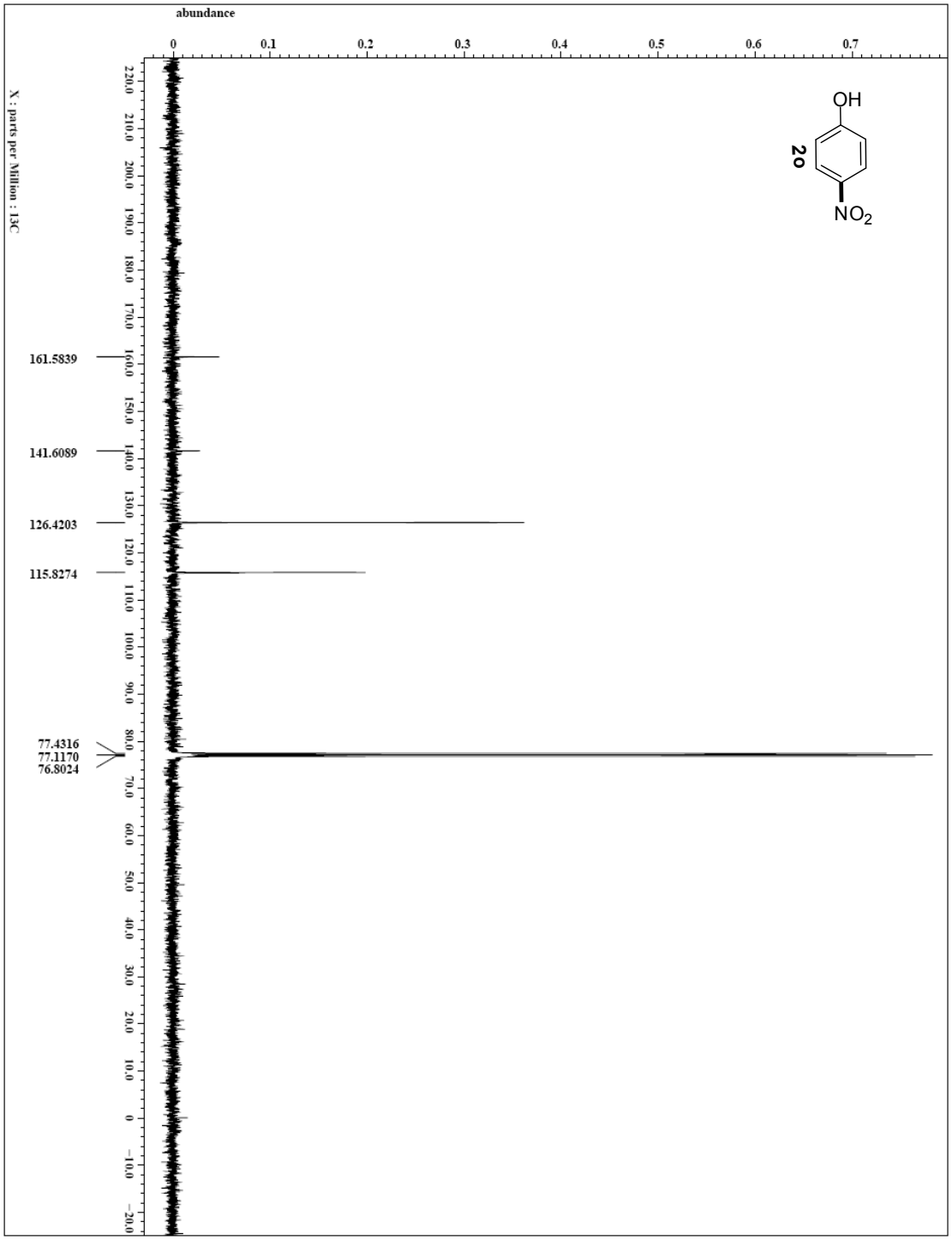

abundance
X : parts per Million : 1H
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
8.0679
8.0530
1.98
7.2502
6.6221
6.6072
2
2.01
−0.0145
NH2
2m
NO2

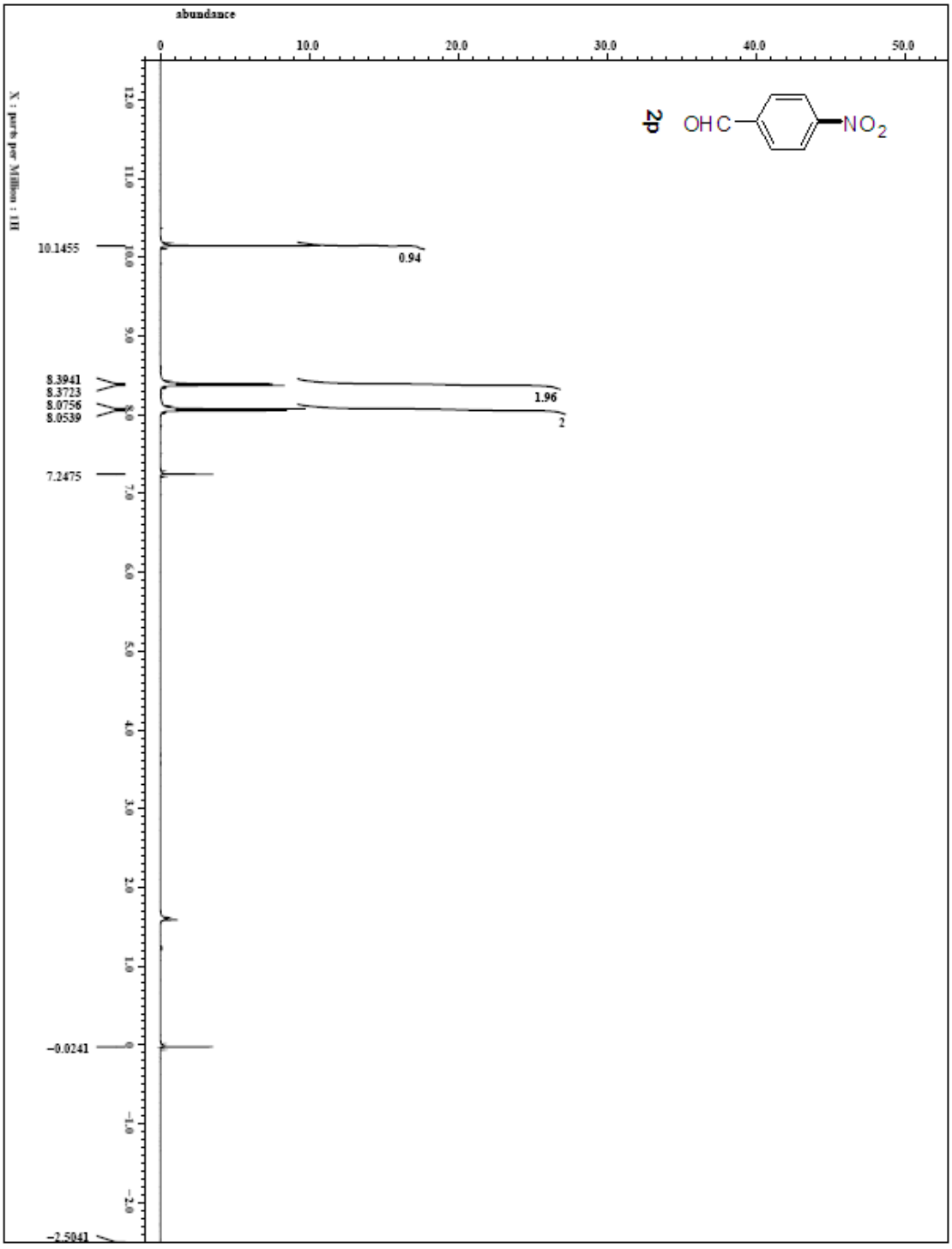


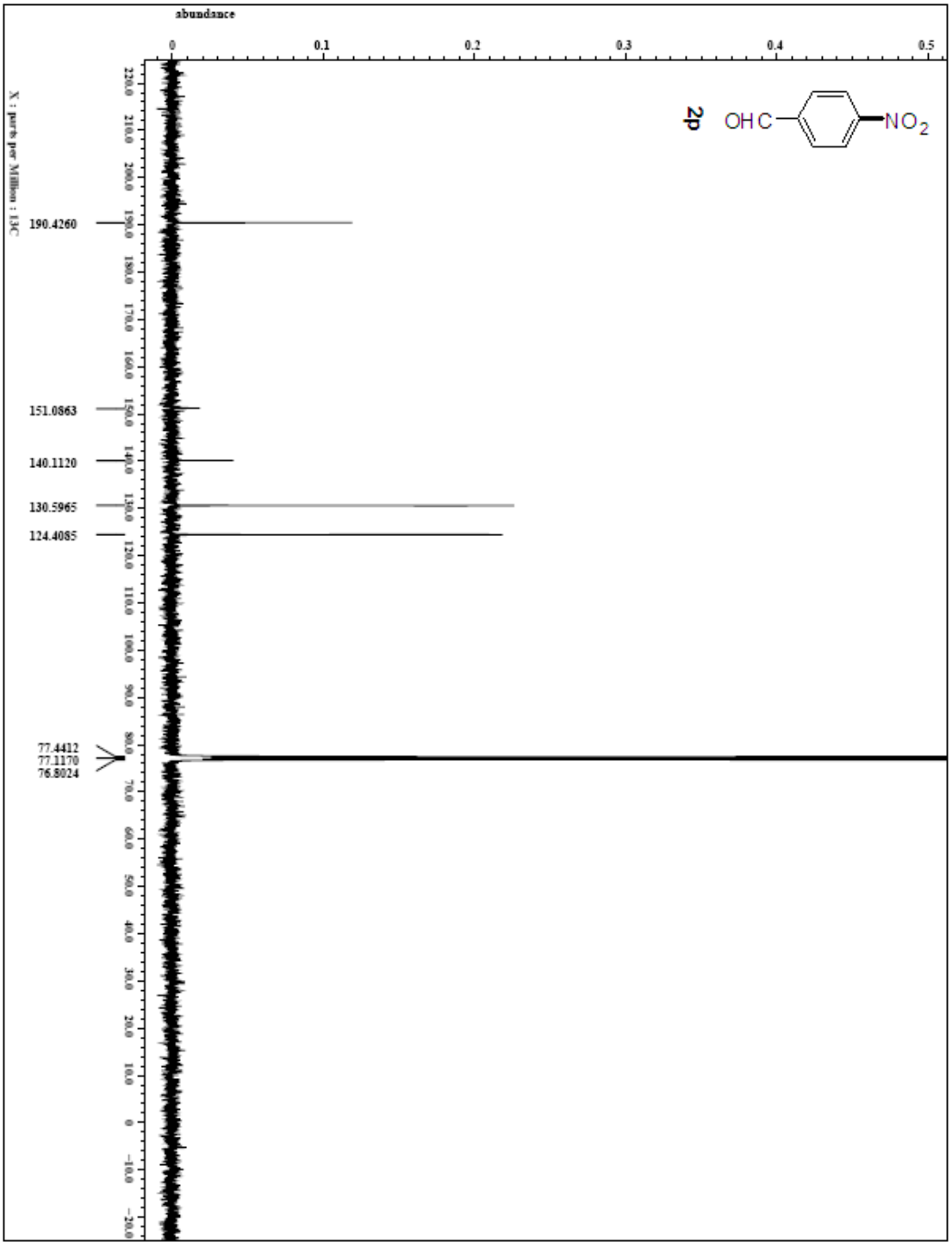

abundance
X : parts per Million : 1H
10.5693
8.0990
8.0876
8.0853
7.5837
7.5699
7.1577
7.1428
7.0019
6.9899
6.9870
6.9756
0.0000
0.99
1
1.03
1.01
1.03
2n
OH
NO2

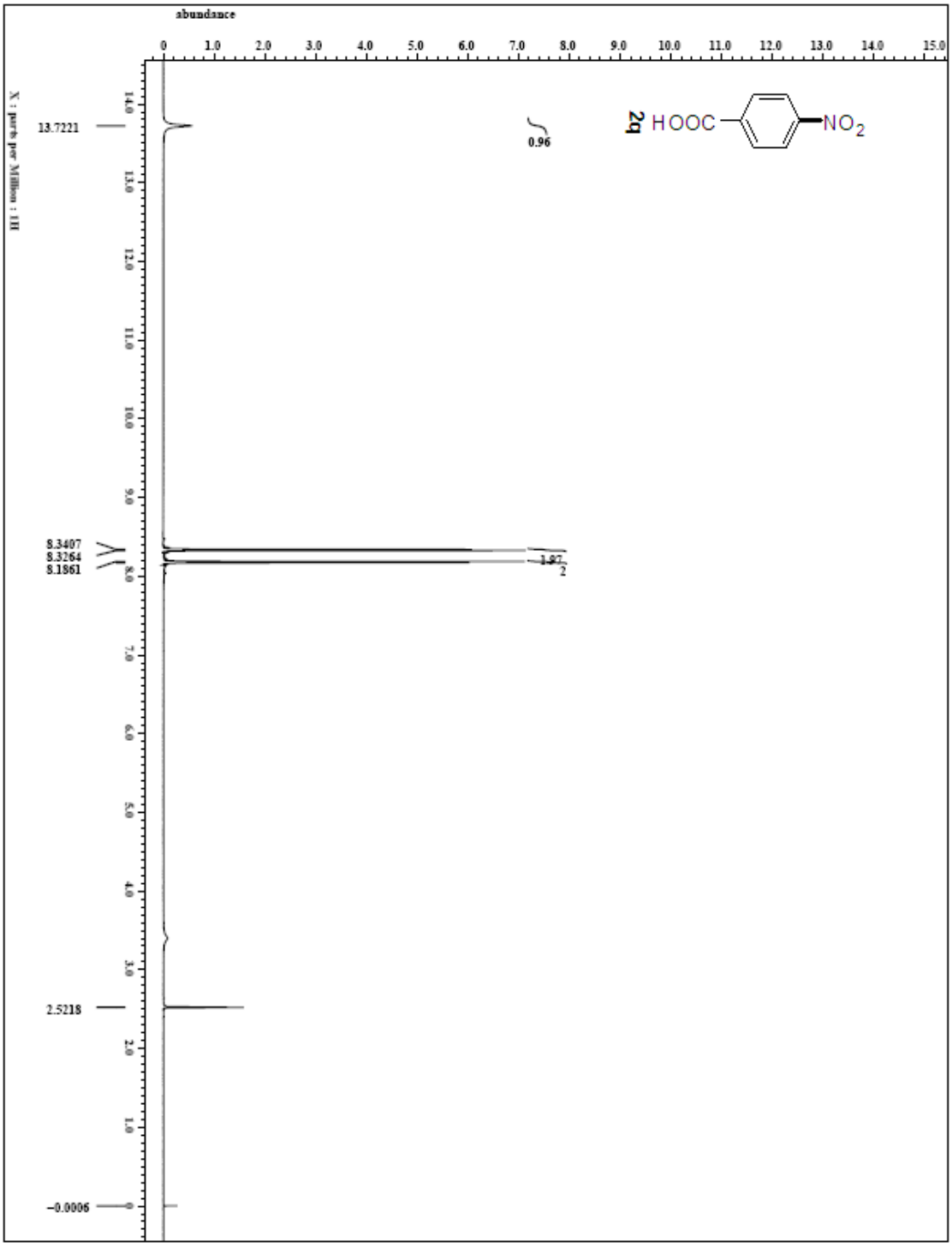

abundance
X : parts per Million : 13C
155.1794
137.6480
133.7511
125.1242
120.2698
120.0017
77.3748
77.1642
76.9535
2n
OH
NO2

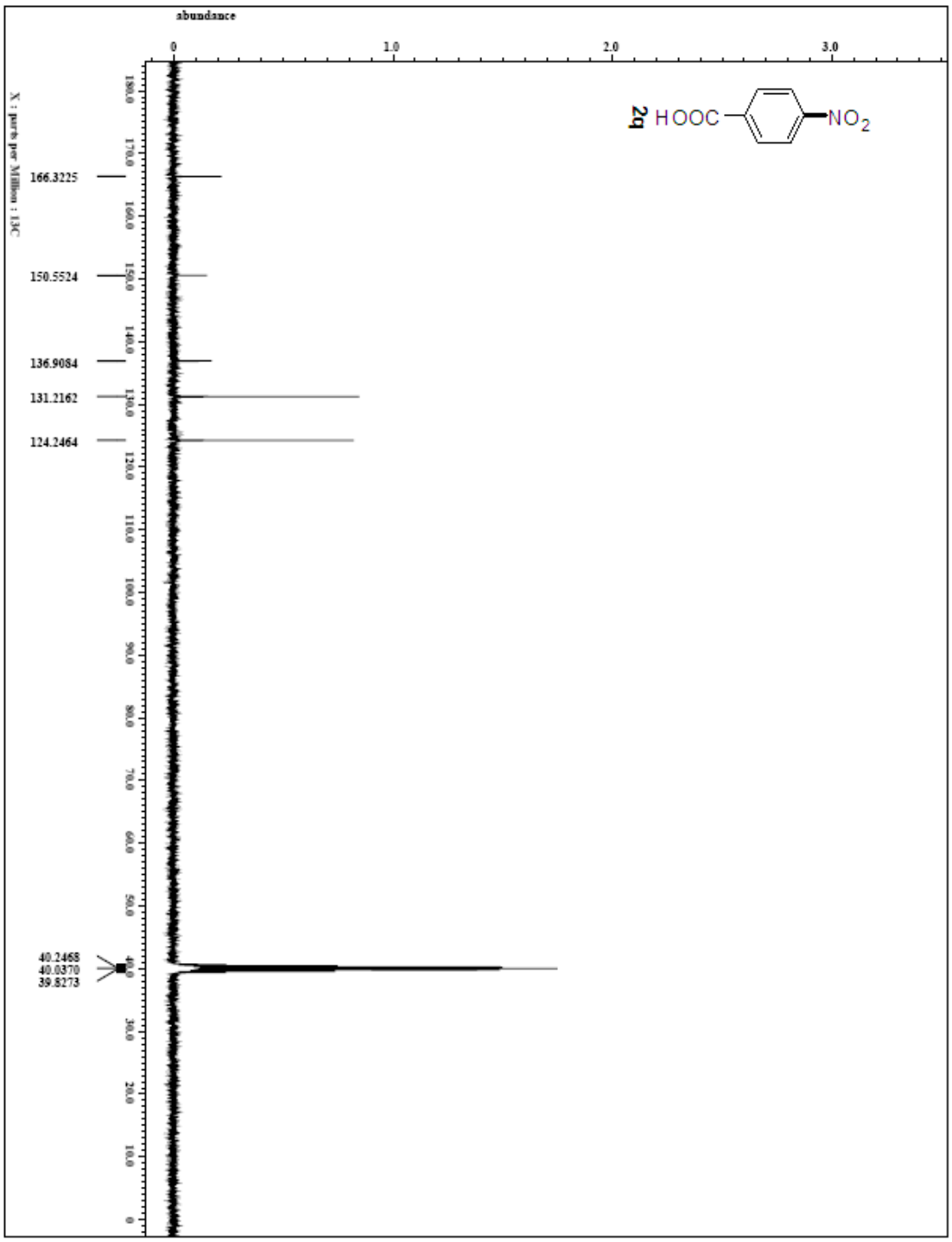


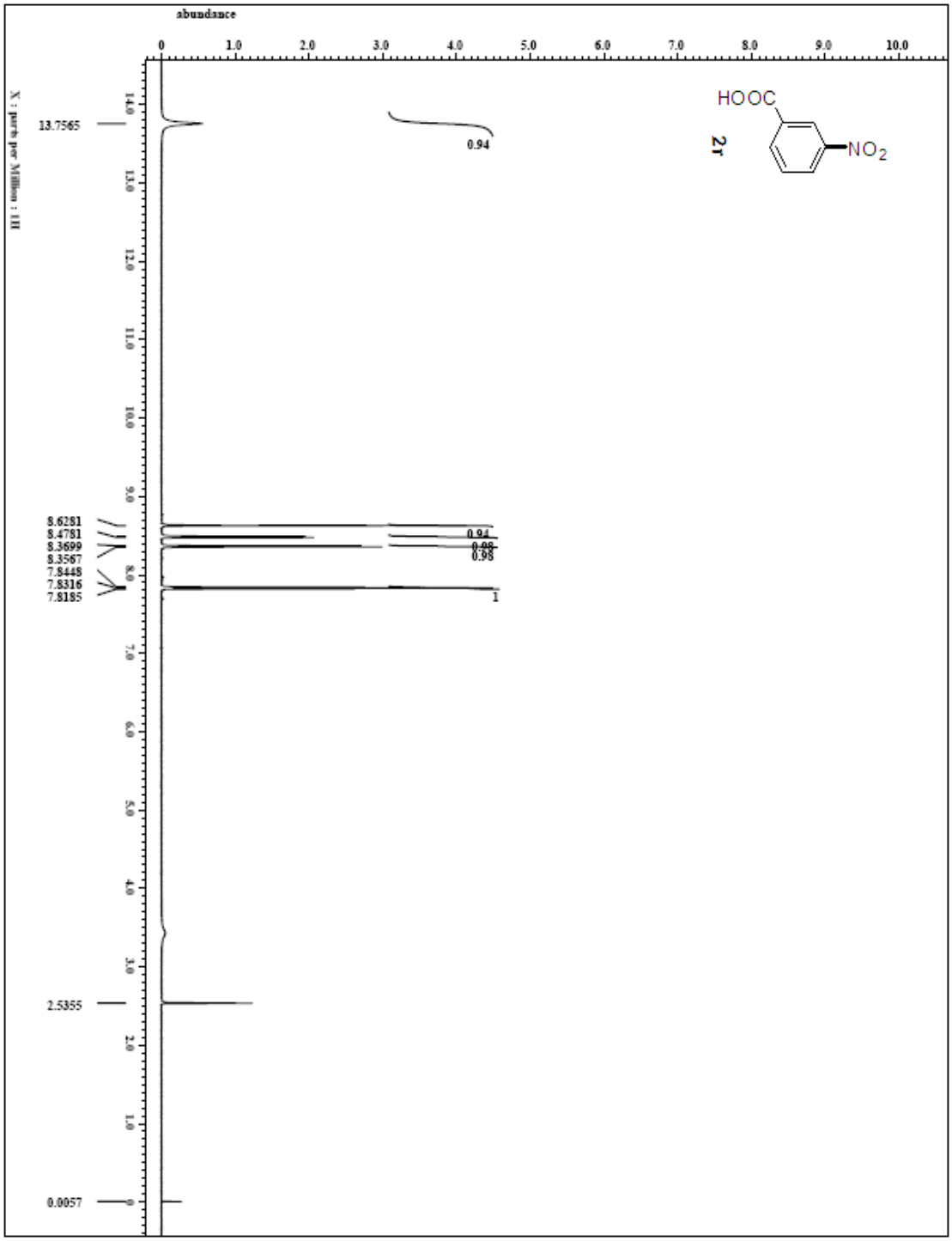


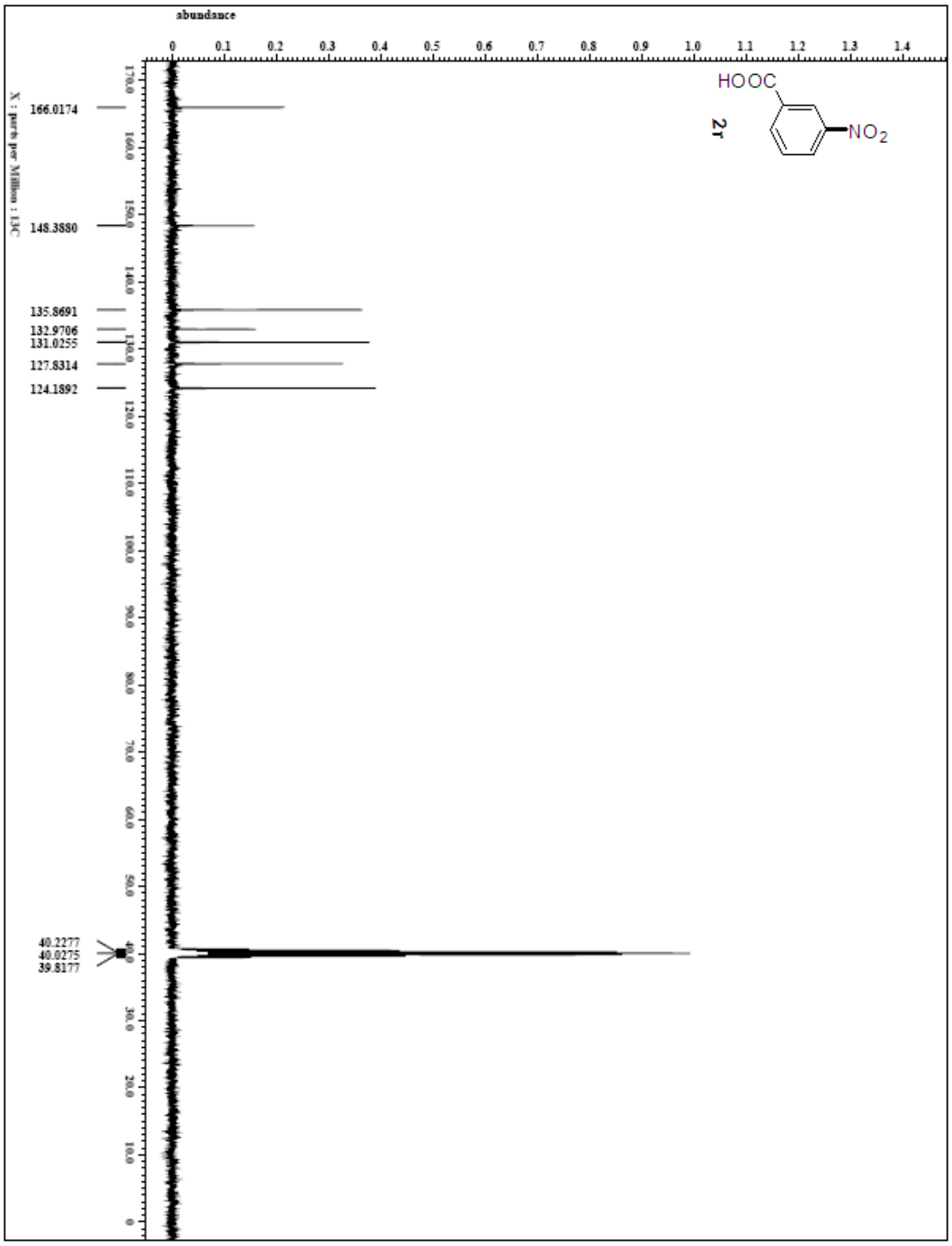

abundance
0
10.0
20.0
30.0
40.0
50.0
X : parts per Million : 1H
2p
OHC
NO2
10.1455
0.94
8.3941
8.3723
8.0756
8.0539
1.96
2
7.2475
-0.0241
-2.5041

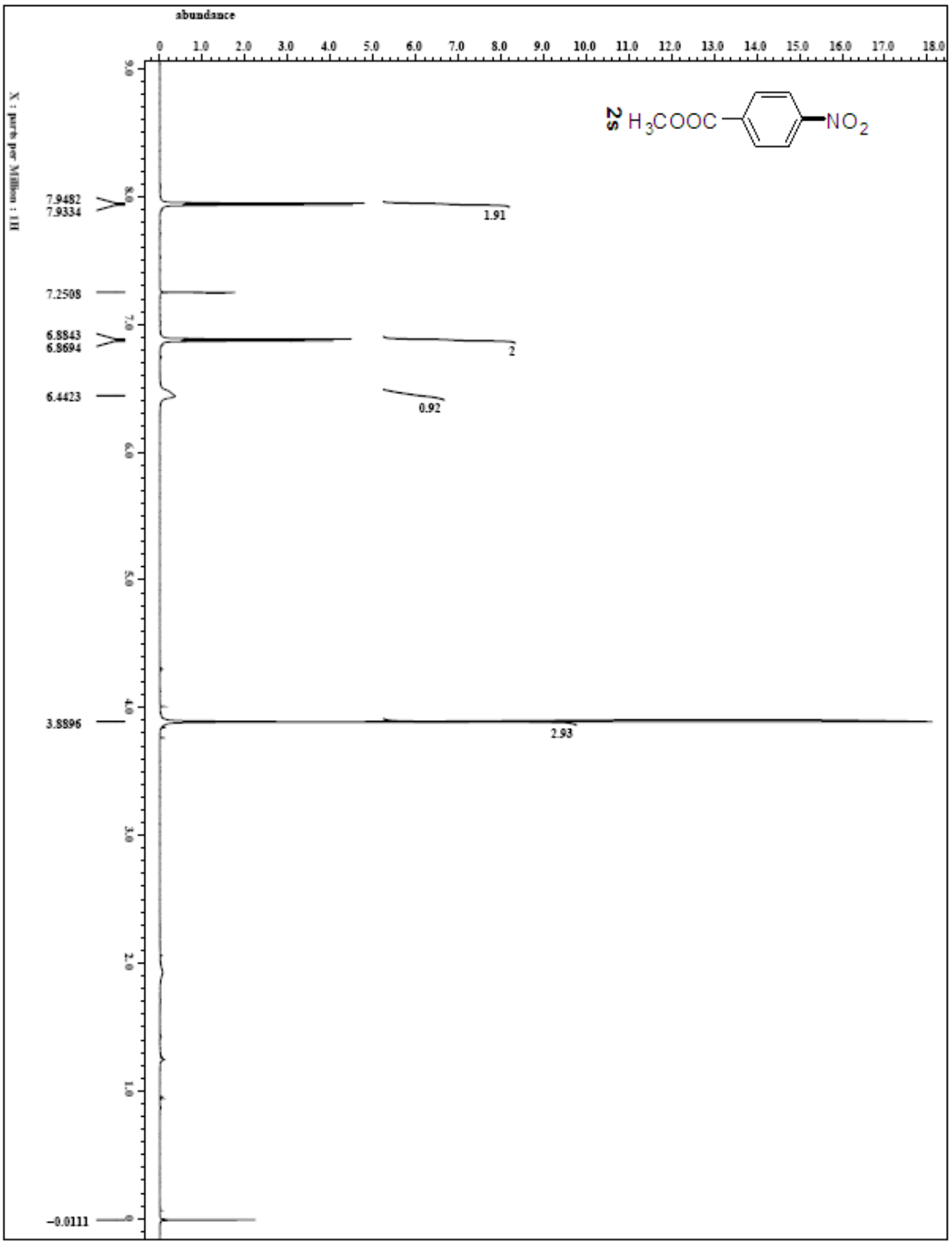

abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : 13C
190.4260
151.0863
140.1120
130.5965
124.4085
77.4412
77.1170
76.8024
2p
OHC
NO2

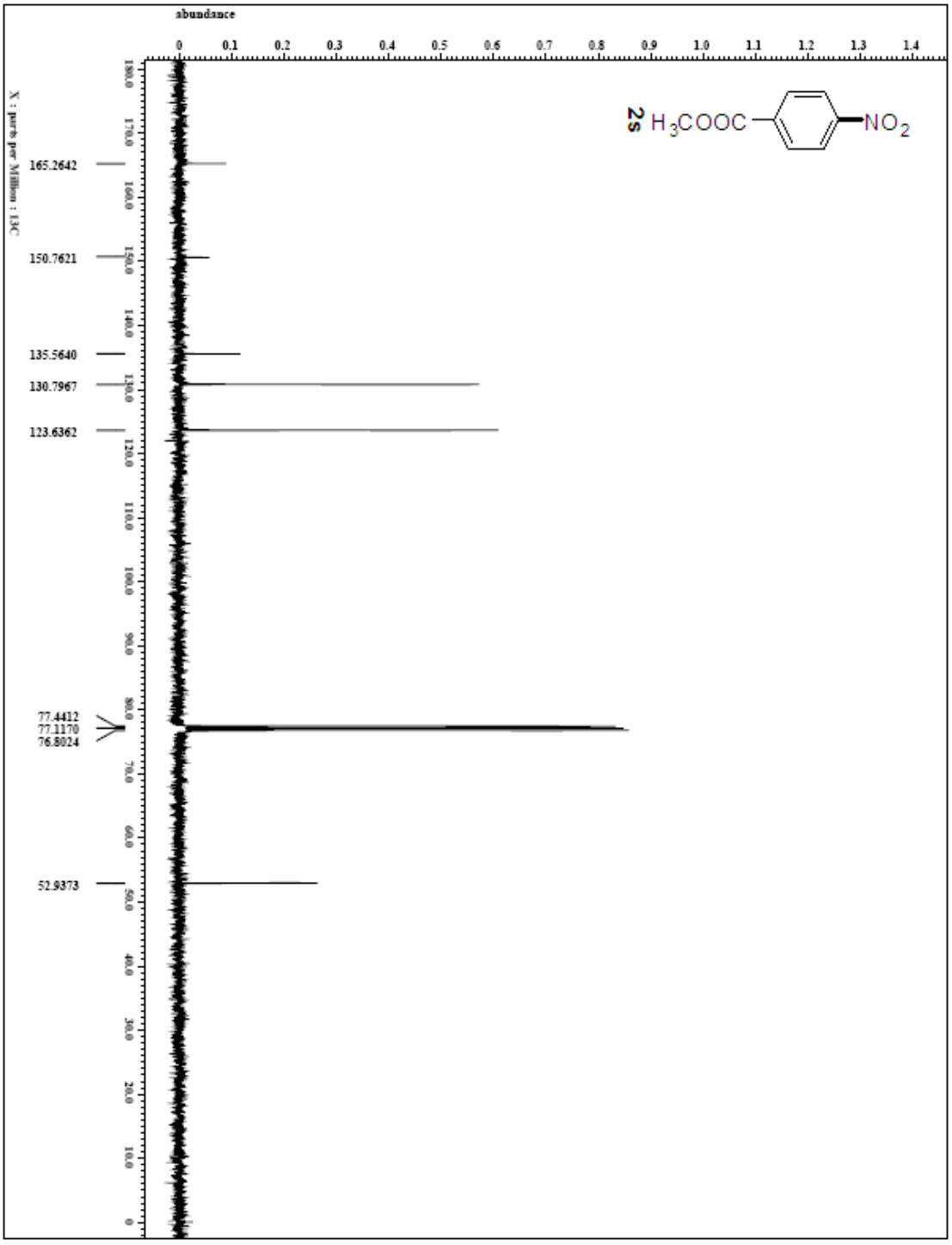

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0
X : parts per Million : 1H
13.7221
8.3407
8.3264
8.1861
2.5218
−0.0006
0.96
1.97
2
2q
HOOC
NO2

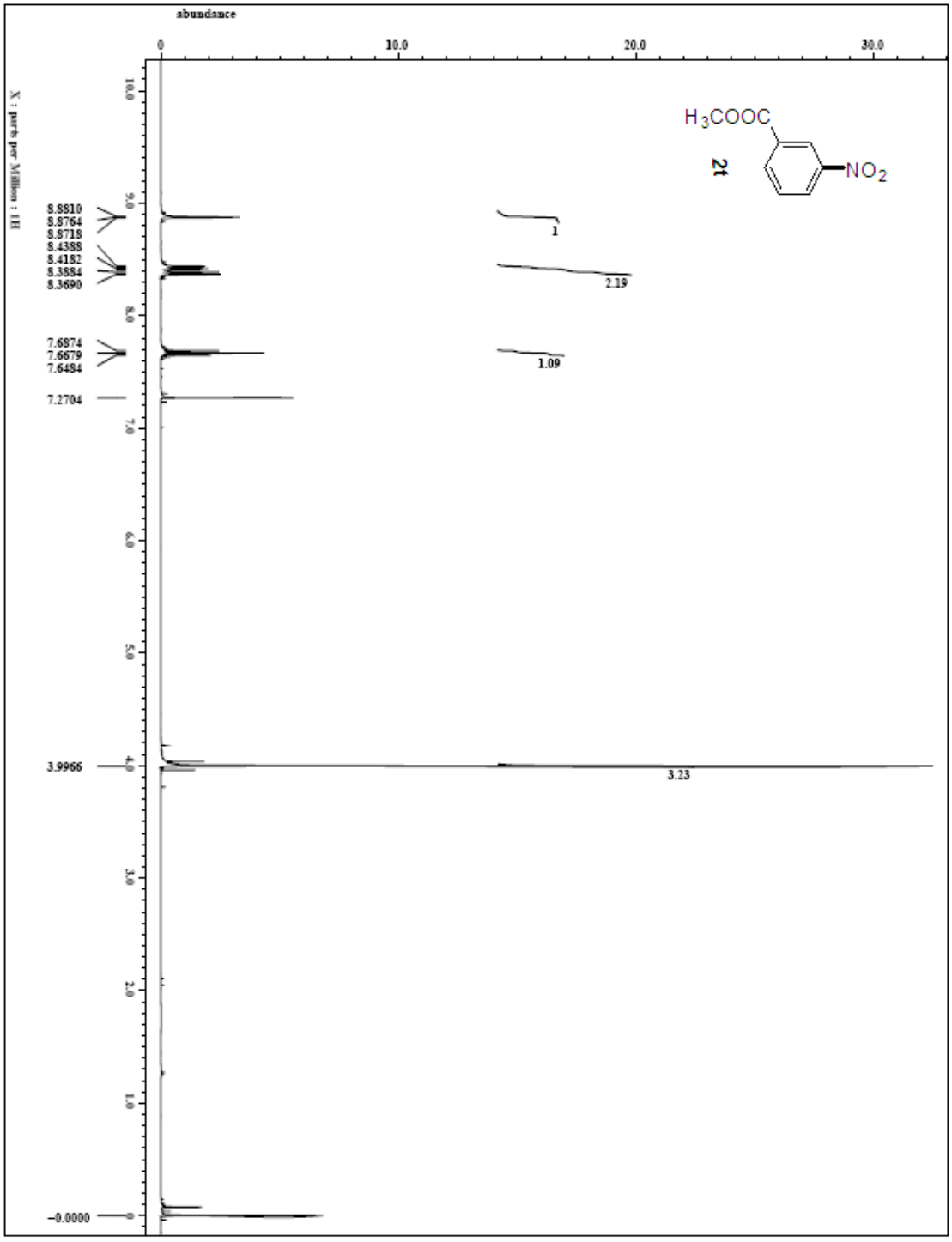

abundance
0
1.0
2.0
3.0
X : parts per Million : 13C
166.3225
150.5524
136.9084
131.2162
124.2464
40.2468
40.0370
39.8273
2q
HOOC
NO2

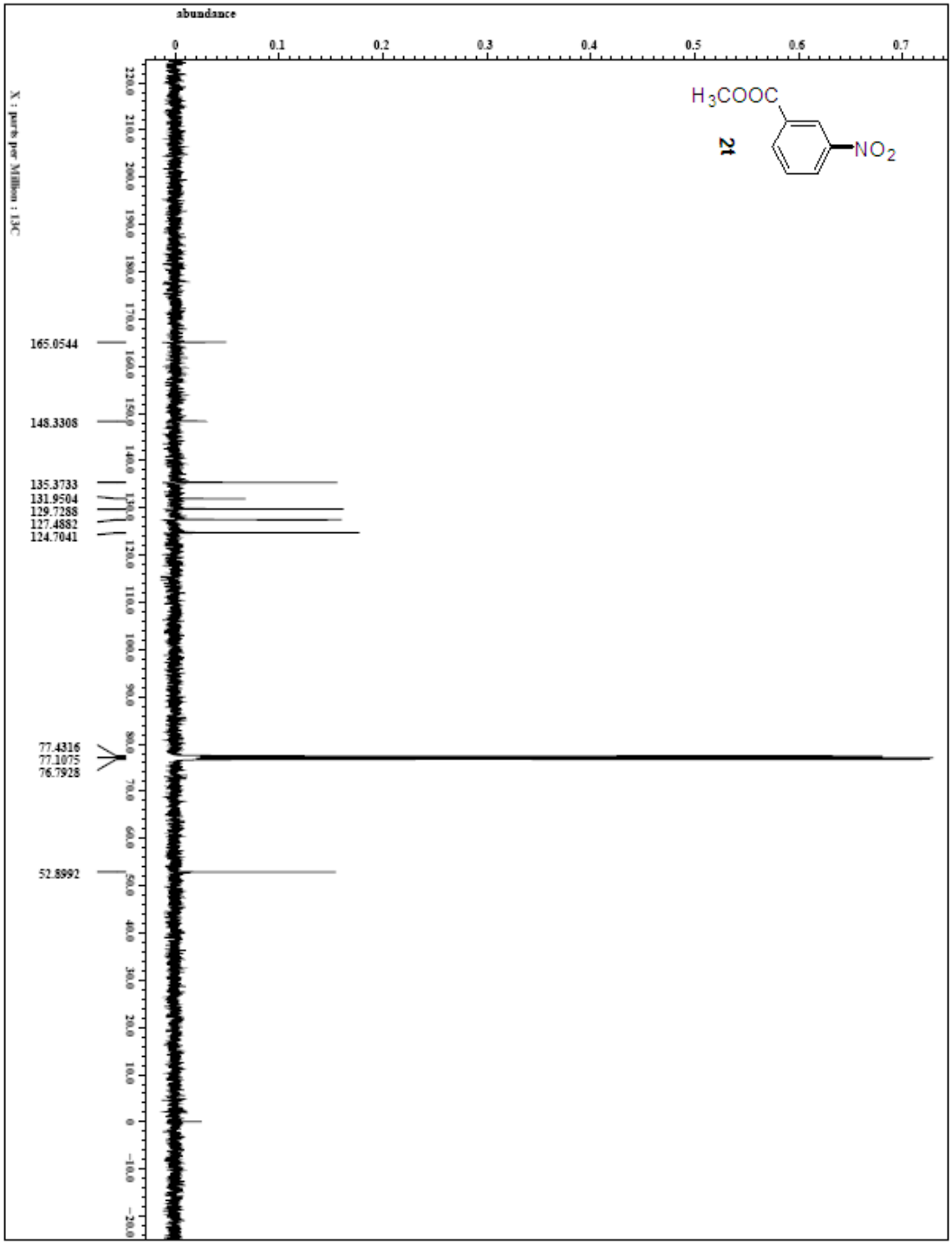


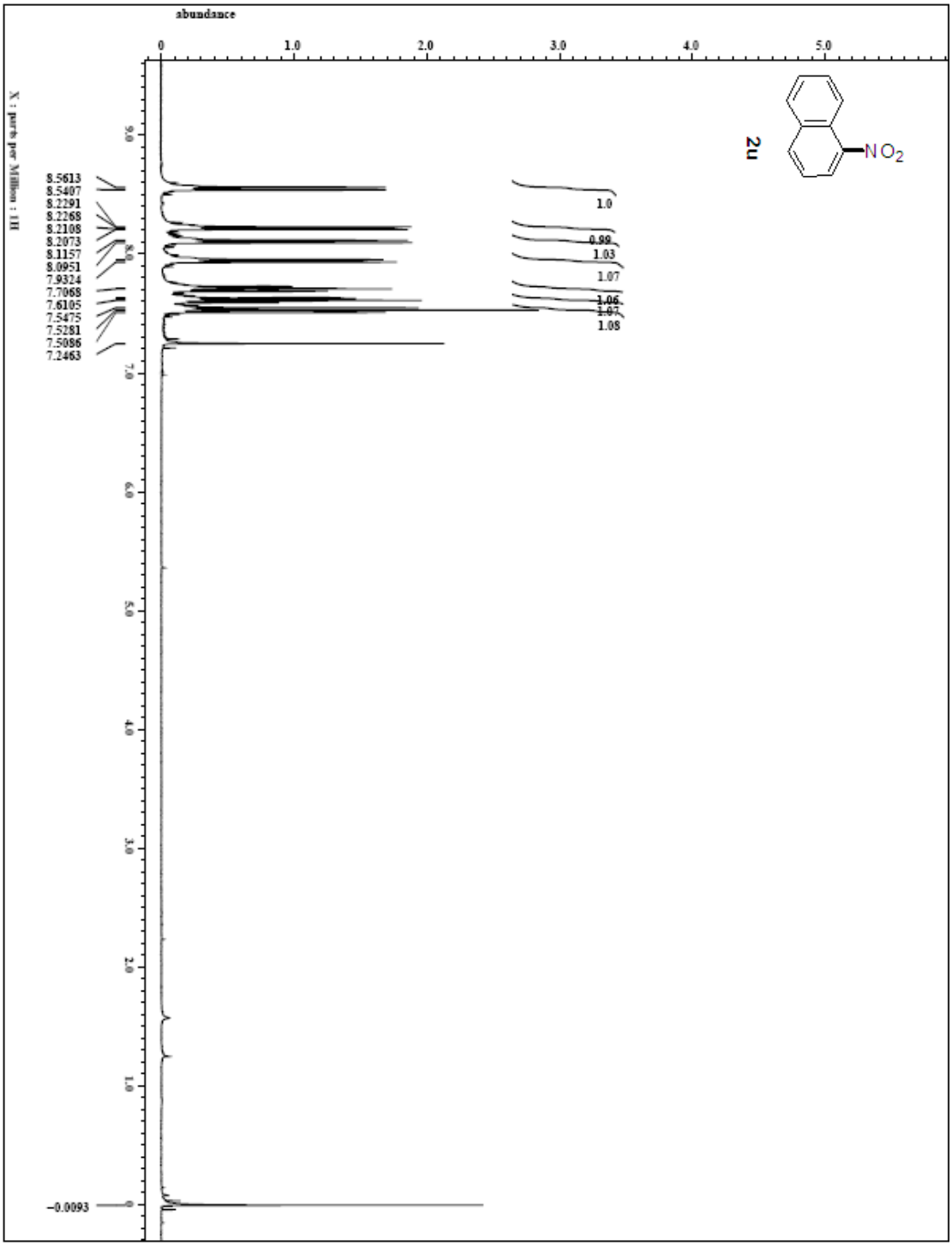


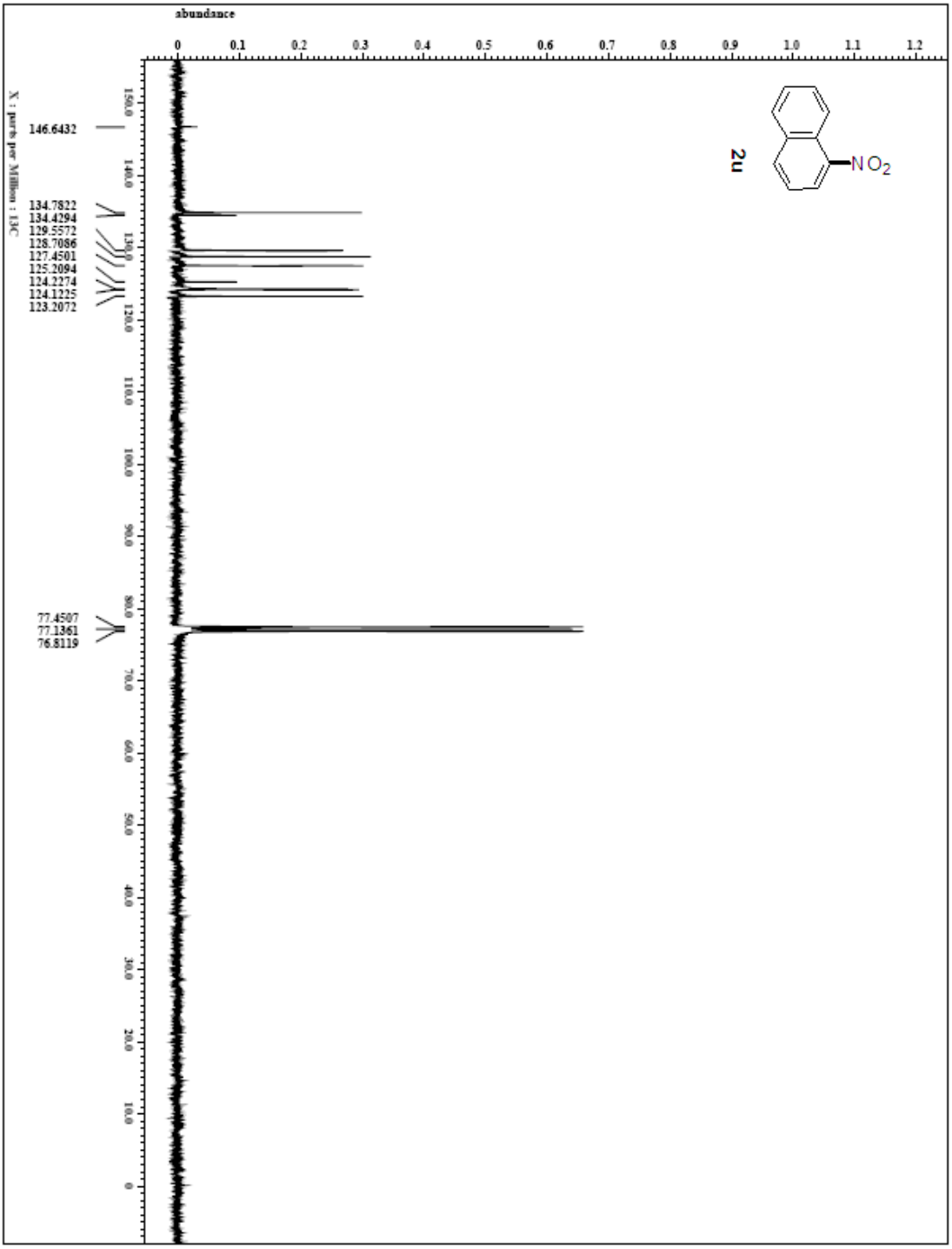

abundance
X : parts per Million : 1H
7.9482
7.9334
7.2508
6.8843
6.8694
6.4423
3.8896
−0.0111
1.91
2
0.92
2.93
H3COOC
NO2

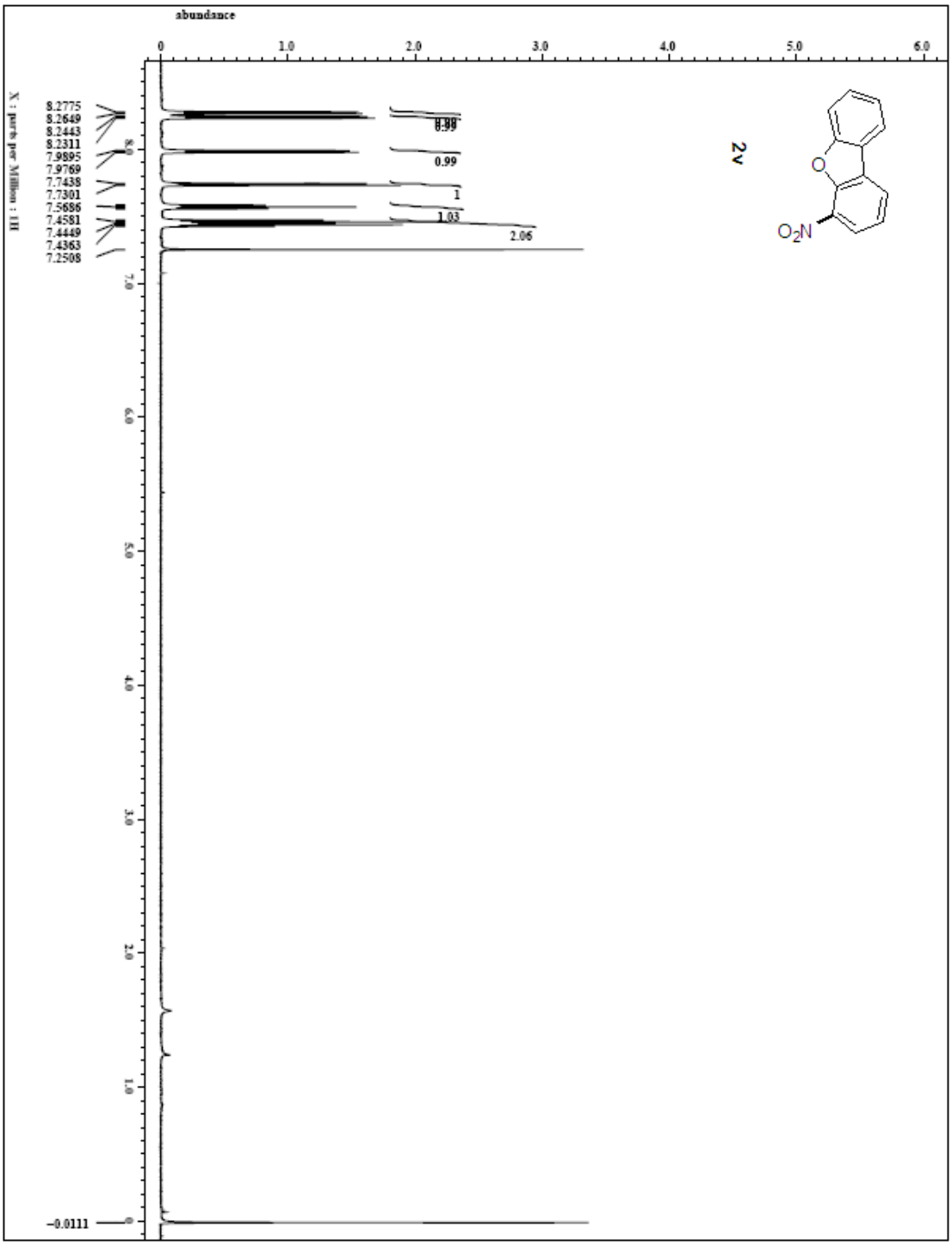

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4
X : parts per Million : 13C
165.2642
150.7621
135.5640
130.7967
123.6362
77.4412
77.1170
76.8024
52.9373
2s
H3COOC
NO2






abundance
X : parts per Million : 1H
8.5613
8.5407
8.2291
8.2268
8.2108
8.2073
8.1157
8.0951
7.9324
7.7068
7.6105
7.5475
7.5281
7.5086
7.2463
−0.0093
1.0
0.99
1.03
1.07
1.06
1.07
1.08
2u
NO2


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
X : parts per Million : 13C
146.6432
134.7822
134.4294
129.5572
128.7086
127.4501
125.2094
124.2274
124.1225
123.2072
77.4507
77.1361
76.8119
2u
NO2


abundance
X : parts per Million : 1H
8.2775
8.2649
8.2443
8.2311
7.9895
7.9769
7.7438
7.7301
7.5686
7.4581
7.4449
7.4363
7.2508
0.99
0.99
1
1.03
2.06
−0.0111
2v
O
O2N