Supporting information for:

Palladium complex immobilized in a SBA-15-supported ionic liquid: an efficient and reusable catalyst for aqueous-phase Suzuki reaction

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Contents:

General information:

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. Liquid NMR was obtained on a 400 MHz Bruker Avance instrument using $CDCl_3$ as solvent and TMS as internal standard. Nitrogen sorption experiments were recorded using a Belsorp-BEL, Inc. analyzer at 77 K. Prior to the measurement, the materials was degassed at 373 K for 12 h. The surface areas were calculated by BET method and the pore size distributions were calculated from the adsorption branch of the isotherms using BJH method. TEM image was taken on a FEI Tecnai 12 BioTWIN microscope operated at 120 kV. DRIFT spectrum was determined using a Brucker-Vector 22. Thermogravimetric analysis was conducted from room temperature to 800 °C in an air flow using a Pheometric Scientific analyzer.

Preparation of SBA-15

The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers.[1] In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =□5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 ºC. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 ºC for 20 h. The mixture was aged at 80 ºC overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhelet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 ºC overnight.

Preparation of SBA-15-amine

Refluxing the SBA-15 (10 g) with 3-aminopropyltrimethoxysilane (10 mmol) in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 90 ºC overnight to give the SBA-15 supported amine (SBA-15-amine).

Preparation of SBA-15-lig

2-acetylpyridine (0.97 g, 8 mmol) was added to a mixture of the oven dried SBA-15-amine (5 g) in super dry ethanol (150 mL) in a 250 mL round bottomed flask. The reaction mixture was stirred at 60 ºC for 24 h. The ligand-grafted silica was filtered at the reaction temperature and the resulting solid was washed thoroughly with hot toluene and ethanol to remove unreacted ketone. It was dried in air at 90 ºC overnight to furnish the corresponding SBA-15 supported bidentate ligand (SBA-15-lig).

Preparation of SBA-15-Pd

SBA-15-lig (3 gr) was added to a solution of palladium acetate (0.035 gr Merck) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, the solid was filtered, washed with acetone, ethanol and ether in order to remove any adsorbed palladium on the surface. It was then dried in an oven at 90 ºC overnight to furnish the corresponding SBA-15 supported complex (SBA-15-Pd).

Preparation of IL@SBA-15- Pd

SBA-15-Pd (3 gr) was added to a solution of 1-butyl-3-methylimidazolium hexafluorophosphate (1.5 cc) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, acetone was slowly removed under reduced pressure. The resulting powder was then dried in an oven at 90 ºC overnight to give final catalyst **IL@SBA-15-Pd** at a loading *ca.*0.032 ± 0.001 mmol g^{-1} (atomic absorption spectroscopy (AA)).

General procedure for the Suzuki coupling reaction using IL@SBA-15-Pd as catalyst:

The Suzuki reaction was performed by using arylboronic acid (1.1 mmol), aryl halide (1.0 mmol), K_2CO_3 (1.5 mmol), and catalyst (0.05-0.2 mol%) in distilled water at 60–80 ºC. The reaction progress was monitored by GC analysis after completion of the reaction;

the mixture was allowed to cool to room temperature and was then filtered and washed with H_2O and ethyl acetate. The organic phase was separated and dried over $MgSO_4$ and the solvent was then removed under reduced pressure. Pure products were obtained after recrystallization or by isolation of the residue by column chromatography on silica

The recovery of the IL@SBA-15-Pd catalyst:

The Suzuki reaction over the **IL@SBA-15-Pd** catalyst was carried out under an argon flow by treatment 0.05 mol% of the catalyst with phenylboronic acid (5.5 mmol), 4-bromobenzaldhyde (5 mmol), K_2CO_3 (7.5 mmol) in distilled water at 60 °C. The reaction progress was monitored by GC using dodecane as internal standard. After completion of the reaction, the resulting mixture was filtered and washed with H_2O and ethylacetate thoroughly. The recovered catalyst was then successfully reused 4 times under the same reaction conditions.

In other method, we added 4-boromobenzaldehyde, phenylboronic acid, and K_2CO_3 to catalyst without separation of previous reaction runs. In this method we can recover the catalyst 5 times.

General procedure for the study of the effects of Hg(0), poly-(4-vinylpyridine) (PVP), and mercaptopropyl silica on the IL@SBA-15-Pd reactivity:

A solution of phenyl boronic acid (1.1 mmol) 4-bromoanisole (1 mmol), K_2CO_3 (1.5 mmol), TBAB (1 mmol) and poisoning agent (400 equivalent to total palladium content) in distilled water (3 mL) was magnetically stirred at 60 °C. Then **IL@SBA-15-Pd** catalyst (containing 0.05 mol % Pd) was rapidly added and the reaction progress was monitored by GC. The results are demonstrated in Figure 1S.

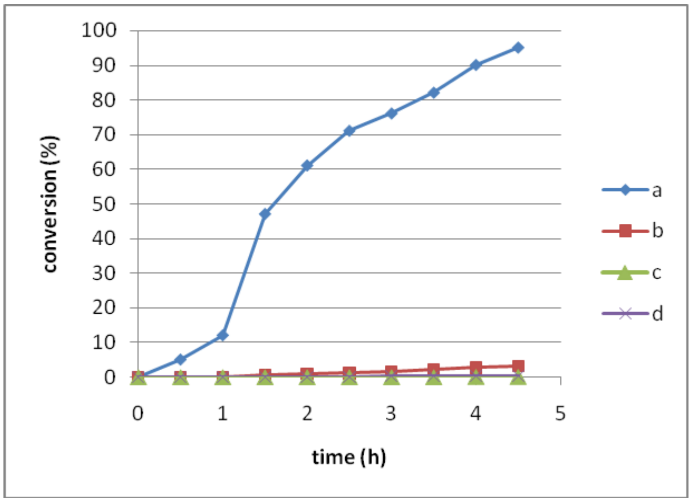


Figure 1S. Reaction progress as a function of time on the Suzuki coupling of 4-bromoanisole with phenylboronic acid by using **IL@SBA-15-Pd** catalyst in water under: a) normal conditions (blue diamond), b) in the presence of 400 equiv Hg^0 (red square), c) in the presence of 400 equiv PVP (violet cross), and d) in the presence of 400 equiv mercaptopropyl silica (green triangle).

Procedure for the hot filtration test:

This experiment was conducted in a water solution containing 1 mmol 4-bromoanisole, 1.1 mmol phenylboronic acid, 0.05 mol% catalyst, 1.5 mmol K_2CO_3 and TBAB (1 mmol) at 60 °C. After 31% of the coupling reaction was completed, the solution was filtered and then filtrate was allowed to progress at 60 °C for 24h. The reaction progress was monitored by GC.

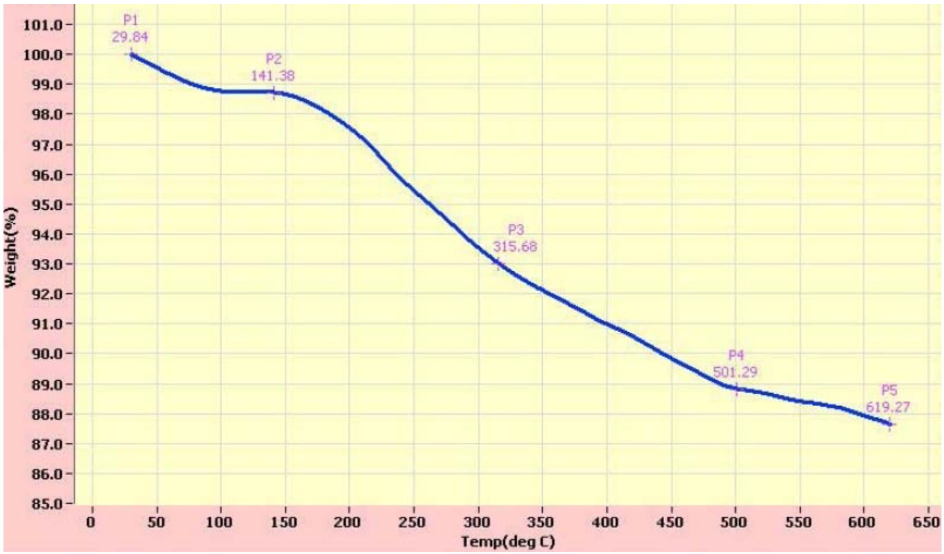


Figure 2S. Thermal gravimetric analysis (TGA) of **SBA-15-Pd**.

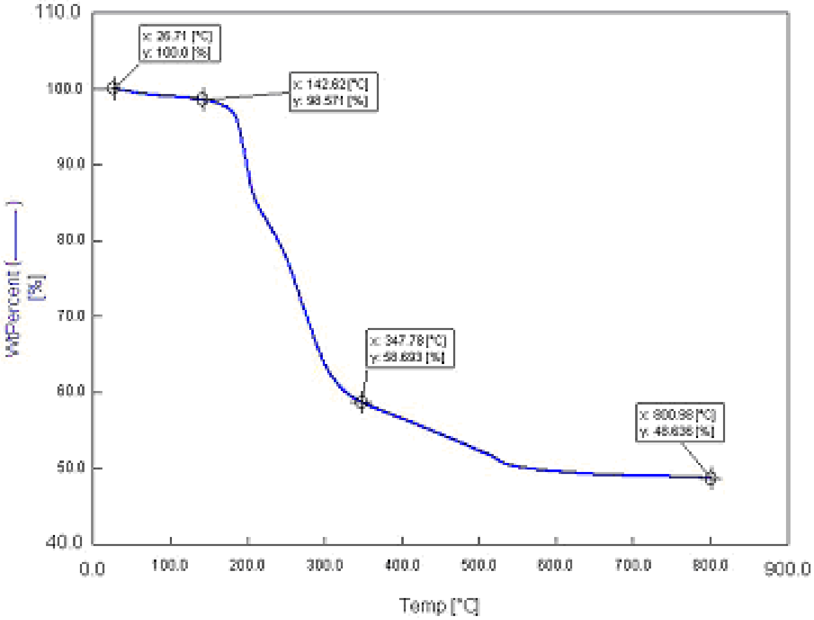


Figure 3S. Thermal gravimetric analysis (TGA) of **IL@SBA-15-Pd**.

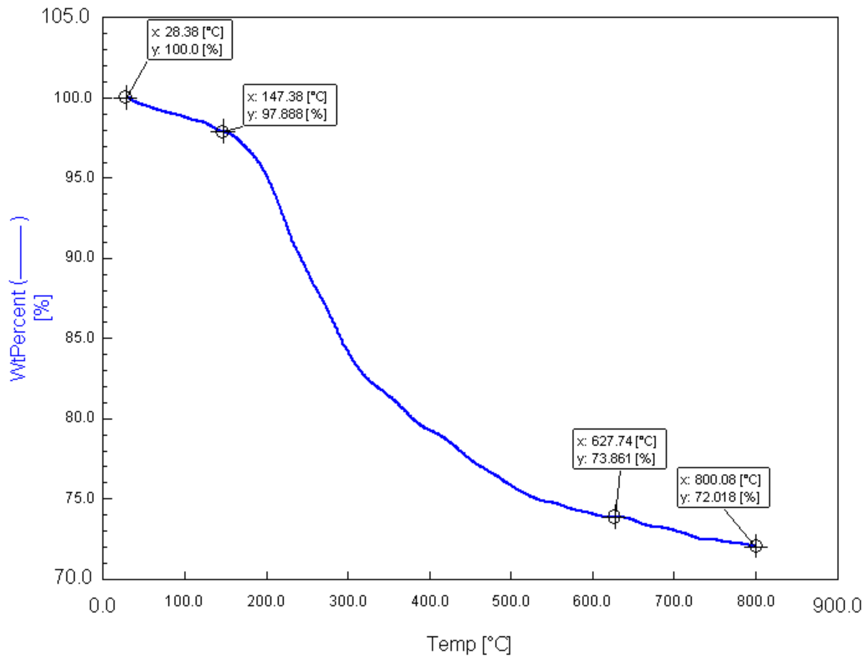


Figure 4S. Thermal gravimetric analysis (TGA) of recovered **IL@SBA-15-Pd**.

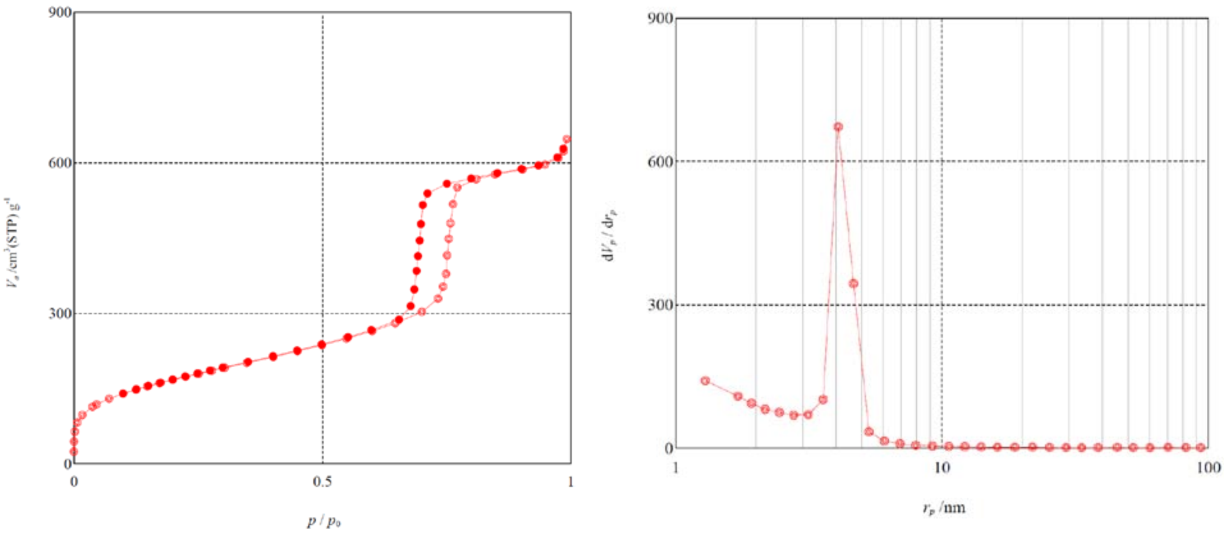


Figure 5S. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the **SBA-15-Pd** material indicating very high uniformity and narrow size distribution of mesochannels.

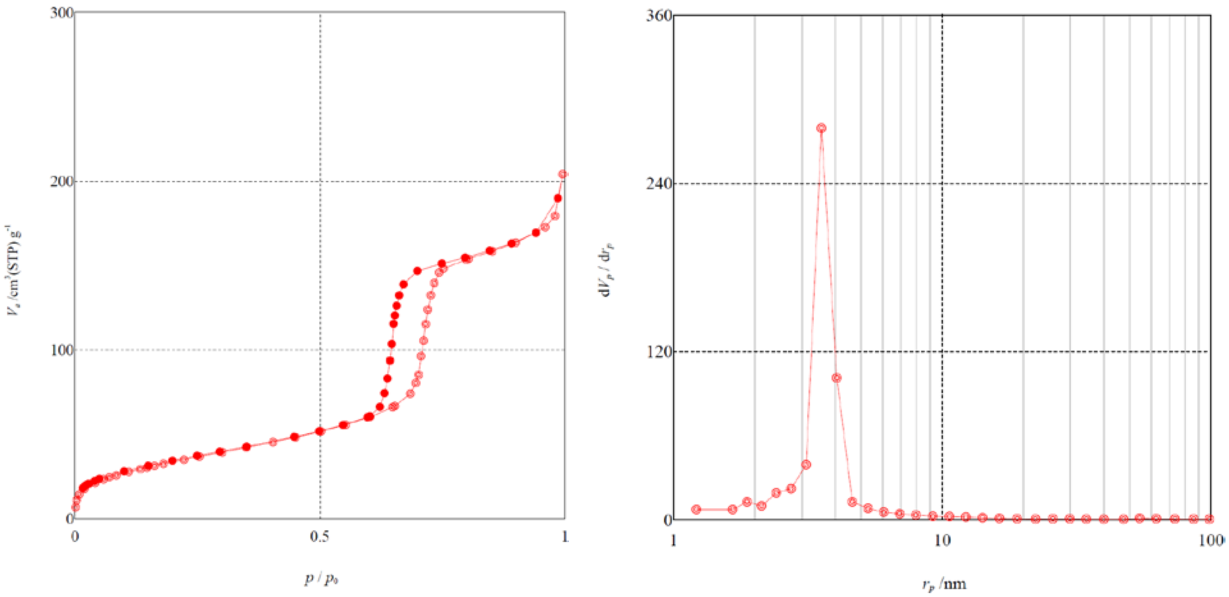


Figure 6S. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the **IL@SBA-15-Pd** material indicating very high uniformity and narrow size distribution of mesochannels.

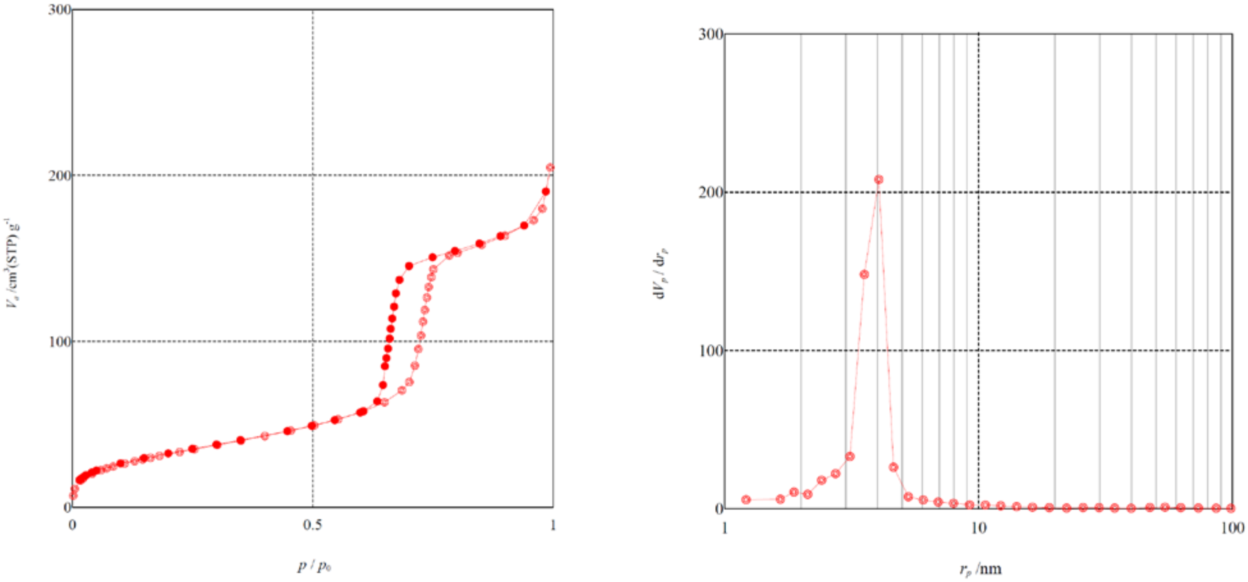


Figure 7S. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the recovered **IL@SBA-15-Pd** material indicating very high uniformity and narrow size distribution of mesochannels.

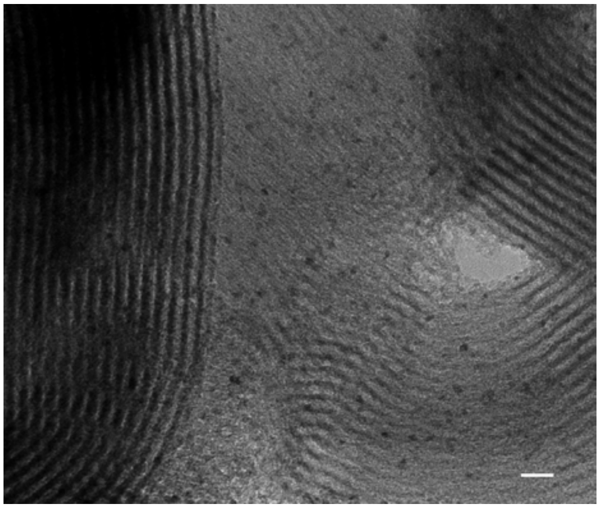


Figure 8S. Transmission electron microscopy (TEM) image of recovered **IL@SBA-15-Pd** material showing two dimensional hexagonal symmetry with superior uniformity of the mesoporous channels

Table 1S. Structural parameters of **SBA-15-Pd**, **IL@SBA-15-Pd** and recovered **IL@SBA-15-Pd** determined from nitrogen sorption experiments:

Sample	BET surface area (m^2/g)	BJH pore diameter (nm)	Pore volume (cm^3/g)
SBA-15-Pd	599	8.2	0.99
IL@SBA-15-Pd	119	6.7	0.30
Recovered **IL@SBA-15-Pd**	113	8.1	0.30

^{1}H NMR and ^{13}C NMR data of the coupling products:

Biphenyl-4-carbaldehyde: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 7.43$-7.54 (m, 3H), 7.65-7.69 (dd, 2H), 7.77-7.80 (d, 2H), 7.97-8.00 (d, 2H), 10.05 (s, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS):127.39, 127.70, 128.48, 129.01, 130.28, 135.18, 139.70, 147.21, 192.04.

4-Nitro-biphenyl: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 7.48$-7.56 (m, 3H), 7.64-7.67 (m, 2H), 7.74-7.78 (m, 2H), 8.30-8.33 (m, 2H),. ^{13}CNMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 124.13, 127.41, 127.81, 128.97, 129.20, 138.76, 147.09, 147.63.

4-Nitro-4'-methyl-biphenyl: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 2.46$ (s, 3H), 7.33-7.35 (d, 2H), 7.55-7.58 (m, 2H), 7.73-7.77 (m, 2H) 8.30-8.33 (m, 2H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 21.24, 124.12, 127.25, 127.50, 129.91, 135.86, 139.12, 146.86, 147.60.

Biphenyl-4-carbonitrile: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS) $\delta = 7.45$-7.55 (m, 5H), 7.62-7.77 (m, 4H). 13C NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 110.94, 118.99, 127.26, 127.76, 128.71, 129.16, 132.63, 139.19, 145.69.

4’-Methyl-biphenyl-4-carbonitrile: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 2.45$ (s, 3H), 7.31-7.33 (d, 2H), 7.52-7.54 (d, 2H), 7.69-7.75 (m, 4H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 21.17, 110.59, 118.88, 127.03, 127.44, 130.01, 132.63, 136.35, 138.93, 145.50.

4-Methoxy-biphenyl: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 3.89$ (s, 3 H), 7.00-7.03 (dd, 2H), 7.31-7.36 (m, 1H), 7.43-7.47 (m, 2H), 7.54-7.60 (m, 4H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 55.33, 114.19, 126.65, 126.72, 128.15, 128.71, 133.82, 140.83, 159.11.

4,4'-Dimethyl-biphenyl: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 2.43 (s, 3H), 2.27-2.29 (d, 2H), 2.51-2.53 (d, 2H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 21.11, 126.83, 129.47, 136.72, 138.30.

3-Phenyl-pyridine: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.31-7.52 (m, 4H), 7.53-7.63 (m, 2H), 7.82-7.89 (m, 1H), 8.57-8.63 (d, 1H), 8.82-8.90 (d, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 123.63, 127.16, 128.14, 129.15, 134.44, 136.67, 137.78, 148.29, 148.47.

3-(4-Methylphenyl)-pyridine: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 2.44 (s, 3H), 7.30-7.35 (m, 2H), 7.36-7.41 (m, 1H), 7.48-7.54 (d, 2H), 7.87-7.92 (m, 1H), 8.56-8.65 (m, 1H), 8.84-8.92 (m, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 21.24, 123.62, 127.05, 129.88, 134.25, 134.97, 136.71, 138.12, 148.20, 150.52.

2-Phenylpyridine: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS) δ = 8.71-8.76 (d, 1H), 8.01-8.07 (d, 2H), 7.71–7.78 (m, 2H), 7.48-7.55 (t, 2H), 7.42-7.48 (t, 1H), 7.20–7.26 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, 25 ºC, TMS) 157.47, 149.71, 139.45, 136.77, 129.00, 128.80, 126.95, 122.14, 120.58.

2-Phenyl-thiophene: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.11-7.14 (dd, 1H), 7.30-7.35 (m, 2H), 7.35-7.37 (dd, 1H), 7.39-7.45 (m, 2H), 7.63-69 (m, 2H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 123.10, 124.84, 125.98, 127.20, 127.49, 128.03, 128.91, 134.42.

2-(4-Methylphenyl)-thiophene: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 2.40 (s, 3H), 7.08-7.12 (dd, 1H), 7.20-7.25 (dd, 2H), 7.26-7.32 (m, 2H), 7.52-757 (m, 2H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 21.20, 122.59, 124.29, 125.89, 126.83, 127.94, 129.57, 131.66, 137.35.

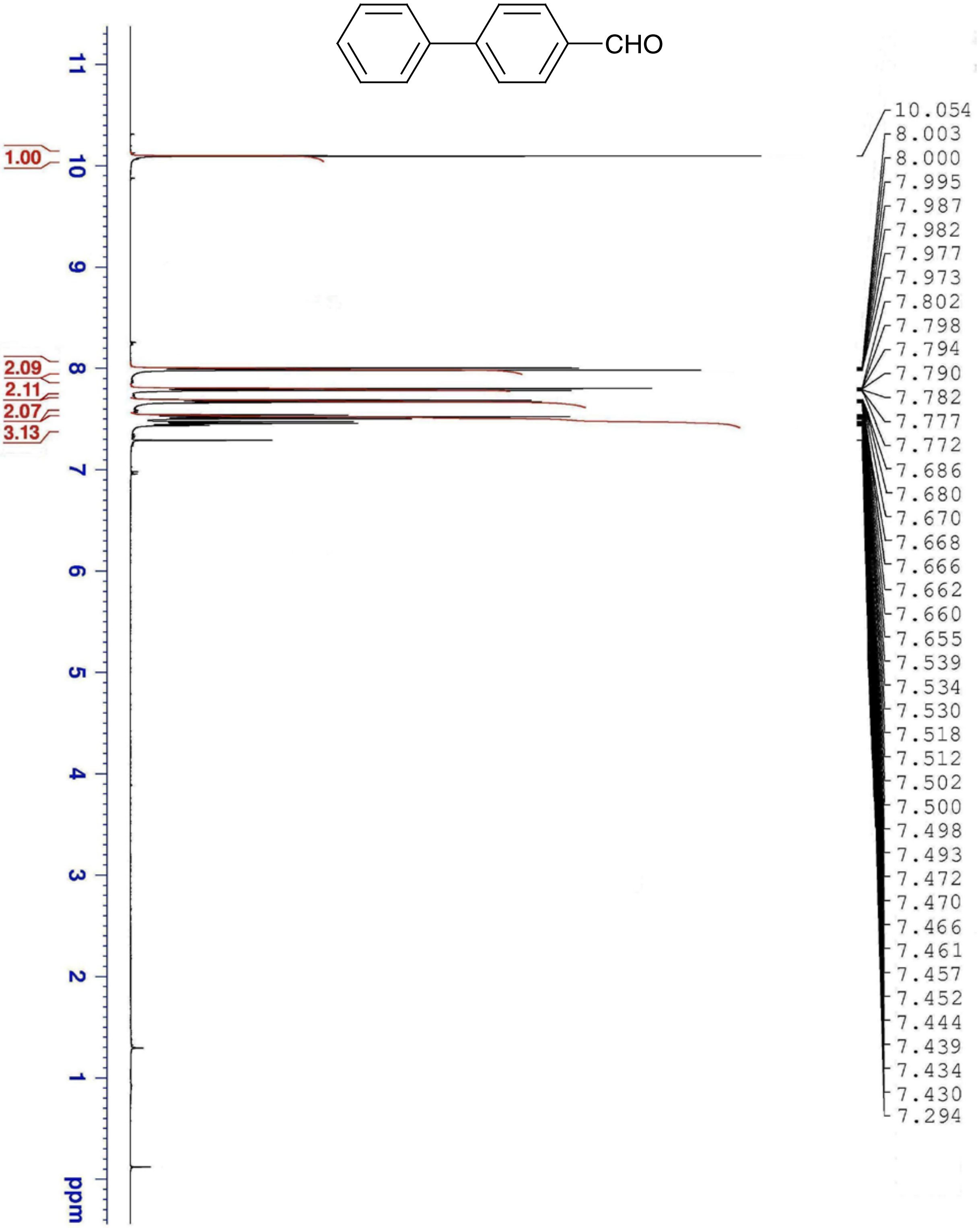
Biphenyl: ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.45-7.53 (t, 2H), 7.54-7.63 (t, 4H), 7.69-7.79 (d, 4H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 127.31, 127.40, 128.90, 141.38.

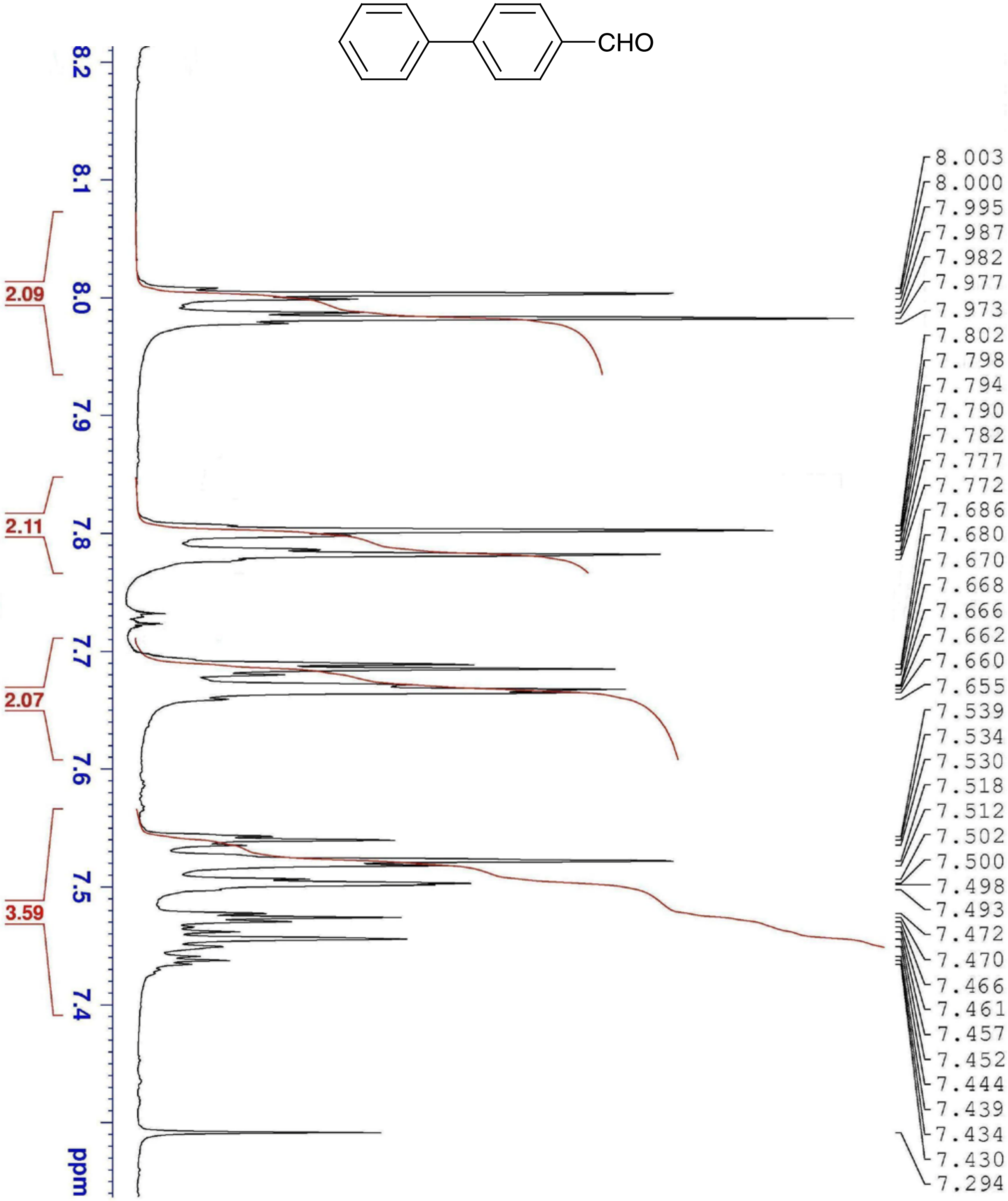
References:

[1] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc*.1998, **120**, 6024.

^{1}H NMR and ^{13}C NMR spectra of the coupling products

Biphenyl-4-carbaldehyde

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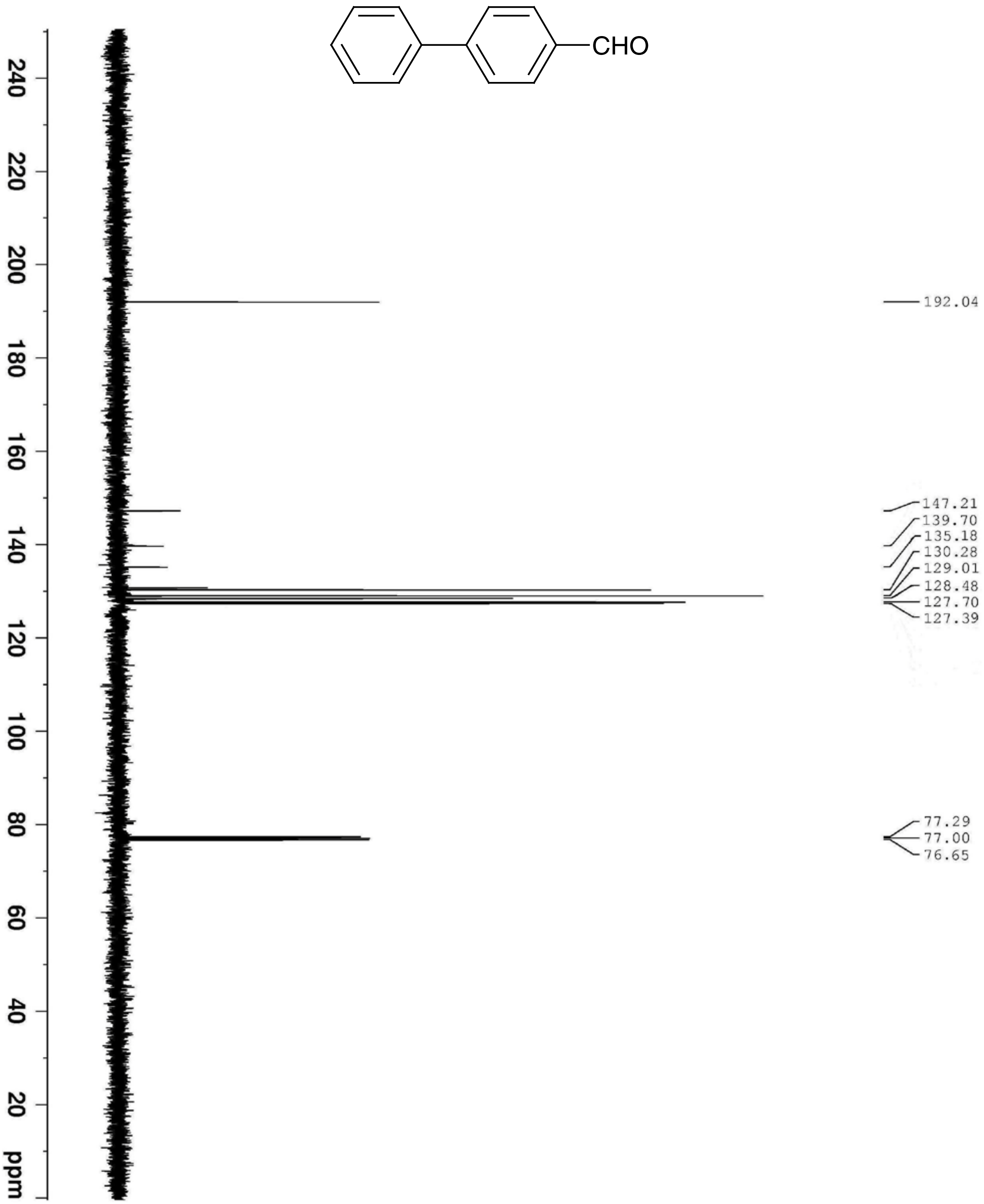
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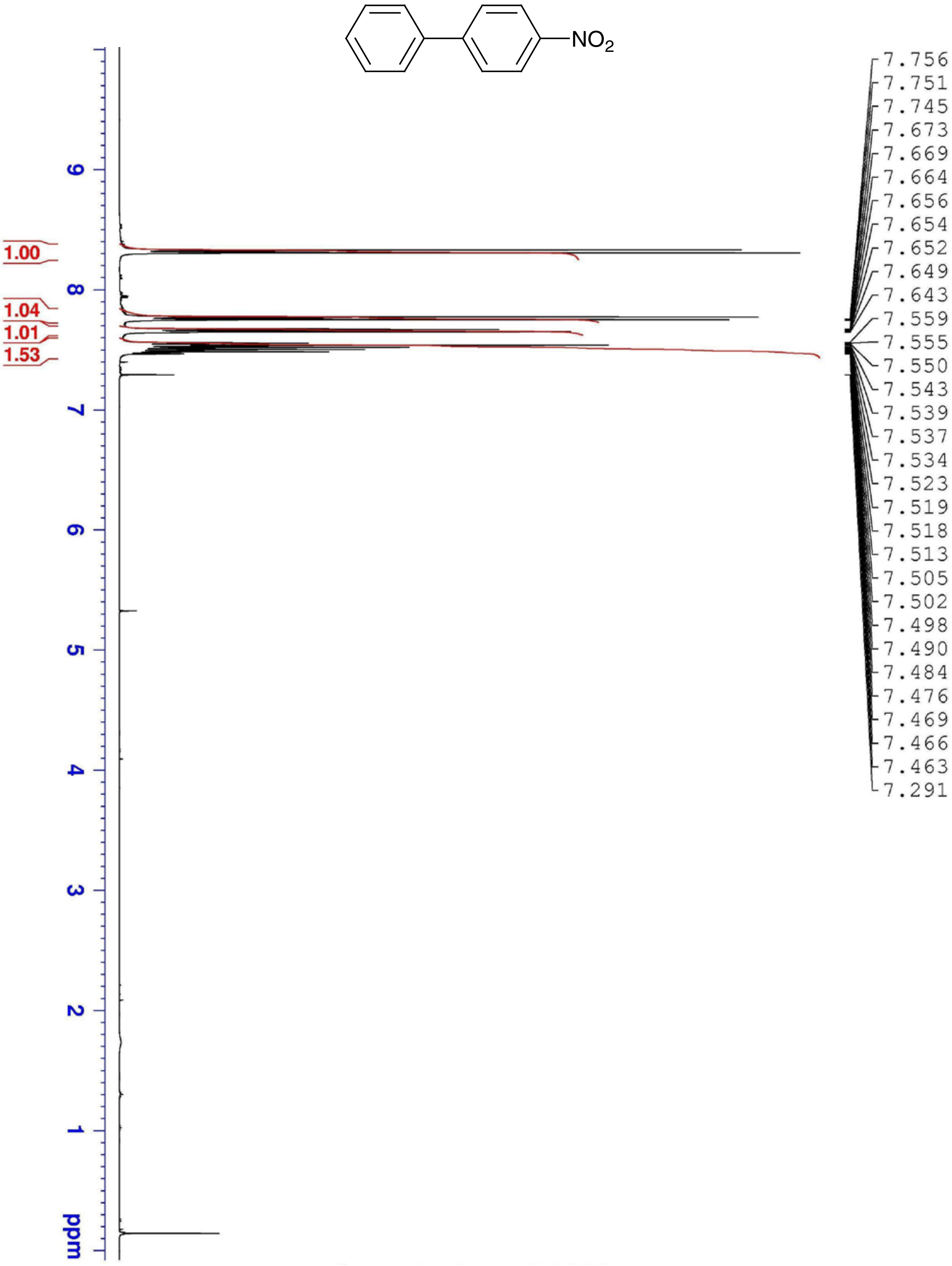

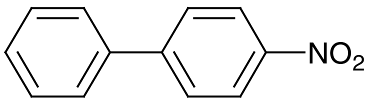
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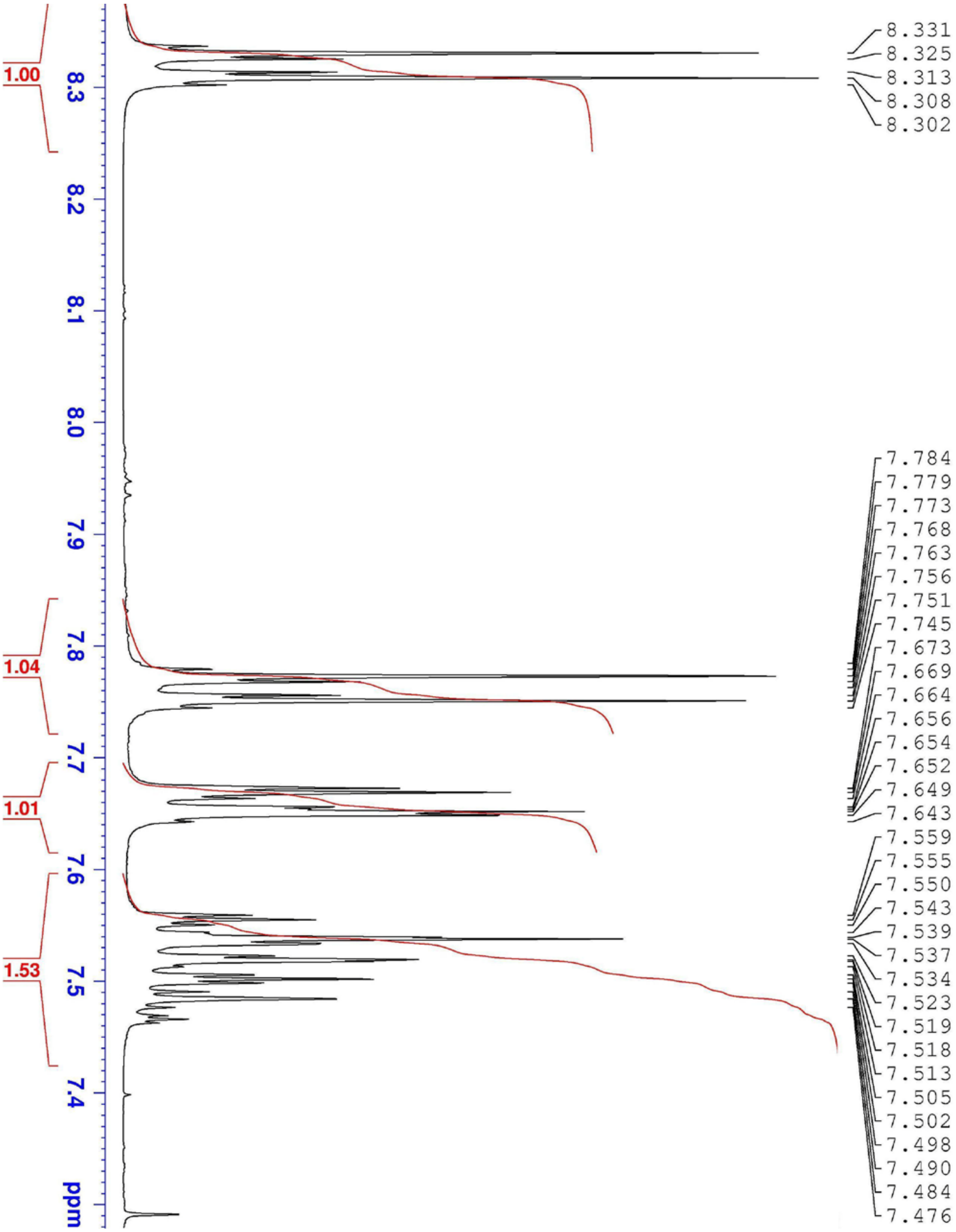
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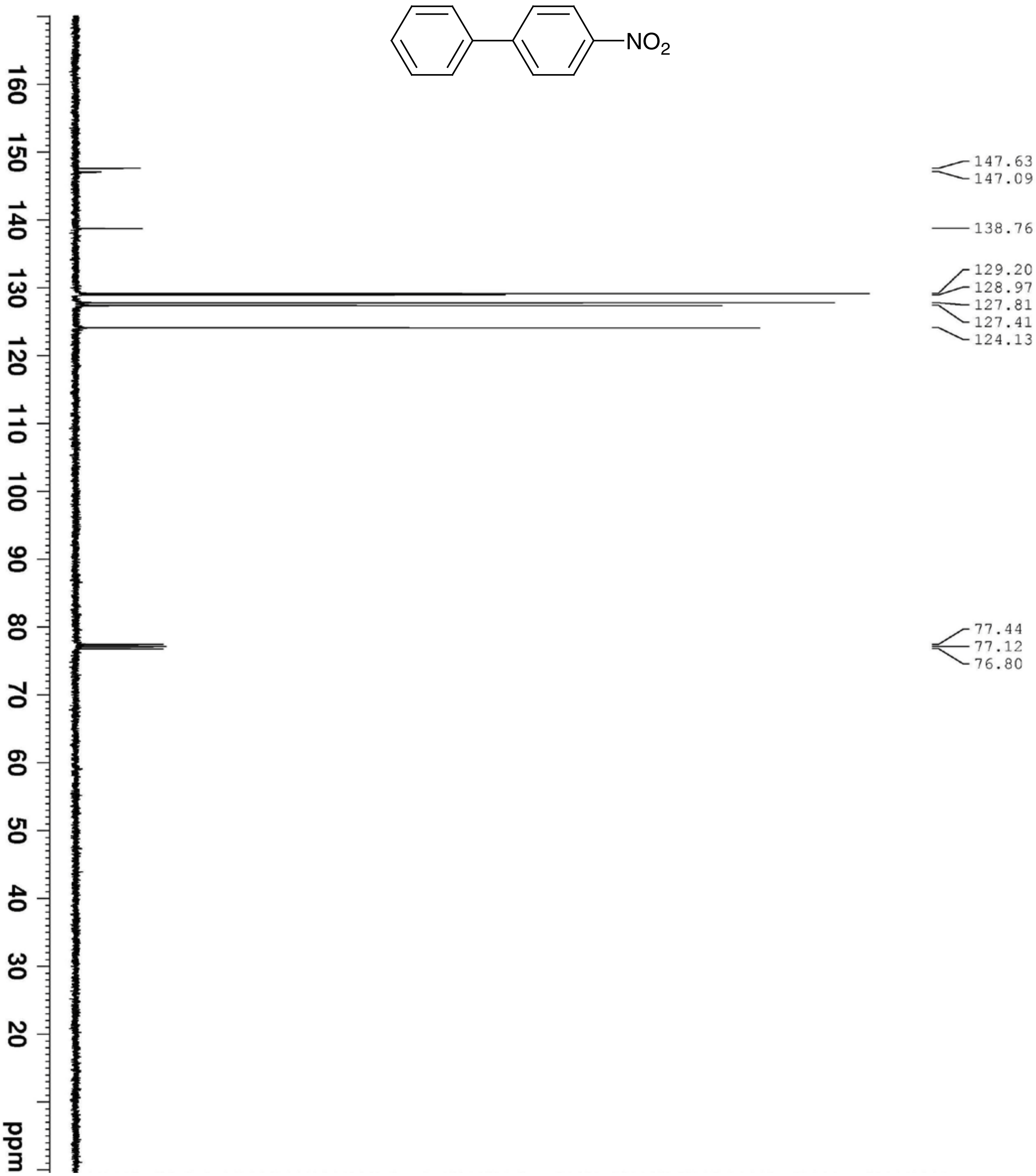
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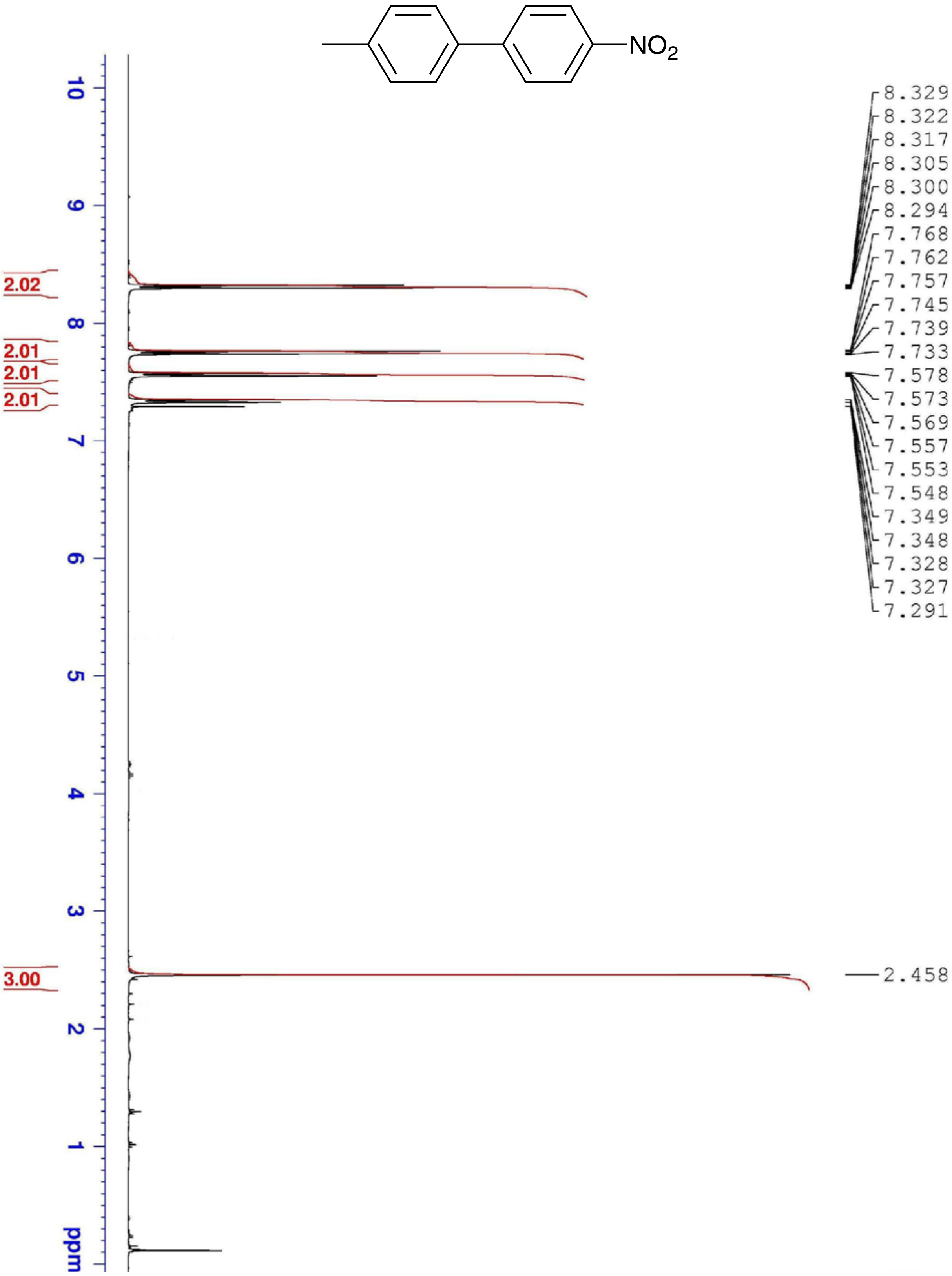

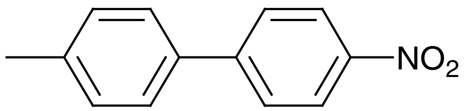
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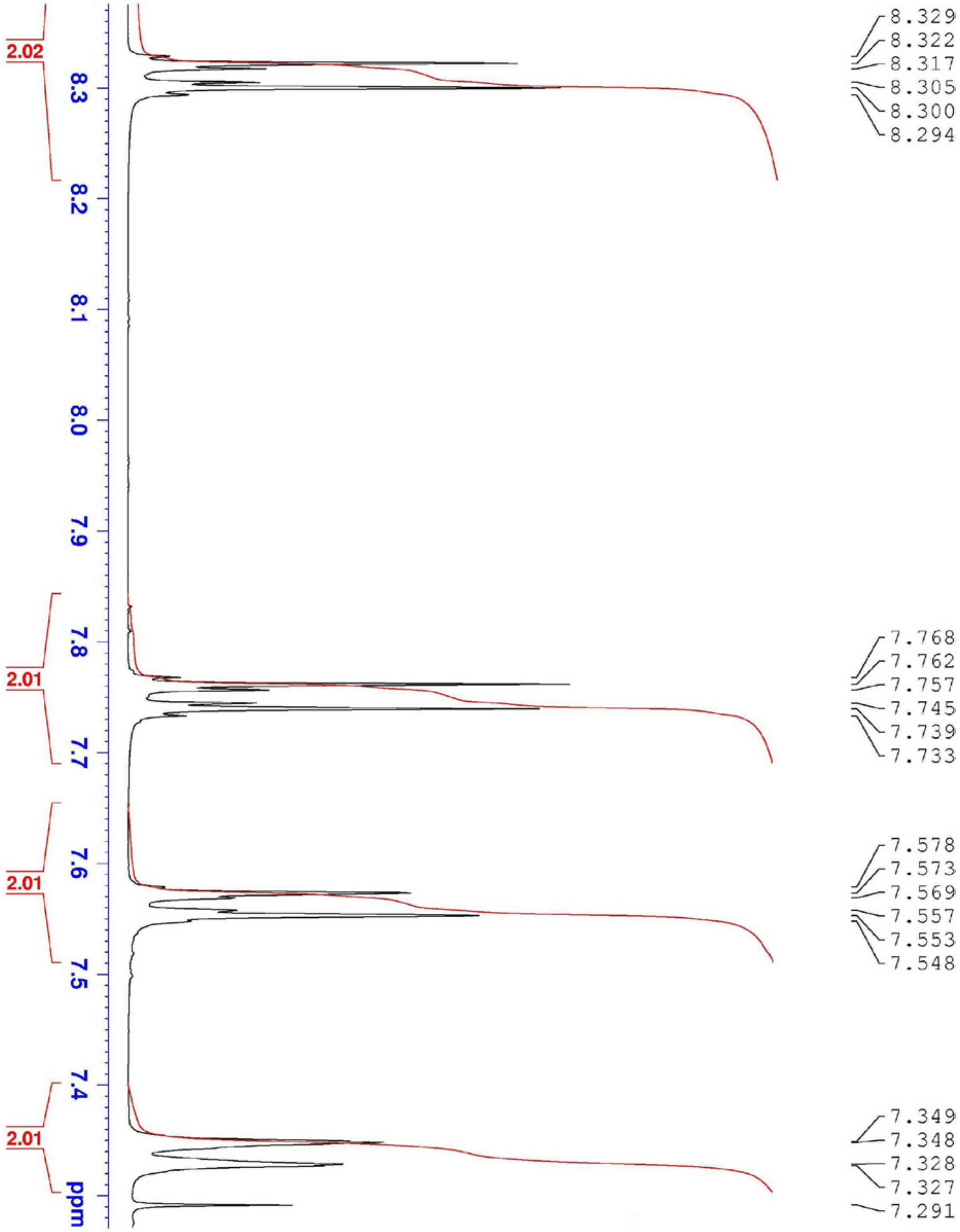
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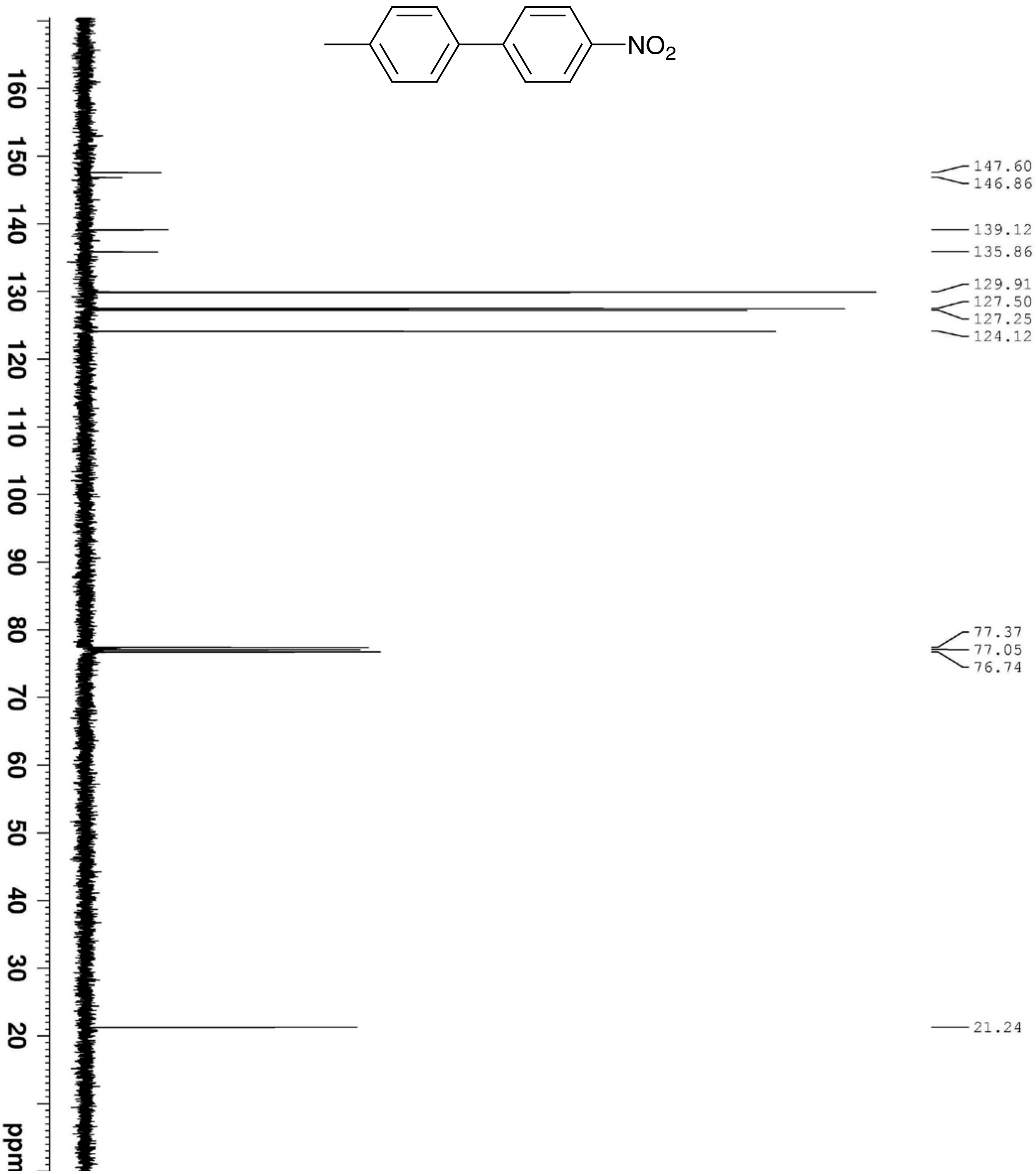
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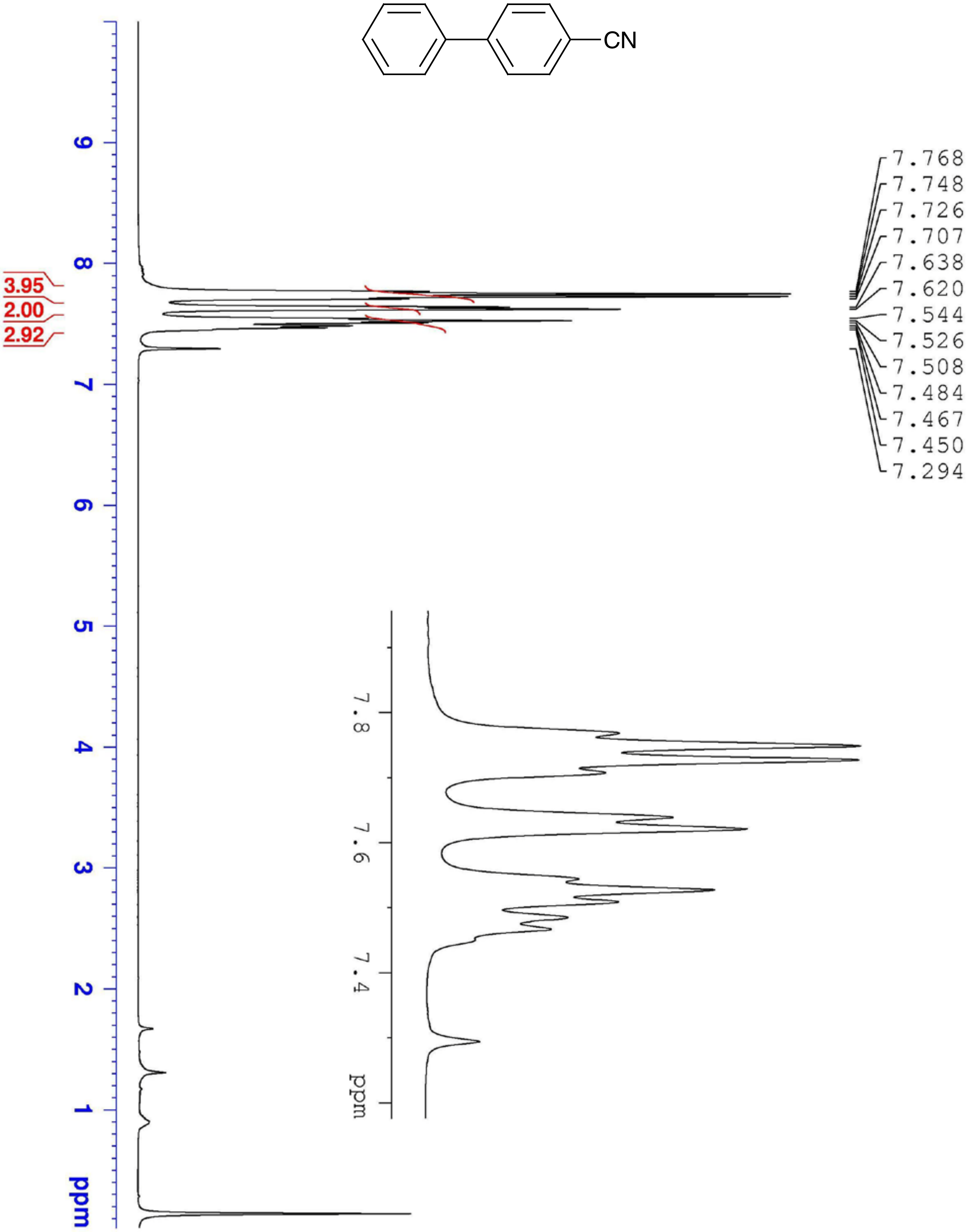

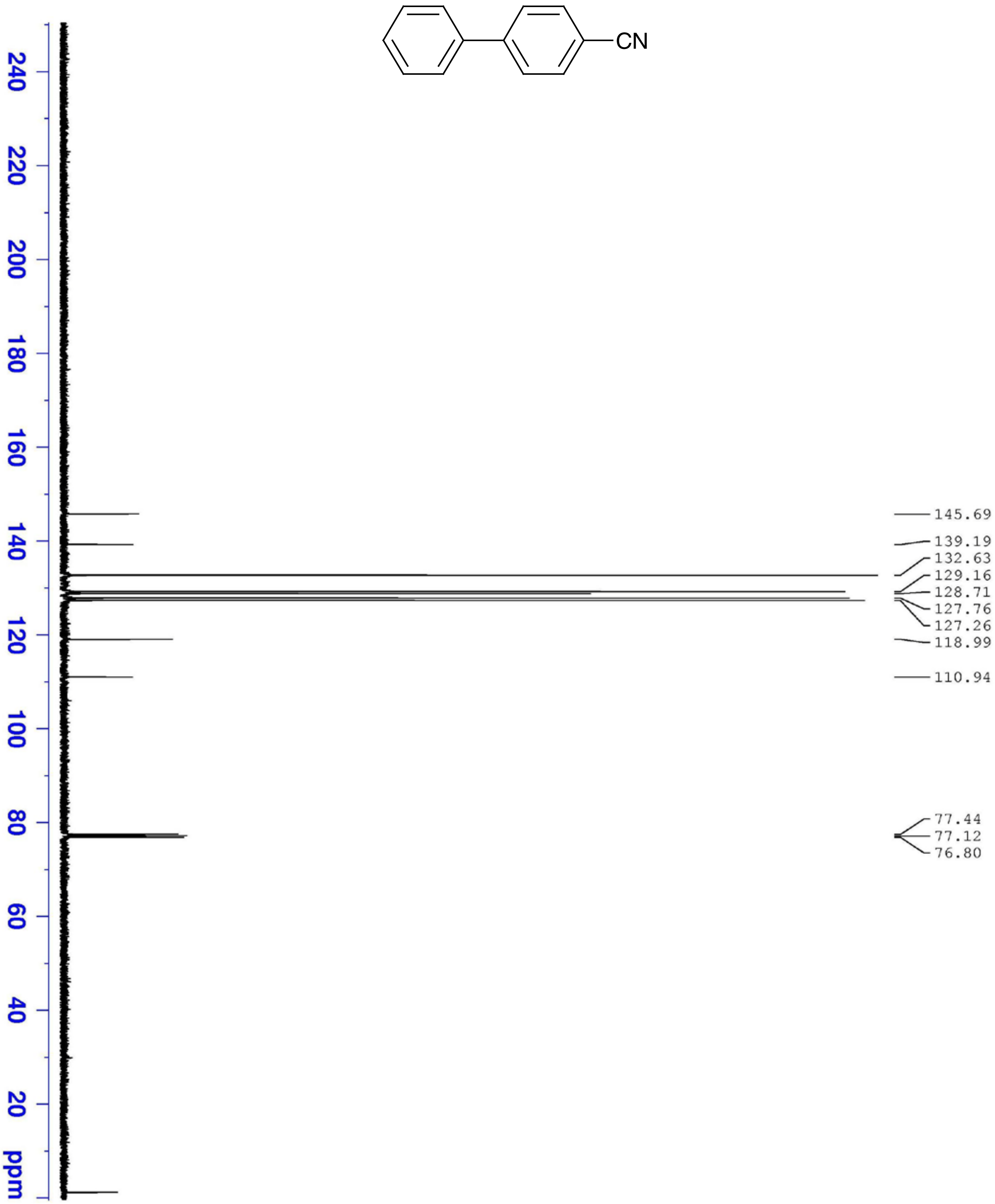
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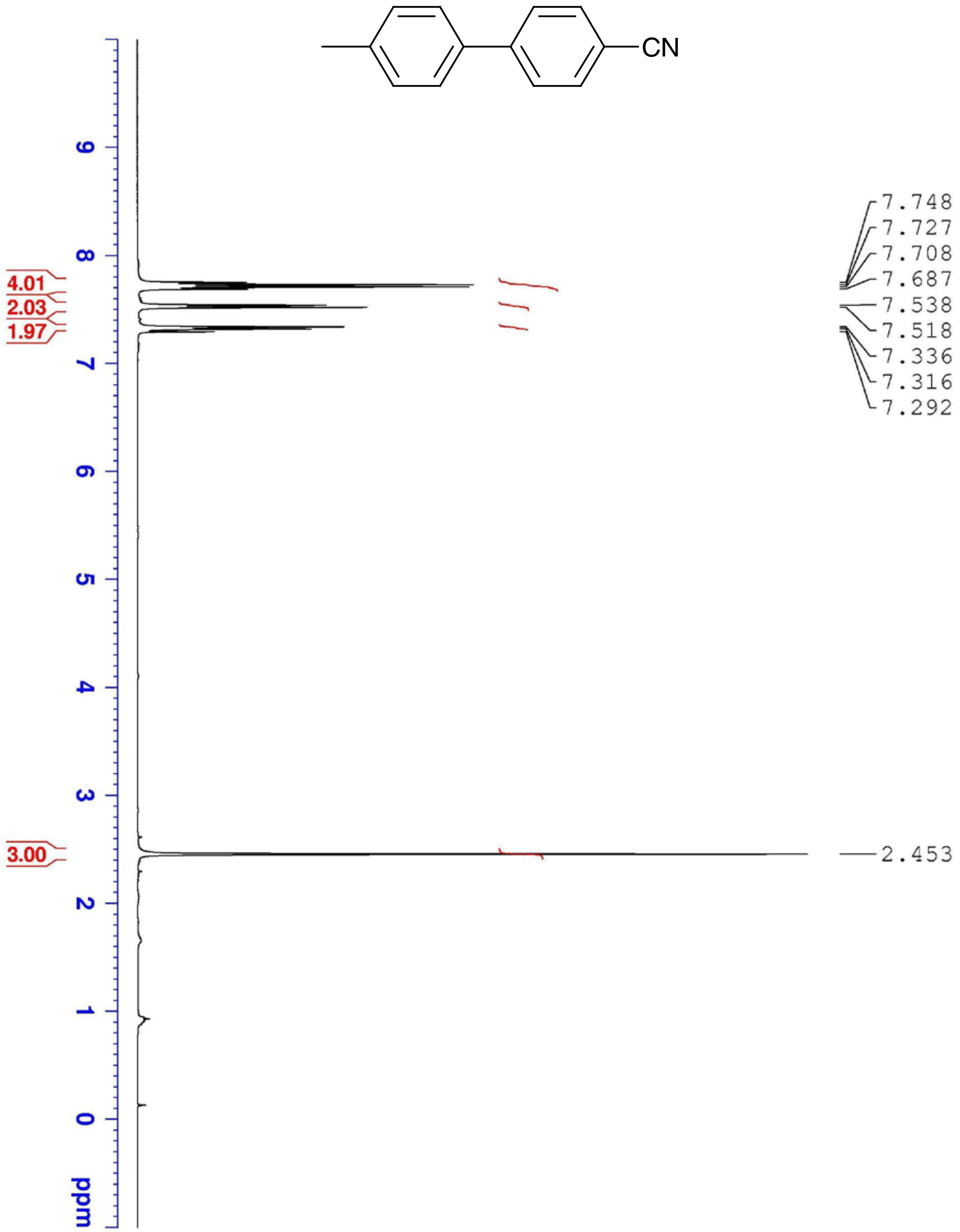

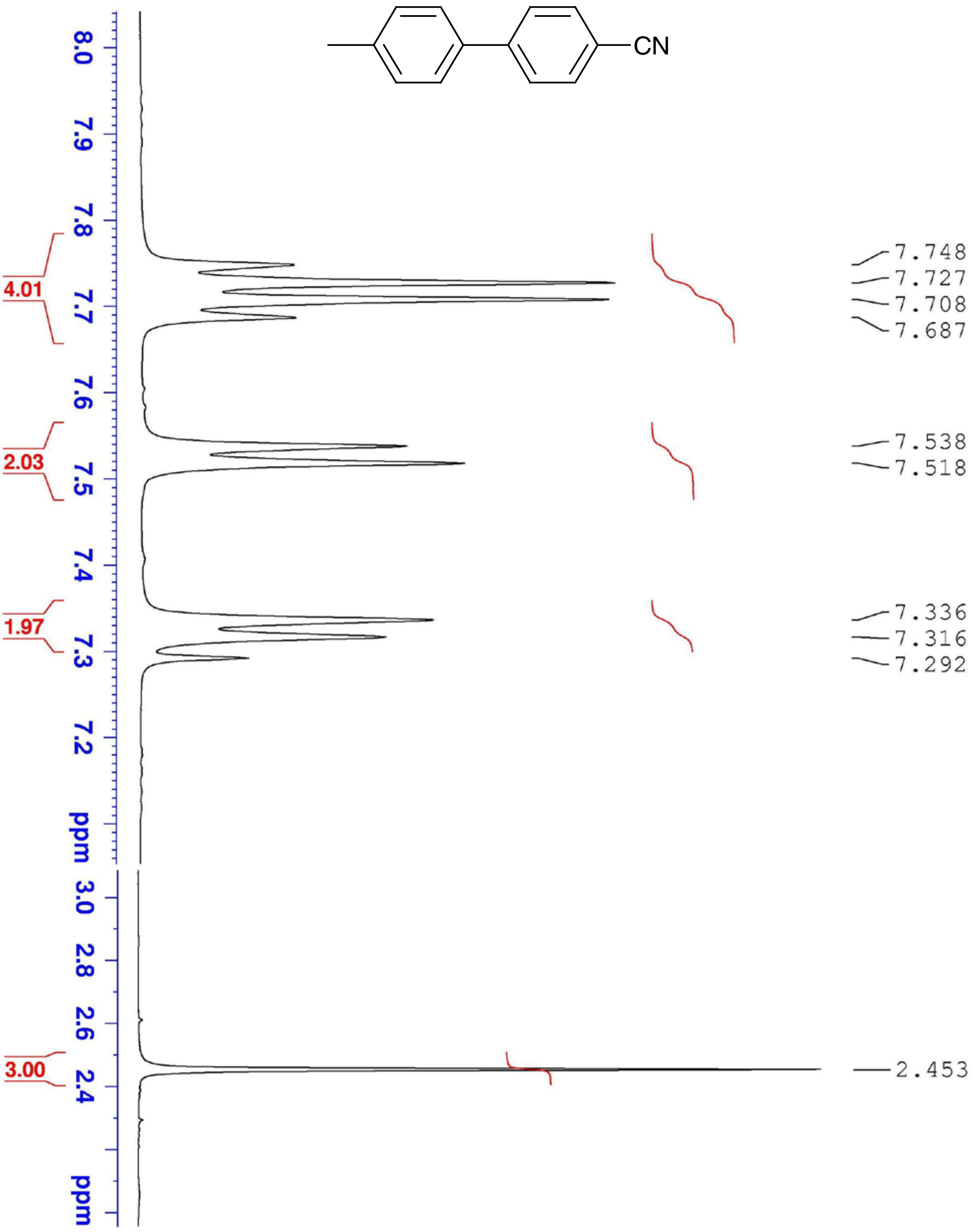
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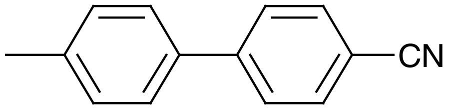
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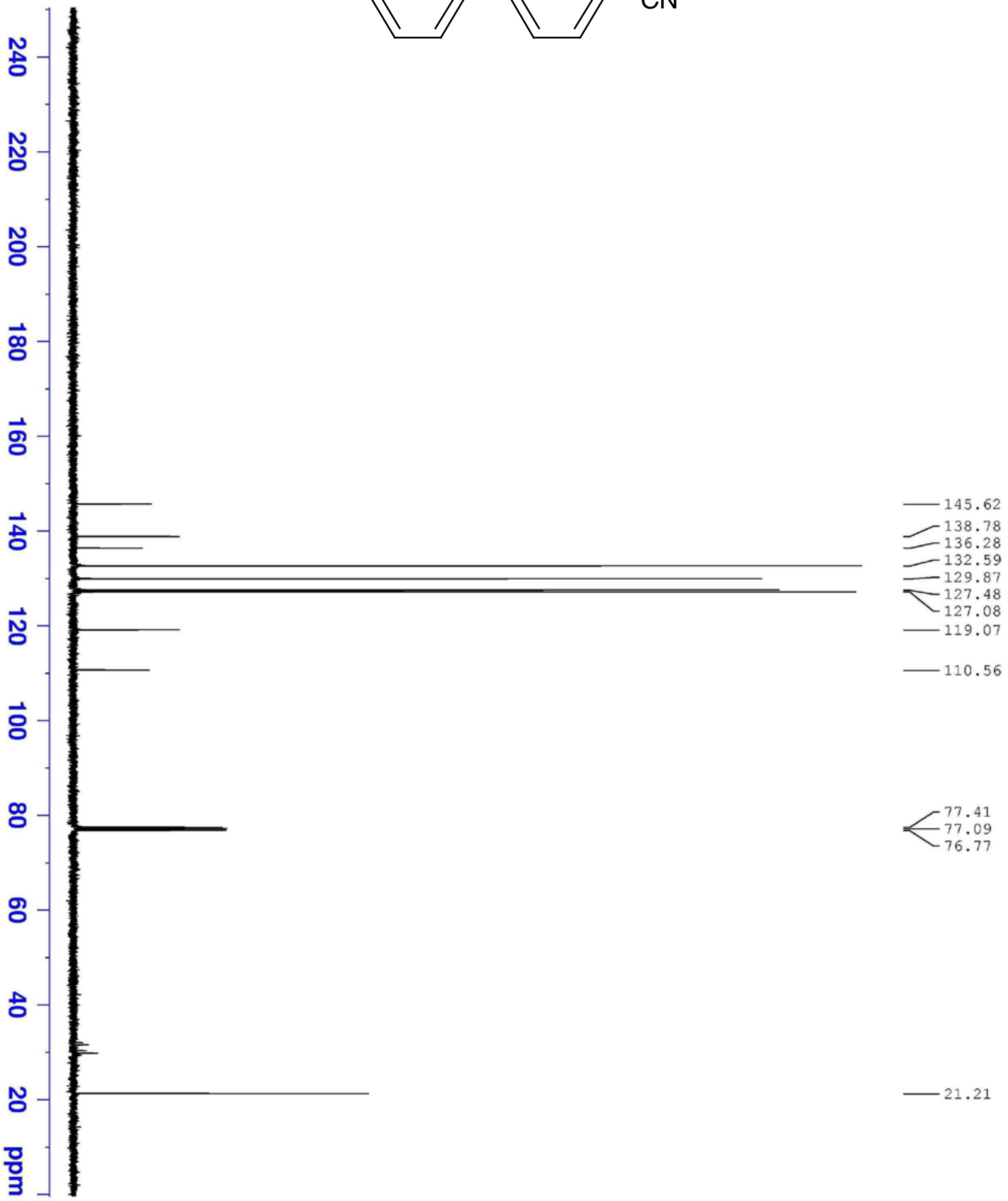
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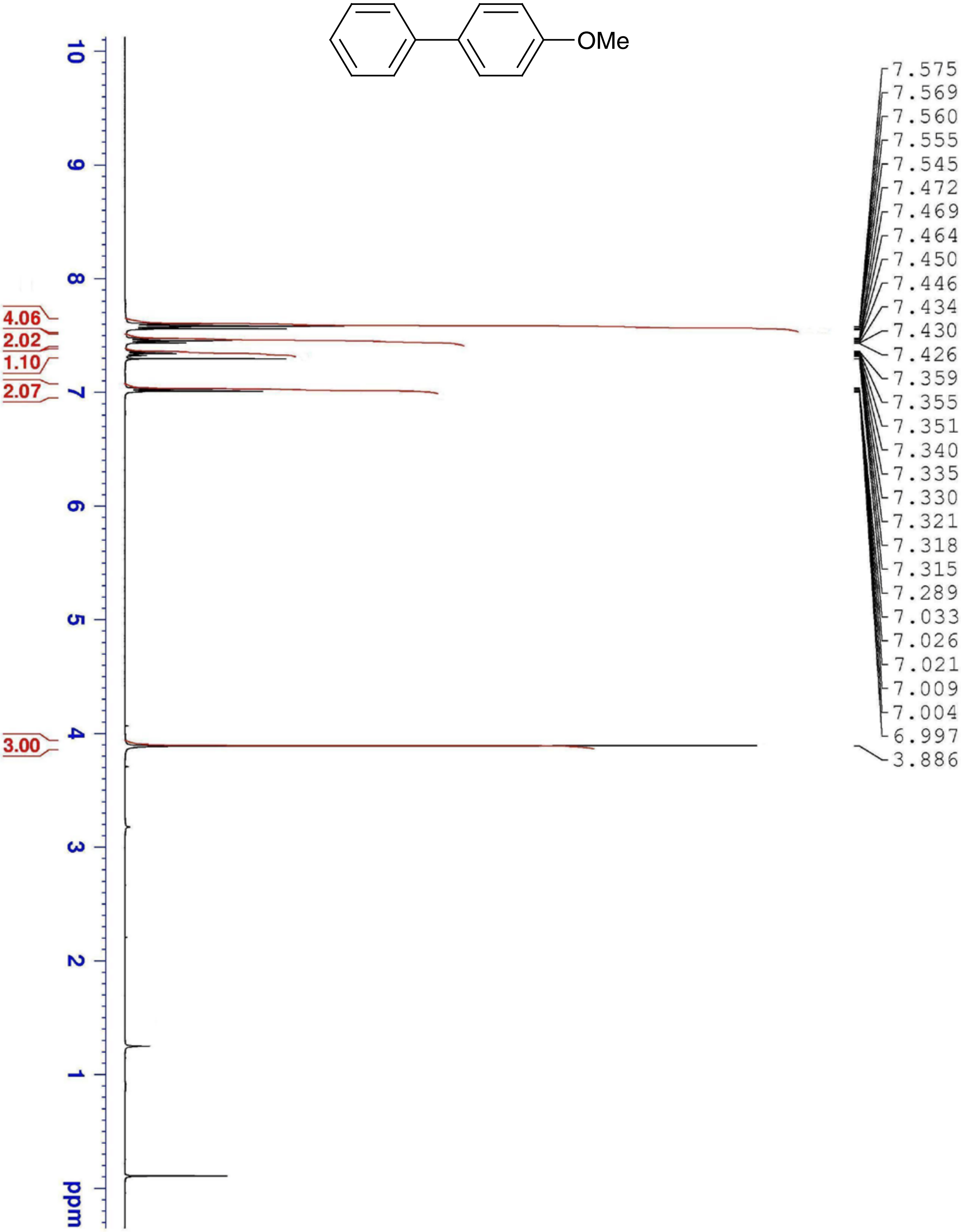
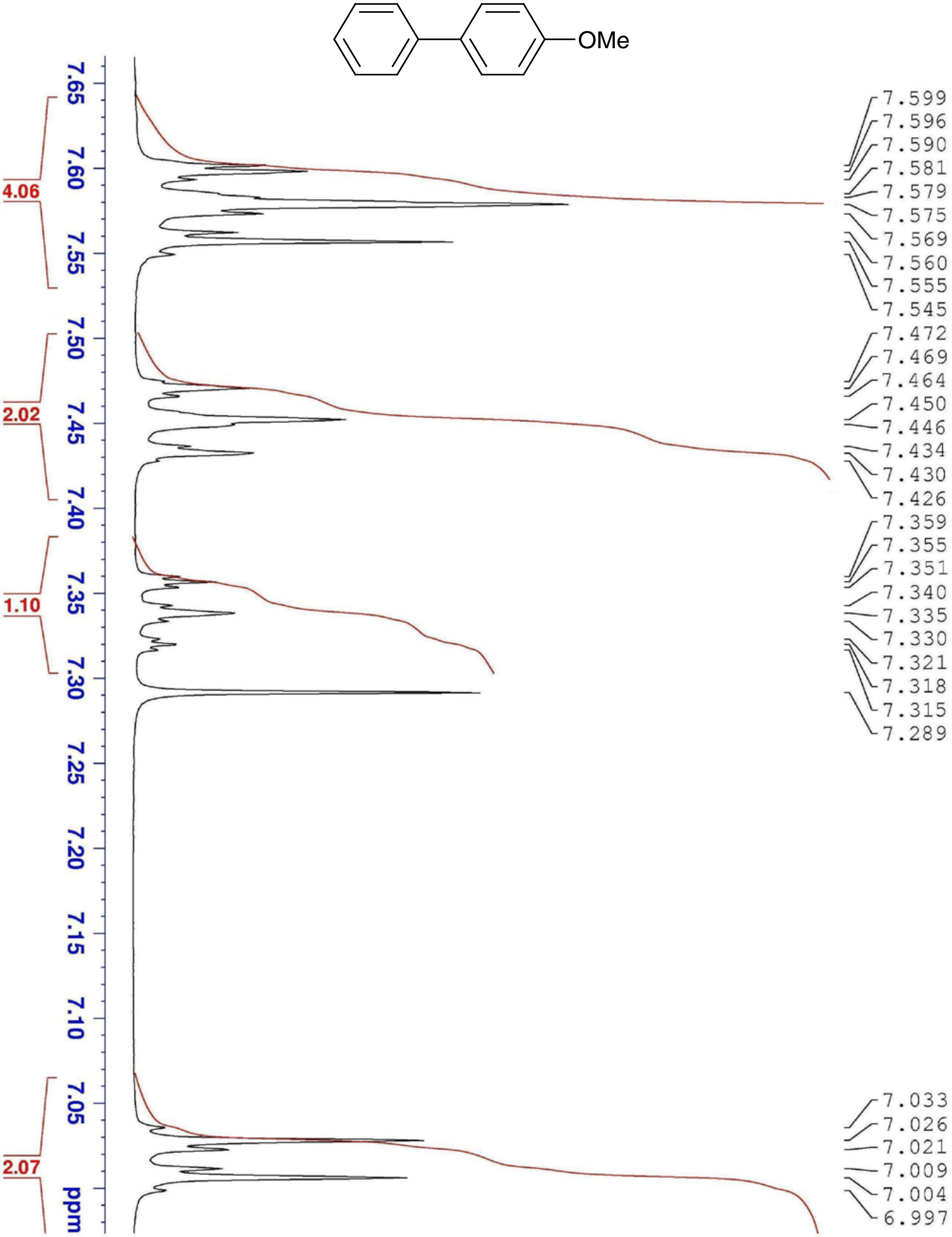
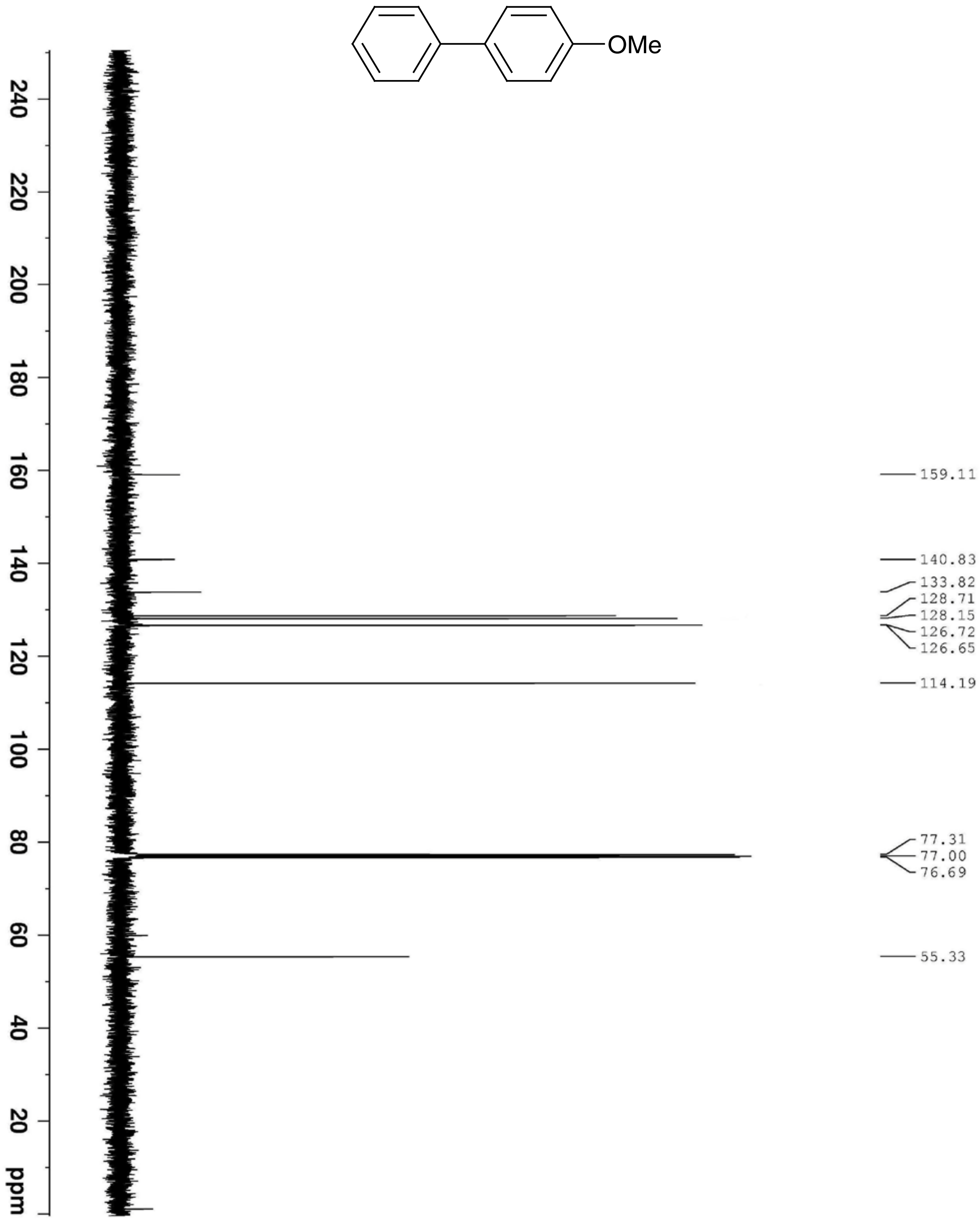
180
160
140
120
100
80
60
40
20
ppm
145.62
138.78
136.28
132.59
129.87
127.48
127.08
119.07
110.56
77.41
77.09
76.77
21.21

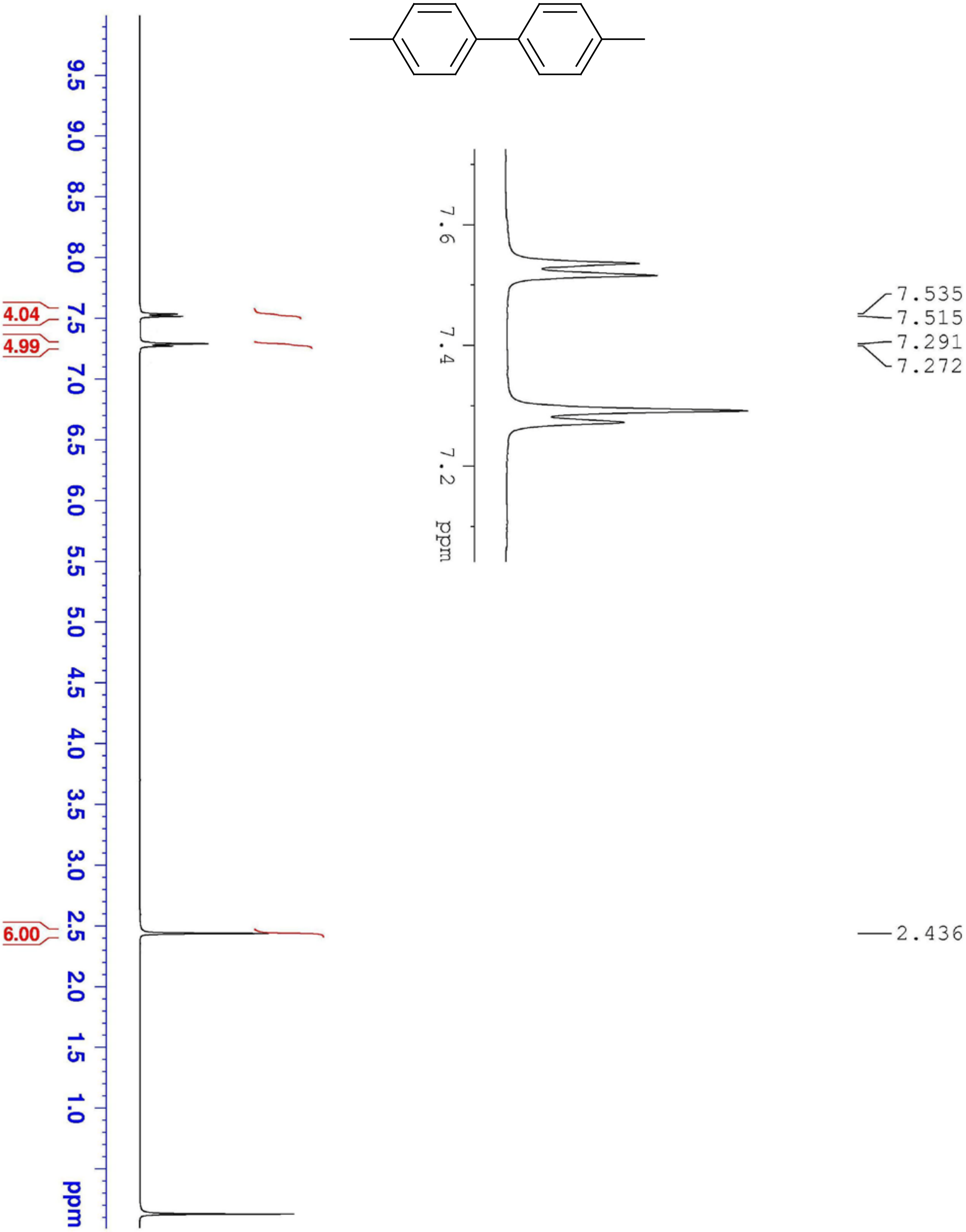
4-Methoxy-biphenyl

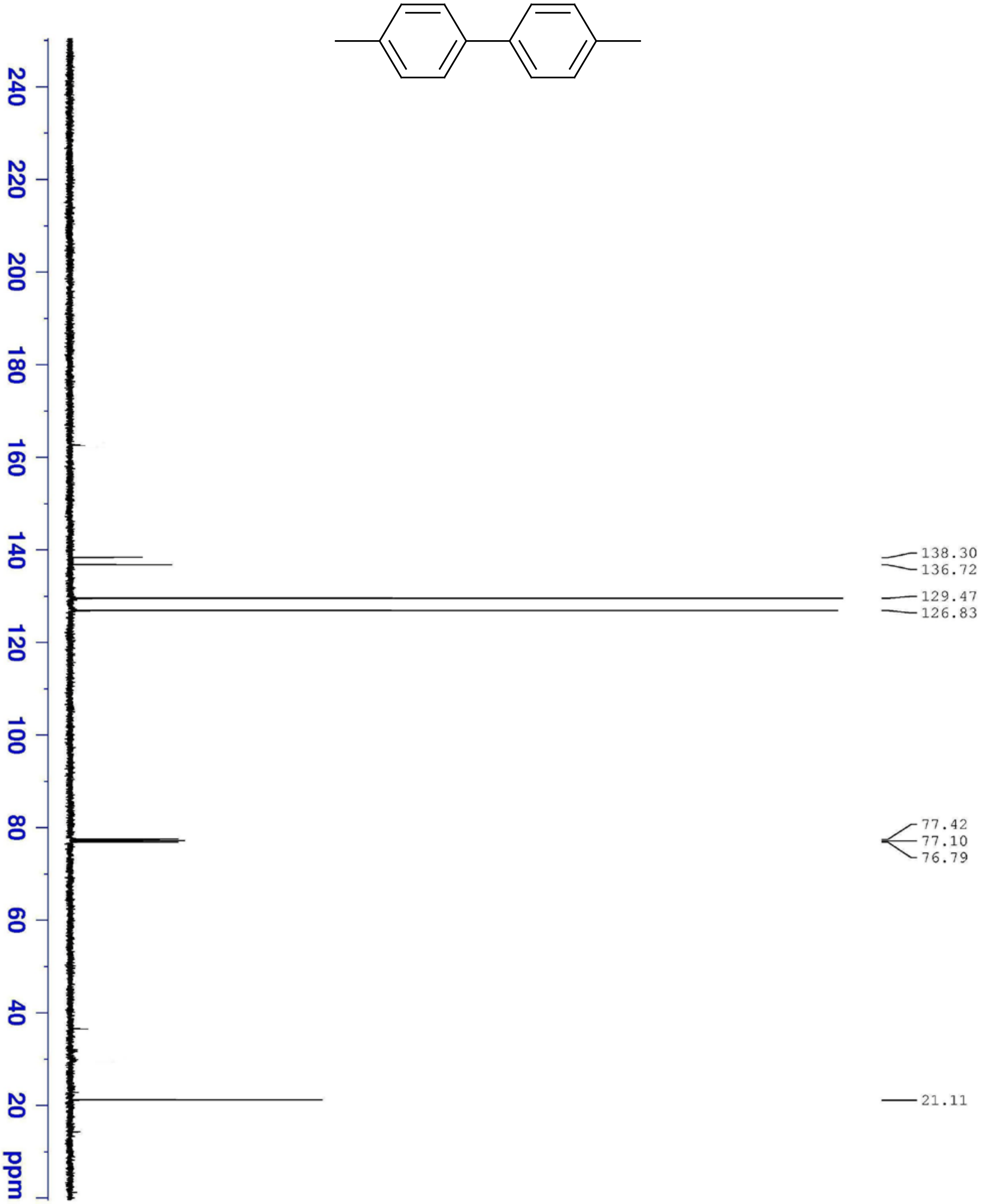



OMe
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
ppm
4.06
2.02
1.10
2.07
7.599
7.596
7.590
7.581
7.579
7.575
7.569
7.560
7.555
7.545
7.472
7.469
7.464
7.450
7.446
7.434
7.430
7.426
7.359
7.355
7.351
7.340
7.335
7.330
7.321
7.318
7.315
7.289
7.033
7.026
7.021
7.009
7.004
6.997

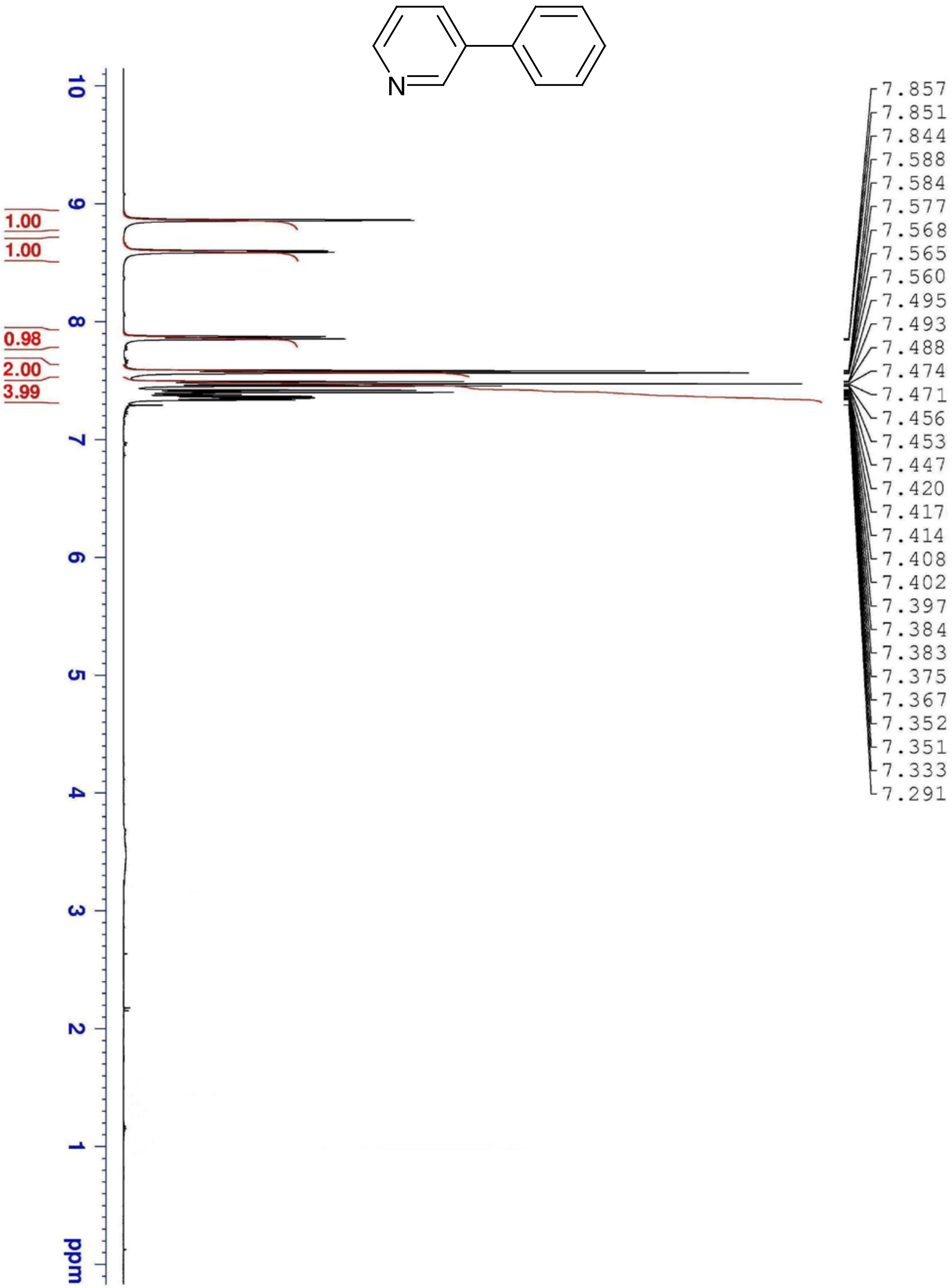

OMe
240
220
200
180
160
140
120
100
80
60
40
20
ppm
159.11
140.83
133.82
128.71
128.15
126.72
126.65
114.19
77.31
77.00
76.69
55.33

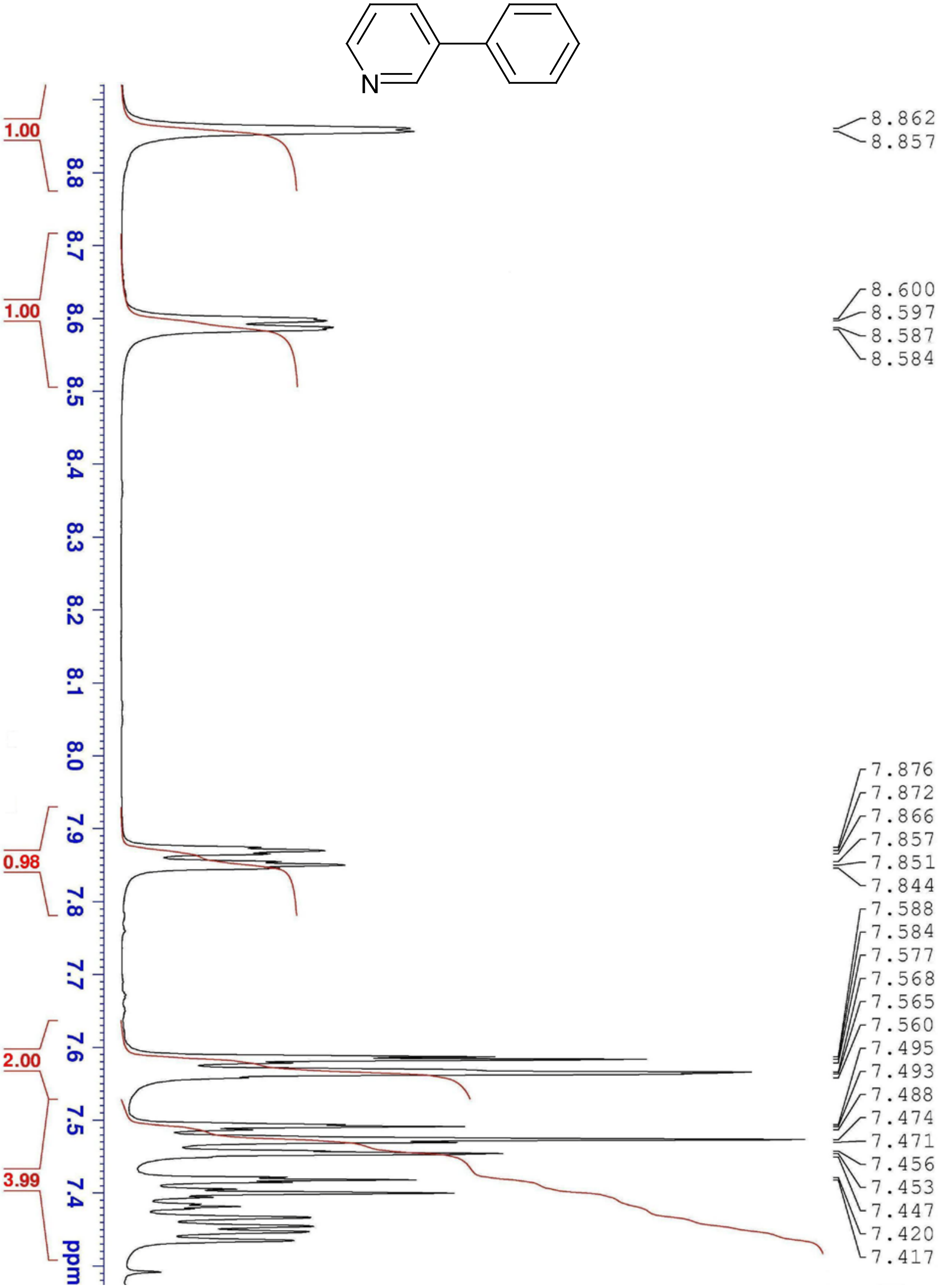
4,4'-Dimethyl-biphenyl

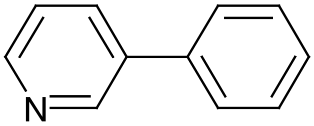


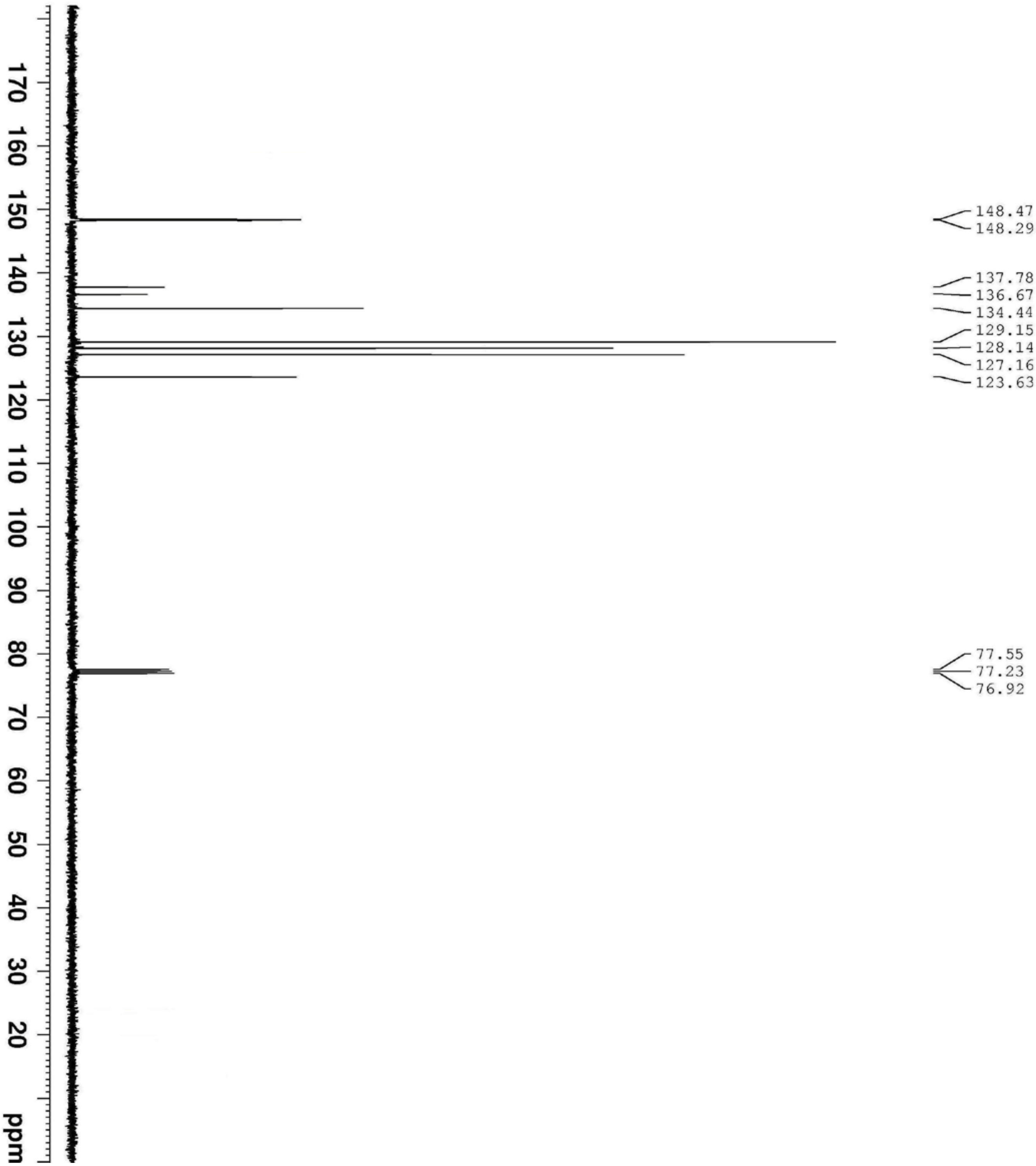

138.30
136.72
129.47
126.83
77.42
77.10
76.79
21.11
240
220
200
180
160
140
120
100
80
60
40
20
ppm

3-Phenylpyridine

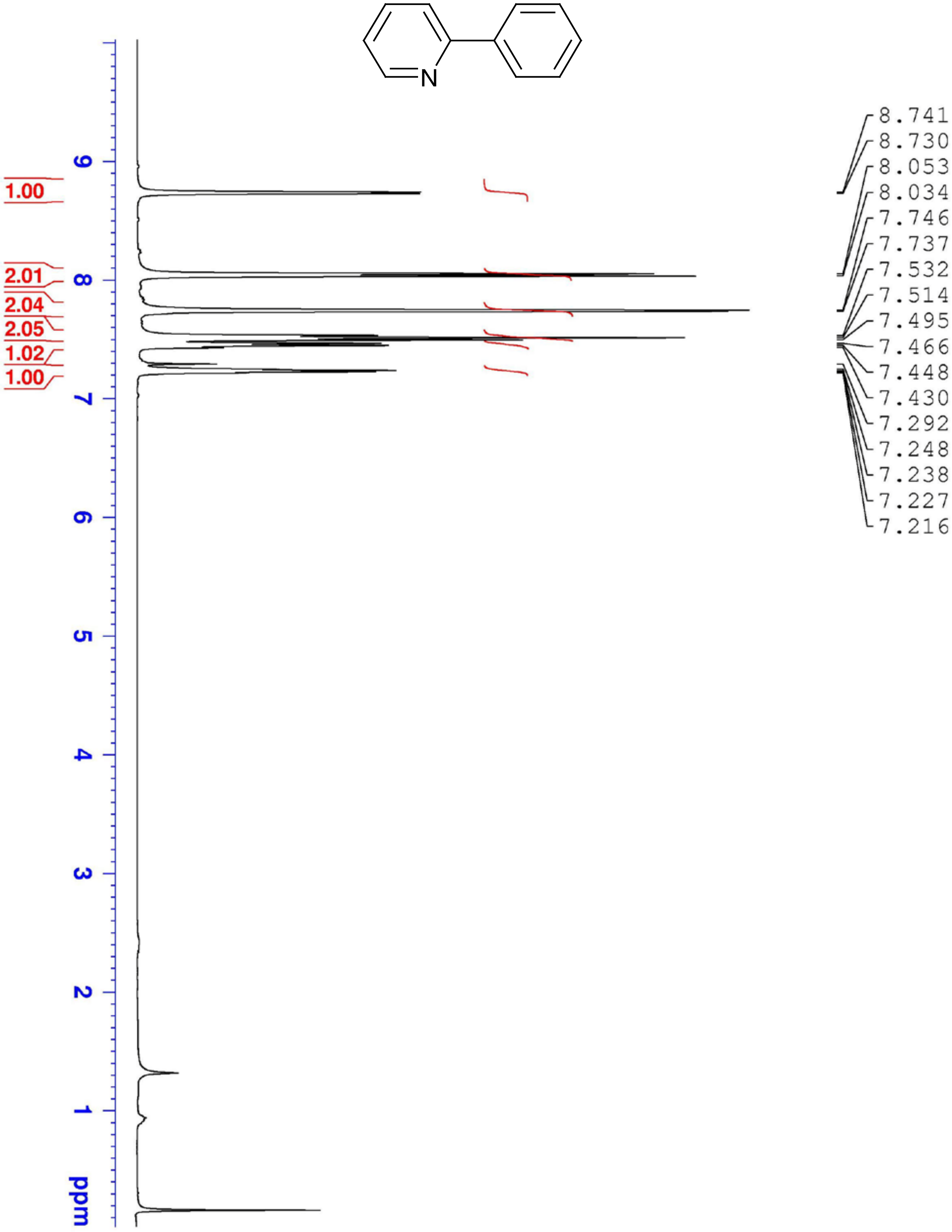


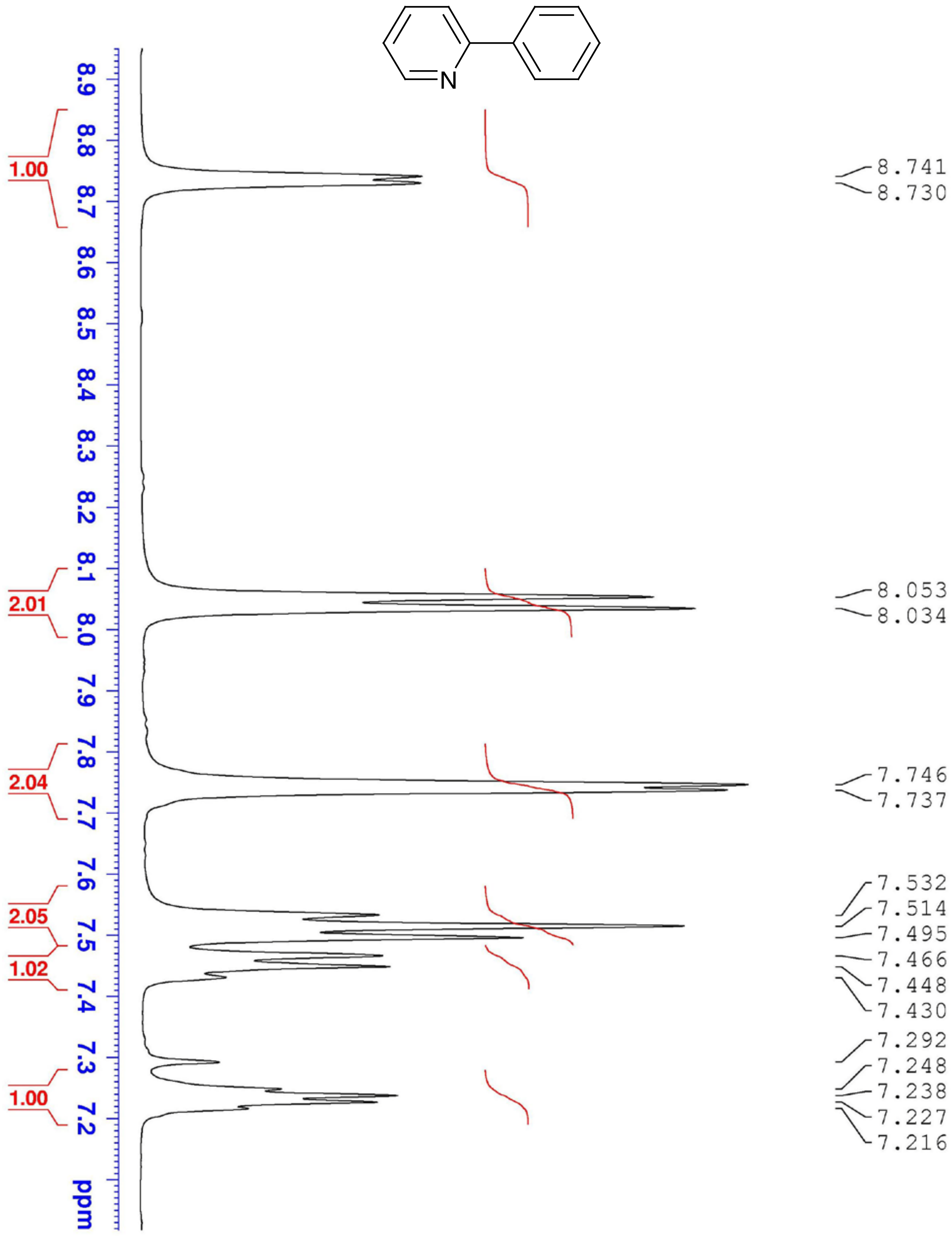

N
1.00
1.00
0.98
2.00
3.99
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
8.862
8.857
8.600
8.597
8.587
8.584
7.876
7.872
7.866
7.857
7.851
7.844
7.588
7.584
7.577
7.568
7.565
7.560
7.495
7.493
7.488
7.474
7.471
7.456
7.453
7.447
7.420
7.417

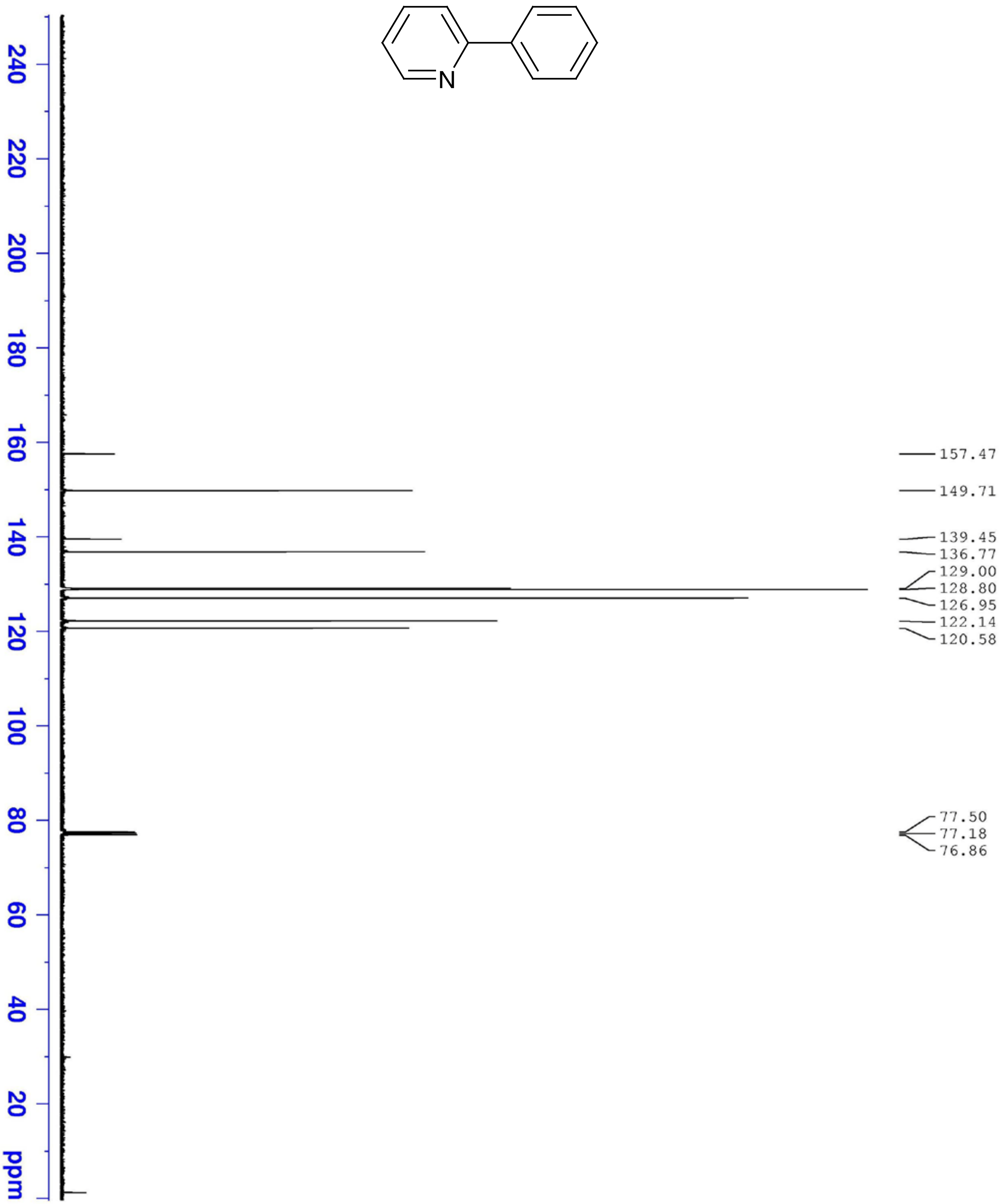

N


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
148.47
148.29
137.78
136.67
134.44
129.15
128.14
127.16
123.63
77.55
77.23
76.92

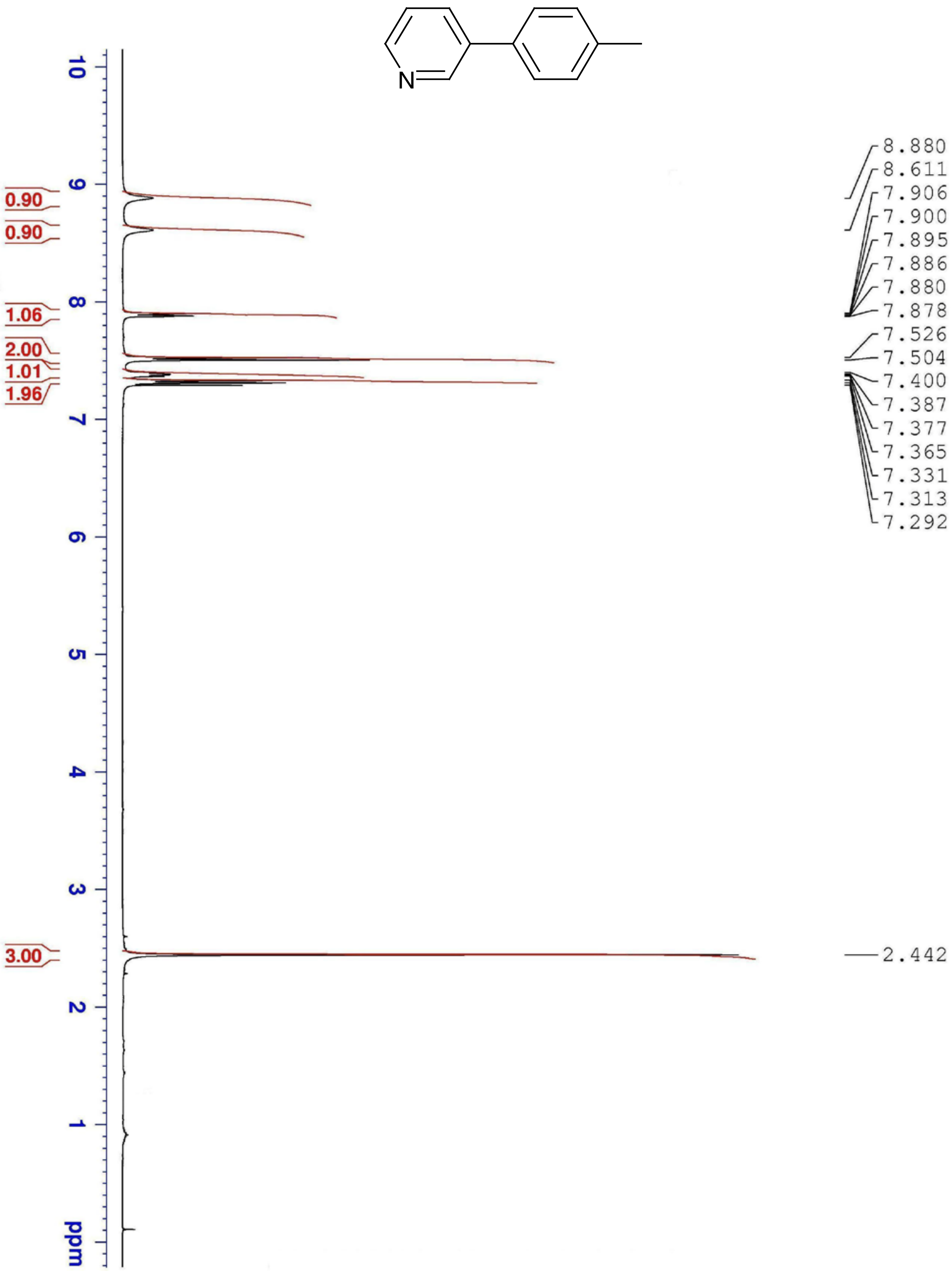
2-Phenylpyridine

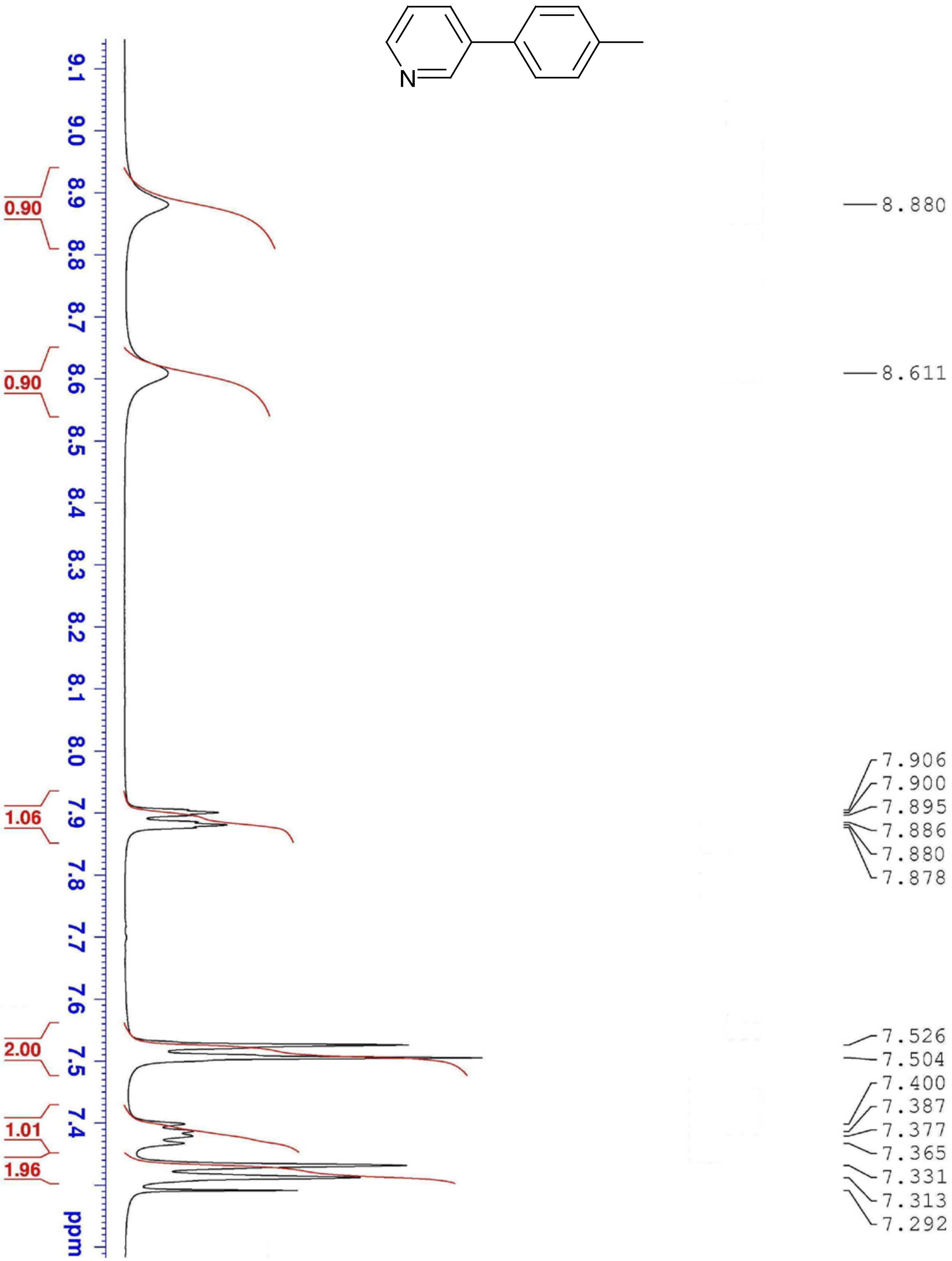


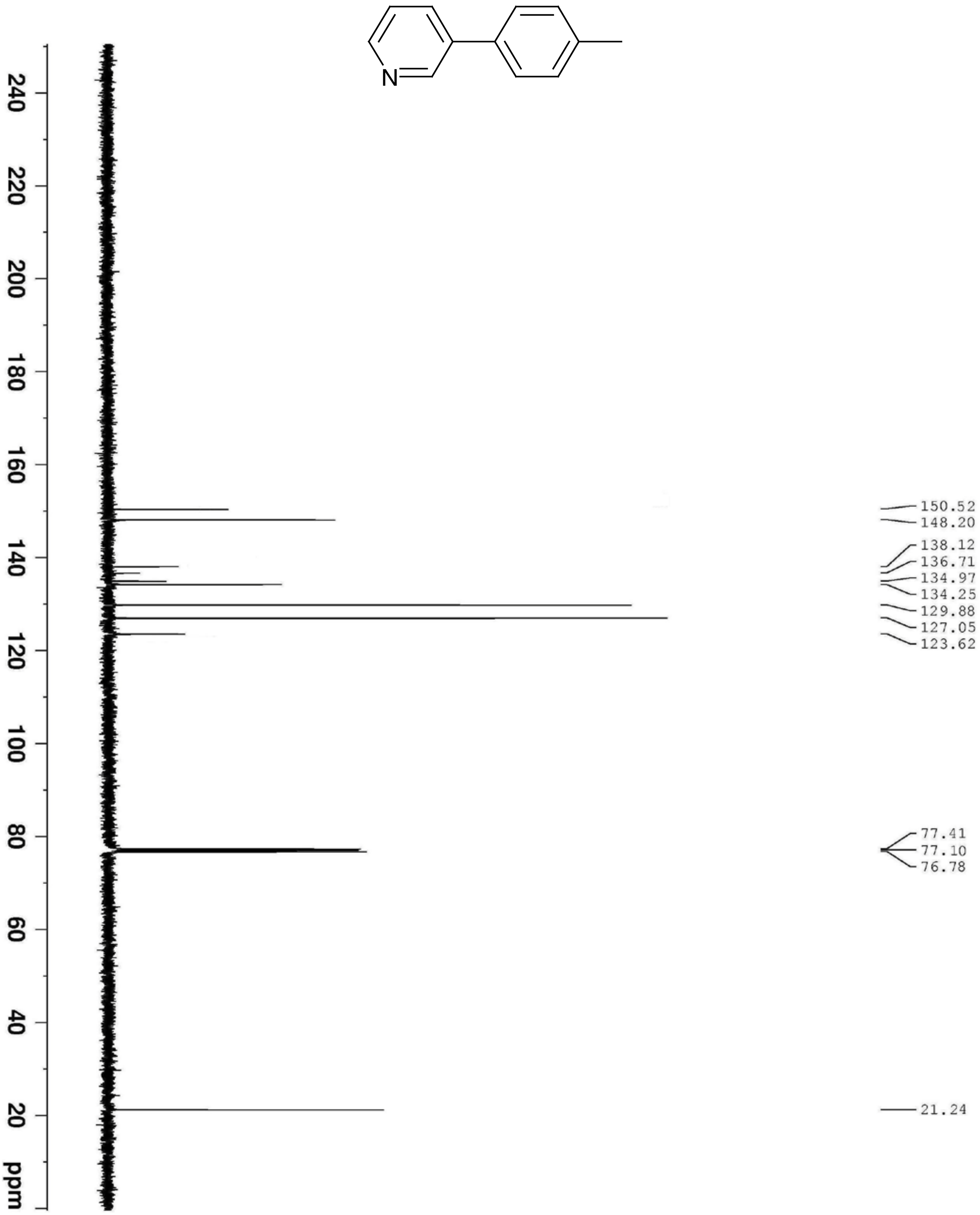

N
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm
1.00
2.01
2.04
2.05
1.02
1.00
8.741
8.730
8.053
8.034
7.746
7.737
7.532
7.514
7.495
7.466
7.448
7.430
7.292
7.248
7.238
7.227
7.216


N
240
220
200
180
160
140
120
100
80
60
40
20
ppm
157.47
149.71
139.45
136.77
129.00
128.80
126.95
122.14
120.58
77.50
77.18
76.86

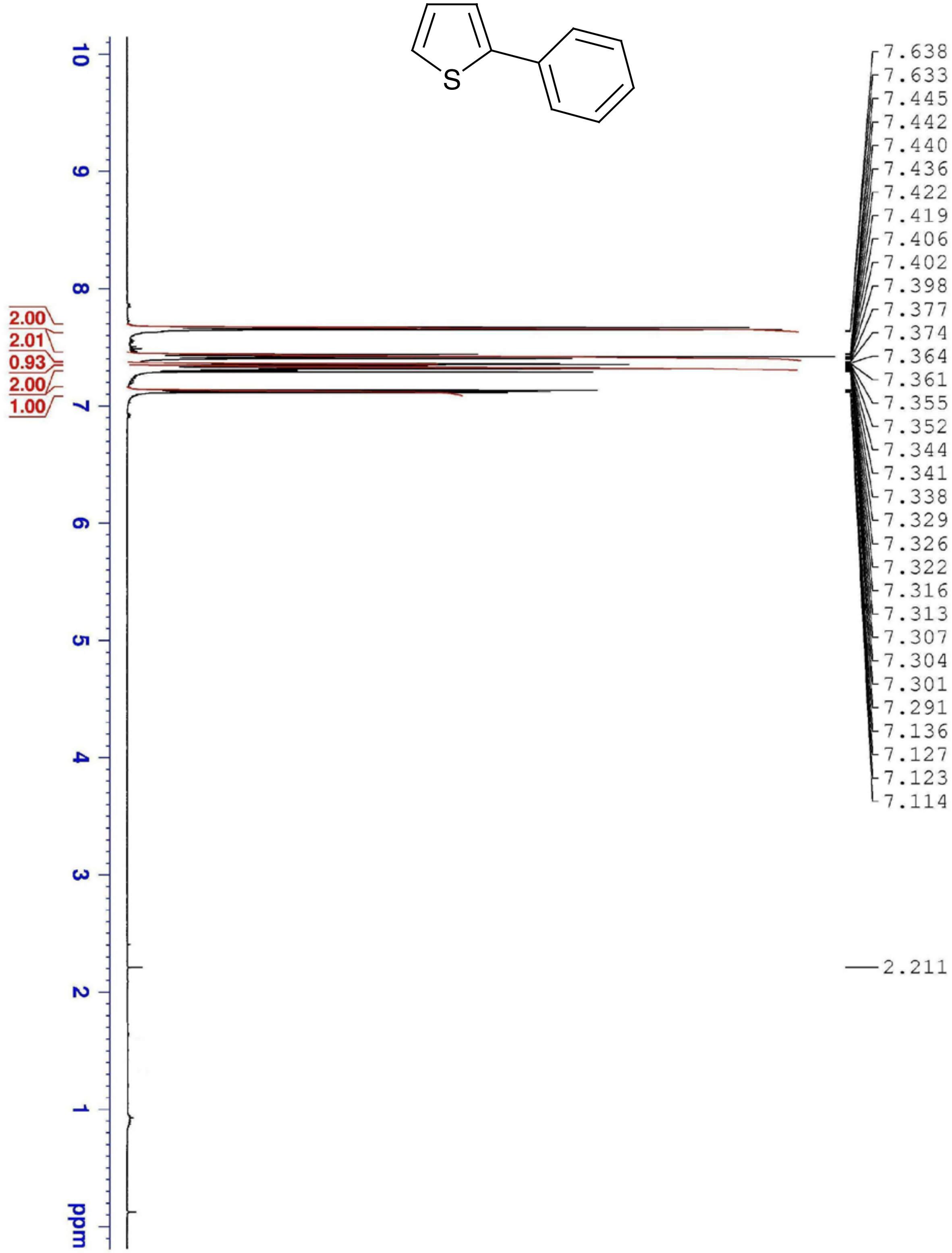
3-(4-Methylphenyl)pyridine

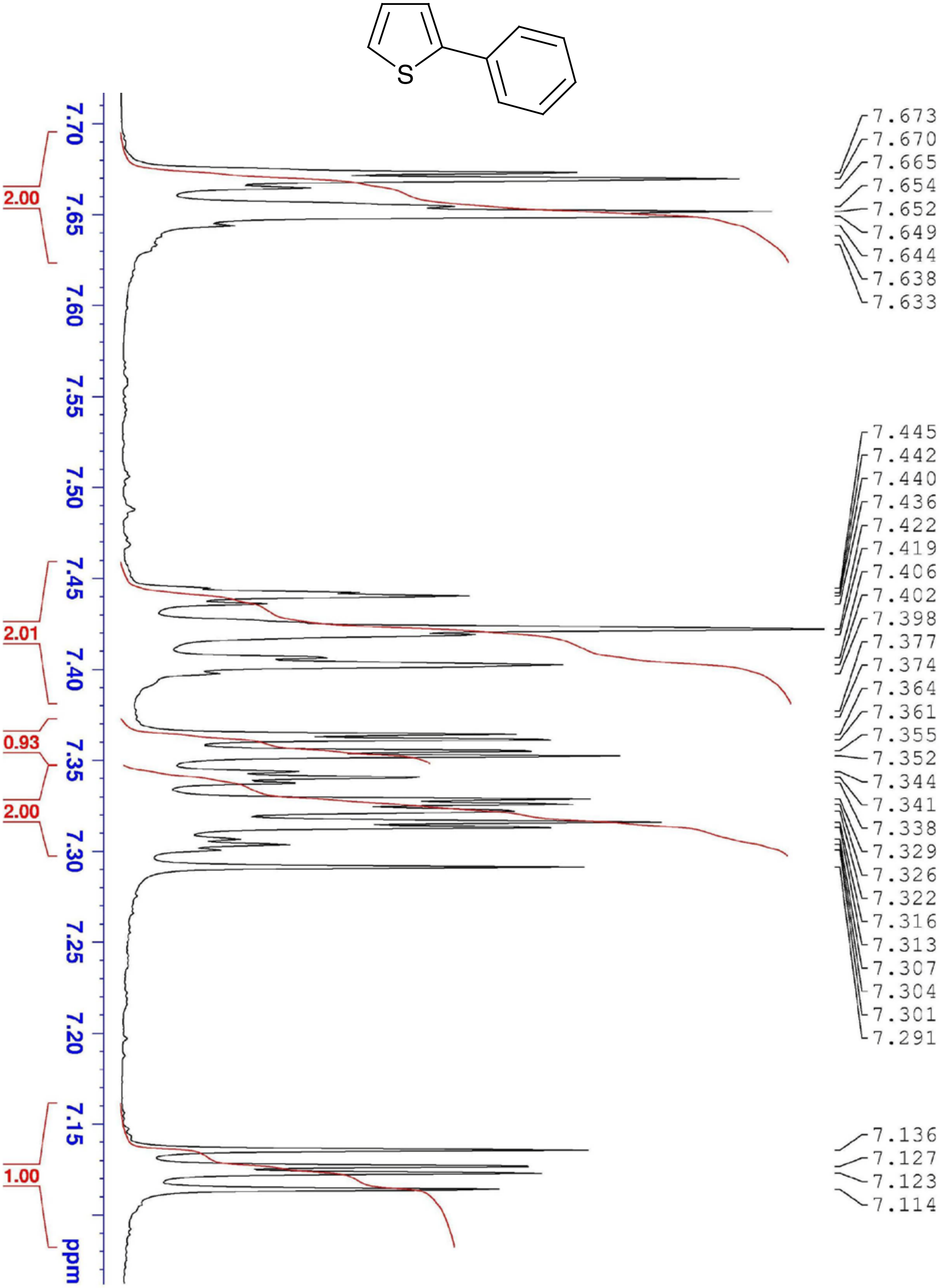


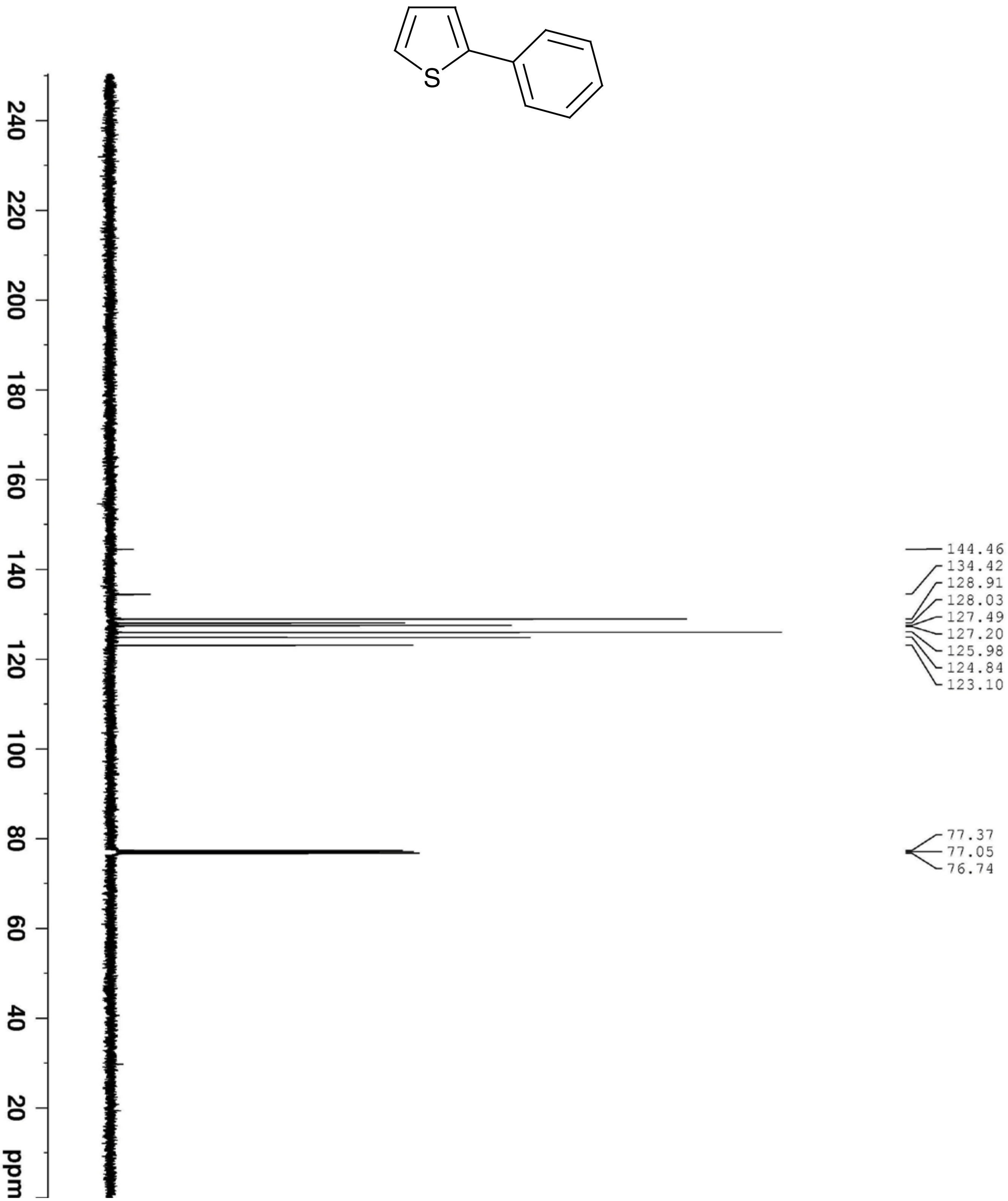

N
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
0.90
0.90
1.06
2.00
1.01
1.96
8.880
8.611
7.906
7.900
7.895
7.886
7.880
7.878
7.526
7.504
7.400
7.387
7.377
7.365
7.331
7.313
7.292


N
240
220
200
180
160
140
120
100
80
60
40
20
ppm
150.52
148.20
138.12
136.71
134.97
134.25
129.88
127.05
123.62
77.41
77.10
76.78
21.24

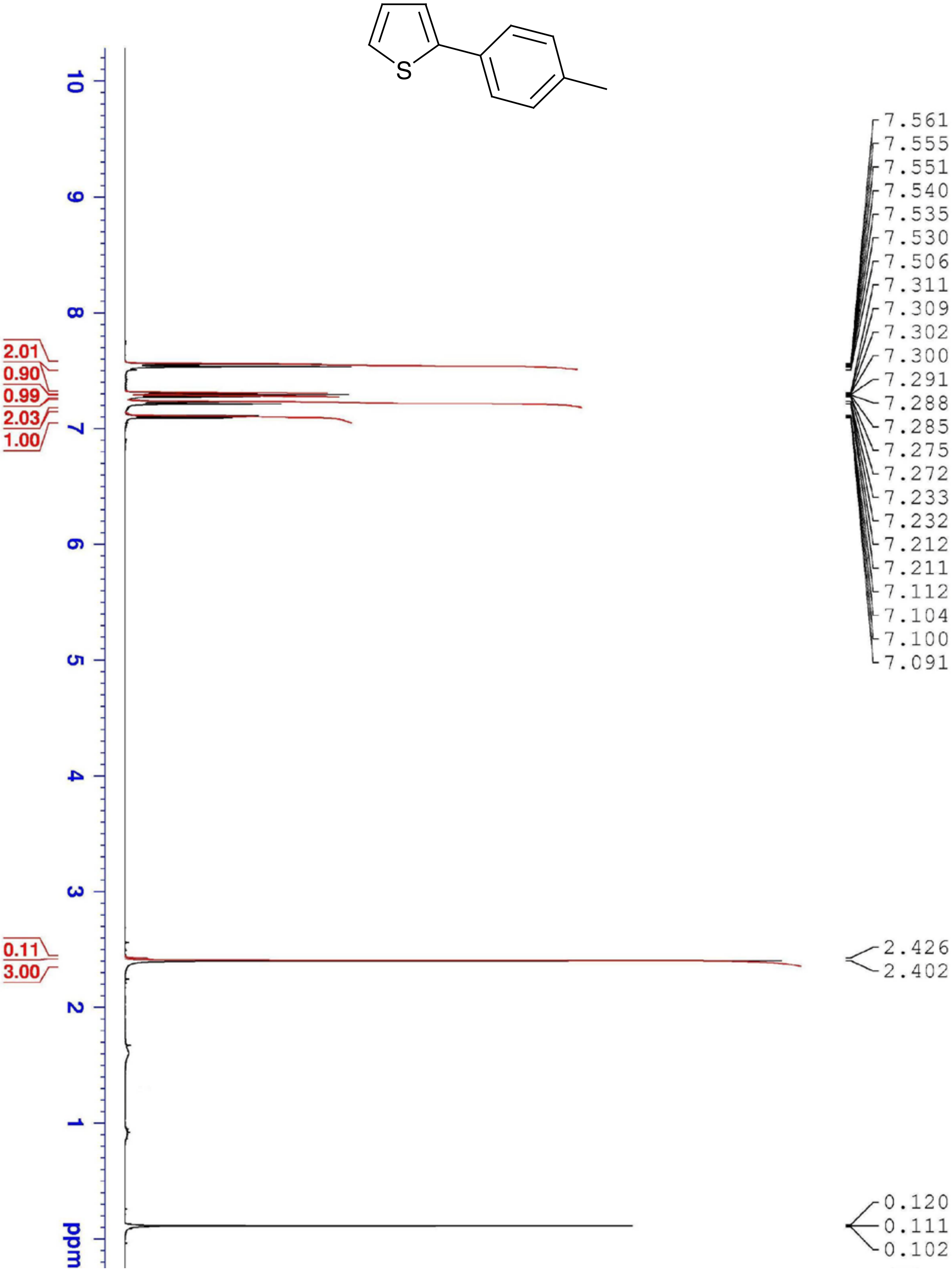
2-Phenylthiophene

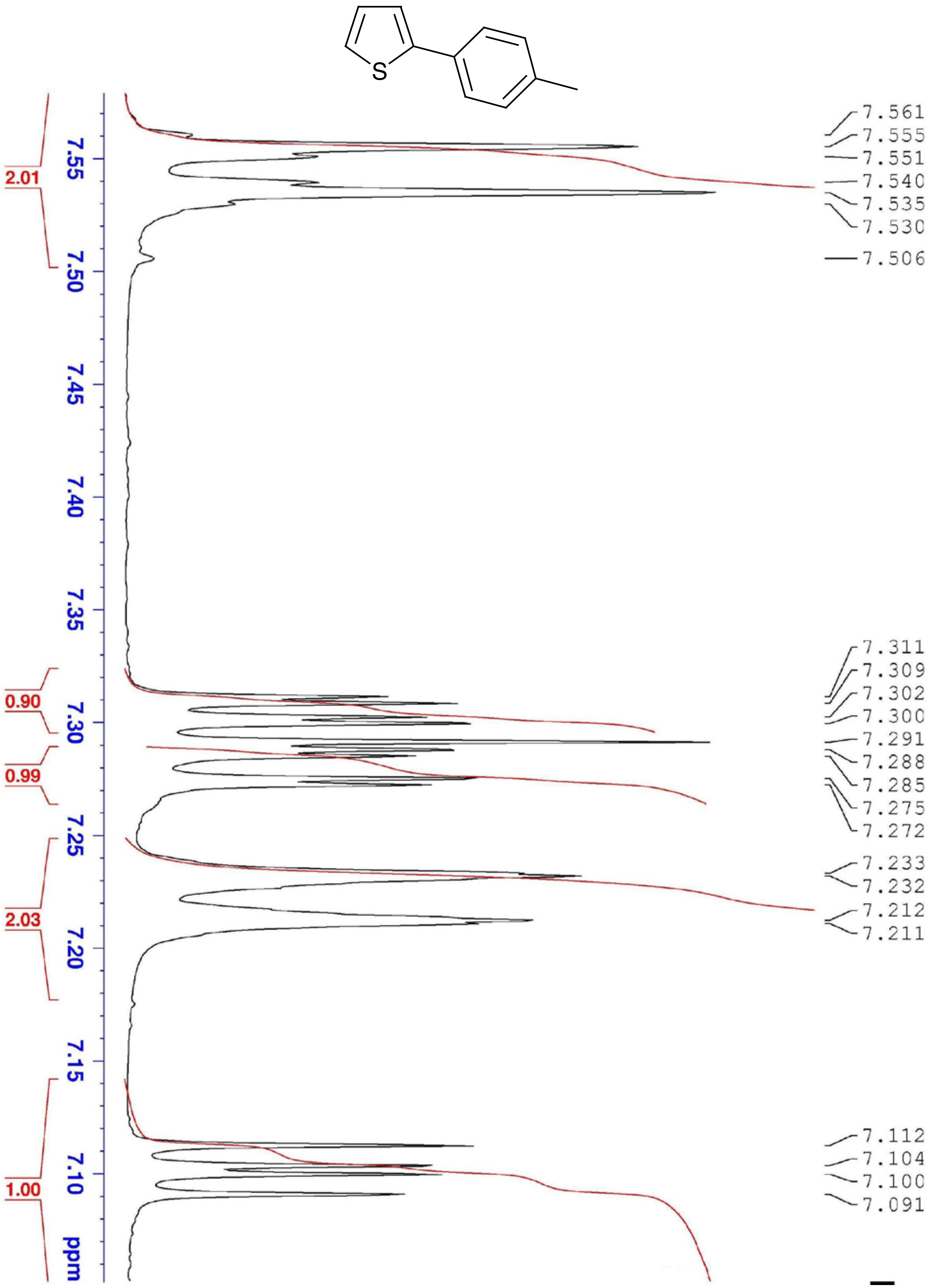


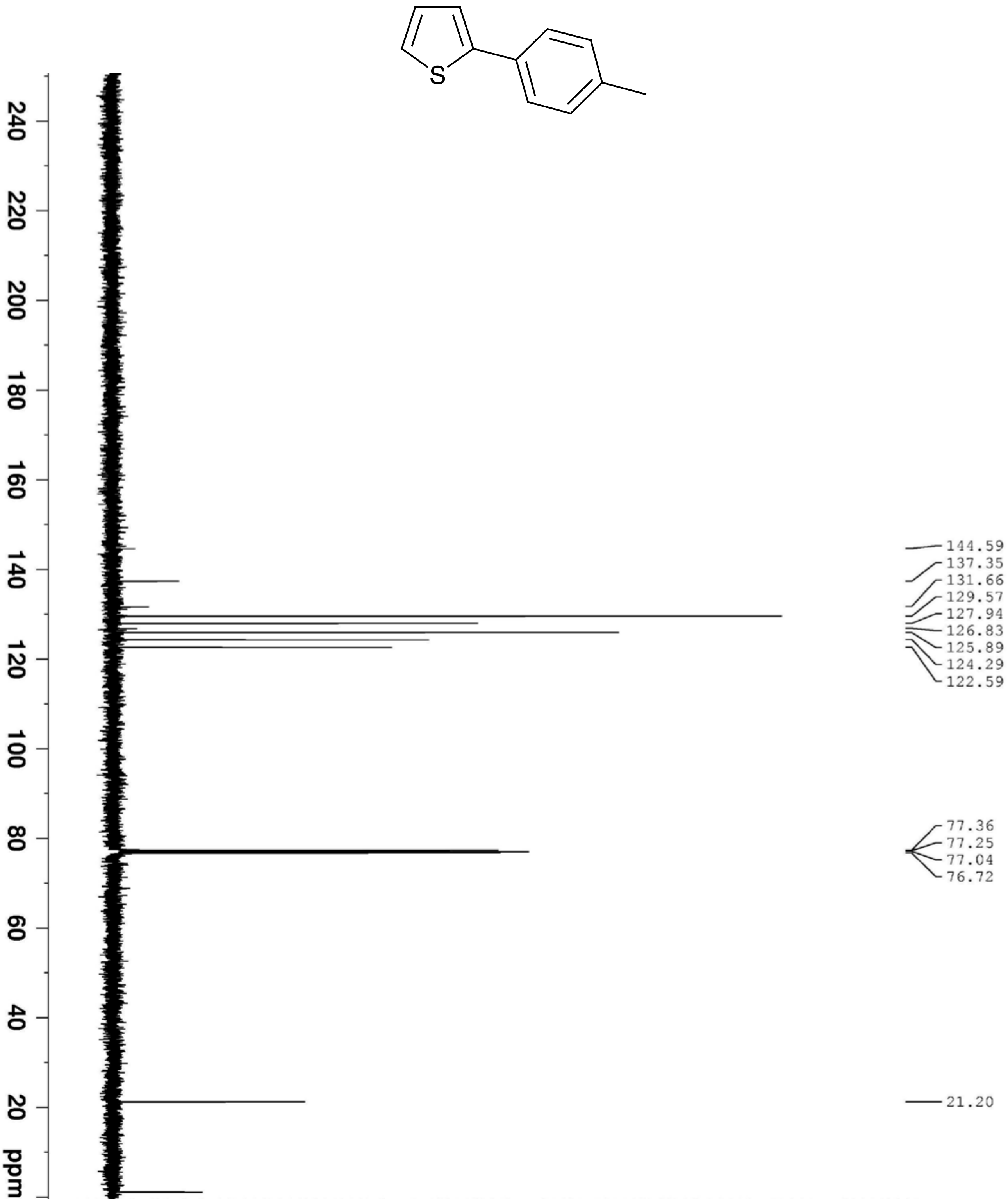

S
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
ppm
2.00
2.01
0.93
2.00
1.00
7.673
7.670
7.665
7.654
7.652
7.649
7.644
7.638
7.633
7.445
7.442
7.440
7.436
7.422
7.419
7.406
7.402
7.398
7.377
7.374
7.364
7.361
7.355
7.352
7.344
7.341
7.338
7.329
7.326
7.322
7.316
7.313
7.307
7.304
7.301
7.291
7.136
7.127
7.123
7.114


S
240
220
200
180
160
140
120
100
80
60
40
20
ppm
144.46
134.42
128.91
128.03
127.49
127.20
125.98
124.84
123.10
77.37
77.05
76.74

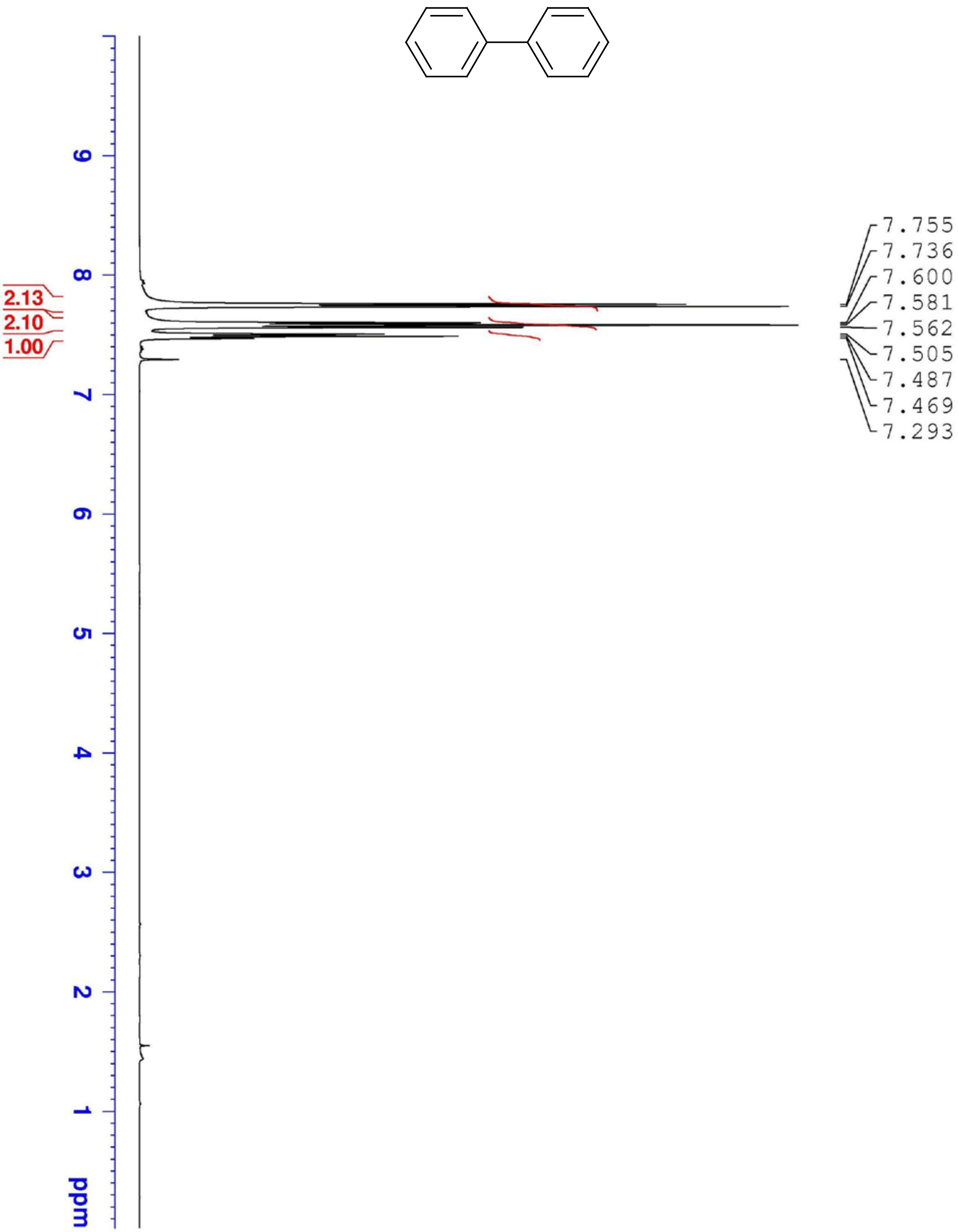
2-(4-Methylphenyl)thiophene

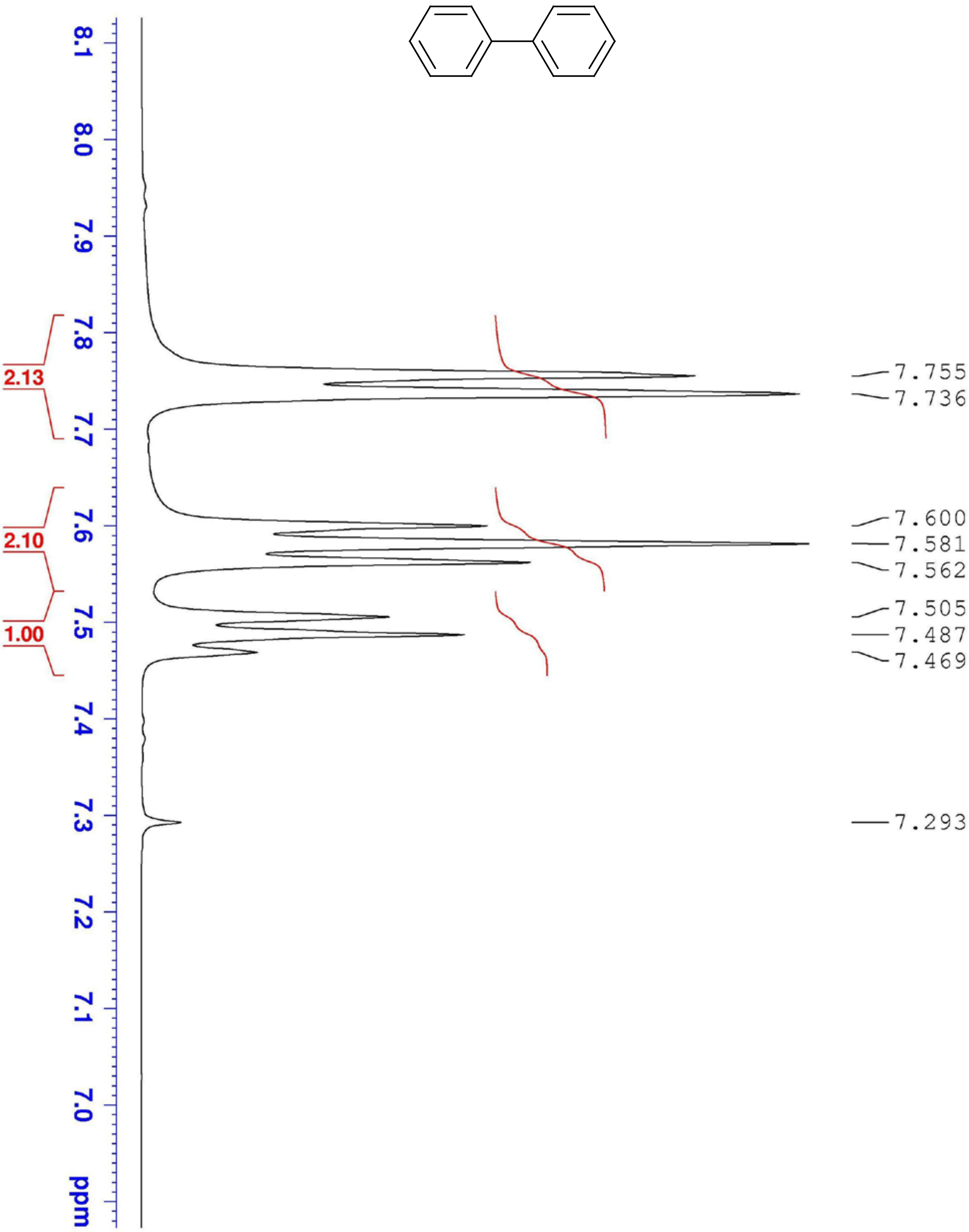


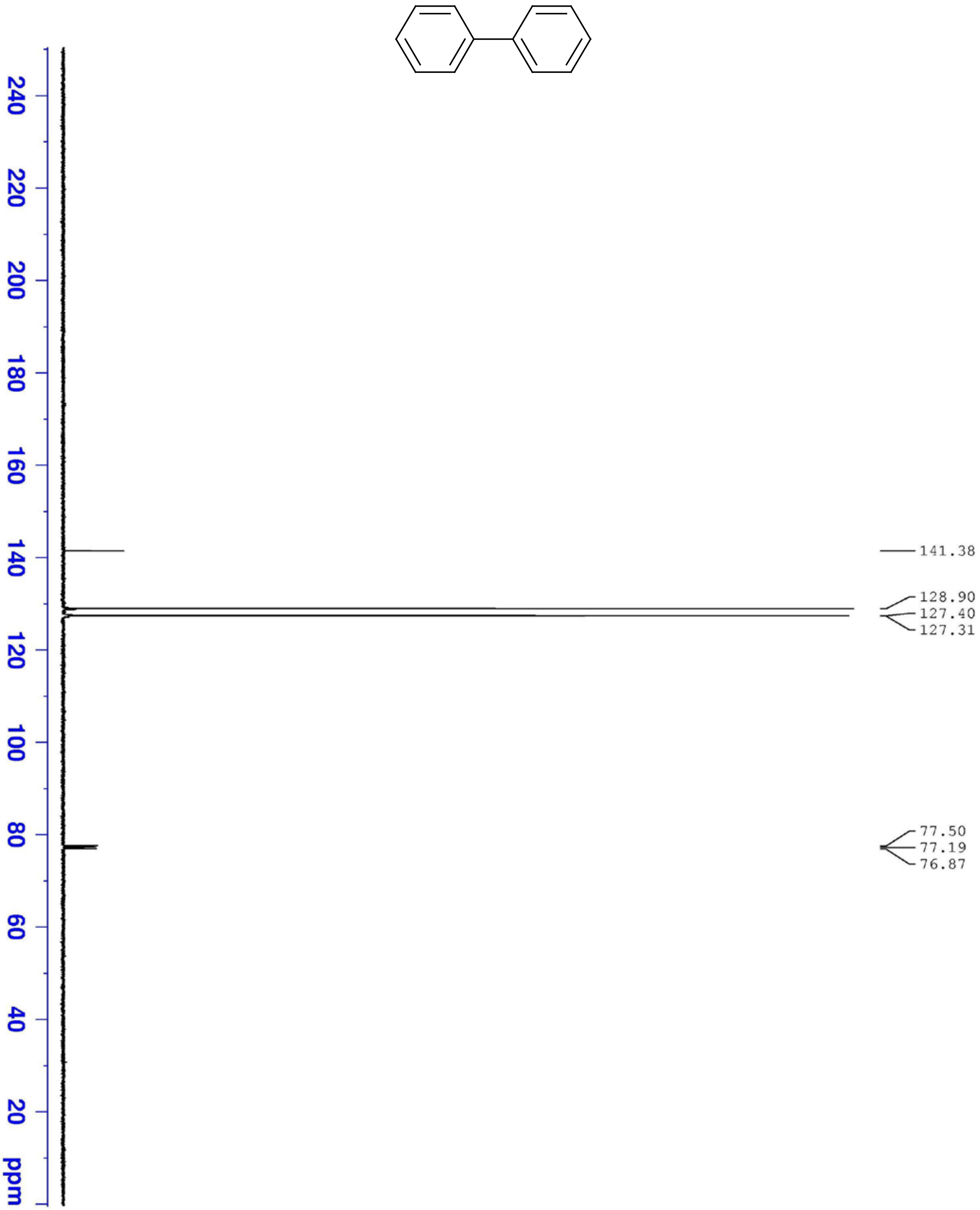

S
7.561
7.555
7.551
7.540
7.535
7.530
7.506
7.311
7.309
7.302
7.300
7.291
7.288
7.285
7.275
7.272
7.233
7.232
7.212
7.211
7.112
7.104
7.100
7.091
2.01
0.90
0.99
2.03
1.00
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
ppm


S
240
220
200
180
160
140
120
100
80
60
40
20
ppm
144.59
137.35
131.66
129.57
127.94
126.83
125.89
124.29
122.59
77.36
77.25
77.04
76.72
21.20

Biphenyl


9
8
7
6
5
4
3
2
1
ppm
2.13
2.10
1.00
7.755
7.736
7.600
7.581
7.562
7.505
7.487
7.469
7.293


7.755
7.736
7.600
7.581
7.562
7.505
7.487
7.469
7.293
2.13
2.10
1.00
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm


240
220
200
180
160
140
120
100
80
60
40
20
ppm
141.38
128.90
127.40
127.31
77.50
77.19
76.87