Supplementary Information

Copper promoted synthesis of tetrazoles and further conversion into diaryl tetrazoles through *C-N* cross-coupling approach

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General Information: Aniline, CS_2, $CuSO_4 \cdot 5H_2O$ (98%), CuI (98%), CuBr (98%), Cu_2O (97%), $CuBr_2$ (99%), $CuCl_2 \cdot 2H_2O$ (99%) and $Cu(OAc)_2 \cdot H_2O$ (98%), Et_3N, Pyridine, sodium bicarbonate, NH_3 and NaN_3 were purchased from Aldrich and used without further purification. The solvents were purchased and dried according to standard procedure prior to use. ^{1}H NMR (400MHz) spectra were recorded with a Varian 400 spectrometer. Infrared (IR) spectra recorded on a Perkin Elmer Spectrum one FT-IR spectrometer. VKSI Medico Centrifuge machine was used for our experimental procedure for the synthesis of Tetrazoles. Isothiocyanates were prepared by using our previous reported procedure.

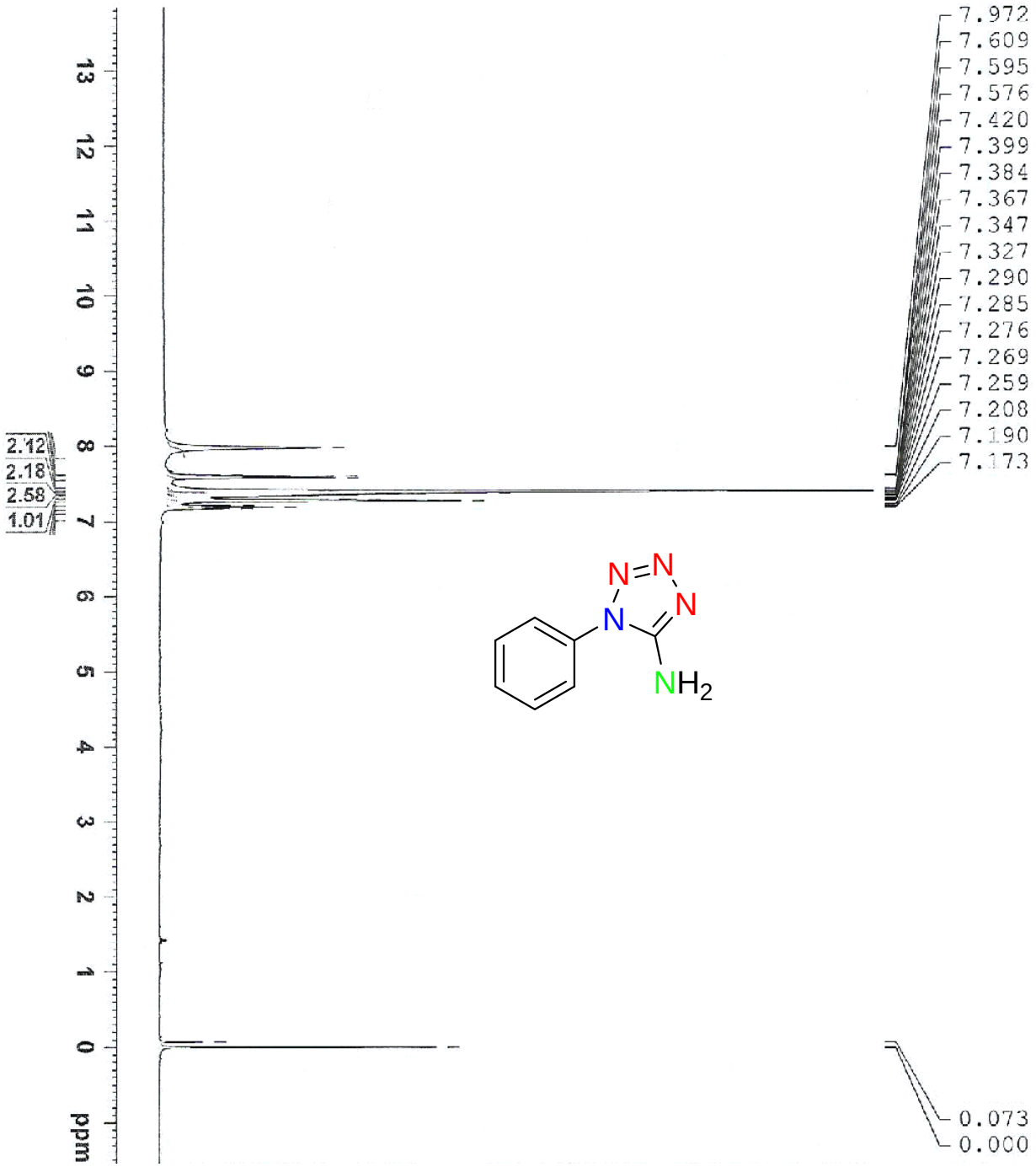
General Procedure for the Synthesis of Phenyl Tetrazoleamine

To a stirred solution of DMSO (4-5 ml)), Phenyl isothiocyanate (2 mmol, 270 mg) was added in slowly and followed by Ammonia (2 ml) was added at room temperature. The whole reaction mixture stirred for one hour at room temperature. Thiourea formation was monitored by TLC. To this, $Cu(OAc)_2.H_2O$ (50 mol %, 125 mg) and $NaHCO_3$ (2 mmol, 168 mg) were added slowly for 5 min and the reaction mixture stirred for 1 hr. During this period, a black color precipitate was

observed and to that reaction mixture sodium azide (2 mmol, 130 mg). Then the reaction mixture stirred for 1 hr. The progress of the reaction was investigated by TLC (30% ethylacetate in hexane). After finishing the reaction, the reaction mixture was transferred into centrifuged tubes and the mixture was centrifuged for 10 min by using centrifugation machine. Black color solid was settled in the bottom of centrifuged tubes. The resulted clear solution was washed with ethyl acetate (10 ml) and water (7 ml) for 3 times. And organic layer was concentrated by using rotary evaporator and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using 30% Ethylacetate in Hexane as eluent to obtain a Phenyl tetrazole amine as a target product, which was characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy analysis.

General Procedure for the Synthesis of diaryl Tetrazoleamine

Phenyl tetrazoleamine was dissolved in DMSO at room temperature. Later, CuI (20 mol %) was added to the prior solution and followed by 1,10-Phen (20 mol%), Cs_2CO_3 (2eq) were added at room temperature. Iodo benzene was incorporated in the previous solution at room temperature. Later, the whole reaction mixture was stirred at 90 ºC for 12 h. Resulting reaction mixture was washed with ethyl acetate (10 ml) and water (7 ml) for 3 to 4 times.Organic layer was concentrated by using rotary evaporator and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using 20% Ethylacetate in Hexane as eluent to obtain a diphenyl tetrazole amine as a target product, which was characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy analysis.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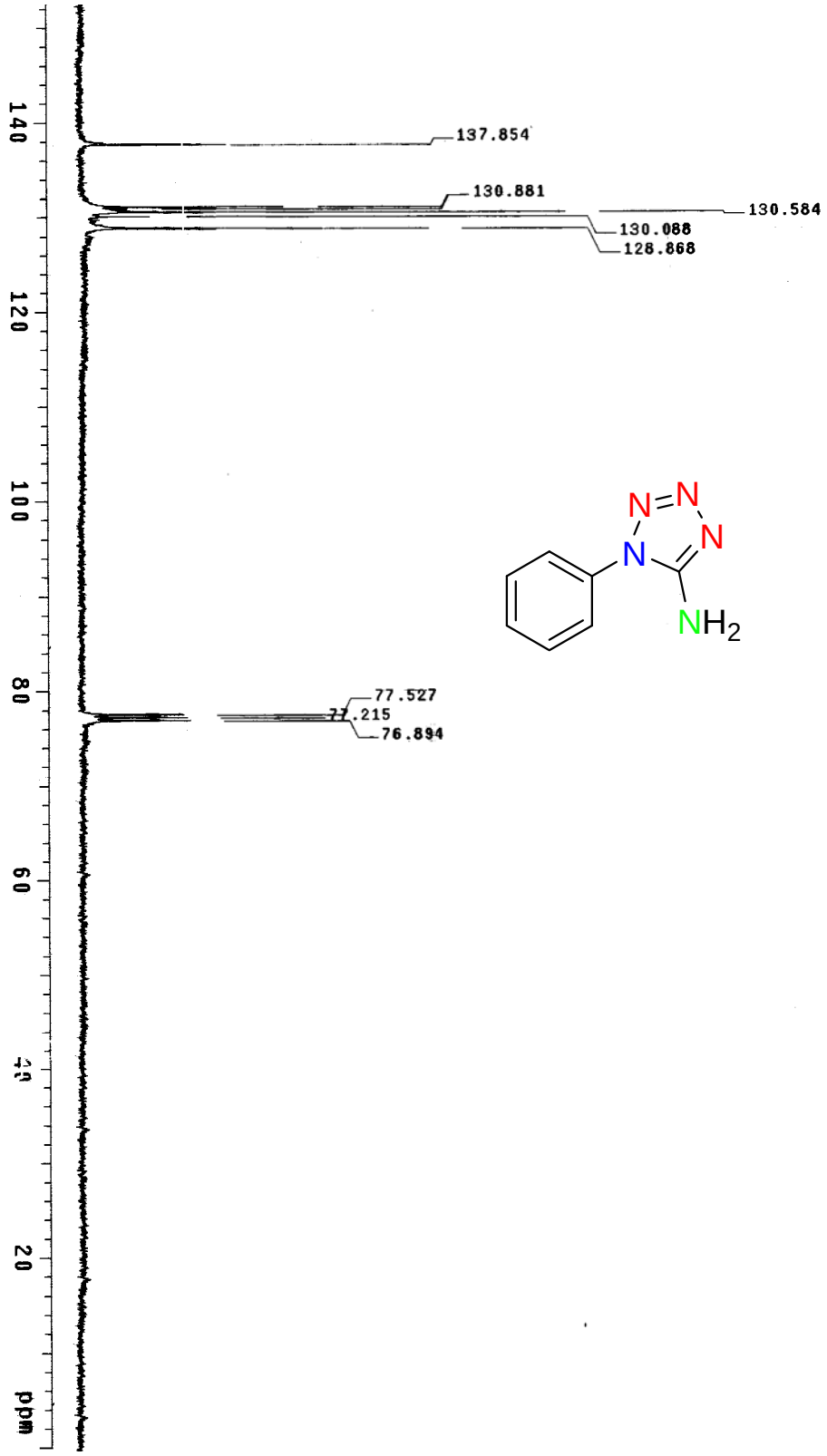
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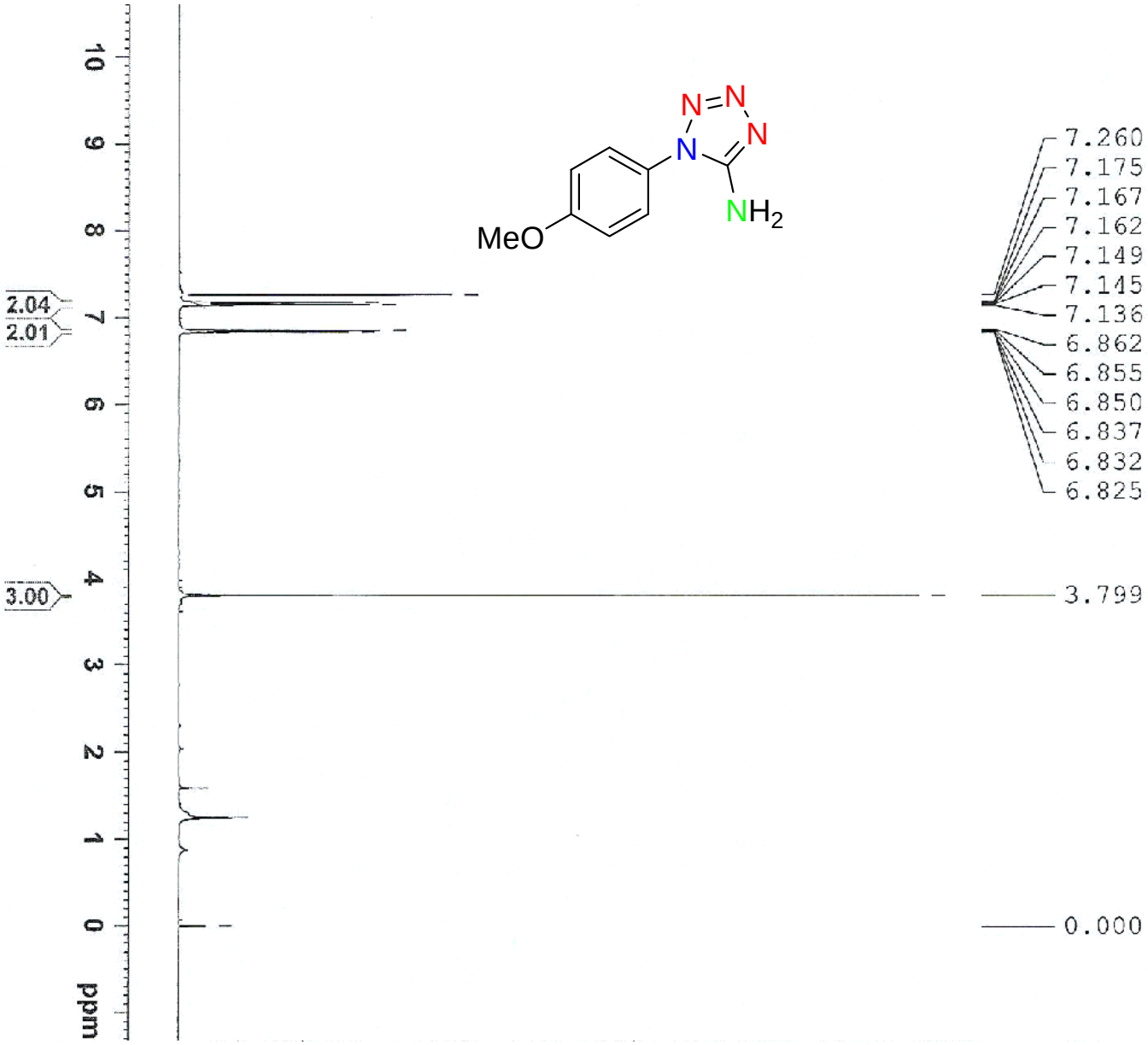
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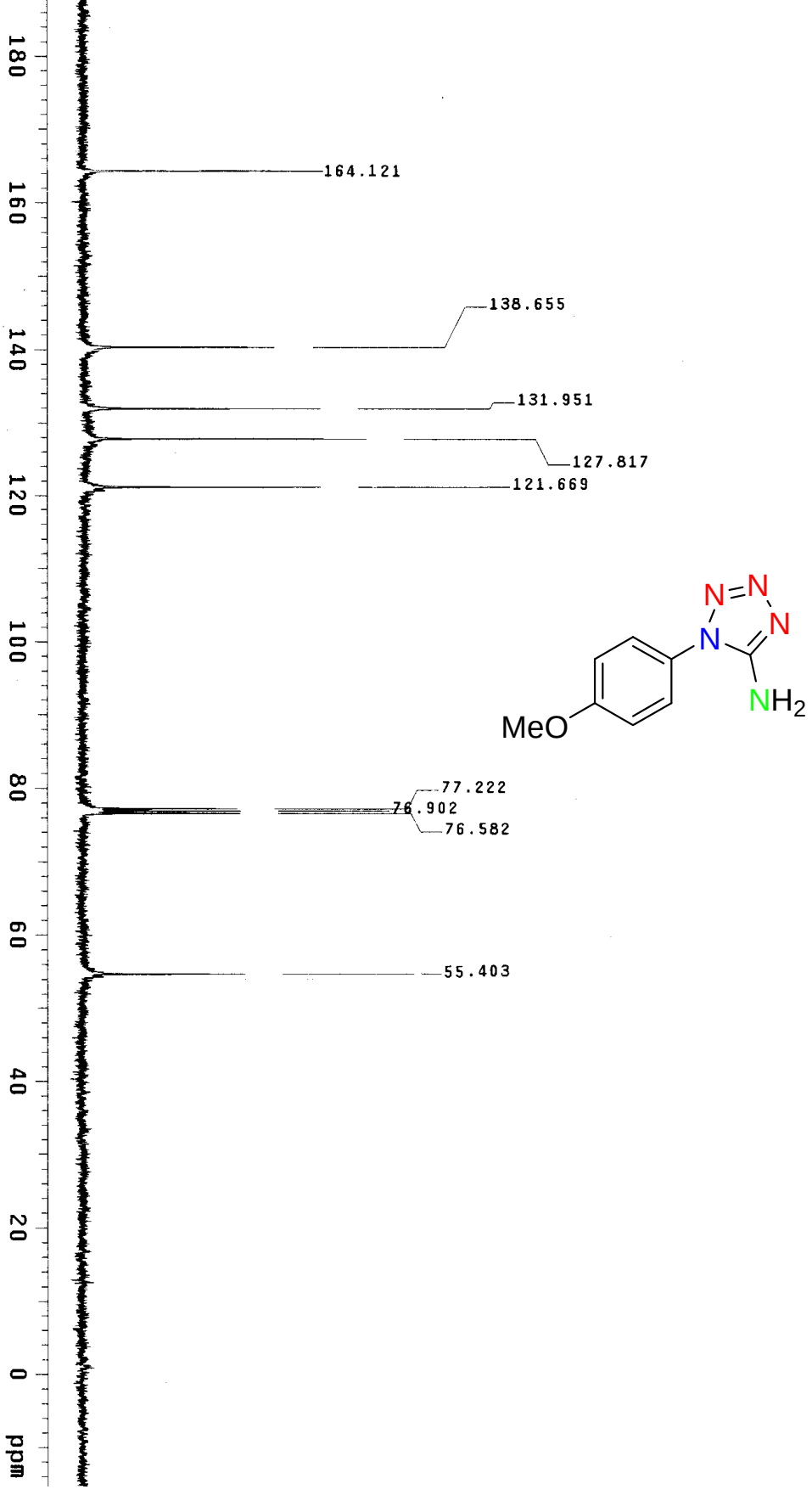
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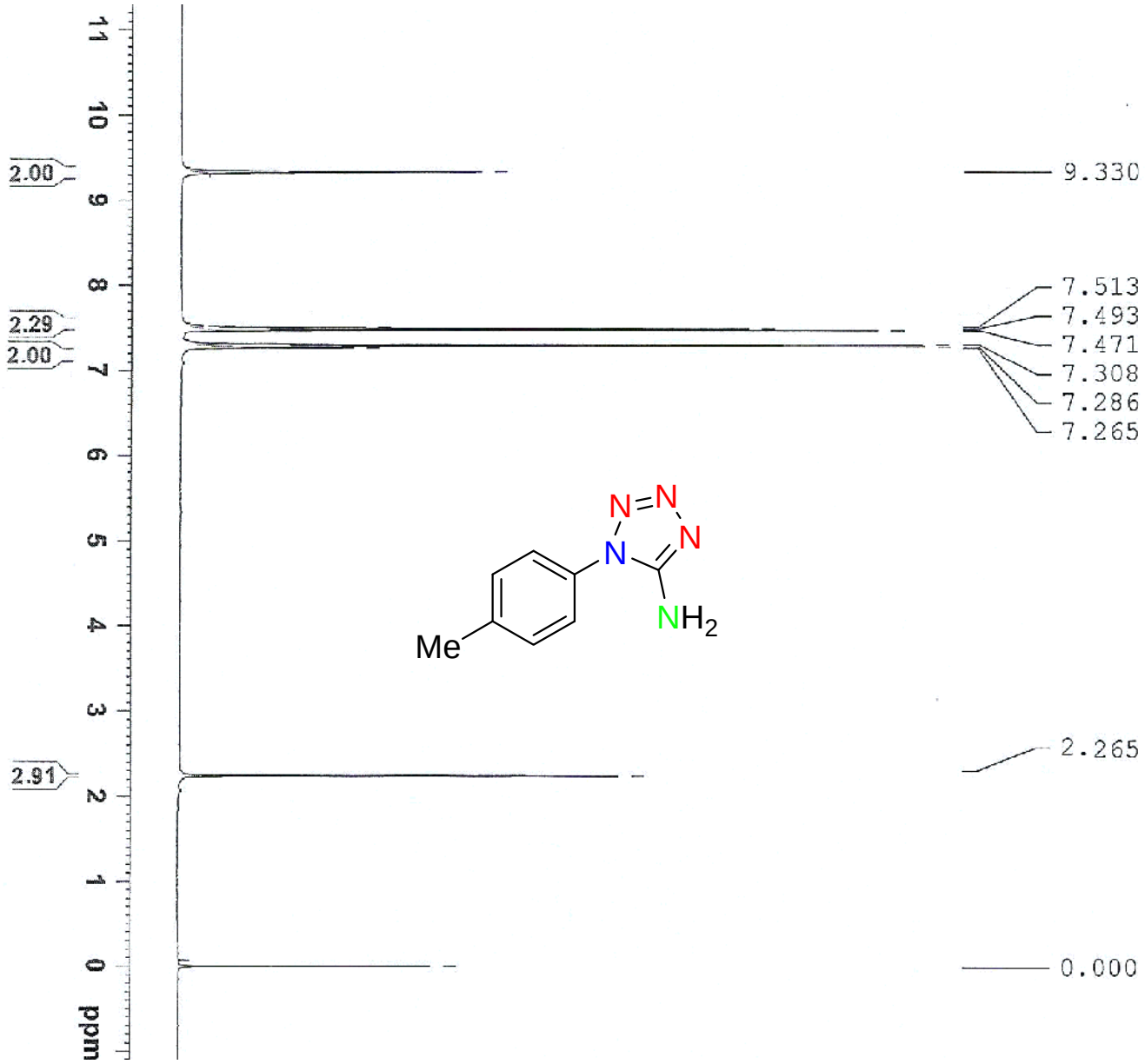
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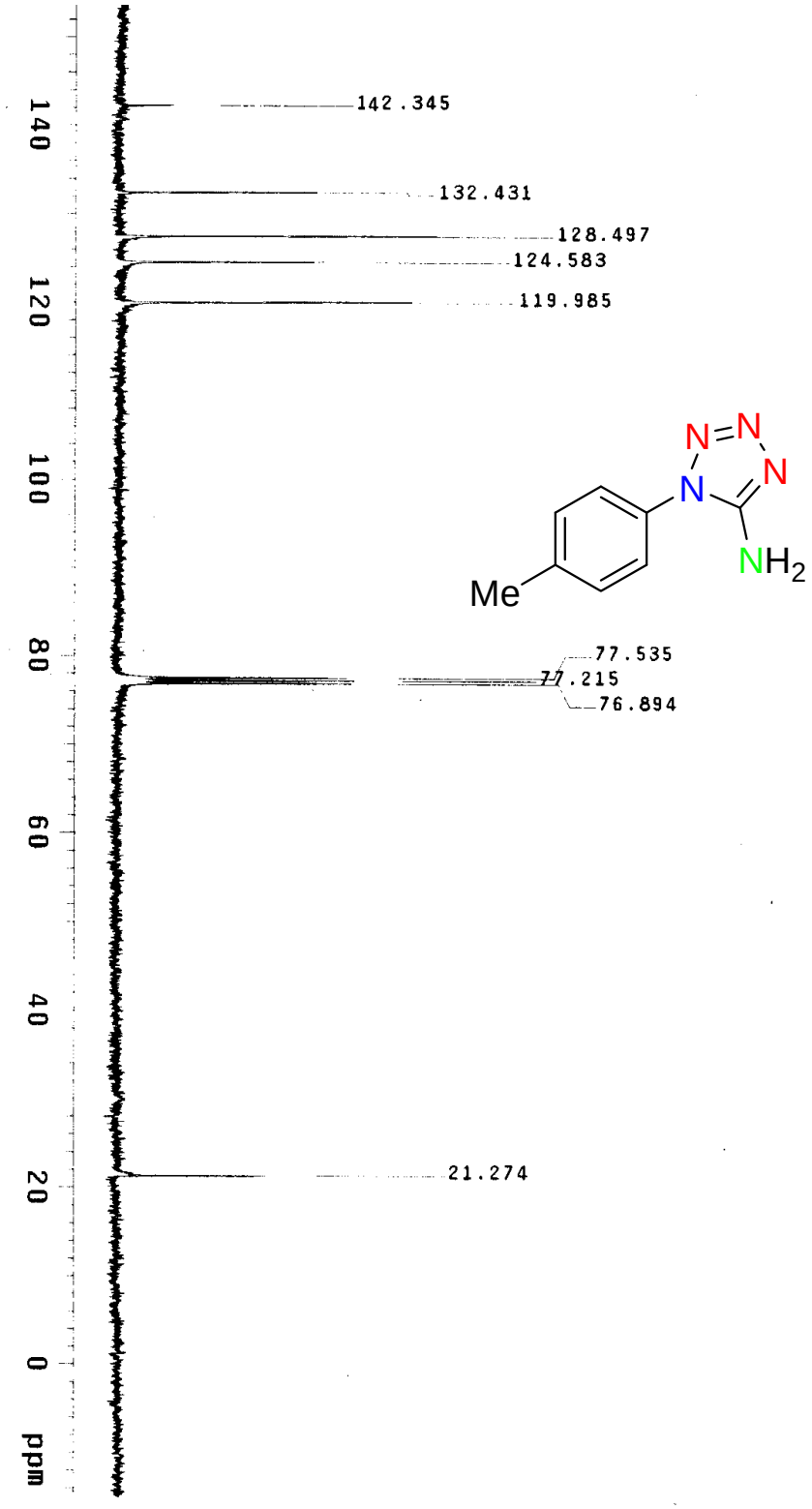
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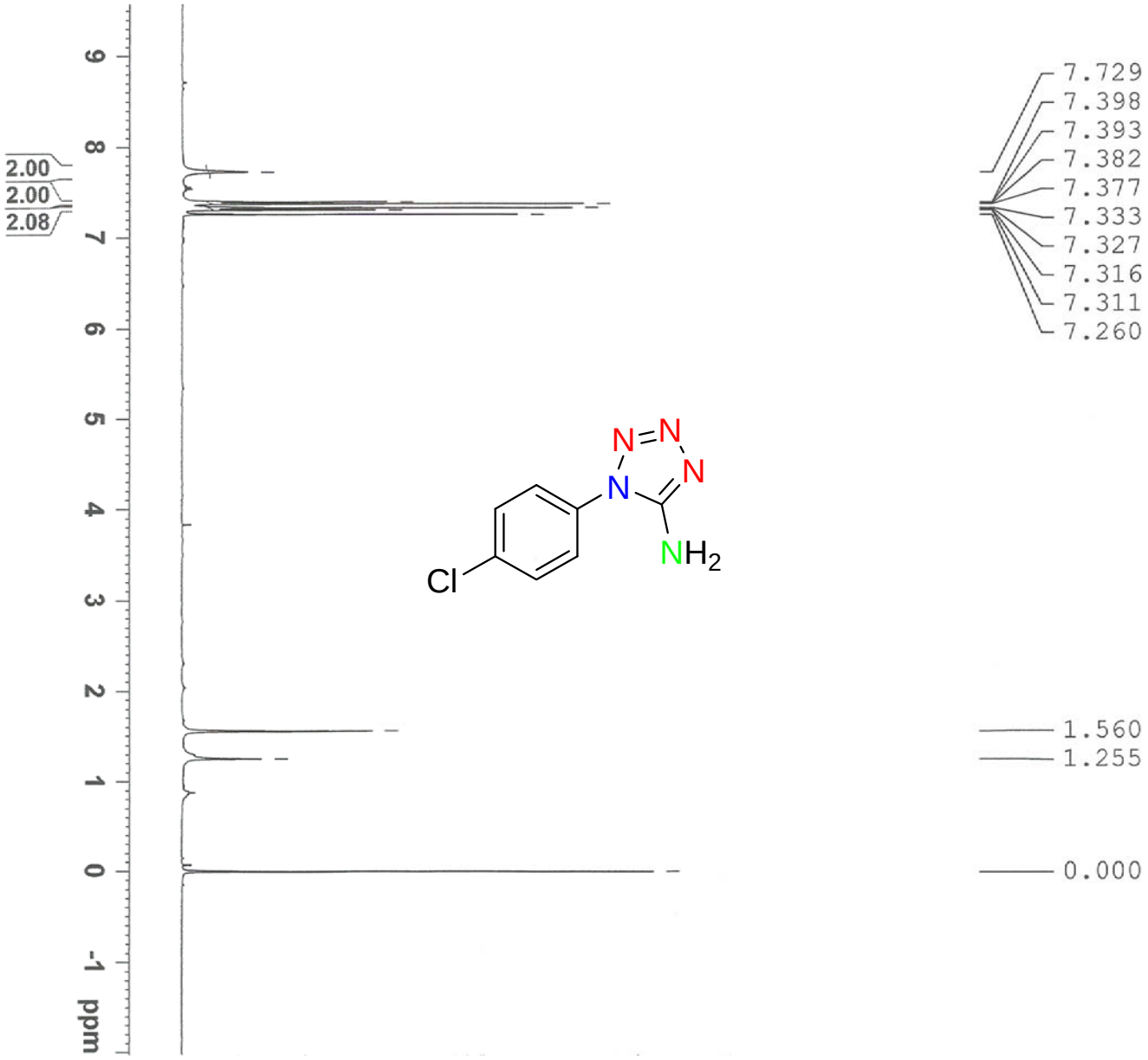
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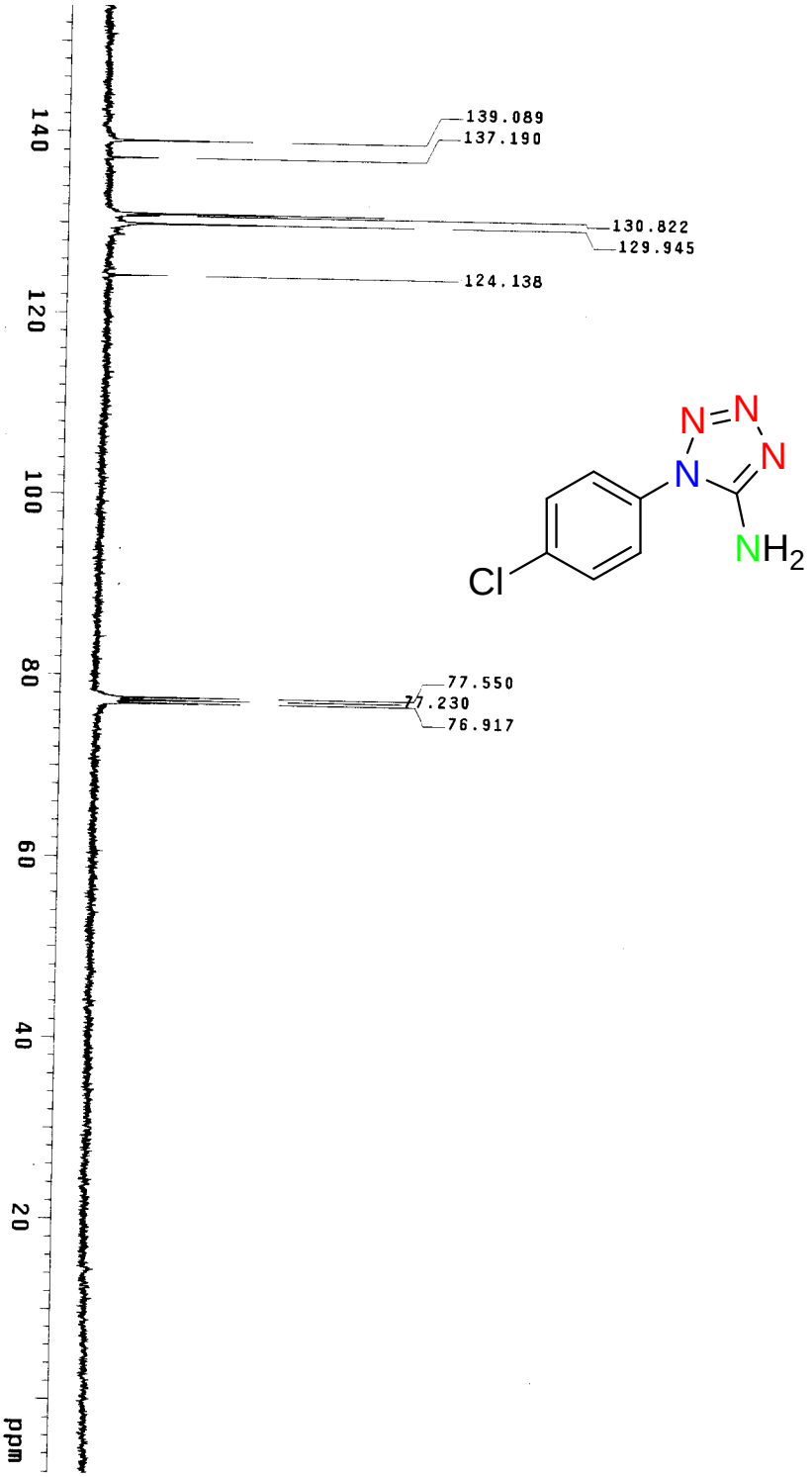
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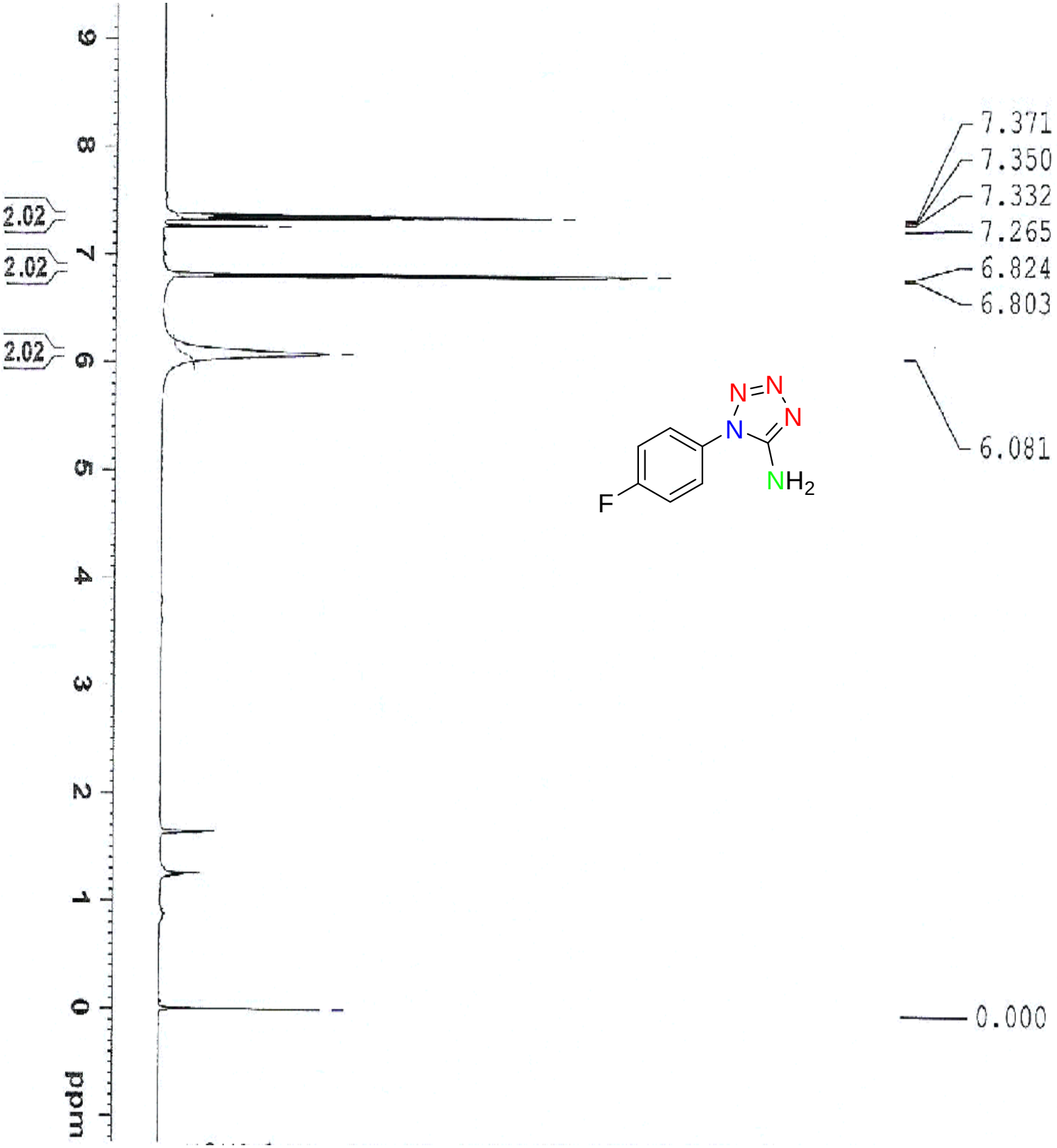
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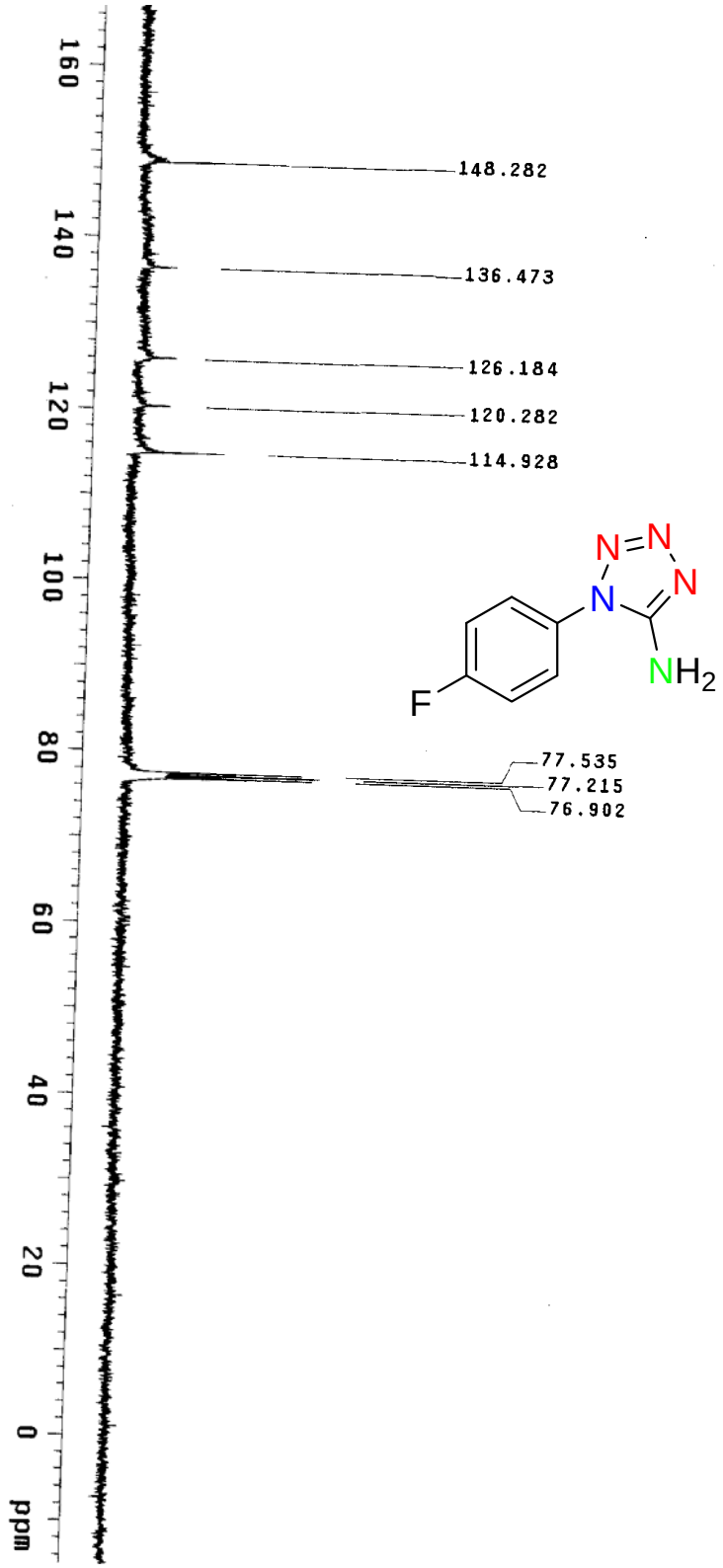
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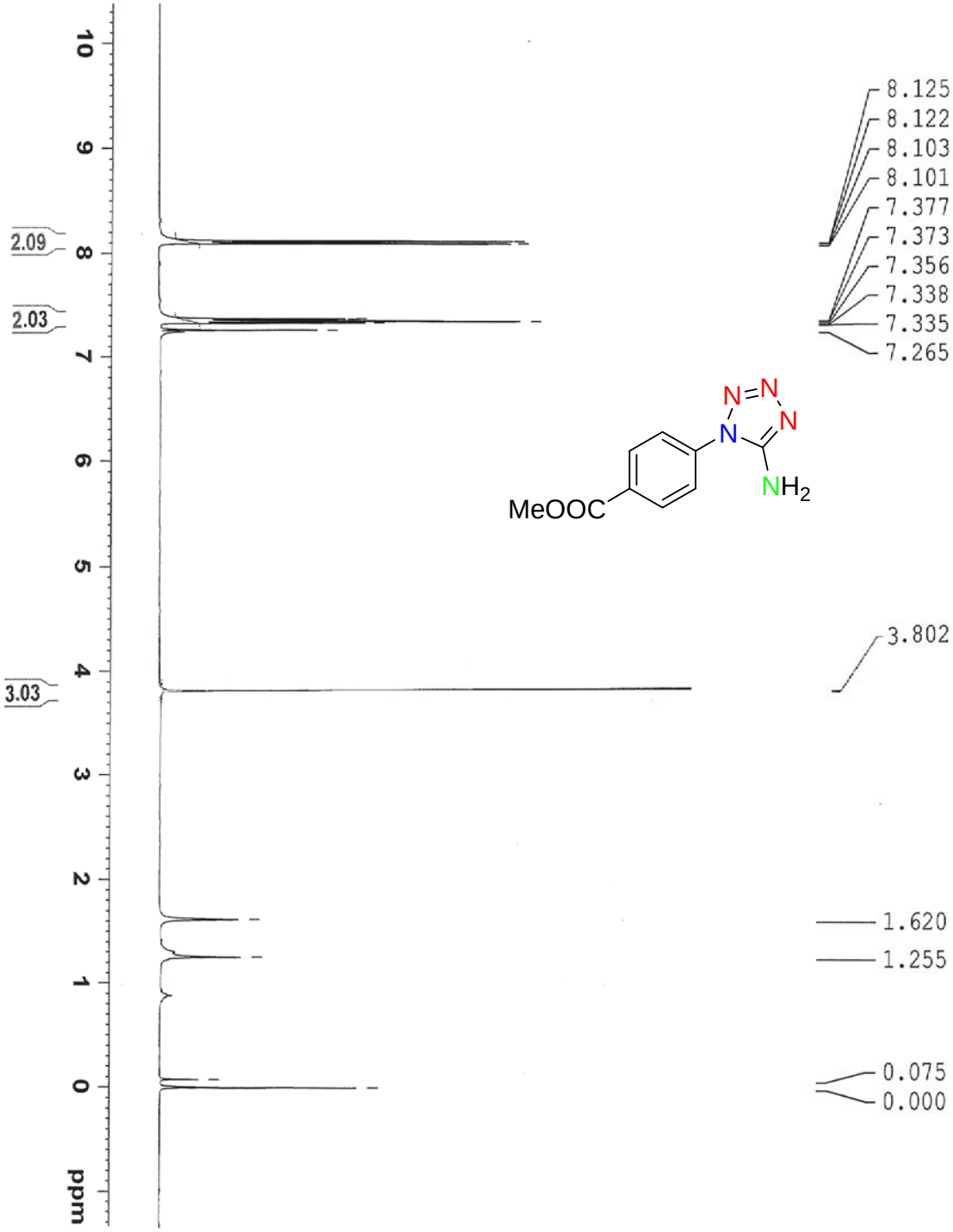
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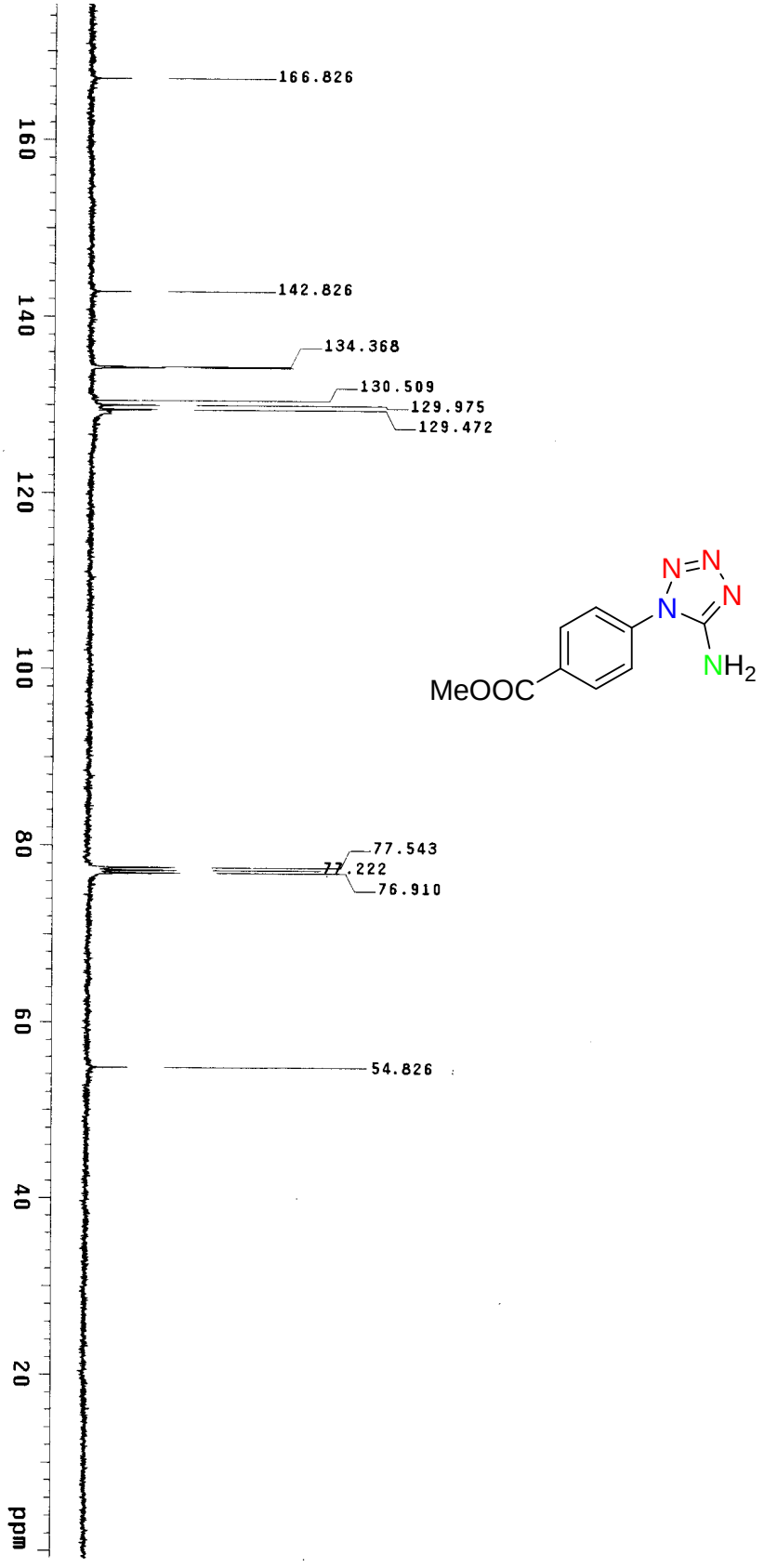
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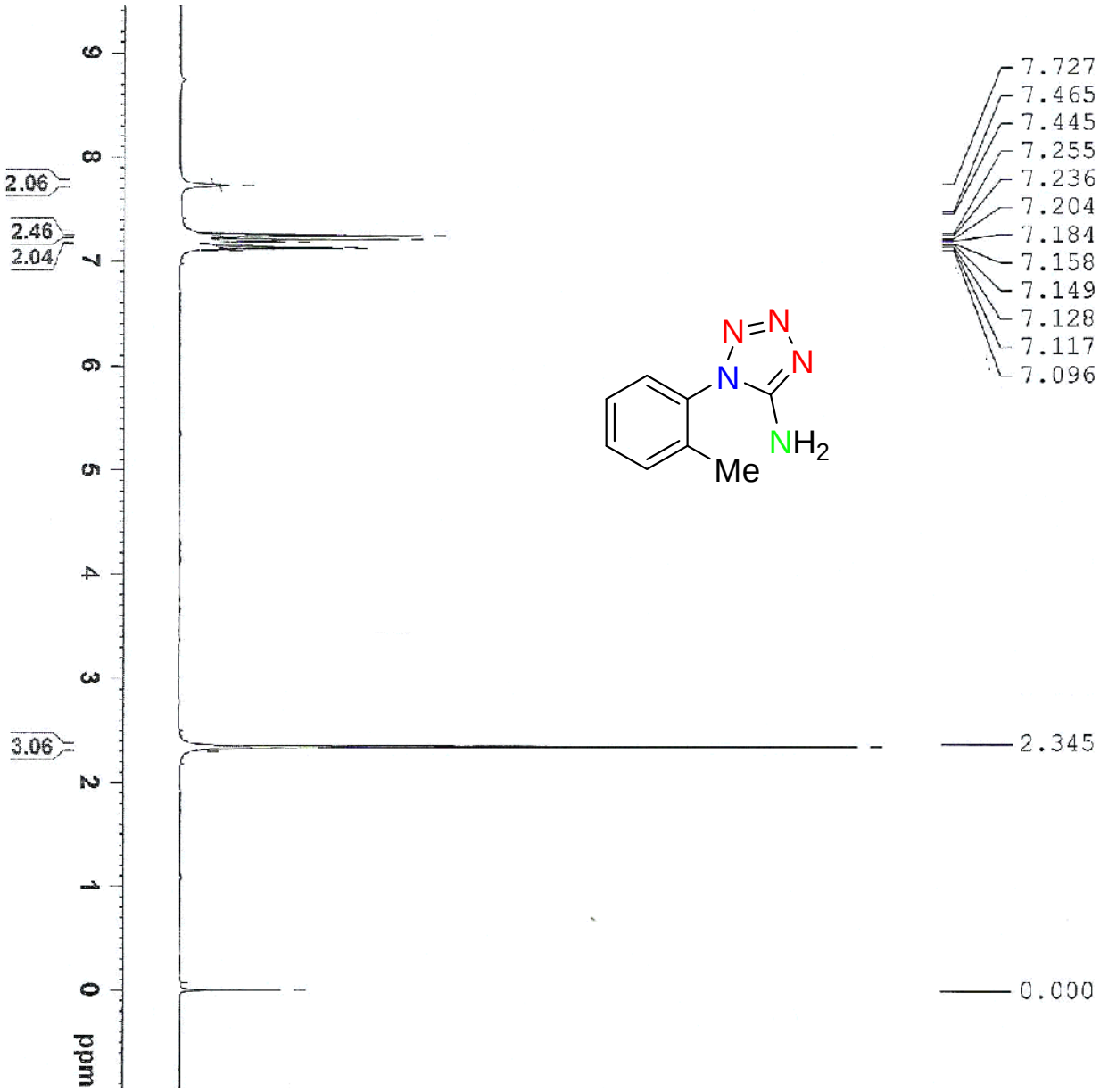
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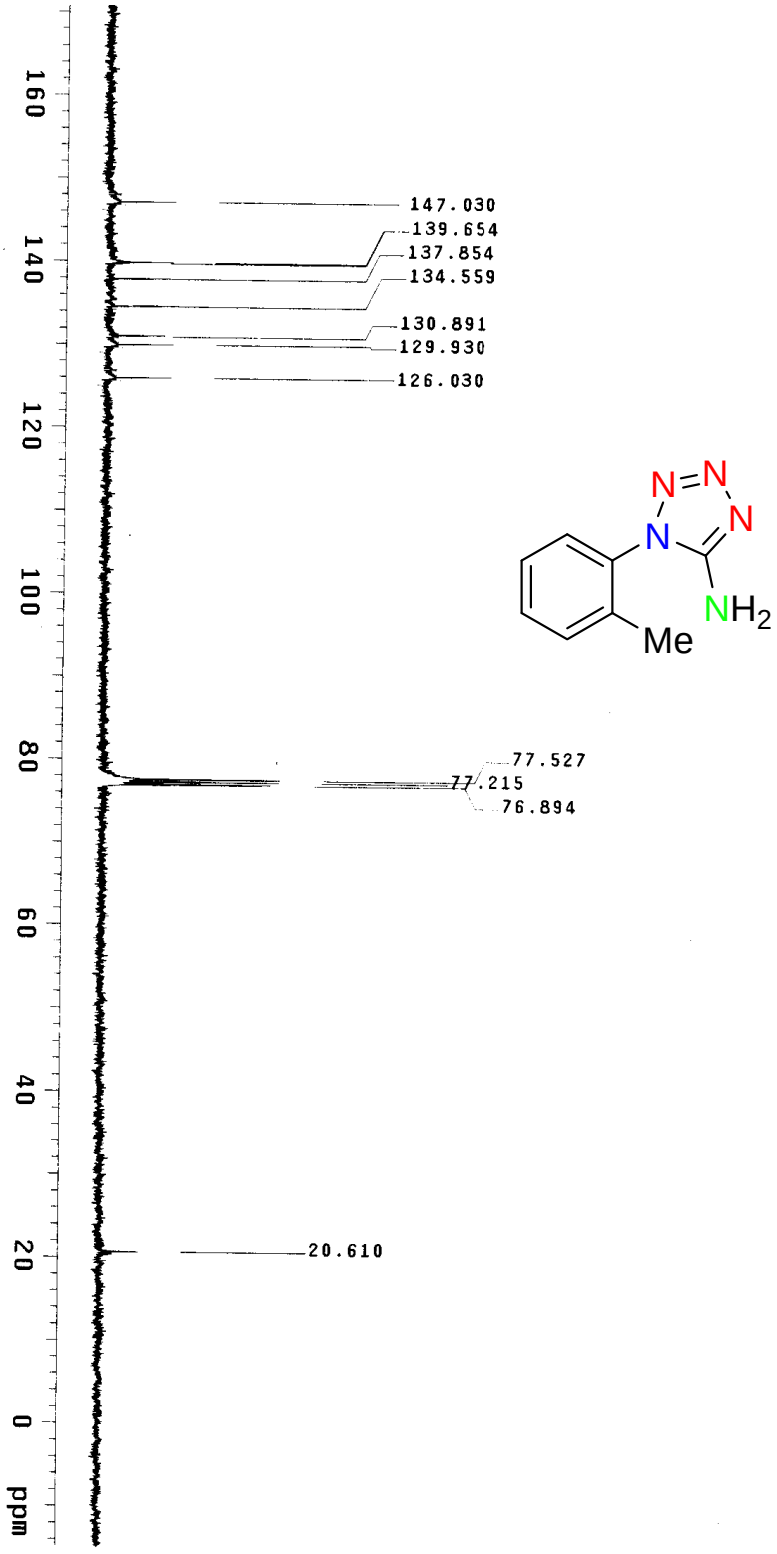
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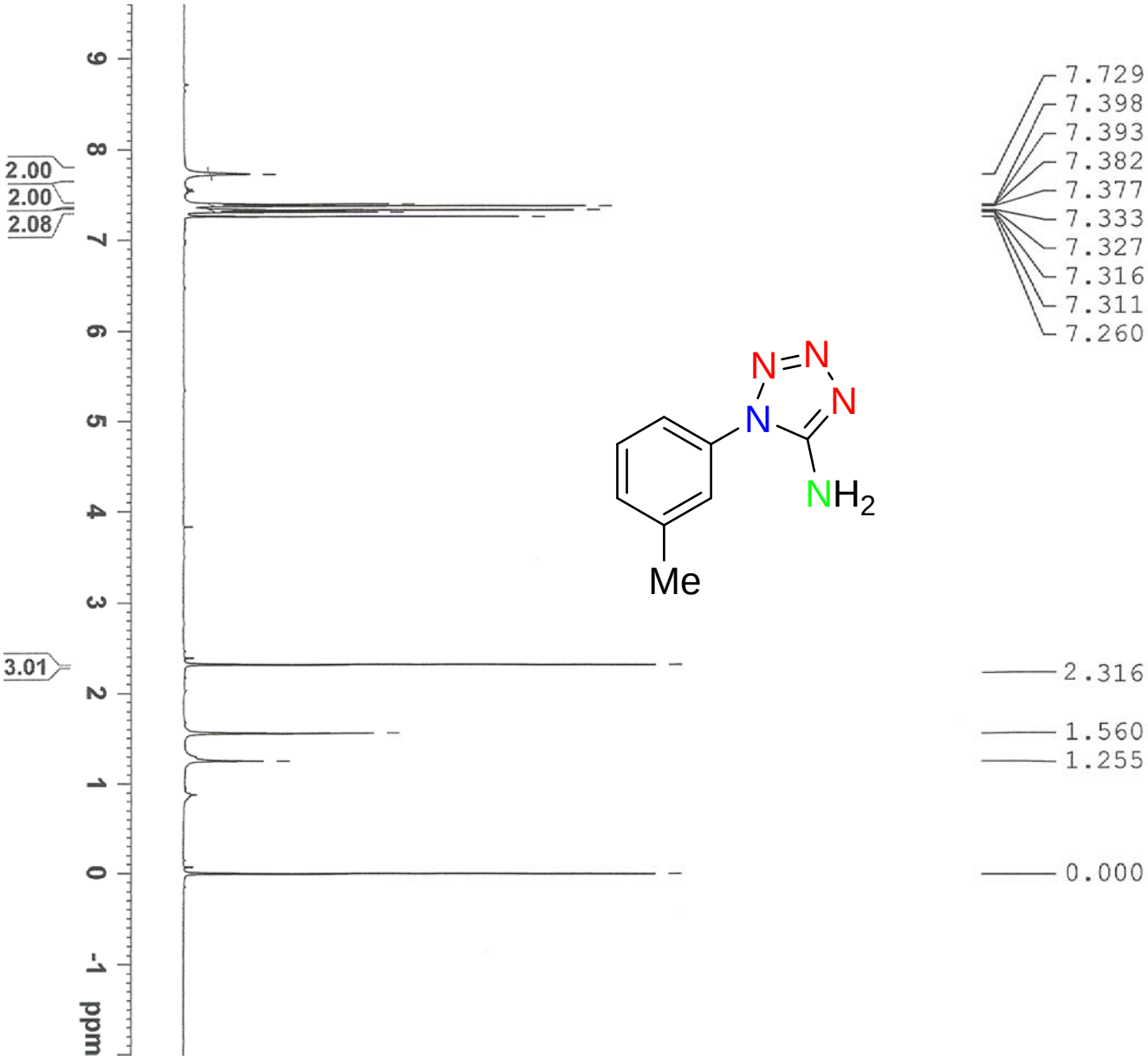
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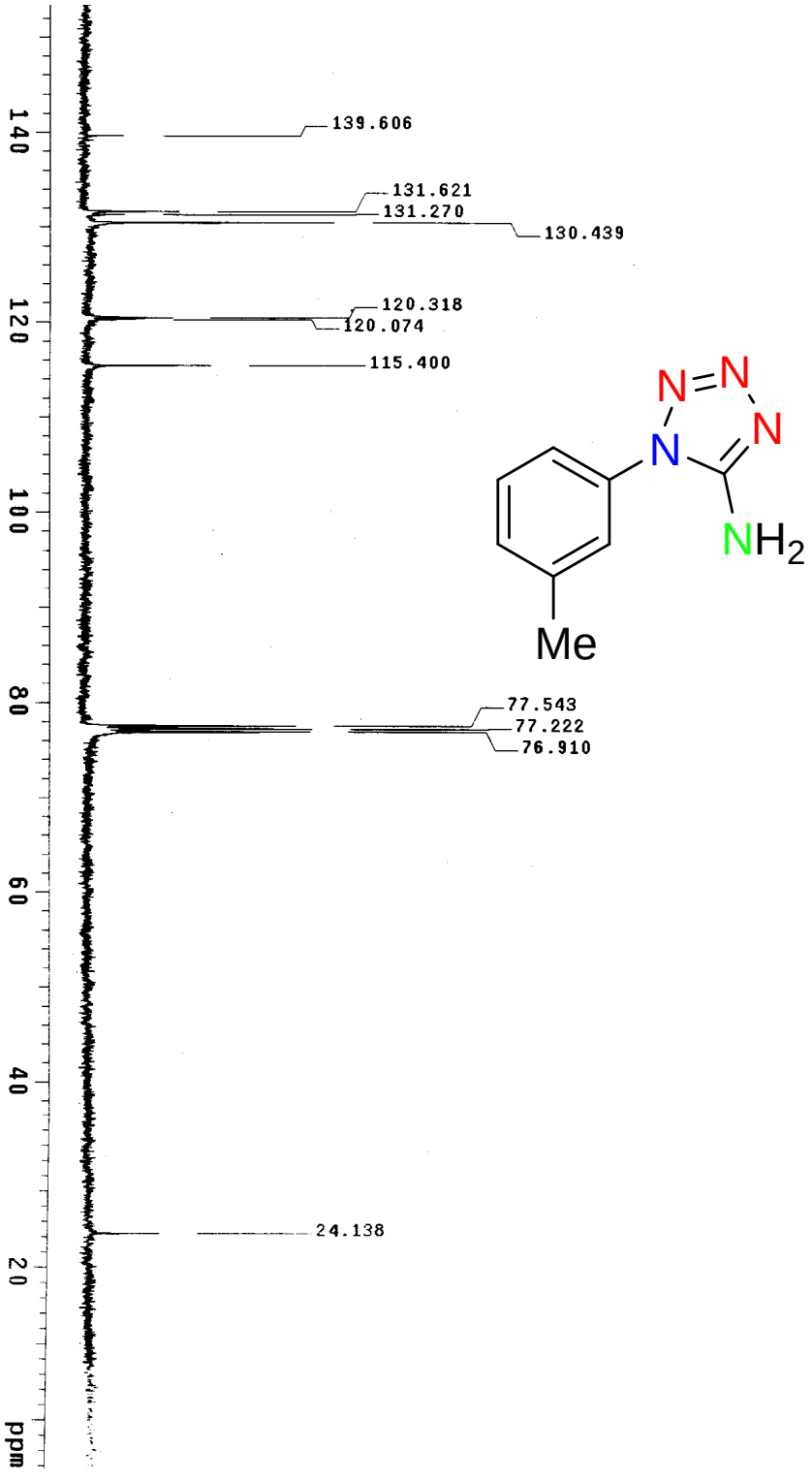
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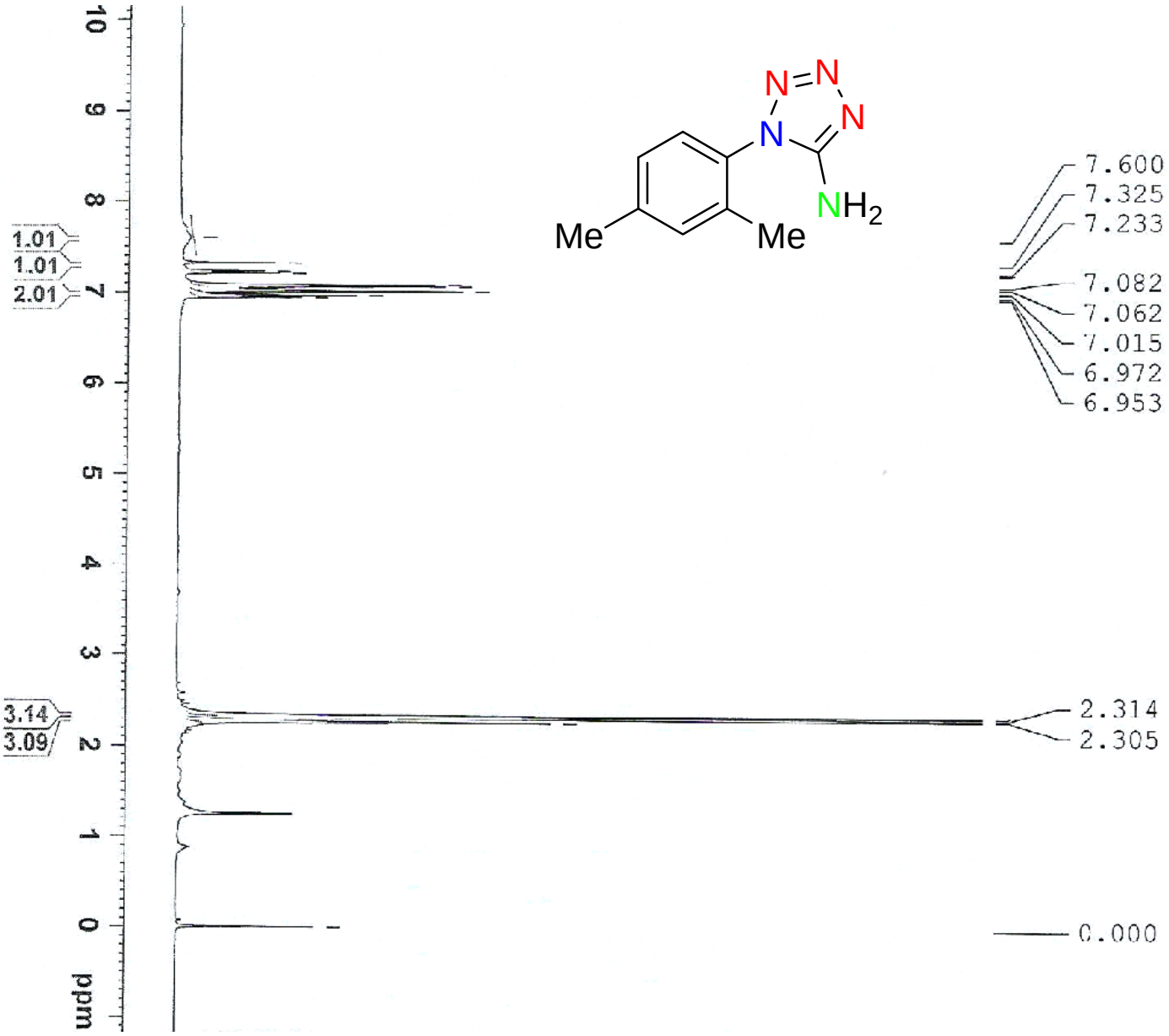
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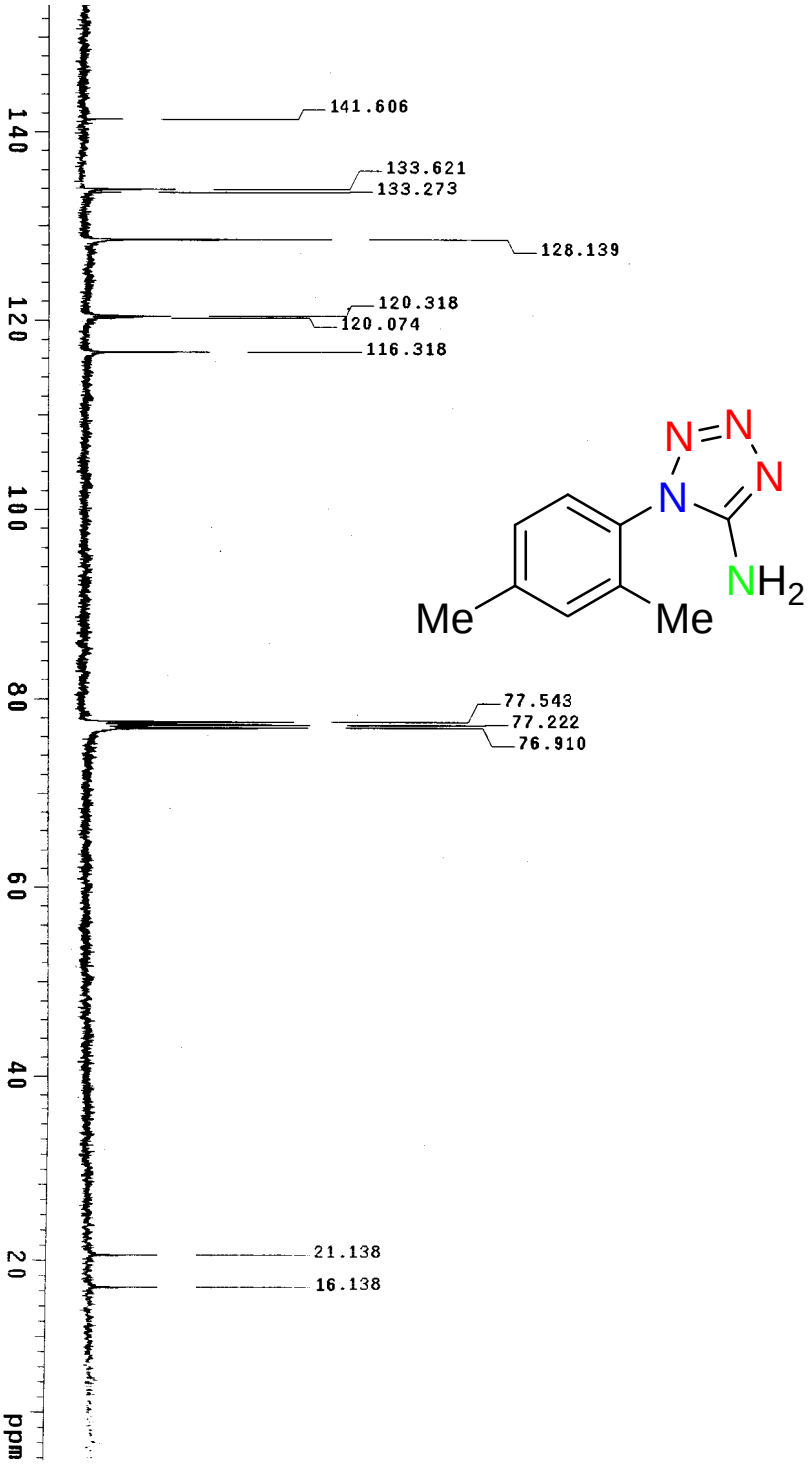
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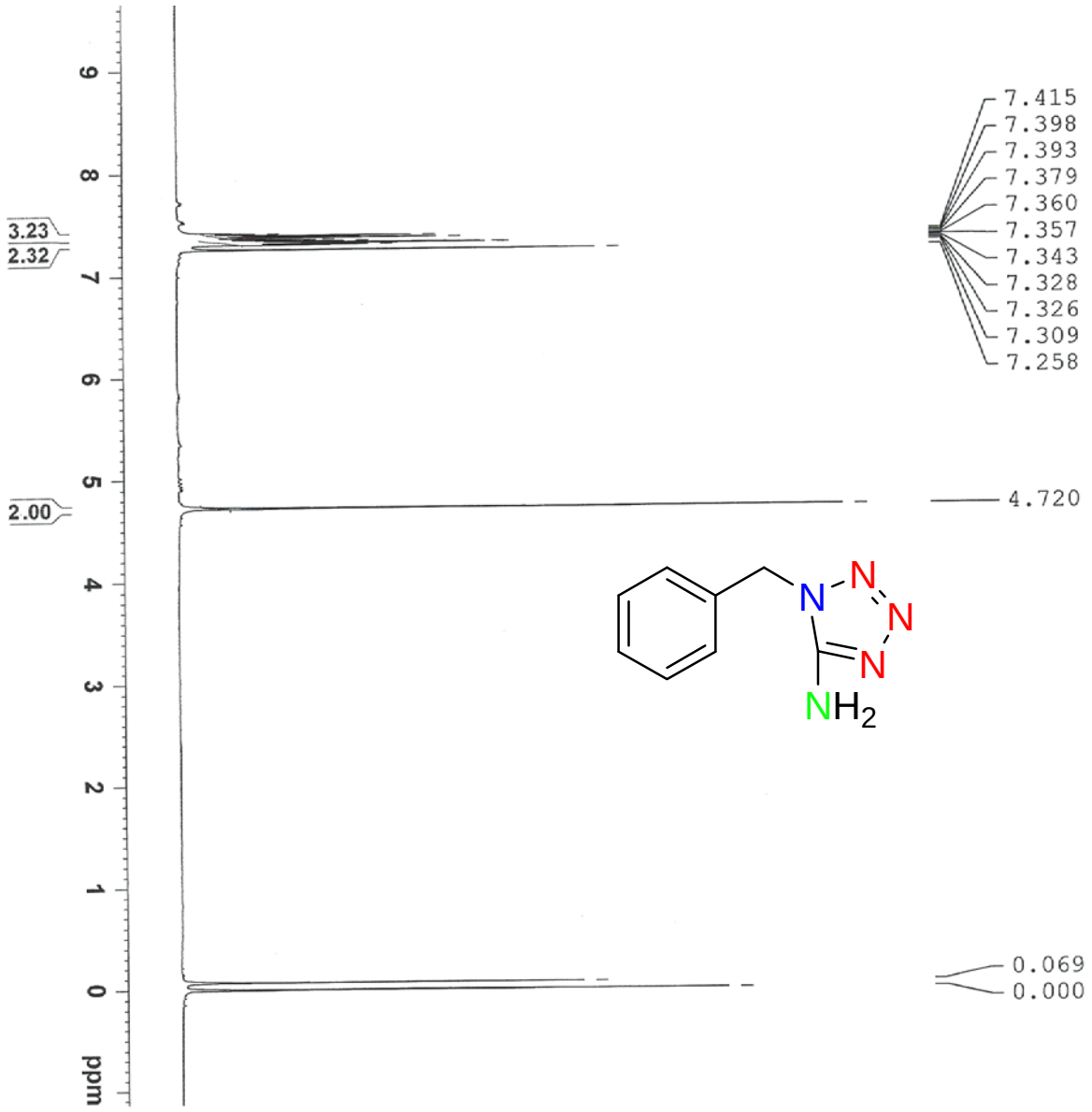
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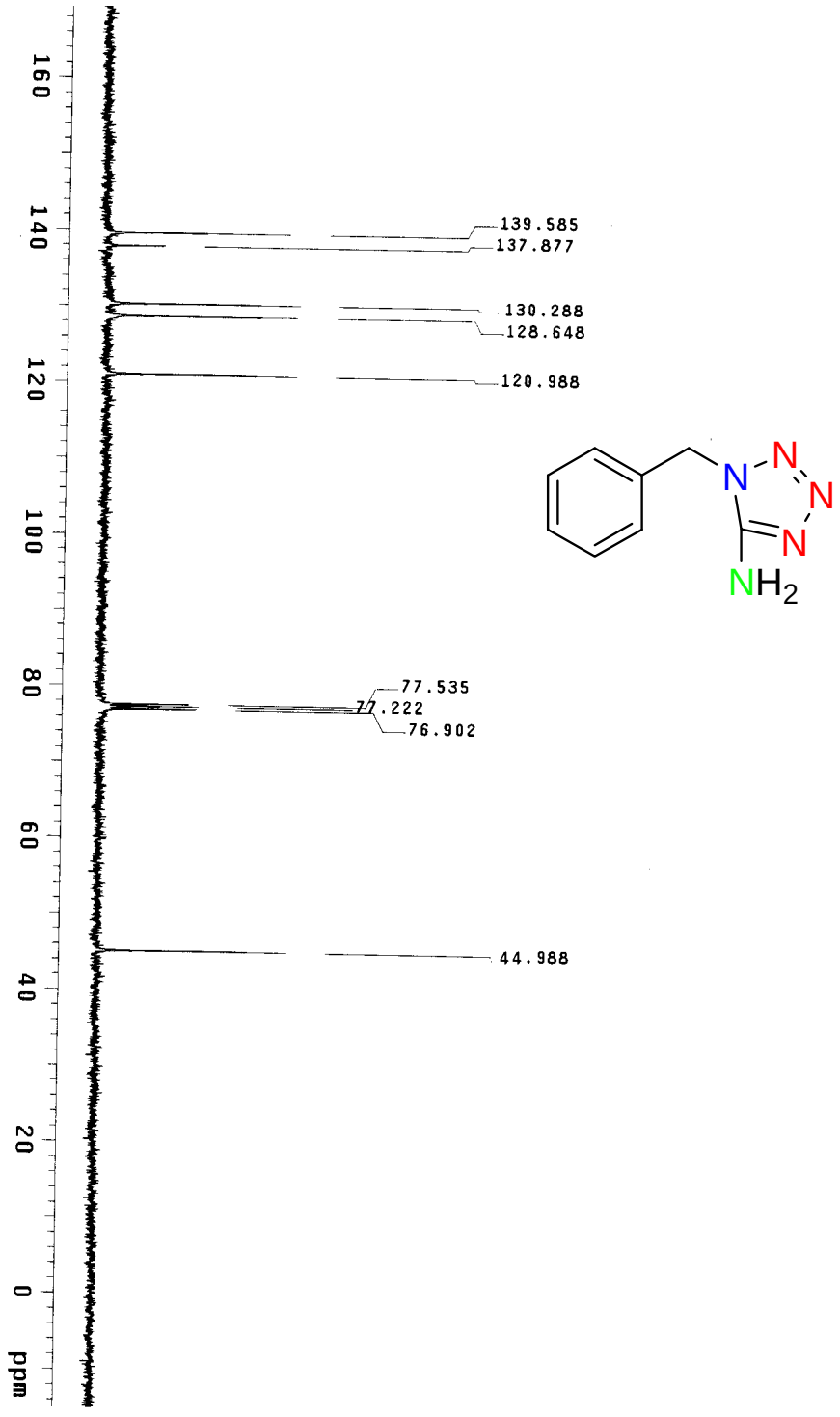
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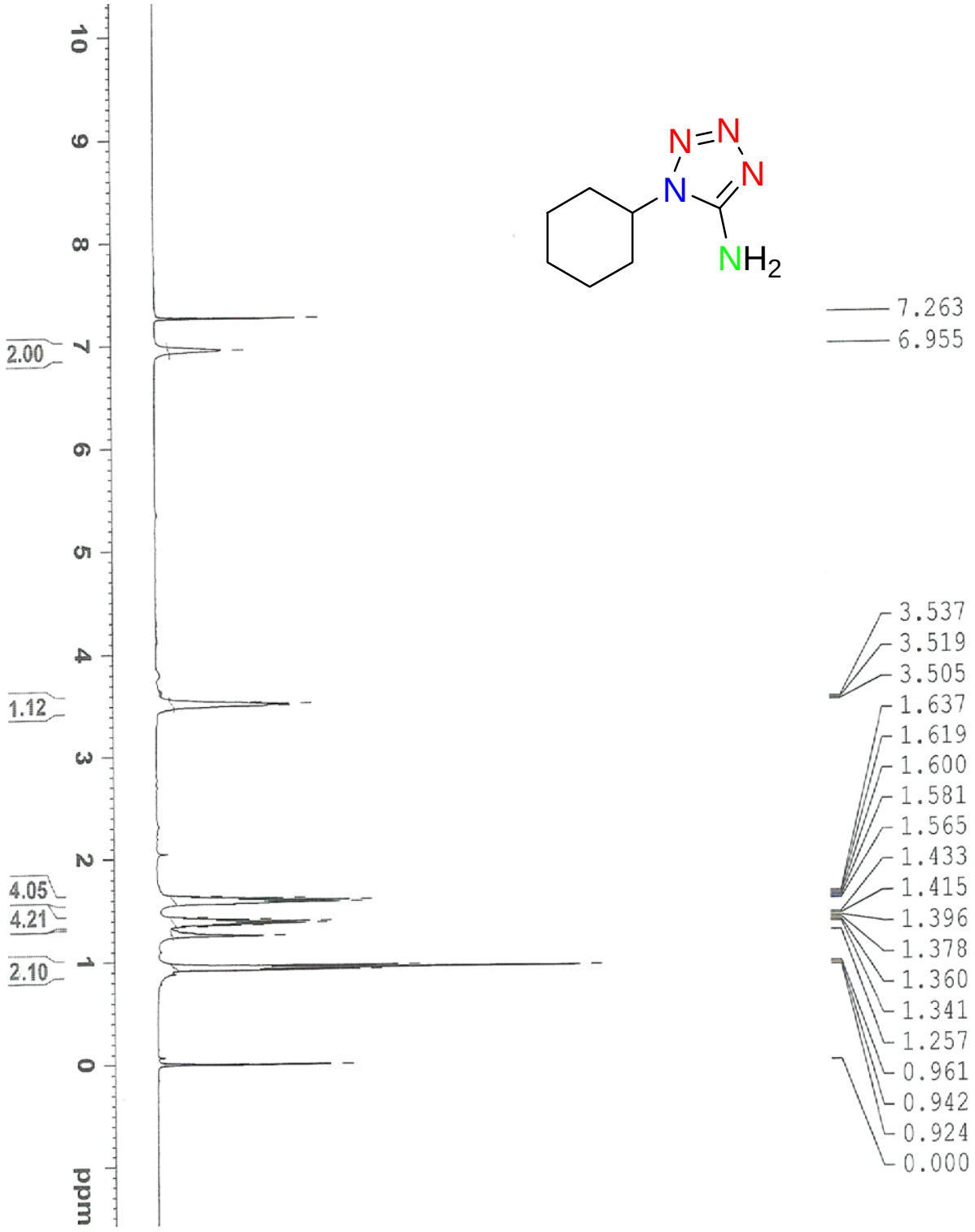
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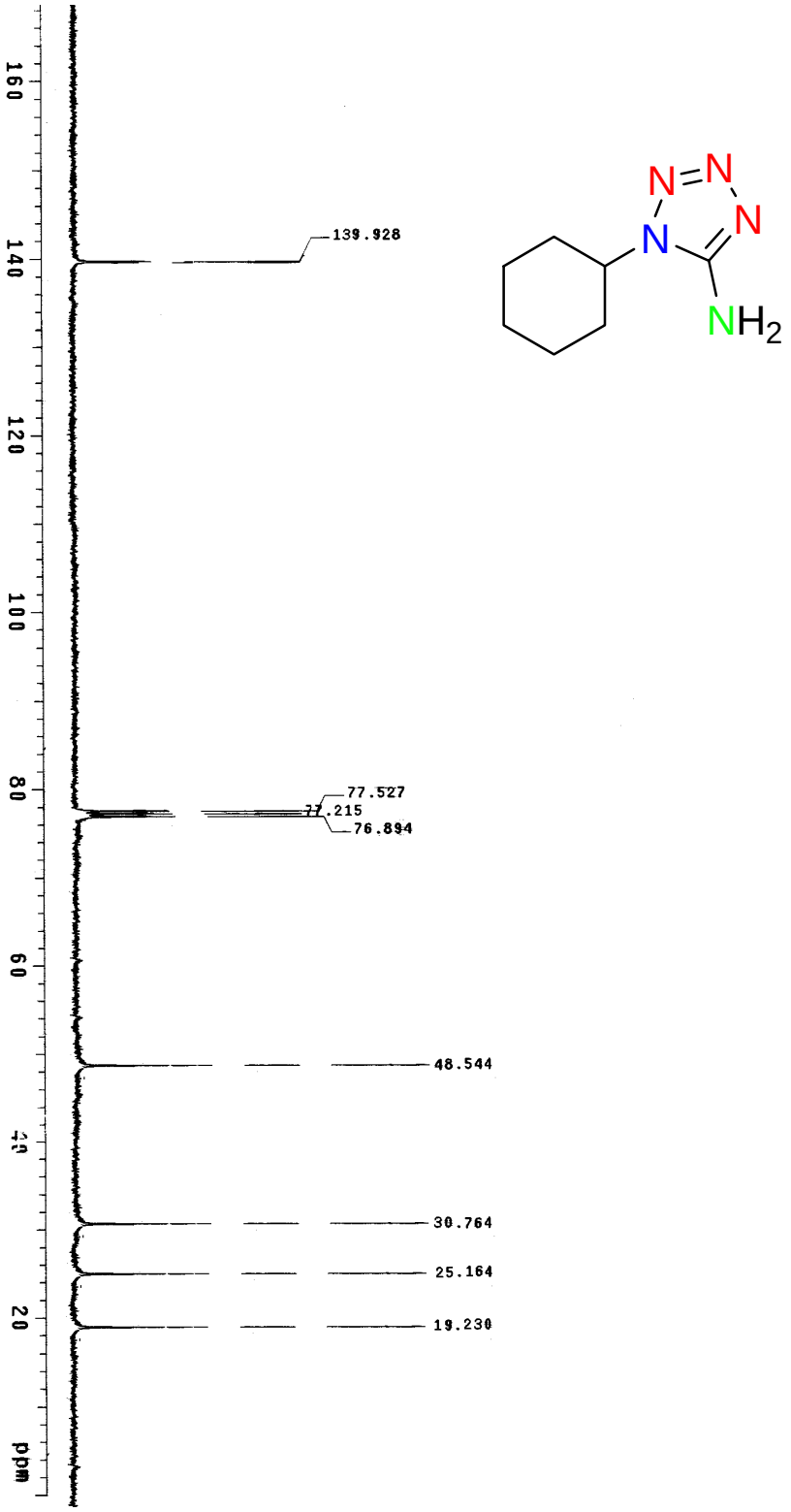
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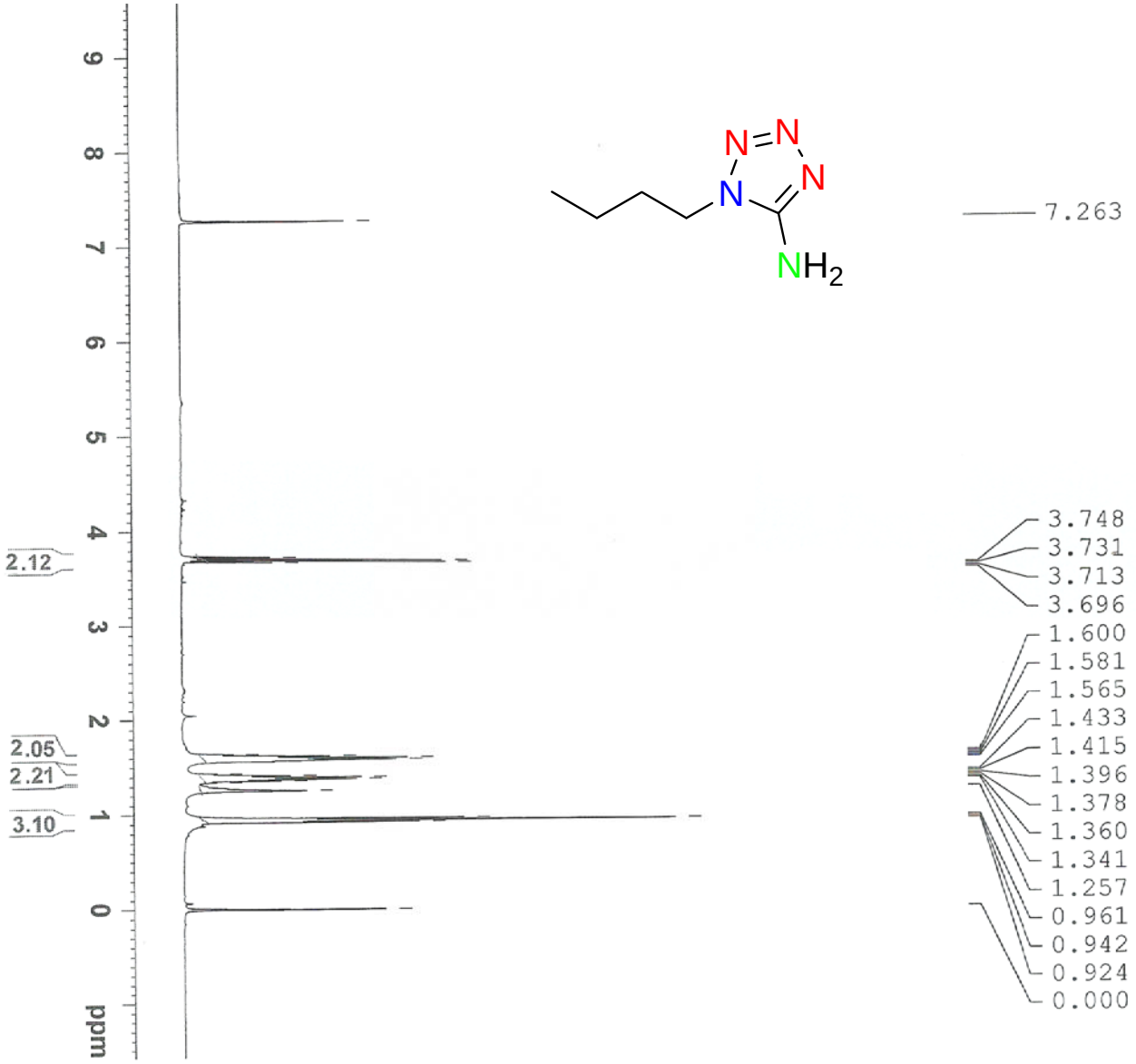
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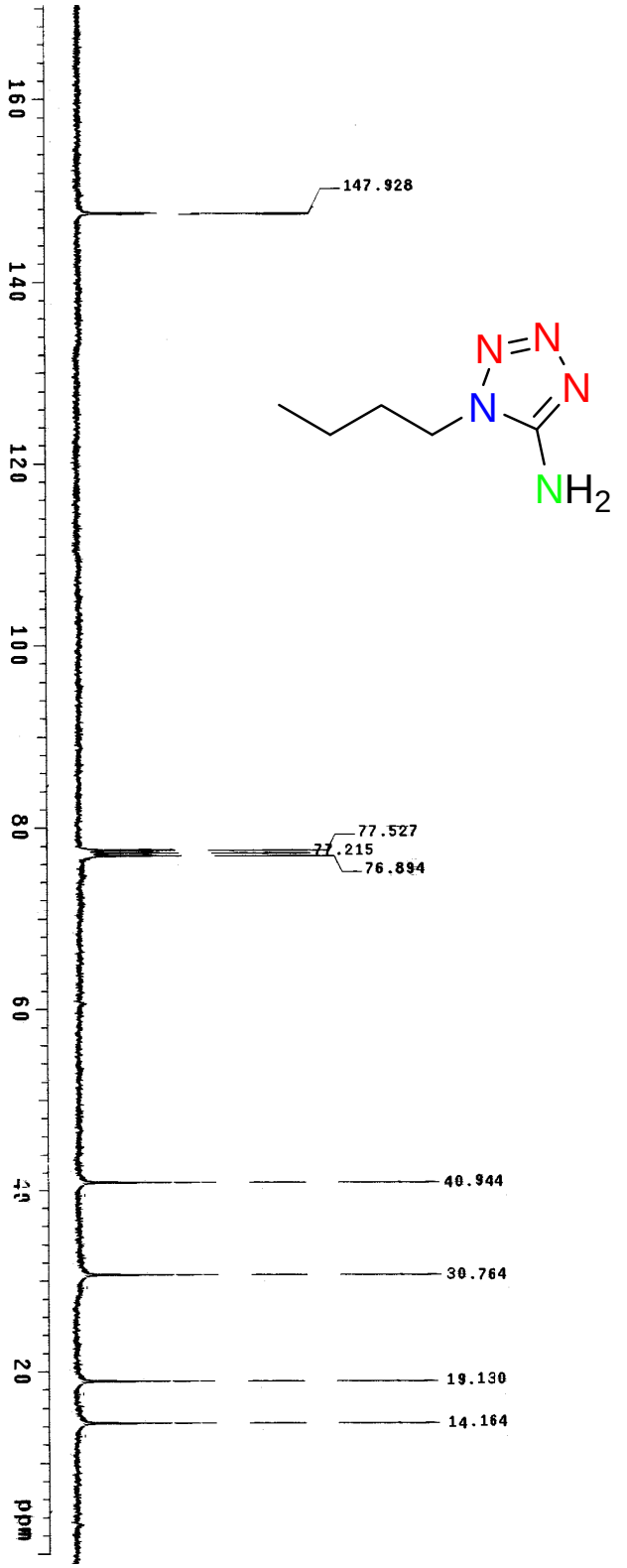
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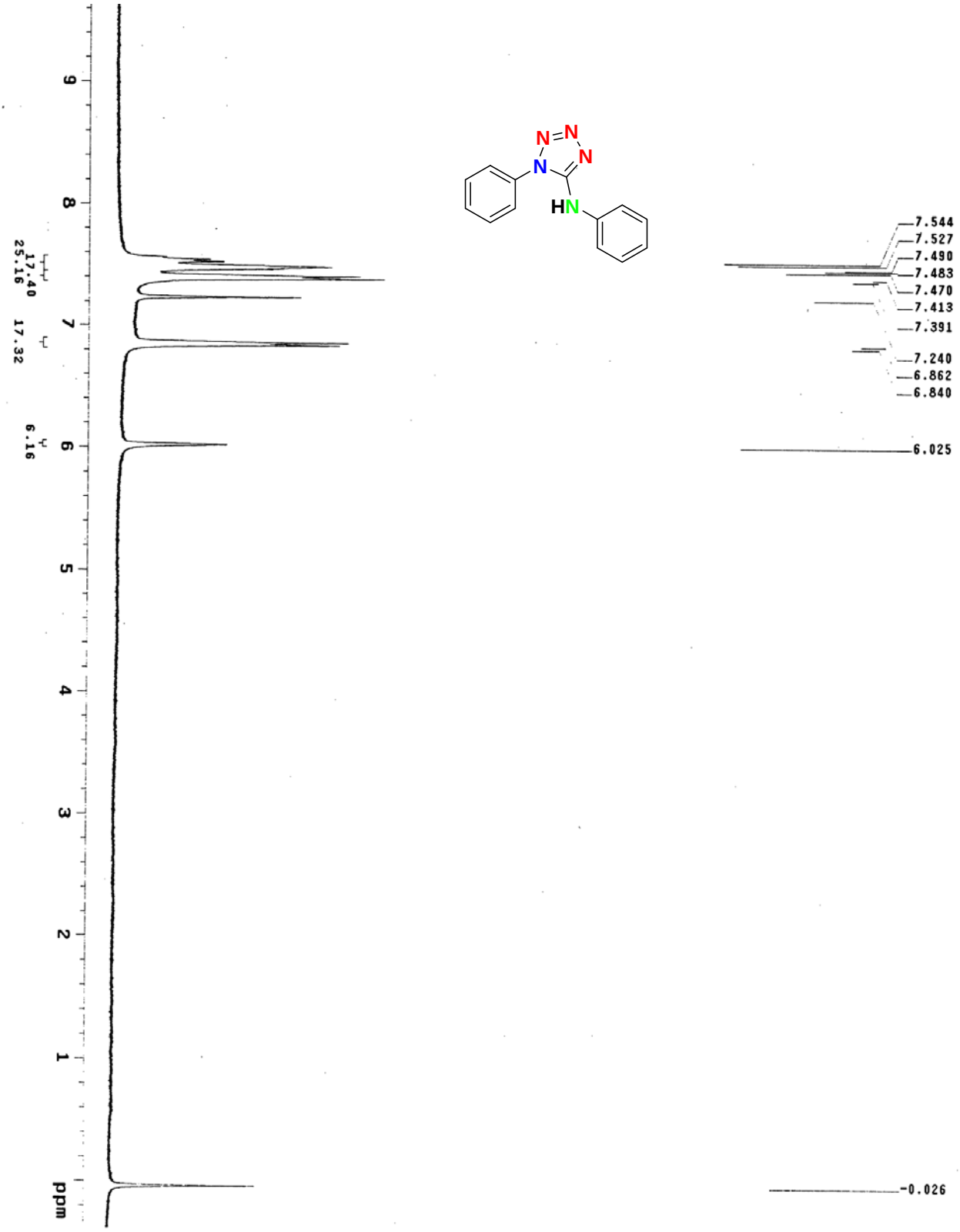
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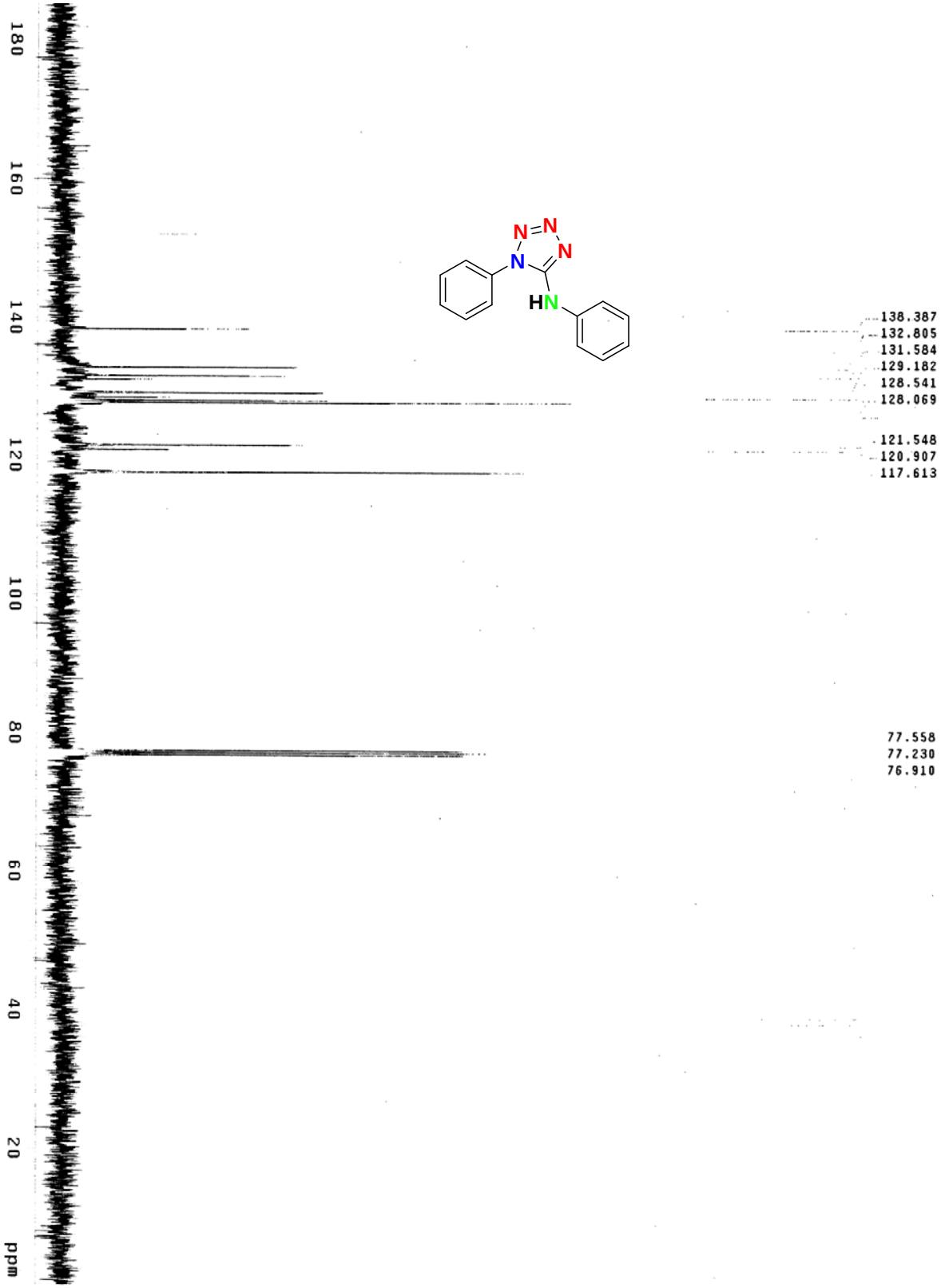
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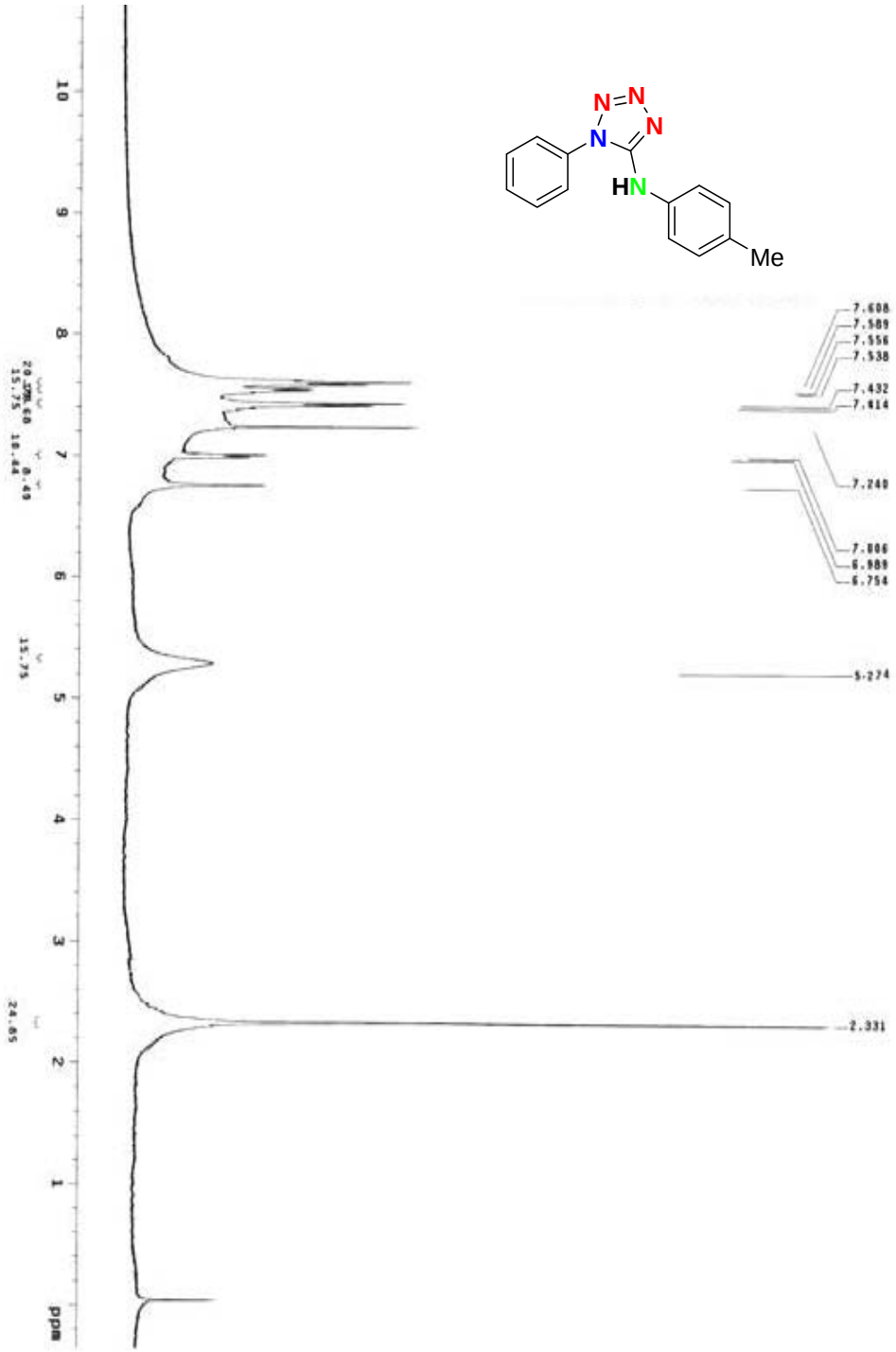
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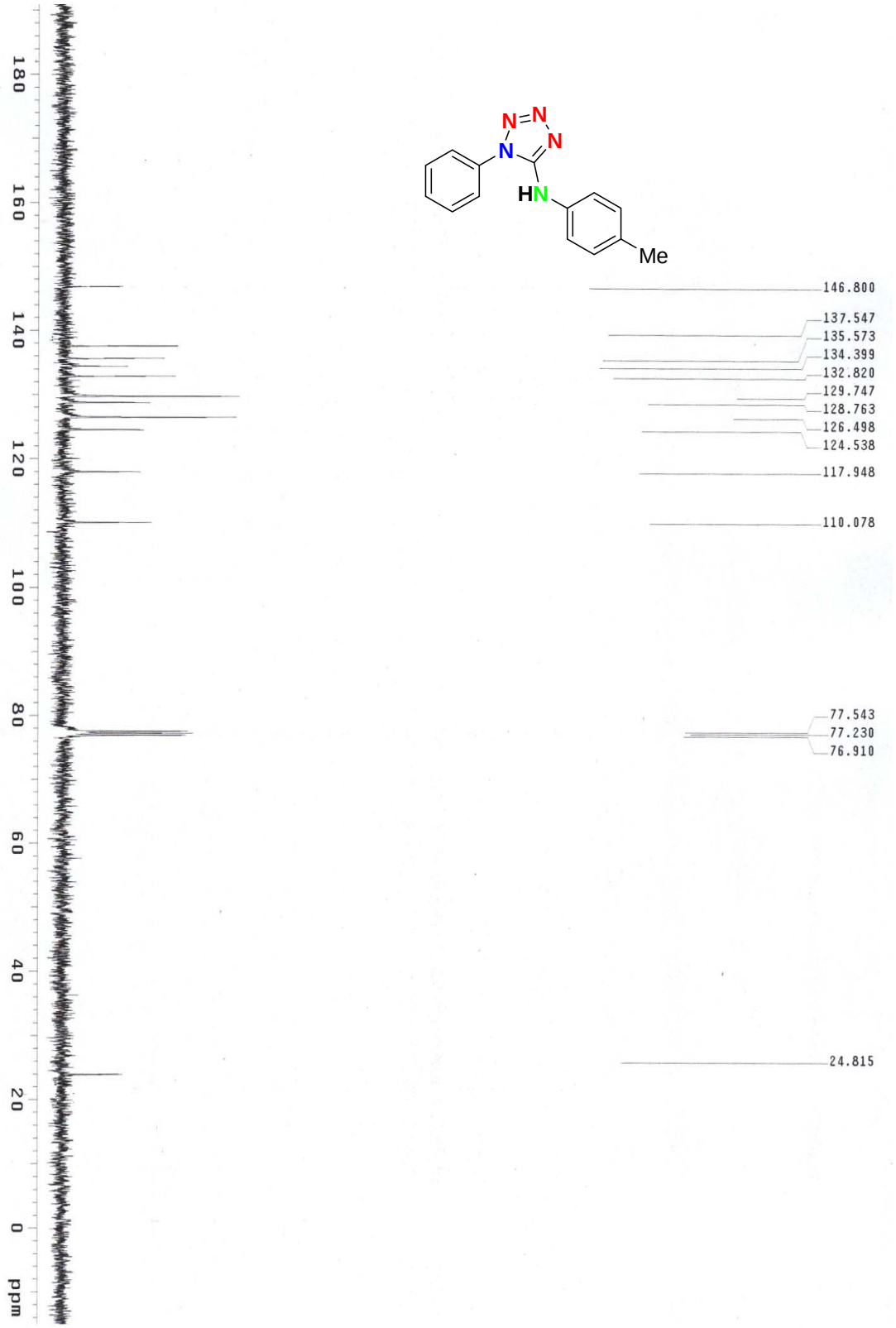
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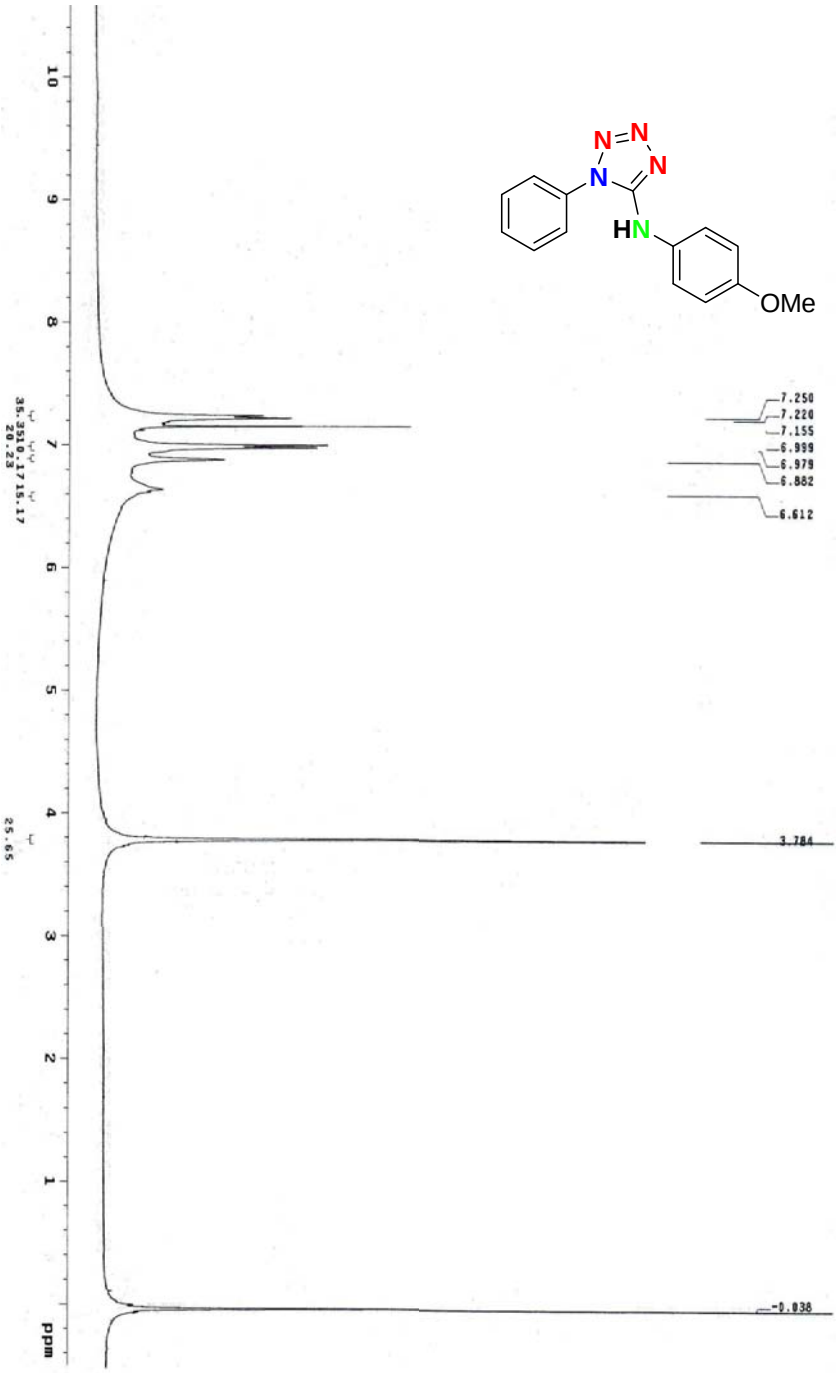
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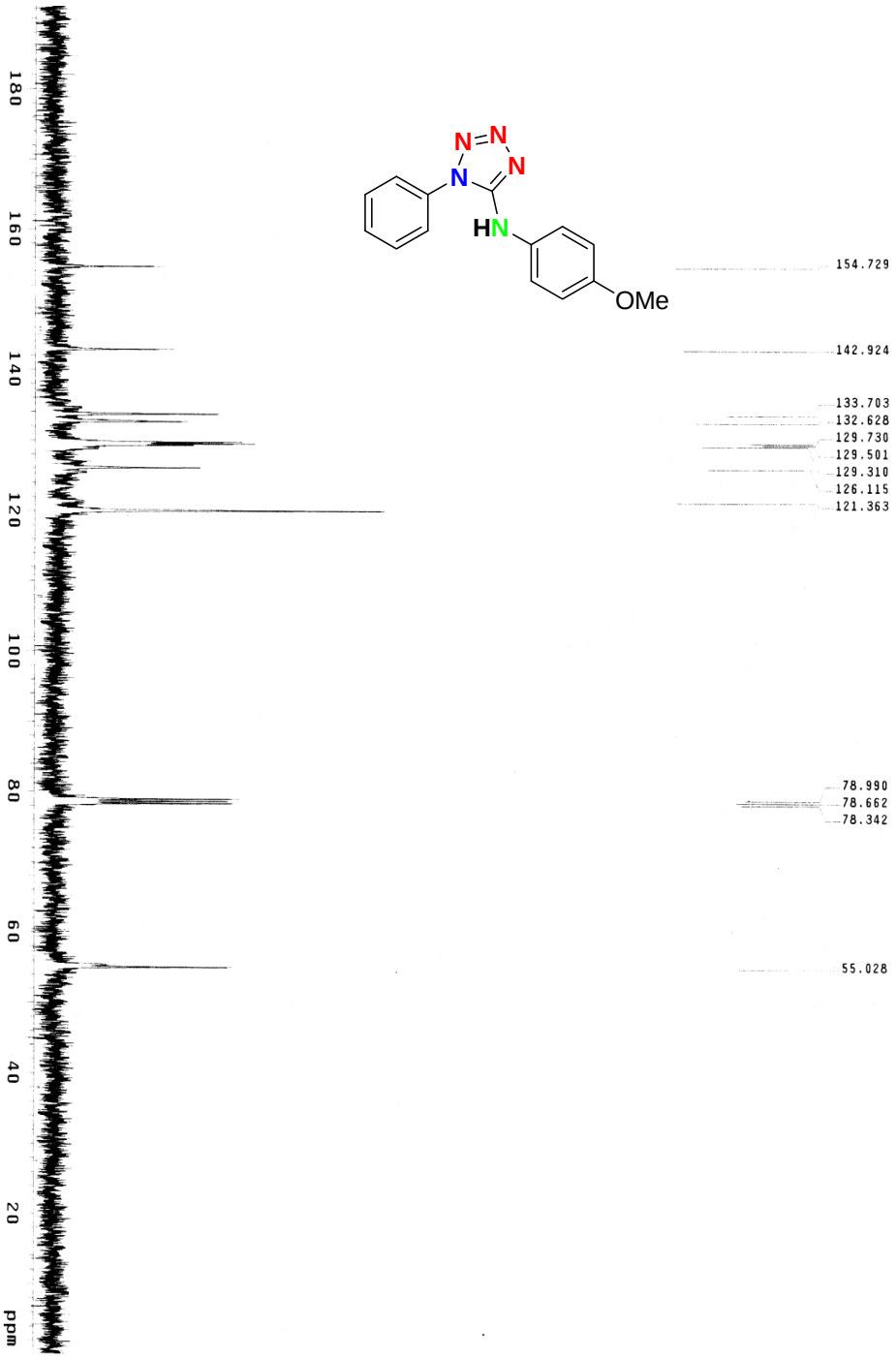
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OMe
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78.662
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55.028
180
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140
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20
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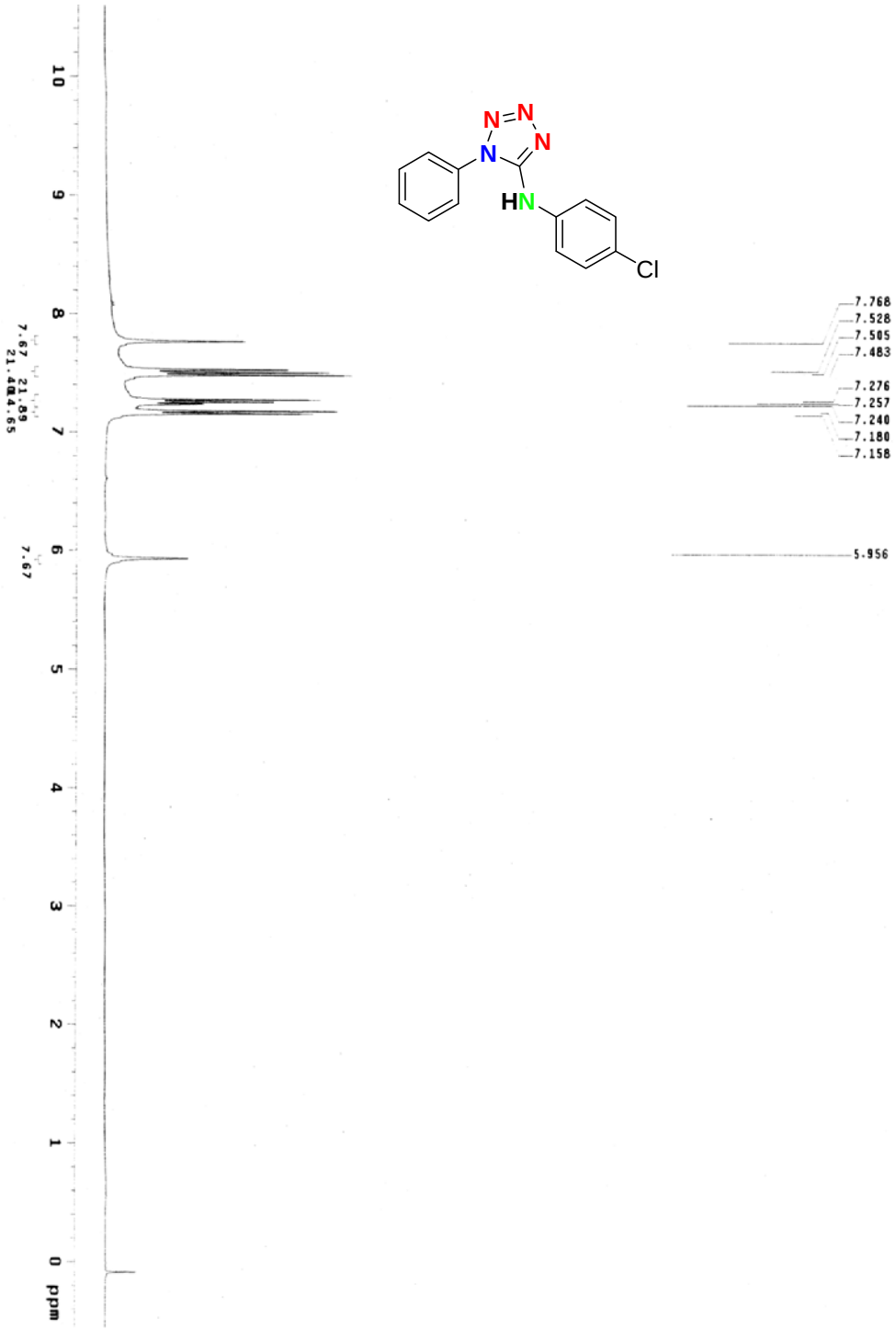
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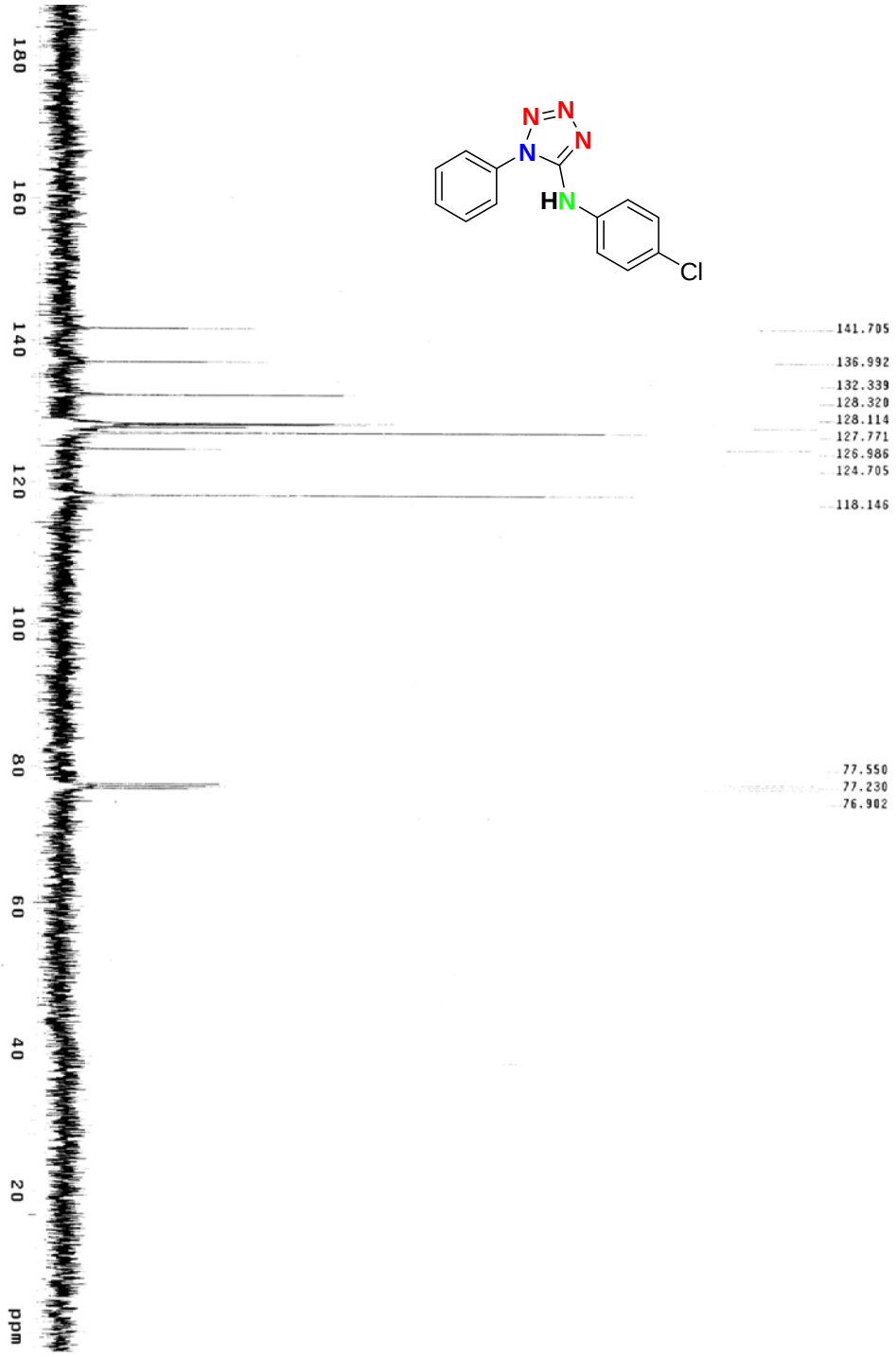
N
N
N
HN
Cl
7.768
7.528
7.505
7.483
7.276
7.257
7.240
7.180
7.158
5.956
7.67
21.89
4.95
10
9
8
7
6
5
4
3
2
1
0
ppm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N
N
N
HN
Cl
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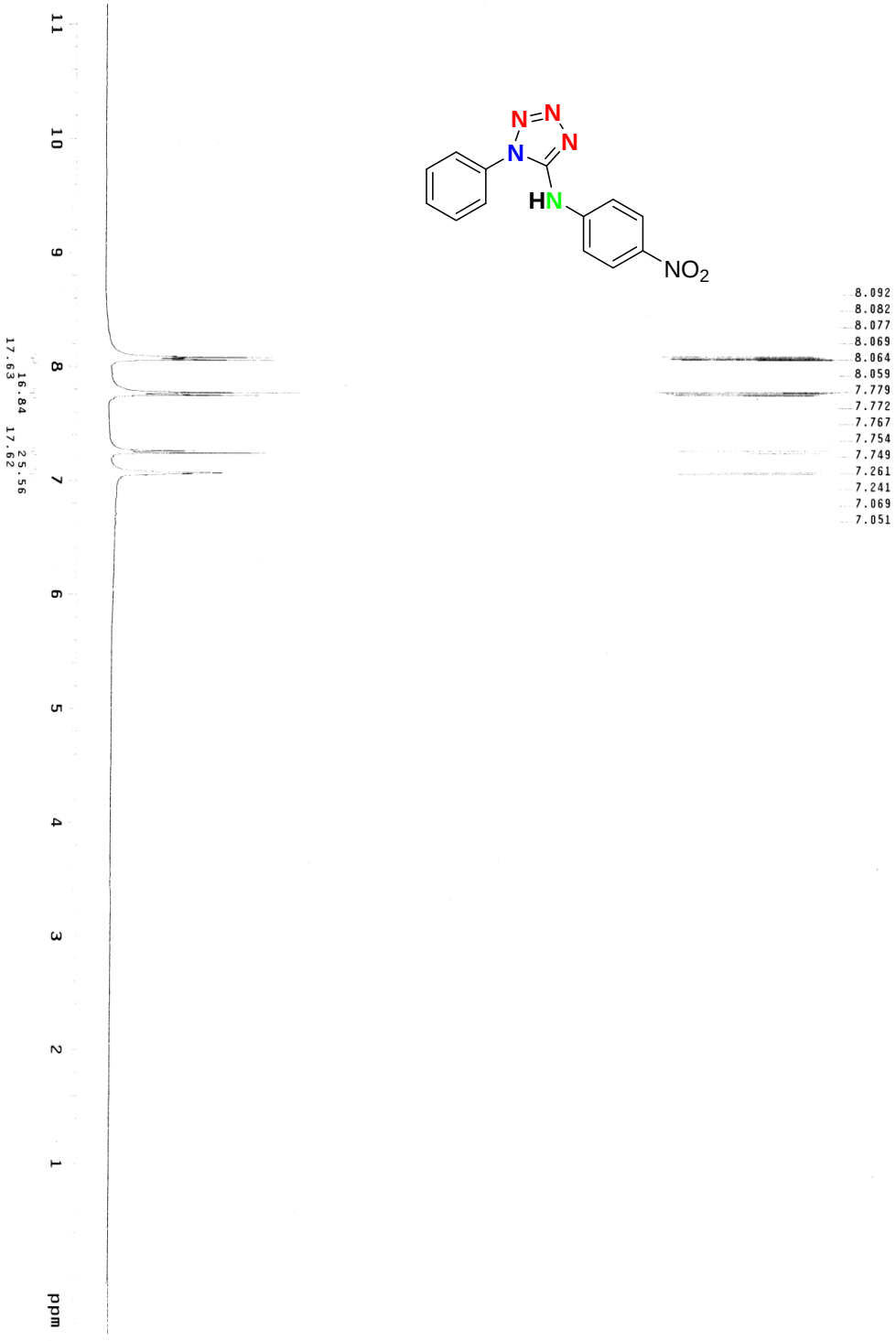
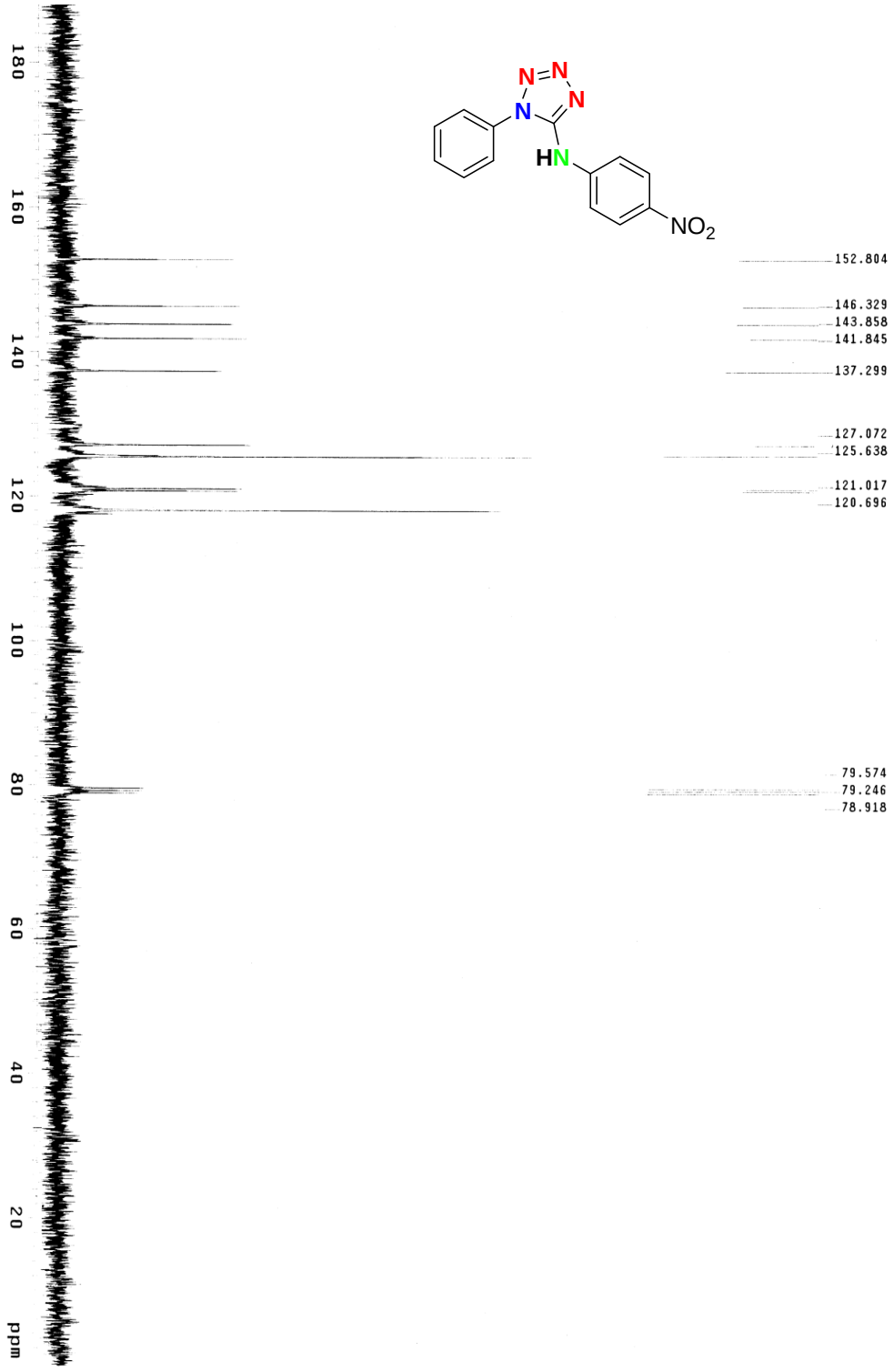
136.992
132.339
128.320
128.114
127.771
126.986
124.705
118.146
77.550
77.230
76.902
180
160
140
120
100
80
60
40
20
ppm


8.092
8.082
8.077
8.069
8.064
8.059
7.779
7.772
7.767
7.754
7.749
7.261
7.241
7.069
7.051
17.63
16.84
25.56
17.62
11
10
9
8
7
6
5
4
3
2
1
ppm
N
N
N
N
HN
NO2


180
160
140
120
100
80
60
40
20
ppm
N
N
N
N
HN
NO2
152.804
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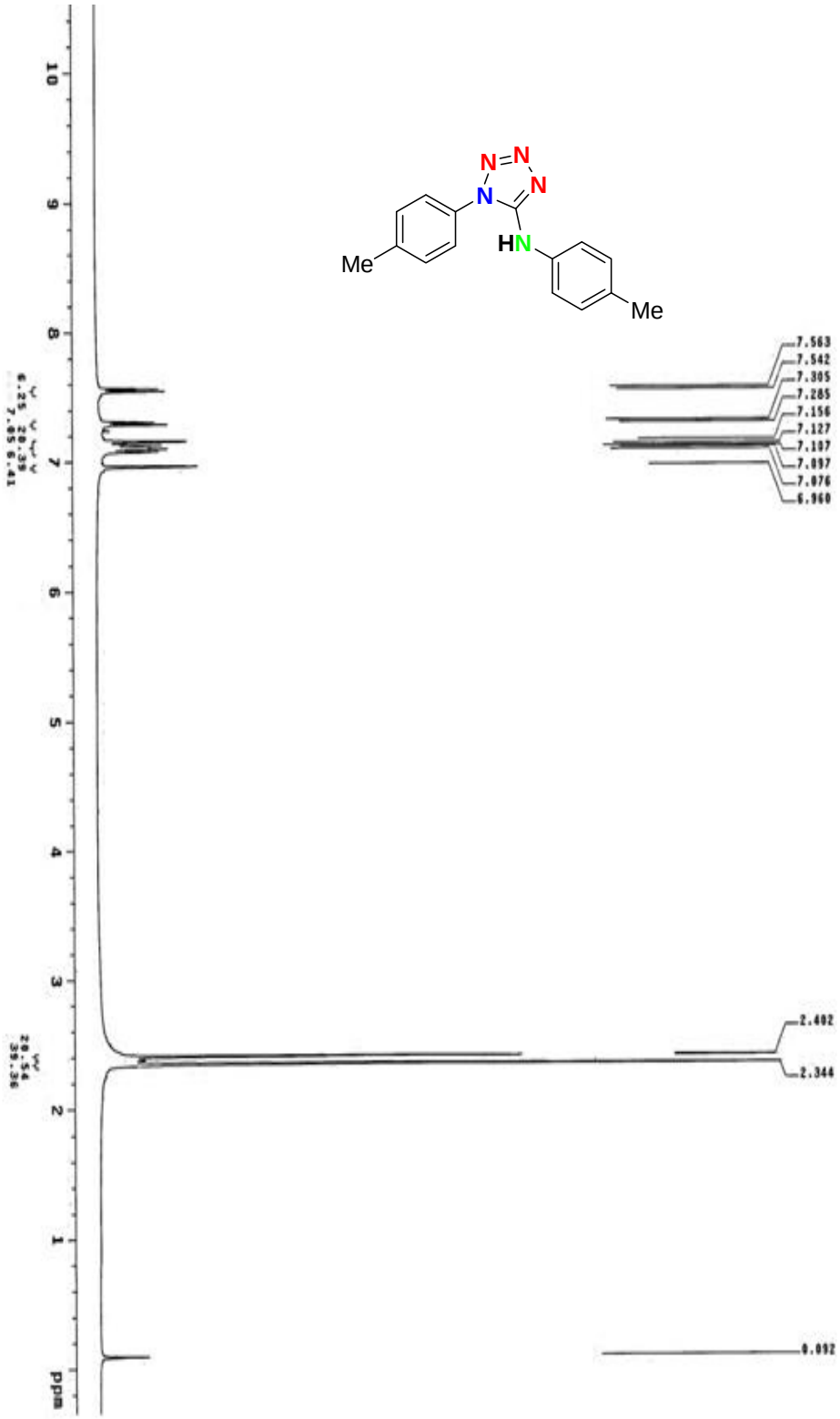
141.845
137.299
127.072
125.638
121.017
120.696
79.574
79.246
78.918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N
N
N
HN
Me
Me
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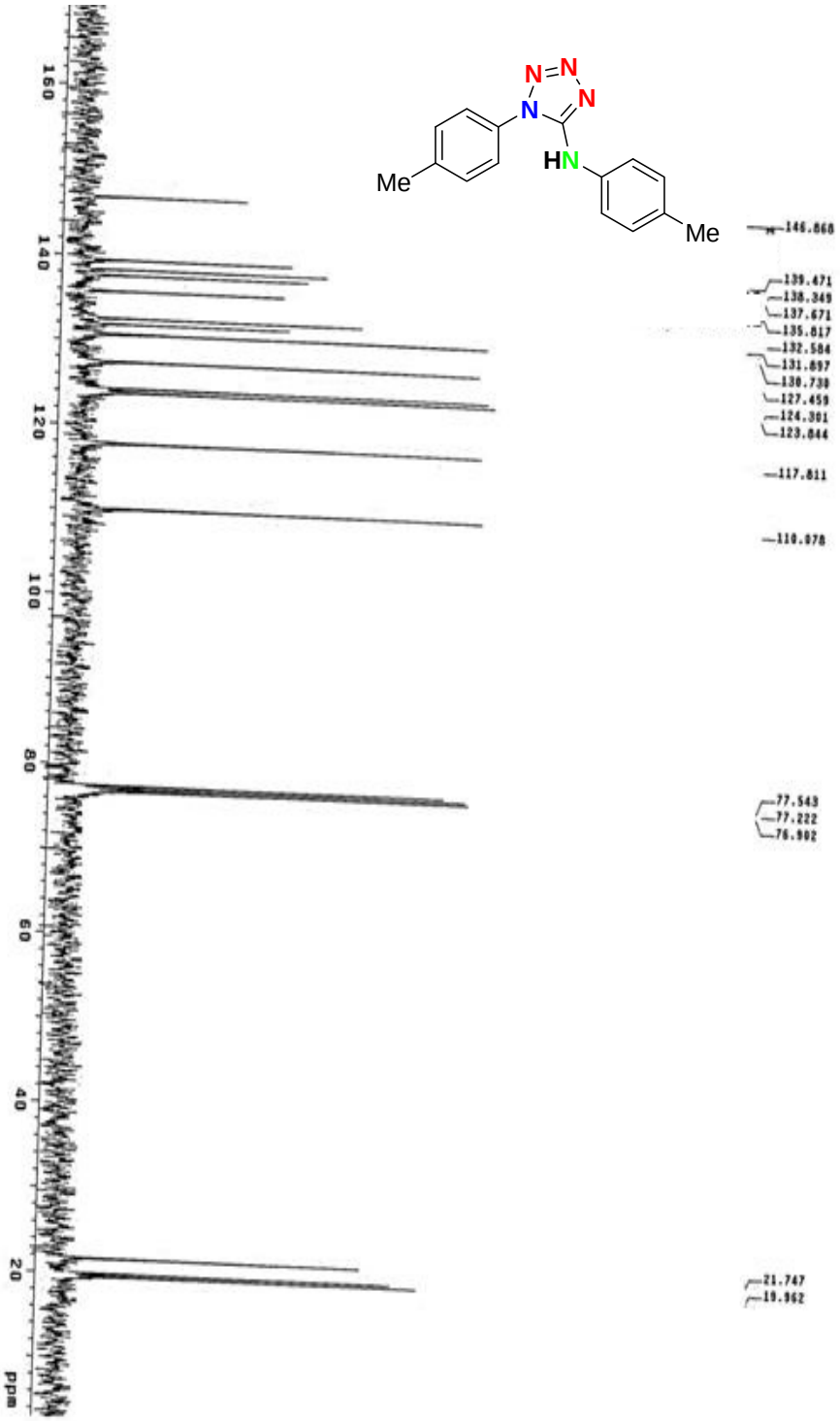
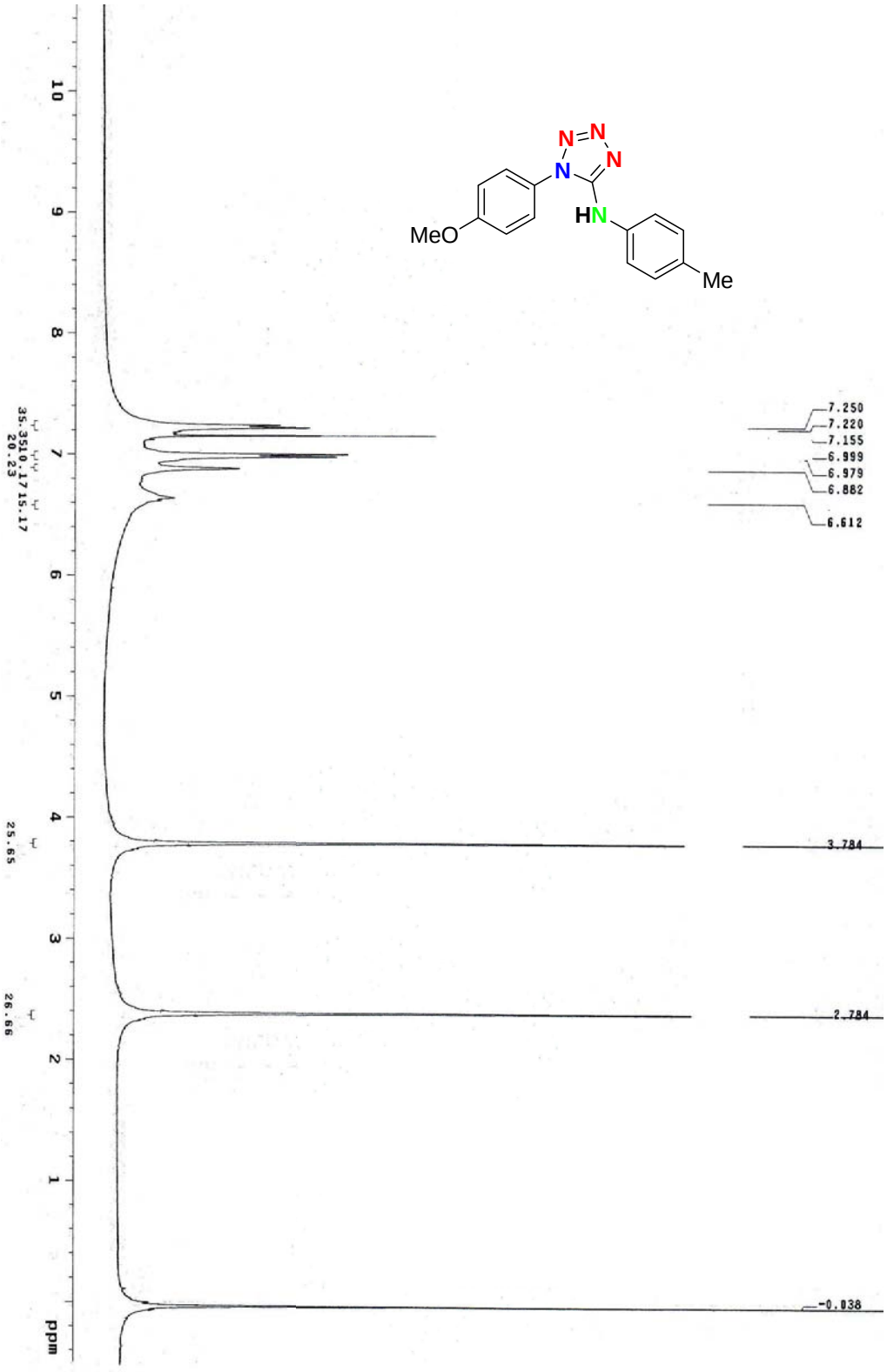
7.305
7.285
7.156
7.127
7.107
7.097
7.076
6.960
2.402
2.344
0.092
ppm


N
N
N
N
HN
Me
Me
146.868
139.471
138.349
137.671
135.817
132.584
131.897
130.739
127.459
124.301
123.844
117.811
110.878
77.543
77.222
76.902
21.747
19.962
160
140
120
100
80
60
40
20
ppm


MeO
HN
Me
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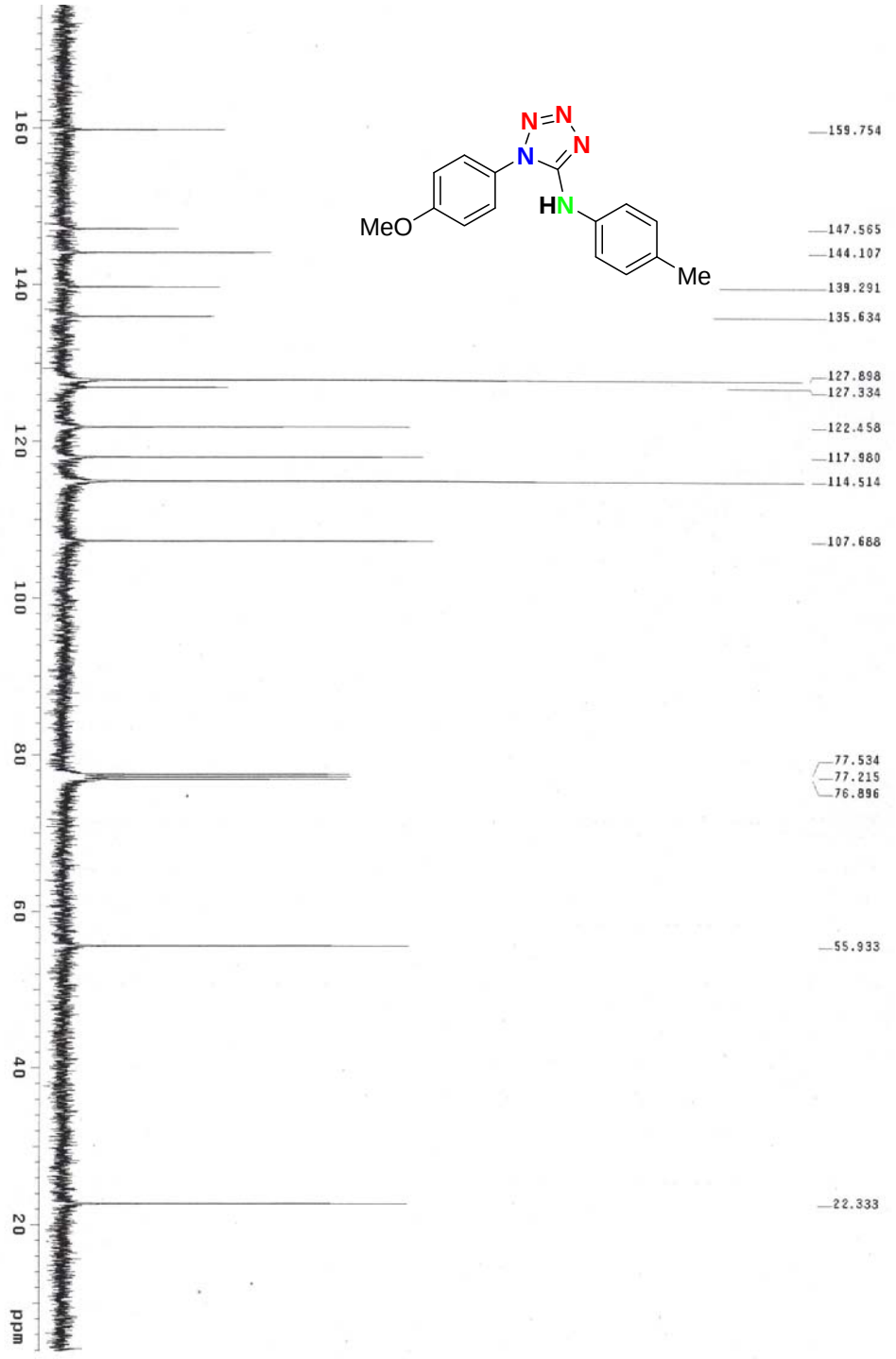
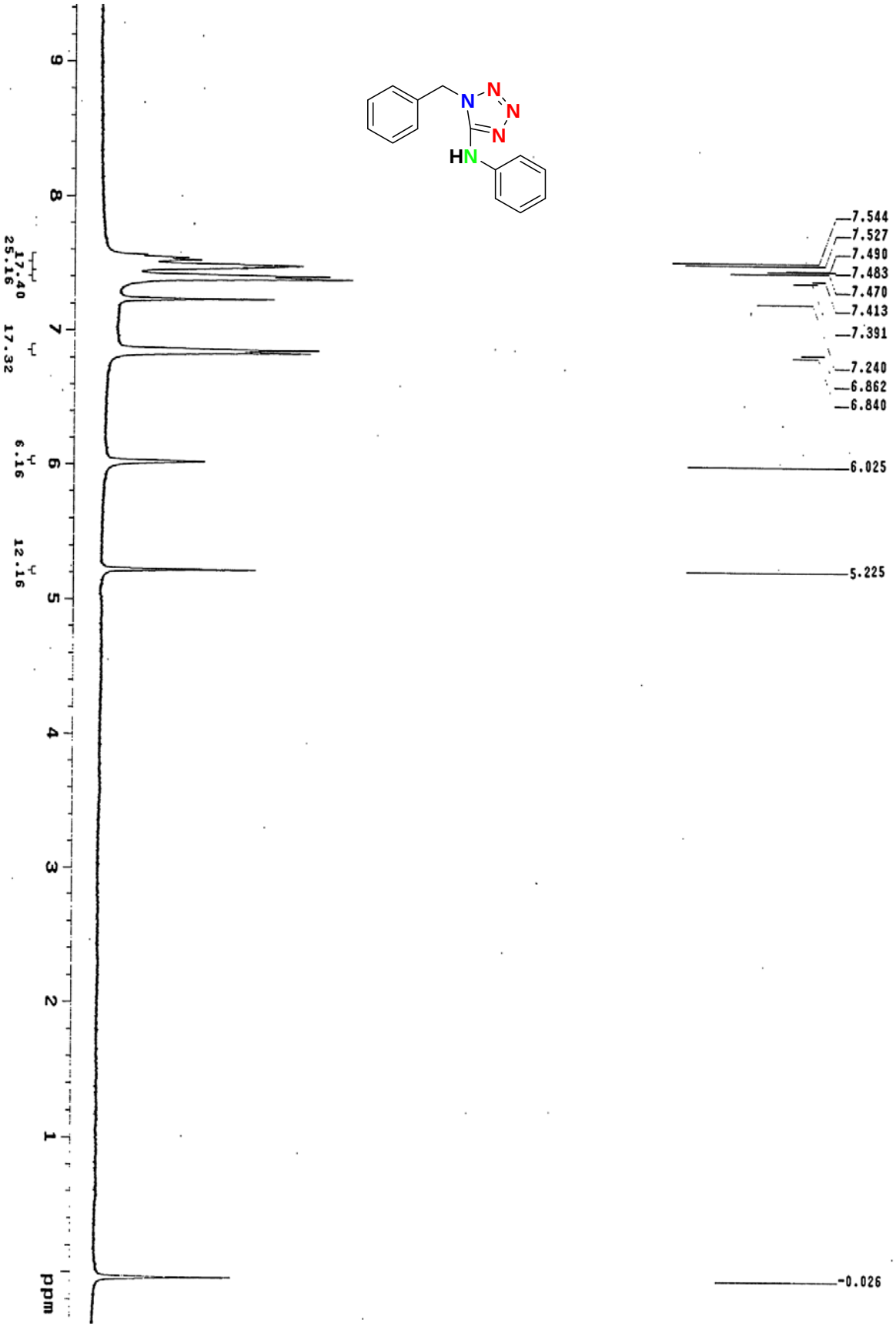
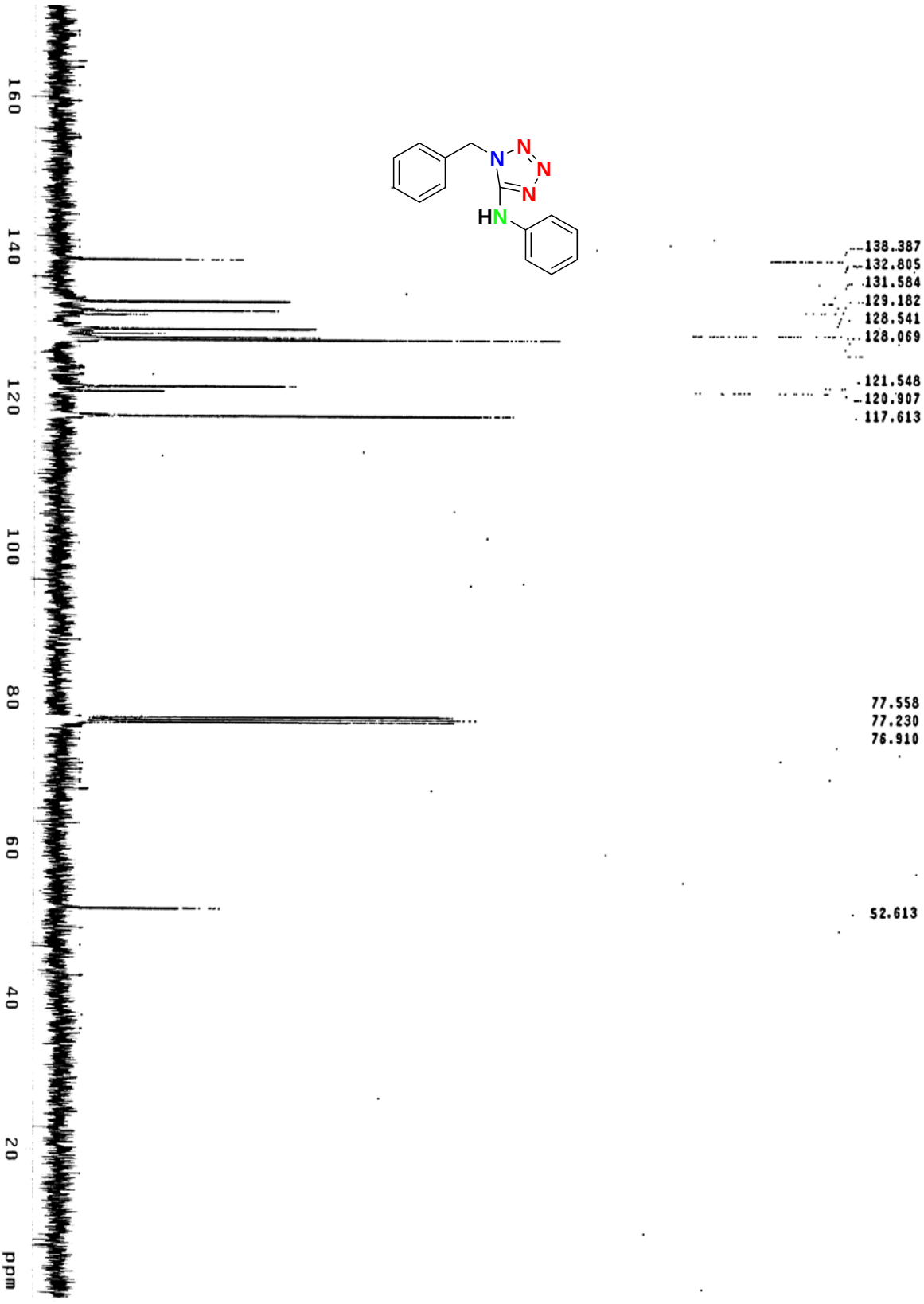
7.220
7.155
6.999
6.979
6.882
6.612
3.784
2.784
-0.038
35.35
10.17
15.17
20.23
25.65
26.66
ppm


MeO
Me
HN
N
N
N
N
159.754
147.565
144.107
139.291
135.634
127.898
127.334
122.458
117.980
114.514
107.688
77.534
77.215
76.896
55.933
22.333
160
140
120
100
80
60
40
20
ppm


N
N
N
N
HN
7.544
7.527
7.490
7.483
7.470
7.413
7.391
7.240
6.862
6.840
6.025
5.225
-0.026
17.40
25.16
17.32
6.16
12.16
ppm


160
140
120
100
80
60
40
20
ppm
N
N
N
N
HN
138.387
132.805
131.584
129.182
128.541
128.069
121.548
120.907
117.613
77.558
77.230
76.910
52.613