Supplementary information

Ecofriendly synthesis of heterogeneous polyvinyl alcohol immobilized copper (II) Schiff base complex as an efficient, reusable catalyst for one-pot three component green preparation of 5-substituted 1H-tetrazoles under mild conditions

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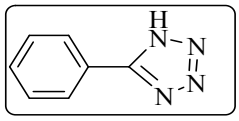
1.1. General synthesis for the preparation of 5-substituted 1*H*-tetrazoles:

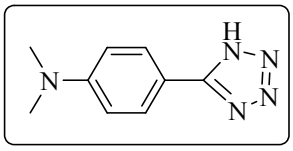
Aldehyde (1 mmol), sodium azide (1.5 mmol) and hydroxylamine hydrochloride (1.5 mmol) in presence of polymeric copper Schiff base complex as a catalyst (10 mg, 0.43 mol%) were mixed together in the water as a solvent. The reaction stirred for sufficient time (generally less than 15 min), which was required for completion of the reaction. The reaction mixture was decanted and the solid residue was washed with 5mL water to remove all of impurities, which are soluble in water. Then 10 mL of hot ethanol (50 ^{o}C) was added to extract the corresponding tetrazole product from the solid residual and leave the catalyst **5** as bright green solid, which could be reused without any purification for the next reaction. The products were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and melting points. We have reported the spectral data of synthesized compounds.

1.2. Physical and spectral data for tetrazole derivatives



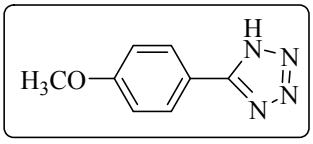
1.2.1. 5-Phenyl-1*H*-tetrazole (9a)

Yellow solid; Yield = 98 %; ***mp:*** 217-219 °C, ***mp*** [1]: 218-220 °C; **IR** (KBr): υ (cm^{-1}): 3126 (C-H, sp^{2}stretch Ar), 1694 (C=N), 1597, 1498 (C=C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.19-7.79 (m, 5H, Ar), 8.62 (s, 1H tetrazole); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 124.96, 126.56, 130.12, 132.46, 156.16; **CHN**: Found %: C 58.33; H 4.02; N 38.12. C9H11N5. Calculated, %: C 57.53; H 4.14; N 38.34



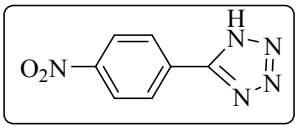
1.2.2. N,N-Dimethyl-4-(1*H*-tetrazol-5-yl)benzenamine (9b)

White solid; Yield = 98 %; ***mp***: 132-134 °C; **IR** (KBr): υ = 570, 739, 1064, 1188, 1527, 1612, 2808, 3263 cm^{-1}; **^{1}H NMR** (250 MHz, $CDCl_3$): δ (ppm) = 2.91 (s, 6H), 6.60 (d, 2H), 7.37 (d, 2H); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 40.2, 11.9, 119.6, 128.3, 150.3, 151.5; **CHN**: Found %: C 56.80; H 5.33; N 37.01. C9H11N5. Calculated, %: C 57.13; H 5.86; N 37.01.



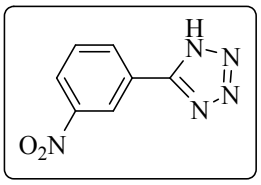
1.2.3. 5-(4-Methoxyphenyl)-1*H*-tetrazole (9c)

White solid; Yield = 98 %; ***mp:*** 233-234 °C, ***mp*** [2]: 234-235 °C; **IR** (KBr): υ = 594, 833, 1026, 1172, 1257, 1512, 1604, 1651, 2839 cm^{-1}; **^{1}H NMR** (250 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 3H), 5.94 (s, 1H), 6.92 (d, 2H), 7.71 (d,2H); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 55.85, 115.51, 123.72, 129.93, 162.63, 165.404; **CHN**: Found %: C 54.12; H 4.05; N 31.25. C9H11N5. Calculated, %: C 54.54; H 4.58; N 31.80.



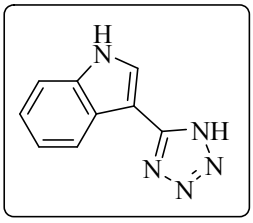
1.2.4 5-(4-Nitrophenyl)-1*H*-tetrazole (9d)

Pale yellow solid; Yield = 98 %; ***mp***: 220-222 °C, ***mp*** [3]: 219-221; **IR** (KBr): υ = 684, 748, 848, 972, 1110, 1342, 1542, 1604, 3340 cm^{-1}; **^{1}H NMR** (250 MHz, $CDCl_3$): δ (ppm) = 4.16 (s, 1H), 7.67 (d, 2H), 8.17 (d, 2H); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 124.04, 127.64, 138.10, 148.35, 160.44; **CHN**: Found %: C 43.11; H 2.50; N 36.60. C9H11N5. Calculated, %: C 43.98; H 2.64; N 36.64.



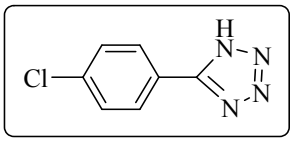
1.2.5. 5-(3-Nitrophenyl)-1*H*-tetrazole (9e)

Pale yellow solid; Yield = 97 %; ***mp***: 155-157 °C, ***mp*** [4]: 156-158 °C; **IR** (KBr): υ = 670, 709, 840, 941, 1103, 1350, 1465, 1535, 1620, 3294 cm^{-1}; **^{1}H NMR** (250 MHz, $CDCl_3$): δ (ppm) = 4.25 (s, 1H), 7.51 (t, 1H), 7.83 (d, 1H), 8.16 (d, 1H), 8.36 (s, 1H); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 121.12, 121.60, 129.93, 130.12, 131.24, 146.45, 165.40; **CHN**: Found %: C 43.55; H 2.60; N 36.52. C9H11N5. Calculated, %: C 43.98; H 2.64; N 36.64.



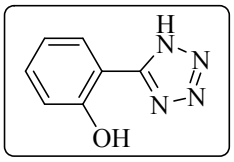
1.2.6. 3-(1*H*-tetrazol-5-yl)-1*H*-indole (9f)

Yellow solid; Yield = 98 %; ***mp***: 161-163 °C; **IR** (KBr): υ = 493, 601, 640, 763, 933, 1118, 1242, 1465, 1519, 1651, 2576, 3070 cm^{-1}; **^{1}H NMR** (250 MHz, $CDCl_3$): δ (ppm) = 7.11-8.26 (aromatic, 5H), 9.92 (s, 1H), 11.21 (s, 1H); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 112.34, 118.09, 120.78, 122.08, 123.42, 130.75, 140.02, 140.22, 184.95; **CHN**: Found %: C 57.81; H 3.81; N 37.50. C9H11N5. Calculated, %: C 58.37; H 3.81; N 37.82.



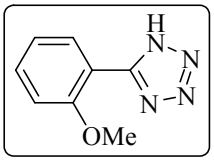
1.2.7. 5-(4-Chlorophenyl)-1*H*-tetrazole (9g)

White solid; Yield = 98 %; ***mp***: 153-155 °C, ***mp*** [5]: 155-156 °C; **IR** (KBr) υ (cm^{-1}): 1485, 1581, 1661, 3057; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 6.98-7.00 (d-2H), 7.27-7.29 (d-2H), 8.01 (s-1H tetrazole); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 120.35, 128.85, 129.47, 143.52, 149.50; **CHN**: Found %: C 46.11; H 2.50; N 19.52. C9H11N5. Calculated, %: C 46.55; H 2.79; N 19.63.



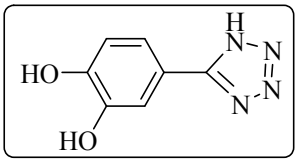
1.2.8. 2-Hydroxyphenyl-1*H*-tetrazole (9h)

White solid; Yield = 80 %; ***mp:*** 219-221 °C, ***mp*** [6]: 219-221 °C; **IR** (KBr) υ (cm^{-1}): 756, 1255, 1488, 1521, 1620, 2988; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 5.2 (s-1H), 7.18-8.15 (aromatic, 4H); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 116.31, 119.31, 123.35, 128.84, 129.33, 156.45, 164.28; **CHN**: Found %: C 52.11; H 3.50; N 34.30. C9H11N5. Calculated, %: C 51.85; H 3.73; N 34.55.



1.2.9. 5-(2-Methoxyphenyl)-1*H*-tetrazole (9i)

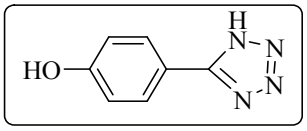
White solid; Yield = 98 %; ***mp***: 154.156 °C; **IR** (KBr) υ (cm^{-1}): 640, 748, 879, 1026, 1110, 1257, 1496, 1596, 1627, 2877, 3001; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 3.79 (s-3H), 6.83-761 (aromatic, 4H); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 56.62, 11.13, 117.14, 125.90, 130.88, 158.77, 164.57, 177.51, 177.63; **CHN**: Found %: C 55.32; H 4.01; N 31.20. C9H11N5. Calculated, %: C 54.54; H 4.58; N 31.80.



1.2.10. 5-(3,4-Dihydroxyphenyl)-1*H*-tetrazole (9j)

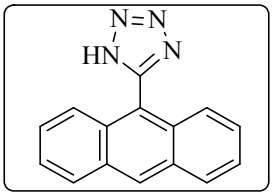
White solid; Yield = 70 %; ***mp***: 213-215 °C; **IR** (KBr) υ (cm^{-1}): 640, 748, 910, 1018, 1118, 1334, 14.73, 1542, 1651, 2923, 3016; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 5.05 (s-2H), 6.98-728 (aromatic, 3H); **^{13}C**

NMR (62.9 MHz, $CDCl_3$) δ (ppm): 115.98, 117.67, 121.07, 124.45, 149.21, 149.69, 163.11 ; **CHN**: Found %: C 47.61; H 3.22; N 31.40. C9H11N5. Calculated, %: C 47.19; H 3.39; N 31.45.



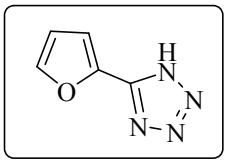
1.2.11. 4-Hydroxyphenyl-1H-tetrazole (9k)

White solid; Yield = 88; ***mp***: 232-235 °C, ***mp*** [7]: 232-234 °C; **IR** (KBr) υ (cm^{-1}): 879, 1273, 1434, 1519, 1604, 2888, 3371; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 4.75 (s-1H), 5.62 (s, 1H), 6.80 (d, 2H), 7.38 (d, 2H); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 116.36, 122.77, 131.86, 156.75, 162.76; **CHN**: Found %: C 52.17; H 3.20; N 34.30. C9H11N5. Calculated, %: C 51.85; H 3.73; N 34.55.



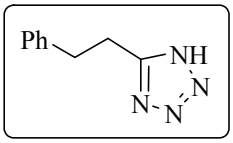
1.2.12. 5-(9-Anthracene)-1H-tetrazole (9l)

Pale yellow solid; Yield = 95 %; ***mp***: 148-150 °C; **IR** (KBr) υ (cm^{-1}): 609, 732, 879, 972, 1157, 1296, 1442, 1519, 1620, 3031; **^{1}H NMR** (250 MHz $CDCl_3$) δ (ppm): 6.47 (s, 1H), 7.25-8.22 (aromatic, 9H); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 124.98, 125.39, 126.79, 128.87, 129.36, 130.20, 134.85, 142.80, 165.05; **CHN**: Found %: C 73.88; H 3.77; N 22.50. C9H11N5. Calculated, %: C 73.16; H 4.09; N 22.75.



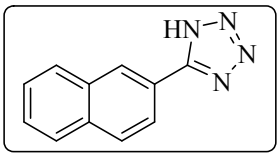
1.2.13. 5-(2-Furfural)-1H-tetrazole (9m)

White solid; Yield = 98 %; ***mp***: 220-222 °C, ***mp*** [3]: 219-221 °C; IR (KBr) υ (cm^{-1}): 1126, 1458, 1558, 2923; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.23 (s-1H), 8.16 (d, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 107.60, 117.75, 144.67, 152.39, 162.19; CHN: Found %: C 45.44; H 3.50; N 41.15. C9H11N5. Calculated, %: C 44.12; H 2.96; N 41.16.



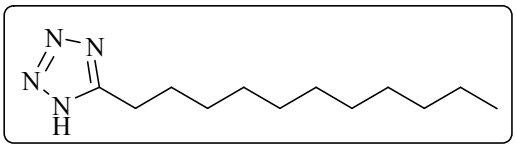
1.2.14. 5-(2-Phenylethyl)-1H-tetrazole (9n)

White solid; Yield = 80 %; ***mp***: 98-100 °C, ***mp*** [8]: 99-101 °C; **IR** (KBr) υ (cm^{-1}): 756, 1126, 1255, 1419, 1521, 3080; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 3.34 (s, 4H), 7.02-7.26 (aromatic, 5H); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 30.55, 38.72, 129.48, 130.90, 132.82, 140.25, 167.79 ; **CHN**: Found %: C 62.72; H 5.13; N 32.00. C9H11N5. Calculated, %: C 62.05; H 5.79; N 32.16.



1.2.15. 5-(Naphthalene-2-yl)-1H-tetrazole (9o)

White solid; Yield: 95 %; ***mp***: 205-207 °C, ***mp*** [9]: 204-206 °C; **IR** (KBr) υ (cm^{-1}): 748, 864, 979, 1172, 1450, 1504, 1596, 2985; **^{1}H NMR** (250 MHz, $CDCl_3$) δ (ppm): 7.17-8.77 (aromatic, 7H); **^{13}C NMR** (62.9 MHz, $CDCl_3$) δ (ppm): 122.41, 126.63, 126.67, 127.45, 127.67, 128.03, 130.69, 132.78, 133.23, 148.12; **CHN**: Found %: C 68.15; H 3.90; N 28.30. C9H11N5. Calculated, %: C 67.34; H 4.11; N 28.55.



1.2.16. Andecane-1H-tetrazole (9p)

white solid; Yield = 80 %; ***mp:*** 215-217 °C; **IR** (KBr): υ = 717, 709, 848, 941, 1041, 1095, 1319, 1465, 1666, 3039, 3093, 3209 cm^{-1}; **^{1}H NMR** (250 MHz, $CDCl_3$): δ (ppm) = 0.821 (t, 3H), 1.18 (m, 19H), 2.19 (m, 2H); **^{13}C NMR** (62.9 MHz, $CDCl_3$): δ (ppm) = 14.024, 22.95, 28.82, 28.88, 30.25, 30.82, 35.03, 161.26; **CHN**: Found %: C 66.07; H 10.10; N 25.01. C9H11N5. Calculated, %: C 64.24; H 10.78; N 24.97.

1.3. References:

1. B. Sreedhar, A. Suresh Kumar, D. Yada, *Tetrahedron. Lett.* **2011**, 52, 3565-3569.

2. D. R. Patil, Y. B. Ingole, K. Singh, D. S. Dalal, New J. Chem. **2013**, 37, 3261-3266.

3. V. Rama, K. Kanagaraj, K. Pitchumani, *J. Org. Chem.* **2011**, 76, 9090-9095.

4. B. S. Jursic, B. W. Leblanc, *J. Heterocycl. Chem.* **1998**, 35, 405-408.

5. A. Najafi Chermahini, A. Teimouri, A. Moaddeli, *Heteroat. Chem*. **2011**, 22, 168-173.

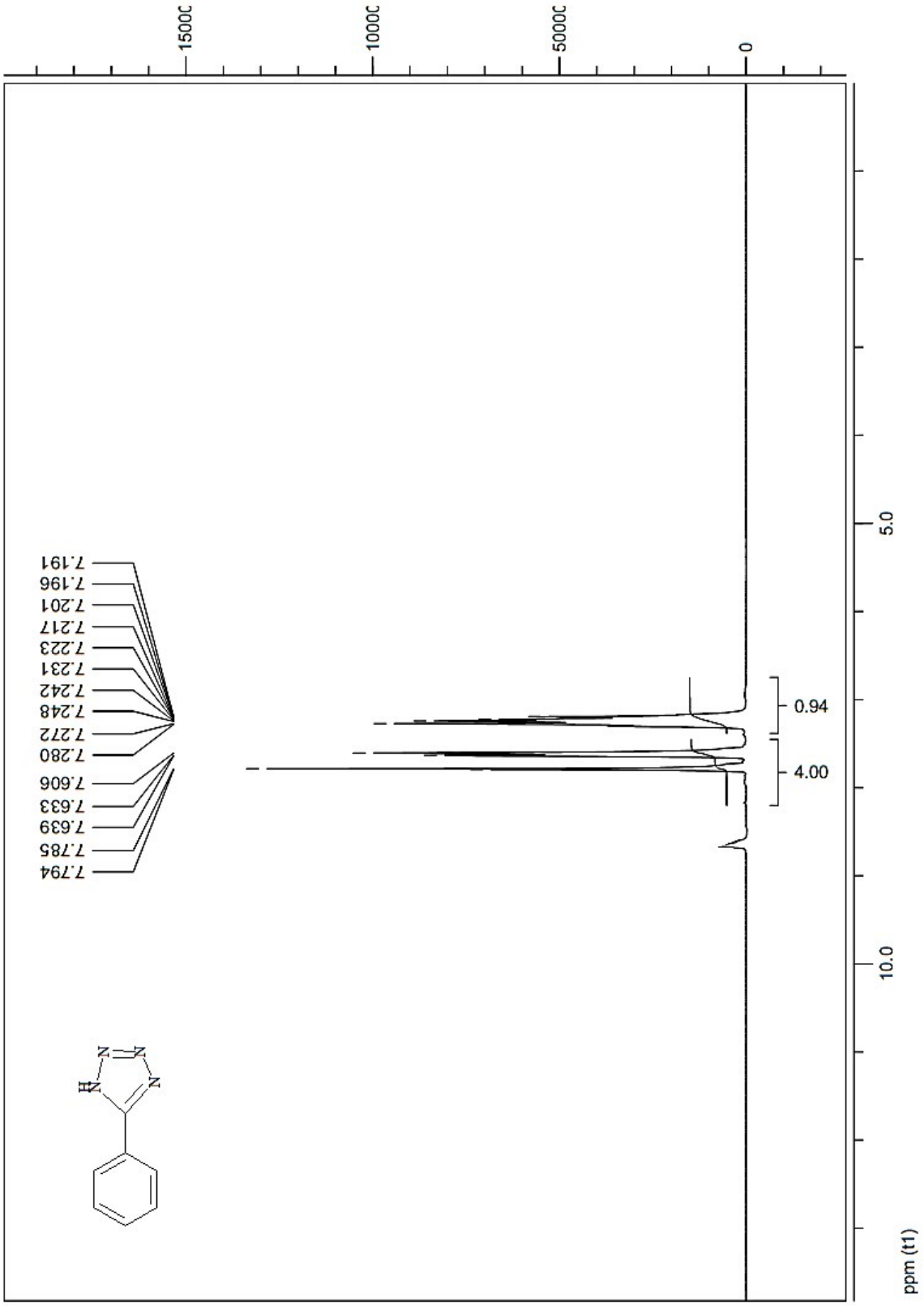
6. V. Aureggi, G. Sedelmeier, Angew. *Chem. Int. Ed.* **2007**, 46, 8440-8444.

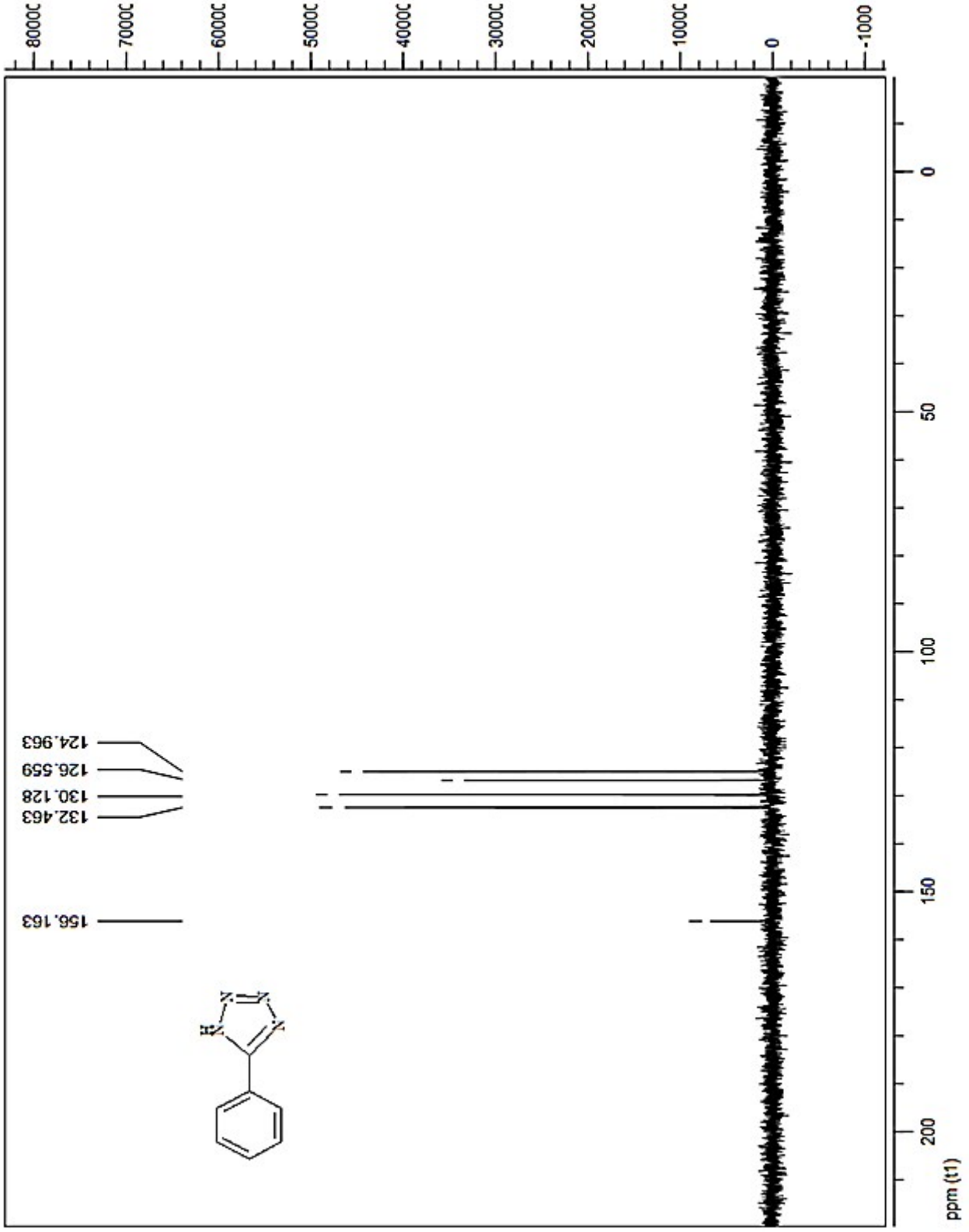
7. T. Jin, F. Kitahara, S. Kamijo, Y. Yamamoto, *Tetrahedron Lett*. **2008**, 49, 2824-2827.

8. D. Amantini, R. Beleggia, F. Fringuelli, F. Pizzo and L. Vaccaro, *J. Org. Chem*. **2004**, 69, 2896-2898.

9. B. Das, C. R. Reddy, D. N. Kumar, M. Krishnaiah, R. Narender, *Synlett*. **2010**, 3, 391-394.

1.4. ^{13}C NMR and ^{1}H NMR spectra of tetrazole derivatives

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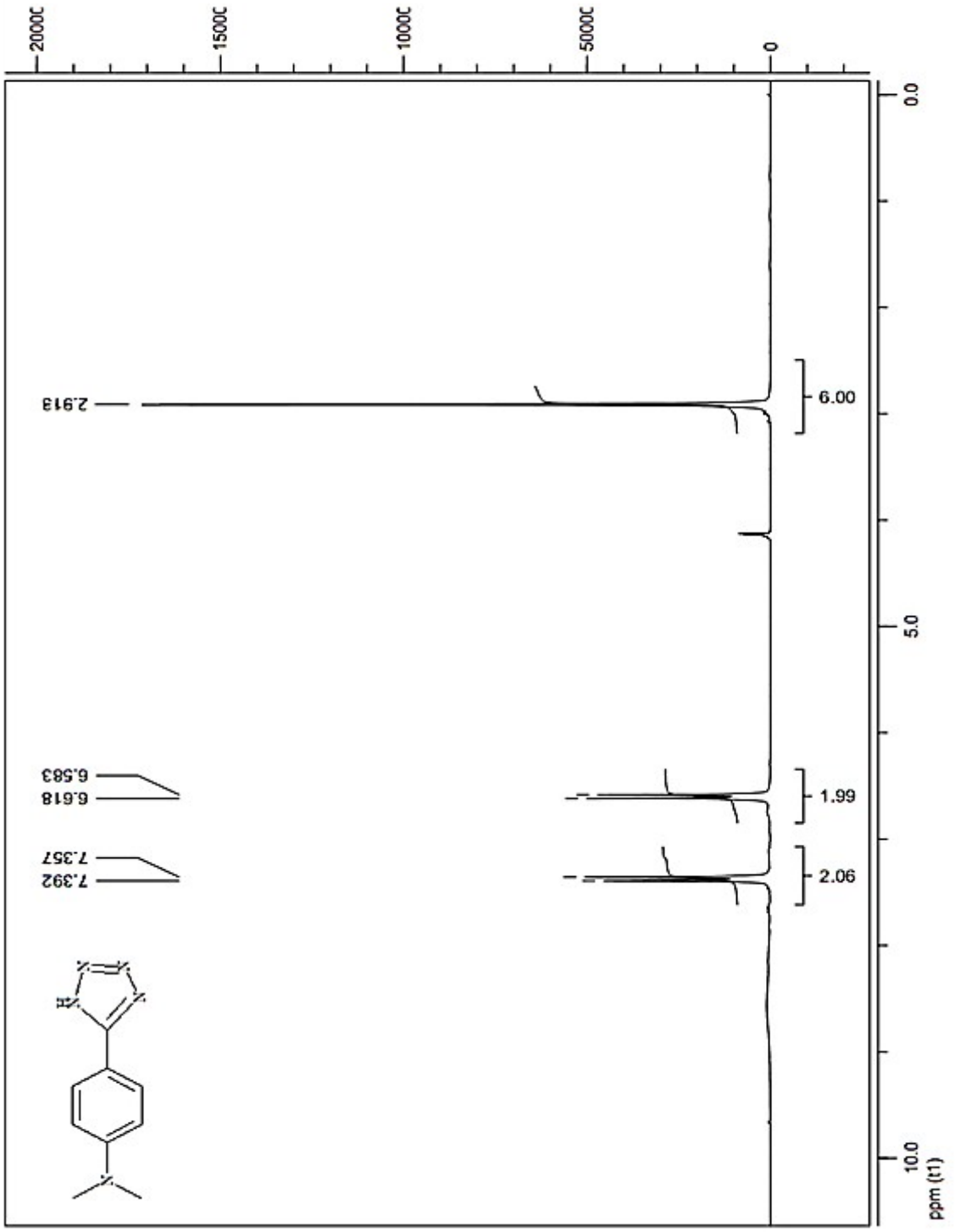
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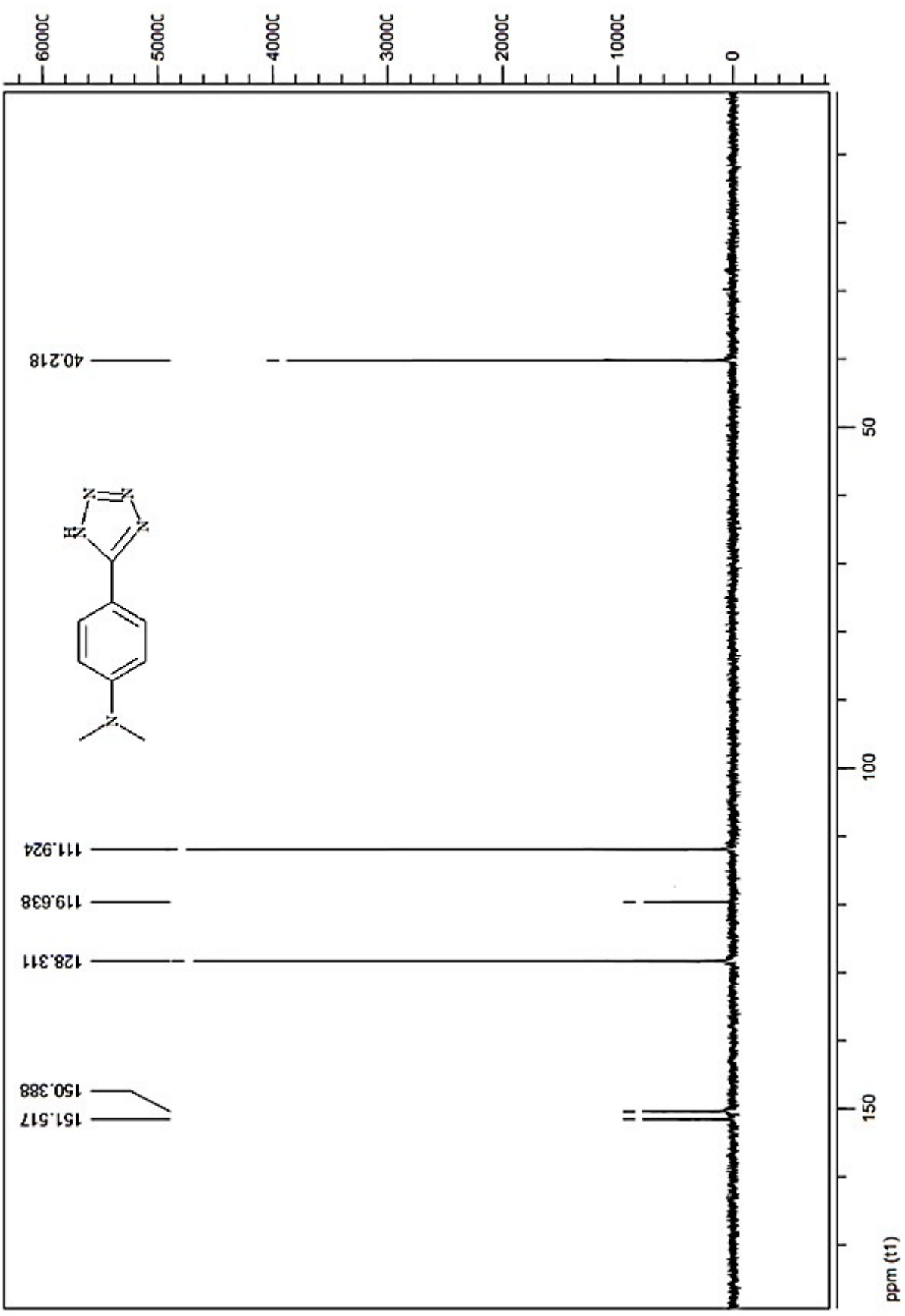
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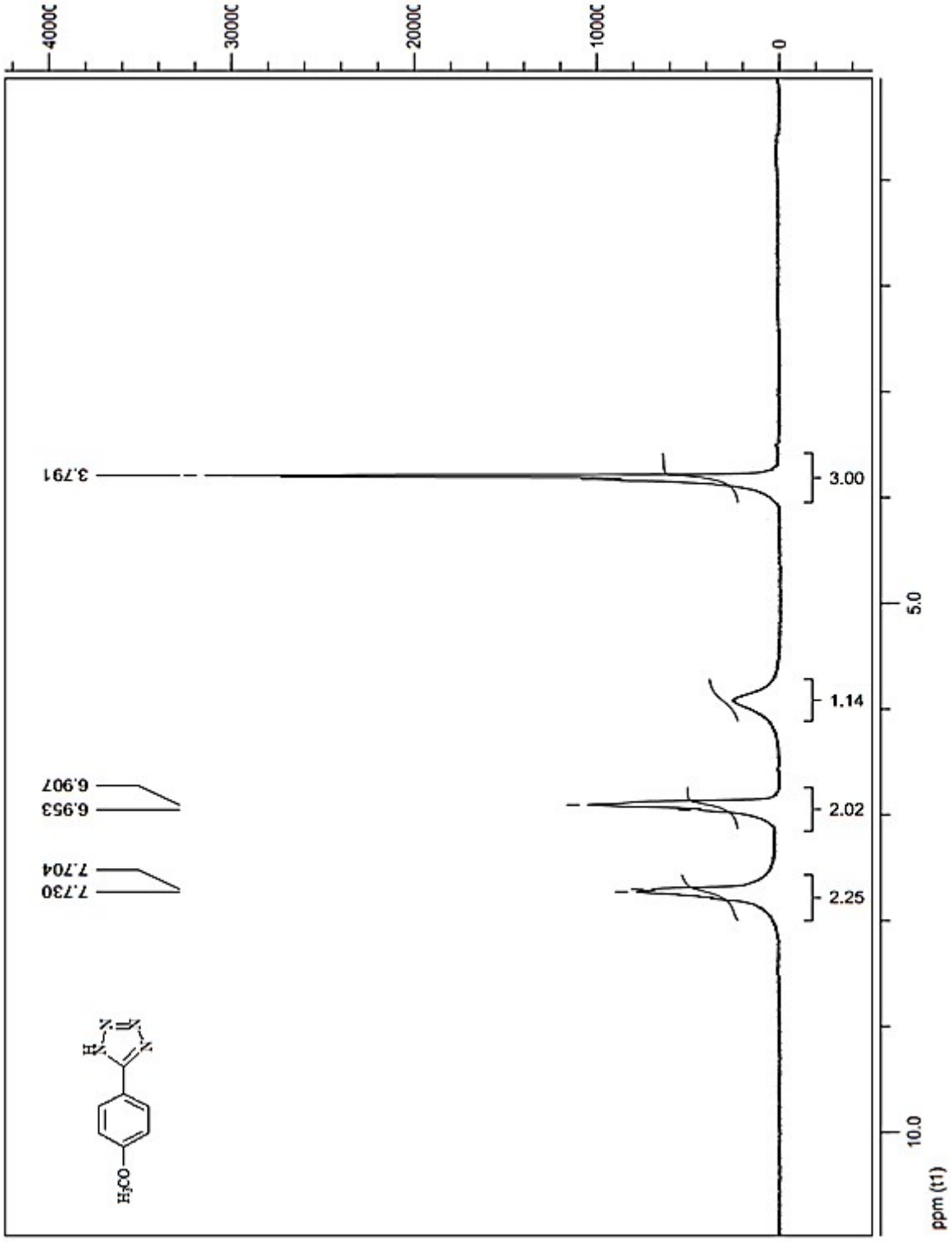
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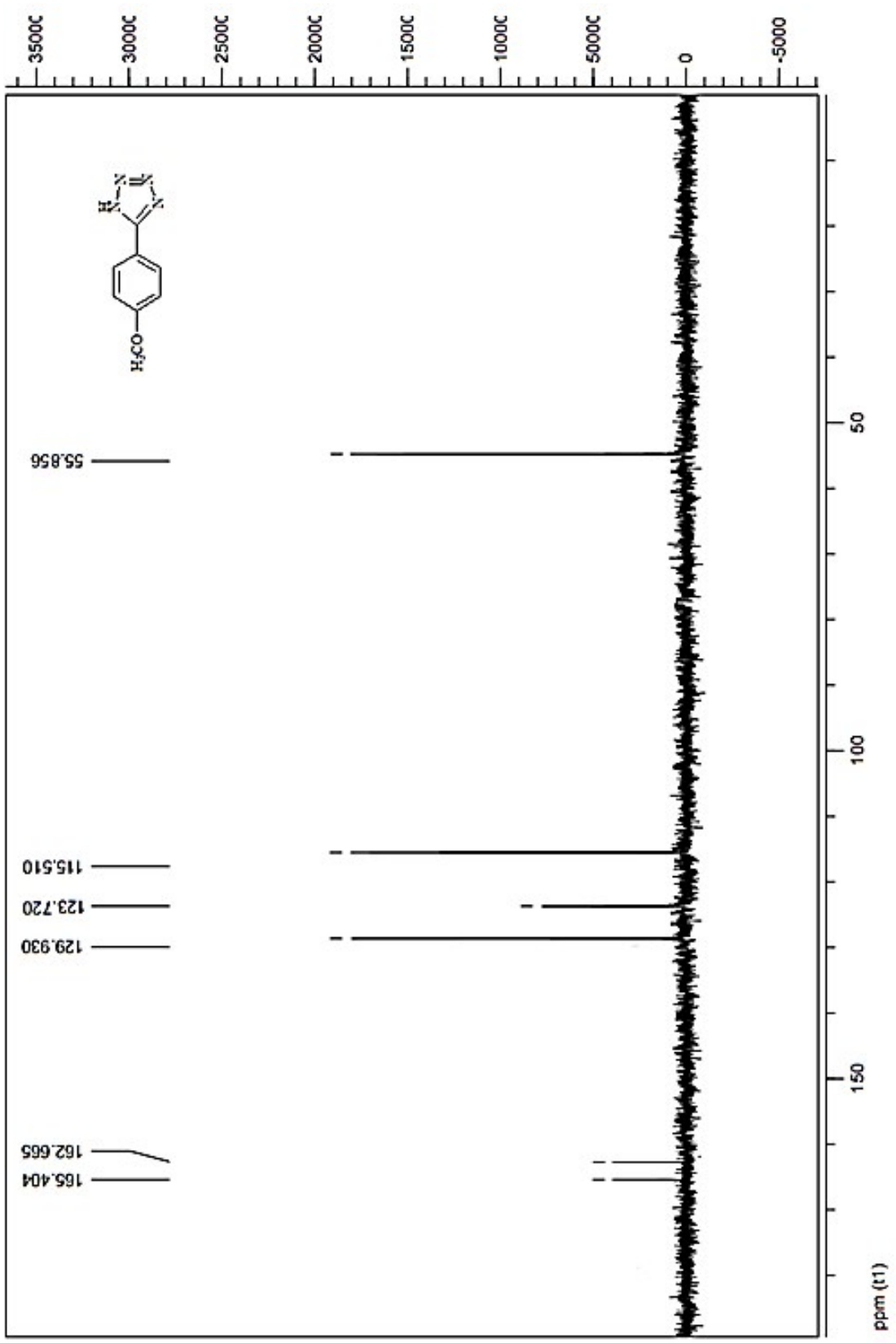
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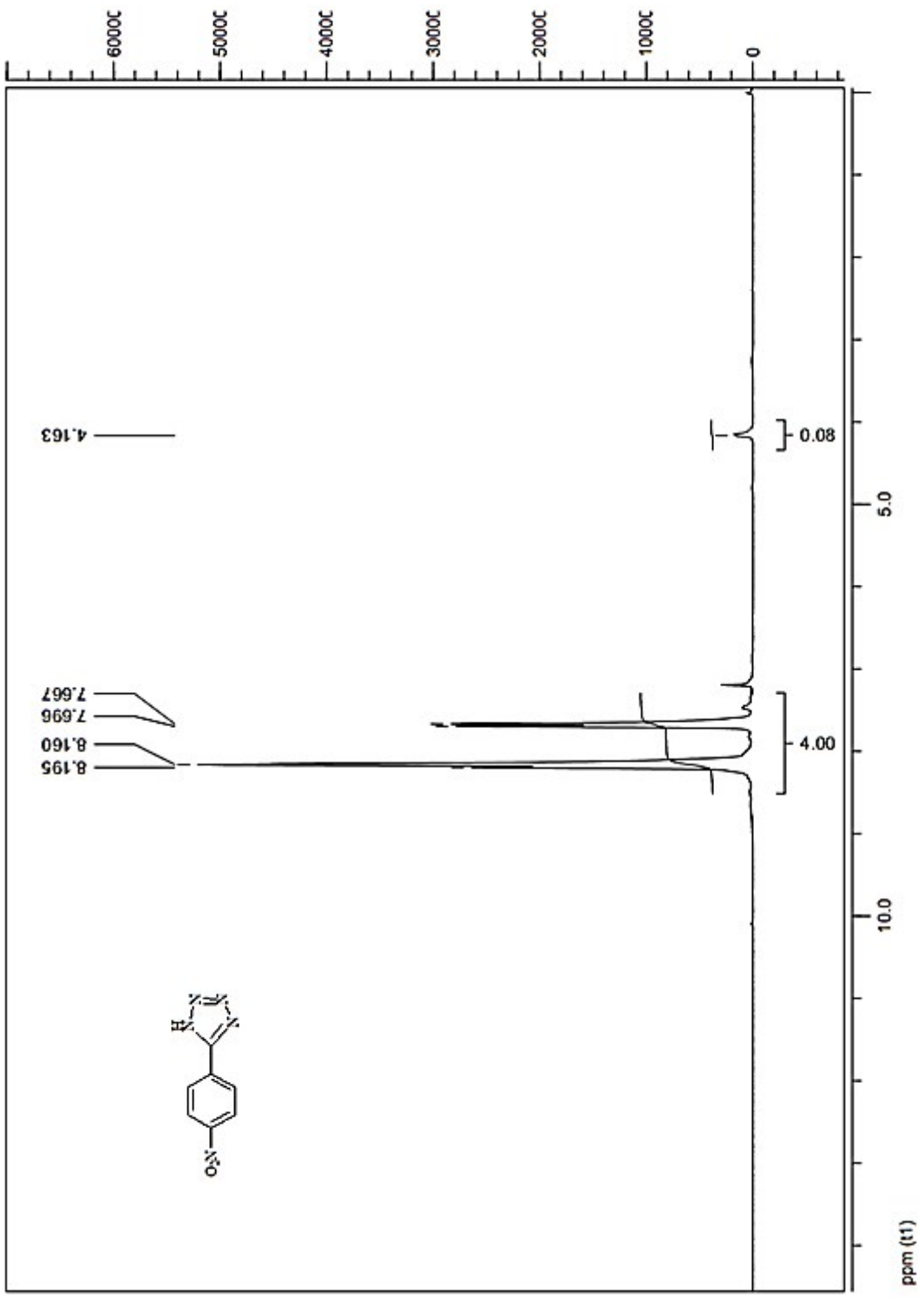
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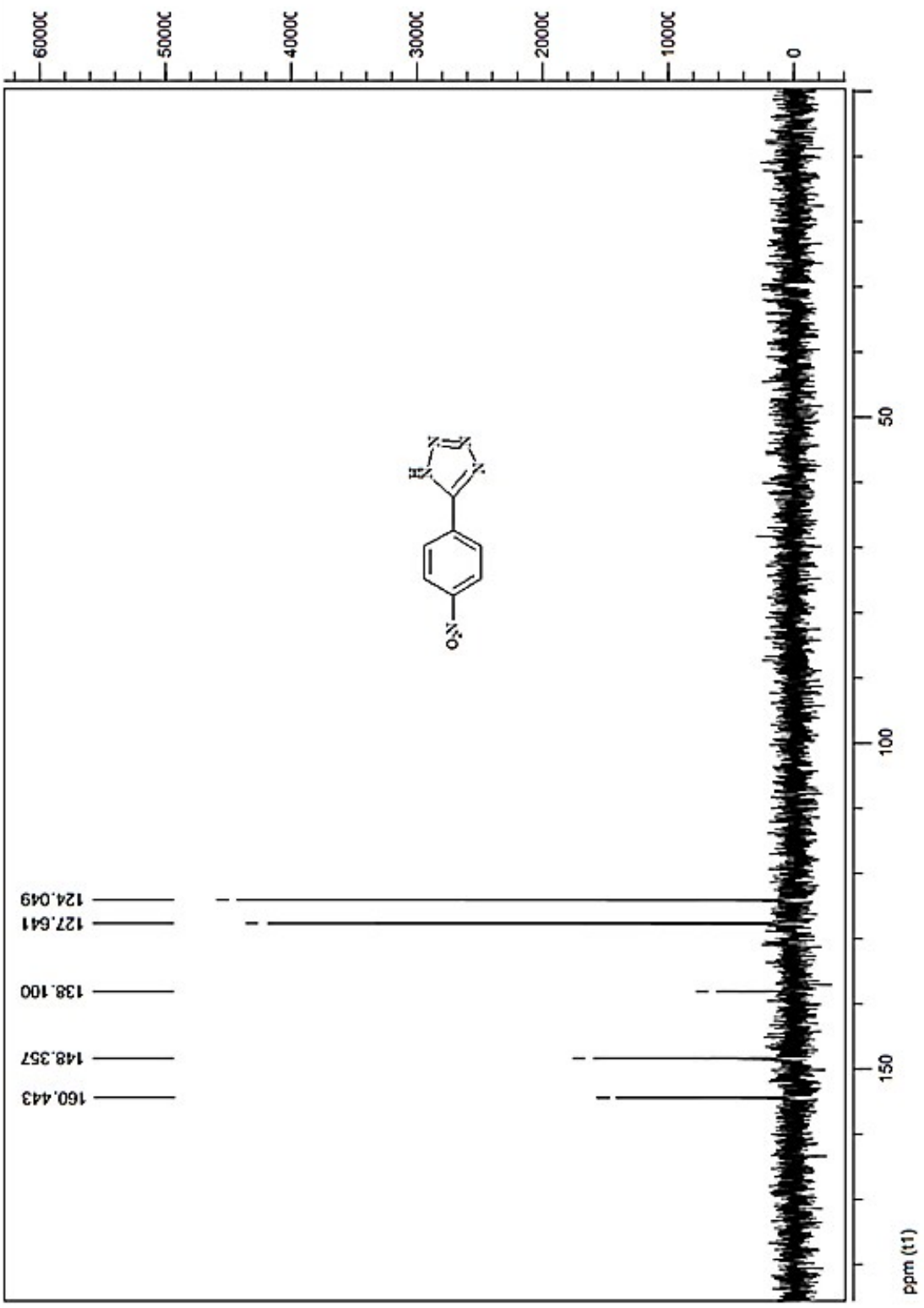
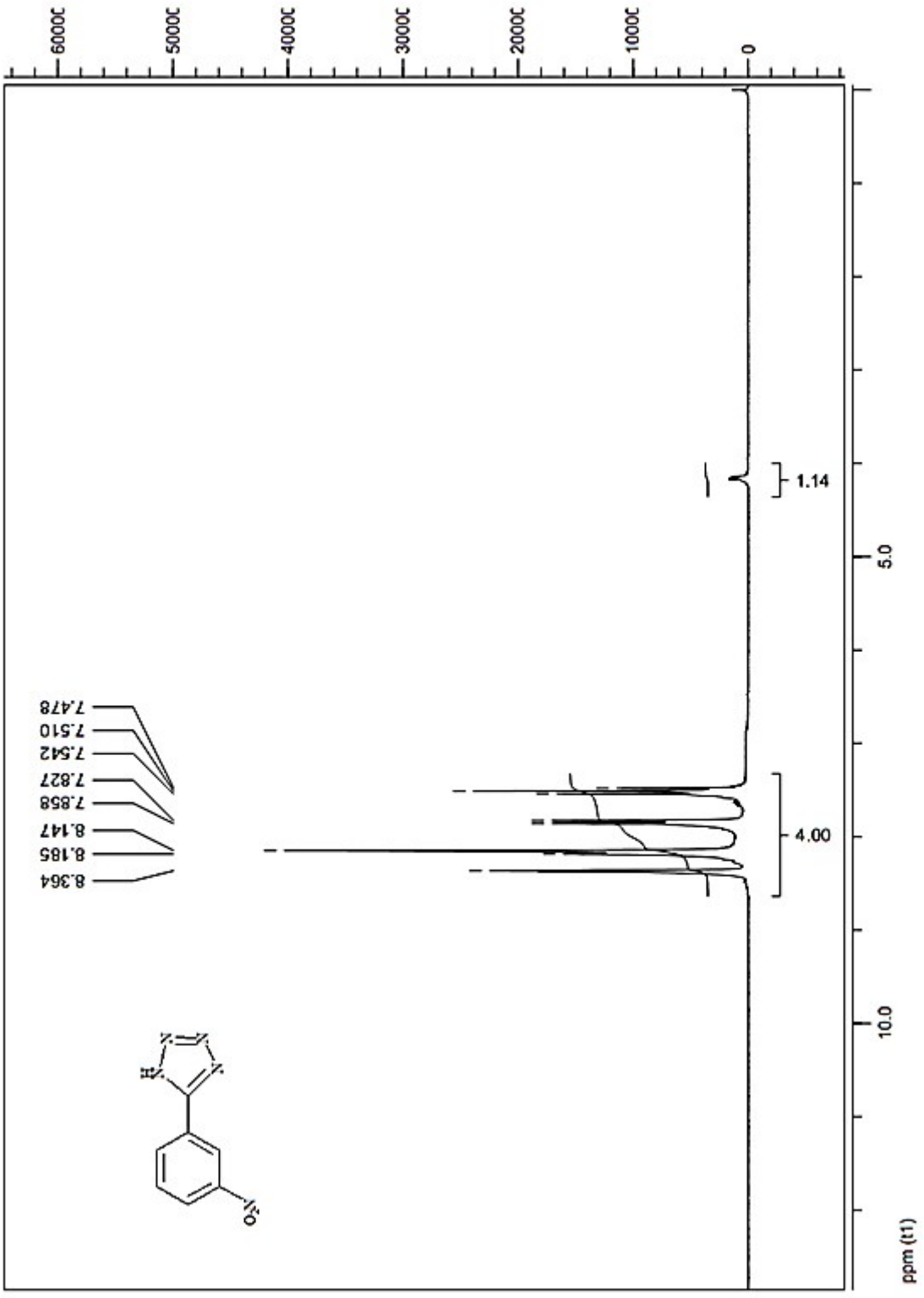
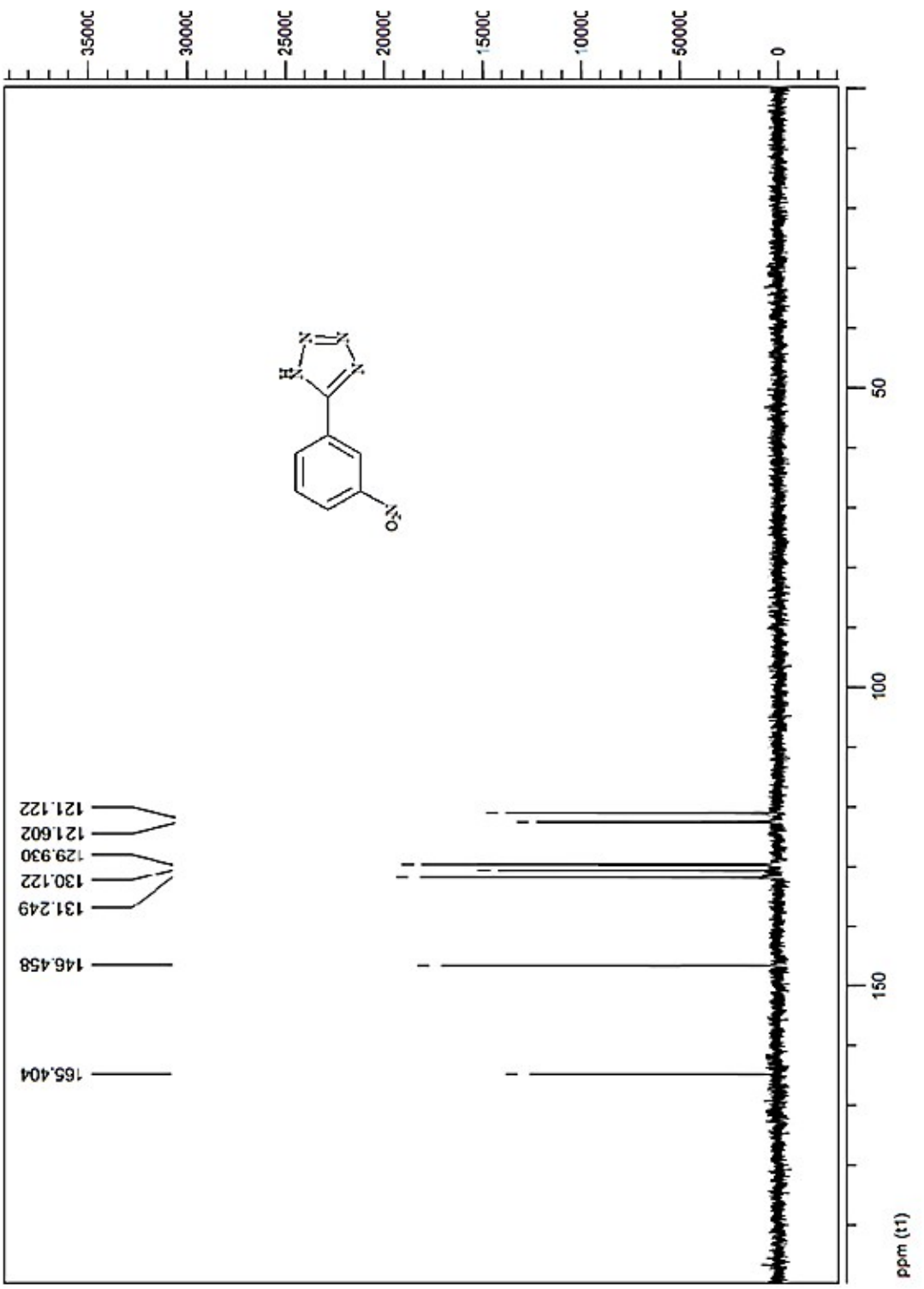
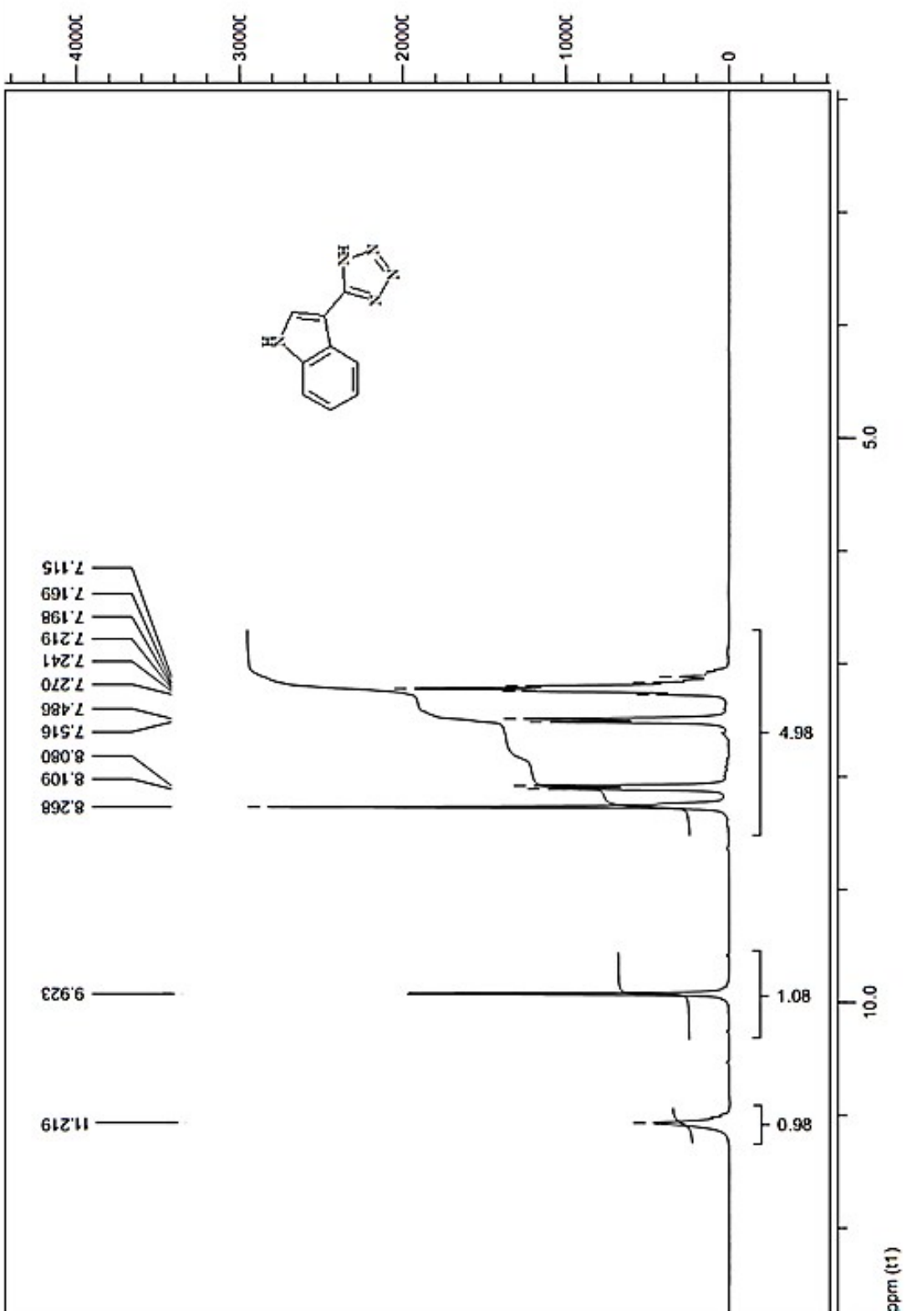
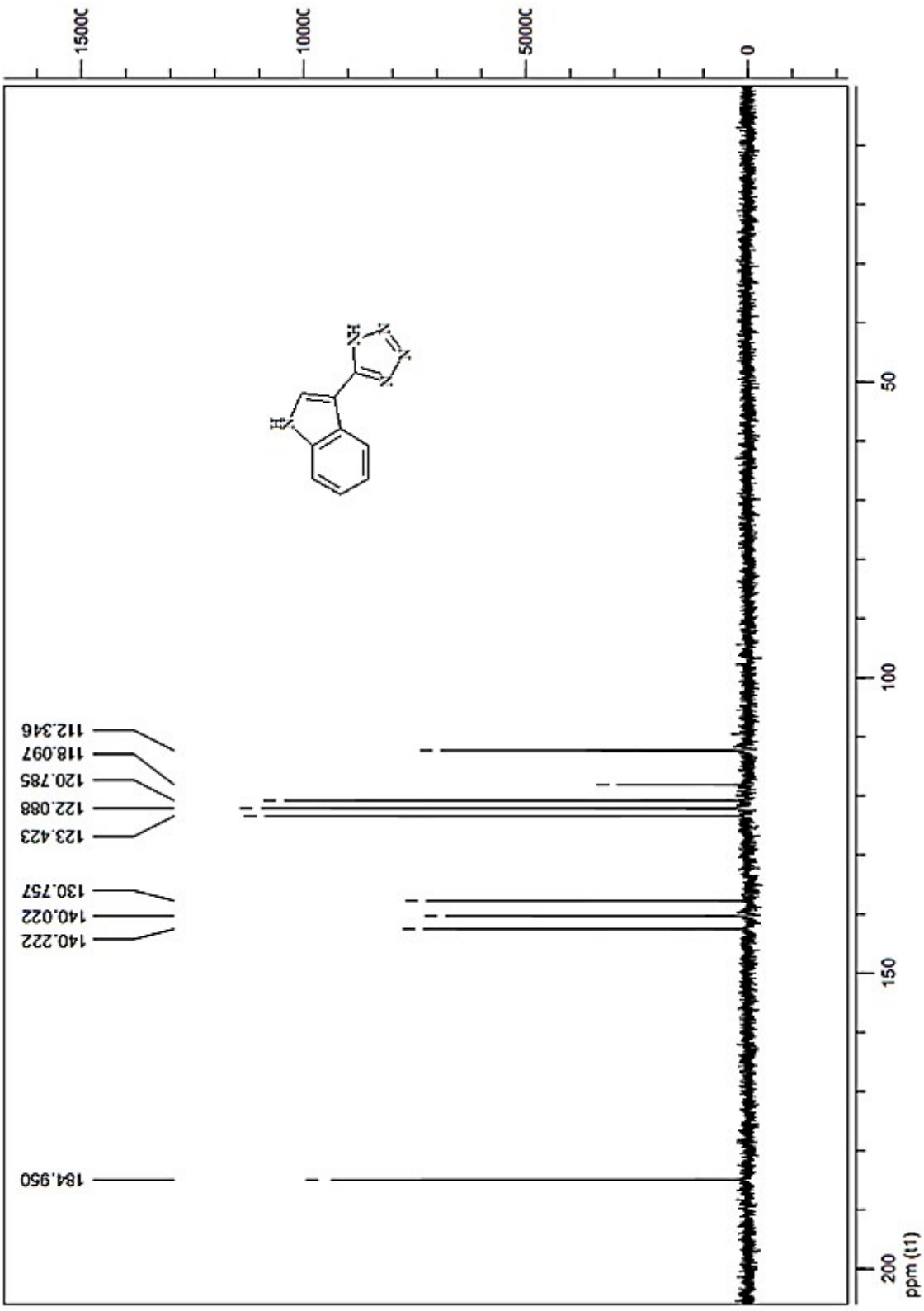
10.0
ppm (t1)

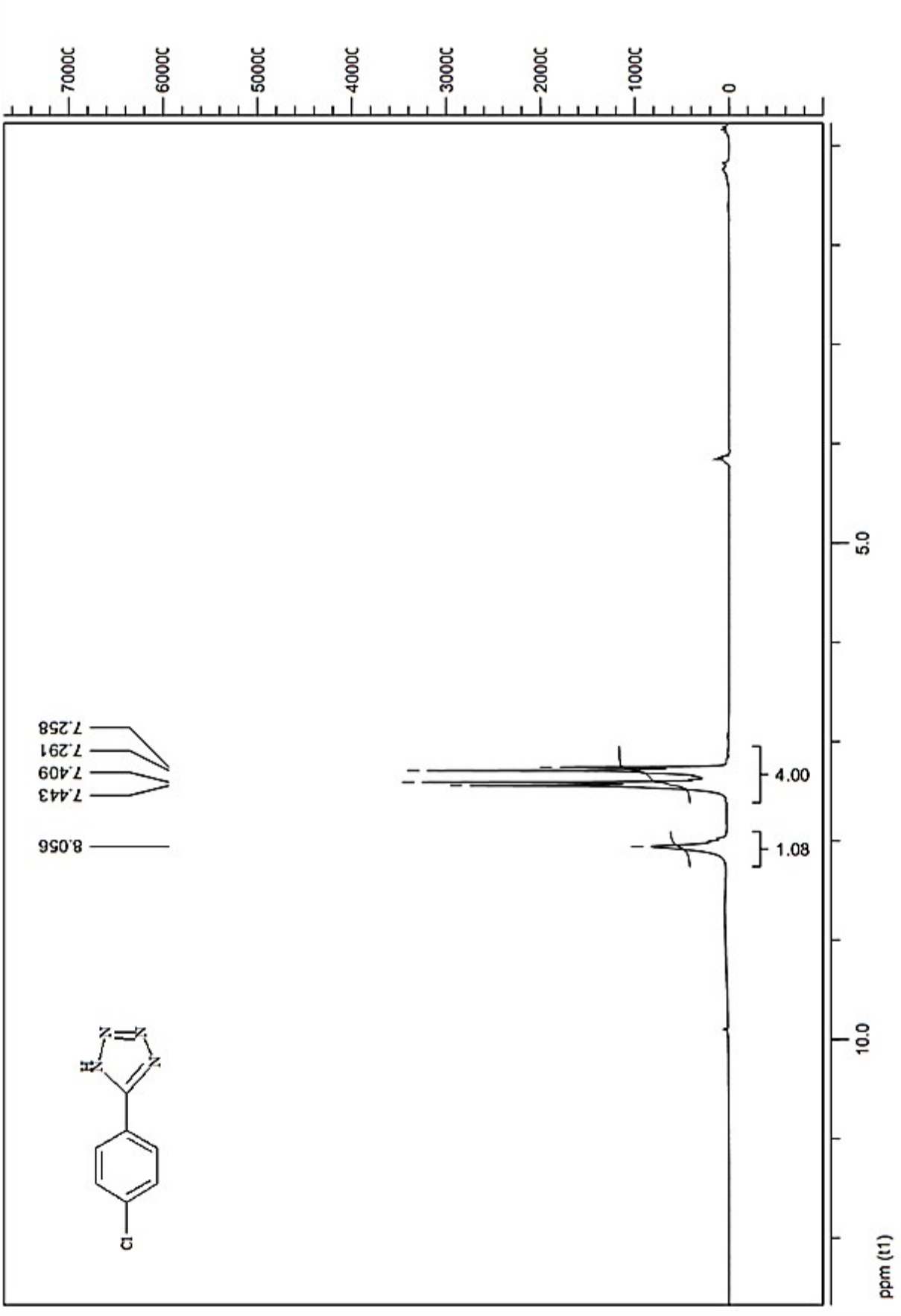

160.443
148.357
138.100
127.641
124.049
ppm (t1)

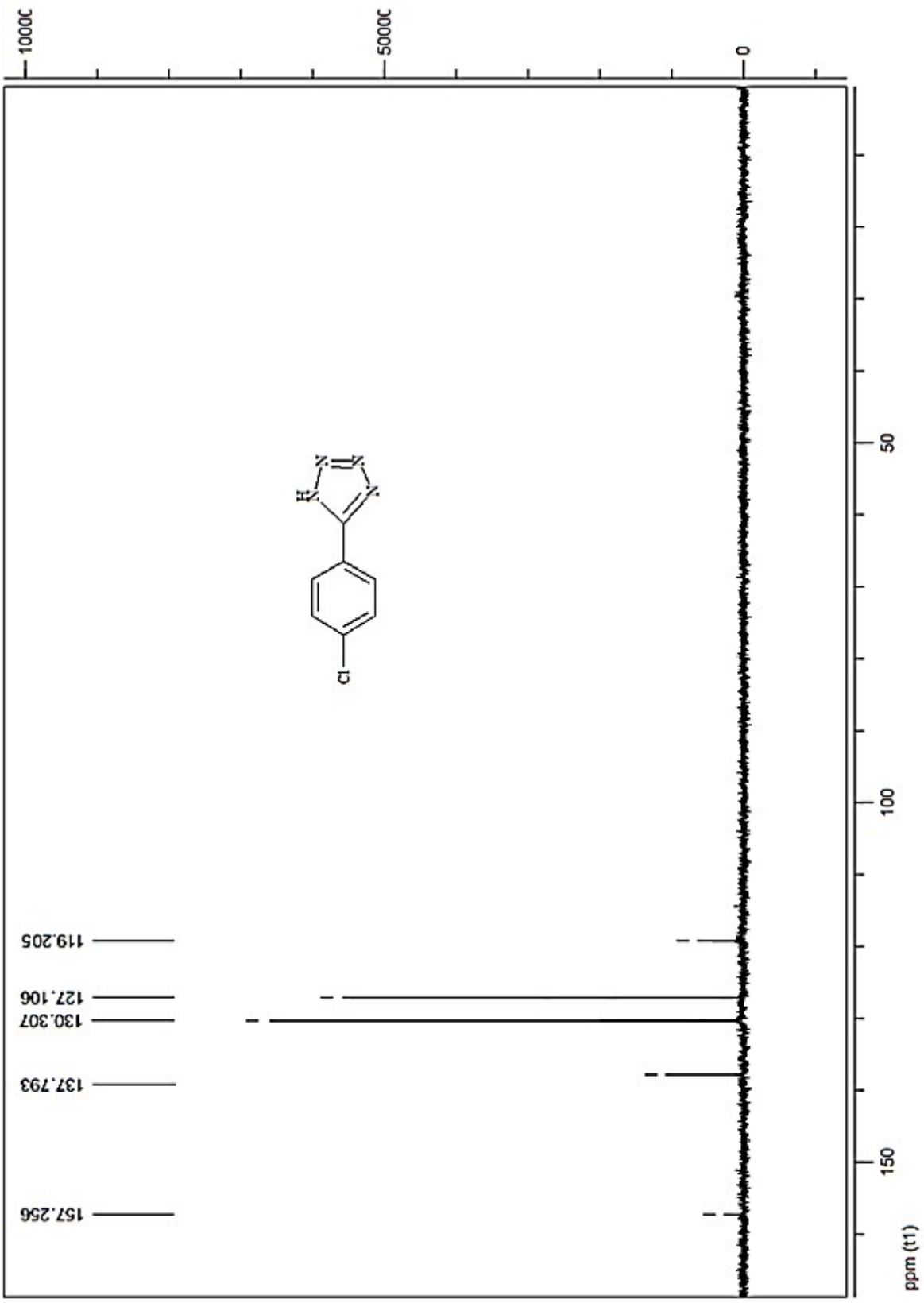

6000
5000
4000
3000
2000
1000
0
8.364
8.185
8.147
7.858
7.827
7.542
7.510
7.478
1.14
4.00
10.0
5.0
ppm (t1)

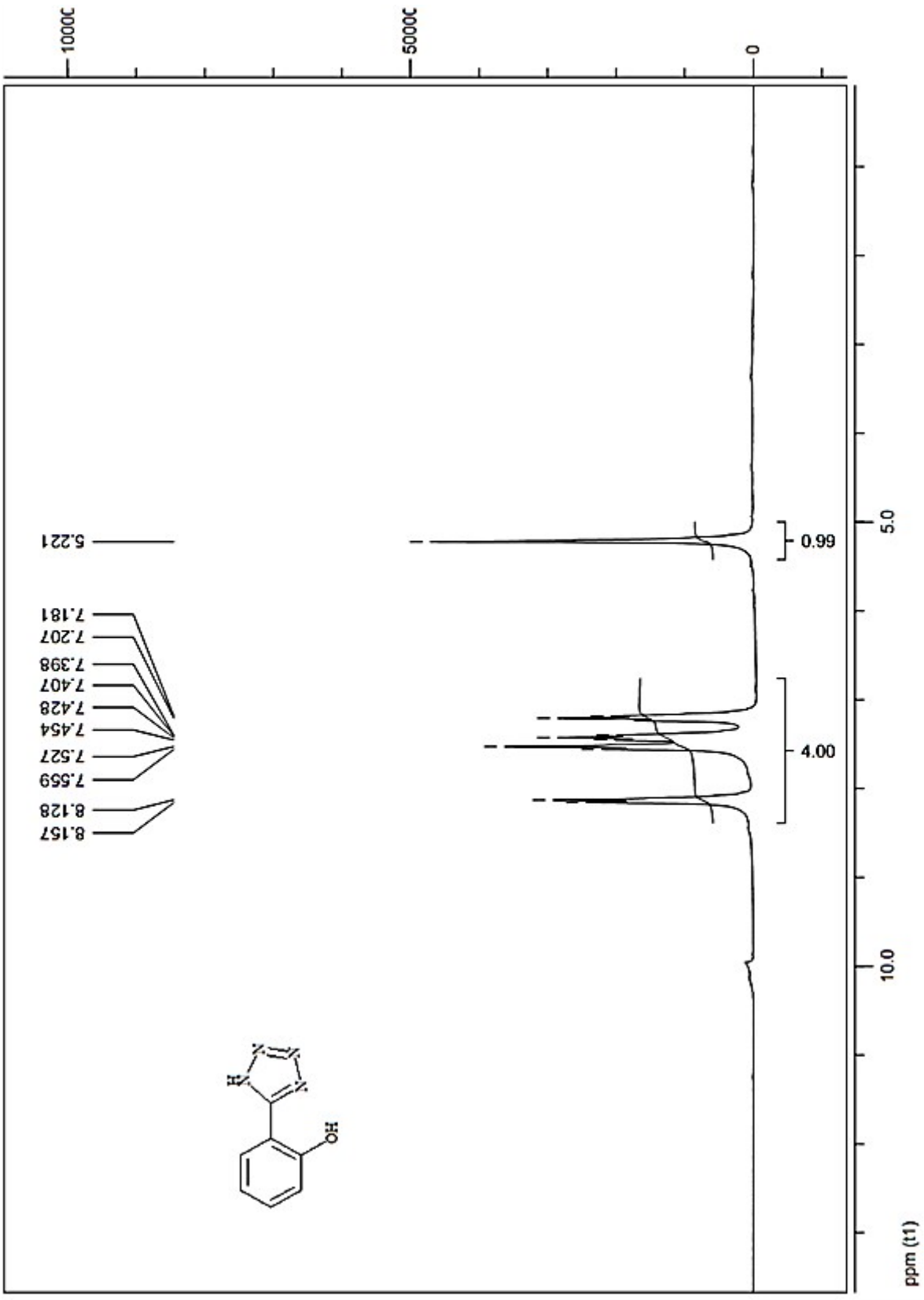

3500
3000
2500
2000
1500
1000
500
0
50
100
150
ppm (t1)
121.122
121.602
129.930
130.122
131.249
146.458
165.404

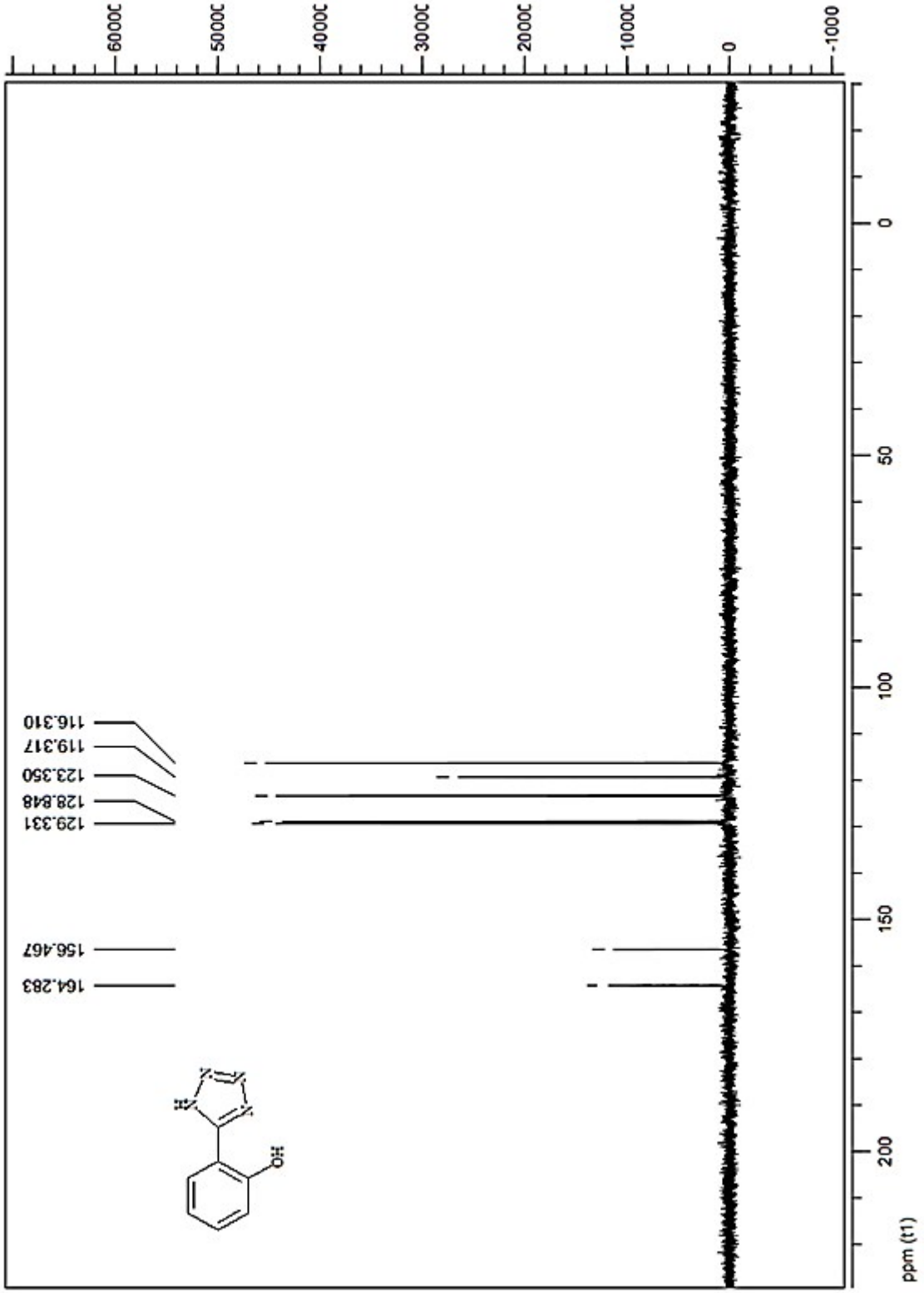

40000
30000
20000
10000
0
11.219
9.923
8.268
8.109
8.080
7.516
7.486
7.270
7.241
7.219
7.198
7.169
7.115
4.98
1.08
0.98
5.0
10.0
ppm (t1)

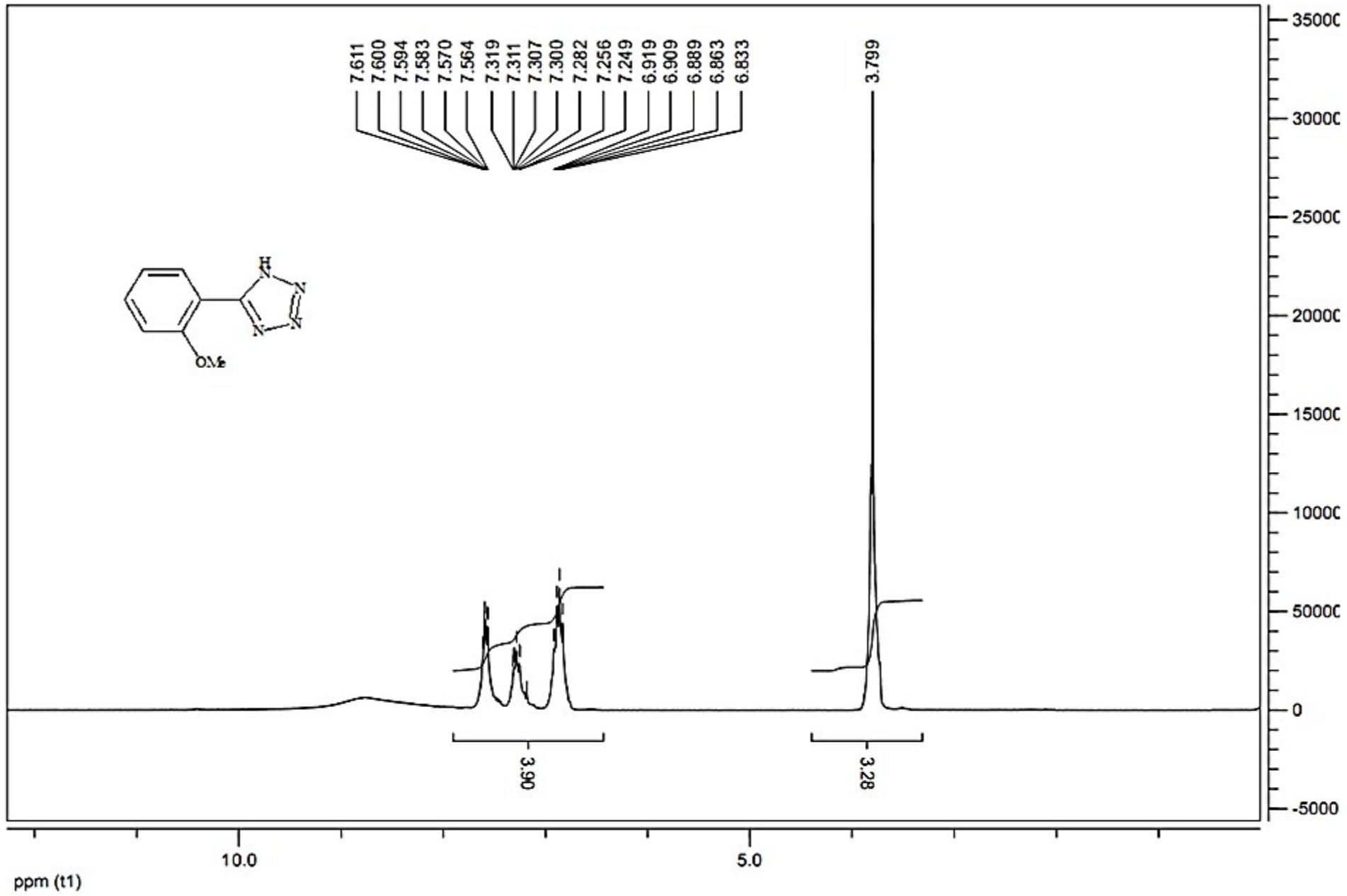

15000
10000
5000
0
184.950
140.222
140.022
130.757
123.423
122.088
120.785
118.097
112.346
200
150
100
50
ppm (t1)

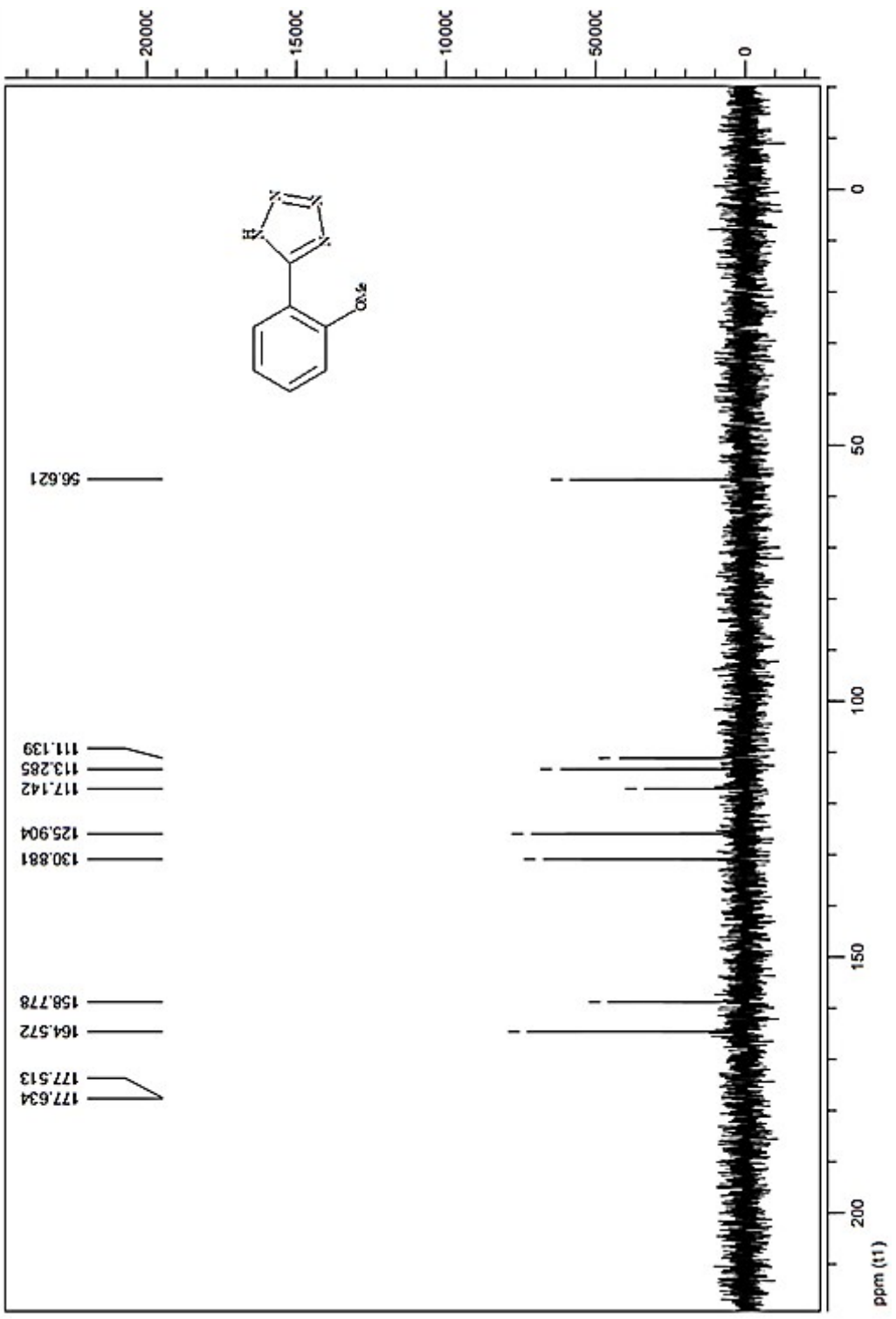

7000
6000
5000
4000
3000
2000
1000
0
5.0
10.0
ppm (t1)
4.00
1.08
8.056
7.443
7.409
7.291
7.258
Cl


10000
5000
0
50
100
150
ppm (t1)
157.256
137.793
130.307
127.106
119.205
Cl

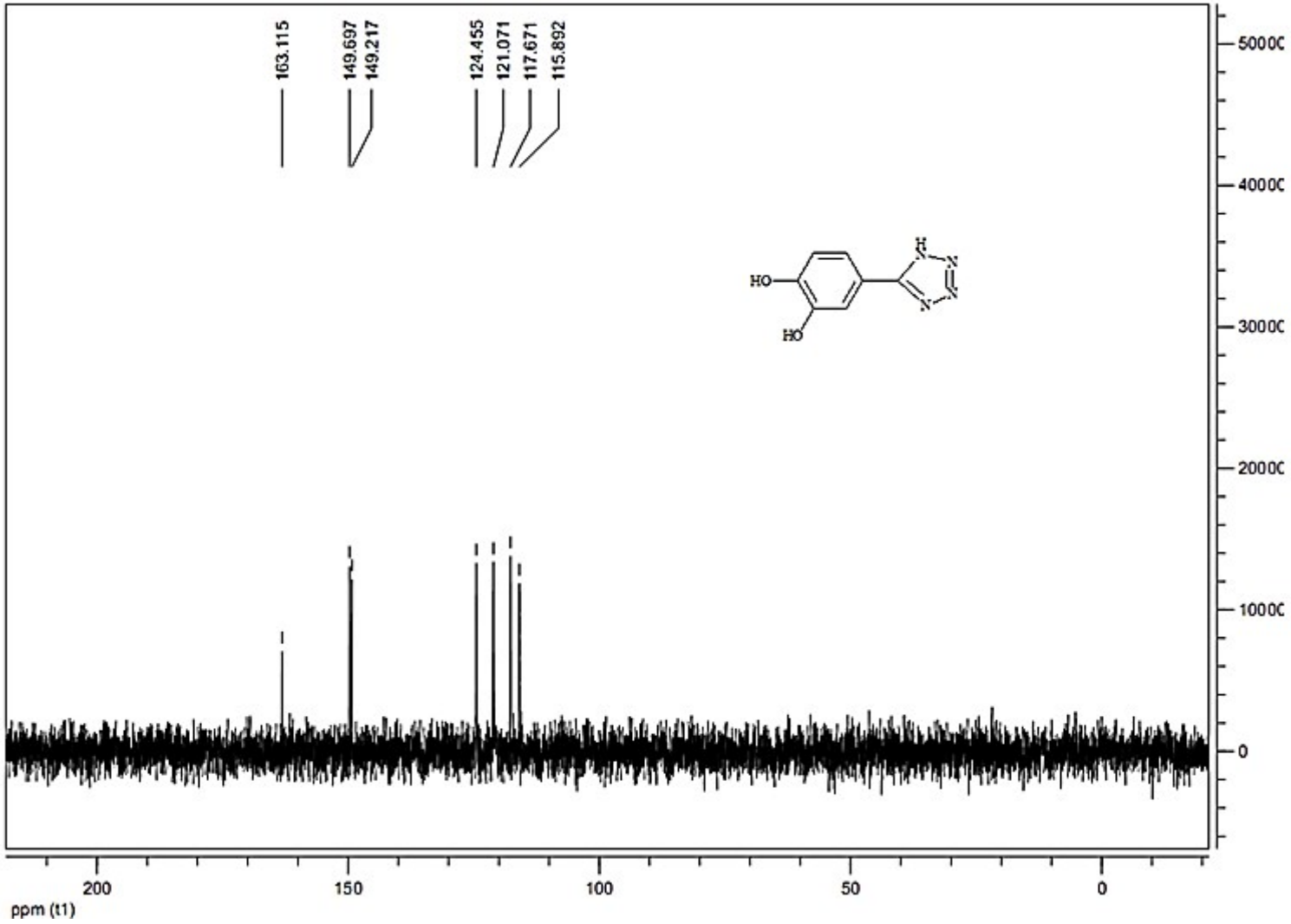

10000
5000
0
5.221
7.181
7.207
7.398
7.407
7.428
7.454
7.527
7.559
8.128
8.157
0.99
4.00
5.0
10.0
ppm (t1)
OH

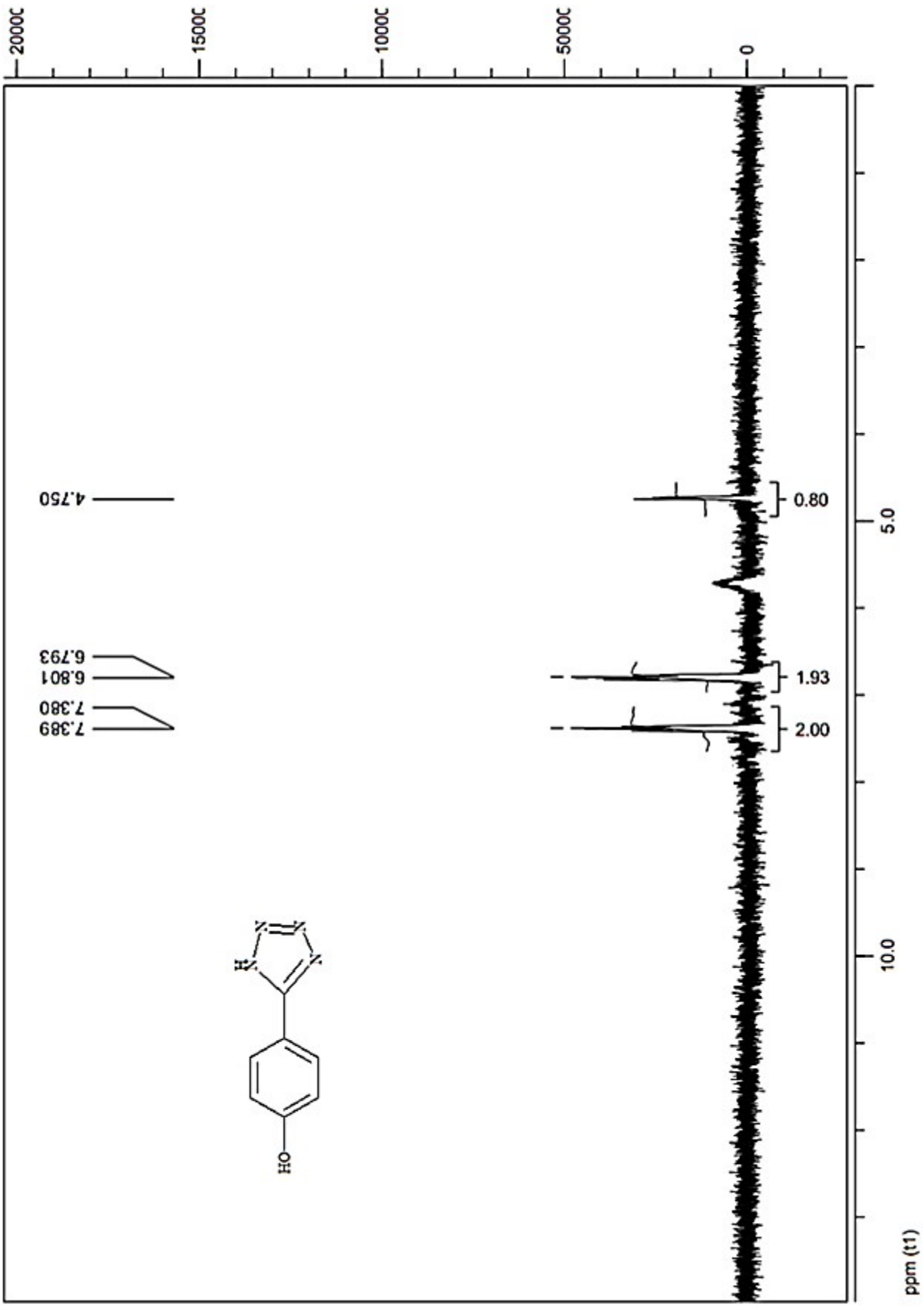

164.283
156.467
129.331
128.848
123.350
119.317
116.310
ppm (t1)

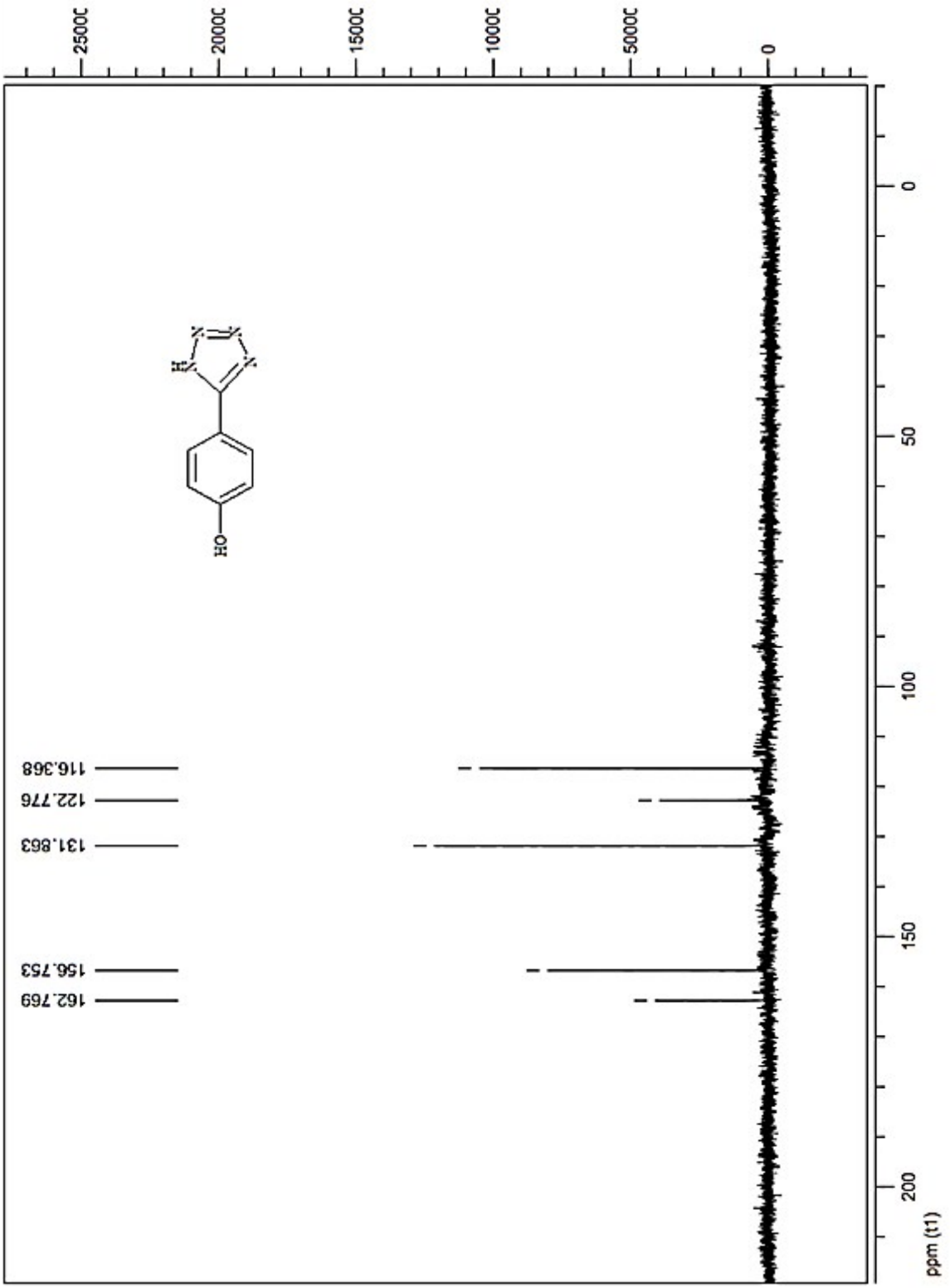

7.611
7.600
7.594
7.583
7.570
7.564
7.319
7.311
7.307
7.300
7.282
7.256
7.249
6.919
6.909
6.889
6.863
6.833
3.799
OMe
3.90
3.28
10.0
5.0
ppm (t1)
35000
30000
25000
20000
15000
10000
5000
0
-5000

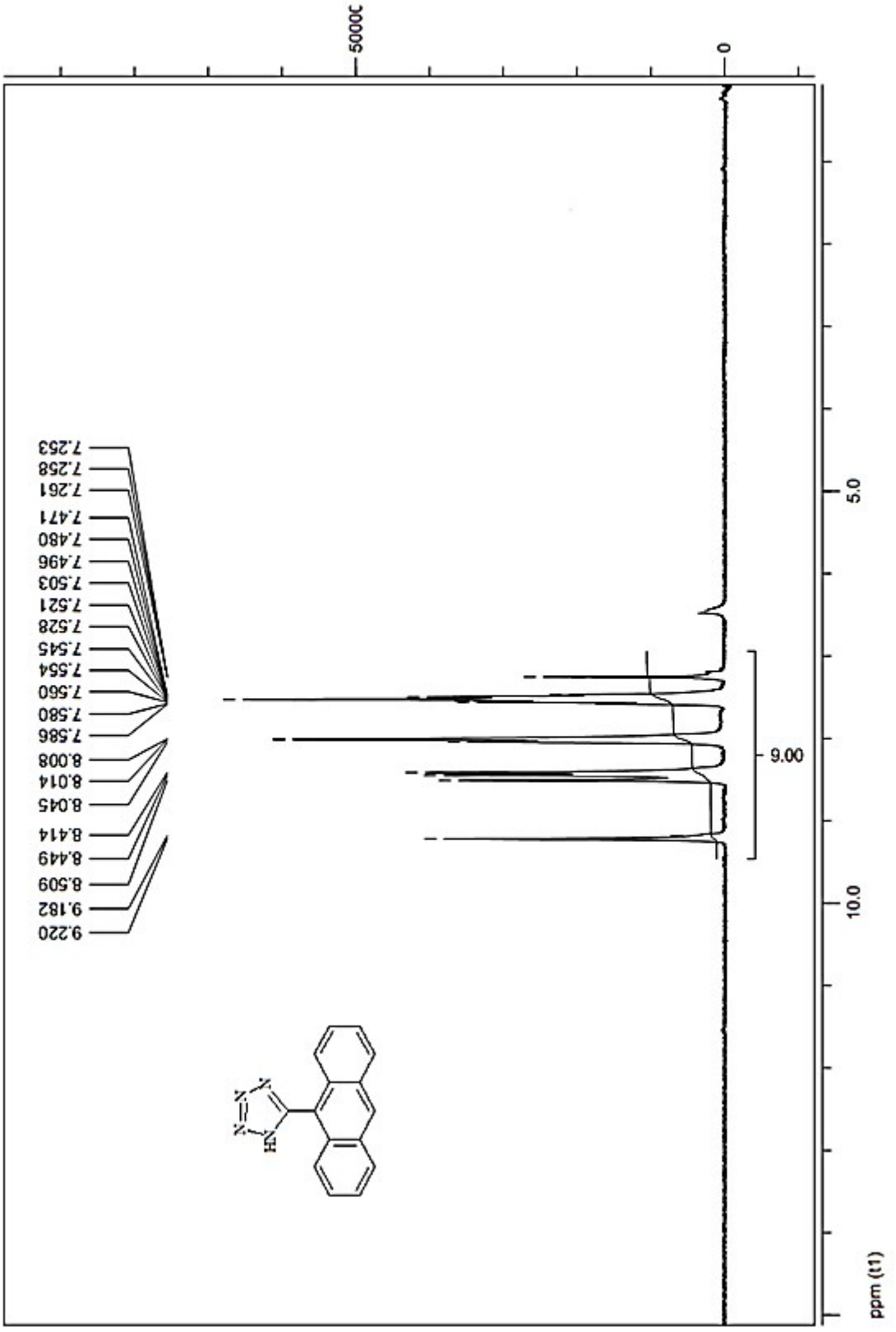

2000
1500
1000
500
0
0
50
100
150
200
ppm (t1)
56.621
111.139
113.285
117.142
125.904
130.881
158.778
164.572
177.513
177.634

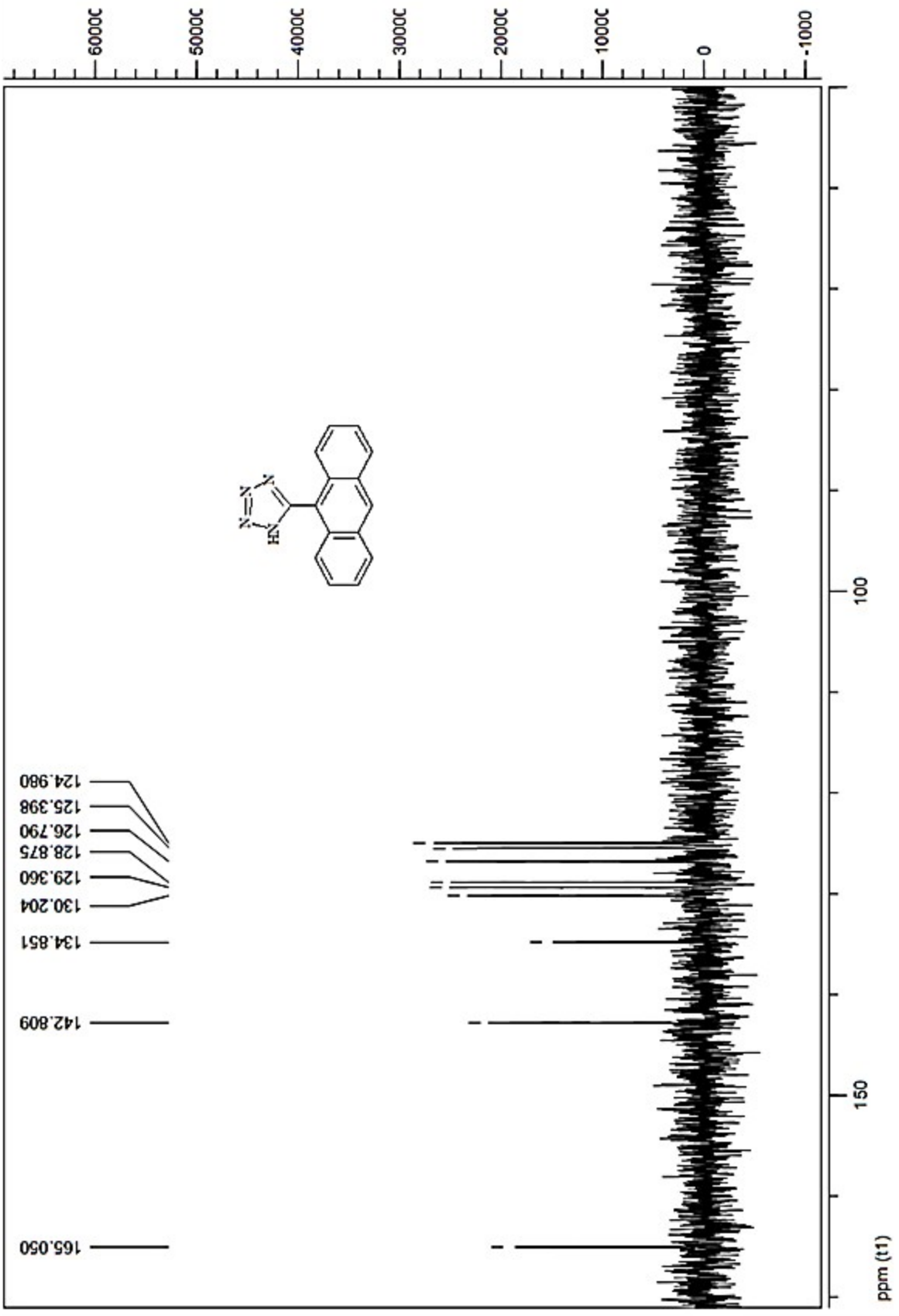
10000
5000
0
5.055
7.286
7.250
7.191
7.016
6.980
2.22
3.00
5.0
10.0
ppm (t1)
HO
HO
N
N
H

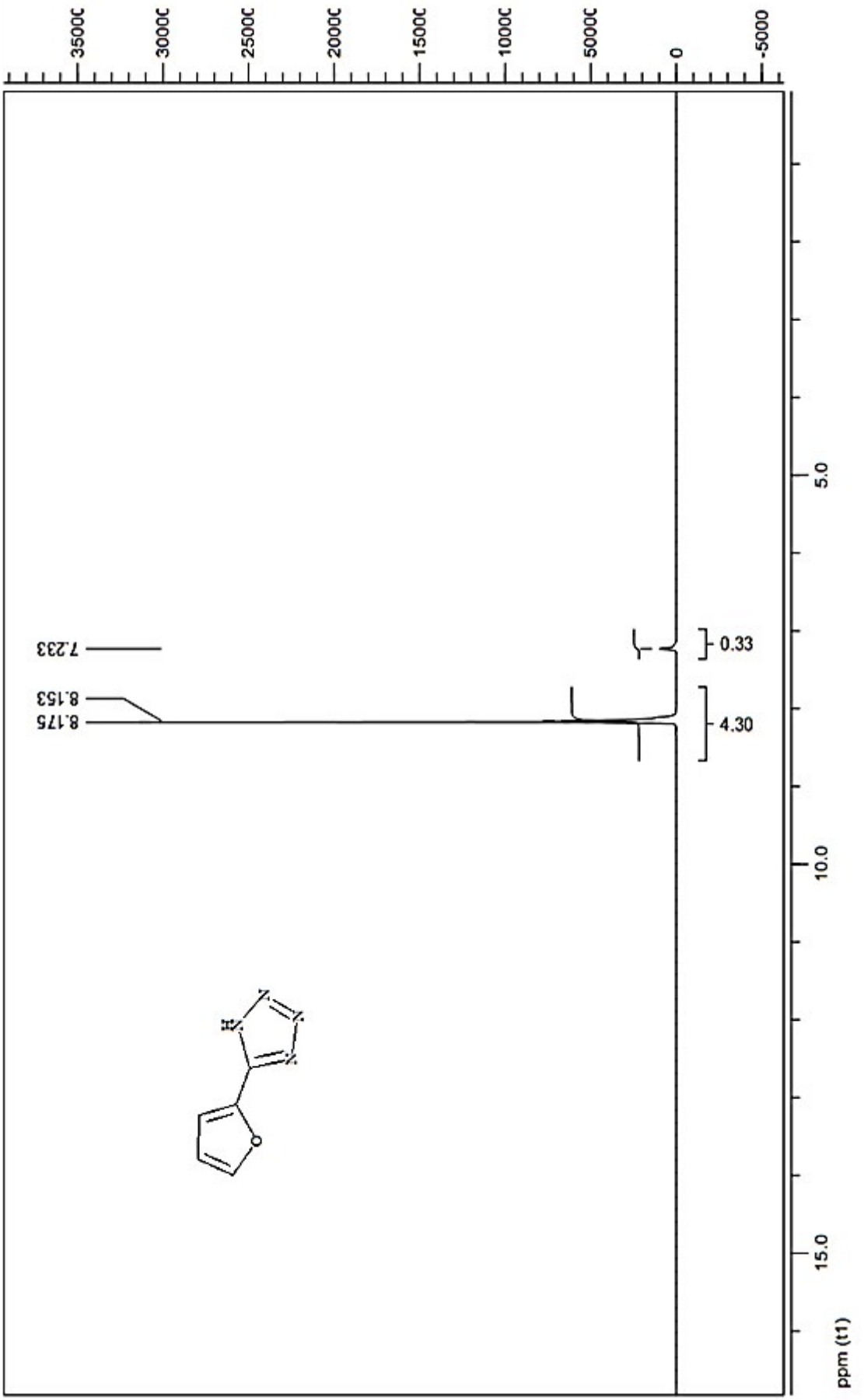

163.115
149.697
149.217
124.455
121.071
117.671
115.892
HO
HO
H
N
N
N
N
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

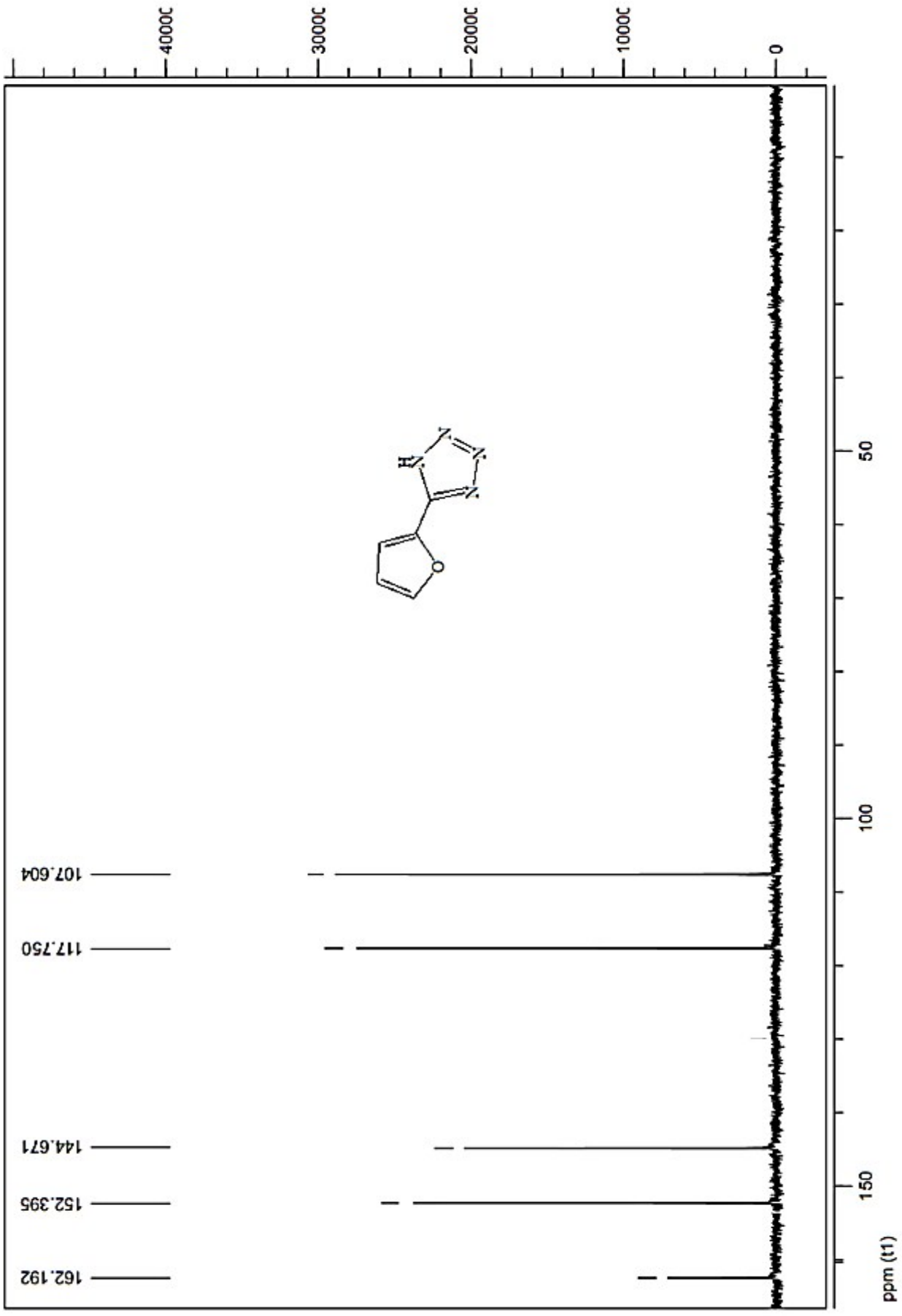

2000
1500
1000
500
0
4.750
7.389
7.380
6.801
6.793
0.80
1.93
2.00
5.0
10.0
ppm (t1)
OH


25000
20000
15000
10000
5000
0
116.368
122.776
131.863
156.753
162.769
0
50
100
150
200
ppm (t1)

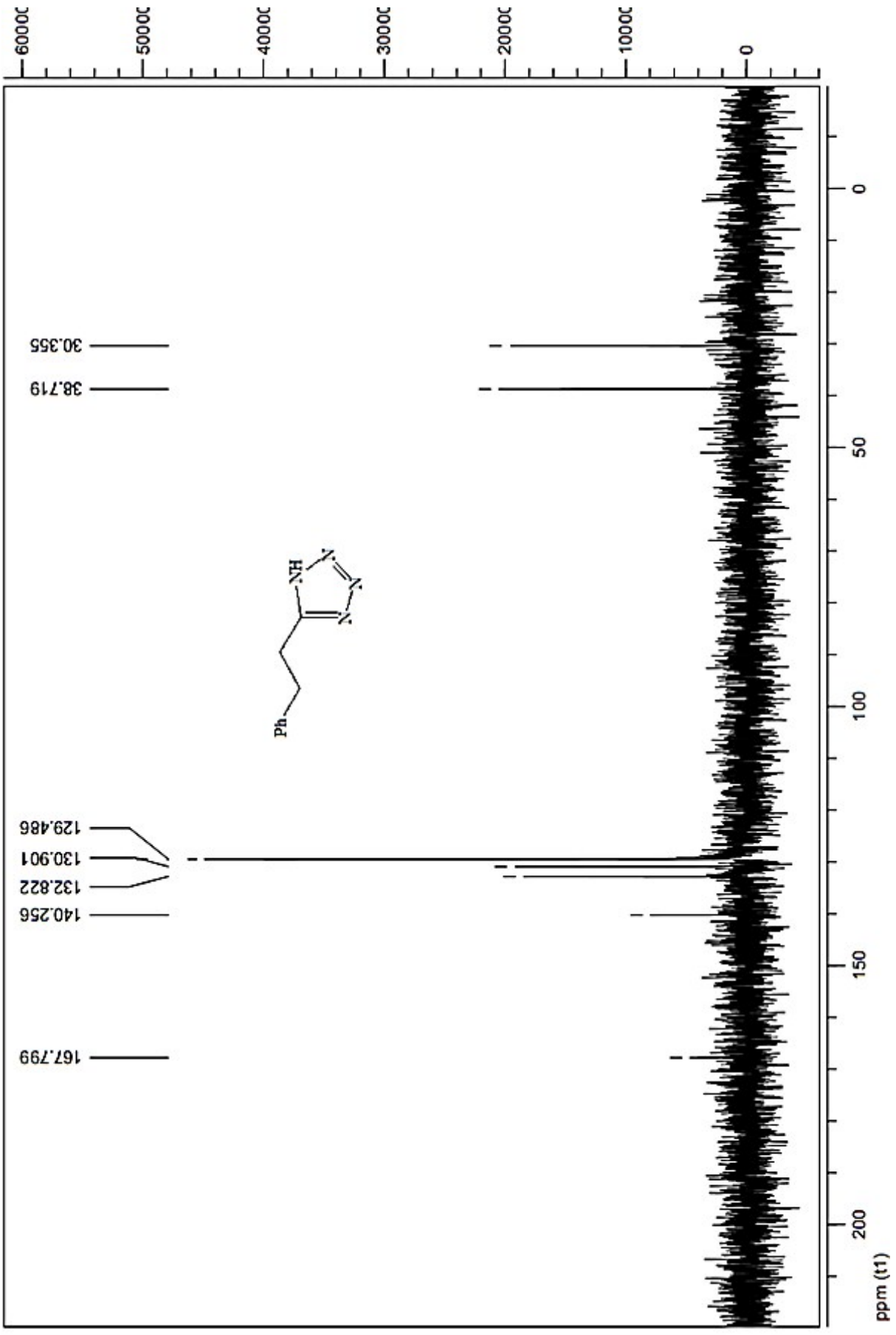

50000
0
7.253
7.258
7.261
7.471
7.480
7.496
7.503
7.521
7.528
7.545
7.554
7.560
7.580
7.586
8.008
8.014
8.045
8.414
8.449
8.509
9.182
9.220
9.00
5.0
10.0
ppm (t1)

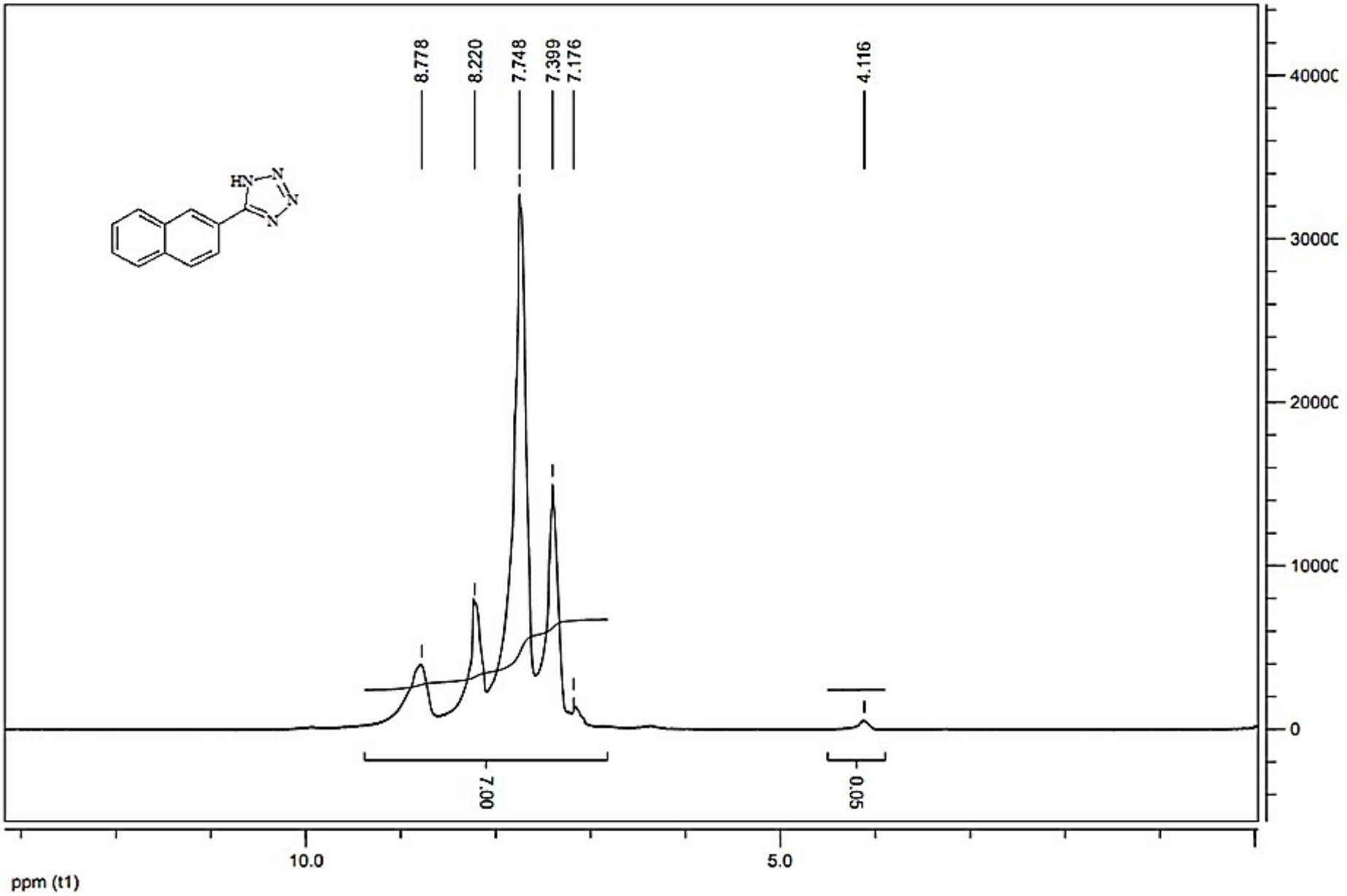

6000
5000
4000
3000
2000
1000
0
-1000
100
150
ppm (t1)
165.050
142.809
134.851
130.204
129.360
128.875
126.790
125.398
124.980

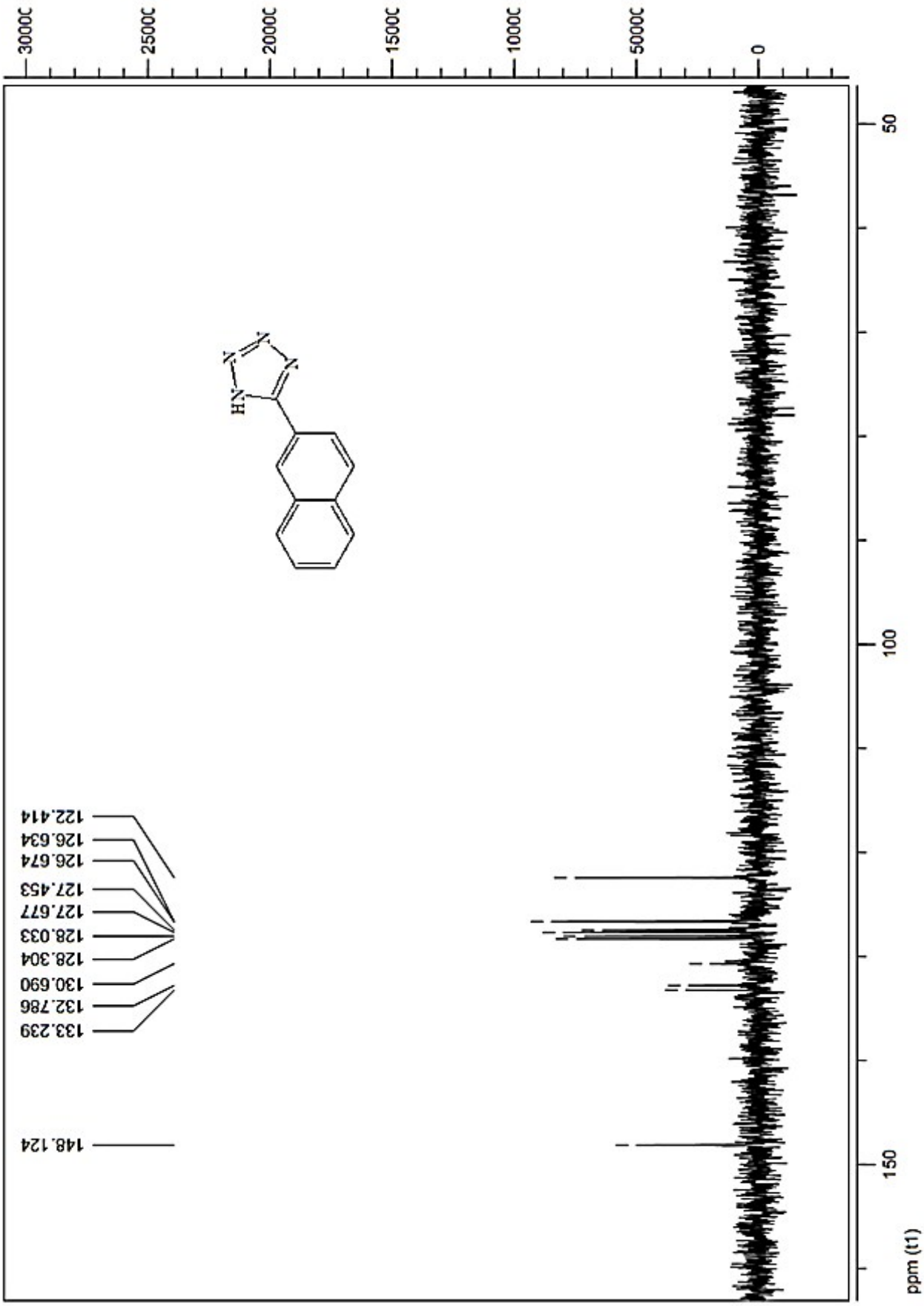

35000
30000
25000
20000
15000
10000
5000
0
-5000
7.233
8.153
8.175
0.33
4.30
5.0
10.0
15.0
ppm (t1)

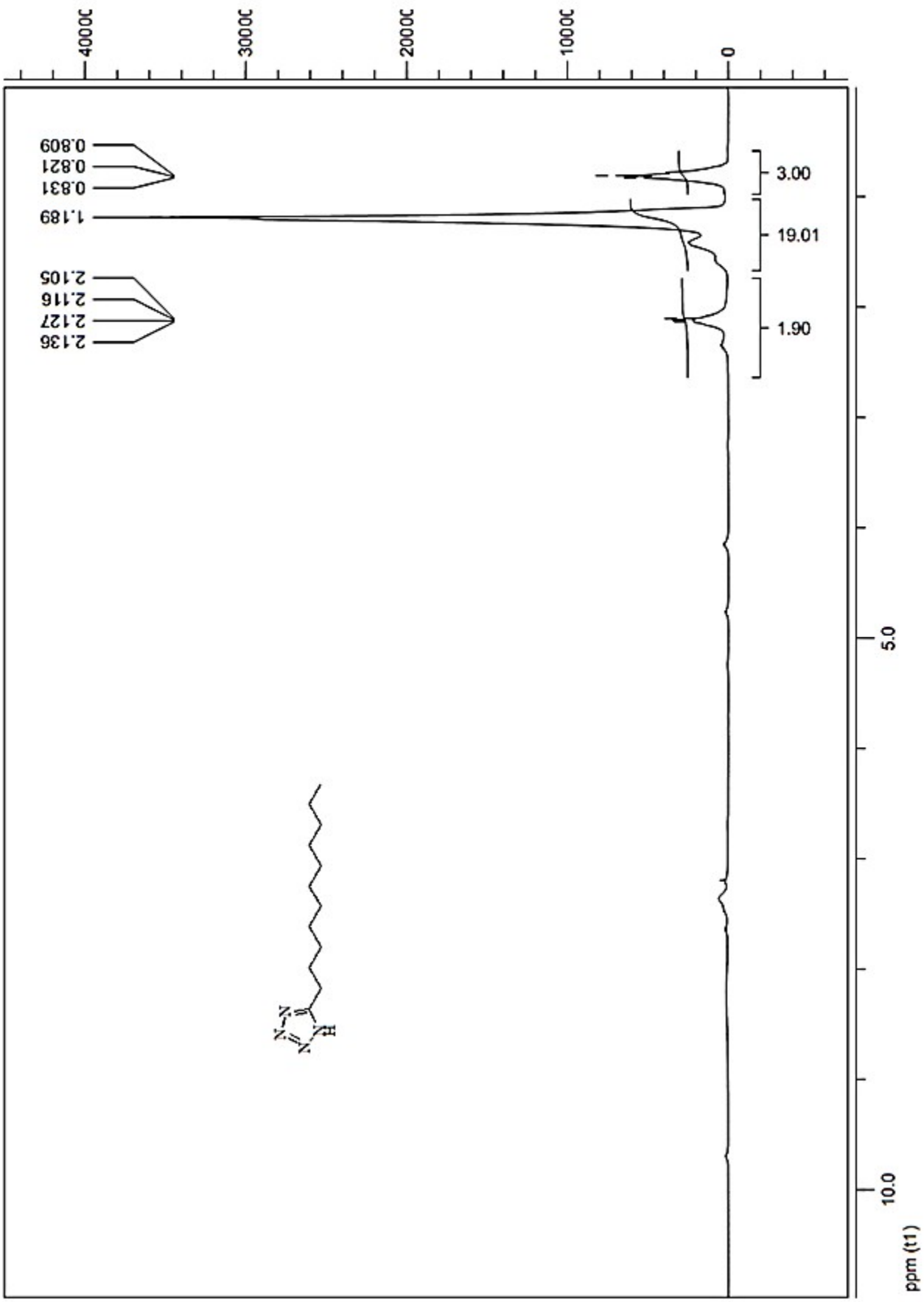

4000
3000
2000
1000
0
50
100
150
ppm (t1)
162.192
152.395
144.671
117.750
107.604

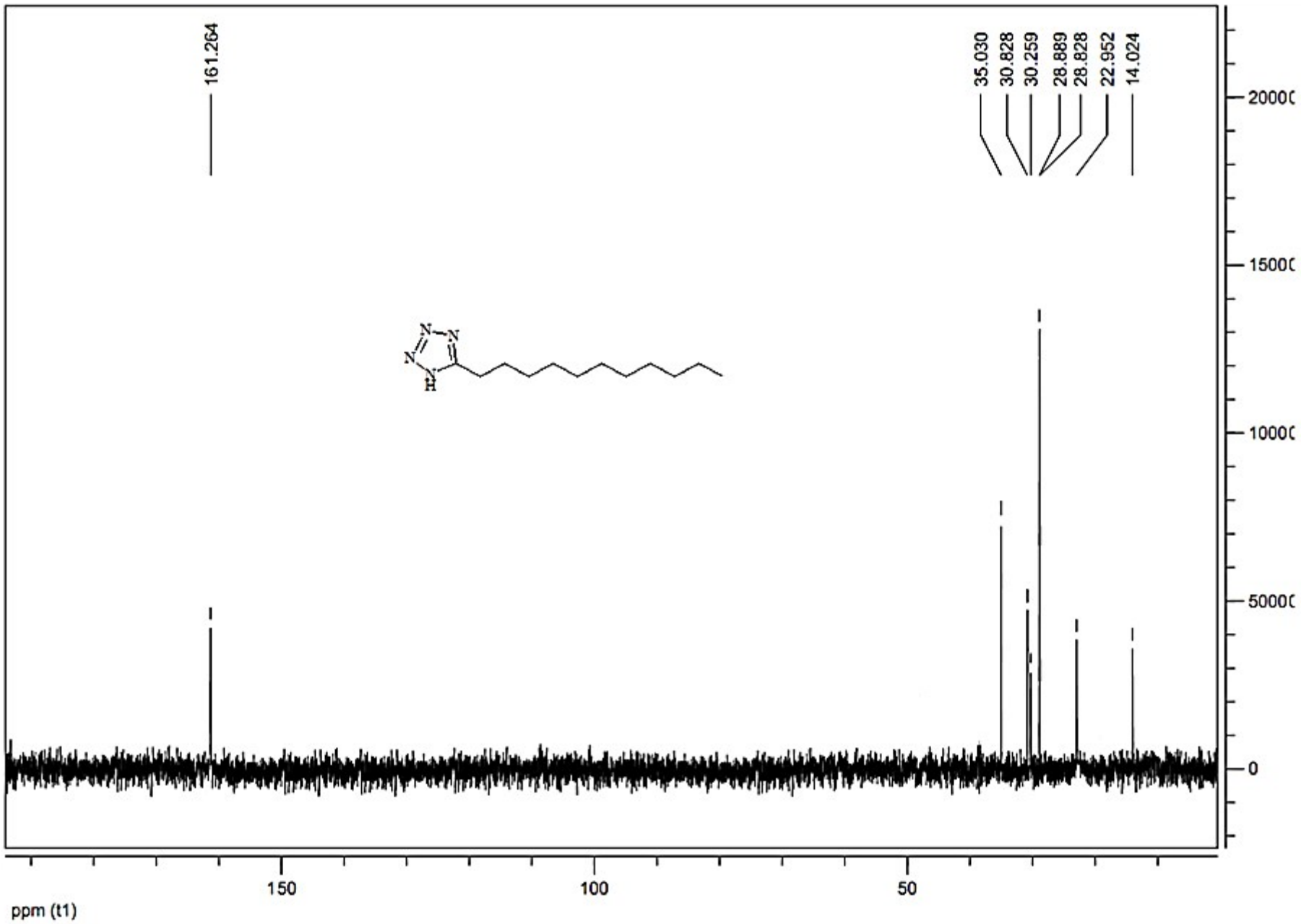
4000
3000
2000
1000
0
3.342
4.00
4.98
7.023
7.056
7.106
7.140
7.166
7.200
7.262
5.0
10.0
ppm (t1)


30.355
38.719
129.486
130.901
132.822
140.256
167.799
Ph
NH
ppm (t1)


8.778
8.220
7.748
7.399
7.176
4.116
HN
N
N
N
4000C
3000C
2000C
1000C
0
7.00
0.05
10.0
5.0
ppm (t1)


3000
2500
2000
1500
1000
500
0
50
100
150
ppm (t1)
148.124
133.239
132.786
130.690
128.304
128.033
127.677
127.453
126.674
126.634
122.414
HN
N
N


4000
3000
2000
1000
0
0.809
0.821
0.831
1.189
2.105
2.116
2.127
2.136
3.00
19.01
1.90
5.0
10.0
ppm (t1)


161.264
35.030
30.828
30.259
28.889
28.828
22.952
14.024
20000
15000
10000
5000
0
150
100
50
ppm (t1)