Supporting Information

THE SYNTHESIS OF DIPYRAZOLYLMETHANE, X-RAY STRUCTURE ANALYSIS AND MECHANISM STUDY

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Content

S1. The detailed spectral analyses of compounds **2a−d** and **2j,k**

(4*Z*)-2,4-Dihydro-4-[(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]-5-methyl-2-phenyl-3*H*-pyrazol-3-one (2a) Yellow solid; Mp 190-192 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz,): δ = 17.95 (s, 1H), 7.92-7.90 (d, *J* = 8.0 Hz, 4H), 7.47-7.43 (m, 4H), 7.30 (s, 1H), 7.29-7.28 (m, 2H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.4, 151.4, 143.2, 137.6, 129.5, 122.5, 118.3, 109.4, 12.9; MS (FAB): m/z = 358.39 $[M+H]^+$; IR (KBr): 3441, 2923, 2855, 1621, 1589, 1549, 1493, 1417, 1381, 1330, 1170, 1111，1005, 753, 668 cm^{-1}. Anal. Calcd for $C_{21}H_{18}N_4O_2$; C, 70.38; H, 5.06; N, 15.63; O, 8.93. Found: C, 70.35; H, 5.03; N, 15.65; O, 8.91.

(4*Z*)-2,4-Dihydro-4-[(5-hydroxy-1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]-2,5-diphenyl-3*H*-pyrazol-3-one (2b) Yellow solid; Mp 267-269 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 17.85 (s, 1H), 8.04-8.02 (m, 4H), 7.76 (s, 1H), 7.56-7.33 (m, 16H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.4, 155.4, 143.2, 137.6, 130.7, 129.6, 129.0, 128.9, 128.7, 126.8, 121.4, 109.2; MS (FAB): m/z = 482.2 $[M+H]^+$; IR (KBr): 3447, 2925, 2854, 1613, 1586, 1516, 1489, 1413, 1344, 1307, 1177, 1107, 861, 756, 694 cm^{-1}. Anal. Calcd for $C_{31}H_{22}N_4O_2$; C, 77.16; H, 4.60; N, 11.61; O, 6.63. Found: C, 77.15; H, 4.63; N, 11.65; O, 6.61.

(4*Z*)-2,4-Dihydro-4-[(5-hydroxy-3-propyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]-5-propyl-2-phenyl-3*H*-pyrazol-3-one (2c) Yellow solid; Mp 201-202 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 17.82 (s, 1H), 7.93-7.90 (d, *J* = 8.2 Hz, 4H), 7.47-7.43 (m, 4H), 7.34 (s, 1H), 7.30-7.28 (m, 2H), 2.72-2.68 (m, 4H), 1.82-1.77 (m, 4H), 1.10-1.06 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.3, 156.1, 137.9, 137.7, 128.8, 126.5, 121.1, 108.7, 29.1, 22.0, 14.1; MS (FAB): m/z = 414.21 $[M+H]^+$; IR (KBr): 3447, 2961, 2927, 1620, 1590, 1538, 1497, 1456, 1385, 1325, 1239, 1111, 1003, 758, 689 cm^{-1}. Anal. Calcd for $C_{25}H_{26}N_4O_2$; C, 72.44; H, 6.32; N, 13.52; O, 7.72. Found: C, 72.45; H, 6.33; N, 13.55; O, 7.71.

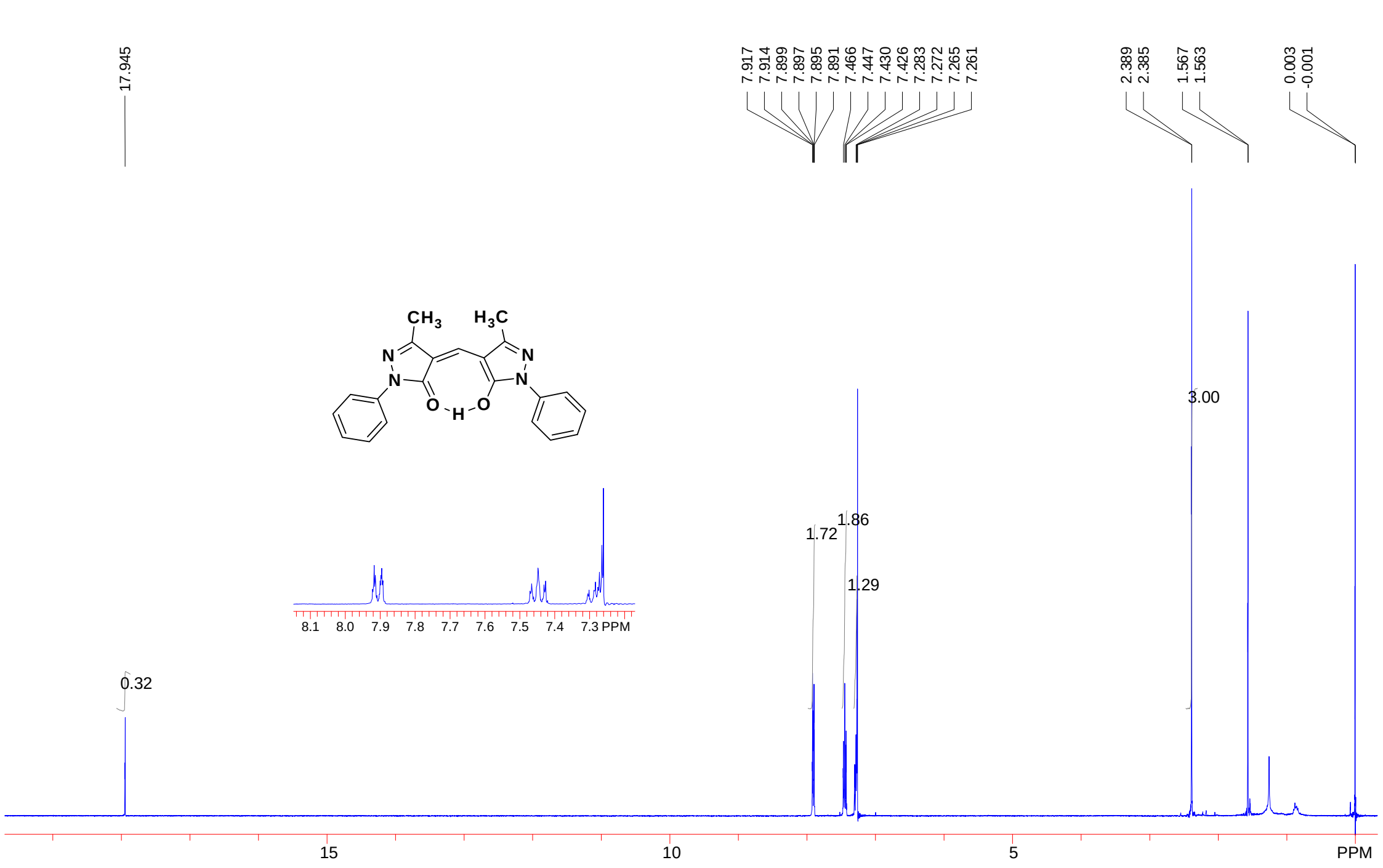
(4*Z*)-2,4-Dihydro-4-[(5-hydroxy-3-isopropyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]-5-isopropyl-2-phenyl-3*H*-pyrazol-3-one (2d) Yellow solid; Mp 101-103 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 17.84 (s, 1H), 7.95-7.92 (d, *J* = 7.6 Hz, 4H), 7.47-7.44 (m, 4H), 7.42 (s, 1H), 7.29-7.27 (m, 2H), 3.14-3.08 (m, 2H), 1.41-1.39 (d, *J* = 7.2 Hz, 12H); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ = 161.6, 160.4, 137.9, 137.3, 128.8, 126.4, 121.2, 107.8, 27.0, 21.6; MS (FAB): m/z = 414.21 [M+H]+; IR (KBr): 3441, 2963, 2924, 1620, 1590, 1536, 1494, 1421, 1382, 1356, 1259, 1107, 993, 760, 691 cm^{-1}. Anal. Calcd for $C_{25}H_{26}N_4O_2$; C, 72.44; H, 6.32; N, 13.52; O, 7.72. Found: C, 72.46; H, 6.31; N, 13.56; O, 7.70.

(4*Z*)-2,4-Dihydro-4-[[5-hydroxy-3-phenyl-1-(4-methoxyphenyl)-1*H*-pyrazol-4-yl]methylene]-5-phenyl-2-(4-methoxyphenyl)-3*H*-pyrazol-3-one (2j) Yellow solid; Mp 267-269 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ = 17.86 (s, 1H), 7.91-7.88 (d, *J* = 8.4 Hz, 4H), 7.73 (s, 1H), 7.55-7.52 (m, 4H), 7.43-7.41(m, 6H), 7.01-7.98 (d, *J* = 8.6 Hz, 4H), 3.86 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.2, 154.4, 149.2, 135.5, 130.4, 129.9, 129.1, 128.5, 126.5. 119.3, 115.0, 109.2, 55.5; MS (FAB): m/z = 542.20 $[M+H]^+$; IR (KBr): 3441, 2926, 2852, 1616, 1511, 1454, 1408, 1346, 1252, 1165, 1111, 1062, 863, 825, 685 cm^{-1}. Anal. Calcd for $C_{33}H_{26}N_4O_4$; C, 73.05; H, 4.83; N, 10.33; O, 11.79. Found: C, 73.01; H, 4.82; N, 10.35; O, 11.78.

(4*Z*)-2,4-Dihydro-4-[[5-hydroxy-3-phenyl-1-(3-methylphenyl)-1*H*-pyrazol-4-yl]methylene]-5-phenyl-2-(3-methylphenyl)-3*H*-pyrazol-3-one (2k) Yellow solid; Mp 187-189 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ = 17.86 (s, 1H), 7.83-7.81 (d, *J* = 7.6 Hz, 4H), 7.74 (s, 1H), 7.55-7.53 (m, 4H), 7.43-7.36 (m, 8H), 7.15-7.13 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.2, 156.7, 149.4, 139.1, 138.8, 137.5, 129.9, 129.4, 129.1, 128.5, 127.4, 122.8, 115.3, 109.4, 21.5; MS (FAB): m/z = 510.21 [M+H]+; IR (KBr): 3451, 2924, 2854, 1603, 1517, 1460, 1389, 1345, 1311, 1105, 1060, 1025, 877, 805, 752, 696 cm^{-1}. Anal. Calcd for $C_{33}H_{26}N_4O_2$; C, 77.63; H, 5.13; N, 10.97; O, 6.27. Found: C, 77.61; H, 5.12; N, 10.95; O, 6.28.

S2. ^1H and ^{13}C NMR spectra of compounds **2a-s, 1a-m, 1o** synthesized in this study.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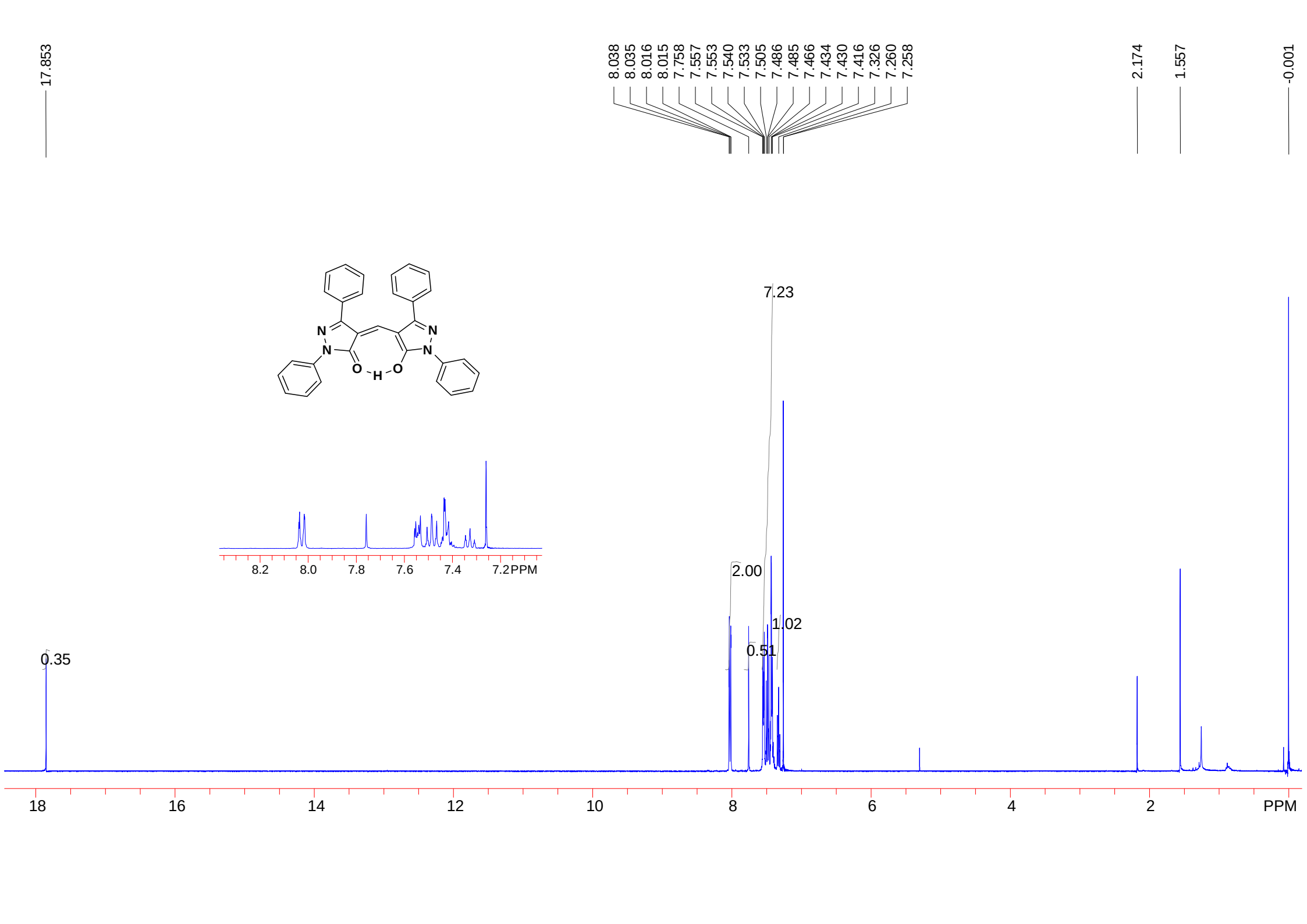
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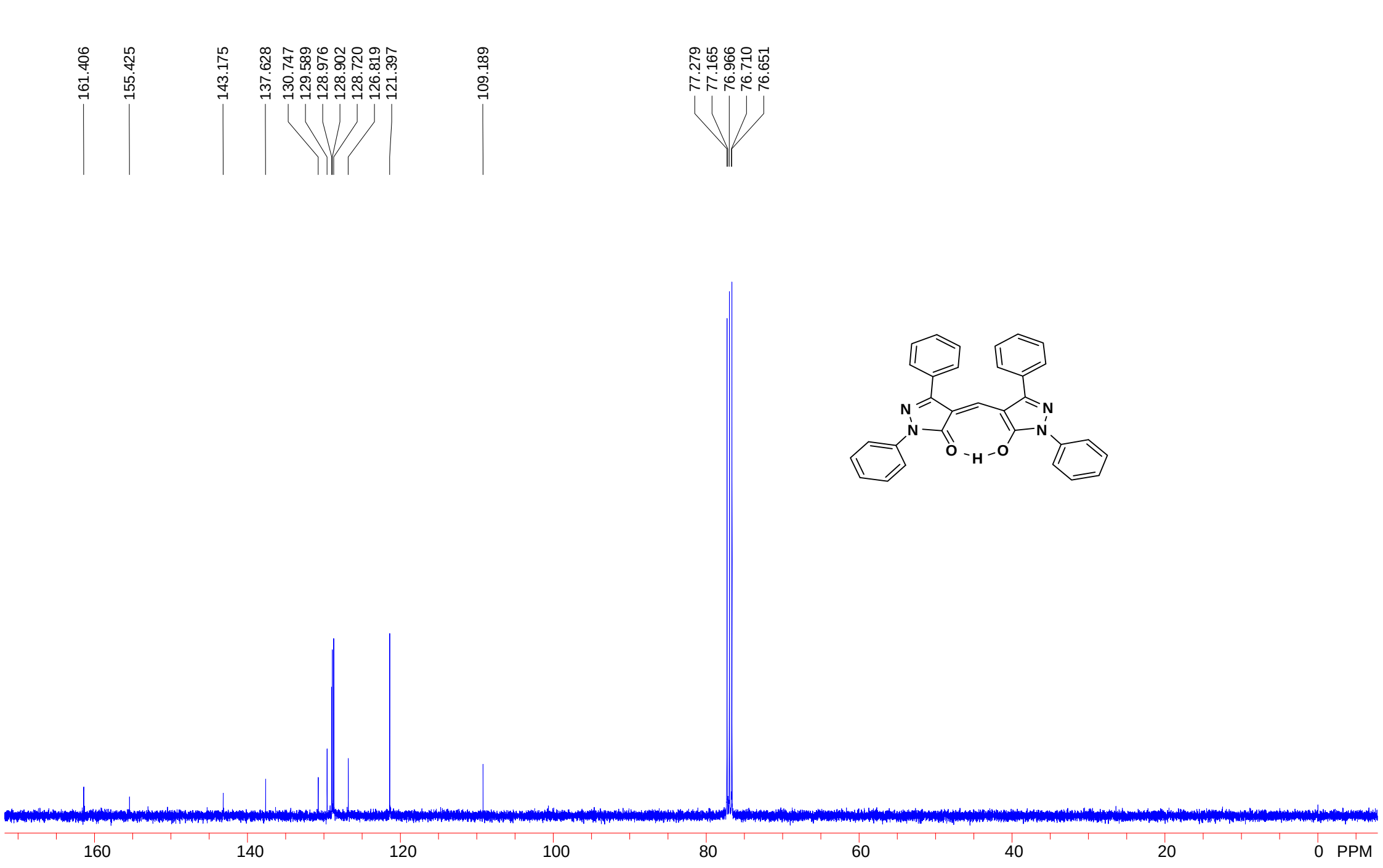
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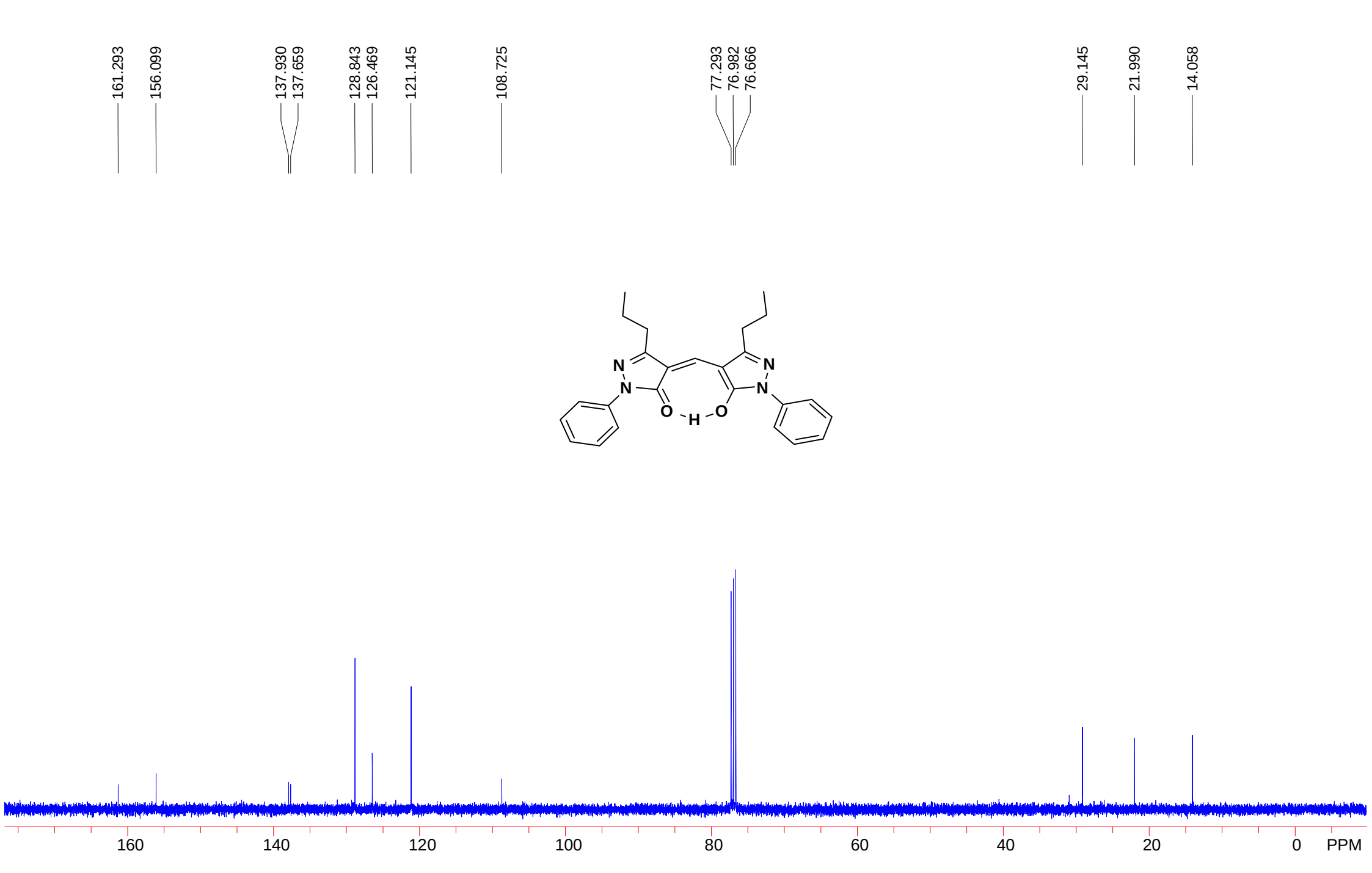
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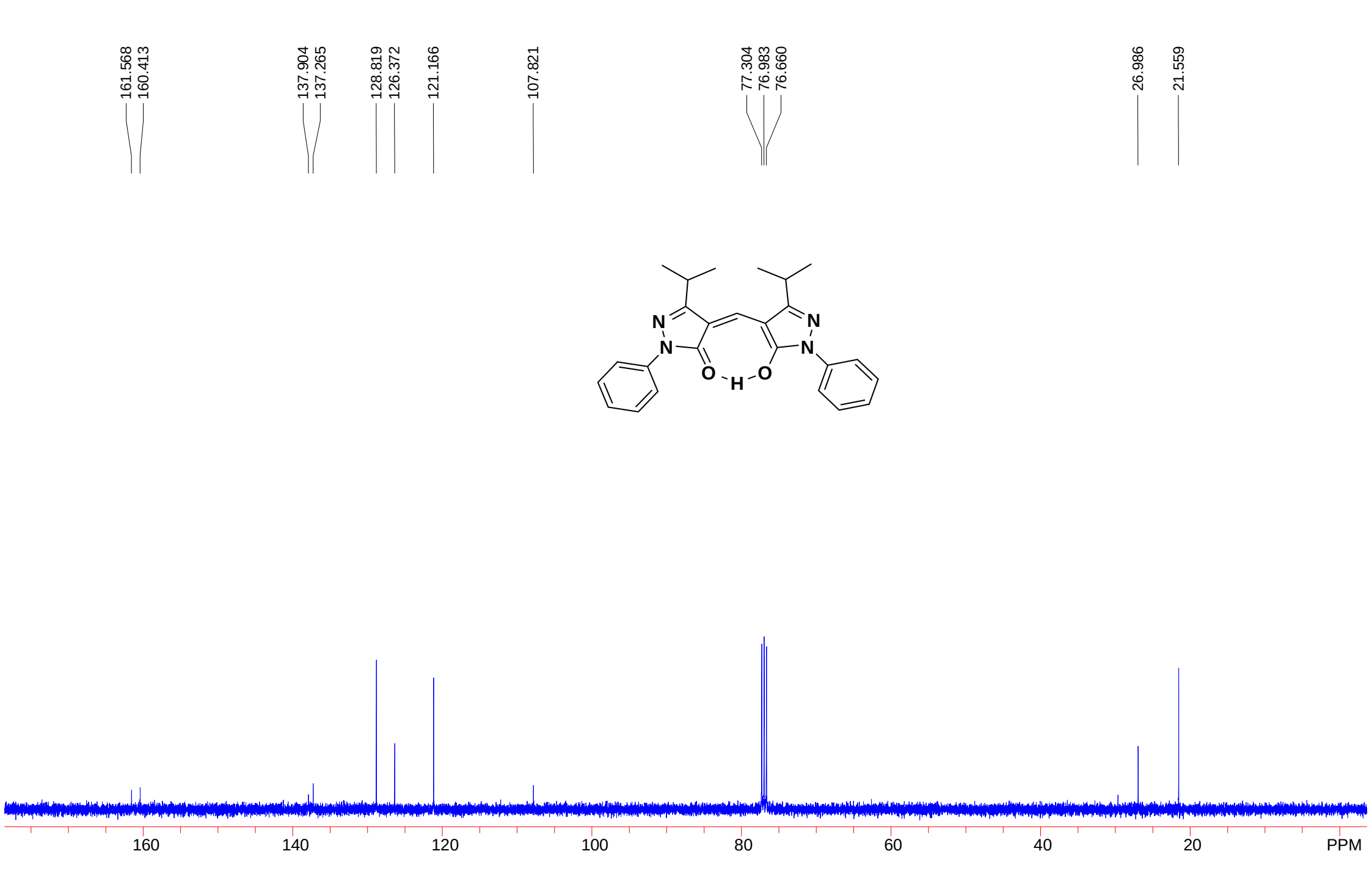
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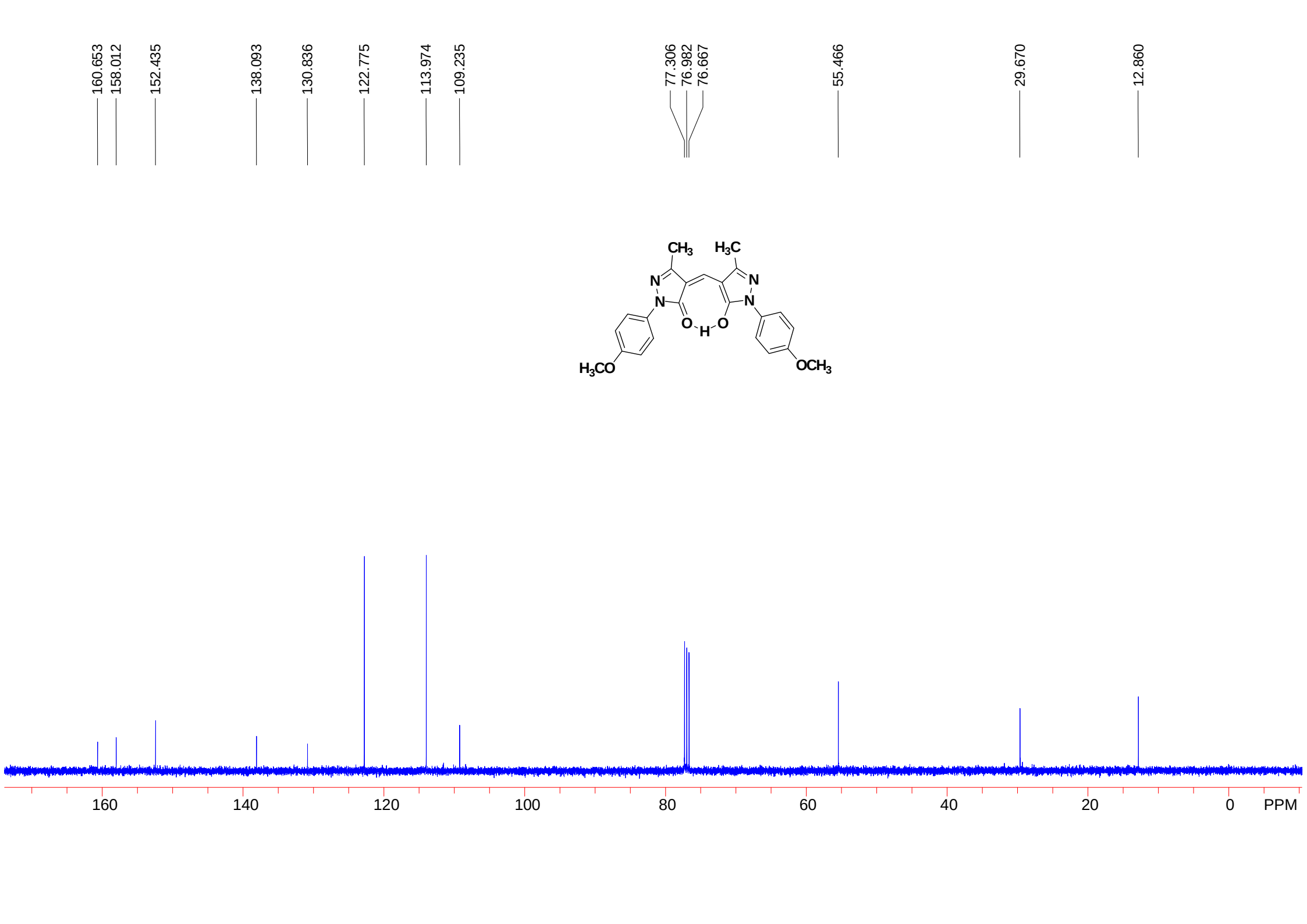
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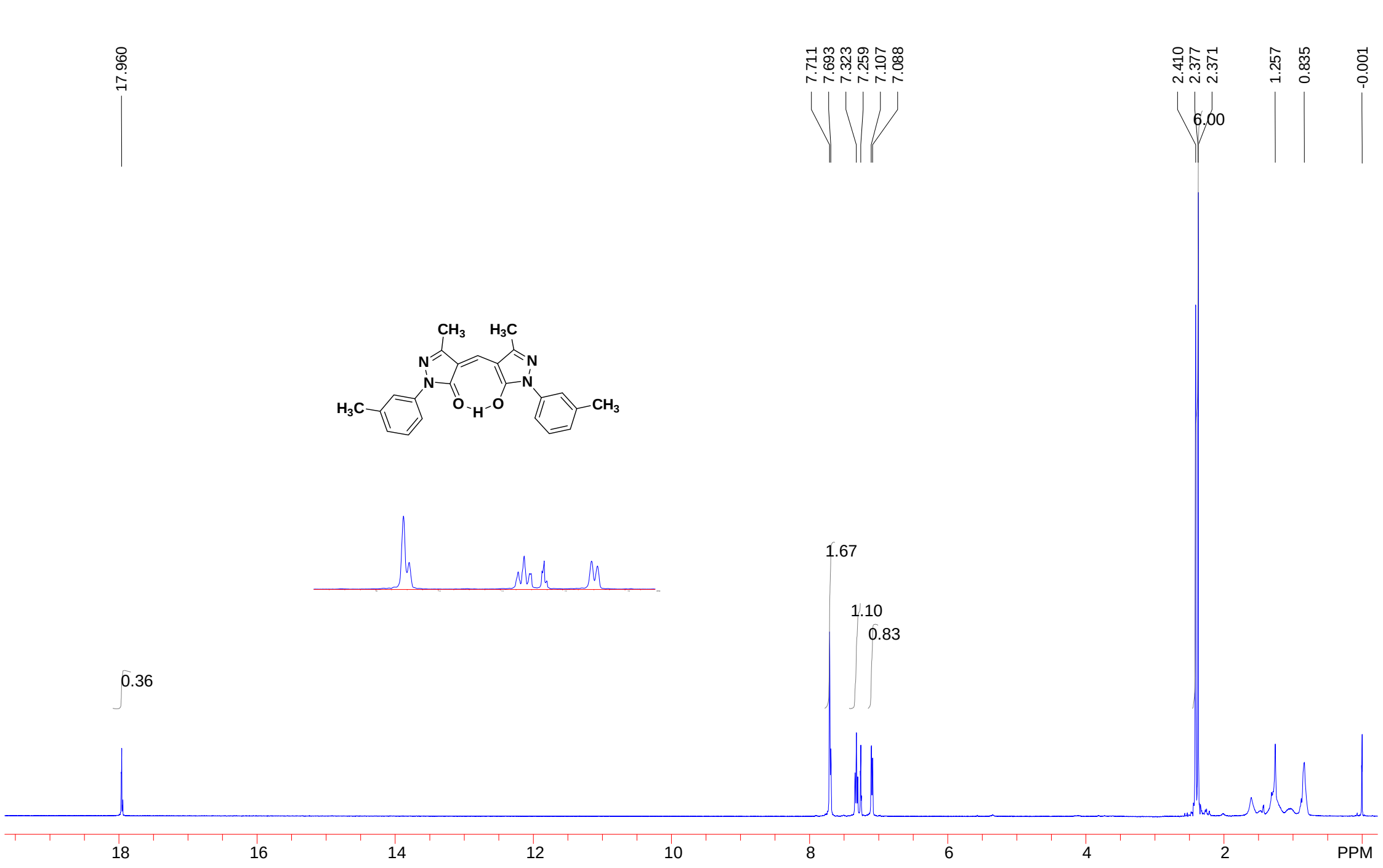
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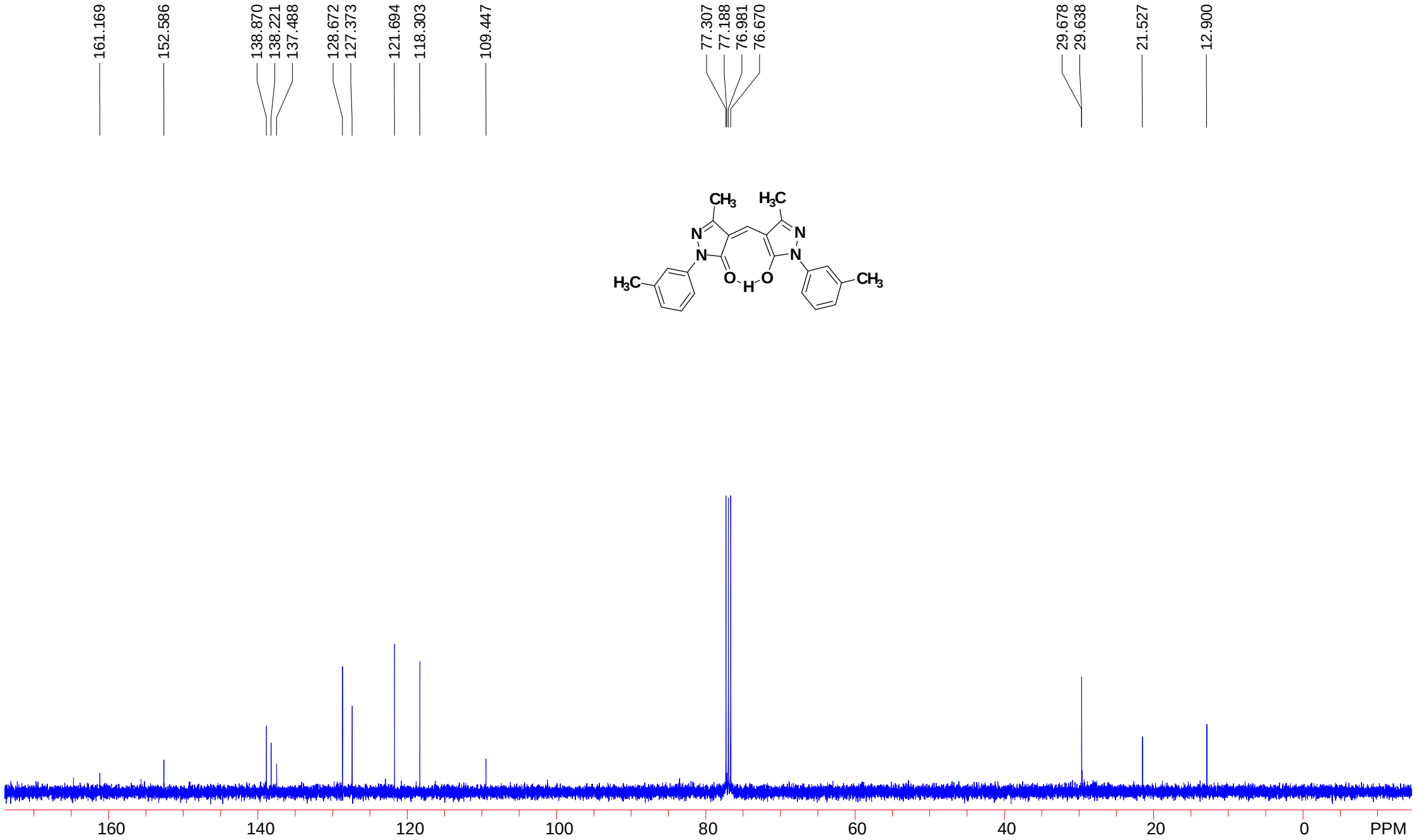
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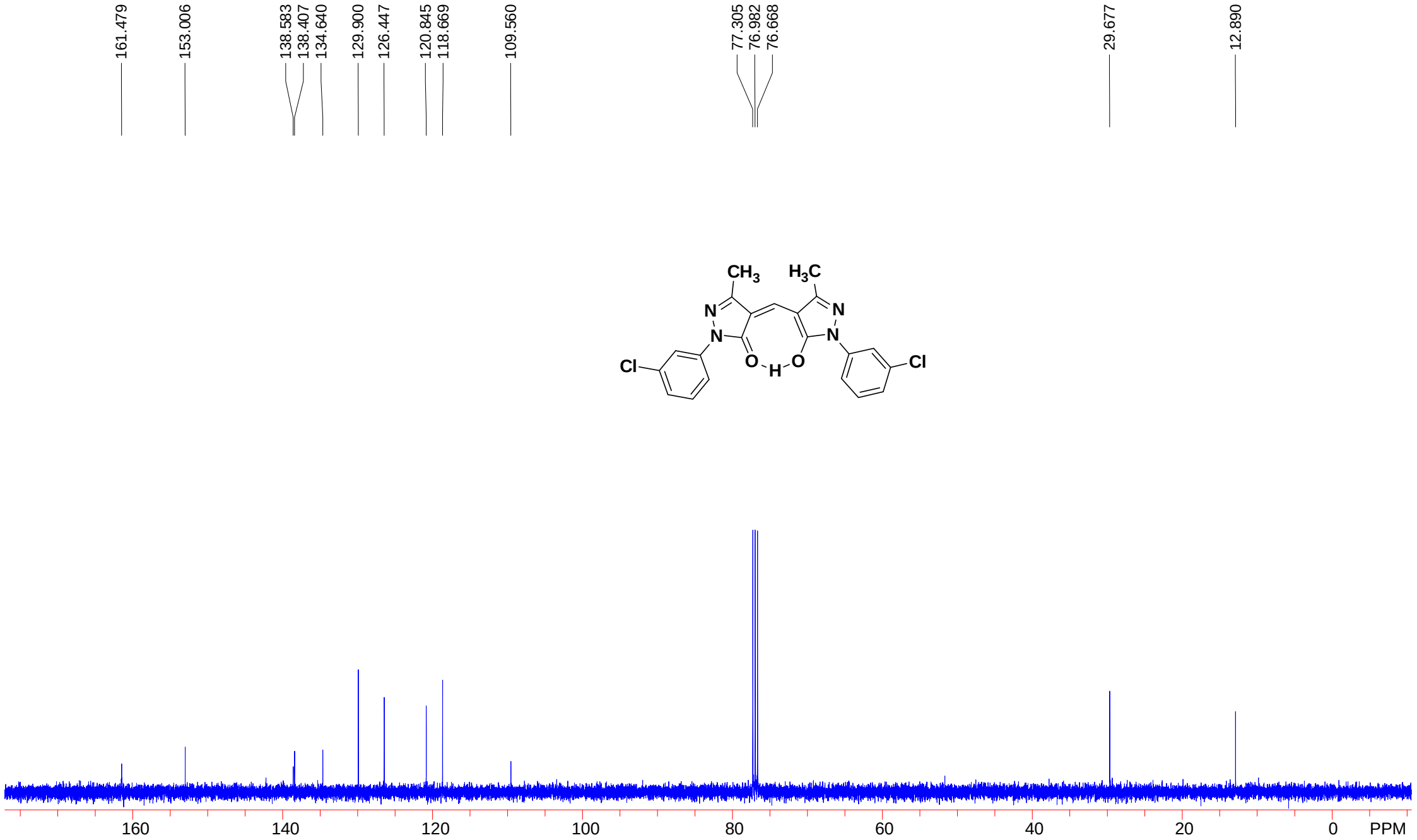
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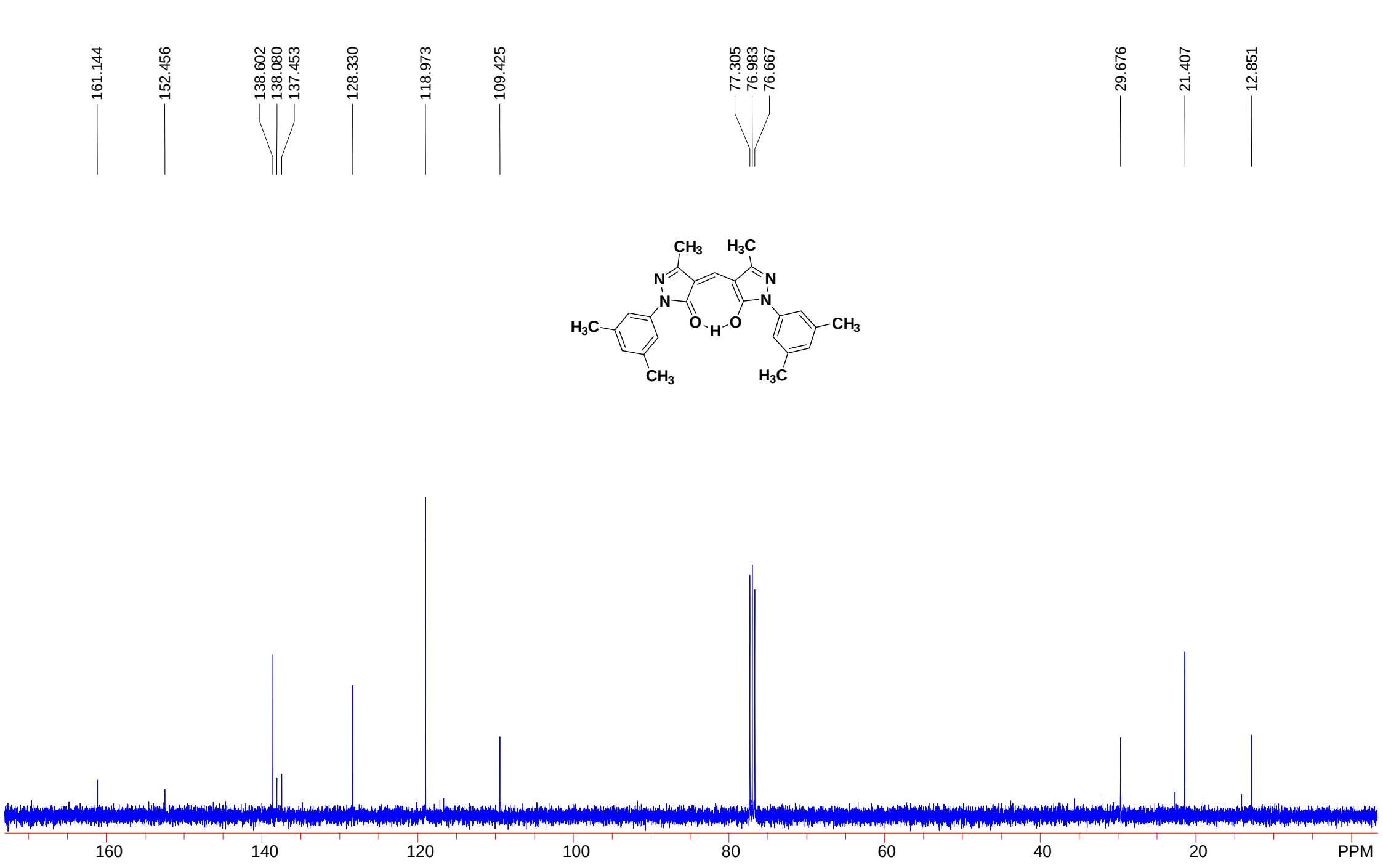
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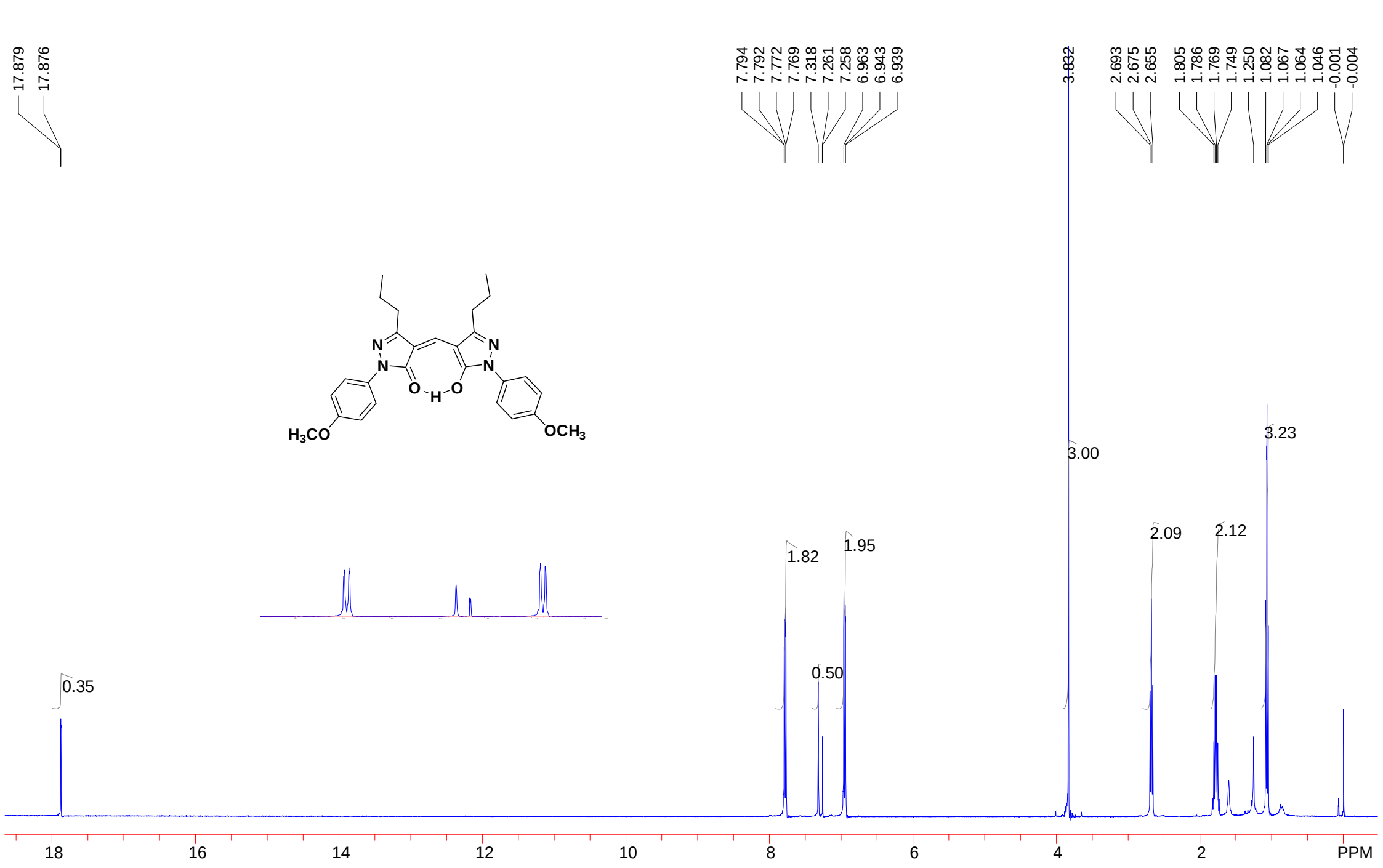
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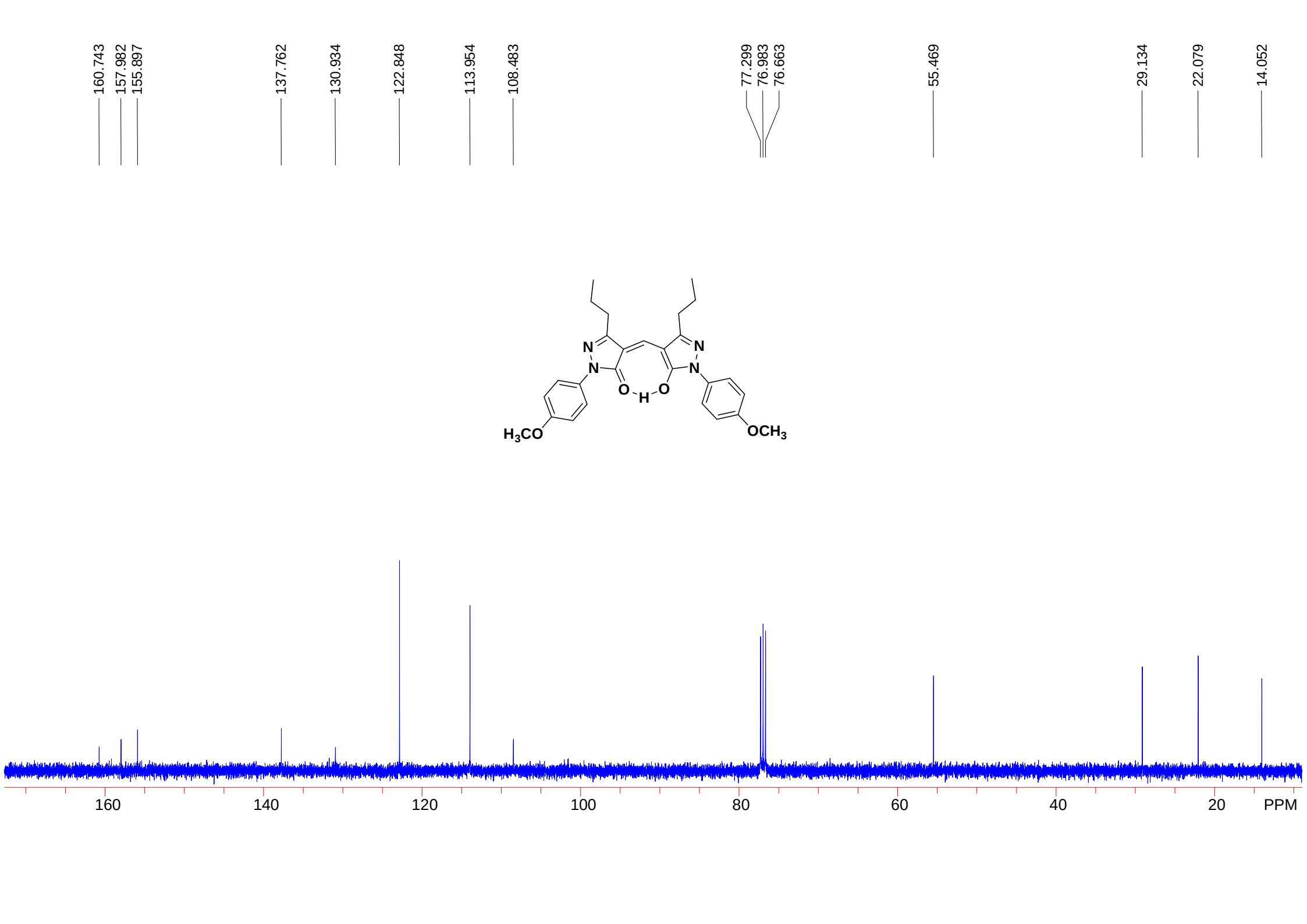
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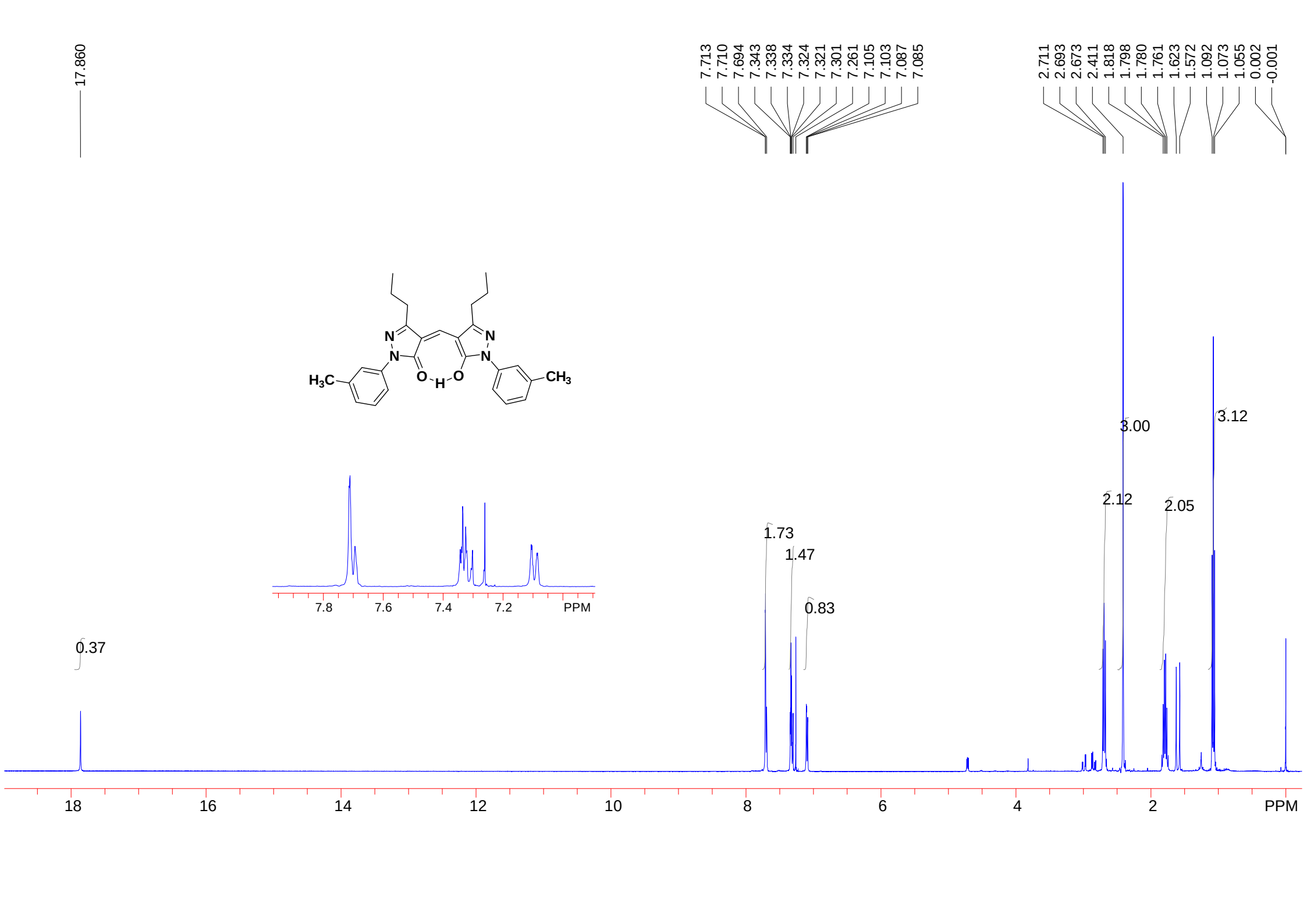
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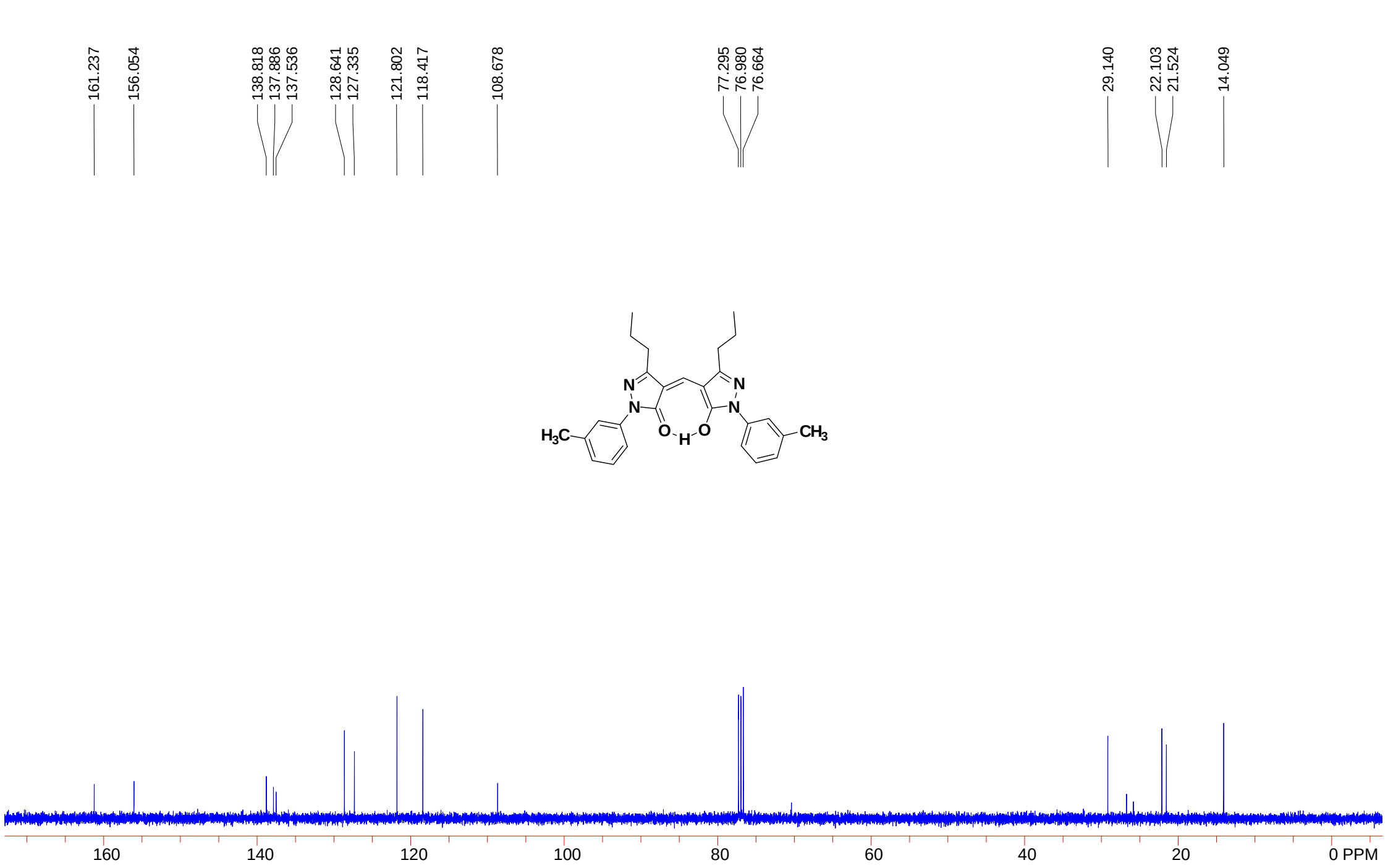
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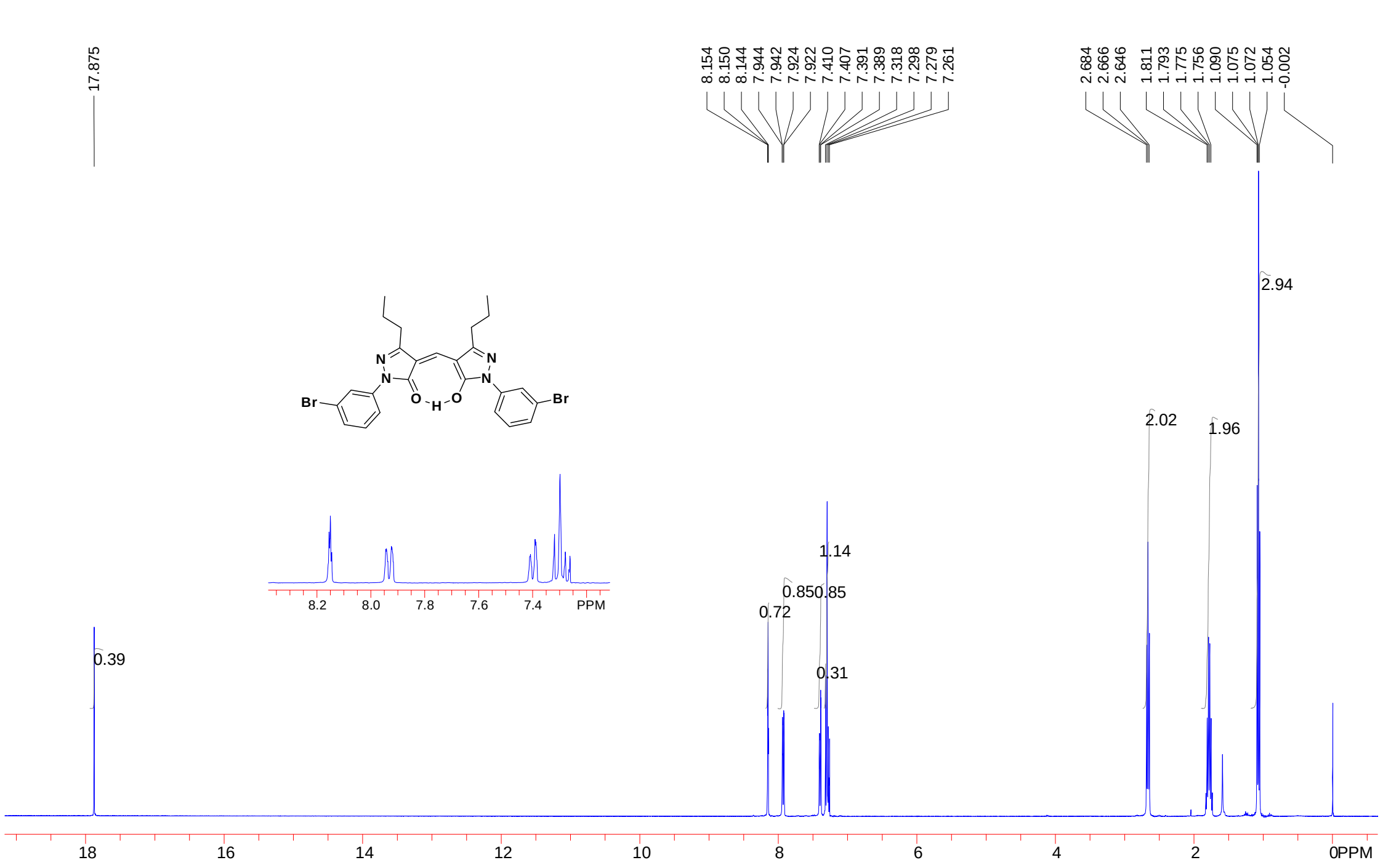
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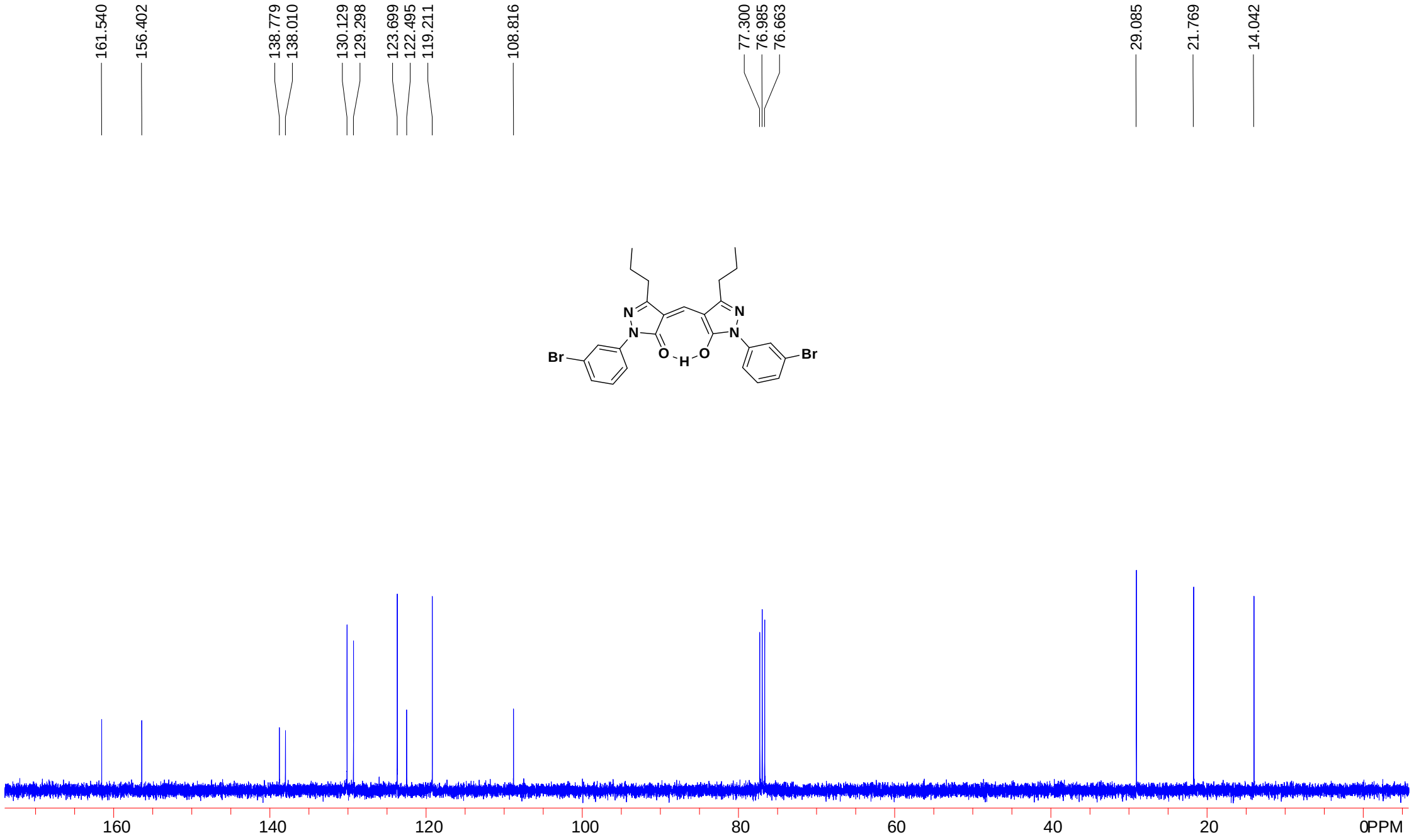
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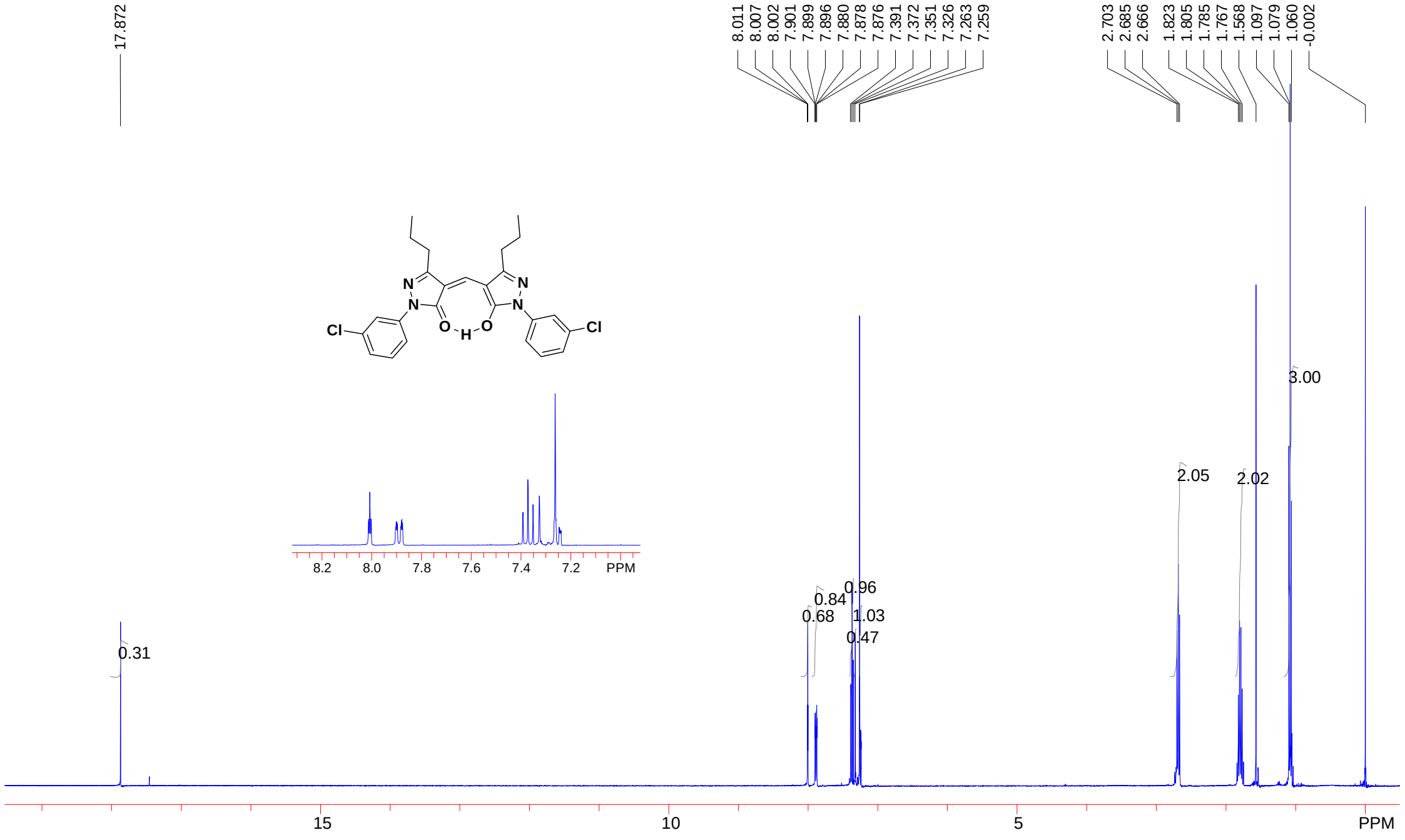
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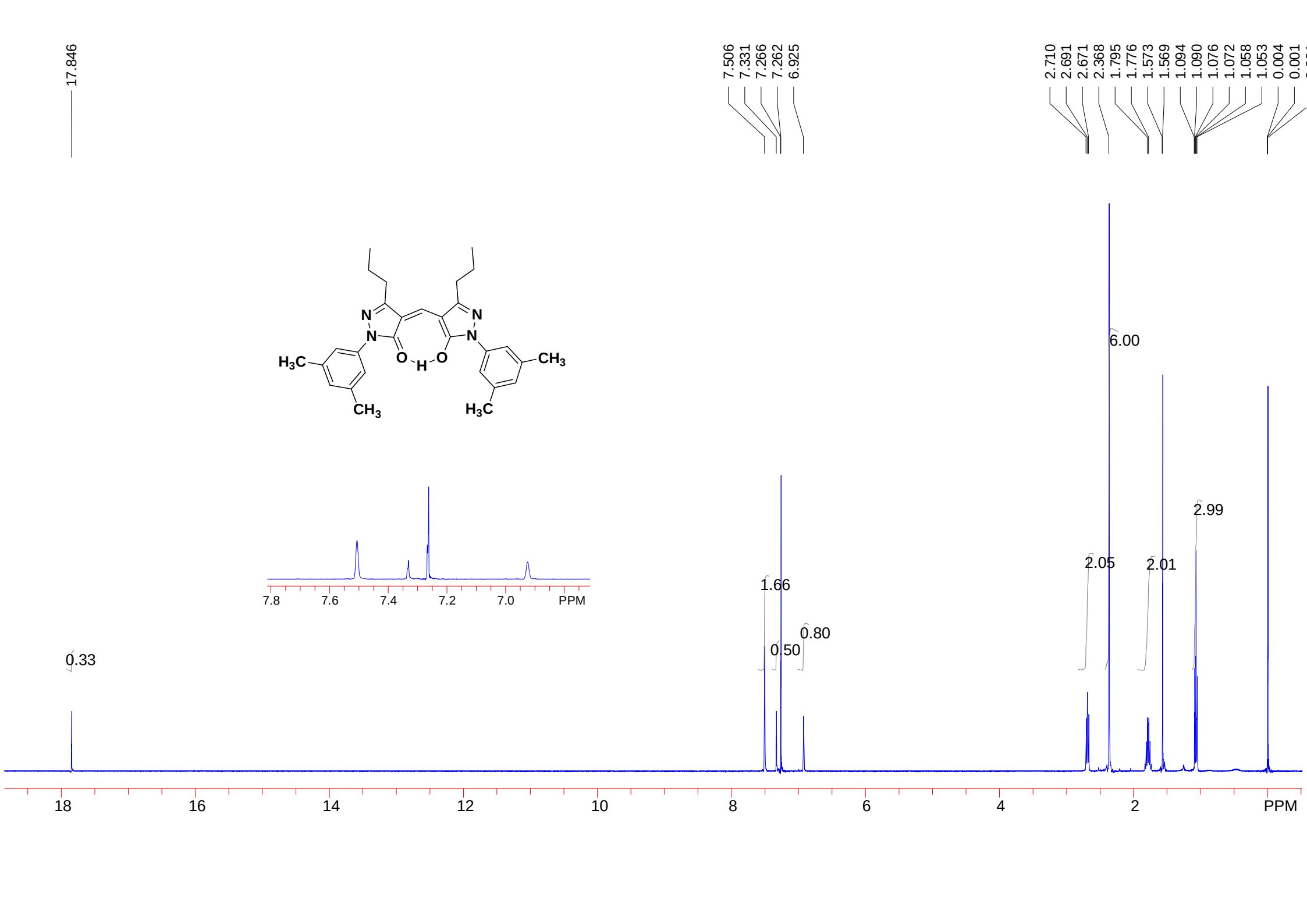
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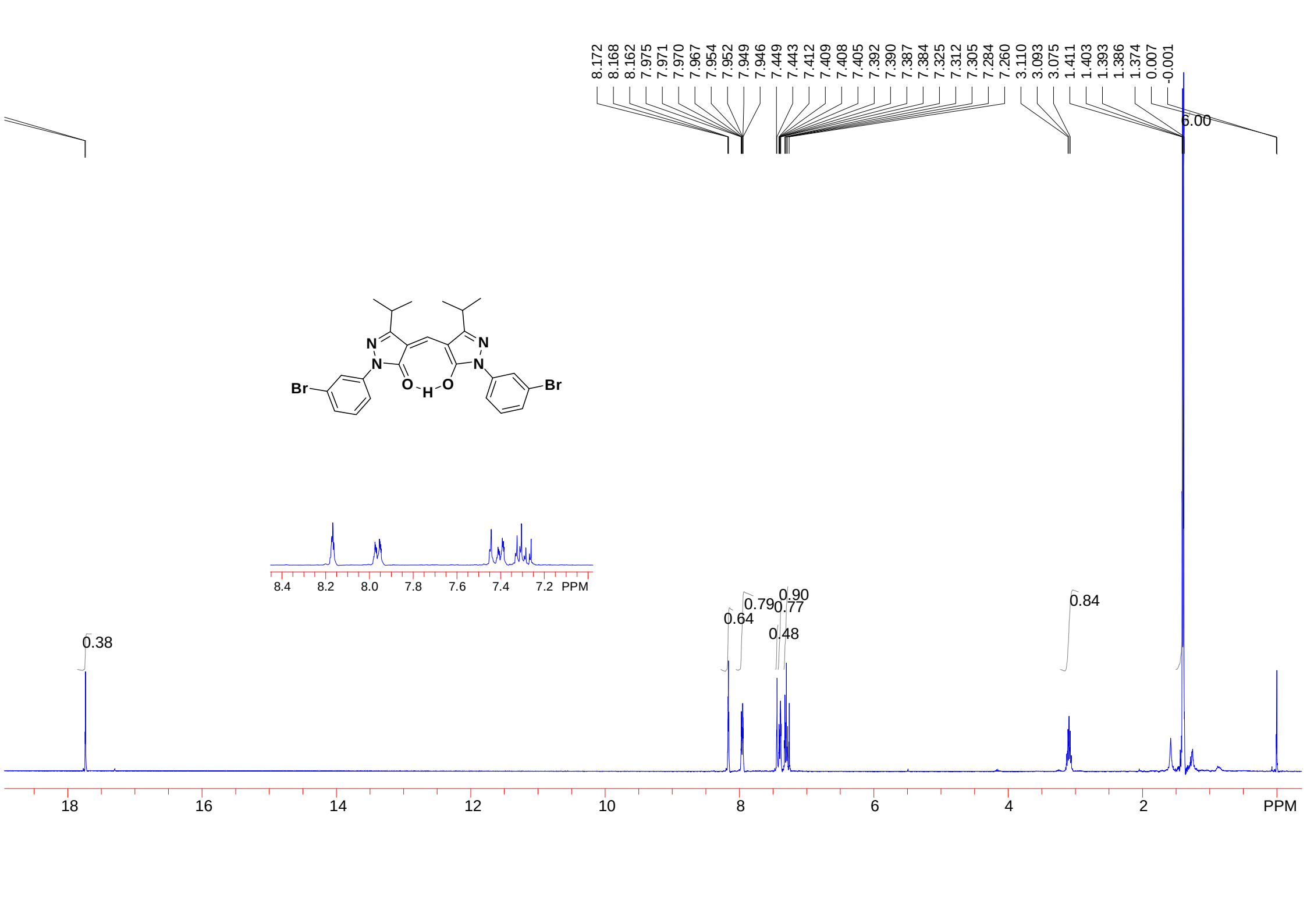
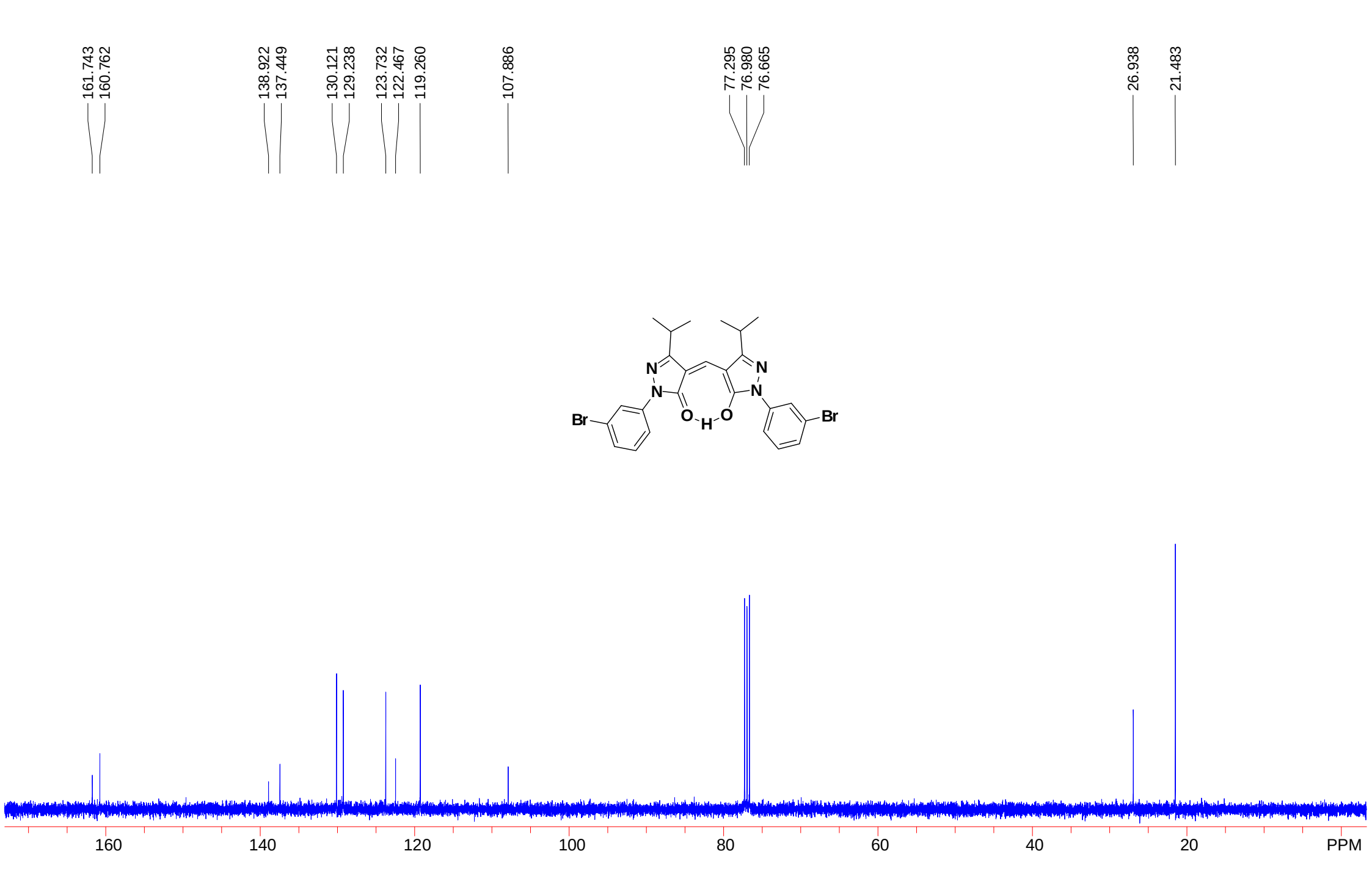
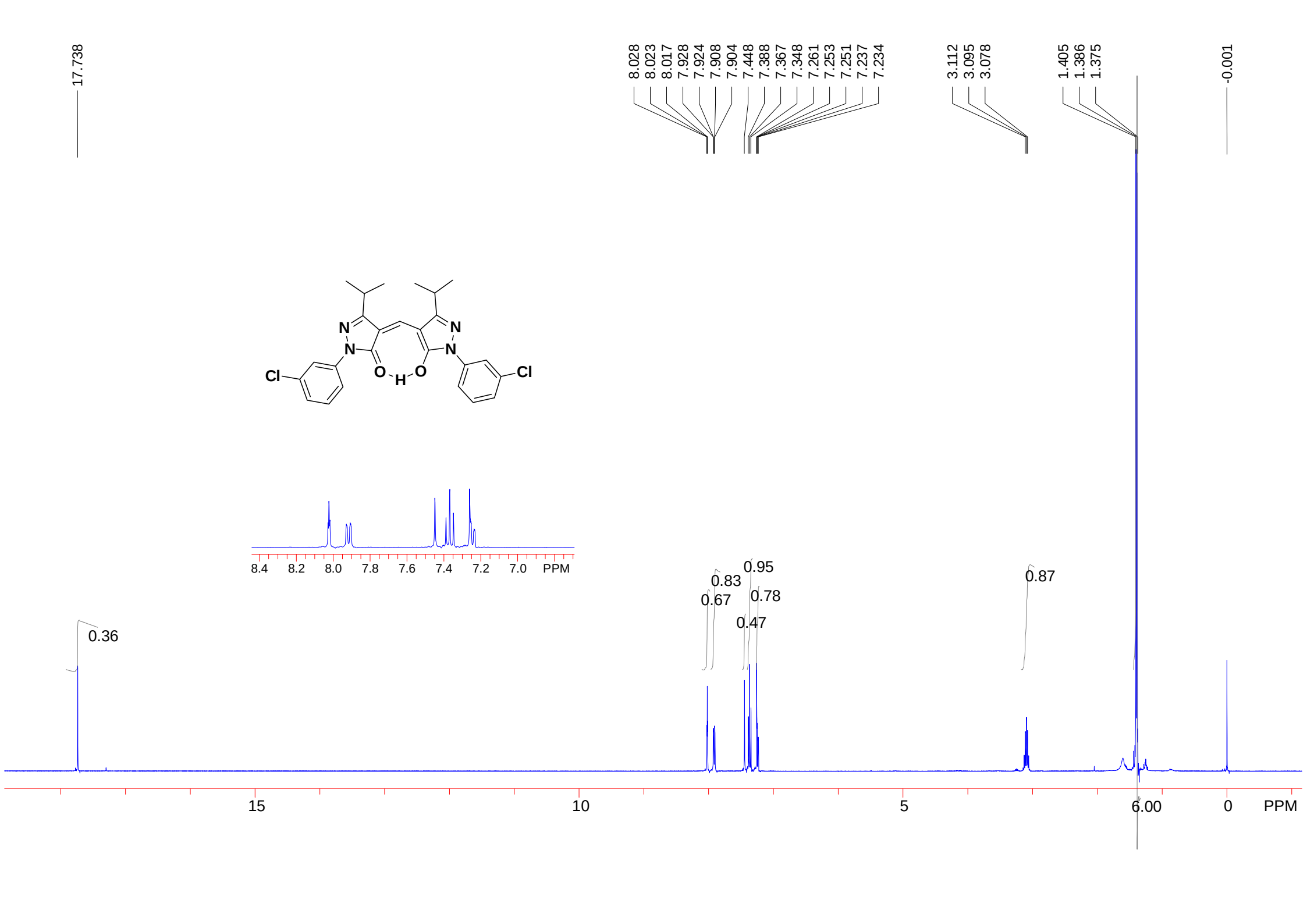
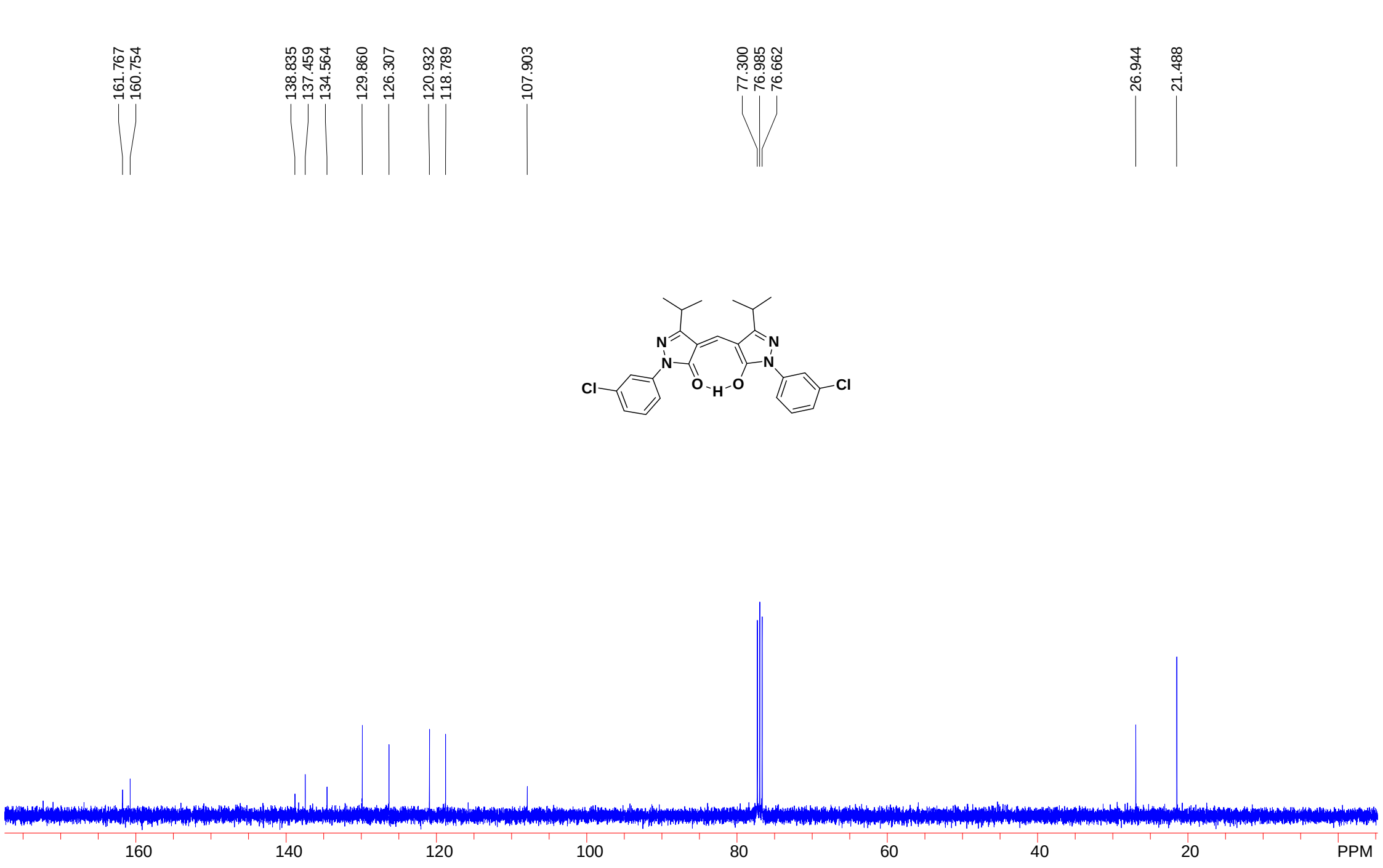
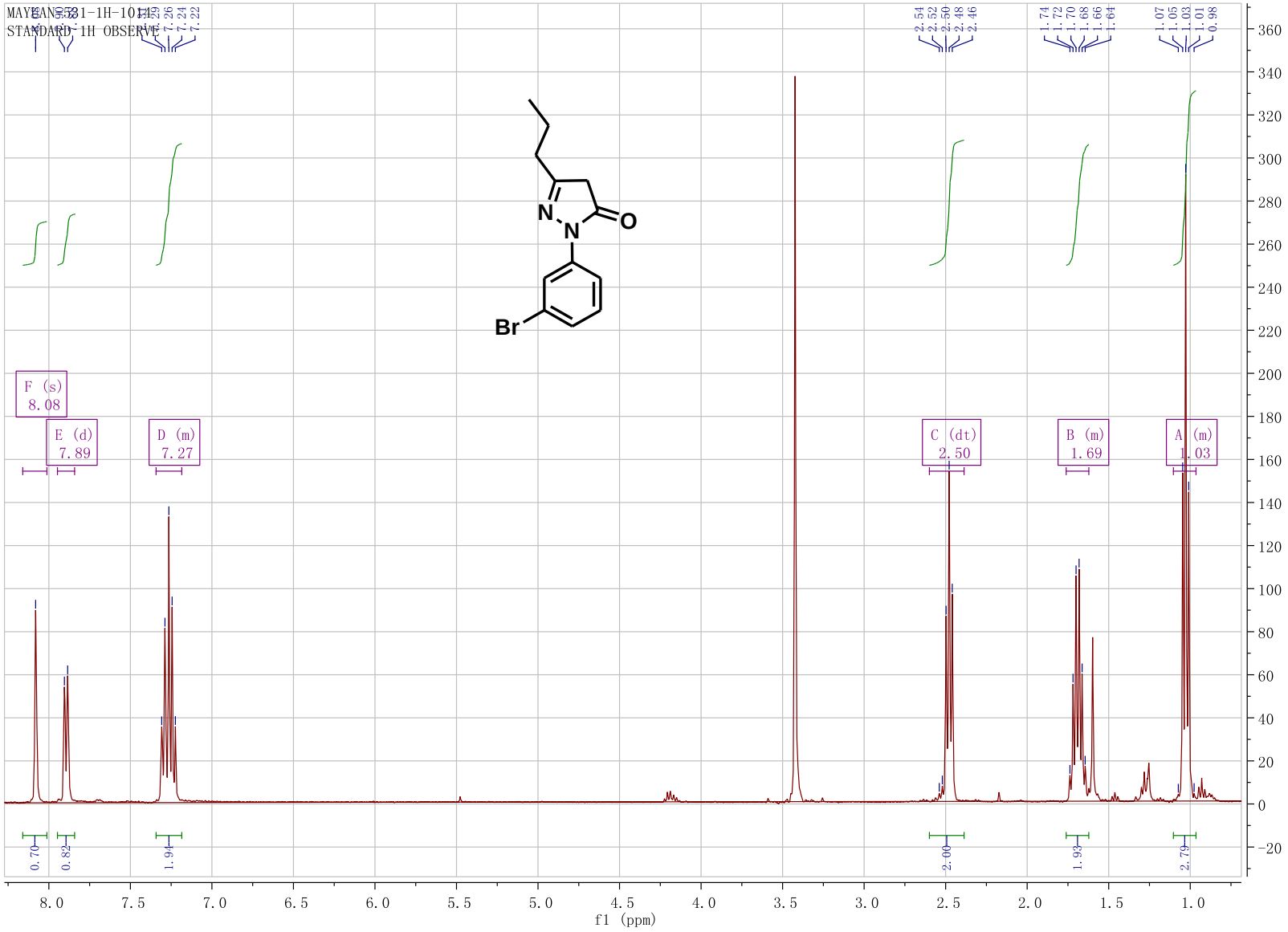
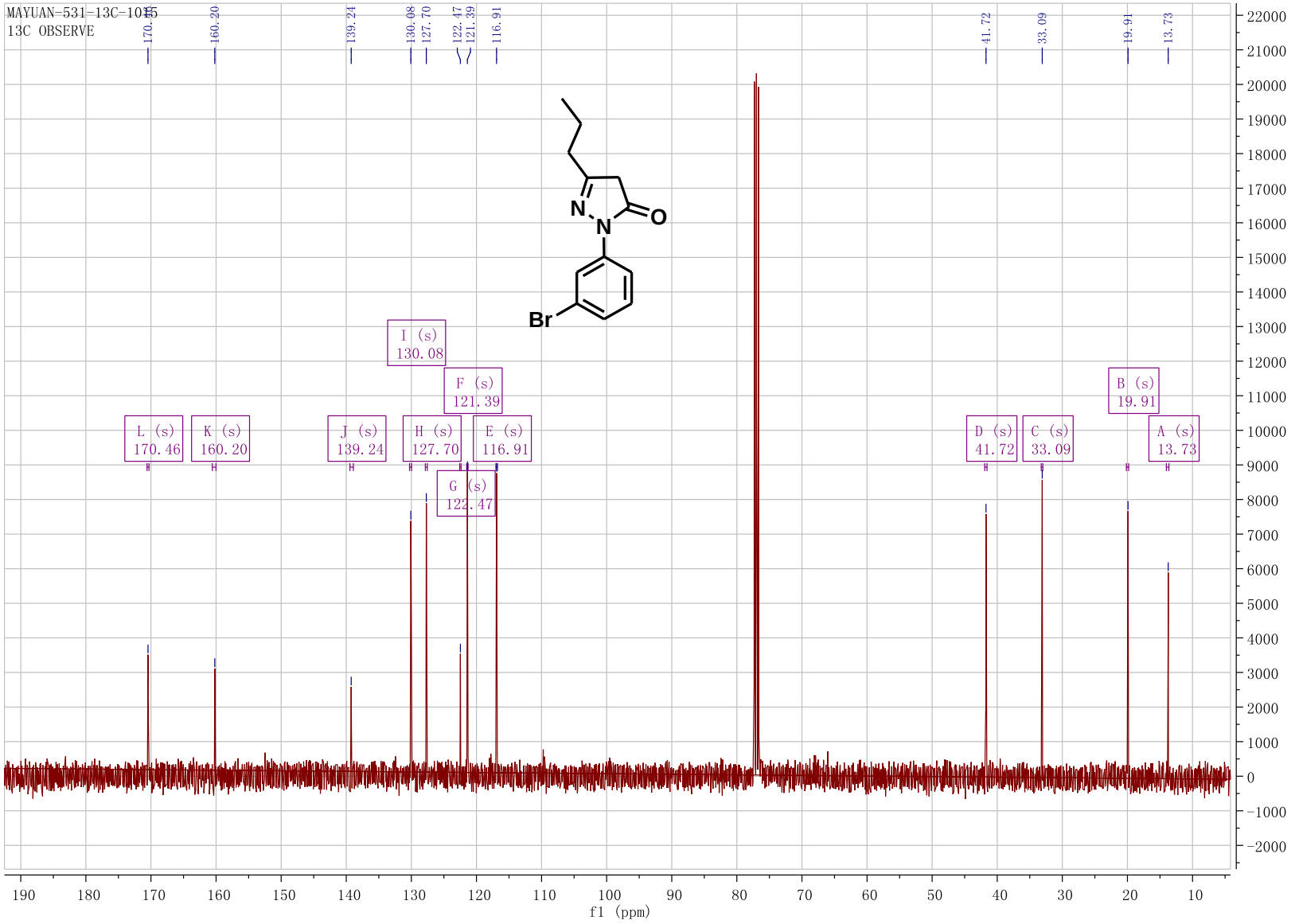

8.172
8.168
8.162
7.975
7.971
7.970
7.967
7.954
7.952
7.949
7.946
7.449
7.443
7.412
7.409
7.408
7.405
7.392
7.390
7.387
7.384
7.325
7.312
7.305
7.284
7.260
3.110
3.093
3.075
1.411
1.403
1.393
1.386
1.374
0.007
-0.001
6.00
Br
Br
N
N
N
N
O
H
O
8.4
8.2
8.0
7.8
7.6
7.4
7.2
PPM
0.38
0.64
0.79
0.77
0.90
0.48
0.84
18
16
14
12
10
8
6
4
2
PPM

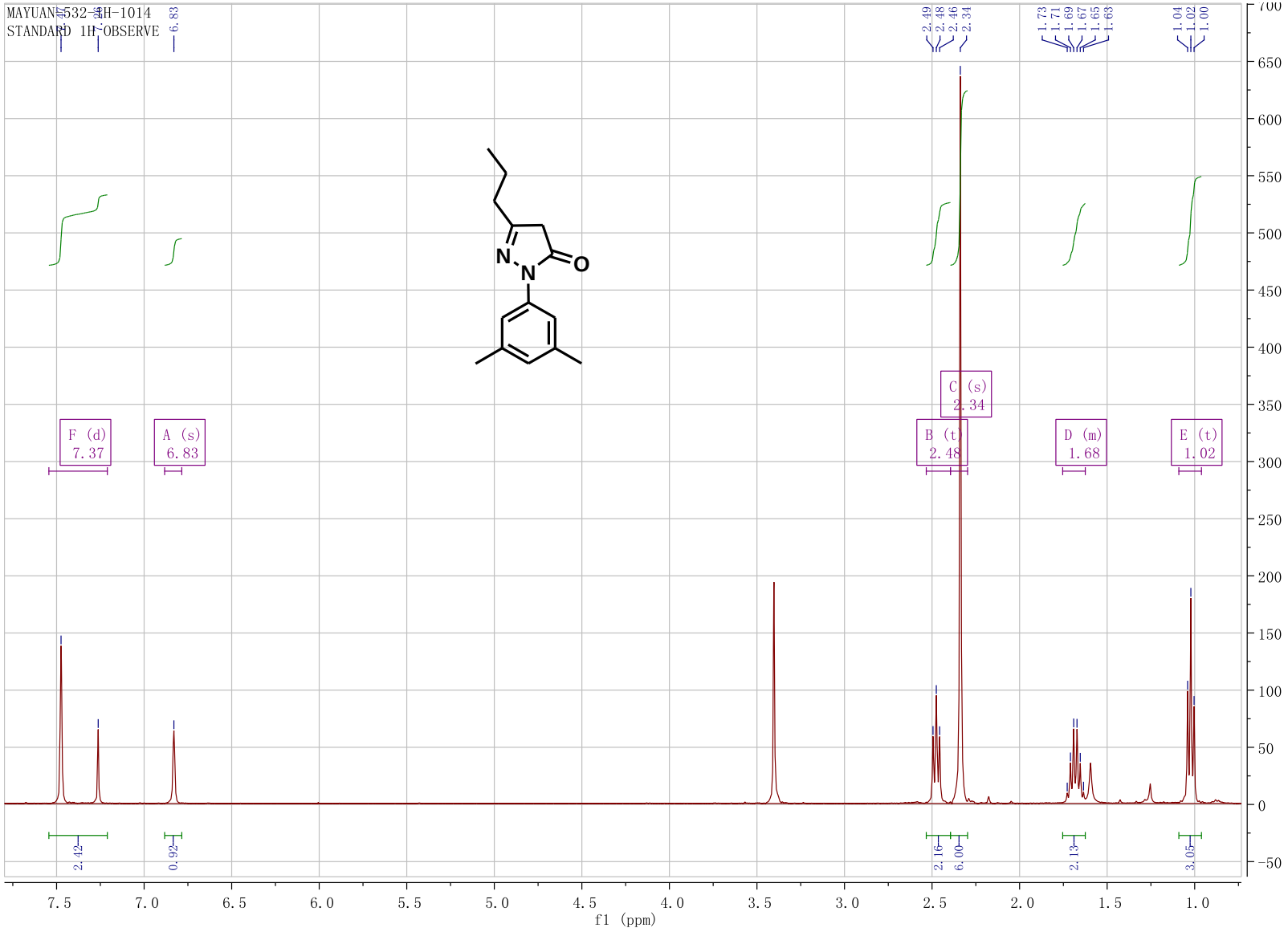

161.743
160.762
138.922
137.449
130.121
129.238
123.732
122.467
119.260
107.886
77.295
76.980
76.665
26.938
21.483
N
N
N
N
O
H
O
Br
Br
160
140
120
100
80
60
40
20
PPM

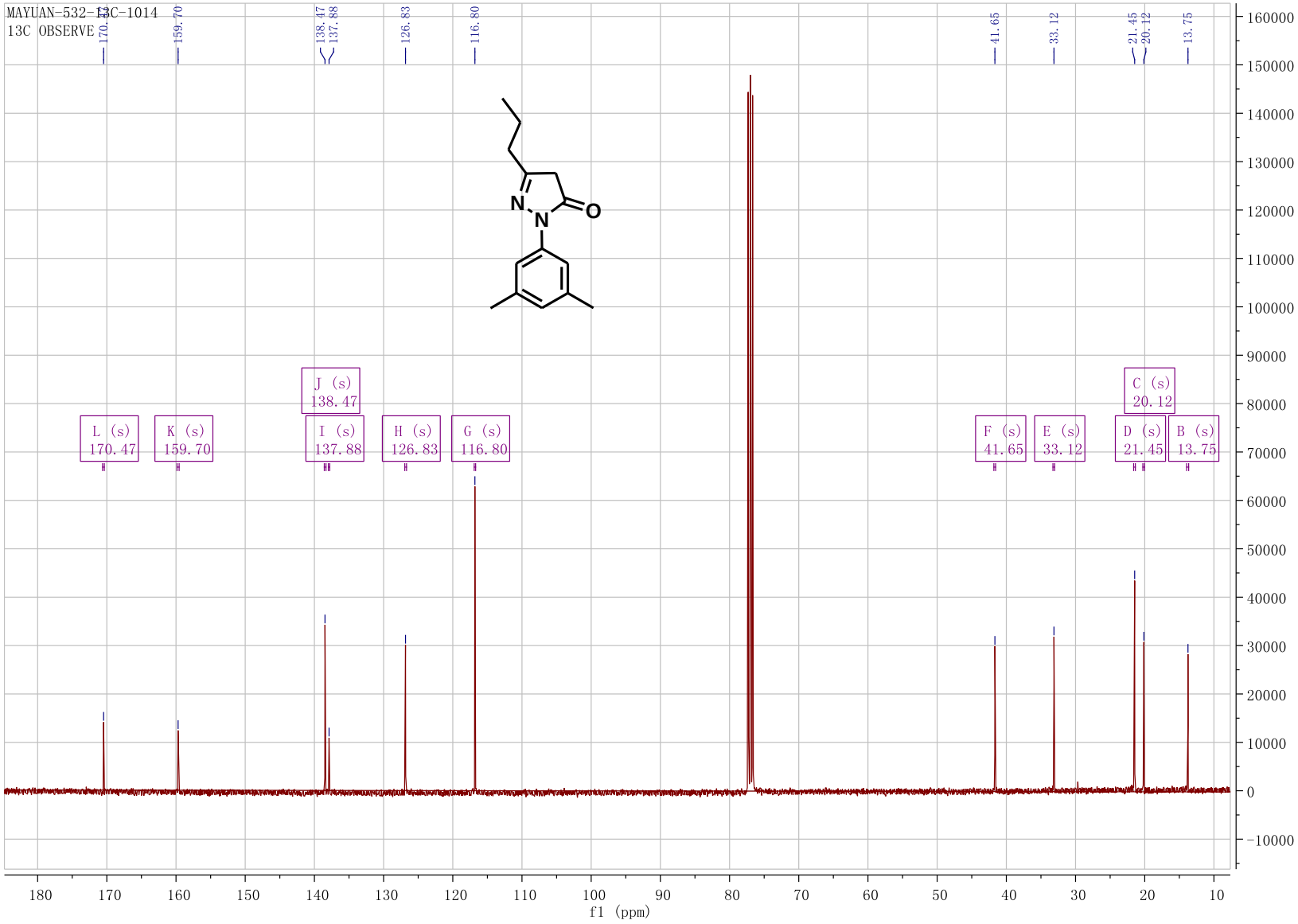

17.738
8.028
8.023
8.017
7.928
7.924
7.908
7.904
7.448
7.388
7.367
7.348
7.261
7.253
7.251
7.237
7.234
3.112
3.095
3.078
1.405
1.386
1.375
-0.001
N
N
N
N
O
H
O
Cl
Cl
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
PPM
0.36
0.67
0.83
0.47
0.95
0.78
0.87
15
10
5
6.00
0
PPM

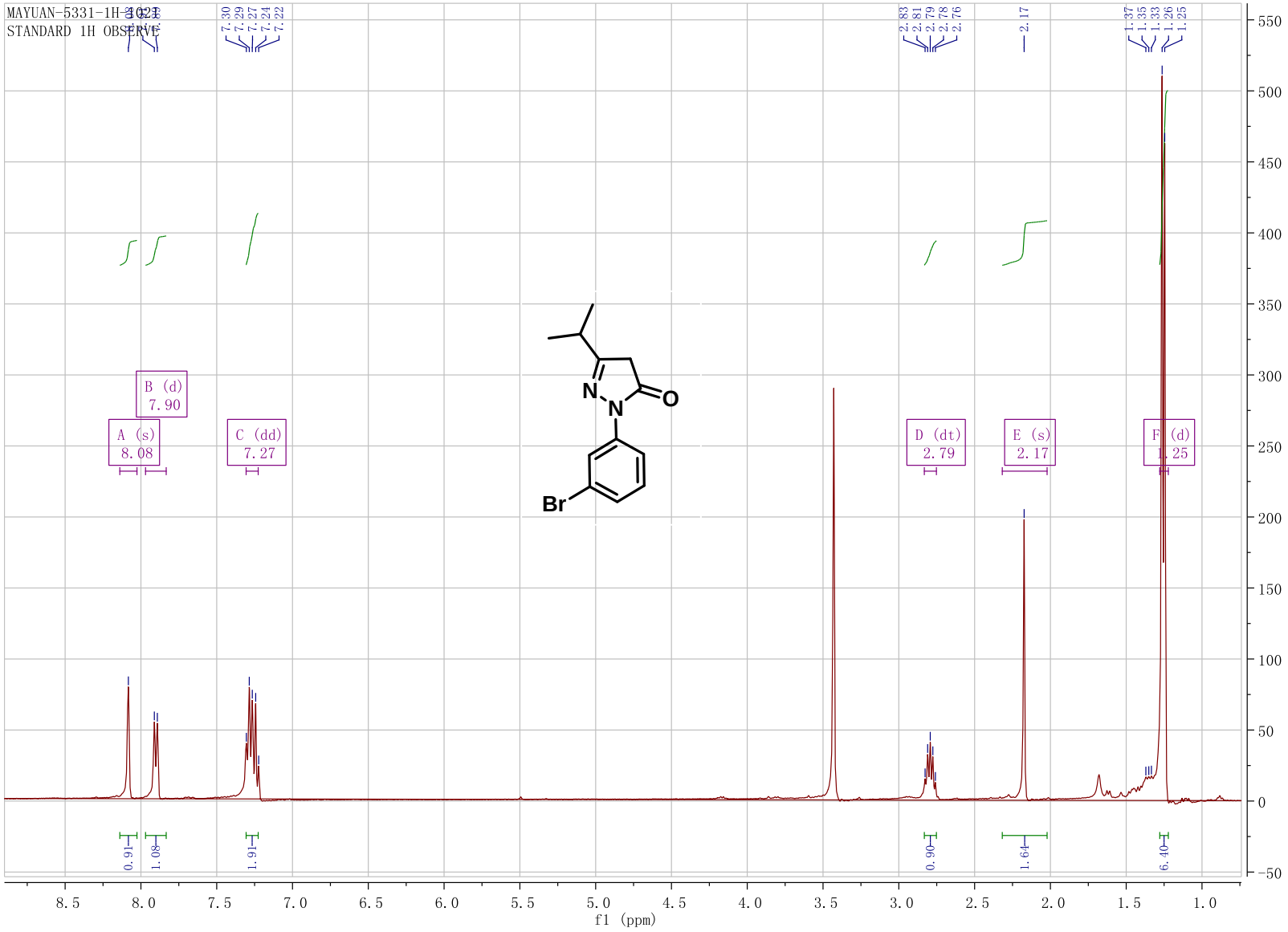

161.767
160.754
138.835
137.459
134.564
129.860
126.307
120.932
118.789
107.903
77.300
76.985
76.662
26.944
21.488
N
N
O
H
O
N
N
Cl
Cl
160
140
120
100
80
60
40
20
PPM

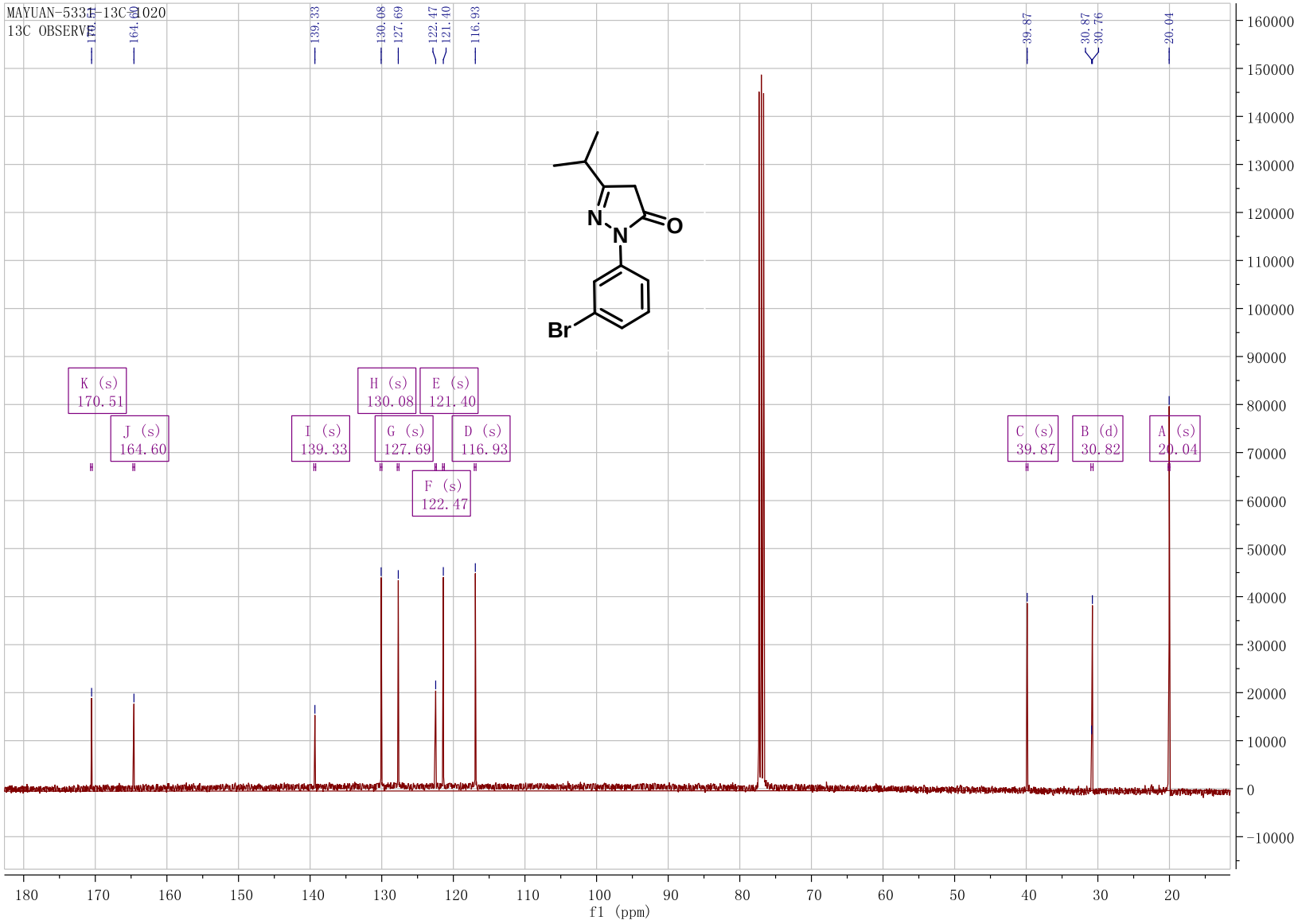

MAYEAN-531-1H-1011
STANDARD 1H OBSERVE
F (s)
8.08
E (d)
7.89
D (m)
7.27
C (dt)
2.50
B (m)
1.69
A (m)
1.03
Br
O
N
N
f1 (ppm)

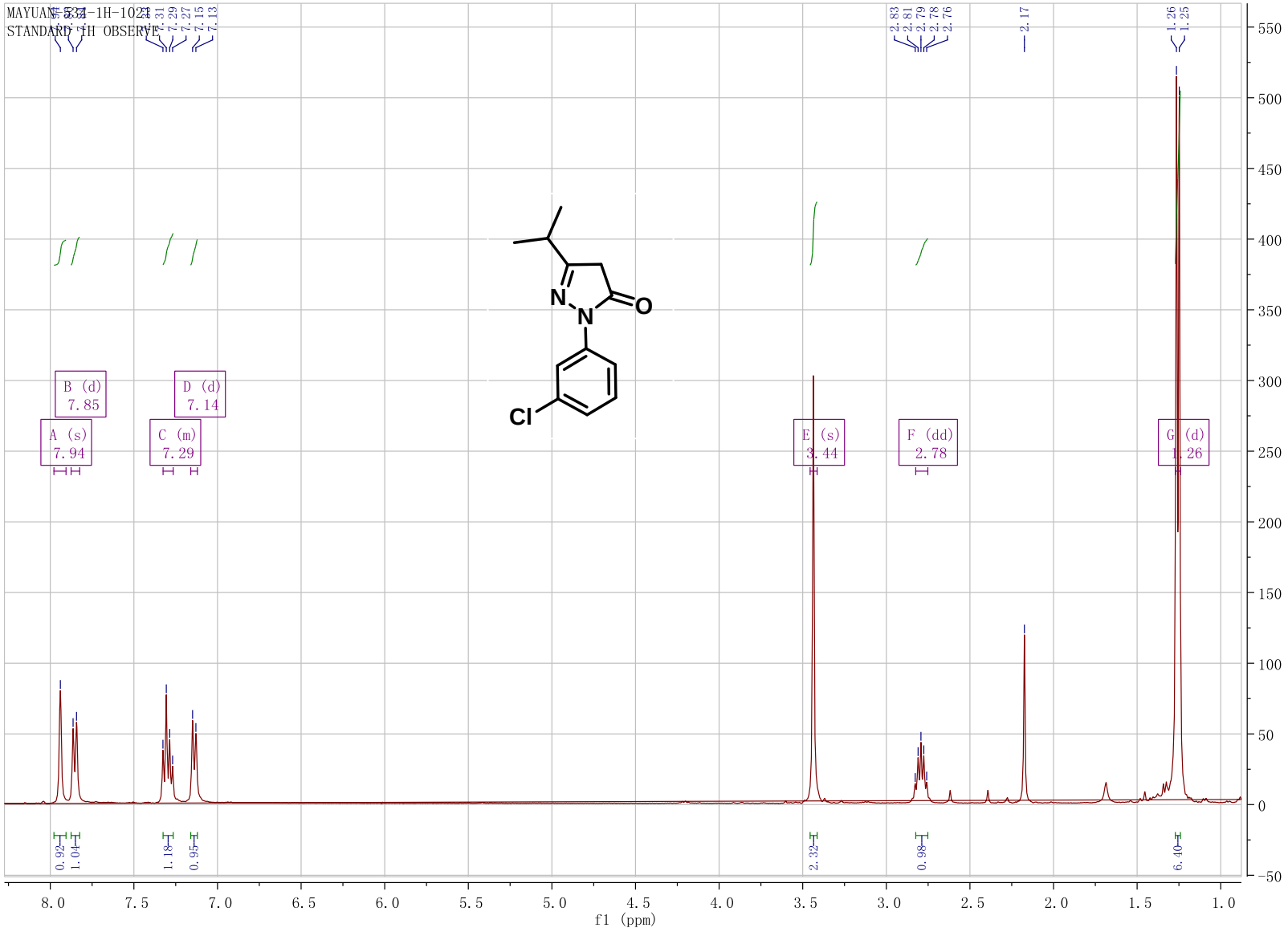

MAYUAN-531-13C-1015
13C OBSERVE
170.46
160.20
139.24
130.08
127.70
122.47
121.39
116.91
41.72
33.09
19.91
13.73
I (s)
130.08
F (s)
121.39
B (s)
19.91
L (s)
170.46
K (s)
160.20
J (s)
139.24
H (s)
127.70
E (s)
116.91
D (s)
41.72
C (s)
33.09
A (s)
13.73
G (s)
122.47
N
N
O
Br
f1 (ppm)

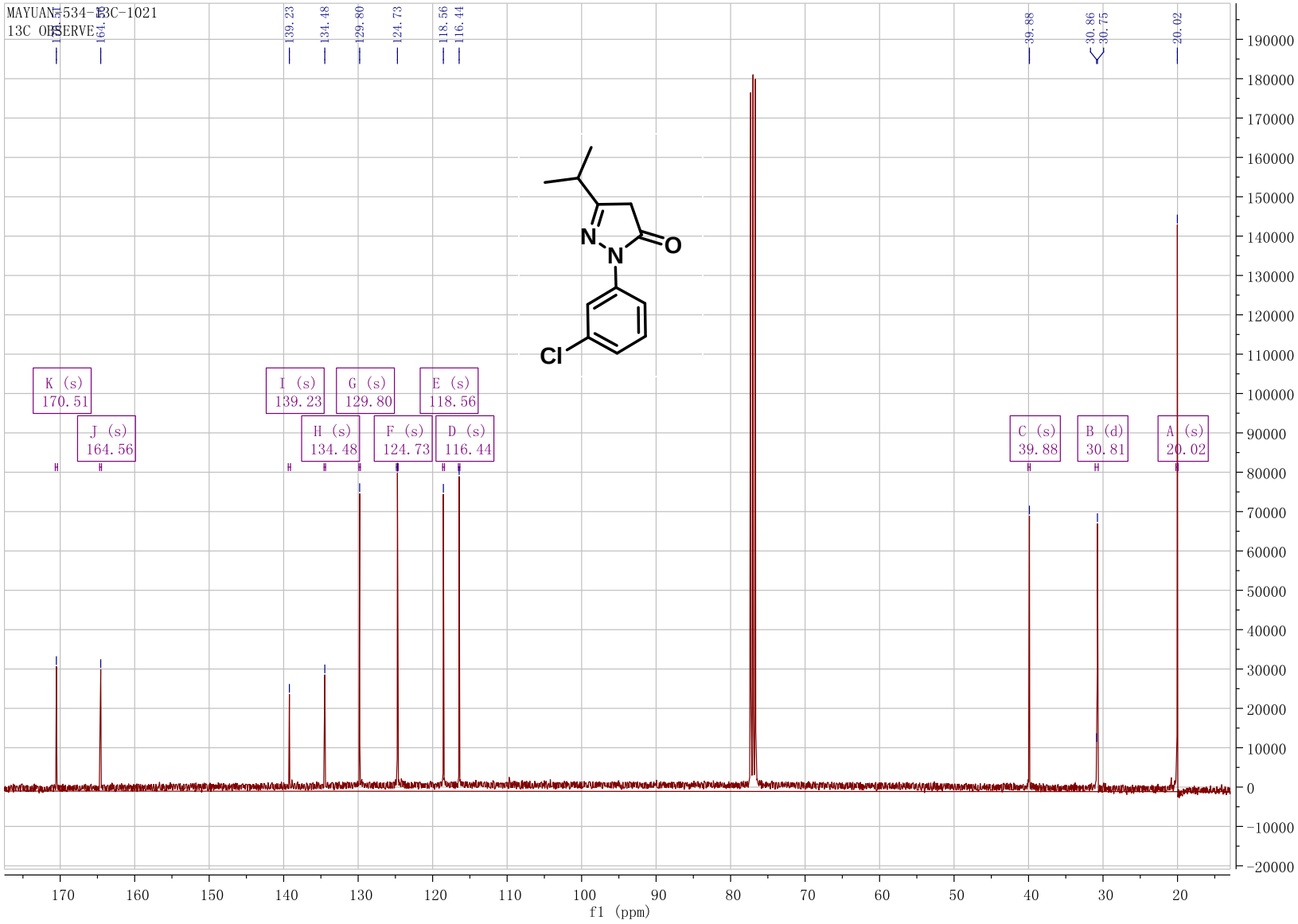

MAYUAN-532-4H-1014
STANDARD 1H-OBSERVE
F (d) 7.37
A (s) 6.83
C (s) 2.34
B (t) 2.48
D (m) 1.68
E (t) 1.02
f1 (ppm)

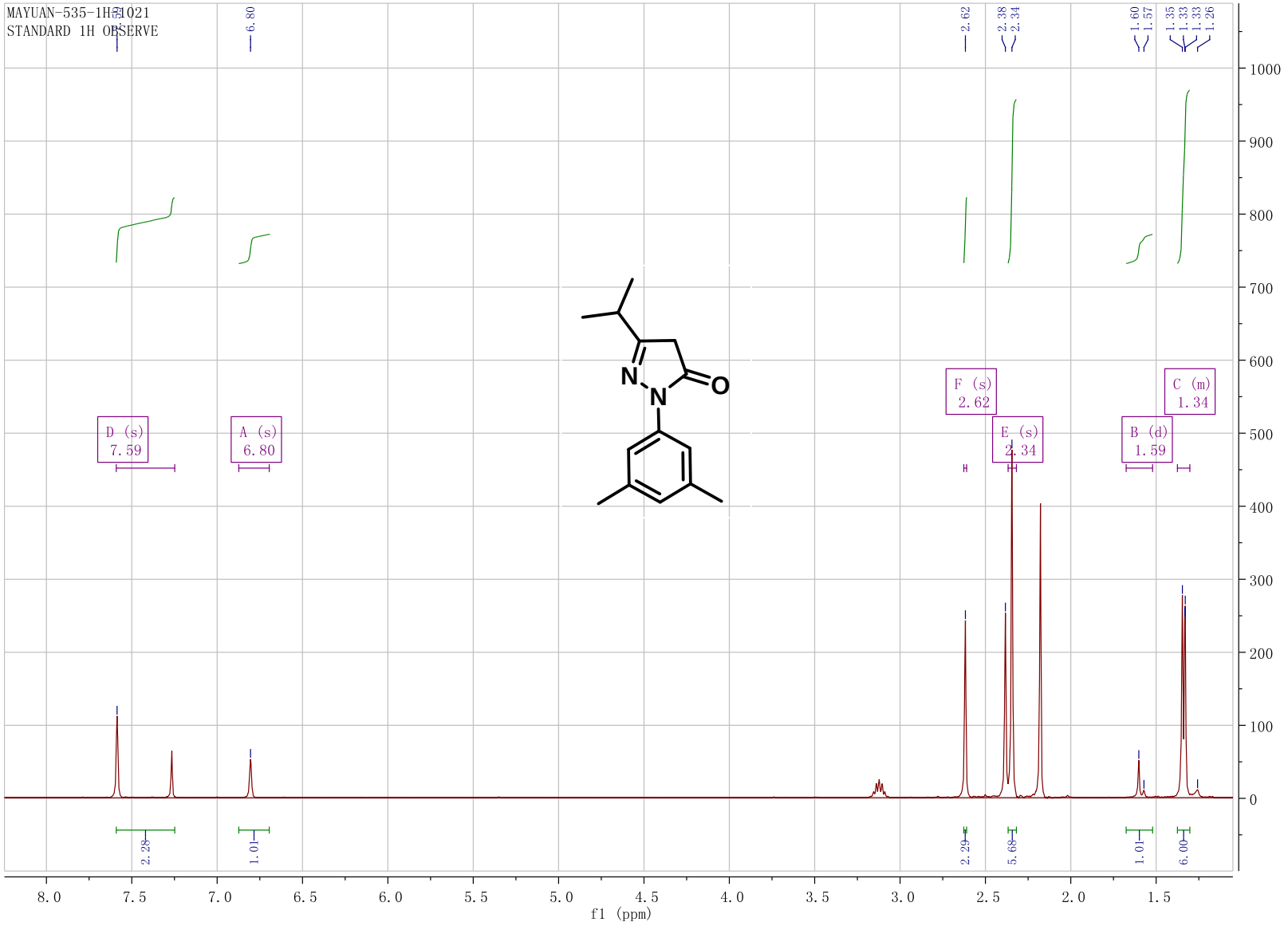

MAYUAN-532-13C-1014
13C OBSERVE
170.47
159.70
138.47
137.88
126.83
116.80
41.65
33.12
21.45
20.12
13.75
L (s) 170.47
K (s) 159.70
J (s) 138.47
I (s) 137.88
H (s) 126.83
G (s) 116.80
F (s) 41.65
E (s) 33.12
C (s) 20.12
D (s) 21.45
B (s) 13.75
N
N
O
f1 (ppm)


MAYUAN-5331-1H-2023
STANDARD 1H OBSERVE
8.08
8.07
7.90
7.88
7.30
7.29
7.27
7.24
7.22
2.83
2.81
2.79
2.78
2.76
2.17
1.37
1.35
1.33
1.26
1.25
A (s)
8.08
B (d)
7.90
C (dd)
7.27
D (dt)
2.79
E (s)
2.17
F (d)
1.25
N
N
O
Br
0.91
1.80
1.91
0.90
1.64
6.40
f1 (ppm)


MAYUAN-533H-13C-1020
13C OBSERVE
170.51
164.60
139.33
130.08
127.69
122.47
121.40
116.93
39.87
30.87
30.76
20.04
K (s) 170.51
J (s) 164.60
I (s) 139.33
H (s) 130.08
G (s) 127.69
F (s) 122.47
E (s) 121.40
D (s) 116.93
C (s) 39.87
B (d) 30.82
A (s) 20.04
N
N
O
Br
f1 (ppm)


MAYUAN-824-1H-1024
STANDARD 1H OBSERVE
7.94
7.85
7.31
7.29
7.27
7.15
7.13
2.83
2.81
2.79
2.78
2.76
2.17
1.26
1.25
B (d)
7.85
D (d)
7.14
A (s)
7.94
C (m)
7.29
E (s)
3.44
F (dd)
2.78
G (d)
1.26
0.92
1.04
1.18
0.95
2.32
0.98
6.40
N
N
O
Cl
f1 (ppm)


MAYUAN-1534-13C-1021
13C OBSERVE
170.51
164.56
139.23
134.48
129.80
124.73
118.56
116.44
39.88
30.86
30.75
20.02
K (s) 170.51
J (s) 164.56
I (s) 139.23
H (s) 134.48
G (s) 129.80
F (s) 124.73
E (s) 118.56
D (s) 116.44
C (s) 39.88
B (d) 30.81
A (s) 20.02
N
N
O
Cl
f1 (ppm)


MAYUAN-535-1H-1021
STANDARD 1H OBSERVE
7.59
6.80
2.62
2.38
2.34
1.60
1.57
1.35
1.33
1.33
1.26
D (s)
7.59
A (s)
6.80
F (s)
2.62
E (s)
2.34
B (d)
1.59
C (m)
1.34
2.28
1.01
2.29
5.68
1.01
6.00
f1 (ppm)

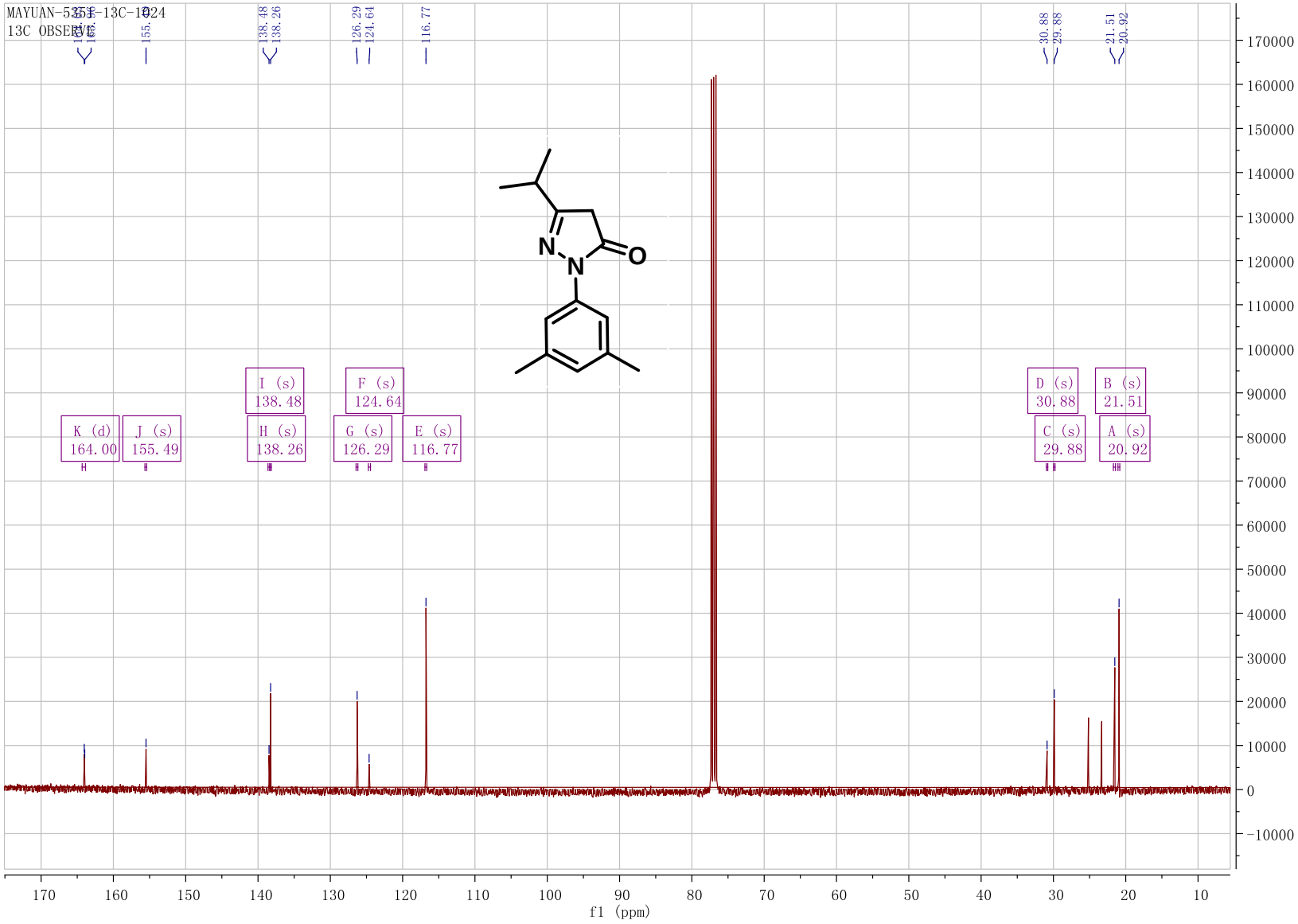

MAYUAN-5355-13C-1024
13C OBSERVE
164.00
155.49
138.48
138.26
126.29
124.64
116.77
30.88
29.88
21.51
20.92
K (d) 164.00
J (s) 155.49
I (s) 138.48
H (s) 138.26
F (s) 124.64
G (s) 126.29
E (s) 116.77
D (s) 30.88
C (s) 29.88
B (s) 21.51
A (s) 20.92
N
N
O
f1 (ppm)

Table S1. Selected bond lengths (Å), and angles(º) for **2f** (room temperature data)

C9-O1	1.281(4)	C32-O3	1.274(4)
C9-N2	1.348(4)	C32-N5	1.348(4)
C8-C9	1.437(4)	C31-C32	1.436(4)
C8-C10	1.382(5)	C31-C33	1.379(5)
C7-C8	1.436(5)	C30-C31	1.435(5)
C7-N1	1.299(4)	C30-N6	1.299(4)
C7-C21	1.499(4)	C30-C44	1.494(4)
N1-N2	1.413(4)	N5-N6	1.410(4)
N2-C6	1.426(4)	N5-C29	1.432(4)
C10-C11	1.381(5)	C33-C34	1.376(5)
C13-O2	1.290(4)	C36-O4	1.296(4)
C13-N4	1.350(4)	C36-N8	1.343(4)
C11-C13	1.434(4)	C34-C36	1.433(5)
C11-C12	1.434(5)	C34-C35	1.440(5)
C12-N3	1.300(4)	C35-N7	1.304(4)
N3-N4	1.412(4)	N7-N8	1.408(4)
O1-H1O	1.23(5)	O3-H2O	1.228(14)
O2-H1O	1.19(5)	O4-H2O	1.204(14)
O1-C9-C8	130.2(3)	O3-C32-C31	130.5(3)
C9-C8-C10	132.7(3)	C32-C31-C33	131.7(3)
C8-C10-C11	137.1(3)	C31-C33-C34	137.1(3)
C10-C11-C13	132.7(3)	C33-C34-C36	133.1(3)
O2-C13-C11	131.3(3)	O4-C36-C34	131.7(3)
C9-O1-H1O	119(2)	C32-O3-H2O	116.0(19)
C10-O2-H1O	117(2)	C36-O4-H2O	113(2)