Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

SYNTHESIS OF STERICALLY SHIELDED STABLE CARBENES OF THE 1,2,4-TRIAZOLE SERIES AND THEIR CORRESPONDING PALLADIUM COMPLEXES: EFFICIENT CATALYSTS FOR CHLOROARENE HYDRODECHLORINATION

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Bis(1-*tert*-butyl-3-phenyl-4-*p*-bromophenyl-1,2,4-triazol-5-ylidene)palladium iodide (**9b**) ($CDCl_3$).

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Bis(1-*tert*-butyl-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-ylidene)palladium iodide (**9d**) (solid state).

1-*tert*-Butyl-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-ylidene)palladium chloride (**10a**) ($CDCl_3$).

[1-*tert*-Butyl-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-ylidene]palladium iodide (**10b**) ($CDCl_3$, solid state).

[1-(1-Adamantyl)-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-ylidene]palladium chloride (**10c**) ($CDCl_3$, solid state).

[1-(1-Adamantyl)-3-phenyl-4-(2,6-diisopropylphenyl)-1,2,4-triazol-5-ylidene]palladium iodide (**10d**) (solid state).

1. Crystallographic data for 8c, 9a,b and 10a

Table 1. Crystal data and structure refinement for **8c**.

Identification code	shelxl	
Empirical formula	C24 H31 N3	
Formula weight	361.52	
Temperature	153(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 13.988(5) Å	α= 90°.
	b = 10.458(4) Å	β= 90.960(5)°.
	c = 15.065(5) Å	γ = 90°.
Volume	2203.5(14) $Å^3$	
Z	4	
Density (calculated)	1.090 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	784	
Crystal size	0.41 x 0.35 x 0.22 mm^3	
Theta range for data collection	2.37 to 27.49°.	
Index ranges	-18<=h<=18, -13<=k<=13, -19<=l<=19	
Reflections collected	22884	
Independent reflections	5057 [R(int) = 0.0804]	
Completeness to theta = 27.49°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9860 and 0.9741	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5057 / 0 / 251
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1326
R indices (all data)	R1 = 0.0587, wR2 = 0.1407
Largest diff. peak and hole	0.267 and -0.236 e.$Å^{-3}$

Table 2. Crystal data and structure refinement for **9a**.

Identification code	shelxl	
Empirical formula	C38 H39 Br2 Cl2 N7 Pd	
Formula weight	930.88	
Temperature	100(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.082(2) Å	α= 86.615(2)°.
	b = 12.898(3) Å	β= 71.761(2)°.
	c = 14.669(3) Å	γ = 63.699(8)°.
Volume	1937.8(7) $Å^3$	
Z	2	
Density (calculated)	1.595 Mg/m^3	
Absorption coefficient	2.716 mm^{-1}	
F(000)	932	
Crystal size	0.22 x 0.11 x 0.07 mm^3	
Theta range for data collection	1.47 to 27.50°.	
Index ranges	-15<=h<=15, -16<=k<=16, -19<=l<=18	

Reflections collected	34348
Independent reflections	8830 [R(int) = 0.0556]
Completeness to theta = 27.50°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8326 and 0.5864
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8830 / 84 / 493
Goodness-of-fit on F^2	1.176
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.0948
R indices (all data)	R1 = 0.0584, wR2 = 0.0978
Largest diff. peak and hole	0.632 and -0.851 e.$Å^{-3}$

Table 3. Crystal data and structure refinement for **9b**.

Identification code	shelxl	
Empirical formula	C36 H36 Br2 I2 N6 Pd	
Formula weight	1072.73	
Temperature	100(2) K	
Wavelength	0.71069 E	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 19.283(3) E	α= 90°.
	b = 12.104(2) E	β= 116.657(2)°.
	c = 18.228(3) E	γ = 90°.
Volume	3802.2(11) E^3	
Z	4	

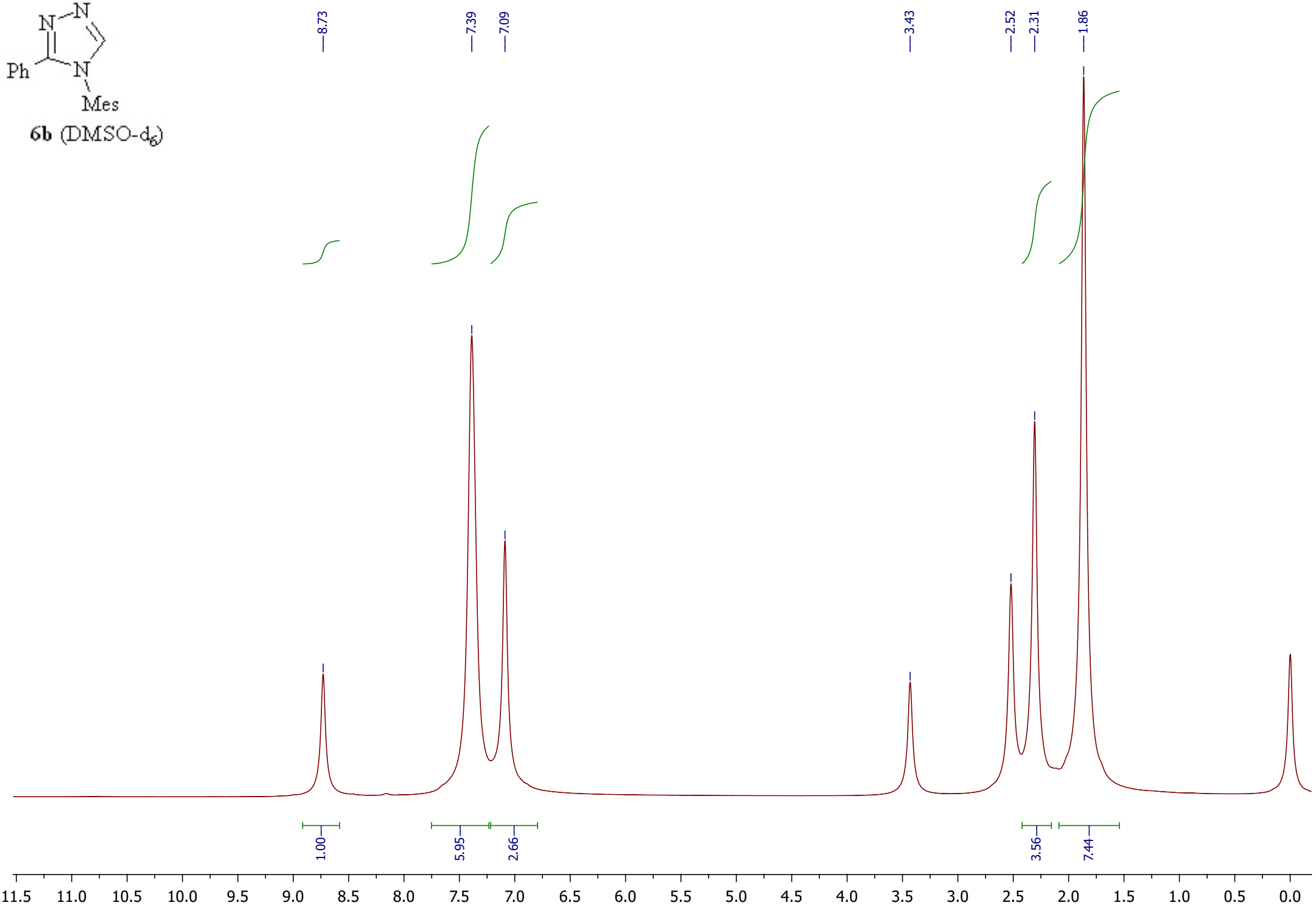
Density (calculated)	1.874 Mg/m^3
Absorption coefficient	4.247 mm^{-1}
F(000)	2064
Crystal size	0.20 x 0.10 x 0.06 mm^3
Theta range for data collection	2.06 to 27.50°.
Index ranges	-25<=h<=25, -15<=k<=15, -23<=l<=23
Reflections collected	84753
Independent reflections	8741 [R(int) = 0.0632]
Completeness to theta = 27.50°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7847 and 0.4838
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8741 / 0 / 430
Goodness-of-fit on F^2	1.331
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1107
R indices (all data)	R1 = 0.0548, wR2 = 0.1110
Largest diff. peak and hole	1.099 and -1.466 $e.E^{-3}$

Table 4. Crystal data and structure refinement for **10a**

Identification code	shelxl
Empirical formula	C28 H37 Cl2 N5 Pd
Formula weight	620.93
Temperature	120(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic

Space group	I 2/a	
Unit cell dimensions	a = 15.164(3) Å	α= 90°.
	b = 11.1580(17) Å	β= 99.668(6)°.
	c = 35.432(5) Å	γ = 90°.
Volume	5909.9(16) $Å^3$	
Z	8	
Density (calculated)	1.396 Mg/m^3	
Absorption coefficient	0.834 mm^{-1}	
F(000)	2560	
Crystal size	0.32 x 0.27 x 0.25 mm^3	
Theta range for data collection	1.92 to 25.00°.	
Index ranges	-18<=h<=18, -13<=k<=13, -42<=l<=42	
Reflections collected	24783	
Independent reflections	5194 [R(int) = 0.0436]	
Completeness to theta = 25.00°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5194 / 0 / 334	
Goodness-of-fit on F^2	1.190	
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.1016	
R indices (all data)	R1 = 0.0376, wR2 = 0.1423	
Largest diff. peak and hole	0.733 and -0.788 $e.Å^{-3}$	

2. ^{1}H and ^{13}C NMR spectra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1.00
5.95
2.66
3.56
7.44
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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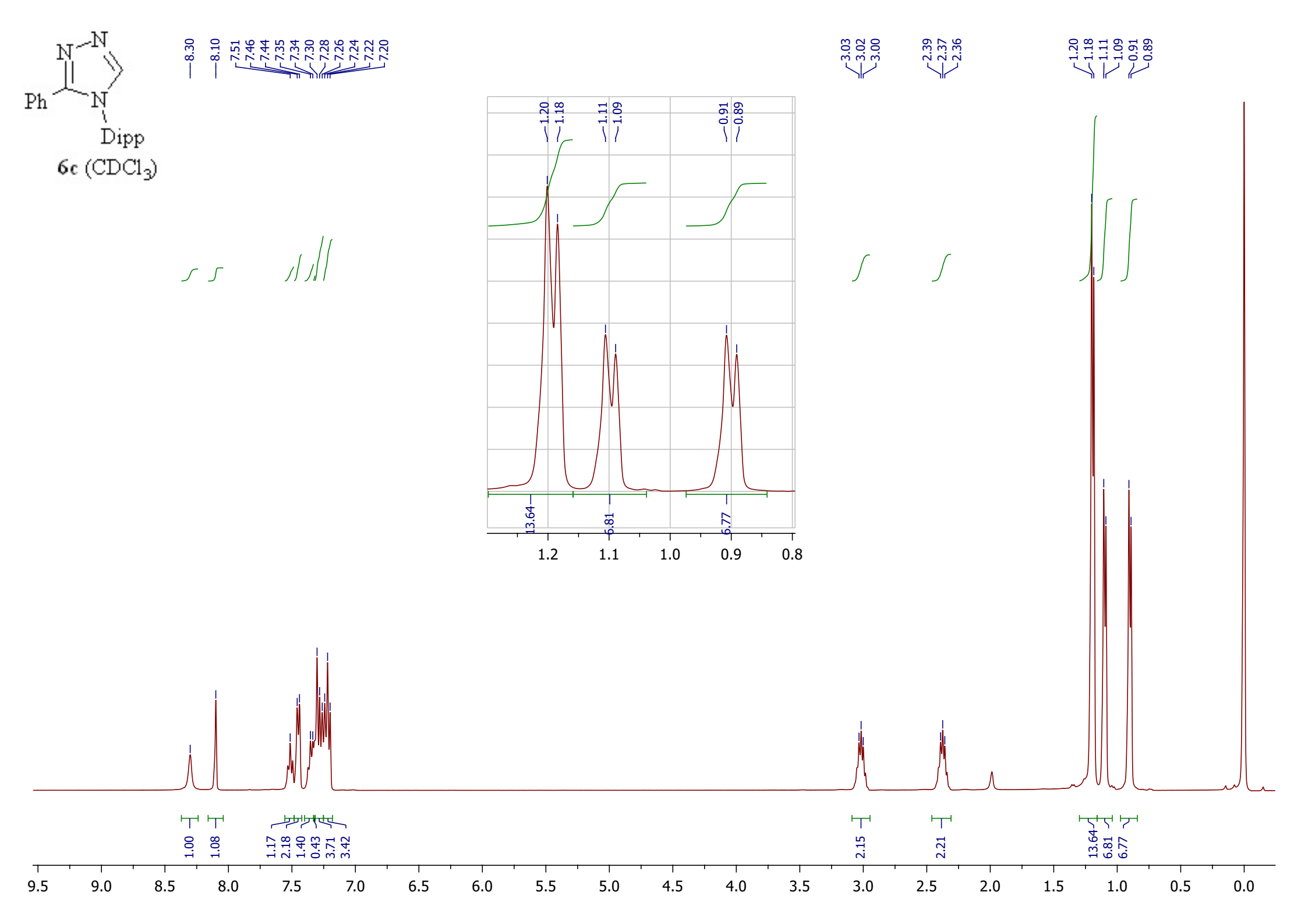
0.0


Ph
Dipp
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7.51
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7.26
7.24
7.22
7.20
3.03
3.02
3.00
2.39
2.37
2.36
1.20
1.18
1.11
1.09
0.91
0.89
13.64
6.81
6.77
1.2
1.1
1.0
0.9
0.8
1.00
1.08
1.17
2.18
1.40
0.43
3.71
3.42
2.15
2.21
13.64
6.81
6.77
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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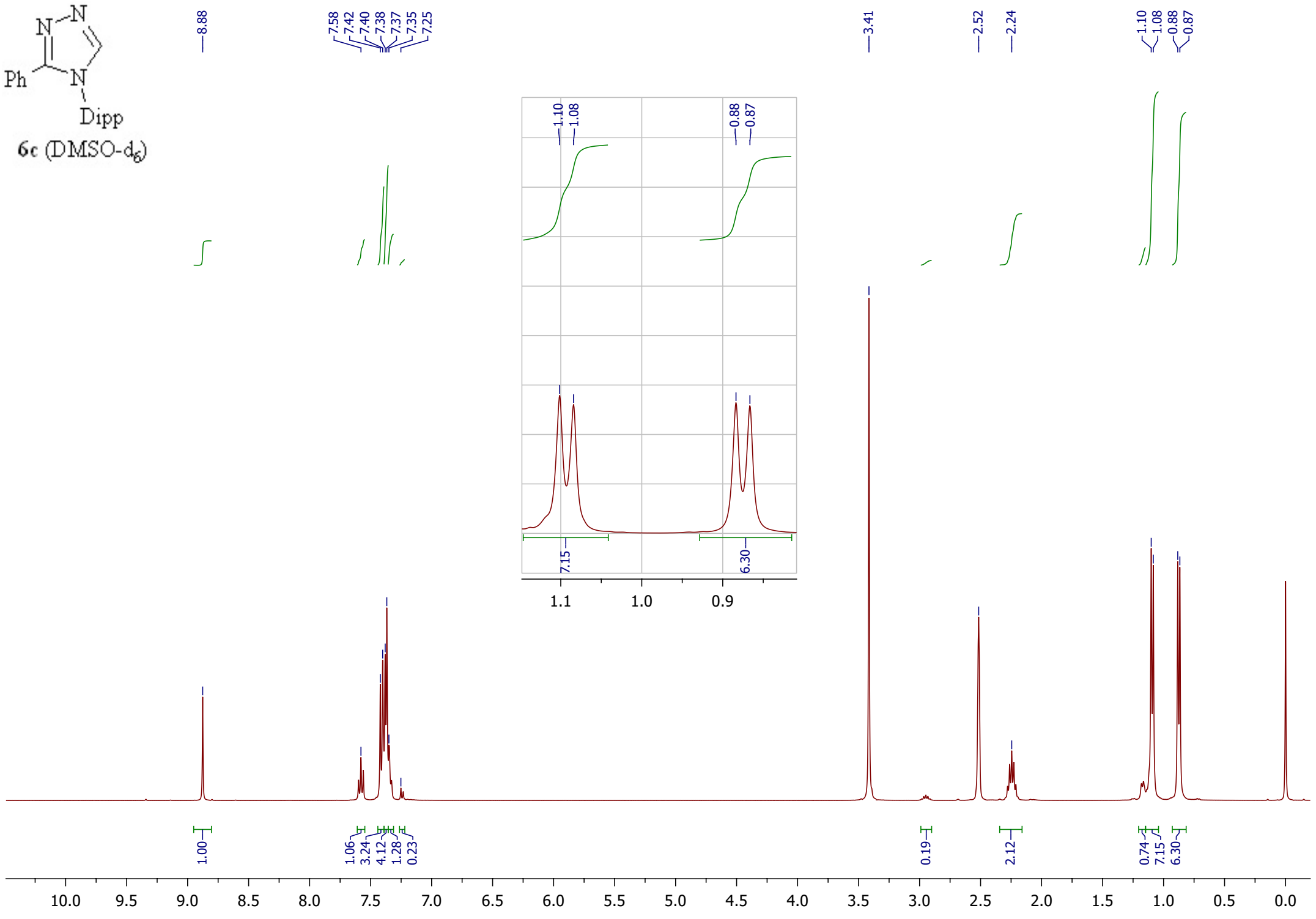
0.0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N
Dipp
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7.25
3.41
2.52
2.24
1.10
1.08
0.88
0.87
7.15
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0.74
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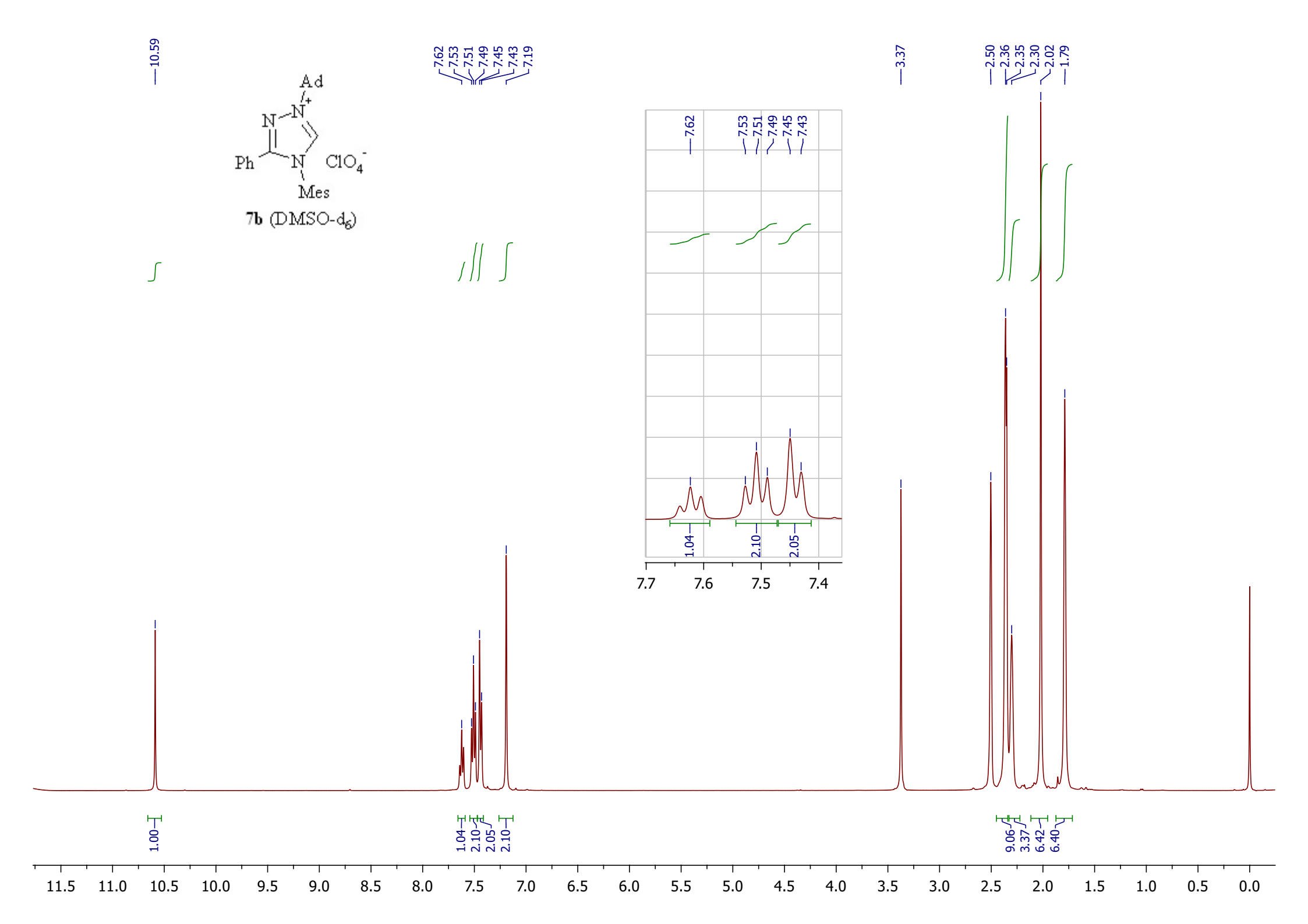
6.30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2.30
2.02
1.79
Ad
Ph
Mes
ClO4
7b (DMSO-d6)
1.00
1.04
2.10
2.05
2.10
9.06
3.37
6.42
6.40
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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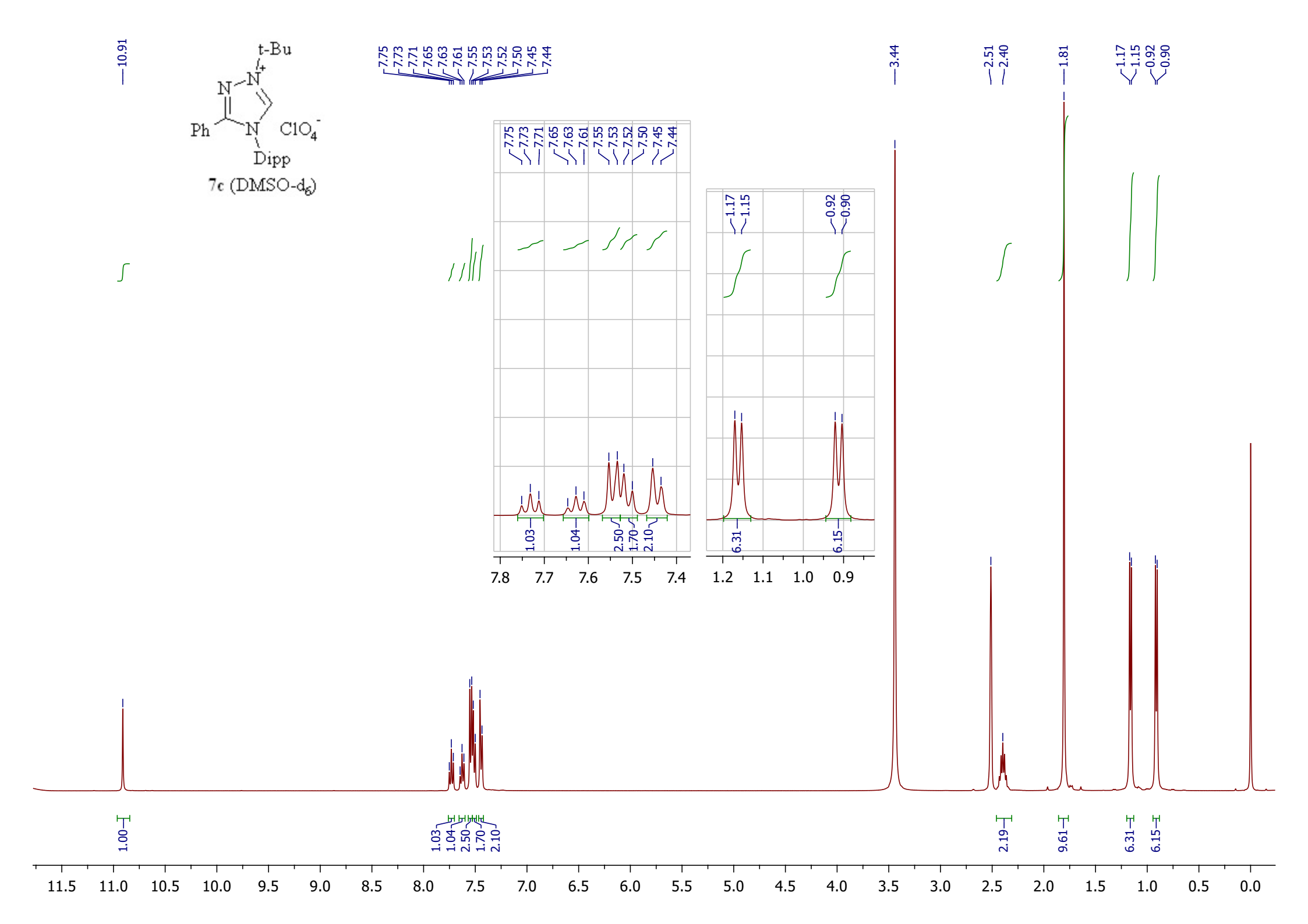
7.6
7.5
7.4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N+
Ph
N
ClO4-
Dipp
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7.65
7.63
7.61
7.55
7.53
7.52
7.50
7.45
7.44
3.44
2.51
2.40
1.81
1.17
1.15
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0.90
1.03
1.04
2.50
1.70
2.10
6.31
6.15
1.00
2.19
9.61
11.5
11.0
10.5
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8.5
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7.5
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6.5
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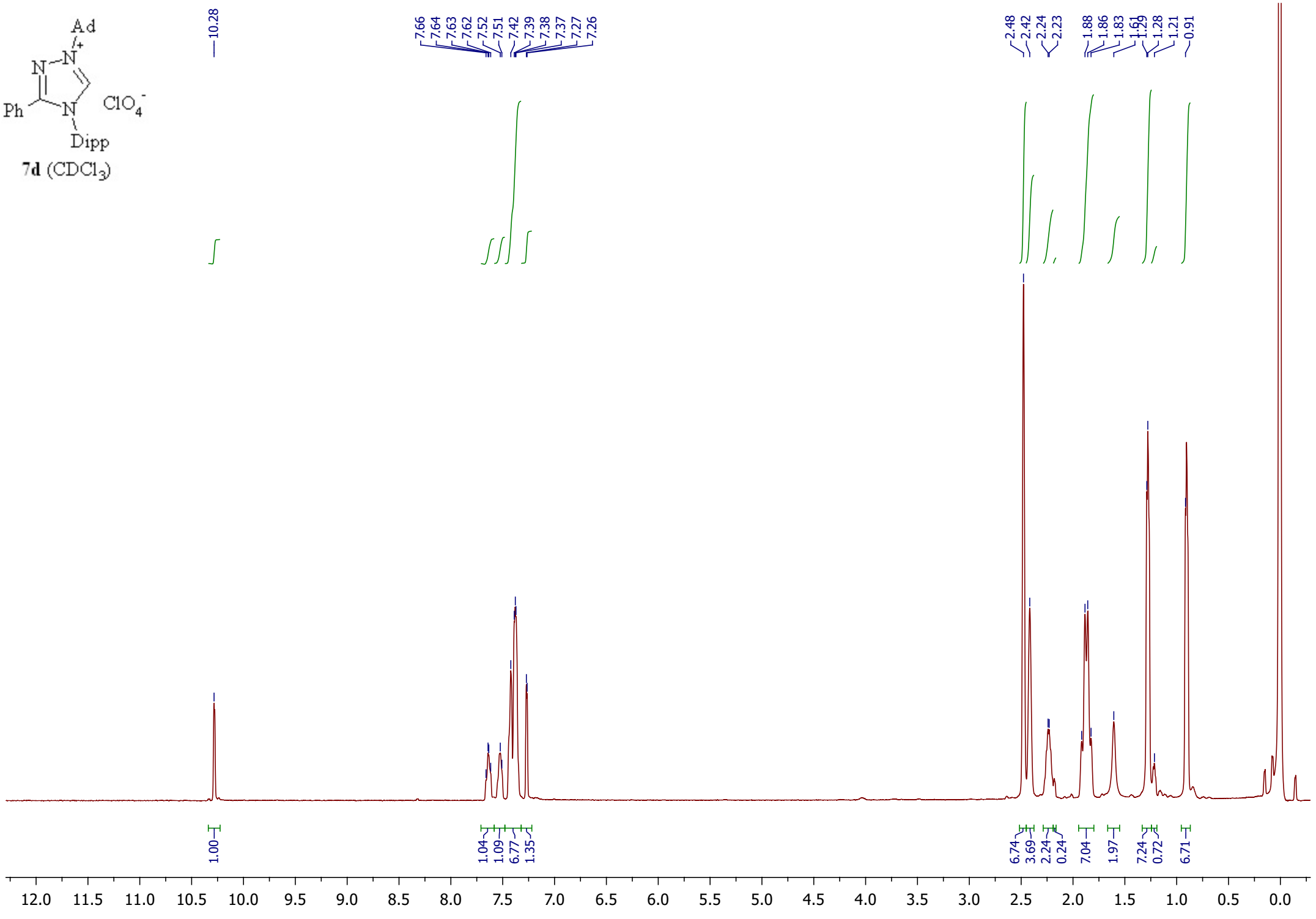
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N
Ph
N
ClO4-
Dipp
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7.51
7.42
7.39
7.38
7.37
7.27
7.26
2.48
2.42
2.24
2.23
1.88
1.86
1.83
1.61
1.29
1.28
1.21
0.91
1.00
1.04
1.09
6.77
1.35
6.74
3.69
2.24
0.24
7.04
1.97
7.24
0.72
6.71
12.0
11.5
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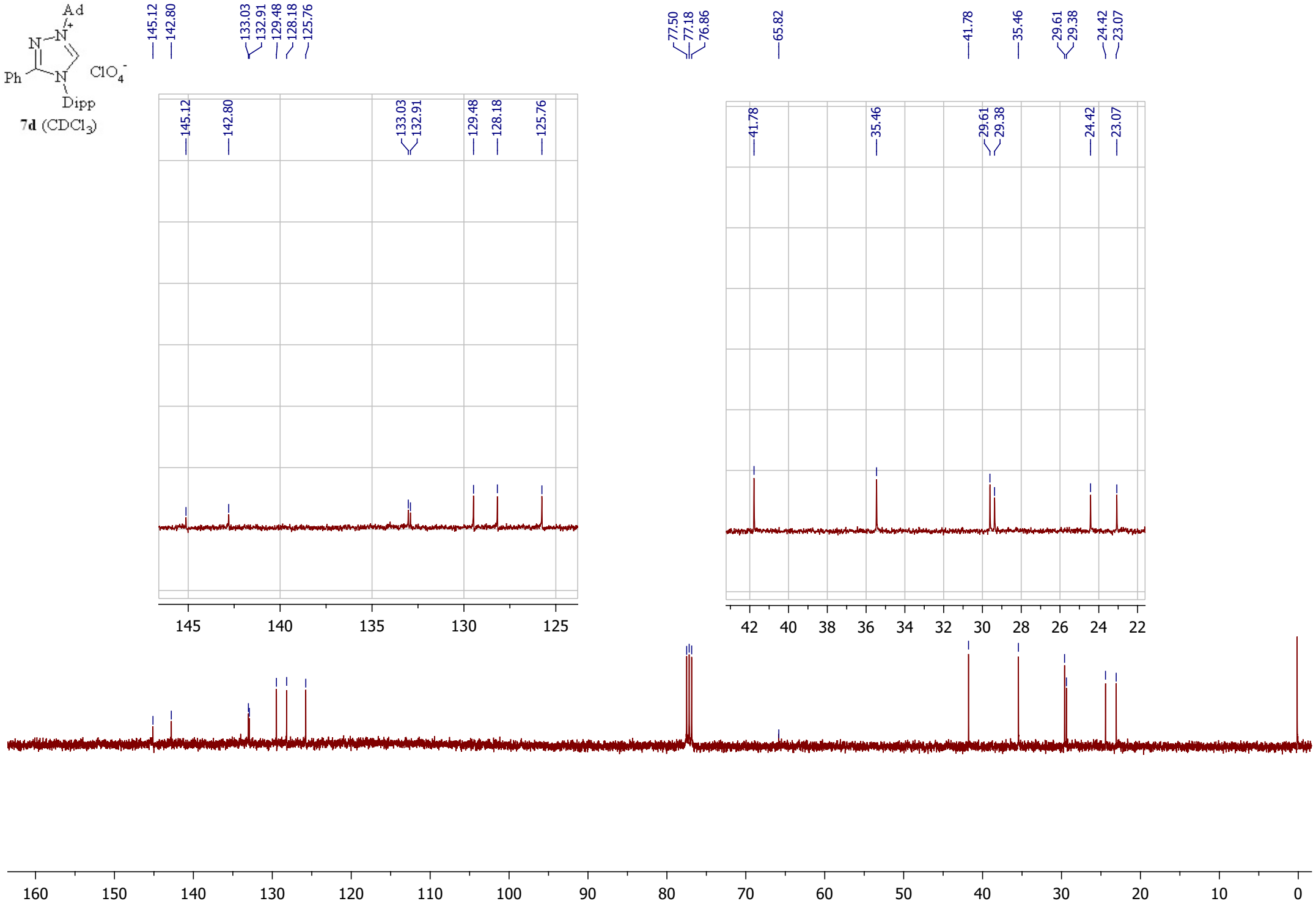
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N
Ph
N
ClO4-
Dipp
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129.48
128.18
125.76
77.50
77.18
76.86
65.82
41.78
35.46
29.61
29.38
24.42
23.07
145
140
135
130
125
42
40
38
36
34
32
30
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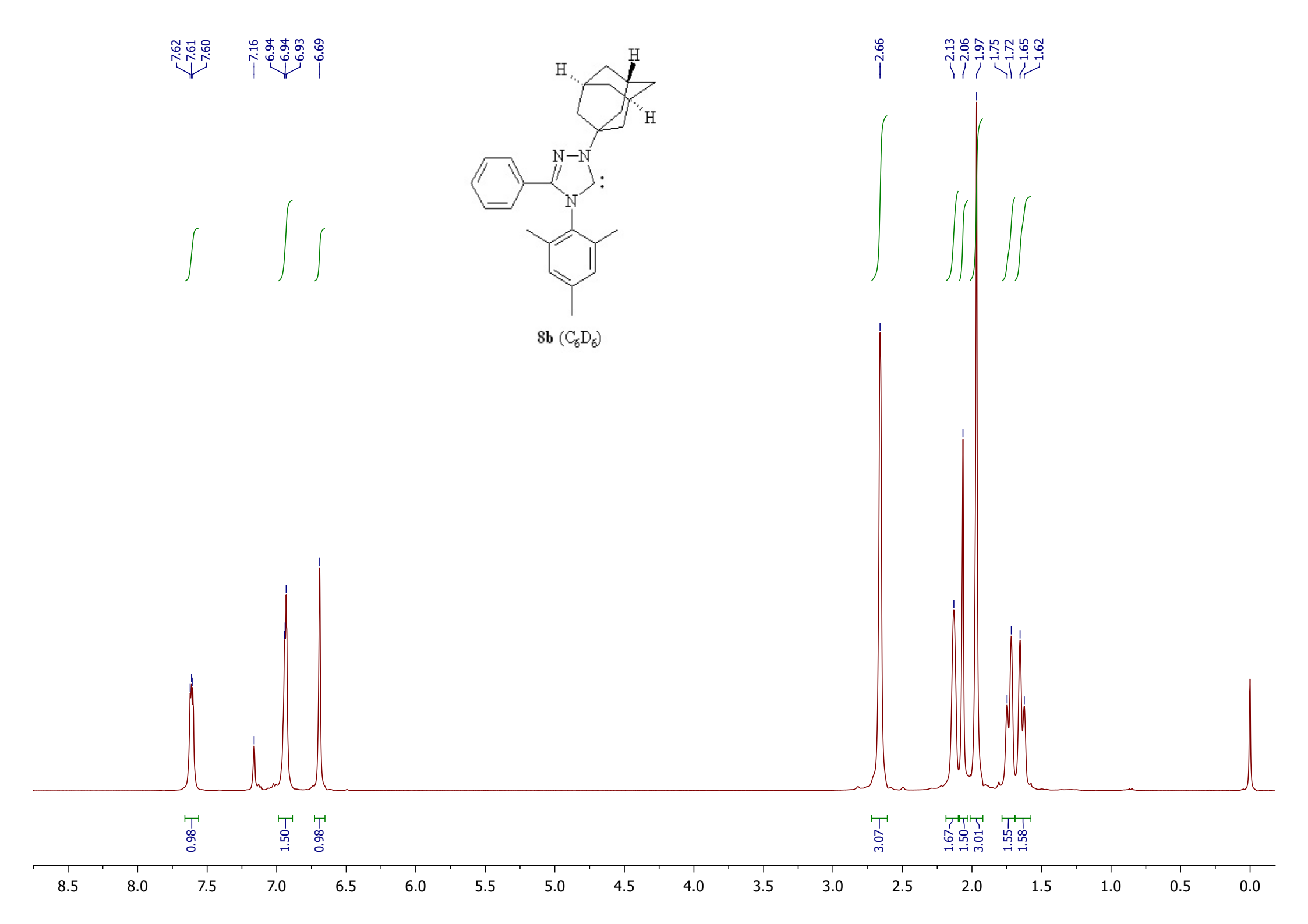
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1.75
1.72
1.65
1.62
H
H
H
N–N
N
0.98
1.50
0.98
3.07
1.67
1.50
3.01
1.55
1.58
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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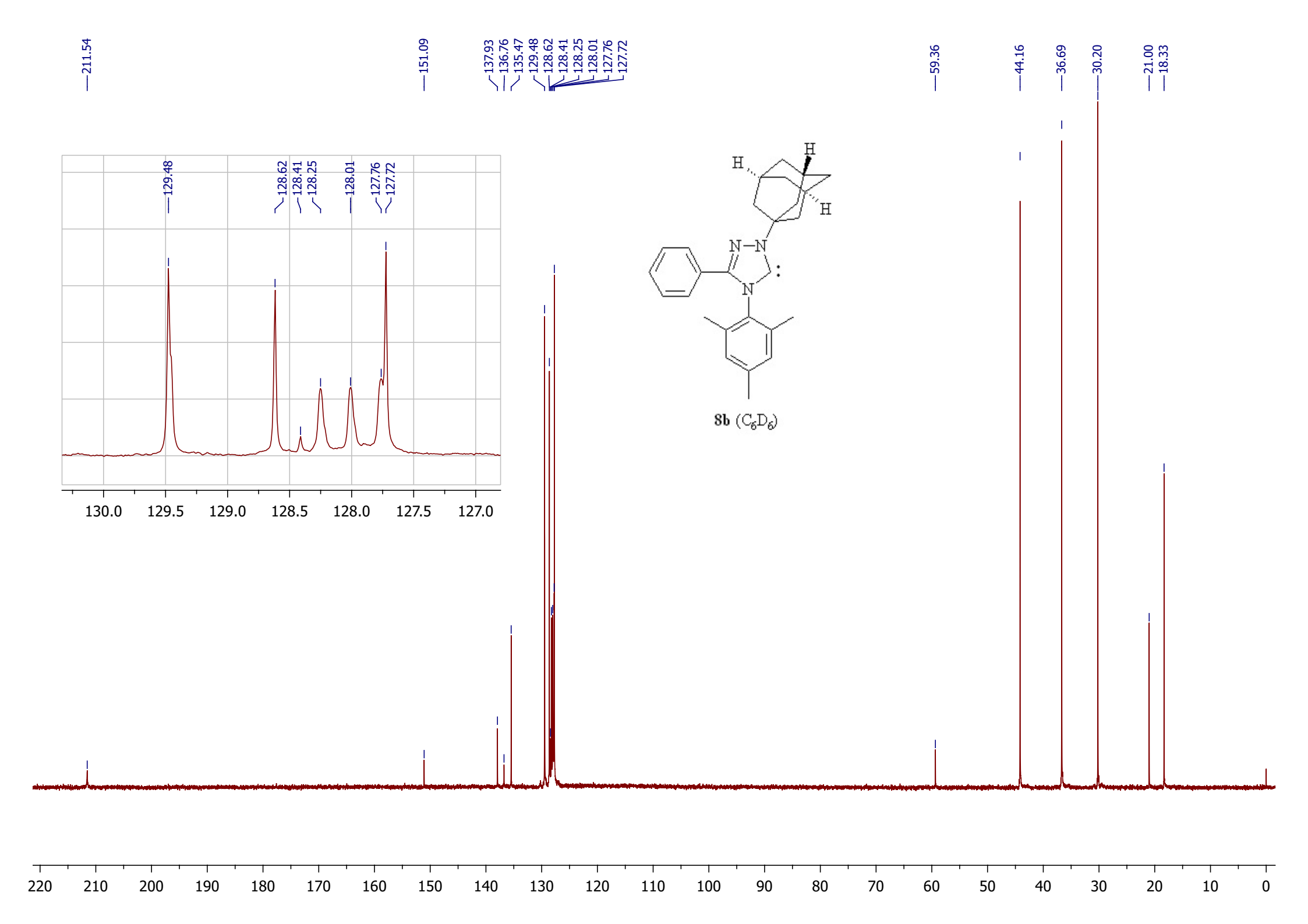
8b (C_6D_6)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59.36
44.16
36.69
30.20
21.00
18.33
H
H
H
N—N
N
:
8b (C6D6)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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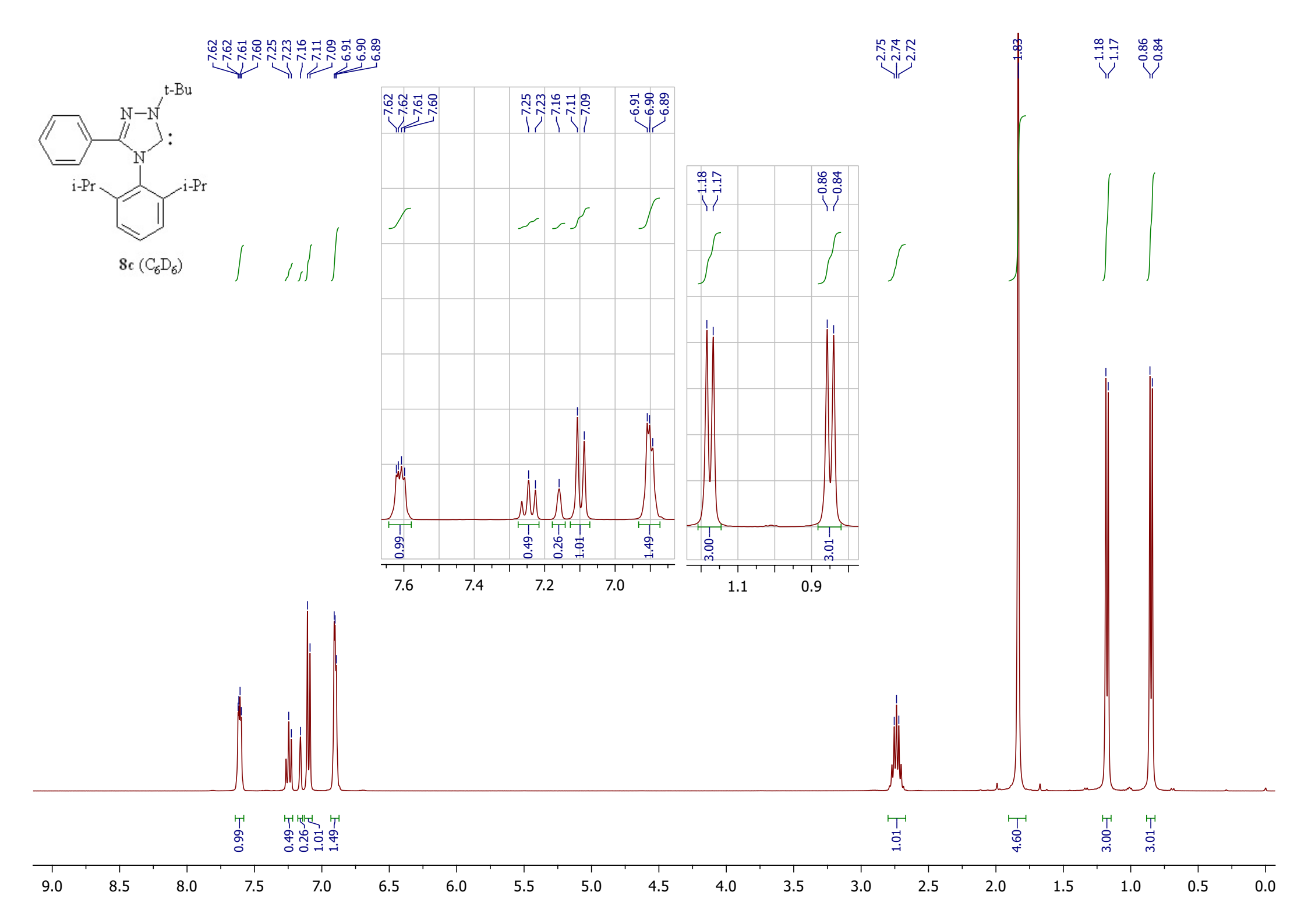
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N
N
i-Pr
i-Pr
8c (C6D6)
7.62
7.62
7.61
7.60
7.25
7.23
7.16
7.11
7.09
6.91
6.90
6.89
2.75
2.74
2.72
1.83
1.18
1.17
0.86
0.84
0.99
0.49
0.26
1.01
1.49
3.00
3.01
4.60
7.6
7.4
7.2
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1.1
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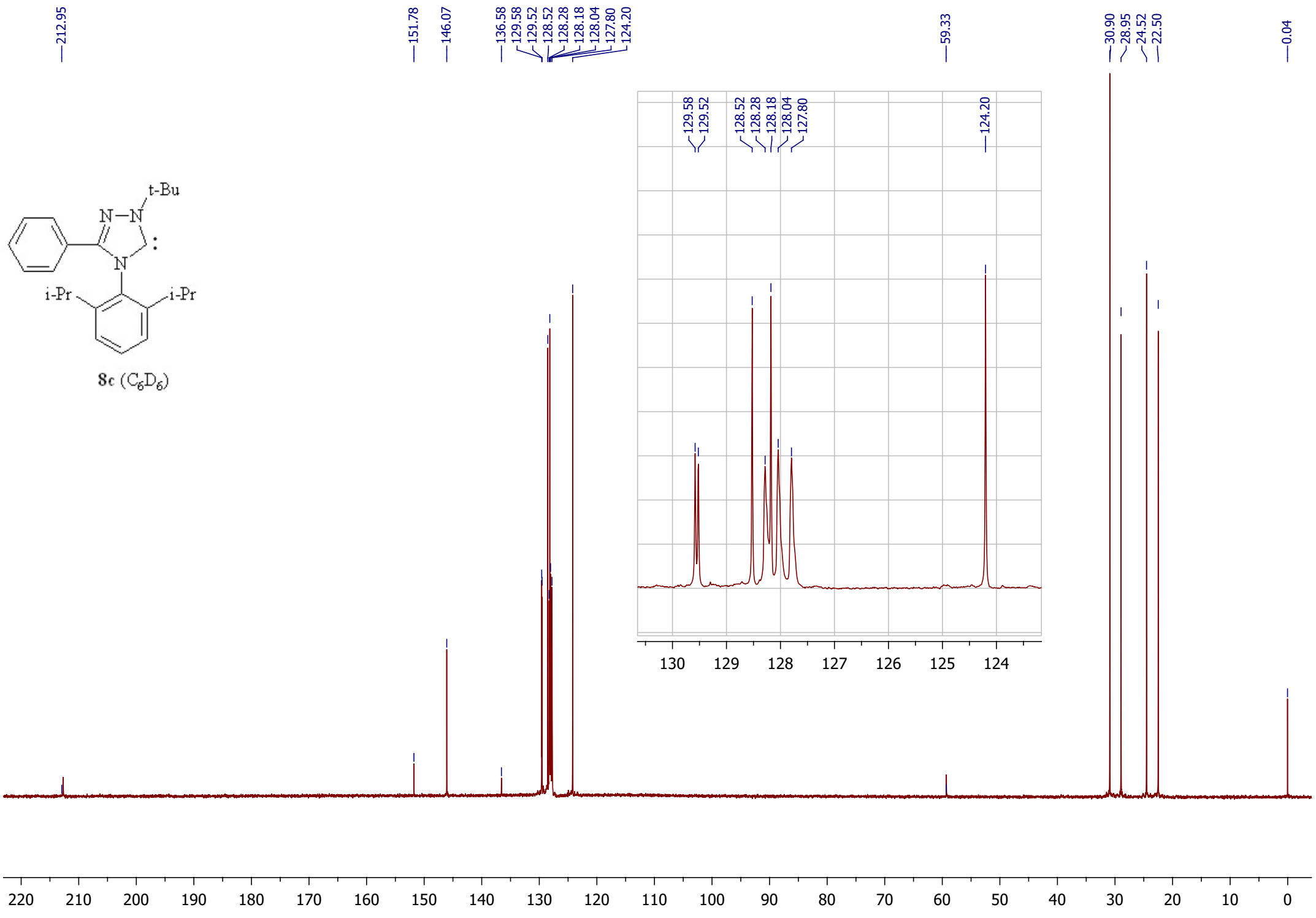
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30.90
28.95
24.52
22.50
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t-Bu
N—N
N
i-Pr
i-Pr
Sc (C6D6)
129.58
129.52
128.52
128.28
128.18
128.04
127.80
124.20
130
129
128
127
126
125
124
220
210
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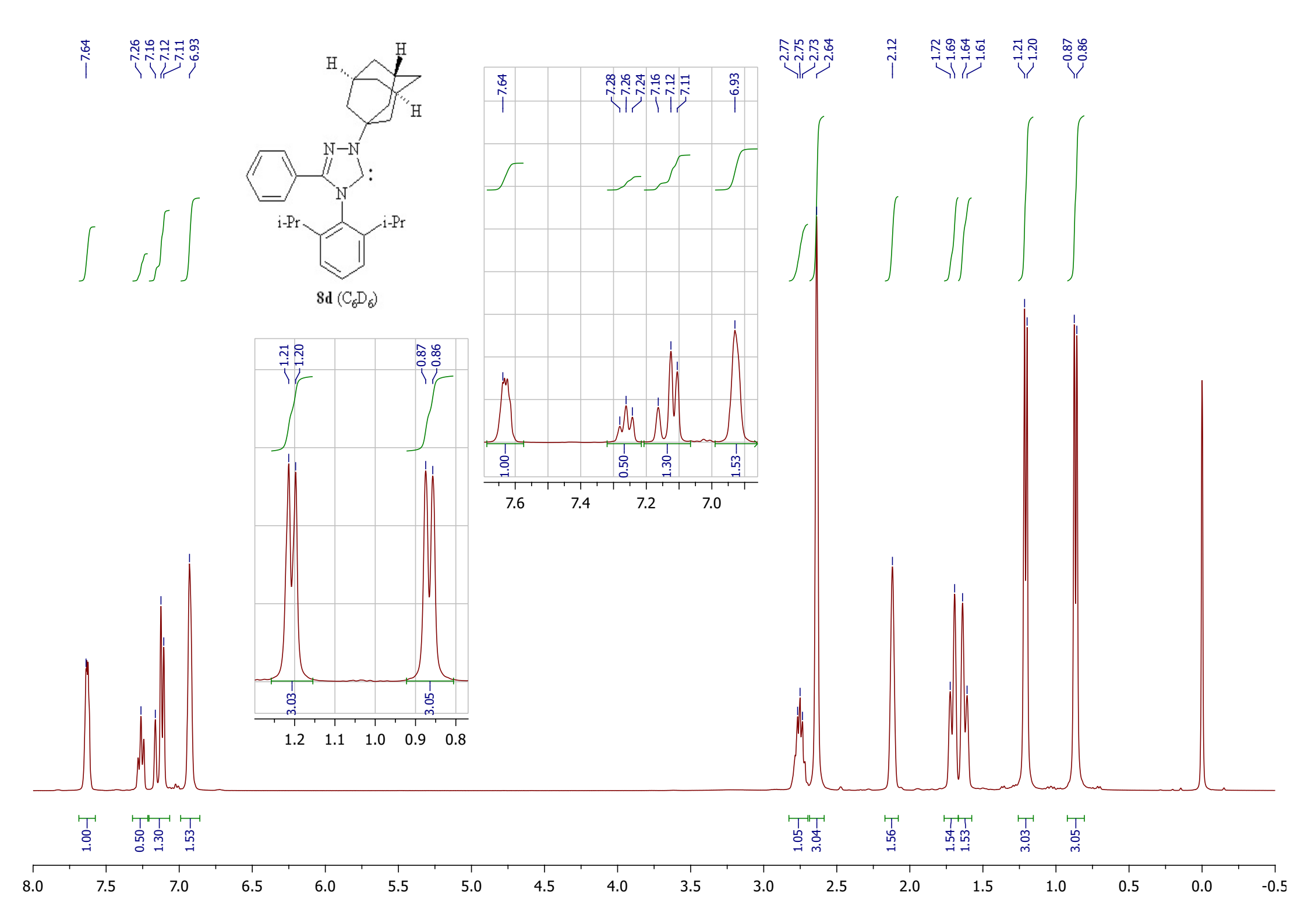
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1.64
1.61
1.21
1.20
0.87
0.86
H
H
H
N–N
N
i-Pr
i-Pr
8d (C6D6)
1.00
0.50
1.30
1.53
1.05
3.04
1.56
1.54
1.53
3.03
3.05
8.0
7.5
7.0
6.5
6.0
5.5
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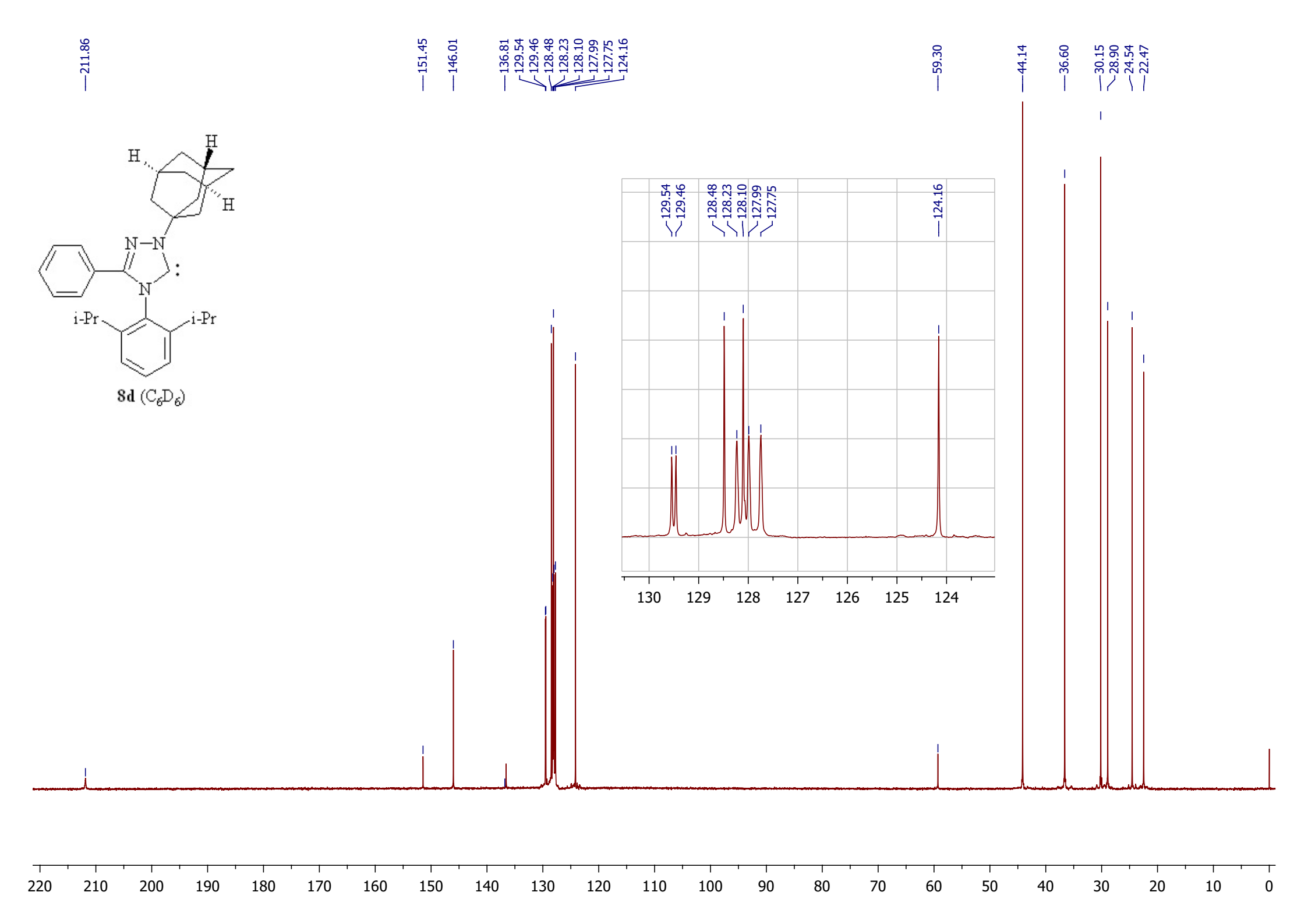
0.0
-0.5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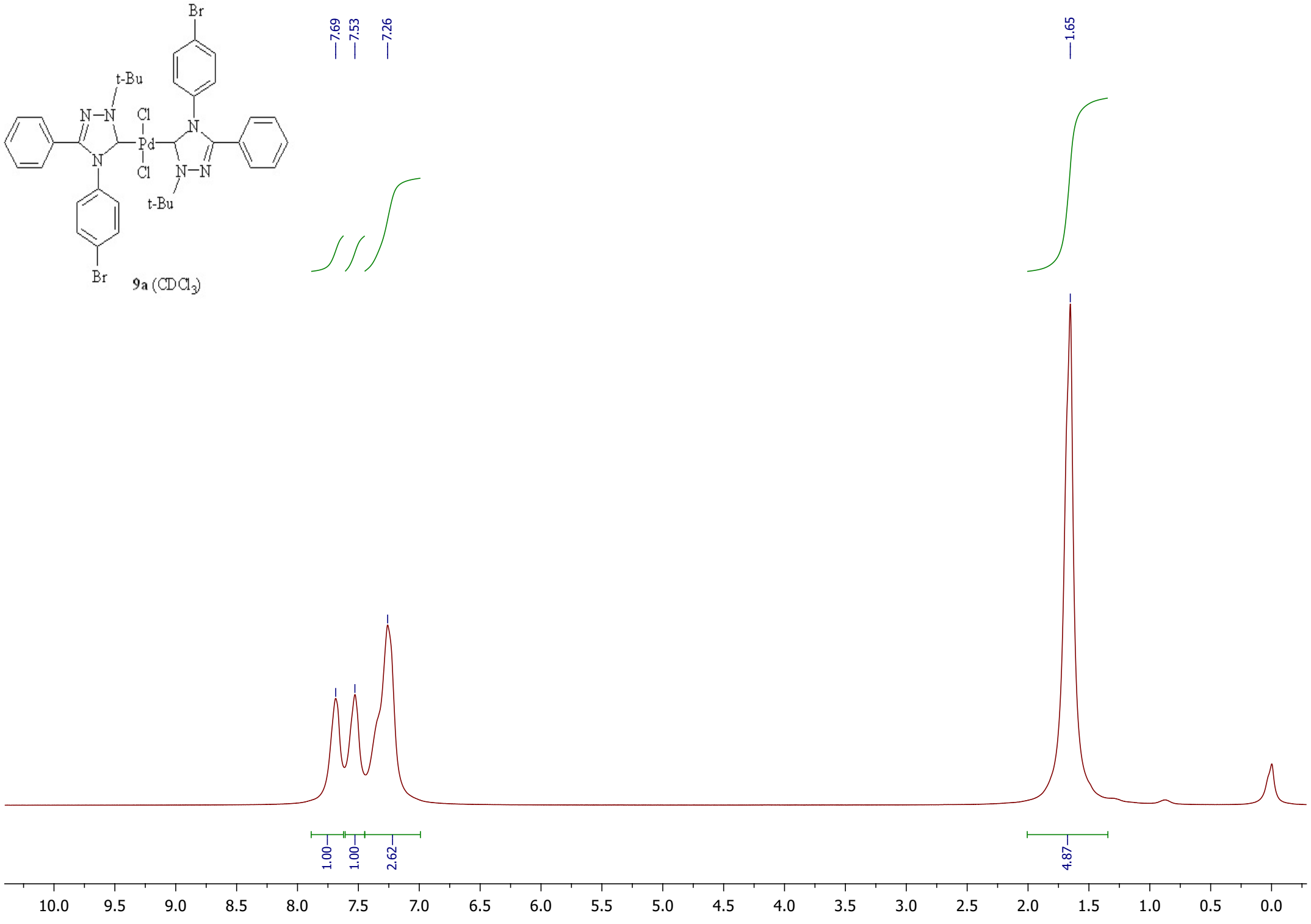
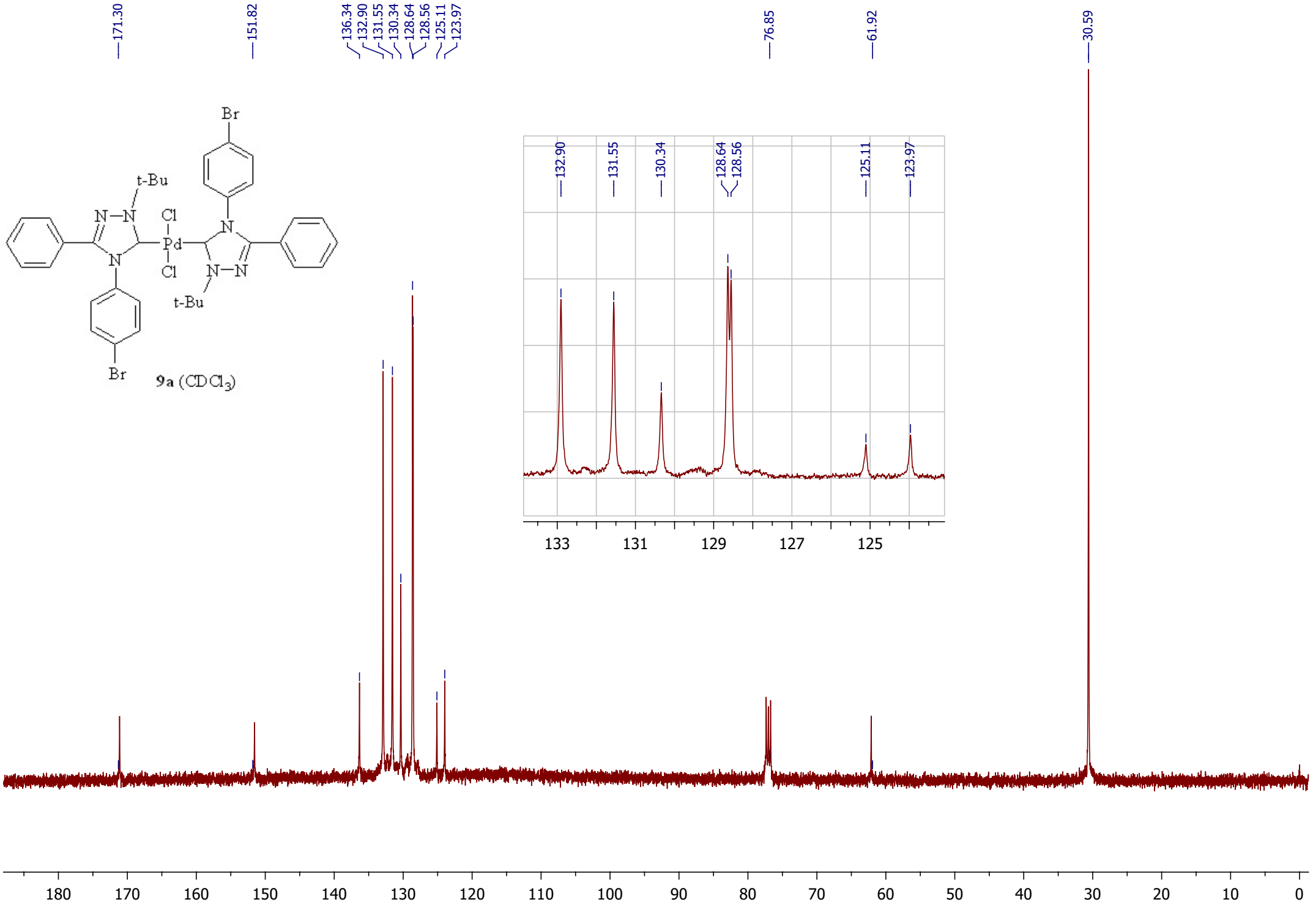
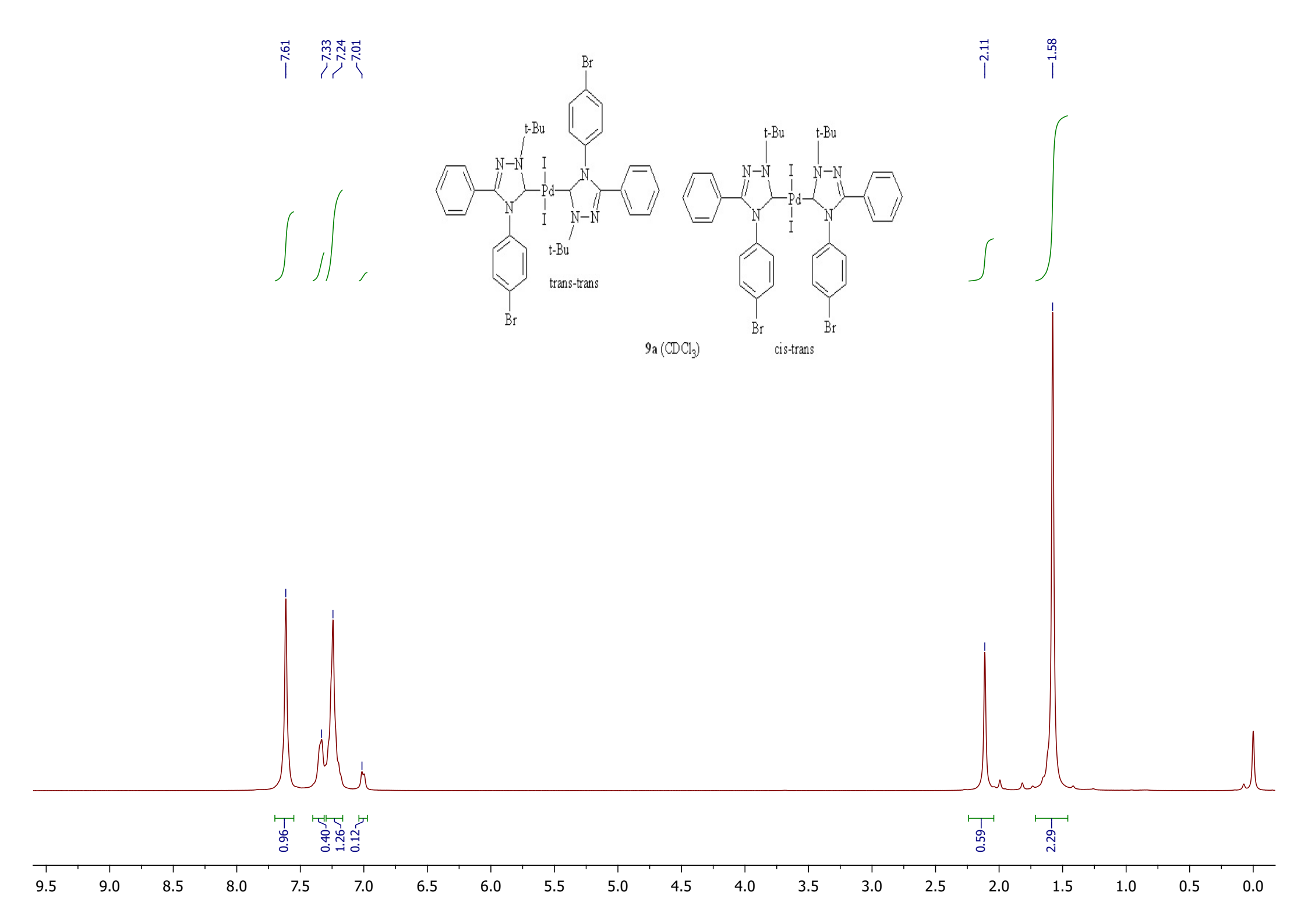
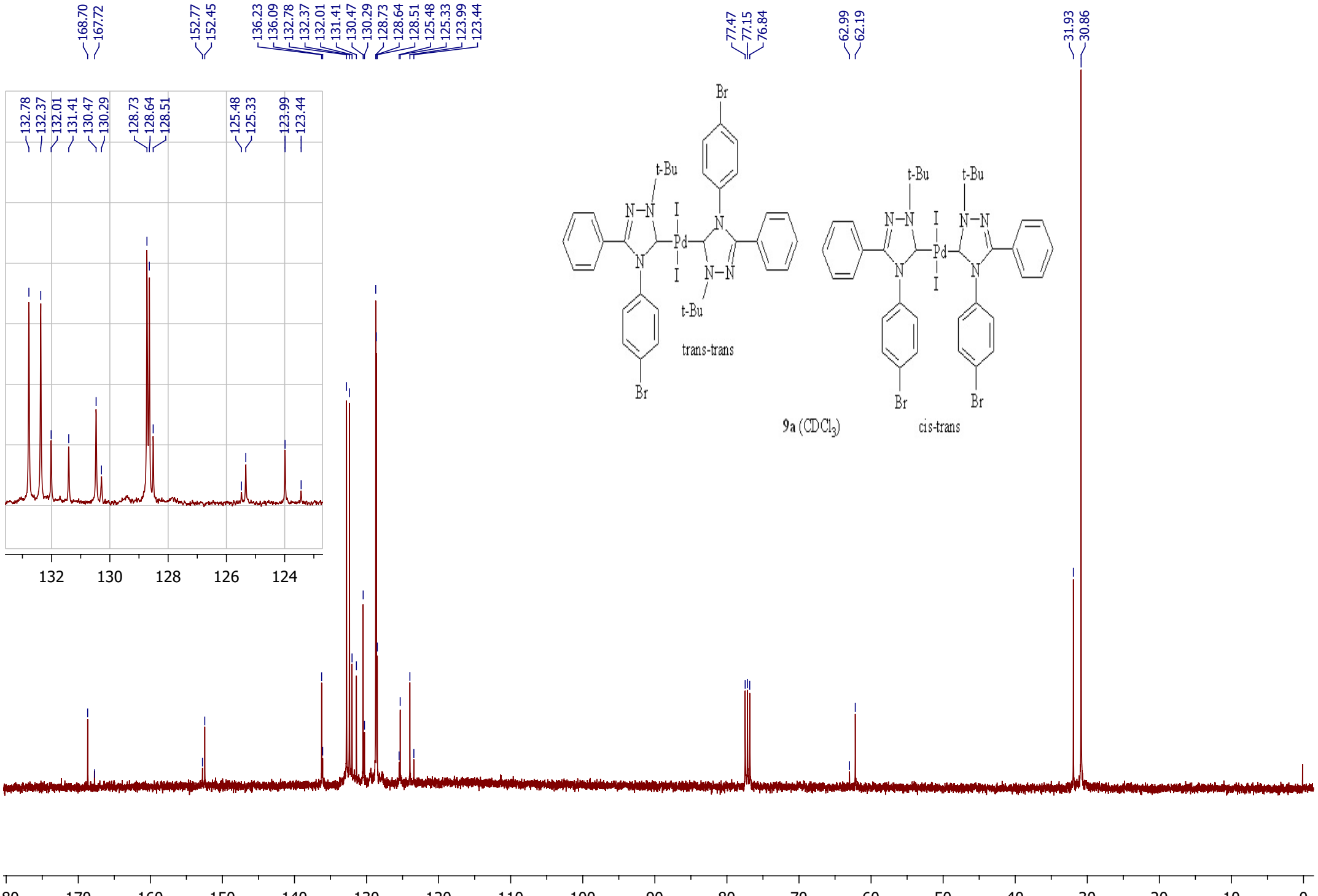
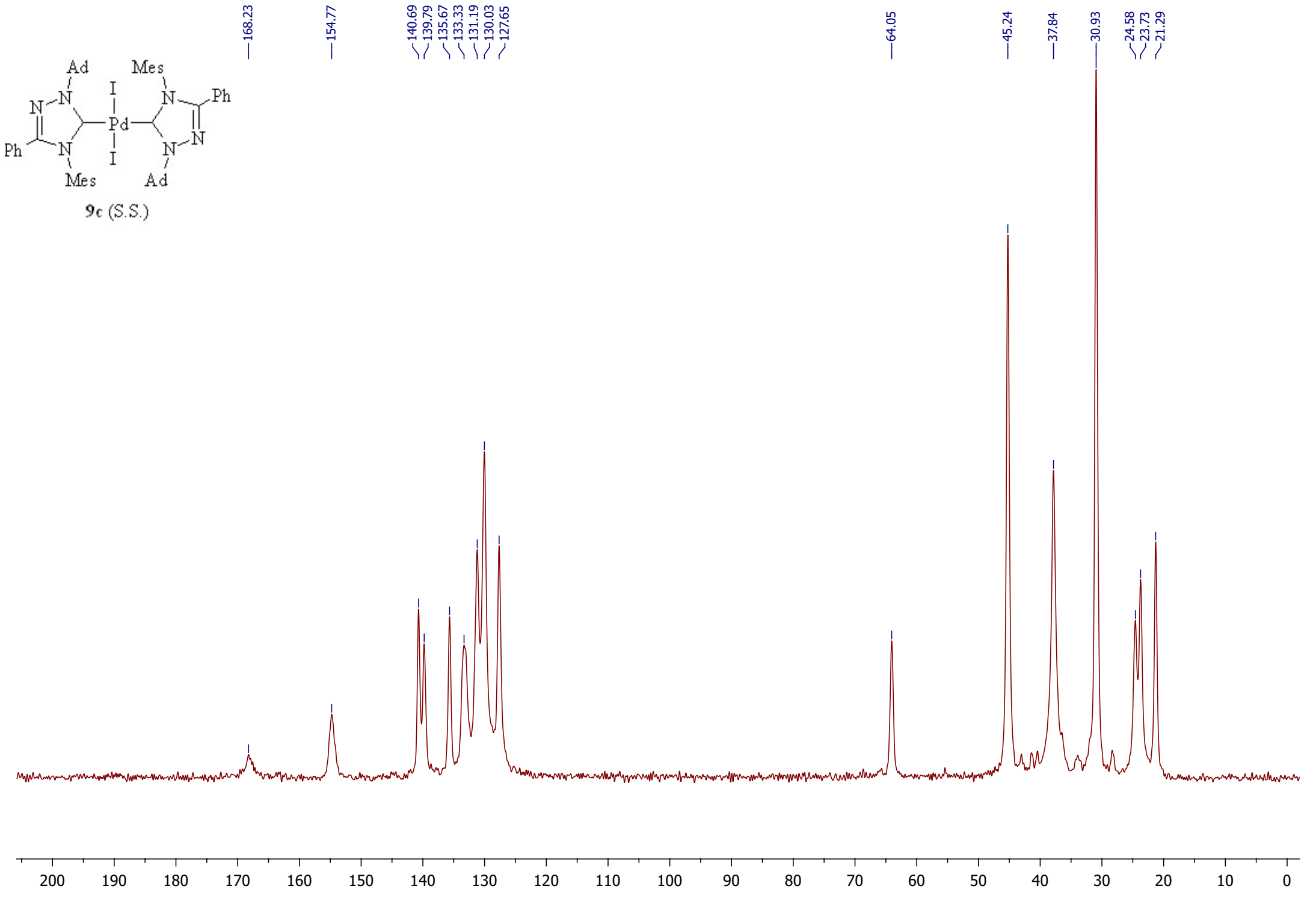
44.14
36.60
30.15
28.90
24.54
22.47
H
H
H
N—N
N
i-Pr
i-Pr
8d (C6D6)
130
129
128
127
126
125
124
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

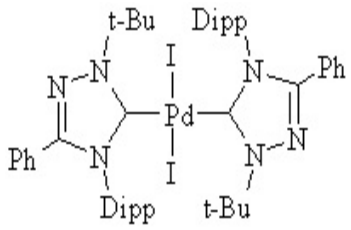

Br
t-Bu
N–N
Cl
Pd
Cl
N
N
N–N
t-Bu
Br
9a (CDCl3)
7.69
7.53
7.26
1.65
1.00
1.00
2.62
4.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.30
151.82
136.34
132.90
131.55
130.34
128.64
128.56
125.11
123.97
76.85
61.92
30.59
Br
t-Bu
N–N
Cl
Pd
Cl
N
N
N–N
t-Bu
Br
9a (CDCl3)
133
131
129
127
125
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.61
7.33
7.24
7.01
2.11
1.58
t-Bu
t-Bu
Br
Br
trans-trans
t-Bu
t-Bu
Br
Br
cis-trans
9a (CDCl3)
0.96
0.40
1.26
0.12
0.59
2.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

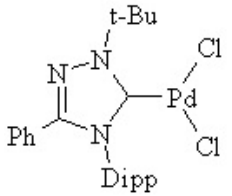

168.70
167.72
152.77
152.45
136.23
136.09
132.78
132.37
132.01
131.41
130.47
130.29
128.73
128.64
128.51
125.48
125.33
123.99
123.44
77.47
77.15
76.84
62.99
62.19
31.93
30.86
t-Bu
t-Bu
trans-trans
t-Bu
t-Bu
cis-trans
9a (CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
132
130
128
126
124


168.23
154.77
140.69
139.79
135.67
133.33
131.19
130.03
127.65
64.05
45.24
37.84
30.93
24.58
23.73
21.29
Ad
Mes
I
N
N
Ph
N
Pd
N
Ph
N
I
N
Mes
Ad
9c (S.S.)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


t-Bu
Dipp
N
N
I
Pd
I
N
N
Ph
Ph
N
N
Dipp
t-Bu

9d (S.S.)

171.87
154.87
147.44
146.74
133.98
132.83
132.07
130.05
128.91
127.15
126.43
64.29
48.07
47.36
32.37
31.64
29.79
27.80
27.06
25.49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



10a ($CDCl_3$)

7.71 7.69 7.40 7.38 7.36 7.35 7.30 7.26 7.18 7.16

2.67 2.61 2.51 2.50 2.35 2.29 2.18 2.13

1.57 1.53 1.38 1.31 1.16

0.70 0.63 0.62 0.58 0.54

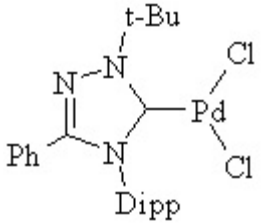
0.96 2.99 4.06

1.00 1.02 5.71 3.40

1.37 1.22 2.09 1.80

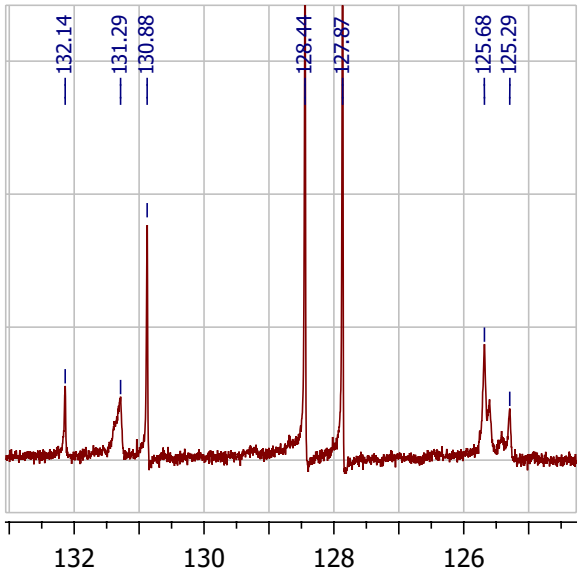
1.12 2.01 2.83

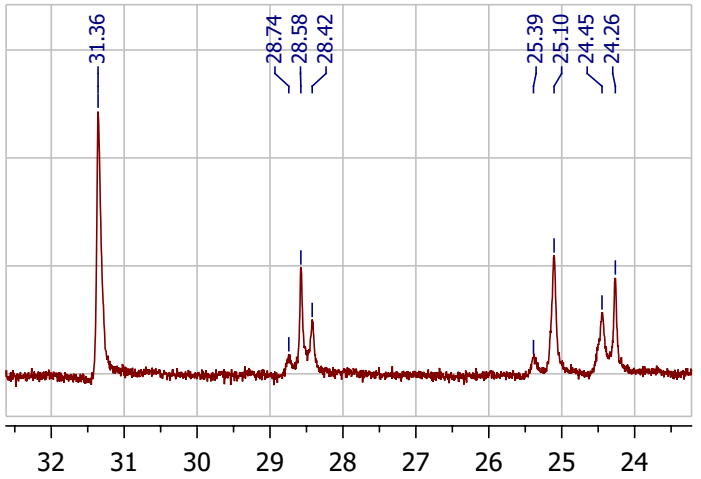
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



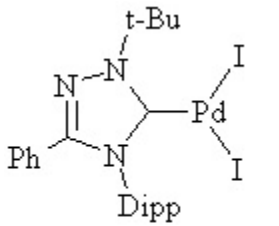
10a ($CDCl_3$)

153.28
149.33
147.17
146.75
132.14
131.29
130.88
128.44
127.87
125.68
125.29
77.34
77.02
76.71
64.26
31.36
28.74
28.58
28.42
25.39
25.10
24.45
24.26



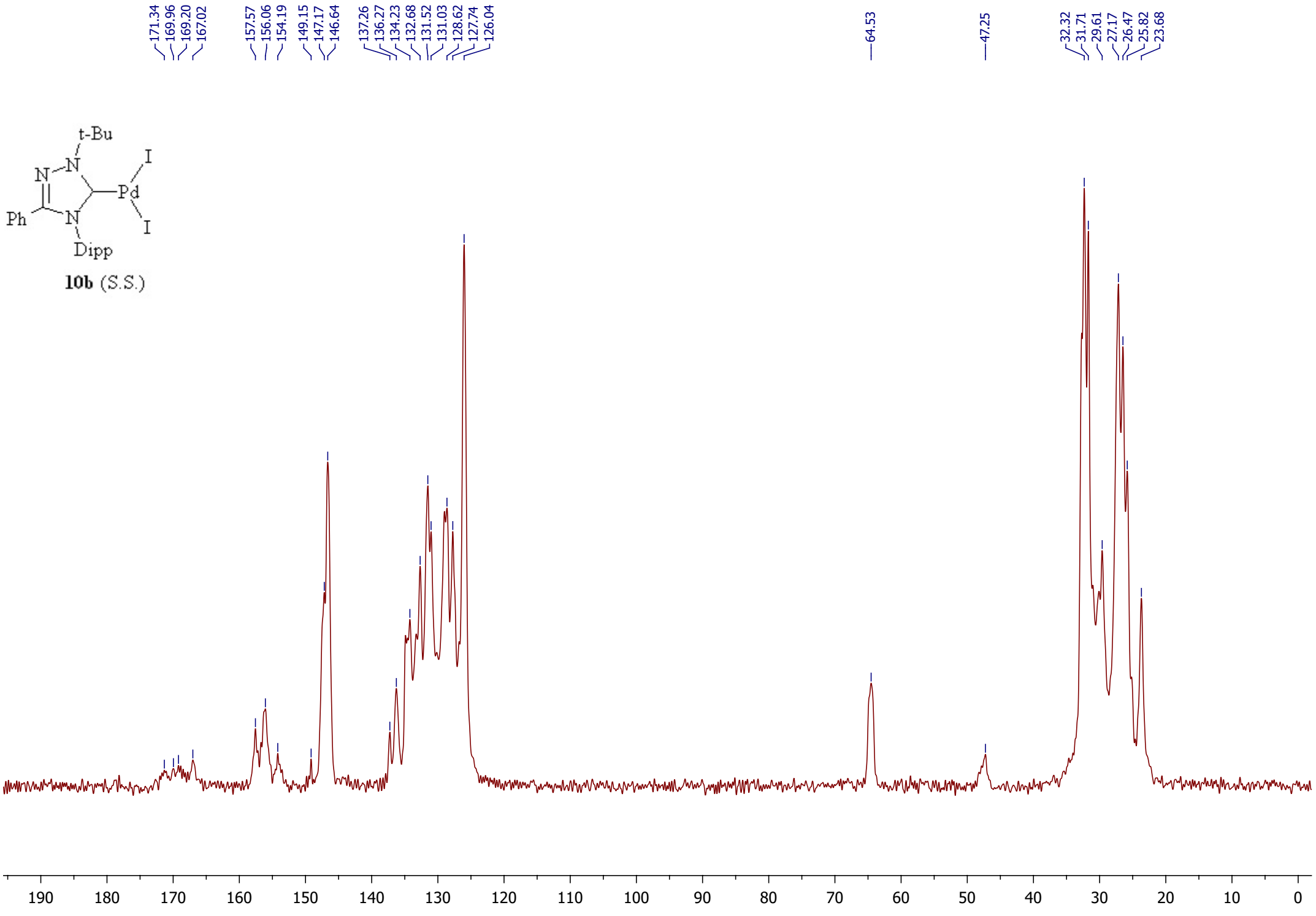


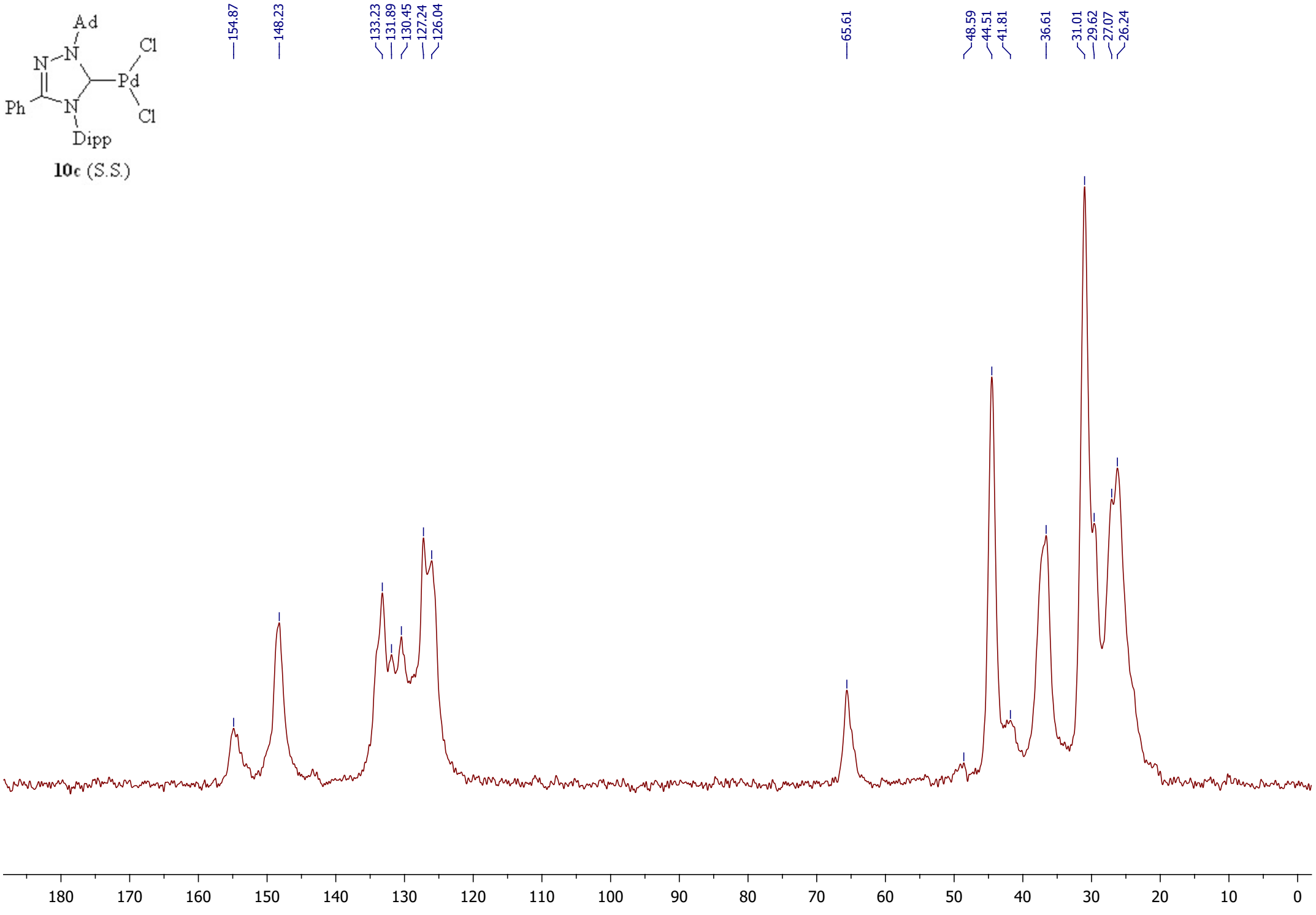
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

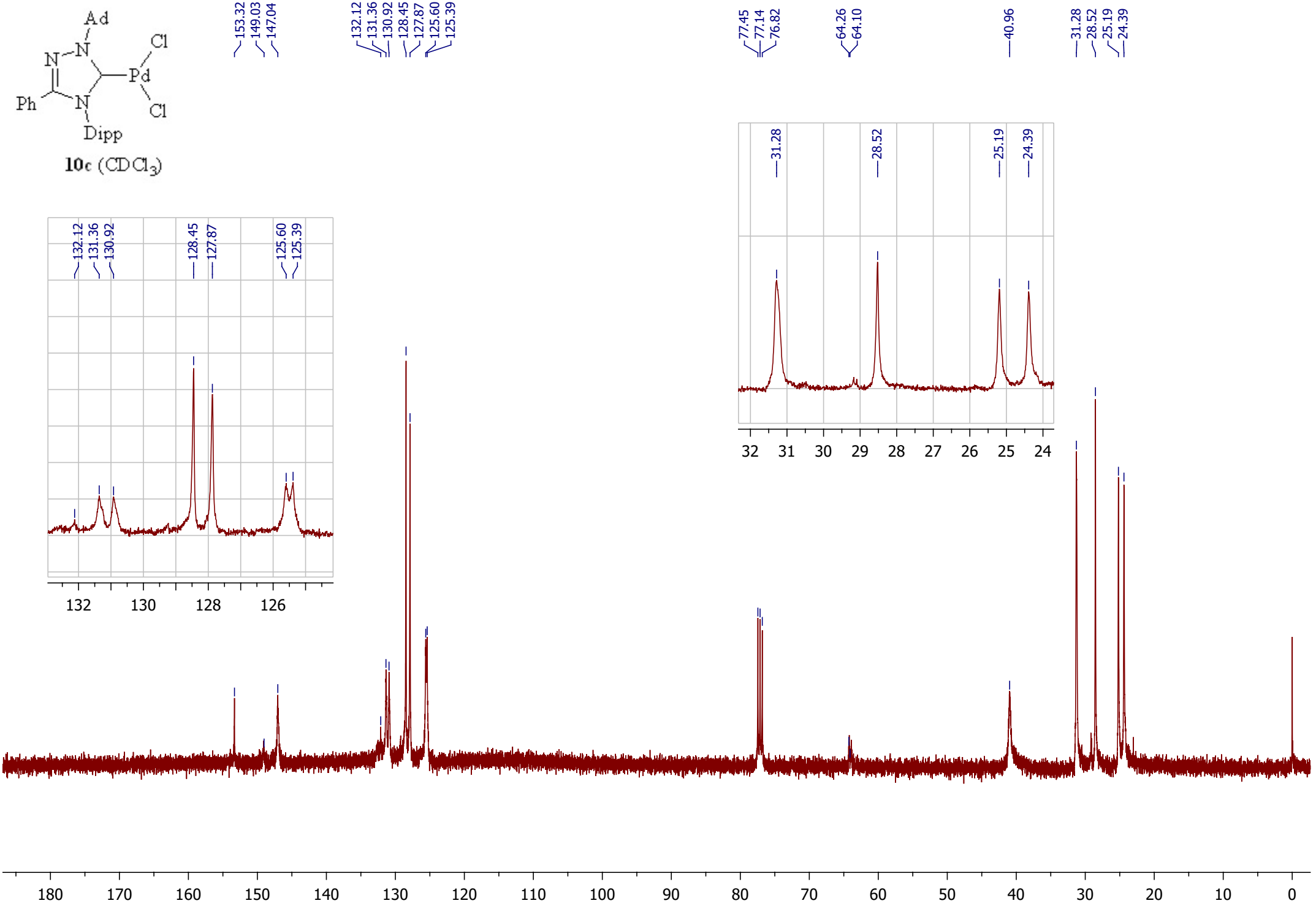

t-Bu
N
N
I
Pd
Ph
N
I
Dipp

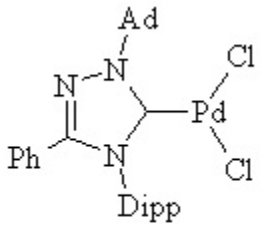
10b (DMSO-d_6)

7.60
7.40
7.38
7.31
7.29
7.20
7.18
4.11
3.32
2.95
2.93
2.48
2.09
1.76
1.57
1.52
1.37
1.35
1.25
0.84
0.83
0.63
0.61
1.11
1.61
0.48
5.01
4.35
3.74
1.00
3.28
14.75
0.41
2.54
10.47
5.61
4.46
9.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.34
169.96
169.20
167.02
157.57
156.06
154.19
149.15
147.17
146.64
137.26
136.27
134.23
132.68
131.52
131.03
128.62
127.74
126.04
64.53
47.25
32.32
31.71
29.61
27.17
26.47
25.82
23.68
t-Bu
N
N
Pd
I
I
Ph
N
Dipp
10b (S.S.)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

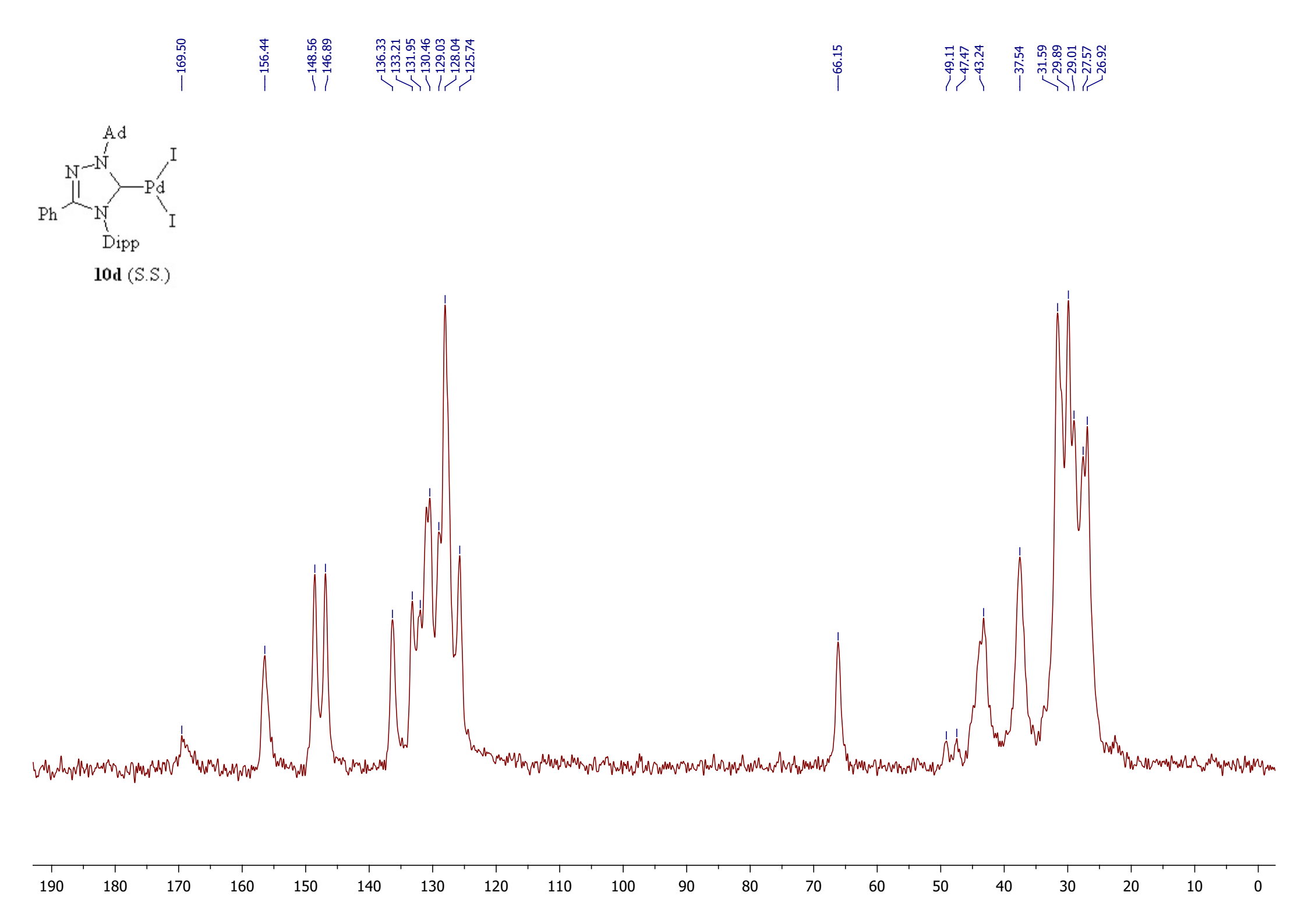

Ad
N
N
Cl
Pd
Cl
Ph
N
Dipp
10c (S.S.)
154.87
148.23
133.23
131.89
130.45
127.24
126.04
65.61
48.59
44.51
41.81
36.61
31.01
29.62
27.07
26.24
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ad
N
N
Cl
Pd
Ph
N
Cl
Dipp
10c (CDCl3)
153.32
149.03
147.04
132.12
131.36
130.92
128.45
127.87
125.60
125.39
77.45
77.14
76.82
64.26
64.10
40.96
31.28
28.52
25.19
24.39
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
32
31
30
29
28
27
26
25
24
132
130
128
126


Ad
N
N
Cl
Pd
Ph
N
Cl
Dipp

10c ($CDCl_3$)

7.69
7.59
7.37
7.31
7.19
2.62
2.25
1.38
0.65
0.00
0.16
0.46
0.59
1.62
1.68
1.00
0.97
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


169.50
156.44
148.56
146.89
136.33
133.21
131.95
130.46
129.03
128.04
125.74
66.15
49.11
47.47
43.24
37.54
31.59
29.89
29.01
27.57
26.92
Ad
N
N
I
Pd
Ph
N
I
Dipp
10d (S.S.)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0