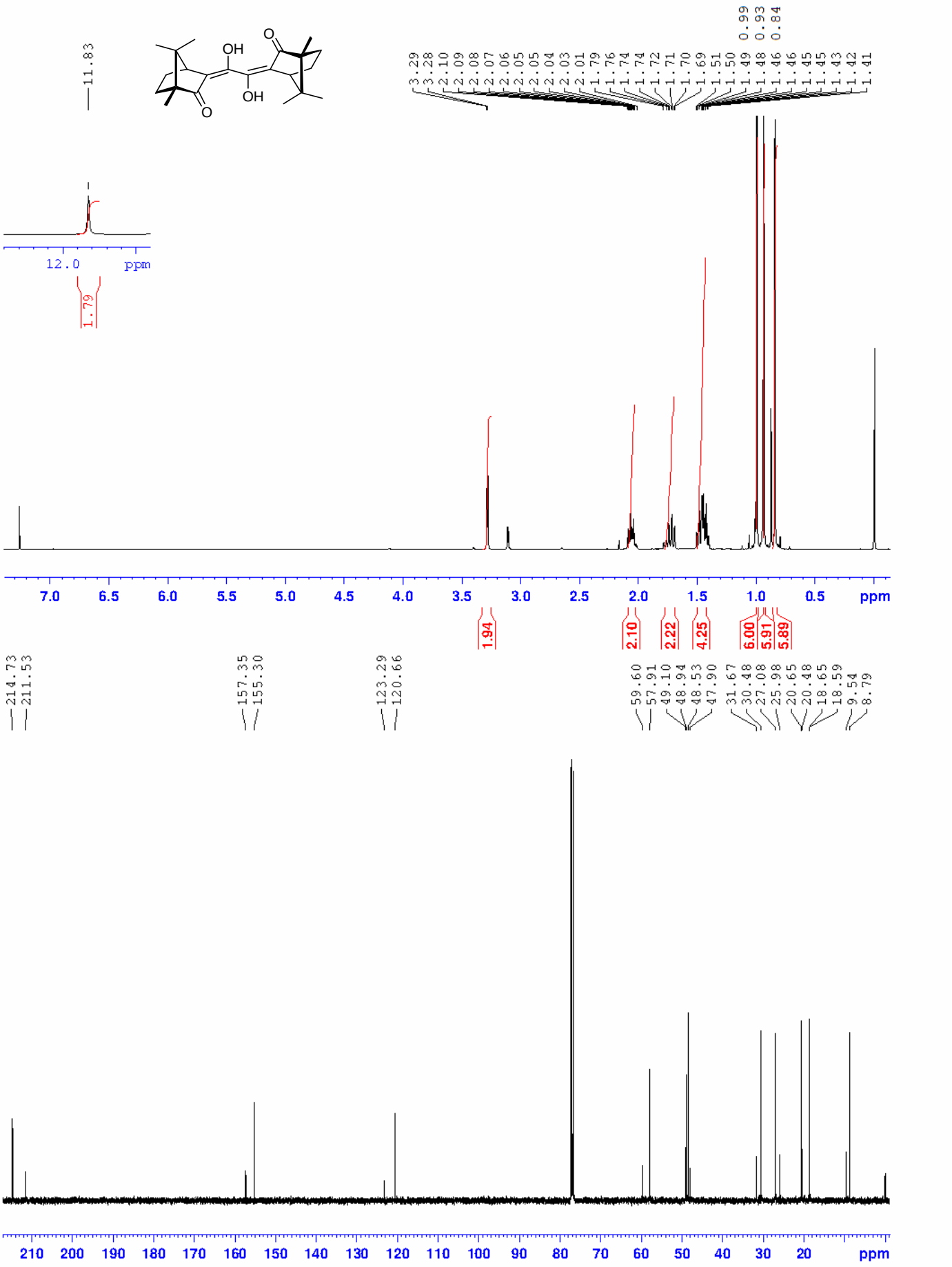
Eur. J. Inorg. Chem. **2011** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2011 · ISSN 1434–1948

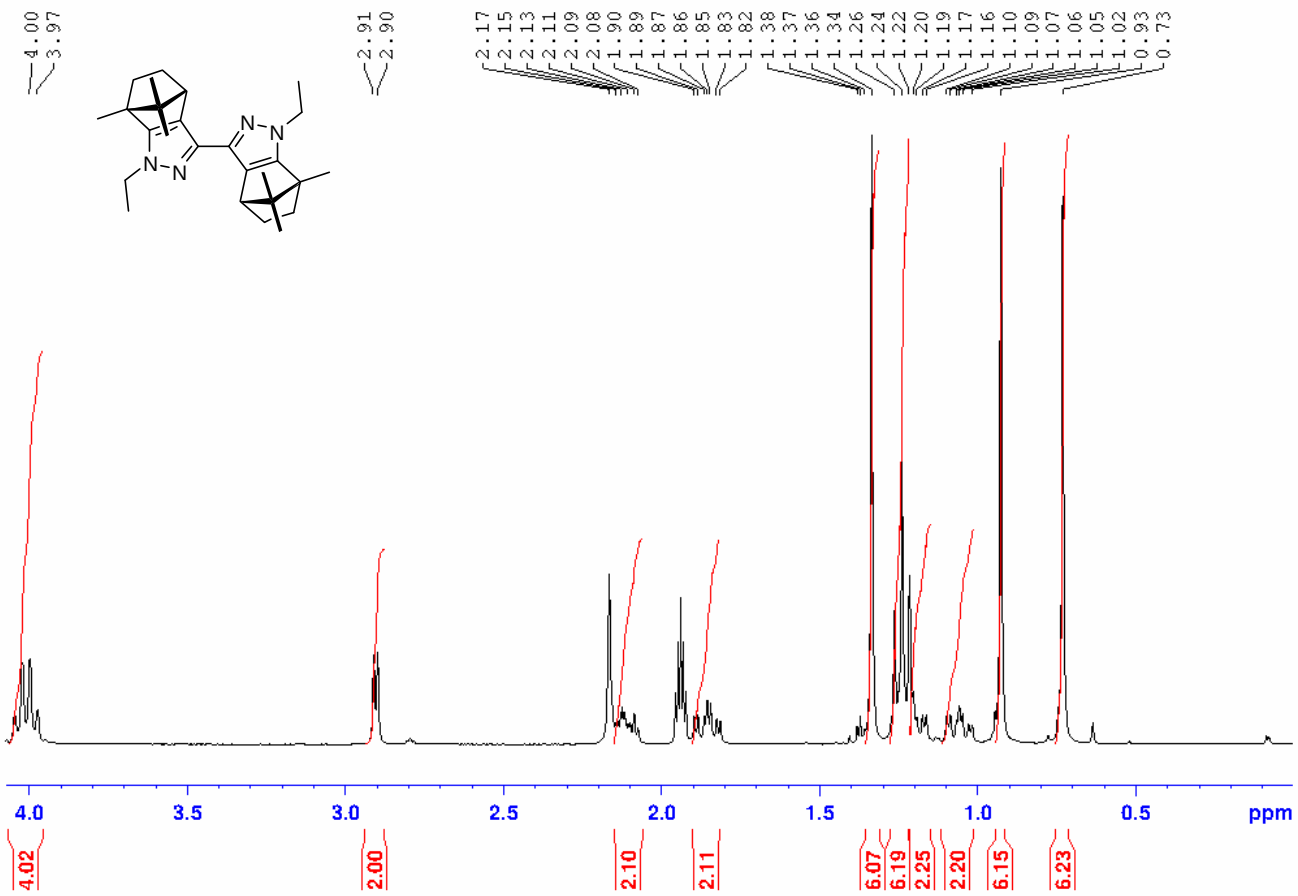
SUPPORTING INFORMATION

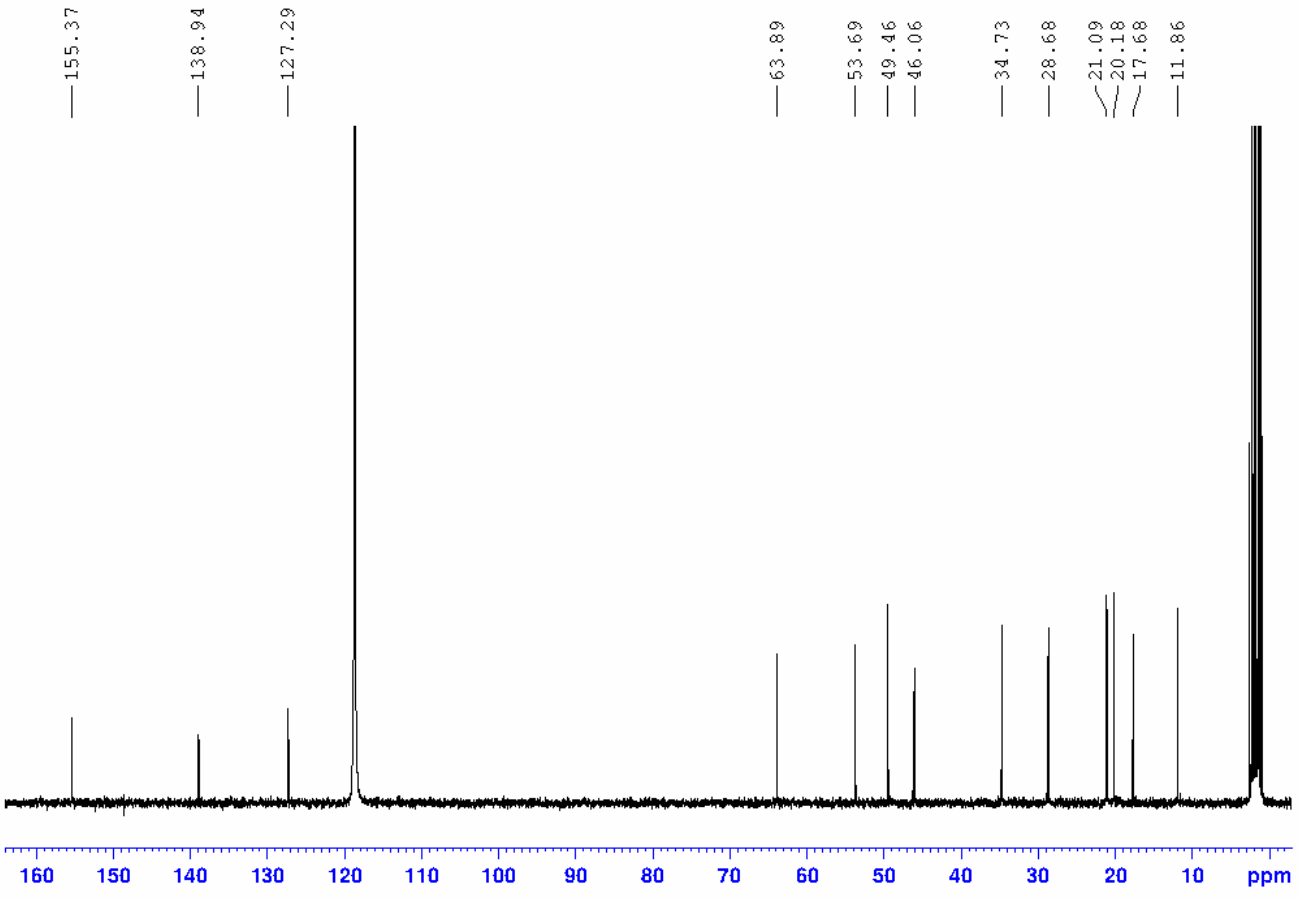
DOI: 10.1002/ejic.201100694
Title: Bulky and Modular 3,3'-Bipyrazoles as Ligands: Synthesis, Characterization, and Catalytic Activity of Pd Complexes
Author(s): Markus J. Spallek, Skrollan Stockinger, Richard Goddard, Frank Rominger, Oliver Trapp*

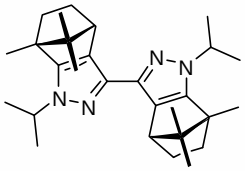
General. All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. Dichloromethane was freshly distilled from calcium hydride under argon atmosphere; THF was freshly distilled from sodium under argon atmosphere. Deuterated solvents were purchased from Euriso-Top. Acetonitrile was dried by a MB SPS-800 with the aid of drying columns. Handling of air- and moisture-sensitive materials was carried out in flame dried flasks under an atmosphere of argon using Schlenk-techniques. Thin layer chromatography (TLC) was performed using Polygram® precoated plastic sheets SIL G/UV254 (SiO_2, 0.20 mm thickness) from Macherey-Nagel. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300 and Bruker ARX-250 spectrometers at RT. Chemical shifts (in ppm) were referenced to residual solvent protons. Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). ^{13}C assignment was achieved via DEPT135 spectra and HSQC experiments. GC-and GC-MS measurements were performed on a Thermo PolarisQ Trace GC-MS, equipped with split injector (250°C), FID (250°C) and a quadrupole ion-trap MS (Thermo, San Jose, CA). MS spectra were recorded on a Finnigan MAT TSQ 700 or a JEOL JMS-700 spectrometer. IR spectra were recorded on a Bruker Vector 22 FT-IR. CD-and UV-Vis spectra were recorded on a JASCO J-810 spectropolarimeter. Crystal structure analysis was accomplished on Bruker Smart CCD and Bruker APEX diffractometers. Melting points were determined on a Büchi melting point apparatus and temperatures were uncorrected. Elemental analysis was performed on an Elementar Vario EL.

^{1}H and ^{13}C NMR spectra of ligands 1 – 3(a–k)

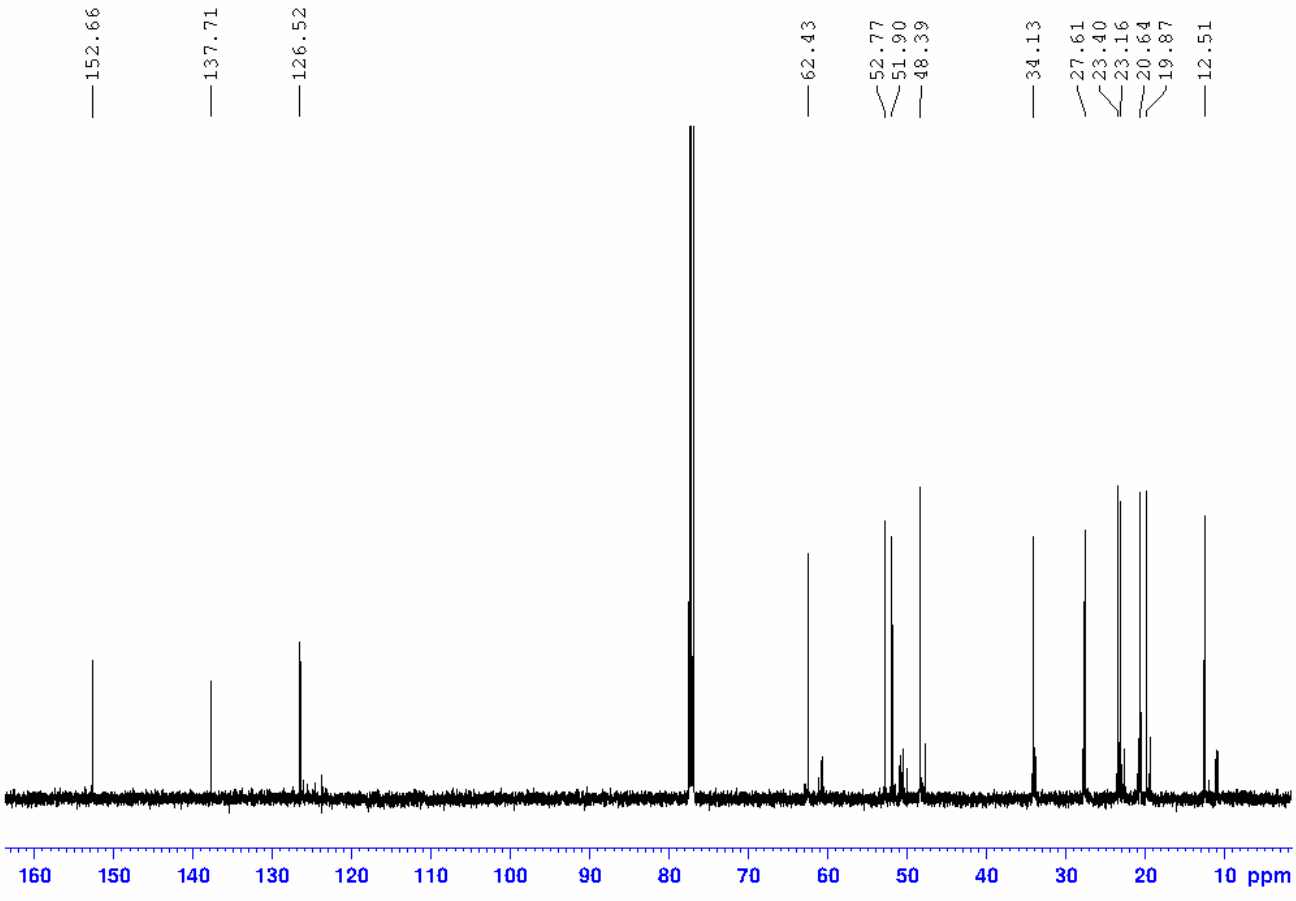


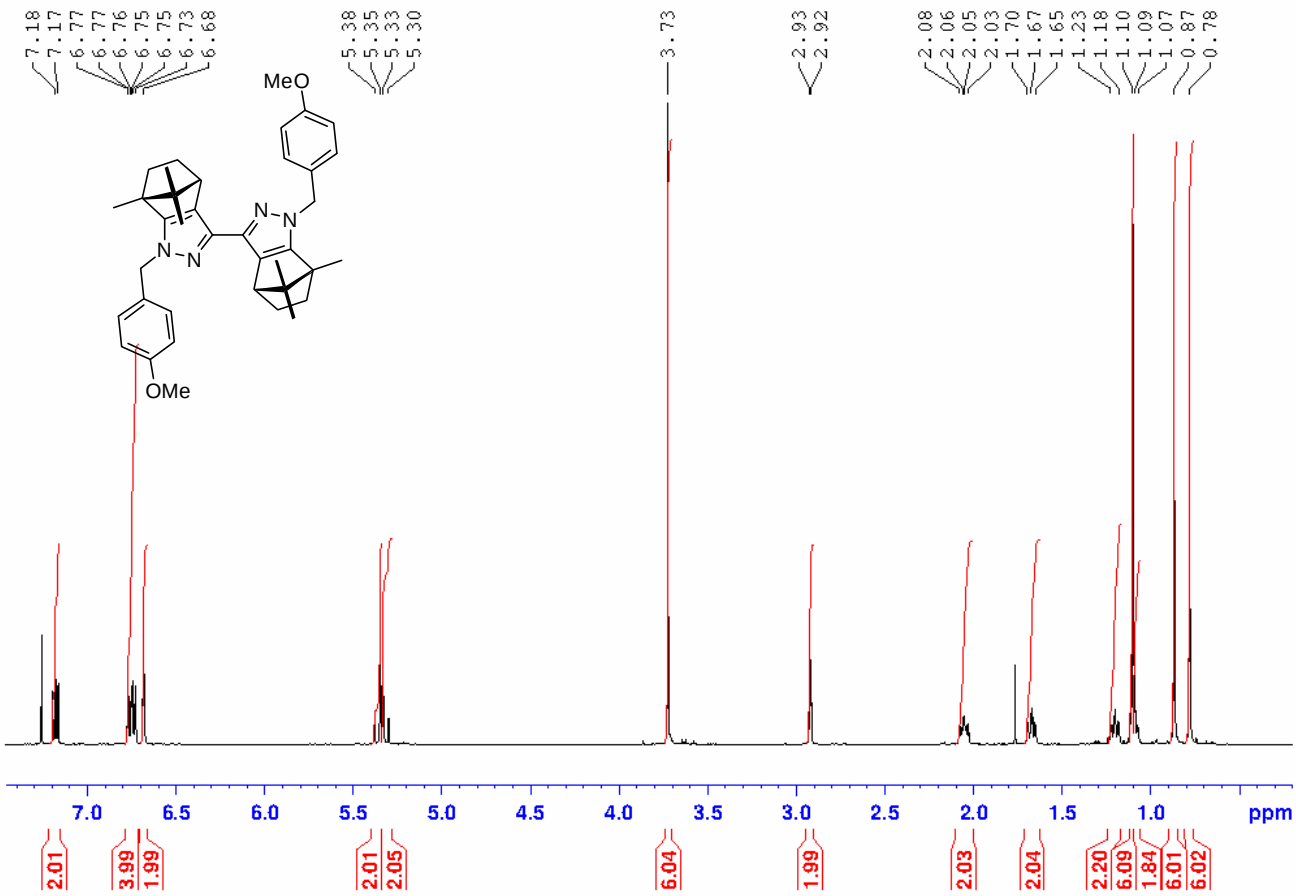

4.00
3.97
2.91
2.90
2.17
2.15
2.13
2.11
2.09
2.08
1.90
1.89
1.87
1.86
1.85
1.83
1.82
1.38
1.37
1.36
1.34
1.26
1.24
1.22
1.20
1.19
1.17
1.16
1.10
1.09
1.07
1.06
1.05
1.02
0.93
0.73
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.02
2.00
2.10
2.11
6.07
6.19
2.25
2.20
6.15
6.23

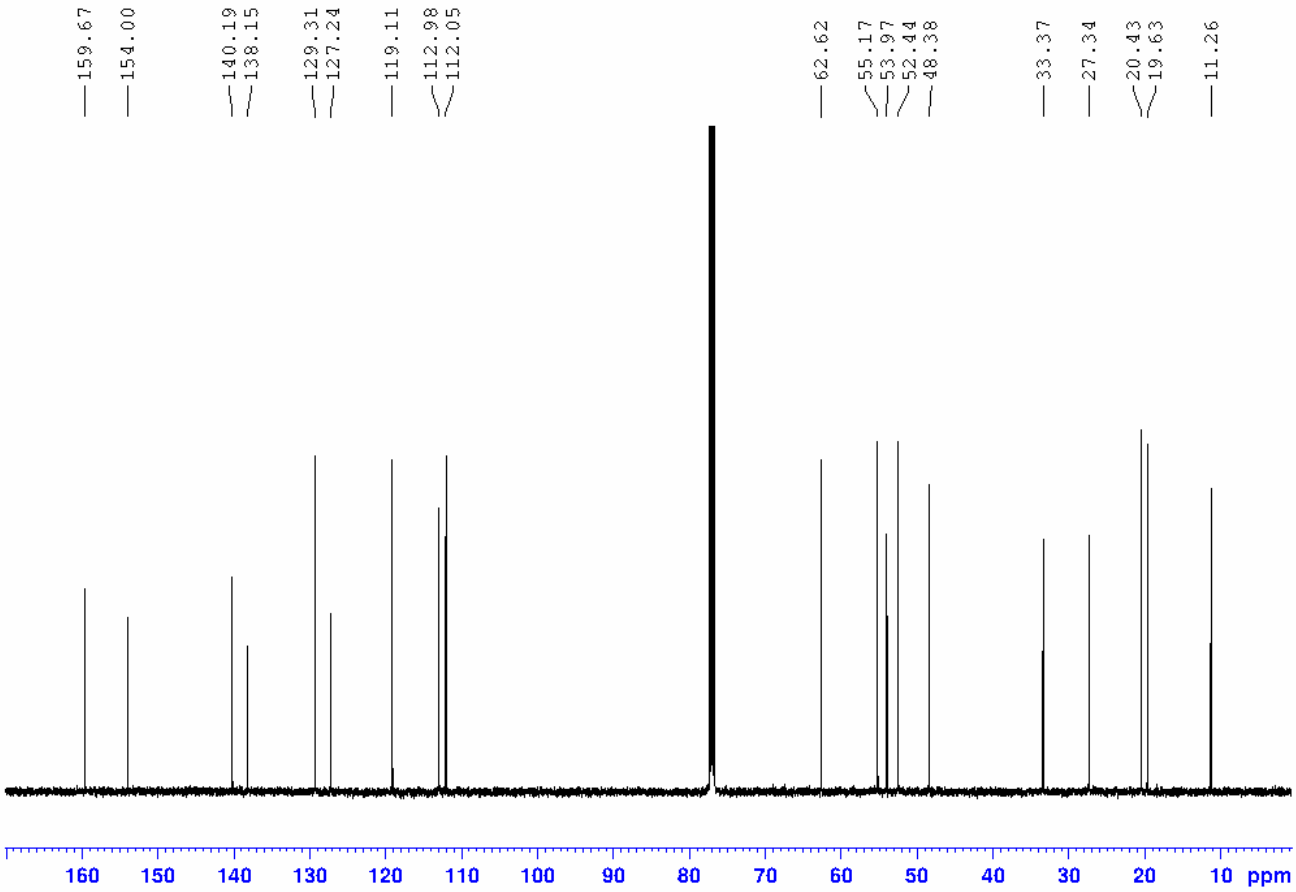

155.37
138.94
127.29
63.89
53.69
49.46
46.06
34.73
28.68
21.09
20.18
17.68
11.86
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

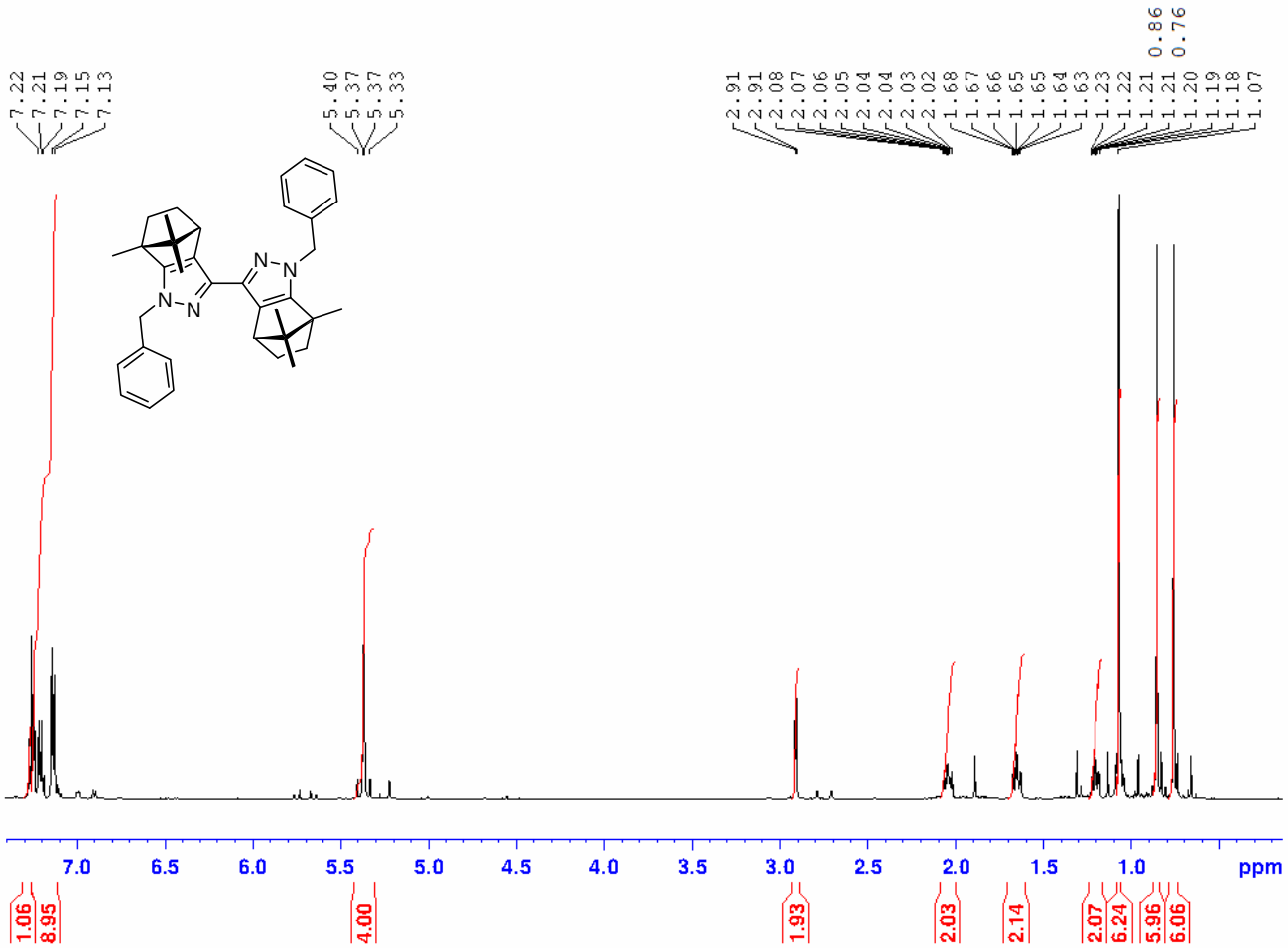


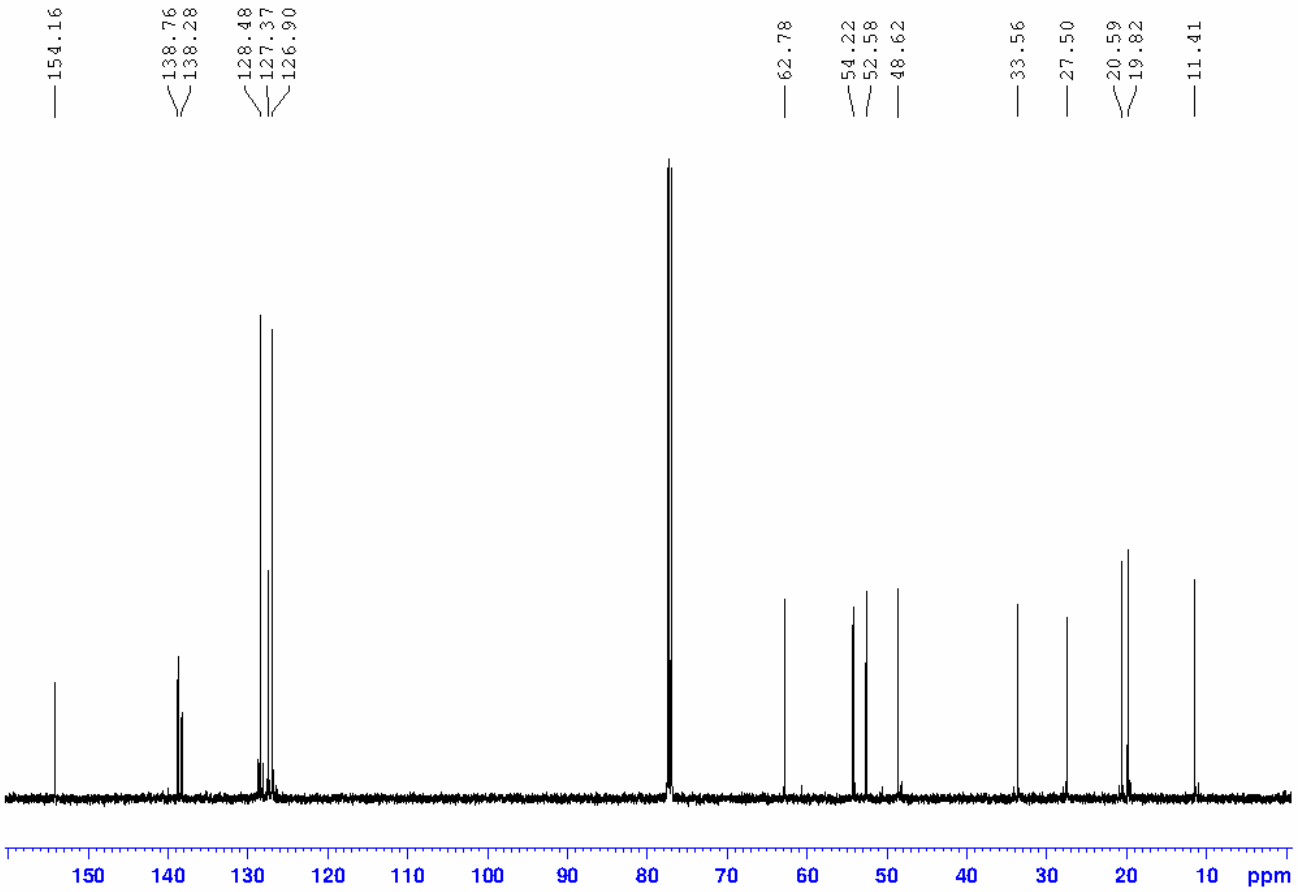
4.53
4.51
4.50
4.49
4.47
4.46
4.44
2.85
2.84
2.14
2.11
2.08
2.06
2.05
2.02
1.89
1.84
1.81
1.79
1.77
1.76
1.74
1.53
1.52
1.50
1.49
1.36
1.32
1.31
0.90
0.78
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
1.91
2.56
2.31
12.23
6.08
2.20
5.92
5.94
2.17

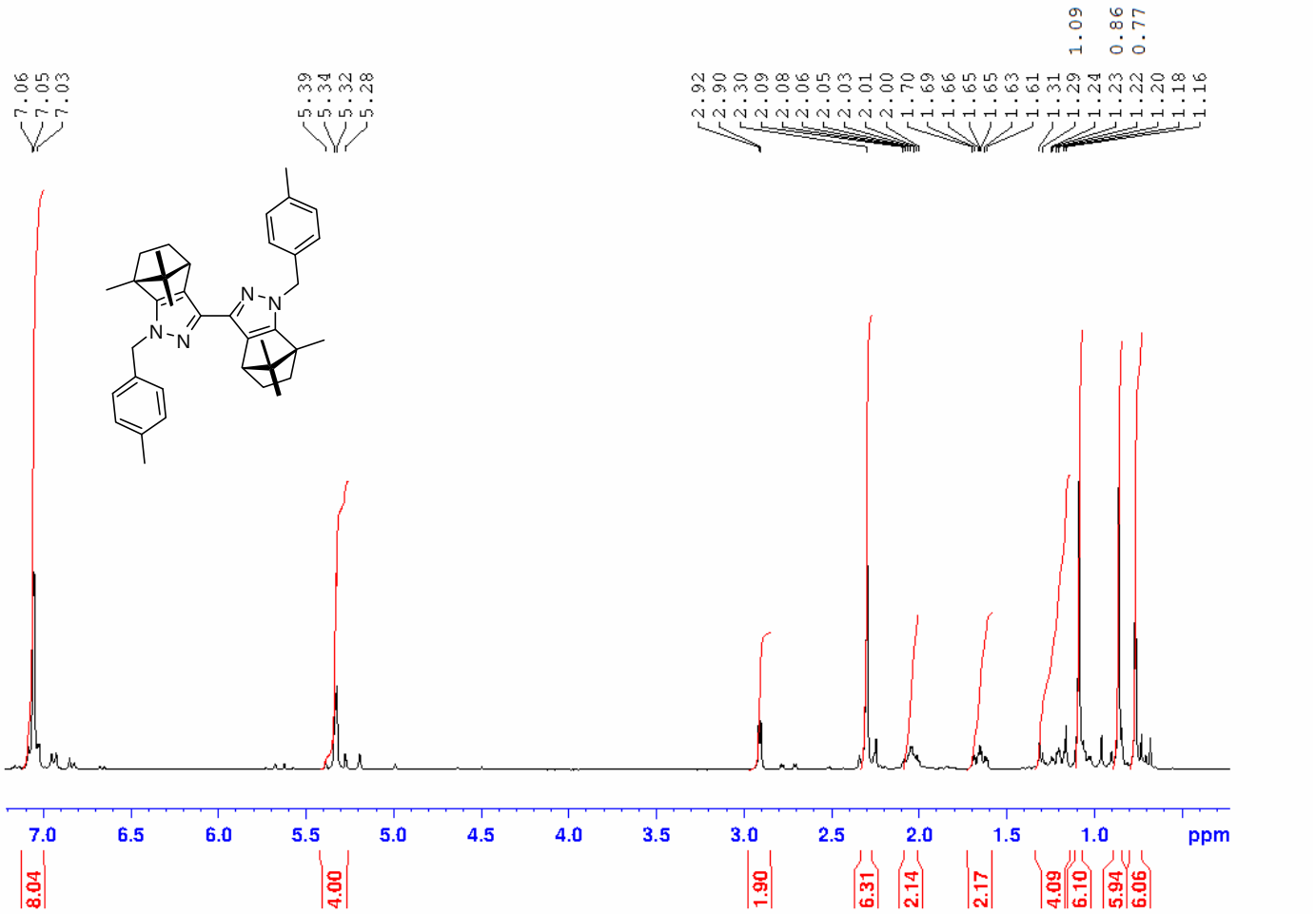

152.66
137.71
126.52
62.43
52.77
51.90
48.39
34.13
27.61
23.40
23.16
20.64
19.87
12.51
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

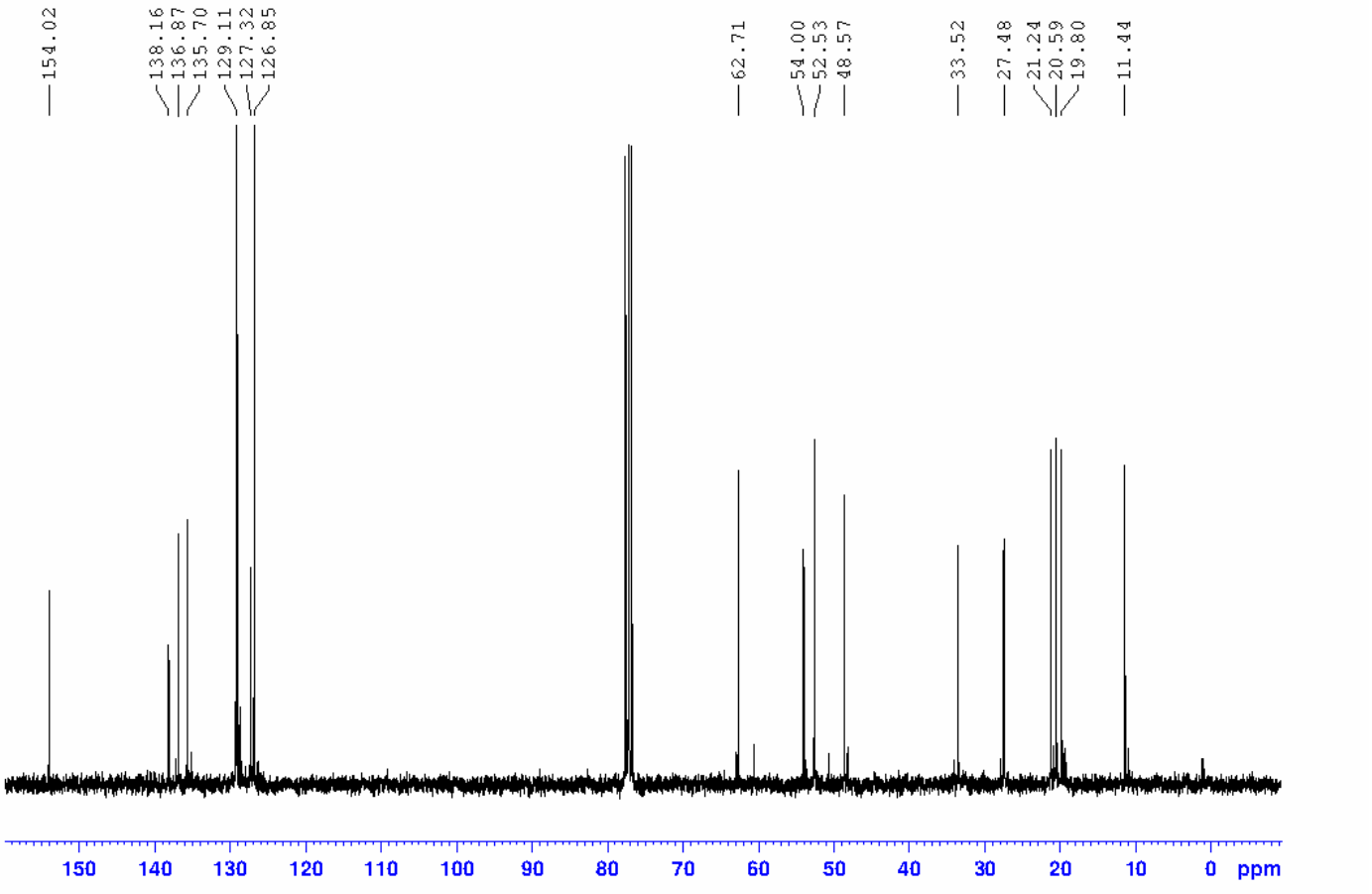

7.18
7.17
6.77
6.77
6.76
6.75
6.75
6.73
6.68
5.38
5.35
5.33
5.30
3.73
2.93
2.92
2.08
2.06
2.05
2.03
1.70
1.67
1.65
1.23
1.18
1.10
1.09
1.07
0.87
0.78
MeO
OMe
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.01
3.99
1.99
2.01
2.05
6.04
1.99
2.03
2.04
2.20
6.09
1.84
6.01
6.02

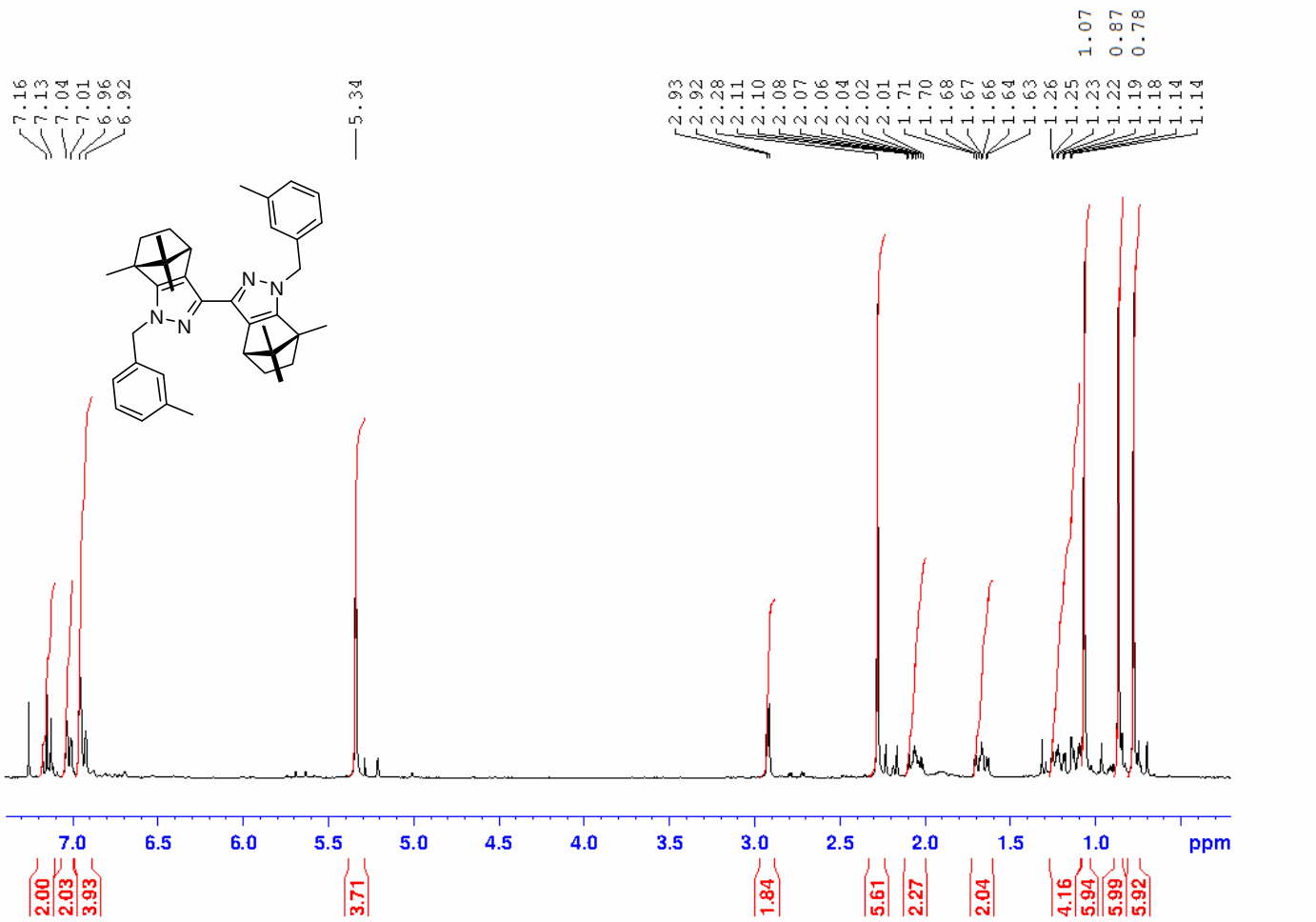

159.67
154.00
140.19
138.15
129.31
127.24
119.11
112.98
112.05
62.62
55.17
53.97
52.44
48.38
33.37
27.34
20.43
19.63
11.26
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

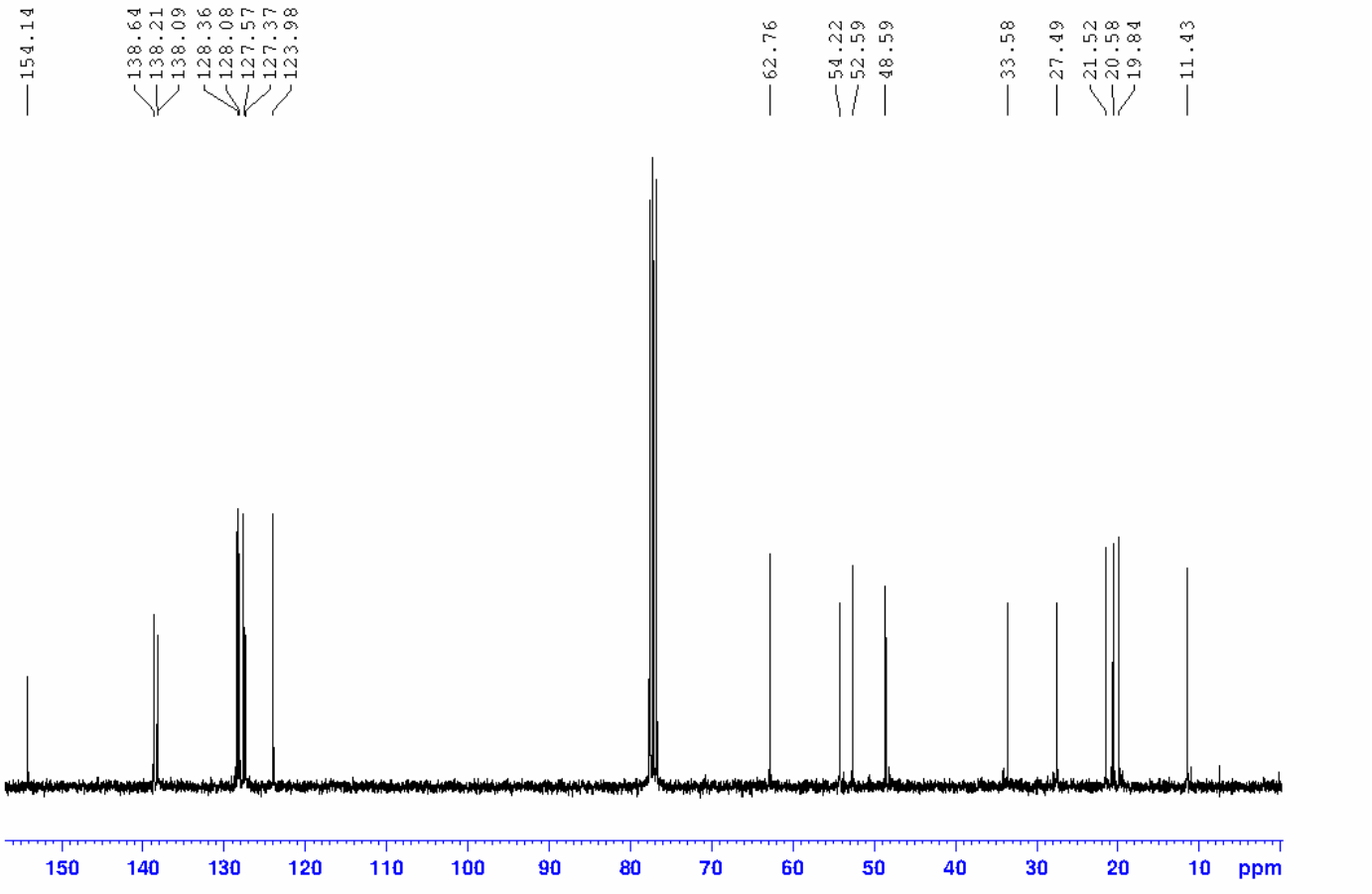

7.22
7.21
7.19
7.15
7.13
5.40
5.37
5.37
5.33
2.91
2.91
2.08
2.07
2.06
2.05
2.04
2.04
2.03
2.02
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.23
1.22
1.21
1.21
1.20
1.19
1.18
1.07
0.86
0.76
N
N
N
N
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.06
8.95
4.00
1.93
2.03
2.14
2.07
6.24
5.96
6.06

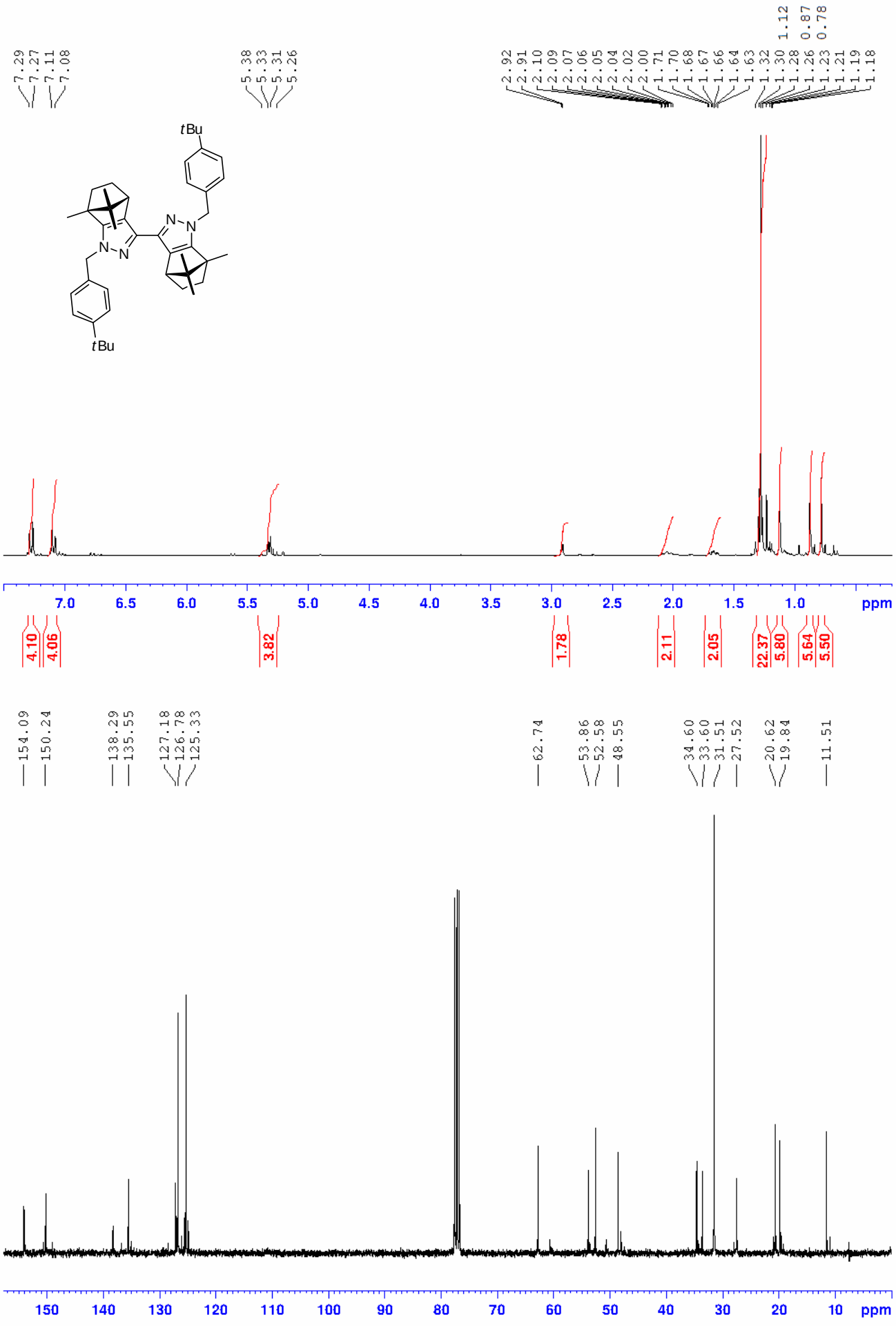

154.16
138.76
138.28
128.48
127.37
126.90
62.78
54.22
52.58
48.62
33.56
27.50
20.59
19.82
11.41
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

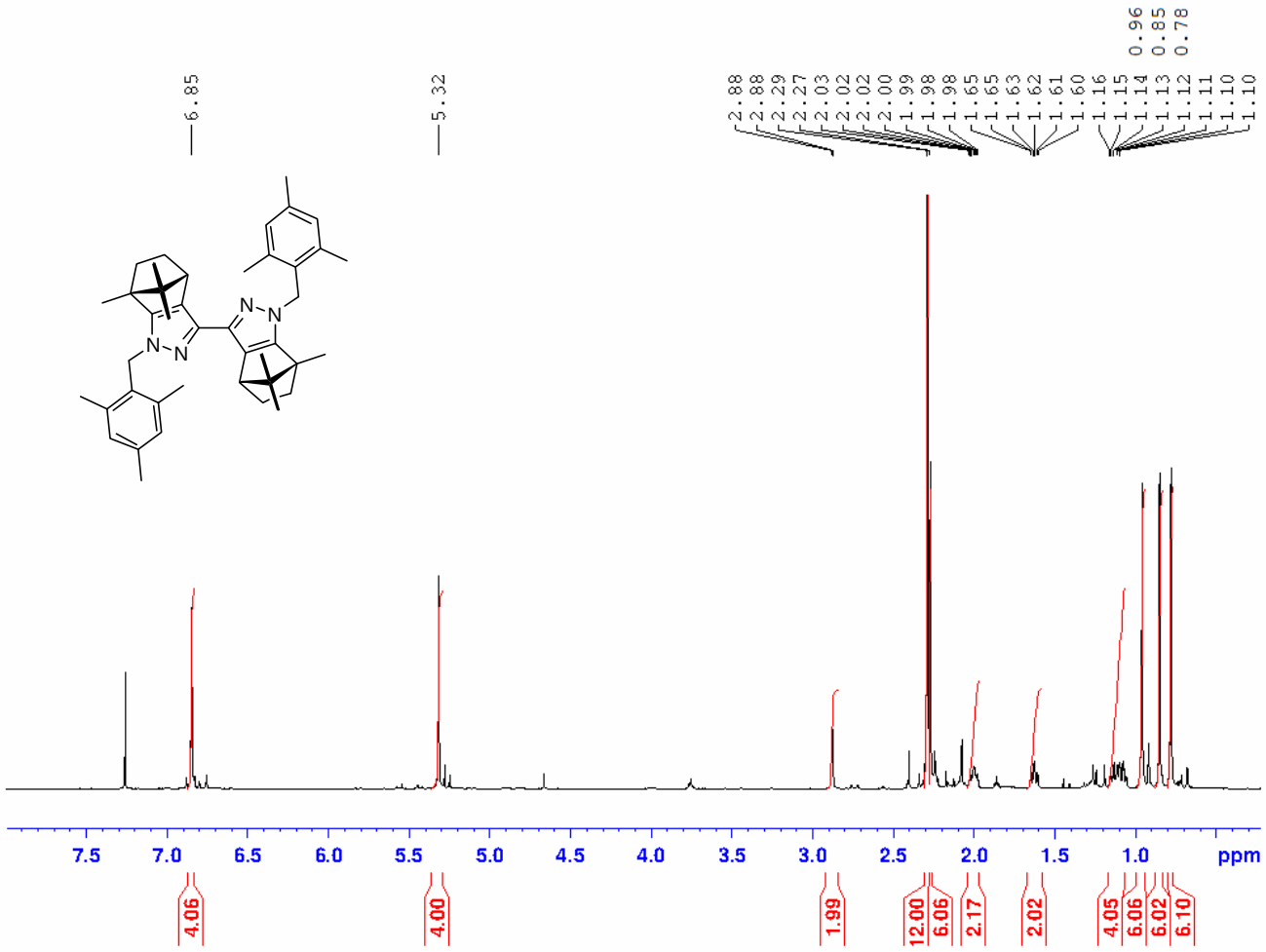

7.06
7.05
7.03
5.39
5.34
5.32
5.28
2.92
2.90
2.30
2.09
2.08
2.06
2.05
2.03
2.01
2.00
1.70
1.69
1.66
1.65
1.65
1.63
1.61
1.31
1.29
1.24
1.23
1.22
1.20
1.18
1.16
1.09
0.86
0.77
N
N
N
N
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
8.04
4.00
1.90
6.31
2.14
2.17
4.09
6.10
5.94
6.06

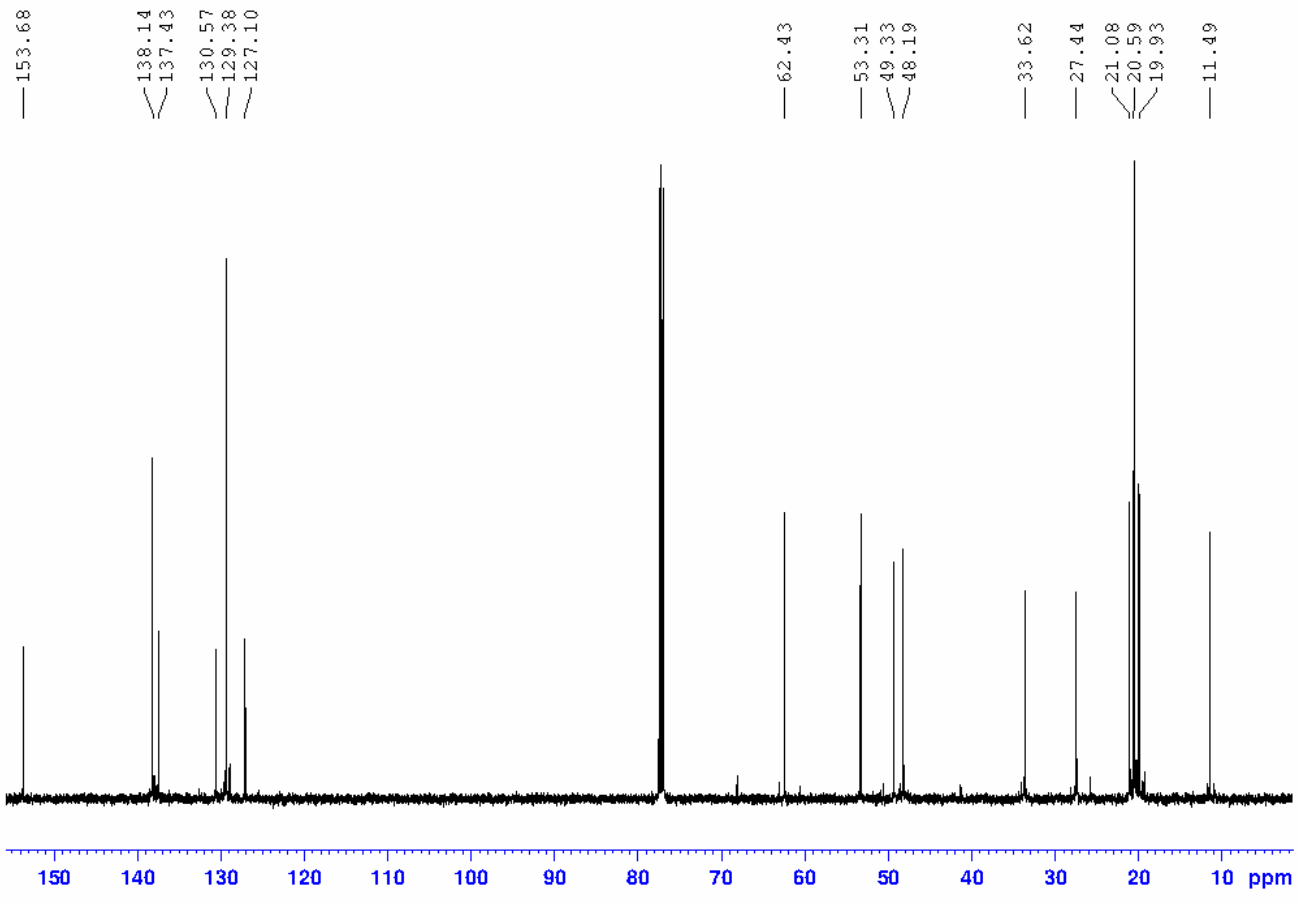

154.02
138.16
136.87
135.70
129.11
127.32
126.85
62.71
54.00
52.53
48.57
33.52
27.48
21.24
20.59
19.80
11.44
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

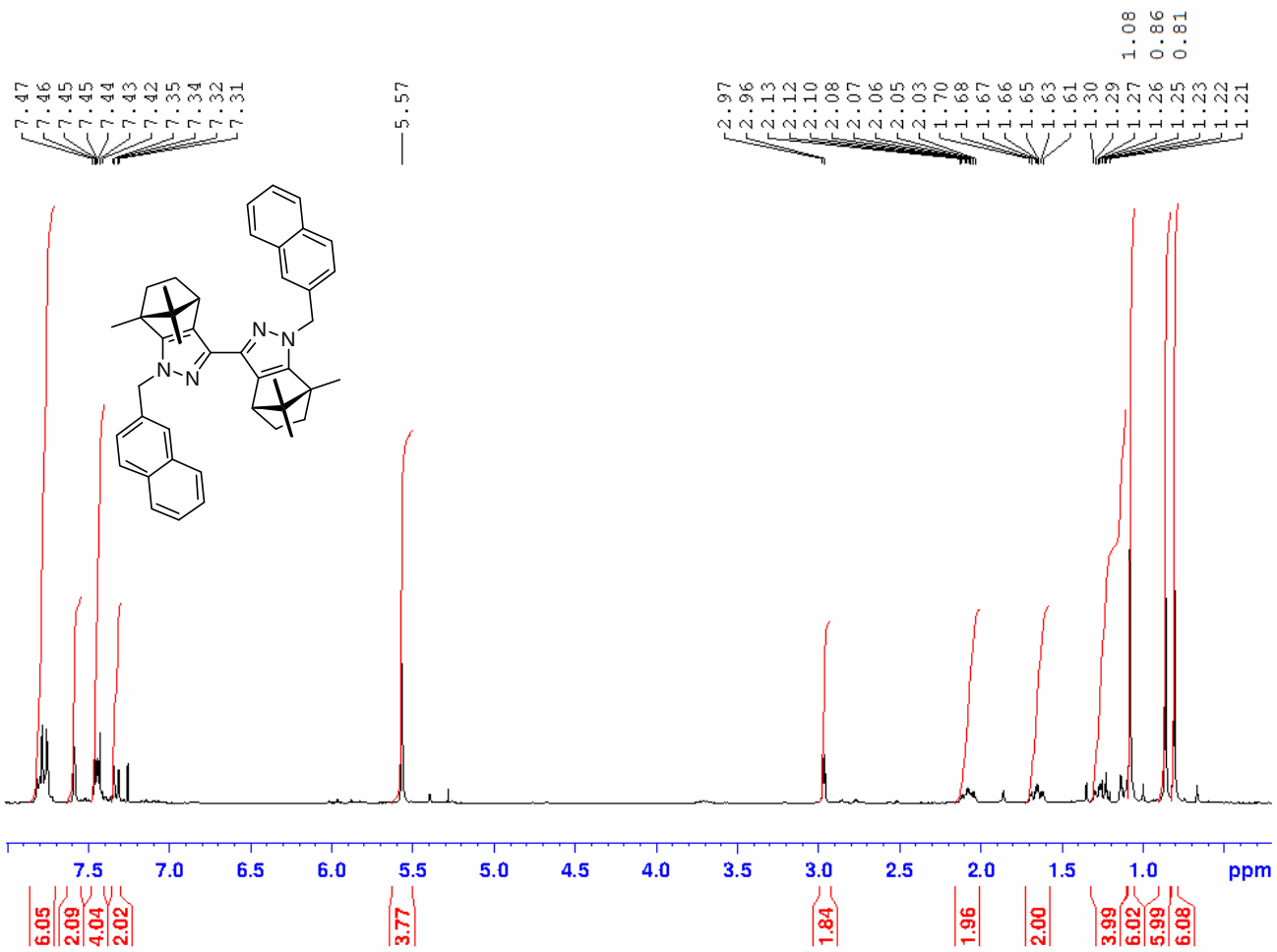

7.16
7.13
7.04
7.01
6.96
6.92
5.34
2.93
2.92
2.28
2.11
2.10
2.08
2.07
2.06
2.04
2.02
2.01
1.71
1.70
1.68
1.67
1.66
1.64
1.63
1.26
1.25
1.23
1.22
1.19
1.18
1.14
1.14
1.07
0.87
0.78
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.03
3.93
3.71
1.84
5.61
2.27
2.04
4.16
5.94
5.99
5.92

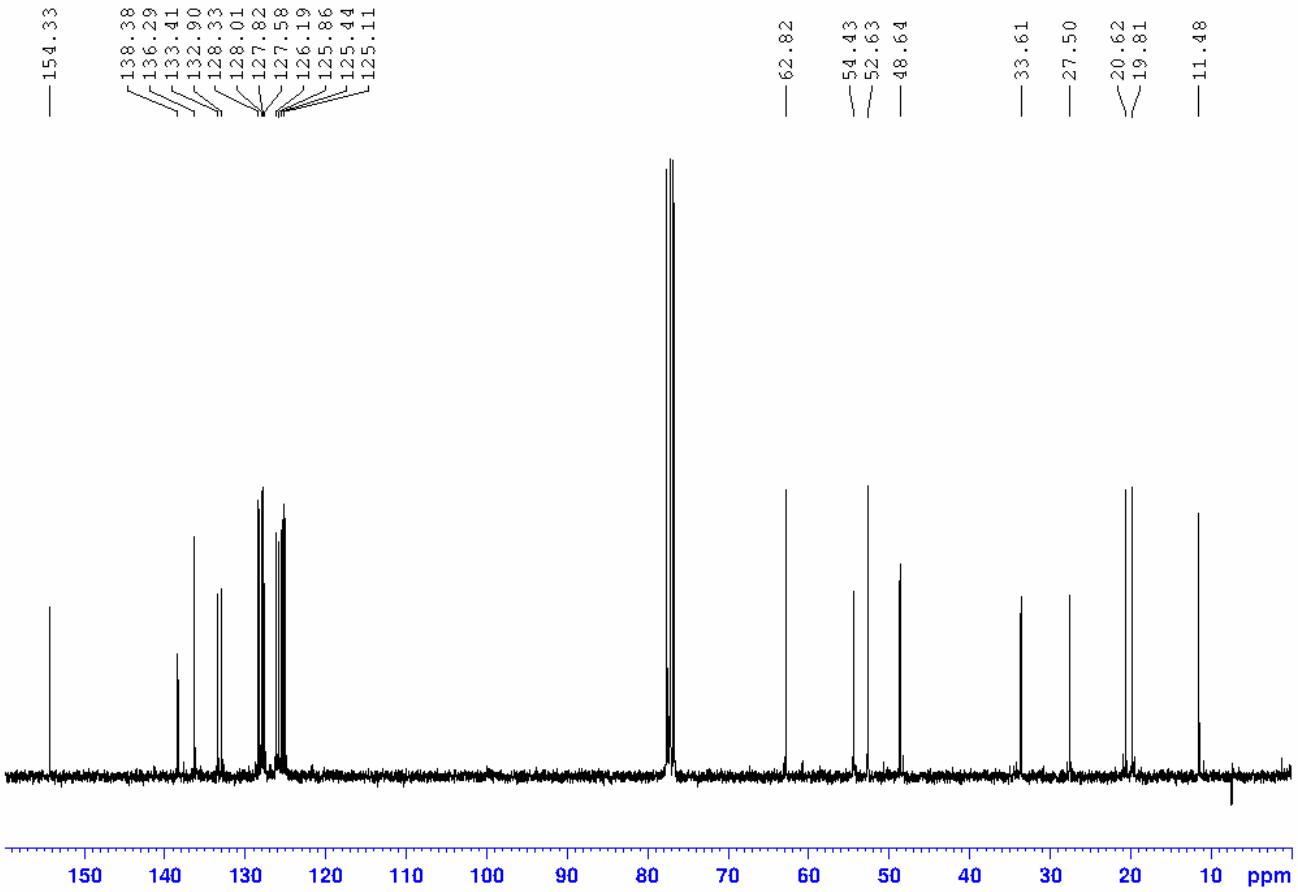

154.14
138.64
138.21
138.09
128.36
128.08
127.57
127.37
123.98
62.76
54.22
52.59
48.59
33.58
27.49
21.52
20.58
19.84
11.43
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

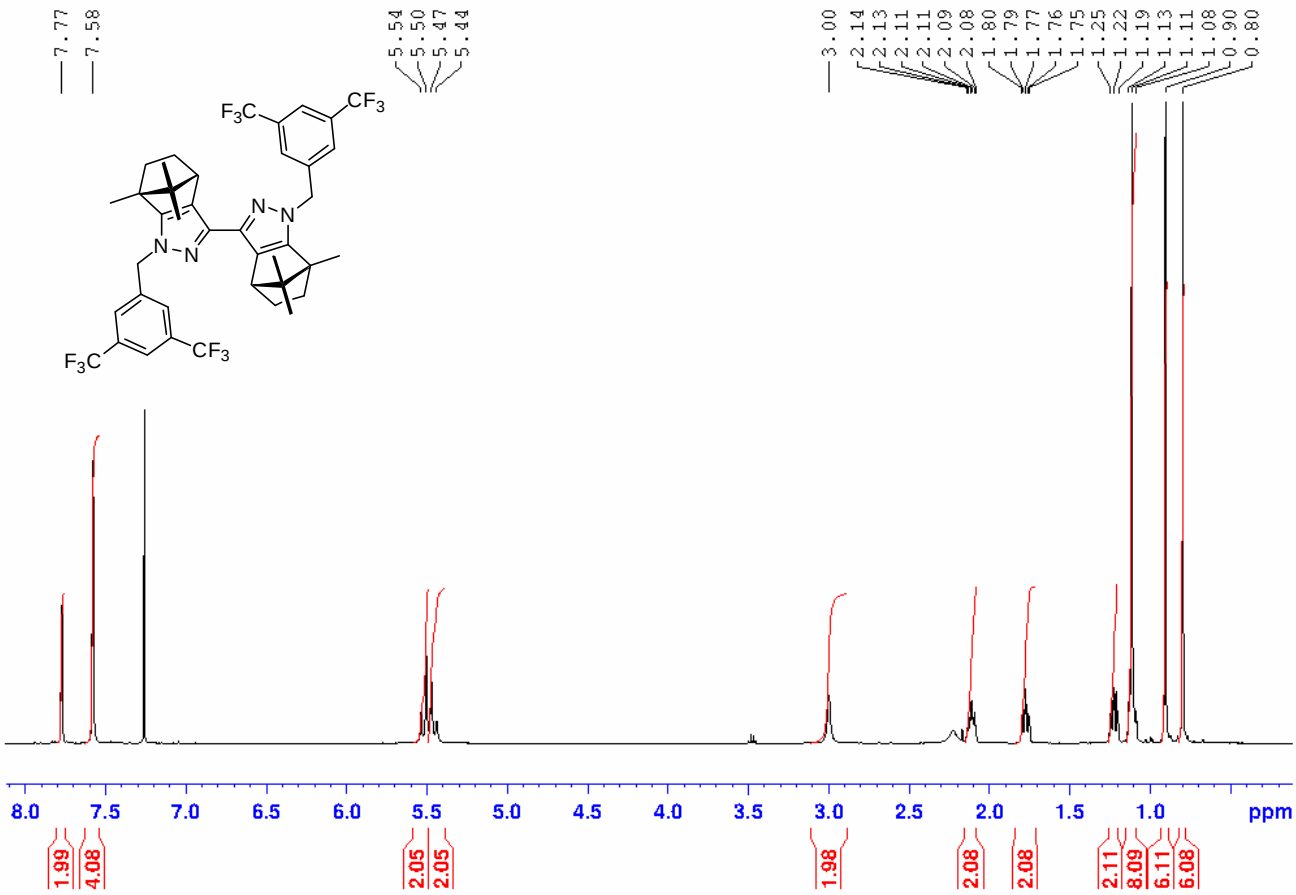

7.29
7.27
7.11
7.08
5.38
5.33
5.31
5.26
2.92
2.91
2.10
2.09
2.07
2.06
2.05
2.04
2.02
2.00
1.71
1.70
1.68
1.67
1.66
1.64
1.63
1.32
1.30
1.28
1.26
1.23
1.21
1.19
1.18
1.12
0.87
0.78
tBu
tBu
N
N
N
N
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.10
4.06
3.82
1.78
2.11
2.05
22.37
5.80
5.64
5.50
154.09
150.24
138.29
135.55
127.18
126.78
125.33
62.74
53.86
52.58
48.55
34.60
33.60
31.51
27.52
20.62
19.84
11.51
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

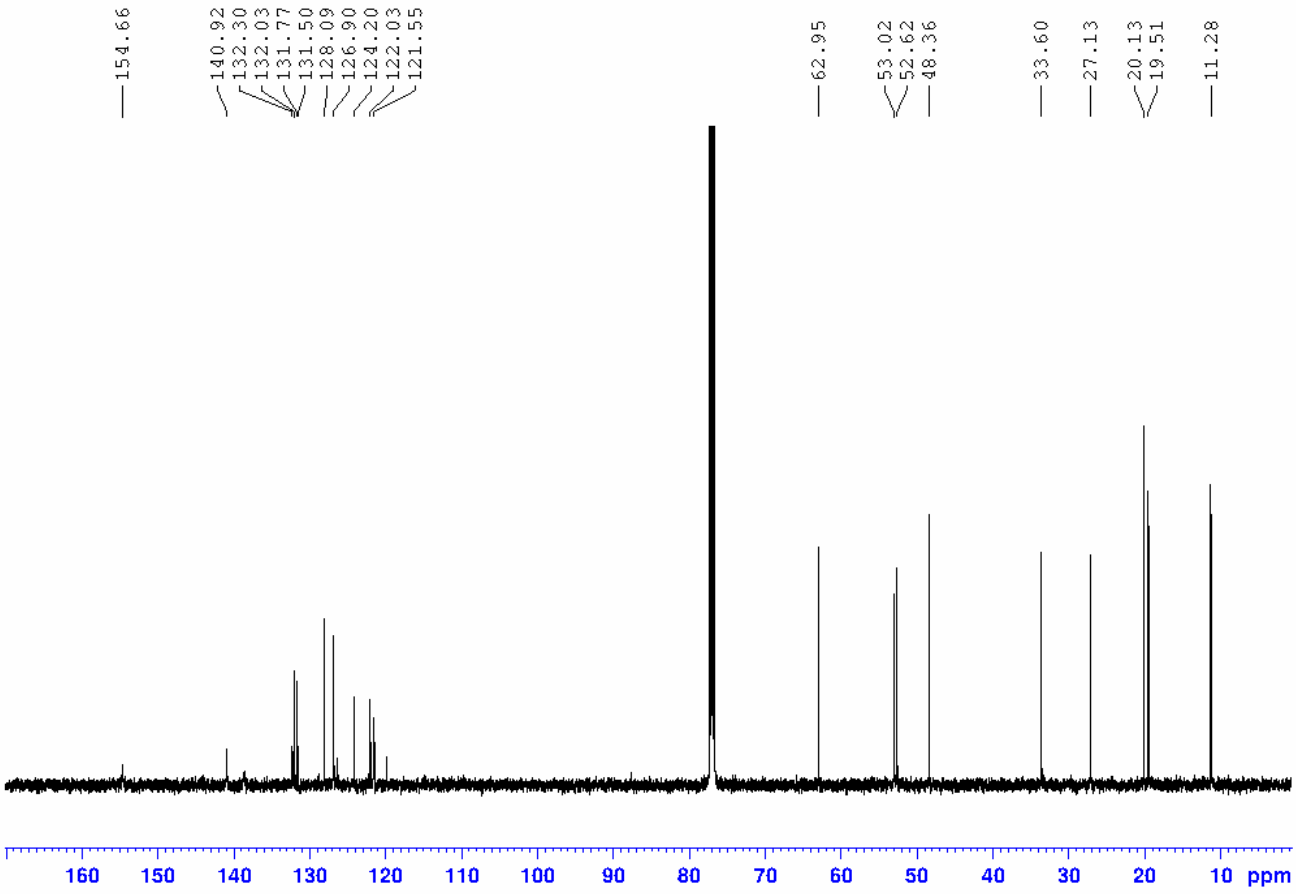

6.85
5.32
2.88
2.88
2.29
2.27
2.03
2.02
2.02
2.00
1.99
1.98
1.98
1.65
1.65
1.63
1.62
1.61
1.60
1.16
1.15
1.14
1.13
1.12
1.11
1.10
1.10
0.96
0.85
0.78
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.06
4.00
1.99
12.00
6.06
2.17
2.02
4.05
6.06
6.02
6.10


153.68
138.14
137.43
130.57
129.38
127.10
62.43
53.31
49.33
48.19
33.62
27.44
21.08
20.59
19.93
11.49
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

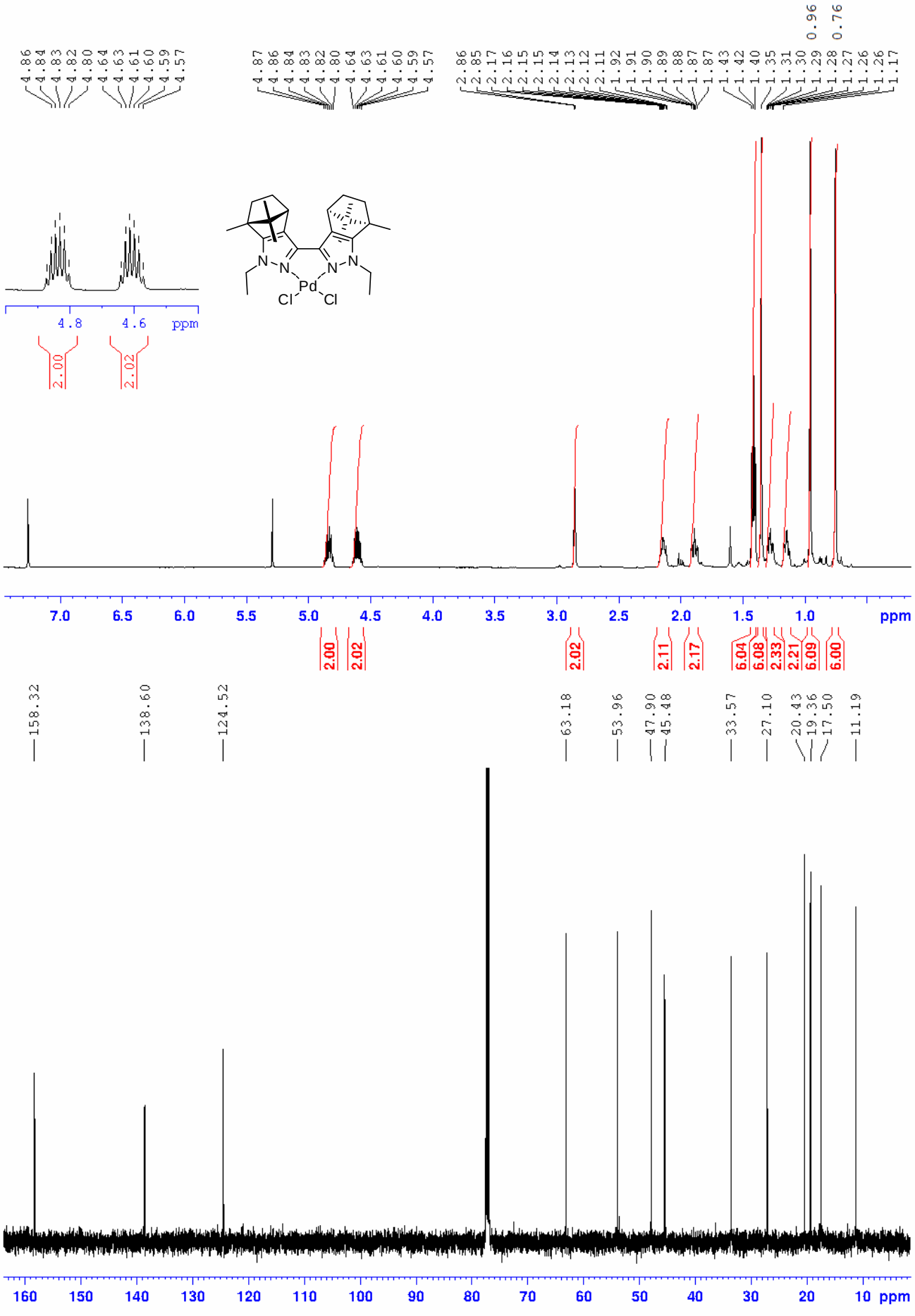

7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.35
7.34
7.32
7.31
5.57
2.97
2.96
2.13
2.12
2.10
2.08
2.07
2.06
2.05
2.03
1.70
1.68
1.67
1.66
1.65
1.63
1.61
1.30
1.29
1.27
1.26
1.25
1.23
1.22
1.21
1.08
0.86
0.81
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
6.05
2.09
4.04
2.02
3.77
1.84
1.96
2.00
3.99
6.02
5.99
6.08

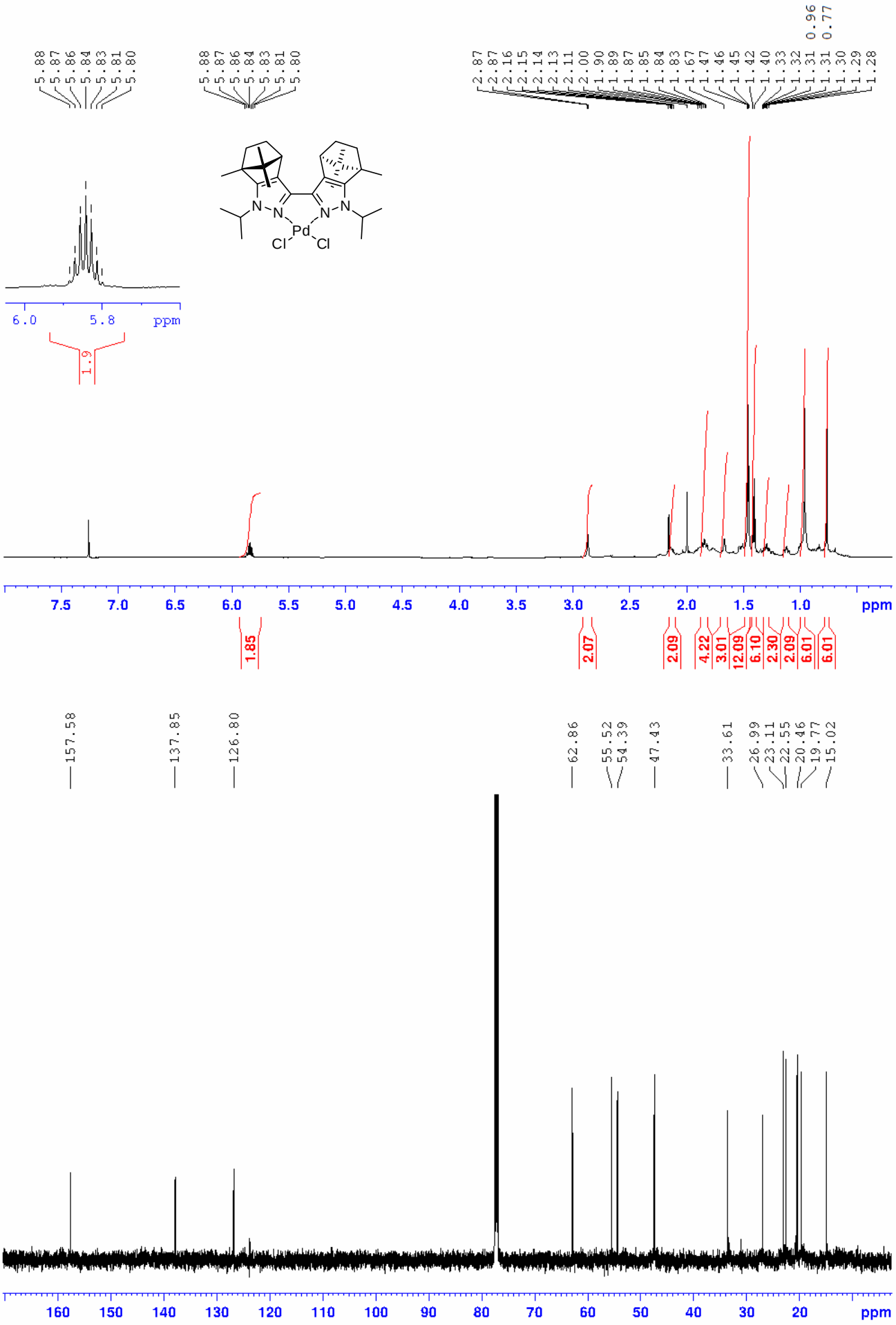

154.33
138.38
136.29
133.41
132.90
128.33
128.01
127.82
127.58
126.19
125.86
125.44
125.11
62.82
54.43
52.63
48.64
33.61
27.50
20.62
19.81
11.48
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

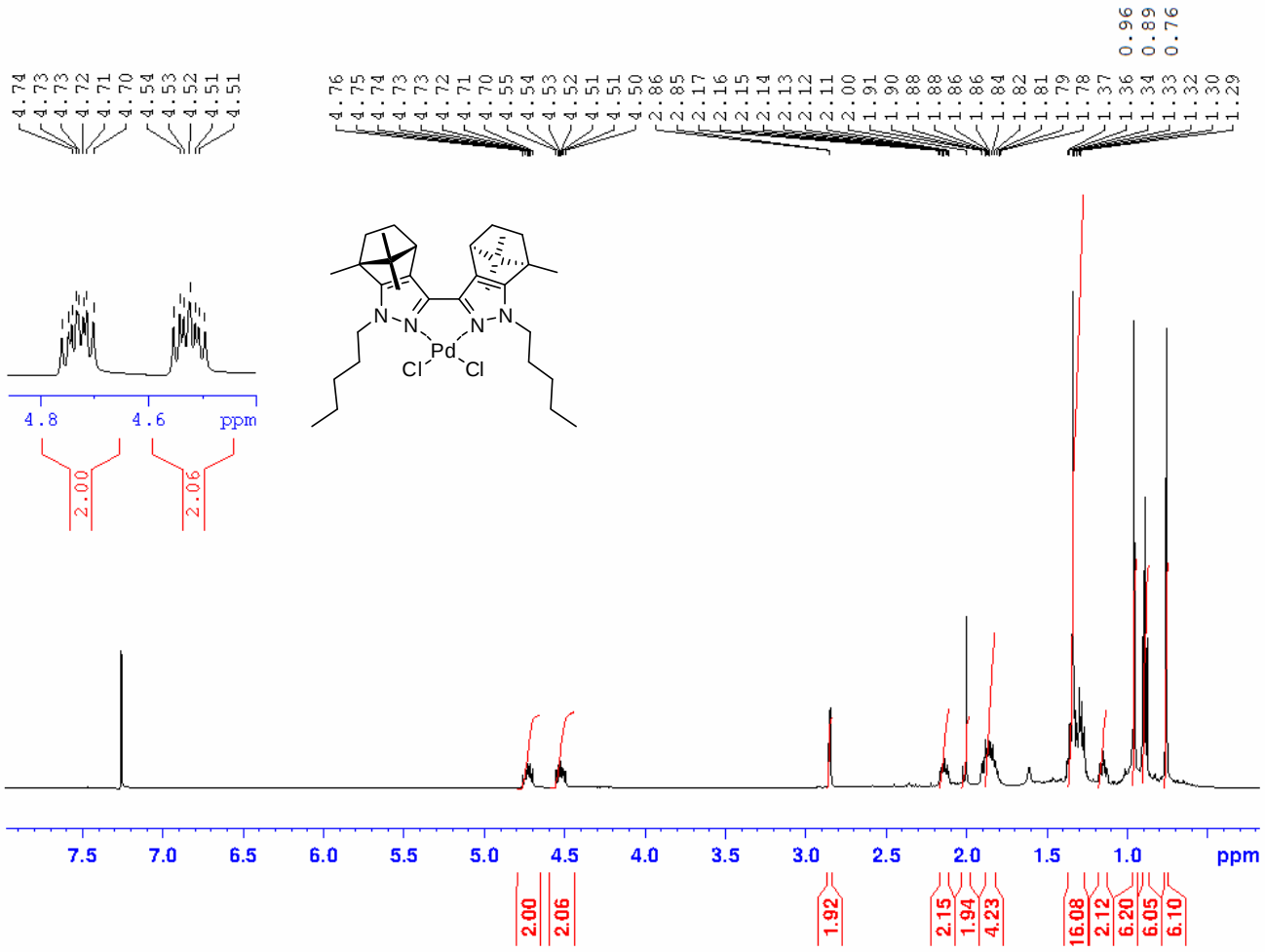

7.77
7.58
5.54
5.50
5.47
5.44
3.00
2.14
2.13
2.11
2.11
2.09
2.08
1.80
1.79
1.77
1.76
1.75
1.25
1.22
1.19
1.13
1.11
1.08
0.90
0.80
F3C
CF3
F3C
CF3
N
N
N
N
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
4.08
2.05
2.05
1.98
2.08
2.08
2.11
8.09
6.11
6.08

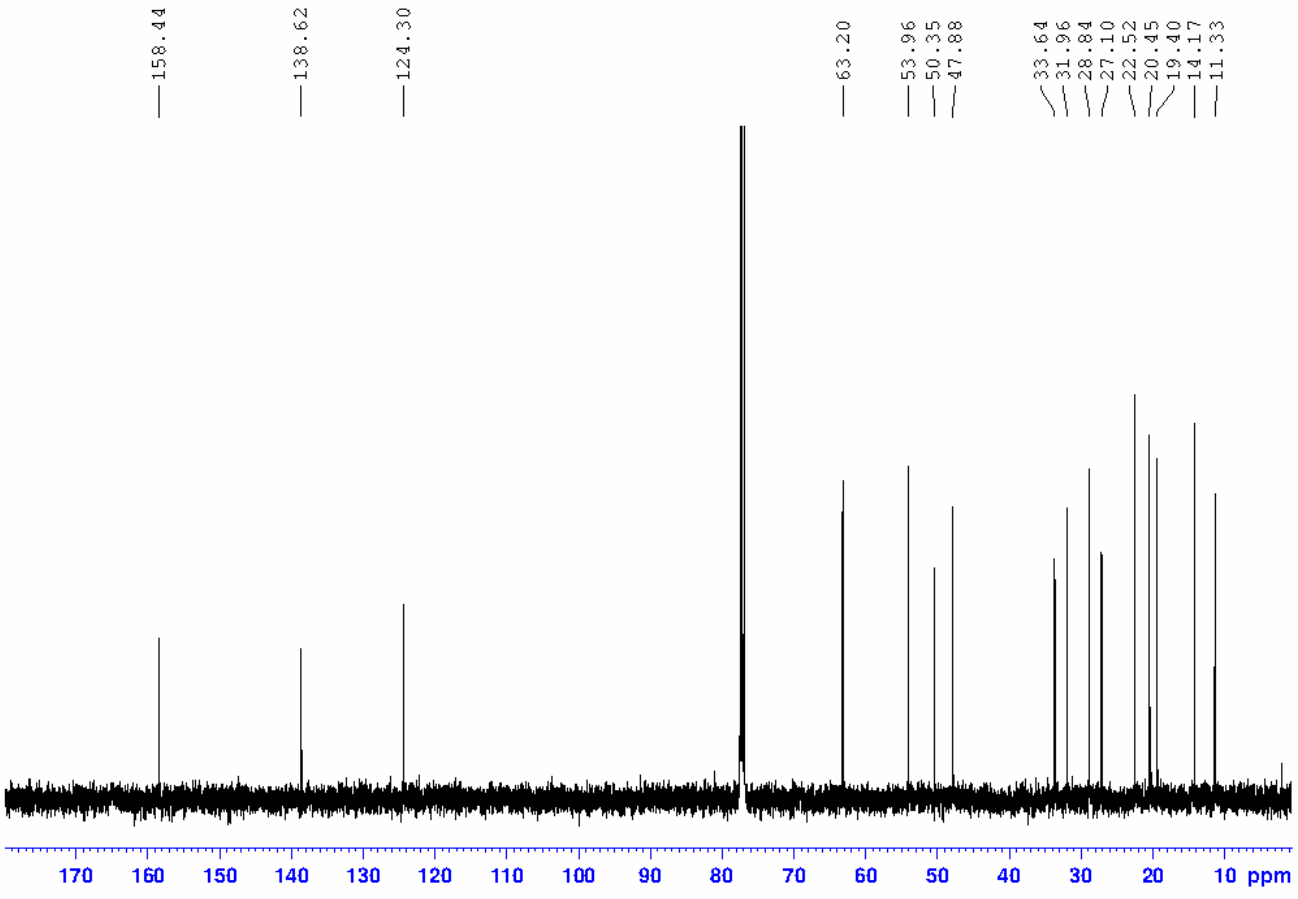

154.66
140.92
132.30
132.03
131.77
131.50
128.09
126.90
124.20
122.03
121.55
62.95
53.02
52.62
48.36
33.60
27.13
20.13
19.51
11.28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

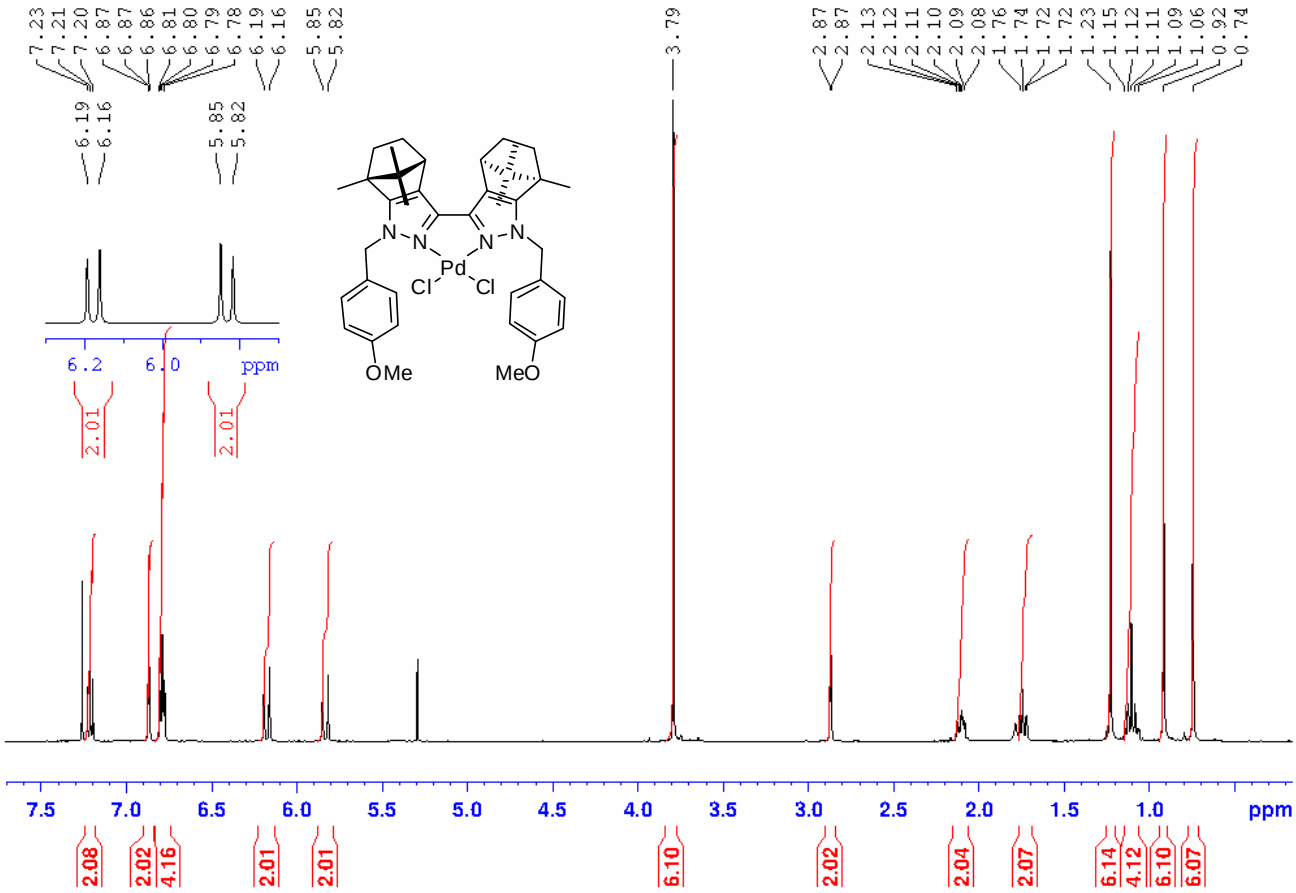
^{1}H and ^{13}C NMR spectra of palladium complexes 4a–k

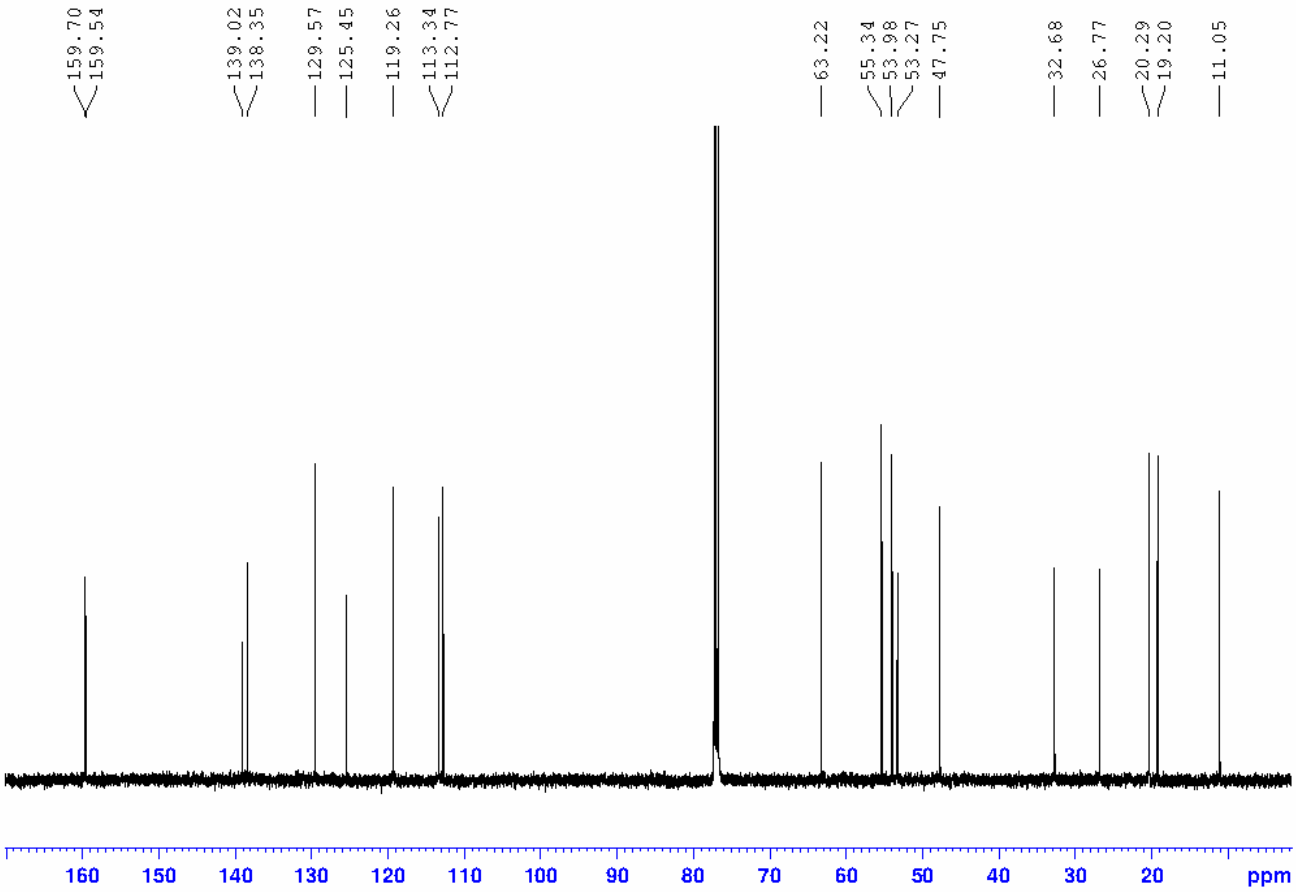


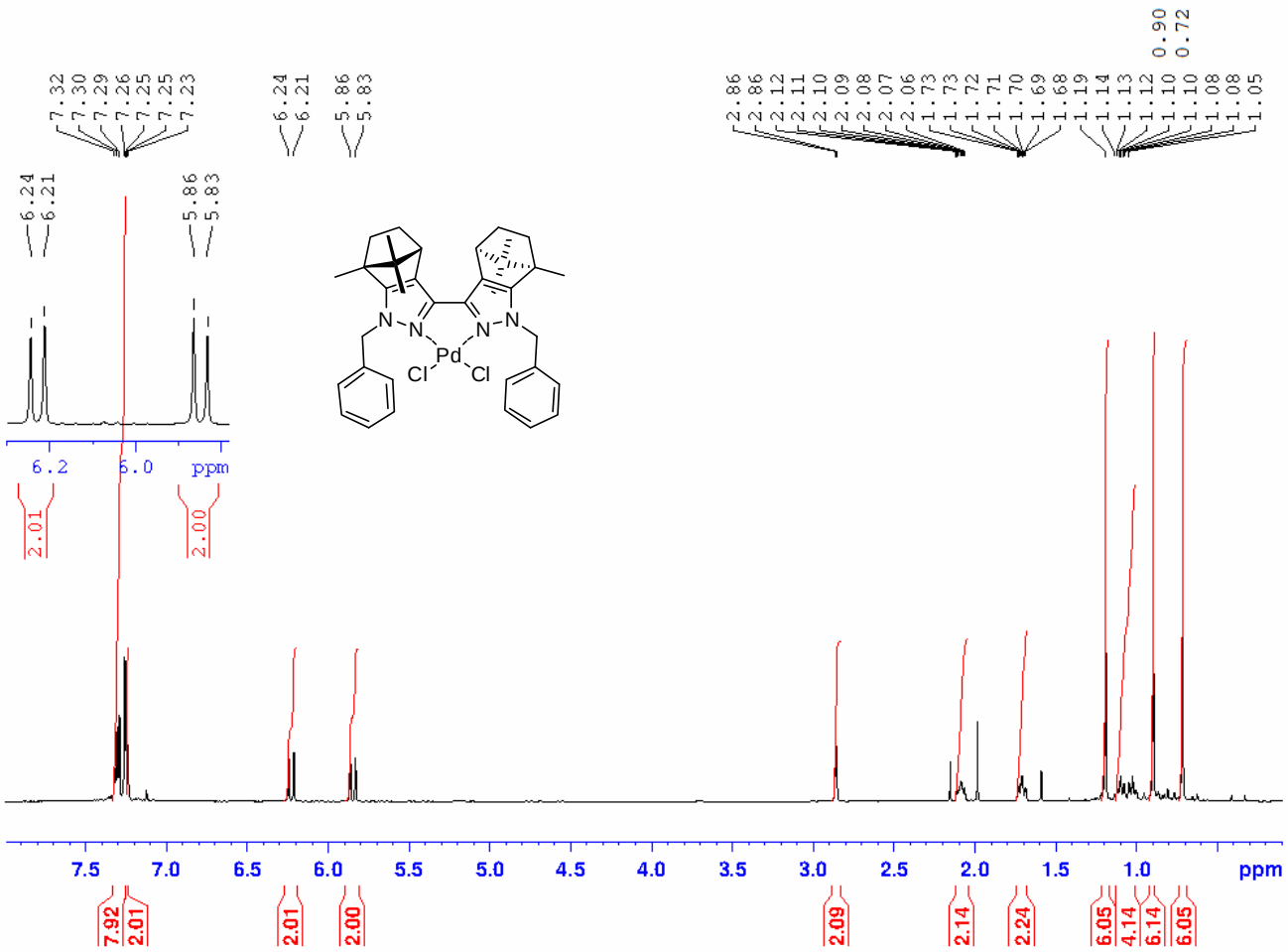

5.88
5.87
5.86
5.84
5.83
5.81
5.80
2.87
2.87
2.16
2.15
2.14
2.13
2.11
2.00
1.90
1.89
1.87
1.85
1.84
1.83
1.67
1.47
1.46
1.45
1.42
1.40
1.33
1.32
1.31
1.31
1.30
1.29
1.28
0.96
0.77
N
N
Pd
Cl
Cl
6.0
5.8
ppm
1.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.85
2.07
2.09
4.22
3.01
12.09
6.10
2.30
2.09
6.01
6.01
157.58
137.85
126.80
62.86
55.52
54.39
47.43
33.61
26.99
23.11
22.55
20.46
19.77
15.02
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

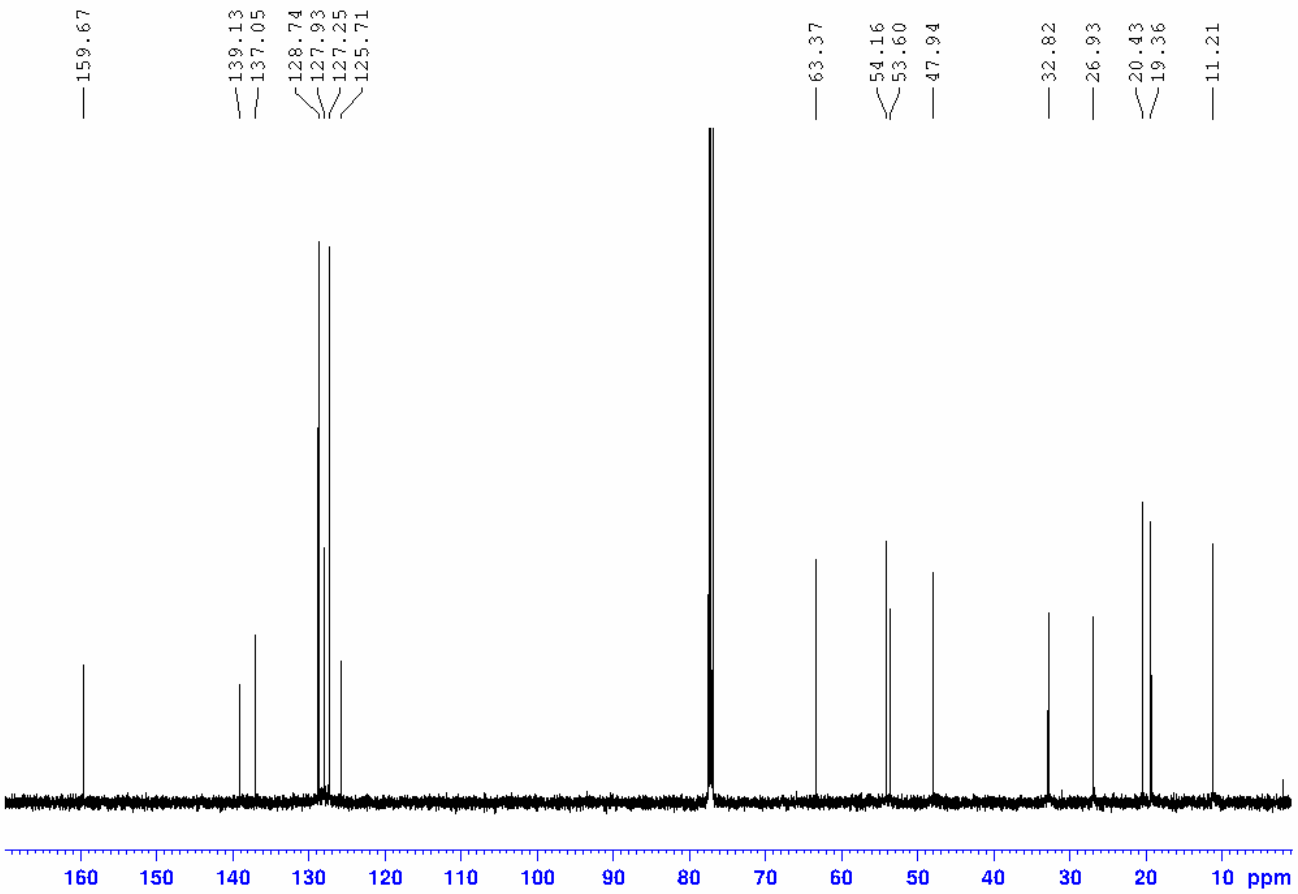

4.74 4.73 4.73 4.72 4.71 4.70 4.54 4.53 4.52 4.51 4.51
4.76 4.75 4.74 4.73 4.73 4.72 4.71 4.70 4.55 4.54 4.53 4.52 4.51 4.51 4.50 2.86 2.85 2.17 2.16 2.15 2.14 2.13 2.12 2.11 2.00 1.91 1.90 1.88 1.88 1.86 1.86 1.84 1.82 1.81 1.79 1.78 1.37 1.36 1.34 1.33 1.32 1.30 1.29
0.96 0.89 0.76
N N N N Pd Cl Cl
4.8 4.6 ppm
2.00 2.06
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 ppm
2.00 2.06 1.92 2.15 1.94 4.23 16.08 2.12 6.20 6.05 6.10

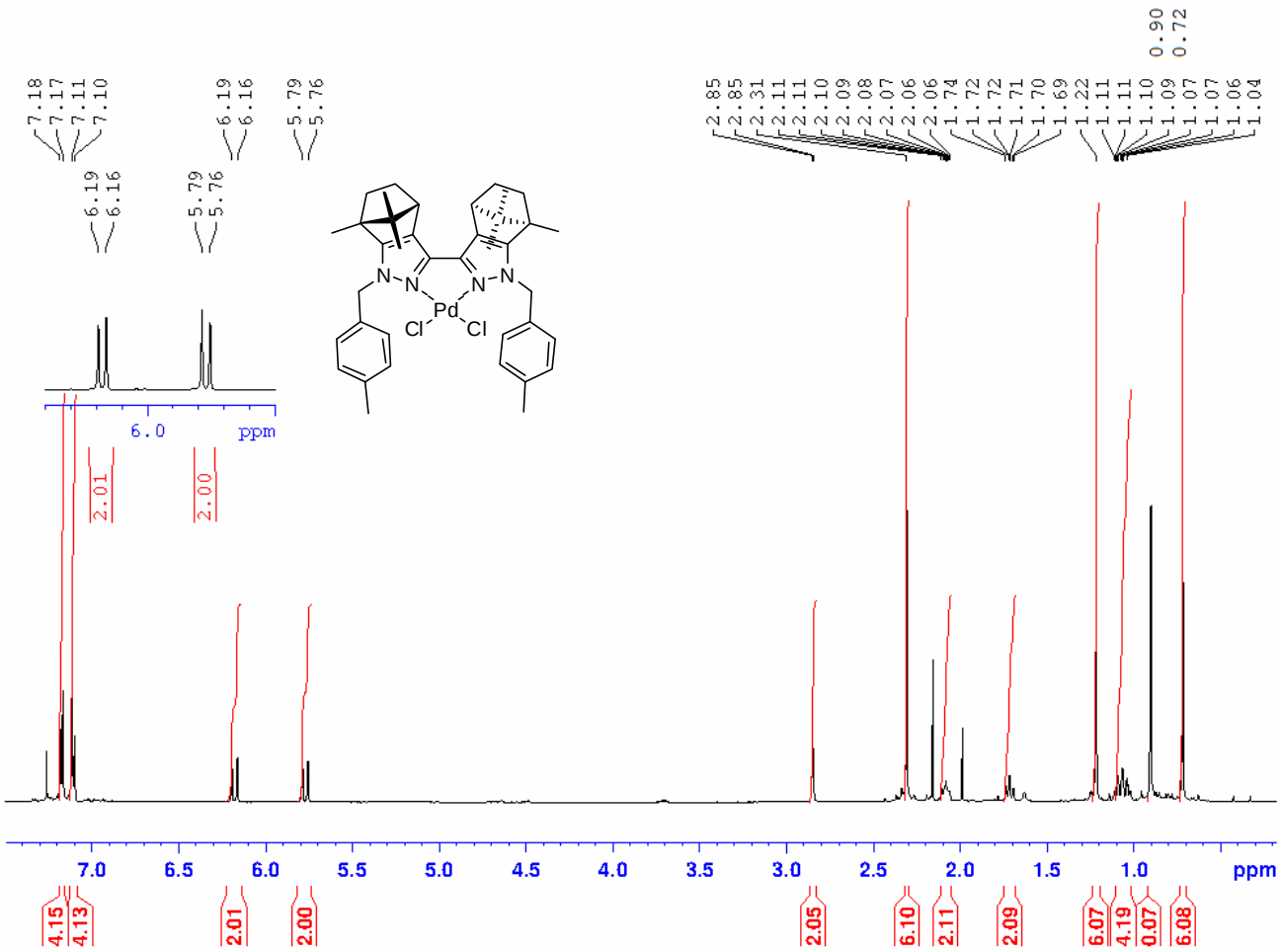

158.44 138.62 124.30 63.20 53.96 50.35 47.88 33.64 31.96 28.84 27.10 22.52 20.45 19.40 14.17 11.33
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

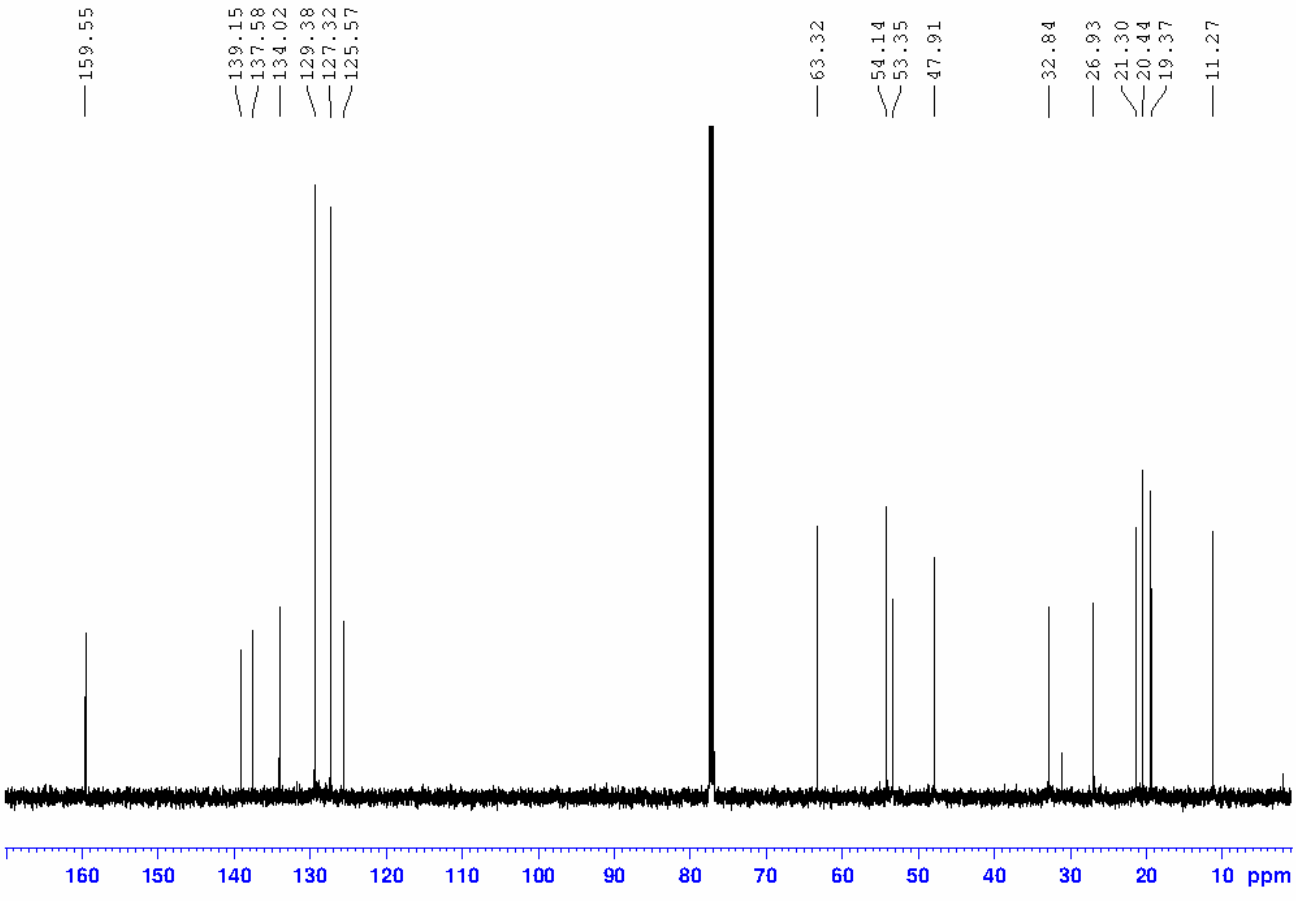

7.23
7.21
7.20
6.87
6.87
6.86
6.81
6.80
6.79
6.78
6.19
6.16
5.85
5.82
3.79
2.87
2.87
2.13
2.12
2.11
2.10
2.09
2.08
1.76
1.74
1.72
1.72
1.23
1.15
1.12
1.11
1.09
1.06
0.92
0.74
6.19
6.16
5.85
5.82
6.2
6.0
ppm
2.01
2.01
N
N
Pd
Cl
Cl
N
N
OMe
MeO
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.08
2.02
4.16
2.01
2.01
6.10
2.02
2.04
2.07
6.14
4.12
6.10
6.07

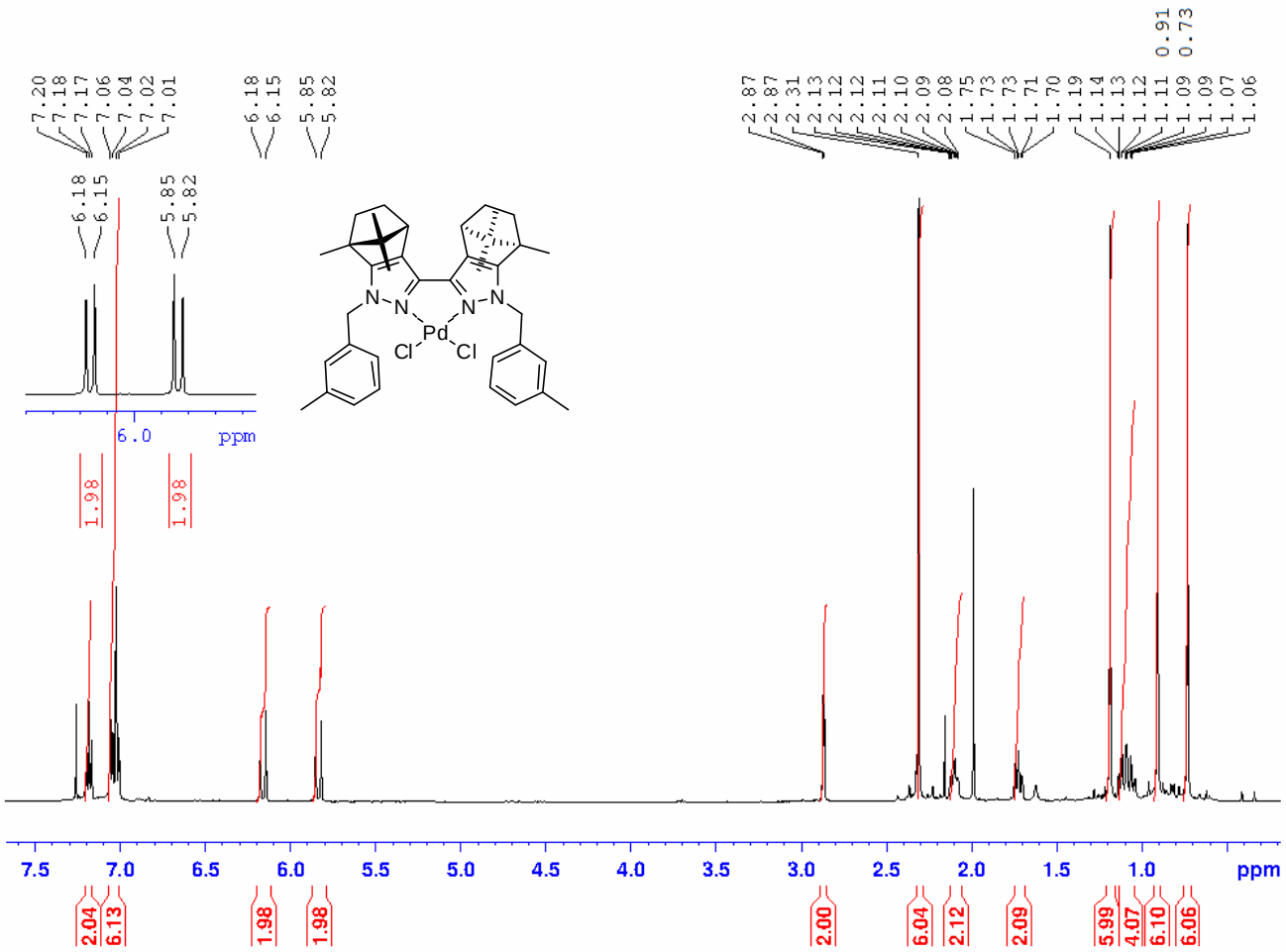

159.70
159.54
139.02
138.35
129.57
125.45
119.26
113.34
112.77
63.22
55.34
53.98
53.27
47.75
32.68
26.77
20.29
19.20
11.05
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

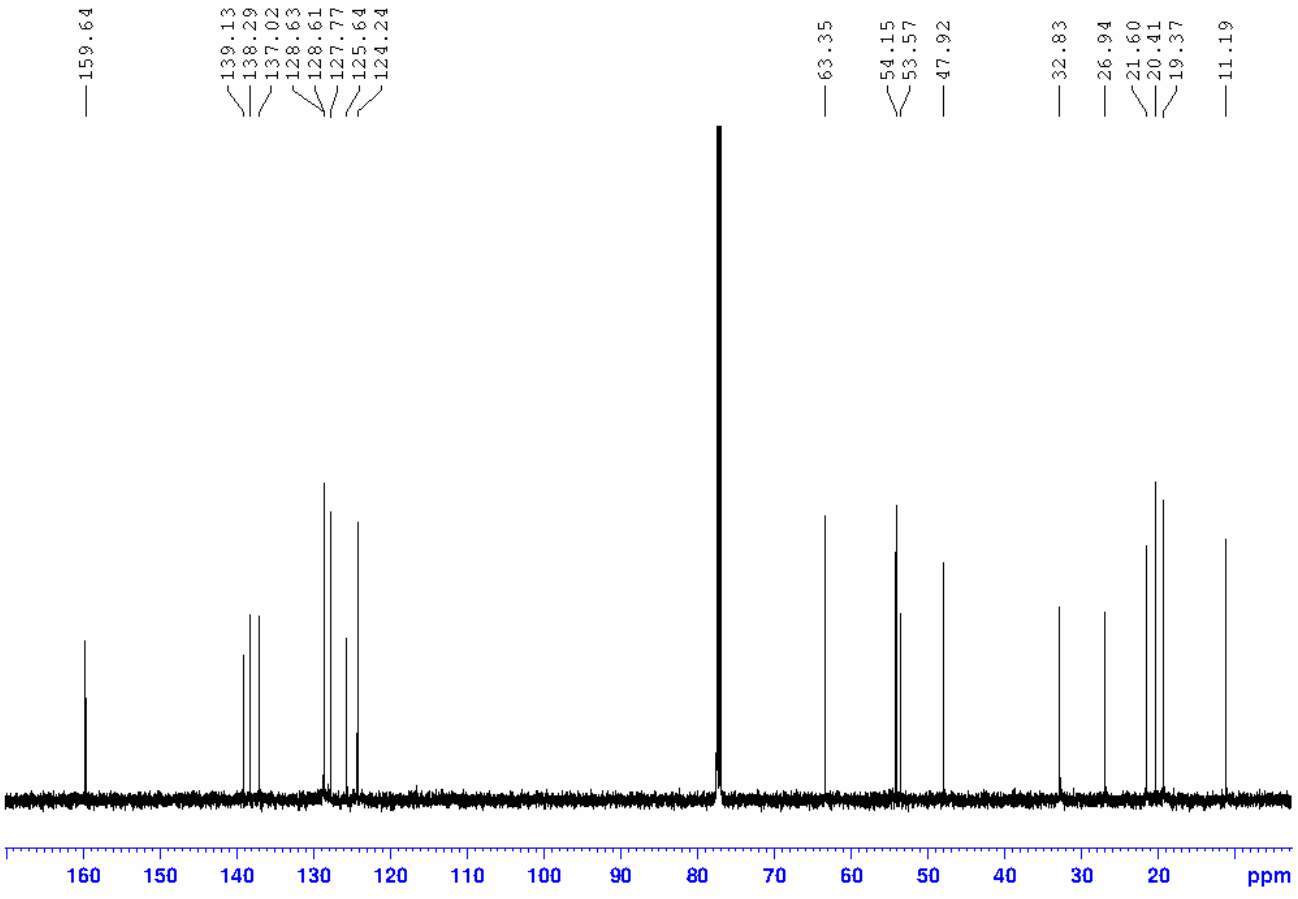

7.32
7.30
7.29
7.26
7.25
7.25
7.23
6.24
6.21
5.86
5.83
2.86
2.86
2.12
2.11
2.10
2.09
2.08
2.07
2.06
1.73
1.72
1.71
1.70
1.69
1.68
1.19
1.14
1.13
1.12
1.10
1.10
1.08
1.08
1.05
0.90
0.72
N
N
Pd
Cl
Cl
N
N
6.2
6.0
ppm
2.01
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
7.92
2.01
2.01
2.00
2.09
2.14
2.24
6.05
4.14
6.14
6.05

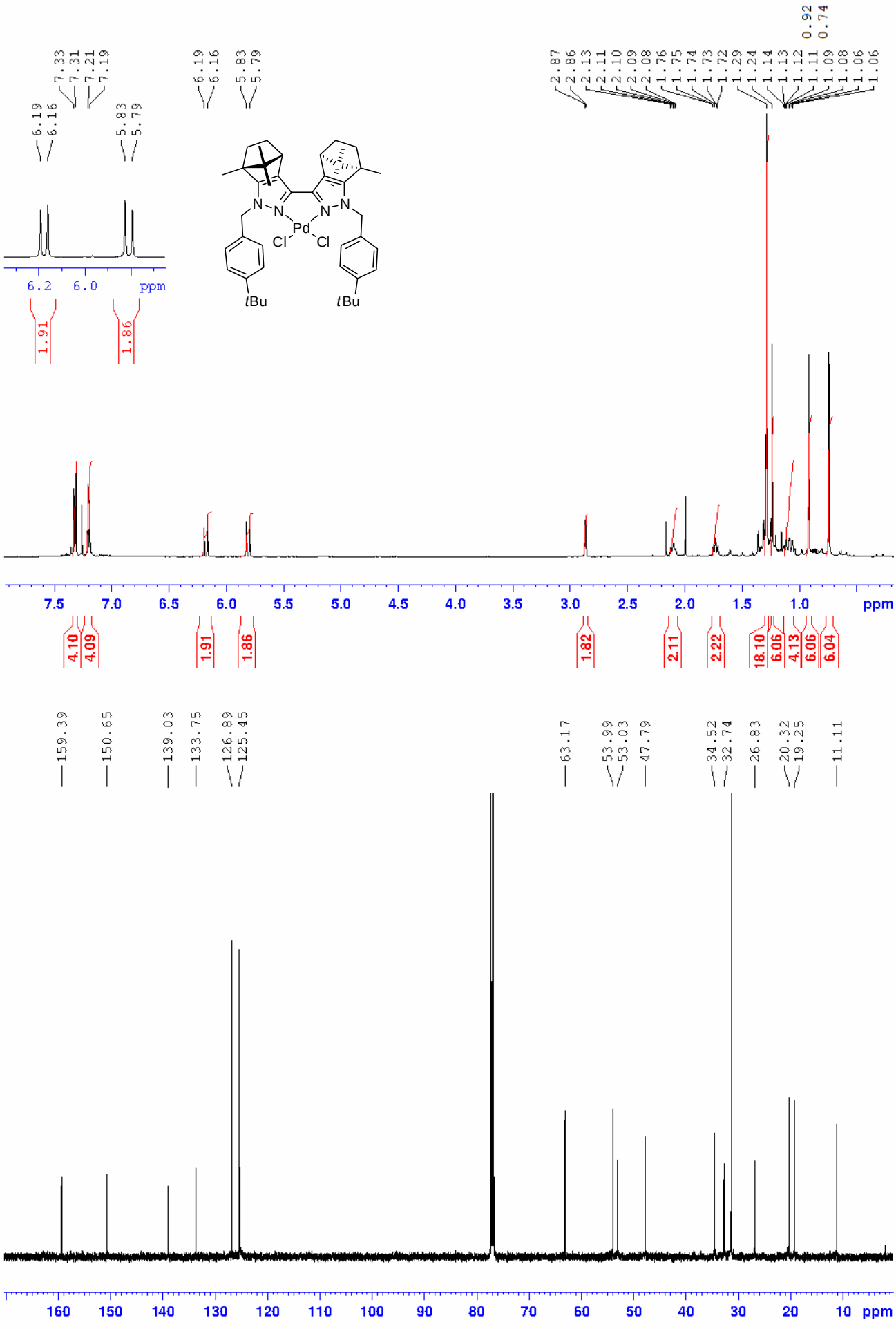

159.67
139.13
137.05
128.74
127.93
127.25
125.71
63.37
54.16
53.60
47.94
32.82
26.93
20.43
19.36
11.21
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

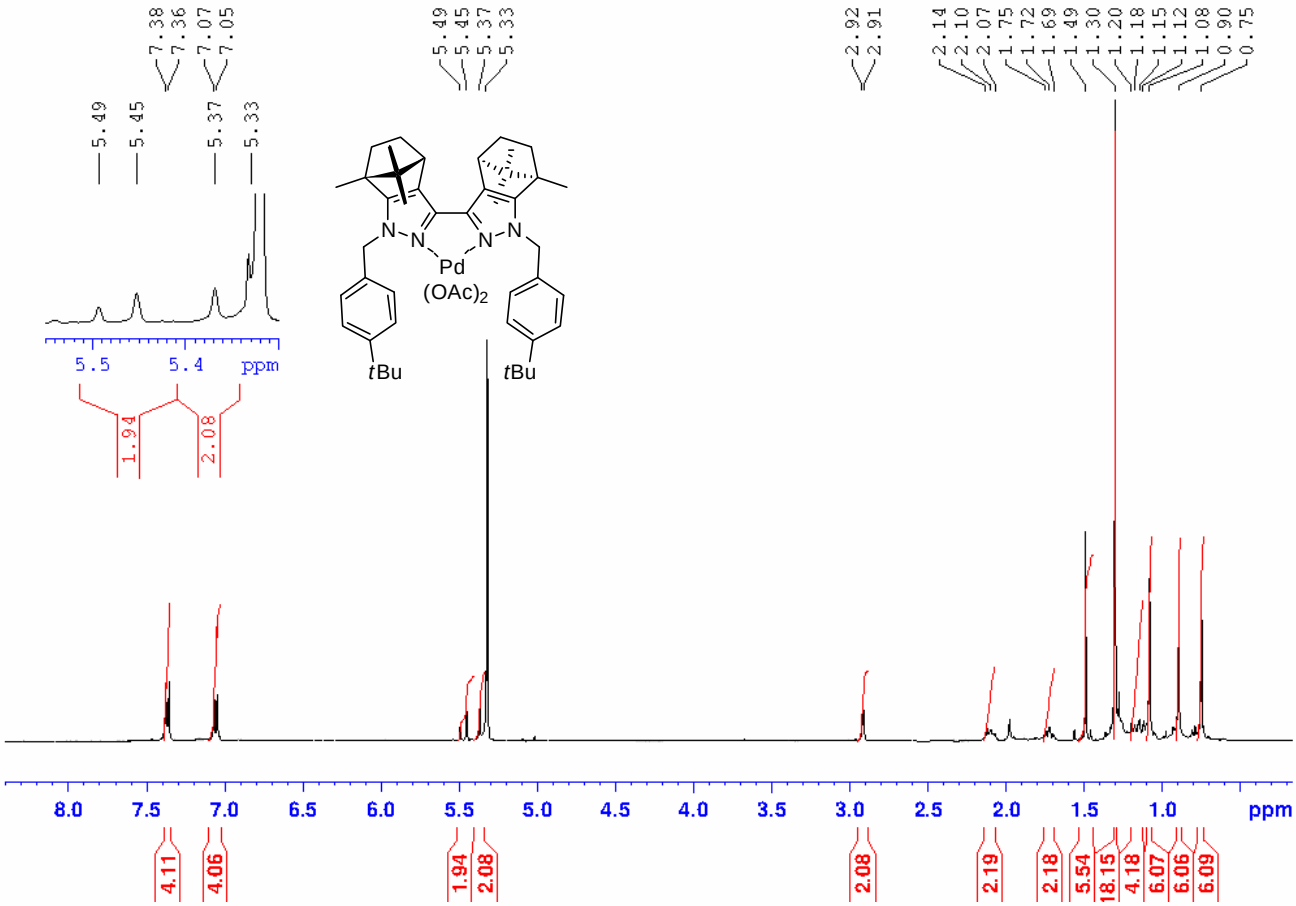

7.18
7.17
7.11
7.10
6.19
6.16
5.79
5.76
2.85
2.85
2.31
2.11
2.11
2.10
2.09
2.08
2.07
2.06
2.06
1.74
1.72
1.72
1.71
1.70
1.69
1.22
1.11
1.11
1.10
1.09
1.07
1.07
1.06
1.04
0.90
0.72
N
N
Pd
Cl
Cl
N
N
6.0
ppm
2.01
2.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.15
4.13
2.01
2.00
2.05
6.10
2.11
2.09
6.07
4.19
0.07
6.08

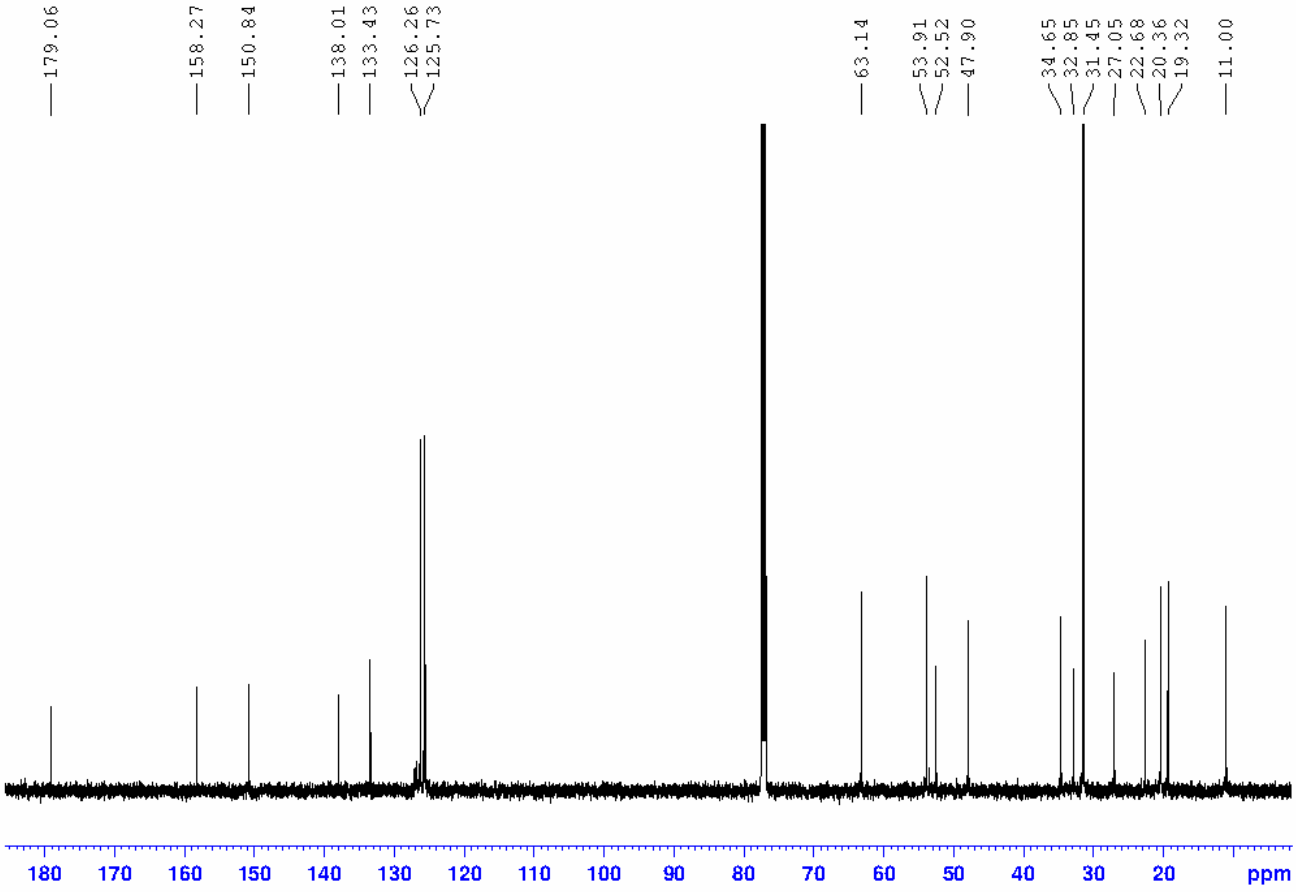

159.55
139.15
137.58
134.02
129.38
127.32
125.57
63.32
54.14
53.35
47.91
32.84
26.93
21.30
20.44
19.37
11.27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

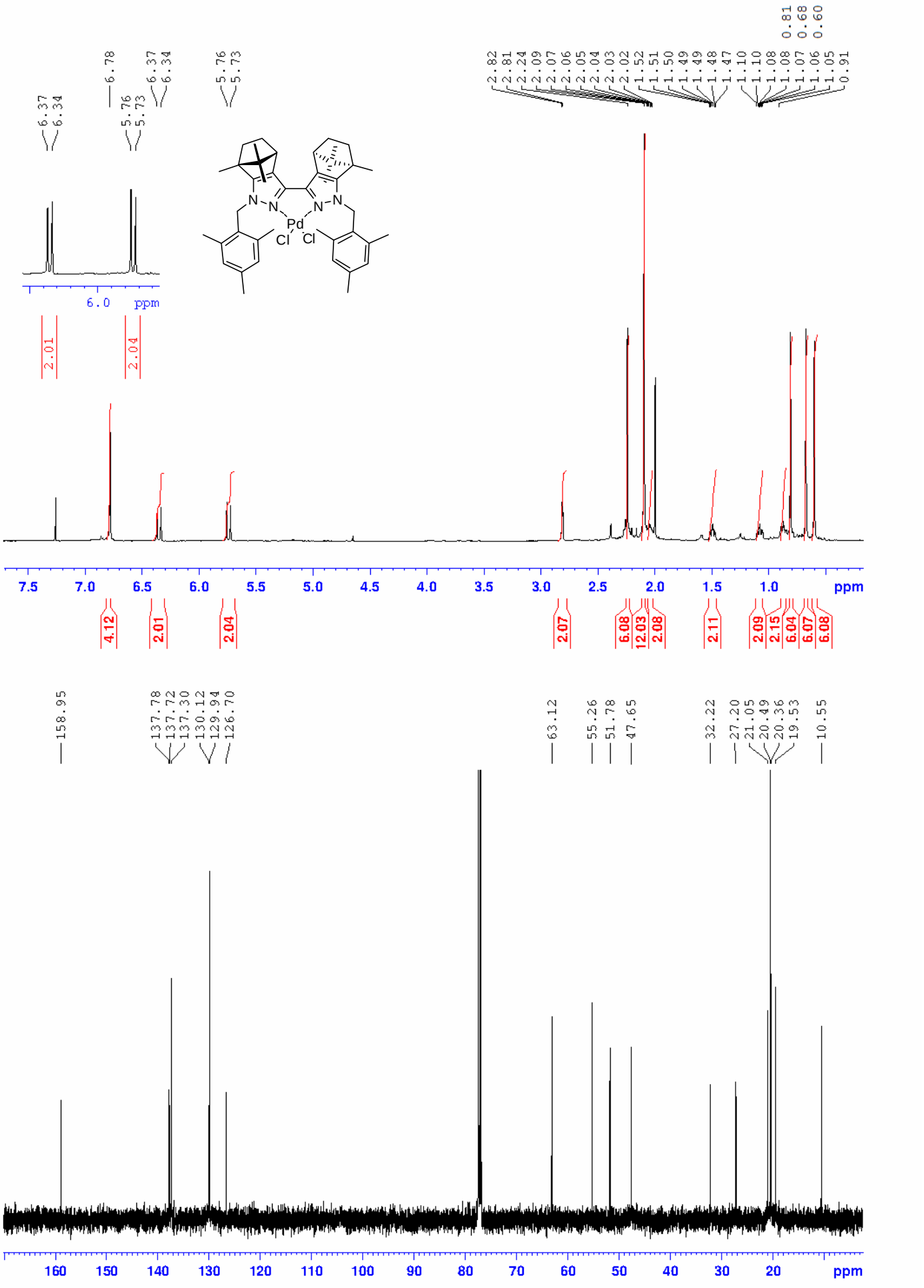

7.20
7.18
7.17
7.06
7.04
7.02
7.01
6.18
6.15
5.85
5.82
2.87
2.87
2.31
2.13
2.12
2.12
2.11
2.10
2.09
2.08
1.75
1.73
1.73
1.71
1.70
1.19
1.14
1.13
1.12
1.11
1.09
1.09
1.07
1.06
0.91
0.73
N
N
Pd
Cl
Cl
N
N
6.0
ppm
1.98
1.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.04
6.13
1.98
1.98
2.00
6.04
2.12
2.09
5.99
4.07
6.10
6.06

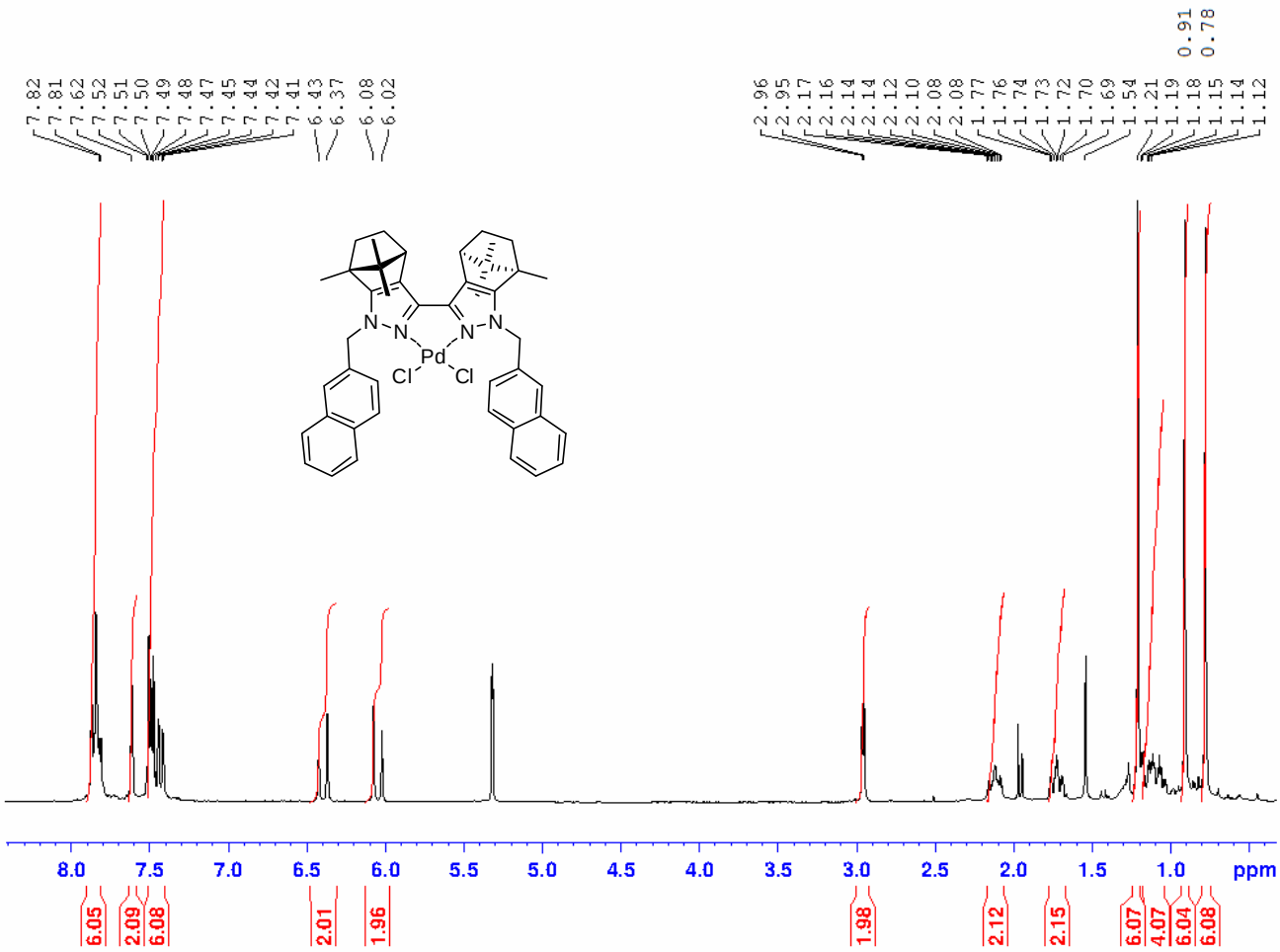

159.64
139.13
138.29
137.02
128.63
128.61
127.77
125.64
124.24
63.35
54.15
53.57
47.92
32.83
26.94
21.60
20.41
19.37
11.19
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

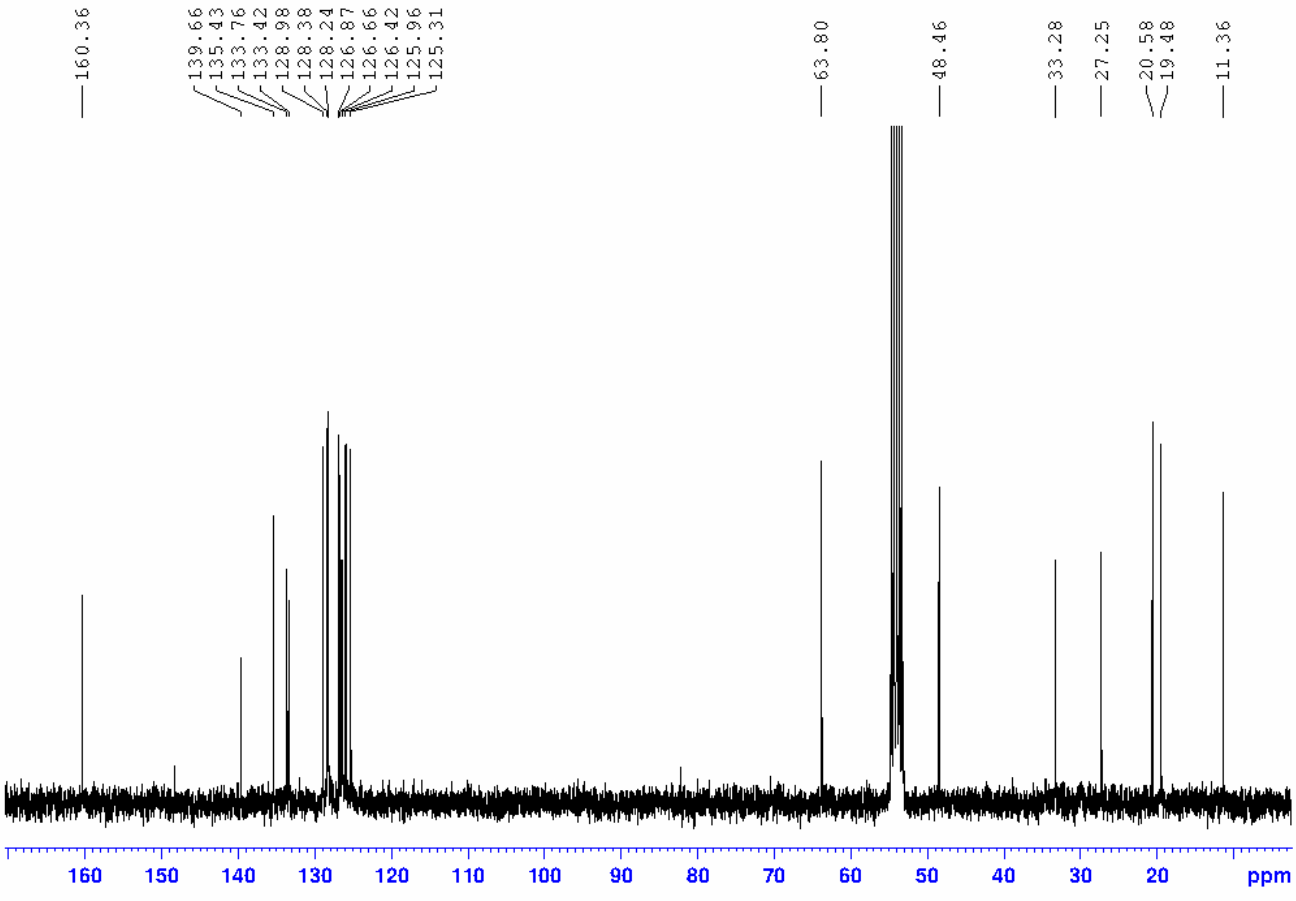

6.19
6.16
7.33
7.31
7.21
7.19
5.83
5.79
6.19
6.16
5.83
5.79
2.87
2.86
2.13
2.11
2.10
2.09
2.08
1.76
1.75
1.74
1.73
1.72
1.29
1.24
1.14
1.13
1.12
1.11
1.09
1.08
1.06
1.06
0.92
0.74
N
N
Pd
Cl
Cl
N
N
tBu
tBu
6.2
6.0
ppm
1.91
1.86
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.10
4.09
1.91
1.86
1.82
2.11
2.22
18.10
6.06
4.13
6.06
6.04
159.39
150.65
139.03
133.75
126.89
125.45
63.17
53.99
53.03
47.79
34.52
32.74
26.83
20.32
19.25
11.11
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

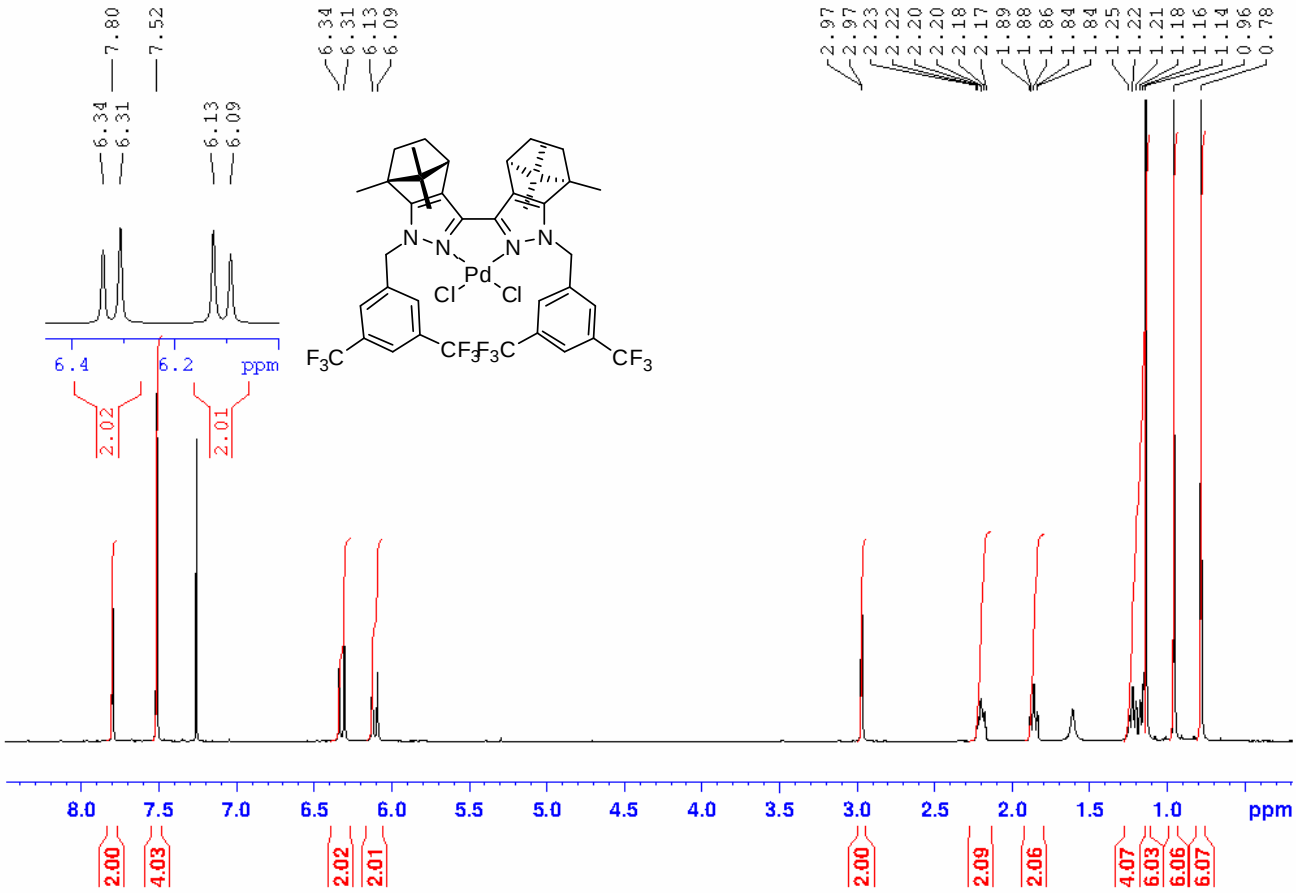

7.38
7.36
7.07
7.05
5.49
5.45
5.37
5.33
2.92
2.91
2.14
2.10
2.07
1.75
1.72
1.69
1.49
1.30
1.20
1.18
1.15
1.12
1.08
0.90
0.75
Pd
(OAc)2
tBu
tBu
5.5
5.4
ppm
1.94
2.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.11
4.06
1.94
2.08
2.08
2.19
2.18
5.54
18.15
4.18
6.07
6.06
6.09

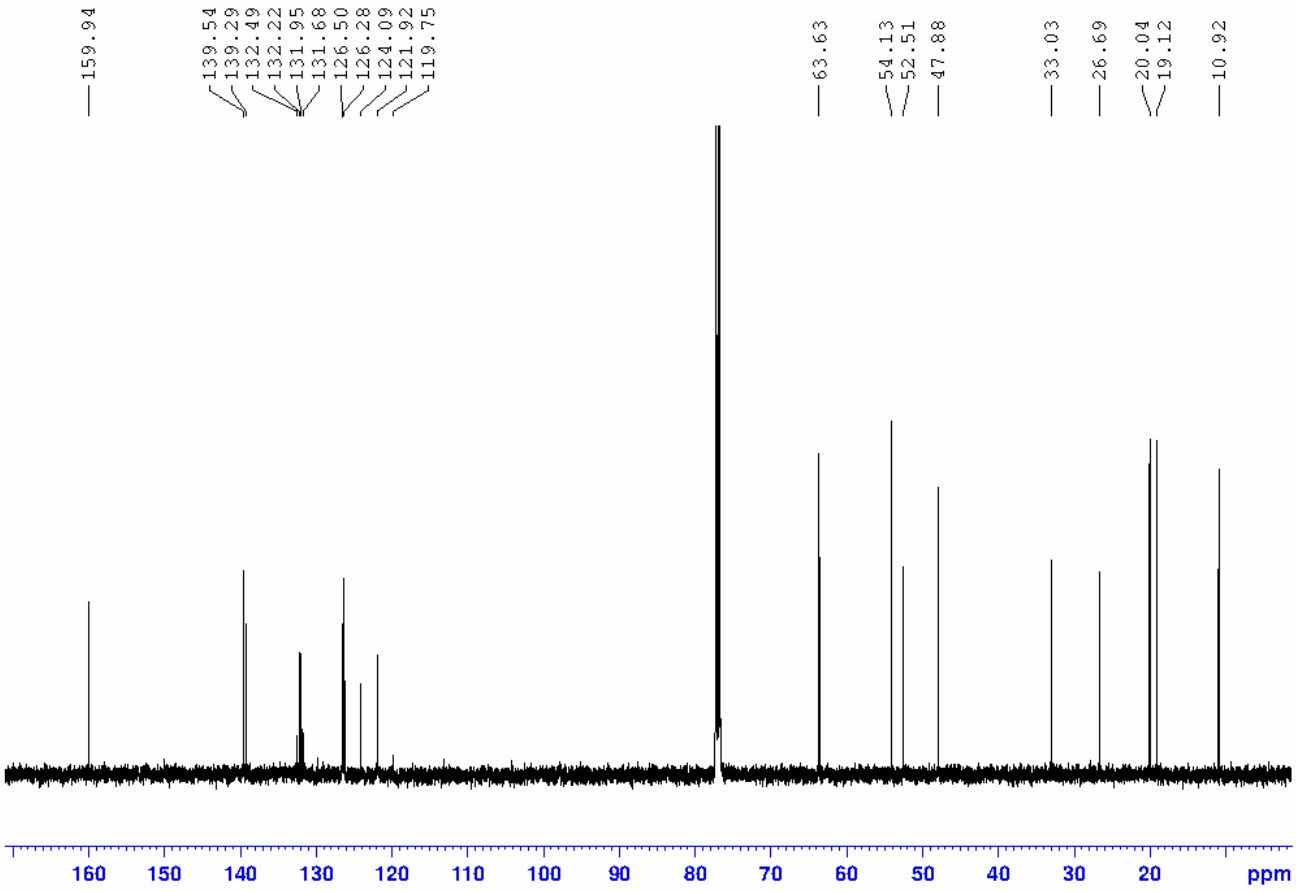

179.06
158.27
150.84
138.01
133.43
126.26
125.73
63.14
53.91
52.52
47.90
34.65
32.85
31.45
27.05
22.68
20.36
19.32
11.00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


6.37
6.34
6.78
5.76
5.73
6.37
6.34
5.76
5.73
2.82
2.81
2.24
2.09
2.07
2.06
2.05
2.04
2.03
2.02
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.10
1.10
1.08
1.08
1.07
1.06
1.05
0.91
0.81
0.68
0.60
N
N
N
N
Pd
Cl
Cl
6.0
ppm
2.01
2.04
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
ppm
4.12
2.01
2.04
2.07
6.08
12.03
2.08
2.11
2.09
2.15
6.04
6.07
6.08
158.95
137.78
137.72
137.30
130.12
129.94
126.70
63.12
55.26
51.78
47.65
32.22
27.20
21.05
20.49
20.36
19.53
10.55
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.82
7.81
7.62
7.52
7.51
7.50
7.49
7.48
7.47
7.45
7.44
7.42
7.41
6.43
6.37
6.08
6.02
2.96
2.95
2.17
2.16
2.14
2.14
2.12
2.10
2.08
2.08
1.77
1.76
1.74
1.73
1.72
1.70
1.69
1.54
1.21
1.19
1.18
1.15
1.14
1.12
0.91
0.78
N
N
N
N
Pd
Cl
Cl
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
ppm
6.05
2.09
6.08
2.01
1.96
1.98
2.12
2.15
6.07
4.07
6.04
6.08

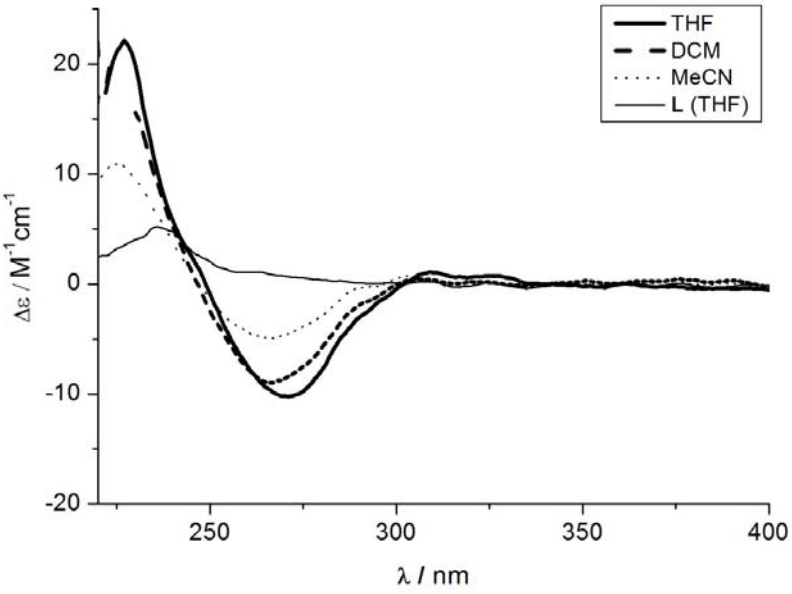

160.36
139.66
135.43
133.76
133.42
128.98
128.38
128.24
126.87
126.66
126.42
125.96
125.31
63.80
48.46
33.28
27.25
20.58
19.48
11.36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.80
7.52
6.34
6.31
6.13
6.09
2.97
2.23
2.22
2.20
2.18
2.17
1.89
1.88
1.86
1.84
1.25
1.22
1.21
1.18
1.16
1.14
0.96
0.78
N
Pd
Cl
F3C
CF3
6.4
6.2
ppm
2.02
2.01
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
ppm
2.00
4.03
2.02
2.01
2.00
2.09
2.06
4.07
6.03
6.06
6.07


159.94
139.54
139.29
132.49
132.22
131.95
131.68
126.50
126.28
124.09
121.92
119.75
63.63
54.13
52.51
47.88
33.03
26.69
20.04
19.12
10.92
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

CD spectra of ligand 3h **and palladium complex** 4h **in various solvents**

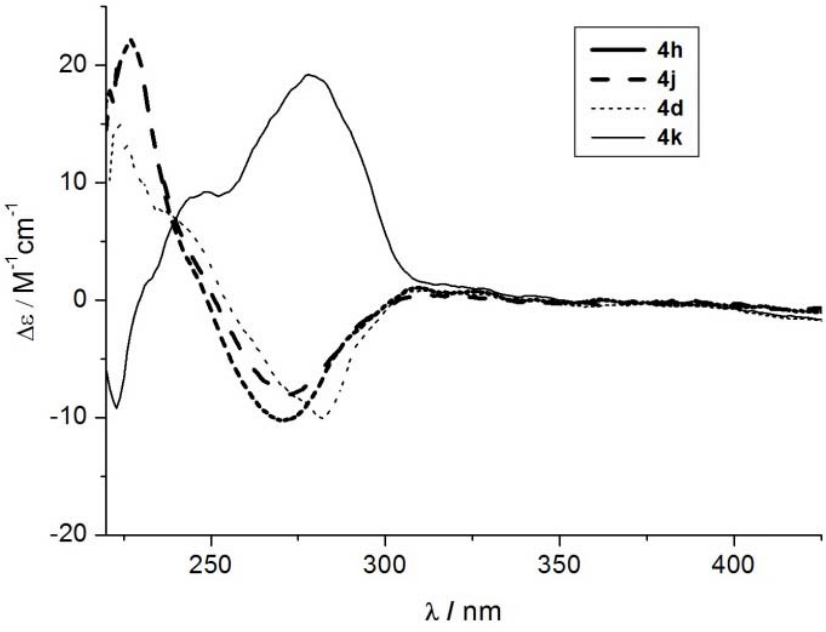
All solution spectra were recorded in distilled solvents.



SI Figure 1: CD spectra of palladium complex 4h **and the free ligand** 3h **in tetrahydrofurane**

CD spectra of palladium complexes 4h, 4j, 4d **and** 4k

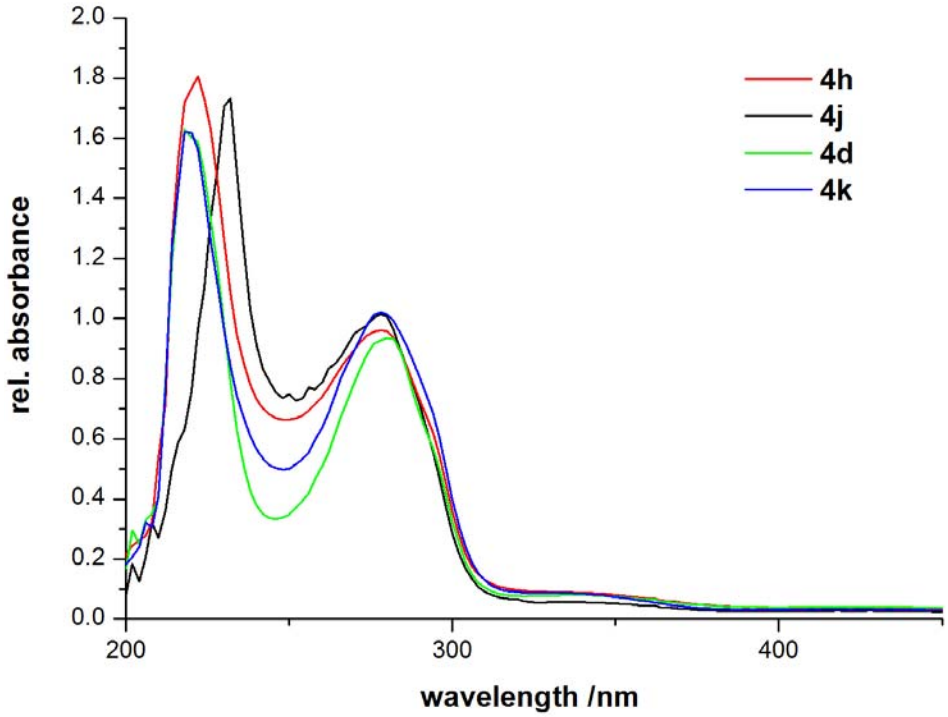
The solution spectra were recorded in distilled tetrahydrofurane.



SI Figure 2: CD spectra of palladium complexes 4h, 4j, 4d **and** 4k **in tetrahydrofurane**

UV-Vis spectra of palladium complexes 4h, 4j, 4d **and** 4k**:**

The solution spectra (c = 0.03 mM) of the palladium complexes were recorded in distilled tetrahydrofurane.



SI Figure 3: UV-Vis spectra of palladium complexes 4h, 4j, 4d **and** 4k **in tetrahydrofurane.**