Supporting Information

Silver-Free Palladium Catalyzed C(sp^3)-H Arylation of Saturated Bicyclic Amine Scaffolds

Charlotte E. Coomber,† Laure Benhamou,† Dejan-Krešimir Bučar,† Peter D. Smith,‡ Michael J. Porter† and Tom D. Sheppard*,†

†Department of Chemistry, University College London, Christopher Ingold Laboratories, 20 Gordon Street, London, WC1H 0AJ

‡Early Chemical Development, Pharmaceutical Sciences, IMED Biotech Unit, AstraZeneca, Macclesfield, UK

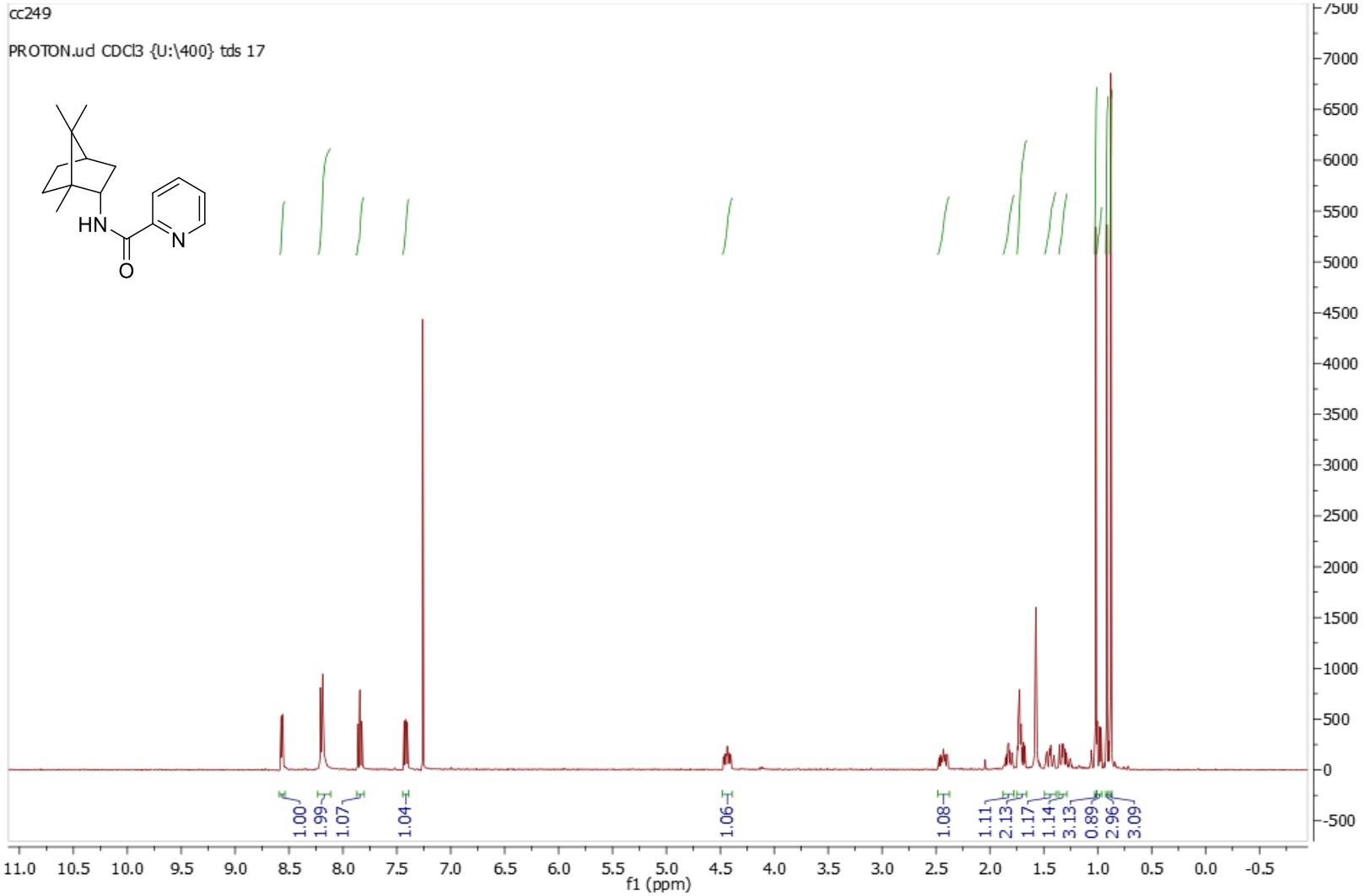
tom.sheppard@ucl.ac.uk

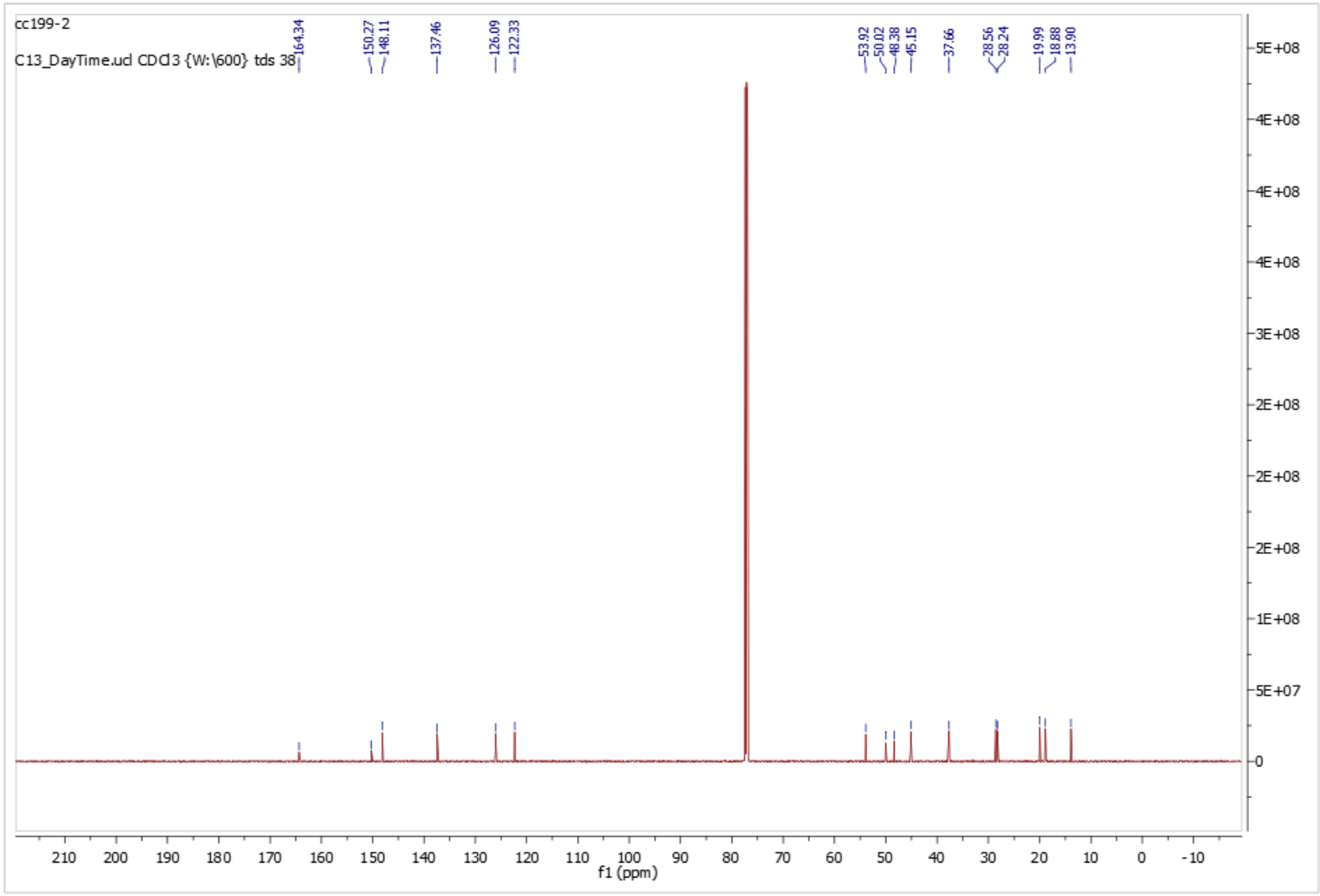
Contents

S2 – S62 ^{1}H and ^{13}C NMR Spectra

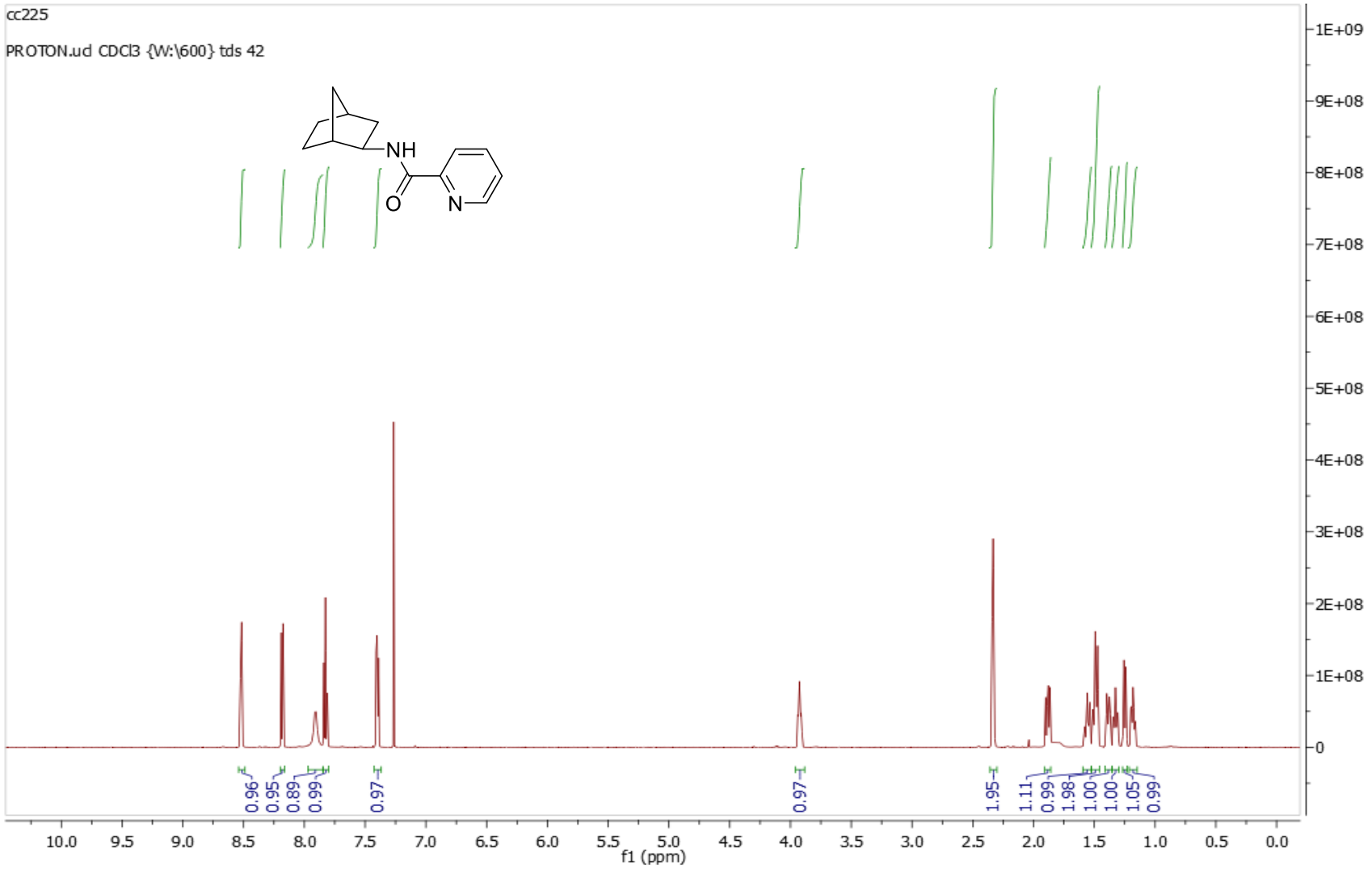
S63 – S64 Crystallographic data for **2a**, **4a** and **8b**

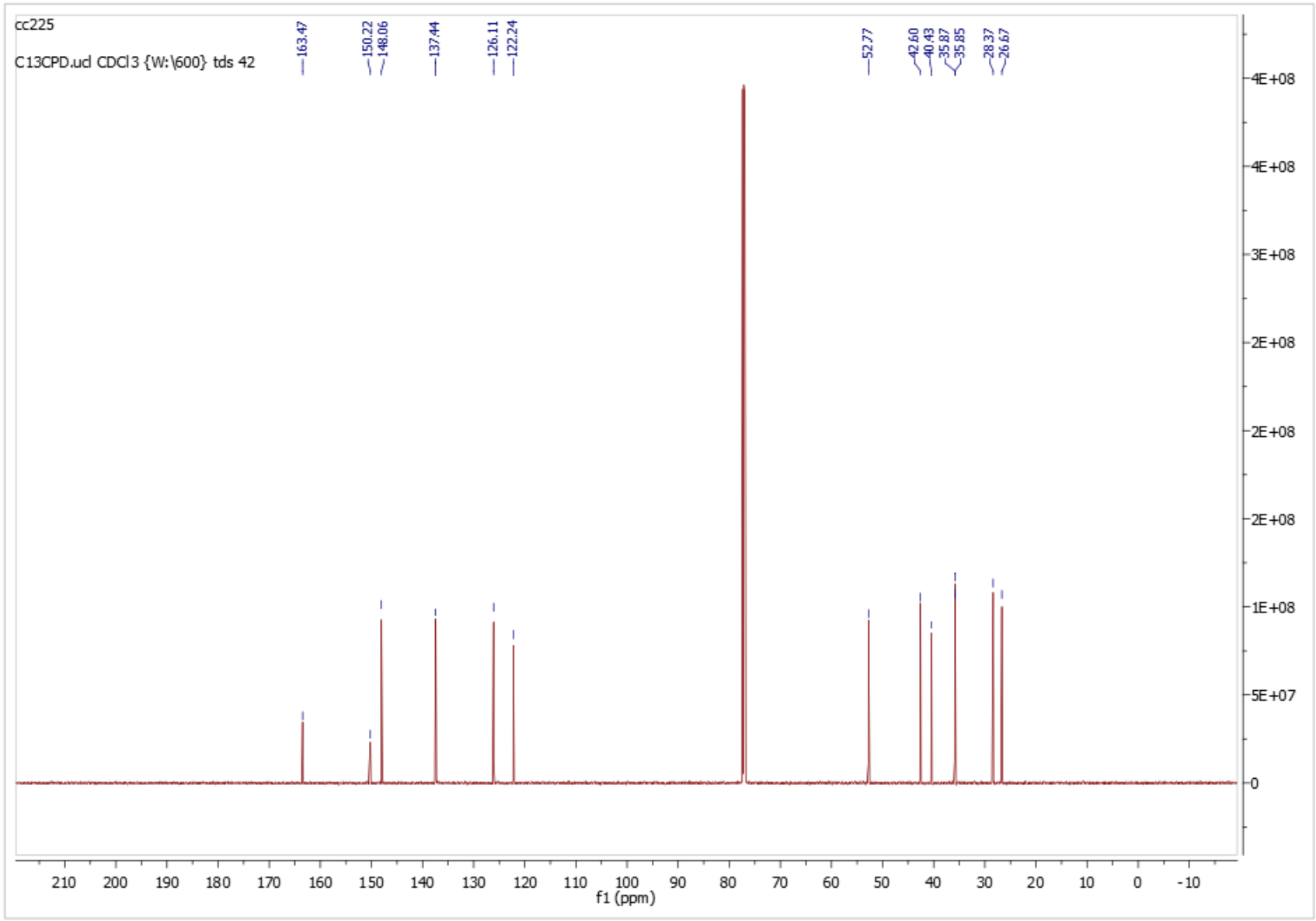
N-((1S,2S,4R)-1,7,7-Trimethylbicyclo[2.2.1] **1**



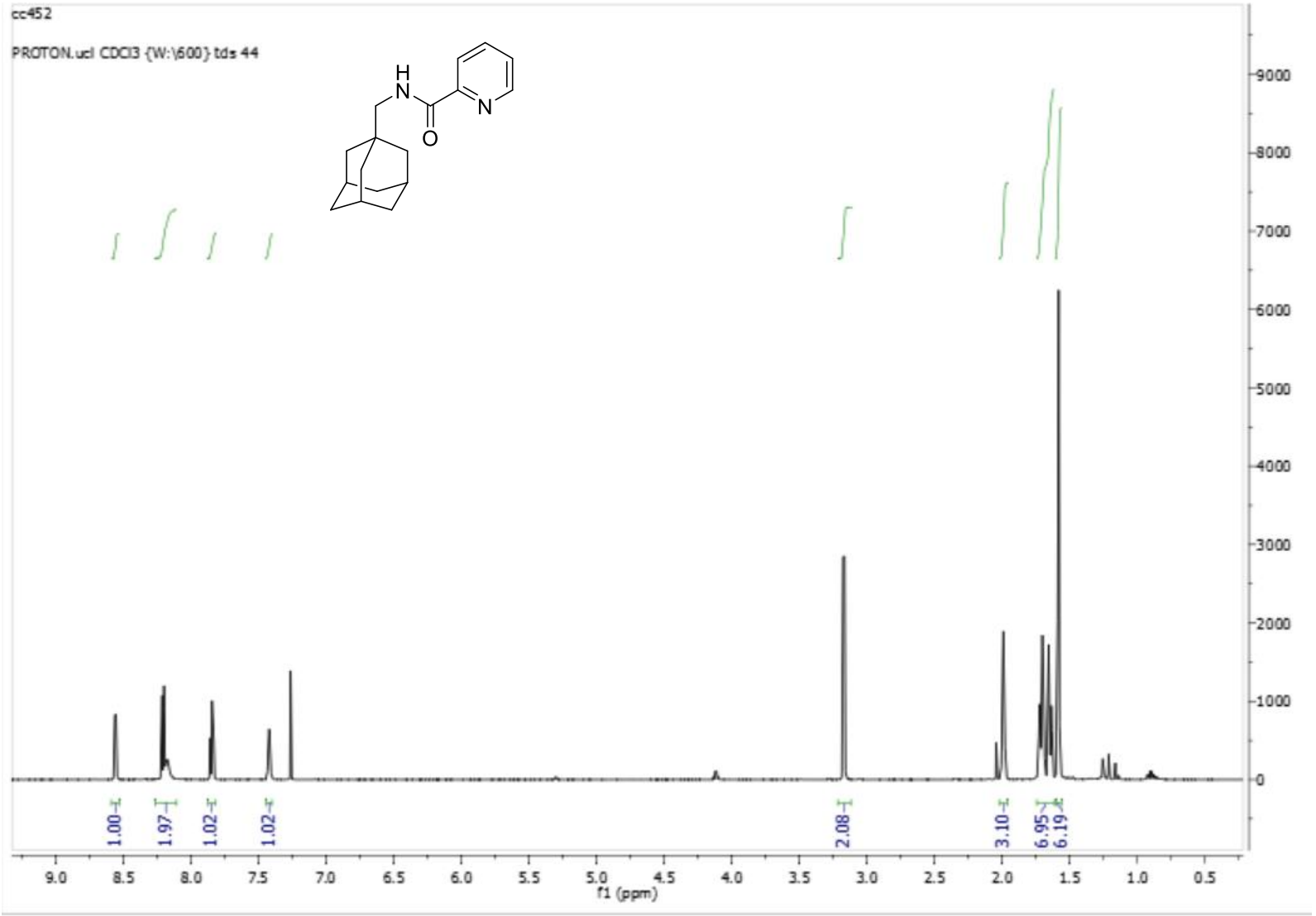

cc199-2
C13_DayTime.ucl CDCl3 {W:\600} tds 38
164.34
150.27
148.11
137.46
126.09
122.33
53.92
50.02
48.38
45.15
37.66
28.56
28.24
19.99
18.88
13.90
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

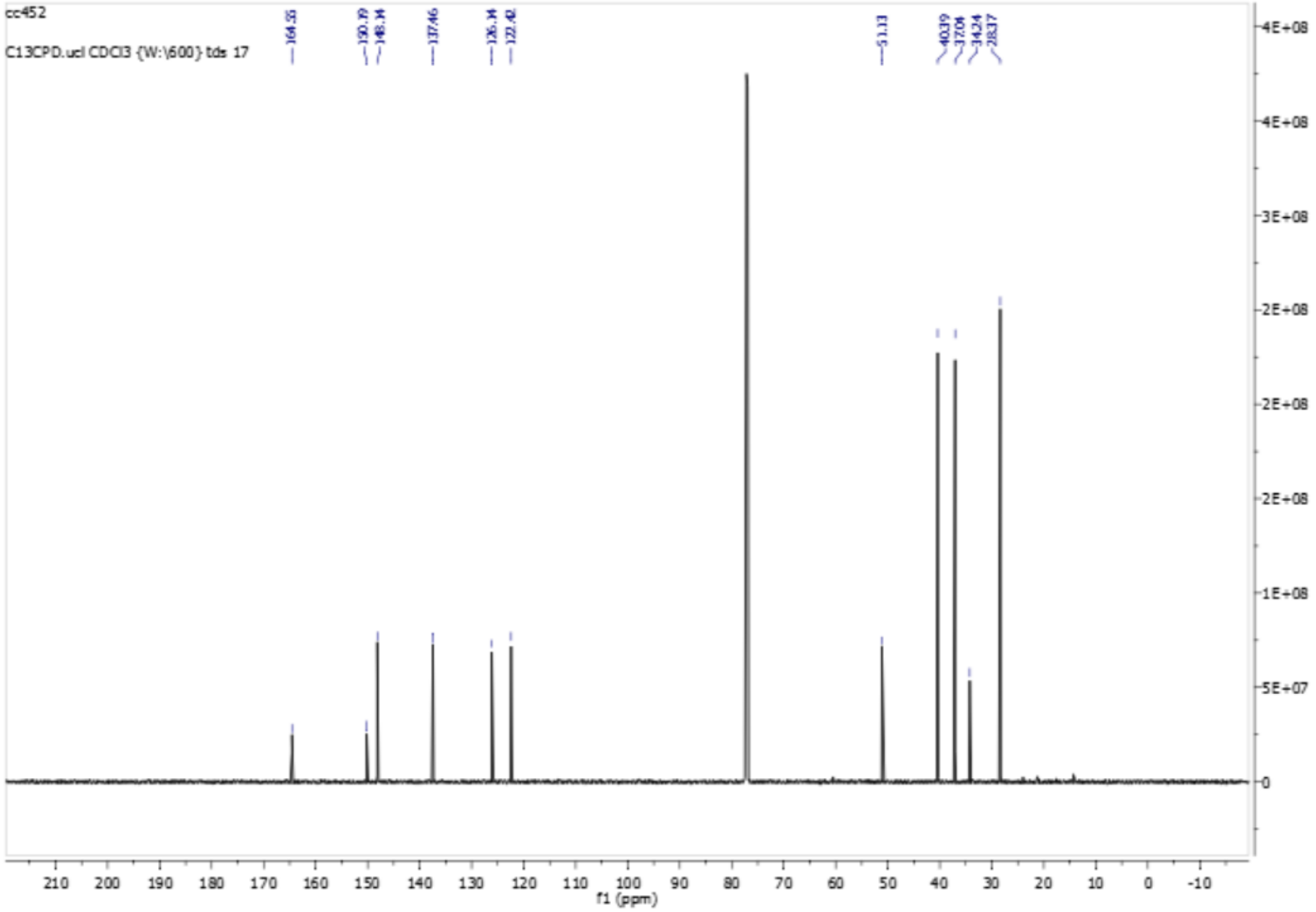
exo-*N*-(Bicyclo[2.2.1]heptan-2-yl)picolinamide ***3***



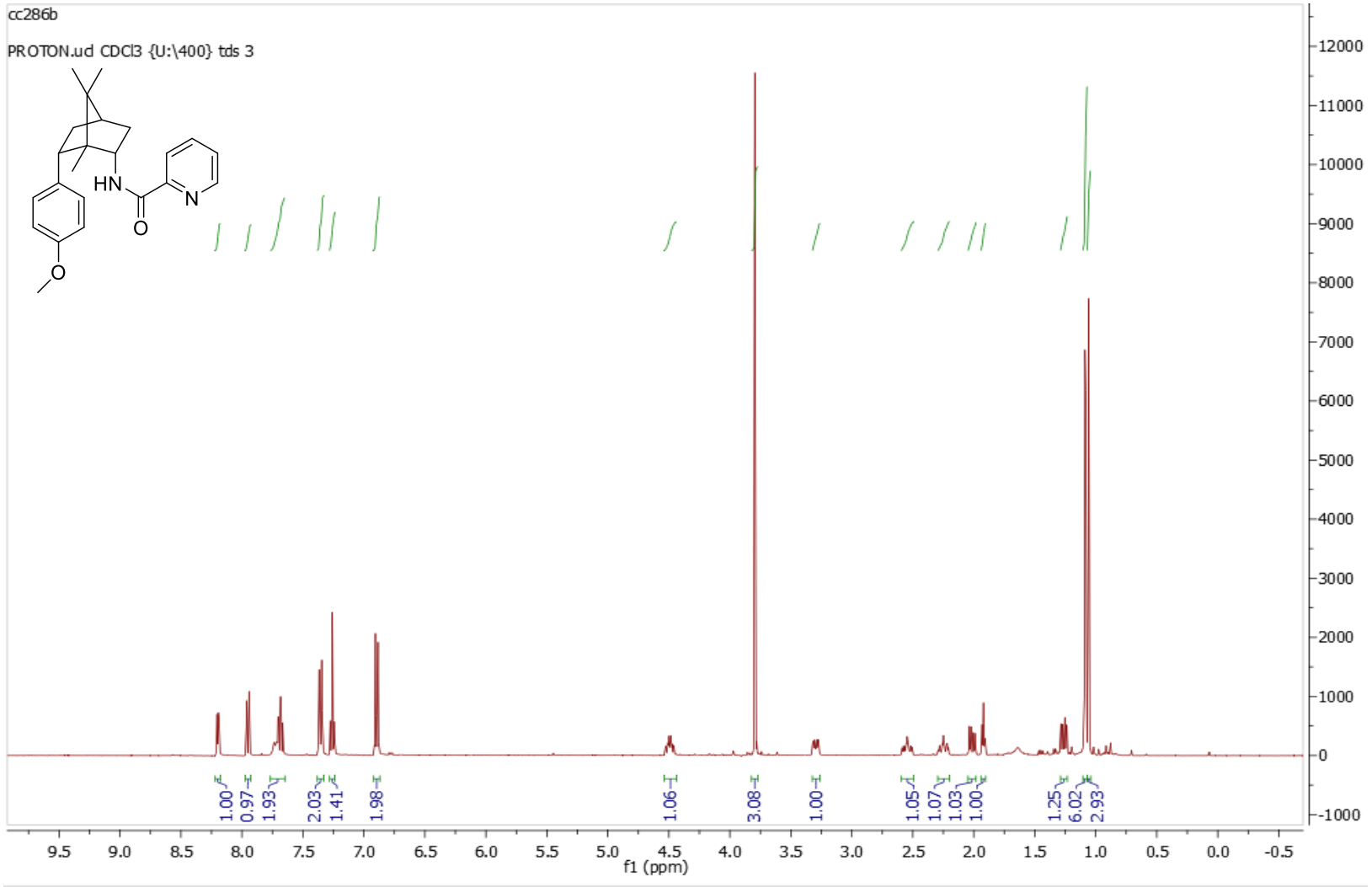

cc225
C13CPD.ucl CDCl3 {W:\600} tds 42
163.47
150.22
148.06
137.44
126.11
122.24
52.77
42.60
40.43
35.87
35.85
28.37
26.67
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

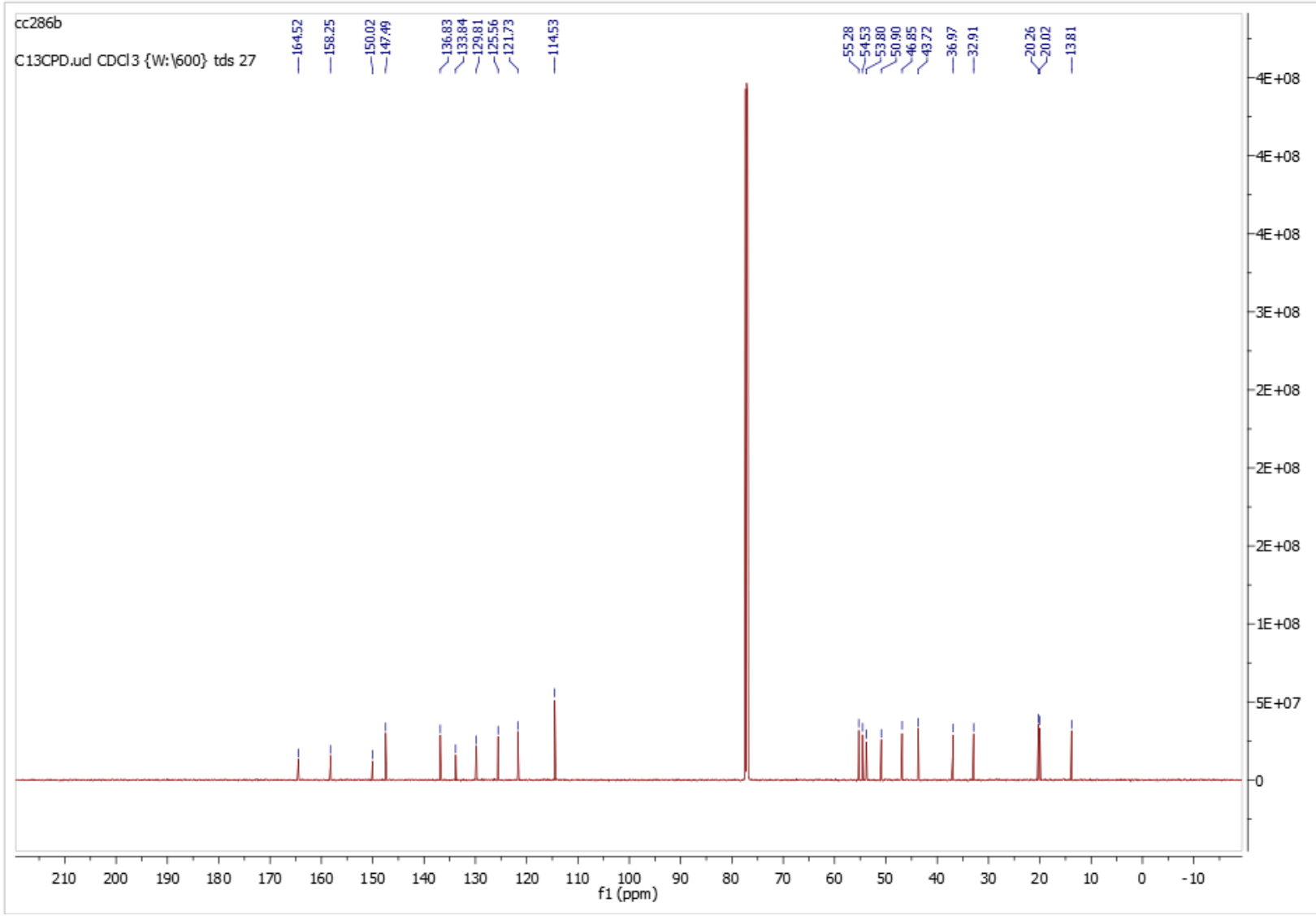
N-(((3R,5R,7R)-adamantan-1-yl)methyl)picolinamide **5**



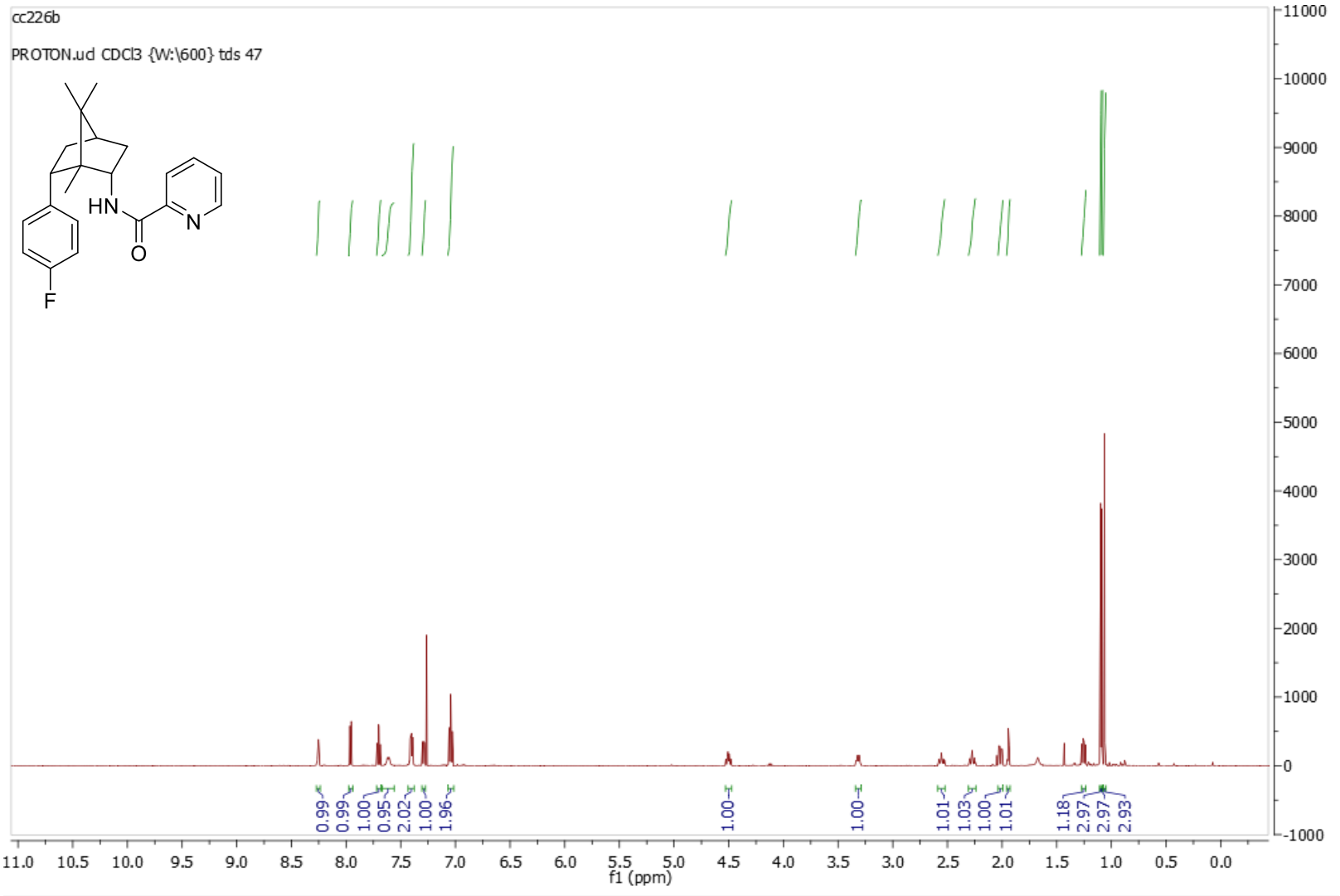

cc452
C13CPD.ucl CDCl3 {W:\600} tds 17
164.55
150.39
148.34
137.46
126.34
122.42
51.13
40.39
37.04
34.24
28.37
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

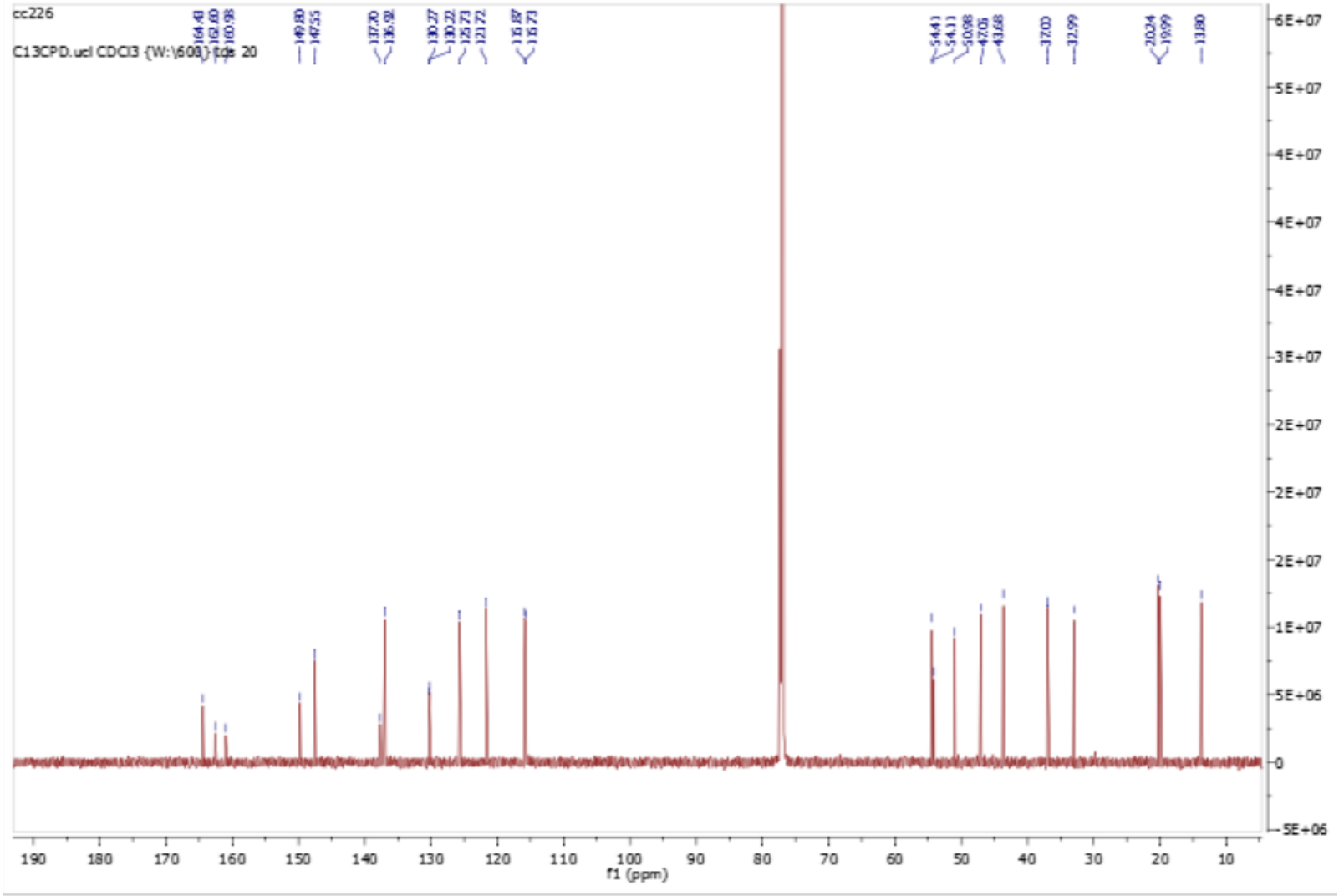
N-((1S,2S,4R,6S)-6-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide[1] **2a**



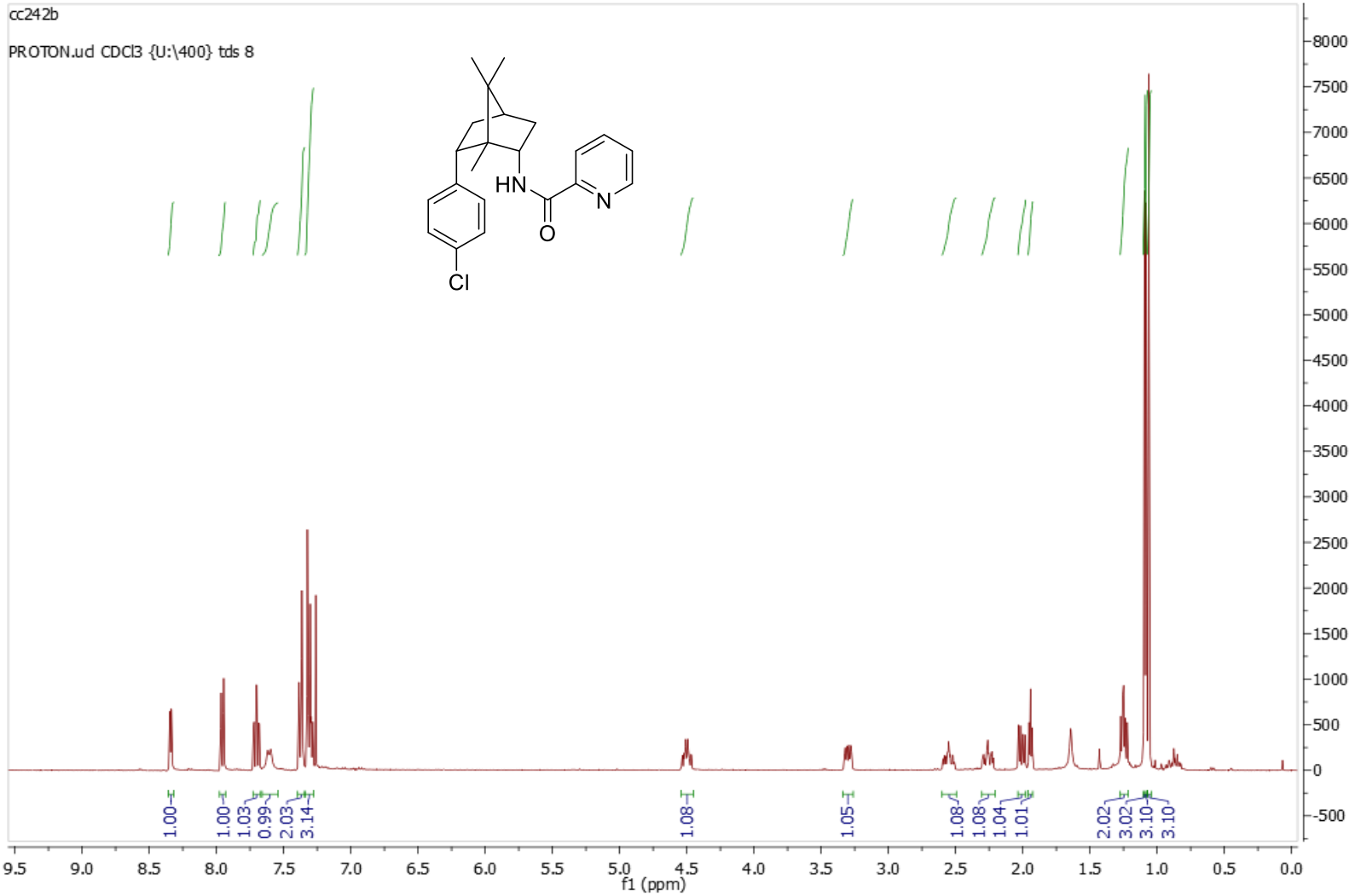

cc286b
C13CPD.ud CDCl3 {W:\600} tds 27
164.52
158.25
150.02
147.49
136.83
133.84
129.81
125.56
121.73
114.53
55.28
54.53
53.80
50.90
46.85
43.72
36.97
32.91
20.26
20.02
13.81
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

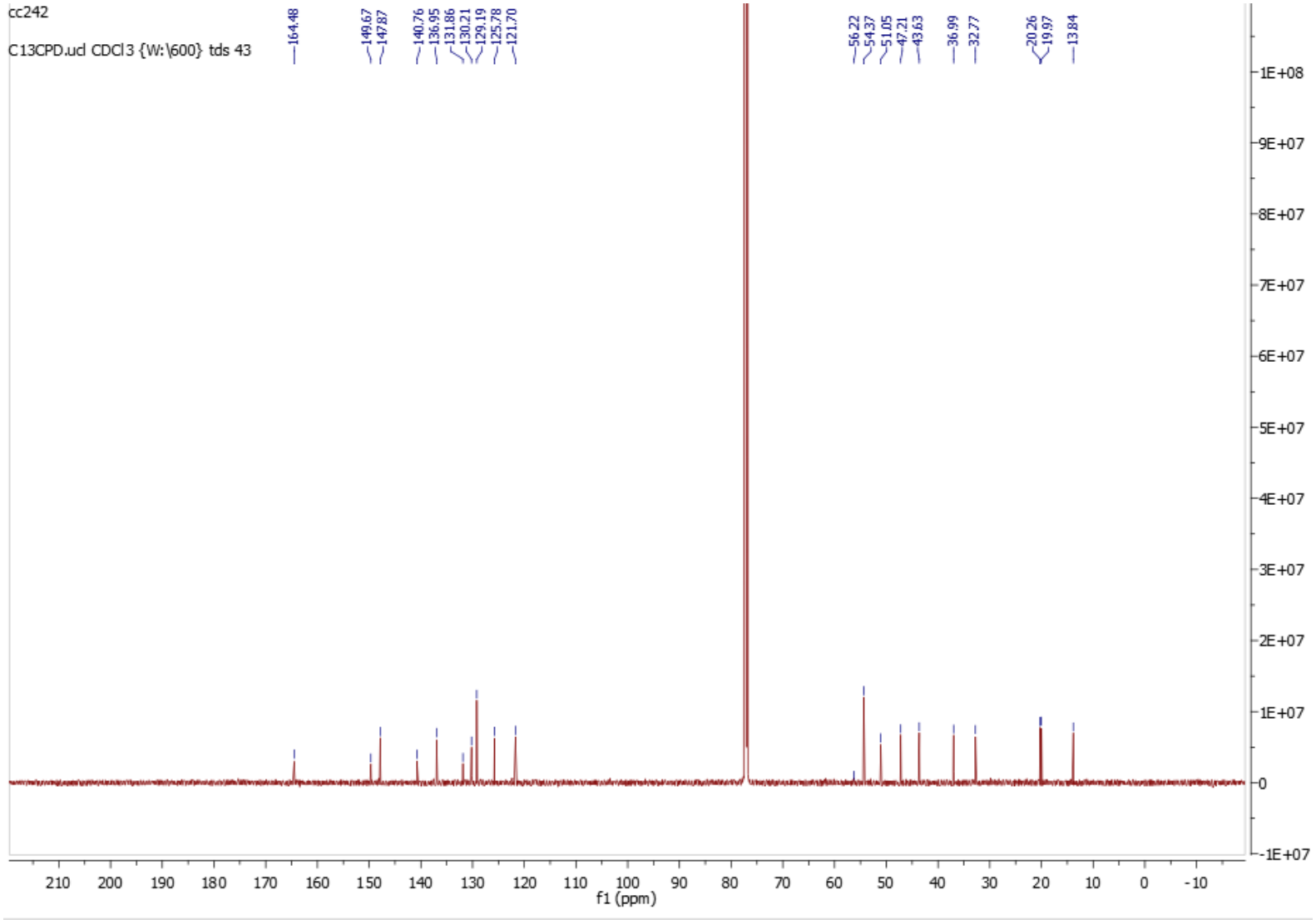
N-((1*S*,2*S*,4*R*,6*S*)-6-(4-fluorophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2b**



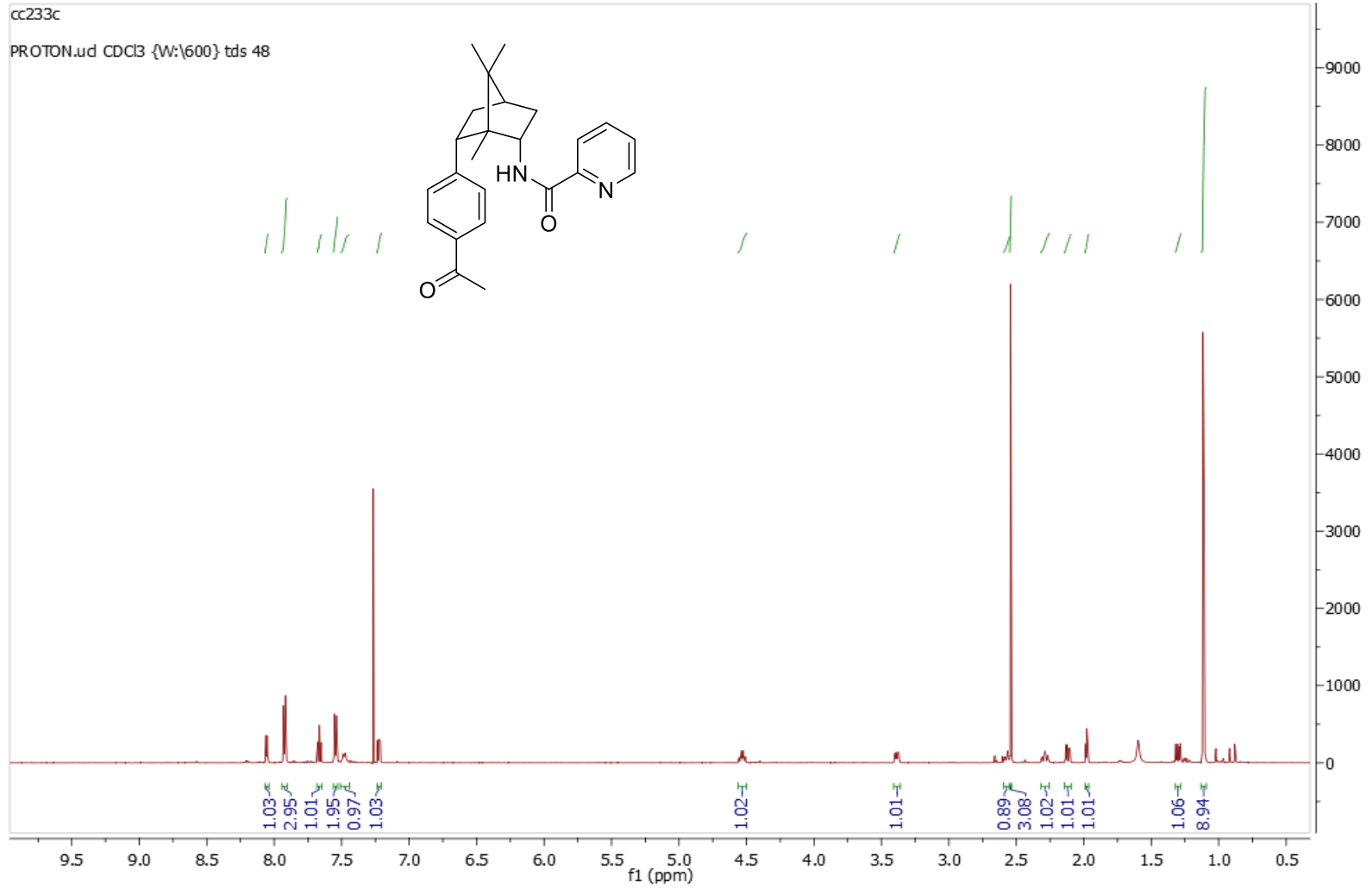

cc226
C13CPD.ucl CDCl3 {W:\600} tde 20
164.41
162.60
160.98
149.80
147.55
137.70
136.92
130.27
130.22
125.73
123.72
116.87
116.73
54.41
54.11
50.98
47.05
43.68
37.03
32.99
20.24
19.99
13.80
6E+07
5E+07
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
-5E+06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

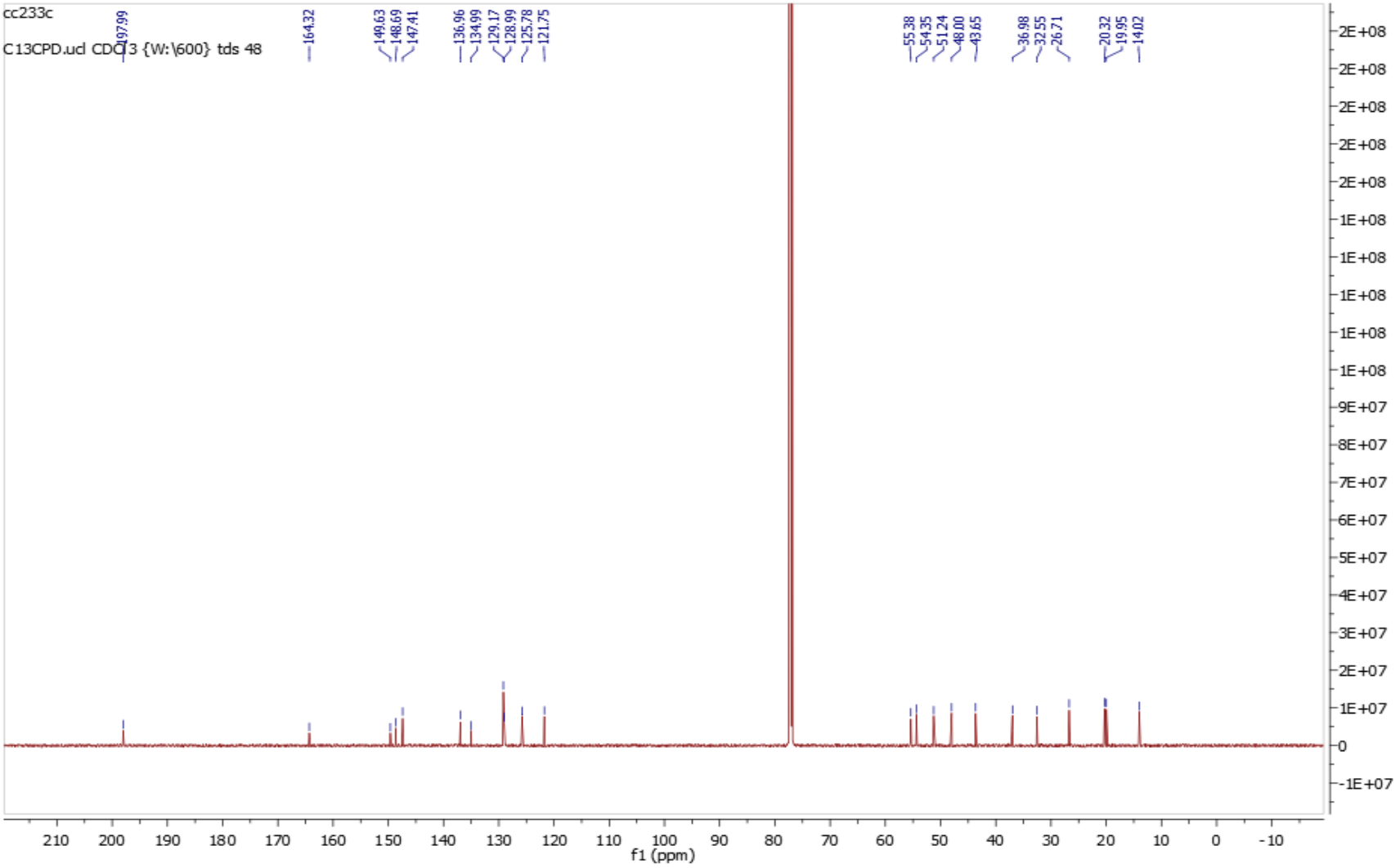
N-((1*S*,2*S*,4*R*,6*S*)-6-(4-chlorophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2c**



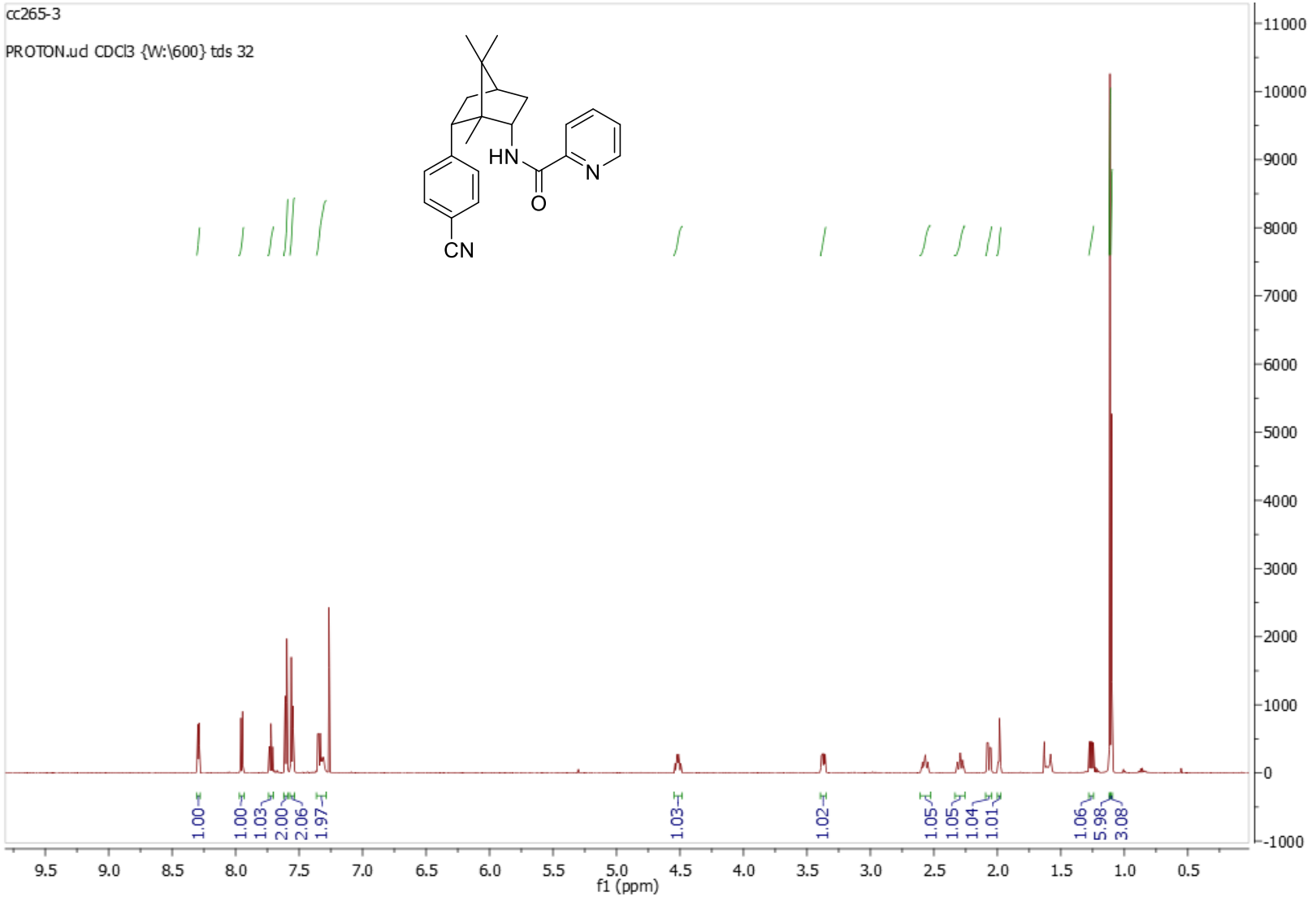

cc242
C13CPD.ucl CDCl3 {W:\600} tds 43
164.48
149.67
147.87
140.76
136.95
131.86
130.21
129.19
125.78
121.70
56.22
54.37
51.05
47.21
43.63
36.99
32.77
20.26
19.97
13.84
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

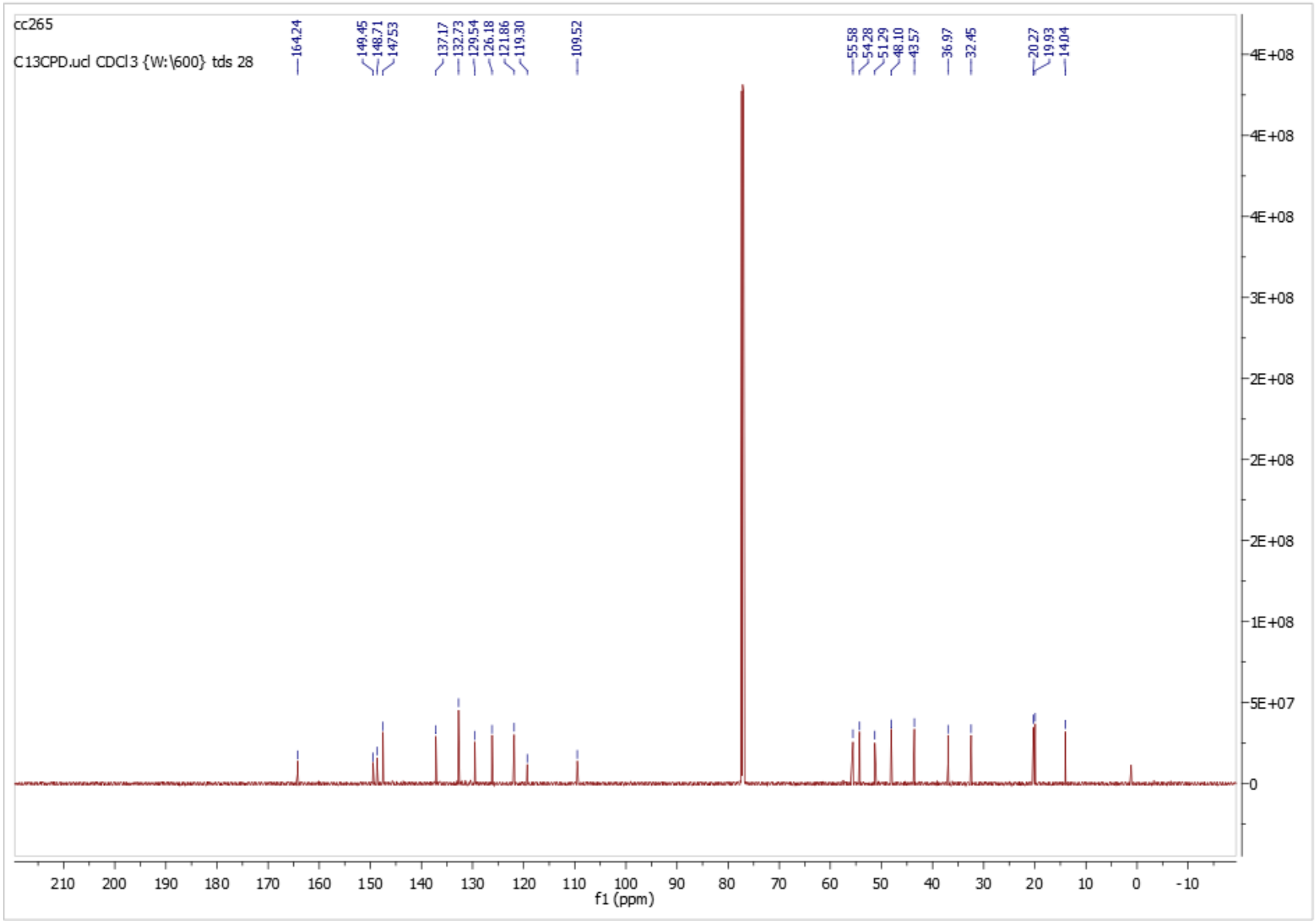
N-((1*S*,2*S*,4*R*,6*S*)-6-(4-Acetylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2d**



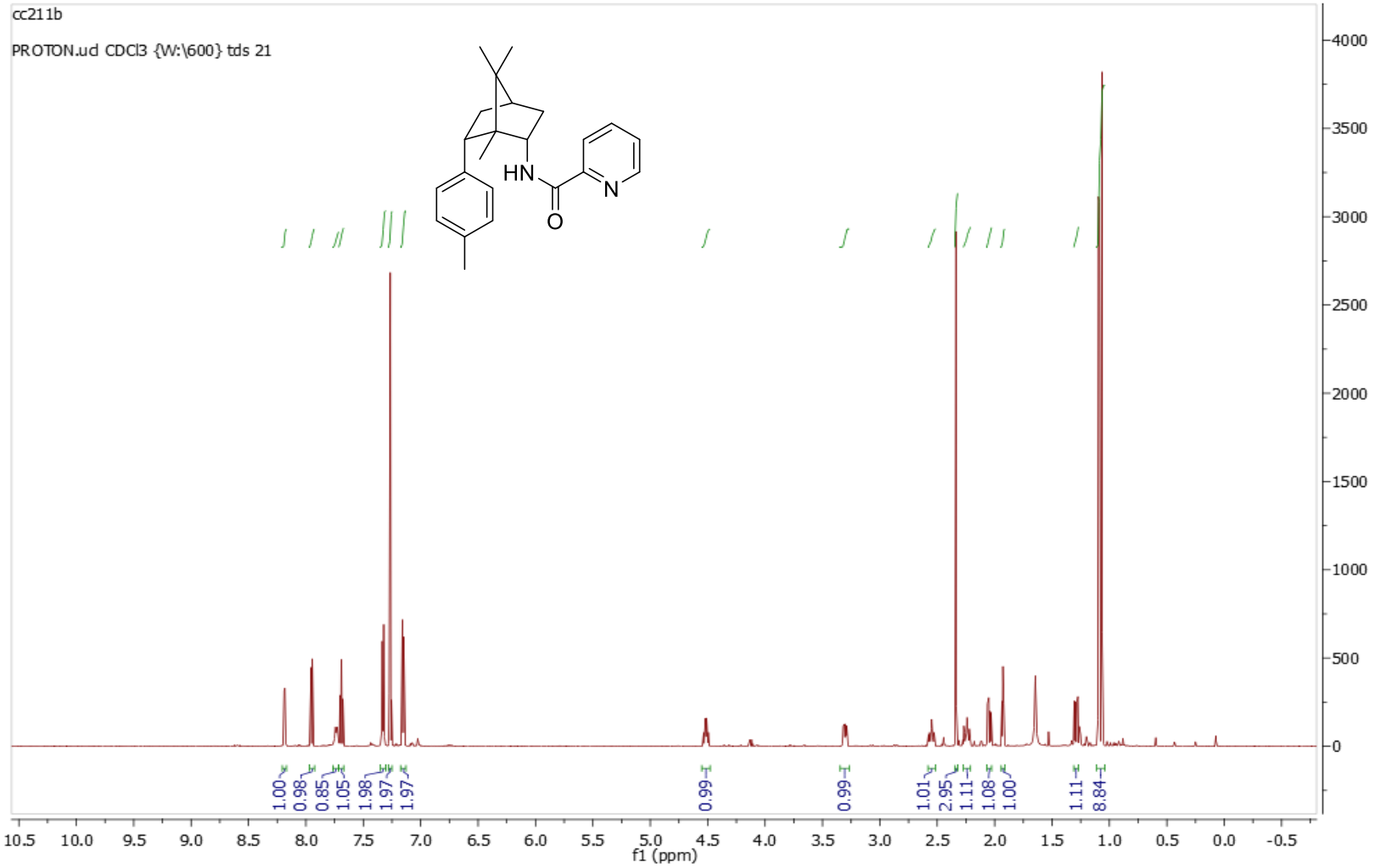

cc233c
C13CPD.ucl CDCl3 {W:\600} tds 48
197.99
164.32
149.63
148.69
147.41
136.96
134.99
129.17
128.99
125.78
121.75
55.38
54.35
51.24
48.00
43.65
36.98
32.55
26.71
20.32
19.95
14.02
f1 (ppm)

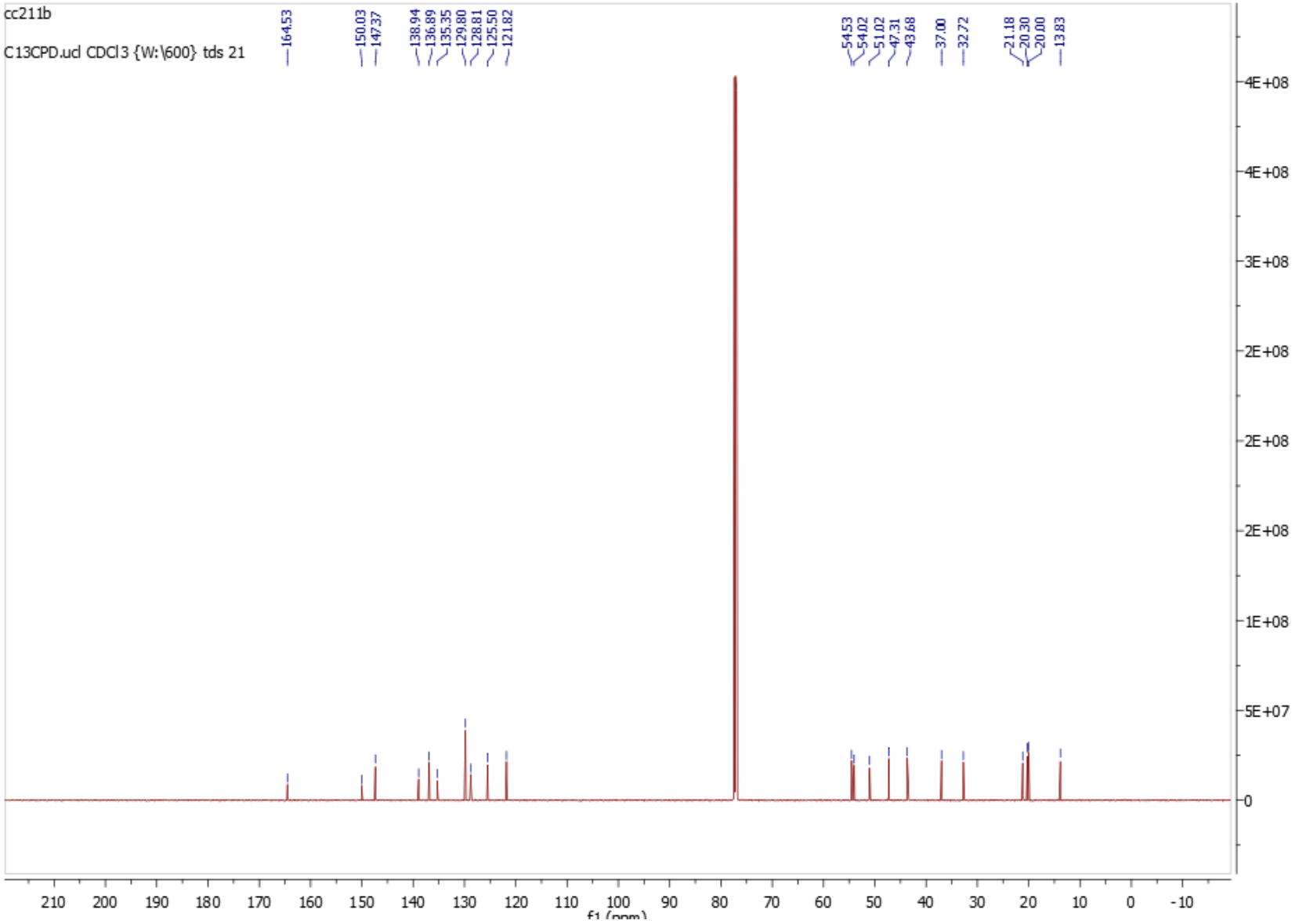
N-((1*S*,2*S*,4*R*,6*S*)-6-(4-Cyanophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2e**



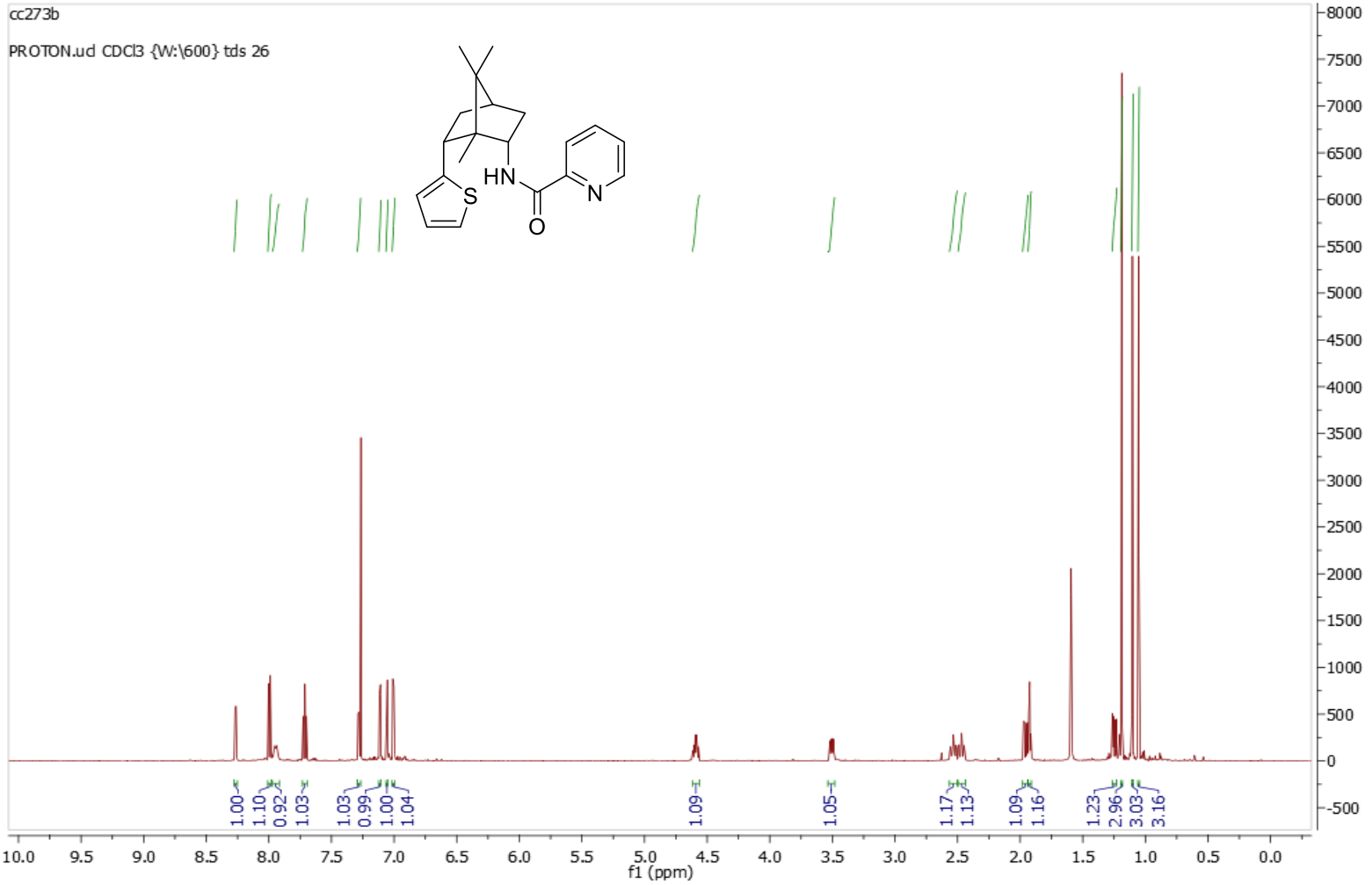

cc265
C13CPD.ucl CDCl3 {W:\600} tds 28
164.24
149.45
148.71
147.53
137.17
132.73
129.54
126.18
121.86
119.30
109.52
55.58
54.28
51.29
48.10
43.57
36.97
32.45
20.27
19.93
14.04
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

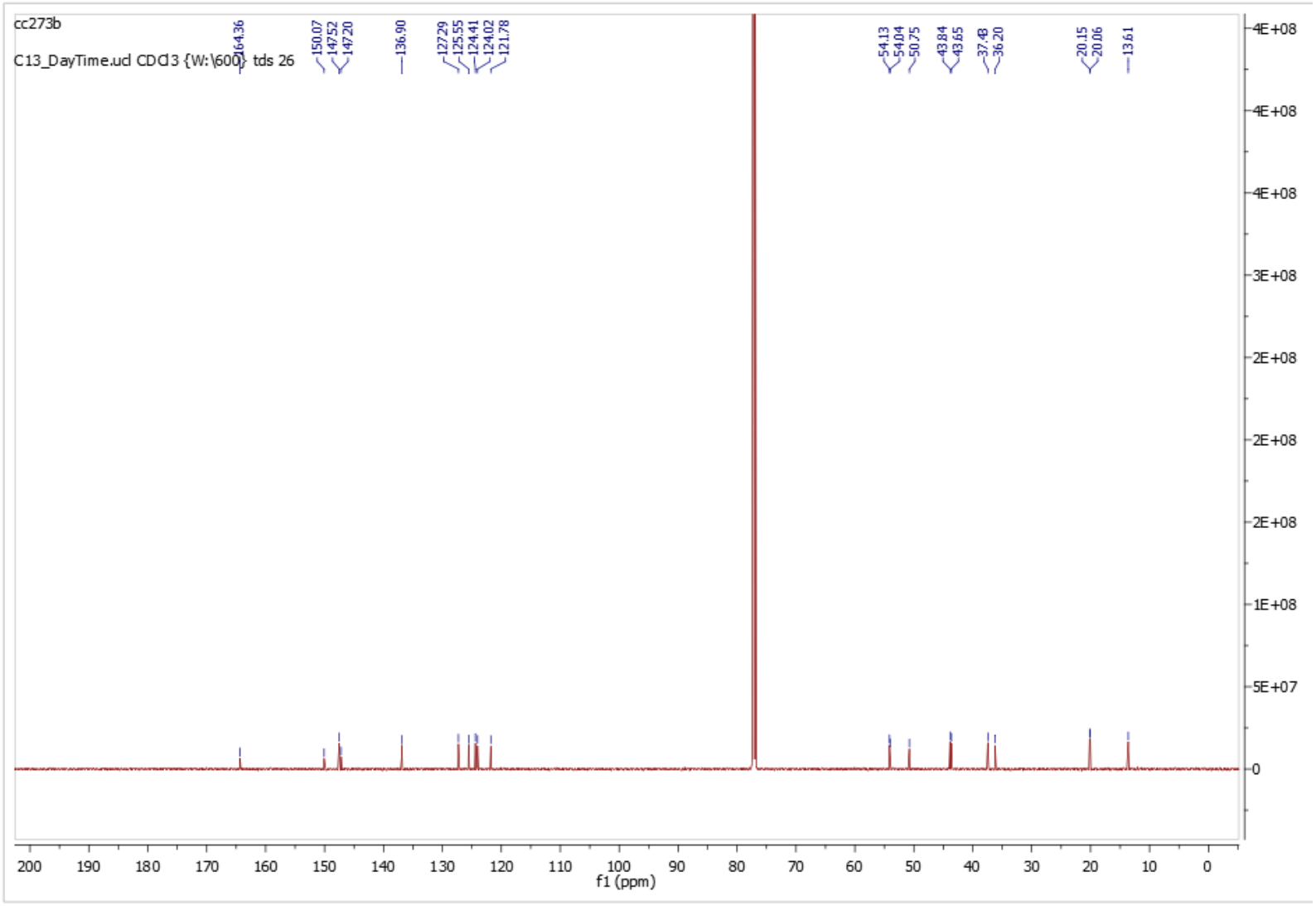
1,7,7-trimethyl-6-(*p*-tolyl)bicycle[2.2.1]heptan-2-yl)picolinamide **2f**



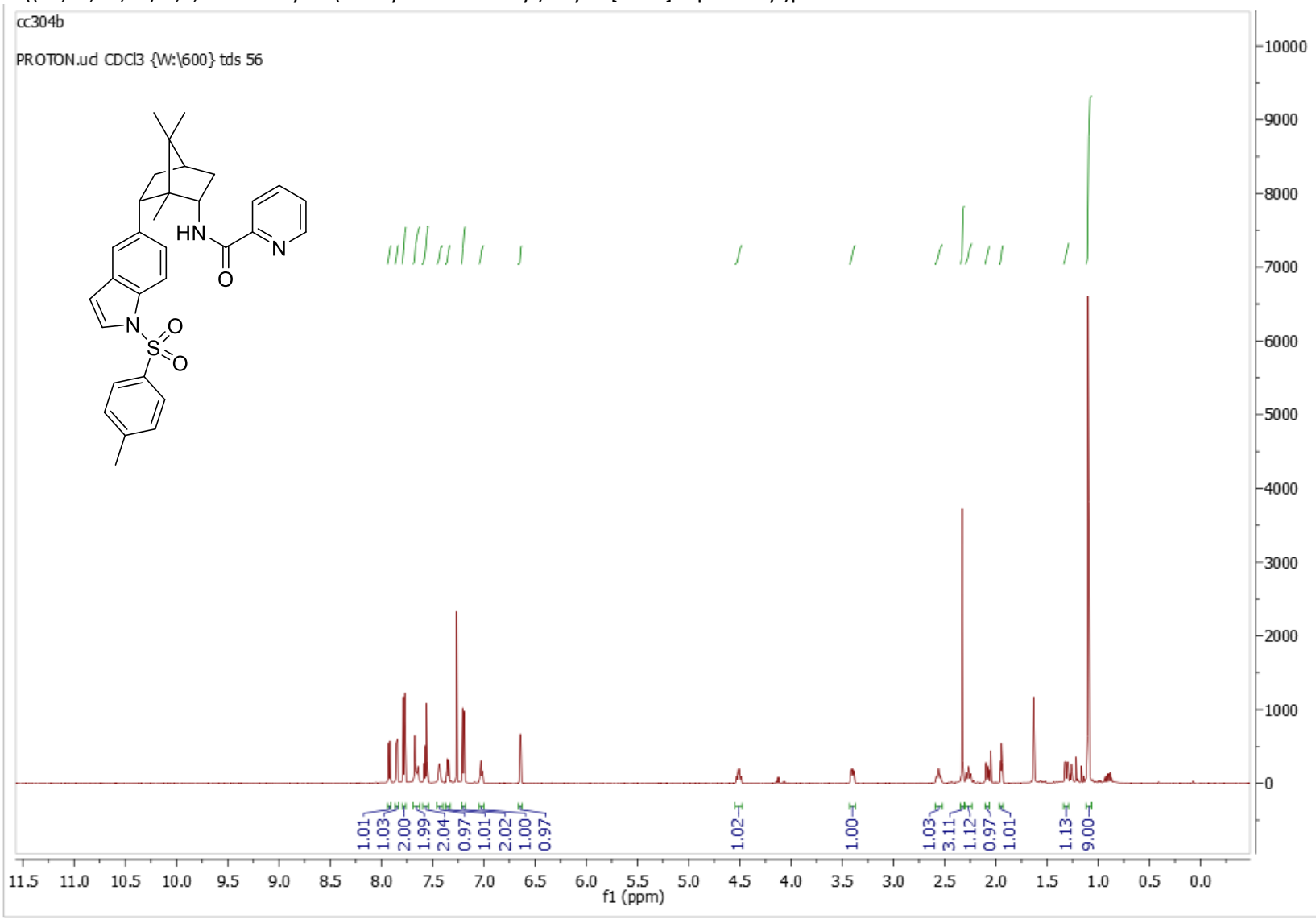

cc211b
C13CPD.ucl CDCl3 {W:\600} tds 21
164.53
150.03
147.37
138.94
136.89
135.35
129.80
128.81
125.50
121.82
54.53
54.02
51.02
47.31
43.68
37.00
32.72
21.18
20.30
20.00
13.83
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

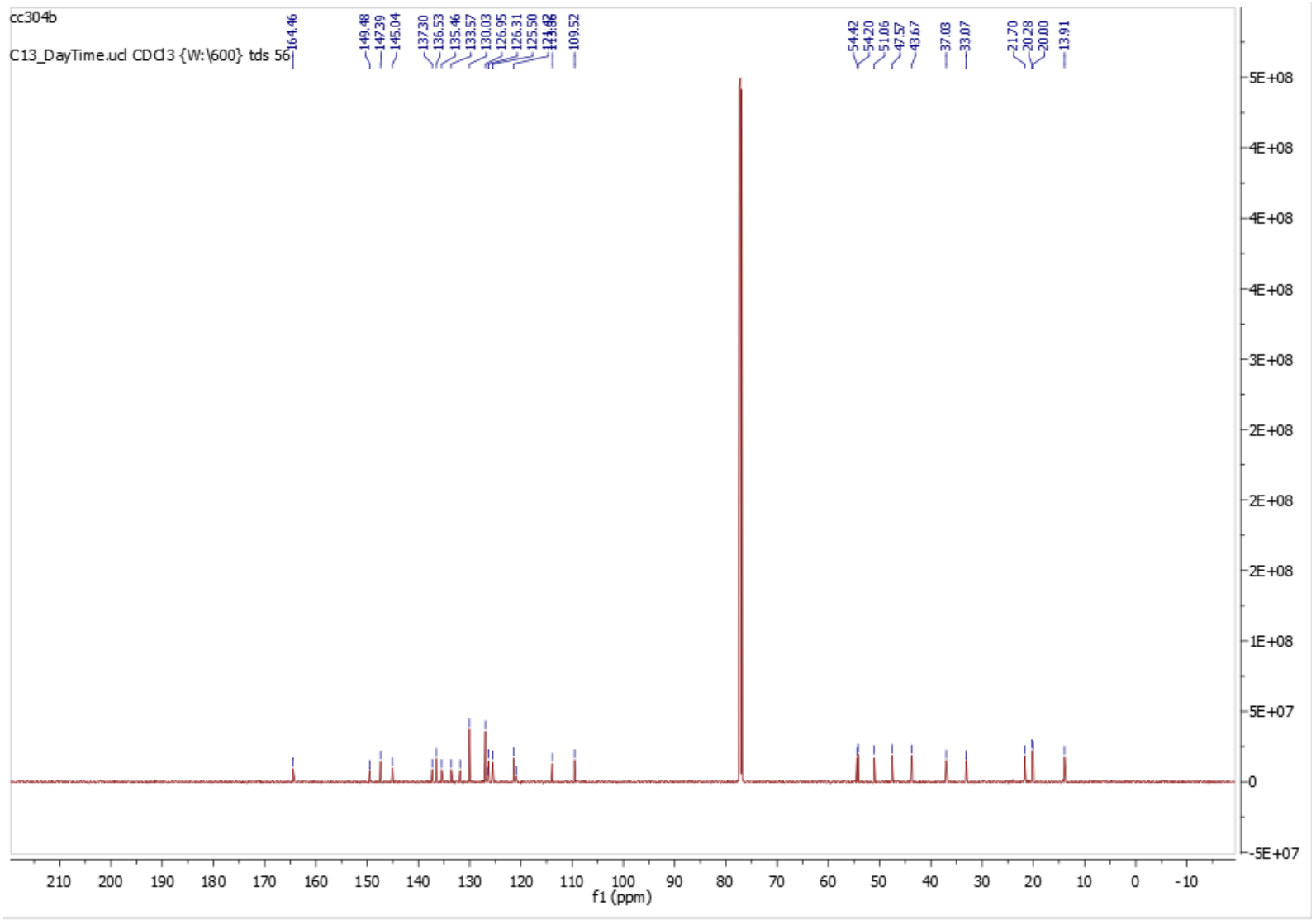
N-((1*S*,2*S*,4*R*,6*R*)-1,7,7-Trimethyl-6-(thiophen-2-yl)bicycle[2.2.1]heptan-2-yl)picolinamide **2g**



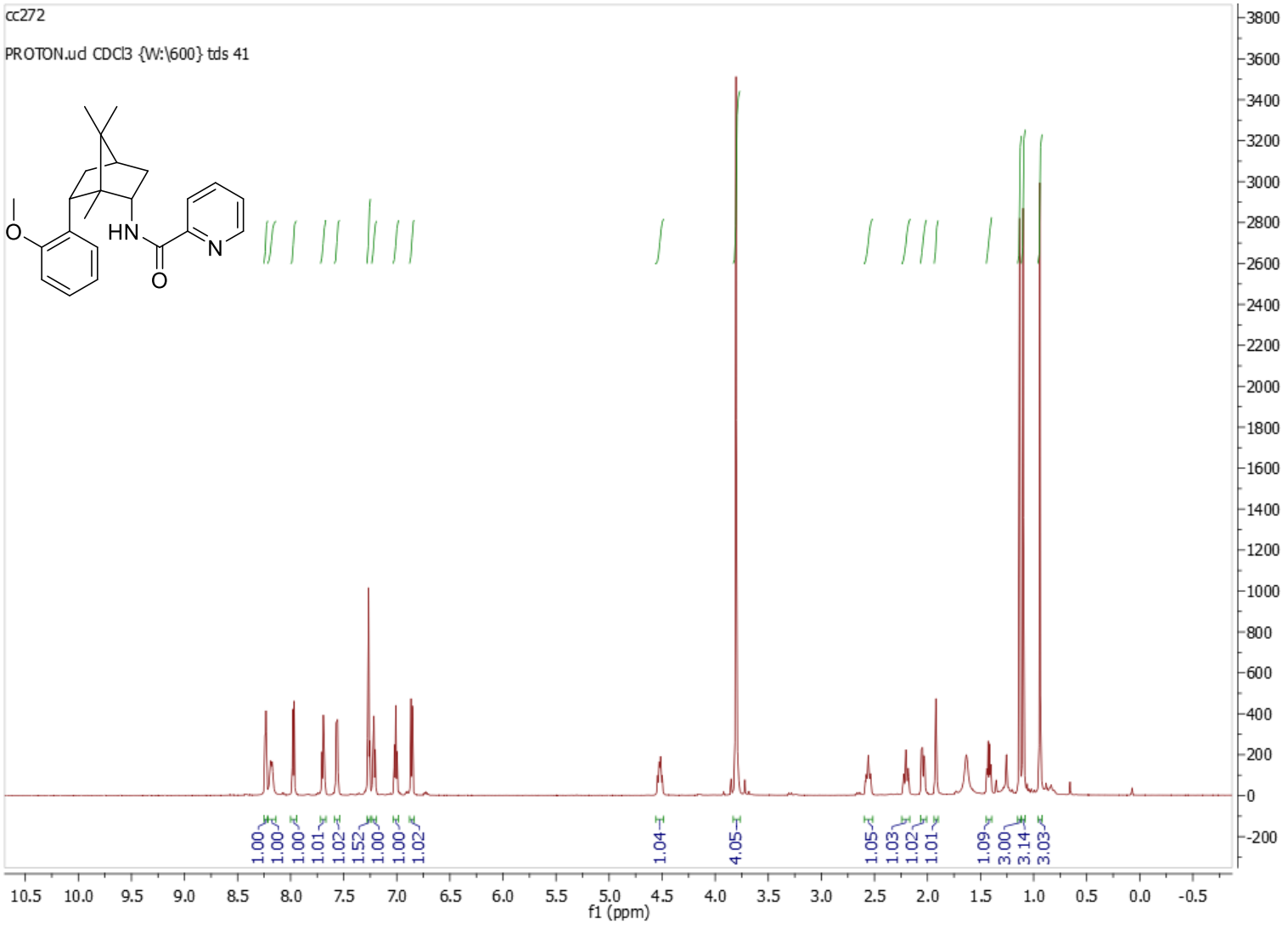

cc273b
C13_DayTime.ucl CDCl3 {W:\600} tds 26
164.36
150.07
147.52
147.20
136.90
127.29
125.55
124.41
124.02
121.78
54.13
54.04
50.75
43.84
43.65
37.48
36.20
20.15
20.06
13.61
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

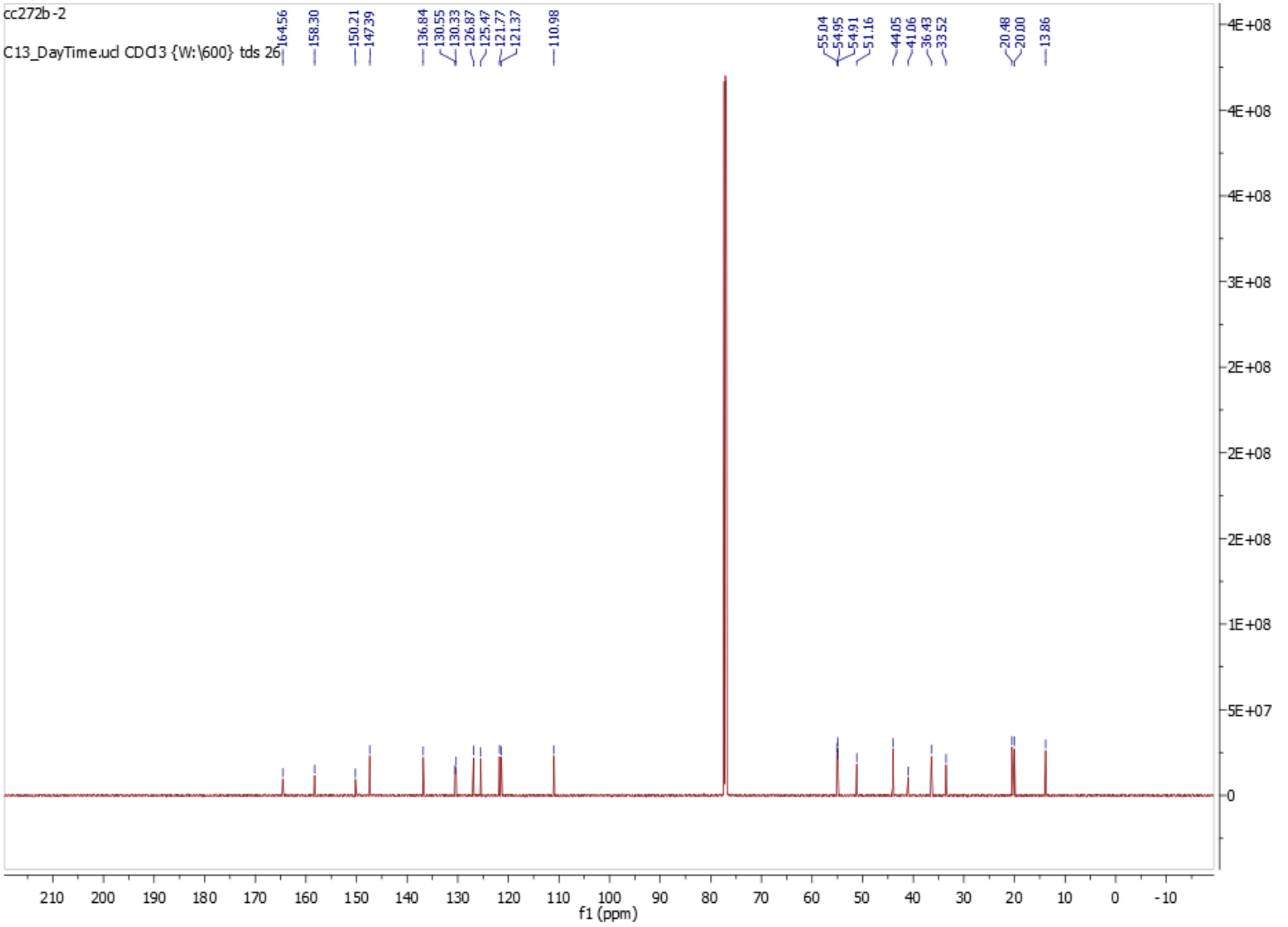
N-((1*S*,2*S*,4*R*,6*S*)-1,7,7-trimethyl-6-(1-tosyl-1*H*-indol-5-yl)bicycle[2.2.1]heptan-2-yl)picolinamide **2h**



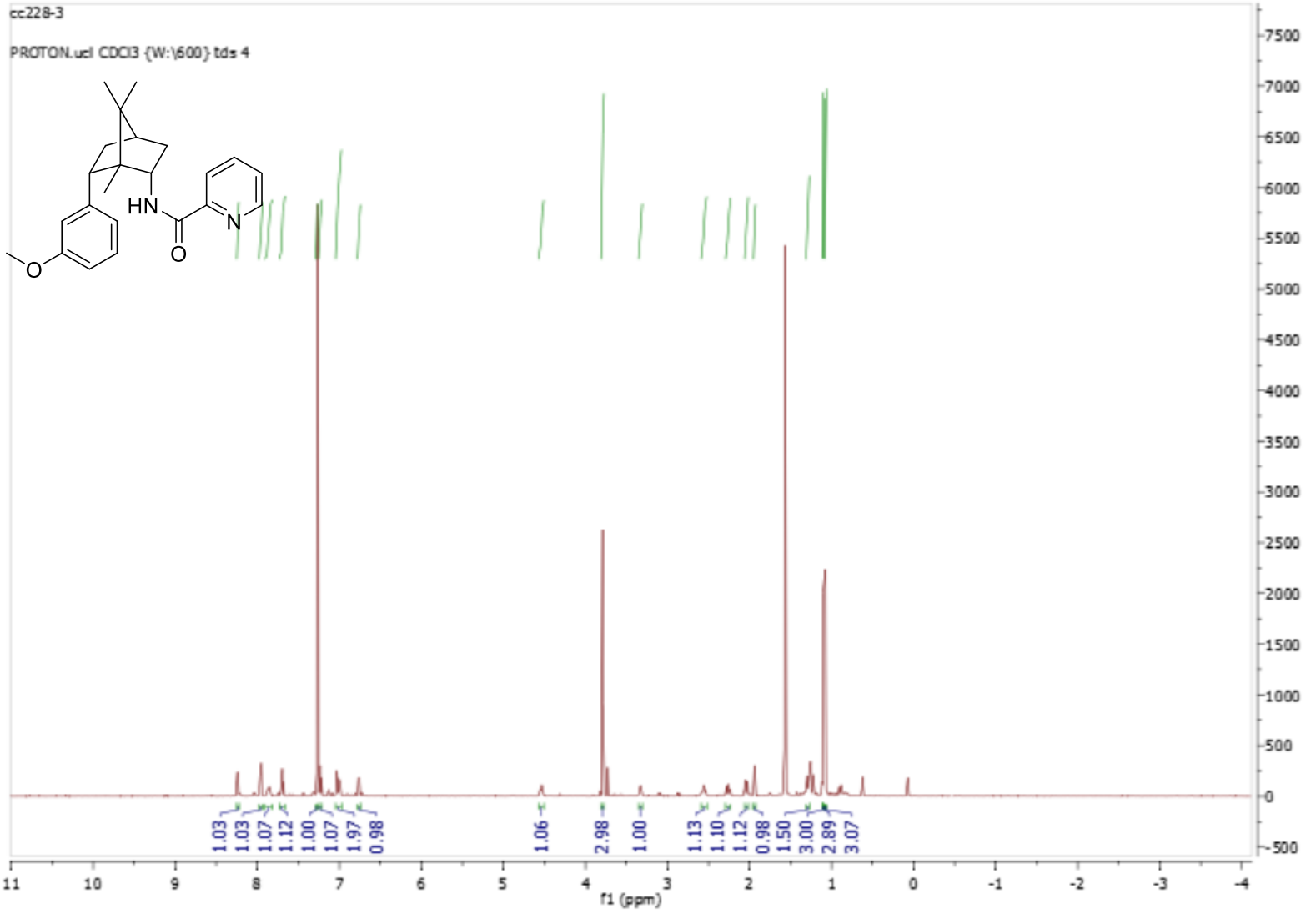

cc304b
C13_DayTime.ucl CDCl3 {W:\600} tds 56
164.46
149.48
147.39
145.04
137.30
136.53
135.46
133.57
130.03
126.95
126.31
125.50
109.52
54.42
54.20
51.06
47.57
43.67
37.03
33.07
21.70
20.28
20.00
13.91
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

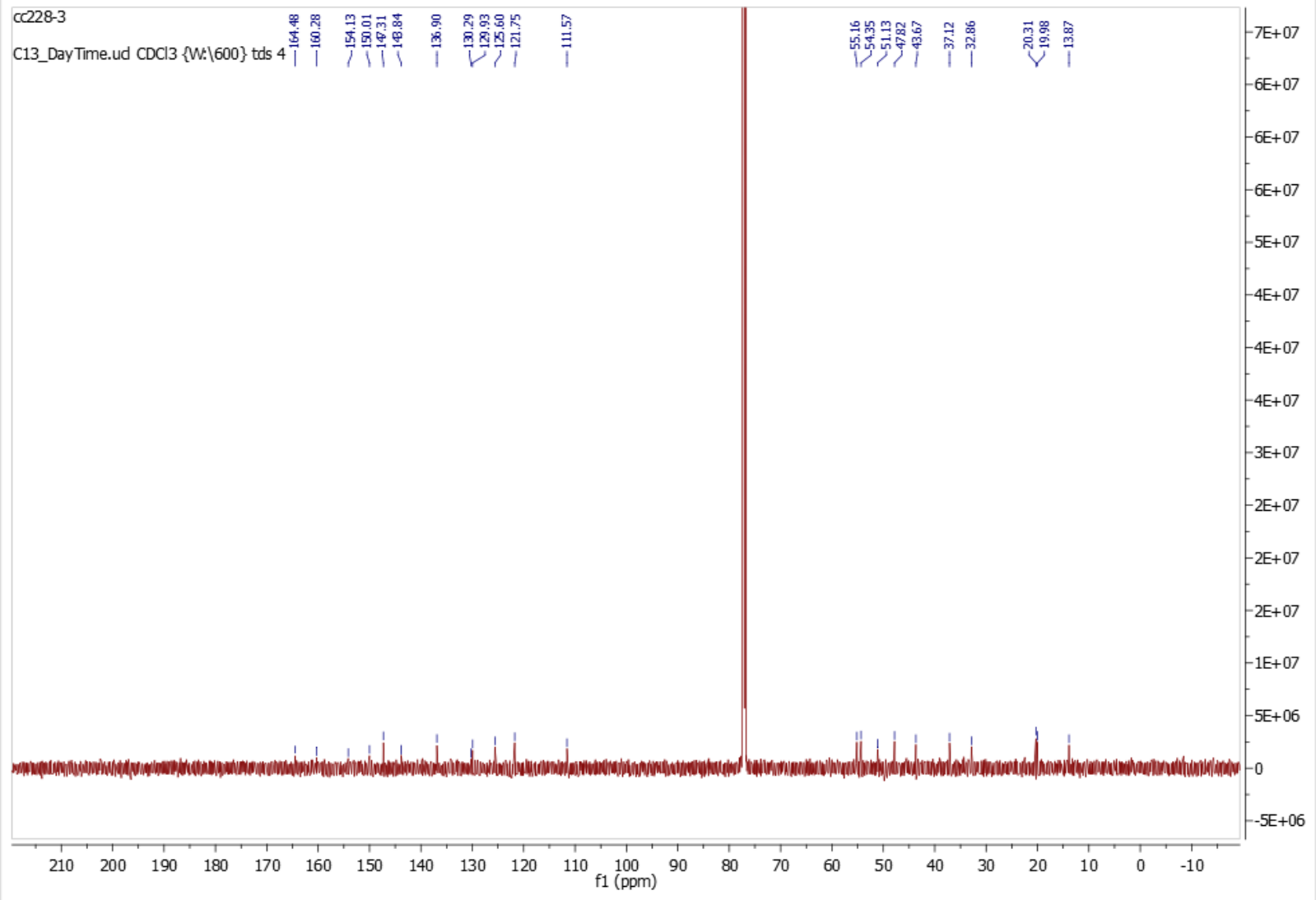
N-((1*S*,2*S*,4*R*,6*R*)-6-(2-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2i**



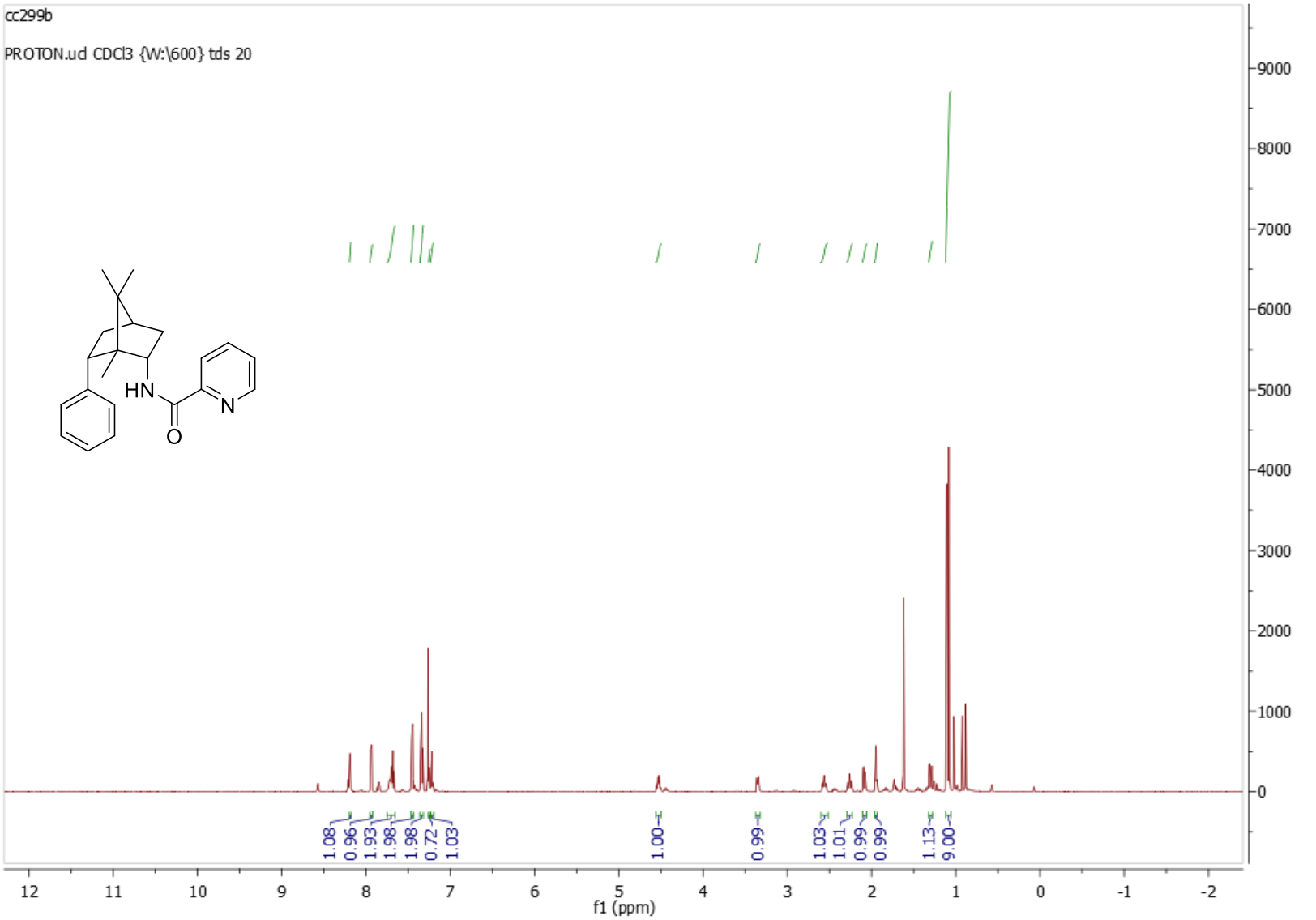

cc272b-2
C13_DayTime.ucl CDCl3 {W:\600} tds 26
164.56
158.30
150.21
147.39
136.84
130.55
130.33
126.87
125.47
121.77
121.37
110.98
55.04
54.95
54.91
51.16
44.05
41.06
36.43
33.52
20.48
20.00
13.86
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

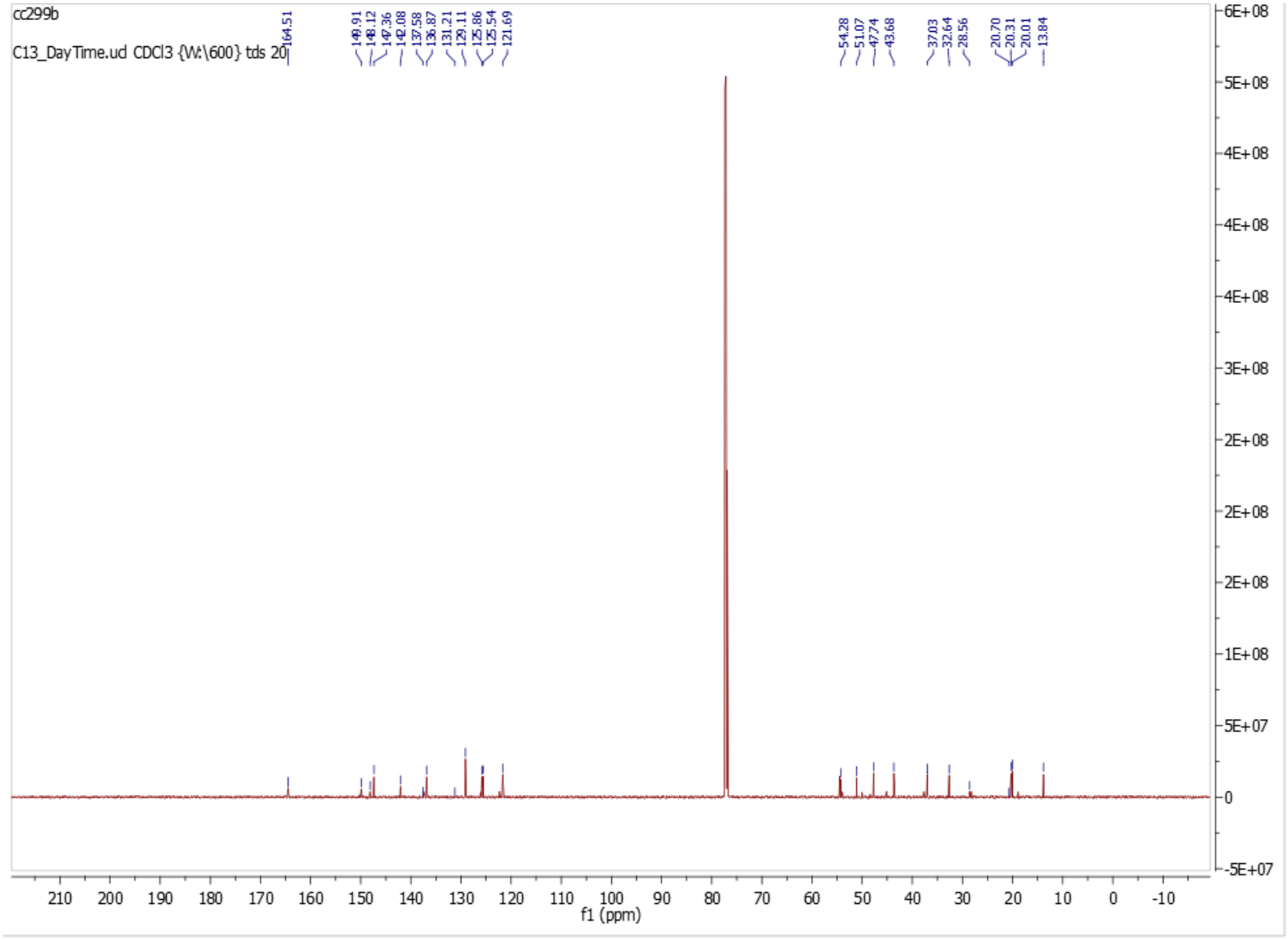
N-((1*S*,2*S*,4*R*,6*R*)-6-(3-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2j**



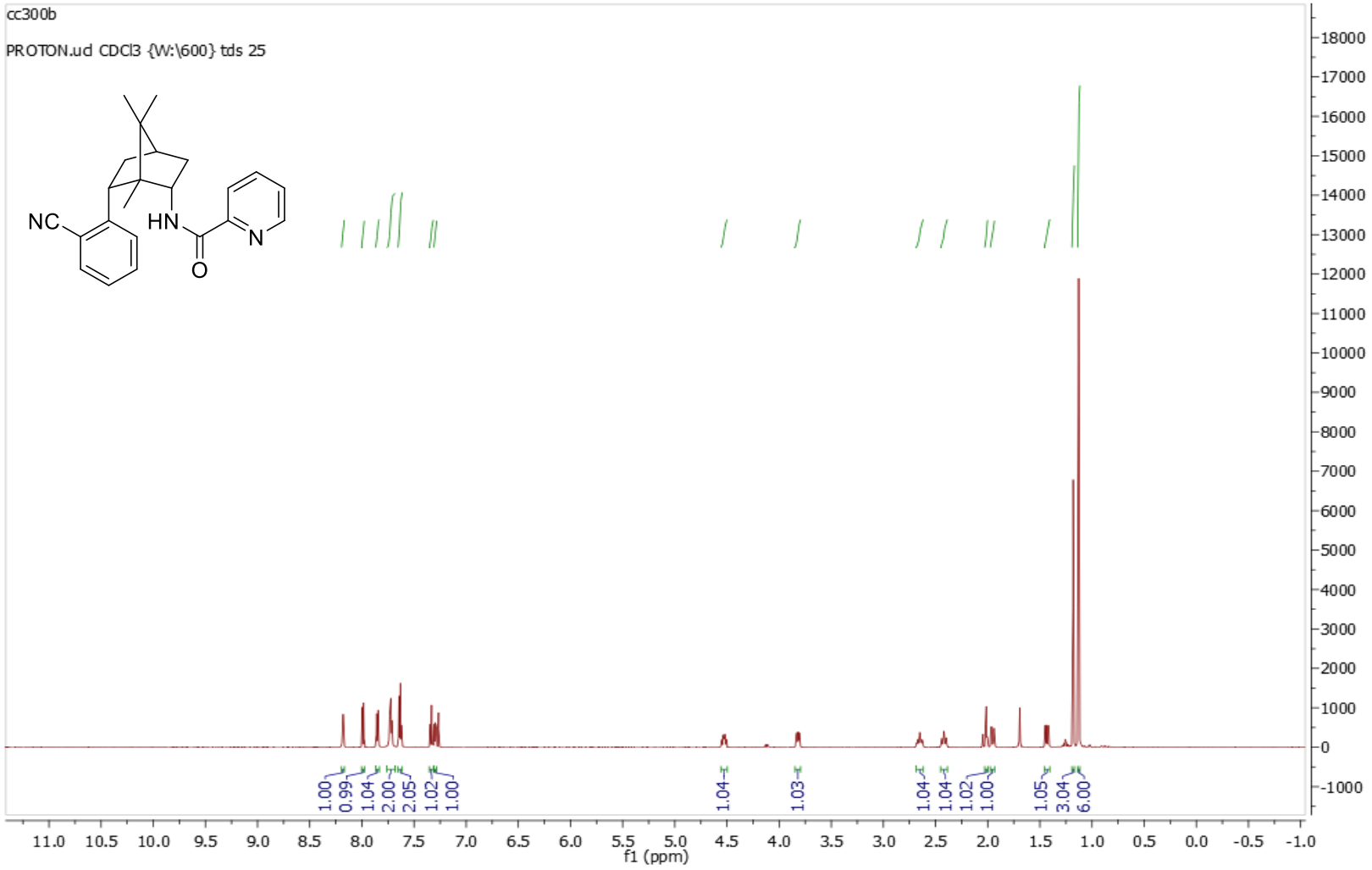

cc228-3
C13_DayTime.ud CDCl3 {W:\600} tds 4
164.48
160.28
154.13
150.01
147.31
148.84
136.90
130.29
129.93
125.60
121.75
111.57
55.16
54.35
51.13
47.82
43.67
37.12
32.86
20.31
19.98
13.87
7E+07
6E+07
6E+07
6E+07
5E+07
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
-5E+06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

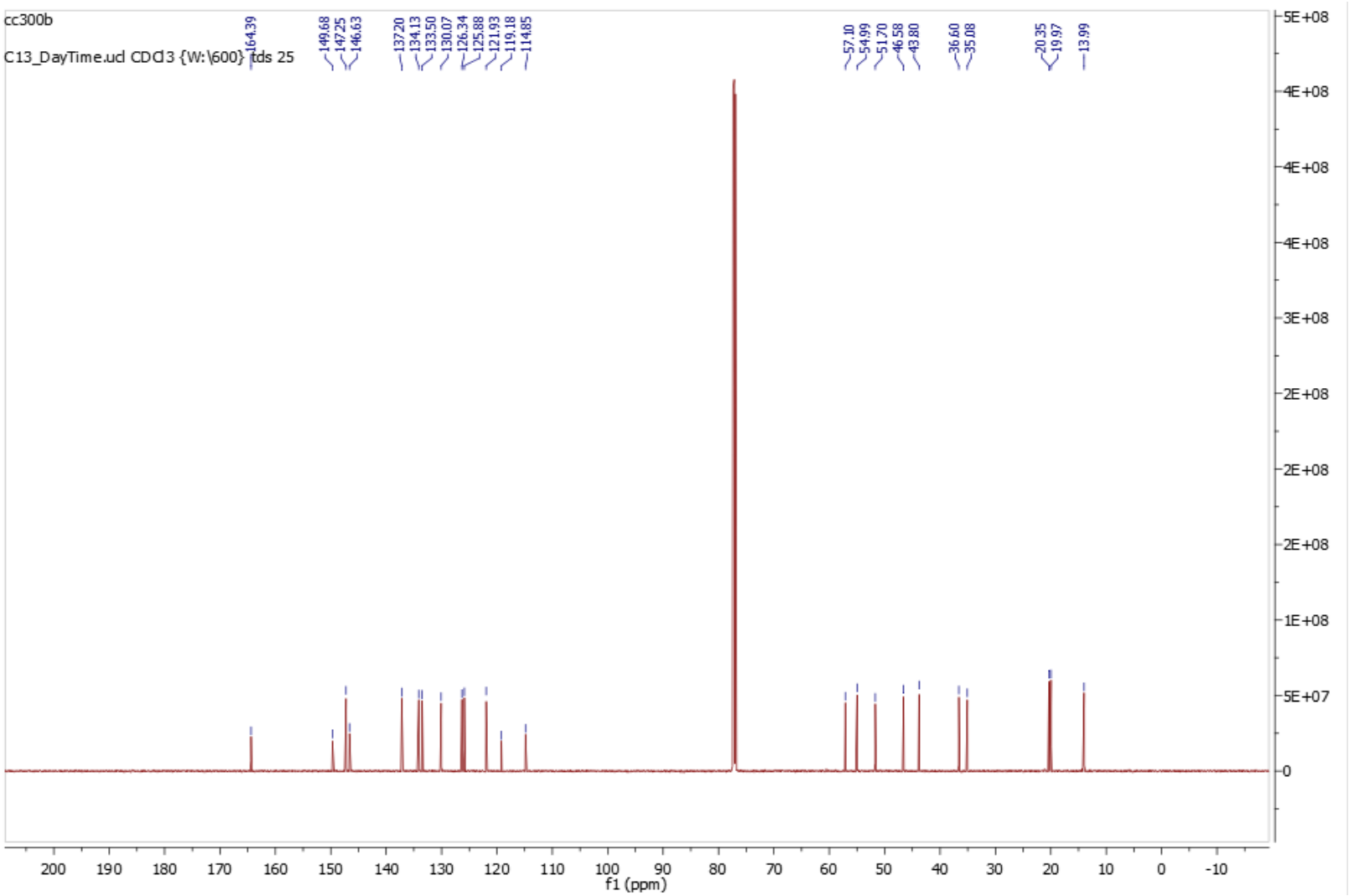
N-((1*S*,2*S*,4*R*,6*S*)-1,7,7-trimethyl-6-phenylbicyclo[2.2.1]heptan-2-yl)picolinamide **2k**



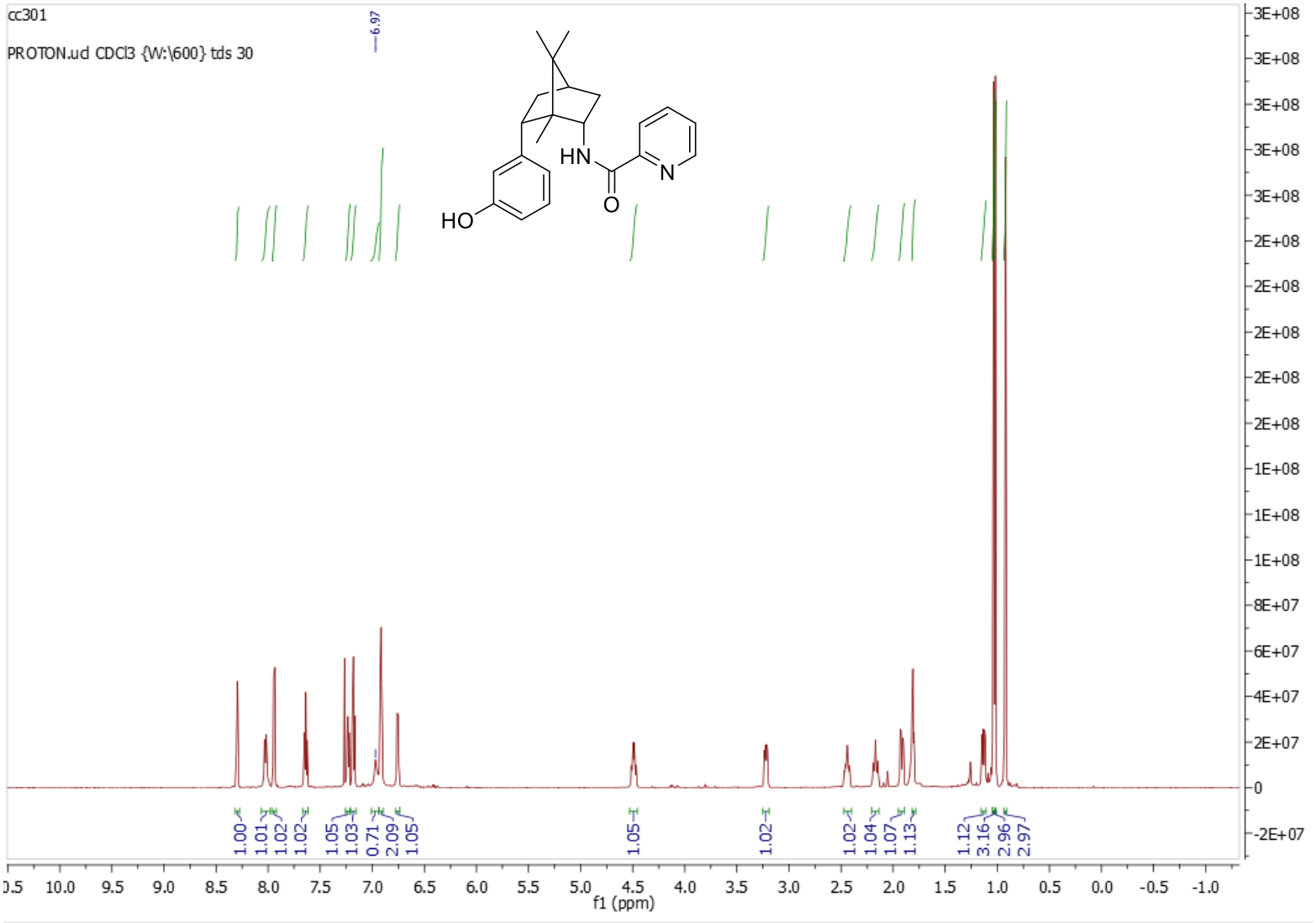

cc299b
C13_DayTime.ud CDCl3 {W:\600} tds 20
164.51
149.91
148.12
147.36
142.08
137.58
136.87
131.21
129.11
125.86
125.54
121.69
54.28
51.07
47.74
43.68
37.03
32.64
28.56
20.70
20.31
20.01
13.84
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

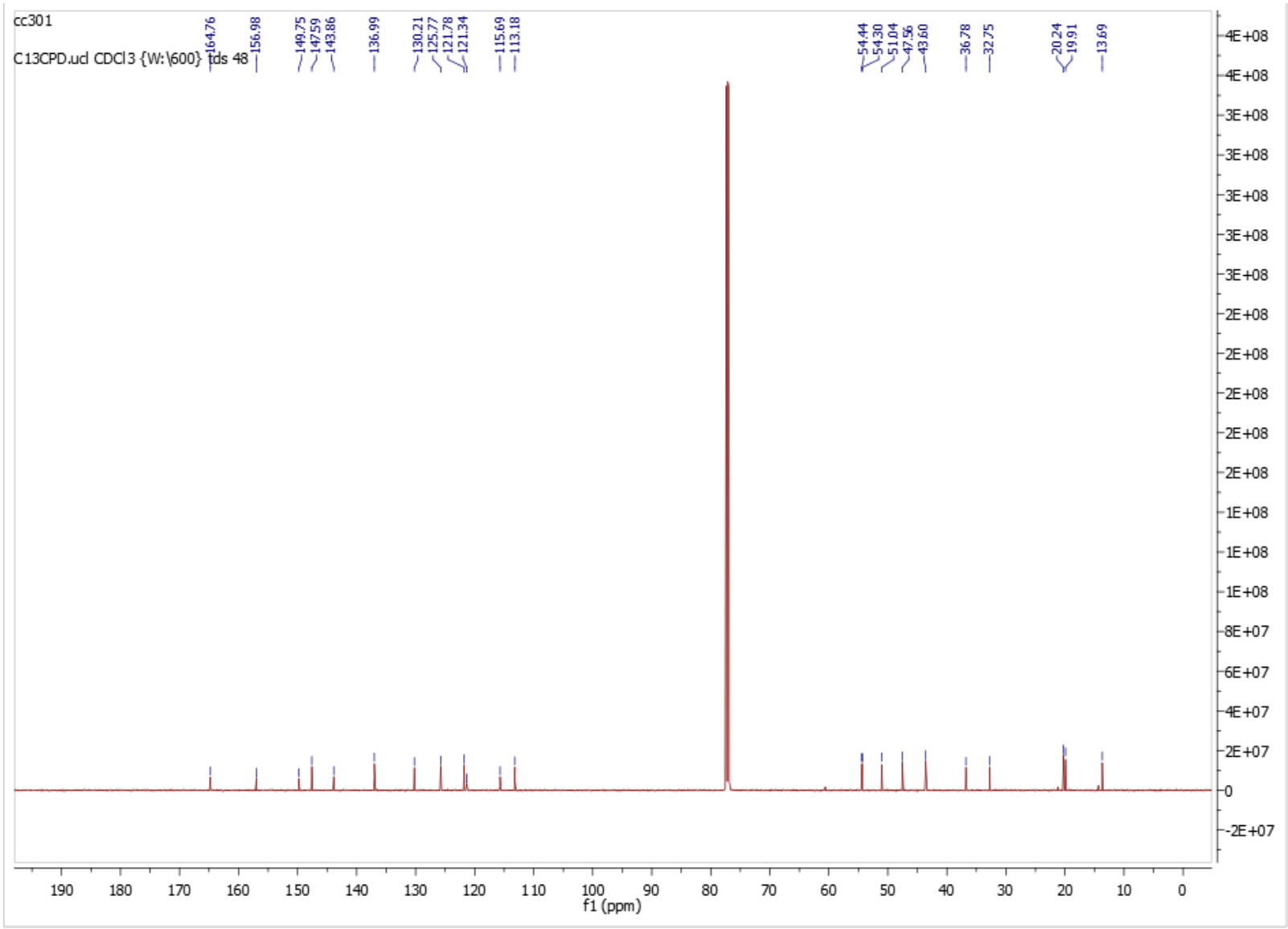
N-((1*S*,2*S*,4*R*,6*S*)-6-(2-cyanophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2l**



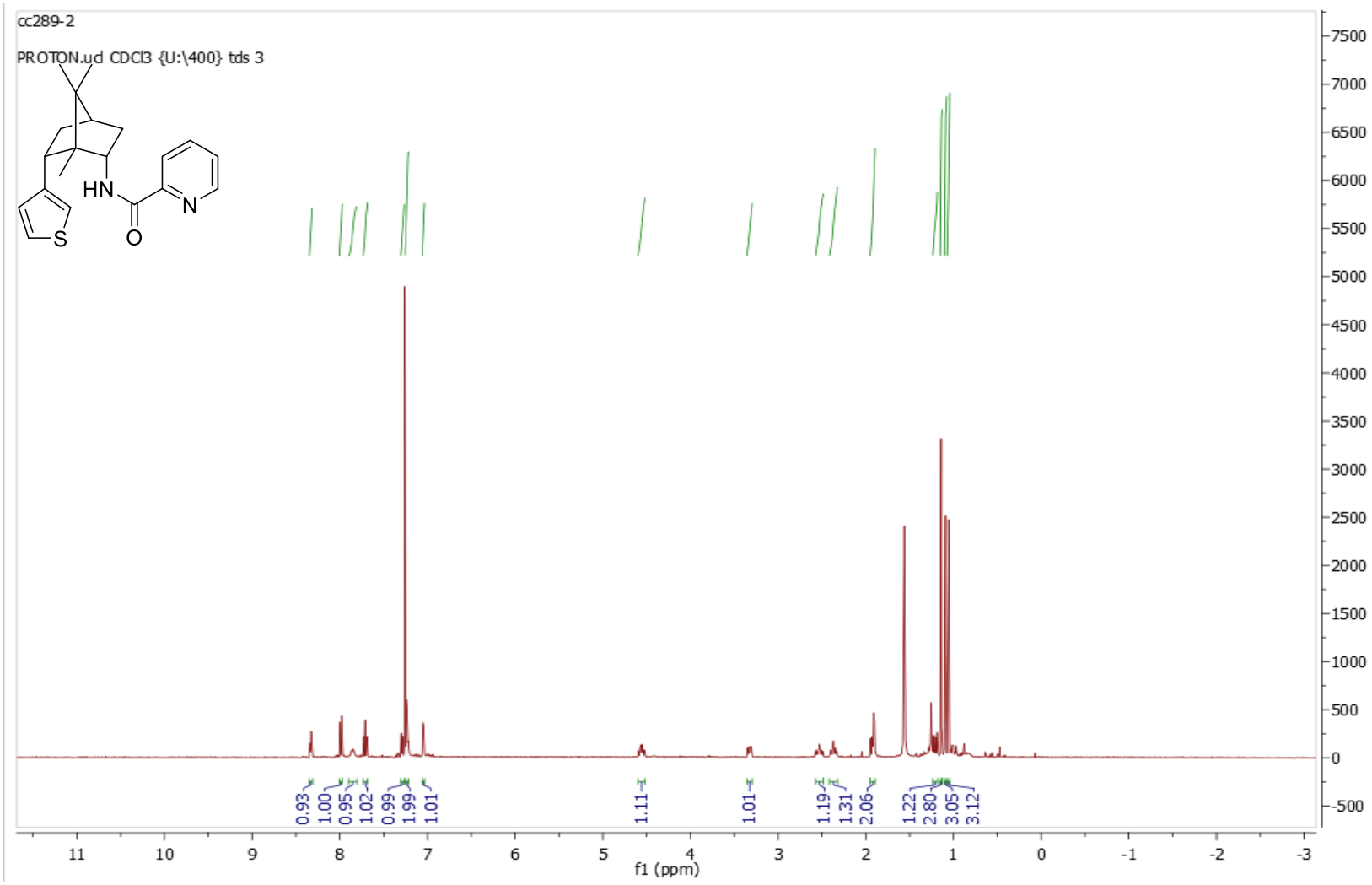

cc300b
C13_DayTime.ucl CDCl3 {W:\600} tds 25
164.39
149.68
147.25
146.63
137.20
134.13
133.50
130.07
126.34
125.88
121.93
119.18
114.85
57.10
54.99
51.70
46.58
43.80
36.60
35.08
20.35
19.97
13.99
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

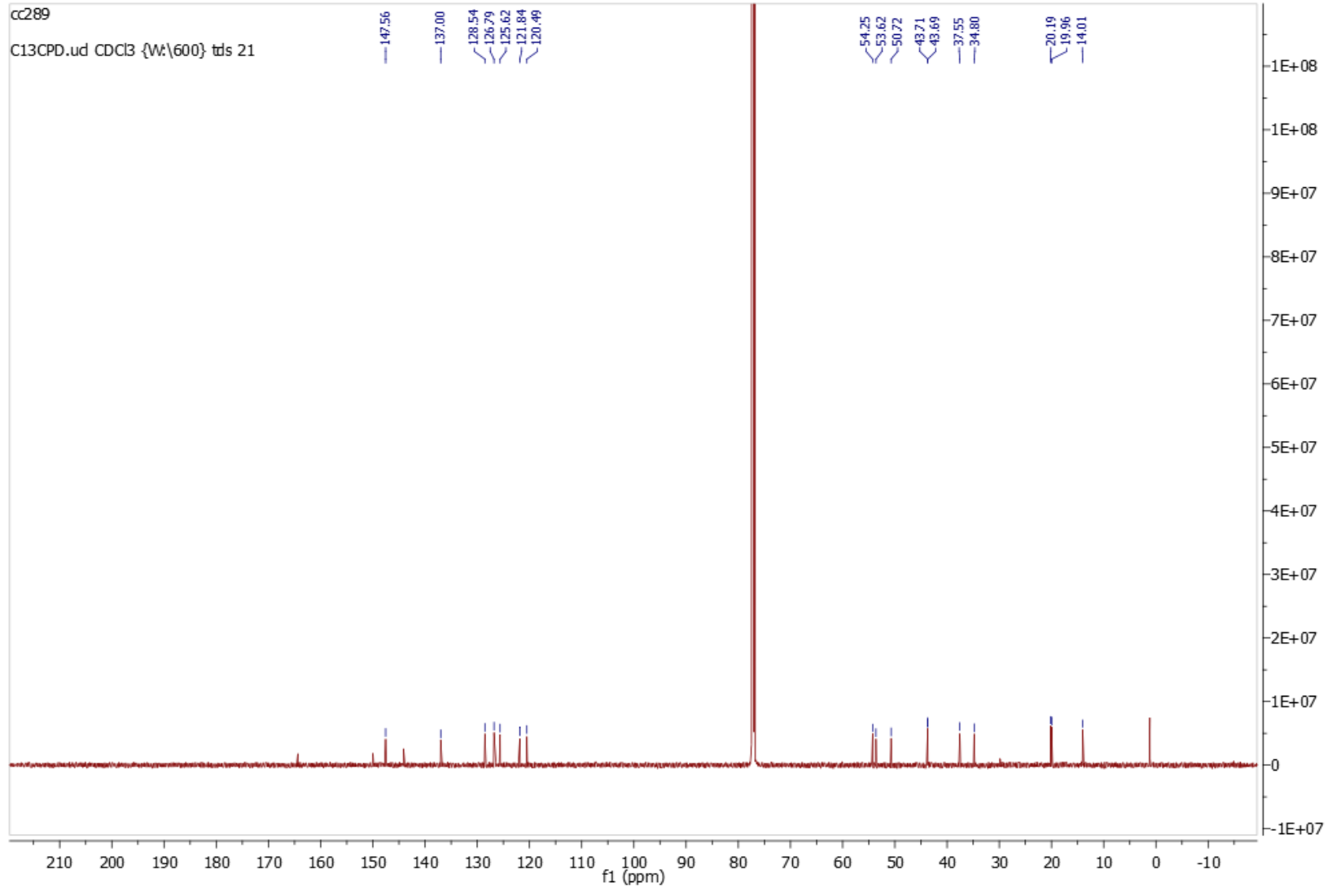
N-((1*S*,2*S*,4*R*,6*S*)-6-(3-hydroxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2m**



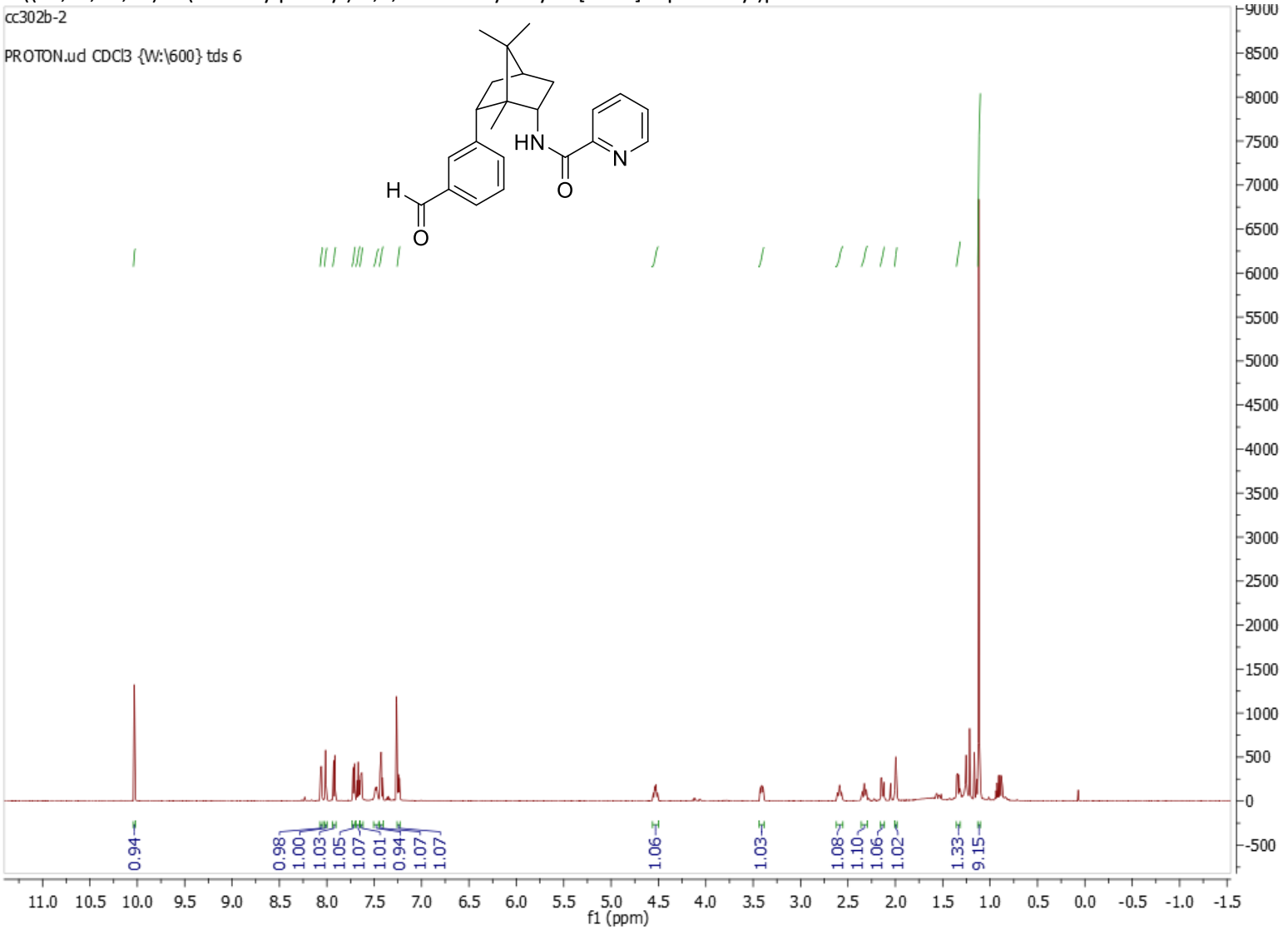

cc301
C13CPD.ud CDCl3 {W:\600} tds 48
164.76
156.98
149.75
147.59
143.86
136.99
130.21
125.77
121.78
121.34
115.69
113.18
54.44
54.30
51.04
47.56
43.60
36.78
32.75
20.24
19.91
13.69
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

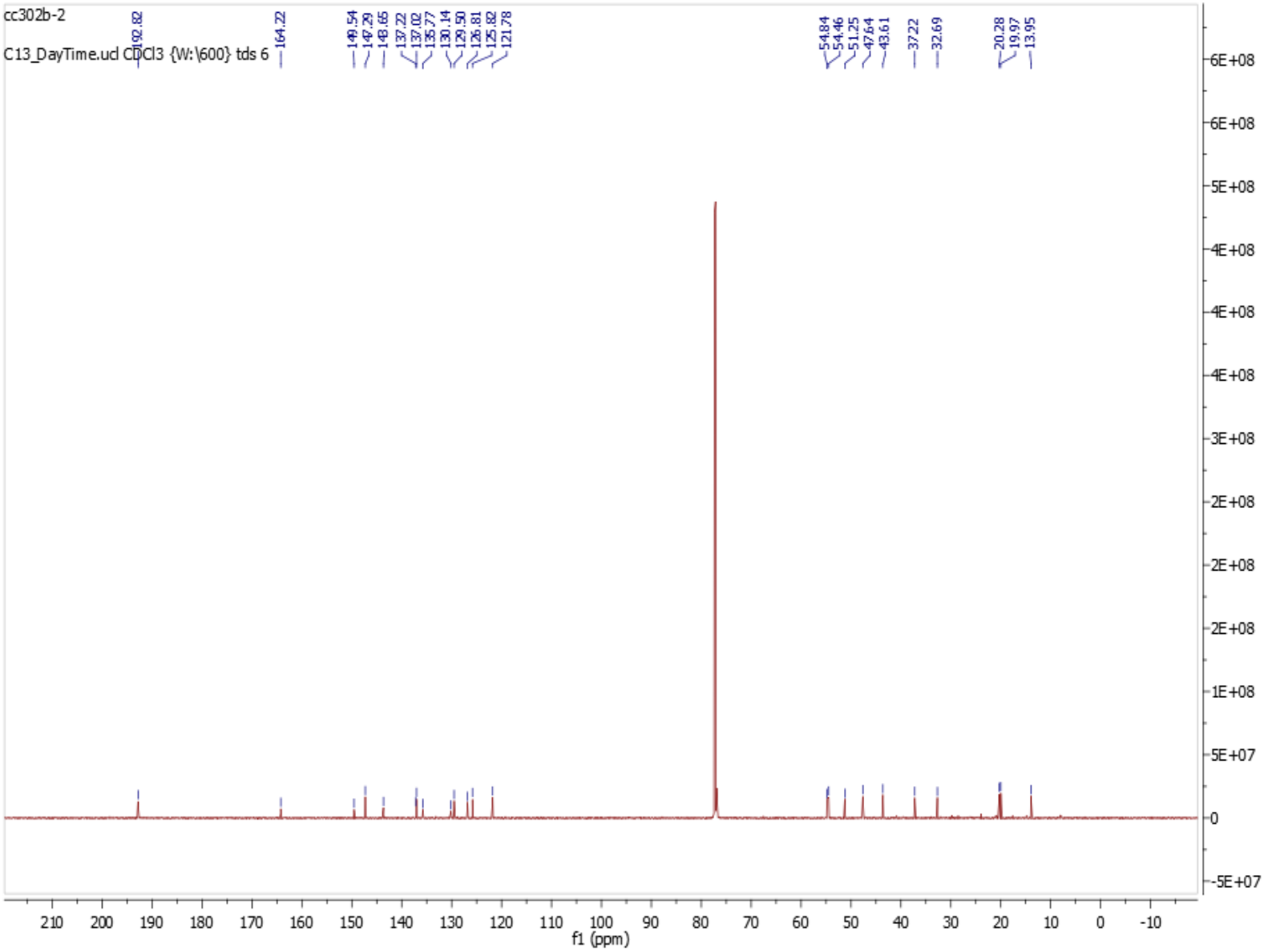
N-((1*S*,2*S*,4*R*,6*S*)-1,7,7-trimethyl-6-(thiophen-3-yl)bicycle[2.2.1]hepten-2-yl)picolinamide **2n**



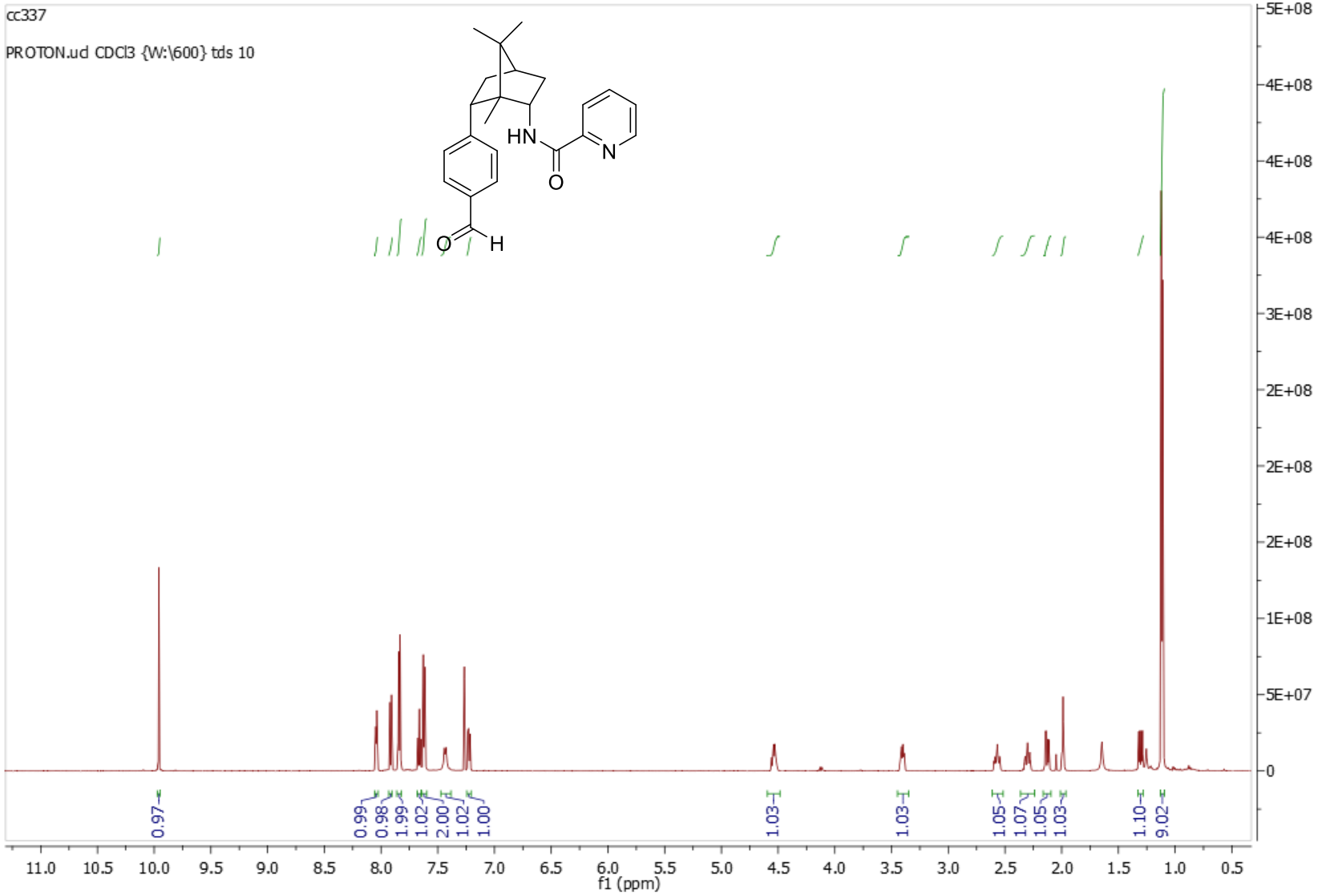

cc289
C13CPD.ud CDCl3 {W:\600} tds 21
147.56
137.00
128.54
126.79
125.62
121.84
120.49
54.25
53.62
50.72
43.71
43.69
37.55
34.80
20.19
19.96
14.01
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

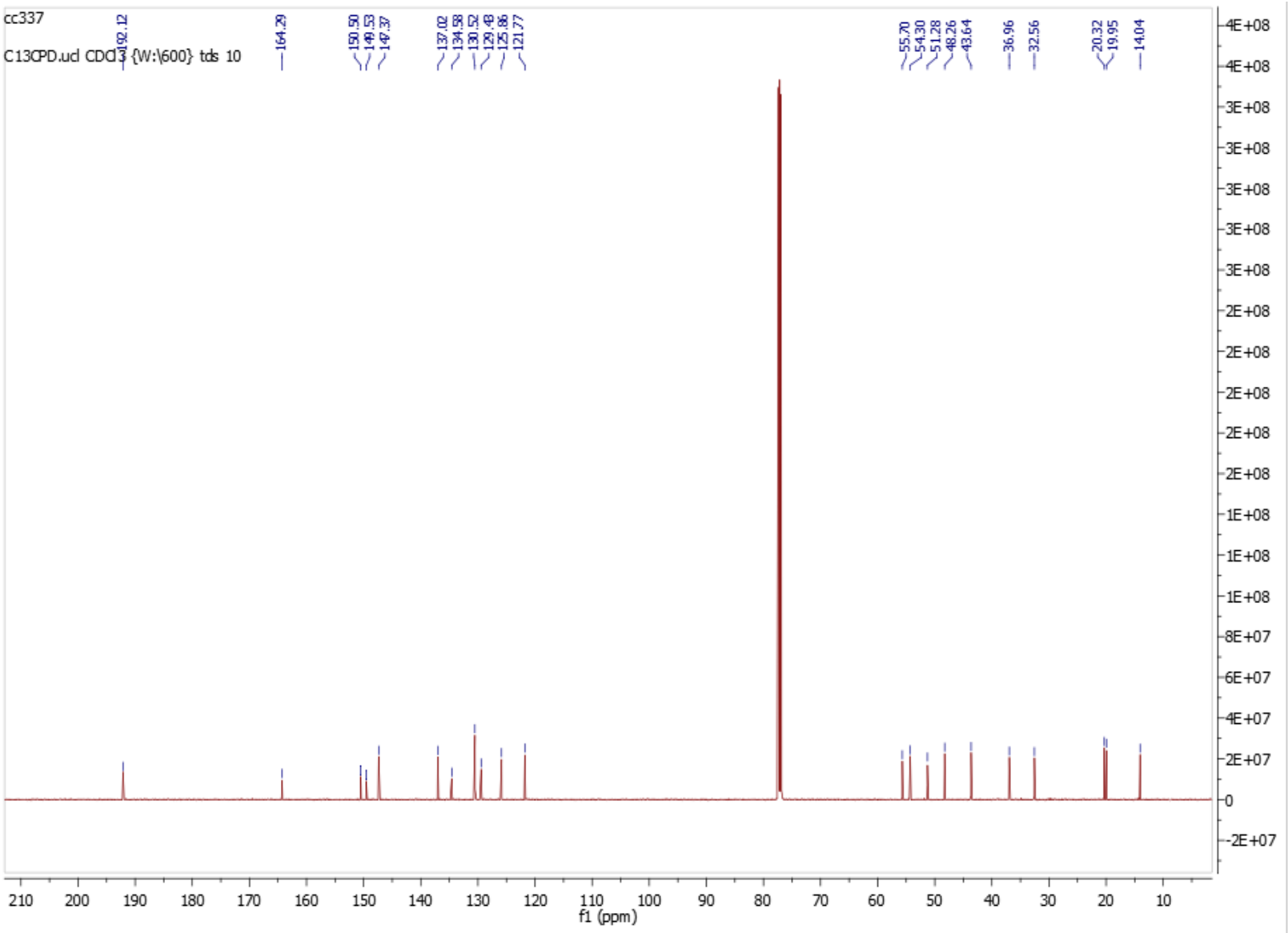
N-((1*S*,2*S*,4*R*,6*S*)-6-(3-formylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2o**



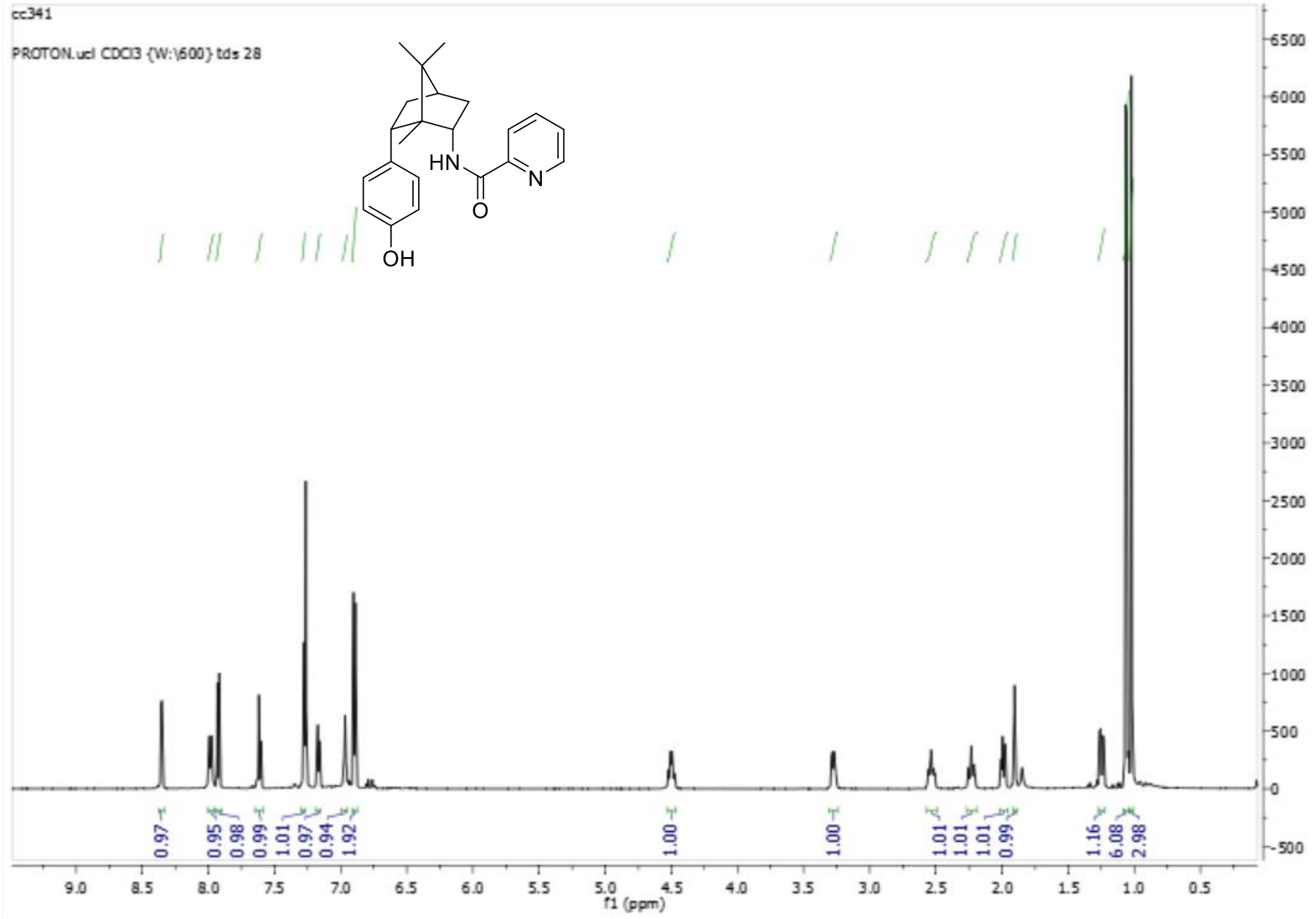

cc302b-2
C13_DayTime.ucl CDCl3 {W:\600} tds 6
192.82
164.22
149.54
149.29
148.65
137.22
137.02
135.77
130.14
129.50
126.81
125.82
121.78
54.84
54.46
51.25
47.64
43.61
37.22
32.69
20.28
19.97
13.95
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

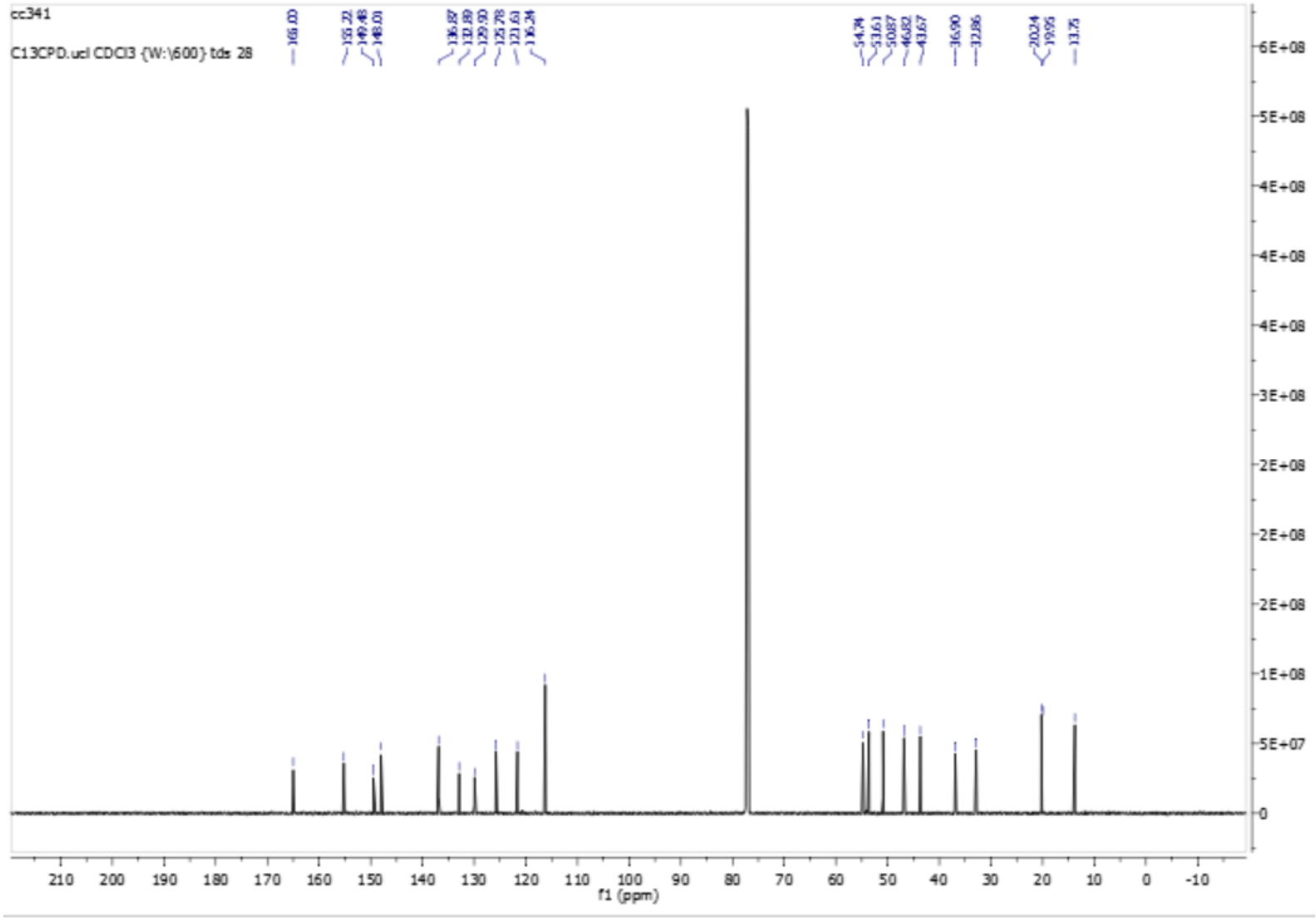
N-((1*S*,2*S*,4*R*,6*S*)-6-(4-formylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide **2p**



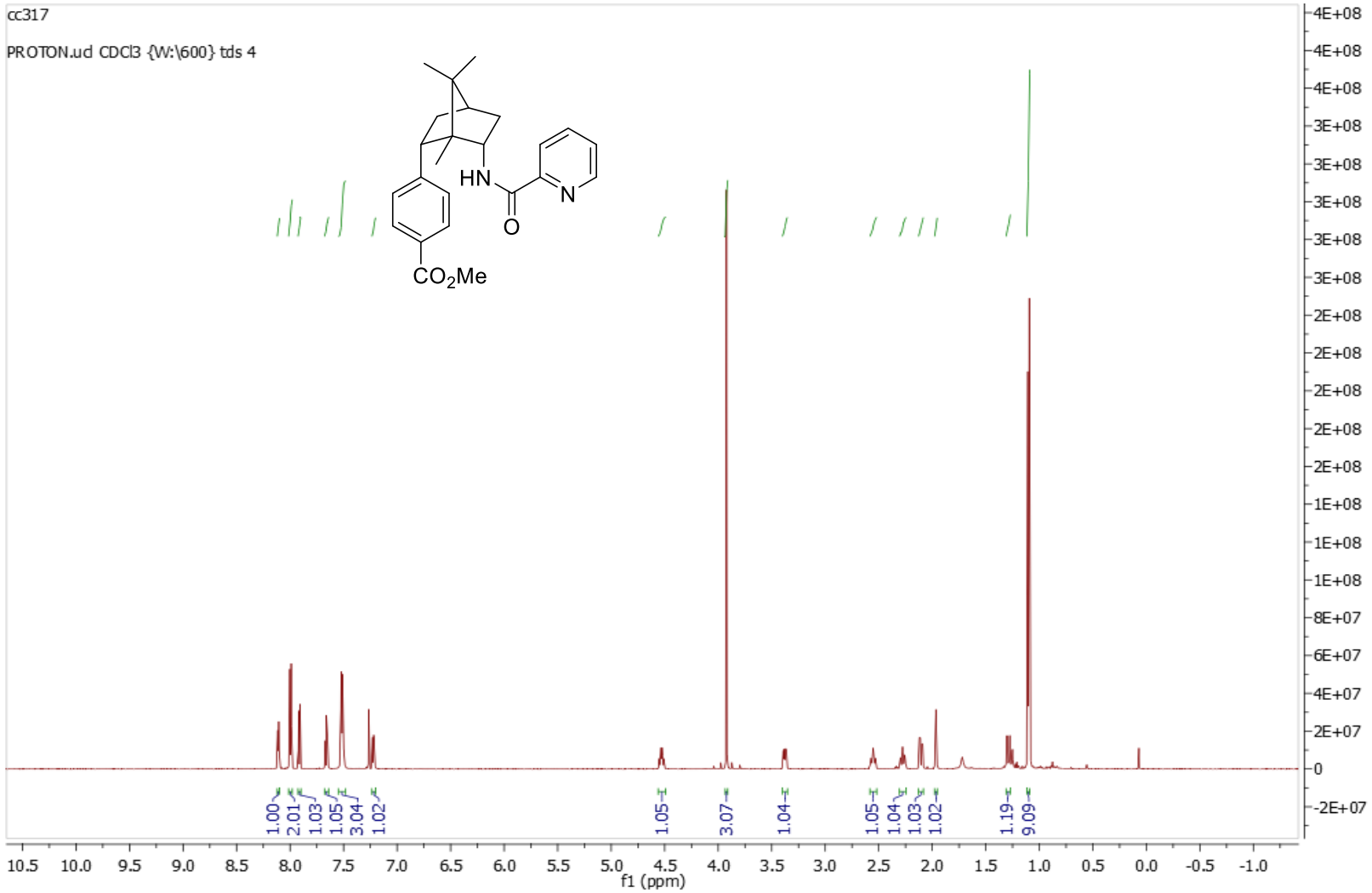

cc337
C13CPD.ucl CDCl3 {W:\600} tds 10
192.12
164.29
150.50
149.53
149.37
137.02
134.58
130.52
129.48
125.86
121.77
55.70
54.30
51.28
48.26
43.64
36.96
32.56
20.32
19.95
14.04
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

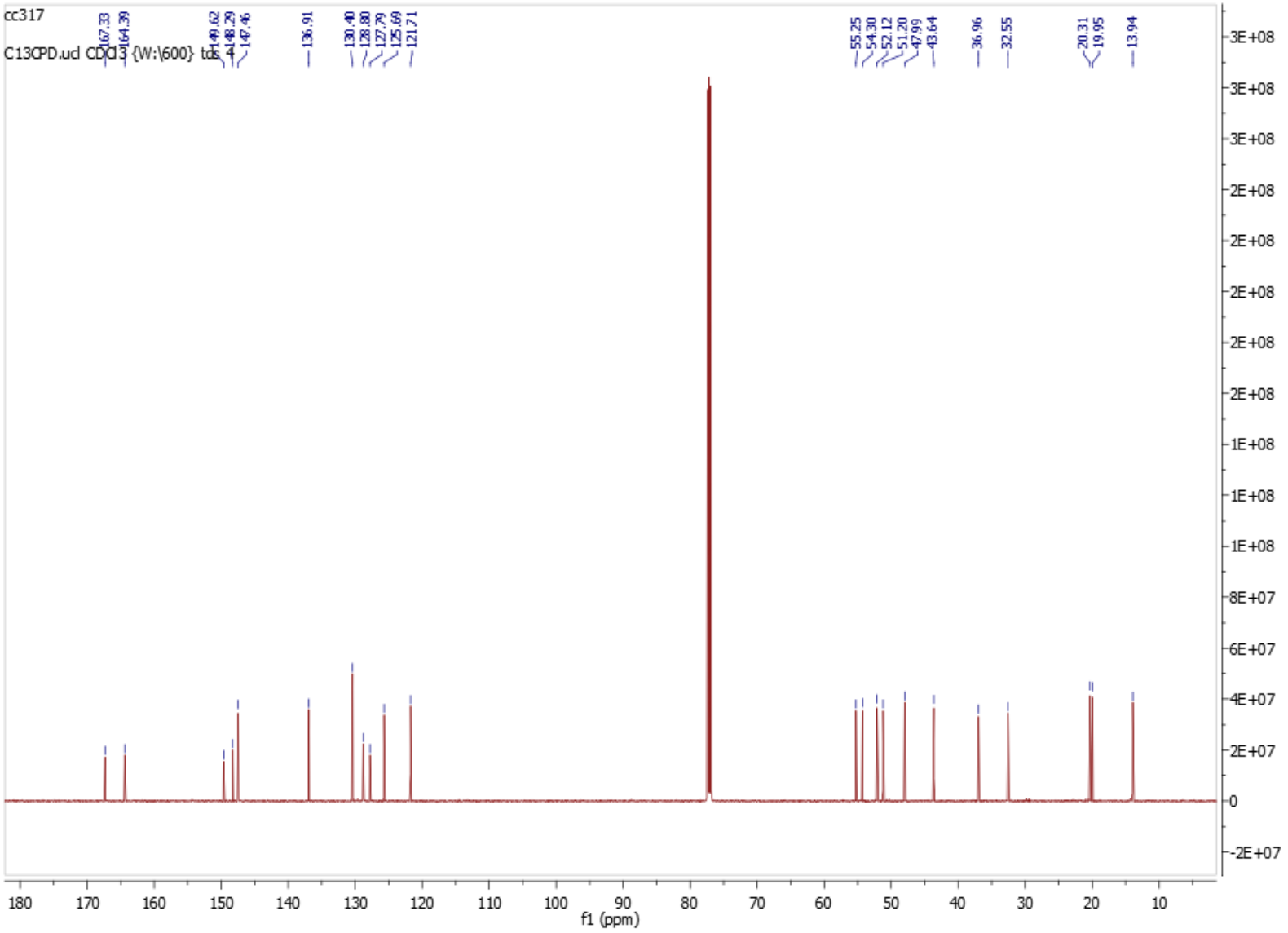
N-((1S,2S,4R,6S)-6-(4-hydroxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)picolinamide (2q).



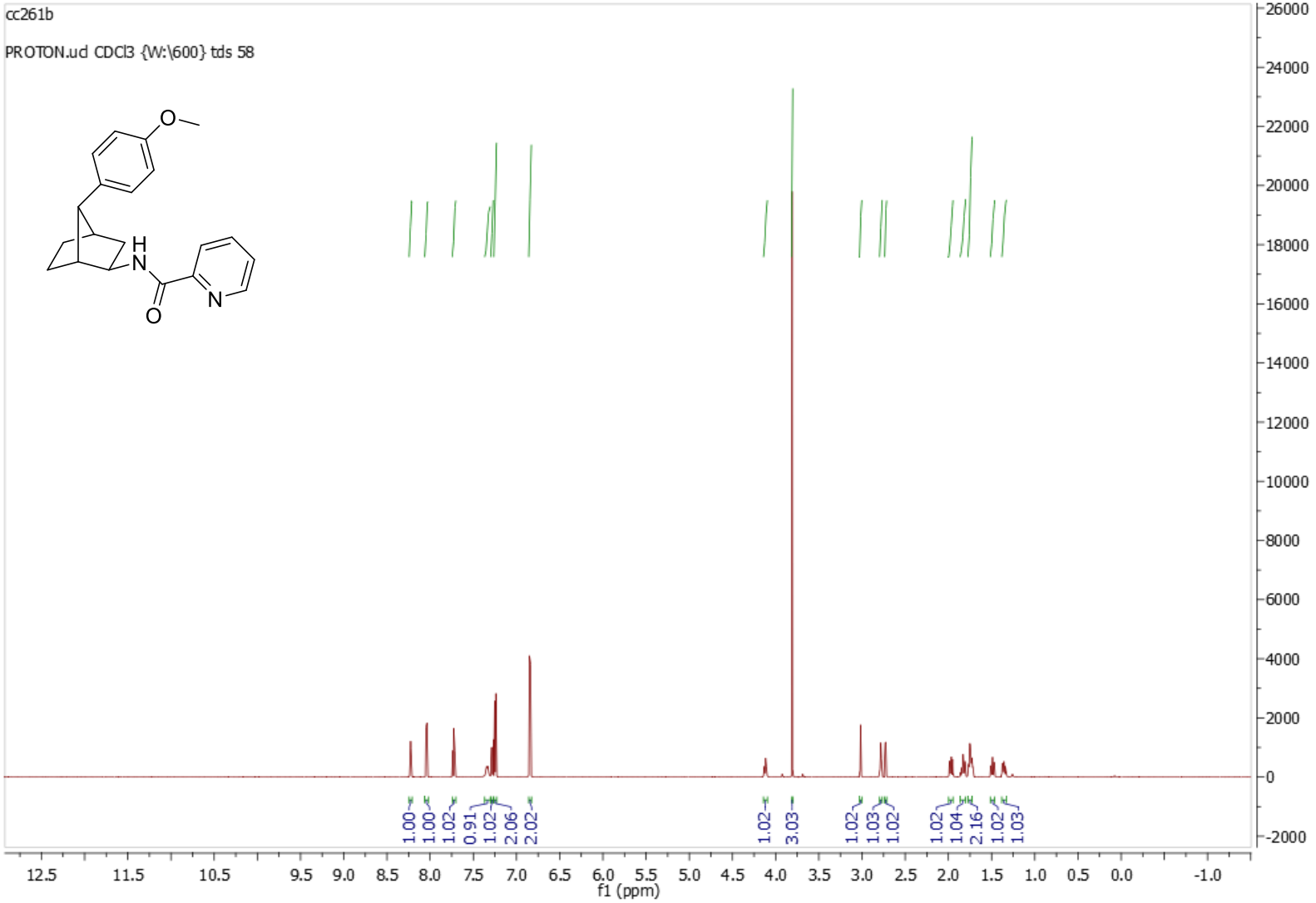

cc341
C13CPD.ucl CDCl3 {W:\600} tds 28
166.00
155.22
149.48
148.01
136.87
132.89
129.90
125.78
123.61
116.24
54.74
53.61
50.87
46.82
43.67
36.90
32.86
20.24
19.95
13.75
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

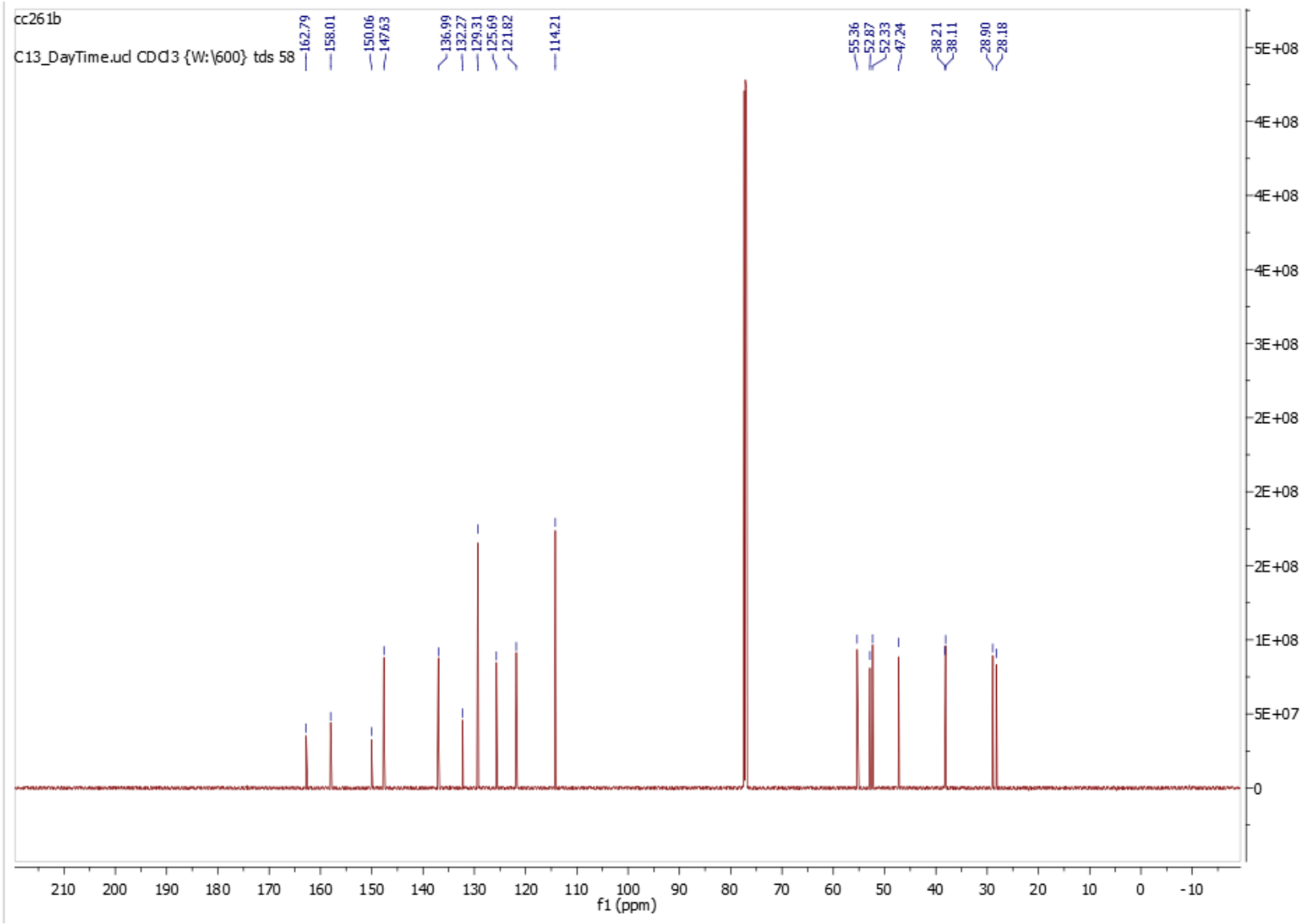
Methyl-4-((1*S*,2*S*,4*R*,6*S*)-1,7,7-trimethyl-6-(picolinamide)bicyclo[2.2.1]heptan-2-yl)benzoate **2r**



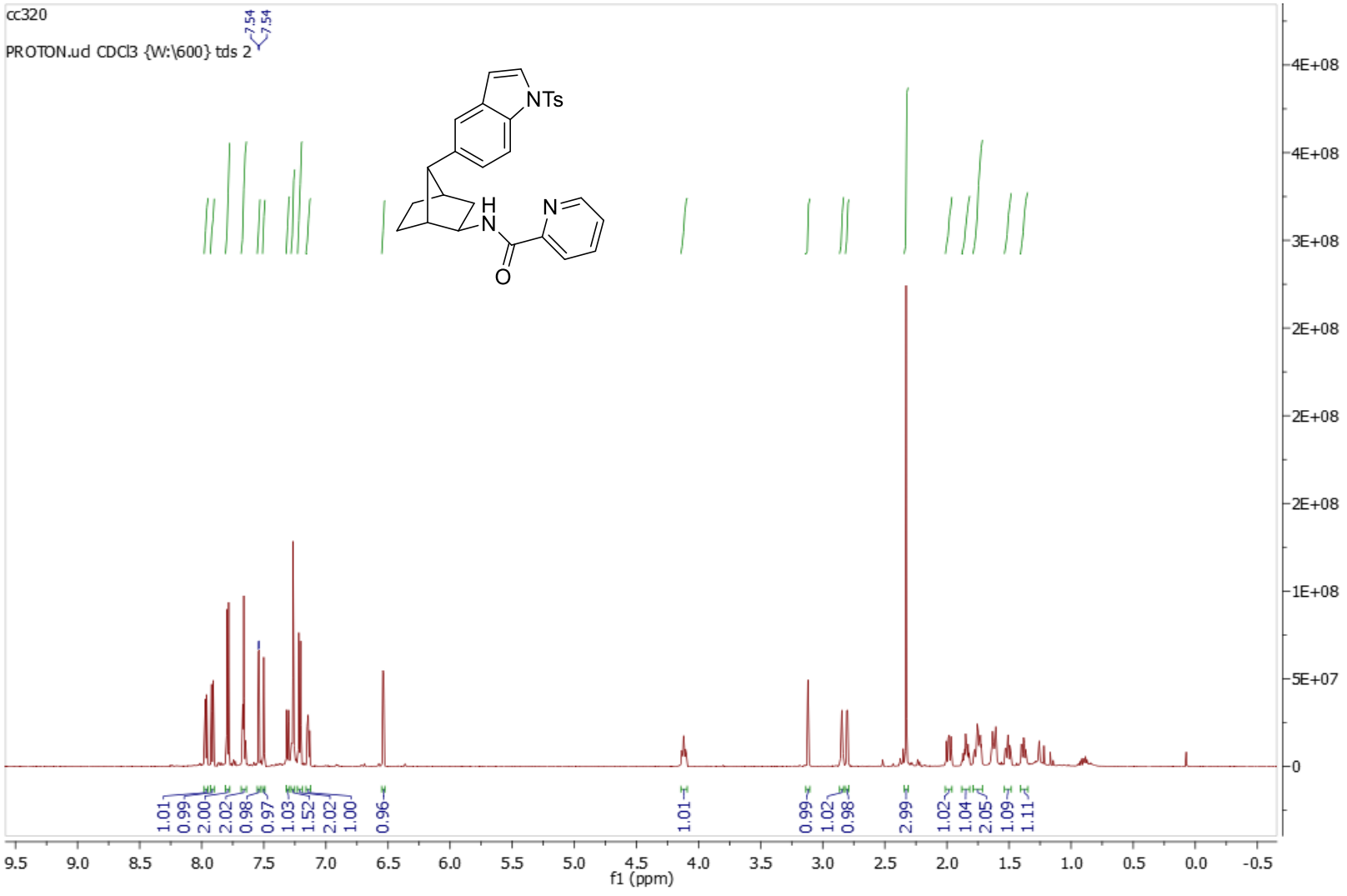

cc317
C13CPD.ud CDCl3 {W:\600} tds 4
167.33
164.39
149.62
148.29
147.46
136.91
130.40
128.80
127.79
125.69
121.71
55.25
54.30
52.12
51.20
47.99
43.64
36.96
32.55
20.31
19.95
13.94
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

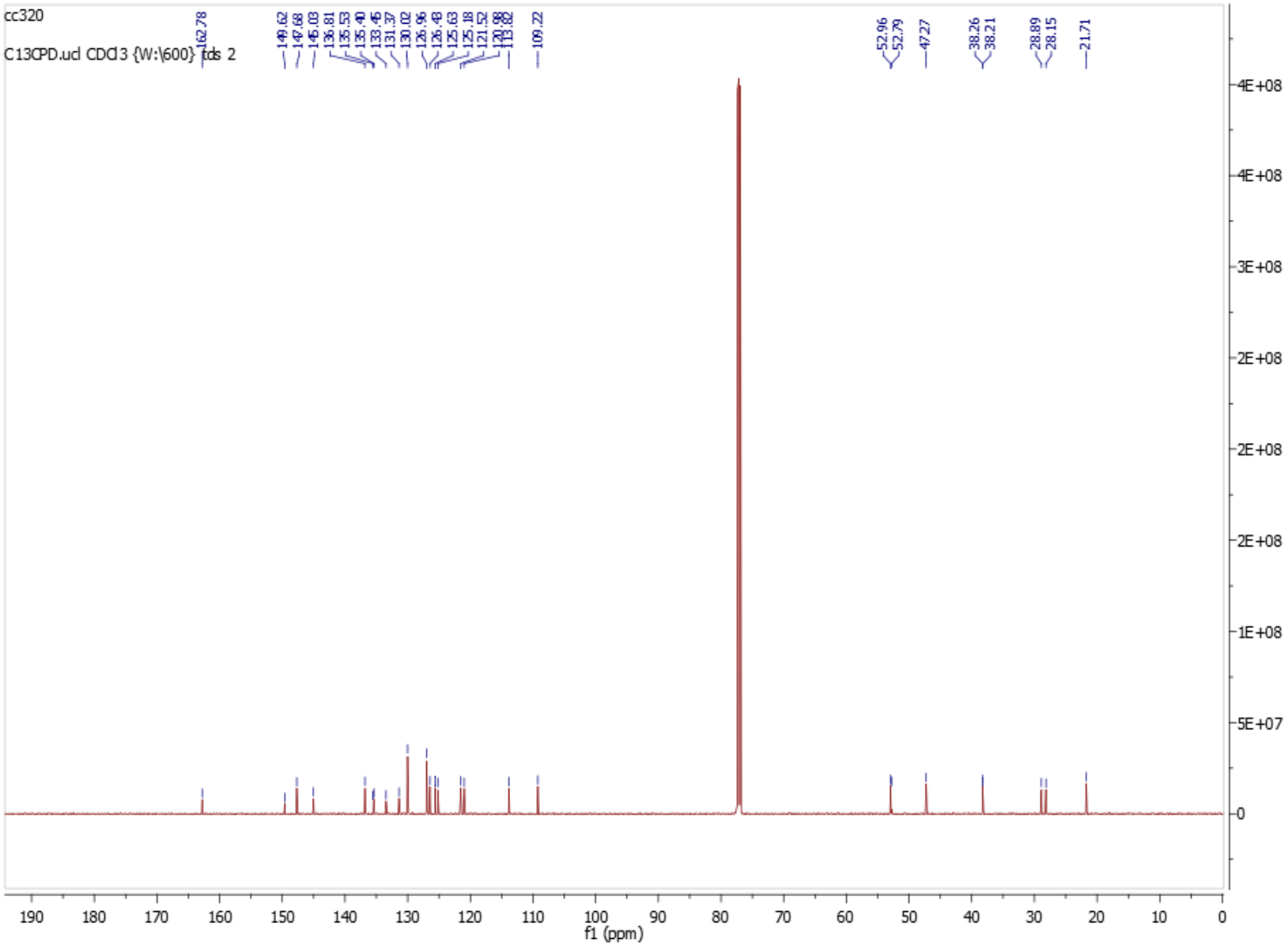
N-7-(4methoxyphenyl)bicycle[2.2.1]heptan-2-yl)picolinamide **4a**



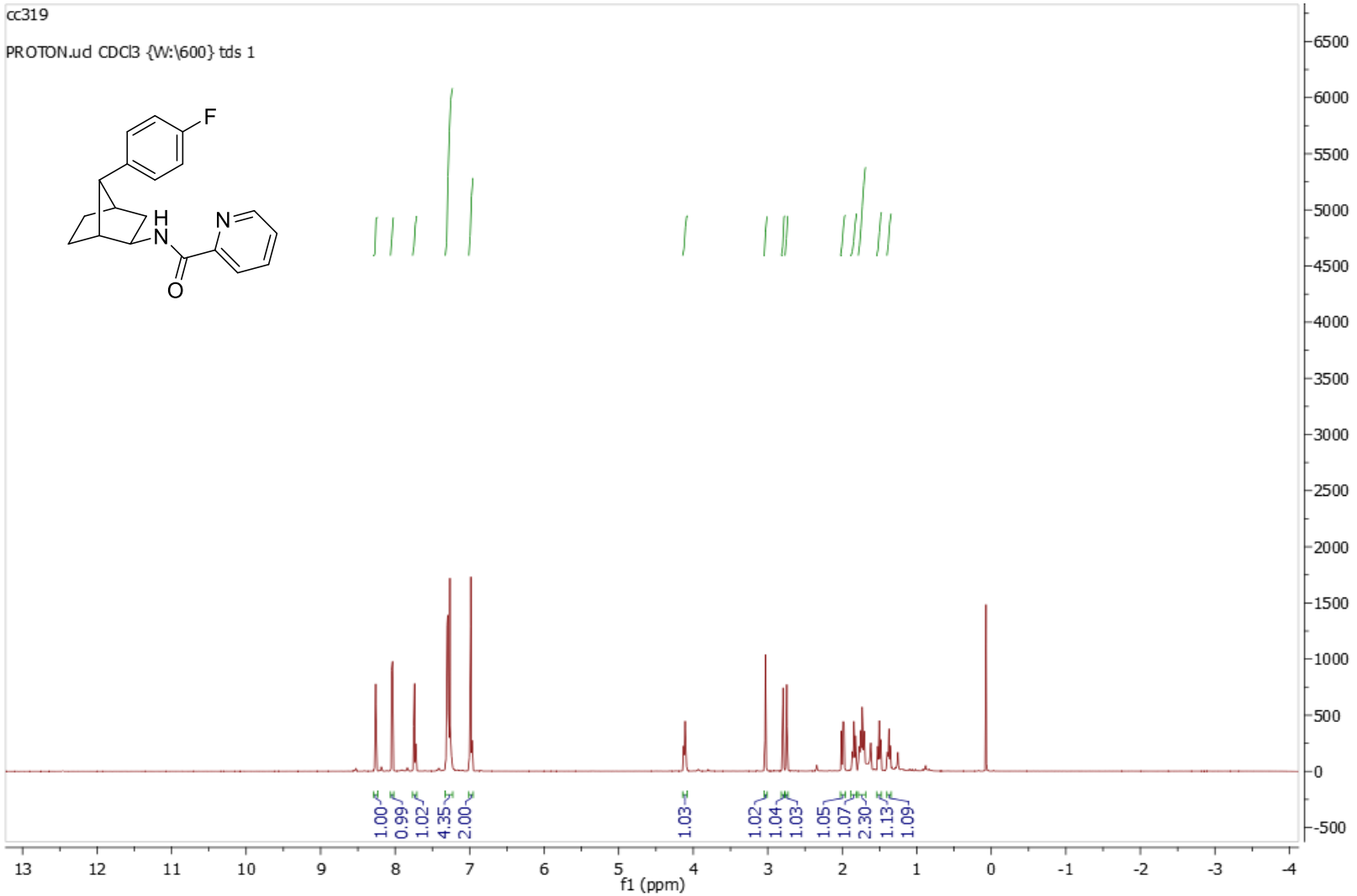

cc261b
C13_DayTime.ucl CDCl3 {W:\600} tds 58
162.79
158.01
150.06
147.63
136.99
132.27
129.31
125.69
121.82
114.21
55.36
52.87
52.33
47.24
38.21
38.11
28.90
28.18
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

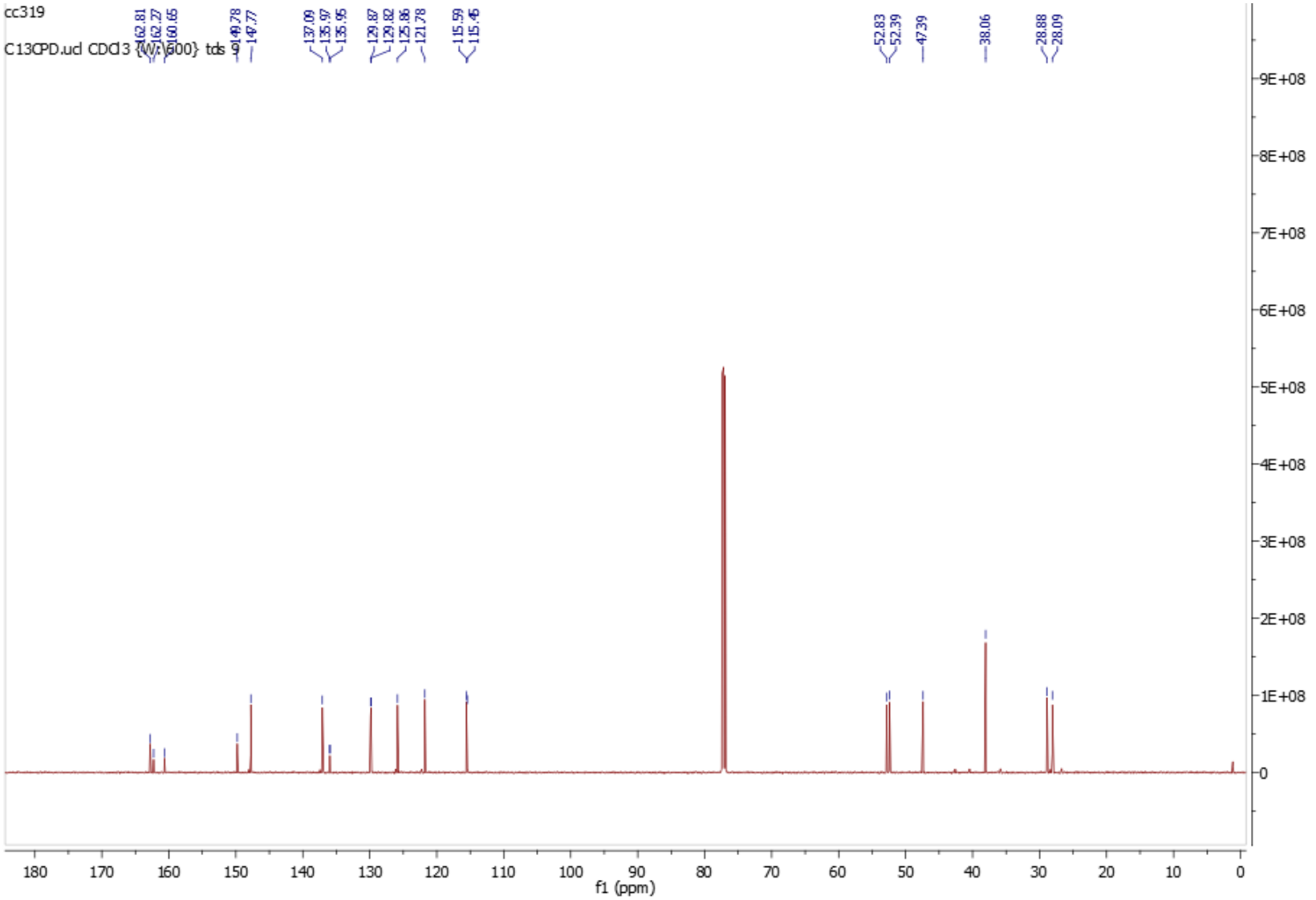
N-7-(1-tosyl-1*H*-indol-5-yl)bicyclo[2.2.1]heptan-2-yl)picolinamide **4b**



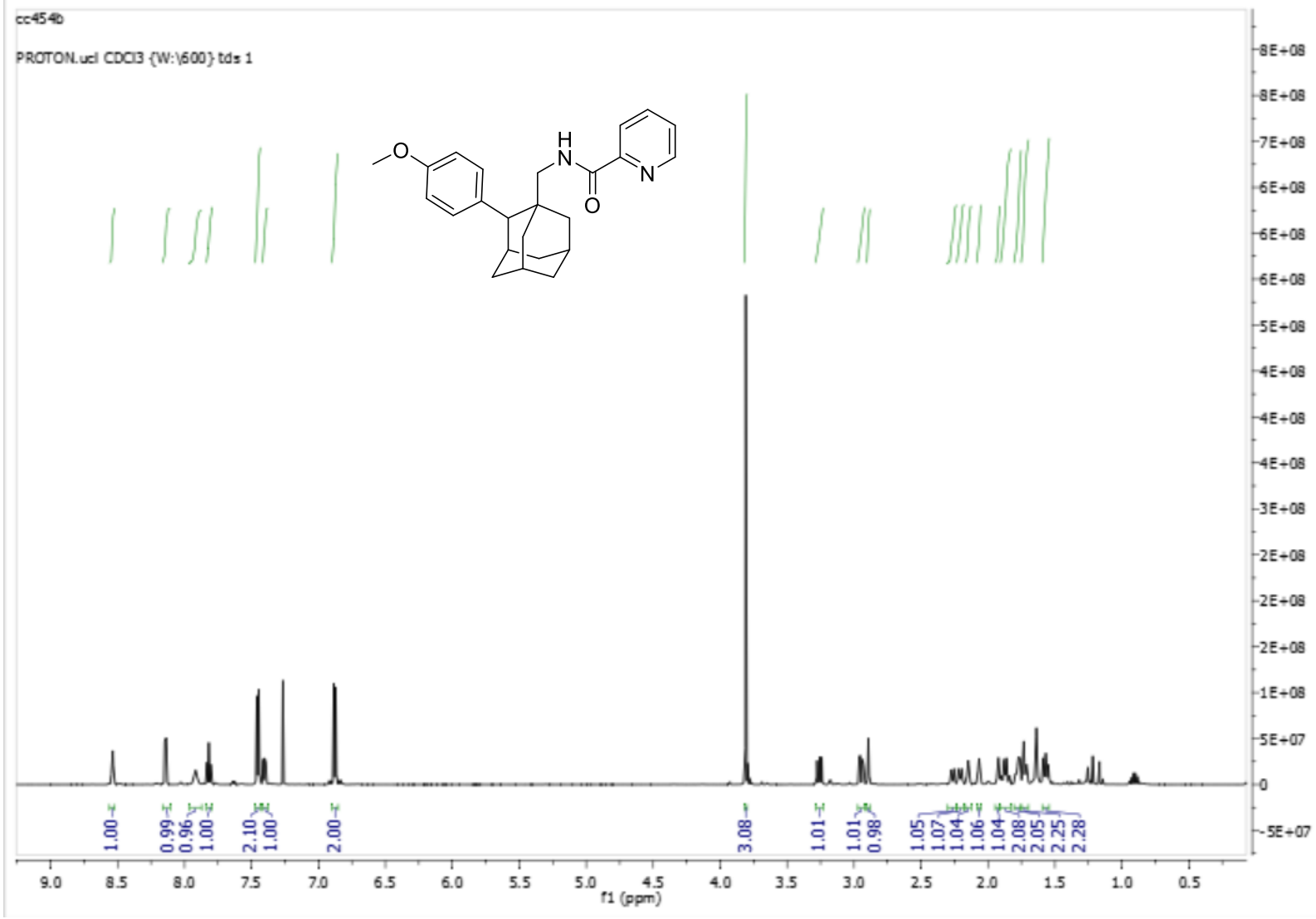

cc320
C13CPD.ud CDCl3 {W:\600} fds 2
162.78
149.62
147.68
145.03
136.81
135.53
135.40
133.45
131.37
130.02
126.96
126.48
125.63
125.18
121.52
113.82
109.22
52.96
52.79
47.27
38.26
38.21
28.89
28.15
21.71
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

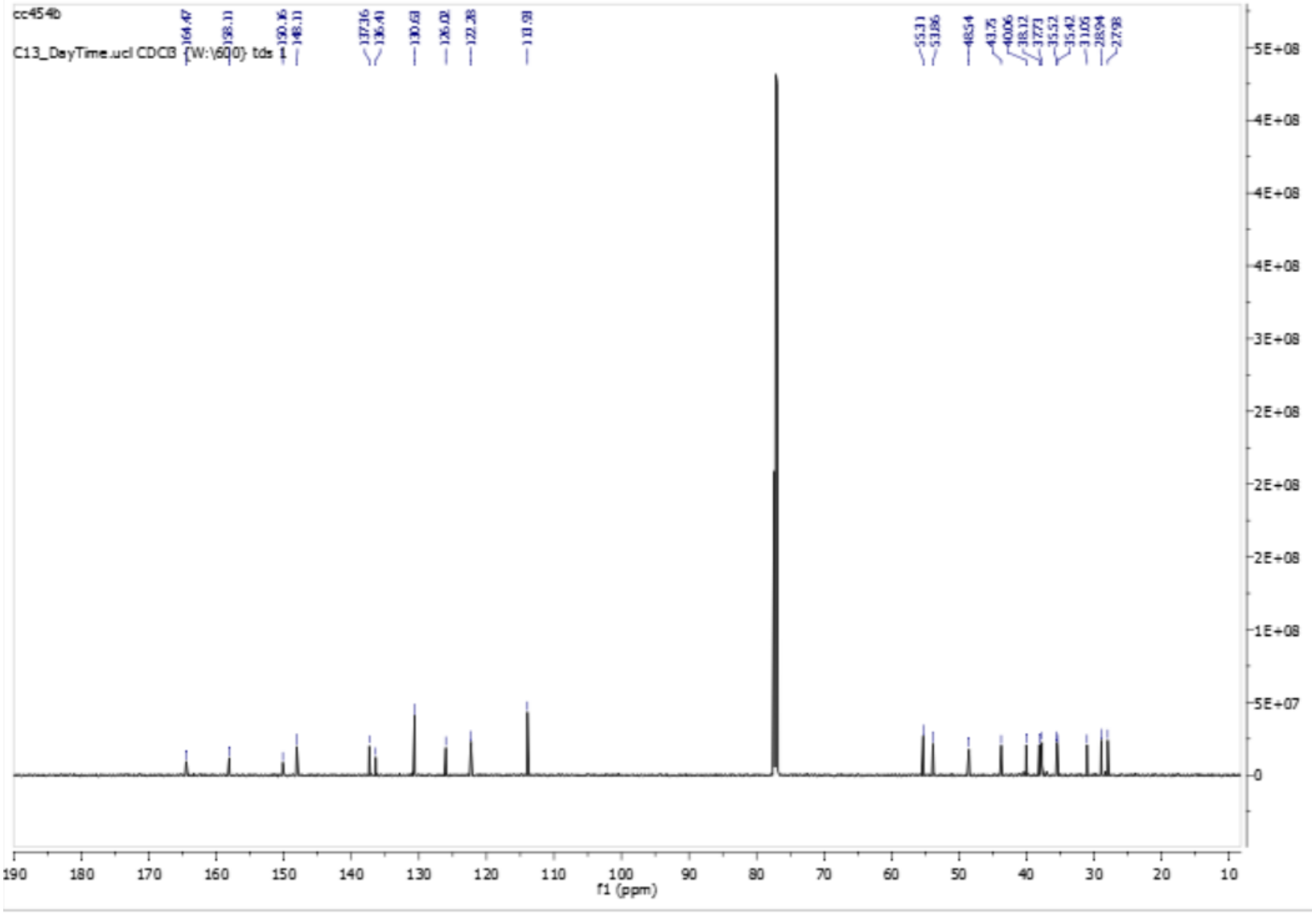
N-7-(4-fluorophenyl)bicyclo[2.2.1]heptan-2-yl)picolinamide **4c**



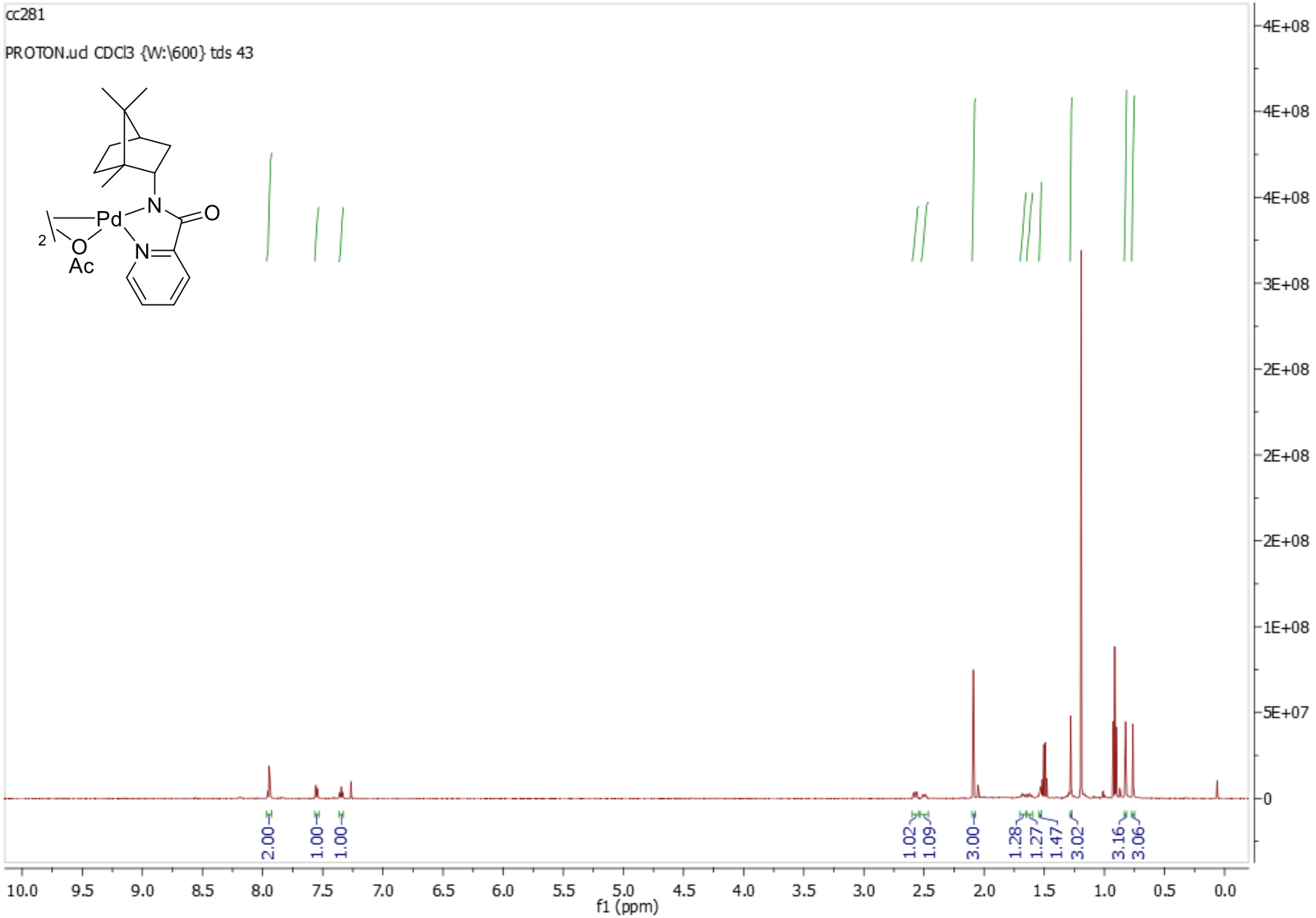

cc319
C13CPD.ucl CDCl3 {W:\600} tds 9
162.81
162.27
160.65
149.78
147.77
137.09
135.97
135.95
129.87
129.82
125.86
121.78
115.59
115.45
52.83
52.39
47.39
38.06
28.88
28.09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

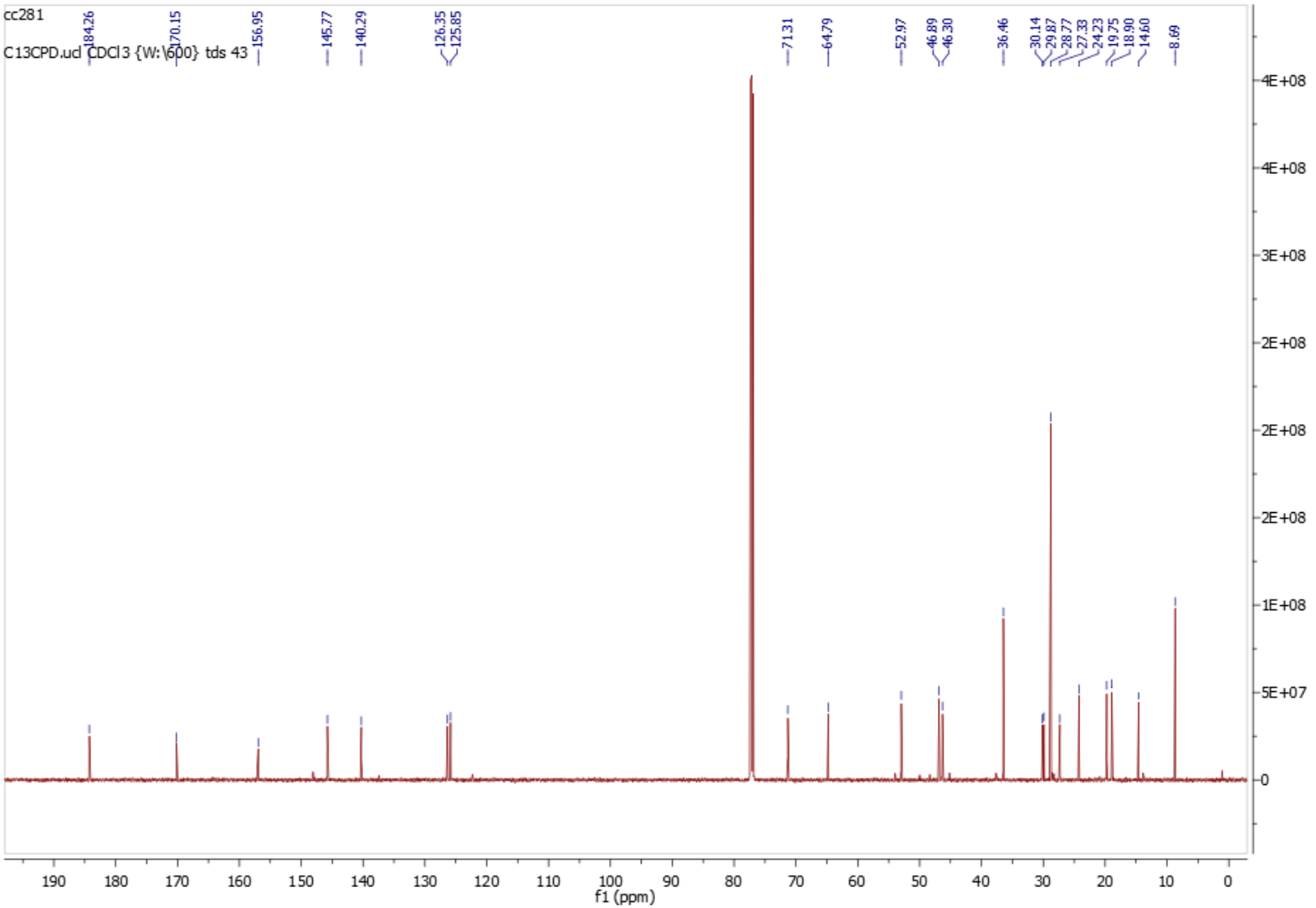
N-2-(4-methoxyphenyl)adamantan-1-yl)methyl)picolinamide **6**



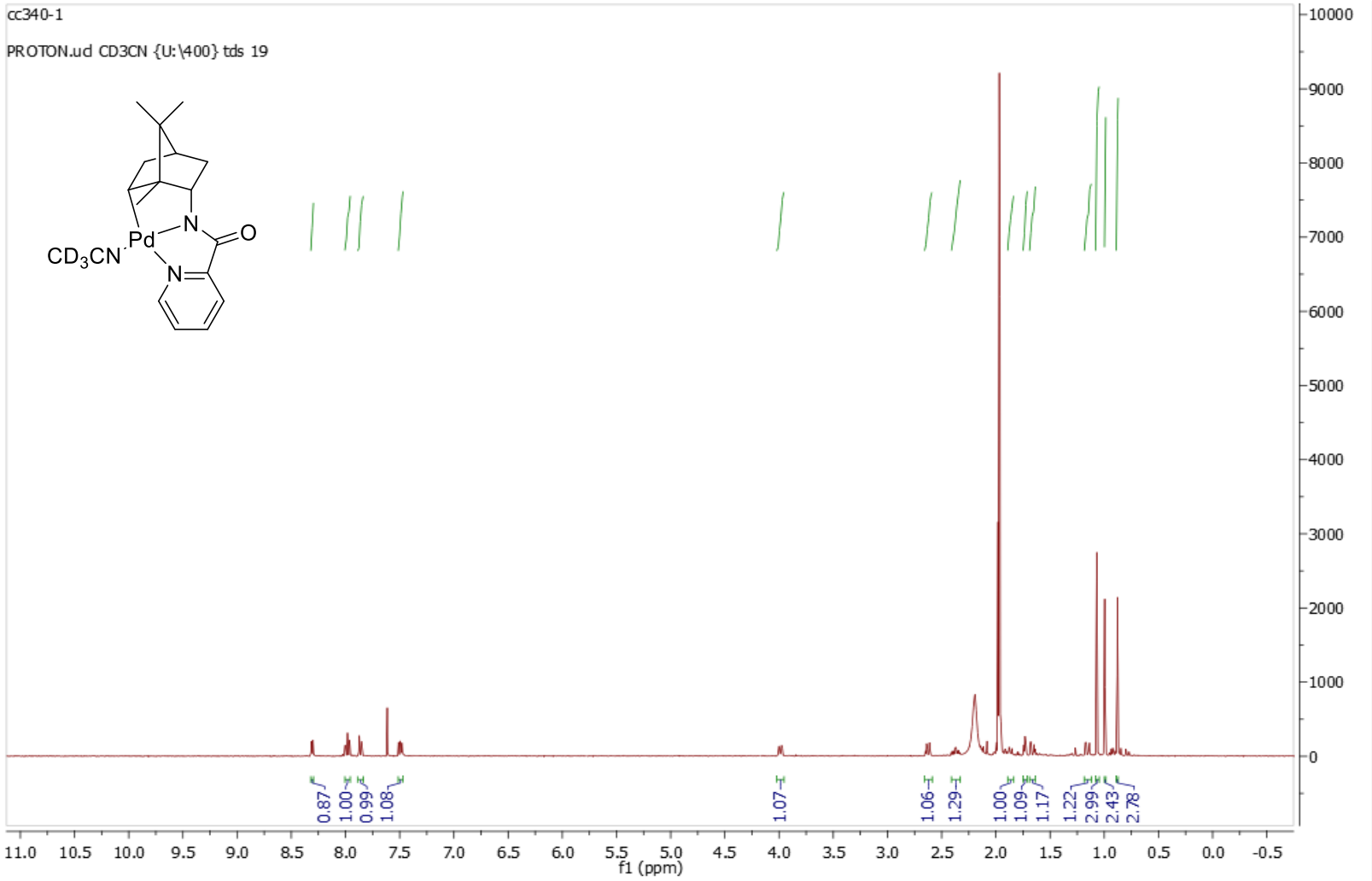

cc4540
C13_DayTime.ucl CDCl3 {W:\600} tds 1
164.47
138.11
130.36
148.11
137.36
136.41
130.63
126.02
122.28
113.91
55.31
53.86
48.54
43.75
40.06
38.12
37.73
35.52
35.42
31.05
28.94
27.98
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

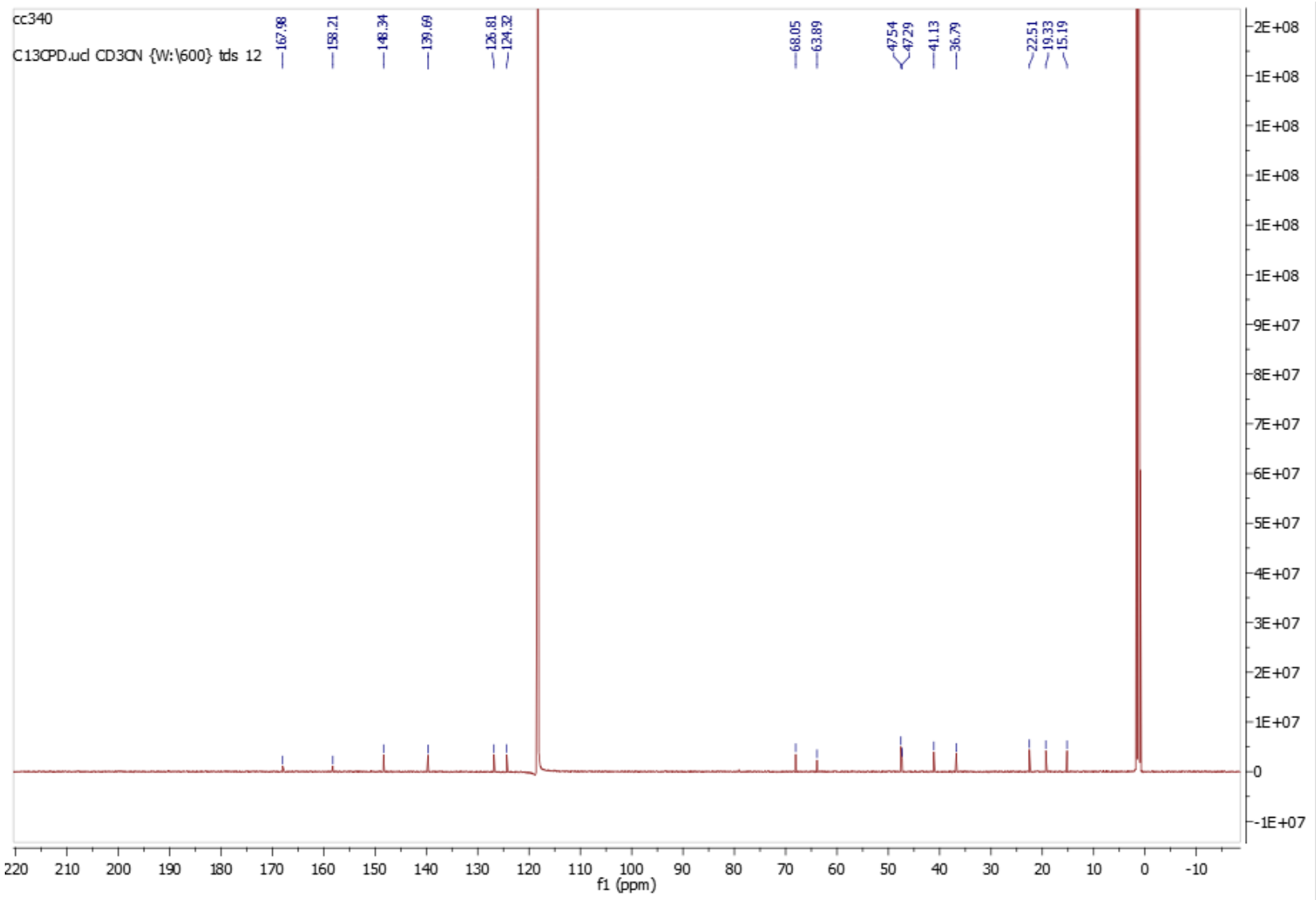
Palladium complex **7**



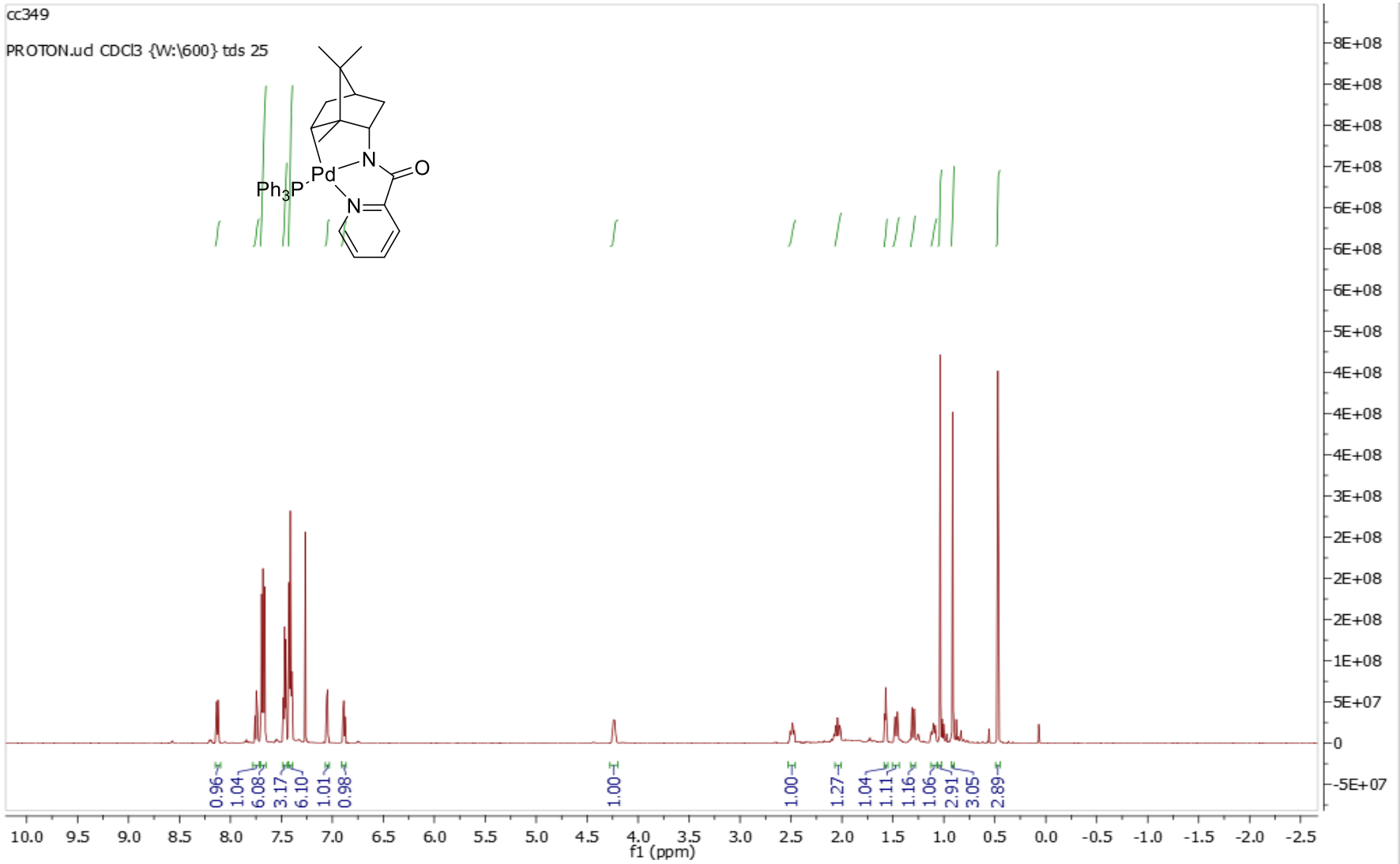

cc281
C13CPD.ucl CDCl3 {W:\600} tds 43
184.26
170.15
156.95
145.77
140.29
126.35
125.85
71.31
64.79
52.97
46.89
46.30
36.46
30.14
29.87
28.77
27.33
24.23
19.75
18.90
14.60
8.69
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

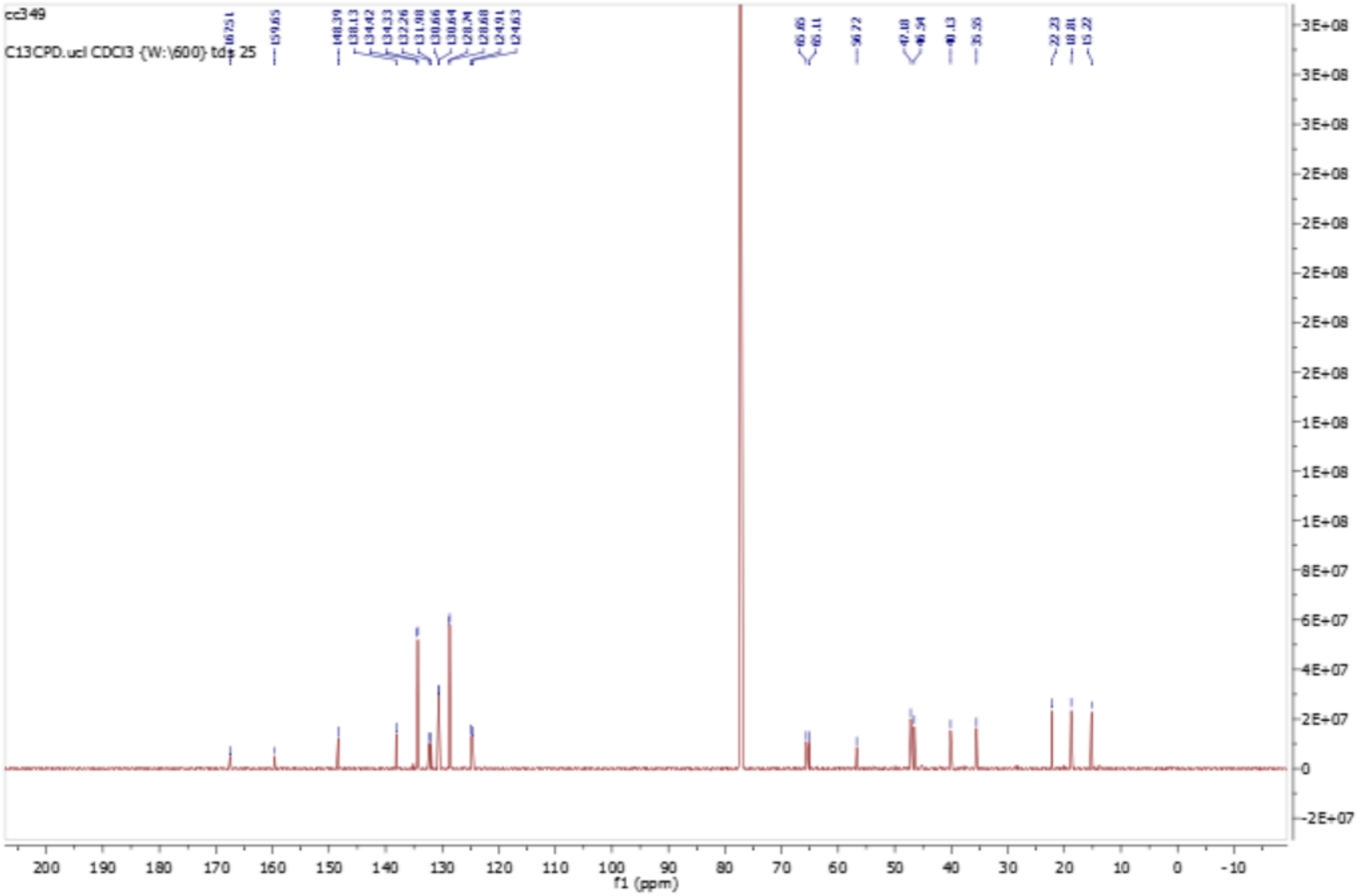
Palladacycle **8a**

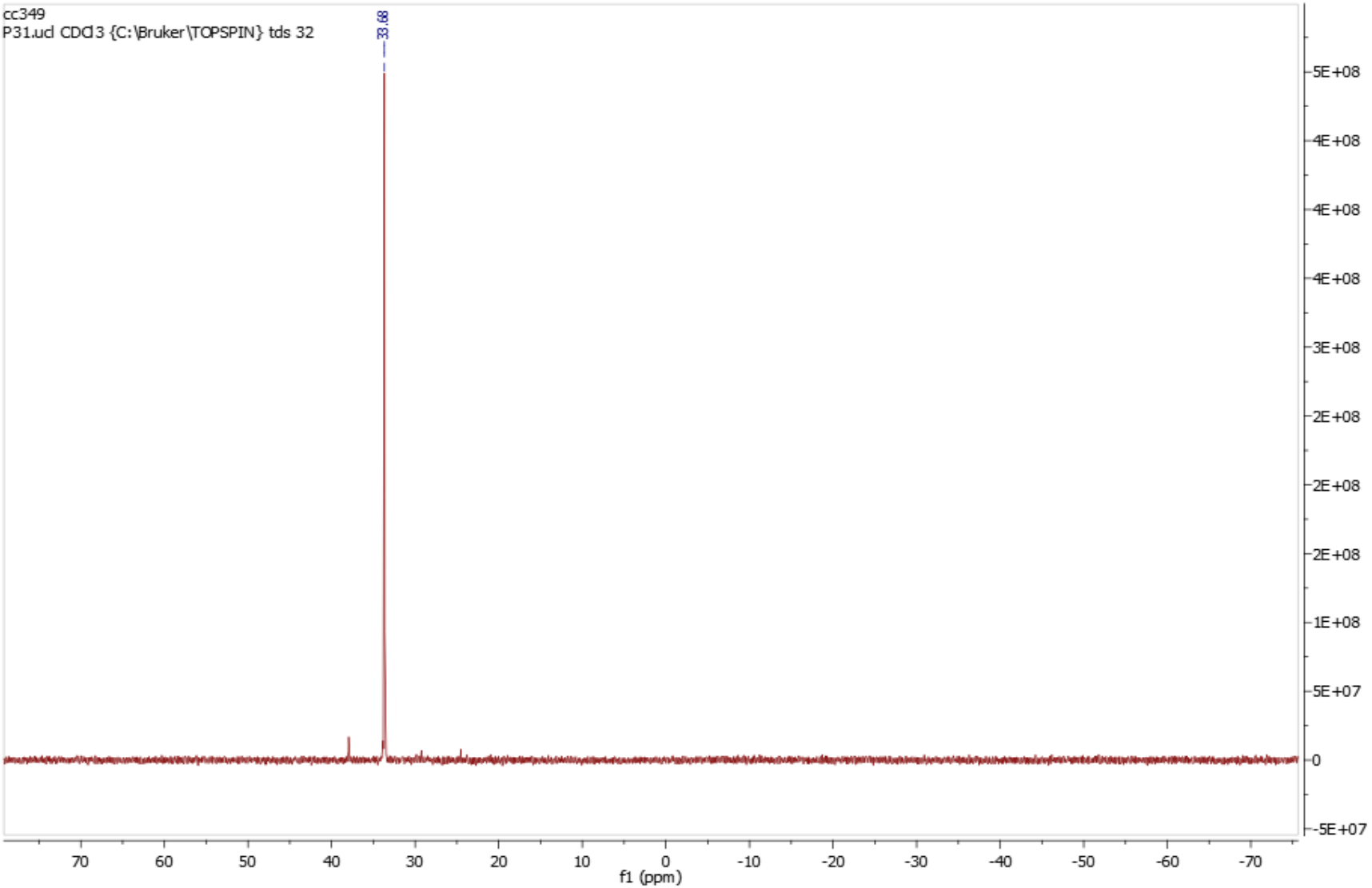



cc340
C13CPD.ucl CD3CN {W:\600} tds 12
167.98
158.21
148.34
139.69
126.81
124.32
68.05
63.89
47.54
47.29
41.13
36.79
22.51
19.33
15.19
f1 (ppm)

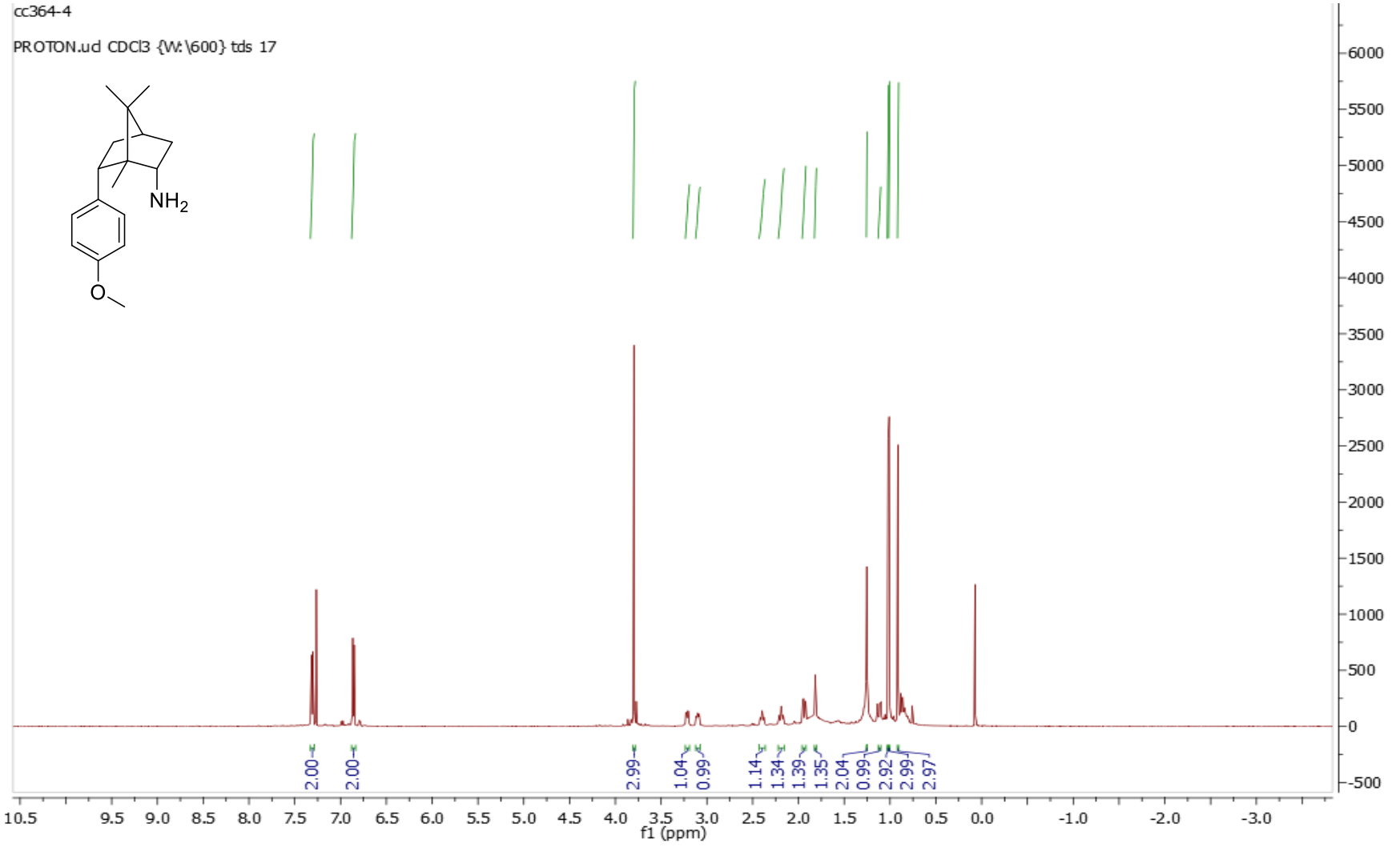
Palladacycle **8b**

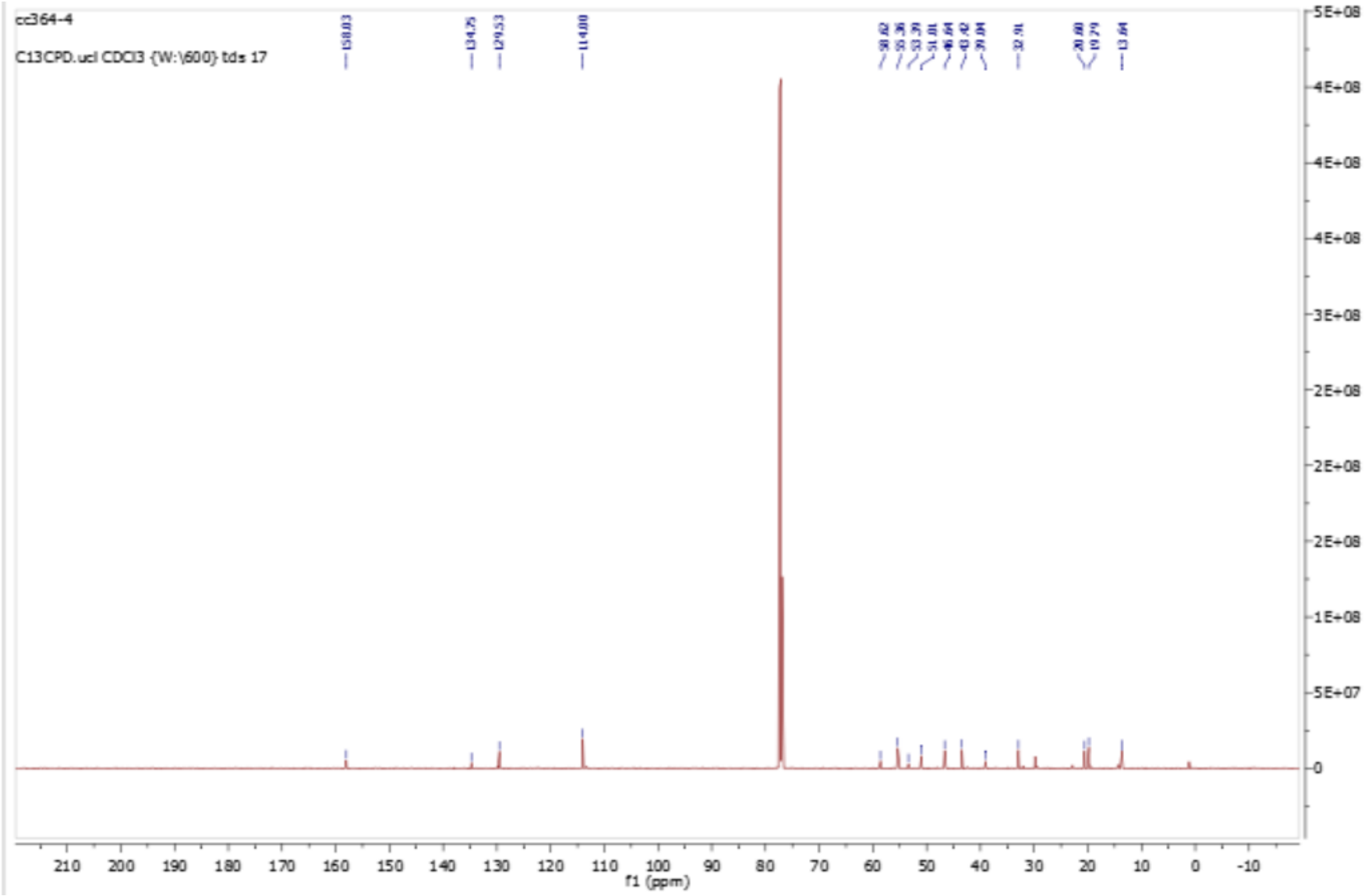



cc349
C13CPD.ucl CDCl3 {W:\600} td= 25
167.51
159.65
148.39
138.13
134.42
134.33
132.26
131.98
130.66
130.64
128.34
126.68
124.91
124.63
65.65
65.11
56.22
47.18
46.54
40.13
35.55
22.23
18.81
15.22
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

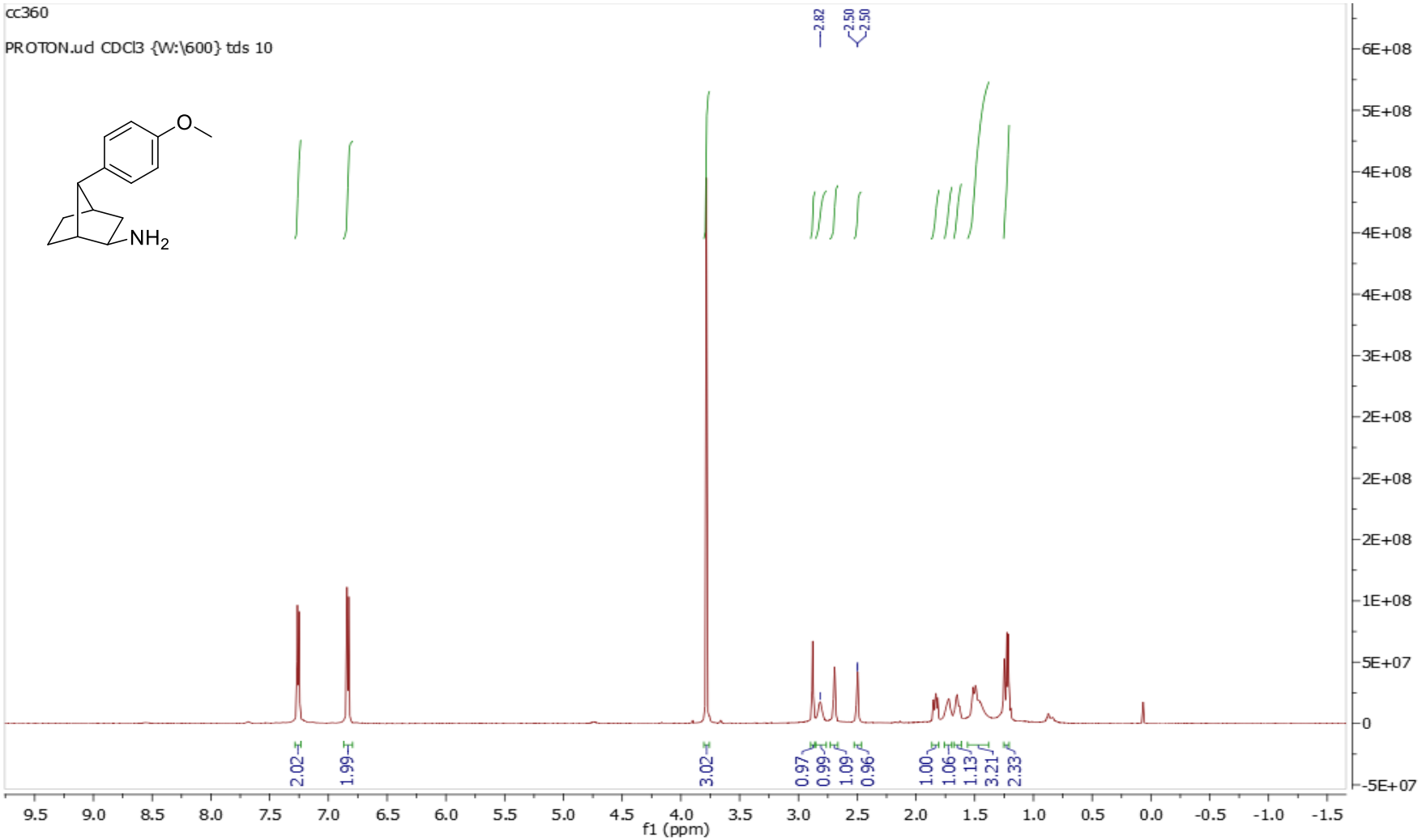

cc349
P31.ucl CDCl3 {C:\Bruker\TOPSPIN} tds 32
33.68
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

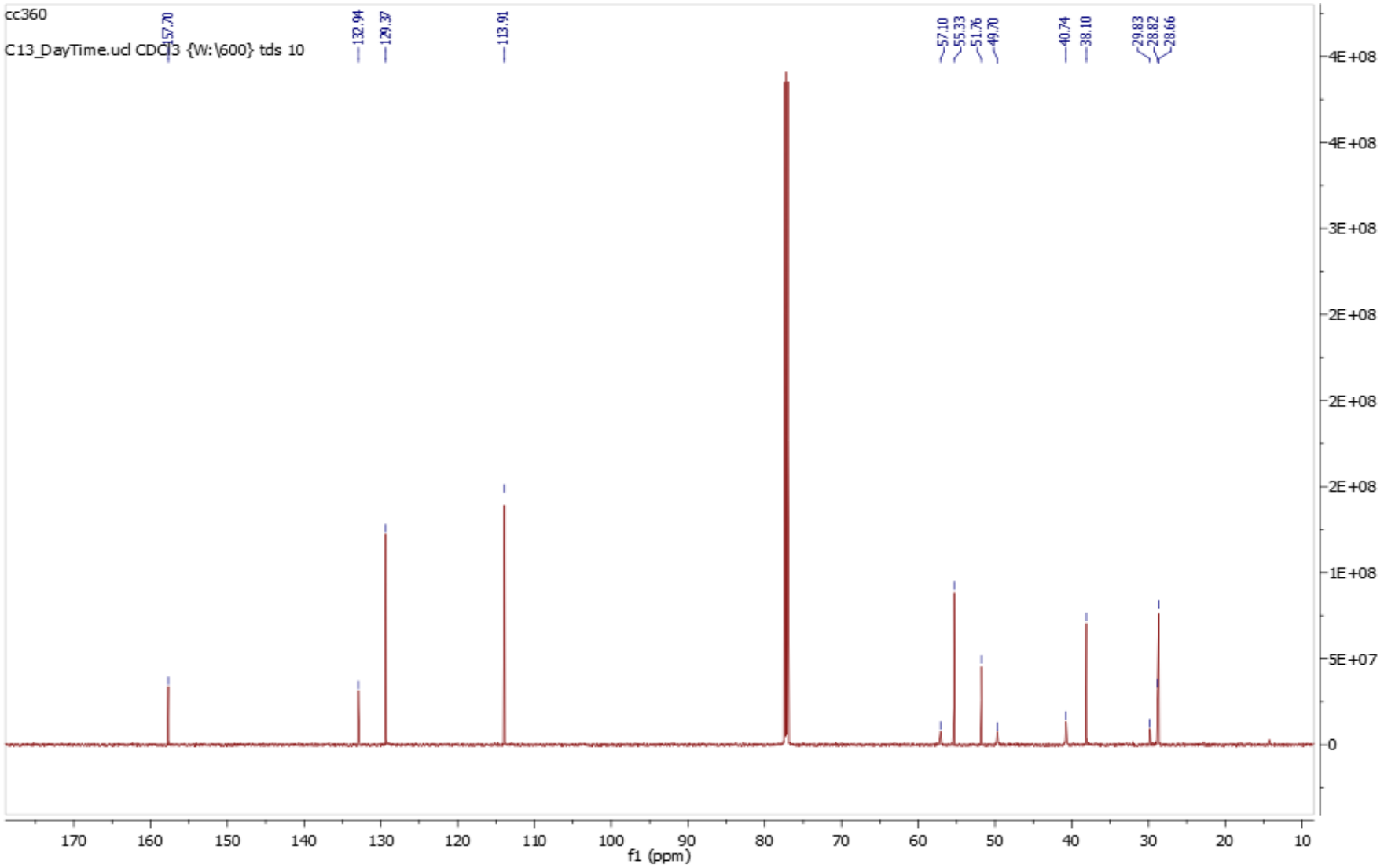
(1*S*,2*S*,4*R*,6*S*)-6-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine **11**




cc364-4
C13CPD.ucl CDCl3 {W:\600} tds 17
158.03
134.75
129.53
114.00
59.62
55.36
53.39
51.01
46.64
43.42
39.04
32.91
20.80
19.79
13.64
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

7-(4-methoxyphenol)bicyclo[2.2.1]heptan-2-amine **12**




cc360
C13_DayTime.ucl CDCl3 {W:\600} tds 10
157.70
132.94
129.37
113.91
57.10
55.33
51.76
49.70
40.74
38.10
29.83
28.82
28.66
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Single Crystal X-ray Diffraction Measurements

Single X-ray diffraction data was collected using an *Agilent SuperNova (Dual Source)* single crystal X-ray diffractometer using a micro-focus CuK_α X-ray beam (50 kV, 0.8 mA) and an *Atlas* detector (135 mm CCD). The temperature was controlled with an *Oxford Instruments Cryojet5*. The data were processed using the *CrysAlisPro* program.[1] Structure solution and refinement were accomplished using the SHELX 2014 programmes.[2] The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms associated with carbon and nitrogen atoms were refined isotropically. Crystallographic and refinement parameters for crystal structures **2a** and **8b** and **4a** are given in Table S1.

1. CrysAlisPro, Agilent Technologies, Version 1.171.36.28 (2014).
2. Sheldrick, G. M. *Acta Crystallogr.* 2015, **C71**, 3–8.

Table S1. Crystallographic and refinement parameters for compounds **2a, 8b** and **4a**.

compound	**2a**	**8b**	**4a**
empirical formula	$C_{23}H_{28}N_2O_2$	$C_{36}H_{37}Cl_6N_2OPPd$	$C_{20}H_{22}N_2O_2$
M_r / g mol^{-1}	364.47	863.74	322.39
T / K	150.0(1)	150.0(1)	150.0(1)
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1$	$P1$	$P\bar{1}$
a / Å	11.30940(10)	11.43580(10)	6.4362(2)
b / Å	10.53060(10)	13.4434(2)	10.8331(4)
c / Å	17.0804(2)	14.17280(10)	11.9492(4)
α / °	90	92.7600(10)	99.468(3)
β / °	104.5610(10)	105.3020(10)	94.704(3)
γ / °	90	112.1750(10)	92.002(3)
V / Å^3	1968.85(4)	1919.36(4)	818.03(5)
Z	4	2	2
ρ_{calc} / g cm^{-3}	1.230	1.495	1.309
μ / mm^{-1}	0.618	8.381	0.676
F(000)	784	876	344
crystal size / mm^3	0.43 × 0.05 × 0.03	0.41 × 0.34 × 0.06	0.37 × 0.22 × 0.21
X-ray radiation	CuK_α (λ = 1.5418 Å)	CuK_α (λ = 1.5418 Å)	CuK_α (λ = 1.5418 Å)
index ranges	$-13 \le h \le 13$	$-14 \le h \le 14$	$-7 \le h \le 7$
	$-12 \le k \le 12$	$-16 \le k \le 15$	$-12 \le k \le 12$
	$-20 \le l \le 20$	$-17 \le l \le 17$	$-14 \le l \le 14$
no. of reflections measured	28886	107520	11079
no. independent reflections	7118	14362	2881
R_{int} [$I \ge 2\sigma(I)$]	0.0420	0.0831	0.0225
goodness-of-fit on F^2	0.989	1.037	1.056
final R_1 values [$I \ge 2\sigma(I)$]	0.0411	0.0513	0.0366
final $wR(F^2)$ values [$I \ge 2\sigma(I)$]	0.0453	0.0520	0.0379
final R_1 values [all data]	0.1109	0.1380	0.0975
final $wR(F^2)$ values [all data]	0.1141	0.1394	0.0986
largest diff. peak/hole / e Å^{-3}	0.040 / −0.202	0.798 / −1.715	0.240 / −0.191
CCDC deposition number	1553200	1553201	1553202

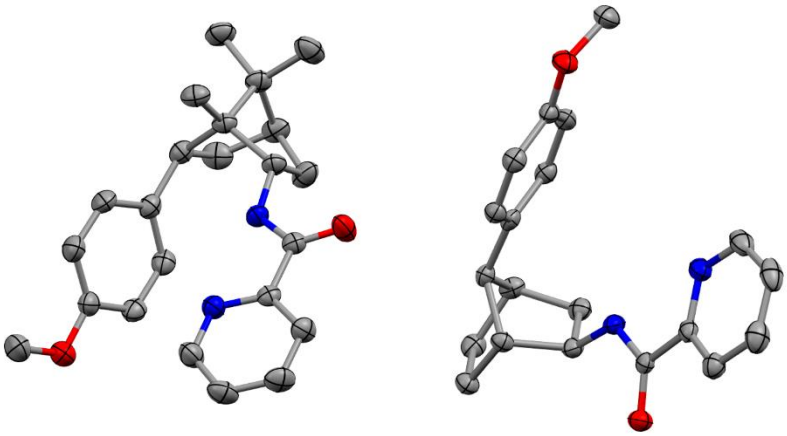


Figure S1. X-ray crystal structures of **2a** and **4a**. The atomic displacement parameters are shown at the 50% probability level. Hydrogen atoms are omitted to enhance clarity. Colour scheme: grey – carbon, blue – nitrogen, red – oxygen.

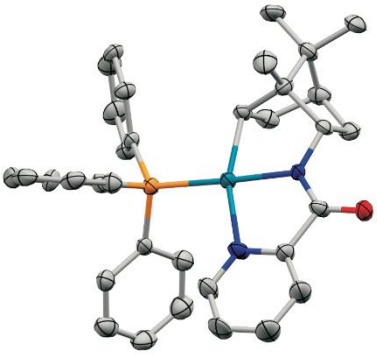


Figure S2. X-ray crystal structure of **8b**. The atomic displacement parameters are shown at the 50% probability level. Hydrogen atoms are omitted to enhance clarity. Colour scheme: grey – carbon, blue – nitrogen, red – oxygen, orange – phosphorus, turquoise – palladium.