Mechanistic Investigations and Substrate Scope Evaluation of Ruthenium-Catalyzed Direct sp^3 Arylation of Benzylic Positions Directed by 3-Substituted Pyridines

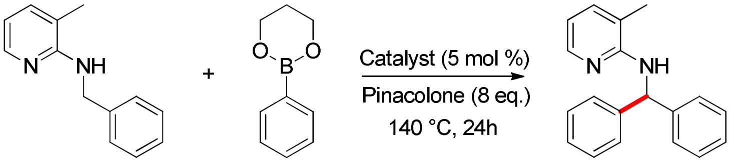
Navid Dastbaravardeh,[†] Karl Kirchner,[†] Michael Schnürch,[*,†] and Marko D. Mihovilovic[†]

Vienna University of Technology, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163-OC, 1060 Vienna (Austria)

E-mail: michael.schnuerch@tuwien.ac.at

Supporting Information

1. Catalyst Screening



4a **17a** **5a**

entry	catalyst	conv.[b]
1	Ru/C	0
2	$Ru_3(CO)_{12}$	86
3	$Ru(PPh_3)_3H_2(CO)$	2
4	$[Ru(p\text{-}cymene)Cl_2]_2$	0
5	$Ru(PPh_3)_3Cl_2$	0
6	$Ru(PPh_3)_2Cl_2(CO)_2$	0

7	$[RuCl_2(cod)]_n$	0
8	$[RuCl_2(CO)_3]_2$	0
9	$RuCl_3$	0
10	$Ru(acac)_3$	0
11	$[Rh(cod)Cl]_2$	0
12	$Rh_4(CO)_{12}$	0
13	$Pd(OAc)_2$	0
14	$PdCl_2$	0
15	$Pd(PPh_3)_4$	0
16	$Fe(CO)_5$	0
17	$Fe_3(CO)_{12}$	0
18	$Fe(CO)_3(PPh_3)_2$	0

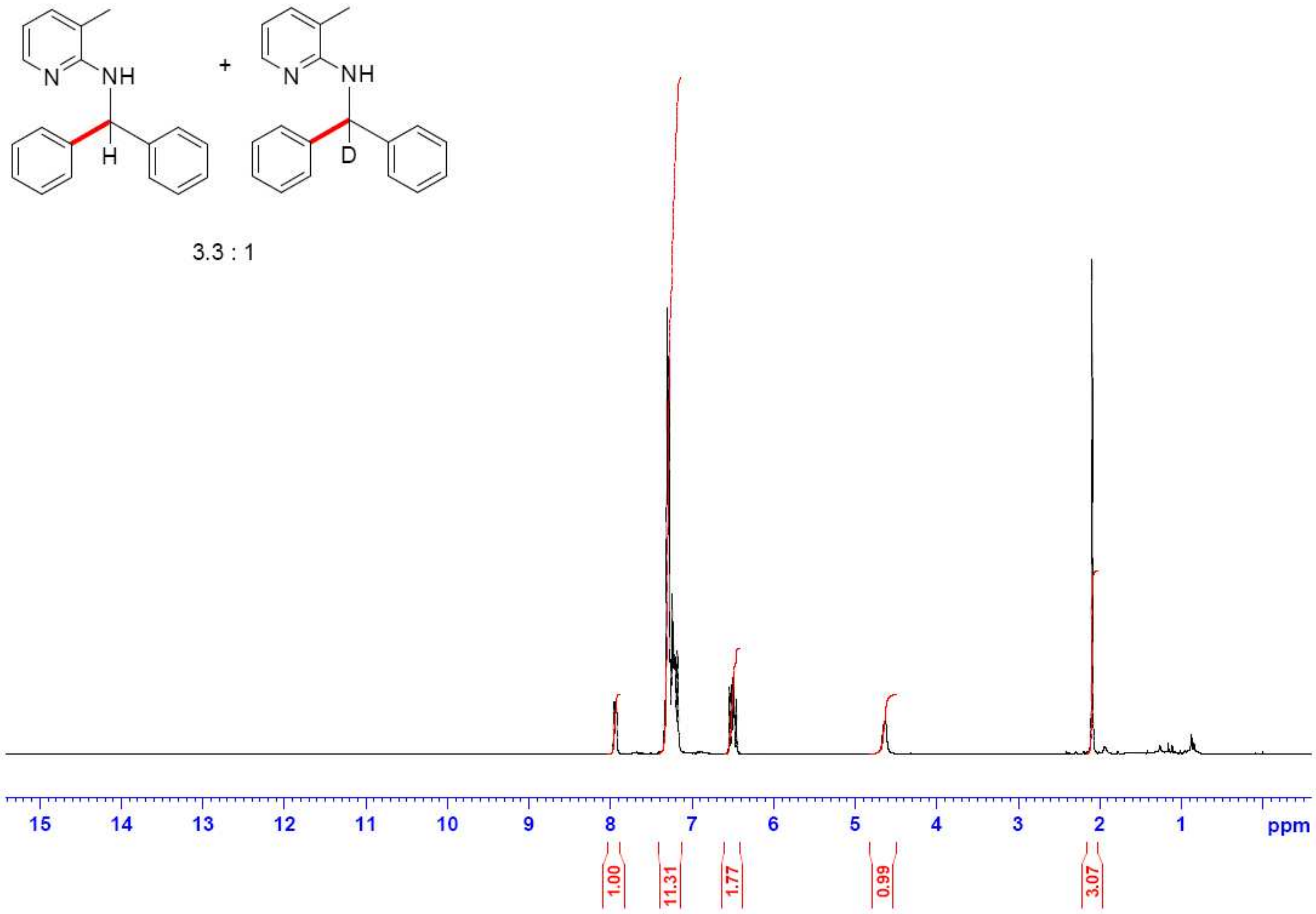
[a] Reaction conditions: **4a** (0.5 mmol), **17a** (0.75 mmol), catalyst (5 mol %) and pinacolone (0.5 mL). [b] Conversion based on GC analysis with respect to **4a** (dodecane as internal standard). [c] Yield determined by GC analysis with respect to **4a** (dodecane as internal standard).

2. DFT Calculations

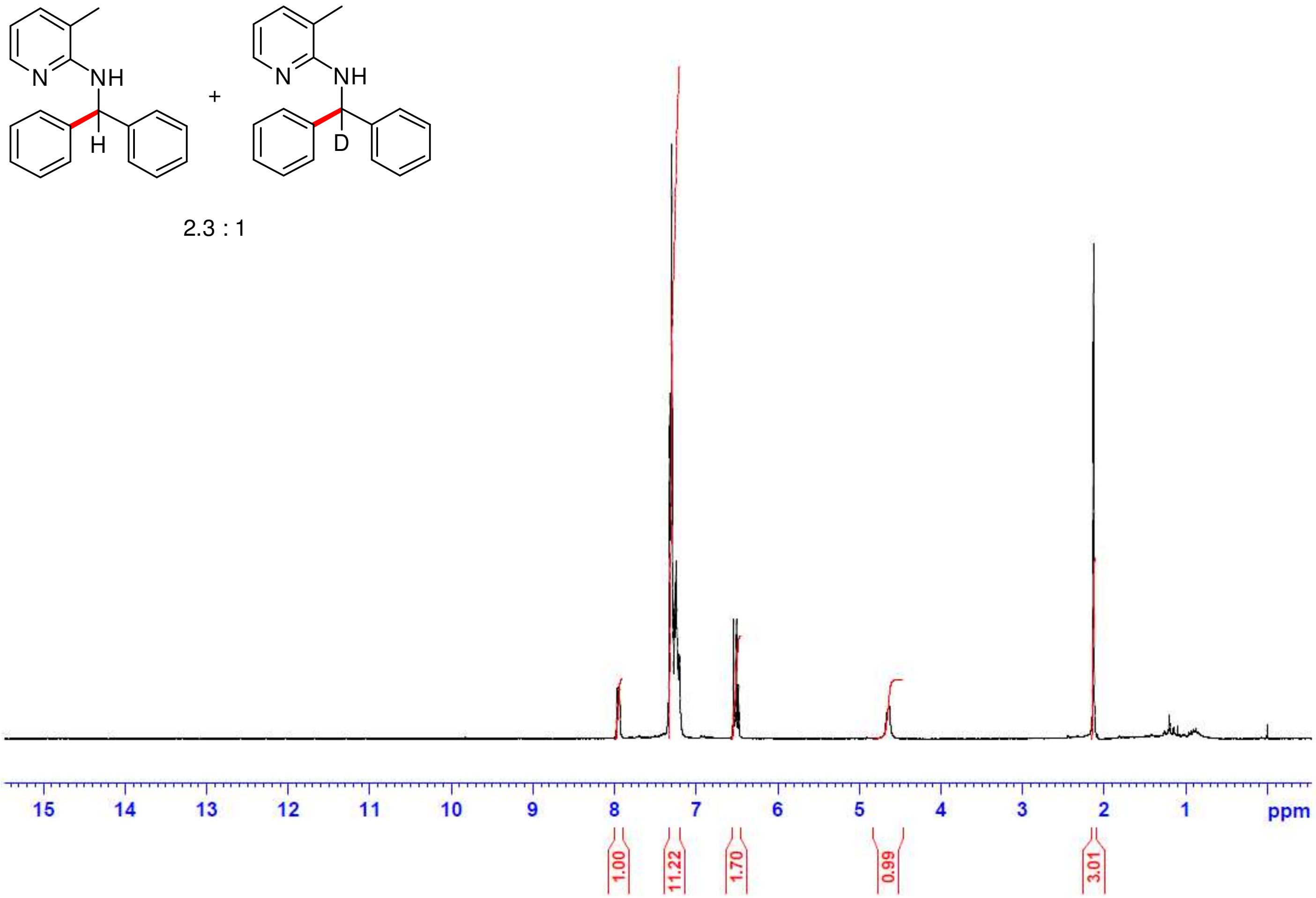
Computational Details. All calculations were performed using the Gaussian 03 software package,[1] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock[2] exchange with DFT exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[3] The optimized geometries were obtained with the 6-31G(d,p) basis sets. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles.

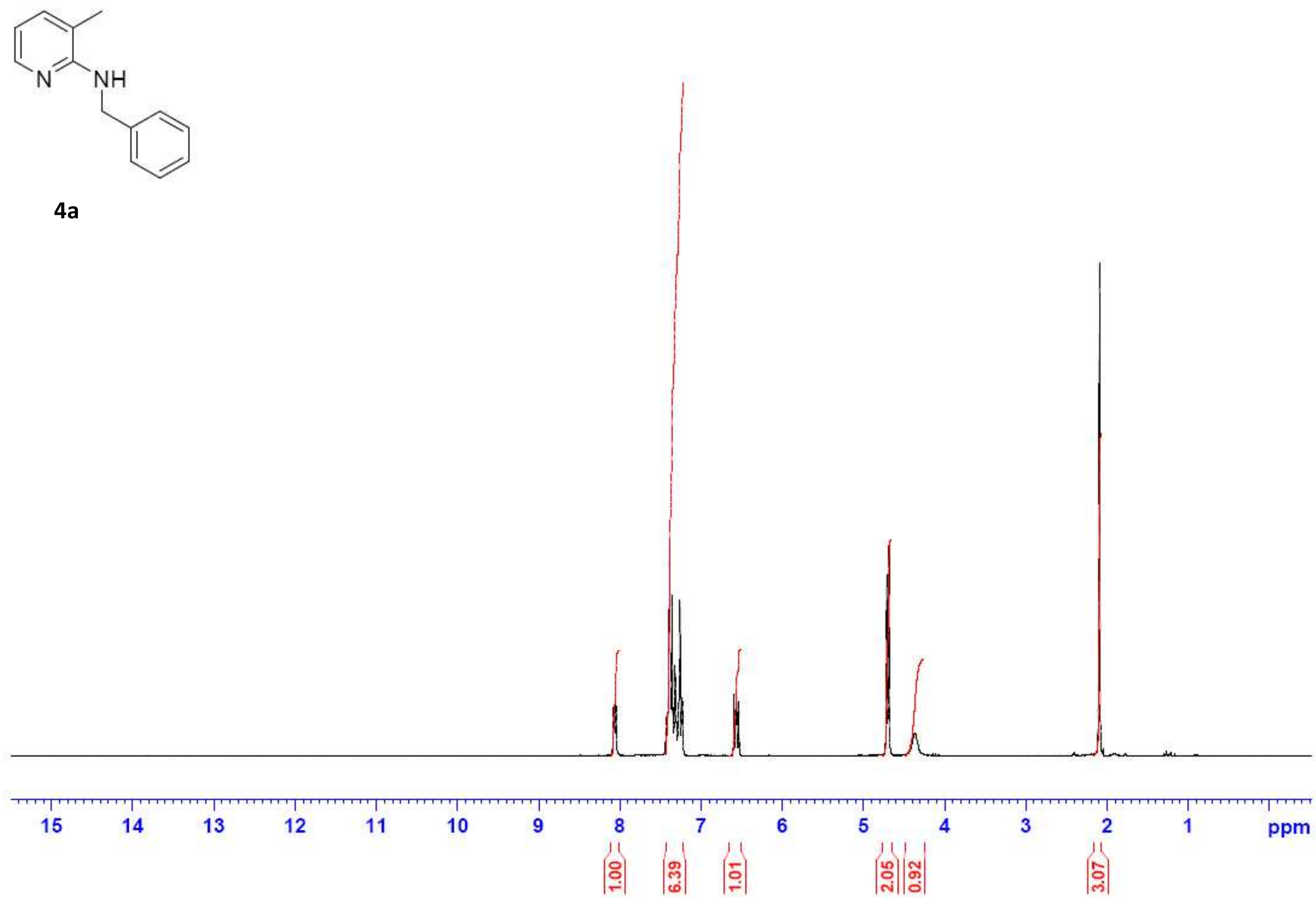
3. NMR Spectra

Intermolecular KIE Experiment -

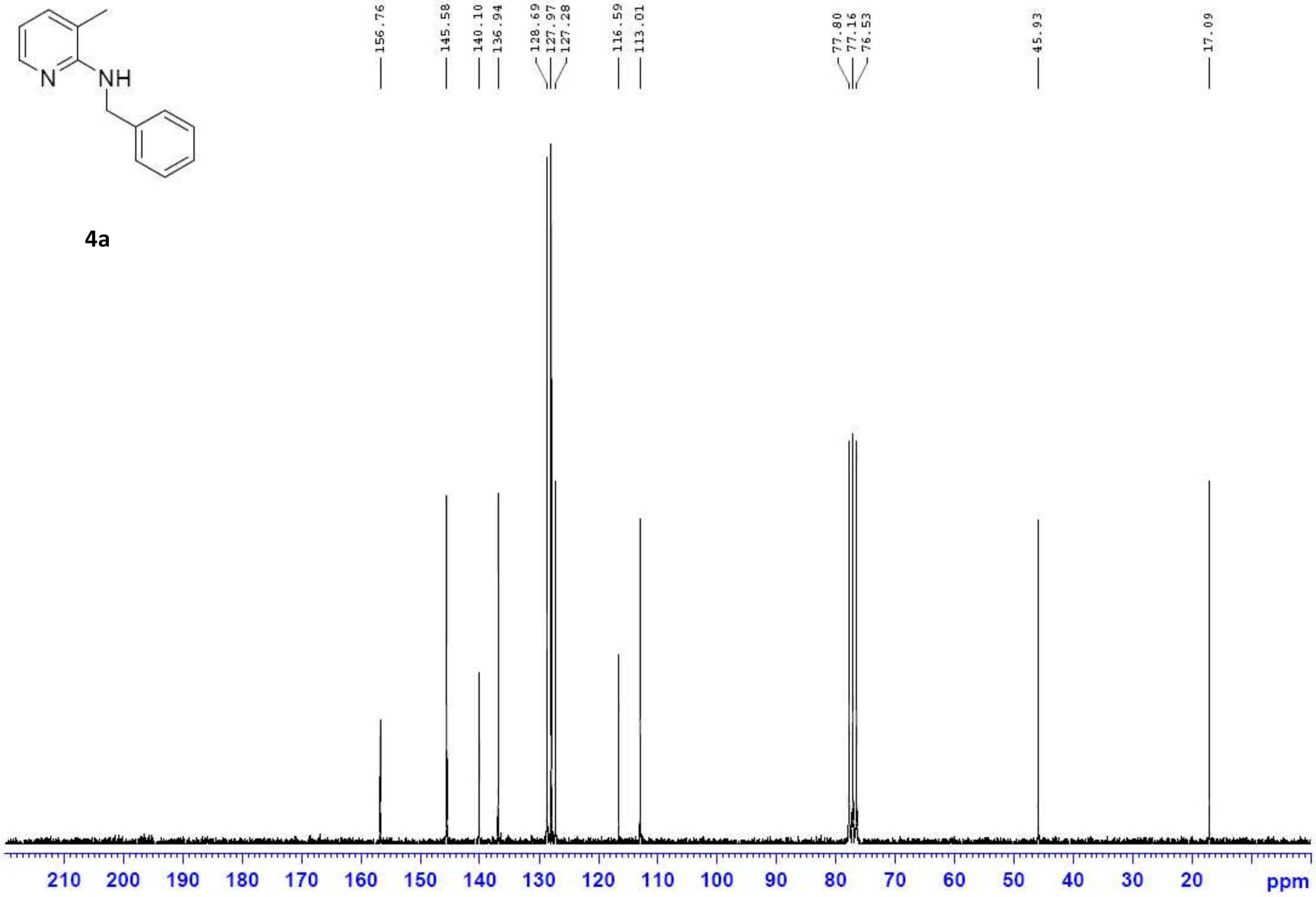


Intramolecular KIE Experiment -

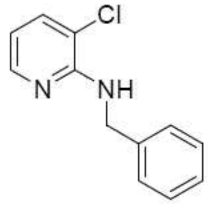




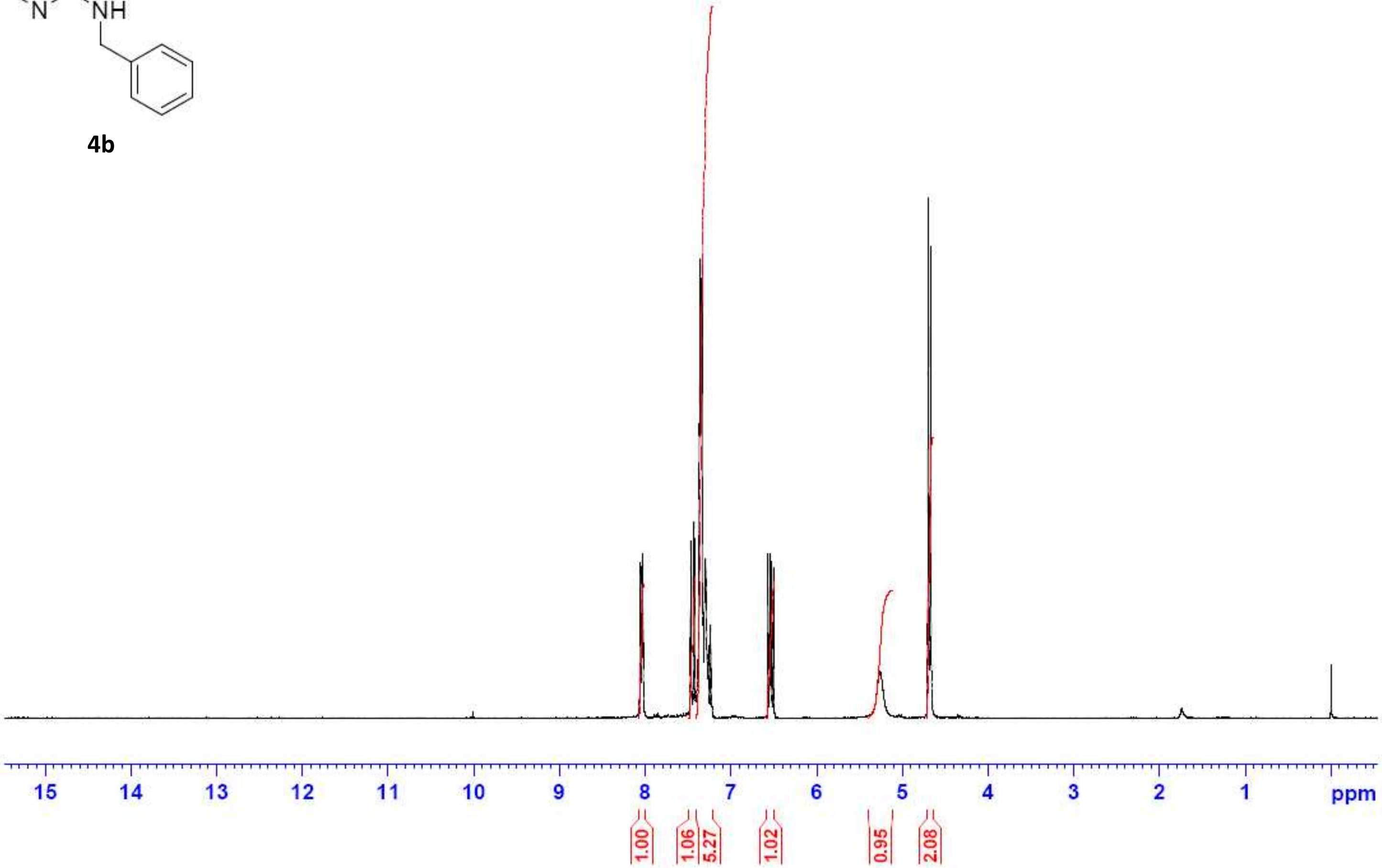
4a

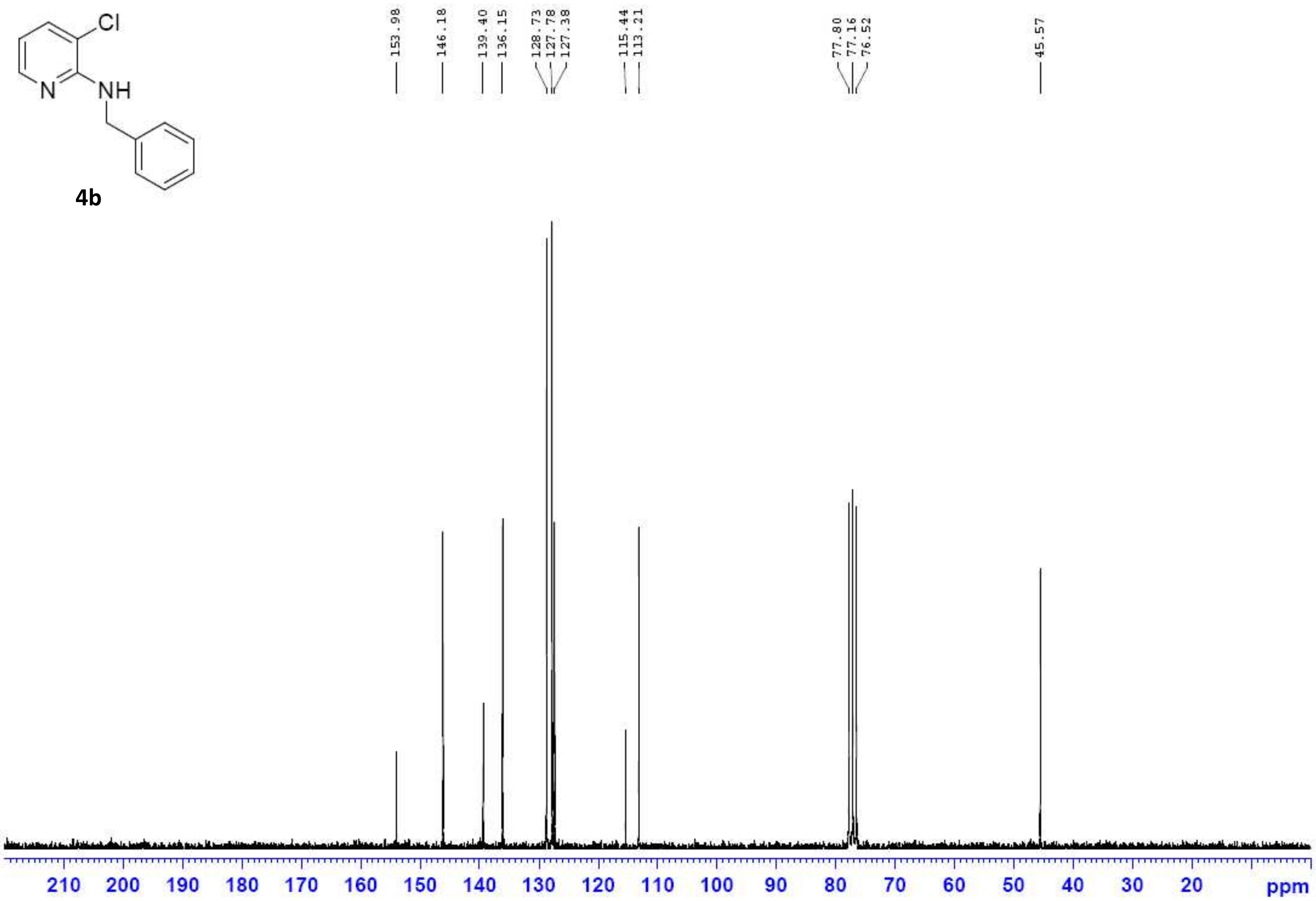

4a

156.76
145.58
140.10
136.94
128.69
127.97
127.28
116.59
113.01
77.80
77.16
76.53
45.93
17.09
NH
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



4b

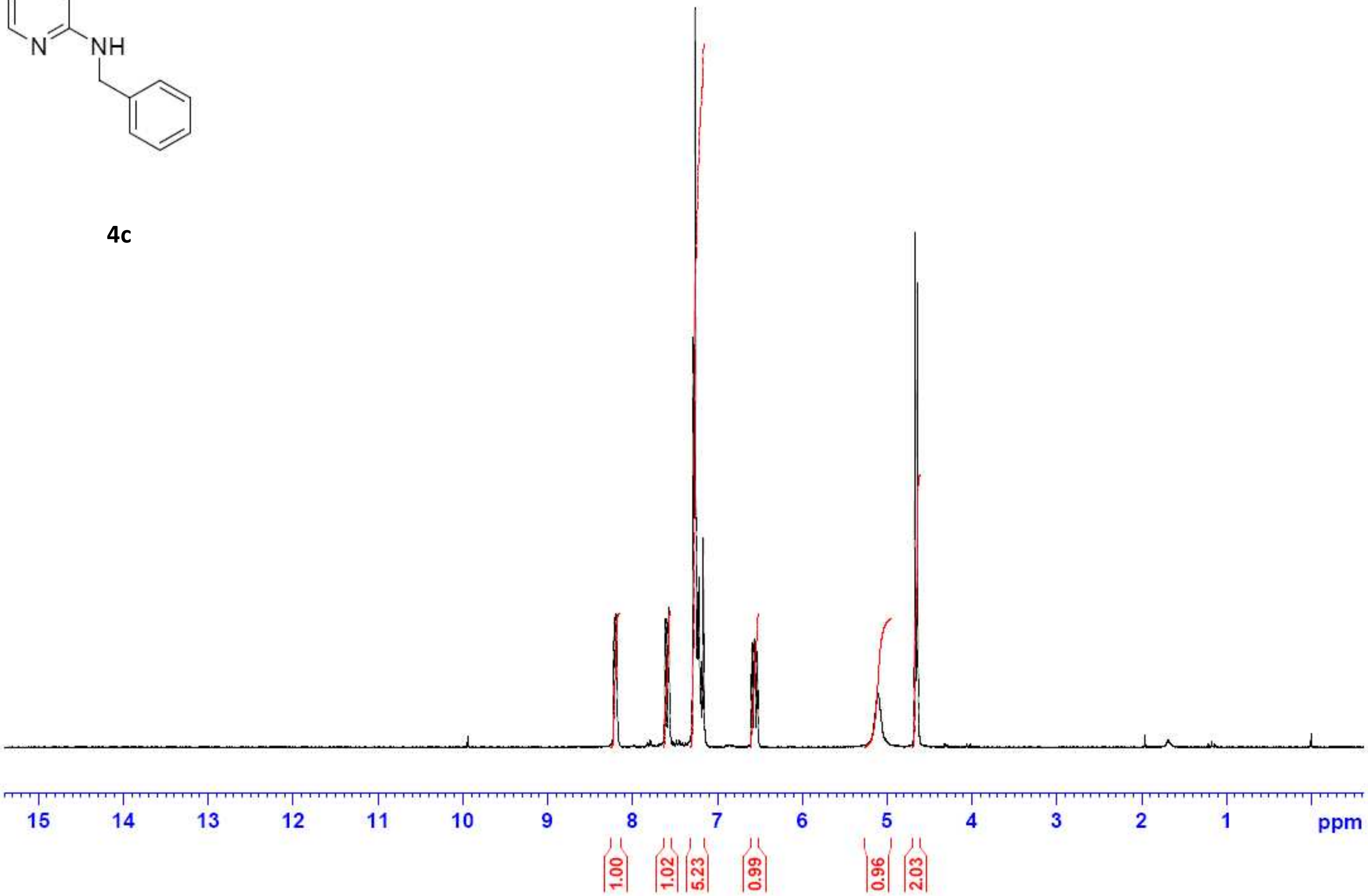




4b

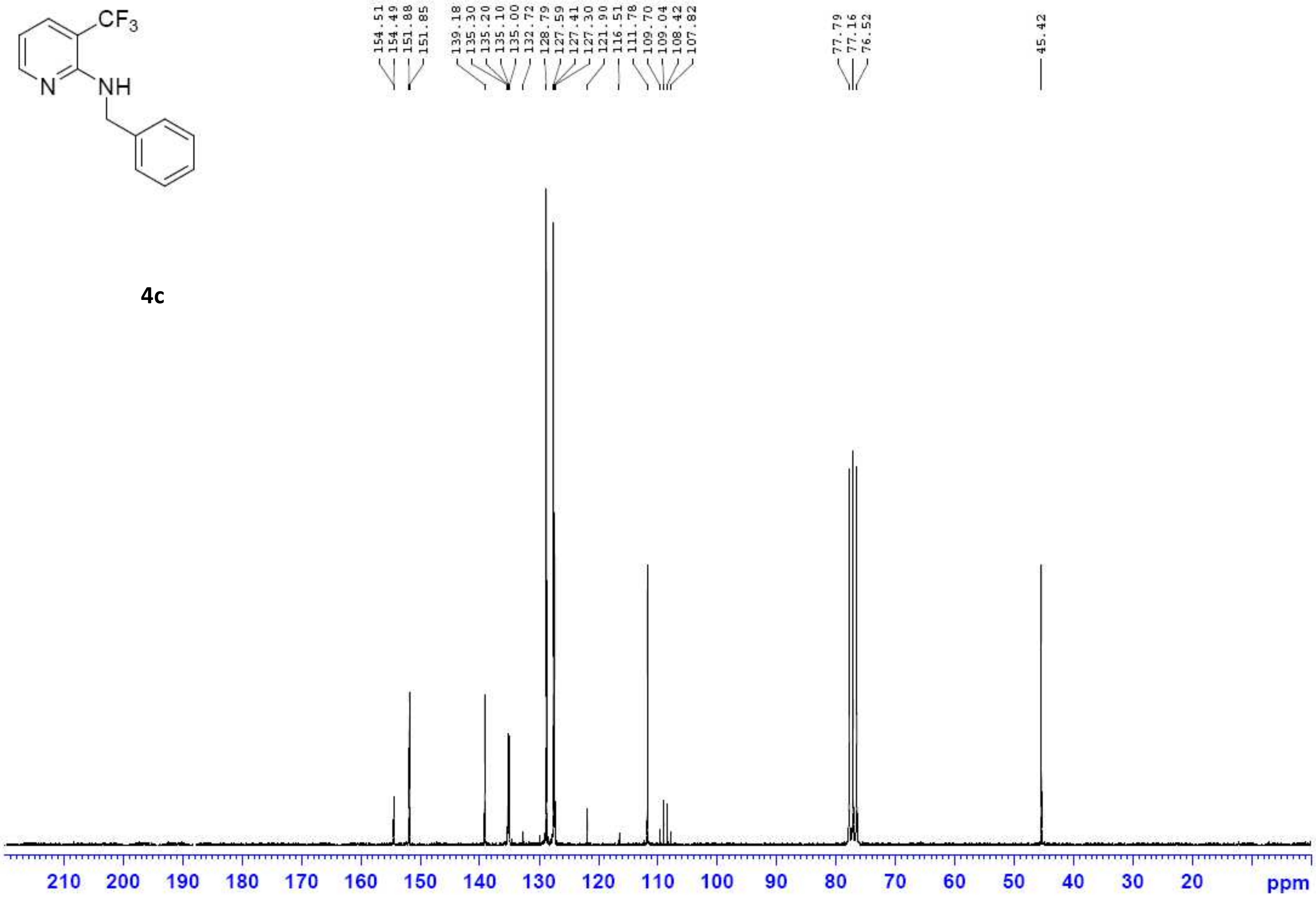
153.98
146.18
139.40
136.15
128.73
127.78
127.38
115.44
113.21
77.80
77.16
76.52
45.57
Cl
N
NH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

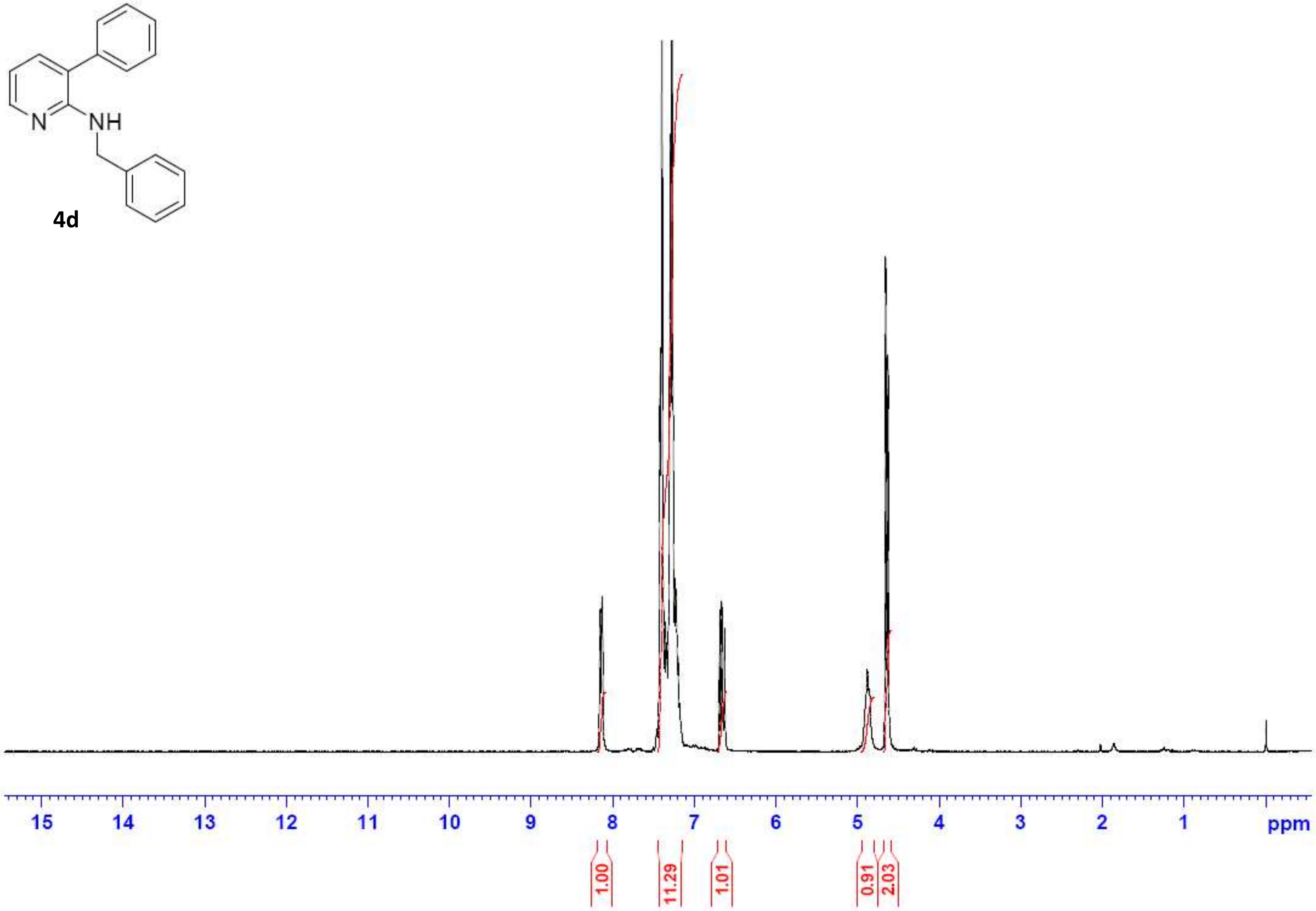
4c



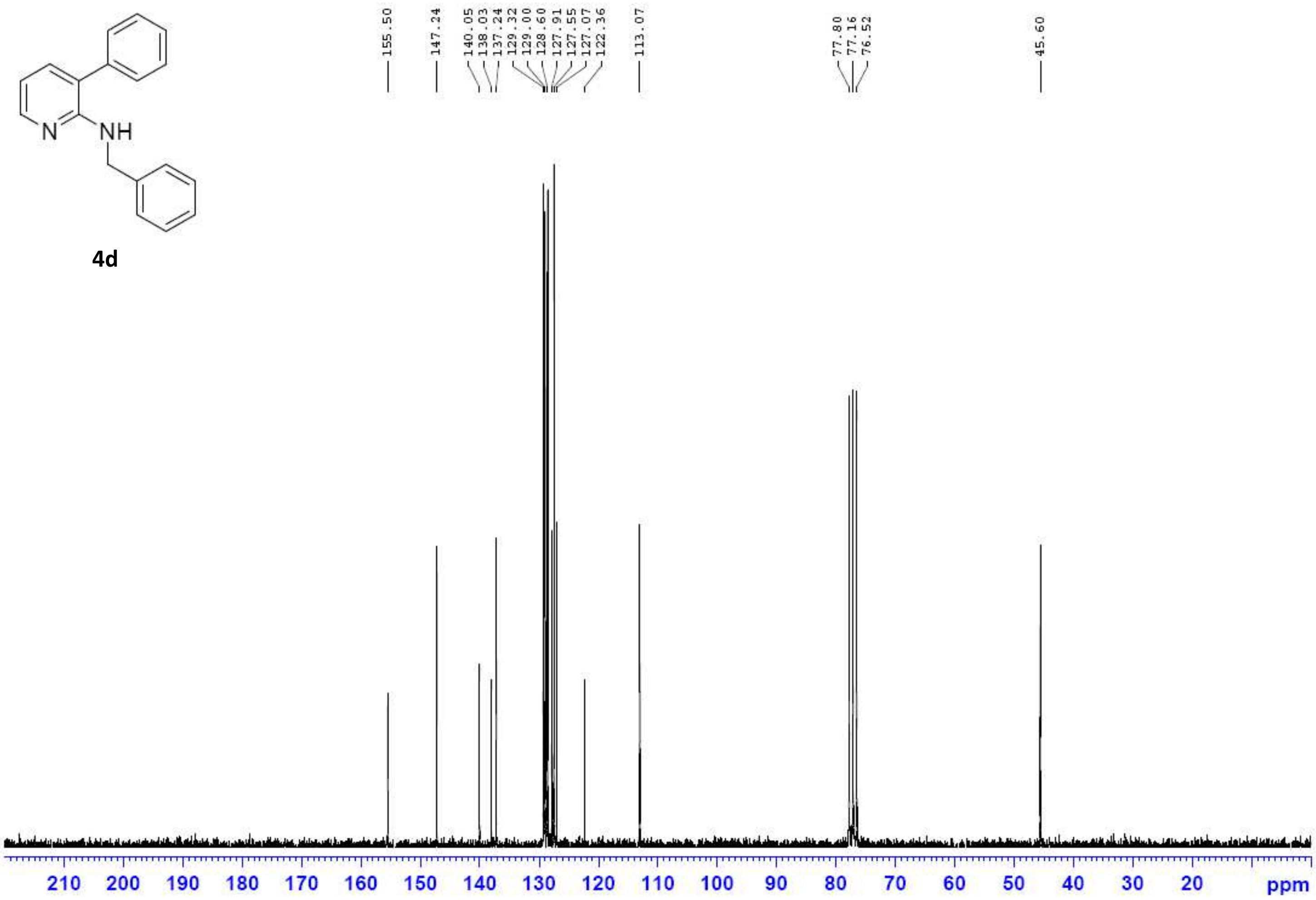

CF3
N
NH

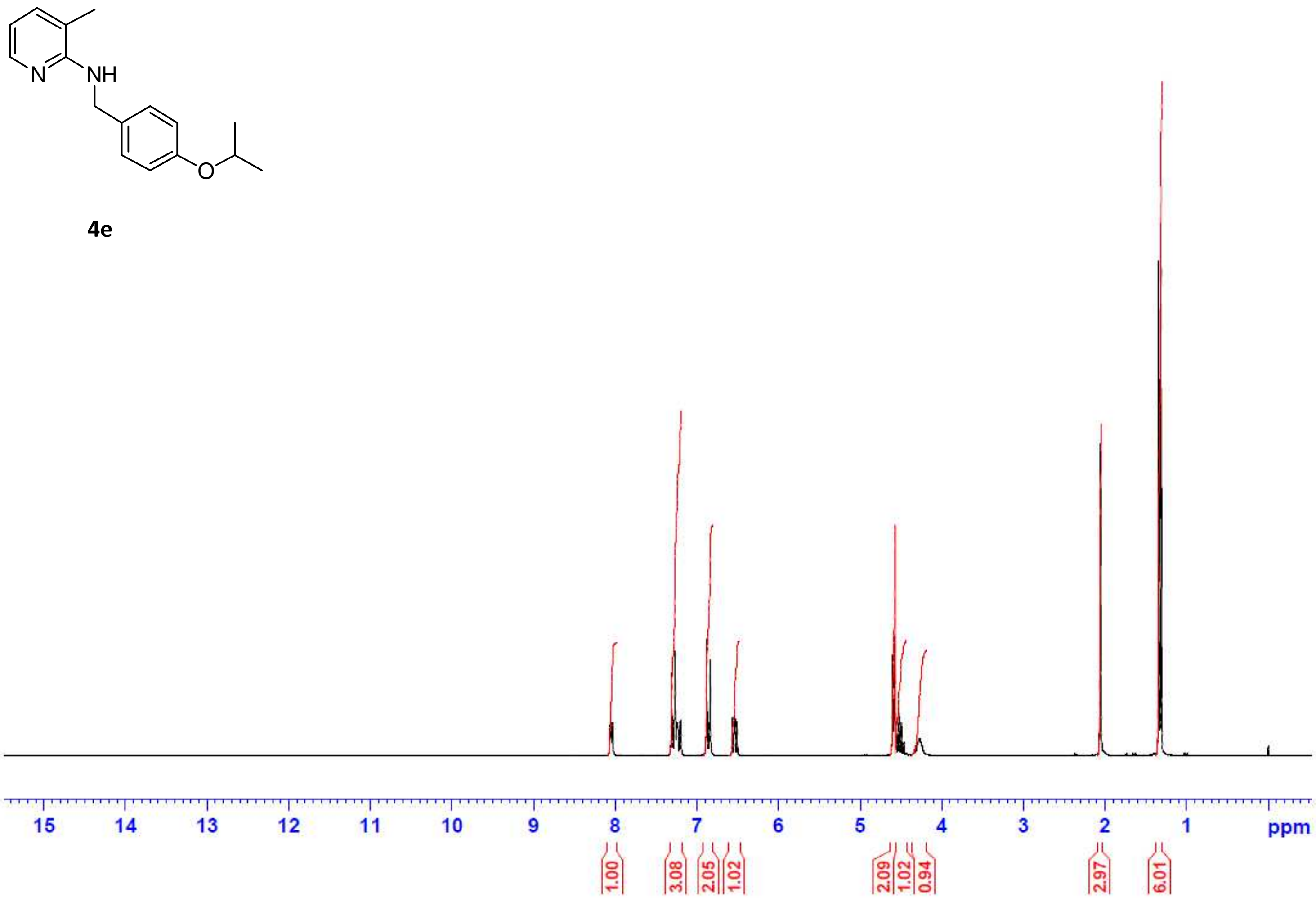
4c


154.51
154.49
151.88
151.85
139.18
135.30
135.20
135.10
135.00
132.72
128.79
127.59
127.41
127.30
121.90
116.51
111.78
109.70
109.04
108.42
107.82
77.79
77.16
76.52
45.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

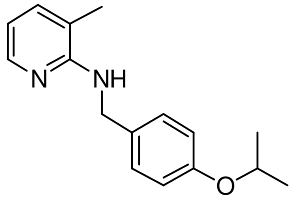


4d

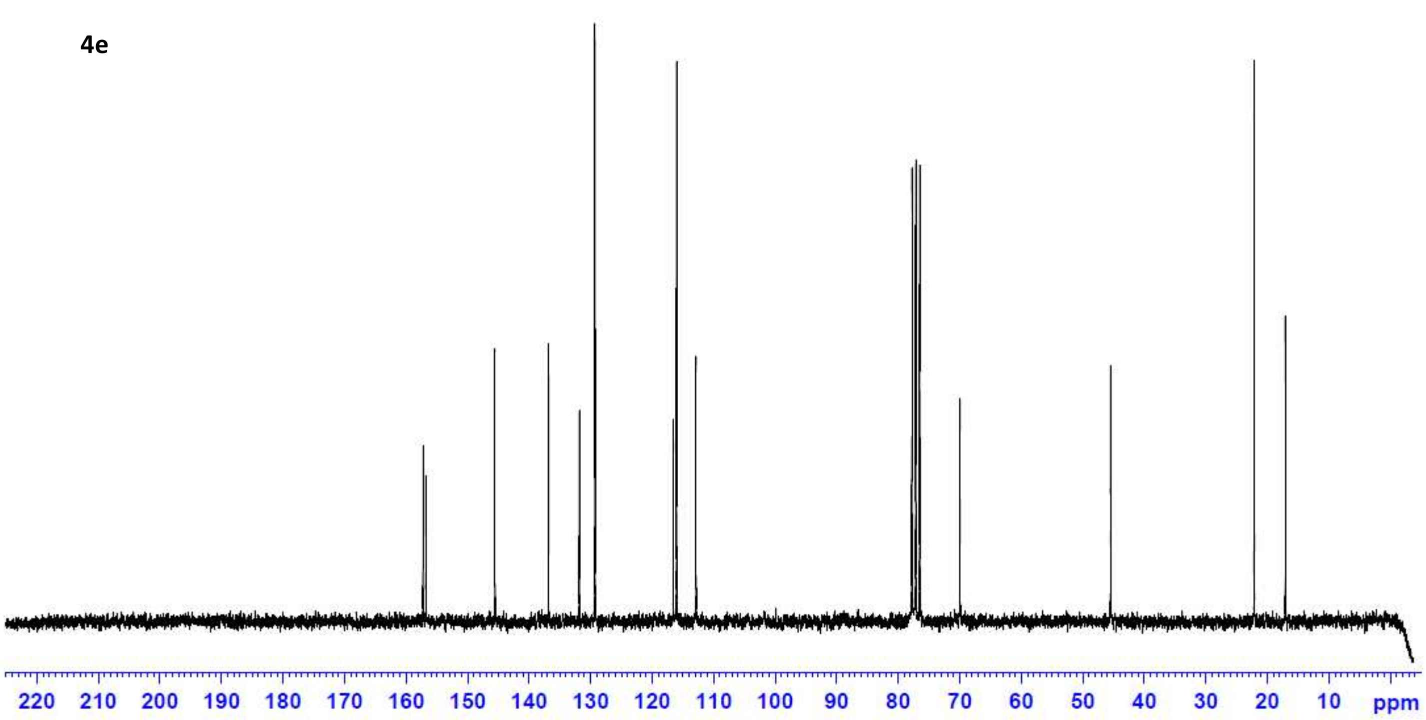

4d
155.50
147.24
140.05
138.03
137.24
129.32
129.00
128.60
127.91
127.55
127.07
122.36
113.07
77.80
77.16
76.52
45.60
NH
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

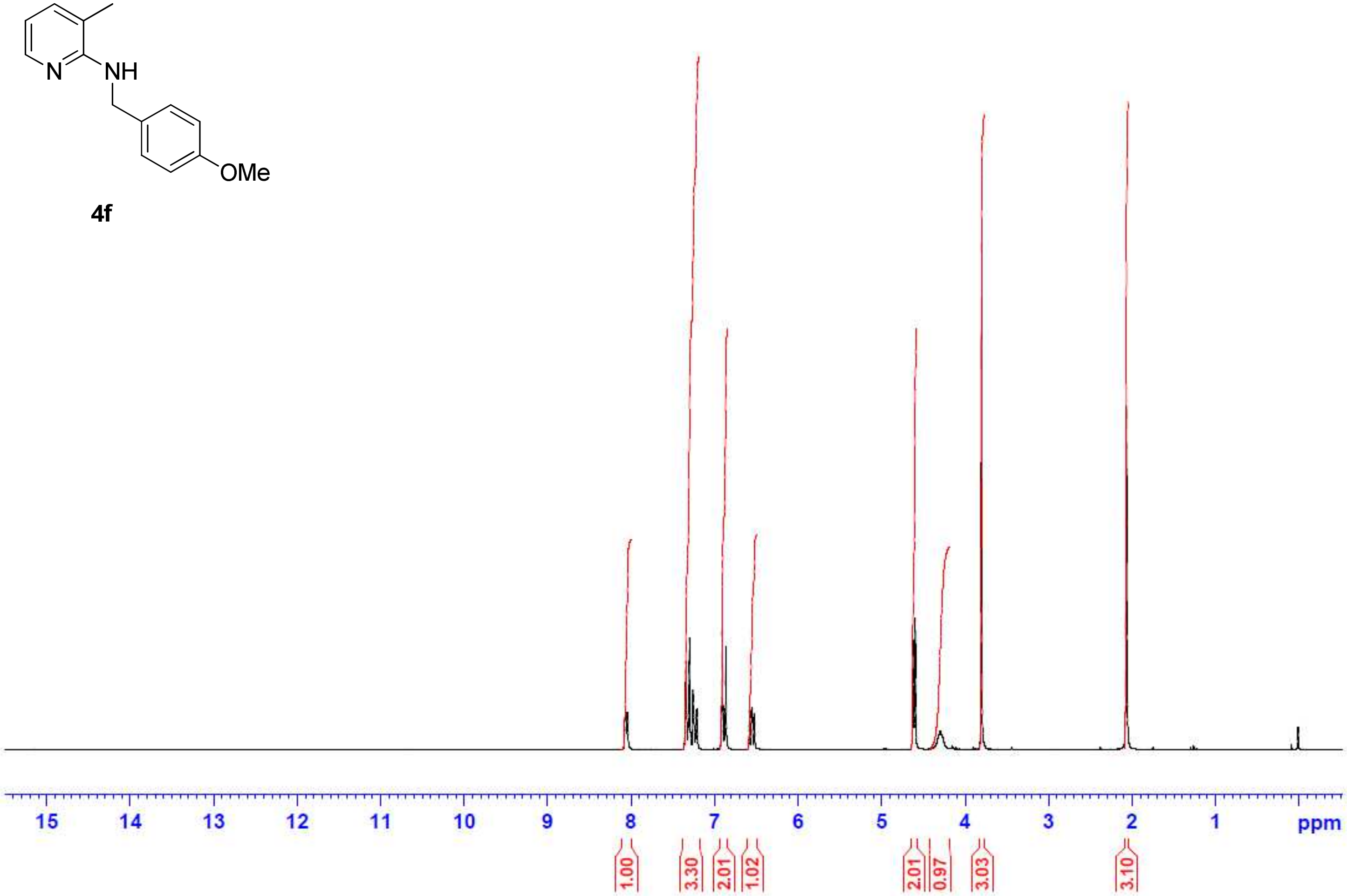
N
NH
O
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.08
2.05
1.02
2.09
1.02
0.94
2.97
6.01

4e

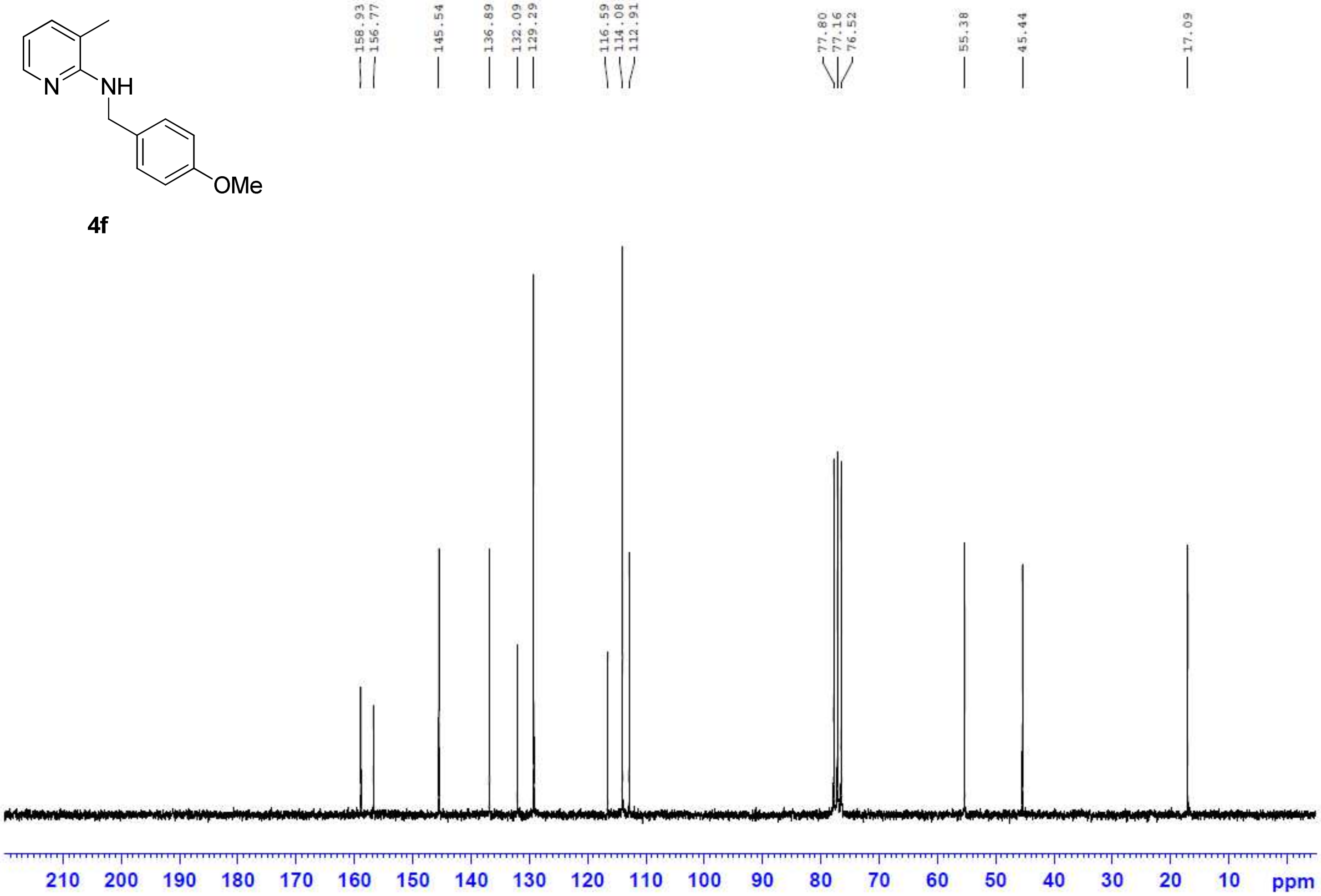

N
NH
O

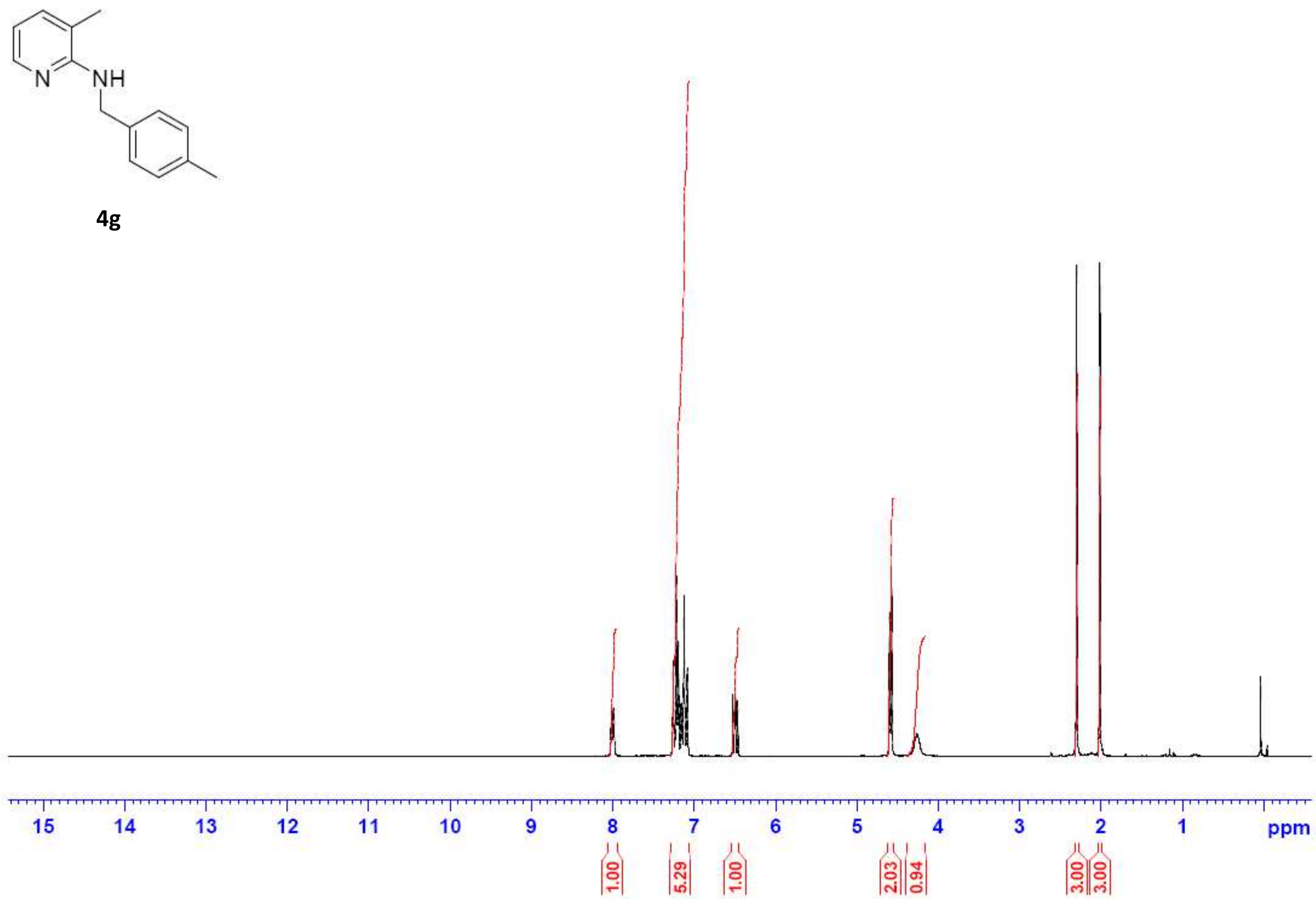
4e


157.25
156.80
145.56
136.87
131.85
129.32
116.58
116.05
112.87
77.79
77.16
76.52
69.98
45.50
22.16
17.11
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

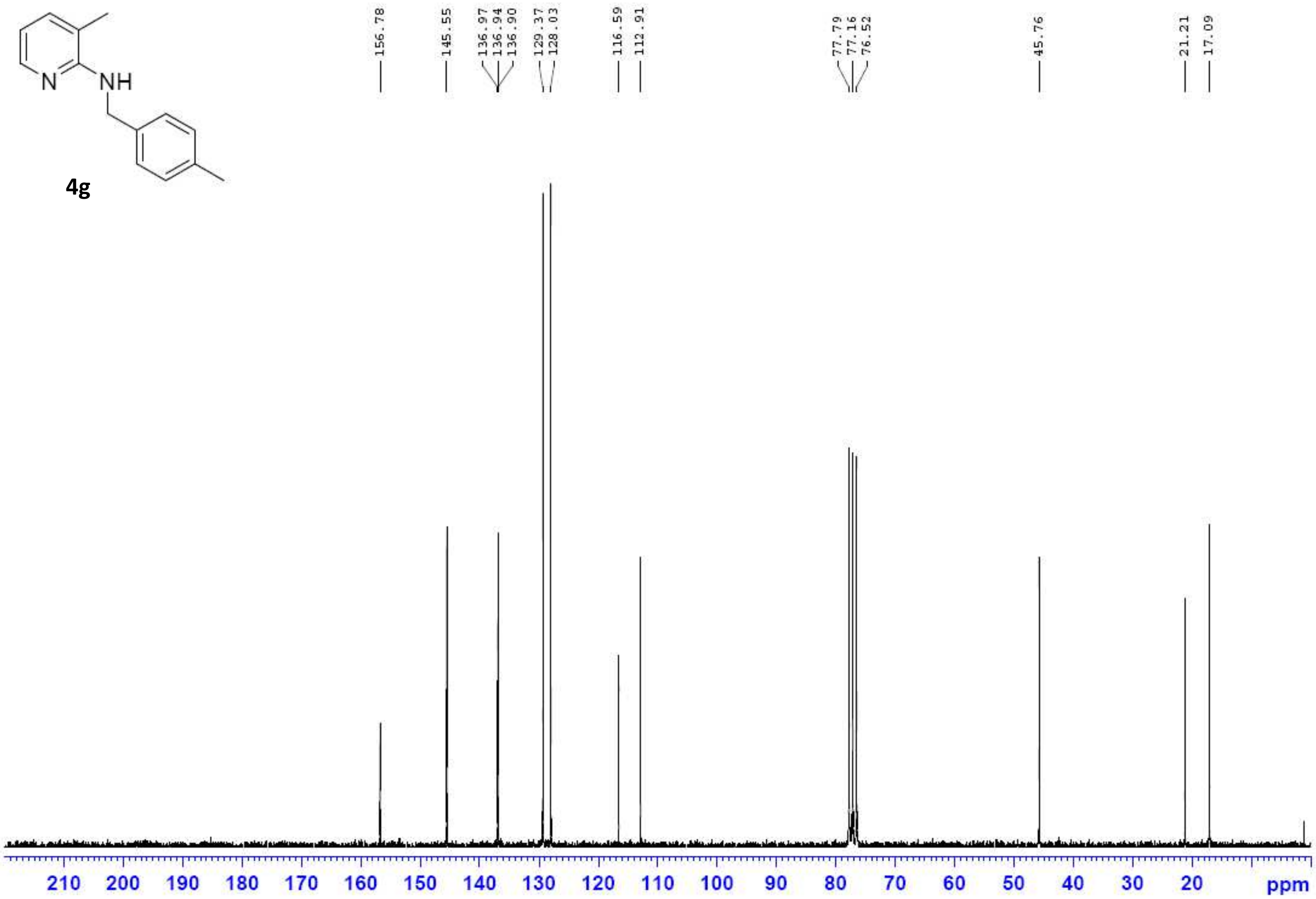


4f


4f
NH
N
OMe
158.93
156.77
145.54
136.89
132.09
129.29
116.59
114.08
112.91
77.80
77.16
76.52
55.38
45.44
17.09
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

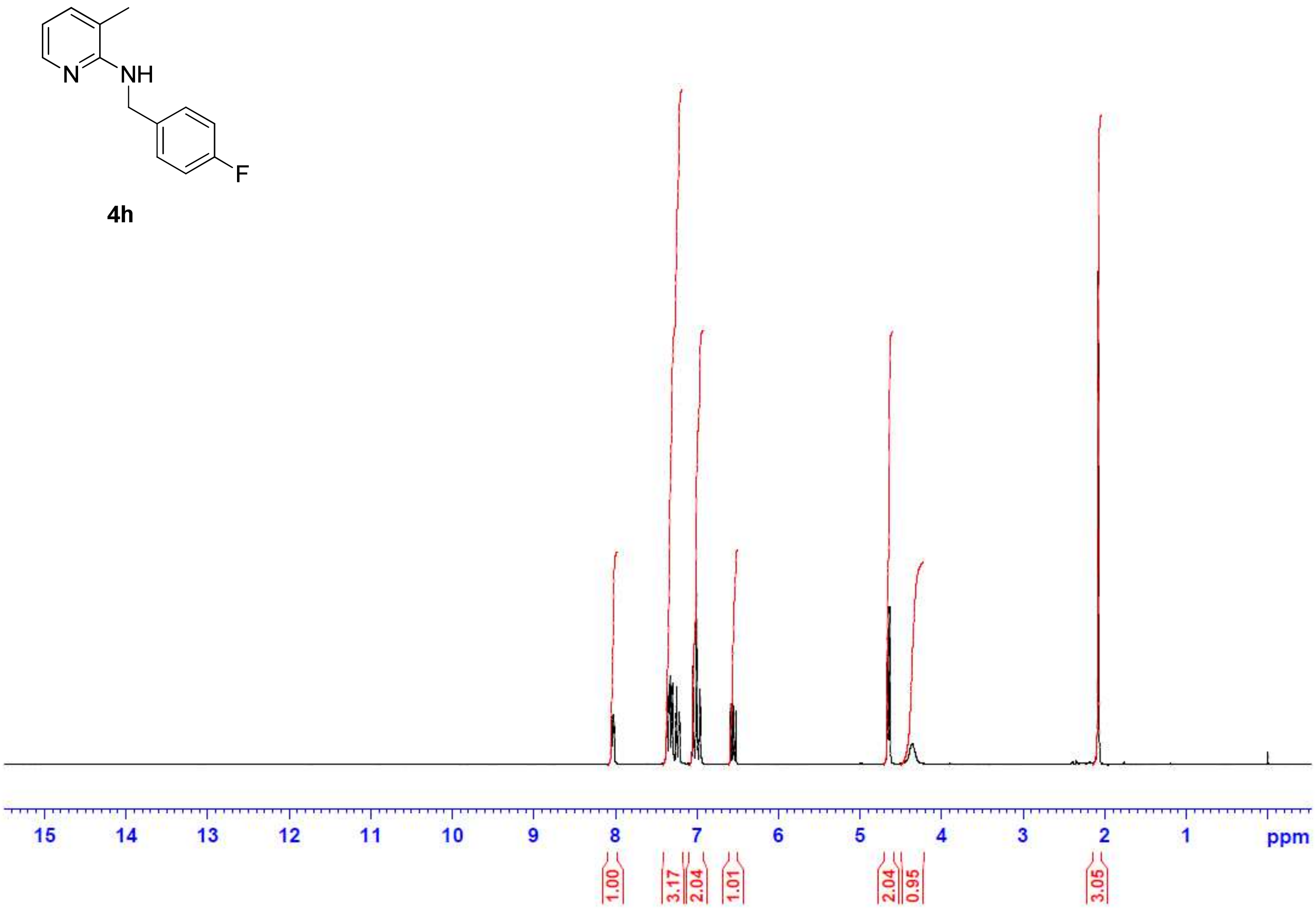


4g

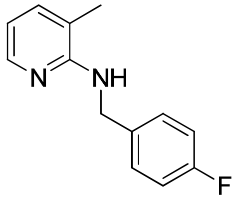


4g

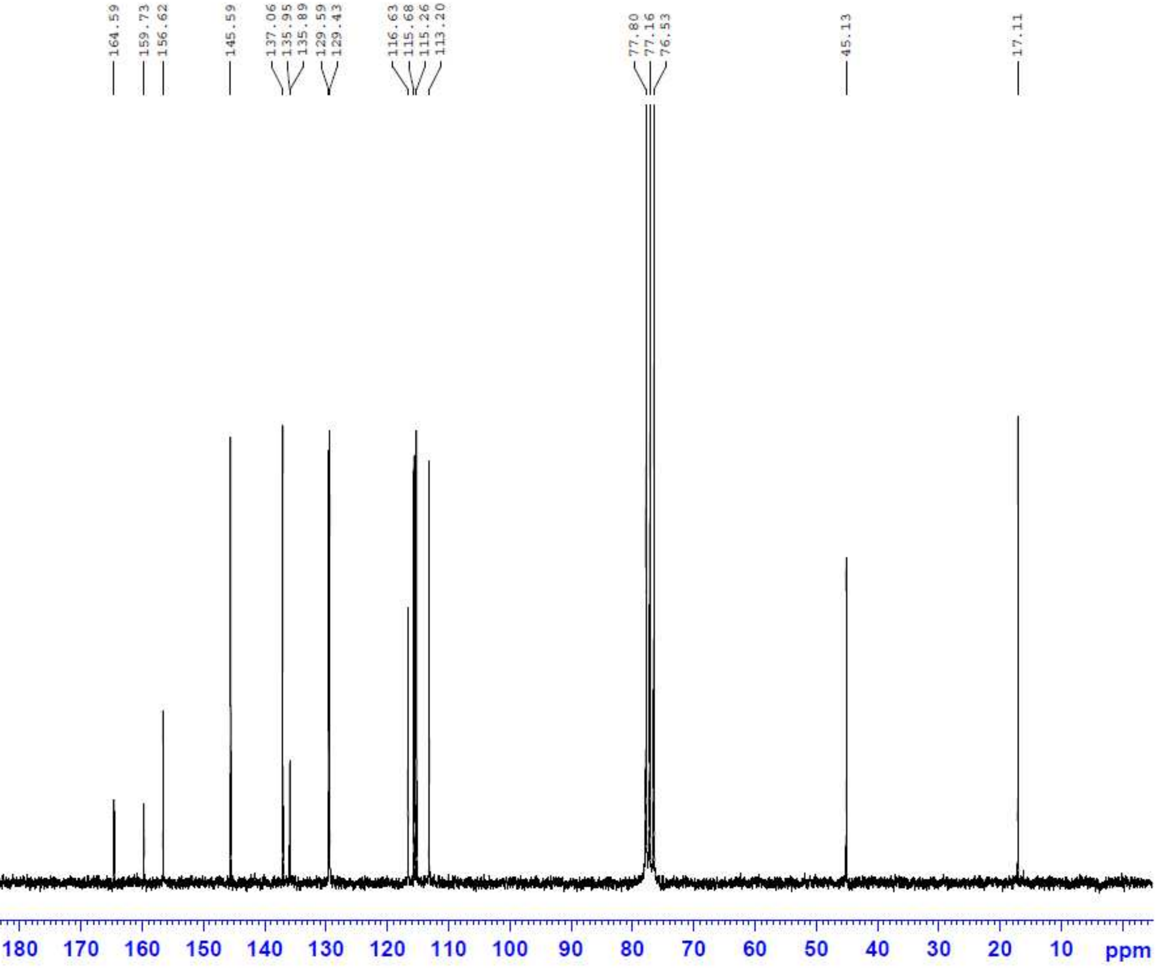
N
NH
156.78
145.55
136.97
136.94
136.90
129.37
128.03
116.59
112.91
77.79
77.16
76.52
45.76
21.21
17.09
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

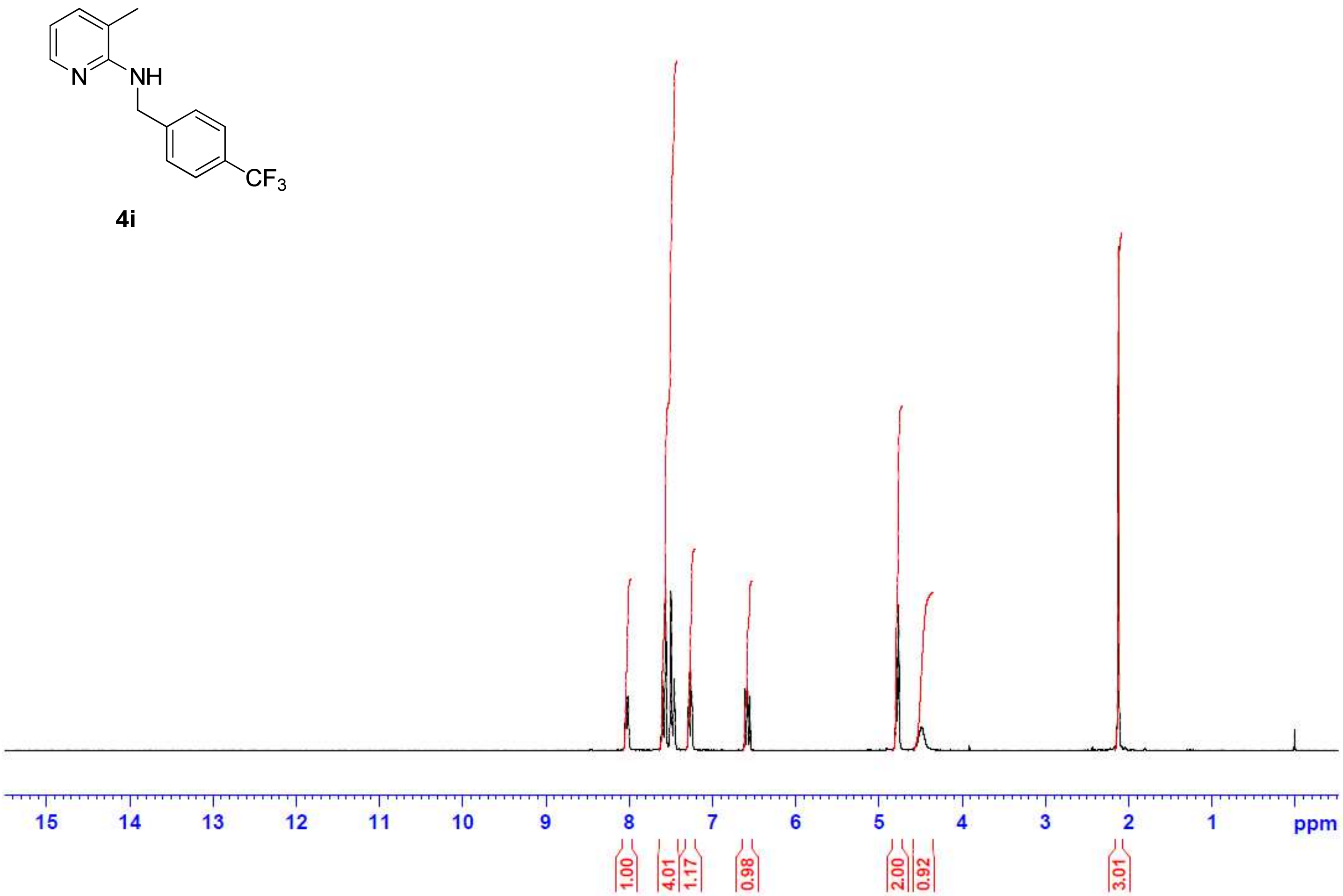


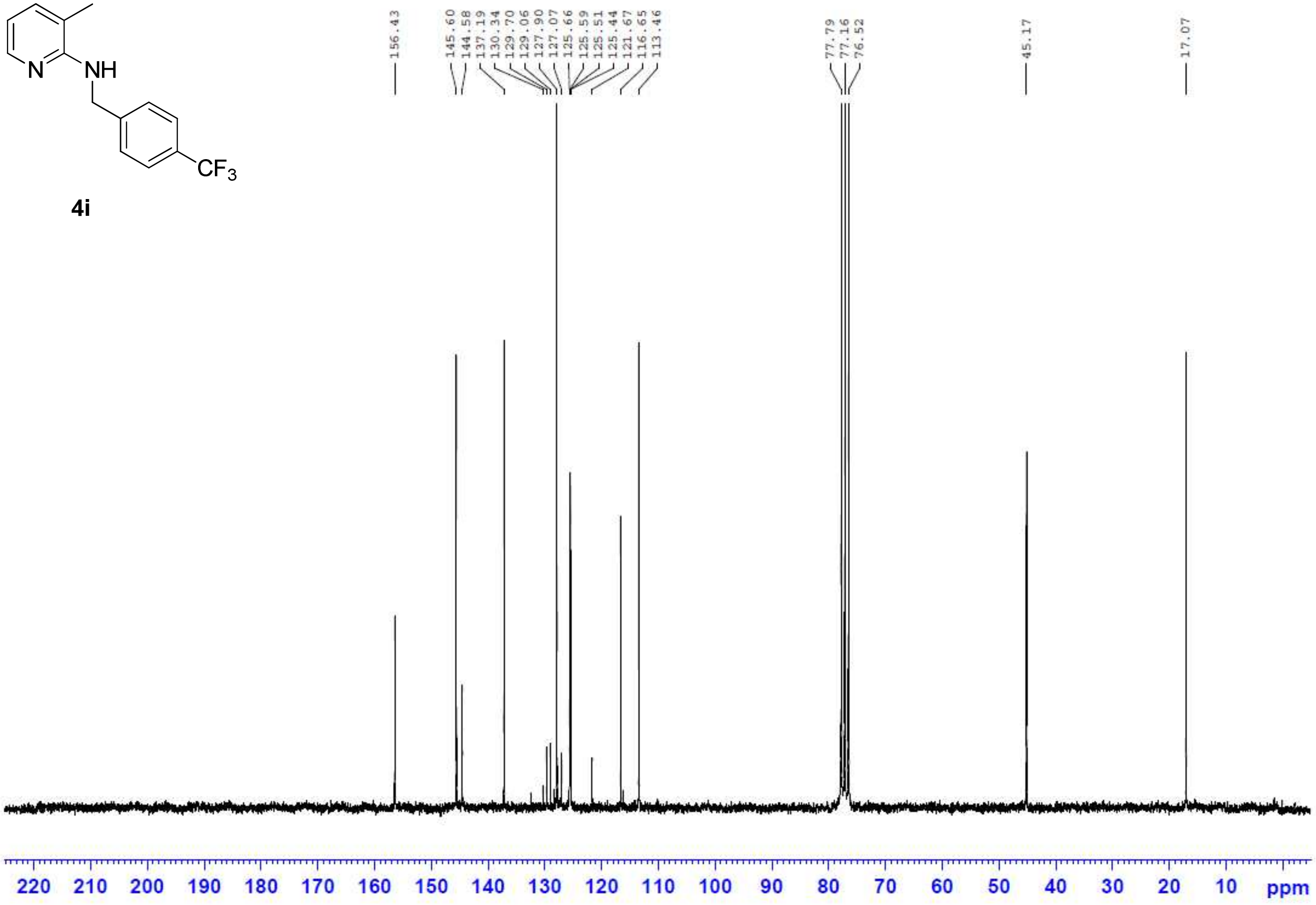
4h


NH
N
F

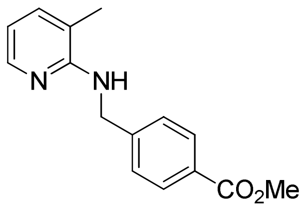
4h


164.59
159.73
156.62
145.59
137.06
135.95
135.89
129.59
129.43
116.63
115.68
115.26
113.20
77.80
77.16
76.53
45.13
17.11
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

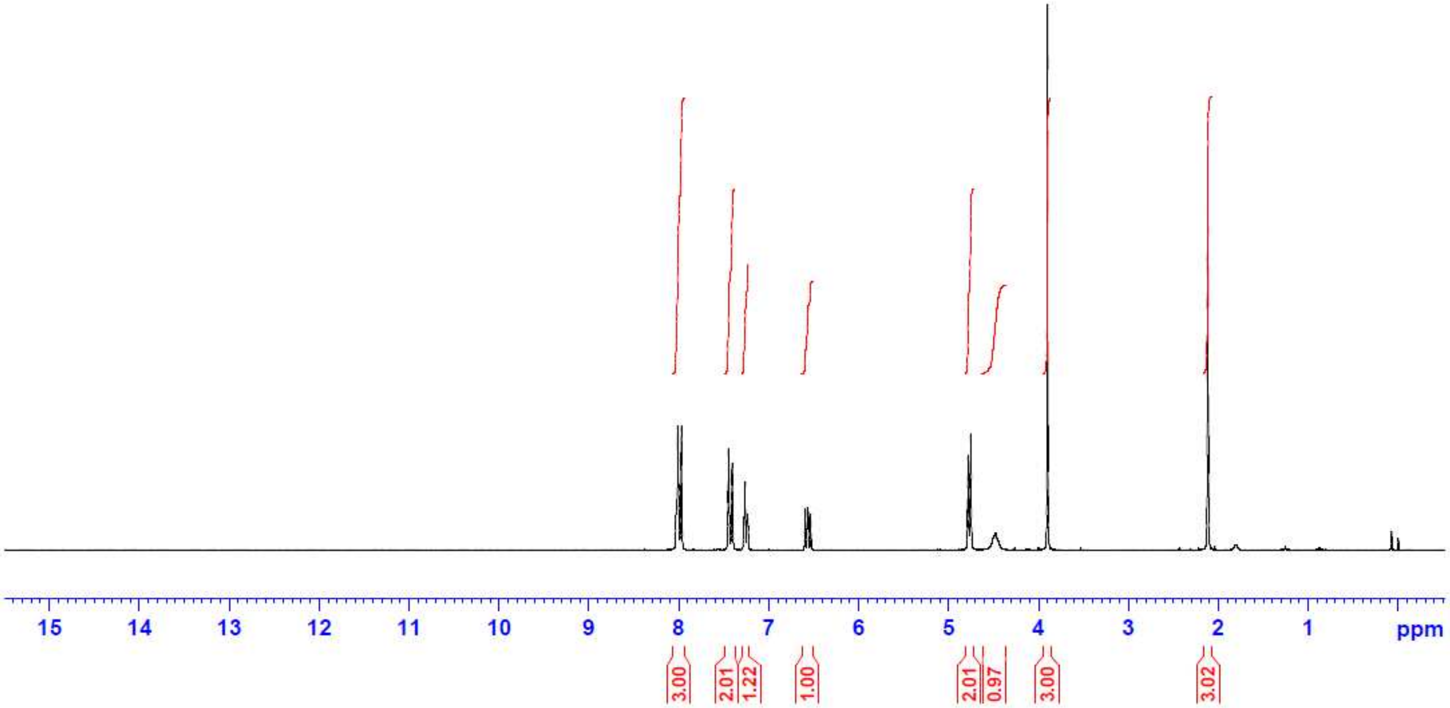

NH
N
CF3
4i
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.01
1.17
0.98
2.00
0.92
3.01

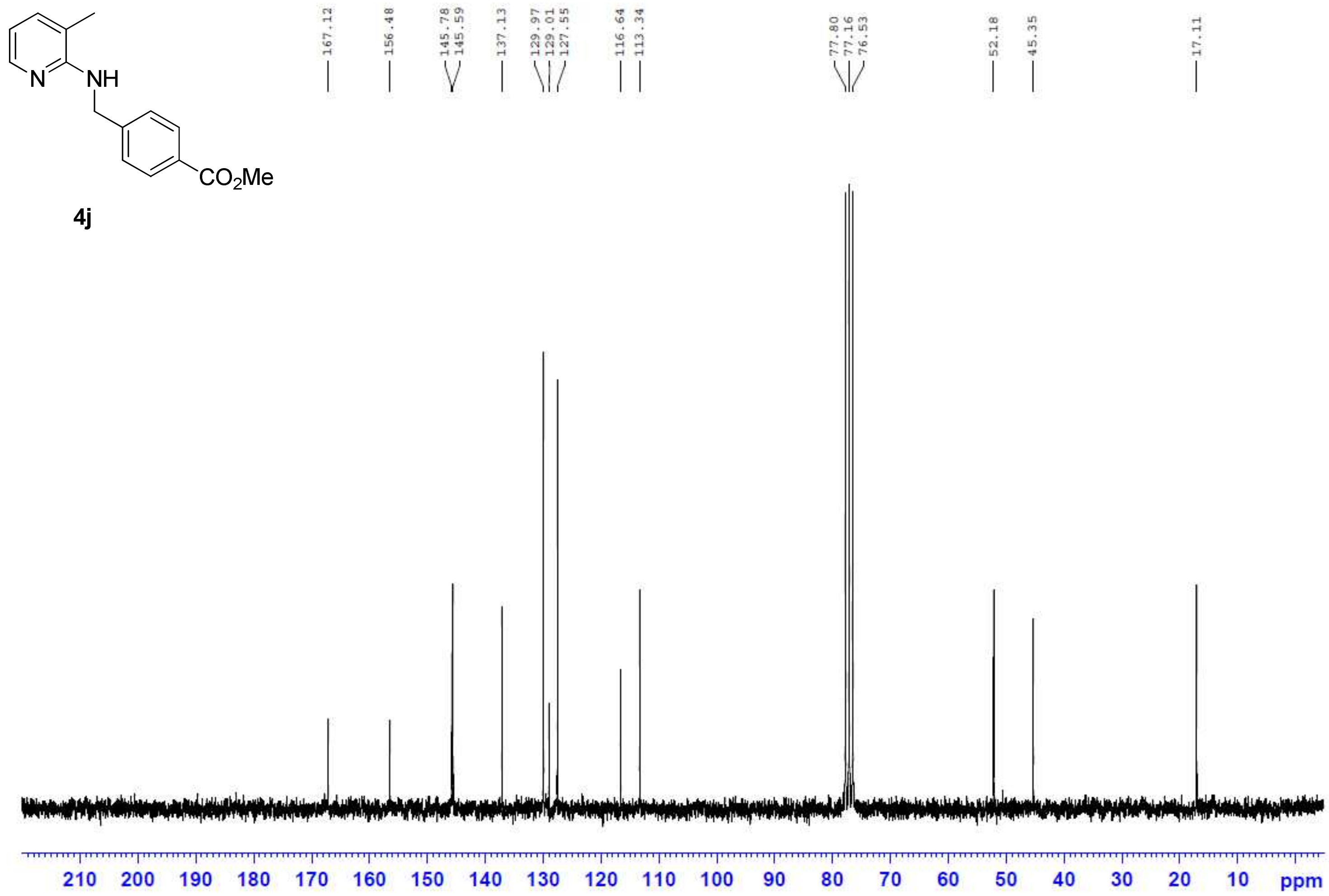

N
NH
CF_3
156.43
145.60
144.58
137.19
130.34
129.70
129.06
127.90
127.07
125.66
125.59
125.51
125.44
121.67
116.65
113.46
77.79
77.16
76.52
45.17
17.07
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4i

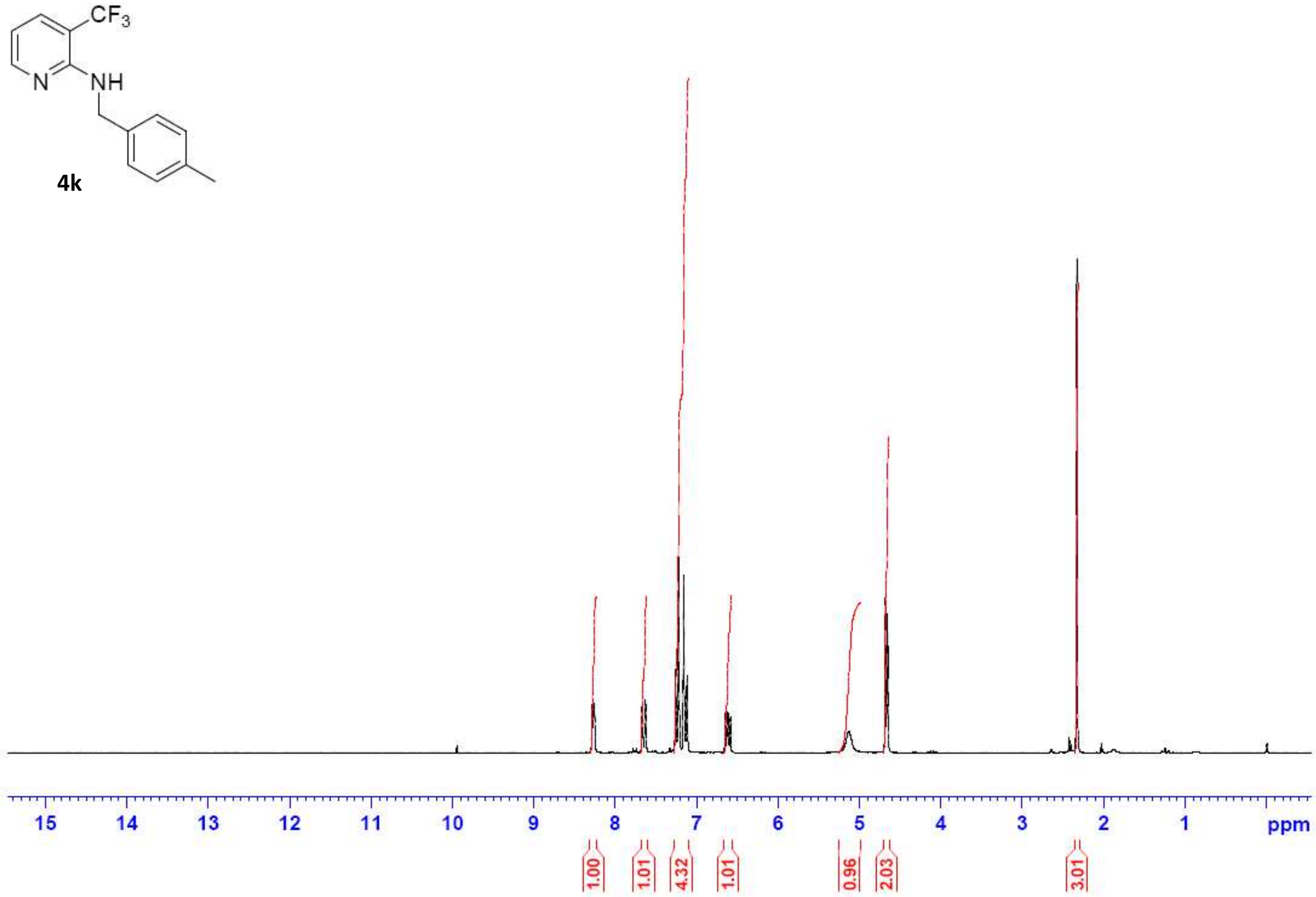

N
NH
CO_2Me

4j


15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
3.00
2.01
1.22
1.00
2.01
0.97
3.00
3.02

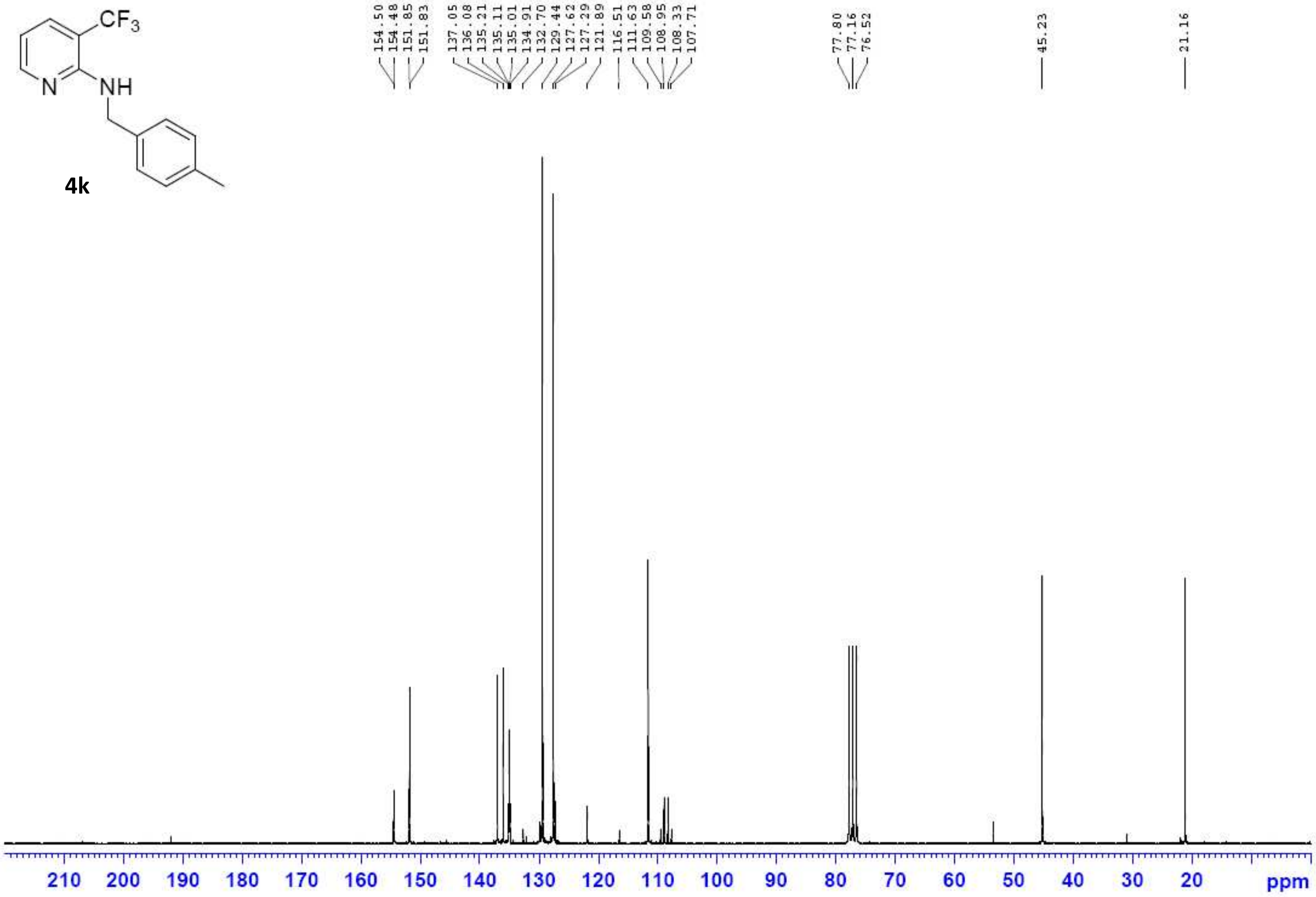

NH
N
CO2Me
167.12
156.48
145.78
145.59
137.13
129.97
129.01
127.55
116.64
113.34
77.80
77.16
76.53
52.18
45.35
17.11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4j

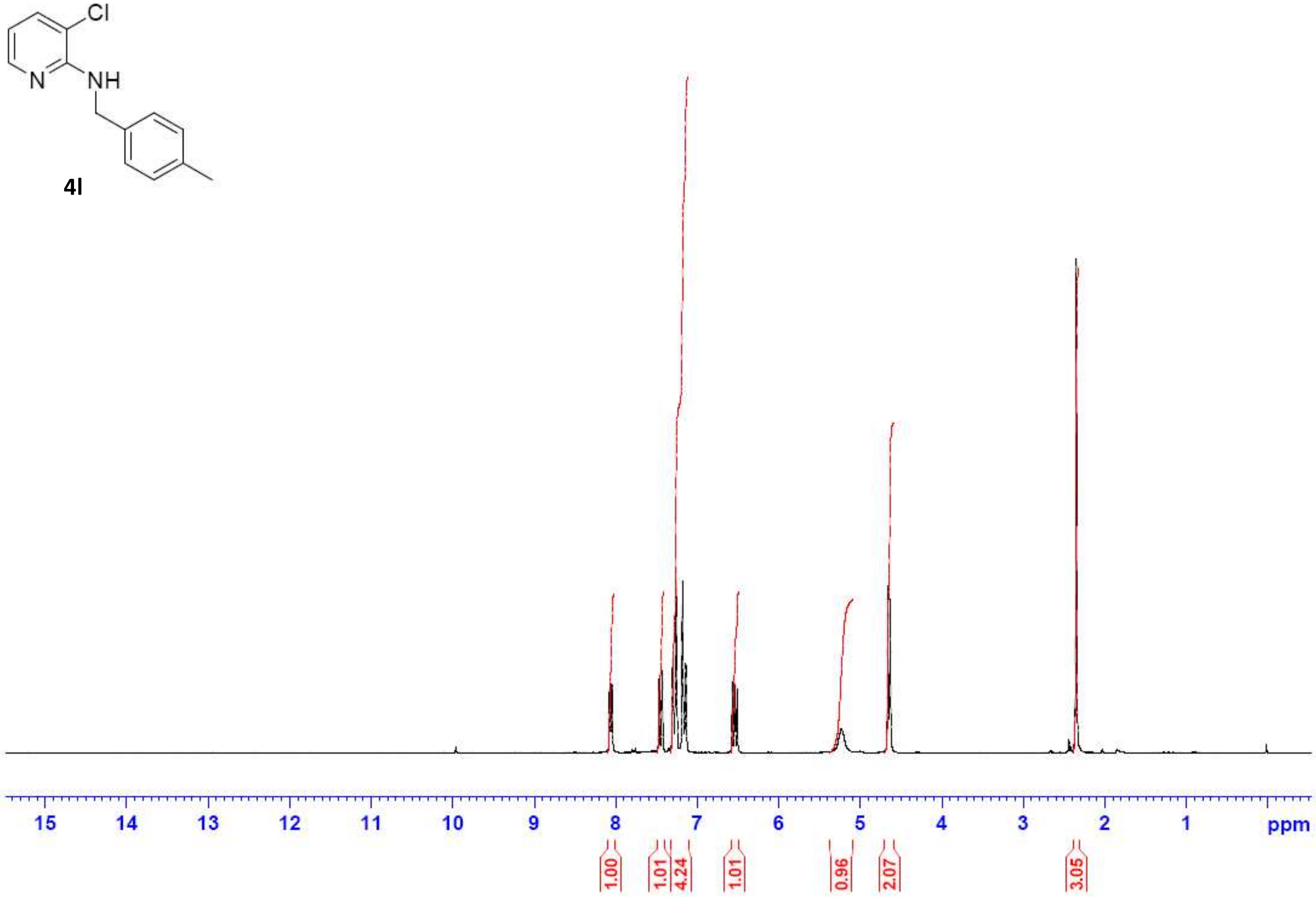


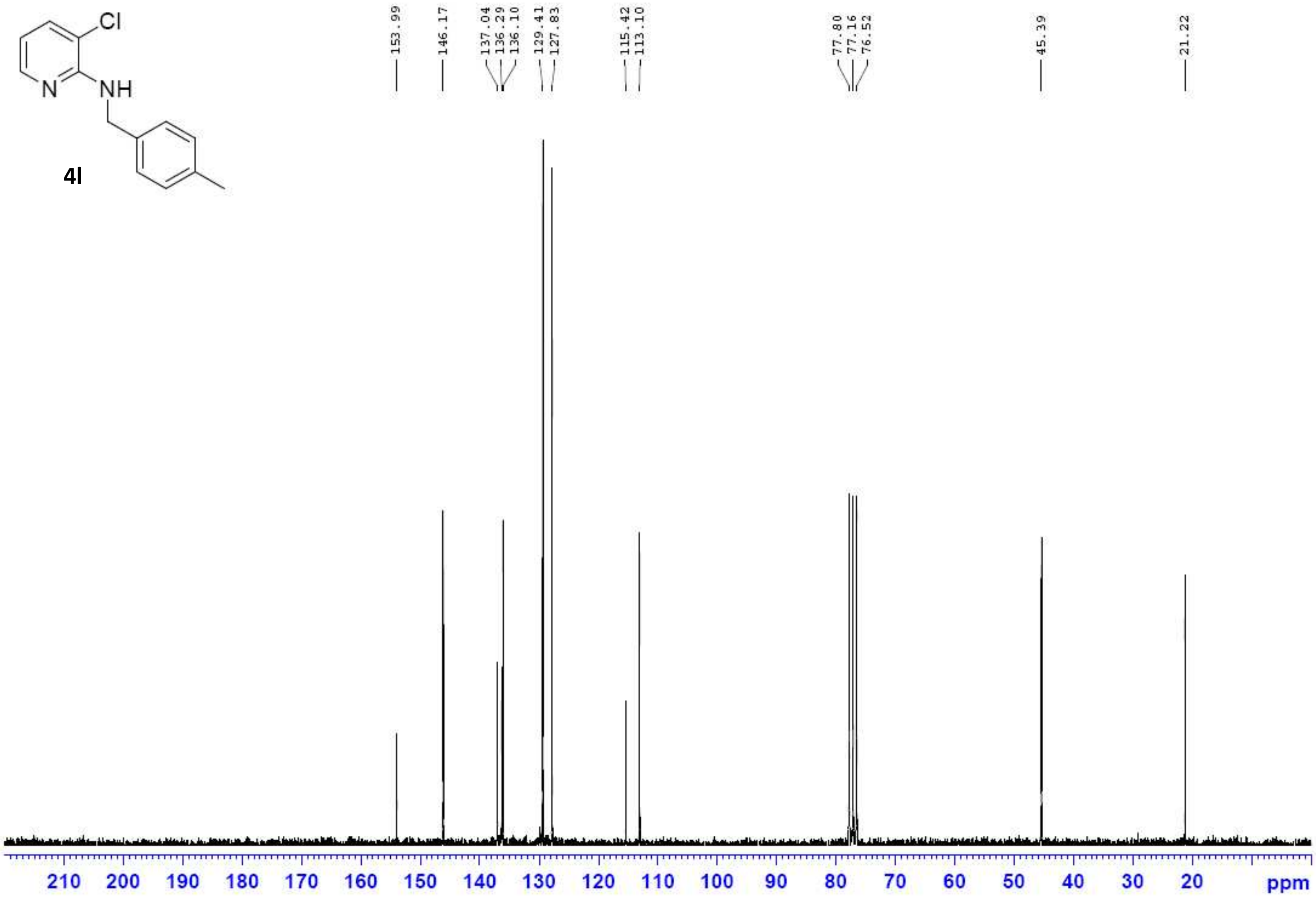
4k

CF3
NH
N
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
4.32
1.01
0.96
2.03
3.01


CF3
N
NH
154.50
154.48
151.85
151.83
137.05
136.08
135.21
135.11
135.01
134.91
132.70
129.44
127.62
127.29
121.89
116.51
111.63
109.58
108.95
108.33
107.71
77.80
77.16
76.52
45.23
21.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

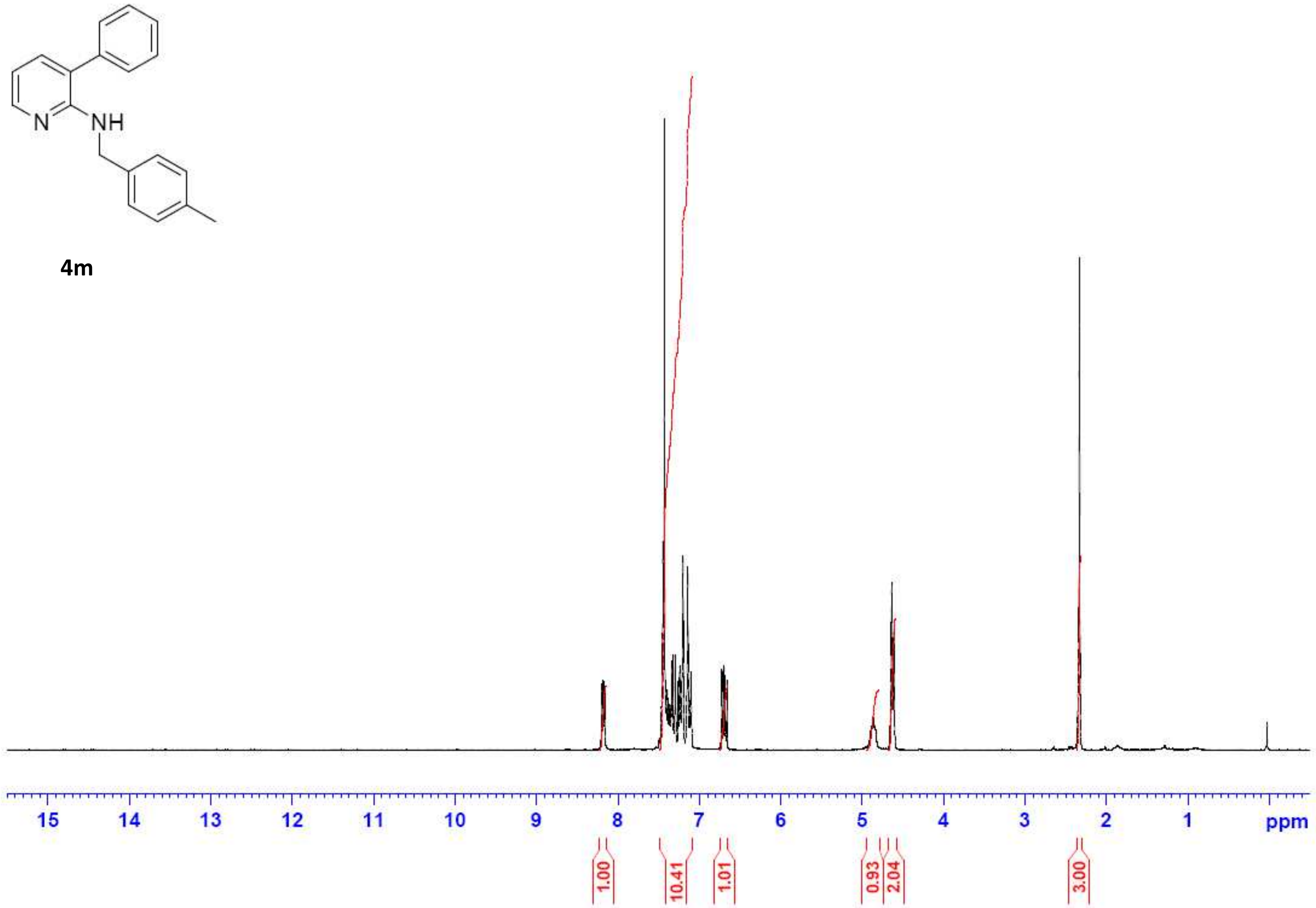
4k


Cl
N
NH
4l
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
4.24
1.01
0.96
2.07
3.05

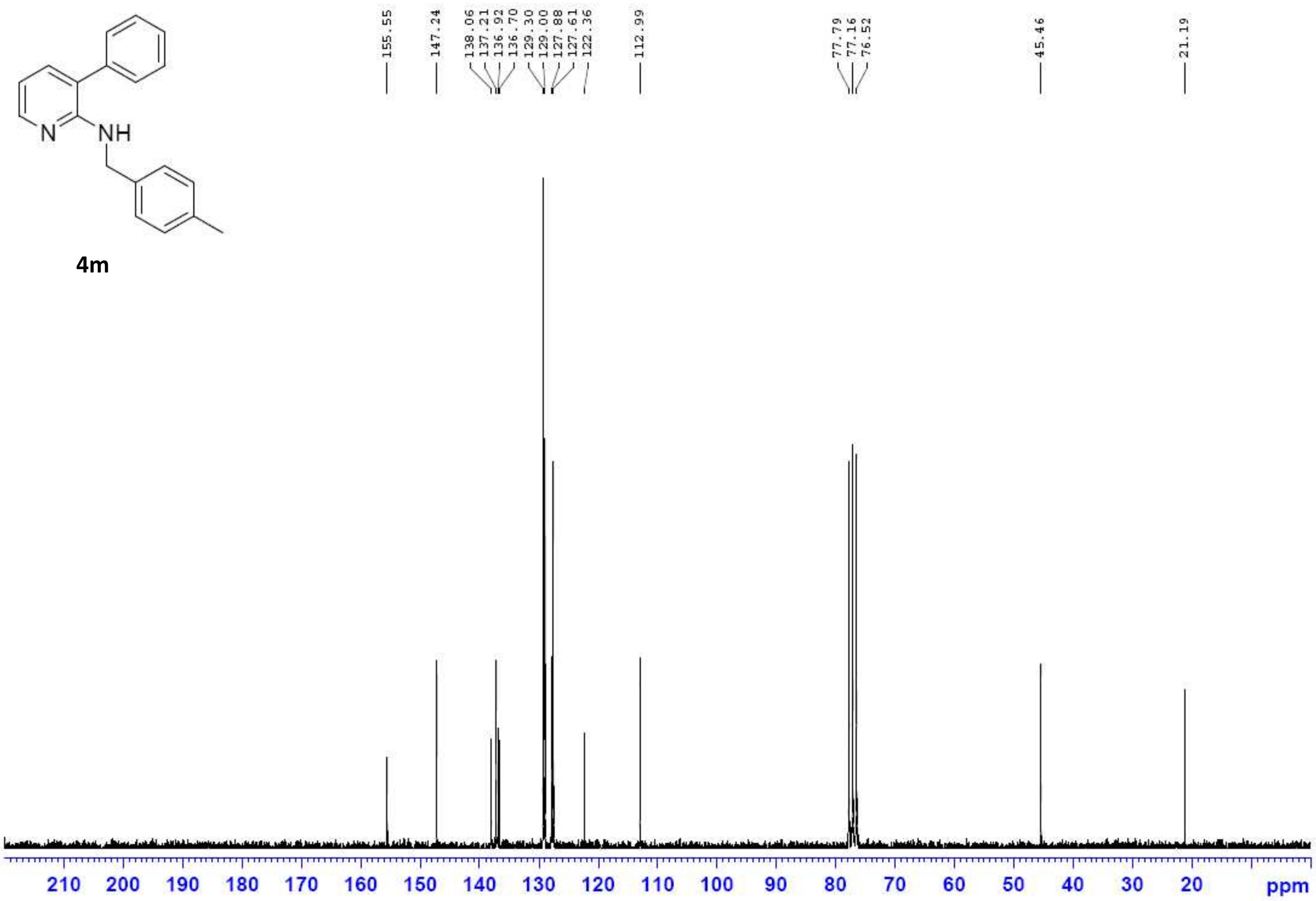


4l

Cl
NH
N
153.99
146.17
137.04
136.29
136.10
129.41
127.83
115.42
113.10
77.80
77.16
76.52
45.39
21.22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

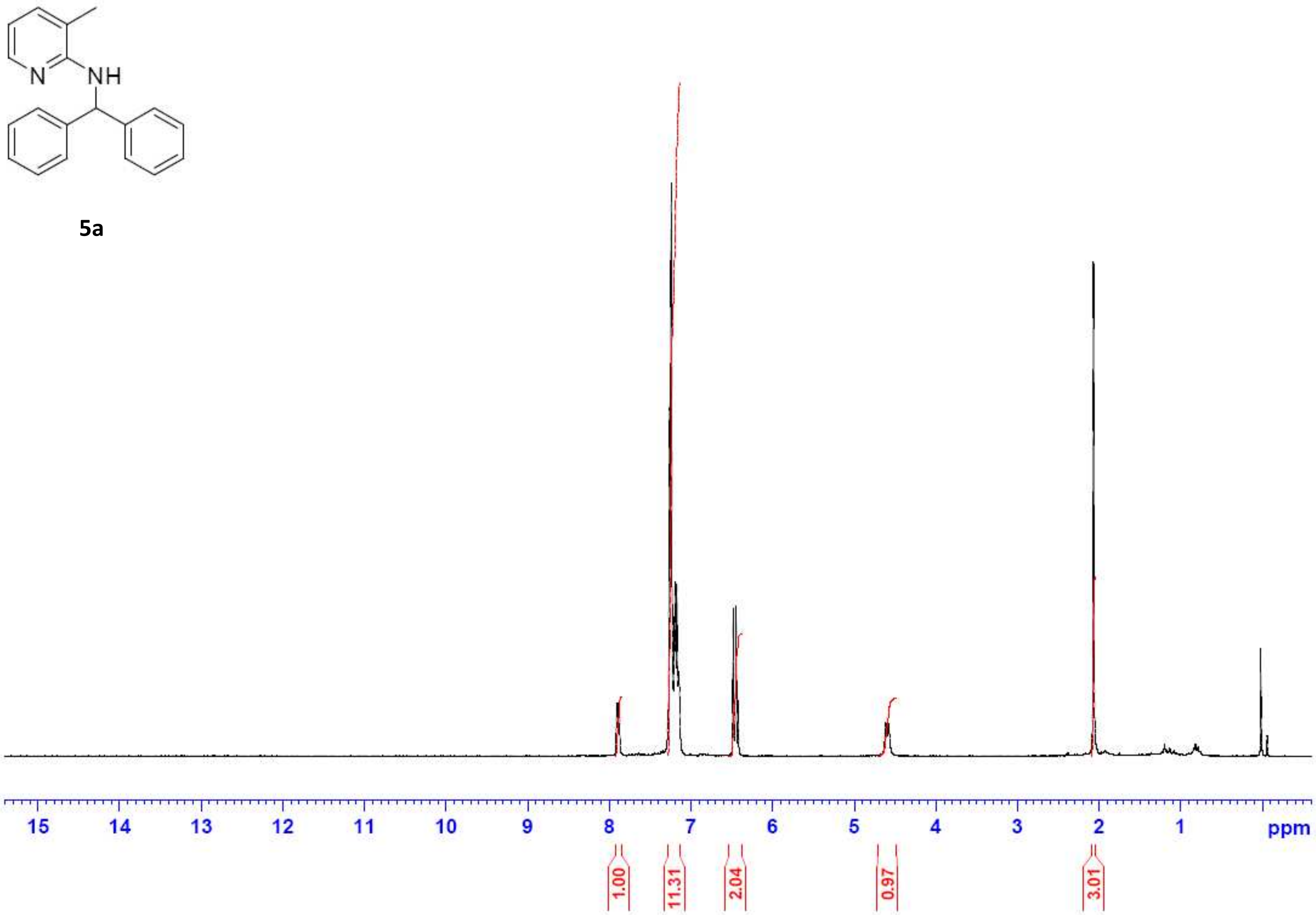


4m

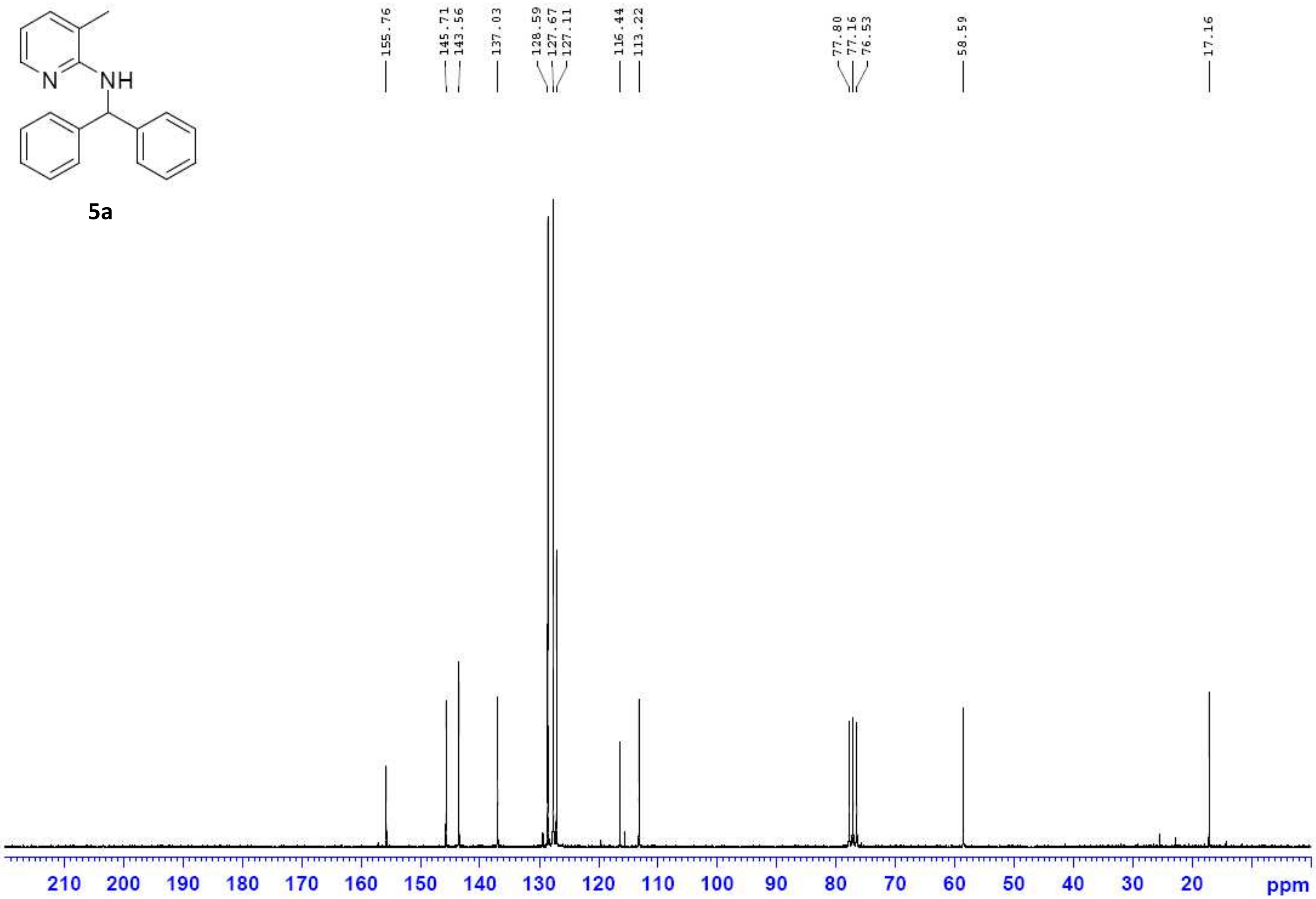


4m

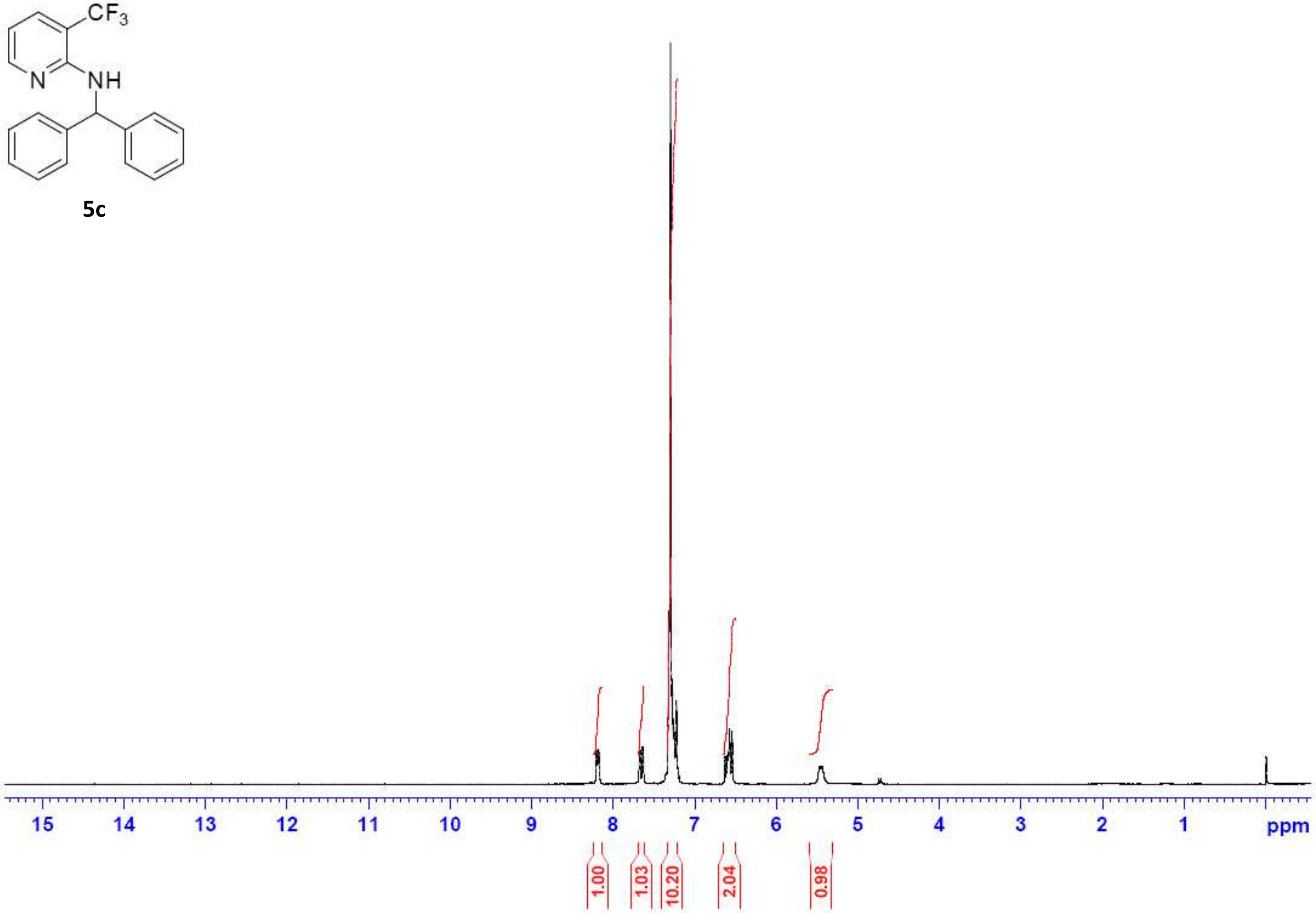
NH
N
155.55
147.24
138.06
137.21
136.92
136.70
129.30
129.00
127.88
127.61
122.36
112.99
77.79
77.16
76.52
45.46
21.19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



5a


N
NH
155.76
145.71
143.56
137.03
128.59
127.67
127.11
116.44
113.22
77.80
77.16
76.53
58.59
17.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

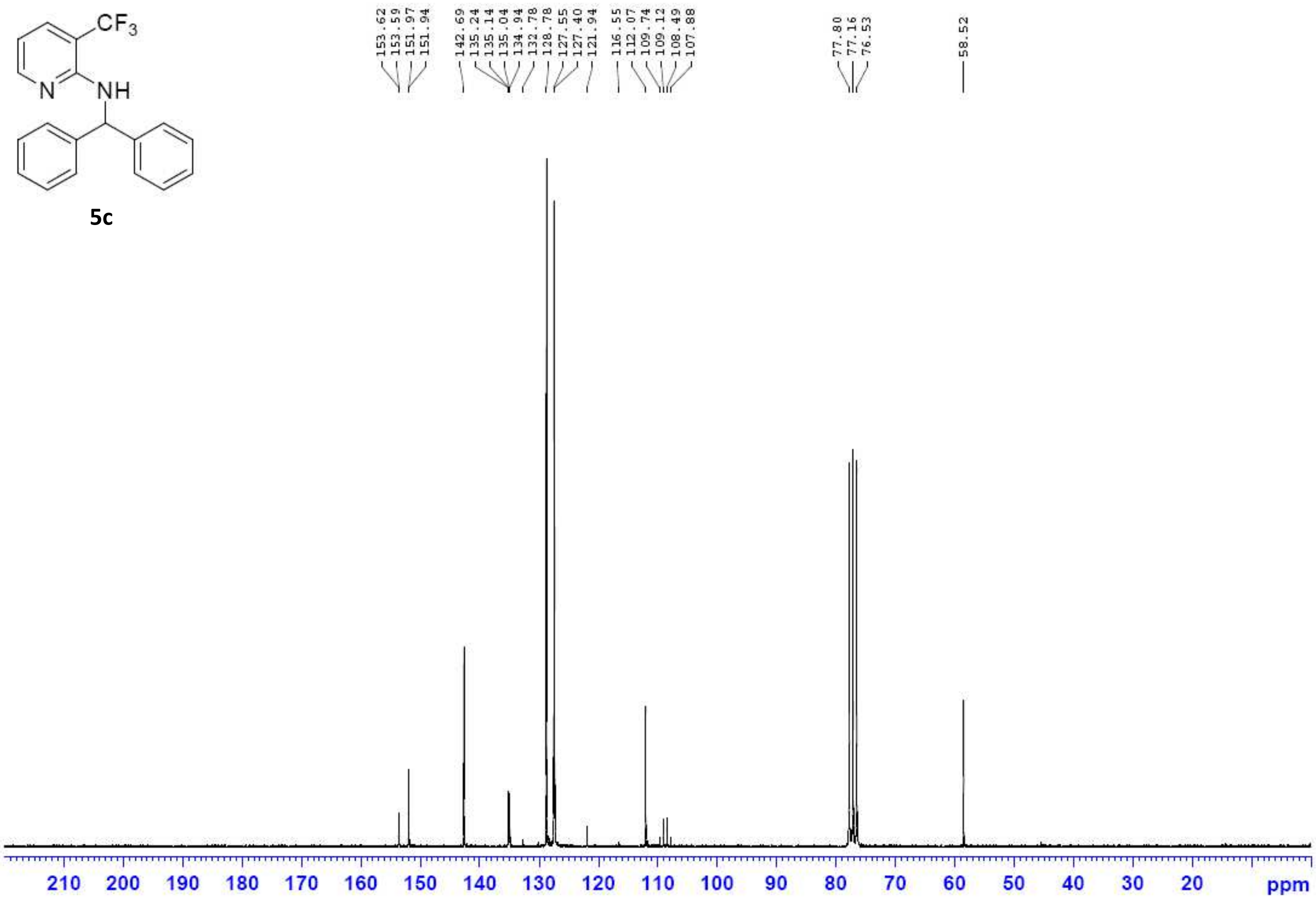
5a

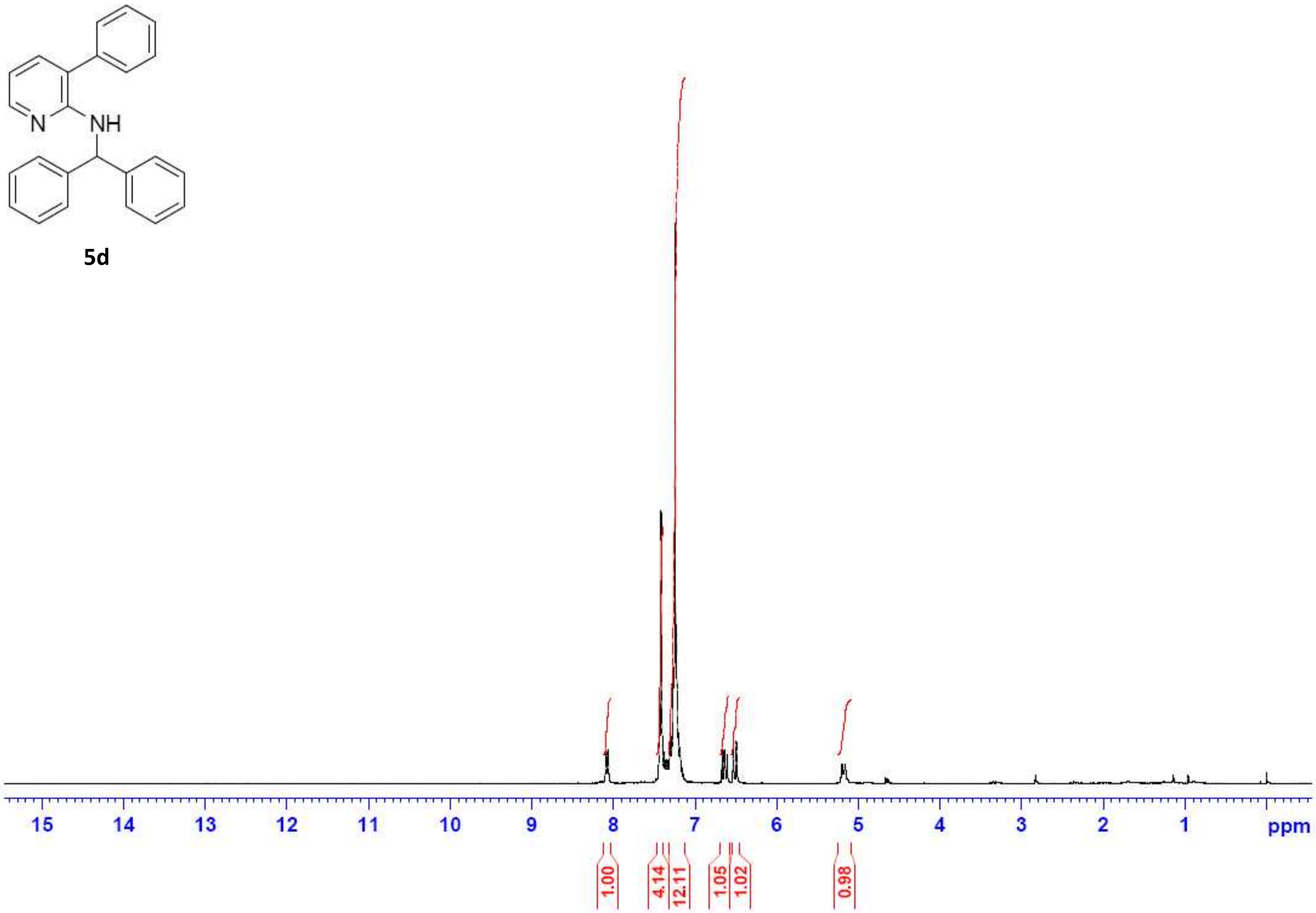


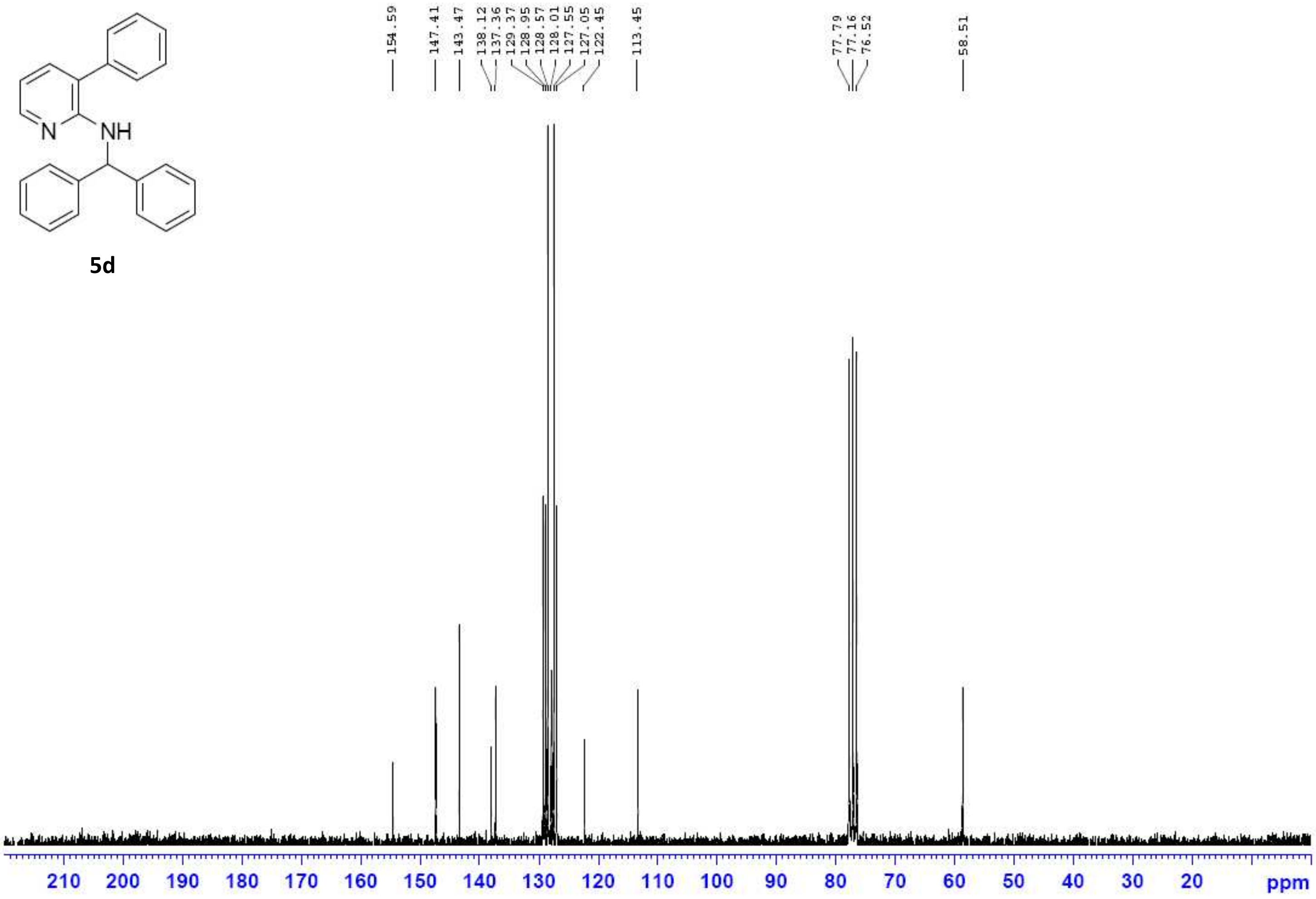
5c

CF3
N
NH

5c

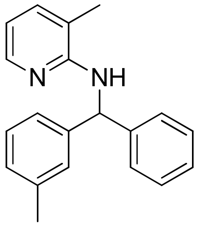

153.62
153.59
151.97
151.94
142.69
135.24
135.14
135.04
134.94
132.78
128.78
127.55
127.40
121.94
116.55
112.07
109.74
109.12
108.49
107.88
77.80
77.16
76.53
58.52
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


NH
N
5d
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.14
12.11
1.05
1.02
0.98

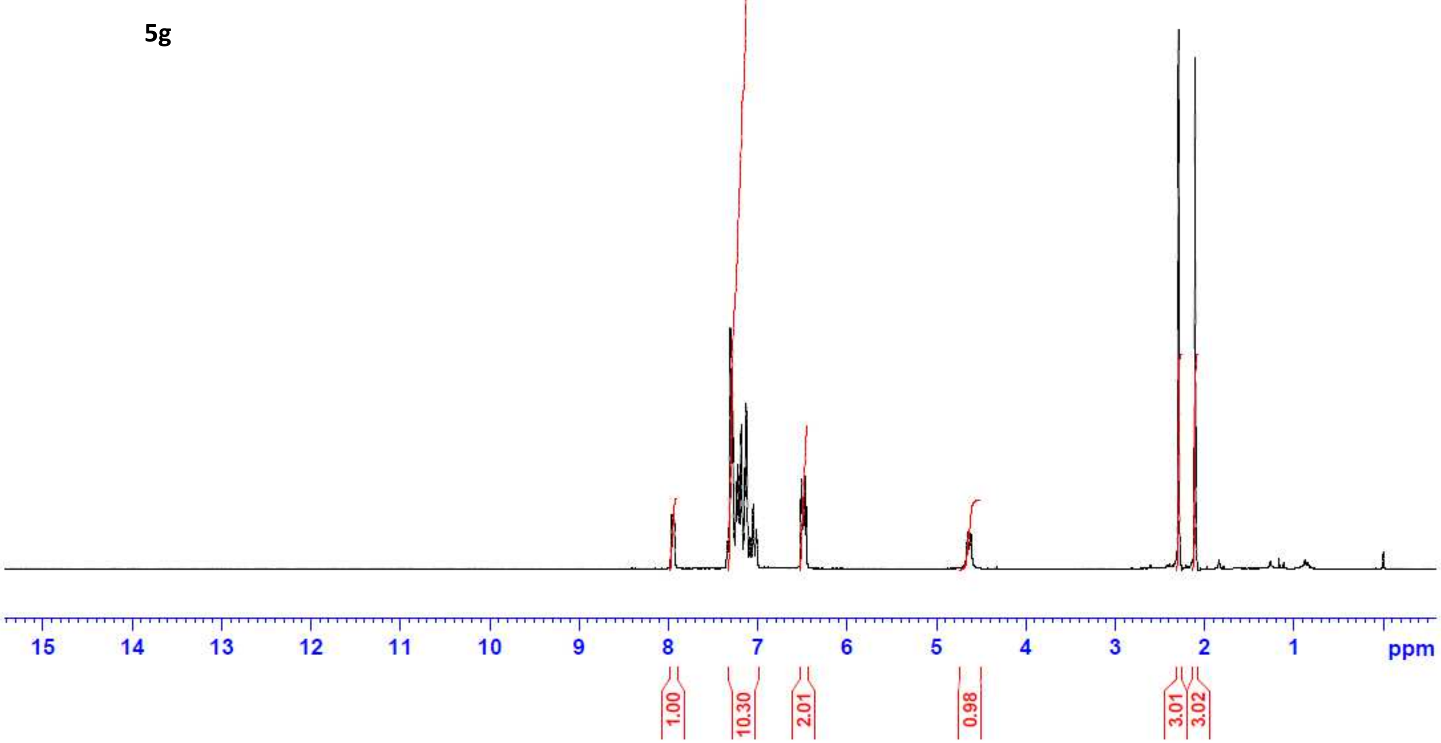


5d

NH
N
154.59
147.41
143.47
138.12
137.36
129.37
128.95
128.57
128.01
127.55
127.05
122.45
113.45
77.79
77.16
76.52
58.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

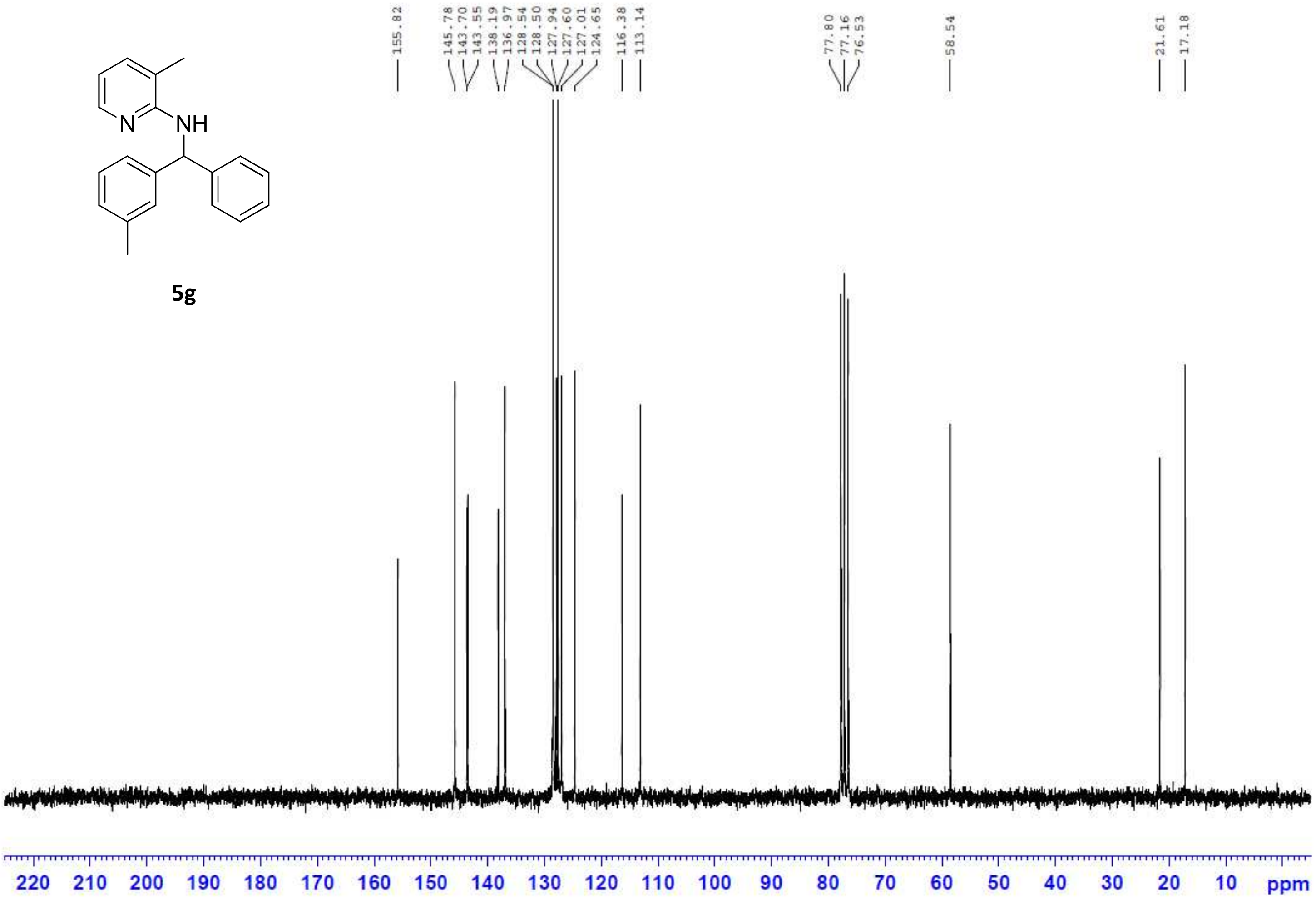


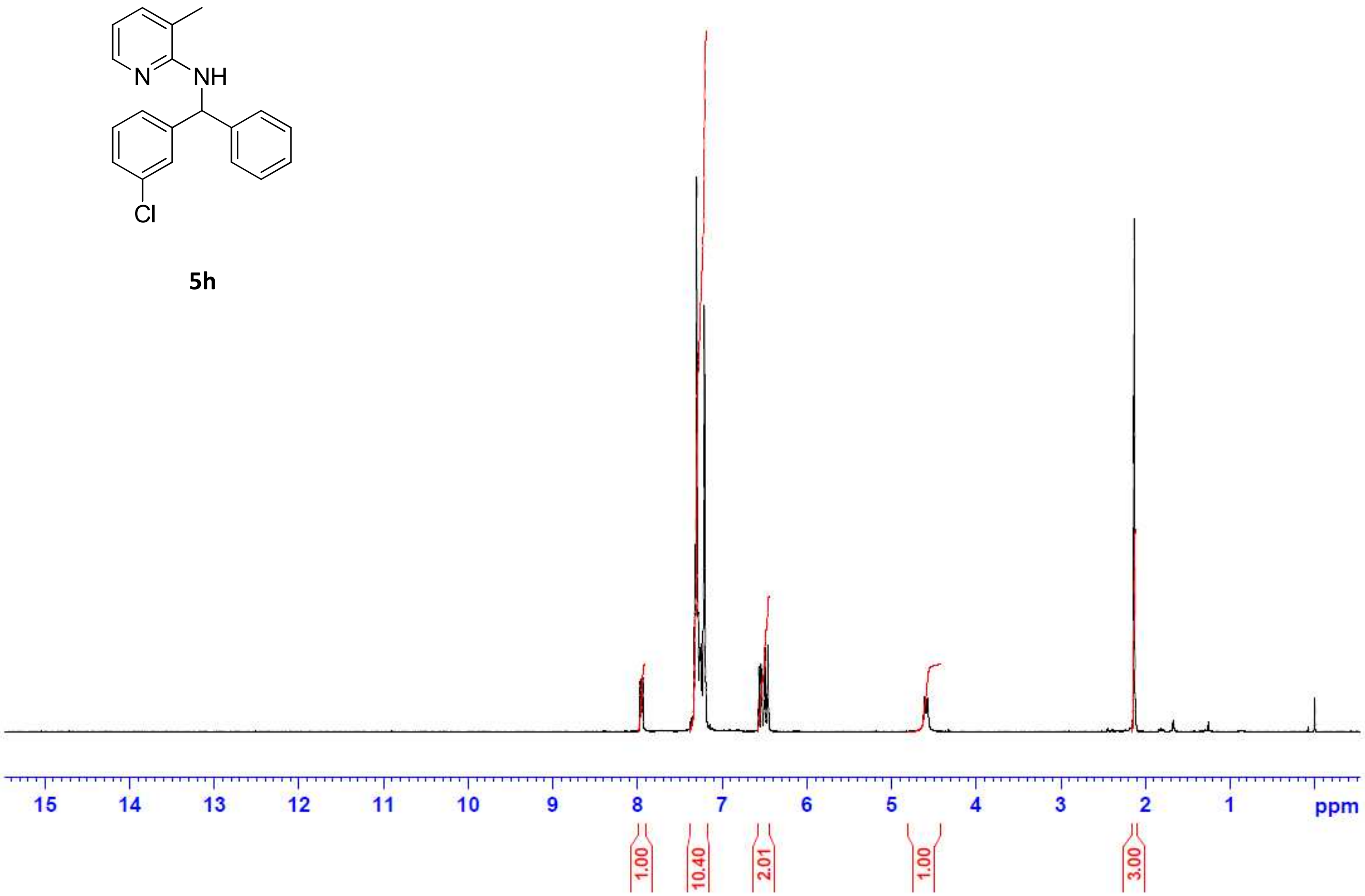
5g



N
NH

5g

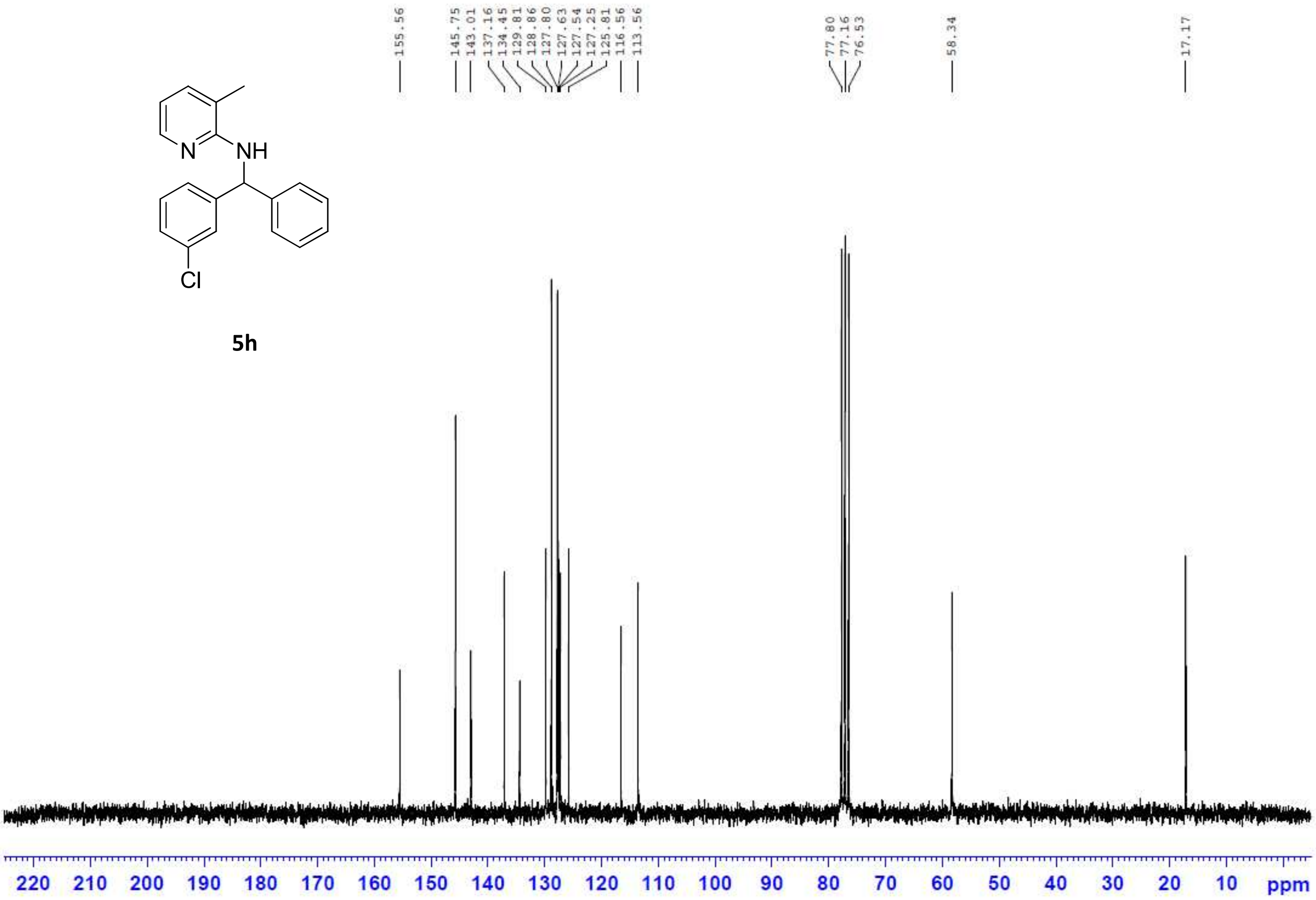

155.82
145.78
143.70
143.55
138.19
136.97
128.54
128.50
127.94
127.60
127.01
124.65
116.38
113.14
77.80
77.16
76.53
58.54
21.61
17.18
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

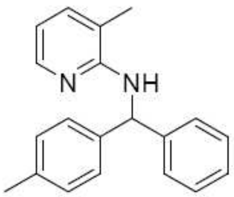


5h

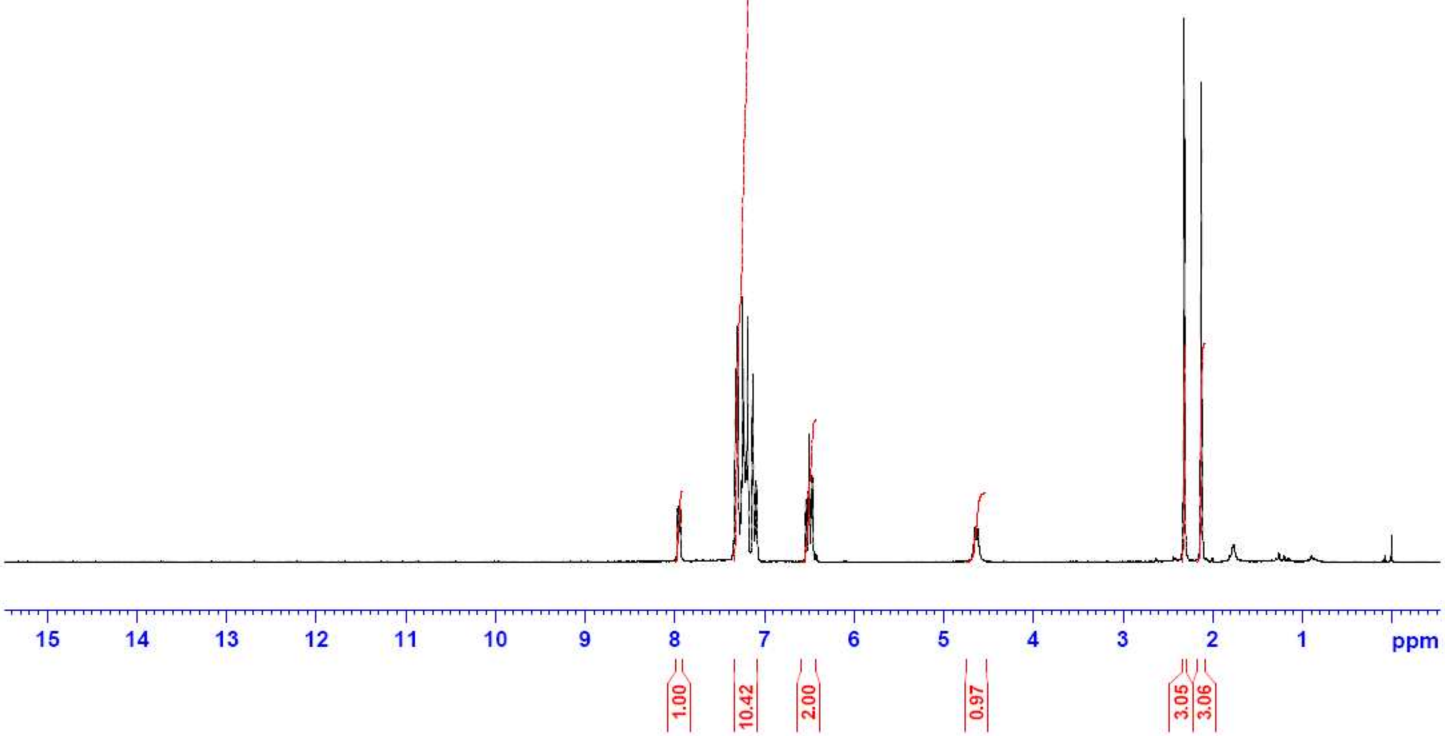
N
NH
Cl

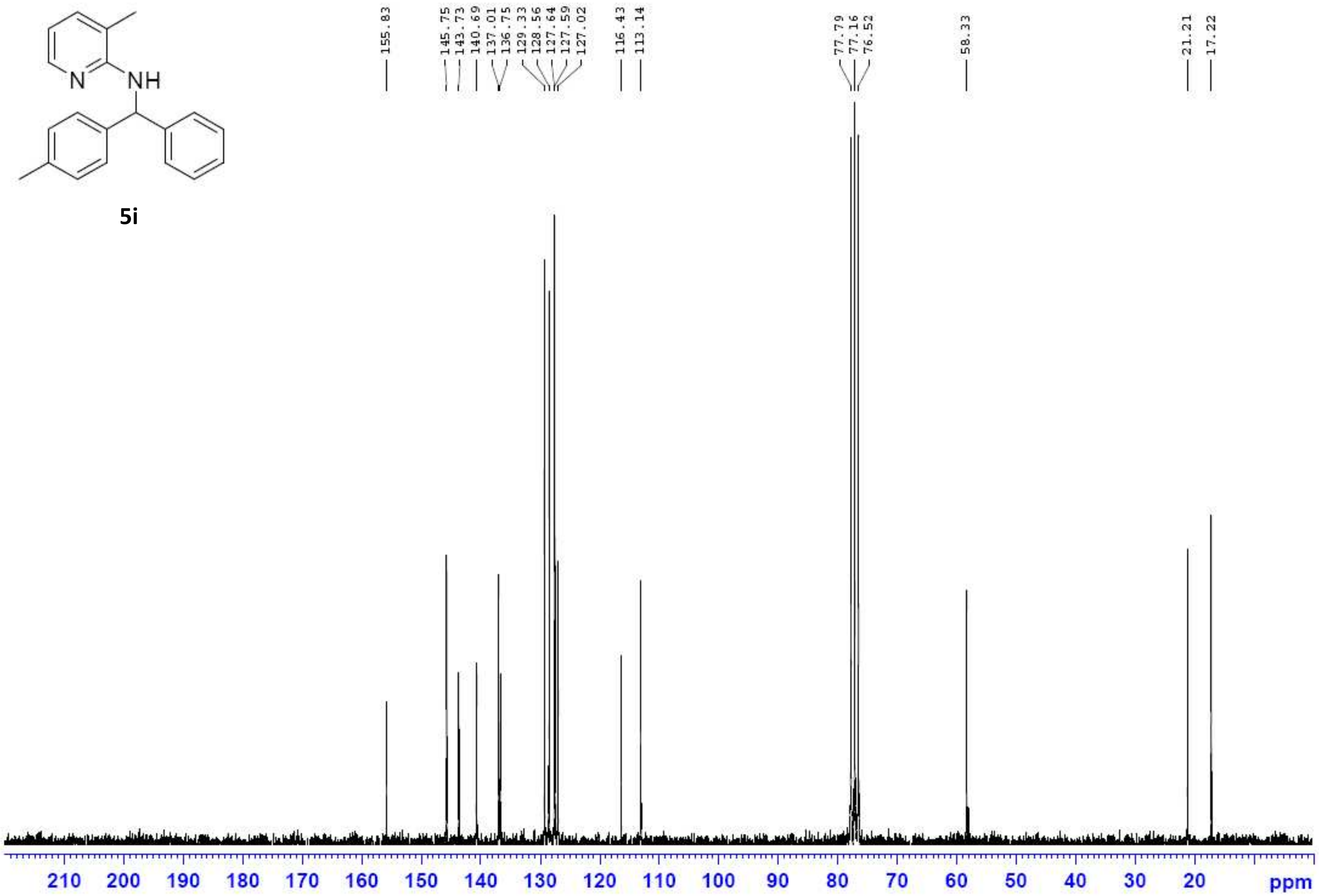
5h


155.56
145.75
143.01
137.16
134.45
129.81
128.86
127.80
127.63
127.54
127.25
125.81
116.56
113.56
77.80
77.16
76.53
58.34
17.17
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

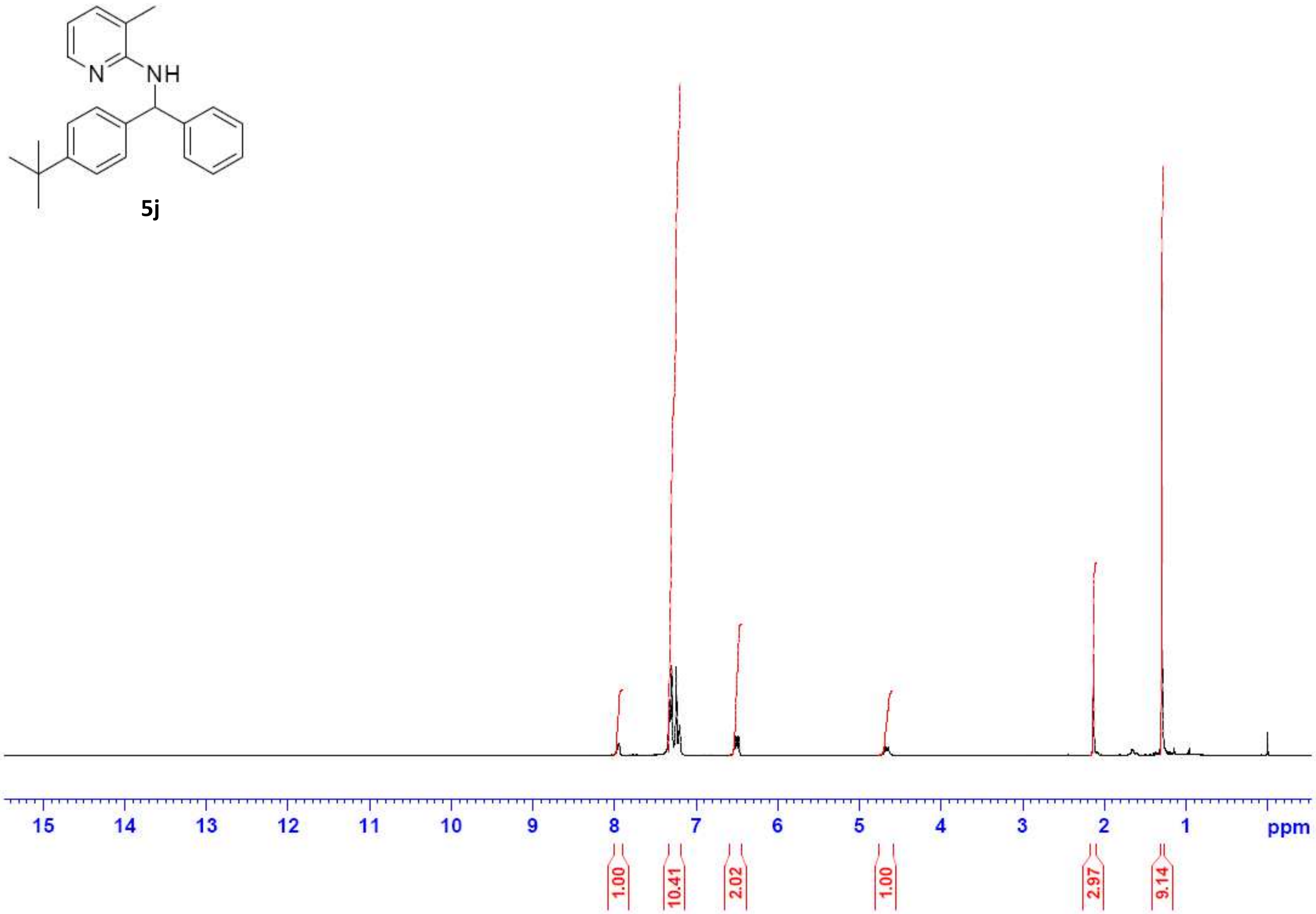


5i

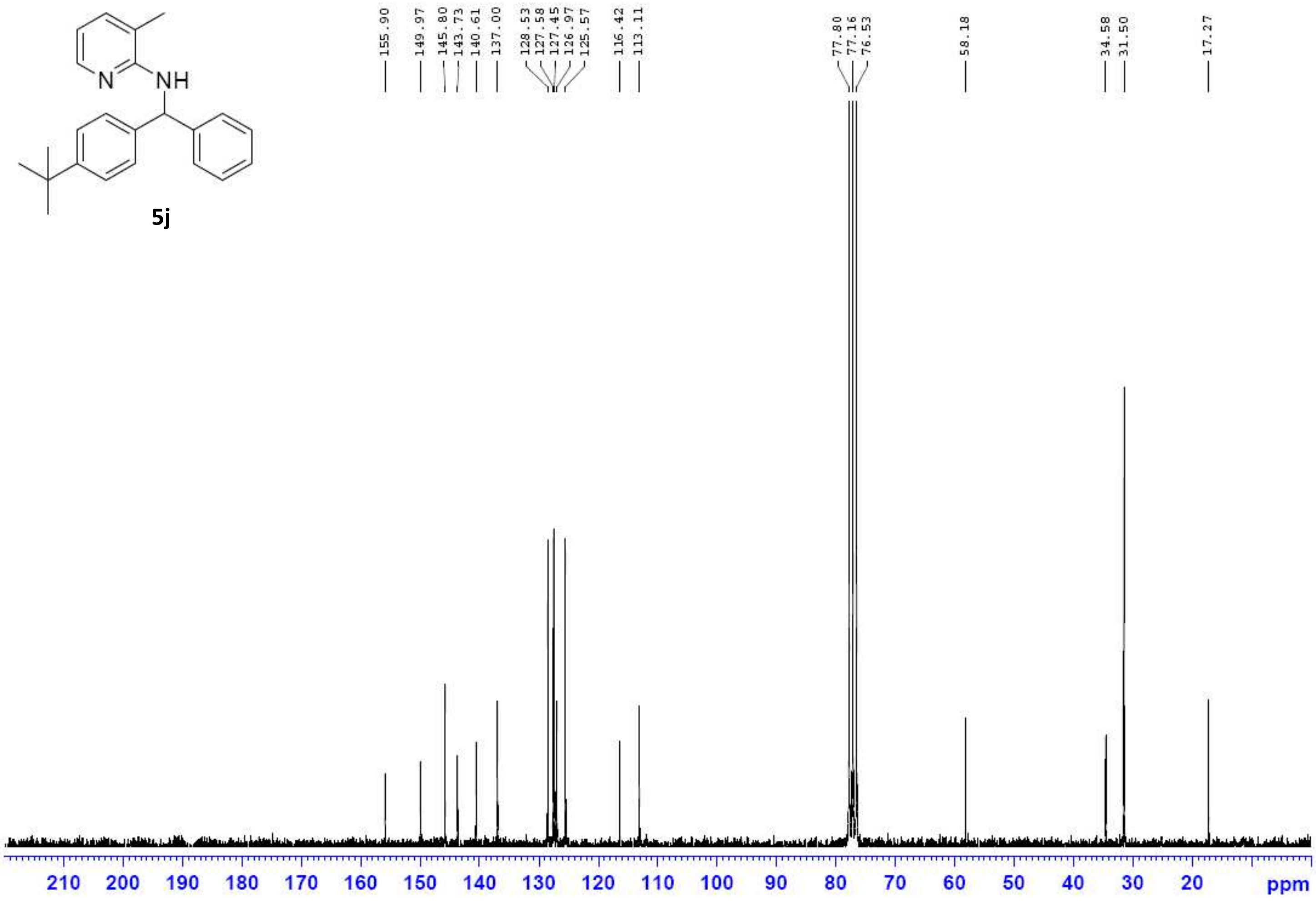




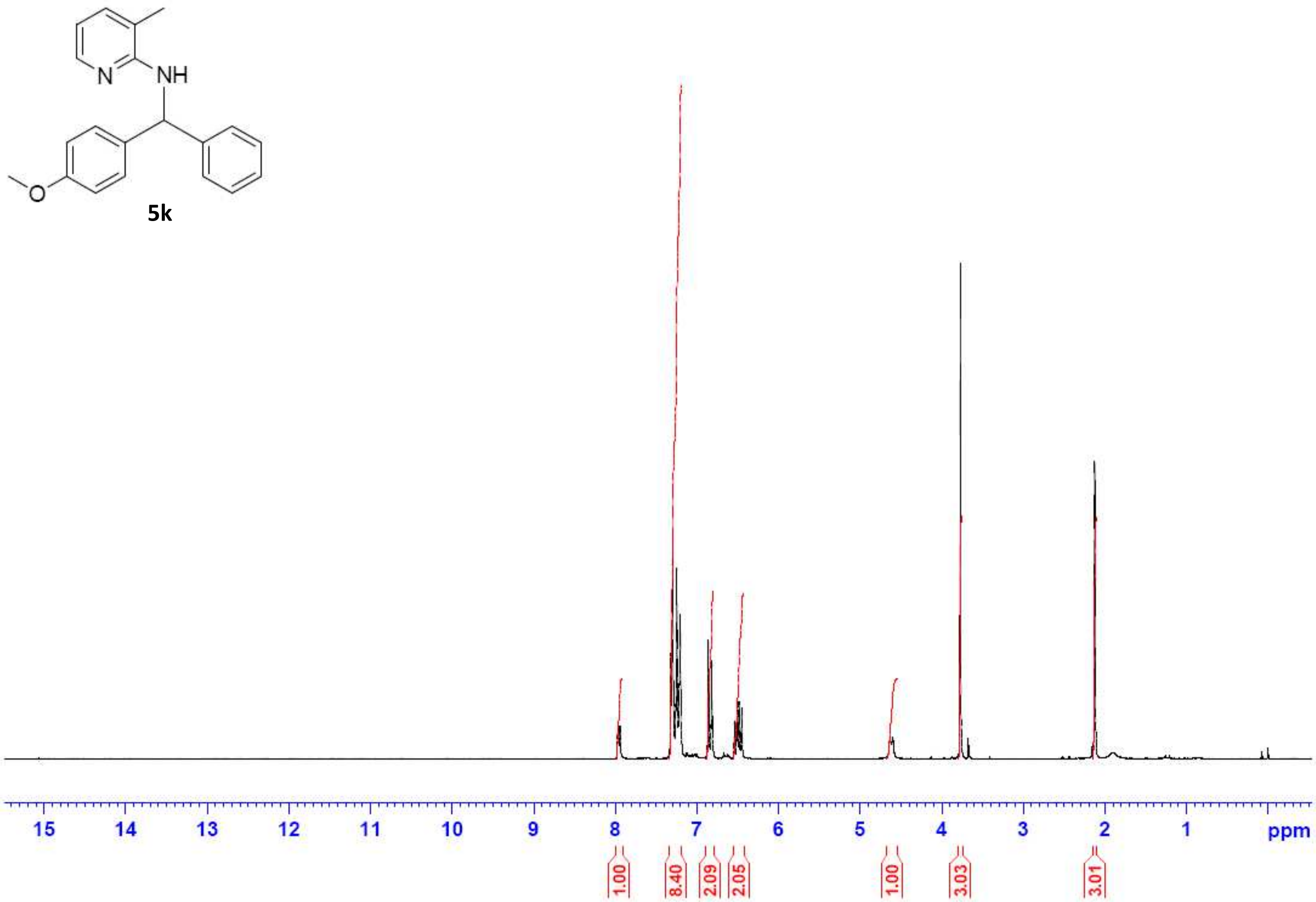
5i
155.83
145.75
143.73
140.69
137.01
136.75
129.33
128.56
127.64
127.59
127.02
116.43
113.14
77.79
77.16
76.52
58.33
21.21
17.22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



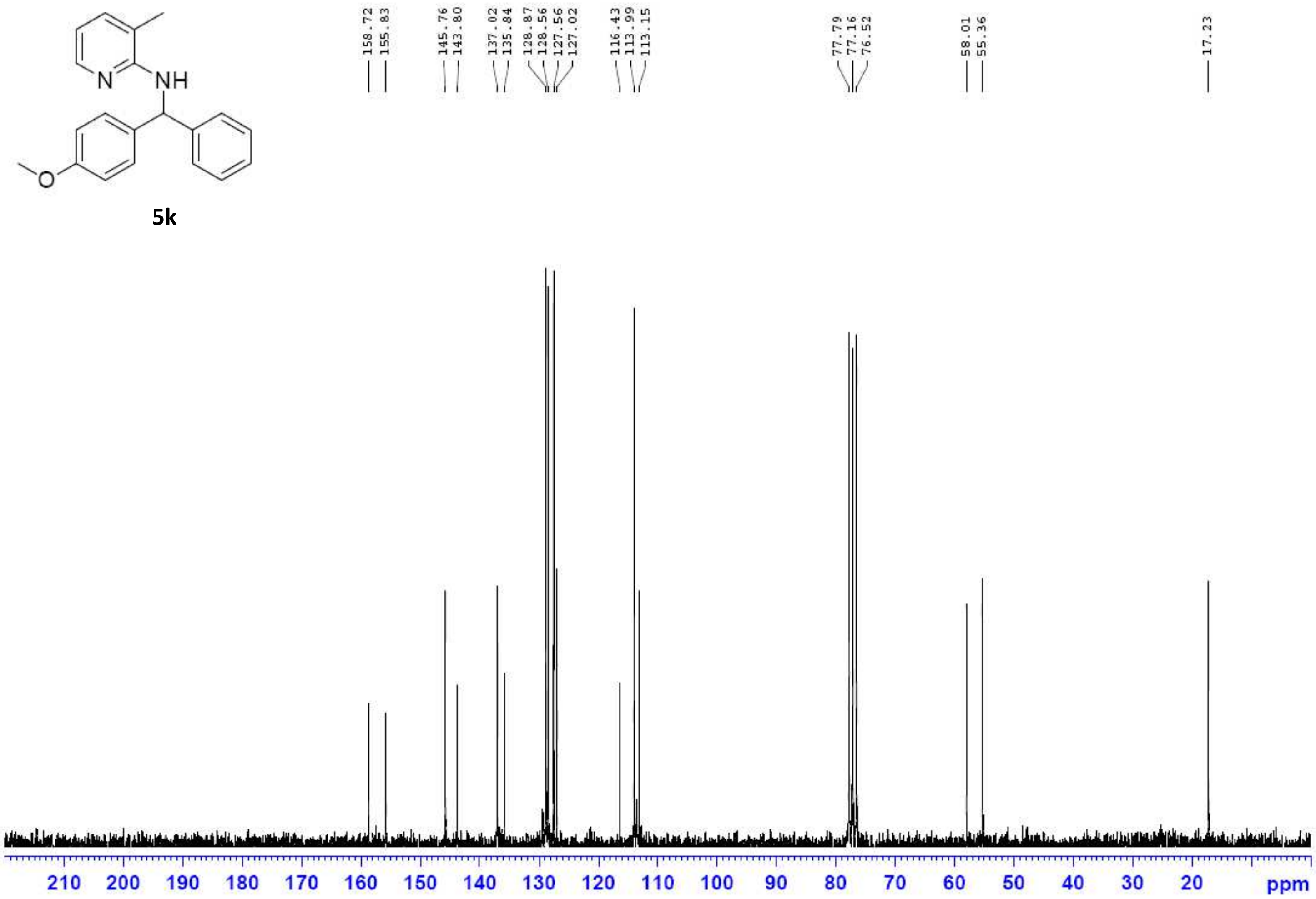
5j


N
NH
155.90
149.97
145.80
143.73
140.61
137.00
128.53
127.58
127.45
126.97
125.57
116.42
113.11
77.80
77.16
76.53
58.18
34.58
31.50
17.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

5j

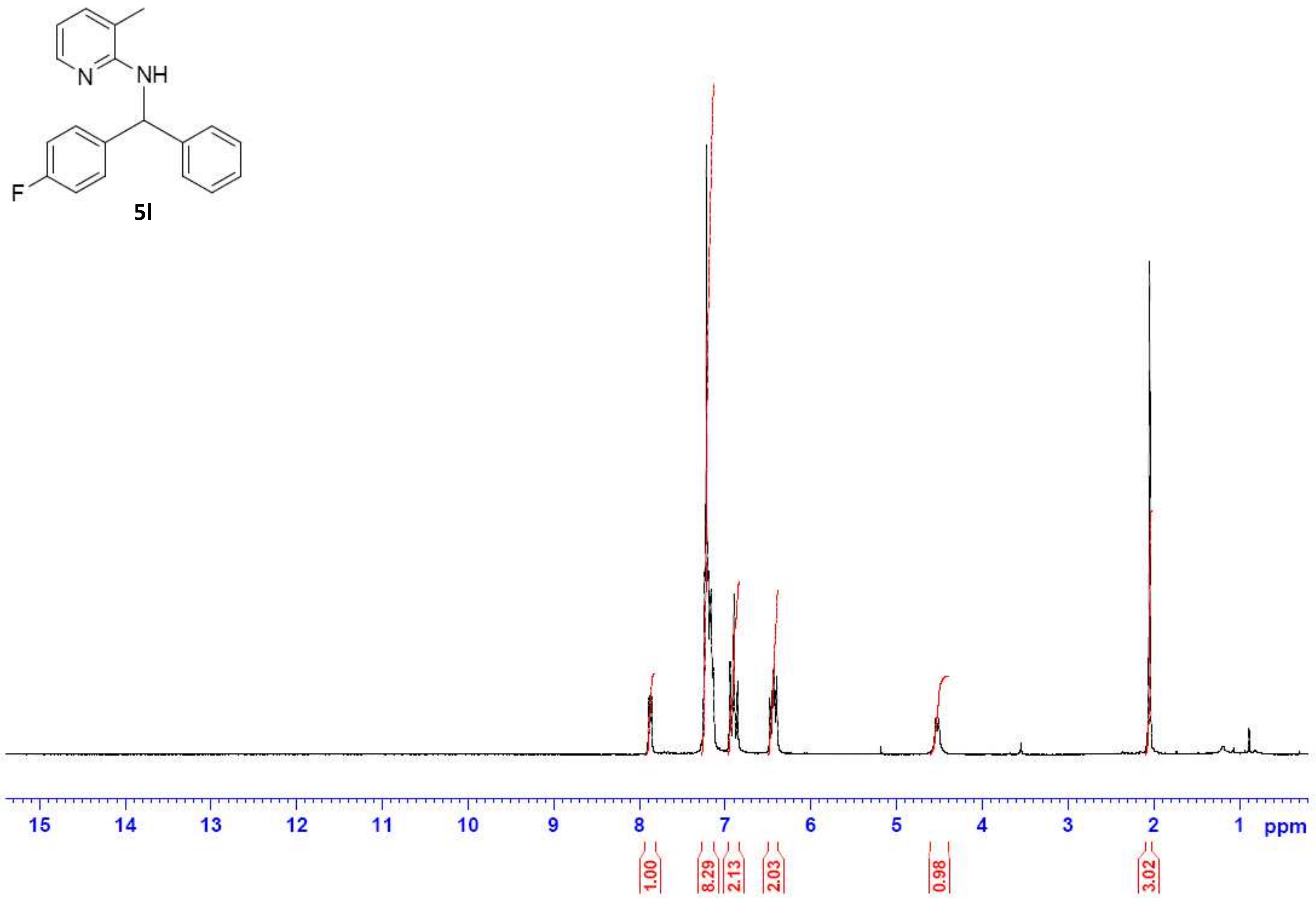


5k

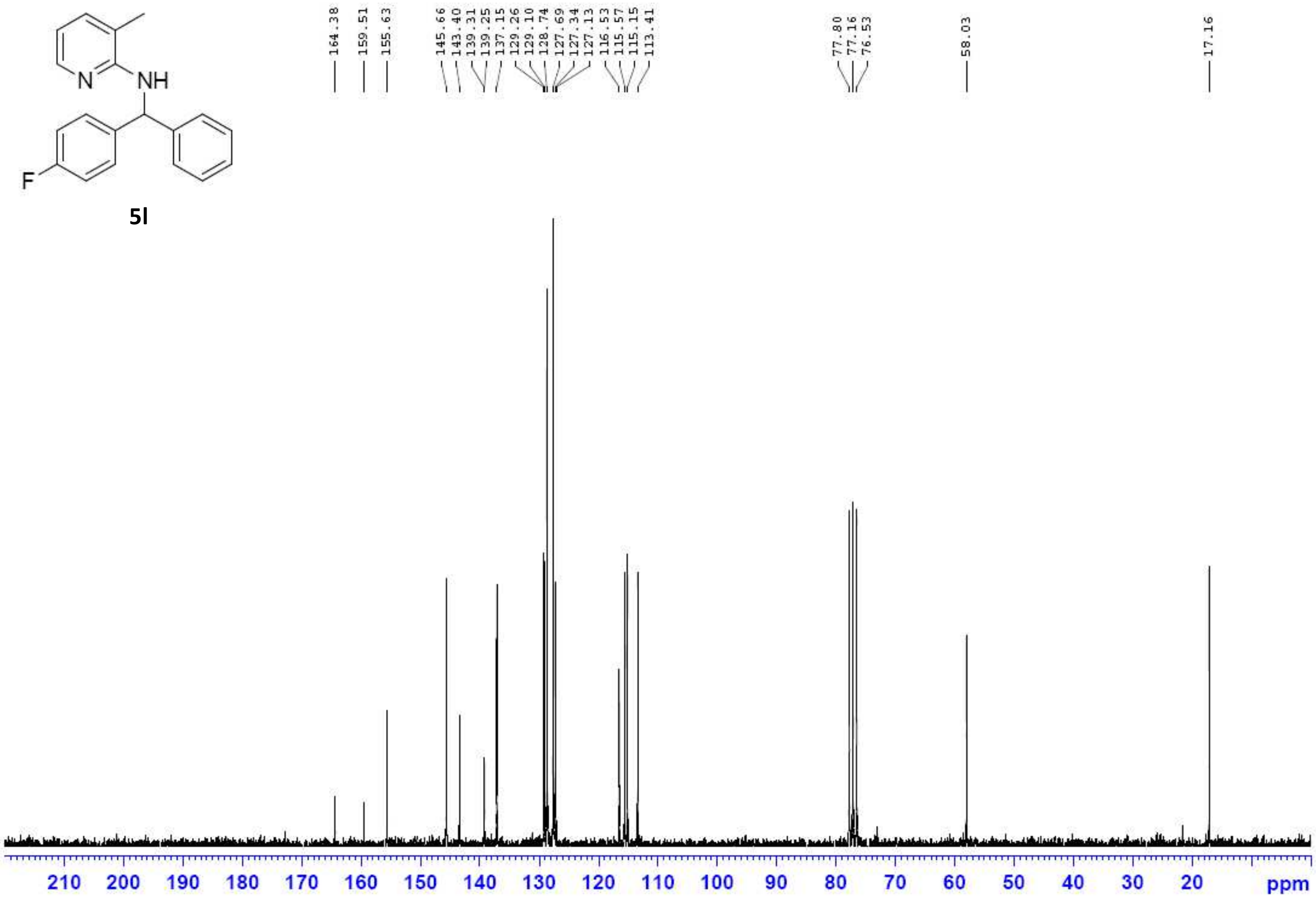


5k

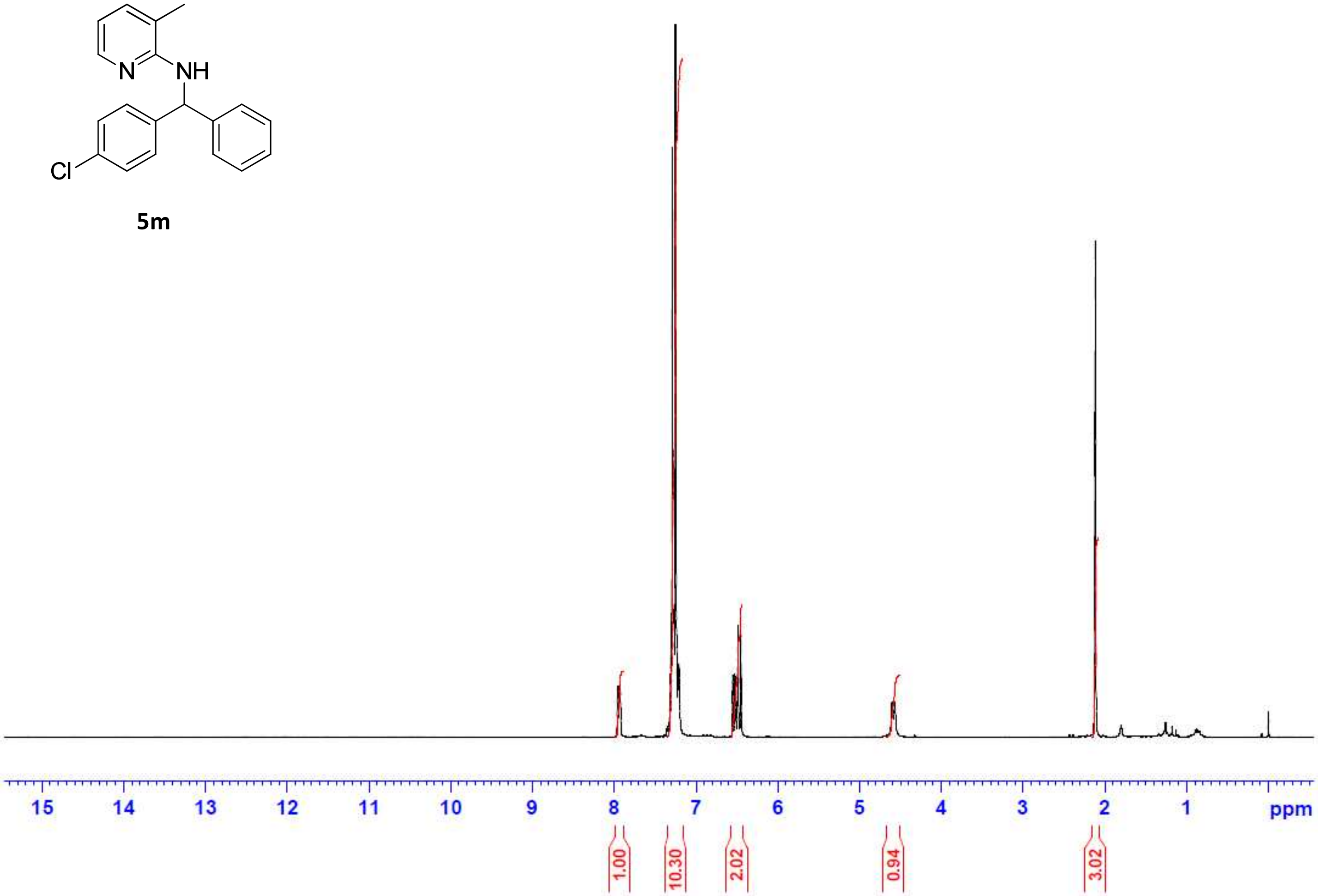
158.72
155.83
145.76
143.80
137.02
135.84
128.87
128.56
127.56
127.02
116.43
113.99
113.15
77.79
77.16
76.52
58.01
55.36
17.23
N
NH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm



5l

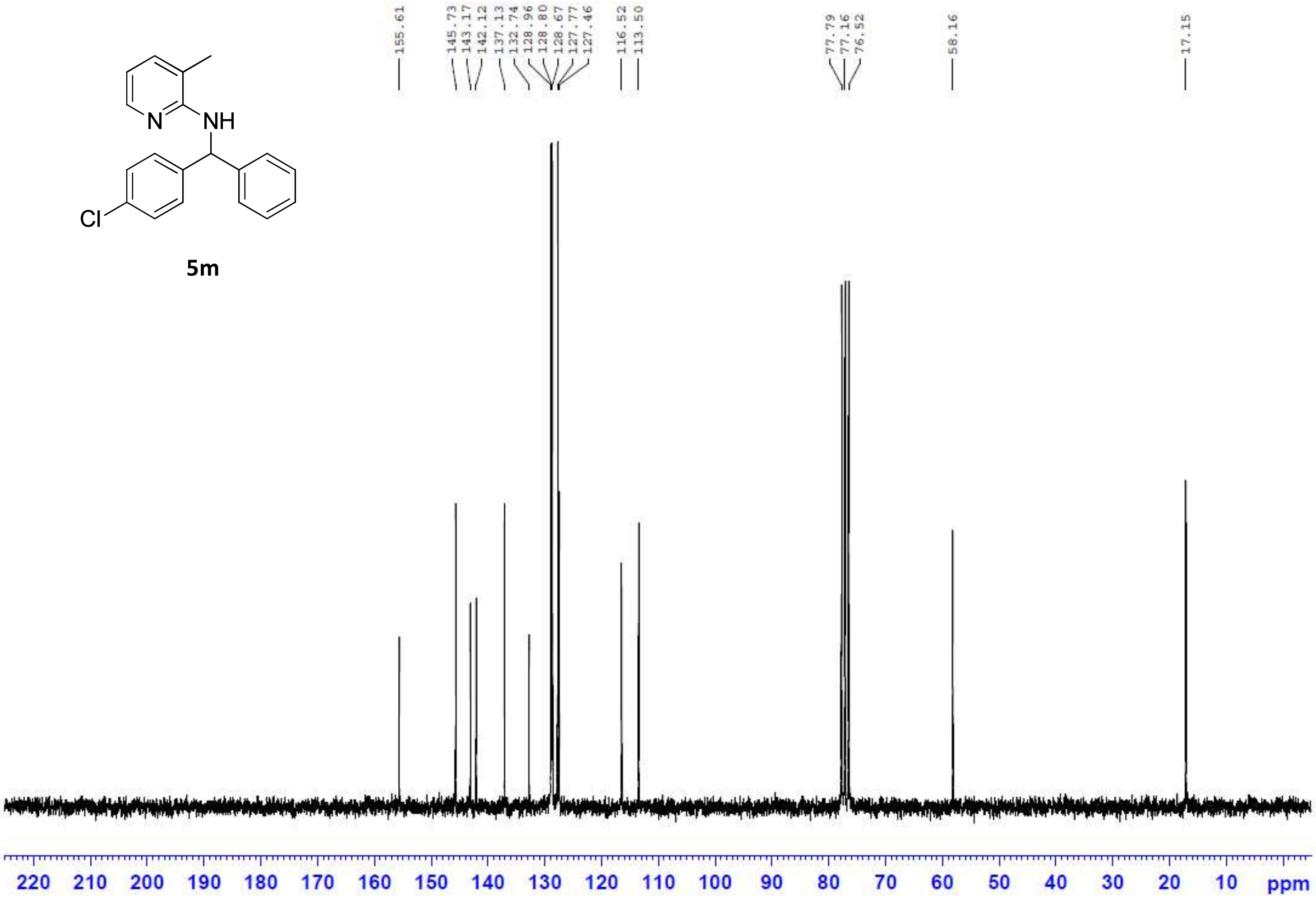

5l

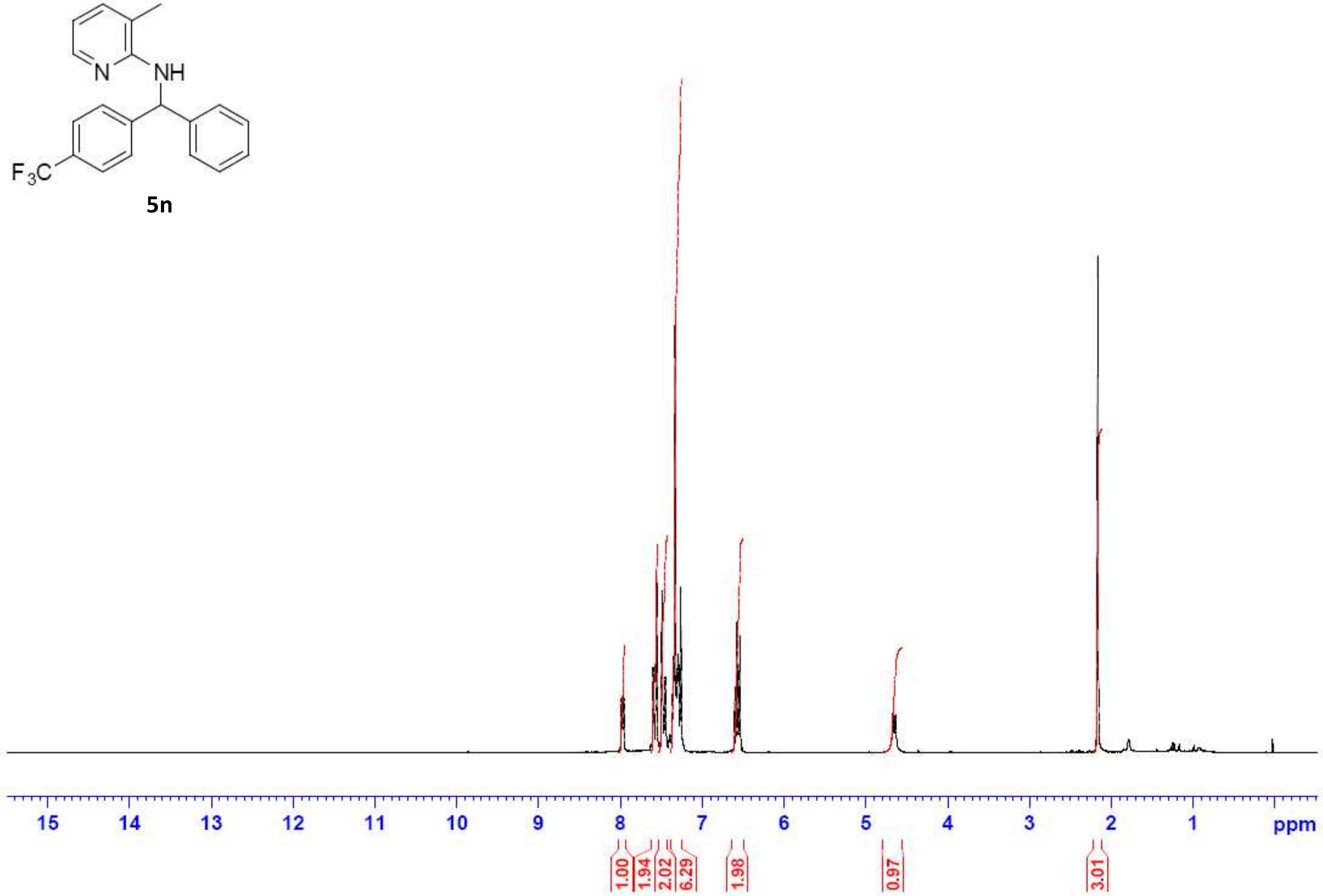
N
NH
F
164.38
159.51
155.63
145.66
143.40
139.31
139.25
137.15
129.26
129.10
128.74
127.69
127.34
127.13
116.53
115.57
115.15
113.41
77.80
77.16
76.53
58.03
17.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



5m

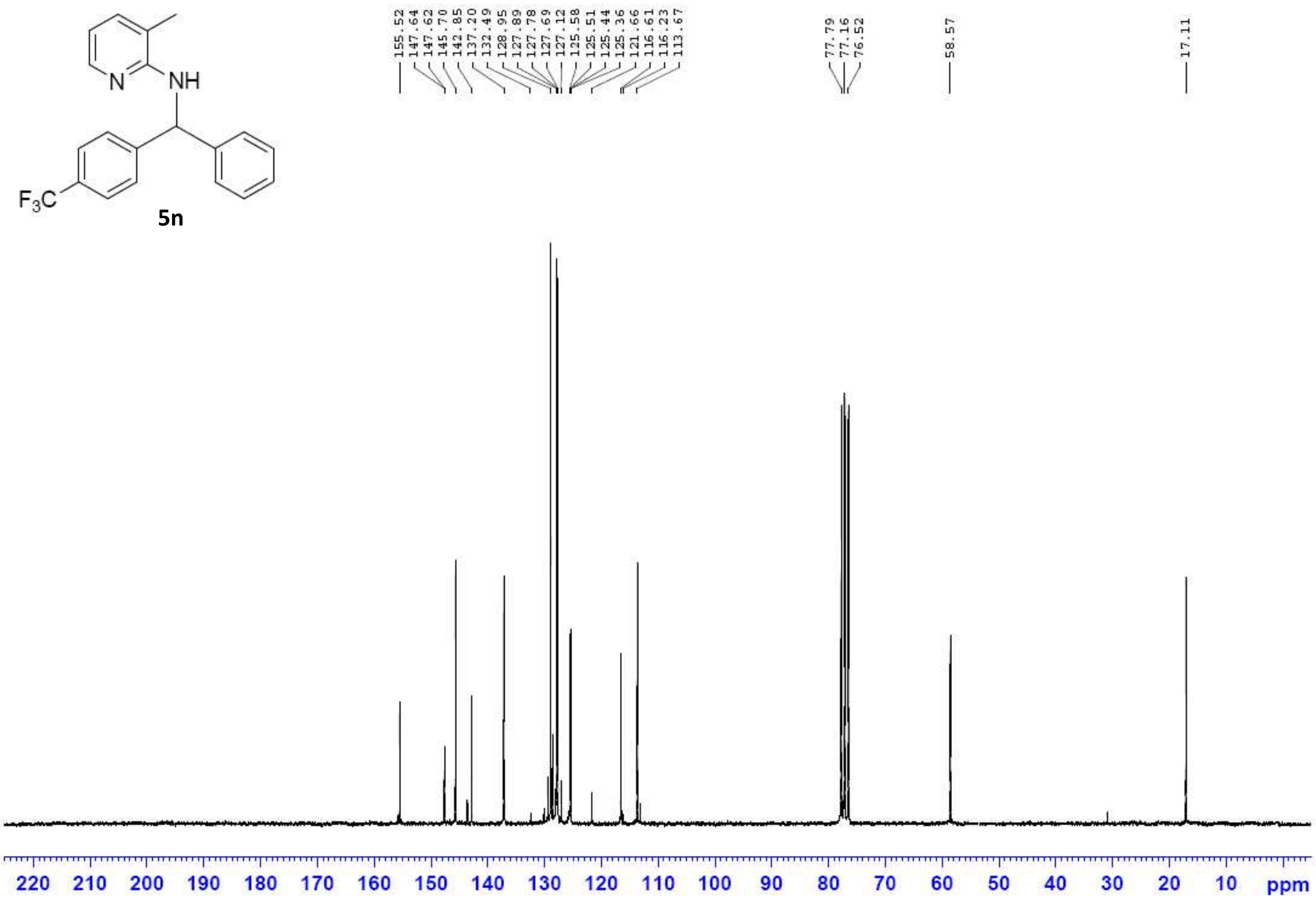
5m


155.61
145.73
143.17
142.12
137.13
132.74
128.96
128.80
128.67
127.77
127.46
116.52
113.50
77.79
77.16
76.52
58.16
17.15
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



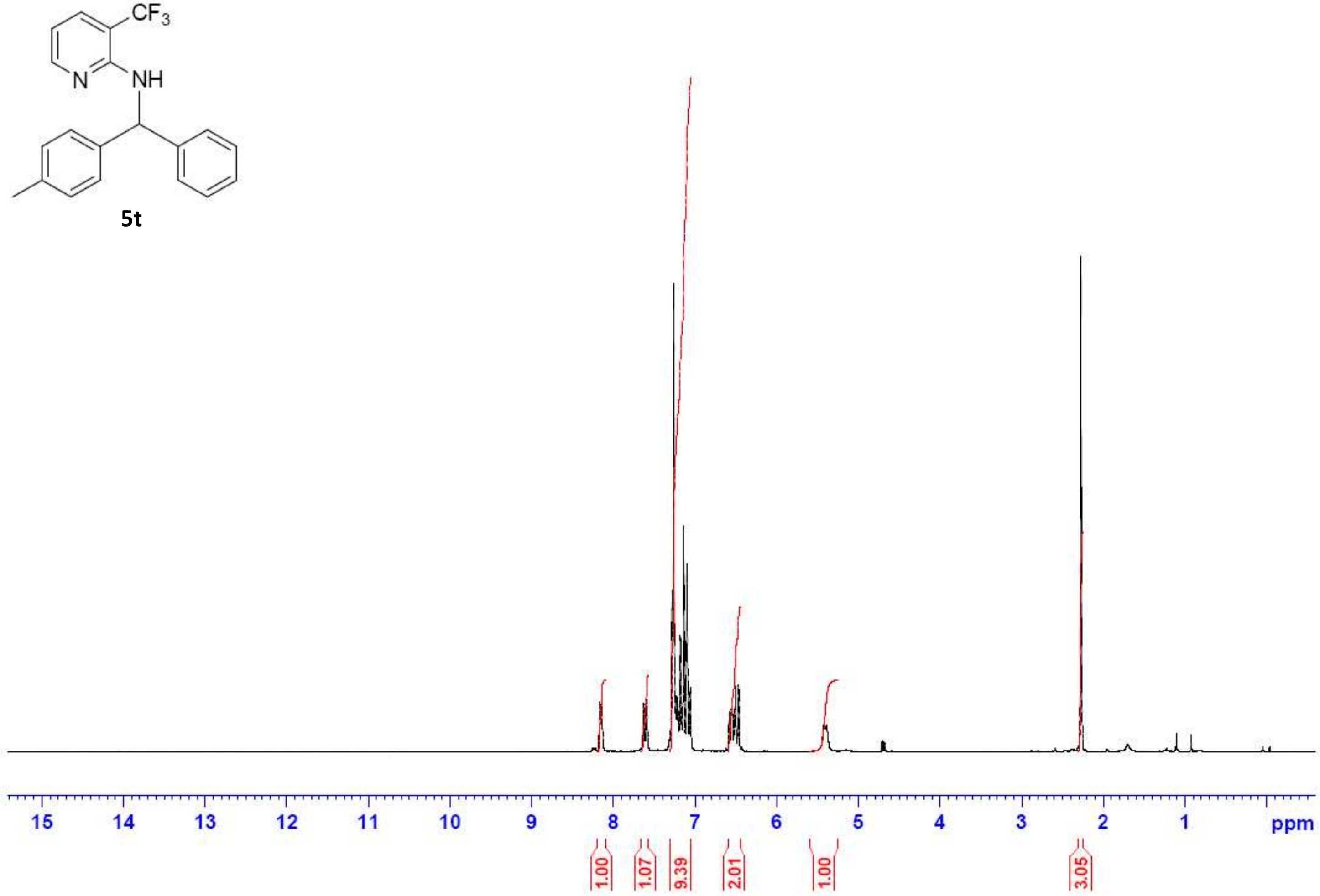
N
NH
F3C
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.94
2.02
6.29
1.98
0.97
3.01

5n

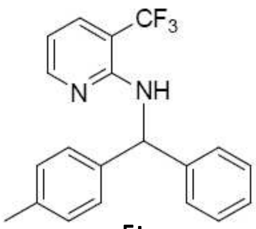


NH
N
F3C
155.52
147.64
147.62
145.70
142.85
137.20
132.49
128.95
127.89
127.78
127.69
127.12
125.58
125.51
125.44
125.36
121.66
116.61
116.23
113.67
77.79
77.16
76.52
58.57
17.11
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

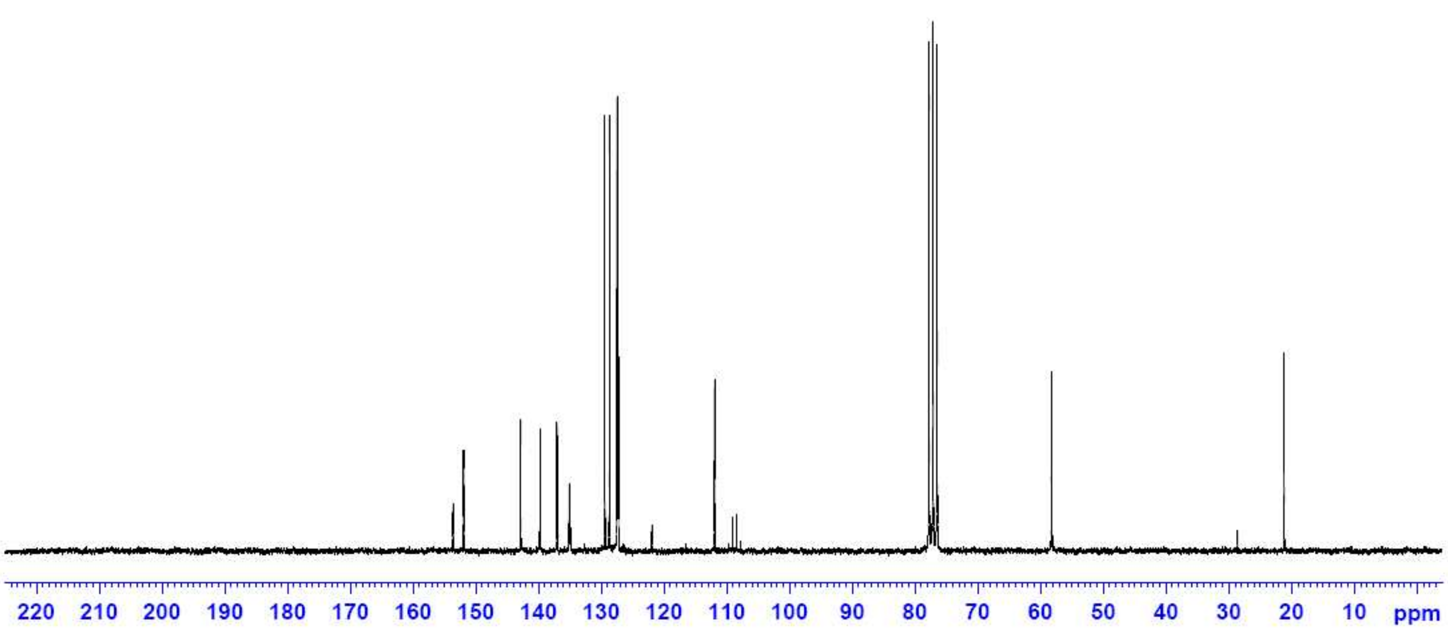
5n

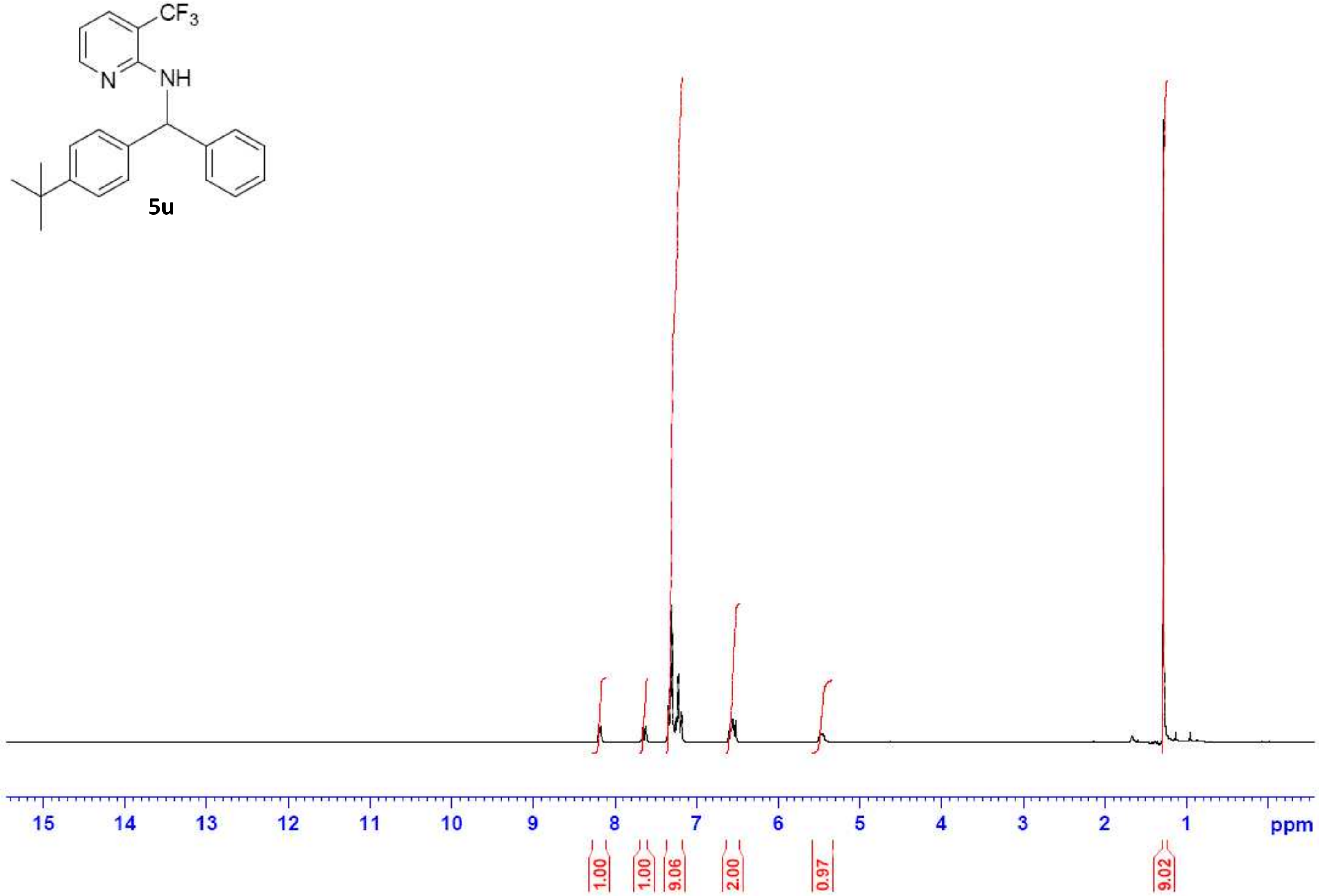


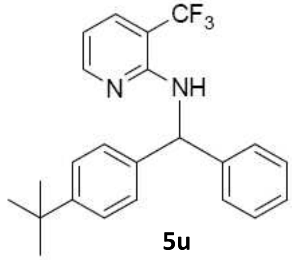
5t


CF3
N
NH

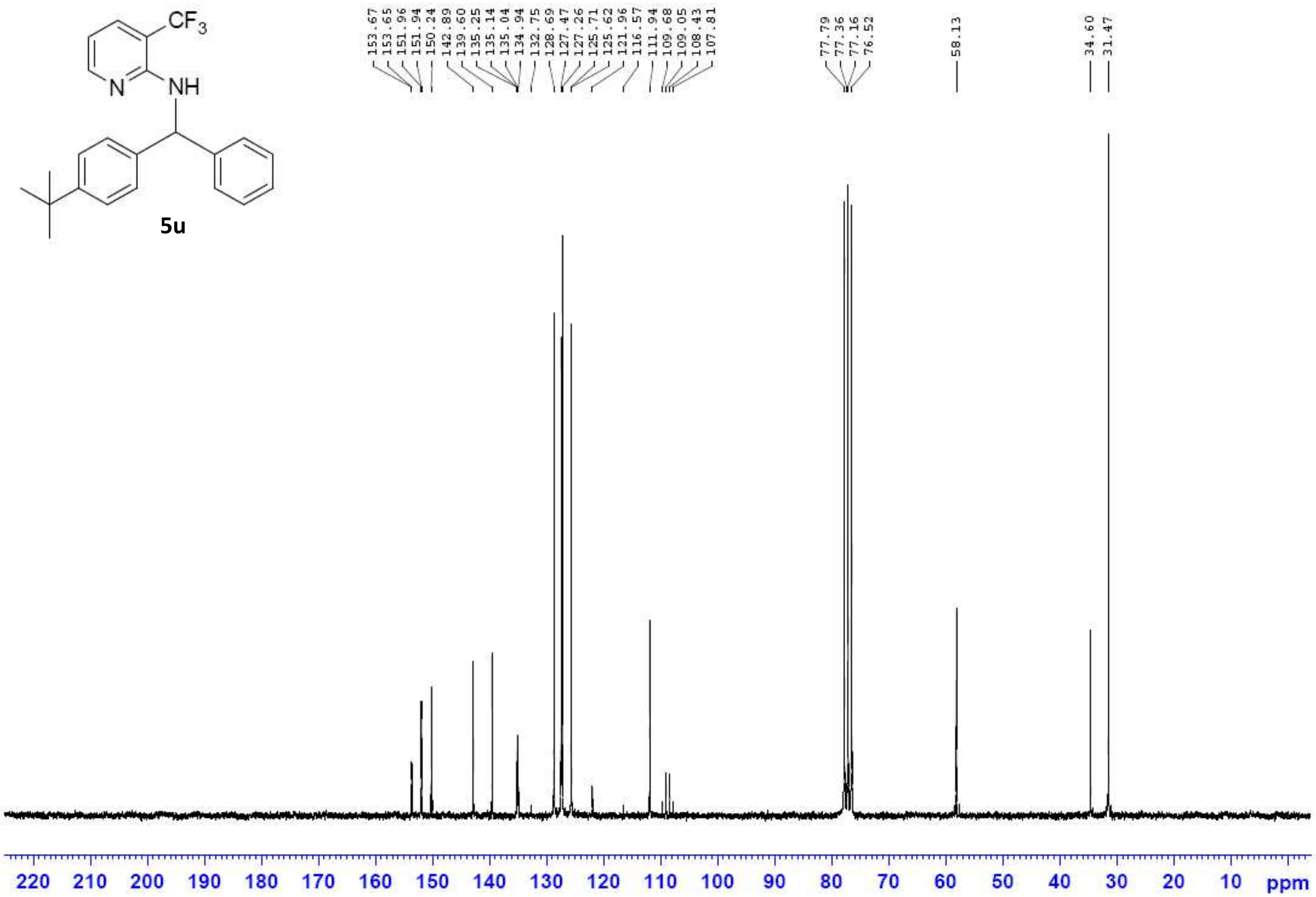
5t

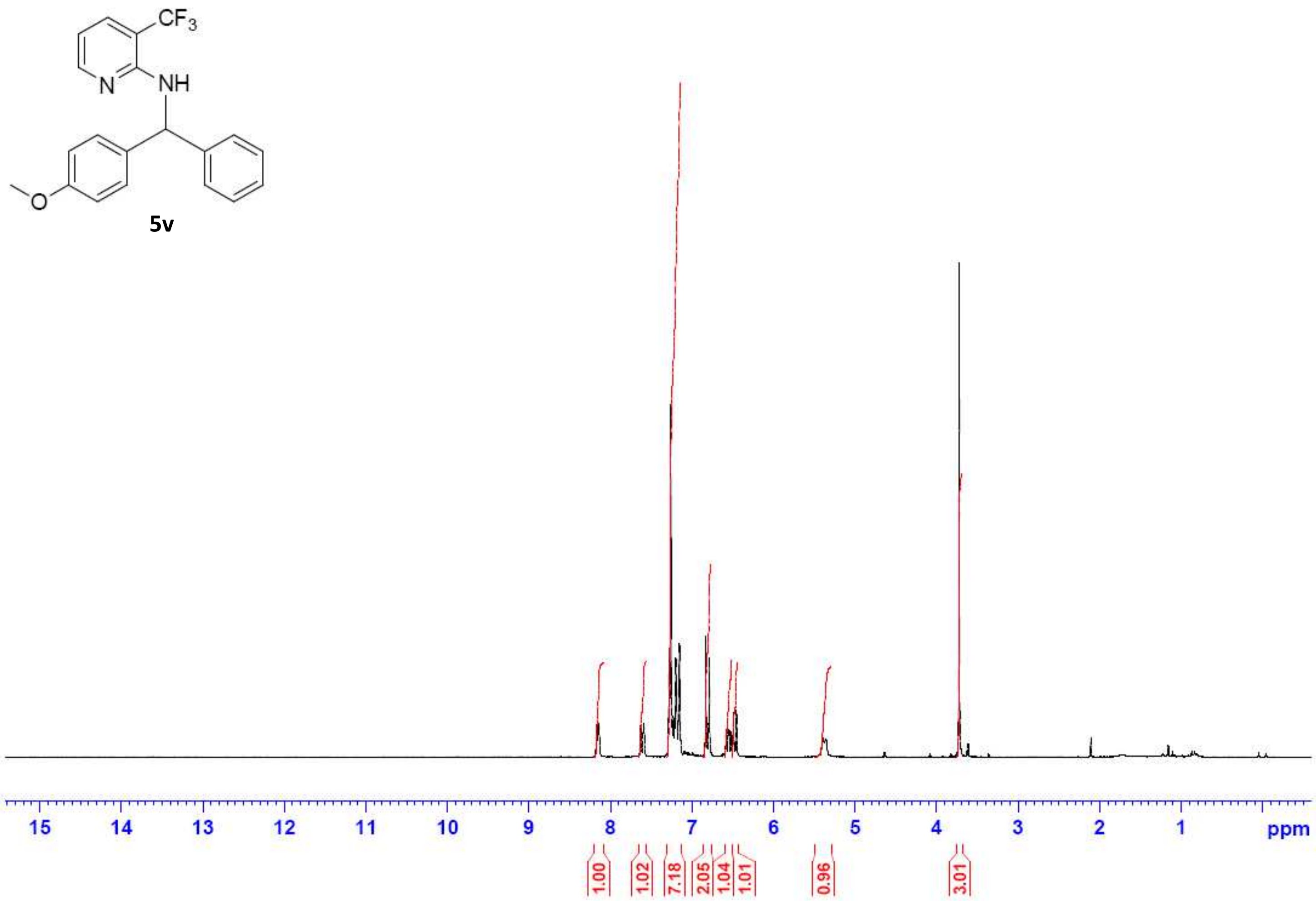

153.64
153.62
151.96
151.93
142.86
139.76
137.06
135.23
135.13
135.03
134.93
132.74
129.49
128.72
127.49
127.45
127.28
111.97
109.08
108.46
77.79
77.16
76.52
58.28
21.20
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


CF3
NH
N
5u
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
9.06
2.00
0.97
9.02

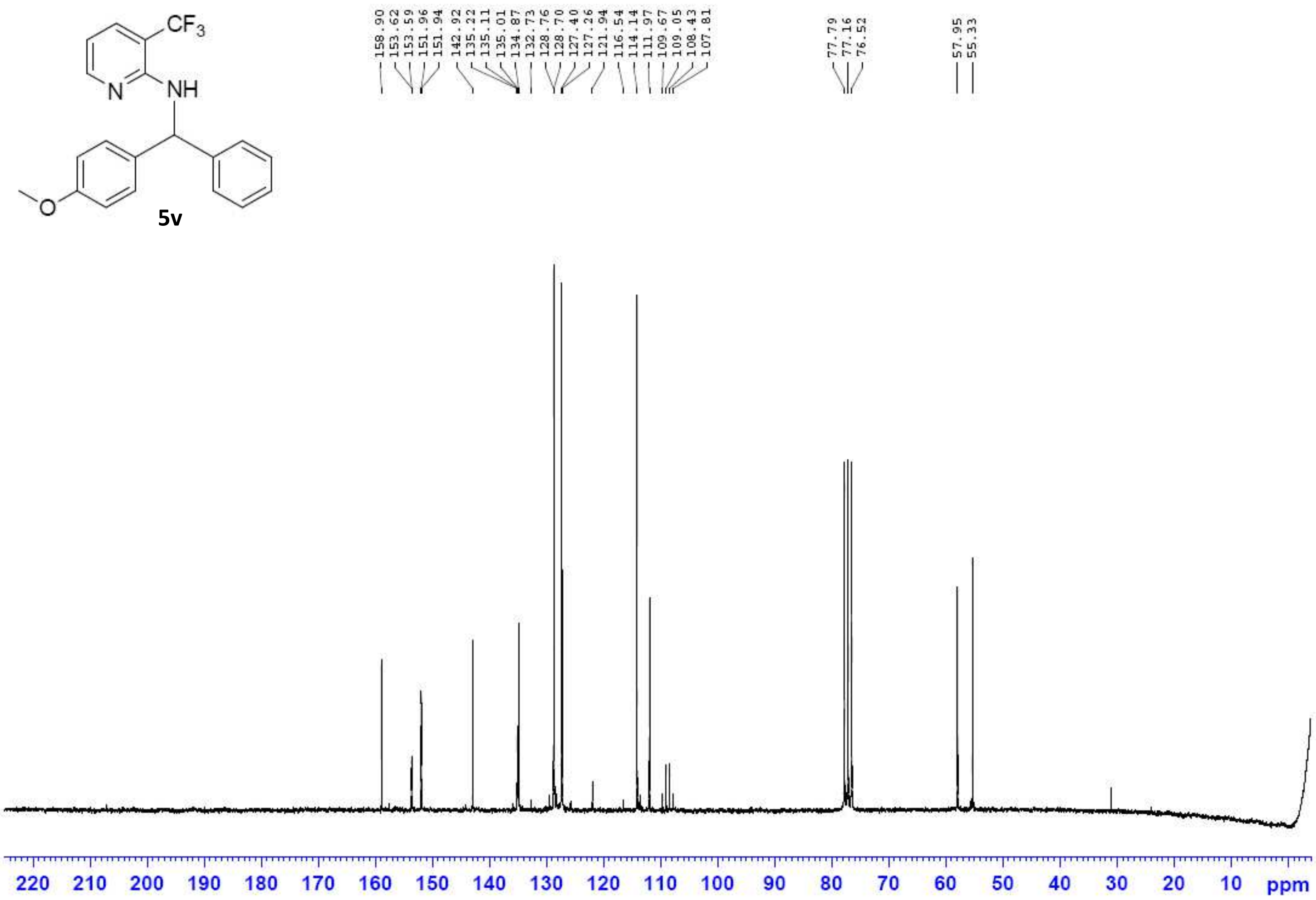

CF3
N
NH

5u


153.67
153.65
151.96
151.94
150.24
142.89
139.60
135.25
135.14
135.04
134.94
132.75
128.69
127.47
127.26
125.71
125.62
121.96
116.57
111.94
109.68
109.05
108.43
107.81
77.79
77.36
77.16
76.52
58.13
34.60
31.47
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

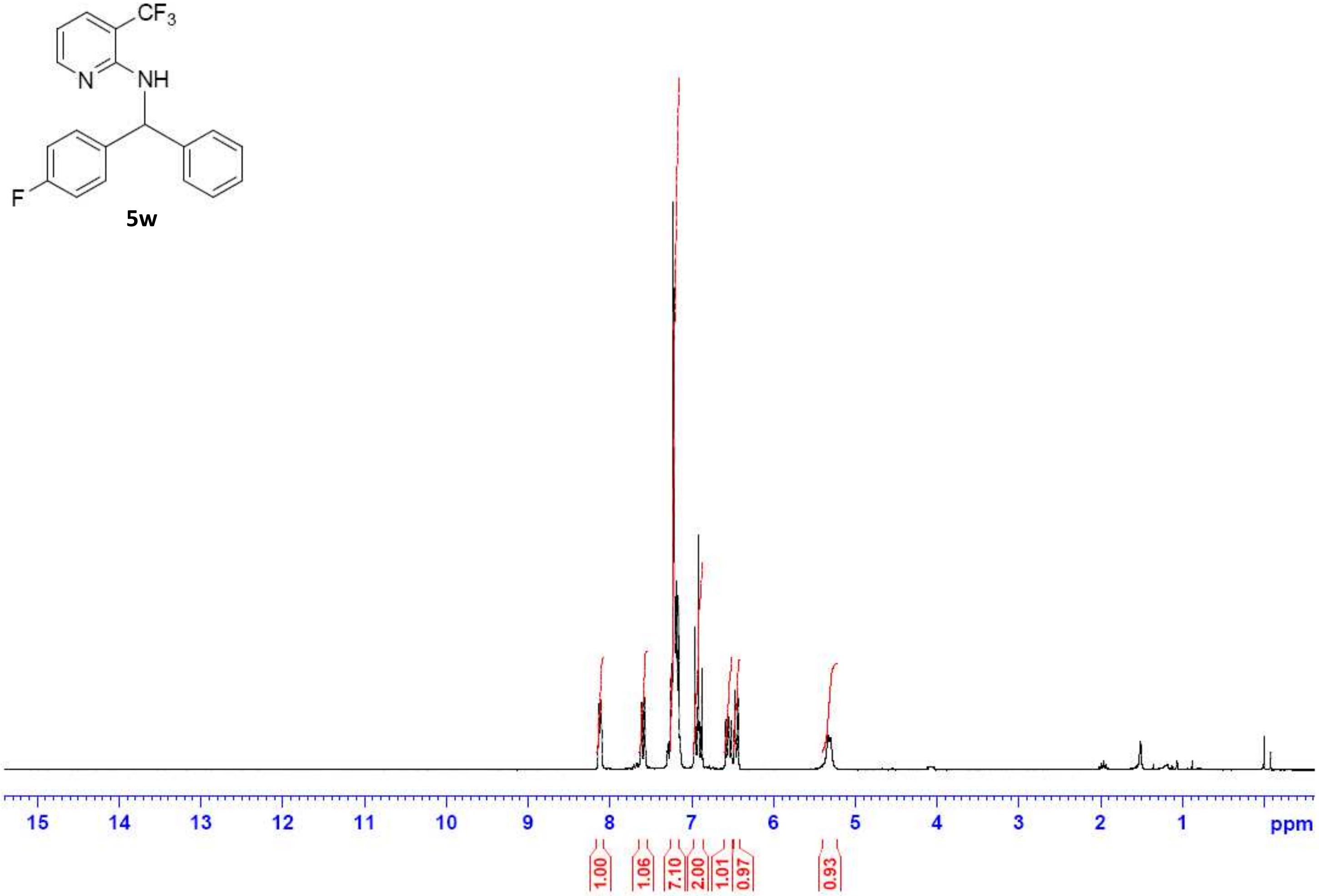

CF_3
NH
N
O
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
7.18
2.05
1.04
1.01
0.96
3.01

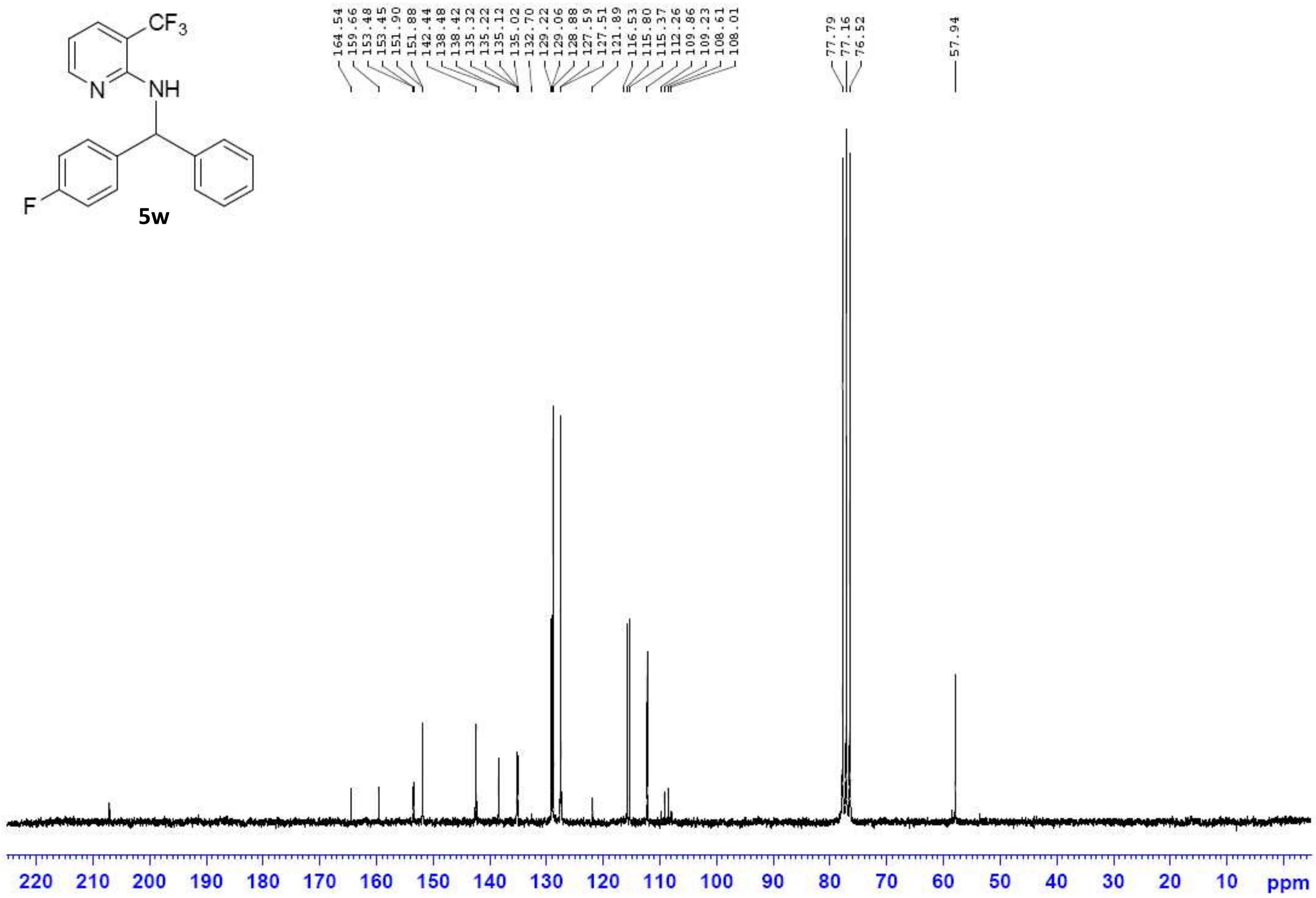
5v

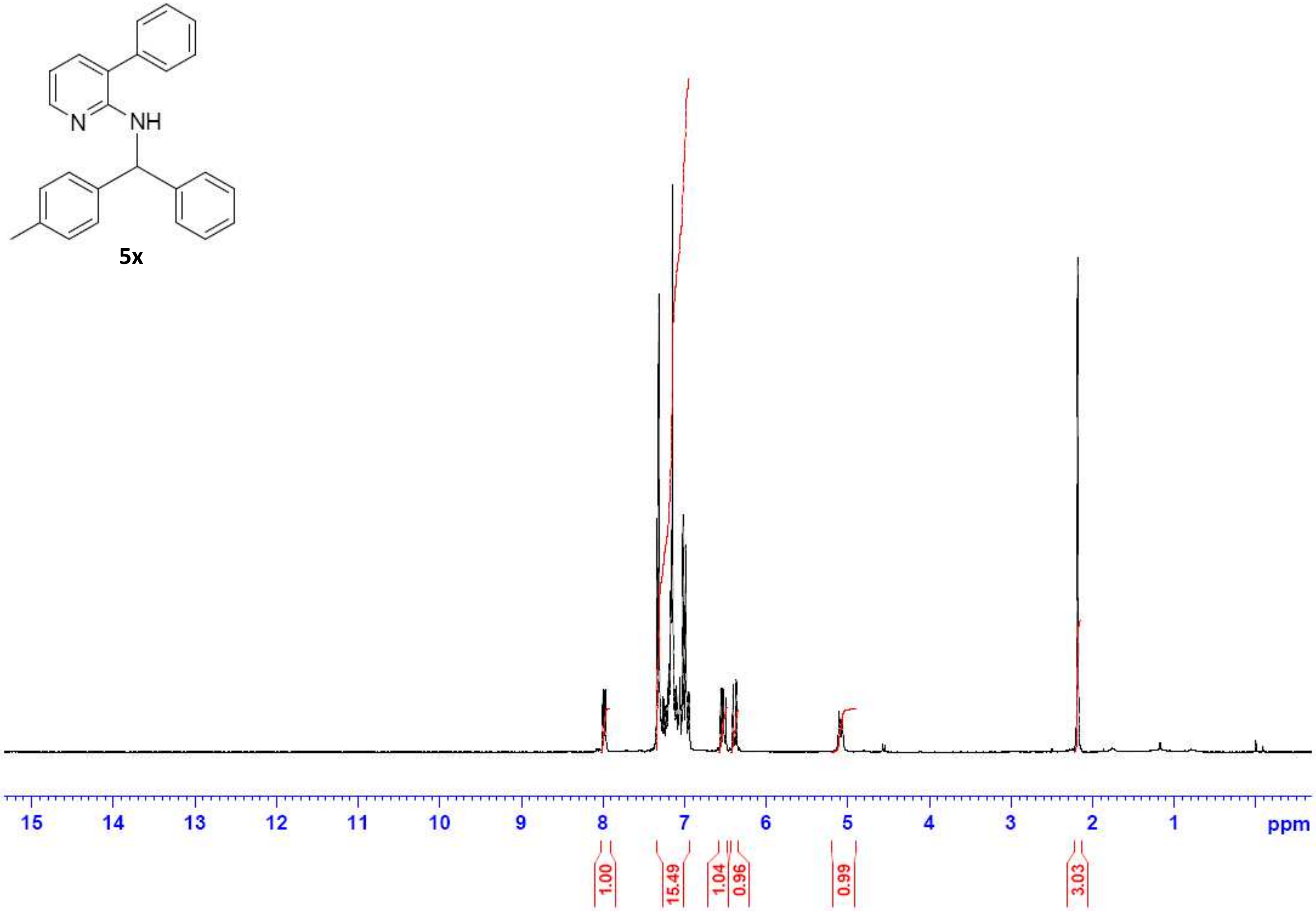


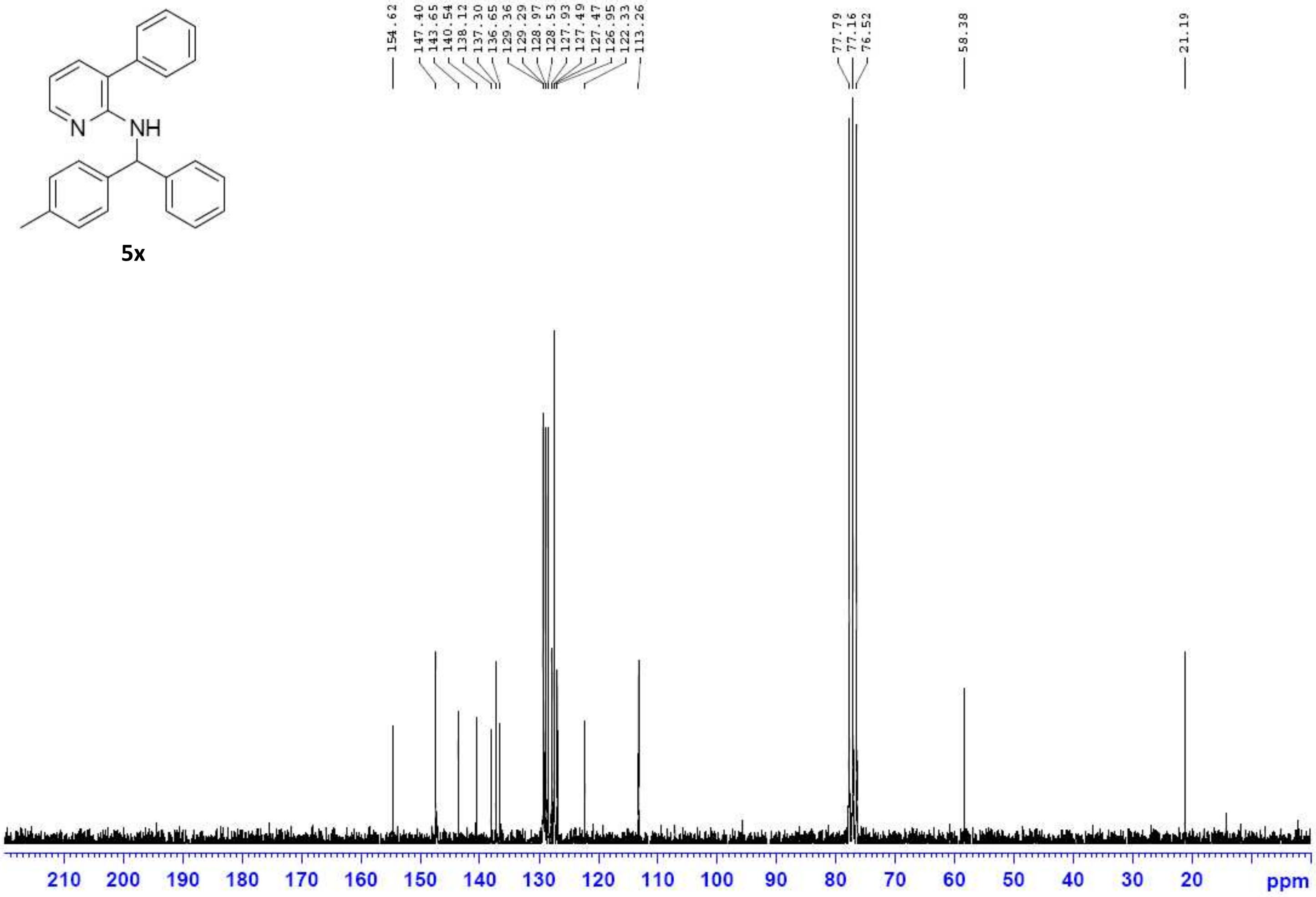
5v

CF3
NH
N
O
158.90
153.62
153.59
151.96
151.94
142.92
135.22
135.11
135.01
134.87
132.73
128.76
128.70
127.40
127.26
121.94
116.54
114.14
111.97
109.67
109.05
108.43
107.81
77.79
77.16
76.52
57.95
55.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CF3
N
NH
F
5w
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
7.10
2.00
1.01
0.97
0.93

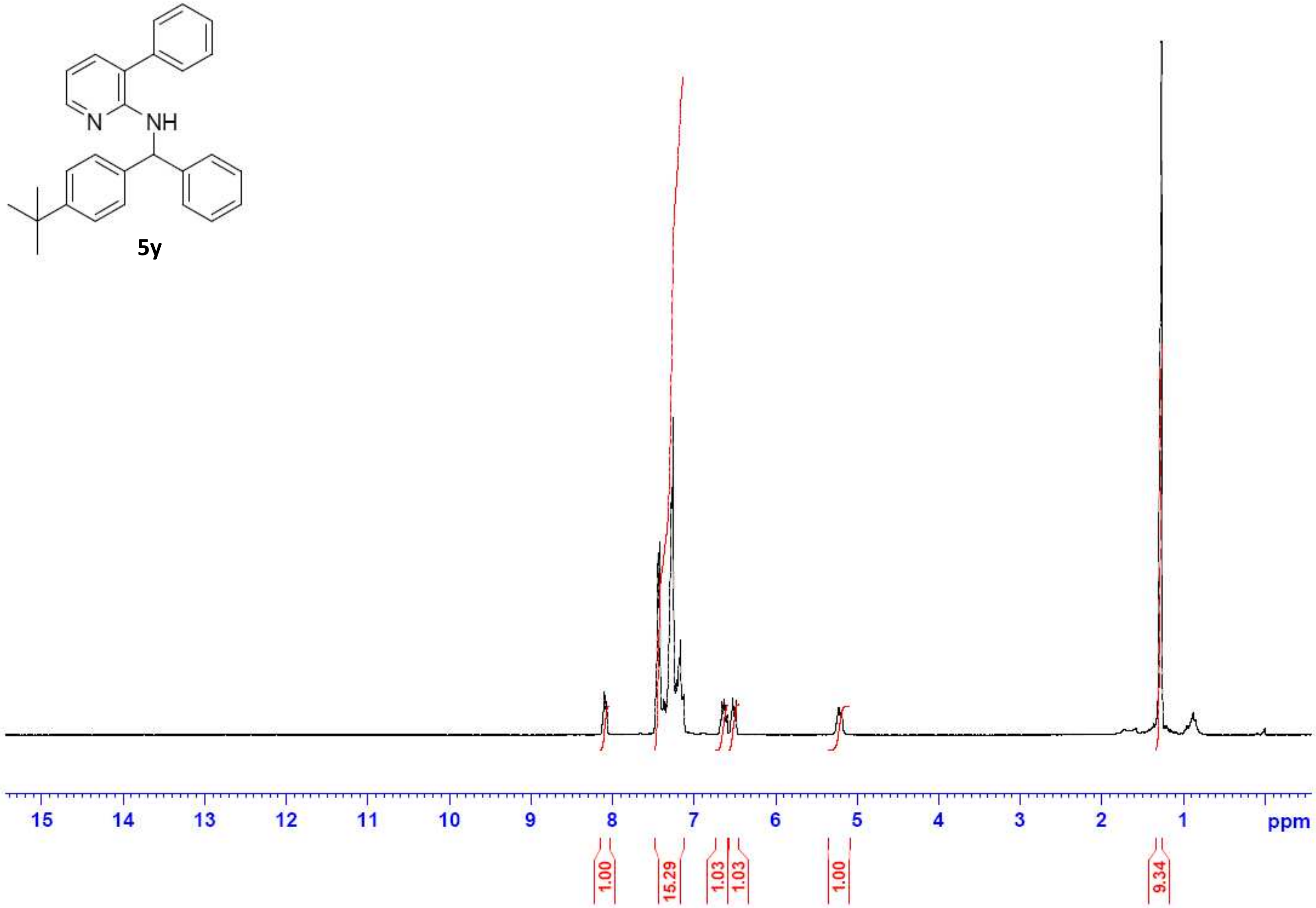

CF3
NH
N
F
5w
164.54
159.66
153.48
153.45
151.90
151.88
142.44
138.48
138.42
135.32
135.22
135.12
135.02
132.70
129.22
129.06
128.88
127.59
127.51
121.89
116.53
115.80
115.37
112.26
109.86
109.23
108.61
108.01
77.79
77.16
76.52
57.94
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


5x

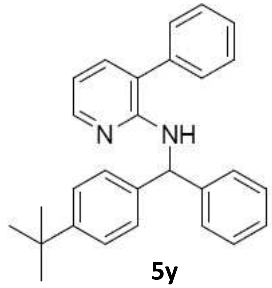


5x

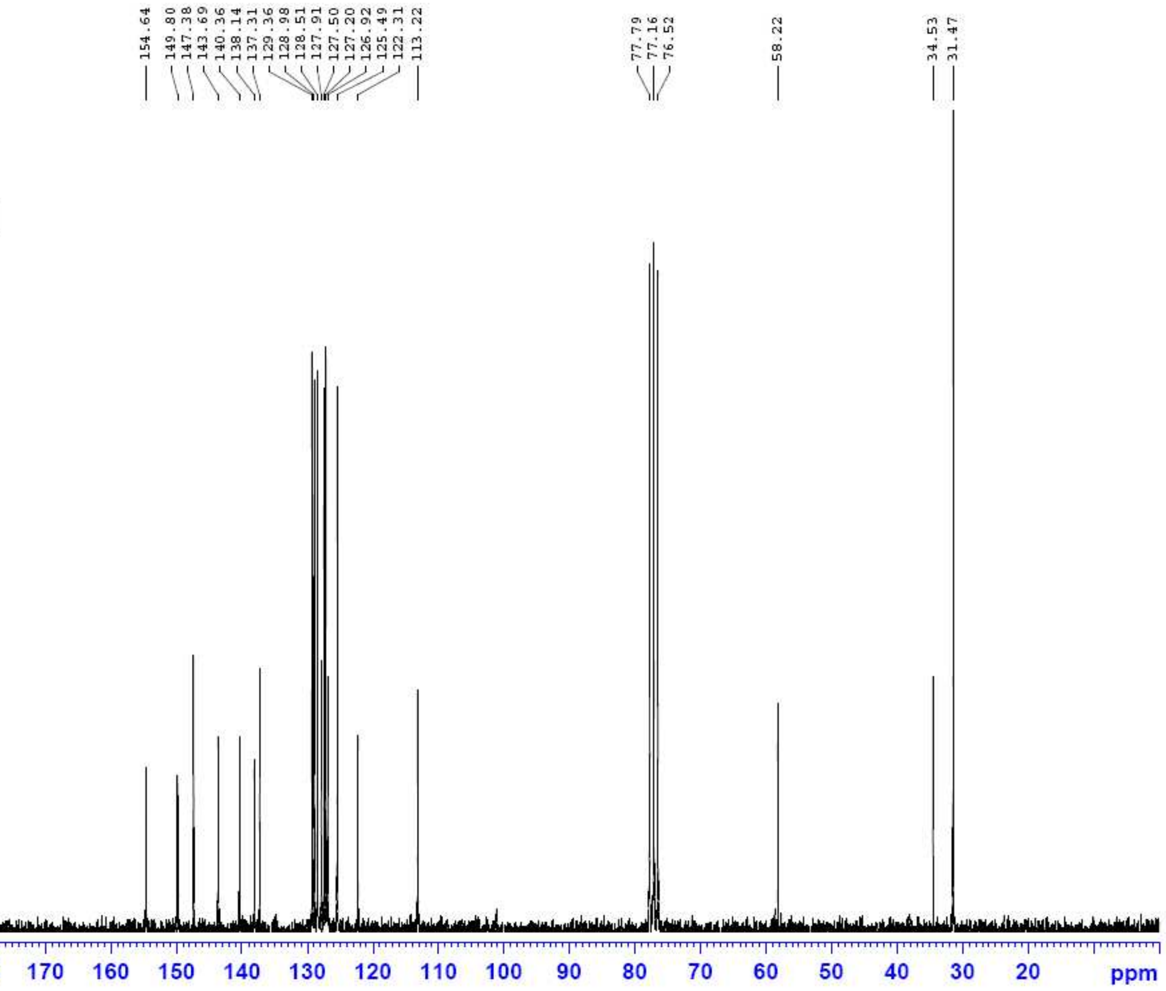
154.62
147.40
143.65
140.54
138.12
137.30
136.65
129.36
129.29
128.97
128.53
127.93
127.49
127.47
126.95
122.33
113.26
77.79
77.16
76.52
58.38
21.19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
N
NH

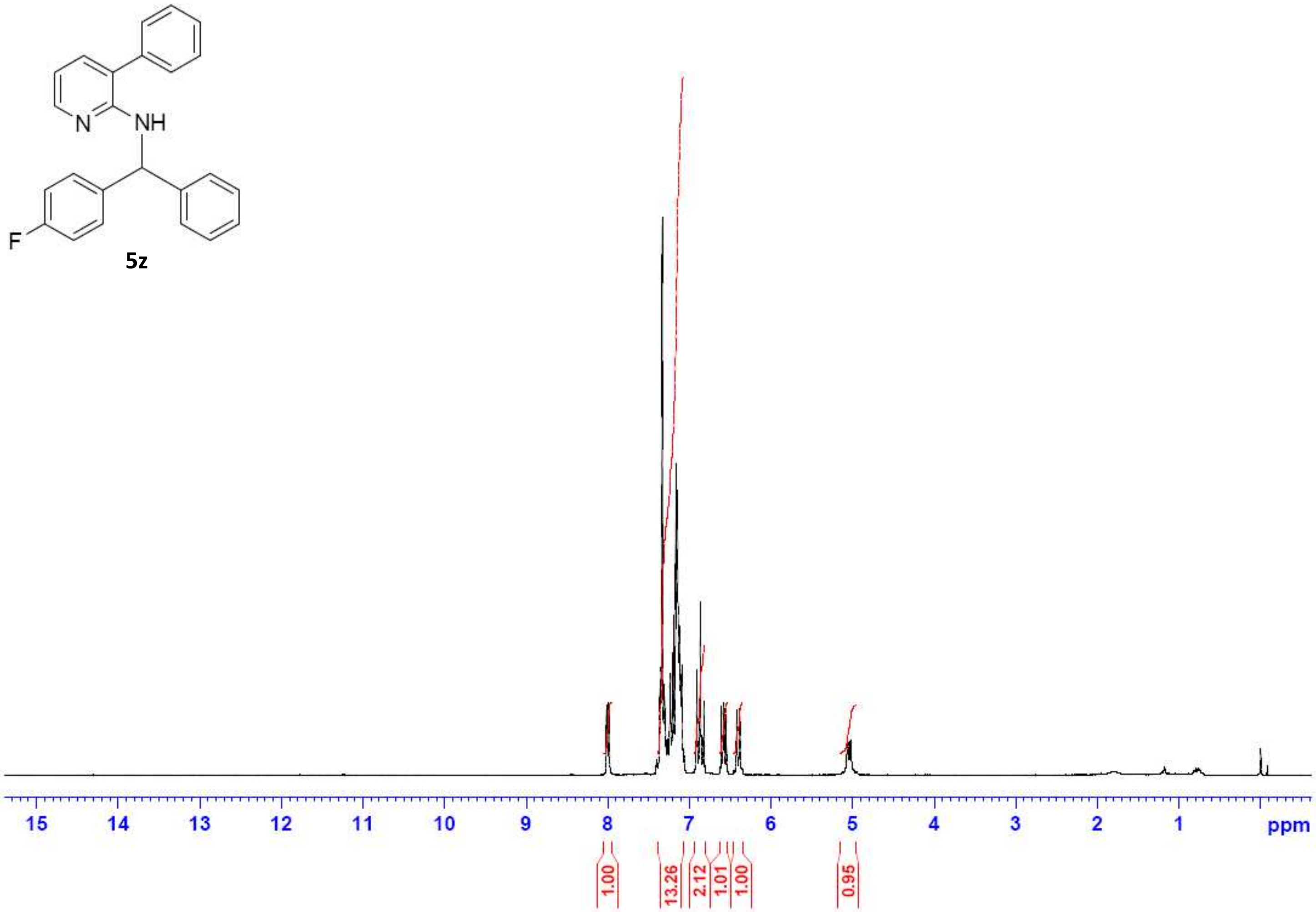


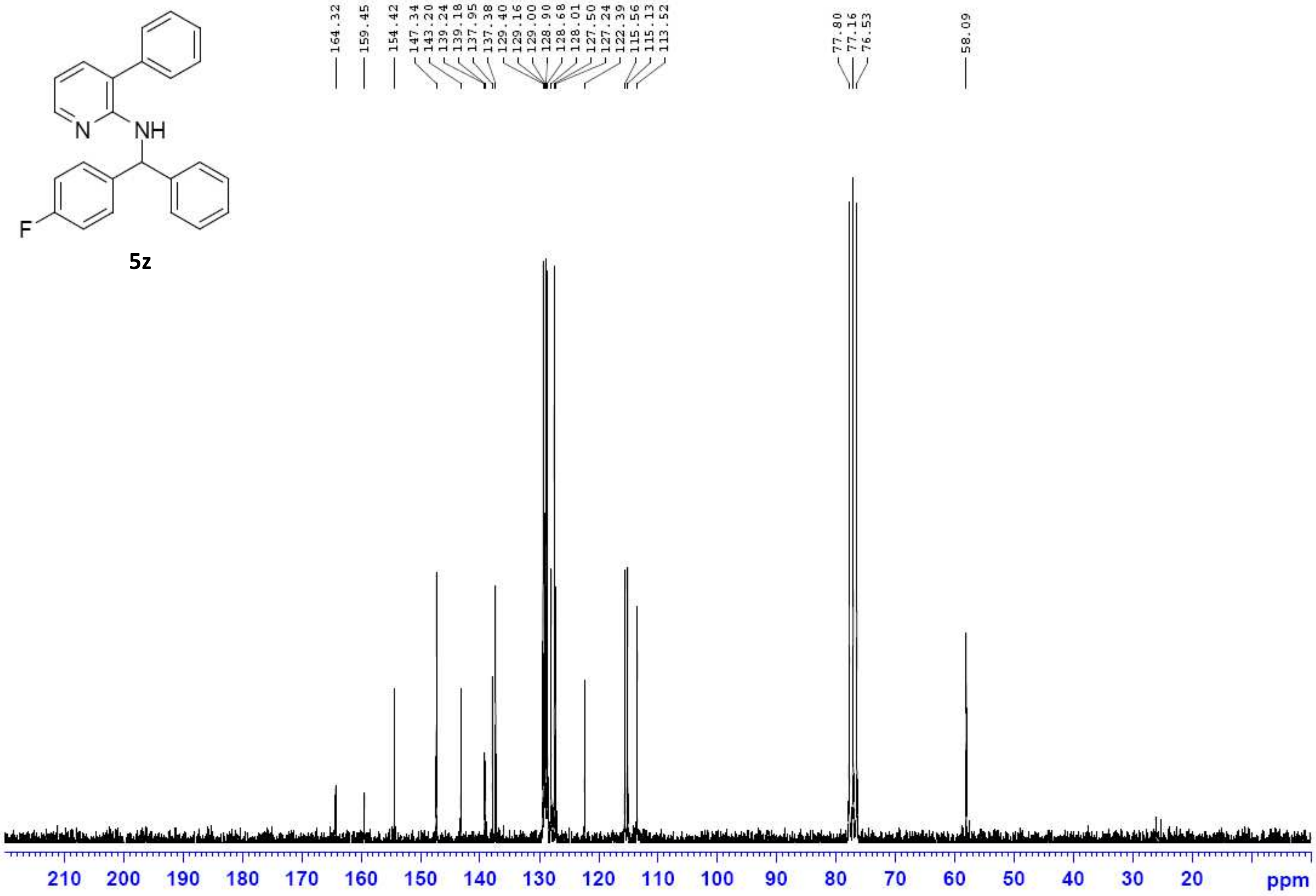
5y



5y

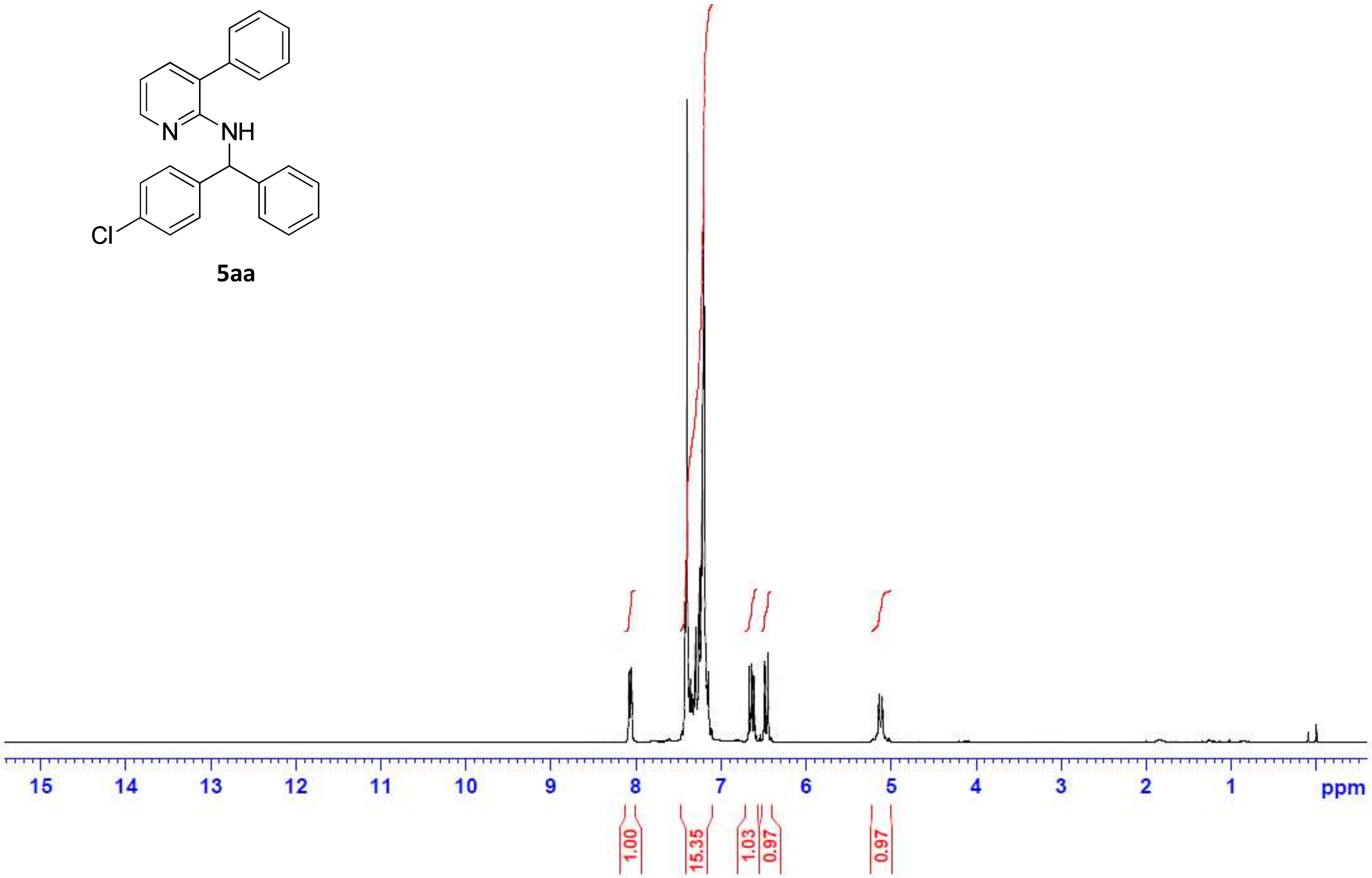

154.64
149.80
147.38
143.69
140.36
138.14
137.31
129.36
128.98
128.51
127.91
127.50
127.20
126.92
125.49
122.31
113.22
77.79
77.16
76.52
58.22
34.53
31.47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5z

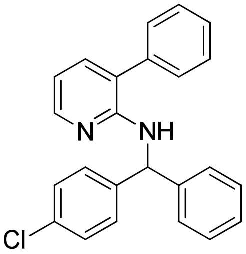


5z

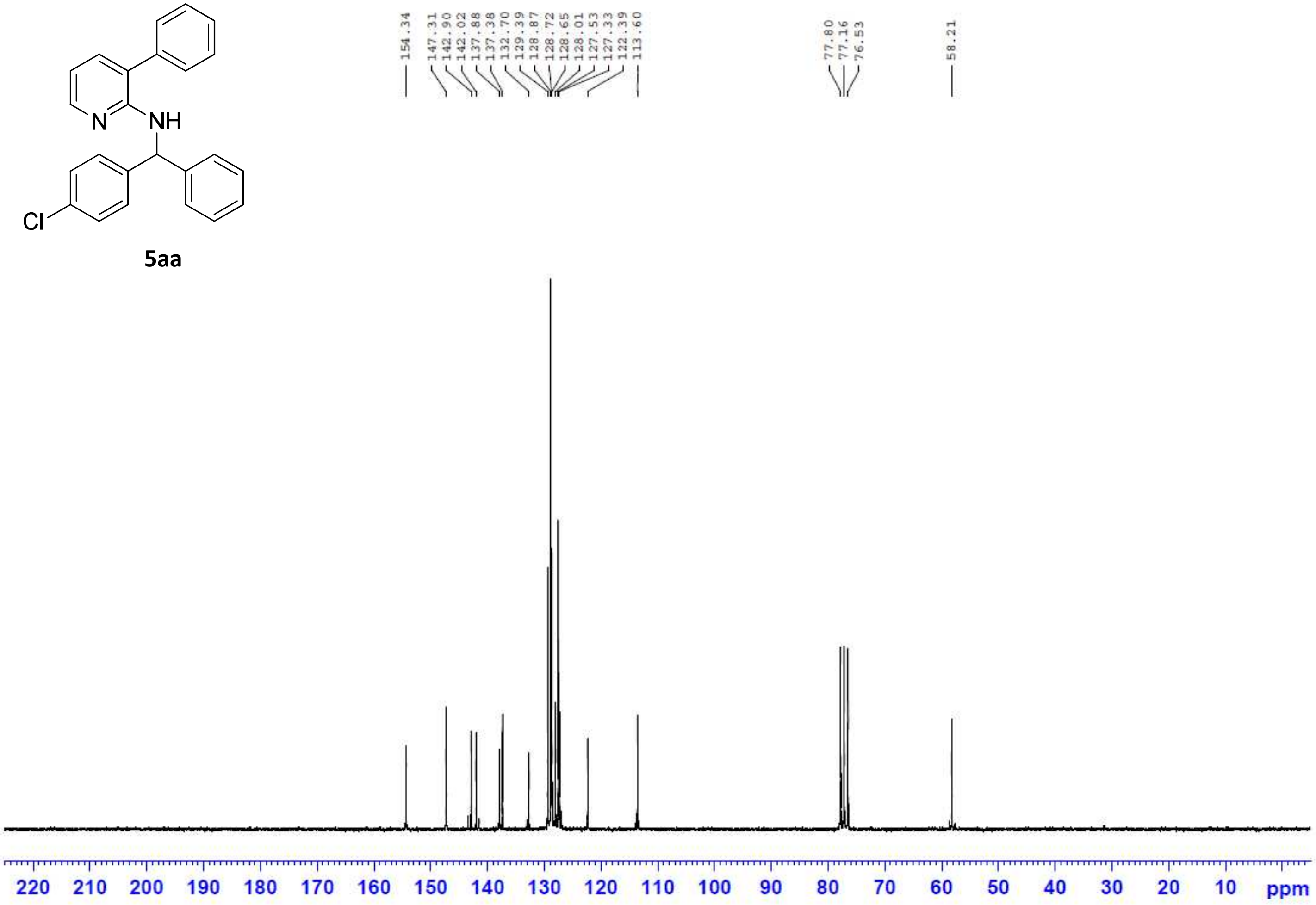
F
N
NH
164.32
159.45
154.42
147.34
143.20
139.24
139.18
137.95
137.38
129.40
129.16
129.00
128.90
128.68
128.01
127.50
127.24
122.39
115.56
115.13
113.52
77.80
77.16
76.53
58.09
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

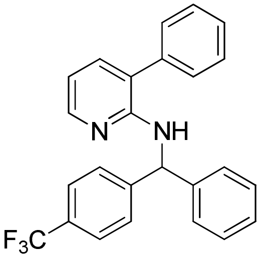


5aa

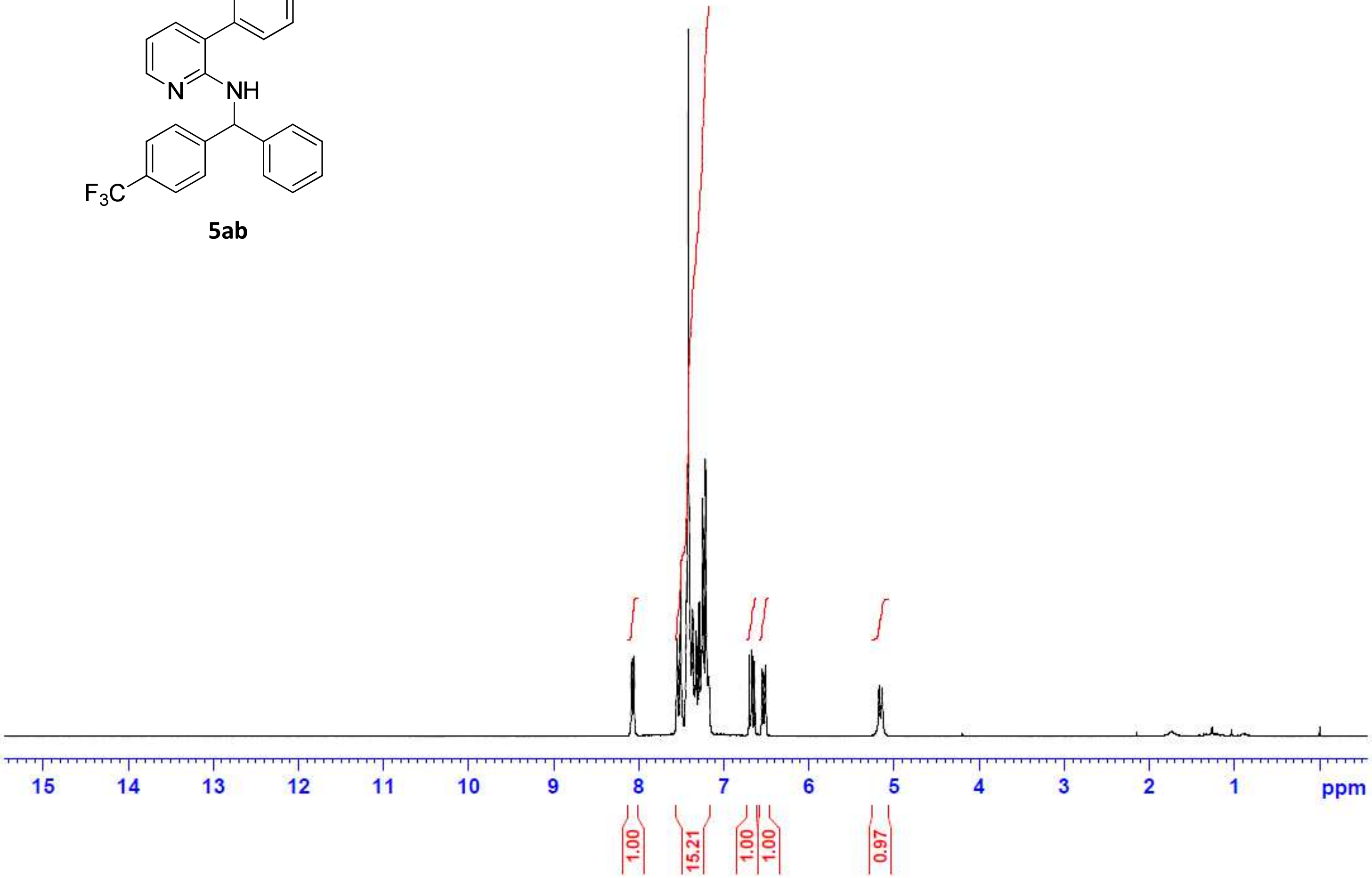

N
NH
Cl

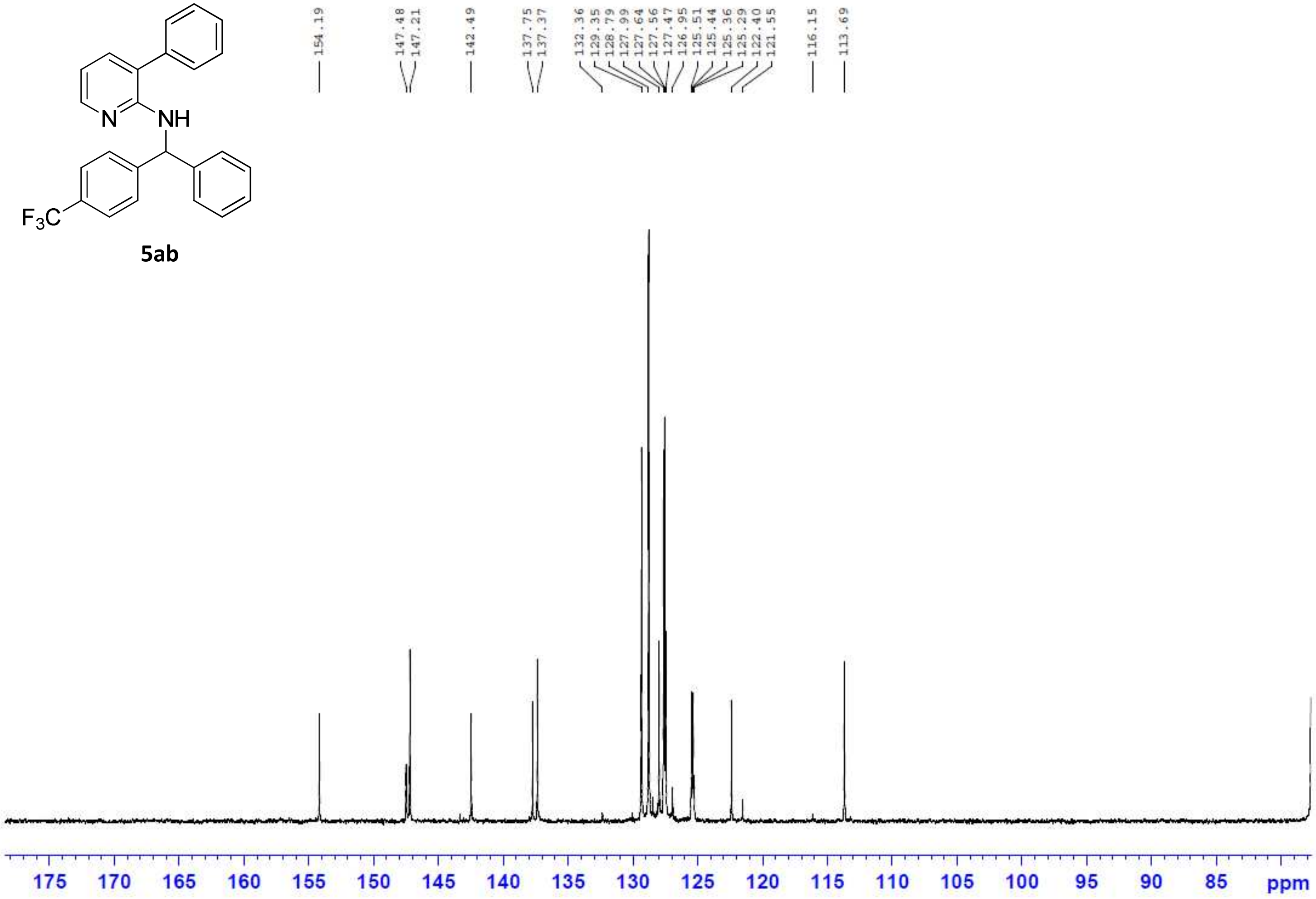
5aa

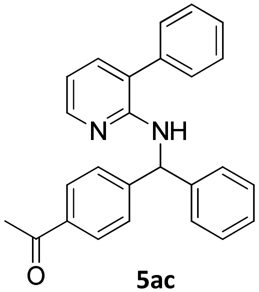

154.34
147.31
142.90
142.02
137.88
137.38
132.70
129.39
128.87
128.72
128.65
128.01
127.53
127.33
122.39
113.60
77.80
77.16
76.53
58.21
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



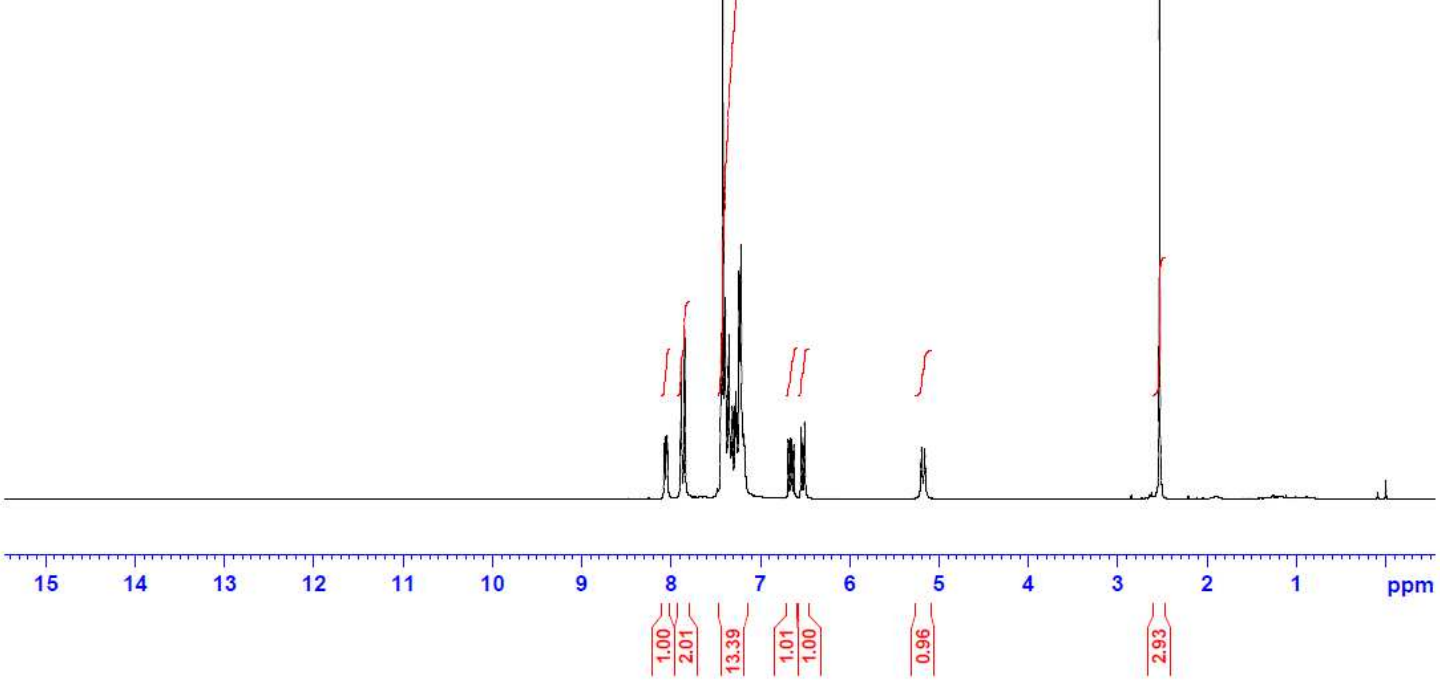
5ab

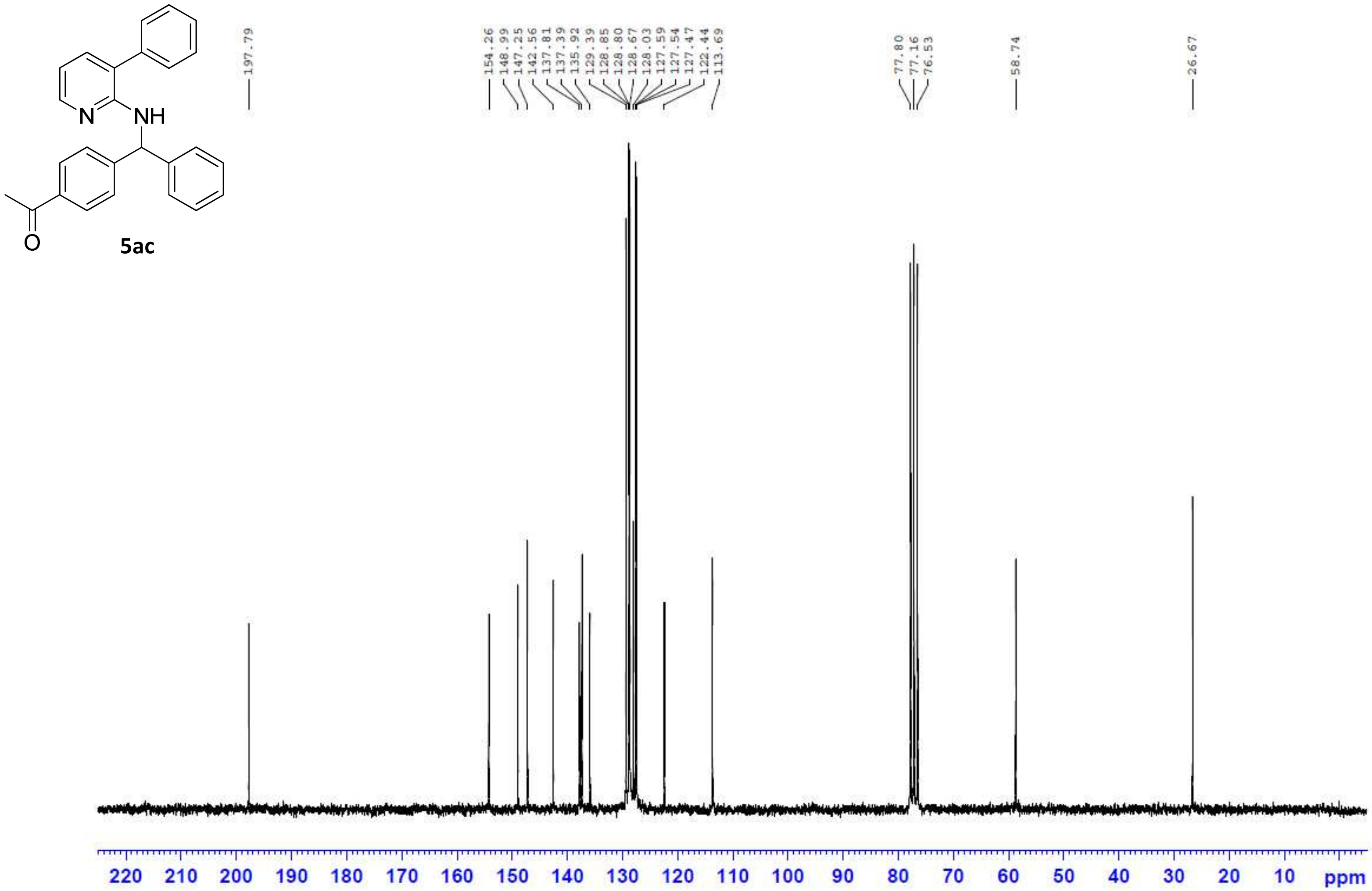



N
NH
F3C
5ab
154.19
147.48
147.21
142.49
137.75
137.37
132.36
129.35
128.79
127.99
127.64
127.56
127.47
126.95
125.51
125.44
125.36
125.29
122.40
121.55
116.15
113.69
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
ppm



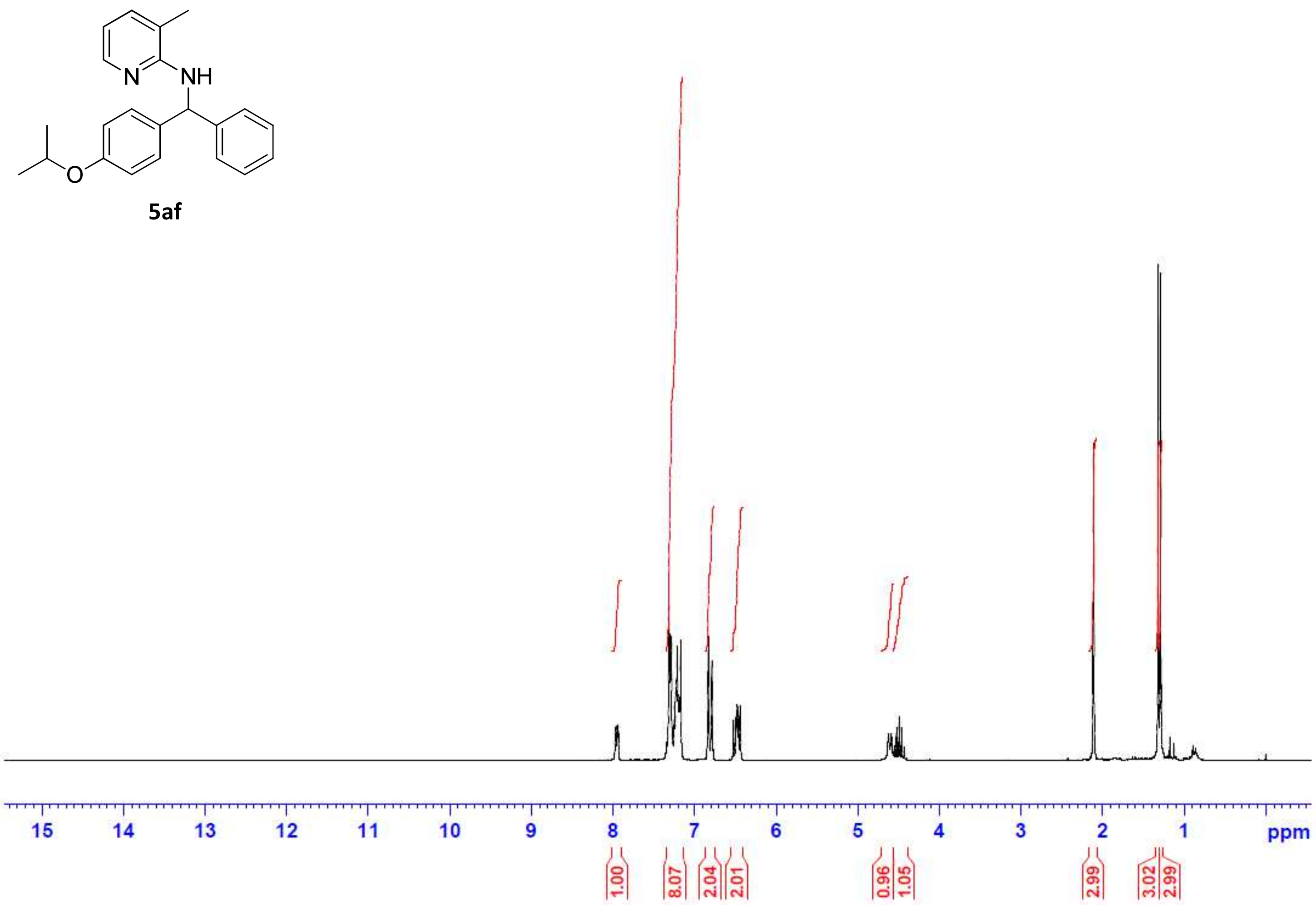
5ac

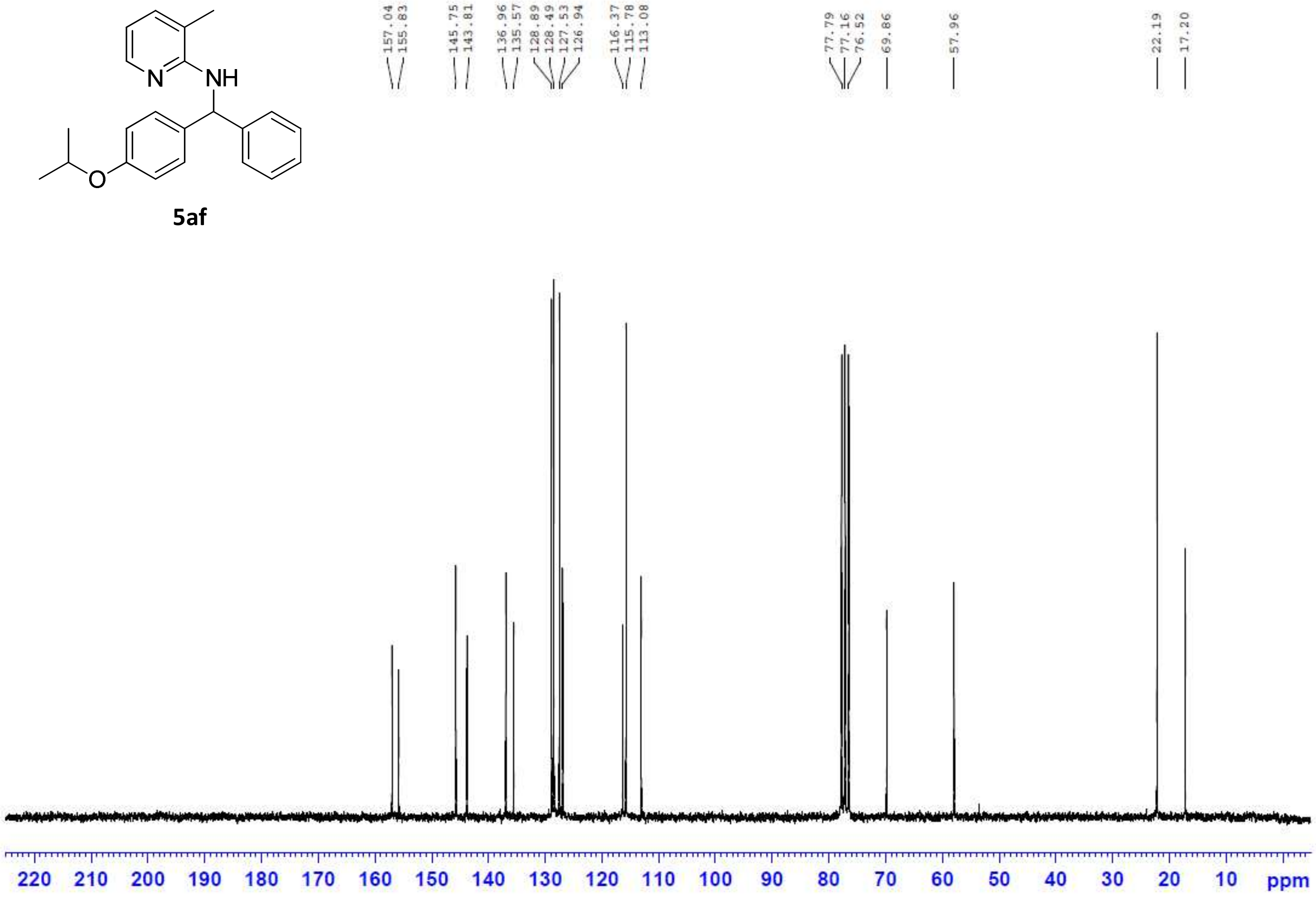




5ac

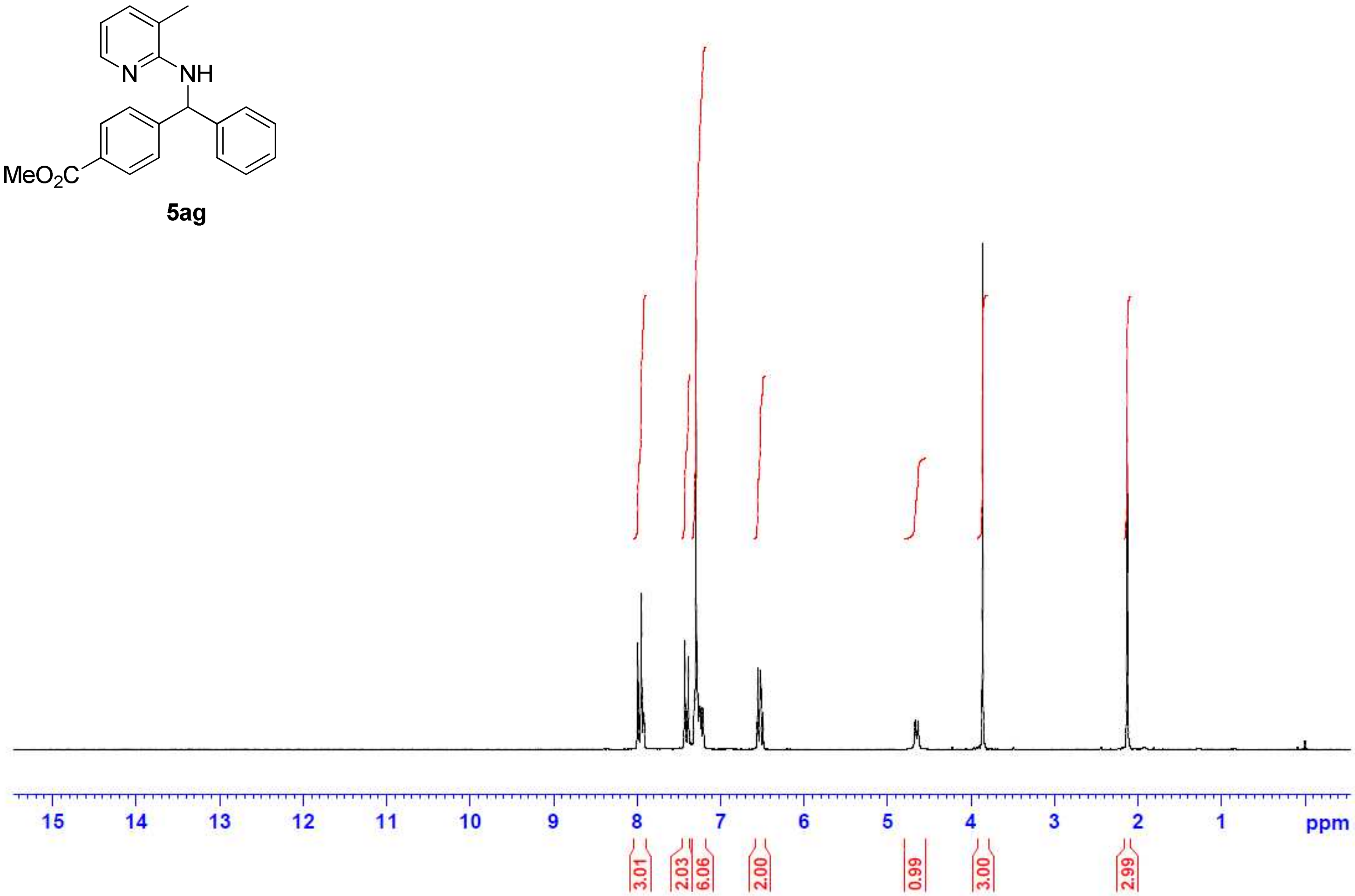
N
NH
O
197.79
154.26
148.99
147.25
142.56
137.81
137.39
135.92
129.39
128.85
128.80
128.67
128.03
127.59
127.54
127.47
122.44
113.69
77.80
77.16
76.53
58.74
26.67
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


NH
N
O
5af
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
8.07
2.04
2.01
0.96
1.05
2.99
3.02
2.99



5af

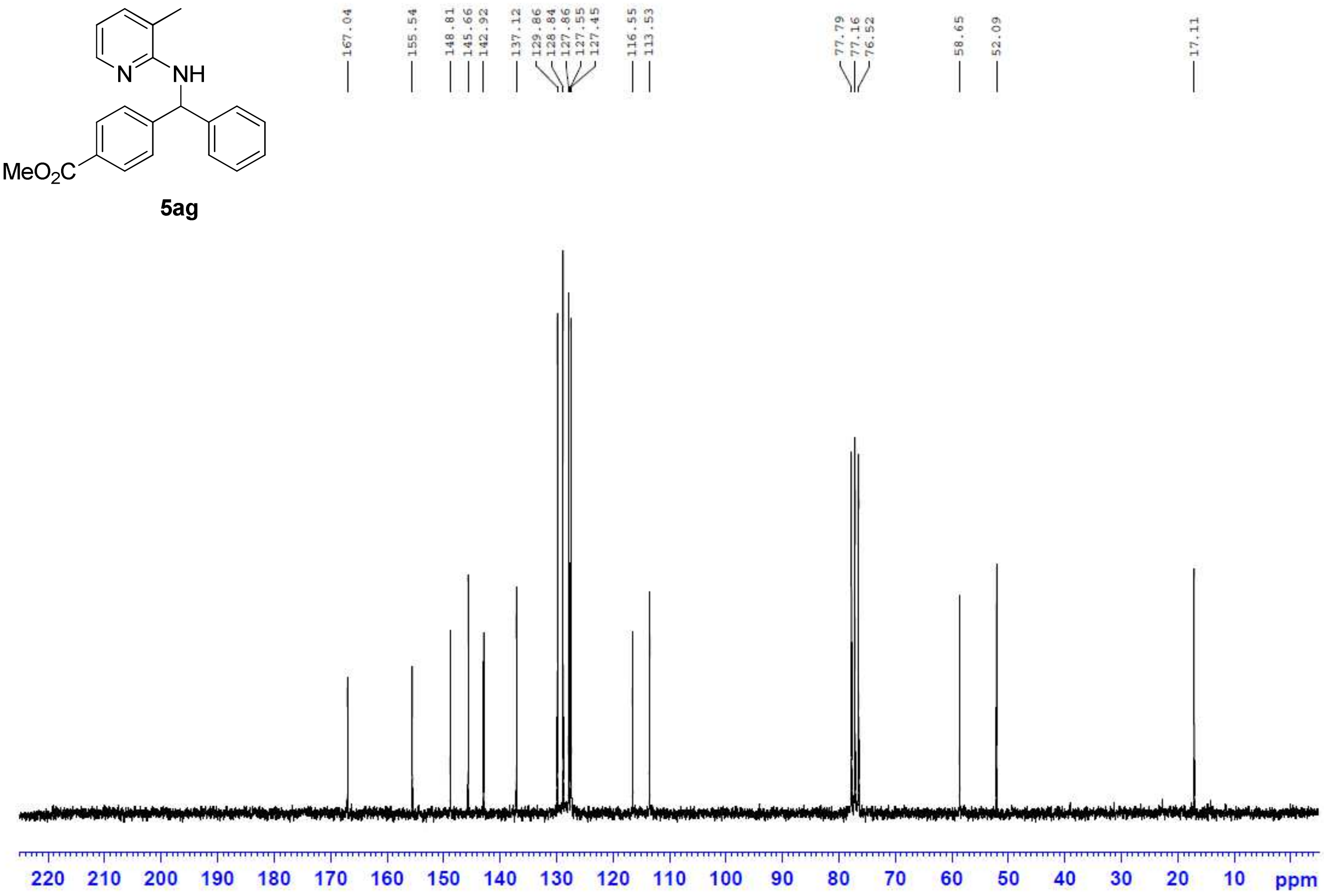
157.04
155.83
145.75
143.81
136.96
135.57
128.89
128.49
127.53
126.94
116.37
115.78
113.08
77.79
77.16
76.52
69.86
57.96
22.19
17.20
N
NH
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

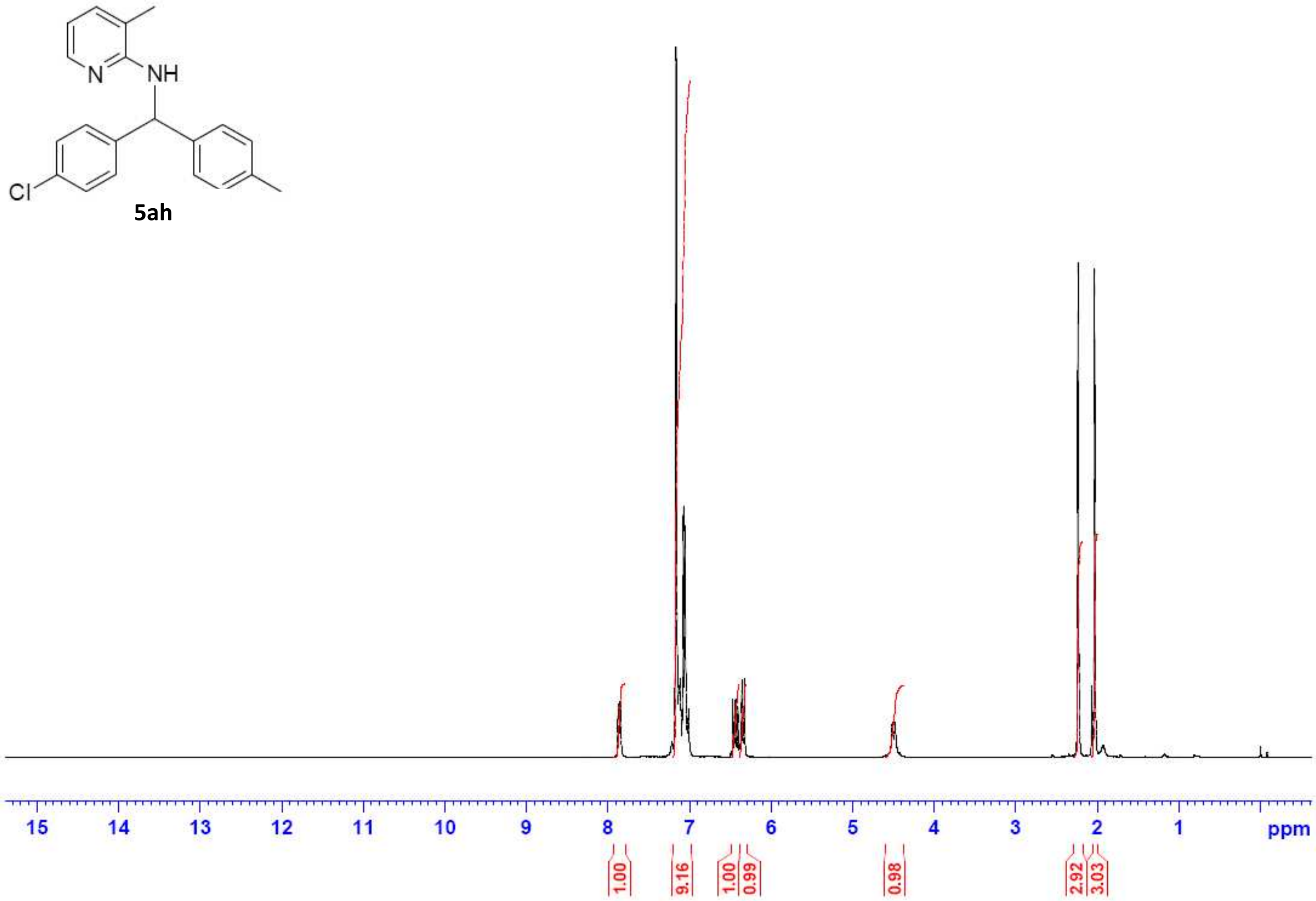


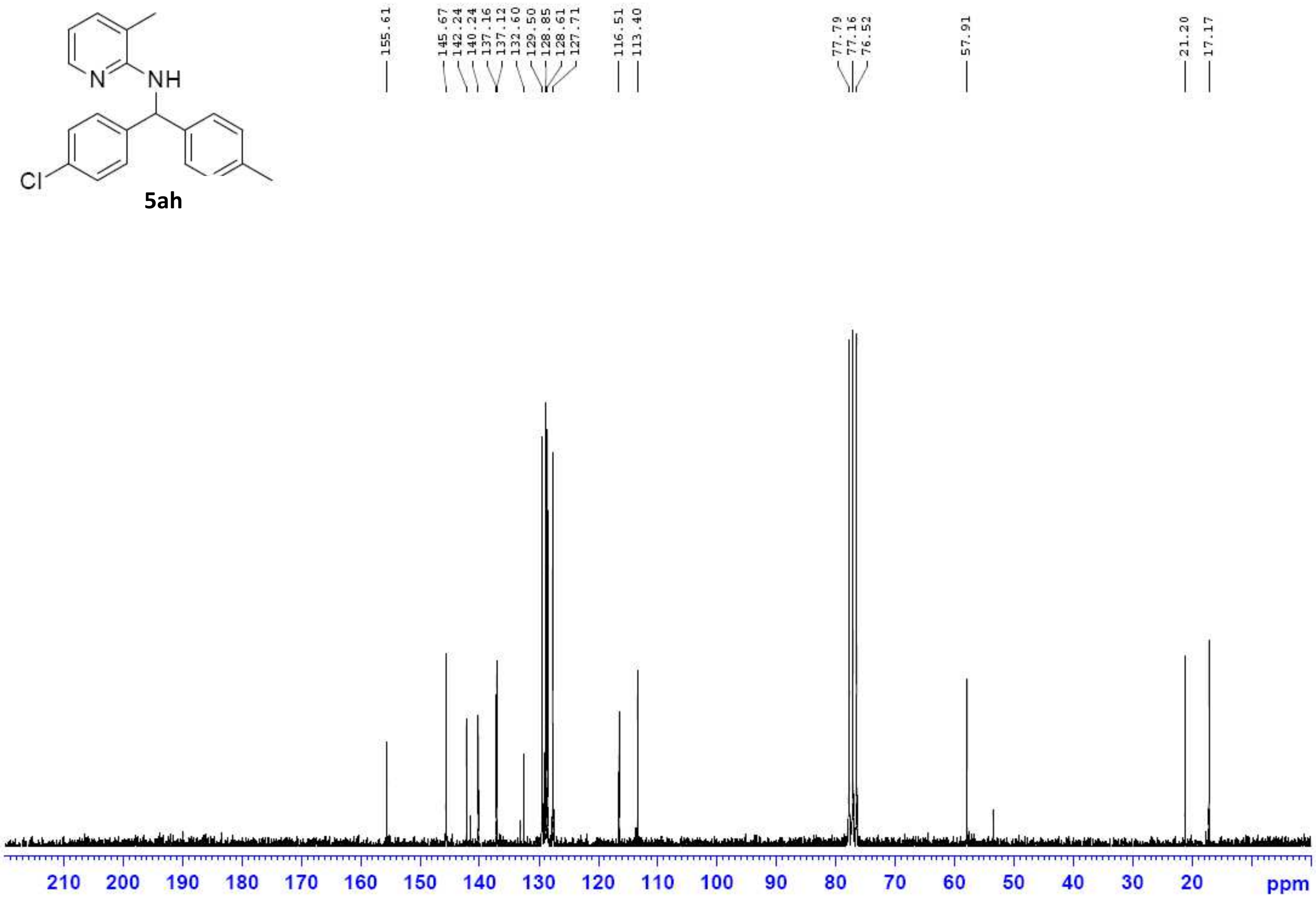
N
NH
MeO$_2$C

5ag

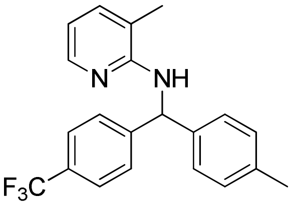
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
3.01
2.03
6.06
2.00
0.99
3.00
2.99


MeO$_2$C
NH
N
5ag
167.04
155.54
148.81
145.66
142.92
137.12
129.86
128.84
127.86
127.55
127.45
116.55
113.53
77.79
77.16
76.52
58.65
52.09
17.11
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


N
NH
Cl
5ah
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
9.16
1.00
0.99
0.98
2.92
3.03

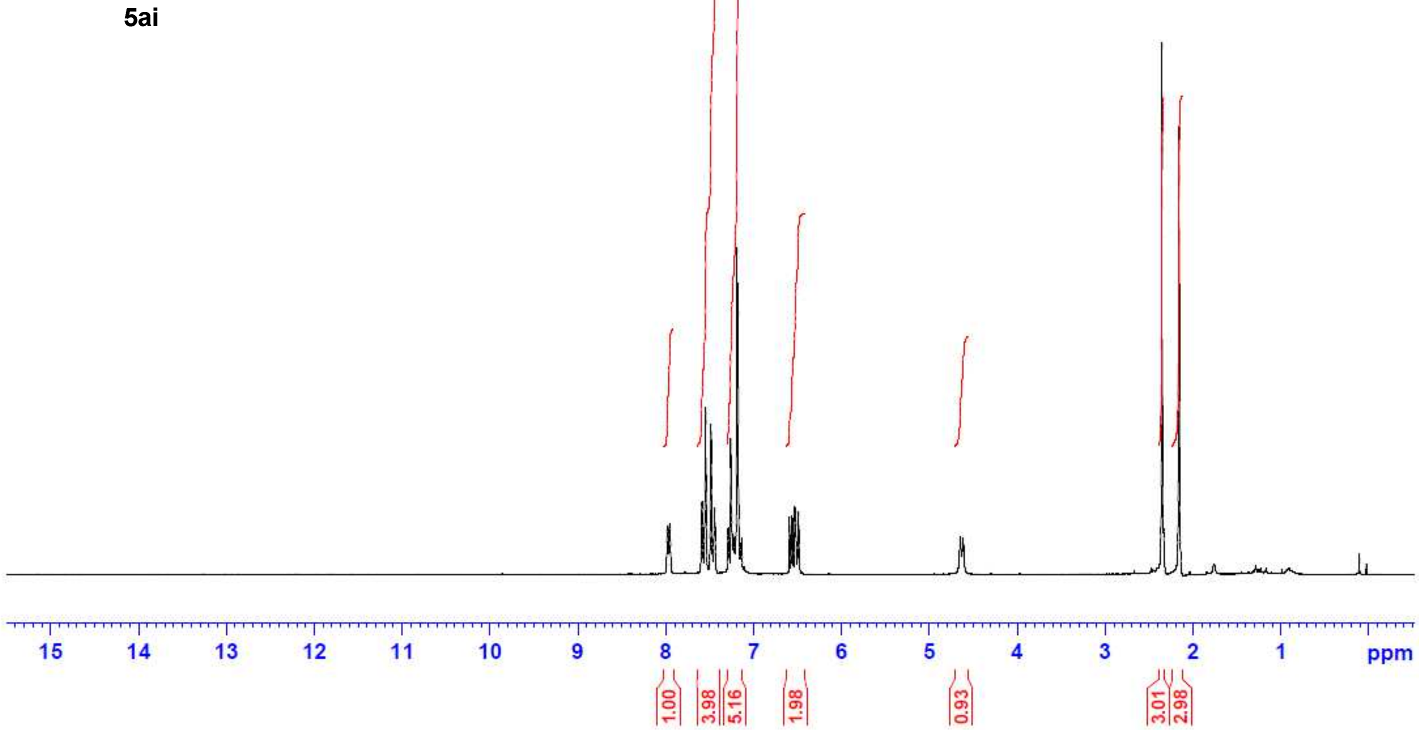

N
NH
Cl
155.61
145.67
142.24
140.24
137.16
137.12
132.60
129.50
128.85
128.61
127.71
116.51
113.40
77.79
77.16
76.52
57.91
21.20
17.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

5ah

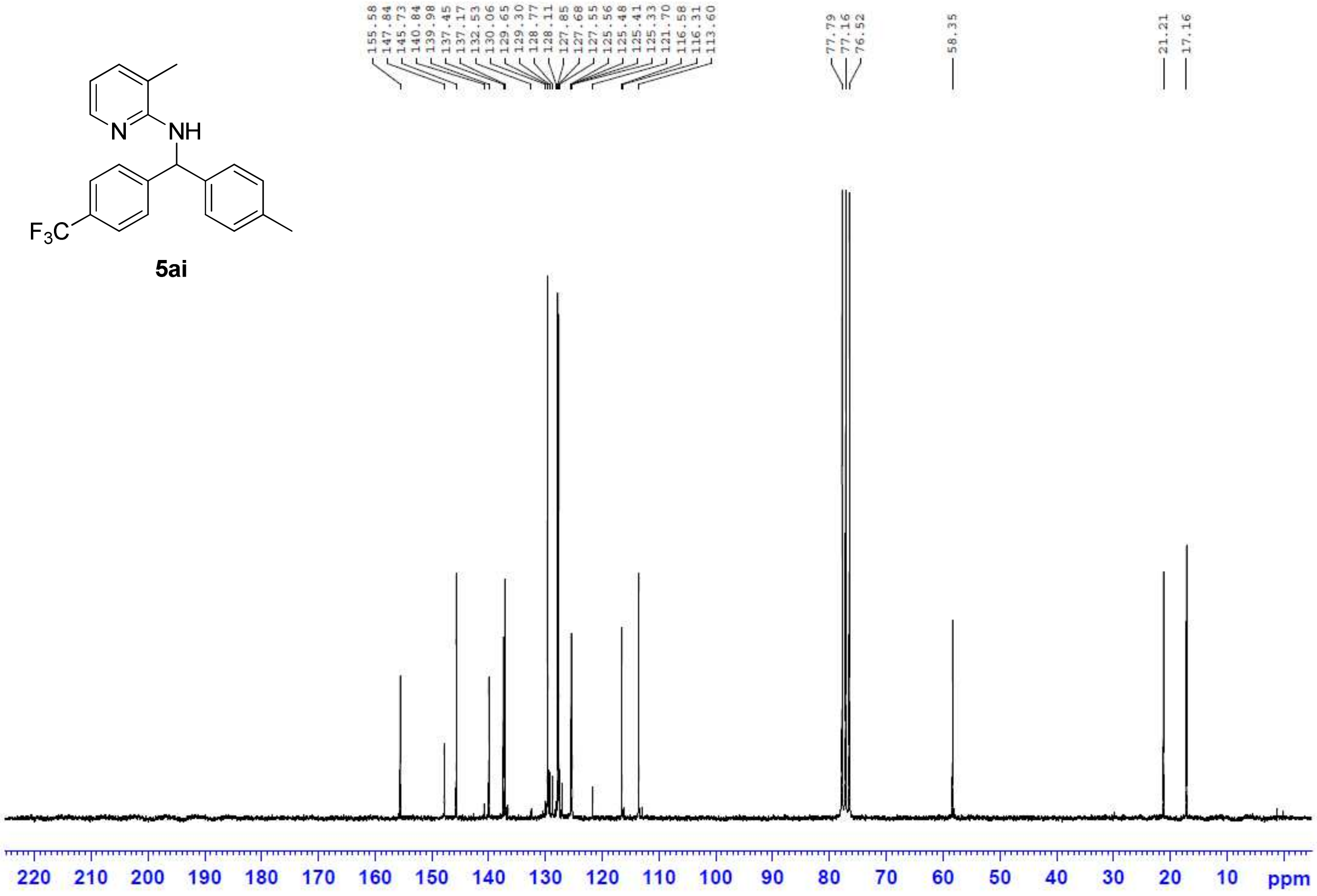


N
NH
F3C

5ai

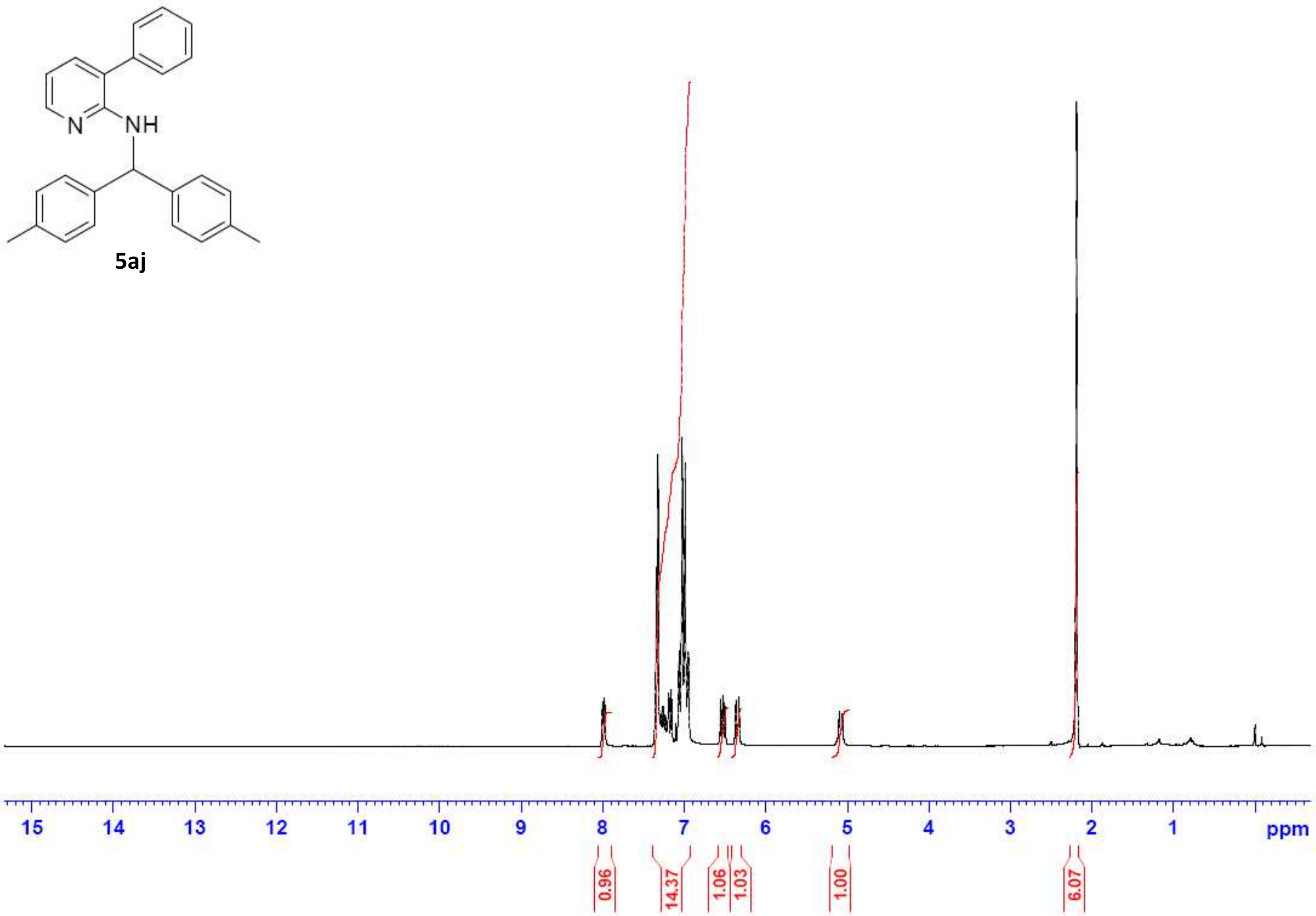


15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.98
5.16
1.98
0.93
3.01
2.98

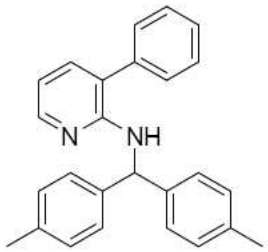

N
NH
F3C

5ai

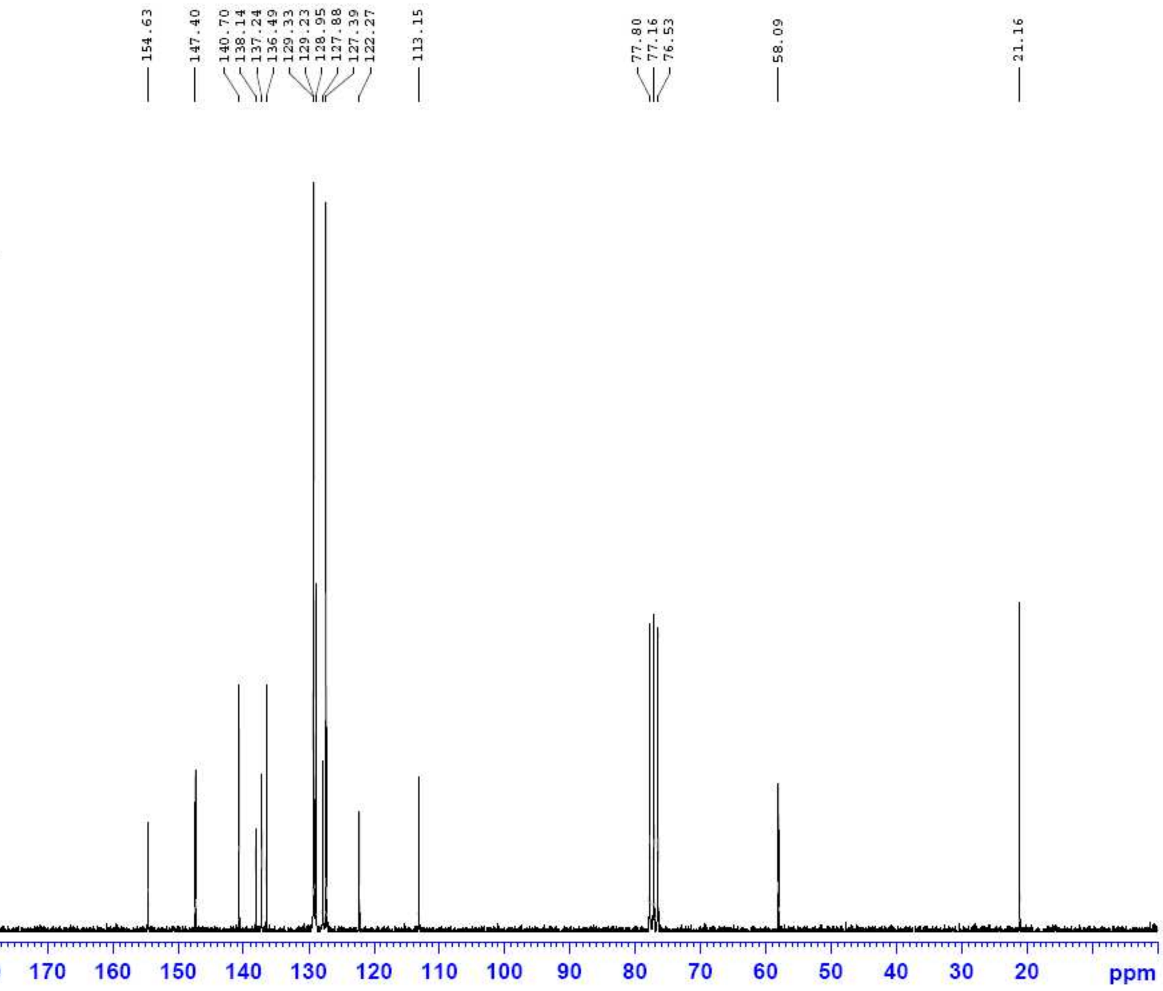
155.58
147.84
145.73
140.84
139.98
137.45
137.17
132.53
130.06
129.65
129.30
128.77
128.11
127.85
127.68
127.55
125.56
125.48
125.41
125.33
121.70
116.58
116.31
113.60
77.79
77.16
76.52
58.35
21.21
17.16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

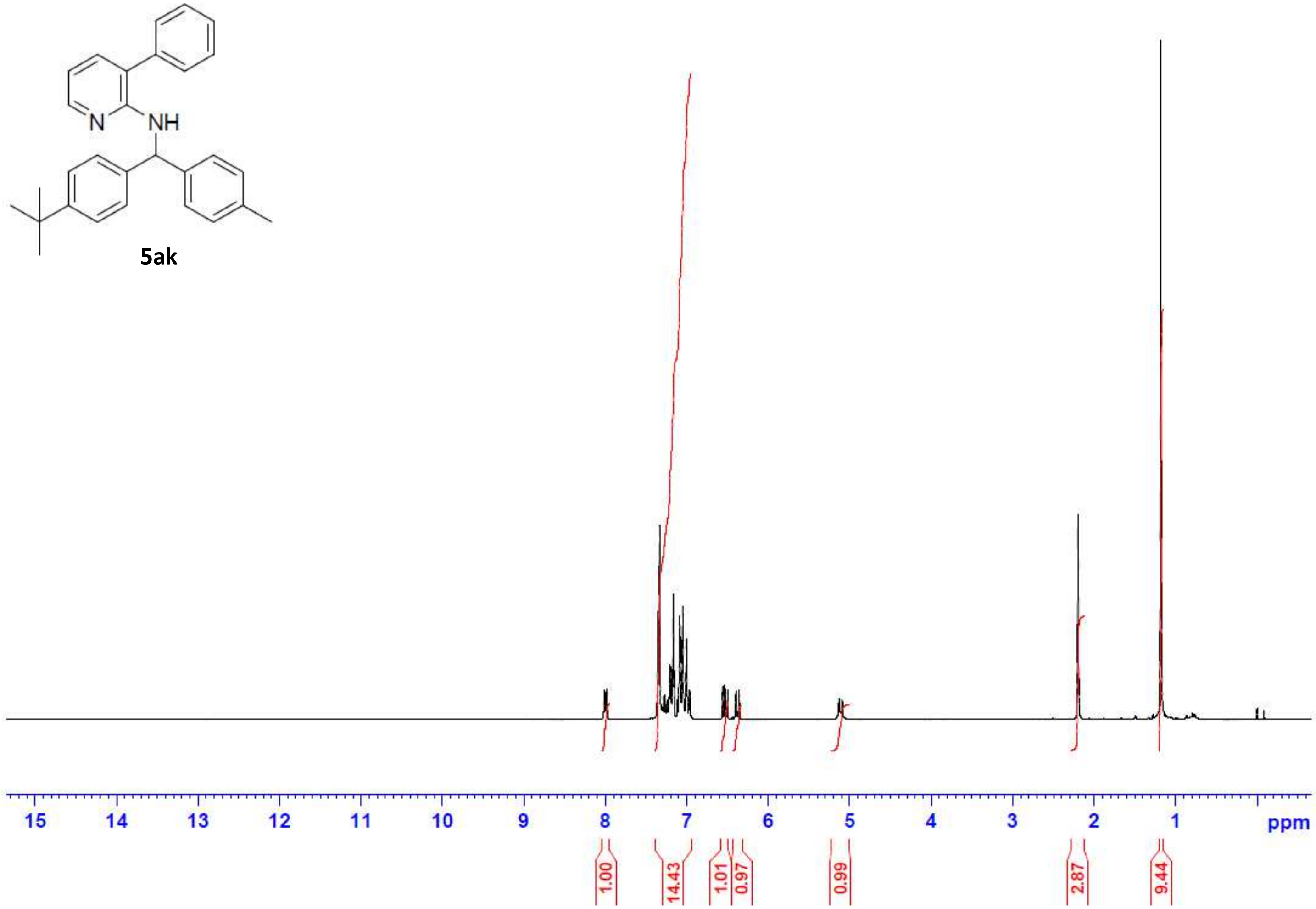


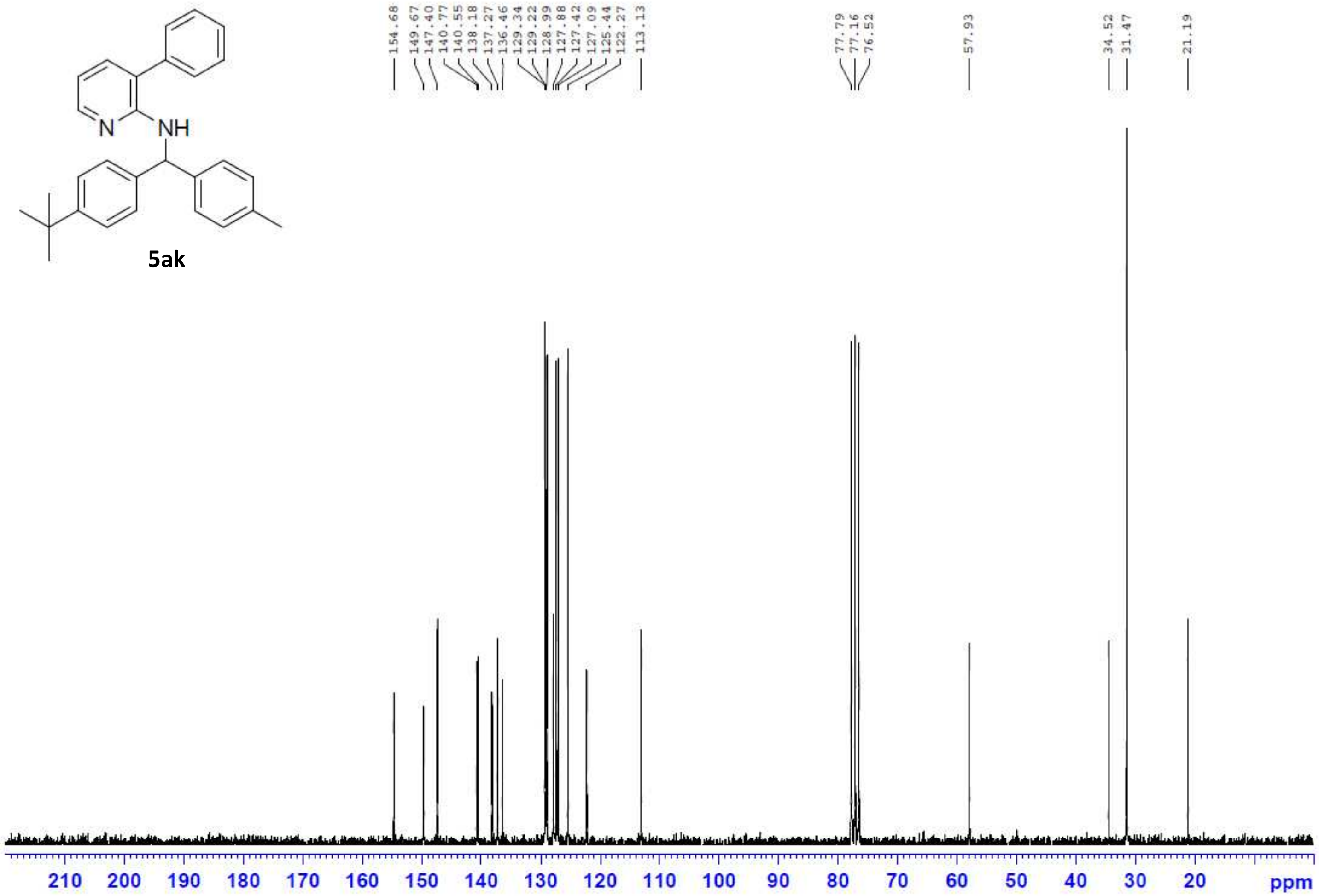
5aj



5aj


154.63
147.40
140.70
138.14
137.24
136.49
129.33
129.23
128.95
127.88
127.39
122.27
113.15
77.80
77.16
76.53
58.09
21.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

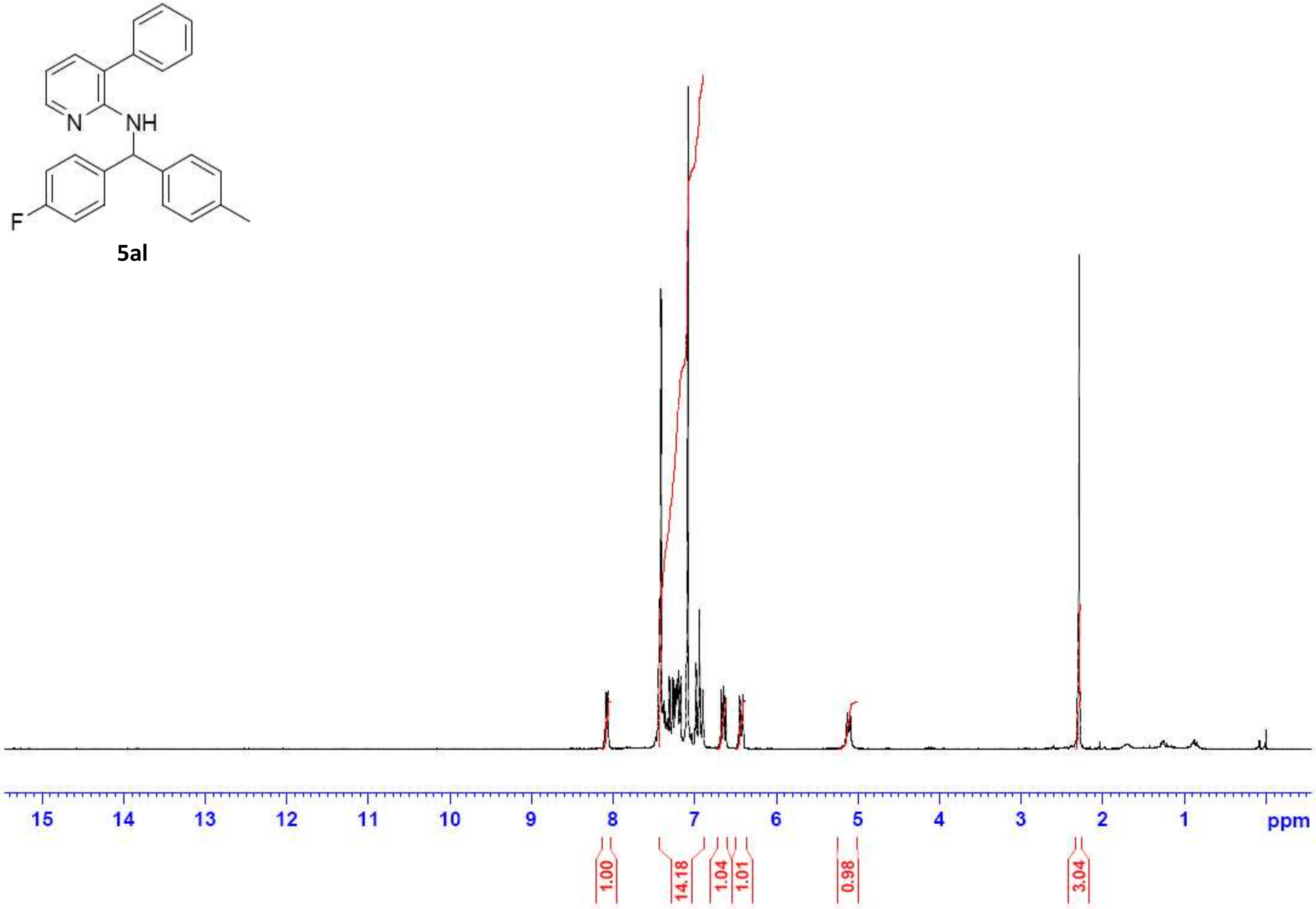

N
NH
5ak
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
14.43
1.01
0.97
0.99
2.87
9.44



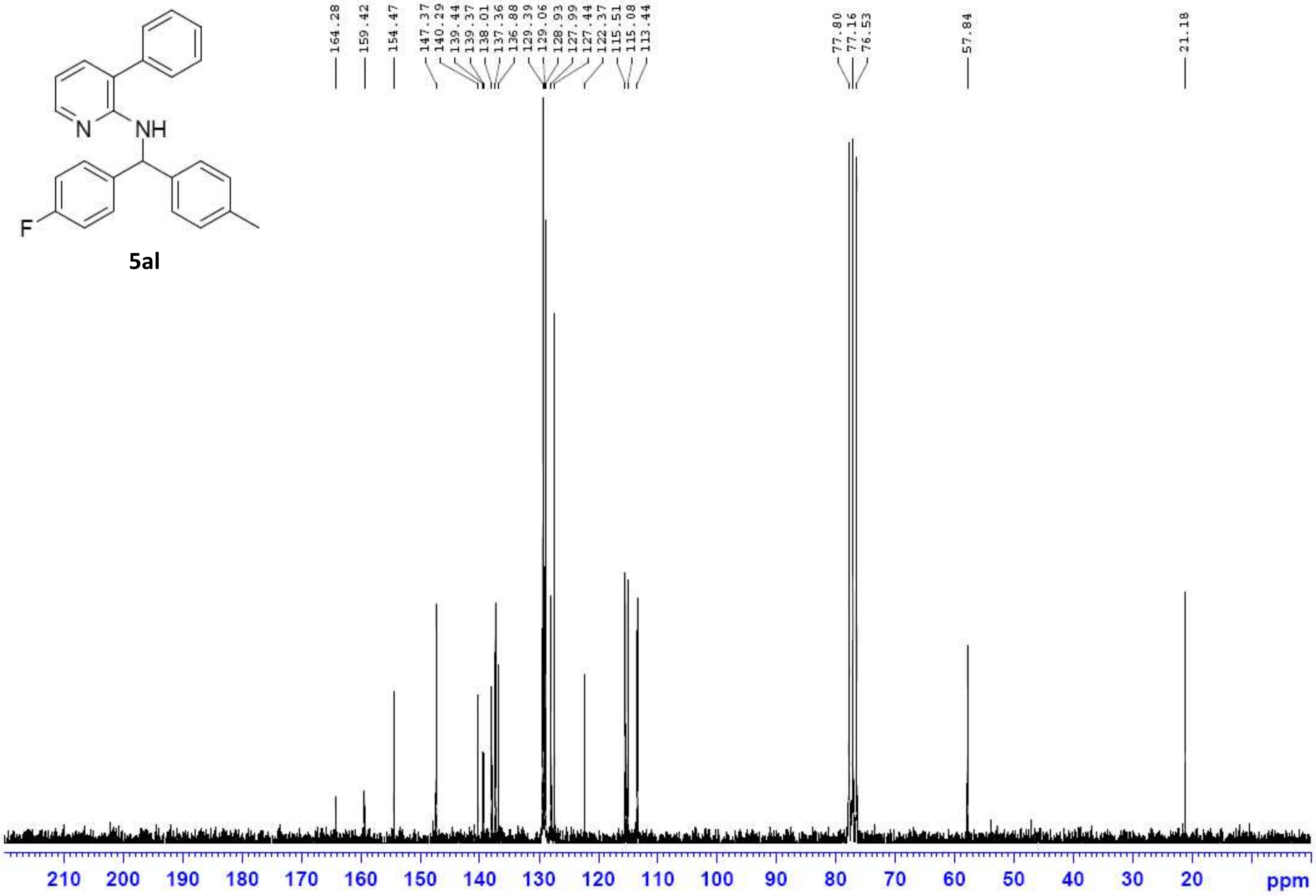
N
NH

5ak

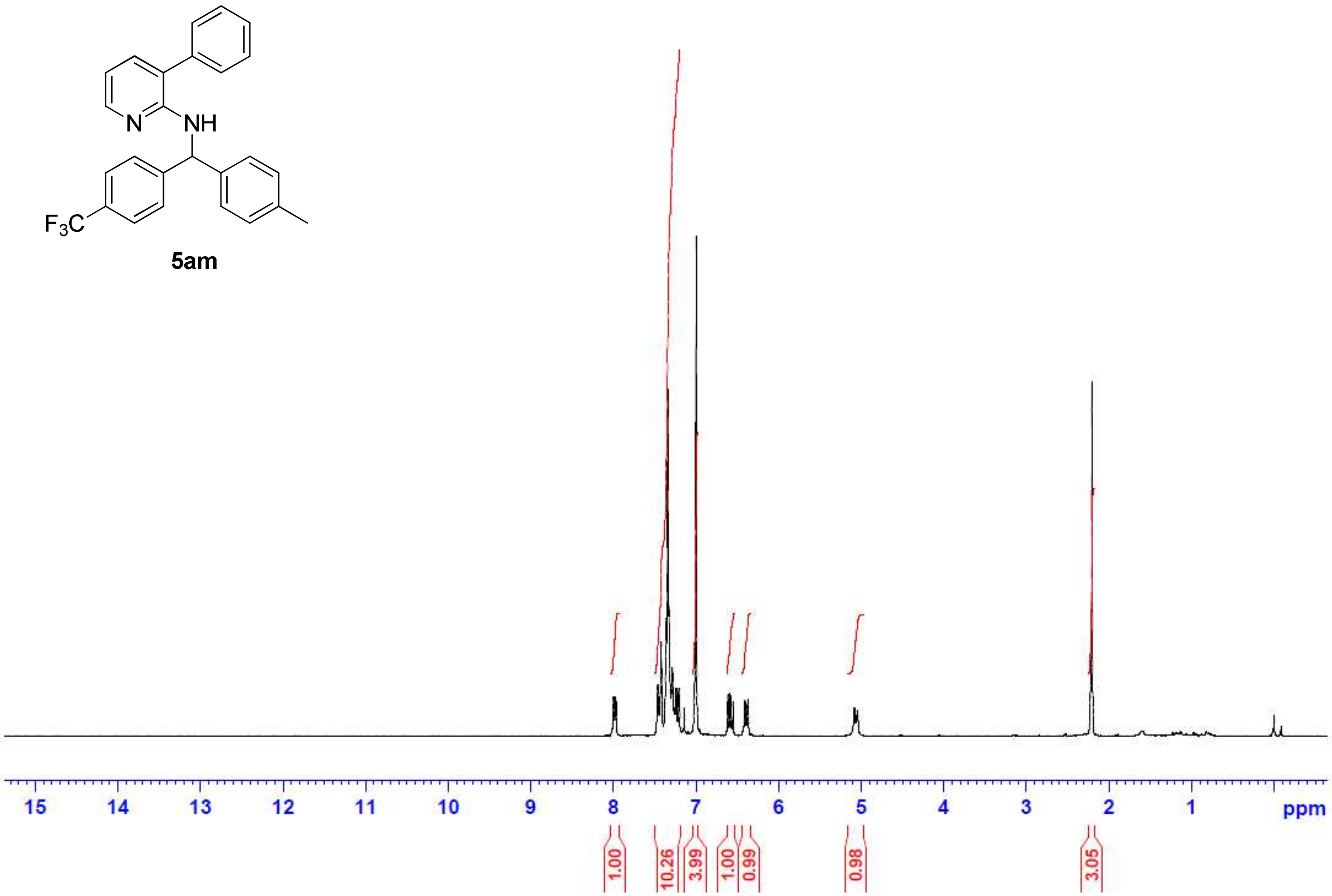
154.68
149.67
147.40
140.77
140.55
138.18
137.27
136.46
129.34
129.22
128.99
127.88
127.42
127.09
125.44
122.27
113.13
77.79
77.16
76.52
57.93
34.52
31.47
21.19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



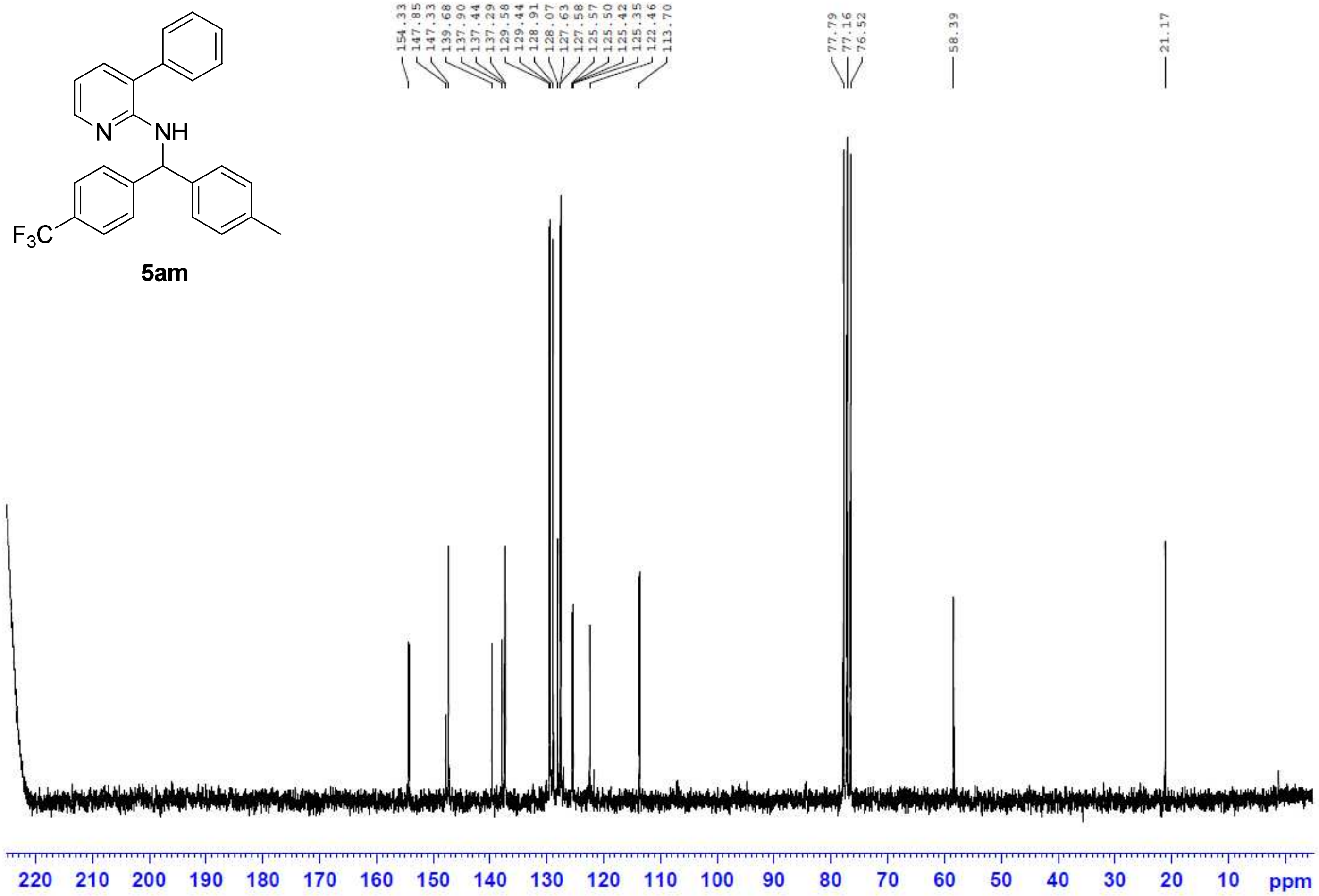
5al


164.28
159.42
154.47
147.37
140.29
139.44
139.37
138.01
137.36
136.88
129.39
129.06
128.93
127.99
127.44
122.37
115.51
115.08
113.44
77.80
77.16
76.53
57.84
21.18
N
NH
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

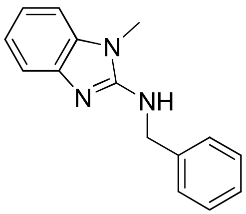
5al


NH
N
F3C
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
10.26
3.99
1.00
0.99
0.98
3.05

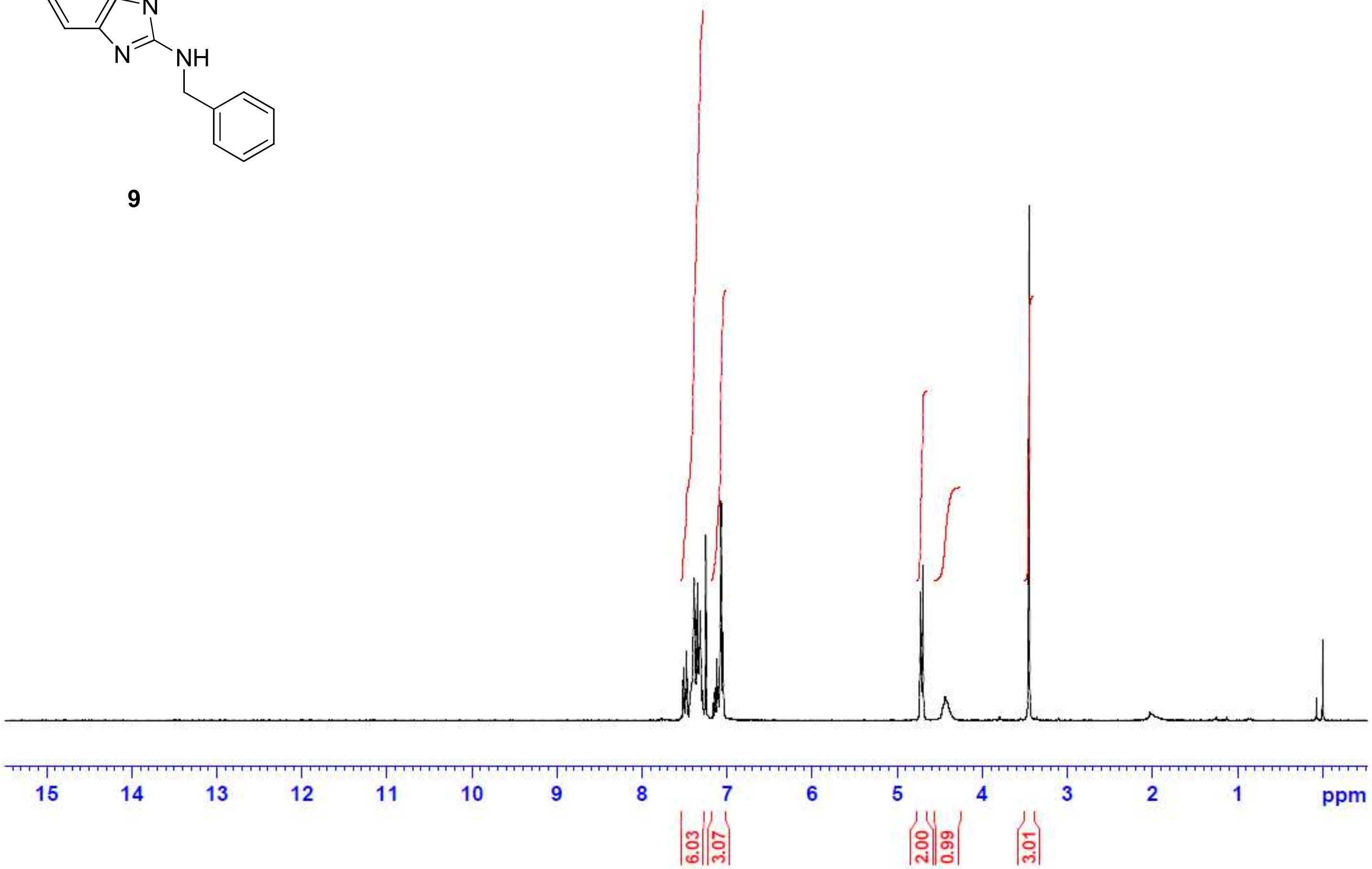
5am

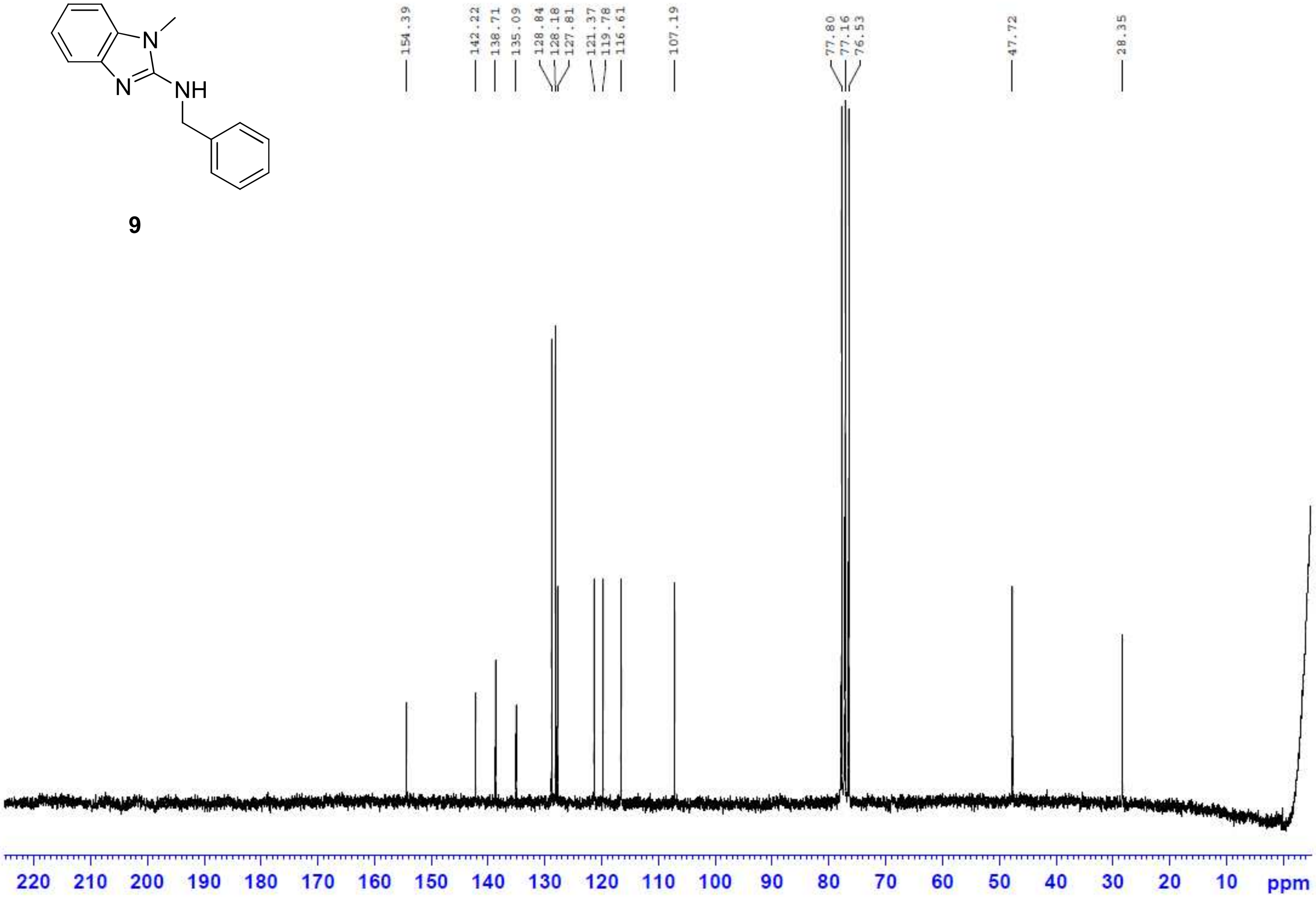

5am

NH
N
F3C
154.33
147.85
147.33
139.68
137.90
137.44
137.29
129.58
129.44
128.91
128.07
127.63
127.58
125.57
125.50
125.42
125.35
122.46
113.70
77.79
77.16
76.52
58.39
21.17
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

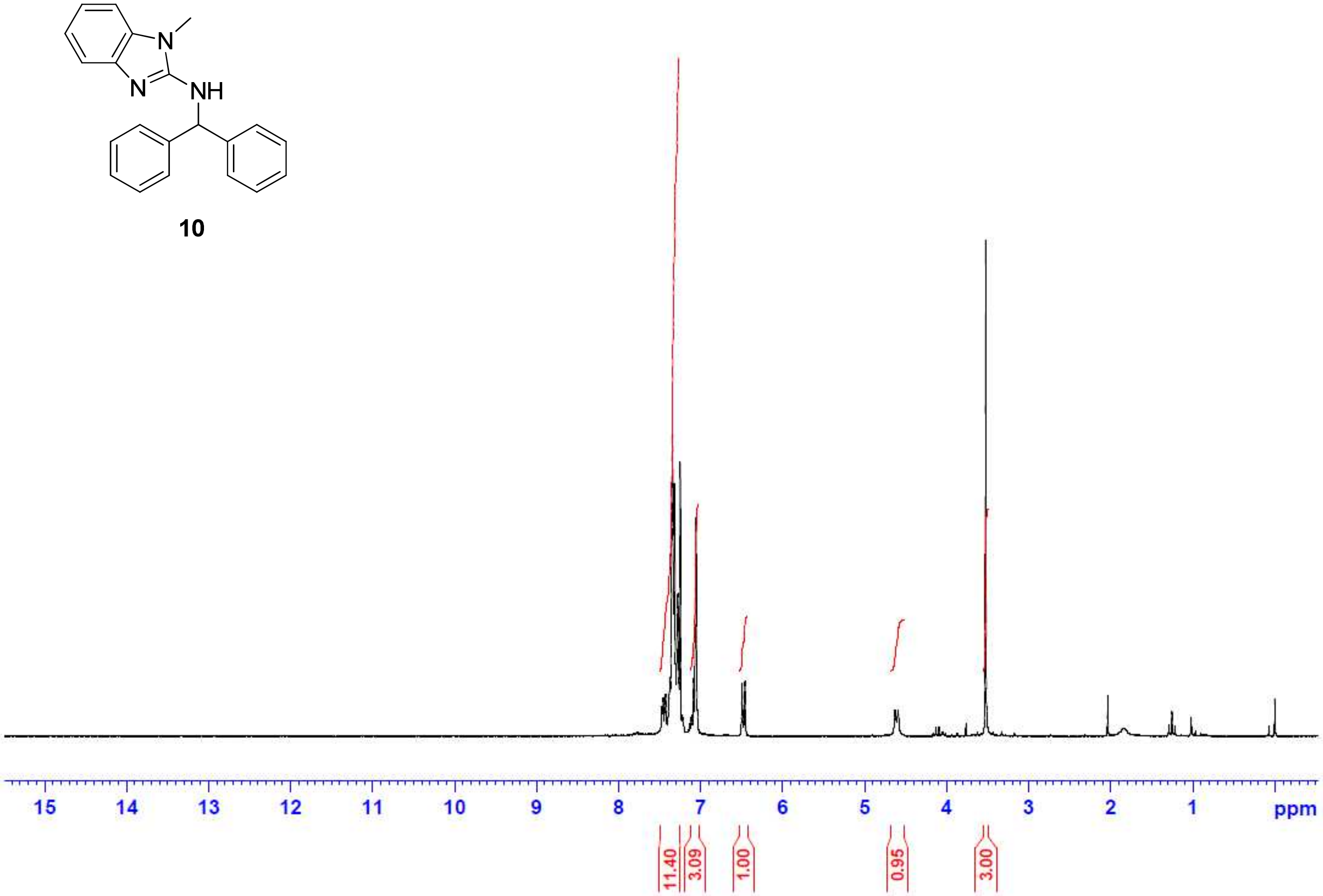


9

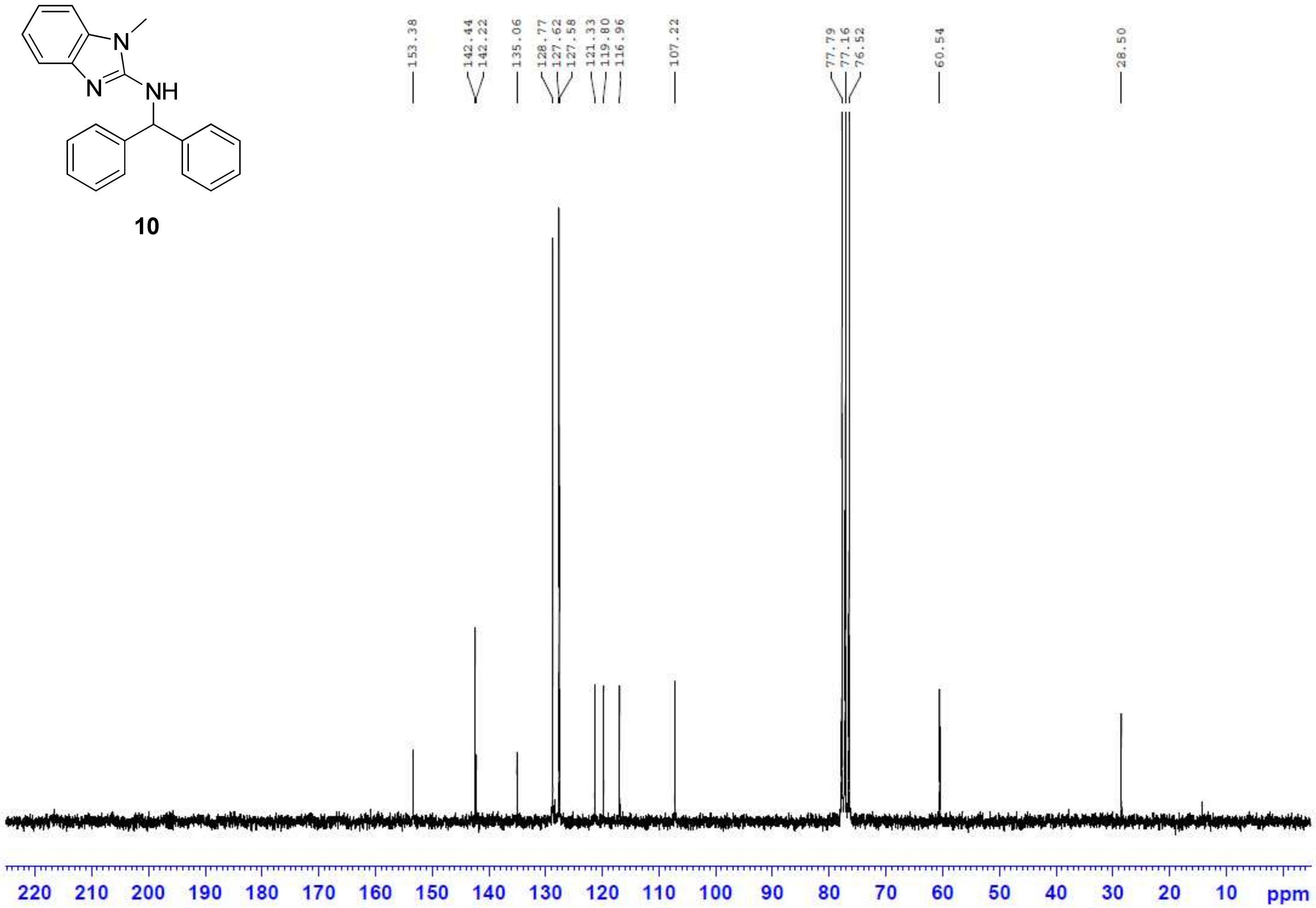



N
N
NH
154.39
142.22
138.71
135.09
128.84
128.18
127.81
121.37
119.78
116.61
107.19
77.80
77.16
76.53
47.72
28.35
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

9

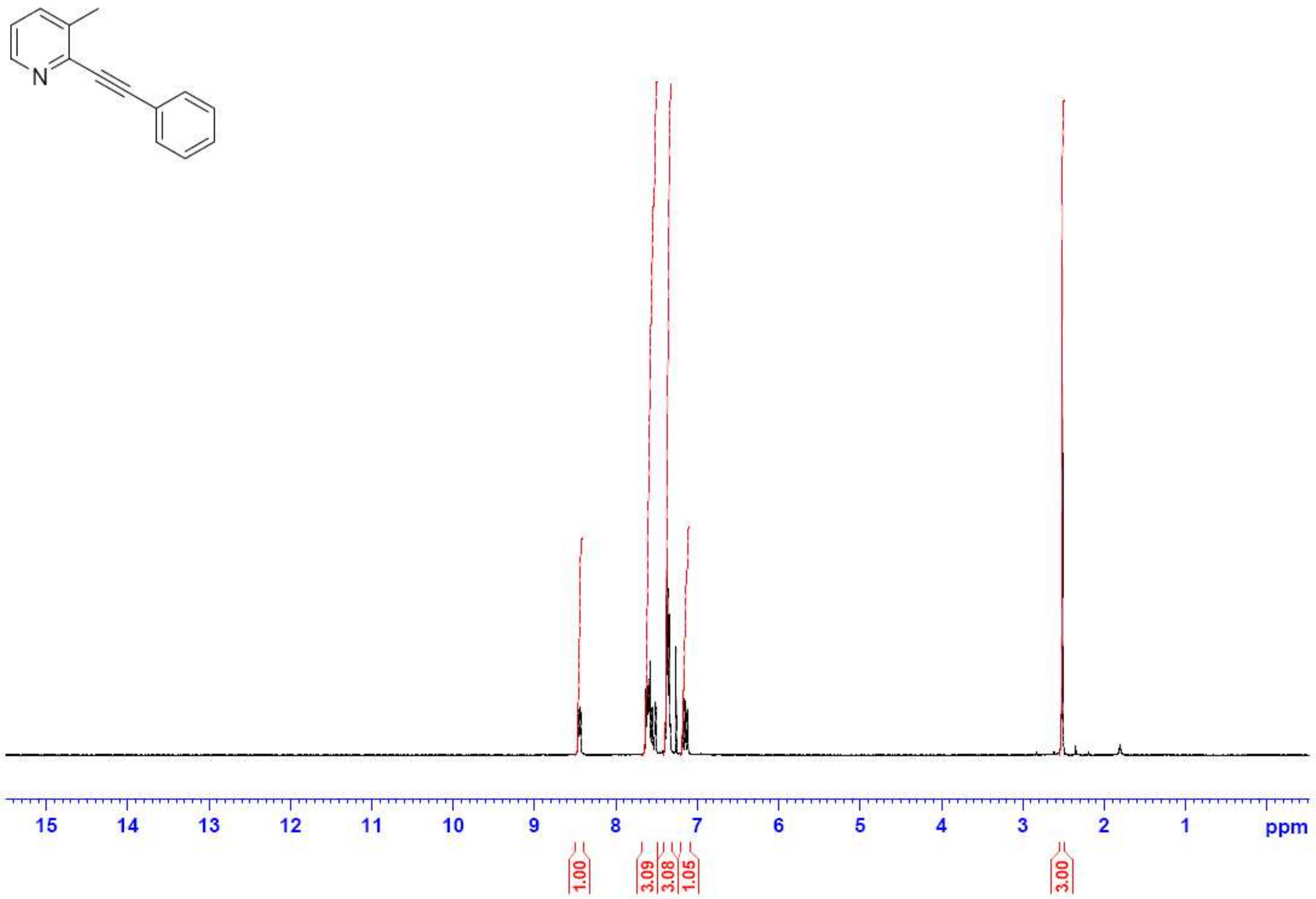


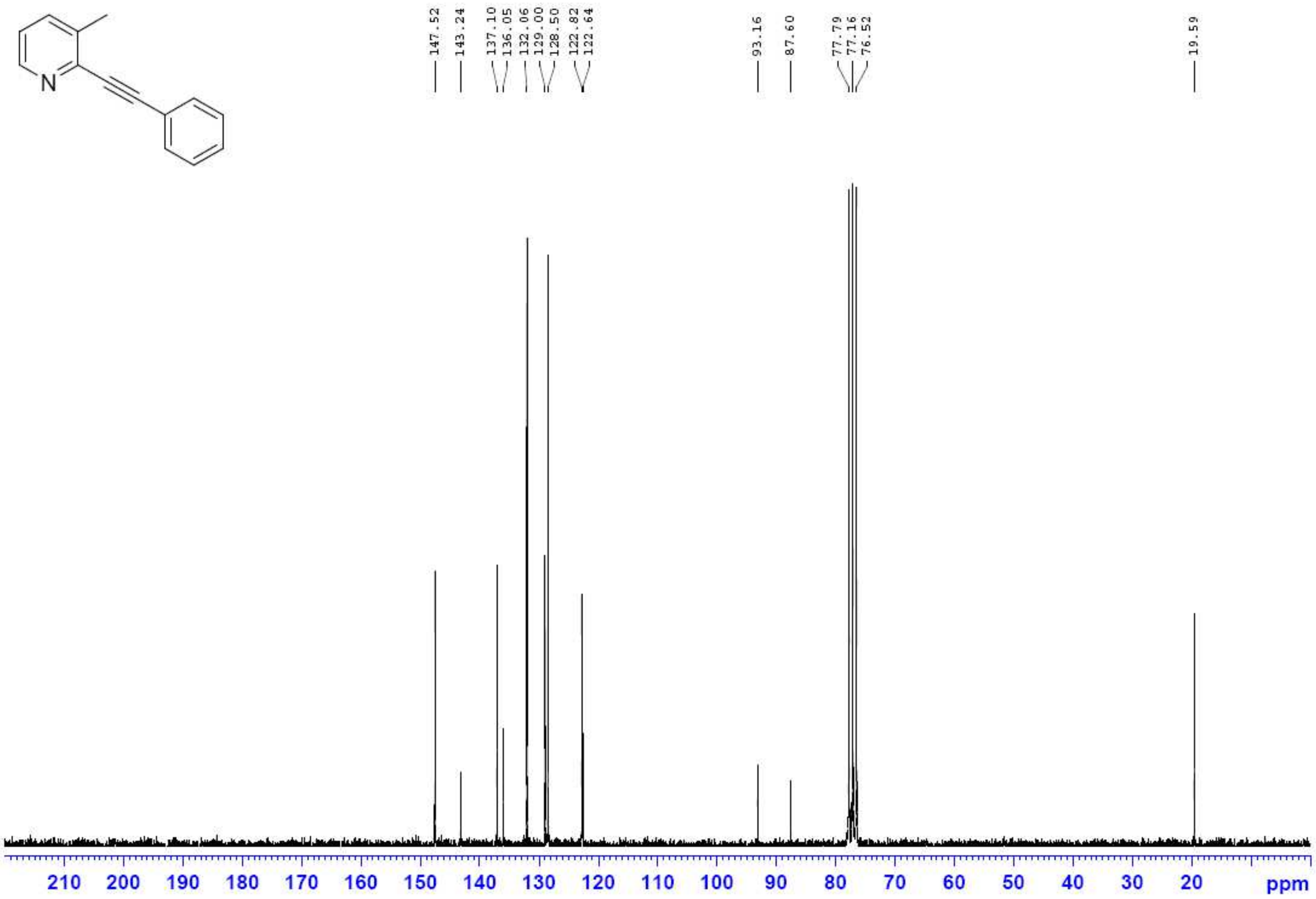
10

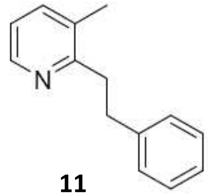


10

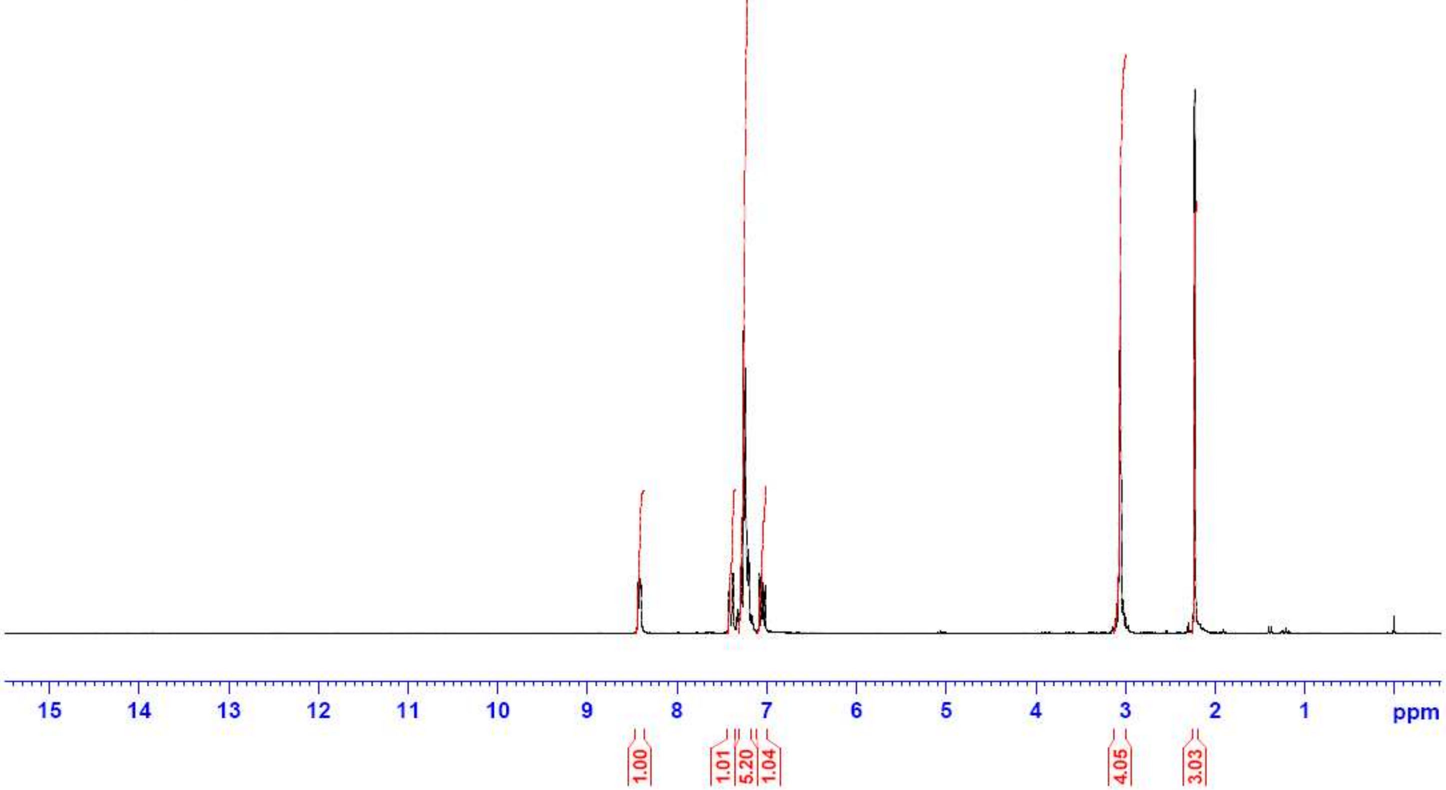
N
NH
N
153.38
142.44
142.22
135.06
128.77
127.62
127.58
121.33
119.80
116.96
107.22
77.79
77.16
76.52
60.54
28.50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

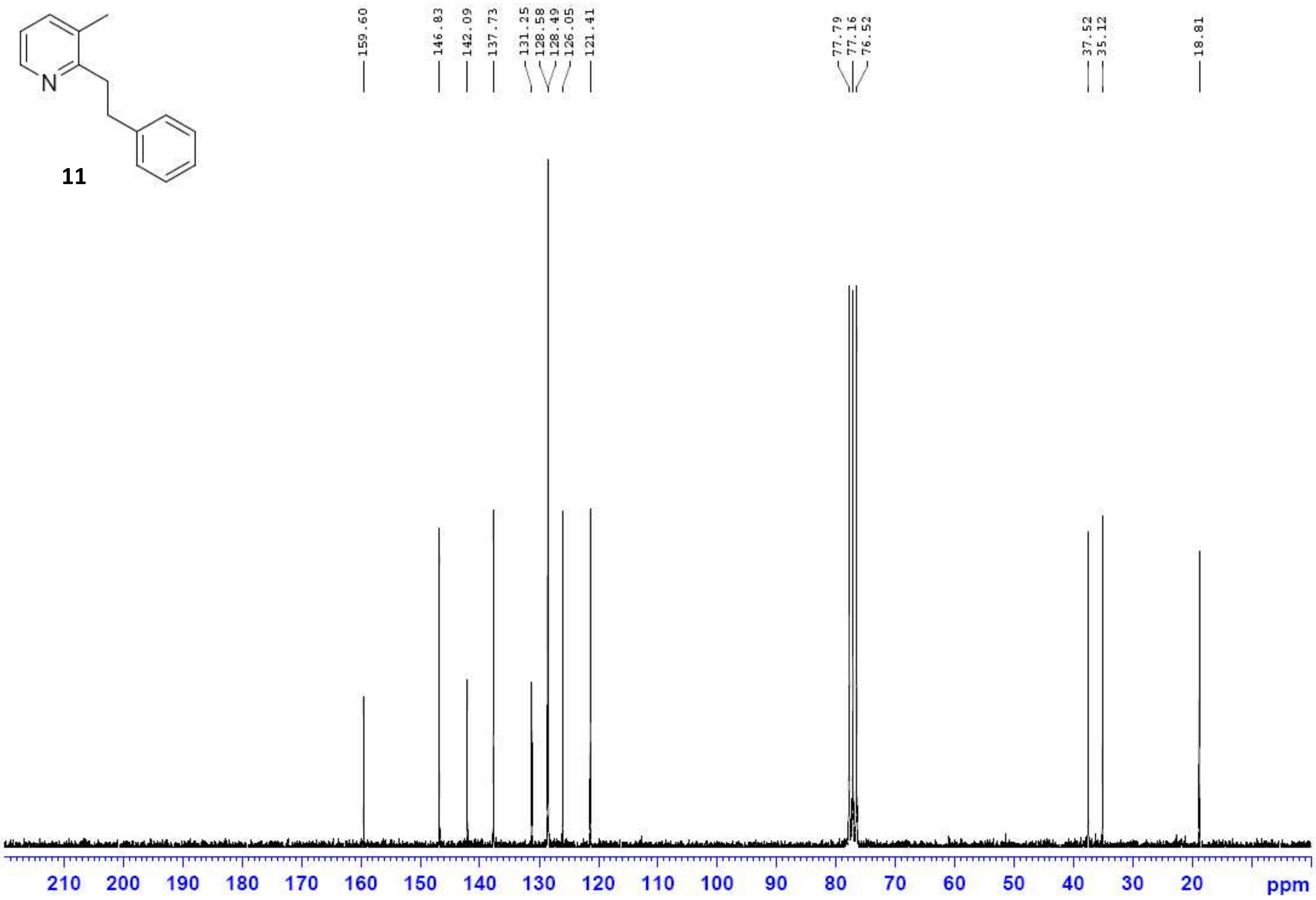

15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.09
3.08
1.05
3.00


147.52
143.24
137.10
136.05
132.06
129.00
128.50
122.82
122.64
93.16
87.60
77.79
77.16
76.52
19.59
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



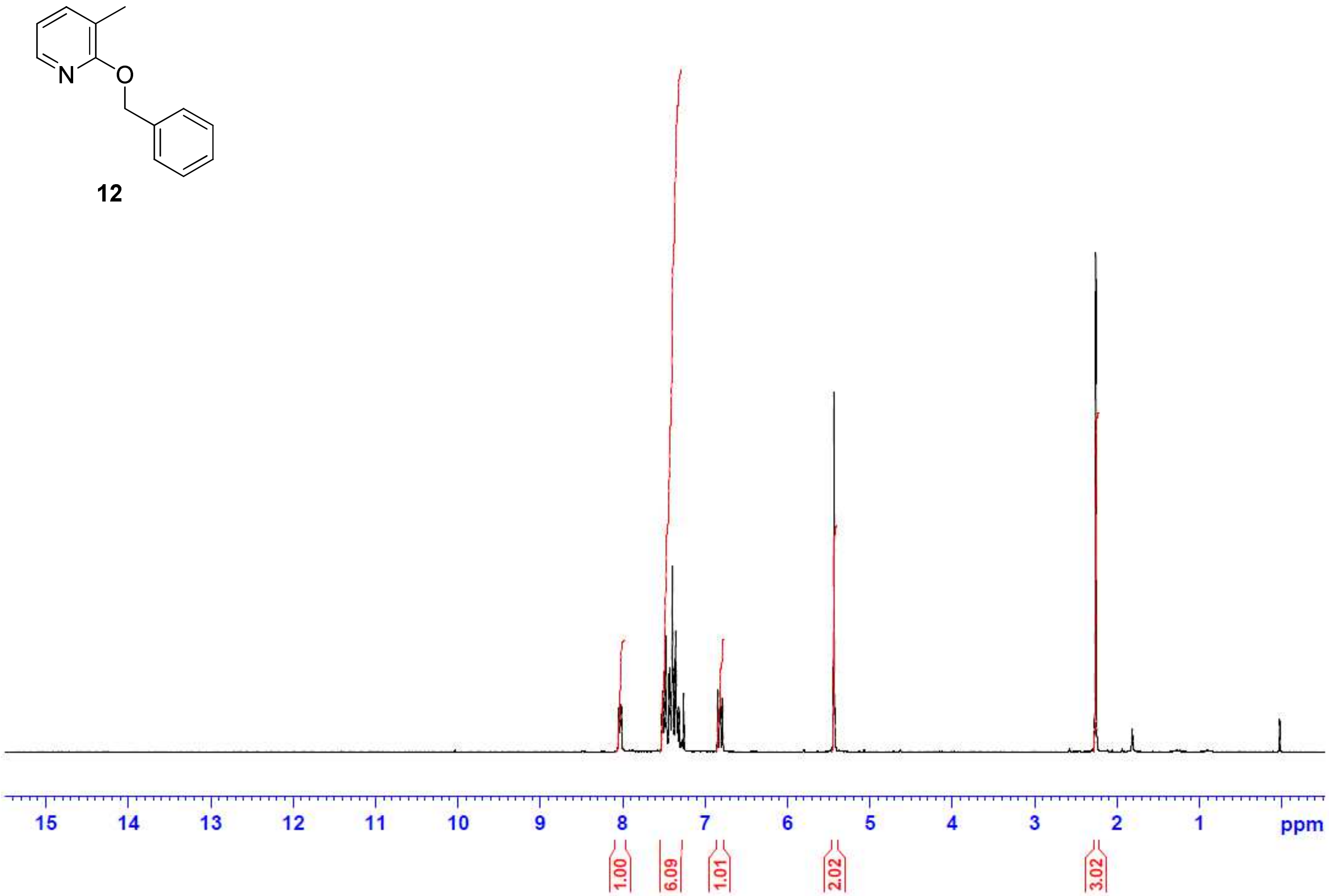
11



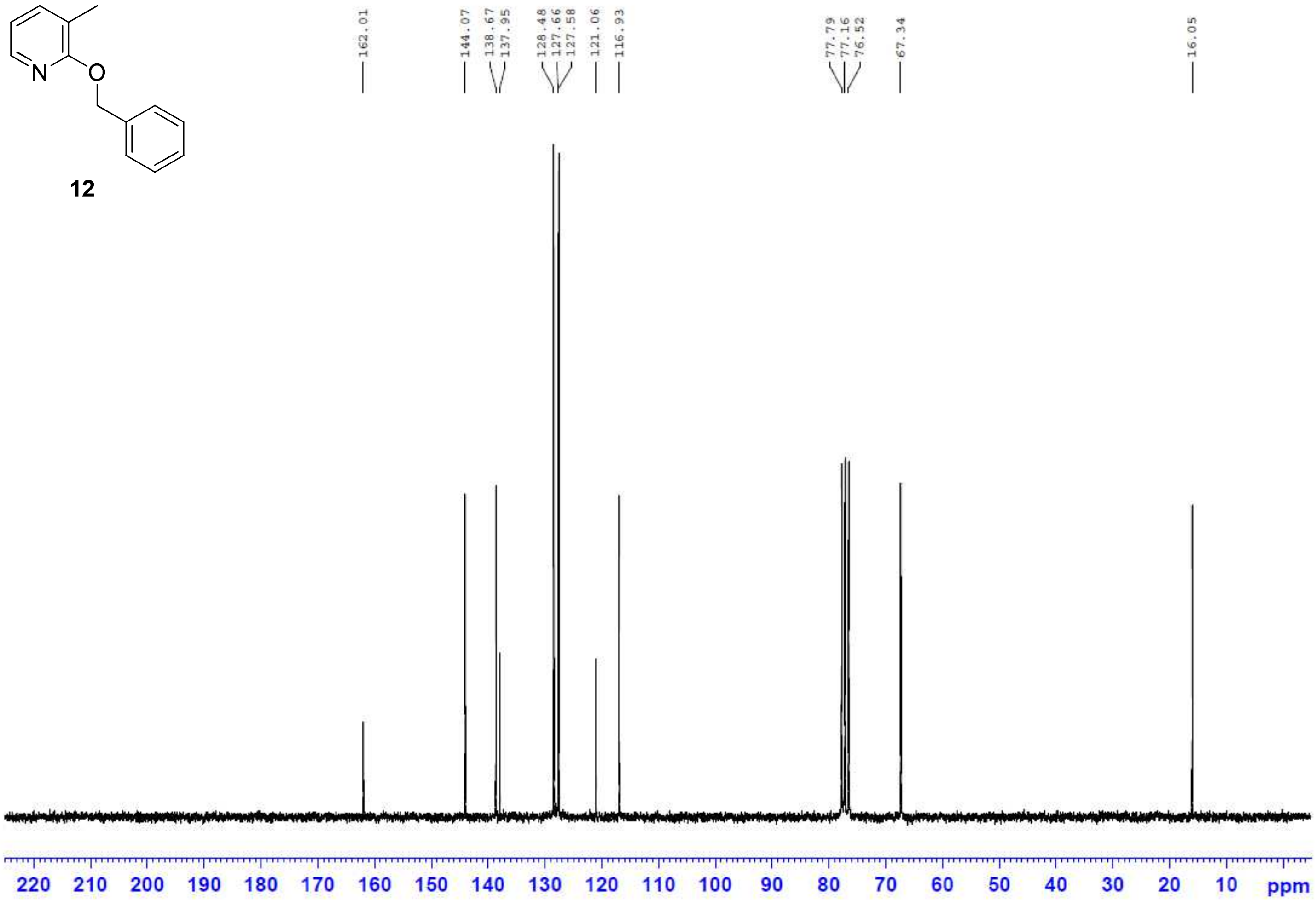


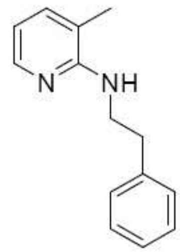
11

N
159.60
146.83
142.09
137.73
131.25
128.58
128.49
126.05
121.41
77.79
77.16
76.52
37.52
35.12
18.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

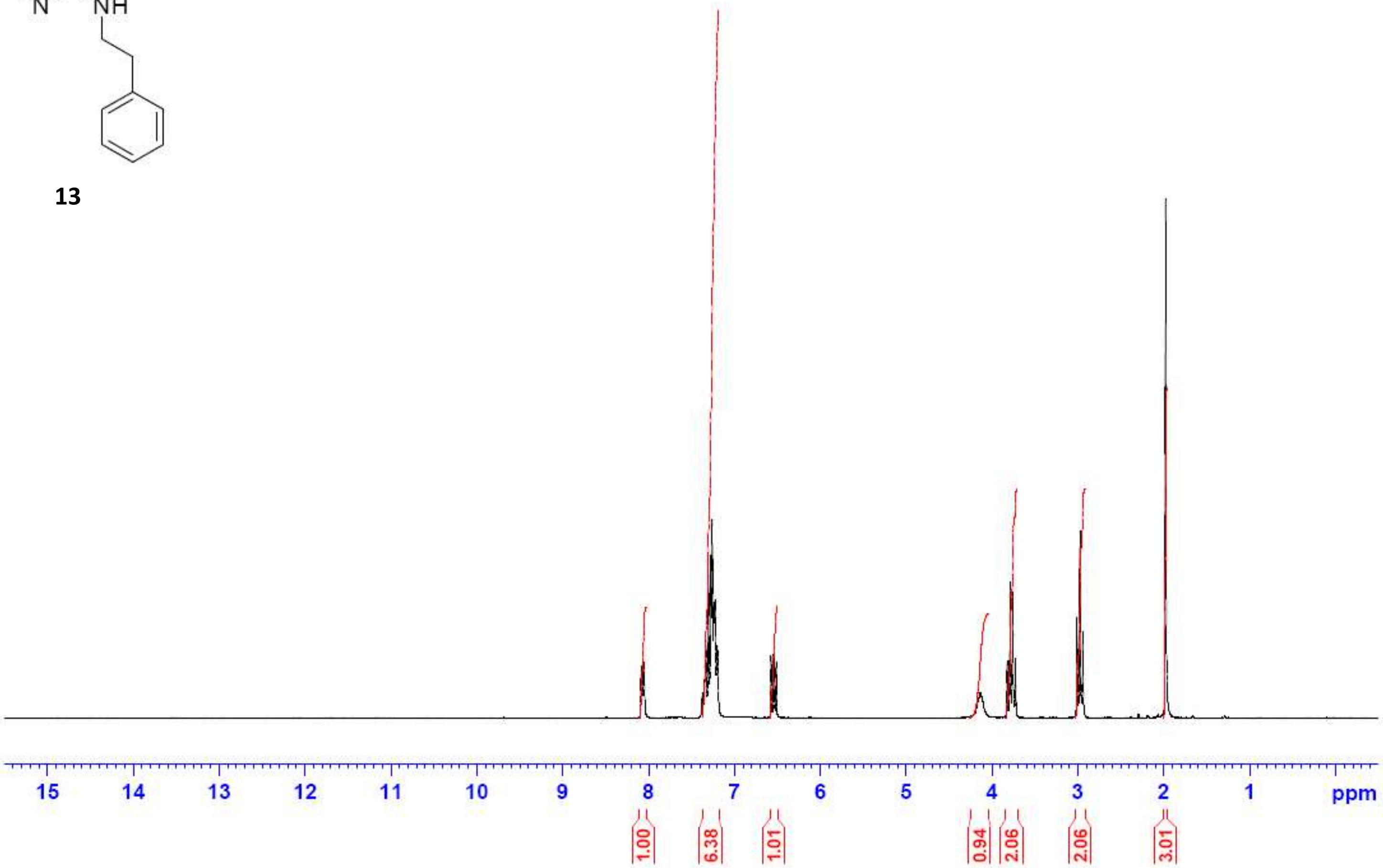


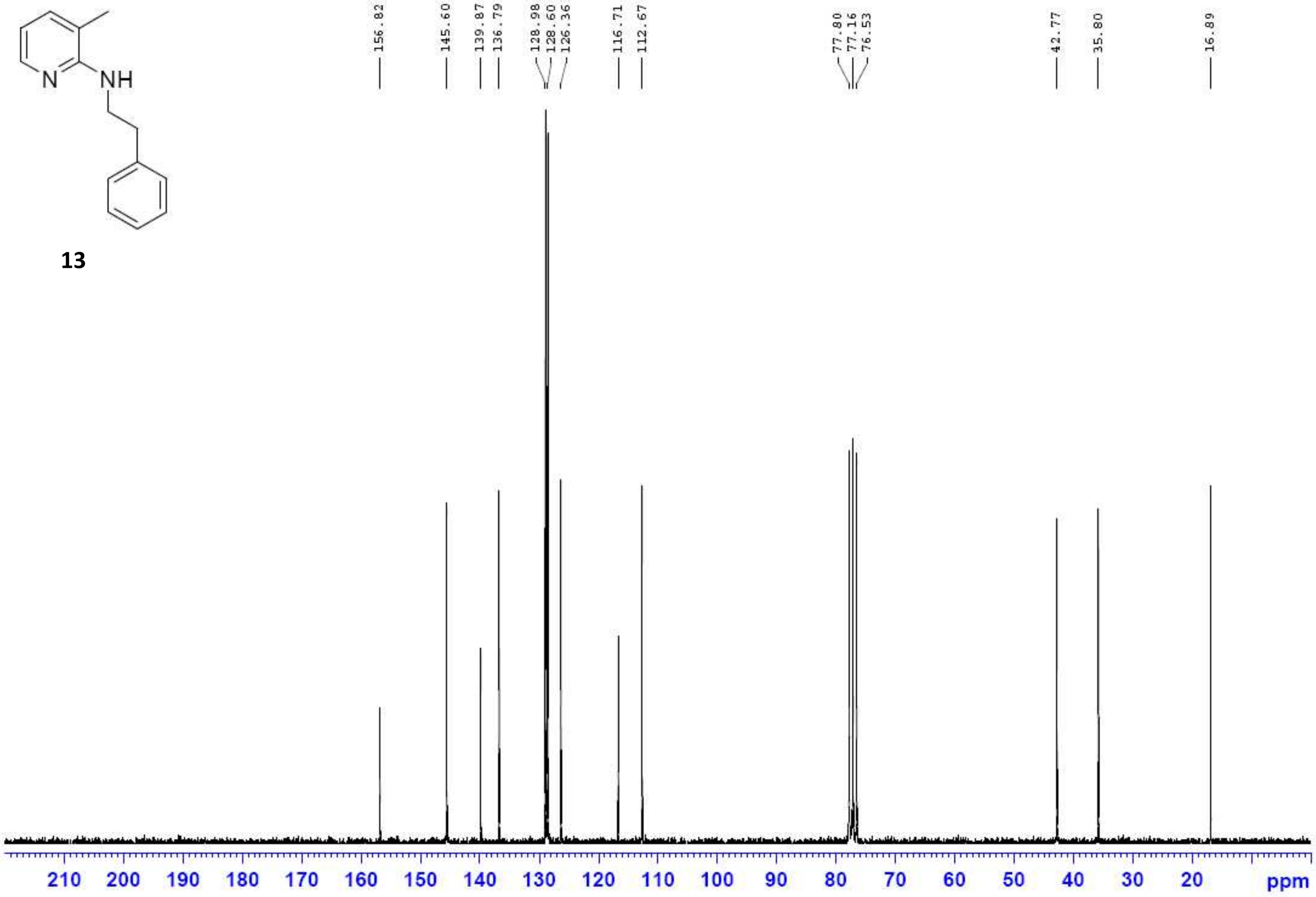
12

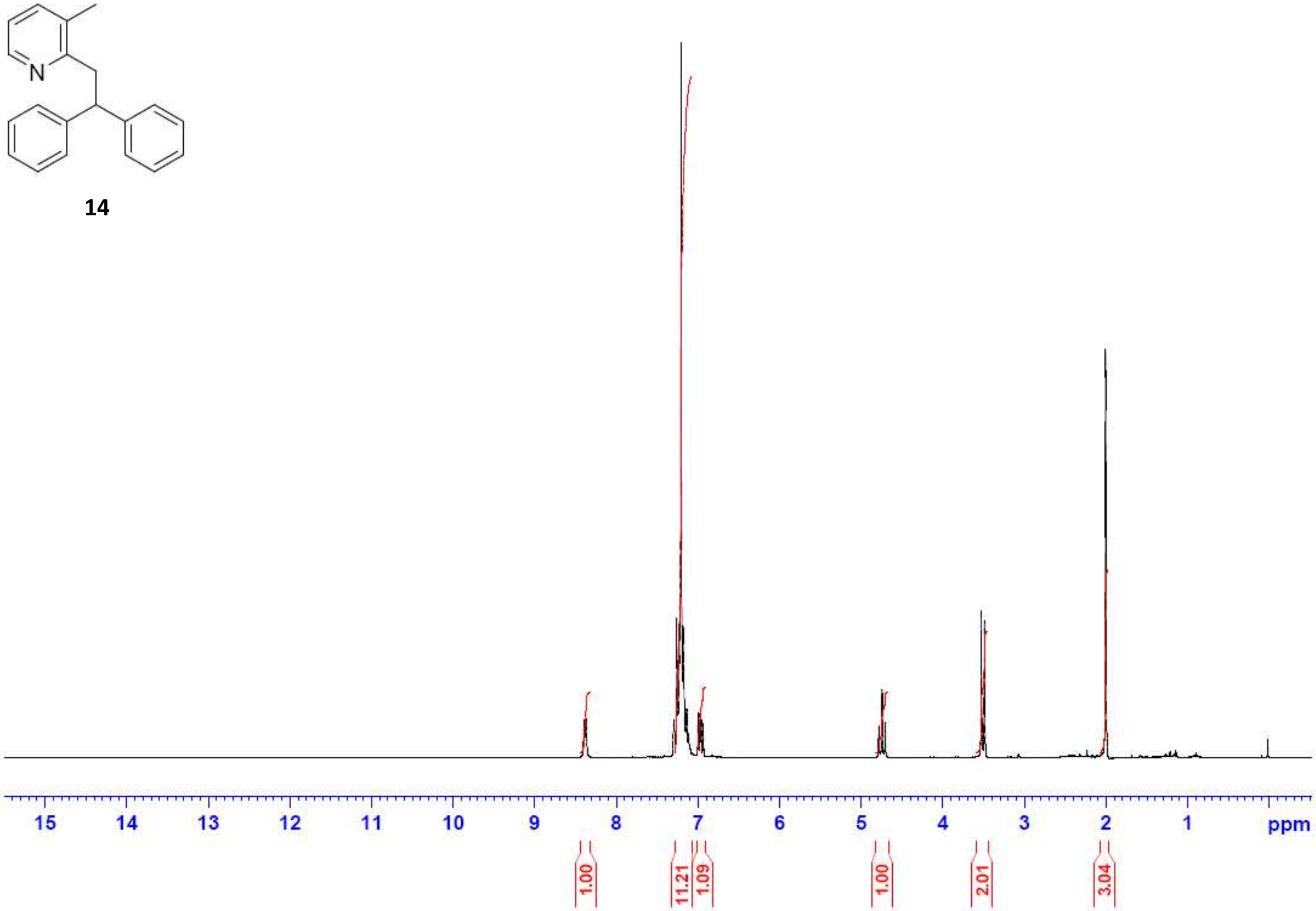

12
162.01
144.07
138.67
137.95
128.48
127.66
127.58
121.06
116.93
77.79
77.16
76.52
67.34
16.05
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



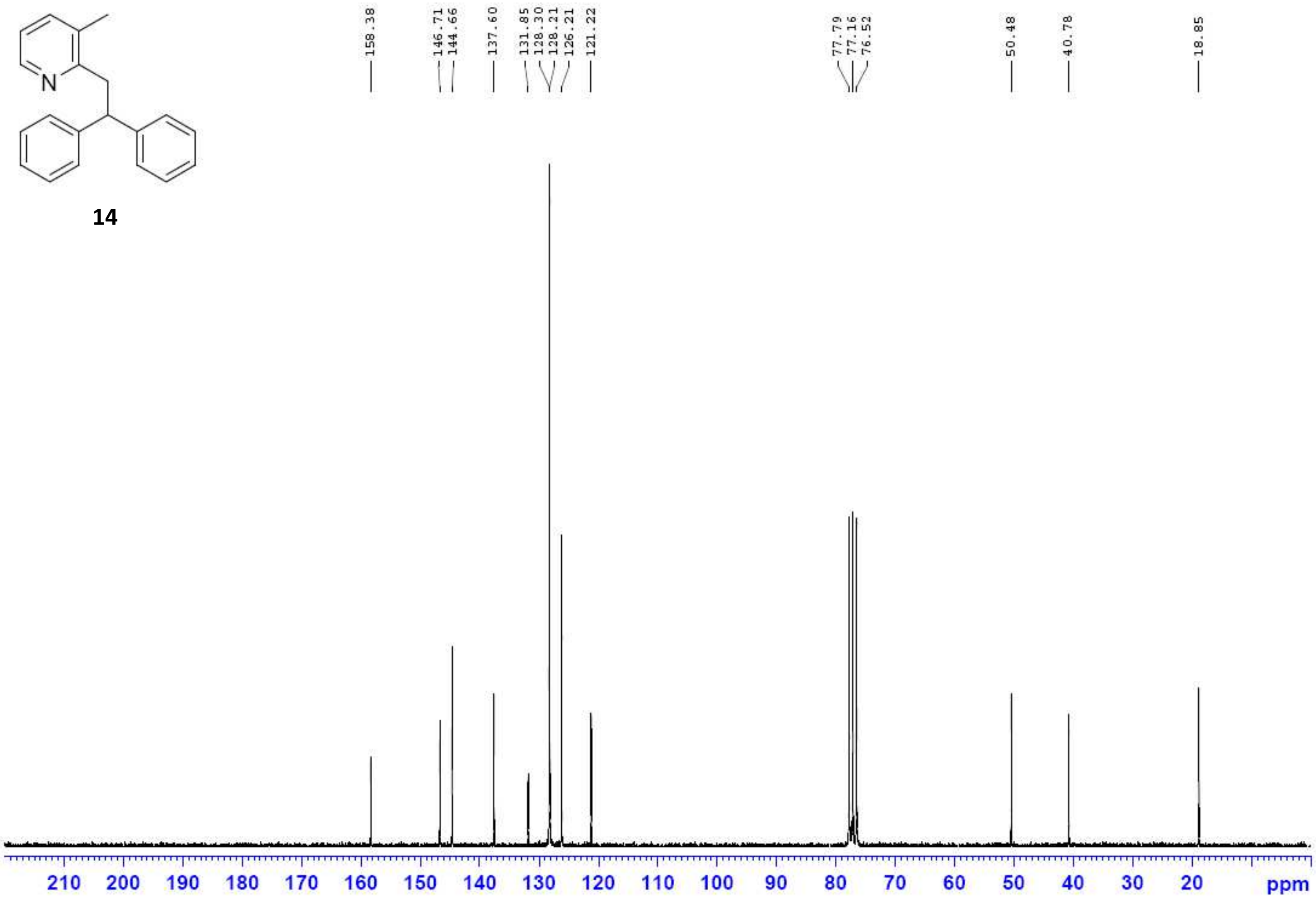
13




13
NH
N
156.82
145.60
139.87
136.79
128.98
128.60
126.36
116.71
112.67
77.80
77.16
76.53
42.77
35.80
16.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

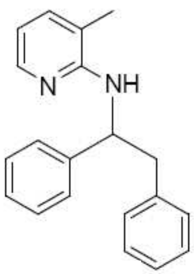


14

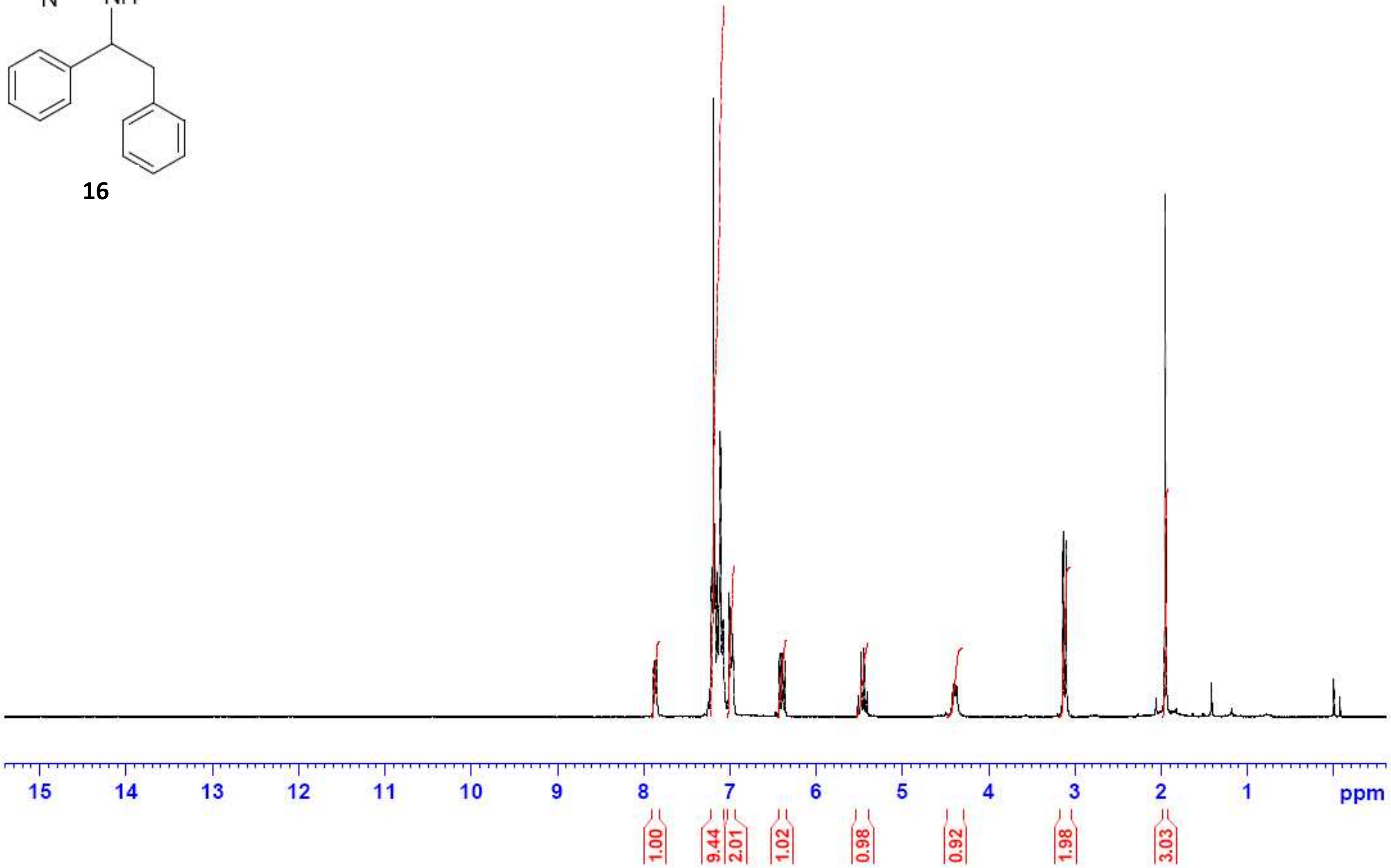


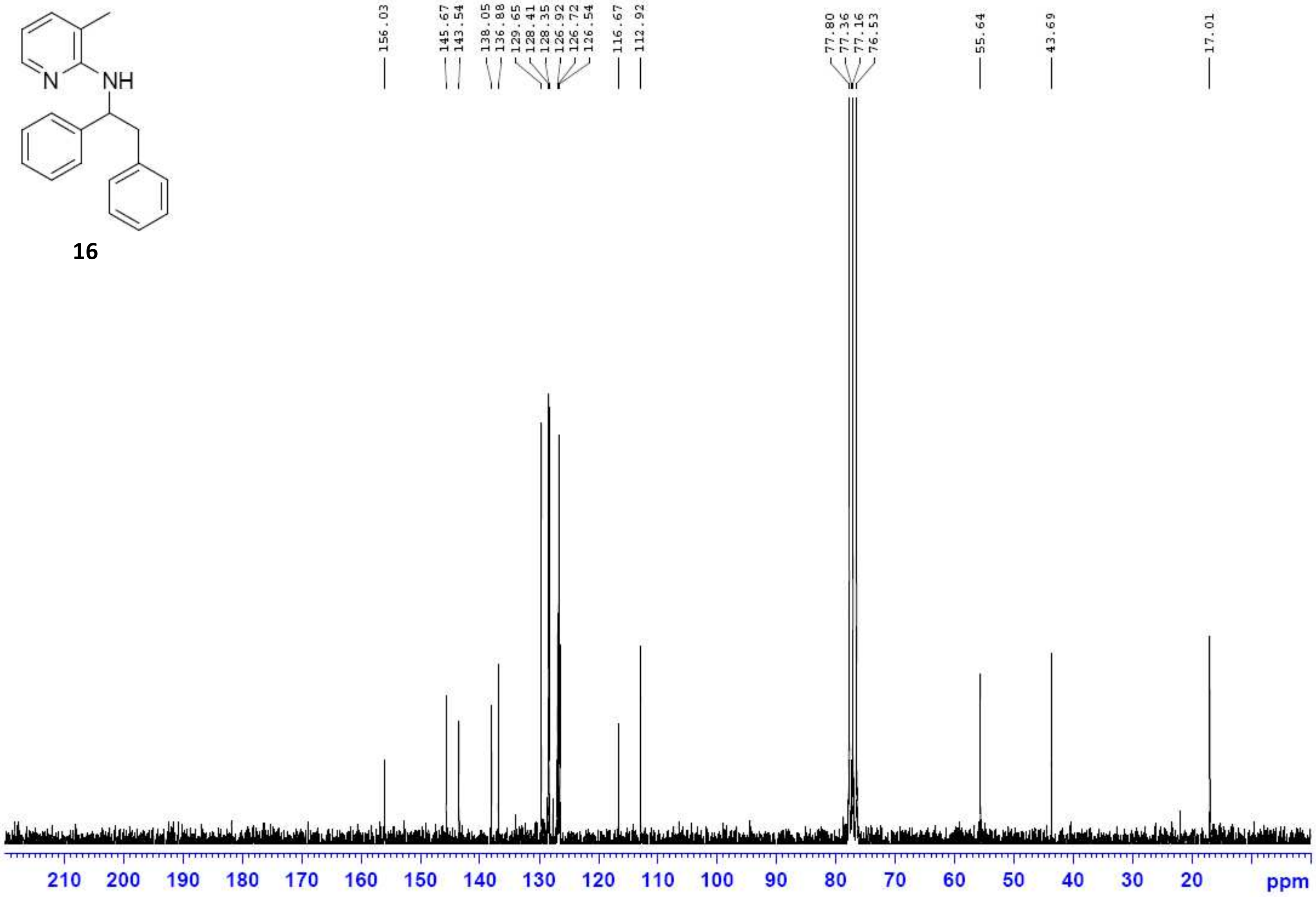
14

N
158.38
146.71
144.66
137.60
131.85
128.30
128.21
126.21
121.22
77.79
77.16
76.52
50.48
40.78
18.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


N
NH

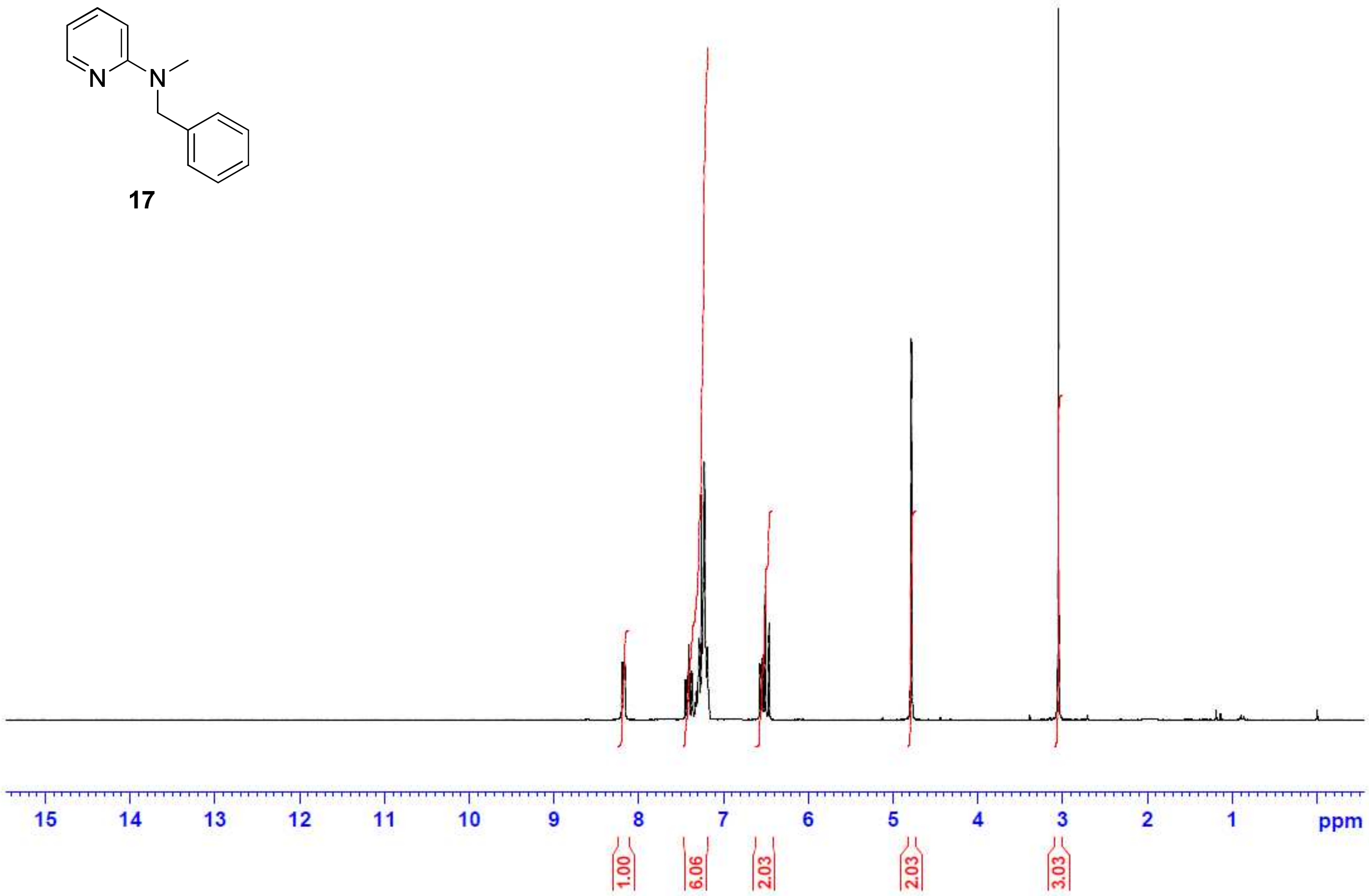
16


15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
9.44
2.01
1.02
0.98
0.92
1.98
3.03

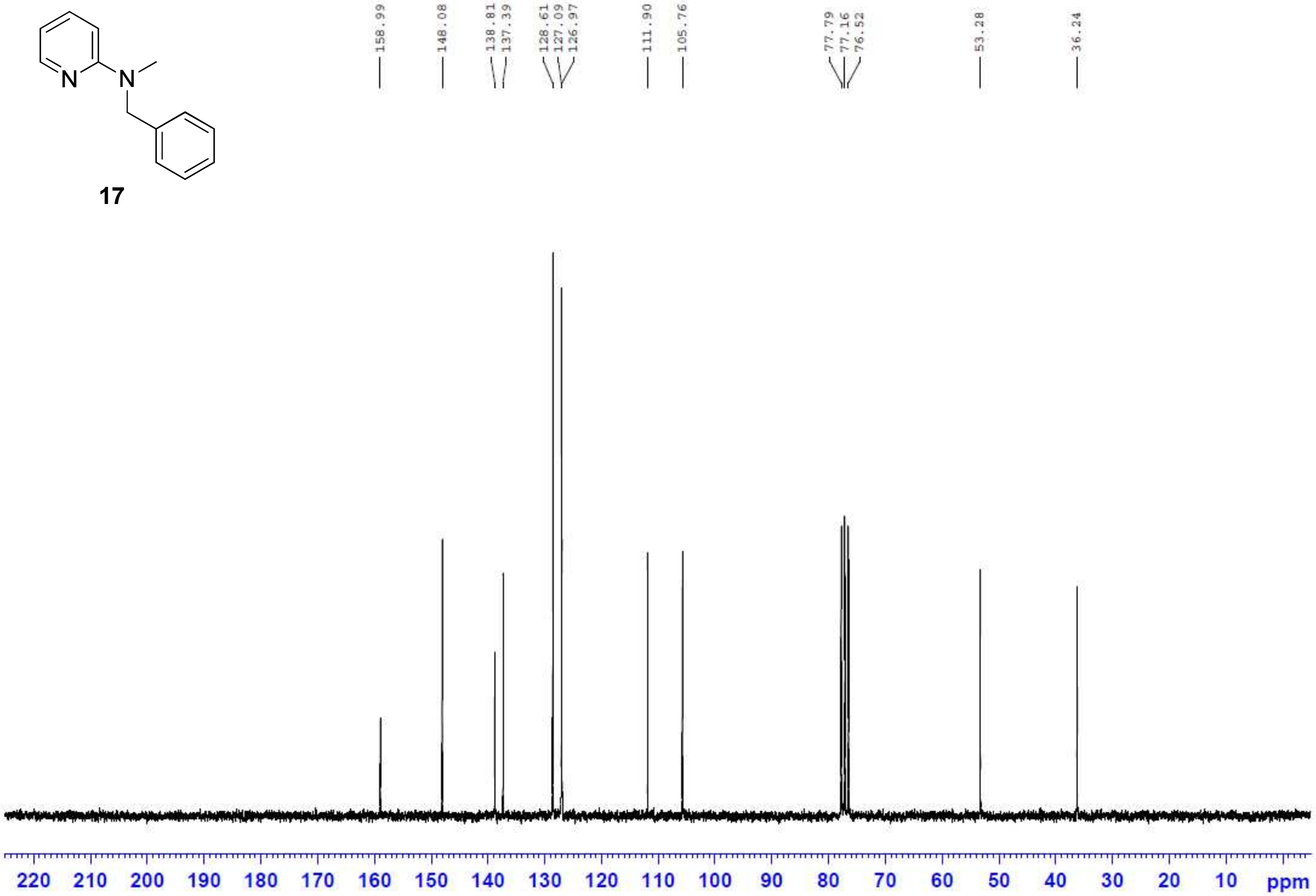


16

NH
N
156.03
145.67
143.54
138.05
136.88
129.65
128.41
128.35
126.92
126.72
126.54
116.67
112.92
77.80
77.36
77.16
76.53
55.64
43.69
17.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

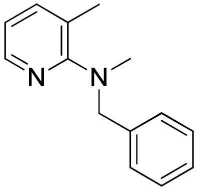


17

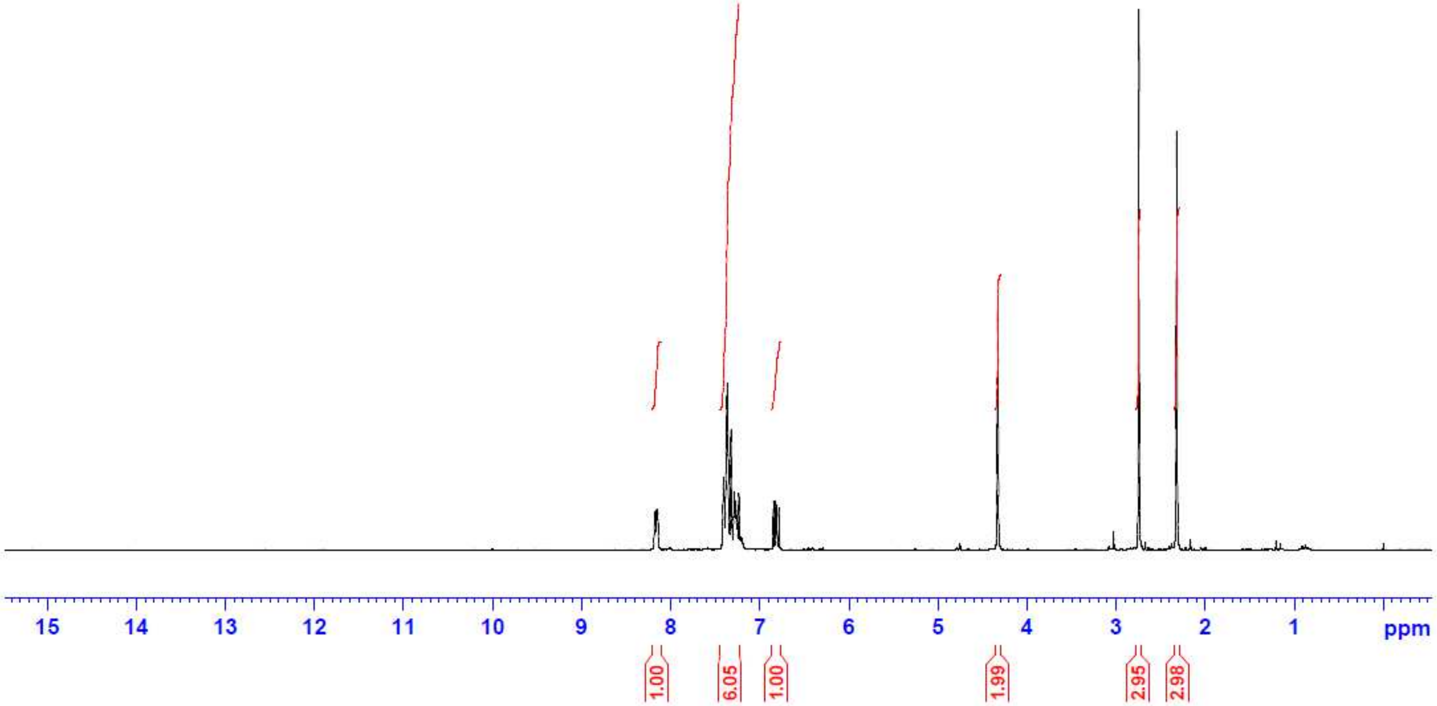


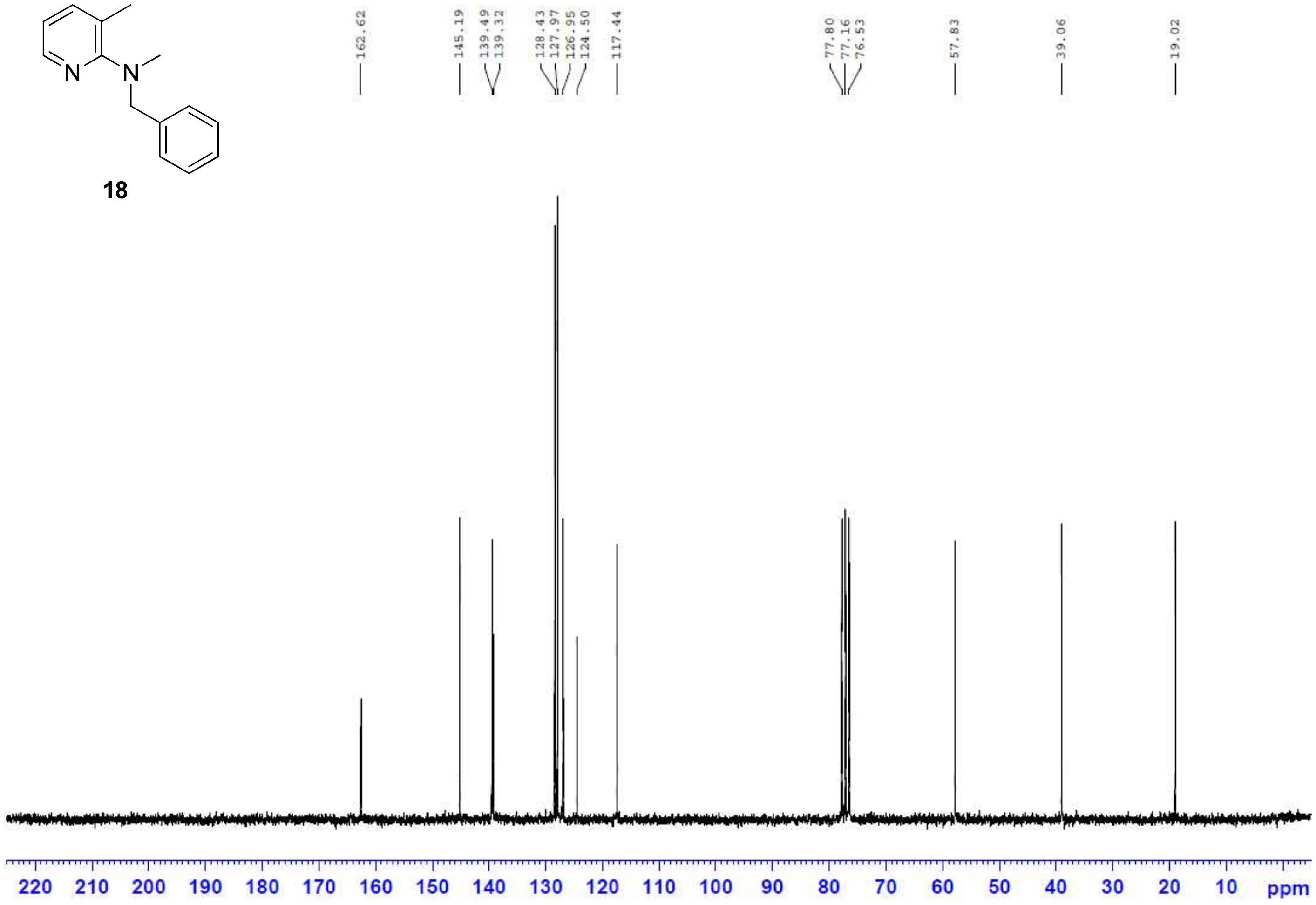
17

158.99
148.08
138.81
137.39
128.61
127.09
126.97
111.90
105.76
77.79
77.16
76.52
53.28
36.24
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



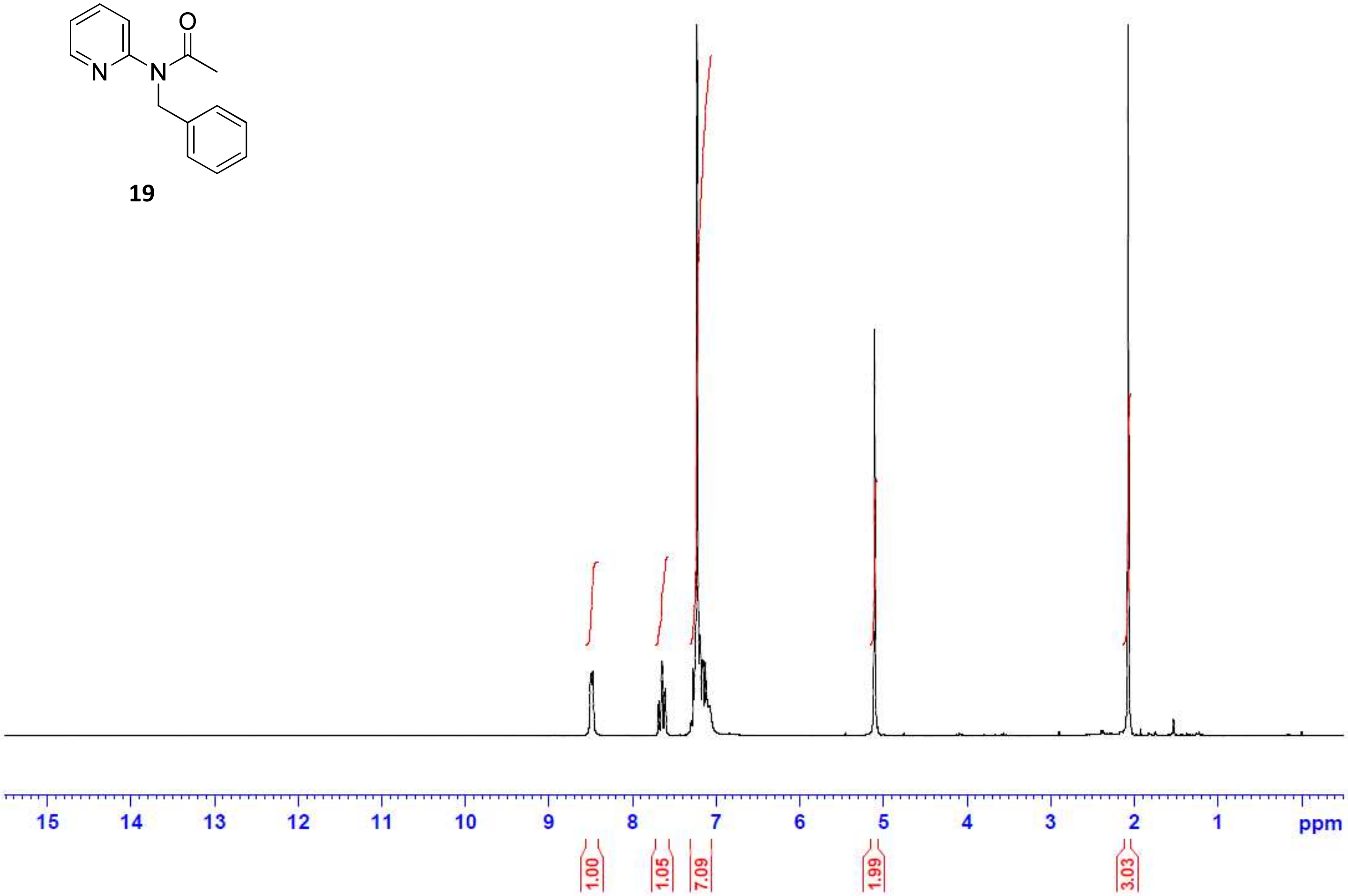
18



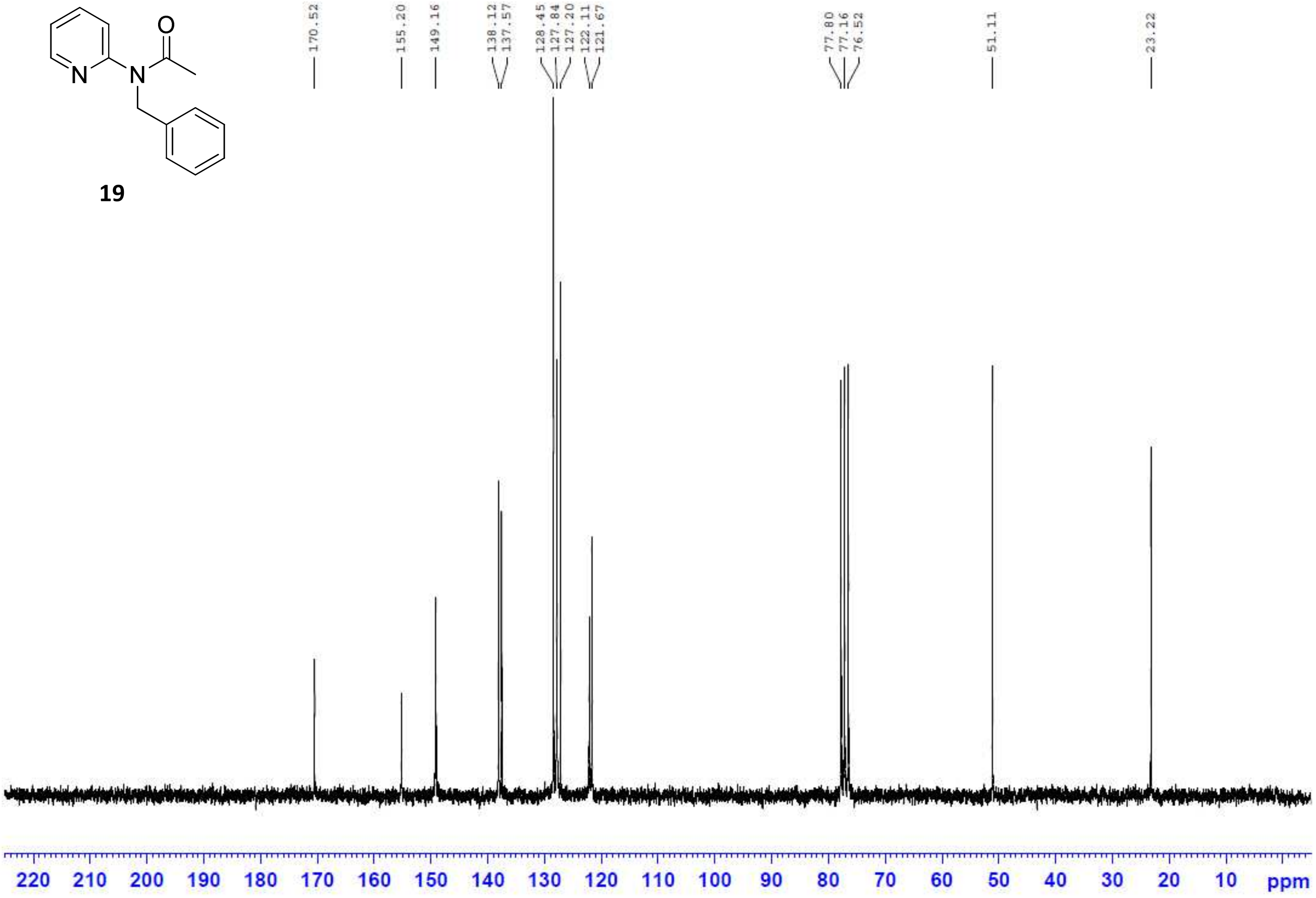


18

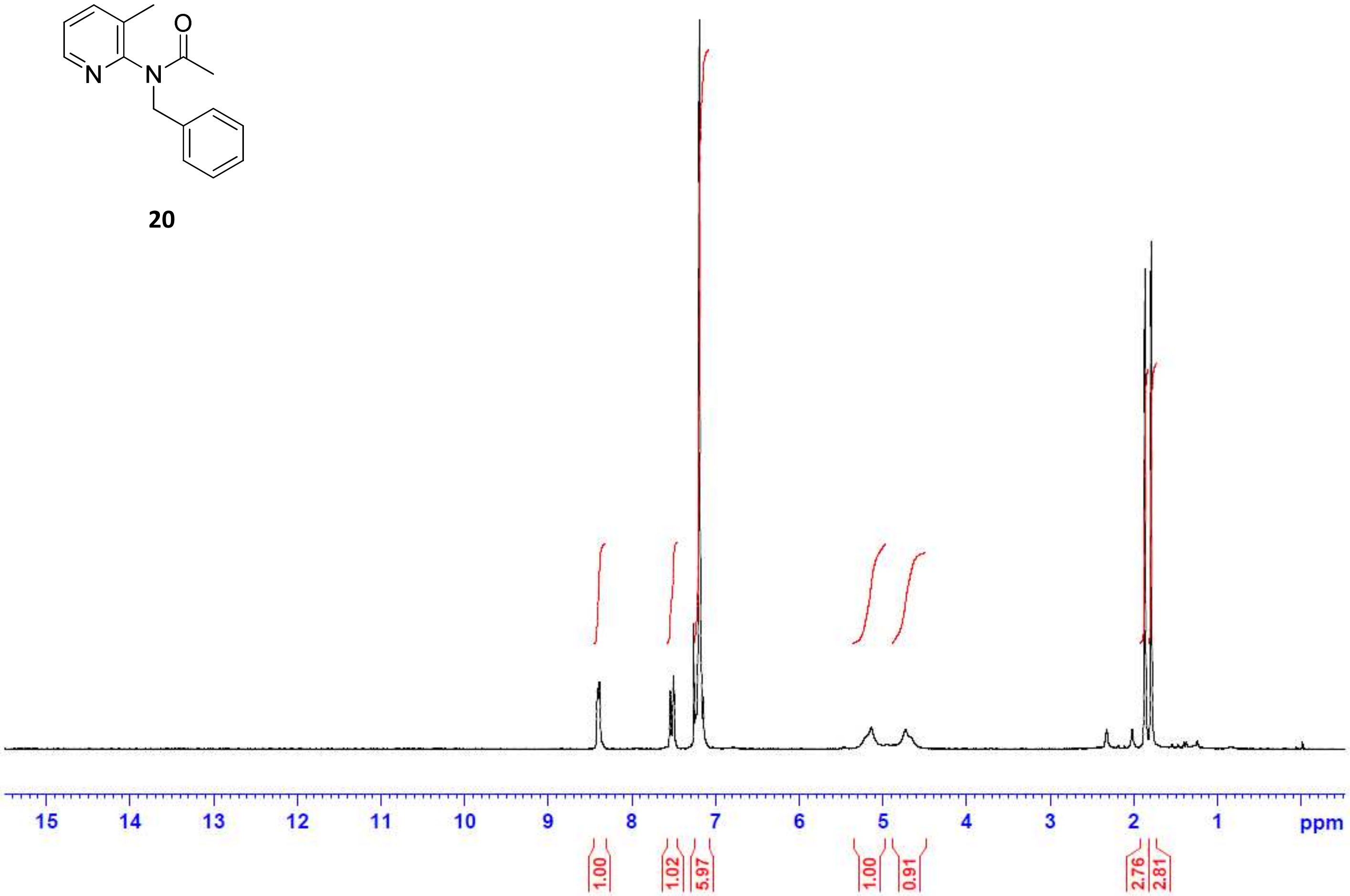
162.62
145.19
139.49
139.32
128.43
127.97
126.95
124.50
117.44
77.80
77.16
76.53
57.83
39.06
19.02
N
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



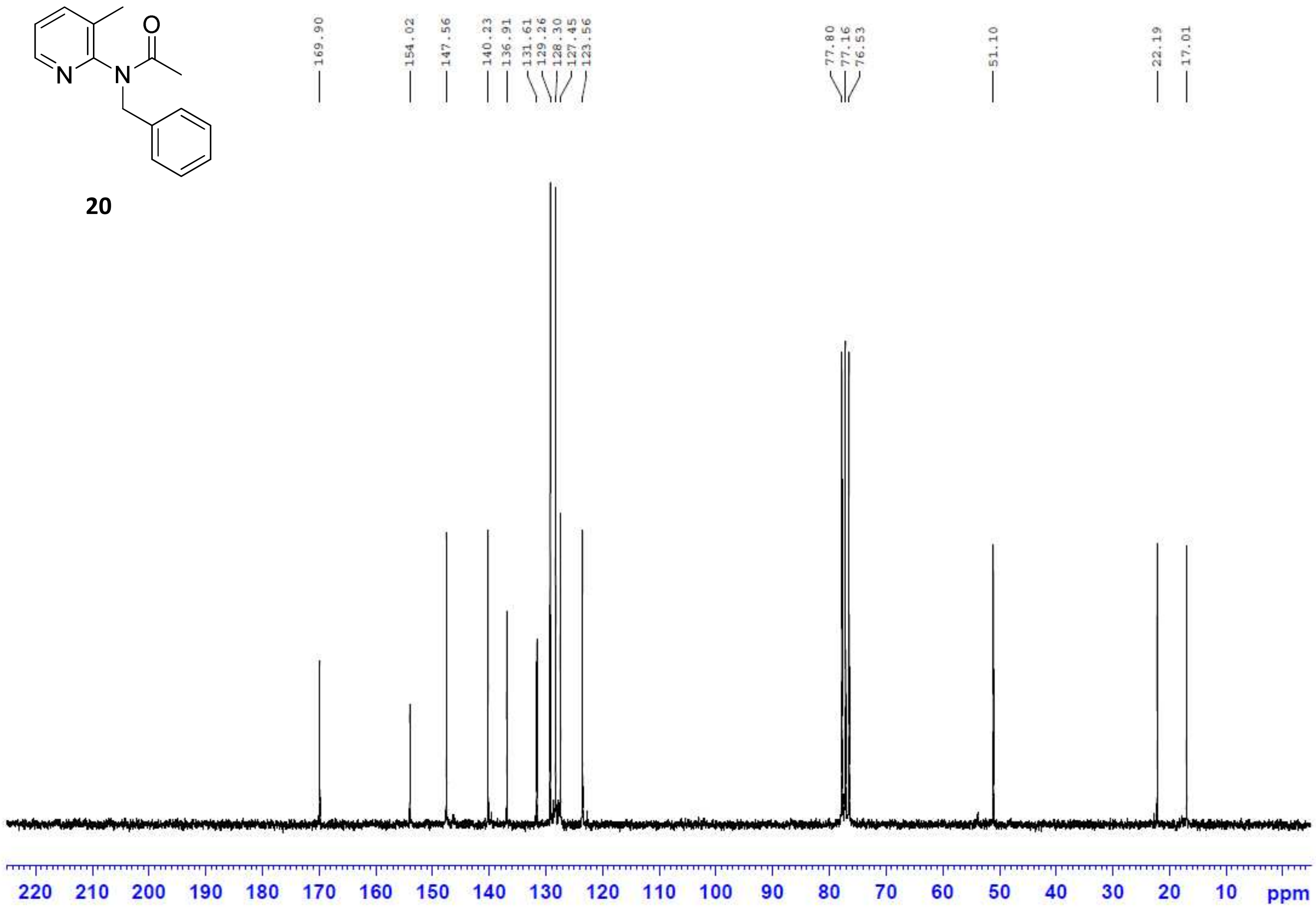
19

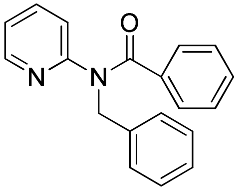

19

N
N
O
170.52
155.20
149.16
138.12
137.57
128.45
127.84
127.20
122.11
121.67
77.80
77.16
76.52
51.11
23.22
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

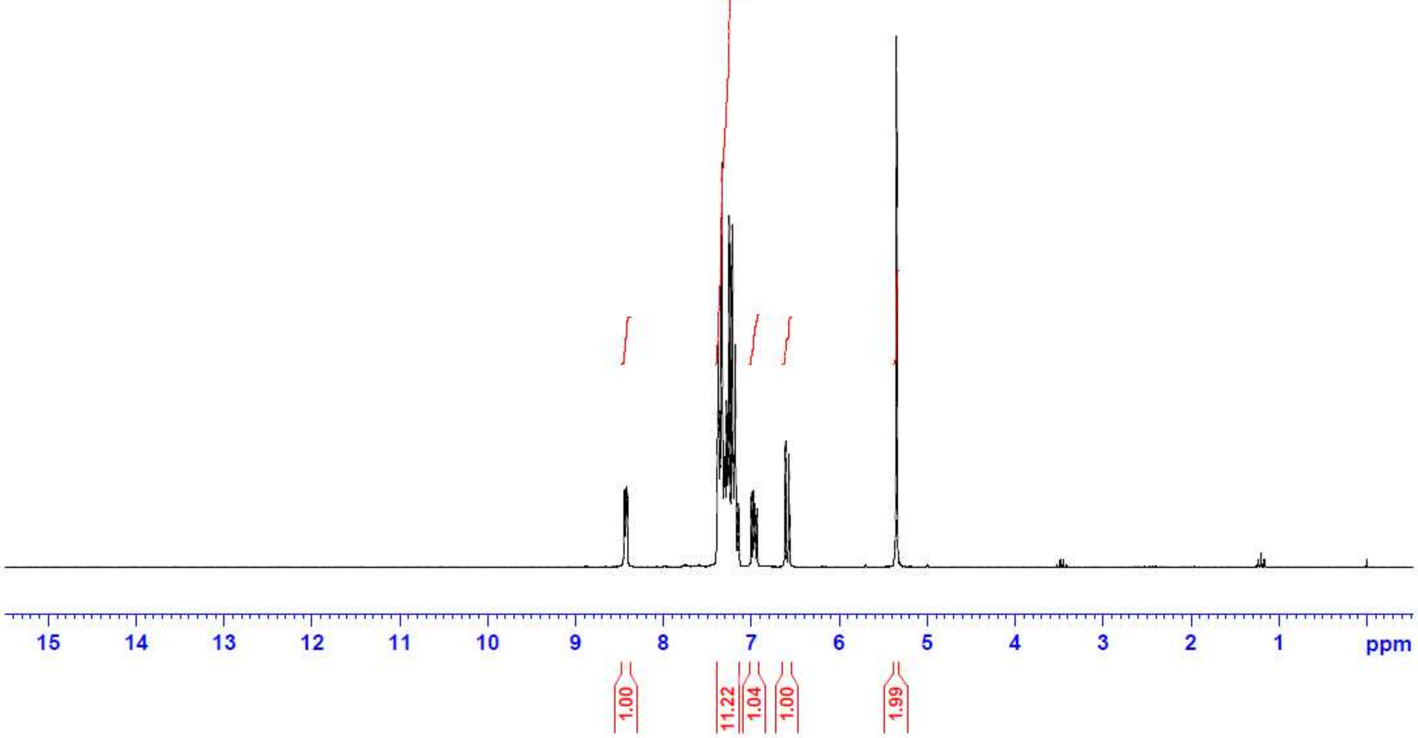


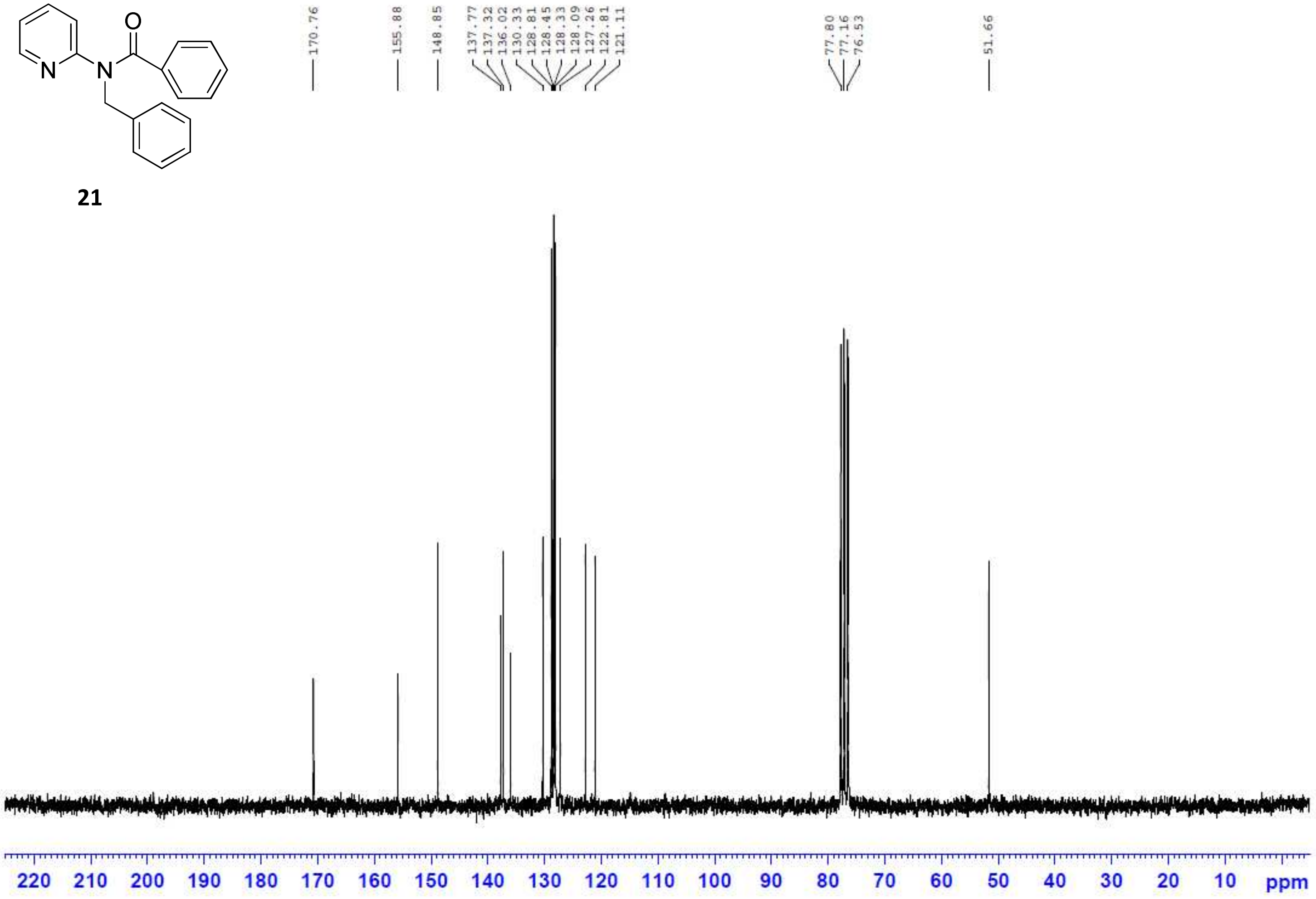
20


20
169.90
154.02
147.56
140.23
136.91
131.61
129.26
128.30
127.45
123.56
77.80
77.16
76.53
51.10
22.19
17.01
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

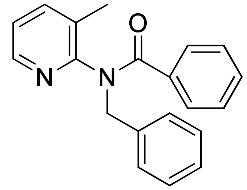


21

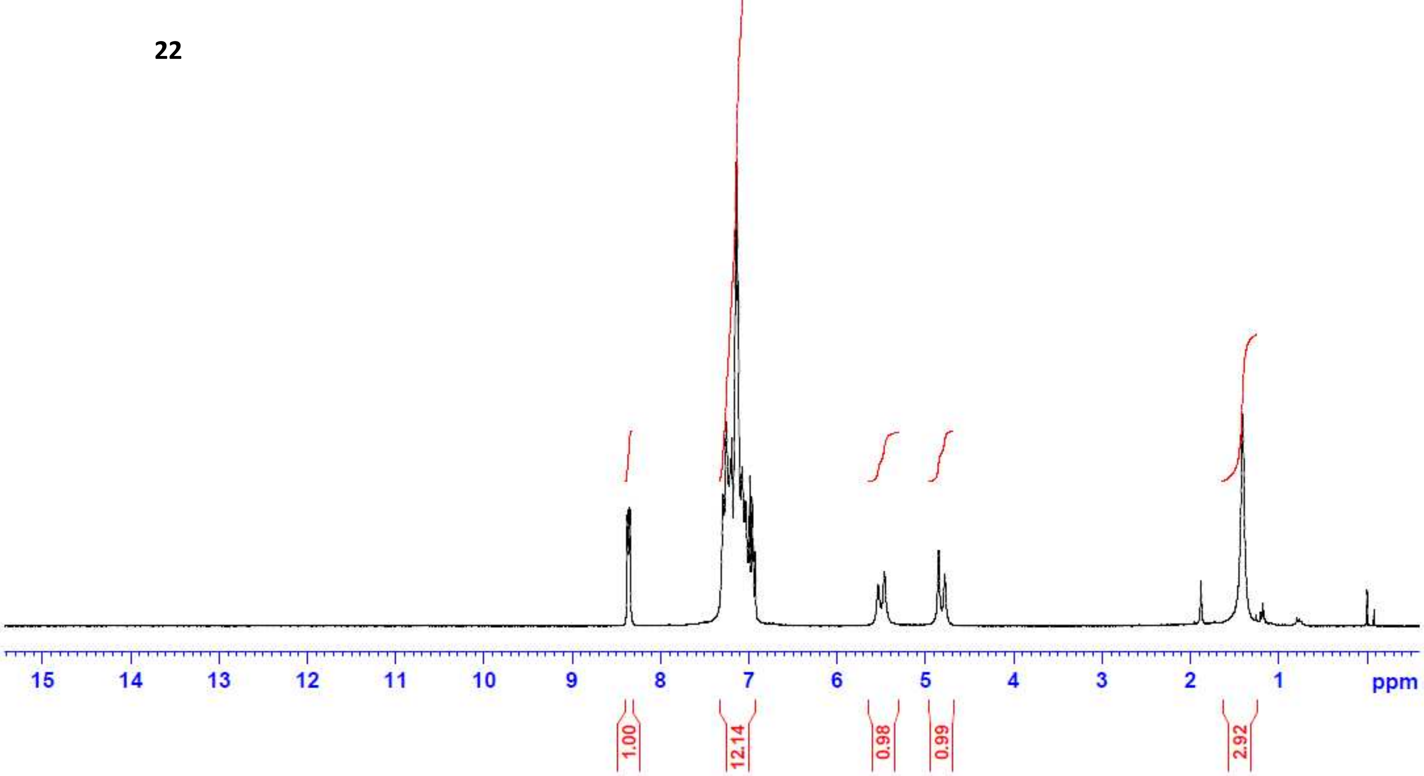


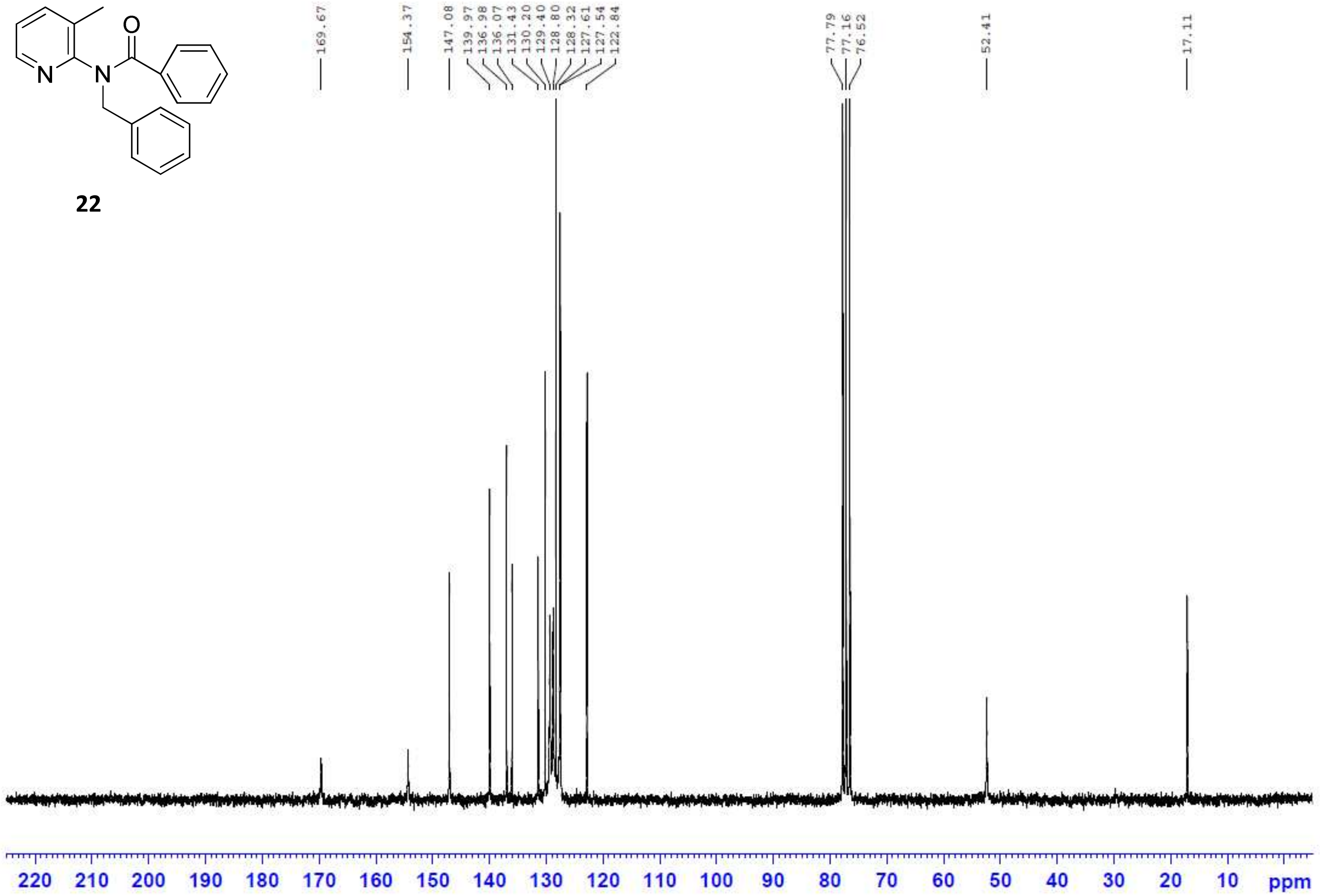

21

170.76
155.88
148.85
137.77
137.32
136.02
130.33
128.81
128.45
128.33
128.09
127.26
122.81
121.11
77.80
77.16
76.53
51.66
O
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

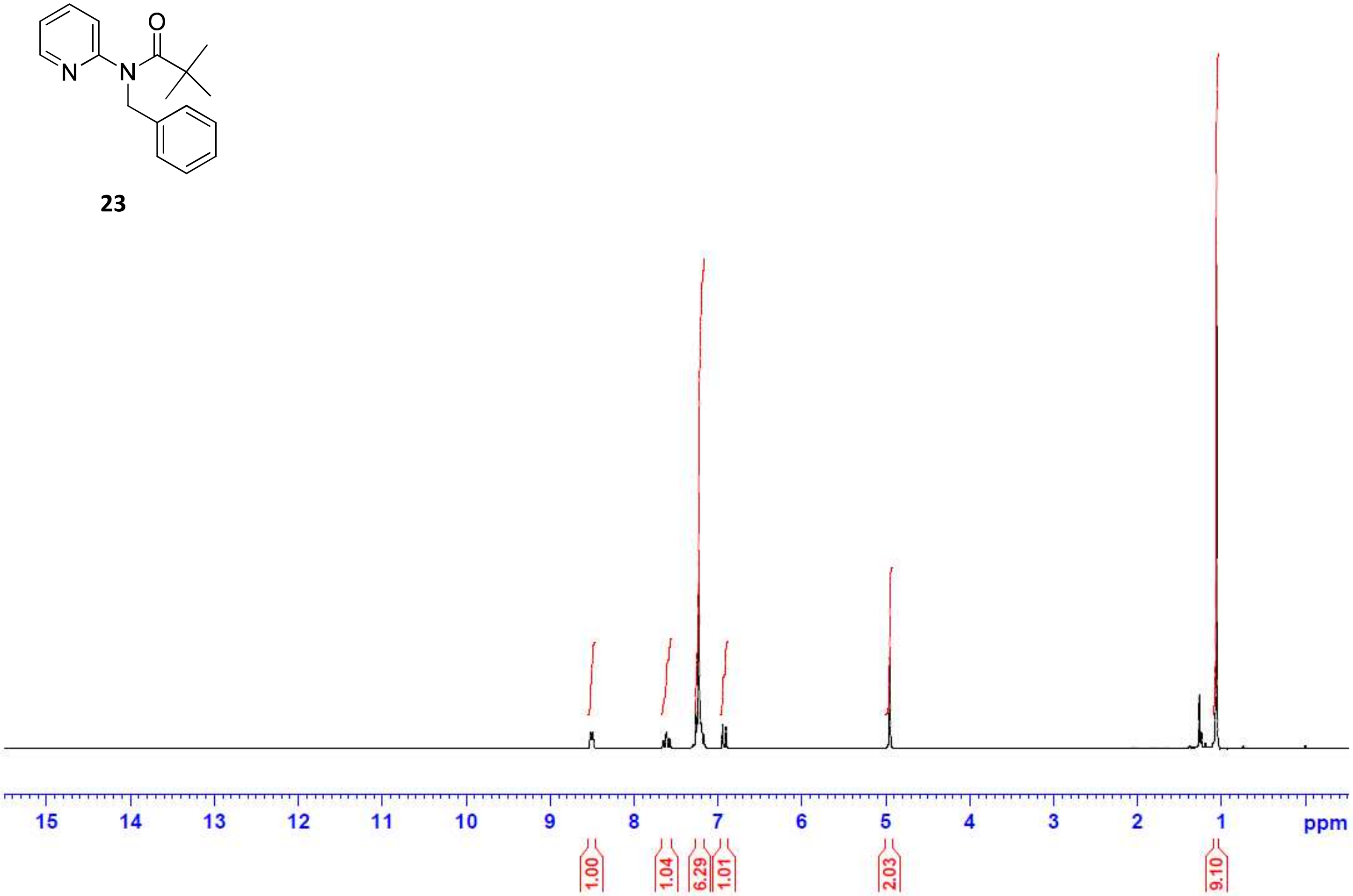


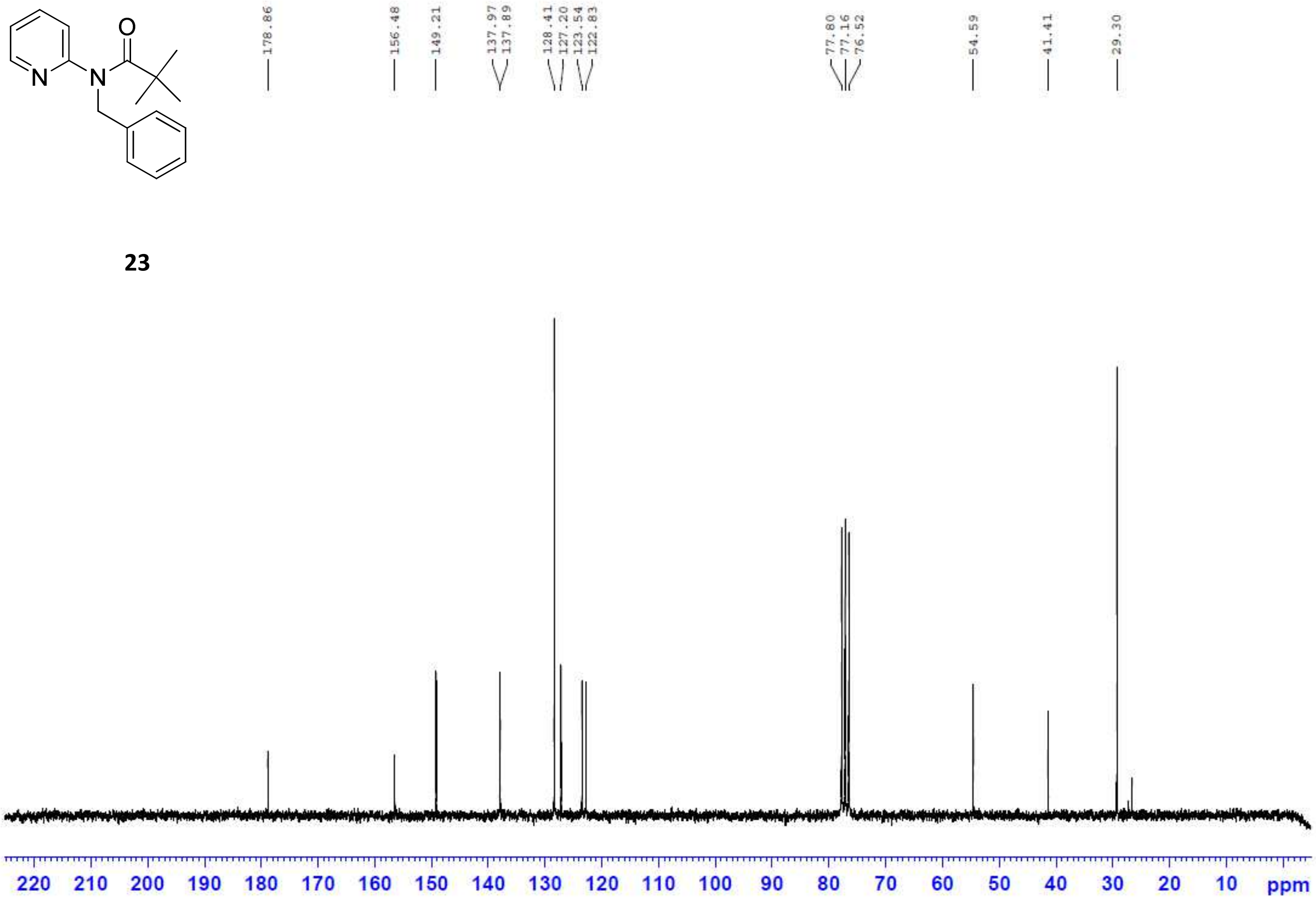
22




O
N
N
169.67
154.37
147.08
139.97
136.98
136.07
131.43
130.20
129.40
128.80
128.32
127.61
127.54
122.84
77.79
77.16
76.52
52.41
17.11
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

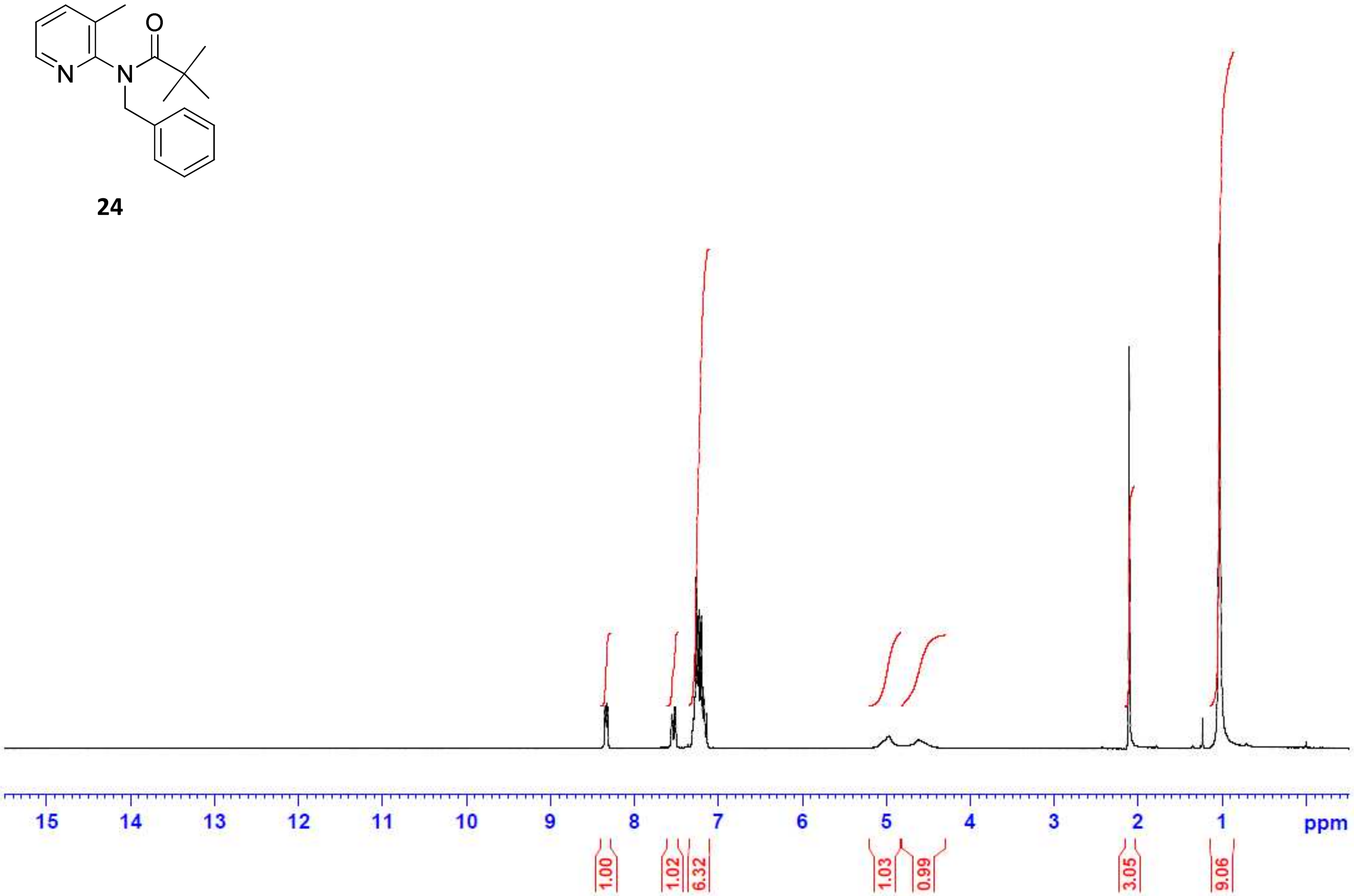
22


23

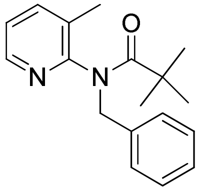


178.86
156.48
149.21
137.97
137.89
128.41
127.20
123.54
122.83
77.80
77.16
76.52
54.59
41.41
29.30
O
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

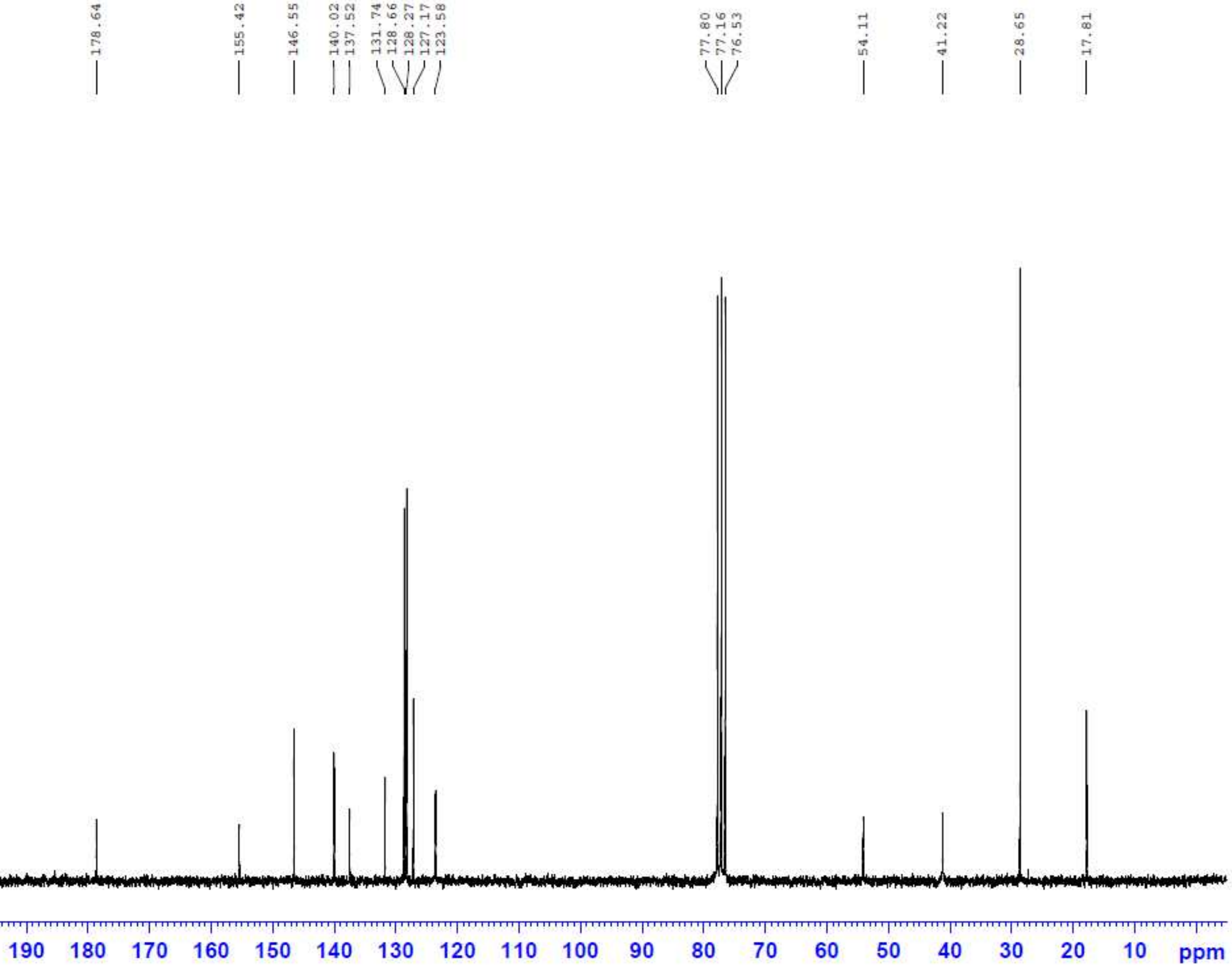
23

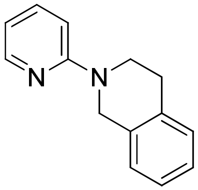


24

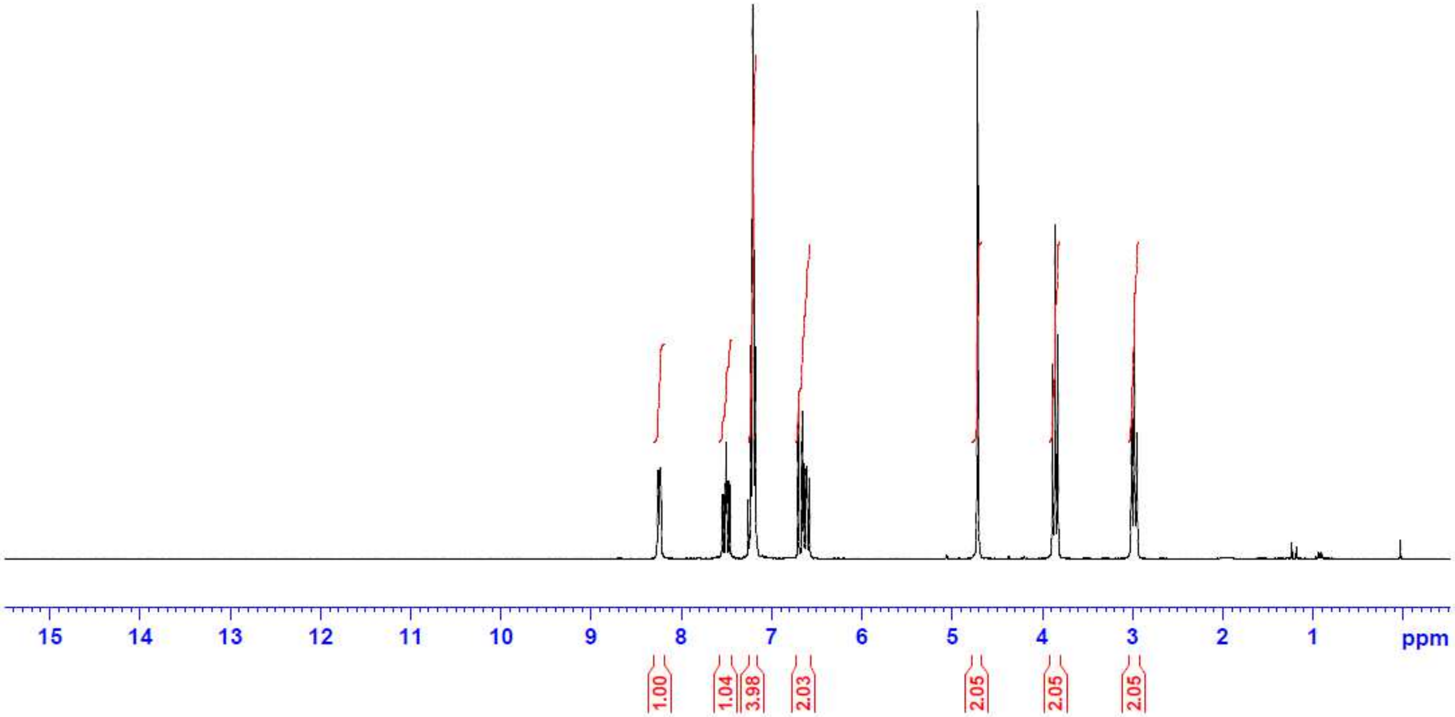


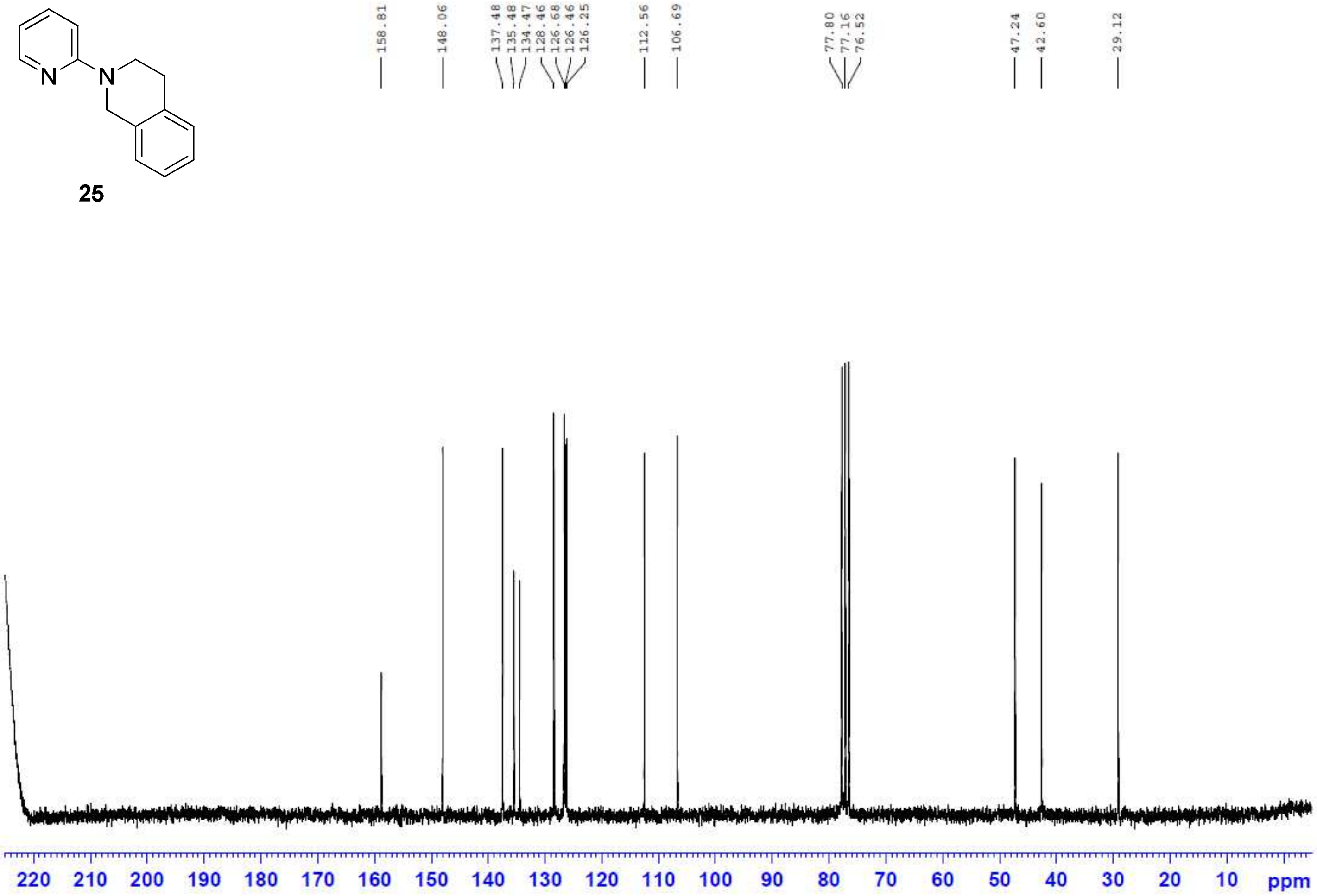
24

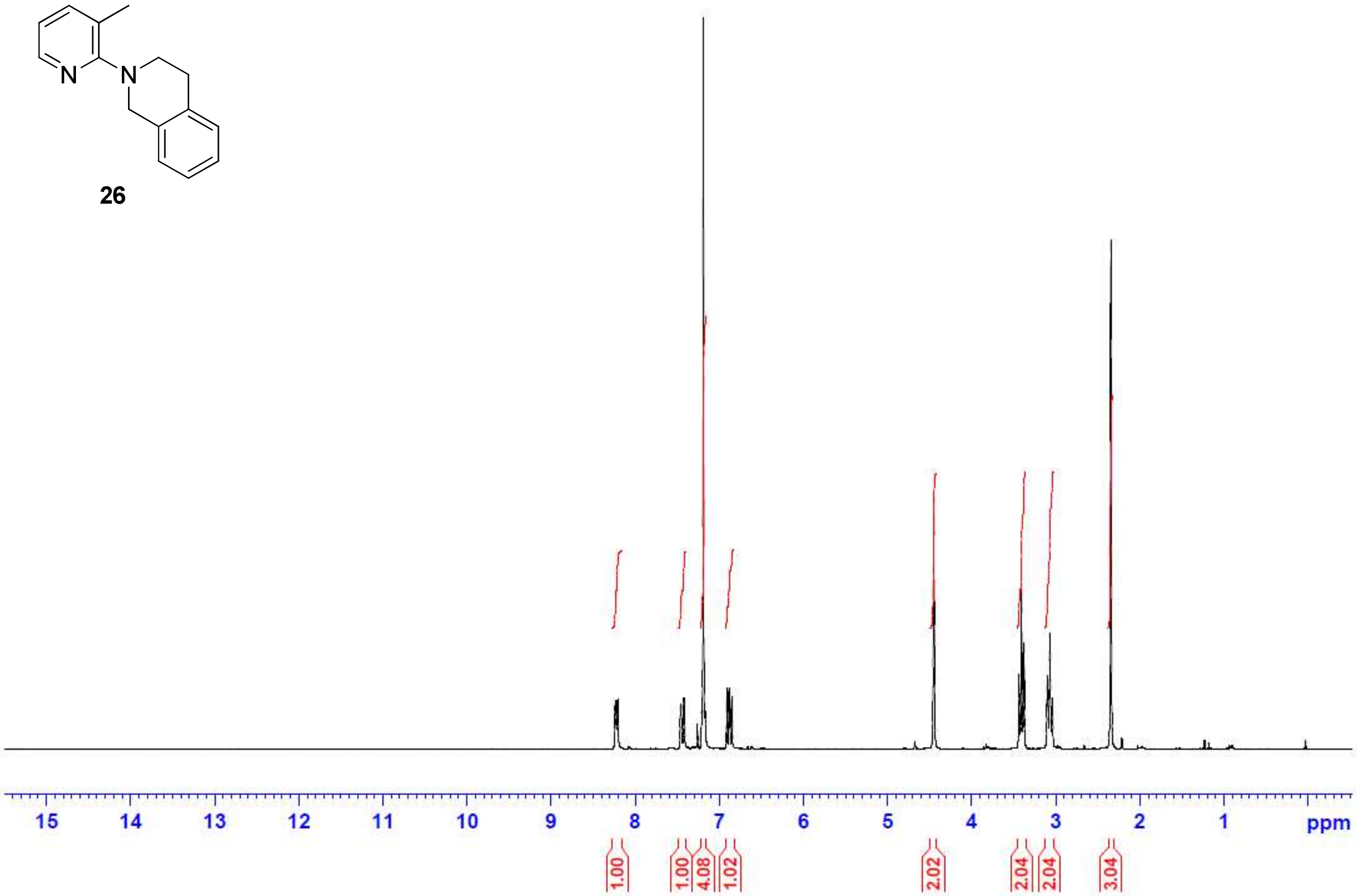

178.64
155.42
146.55
140.02
137.52
131.74
128.66
128.27
127.17
123.58
77.80
77.16
76.53
54.11
41.22
28.65
17.81
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



25

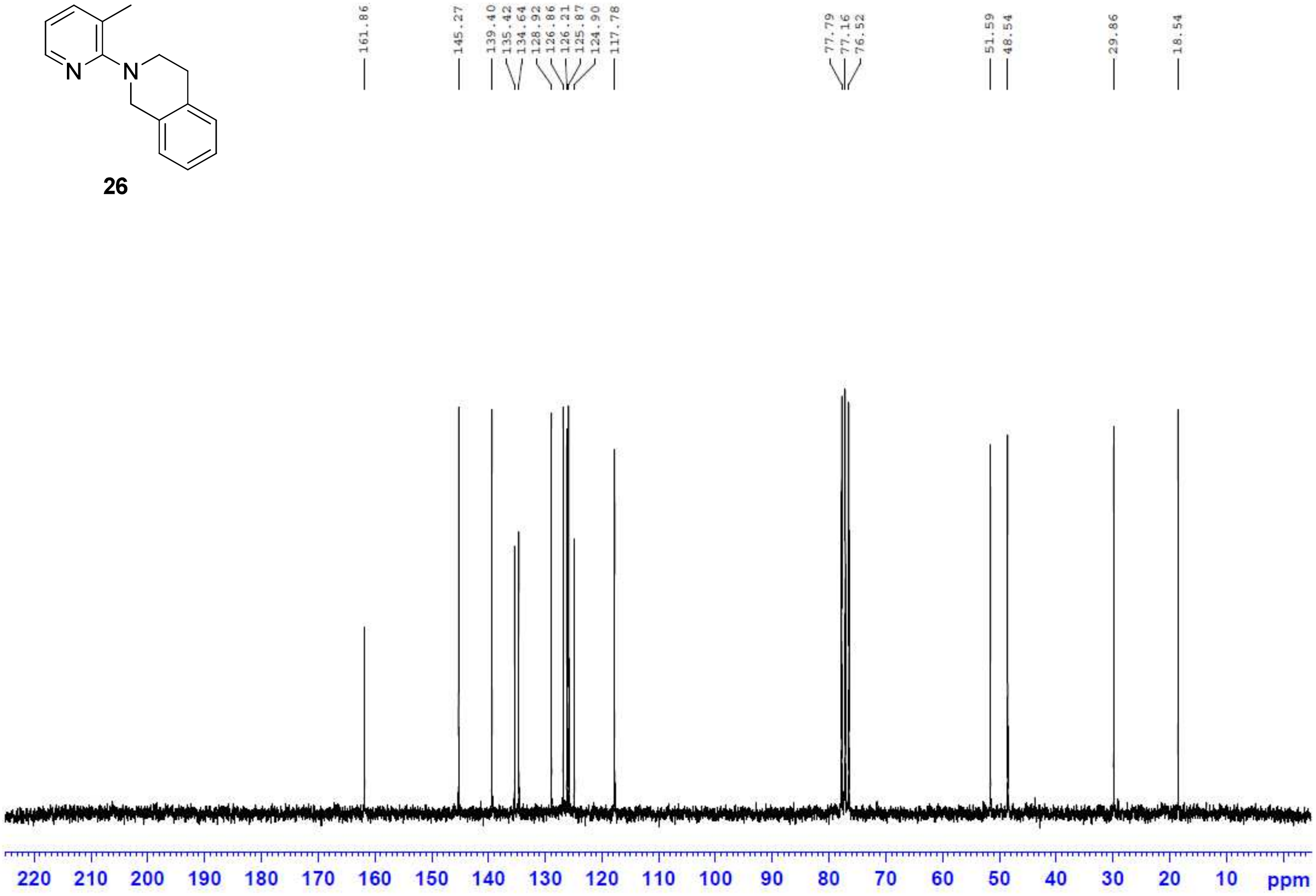



N
N
25
158.81
148.06
137.48
135.48
134.47
128.46
126.68
126.46
126.25
112.56
106.69
77.80
77.16
76.52
47.24
42.60
29.12
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



26

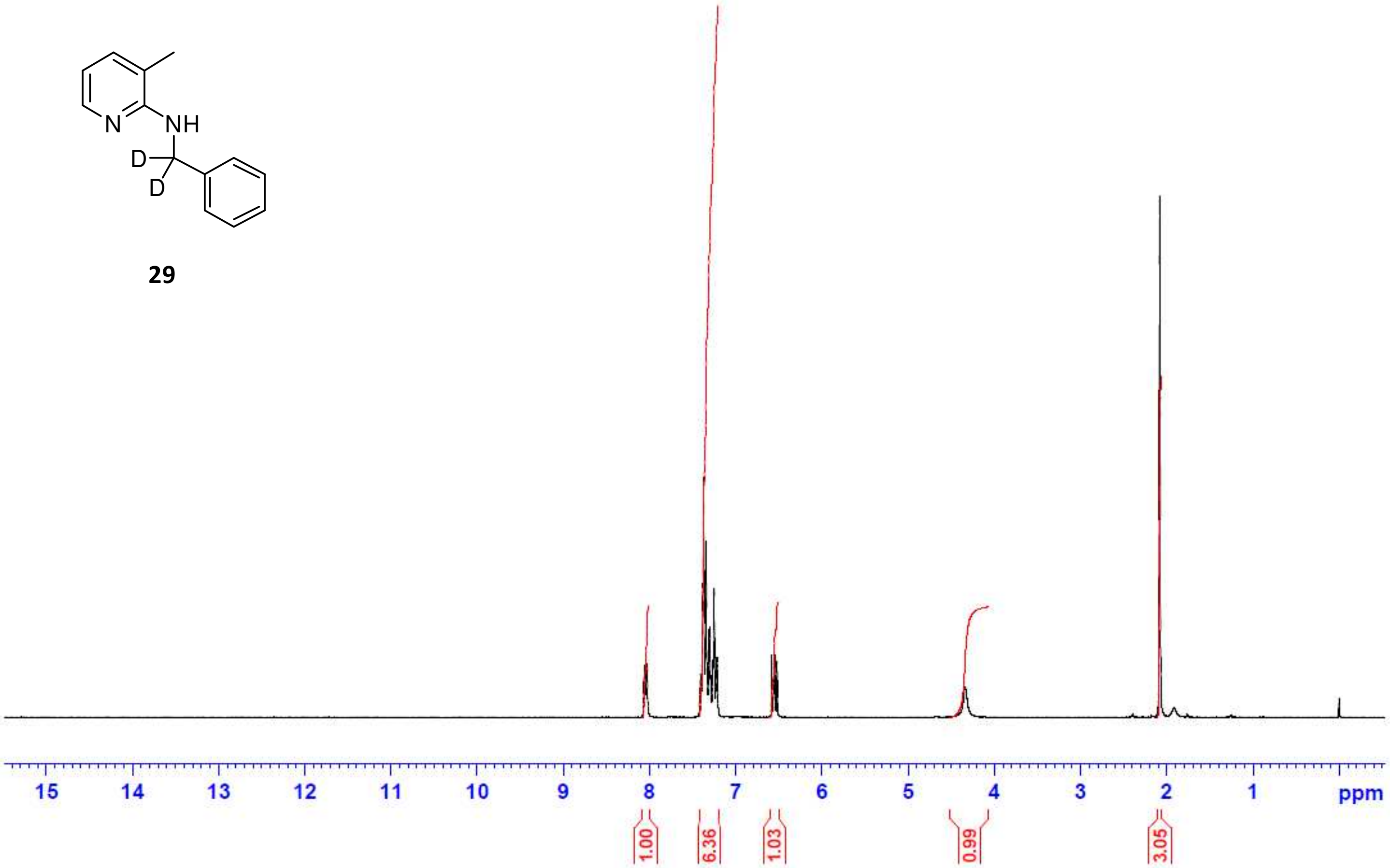
1.00
1.00
4.08
1.02
2.02
2.04
2.04
3.04
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
N
N

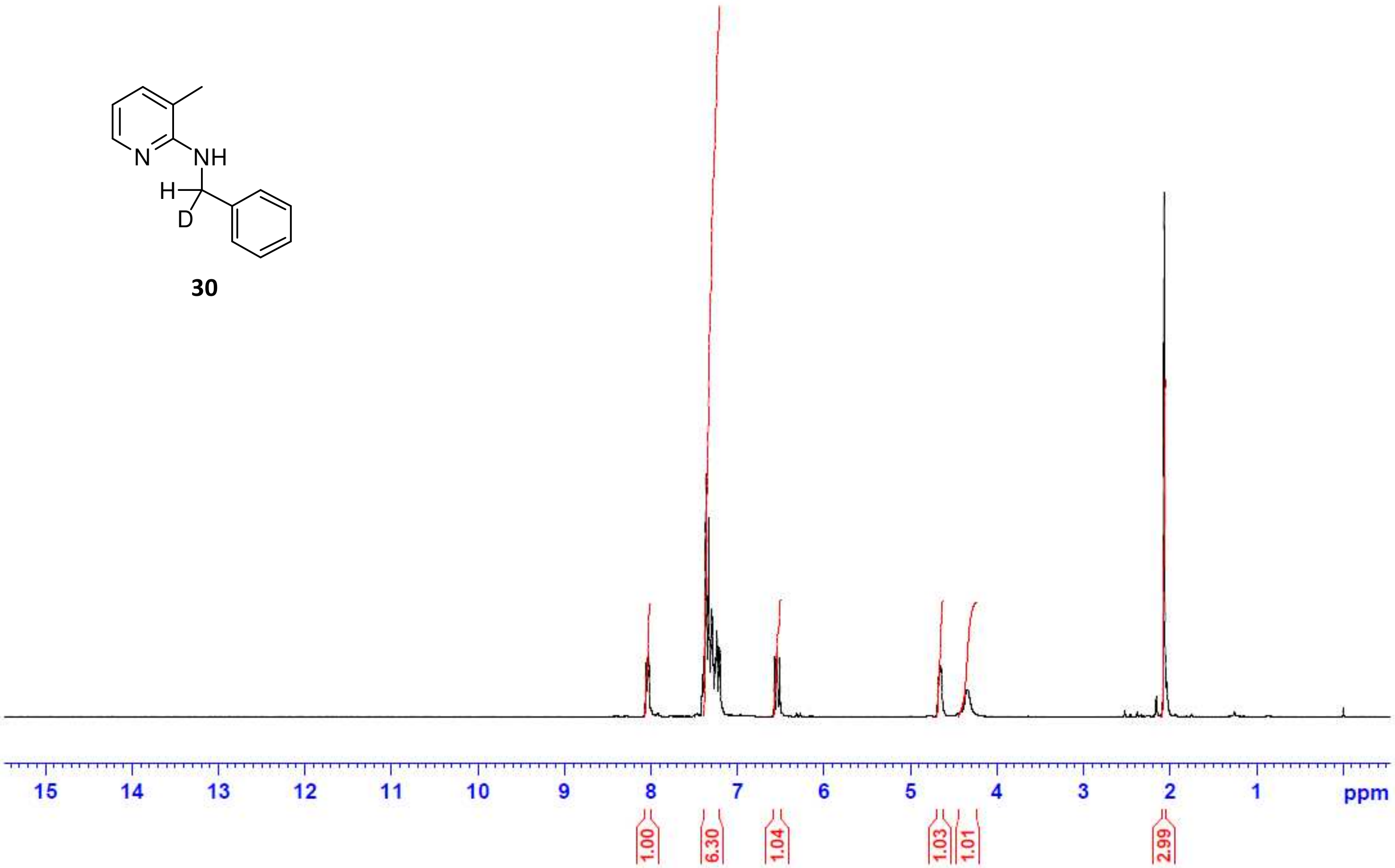


26

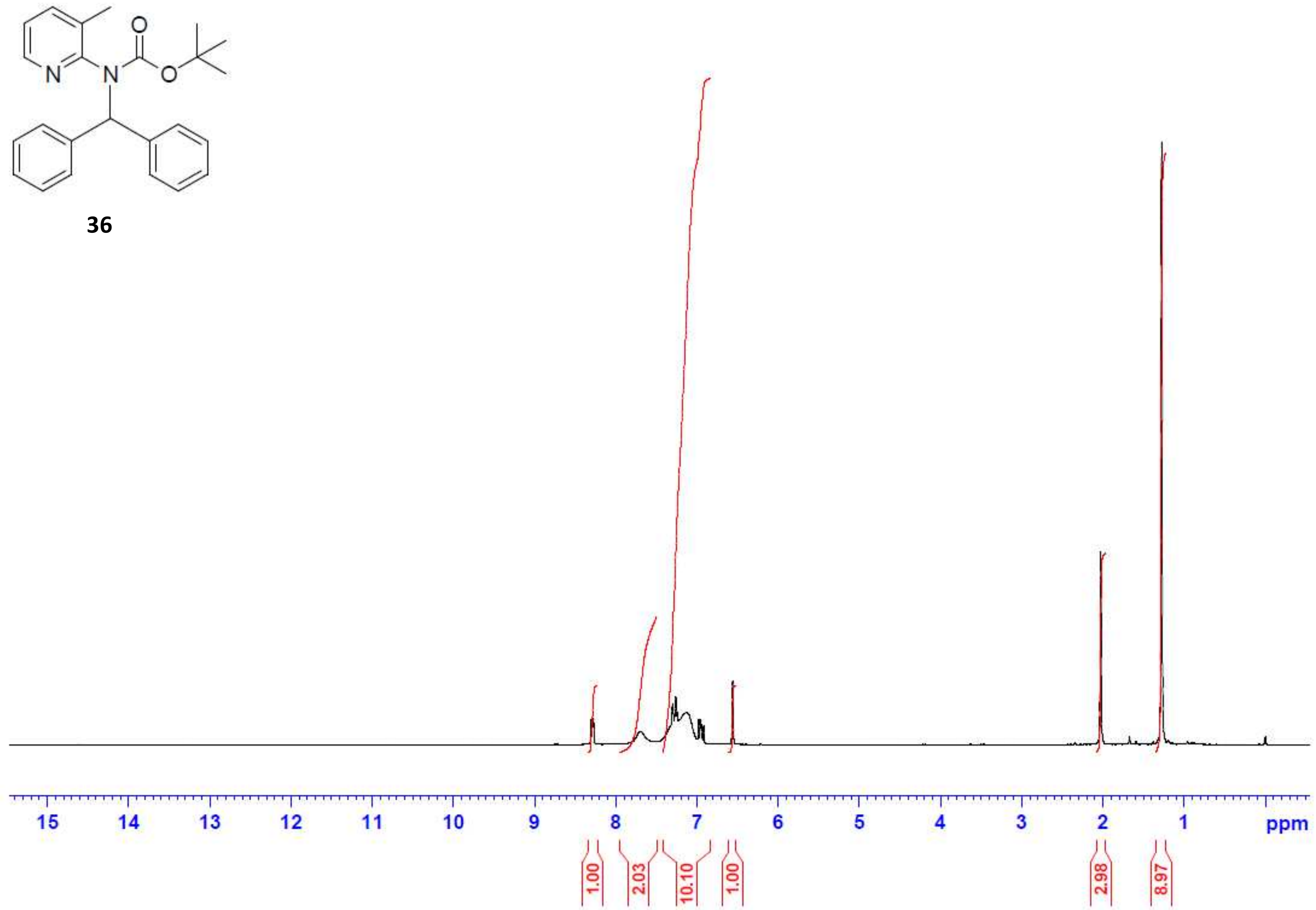
161.86
145.27
139.40
135.42
134.64
128.92
126.86
126.21
125.87
124.90
117.78
77.79
77.16
76.52
51.59
48.54
29.86
18.54
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

29

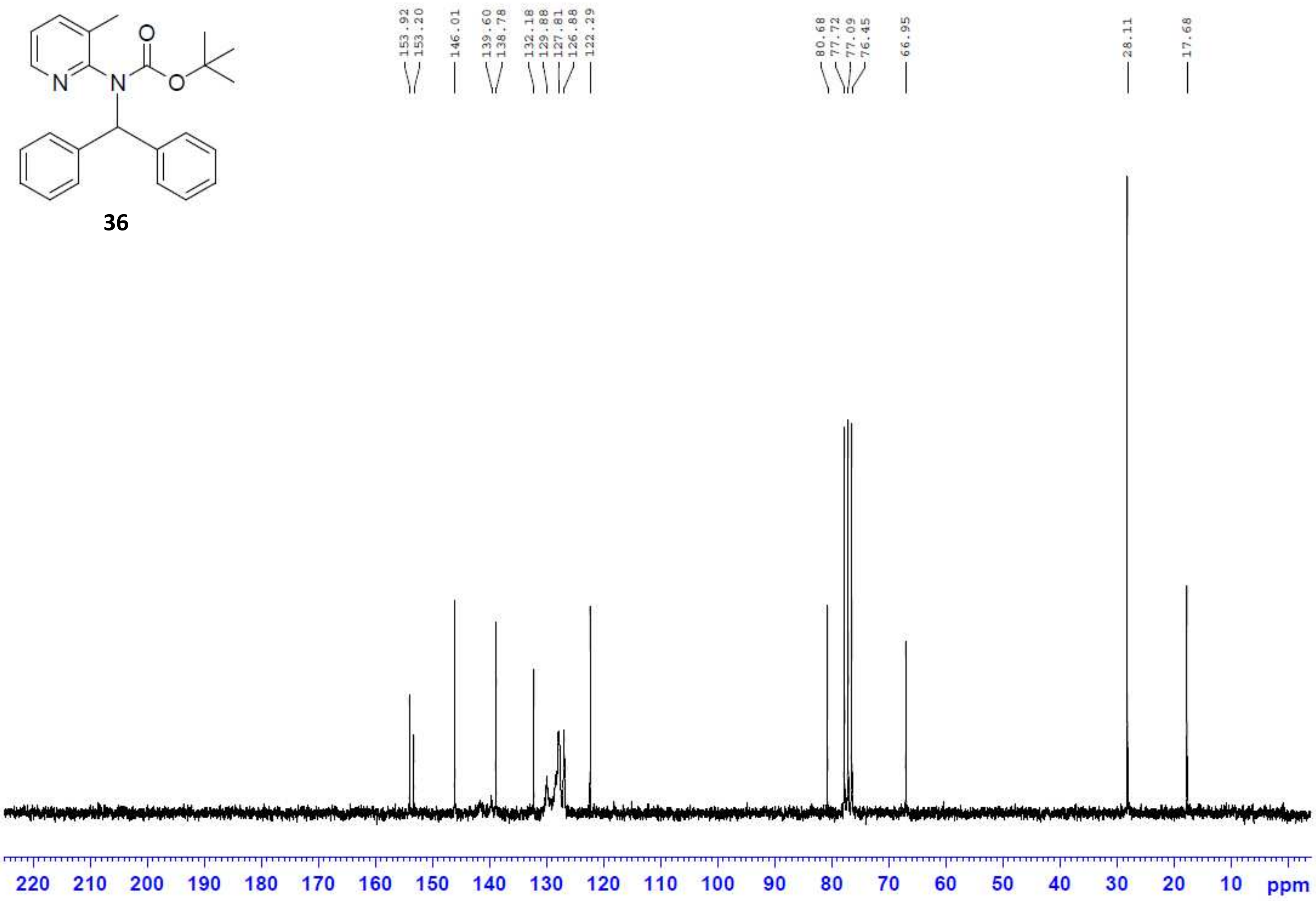




30

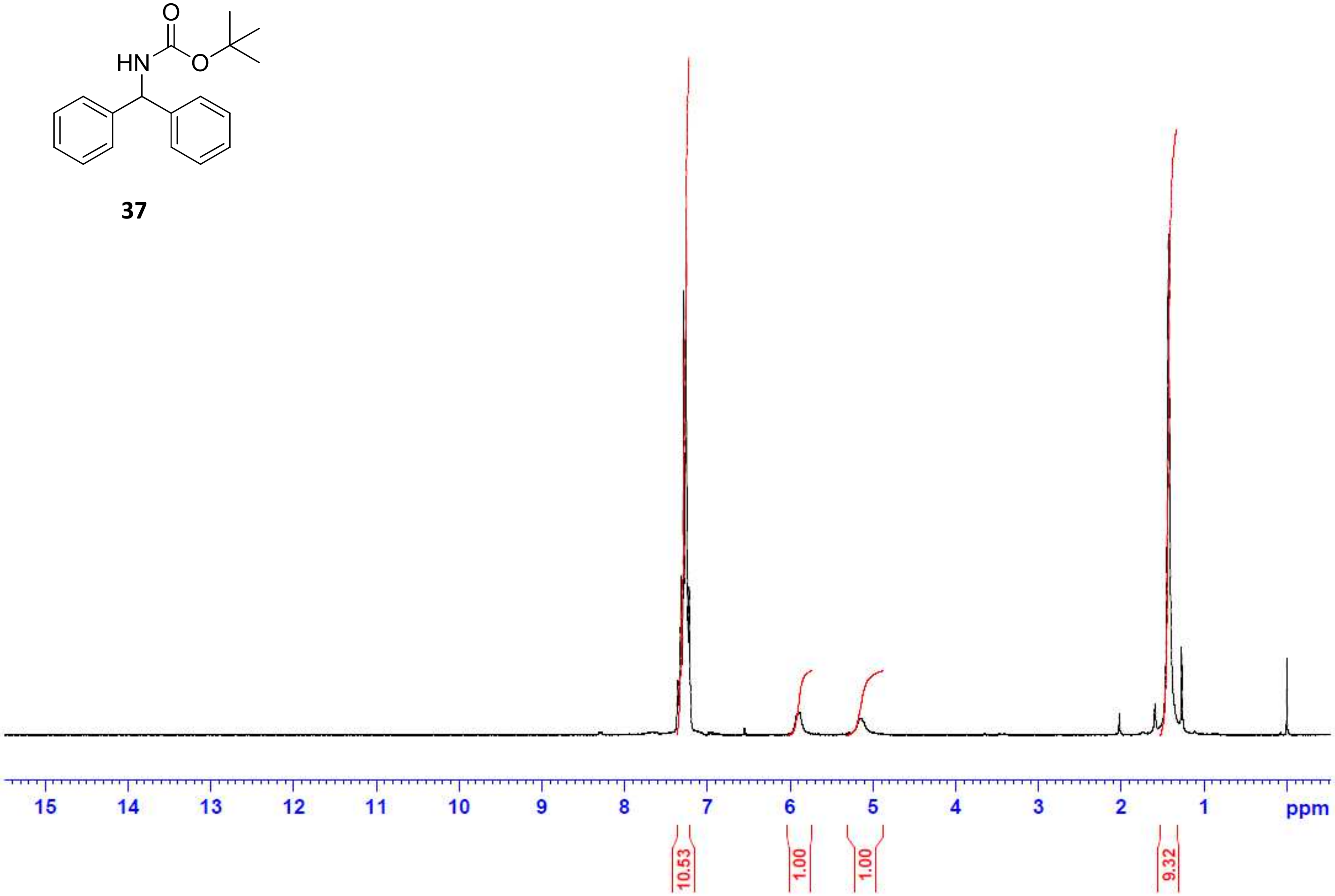


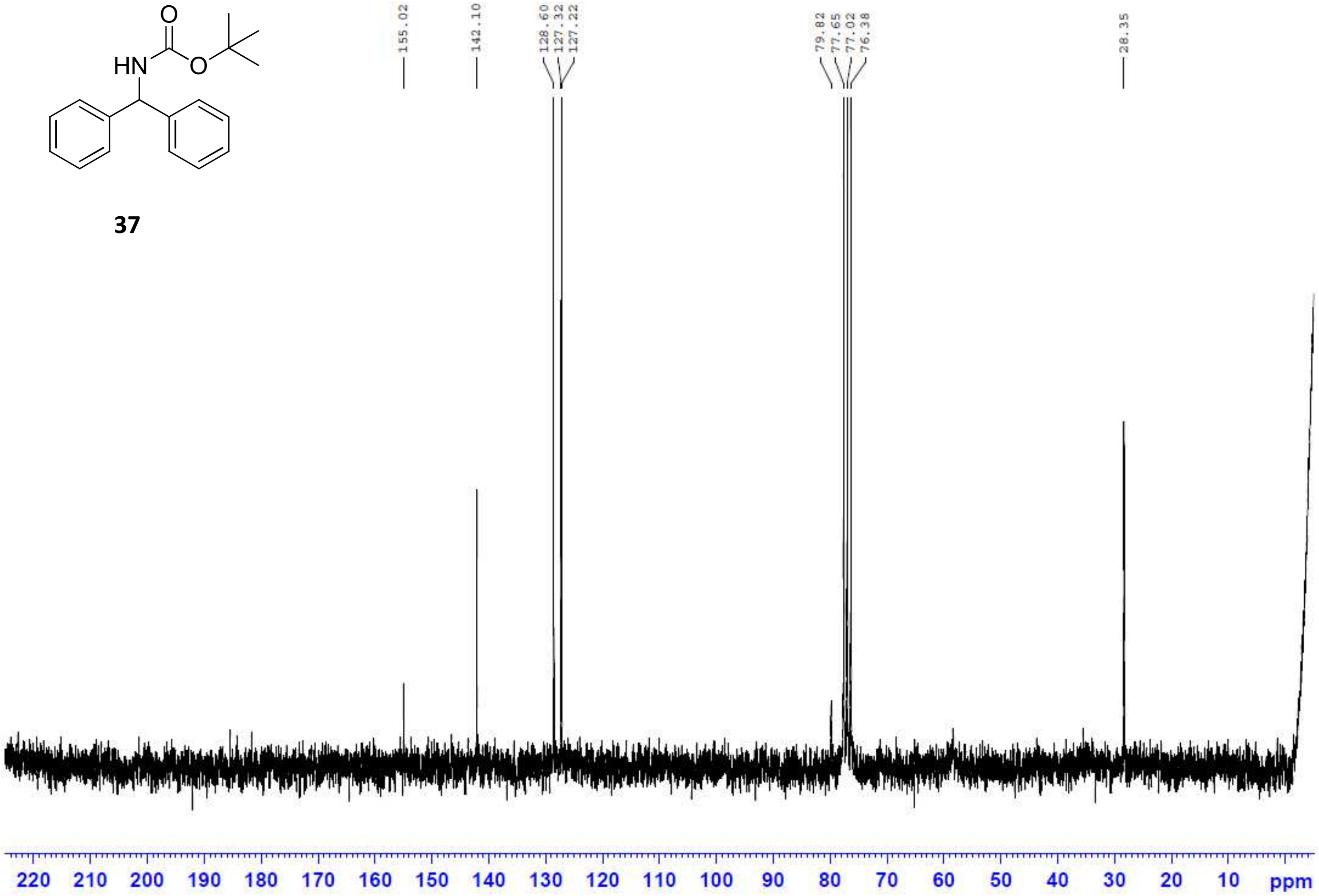
36



36

153.92
153.20
146.01
139.60
138.78
132.18
129.88
127.81
126.88
122.29
80.68
77.72
77.09
76.45
66.95
28.11
17.68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
N
N
O
O


37


HN
O
O
155.02
142.10
128.60
127.32
127.22
79.82
77.65
77.02
76.38
28.35
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

37

4. References

---

[1] *Gaussian 03,* R. C., Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. ; S.; Tomasi, J. B., V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.; Wallingford CT: 2004.

[2] Hehre, W. J. R., L.; Schleyer, P. v.R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: NY, 1986.

[3] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* 1997, *78*, 1396.