Supporting Information

Manganese(I)-Catalyzed Direct C-H Allylation of Arenes with Allenes

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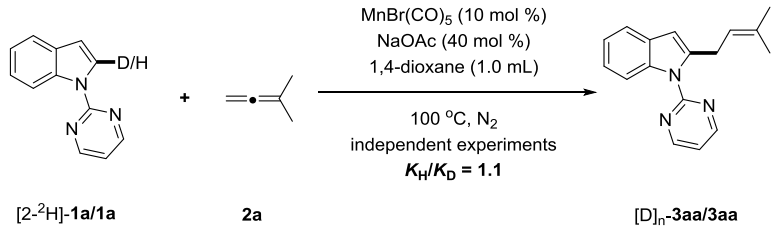
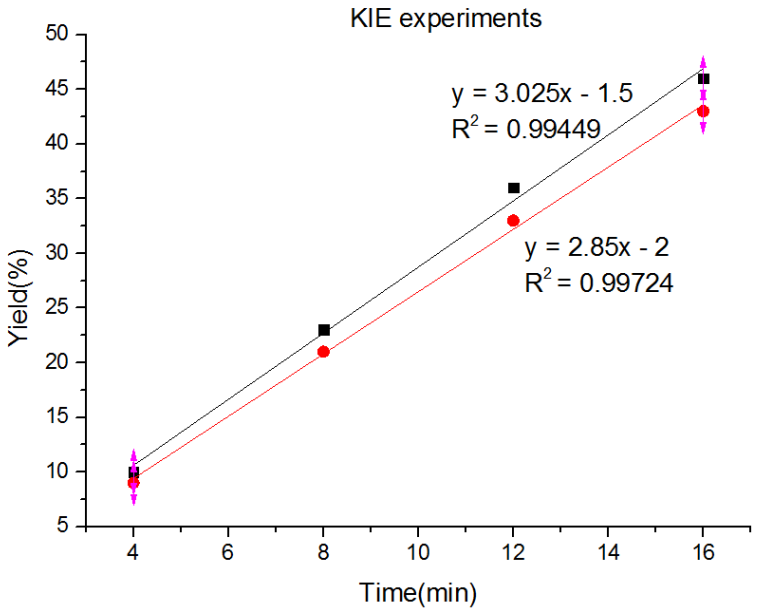
1. Mechanistic studies

1.1 Intermolecular KIE by independent experiments



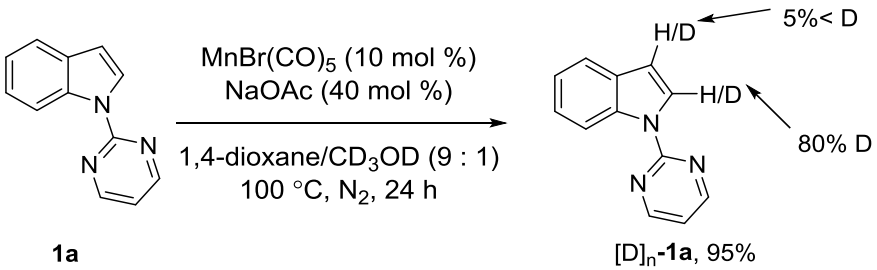
Two parallel reactions of 1,1-dimethylallene **2a** with **1a** and [2-^{2}H]-**1a** respectively were performed to determine the corresponding ***KIE*** value. **1a** (39.0 mg, 0.2 mmol) or [2-^{2}H]-**1a** (39.2 mg, 0.2 mmol), $MnBr(CO)_5$ (5.5 mg, 10 mol %), NaOAc (6.6 mg, 40 mol %), 1,4-dioxane (1.0 mL) and 1,1-dimethylallene **2a** (30 μL, 1.5 mmol) were placed in a 15 mL Schlenk tube. The mixture was stirred at 100 ℃. The crude yield was analysed by ^{1}H NMR using 1-iodo-4-methoxybenzene as the internal standard. The initial reaction rate was obtained by plotting the four points to obtain ***KIE***:

Time (min)	4	8	12	16
3aa	10	23	36	46
[D]$_n$-**3aa**	9	21	33	43

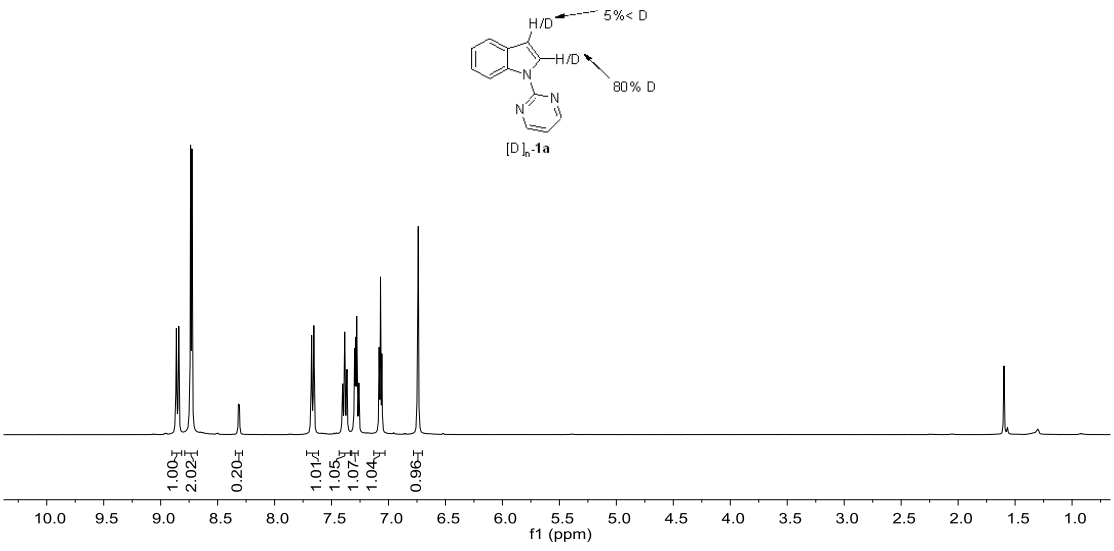


1.2 Manganese-catalyzed H/D exchange experiments

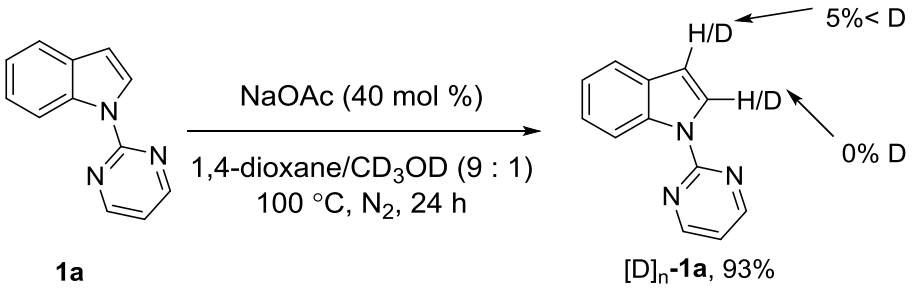
(a)



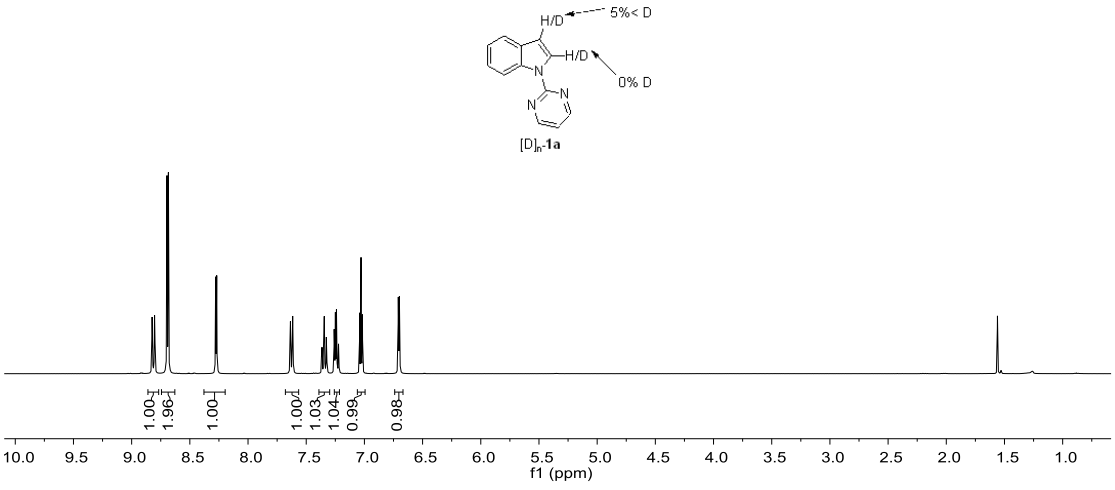
1-(Pyrimidin-2-yl)-1*H*-indole **1a** (0.2 mmol), NaOAc (6.6 mg, 40 mol %), $MnBr(CO)_5$ (5.5 mg, 10 mol %), 1,4-dioxane (0.9 mL) and CD_3OD (0.1 mL) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc (10 mL) and H_2O (5 mL). The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (10 mL), and then dried over Na_2SO_4. After concentration under reduced pressure, purification by column chromatography on silica gel (PE/EtOAc = 50/1) yielded $[D]_n$-**1a** (37.0 mg, 95%). The D incorporation was determined by ^{1}H-NMR spectroscopy.



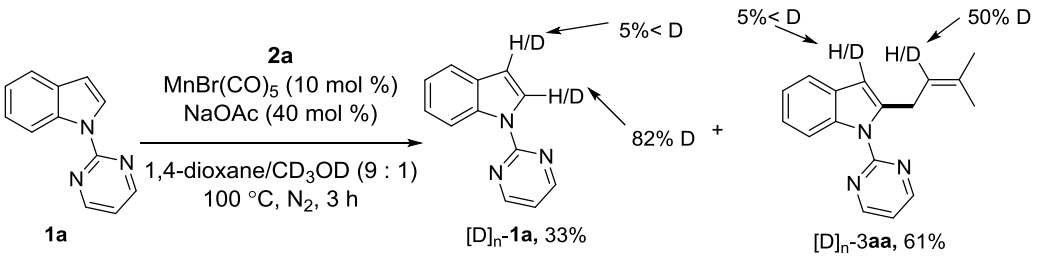
(b)



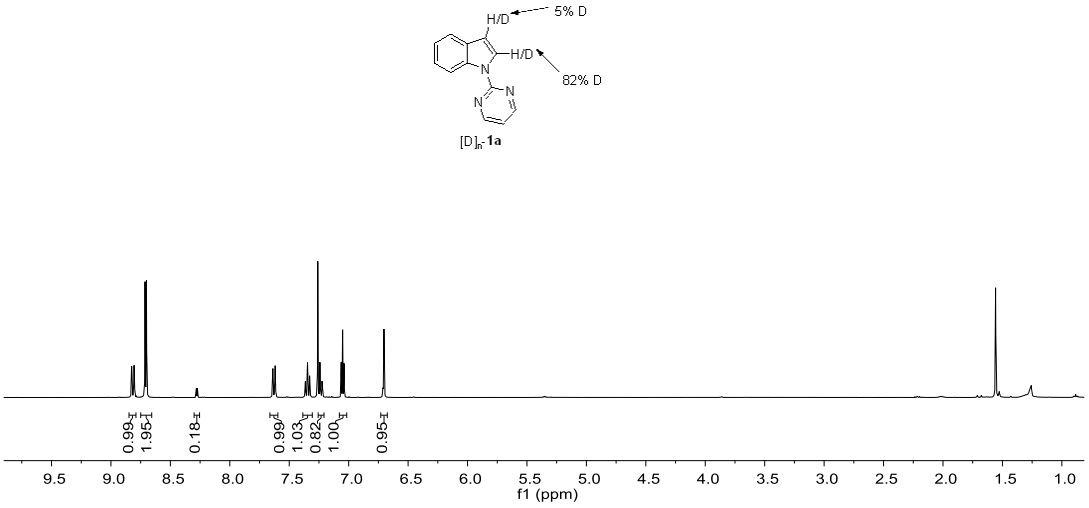
1-(Pyrimidin-2-yl)-1*H*-indole **1a** (0.2 mmol), NaOAc (6.6 mg, 40 mol %), 1,4-dioxane (0.9 mL) and CD_3OD (0.1 mL) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc (10 mL) and H_2O (5 mL). The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (10 mL), and then dried over Na_2SO_4. After concentration under reduced pressure, purification by column chromatography on silica gel (PE/EtOAc = 50/1) yielded $[D]_n$-**1a** (36.5 mg, 96%). The D incorporation was determined by ^{1}H-NMR spectroscopy.

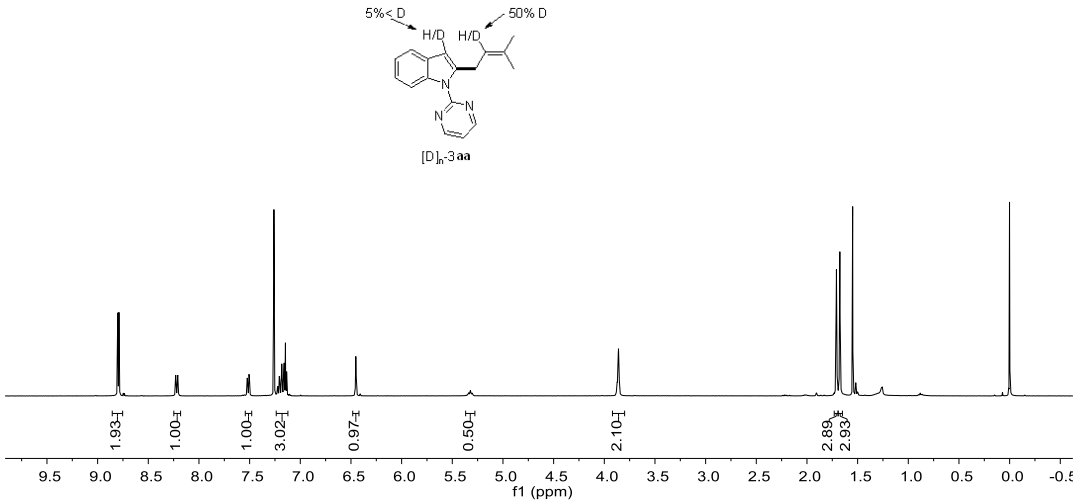


(c)

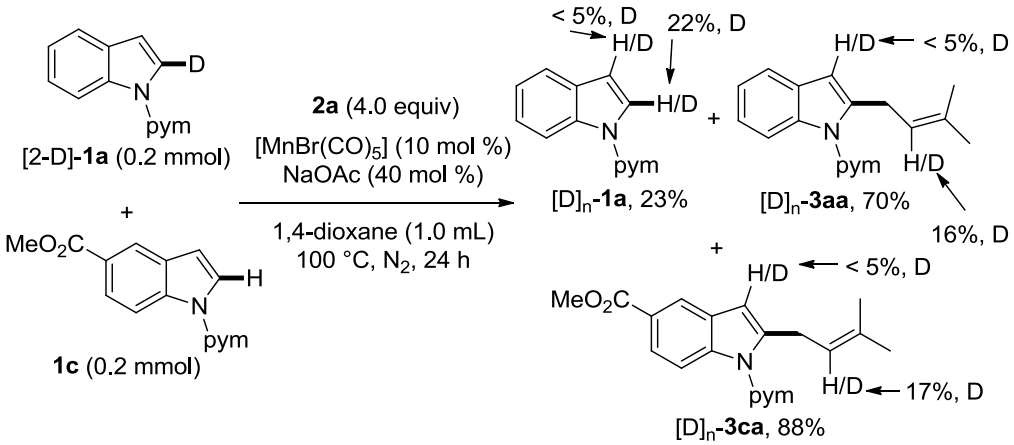


1-(Pyrimidin-2-yl)-1*H*-indole **1a** (0.2 mmol), NaOAc (6.6 mg, 40 mol %), $MnBr(CO)_5$ (5.5 mg, 10 mol %), 1,4-dioxane (1.0 mL) and 1,1-dimethylallene **2a** (0.3 mmol, 1.5 equiv) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc (10 mL) and H_2O (5 mL). The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (10 mL), and then dried over Na_2SO_4. After concentration under reduced pressure, purification by column chromatography on silica gel (PE/EtOAc = 64/1) yielded $[D]_n$-**1a** (13.0 mg, 33%) and $[D]_n$-**3aa** (31.5 mg, 61%). The D incorporation was determined by ^{1}H-NMR spectroscopy.



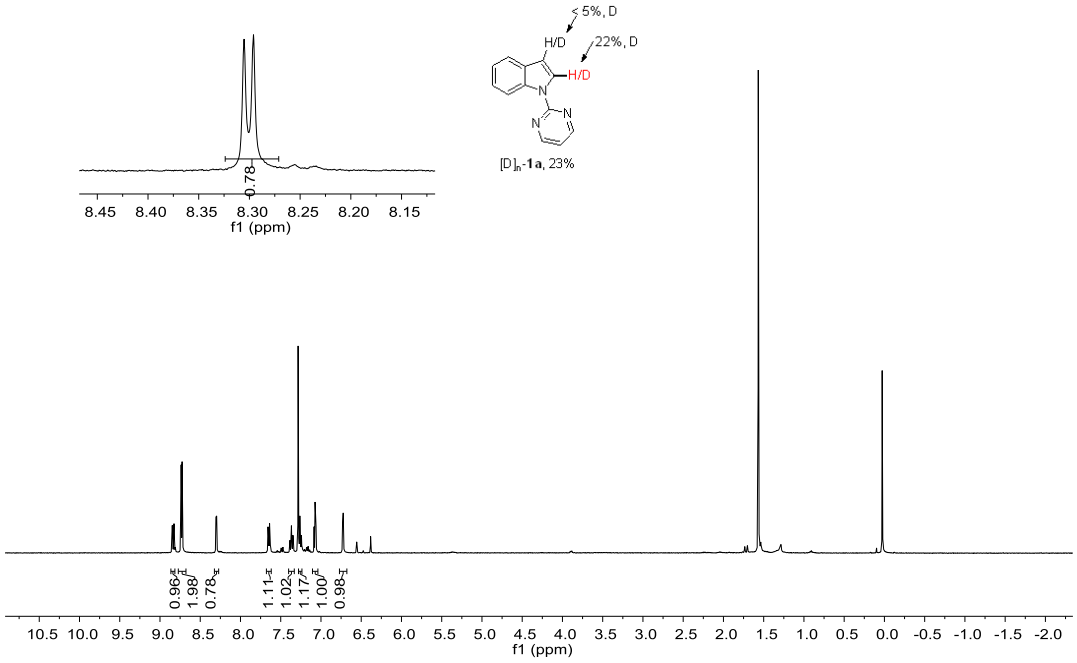


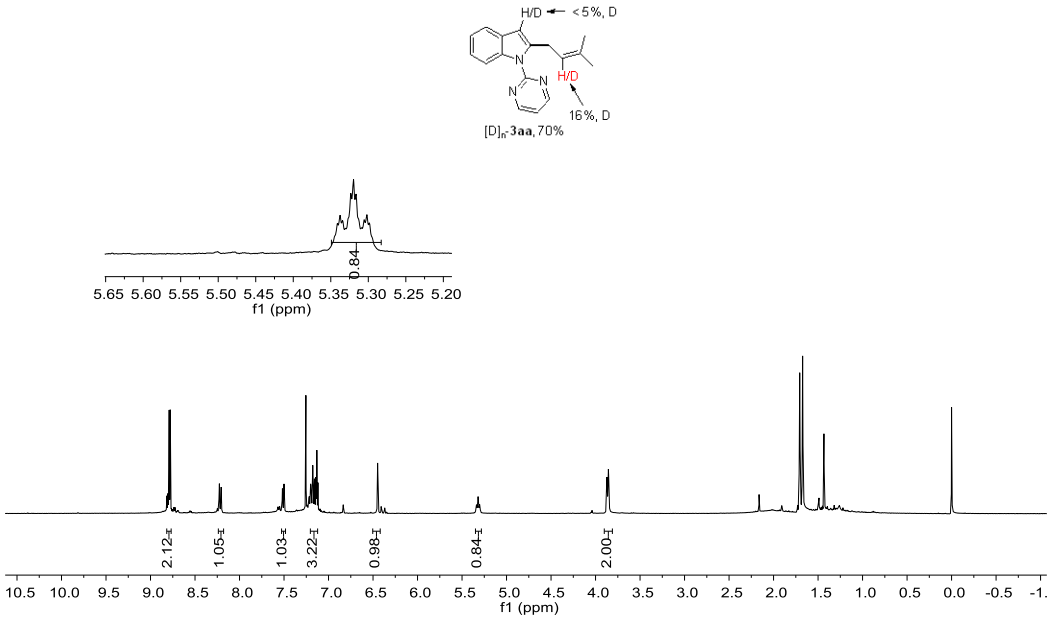
(d)

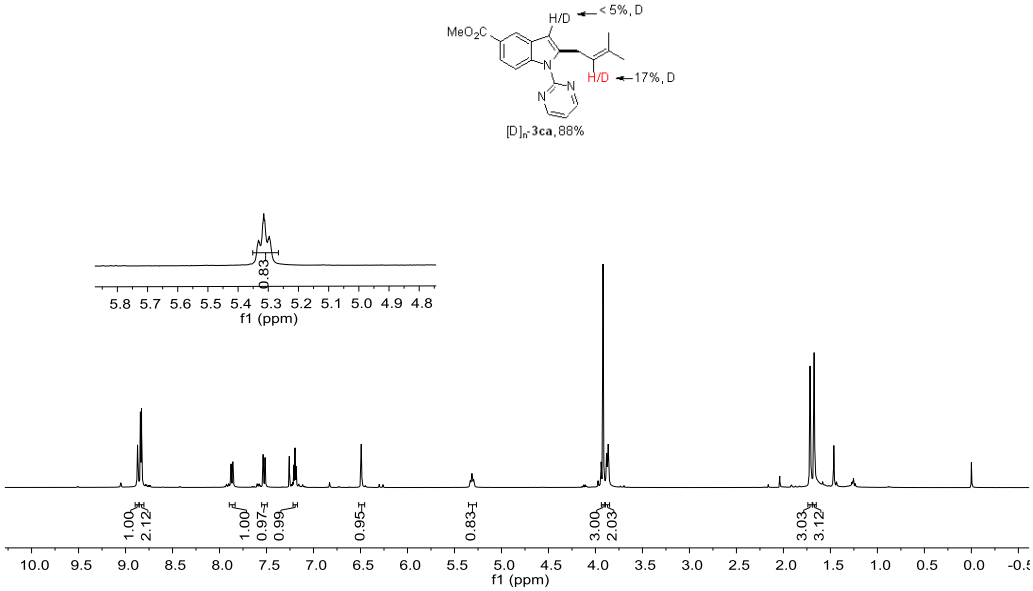


[2-^{2}H]-**1a** (0.2 mmol), **1c**, NaOAc (6.6 mg, 40 mol %), $MnBr(CO)_5$ (5.5 mg, 10 mol %), 1,4-dioxane (1.0 mL) and 1,1-dimethylallene **2a** (0.8 mmol, 4.0 equiv) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc (10 mL) and H_2O (5 mL). The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (10 mL), and then dried over Na_2SO_4. After concentration under reduced pressure, purification by column chromatography on silica gel (PE/EtOAc = 64/1→16/1) yielded $[D]_n$-**1a** (9.0 mg, 23%), $[D]_n$-**3aa** (36.7

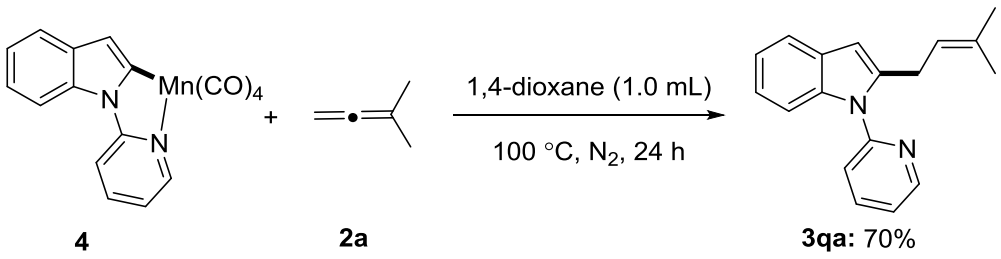
mg, 70%) and $[D]_n$-**3ca** (56.5 mg, 88%). The D incorporation was determined by ^{1}H-NMR spectroscopy.





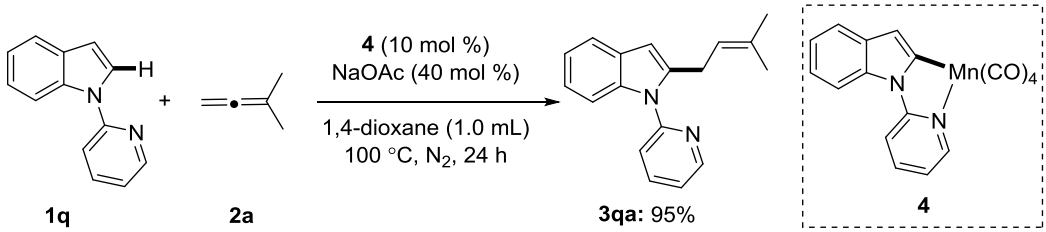


1.3 Stoichiometric prenylation with cyclometalated complex 4[1]



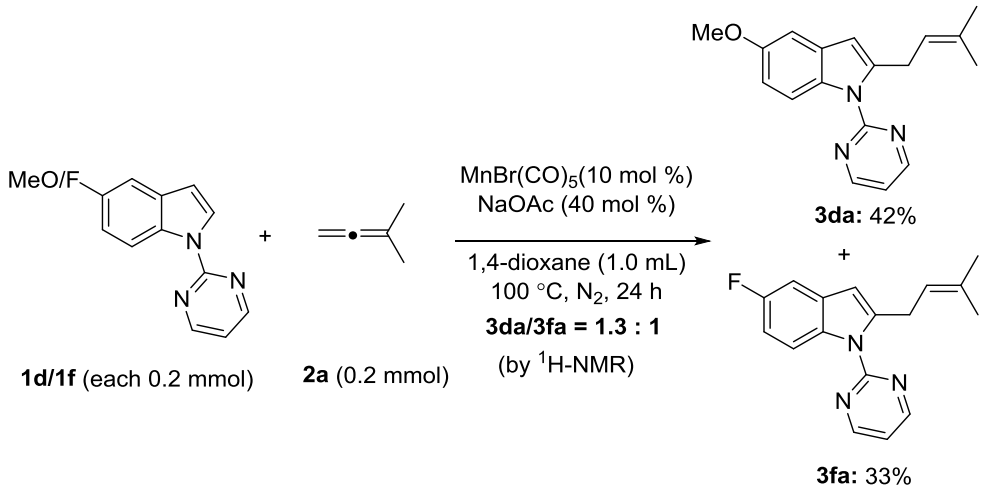
4 (72 mg, 0.2 mmol), 1,1-dimethylallene **2a** (30 μL, 0.3 mmol), and 1,4-dioxane (1.0 mL) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was transferred into a round flask with EtOAc and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (PE/EtOAc = 64/1) afforded product **3qa** (36.7, 70%).

1.4 Catalytic reactivity of cyclometalated complex 4



1-(Pyridin-2-yl)-1*H*-indole **1q** (38.8 mg, 0.2 mmol), 1,1-dimethylallene **2a** (30 μL, 0.20 mmol), **4** (7.2 mg, 10 mol %), NaOAc (6.6 mg, 40 mol %) and 1,4-dioxane (1.0 mL) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was transferred into around flask with EtOAc and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (PE/EtOAc = 64/1) afforded the desired product **3qa** (49.8 mg, 95% based on 0.20 mmol).

1.5 Intermolecular competition experiments between arenes 1d and 1f:

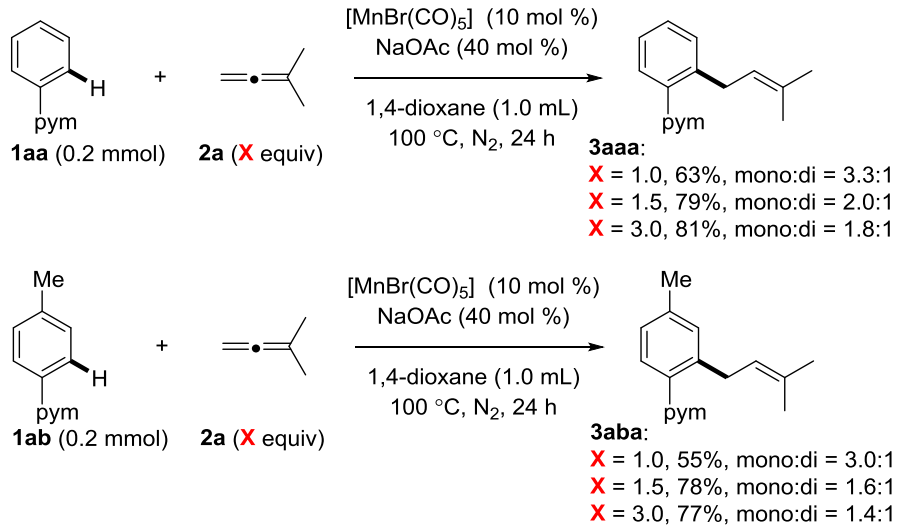


5-Methoxy-1-(pyrimidin-2-yl)-1*H*-indole (**1d**) (45 mg, 0.20 mmol), 5-fluoro-1-(pyrimidin-2-yl)-1*H*-indole (**1f**) (43 mg, 0.20 mmol), 1,1-dimethylallene (**2a**) (20 μL, 0.20 mmol), $MnBr(CO)_5$ (5.5 mg, 10 mol %), NaOAc (6.6 mg, 40 mol %) and 1,4-dioxane (1.0 mL) were placed in a 15 mL Schlenk tube under N_2. The mixture was stirred at 100 ℃ for 24 h. At ambient temperature, the reaction mixture was

diluted with EtOAc (10 mL), then 1-iodo-4-methoxybenzene (46.8 mg, 0.2 mmol) was added as internal standard, the crude mixture was analyzed to obtain the ^{1}H-NMR conversion of the products **3da** (42%) and **3fa** (33%).

2. The mono- and diprenylation selectivity by using different equivalents of 2a

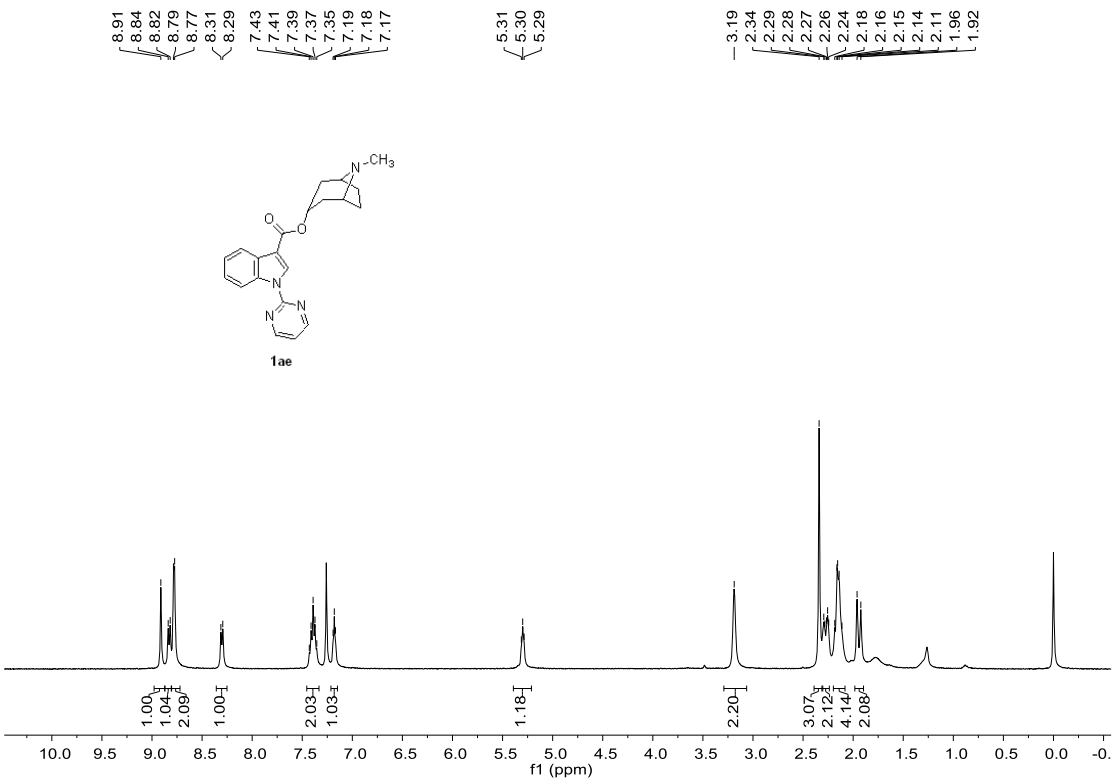
Scheme 2



3. Reference

1. Liu, W.; Richter, S. C.; Zhang, Y.; Ackermann, L. *Angew. Chem. Int. Ed*. **2016**, *55*, 7747.

4. NMR spectrum of some starting materials and products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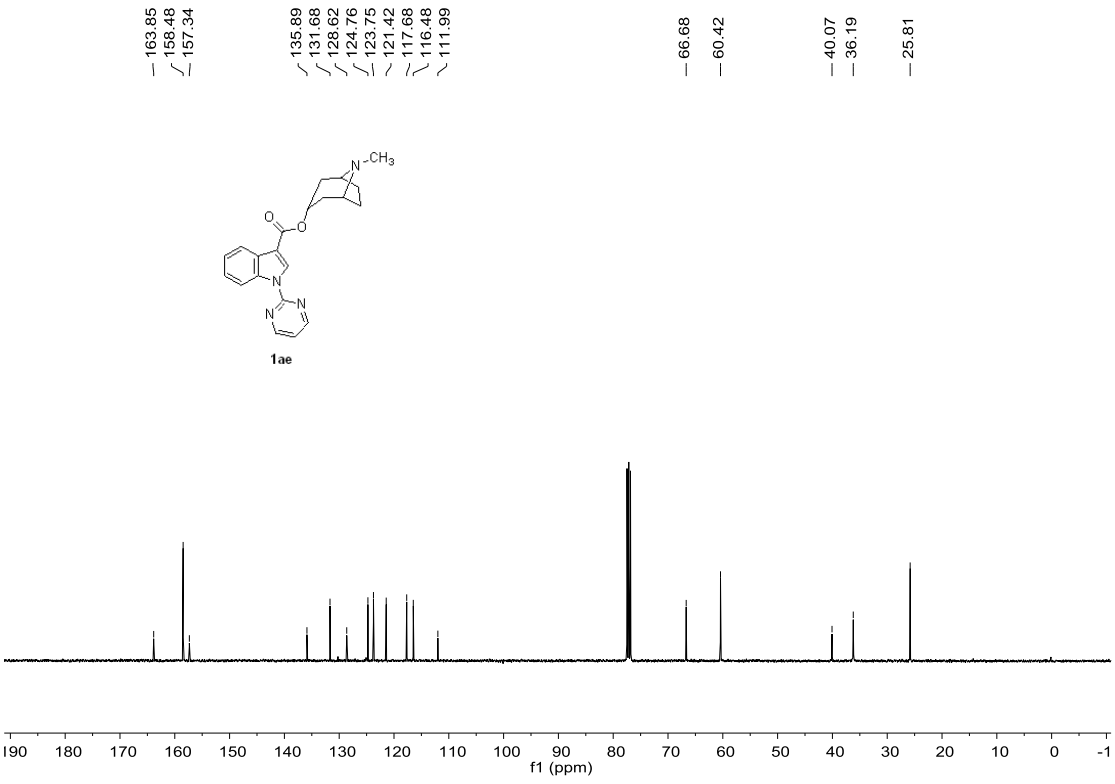
8.84
8.82
8.79
8.77
8.31
8.29
7.43
7.41
7.39
7.37
7.35
7.19
7.18
7.17
5.31
5.30
5.29
3.19
2.34
2.29
2.28
2.27
2.26
2.24
2.18
2.16
2.15
2.14
2.11
1.96
1.92
1ae
1.00
1.04
2.09
1.00
2.03
1.03
1.18
2.20
3.07
2.12
4.14
2.08
f1 (ppm)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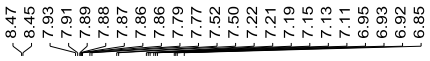
157.34
135.89
131.68
128.62
124.76
123.75
121.42
117.68
116.48
111.99
66.68
60.42
40.07
36.19
25.81
1ae
f1 (ppm)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8.45
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7.87
7.86
7.86
7.79
7.77
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7.22
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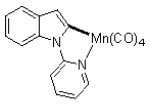
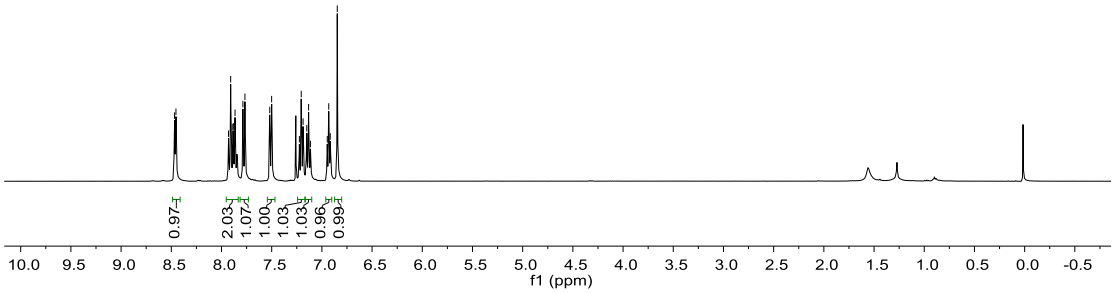
6.93
6.92
6.85


Mn(CO)4
N
N

4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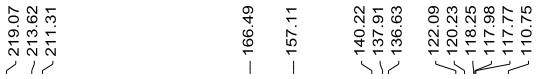
2.03
1.07
1.00
1.03
1.03
0.96
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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213.62
211.31
166.49
157.11
140.22
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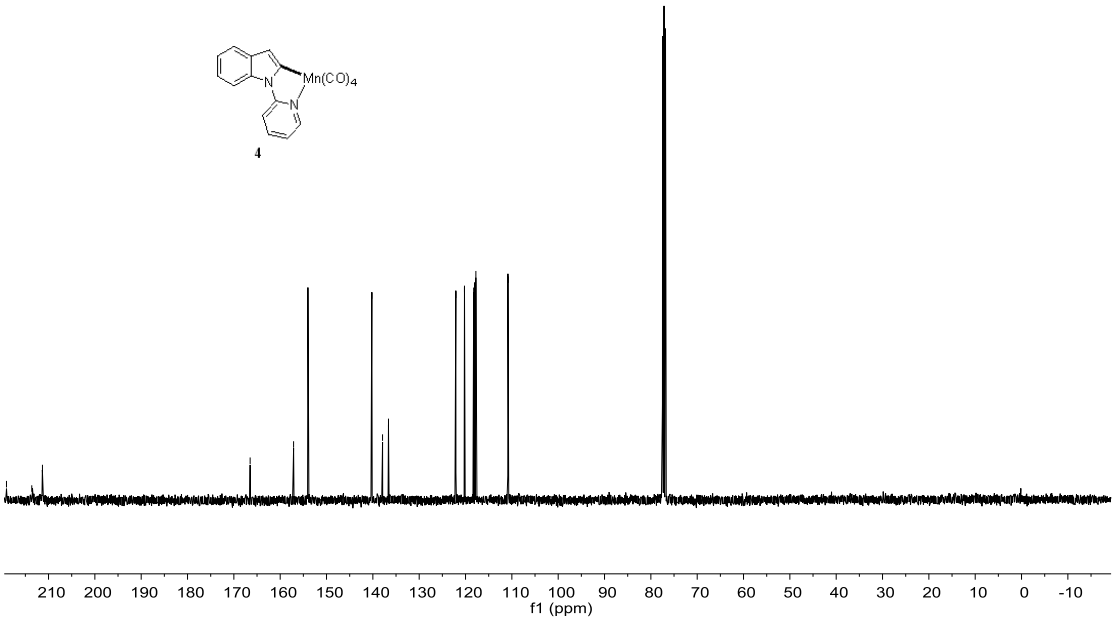
122.09
120.23
118.25
117.98
117.77
110.75

Mn(CO)4
N
N

4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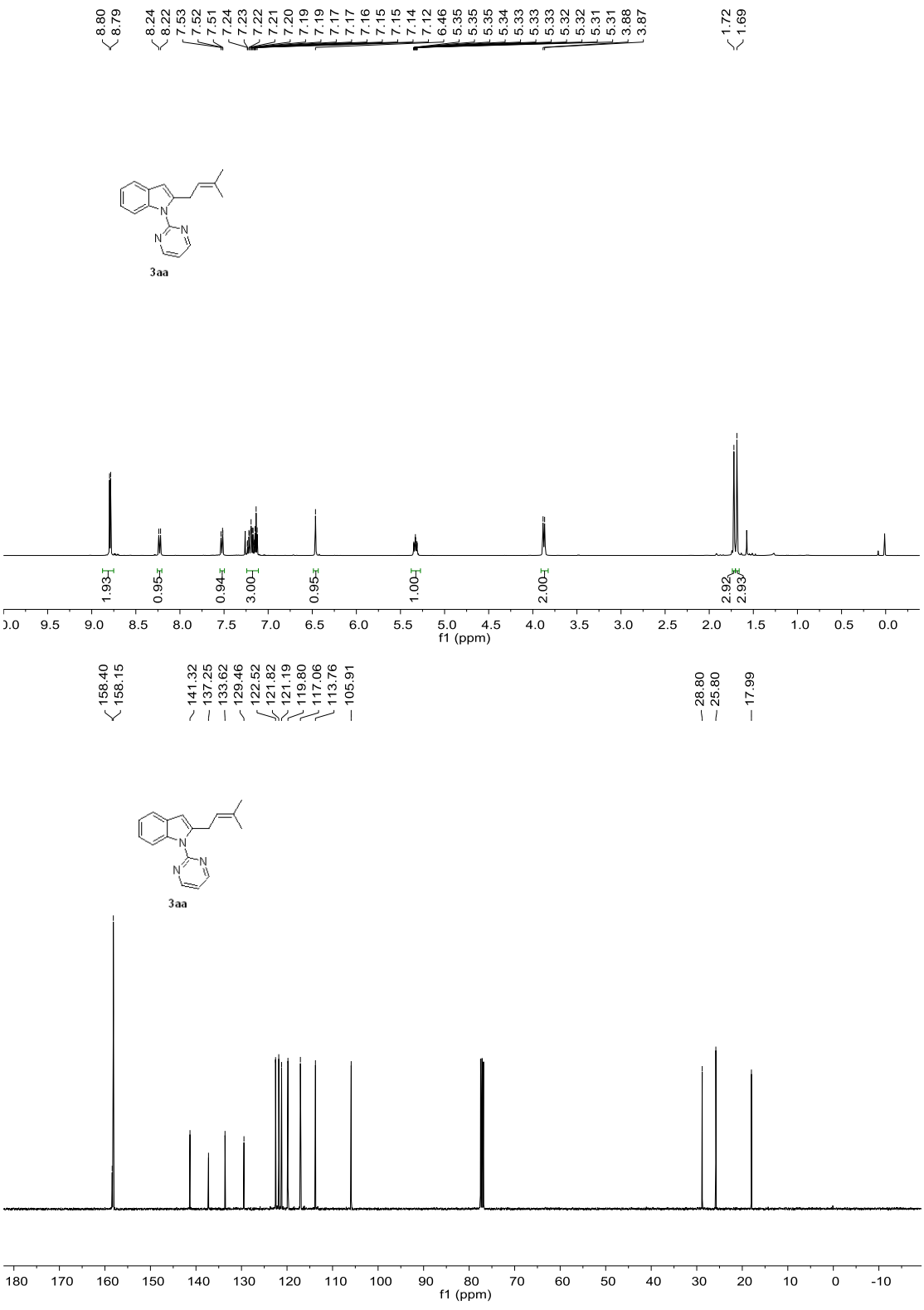
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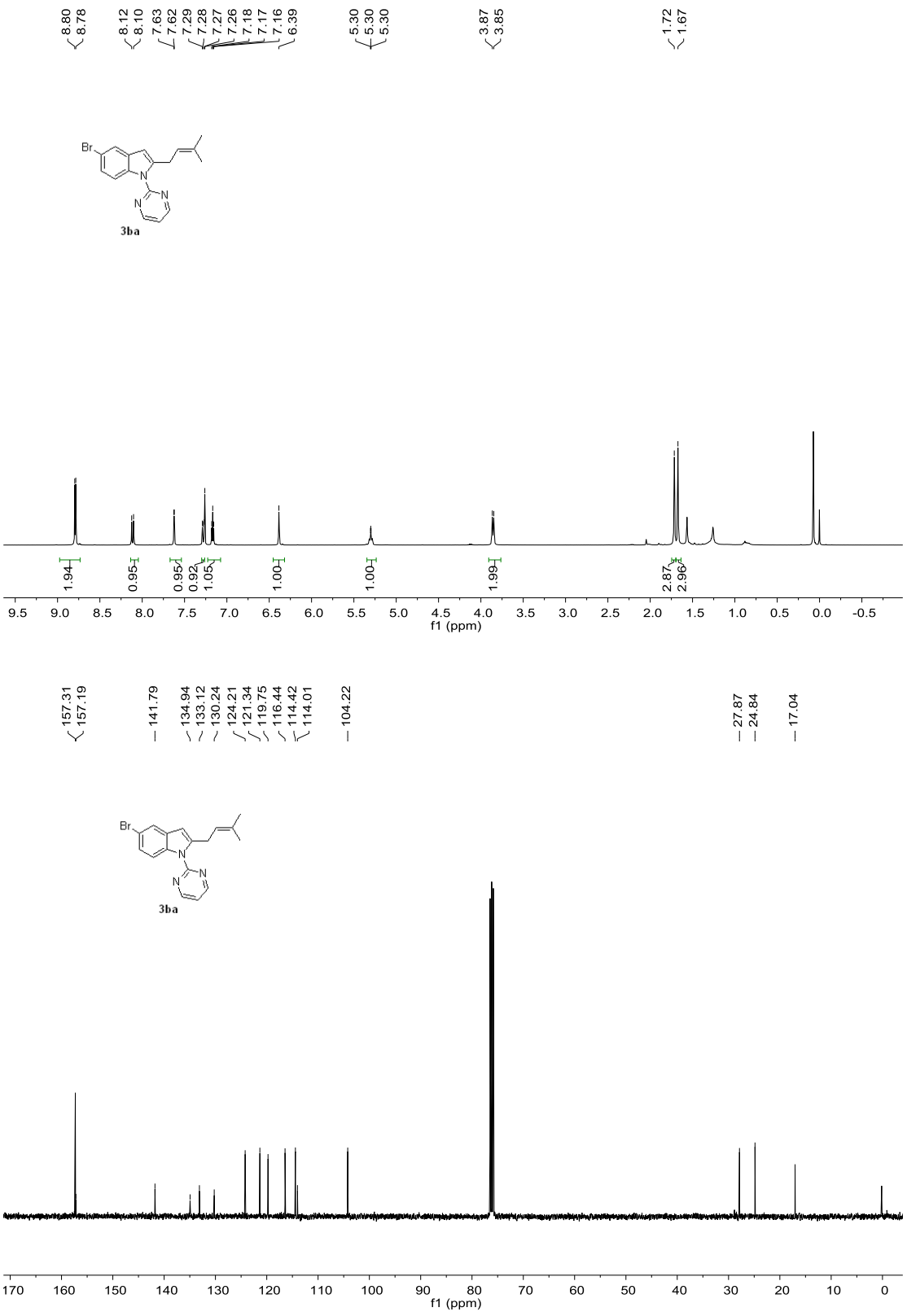
7.52
7.51
7.24
7.23
7.22
7.21
7.20
7.19
7.19
7.17
7.17
7.16
7.15
7.15
7.14
7.12
6.46
5.35
5.35
5.35
5.34
5.33
5.33
5.33
5.32
5.32
5.31
5.31
3.88
3.87
1.72
1.69
3aa
1.93
0.95
0.94
3.00
0.95
1.00
2.00
2.92
2.93
f1 (ppm)
158.40
158.15
141.32
137.25
133.62
129.46
122.52
121.82
121.19
119.80
117.06
113.76
105.91
28.80
25.80
17.99
3aa
f1 (ppm)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8.78
8.12
8.10
7.63
7.62
7.29
7.28
7.27
7.26
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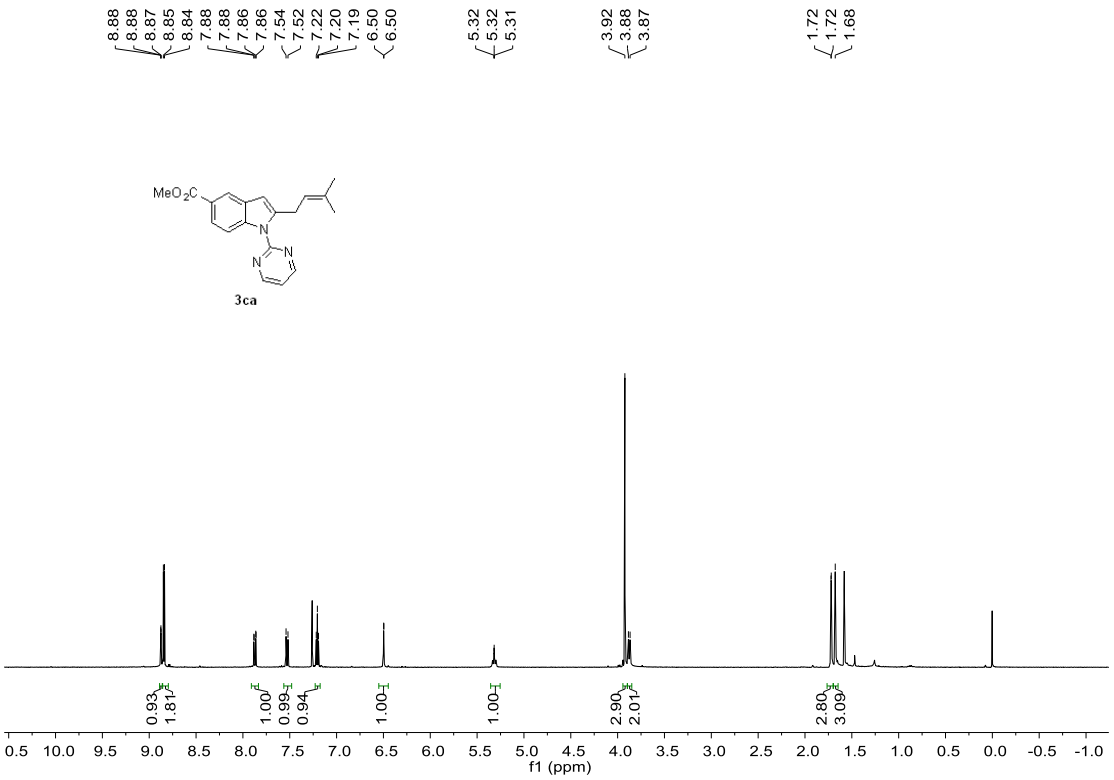
7.17
7.16
6.39
5.30
5.30
5.30
3.87
3.85
1.72
1.67
Br
N
N
N
3ba
1.94
0.95
0.95
0.92
1.05
1.00
1.00
1.99
2.87
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
157.31
157.19
141.79
134.94
133.12
130.24
124.21
121.34
119.75
116.44
114.42
114.01
104.22
27.87
24.84
17.04
Br
N
N
N
3ba
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.88
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8.85
8.84
7.88
7.88
7.86
7.86
7.54
7.52
7.22
7.20
7.19
6.50
6.50
5.32
5.32
5.31
3.92
3.88
3.87
1.72
1.72
1.68
MeO2C
N
N
N
3ca
0.93
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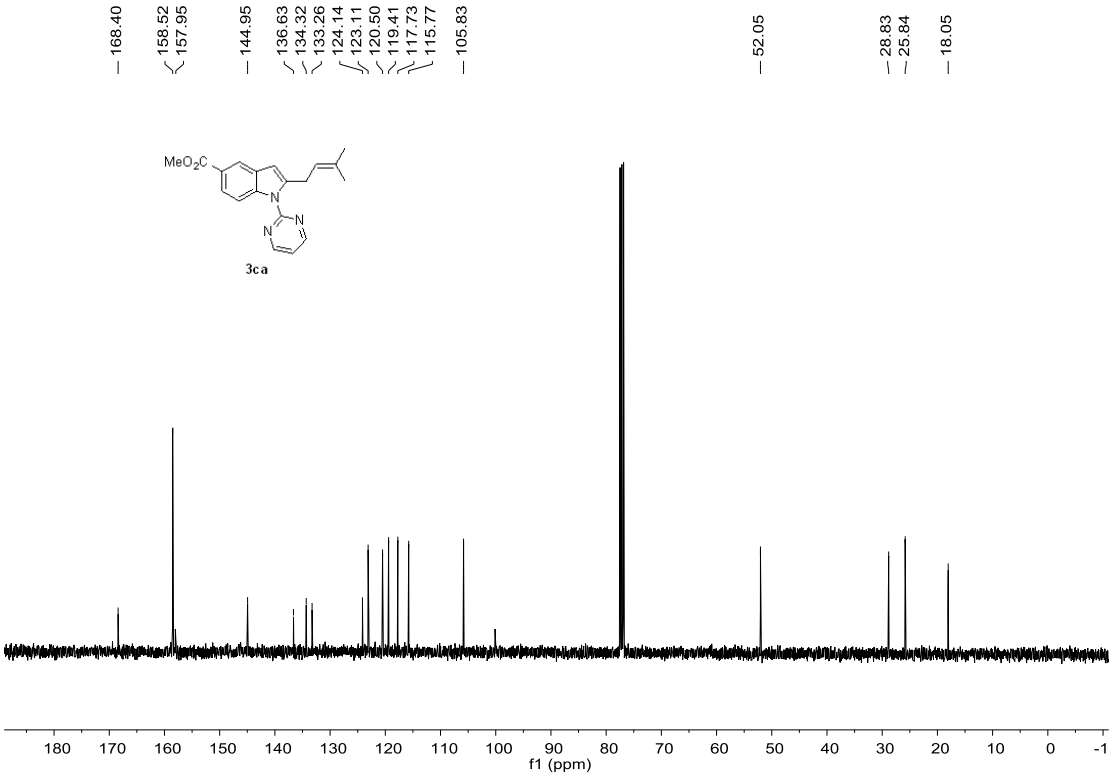
1.00
0.99
0.94
1.00
1.00
2.90
2.01
2.80
3.09
f1 (ppm)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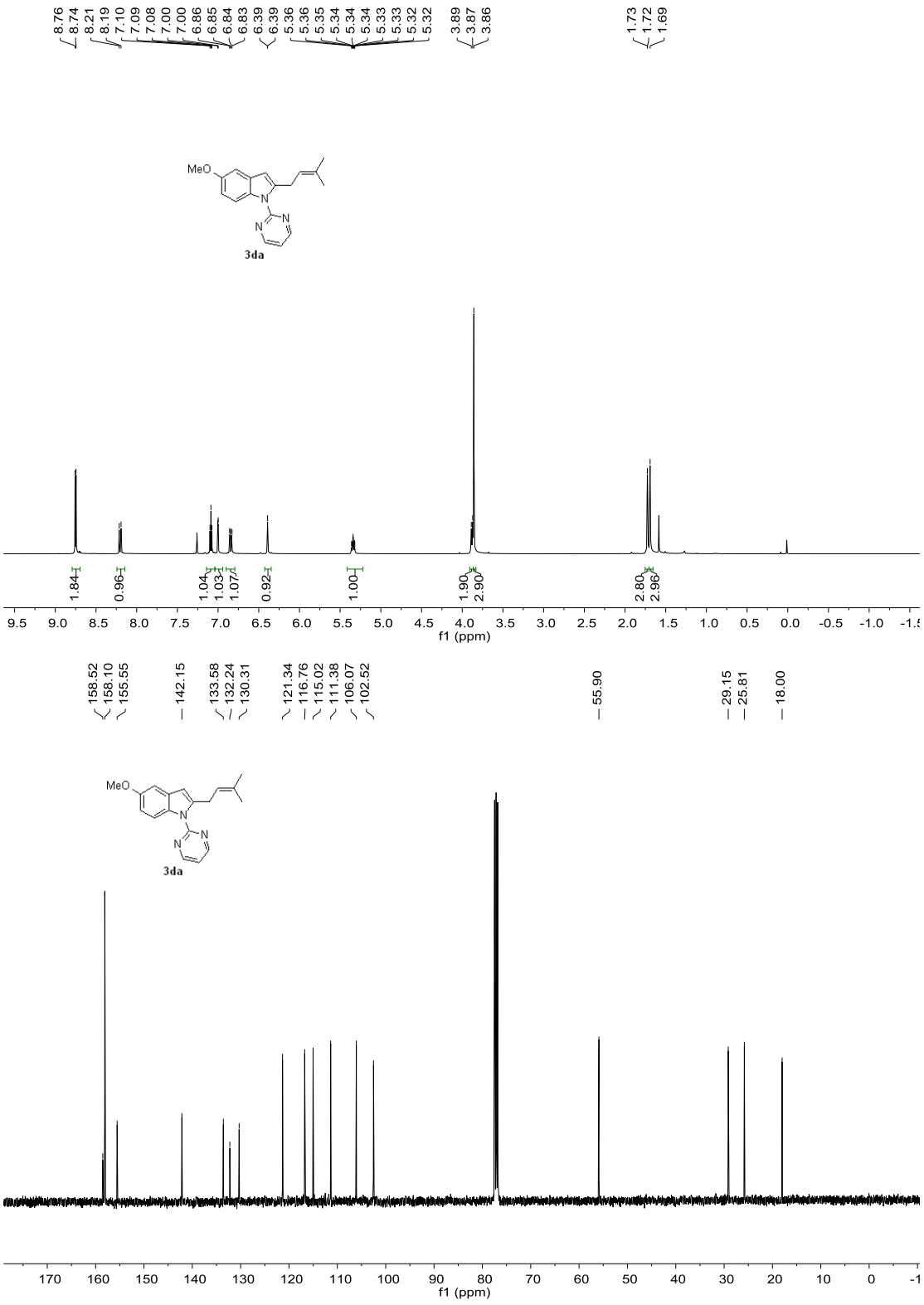
MeO2C
N
N
N
3ca
f1 (ppm)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5.36
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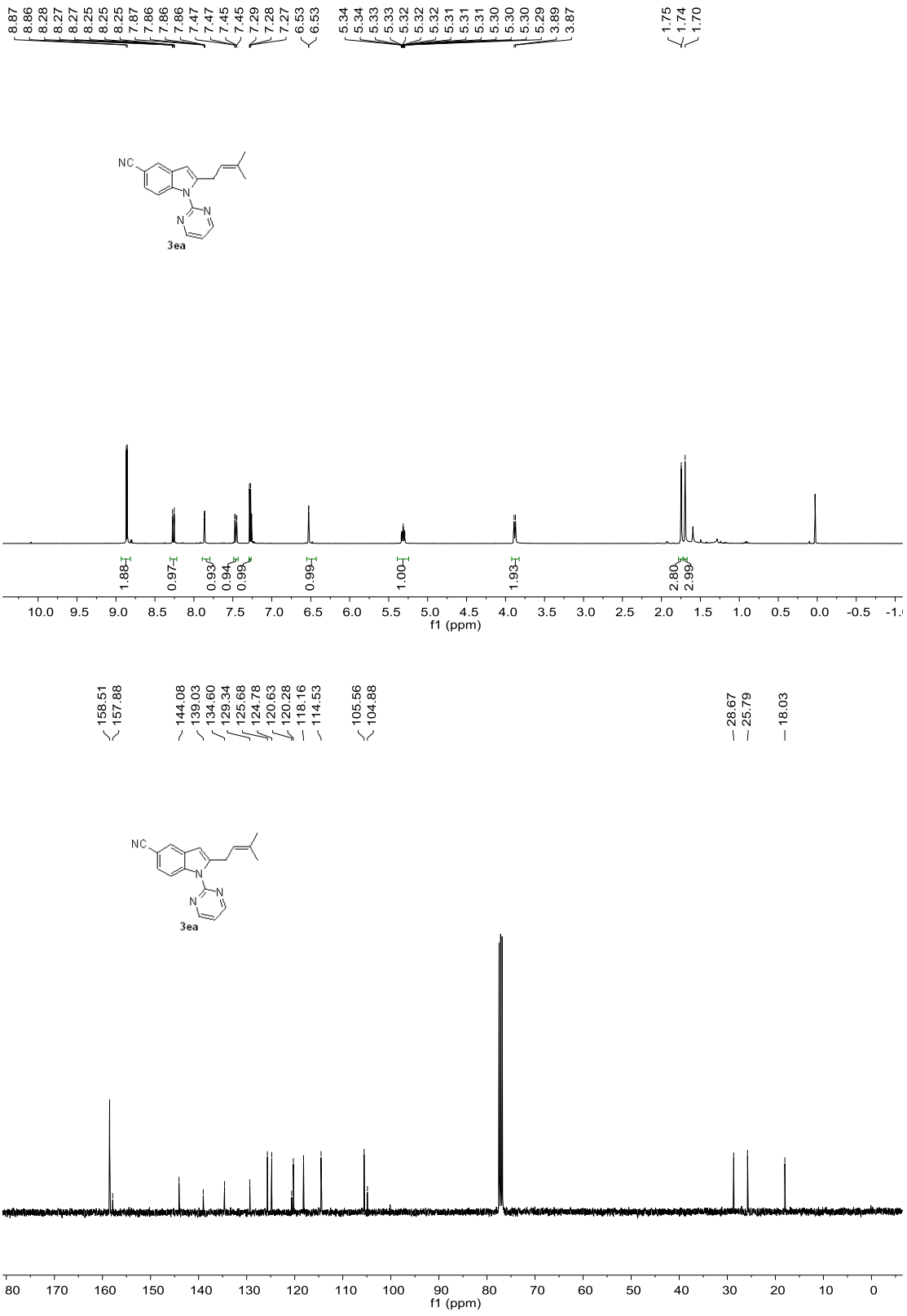
5.34
5.34
5.33
5.33
5.32
5.32
3.89
3.87
3.86
1.73
1.72
1.69
MeO
N
N
N
3da
1.84
0.96
1.04
1.03
1.07
0.92
1.00
1.90
2.90
2.80
2.96
f1 (ppm)
158.52
158.10
155.55
142.15
133.58
132.24
130.31
121.34
116.76
115.02
111.38
106.07
102.52
55.90
29.15
25.81
18.00
MeO
N
N
N
3da
f1 (ppm)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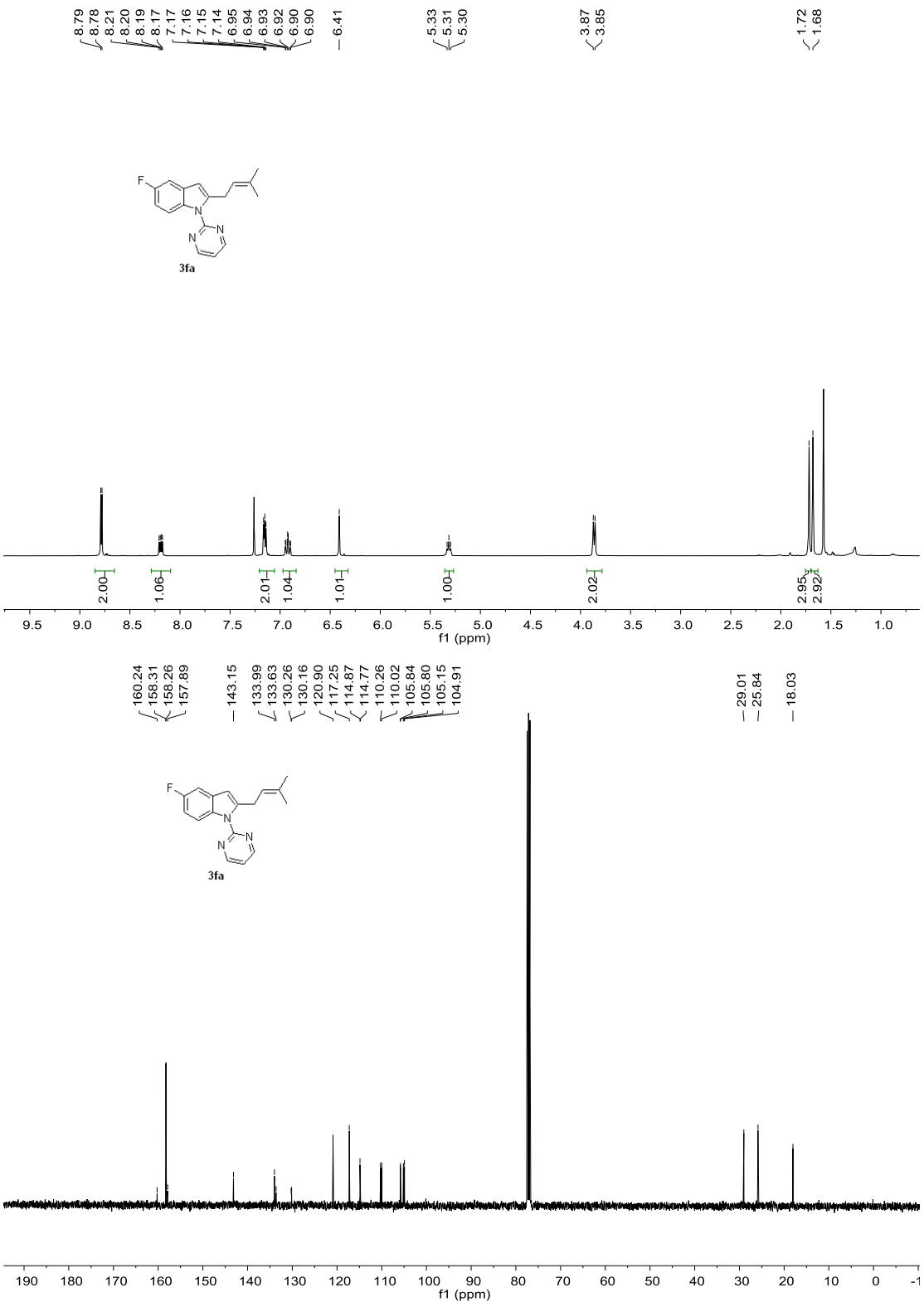
8.86
8.28
8.27
8.27
8.25
8.25
8.25
7.87
7.86
7.86
7.86
7.47
7.47
7.45
7.45
7.29
7.28
7.27
6.53
6.53
5.34
5.34
5.33
5.33
5.32
5.32
5.32
5.31
5.31
5.31
5.30
5.30
5.30
5.29
3.89
3.87
1.75
1.74
1.70
NC
N
N
N
3ea
1.88
0.97
0.93
0.94
0.99
0.99
1.00
1.93
2.80
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
158.51
157.88
144.08
139.03
134.60
129.34
125.68
124.78
120.63
120.28
118.16
114.53
105.56
104.88
28.67
25.79
18.03
NC
N
N
N
3ea
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.78
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8.17
7.17
7.16
7.15
7.14
6.95
6.94
6.93
6.92
6.90
6.90
6.41
5.33
5.31
5.30
3.87
3.85
1.72
1.68
F
N
N
3fa
2.00
1.06
2.01
1.04
1.01
1.00
2.02
2.95
2.92
f1 (ppm)
160.24
158.31
158.26
157.89
143.15
133.99
133.63
130.26
130.16
120.90
117.25
114.87
114.77
110.26
110.02
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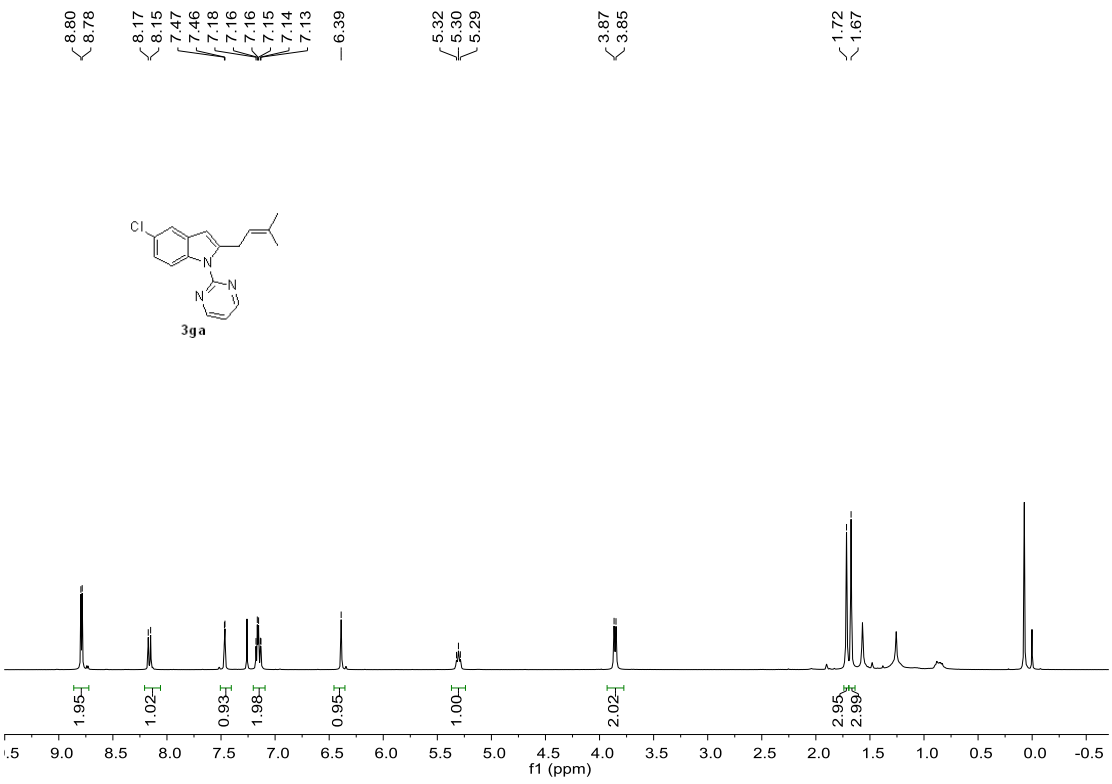
105.80
105.15
104.91
29.01
25.84
18.03
F
N
N
3fa
f1 (ppm)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8.78
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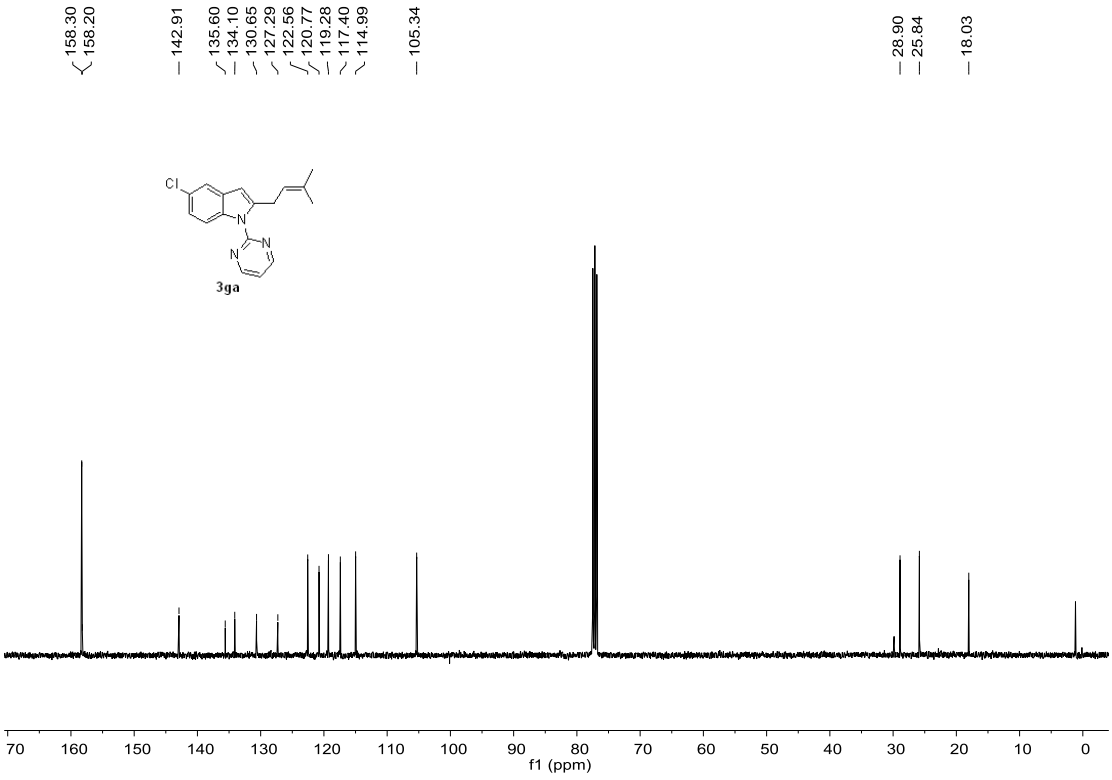
7.46
7.18
7.16
7.16
7.15
7.14
7.13
6.39
5.32
5.30
5.29
3.87
3.85
1.72
1.67
Cl
N
N
N
3ga
1.95
1.02
0.93
1.98
0.95
1.00
2.02
2.95
2.99
f1 (ppm)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158.20
142.91
135.60
134.10
130.65
127.29
122.56
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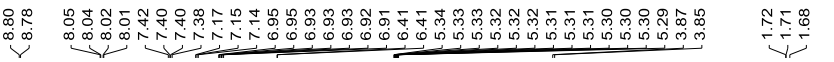
114.99
105.34
28.90
25.84
18.03
Cl
N
N
N
3ga
f1 (ppm)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8.78
8.05
8.04
8.02
8.01
7.42
7.40
7.40
7.38
7.17
7.15
7.14
6.95
6.95
6.93
6.93
6.92
6.91
6.41
6.41
5.34
5.33
5.33
5.32
5.32
5.32
5.31
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5.30
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5.30
5.29
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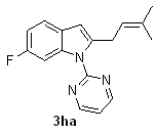
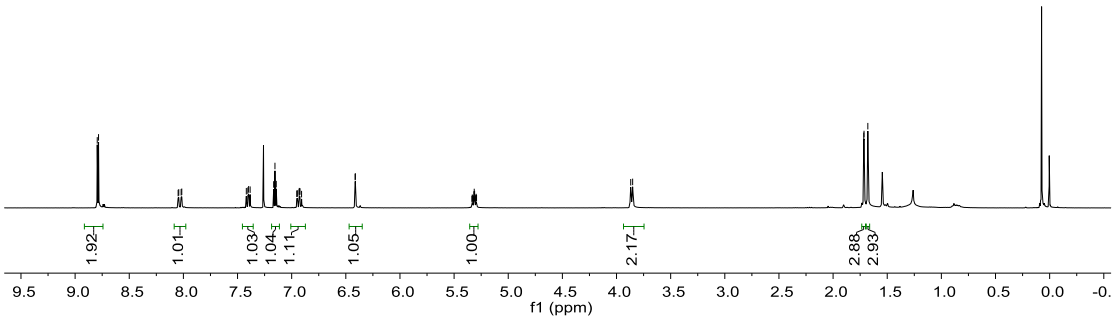
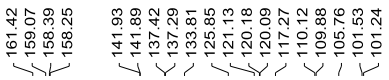
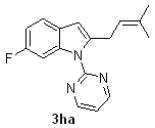
3.85
1.72
1.71
1.68


F
N
N
N

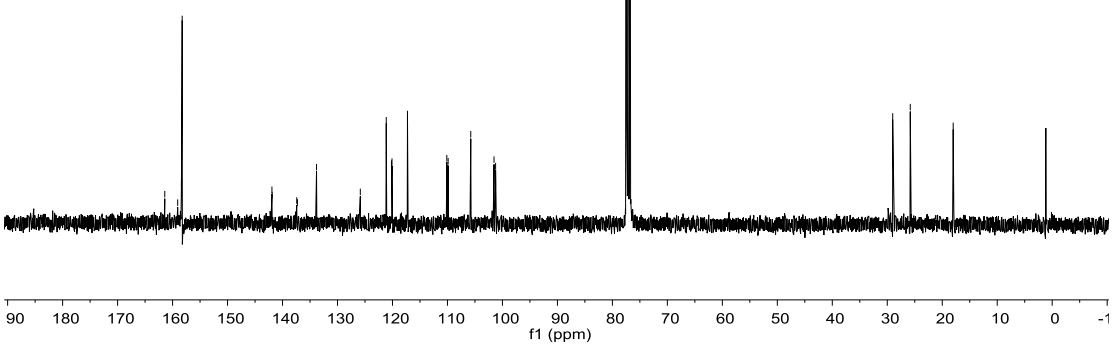
3ha

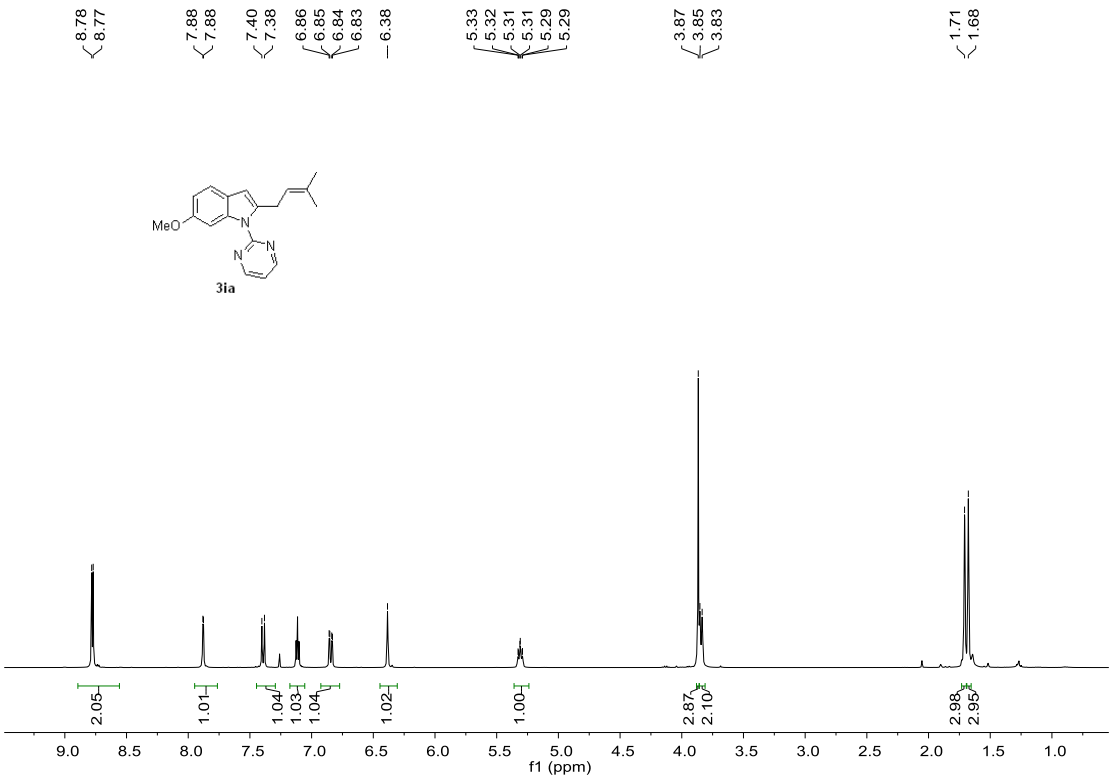

1.92
1.01
1.03
1.04
1.11
1.05
1.00
2.17
2.88
2.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


161.42
159.07
158.39
158.25
141.93
141.89
137.42
137.29
133.81
125.85
121.13
120.18
120.09
117.27
110.12
109.88
105.76
101.53
101.24
29.01
25.81
18.01


F
N
N
N

3ha


90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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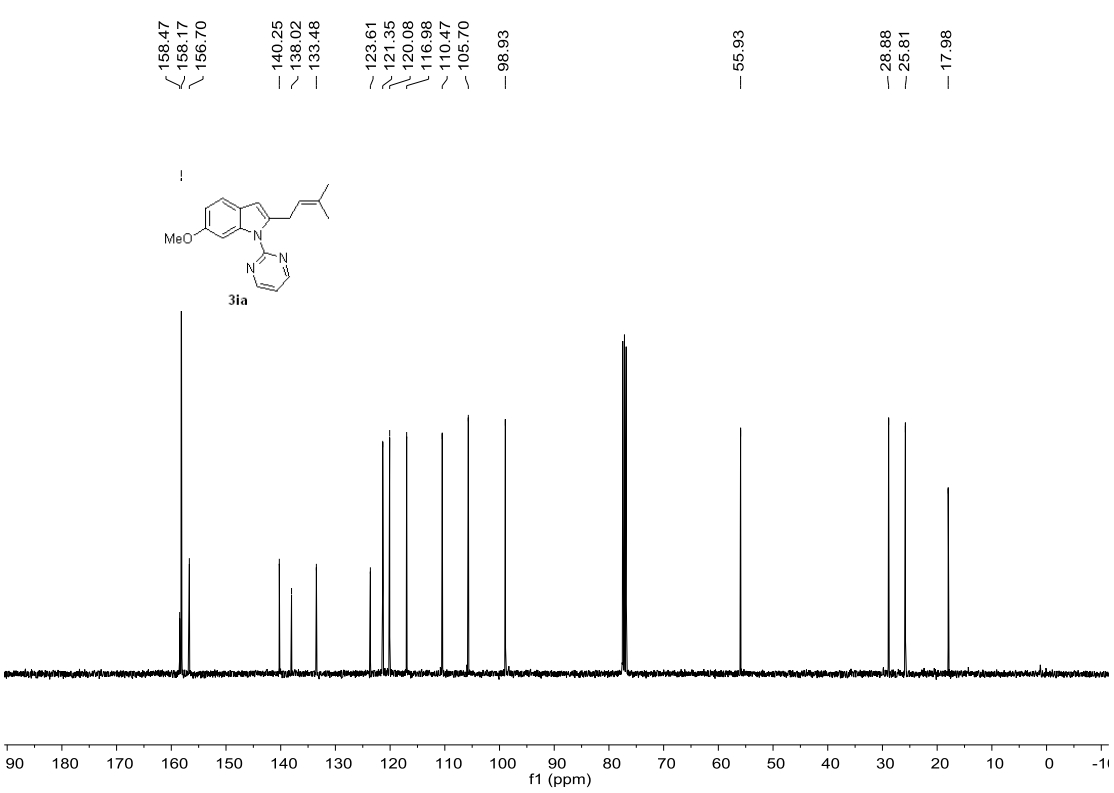
7.40
7.38
6.86
6.85
6.84
6.83
6.38
5.33
5.32
5.31
5.31
5.29
5.29
3.87
3.85
3.83
1.71
1.68
MeO
N
N
3ia
2.05
1.01
1.04
1.03
1.04
1.02
1.00
2.87
2.10
2.98
2.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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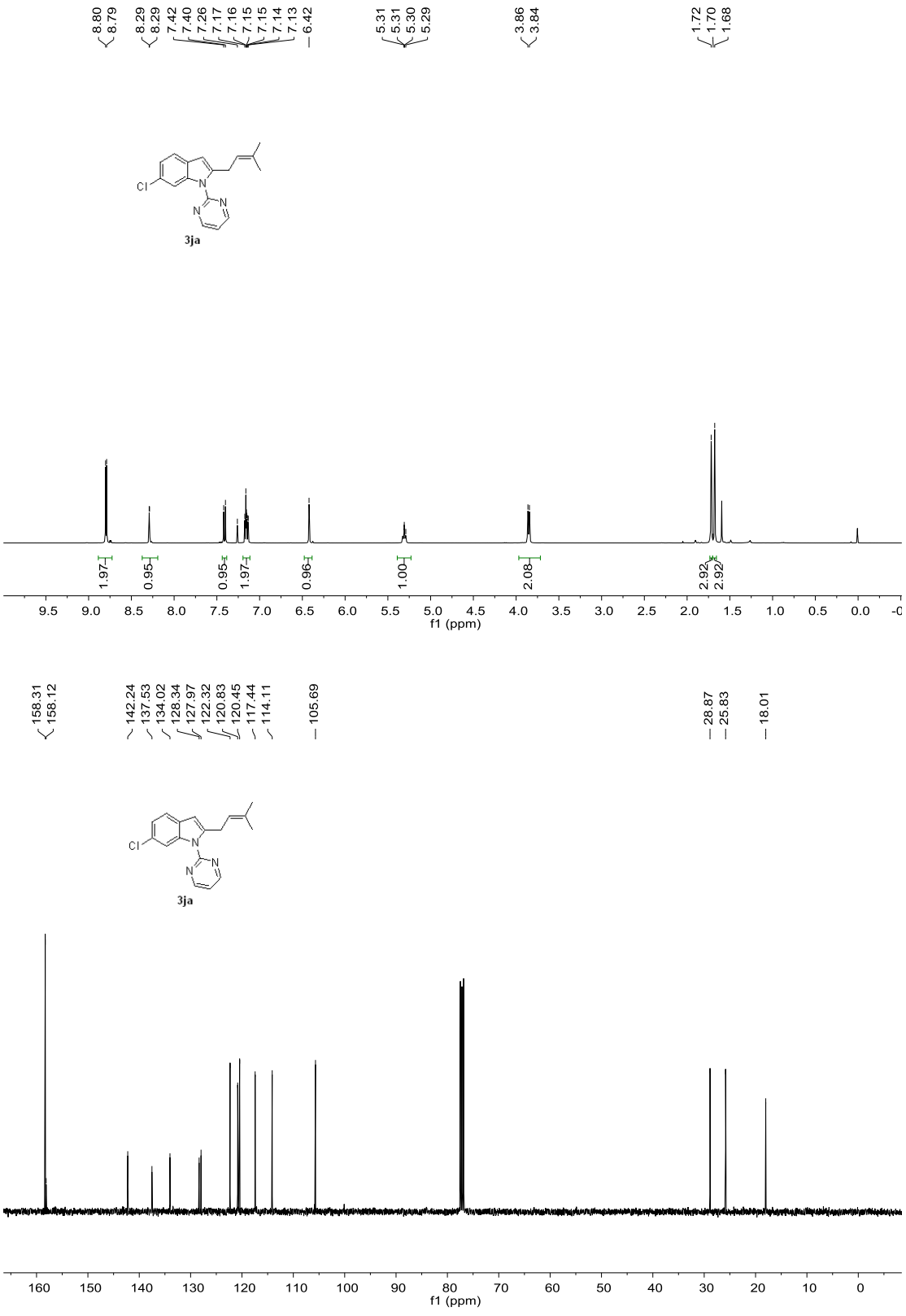
158.17
156.70
140.25
138.02
133.48
123.61
121.35
120.08
116.98
110.47
105.70
98.93
55.93
28.88
25.81
17.98
MeO
N
N
3ia
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.79
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8.29
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7.40
7.26
7.17
7.16
7.15
7.15
7.14
7.13
6.42
5.31
5.31
5.30
5.29
3.86
3.84
1.72
1.70
1.68
Cl
N
N
N
3ja
1.97
0.95
0.95
1.97
0.96
1.00
2.08
2.92
2.92
f1 (ppm)
158.31
158.12
142.24
137.53
134.02
128.34
127.97
122.32
120.83
120.45
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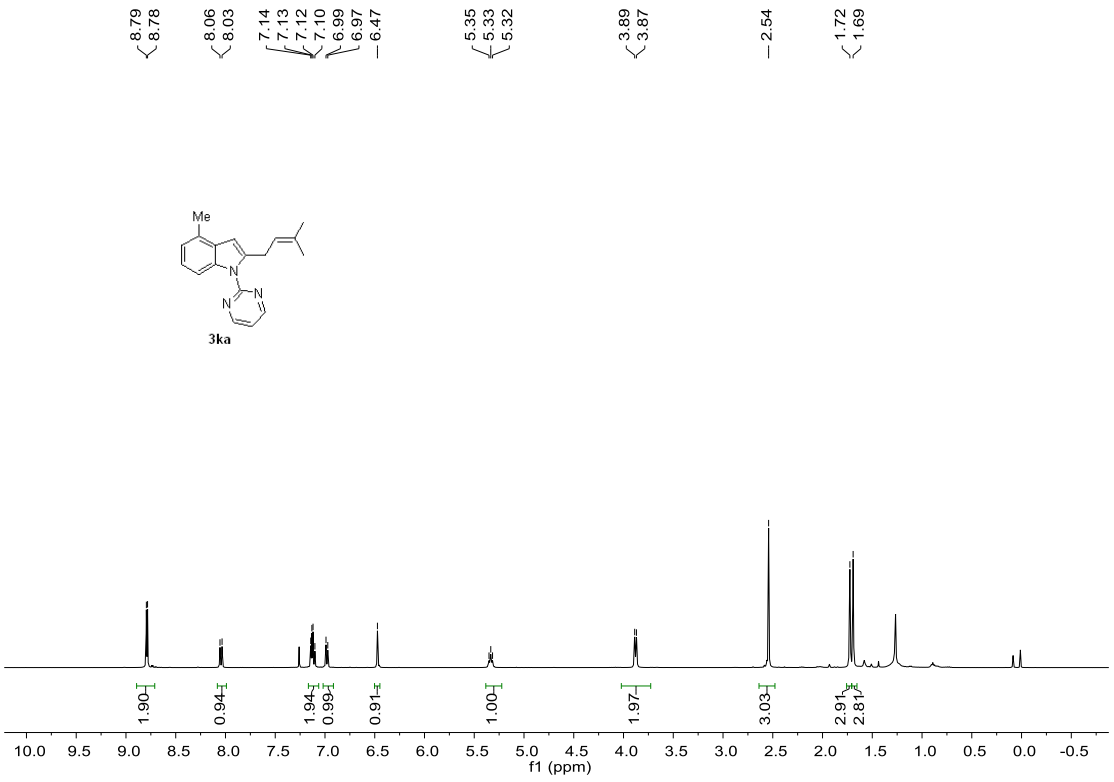
114.11
105.69
28.87
25.83
18.01
Cl
N
N
N
3ja
f1 (ppm)


8.79
8.78
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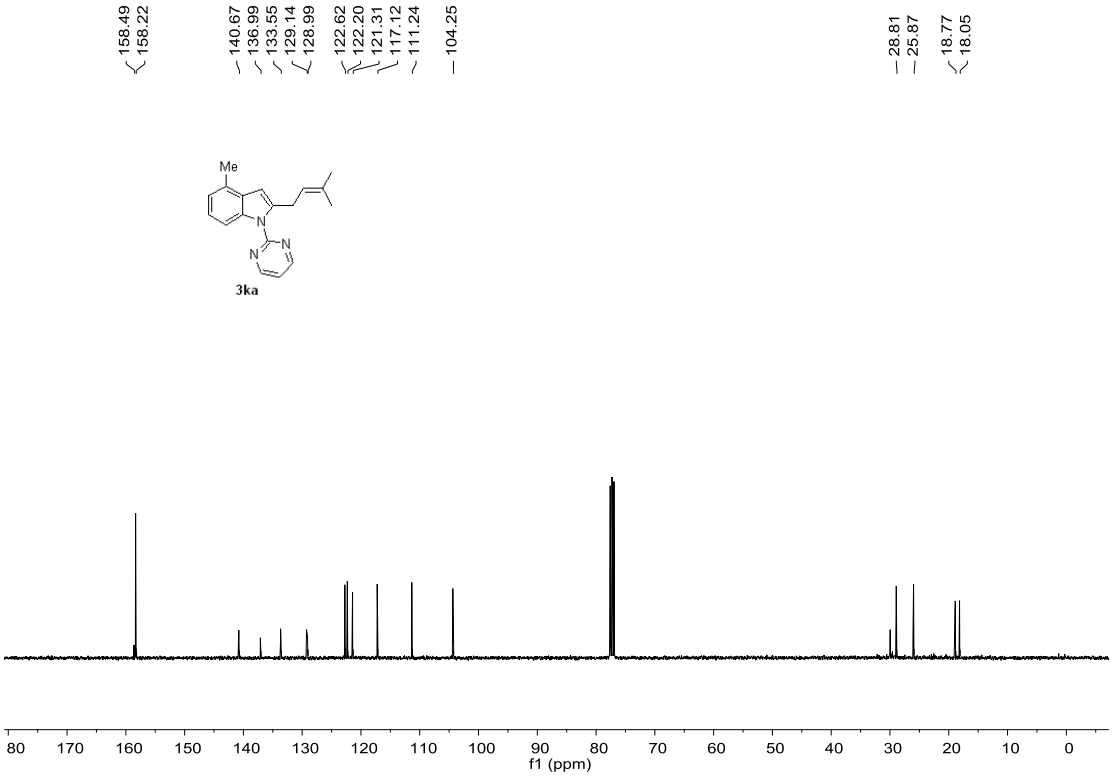
8.03
7.14
7.13
7.12
7.10
6.99
6.97
6.47
5.35
5.33
5.32
3.89
3.87
2.54
1.72
1.69
Me
N
N
3ka
1.90
0.94
1.94
0.99
0.91
1.00
1.97
3.03
2.91
2.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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158.22
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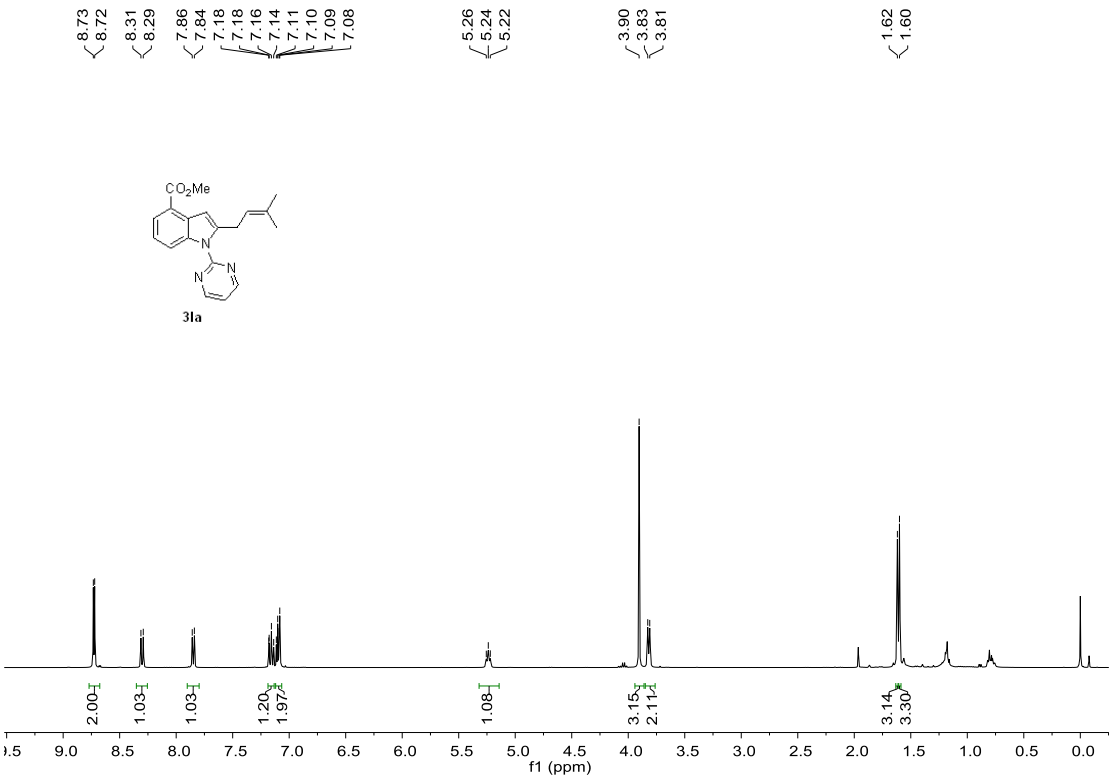
136.99
133.55
129.14
128.99
122.62
122.20
121.31
117.12
111.24
104.25
28.81
25.87
18.77
18.05
Me
N
N
3ka
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.73
8.72
8.31
8.29
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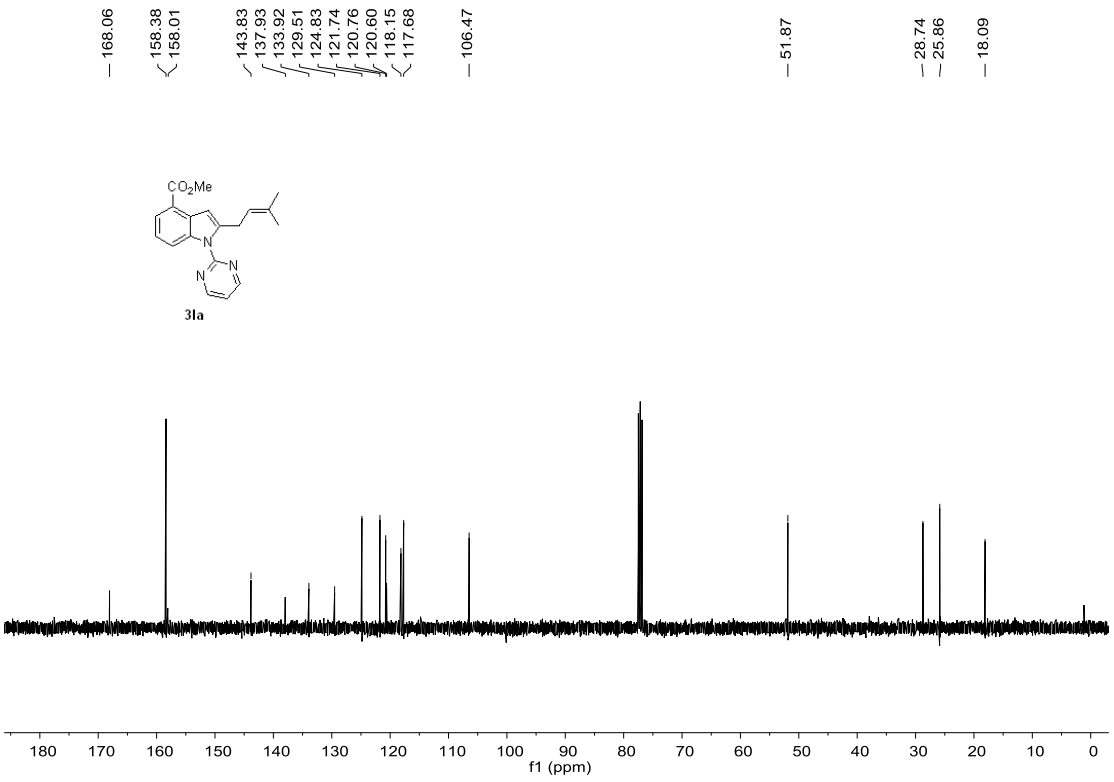
7.84
7.18
7.18
7.16
7.14
7.11
7.10
7.09
7.08
5.26
5.24
5.22
3.90
3.83
3.81
1.62
1.60
CO2Me
N
N
3la
2.00
1.03
1.03
1.20
1.97
1.08
3.15
2.11
3.14
3.30
f1 (ppm)


168.06
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137.93
133.92
129.51
124.83
121.74
120.76
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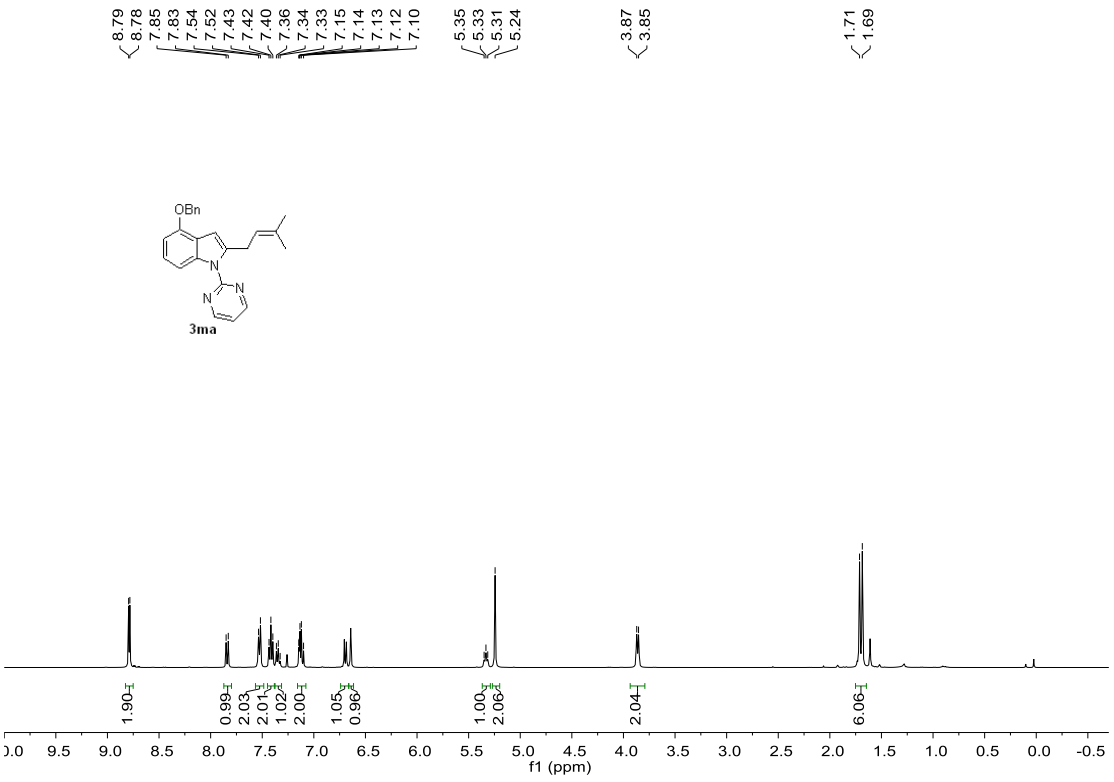
106.47
51.87
28.74
25.86
18.09
CO2Me
N
N
3la
f1 (ppm)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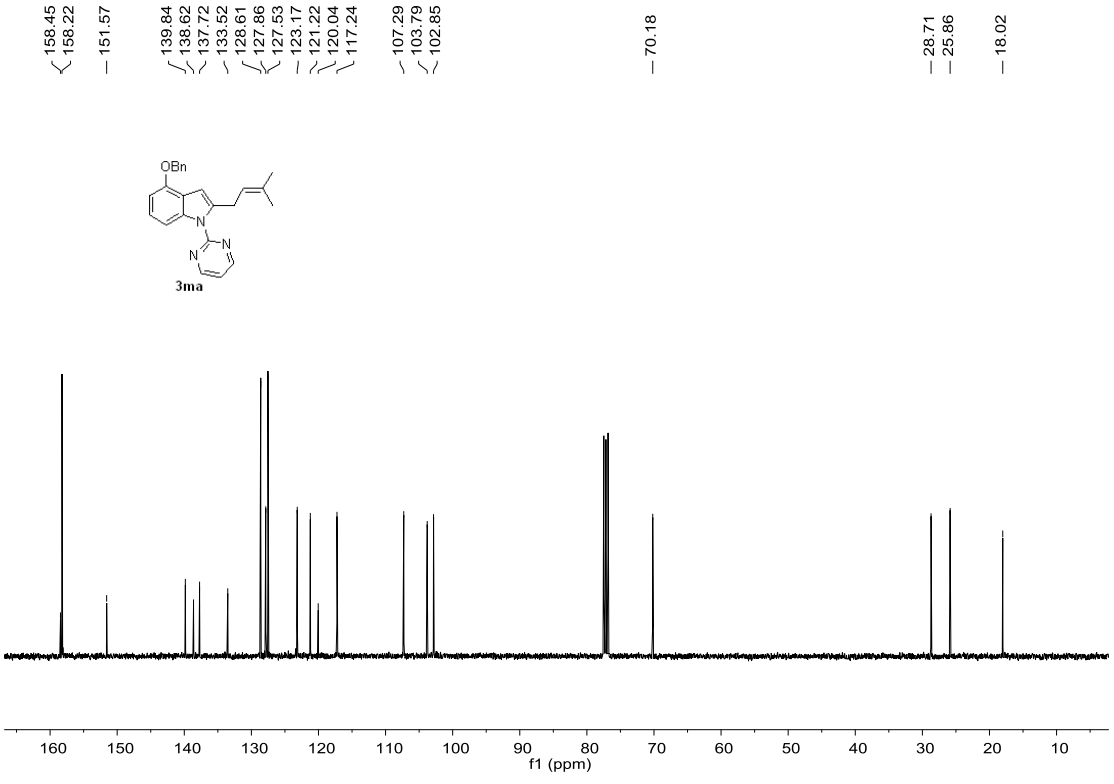
7.42
7.40
7.36
7.34
7.33
7.15
7.14
7.13
7.12
7.10
5.35
5.33
5.31
5.24
3.87
3.85
1.71
1.69
OBn
N
N
3ma
1.90
0.99
2.03
2.01
1.02
2.00
1.05
0.96
1.00
2.06
2.04
6.06
f1 (ppm)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128.61
127.86
127.53
123.17
121.22
120.04
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107.29
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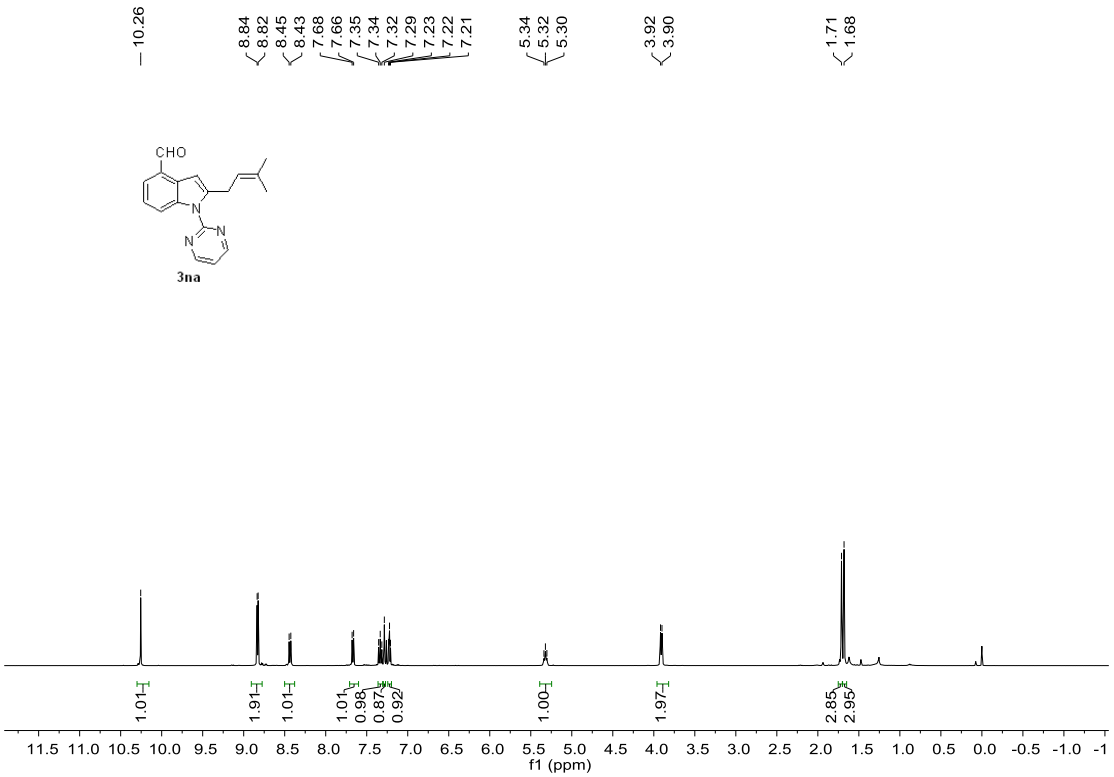
102.85
70.18
28.71
25.86
18.02
OBn
N
N
3ma
f1 (ppm)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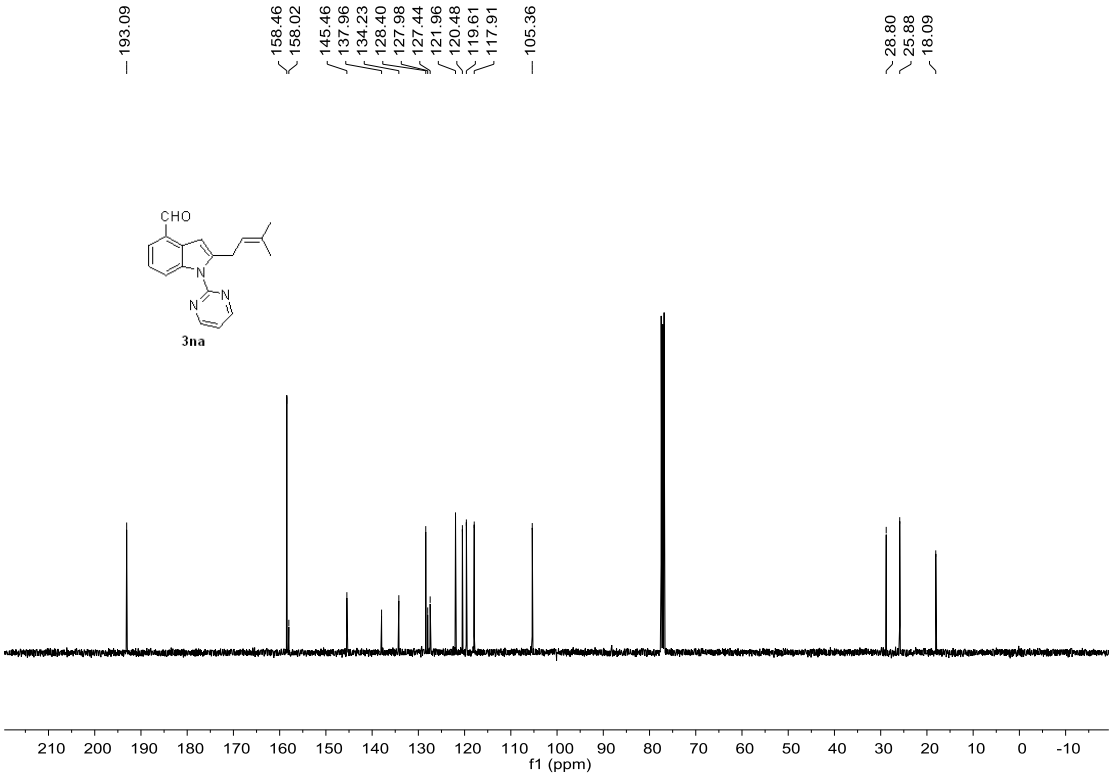
7.34
7.32
7.29
7.23
7.22
7.21
5.34
5.32
5.30
3.92
3.90
1.71
1.68
CHO
N
N
N
3na
1.01
1.91
1.01
1.01
0.98
0.87
0.92
1.00
1.97
2.85
2.95
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)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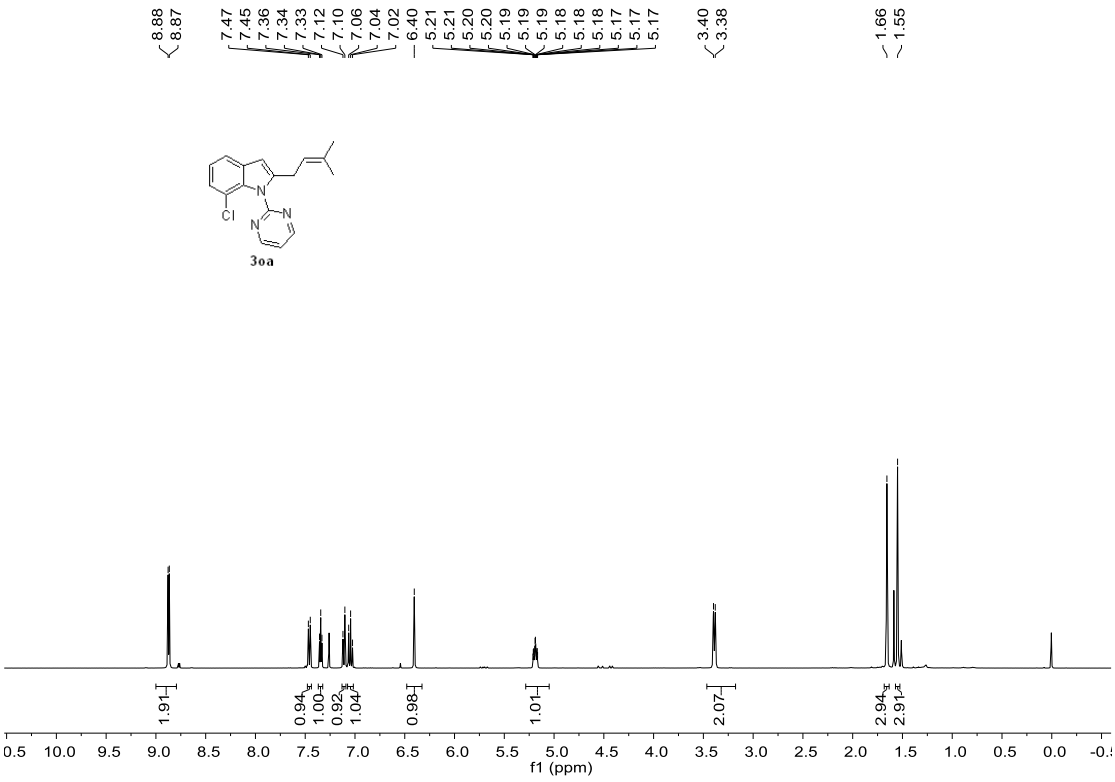
134.23
128.40
127.98
127.44
121.96
120.48
119.61
117.91
105.36
28.80
25.88
18.09
CHO
N
N
N
3na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.88
8.87
7.47
7.45
7.36
7.34
7.33
7.12
7.10
7.06
7.04
7.02
6.40
5.21
5.21
5.20
5.20
5.19
5.19
5.19
5.18
5.18
5.17
5.17
5.17
3.40
3.38
1.66
1.55
Cl
N
N
3oa
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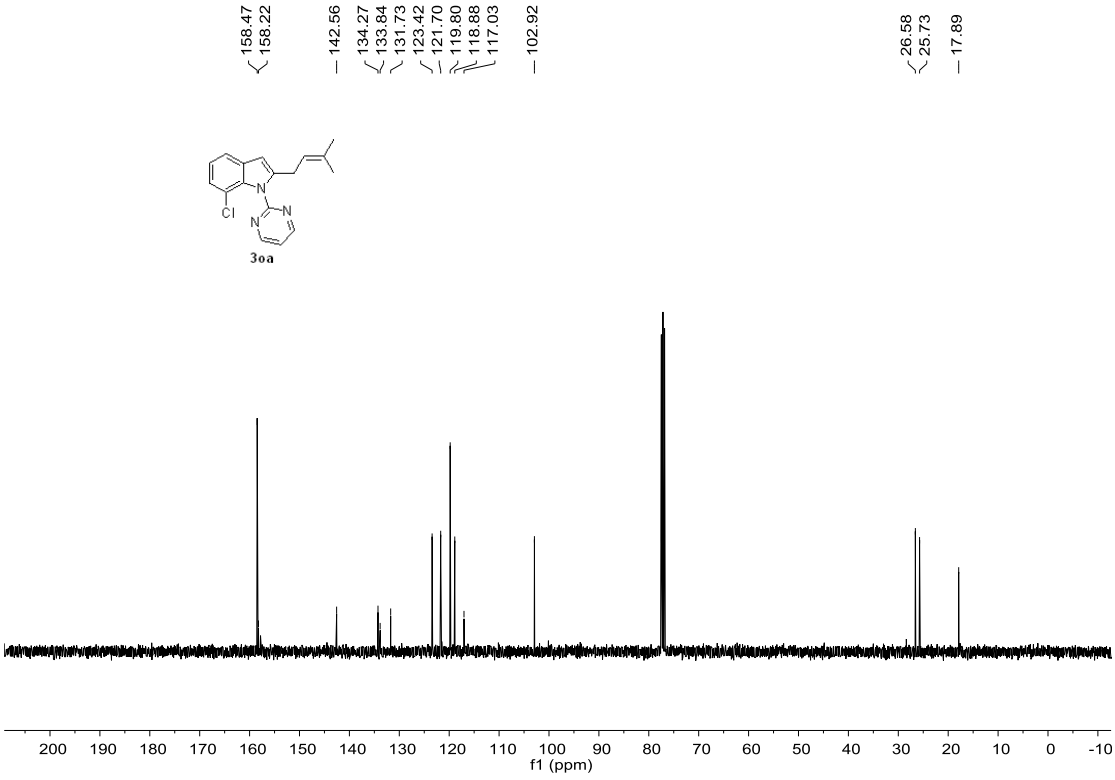
1.00
0.92
1.04
0.98
1.01
2.07
2.94
2.91
f1 (ppm)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158.22
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134.27
133.84
131.73
123.42
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117.03
102.92
26.58
25.73
17.89
Cl
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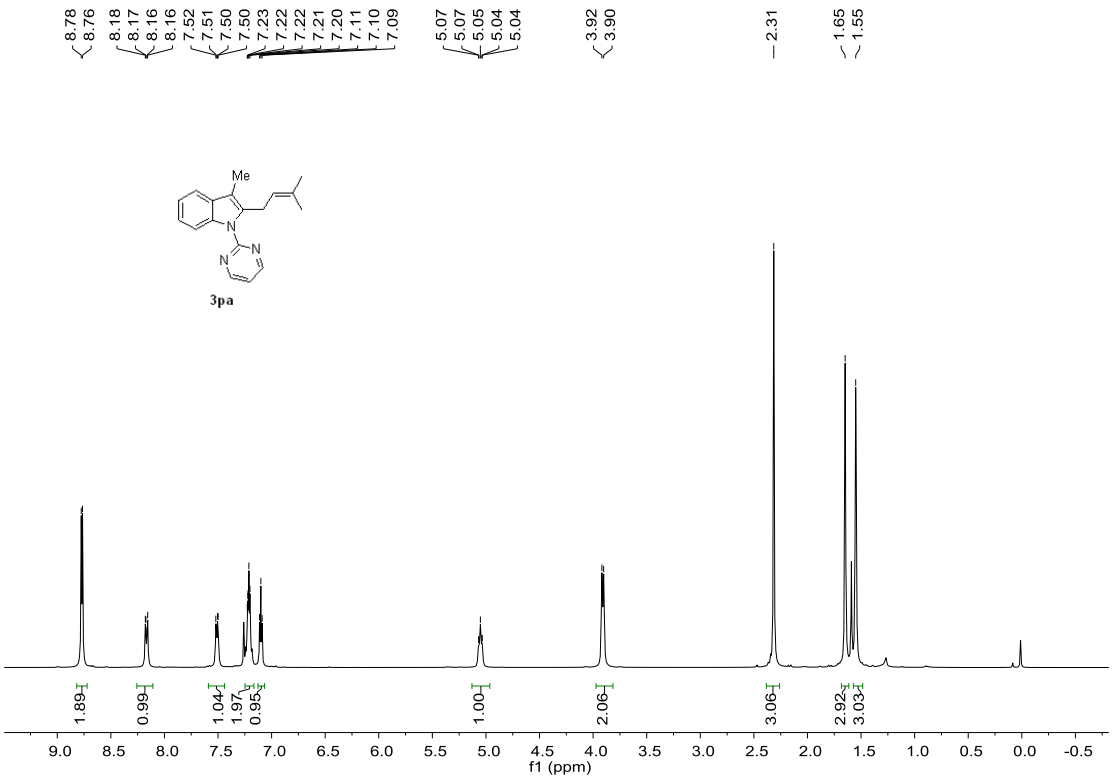
N
3oa
f1 (ppm)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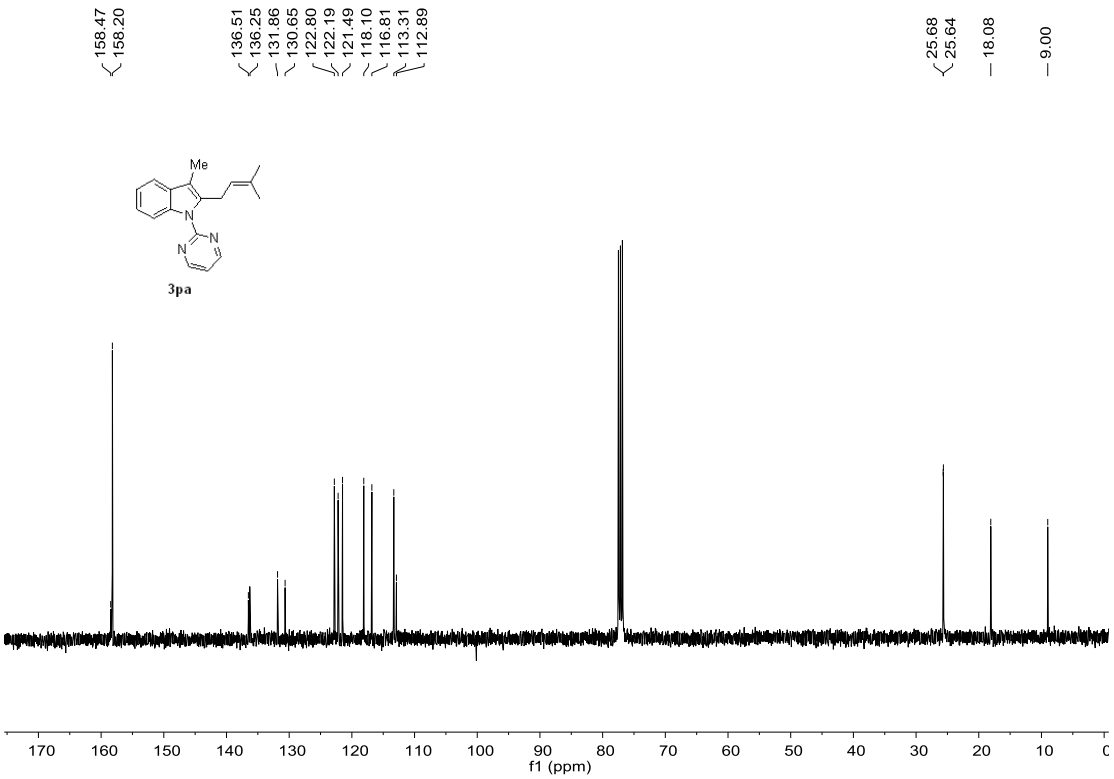
7.52
7.51
7.50
7.50
7.23
7.22
7.22
7.21
7.20
7.11
7.10
7.09
5.07
5.07
5.05
5.04
5.04
3.92
3.90
2.31
1.65
1.55
Me
N
N
N
3pa
1.89
0.99
1.04
1.97
0.95
1.00
2.06
3.06
2.92
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.47
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136.25
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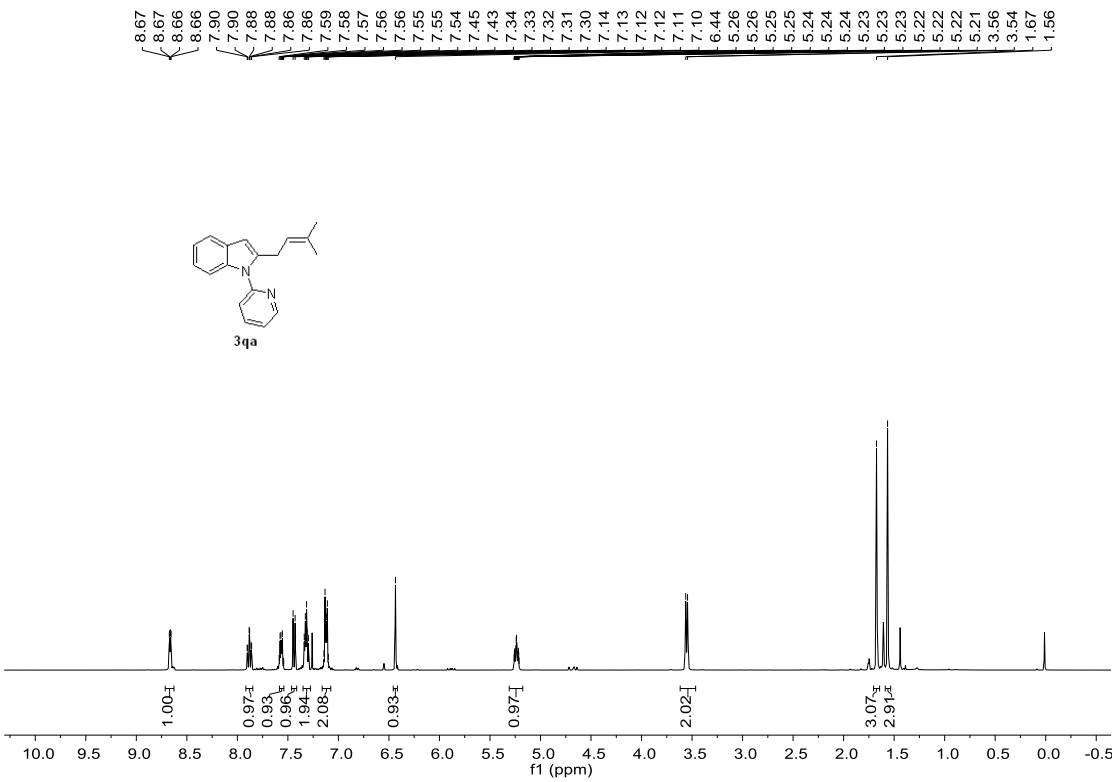
130.65
122.80
122.19
121.49
118.10
116.81
113.31
112.89
25.68
25.64
18.08
9.00
Me
N
N
N
3pa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.88
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7.86
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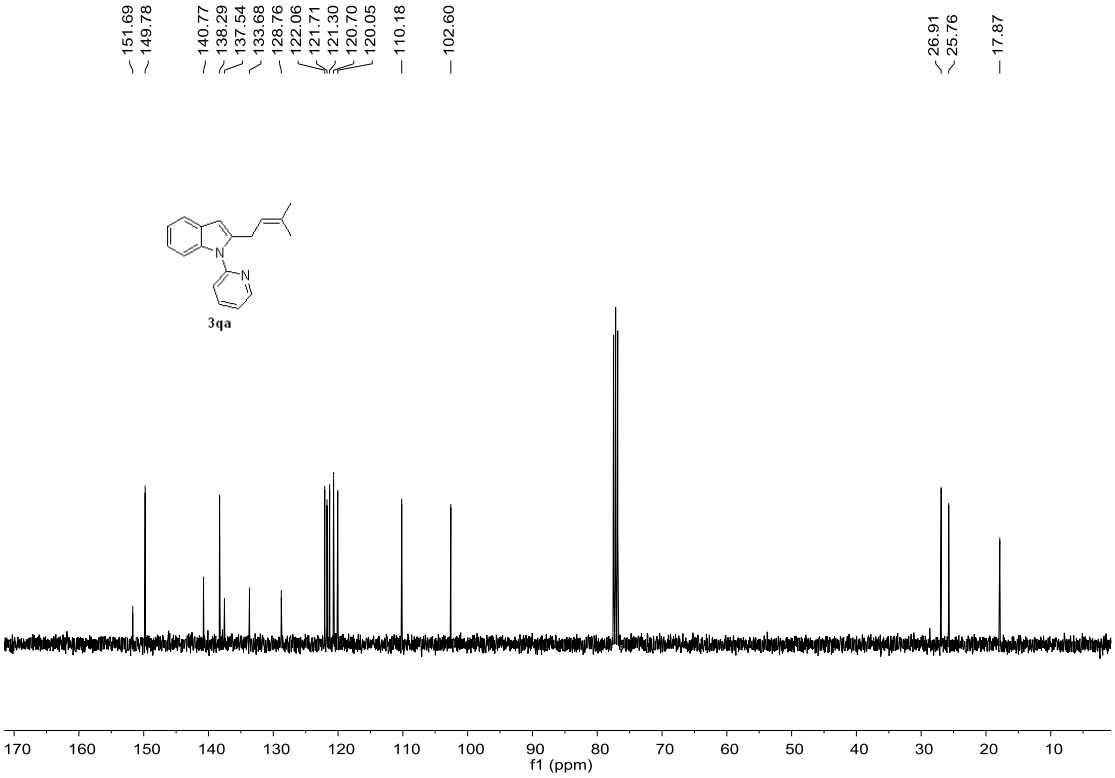
7.57
7.56
7.56
7.55
7.55
7.54
7.45
7.43
7.34
7.33
7.32
7.31
7.30
7.14
7.13
7.12
7.12
7.11
7.10
6.44
5.26
5.25
5.25
5.24
5.24
5.24
5.23
5.23
5.23
5.22
5.22
5.22
5.21
3.56
3.54
1.67
1.56
3qa
1.00
0.97
0.93
0.96
1.94
2.08
0.93
0.97
2.02
3.07
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.06
121.71
121.30
120.70
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110.18
102.60
26.91
25.76
17.87
3qa
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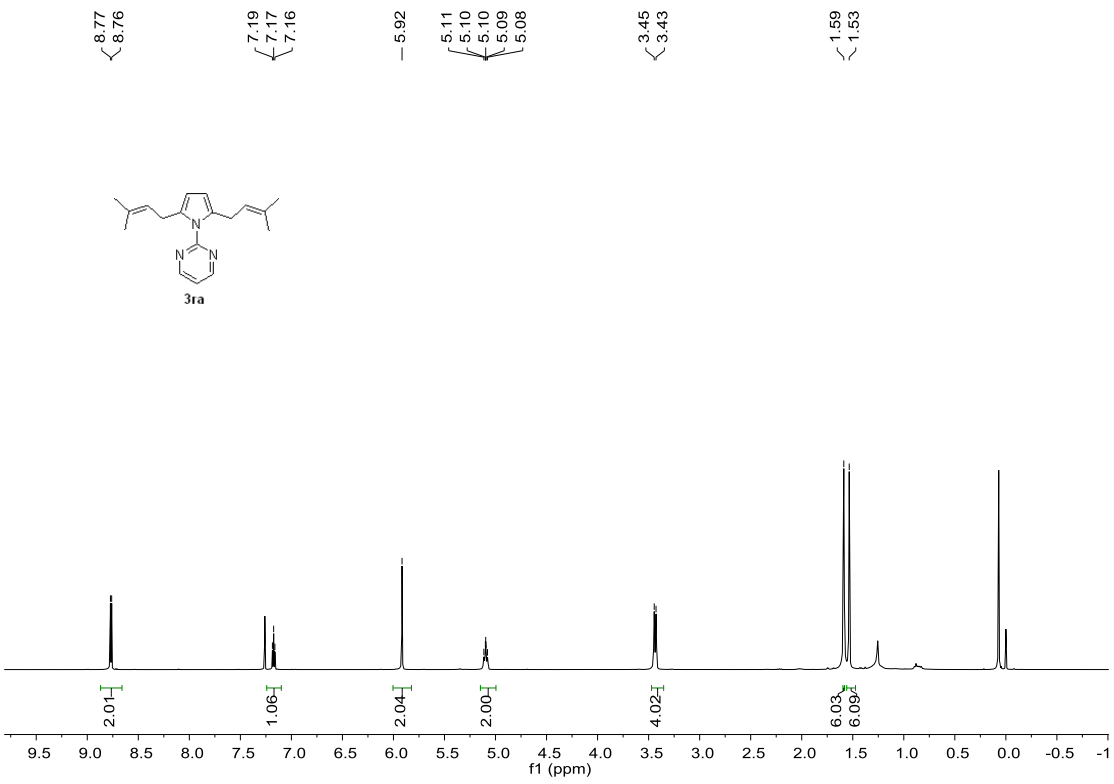
f1 (ppm)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5.09
5.08
3.45
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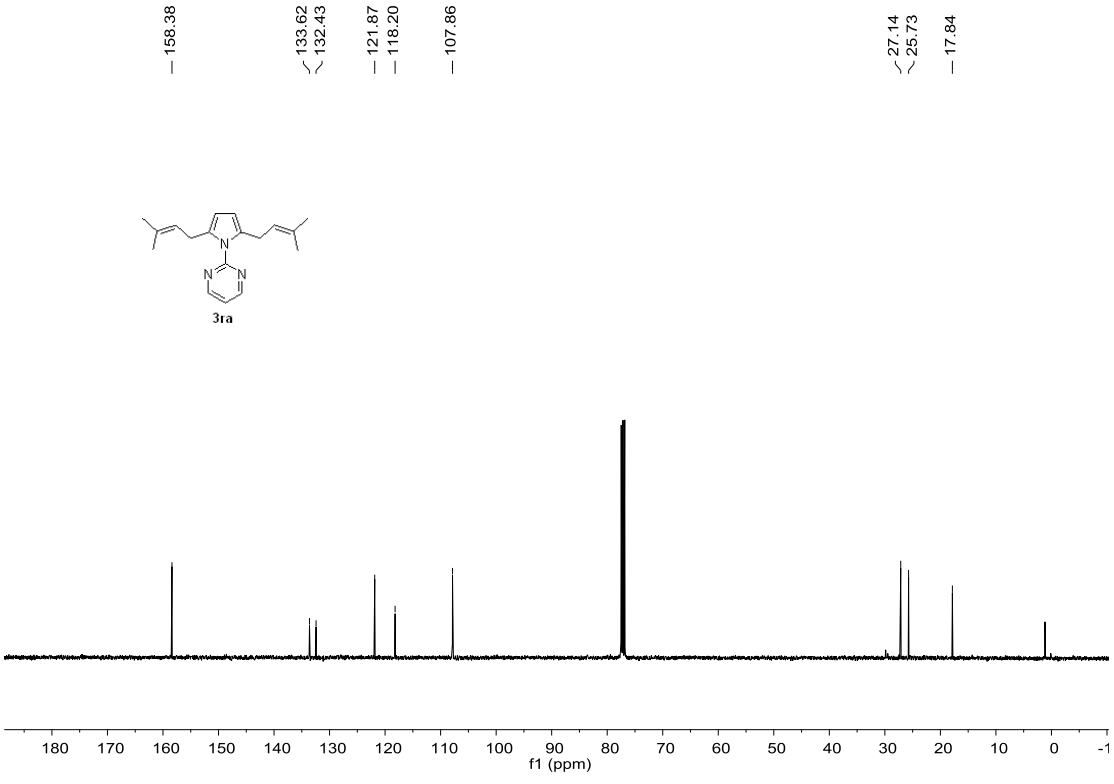
1.53
3ra
2.01
1.06
2.04
2.00
4.02
6.03
6.09
f1 (ppm)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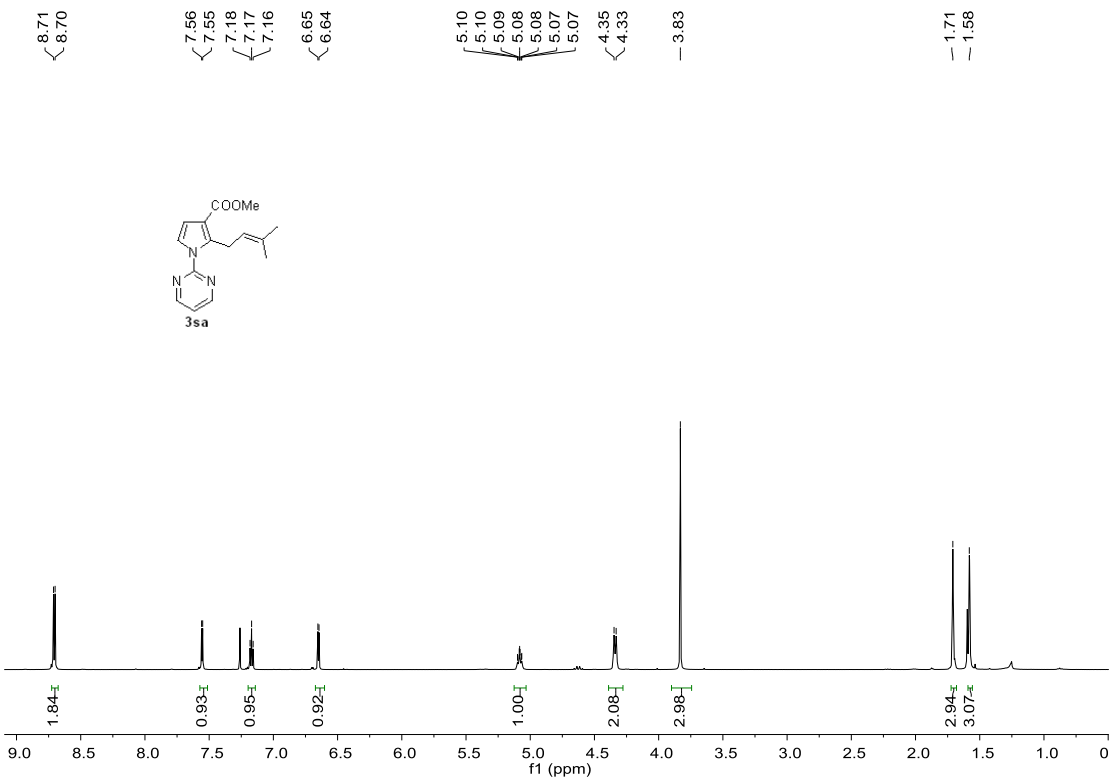
f1 (ppm)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5.10
5.09
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5.08
5.07
5.07
4.35
4.33
3.83
1.71
1.58
COOMe
3sa
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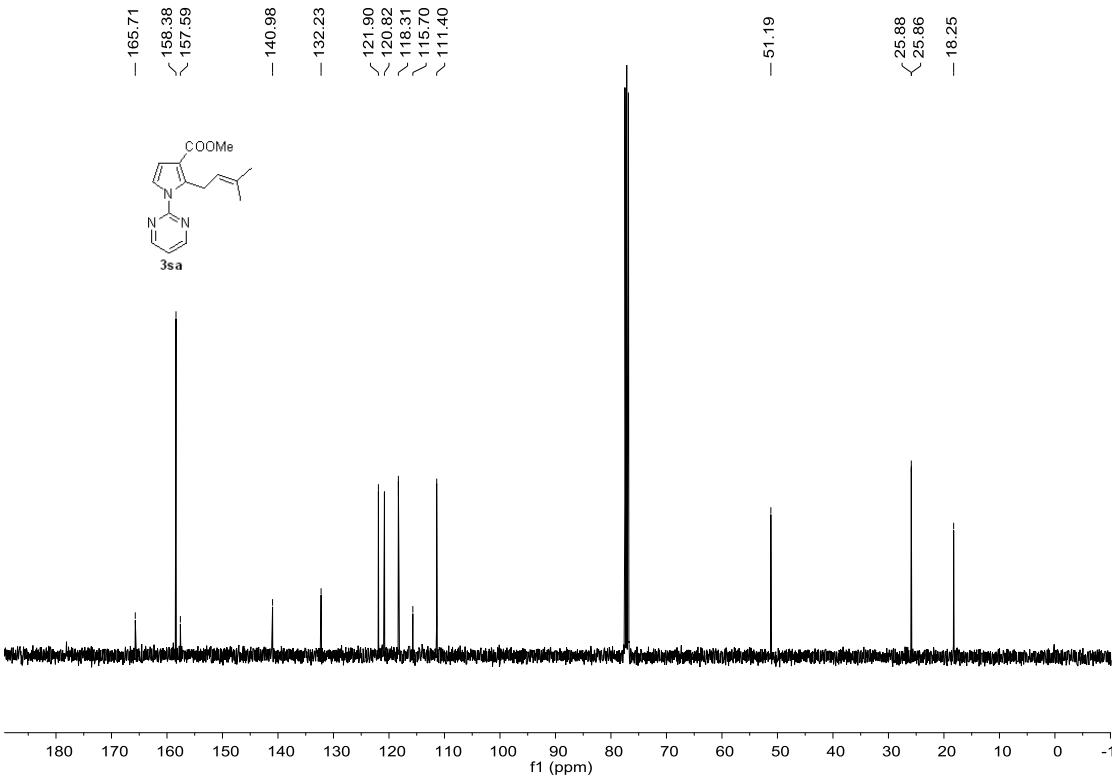
0.95
0.92
1.00
2.08
2.98
2.94
3.07
f1 (ppm)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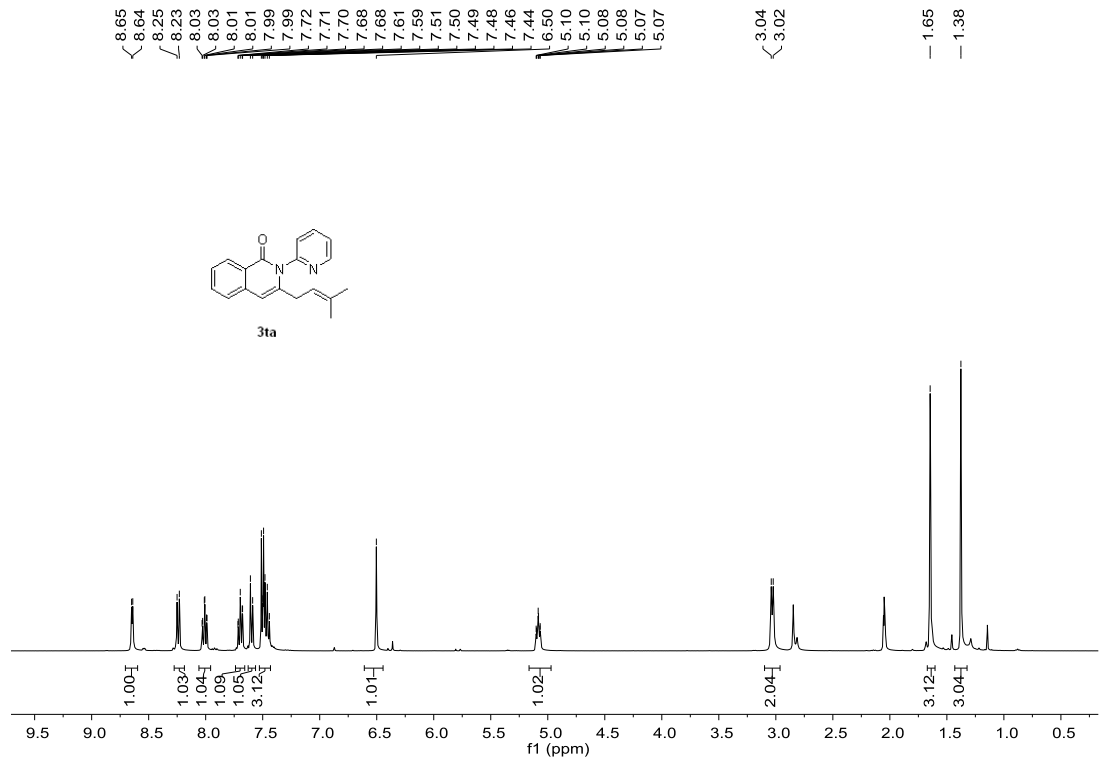
25.86
18.25
COOMe
3sa
f1 (ppm)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7.68
7.61
7.59
7.51
7.50
7.49
7.48
7.46
7.44
6.50
5.10
5.10
5.08
5.08
5.07
5.07
3.04
3.02
1.65
1.38
3ta
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1.09
1.05
3.12
1.01
1.02
2.04
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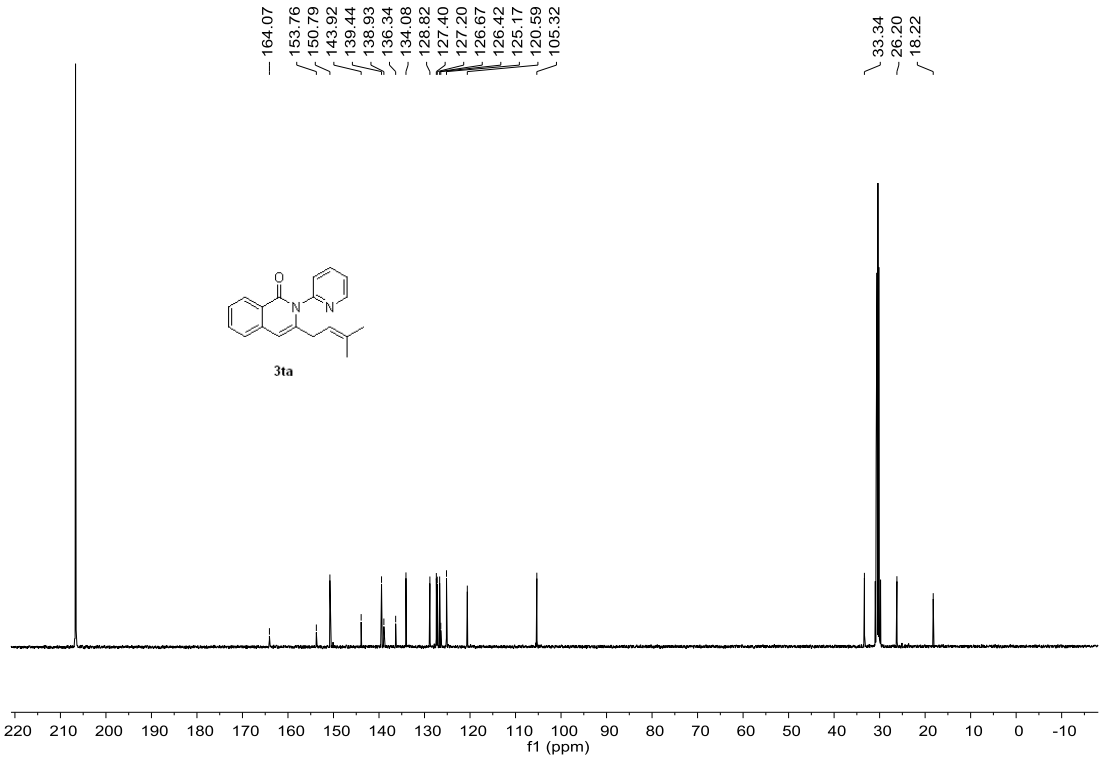
3.04
f1 (ppm)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138.93
136.34
134.08
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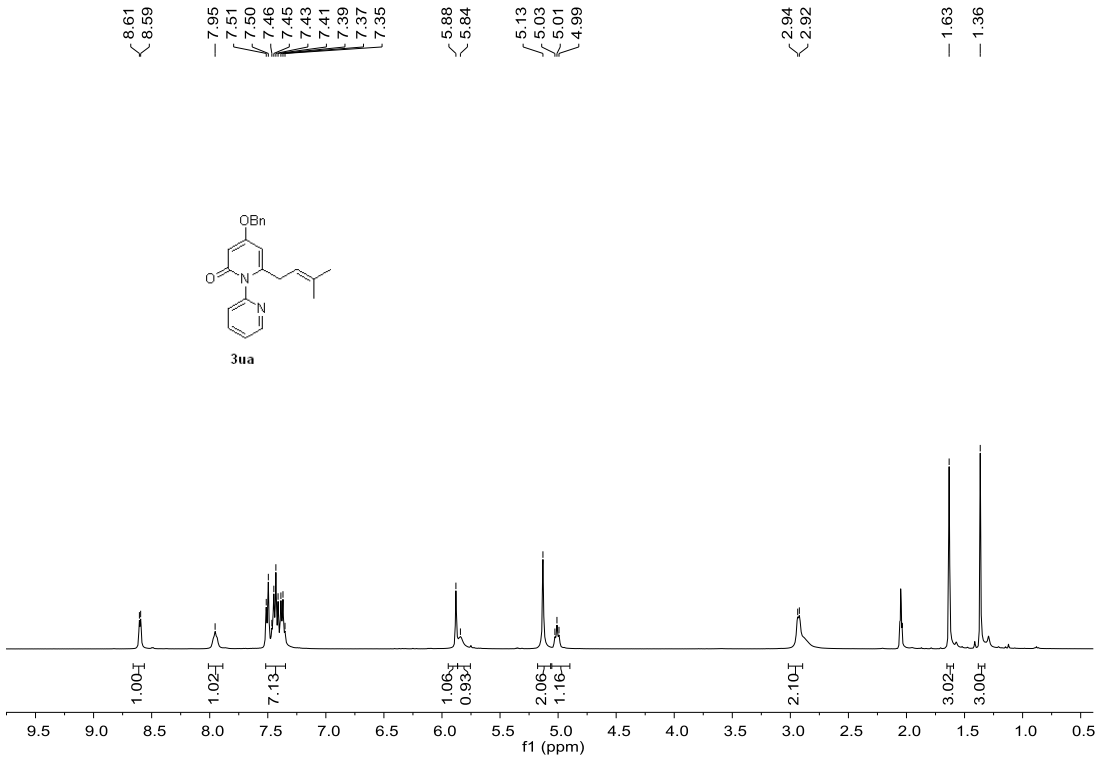
126.42
125.17
120.59
105.32
33.34
26.20
18.22
3ta
f1 (ppm)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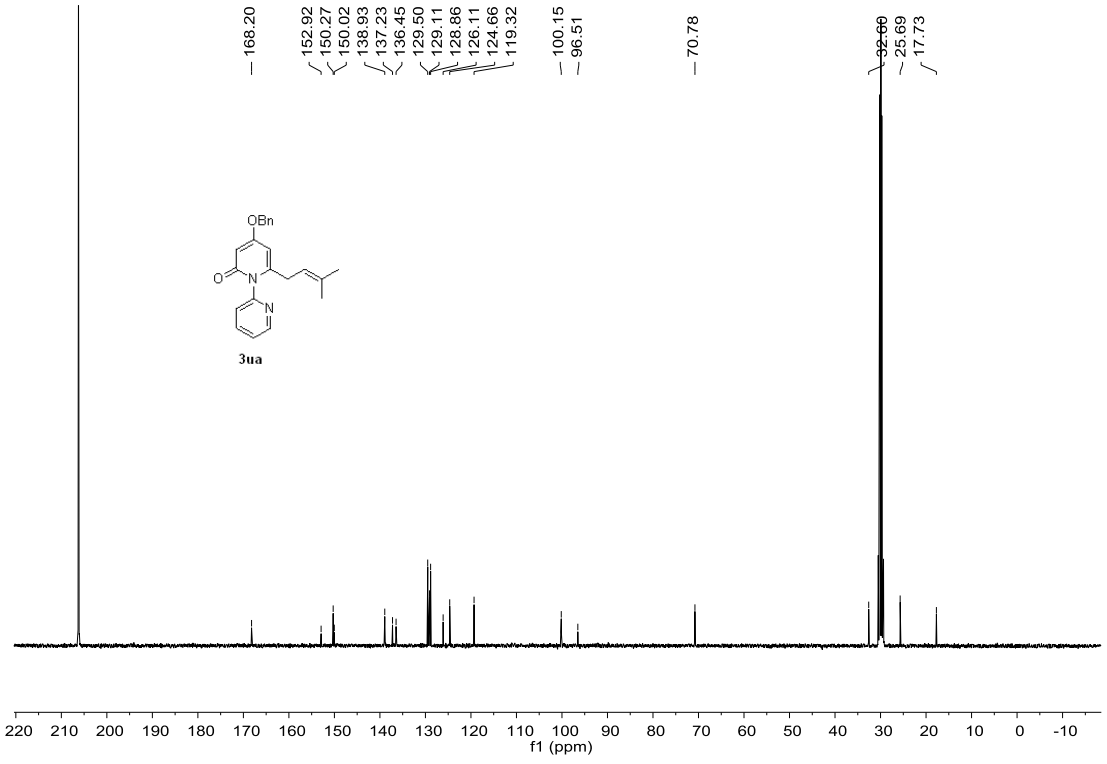
7.46
7.45
7.43
7.41
7.39
7.37
7.35
5.88
5.84
5.13
5.03
5.01
4.99
2.94
2.92
1.63
1.36
OBn
O
N
N
3ua
1.00
1.02
7.13
1.06
0.93
2.06
1.16
2.10
3.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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150.02
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137.23
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129.11
128.86
126.11
124.66
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100.15
96.51
70.78
32.00
25.69
17.73
OBn
O
N
N
3ua
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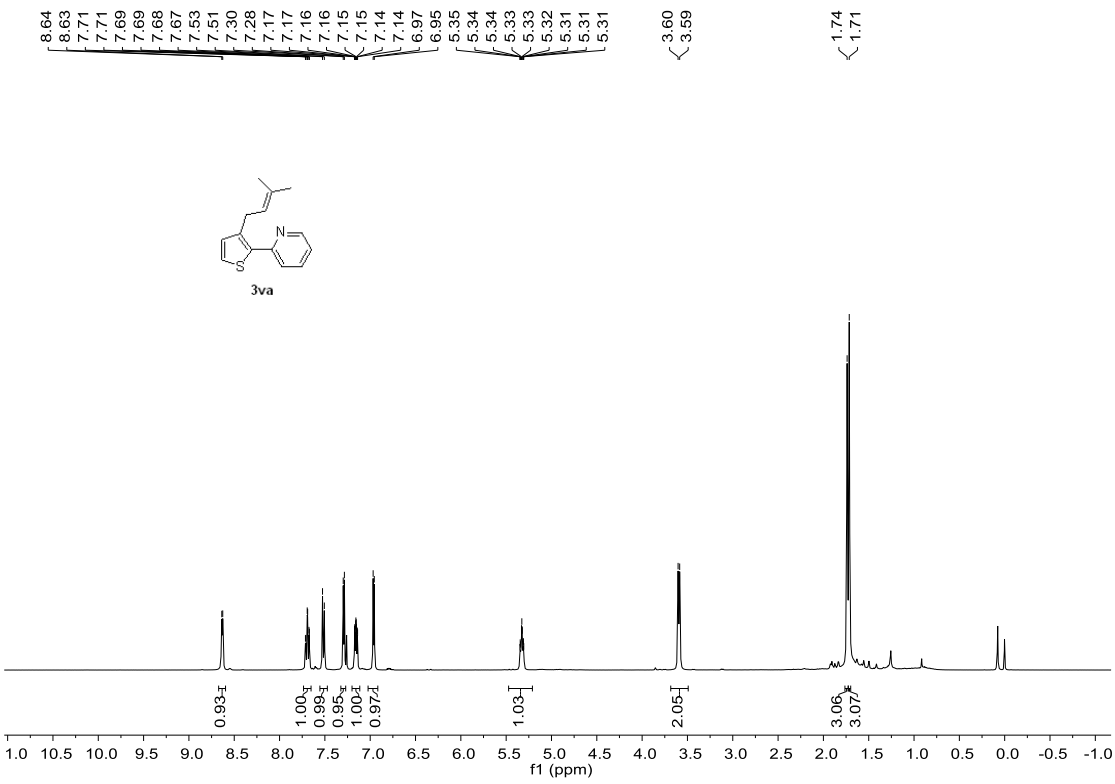
f1 (ppm)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7.51
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7.17
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7.14
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5.33
5.33
5.32
5.31
5.31
5.31
3.60
3.59
1.74
1.71
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0.93
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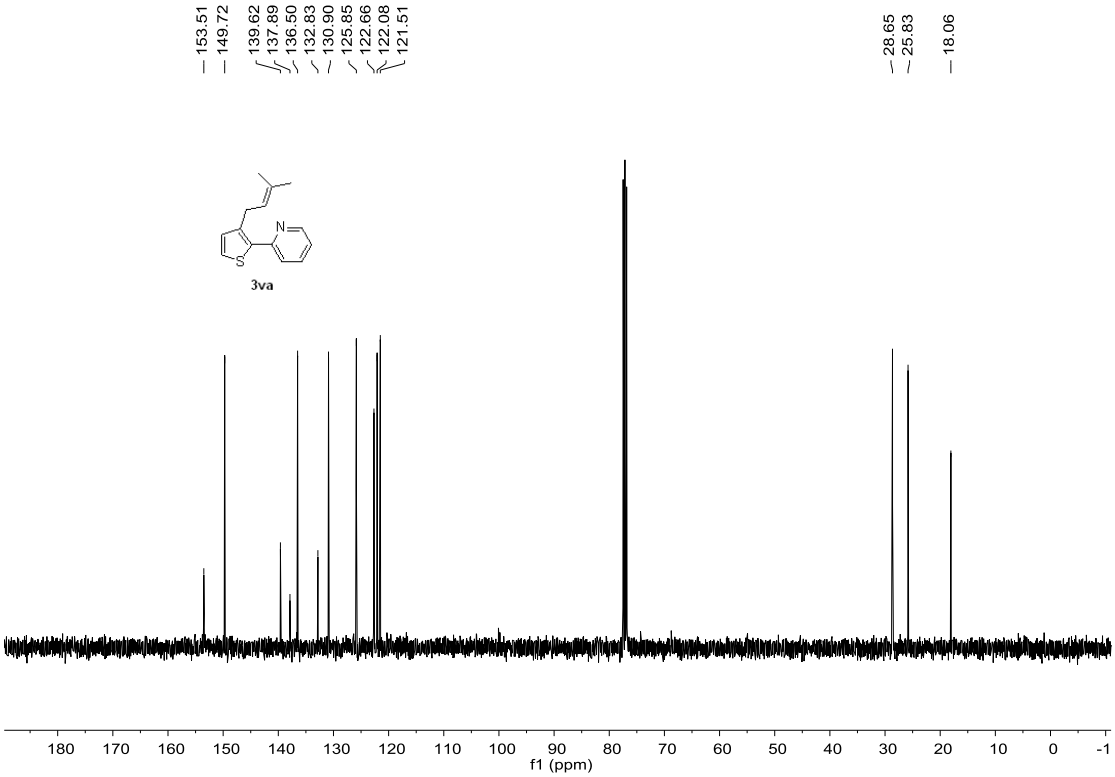
0.99
0.95
1.00
0.97
1.03
2.05
3.06
3.07
f1 (ppm)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121.51
28.65
25.83
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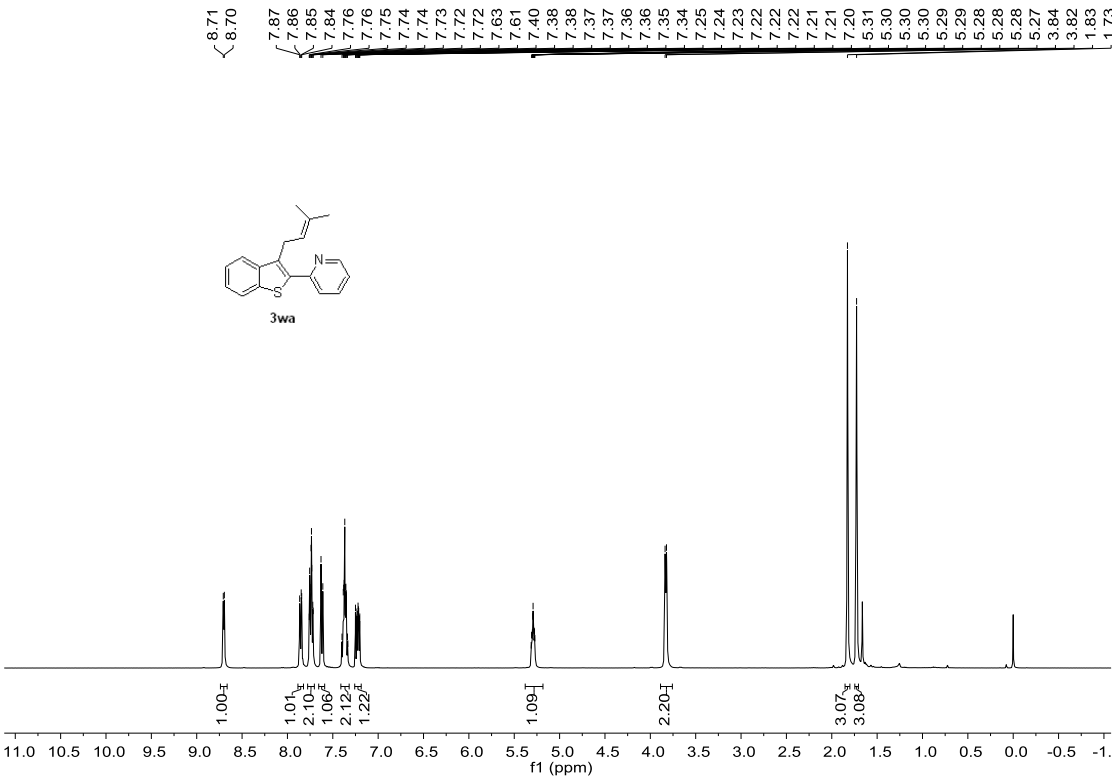
3va
f1 (ppm)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7.72
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7.37
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5.29
5.28
5.28
5.28
5.27
3.84
3.82
1.83
1.73
3wa
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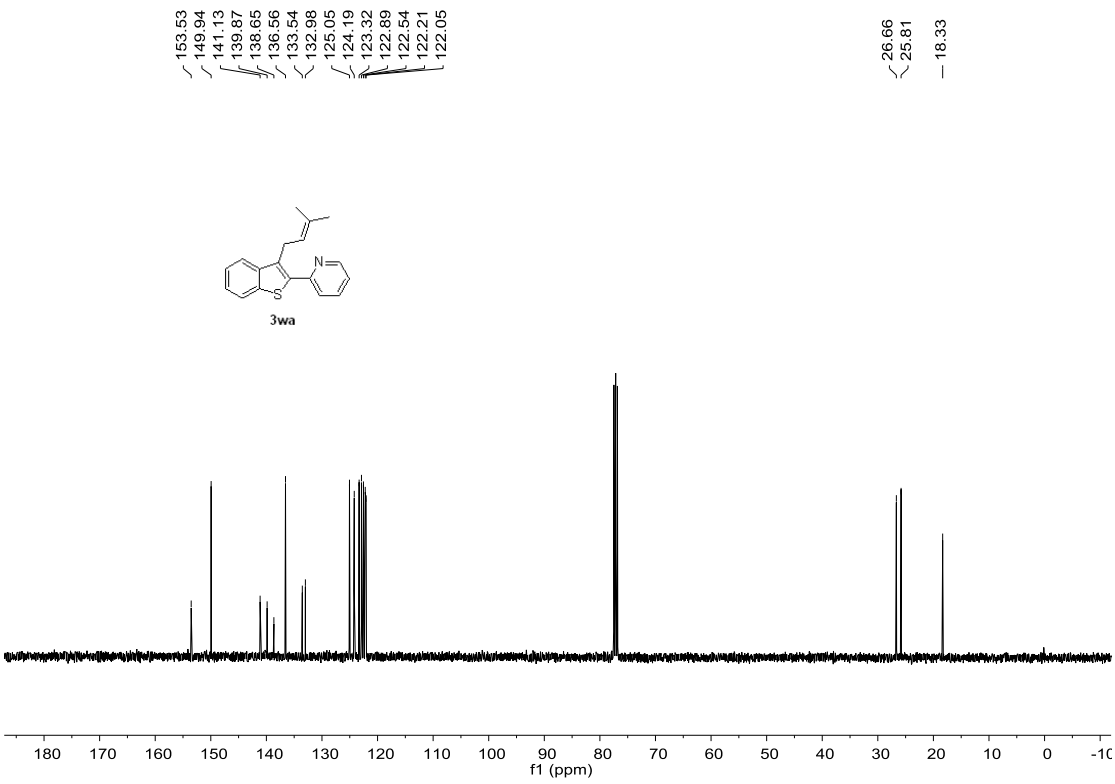
1.01
2.10
1.06
2.12
1.22
1.09
2.20
3.07
3.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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123.32
122.89
122.54
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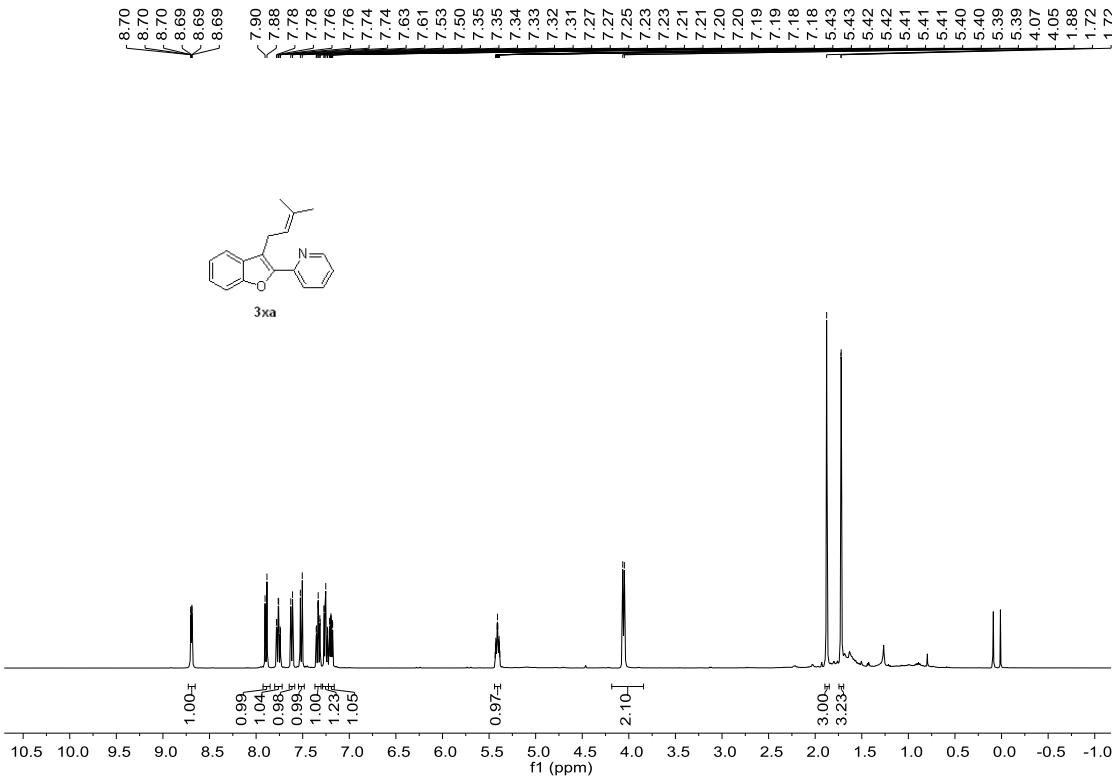
26.66
25.81
18.33
3wa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.76
7.74
7.74
7.63
7.61
7.53
7.50
7.35
7.34
7.33
7.32
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7.25
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7.20
7.19
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5.43
5.42
5.42
5.41
5.41
5.41
5.40
5.40
5.39
5.39
4.07
4.05
1.88
1.72
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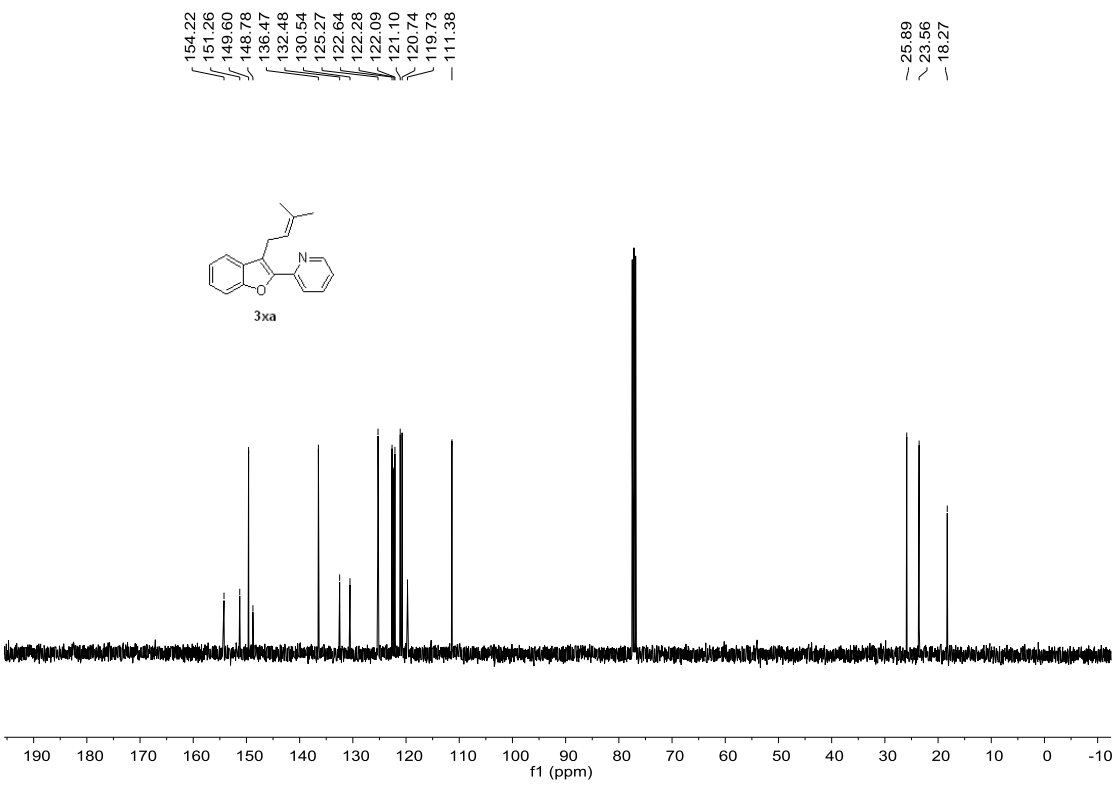
0.99
1.04
0.98
0.99
1.00
1.23
1.05
0.97
2.10
3.00
3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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125.27
122.64
122.28
122.09
121.10
120.74
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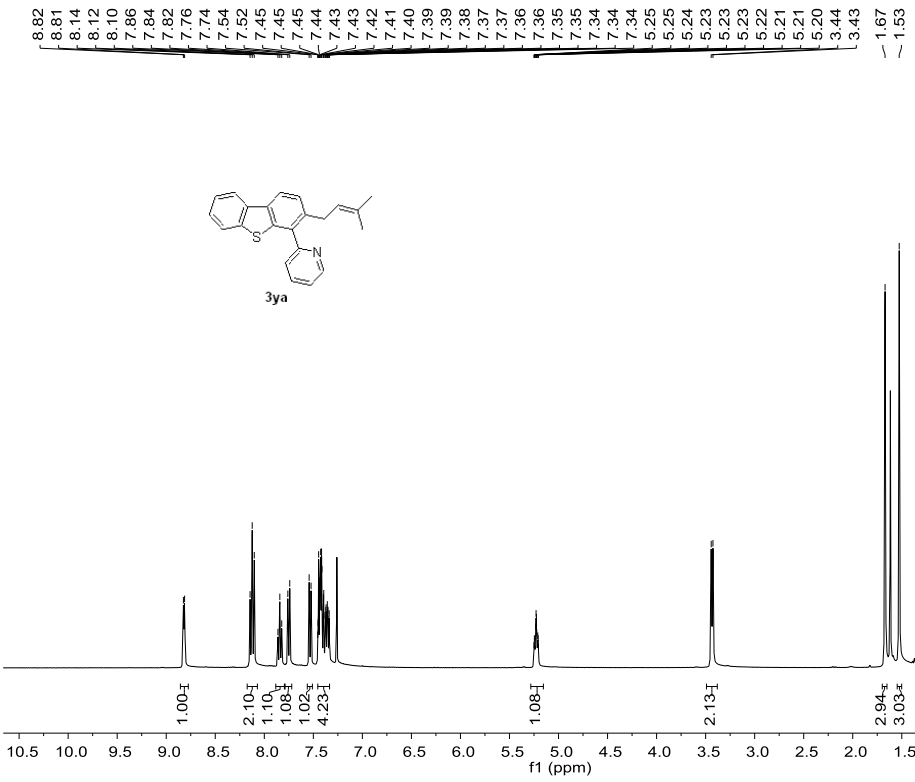
111.38
25.89
23.56
18.27
3xa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.45
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7.43
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5.21
5.21
5.20
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3.43
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1.53
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1.02
4.23
1.08
2.13
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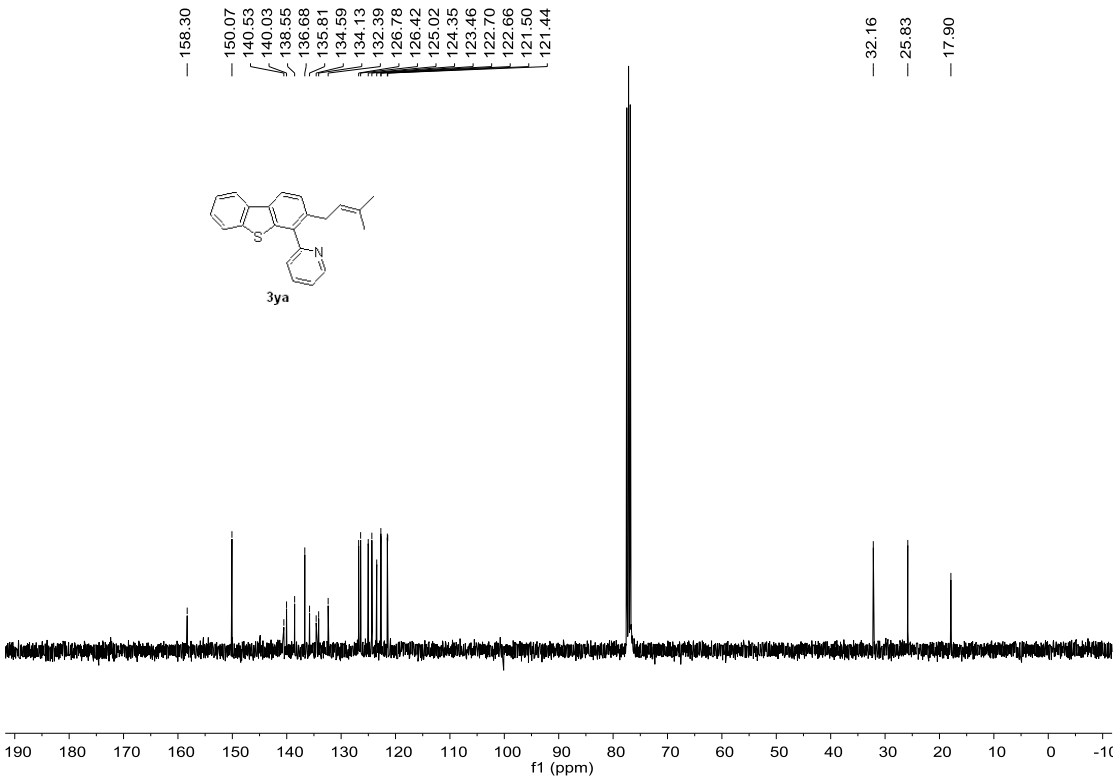
3.03
f1 (ppm)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126.78
126.42
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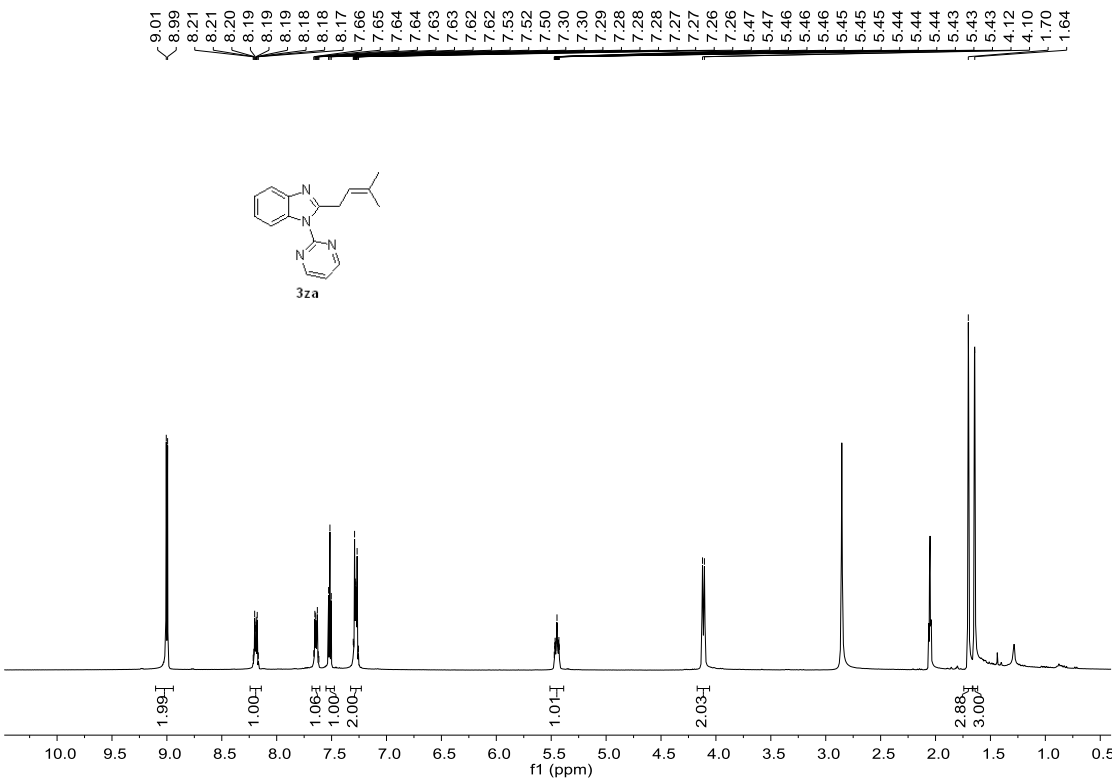
121.44
32.16
25.83
17.90
3ya
f1 (ppm)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1.70
1.64
3za
1.99
1.00
1.06
1.00
2.00
1.01
2.03
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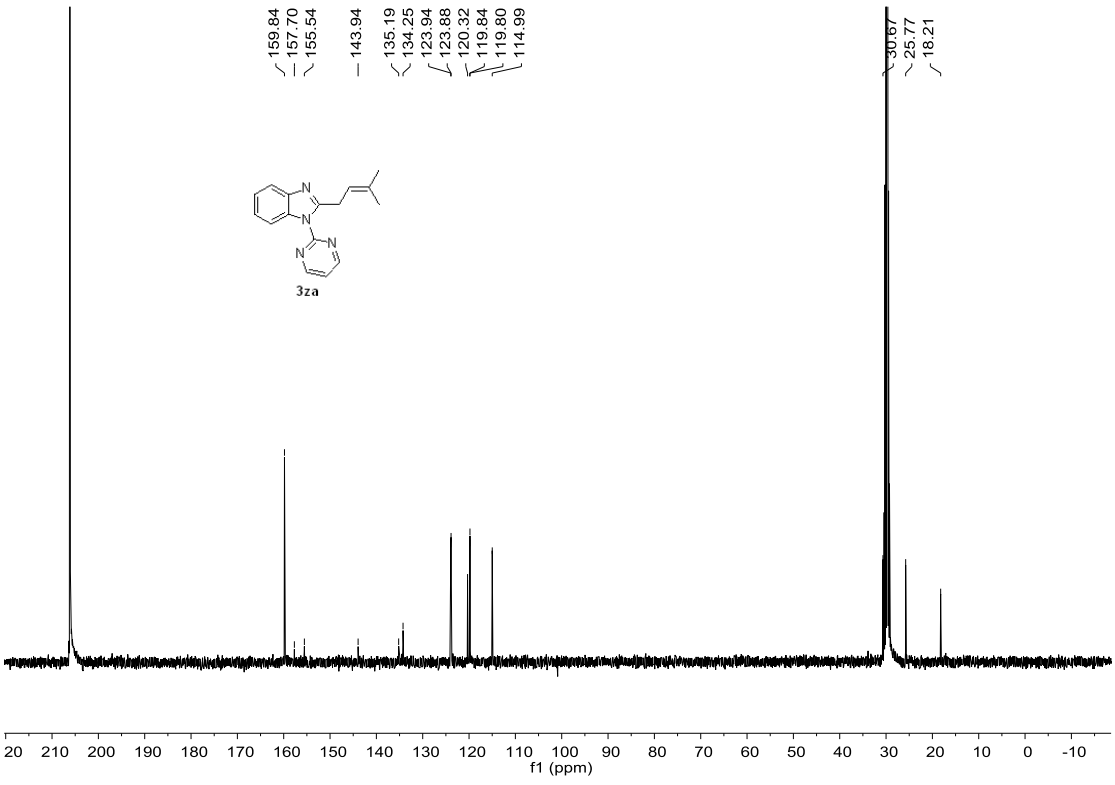
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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25.77
18.21
3za
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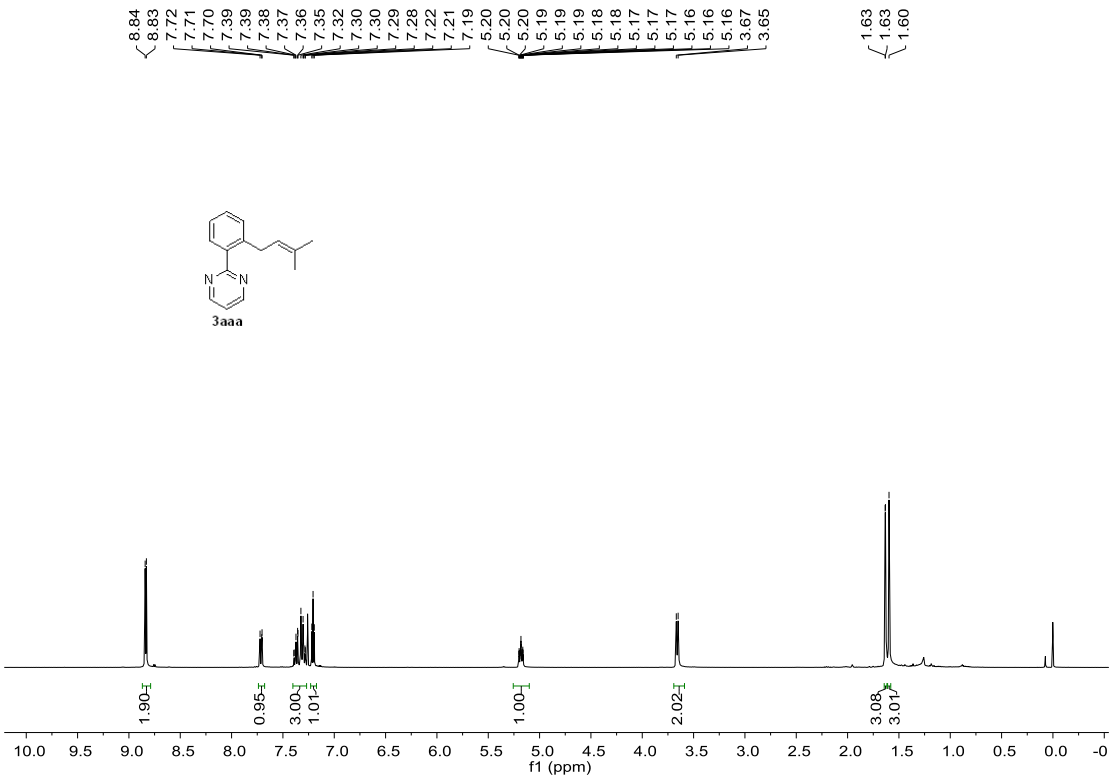
f1 (ppm)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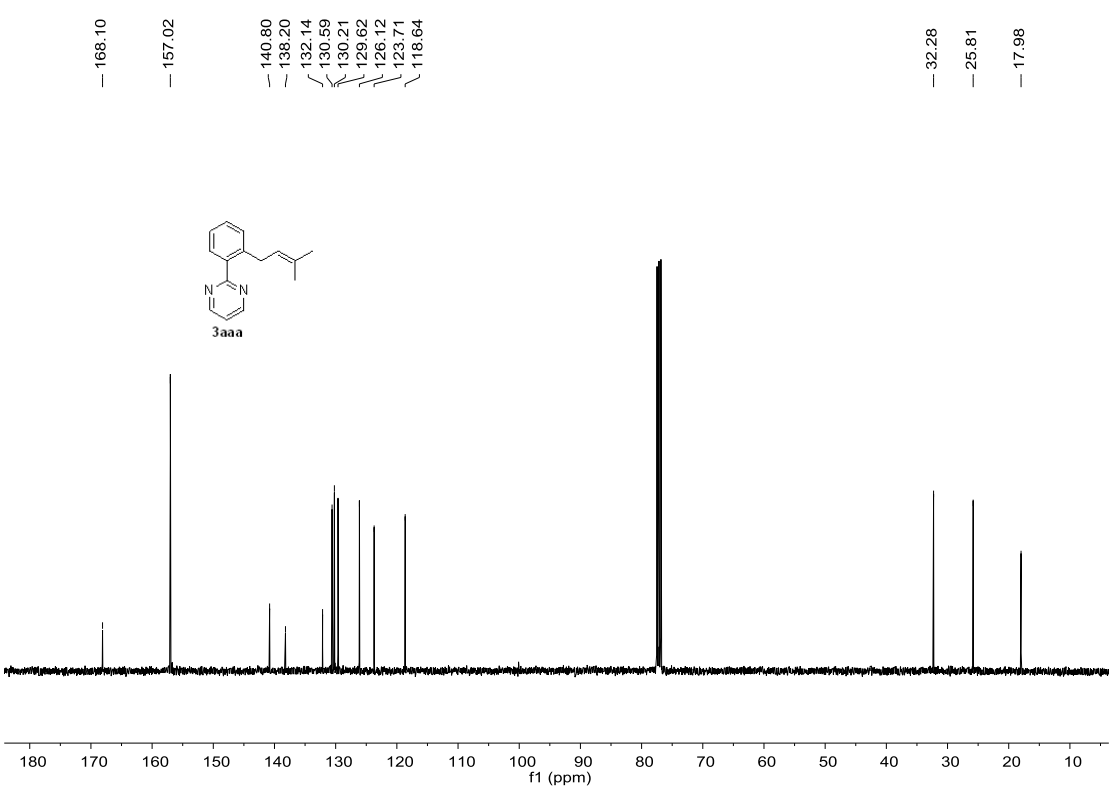
5.17
5.17
5.16
5.16
5.16
3.67
3.65
1.63
1.63
1.60
3aaa
1.90
0.95
3.00
1.01
1.00
2.02
3.08
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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130.59
130.21
129.62
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123.71
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32.28
25.81
17.98
3aaa
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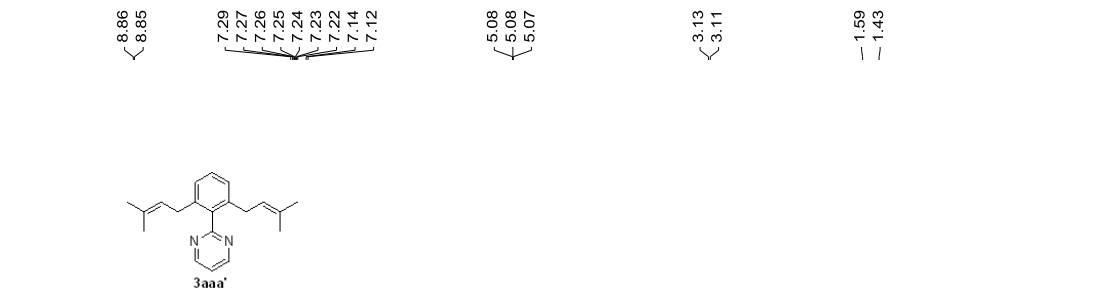
f1 (ppm)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7.12
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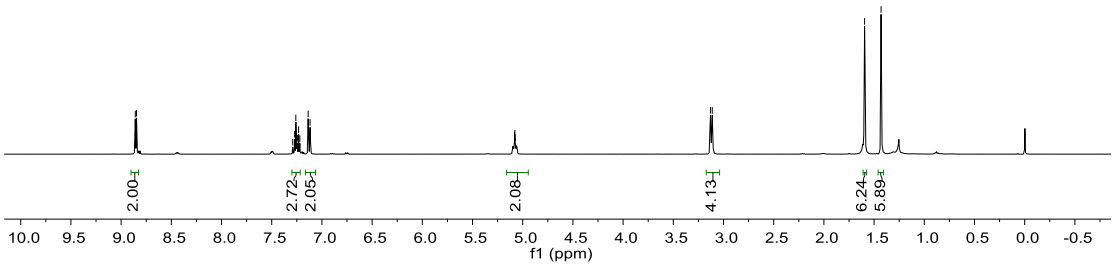
5.08
5.07
3.13
3.11
1.59
1.43

3aaa'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6.24
5.89
f1 (ppm)

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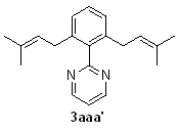
17.78



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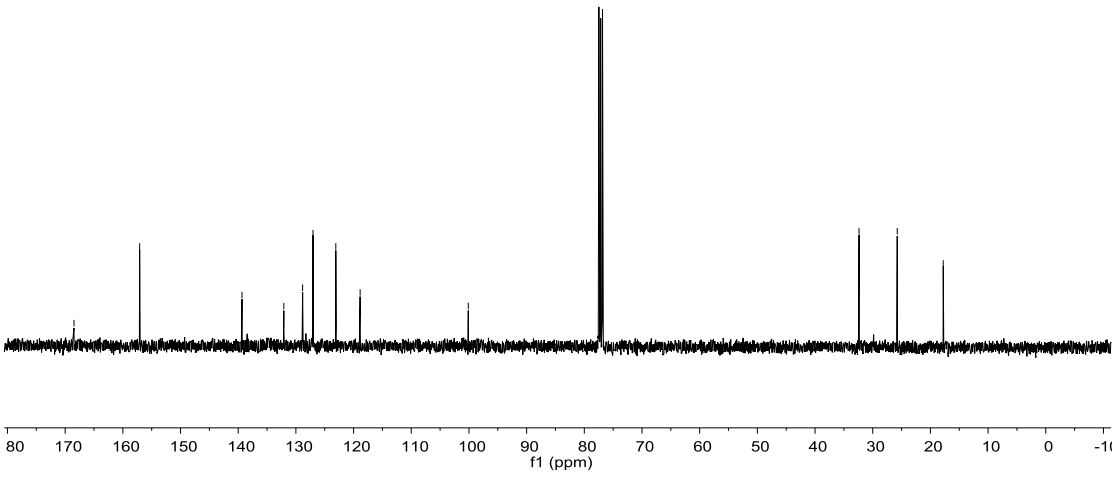
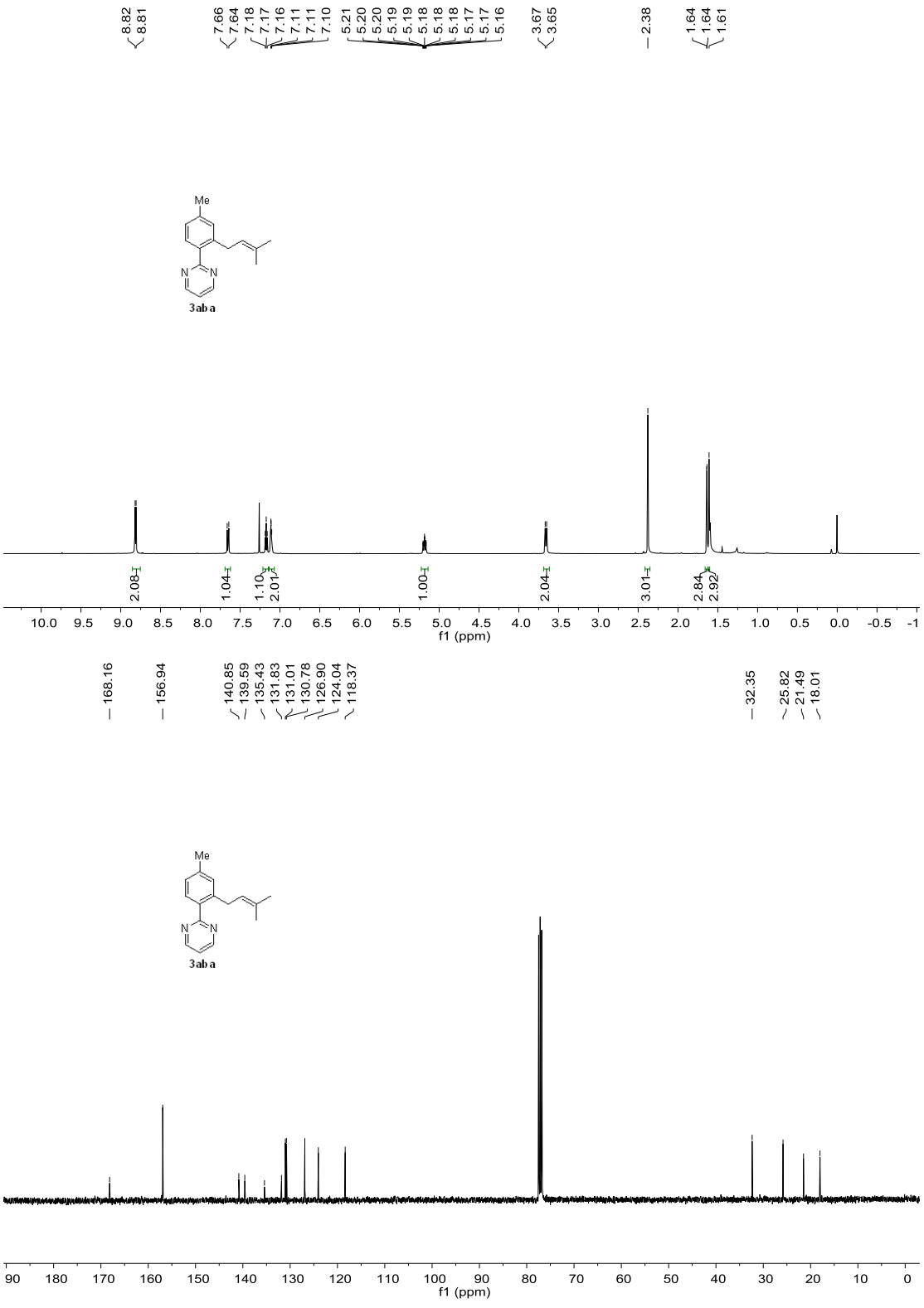

f1 (ppm)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8.81
7.66
7.64
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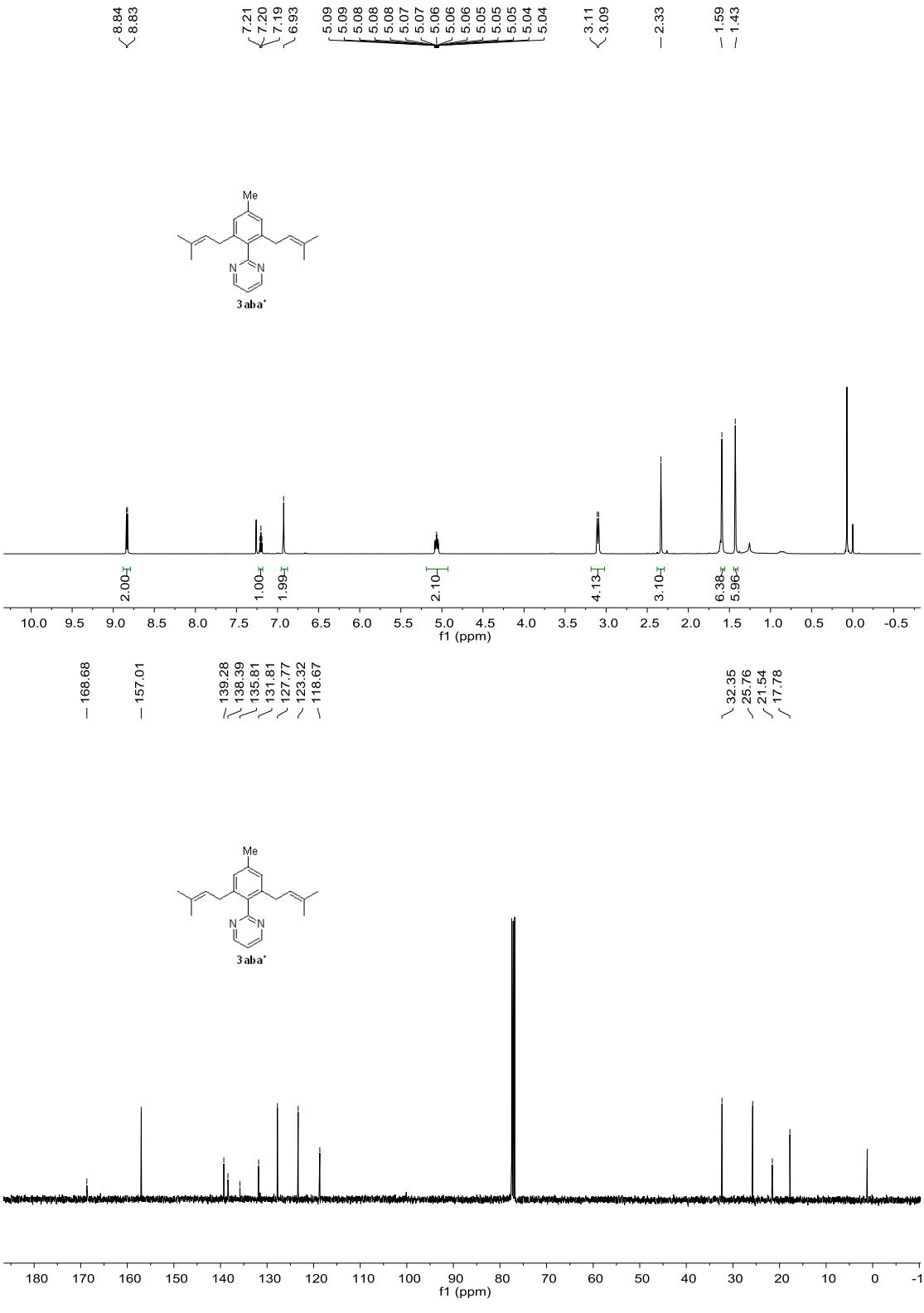
7.17
7.16
7.11
7.11
7.10
5.21
5.20
5.20
5.19
5.19
5.18
5.18
5.18
5.17
5.17
5.16
3.67
3.65
2.38
1.64
1.64
1.61
Me
N
N
3aba
2.08
1.04
1.10
2.01
1.00
2.04
3.01
2.84
2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)
168.16
156.94
140.85
139.59
135.43
131.83
131.01
130.78
126.90
124.04
118.37
32.35
25.82
21.49
18.01
Me
N
N
3aba
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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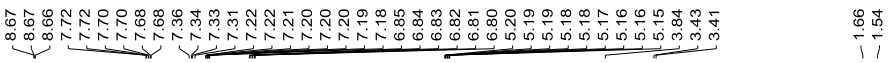
8.83
7.21
7.20
7.19
6.93
5.09
5.09
5.08
5.08
5.08
5.07
5.07
5.06
5.06
5.06
5.05
5.05
5.05
5.04
5.04
3.11
3.09
2.33
1.59
1.43
Me
N
N
3aba'
2.00
1.00
1.99
2.10
4.13
3.10
6.38
5.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
168.68
157.01
139.28
138.39
135.81
131.81
127.77
123.32
118.67
32.35
25.76
21.54
17.78
Me
N
N
3aba'
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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8.66
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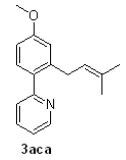
7.72
7.70
7.70
7.68
7.68
7.36
7.34
7.33
7.31
7.22
7.22
7.21
7.20
7.20
7.20
7.19
7.18
6.85
6.84
6.83
6.82
6.81
6.80
5.20
5.19
5.19
5.18
5.18
5.17
5.16
5.16
5.15
3.84
3.43
3.41
1.66
1.54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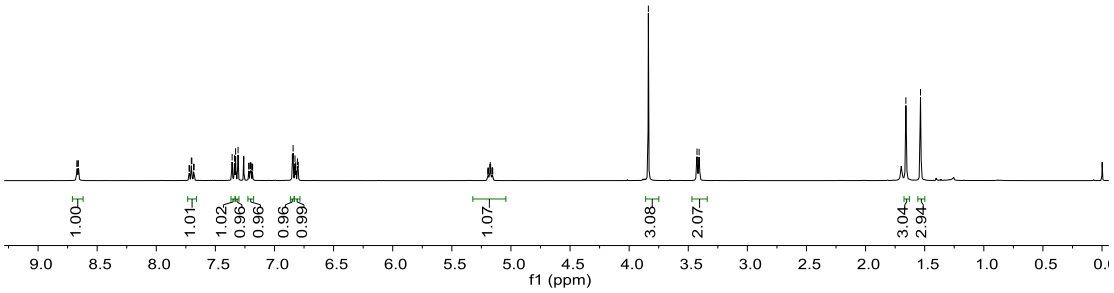
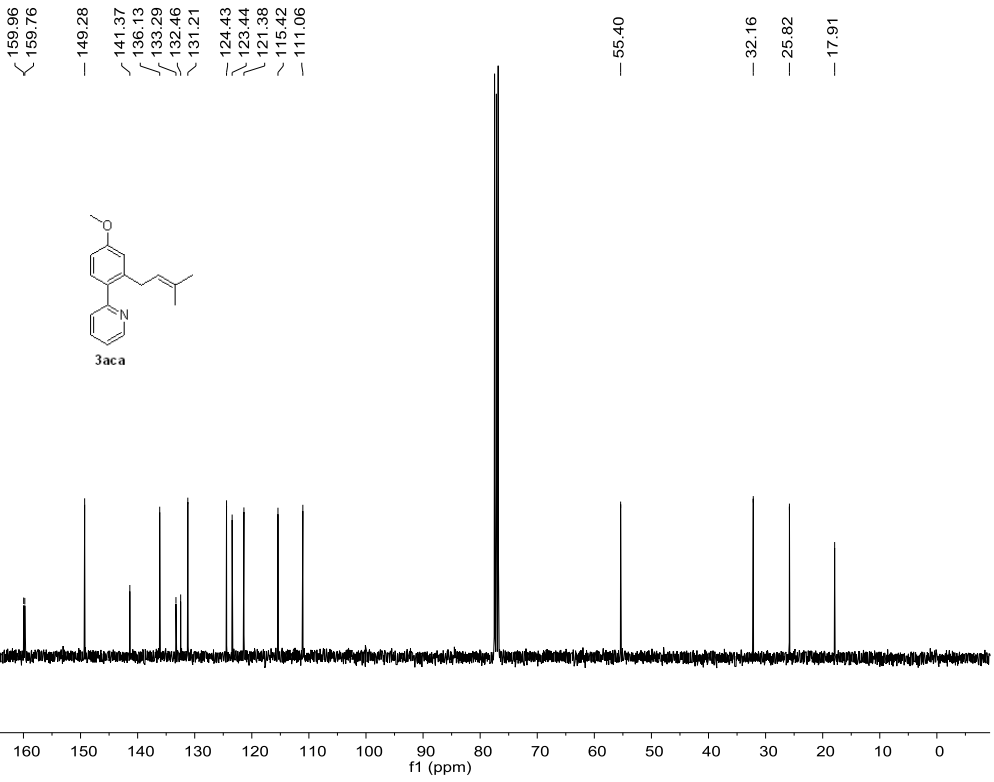
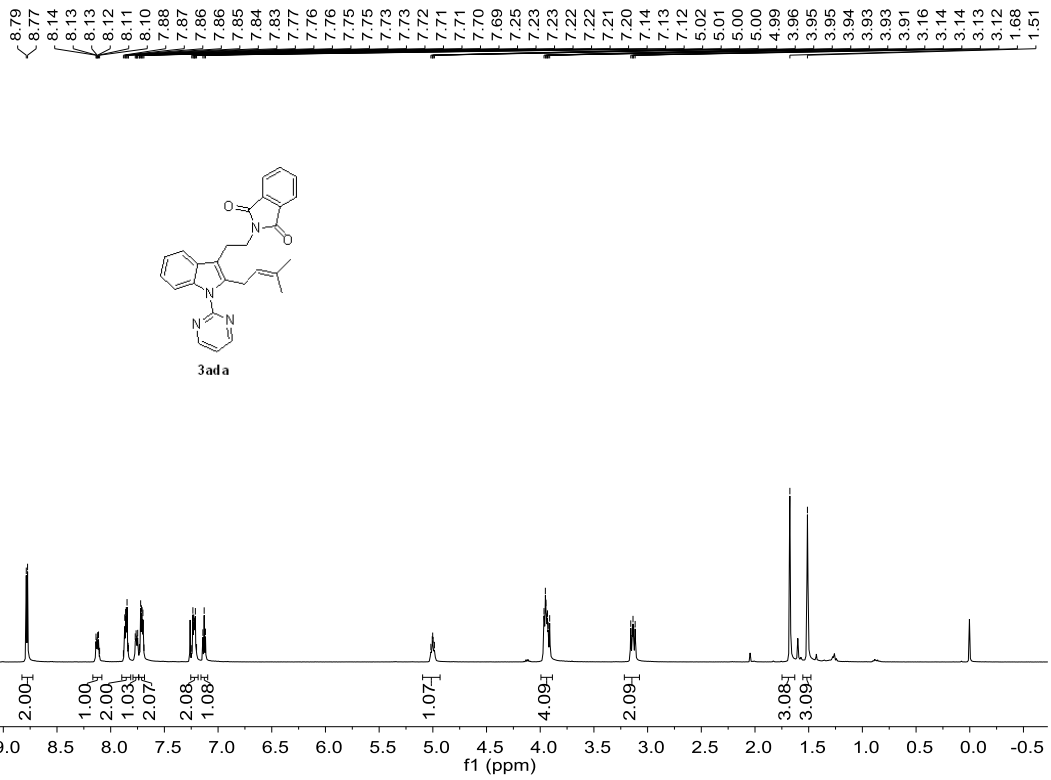
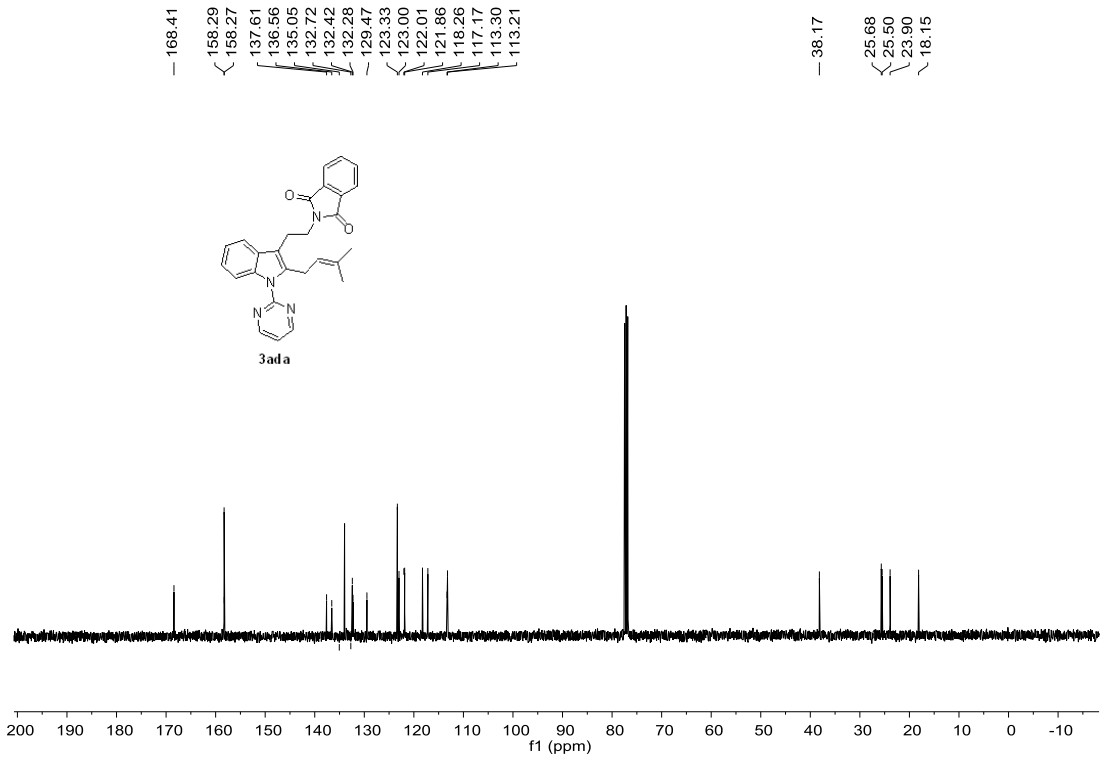
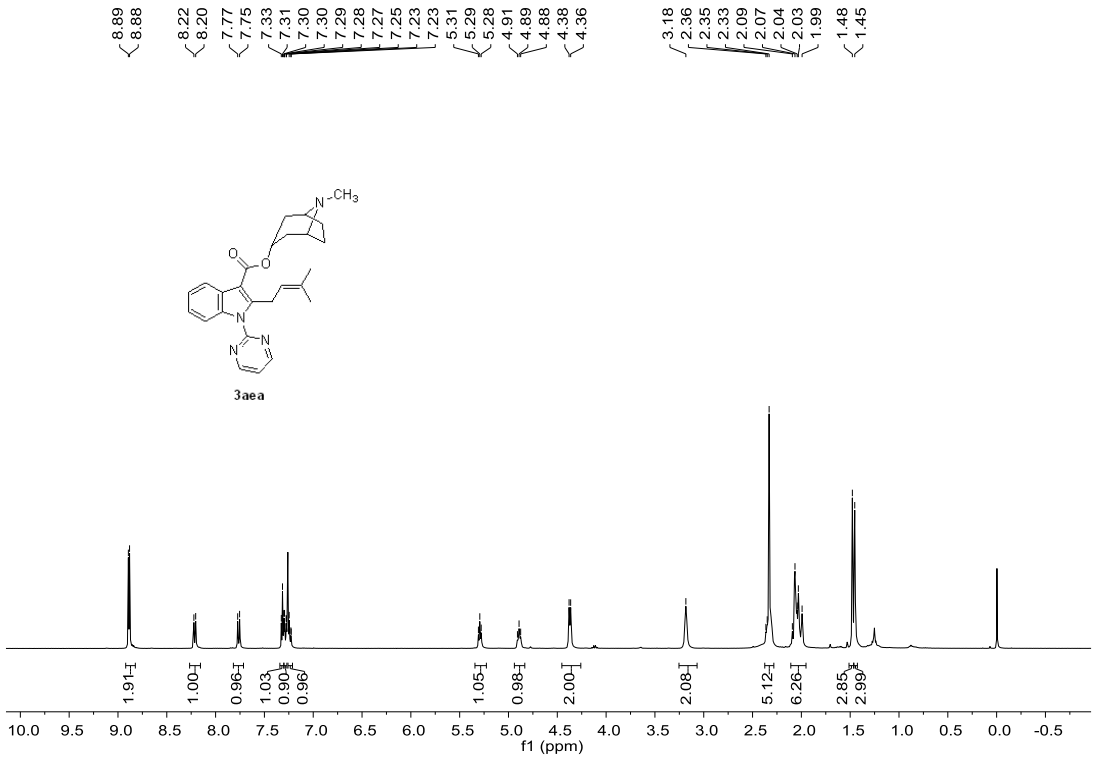

1.00
1.01
1.02
0.96
0.96
0.96
0.99
1.07
3.08
2.07
3.04
2.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


159.96
159.76
149.28
141.37
136.13
133.29
132.46
131.21
124.43
123.44
121.38
115.42
111.06
55.40
32.16
25.82
17.91
3aca
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.79 8.77 8.14 8.13 8.13 8.12 8.11 8.10 7.88 7.87 7.86 7.86 7.85 7.84 7.83 7.77 7.76 7.76 7.75 7.75 7.73 7.72 7.71 7.71 7.70 7.69 7.25 7.23 7.23 7.22 7.22 7.21 7.20 7.14 7.13 7.12 5.02 5.01 5.00 5.00 4.99 3.96 3.95 3.95 3.94 3.93 3.93 3.91 3.16 3.14 3.14 3.13 3.12 1.68 1.51
3ada
2.00 1.00 2.00 1.03 2.07 2.08 1.08 1.07 4.09 2.09 3.08 3.09
f1 (ppm)


168.41 158.29 158.27 137.61 136.56 135.05 132.72 132.42 132.28 129.47 123.33 123.00 122.01 121.86 118.26 117.17 113.30 113.21 38.17 25.68 25.50 23.90 18.15
3ada
f1 (ppm)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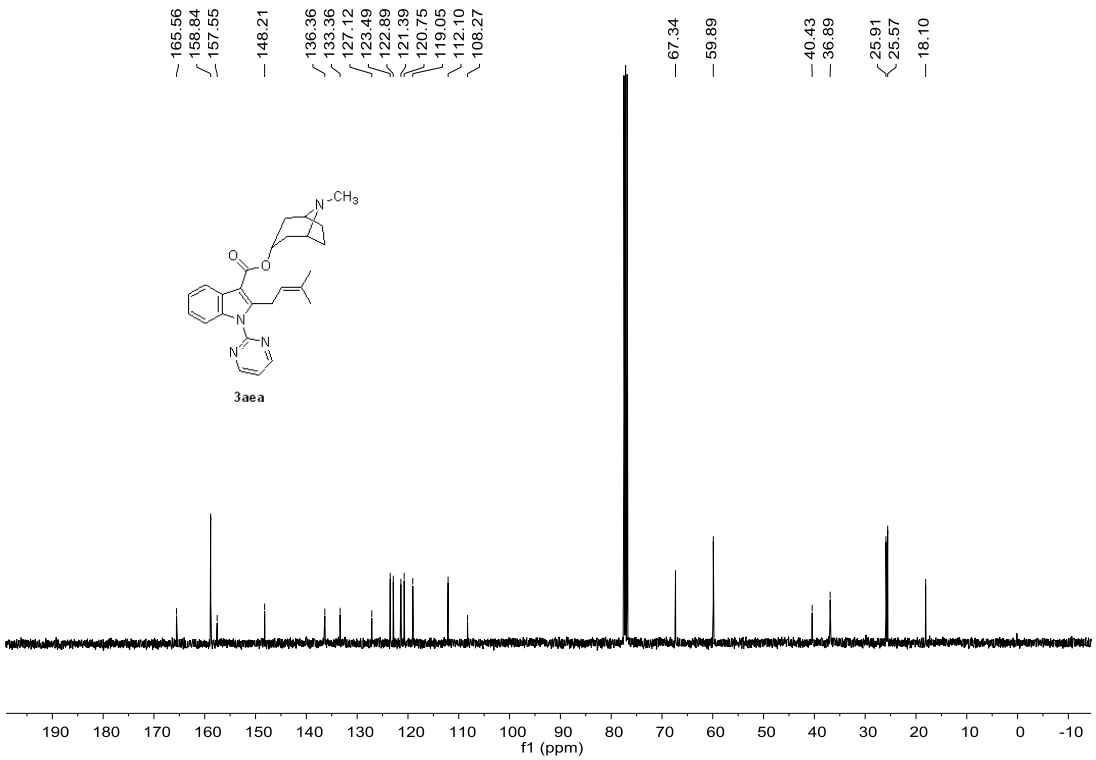
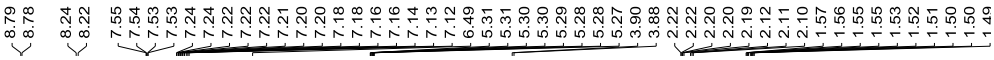
8.88
8.22
8.20
7.77
7.75
7.33
7.31
7.30
7.30
7.29
7.28
7.27
7.25
7.23
7.23
5.31
5.29
5.28
4.91
4.89
4.88
4.38
4.36
3.18
2.36
2.35
2.33
2.09
2.07
2.04
2.03
1.99
1.48
1.45
3aea
1.91
1.00
0.96
1.03
0.90
0.96
1.05
0.98
2.00
2.08
5.12
6.26
2.85
2.99
f1 (ppm)


165.56
158.84
157.55
148.21
136.36
133.36
127.12
123.49
122.89
121.39
120.75
119.05
112.10
108.27
67.34
59.89
40.43
36.89
25.91
25.57
18.10
3aea
f1 (ppm)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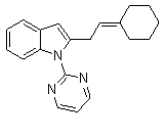
8.78
8.24
8.22
7.55
7.54
7.53
7.53
7.24
7.24
7.22
7.22
7.21
7.20
7.20
7.18
7.18
7.16
7.16
7.14
7.13
7.12
6.49
5.31
5.31
5.30
5.30
5.29
5.28
5.28
5.27
3.90
3.88
2.22
2.22
2.20
2.20
2.19
2.12
2.11
2.10
1.57
1.56
1.55
1.55
1.53
1.52
1.51
1.50
1.50
1.49



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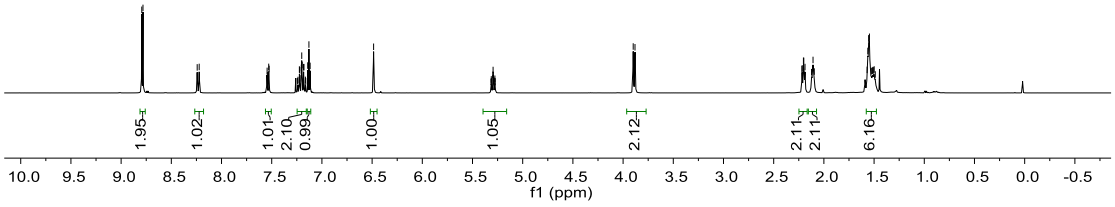
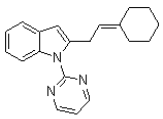
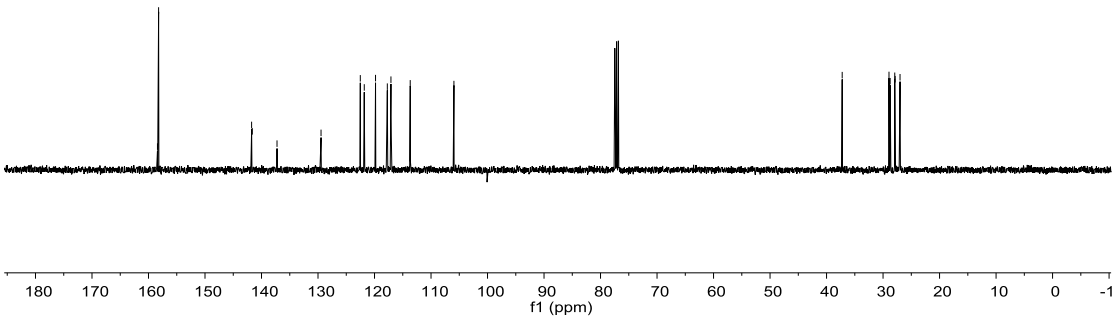

1.95
1.02
1.01
2.10
0.99
1.00
1.05
2.12
2.11
2.11
6.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

158.41
158.21
141.75
141.63
137.26
129.46
122.52
121.81
119.82
117.73
117.09
113.68
105.95
37.23
28.95
28.74
27.93
27.86
27.00



3ab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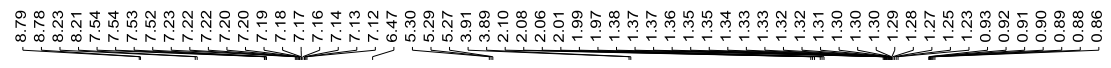
f1 (ppm)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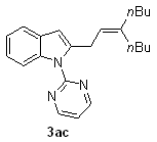
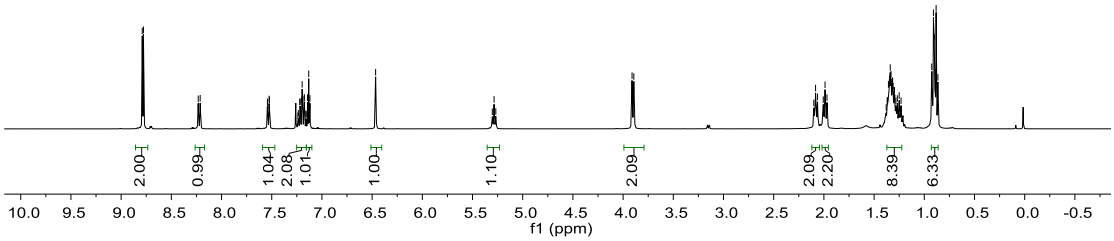
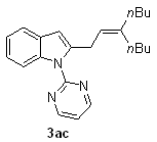
8.78
8.23
8.21
7.54
7.54
7.53
7.52
7.23
7.22
7.22
7.20
7.20
7.19
7.18
7.17
7.16
7.14
7.13
7.12
6.47
5.30
5.29
5.27
3.91
3.89
2.10
2.08
2.06
2.01
1.99
1.97
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.33
1.33
1.32
1.32
1.31
1.30
1.30
1.30
1.29
1.28
1.27
1.25
1.23
0.93
0.92
0.91
0.90
0.89
0.88
0.86


nBu
nBu
N
N
N

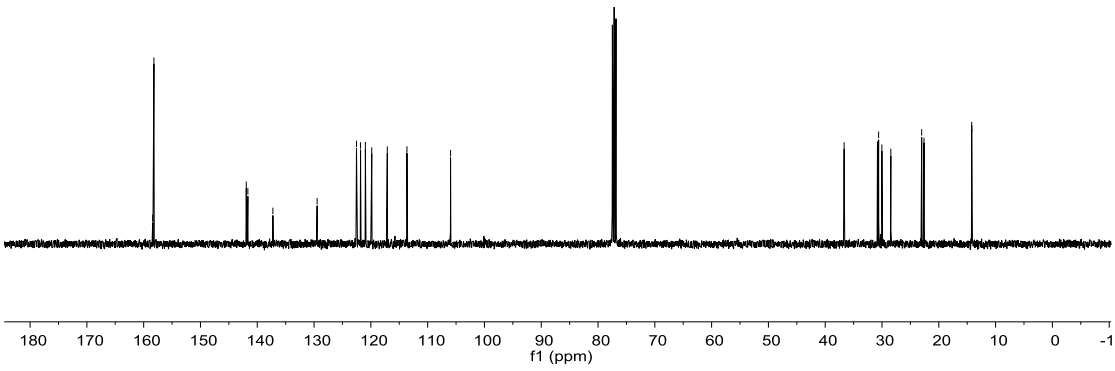
3ac

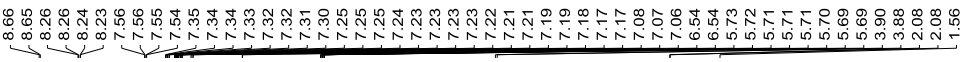

2.00
0.99
1.04
2.08
1.01
1.00
1.10
2.09
2.09
2.20
8.39
6.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

158.42
158.19
141.94
141.65
137.25
129.46
122.53
121.82
120.96
119.84
117.10
113.64
105.96
36.67
30.80
30.60
30.02
28.44
23.01
22.61
14.21
14.18


nBu
nBu
N
N
N

3ac


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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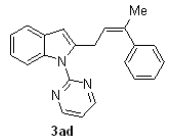
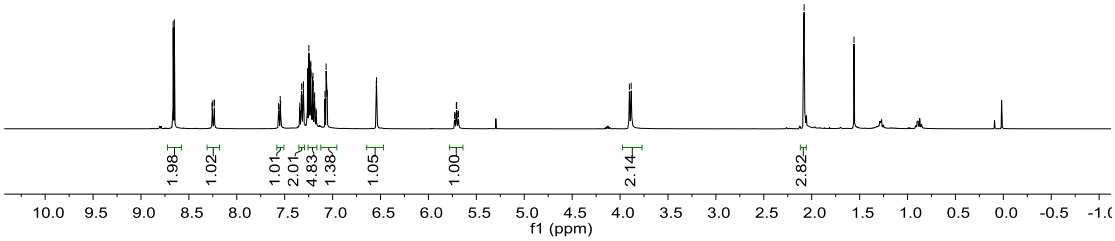
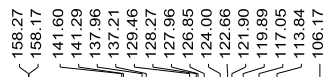
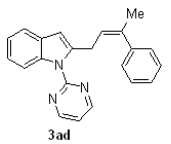
7.56
7.56
7.55
7.54
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.21
7.21
7.19
7.19
7.18
7.17
7.17
7.08
7.07
7.06
6.54
6.54
5.73
5.72
5.71
5.71
5.71
5.70
5.69
5.69
3.90
3.88
2.08
2.08
1.56


Me
N
N
N

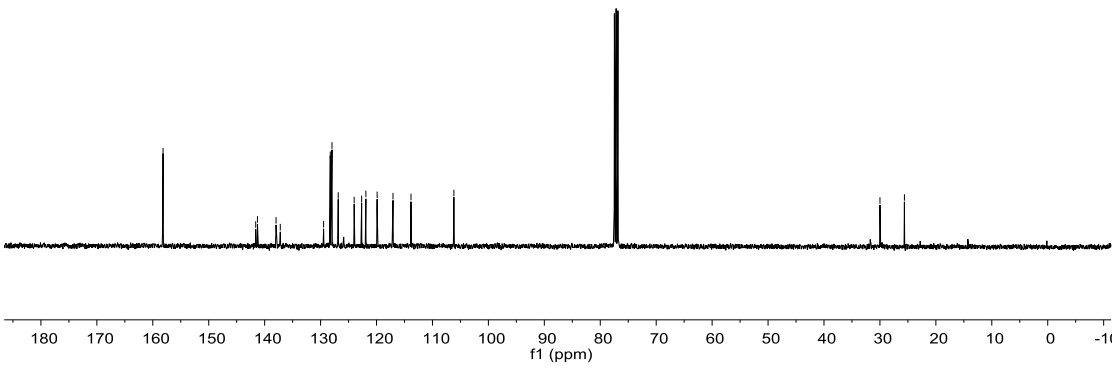
3ad

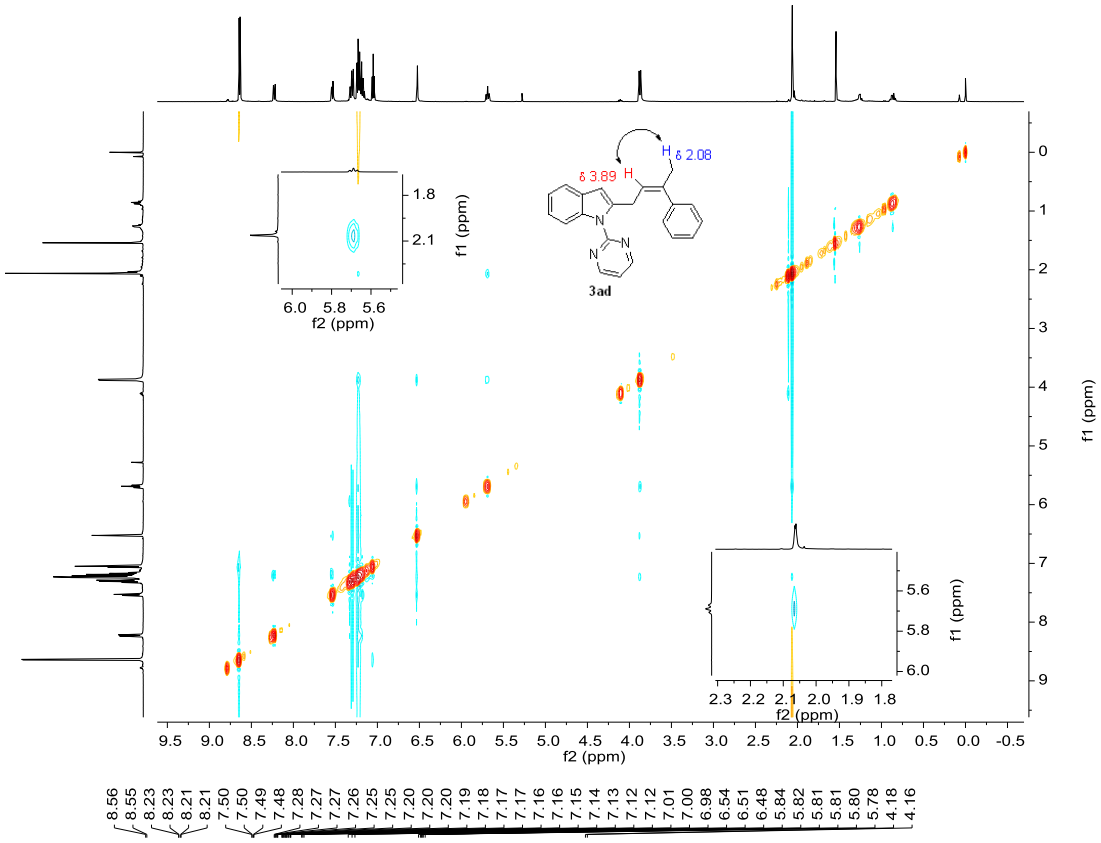

1.98
1.02
1.01
2.01
4.83
1.38
1.05
1.00
2.14
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.27
158.17
141.60
141.29
137.96
137.21
129.46
128.27
127.96
126.85
124.00
122.66
121.90
119.89
117.05
113.84
106.17
29.99
25.62


Me
N
N
N

3ad


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


δ 3.89
H
δ 2.08
3ad
f1 (ppm)
f2 (ppm)

8.56
8.55
8.23
8.23
8.21
8.21
7.50
7.50
7.49
7.48
7.28
7.27
7.27
7.26
7.25
7.25
7.20
7.20
7.20
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.13
7.12
7.12
7.01
7.00
6.98
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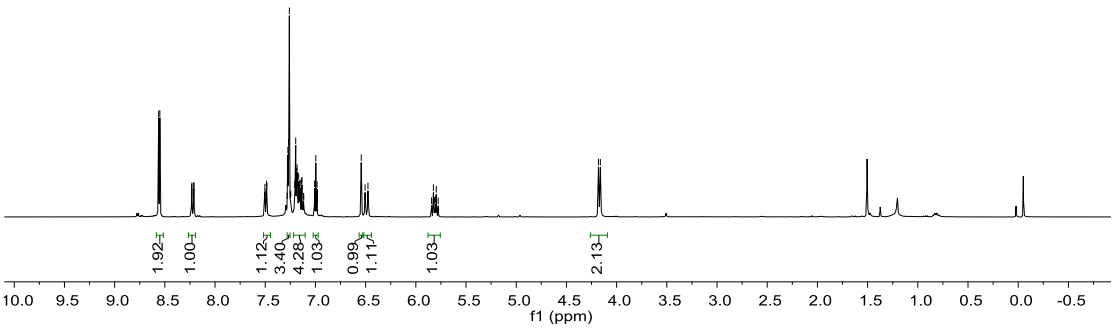
6.48
5.84
5.82
5.81
5.81
5.80
5.78
4.18
4.16

3ae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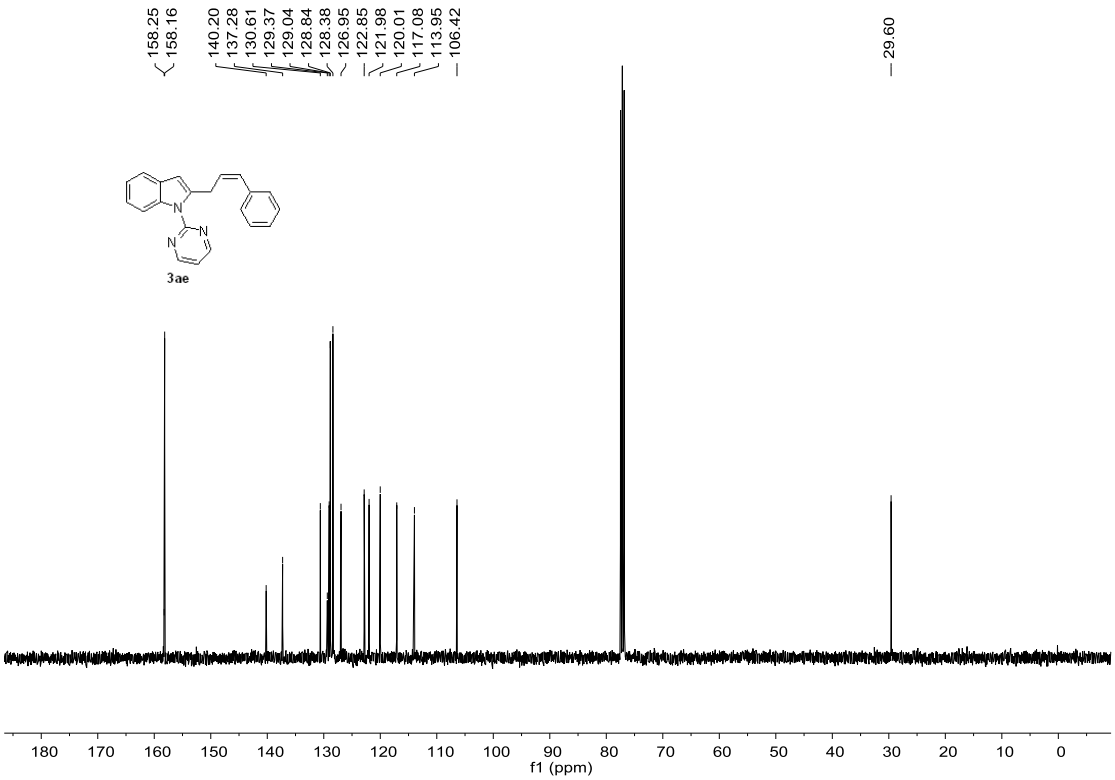
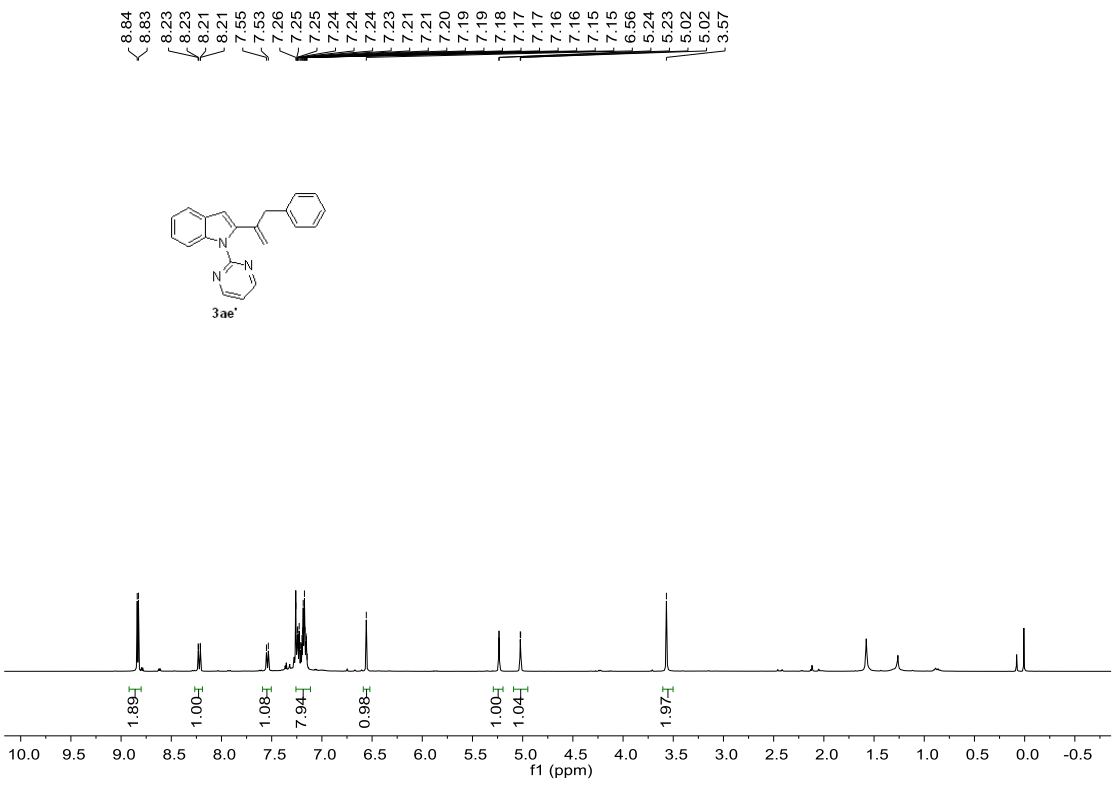
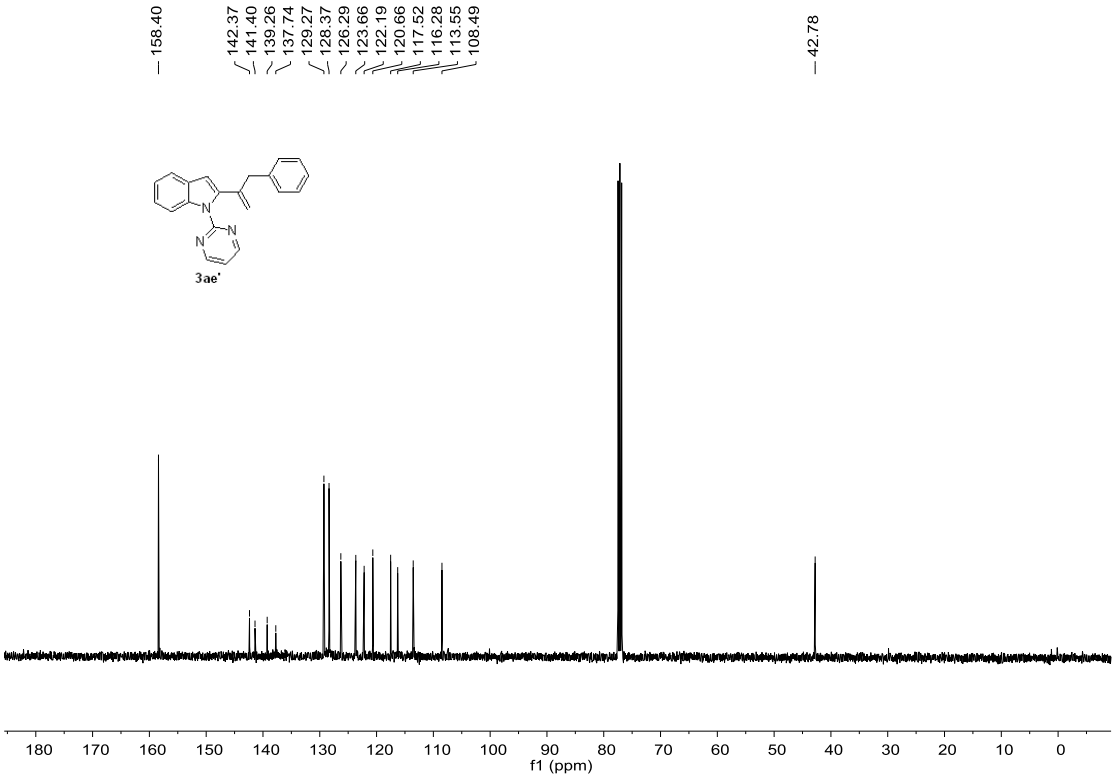
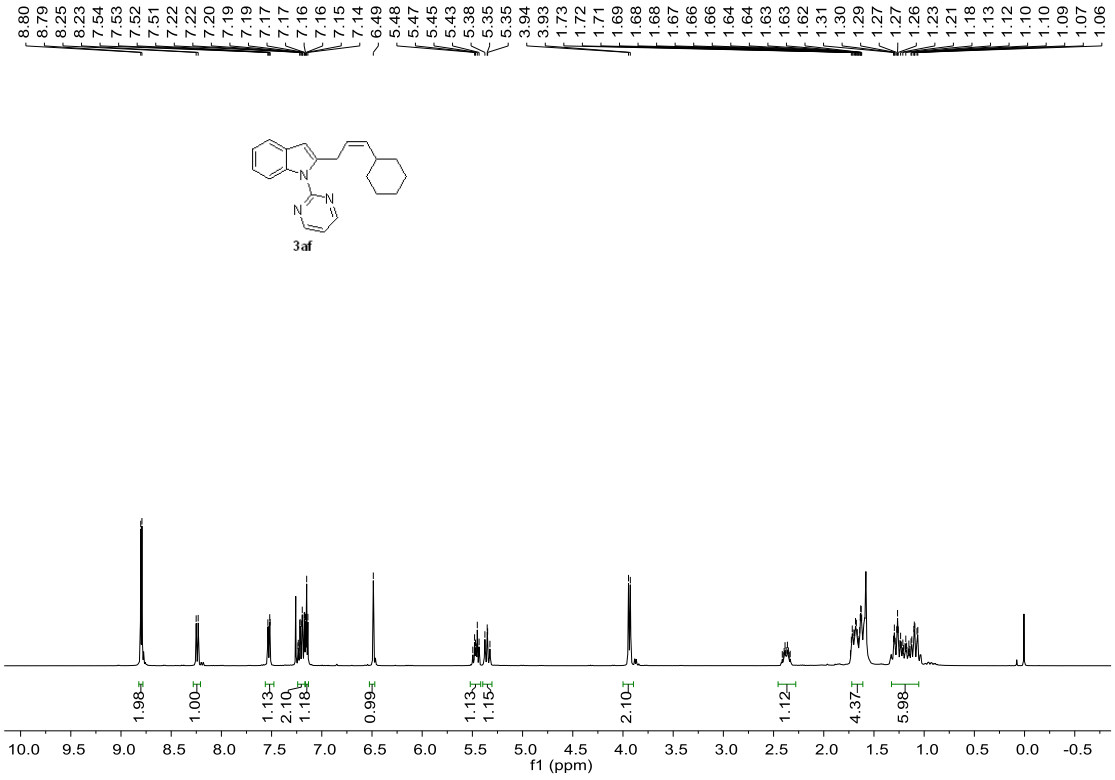
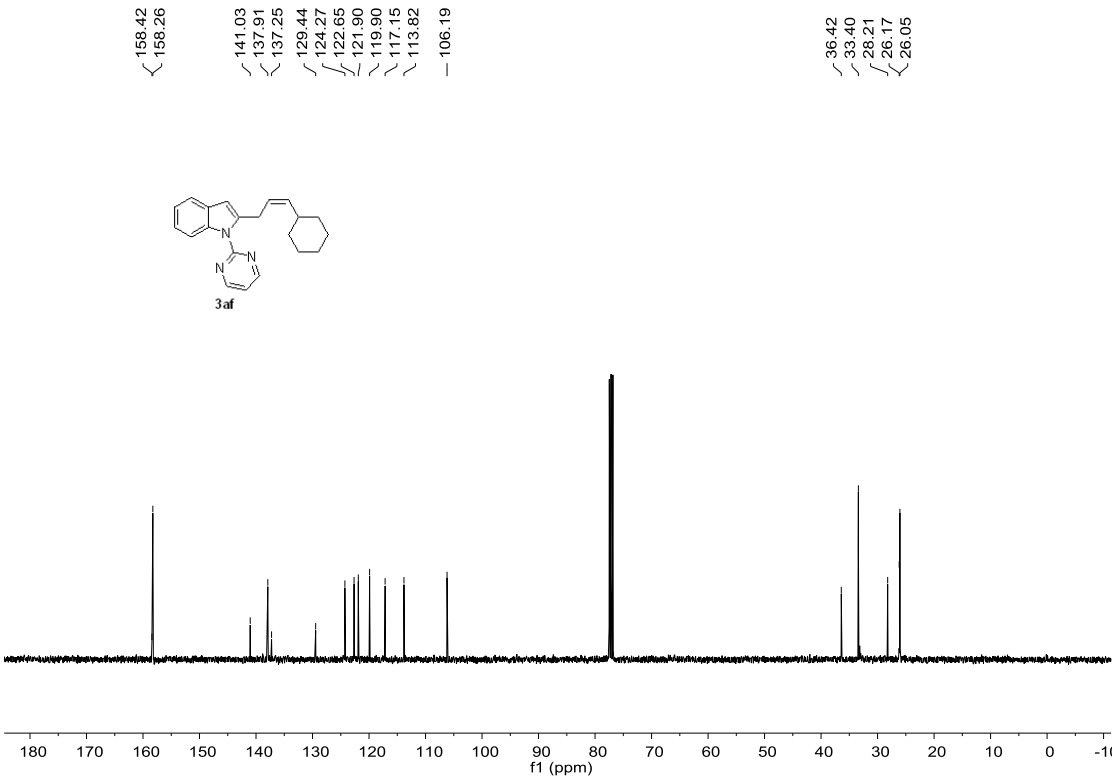
1.03
0.99
1.11
1.03
2.13
f1 (ppm)

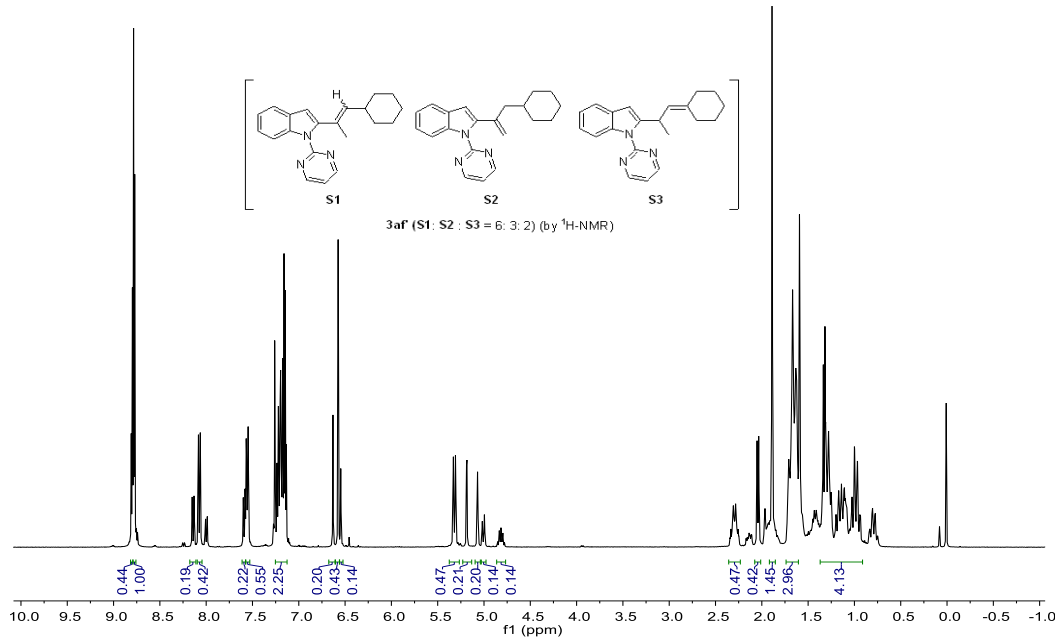

158.25
158.16
140.20
137.28
130.61
129.37
129.04
128.84
128.38
126.95
122.85
121.98
120.01
117.08
113.95
106.42
29.60
3ae
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.84
8.83
8.23
8.23
8.21
8.21
7.55
7.53
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
6.56
5.24
5.23
5.02
5.02
3.57
3ae'
1.89
1.00
1.08
7.94
0.98
1.00
1.04
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.40
142.37
141.40
139.26
137.74
129.27
128.37
126.29
123.66
122.19
120.66
117.52
116.28
113.55
108.49
42.78
3ae'
f1 (ppm)


8.80
8.79
8.25
8.23
7.54
7.53
7.52
7.51
7.22
7.20
7.19
7.19
7.17
7.17
7.16
7.16
7.15
7.14
6.49
5.48
5.47
5.45
5.43
5.38
5.35
5.35
3.94
3.93
1.73
1.72
1.71
1.69
1.68
1.68
1.67
1.66
1.66
1.64
1.64
1.63
1.63
1.62
1.31
1.30
1.29
1.27
1.27
1.26
1.23
1.21
1.18
1.13
1.12
1.10
1.10
1.09
1.07
1.06
3af
1.98
1.00
1.13
2.10
1.18
0.99
1.13
1.15
2.10
1.12
4.37
5.98
f1 (ppm)


158.42
158.26
141.03
137.91
137.25
129.44
124.27
122.65
121.90
119.90
117.15
113.82
106.19
36.42
33.40
28.21
26.17
26.05
3af
f1 (ppm)


S1
S2
S3
3af' (S1 : S2 : S3 = 6: 3: 2) (by 1H-NMR)
0.44
1.00
0.19
0.42
0.22
0.55
2.25
0.20
0.43
0.14
0.47
0.21
0.20
0.14
0.14
0.47
0.42
1.45
2.96
4.13
f1 (ppm)