Supplementary Materials: An Expeditious and Greener Synthesis of 2-Aminoimidazoles in Deep Eutectic Solvents

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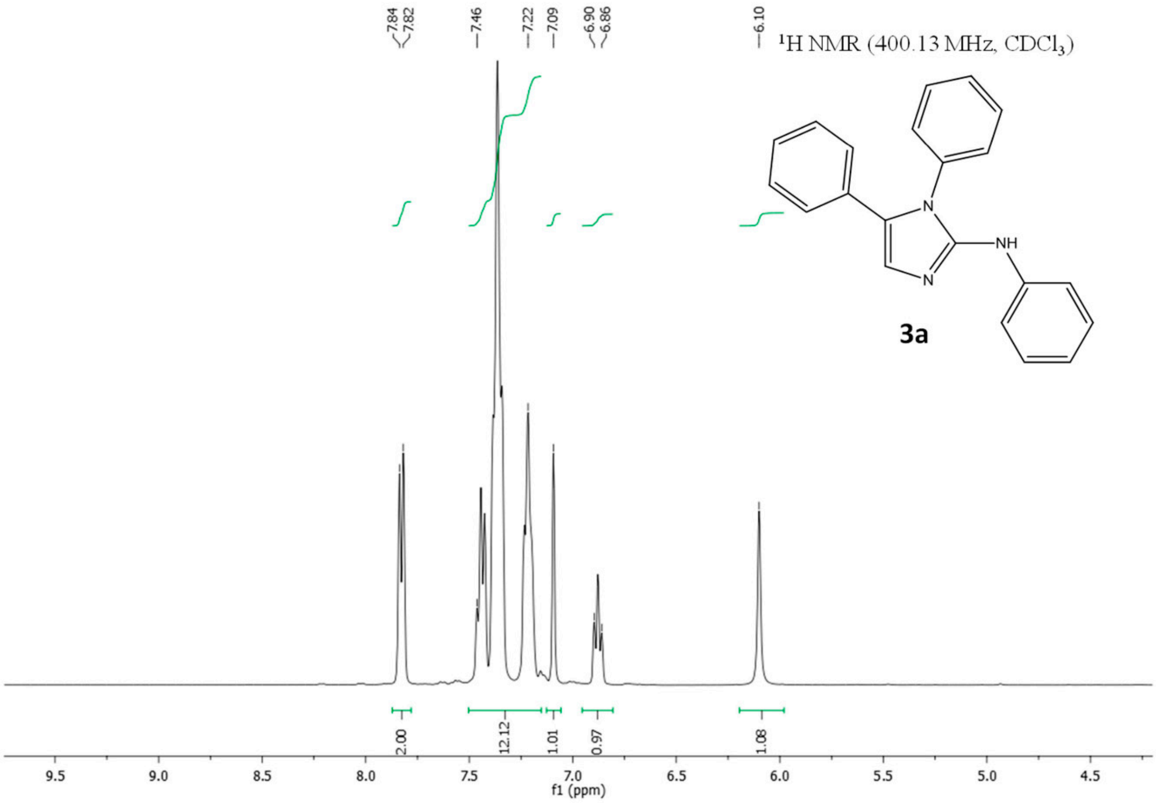
Synthesis of 2-Aminoimidazoles **3a–g** *in THF (Table 1, Main Manuscript)*

The appropriate α-chloroketone **1** (1.0 mmol), guanidine **2a** (1.3 mmol) and Et_3N (1 mmol) were added to dry THF (6 mL), under an argon atmosphere and magnetic stirring, and the mixture was then heated under reflux for a period of 10–12 h, until the ketone **1** disappeared, as revealed by GC-MS analysis. After this time, the mixture was cooled to room temperature and 10 mL of H_2O were added. The resulting aqueous solution was then extracted with AcOEt (3 × 10 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash-chromatography (silica gel; petroleum ether/AcOEt 80:20–95:5) to give products **3a**–**g**.

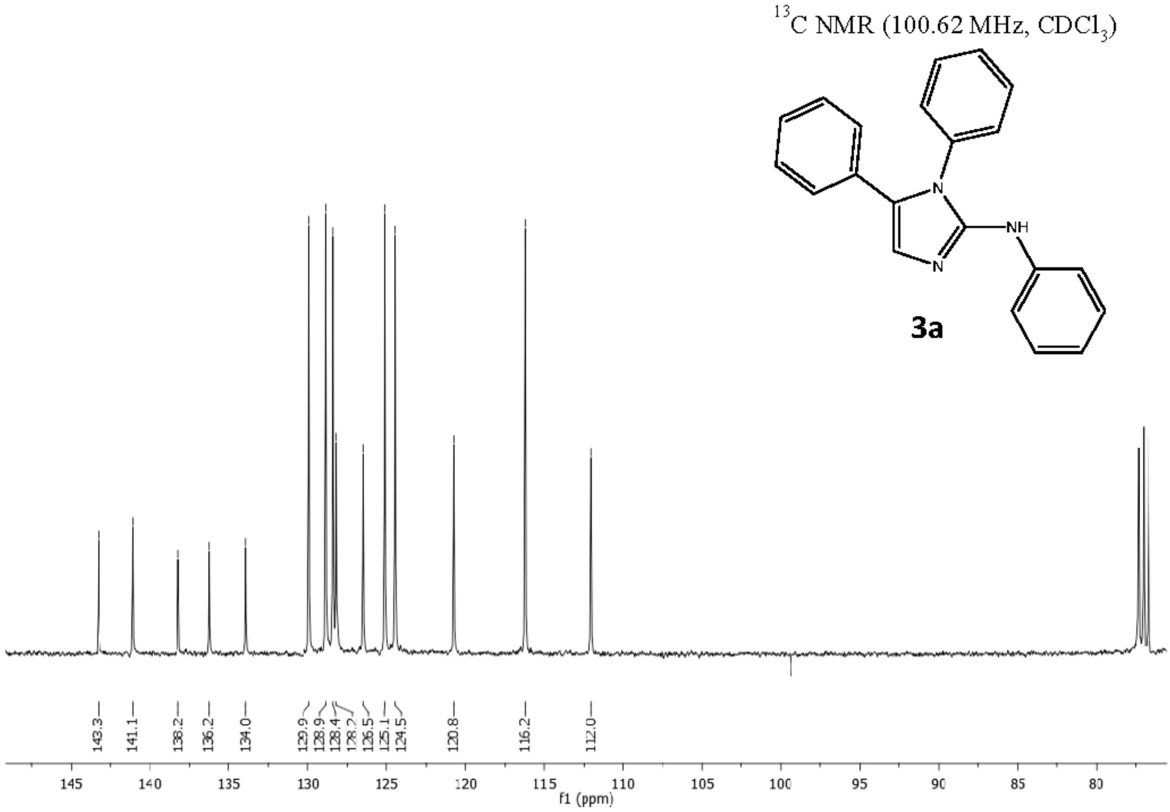
Synthesis of 2-Aminoimidazoles **3h**,**i** *in EtOH (Table 1, Main Manuscript)*

Guanidinium carbonate **2b**·H_2CO_3 (1.3 mmol) and KOH (1.3 mmol) were added to EtOH (6 mL) under magnetic stirring, and the mixture was then heated under reflux for a period of 30 min, so as to liberate the free base of guanidine **2b** in situ. After this time, α-chloroketone **1** and triethylamine (1.3 mmol) were added and the reaction stirred at reflux for 10–12 h until the ketone **1** disappeared, as revealed by GC-MS analysis. The reaction mixture was then cooled to room temperature and 10 mL of H_2O were added. The resulting aqueous solution was extracted with AcOEt (3 × 10 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash-chromatography (silica gel; petroleum ether/AcOEt 20:80–40:60) to give products **3h**–**i**.



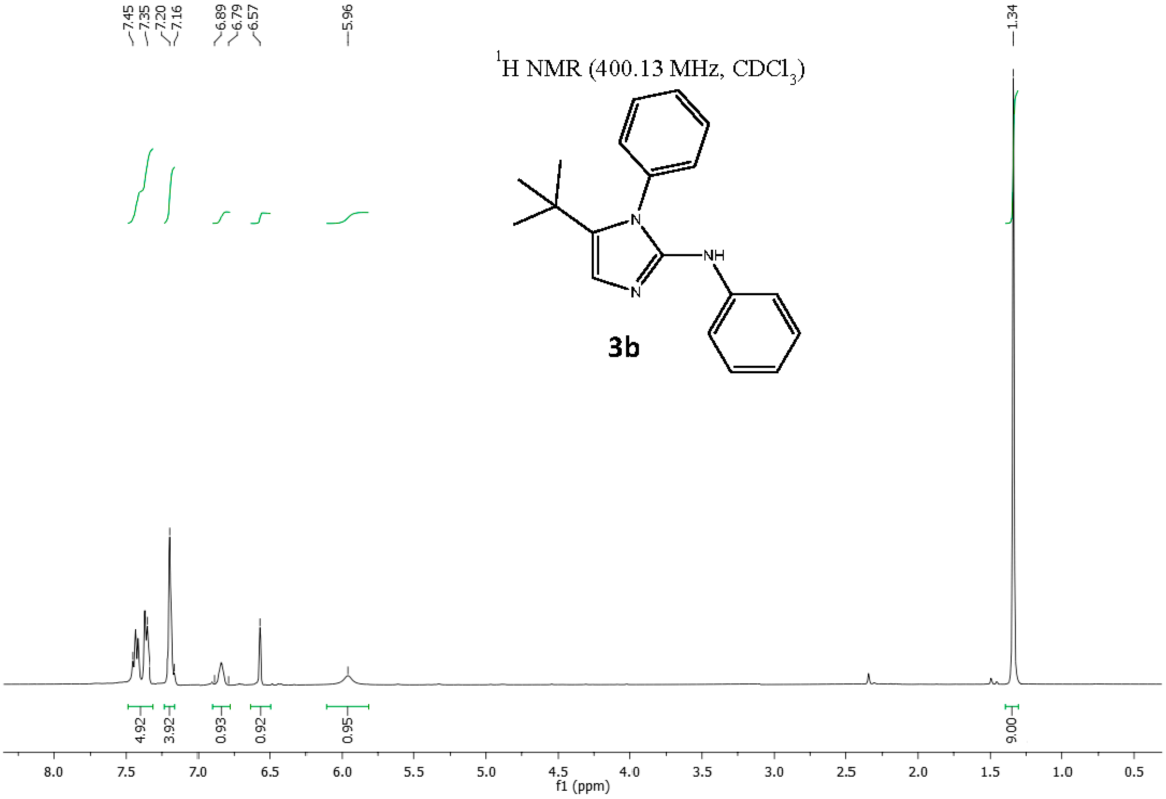
^{1}H NMR (400.13 MHz, $CDCl_3$)

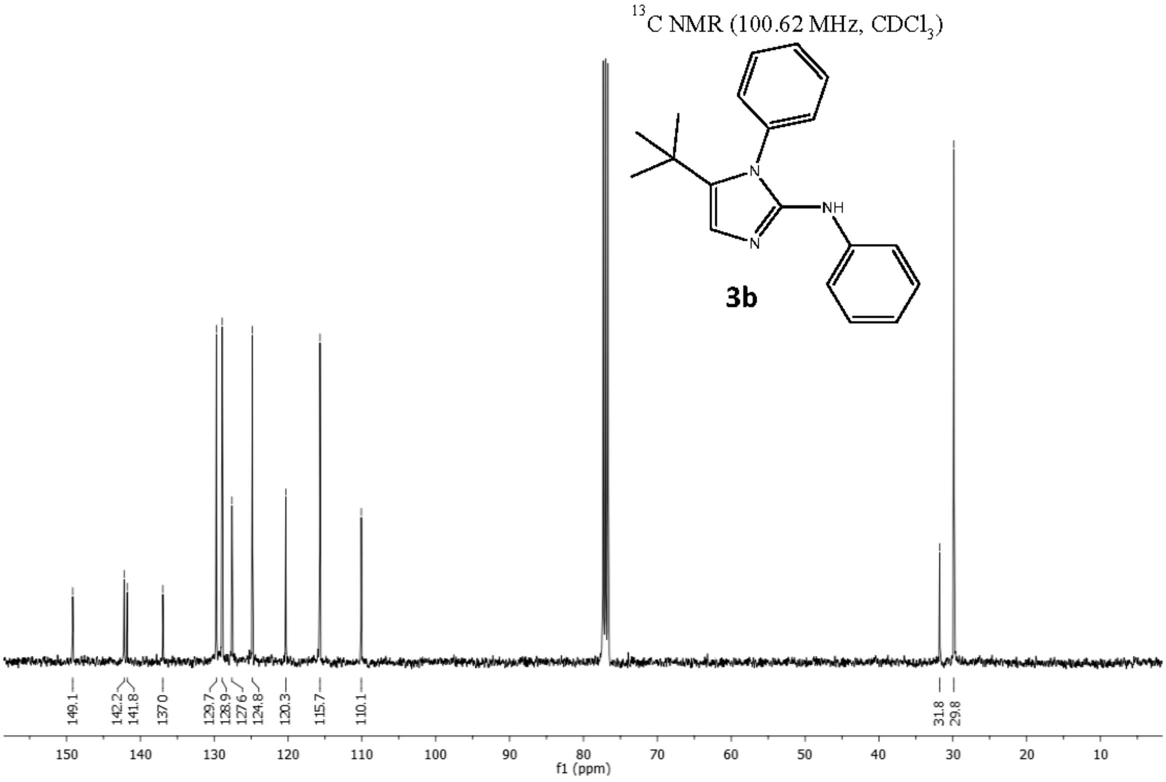
3a

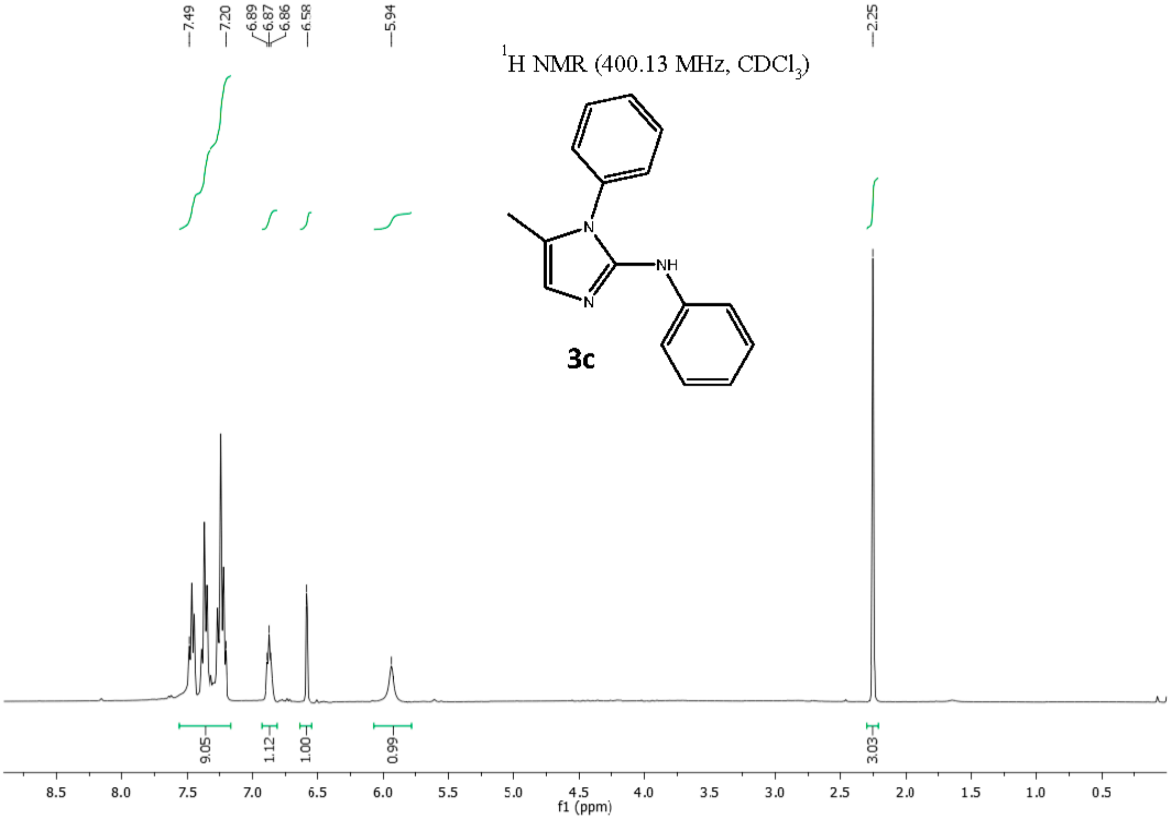


^{13}C NMR (100.62 MHz, $CDCl_3$)

3a

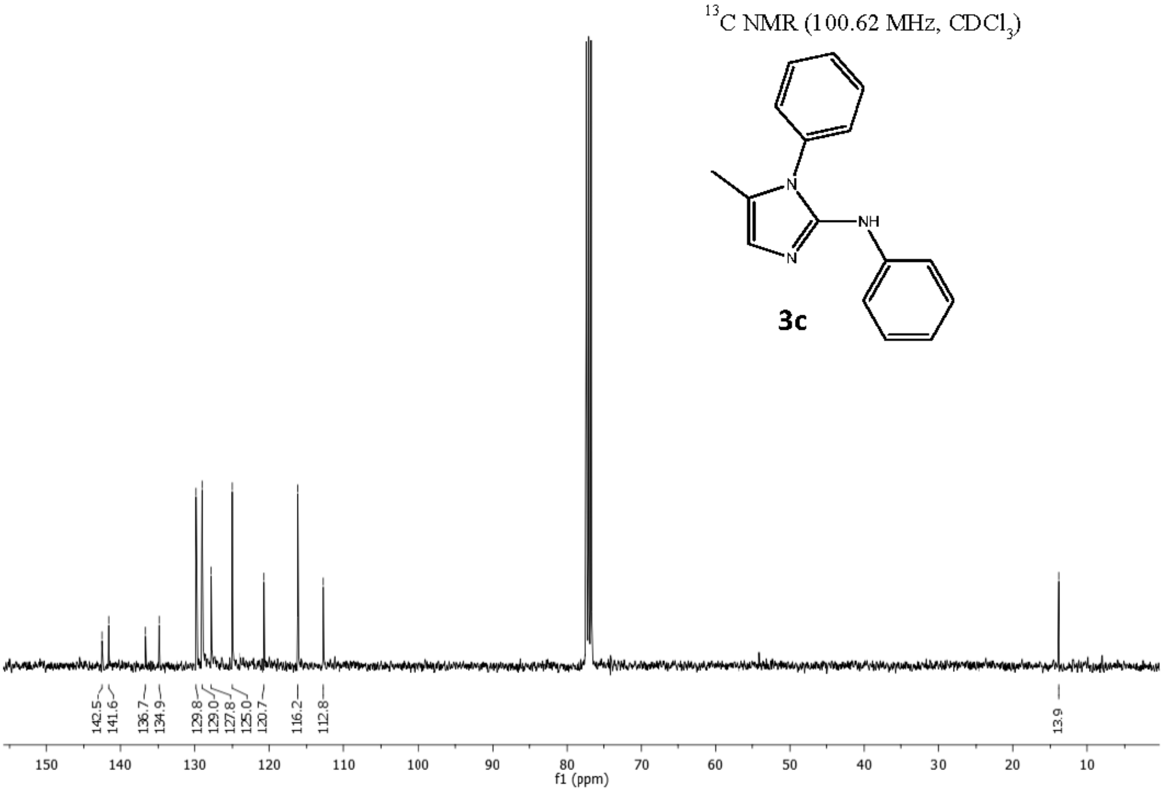

7.45
7.35
7.20
7.16
6.89
6.79
6.57
5.96
1.34
^{1}H NMR (400.13 MHz, CDCl$_3$)
N
N
NH
3b
4.92
3.92
0.93
0.92
0.95
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


^{13}C NMR (100.62 MHz, CDCl$_3$)
N
N
NH
3b
149.1
142.2
141.8
137.0
129.7
128.9
127.6
124.8
120.3
115.7
110.1
31.8
29.8
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



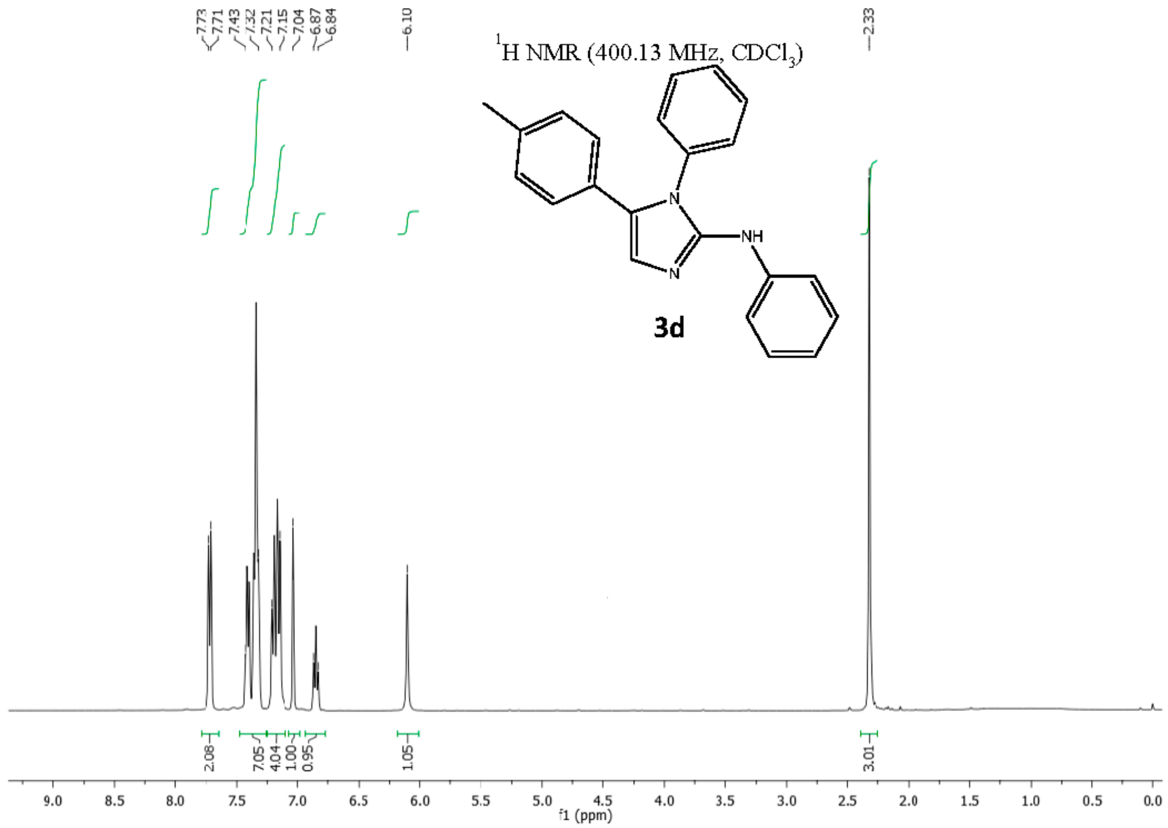
^{1}H NMR (400.13 MHz, $CDCl_3$)

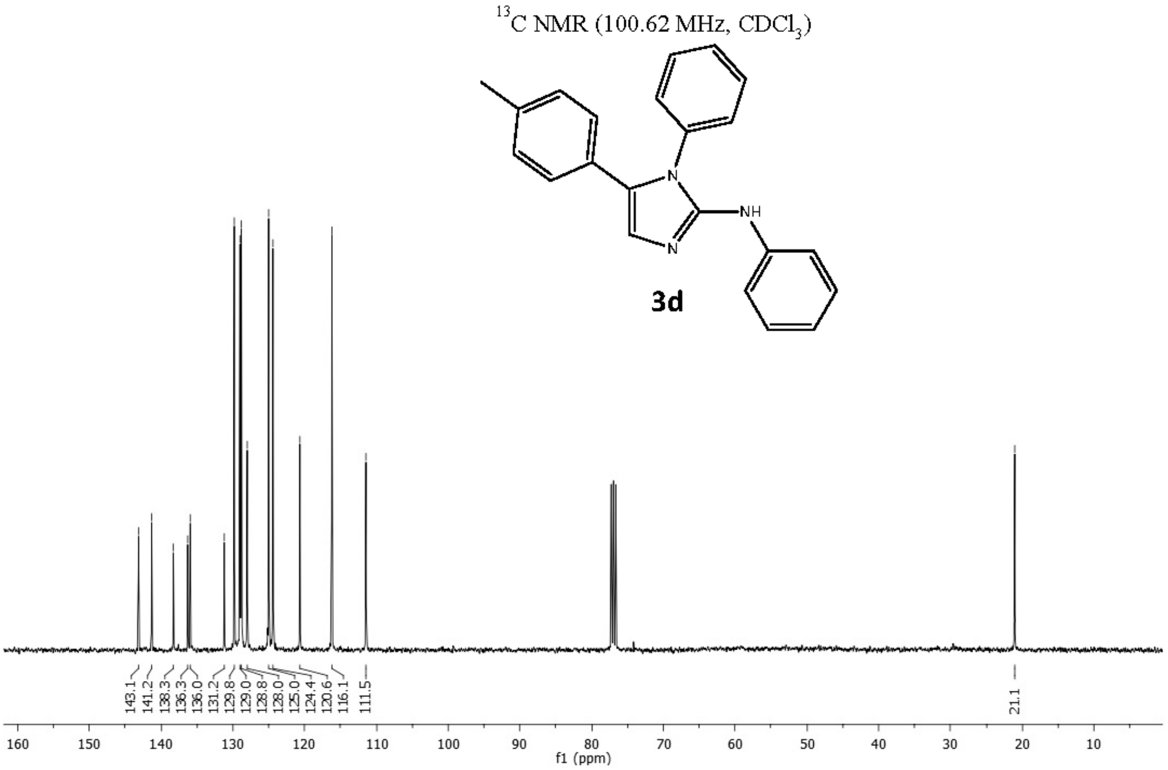
3c

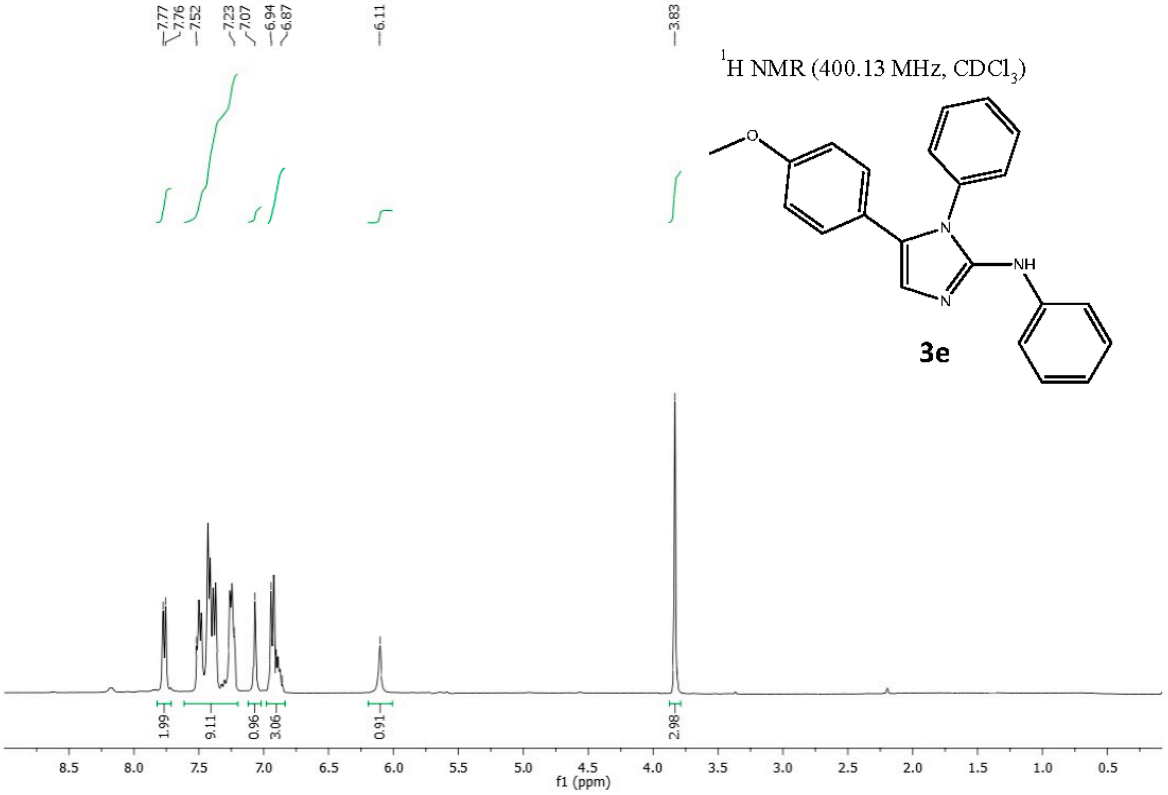


^{13}C NMR (100.62 MHz, $CDCl_3$)

3c

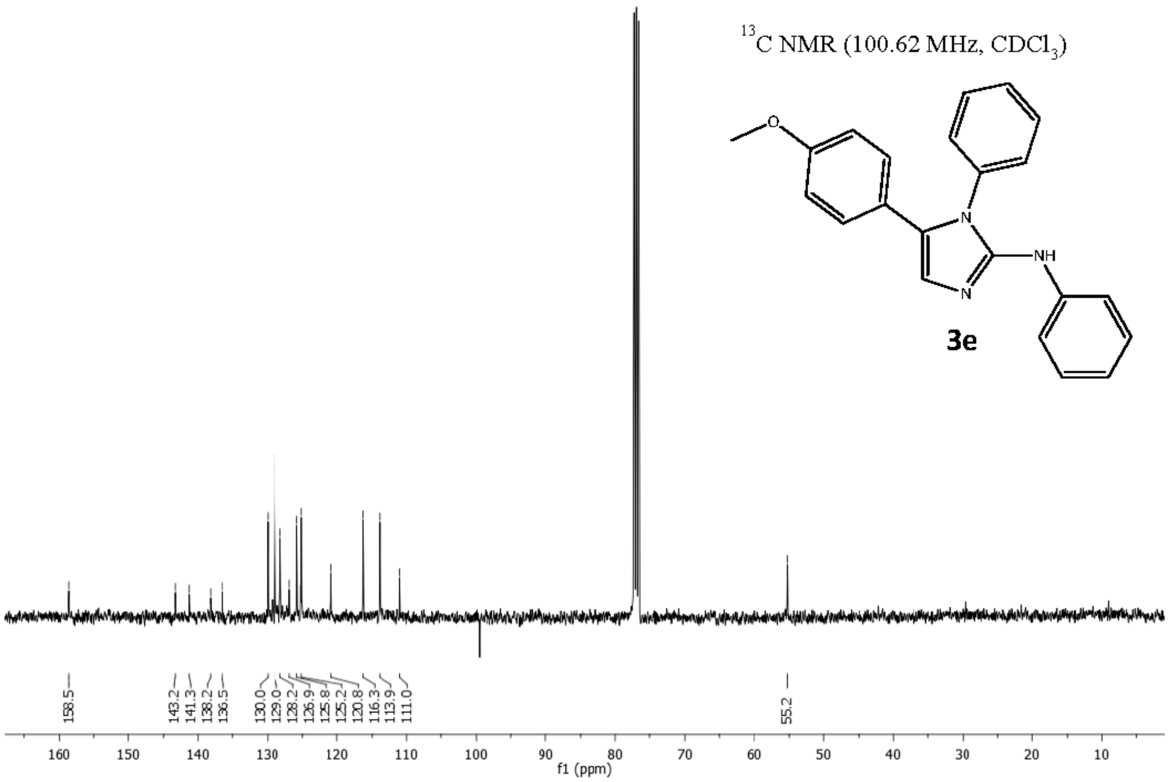

7.73
7.71
7.43
7.32
7.21
7.15
7.04
6.87
6.84
6.10
2.33
^{1}H NMR (400.13 MHz, CDCl$_3$)
N
N
NH
3d
2.08
7.05
4.04
1.00
0.95
1.05
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


^{13}C NMR (100.62 MHz, CDCl$_3$)
N
N
NH
3d
143.1
141.2
138.3
136.3
136.0
131.2
129.8
129.0
128.8
128.0
125.0
124.4
120.6
116.1
111.5
21.1
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



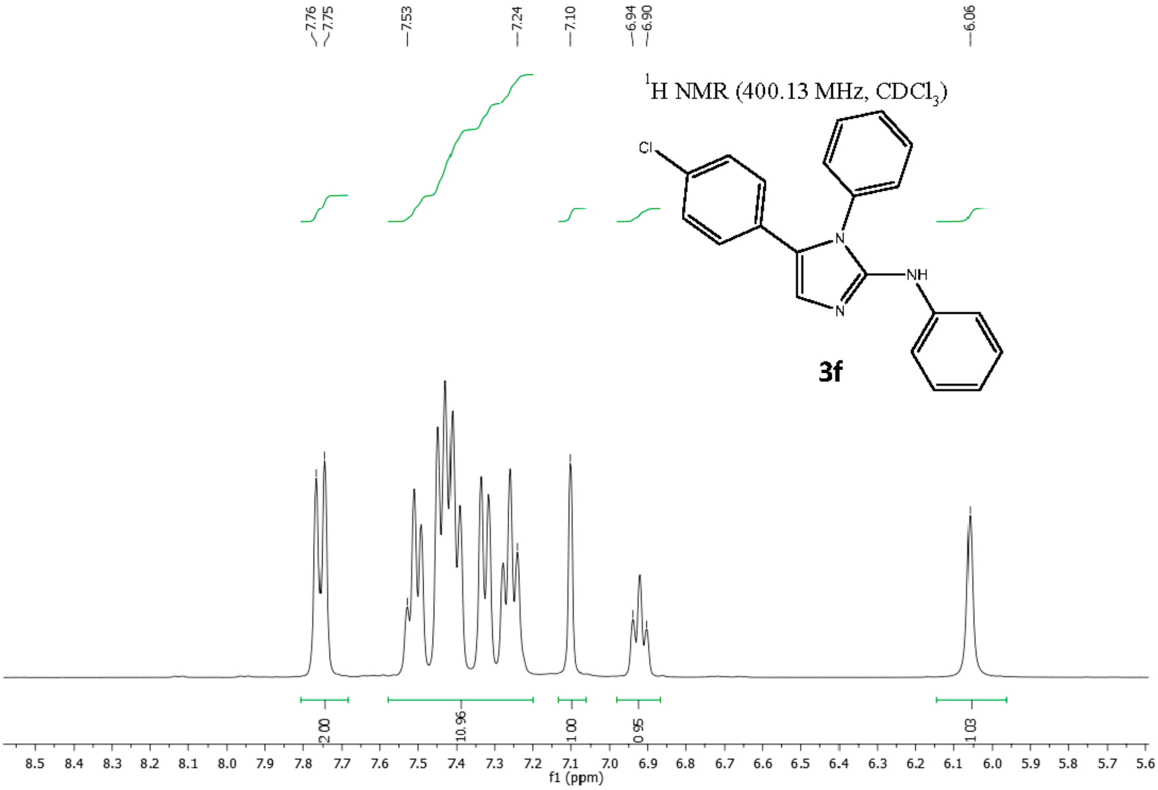
^{1}H NMR (400.13 MHz, $CDCl_3$)

3e



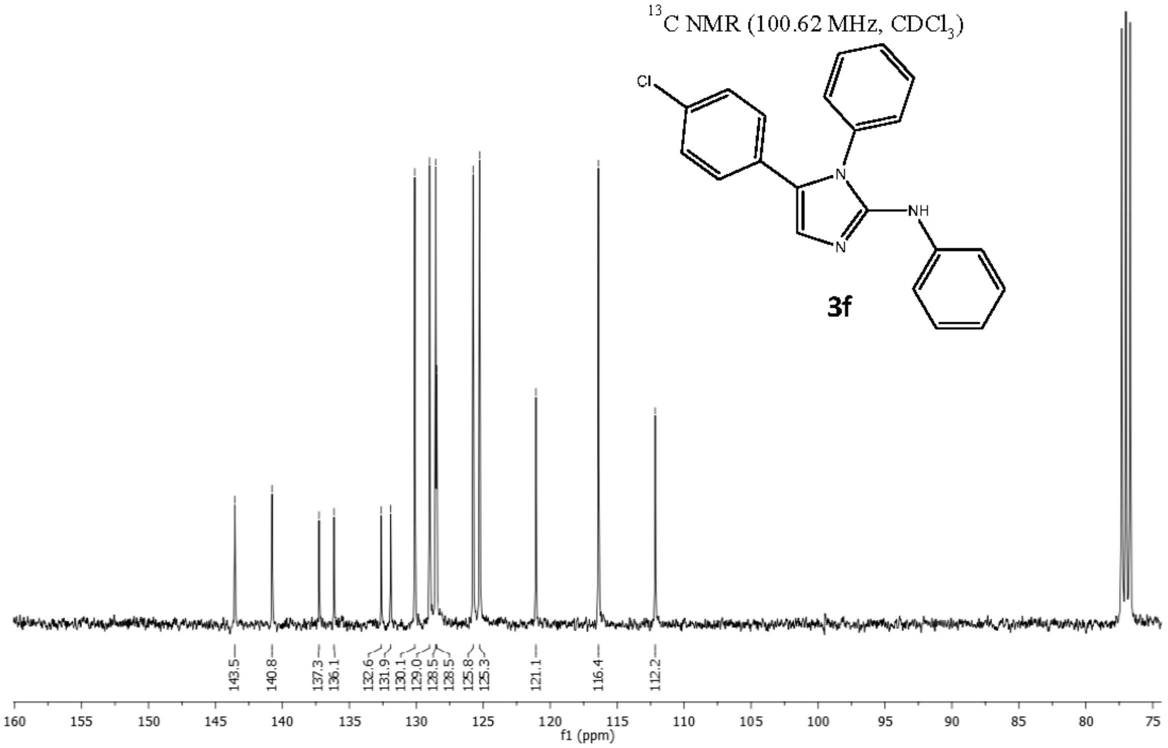
^{13}C NMR (100.62 MHz, $CDCl_3$)

3e



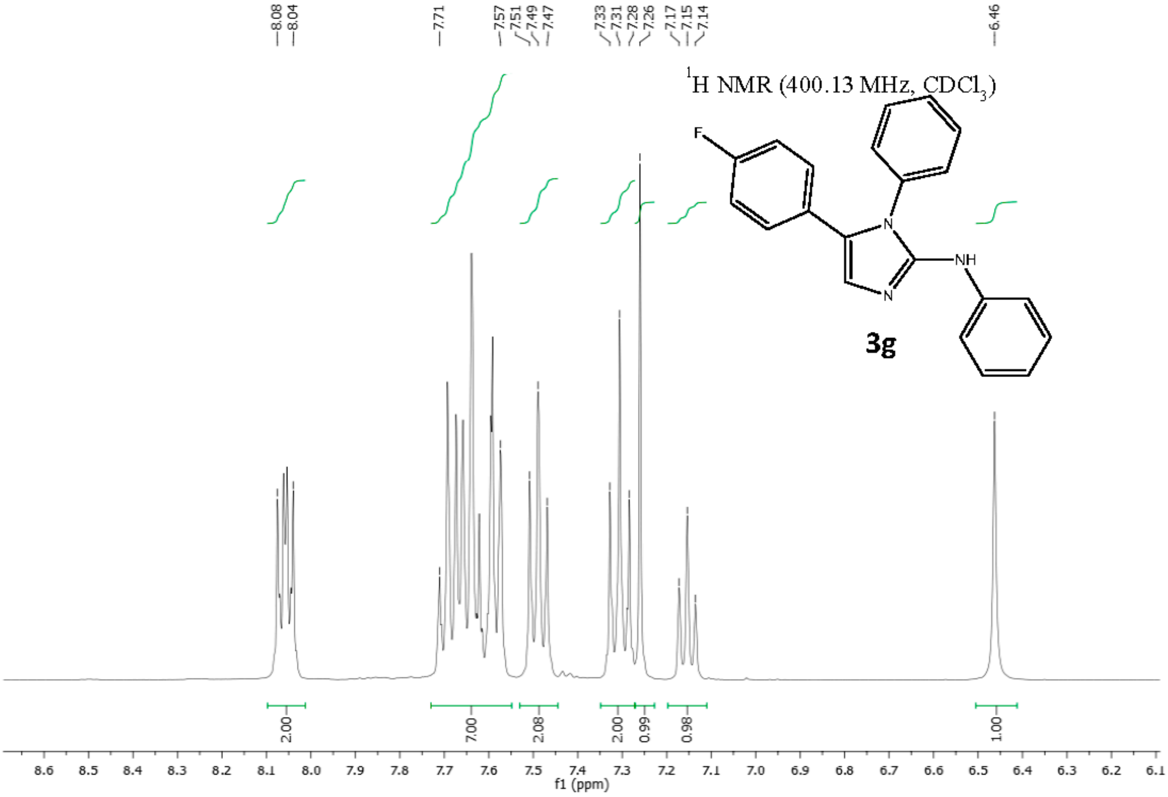
^{1}H NMR (400.13 MHz, $CDCl_3$)

3f



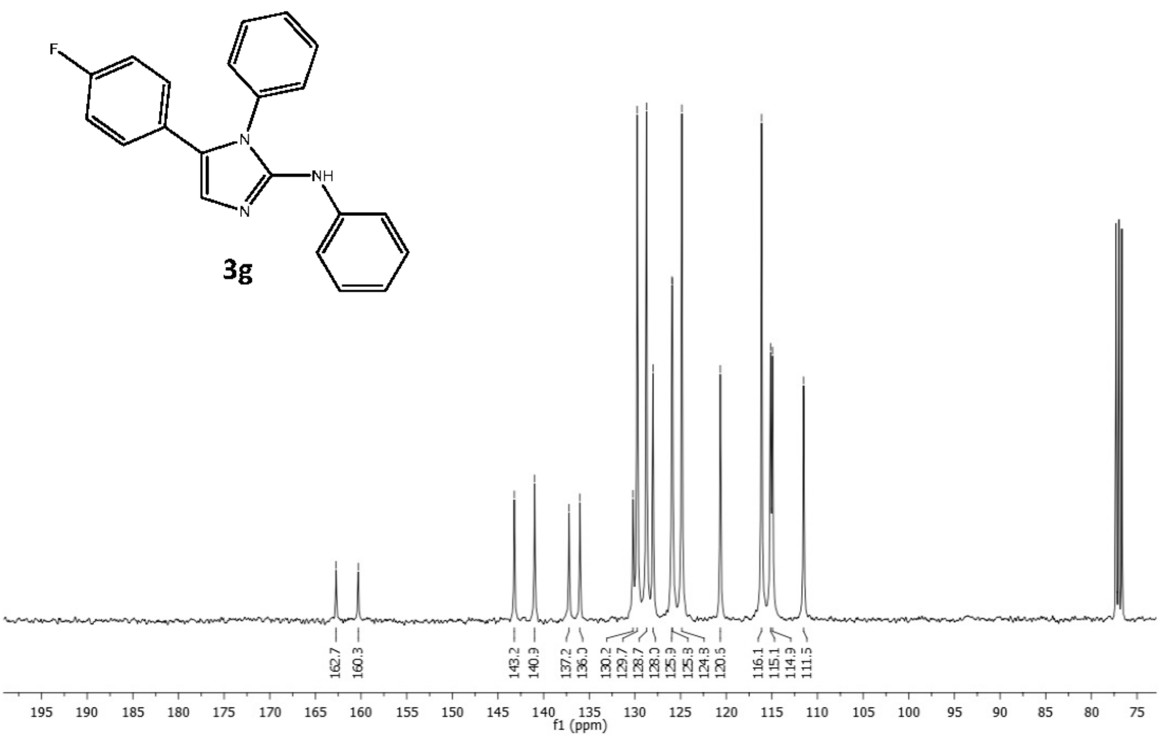
^{13}C NMR (100.62 MHz, $CDCl_3$)

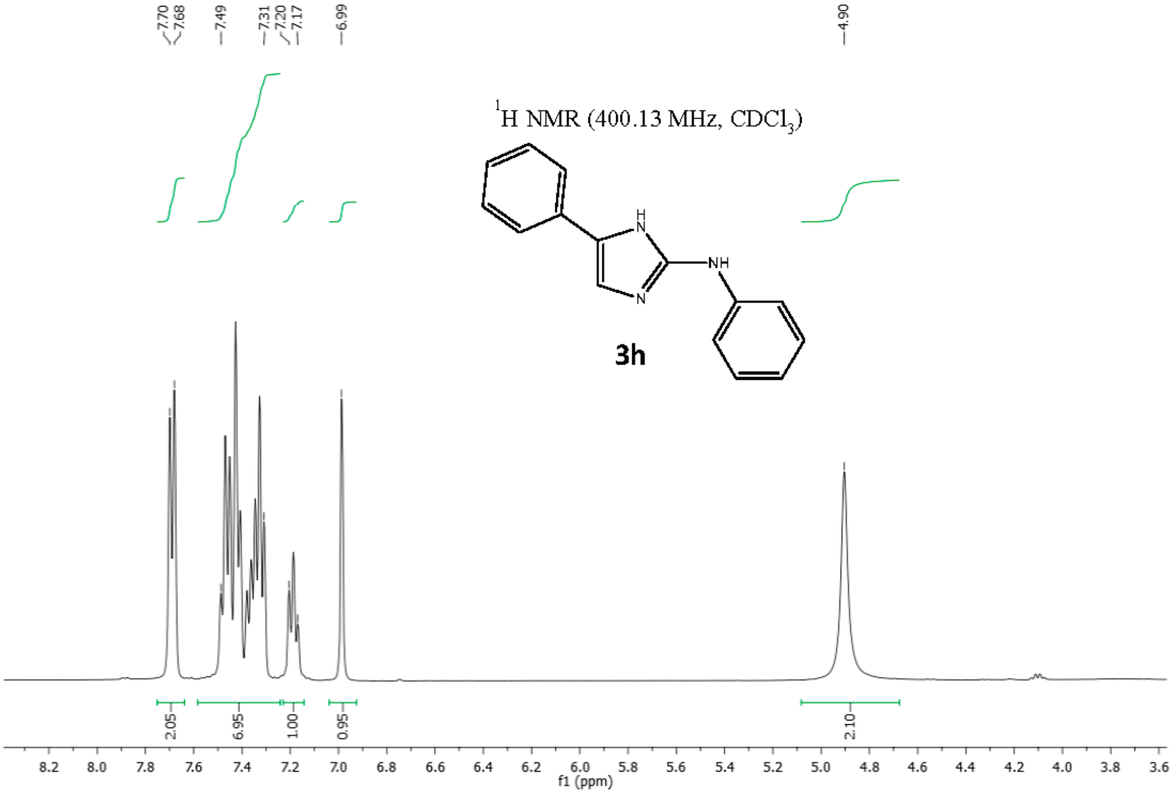
3f



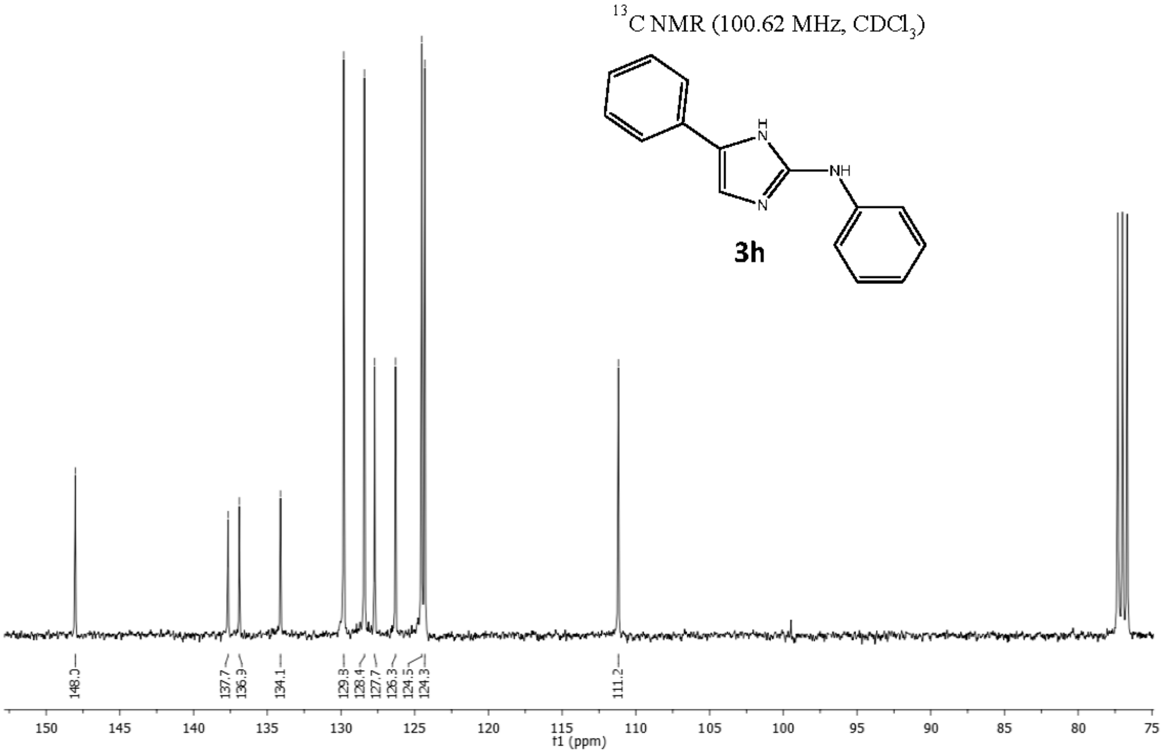
^{1}H NMR (400.13 MHz, $CDCl_3$)

^{13}C NMR (100.62 MHz, $CDCl_3$)

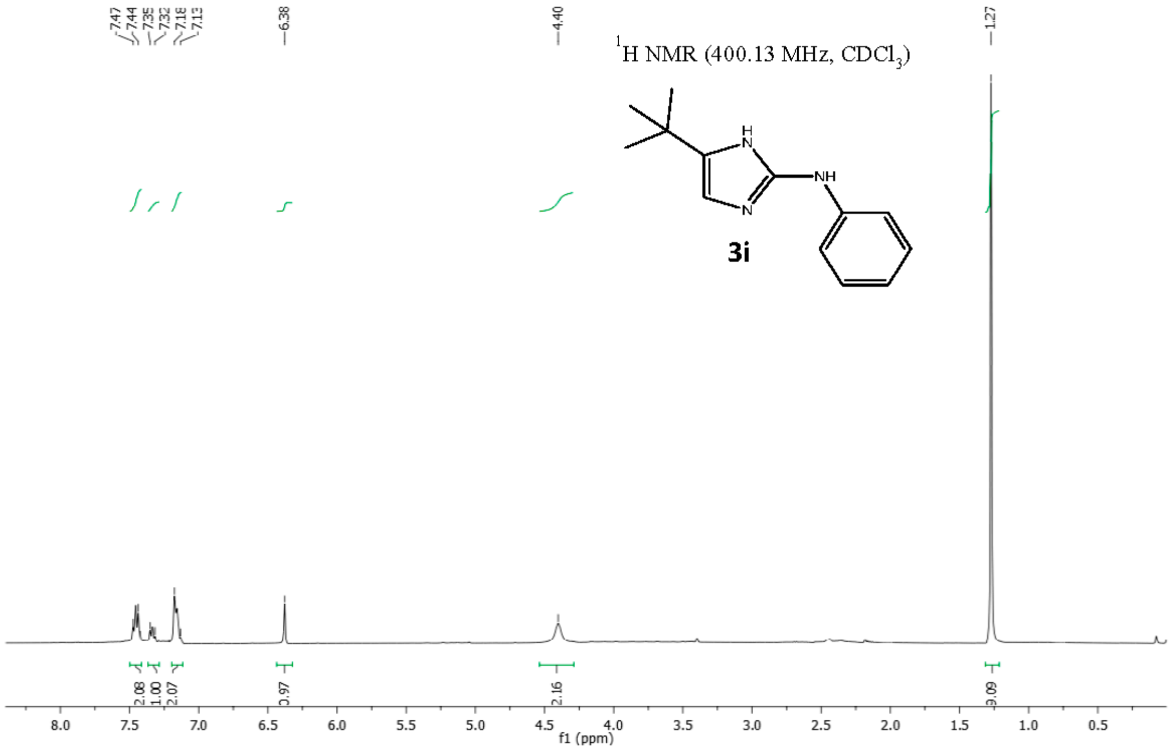


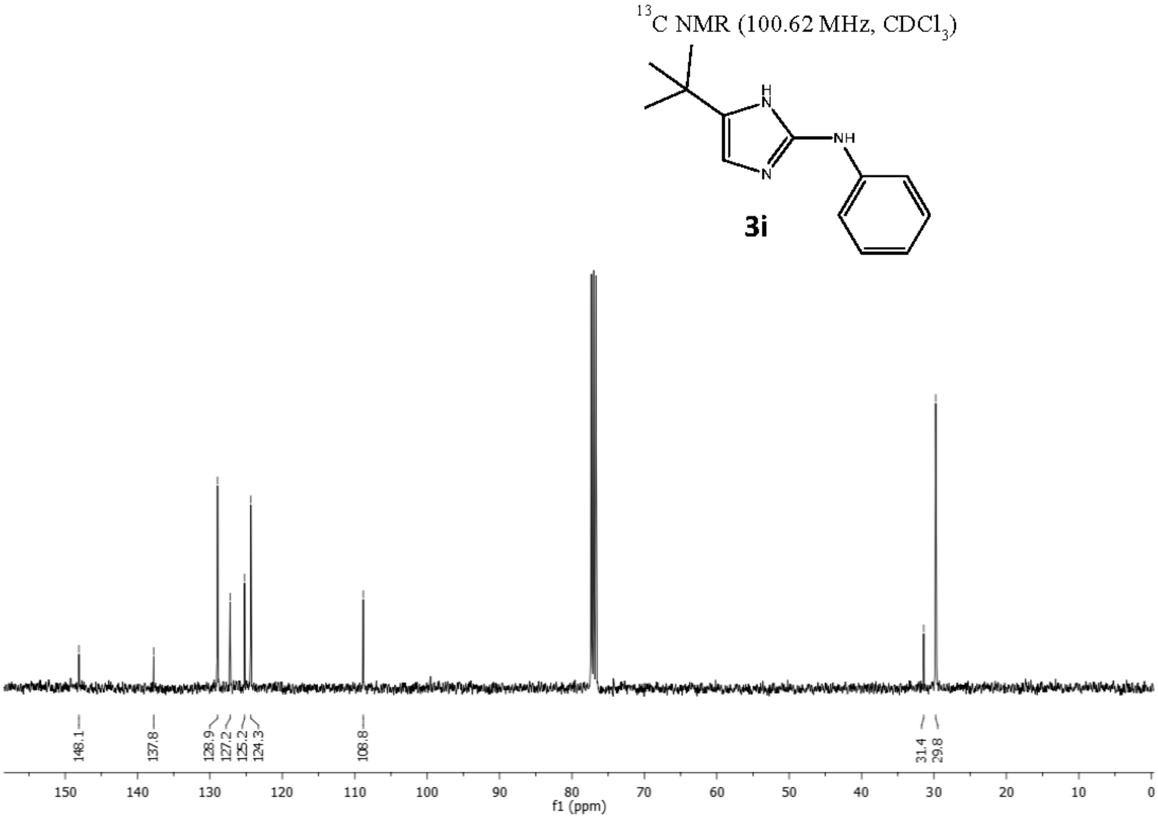

^{1}H NMR (400.13 MHz, $CDCl_3$)

3h


^{13}C NMR (100.62 MHz, $CDCl_3$)

3h


^{1}H NMR (400.13 MHz, CDCl$_3$)
3i
H
N
NH
N
7.47
7.44
7.35
7.32
7.18
7.13
6.38
4.40
1.27
2.08
1.00
2.07
0.97
2.16
9.09
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)


^{13}C NMR (100.62 MHz, CDCl$_3$)
3i
H
N
NH
N
148.1
137.8
128.9
127.2
125.2
124.3
108.8
31.4
29.8
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)