Supporting Information

CO_2 as C1 Source: $B(C_6F_5)_3$ Catalyzed Cyclization of *o*-Phenylenediamines to Construct Benzimidazoles in the Presence of Hydrosilane

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Table of Contents

1. General remarks……2

2. General procedure for the synthesis of products **2a-m**……2

3. Characterization data for all products……2

4. Synthesis of the adduct from *o*-phenylenediamine and $B(C_6F_5)_3$……6

5. The generation of species **7** from *o*-phenylenediamine, $B(C_6F_5)_3$ and CO_2……7

6. ^1H and ^{13}C NMR spectra of the products……9

General remarks

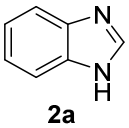
All solvents before used were dehydration under standard methods and stored under argon. Other reagents were obtained from commercial sources and used without further purification, unless otherwise noted. All reactions were monitored by TLC with GF254 silica gel coated plates. Flash column chromatography was carried out by using 200-300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III NMR spectrometer (400 MHz) in $CDCl_3$ or DMSO-d_6 internally referenced to tetramethylsilane (TMS) or $CDCl_3$ (DMSO-d_6) signals. Chemical shifts are reported in ppm and coupling constants (*J*) in Hz. The high resolution mass spectra were measured on an Agilent 6530 Q-TOF mass spectrometer. All substrates (**1a-1m**) are known compounds and prepared according to the literature.

General procedure for the synthesis of products 2a-m.

To a PTFE-lined autoclave equipped with a magnetic stirrer was charged with **1a** (**1b-p**, 0.2 mmol), $B(C_6F_5)_3$ (0.02 mmol) and $PhSiH_3$ (0.8 mmol) in 2 mL THF, Then the sealed mixture was charged with 1 MPa CO_2 and heated with stirring at 120 ^{o}C for 24 h. Water (15 mL) was then added to the mixture when the reaction was completed and cool down to ambient temperature. The aqueous layer was extracted with 3×10 mL of DCM. The combined organic layer was dried over anhydrous $MgSO_4$, after which the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (1:2-1:3) as the eluent to afford the desired product **2a** (**2b-l**).

Characterization data for all products

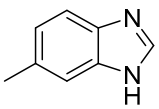
1*H*-Benzo[*d*]imidazole (2a)[1]



2a

19.6 mg, 83% yield, white solid; Spectral data of **2a**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 8.14 (s, 1H), 7.68 (dd, *J* = 5.0, 3.2 Hz, 2H), 7.31 (dd, *J* = 6.0, 3.2 Hz, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.6, 137.6, 123.2, 115.7. HRMS (ESI) calcd for $C_7H_7N_2$ $[M+H]^+$ 119.0604, found: 119.0603.

6-Methyl-1*H*-benzo[*d*]imidazole (2b)[2]

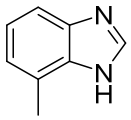


2b

22.4 mg, 85% yield, yellow solid; Spectral data of **2b**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.07 (s, 1H), 8.01 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.36 (s, 1H), 7.07 – 7.00 (dd,*J* = 8.4, 1.2, 1H), 2.39 (s, 3H).^{13}C

NMR (100 MHz, Chloroform-*d*) δ 140.4, 137.2, 136.0, 133.1, 124.7, 115.5, 114.9, 21.8. HRMS (ESI) calcd for $C_8H_9N_2$ $[M+H]^+$ 133.0760, found: 133.0760.

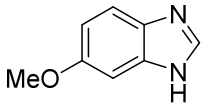
7-Methyl-1*H*-benzo[*d*]imidazole (2c)[3]



2c

15.4 mg, 58% yield, yellow solid; Spectral data of **2c**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 2.61 (s, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.3, 137.6, 136.8, 126.0, 123.5, 123.1, 112.6, 17.3. HRMS (ESI) calcd for $C_8H_9N_2$ $[M+H]^+$ 133.0760, found: 133.0758.

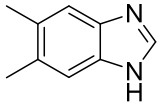
6-Methoxy-1*H*-benzo[*d*]imidazole (2d)[4]



2d

18.2 mg, 61% yield, yellow solid; Spectral data of **2d**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.93 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.10 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.0, 140.2, 137.3, 132.3, 116.5, 113.3, 97.6, 56.0. HRMS (ESI) calcd for $C_8H_9N_2O$ $[M+H]^+$ 149.0709, found: 149.0711.

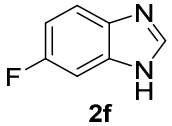
5,6-Dimethyl-1*H*-benzo[*d*]imidazole (2e)[4]



2e

18.0 mg, 62% yield, yellow solid; Spectral data of **2e**:^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.43 (s, 2H), 2.36 (s, 6H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.1, 136.4, 132.0, 115.6, 20.5. HRMS (ESI) calcd for $C_9H_{11}N_2$ $[M+H]^+$ 147.0917, found: 147.0919.

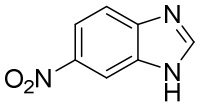
6-Fluoro-1*H*-benzo[*d*]imidazole (2f)[4]



2f

20.6 mg, 76% yield, yellow solid; Spectral data of **2f**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.16 (s, 1H), 7.58 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.32 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.05 (td, *J* = 8.8, 1.2 Hz 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ159.9 (d, *J* = 237.6 Hz), 141.9, 137.7(d, *J* = 13.6 Hz), 134.5, 116.4 (d, *J* = 10.3 Hz), 111.6(d, *J* = 25.5 Hz), 101.5 (d, *J* = 25.8 Hz). HRMS (ESI) calcd for $C_7H_6FN_2$ $[M+H]^+$ 137.0510, found: 137.0509.

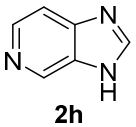
6-Nitro-1*H*-benzo[*d*]imidazole (2g)[4]



2g

8.2 mg, 25% yield, yellow solid; Spectral data of **2g**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (d, *J* = 14.8 Hz, 2H), 8.13 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.8, 142.9, 142.6, 117.6, 115.6, 111.6. HRMS (ESI) calcd for $C_7H_6N_3O_2$ $[M+H]^+$ 164.0455, found: 164.0457.

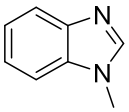
3*H*-Imidazo[4,5-*c*]pyridine (2h)[5]



2h

20.8 mg, 87%, yellow solid; Spectral data of **2h**:^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (s, 1H), 8.39 (s, 1H), 8.30 (d, *J* = 3.2 Hz, 1H), 7.59 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3, 141.2, 139.8, 109.4. HRMS (ESI) calcd for $C_6H_6N_3$ $[M+H]^+$ 120.0556, found: 120.0555.

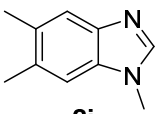
1-Methyl-1*H*-benzo[*d*]imidazole (2i)[1]



2i

25.1 mg, 95% yield, yellow solid; Spectral data of **2i**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.83 – 7.79 (m, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.27 (m, 2H), 3.84 (s, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.6, 134.6,123.1, 122.3, 120.3, 109.5, 31.2.HRMS (ESI) calcd for $C_8H_9N_2$ $[M+H]^+$ 133.0760, found: 133.0761.

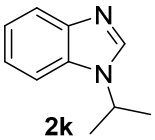
1,5,6-Trimethyl-1*H*-benzo[*d*]imidazole (2j)[3]



2j

30.1mg, 94% yield, yellow solid; Spectral data of **2j**:^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.55 (s, 1H), 7.14 (s, 1H), 3.77 (s, 3H), 2.38 (d, *J* = 9.6 Hz, 6H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 142.2, 133.2, 132.2, 131.1, 120.2, 109.6, 31.1, 20.7, 20.4. HRMS (ESI) calcd for $C_{10}H_{13}N_2$ $[M+H]^+$ 161.1073, found: 161.1075.

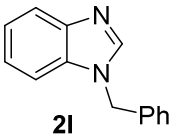
1-Isopropyl-1*H*-benzo[*d*]imidazole (2k)[6]



2k

17.0 mg, 53% yield, red oil; Spectral data of **2k**:^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.38 (t, *J* = 8.4 Hz 1H), 4.86 – 4.75 (m, 1H), 1.71 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.4, 136.3, 131.7, 126.2, 125.8, 116.8, 112.1, 50.3, 29.9. HRMS (ESI) calcd for $C_{10}H_{13}N_2$ $[M+H]^+$ 161.1073, found: 161.1073.

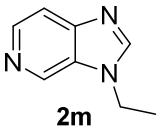
1-Benzyl-1*H*-benzo[*d*]imidazole (2l)[7]



2l

32.9 mg, 79% yield, orange oil; Spectral data of **2l**:^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.25 (m, 5H), 6.82 – 6.73 (m, 1H), 6.72 – 6.59 (m, 3H), 4.27 (s, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.5, 137.8, 134.3, 128.7, 127.9, 127.4, 120.8, 118.9, 116.6, 112.1, 48.7. HRMS (ESI) calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found: 209.1070.

3-Ethyl-3*H*-imidazo[4,5-*c*]pyridine (2m)



2m

25.8 mg, 88% yield, yellow solid; Spectral data of **2n**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.92 (s, 1H), 7.78 (s, 1H), 6.88 (s, 1H), 3.28 – 3.20 (m, 2H), 1.20 (d, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.5, 140.8, 139.2, 137.5,128.6 , 103.5, 41.8, 12.1. HRMS (ESI) calcd for $C_8H_{10}N_3$ $[M+H]^+$ 148.0869, found: 148.0871.

References

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Synthesis of the adduct from *o*-phenylenediamine and $B(C_6F_5)_3$

To a PTFE-lined autoclave equipped with a magnetic stirrer was charged with **1a** (0.2 mmol) and $B(C_6F_5)_3$ (0.2 mmol) in 2 mL THF. Then the sealed mixture was charged with 1 MPa CO_2 and heated with stirring at 60 °C for 12 h. After that the solvent was removed under reduced pressure and to measure the NMR directly in $CDCl_3$.

^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.0, 146.7, 138.3, 137.7, 136.0, 135.7, 129.2, 128.2, 124.0 (d, J = 16.6 Hz), 123.1, 119.2. ^{11}B NMR (128 MHz, Chloroform-*d*) δ -4.08 (s), -6.59 (s).

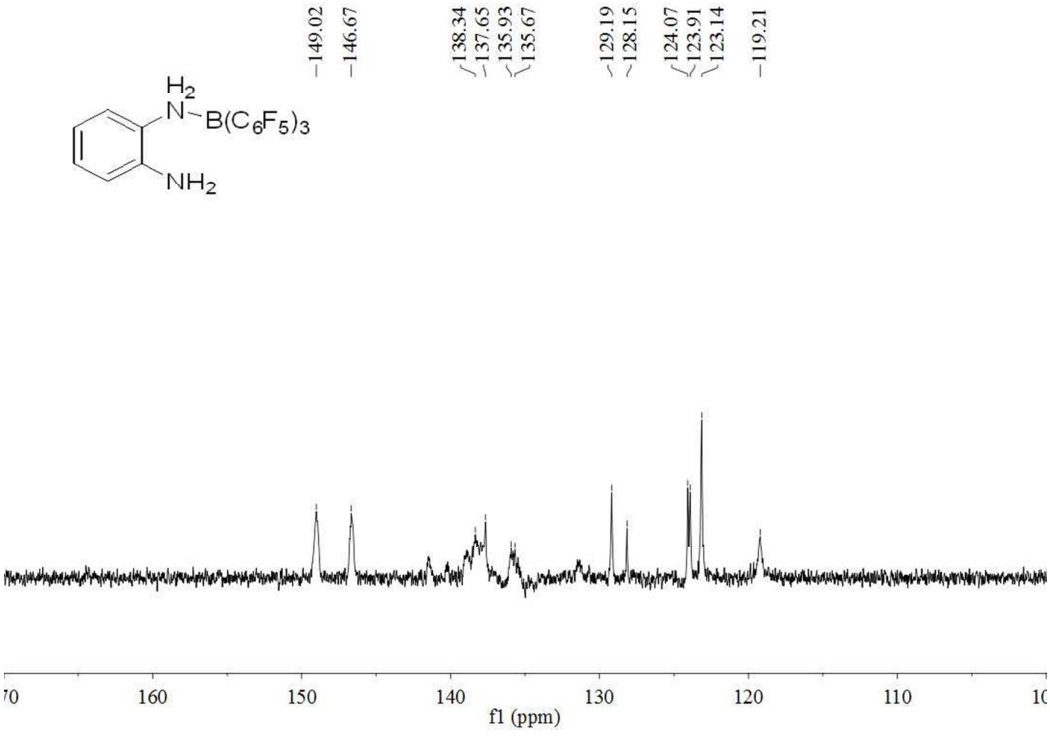


Figure S1 ^{13}C NMR spectra of the adduct from *o*-phenylenediamine and $B(C_6F_5)_3$

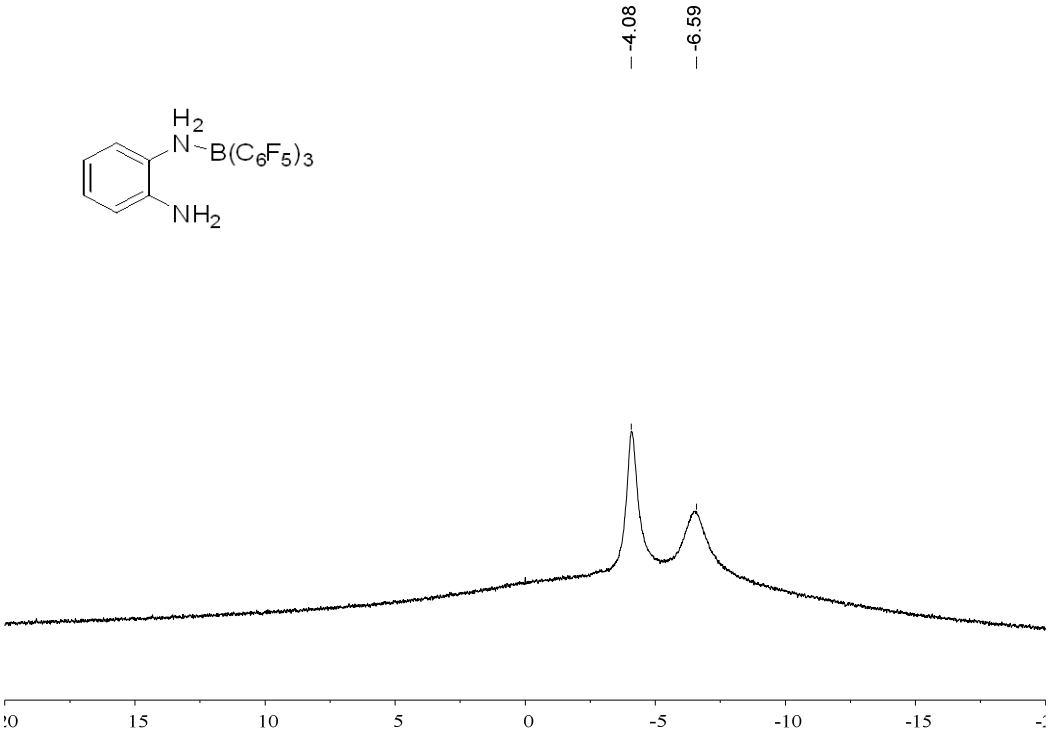


Figure S2 ^{11}B NMR spectra of the adduct from *o*-phenylenediamine and $B(C_6F_5)_3$

The generation of species 7 from *o*-phenylenediamine, $B(C_6F_5)_3$ and CO_2.

To a PTFE-lined autoclave equipped with a magnetic stirrer was charged with **1a** (0.2 mmol) and $B(C_6F_5)_3$ (0.2 mmol) in 2 mL THF. Then the sealed mixture was charged with 1 MPa CO_2 and heated with stirring at 120 °C for 6 h. After that the solvent was removed under reduced pressure and to measure the NMR directly in $CDCl_3$.

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.1 (*C*O), 149.1, 146.8, 137.9, 135.7, 134.1, 133.9, 127.9, 123.7 (d, *J* = 14.2 Hz), 123.3, 121.2, 117.6. ^{11}B NMR (128 MHz, Chloroform-*d*) δ -2.79 (s), 4.01 (s), -6.58 (s).

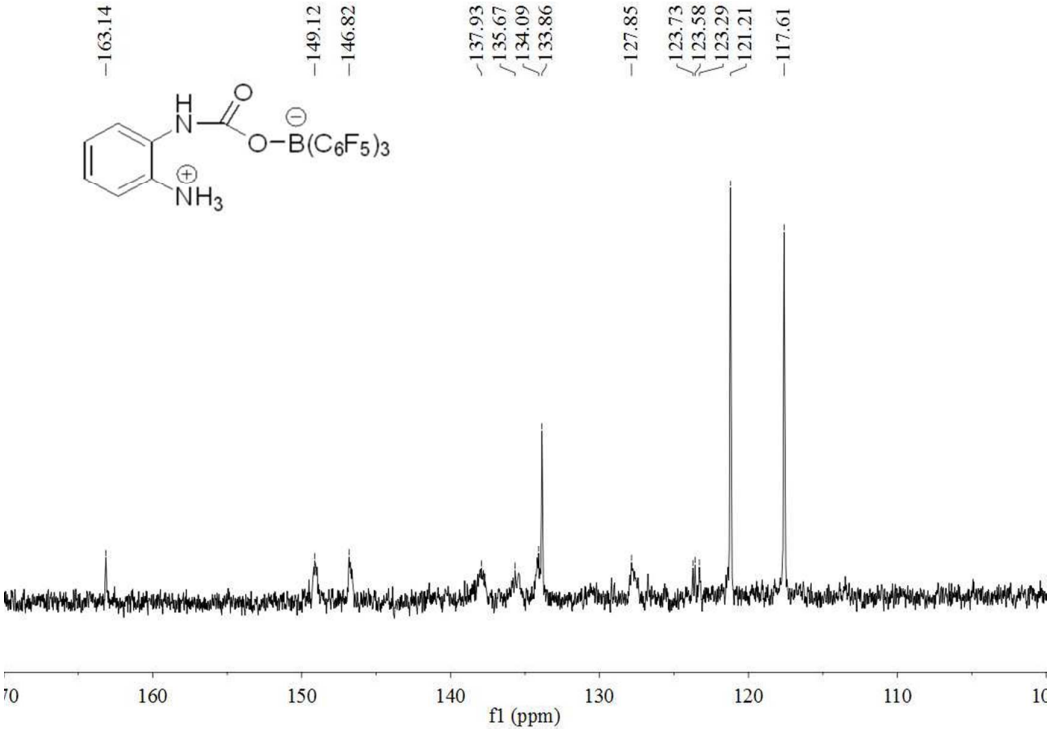


Figure S3 ^{13}C NMR spectra of species 7 from *o*-phenylenediamine, $B(C_6F_5)_3$ and CO_2.

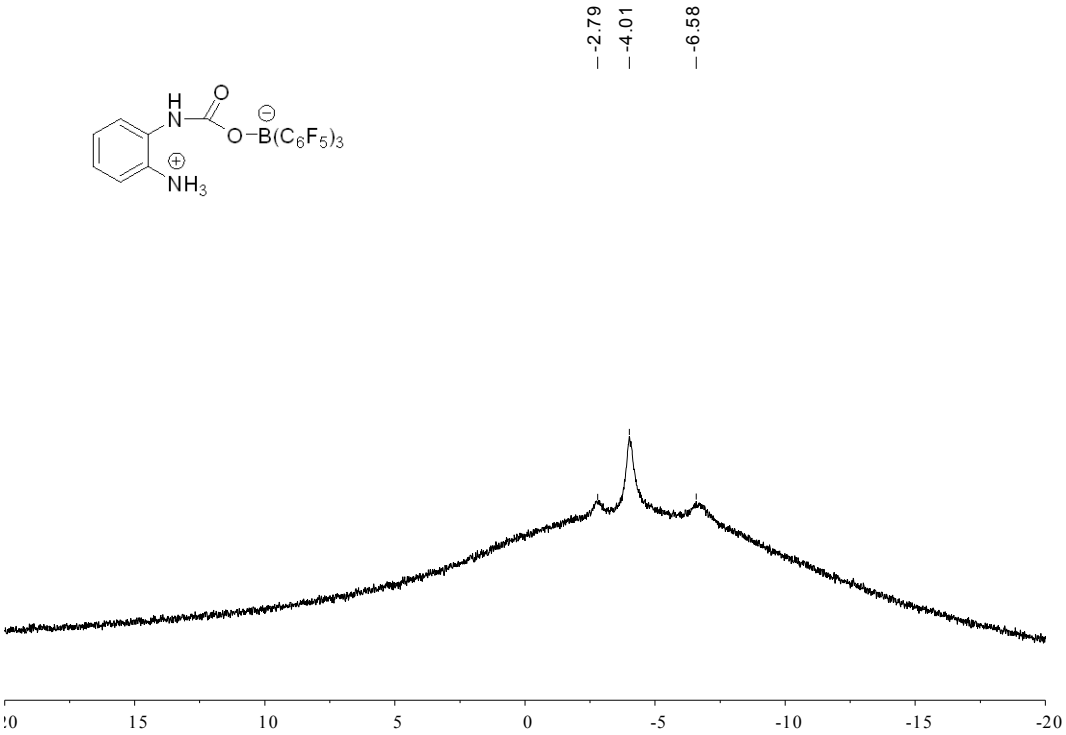
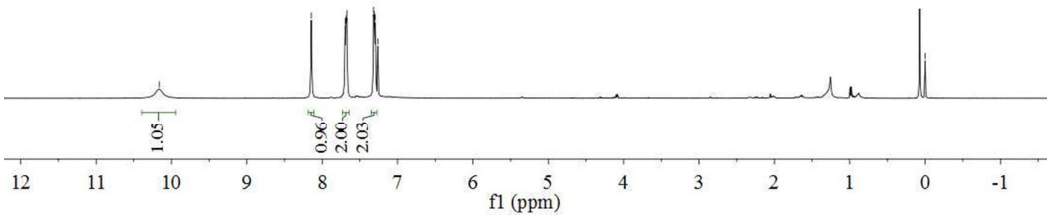
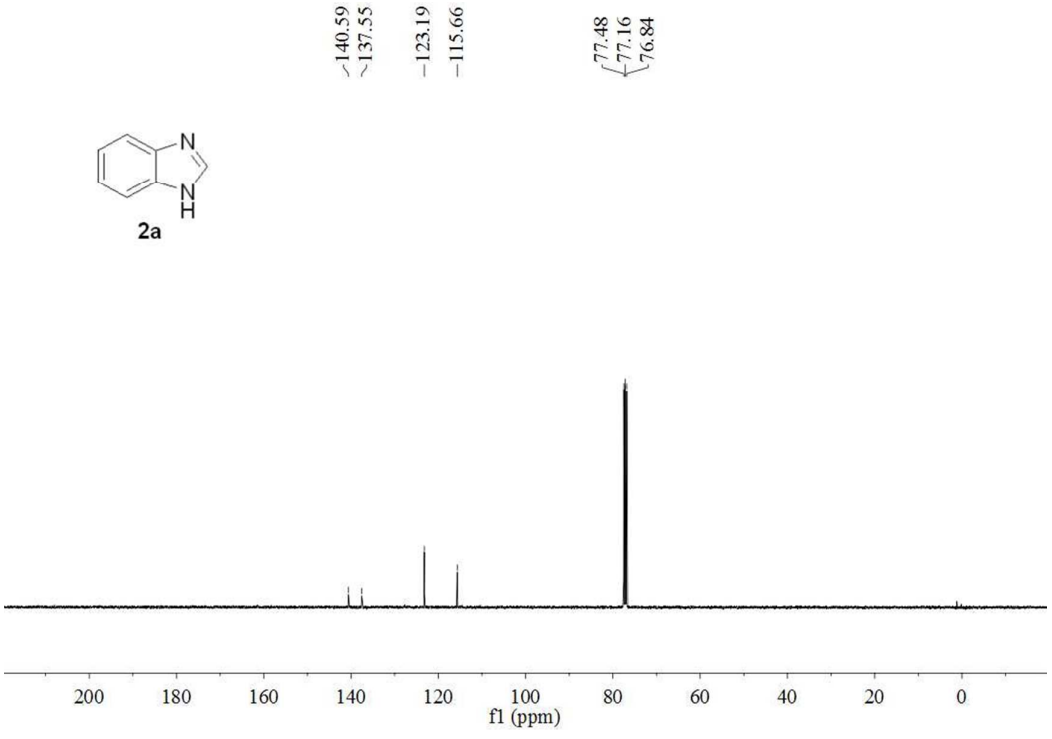


Figure S4 ^{11}B NMR spectra of species 7 from *o*-phenylenediamine, $B(C_6F_5)_3$ and CO_2.

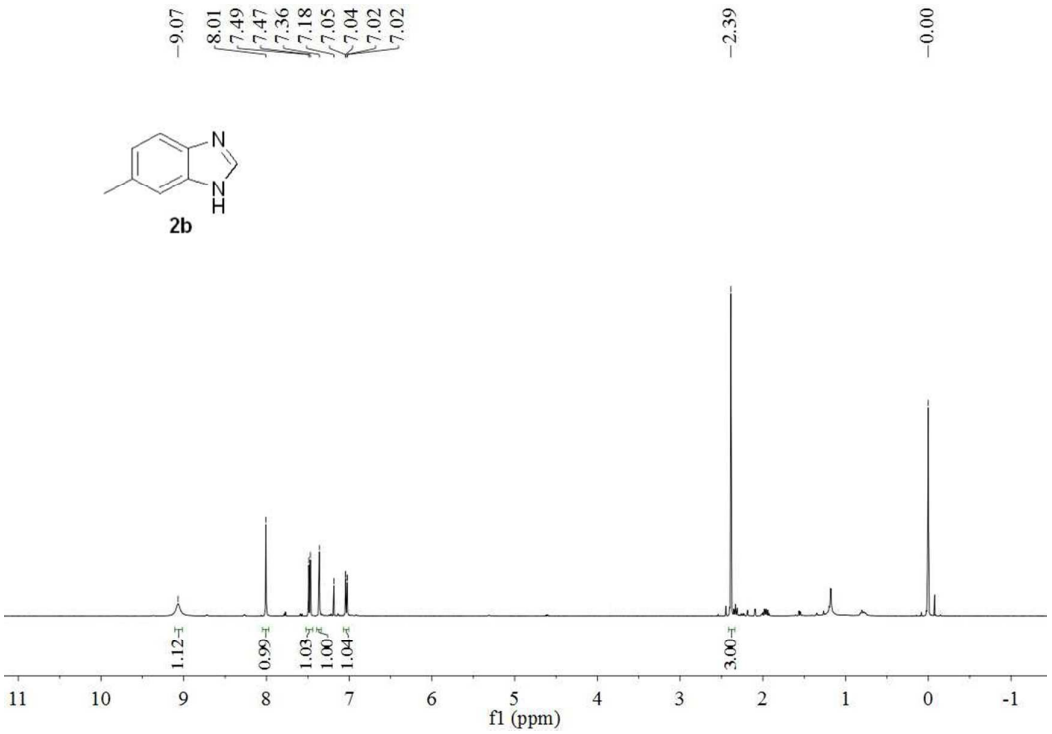
Copies of NMR

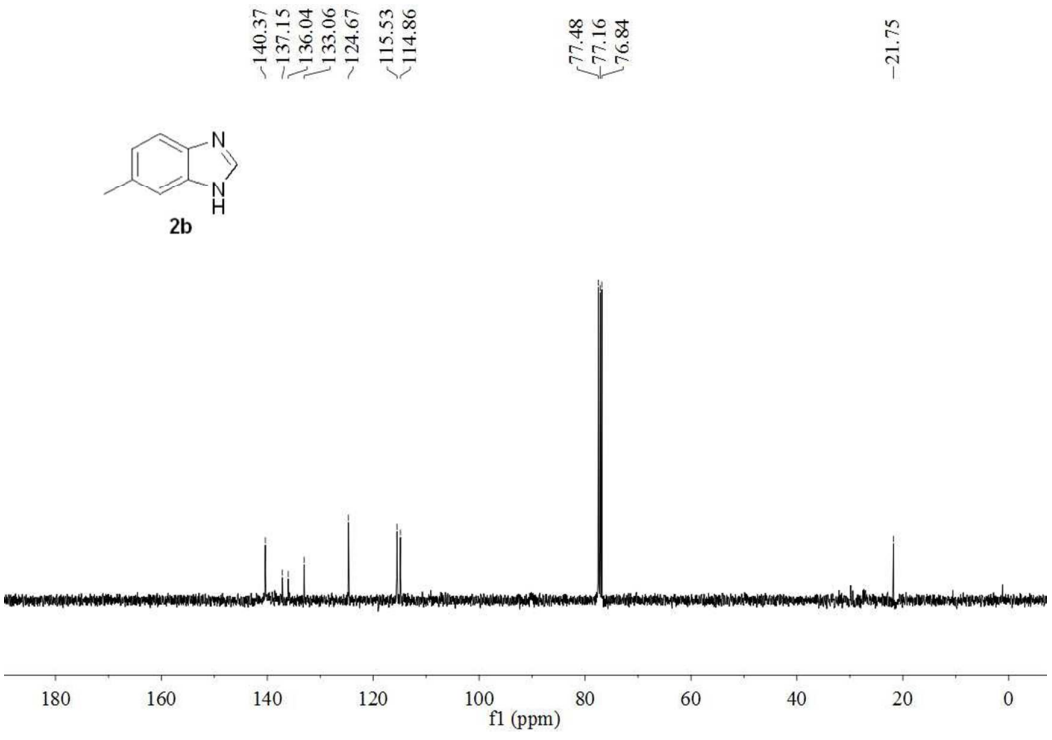
2a

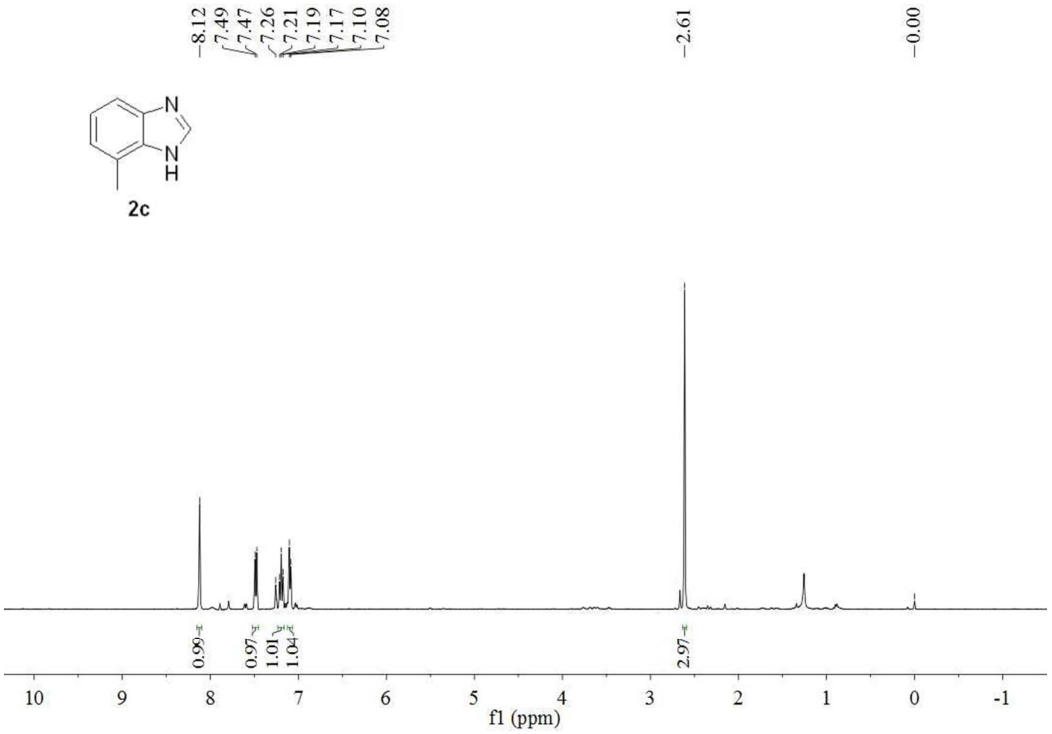




2a


9.07
8.01
7.49
7.47
7.36
7.18
7.05
7.04
7.02
7.02
2.39
0.00
2b
1.12
0.99
1.03
1.00
1.04
3.00
f1 (ppm)


140.37
137.15
136.04
133.06
124.67
115.53
114.86
77.48
77.16
76.84
21.75
2b
f1 (ppm)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7.47
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7.21
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7.08
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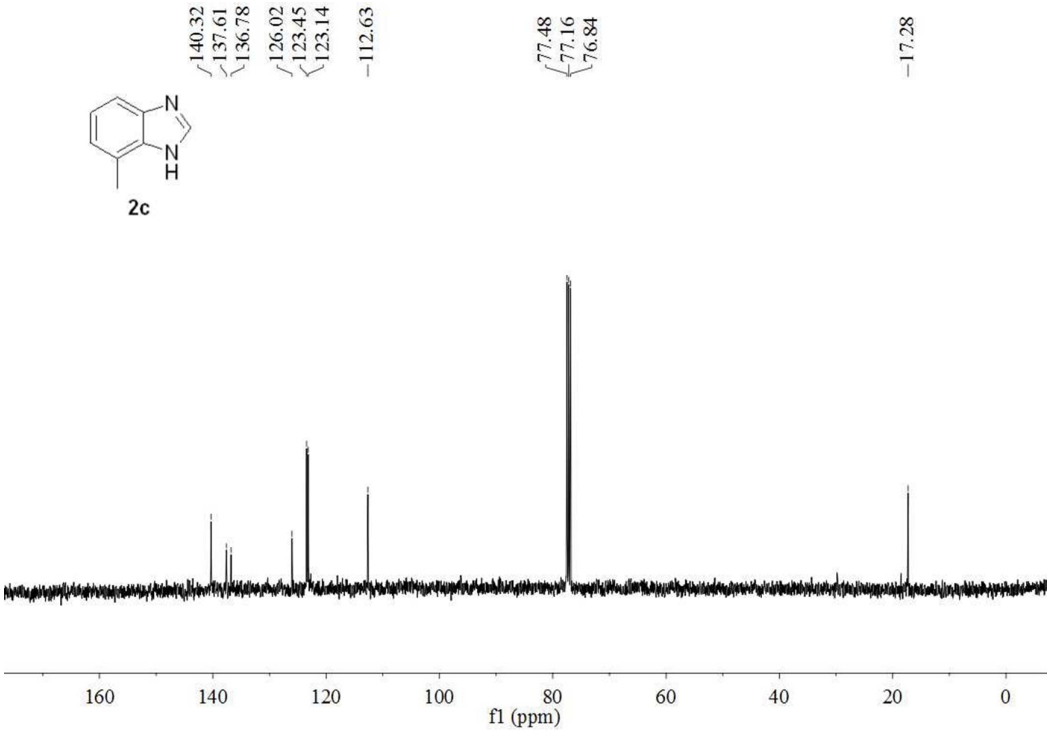
2c
0.99
0.97
1.01
1.04
2.97
f1 (ppm)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126.02
123.45
123.14
112.63
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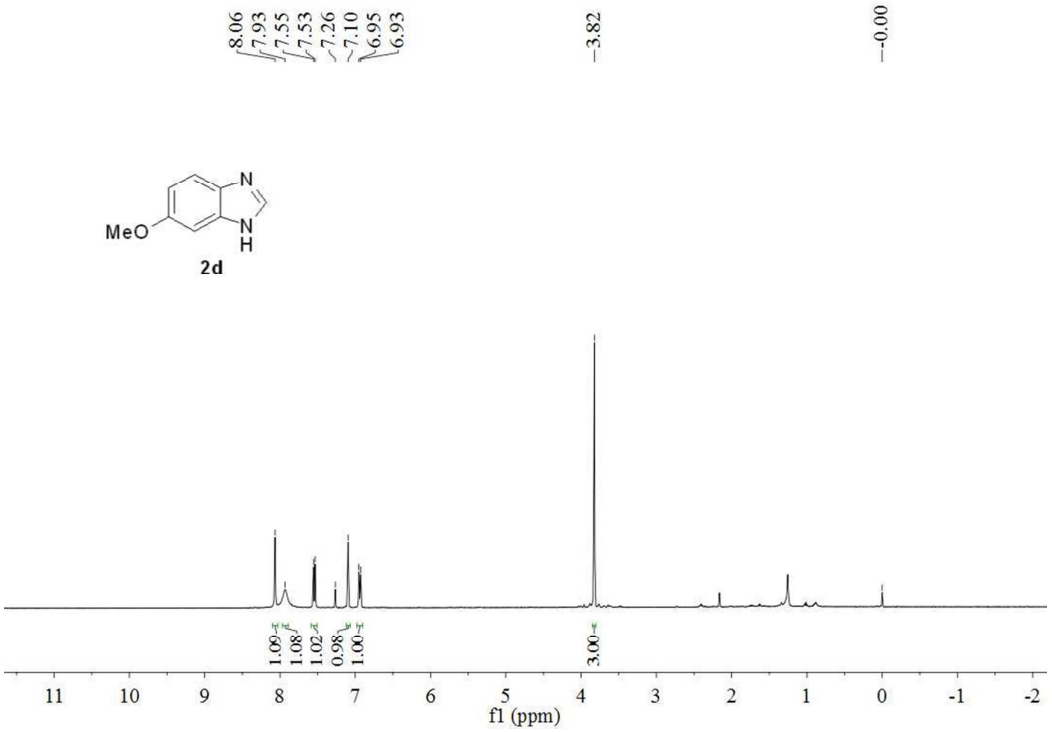
76.84
17.28
2c
f1 (ppm)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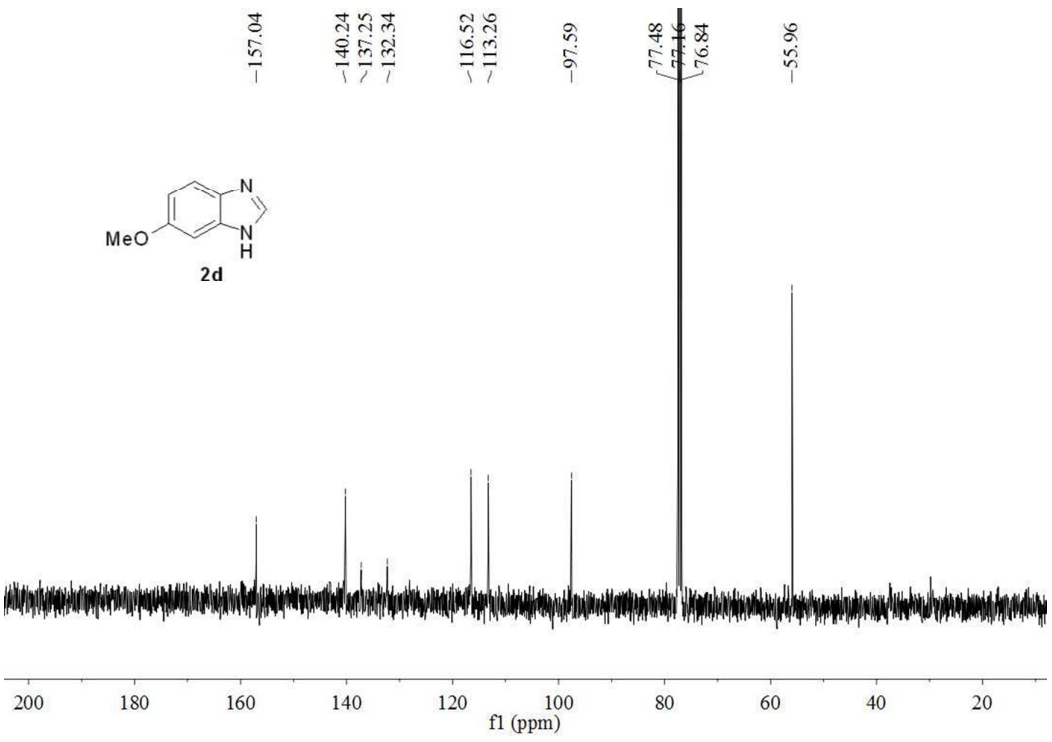
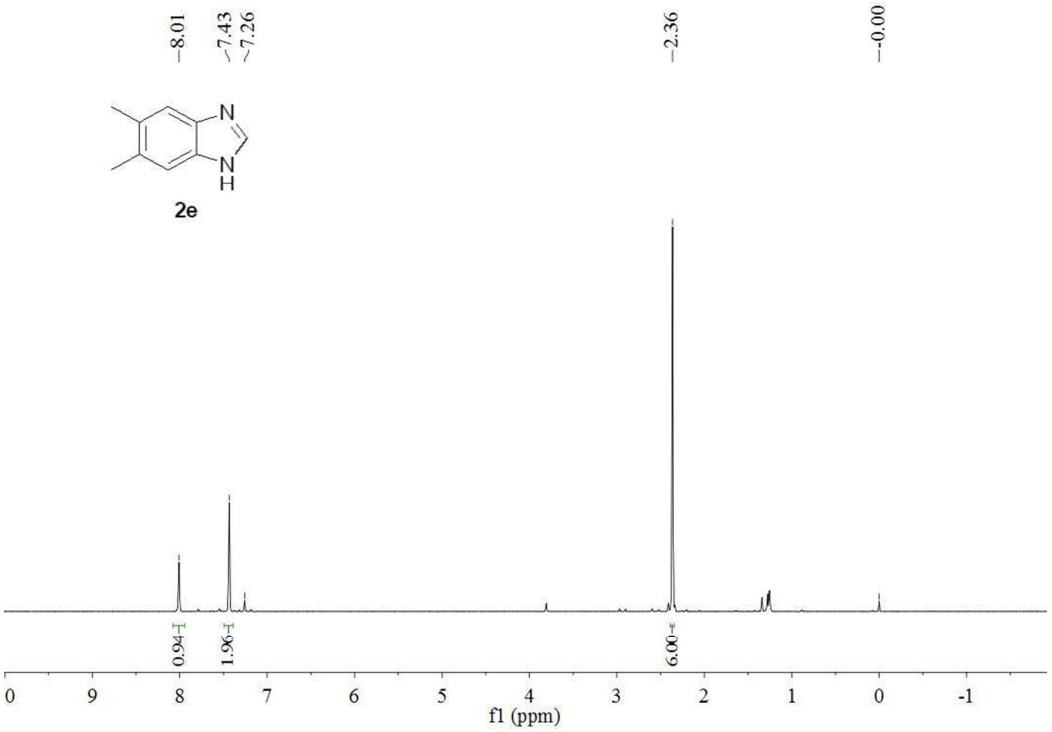
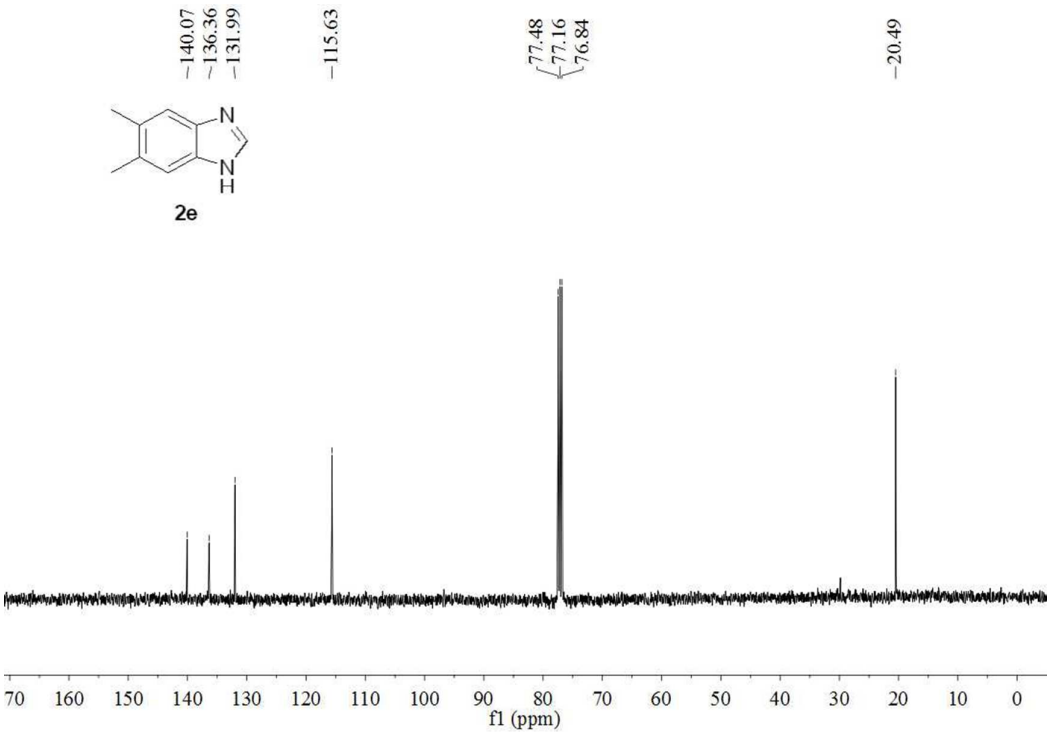
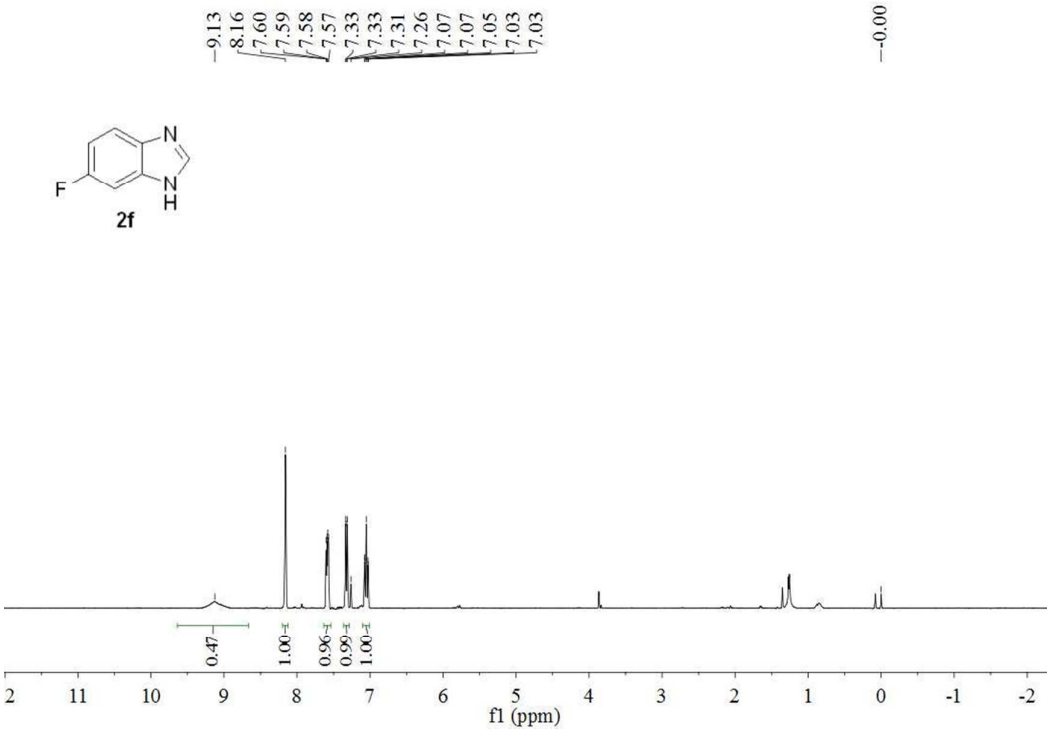
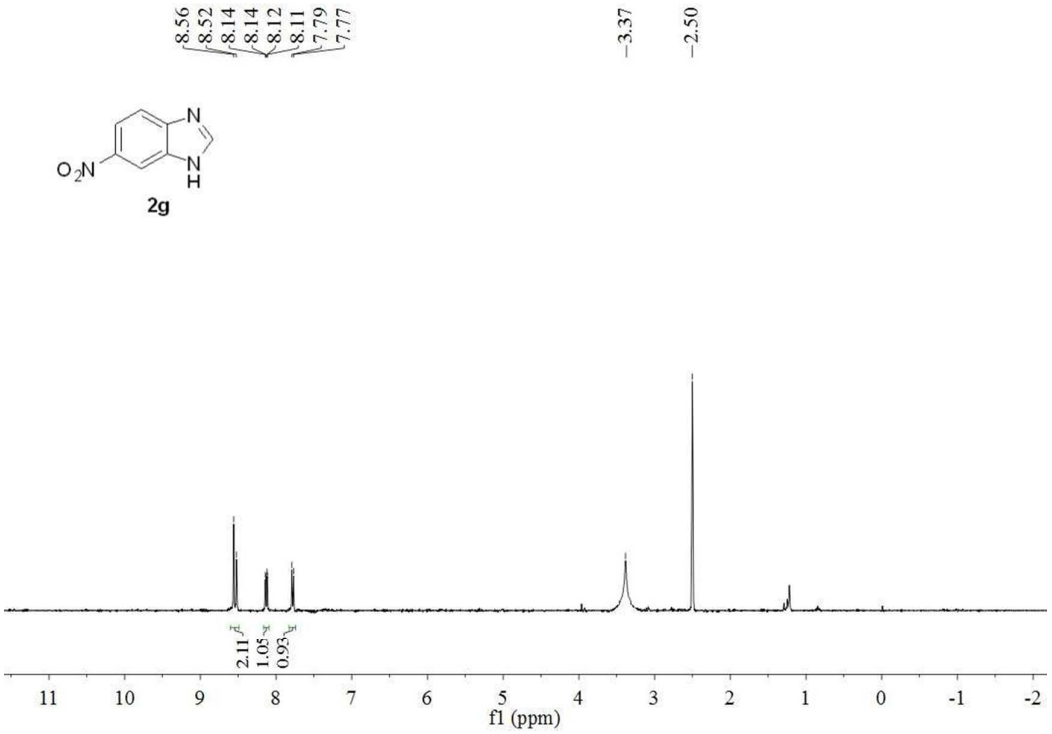
7.93
7.55
7.53
7.26
7.10
6.95
6.93
3.82
0.00
MeO
2d
1.09
1.08
1.02
0.98
1.00
3.00
f1 (ppm)

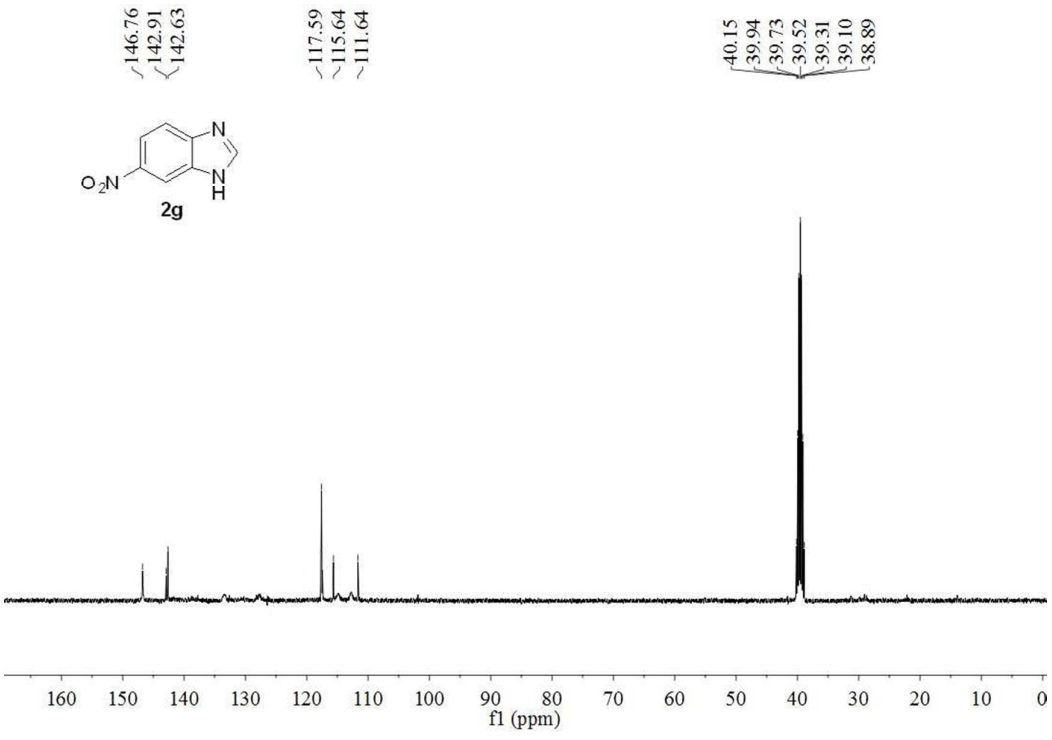

157.04
140.24
137.25
132.34
116.52
113.26
97.59
77.48
77.16
76.84
55.96
MeO
2d
f1 (ppm)

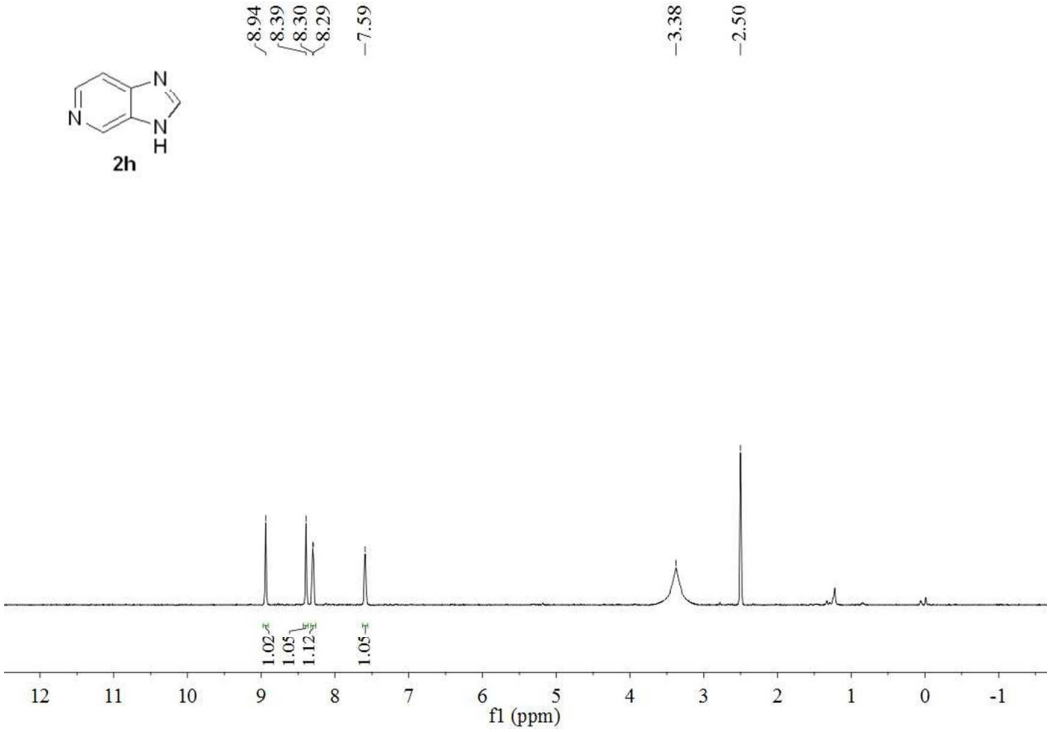

8.01
7.43
7.26
2.36
0.00
2e
0.94
1.96
6.00
f1 (ppm)

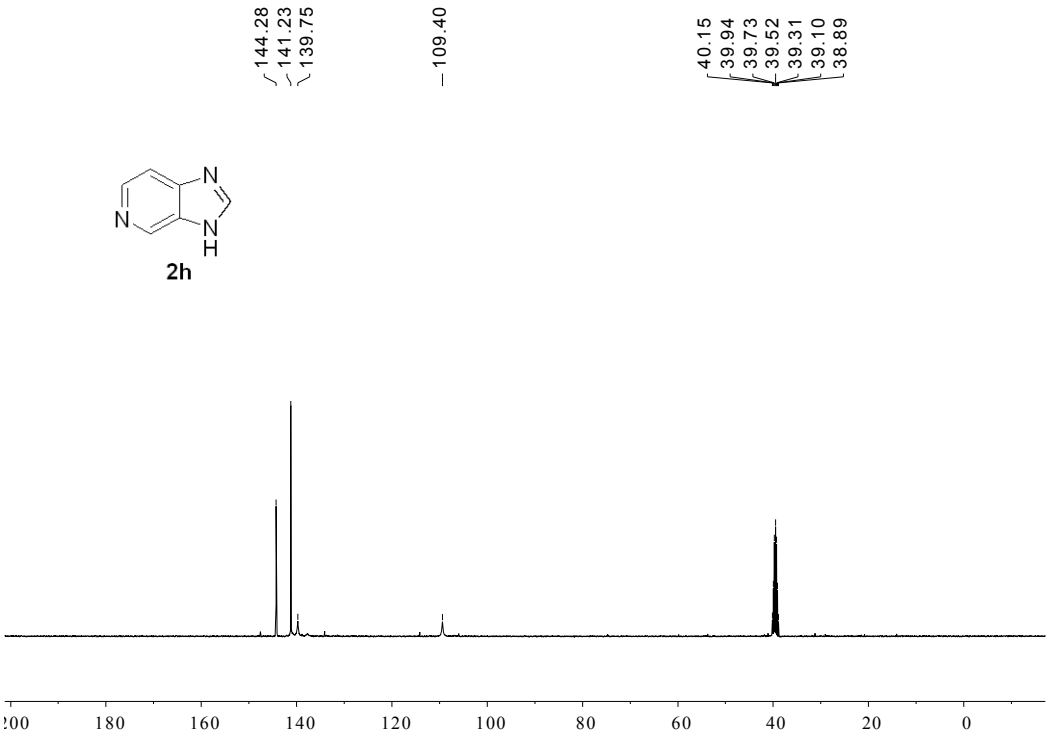

140.07
136.36
131.99
115.63
77.48
77.16
76.84
20.49
2e
f1 (ppm)


9.13
8.16
7.60
7.59
7.58
7.57
7.33
7.33
7.31
7.26
7.07
7.07
7.05
7.03
7.03
0.00
F
N
H
2f
0.47
1.00
0.96
0.99
1.00
2
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
161.04
158.66
141.90
137.79
137.65
134.52
116.42
116.32
111.74
111.49
101.59
101.33
77.48
77.16
76.84
F
N
H
2f
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.56
8.52
8.14
8.14
8.12
8.11
7.79
7.77
3.37
2.50
2g
2.11
1.05
0.93
11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


146.76
142.91
142.63
117.59
115.64
111.64
40.15
39.94
39.73
39.52
39.31
39.10
38.89
2g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.94
8.39
8.30
8.29
7.59
3.38
2.50
2h
1.02
1.05
1.12
1.05
f1 (ppm)


144.28
141.23
139.75
109.40
40.15
39.94
39.73
39.52
39.31
39.10
38.89
2h


7.86
7.82
7.82
7.82
7.81
7.80
7.80
7.40
7.40
7.40
7.39
7.38
7.38
7.34
7.34
7.33
7.32
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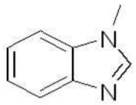
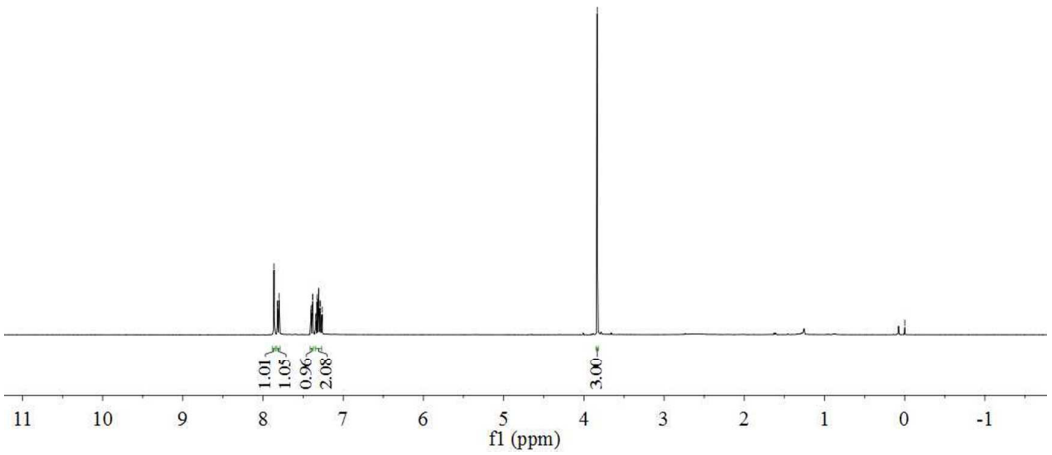
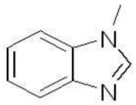
7.30
7.29
7.29
7.27
7.27
7.27
7.26
3.83
0.00



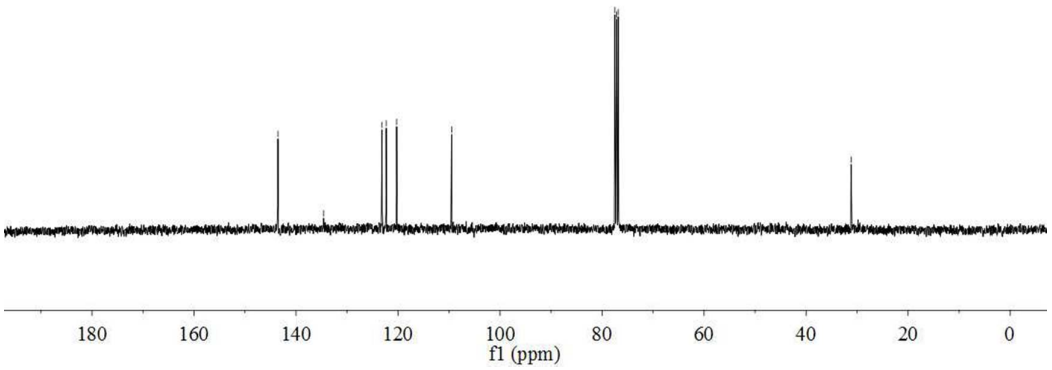
2i

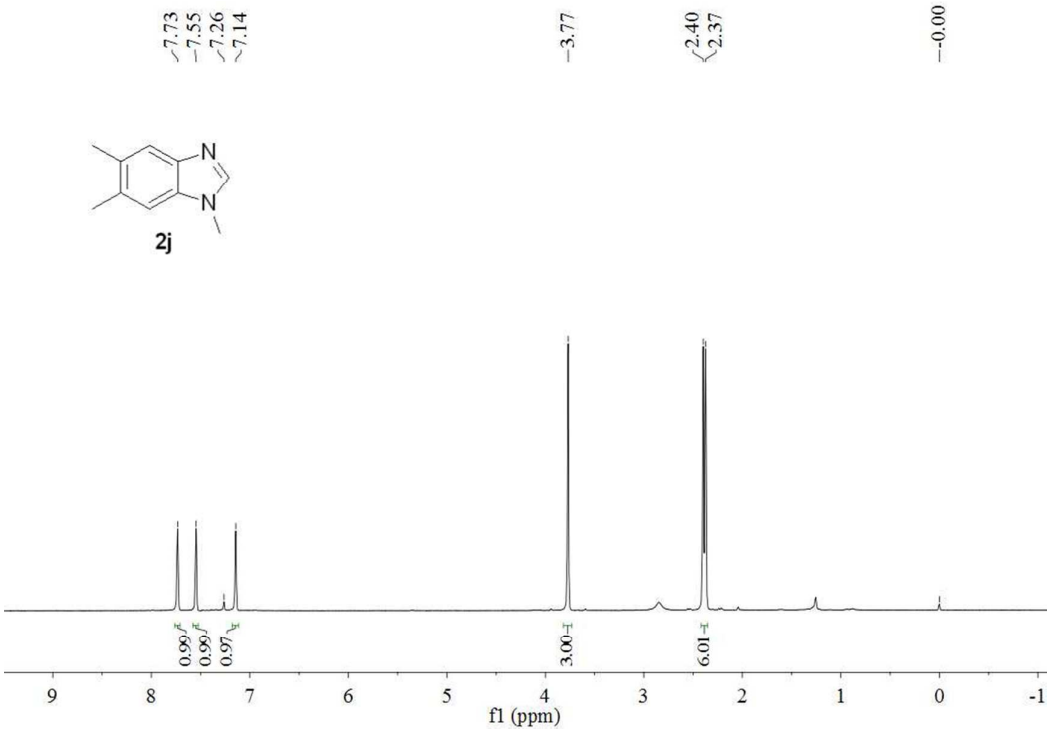

1.01
1.05
0.96
2.08
3.00
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

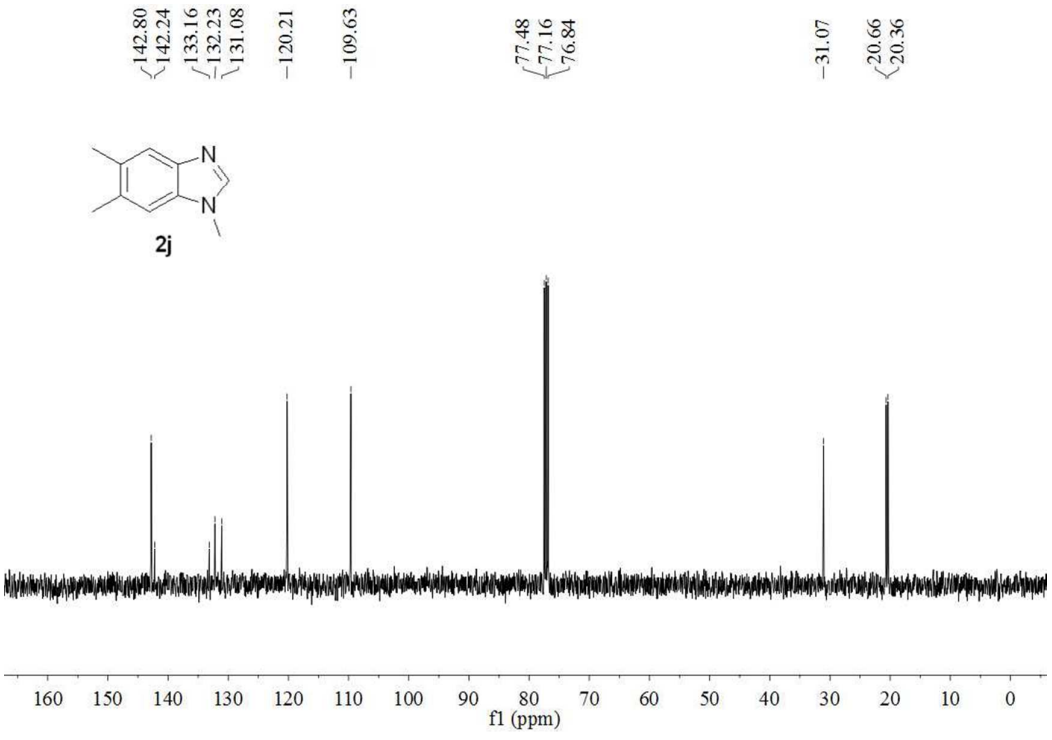

143.55
134.57
123.14
122.32
120.27
109.49
77.48
77.16
76.84
31.17

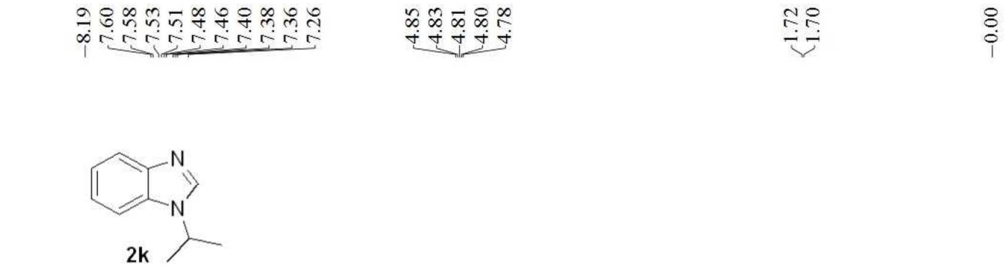


2i


180
160
140
120
100
80
60
40
20
0
f1 (ppm)

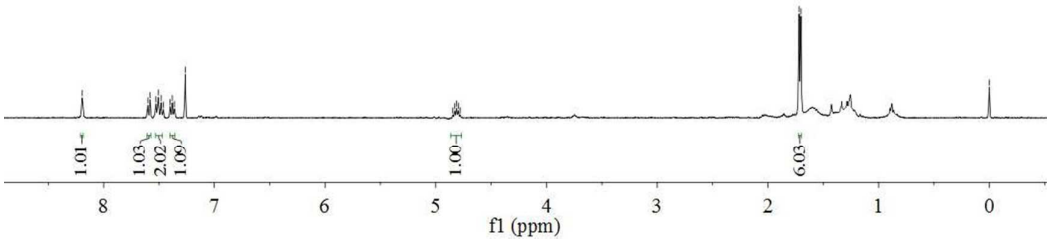

7.73
7.55
7.26
7.14
3.77
2.40
2.37
0.00
2j
0.99
0.99
0.97
3.00
6.01
f1 (ppm)

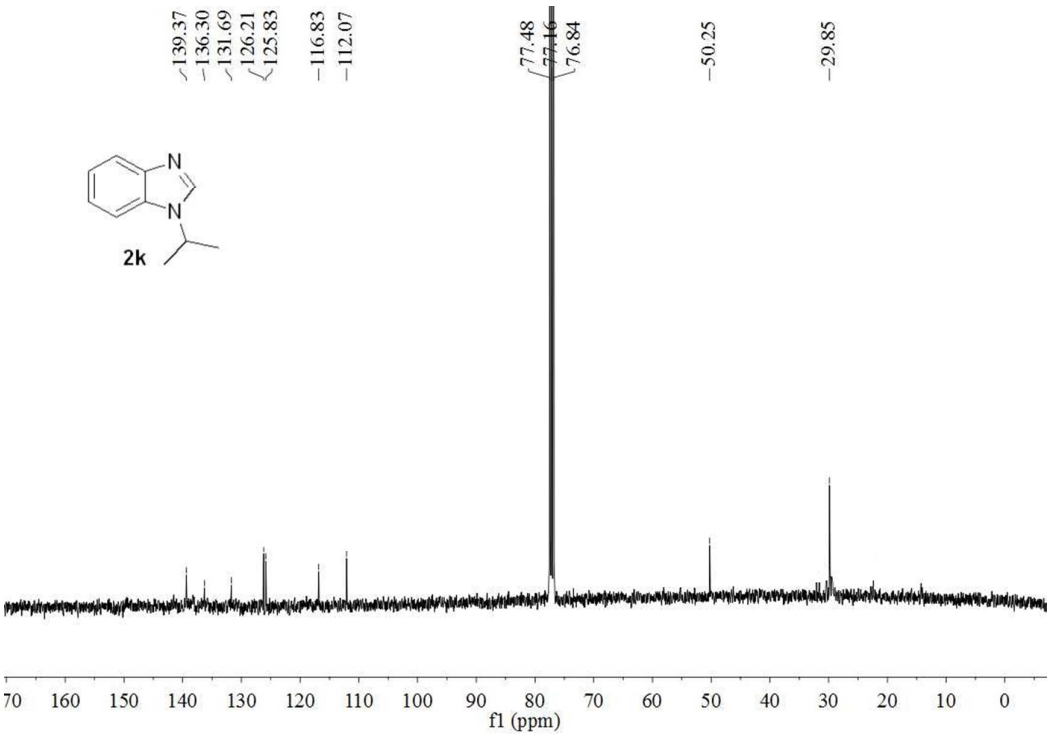

142.80
142.24
133.16
132.23
131.08
120.21
109.63
77.48
77.16
76.84
31.07
20.66
20.36
2j
f1 (ppm)


8.19
7.60
7.58
7.53
7.51
7.48
7.46
7.40
7.38
7.36
7.26
4.85
4.83
4.81
4.80
4.78
1.72
1.70
0.00

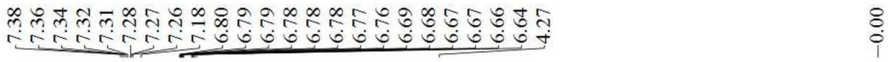
N
N

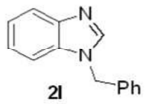
2k


1.01
1.03
2.02
1.00
1.00
6.03
8
7
6
5
4
3
2
1
0
f1 (ppm)

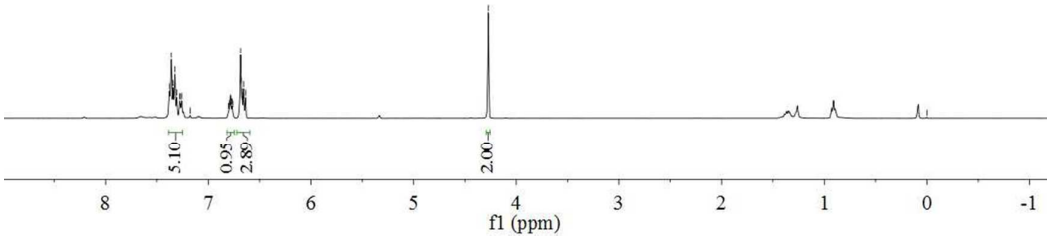

139.37
136.30
131.69
126.21
125.83
116.83
112.07
77.48
77.16
76.84
50.25
29.85
N
N
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2k

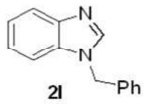

7.38
7.36
7.34
7.32
7.31
7.28
7.27
7.26
7.18
6.80
6.79
6.79
6.78
6.78
6.78
6.77
6.76
6.69
6.68
6.67
6.67
6.66
6.64
4.27
0.00


N
N
Ph

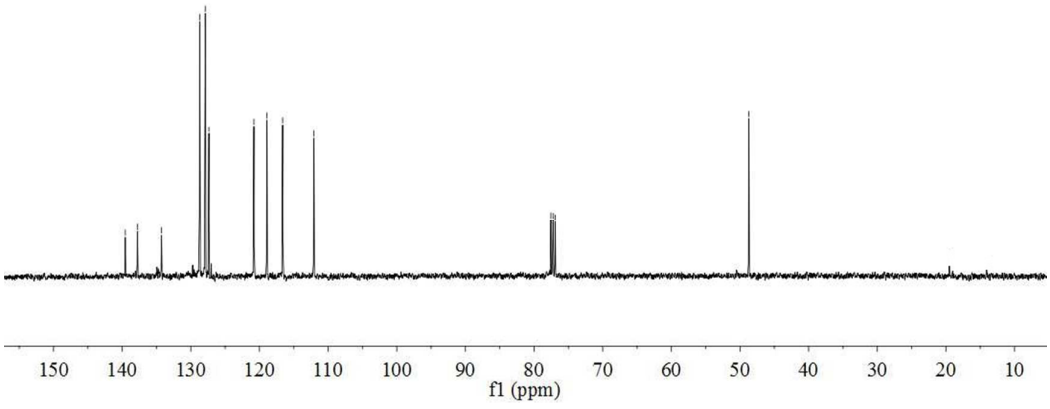
2l

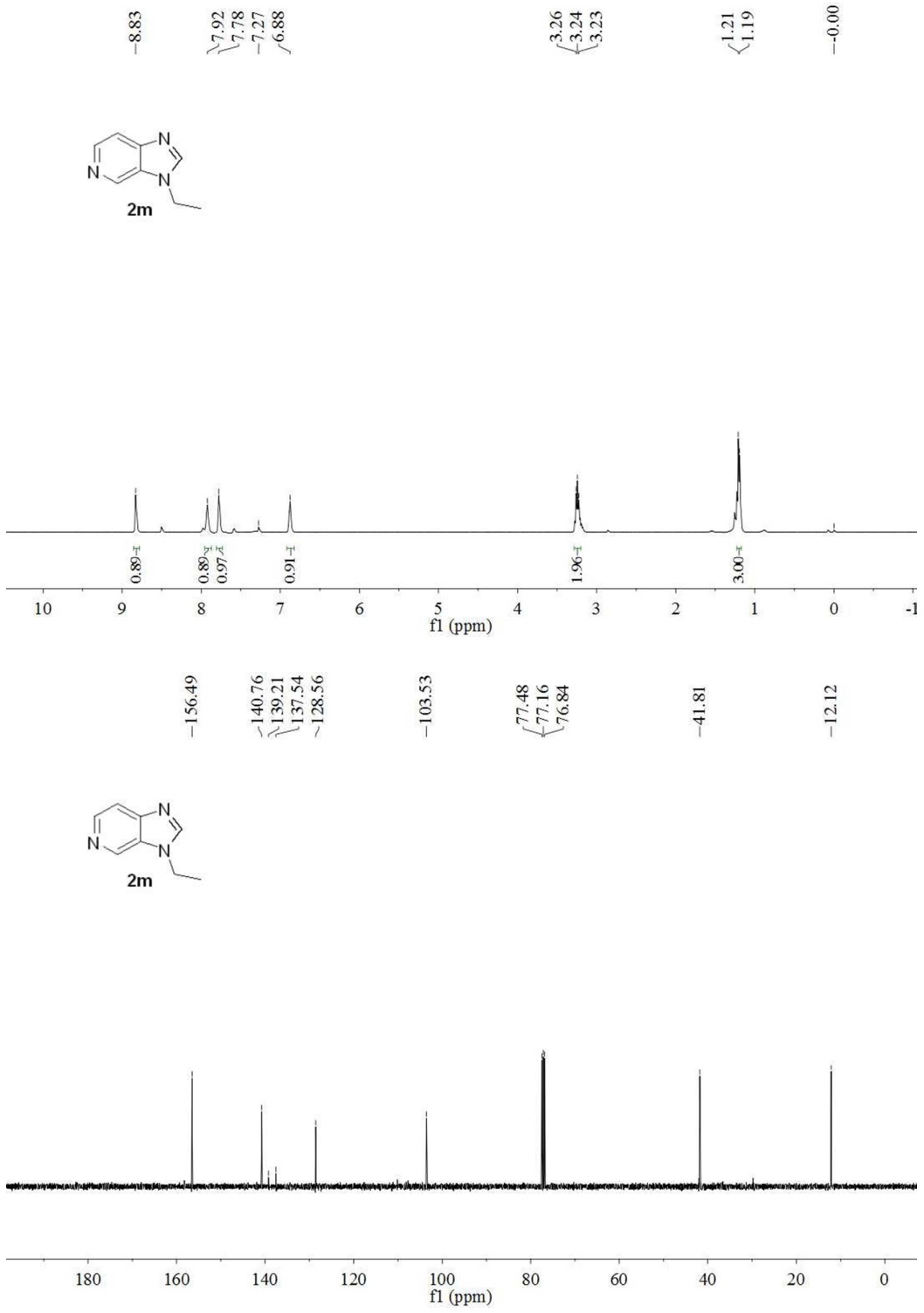

5.10
0.95
2.89
2.00
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


139.54
137.79
134.28
128.71
127.90
127.36
120.81
118.91
116.62
112.07
77.55
77.23
76.91
48.71


N
N
Ph

2l


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.83
7.92
7.78
7.27
6.88
3.26
3.24
3.23
1.21
1.19
0.00
2m
0.89
0.89
0.97
0.91
1.96
3.00
f1 (ppm)
156.49
140.76
139.21
137.54
128.56
103.53
77.48
77.16
76.84
41.81
12.12
2m
f1 (ppm)