Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 579–580

Electrochemical C–H arylation of heteroarenes with *in situ* diazotizated anilines

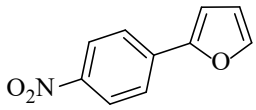
Zhen-Xiang Liu, Hui Mao, Hang-Cheng Ni and Tai-Jin Chen

Experimental Procedures

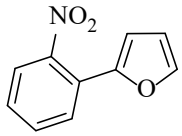
General procedure for the synthesis of 3a~3m

An undivided cell was equipped with a graphite felt anode (2×1 cm^2 plate) and a Ni foam cathode (2×1 cm^2 plate) and connected to a direct (DC) regulated power supply. To the cell was added aryl amine (**1**, 0.2 mmol), heteroarene (**2**, 2 mmol), Bu^tONO (0.3 mmol), $MeSO_3H$ (0.2 mmol), Bu_4NBF_4 (0.2 mmol) and DMSO (5 ml). The mixture was electrolyzed using constant current conditions (I = 10 mA) at room temperature under magnetic stirring. After reaction, the reaction mixture was poured into water, extracted with EtOAc (3 × 5 ml) and dried over Na_2SO_4. The organic phase was then concentrated under reduced pressure, which was further purified by column chromatography using petroleum ether/ethyl acetate (9:1, *v*/*v*) as eluent.

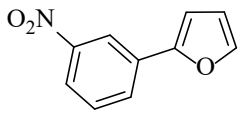
Characterization data



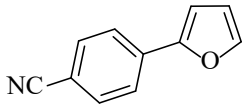
2-(4-Nitrophenyl)furan (3a).[S1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 1.7 Hz, 1H), 6.87 (d, J = 3.5 Hz, 1H), 6.55 (dd, J = 3.5, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 146.4, 144.2, 136.4, 124.3, 123.9, 112.5, 109.0; MS (ESI) *m/z* 212 $[M + Na]^+$.



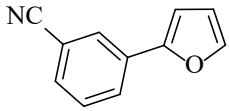
2-(2-Nitrophenyl)furan (3b).[S2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.64 (m, 2H), 7.56 (td, J = 7.7, 1.3 Hz, 1H), 7.50 (dd, J = 1.8, 0.7 Hz, 1H), 7.45-7.34 (m, 1H), 6.66 (dd, J = 3.5, 0.6 Hz, 1H), 6.49 (dd, J = 3.5, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 147.5, 143.8, 131.9, 128.9, 128.3, 124.1, 123.8, 111.9, 109.7; MS (ESI) *m/z* 212 $[M + Na]^+$.



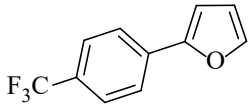
2-(3-Nitrophenyl)furan (3c).[S3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (t, J = 1.9 Hz, 1H), 8.08 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.95 (ddd, J = 7.8, 1.6, 1.1 Hz, 1H), 7.64-7.46 (m, 2H), 6.80 (dd, J = 3.4, 0.6 Hz, 1H), 6.52 (dd, J = 3.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 148.7, 143.3, 132.4, 129.7, 129.2, 121.7, 118.5, 112.1, 107.3; MS (ESI) *m/z* 212 $[M + Na]^+$.



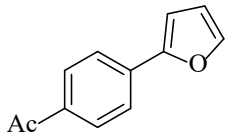
4-(Furan-2-yl)benzonitrile (3d).[S4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75- 7.68 (m, 2H), 7.66-7.60 (m, 2H), 7.53 (dd, *J* = 1.7, 0.6 Hz, 1H), 6.80 (dd, *J* = 3.5, 0.6 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 143.7, 134.6, 132.6, 123.9, 119.0, 112.3, 110.2, 108.2; MS (ESI) *m/z* 192 $[M + Na]^+$.



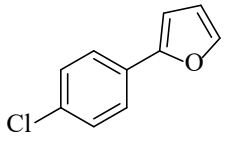
3-(Furan-2-yl)benzonitrile (3e).[S1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.2 Hz, 1H), 7.85 (dt, *J* = 7.3, 1.8 Hz, 1H), 7.56-7.43 (m, 3H), 6.73 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 143.2, 131.9, 130.4, 129.6, 127.7, 127.1, 118.7, 113.0, 112.1, 106.9; MS (ESI) *m/z* 192 $[M + Na]^+$.



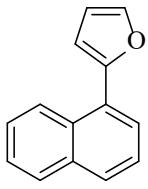
2-(4-(Trifluoromethyl)phenyl)furan (3f).[S2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.54-7.49 (m, 1H), 6.76 (d, *J* = 3.4 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 143.2, 134.0 (d, *J* = 1.3 Hz), 129.1 (q, *J* = 32.5 Hz), 125.8 (q, *J* = 3.9 Hz), 124.3 (d, *J* = 271.8 Hz), 123.9, 112.0, 107.0; MS (ESI) *m/z* 235 $[M + Na]^+$.



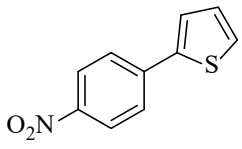
1-(4-(Furan-2-yl)phenyl)ethanone (3g).[S5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.93 (m, 2H), 7.77-7.68 (m, 2H), 7.52 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.79 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 152.8, 143.3, 135.5, 134.9, 129.0, 123.6, 112.1, 107.5, 26.6; MS (ESI) *m/z* 209 $[M + Na]^+$.



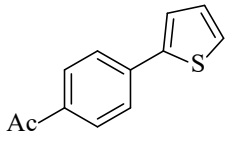
2-(4-Chlorophenyl)furan (3h).[S5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.57 (m, 2H), 7.48 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.40-7.33 (m, 2H), 6.64 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 142.3, 133.0, 129.4, 128.9, 125.0, 111.8, 105.5; MS (ESI) *m/z* 201 $[M + Na]^+$.



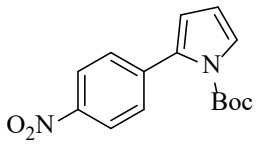
2-(Naphthalen-1-yl)furan (3i).[S6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.95-7.82 (m, 2H), 7.75 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.64 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.58-7.50 (m, 3H), 6.75 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.61 (dd, *J* = 3.3, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.5, 134.0, 130.5, 128.7, 128.6 (2C), 126.6, 126.2, 126.0, 125.6, 125.4, 111.4, 109.3; MS (ESI) *m/z* 217 $[M + Na]^+$.



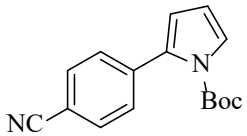
2-(4-Nitrophenyl)thiophene (3j).[S4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28-8.17 (m, 2H), 7.78-7.67 (m, 2H), 7.50-7.38 (m, 2H), 7.14 (dd, *J* = 5.1, 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 141.6, 140.6, 128.7, 127.7, 126.0, 125.8, 124.4; MS (ESI) *m/z* 228 $[M + Na]^+$.



1-(4-(Thiophen-2-yl)phenyl)ethanone (3k).[S5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.92 (m, 2H), 7.72-7.65 (m, 2H), 7.43 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 143.0, 138.9, 135.8, 129.2, 128.5, 126.6, 125.8, 124.7, 26.7; MS (ESI) *m/z* 225 $[M + Na]^+$.



***tert*-Butyl 2-(4-nitrophenyl)-1*H*-pyrrole-1-carboxylate (3l)**.[S3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30-8.06 (m, 2H), 7.68-7.43 (m, 2H), 7.37 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.29 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.24 (t, *J* = 3.3 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 146.6, 140.7, 132.8, 129.6, 124.4, 123.0, 116.6, 111.2, 84.6, 27.8; MS (ESI) *m/z* 311 $[M + Na]^+$.



***tert*-Butyl 2-(4-cyanophenyl)-1*H*-pyrrole-1-carboxylate (3m)**.[S3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.59 (m, 2H), 7.49-7.42 (m, 2H), 7.38 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.29- 6.23 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 138.9, 133.2, 131.5, 129.6, 124.0, 119.1, 116.1, 111.1, 110.6, 84.4, 27.8; MS (ESI) *m/z* 291 $[M + Na]^+$.

References

S1.D. Hata, T. Moriuchi, T. Hirao and T. Amaya, *Chem. - Eur. J.*, 2017, **23**, 7703.

S2.D. M. Monzón, T. Santos, F. Pinacho-Crisóstomo, V. S. Martin and R. Carrillo, *Chem. - Asian J.*, 2018, **13**, 325.

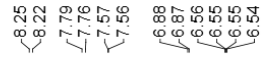
S3.D. P. Hari, P. Schroll and B. König, *J. Am. Chem. Soc.*, 2012, **134**, 2958.

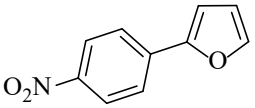
S4.S. Shaaban, A. Jolit, D. Petkova and N. Maulide, *Chem. Commun.*, 2015, **51**, 13902.

S5.S. Crespi, S. Protti and M. Fagnoni, *J. Org. Chem.,* 2016, **81**, 9612.

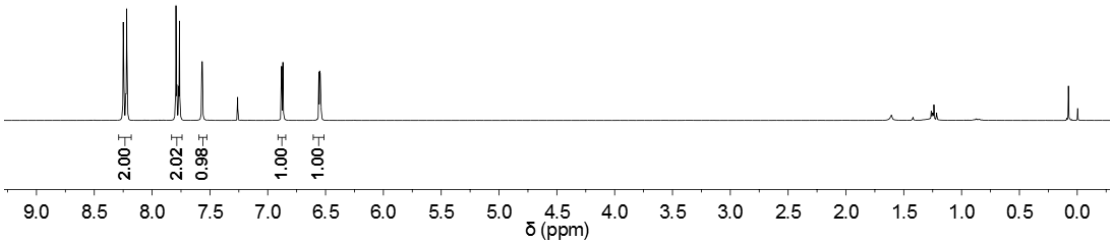
S6.P. R. Melvin, N. Hazari, M. M. Beromi, H. P. Shah and M. J. Williams, *Org. Lett.*, 2016, **18**, 5784.

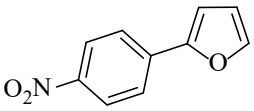
Copies of ^{1}H and ^{13}C NMR Spectra



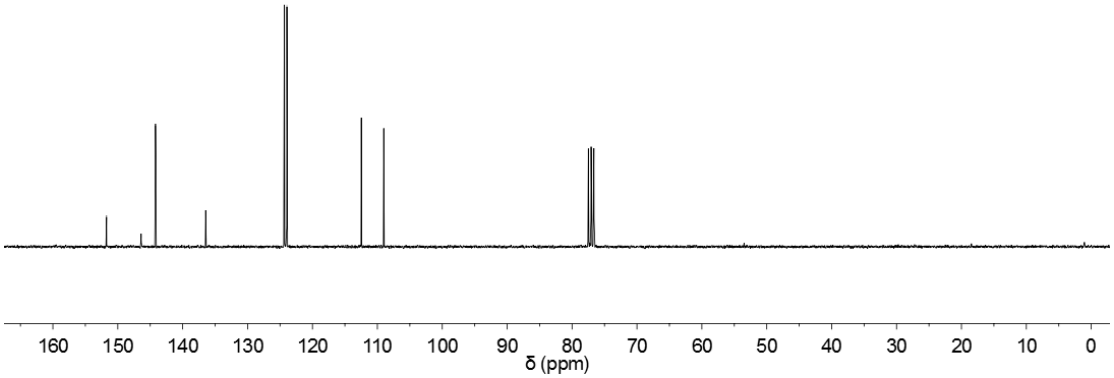


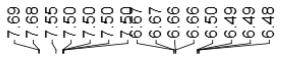
3a

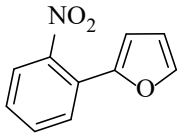




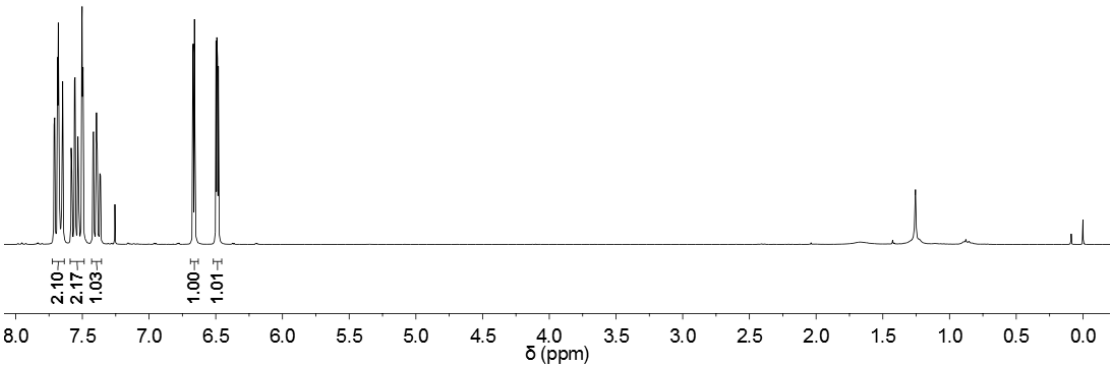
3a

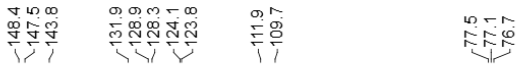


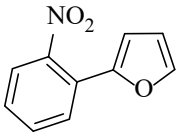

7.69
7.68
7.55
7.50
7.50
7.50
6.67
6.66
6.66
6.50
6.49
6.49
6.48


NO2
O

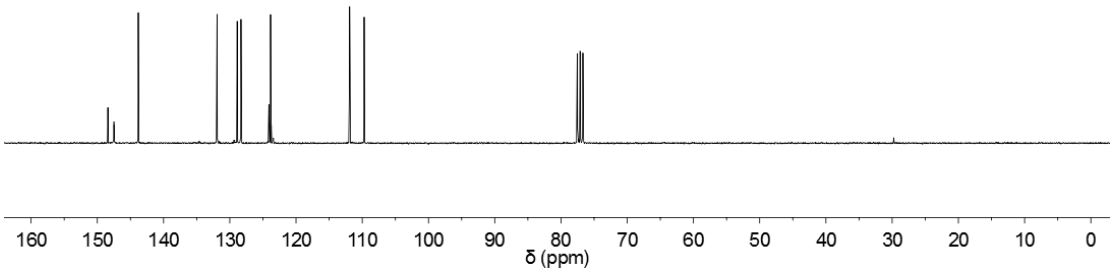
3b

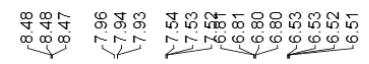

2.10
2.17
1.03
1.00
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

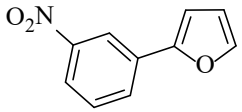

148.4
147.5
143.8
131.9
128.9
128.3
124.1
123.8
111.9
109.7
77.5
77.1
76.7


NO2
O

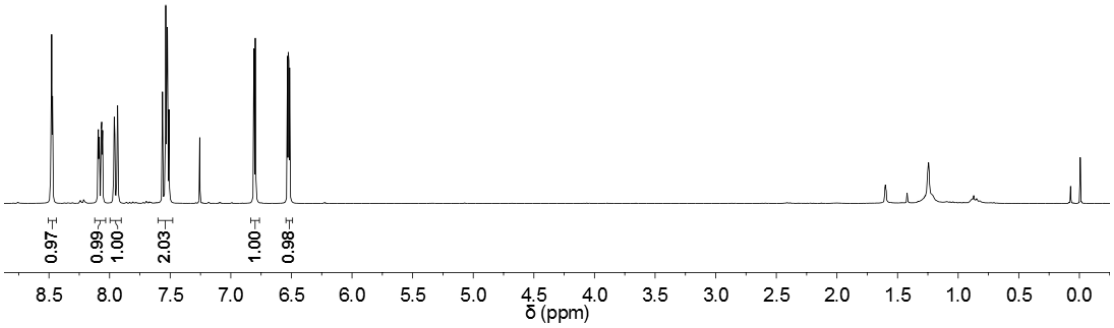
3b


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

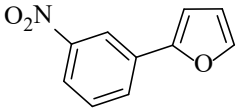

8.48
8.48
8.47
7.96
7.94
7.93
7.54
7.53
7.52
6.81
6.80
6.80
6.53
6.53
6.52
6.51


O2N
O

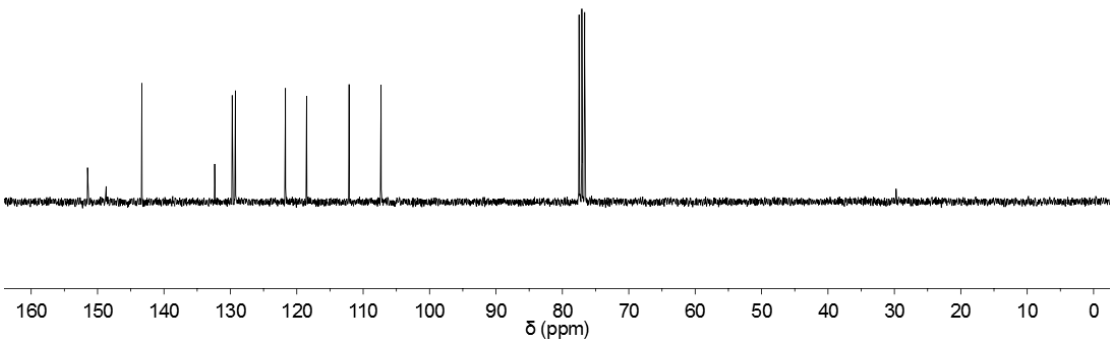
3c

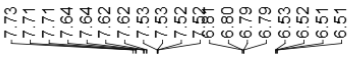

0.97
0.99
1.00
2.03
1.00
0.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

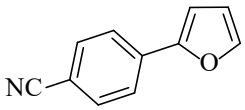

151.5
148.7
143.3
132.4
129.7
129.2
121.7
118.5
112.1
107.3
77.5
77.1
76.6


O2N
O

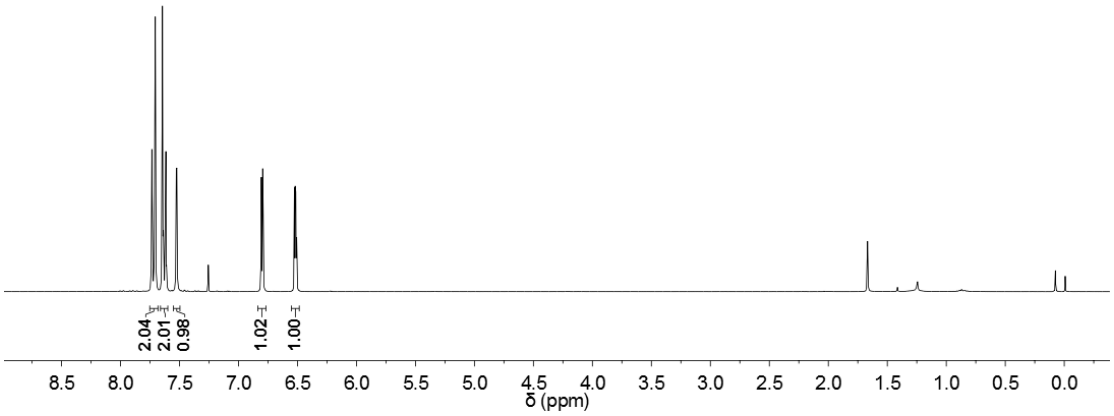
3c

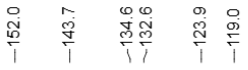

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.73
7.71
7.71
7.64
7.64
7.62
7.62
7.53
7.53
7.52
6.80
6.79
6.79
6.53
6.52
6.51
6.51

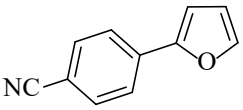

NC
O

3d

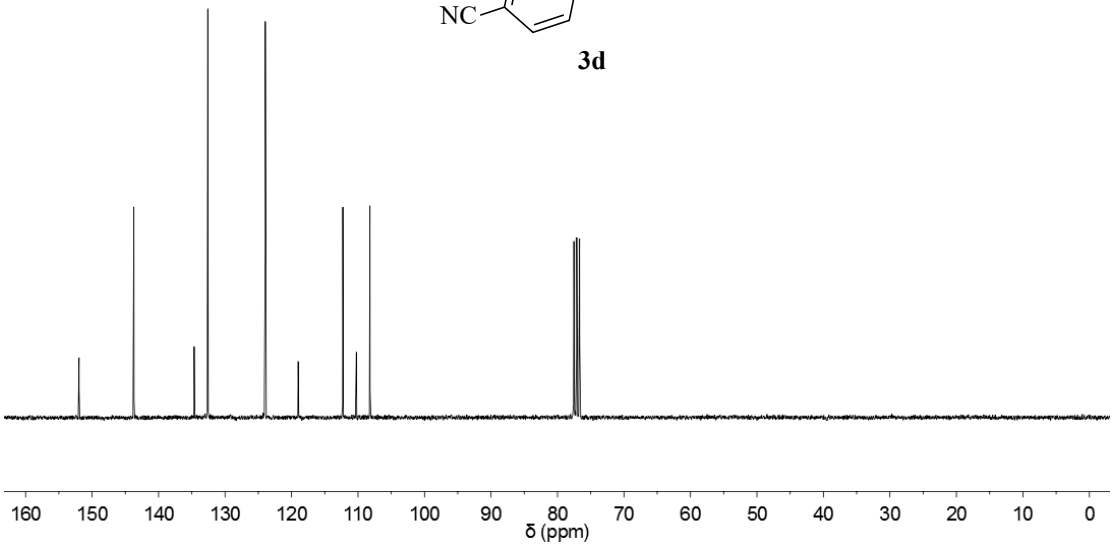

2.04
2.01
0.98
1.02
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

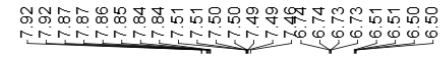

152.0
143.7
134.6
132.6
123.9
119.0
112.3
110.3
108.2

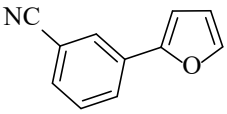

77.5
77.1
76.7


NC
O

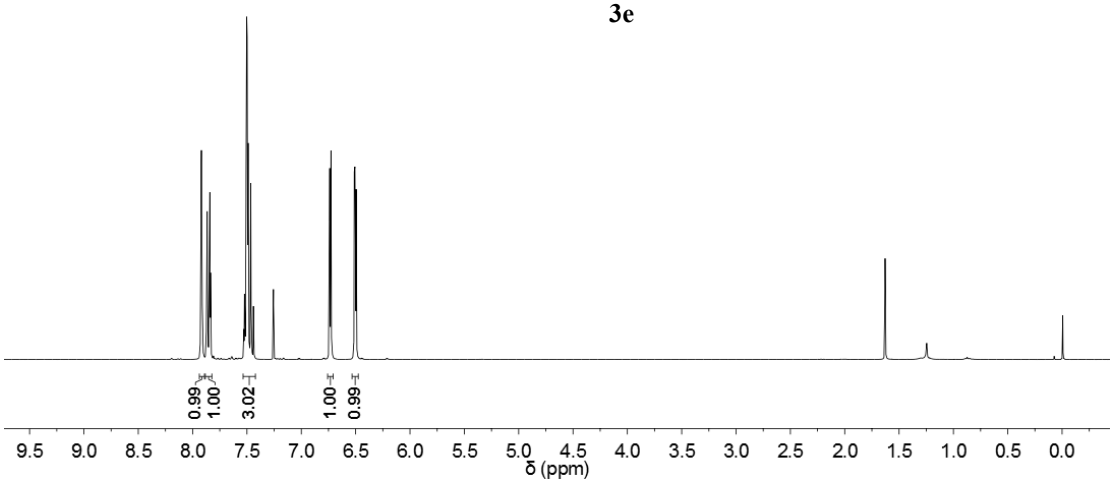
3d

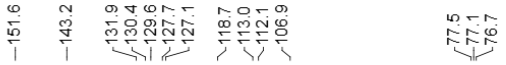

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

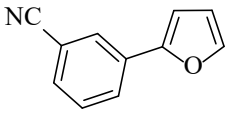

7.92
7.92
7.87
7.87
7.86
7.85
7.84
7.84
7.51
7.51
7.50
7.50
7.49
7.46
6.74
6.73
6.51
6.51
6.50
6.50


NC
O

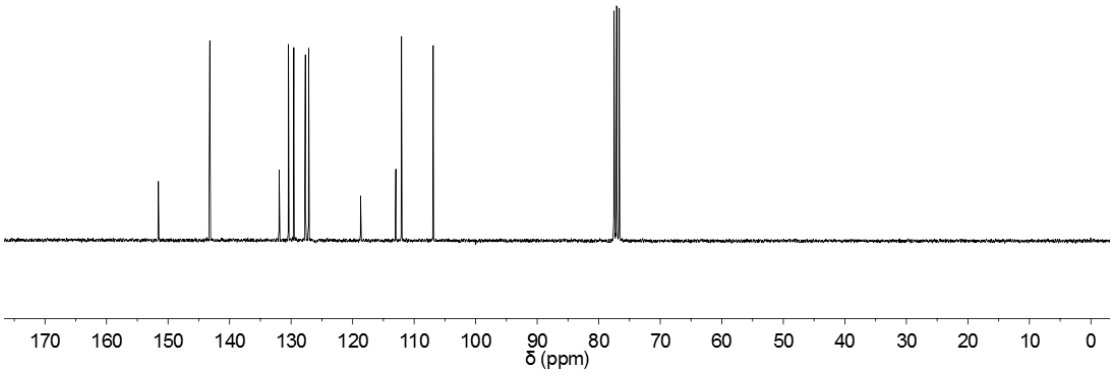
3e

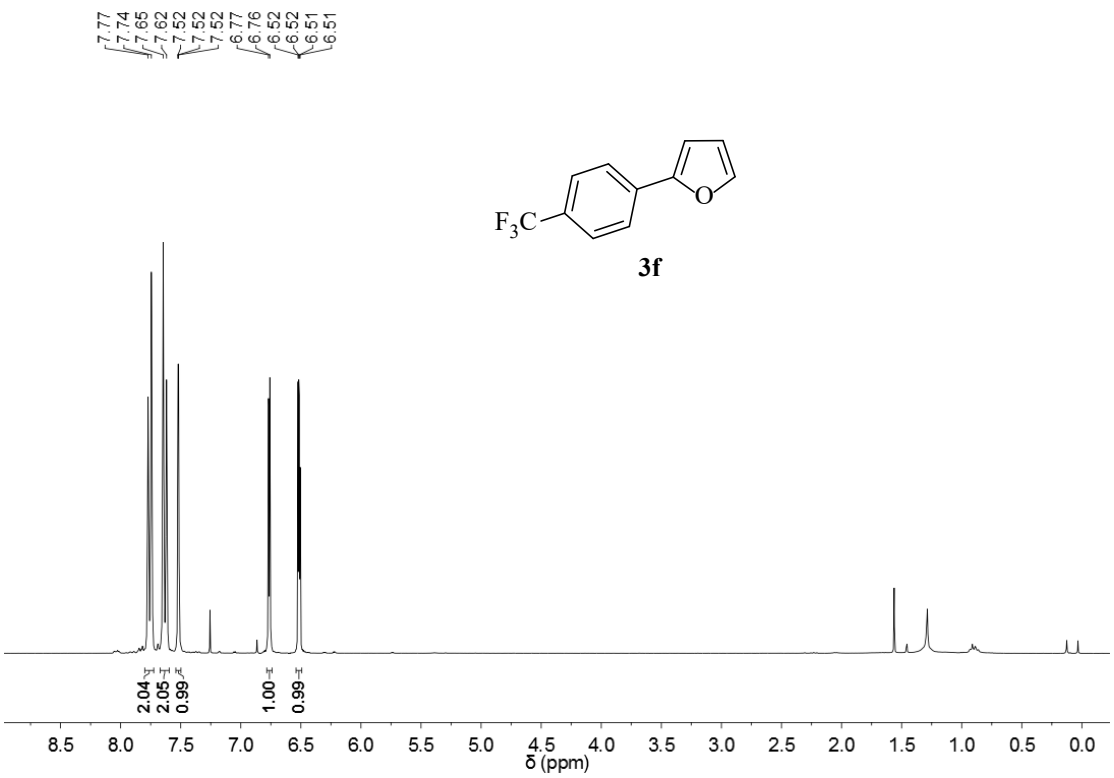

0.99
1.00
3.02
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

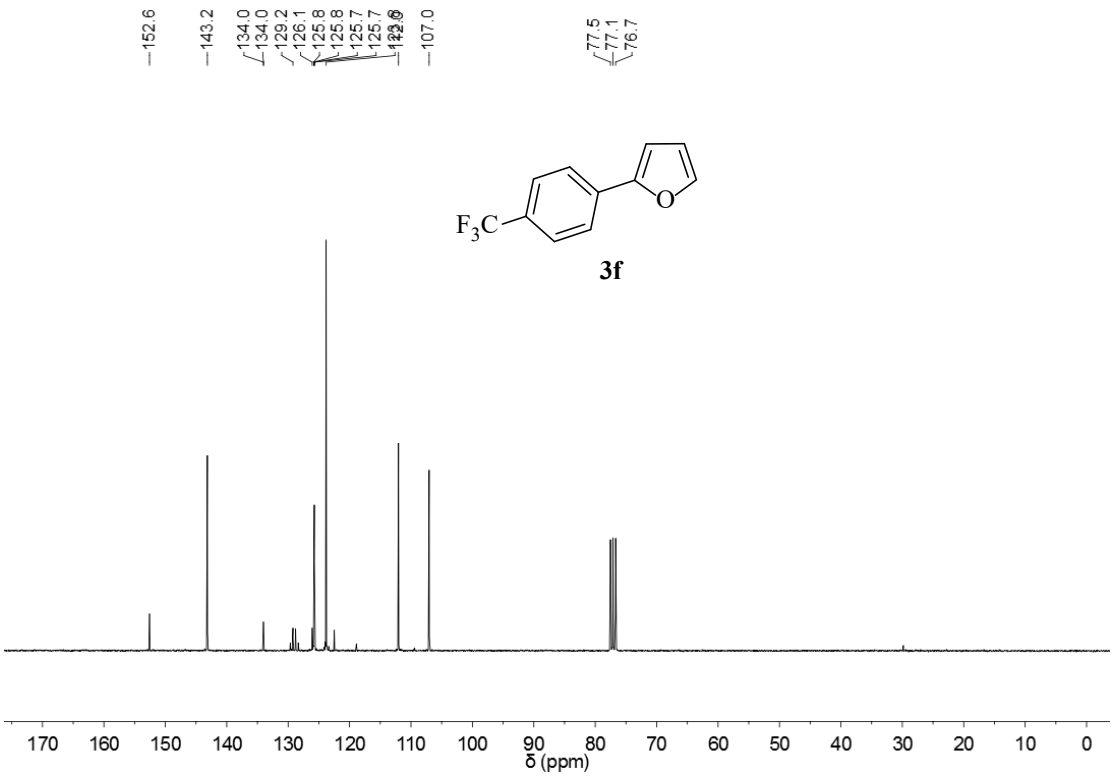

151.6
143.2
131.9
130.4
129.6
127.7
127.1
118.7
113.0
112.1
106.9
77.5
77.1
76.7

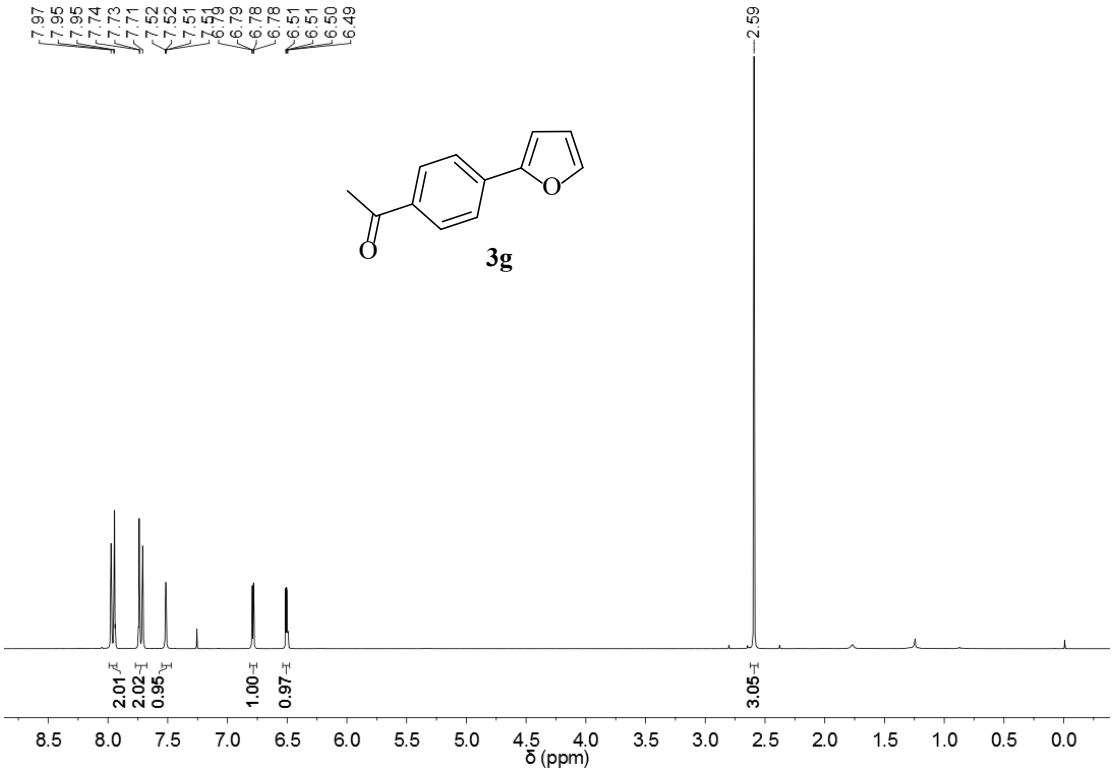

NC
O

3e

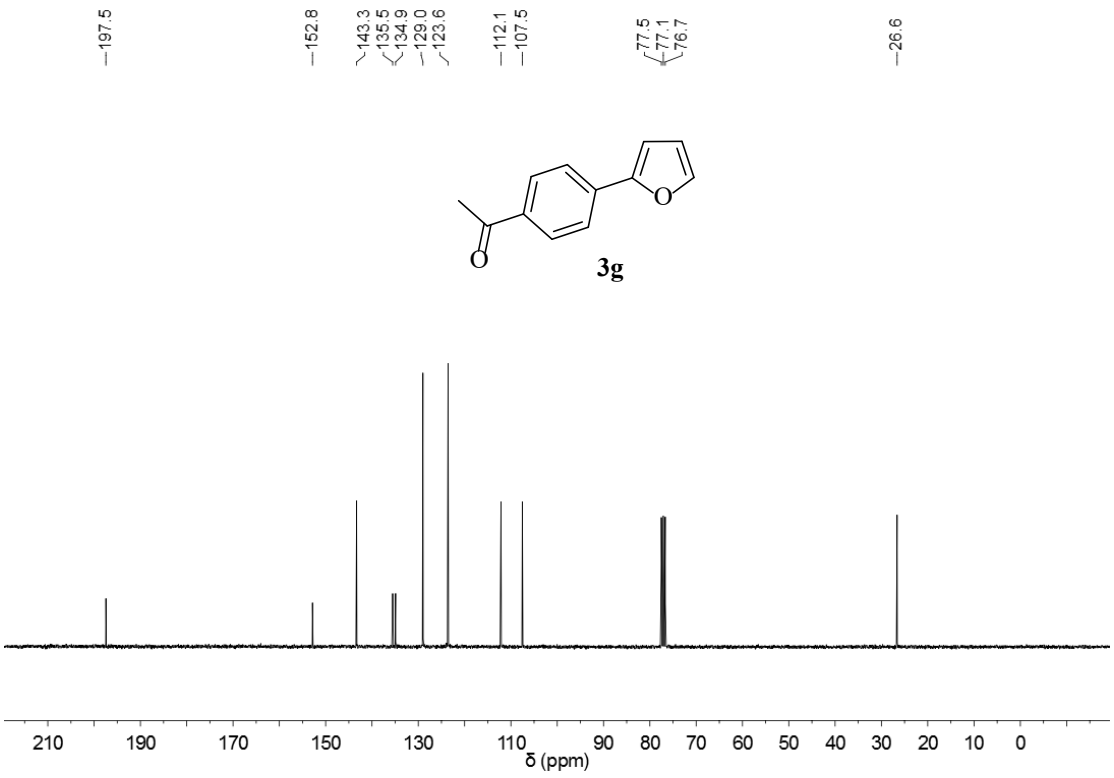

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.77
7.74
7.65
7.62
7.52
7.52
7.52
6.77
6.76
6.52
6.52
6.51
6.51
F3C
O
3f
2.04
2.05
0.99
1.00
0.99
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
δ (ppm)

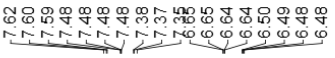

152.6
143.2
134.0
134.0
129.2
126.1
125.8
125.8
125.7
125.7
107.0
77.5
77.1
76.7
F3C
O
3f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

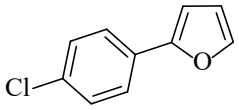

7.97
7.95
7.95
7.74
7.73
7.71
7.52
7.52
7.51
7.51
6.79
6.79
6.78
6.78
6.51
6.51
6.50
6.49
2.59
2.01
2.02
0.95
1.00
0.97
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

3g

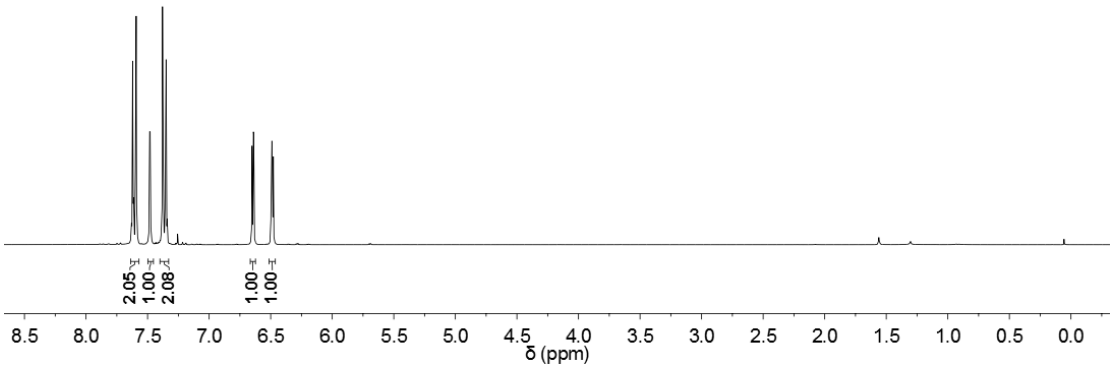

197.5
152.8
143.3
135.5
134.9
129.0
123.6
112.1
107.5
77.5
77.1
76.7
26.6
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
δ (ppm)

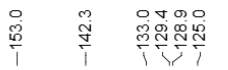
3g

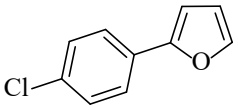

7.62
7.60
7.59
7.48
7.48
7.48
7.48
7.38
7.37
6.65
6.64
6.64
6.50
6.49
6.48
6.48


Cl
O

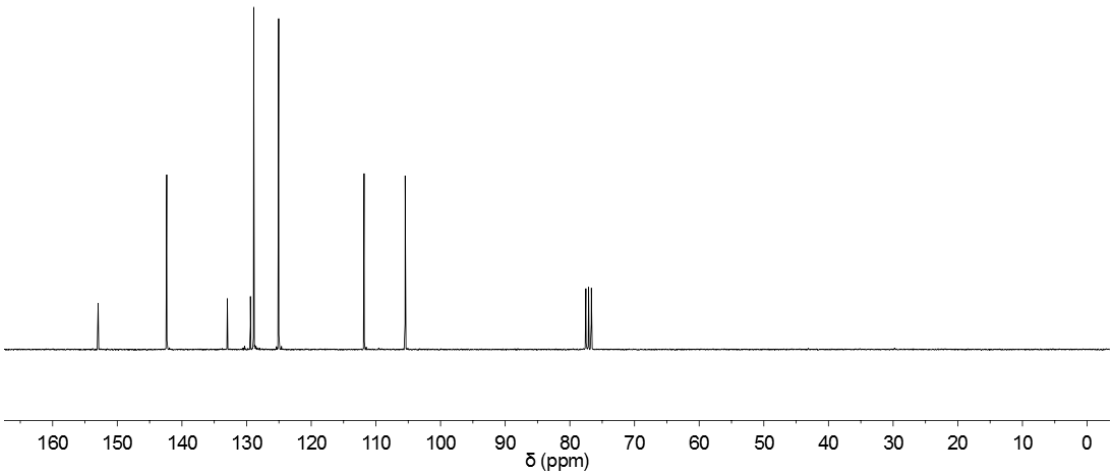
3h

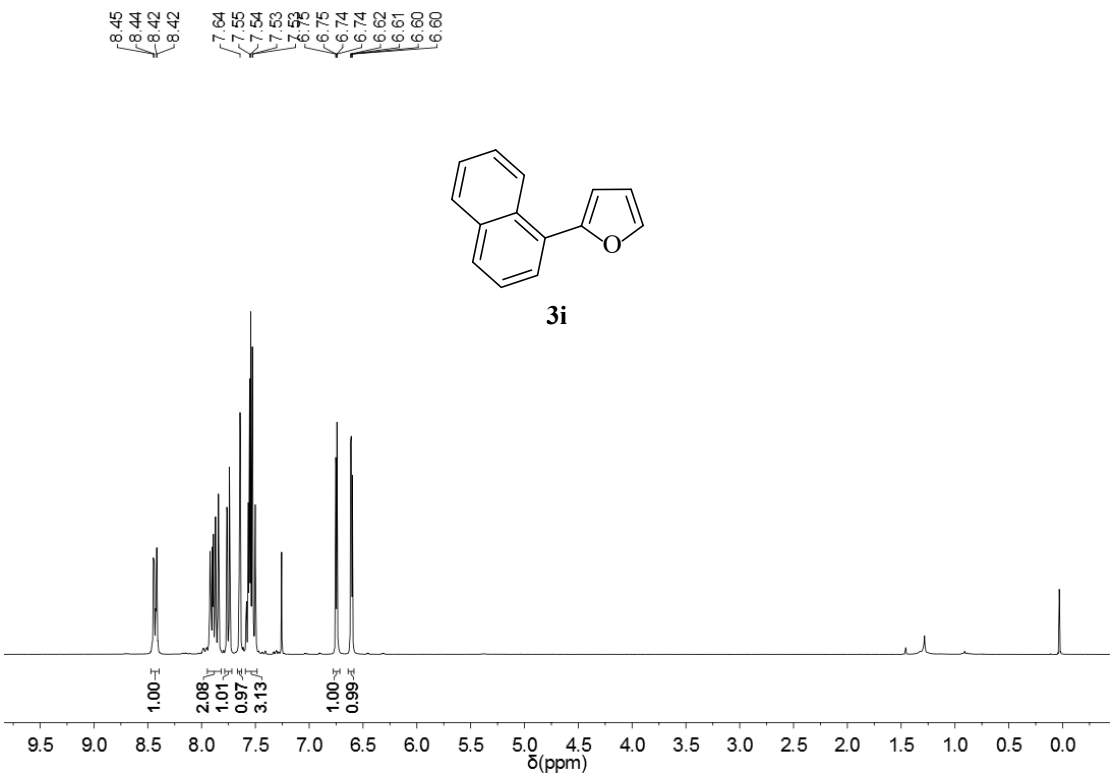

2.05
1.00
2.08
1.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

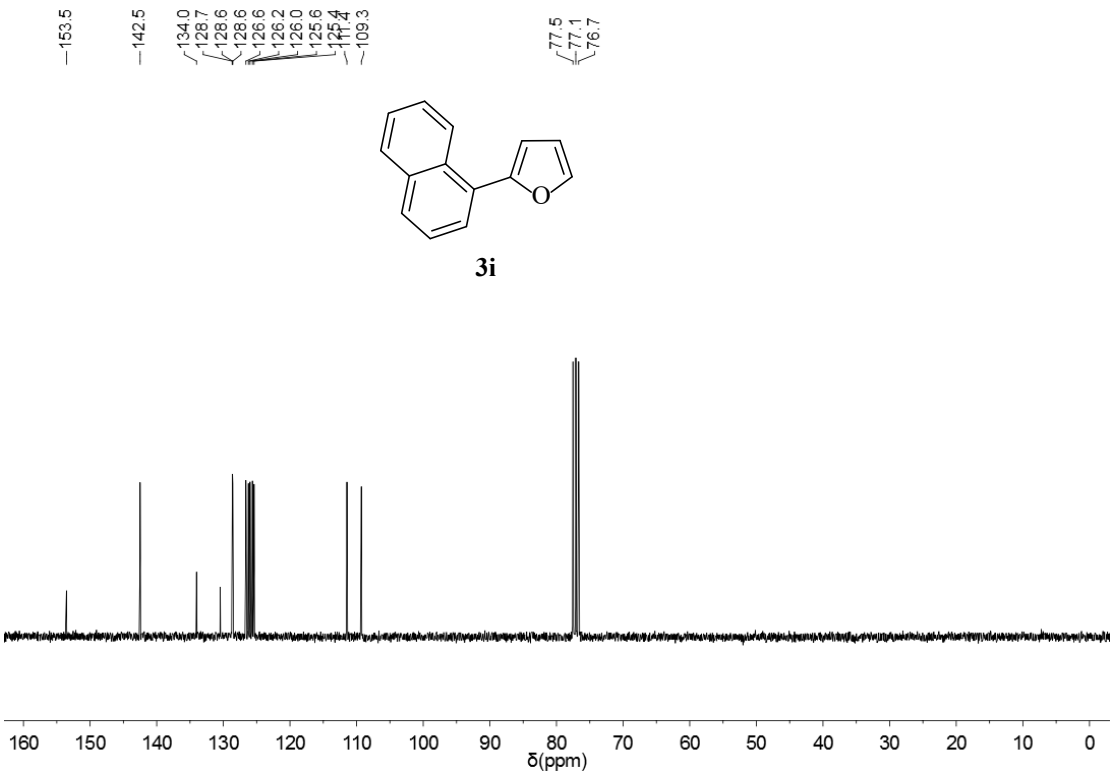

153.0
142.3
133.0
129.4
128.9
125.0
111.8
105.5
77.5
77.1
76.7


Cl
O

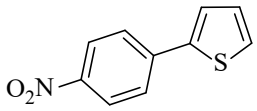
3h


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

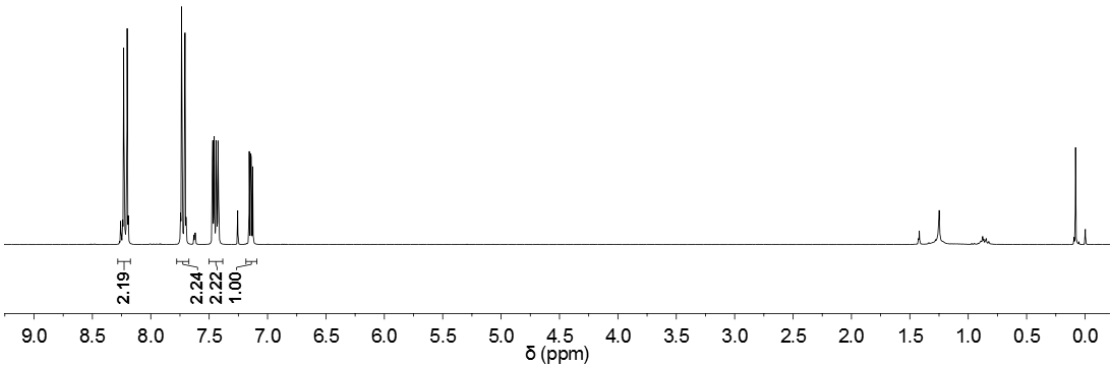

8.45
8.44
8.42
8.42
7.64
7.55
7.54
7.53
7.53
6.75
6.74
6.74
6.62
6.61
6.60
6.60
O
3i
1.00
2.08
1.01
0.97
3.13
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)


153.5
142.5
134.0
128.7
128.6
128.6
126.6
126.2
126.0
125.6
77.5
77.1
76.7
109.3
O
3i
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

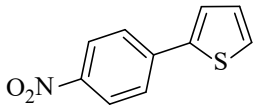

8.26
8.24
8.23
8.23
8.21
8.20
8.19
7.75
7.74
7.73
7.71
7.71
7.70
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.16
7.14
7.14
7.13


O2N
S

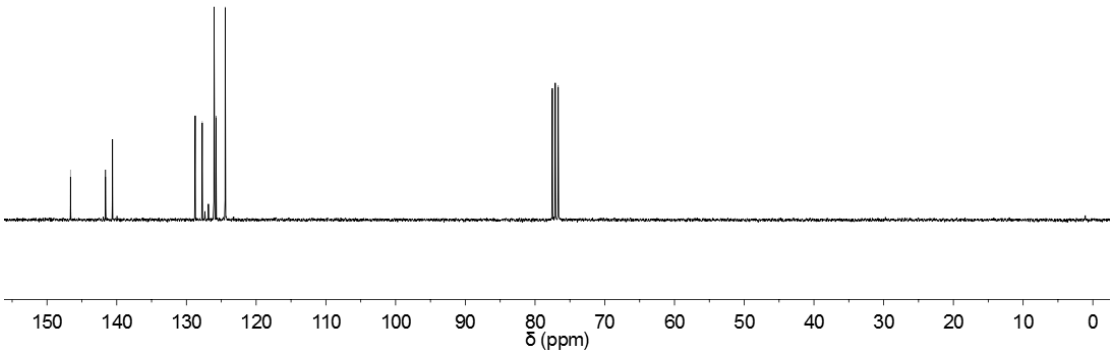
3j

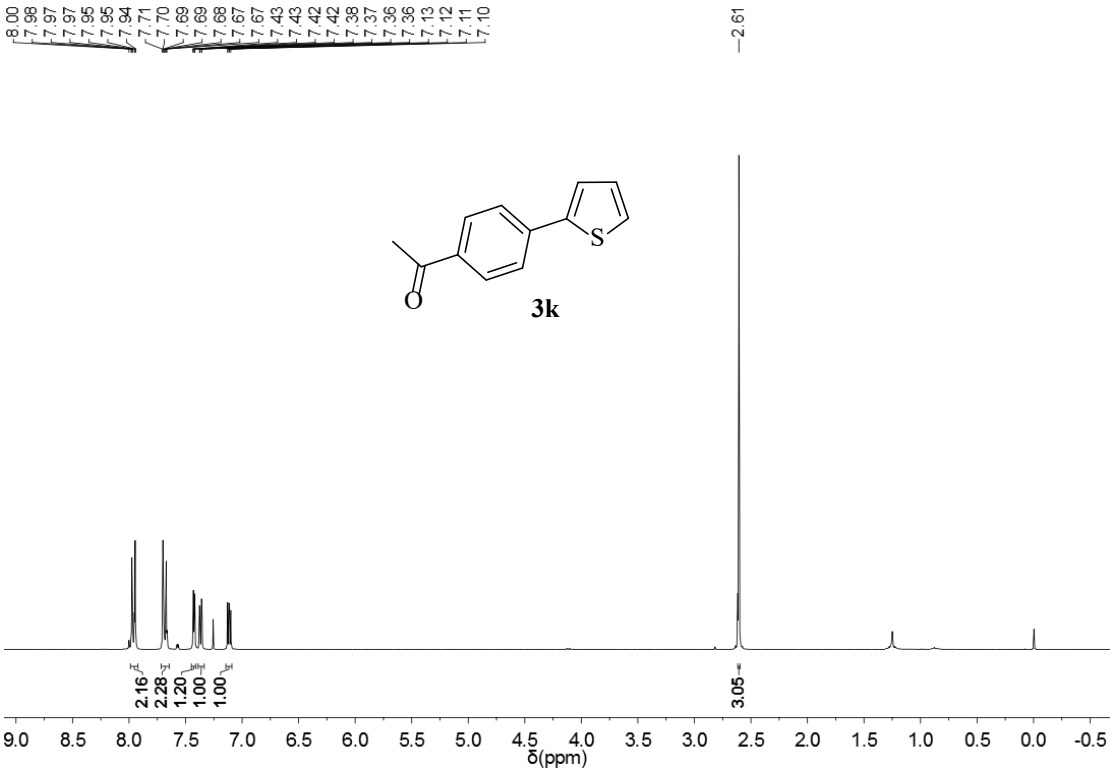

2.19
2.24
2.22
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

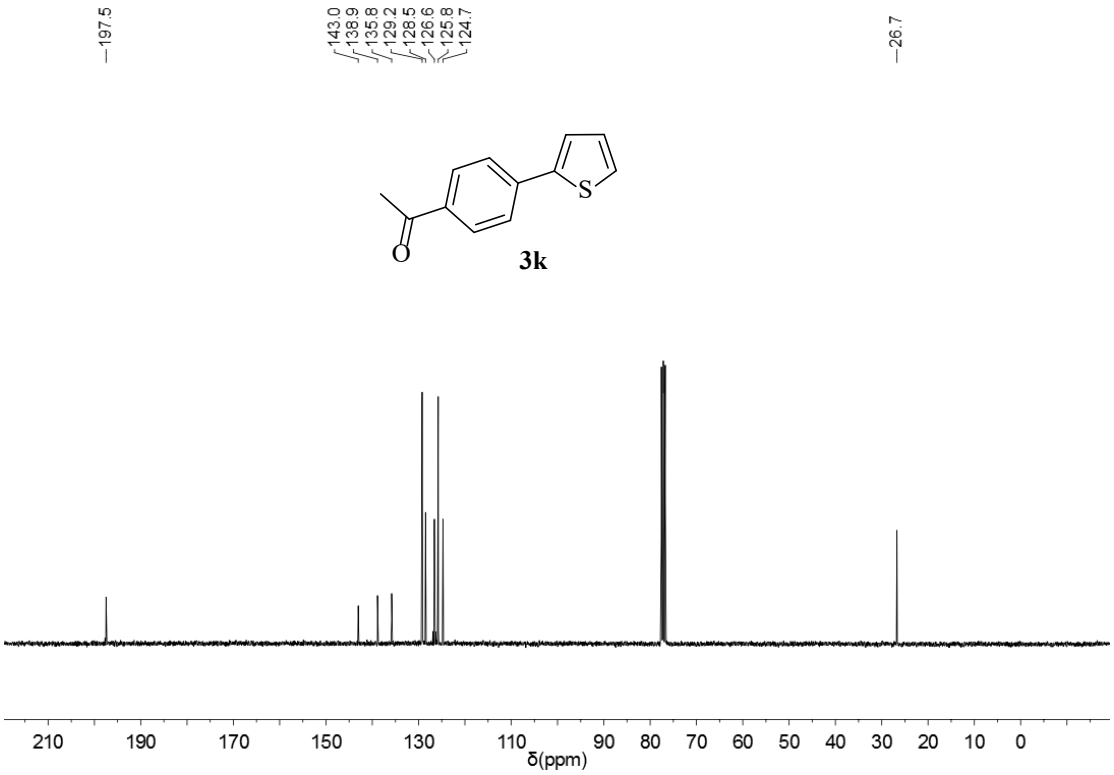

146.6
141.6
140.6
128.7
127.7
126.0
125.8
124.4
77.5
77.1
76.7

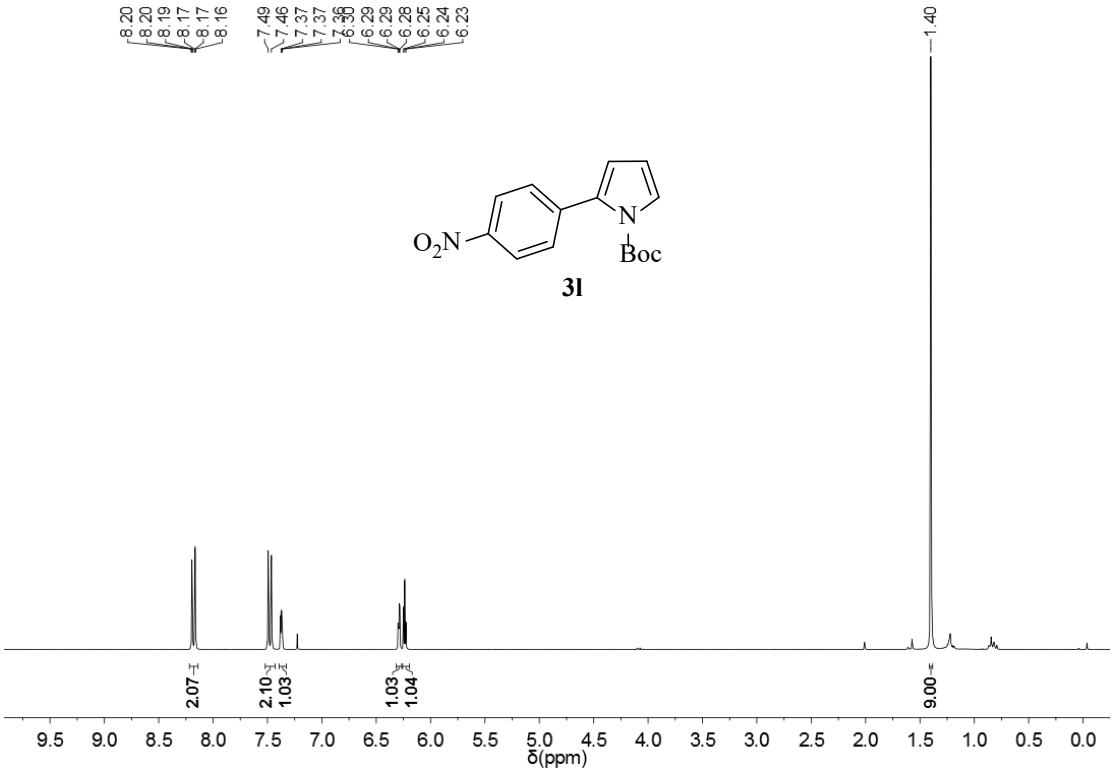

O2N
S

3j

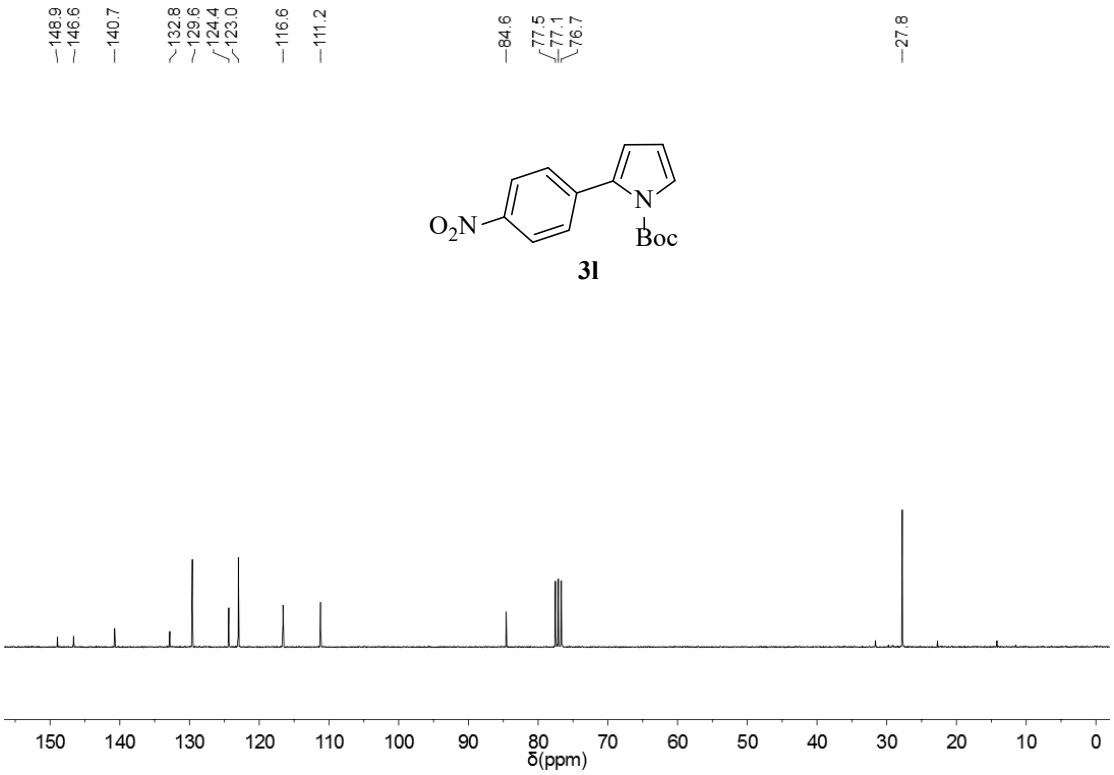

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.00
7.98
7.97
7.97
7.95
7.95
7.94
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.43
7.43
7.42
7.42
7.38
7.37
7.36
7.36
7.13
7.12
7.11
7.10
2.61
O
S
3k
2.16
2.28
1.20
1.00
1.00
3.05
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
δ(ppm)

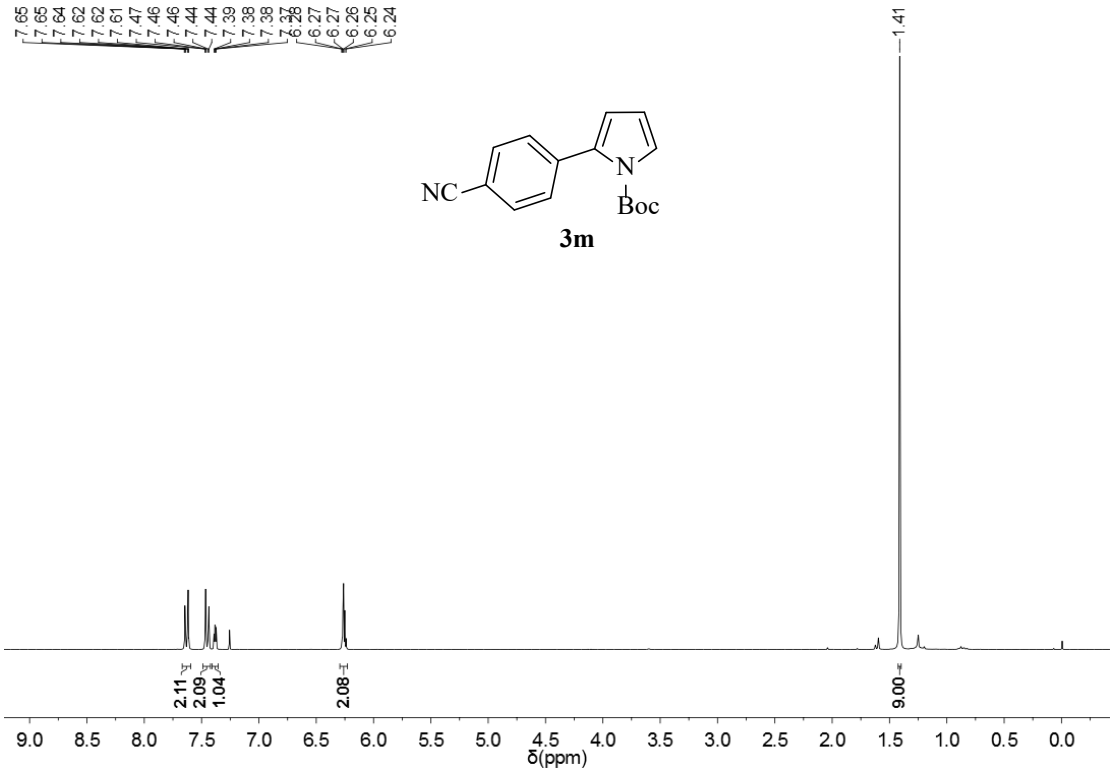

197.5
143.0
138.9
135.8
129.2
128.5
126.6
125.8
124.7
26.7
O
S
3k
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
δ(ppm)


8.20
8.20
8.19
8.17
8.17
8.16
7.49
7.46
7.37
7.37
7.36
6.29
6.29
6.28
6.25
6.24
6.23
1.40
O2N
N
Boc
2.07
2.10
1.03
1.03
1.04
9.00
δ(ppm)

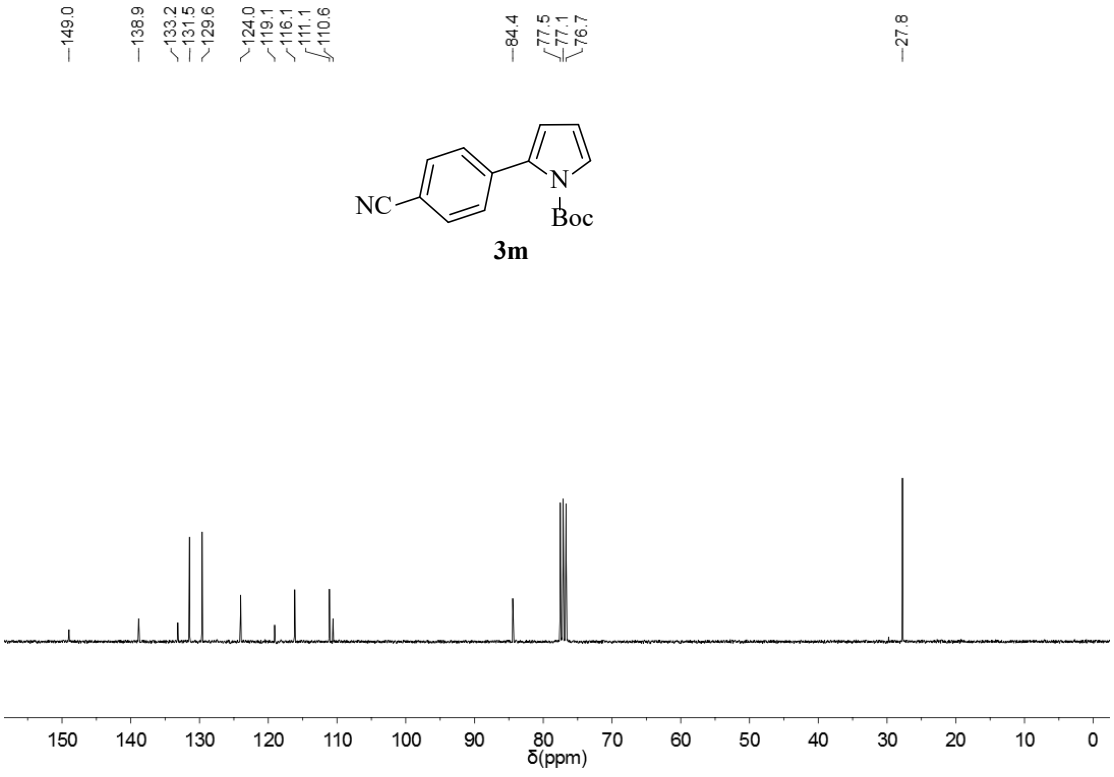
3l


148.9
146.6
140.7
132.8
129.6
124.4
123.0
116.6
111.2
84.6
77.5
77.1
76.7
27.8
O2N
N
Boc
δ(ppm)

3l


7.65
7.65
7.64
7.62
7.62
7.61
7.47
7.46
7.46
7.44
7.44
7.39
7.38
7.38
7.37
7.28
6.27
6.27
6.26
6.25
6.24
1.41
NC
N
Boc
2.11
2.09
1.04
2.08
9.00
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
δ(ppm)

3m


149.0
138.9
133.2
131.5
129.6
124.0
119.1
116.1
111.1
110.6
84.4
77.5
77.1
76.7
27.8
NC
N
Boc
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

3m