Supporting Information

The Palladium-Catalyzed Cyanation of Indole C-H Bonds with the Combination of NH_4HCO_3 and DMSO as a Safe Cyanide Source

Xinyi Ren, Jianbin Chen, Fan Chen* and Jiang Cheng*

E-mail: jiangcheng@wzu.edu.cn; fanchen@wzu.edu.cn

1) General experimental details:

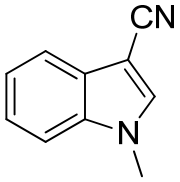
Chemicals were either purchased or purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^{1}H 500 MHz, ^{13}C 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz.

General procedure:

Under O_2, a sealed tube was charged with 1-methyl-1*H*-indole (0.2 mmol), NH_4HCO_3 (0.3 mmol, 1.5 equiv.), $PdCl_2$ (10 mol %), $Cu(OAc)_2$ (1.1 equiv.), and DMSO (1.5 mL). The tube was kept stirring at 140 ^{o}C for 6 h. After the completion of the reaction, as monitored by TLC, brine was added (10 mL), and the reaction mixture was extracted with ethyl acetate (3×5 mL). The ethyl acetate extract was purified by flash column chromatography on silica gel to give the product.

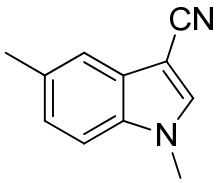
2) Spectral data for the products

1-methyl-1*H*-indole-3-carbonitrile (2a)[1]



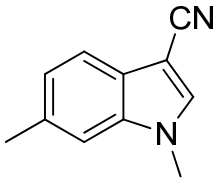
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.56 (s, 1H), 7.41-7.29 (m, 3H), 3.85 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.0, 135.5, 127.8, 123.8, 122.1, 119.8, 115.9, 110.3, 85.5, 33.6.

1,5-dimethyl-1*H*-indole-3-carbonitrile (2b)[1]



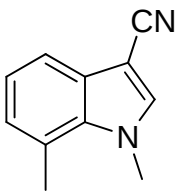
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (s, 1H), 7.43 (s, 1H), 7.21-7.19 (m, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 3.75 (s, 3H), 2.41 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.3, 134.4, 131.8, 128.1, 125.5, 119.5, 116.1, 109.9, 84.8, 33.6, 21.3.

1,6-dimethyl-1*H*-indole-3-carbonitrile (2c)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 7.17 (s, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 2.51 (s, 3H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.4, 135.0, 133.9, 125.5, 123.8, 119.3, 116.1, 110.2, 85.1, 33.4, 21.8.
IR (prism, cm^{-1}): 3039, 2208, 1532, 1251, 738.
MS(EI) 170 (M^+); HRMS Calcd. for $C_{11}H_{10}N_2$ (M^+) 170.0844, found 170.0850.

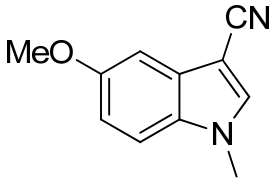
1,7-dimethyl-1*H*-indole-3-carbonitrile (2d)[2]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.14 (t, *J* = 7.5

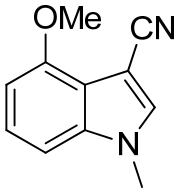
Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 4.09 (s, 3H), 2.76 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.7, 134.8, 129.0, 126.4, 122.3, 122.2, 117.9, 115.9, 85.3, 37.6, 19.4.

5-methoxy-1-methyl-1*H*-indole-3-carbonitrile (2e)[1]



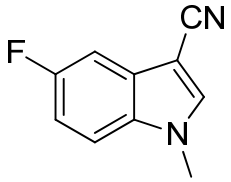
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (s, 1H), 7.19 (d, J = 9.0 Hz, 1H), 7.09 (s, 1H), 6.90 (d, J = 9.0 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.0, 135.3, 131.0, 128.7, 116.1, 114.6, 111.2, 100.8, 85.0, 55.8, 33.8.

4-methoxy-1-methyl-1*H*-indole-3-carbonitrile (2f)



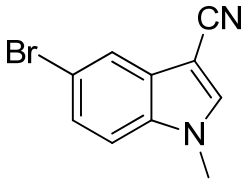
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (s, 1H), 7.20-7.17 (m, 1H), 6.90 (d, J = 8.5 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.74 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.7, 137.5, 135.0, 124.9, 117.5, 116.7, 103.1, 101.8, 84.0, 55.6, 33.8.
IR (prism, cm^{-1}): 3122, 2215, 1527, 1264, 733.
MS(EI) 186 (M^+); HRMS Calcd. for $C_{11}H_{10}N_2O$ (M^+) 186.0793, found 186.0797.

5-fluoro-1-methyl-1*H*-indole-3-carbonitrile (2g)



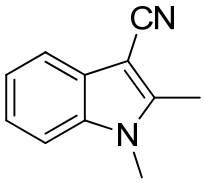
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (s, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.09 (t, J = 9.0 Hz, 1H), 3.85 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.2 (d, $J_{C\text{-}F}$ = 238.4 Hz), 136.7, 132.6, 128.4, (d, $J_{C\text{-}F}$ = 10.8 Hz), 115.4, 112.6 (d, $J_{C\text{-}F}$ = 26.4 Hz), 111.4 (d, $J_{C\text{-}F}$ = 9.6 Hz), 105.1 (d, $J_{C\text{-}F}$ = 24.8 Hz), 85.6 (d, $J_{C\text{-}F}$ = 4.6 Hz), 33.9.
IR (prism, cm^{-1}): 3051, 2220, 1534, 1191, 740.
MS(EI) 174 (M^+); HRMS Calcd. for $C_{10}H_7N_2F$ (M^+) 174.0593, found 174.0585.

5-bromo-1-methyl-1*H*-indole-3-carbonitrile (2h)



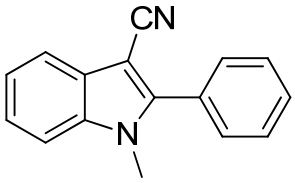
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89 (s, 1H), 7.55 (s, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.26 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.3, 134.7, 129.2, 127.0, 122.5, 115.8, 115.1, 111.8, 85.3, 33.8.
IR (prism, cm^{-1}): 3053, 2219, 1540, 1266, 740.
MS(EI) 233 (M^+); HRMS Calcd. for $C_{10}H_7N_2Br$ (M^+) 233.9793, found 233.9798.

1,2-dimethyl-1*H*-indole-3-carbonitrile (2i)[1]



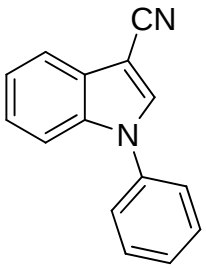
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.32-7.23 (m, 3H), 3.70 (s, 3H), 2.58 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.6, 136.3, 127.0, 123.0, 121.9, 119.0, 116.6, 109.7, 84.9, 30.1, 12.0.

1-methyl-2-phenyl-1*H*-indole-3-carbonitrile (2j)[1]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.59-7.53 (m, 5H), 7.45-7.32 (m, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.1, 136.8, 129.9, 129.8, 129.0, 128.7, 127.6, 123.9, 122.4, 119.6, 116.6, 110.5, 85.6, 31.7.

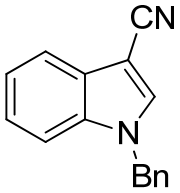
1-phenyl-1*H*-indole-3-carbonitrile (2k)[1]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.85-7.83 (m, 1H), 7.81 (s, 1H), 7.60-7.57 (m, 2H), 7.53-7.48 (m, 4H), 7.36-7.34 (m, 2H).

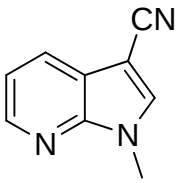
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.8, 135.6, 134.6, 130.0, 128.4, 128.0, 124.9, 124.5, 122.8, 120.0, 115.5, 111.5, 88.1.

1-benzyl-1*H*-indole-3-carbonitrile (2l)[1]



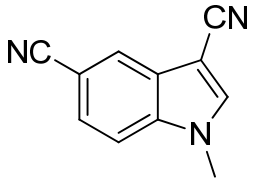
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80-7.78 (m, 1H), 7.61 (s, 1H), 7.38-7.29 (m, 6H), 7.16-7.14 (m, 2H), 5.35 (s, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.6, 135.2, 134.9, 129.1, 128.4, 128.0, 127.1, 124.0, 122.3, 120.0, 115.8, 110.8, 86.3, 50.9.

1-methyl-1*H*-pyrrolo[2,3-b]pyridine-3-carbonitrile (2m)



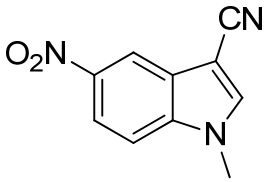
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.41 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.21-7.19 (m, 1H); 3.90 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.8, 145.1, 135.9, 128.3, 120.1, 118.1, 115.1, 84.3, 32.1.
IR (prism, cm^{-1}): 3051, 2219, 1533, 1266, 740.
MS(EI) 157 (M^+); HRMS Calcd. for $C_9H_7N_3$ (M^+) 157.0640, found 157.0639.

1-methyl-1*H*-indole-3,5-dicarbonitrile (2n and 2o)



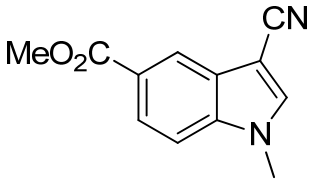
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10 (s, 1H), 7.72 (s, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 3.92 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.7, 137.5, 127.4, 126.8, 125.2, 119.3, 114.2, 111.5, 105.9, 87.1, 34.0.
IR (prism, cm^{-1}): 3051, 2219, 1533, 1267, 737.
MS(EI) 181 (M^+); HRMS Calcd. for $C_{11}H_7N_3$ (M^+) 181.0640, found 181.0637.

1-methyl-5-nitro-1*H*-indole-3-carbonitrile (2p)



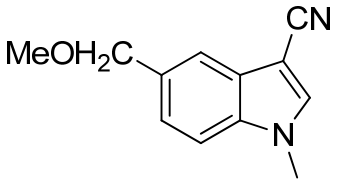
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.72 (s, 1H), 8.27 (d, J = 9.0 Hz, 1H), 7.75 (s, 1H), 7.49 (d, J = 9.0 Hz, 1H), 3.95 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.6, 138.6, 138.5, 127.1, 119.4, 116.9, 114.0, 110.8, 88.6, 34.2.
IR (prism, cm^{-1}): 3051, 2220, 1533, 1266, 738.
MS(EI) 201 (M^+); HRMS Calcd. for $C_{10}H_7N_3O_2$ (M^+) 201.0538, found 201.0537.

methyl 3-cyano-1-methyl-1*H*-indole-5-carboxylate (2q)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.63 (s, 1H), 7.41 (d, J = 8.5 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 138.3, 136.9, 127.2, 125.1, 124.3, 122.4, 115.0, 110.2, 87.2, 52.2, 33.8.
IR (prism, cm^{-1}): 3109, 2209, 1700, 1530, 1239, 742.
MS(EI) 214 (M^+); HRMS Calcd. for $C_{12}H_{10}N_2O_2$ (M^+) 214.0742, found 214.0749.

5-(methoxymethyl)-1-methyl-1*H*-indole-3-carbonitrile (2r)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (s, 1H), 7.56 (s, 1H), 7.37 (d, J = 8.5 Hz, 2H), 4.58 (s, 2H), 3.85 (s, 3H), 3.40 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.8, 135.6, 132.3, 127.8, 124.1, 119.3, 115.8, 110.4, 85.6, 74.8, 58.0, 33.7, 29.7.
IR (prism, cm^{-1}): 3115, 2217, 1529, 1248, 741.
MS(EI) 200 (M^+); HRMS Calcd. for $C_{12}H_{12}N_2O$ (M^+) 200.0950, found 200.0951.

3) The CN^- was detected by indicator paper

(1) Principle:

The combination of CN^- with acids produces hydrocyanic acid, which reacts with picric acid showed rose-red colour.

(2) Detection of CN^-: A picric acid test strip was inserted into a glass tube, and drops of saturated sodium carbonate solution was dropped on it to make it wet. Then, the glass tube was inserted into the rubber stopper with a suitable hole. 0.2 g of tartrate solid and 1.5 mL of the reaction solution were added to flask, which was stuffed by rubber stopper fitted with glass tube, immediately. The flask was heated in the water bath under 80 ^oC for 20 minutes. The test paper appeared rose-red, which proved the existence of CN^-.

Table S1 Detection of CN^- by indicator paper[a]

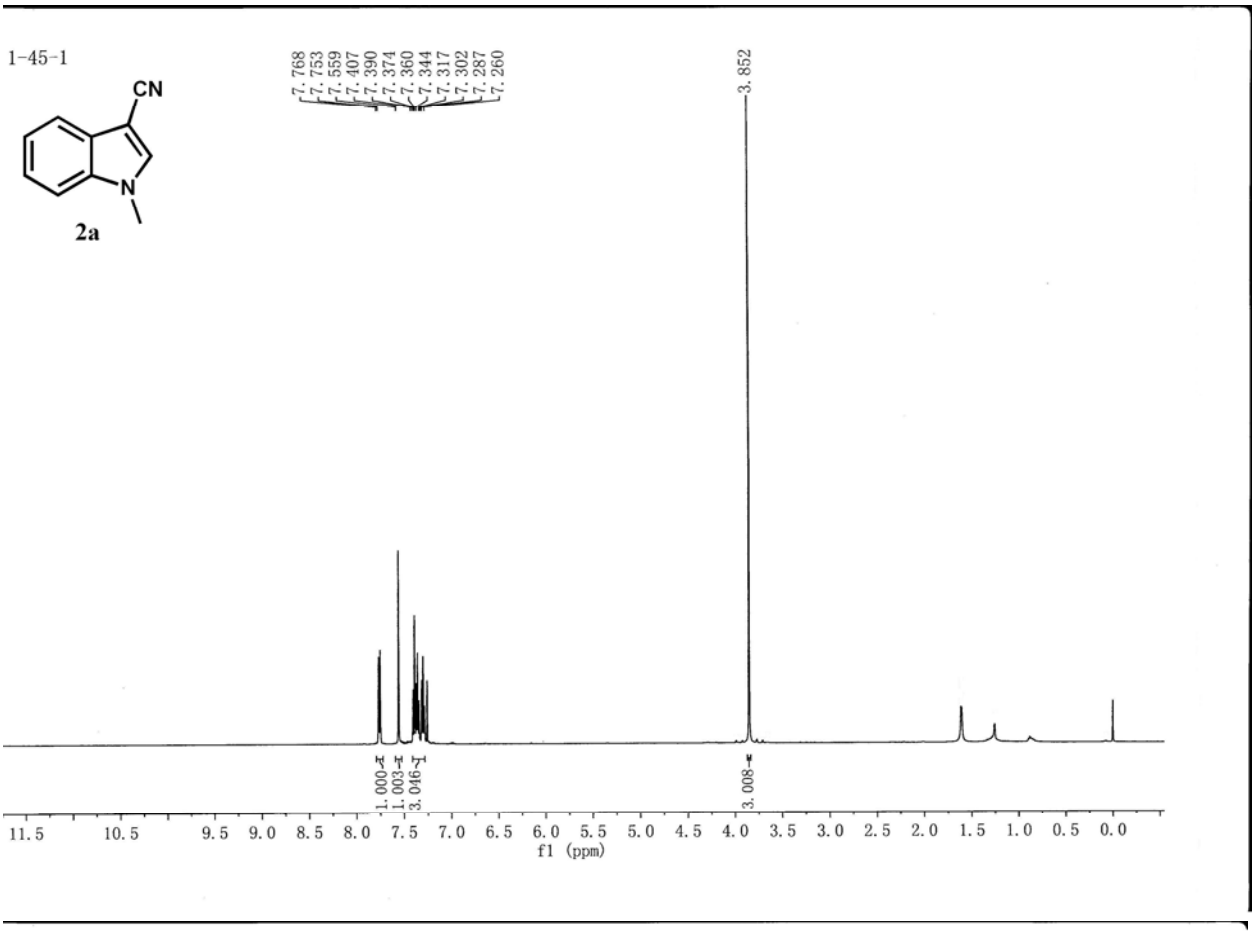
DMSO	NH_4HCO_3	O_2			-
DMSO	NH_4HCO_3	O_2	$PdCl_2$		-
DMSO	NH_4HCO_3	O_2		$Cu(OAc)_2$	+
DMSO	NH_4HCO_3	O_2	$PdCl_2$	$Cu(OAc)_2$	+

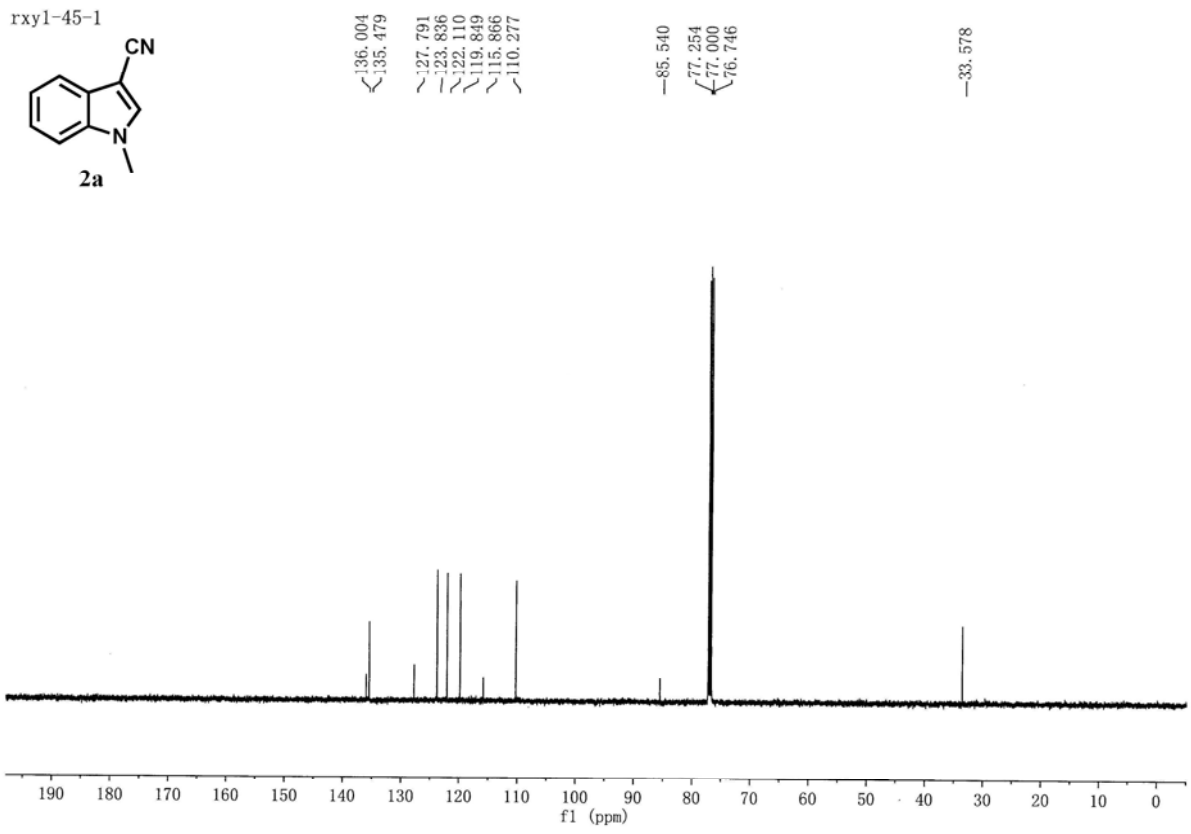
[a] Reaction conditions: the mixture was heated under 140 ^oC for 3 h. "-" means negative; "+" means positive.

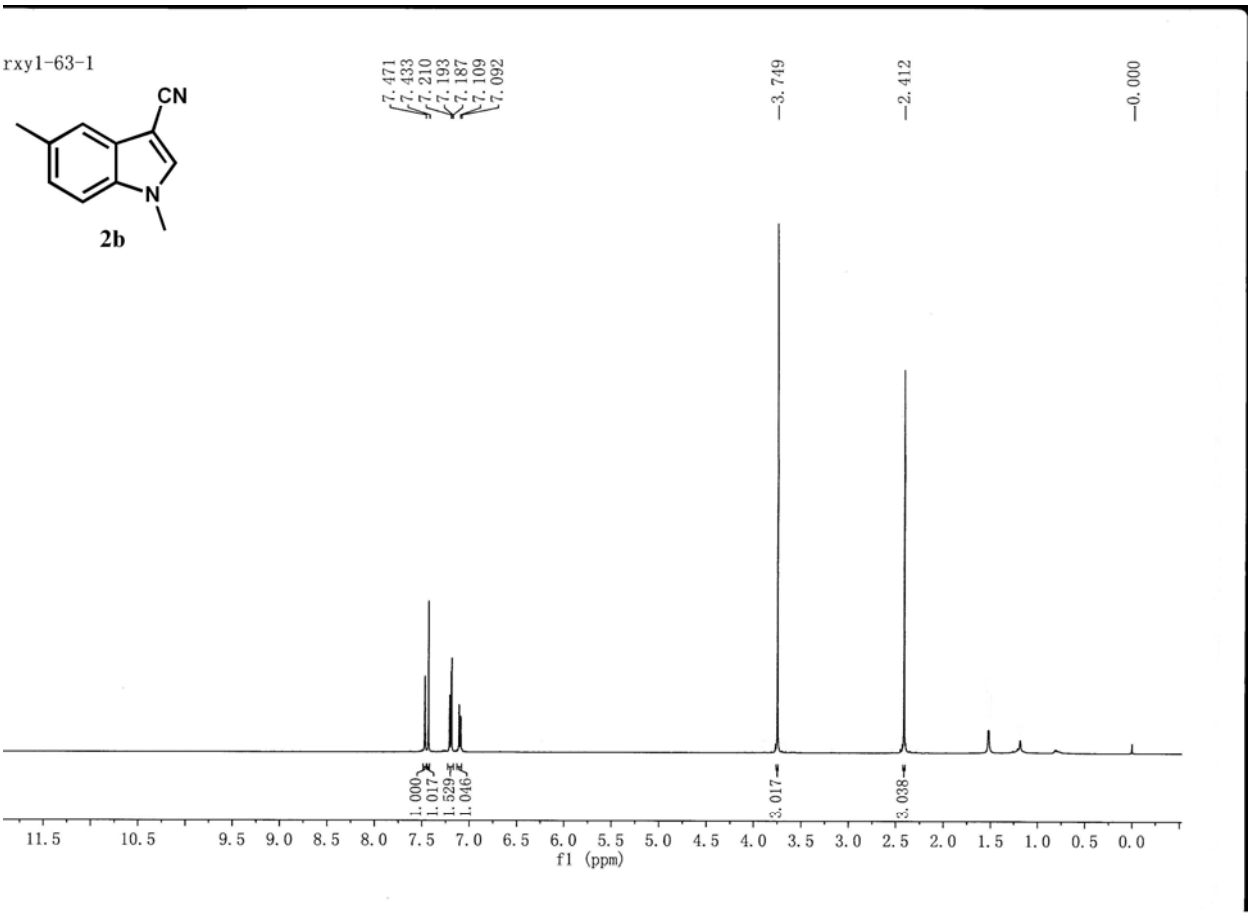
4) References

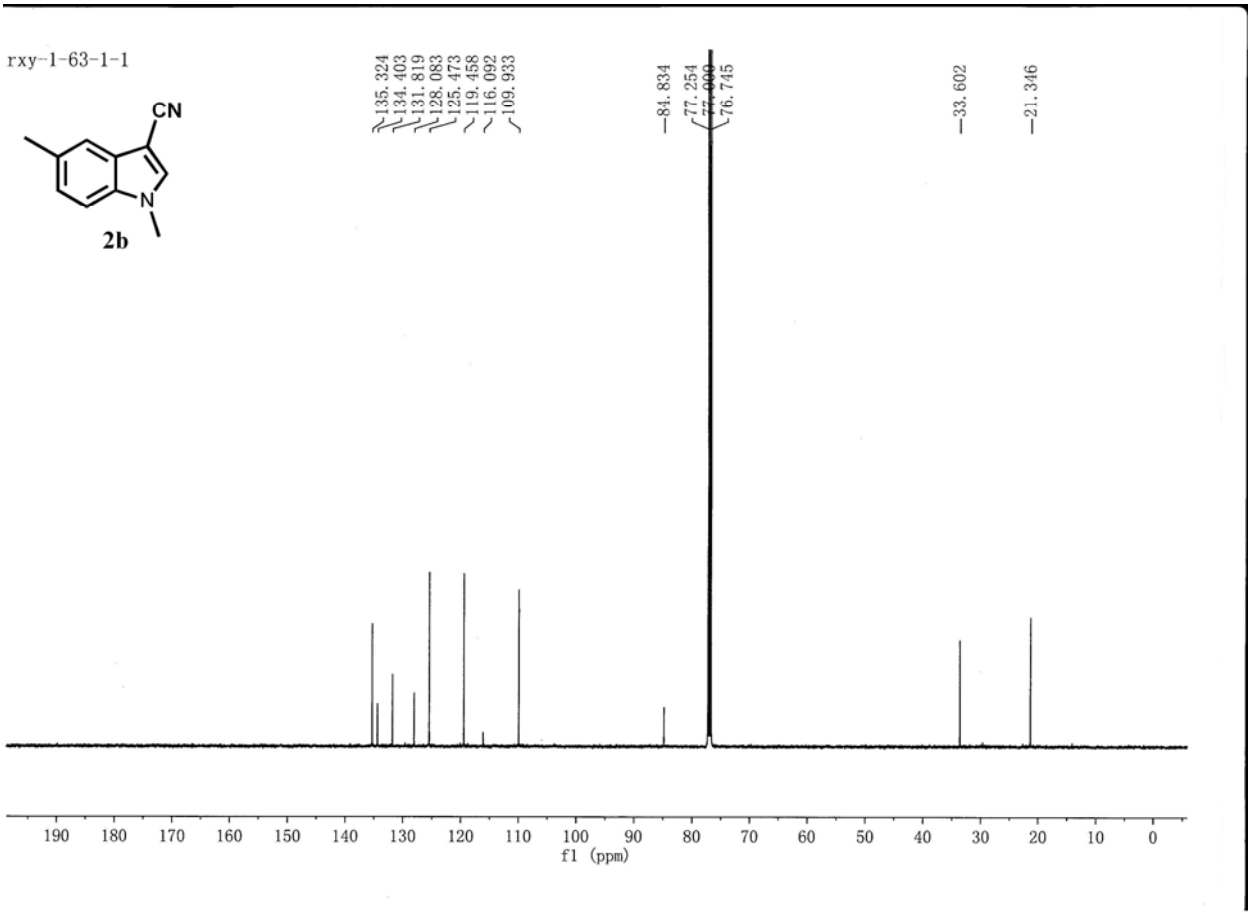
(1) G. Yan, C. Kuang, Y. Zhang and J. Wang, *Org. Lett*., 2010, **12**, 1052..

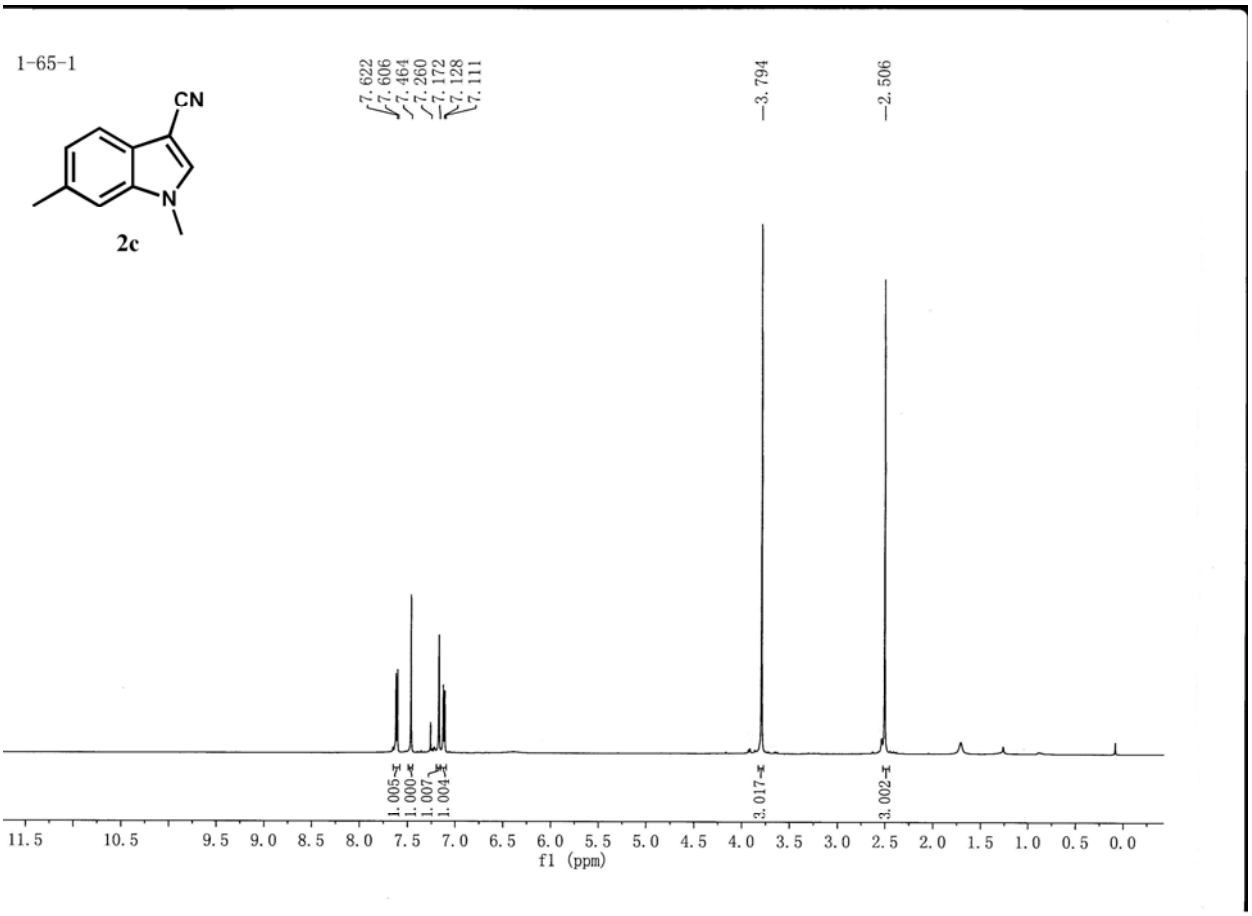
(2) C. J. Swain, R. Baker, C. Kneen, J. Moseley, J. Saunders, E. M. Seward, G. Stevenson, M. Beer and J. Stanton, *J. Med. Chem*., 1991, **34**, 140.

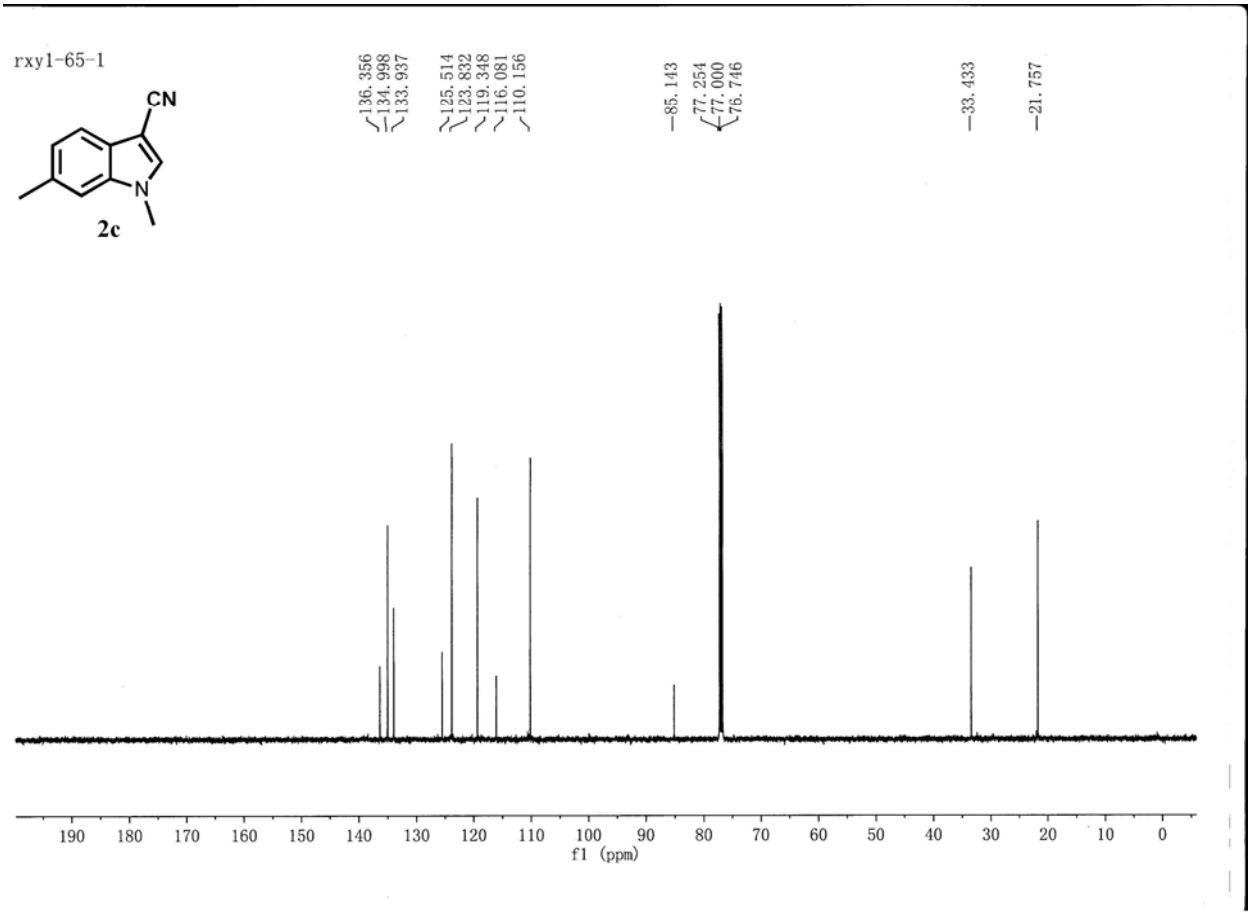

1-45-1
CN
N
2a
7.768
7.753
7.559
7.407
7.390
7.374
7.360
7.344
7.317
7.302
7.287
7.260
3.852
1.000
1.003
3.046
3.008
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

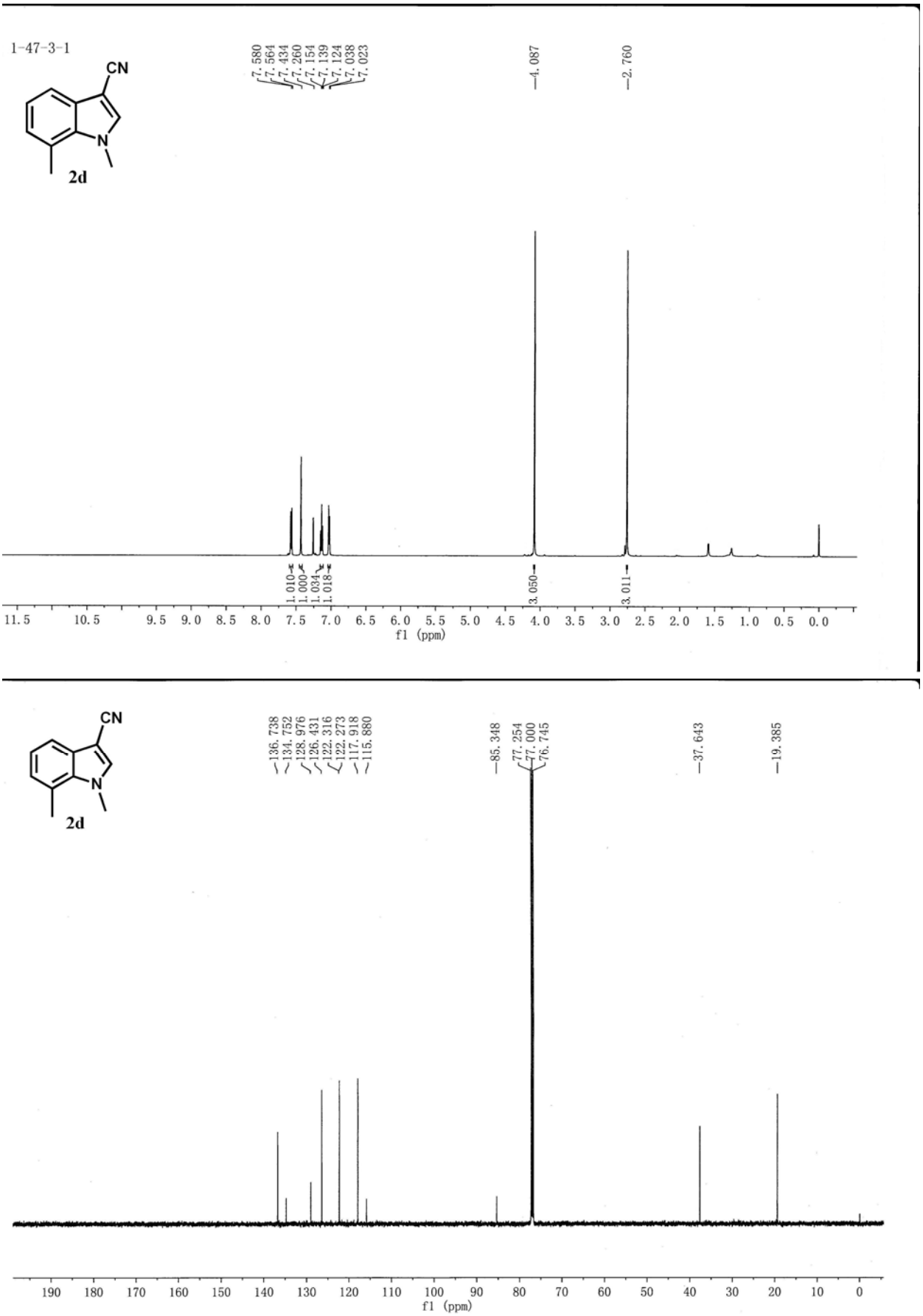

rxy1-45-1
CN
N
2a
136.004
135.479
127.791
123.836
122.110
119.849
115.866
110.277
85.540
77.254
77.000
76.746
33.578
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

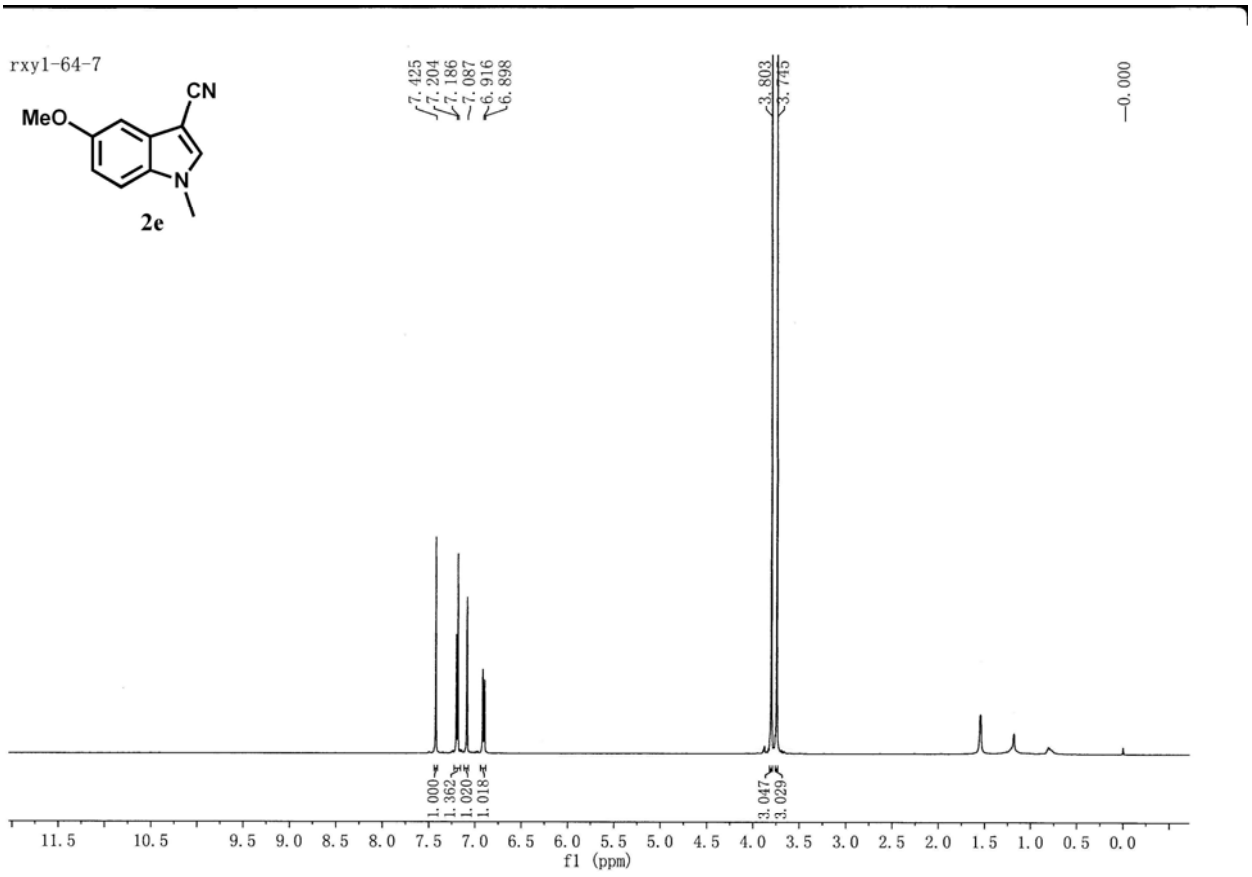

rxy1-63-1
CN
N
2b
7.471
7.433
7.210
7.193
7.187
7.109
7.092
3.749
2.412
0.000
1.000
1.017
1.529
1.046
3.017
3.038
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

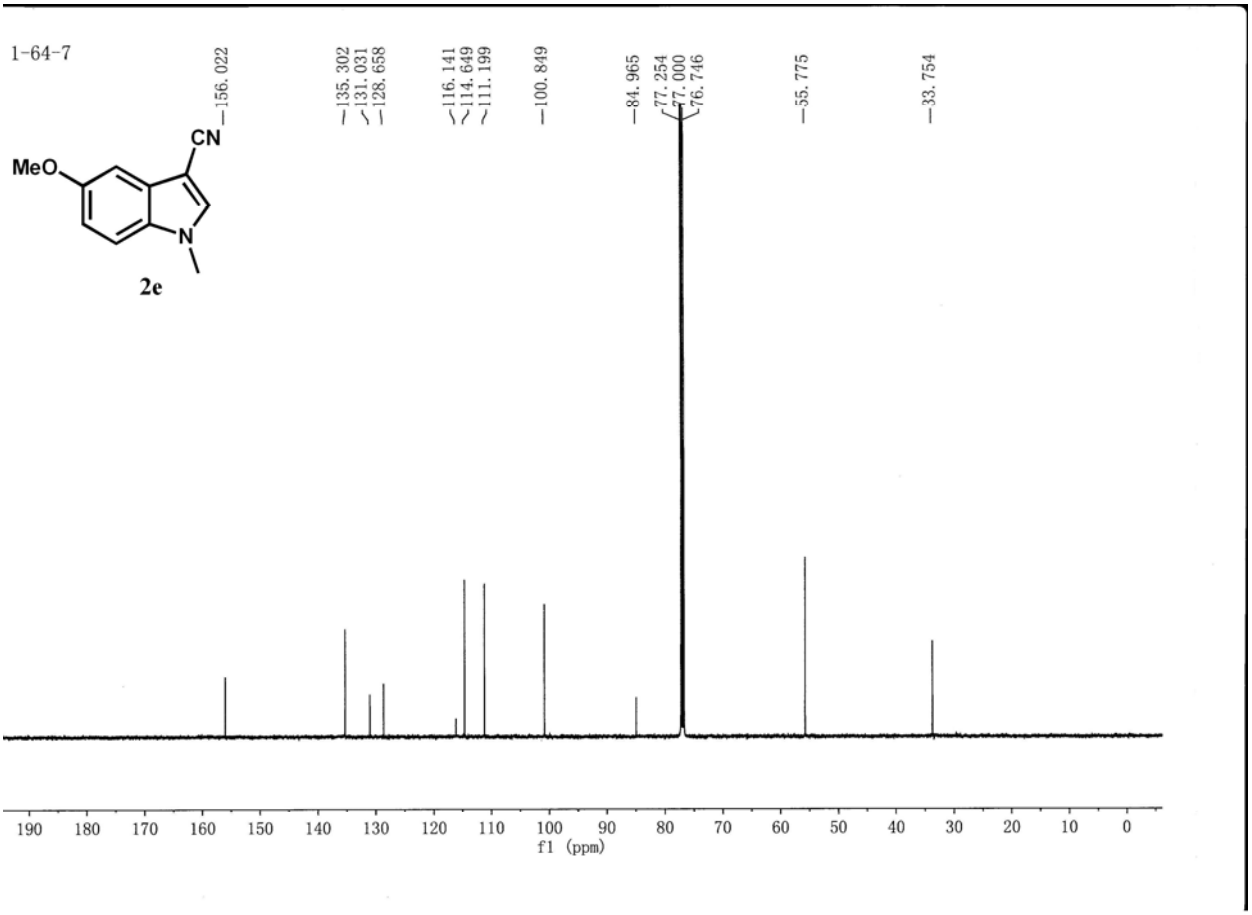

rxy-1-63-1-1
CN
N
2b
135.324
134.403
131.819
128.083
125.473
119.458
116.092
109.933
84.834
77.254
77.000
76.745
33.602
21.346
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

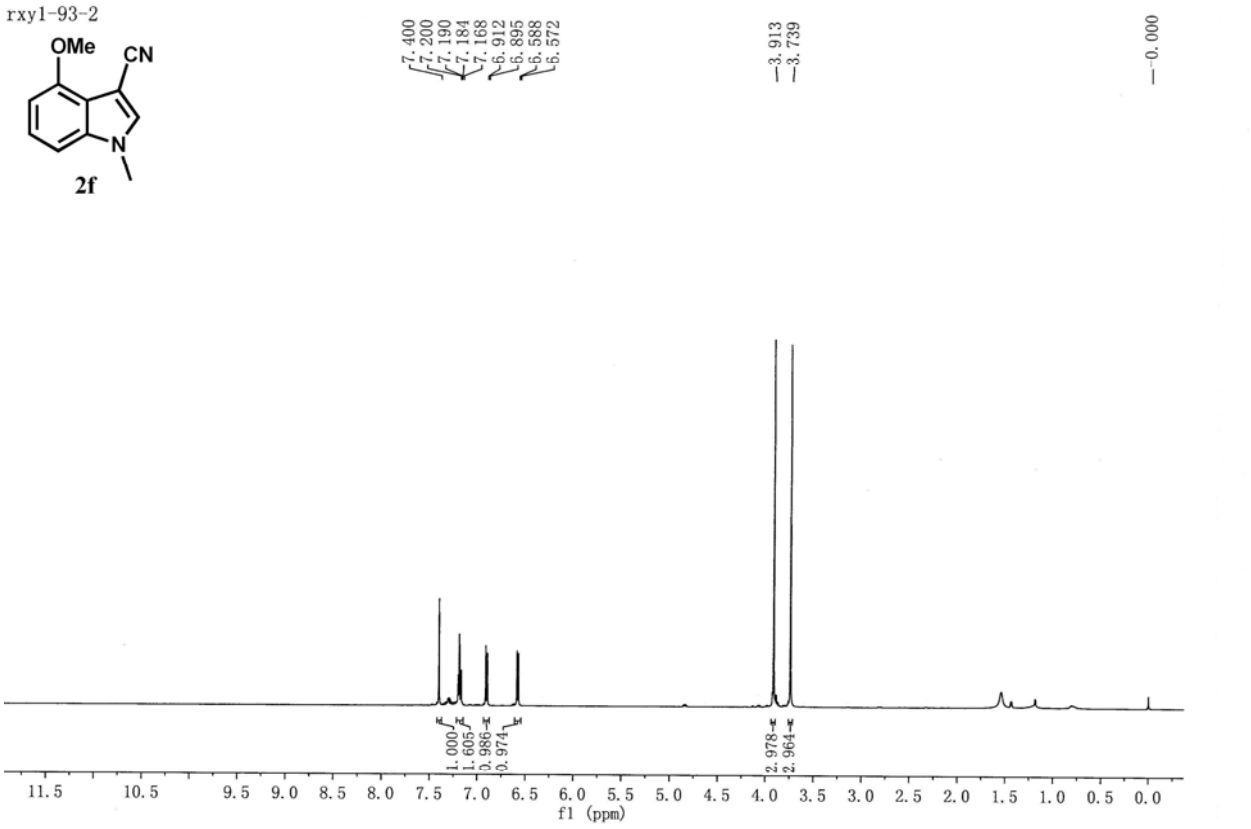

1-65-1
CN
N
2c
7.622
7.606
7.464
7.260
7.172
7.128
7.111
3.794
2.506
1.005
1.000
1.007
1.004
3.017
3.002
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

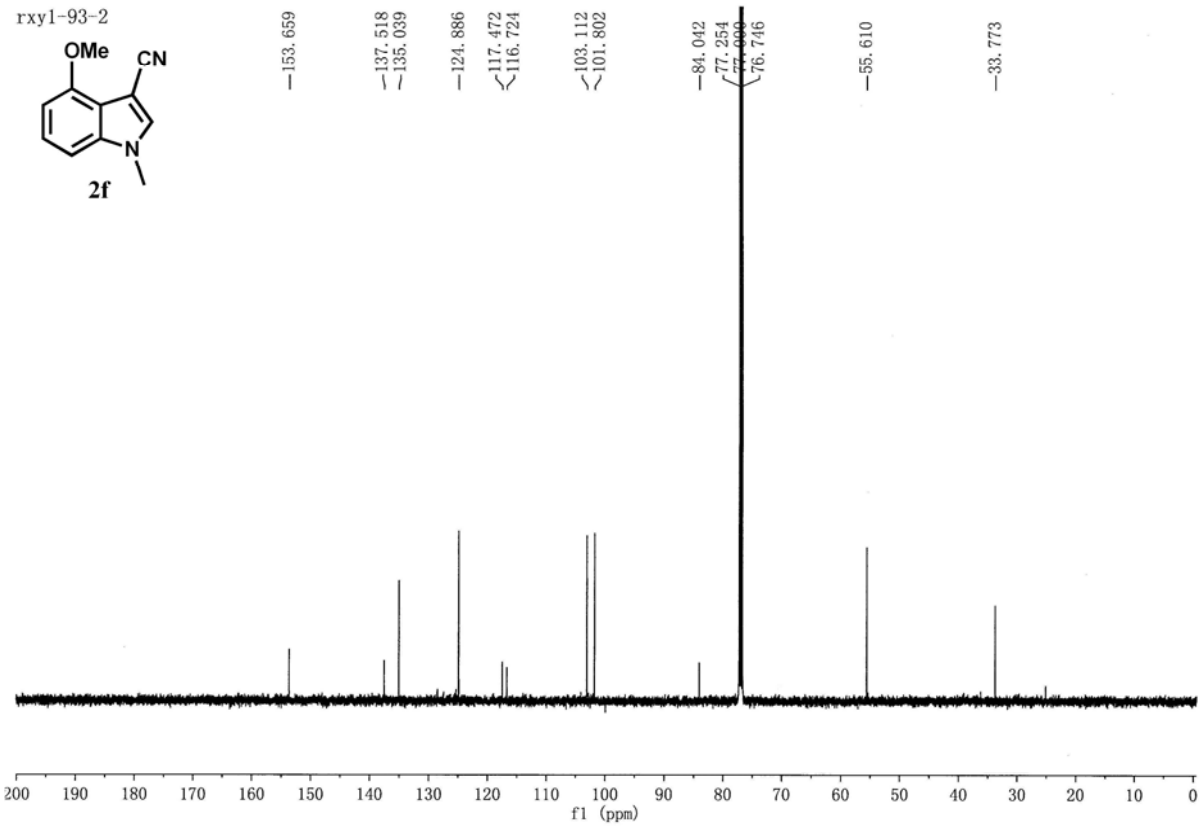

rxy1-65-1
CN
N
2c
136.356
134.998
133.937
125.514
123.832
119.348
116.081
110.156
85.143
77.254
77.000
76.746
33.433
21.757
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

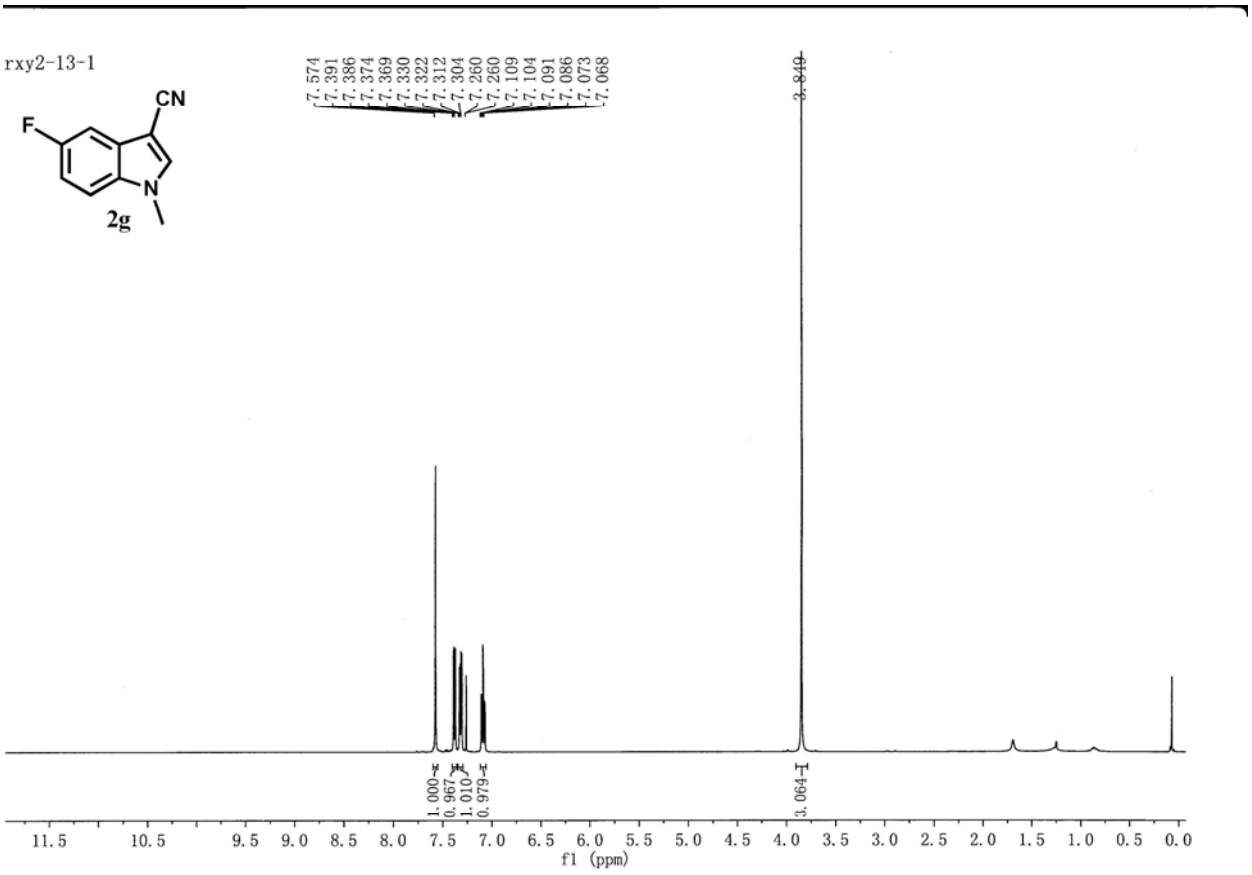

1-47-3-1
CN
N
2d
7.580
7.564
7.434
7.260
7.154
7.139
7.124
7.038
7.023
4.087
2.760
1.010
1.000
1.034
1.018
3.050
3.011
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
CN
N
2d
136.738
134.752
128.976
126.431
122.316
122.273
117.918
115.880
85.348
77.254
77.000
76.745
37.643
19.385
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

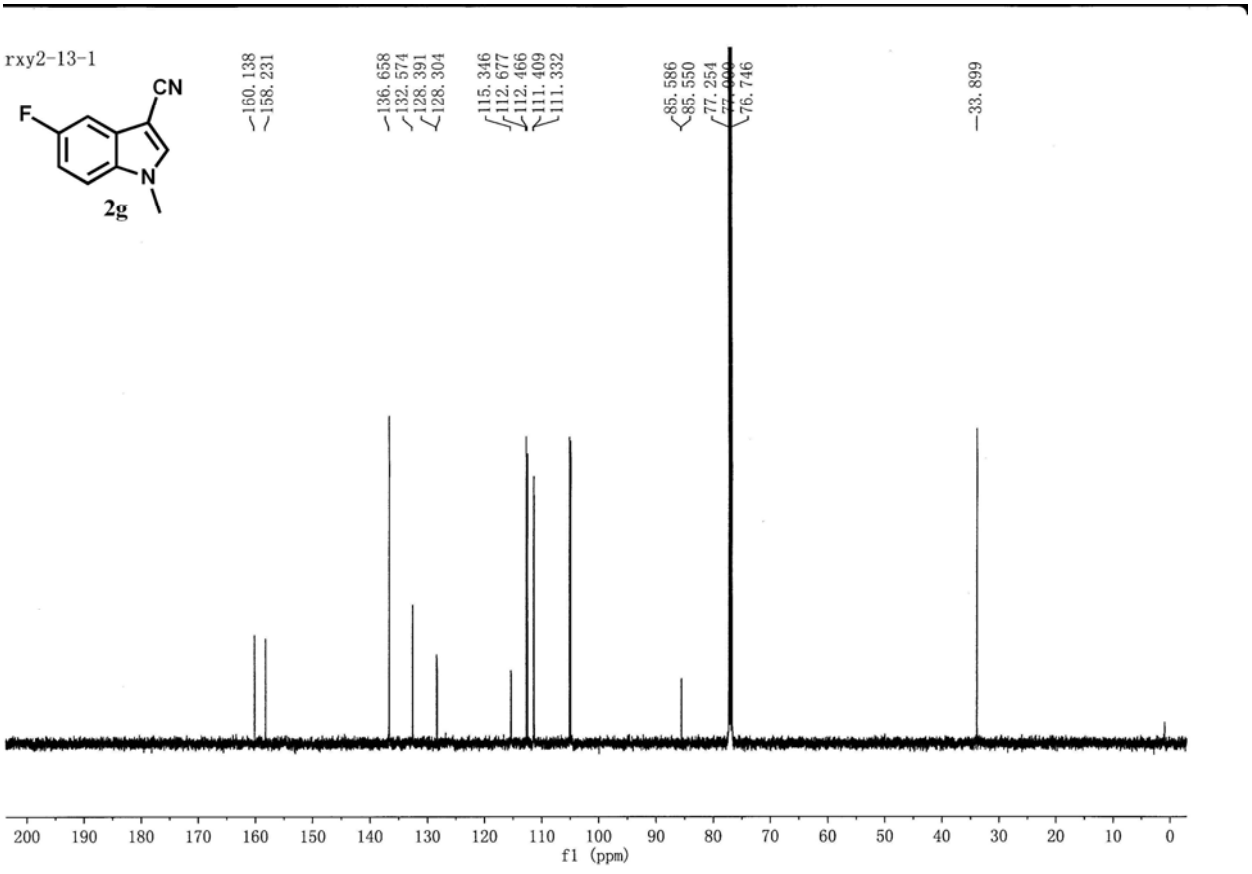

rxy1-64-7
MeO
CN
N
2e
7.425
7.204
7.186
7.087
6.916
6.898
3.803
3.745
0.000
1.000
1.362
1.020
1.018
3.047
3.029
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

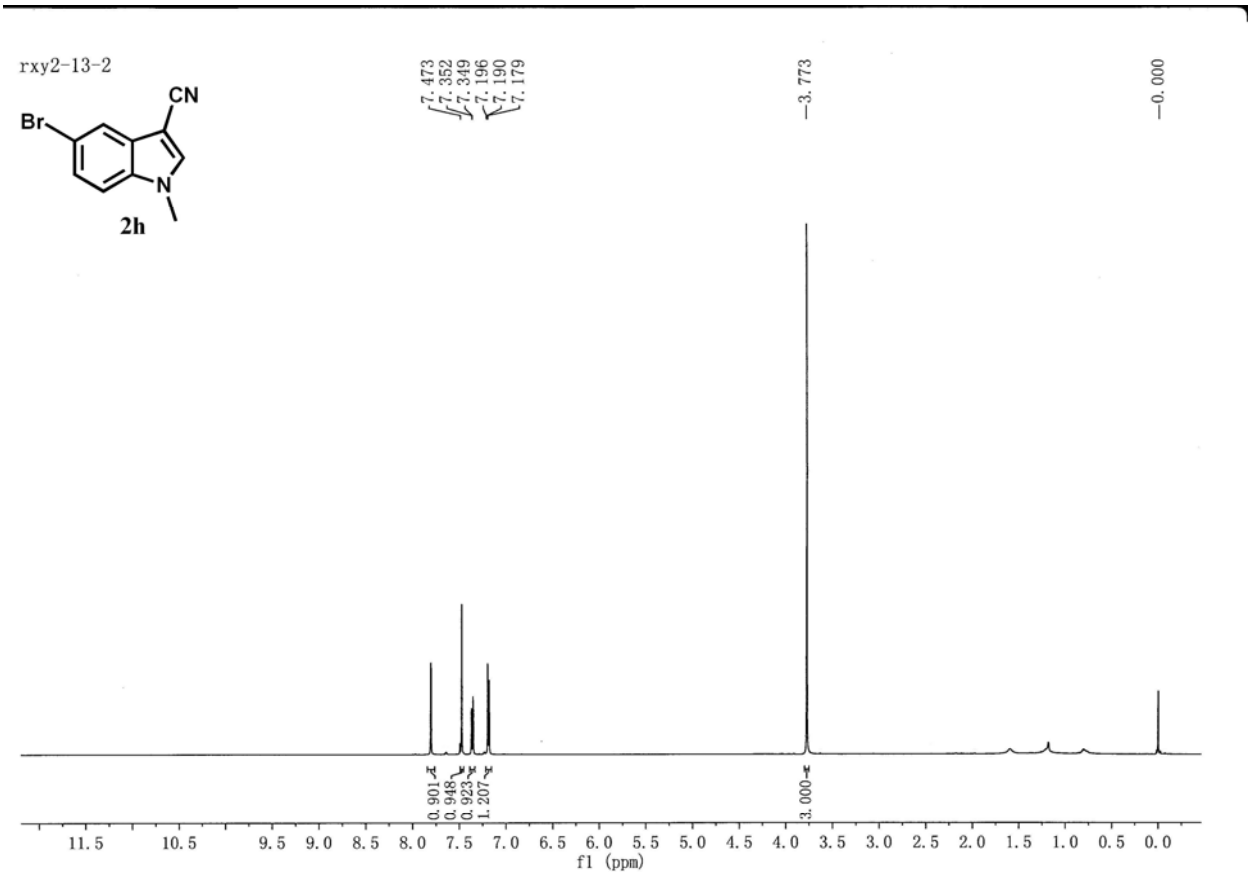

1-64-7
MeO
CN
N
2e
156.022
135.302
131.031
128.658
116.141
114.649
111.199
100.849
84.965
77.254
77.000
76.746
55.775
33.754
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

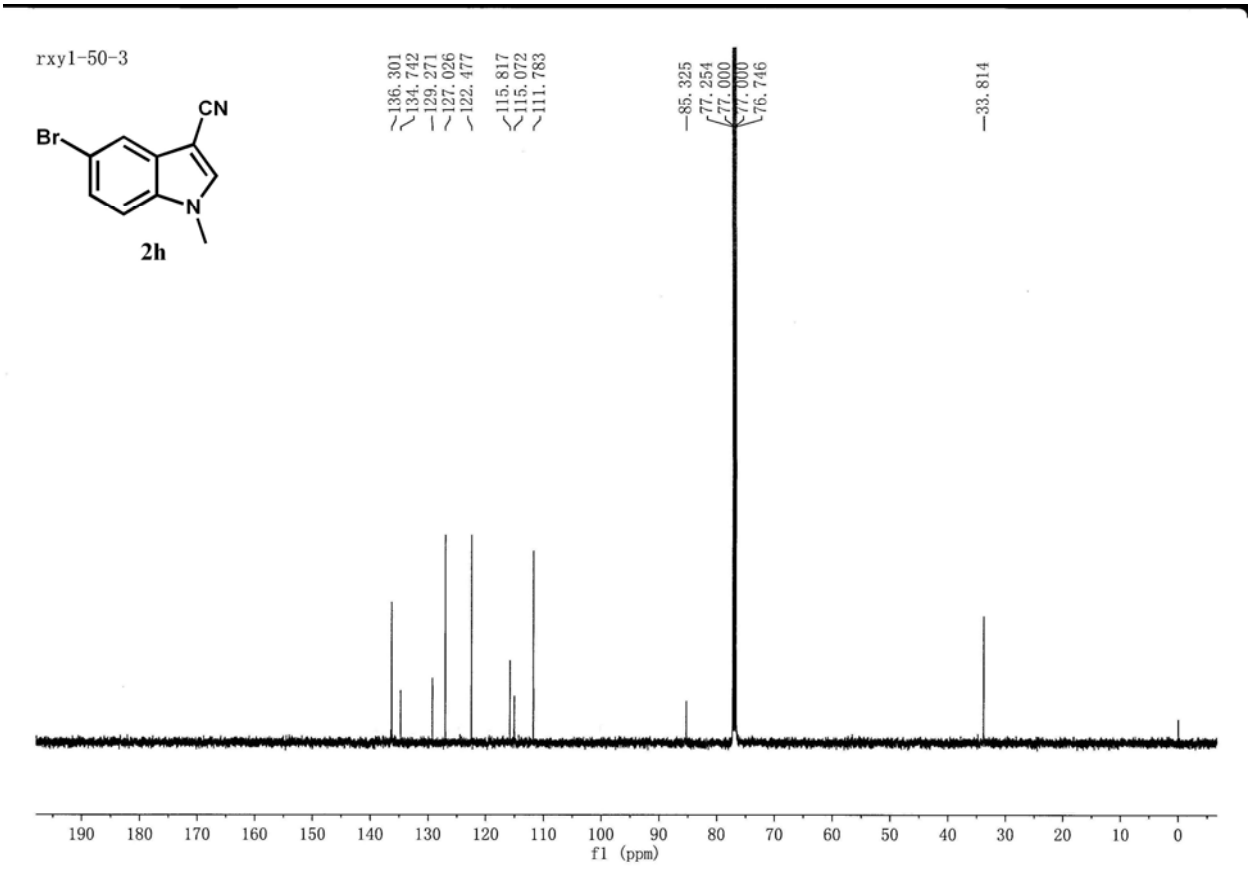

rxy1-93-2
OMe
CN
N
2f
7.400
7.200
7.190
7.184
7.168
6.912
6.895
6.588
6.572
3.913
3.739
0.000
1.000
1.605
0.986
0.974
2.978
2.964
f1 (ppm)

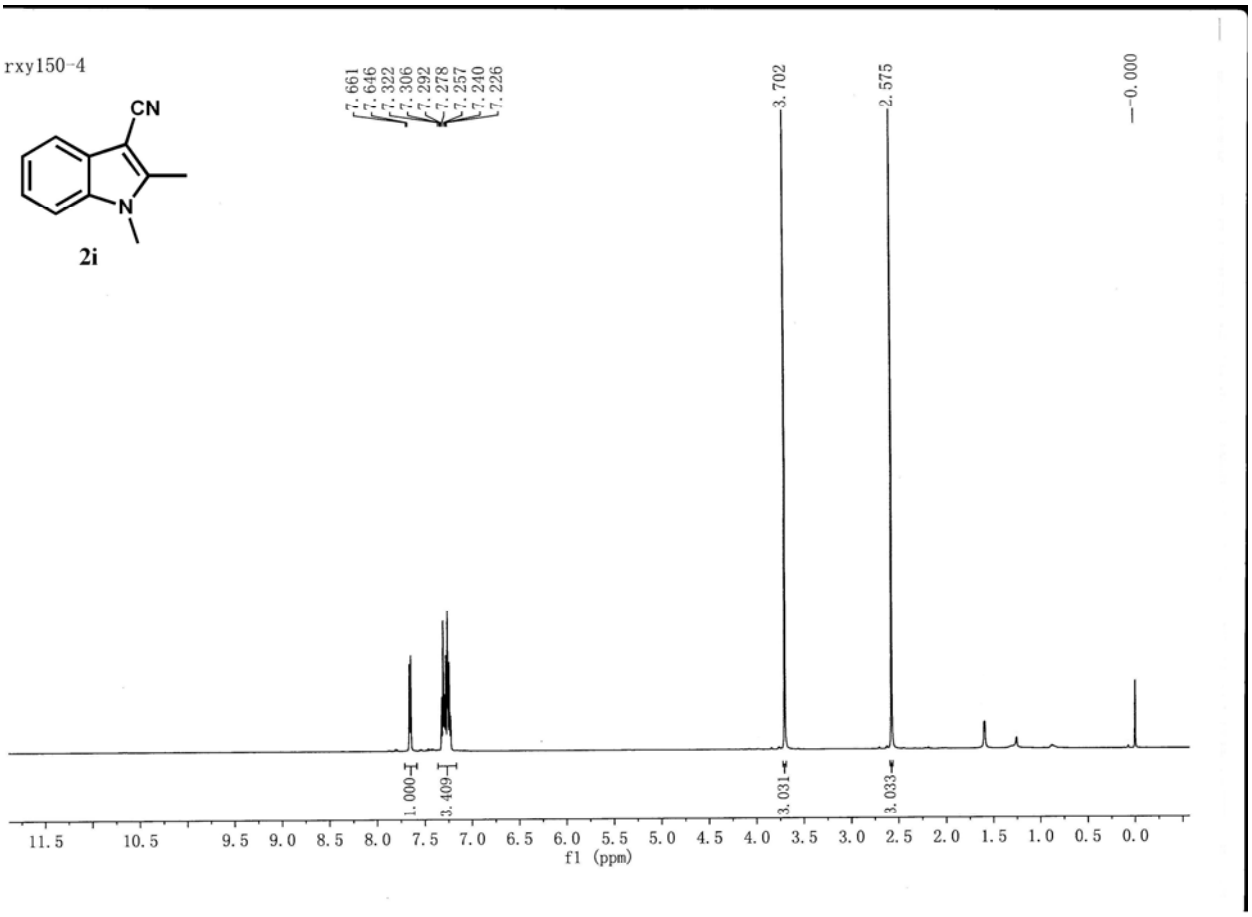

rxy1-93-2
OMe
CN
N
2f
153.659
137.518
135.039
124.886
117.472
116.724
103.112
101.802
84.042
77.254
77.000
76.746
55.610
33.773
f1 (ppm)

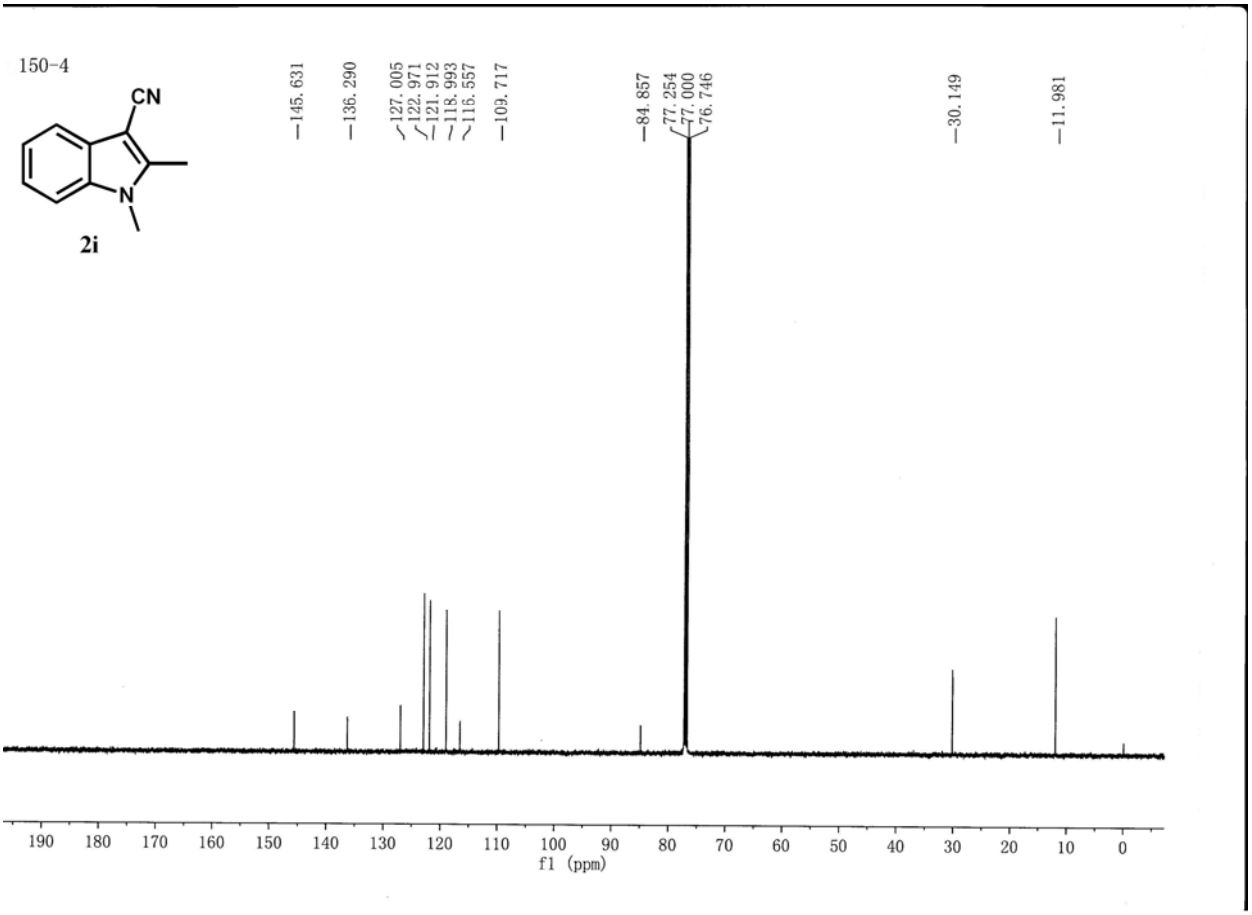

rxy2-13-1
F
CN
N
2g
7.574
7.391
7.386
7.374
7.369
7.330
7.322
7.312
7.304
7.260
7.260
7.109
7.104
7.091
7.086
7.073
7.068
3.849
1.000
0.967
1.010
0.979
3.064
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

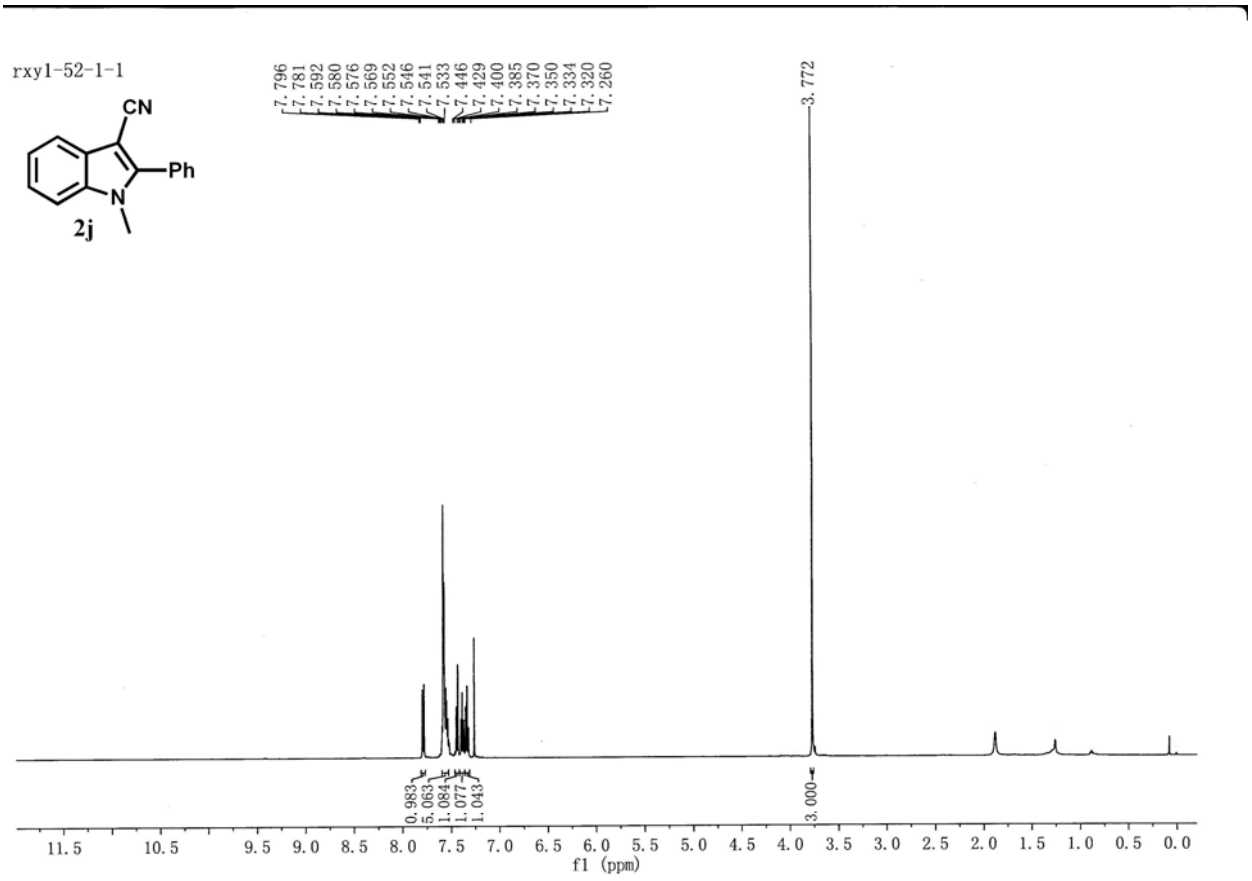

rxy2-13-1
F
CN
N
2g
160.138
158.231
136.658
132.574
128.391
128.304
115.346
112.677
112.466
111.409
111.332
85.586
85.550
77.254
77.000
76.746
33.899
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

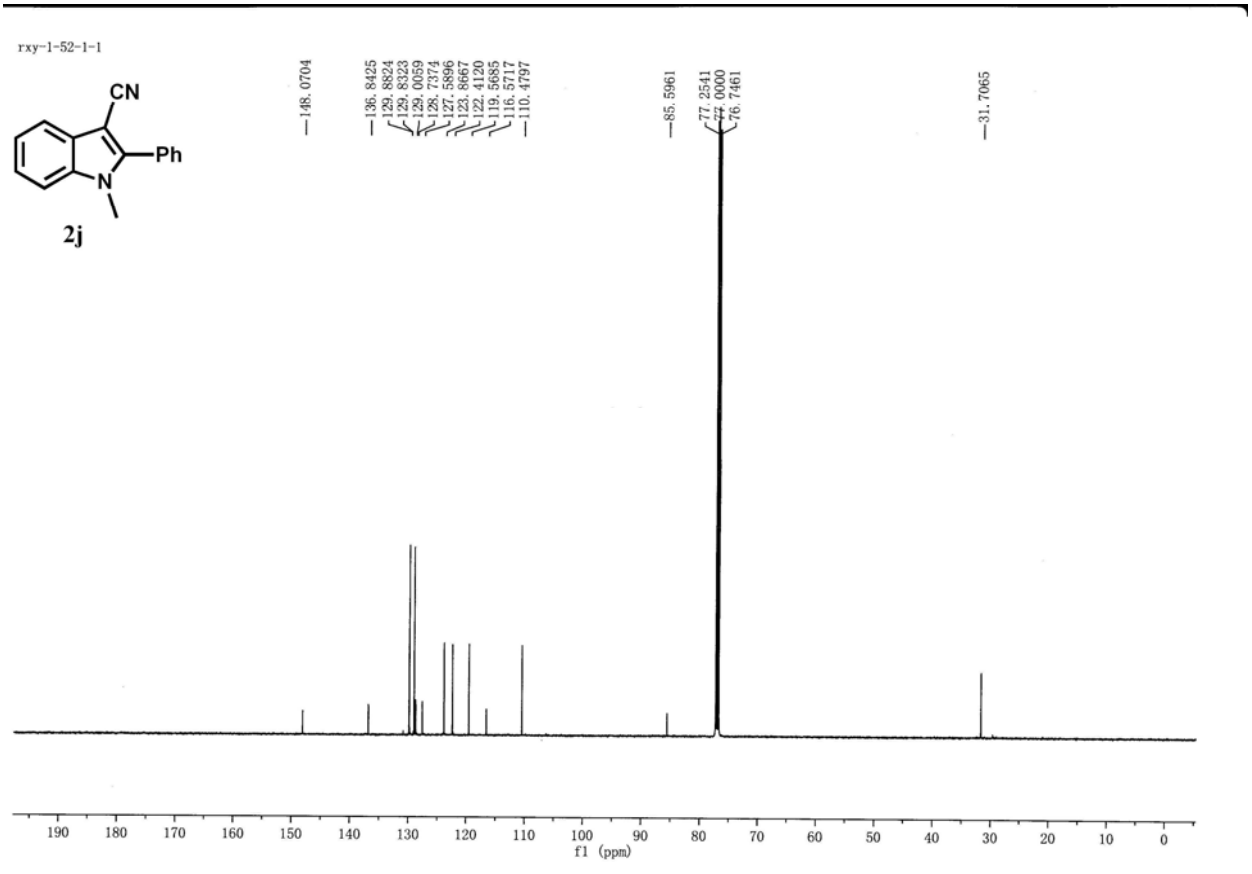

rxy2-13-2
Br
CN
N
2h
7.473
7.352
7.349
7.196
7.190
7.179
3.773
0.000
0.901
0.948
0.923
1.207
3.000
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

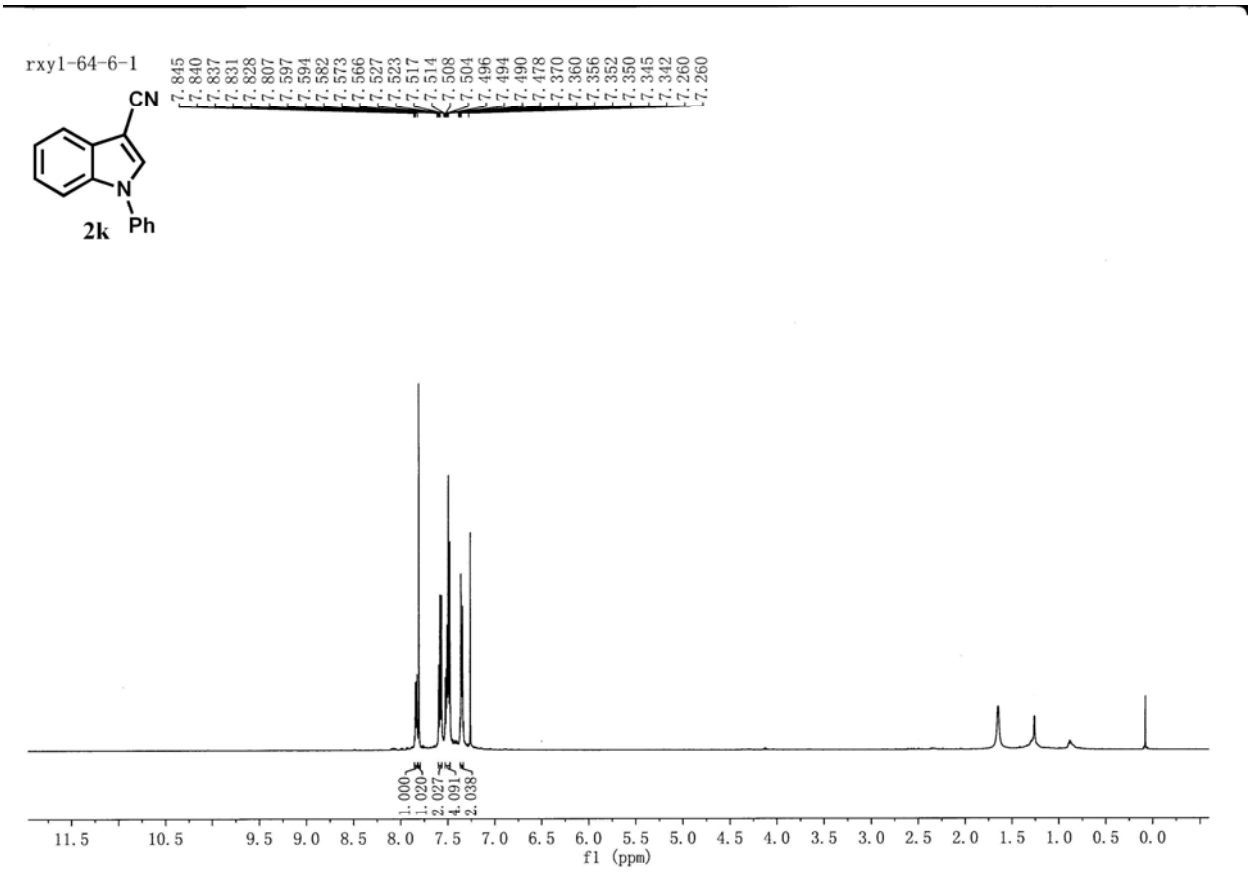

rxy1-50-3
Br
CN
N
2h
136.301
134.742
129.271
127.026
122.477
115.817
115.072
111.783
85.325
77.254
77.000
76.746
33.814
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

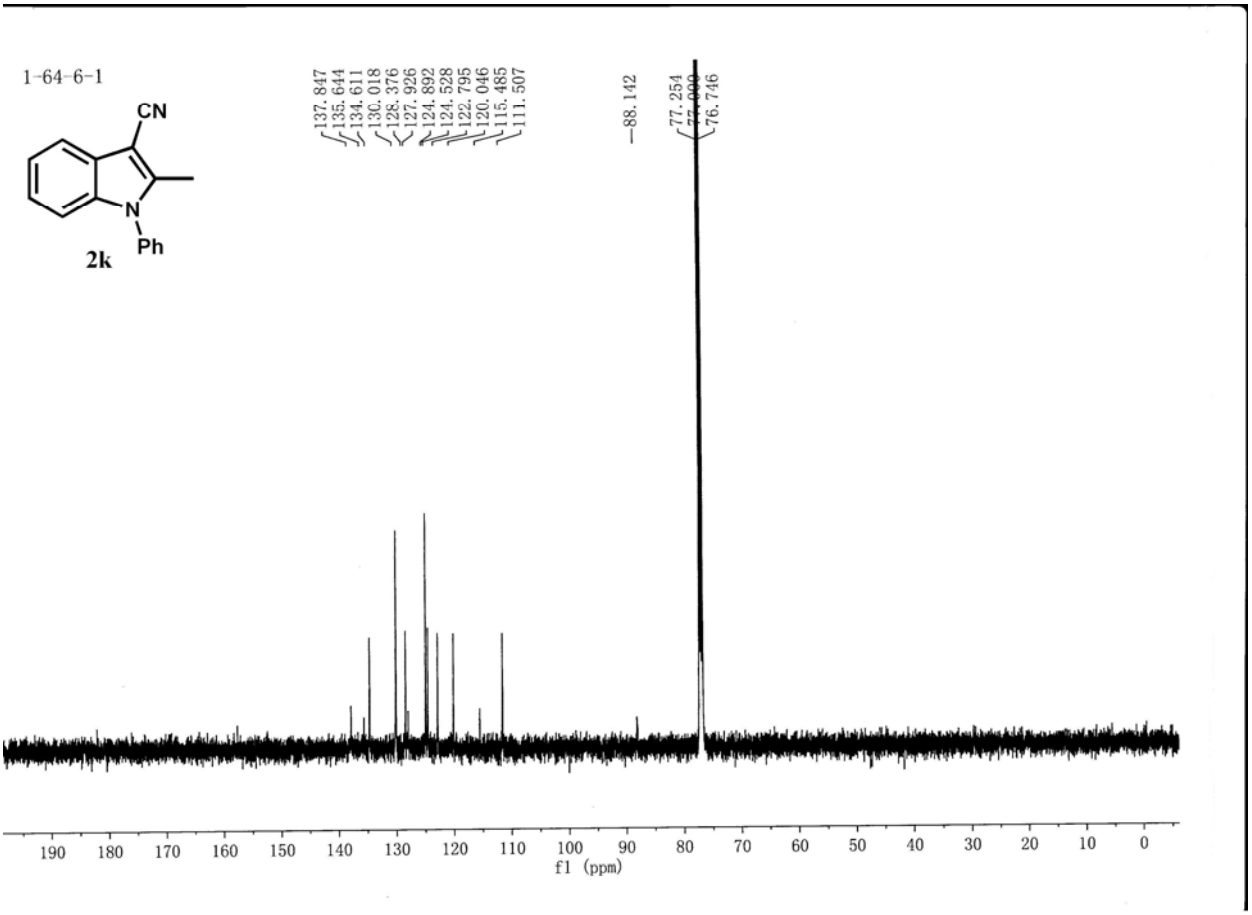

rxy150-4
CN
N
2i
7.661
7.646
7.322
7.306
7.292
7.278
7.257
7.240
7.226
3.702
2.575
0.000
1.000
3.409
3.031
3.033
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

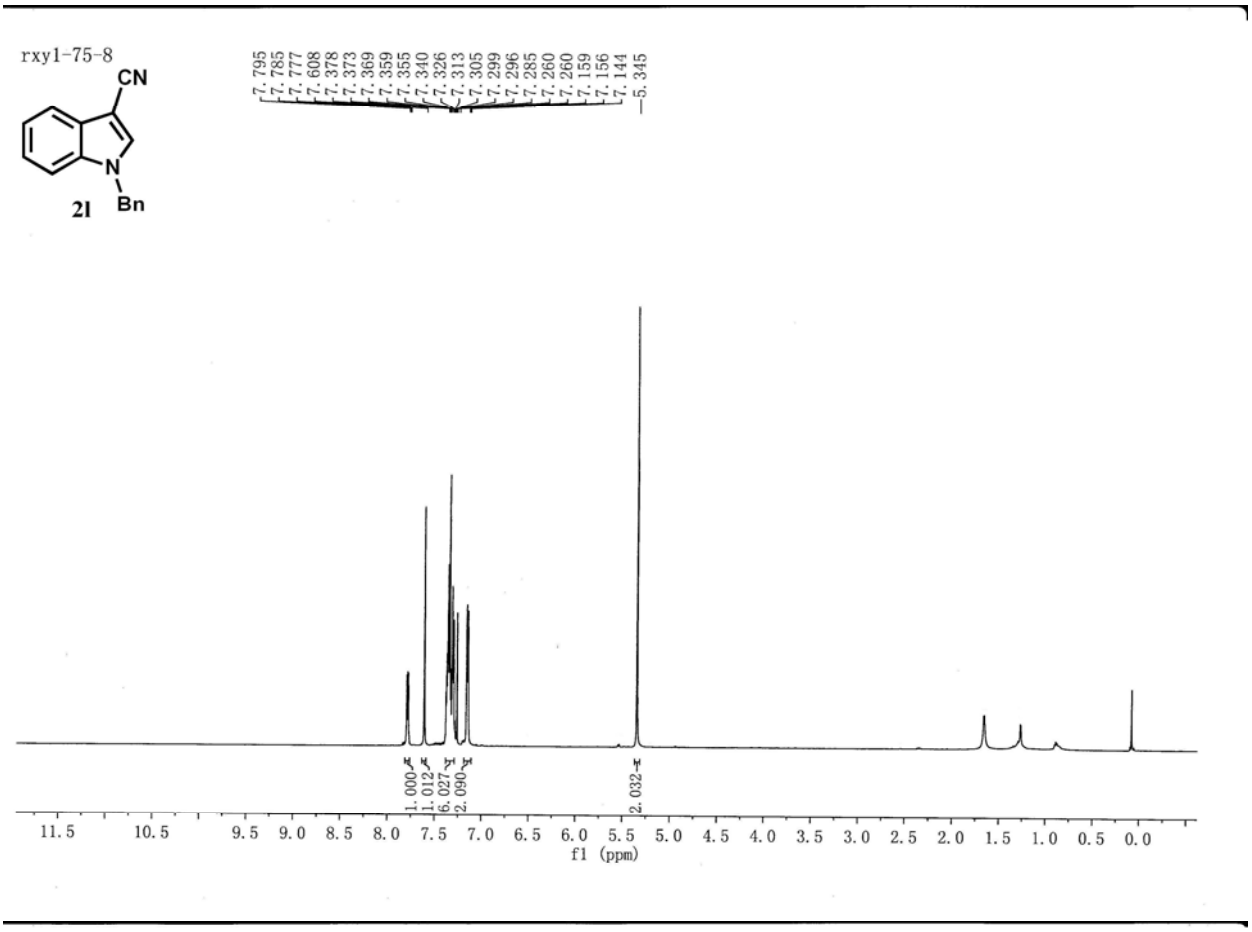

150-4
CN
N
2i
145.631
136.290
127.005
122.971
121.912
118.993
116.557
109.717
84.857
77.254
77.000
76.746
30.149
11.981
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

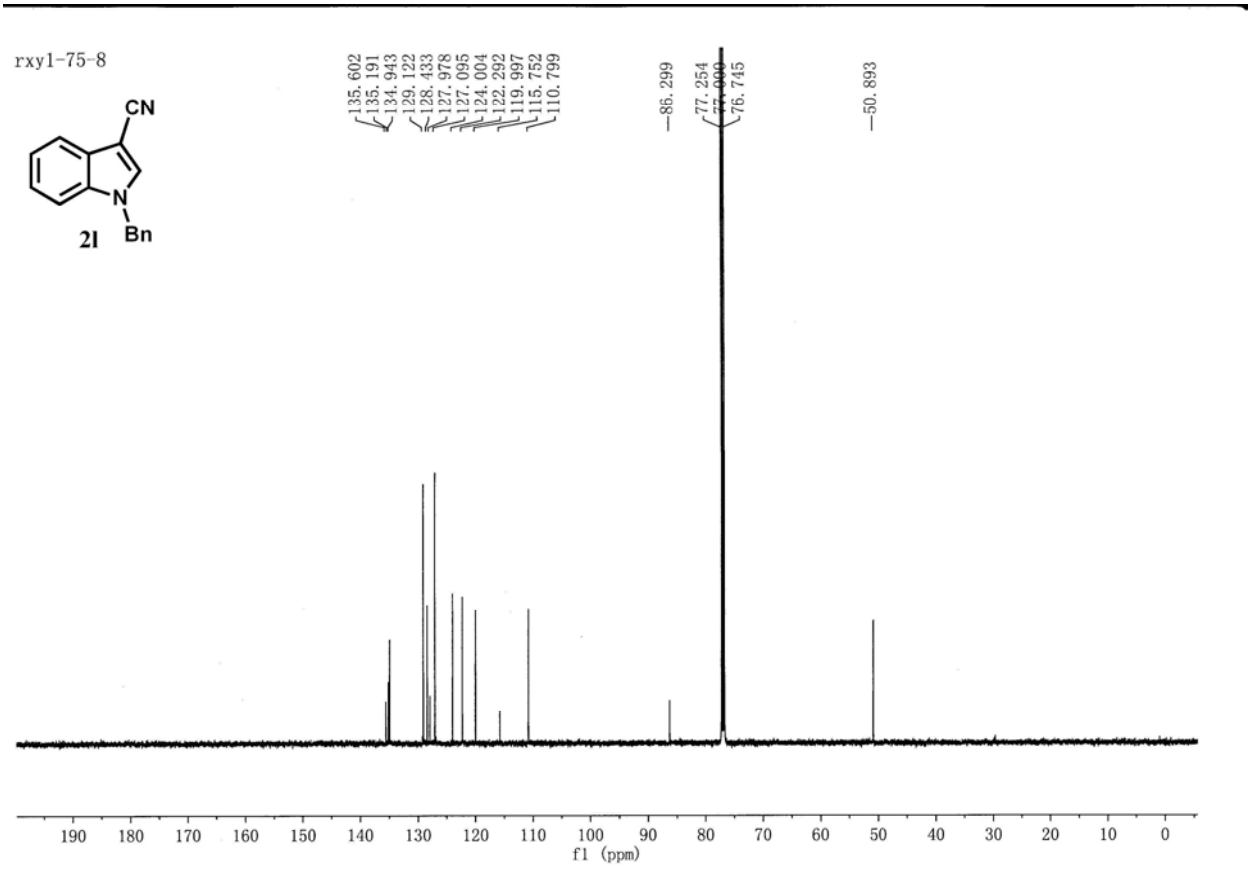

rxy1-52-1-1
CN
Ph
N
2j
7.796
7.781
7.592
7.580
7.576
7.569
7.552
7.546
7.541
7.533
7.446
7.429
7.400
7.385
7.370
7.350
7.334
7.320
7.260
3.772
0.983
5.063
1.084
1.077
1.043
3.000
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

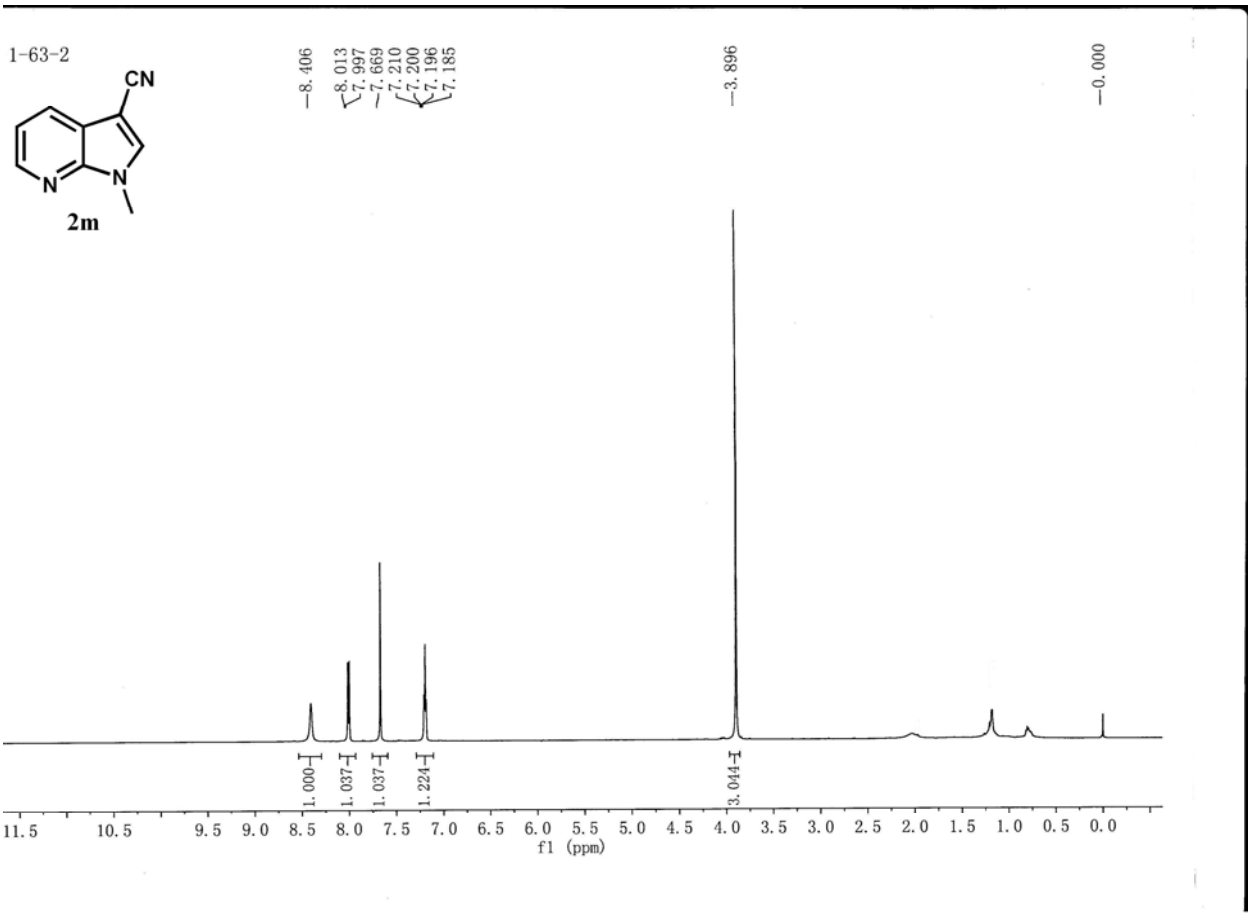

rxy-1-52-1-1
CN
Ph
N
2j
148.0704
136.8425
129.8824
129.8323
129.0059
128.7374
127.5896
123.8667
122.4120
119.5685
116.5717
110.4797
85.5961
77.2541
77.0000
76.7461
31.7065
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

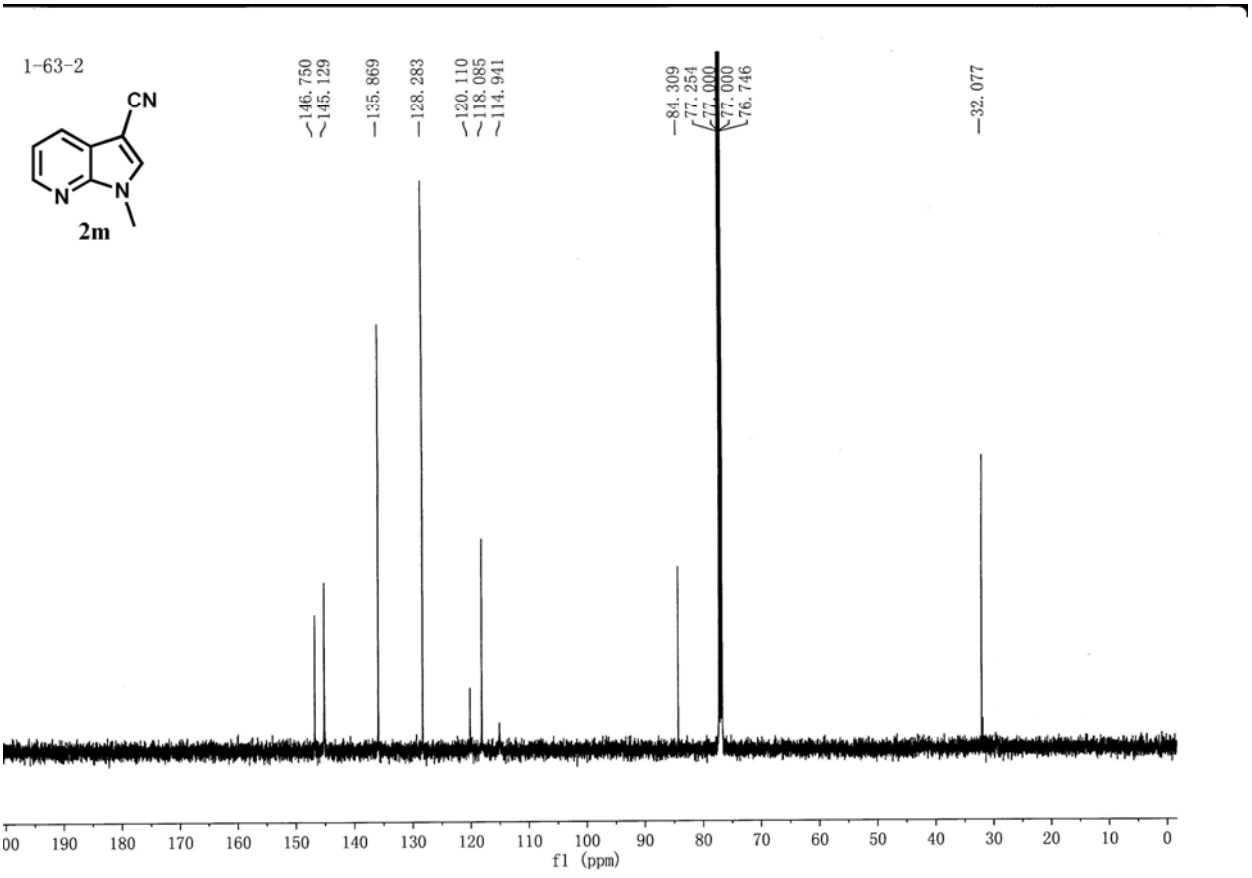

rxy1-64-6-1
7.845
7.840
7.837
7.831
7.828
7.807
7.597
7.594
7.582
7.573
7.566
7.527
7.523
7.517
7.514
7.508
7.504
7.496
7.494
7.490
7.478
7.370
7.360
7.356
7.352
7.350
7.345
7.342
7.260
7.260
CN
N
Ph
2k
1.000
1.020
2.027
4.091
2.038
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

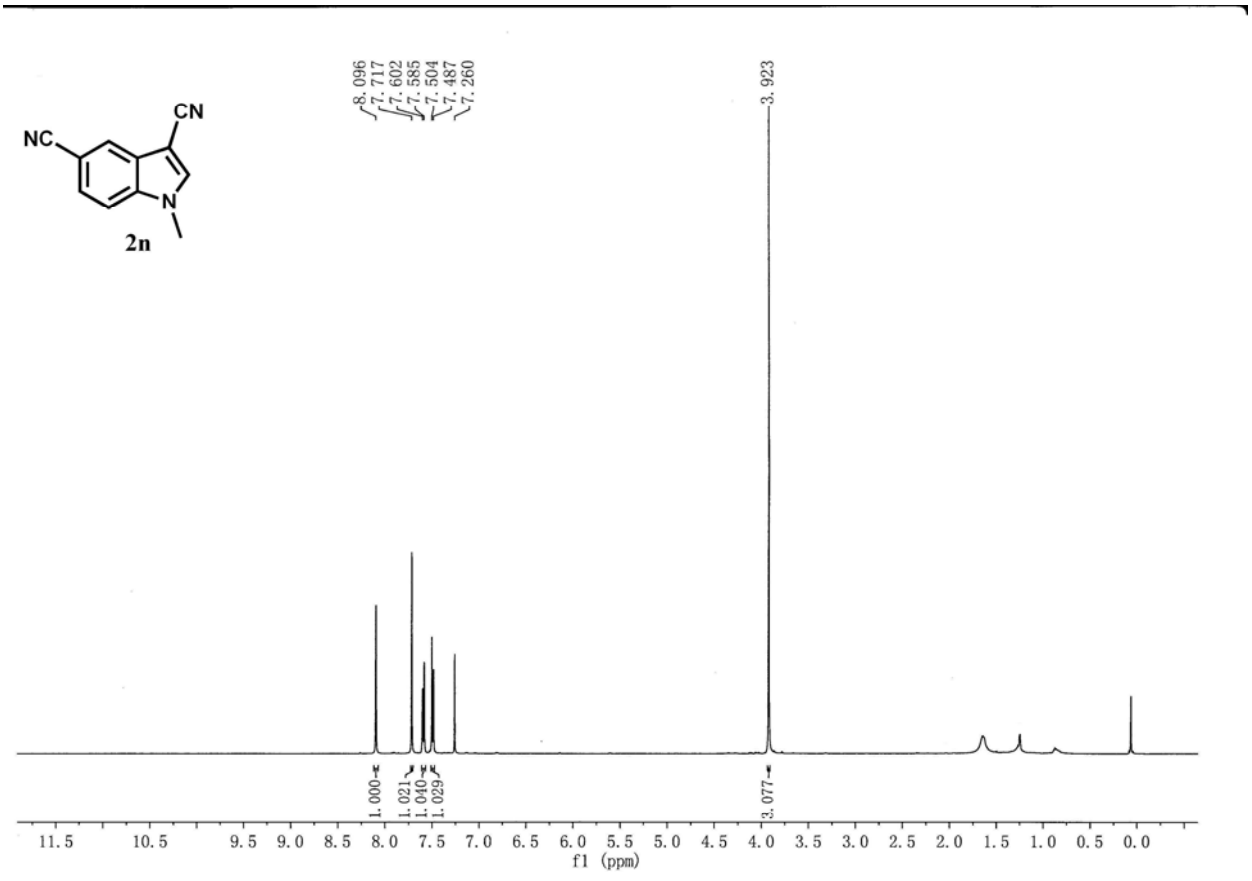

1-64-6-1
CN
N
Ph
2k
137.847
135.644
134.611
130.018
128.376
127.926
124.892
124.528
122.795
120.046
115.485
111.507
88.142
77.254
77.000
76.746
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

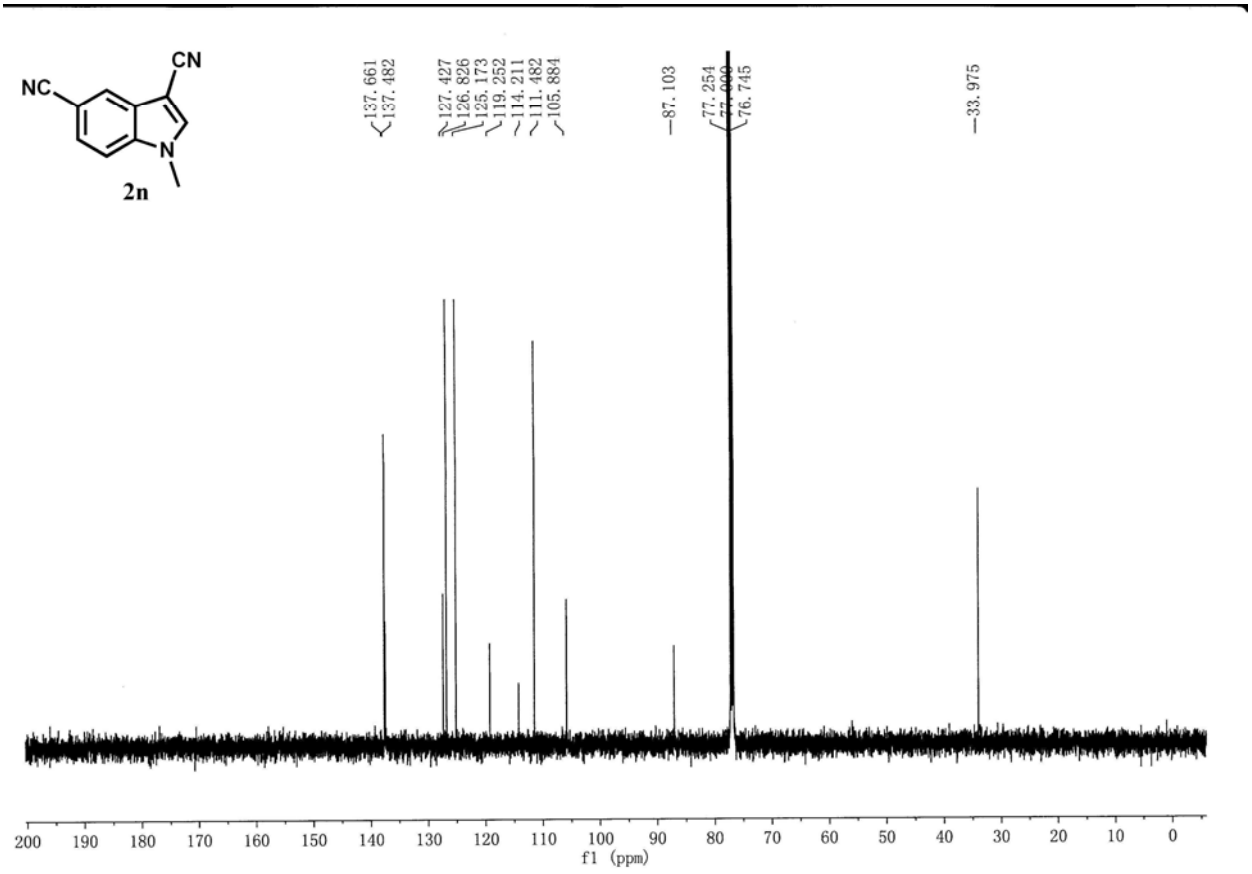

rxy1-75-8
CN
N
Bn
21
7.795
7.785
7.777
7.608
7.378
7.373
7.369
7.359
7.355
7.340
7.326
7.313
7.305
7.299
7.296
7.285
7.260
7.260
7.159
7.156
7.144
5.345
1.000
1.012
6.027
2.090
2.032
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

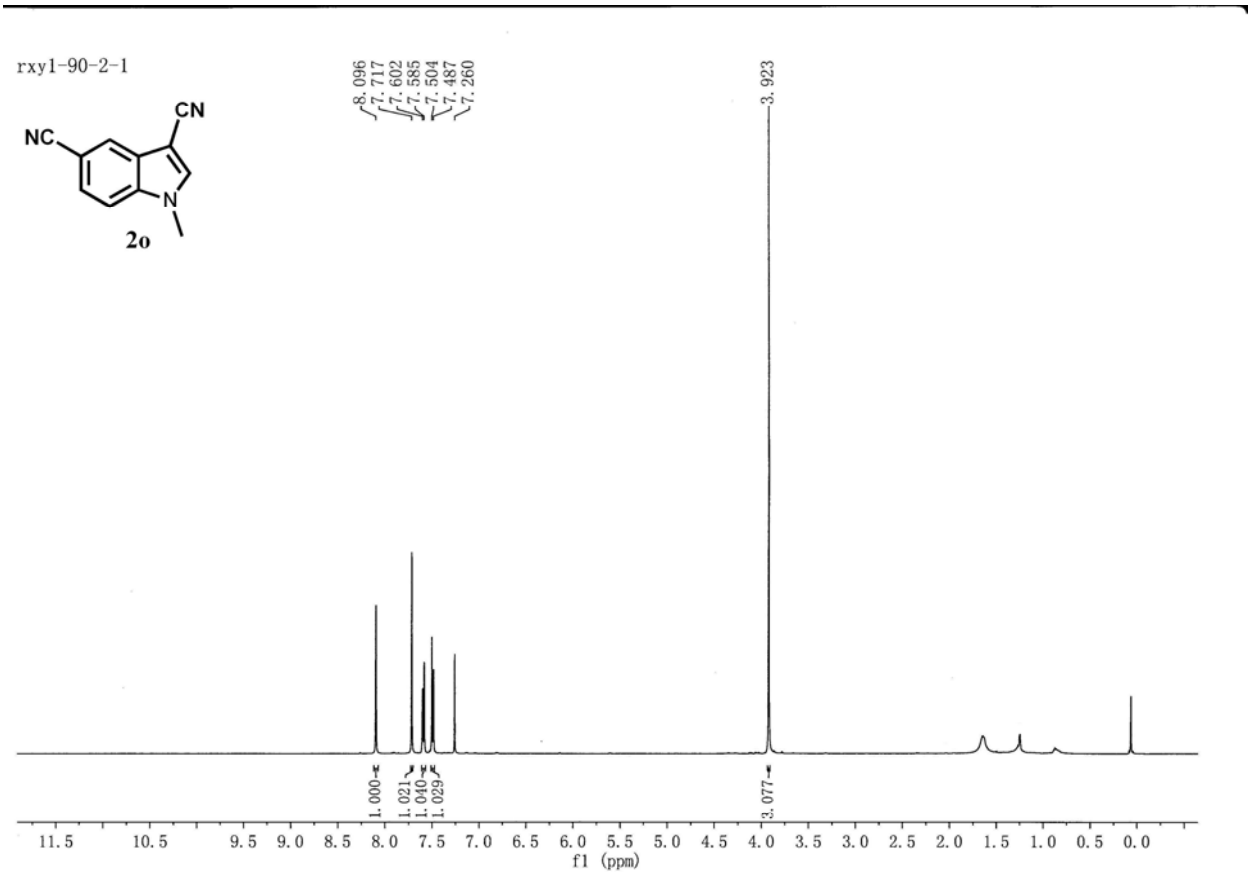

rxy1-75-8
CN
N
Bn
21
135.602
135.191
134.943
129.122
128.433
127.978
127.095
124.004
122.292
119.997
115.752
110.799
86.299
77.254
77.000
76.745
50.893
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

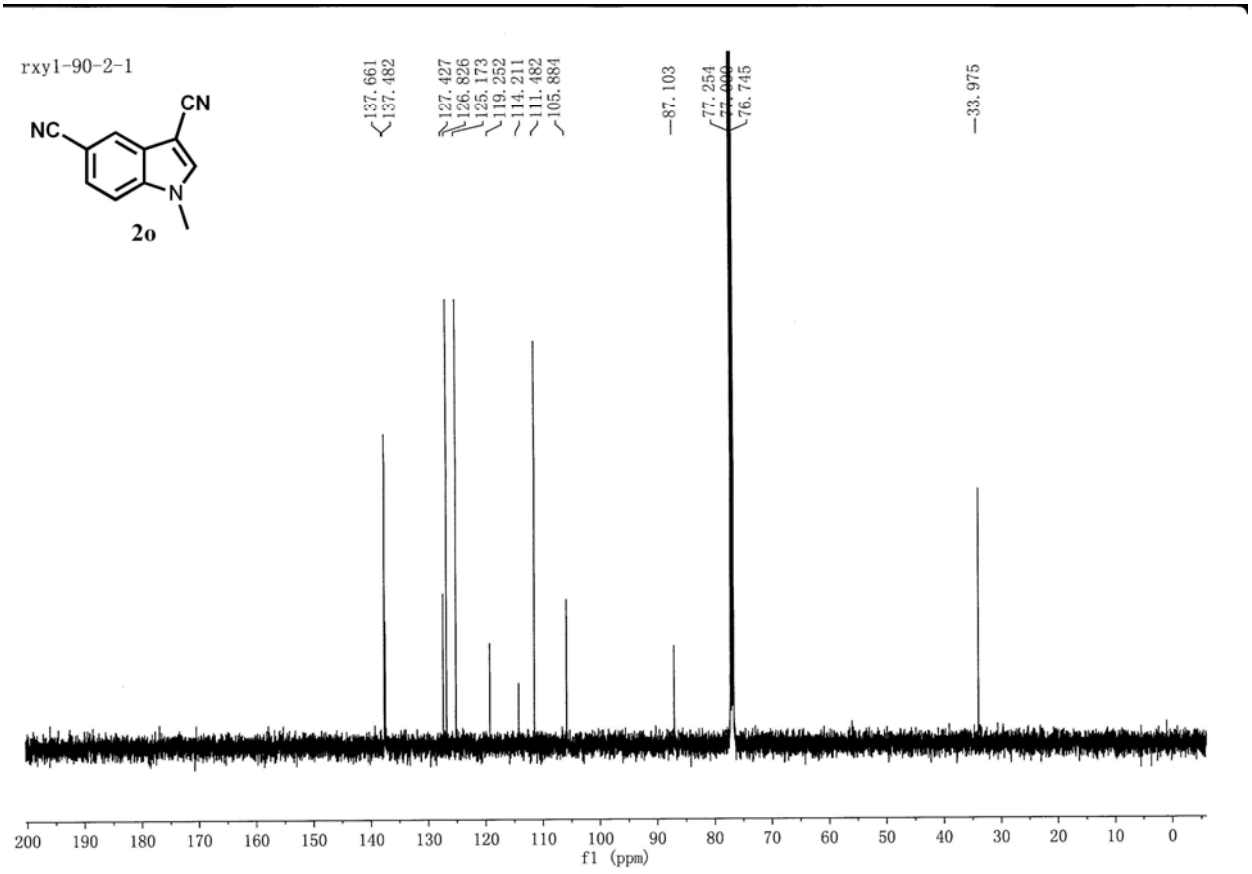

1-63-2
CN
N
N
2m
8.406
8.013
7.997
7.669
7.210
7.200
7.196
7.185
3.896
0.000
1.000
1.037
1.037
1.224
3.044
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

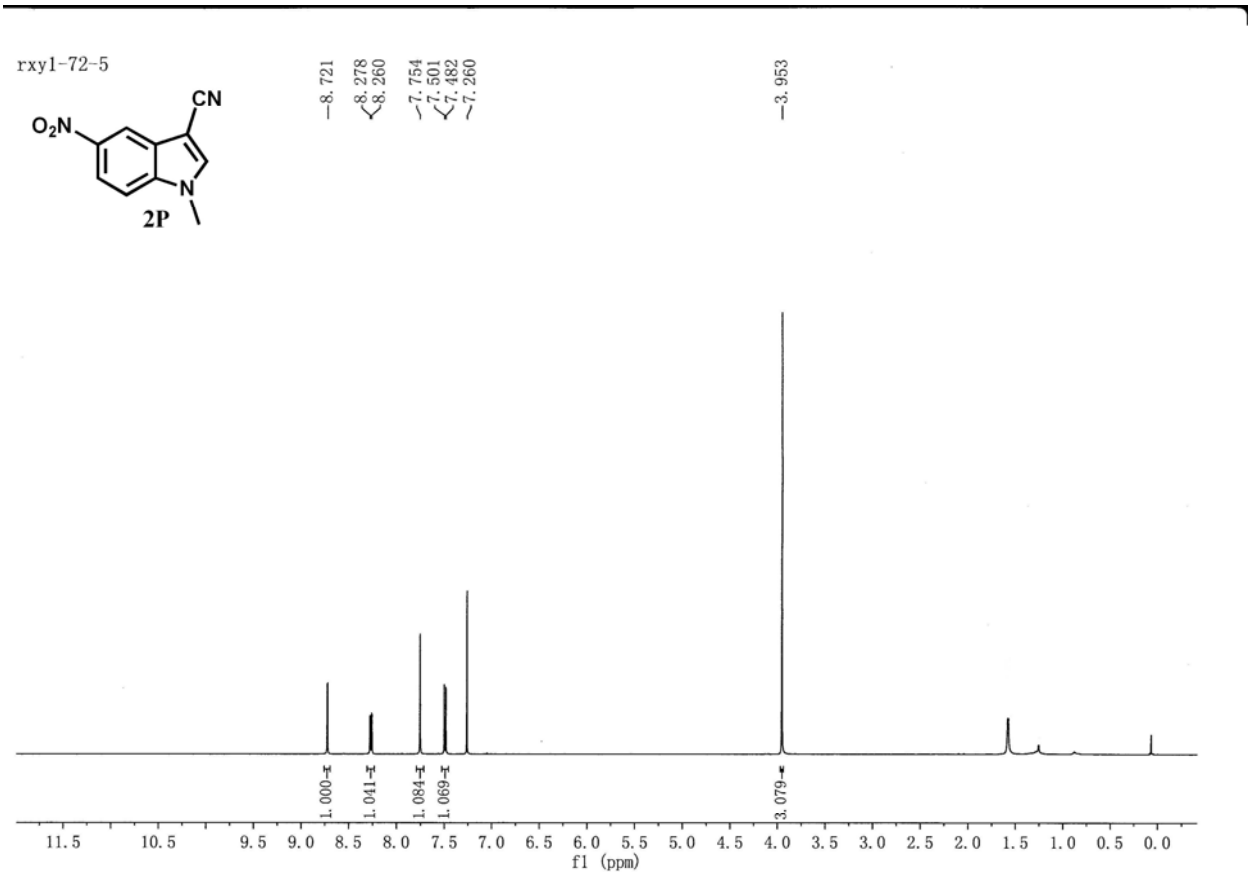

1-63-2
CN
N
N
2m
146.750
145.129
135.869
128.283
120.110
118.085
114.941
84.309
77.254
77.000
76.746
32.077
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CN
NC
N
2n
8.096
7.717
7.602
7.585
7.504
7.487
7.260
3.923
1.000
1.021
1.040
1.029
3.077
11.5
10.5
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
f1 (ppm)

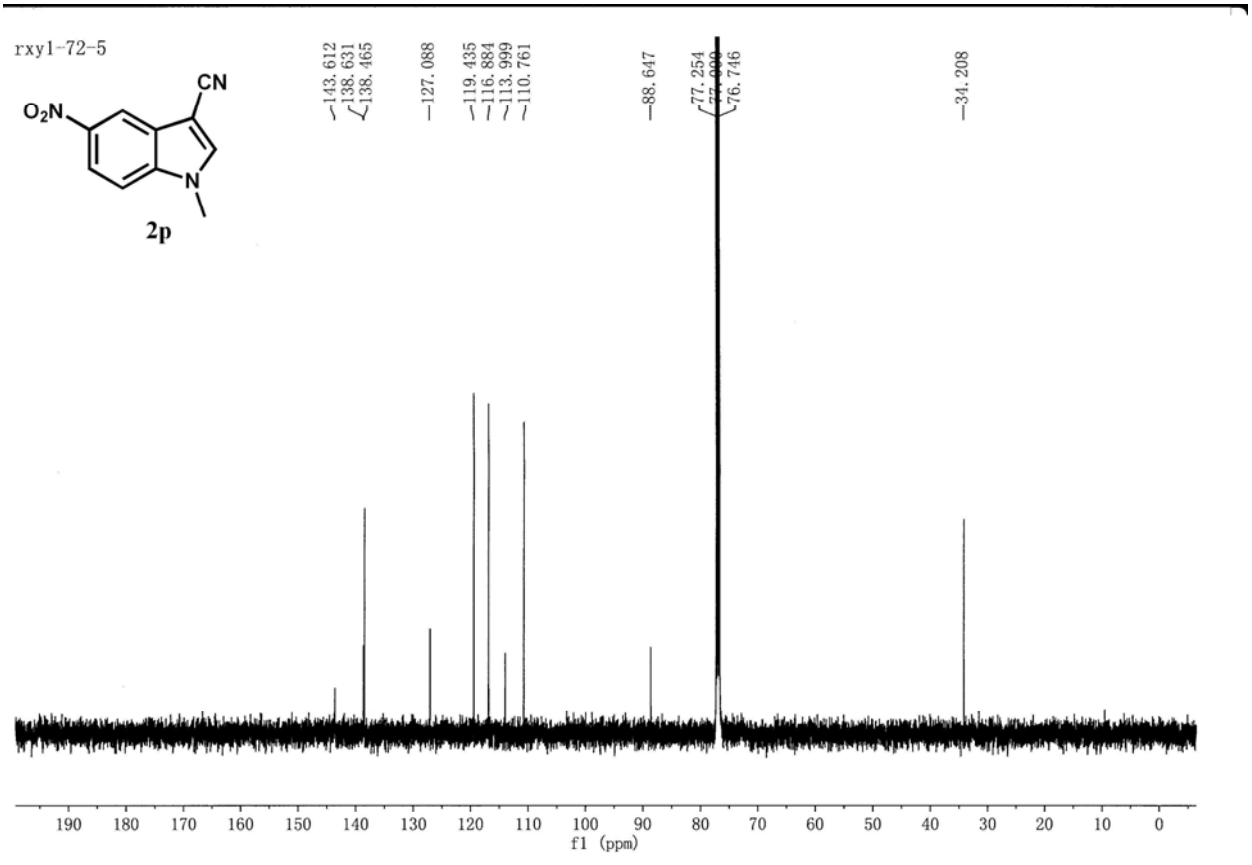

CN
NC
N
2n
137.661
137.482
127.427
126.826
125.173
119.252
114.211
111.482
105.884
87.103
77.254
77.000
76.745
33.975
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


rxy1-90-2-1
NC
CN
N
2o
8.096
7.717
7.602
7.585
7.504
7.487
7.260
3.923
1.000
1.021
1.040
1.029
3.077
11.5 10.5 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
f1 (ppm)

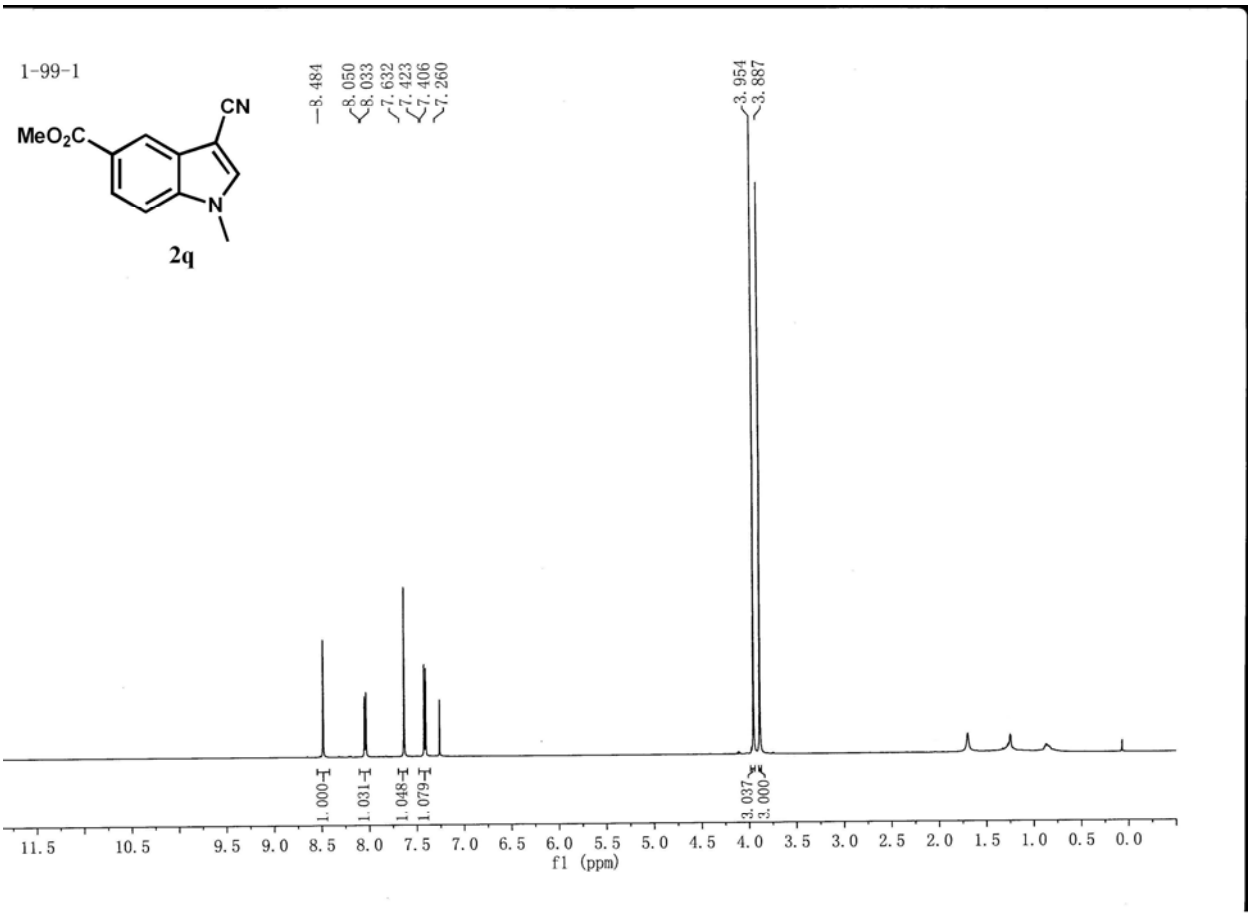

rxy1-90-2-1
NC
CN
N
2o
137.661
137.482
127.427
126.826
125.173
119.252
114.211
111.482
105.884
87.103
77.254
77.000
76.745
33.975
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

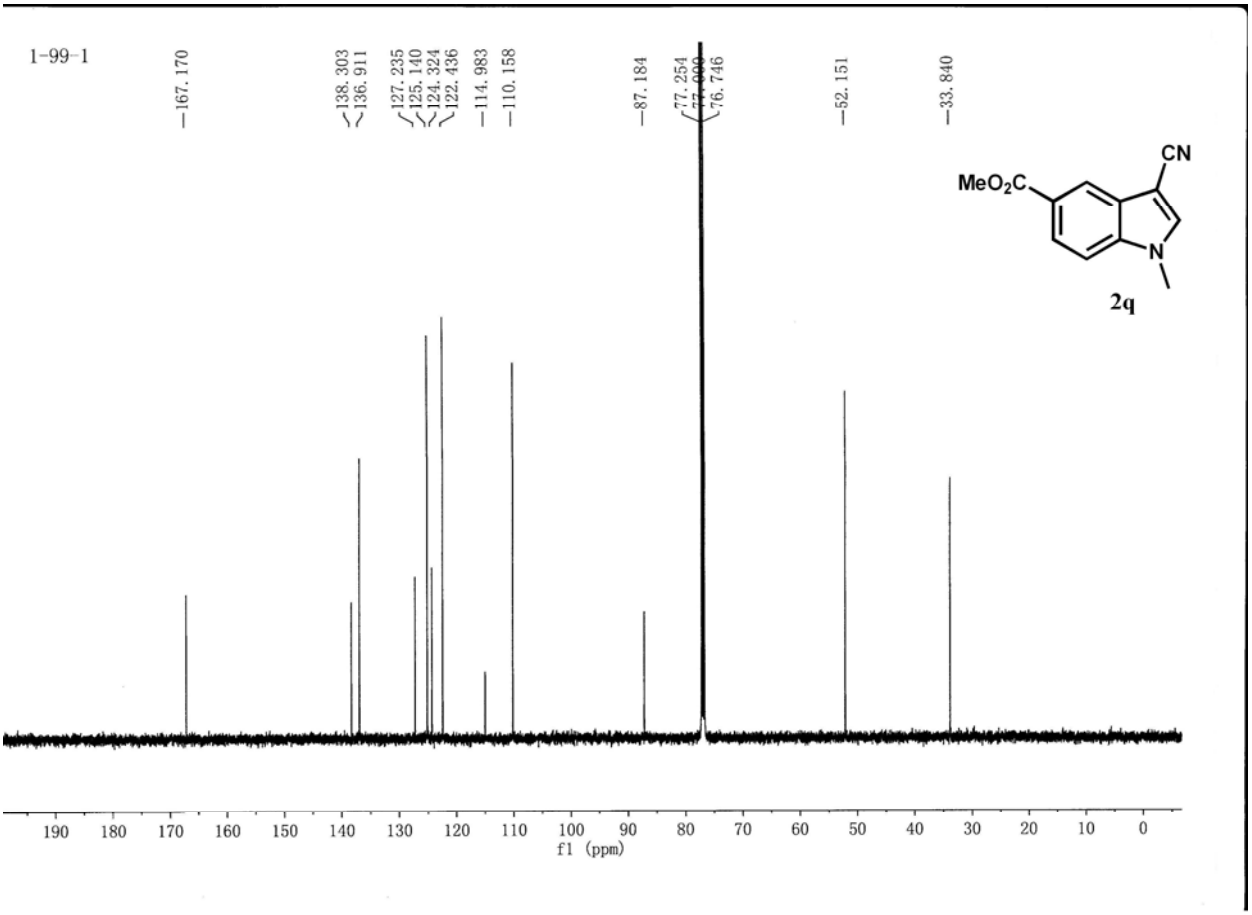

rxy1-72-5
8.721
8.278
8.260
7.754
7.501
7.482
7.260
3.953
1.000
1.041
1.084
1.069
3.079
f1 (ppm)

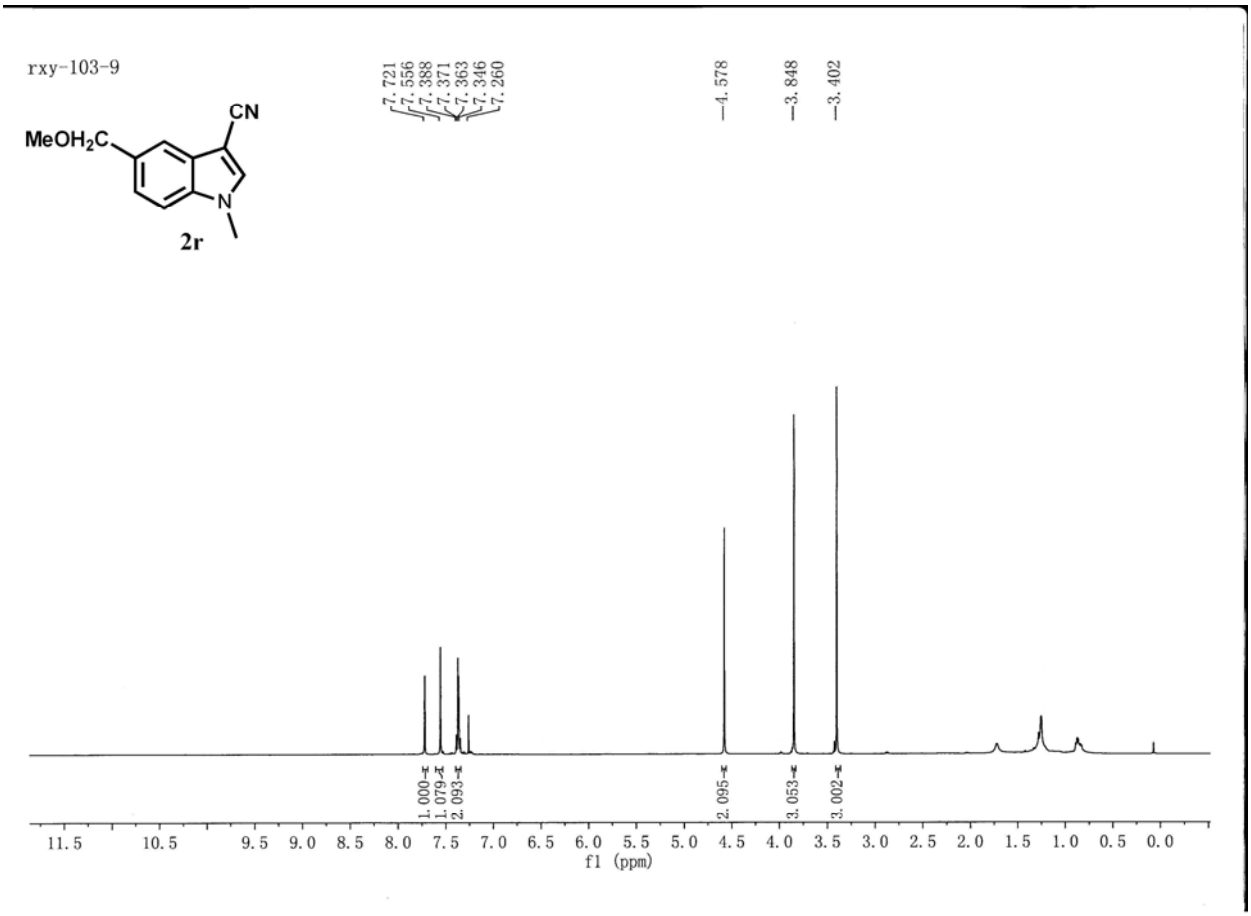
2P

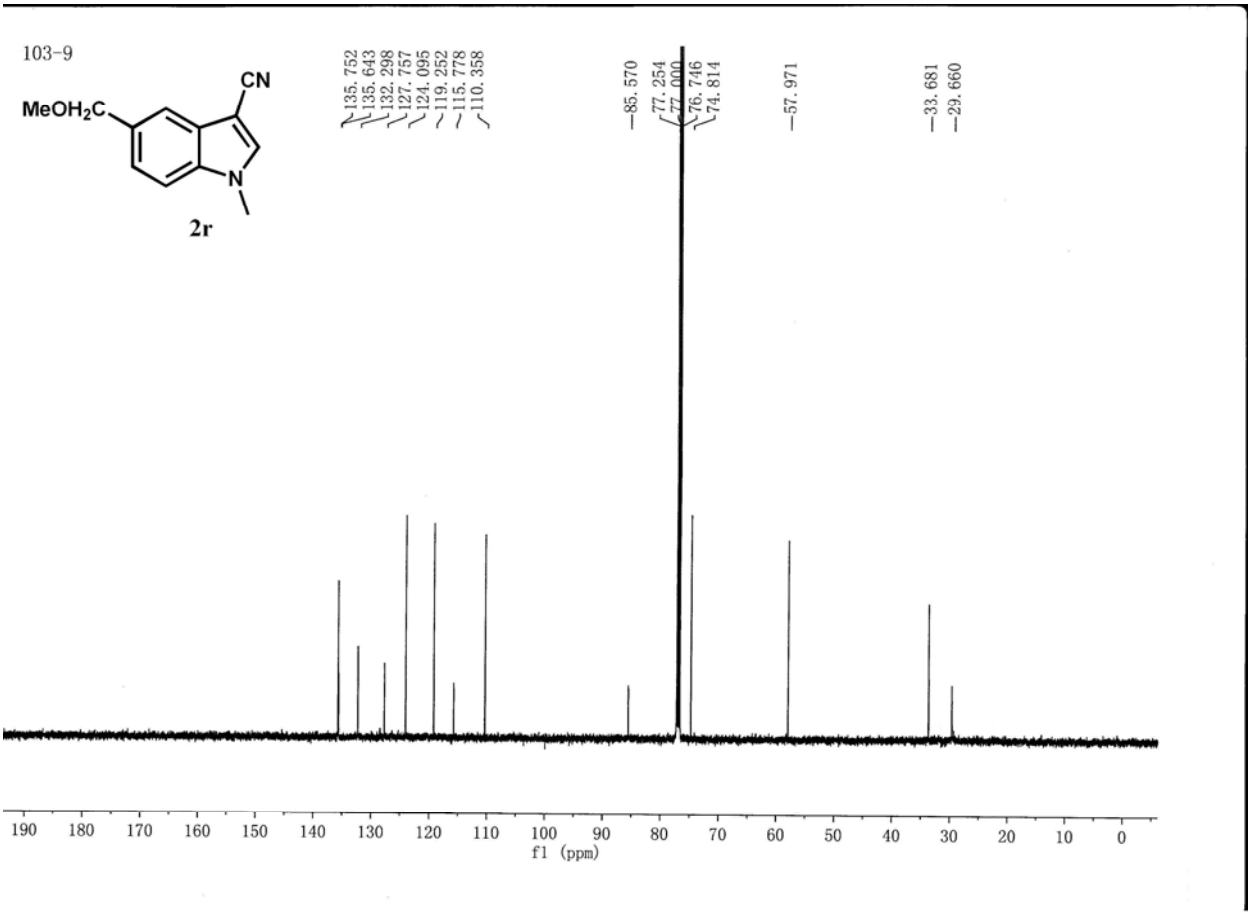

rxy1-72-5
143.612
138.631
138.465
127.088
119.435
116.884
113.999
110.761
88.647
77.254
76.746
34.208
f1 (ppm)

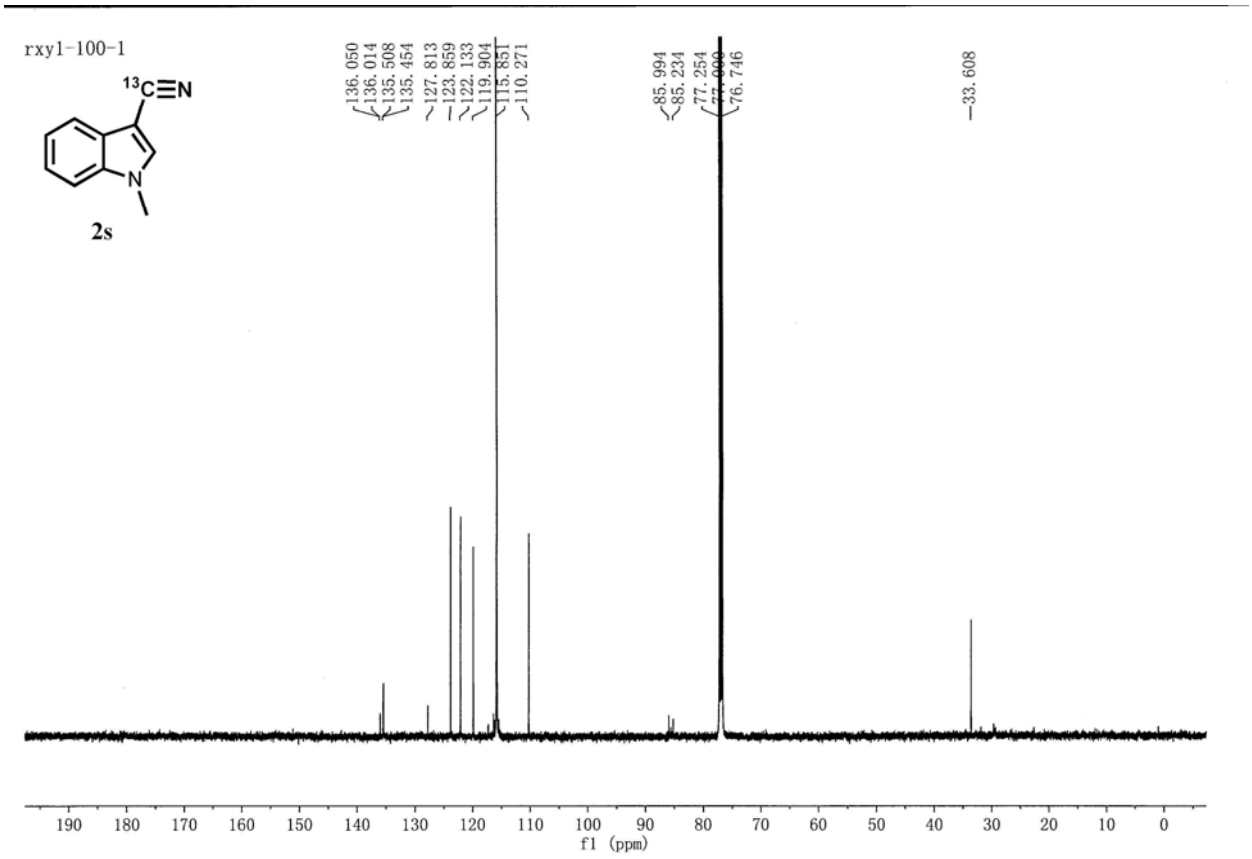
2p


1-99-1
MeO2C
CN
N
2q
8.484
8.050
8.033
7.632
7.423
7.406
7.260
3.954
3.887
1.000
1.031
1.048
1.079
3.037
3.000
11.5
10.5
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
f1 (ppm)


1-99-1
167.170
138.303
136.911
127.235
125.140
124.324
122.436
114.983
110.158
87.184
77.254
77.000
76.746
52.151
33.840
MeO2C
CN
N
2q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


rxy-103-9
MeOH2C
CN
N
2r
7.721
7.556
7.388
7.371
7.363
7.346
7.260
4.578
3.848
3.402
1.000
1.079
2.093
2.095
3.053
3.002
11.5
10.5
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
f1 (ppm)


103-9
MeOH2C
CN
N
2r
135.752
135.643
132.298
127.757
124.095
119.252
115.778
110.358
85.570
77.254
77.000
76.746
74.814
57.971
33.681
29.660
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


rxy1-100-1
$^{13}C\equiv N$
N
2s
136.050
136.014
135.508
135.454
127.813
123.859
122.133
119.904
115.851
110.271
85.994
85.234
77.254
76.746
33.608
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)