Supporting Information

Ruthenium-carbamato-complex derived from siloxylated amine and carbon dioxide for the oxidative α-cyanation of aromatic and cyclic tertiary amines.

Subodh Kumar,[a] Suman L. Jain[a*]

Chemical Sciences Division

CSIR-Indian Institute of Petroleum, Mohkampur, Dehradun-248005 (India)

suman@iip.res.in

Contents

General

The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. The ^{1}H NMR and ^{13}C NMR Spectra were recorded on Bruker 400 MHz spectrometer and the chemical shifts are expressed in δ parts per million relative to tetramethylsilane (TMS) as internal standard. The conversions and selectivity of the products were determined by high resolution GCMSD, EI, quadrapole mass analyzer, EM detector.

General experimental procedure: A 25 mL round bottomed flask equipped with a magnetic stirrer bar was charged with tertiary amine (1 mmol), NaCN (1.2 mmol), MeOH (2 mL), catalyst **3** (2 mol %) and AcOH (1 mL). To the resulting stirred reaction mixture aqueous hydrogen peroxide (1.5 mmol, 35 wt-%) was added drop wise over a period of 30 min and the stirring was continued at room temperature. The progress of the reaction was monitored by TLC (SiO_2). After completion of the reaction, the catalyst was recovered by precipitation with diethyl ether followed by filtration. The obtained organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under vacuum to give crude product, which was purified by flash chromatography to afford pure α-aminonitrile. The conversion of tertiary amines into corresponding α-aminonitriles and their selectivity was determined by GC-MS (EI quadrupol mass analyzer, EM detector) and the identity of the selected products was established by comparing their spectral data with authentic samples. The values of ^{1}H and ^{13}C NMR spectra of the products are given as below:

N-Methyl-*N*-phenylaminoacetonitrile (Table 2, entry 1; **6a)**: ^{1}H NMR ($CDCl_3$) δ: 3.03 (s, 3 H), 4.20 (s, 2 H), 6.80 (dd, *J* = 8.5 and 1.2 Hz, 1H), 6.89 (dd, *J* = 6.2 and 0.92 Hz, 1H), 6.95-7.20 (m, 3H); ^{13}C NMR ($CDCl_3$) δ: 147.5, 128.9, 120.0, 114.9, 42.6, 39.0 ppm.

N-Methyl-*N*-(4-methylphenyl)aminoacetonitrile (Table 2, entry 2; **6b)**: ^{1}H NMR ($CDCl_3$) δ: 2.20 (s, 3 H), 3.01 (s, 3 H), 4.12 (s, 2 H), 6.83 (d, J=8.5 Hz, 2 H), 7.12 (d, J=8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ: 145.8, 130.0, 129.9, 115.5, 115.4, 42.8, 39.5, 20.3 ppm.

N-Methyl-N-(3-methylphenyl)aminoacetonitrile (Table 2, entry 3; **6c):** ^{1}H NMR ($CDCl_3$) δ: 2.31 (s, 3 H), 2.98 (s, 3 H), 4.25 (s, 2 H), 6.66-6.68 (m, 2 H), 6.74 (d, *J* 6.0 Hz, 1H)), 7.16-7.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ: 21.8, 39.2, 42.3, 112.0, 115.5, 115.6,121.1, 129.2, 139.2, 147.8 ppm;

N-Methyl-*N*-(2-bromophenyl)aminoacetonitrile (Table 2, entry 4; **6d):** viscous oil; ^{1}H NMR ($CDCl_3$) δ: 2.92 (s, 3 H), 4.07 (s, 2 H), 6.98-7.04 (m, 1 H), 7.25-7.35 (m, 2 H) , 7.55-7.58 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ: 40.6, 44.8, 115.1, 119.7, 122.8, 126.3, 128.5, 133.9, 147.3 ppm.

N-Methyl-*N*-(4-bromophenyl)aminoacetonitrile (Table 2, entry 5; **6e)**: ^{1}H NMR ($CDCl_3$) δ: 3.12 (s, 3 H), 4.16 (s, 2 H), 6.73 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2H) ; ^{13}C NMR ($CDCl_3$) δ: 146.2, 130.2, 125.4, 116.2, 115.0, 42.6, 39.2 ppm.

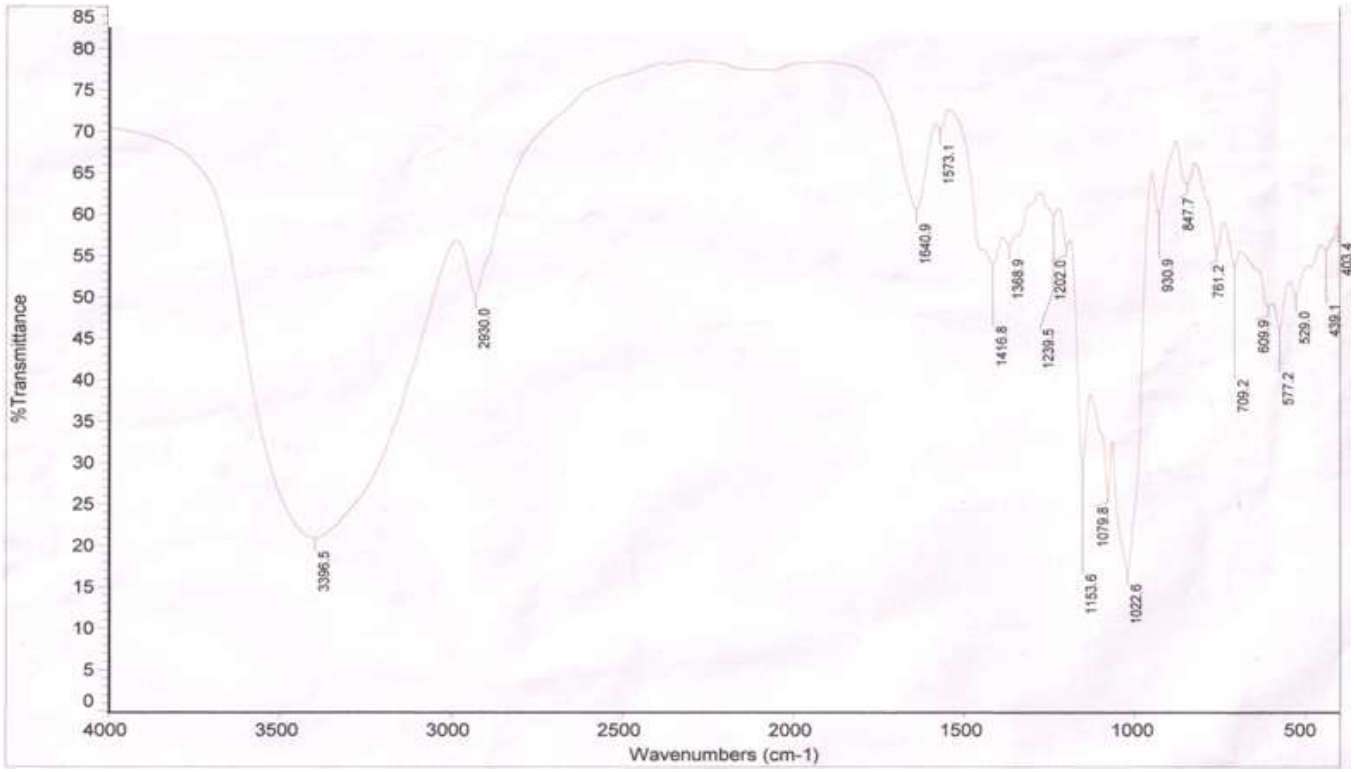
Anilinoacetonitrile (Table 2, entry 6; **6f)*:*** ^{1}H NMR ($CDCl_3$) δ: 1.52 (broad s, 1H), 4.24 (s, 2 H), 6.88 (dd, *J* = 7.9 and 1.2 Hz, 1H), 7.12 (dd, *J* = 8.2 and 0.82 Hz, 1H), 7.15-7.20 (m, 3H) ; ^{13}C NMR ($CDCl_3$) δ: 149.5, 126.9, 120.2, 115.9, 40.6 ppm.

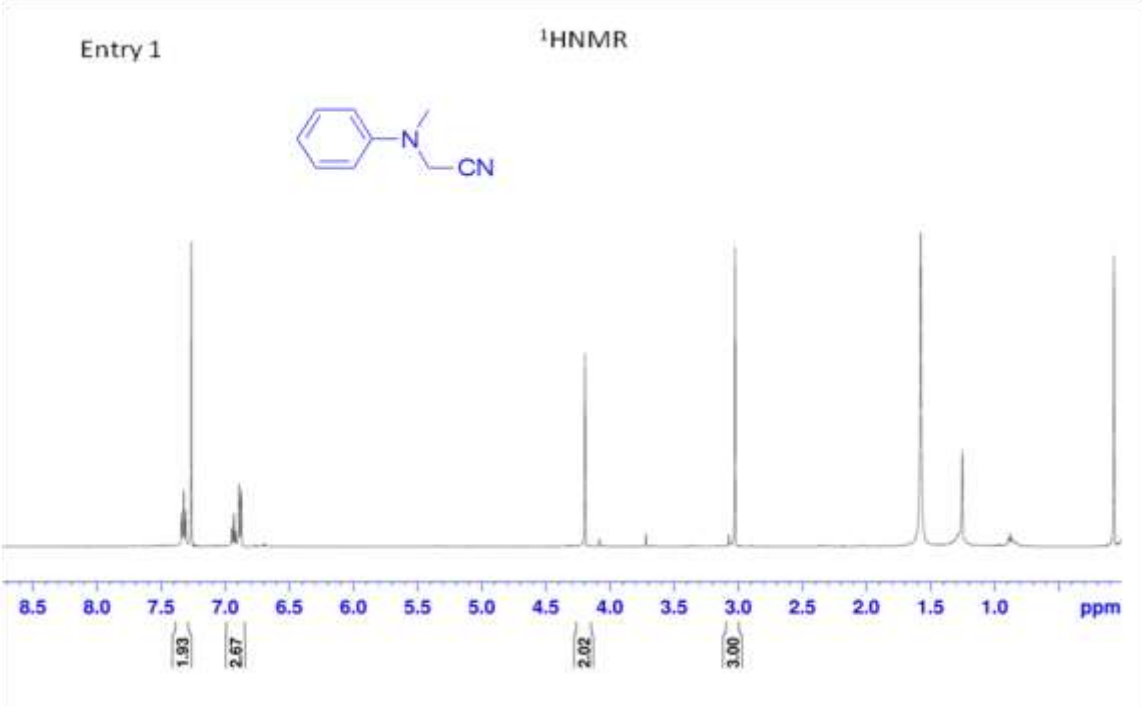
2-Cyano-*N*-phenylpiperidine (Table 2, entry 7; **6g)**: ^{1}H NMR ($CDCl_3$) δ: 1.58-1.88 (m, 4H), 1.90-2.10 (m, 2H), 2.98-3.13 (m, 1H), 3.44-3.47 (m, 1H), 4.58 (t, *J* = 3.4 Hz, 1H), 6.72-7.00 (m, 2H), 7.13-7.21 (m, 3H) ; ^{13}C NMR ($CDCl_3$)δ: 149.0, 128.6, 120.8, 118.0, 117.2, 52.6, 45.8, 29.1, 25.0, 20.4 ppm.

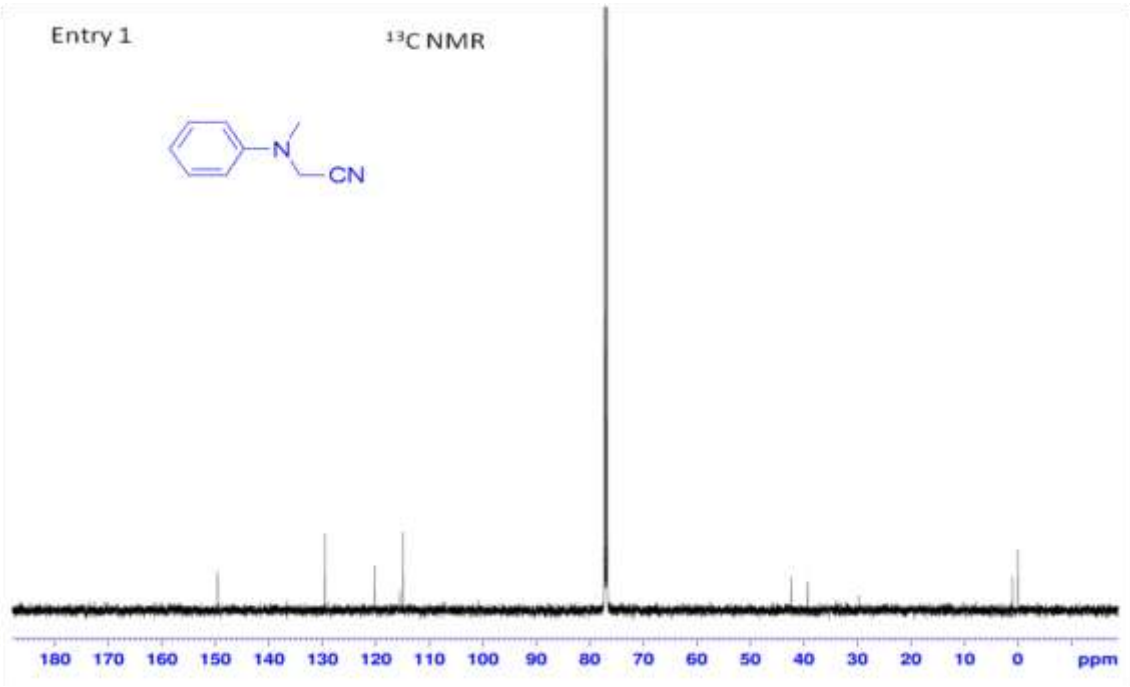
2-Cyano-*N*-phenylpyrolidine(Table 2, entry 8; **6h)**: mp 60-61°C; ^{1}H NMR ($CDCl_3$) δ: 2.08-2.40 (m, 4H), 3.26-3.38 (m, 2H), 4.28 (dd, *J* = 4.7 and 2.5 Hz, 1H), 6.60-6.67 (m, 2H), 6.82-6.92 (m, 3H) ; ^{13}C NMR ($CDCl_3$) δ: 150.7, 137.8, 119.2, 115.0, 114.6, 52.5, 47.6, 32.4, 23.6 ppm.

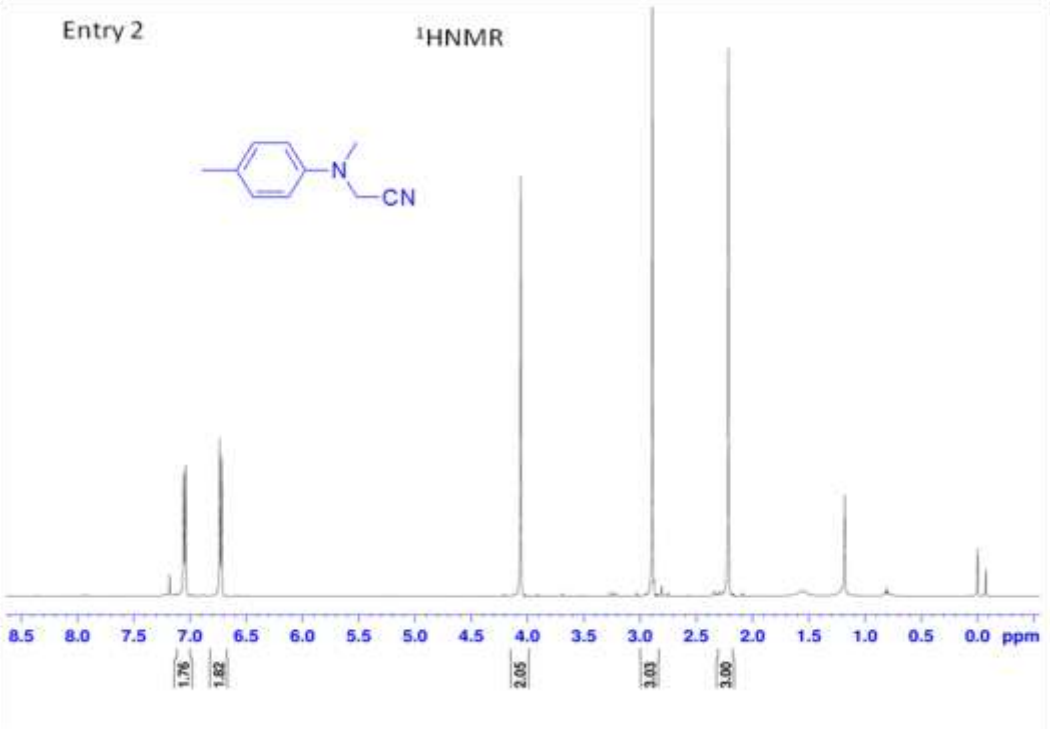
2-Cyano-1-phenyl-1,2,3,4-tetrahydroisoquinoline (Table 2, entry 9; **6i)**: mp 101-102°C; ^{1}H NMR ($CDCl_3$) δ 2.91 (dt, *J* = 15.8 and 3.2Hz, 1 H), 3.08, (ddd, *J* = 15.8, 9.5, and 5.4 Hz, 1H), 3.38 (ddd, *J* = 12.5, 9.5, and 3.2 Hz, 1H), 3.79-3.84 (m, 1H), 5.52 (s, 1H), 7.00-7.06 (m, 1H), 7.09-7.12 (m, 2H), 7.22-7.26 (m, 6H) ; ^{13}C NMR ($CDCl_3$) δ: 149.4, 132.8, 129.2, 129.0, 128.4, 128.1, 126.6, 117.5, 117.1, 52.6, 45.2, 27.2 ppm.

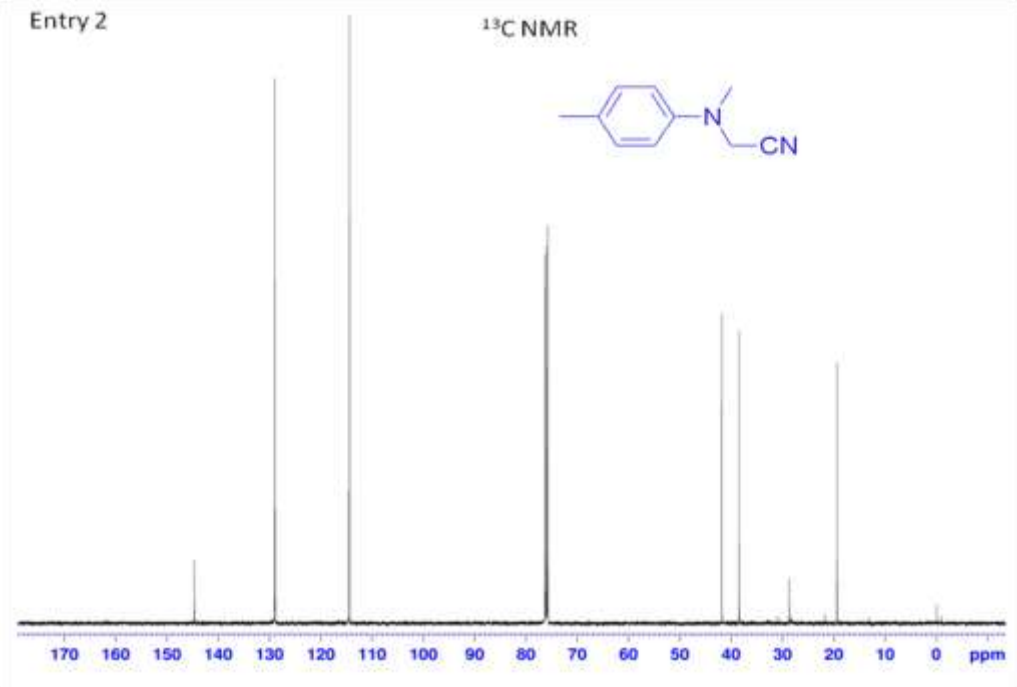
Fig. 1: IR spectra of the rithenium carbamato complex **3**

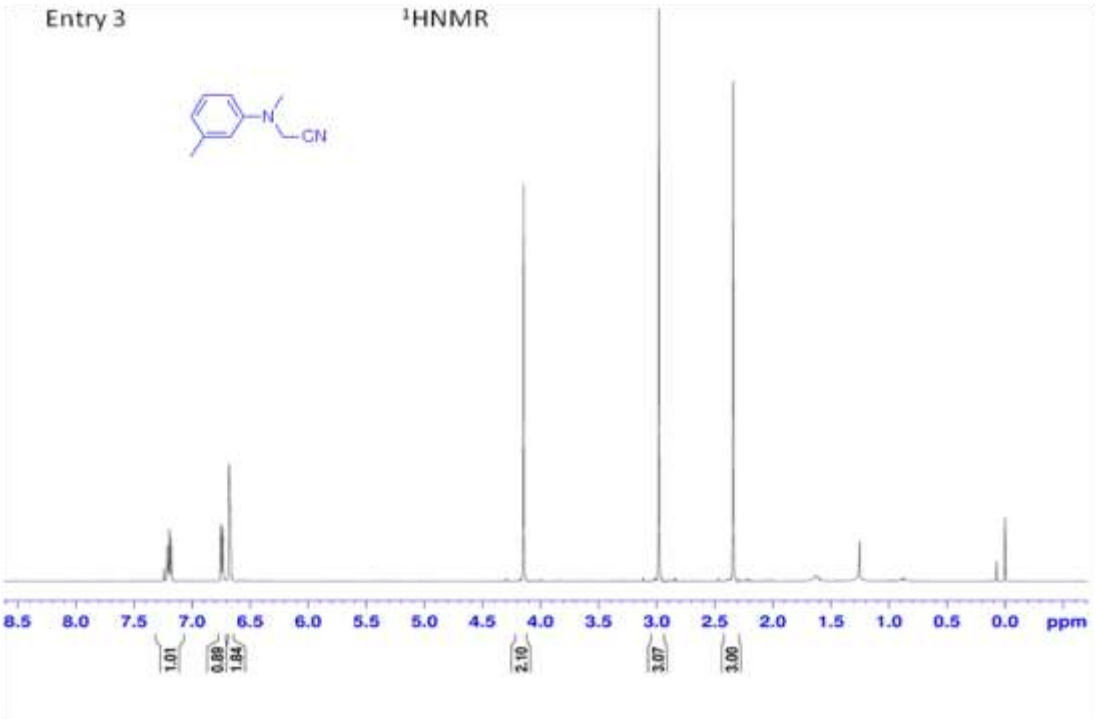


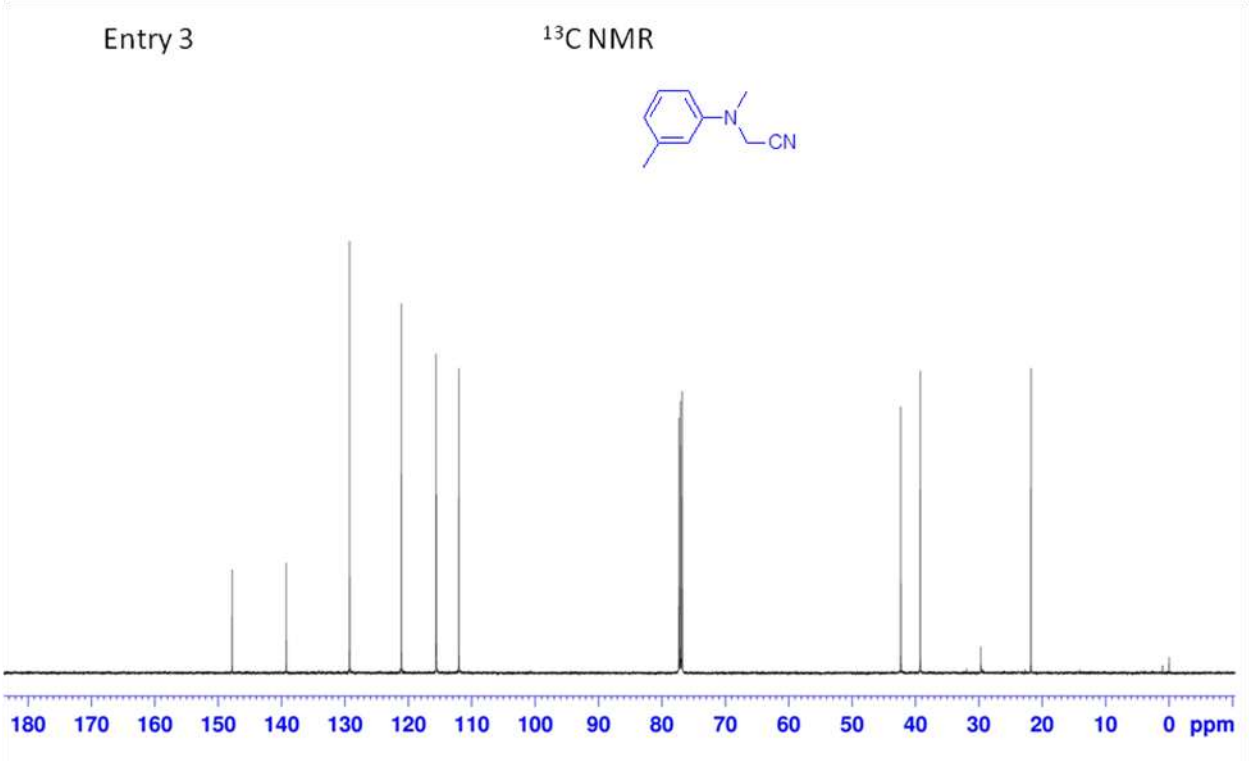

Entry 1
¹HNMR
N
CN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.93
2.67
2.02
3.00

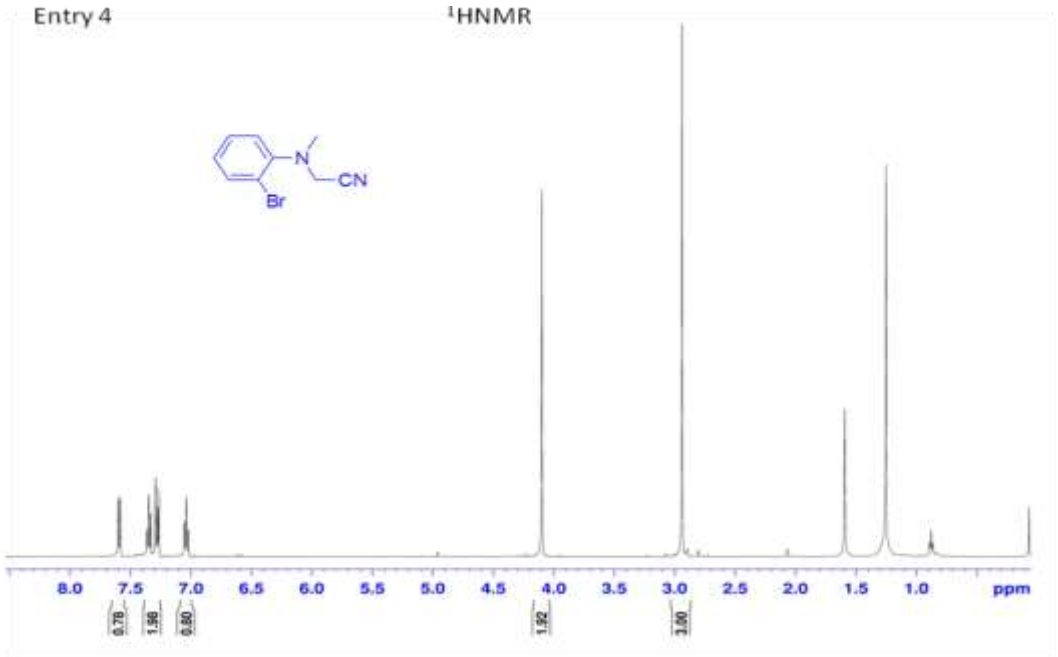

Entry 1
¹³C NMR
N
CN
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

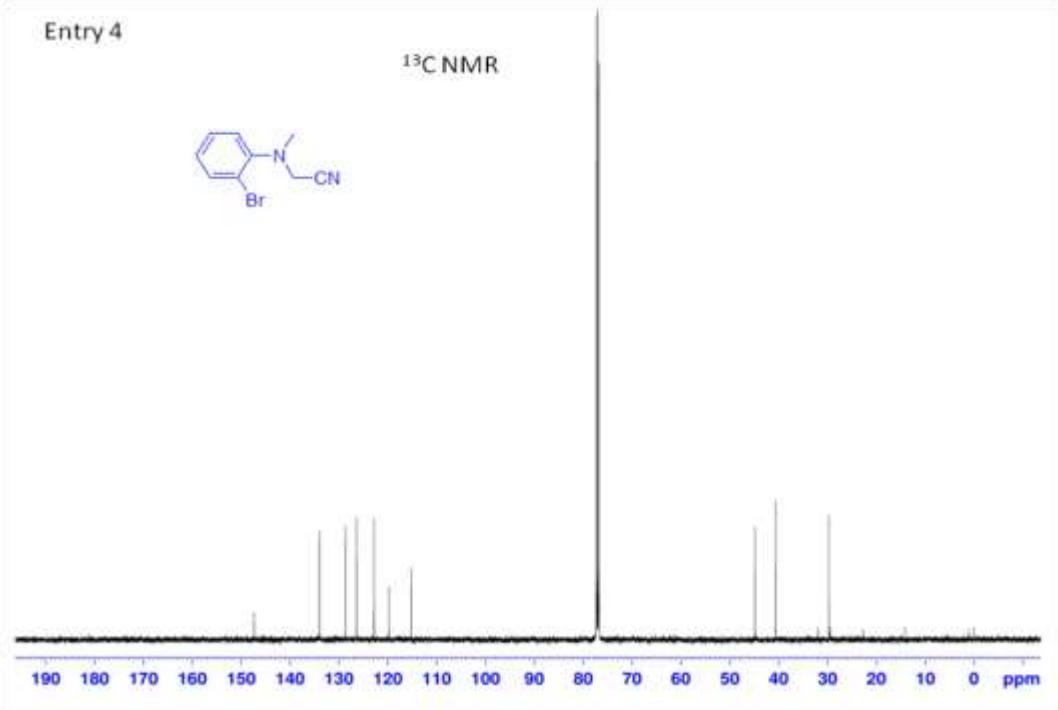


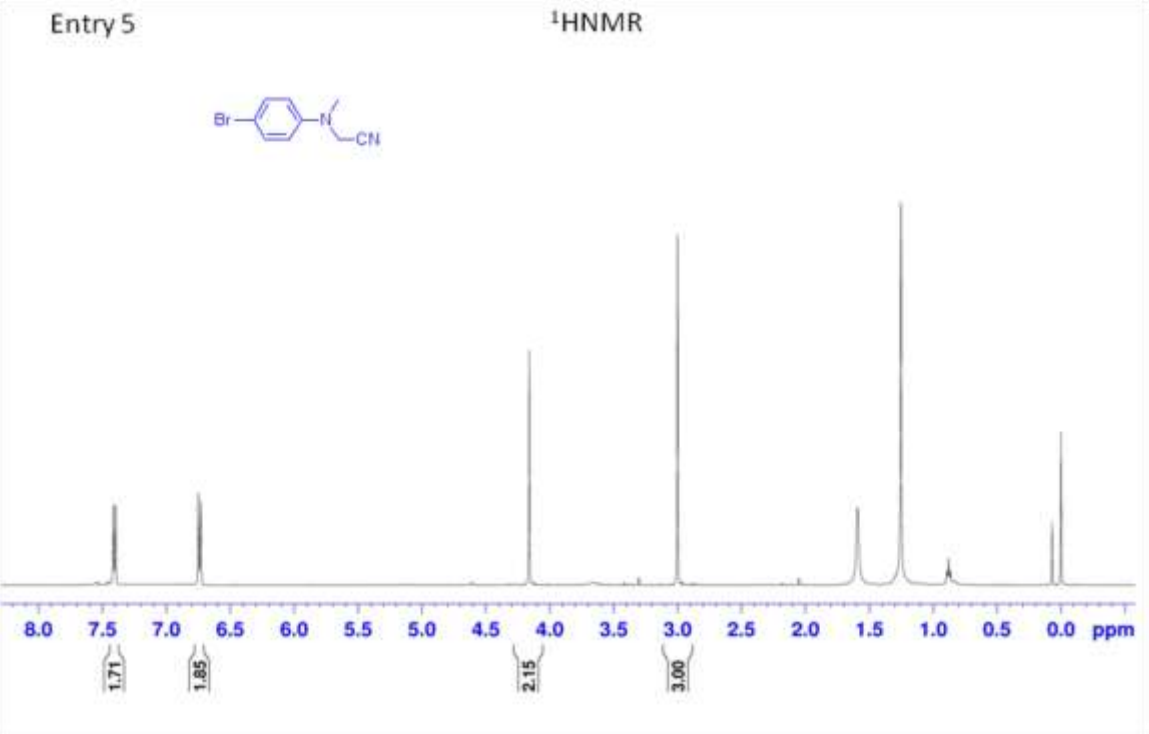


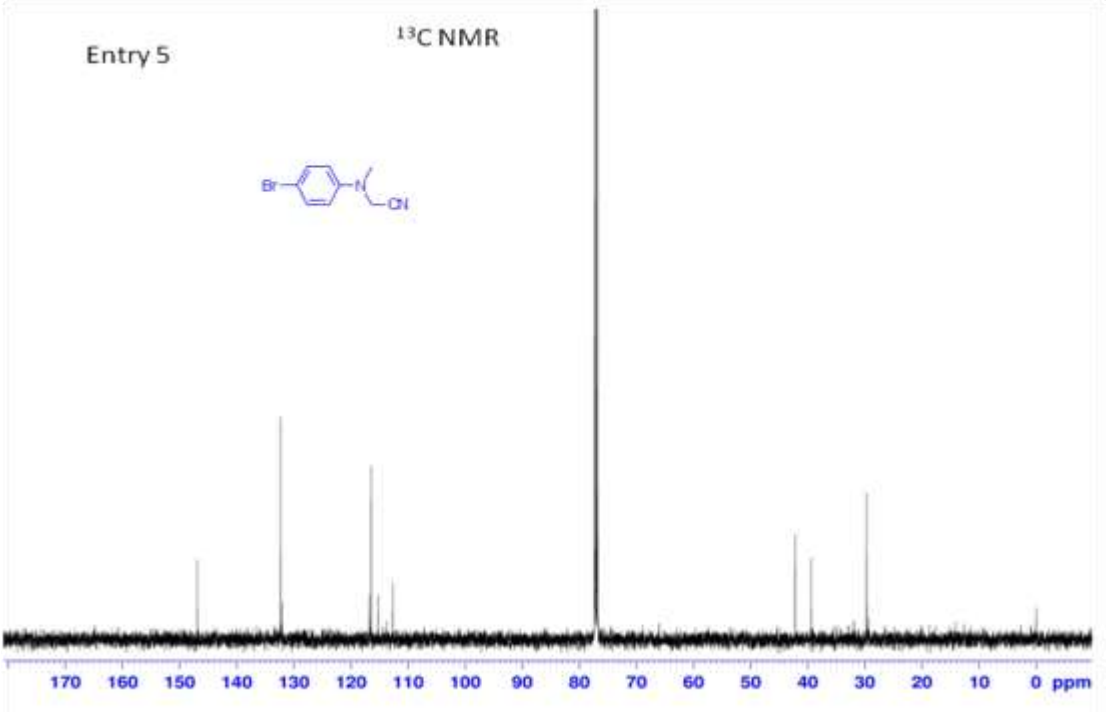

Entry 3
¹HNMR
N
CN
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
0.89
1.84
2.10
3.07
3.06


Entry 3
¹³C NMR
N
CN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

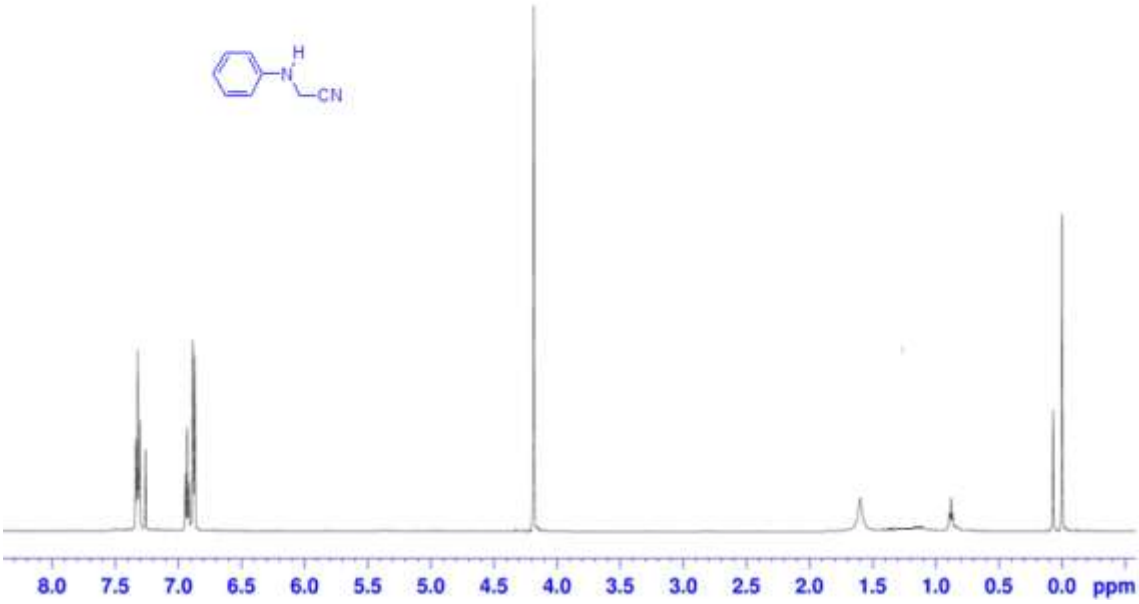








Entry 6 ^{1}HNMR



Entry 6 ^{13}C NMR