Supporting information

Rhodium Catalyzed Cyanation of Chelation Assisted C-H Bonds

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1. General Comments:

All reactions were carried out under an atmosphere of dry nitrogen using reaction tubes. Dry toluene was prepared by distilling over sodium ketyl and stored over using molecular sieves 4Å under N_2 atmosphere. All the arylpyridine derivatives were synthesized from 2-bromopyridine derivatives and arylboronic acids employing literature procedure.[1] Synthesis of *N*-cyano-N-phenyl-p-methylbenzenesulfonamide was achieved from phenylurea and tosyl chloride utilizing the protocol reported in the literature.[2] $[Cp^*RhCl_2]_2$, $AgSbF_6$ and $AgClO_4$ were obtained from Aldrich and they were used as received. $NaBF_4$ was purchased from spectrochem and used as received.

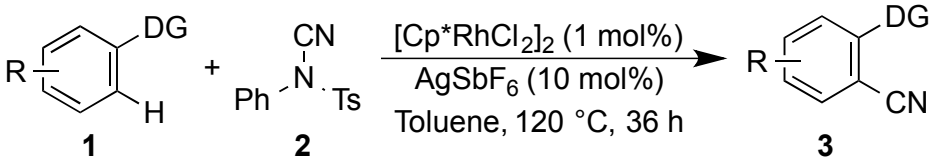
Column chromatography was performed using Rankem Silicagel (100-200 mesh) and the solvent system used unless otherwise specified, was ethylacetate-hexanes with various percentage of polarity depending on the nature of the substrate.

2. Analytical Methods:

NMR data were recorded on Bruker DPX 400 and AVC 500 MHz spectrometers. ^{13}C and ^{1}H NMR spectra were referenced to signals of deutero solvents and residual protiated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectormeter. HRMS were recorded by electron spry ionization (ESI) method on a Q-TOF Micro with lock spray source. Melting points are corrected. The crystal data were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

[1] Rao, X.; Liu, C.; Qiu, J.; Jin, Z. *Org. Biomol. Chem.* **2012**, *10*, 7875-7883.
[2] a) Kurzer, F. *J. Chem. Soc.* **1949**, 1034-1038; b) Kurzer, F. *J. Chem. Soc.* **1949**, *0*, 3029-3033

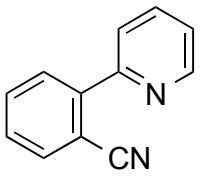
3. General procedure for rhodium catalyzed cyanation of chelation assisted C-H bonds:



A dry reaction tube was charged with arenes **1** (0.2 mmol), *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.002 mmol, 1 mol%), $AgSbF_6$ (0.02 mmol, 10 mol%) and dry toluene (2 mL) under nitrogen atmosphere. The reaction tube was sealed under nitrogen atmosphere and kept at 120 °C and continued stirring for 36h. After the completion of the reaction, as monitored by TLC the reaction mixture was cooled to room temperature and purified by column chromatography using mixture of hexane and ethyl acetate as eluent to afford the analytically pure mono and dicyanated products.

4. Properties of isolated benzonitriles (3a-v):

2-(pyridin-2-yl)benzonitrile (3a):



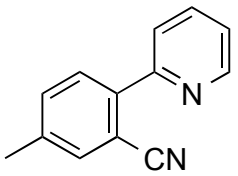
According to the general procedure the mono and dicyanated products were isolated in 84% and 7% yield, respectively using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.77 (d, 1H, *J* = 3.7 Hz, HPy), 7.91-7.73 (m, 4H, HAr), 7.69 (t, 1H, *J* = 7.7 Hz, HAr), 7.51 (t, 1H, *J* = 7.4 Hz, HAr), 7.36 (t, 1H, *J* = 6.1 Hz, HAr).

[3] a) Kim, J.; Chang, S. *J. Am. Chem. Soc.* **2010**, *132*, 10272-10274; b) Kim, J.; Kim, H.; Chang, S. *Org. Lett.* **2012**, *14*, 3924-3927; c) Xu, H.; Liu, P.-T.; Li, Y.-H.; Han, F.-S. *Org. Lett.* **2013**, *15*, 3354-3357.

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.2 (C), 149.9 (CH), 143.4 (C), 136.9 (CH), 134.1 (CH), 132.8 (CH), 129.9 (CH), 128.8 (CH), 123.4 (CH), 123.3 (CH), 118.7 (CN), 111.0 (C).

5-Methyl-2-(pyridin-2-yl)benzonitrile (3b):

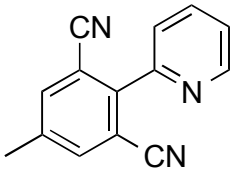


According to the general procedure the mono and dicyanated products were isolated in 74% and 18% yield, respectively using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.75 (d, 1H, J = 4.8 Hz, HPy), 7.81 (td, 1H, J = 7.8, 1.5 Hz, HAr), 7.78 (m, 2H, HAr), 7.59 (s, 1H, HAr), 7.48 (d, 1H, J = 7.8 Hz, HAr), 7.36-7.29 (m, 1H, HAr), 2.43 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.2 (C), 149.8 (CH), 140.7 (C), 139.1 (C), 136.7 (CH), 134.4 (CH), 133.7 (CH), 129.8 (CH), 123.1 (2 × CH), 118.9 (CN), 110.8 (C), 20.8 (CH_3).

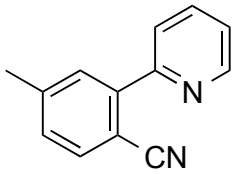
5-Methyl-2-(pyridin-2-yl)isophthalonitrile (3b'):



^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.87-80 (m, 1H, HPy), 7.90 (td, 1H, J = 7.6, 2.0 Hz, HAr), 7.80 (s, 2H, HAr), 7.72-7.67 (m, 1H, HAr), 7.48-7.42 (m, 1H, HAr), 2.51 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.2 (C), 150.2 (CH), 144.2 (C), 140.1 (C), 137.8 (CH), 136.9 (CH), 124.5 (CH), 123.1 (C) 116.6 (CN), 113.9 (C), 20.7 (CH_3).

4-Methyl-2-(pyridin-2-yl)benzonitrile (3c):

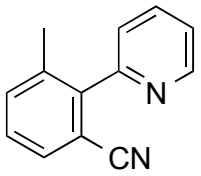


According to the general procedure the mono cyanated product was isolated in 78% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.67 (d, 1H, *J* = 4.3 Hz, HPy), 7.78-7.65 (m, 2H, HAr), 7.62-7.53 (m, 2H, HAr), 7.30-7.16 (m, 2H, HAr), 2.38 (s, 3H, -CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.4 (C), 149.9 (CH), 143.8 (C), 143.3 (C), 136.7 (CH), 133.9 (CH), 130.7 (CH), 129.5 (CH), 123.3 (CH), 123.2 (CH), 118.9 (CN), 108.0 (C), 21.8 (CH_3).

3-Methyl-2-(pyridin-2-yl)benzonitrile (3d):

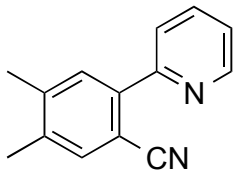


According to the general procedure the mono cyanated product was isolated in 60% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.77 (bs, 1H, HPy), 7.85 (t, 1H, *J* = 7.7 Hz, HAr), 7.60 (d, 1H, *J* = 7.4 Hz, HAr), 7.51 (d, 1H, *J* = 7.7 Hz, HAr), 7.47-7.31 (m, 3H, HAr), 2.22 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 156.0 (C), 149.7 (CH), 143.4 (C), 137.8 (C), 136.8 (CH), 134.8 (CH), 130.6 (CH), 128.5 (CH), 124.6 (CH), 123.2 (CH), 118.2 (CN), 112.7 (C), 20.0 (CH_3).

4,5-Dimethyl-2-(pyridin-2-yl)benzonitrile (3e):

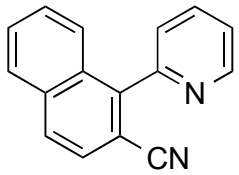


According to the general procedure the mono cyanated product was isolated in 45% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.75 (d, 1H, *J* = 4.1 Hz, HPy), 7.86-7.74 (m, 2H, HAr), 7.63 (s, 1H, HAr), 7.54 (s, 1H, HAr), 7.37-7.29 (m, 1H, HAr), 2.38 (s, 3H, -CH_3), 2.34 (s, 3H, -CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.3 (C), 149.8 (CH), 142.7 (C), 140.9 (C), 137.9 (C), 136.8 (CH), 134.8 (CH), 131.1 (CH), 123.2 (CH), 123.0 (CH), 119.1 (CN), 107.9 (C), 20.1 (CH_3), 19.3 (CH_3).

1-(Pyridin-2-yl)-2-naphthonitrile (3f):

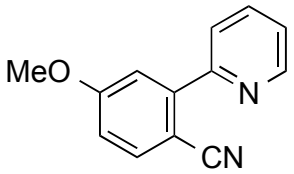


According to the general procedure the mono cyanated product was isolated in 54% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.86 (d, 1H, *J* = 4.3 Hz, HPy), 8.01-7.87 (m, 3H, HAr), 7.71 (d, 2H, *J* = 8.6 Hz, HAr), 7.67-7.57 (m, 2H, HAr), 7.56-7.49 (m, 1H, HAr), 7.49-7.42 (m, 1H, HAr).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.3 (C), 150.0 (CH), 144.4 (C), 136.8 (CH), 135.0 (C), 131.1 (C), 129.4 (CH), 128.8 (CH), 128.3 (CH), 127.9 (CH), 126.8 (CH), 126.7 (CH), 125.7 (CH), 123.5 (CH), 118.5 (CN), 109.7 (C).

4-Methoxy-2-(pyridin-2-yl)benzonitrile (3g):

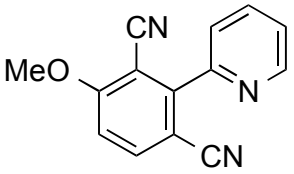


According to the general procedure the mono and dicyanated products were isolated in 61% and 20% yield, respectively using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.68 (d, 1H, *J* = 4.0 Hz, HPy), 7.79-7.68 (m, 2H, HAr), 7.62 (d, 1H, *J* = 8.5 Hz, HAr), 7.32-7.22 (m, 2H, HAr), 6.91 (d, 1H, *J* = 8.5 Hz, HAr), 3.83 (s, 3H, $-OCH_3$).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 162.8 (C), 155.1 (C), 149.9 (CH), 145.6 (C), 136.8 (CH), 135.7 (CH), 123.4 (CH), 123.3 (CH), 119.1 (CN), 115.1 (CH), 115.0 (CH), 102.7 (C), 55.7 (CH_3).

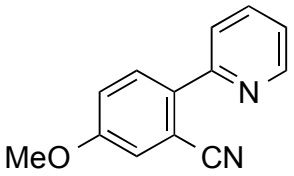
4-Methoxy-2-(pyridin-2-yl)isophthalonitrile (3g'):



^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.76 (d, 1H, *J* = 4.6 Hz, HPy), 7.91-7.76 (m, 2H, HAr), 7.61 (d, 1H, *J* = 8.2 Hz, HAr), 7.43-7.35 (m, 1H, HAr), 7.04 (d, 1H, *J* = 8.8 Hz, HAr), 3.99 (s, 3H, $-OCH_3$).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 164.3 (C), 152.3 (C), 150.2 (CH), 149.3 (C), 138.8 (CH), 136.9 (CH), 124.6 (CH), 124.4 (CH), 116.7 (CN), 113.5 (CN), 111.4 (CH), 105.5 (C), 103.8 (C), 57.0 (CH_3).

5-Methoxy-2-(pyridin-2-yl)benzonitrile (3h):

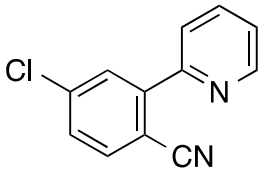


According to the general procedure the mono cyanated product was isolated in 76% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.74 (d, 1H, J = 3.8 Hz, HPy), 7.86-7.70 (m, 3H, HAr), 7.36-7.16 (m, 3H, HAr), 3.88 (s, 3H, -OCH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.5 (C), 155.0 (C), 149.8 (CH), 136.7 (CH), 136.0 (C), 131.3 (CH), 122.86 (CH), 122.83 (CH), 119.4 (CH), 118.7 (CN), 118.5 (CH), 111.7 (C), 55.7 (CH_3).

4-Chloro-2-(Pyridin-2-yl)benzonitrile (3i):

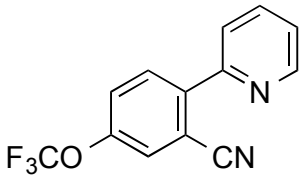


According to the general procedure the mono cyanated product was isolated in 47% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.78 (d, 1H, J = 4.7 Hz, HPy), 7.91-7.77 (m, 3H, HAr), 7.73 (d, 1H, J = 8.3 Hz, HAr), 7.49 (d, 1H, J = 8.3 Hz, HAr), 7.39 (t, 1H, J = 6.0 Hz, HAr).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.9 (C), 150.1 (CH), 144.9 (C), 139.5 (C), 137.0 (CH), 135.2 (CH), 130.3 (CH), 129.1 (CH), 123.9 (CH), 123.2 (CH), 117.9 (CN), 109.3 (C).

2-(Pyridin-2-yl)-5-(trifluoromethoxy)benzonitrile (3j):

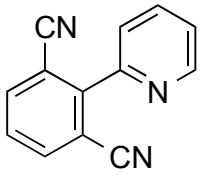


According to the general procedure the mono cyanated product was isolated in 38% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.78 (d, 1H, *J* = 4.0 Hz, HPy), 7.96-7.83 (m, 2H, HAr), 7.79 (d, 1H, *J* = 7.5 Hz, HAr),7.65 (s, 1H, HAr), 7.55 (d, 1H, *J* = 8.8 Hz, HAr), 7.44-7.36 (m, 1H, HAr).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.9 (C), 150.1 (CH), 148.9 (C), 142.0 (C), 137.0 (CH), 131.8 (CH), 125.9 (CH), 125.4 (CH), 123.7 (CH), 123.2 (CH), 118.9 (CN), 117.6 (q, *J* = 261 Hz, C), 112.5 (C).

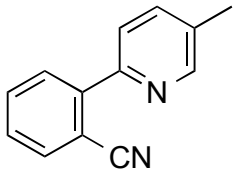
2-(Pyridin-2-yl)isophthalonitrile (3k):



^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.84 (d, 1H, *J* = 4.6 Hz, HPy), 8.00 (d, 2H, *J* = 7.9 Hz, HAr), 7.93 (td, 1H, *J* = 7.8, 1.7 Hz, HAr), 7.73 (d, 1H, *J* = 7.8 Hz, HAr), 7.65 (t, 1H, *J* = 7.8 Hz, HAr), 7.48 (ddd, 1H, *J* = 7.7, 4.8, 0.9 Hz, HAr).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.1 (C), 150.3 (CH), 146.9 (C), 137.3 (CH), 137.1 (CH), 129.3 (CH), 124.7 (CH), 124.5 (CH), 116.5 (CN), 114.2 (C).

2-(5-Methylpyridin-2-yl)benzonitrile (3n):

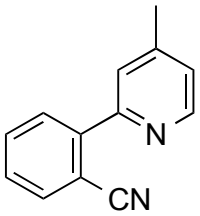


According to the general procedure the mono cyanated product was isolated in 66% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.50 (s, 1H, HPy), 7.73 (d, 1H, *J* = 7.9 Hz, HAr), 7.69 (d, 1H, *J* = 7.6 Hz, HAr), 7.62-7.50 (m, 3H, HAr), 7.38 (t, 1H, *J* = 7.6 Hz, HAr), 2.31 (s, 3H, -CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.4 (C), 150.4 (CH), 143.5 (C), 137.3 (CH), 134.0 (CH), 133.2 (C), 132.8 (CH), 129.8 (CH), 128.4 (CH), 122.7 (CH), 118.8 (CN), 110.9 (C), 18.2 (CH_3).

2-(4-Methylpyridin-2-yl)benzonitrile (3o):

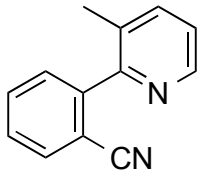


According to the general procedure the mono cyanated product was isolated in 82% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.60 (d, 1H, *J* = 4.3 Hz, HPy), 7.85-7.72 (m, 2H, HAr), 7.66 (t, 1H, *J* = 7.6 Hz, HAr), 7.57 (s, 1H, HAr), 7.47 (t, 1H, *J* = 7.6 Hz, HAr), 7.16 (d, 1H, *J* = 4.0 Hz, HAr), 2.43 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.1 (C), 149.5 (CH), 148.2 (C), 143.5 (C), 134.0 (CH), 132.8 (CH), 129.9 (CH), 128.6 (CH), 124.3 (CH), 124.2 (CH), 118.7 (CN), 111.1 (C), 21.2 (CH_3).

2-(3-Methylpyridin-2-yl)benzonitrile (3p):



According to the general procedure the mono cyanated product was isolated in 70% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.48 (s, 1H, HPy), 7.69 (d, 1H, J = 7.3 Hz, HAr), 7.64-7.53 (m, 2H, HAr), 7.47-7.37 (m, 2H, HAr), 7.24-7.17 (m, 1H, HAr), 2.18 (s, 3H, -CH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.5 (C), 147.1 (CH), 144.3 (C), 138.5 (CH), 133.0 (CH), 132.6 (CH), 131.7 (C), 129.9 (CH), 128.4 (CH), 123.5 (CH), 117.8 (CN), 112.4 (C), 19.0 (CH_3).

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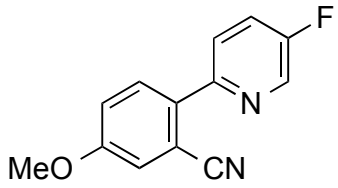
2-(5-Fluoropyridin-2-yl)-5-methoxybenzonitrile (3q):



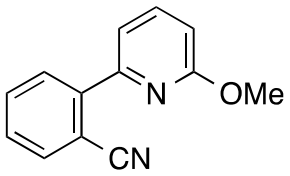
According to the general procedure the mono cyanated product was isolated in 42% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography.

IR (KBr): 2223 cm^{-1} (C≡N).

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.51 (d, 1H, *J* = 2.8 Hz, HAr), 7.72-7.63 (m, 2H, HAr), 7.44 (td, 1H, *J* = 8.1, 2.9 Hz, HAr), 7.20-7.17 (m, 1H, HAr), 7.13 (dd, 1H, *J* = 8.7, 2.7 Hz, HAr), 3.81 (s, 3H, OCH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.6 (C), 157.9 (d, *J* = 258.1 Hz, C), 150.2 (d, J = 3.8 Hz, C), 137.1 (d, *J* = 23.9 Hz, CH), 133.9 (C), 130.3 (CH), 122.8 (d, *J* = 4.2 Hz, C), 122.5 (d, *J* = 18.1 Hz, C), 118.4 (CH), 117.5 (CN), 117.4 (CH), 110.6 (C), 54.7 (CH_3).

2-(6-Methoxypyridin-2-yl)benzonitrile (3r):

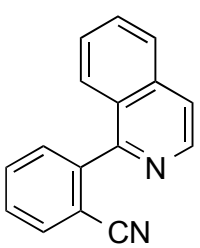


According to the general procedure the mono cyanated product was isolated in 24% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.80-7.69 (m, 2H, HAr), 7.66-7.54 (m, 2H, HAr), 7.41 (t, 1H, *J* = 7.7 Hz, HAr), 7.24 (d, 1H, *J* = 7.5 Hz, HAr), 6.73 (d, 1H, *J* = 8.2 Hz, HAr), 4.01 (s, 3H, OCH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 163.8 (C), 161.5 (C), 152.5 (C), 143.0 (C), 139.2 (CH), 134.7 (CH), 132.5 (CH), 129.4 (CH), 128.5 (CH), 119.2 (CN), 115.3 (CH), 111.1 (C), 54.0 (CH_3).

2-(Isoquinolin-1-yl)benzonitrile (3s):

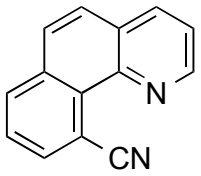


According to the general procedure the mono cyanated product was isolated in 74% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.57 (d, 1H, *J* = 5.5 Hz, HAr), 7.82 (d, 1H, *J* = 8.0 Hz, HAr), 7.77 (d, 1H, *J* = 7.5 Hz, HAr), 7.70-7.58 (m, 4H, HAr), 7.55 (d, 1H, *J* = 7.3 Hz, HAr), 7.52-7.39 (m, 2H, HAr).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 156.9 (C), 143.0 (C), 142.2 (CH), 136.7 (C), 133.5 (CH), 132.4 (CH), 130.9 (CH), 130.5 (CH), 128.9 (CH), 127.8 (CH), 127.3 (CH), 126.8 (C), 126.5 (CH), 121.3 (CH), 117.8 (CN), 113.2 (C).

Benzo[*h*]isoquinoline-10-carbonitrile (3t):

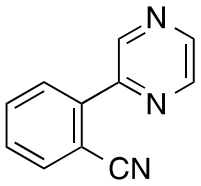


According to the general procedure the reaction mixture was stirred at 120 ^{o}C for 48h, the mono cyanated product was isolated in 82% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 9.14-9.05 (m, 1H, HAr), 8.18 (d, 1H, *J* = 8.0 Hz, HAr), 8.14-8.02 (m, 2H, HAr), 7.82-7.64 (m, 3H, HAr), 7.59 (dd, 1H, *J* = 8.1, 4.4 Hz, HAr).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 147.4 (CH), 143.3 (C), 135.2 (CH), 134.6 (CH), 132.9 (C), 131.7 (CH), 129.6 (C), 126.3 (CH), 126.2 (CH), 126.0 (CH), 125.9 (C), 122.0 (CH), 119.8 (CN), 107.8 (C).

2-(Pyrazin-2-yl)benzonitrile (3u):



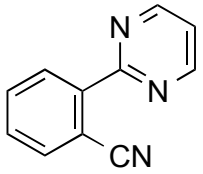
According to the general procedure the reaction was done by using 2 mol% of catalyst. The mono cyanated product was isolated in 51% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography.

IR (KBr): 2220 cm^{-1} (C≡N).

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 9.04 (s, 1H, HAr), 8.75 (s, 1H, HAr), 8.66 (s, 1H, HAr), 7.91 (m, 2H, HAr), 7.75 (t, 1H, *J* = 7.6 Hz, HAr), 7.59 (t, 1H, *J* = 7.6 Hz, HAr).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 151.1 (C), 144.3 (2 × CH), 144.0 (CH), 140.0 (C), 134.5 (CH), 133.0 (CH), 129.4 (CH), 129.7 (CH), 118.1 (CN), 111.4 (C).

2-(Pyrimidin-2-yl)benzonitrile (3v):

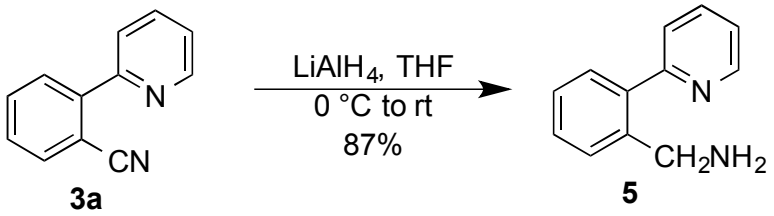


According to the general procedure the reaction was done by using 2 mol% of catalyst. The mono cyanated product was isolated in 42% yield using the mixture of ethyl acetate/hexane as an eluent for column chromatography. The spectra data are in agreement with the literature report.[3]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.91 (d, 2H, *J* = 4.8 Hz, HAr), 8.36 (d, 1H, *J* = 7.9 Hz, HAr), 7.84 (d, 1H, *J* = 7.7 Hz, HAr), 7.71 (t, 1H, *J* = 7.5 Hz, HAr), 7.57 (d, 1H, *J* = 7.7 Hz, HAr), 7.32 (t, 1H, *J* = 5.0 Hz, HAr).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 161.8 (C), 156.3 (CH), 139.3 (C), 134.0 (CH), 131.5 (CH), 129.4 (CH), 129.2 (CH), 119.1 (CH), 117.9 (CN), 110.8 (C).

5. Synthesis of 2-(pyridin-2-yl)benzylamine (5):[4]



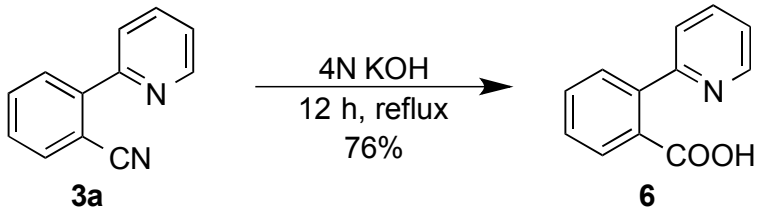
3a **5**

To a solution of 2-(pyridine-2-yl)benzonitrile (**3a**) (0.2 mmol, 1eq) in THF (2 mL) was added LAH (0.25 mmol, 1.25 eq) in portion wise. After stirring the reaction mixture for 1h, it was quenched with Na_2SO_4 until it forms precipitate. To the resulting mixture add 2 mL of ethylacetate filtered, dried over Na_2SO_4 and concentrated in *vacuo* to afford product **5** with 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.64 (d, 1H, *J* = 4.2 Hz, HPy), 7.81-7.76 (m, 1H, HAr), 7.50-7.46 (m, 1H, HAr), 7.44-7.40 (m, 1H, HAr), 7.39-7.36 (m, 3H, HAr), 7.29-7.26 (m, 1H, HAr), 3.84 (s, 2H, -CH_2), 3.62 (s, 2H, -NH_2).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.3 (C), 148.8 (CH), 140.1 (C), 138.8(C), 137.3(CH), 131.0 (CH), 130.2 (CH), 129.3 (CH), 128.2 (CH), 124.0 (CH), 122.4 (CH), 44.6 (CH_2).

6. Synthesis of 2-(Pyridin-2-yl)benzoic acid (6):[5]



3a **6**

The mixture of 2-(pyridine-2-yl)benzonitrile (**3a**) (0.2 mmol, 1eq) and 4N KOH (0.5 mL) was refluxed for 12 h. After the reaction completion, as monitored by TLC, the reaction mixture was diluted with 5 mL of ethyl acetate. Then the mixture was neutralized by dil. HCl. The

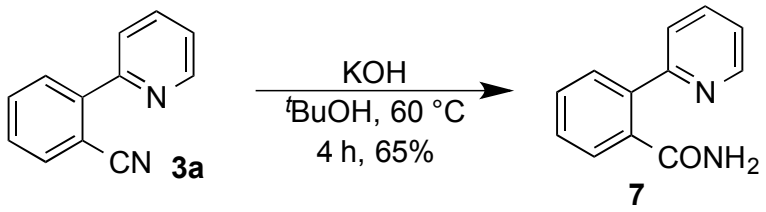
[4] Liskey, C. W.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 11389-11391.

organic layer was collected and dried over Na_2SO_4. The solvent was concentrated in vacuo and purified by column chromatography to afford the product **6** with 76% yield. The spectra data are in agreement with the literature report.[5]

^{1}H NMR (400 MHz, MeOH-d_4, 24 °C): δ 8.63 (m, 1H, *J* = 4.2 Hz, HPy), 8.01 (m, 2H, HAr), 7.72-7.70 (m, 1H, HAr), 7.61 (m, 3H, HAr), 7.49 (m, 1H, HAr).

^{13}C{^{1}H} NMR (100 MHz, MeOH-d_4, 24 °C): δ 171.5 (C=O), 160.3 (C), 149.1 (CH), 142.0 (C), 138.5 (CH), 133.2(CH), 132.4 (CH), 131.3(CH), 131.1 (CH), 129.7 (CH), 125.1 (CH), 125.1 (CH), 123.7 (CH).

7. Synthesis of 2-(pyridin-2-yl)benzamide (7):[4]



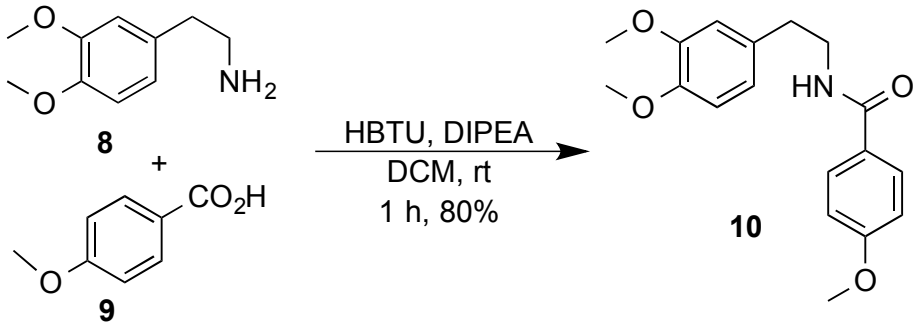
In a reaction tube 2-(pyridine-2-yl)benzonitrile (**3a**) (0.172 mmol, 1eq) was dissolved in *t*-BuOH (0.5 mL). Solid KOH (3.225 mmol, 18.75 eq) was added and the reaction mixture was heated at 60 ^{o}C for 4h. Then the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, concentrated in *vacuo* and purified by column chromatography to afford product **7** with 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.62 (d, 1H, *J* = 4.2 Hz, HPy), 7.77-7.72 (m, 1H, HAr), 7.68-7.66 (m, 1H, HAr), 7.52-7.50 (m, 3H, HAr), 7.46-7.42 (m, 1H, HAr), 7.29-7.26 (m, 1H, HAr), 6.36 (s, 1H, -NH), 5.95 (s, 1H, -NH).

[5] Rebstock, A.-S.; Mongin, F.; Trécourt, F.; Quéguiner, G. *Tetrahedron*, **2003**, *59*, 4973-4977.

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 172.0 (C=O), 158.4 (C), 149.1 (CH), 138.8(C), 136.8(CH), 135.4 (C), 130.4 (CH), 130.2 (CH), 128.65 (CH), 128.65 (CH), 124.0 (CH), 122.5 (CH).

8. Synthesis of *N*-(3,4-Dimethoxyphenethyl)-4-methoxybenzamide (10):



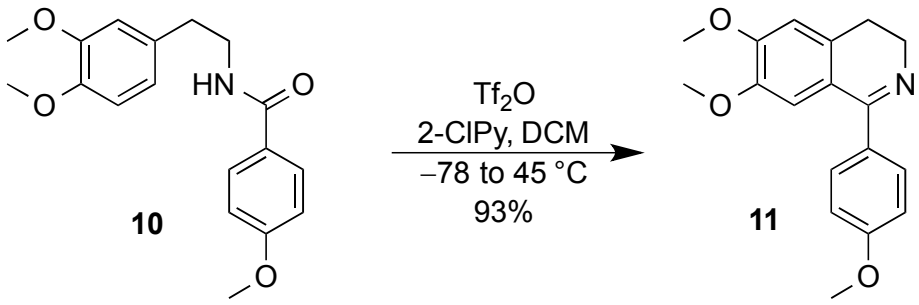
In a 25 mL round-bottom flask 2-(3,4-dimethoxyphenyl)ethanamine **8** (1.77 mmol, 1eq) and dry dichloromethane (10 mL) was added followed by *p*-methoxy benzoic acid **9** (1.77mmol, 1eq), HBTU (2.124 mmol, 1.2eq) and diisopropyl ethylamine (2.12 mmol, 1.2 eq) under nitrogen atmosphere. Then the reaction mixture was stirred at room temperature for 1h. After the completion of reaction, as monitored by TLC the reaction mixtture was extracted with dichloromethane. The combined organic layers was dried over Na_2SO_4 and concentrated in *vacuo*. The resulting mixture was purified by column chromatography to afford product **10** with 80% yield. The spectra data are in agreement with the literature report.[6]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.65(d, 1H, J = 8.7 Hz HAr), 6.88 (d, 2H, J = 8.6 Hz, HAr), 6.81 (d, 1H, J = 8.0 Hz, HAr), 6.76-6.73 (m, 2H, HAr), 6.13 (s, 1H, -NH), 3.85 (s, 3H, $-OCH_3$), 3.82 (s, 6H, $-OCH_3$), 3.68-3.63 (m, 2H, $-C\mathbf{H}_2CH_2NH$), 2.85 (t, 2H, J = 6.9 Hz - $CH_2C\mathbf{H}_2NH$),

[6] Jia, X.; Yang, D.; Zhang, S.; Cheng, J. *Org. Lett.* **2009**, *11*, 4716-4719.

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.0 (C=O), 162.2(C), 149.1 (C), 147.7 (C), 131.6 (C), 128.6 (CH), 126.9 (C), 120.7 (CH), 113.8 (CH), 112.0 (CH), 111.5 (CH), 56.0 (OCH_3), 56.0 (OCH_3), 55.5 (OCH_3), 41.3 (CH_2), 35.4 (CH_2).

9. Synthesis of 6,7-Dimethoxy-1-(4-methoxyphenyl)-3,4-dihydroisoquinoline (11):

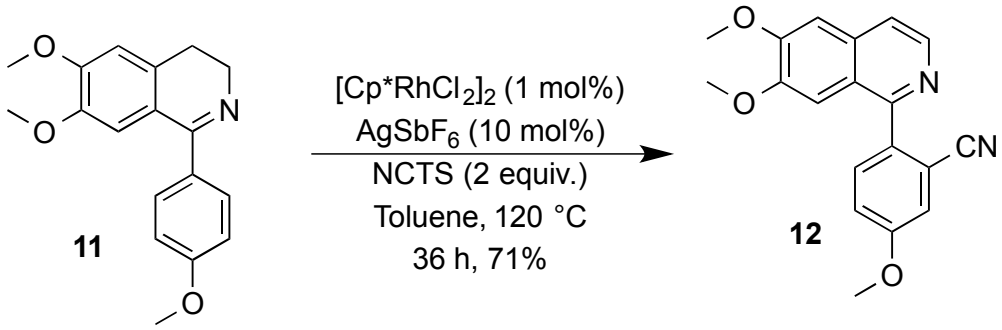


To a stirred mixture of amide **10** (0.79 mmol, 1eq) and 2-chloropyridine (0.094 mmol, 1.2 eq) in dichloro methane (5 mL) triflouromethanesulfonic anhydride (0.88 mmol, 1.12 eq) was introduced over 1 min at -78 ^{o}C. After 5 min, the resulting solution was allowed to warm to room temperture, susequently kept at 45 °C. After 1h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. The reaction mixture was diluated with dichloromethane (5 mL) and washed with brine, died over anhydrous sodium sulfate. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography on alumina gel to afford the product **11** as a pale yellow solid product with 93% yield. The spectra data are in agreement with the literature report.[5]

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.61(d, 2H, J = 8.5 Hz, HAr), 6.95 (d, 2H, J = 8.5 Hz, HAr), 6.83 (s, 1H, HAr), 6.78 (s, 1H, HAr), 3.94 (s, 3H, -OCH_3), 3.84 (s, 3H, -OCH_3), 3.84-3.82 (m, 2H, -C**H**$_2$CH_2N), 3.73 (s, 3H, -OCH_3), 2.75 (t, 2H, J = 6.9 Hz -CH_2C**H**$_2$N).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 166.9 (C), 161.2 (C), 147.3 (C), 143.3 (C), 133.3 (C), 130.9 (CH), 130.1 (C), 121.2 (CH), 113.8 (CH), 112.3 (CH), 110.5 (CH), 56.3 (OCH_3), 56.2 (OCH_3), 55.4 (OCH_3), 46.5 (CH_2), 26.1 (CH_2).

10. Synthesis of 2-(6,7-dimethoxyisoquinolin-1-yl)-5-methoxybenzonitrile (12):



A dry reaction tube was charged with arenes **11** (0.2 mmol), *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide (NCTS) **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.002 mmol, 1 mol%), $AgSbF_6$ (0.02 mmol, 10 mol%) and dry toluene (2 mL) under nitrogen atmosphere. The reaction tube was sealed under nitrogen atmosphere and kept at 120 °C and continued stirring for 36h. After the completion of the reaction, as monitored by TLC the reaction mixture was cooled to room temperature and purified by preparative TLC using mixture of hexane and ethyl acetate as eluent to afford the cyanated product **12** in 71% yield. The spectra data are in agreement with the literature report.[5]

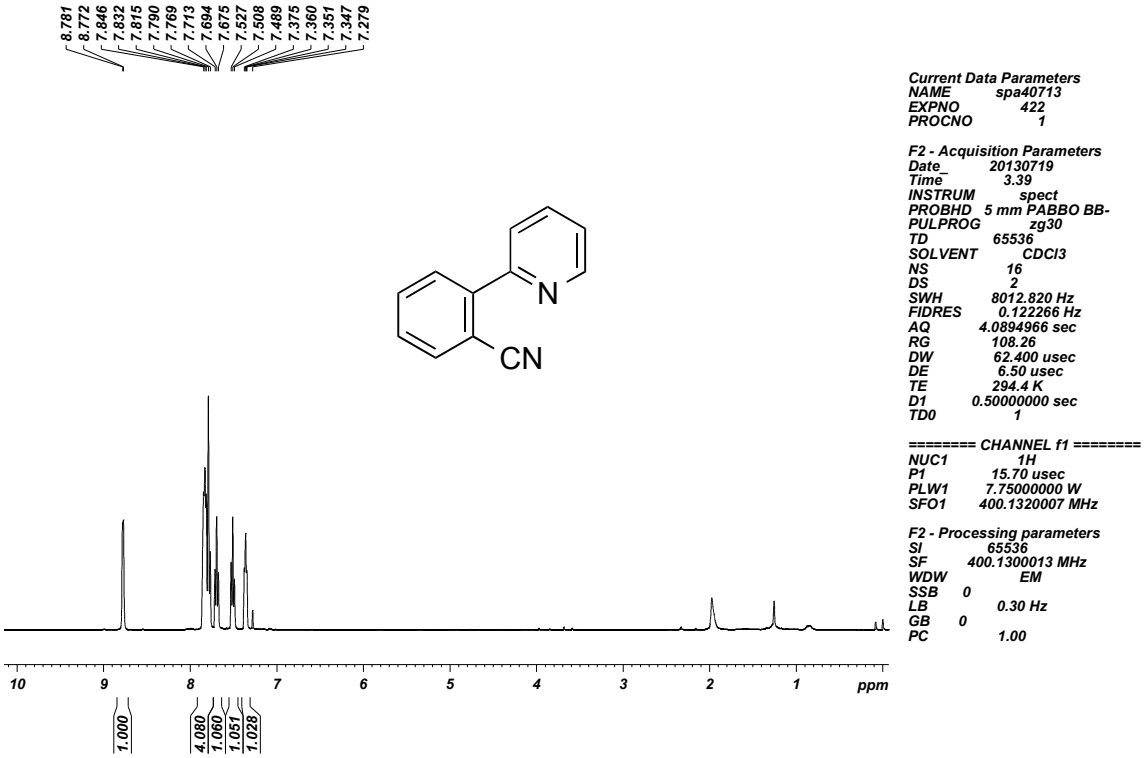
^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.51 (d, 1H, J = 5.7 Hz, HAr), 7.63-7.55 (m, 2H, HAr), 7.34 (s, 1H, HAr), 7.27 (s, 1H, HAr), 7.15 (s, 1H, HAr), 6.98 (s, 1H, HAr), 4.05 (s, 3H, -OCH_3), 3.93 (s, 3H, -OCH_3), 3.86 (s, 3H, -OCH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.4 (C), 154.2 (C), 153.0 (C), 150.5 (C), 141.3 (CH), 135.8 (C), 133.8 (C), 132.1 (CH), 123.0 (C), 119.9 (CH), 118.9 (CH), 117.9 (CH), 117.7 (C), 113.9 (CN), 105.1 (CH), 104.6 (CH), 56.1 (OCH_3), 55.9 (OCH_3), 55.8 (OCH_3).

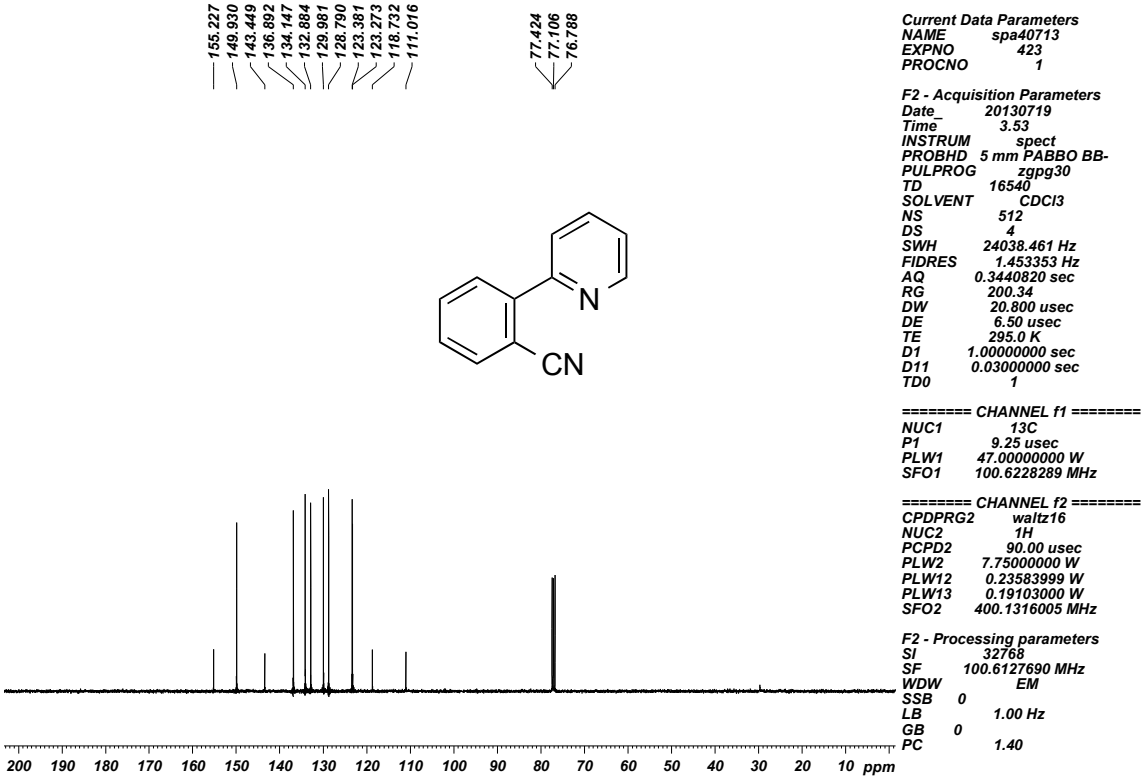
11. NMR spectra of isolated benzonitriles:

2-(pyridin-2-yl)benzonitrile (3a):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

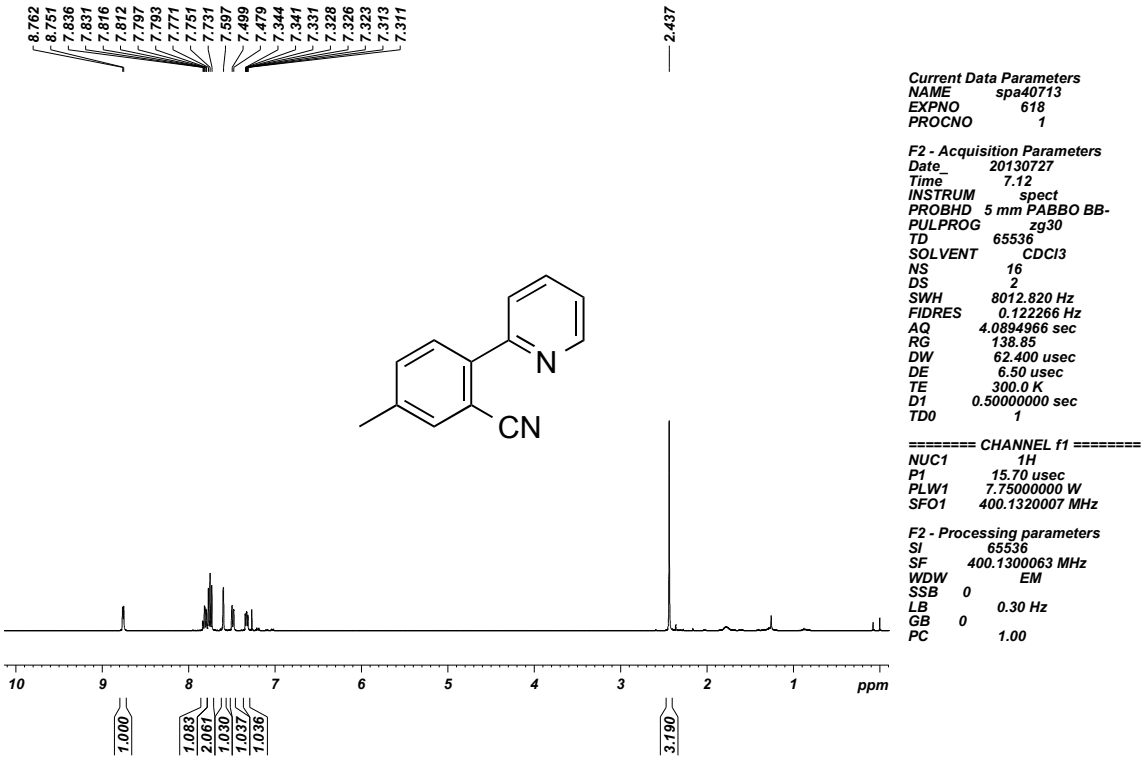


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

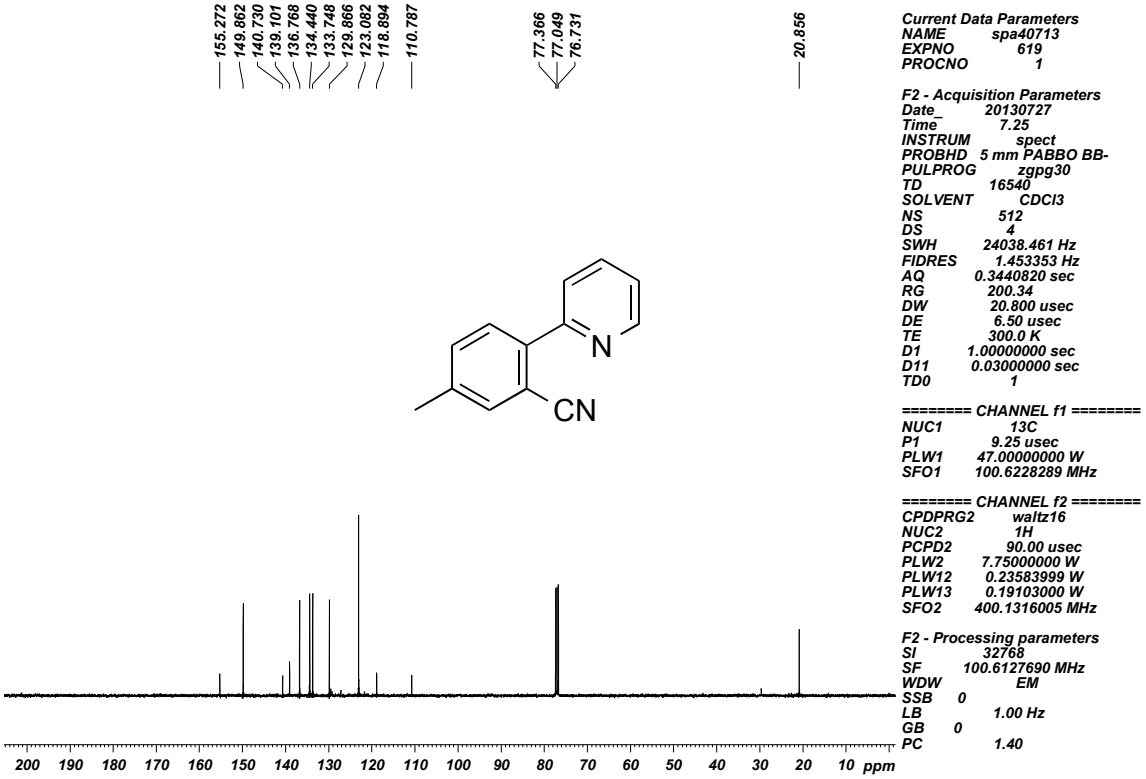


5-Methyl-2-(pyridin-2-yl)benzonitrile (3b):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

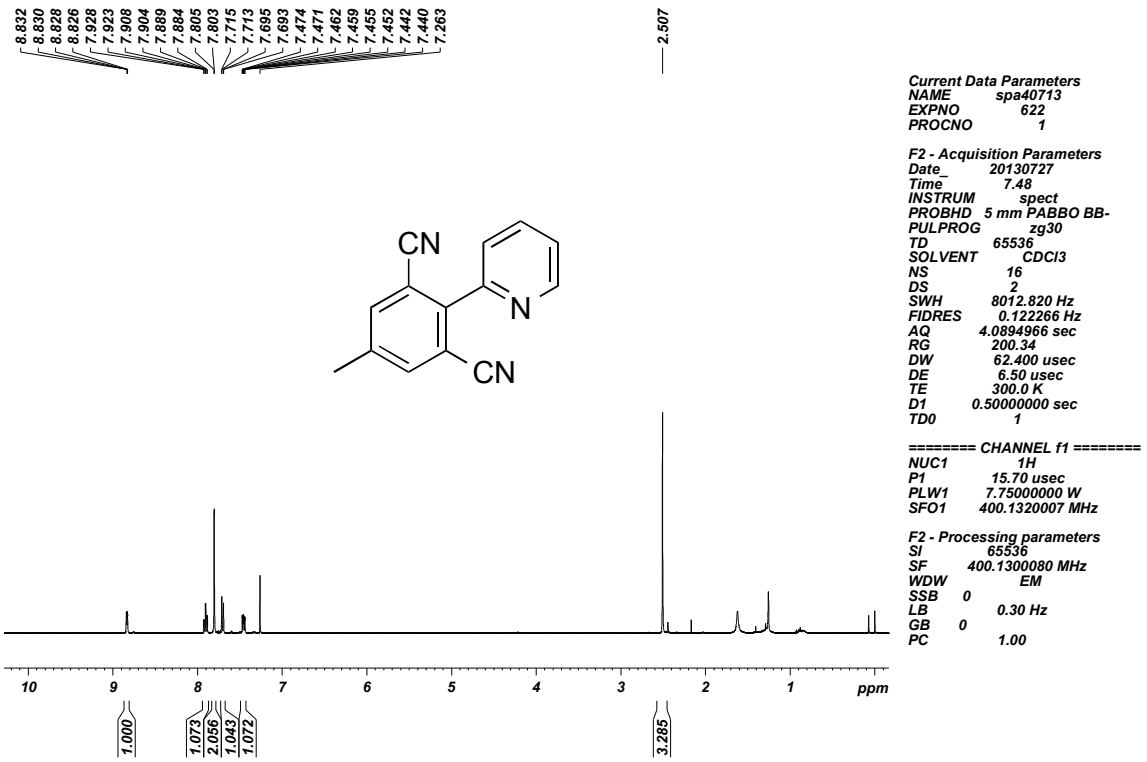


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

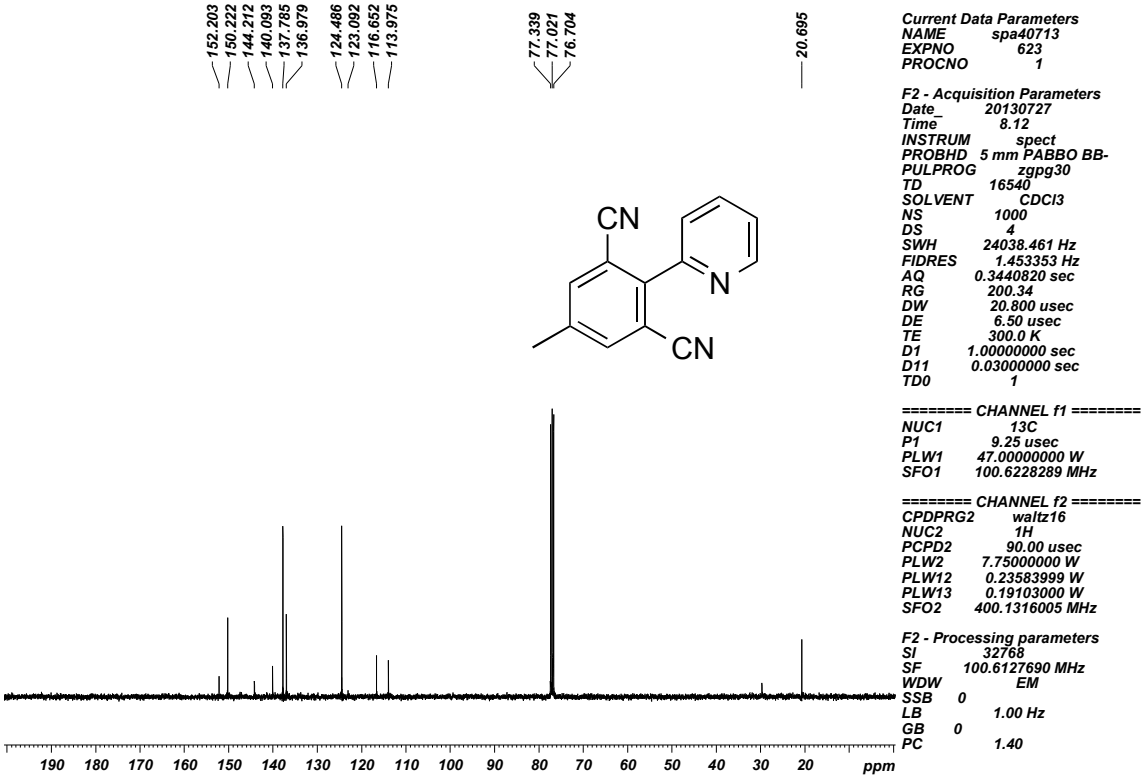


5-Methyl-2-(pyridin-2-yl)isophthalonitrile (3b'):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

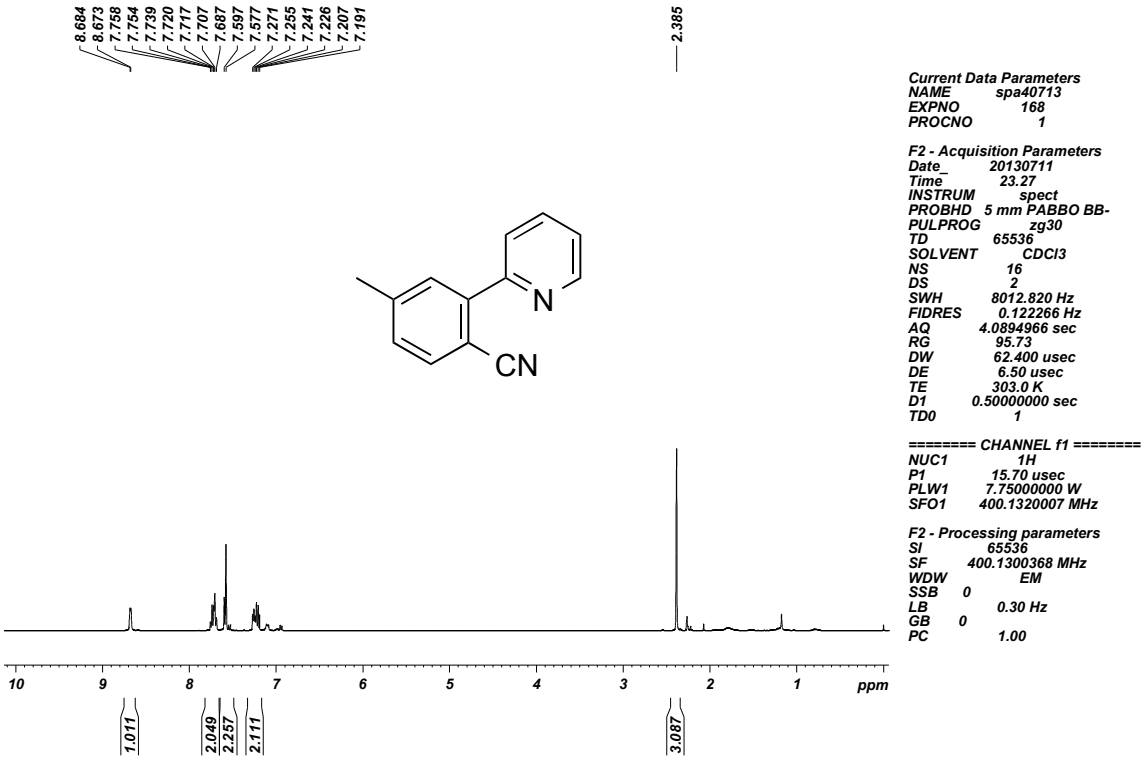


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

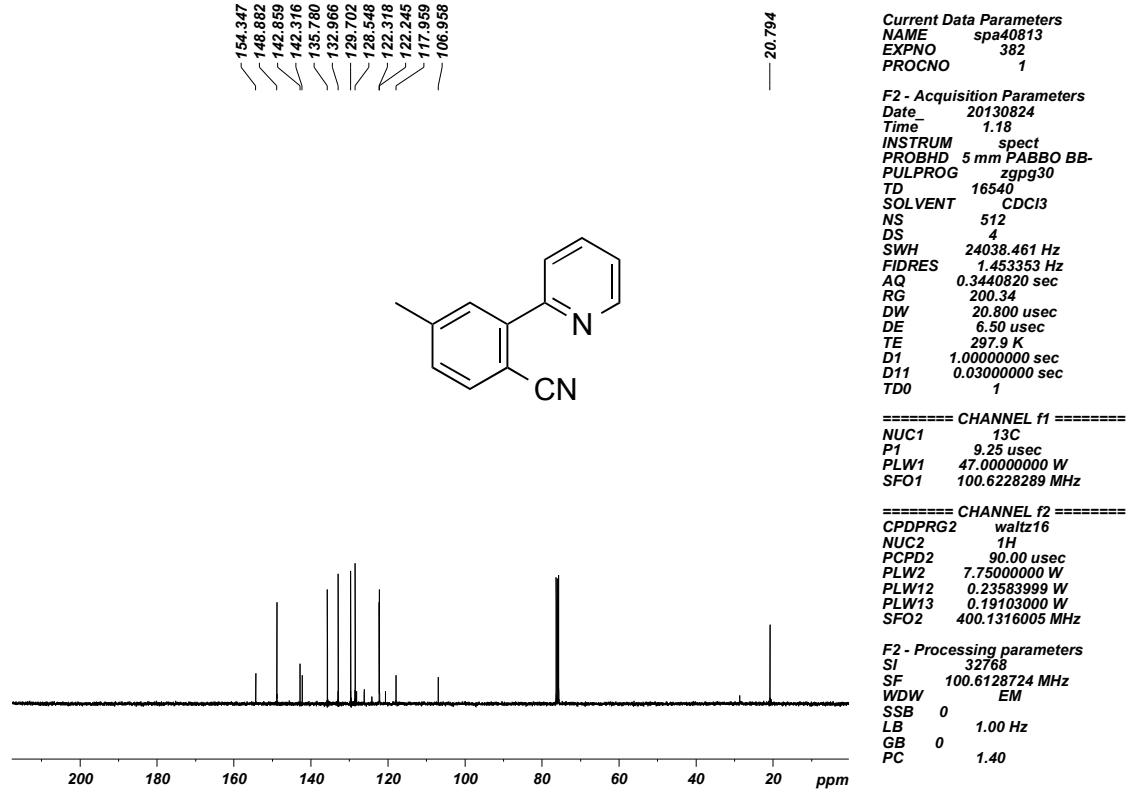


4-Methyl-2-(pyridin-2-yl)benzonitrile (3c):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

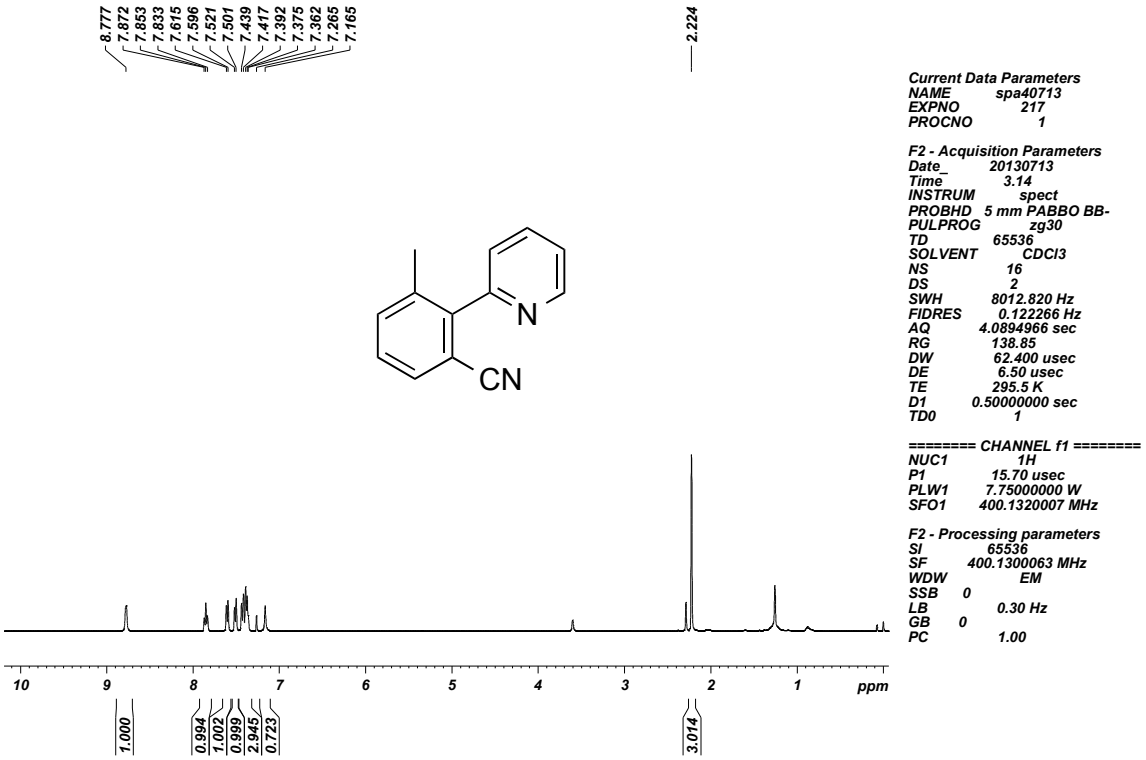


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

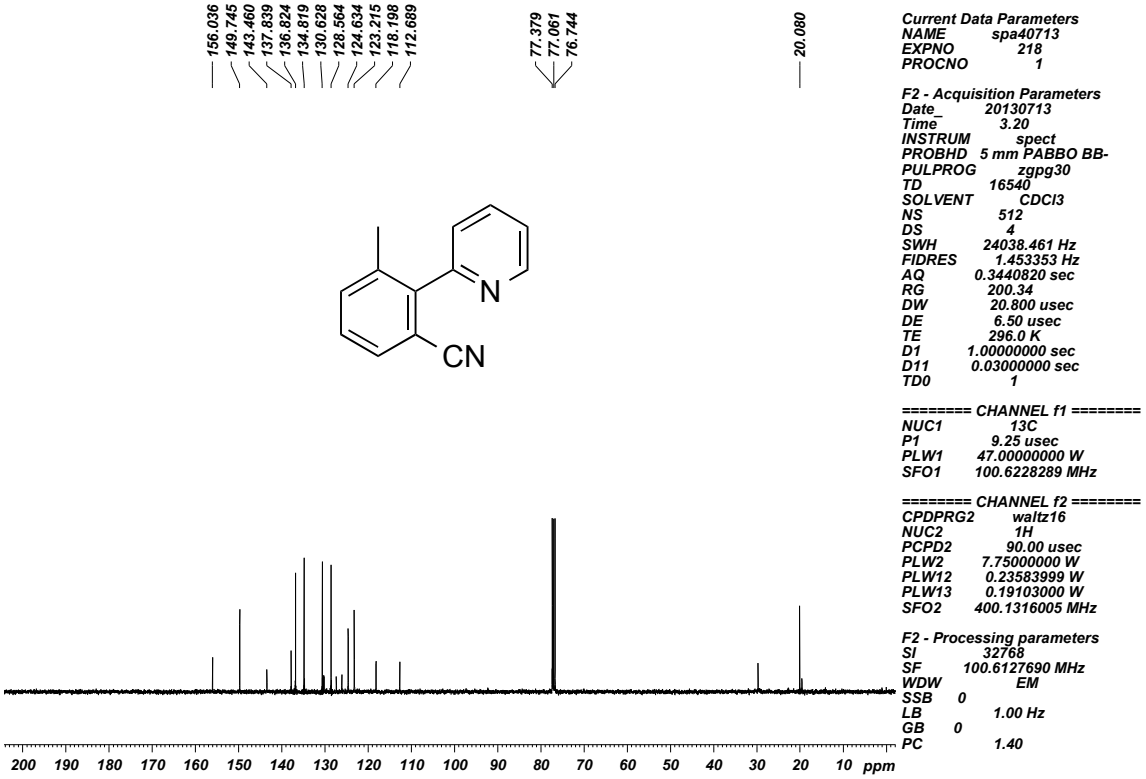


3-Methyl-2-(pyridin-2-yl)benzonitrile (3d):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

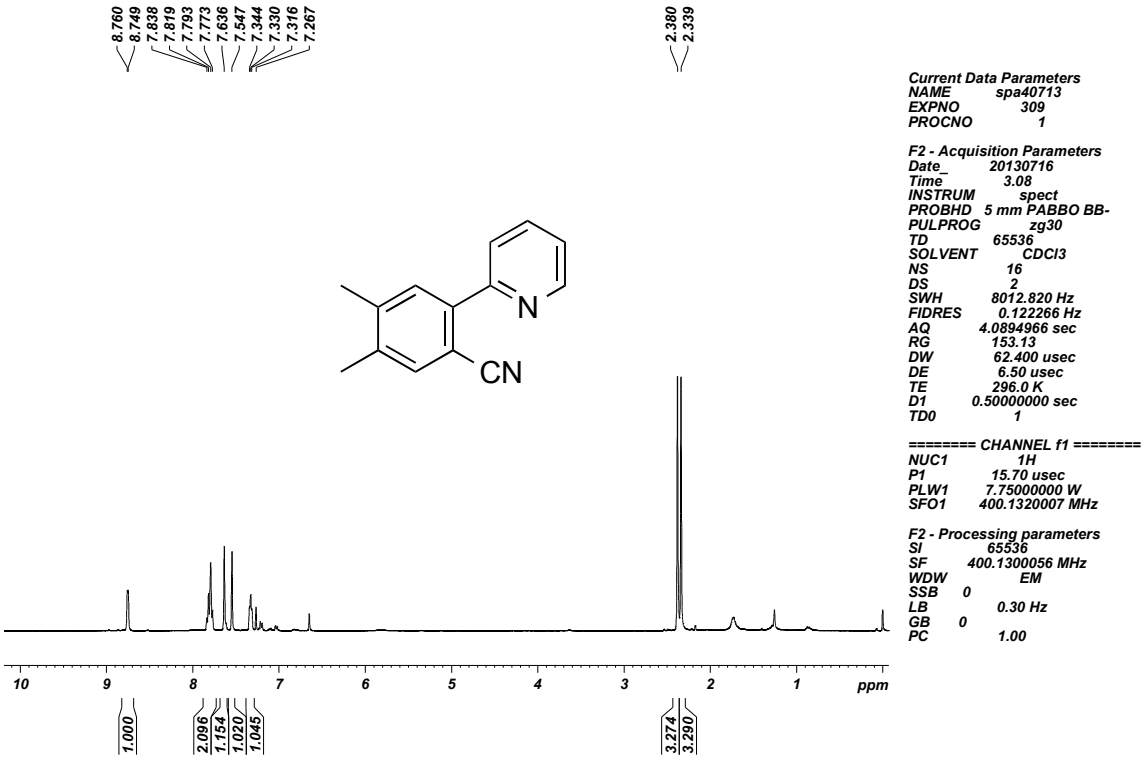


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

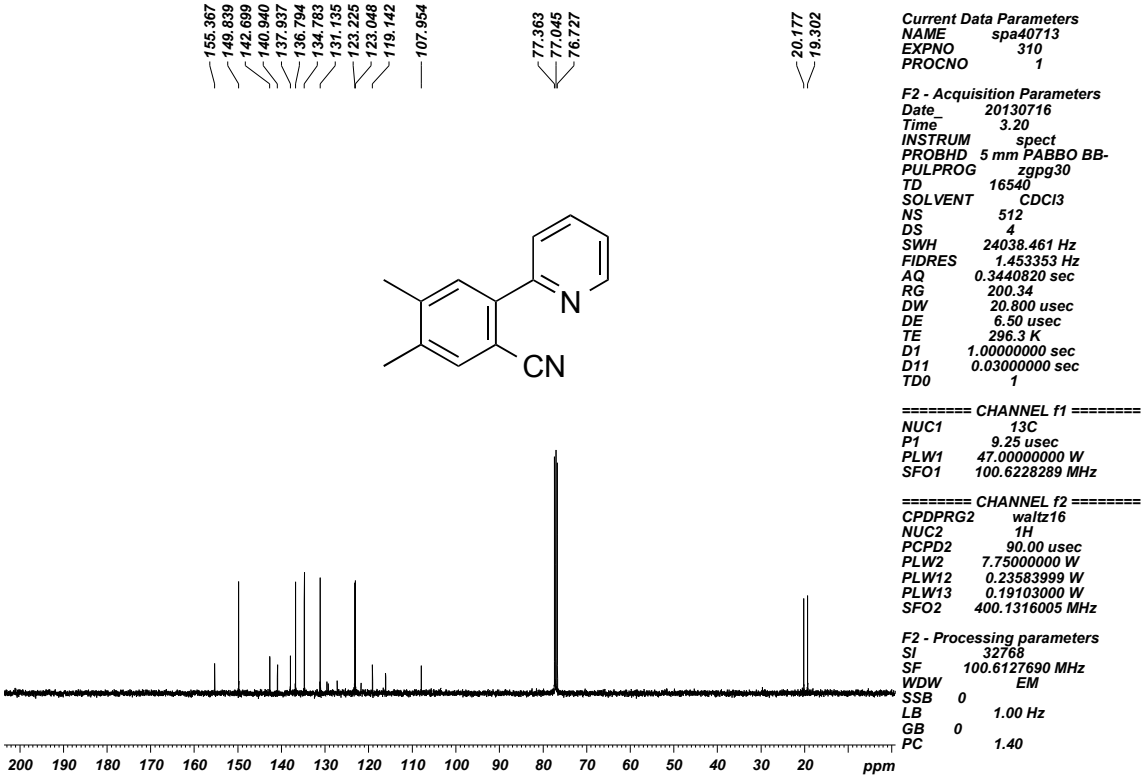


4,5-Dimethyl-2-(pyridin-2-yl)benzonitrile (3e):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

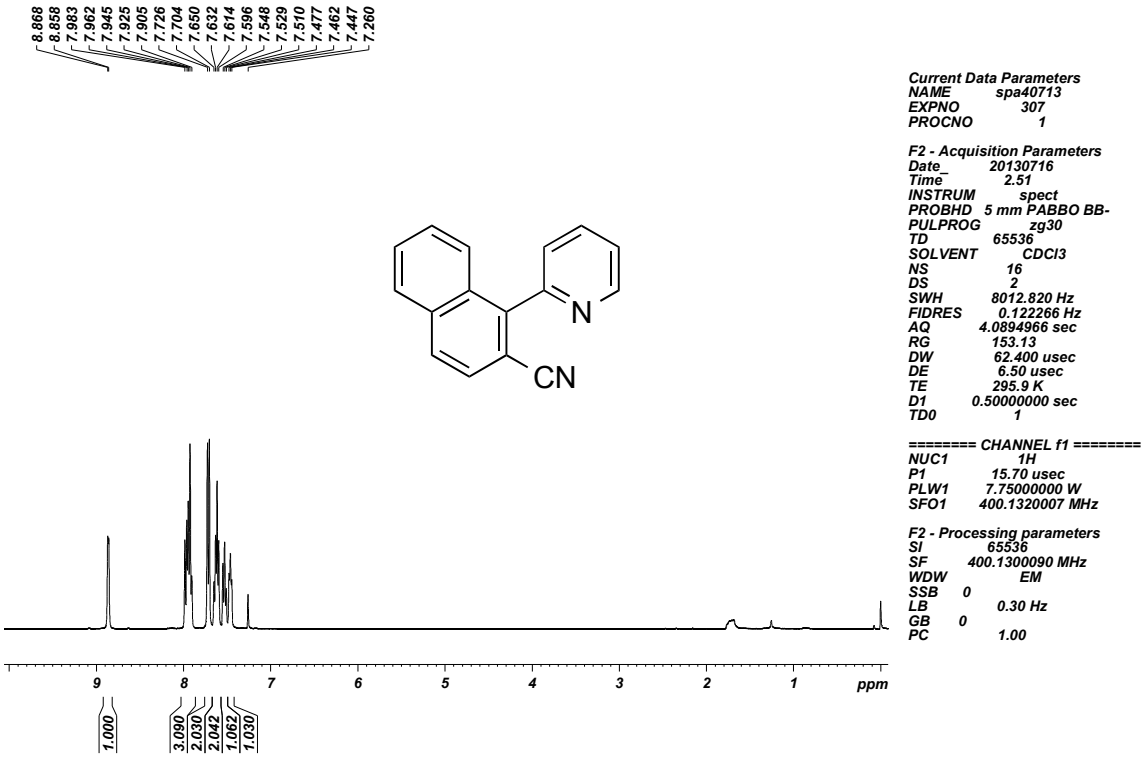


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

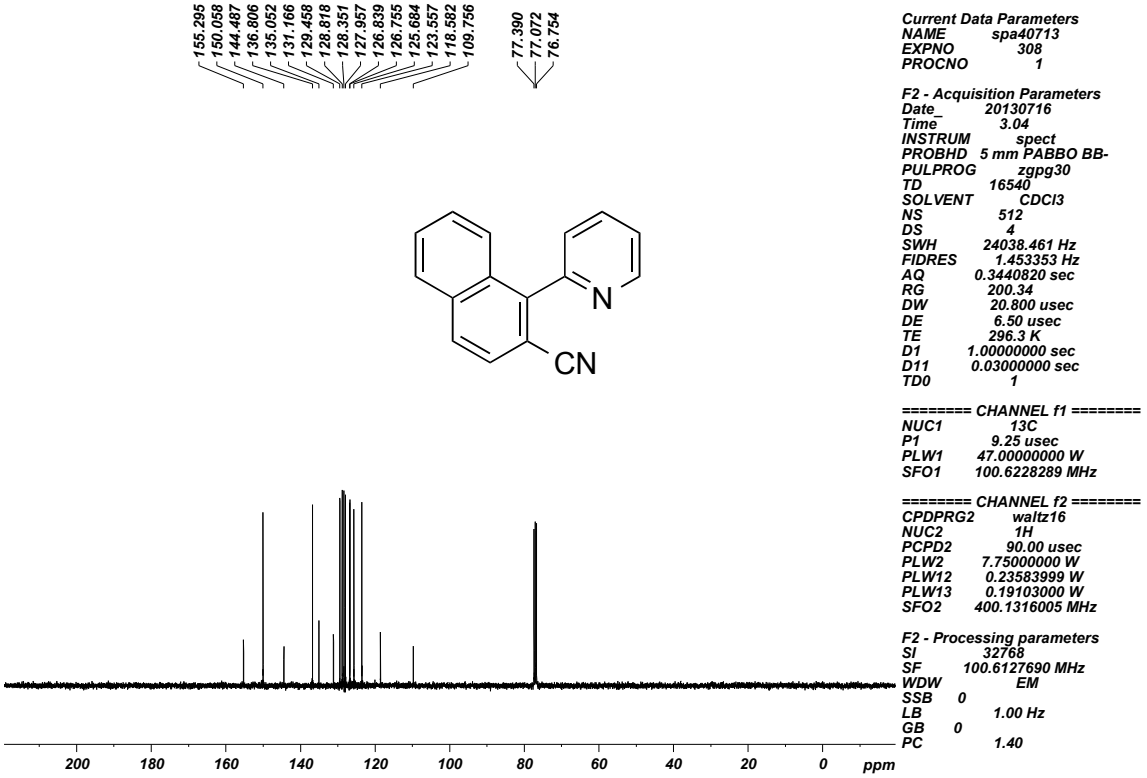


1-(Pyridin-2-yl)-2-naphthonitrile (3f):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

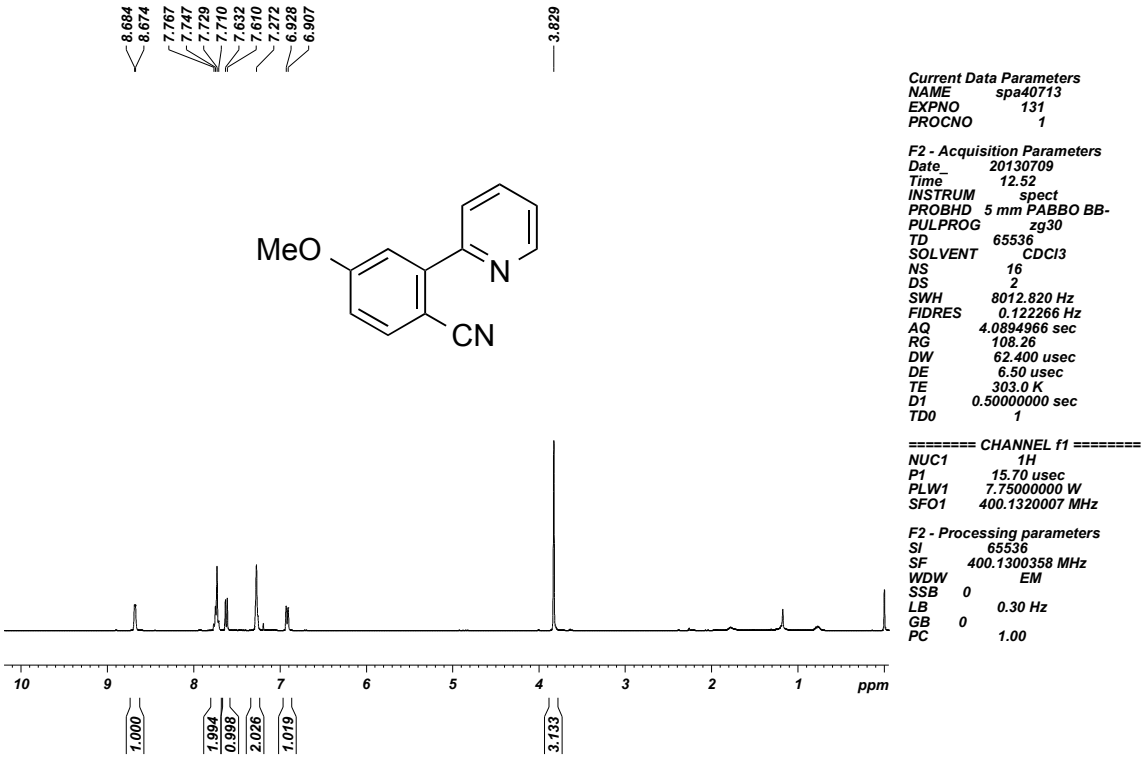


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

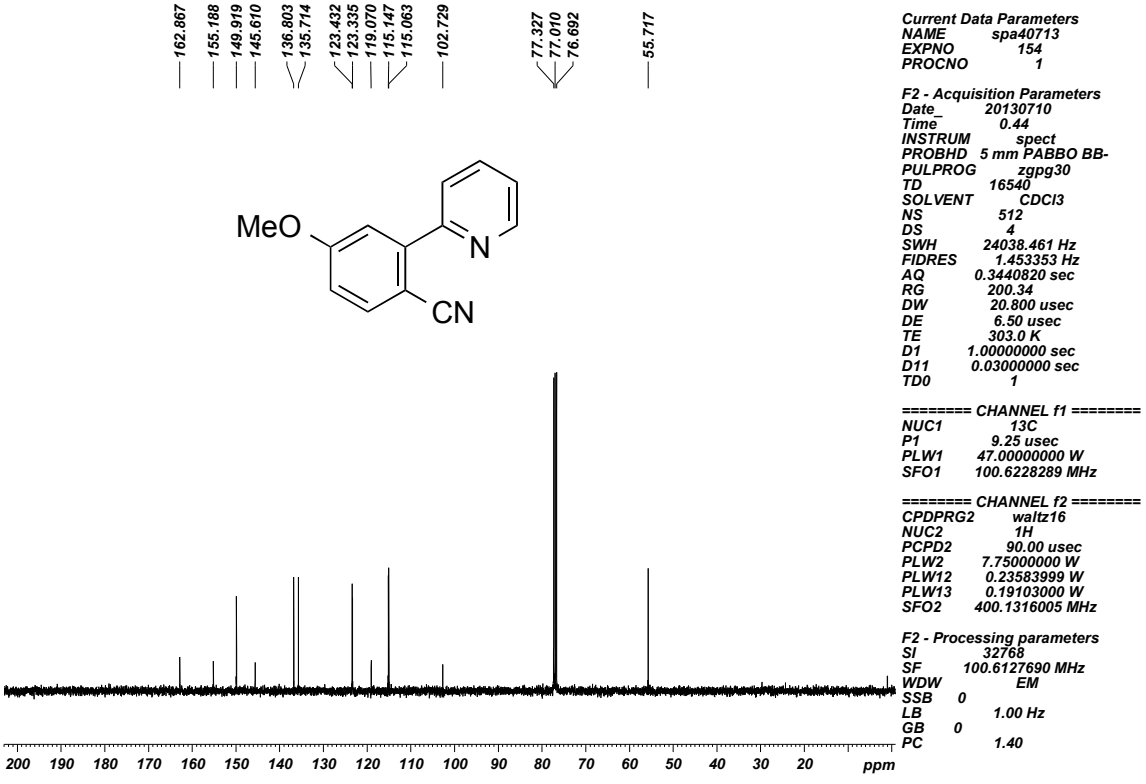


4-Methoxy-2-(pyridin-2-yl)benzonitrile (3g):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

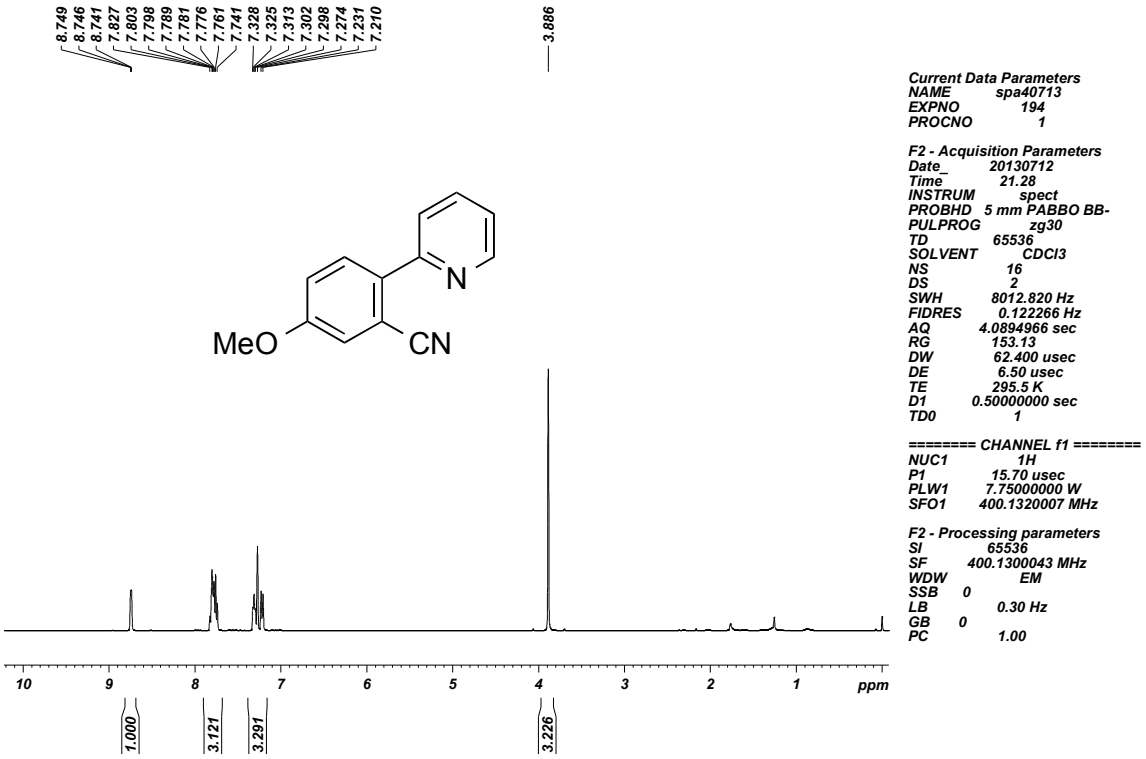


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

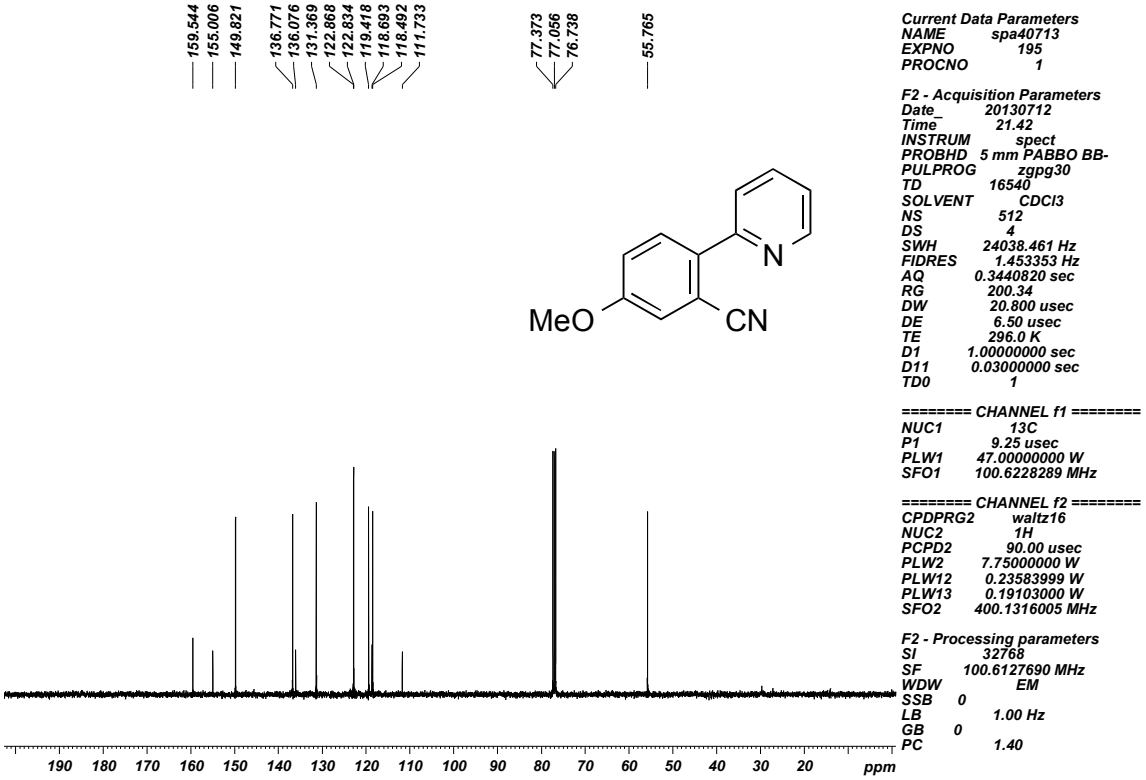


5-Methoxy-2-(pyridin-2-yl)benzonitrile (3h):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

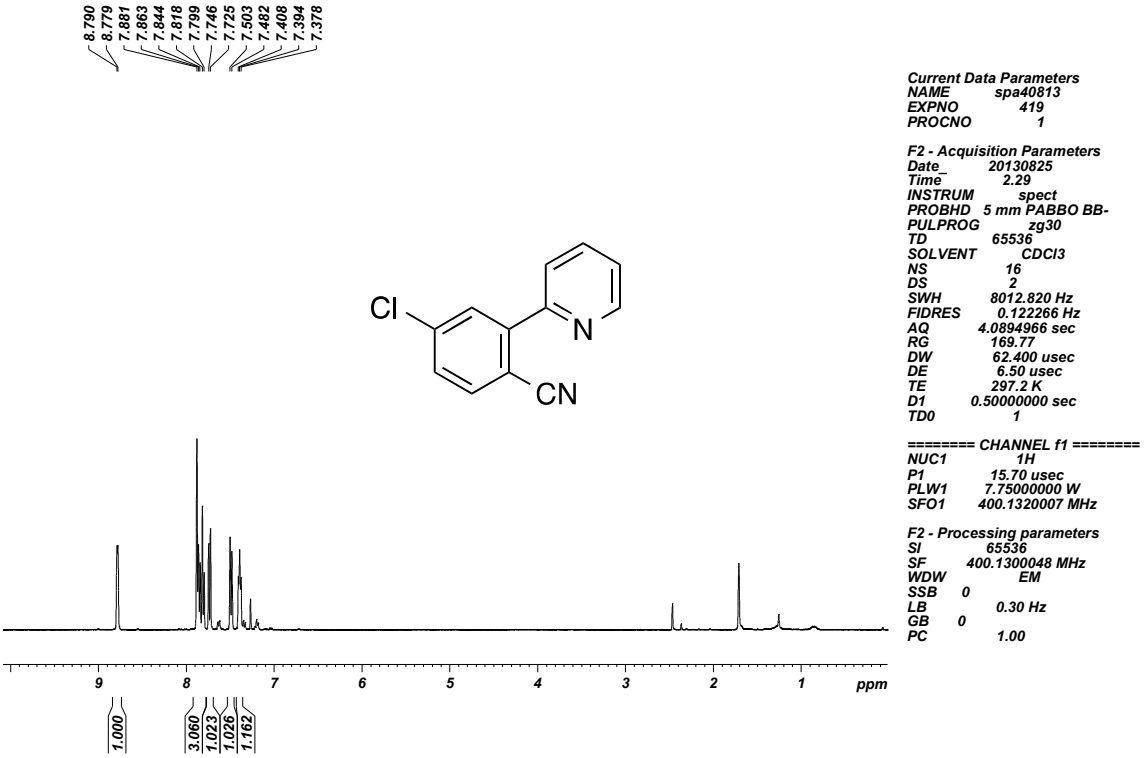


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

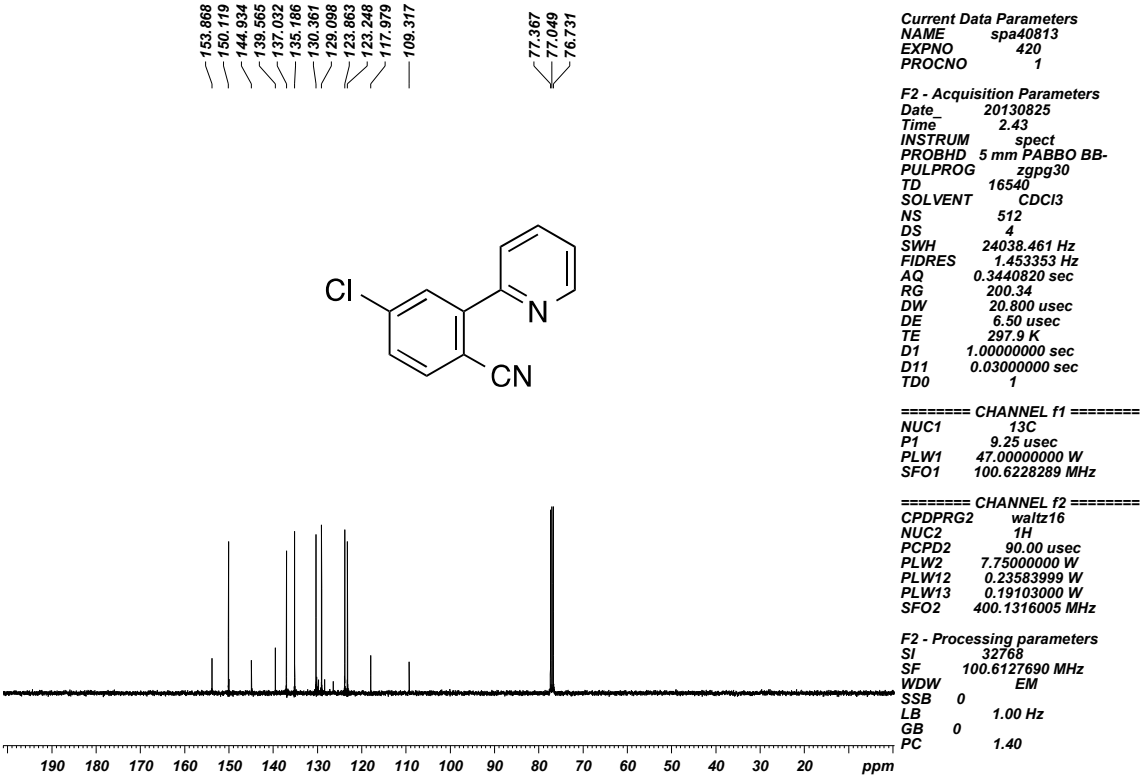


4-Chloro-2-(Pyridin-2-yl)benzonitrile (3i):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

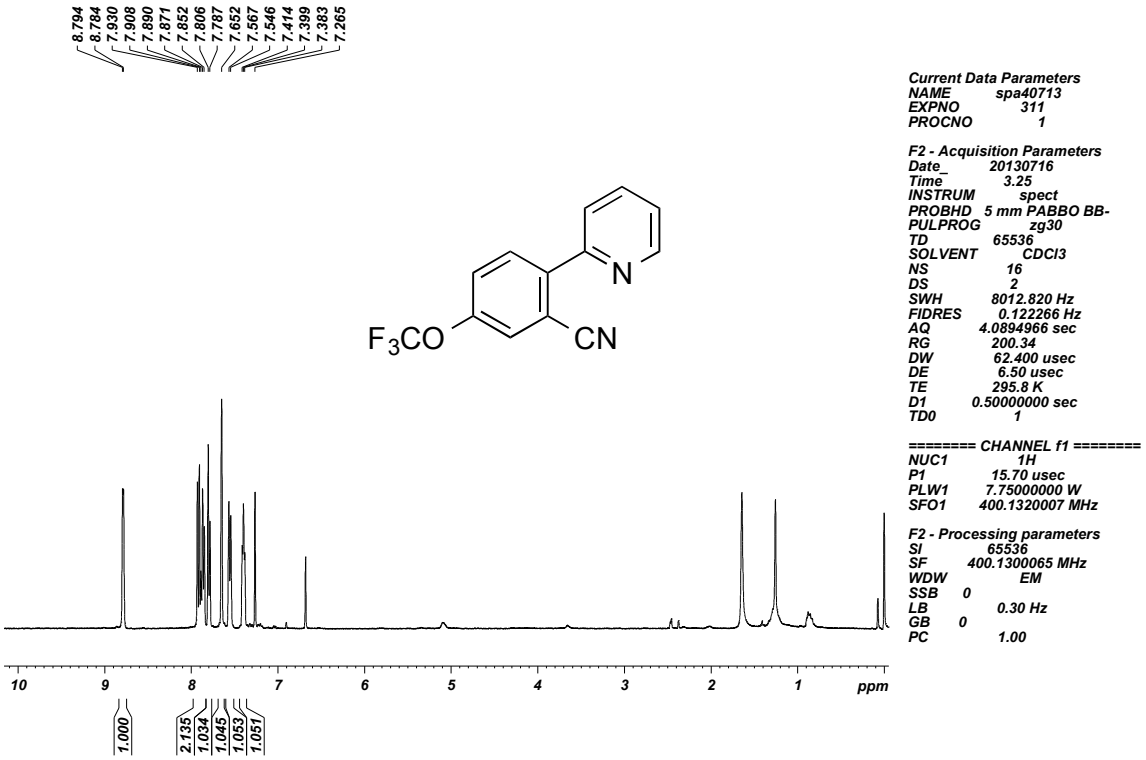


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

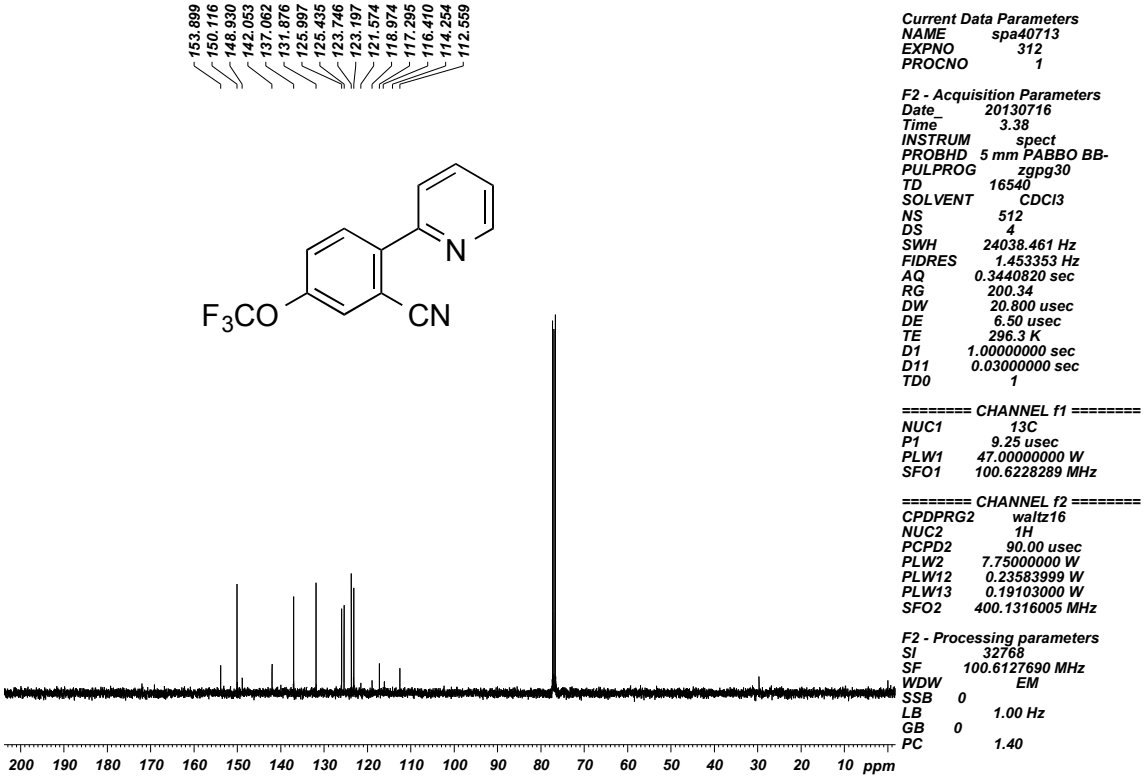


2-(Pyridin-2-yl)-5-(trifluoromethoxy)benzonitrile (3j):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

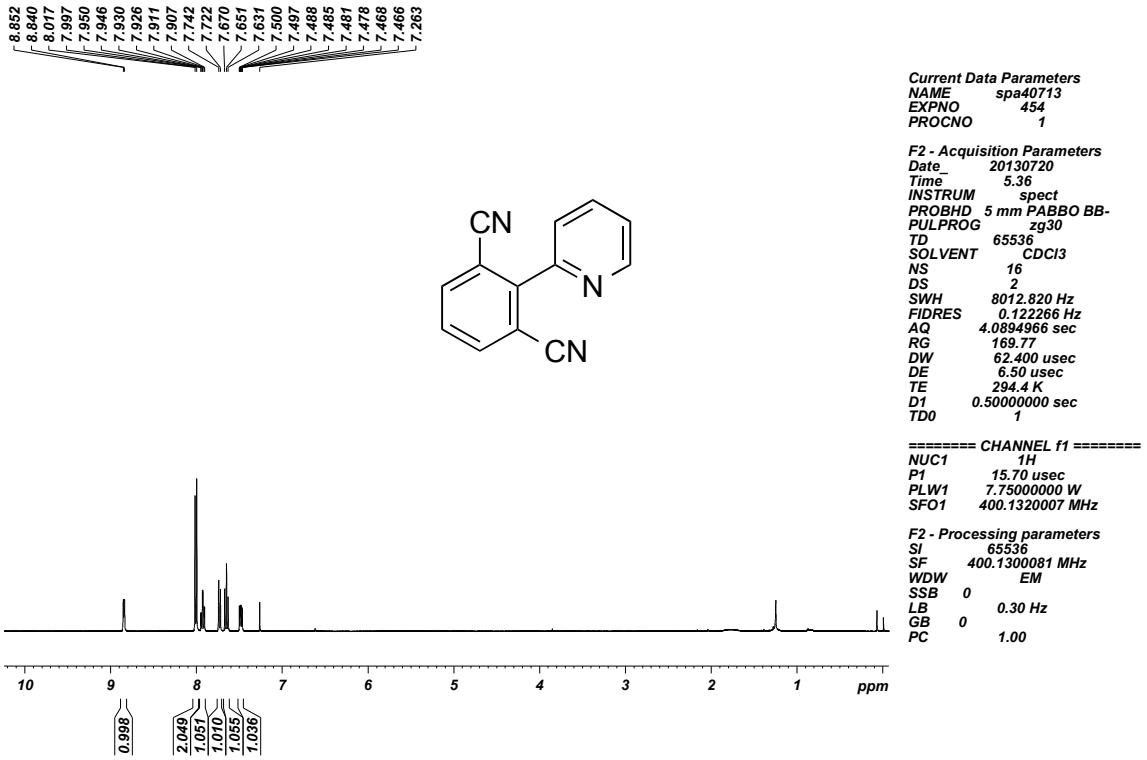


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

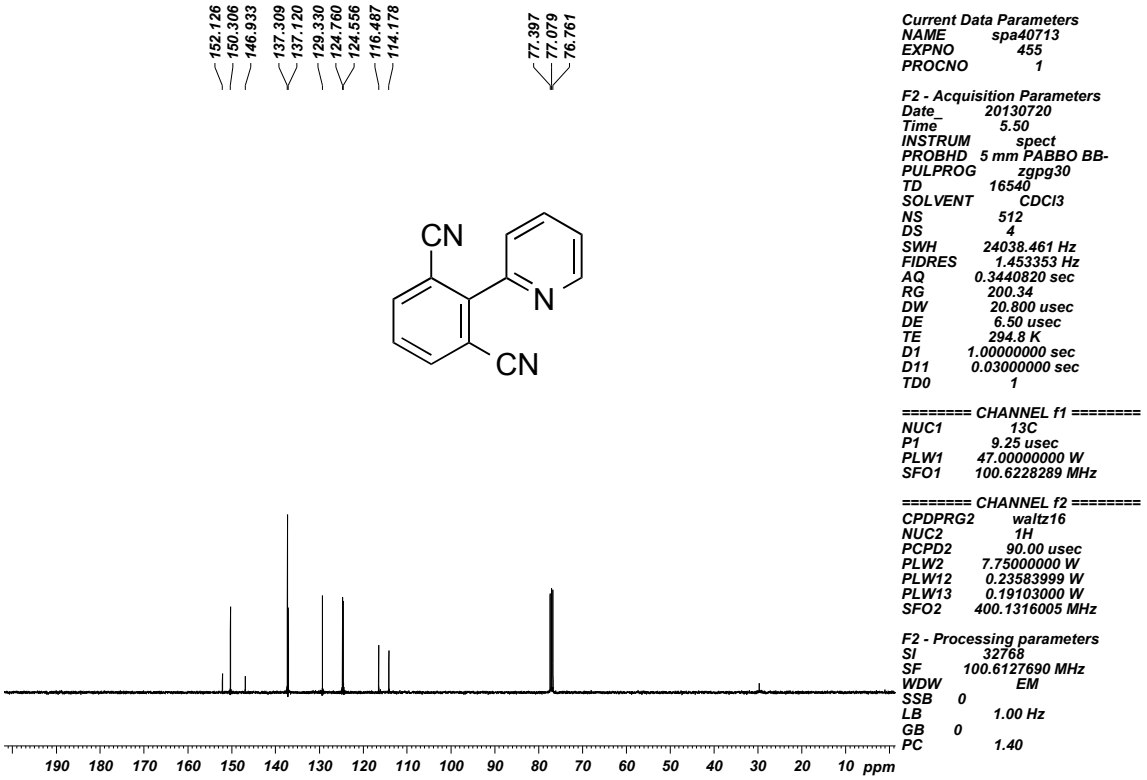


2-(Pyridin-2-yl)isophthalonitrile (3k):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

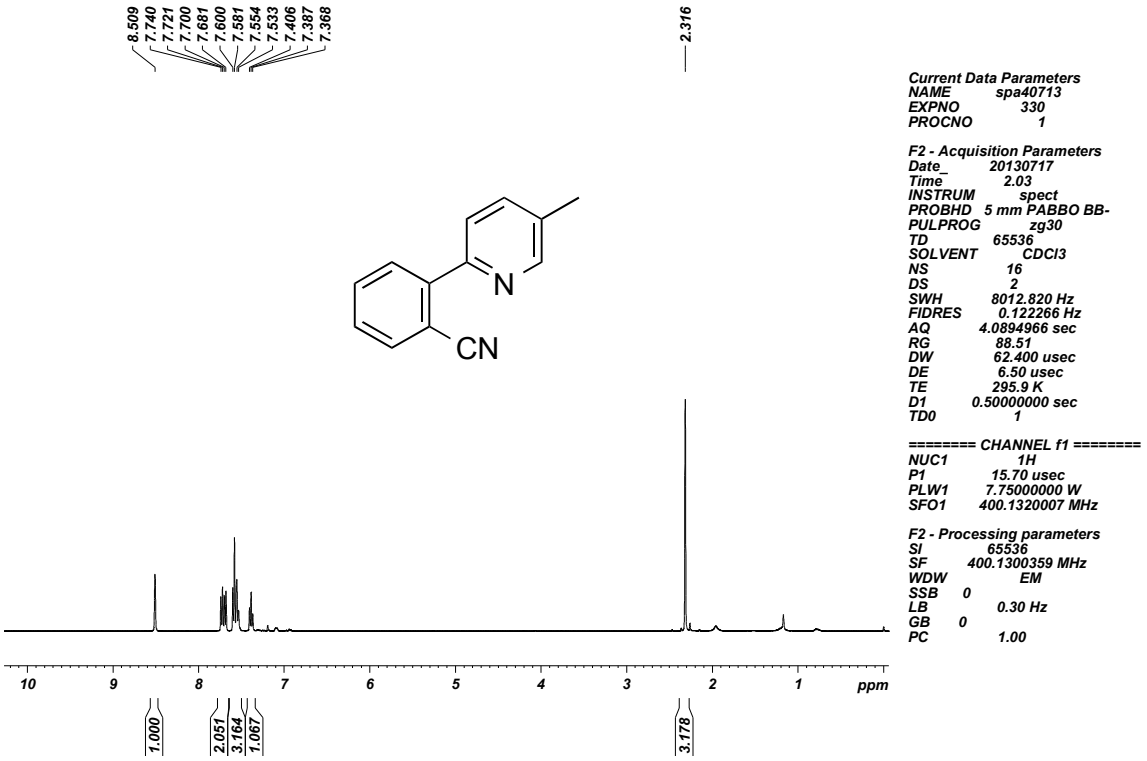


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

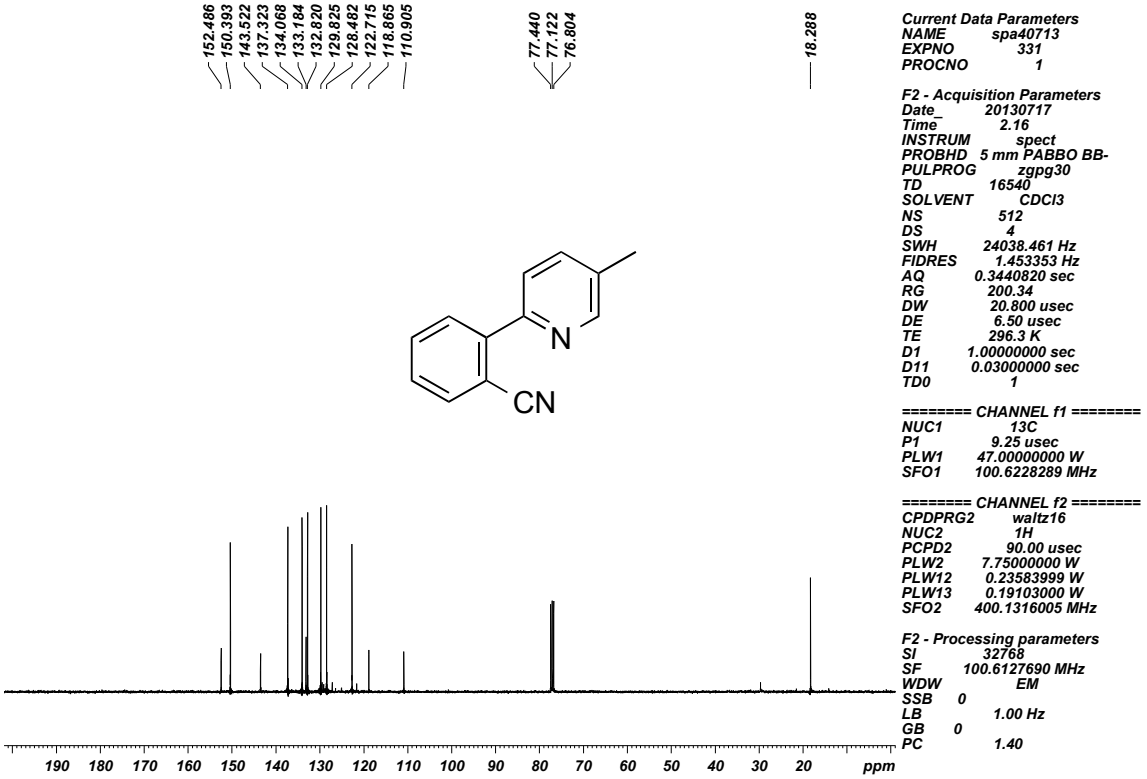


2-(5-Methylpyridin-2-yl)benzonitrile (3n):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

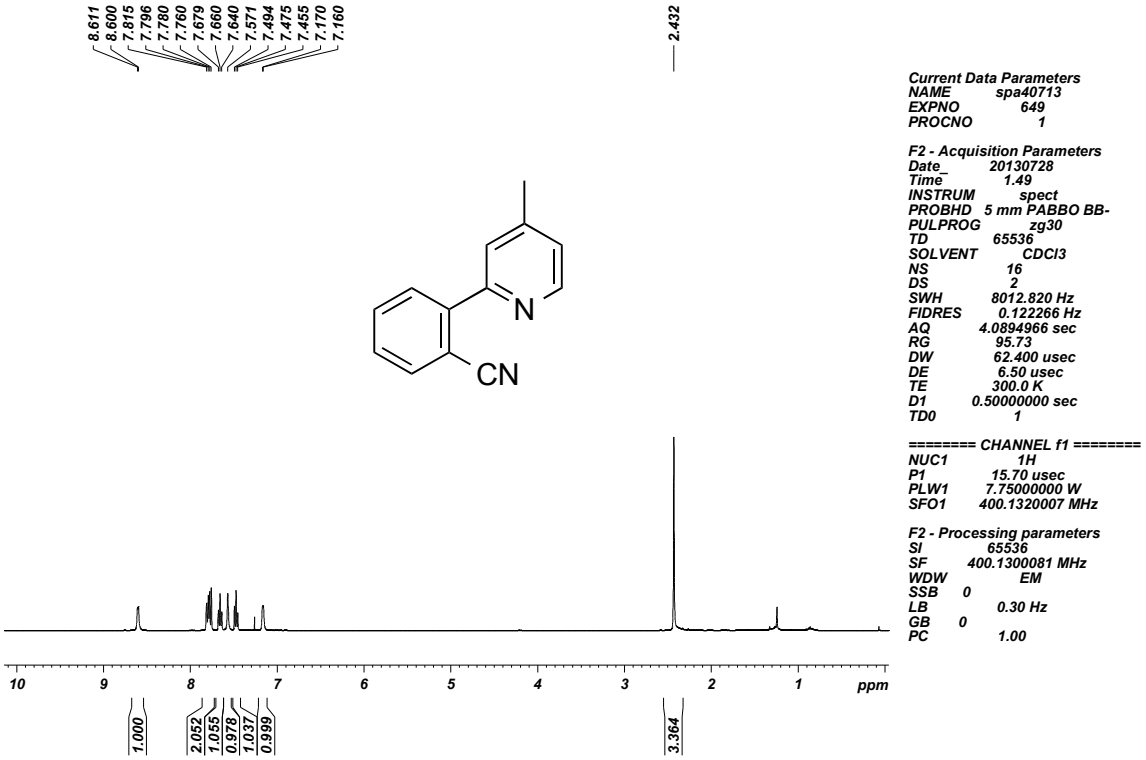


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

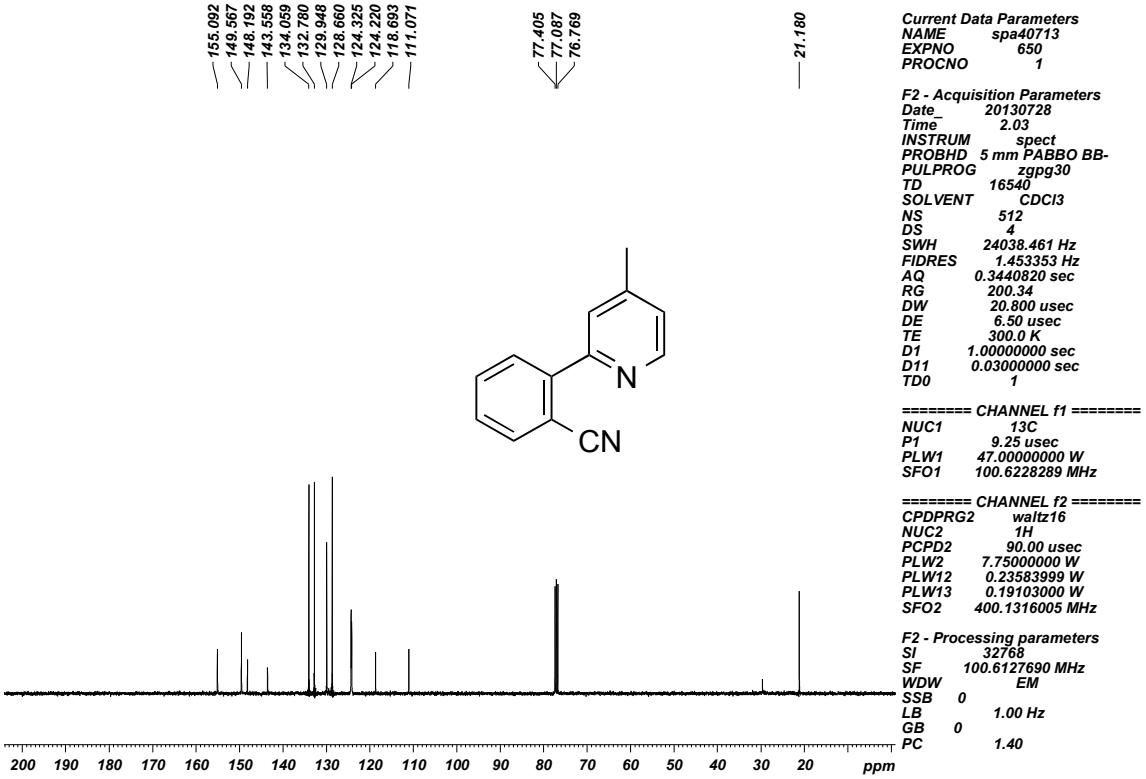


2-(4-Methylpyridin-2-yl)benzonitrile (3o):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

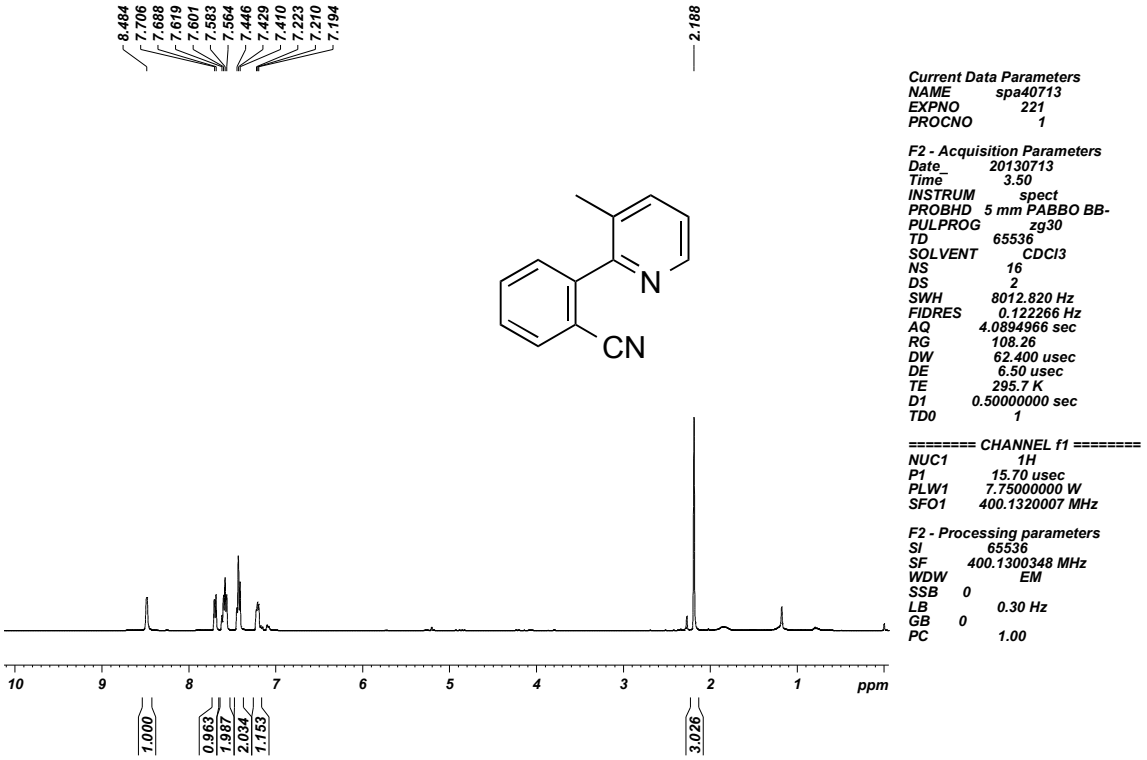


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

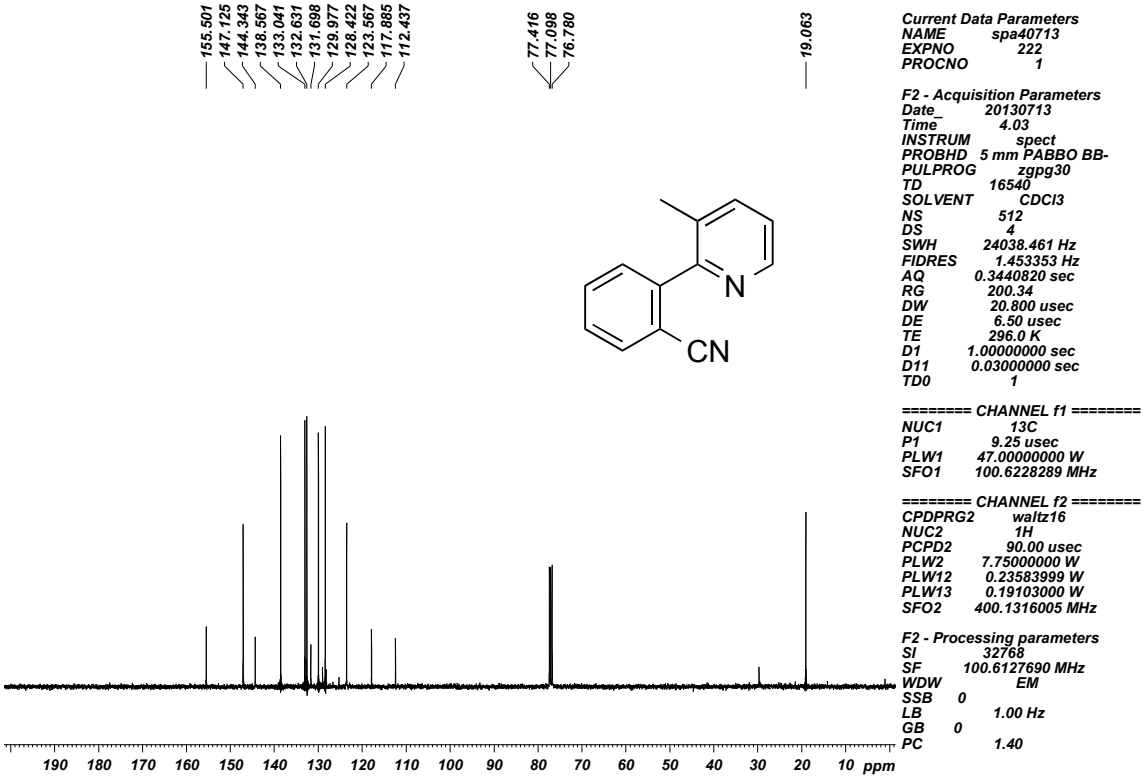


2-(3-Methylpyridin-2-yl)benzonitrile (3p):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

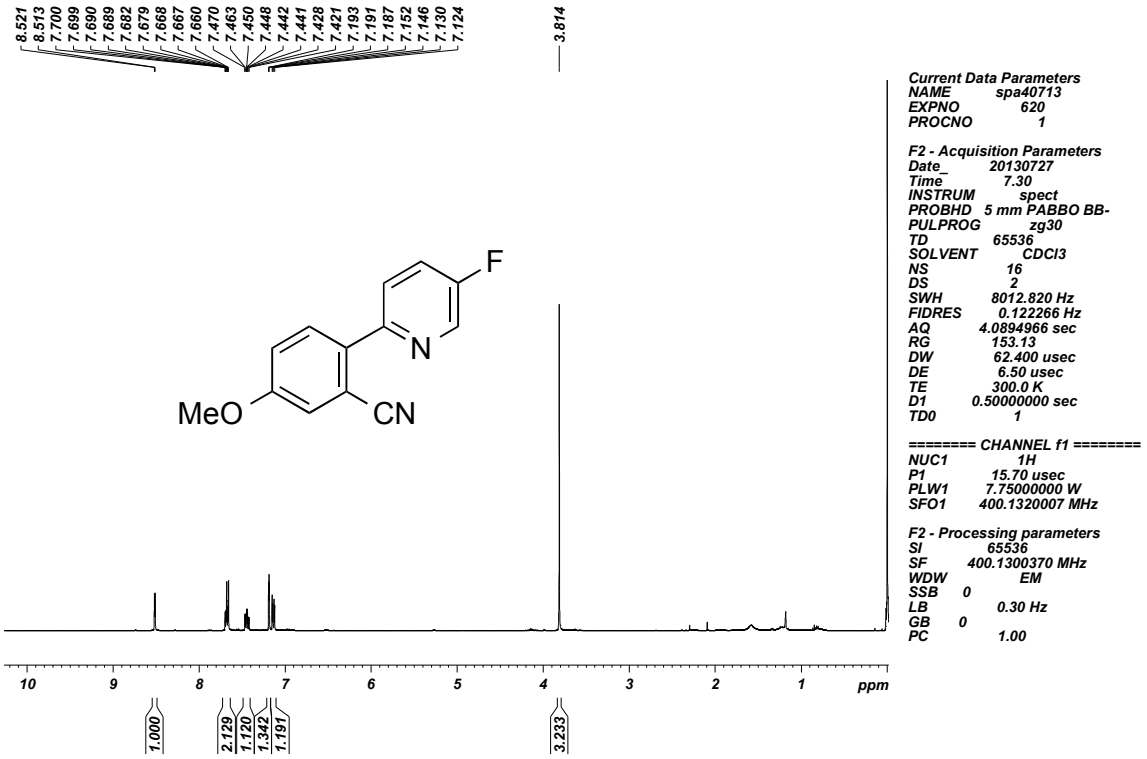


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

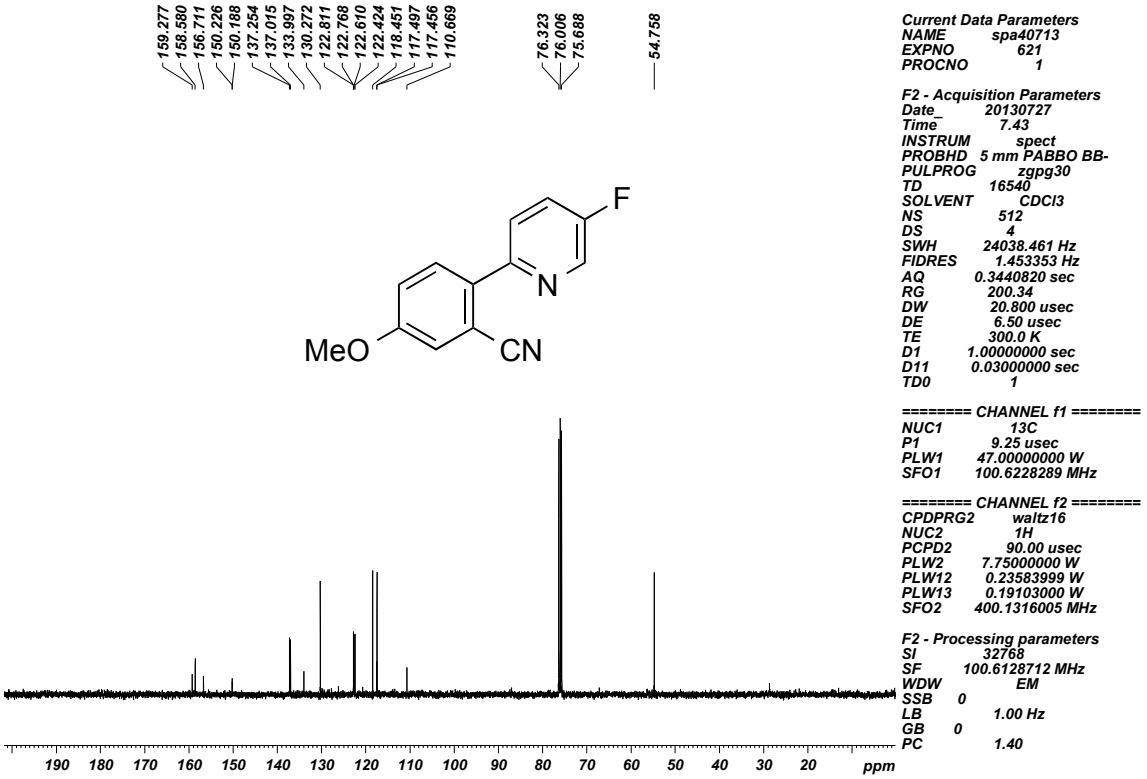


2-(5-Fluoropyridin-2-yl)-5-methoxybenzonitrile (3q):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

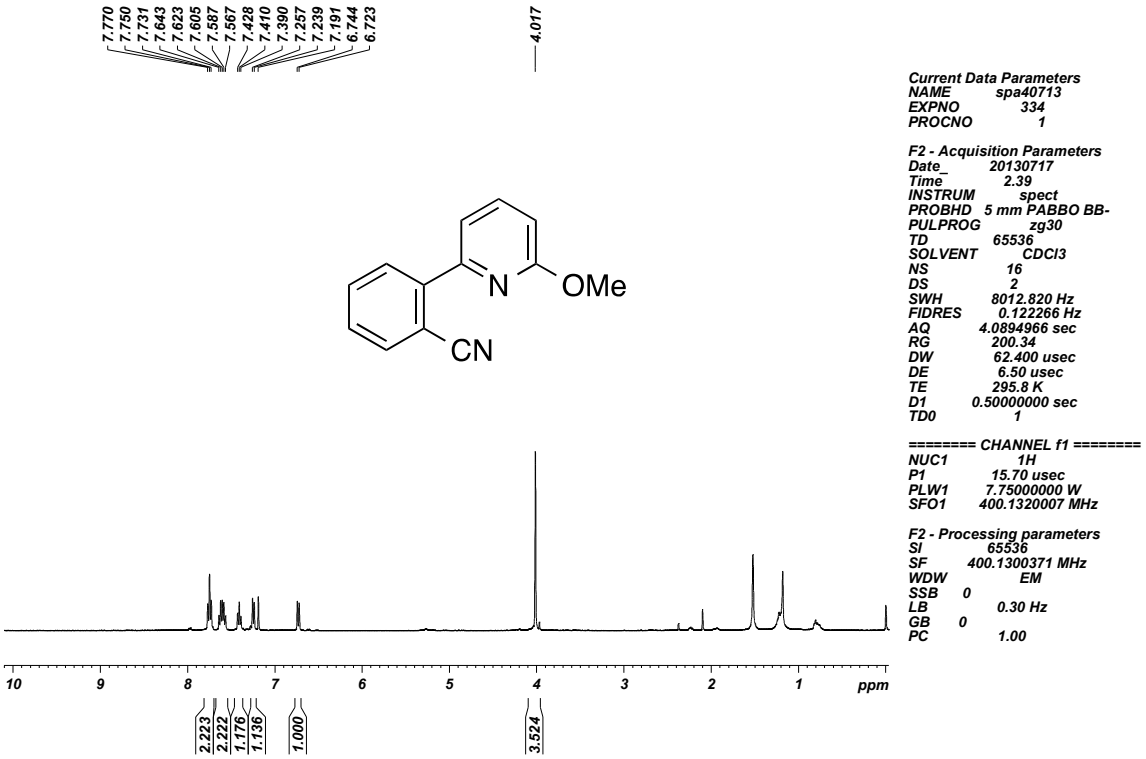


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

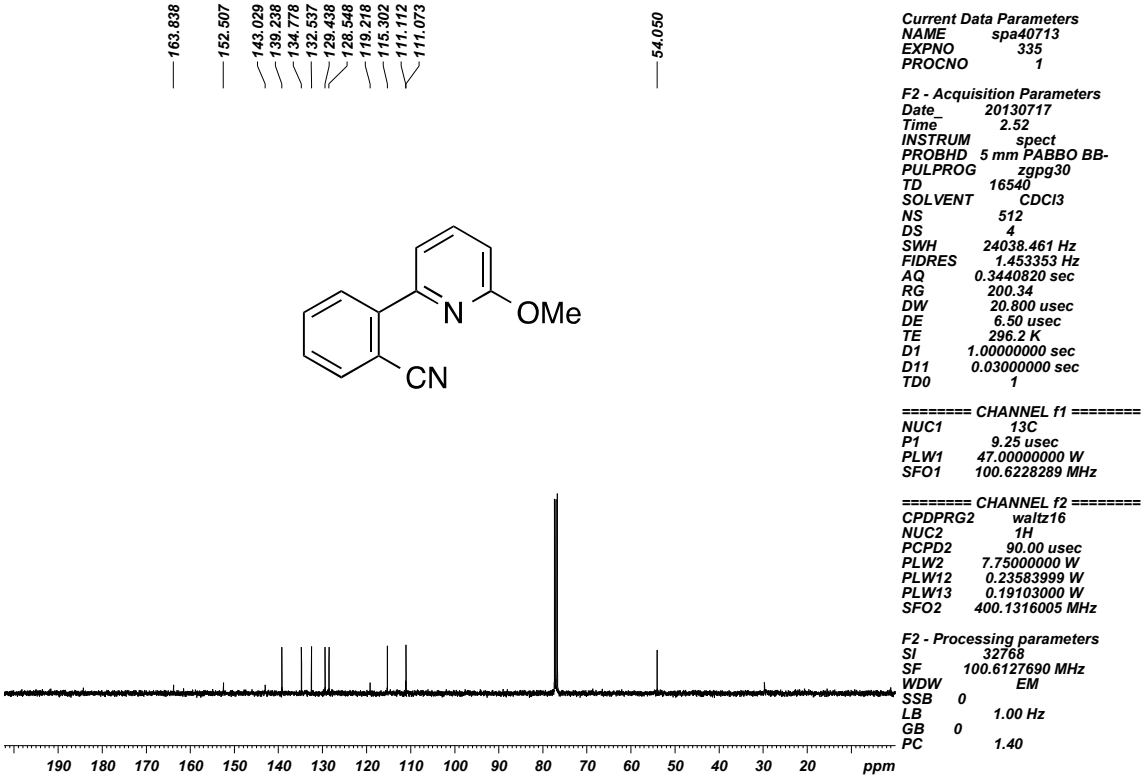


2-(6-Methoxypyridin-2-yl)benzonitrile (3r):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

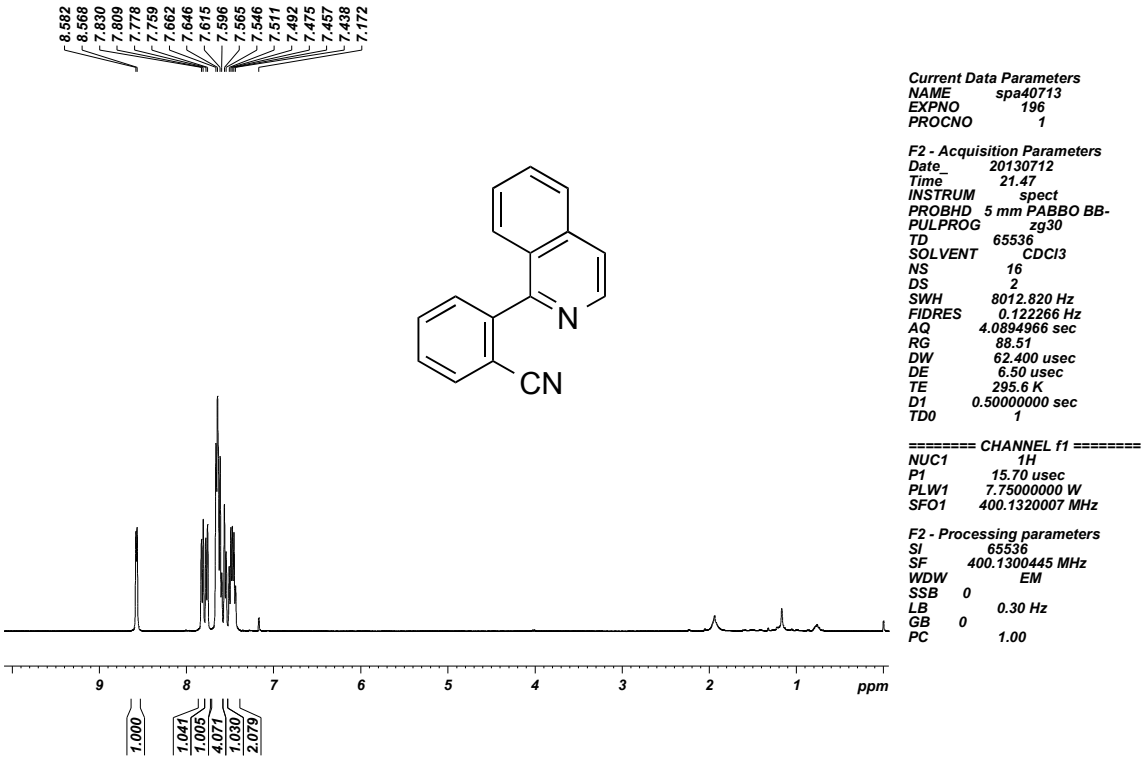


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

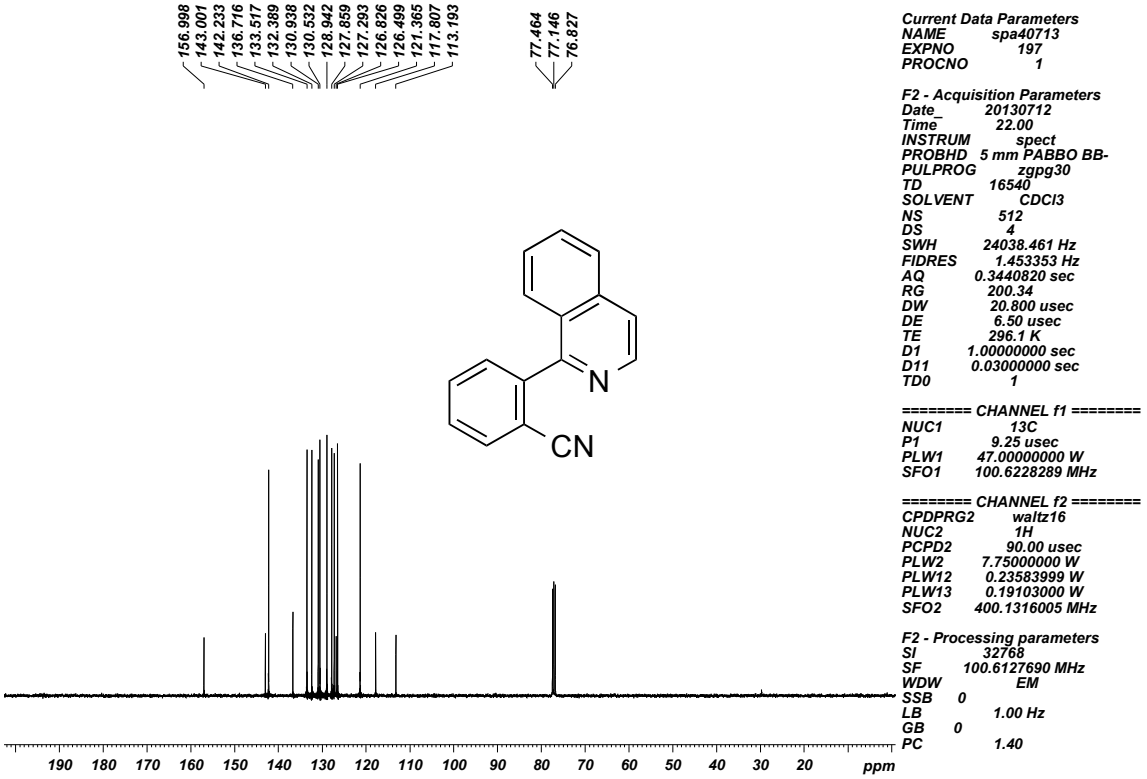


2-(Isoquinolin-1-yl)benzonitrile (3s):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

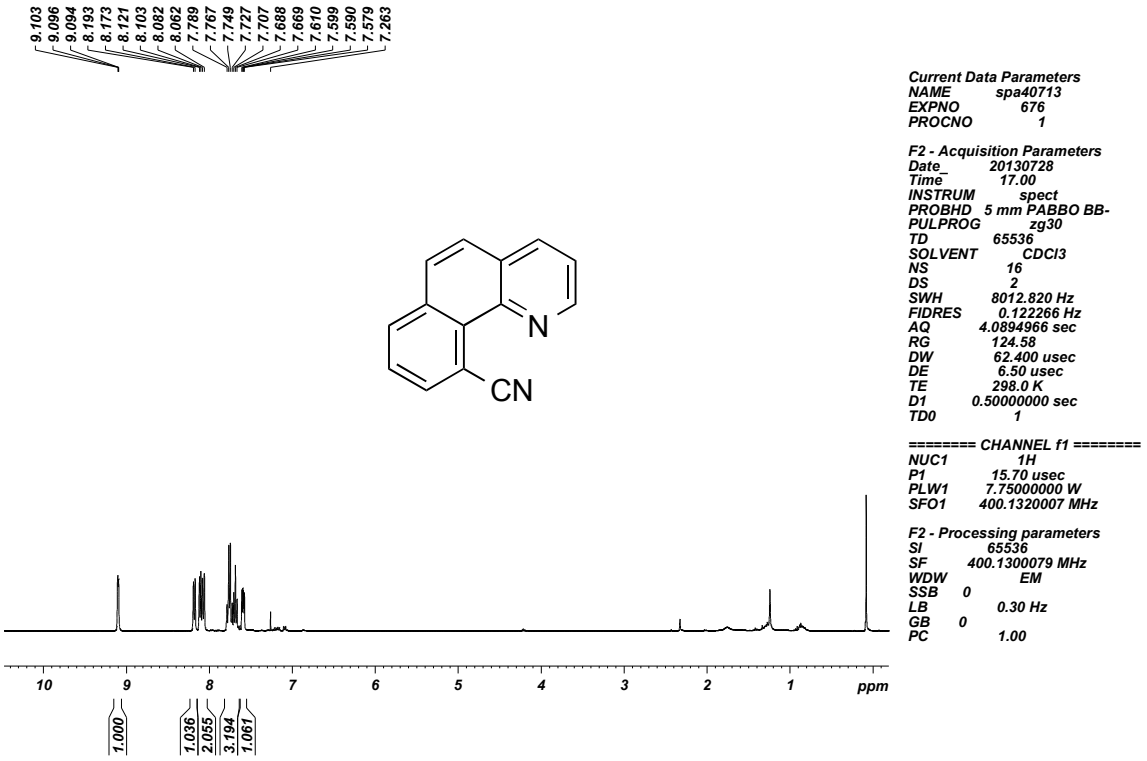


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

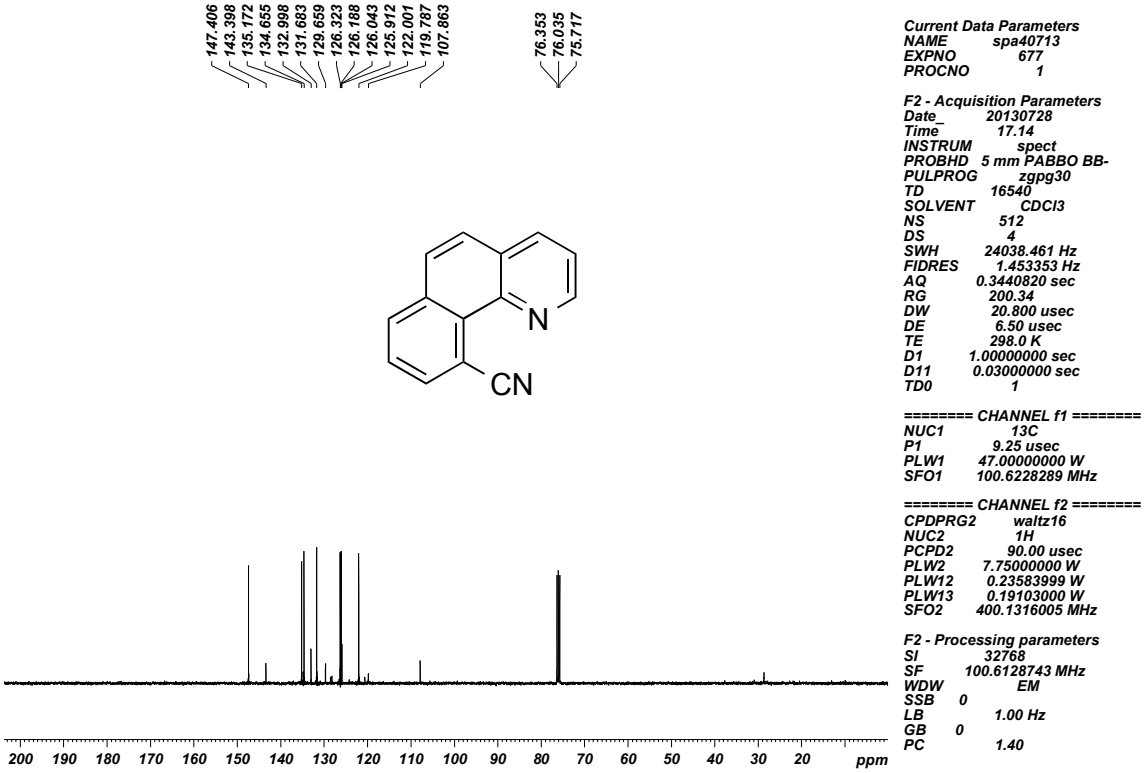


Benzo[*h*]isoquinoline-10-carbonitrile (3t):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

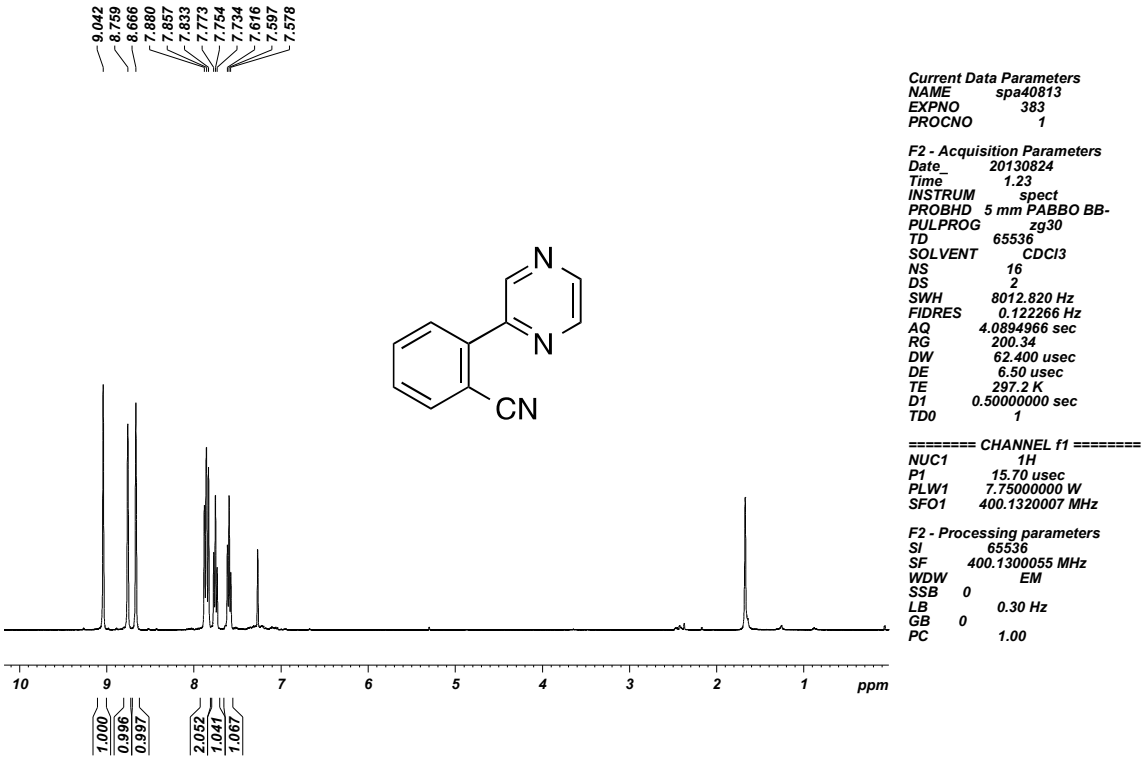


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

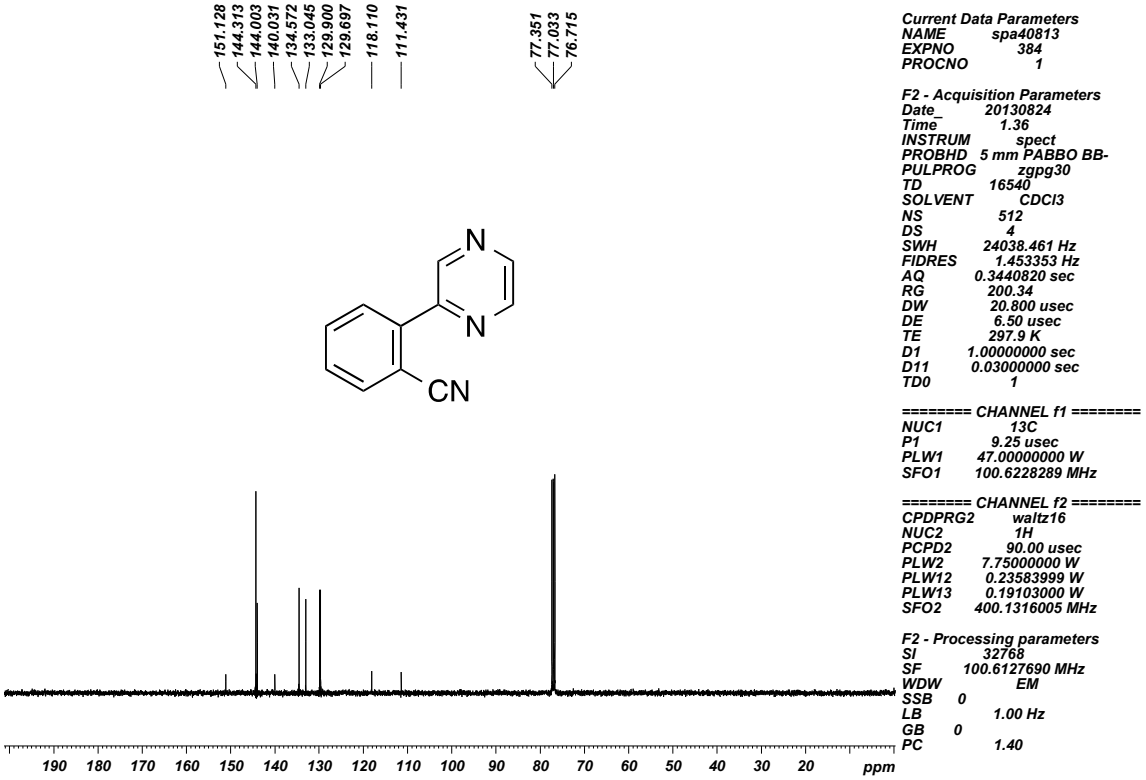


2-(Pyrazin-2-yl)benzonitrile (3u):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

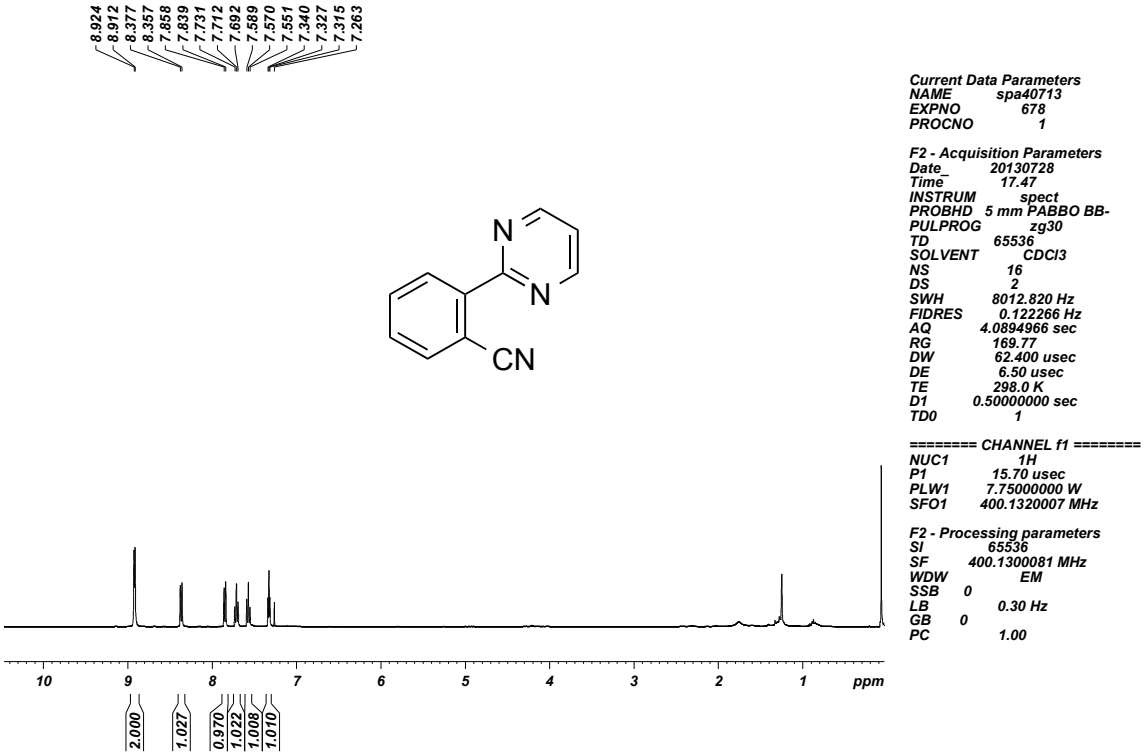


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)

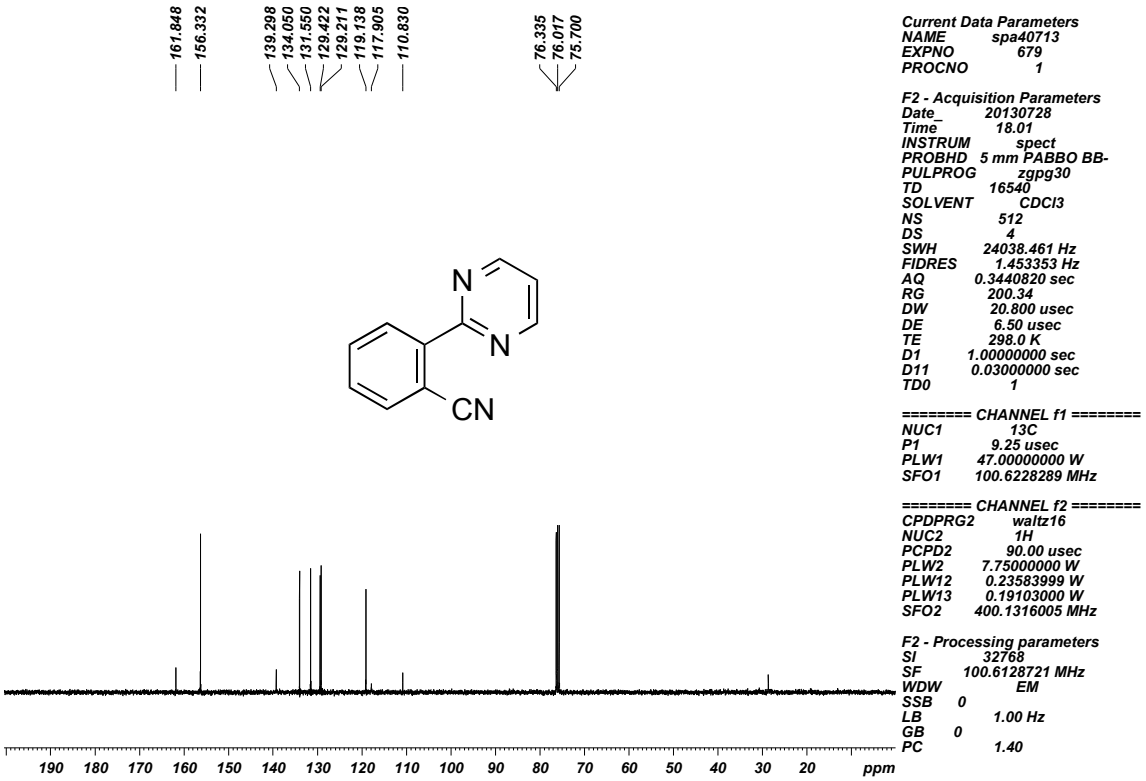


2-(Pyrimidin-2-yl)benzonitrile (3v):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)

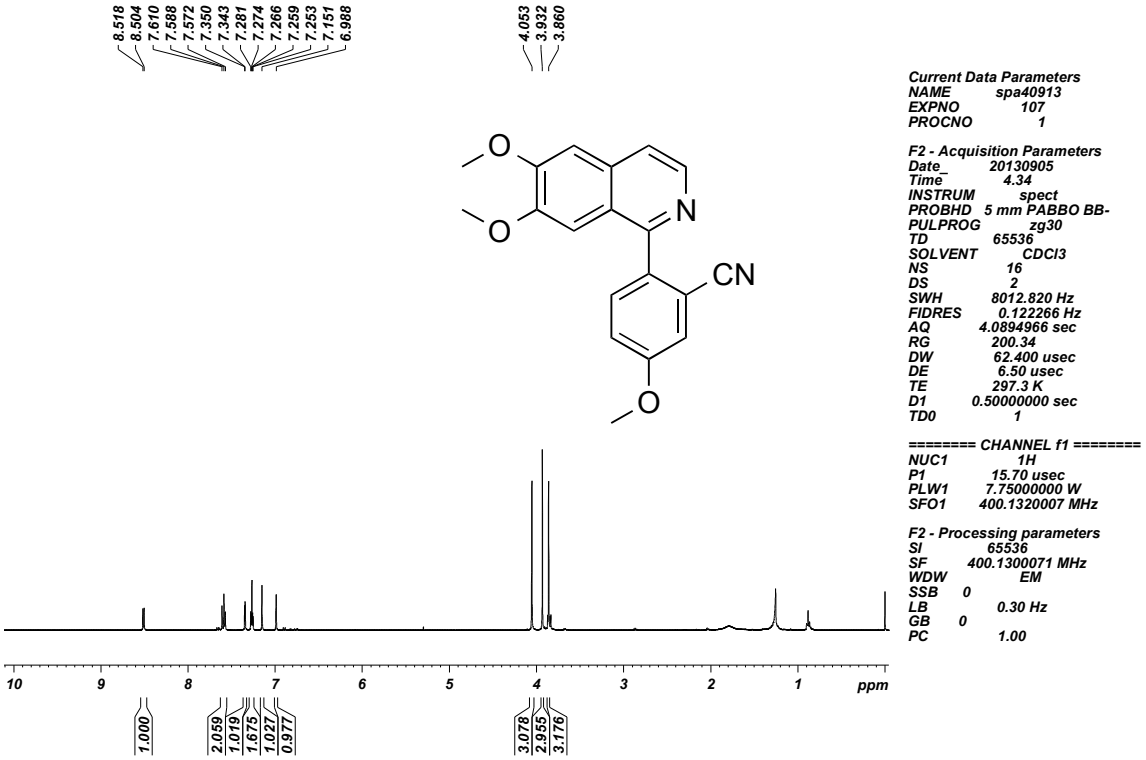


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)



2-(6,7-dimethoxyisoquinolin-1-yl)-5-methoxybenzonitrile (12):

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C)