Supporting Information

Mild and General Methods for the Palladium-Catalyzed Cyanation of Aryl and Heteroaryl Chlorides

Adam Littke,^{*,†} Maxime Soumeillant,^{*,‡} Robert F. Kaltenbach III,[§] Robert J. Cherney,[§] Christine M. Tarby[§] and Susanne Kiau[†]

[†]*Process Research and Development, Bristol-Myers Squibb Pharmaceutical Research Institute, 1 Squibb Drive, P.O. Box 191, New Brunswick, New Jersey 08903-0191*

[‡]*Process Research and Development, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 4000, Princeton, New Jersey 08543-4000*

[§]*Discovery Chemistry, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 4000, Princeton, New Jersey, 08543-4000*

Table of contents:

1- General	pages S1 – S2
2- Cyanation of Aryl and Heteroaryl Chlorides.	
Representative experimental procedure.	page S2
3- Reaction times and temperatures for all entries in tables 2 and 3	pages S2 – S3
4- In-process HPLC spectra versus commercially available HPLC markers	pages S3 – S18
5- Work-up procedures and isolated yields	pages S18 – S25
6- Copies of ¹H and ¹³C NMR of isolated compounds	pages S26 - S65

1- General

All reagents and catalysts were purchased from commercial suppliers (Aldrich, Alfa-Aesar, Strem) and used as received. Pd[P(*t*-Bu)₃]₂, which is reported as air-sensitive, was stored at room temperature on the bench, except during weekends, during which time it was kept in a dessicator under nitrogen. Older

batches of $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ would typically become orangish in color, however, cyanations would proceed normally using these older batches. DMAC (anhydrous, 99.8%, Aldrich) was gently sparged with nitrogen for 20 minutes to 1 hour at room temperature prior to use. HPLC solution yields are the average of two runs, isolated yields are one run.

2- Cyanation of Aryl and Heteroaryl Chlorides. Representative experimental procedure.

Table 2, entry 1: Palladium(II)trifluoroacetate ($\text{Pd}(\text{TFA})_2$; 9.6 mg, 0.0289 mmol, 4.3 mol %), zinc flakes, 1.1 μm thick -325 mesh (8.3 mg, 0.127 mmol, 19 mol %), racemic-2-di-tert-butylphosphino-1,1'-binaphthyl (23.5 mg, 0.059 mmol, 8.8 mol %), 4-chloroaniline (85.4 mg, 0.669 mmol, 100 mol %), and $\text{Zn}(\text{CN})_2$ (43.9 mg, 0.374 mmol, 56 mol %) were charged successively to a 25 x 90 mm glass test-tube equipped with a magnetic stir bar and Teflon screw-cap. The test-tube was evacuated and back-filled with nitrogen. DMAC (anhydrous, 99.8%, 3.6 mL) was added via syringe and the resulting reaction mixture was stirred at room temperature for 20 mins while performing 3 evacuation-nitrogen refill cycles. The reaction mixture was then heated to 95 °C over 45 minutes and held at that temperature for 14 hours. The reaction mixture was then cooled to room temperature, diluted with acetonitrile, filtered through a 45 μm HPLC syringe filter and the supernatant was analyzed by HPLC. HPLC analysis indicated a solution yield of 97.8% of 4-aminobenzonitrile. For workup procedures used to obtain isolated yields, please refer to Section 5.

3- Reaction times and temperatures for all entries in tables 2 and 3

Table 2, entry 1. 4-aminobenzonitrile. 14 hours at 95 °C

Table 2, entry 2. 2-cyanophenol. 3 hours at 95 °C

Table 2, entry 3. 2-cyanothioanisole. 5 hours at 95 °C

Table 2, entry 4. 4'-cyanoacetanilide. 2 hours at 95 °C

Table 2, entry 5. 3-cyanotoluene. 5 hours at 95 °C

Table 2, entry 6. 9-cyanoanthracene. 6 hours at 80 °C

Table 2, entry 7. 2,4-difluorobenzonitrile. 5 hours at 95 °C

Table 2, entry 8. 2-cyano-3-nitrotoluene. 4 hours at 95 °C

Table 2, entry 9. methyl 4-cyanobenzoate. 4 hours at 80 °C

Table 2, entry 10. 4-cyanobenzoic acid. 5 hours at 80 °C

Table 2, entry 11. 4-cyanophenylboronic acid. 5 hours at 80 °C

Table 3, entry 1. 5-cyanoindole. 7 hours at 95 °C

Table 3, entry 2. 4-cyanoindole. 7 hours at 95 °C

Table 3, entry 3. 2-methyl-6-cyanopyridine. 3 hours at 80 °C

Table 3, entry 4. 2-methoxy-5-cyanopyridine. 3 hours at 80 °C

Table 3, entry 5. 2-amino-4-cyanopyridine. 18 hours at 80 °C

Table 3, entry 6. 2,4-dicyanopyridine. 17 hours at 80 °C

Table 3, entry 7. 2-pyrimidinecarbonitrile. 6 hours at 80 °C

Table 3, entry 8. pyrazinecarbonitrile. 16 hours at 80 °C

Table 3, entry 9. 2-cyano-3-methylthiophene. 6 hours at 95 °C

4- In-process HPLC spectra versus commercially available HPLC markers

Included are copies of HPLC spectra for all products in tables 2 and 3. For all entries, the first HPLC spectrum shown is the spectra of the reaction product and the second HPLC spectrum is of an authentic sample of the reaction product and supplier (in parenthesis). For table 2, entries 4, 5 and 7, the HPLC method (HPLC column, mobile phase, flow rate and wavelength of detection) is given under table 2, entry 4, page S6. For all other entries, the HPLC method is given under table 2, entry 1 page S4.

Table 2, entry 1: 4-cyanoaniline

Method Description (this method was used for all entries in tables 2 and 3 EXCEPT table 2, entries 4, 5 and 7):

Inj. Vol. = 10 uL

Start % B = 20

15 Min. 90%

Flow Rate = 1 ml/min

Wavelength1 = 220

Wavelength2 = 254

Solvent Pair = TFA

Solvent A = A1=0.05% TFA in Water

Solvent B = B1=0.05% TFA in CH3CN

Column 3 : Zorbax SB-C18 5 um 4.6 x 150 mm

Note: 13.13 min peak is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂)

Authentic 4-cyanoaniline (Aldrich)

Table 2, entry 2: 2-cyanophenol

Note: 13.13 min peak is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂)

Authentic 2-cyanophenol (Aldrich)

Table 2, entry 3: 2-cyanothioanisole

Note: peak at 13.58 min is for unreacted starting material 2-chlorothiophenol

Authentic 2-cyanothiophenol (Alfa Aesar)

Table 2, entry 4: 4'-cyanoacetanilide

Method Description (this method was used for entries 4, 5 and 7 in table 2):

Inj. Vol. = 10 uL

Start % B = 35

2 Min. 35%

16 Min. 75%

20 Min. 100%

25 Min. 100%

Flow Rate = 1 ml/min

Wavelength1 = 220

Wavelength2 = 254

Solvent Pair = TFA

Solvent A = A1=0.05% TFA in CH3CN:water (5:95)

Solvent B = B1=0.05% TFA in CH3CN:water (95:15)

Column 2 : 2: YMC Pro C18 3 um 4.6 x 150 mm

Authentic 4'-cyanoacetanilide (Lancaster)

Table 2, entry 5: 3-cyanotoluene

Note: 10.98 min peak is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂)

Authentic 3-cyanotoluene (Aldrich)

Table 2, entry 6: 9-cyanoanthracene

Authentic 9-cyanoanthracene (Aldrich)

Table 2, entry 7: 2,4-difluorobenzonitrile

Note: peak at 10.99 min is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂) and the peak at 14.73 is for ligand-oxide

Authentic 2,4-difluorobenzonitrile (Aldrich)

Table 2, entry 8: 2-cyano-3-nitrotoluene

Authentic 2-cyano-3-nitrotoluene (Aldrich)

Table 2, entry 9: methyl-4-cyanobenzoate

Authentic methyl-4-cyanobenzoate (Aldrich)

Table 2, entry 10: 4-cyanobenzoic acid

Authentic 4-cyanobenzoic acid (Aldrich)

Table 2, entry 11: 4-cyanophenylboronic acid

Note: 13.10 min peak is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂)

Authentic 4-cyanophenylboronic acid (Aldrich)

Table 3, entry 1: 5-cyanoindole

Note: peak at 13.13 min is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂) and the peak at 11.95 is for unreacted 5-chloroindole

Authentic 5-cyanoindole (Aldrich)

Table 3, entry 2: 4-cyanoindole

Note: peak at 13.17 min is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂) and the peak at 17.5 is for ligand-oxide

Authentic 4-cyanoindole (Aldrich)

Table 3, entry 3: 2-cyano-6-methylpyridine

Authentic 2-cyano-6-methylpyridine (Aldrich)

Table 3, entry 4: 3-cyano-6-methoxypyridine

Authentic 3-cyano-6-methoxypyridine (Aldrich)

Table 3, entry 5: 4-cyano-2-aminopyridine

Authentic 4-cyano-2-aminopyridine (Alfa Aesar)

Table 3, entry 6: 2,4-dicyanopyridine

Note: 13.06 min peak is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂)

Authentic 2,4-dicyanopyridine (Alfa Aesar)

Table 3, entry 7: 2-cyanopyrimidine

Note: peak at 13.08 min is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂) and the peak at 17.47 is for ligand-oxide

Authentic 2-cyanopyrimidine (Aldrich)

Table 3, entry 8: 2-cyanopyrazine

Note: 13.02 min peak is for the ligand racemic-2-di-*t*-butylphosphino-1,1'-binaphthyl ((binaphthyl)P(*t*-Bu)₂)

Authentic 2-cyanopyrazine (Aldrich)

Table 3, entry 9: 2-cyano-3-methylthiophene

Authentic 2-cyano-3-methylthiophene (Alfa Aesar)

5- Work-up procedures and isolated yields

Upon completion of the cyanation, the reaction mixtures were allowed to cool down to room temperature and worked up according to one of the following four protocols which will be referenced to as method A, B, C or D in the yield and spectral data summary of each compound.

2-A/ Method A: the reaction mixture was further cooled down to 15°C and quenched slowly with 3N aqueous ammonia until pH 10.5-11.0. After no less than 1.5 hour stirring at room temperature, the slurry was polish filtered on a bed of Celite 545 and the filtrate was partitioned between ethyl acetate (EtOAc) and saturated aqueous ammonium chloride (NH₄Cl) and the aqueous layer was back extracted with EtOAc. The combined extracts were washed 3-4 times with water, dried over MgSO₄ and concentrated to an oily residue which was purified on a REDISEPP column (silica 35-60 µm) by elution with heptane/EtOAc gradients using a ISCO Teledyne automate. The pure fractions were collected together and the solvents evaporated to obtain the title compound.

2-B/ Method B: the solids were removed by polish filtration on a bed of Celite 545 and the DMAC filtrate was concentrated down from 17-19 mL/g to approximately 4-6 mL/g by distillation under 20 Torr. The distillation residue was cooled to 10-15°C and quenched slowly with 3N aqueous ammonia until pH 10.5-11.0. The resulting slurry was further diluted with water and the mixture was stirred for 2-5 hours at room temperature. The solid was collected by filtration, rinsed several times with water and air-dried on the filter with vacuum suction for at least 45 minutes to 1 hour. The cake was washed 3 times with heptane and dried in a vacuum oven until constant weight to yield the desired aryl or heteroaryl nitrile.

2-C/ Method C: the solids were removed by polish filtration on a bed of Celite 545 and the filtrate was diluted with 45 to 60 mL of EtOAc/g of substrate, 3N aqueous ammonia and saturated aqueous NH_4Cl and the layers were separated. **Note:** when aqueous layer losses were too significant, the product could be fully extracted in the organic layer by either adjusting the pH to 7.0 with 1N aqueous HCl or by back extraction of the aqueous layer. The EtOAc extract was washed 3-4 times with water, dried over MgSO_4 and concentrated to an oily or solid residue which was purified on a REDISEPP column (silica 35-60 μm) by elution with heptane/EtOAc gradients using a ISCO Teledyne automate. The pure fractions were collected together and the solvents evaporated to obtain the title compound.

2-D/ Method D: the solids were removed by polish filtration on a bed of Celite 545 and the filtrate was concentrated down to 3-4 mL/g of substrate by vacuum distillation (25-35 Torr and 78-85°C). The distillation residue was immobilized on Celite and the residual dimethylacetamide was removed on a Speedvac apparatus. The product was separated by chromatography on a REDISEPP column (silica 35-60 μm) by elution with heptane/EtOAc gradients using a ISCO Teledyne automate. The pure fractions were collected together and the solvents evaporated to obtain the title compound.

Table 2, entry 1: 4-cyanoaniline

Method B: input 4-chloroaniline: 1.850 g (theoretical output: 1.687 g); output: 1.569 g (93.0 % yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.39 (2 H, dt, $J=8.68, 2.42, 2.09$ Hz), 6.63 (2 H, dt, $J=8.68, 2.42, 2.09$ Hz), 4.18 (2 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 150.40, 133.72 (2 C), 120.09, 114.38 (2 C), 100.06.

Table 2, entry 2: 2-cyanophenol

Method C with pH adjustment to 7.00 prior to first phase split and chromatography from heptane/EtOAc. Input 2-chlorophenol: 1.423 g (theoretical output: 1.318); output: 1.165 g (88.4 % yield). ^1H NMR (400 MHz, *dms**o*-*d*6) δ ppm 11.04 (1 H, s), 7.58 (1 H, dd, $J=7.69$, 1.54 Hz), 7.44 - 7.51 (1 H, m), 7.00 (1 H, d, $J=8.35$ Hz), 6.88 - 6.94 (1 H, m). ^{13}C NMR (101 MHz, *dms**o*-*d*6) δ ppm 160.09, 134.65, 133.18, 119.50, 116.96, 116.11, 98.80.

Table 2, entry 3: 2-cyanothioanisole

Method C with chromatography from heptane/EtOAc. Input 2-chlorothioanisole: 534.6 mg (theoretical output: 502.7 mg); output: 282.0 mg (56.1 % yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.57 (1 H, dd, $J=7.91$, 1.32 Hz), 7.51 (1 H, td, $J=7.91$, 1.32 Hz), 7.29 (1 H, d, $J=7.91$ Hz), 7.19 (1 H, td, $J=7.58$, 1.10 Hz), 2.54 (3 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 143.55, 133.40, 132.88, 126.16, 125.05, 116.88, 111.53, 15.70.

Table 2, entry 4: 4'-cyanoacetanilide

Method B: this compound was further purified by suspending the solid at 50°C in heptane/EtOAc 1:1 v/v. The slurry was cooled down to room temperature for 3 hours, the solid was collected by filtration and rinsed twice with heptane/EtOAc 9:1 v/v and dried.

For normal catalyst loading: input 4'-chloroacetanilide: 3.006 g (theoretical output: 2.839 g); output: 2.625 g (92.5% yield).

Cyanation with 1.9 mol% $\text{Pd}(\text{TFA})_2$, 3.7 mol% ligand and 8.3 mol% Zinc flake: input 4'-chloroacetanilide: 3.024 g (theoretical output: 2.856 g); output: 2.625 g (91.9% yield).

^1H NMR (400 MHz, *Methanol-d*4) δ ppm 7.66 (2 H, d, $J=8.35$ Hz), 7.56 (2 H, d, $J=8.35$ Hz), 2.07 (3 H, s). ^{13}C NMR (101 MHz, *Methanol-d*4) δ ppm 171.76, 144.21, 133.96 (2 C), 120.55 (2 C), 119.62, 107.28, 23.81.

Table 2, entry 5: 3-cyanotoluene

Method A with chromatography from heptane/EtOAc. Input 3-chlorotoluene: 1.330 g (theoretical output: 1.231 g); output: 1.025 g (83.3 % yield). ^1H NMR (400 MHz, *dms**o*-*d*₆) δ ppm 7.64 (1 H, d, *J*=0.88 Hz), 7.61 (1 H, d, *J*=7.47 Hz), 7.50 - 7.55 (1 H, m), 7.45 (1 H, t, *J*=7.69 Hz), 2.34 (3 H, s). ^{13}C NMR (101 MHz, *dms**o*-*d*₆) δ ppm 139.21, 133.98, 132.29, 129.32, 129.24, 118.87, 111.13, 20.48.

Table 2, entry 6: 9-cyanoanthracene

Method B: input 9-chloroanthracene: 0.959 g (theoretical output: 0.920 g); output: 0.911 g (99.0 % yield). ^1H NMR (400 MHz, *CDCl*₃) δ ppm 8.67 (1 H, s), 8.41 (2 H, dd, *J*=8.79, 0.88 Hz), 8.07 (2 H, d, *J*=8.57 Hz), 7.68 - 7.74 (2 H, m), 7.55 - 7.61 (2 H, m). ^{13}C NMR (101 MHz, *CDCl*₃) δ ppm 133.30 (2 C), 132.71 (1 C), 130.62 (2 C), 128.92 (4 C), 126.34 (2 C), 125.29 (2 C), 117.22 (1 C), 105.44 (1 C).

Table 2, entry 7: 2,4-difluorobenzonitrile

Method A with chromatography from heptane/EtOAc. Input 1-chloro-2,4-difluorobenzene: 1.531 g (theoretical output: 1.449g); output: 1.050 g (72.5 % yield). **Note:** upon evaporating the bulk of the solvent from the clean chromatography fractions, the product started to sublime on the walls of the flasks. To minimize the losses in the rotary evaporator, the residual solution was placed on a glass watch topped with a thin stem funnel connected to a gentle air-stream to complete the evaporation. ^1H NMR (400 MHz, *CDCl*₃) δ ppm 7.65 (1 H, ddd, *J*=8.57, 7.25, 6.15 Hz), 6.99 - 7.05 (1 H, m), 6.97 (1 H, dt, *J*=8.79, 2.64 Hz). ^{13}C NMR (101 MHz, *CDCl*₃) δ ppm 165.77 (1 C, dd, *J*=259.55, 10.14 Hz), 164.13 (1 C, dd, *J*=261.58, 12.17 Hz), 134.98 (1 C, d,

$J=10.14$ Hz), 112.93 - 113.37 (1 C, m), 112.82 (1 C, $J=4.06$ Hz), 105.45 (1 C, dd, $J=26.34$, 4.06 Hz), 98.18 (1 C, $J=4.06$ Hz).

Table 2, entry 8: 2-cyano-3-nitrotoluene

Method C with chromatography from heptane/EtOAc. Input 2-chloro-3-nitrotoluene: 0.789 g (theoretical output: 0.746 g); output: 0.634 g (85.0 % yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.12 (1 H, dd, $J=6.81$, 2.42 Hz), 7.64 - 7.71 (2 H, m), 2.70 (3 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 145.76, 135.50, 132.63 (2 C), 122.89, 113.71, 107.96, 21.08.

Table 2, entry 9: methyl-4-cyanobenzoate

Method C with chromatography with heptane/EtOAc. Input methyl-4-chlorobenzoate: 781.1 mg (theoretical output: 738 mg); output: 635.4 mg (86.1 % yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.10 - 8.14 (2 H, m), 7.71 - 7.75 (2 H, m), 3.94 (3 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 165.39, 133.90, 132.19 (2 C), 130.07 (2 C), 117.93, 116.39, 52.69.

Table 2, entry 10: 4-cyanobenzoic acid

Method B: input 4-chlorobenzoic acid: 0.987 g (theoretical output: 0.925 g); output: 0.777 g (84.0 % yield). ^1H NMR (400 MHz, $\text{dms}\text{-}d_6$) δ ppm 13.55 (1 H, s), 8.04 - 8.09 (2 H, m), 7.94 - 7.98 (2 H, m). ^{13}C NMR (101 MHz, $\text{dms}\text{-}d_6$) δ ppm 166.44, 135.25, 133.06 (2 C), 130.31 (2 C), 118.57, 115.47.

Table 2, entry 11: 4-cyanophenylboronic acid

Method C *except* that the crude 4-cyanophenylboronic acid was purified via recrystallization from hot water. Input 4-chlorophenylboronic acid: 0.778 g (theoretical output: 0.730 g); output: 0.540 g (74.0 % yield). ^1H NMR (400 MHz, $\text{dms}\text{-}d_6$) δ ppm 8.39 (2 H, s), 7.92 (2 H, d, $J=8.35$

Hz), 7.77 (2 H, d, $J=8.35$ Hz). ^{13}C NMR (101 MHz, *dms**o*-*d*6) δ ppm 134.39 (2 C), 132.33 (1 C, d, $J=287.94$ Hz), 130.76 (2 C), 118.77, 112.20.

Table 3, entry 1: 5-cyanoindole

Method C with back extraction of the basic aqueous layer and chromatography from heptane/EtOAc. Input 5-chloro-1*H*-indole: 1.455 g (theoretical output: 1.344 g); output: 0.594 g (44.2% yield). ^1H NMR (400 MHz, *dms**o*-*d*6) δ ppm 11.66 (1 H, s), 8.07 (1 H, d, $J=0.88$ Hz), 7.52 - 7.57 (2 H, m), 7.41 (1 H, dd, $J=8.57, 1.54$ Hz), 6.55 - 6.59 (1 H, m). ^{13}C NMR (101 MHz, *dms**o*-*d*6) δ ppm 137.37, 127.81, 127.19, 125.47, 123.41, 120.55, 112.42, 101.83, 100.68.

Table 3, entry 2: 4-cyanoindole

Method C with back extraction of the basic aqueous layer and chromatography from heptane/EtOAc. Input 4-chloro-1*H*-indole: 0.770 g (theoretical output: 0.722 g); output: 0.648 g (89.3% yield). ^1H NMR (400 MHz, *dms**o*-*d*6) δ ppm 11.74 (1 H, s), 7.75 (1 H, d, $J=8.35$ Hz), 7.64 (1 H, d, $J=3.08$ Hz), 7.52 (1 H, d, $J=0.88$ Hz), 7.19 - 7.26 (1 H, m), 6.58 (1 H, d, $J=3.08$ Hz). ^{13}C NMR (101 MHz, *dms**o*-*d*6) δ ppm 135.60, 128.84, 128.48, 124.50, 120.91, 118.81, 116.86, 101.04, 99.37.

Table 3, entry 3: 2-cyano-6-methylpyridine

Method D: input 2-chloro-6-methylpyridine: 0.875 g (theoretical output: 0.802 g); output: 0.779 g (97.1% yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.70 (1 H, t, $J=7.69$ Hz), 7.50 (1 H, d, $J=7.47$ Hz), 7.36 (1 H, d, $J=7.91$ Hz), 2.59 (3 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 160.65, 137.01, 133.16, 126.82, 125.65, 117.34, 24.33.

Table 3, entry 4: 3-cyano-6-methoxypyridine

Method B: input 5-chloro-2-methoxypyridine: 0.465 g (theoretical output: 0.434 g); output: 0.409 g (94.1 % yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.47 (1 H, d, $J=2.20$ Hz), 7.75 (1 H, dd, $J=8.57, 2.42$ Hz), 6.80 (1 H, d, $J=8.79$ Hz), 3.97 (3 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 166.00, 151.94, 140.82, 117.22, 111.80, 102.38, 54.23.

Table 3, entry 5: 4-cyano-2-aminopyridine

Method B: input 5-chloro-2-methoxypyridine: 0.356 g (theoretical output: 0.330 g); output: 0.293 g (88.9 % yield). ^1H NMR (400 MHz, $\text{dms}\text{-}d_6$) δ ppm 8.09 (1 H, dd, $J=5.16, 0.55$ Hz), 6.78 (1 H, dd, $J=5.16, 1.43$ Hz), 6.71 - 6.74 (1 H, m), 6.53 (2 H, s). ^{13}C NMR (101 MHz, $\text{dms}\text{-}d_6$) δ ppm 159.50, 149.19, 119.32, 117.06, 111.55, 109.39.

Table 3, entry 6: 2,4-dicyanopyridine

Method B: input 2,4-dichloropyridine: 0.5456 g (theoretical output: 0.476 g); output: 0.3251 g (68.3 % yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.92 - 8.96 (1 H, m), 7.91 - 7.94 (1 H, m), 7.77 (1 H, dd, $J=4.83, 1.32$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 152.16, 135.30, 129.53, 128.34, 122.10, 115.49, 114.52.

Table 3, entry 7: 2-cyanopyrimidine

Method D with chromatography from heptane/EtOAc. Input 2-chloropyrimidine: 1.420 g (theoretical output: 1.277 g); output: 1.106 g (86.6% yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.86 (2 H, d, $J=4.83$ Hz), 7.55 (1 H, t, $J=5.05$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 158.03 (2 C), 145.30, 123.58, 115.53.

Table 3, entry 8: 2-cyanopyrazine

Method D with chromatography from heptane/EtOAc. Input 2-chloropyrazine: 0.955 g (theoretical output: 0.859 g); output: 0.627 g (73.0% yield). ^1H NMR (400 MHz, CDCl_3) δ ppm

8.92 (1 H, d, $J=1.32$ Hz), 8.79 (1 H, d, $J=2.64$ Hz), 8.72 (1 H, dd, $J=2.64, 1.32$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 148.29, 147.32, 145.44, 131.06, 115.20.

Table 3, entry 9: 2-cyano-3-methylthiophene

Method C with chromatography with heptane/EtOAc. Input 2-chloro-3-methylthiophene: 689.5 mg (theoretical output: 640.5 mg); output: 553.4 mg (86.4% yield). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.45 (1 H, d, $J=5.27$ Hz), 6.93 (1 H, d, $J=4.83$ Hz), 2.43 (3 H, s). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 149.48, 131.52, 129.51, 114.20, 105.85, 15.19.

6- Copies of ^1H and ^{13}C NMR of isolated compounds

Table 2, entry 1: 4-cyanoaniline

No.	(ppm)	(Hz)	Height
1	4.18	1672.0	0.1648
2	6.61	2643.1	0.1438
3	6.62	2645.8	0.9376
4	6.62	2647.5	0.2994
5	6.63	2652.3	0.3457
6	6.64	2654.1	0.9671
7	6.65	2656.7	0.1148

No.	(ppm)	(Hz)	Height
8	7.37	2946.8	0.1551
9	7.38	2949.0	1.0000
10	7.38	2950.7	0.3016
11	7.39	2955.5	0.3277
12	7.40	2957.3	0.8806
13	7.40	2959.9	0.1094

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M01	4.18	[4.11 .. 4.25]	-	s	2
2	M02	6.63	[6.60 .. 6.66]	-	dt	2
3	M00	7.39	[7.36 .. 7.41]	8.68	dt	2
4	M00	7.39	[7.36 .. 7.41]	2.42	dt	2
5	M00	7.39	[7.36 .. 7.41]	2.09	dt	2

No.	(ppm)	(Hz)	Height
1	76.68	7708.0	1.0000
2	77.00	7740.4	0.8934
3	77.30	7770.9	0.8458
4	100.06	10058.2	0.0995
5	114.38	11497.9	0.9189
6	120.09	12071.7	0.1236
7	133.72	13442.5	0.9045
8	150.40	15119.4	0.1826

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M04	100.06	[99.95 .. 100.14]	s	1
2	M03	114.38	[114.22 .. 114.52]	s	2
3	M02	120.09	[119.98 .. 120.19]	s	1
4	M01	133.72	[133.54 .. 133.89]	s	2
5	M00	150.40	[150.30 .. 150.49]	s	1

Table 2, entry 2: 2-cyanophenol

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	2.49	995.5	0.2000	12	7.46	2981.2	0.2266	1	M04	6.91	[6.88 .. 6.94]	-	m	1
2	3.36	1342.6	0.0190	13	7.47	2986.9	0.2401	2	M03	7.00	[6.97 .. 7.03]	8.35	d	1
3	6.89	2754.0	0.2131	14	7.47	2988.2	0.3191	3	M02	7.47	[7.44 .. 7.51]	-	m	1
4	6.89	2754.9	0.2305	15	7.48	2989.5	0.2567	4	M01	7.58	[7.55 .. 7.60]	7.69	dd	1
5	6.91	2761.5	0.4255	16	7.49	2995.2	0.1850	5	M01	7.58	[7.55 .. 7.60]	1.54	dd	1
6	6.91	2762.4	0.4406	17	7.50	2997.0	0.1872	6	M00	11.04	[11.02 .. 11.05]	-	s	1
7	6.93	2768.9	0.2472	18	7.57	3024.7	0.3686							
8	6.93	2769.8	0.2542	19	7.57	3026.4	0.3407							
9	6.99	2794.0	0.4134	20	7.59	3032.6	0.3375							
10	7.01	2802.3	0.4506	21	7.59	3033.9	0.3066							
11	7.45	2979.4	0.2140	22	11.04	4411.9	1.0000

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	38.87	3907.9	0.1412	8	98.80	9932.3	0.0863
2	39.08	3928.2	0.4241	9	116.11	11672.1	0.2667
3	39.30	3950.5	0.7821	10	116.96	11757.3	0.1096
4	39.50	3970.7	1.0000	11	119.50	12012.8	0.2666
5	39.70	3991.0	0.8474	12	133.18	13387.6	0.3008
6	39.92	4013.3	0.4042	13	134.65	13535.6	0.3424
7	40.13	4033.6	0.1480	14	160.09	16092.6	0.1314

Table 2, entry 3: 2-cyanothioanisole

No.	(ppm)	(Hz)	Height
1	2.54	1015.5	1.0000
2	7.17	2867.7	0.0428
3	7.18	2869.0	0.0424
4	7.19	2875.6	0.0876
5	7.20	2876.4	0.0979
6	7.21	2883.0	0.0544
7	7.21	2883.9	0.0551
8	7.28	2912.0	0.0773
9	7.30	2920.0	0.0929
10	7.49	2992.5	0.0530

No.	(ppm)	(Hz)	Height
11	7.49	2993.8	0.0503
12	7.51	3000.4	0.0667
13	7.51	3001.7	0.0724
14	7.52	3008.3	0.0379
15	7.53	3009.6	0.0430
16	7.55	3020.1	0.0804
17	7.56	3021.5	0.0698
18	7.57	3028.0	0.0731
19	7.58	3029.4	0.0651

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M04	2.54	[2.52 .. 2.55]	-	s	3
2	M03	7.19	[7.17 .. 7.22]	7.58	td	1
3	M03	7.19	[7.17 .. 7.22]	7.58	td	1
4	M03	7.19	[7.17 .. 7.22]	1.10	td	1
5	M02	7.29	[7.27 .. 7.31]	7.91	d	1
6	M01	7.51	[7.48 .. 7.53]	7.91	td	1
7	M01	7.51	[7.48 .. 7.53]	7.91	td	1
8	M01	7.51	[7.48 .. 7.53]	1.32	td	1
9	M00	7.57	[7.55 .. 7.59]	7.91	dd	1
10	M00	7.57	[7.55 .. 7.59]	1.32	dd	1

No.	(ppm)	(Hz)	Height
1	15.70	1578.1	0.5953
2	76.68	7708.0	1.0000
3	77.00	7740.4	0.9952
4	77.32	7772.9	0.8498
5	111.53	11212.0	0.0810
6	116.88	11749.3	0.1401
7	125.05	12570.5	0.6318
8	126.16	12682.1	0.3784
9	132.88	13357.3	0.8648
10	133.40	13410.0	0.7850
11	143.55	14430.0	0.2167

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M07	15.70	[15.18 .. 16.04]	s	1
2	M06	111.53	[111.14 .. 111.77]	s	1
3	M05	116.88	[116.54 .. 117.20]	s	1
4	M04	125.05	[124.68 .. 125.44]	s	1
5	M03	126.16	[125.83 .. 126.49]	s	1
6	M02	132.88	[132.61 .. 133.08]	s	1
7	M01	133.40	[133.21 .. 133.70]	s	1
8	M00	143.55	[143.28 .. 143.81]	s	1

Table 2, entry 4: 4'-cyanoacetanilide

No.	(ppm)	(Hz)	Height
1	2.07	827.4	1.0000
2	4.78	1911.0	0.3664
3	7.55	3020.0	0.2047
4	7.58	3028.4	0.3030
5	7.65	3060.0	0.2955
6	7.68	3068.4	0.1972

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M02	2.07	[2.03 .. 2.10]	-	s	3
2	M01	7.56	[7.54 .. 7.60]	8.35	d	2
3	M00	7.66	[7.63 .. 7.70]	8.35	d	2

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	23.81	2393.1	0.0724	8	49.42	4968.3	0.1348	1	M06	23.81	[23.73 .. 23.89]	m	1
2	48.13	4838.5	0.1131	9	107.28	10783.9	0.0358	2	M05	107.28	[107.21 .. 107.34]	m	1
3	48.35	4860.8	0.4311	10	119.62	12024.9	0.0292	3	M04	119.62	[119.55 .. 119.69]	m	1
4	48.58	4883.2	0.6103	11	120.55	12118.1	0.1695	4	M03	120.56	[120.45 .. 120.67]	m	2
5	48.78	4903.4	1.0000	12	133.96	13466.6	0.2056	5	M02	133.85	[133.12 .. 134.57]	m	2
6	49.00	4925.7	0.7121	13	144.21	14496.7	0.0388	6	M01	144.26	[143.54 .. 144.99]	m	1
7	49.20	4946.0	0.4098	14	171.76	17266.6	0.0375	7	M00	171.76	[170.95 .. 172.56]	m	1

Table 2, entry 5: 3-cyanotoluene

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.34	935.7	1.0000	8	7.52	3005.4	0.1148
2	2.49	993.7	0.0554	9	7.54	3012.8	0.0674
3	2.49	995.5	0.0773	10	7.60	3039.6	0.1078
4	3.32	1328.1	0.0785	11	7.62	3047.1	0.0853
5	7.43	2971.5	0.0733	12	7.64	3054.1	0.1467
6	7.45	2979.4	0.1926	13	7.64	3055.0	0.1668
7	7.47	2986.9	0.1487				

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M04	2.34	[2.32 .. 2.36]	-	s	3
2	M03	7.45	[7.42 .. 7.48]	7.69	t	1
3	M03	7.45	[7.42 .. 7.48]	7.69	t	1
4	M02	7.53	[7.50 .. 7.55]	-	m	1
5	M01	7.61	[7.59 .. 7.63]	7.47	d	1
6	M00	7.64	[7.63 .. 7.65]	0.88	d	1

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	20.48	2058.6	0.2280	8	111.13	11171.3	0.0793	1	M00	20.48	[20.45 .. 20.51]	s	1
2	38.87	3907.9	0.1446	9	118.87	11949.9	0.1196	2	M07	111.13	[111.10 .. 111.16]	s	1
3	39.08	3928.2	0.4153	10	129.24	12992.2	0.4139	3	M08	118.87	[118.84 .. 118.90]	s	1
4	39.30	3950.5	0.8142	11	129.32	13000.3	0.3613	4	M09	129.24	[129.21 .. 129.27]	s	1
5	39.70	3991.0	0.8100	12	132.29	13298.4	0.3917	5	M10	129.32	[129.29 .. 129.35]	s	1
6	39.92	4013.3	0.4103	13	133.98	13468.7	0.4739	6	M11	132.29	[132.26 .. 132.32]	s	1
7	40.13	4033.6	0.1449	14	139.21	13993.9	0.1090	7	M12	133.98	[133.95 .. 134.01]	s	1
								8	M13	139.21	[139.18 .. 139.24]	s	1

Table 2, entry 6: 9-cyanoanthracene

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	7.25	2898.4	0.2511	12	7.71	3082.5	0.7733	1	M04	7.58	[7.55 .. 7.61]	-	m	2
2	7.56	3021.7	0.4623	13	7.71	3083.9	0.6913	2	M03	7.71	[7.68 .. 7.74]	-	m	2
3	7.56	3022.8	0.4826	14	7.73	3089.1	0.5067	3	M02	8.07	[8.05 .. 8.09]	8.57	d	2
4	7.58	3028.5	0.6365	15	7.73	3090.4	0.5125	4	M01	8.41	[8.39 .. 8.44]	8.79	dd	2
5	7.58	3029.6	0.7595	16	8.06	3221.4	1.0000	5	M01	8.41	[8.39 .. 8.44]	0.88	dd	2
6	7.58	3031.1	0.5681	17	8.08	3230.0	0.9092	6	M00	8.67	[8.65 .. 8.68]	-	s	1
7	7.60	3036.8	0.6321	18	8.40	3358.1	0.9356							
8	7.60	3037.9	0.6296	19	8.40	3358.9	0.9602							
9	7.69	3074.0	0.6078	20	8.42	3366.8	0.8828							
10	7.69	3075.1	0.6548	21	8.42	3367.7	0.8930							
11	7.71	3080.6	0.5392	22	8.67	3464.2	0.9241

No.	(ppm)	(Hz)	Height
1	76.68	7708.0	1.0000
2	77.00	7740.4	0.8799
3	77.30	7770.9	0.8377
4	105.44	10599.6	0.0178
5	117.22	11783.8	0.0260
6	125.29	12594.9	0.2778
7	126.34	12700.3	0.3347
8	128.92	12959.9	0.5694
9	130.62	13130.2	0.1030
10	132.71	13341.1	0.1516
11	133.30	13399.9	0.0933

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M07	105.44	[105.31 .. 105.55]	s	1
2	M06	117.22	[117.10 .. 117.33]	s	1
3	M05	125.29	[125.08 .. 125.41]	s	2
4	M04	126.34	[126.21 .. 126.45]	s	2
5	M03	128.92	[128.73 .. 129.07]	s	4
6	M02	130.62	[130.45 .. 130.74]	s	2
7	M01	132.71	[132.52 .. 132.83]	s	1
8	M00	133.30	[133.14 .. 133.44]	s	2

Table 2, entry 7: 2,4-difluorobenzonitrile

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	6.95	2778.0	0.4700	9	7.01	2803.1	0.5600	17	7.62	3045.6	0.5256
2	6.96	2780.7	0.5311	10	7.01	2804.4	0.5511	18	7.63	3051.8	0.5489
3	6.97	2786.8	0.7051	11	7.02	2804.8	0.4203	19	7.64	3053.1	0.5504
4	6.98	2789.4	1.0000	12	7.03	2809.7	0.3840	20	7.64	3054.4	0.5340
5	6.99	2793.4	0.4712	13	7.03	2810.5	0.3807	21	7.65	3058.8	0.5330
6	6.99	2795.6	0.5902	14	7.03	2811.9	0.2844	22	7.65	3060.1	0.5615
7	7.00	2797.8	0.6457	15	7.04	2812.7	0.2995	23	7.66	3061.4	0.5223
8	7.01	2801.7	0.7478	16	7.25	2898.4	0.0866	24	7.67	3067.6	0.4374

No.	(ppm)	Value	Absolute Value
1	[6.94 .. 6.99]	0.286	1.93674e+8
2	[6.99 .. 7.04]	0.354	2.39884e+8

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M02	6.97	[6.94 .. 7.00]	8.79	dt	1
2	M02	6.97	[6.94 .. 7.00]	8.79	dt	1
3	M02	6.97	[6.94 .. 7.00]	2.64	dt	1
4	M01	7.02	[6.99 .. 7.05]	-	m	1
5	M00	7.65	[7.60 .. 7.68]	8.57	ddd	1
6	M00	7.65	[7.60 .. 7.68]	7.25	ddd	1
7	M00	7.65	[7.60 .. 7.68]	6.15	ddd	1

Table 2, entry 8: 2-cyano-3-nitrotoluene

No.	(ppm)	(Hz)	Height
1	2.70	1078.4	1.0000
2	7.25	2898.4	0.0143
3	7.65	3058.8	0.0348
4	7.67	3066.7	0.1612
5	7.68	3071.1	0.1342
6	7.69	3073.7	0.3618
7	7.70	3079.0	0.0294
8	8.11	3242.0	0.0742
9	8.12	3244.7	0.0811
10	8.13	3249.1	0.0539
11	8.13	3251.3	0.0645

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M02	2.70	[2.67 .. 2.72]	-	s	3
2	M01	7.68	[7.64 .. 7.71]	-	m	2
3	M00	8.12	[8.10 .. 8.14]	6.81	dd	1
4	M00	8.12	[8.10 .. 8.14]	2.42	dd	1

No.	(ppm)	(Hz)	Height
1	21.08	2119.5	0.1805
2	76.68	7708.0	1.0000
3	77.00	7740.4	0.9377
4	77.30	7770.9	0.7855
5	107.96	10853.0	0.0342
6	113.71	11430.9	0.0784
7	122.89	12353.6	0.3356
8	132.63	13333.0	0.3464
9	135.50	13620.9	0.2499
10	145.76	14653.0	0.1062

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M06	21.08	[20.78 .. 21.41]	s	1
2	M05	107.96	[107.65 .. 108.24]	s	1
3	M04	113.71	[113.37 .. 113.96]	s	1
4	M03	122.89	[122.61 .. 123.20]	s	1
5	M02	132.63	[132.28 .. 133.10]	s	2
6	M01	135.50	[135.13 .. 135.83]	s	1
7	M00	145.76	[145.28 .. 146.13]	s	1

Table 2, entry 9: methyl 4-cyanobenzoate

No.	(ppm)	(Hz)	Height
1	3.94	1576.7	1.0000
2	7.72	3086.1	0.1966
3	7.72	3087.8	0.0846
4	7.74	3094.4	0.2119
5	8.11	3242.9	0.2218
6	8.12	3244.7	0.0912
7	8.13	3249.5	0.0776
8	8.13	3251.3	0.2008

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	H's
1	M02	3.94	[3.94 .. 3.96]	s	3
2	M01	7.73	[7.71 .. 7.75]	m	2
3	M00	8.12	[8.10 .. 8.14]	m	2

No.	(ppm)	(Hz)	Height
1	52.69	5297.0	0.4431
2	76.70	7710.0	0.9975
3	77.00	7740.4	0.8620
4	77.32	7772.9	1.0000
5	116.39	11700.6	0.1338
6	117.93	11854.7	0.1445
7	130.07	13075.4	0.9873
8	132.19	13288.4	0.9155
9	133.90	13460.7	0.1056
10	165.39	16626.0	0.1446

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M06	52.69	[51.42 .. 53.76]	s	1
2	M05	116.39	[115.35 .. 117.14]	s	1
3	M04	117.93	[117.14 .. 118.79]	s	1
4	M03	130.07	[129.12 .. 130.64]	s	2
5	M02	132.19	[131.47 .. 132.98]	s	2
6	M01	133.90	[133.26 .. 134.77]	s	1
7	M00	165.39	[164.39 .. 166.18]	s	1

Table 2, entry 10: 4-cyanobenzoic acid

No.	(ppm)	(Hz)	Height
1	2.49	993.7	0.1176
2	2.49	995.5	0.1620
3	7.95	3178.0	0.5769
4	7.95	3179.8	0.2554
5	7.97	3184.6	0.2836
6	7.97	3186.4	1.0000
7	8.05	3219.8	0.9178
8	8.06	3221.5	0.3004
9	8.07	3226.4	0.2391
10	8.07	3228.1	0.6645
11	13.55	5418.2	0.0776

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	H's
1	M02	7.96	[7.94 .. 7.98]	m	2
2	M01	8.06	[8.04 .. 8.09]	m	2
3	M00	13.55	[13.51 .. 13.59]	s	1

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	39.30	3950.5	0.1426	8	115.47	11607.2	0.0743	1	M05	115.47	[115.28 .. 115.60]	s	1
2	39.50	3970.8	0.4278	9	118.57	11919.5	0.0720	2	M04	118.57	[118.38 .. 118.66]	s	1
3	39.70	3991.0	0.7715	10	130.31	13099.7	0.3475	3	M03	130.31	[130.11 .. 130.47]	s	2
4	39.92	4013.3	1.0000	11	133.06	13375.4	0.4002	4	M02	133.06	[132.79 .. 133.24]	s	2
5	40.13	4033.6	0.8516	12	135.25	13596.5	0.0982	5	M01	135.25	[135.04 .. 135.39]	s	1
6	40.35	4055.9	0.3920	13	166.44	16731.4	0.1377	6	M00	166.44	[166.26 .. 166.62]	s	1
7	40.55	4076.2	0.1420										

Table 2, entry 11: 4-cyanophenylboronic acid

No.	(ppm)	(Hz)	Height
1	2.48	993.3	0.2047
2	2.49	995.5	0.2863
3	2.49	997.2	0.2134
4	7.76	3103.8	0.7500
5	7.78	3112.1	1.0000
6	7.91	3163.1	0.9021
7	7.93	3171.5	0.6924
8	8.39	3354.3	0.0227

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M01	7.77	[7.75 .. 7.79]	8.35	d	2
2	M00	7.92	[7.89 .. 7.95]	8.35	d	2
3	M02	8.39	[8.20 .. 8.54]	-	s	2

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	C's
1	38.67	3887.6	0.1389	8	112.20	11278.8	0.0758	1	M04	112.20	[112.12 .. 112.28]	-	s	1
2	38.87	3907.9	0.4287	9	118.77	11939.8	0.0593	2	M03	118.77	[118.69 .. 118.85]	-	s	1
3	39.08	3928.2	0.7928	10	130.76	13144.3	0.2352	3	M02	130.76	[130.65 .. 130.84]	-	s	2
4	39.30	3950.5	1.0000	11	130.90	13158.5	0.0511	4	M01	132.33	[130.86 .. 133.86]	287.94	d	1
5	39.50	3970.8	0.8618	12	133.76	13446.4	0.0440	5	M00	134.39	[134.26 .. 134.50]	-	s	2
6	39.70	3991.0	0.3998	13	134.39	13509.3	0.3107							
7	39.92	4013.3	0.1539											

Table 3, entry 1: 5-cyanoindole

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	2.49	995.5	0.1765	11	7.42	2966.7	0.4746	1	M04	6.57	[6.55 .. 6.59]	-	m	1
2	2.49	997.2	0.1279	12	7.42	2968.0	0.4938	2	M03	7.41	[7.39 .. 7.44]	8.57	dd	1
3	6.57	2625.7	0.2809	13	7.54	3014.6	1.0000	3	M03	7.41	[7.39 .. 7.44]	1.54	dd	1
4	6.57	2626.6	0.3161	14	7.55	3017.7	0.5749	4	M02	7.55	[7.52 .. 7.57]	-	m	2
5	6.57	2627.5	0.4365	15	7.55	3020.3	0.4280	5	M01	8.07	[8.05 .. 8.08]	0.88	d	1
6	6.58	2628.8	0.3072	16	7.56	3022.9	0.4603	6	M00	11.66	[11.62 .. 11.70]	-	s	1
7	6.58	2629.7	0.2946	17	8.07	3225.5	0.5664							
8	6.58	2630.5	0.2677	18	8.07	3226.4	0.5634							
9	7.40	2957.9	0.3495	19	11.66	4661.5	0.1260							
10	7.40	2959.7	0.3860

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	38.65	3885.6	0.1474	9	101.83	10236.5	0.2629	1	M08	100.68	[100.51 .. 100.82]	s	1
2	38.87	3907.9	0.4053	10	112.42	11301.1	0.3626	2	M07	101.83	[101.67 .. 102.01]	s	1
3	39.08	3928.2	0.8755	11	120.55	12118.2	0.1335	3	M06	112.42	[112.24 .. 112.60]	s	1
4	39.28	3948.4	1.0000	12	123.41	12406.2	0.2980	4	M05	120.55	[120.41 .. 120.67]	s	1
5	39.50	3970.8	0.8113	13	125.47	12613.0	0.3657	5	M04	123.41	[123.24 .. 123.54]	s	1
6	39.70	3991.0	0.4356	14	127.19	12785.4	0.1432	6	M03	125.47	[125.33 .. 125.60]	s	1
7	39.90	4011.3	0.1357	15	127.81	12848.2	0.2543	7	M02	127.19	[127.04 .. 127.31]	s	1
8	100.68	10120.9	0.1406	16	137.37	13809.4	0.1485	8	M01	127.81	[127.67 .. 127.97]	s	1
								9	M00	137.37	[136.98 .. 137.95]	s	1

Table 3, entry 2: 4-cyanoindole

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	2.48	993.3	0.2140	9	7.24	2896.4	0.6838	1	M05	6.58	[6.55 .. 6.61]	3.08	d	1
2	2.49	995.5	0.2868	10	7.52	3005.4	0.7291	2	M04	7.23	[7.19 .. 7.26]	-	m	1
3	2.49	997.2	0.2127	11	7.52	3006.2	0.7366	3	M03	7.52	[7.48 .. 7.54]	0.88	d	1
4	3.35	1340.8	0.1970	12	7.64	3053.3	1.0000	4	M02	7.64	[7.62 .. 7.66]	3.08	d	1
5	6.58	2629.2	0.7381	13	7.64	3056.3	0.9886	5	M01	7.75	[7.72 .. 7.78]	8.35	d	1
6	6.58	2632.3	0.7285	14	7.74	3095.9	0.8003	6	M00	11.74	[11.67 .. 11.81]	-	s	1
7	7.21	2881.0	0.5802	15	7.76	3104.2	0.7650							
8	7.23	2888.9	0.8471	16	11.74	4692.7	0.2073

No.	(ppm)	(Hz)	Height
1	38.87	3907.9	0.1355
2	39.08	3928.2	0.4347
3	39.28	3948.4	0.8173
4	39.50	3970.8	1.0000
5	39.70	3991.0	0.8789
6	39.90	4011.3	0.4096
7	40.13	4033.6	0.1488
8	99.37	9989.1	0.3158

No.	(ppm)	(Hz)	Height
9	101.04	10157.4	0.0962
10	116.86	11747.2	0.3233
11	118.81	11943.8	0.0961
12	120.91	12154.7	0.3171
13	124.50	12515.7	0.3066
14	128.48	12915.1	0.0916
15	128.84	12951.6	0.2472
16	135.60	13630.9	0.1181

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M08	99.37	[99.28 .. 99.45]	s	1
2	M07	101.04	[100.98 .. 101.12]	s	1
3	M06	116.86	[116.79 .. 116.96]	s	1
4	M05	118.81	[118.74 .. 118.87]	s	1
5	M04	120.91	[120.83 .. 121.02]	s	1
6	M03	124.50	[124.43 .. 124.60]	s	1
7	M02	128.48	[128.41 .. 128.55]	s	1
8	M01	128.84	[128.78 .. 128.93]	s	1
9	M00	135.60	[134.61 .. 136.85]	s	1

Table 3, entry 3: 2-cyano-6-methylpyridine

No.	(ppm)	(Hz)	Height
1	2.59	1035.7	1.0000
2	7.25	2898.4	0.0095
3	7.35	2939.7	0.1196
4	7.37	2947.6	0.1344
5	7.49	2994.2	0.1104
6	7.51	3001.7	0.1347
7	7.68	3070.2	0.1113
8	7.70	3077.7	0.1852
9	7.72	3085.6	0.0852

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M03	2.59	[2.57 .. 2.60]	-	s	3
2	M02	7.36	[7.34 .. 7.38]	7.91	d	1
3	M01	7.50	[7.48 .. 7.52]	7.47	d	1
4	M00	7.70	[7.67 .. 7.72]	7.69	t	1
5	M00	7.70	[7.67 .. 7.72]	7.69	t	1

No.	(ppm)	(Hz)	Height
1	24.33	2446.0	0.2108
2	76.68	7708.0	0.9462
3	77.00	7740.4	1.0000
4	77.32	7772.9	0.9184
5	117.34	11795.9	0.1051
6	125.65	12631.4	0.3149
7	126.82	12749.0	0.4756
8	133.16	13385.7	0.0776
9	137.01	13773.0	0.3525
10	160.65	16149.5	0.1436

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M06	24.33	[23.99 .. 24.64]	s	1
2	M05	117.34	[116.97 .. 117.59]	s	1
3	M04	125.65	[125.26 .. 125.95]	s	1
4	M03	126.82	[126.53 .. 127.08]	s	1
5	M02	133.16	[132.89 .. 133.44]	s	1
6	M01	137.01	[136.74 .. 137.25]	s	1
7	M00	160.65	[160.32 .. 160.90]	s	1

Table 3, entry 4: 3-cyano-6-methoxypyridine

No.	(ppm)	(Hz)	Height
1	3.97	1589.0	1.0000
2	6.79	2714.7	0.1232
3	6.81	2723.5	0.1248
4	7.74	3094.4	0.0828
5	7.75	3097.0	0.0848
6	7.76	3103.2	0.0823
7	7.77	3105.4	0.0770
8	8.47	3385.7	0.1082
9	8.47	3387.9	0.1043

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M03	3.97	[3.96 .. 3.99]	-	s	3
2	M02	6.80	[6.78 .. 6.82]	8.79	d	1
3	M01	7.75	[7.73 .. 7.78]	8.57	dd	1
4	M01	7.75	[7.73 .. 7.78]	2.42	dd	1
5	M00	8.47	[8.46 .. 8.49]	2.20	d	1

No.	(ppm)	(Hz)	Height
1	54.23	5451.1	0.5297
2	76.68	7708.0	0.9889
3	77.00	7740.4	1.0000
4	77.32	7772.9	0.8632
5	102.38	10291.4	0.1001
6	111.80	11238.3	0.4757
7	117.22	11783.8	0.1149
8	140.82	14156.2	0.5170
9	151.94	15273.5	0.4501
10	166.00	16686.9	0.1049

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M06	54.23	[54.07 .. 54.35]	s	1
2	M05	102.38	[102.20 .. 102.48]	s	1
3	M04	111.80	[111.60 .. 111.90]	s	1
4	M03	117.22	[117.09 .. 117.34]	s	1
5	M02	140.82	[140.60 .. 140.97]	s	1
6	M01	151.94	[151.74 .. 152.08]	s	1
7	M00	166.00	[165.83 .. 166.13]	s	1

Table 3, entry 5: 4-cyano-2-aminopyridine

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.49	997.2	0.2188	9	6.78	2708.7	0.5137
2	2.50	999.0	0.2959	10	6.78	2712.5	0.5804
3	2.50	1001.0	0.2142	11	6.79	2713.8	0.5365
4	6.53	2609.2	0.6898	12	8.08	3231.7	0.6148
5	6.72	2686.6	0.6729	13	8.08	3232.1	0.6346
6	6.72	2687.9	1.0000	14	8.10	3236.7	0.6062
7	6.73	2688.8	0.7503	15	8.10	3237.4	0.6250
8	6.77	2707.2	0.5848				

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M03	6.53	[6.48 .. 6.57]	-	s	2
2	M02	6.72	[6.71 .. 6.74]	-	m	1
3	M01	6.78	[6.76 .. 6.80]	5.16	dd	1
4	M01	6.78	[6.76 .. 6.80]	1.43	dd	1
5	M00	8.09	[8.06 .. 8.12]	5.16	dd	1
6	M00	8.09	[8.06 .. 8.12]	0.55	dd	1

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	38.45	3865.3	0.1488	8	109.39	10996.9	0.2844	1	M05	109.39	[109.07 .. 109.70]	s	1
2	38.67	3887.6	0.4457	9	111.55	11213.9	0.2947	2	M04	111.55	[111.27 .. 111.91]	s	1
3	38.87	3907.9	0.9063	10	117.06	11767.4	0.0930	3	M03	117.06	[116.78 .. 117.32]	s	1
4	39.08	3928.2	1.0000	11	119.32	11994.5	0.1114	4	M02	119.32	[119.05 .. 119.59]	s	1
5	39.30	3950.5	0.8773	12	149.19	14997.6	0.2861	5	M01	149.19	[148.87 .. 149.65]	s	1
6	39.50	3970.8	0.4492	13	159.50	16033.8	0.1332	6	M00	159.50	[159.13 .. 159.86]	s	1
7	39.70	3991.0	0.1304										

Table 3, entry 6: 2,4-dicyanopyridine

No.	(ppm)	(Hz)	Height
1	7.25	2898.4	0.0560
2	7.77	3104.5	0.6178
3	7.77	3105.8	0.7157
4	7.78	3109.3	0.7075
5	7.78	3110.7	0.6242
6	7.92	3165.1	0.7618
7	7.92	3166.5	1.0000
8	7.92	3167.8	0.7009
9	8.93	3569.9	0.6951
10	8.94	3574.7	0.7094
11	8.94	3575.6	0.6717

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M02	7.77	[7.76 .. 7.79]	4.83	dd	1
2	M02	7.77	[7.76 .. 7.79]	1.32	dd	1
3	M01	7.92	[7.91 .. 7.94]	-	m	1
4	M00	8.94	[8.92 .. 8.96]	-	m	1

No.	(ppm)	(Hz)	Height
1	76.68	7708.0	1.0000
2	77.00	7740.4	0.9663
3	77.32	7772.9	0.7976
4	114.52	11512.1	0.1456
5	115.49	11609.4	0.0953
6	122.10	12274.5	0.1151
7	128.34	12901.1	0.4207
8	129.53	13020.7	0.4812
9	135.30	13600.6	0.0838
10	152.16	15295.8	0.4916

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M06	114.52	[114.30 .. 114.70]	s	1
2	M05	115.49	[115.31 .. 115.61]	s	1
3	M04	122.10	[121.87 .. 122.26]	s	1
4	M03	128.34	[128.06 .. 128.54]	s	1
5	M02	129.53	[129.25 .. 129.77]	s	1
6	M01	135.30	[135.03 .. 135.53]	s	1
7	M00	152.16	[151.88 .. 152.38]	s	1

Table 3, entry 7: 2-cyanopyrimidine

No.	(ppm)	(Hz)	Height
1	7.54	3014.0	0.3588
2	7.55	3018.8	0.6834
3	7.56	3024.1	0.3079
4	8.85	3540.0	0.9986
5	8.87	3544.8	1.0000

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M01	7.55	[7.53 .. 7.58]	5.05	t	1
2	M01	7.55	[7.53 .. 7.58]	5.05	t	1
3	M00	8.86	[8.84 .. 8.89]	4.83	d	2

No.	(ppm)	(Hz)	Height
1	76.70	7710.0	0.8587
2	77.00	7740.4	0.9150
3	77.32	7772.9	1.0000
4	115.53	11613.4	0.0940
5	123.58	12422.5	0.6728
6	145.30	14606.4	0.1003
7	158.03	15885.9	0.9275

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M03	115.53	[114.74 .. 116.10]	s	1
2	M02	123.58	[122.63 .. 124.21]	s	1
3	M01	145.30	[144.45 .. 145.74]	s	1
4	M00	158.03	[157.22 .. 158.52]	s	2

Table 3, entry 8: 2-cyanopyrazine

No.	(ppm)	(Hz)	Height
1	7.25	2898.4	0.0390
2	8.72	3484.2	0.5188
3	8.72	3486.4	0.8020
4	8.73	3488.1	0.6153
5	8.79	3513.6	1.0000
6	8.80	3516.2	0.8662
7	8.92	3565.0	0.9898
8	8.92	3566.3	0.9897

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M02	8.72	[8.71 .. 8.74]	-	dd	1
2	M01	8.79	[8.78 .. 8.81]	2.64	d	1
3	M00	8.92	[8.91 .. 8.93]	1.32	d	1

No.	(ppm)	(Hz)	Height
1	76.68	7708.0	1.0000
2	77.00	7740.4	0.9876
3	77.32	7772.9	0.8533
4	115.20	11581.0	0.1203
5	131.06	13174.8	0.0986
6	145.44	14620.6	0.4478
7	147.32	14809.2	0.5466
8	148.29	14906.5	0.5859

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M04	115.20	[114.84 .. 115.43]	s	1
2	M03	131.06	[130.84 .. 131.28]	s	1
3	M02	145.44	[145.14 .. 145.64]	s	1
4	M01	147.32	[146.91 .. 147.67]	s	1
5	M00	148.29	[147.85 .. 148.59]	s	1

Table 3, entry 9: 2-cyano-3-methylthiophene

No.	(ppm)	(Hz)	Height
1	2.43	969.8	1.0000
2	6.92	2766.6	0.1542
3	6.93	2771.4	0.1588
4	7.44	2975.8	0.1631
5	7.46	2981.0	0.1561

No.	Multiplet1	Shift1 (ppm)	(ppm)	J (Hz)	Type	H's
1	M02	2.43	[2.40 .. 2.45]	-	s	3
2	M01	6.93	[6.90 .. 6.95]	4.83	d	1
3	M00	7.45	[7.43 .. 7.47]	5.27	d	1

No.	(ppm)	(Hz)	Height
1	15.19	1527.4	0.6726
2	76.68	7708.0	0.7903
3	77.00	7740.4	0.8524
4	77.32	7772.9	0.7775
5	105.85	10640.1	0.1168
6	114.20	11479.6	0.2077
7	129.51	13018.7	1.0000
8	131.52	13221.4	0.9537
9	149.48	15026.1	0.2829

No.	Multiplet1	Shift1 (ppm)	(ppm)	Type	C's
1	M05	15.19	[14.89 .. 15.50]	s	1
2	M04	105.85	[105.41 .. 106.09]	s	1
3	M03	114.20	[113.85 .. 114.47]	s	1
4	M02	129.51	[128.97 .. 129.99]	s	1
5	M01	131.52	[131.11 .. 131.90]	s	1
6	M00	149.48	[149.09 .. 149.84]	s	1