Supporting Information

Synthesis

2-Methyl-3-hydroxypyridine, 2-chloro-3-hydroxypyridine, 2-bromo-3-hydroxypyridine, 2-chloro-3-aminopyridine and 2-bromo-3-aminopyridine were purchased from Lancaster and/or Acros Chemicals and used as such for crystallization. Compounds are named as halo derivatives of the parent hydroxy-/ amino-pyridine.

2-Iodo-3-hydroxypyridine: 3-Hydroxypyridine, KOH and NaI (1.0 equiv each) were dissolved in MeOH (15 mL), 4% NaOCl solution (1.0 equiv) was slowly added at 0 °C. The solution was neutralised after 2 h and the solid product was separated by filtration. ^{1}H NMR: ($CDCl_3$, 200 MHz) δ 7.98 (d, J 5 Hz, 1H), 7.22 (d, J 8 Hz, 1H), 7.16 (dd, J 8, 5 Hz, 1H), 5.49 (s, 1H).

3-Hydroxypyridine-*N*-oxide: 3-Hydroxypyridine and *m*-CPBA (1.0 equiv each) were dissolved in EtOAc (10 mL) and stirred at room temperature for 2 h. The precipitated solid product was collected by filtration. The other *N*-oxides were prepared by the same procedure.

H^1-NMR:

3-Hydroxypyridine-*N*-oxide: (DMSO-d_6, 200 MHz) δ 10.49 (s, 1H), 7.75 (s, 1H), 7.73 (d, J 6 Hz, 1H), 7.21 (dd, J 8, 6 Hz, 1H), 6.81 (d, J 8 Hz, 1H).

2-Methyl-3-hydroxypyridine-*N*-oxide: (DMSO-d_6, 400MHz) δ 10.46 (s, 1H), 7.81 (d, J 6 Hz, 1H), 7.06 (dd, J 8, 6 Hz, 1H), 6.81 (d, J 8 Hz, 1H), 2.24 (s, 3H).

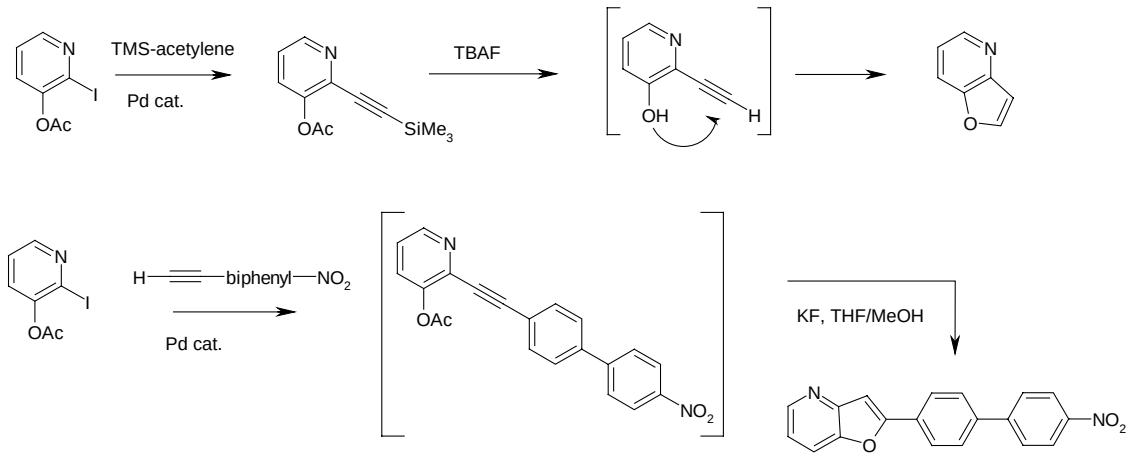
2-Chloro-3-hydroxypyridine-*N*-oxide: (DMSO-d_6, 400MHz) δ 11.36 (s, 1H), 8.00 (d, J 6 Hz, 1H), 7.20 (dd, J 8, 6 Hz, 1H), 6.94 (d, J 8 Hz, 1H).

2-Bromo-3-hydroxypyridine-*N*-oxide: (DMSO-d_6, 200MHz) δ 10.90 (s, 1H), 7.85 (d, J 5 Hz, 1H), 6.99 (dd, J 7, 5 Hz, 1H), 6.81 (d, J 7 Hz, 1H).

Attempted synthesis of 2-ethynyl derivatives of 3-pyridinol **1** resulted in cyclized benzofuran products (Scheme S1). For other examples of this facile reaction, see:

(1) Chakrabarty, M.; McConville, D. B.; Saito, T.; Meng, H.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *Tetrahedron Lett.* **1998**, *39*, 8237.

(2) Arcadi, A.; Cacchi, S.; Giuseppe, S. D.; Fabrizi, G.; Marinelli, F. *Org. Lett.* **2002**, *4*, 2409.



Scheme S1 Attempted synthesis of 2-ethynyl derivatives was unsuccessful due to cyclization from proximal hydroxyl group to benzofuran ring.

Crystallographic data

Crystal data was collected on Bruker SMART APEX CCD with Mo-Kα radiation (λ = 0.71073 Å).

2-Chloro-3-hydroxypyridine (**1Cl**)**:** C_5H_4ClNO, *Mr* = 129.54, orthorhombic, *Fdd*2, *a* = 23.069(4), *b* = 25.231(4), *c* = 3.8429(6) Å, *V* = 2236.8(6) Å^3, *Z* = 16, *R*1 = 0.0295, *wR*2 = 0.0764, *T* = 298 K.

2-Bromo-3-hydroxypyridine (**1Br**)**:** C_5H_4BrNO, *Mr* = 174.00, orthorhombic, *Pna*2$_1$, *a* = 11.5563(12), *b* = 12.7285(13), *c* = 3.8875(4) Å, *V* = 571.83(10) Å^3, *Z* = 4, *R*1 = 0.0198, *wR*2 = 0.0507, *T* = 100 K.

2-Iodo-3-hydroxypyridine (**1I**)**:** C_5H_4INO, *Mr* = 220.99, orthorhombic, *Pna*2$_1$, *a* = 11.5329(11), *b* = 12.8331(12), *c* = 4.2475(4) Å, *V* = 628.64(10) Å^3, *Z* = 4, *R*1 = 0.0172, *wR*2 = 0.0457, *T* = 100 K.

2-Methyl-3-hydroxypyridine (**1Me**)**:** C_6H_7NO, *Mr* = 109.13, monoclinic, *C*2/*c*, *a* = 11.053(2), *b* = 9.6151(19), *c* = 11.316(2) Å, *β* = 100.64(3)º, *V* = 1181.9(4)Å^3, *Z* = 8 , *R*1 = 0.1495, *wR*2= 0.3050, *T* = 100K.

2-Chloro-3-hydroxypyridine-*N*-oxide (2Cl): $C_5H_4ClNO_2$, *Mr* = 145.54, orthorhombic, *Pna*2$_1$, *a* = 11.2712(14), *b* = 12.7754(16), *c* = 3.7794(5) Å, *V* = 544.21(12) Å^3, *Z* = 4, *R*1 = 0.0266, *wR*2 = 0.0617, *T* = 100K.

2-Bromo-3-hydroxypyridine-*N*-oxide (2Br): $C_5H_4BrNO_2$, *Mr* = 190.00, orthorhombic, *P*2$_1$2$_1$2$_1$, *a* = 3.8571(5), *b* = 12.3235(15), *c* = 12.5884(15) Å, *V* = 598.36(13) Å^3, *Z* = 4, *R*1 = 0.0252, *wR*2 = 0.0589, *T* = 298 K.

2-Methyl-3-hydroxypyridine-*N*-oxide (2Me): $C_6H_7NO_2$, Mr = 125.13, monoclinic, $P2_1/c$, a = 4.6258(9), b = 10.3353(19), c = 12.677(2) Å, β = 99.270(3)°, V = 598.18(19) Å^3, Z = 4, $R1$ = 0.0487, $wR2$ = 0.1346, T = 298 K.

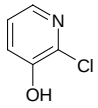
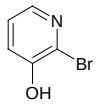
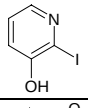
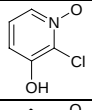
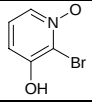
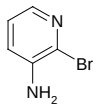
3-Hydroxypyridine-*N*-oxide (2H): $C_5H_5NO_2$, Mr = 111.10, triclinic, P-1, a = 6.3536(8), b = 6.5014(8), c = 6.9499(8)Å, α = 113.794(2), β = 99.650(2), γ = 106.930(2)º, V = 237.59(5) Å^3, Z = 2, $R1$ = 0.0398, $wR2$ = 0.1055, T = 298 K. C2 is disordered over two positions (C2A, C2B) with 0.5 occupancy. Similarly N1 and OH hydrogen are disordered over two positions (N1A, N1B and H1, H2) with 0.5 occupancy.

2-Chloro-3-aminopyridine (3Cl): $C_5H_5ClN_2$, Mr = 128.56, monoclinic, $P2_1/n$, a = 6.446(5), b = 8.022(6), c = 11.991(8)Å, β = 104.510(11)º, V = 600.3(7) Å^3, Z = 4 , $R1$ = 0.0429, $wR2$ = 0.1222, T = 298K.

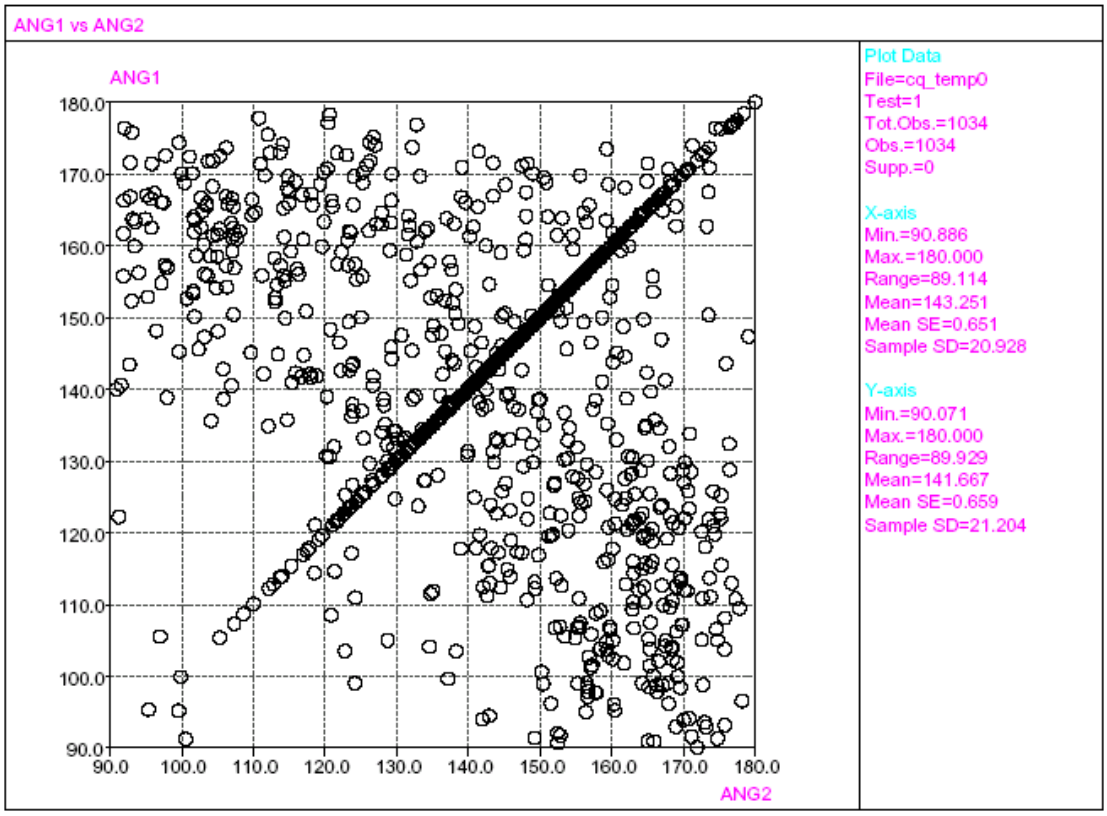
2-Bromo-3-aminopyridine (3Br): $C_5H_5BrN_2$, Mr = 173.02, monoclinic, $P2_1$, a = 7.9689(5), b = 13.1908(8), c = 11.6096(7) Å, β = 104.6860(10)º, V = 1180.49(13) Å^3, Z = 8, $R1$ = 0.0243, $wR2$ = 0.0588, T = 100K.

Intensities were corrected for absorption effects using the multi-scan technique SADABS. All non-hydrogen atoms were refined anisotropically. H atoms connected to C were generated by riding model and H atoms connected to oxygen were located in difference electron density maps. Structure solution and refinement were carried out with Bruker SHELXTL.

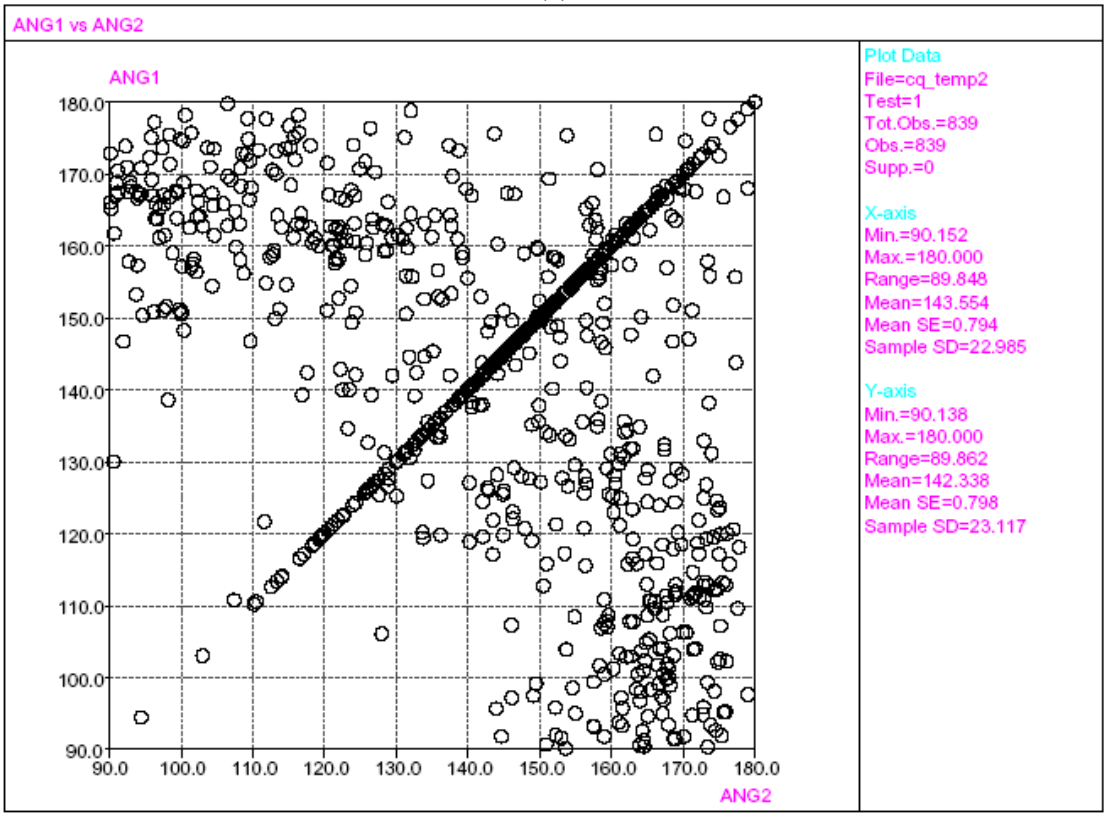
Table S1 Inter-halogen interaction geometry in crystal structures **1-3**.

Compound	Space group	X···X (Å)	C–X···X–C (º)	Geometry[a]
	*Fdd*2	3.350	158.94, 158.94	V-shape
	*Pna*2$_1$	3.637	170.20, 121.25	L-shape
	*Pna*2$_1$	3.738	174.45, 114.52	L-shape
	*Pna*2$_1$	3.510	132.96, 101.41	Borderline L/V
	$P2_12_12_1$	3.931	171.52, 126.06	L-shape
	$P2_1$	3.636 3.634	177.76, 102.57 148.15, 102.48	L-shape Borderline L/V

[a] See Scheme 1a for classification.


ANG1 vs ANG2
ANG1
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0 170.0 180.0
ANG2
Plot Data
File=cq_temp0
Test=1
Tot.Obs.=1034
Obs.=1034
Supp.=0
X-axis
Min.=90.886
Max.=180.000
Range=89.114
Mean=143.251
Mean SE=0.651
Sample SD=20.928
Y-axis
Min.=90.071
Max.=180.000
Range=89.929
Mean=141.667
Mean SE=0.659
Sample SD=21.204

(a)


ANG1 vs ANG2
ANG1
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0 170.0 180.0
ANG2
Plot Data
File=cq_temp2
Test=1
Tot.Obs.=839
Obs.=839
Supp.=0
X-axis
Min.=90.152
Max.=180.000
Range=89.848
Mean=143.554
Mean SE=0.794
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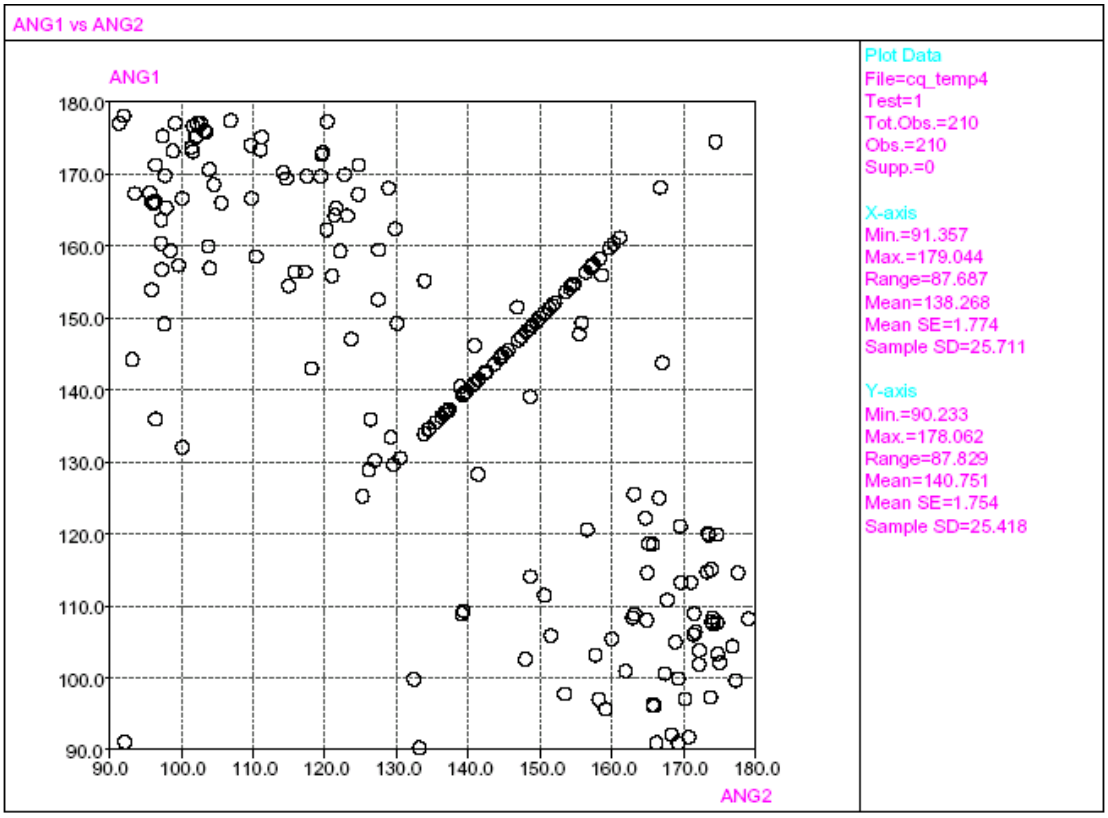
Mean=142.338
Mean SE=0.798
Sample SD=23.117

(b)

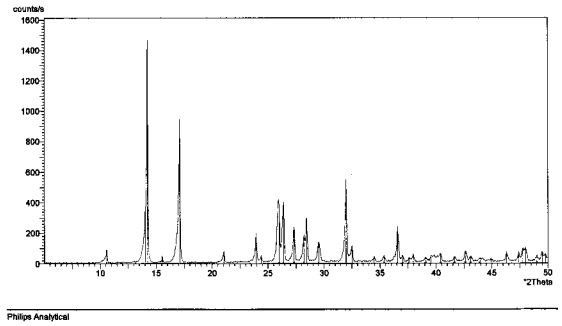


(c)

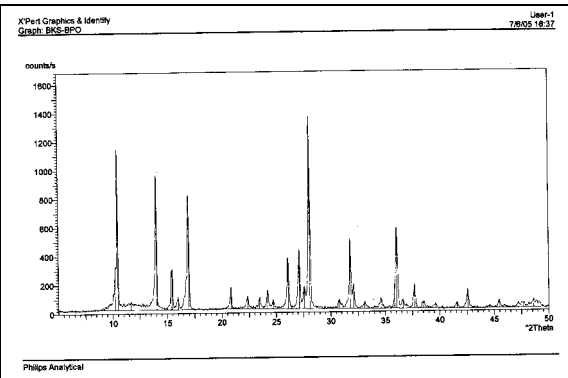
Figure S1 Geometrical parameters of halogen···halogen interactions (C–X···X–C fragment) in accurate (3D coordinates determined, no disorder, no ions, no errors, no powder structures, not polymeric) organic crystal structures extracted from the Cambridge Structural Database (ConQuest 1.8, November 2005 update, Vista plot): (a) Cl···Cl, 3.0-3.5 Å, $R \leq 0.05$; (b) Br···Br, 3.0-3.7 Å, $R \leq 0.10$; (c) I···I, 3.0-4.0 Å, $R \leq 0.10$. Note that the proportion of L-shaped contacts ($\theta 1$ = 150-180º, $\theta 2$ = 90-130º) is larger for the more polarizable Br, I halogens compared to greater number of $\theta 1 = \theta 2$ contacts for the electrostatic Cl atoms. See Scheme 1a for inter-halogen geometry types.

For CSD data analysis, see:

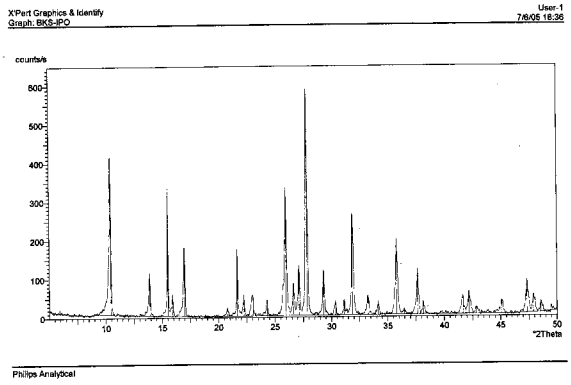
(3) Allen, F. H. *Acta. Crystallogr., Sect. B* **2002**, *58*, 380.



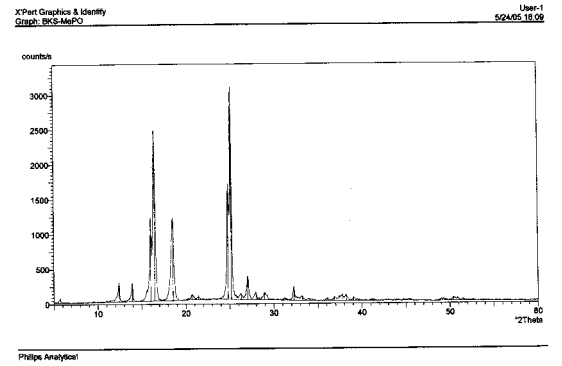
(a) 2-Chloro-3-hydroxypyridine, **1**Cl



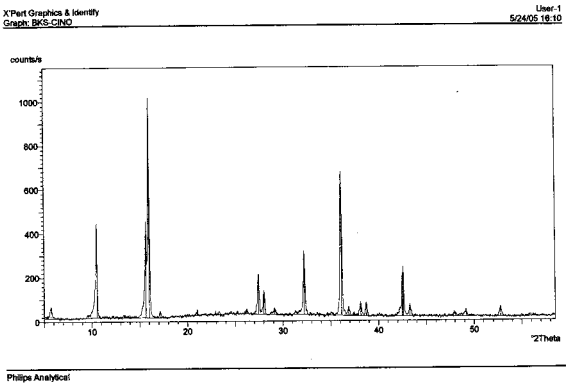
(b) 2-Bromo-3-hydroxypyridine, **1**Br



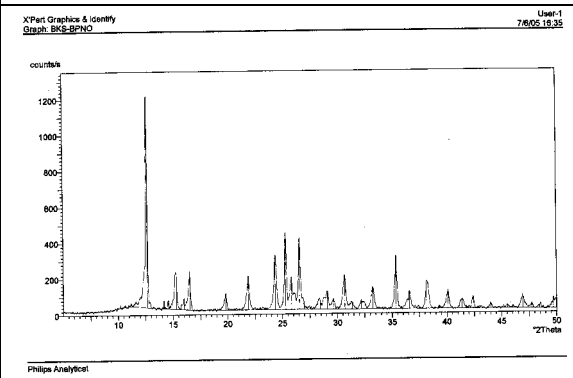
(c) 2-Iodo-3-hydroxypyridine, **1**I



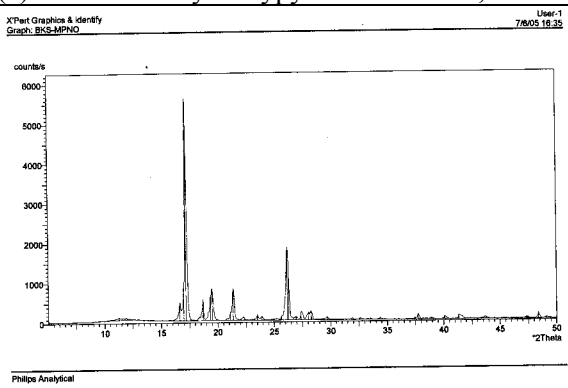
(d) 2-Methyl-3-hydroxypyridine, **1**Me



(e) 2-Chloro-3-hydroxypyridine-*N*-oxide, **2**Cl



(f) 2-Bromo-3-hydroxypyridine-*N*-oxide, **2**Br



(g) 2-Methyl-3-hydroxypyridine-*N*-oxide, **2**Me

Figure S2 Powder XRD of **1** and **2** solids recorded on a PANlytical 1830 (Philips Analytical) diffractometer using Cu-*K*α X-radiation at 35 kV and 25 mA. Diffraction intensities were collected over 2θ range 5-50º at scan rate 2º/min. The powdered bulk material matches reasonably well with the simulated powder pattern from X-ray data w.r.t. 2θ but peak intensities vary, perhaps due to microcrystalline orientation and/or texture effects.