Supporting Information

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively, with TMS as internal standard and $CDCl_3$ as solvent. *J* Values are given in Hz. GC analysis were performed (with an internal standard) on a Shimadzu GC-14A apparatus using a HP1 20m column and temperature programming. GC/MS (EI) spectra were recorded on a HP5871 spectrometer. Melting-point were performed on a Totoli apparatus and are uncorrected. Elemental and HRMS analyses were performed by the Service Central d´Analyse du CNRS (Vernaison, France).

Materials and solvents

BuLi (1.6 M solution in Hexane) and 2-chloropyridine were purchased from Aldrich and Acros, respectively. Dimethylaminoethanol was commercially available and distilled before use. Hexane, THF, xylene and toluene were distilled and stored on sodium wire before use. All other reagents were commercially available and were purified or used as such.

Typical procedure for C-6 functionalisation of 2-chloropyridine : Preparation of silane (2a)

A solution of 2-(dimethylamino)ethanol (0.8ml, 8 mmoles) in hexane (5ml) was cooled at ca. -5°C and BuLi (10ml, 16 mmoles) was added dropwise under a nitrogen atmosphere. After 30 min at 0°C, the solution was cooled at –78°C and a solution of 2-chloropyridine (0.306 g, 2.67 mmoles) in hexane (5ml) was added dropwise. After 1h of stirring a deep rust colored solution was observed. Then a solution of chlorotrimethylsilane (1.17 g, 1.36 ml, 10.67 mmoles) in THF (20ml) was introduced dropwise. After addition, the reaction medium was allowed to warm slowly at room temperature (1h). The mixture was hydrolysed at 0°C with H_2O (40ml). The aqueous layer was then extracted with ether (20ml) and dichloromethane (20ml). The combined layer were dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was analysed by GC and purified by column chromatography (Hexane/AcOEt 95:5, as eluent) to give 2-chloro-6-trimethylsilylpyridine **2a** as a colorless oil (0.51g, 90%).

6-chloro-2-pyridyl(trimethyl)silane (2a) : colorless oil, eluent : hexane/AcOEt (95:5), δ_H 0.3 (s, 9H), 7.20 (d, J 8, 1H), 7.40 (d, J 7.2, 1H), 7.52 (t, J 8, 1H); δ_C –1.66, 123.33, 127.15. 136.64, 151.97, 170.15. MS (EI) m/z 187 (5, M^++1), 186 (9, M^+), 185 (16, M^+-1), 150 (64), 112 (8), 95 (21), 93 (61), 78 (22) , 72 (44), 65 (31), 51 (15). ($C_8H_{12}NSiCl$ requires C, 51.74; H, 6.51; N, 7.54 : Found: C, 52.13; H, 6.45; N, 7.38%).

6-chloro-[2-^{2}H]pyridine (2b) : δ_H 7.22 (d, J 7.6, 1H), 7.32 (d, J 8.4, 1H), 7.65 (t, J 7.6 and 8,1H); δ_C 122.04, 124.20. 138.52, 148.87, 149.15, 149.43, 151.19.

2-(6-chloro-2-pyridyl)-2-butanol (2f) : colorless oil, eluent : Hexane/AcOEt (70:30), δ_H 0.85 (t, J 7.3 and 7.7, 3H), 1.5 (s, 3H), 1,85 (q, J 7.3 and 7.7, 2H), 4.4 (s, 1H), 7.2 (d, J 7.7, 1H), 7.35 (d, J 7.7, 1H), 7,75 (t, J 7.7, 1H); δ_C 7.5, 28.0, 35.95, 76.68, 117.59, 122.06, 139.18, 149.46, 166.44. MS (EI) m/z 170 (6, M^+-16), 158 (30), 156 (100), 138 (24), 113 (19), 78 (56) , 76 (17), 51 (25). ($C_9H_{12}NOCl$ requires C, 58.23 ; H, 6.52 ; N, 7.54 : Found: C, 58.29; H, 6.84; N, 7.25%).

Tributyl(6-chloro-2-pyridyl)stannane (2i) : colourless oil, eluent : Hexane/AcOEt (95:5), δ_H 0.85 (t, J 8.0, 9H), 1.15 (t, J 8.0, 6H), 1.3 (m, 6H), 1.55 (m, 6H), 7,15 (dd, J 4.0, 1H), 7.30 (dd, J 8.0, 1H), 7.45 (t, J 8.0, 1H); δ_C 10,01, 13.62, 29.06, 122.53, 130.83, 135.91, 152.16, 175.84. ($C_{17}H_{30}NSnCl$ requires C, 50.72 ; H, 7.46 ; N, 3.48 : Found: C, 50.88; H, 7.58; N, 3.45%).

6-iodo-2-pyridyl chloride (2l): yellow solid, eluent : Hexane/AcOEt (90:10), mp : 82-85°C, δ_H 7.35 (m, 2H) 7.45 (dd, J 7.3, 1H); δ_C 115.49, 123.52, 133.56. 139.48, 150.97. MS (EI) m/z 241 (8, M^++1), 240 (1, M^+), 239 (27, M^+-1), 127 (100), 114 (25), 112 (83), 76 (88), 75 (26) , 51 (27). (C_5H_3NI requires C, 25.08 ; H, 1.26 ; N, 5.85 : Found: C, 25.16; H, 1.33; N, 5.51%).

2-(6-chloro-2-pyridyl)pyrazine (2m): white solid, eluent : Hexane/AcOEt (70/30), mp : 93-94°C, δ_H 7.4 (d, J 8, 1H), 7.8 (t, J 4 and 8, 1H), 8.3 (d, J 7.7, 1H); 8.6 (m, 2H), 9,6 (s, 1H); δ_C 120.28, 125.04, 139.61, 143.42. 143.58, 144.98, 149.62, 154.78. MS (EI) m/z 192 (6, M^++1), 191 (67, M^+), 139 (45), 113 (34), 103 (50), 76 (69), 75 (41) , 52 (100), 51 (78). HRMS Calcd for $C_9H_6N_3Cl$ requires: 191.0250, found: 191.0252.

4-(6-chloro-2-pyridyl)pyrimidine (2n): white solid, eluent : Hexane/AcOEt (70/30), mp : 120-121°C, δ_H 7.4 (d, J 7.3, 1H), 7.8 (t, J 7.3 and 7.9, 1H), 8.35 (d, J 4.9, 1H); 8.4 (d, J 7.9, 1H), 8.85 (d, J 4.9, 1H), 9,3 (s, 1H); δ_C 117.51, 119.99, 126.10, 139.67, 151.28. 154.26, 158.15, 158.60, 161.04. MS (EI) m/z 192 (3, M^++1), 191 (37, M^+), 190 (1, M^+-1), 137 (32), 79 (31), 76 (57), 75 (35) , 52 (100), 51 (63).

6-chloro-2-pyridyl methyl sulfide **2c**,[1] 6-methyl-2-pyridyl chloride **2d**,[2] 1-(6-chloro-2-pyridyl)-2,2-dimethyl-1-propanol **2e**,[3] 6-chloro-2-pyridinecarbaldehyde **2g**,[4] 6-chloro-2-pyridyl-

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phenylmethanone **2h**,[5] 6-chloro-2-pyridyl chloride **2j**[6] and 6-bromo-2-pyridyl chloride **2k**[6] were found identical (spectroscopic and physical data) to authentic or commercial samples.

Typical procedure for coupling of 2-chloro-6-(tributylstannyl)pyridine (2i)

To a mixture of $Pd(PPh_3)_4$ (60mg, 0.055mmoles, 5mol%) and the appropriate (hetero)arylhalide (1.32mmoles) in xylene or toluene (15ml) was added **2i** (440mg, 1.1mmoles) in the appropriate solvent (5ml). The mixture was refluxed for 12h. After cooling at room temperature, the mixture was poured into a satured solution of KF (25ml). The organic layer was then extracted twice with ether (20ml), washed with H_2O (25ml) and dried ($MgSO_4$). After evaporatíon of the solvent under reduced pressure, the crude product was purified on a chromatotron using Hexane/AcOEt mixture as eluent.

3-(6-chloro-2-pyridyl)quinoline (5c): white solid, eluent : Hexane/AcOEt (60/40), mp : 161-162°C, δ_H 7.35 (d, J 7.0, 1H), 7.6 (t, J 7.3, 1H), 7.75 (m, 3H), 7.9 (d, J 8.0, 1H); 8.15 (d, J 8.4, 1H), 8.8 (s, 1H), 9,5 (s, 1H); δ_C 118.71, 123.30, 127.61, 128.44, 128.58, 129.22, 130.23, 130.29, 134.30, 139.54, 148.37. 148.73, 151.84, 155.37. MS (EI) m/z 242 (30, M^++1), 241 (23, M^+), 240 (100, M^+-1), 205 (45), 177 (19), 151 (20), 102 (41), 76 (48), 75 (59), 63 (32), 51 (62). HRMS Calcd for C14H9N2Cl requires 240.0454, found: 240.0455.

5-(6-chloro-2-pyridyl)pyrimidine (5d): white solid, eluent : Hexane/AcOEt (70/30), mp : 140-142°C, δ_H 7.4 (d, J 7.9, 1H), 7.7 (d, J 7.7, 1H), 7.85 (t, J 7.7 and 7.9, 1H); 9.25 (s, 1H), 9.3 (s, 2H) ; δ_C 118.78, 123.20, 130.97, 139.84, 152.59. 155.24, 159.05, 163.08. MS (EI) m/z 192 (16, M^++1), 191 (80, M^+), 190 (24, M^+-1), 164 (83), 113 (100), 102 (70), 76 (59), 75 (78), 52 (43), 51 (97). HRMS Calcd for $C_9H_6N_3Cl$ requires: 191.0250, found: 191.0253.

2-chloro-6-phenylpyridine **5a**,[7] 2-chloro-6-(2-pyridyl)pyridine **5b**,[8] 2-chloro-6-(6-chloro-2-pyridyl)pyridine **4**[9] were found identical (spectroscopic and physical data) to authentic samples.

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