Supplementary Material (ESI) for Chemical Communications

Bromine-lithium Exchange under Non Cryogenic Conditions : $TMSCH_2Li$-LiDMAE promoted C-2 lithiation of 2,3-Dibromopyridine

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General considerations.

2-Dimethylaminoethanol was distilled over KOH under nitrogen and stored over molecular sieves. *n*-BuLi (1.6M solutions in hexanes) was obtained from ACROS. $TMSCH_2Li$ (0.92 M solution in hexanes) was kindly offered by FMC Lithium. All reagents were commercially available and used as such or purified if needed. All solvents were distilled and stored over sodium wire before use. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ (TMS as internal standard) on a Bruker AC200 instrument at 200 and 50 MHz respectively. GC experiments were performed on a Shimadzu chromatograph (FID detection) through a 15m capillary HP1 column. HRMS (ESI) were performed on a Bruker MICROTOF spectrometer.

General Procedure for selective C-2 lithiation of 2,3-dibromopyridine

To a solution of of 2-dimethylaminoethanol (164 mg, 1.84 mmoles) in hexane (6 mL) cooled at 0°C was added drop-wise $TMSCH_2Li$ (6 mL, 5.52 mmoles,) under a nitrogen atmosphere. After stirring for 30 min. at the same temperature, a solution of 2,3-dibromopyridine (436 mg, 1.84 mmoles) in toluene (2 mL) was added drop-wise. The obtained red solution was then stirred for 30 min. at 0°C and treated drop-wise with a solution of the appropriate electrophile (2.2 mmoles) in THF (2 mL) at -20°C. After 1h of stirring the mixture was hydrolyzed with water (10 mL). The organic layer was then extracted with diethylether (10 mL), dried over $MgSO_4$ and the solvents were evaporated. The crude product was subjected to GC analysis and finally purified by column chromatography using hexane-AcOEt mixtures as eluent.

Products

3-bromo-2-(trimethylsilyl)pyridine (2a). Obtained by the general procedure using $ClSiMe_3$ as electrophile. Purification by column chromatography (hexane/AcOEt:8/2) gave **2a** (76%) as a colorless oil. δ_H 0.44 (s, 9H), 7.09 (dd, *J*=8.0 and 4.6 Hz, 1H), 7.73 (dd, *J*=8.2 and 1.5 Hz, 1H), 8.67 (dd, *J*=4.6 and 1.2 Hz, 1H). δ_C -0.6, 124.3, 129.6, 138.7, 148.1, 167.6. HRMS (ESI), [M+H], Calcd(found) : 229.9995 (230.0020).

3-bromo-2-chloro-pyridine (2b).[1] Obtained by the general procedure using C_2Cl_6 as electrophile. Purification by column chromatography (hexane/AcOEt:8/2) gave **2b** (65%) as a yellow oil which solidified upon standing (mp°C, 53-56, lit.[1], 54-56). δ_H 7.14 (dd, J= 7.9 and 4.7 Hz, 1H), 7.96 (dd, *J*=8.0 and 1.8 Hz, 1H), 8.36 (dd, *J*=4.6 and 1.6 Hz, 1H). δ_C 120.4 , 123.5 , 140.5 , 142.3 , 148.0

3-bromo-2-iodo-pyridine (2c).[1] Obtained by the general procedure using I_2 as electrophile. Purification by column chromatography (hexane/AcOEt:8/2) gave **2c** (58%) as a yellow oil which solidified upon standing (mp°C, 50-53, lit.[1], 50-52). δ_H 7.18 (dd, J= 7.9 and 4.6 Hz, 1H), 7.85 (dd, J=7.9 and 1.6 Hz, 1H), 8.32 (dd, J= 4.6 and 1.9 Hz, 1H). δ_C 110.1, 124.0, 130.2 , 140.0, 148.6.

3-bromo-2-(tributylstannyl)pyridine (2d). Obtained by the general procedure using $ClSnBu_3$ as electrophile. Purification by column chromatography (hexane/AcOEt:7/3) gave **2d** (65%) as a colorless oil. δ_H 0.87 (m, 9H), 1.30 (m, 12H), 1.57 (m, 6H), 7.01(dd, *J*=8.4 and 4.9 Hz, 1H), 7.68 (dd, *J*=8.4 and 1.6 Hz, 1H), 8.64 (dd, *J*=4.6 and 1.2 Hz, 1H). δ_C 11.4 , 14.3 , 27.7 , 29.4 , 121.9 , 123.5, 133.0 , 136.9, 148.4. HRMS (ESI), [M+H], Calcd(found): 448.0648 (448.0650).

(3-bromopyridin-2-yl)(phenyl)methanone (2e). Obtained by the general procedure using $PhCONMe_2$ as electrophile. Purification by column chromatography (hexane/AcOEt:7/3) gave **2e** (60%) as a pale yellow solid (mp°C, 83). δ_H 7.33 (dd, *J*=8.4 and 3.5 Hz, 1H), 7.40 (t, *J*=7.2 Hz, 2H), 7.60 (m, 2H), 7.80 (d, *J*= 6.8Hz, 1H), 8.06 (dd, *J*=8.3 and 1.2 Hz, 1H), 8.65 (dd, *J*=4.6 and 1.2 Hz, 1H). δ_C 117.8, 125.8, 128.8, 130.4, 134.2, 134.96, 141.1, 147.6, 156.1, 193.3. HRMS (ESI), [M+Na], Calcd(found): 283.9681 (283.9690).

1-(3-bromopyridin-2-yl)-2,2-dimethylpropan-1-one (2f). Obtained by the general procedure using *t*-BuCN as electrophile. Purification by column chromatography (hexane/AcOEt:7/3) gave **2f** (73%) as a pale orange oil. δ_H 1.51 (s, 9H), 7.38 (dd, J=8.4 and

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4.6 Hz, 1H), 8.16 (dd, *J*=8.0 and 1.2 Hz, 1H), 8.74 (dd, *J*=4.7 and 1.2 Hz, 1H). δ_C 27.2, 28.7, 125.1, 126.9, 141.2, 147.2, 147.4, 219.7. HRMS (ESI), [M+Na], Calcd(found): 263.9994 (264.0020).

(3-bromopyridin-2-yl)(phenyl)methanol (2g). Obtained by the general procedure using PhCHO as electrophile. Purification by column chromatography (hexane/AcOEt:7/3) gave **2g** (59 %) as a yellow solid (mp°C, 61). δ_H 5.32 (d, *J*=7.6 Hz, 1H), 5.95 (d, *J*=7.5 Hz, 1H), 7.07 (dd, *J*=8.0 and 4.0 Hz, 1H), 7.27 (m, 5H), 7.81 (dd, *J*=8.0 and 1.2 Hz, 1H), 8.54 (dd, *J*=4.7 and 1.2 Hz, 1H). δ_C 73.7, 120.0, 124.3, 127.1, 127.9, 128.6, 141.3, 141.8, 146.9, 158.70. HRMS (ESI), [M+Na], Calcd(found): 285.9838 (285.9855)

(3-bromopyridin-2-yl)(2-methoxyphenyl)methanol (2h). Obtained by the general procedure using o-AnisylCHO as electrophile. Purification by column chromatography (hexane/AcOEt:7/3) gave **2h** (79 %) as a yellow solid (mp°C, 98). δ_H 3.88 (s, 3H), 4.69 (brs, 1H), 5.14 (d, *J*=7.20 Hz, 1H), 6.40 (d, *J*=7.20 Hz, 1H), 6.81-6.94 (m, 3H), 7.20-7.26 (m, 2H), 7.86 (dd, *J*=8.0 and 1.2 Hz, 1H), 8.61 (dd, *J*=4.7 and 1.2 Hz, 1H). δ_C 55.9, 68.3, 111.2, 120.2, 120.6, 124.0, 128.3, 129.4, 130.1, 141.2, 146.5, 158.1, 159.0. HRMS (ESI), [M+Na], Calcd(found): 315.9944 (315.9960).