**Supplementary Materials and Methods**

**Preparation of 2-chloro-1-{6-[(4-fluorophenyl)methyl]-5-(hydroxymethyl)-3,3-dimethyl-1H,2H,3H-pyrrolo[3,2-b]pyridin-1-yl}ethan-1-one (S4)**

The title compound was prepared according to the scheme below. Treatment of 6-(4-fluorobenzyl)-3,3-dimethyl-2,3-dihydro-1H-pyrrolo[3,2-b]pyridine **S1** [Tamanini et al.] with N-bromosuccinimide gave 5-bromo compound **S2** in high yield, then two-stage lithiation using methyllithium followed by tert-butyllithium and subsequent quench at low temperature with N,N-dimethylformamide gave the C5 substituted aldehyde. This product, used without further purification, was reduced with sodium borohydride to afford primary alcohol **S3**. Subsequent chloroacetylation gave 2-chloro-1-{6-[(4-fluorophenyl)methyl]-5-(hydroxymethyl)-3,3-dimethyl-1H,2H,3H-pyrrolo[3,2-b]pyridin-1-yl}ethan-1-one **S4**.



Reagents and conditions: (a) N-bromosuccinimide, DMF, 5 oC – RT, 95%; (b) 1. MeLi, Et2O, THF, -78 oC; 2. tert-BuLi, hexane; 3. DMF, -78 oC, used without purification; (c) NaBH4, MeOH, ~5 oC, 76% over 2 steps; (d) ClCH2COCl, MeCN, ~5 oC.