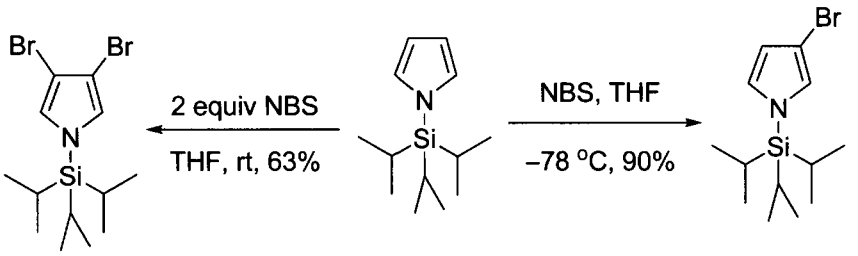
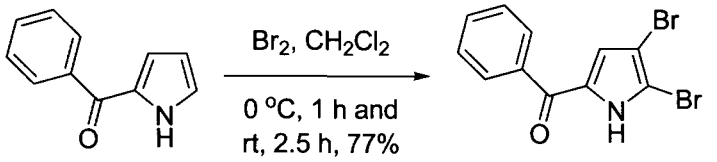
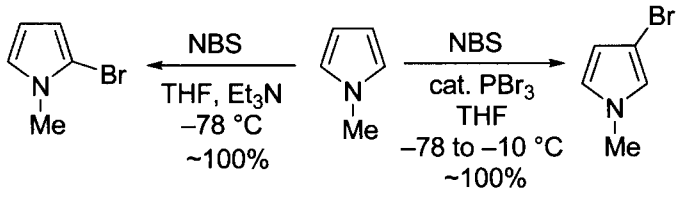
There are exceptions to the rule. For instance, when there is a bulky group on the nitrogen such as triisopropylsilyl group (TIPS), bromination occurs predominantly on the C3 (β) position instead of on the C2 (α) position.[3]



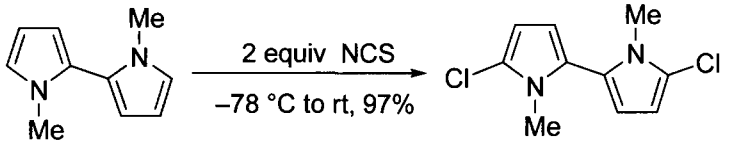
Bromination on both α- and β-positions is also possible[4]:



Depending on the reaction conditions, 1-methylpyrrole can be brominated at C2 with NBS (*N*-bromosuccinate) to give 2-bromo-1-methylpyrrole or at C3 with NBS and catalytic PBr_3 to give 3-bromo-1-methylpyrrole. Both reactions are essentially quantitative, but both bromides decompose on silica gel.[5]



Methyl-protected bipyrrole was chlorinated at both C2 positions on treatment with NCS (*N*-chlorosuccinate) in excellent yield.[6]



Mannich reaction

For the Mannich reaction with pyrrole, the substitution occurs predominantly at the C2 position as well.[7]