

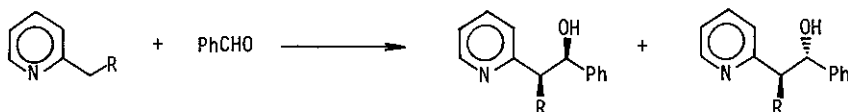
STEREO- AND REGIOSELECTIVE ALDOL-TYPE REACTION OF ACTIVE METHYLENE GROUPS
OF NITROGEN-CONTAINING HETEROAROMATIC COMPOUNDS

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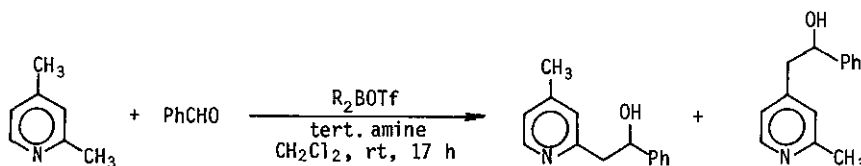
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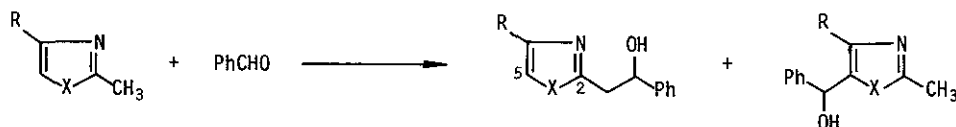
The combination of dialkylboryl triflates and aliphatic tertiary amines was successively applied to the aldol-type reaction of "active methylene groups" of nitrogen-containing heteroaromatic compounds with benzaldehyde. The stereoselectivity and regioselectivity were much better than those of conventional methods using strong bases such as *n*-butyllithium or lithium diisopropylamide as shown below.



R	Reaction conditions	Yield (%)	erythro	threo
Me	i) LDA/THF/-78° $\rightarrow$ rt, ii) PhCHO/-78° $\rightarrow$ rt	78	26	74
Me	i) <i>n</i> -Bu ₂ BOTf/-78°, ii) Et ₃ N, PhCHO/rt/17 h	50	94	6
Ph	i) 9-BBN-OTf/-78°, ii) Et ₃ N, PhCHO/rt/17 h	66	100	0



R ₂ BOTf	tert. amine	Yield (%)	2-Substituted	4-Substituted
<i>n</i> -Bu ₂ BOTf	Et ₃ N	68	100	0
9-BBN-OTf	<i>i</i> -Pr ₂ NEt	73	0	100



R	X	Reaction conditions	Yield (%)	2-Substituted	5-Substituted
H	S	i) <i>n</i> -BuLi/THF/-78° $\rightarrow$ rt, ii) PhCHO/-78° $\rightarrow$ rt	43	0	100
Ph	O	i) <i>n</i> -BuLi/THF/-78° $\rightarrow$ rt, ii) PhCHO/-78° $\rightarrow$ rt	60	0	100
H	S	i) 9-BBNOTf/-78°, ii) <i>i</i> -Pr ₂ NEt, PhCHO/rt/17 h	77	100	0
Ph	O	i) 9-BBNOTf/-78°, ii) Et ₃ N, PhCHO/rt/17 h	70	100	0