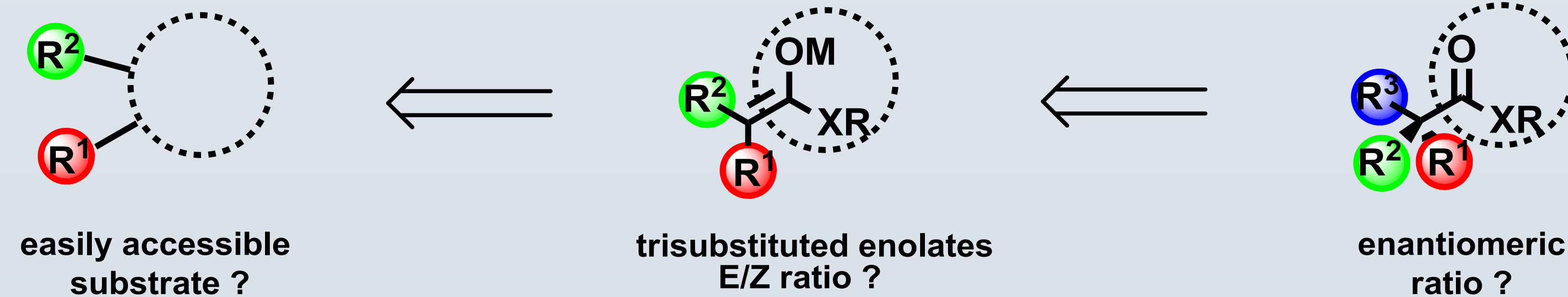


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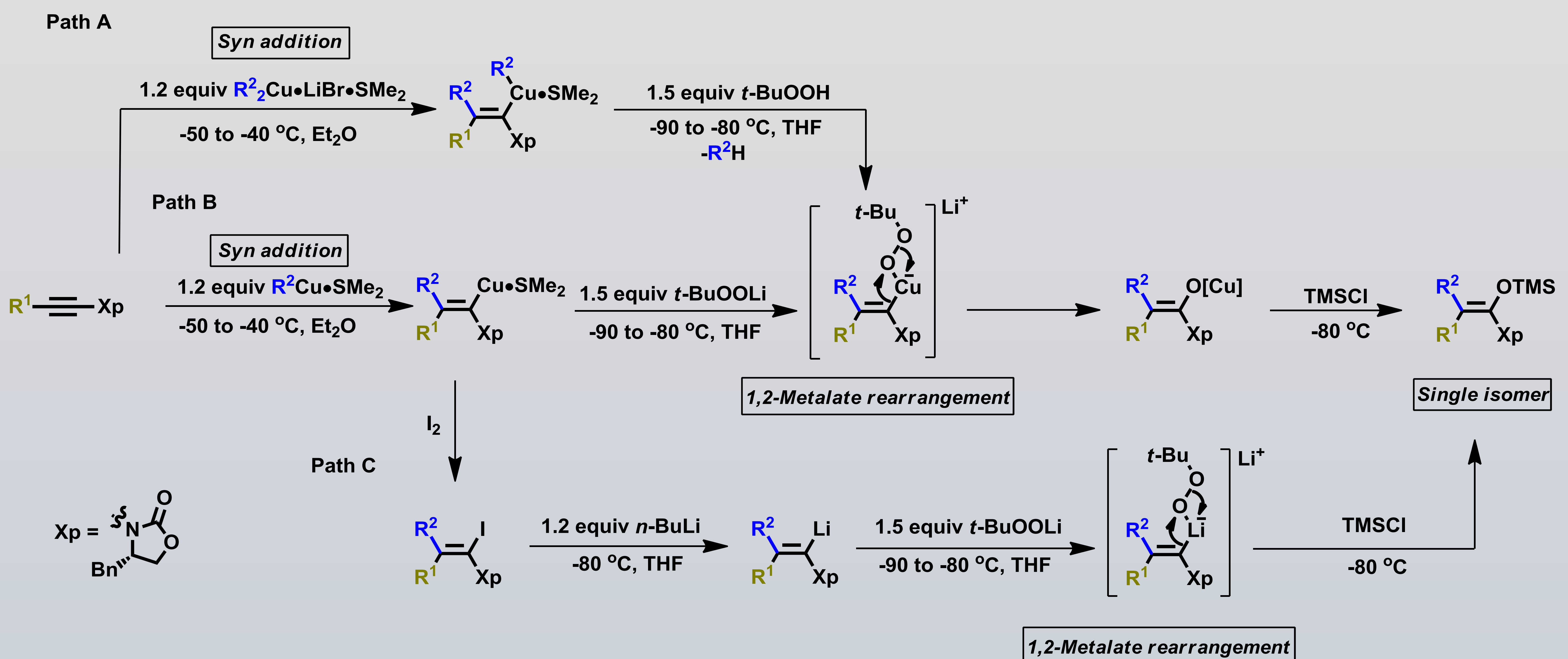
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Formation of enantiomerically pure quaternary carbon center α to a carbonyl group remains a challenge in modern synthetic organic chemistry. The aldol reaction could provide access to such molecular framework. However, the main problem that limits the formation of these stereocenters is the difficulty to prepare stereodefined trisubstituted enolates in acyclic systems. The most prominent examples reported to date require either the preparation of an enantiomerically pure sp^3 -stereocenter that is subsequently enolized into stereodefined trisubstituted enolates of amides and esters, or the preparation of unsaturated conjugated amides which are deprotonated or hydroborated forming stereodefined enolates¹. Despite the variety of methods, their application to the diastereoselective aldol reaction remains challenging.



As the formation of trisubstituted stereodefined enolates represents a challenging issue, we developed a simple and reliable stereoselective approach based on carbometalation/ oxidation sequence² of organocopper, organocuprate and organolithium species that were subsequently trapped as trisubstituted silyl enol ether. The Mukaiyama aldol reaction with aliphatic and aromatic aldehydes opened a straight forward access to the formation of the aldol products possessing the expected quaternary stereocenter in high yields and diastereoselectivities³.

Formation of stereodefined trisubstituted silyl enol ether



The Mukaiyama aldol reaction

