

Multivalent Activation in Temporary Phosphate Tethers:
A New Tether For Small Molecule Synthesis
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Summary : Free multivalent activation in temporary phosphate tethers a new tether for small molecule synthesis pdf download - the use of phosphate esters as temporary tethers capable of multivalent activation is the broad focus of the dissertation research reported herein specifically the utility of phosphate tethers has been demonstrated through the divalent activation of allylic c2-symmetric monocyclic phosphates within these systems the temporary phosphate tether mediates a highly diastereoselective desymmetrization event via copper-mediated allylic alkylation studies were extended to include c 2-unsymmetric monocyclic phosphates in which steric and electronic effects were further probed in general the method provided access to both syn- and anti-1 2-homoallylic alcohols we next explored multivalent activation via a temporary phosphate tether in which all three phosphate ester appendages have been activated this was achieved through the formation of a triply allylic bicyclic phosphate containing unique steric and stereoelectronic properties enabling our study of selective cleavage reactions mediated by a temporary phosphate tether several selective reactions were realized taking advantage of the diverse reactivity profile possessed within the bicyclic phosphate the application of these selective cleavage reactions towards the synthesis of non-phosphorus polyketide fragments was further shown with the methodology in place we turned our attention towards the synthesis of the c1-c15 fragment of the dolabelide family of macrolides two routes were realized both taking advantage of the protecting group aspect and latent leaving group ability of the temporary phosphate tether supplying the c15-c30 fragment in 12-steps from the bicyclic phosphate lastly the use of a ring-closing metathesis rcm template based approach towards the production of p-chiral phosphono sugars was explored the method took advantage of a diastereoselective displacement reaction at phosphorus with chiral secondary allylic alcohols followed by rcm to afford an allylic phostone template these templates could subsequently be stereoselectively reacted with oxygen and nitrogen nucleophiles to afford an array of fully substituted phosphono sugars

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