

**New Methods for the Formation of Methyl Bearing Stereogenic
Centers via Methylketene Dimerization and Free Radical
Additions to Allyl Bromides**

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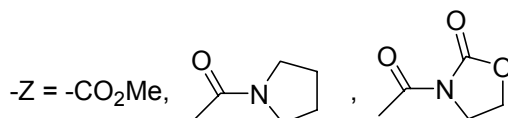
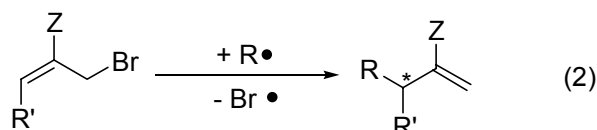
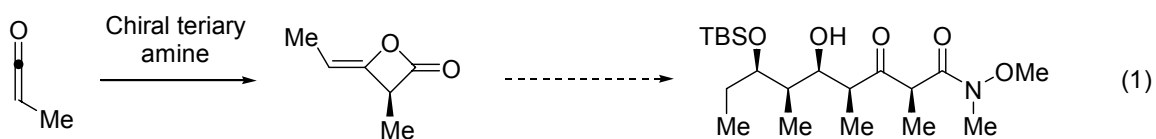
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New Methods for the Formation of Methyl Bearing Stereogenic Centers via Methylketene Dimerization and Free Radical Additions to Allyl Bromides

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(Abstract)

Two organic synthetic methods for the generation of methyl bearing chiral centers have been developed using: 1) dimerization of methylketene and 2) a free radical-based addition/elimination reaction involving allyl bromides. The first method, the asymmetric dimerization of methyl ketene, followed by an asymmetric aldol reaction and the appropriate functional group manipulations enabled us to construct the (2*S*, 4*S*, 6*S*) trimethylnonyl subunit found in the siphonariene class of natural products (eq 1). The latter method explored the stereoselective potential of a free radical-based condensation reaction by examining compounds which are known to be able to support chiral auxiliaries and chiral Lewis acids (eq 2). Additionally, substituent effect on the rates of this reaction were examined closely and found to be comparable to similar, previously examined systems. The synthetic utility, magnitude and scope of this reaction are discussed.



R = benzyl or phenethyl radical

R' = -H or -Me