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Stereoselective Synthesis of All-Carbon Tetrasubstituted Alkenes from In Situ Generated Ketenes and Organometallic Reagents
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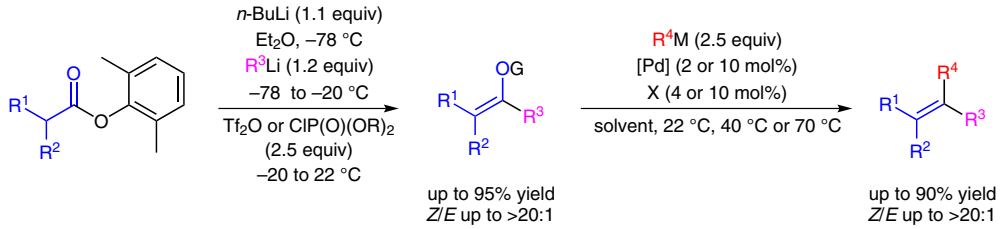
Category
Metal-Mediated Synthesis

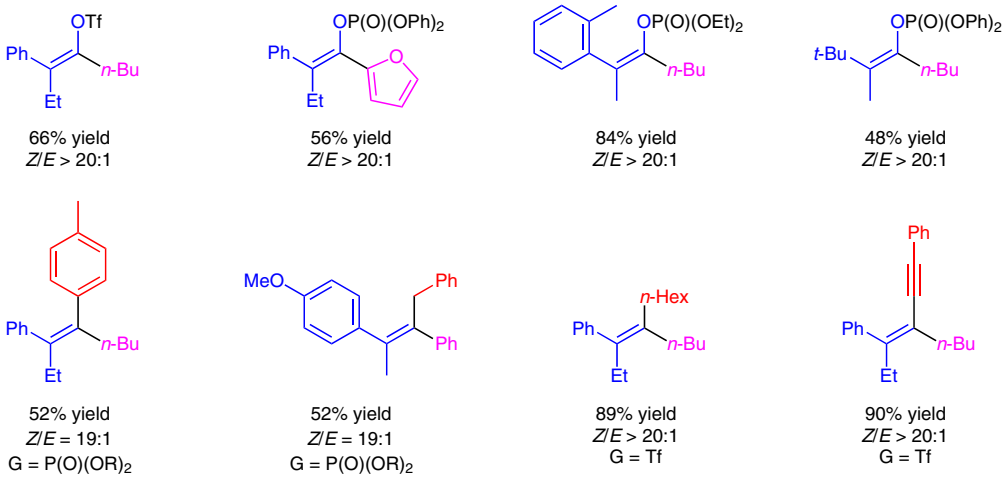
Key words
lithium
magnesium
palladium
tetrasubstituted alkenes

Stereoselective Synthesis of All-Carbon Tetrasubstituted Alkenes



G = Tf or $P(O)(OR)_2$ (R = Et, Ph)
M = MgBr [G = $P(O)(OR)_2$]; 9-BBN, $B(OH)_2$, H (G = Tf)
[Pd] = $Pd(dba)_2$ [G = $P(O)(OR)_2$]; $Pd(OAc)_2$, $PdCl_2(PPh)_3$ (G = Tf)
X = XPhos [G = $P(O)(OR)_2$]; SPhos, CuI (G = Tf)
R^1 = Ph, 4-$MeOC_6H_4$, 2-MeC_6H_4, 3-thienyl, *i*-Pr, *t*-Bu
R^2 = Et, Me, Bn, *i*-Pr
R^3 = *n*-Bu, Ph, C(Me)=CH_2, 2-furanyl
R^4 = Ph, Tol, Me, Bn, *n*-Hex, ethynylphenyl

Selected examples:



Significance: The stereoselective synthesis of various all-carbon tetrasubstituted alkenes is disclosed, employing a two-step protocol which includes the stereoselective generation of an alkenyl pseudohalide followed by stereospecific palladium-catalyzed cross-coupling. The appropriate tetrasubstituted alkenes are obtained in good yield and with good diastereomeric ratios, providing mainly the *Z*-isomers.

Comment: The reaction is proposed to proceed via a ketene intermediate which is stereospecifically attacked by a lithium organyl to form the trisubstituted enolate moiety attached to a pseudohalide group [OTf or $OP(P)(OR)_2$]. This moiety may be converted into other functional groups by palladium-catalyzed cross-couplings to give the corresponding all-carbon tetrasubstituted alkenes.

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