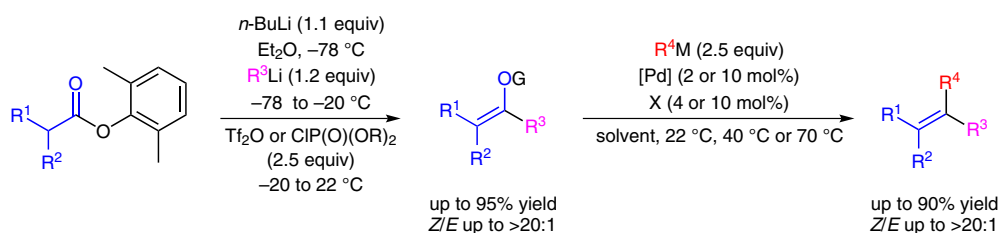
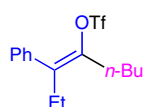


Stereoselective Synthesis of All-Carbon Tetrasubstituted Alkenes

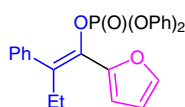


G = Tf or P(O)(OR)₂ (R = Et, Ph)
M = MgBr [G = P(O)(OR)₂]; 9-BBN, B(OH)₂, H (G = Tf)
[Pd] = Pd(dba)₂ [G = P(O)(OR)₂]; Pd(OAc)₂, PdCl₂(PPh)₃ (G = Tf)
X = XPhos [G = P(O)(OR)₂]; SPhos, Cul (G = Tf)
R¹ = Ph, 4-MeOC₆H₄, 2-MeC₆H₄, 3-thienyl, *i*-Pr, *t*-Bu
R² = Et, Me, Bn, *i*-Pr
R³ = *n*-Bu, Ph, C(Me)=CH₂, 2-furanyl
R⁴ = Ph, Tol, Me, Bn, *n*-Hex, ethynylphenyl

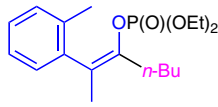
Selected examples:



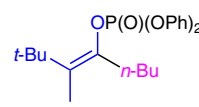
66% yield
 $Z/E > 20:1$



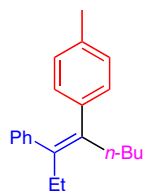
56% yield
 $Z/E > 20:1$



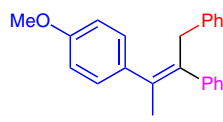
84% yield
 $Z/E > 20:1$



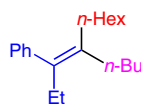
48% yield
 $Z/E > 20:1$



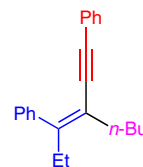
52% yield
 $Z/E = 19:1$
G = P(O)(OR)₂



52% yield
 $Z/E = 19:1$
G = P(O)(OR)₂



89% yield
 $Z/E > 20:1$
G = Tf



90% yield
 $Z/E > 20:1$
G = Tf

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 tri-substituted enolate moiety attached to a pseudo-halide 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.