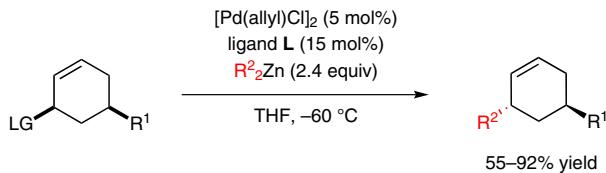


Personal Copy

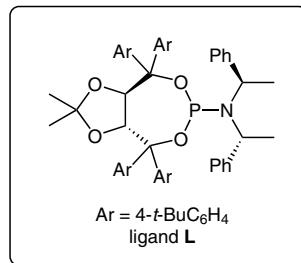


Thieme

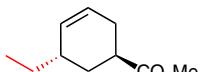
Asymmetric Palladium-Catalyzed Allylic Substitution Using Dialkylzinc Reagents



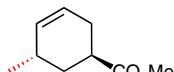
R¹ = CO₂Me, CO₂Bn, Ph, CON(OMe)Me, CHO, COPh
R² = Me, Et,
LG = OAc, OCO₂Me, Cl



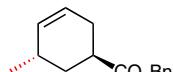
Selected examples:



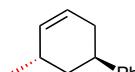
78% yield
dr = 99:1, er = 94:6
(LG = OAc)



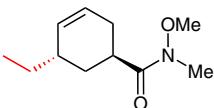
60% yield
dr = 99:1, er = 87:13
(LG = OCO₂Me)



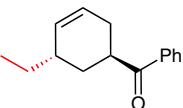
55% yield
dr = 99:1, er = 84:16
(LG = OCO₂Me)



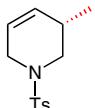
92% yield
dr = 97:3, er = 89:11
(LG = OAc)



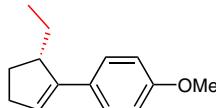
86% yield
dr = 99:1, er = 93:7
(LG = OAc)



75% yield
dr = 99:1, er = 87:13
(LG = OAc)



81% yield
er = 90:10
(LG = OAc)



80% yield
er = 88:12
(LG = OAc)

Significance: Maulide and co-workers present an enantioselective palladium-catalyzed alkylation of racemic allylic electrophiles employing dialkylzinc reagents as nucleophiles. The reaction proceeds under mild conditions and shows broad functional group tolerance.

Comment: This new transformation, that prevents the standard ‘umpolung’ reactivity of allyl–palladium species, hinges on the effect of the TADDOL-derived phosphoramidite ligand L.