

SYNFACTS Highlights in Current Synthetic Organic Chemistry

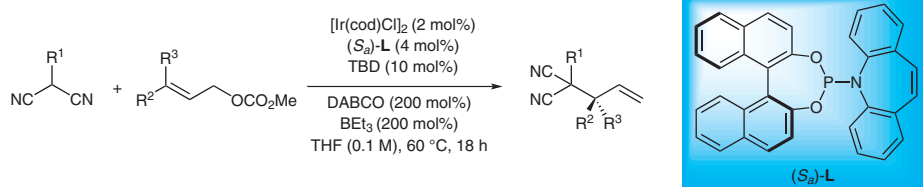
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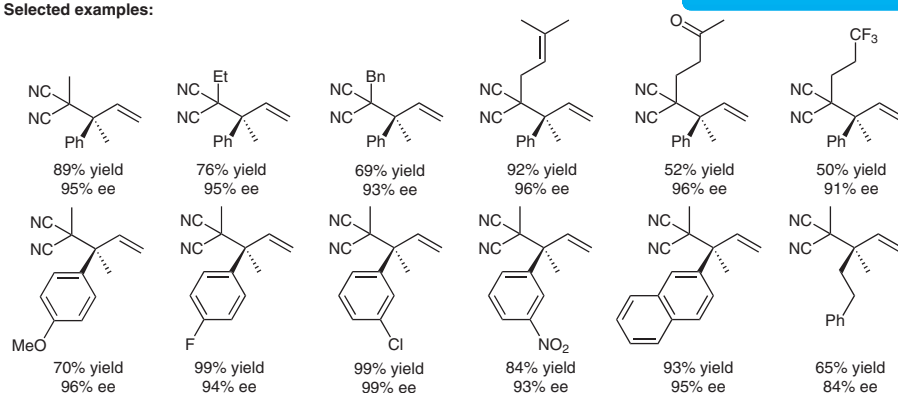
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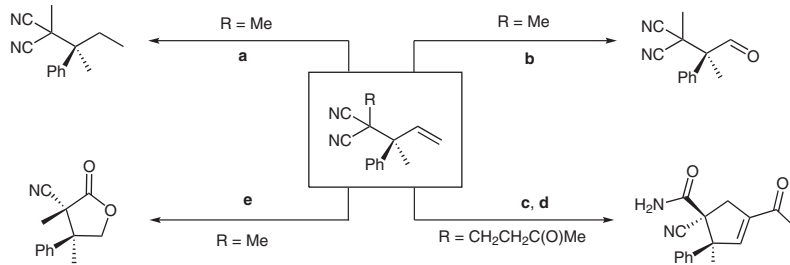
Iridium-Catalyzed Enantioselective Allylic Alkylation



Selected examples:



Product transformations:



Reaction conditions: **a)** RhCl(PPh₃)₃, H₂ (balloon), benzene, 23 °C, 18 h, 92% yield; **b)** O₃, pyridine, CH₂Cl₂, -78 °C, 4 min, 93% yield; **c)** i. O₃, pyridine, CH₂Cl₂, -78 °C, 4 min, ii. *p*-TsOH, benzene, reflux, 18 h, 47% yield; **d)** NaOH, EtOH-H₂O (1:1), 60 °C, 18 h, 38% yield, dr = 1:1:1; **e)** i. O₃, MeOH, -78 °C, 0.5 h, ii. NaBH₄, 0 °C, 3 h, 65% yield, dr = 1:2:5

Significance: Enantioselective construction of all-carbon quaternary stereocenters is a formidable challenge in organic chemistry. Stoltz and co-workers report the first enantioselective iridium-catalyzed allylic alkylation to give acyclic products bearing vicinal all-carbon quaternary centers. Moreover, the allylic alkylation products can be transformed into various valuable and densely functionalized building blocks in a chemo- and diastereoselective way.

Comment: The present iridium-catalyzed allylic alkylation reaction proceeds with excellent yields and enantioselectivities with various malononitrile-derived nucleophiles and allylic electrophiles. The catalyst prepared from [Ir(cod)Cl]₂, (S_a)-L, and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in the presence of DABCO and triethylborane furnished the allylic alkylation products.

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