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Metal-Free Enantioselective Electrophilic Activation of Allenamides: Stereoselective Dearomatization of Indoles
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Category

Organo- and Biocatalysis

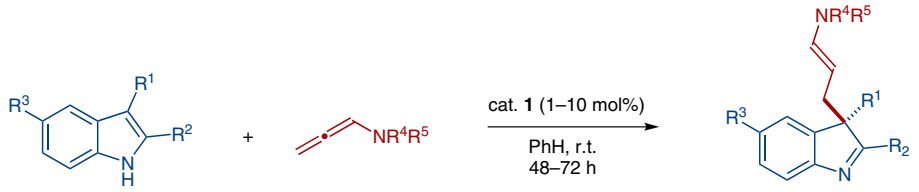
Key words

allenamides

dearomatization

quaternary carbon centers

Enantioselective Dearomatization of Indoles

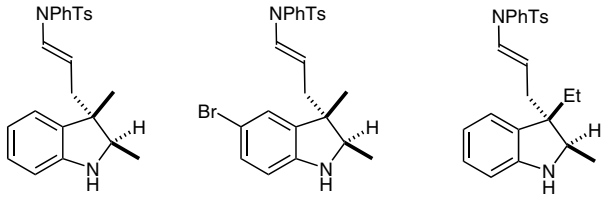


R^1 = Alk, Bn
R^2 = Alk
R^3 = H, Hal, OAlk, Alk

R^4 = Ts, Bs

15 examples
44–98% yield
er from 86:14 to 97:3

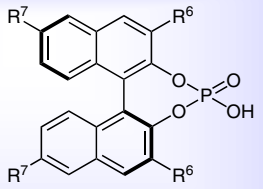
Selected examples of dearomatization–hydrogen transfer cascade:



51% yield
er_{trans} = 99:1
er_{cis} = 91:9
dr = 19:1

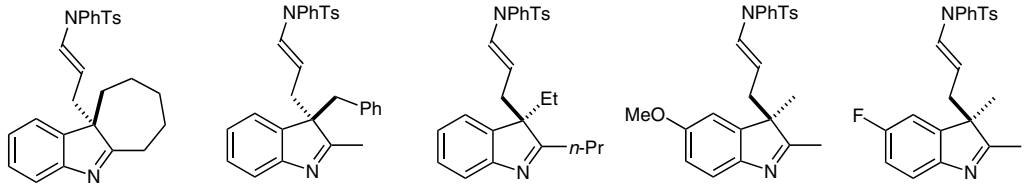
60% yield
er_{trans} = 97.5:2.5
er_{cis} = 91:9
dr = 10:1

49% yield
er_{trans} = 99.5:0.5
er_{cis} = 66.5:33.5
dr = 15:1



R^6 = 2,4,6-$Cy_3C_6H_2$ (*R*)-cat. **1**
R^7 = H, C_8H_{17}

Selected examples:



51% yield
er = 95.5:4.5

87% yield
er = 97:4

69% yield
er = 93.5:6.5
using (*S*)-cat. **1**

60% yield
er = 96:4
using (*S*)-cat. **1**

64% yield
er = 95.5:4.5
using (*S*)-cat. **1**

Significance: Bandini and co-workers report an enantioselective dearomatization of indoles. Using 1 to 10 mol% of chiral phosphoric acid catalyst **1**, the desired 3,3-disubstituted indolenines are obtained in moderate to high yields and good to excellent enantioselectivities.

Comment: The authors developed an enantioselective electrophilic activation of allenamides, generating enantioenriched dearomatized 3,3-disubstituted indolenines as products. Additionally, a dearomatization–hydrogen transfer cascade was conducted. Performing the reaction in the presence of molecular sieves and Hantzsch ester, the corresponding indolines are obtained in good yields and with high diastereo- and enantioselectivities.

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