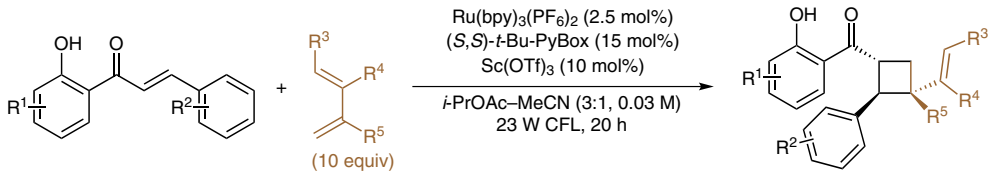
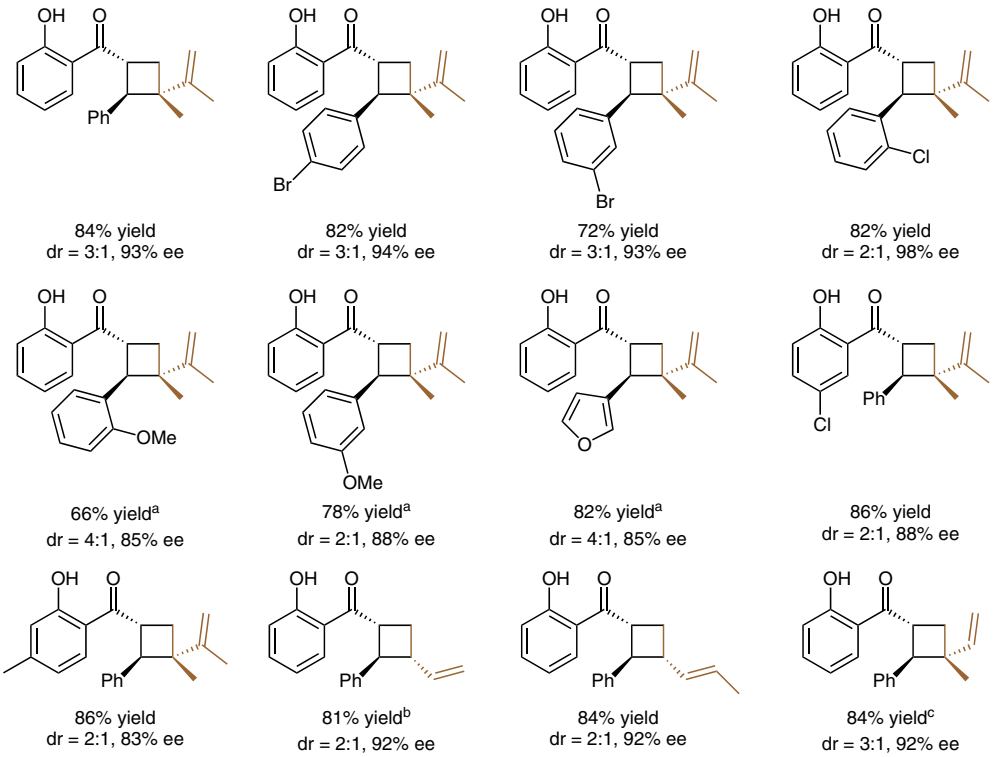
T. R. BLUM, Z. D. MILLER, D. M. BATES, I. A. GUZEI, T. P. YOON* (UNIVERSITY OF WISCONSIN-MADISON, USA)

Enantioselective Photochemistry through Lewis Acid-Catalyzed Triplet Energy Transfer
Science **2017**, *354*, 1391–1395.

Ruthenium-Catalyzed Asymmetric Photocycloaddition of 2′-Hydroxychalcones



Selected examples:



84% yield
dr = 3:1, 93% ee

82% yield
dr = 3:1, 94% ee

72% yield
dr = 3:1, 93% ee

82% yield
dr = 2:1, 98% ee

66% yield[a]
dr = 4:1, 85% ee

78% yield[a]
dr = 2:1, 88% ee

82% yield[a]
dr = 4:1, 85% ee

86% yield
dr = 2:1, 88% ee

86% yield
dr = 2:1, 83% ee

81% yield[b]
dr = 2:1, 92% ee

84% yield
dr = 2:1, 92% ee

84% yield[c]
dr = 3:1, 92% ee

[a] Irradiation with a blue LED lamp instead of a 23 W CFL bulb (irradiation time: 2 h).
[b] Irradiation time: 40 h. [c] Isolated as a 6:1 mixture of regioisomers.

Significance: A chiral scandium–ligand complex was shown to catalyze triplet energy transfer from an electronically excited photosensitizer. This strategy can be applied to the asymmetric [2+2] photocycloaddition of 2′-hydroxychalcones and dienes with tris(bipyridyl)ruthenium(II) as a sensitizer.

Comment: This protocol permits ready access to chiral [2+2] cycloadducts bearing three contiguous stereocenters in good yields and with high enantioselectivities. Several lines of evidence support a mechanism in which the coordination of the scandium catalyst dramatically lowers the triplet energy of the 2′-hydroxychalcone.

SYNFACTS Contributors: Hisashi Yamamoto, Wataru Muramatsu
Synfacts 2017, 13(03), 0265 Published online: 15.02.2017
DOI: 10.1055/s-0036-1589975; **Reg-No.:** H01317SF

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

ruthenium catalysis
photocatalysis
photocycloaddition
hydroxychalcones
dienes