Ruthenium-Catalyzed Asymmetric Yne–Enone Cyclizations

Significance: The authors report asymmetric yne–enone cyclizations catalyzed by chiral cationic CpXRu(II) complexes. A variety of 4H-pyrans were obtained in good yields (≤95%) and high enantioselectivities (er ≤ 99:1).

Comment: A new class of chiral CpXRu(II) complexes was synthesized that provide opportunities for the development of synthetically valuable enantioselective transformations.

Selected examples:

71% yield  
er = 97:3

87% yield  
er = 98.5:1.5

95% yield  
er = 89:11

78% yield  
er = 99:1

72% yield  
er = 98:2

95% yield  
er = 98:2

Synthesis of the chiral CpXRu(II) complexes:

1. TiOEt, C6H6, 80 °C then [(C6H6)RuCl2]2, MeCN, r.t.  
21–77% yield

2. AgX  
61–99% yield

hv, MeCN  
>95% yield

MeCN  
NCMe

(5 mol%)

THF, –20 °C, 20–60 min

(5 mol%)

O

MeO2C

MeO2C

O

MeO2C

MeO2C

O

MeO2C

MeO2C

O

MeO2C

MeO2C

O

MeO2C

MeO2C

O

MeO2C

MeO2C

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MeO2C

MeO2C

O