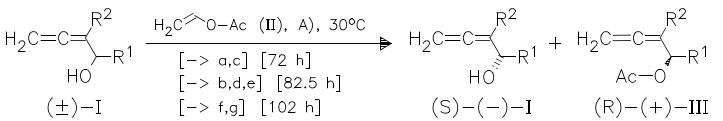
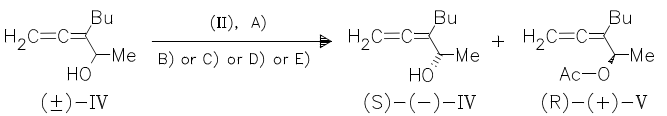
Allenes
P 0025
07- 062

Efficient Preparation of Highly Optically Active (S)-(-)-2,3-Allenols and (R)-(+)-2,3-Allenyl Acetates by a Clean Novozym-435-Catalyzed Enzymatic Separation of Racemic 2,3-Allenols. — Novozym 435 is found to be an effective biocatalyst for the reaction of racemic allenols with vinyl acetate to give both the resolved allenols and the acetates with high enantioselectivities even at relatively high substrate concentrations and low catalyst loading. The conversion of resolved allenol (S)-(IV) into enantiopure dihydrofurans and an epoxide is demonstrated. — (XU, D.; LI, Z.; MA*, S.; Chem. Eur. J. 8 (2002) 21, 5012-5018; State Key Lab. Organomet. Chem., Shanghai Inst. Org. Chem., Chin. Acad. Sci., Shanghai 200032, Peop. Rep. China; Eng.) — Klein

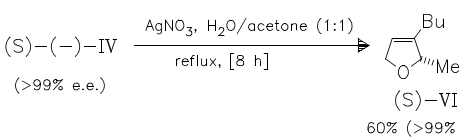


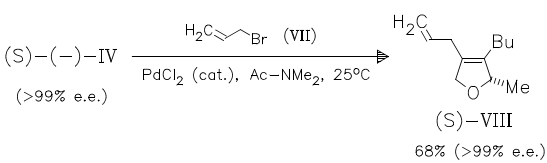
a R^1: –Me ; R^2: –Pr	36% (>99% e.e.)	36% (95% e.e.)
b R^1: –Me ; R^2: –$(CH_2)_5$–Me	40% (99% e.e.)	31% (99% e.e.)
c R^1: –Me ; R^2: –CH_2–Ph	42% (96% e.e.)	45% (>99% e.e.)
d R^1: –Me ; R^2: –$(CH_2)_2$–Ph	50% (99% e.e.)	44% (94% e.e.)
e R^1: –Me ; R^2: –CH_2–CH=CH_2	31% (>99% e.e.)	38% (99% e,e,)
f R^1: –Et ; R^2: –Bu	49% (>99% e.e.)	43% (>99% e.e.)
g R^1: –Et ; R^2: –$(CH_2)_6$–Me	49% (>99% e.e.)	47% (>99% e.e.)

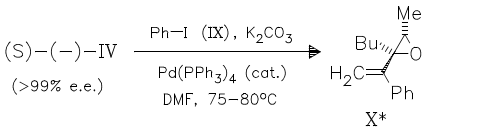
A): Novozym 435, neat



B): 30°C, [96 h]	39% (99% e.e.)	31% (99% e.e.)
C): 40°C, [48 h]	40% (>99% e.e.)	45% (99% e.e.)
D): 50°C, [40 h]	40% (>99% e.e.)	43% (98% e.e.)
E): 60°C, [24.5 h]	36% (>99% e.e.)	39% (>99% e.e.)






(S)–(–)–IV
(>99% e.e.)
Ph–I (IX), K2CO3
Pd(PPh3)4 (cat.)
DMF, 75–80°C
Me
Bu
O
H2C
Ph
X*
59% (94% d.e., >99% e.e.)