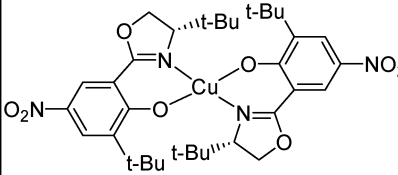
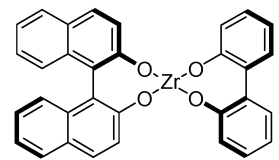
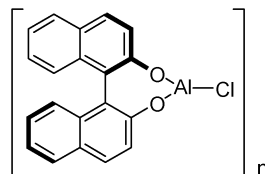
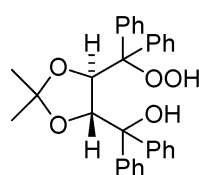


Table 2. Comparison of Chiral Oxidation Catalysts in BV Oxidation of Bicyclo[4.2.0]octanone

entry	Catalyst/ reagent	Conditions	yield/e.e. versus 1a+b (see <i>fig. 29</i>)	ref
1		O ₂ /t-BuCHO 1mol% (S,S) Cu-complex benzene, RT	92% e.e. (15 % yld) (R,S); 67% e.e. (46% yld) (R,R).	77
2		1.5 eq. TBHP 100% Zr-complex toluene	87% e.e. (R,S), 14% e.e. (R,R) (ratio 1a:1b = 1:6)	77
3		1 eq. TBHP, 25mol% Me ₂ AlCl + R-BINOL, conv <100%	90% e.e. (R,S) 25% e.e. (R,R)	77
4		0.7 eq. ROOH, -30°C, 60h, DBU /LiCl, conv. 70%	55% e.e.(R,R) (66% yld)	78
5	acinetobacter NCIMB 9871 (whole cells)		>95% e.e. (18% yld) (R,S); 61% e.e. (30% yld) (R,R)	79
6	acinetobacter TD 63 (whole cells)		>95% e.e. (12% yld) (R,S); 53% e.e. (24% yld) (R,R)	79

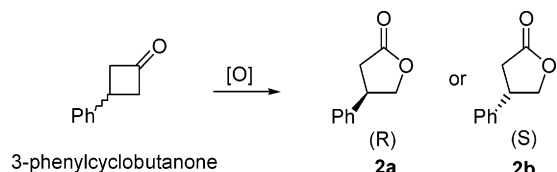


Figure 30. Asymmetric BV oxidation of prochiral 3-phenylcyclobutanone.

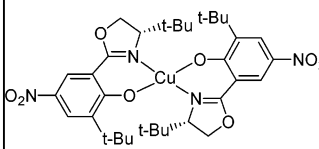
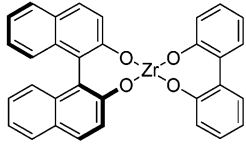
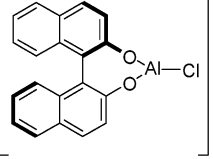
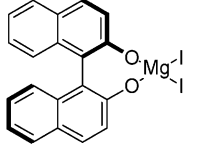
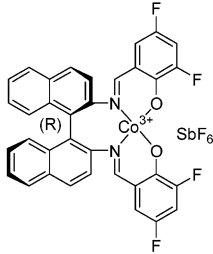
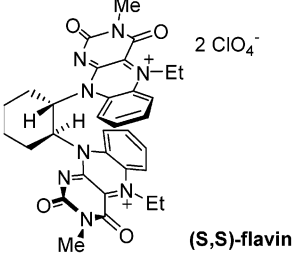
hardly provide an advantage over metal-catalyzed BV reactions.

Another often used substrate is the prochiral 3-phenylcyclobutanone (Figure 30 and Table 3), and

with some exceptions,⁸⁰ better results are obtained.

The chiral BINOL complexes of zirconium,⁷⁶ aluminum,⁷⁷ and magnesium⁸¹ are not only active in the asymmetric oxidation of racemic ketones, they also catalyze the asymmetric BV oxidation of prochiral substrates (see Table 3). The cobalt salen catalyst developed in the group of Katsuki is by far the most effective catalyst. Good results are obtained with only 1 mol % of cobalt catalyst in combination with the UHP adduct or with aqueous hydrogen peroxide.⁸² Alternatively, the ketone can be modified with a C2-symmetric 2,4-pentanediol to form a ketal, which is

Table 3. BV Oxidation of 3-Phenylcyclobutanone

entry	reagent / catalyst	Conditions	yield/e.e. versus 2a+b	Ref
1		1 mol% (S,S)-Cu-complex O ₂ /t-BuCHO	44% e.e. (S) 66-88% yld	87
2		1 eq. Zr- (S)-BINOL complex, 1.5 eq. TBHP, toluene, -25 °C to RT, 12 h	31% e.e. (R)	76
3		15 mol% Al-(R)-BINOL complex CHP	68% e.e. (R) 100% yld	77
4		50 mol% (R)- BINOL- MgI ₂ , 1.5 eq. CHP, CH ₂ Cl ₂ , -25 °C, 8 h	65% e.e. (R) 91% yld	81
5		5 mol% Co-complex, 1.3 eq. 30% H ₂ O ₂ , EtOH, 24 h, 0 °C	75% e.e. (S) 85% yld	82
6	 (S,S)-flavin	10 mol% (SS) flavin- catalyst, 1.5 eq. H ₂ O ₂ (30%), 25 mol% AcONa, CF ₃ CH ₂ OH/MeOH/H ₂ O (6:3:1), -30°C, 6 dys	63% ee (S) 67% yld (62% ee (R) when using RR flavin)	85
7	Cunninghamella echinulata (whole cells)	28°C, pH = 8, cell conc.: 5 g/l, 3.4 mM ketone.	>98% e.e. (R) 71% yld	86