As conceptually new chiral ligands, we have been developing enantiomerically pure C2-symmetric chiral dienes, whose basic diene skeleton is bicyclo-[2.2.1]-hepta-2,5-diene (nbd) or bicyclo-[2.2.2]octa-2,5-diene (bod). They have two alkyl or aryl substituents on the double bonds, one on each of the two double bonds. The chiral diene ligands were found to be better than the conventional chiral ligands represented by chiral bisphosphines in terms of both catalytic activity and enantioselectivity in some of the catalytic asymmetric reactions. Their high performance was observed in rhodium-catalyzed asymmetric addition of organoboron reagents to α,β-unsaturated ketones, N-sulfonylimines, and so on. Recently, we have developed two new chiral diene ligands: One is (R)-diene* readily obtained through [4+2] cycloaddition of (R)-α-phellandrene with 2-naphthyl acetylene carboxylate. The other is that based on tetrafluorobenzobarrelene (tfb) skeleton. They were found to be excellent chiral ligands for the rhodium-catalyzed asymmetric arylation reactions including the conjugate addition to β,β-disubstituted α,β-unsaturated ketones and ketimines forming quaternary carbon centers with high enantioselectivity.