Electronic Supplementary Information

**General procedure for the asymmetric DA reaction of cyclopentadiene 2 with acryloyl-1,3-oxazolidin-2-one 3a using cationic Pd-POZ catalyst 1c in [bmim][BF₄]**

(Table 2, entry 1); PdCl₂-POZ complex (12 mg, 0.018 mmol) and AgSbF₆ (18 mg, 0.053 mmol) were dissolved in CH₂Cl₂ (1.0 cm³) and the mixture was stirred for 1 h at room temperature under Ar to produce a yellow solution with a white AgCl precipitate. The mixture was filtered in air through filter paper, and evaporated. To the resulting antimonate catalyst 1c was added [bmim][BF₄] (0.5 cm³) and a solution of acryloyl-1,3-oxazolidin-2-one 3a (50 mg, 0.35 mmol) in CH₂Cl₂ (0.5 cm³). After stirring a few minutes, CH₂Cl₂ was removed under reduced pressure and cyclopentadiene 2 (0.12 cm³, 1.77 mmol) was added. The reaction mixture was stirred at room temperature under Ar. After 48 h, the reaction mixture was quenched with saturated NaHCO₃ solution and extracted twice with ether. The combined organic layer was washed with brine, dried with anhydrous MgSO₄ and concentrated. The crude product was purified by preparative TLC on silica gel (1:1 hexane:AcOEt) to give the DA adduct 4 (65 mg, 89 %) as white solid. HPLC analysis (Daicel Chiralcel OD-H) indicated that the endo/exo ratio was 96:4 and the enantiomeric excess of the product was 96 %.

**General procedure for reuse of cationic Pd-POZ catalyst 1c in [bmim][BF₄] and CH₂Cl₂ (Table 4);** To a solution of Pd-POZ catalyst 1c (0.036 mmol) in [bmim][BF₄] (0.5 cm³) was added a solution of acryloyl-1,3-oxazolidin-2-one 3a (50 mg, 0.35 mmol)
in CH₂Cl₂ (1.0 cm³). After the mixture was cooled to −40°C, cyclopentadiene 2 (0.12 cm³, 1.77 mmol) was added. The reaction mixture was stirred at −40°C for 12 h and subsequently the reaction temperature was raised to 0°C. After 24 h of stirring at 0°C, the temperature was allowed to warm to room temperature. After the reaction, CH₂Cl₂ was removed under reduced pressure and the ionic liquid was washed with diethyl ether (1.0 cm³ ×10). The resulting ionic liquid was dried under reduced pressure for 2 h and charged with a solution of acryloyl-1,3-oxazolidin-2-one 3a (50 mg, 0.35 mmol) in CH₂Cl₂ (1.0 cm³). The mixture was cooled to −40°C, added cyclopentadiene 2 (0.12 cm³, 1.77 mmol) and continued to next cycle. On another hand, the combined diethyl ether layer was purified according to above procedure, giving the DA adduct 4 (73 mg, 99%, 95% ee).