

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).