Supporting Information

For

Asymmetric Hydrogenation of Itaconic Acid and Enol Acetate Derivatives with the Rh-TangPhos Catalyst

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General procedures for hydrogenation of itaconic acid derivatives

In a glovebox filled with nitrogen, to a solution of β -substituted itaconic acid derivative (0.5 mmol) in 4 mL of degassed THF was added Rh[(TangPhos)nbd]SbF₆ (2.5 μ mol). The whole solution was transferred into an autoclave. The autoclave was then purged three times with hydrogen and filled with hydrogen to 20 psi pressure. The resulting reactor was stirred at room temperature for 24 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. The residue was passed through a short silica gel plug to give hydrogenation product 2-substituted succinic acid derivative in quantitative yield. If the product was an ester, a small amount of sample was directly subjected to chiral GC or HPLC analysis. If the product was an acid, a small amount of the acid product was converted to its methyl ester by treatment with strong acidic resin (DOWEX 50WX2-400 ion-exchange resin) in methanol. The methyl ester was sampled for chiral HPLC analysis.

GC or HPLC conditions for itaconic acid derivatives

Chiral GC: γ -DEX 225, 100°C, 23.9 min (*S*), 24.7 min (*R*)

Chiral GC: γ -DEX 225, 85°C for 30 min then 2°C/min to 125°C
for 30 min, 62.2 min (*S*), 62.3 min (*R*).

Chiral HPLC: Chiralcel OD-H, hexane: isopropanol = 95: 5, 10.6
min (*R*), 12.4 min (*S*).

Chiral HPLC: Chiralcel OD-H, hexane:isopropanol = 95:5,
16.0 min (*R*), 22.4 min (*S*).

Chiral HPLC: Chiralcel OD-H, hexane:isopropanol = 95:5,
11.0 min (*R*), 15.6 min (*S*).

Chiral HPLC: Chiralcel OD-H, hexane:isopropanol = 95:5,
14.7 min (*R*), 17.1 min (*S*).

Chiral HPLC: Chiralcel OD-H, hexane:isopropanol = 95:5, 14.6
min (*R*), 16.9 min (*S*).

Chiral HPLC: Chiralcel OD-H, hexane:isopropanol = 95:5, 19.7 min (*R*), 28.1 min (*S*).

Chiral HPLC: Chiralcel OD-H, hexane:isopropanol = 95:5, 16.4 min (*R*), 23.3 min (*S*).

General procedures for hydrogenation of enol acetates

In a glovebox filled with nitrogen, to a solution of an enol acetate (0.5 mmol) in 4 mL of degassed THF was added Rh[(TangPhos)nbd]SbF₆ (2.5 μmol). The whole solution was transferred into an autoclave. The autoclave was then purged three times with hydrogen and filled with hydrogen to 20 psi pressure. The resulting reactor was stirred at room temperature for 24 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. The residue was passed through a short silica gel plug to give hydrogenation product chiral acetate in quantitative yield. The enantiopurity was analyzed by chiral GC on a chiralselect 1000 column.

GC or HPLC conditions for chiral acetates

Chiral GC: Chiralselect 1000, 155°C, 54.4 min (*S*), 56.3 (*R*).

Chiral GC: β -DEX 120, 125°C, 10.3 min (*S*), 10.6 min (*R*).

Chiral GC: Chiralselect 1000, 140°C, 7.5 min (*S*), 8.4 min (*R*).

Chiral GC: Chiralselect 1000, 150°C, 13.6 min (*S*), 14.9 min (*R*).

Chiral GC: Chiralselect 1000, 110°C, 8.2 min (*S*), 9.9 min (*R*).

Chiral GC: Chiralselect 1000, 160°C, 39.5 min (*S*), 42.8 min (*R*).