Supporting Information for

Oxidative Kinetic Resolution of Racemic Secondary Alcohols in Water with Chiral PNNP/Ir catalyst

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1. General methods

All experiments were carried out under nitrogen atmosphere with Schlenk techniques. All racemic alcohols were synthesized by NaBH₄ reduction in ethanol from their respective ketones. The conversion of the products was determined by GC. The ee of the products was determined by GC or HPLC.

2. A typical procedure for oxidative kinetic resolution of racemic secondary alcohols

An example is given by the oxidative kinetic resolution of racemic 1-phenylpropanol using chiral PNNP/Ir catalyst. Under nitrogen atmosphere, (S,S)-PNNP (0.005 mmol) and [Ir(COD)Cl]₂ (0.0025 mmol) were placed in a Schlenk tube equipped with a Teflon-coated magnetic stirring bar. Dichloromethane (0.5 mL) was then added and the mixture was stirred for a few minutes to generate catalyst in situ. Subsequently, acetone (2.2 mL), PPNCl (0.05 mmol), and water (8.0 mL) were successively introduced. After the mixture was stirred for 1 h, appropriate amount of KOH/iPrOH solution was added. About 0.5 h, the racemic 1-phenylpropanol was added and the mixture was continually stirred at 28 °C for about 16 h. At the end of the reaction, the product was extracted with ethyl acetate and then passed through a short silica gel column. The conversion and the ee of the product were determined by GC.
3. **Chromatograph analytical data for chiral aromatic alcohols**

![Chemical structure of the aromatic alcohol](image)

**GC analysis:** Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 115 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

**Racemic a:**

![Chromatogram of racemic a](image)

**Resolved a (Table 4, Entry 1):**

![Chromatogram of resolved a](image)
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 110 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic b:

Resolved b (Table 4, Entry 2):
HPLC analysis: Daicel Chiralcel OD column, 4.6 mm i. d. × 250 mm; Eluent: \( n \)-hexane/\( i \)-PrOH = 98:2; flow rate = 0.9 mL/min; Temp., 25 °C; detection, 254 nm, \( t_1 = 16.86 \) min, \( t_2 = 19.12 \) min)

Racemic \( c \):

Resolved \( c \) (Table 4, Entry 3):
HPLC analysis: Daicel Chiralcel OD column, 4.6 mm i. d. × 250 mm; Eluent: n-hexane/i-PrOH = 98:2; flow rate = 0.9 mL/min; Temp., 25 °C; detection, 254 nm, (t₁ = 11.55 min, t₂ = 14.03 min)

Racemic d:

Resolved d (Table 4, Entry 4):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 100 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic e:

Resolved e (Table 4, Entry 5):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 130 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic f:

Resolved f (Table 4, Entry 6):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 130 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic g:

Resolved g (Table 4, Entry 7):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic h:

Resolved h (Table 4, Entry 8):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 130 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic i:

Resolved i (Table 4, Entry 9):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 130 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic j:

Resolved j (Table 4, Entry 10):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic k:

Resolved k (Table 4, Entry 11)
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic I:

Resolved I (Table 4, Entry 12)
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 110 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic m:

Resolved m (Table 4, Entry 13):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic n

Resolved n (Table 4, Entry 14):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic o:

Resolved o (Table 4, Entry 15):
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic p:

Resolved p (Table 4, Entry 16)
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic $q$:

Resolved $q$ (Table 4, Entry 17)
GC analysis: Chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 120 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa.

Racemic r:

Resolved r (Table 4, Entry 18)