Supporting Information for

Unsymmetrical Iron Catalyst for the Asymmetric Transfer Hydrogenation of Ketones.

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Figure S2 The FT-IR spectrum (KBr pellet) of 4. The peak at 1951 cm\(^{-1}\) was assigned to the CO stretch.
Figure S3 Entry 3 reaction profile and ee of the catalytic reduction of acetophenone.
**Figure S4.1** Reaction for entry 1, Table 1

\[
\text{4, KOTBu, iPrOH} \quad \text{28°C}
\]

GC analysis conditions: Oven temperature 130 °C

Retention time: (R)-isomer = 6.693; (S)-isomer = 7.193; starting material = 4.093.

**Figure S4.2**

10 min

![Graph](image)

**Figure S5.1** Reaction for entry 2, Table 1

\[
\text{4, KOTBu, iPrOH} \quad \text{28°C}
\]

GC analysis conditions: Oven temperature 130 °C

Retention time: (R)-isomer = 6.758; (S)-isomer = 7.239; starting material = 4.072.

**Figure S5.2**

50 min
Figure S6.1 Reaction for entry 3, Table 1

![Diagram](image)

GC analysis conditions: Oven temperature 130 °C
Retention time: (R)-isomer = 6.703; (S)-isomer = 7.193; starting material = 4.092.

Figure S6.2

120 min

![Diagram](image)

Figure S7.1 Reaction for entry 4, Table 1

![Diagram](image)
GC analysis conditions: Oven temperature 120 °C
Retention time: (R)-isomer = 10.966; (S)-isomer = 11.992; starting material = 5.349.

**Figure S7.2**
60 min

![Graph showing GC analysis results for Figure S7.2](image)

**Figure S8.1** Reaction for entry 6, Table 1

\[
\text{Ph-CH=Cl + 4, KOTBu, iPrOH} \xrightarrow{28^\circ C} \text{Ph-CH(OH)Cl}
\]

GC analysis conditions: Oven temperature 120 °C
Retention time: (R)-isomer = 14.530; (S)-isomer = ; starting material = 3.672.

**Figure S8.2**
2 min

![Graph showing GC analysis results for Figure S8.2](image)
**Figure S9.1** Reaction for entry 7, Table 1

\[
\begin{array}{c}
\text{Cl} \quad \text{O} \\
\text{Cl} \\
\end{array}
\xrightarrow{4, \text{KOTBu, iPrOH}}
\begin{array}{c}
\text{Cl} \quad \text{OH} \\
\text{Cl} \\
\end{array}
\]

28°C

GC analysis conditions: Oven temperature 145 °C

Retention time: (R)-isomer = 5.654; (S)-isomer = 6.924; starting material = 2.752.

**Figure S9.2**

10 min

**Figure S10.1** Reaction for entry 8, Table 1

\[
\begin{array}{c}
\text{Cl} \quad \text{O} \\
\text{Cl} \\
\end{array}
\xrightarrow{4, \text{KOTBu, iPrOH}}
\begin{array}{c}
\text{Cl} \quad \text{OH} \\
\text{Cl} \\
\end{array}
\]

28°C

GC analysis conditions: Oven temperature 145 °C

Retention time: (R)-isomer = 4.737; (S)-isomer = 5.213; starting material = 2.588.

**Figure S10.2**

10 min
**Figure S11.1** Reaction for entry 9, Table 1

\[
\begin{align*}
\text{R} & \rightarrow 4, \text{KOTBu, iPrOH} \\
& \text{28°C} \\
\text{O} & \rightarrow \text{OH}
\end{align*}
\]

GC analysis conditions: Oven temperature 130 °C

Retention time: \((R)\)-isomer = ; \((S)\)-isomer = ; starting material = .

**Figure S11.2**

20 min

**Figure S12.1** Reaction for entry 10, Table 1
GC analysis conditions: Oven temperature 140 °C
Retention time: (R)-isomer = 2.735; (S)-isomer = 2.606; starting material = 1.399.

**Figure S12.2**
40 min

![Graph showing GC analysis results](image)

**Figure S13.1** Reaction for entry 11, Table 1

GC analysis conditions: Oven temperature 100 °C
Retention time: (R)-isomer = 13.779; (S)-isomer = 14.208; starting material = 5.865.

**Figure S13.2**
20 min
Figure 13.3

20 mins, after isolation ee was obtainable

Figure S14.1 Reaction for entry 13, Table 1

\[
\begin{align*}
\text{O} & \quad \text{4, KOtBu, iPrOH} \\
& \quad 28^\circ\text{C}
\end{align*}
\]

GC analysis conditions: Oven temperature 60 °C
Retention time: (R)-isomer = 9.41; (S)-isomer = 9.92; starting material = 3.74.

Figure S14.2

50 min
Figure S15.1 Reaction for entry 16, Table 1

\[
\begin{align*}
\text{O} & \quad \rightarrow \\
\text{4, KOTBu, iPrOH} & \quad \text{OH} \\
28^\circ\text{C} & \quad \text{product} = 5.013; \text{starting material} = 3.228.
\end{align*}
\]

GC analysis conditions: Oven temperature 180 °C

Figure S15.2

30 min

Figure S16.1 Reaction for entry 17, Table 1

\[
\begin{align*}
\text{O} & \quad \rightarrow \\
\text{4, KOTBu, iPrOH} & \quad \text{OH} \\
28^\circ\text{C} & \quad \text{product} = 5.013; \text{starting material} = 3.228.
\end{align*}
\]
GC analysis conditions: Oven temperature 150 °C
Retention time: (R)-isomer = 6.119; (S)-isomer = 6.378; starting material = 4.403.

**Figure S16.2**
20 min

![GC analysis graph]

**Figure S17.1** Reaction for entry 18, Table 1

![Reaction scheme]

GC analysis conditions: Oven temperature 125 °C
Retention time: (R)-isomer = 15.743; (S)-isomer = 16.157; RED-(R)-isomer = 10.677; RED-(S)-isomer = 11.051; REDK = 6.416; starting material = 12.175.

**Figure S17.2**
20 min
Figure S18.1 Reaction for entry 19, Table 1

\[
\begin{align*}
\text{R} & \quad \text{4, KOTBu, iPrOH} \\
28^\circ \text{C} & \quad \rightarrow \quad \text{R'}
\end{align*}
\]

GC analysis conditions: Oven temperature 160 °C
Retention time: product = 7.04; starting material = 5.28.

Figure S18.2

10 min