Supporting Information

Highly Enantioselective Catalytic $\text{aza}$-Morita-Baylis-Hillman Reaction

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**General Remarks:**

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; [α]D-values are given in unit of 10 deg⁻¹ cm² g⁻¹. ¹H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in CDCl₃ with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. ¹³C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers (CDCl₃: 77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm⁻¹. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, OD-H, and IC columns 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)) and chiral column (Phenomenex Lux 5µ Amylose-2 column 4.6 × 250 mm (PA-2), Phenomenex Lux 5µ Cellulose-2 column 4.6 × 250 mm (PC-2), (Phenomenex Ind., Ltd.)). Mass spectra were recorded by EI, ESI, MALDI and HRMS was measured on a HP-5989 instrument.
General procedure for the phosphine-catalyzed asymmetric aza-MBH reaction of N-alkoxycarbonyl ketimine 61 with MVK:

Into a 100 mL oven-dried reaction flask under argon atmosphere were added N-alkoxycarbonyl Ketimine 61 (1 g, 3.5 mmol), catalyst CP1 (0.7 mmol, 318 mg), chloroform (70 mL) and MVK (7 mmol, 556 μL). The reaction mixture was stirred at 25 °C for 48 h, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.
## 分析结果表

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<th>峰号</th>
<th>峰名</th>
<th>保留时间 (min)</th>
<th>峰高</th>
<th>峰面积 (mm²)</th>
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Translation: Enantiomeric excess was determined by HPLC with a Chiralcel IC column ($\lambda = 230$ nm); eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; $t_{major} = 32.93$ min, $t_{minor} = 37.76$ min; ee% = 84%.

$$\begin{align*}
\text{N} & \text{Boc} \\
\text{O} & \text{O} \\
+ & \text{(R)-CP1 (20 mol\%)} \\
\text{Allyl} & \text{Chloroform, rt, 24h} \\
\text{into a 50 mL oven-dried reaction flask under argon atmosphere were added 4Å MS (150 mg),} \\
\text{N-alkoxycarbonyl Ketimine 61 (200 mg, 0.7 mmol), catalyst CP1 (0.14 mmol, 64 mg),} \\
\text{chloroform (14 mL) and MVK (7 mmol, 113 µL). The reaction mixture was stirred at 25 °C} \\
\text{into a 50 mL oven-dried reaction flask under argon atmosphere were added 4Å MS (150 mg),} \\
\text{N-alkoxycarbonyl Ketimine 61 (200 mg, 0.7 mmol), catalyst CP1 (0.14 mmol, 64 mg),} \\
\text{chloroform (14 mL) and MVK (7 mmol, 113 µL). The reaction mixture was stirred at 25 °C} \\
\end{align*}$$
for 24 h, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.
Translation: Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 230$ nm]; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; $t_{major} = 33.88$ min, $t_{minor} = 39.16$ min; ee% = 91%.
General procedure for the phosphine-catalyzed asymmetric *aza*-MBH reaction of *N*-sulfonated imine 59 with MVK:

![Reaction Equation]

Into a 100 mL oven-dried reaction flask under argon atmosphere were added *N*-sulfonated imine 59 (1 g, 3.4 mmol), catalyst (S)-**CP1** (0.34 mmol, 155 mg) and THF (28 mL), and MVK (10.2 mmol, 827 μL) was added at -30 °C. The reaction mixture was stirred at -30 °C for 96 h, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

**HPLC REPORT**

Sample Name: hfl-12-57Race Date:####
Column: AS-H Mobile Phase: hex/ipr=65/35
Velocity(ml/min): 0.7 Detection Wavelength(nm):254

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Sample Name: hfl-12-57Ch      Date:####
Column: AS-H                 Mobile Phase: hex/ipr=65/35
Velocity(ml/min): 0.7           Detection Wavelength(nm): 254

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References
