

Supporting Information

Highly Enantioselective Catalytic *aza*-Morita-Baylis-Hillman Reaction

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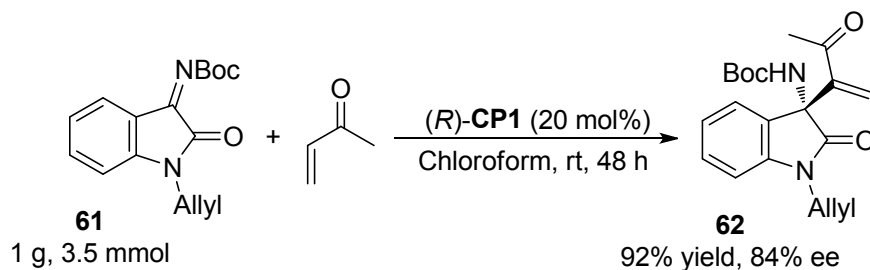
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General Remarks:

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; $[\alpha]_D$ -values are given in unit of $10 \text{ deg}^{-1} \text{ cm}^2 \text{ g}^{-1}$. ^1H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in CDCl_3 with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers (CDCl_3 : 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 $4.6 \times 250 \text{ mm}$, (Daicel Chemical Ind., Ltd.)) and chiral column (Phenomenex Lux 5μ Amylose-2 column $4.6 \times 250 \text{ mm}$ (PA-2), Phenomenex Lux 5μ Cellulose-2 column $4.6 \times 250 \text{ mm}$ (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:**

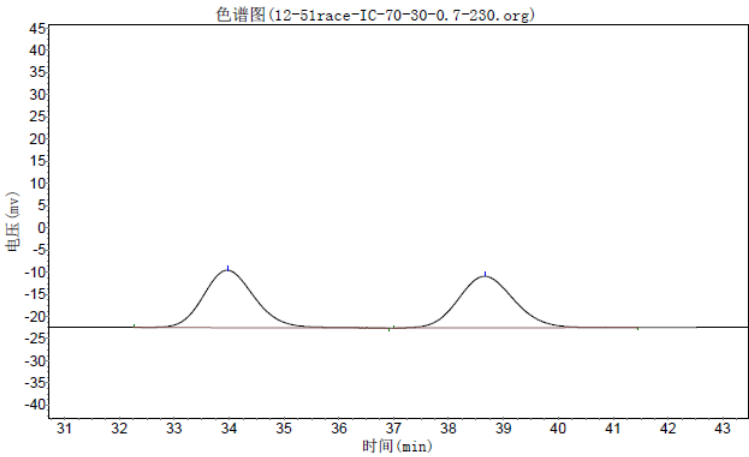


Into a 100 mL oven-dried reaction flask under argon atmosphere were added *N*-alkoxycarbonyl Ketimine **61** (1 g, 3.5 mmol), catalyst **CP1** (0.7 mmol, 318 mg), chloroform (70 mL) and MVK (7 mmol, 556 μ L). The reaction mixture was stirred at 25 $^{\circ}$ C for 48 h, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

实验时间: 2014-01-20, 18:13:45
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实验者:
报告时间: 2014-01-21, 15:19:50
积分方法: 面积归一法

使用仪器类型: 气相色谱 检测器: FID 进样器: 分流
柱温: 程序升温



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		33.965	12927.666	830348.813	50.3430
2		38.655	11609.821	819032.875	49.6570
总计			24537.487	1649381.688	100.0000

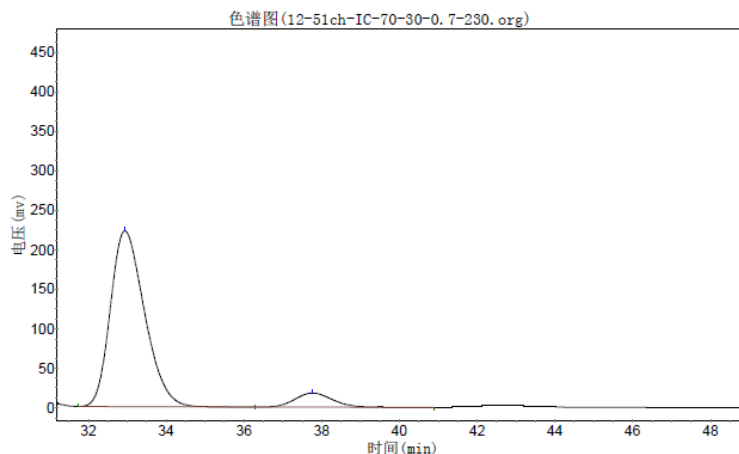
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实验者:
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积分方法: 面积归一法

使用仪器类型: 气相色谱
柱温: 程序升温

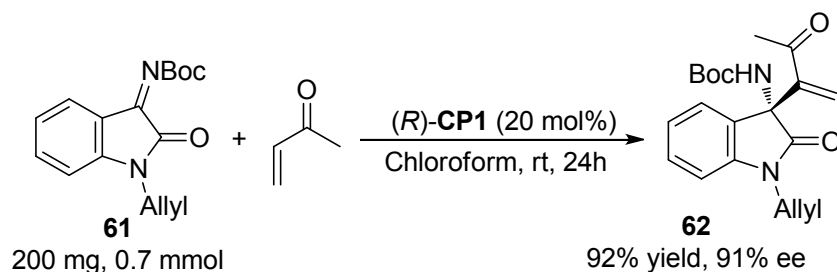
检测器: FID

进样器: 分流



分析结果表					
峰号	峰名	保留时间	峰高	峰面积	含量
1		32.933	222765.938	13622910.000	91.9383
2		37.758	17813.131	1194545.875	8.0617
总计			240579.068	14817455.875	100.0000

Translation: Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 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%.



Into a 50 mL oven-dried reaction flask under argon atmosphere were added 4Å MS (150 mg), *N*-alkoxycarbonyl Ketimine **61** (200 mg, 0.7 mmol), catalyst **CP1** (0.14 mmol, 64 mg), chloroform (14 mL) and MVK (7 mmol, 113 μ L). The reaction mixture was stirred at 25 °C

for 24 h, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

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实验时间: 2014-01-20, 18:13:45
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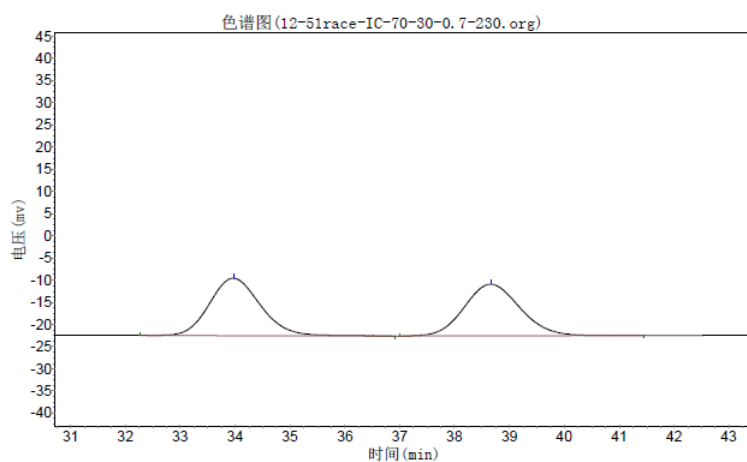
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积分方法: 面积归一法

使用仪器类型: 气相色谱

检测器: FID

进样器: 分流

柱温: 程序升温



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		33.965	12927.666	830348.813	50.3430
2		38.655	11609.821	819032.875	49.6570
总计			24537.487	1649381.688	100.0000

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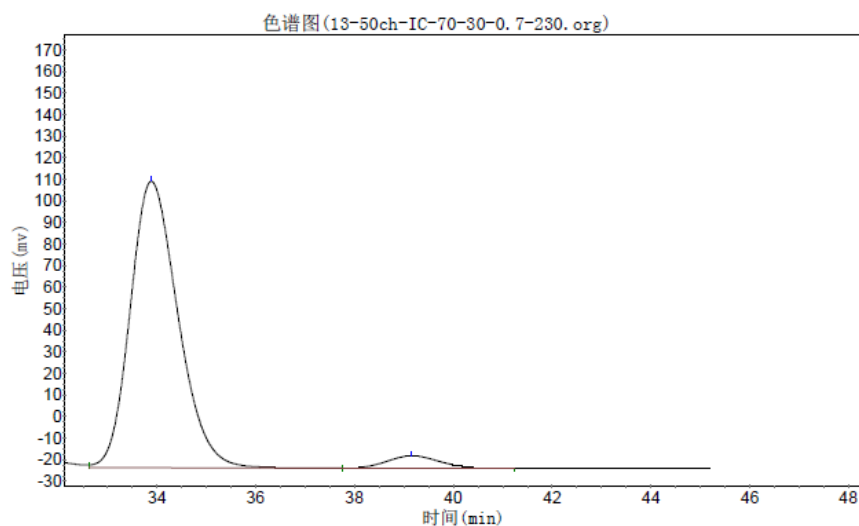
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积分方法: 面积归一法

使用仪器类型: 气相色谱

检测器: FID

进样器: 分流

柱温: 程序升温

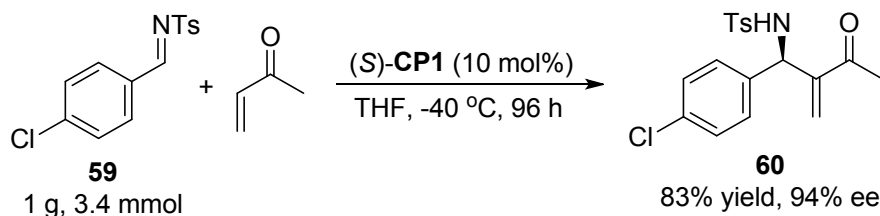


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		33.883	132804.719	8916825.000	95.5046
2		39.157	5710.299	419714.906	4.4954
总计			138515.018	9336539.906	100.0000

Translation: Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 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%.

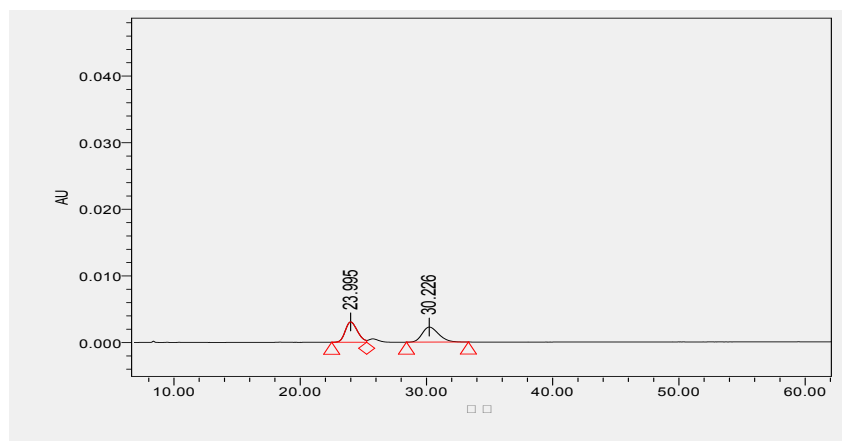
General procedure for the phosphine-catalyzed asymmetric *aza*-MBH reaction of *N*-sulfonated imine **59 with MVK:**



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 μ L) was added at -30 $^\circ$ C. The reaction mixture was stirred at -30 $^\circ$ C for 96 h, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

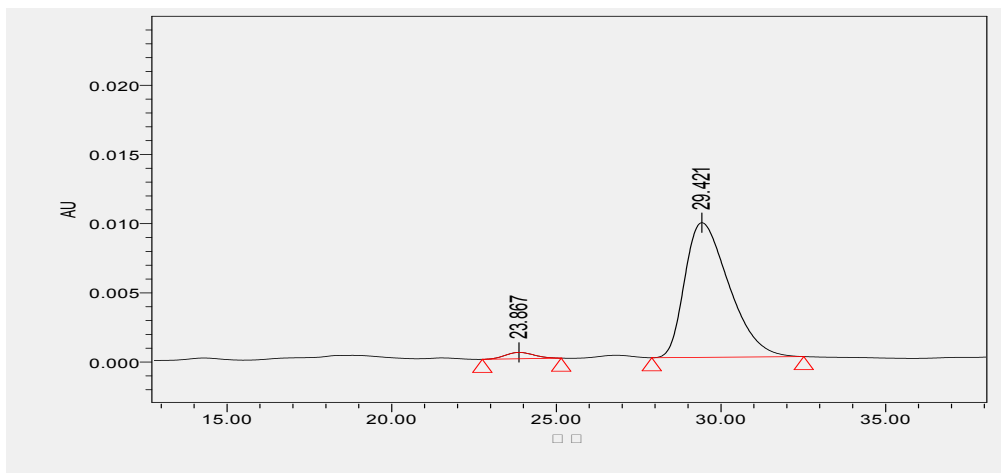
HPLC REPORT

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



NO	R. Time	Peak Area	Percent	Peak Height
1	23.995	203897	49.77	3046
2	30.226	205790	50.23	2257

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



NO	R. Time	Peak Area	Percent	Peak Height
1	23.867	28323	3.02	464
2	29.421	909826	96.98	9736

References

1. M. Shi, L.-H. Chen, C.-Q. Li, *J. Am. Chem. Soc.*, 2005, **127**, 3790.
2. F.-L. Hu, Y. Wei, M. Shi, S. Pindi and G. Li, *Org. Biomol. Chem.*, 2013, **11**, 1921.