Supporting Information
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Chelating Hydroxyalkyl-NHCs as efficient chiral ligands for room temperature Copper-Catalyzed Asymmetric Allylic Alkylation

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1. General information

1.1 Equipment and chemicals used

Unless otherwise stated all commercial materials were used without further purification. All reactions were carried out under N₂ (or argon) atmosphere in pre-dried glassware. The solvents: Toluene and Methanol were dried by distillation over sodium metal under nitrogen (or argon). Dichloromethane and ethyl acetate were dried by distillation over CaH₂ under nitrogen (or argon) and stored under inert atmosphere. Analytical thin-layer chromatography (TLC) of all reactions was performed on silica gel 60 F₂₅₄ TLC plates. Visualization was performed with standard potassium permanganate stains or UV light. Flash column were performed using silica gel 60 (230-400 mesh). NMR spectra were recorded with Bruker machines in CDCl₃ or CD₂Cl₂; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) are in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), septet (sept), multiplet (m), and broad (br).

Enantiomeric ratios were determined by chiral GLC analysis [Chiraldex G-TA column (30m × 0.25mm) and Cyclodex β] in comparison with authentic materials. Diethylzinc and dibutylzinc reagent were purchased from Aldrich Chemical Co, dimethylzinc was purchased from Acros Organics and used without purifications. (CuOTf)₂•C₆H₆ was purchased from Aldrich Chemical Co and used without purification. Substrate precursors were purchased from Aldrich Chemical Co and Alfa Aesar and used without purification. The allylic alcohols were prepared from the corresponding aldehydes and ketones using a two steps Horner-Emmons olefination / Dibal-H reduction sequence.

All glassware was either oven dried or flame dried, and reactions were done under an atmosphere of argon unless otherwise specified.

1. 2 Synthesis of oxalamide of L7

The oxalamide precursor of L7 was prepared following a protocol adapted from an already reported one\(^1\), using aniline and L-\textit{tert}-Leucinol as reagents.

The desired product was obtained as a white solid in 97% yield.

\(^{1}\text{H NMR}\) (CDCl\(_3\), 400 MHz): 9.36 (bs, 1H), 7.74 (bd, \(J = 9.6\), 1H), 7.61 (d, \(J = 7.6\) Hz, 2H), 7.34 (m, 2H), 7.16 (t, \(J = 7.6\) Hz, 1H), 3.91 (bd, \(J = 11.3\) Hz, 1H), 3.86-3.81 (m, 1H), 3.64 (bt, \(J = 9.2\) Hz, 1H), 2.42 (bs, 1H), 0.98 (s, 9H)

\(^{13}\text{C NMR}\) (CDCl\(_3\), 400 MHz): 160.8 (CON), 157.5 (CON), 136.3 (1C), 129.1 (2C), 125.3 (1C), 119.8 (2C), 62.2 (CH\(_2\)), 60.8 (CH), 33.8 (C), 26.8 (3CH\(_3\)).

\([\alpha]_D^{20} = -1.0\) (c = 1, CHCl\(_3\))

1. 3 Synthesis of oxalamide of L8

The oxalamide precursor of L8 was prepared following a protocol adapted from an already reported one\(^1\), using of 2,5-diisopropylaniline and L-\textit{tert}-Leucinol as reagents.

Desired product was obtained as a white solid in quantitative yield (mp = 190 – 191°C).

\(^{1}\text{H NMR}\) (CDCl\(_3\), 400 MHz): 8.81 (bs, 1H), 7.67 (bd, \(J = 9.6\), 1H), 7.33 (dd, \(J = 7.6\) Hz, \(J = 7.6\) Hz, 1H), 7.20 (d, \(J = 7.6\) Hz, 2H), 3.95-3.82 (m, 2H), 3.00 (sept, \(J = 6.8\) Hz, 2H), 2.08 (t, \(J = 6\) Hz, 1H), 1.20 (dd, \(J = 6.8\) Hz, \(J = 10.0\) Hz, 12H), 1.01 (s, 9H)

\(^{13}\text{C NMR}\) (CDCl\(_3\), 400 MHz): 160.7 (CON), 159.2 (CON), 145.8 (2C), 129.6 (C), 128.8 (CH), 123.6 (2CH), 62.4 (CH\(_2\)), 60.9 (CH), 33.8 (C), 28.9 (2CH), 26.8 (3CH\(_3\)), 23.7 (2CH\(_3\)), 23.5 (2CH\(_3\)).

\([\alpha]_D^{20} = -4.6\) (c = 1, CHCl\(_3\))

\(\text{HMRS: m/z calcd for } [\text{C}_{20}\text{H}_{32}\text{N}_{2}\text{O}_{3}\text{Na}]^{+}: 371.23106, \text{found: 371.2300}; m/z \text{calcd for } [\text{C}_{20}\text{H}_{31}\text{N}_{2}\text{O}_{3}\text{Na}_{2}]^{2+}: 393.21301, \text{found: 393.2133};\)

1. 4 Synthesis of imidazolium salt L7

The imidazolium salt was prepared following a protocol adapted from an already reported one\(^1\).

L7 was obtained as a white solid (mp = 178°C) in 83% overall yield.

\(^{1}\text{H NMR}\) ((CD\(_3\))\(_2\)CO, 400 MHz): 9.42 (s, 1H), 7.53 (s, 2H), 7.52 (bd, \(J = 1.6\), 2H), 7.38-7.34 (m, 1H), 4.77 (t, \(J = 5.2\) Hz, 1H), 4.73-4.68 (m, 2H), 4.59-4.46 (m, 2H), 4.03-4.00 (m, 2H), 3.91 (dd, \(J = 6.0\), 8.0, 1H), 1.14 (s, 9H).
1^3C NMR ((CD$_3$)$_2$CO, 100 MHz): 157.0 (CH), 137.6 (1C$_{Ar}$), 130.9 (2C$_{Ar}$), 127.8 (1C$_{Ar}$), 118.9 (2C$_{Ar}$), 72.3 (CH), 58.2 (CH$_2$), 49.9 (CH$_2$), 49.4 (CH$_2$), 34.5 (C), 27.7 (3CH$_3$).

3^1P NMR ((CD$_3$)$_2$CO, 162 MHz): -144.3 (sept, $J = 707$, 1P)

1^9F NMR ((CD$_3$)$_2$CO, 376 MHz):-72.65 (d, $J = 707$, 6F)

1.5 Synthesis of imidazolium salt L8

The Imidazolium salt L8 was prepared following a protocol adapted from an already reported one$^1$. L8 was obtained as a white solid (mp = 145°C) in 71% overall yield.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): 7.73 (s, 1H), 7.40 (t, $J = 7.8$, 1H), 7.22-7.19 (m, 2H), 4.31-4.10 (m, 4H), 3.93 (dd, $J = 11.9$, 3.8, 1H), 3.73 (dd, $J = 1.09$, 10.4, 1H), 3.62 (dd, $J = 10.4$, 3.8, 1H), 2.86-2.73 (m, 2H), 2.03 (s, 1H), 1.22 (d, $J = 6.8$, 3H), 1.20 (d, $J = 6.8$, 3H), 1.13 (d, $J = 5.2$, 3H), 1.11 (d, $J = 5.2$, 3H), 0.99 (s, 9H).

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz): 159.9 (CH), 147.1(C), 146.8(C), 131.7 (CH), 129.9 (C), 125.4 (CH), 125.2 (CH), 70.7 (CH), 57.6 (CH$_2$), 48.5 (CH$_2$), 37.8 (CH$_2$), 31.0 (C), 29.2 (CH), 29.0 (CH), 27.4 (3CH$_3$), 24.9 (CH$_3$), 24.8 (CH$_3$), 24.0 (CH$_3$), 23.9 (CH$_3$).

$^{31}$P NMR (CD$_2$Cl$_2$, 162 MHz): -144.5 (sept, $J = 711$, 1P)

$^{19}$F NMR (CD$_2$Cl$_2$, 376 MHz): -71.53 (d, $J = 711$, 6F)

$[\alpha]_D^{20} = +5.4$ (c = 1, acetone)

EA : calcd (%) for C21H35F6N2OP (476.24): C, 52.94; H, 7.40; N, 5.88; found : C, 52.97; H, 7.54; N, 5.89

1.6 Representative procedure for the copper-catalysed allylic alkylation of dialkylzinc reagents to allylic phosphates.

An dried Schlenk tube, under an argon atmosphere, was charged with (CuOTf)$_2$$\cdot$C$_6$H$_6$ (0.005 mmol) and ligand Lx (0.01 mmol). 0.5 mL of freshly distillated ethyl acetate was then added followed by the addition of $n$-BuLi (0.025 mmol). After stirring at room temperature for 10 min, Et$_2$Zn (3.0 mmol) was added dropwise at this temperature. After cooling the reaction vessel to 0°C, the phosphate (1 mmol) was added. As soon as the addition of the substrate was completed, the ice bath was removed. The reaction mixture was stirred for 30min at room temperature. Upon completion of the reaction, HCl 1N was added and the compound was extracted with diethylether. The combined organic layers
were then washed with saturated NaHCO₃ aqueous solution, brine, and dried over MgSO₄. The solvents were carefully removed under vacuo. The crude product was purified by silica gel chromatography (100% pentane) to afford the corresponding product as a colorless oil.
2. Copy of $^1$H, $^{13}$C NMR, $^{31}$P NMR, and $^{19}$F NMR analysis
3. Copy of the GLC analysis

![Chiraldex G-TA](image)

**Chiraldex G-TA**

Pressure = 109.3 kPa

45°C-90min-0.5°C/min-50°C-10°C/min-160°C-10min

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100°C-120°C-10°C/min-120°C-5°C/min-5°C/min-180°C-10min

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Chromatogram 2-6j120 C:GCsolution/Data/Tfalkylation allylique/naphthy12-6j120c.ged - Channel 1

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45°C-90min-0.5°C/min-50°C-15min-10°C/min-180-10min

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