Supporting Information for

Cu-catalyzed Asymmetric Hydroamination of Styrenes with $\text{pivZPhos}$ as Ligand

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1. General remarks

All NMR spectra were collected on Bruker Avance spectrometers equipped with a 5 mm BBI probe (1H, 13C, 31P), each with z-gradient, at 30 °C, unless otherwise indicated. 1H and 13C chemical shifts were calibrated vs. the deuterated solvent used. MS was measured on Agilent 1100 Series LC/MSD mass spectrometer. Accurate mass measurements were performed on a Time of Flight mass spectrometer (LC/MSD TOF) operating in a positive electrospray ionization mode with the capillary voltage of 3 kV. The mass spectrometer was tuned and calibrated using a tuning mix prior to sample analysis. Samples were introduced to the mass spectrometer by flow injection using an HPLC system. Solvents and reagents were used as received without additional purification unless otherwise indicated. Ligand pivZPhos was prepared according to our previous paper. Alkenes are all known compounds and they are either commercially available or could be prepared from Wittig reaction. O-Benzoyl hydroxylamines 2a, 2b, 2c and 2d were prepared according to literatures. The enantiomeric excesses of the products were determined by chiral SFC or GC with a chiral stationary phase. The mobile phase for SFC (3ml/min) is mixture of CO2 (A) and IPA (or MeOH) (B). The chiral stationary phase for SFC is Phenomenex Lux Cellulose-3. Gradient for SFC: 1%B to 3%B in 3min; then to 50%B in 5min; hold at 50%B for 1min; to 1%B in 0.5min; hold at 1%B for 0.5min.

2. Copper-catalyzed hydroamination of alkenes procedure

Typical procedure A:

To a sealed tube was added Cu(OAc)2 (10 mol%), pivZPhos (10 mol%), LiOtBu (3.0 eq.) and anhydrous THF (2.0 ml). The tube was evacuated and refilled with argon and stirred for 15 min. A solution of alkene (1.0 eq., 0.40 mmol) and O-benzoyl hydroxylamine (3.0 eq.) in anhydrous THF (2.0 ml) was added to the tube followed by the addition of silane Ph2MeSiH. The reaction was stirred at 20 °C for 16h before being quenched with water (20 ml). The mixture was extracted with EtOAc (20 ml X 2) and dried over anhydrous Na2SO4. After filtration and concentration, the product was purified by silica gel column chromatography.
3. Substrates scope and analytical data

\((S)-N,N\text{-dibenzyl-1-phenylethan-1-amine}\)

Prepared according to the typical procedure A from styrene (0.40 mmol) and \(O\)-benzoyl-\(N,N\)-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (94 mg, 78% yield) with 86% ee. \(^{1}\text{H}NMR\) is identical to the one reported in literature.\(^{4}\) Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO\(_2\)/MeOH, 3 mL/min, 220 nm); \(t_r = 2.32, 3.09\) min. \([\alpha]\)\(^{20}_D = -47.0\) (c = 1.30, CHCl\(_3\)).
(S)-N,N-dibenzyl-1-(naphthalen-2-yl)ethan-1-amine

Prepared according to the typical procedure A from 2-vinyl naphthalene (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (106 mg, 75% yield) with 78% ee. $^1$H NMR is identical to the one reported in literature. Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO$_2$/IPA, 3 mL/min, 220 nm); tr = 5.18, 6.55 min. [α]$^2_0 = -53.6$ (c = 0.80, CHCl$_3$)
(S)-N,N-dibenzyl-1-(o-tolyl)ethan-1-amine

Prepared according to the typical procedure A from 2-methylstyrene (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (76 mg, 60% yield) with 84% ee. $^1$H NMR is identical to the one reported in literature.$^5$ Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO$_2$/IPA, 3 mL/min, 220 nm); $t_{r} = 2.37$, 2.97 min. $[\alpha]_{D}^{20} = 43.3$ (c = 1.15, CHCl$_3$)
Prepared according to the typical procedure A from 2-chlorostyrene (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (97 mg, 72% yield) with 62% ee. $^1$HNMR is identical to the one reported in literature. Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO$_2$/IPA, 3 mL/min, 220 nm); $t_r$ = 2.96, 3.51 min. $[\alpha]^{20}_D = 46.6$ (c = 0.75, CHCl$_3$)
Prepared according to the typical procedure A from 4-methoxystyrene (0.40 mmol) and O-benzoyl-NN-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (93 mg, 70% yield) with 90% ee. 1HNMR is identical to the one reported in literature. Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO2/IPA, 3 mL/min, 220 nm); tr = 4.27, 5.18 min. [α]20° = -73.0 (c = 0.20, CHCl3)
(S)-N,N-dibenzyl-1-(4-fluorophenyl)ethan-1-amine

Prepared according to the typical procedure A from 4-fluorostyrene (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (100 mg, 78% yield) with 83% ee. \(^{1}\)HNMR is identical to the one reported in literature.\(^{5}\) Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO\(_2\)/MeOH, 3 mL/min, 220 nm); \(\text{tr} = 2.18, 3.63\) min. \([\alpha]_{D}^{20} = -35.8\) (c = 0.55, CHCl\(_3\))
(S)-1-(benzofuran-5-yl)-N,N-dibenzylethan-1-amine

Prepared according to the typical procedure A from 5-vinylbenzofuran (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (122 mg, 89% yield) with 88% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.60 (d, $J = 2.2$ Hz, 1H), 7.57-7.56 (m, 1H), 4.47 (d, $J = 8.6$ Hz, 1H), 7.40-7.35 (m, 5H), 7.32-7.28 (m, 4H), 7.22-7.28 (m, 2H), 6.76 (dd, $J = 2.2$, 0.9 Hz, 1H), 4.02 (q, $J = 6.8$ Hz, 1H), 3.62 (d, $J = 13.8$ Hz, 2H), 3.48 (d, $J = 13.8$ Hz, 2H), 1.48 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 154.0, 145.0, 140.5, 137.4, 128.7, 128.2, 126.7, 125.0, 120.0, 110.7, 106.7, 56.2, 53.6, 14.3. HRMS (ESI$^+$) calcd for C$_{24}$H$_{24}$NO [M+H]$^+$: 342.1852; found: 342.1853. Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO$_2$/MeOH, 3 mL/min, 220 nm); tr = 4.11, 5.62 min. $[\alpha]_{20}^D = -90.4$ (c = 0.20, MeOH).
Prepared according to the typical procedure A from 5-vinylbenzo[b]thiophene (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). After column, impurity could be washed off by acid/base extraction. The product was isolated as a colorless oil (122 mg, 85% yield) with 91% ee. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.88 (d, $J = 4.2$, 1.7 Hz, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 7.88 (dd, $J = 8.8$, $J = 1.9$ Hz, 1H), 7.72 (s, 1H), 7.40-7.37 (m, 5H), 7.33-7.29 (m, 4H), 7.24-7.20 (m, 2H), 4.1 (q, $J = 6.8$ Hz, 1H), 3.58 (d, $J = 3.5$ Hz, 4H), 1.54 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 150.0, 147.7, 141.8, 140.1, 136.0, 130.9, 129.0, 128.7, 128.3, 126.9, 125.6, 121.0, 55.9, 53.6, 12.5. HRMS (ESI⁺) calcd for C$_{24}$H$_{24}$NS [M+H]$^+$: 358.1624; found: 358.1623. Enantiomeric excess was determined by SFC with a Lux Cellulose-3 column (CO$_2$/MeOH, 3 mL/min, 220 nm); tr = 5.50, 8.19 min. [α]$^D_{20}$ = -69.4 (c = 1.30, MeOH).
(S)-N,N-dibenzyl-1-(quinolin-6-yl)ethan-1-amine

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Prepared according to the typical procedure A from 6-vinylquinoline (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (59 mg, 42% yield) with 57% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.88 (dd, $J = 4.2$, 1.8 Hz, 1H), 8.15-8.12 (m, 1H), 8.09 (d, $J = 9.2$ Hz,
1H), 7.88 (dd, J = 8.8, 2.0 Hz, 1H), 7.72 (br, 1H), 7.39-7.29 (m, 9H), 7.24-7.20 (m, 2H), 4.10 (q, J = 6.9 Hz, 1H), 3.58 (q, J = 3.60 Hz, 4H), 1.54 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 149.0, 146.7, 140.8, 139.1, 135.0, 129.9, 128.0, 127.7, 127.2, 126.8, 125.9, 124.5, 120.0 54.8, 52.6, 28.7. HRMS (ESI$^+$) calcd for C$_{25}$H$_{25}$N$_{2}$ [M+H]$^+$ : 353.2012; found: 353.2013. Enantiomeric excess was determined by SFC with a Lux Cellulose-4 column (CO$_2$/MeOH, 3 mL/min, 220 nm); tr = 4.69, 5.44 min. [α]$^{20}_D$ = 8.0 (c = 0.30, MeOH).
(S)-N,N-dibenzyl-1-(2-methylpyridin-3-yl)ethan-1-amine

Prepared according to the typical procedure A from 2-methyl-3-vinylpyridine (0.40 mmol) and O-benzoyl-N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (41 mg, 32% yield) with 49% ee. ^1H NMR (400 MHz, CDCl₃) δ: 8.35 (dd, J = 4.8, 1.6 Hz, 1H), 7.73 (dd, J = 7.8, 1.5 Hz, 1H), 7.29-7.21 (m, 10H), 7.09 (dd, J = 7.8, 4.8 Hz, 1H), 4.09 (q, J = 6.8 Hz, 1H), 3.58 (q, J = 13.8 Hz, 1H), 2.35 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ: 157.8, 147.1, 139.6, 137.1, 134.7, 129.0, 128.1, 126.9, 120.8, 54.2, 29.7, 22.2, 13.2. HRMS (ESI⁺) calc for C₂₂H₂₅N₂ [M+H]^+: 317.2012; found: 317.2013. Enantiomeric excess was determined by SFC with a Lux Cellulose-4 column (CO₂/MeOH, 3 mL/min, 220 nm); tr = 2.29, 2.82 min. [α]²⁰₀ = 103.3 (c = 0.50, MeOH).
Prepared according to the typical procedure A from trans-β-methylstyrene (0.40 mmol) and O-benzoyl-
N,N-dibenzylhydroxylamine (1.20 mmol). The product was isolated as a colorless oil (78 mg, 60 % yield) 
with 92% ee. $^1$H NMR is identical to the one reported in literature. $^5$ Enantiomeric excess was determined 

(5)-N,N-dibenzyl-1-phenylpropan-1-amine

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by SFC with a Lux Cellulose-4 column (CO₂/MeOH, 3 mL/min, 220 nm); tr = 1.81, 2.41 min. \([\alpha]^{20}_D = -33.0\) (c = 0.10, CHCl₃)
(S)-1-(1-phenylethyl)piperidine

Prepared according to the typical procedure A from styrene (0.40 mmol) and piperidin-1-yl benzoate (1.20 mmol). The product was isolated as a colorless oil (25 mg, 33 % yield) with 94% ee. **$^1$HNMR** is identical to the one reported in literature. Enantiomeric excess was determined by chiral GC with a Supelco beta-DEX325 column (30 m $\times$ 0.25 mm $\times$ 0.25 μm), He 1.0 ml/min, 100 °C; tr = 23.05, 23.32 min. $[\alpha]^2_{20} = -32.0$ (c = 0.60, CHCl$_3$)
Prepared according to the typical procedure A from styrene (0.40 mmol) and morpholino benzoate (1.20 mmol). The product was isolated as a colorless oil (45 mg, 59 % yield) with 84% ee. \(^1\)HNMR is identical to the one reported in literature.\(^4\) Enantiomeric excess was determined by chiral GC with a Supelco beta-DEX325 column (30 m × 0.25 mm × 0.25 μm), He 1.0 ml/min, 120 °C; tr = 32.20, 32.72 min. \([\alpha]^{20}_D = -63.2 \text{ (c = 0.25, CHCl}_3\text{)}\)
Prepared according to the typical procedure A from styrene (0.40 mmol) and azepan-1-yl benzoate (1.20 mmol). The product was isolated as a colorless oil (34 mg, 42 % yield) with 84% ee. $^1$HNMR is identical to the one reported in literature. Enantiomeric excess was determined by chiral GC with a Supelco beta-DEX3254 column (30 m × 0.25 mm × 0.25 μm), He 1.0 ml/min, 100 °C; tr = 31.85, 32.37 min. [$\alpha$]$^20_D = 0.67$ (c = 0.30, CHCl₃)
4. Literatures
