

Electronic Supporting Information

An NHC-CuCl functionalized metal-organic framework for catalyzing β -boration of α,β -unsaturated carbonyl compounds

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S1 - Materials and Instruments

All chemicals except the ligand were purchased and used without further purification. IR spectra were recorded on a Nicolet-5700 FT-IR spectrophotometer with KBr pellets in the region of 4000 - 400 cm^{-1} . The powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractionmeter with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator at 298 K. Elemental analysis (C, H, and N) were performed on a Perkin-Elmer 2400 II analyzer. Thermogravimetric analysis (TGA) and mass spectrum was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C simultaneous TG/DSC-QMS analyzer with a heating rate of 20 $^{\circ}\text{C}/\text{min}$. The nitrogen adsorption-desorption isotherm was recorded on a Quantachrome Autosorb iQ analyzer.

S2 - Synthesis of the ligands

Synthesis of the ligand 1,3-bis(2-methyl-4-carboxyphenyl)imidazolium chloride (H_2LCl) was achieved in several steps following a literature procedure¹ after slight modification.

(a) Synthesis of *N, N'*-bis(2-methyl-4-carboxyphenyl)ethylenediimine.

3-Methyl-4-aminobenzoic acid (3.20 g, 21.6 mmol) and formic acid (2 drops) was added in dry ethanol (10 mL). The solvent was completely dissolved by ultrasound shaking. 40% aqueous solution of glyoxal (1.48 mL, 13.0 mmol, 0.6 equiv) was added dropwisely. The solution was stirred at 35 $^{\circ}\text{C}$ for 24 h. The solid was collected by filtration, washed with water, and dried in vacuum to afford a white powder (2.28 g, 65.2 %).

(b) Synthesis of 1,3-bis(2-methyl-4-carboxyphenyl)imidazolium Chloride (H_2LCl).

The compound (2.283 g, 7.0 mmol), as obtained above, was dissolved in anhydrous THF (5 mL) under the sealed vial followed by addition of paraformaldehyde (0.2830 g, 9.4 mmol, 1.34 equiv) in 12 N HCl (0.94 mL, 11.28 mmol, 1.6 equiv) in dioxane (1.8 mL) at 0 $^{\circ}\text{C}$. The reaction mixture was stirred at 35 $^{\circ}\text{C}$ for 12 h. The solid was collected by filtration, and dried in vacuum to afford H_2LCl (1.43 g, 58.4%) as light pink powder. ¹H NMR (400 MHz, DMSO) δ 13.36 (s, 2H), 10.06

(s, 1H), 8.41 (d, J = 1.2 Hz, 2H), 8.09 (s, 2H), 8.01 (d, J = 9.3 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 2.41 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 166.18, 139.05, 137.27, 134.08, 132.81, 132.48, 128.08, 127.20, 123.90, 17.26.

(c) Synthesis of 1,3-bis(2-methyl-4-carboxyphenyl)imidazolium Nitrate [$\text{H}_2\text{L}(\text{NO}_3)$].

H_2LCl (0.3720 g, 1.0 mmol) was stirred in 10.0 mL water and was deprotonated by adding NaOH (0.12 g, 3.0 mmol), resulting in yellow solution. After filtration, 15.0 mL diluted HNO_3 (1.0 M) was added into the filtrate and white precipitation formed. The resultant solids were collected by filtration, washed with 30.0 mL water, and further dried in vacuum overnight to give crude product of $\text{H}_2\text{L}(\text{NO}_3)$ (0.2745 g).

The crude $\text{H}_2\text{L}(\text{NO}_3)$ (0.3990 g, 1.0 mmol) was treated with the same procedure as described above to give fine product of $\text{H}_2\text{L}(\text{NO}_3)$ (0.3550 g). ^1H NMR (400 MHz, DMSO) δ 13.37 (s, 2H), 9.97 (s, 1H), 8.41 (d, J = 1.2 Hz, 2H), 8.11 (s, 2H), 8.03 (d, J = 9.3 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 2.42 (s, 6H).

The quality of the fine product of $\text{H}_2\text{L}(\text{NO}_3)$ can be simply checked by following steps:

40.0 mg fine $\text{H}_2\text{L}(\text{NO}_3)$ was dissolved in $\text{H}_2\text{O}/\text{MeOH}$ (v/v, 5 mL/5 mL) and filtered to give a clear solution. After addition of AgNO_3 (0.1 mmol), the solution still remained clear, suggesting most Cl^- anions have been exchanged with NO_3^- anions in the product.

For comparison, 37.0 mg H_2LCl was dissolved in $\text{H}_2\text{O}/\text{MeOH}$ (v/v, 5.0 mL/5.0 mL) and filtered to give a clear solution. The solution was added by AgNO_3 (0.1 mmol) and a large amount of white precipitate appeared, suggesting the presence of Cl^- anions.

S3 - Synthesis of the MOF 1 and 1-im

Synthesis of $[\text{Cu}(\text{L})_{0.69}(\text{LCuCl})_{0.31}(\text{H}_2\text{O})] \cdot (\text{Cl})_x \cdot (\text{NO}_3)_{0.69-x} \cdot (\text{solvent})$ (1): H_2LCl (11.6 mg, 0.031 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_3$ (18.2 mg, 0.075 mmol) were dissolved in 2.0 mL DMF. The mixture sealed tightly in a 20 mL vial was heated at 120 °C for 24-48 hours to afford elongated prism greenish-blue crystals. The collected crystals (ca. 10.2 mg) were washed thoroughly by DMF and kept in fresh DMF.

Synthesis of $[\text{Cu}(\text{L})] \cdot (\text{NO}_3) \cdot (\text{solvent})$ (1-im): $\text{H}_2\text{L}(\text{NO}_3)$ (10.5 mg, 0.026 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_3$ (10.0 mg, 0.042 mmol) were dissolved in 1.0 mL DMA. The mixture sealed tightly in a 20 mL vial was heated at 110 °C for 12 hours to afford greenish-blue microcrystals. The collected crystals were washed thoroughly by DMA and kept in fresh DMA.

S4 - Single-crystal X-ray diffraction analysis of MOF 1

Crystal structure determination: Single crystal X-ray diffraction data were recorded at room temperature on a Bruker SMART-1000 CCD diffractionmeter with graphite-monochromated with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω scan mode. Data reduction was performed using the SAINT program.² The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELX program.³ All non-hydrogen framework atoms were refined with anisotropic displacement parameters, while the hydrogen atoms on the organic ligand were placed in idealized positions with isotropic displacement parameters. The two high residual electron densities close to carbon atom of imidazolium ring were properly assigned as copper and

chloride with 31% site occupation, and R_1 is convergent to a reasonable level. Due to the high disorder and low residual electron density, it was impossible to locate counterions (NO_3^- or Cl^-) and guest molecules (DMF and H_2O) in the pores. The *PLATON/SQUEEZE* program was used to remove scattering contribution from disordered guest molecules and to produce solvent-free diffraction intensities, which were used in the final structure refinement.⁴ Full crystallographic data for **1** have been deposited with the CCDC 1572628.

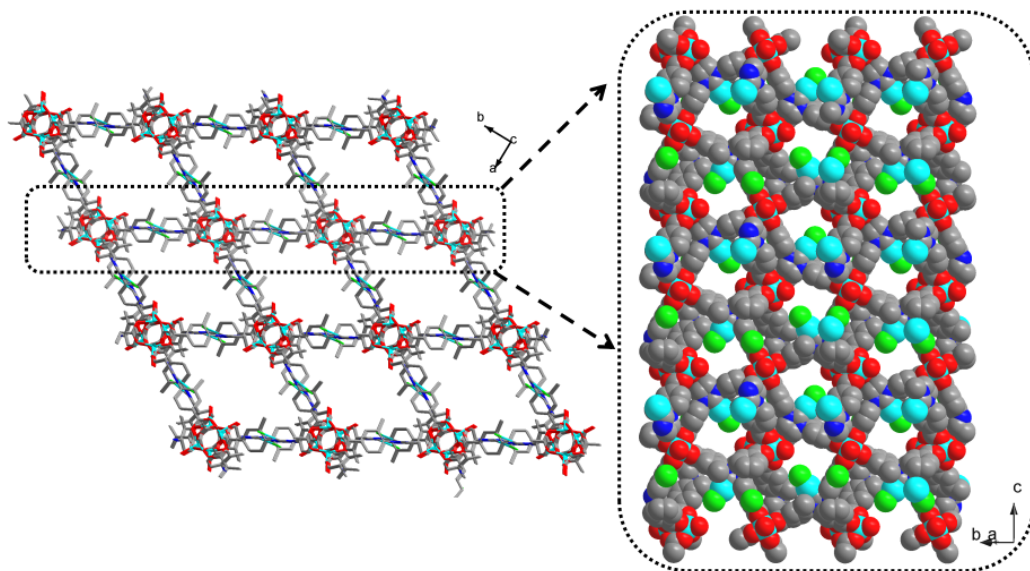
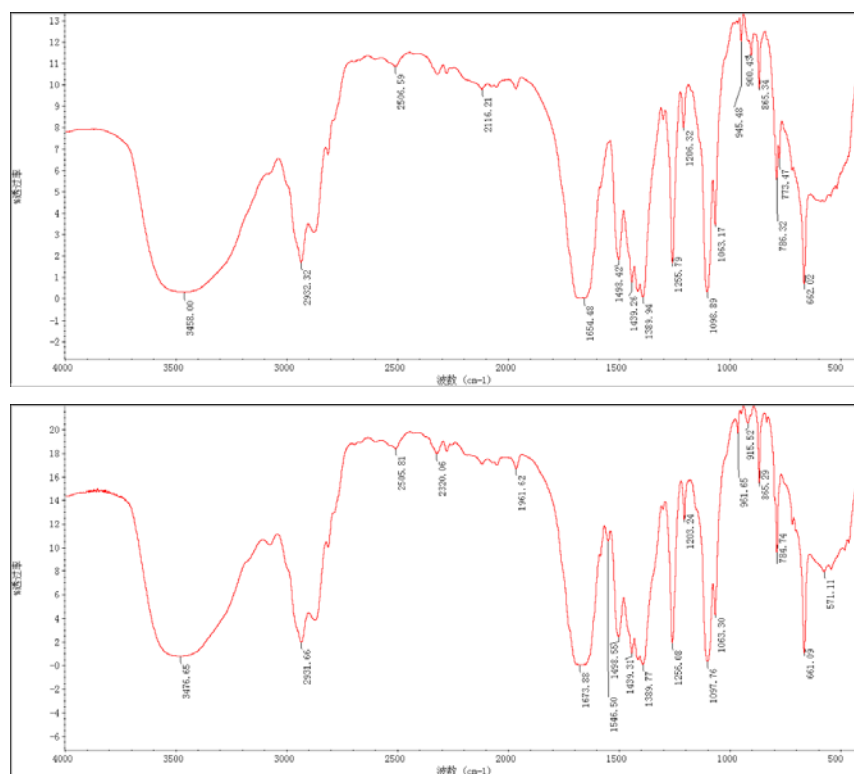


Fig. S1 The small windows on the wall of channels along the c-axis.

S5 - Fourier-Transform infrared spectrum



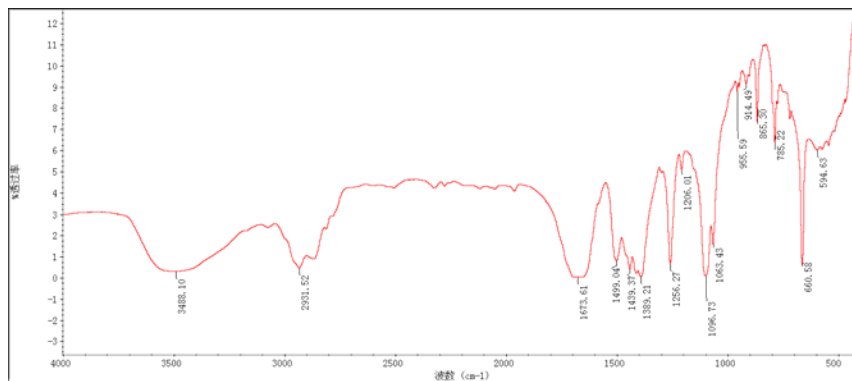


Fig. S2 The FT-IR spectrum of **1**(top), **1-im** (middle), and recovered **1** by DMF (bottom) showing almost identical .

S6 - Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C. TGA plot (green line) shows the sample loses all solvents (water, DMF) with a weight loss of 30.2% before 280 °C. Then, without clear plateau, it started to decompose.

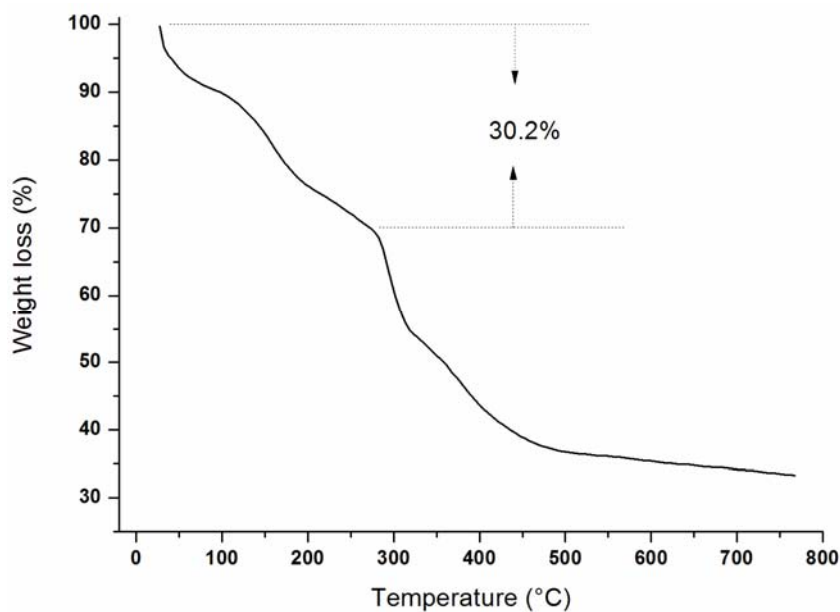


Fig. S3 TG plot of as-synthesized MOF **1**.

S7 - Nitrogen adsorption measurement

The sample for N₂ adsorption was exchanged with CH₂Cl₂, 20 mL × 3 times for 3 days and then activated by heating at 100 °C overnight. The nitrogen adsorption-desorption isotherm was recorded at 77 K on a Quantachrome Autosorb iQ analyzer.

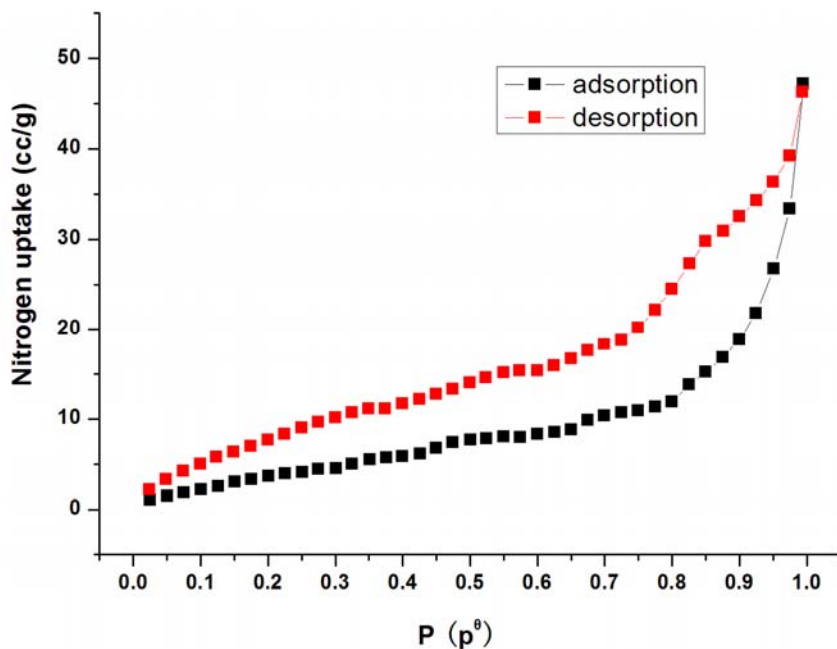
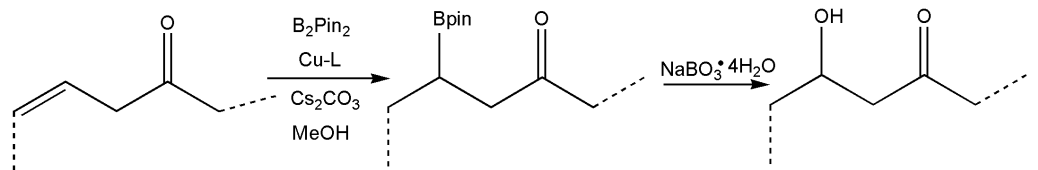


Fig. S4 Nitrogen adsorption-desorption isotherm of **1** at 77 K, indicating negligible adsorption.

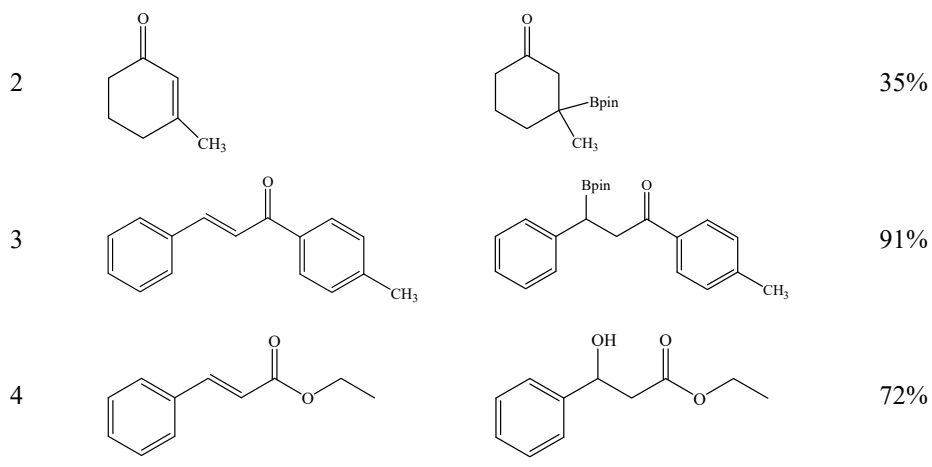
S8 - General procedure for the catalyzed β -boration of α, β -unsaturated compounds by MOF **1**.⁵⁻⁷

MOF **1** (ca. 10 mg, 2×10^{-2} mmol), Cs_2CO_3 (7.8 mg, 2.4×10^{-2} mmol), and bis(pinacolato)diboron (112 mg, 0.44 mmol) were added to 2.0 mL of anhydrous THF in an oven-dried Schlenk flask under an N_2 atmosphere. The mixture was stirred at room temperature for 10 min. Then α, β -unsaturated carbonyl compounds (0.4 mmol) and MeOH (32 μL , 0.8 mmol) were added simultaneously to the stirred mixture. After the mixture was stirred for 24 h at 25 $^\circ\text{C}$, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1–10:1) to give the corresponding compound.

Table S1. β -boration reactions of various α, β -unsaturated carbonyl compounds catalyzed by MOF **1**.^[a]



Entry	Substrate	Product	Yield (%) ^[b]
1			95%



[a]. Unless otherwise noted, α,β -unsaturated carbonyl compounds (0.4 mmol), Cs_2CO_3 (7.8 mg, 2.4×10^{-2} mmol), and bis(pinacolato)diboron (112 mg, 0.44 mmol), MeOH (32 μL , 0.8 mmol), and MOF **1** (10 mg, 2×10^{-2} mmol) were suspended in 2.0 mL of anhydrous THF in an oven-dried Schlenk flask under an N_2 atmosphere. The mixture was stirred for 24 h at 25 $^\circ\text{C}$. [b] Isolated yield of the product.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-one (**1**)⁵

Yield: 95% for reaction time 24 h.

¹H NMR (400 MHz, CDCl_3) δ 2.42 – 2.20 (m, 4H), 2.12 – 1.96 (m, 1H), 1.86 (dd, $J = 12.9, 3.5$ Hz, 1H), 1.80 – 1.67 (m, 1H), 1.61 (ddd, $J = 24.3, 11.0, 3.1$ Hz, 1H), 1.52 – 1.33 (m, 1H), 1.22 (s, 12H); ¹³C NMR (101 MHz, CDCl_3) δ 212.25, 83.41, 42.52, 41.81, 28.36, 26.46, 24.70, 24.66.

Recycling experiments on β -boration of 2-cyclohexen-1-one

We examined the recyclability of the MOF **1** in catalytic β -boration of 2-cyclohexen-1-one for five runs under the same conditions. After each run, the recovered MOF **1** are thoroughly washed and activated by THF, and then reused for next run. The catalytic yields are summarized in Table S2.

Table S2 Recycling experiments on β -boration of 2-cyclohexen-1-one. Reaction time of each run is 24 h.

Entry	Runs	Yield (%)
1	1st	95
2	2nd	93.4
3	3rd	92
4	4th	92.5
5	5th	93

3-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-one(**2**)⁵

Yield: 35%. ¹H NMR (400 MHz, CDCl_3) δ 2.50 (d, $J = 13.9$ Hz, 1H), 2.35 – 2.15 (m, 2H), 2.00 – 1.90 (m, 2H), 1.85 – 1.71 (m, 1H), 1.45 – 1.27 (m, 2H), 1.21 (s, 12H), 1.03 (d, $J = 9.7$ Hz, 3H); ¹³C NMR (101 MHz, CDCl_3) δ 211.77, 83.47, 41.11, 34.19, 29.67, 24.61, 24.55, 24.13, 23.80.

3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-p-tolylpropan-1-one (3)⁶

Yield: 91%.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.2 Hz, 2H), 7.29 (dd, J = 8.6, 6.8 Hz, 4H), 7.23 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 9.2, 4.4 Hz, 1H), 3.52 (dd, J = 18.2, 10.9 Hz, 1H), 3.40 (dd, J = 18.2, 5.1 Hz, 1H), 2.78 (dd, J = 10.8, 5.1 Hz, 1H), 2.40 (d, J = 6.0 Hz, 3H), 1.24 (s, 6H), 1.16 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 199.33, 143.64, 142.02, 134.28, 129.13, 128.47, 128.36, 128.15, 125.53, 83.34, 43.13, 24.55, 24.51, 21.62.

Recycling experiments on β -boration of 3-phenyl-1-p-tolylpropan-1-one

We examined the recyclability of the MOF 1 in catalytic β -boration of 3-phenyl-1-p-tolylpropan-1-one for five runs under the same conditions. After each run, the recovered MOF 1 are thoroughly washed and activated by THF, and then reused for next run. The catalytic yields are summarized in Table S3.

Table S3 Recycling experiments on β -boration of 3-phenyl-1-p-tolylpropan-1-one. Reaction time of each run is 24 h.

<i>Entry</i>	<i>Runs</i>	<i>Yield (%)</i>
<i>1</i>	<i>1st</i>	<i>91</i>
<i>2</i>	<i>3rd</i>	<i>88</i>
<i>3</i>	<i>5th</i>	<i>89</i>

Ethyl 3-hydroxy-3-phenylpropanoate (4)⁷

After the β -boration of α,β -unsaturated ester, the solvent was removed under reduced pressure and the crude product was subjected to the oxidation with sodium peroxoborate (305 mg, 5.0 equiv) in THF (2.0 mL) and H₂O (2.0 mL) at room temperature for 3 h. After the reaction was completed, dichloromethane (3 mL) were added to the mixture. The aqueous layer was separated and back extracted with dichloromethane (2 \times 3 mL). The organic layers were then combined and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the corresponding compound 4. Yield: 72%.

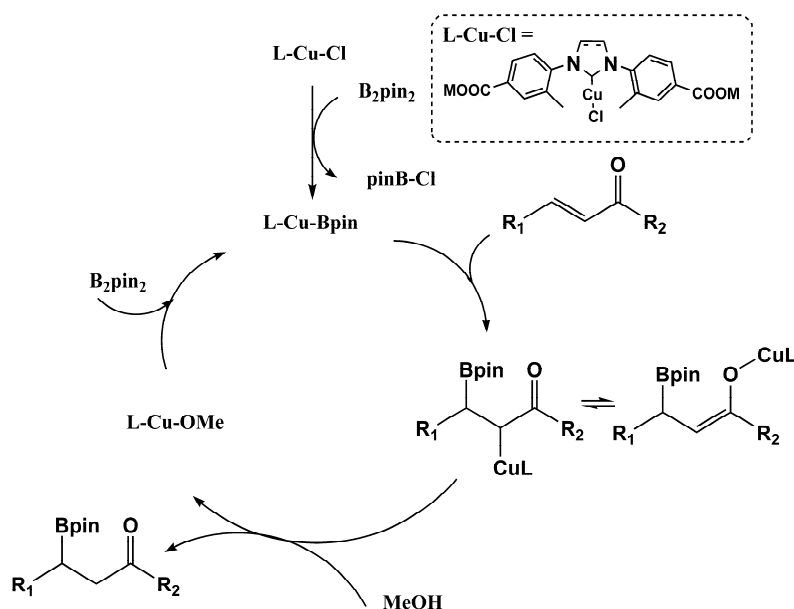
¹H NMR (400 MHz, CDCl₃) δ 7.36 (q, J = 8.0 Hz, 4H), 7.29 (d, J = 6.8 Hz, 1H), 5.19 – 5.08 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.25 (d, J = 3.3 Hz, 1H), 2.83 – 2.64 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.40, 142.47, 128.52, 127.78, 125.64, 70.31, 60.86, 43.30, 14.13.

S9 Proposed mechanism for NHC-CuCl catalyzed β -boration of α,β -unsaturated carbonyl compounds

Since the seminal works reported independently by Hosomi et al and Miyaura et al in 2000,^{8,9} various cuprous systems for catalyzing β -boration of α,β -unsaturated carbonyl compounds have been substantially developed, including NHC-Cu(I) systems.^{10,11}

Meanwhile, several key reports shed light on the possible mechanisms for the copper-catalyzed β -boration of α,β -unsaturated carbonyl compounds based on experiments and DFT calculations.^{9,12-16} Intermediate copper-boryl complexes are initially postulated,⁹ then isolated experimentally,¹³ and now generally believed to be the catalytically active species during the catalytic cycle.^{12,15,16} A number of organic transformations mediated by copper-boryl complexes have been reported and summarized in a recent review.¹⁵ In addition, the use of MeOH as an additive enables the reaction to occur quickly at room temperature.¹²

Considering the above critical observations and the important role of MeOH in our case, we propose a possible mechanism (Scheme S1) based on Yun's model.¹² Our current view is that an NHC bound copper-boryl complex is the catalytically active intermediate and its conjugate addition reaction to α,β -unsaturated carbonyl compounds takes place. The resulting organocopper species react with MeOH to afford the protonated product and a copper alkoxide. The latter then regenerate the active catalyst with bis(pinacolato)diboron.



Scheme S1 Proposed catalytic cycle for NHC-CuCl catalyzed β -boration of α,β -unsaturated carbonyl compounds

Reference:

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