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Planar-chiral ferrocene-based triazolylidene copper complexes: synthesis, characterization, and catalysis in asymmetric borylation of α,β-unsaturated ester†

Ryosuke Haraguchi, *[a] Tatsuro Yamazaki,[b] Koki Torita,[b] Tatsuki Ito[b] and Shin-ichi Fukuzawa *[b]

1,2,3-Triazol-5-ylidenes have recently attracted considerable attention as versatile ligands because of their strong electron-donating properties and structural diversities. While some efforts have been devoted to the development of chiral triazolylidene-metal complexes, there is no example achieving asymmetric induction by base-metal complexes with triazolylidene ligands. Herein, we synthesized planar-chiral ferrocene-based triazolylidene copper complexes, which enabled the asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron with good enantioselectivity.

Introduction

Over the last three decades, N-heterocyclic carbenes (NHCs) have significantly contributed to the progress in many research fields, including organometallic chemistry[1] and homogeneous catalysis.[2] Moreover, many NHC-metal complexes have been utilized as biologically active molecules[3] in medicinal chemistry and as promising photosensitizers in material sciences.[4] While imidazol-2-ylidenes hold an important position in the history of NHC chemistry, 1,2,3-triazol-5-ylidenes have emerged as versatile ligands for transition-metal complexes.[5] These carbenes are referred to as mesoionic carbenes (MICs), because no canonical resonance form of MICs without introducing formal charges can be drawn. The anionic carbon at the C4-position of a triazole ring endows the C5-carbene carbon with stronger electron-donating property than those of normal NHCs such as imidazol-2-ylidenes. In addition, the precursors of 1,2,3-triazol-5-ylidenes, that is 1,2,3-triazolium salts, are readily prepared in a structurally diverse manner *via* the Huisgen reaction[6] of azides and alkynes followed by a subsequent alkylation. Oxidative [3 + 2] cycloadditions of triazenes and alkynes can also provide 1,2,3-triazolium salts.[7] Since the pioneering work by Albrecht,[8a] various triazole-based MIC-metal complexes have been developed.[8] However, despite the progress, there are limited reports on the synthesis of chiral 1,2,3-triazol-5-ylidene-metal complexes,[9] and only few examples of asymmetric catalysis using chiral 1,2,3-triazol-5-ylidene-metal complexes have been reported. Sankararaman reported the asymmetric hydrogenation of alkenes using a [2.2]paracyclophane-based planar-chiral palladium complex as a catalyst (Scheme 1a).[9b] Elsevier developed axially chiral triazolylidene rhodium complexes with a binaphthyl backbone for the asymmetric hydrosilylation of ketones (Scheme 1b).[9c] Chen showed that chiral dinuclear gold complexes exhibited high enantioselectivity for the [2 + 2] cycloaddition of allenamides and styrenes (Scheme 1d).[9e] Our group recently developed a chiral triazolylidene-Pd-PEPPSI (PEPPSI = pyridine, enhanced, precatalyst, preparation, stabilization, initiation) complex with ferrocene-based planar chirality[10] for the asymmetric Suzuki–Miyaura cross-coupling reaction.[9d] However, all of these studies are based on the use of noble metals as catalysts; thus, the development of asymmetric catalysis by base-metal complexes with chiral mesoionic triazolylidenes is highly desired. Herein, we synthesized triazolylidene copper complexes with planar-chiral ferrocenyl groups in different substitution patterns (Fig. 1) and compared their catalytic activity and enantioselectivity for the asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron. All copper complexes **1a–c** showed moderate to good enantioselectivity. This study provides the first example to achieve asymmetric induction in catalysis by triazolylidene base-metal complexes.

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[a] Department of Applied Chemistry, Faculty of Engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan.
E-mail: haraguchi.ryosuke@p.chibakoudai.jp

[b] Department of Applied Chemistry, Institute of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

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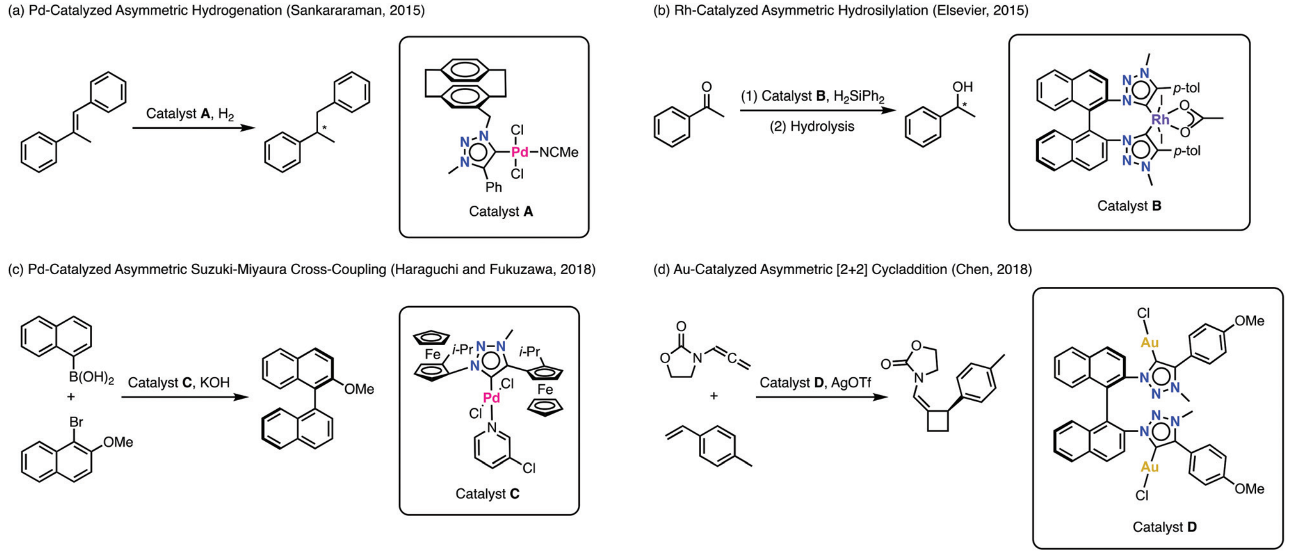
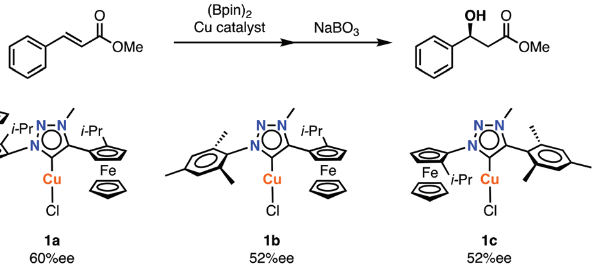


Scheme 1 Examples of asymmetric catalysis by chiral triazolylidene-metal complexes.



1a 60%ee

1b 52%ee

1c 52%ee

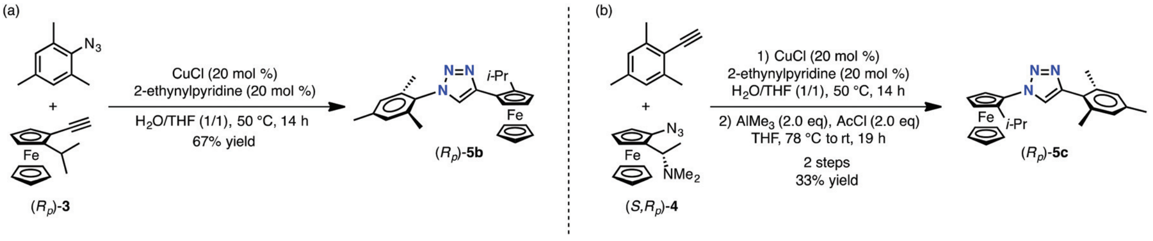
Fig. 1 Planar-chiral ferrocene-based triazolylidene complexes investigated in this study.

Results and discussion

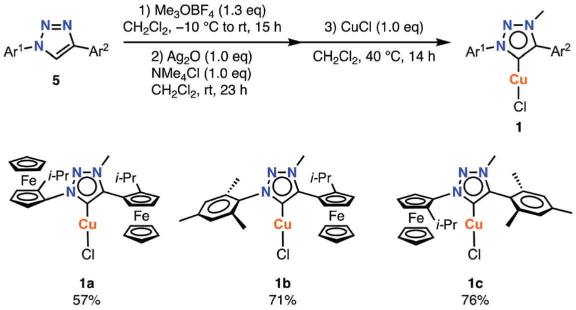
Optically active triazoles **5a–c** were synthesized according to the slightly modified procedure from that previously reported by our group.[9d] Both planar-chiral alkyne **3** and azide **4** were prepared from commercially available Ugi's amine in 77% yield and 60% yield, respectively (see Scheme S1 in the ESI†). As shown in Scheme 2a, treatment of optically active alkyne **3** with mesityl azide in a mixture of H_2O/THF (1/1) in the presence of a catalytic amount of copper(I) chloride and 2-ethynylpyridine at 50 °C for 14 h afforded the corresponding triazole **5b** in 67% yield.[11] On the other hand, **5a** and **5c** were prepared by a two-step protocol consisting of copper-catalyzed [3 + 2] cycloaddition and the subsequent methylation, given that planar-chiral azide **4** is unstable under the reaction conditions for the methylation. While this methylation step in the previously reported method was achieved by the use of dimethylzinc, we found that trimethylaluminium was also successfully employed to afford the corresponding methylated products. This finding improved the synthetic route to chiral triazoles with respect to cost because of trimethylaluminium is much inexpensive than dimethylzinc.

The two-step protocol gave **4a** and **4c** in 46% and 33% yields, respectively (see Scheme S1 in the ESI† for synthesis of **4a**). The reaction of **4a–c** with trimethyloxonium tetrafluoroborate afforded the corresponding triazolium salts, which underwent metalation at the 5-position of the triazolium rings in the presence of silver oxide and tetramethylammonium chloride to give triazolylidene silver complexes *in situ*. Finally, the subsequent transmetalation using copper(I) chloride furnished the triazolylidene copper complexes **1a–c** (Scheme 3) as orange solids in good yields.

All complexes were stable toward air and moisture for three months. The formation of Cu–C_{trz} bonds (trz = triazolylidene) was confirmed by the appearance of a new peak for carbene



Scheme 2 Preparation of planar-chiral triazoles **5**.



Scheme 3 Preparation of chiral triazolylidene copper complexes.

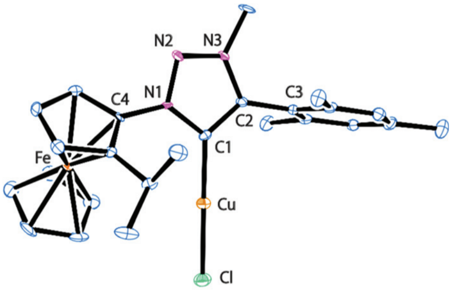
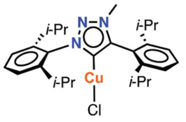


Fig. 3 ORTEP representation of compound **1c**. Thermal ellipsoids are at 50% probability level with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angle (°): C(1)–Cu(1) 1.875(7), Cu(1)–Cl(1) 2.107(2), C(1)–Cu(1)–Cl(1) 179.2(2).

Table 1 Comparison of **1b** and **1c** with other [Cu(NHC)Cl] complexes

Complex	Cu–Cl (Å)	$\%V_{\text{bur}}$[a]
1b	2.117(3)	48.8
1c	2.137(2)	47.9
6[13d]	2.132(6)	43.8
7[13e]	2.111(2)	36.2
8[13f]	2.115(1)	51.3

[a] Parameters applied for Samb*V*ca calculations: sphere radius 3.50 Å; bond length 2.00 Å; mesh spacing 0.10 Å; Bondi radius 1.17; H atoms are excluded.



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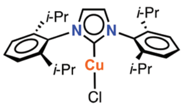

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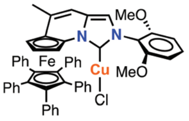

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carbon in **1a–c** at 165–167 ppm in the ^{13}C NMR spectrum, which is consistent with the reported values in the range of 160–170 ppm for triazolylidene copper complexes.[12] High-resolution of electrospray mass spectra of **1a–c** provided the additional evidence for the formation of triazolylidene copper complexes, with the fragment peaks at *m*/*z* 656.0257 (calculated for $[\mathbf{1a} + \text{Na}]^+$ 656.0256), *m*/*z* 917.2748 (calculated for $[2{*}\mathbf{1b} - \text{CuCl}_2]^+$ 917.2718), and *m*/*z* 917.2690 (calculated for $[2{*}\mathbf{1c} - \text{CuCl}_2]^+$ 917.2718) being observed.

While the molecular structures of triazolylidene copper complexes **1b** and **1c** were unambiguously determined by X-ray diffraction analysis (Fig. 2 and 3), several attempts to grow single crystals of **1a** suitable for X-ray diffraction were unsuccessful. Single crystals of **1b** and **1c** were grown by slow diffusion of diethyl ether into a saturated chloroform solution of the corresponding complexes.

The copper complexes exhibited the expected linear geometry with C_{trz}–Cu–Cl angles of 177.3(3)° and 179.2(2)° in **1b** and **1c**, respectively. The bond length of Cu–Cl in **1b** was slightly longer than that in **1c**, which was probably because of a stronger trans-effect in **1b**. This indicates that the position of the ferrocenyl group on the triazolium ring influences the electron-donating properties of triazolylidene ligands.

The steric properties of **1b** and **1c** were evaluated by means of the percent buried volume analysis ($\%V_{\text{bur}}$), as shown in Table 1.[13a] The obtained $\%V_{\text{bur}}$ values of 48.8% in **1b** and 47.9% in **1c** are close to that for the bulkiest NHC copper complex **8**[13f] and significantly higher than those for bulky NHC copper complexes **6**[13d] and **7**.[13e]

The catalytic activity of triazolylidene copper complexes **1a–c** for the asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron were examined.[14] The results are shown in Table 2. Treatment of methyl cinnamate (**9**) with bis(pinacolato)diboron (1.1 eq.) in the presence of copper complex **1c** (5.0 mol%) and sodium *tert*-butoxide (1.1 eq.) in THF at 0 °C for 2 h gave the borylated compound, which underwent oxidation with $NaBO_3 \cdot 4H_2O$ to afford methyl 3-hydroxy-3-phenylpropanoate (**10**) in 53% yield with 47% ee (entry 1). This is the first time that asymmetric induction was observed using a chiral triazolylidene copper complex as a catalyst. The use of 1,4-dimesityl-3-methyl-1,2,3-triazol-5-ylidene copper chloride complex (**1d**)[12a] as a catalyst decreased the yield of **10** by 30% compared to **1c**, which suggests that the planar-chiral ferrocenyl moiety is crucial for both good catalytic efficiency and enantioselectivity (entry 2). When bases other than sodium *tert*-butoxide were used in the reaction, the enantioselectivity was improved without loss of product yield (entries 3 and 4). The use of a catalytic amount of sodium *tert*-butoxide slightly

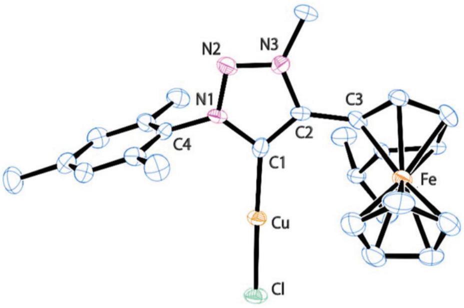
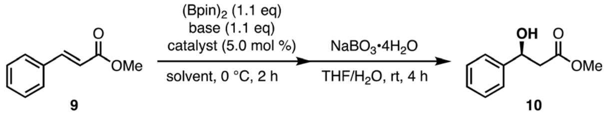


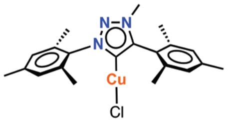
Fig. 2 ORTEP representation of compound **1b**. Thermal ellipsoids are at 50% probability level with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angle (°): C(1)–Cu(1) 1.888(8), Cu(1)–Cl(1) 2.111(2), C(1)–Cu(1)–Cl(1) 177.3(3).

Table 2 Asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron[a]

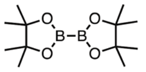


Entry	[Cu]	Base	Solvent	Yield[b] (%)	ee[c] (%)
1	**1c**	NaO*t*Bu	THF	53	47
2	**1d**	NaO*t*Bu	THF	23	—
3	**1c**	KO*t*Bu	THF	53	52
4	**1c**	LiO*t*Bu	THF	52	52
5[d]	**1c**	NaO*t*Bu	THF	48	48
6	**1c**	NaO*t*Bu	CH_2Cl_2	51	44
7	**1c**	NaO*t*Bu	Et_2O	38	53
8	**1c**	NaO*t*Bu	Toluene	36	25
9	**1b**	LiO*t*Bu	THF	50	52
10	**1a**	LiO*t*Bu	THF	45	60

[a] Standard conditions: **9** (0.20 mmol), (Bpin)$_2$ (0.22 mmol), base (0.22 mmol), catalyst (0.010 mmol) in THF (2.0 mL) at 0 °C for 2 h. [b] Isolated yields. [c] Determined by HPLC analysis of the isolated **10** using a chiral stationary phase column (Chiralcel OJ-H). [d] 5 mol% of NaO*t*Bu was used.



1d



(Bpin)$_2$

decreased the yield of **10** without loss of enantioselectivity (entries 1 and 5). Moreover, the effect of solvents on catalytic activity and enantioselectivity was investigated. Among the solvents investigated, THF gave the best result with respect to both yield and enantioselectivity (entries 1, 6–8). It is noteworthy that switching the positions of the chiral ferrocenyl substituent and the mesityl group had negligible influence on both yield and enantioselectivity (entries 1 and 9). Furthermore, the enantioselectivity was slightly improved when copper complex **1a** bearing two planar-chiral ferrocenyl units was used (entry 10).[15,16]

Conclusions

Planar-chiral ferrocene-based triazolylidene copper complexes were successfully prepared and characterized by NMR, HRMS, and X-ray diffraction analysis. The catalytic performance of the copper complexes was evaluated for the asymmetric borylation of methyl cinnamate with bis(pinacolato) diboron. All copper complexes were found to exhibit moderate enantioselectivity for the reaction. To the best of our knowledge, this is the first example that achieved asymmetric induction employing a triazolylidene base-metal complex as a catalyst. To provide a more effective chiral environment within proximity of metal center, the development of triazolylidene ligands with bulkier planar-chiral ferrocenyl groups is currently in progress.

Experimental section

General

All manipulations of oxygen- and moisture-sensitive materials were conducted under argon or nitrogen atmosphere in a flame dried Schlenk flask. Nuclear magnetic resonance spectra were taken on a JEOL ECA spectrometer using tetramethylsilane for ^{1}H NMR as an internal standard (δ = 0 ppm) when $CDCl_3$ was used as a solvent, and using $CDCl_3$ for ^{13}C NMR as an internal standard (δ = 77.16 ppm) when $CDCl_3$ was used as a solvent. ^{1}H NMR and ^{13}C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra (HRMS) were measured by a JEOL JMS-T100LC AccuTOF. Infrared (IR) spectra were measured by an FT/IR-4100ST spectrometer. High performance liquid chromatography (HPLC) was performed on a JASCO MD-2010 Plus system with UV and CD detectors and chiral column of Daicel, Chiralpak OJ-H. X-ray crystallographic analysis was performed on VariMax/Saturn CCD diffractometer.

General procedure for preparation of chiral triazolylidene copper complexes 1a

To a 50 mL Schlenk flask were added sequentially triazolium salt, silver(I) oxide (1.0 eq.), NMe_4Cl (1.0 eq.), and dry CH_2Cl_2 under a nitrogen atmosphere. The mixture was stirred in the dark at room temperature for 23 h. To the mixture was added CuCl (1.0 eq.), and the resulting mixture was stirred at 40 °C for 14 h followed by filtration through a pad of Celite. The filtrate was concentrated *in vacuo* to afford the crude product. Purification by silica gel column chromatography gave **1** as an orange solid.

1a

Yield: 57% (0.12 g); orange solid; R_f 0.23 (hexane/ethyl acetate = 5/1); $[\alpha]_D^{25}$ +90.7 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.16 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.44 (s, 5H), 4.39–4.33 (m, 2H), 4.35 (s, 5H), 4.33–4.31 (m, 1H), 4.27–4.25 (m, 1H), 4.24–4.21 (m, 1H), 3.94 (s, 3H), 3.60 (qq, *J* = 6.8, 6.8 Hz, 1H), 3.06 (qq, *J* = 6.8, 6.8 Hz, 1H), 1.40–1.34 (m, 6H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: ^{13}C NMR (125 MHz, $CDCl_3$)δ: 166.7($C_{carbene}$), 146.2($C_{trz\text{-}4}$), 98.0(C_{Fero}), 96.1 (C_{Fero}), 91.8(C_{Fero}), 71.2(C_{Fero}), 71.1(C_{Fero}), 71.1(C_{Fero}), 67.6(C_{Fero}), 67.1(C_{Fero}), 66.4(C_{Fero}), 66.3(C_{Fero}), 65.3(C_{Fero}), 64.8(C_{Fero}), 37.0 (C_{Me}), 26.7($C_{i\text{-}Pr}$), 25.9($C_{i\text{-}Pr}$), 25.4($C_{i\text{-}Pr}$), 24.6($C_{i\text{-}Pr}$), 22.1($C_{i\text{-}Pr}$), 21.6 ($C_{i\text{-}Pr}$) ppm IR (KBr): 3455.8, 3092.3, 2958.3, 2924.5, 2866.7, 1628.6, 1560.1, 1542.8, 1457.9, 1424.2, 1410.7, 1380.8, 1360.5, 1262.2, 1231.3, 1170.6, 1106.9, 1067.4, 1036.5, 1000.9, 970.0, 946.9, 875.5, 824.4, 749.2, 733.8, 720.3, 688.5, 678.8, 669.2, 644.1, 621.9, 566.0, 540.0 cm^{-1}; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{29}H_{33}N_3ClCuFe_2Na$ 656.0256, found 656.0257.

1b

Yield: 71% (0.047 g); orange solid; R_f 0.69 (dichloromethane); $[\alpha]_D^{25}$ −40.3 (*c* 0.01, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.02 (s, 1H), 6.99 (s, 1H), 4.42 (s, 5H), 4.40–4.36 (m, 2H), 4.36–4.33

(m, 1H), 3.98 (s, 3H), 3.79–3.68 (m, 1H), 2.36 (s, 3H), 2.16 (s, 3H), 2.00 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.8(C_{carbene}), 146.9 ($C_{\text{trz-4}}$), 140.5(C_{benz}), 136.4(C_{benz}), 134.1(C_{benz}), 133.9(C_{benz}), 129.6(C_{benz}), 129.6(C_{benz}), 98.0(C_{Fero}), 71.2(C_{Fero}), 70.8(C_{Fero}), 67.7(C_{Fero}), 67.2(C_{Fero}), 66.6(C_{Fero}), 37.0(C_{Me}), 26.9(C_{Me}), 25.3 (C_{Me}), 21.5(C_{Me}), 21.3($C_{\text{i-Pr}}$), 17.9($C_{\text{i-Pr}}$), 17.5($C_{\text{i-Pr}}$) ppm; IR (KBr): 3464.5, 3092.3, 3080.7, 2956.3, 2920.7, 2862.8, 1654.6, 1638.2, 1628.6, 1618.0, 1609.3, 1560.1, 1542.8, 1509.0, 1490.7, 1458.9, 1449.2, 1439.6, 1407.8, 1337.9, 1360.5, 1322.0, 1291.1, 1266.0, 1230.4, 1185.0, 1131.1, 1106.0, 1071.3, 1035.6, 1001.8, 960.4, 852.4, 823.5, 812.8, 756.9, 737.6, 681.7, 671.1, 654.7, 622.9, 594.9, 583.4, 569.9, 537.1 cm^{-1}; ESI-HRMS (*m*/*z*): $[2M - CuCl_2]^+$ calcd for $C_{50}H_{58}N_6CuFe_2$ 917.2718, found 917.2748.

1c

Yield: 76% (0.40 g); orange solid; R_f 0.19 (dichloromethane); $[\alpha]_D^{25}$ +83.1 (*c* 0.008, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.99 (s, 1H), 6.98 (s, 1H), 5.22–5.11 (m, 1H), 4.35 (s, 5H), 4.30–4.21 (m, 2H), 3.81 (s, 3H), 3.32–3.12 (m, 1H), 2.34 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9(C_{carbene}), 146.8 ($C_{\text{trz-4}}$), 140.6(C_{benz}), 138.0(C_{benz}), 138.0(C_{benz}), 129.1(C_{benz}), 129.1(C_{benz}), 123.2(C_{benz}), 95.8(C_{Fero}), 91.7(C_{Fero}), 71.2(C_{Fero}), 66.2(C_{Fero}), 65.4(C_{Fero}), 64.9(C_{Fero}), 36.1(C_{Me}), 26.2(C_{Me}), 24.7 (C_{Me}), 22.1(C_{Me}), 21.4($C_{\text{i-Pr}}$), 20.6($C_{\text{i-Pr}}$), 20.4($C_{\text{i-Pr}}$) ppm; IR (KBr): 2962.1, 2947.7, 2919.7, 2859.2, 2126.1, 1654.6, 1647.9, 1637.3, 1611.2, 1560.1, 1458.9, 1439.6, 1406.8, 1379.8, 1364.4, 1324.9, 1304.6, 1262.2, 1235.2, 1170.6, 1148.4, 1106.0, 1064.5, 1038.5, 1024.0, 998.0, 960.4, 874.6, 853.3, 845.6, 826.3, 813.8, 763.7, 691.4, 672.1, 661.5, 641.2, 623.9, 592.0, 568.9, 557.3, 539.0 cm^{-1}; ESI-HRMS (*m*/*z*): $[2M - CuCl_2]^+$ calcd for $C_{50}H_{58}N_6CuFe_2$ 917.2718, found 917.2690.

Representative procedure for the asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron

To a 5 mL vial were added sequentially lithium *tert*-butoxide (0.22 mmol, 18 mg) and catalyst **1a** (0.010 mmol, 6.3 mg) in a glovebox. After the vial was taken out of the glovebox, THF (1 mL) was added to the reaction mixture. The mixture was stirred at room temperature for 20 min, and a THF (0.5 mL) solution of bis(pinacolato)diboron (0.22 mmol, 56 mg) was added to the reaction mixture at 0 °C. After the resulting mixture was stirred at 0 °C for 10 min, a THF solution of methyl cinnamate (0.20 mmol, 32 mg) was added to the mixture. The mixture was stirred at 0 °C for 2 h and then was quenched with $NaBO_3 \cdot 4H_2O$ and water. After the resulting mixture was stirred at room temperature for 4 h, the mixture was extracted by ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated *in vacuo*. Purification by preparative TLC (PTLC) (hexane/ethyl acetate = 4/1) gave **10** as a colorless oil. Enantio excess of **10** was determined by HPLC analysis with a chiral stationary phase column (Daicel, Chiralpak OD-H, *n*-hexane/i-PrOH = 95/5, flow rate = 0.5 mL min^{-1}, λ = 225 nm, 30 °C): t_{major} = 31.1 min, t_{minor} = 46.7 min.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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16 The reaction did not proceed in the absence of copper complexes. In contrast, the use of copper chloride (CuCl) as a catalyst in the borylation reaction provided **10** in 51% yield. The elemental analysis of **1a** revealed that some impurity was included in **1a**, which indicated the possibility that residual CuCl may promote the background reaction to decrease the enantioselectivity in the asymmetric borylation.