

# Enantioselective Synthesis of Planar Chiral Ferrocenes via Palladium-Catalyzed Direct Coupling with Arylboronic Acids

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**S** Supporting Information

**ABSTRACT:** Enantioselective Pd(II)-catalyzed direct coupling of aminomethylferrocene derivatives with boronic acids was realized. With commercially available Boc-L-Val-OH as a ligand, planar-chiral ferrocenes could be synthesized in yields of 14–81% with up to 99% ee under mild conditions.

Chiral ferrocenes are of great interest in the fields of asymmetric catalysis, materials science, biomedical research, and so on.<sup>1</sup> In particular, ferrocenes bearing planar chirality, in some cases with additional central chirality, have been demonstrated to be highly efficient ligands or catalysts in asymmetric catalysis.<sup>2</sup> Consequently, the development of methods to introduce planar chirality into the ferrocene backbone has attracted intense attention. To date, the most widely used strategy is diastereoselective directed ortho metalation (DoM) induced by various chiral auxiliaries (or chiral directing groups), and in this approach, central chirality in general must be preinstalled.<sup>3</sup> Notably, Snieckus and co-workers developed an enantioselective DoM of ferrocene derivatives with an external chiral base such as (–)-sparteine, which provides a straightforward route to ferrocenes with only planar chirality.<sup>4</sup> Recently, Ogasawara and co-workers reported an elegant method for the synthesis of planar-chiral ferrocenes through ring-closing metathesis reactions.<sup>5</sup> However, the catalytic enantioselective synthesis of planar-chiral ferrocenes remains rare.<sup>6</sup> Developing such a process with readily available starting materials and catalysts is challenging but highly desirable.

Significant progress on palladium-catalyzed direct functionalization of inert C–H bonds has been made during the past decade.<sup>7</sup> However, despite continuous efforts, the highly challenging topic of catalytic enantioselective C–H activation has progressed rather slowly.<sup>8</sup> Breakthroughs recently have been achieved by Yu and co-workers,<sup>9</sup> who discovered that chiral monoprotected amino acids can serve as efficient ligands to enable enantioselective C–H activation of series of prochiral substrates. Inspired by these results, we recently explored the enantioselective synthesis of planar-chiral ferrocenes as part of our ongoing program devoted to direct functionalization of ferrocenes.<sup>10,11</sup> Commercially available amino acid derivatives were found to be highly efficient ligands for Pd-catalyzed direct functionalization of ferrocene with boronic acids. The conditions developed tended to be mild, general, and practical for the synthesis of enantiopure planar-chiral ferrocenes. Here

we report such a highly enantioselective synthesis of planar-chiral ferrocenes via Pd-catalyzed C–H bond activation process.

We began our studies by using dimethylaminomethylferrocene (**1a**) as a model substrate. Pd-catalyzed direct arylation of **1a** with phenylboronic acid (**2a**)<sup>12</sup> was then carried out in the presence of 10 mol % Pd(OAc)<sub>2</sub>, 20 mol % Boc-L-Val-OH, and 1 equiv of K<sub>2</sub>CO<sub>3</sub> in *N,N*-dimethylacetamide (DMA) at 80 °C under air. To our great delight, the reaction proceeded smoothly to afford the desired product **3a** in 58% yield with 97% ee, along with trace amount of diarylation product **3a'** (Table 1, entry 1). The addition of 25 mol % tetrabutylammonium bromide (TBAB) as an additive improved the yield of **3a** to 74% without affecting the enantioselectivity

**Table 1. Screening of Protected Amino Acids<sup>a</sup>**

Reaction scheme: **1a** (ferrocene with NMe<sub>2</sub> group) reacts with PhB(OH)<sub>2</sub> (**2a**) (2 equiv) in the presence of Pd(OAc)<sub>2</sub> (10 mol %), ligand (20 mol %), K<sub>2</sub>CO<sub>3</sub> (1 equiv), TBAB (0.25 equiv) in DMA at 80 °C, air, 4h to yield **3a** (monarylated ferrocene) and **3a'** (diarylated ferrocene).

entry	ligand	3a:3a' <sup>b</sup>	yield (%) <sup>c</sup>	ee (%) <sup>d</sup>
1 <sup>e</sup>	Boc-L-Val-OH	42:1	58	97
2	Boc-L-Val-OH	8.3:1	74	98
3	Boc-L-Phe-OH	8.7:1	71	98
4	Boc-L-Abu-OH	10:1	64	94
5	Boc-L-Ala-OH	4.2:1	61	92
6	Boc-L-Leu-OH	20:1	51	96
7	Boc-L-Ile-OH	9.5:1	70	97
8	Boc-L-Tle-OH	9:1	75	98
9	Boc-L-Nva-OH	6.4:1	69	96
10	Boc-L-Phg-OH	6.5:1	48	81
11	Ac-L-Val-OH	10:1	60	88
12	Cbz-L-Val-OH	25:1	52	96
13	Fmoc-L-Val-OH	–	19 <sup>b</sup>	–
14 <sup>f</sup>	<b>Boc-L-Val-OH</b>	<b>20:1</b>	<b>79</b>	<b>98</b>
15 <sup>g</sup>	Boc-L-Val-OH	50:1	59	97

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd(OAc)<sub>2</sub> (10 mol %), ligand (20 mol %), K<sub>2</sub>CO<sub>3</sub> (1 equiv), and TBAB (0.25 equiv) in DMA at 80 °C under air. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis with CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>c</sup>Isolated yields. <sup>d</sup>Determined by HPLC analysis. <sup>e</sup>Without TBAB. <sup>f</sup>At 60 °C. <sup>g</sup>At 40 °C.

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(98% ee; entry 2). Next, commercially available *N*-Boc-protected *L*-amino acids as ligands were systematically examined, and the results are summarized in Table 1. The reactions all gave the desired product in yields ranging from 48 to 75% with excellent enantioselectivity ranging from 81 to 98% ee (entries 2–10). Boc-*L*-Val-OH and Boc-*L*-Tle-OH proved to be the most efficient chiral ligands in terms of enantioselectivity and reactivity, giving the desired product in 74–75% yield with 98% ee (entries 2 and 8). Boc-*L*-Val-OH was chosen for further studies given its cheapness. The protecting group on the nitrogen of *L*-valine was found to have a dramatic impact on the reactivity and enantioselectivity (Ac, 60% yield, 88% ee; Cbz, 52% yield, 96% ee; Fmoc, 19% yield; entries 11–13, Table 1). Lowering the reaction temperature to 60 °C slightly improved the yield to 79% (entry 14). Notably, there was a moderate kinetic resolution for the formation of bisphenylation product **3a'**. Along with the reaction time, both the ratio of bisphenylation byproduct **3a'** and the ee of **3a** increased slightly [for details, see the Supporting Information (SI)]. Further screening of other reaction parameters, including the oxidant, base, solvent, catalyst loading, and amount of phenylboronic acid did not improve the results (for details, see the SI). Thus the optimized conditions were obtained as the following: 10 mol % Pd(OAc)<sub>2</sub>, 20 mol % Boc-*L*-Val-OH, 2 equiv of boronic acid, 1 equiv of K<sub>2</sub>CO<sub>3</sub>, and 25 mol % TBAB in DMA at 60 °C under air (Table 1, entry 14).

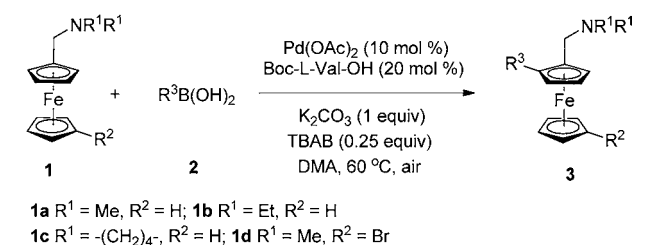
Under the above optimized reaction conditions, various aminomethylferrocene derivatives and boronic acids were examined to test the generality of the current reaction. The results are summarized in Table 2. Various substituted arylboronic acids bearing either an electron-donating group

or an electron-withdrawing group were well-tolerated and afforded their corresponding products in good yields (55–81%) with excellent enantioselectivity (94–99% ee) (entries 2–3, 5, and 7–10) except for *o*-tolylboronic acid **2d** (33% yield, 94% ee; entry 4). Notably, the reaction with 2-naphthylboronic acid (**2f**) also led to product **3f** in 75% yield and 96% ee (entry 6). The reaction of methylboronic acid required a higher temperature and prolonged reaction time, giving the desired product in a moderate yield (entry 11). In addition, the reaction was general for aminomethylferrocenes with different alkyl groups on the nitrogen atom (R<sup>1</sup> = Et, 67% yield, 90% ee; R<sup>1</sup>R<sup>1</sup> = -(CH<sub>2</sub>)<sub>4</sub>-, 71% yield, 98% ee; entries 12 and 13). Introduction of a substituent on the other Cp ring could also be tolerated. For instance, when 1-aminomethyl-1'-bromoferrocene (**1d**) was used, the arylation product **3n** was obtained in 69% yield with 97% ee (entry 14). The wide tolerance of substituents provides the opportunity for further transformation of the products into useful ligands or catalysts.

The absolute configuration of the product **3a** was assigned as S<sub>p</sub> by comparing the optical rotation of the enantiomer of 1-methyl-2-phenylferrocene obtained from **3a** with that for the enantiomer of 1-methyl-2-phenylferrocene obtained from a literature-reported compound with known absolute configuration (for details, see the SI).

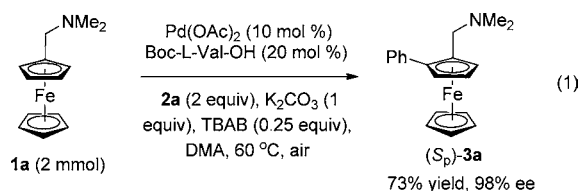
To test the practicality of the methodology, a relatively large scale reaction was carried out. The arylation of **1a** on a 2 mmol scale with **2a** afforded the desired product [(S<sub>p</sub>)-**3a**] without notable erosion in either the yield (73%) or enantioselectivity (98% ee) (eq 1). However, addition of **2a** in five portions (every 2 h) had a beneficial effect for achieving a higher yield compared with addition of **2a** all at once.

**Table 2. Enantioselective Synthesis of Planar-Chiral Ferrocenes via C–H Activation<sup>a</sup>**

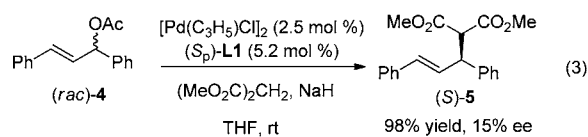
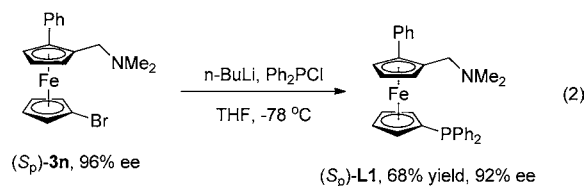


entry	1	R <sup>3</sup> (2)	time (h)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>1a</b>	C <sub>6</sub> H <sub>5</sub> ( <b>2a</b> )	10	79 ( <b>3a</b> )	98
2	<b>1a</b>	4-MeC <sub>6</sub> H <sub>4</sub> ( <b>2b</b> )	10	70 ( <b>3b</b> )	97
3	<b>1a</b>	3-MeC <sub>6</sub> H <sub>4</sub> ( <b>2c</b> )	10	81 ( <b>3c</b> )	99
4	<b>1a</b>	2-MeC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )	75	33 ( <b>3d</b> )	94
5	<b>1a</b>	4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>2e</b> )	10	59 ( <b>3e</b> )	96
6	<b>1a</b>	2-naphthyl ( <b>2f</b> )	3.5	75 ( <b>3f</b> )	96
7	<b>1a</b>	4-ClC <sub>6</sub> H <sub>4</sub> ( <b>2g</b> )	10	72 ( <b>3g</b> )	97
8	<b>1a</b>	4-FC <sub>6</sub> H <sub>4</sub> ( <b>2h</b> )	10	55 ( <b>3h</b> )	97
9	<b>1a</b>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ( <b>2i</b> )	10	61 ( <b>3i</b> )	94
10	<b>1a</b>	4-EtOCOC <sub>6</sub> H <sub>4</sub> ( <b>2j</b> )	8	72 ( <b>3j</b> )	95
11 <sup>d</sup>	<b>1a</b>	Me ( <b>2k</b> )	24	14 ( <b>3k</b> )	ND
12	<b>1b</b>	C <sub>6</sub> H <sub>5</sub> ( <b>2a</b> )	22	67 ( <b>3l</b> )	90
13	<b>1c</b>	C <sub>6</sub> H <sub>5</sub> ( <b>2a</b> )	10	71 ( <b>3m</b> )	98
14	<b>1d</b>	C <sub>6</sub> H <sub>5</sub> ( <b>2a</b> )	16	69 ( <b>3n</b> )	97

<sup>a</sup>Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), Pd(OAc)<sub>2</sub> (10 mol %), Boc-*L*-Val-OH (20 mol %), K<sub>2</sub>CO<sub>3</sub> (1 equiv), and TBAB (0.25 equiv) in DMA at 60 °C under air. <sup>b</sup>Isolated yields. <sup>c</sup>Determined by HPLC analysis. <sup>d</sup>At 90 °C.



As a further demonstration of the utility of our methodology, the planar-chiral *P,N*-ligand **L1** was prepared from product **3n** obtained in the current study. Starting from **3n** (96% ee), lithiation with *n*-BuLi followed by quenching with Ph<sub>2</sub>PCL afforded **L1** in 68% yield with 92% ee (eq 2). A preliminary



examination of **L1** (92% ee) in a palladium-catalyzed allylic alkylation reaction (eq 3) disclosed that this type of *P,N*-ligand is highly efficient, although the enantioselectivity needs further improvement (98% yield, 15% ee).

In summary, we have developed an asymmetric Pd-catalyzed method for direct functionalization of aminomethylferrocene derivatives with boronic acids. The new methodology provides a highly enantioselective synthesis of planar-chiral ferrocenes from readily available starting materials under mild reaction conditions. The requirement of commercially available and cheap *N*-Boc-protected amino acids as efficient ligands and air as the oxidant makes the current access to enantiopure ferrocene compounds potentially practical. Further mechanistic investigations, applications of these enantiopure ferrocenes, and the development of a more efficient catalytic system are currently underway in our laboratory.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental procedures and analysis data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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