Rhodium-Catalyzed Asymmetric Phenylation of N-
Phosphinoylarylimines with Triphenylborane.\textsuperscript{a}

Xinyu Hao,\textsuperscript{b} Qian Chen,\textsuperscript{c} Masami Kuriyama,\textsuperscript{b} Ken-ichi Yamada,\textsuperscript{b} Yasutomo Yamamoto\textsuperscript{d} and Kiyoshi Tomioka\textsuperscript{d,\textsuperscript{e}}

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Triphenylborane asymmetrically transfers its phenyl group to N-
diphenylphosphinoylarylimines to give diarylmethylamines with
high ee in high yield without imine hydrolysis under the catalysis
of a chiral amidonophosphane–rhodium(I) complex.

The success in the chiral amidonophosphane–rhodium-
catalyzed asymmetric arylation of N-diphenylphosphinoyl
(Dpp) imines with aryloboroxines\textsuperscript{1,2} relied on the use of
molecular sieves 4A (MS 4A) as a dehydrating agent to realize
almost water-free conditions, giving the corresponding
diarylmethylamines with extremely high enantioselectivity
in satisfactory high yield.\textsuperscript{3,4} For example, the arylation of
benzaldehyde N-Dpp-imine 2a with 4-methylphenyl and 4-
methoxyphenylboroxines 3b and 3c in a 5:1 mixture
of dioxane and propanol in the presence of the 1Rh(I) catalyst
and MS 4A at 80 °C for 12 h gave the corresponding aryldated
amines (S)-4b and (S)-4c with 98% ee each in 96% and 92%
yields, respectively (Table 1, entries 1 and 2).\textsuperscript{4} Continuing
scope and limitation studies, however, revealed that the
reaction of less reactive 4-methyl- and 4-methoxybenzaldehyde
N-Dpp-imines 2b and 2c with phenylboroxine 3a gave the
products (R)-4b and (R)-4c with lower 84% and 83% ee
decreased 79% and 10% yields, respectively, probably due to
in competitive hydrolysis of the imines (entries 3 and 4). Then,
our problem solving research was focused on the survey of
arylation conditions that give shorter reaction time to avoid
the hydrolysis.

Table 1 Scope and Limitation of Asymmetric Arylation of N-Dpp-
arylimines\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar\textsuperscript{1}</th>
<th>Ar\textsuperscript{2}</th>
<th>time</th>
<th>yield ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{a}</td>
<td>2a</td>
<td>Ph</td>
<td>3b</td>
<td>4-MeOC\textsubscript{6}H\textsubscript{4}CH\textsubscript{3}</td>
</tr>
<tr>
<td>2\textsuperscript{a}</td>
<td>2a</td>
<td>Ph</td>
<td>3c</td>
<td>4-MeOC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}</td>
</tr>
<tr>
<td>3</td>
<td>2b</td>
<td>4-MeOC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}</td>
<td>3a</td>
<td>Ph</td>
</tr>
<tr>
<td>4</td>
<td>2c</td>
<td>4-MeOC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}</td>
<td>3a</td>
<td>Ph</td>
</tr>
<tr>
<td>5\textsuperscript{b}</td>
<td>2e</td>
<td>4-MeOC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}</td>
<td>3a</td>
<td>Ph</td>
</tr>
<tr>
<td>6\textsuperscript{b}</td>
<td>2b</td>
<td>4-MeOC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{5}</td>
<td>3d</td>
<td>Ph</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The reaction was conducted with 1.67 equiv of (Ar\textsubscript{3}BO\textsubscript{3}) in the presence of 6.6 mol % of I, and 6.0 mol % of the Rh(I) exceeding entry 6. The ee was determined by chiral stationary phase HPLC analysis. See ref 4. Microwave irradiation. 5 equiv of trisuborate 3d was used. Without MS 4A. Racemic phenyl(4-tolyl)methanol, aldehyde adduct, was obtained in 76% yield.

Microwave irradiation of a mixture of 2c and phenylboroxine 3a at 220 °C for 10 min was apparently beneficial but not satisfactory to give (R)-4b with 68% ee in improved 45% yield (entry 5). A cyclic triolborate 3d failed to give an imine adduct (R)-4b but gave the corresponding racemic aldehyde adduct, phenyl(4-tolyl)methanol, in 76% yield (entry 6). Finally, we found triphenylborane as a reactive phenylation reagent to give phenylated amines (R)-4b and (R)-4c with 93% ee each in 92% and 91% yields, respectively, without imine hydrolysis. Herein, we report a catalytic asymmetric phenylation of N-Dpp-arylimines 2 with triphenylborane. In contrast to the widely used boronic reagents, triarylboranes have not been utilized as an aryl source in asymmetric catalysis,\textsuperscript{5} although a mixture of triphenylborane and diethylzinc has been employed for in situ generation of diphenylzinc.\textsuperscript{6}

When a mixture of 4-tolylaldehyde N-Dpp-imine 2b and triphenylborane (1.67 equiv) was heated in propan-1-ol at 100 °C for 12 h in the presence of a catalytic amount of I (6.6 mol %) and acetylacetonatobis(ethylene)rhodium(I) (6.0 mol %), the phenylated product (R)-4b with 81% ee was obtained in 63% yield (Table 2, entry 1). The reaction was then performed in the presence of KF because promotion of a transmetalation process of organoboron reagents by fluoride was described.\textsuperscript{7} The reactions with anhydrous KF and KF on alumina resulted in less satisfactory 39% and 44% yields, and 60% and 81% enantioselectivity, respectively (entries 2 and 3). When the reaction was conducted in the presence of KF on Celite, the reaction more smoothly proceeded to give (R)-4b with 89% ee in increased 72% yield (entry 4). A mixture of dioxane and propanol\textsuperscript{4} was not suitable solvent for the reaction with triphenylborane, and only a trace amount of the product was produced (entry 5). Finally, tert-butanol was found to be the choice to complete the reaction in only 1 h at 100 °C, giving (R)-4b with 93% ee in 92% yield (entry 6).

Table 2 Survey of Reaction Conditions\textsuperscript{6}

<table>
<thead>
<tr>
<th>entry</th>
<th>Solvent</th>
<th>KF source</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PrOH</td>
<td>-</td>
<td>12</td>
<td>63</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>PrOH</td>
<td>KF</td>
<td>6</td>
<td>39</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>PrOH</td>
<td>KF/Al\textsubscript{2}O\textsubscript{3}</td>
<td>6</td>
<td>44</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>PrOH</td>
<td>KF/Celite</td>
<td>6</td>
<td>72</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>dioxane/PrOH (1:1)</td>
<td>KF/Celite</td>
<td>6</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>t-ButOH</td>
<td>KF/Celite</td>
<td>1</td>
<td>92</td>
<td>93</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The reaction was conducted with 1.67 equiv of PrOH in the presence of 2.0 equiv of the indicated KF source, 6.6 mol % of I, and 6.0 mol % of Rh(acac)(C\textsubscript{6}H\textsubscript{4}H\textsubscript{5})\textsubscript{2}. The ee was determined by chiral stationary phase HPLC analysis.

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This asymmetric phenylation with triphenylborane was applicable to other N-Dpp-arylimines (Table 3). Phenylation of 3-tolylimine 2d gave the corresponding 4d with 96% ee in high 92% yield (entry 2). Electron-deficient 4-chlorobenzaldimine 2f bearing a chlorine atom was converted to 4f with 92% ee in 91% yield (entry 4). Although the reaction of sterically demanding ortho-substituted arylimines 2e and 2g was slower, the reaction proceeded in highly enantioselective manner to give 4e and 4g with 90% ee and 93% ee in 86% and 84% yield, respectively (entries 3 and 5). It is noteworthy that the reaction of 4-methoxybenzaldimine 2c, miserable results of which were the starting point for this study (Table 1, entry 4), also successfully proceeded for 12 h to give 4c with 93% ee in 91% yield (entry 6). Polyaromatic 2-naphthalaldimine 2h and heteroaromatic 2-furancarboaldimine 2i were also good substrates to give 4h and 4i with 90% and 91% ee in 94% and 86% yield, respectively (entries 7 and 8).

![Table 3 Catalytic Asymmetric Phenylation of N-Dpp-arylimines 2 with Triphenylborane](image)

In conclusion, we have developed a widely applicable chiral amidomonomophosphine–rhodium-catalyzed enantioselective phenylation of aryl-N-Dpp-imes with triphenylborane. The results clearly indicate the utility of triarylborane in avoiding in situ water generation. Because a Dpp group is cleaved under milder acidic conditions than a Boc group, this reaction provides a versatile methodology to access a variety type of optically active diarylmethanes.

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**Notes and references**

1. Dedicated to the celebration of her 60th birthday of Prof. Carmen Nájera Domingo.

2. Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan. Fax: 81 75 753 4604; Tel: 81 75 753 4573; E-mail: yamaki@pharm.kyoto-u.ac.jp

3. The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin, Heilongjiang, 150008, P. R. China. E-mail: chenqian@hiat.phepicac.ac.cn

4. Faculty of Pharmaceutical Sciences, Doshisha Women’s College of Liberal Arts, Kado, Kyotanabe 610-0395, Japan. Fax: 81 774 65 8658; Tel: 81 774 65 8676; E-mail: tomioka@pharm.kyoto-u.ac.jp

5. General procedure of the catalytic asymmetric phenylation: Under argon atmosphere, a round-bottom flask was charged with Rh(acac)(C=C)(3.1 mg, 0.012 mmol), I (6.5 mg, 0.013 mmol), 2 (0.200 mmol), triphenylborane (0.334 mmol), and 50% KO on celite (40 mg). To the flask was added t-BuOH (0.5 mL), and the mixture was stirred at 100 °C. After the indicated reaction time, the mixture was diluted with AcOEt, washed with brine, dried over NaSO₄, and then concentrated. The resulting residue was purified through silica gel column chromatography.


