

## Palladium(0)-catalyzed intramolecular dearomative arylation of pyrroles†

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The palladium(0)-catalyzed dearomative arylation of pyrroles has been accomplished to afford the spironaphthalenepyrrole derivatives in good to excellent yields.

Dearomatization<sup>1</sup> of aromatic compounds has made great progress in developing molecular complexity in recent years.<sup>2</sup> Beyond the traditional methods such as oxidation,<sup>3</sup> electrophilic alkylation<sup>4</sup> and cycloaddition,<sup>5</sup> in which a stoichiometric amount of reagents is indispensable, transition-metal-catalyzed dearomatization reaction<sup>6</sup> is an attractive approach in which only a catalytic amount of metal complex is required. Among them, Pd-catalyzed cross-coupling reaction has been demonstrated to be successful in dearomative processes. Since 2009, Buchwald and co-workers have realized the Pd-catalyzed dearomatization reaction of aniline derivatives and phenols.<sup>7</sup> Bedford *et al.* have also independently accomplished this type of reaction by employing anilines and 2-amino-1-methylindoles as suitable substrates.<sup>8</sup> In 2012, we reported the Pd-catalyzed intramolecular dearomative arylation of indoles.<sup>9</sup>

On the other hand, the pyrrole and pyrroline structural cores exist widely in bioactive compounds and pharmaceuticals (Fig. 1).<sup>10</sup> Therefore, great efforts have been made for the synthesis of pyrroles, pyrrolines and their derivatives.<sup>11</sup> With our continuing interest in developing catalytic dearomatization reactions,<sup>12</sup>



Scheme 1 Dearomative arylation of 2,5-disubstituted pyrroles.

we envision that the dearomatization of pyrroles could be achieved through the Pd-catalyzed intramolecular dearomative arylation reaction (Scheme 1), providing the spironaphthalenepyrrole compounds. Herein we report our results on this subject.

With substrate **1a**, we began to examine the palladium precursors and the ligands in the dearomative arylation reaction. The results are summarized in Table 1. With the catalytic system consisting of [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (2.5 mol%), PPh<sub>3</sub> (7.5 mol%), and K<sub>2</sub>CO<sub>3</sub> (1.5 equiv.), the dearomative arylation of **1a** in refluxing toluene (0.2 M) afforded the desired product **2a** in 81% yield (entry 1). Other readily available palladium sources led to much lower yields (entries 2–4). Various ligands such as SIPr-HBF<sub>4</sub>, phosphoramidite **L1**, XPhos, XPhos(<sup>t</sup>Bu), QPhos, and **P1** were then screened (entries 5–10). Phosphoramidite **L1** performed best to give the dearomatization product in 91% yield (entry 6).

In the presence of 2.5 mol% of [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> and 7.5 mol% of **L1**, reaction parameters such as bases and solvents were further optimized. Among the inorganic bases tested, K<sub>2</sub>CO<sub>3</sub> remained to be the best option (entries 11–15). The use of organic bases such as Et<sub>3</sub>N did not lead to the formation of the desired product (entry 16). The reaction in dioxane or DMF could give the dearomatization product in good yields (entries 17 and 18). It is worth mentioning that the reaction proceeded smoothly in refluxed THF (entry 19). The desired product could be obtained in 90% yield with 2 mol% of catalyst (entry 20), while 1 mol% of catalyst resulted in only 49% conversion (entry 21).

Under the optimized reaction conditions, {[Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (1.0 mol%), **L1** (3.0 mol%), and K<sub>2</sub>CO<sub>3</sub> (1.5 equiv.) in refluxed toluene (0.2 M)}, the substrate scope was investigated. The results

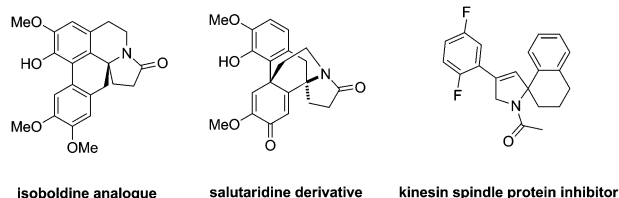


Fig. 1 Selected bioactive compounds bearing spironaphthalene-pyrrolidine units.

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**Table 1** Optimization of the reaction conditions<sup>a</sup>

| Entry           | [Pd]  | L                       | Base                            | Solvent | Yield <sup>b</sup> (%) |
|-----------------|---|-------------------------|---------------------------------|---------|------------------------|
| 1               | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | PPh <sub>3</sub>        | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 81                     |
| 2               | Pd(OAc) <sub>2</sub>  | PPh <sub>3</sub>        | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 66                     |
| 3 <sup>c</sup>  | Pd <sub>2</sub> (dba) <sub>3</sub>                                  | PPh <sub>3</sub>        | K <sub>2</sub> CO <sub>3</sub>  | Toluene | < 5                    |
| 4               | Pd(PPh <sub>3</sub> ) <sub>4</sub>                                  | —                       | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 24                     |
| 5               | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | SIPr-HBF <sub>4</sub>   | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 82                     |
| 6               | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 91                     |
| 7               | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | XPhos                   | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 62                     |
| 8               | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | XPhos( <sup>t</sup> Bu) | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 19                     |
| 9               | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | QPhos                   | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 52                     |
| 10              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | P1                      | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 15                     |
| 11              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | CS <sub>2</sub> CO <sub>3</sub> | Toluene | 83                     |
| 12              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>3</sub> PO <sub>4</sub>  | Toluene | 66                     |
| 13              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | Li <sub>2</sub> CO <sub>3</sub> | Toluene | 11                     |
| 14              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | NaOAc                           | Toluene | 37                     |
| 15 <sup>c</sup> | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | KO <sup>t</sup> Bu              | Toluene | < 5                    |
| 16 <sup>c</sup> | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | Et <sub>3</sub> N               | Toluene | N.D.                   |
| 17              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>2</sub> CO <sub>3</sub>  | Dioxane | 87                     |
| 18              | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>2</sub> CO <sub>3</sub>  | DMF     | 74                     |
| 19 <sup>d</sup> | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>2</sub> CO <sub>3</sub>  | THF     | 80                     |
| 20 <sup>e</sup> | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 90                     |
| 21 <sup>f</sup> | [Pd(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub> | <i>rac</i> -L1          | K <sub>2</sub> CO <sub>3</sub>  | Toluene | 49                     |

<sup>a</sup> Reaction conditions: [Pd] (5.0 mol%), L (7.5 mol%), base (1.5 equiv.) and **1a** (0.2 mmol) in solvent (0.2 M) at 110 °C. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by <sup>1</sup>H NMR. <sup>d</sup> Refluxed at 75 °C. <sup>e</sup> [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (1.0 mol%) was used. <sup>f</sup> [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (0.5 mol%) was used.

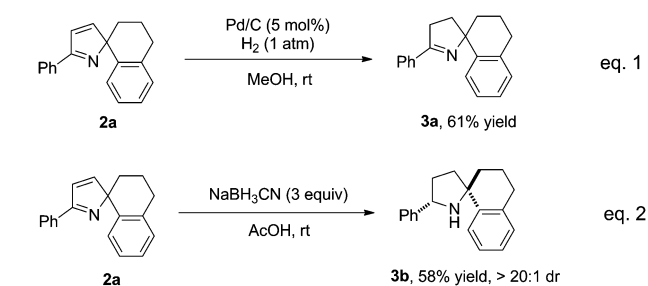
are summarized in Table 2. 2-Aryl pyrrole substrates bearing either an electron-donating group (4'-MeO, **2b**) or an electron-withdrawing group (4'-F, **2c**) on the benzene ring were well tolerated to afford dearomatization products in excellent yields (91–93%). Notably, alkyl substituents could also be present on the pyrrole ring without attenuating its nucleophilicity. When the phenyl group was replaced by an ethyl group (5-Et, **2d**), the reaction proceeded smoothly, giving the desired product in 84% yield. In the case of product **2e** featuring more steric hindrance due to the 3-methyl substituent, only 32% yield was obtained with *rac*-L1 as a ligand. To our delight, the yield could be improved to 73% when XPhos was utilized instead of *rac*-L1.

Substrates having substituents (R<sup>2</sup>) on the bromobenzene ring varying the electronic properties (**2f–2h**) were all tolerated, leading to the dearomatized products in 87–94% yields. The naphthyl ring containing substrate was also applicable, and the

**Table 2** Substrate scope of dearomative arylation of pyrroles<sup>a,b</sup>

|  |     |           |                         |           |     |
|--|-----|-----------|-------------------------|-----------|-----|
|  |     |           |                         |           |     |
| <b>2a</b>  | 90% | <b>2b</b> | 93%                     | <b>2c</b> | 91% |
| <b>2d</b>  | 84% | <b>2e</b> | 32% (73% <sup>c</sup> ) | <b>2f</b> | 89% |
| <b>2g</b>  | 94% | <b>2h</b> | 87%                     | <b>2i</b> | 79% |
|  |     |           |                         |           |     |
| R = Me, <b>2j</b> 93%;<br>= Et, <b>2k</b> 92%;<br>= <sup>t</sup> Bu, <b>2l</b> 87% |     |           |                         |           |     |

<sup>a</sup> Reaction conditions: [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (1.0 mol%), *rac*-L1 (3.0 mol%), K<sub>2</sub>CO<sub>3</sub> (1.5 equiv.) and **1a** (0.4 mmol) in toluene (0.2 M) at reflux. <sup>b</sup> Isolated yields. <sup>c</sup> XPhos was used as the ligand.

**Scheme 2** Transformations of dearomatization product **2a**.

desired product **2i** was obtained in 79% yield. When the malonate diester linked substrates were used, much higher reactivity was observed. The dearomatization products were obtained in excellent yields (87–93% in 10 h, **2j–2l**).

To explore the utility of the product obtained here, several transformations of the dearomatization product **2a** were then carried out. As summarized in Scheme 2, hydrogenation of **2a** by using Pd/C as the catalyst under 1 atm of hydrogen atmosphere smoothly led to product **3a** in 61% yield, with the imine functionality intact (eqn (1)). The dearomatization product **2a** could also be subjected to 3 equivalents of NaBH<sub>3</sub>CN in acetic acid, and the spironaphthalenepyrroline product **3b** was obtained in 58% yield with >20:1 dr (eqn (2)).<sup>13</sup>

In summary, we have realized the Pd-catalyzed intramolecular dearomative arylation of 2-substituted pyrroles, leading to spironaphthalene-1,2'-pyrrole derivatives in good to excellent yields. Further extension of the reaction scope and development of an enantioselective variant are currently under investigation in our lab.

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- The relative configuration of compound **3b** was determined by H-H COSY and 2D NOESY NMR analysis, see the ESI.†