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# Regioselective C–H alkenylation of imidazoles and its application to the synthesis of unsymmetrically substituted benzimidazoles†

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A palladium-catalyzed C–H alkenylation of imidazoles has been developed. High C5 selectivity was achieved for C2-unsubstituted and C2-substituted imidazoles using oxygen and copper(II) acetate, respectively, as oxidants. The obtained products were applied to benzannulation through a sequence involving transposition of *N*-alkyl groups to give C4-alkenyl imidazoles, alkenylation, thermal 6π-electrocyclization, and oxidation, affording unsymmetrically substituted benzimidazoles.

Imidazoles and their benzannulated forms, benzimidazoles, are an important class of heterocycles, which are found in a number of commercial drugs, biologically active compounds, *N*-heterocyclic carbene ligands, and ionic liquids.<sup>1</sup> Thus, selective syntheses of (benz)imidazoles have been essential to provide a wide range of derivatives containing a chosen functional group at a desired position. Particularly, parent (NH)-(benz)imidazoles are in tautomeric equilibrium, being formally symmetric, and approaches to access unsymmetrically substituted (benz)imidazoles have been of great interest in organic synthesis. However, most of the available methods rely on the formation of C–N bonds, which presents difficulties in the preparation of more sterically hindered regioisomers (Fig. 1A).<sup>2,3</sup> The synthesis of unsymmetrically substituted benzimidazoles also depends on C–N bond forming processes, such as the installation of primary amines onto multi-substituted aromatic rings and subsequent ring closure, making it challenging to increase structural diversity in the aromatic ring (Fig. 1B).<sup>4</sup> Alternatively, the regioselective formation of C–C bonds *via* direct C–H functionalization of *N*-substituted imidazoles could provide a systematic access to functionalized (benz)imidazoles.<sup>5</sup> In fact, notable progress has been made in the installation of aryl groups to afford C5-arylated imidazoles.<sup>6,7</sup> However, C–H alkenylation, also known as the Fujiwara–Moritani



Fig. 1 (A) (NH)-Imidazoles in tautomeric equilibrium leading to regioisomeric mixtures of *N*-substituted products. (B) Synthesis of benzimidazoles from multi-substituted arenes *via* C–N bond formation. (C) Synthesis of C5-alkenyl imidazoles and functionalized benzimidazoles *via* regioselective C–C bond forming reactions.

reaction, has been much less successful than arylation.<sup>8–10</sup> Despite the importance of alkenyl imidazoles in drug discovery and natural product synthesis, either as chemical motifs or as latent functional groups, the regioselective C5-alkenylation of *N*-alkylimidazoles using readily available olefins has not been reported to the best of our knowledge.<sup>11</sup> Furthermore, the installed alkenyl groups offer a great opportunity to build unsymmetrically substituted benzimidazoles; however, this possibility has been underexplored.<sup>12</sup>

The underdevelopment of imidazole C–H alkenylation is attributed to the unique reactivity of this heterocyclic core. Compared to the other two-nitrogen-containing five-membered heterocycle, pyrazole, imidazole is significantly basic, undergoing protonation at the nitrogen atom in the presence of acids and outcompeting nitrogen-based ligands that are frequently used in aerobic oxidation reactions.<sup>13,14</sup> Instead of searching for ligands that could compete with imidazoles, we envisioned that an imidazole substrate itself could be a competent ligand to facilitate dehydrogenative alkenylation of imidazoles.<sup>15</sup> More specifically, we hypothesized that imidazole-ligated Pd(II) carboxylate complexes should enable palladation at the more nucleophilic C5 position in preference to the C2 position of imidazoles, which requires strong bases and/or Lewis acidic metal additives.<sup>16,17</sup>

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Herein, we report the regioselective C5-alkenylation of imidazoles and its application to the construction of unsymmetrically substituted benzimidazoles (Fig. 1C).

In order to develop a general protocol for the alkenylation of imidazoles, the optimization process was performed with a 1-alkylimidazole and a 1,2-dialkylimidazole in parallel (Table 1, see the ESI† for details). Simple imidazole **1a** was reacted with two equivalents of olefins, whereas the amount of olefins was increased to three equivalents for C2-substituted imidazole **2a**. Employing the C2-alkenylation conditions reported by Ong's group did not provide the corresponding C5-alkenylated imidazoles (entries 1 and 2).<sup>9a</sup> Only when we replaced the Ag salt by oxygen, we observed some selectivity towards the C5 position, and the reaction was more efficient in DMA than in 1,4-dioxane (entries 3 and 4). The presence of carboxylate salts was critical for the conversion, and potassium pivalate was superior to potassium acetate (entries 5 and 6).<sup>18</sup> The kinetic isotope effect (KIE) was measured under the conditions of entry 6 ( $k_{\text{H}}/k_{\text{D}} = 2.76$ ; see the ESI†), suggesting that the cleavage of the C–H bond at C5 was rate-limiting. In addition, it is notable that these aerobic conditions were not compatible with related 1,3-azoles (not shown), *i.e.* thiazoles and oxazoles, indicating the distinctive ligand effect of imidazole. Cesium pivalate was as competent as potassium pivalate, however, the same efficiency was not achieved with a combination of potassium carbonate and pivalic acid (entries 7 and 8, respectively). Aerobic conditions using air instead of oxygen reduced the conversion of both substrates (entry 9). To increase the conversion of C2-substituted imidazole **2a**, where the regioselectivity issue is alleviated, the addition of Cu salts was investigated. As anticipated,

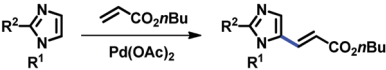
the alkenylation product **2b** was formed in high yields in the presence of  $\text{Cu}(\text{OAc})_2$ , which was slightly more efficient than its hydrate form (entries 11 and 10, respectively). The addition of pyridine as a ligand did not increase the conversion, presumably due to the strong ligand effect of imidazoles (entry 12). Heating the reaction mixture at 120 °C promoted the alkenylation at both C4 and C5 positions, resulting in a decreased yield of **2b** (entry 13). It should be noted that under the Cu conditions, the selectivity was generally low for simple imidazole **1a** and a significant amount of the C2-alkenylation product was formed. For example, the reaction of **1a** using the conditions described in entry 11 gave 38% yield of the corresponding C2-alkenylation product along with 12% of C5-alkenylation product **1b**. This result is consistent with the fact that copper salts activate the C2 position of imidazoles, an effect that has been observed since the pioneering reports on the C–H arylation of imidazoles.<sup>17</sup> Therefore, the conditions described in entries 6 and 11 were used for the C5-alkenylation of C2-unsubstituted and C2-substituted imidazoles, respectively.

The scope of C5-alkenylation of C2-unsubstituted imidazoles was examined using the catalytic system derived from  $\text{Pd}(\text{OAc})_2$ , KOPIV,  $\text{O}_2$ , and DMA (Table 2). Reactions with acrylates and acrylamides gave good yields of C5-alkenylation products (**1b–1g**, **3b**, and **3c**). Styrene derivatives were also used to afford the corresponding products (**3d** and **3e**). Furthermore, imidazoles substituted with different alkyl groups at the N1 nitrogen were well tolerated (**4b** and **5b**). C5-Alkenyl imidazoles have previously been accessible *via* the Horner–Wadsworth–Emmons and Heck reactions of the corresponding C5-prefunctionalized imidazoles, which, however, are difficult to access.<sup>11</sup> Thus, our strategy based on the direct C–H alkenylation of readily available imidazoles offers a highly useful alternative access to a range of these structural motifs.

When the C2 position was substituted with alkyl and aryl groups, the Pd-catalyzed and Cu-mediated alkenylation worked well with a variety of alkenes, including acrylates, acrylamides, and styrene (Table 3). Substituents at the N1 and C2 positions were varied to readily provide a range of C5-alkenylated imidazoles.

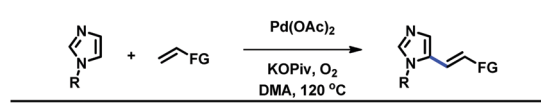
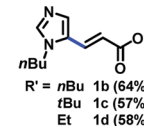
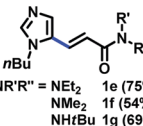
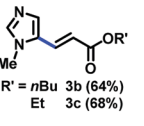
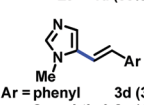
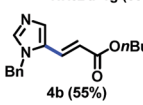
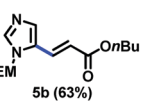
Next, the resulting C5-alkenylated imidazoles were subjected to additional alkenylation. Despite various attempts, the yield

Table 1 C5-Alkenylation of imidazoles<sup>a</sup>

<div><p>1a: R<sup>1</sup> = <i>n</i>Bu, R<sup>2</sup> = H 2a: R<sup>1</sup> = Bn, R<sup>2</sup> = Me</p><p>1b 2b</p></div>						
Entry	Additive	Oxidant	Solvent	Temp. (°C)	Yield (%)	
					1b <sup>b</sup>	2b <sup>c</sup>
1 <sup>d</sup>	1,10-Phenanthroline	AgTFA	Toluene	130	<5	<1
2	—	AgTFA	1,4-Dioxane	100	<5	<1
3	—	O <sub>2</sub> (1 atm)	1,4-Dioxane	120	11	7
4	—	O <sub>2</sub> (1 atm)	DMA	120	32	50
5	KOAc	O <sub>2</sub> (1 atm)	DMA	120	57	61
6	KOPiv	O <sub>2</sub> (1 atm)	DMA	120	67	67
7	CsOPiv	O <sub>2</sub> (1 atm)	DMA	120	64	64
8 <sup>e</sup>	K <sub>2</sub> CO <sub>3</sub> /PivOH	O <sub>2</sub> (1 atm)	DMA	120	54	40
9	KOPiv	Air	DMA	120	52	50
10	—	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	1,4-Dioxane	100	20	68
11	—	Cu(OAc) <sub>2</sub>	1,4-Dioxane	100	12	76
12	Pyridine (20 mol%)	Cu(OAc) <sub>2</sub>	1,4-Dioxane	100	14	72
13	—	Cu(OAc) <sub>2</sub>	1,4-Dioxane	120	6	62

<sup>a</sup> Reaction conditions: imidazole (1.0 mmol), *n*-butyl acrylate (2.0 and 3.0 mmol for **1a** and **2a**, respectively),  $\text{Pd}(\text{OAc})_2$  (0.10 mmol), additive (2.0 mmol), oxidant (2.0 mmol or  $\text{O}_2$  balloon), solvent (0.33 M), 120 °C, 24 h. <sup>b</sup> GC yield. <sup>c</sup> <sup>1</sup>H NMR yield. <sup>d</sup> Reaction conditions: imidazole (1.0 mmol), *n*-butyl acrylate (5.0 mmol),  $\text{Pd}(\text{TFA})_2$  (0.10 mmol), 1,10-phenanthroline (0.15 mmol), AgTFA (2.0 mmol), toluene (0.50 M), 130 °C (ref. 9a). <sup>e</sup> PivOH (0.50 mmol) was used.

Table 2 Regioselective C–H alkenylation of 1-alkylimidazoles

		
 <b>1b</b> (64%) <b>1c</b> (57%) <b>1d</b> (58%)	 <b>1e</b> (75%) <b>1f</b> (54%) <b>1g</b> (69%)	 <b>3b</b> (64%) <b>3c</b> (68%)
 <b>3d</b> (37%) <b>3e</b> (46%)	 <b>4b</b> (55%)	 <b>5b</b> (63%)

Reaction conditions: imidazole (1.0 mmol), alkene (2.0 mmol),  $\text{Pd}(\text{OAc})_2$  (0.10 mmol), KOPIV (2.0 mmol),  $\text{O}_2$  balloon (1.0 atm), DMA (3.0 mL), 120 °C, 24 h.

Table 3 C–H alkenylation of 1,2-substituted imidazoles



Reaction conditions: imidazole (0.50 mmol), alkene (1.5 mmol), Pd(OAc)<sub>2</sub> (0.050 mmol), Cu(OAc)<sub>2</sub> (1.0 mmol), 1,4-dioxane (1.5 mL), 100 °C, 15 h.

of C4-alkenylation of C5-alkenylated imidazoles remained modest (<40%). Thus, an alternative strategy based on the SEM-group switch, which had previously been demonstrated for the preparation of C4,5-diarylated imidazoles, was adopted.<sup>2b,16</sup> Heating the C5-alkenyl imidazoles in the presence of a catalytic amount of 2-(trimethylsilyl)ethoxymethyl chloride (SEM-Cl) afforded the corresponding C4-alkenyl imidazoles in good-to-high yields (Table 4, step a). For imidazoles bearing a substituent at the C2 position, the alkenylation at the C5 position using Pd(OAc)<sub>2</sub> and Cu(OAc)<sub>2</sub> was applied to smoothly generate the corresponding dialkenylated products (**11b**, **12b**, and **13b**; step b). For the subsequent ring closure, the oxidative conditions developed by Langer's group gave a mixture of products, resulting from undesired pathways, including SEM-switch, removal of the SEM group, and most significantly, incomplete oxidation.<sup>12</sup> Other oxidizing reagents that could enable thermal 6π-electrocyclization and oxidation were tested; the desired benzimidazoles were ultimately formed employing catalytic amounts of DDQ and

Table 4 Sequential alkenylation and cyclization for the synthesis of substituted benzimidazoles



Step a: imidazole (1.0 equiv.), SEM-Cl (0.050 equiv.), CH<sub>3</sub>CN (0.10 M), 100 °C, 24 h. Step b: imidazole (1.0 equiv.), alkene (3.0 equiv.), Pd(OAc)<sub>2</sub> (0.10 equiv.), Cu(OAc)<sub>2</sub> (2.0 equiv.), 1,4-dioxane (0.33 M), 100 °C, 15 h. Step c: DDQ (0.10 equiv.), NaNO<sub>2</sub> (0.10 equiv.), Ph<sub>2</sub>O (0.10 M), 180 °C, 36 h; 3 N HCl, 80 °C.



Scheme 1 Benzannulation of a C2-unsubstituted imidazole using N-methylation.

NaNO<sub>2</sub> under an oxygen atmosphere (step c).<sup>19</sup> However, high temperatures (200 °C) were required and thus, the scrambling of the SEM group could not be eliminated. Hence, SEM deprotection was performed to obtain the final (NH)-free benzimidazoles (**11c**, **12c**, and **13c**).

This strategy using sequential alkenylation, switch of the N-substituent, and cyclization was useful for the regioselective formation of N-methylbenzimidazoles. For example, the alkenylation product **5b** was subjected to trimethyloxonium tetrafluoroborate, and the obtained product was subsequently treated with TFA at ambient temperature, giving 1-methyl-4-alkenyl imidazole **14a** (Scheme 1). Remarkably, the next alkenylation of imidazole **14a** bearing an electron-withdrawing group at the C4 position took place preferentially at the C5 position, giving **14b**. Ring closure led to the formation of benzimidazole **14c**, which has different substituents at the C5 and C6 positions and fixed regiochemistry at the N1 position.

In conclusion, we have demonstrated Pd-catalyzed C–H alkenylation reactions of imidazoles at the C5 position. Imidazole substrates served as effective ligands in the palladium-catalyzed system, allowing the oxidative coupling to olefins. A variety of alkenylated imidazoles were easily prepared from readily available simple imidazoles and olefins in a single step. Furthermore, the resulting imidazoles were converted to unsymmetrically substituted benzimidazoles in a systematic way. In addition to the importance in the synthesis of imidazole and benzimidazole derivatives, these results suggest the potential role of imidazoles as ligands in dehydrogenative C–C bond forming reactions, which are currently being investigated in our laboratory and will be reported in due course.

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## Conflicts of interest

There are no conflicts to declare.

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