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An efficient synthesis of 2-arylimidazoles by oxidation of 2-arylimidazolines using activated carbon–O_2 system and its application to palladium-catalyzed Mizoroki–Heck reaction

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Abstract—Oxidative conversion of 2-substituted imidazoline (dihydroimidazole) to the corresponding imidazole was achieved by an activated carbon–O_2 system. Also, the 2-arylimidazolines and 2-arylimidazoles have been found to work as simple ligands in the palladium-catalyzed Mizoroki–Heck reaction.

1. Introduction

We have recently reported an activated carbon–O_2 oxidation system. That is, a variety of 2-arylbenzoxazoles, 2-arylbenzimidazoles and 2-arylbenzothiazoles were directly synthesized from the reaction of the substituted 2-aminophenols, 1,2-phenylenediamines, or 2-aminobenzenethiols with aldehydes in the presence of activated carbon (Darco® KB or Shirasagi KL) in xylene under an oxygen atmosphere.[1] Hantzsch 1,4-dihydropyridines and 1,3,5-trisubstituted pyrazolines were also oxidized to the corresponding aromatic compounds by the aid of activated carbon in both acetic acid and xylene.[2] Furthermore, oxidative aromatization of 9,10-dihydroanthracenes to anthracenes using molecular oxygen was also promoted by activated carbon.[3]

Substituted imidazoles are important moieties constituted in pharmaceuticals, pesticides and bioactive compounds. Furthermore, recently, imidazoles have been found to be attractive as a skeleton of ionic liquids in many fields such as environmentally friendly solvents in organic synthesis, electrolytes, liquid crystals and so on. Therefore, there have been many reports for the synthesis of imidazole derivatives. Among those, oxidative conversion of imidazoline to imidazole is a general and reliable method. Actually, $KMnO_4$,[4] MnO_2,[5] $BaSO_4$,[6] Pd/C,[7] Pd/C–DMSO,[8] $(COCl)_2$–DMSO,[9] trichloroisocyanuric acid (TCCA)[10] and *o*-iodoxybenzoic acid (IBX)[11] have been used as oxidizing agents. Very recently, Togo and Ishihara reported an efficient method using (diacetoxyiodo)benzene (DIB) in the presence of K_2CO_3.[12] Encouraged by these reports, as an extension of our activated carbon–O_2 oxidation system, we examined the oxidation of imidazolines to imidazoles.

On the other hand, the Mizoroki–Heck reaction has been widely used for construction of a carbon–carbon bond since the first report in 1971.[13] As ligands, phosphine and related compounds are often used. Recently, electron-rich and bulky alkyl phosphines, such as P(*t*-Bu)$_3$, were developed as highly effective ligands.[14] Especially, in view of the advances made in the field of palladacycles,[15] *N*-heterocyclic carbenes should be noteworthy.[16,17] We are interested in the use of non-phosphine ligands, namely, nitrogen-based ligands such as imidazole and imidazoline in palladium-catalyzed coupling reaction. Among the nitrogen-based ligands, we focused on 2-arylimidazole derivatives, because their structures are simple, they are easy to treat and inexpensive. Furthermore, the introduction of a variety of substituents at the 2-position of imidazole is also easily possible. There are some reports on the compounds containing imidazole moieties used as ligands in the Mizoroki–Heck reaction; however, most of them are palladium carbene complexes possessing a carbon–palladium bond.

Here, we report an efficient oxidative synthesis of 2-substituted imidazoles from the corresponding imidazolines and the Mizoroki–Heck reaction catalyzed by $PdCl_2$–2-arylimidazoline and $PdCl_2$–2-arylimidazole complexes.

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2. Results and discussion

2.1. Oxidative conversion of 2-arylimidazolines to 2-arylimidazoles

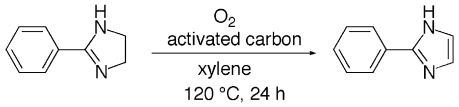
The starting 2-arylimidazolines were prepared by the reported methods. They are classified into two methods. One is the reaction of nitrile with ethylenediamine in the presence of a catalytic amount of S,[18] and the other is the reaction of aldehyde with ethylenediamine in the presence of a stoichiometric amount of NBS,[19] or molecular iodine in the presence of K_2CO_3.[12,20,21] 2-Arylimidazolines prepared by the above methods were treated with 100 wt % of activated carbon (Shirasagi KL, Japan EnviroChemicals, Ltd.) in xylene at 120 °C under oxygen atmosphere. The results in Table 1 clearly show that combination of activated carbon and oxygen accelerated oxidative conversion of imidazolines to the corresponding imidazoles.[22] As shown in Table 2, a variety of imidazolines having aryl groups at the 2-position were smoothly converted to the corresponding imidazoles in good to high yield. Unfortunately, in the case of an aliphatic substituent at the 2-position, only 2-*tert*-butyl imidazoline was converted to the corresponding imidazole in 62% yield.[23] It should be noted that we confirmed the possibility of reuse of activated carbon.

2.2. Mizoroki–Heck reaction of 4-bromotoluene with some olefins

We examined the reaction of 4-bromotoluene with methyl acrylate and *tert*-butyl acrylate under the conventional conditions using *N*,*N*-dimethylformamide (DMF) as a solvent and K_2CO_3 as a base at 120 °C. As for the palladium source, $PdCl_2$ was the choice in our reaction system, because $PdCl_2$ showed higher reactivity than $Pd(OAc)_2$. We confirmed that $PdCl_2$ alone, without a ligand almost did not catalyze the reaction (only 9% yield). Therefore, it is clear that 2-arylimidazoline and 2-arylimidazole ligands accelerated the Mizoroki–Heck reaction as shown in Table 3. Generally, 2-arylimidazoline–palladium complexes showed higher catalytic activity than 2-arylimidazole–palladium complexes in Mizoroki–Heck reaction only except for entry 1. This phenomenon was remarkable in the reaction of 4-bromotoluene with styrene (1.25 equiv) as shown in Scheme 1. That is, when 2-phenylimidazoline was used as a ligand, the product was obtained in 62% yield, whereas, only 6% of the product was obtained by the use of 2-phenylimidazole (Scheme 1).

It is noteworthy that when the reaction proceeded smoothly, the formation of a precipitate, Pd black, was not observed.

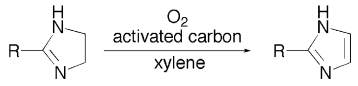
Table 1. Oxidative conversion of 2-phenylimidazoline to 2-phenylimidazole[a]

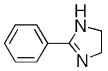
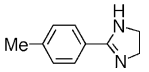
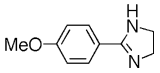
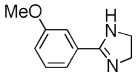
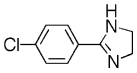
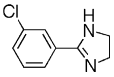
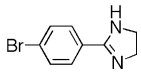
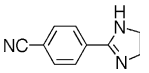
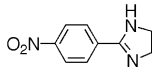
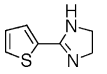


Entry	Activated carbon	Atmosphere	Yield[b]/%
1	None	O_2	21 (79)
2	Shirasagi KL	O_2	84 (0)
3	Shirasagi KL	Air	51 (15)
4	Shirasagi KL	Ar	10 (74)

[a] All reactions were carried out using 100 wt % of activated carbon (Shirasagi KL) in xylene at 120 °C for 24 h.
[b] Yield was determined by ^{1}H NMR analysis. The values in parentheses indicate the yield of recovered starting material.

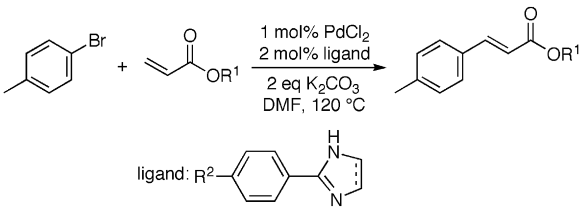
Table 2. Oxidative aromatization of 2-arylimidazolines to the corresponding imidazoles[a]



Entry	Imidazoline	Time/h	Yield[b]/%
1		24	84
2		24	80
3		24	72
4		24	77
5		24	80
6		24	84
7		25	78
8		24	84
9		25	82
10		24	70

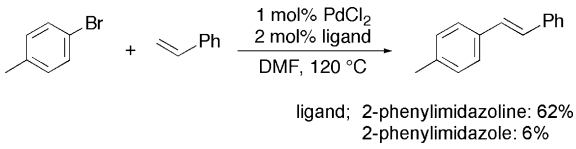
[a] All reactions were carried out using 100 wt % of activated carbon (Shirasagi KL) in xylene at 120 °C.
[b] Isolated yield.

Table 3. Mizoroki–Heck reaction using 2-arylimidazolines or 2-arylimidazole–palladium complexes[a]



Entry	R^1	R^2	Yield[b]/%	
			Imidazoline	Imidazole
1	Me	OMe	54	87
2	Me	H	86	85
3	Me	CN	92	81
4	*t*-Bu	OMe	89	77
5	*t*-Bu	H	95	70
6	*t*-Bu	CN	64	62

[a] All reactions were carried out in a ratio of 4-bromotoluene–acrylate–$PdCl_2$–ligand=1:2:0.01:0.02 in DMF at 120 °C.
[b] Isolated yield.



Scheme 1.

We assumed that two 2-arylimidazolines or two 2-arylimidazoles could coordinate to the palladium atom. It is also noted that these complexes are stable and insensitive to air.

3. Conclusion

In this paper we have disclosed a facile conversion of 2-arylimidazolines to 2-arylimidazoles by the aid of an activated carbon–O_2 system. Furthermore, simple $PdCl_2$–2-arylimidazoline and $PdCl_2$–2-arylimidazole catalyst systems for the Mizoroki–Heck reaction have been developed. Further investigation on application of the new catalyst to other coupling reactions is now in progress.

4. Experimental

4.1. General procedure for oxidation of 2-arylimidazolines to 2-arylimidazoles

2-Arylimidazoline (1 mmol), activated carbon (100 wt %; Shirasagi KL) and xylene (4 mL) were placed in a 100 mL three-necked flask and the mixture was heated at 120 °C. After decreasing pressure inside the flask, it was filled with oxygen using 1 L balloon. After confirmation of the completion of the reaction, the mixture was filtrated using Celite and washed with methanol. The filtrate was concentrated to obtain the product in analytically pure form.

4.1.1. 2-Phenylimidazole. R_f 0.53 (ethyl acetate). Mp 144–146 °C (lit.[4] 140–142 °C). IR (KBr): ν_{max} (cm^{-1}) 3567, 3053, 2989, 1670, 1560, 1506, 1461, 1106, 948, 705, 683. ^1H NMR (400 MHz, DMSO-d_6): δ 7.0 (br s, 1H), 7.2 (br s, 1H), 7.33 (t, J=8.0 Hz, 1H), 7.44 (dd, J=8.0 Hz, J=8.0 Hz, 2H), 7.93 (d, J=8.0 Hz, 2H), 12.49 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 124.8, 128.0, 128.8, 130.8, 145.6. MS m/z: 145.4 (M^+).

4.1.2. 2-(4′-Methoxyphenyl)imidazole. R_f 0.39 (ethyl acetate). Mp 155–157 °C (lit.[24] 152–154 °C). IR (KBr): ν_{max} (cm^{-1}) 3444, 3073, 2840, 1616, 1518, 1439, 1253, 1101, 1029, 840. ^1H NMR (400 MHz, DMSO-d_6): δ 3.79 (s, 3H), 7.00 (d, J=8.8 Hz, 2H), 7.1 (br s, 2H), 7.85 (d, J=8.8 Hz, 2H), 12.31 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 55.3, 114.2, 123.7, 126.3, 145.7, 159.2. MS m/z: 175.4 (M^+).

4.1.3. 2-(3′-Methoxyphenyl)imidazole. R_f 0.50 (ethyl acetate). Mp 155–156 °C. IR (KBr): ν_{max} (cm^{-1}) 3448, 3141, 3017, 1618, 1587, 1231, 1109, 945, 773. ^1H NMR (400 MHz, DMSO-d_6): δ 3.79 (s, 3H), 6.90 (dd, J=8.0 Hz, J=2.4 Hz, 1H), 7.0 (br s, 1H), 7.2 (br s, 1H), 7.34 (dd, J=8.0 Hz, J=8.0 Hz, 1H), 7.50–7.52 (m, 2H), 12.48 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 55.2, 110.1, 113.8, 117.2, 129.9, 132.1, 145.5, 159.6. MS m/z: 175.5 (M^+). Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.94; H, 5.79; N, 16.08. Found: C, 68.78; H, 5.76; N, 15.82.

4.1.4. 2-(2′-Thienyl)imidazole. R_f 0.66 (ethyl acetate). Mp 196–197 °C. IR (KBr): ν_{max} (cm^{-1}) 3435, 3107, 2913, 1651, 1558, 1520, 1471, 1102. ^1H NMR (400 MHz, DMSO-d_6): δ 6.9 (br s, 1H), 7.10 (dd, J=4.8 Hz, J=4.0 Hz, 1H), 7.2 (br s, 1H), 7.48 (dd, J=4.8 Hz, J=1.6 Hz, 1H), 7.49 (dd, J=4.0 Hz, J=1.6 Hz, 1H), 12.50 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 123.3, 125.6, 127.8, 134.6, 141.5. MS m/z: 151.4 (M^+). Anal. Calcd for $C_7H_6N_2S$: C, 55.97; H, 4.03; N, 18.65. Found: C, 55.95; H, 4.21; N, 18.37.

4.1.5. 2-(4′-Methylphenyl)imidazole. R_f 0.53 (ethyl acetate). Mp 219–221 °C (lit.[8] 223 °C). IR (KBr): ν_{max} (cm^{-1}) 3687, 1578, 1517, 1443, 1104, 822, 731. ^1H NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H), 7.0 (br s, 1H), 7.2 (br s, 1H), 7.24 (d, J=8.0 Hz, 2H), 7.81 (d, J=8.0 Hz, 2H), 12.39 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 20.8, 124.7, 128.2, 129.2, 137.2, 145.7. MS m/z: 159.5 (M^+). Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.03; H, 6.45; N, 17.39.

4.1.6. 2-(4′-Cyanophenyl)imidazole. R_f 0.59 (ethyl acetate). Mp 264–266 °C. IR (KBr): ν_{max} (cm^{-1}) 3446, 3161, 2981, 2222, 1654, 1610, 1506, 1448, 1067, 837. ^1H NMR (400 MHz, DMSO-d_6): δ 7.1 (br s, 1H), 7.4 (br s, 1H), 7.91 (d, J=8.0 Hz, 2H), 8.10 (d, J=8.0 Hz, 2H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 109.9, 118.9, 125.1, 132.8, 134.7, 143.9. MS m/z: 170.5 (M^+). Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.83. Found: C, 71.17; H, 4.33; N, 24.55.

4.1.7. 2-(4′-Chlorophenyl)imidazole. R_f 0.61 (ethyl acetate). Mp 250–251 °C (lit.[8] 248 °C). IR (KBr): ν_{max} (cm^{-1}) 3455, 1640, 1499, 1449, 1096, 826, 724. ^1H NMR (400 MHz, DMSO-d_6): δ 7.0 (br s, 1H), 7.30 (br s, 1H), 7.50 (d, J=8.8 Hz, 2H), 7.94 (d, J=8.8 Hz, 2H), 12.58 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 126.4, 128.7, 129.7, 132.3, 144.5. MS m/z: 179.3 (M^+).

4.1.8. 2-(3′-Chlorophenyl)imidazole. R_f 0.53 (ethyl acetate). Mp 134–135 °C (lit.[8] 133 °C). IR (KBr): ν_{max} (cm^{-1}) 3451, 3061, 2807, 1668, 1606, 1556, 1466, 1108, 768, 680. ^1H NMR (400 MHz, DMSO-d_6): δ 7.1 (br s, 1H), 7.3 (br s, 1H), 7.39 (d, J=8.0 Hz, 1H), 7.47 (dd, J=8.0 Hz, J=8.0 Hz, 1H), 7.90 (d, J=8.0 Hz, 1H), 7.98 (m, 1H), 12.64 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 123.3, 124.4, 127.7, 130.8, 132.8, 133.6, 144.2. MS m/z: 179.5 (M^+).

4.1.9. 2-(4′-Bromophenyl)imidazole. R_f 0.57 (ethyl acetate). Mp 247–249 °C. IR (KBr): ν_{max} (cm^{-1}) 3436, 2964, 2873, 1605, 1560, 1495, 1446, 1107, 824, 724. ^1H NMR (400 MHz, DMSO-d_6): δ 7.0 (br s, 1H), 7.3 (br s, 1H), 7.64 (d, J=8.8 Hz, 2H), 7.87 (d, J=8.8 Hz, 2H), 12.59 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 120.9, 126.7, 130.0, 131.6, 144.5. MS m/z: 225.4 (M^+). Anal. Calcd for $C_9H_7BrN_2$: C, 48.46; H, 3.16; N, 12.56. Found: C, 48.17; H, 3.16; N, 12.75.

4.1.10. 2-(4′-Nitrophenyl)imidazole. R_f 0.68 (ethyl acetate). Mp 309–311 °C (lit.[25] 310–312 °C). IR (KBr): ν_{max}

(cm^{-1}) 3694, 1515, 1333, 1107, 856. ^1H NMR (400 MHz, DMSO-d_6): δ 7.2 (br s, 1H), 7.4 (br s, 1H), 8.16 (d, J= 9.2 Hz, 2H), 8.30 (d, J=9.2 Hz, 2H), 12.97 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 124.3, 125.3, 136.6, 143.6, 146.4. MS m/z: 190.5 (M^+).

4.1.11. 2-*tert*-Butylimidazole. R_f 0.50 (4:1 ethyl acetate–methanol). Mp 151–152 °C. IR (KBr): ν_{max} (cm^{-1}) 3566, 2960, 1661, 1568, 1430, 1372, 1103, 974, 735. ^1H NMR (400 MHz, DMSO-d_6): δ 1.27 (s, 9H), 6.7 (br s, 1H), 6.9 (br s, 1H), 11.57 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 29.6, 32.4, 155.0. MS m/z: 125.6 (M^+). Anal. Calcd for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.99; H, 9.80; N, 22.23.

4.2. General procedure for Mizoroki–Heck reaction

$PdCl_2$ (0.02 mmol), 2-arylimidazoline (or 2-arylimidazole) (0.04 mmol) and K_2CO_3 (2 equiv) were mixed in DMF (10 mL) and the mixture was stirred at 50 °C for 1 h. 4-Bromotoluene (2 mmol) and methyl acrylate (or *tert*-butyl acrylate) (4 mmol) were added. The mixture was then stirred at 120 °C for 24 h. The reaction mixture was cooled, and then precipitates were removed by filtration and extracted with diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. After evaporation, the obtained residue was purified by silica gel column chromatography to give the coupling products.

4.2.1. (*E*)-Methyl 4-methylcinnamate. R_f=0.53 (5:1 hexane–ethyl acetate). Mp 54–55 °C. IR (KBr): ν_{max} (cm^{-1}) 3401, 3028, 2948, 1712, 1634, 1606, 1515, 1436, 1332, 1319, 1281, 1210, 1193, 1170, 999, 818, 521, 511, 493. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, 1H, J=16.4 Hz), 7.42 (d, 2H, J=8.0 Hz), 7.19 (d, 2H, J=7.6 Hz), 6.40 (d, 1H, J=16.0 Hz), 3.80 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 167.6, 144.8, 140.7, 131.6, 129.6, 128.0, 116.7, 51.6, 21.4. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.83; H, 6.92.

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References and notes

1. (a) Kawashita, Y.; Nakamichi, N.; Kawabata, H.; Hayashi, M. *Org. Lett.* **2003**, *5*, 3713; (b) Kawashita, Y.; Ueba, C.; Hayashi, M. *Tetrahedron Lett.* **2006**, *47*, 4231.
2. (a) Nakamichi, N.; Kawashita, Y.; Hayashi, M. *Org. Lett.* **2002**, *4*, 3955; (b) Nakamichi, N.; Kawashita, Y.; Hayashi, M. *Synthesis* **2004**, 1015.
3. Nakamichi, N.; Kawabata, H.; Hayashi, M. *J. Org. Chem.* **2003**, *68*, 8272.
4. Mohammadpoor-Baltork, I.; Zolfigol, M. A.; Abdollahi-Alibeik, M. *Tetrahedron Lett.* **2004**, *45*, 8687.
5. Martin, P. K.; Matthews, H. R.; Rapoport, H.; Thyagarajan, G. *J. Org. Chem.* **1968**, *33*, 3758.
6. Hughey, J. L. I. V.; Knapp, S.; Schugar, H. *Synthesis* **1980**, 489.
7. Amemiya, Y.; Miller, D. D.; Hsu, F. L. *Synth. Commun.* **1990**, *20*, 2483.
8. Anastassiadou, M.; Baziard-Mouysset, G.; Payard, M. *Synthesis* **2000**, 1814.
9. Huh, D. H.; Ryu, H.; Kim, Y. G. *Tetrahedron* **2004**, *60*, 9857.
10. Mohammadpoor-Baltork, I.; Zolfigol, M. A.; Abdollahi-Alibeik, M. *Synlett* **2004**, 2803.
11. Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 4077.
12. Ishihara, M.; Togo, H. *Synlett* **2006**, 227.
13. (a) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581; (b) Heck, R. F.; Nolley, J. P., Jr. *J. Org. Chem.* **1972**, *37*, 2320.
14. (a) Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10; (b) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989; For N-donating ligand–palladium-catalyzed Heck reaction, see: Done, M. C.; Rüther, T.; Cavell, K. J.; Kilner, M.; Peacock, E. J.; Braussaud, N.; Skelton, B. W.; White, A. *J. Organomet. Chem.* **2000**, *607*, 78.
15. (a) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844; (b) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23.
16. (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290; (b) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, C. S. P. *J. Organomet. Chem.* **2002**, *653*, 69.
17. See also for recent palladium-catalyzed coupling reactions: (a) Review: Phan, N. T. S.; Sluys, M. V. D.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609; (b) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481; (c) Beller, M.; Zapf, A. *Synlett* **1998**, 792.
18. Mohammadpoor-Baltork, I.; Abdollahi-Alibeik, M. *Bull. Korean Chem. Soc.* **2003**, *24*, 1354.
19. Fujioka, H.; Murai, K.; Ohba, Y.; Hiramatsu, A.; Kita, Y. *Tetrahedron Lett.* **2005**, *46*, 2197.
20. Other methods for imidazoline synthesis: (a) Neef, G.; Eder, U.; Sauer, G. *J. Org. Chem.* **1981**, *46*, 2824; (b) Mitchell, J. M.; Finney, N. S. *Tetrahedron Lett.* **2000**, *41*, 8431; (c) Peddibhotla, S.; Tape, J. J. *Synthesis* **2003**, 1433; (d) You, S.; Kelly, J. W. *Org. Lett.* **2004**, *6*, 1681; (e) Gogoi, P.; Konwar, D. *Tetrahedron Lett.* **2006**, *47*, 79; (f) Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Kargar, H. *Tetrahedron Lett.* **2006**, *47*, 2129.
21. In the case of 1,2-phenylenediamine and aldehydes, the corresponding intermediate dihydro-cyclic benzimidazolines could not be isolated, because successive oxidation step proceeded very rapidly. On the other hand, in the present case, the product of ethylenediamine and aldehydes, that is, 2-arylimidazolines were stable and were isolated, and can be used as a substrate of oxidation leading to the formation of 2-arylimidazoles.
22. As for the role of activated carbon in oxidative aromatization, we found that surface area of micropore is one of the important factors. The details will be published in a separate full paper.
23. We examined oxidation of a variety of imidazolines having alkyl groups at the 2-position such as methyl, *n*-pentyl, dihydrocinnamyl, cyclohexyl; however, all of them gave only low yield of the corresponding imidazole. Only 2-*tert*-butyl imidazoline was oxidized to the corresponding imidazole in 62% yield.
24. Jones, H.; Fordice, M. W.; Greenwald, R. B.; Hannah, J.; Jacob, A.; Ruyle, W. V.; Walford, G. L.; Shen, T. Y. *J. Med. Chem.* **1978**, *21*, 1100.
25. Hurst, D. T. *Heterocycles* **1988**, *27*, 371.