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# Palladium-catalyzed direct 5-arylation of 1,3-dimethyluracil with aryl bromides: an electrophilic metalation–deprotonation with electrophilic arylpalladium intermediate

Ko Hoon Kim, Hyun Seung Lee, Jae Nyoung Kim *

*Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Republic of Korea*

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ABSTRACT

An efficient method of palladium-catalyzed direct 5-arylation of 1,3-dimethyluracil was developed with a various range of aryl bromides including electron-deficient aryl bromides. 5-Aryluracil derivatives were obtained in moderate to good yields regioselectively most likely via an electrophilic metalation–deprotonation process.



5-Aryluracil and its nucleoside derivatives have received much attention due to their wide range of biological activities[1] and applications in bioanalysis or chemical biology.[2] Most frequently, these compounds were prepared by palladium-catalyzed cross-coupling reactions of 5-halouracils with arylboronic acids[3] or arylstannanes.[4] However, the yields of 5-aryluracil derivatives were moderate and highly toxic stannane impurities would be a problem for the biological study with the product obtained from arylstannane. Recently, Hocek and co-workers reported an elegant palladium-catalyzed direct arylation of N–H protected uracils with aryl halides.[5,6] However, the yields of 5-aryluracils were moderate and the selectivity between 5- and 6-aryluracils was not satisfactory. In addition, aryl halides bearing an electron-withdrawing substituent failed in the reaction.

In these respects, we decided to develop a more efficient protocol for the 5-arylation of 1,3-dimethyluracil (**1a**). At the outset of this study, we focused our attention to a palladium-catalyzed direct arylations of indole derivatives, which have been studied deeply by many research groups.[7,8] As shown in Scheme 1, the reactivity of 1,3-dimethyluracil (**1a**) toward an electrophile would be very similar with that of indole, in that both compounds have an enamine moiety and attack an electrophile at the 3-position of indole and the 5-position of uracil. Thus most of the reported palladium-catalyzed arylations of indole used an electrophilic palladium intermediate,[7] while the concept has not been examined with uracil derivatives, to the best of our knowledge.[9] Actually, however, the palladium intermediate **I** of indole was converted to a more stable benzylic carbocation intermediate **II** via a 1,2-palladium migration[8] and eventually provided 2-arylindole. A similar 1,2-migration of palladium in the case of uracil (**III** to **IV**) would be difficult because the carbocation intermediate **IV** is not stable due to the presence of nearby electron-deficient carbon atom of carbonyl moiety. In addition, the hydrogen at the 5-position of intermediate **III** is acidic, thus the intermediate **III** could be converted to an aryluracilpalladium intermediate **V** readily, and eventually to 1,3-dimethyl-5-aryluracil (**3a**) via a reductive elimination of $Pd^0$. Thus the formation **3a** would be a major pathway when the electrophilic palladation of **1a** operates effectively.

Thus we expected that we could increase the yield of **3a** and improve the ratio of **3a**/**4a** at the same time, by using an electrophilic arylpalladium species. The use of a relatively poorly coordinating carboxylate as the counterion could allow the dissociation of ArPdBr into more electrophilic arylpalladium species $ArPd^+[OCOR]^-$.[7a] Subsequently, a proportion of an electrophilic palladation process could be increased while a Heck-type carbopalladation process (vide infra) decreased. Based on the assumption we decided to use pivalic acid (PivOH) as a carboxylate ion source, and examined the reaction of **1a** as summarized in Table 1.

Initially, the reaction of **1a** and bromobenzene (**2a**) was examined under three typical palladium-catalyzed reaction conditions (entries 1–3). When we use $Cs_2CO_3$, **3a** was isolated in low yield (18%) along with **4a** (8%). In the reaction, biphenyl was produced in appreciable amounts by Ullmann type aryl–aryl reductive

* Corresponding author. Tel.: +82 62 530 3381; fax: +82 62 530 3389.
*E-mail address:* kimjn@chonnam.ac.kr (J.N. Kim).

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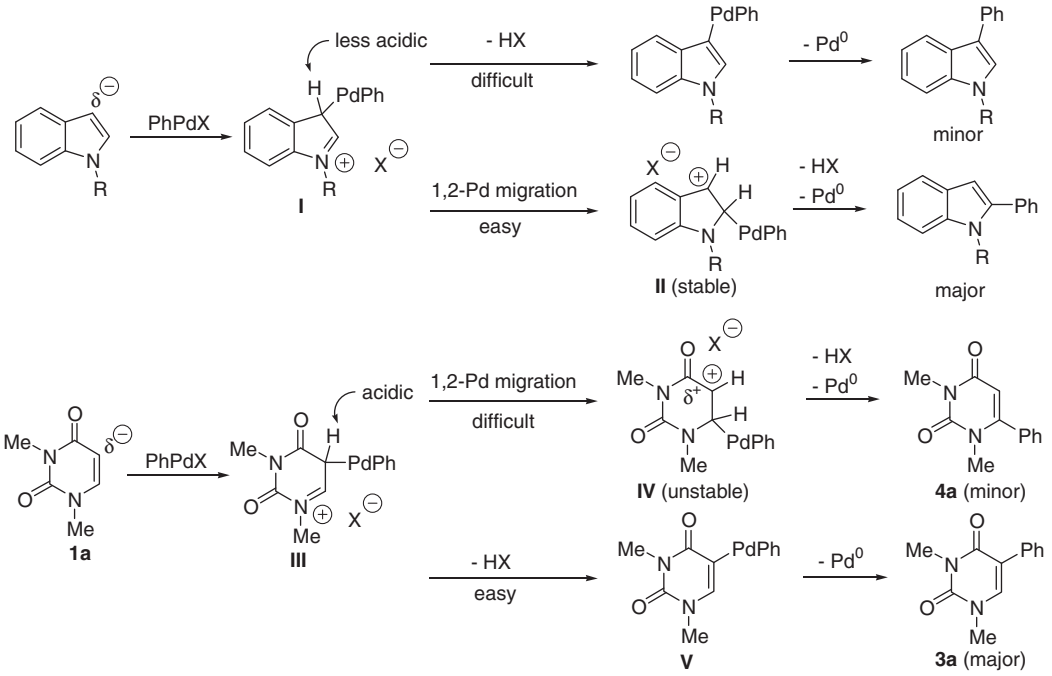



**Scheme 1.** Similarity and difference between indole and 1,3-dimethyluracil (**1a**) in their Pd-catalyzed arylation.

**Table 1**
Optimization of reaction conditions for the synthesis of 1,3-dimethyl-5-phenyluracil (**3a**)

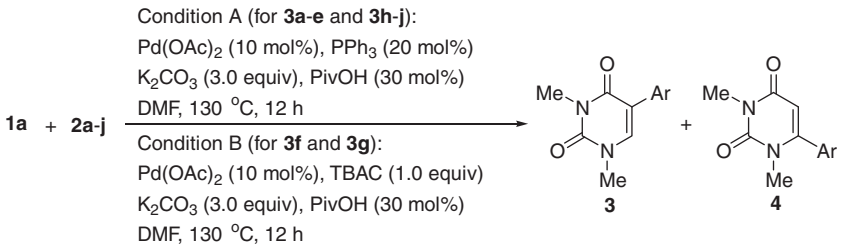
| Entry | Conditions[a] | 3a (%) | 4a (%) |
|---|---|---|---|
| 1 | $PPh_3$ (20 mol %), $Cs_2CO_3$ (3.0 equiv), DMF, 130 °C, 12 h | 18 | 8 |
| 2 | $PPh_3$ (20 mol %), $K_2CO_3$ (3.0 equiv), DMF, 130 °C, 12 h | 42 | 8 |
| 3 | TBAC (1.0 equiv), $K_2CO_3$ (3.0 equiv), DMF, 130 °C, 12 h | 29 | 10 |
| 4[b] | $PPh_3$ (20 mol %), $K_2CO_3$ (3.0 equiv), PivOH (30 mol %), DMF, 130 °C, 12 h | 79 | 10 |
| 5 | $PPh_3$ (20 mol %), $K_2CO_3$ (3.0 equiv), PivOH (100 mol %), DMF, 130 °C, 12 h | 71 | 8 |
| 6 | $PPh_3$ (20 mol %), $K_2CO_3$ (3.0 equiv), PivOH (30 mol %), DMF, 100 °C, 12 h | 73 | 8 |
| 7[c] | $PPh_3$ (10 mol %), $K_2CO_3$ (3.0 equiv), PivOH (30 mol %), DMF, 100 °C, 12 h | 70 | 10 |
| 8[d] | TBAC (1.0 equiv), $K_2CO_3$ (3.0 equiv), PivOH (30 mol %), DMF, 130 °C, 12 h | 77 | 9 |
| 9 | $PPh_3$ (20 mol %), $Na_2CO_3$ (3.0 equiv), PivOH (30 mol %), DMF, 130 °C, 12 h | 14 | 25 |
| 10 | $PPh_3$ (20 mol %), $AgNO_3$ (1.0 equiv), $K_2CO_3$ (3.0 equiv), DMF, 130 °C, 12 h | 42 | 6 |
| 11 | $PPh_3$ (20 mol %), $Ag_2O$ (1.0 equiv), $K_2CO_3$ (3.0 equiv), PivOH (30 mol %), DMF, 130 °C, 12 h | 44 | 6 |

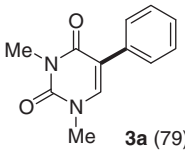
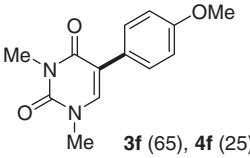
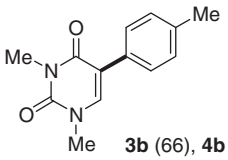
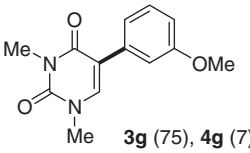
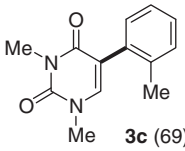
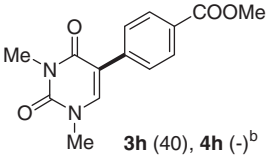
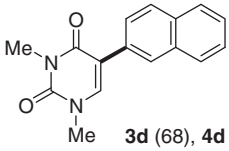
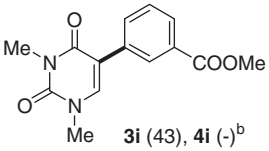
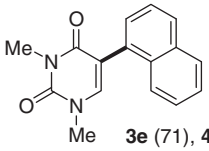
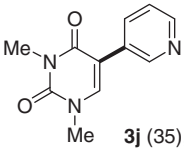
[a] PhBr (2.0 equiv) and $Pd(OAc)_2$ (10 mol %) are common, unless otherwise noted.
[b] Selected as condition A.
[c] $Pd(OAc)_2$ (5 mol %) was used.
[d] Selected as condition B.

coupling reaction.[10] Replacing the base to $K_2CO_3$[11] increased the yield of **3a** to 42%; however, the result was not satisfactory (entry 2). The use of ligandless conditions employing TBAC (tertabutylammonium chloride) was not effective (entry 3). The use of PivOH dramatically improved the yield of **3a**, as shown in entries 4–8, as compared to the reactions carried out without PivOH (entries 1–3). When we use $K_2CO_3$/PivOH combination (entry 4), the yield of **3a** increased to 79%; however, **4a** was also formed albeit in low yield (10%).[12] Increasing the amounts of PivOH (entry 5) was not effective. Lowering the reaction temperature did not improve the selectivity (entry 6). Lower loading of Pd/$PPh_3$ decreased the yield of **3a** slightly (entry 7). The use of TBAC in the presence of PivOH (entry 8) showed a similar result with that of entry 4. The use of $Na_2CO_3$ was not effective even in the presence of PivOH (entry 9). In order to abstract a bromide ion effectively from ArPdBr and generate a more electrophilic arylpalladium intermediate,[7a] the addition of silver salts such as $AgNO_3$ or $Ag_2O$ was examined; however, it was not helpful (entries 10 and 11). With the optimization experiments, we found that the conditions employing $K_2CO_3$/PivOH in the presence of $PPh_3$ (entry 4: condition A) or TBAC (entry 8: condition B) were the best. Although the selectivity was not high enough, we could certainly increase the yield of **3a**.[5,13]

In order to examine the generality, we performed the reactions of **1a** with various aryl bromides **2a–j**, and the results are summarized in Table 2. The reactions with 4-bromotoluene (**2b**), 2-bromotoluene (**2c**), 2-bromonaphthalene (**2d**), and 1-bromonaphthalene (**2e**) afforded the corresponding 5-aryl products **3b–e** in good yields (66–71%) along with low yields of 6-aryl derivatives **4b–d** (8–10%). The reaction with 4-bromoanisole (**2f**), however, showed a quite different result. Under the conditions employing $PPh_3$ (entry 4 in Table 1: condition A), 5-aryl **3f,** and 6-aryl **4f** were isolated in 38% and 40%, respectively. We thought that the moderate combined yield (78%) and low selectivity between **3f**/**4f** (almost 1:1) might be ascribed to the low electrophilicity of 4-MeOPhPdX species which renders the electrophilic palladation difficult. An electron-donating methoxy group made the arylpalladium intermediate less electrophilic. In addition, the presence of electron-rich $PPh_3$ ligand could make the arylpalladium species less electrophilic.[7b] Thus we examined a ligandless condition (entry 8 in Table 1: condition B), and we could improve both the yield and selectivity (**3f**: 65% and

**Table 2**
Palladium-catalyzed direct 5-arylation of 1,3-dimethyluracil




| Entry | Product[a] (%) | Entry | Product[a] (%) |
|---|---|---|---|
| 1 |  **3a** (79), **4a** (10) | 6 |  **3f** (65), **4f** (25) |
| 2 |  **3b** (66), **4b** (9) | 7 |  **3g** (75), **4g** (7) |
| 3 |  **3c** (69), **4c** (10) | 8 |  **3h** (40), **4h** (-)[b] |
| 4 |  **3d** (68), **4d** (8) | 9 |  **3i** (43), **4i** (-)[b] |
| 5 |  **3e** (71), **4e** (-)[b] | 10 |  **3j** (35), **4j** (-)[b] |

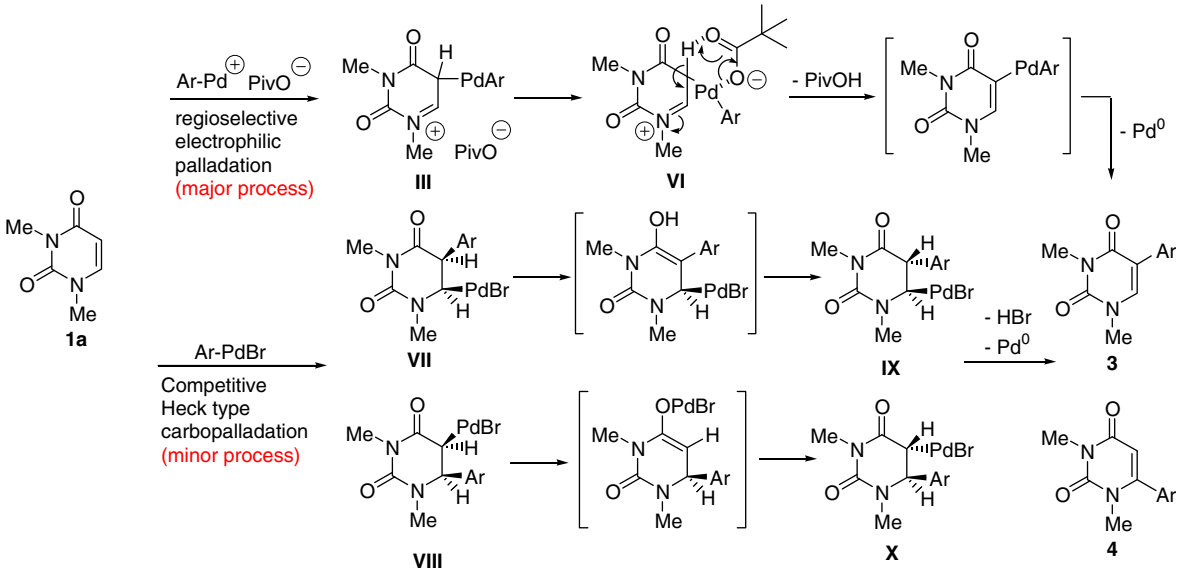
[a] 5-Aryl derivatives **3a–j** are shown in Table, and the yields of **3** and **4** are isolated.
[b] Failed to isolate.

**4f**: 25%), as shown in entry 6. Similarly, the reaction with 3-bromoanisole (**2g**) provided **3g** in good yield (75%). The reactions with aryl bromides bearing an electron-withdrawing group showed sluggish reactivity. Methyl 4-bromobenzoate (**2h**), methyl 3-bromobenzoate (**2i**), and 3-bromopyridine (**2j**) produced the desired compounds **3h–j** in low to moderate yields (35–43%). We could obtain the corresponding 5-aryluracil derivatives from aryl bromides bearing an EWG group, albeit in moderate yields, in contrast to the paper of Hocek.[5]

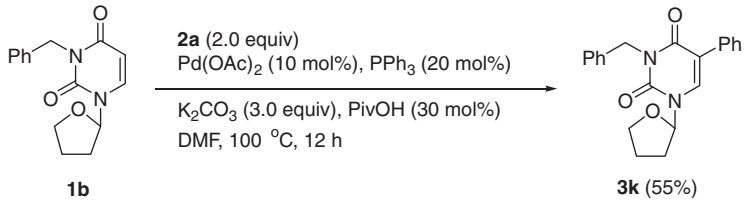
The reaction mechanism for the selective formation of 5-aryluracils **3a–j** could be postulated as shown in Scheme 2. Heck-type carbopalladation (vide supra) of 5,6-double bond of **1a** with ArPdBr species could occur in two ways to form **VII** and **VIII**. Epimerization of **VII** and **VIII** at the 5-position could provide **IX** and **X** via the corresponding enol or palladium enolate, respectively, and a following syn β-H elimination would produce **3** and **4**, respectively. However, another important pathway must be involved for the exclusive formation of **3**. The pathway could be an electrophilic metalation–deprotonation (EMD) mechanism. The ionization of arylpalladium bromide ArPdBr to a cationic palladium intermediate $ArPd^+$ could be facilitated in the presence of PivOK,[7a] especially in a polar solvent such as DMF, as Sharp and co-workers reported in their regioselective arylation of furan.[14] A subsequent electrophilic palladation could occur easily and regioselectively at the electron-rich 5-position of **1a** to form aryluracilpalladium intermediate **VI**, and a following re-aromatization provided **3** after a reductive elimination of $Pd^0$.

As another entry, we examined 5-phenylation of 1-(tetrahydrofuran-2-yl)-3-benzyluracil (**1b**)[15] with bromobenzene (**2a**) under the same reaction conditions; however, a severe decomposition was observed at 130 °C. By lowering the reaction temperature to 100 °C, we could isolate **3k** in 55%,[12] as shown in Scheme 3. In the reaction, the corresponding 6-phenyl derivative was not formed in any trace amount presumably due to the steric hindrance caused by tetrahydrofuranyl moiety.

As we started the 5-arylation of **1a** by deep consideration of indole derivatives, we decided to examine the feasibility of selective synthesis of 6-aryl derivative **4a** by applying the reported method of oxidative arylation of indoles. Fagnou[16a,b] and DeBoef[16c,d] have reported oxidative arylations of indoles with arenes. As shown in Scheme 4, the reaction of **1a** was examined in the presence of



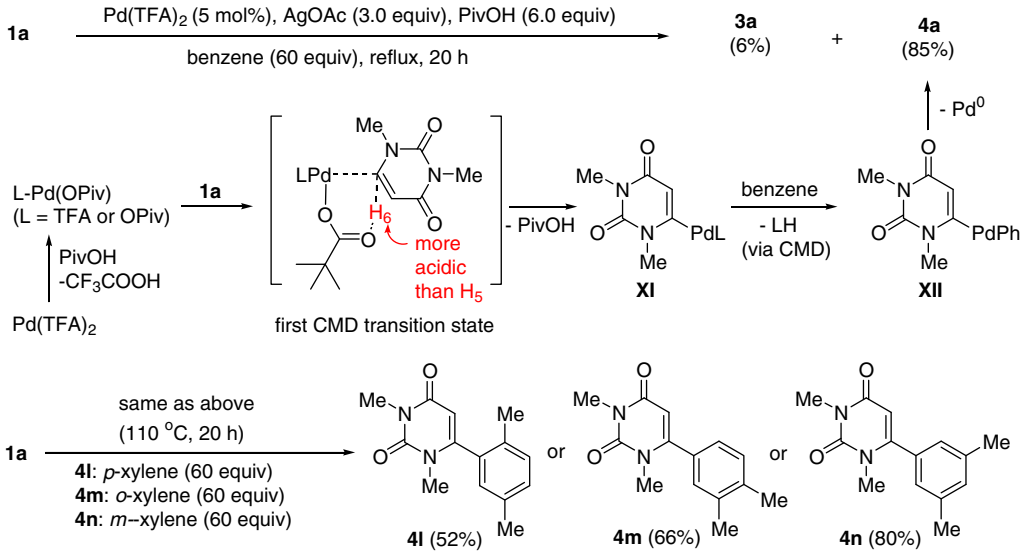

**Scheme 2.**




**Scheme 3.**

$Pd(TFA)_2$, AgOAc, and PivOH in benzene (reflux, 20 h). To our delight, **4a** was obtained in high yield (85%) along with a trace amount of **3a** (6%). The mechanism for the selective formation of **4a** could be proposed as follows based on the works of Fagnou and DeBoef.[16] A regioselective palladation occurred at the 6-position of **1a** to form **XI**, most likely via a concerted metalation–deprotonation (CMD) process by $Pd^{II}(L)(OPiv)$ species involving a deprotonation of more acidic hydrogen atom at the 6-position.[5] A subsequent arylation of uracilpalladium intermediate **XI** with benzene via a second CMD process produced **4a** after reductive elimination of $Pd^0$, which was oxidized to $Pd^{II}$ by AgOAc.[17] Similarly, the reactions of **1a** and three xylene isomers under the similar conditions[18] afforded the corresponding 6-xylyluracil derivatives **4l–n** in moderate to good yields (52–80%), as also shown in Scheme 4.

In summary, we disclosed a palladium-catalyzed direct 5-arylation of 1,3-dimethyluracil with various range of aryl




**Scheme 4.**

bromides including electron-deficient aryl bromides. 5-Aryluracils were formed exclusively most likely via an electrophilic metalation–deprotonation process while the 6-aryl derivatives via a Heck-type mechanism as minor products. In addition, 1,3-dimethyl-6-phenyluracil (**4a**) was also synthesized in high yield by oxidative arylation with benzene via a CMD mechanism. Further studies on the reaction mechanism and the scope of this reaction are currently underway including an intramolecular version.

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9. In the papers of Hocek,[5] an electron-deficient tris(pentafluorophenyl)-phosphine might be helpful for the increase of the electrophilicity of an arylpalladium intermediate.
10. For our recent example of palladium-catalyzed benzoin-mediated Ullmann type coupling of aryl bromides to biaryls Park, B. R.; Kim, K. H.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2011**, *52*, 4405–4407. and further references were cited therein. In the reaction, biaryls and trace amount of arenes were formed but the yields of these compounds were not determined.
11. The use of $K_2CO_3$ afforded higher yield of product in many palladium-catalyzed reactions with aryl bromides than $Cs_2CO_3$, see: (a) Pivsa-Art, S.; Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 467–473; (b) Watanabe, M.; Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **2000**, *41*, 481–483; (c) Safin, D. A.; Babashkina, M. G.; Klein, A. *Catal. Lett.* **2009**, *129*, 363–366; (d) Safin, D. A.; Babashkina, M. G. *Catal. Lett.* **2009**, *130*, 679–682.
12. *Typical procedure for the synthesis of 1,3-dimethyl-5-phenyluracil (**3a**)*: A stirred mixture of 1,3-dimethyluracil (**1a**, 140 mg, 1.0 mmol), bromobenzene (**2a**, 315 mg, 2.0 equiv), $Pd(OAc)_2$ (22 mg, 10 mol %), $PPh_3$ (52 mg, 20 mol %), PivOH (30 mg, 30 mol %), $K_2CO_3$ (415 mg, 3.0 equiv) in DMF (1.5 mL) was heated to 130 °C for 12 h under nitrogen atmosphere. After the usual aqueous extractive workup with chloroform and column chromatographic purification process (hexanes/THF, 4:1) compounds **3a** (171 mg, 79%) and **4a** (21 mg, 10%) were obtained as white solids.[5] Other compounds were synthesized analogously, and the known compounds **3a–d**[5,19a] and **3f**,[5,19a] **4a–d**,[5,19a] **4f**,[5,19a] **4g**[19a] were identified by comparison their mp, IR, $^1$H NMR and/or mass data with the reported. The selected spectroscopic data of **3e** and **3g–k** are as follows.
*Compound **3e***:[19b] 71%; white solid, mp 203–204 °C; IR (KBr) 2945, 1700, 1646, 1450, 1346 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.43 (s, 3H), 3.44 (s, 3H), 7.25 (s, 1H), 7.33 (dd, $J$ = 6.9 and 1.2 Hz, 1H), 7.44–7.50 (m, 3H), 7.68–7.71 (m, 1H), 7.85–7.88 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.22, 36.90, 113.54, 125.18, 125.25, 125.90, 126.22, 128.12, 128.36, 128.97, 130.57, 132.29, 133.58, 142.13, 151.72, 162.57; ESIMS $m/z$ 267 [M+H]$^+$. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.43; H, 5.57; N, 10.29.
*Compound **3g***:[19a] 75%; white solid, mp 122–124 °C; IR (KBr) 2946, 1702, 1656, 1603, 1491, 1451, 1350 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.42 (s, 3H), 3.47 (s, 3H), 3.83 (s, 3H), 6.88 (d, $J$ = 7.2 Hz, 1H), 7.00–7.12 (m, 2H), 7.22–7.36 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.25, 37.10, 55.29, 113.57, 113.96, 114.16, 120.50, 129.41, 134.20, 140.53, 151.42, 159.56, 162.23; ESIMS $m/z$ 247 [M+H]$^+$. Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.75; H, 5.96; N, 11.13.
*Compound **3h***: 40%; white solid, mp 180–181 °C; IR (KBr) 1707, 1651, 1607, 1279, 1112 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.43 (s, 3H), 3.50 (s, 3H), 3.92 (s, 3H), 7.40 (s, 1H), 7.60 (d, $J$ = 8.4 Hz, 2H), 8.04 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.25, 37.21, 52.10, 113.21, 127.97, 129.25, 129.64, 137.54, 141.13, 151.24, 161.89, 166.72; ESIMS $m/z$ 275 [M+H]$^+$. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.39; H, 5.45; N, 10.06.
*Compound **3i***: 43%; white solid, mp 158–159 °C; IR (KBr) 2953, 1713, 1652, 1253 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.42 (s, 3H), 3.49 (s, 3H), 3.92 (s, 3H), 7.39 (s, 1H), 7.46 (dd, $J$ = 7.8 and 7.8 Hz, 1H), 7.79 (ddd, $J$ = 7.8, 1.8 and 1.2 Hz, 1H), 7.99 (ddd, $J$ = 7.8, 1.8 and 1.2 Hz, 1H), 8.10–8.11 (m, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.17, 37.08, 52.13, 113.13, 128.42, 128.75, 128.86, 130.28, 132.91, 133.19, 140.86, 151.26, 162.05, 166.72; ESIMS $m/z$ 275 [M+H]$^+$. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.64; H, 5.45; N, 10.13.
*Compound **3j***:[19c] 35%; white solid, mp 198–200 °C; IR (KBr) 1693, 1650, 1483, 1350 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.43 (s, 3H), 3.51 (s, 3H), 7.28–7.38 (m, 1H), 7.39 (s, 1H), 7.95 (d, $J$ = 8.1 Hz, 1H), 8.57 (br s, 1H), 8.65 (br s, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.25, 37.24, 111.02, 123.14, 129.00, 136.07, 140.68, 148.30, 148.88, 151.26, 162.03; ESIMS $m/z$ 218 [M+H]$^+$. Anal. Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 60.64; H, 5.49; N, 19.12.
*Compound **3k***: 55%; sticky oil; IR (film) 3060, 2960, 2892, 1702, 1658, 1494, 1458, 1440, 1291, 1076 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.85–2.14 (m, 3H) 2.37–2.49 (m, 1H), 3.95–4.02 (m, 1H), 4.17–4.23 (m, 1H), 5.14 (d, $J$ = 13.5 Hz, 1H), 5.23 (d, $J$ = 13.5 Hz, 1H), 6.08 (dd, $J$ = 6.3 and 3.3 Hz, 1H), 7.22–7.42 (m, 6H), 7.44 (s, 1H), 7.46–7.57 (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 23.90, 33.11, 44.54, 70.19, 88.05, 114.14, 127.62, 127.78, 128.36, 128.41 (2C), 129.41, 133.39, 134.71, 136.85, 150.43, 161.83; ESIMS $m/z$ 349 [M+H]$^+$. Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.23; H, 5.96; N, 7.89.
13. We also examined the reaction of **1a** under the modified condition A, by simply replacing $PPh_3$ with tris(pentafluorophenyl)phosphine:[5] however, the results were not satisfactory (**3a**: 73% and **4a**: 18%). Replacement of $PPh_3$ with an electron-poor triethyl phosphite ligand was also examined in order to make the arylpalladium intermediate more electrophilic, however, the yield and selectivity were similar (**3a**: 74% and **4a**: 16%) with those of $(C_6F_5)_3P$. In addition, the reaction of **1a** and iodobenzene produced biphenyl as a major product along with a low yield of **3a** (<15%).
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Gorelsky, S. I.; Pike, A.; LeBris, A. P.; DeBoef, B. *J. Am. Chem. Soc.* **2010**, *132*, 14676–14681; (d) Dwight, T. A.; Rue, N. R.; Charyk, D.; Josselyn, R.; DeBoef, B. *Org. Lett.* **2007**, *9*, 3137–3139.

17. The yields of **4a** and **3a** were 60% and 16%, respectively, when we used $Pd(OAc)_2$ instead of $Pd(TFA)_2$.
18. The reaction at 80 °C was so sluggish that we raised the temperature to 110 °C. The yield of **4l** was moderate due to steric crowdedness during the second CMD process between uracilpalladium intermediate **XI** and *p*-xylene, as reported in the oxidative arylation of indoles.[16] The corresponding 5-xylyl derivative was not observed at all. When we used *o*-xylene, compound **4m** was obtained in 66% along with a low yield of the corresponding 5-xylyl derivative (17%). In the case of *m*-xylene, **4n** was obtained in high yield (80%) along with a low yield of the corresponding 5-xylyl derivative (11%).
*Compound* ***4l***:[19a] 52%; colorless oil; IR (film) 2952, 1706, 1662, 1438, 1367 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.19 (s, 3H), 2.35 (s, 3H), 3.08 (s, 3H), 3.42 (s, 3H), 5.64 (s, 1H), 6.96 (s, 1H), 7.19 (s, 2H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 18.70, 20.79, 27.95, 33.17, 101.95, 128.34, 130.48, 130.78, 131.97, 132.78, 136.17, 152.52, 154.35, 162.60; ESIMS *m*/*z* 245 $[M+H]^+$. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.96; H, 6.89; N, 11.23.
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