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EFFECT OF OXYGEN SUBSTITUENT IN THE ANILINE PART OF BENZANILIDE ON THE REGIOSELECTIVITY IN DIRECT ARYLATION USING PALLADIUM-PHOSPHINE REAGENTS

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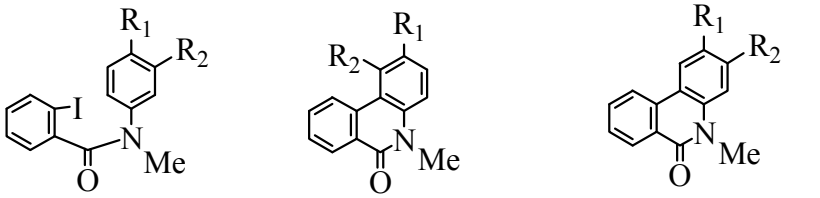
Abstract – This study investigated the effect of oxygen substituents at the 3'-position in the aniline part of 2-iodobenzanilides on the coupling position in its Pd-assisted direct arylation. Benzanilide with methylenedioxy and acetoxy groups yielded the *ortho*-product formed predominantly by connection to a more hindered carbon. The mechanism is discussed from the perspectives of both steric and coordinated effects.

Direct arylation[1a] (aryl-aryl coupling reaction) of a nonactivated aryl C-H bond with an activated arene by palladium-phosphine reagent has been used to synthesize many condensed aromatic compounds.[1] Recently, we reported that an intramolecular direct arylation of 2-halo-*N*-arylbenzamides using palladium reagents was a convenient method for synthesizing polycyclic aromatic lactams, some of which can be transformed into aromatic alkaloids.[2] Moreover, we successfully synthesized benzonaphthazepine, a new skeletal compound, and pyrrolophenanthridine (Amaryllidaceae) alkaloids, utilizing a Pd-assisted biaryl coupling reaction with regioselective C–H activation *via* the intramolecular coordination of an amine to Pd.[3] Subsequently, we applied the direct arylation using Pd to the synthesis of quinazoline alkaloids[4,5] and benzpyranones.[4,5]

Examining the synthesis of trisphaeridine, we found that the Pd-mediated coupling reaction of *N*-(2-iodophenyl)benzamide possessing a methylenedioxy group in the benzoyl part produced the

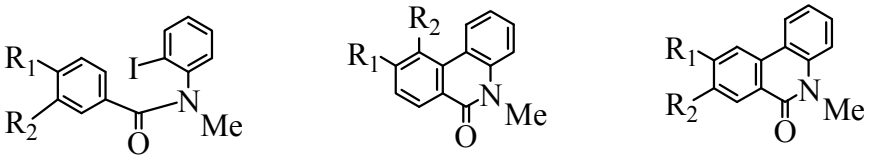
ortho-product, which was formed by connection to a more hindered carbon and the *para*-product in a 4 to 1 ratio.[6] Subsequently, we investigated the effect of several oxygen substituents in the benzoyl part of *N*-(2-iodophenyl)benzamide (**A**) on the coupling position in its Pd-assisted biaryl coupling reaction. We reported that benzamide with methylenedioxy and acyloxy groups yielded the *ortho*-product (**B**) formed predominantly by connection to a more hindered carbon and benzamide with methoxy and phenol groups gave the *ortho*-product (**B**) and the *para*-product (**C**) in almost equal amounts.[7]

In order to investigate the generality of oxygen-substituent effect on coupling position, we examined biaryl coupling reaction of 2-iodo-*N*-methylbenzanilides (**1**) possessing oxygen-substituents in the aniline part.



1 **2** (*ortho*-product) **3** (*para*-product)

a : $R_1 + R_2 = OCH_2O$ **c** : R_1=H, R_2 =OAc
b : R_1=H, R_2 =OMe **d** : R_1=H, R_2 =OH



A **B** (*ortho*-product) **C** (*para*-product)

a : $R_1 + R_2 = OCH_2O$ **c** : R_1=H, R_2 =OAc
b : R_1=H, R_2 =OMe **d** : R_1=H, R_2 =OH

Scheme 1

The results of the coupling reactions using methods A [$Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), and K_2CO_3 (200 mol%)], B[8] [$Pd(OAc)_2$ (100 mol%), DPPP (100 mol%), *n*-Bu_3P (100 mol%), and Ag_2CO_3 (200 mol%)], and C [$Pd(OAc)_2$ (10 mol%), (*o*-tol)$_3$P (20 mol%), and K_2CO_3 (200 mol%)] in DMF under reflux are summarized in Table 1.

First, the direct arylations of **1** using Method A were examined. The compound (**1a**) possessing a methylenedioxy group gave the *ortho*-product (**2a**) as the major product, and the acetate (**1c**) gave the *ortho*-product (**2d**) selectively.[9] Interestingly, these products are formed by connection to a more hindered carbon. By contrast, the reaction of benzamides (**1b** and **d**) possessing methoxy and hydroxyl group under the same reaction conditions gave the corresponding coupling products (**2** and **3**) in a ratio of 1.1~1.4 to 1, showing nearly equal selectivity. (See Table 1)

The regioselectivity of the coupling reaction involving two possible positions, C_2 (*ortho*) and C_6 (*para*), can be discussed based on steric and electronic effects. The difference in the regioselectivity of methoxy

and methylenedioxy groups reflects the steric bulkiness of the methoxy group[10] and the fact that the lone pair of electrons in the methylenedioxy oxygen atom is more electronegative than that in the methoxy oxygen atom because of reduced resonance of the π-electron on the benzene ring.[11] Therefore, the lone pair of electrons in the methylenedioxy oxygen atom would coordinate to the Pd^{II} more tightly to produce the *ortho*-product predominantly.

Table1. Results of biaryl coupling reactions of benzanilides (**1** and **A**).[a)]

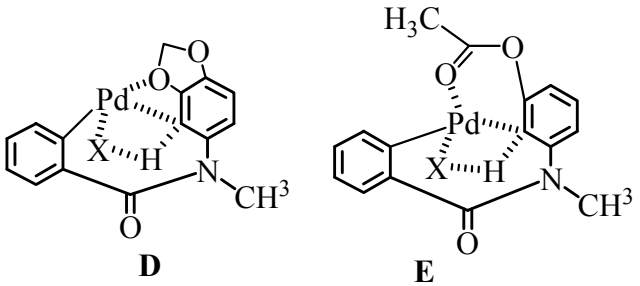
Method	substrate	yield(%) **2** + **3**	ratio[b)] **2** : **3**	substrate[d)]	yield(%)[d)] **B**+ **C**	ratio[d)] **B** : **C**
A	**1a**	92	7.6 : 1	**Aa**	quant	7.5 : 1
B		79	15.0 : 1		84	11.5 : 1
C		quant	4.0 : 1		96	5.6 : 1
A	**1b**	96	1.4 : 1	**Ab**	93	1.0 : 1
B		97	2.2 : 1		98	1.3 : 1
C		98	1.4 : 1		quant	0.6 : 1
A	**1c**	quant	7.9 : 1	**Ac**	76	7.0 : 1
B		quant	9.9 : 1		quant	8.3 : 1
C		95	2.9 : 1		96	2.9 : 1
A	**1d**	94	1.1 : 1	**Ad**	79	1.0: 1
B[c)]		85	2.2 : 1		83	1.4 : 1
C		quant	0.9 : 1		quant	1.2 : 1

a) All reactions were carried out in DMF under Ar atmosphere and reflux for 15~30 min.
Method A : [$Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), and K_2CO_3 (200 mol%)]
Method B: [$Pd(OAc)_2$ (100 mol%), DPPP (100 mol%), *n*-Bu_3P (100mol%), and Ag_2CO_3 (200 mol%)]
Mehtod C: [$Pd(OAc)_2$ (10 mol%), *(o*-tol)$_3$P(20 mol%), and K_2CO_3 (200 mol%)]
b) Determined by HPLC and NMR analysis.
c) K_2CO_3 (200 mol%) as a base in place of Ag_2CO_3, because **1d** was gradually decomposed by using Ag_2CO_3.
d) See reference 7.

All of the reactions using our new method (Method B)[8] yielded the *ortho*-product (**2**) as the major product; which was more sterically hindered than the *para*-product (**3**), in comparison with Method A. This indicates that a bidentate ligand (DPPP) is sterically smaller than two monodentate ligands (PPh_3) and suggests that the bulkiness of the ligand affects the regioselectivity. Therefore, reactions were carried out using Method C with (*o*-tol)$_3$P, which has a larger cone angle and is bulkier than PPh_3 as the ligand.[12] Table 1 summarizes the results using Method C. The general decrease in *ortho*-products (**2**) from the coupling reaction at the sterically hindered position indicates that ligand bulkiness influences regioselectivity.[13] These results are very similar to those of direct arylation of benzamides (**A**) possessing oxygen substituents in the benzoyl part.[7,14]

Recently, several mechanistic pathways for direct arylation (aryl-aryl coupling reaction) have been

proposed.[1a, 15] We presented that the formation of aryl-aryl bond would proceed *via* a σ-bond metathesis (C-H activation). [16] According to our proposal, the *ortho*-product (**2**) would be predominantly formed *via* the intermediate (**D**) and (**E**), respectively.



D **E** Pd : Pd(II)

Chart 1

In conclusion, the ratio of **2** to **3** was influenced by the coordinating ability of substituent(s) to the Pd^{II} complex and by the steric relationship between the substituent(s) and the phosphine ligand. More detailed investigations of direct arylation mechanism are now in progress.

EXPERIMENTAL

Melting points were measured on a micro-melting point hot-stage apparatus (Yanagimoto) and are uncorrected. IR spectra were recorded on a JASCO FT/IR 350 spectrophotometer and ^{1}H-NMR spectra in deuteriochloroform on Varian Mercury 300 or VXR-500 spectrometers. NMR spectral data are reported in parts per million downfield from tetramethylsilane as the internal standard (δ 0.0), and the coupling constants are given in Hertz. MS spectra were obtained on a VG-70SE. Analytical HPLC was performed with a Shimadzu SPD-6A on a silica gel column (Chemcosorb 5Si-U). Column chromatography was carried out on a Merck silica gel (230–400 mesh). All the extracts were washed with brine, dried over anhydrous $MgSO_4$, and filtered; the filtrate was concentrated to dryness under reduced pressure.

N-(1,3-Benzodioxol-yl)-2-iodo-*N*-methylbenzanilide (1a)

A mixture of 3,4-methylenedioxyaniline(2.06 g, 15.0 mmol), 2-iodobenzoic acid (4.84 g, 19.5 mmol), *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide (EDC) (4.95 g, 25.8 mmol), and 4-dimethylaminopyridine (0.40 g, 3.3 mmol) in dry CH_2Cl_2 (12 mL) was stirred at rt for 30 min under an argone atmosphere. The reaction mixture was poured into water and the aqueous layer was extracted with AcOEt.. The organic layer was washed with 10% HCl, 5% aqueous $NaHCO_3$ solution, and brine. The residue was recrystalized from AcOEt to give *N*-(1,3-benzodioxol-5-yl)-2-iodobenzanilide (3.25 g, 59 %) as colorless needles, mp 204–206 ˚C. IR (KBr) cm^{-1}: 3050, 1650, 1450. *Anal*. Calcd for $C_{14}H_{10}NO_3I$: C, 45.80; H, 2.75; N, 3.82. Found: C, 45.82; H, 2.97; N, 3.84.

Methyl iodide (0.30 mL, 4.5 mmol) was added to a suspension of *N*-(1,3-benzodioxol-5-yl)-2-

iodobenzanilide (1.10 g, 3.0 mmol) and NaH (60%, 0.46 g, 9.0 mmol) in dry DMF (32 mL). After stirring at rt for 15 min, the excess NaH was decomposed with ice water, and the aqueous layer was extracted with AcOEt. The residue in AcOEt was subjected to column chromatography on a silica gel. Elution with hexane:AcOEt (2:1) gave **1a** (1.10 g, 96.7%) as colorless prisms (from hexane:AcOEt), mp 71-74 ˚C. IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (500 MHz) : 3.44 (3H, s), 5.90 (2H, s), 6.57 (1H, d, *J* = 8.5 Hz), 6.66 (1H, dd, *J* = 8.5, 2.0 Hz), 6.72 (1H, d, *J* = 2.0 Hz), 6.88 (1H, ddd, *J* = 7.5, 7.5, 1.5 Hz), 7.05 (1H, dd, *J* = 7.5, 1.5 Hz), 7.15 (1H, dd, *J* = 7.5, 7.5 Hz), 7.68 (1H, br d, *J* =8.0 Hz). *Anal*. Calcd for $C_{15}H_{12}NO_3I$: C, 47.27; H, 3.17; N, 3.67. Found: C, 47.31; H, 3.26; N, 3.60.

2-Iodo-3'-methoxy-*N*-methylbenzanilide (1b)

Methyl iodide (0.55 mL, 8.16 mmol) was added to a suspension of 2-iodo-3-methoxybenzanilide[17] (2.0 g, 5.44 mmol) and NaH (60%, 0.65 g, 16.32 mmol) in dry DMF (30 mL). After stirring for 15 min at rt, the excess NaH was decomposed with ice water, and the aqueous layer was extracted with AcOEt. The residue in AcOEt was subjected to column chromatography on a silica gel. Elution with hexane:AcOEt (1:1) gave **1b** (1.10 g, 96.7%) as colorless oil. IR (KBr) cm^{-1}: 1640. ^{1}H-NMR (500 MHz) : 3.51 (3H, s), 3.69 (3H, s), 6.65 (1H, dd, *J* = 8.5, 2 Hz), 6.73 (1H, dd, *J* = 2.0, 2.0 Hz), 6.76 (1H, br. d, *J* = 8.0 Hz), 6.87 (1H, br t, *J* = 7.5 Hz), 7.04 (1H, br d, *J* = 7.5 Hz), 7.09 (1H, br t, *J* = 8.5 Hz), 7.13 (1H, br t, *J* = 7.5 Hz),, 7.68 (1H, d, *J* = 7.5 Hz). High resolution MS (FAB) *m*/*z*: Calcd for $C_{15}H_{14}NO_3I$ $[M+1]^+$: 368.0148. Found: 368.0102.

3-(2-Iodo-*N*-methylbenzamido)phenyl acetate (1c)

A mixture of *m*-aminophenol (3.27 g, 30.0 mmol), 2-iodobenzoic acid (9.67 g, 39.0 mmol), EDC (9.78 g, 51.0 mmol), and 4-dimethylaminopyridine (0.73 g, 6.0 mmol) in dry CH_2Cl_2 (300 mL) was stirred at rt for 30 min under an argone atmosphere. The reaction mixture was poured into water and the aqueous layer was extracted with AcOEt. The extracts were washed with 10% HCl, 5% aqueous $NaHCO_3$ solution, and brine. A solution of the residue in EtOH (50 mL) and 5% aqueous NaOH solution (50 mL) was stirred at rt for 30 min and was acidified with 10% HCl solution. The mixture was concentrated under reduced pressure and was extracted with AcOEt. The organic layer was washed with 5% aqueous $NaHCO_3$ solution and brine. The residue was recrystalized from AcOEt to give 2'-iodo-3-hydroxybenzanilide (3.54 g, 34.8 %) as colorless prisms, mp 171–173 ˚C. IR (KBr) cm^{-1}: 3200, 1650, 1440. *Anal*. Calcd for $C_{13}H_{10}NO_2I$: C, 46.04; H, 2.97; N, 4.13. Found: C, 45.92; H, 2.97; N, 4.08.

A solution of 2'-iodo-3-hydroxybenzanilide (890 mg, 2.62 mmol) in acetic anhydride (0.58 mL), 5.24 mmol) and pyridine (5 mL) was stirred for 45 min at rt. The reaction mixture was made acidic with 10% HCl solution and the aqueous layer was extracted with AcOEt. The organic layer was washed with 5% aqueous $NaHCO_3$ solution and brine. The residue was recrystallized from AcOEt-hexane to afford 3-(2-iodobenzamido)phenyl acetate (909 mg, 91%), as colorless prisms, mp 115–118 ˚C. IR (KBr) cm^{-1}:

3250, 1760, 1660. *Anal*. Calcd for $C_{15}H_{12}NO_3I$: C, 47.27; H, 3.17; N, 3.67. Found: C, 47.42; H, 3.26; N, 3.62.

Methyl iodide (0.45 mL, 6.75 mmol) was added to a suspension of 3-(2-iodobenzamido)phenyl acetate (1.72 g, 4.5 mmol) and NaH (60%, 0.20 g, 5.0 mmol) in dry DMF (45 mL). After stirring for 15 min under ice cooling, the excess NaH was decomposed with ice water, and the quenched mixture was made acidic with 10% HCl solution, and then extracted with AcOEt. The residue in AcOEt was subjected to column chromatography on a silica gel. Elution with $CHCl_3$:hexane:AcOEt (5:3:1) gave **1c** (1.63 g, 91.7%) as oil. IR (KBr) cm^{-1}: 1760, 1650. ^{1}H-NMR (500 MHz) : 2.26 (3H, s), 3.51 (3H, s), 6.87 (2H, m), 6.97 (1H, br. s), 7.01 (1H, br d, J = 7.0 Hz), 7.05 (1H, br d, J = 6.0 Hz), 7.15 (2H, m), 7.67 (1H, br d, J = 7.5 Hz). High resolution MS (FAB) m/z : Calcd for $C_{16}H_{14}NO_3I$ $[M+1]^+$: 396.0096. Found: 396.0095.

3-(2'-Iodo-*N*-methylbenzamido)phenol (1d)

Aqueous 5% $NaHCO_3$ solution (18 mL) was added to a solution of **1c** (1.0 g, 2.53mmol) in MeOH (36 mL) under ice cooling and the mixture was stirred at rt over night. The reaction mixture was made acidic with 10% HCl solution and extracted with AcOEt. The residue was recrystallized from AcOEt-hexane to afford **1d** (0.89 g, 89.3 %) as colorless prisms, mp 171-173 ˚C. IR (KBr) cm^{-1}: 3200, 1626, 1591. ^{1}H-NMR (300 MHz, d_6-DMSO): 3.29 (3H, s), 6.60 (1H, d, J = 7.9 Hz), 6.73 (1H, br d, J = 8.0 Hz), 6.75 (1H, br s), 7.00 (1H, t, J = 7.2 Hz), 7.04 (1H, t, J = 7.9 Hz), 7.21 (1H, br d, J = 7.2 Hz), 7.28 (1H, t, J = 7.2 Hz), 7.75 (1H, d, J = 8.0 Hz), 9.19 (1H, s),. *Anal*. Calcd for $C_{14}H_{12}NO_2I$: C, 47.61; H, 3.43; N, 3.97. Found: C, 47.53; H, 3.49; N, 3.88.

General Procedure for the Coupling Reaction of Benzanilides (1)

Coupling reaction was carried out under the reaction conditions indicated in Table 1. Then, the reaction mixture of **1a**, **1b**, and **1d** was diluted with AcOEt, and the precipitates were removed by filtration. The filtrate was washed with brine.

Biaryl Coupling Reaction of *N*-(1,3-benzodioxol-yl)-2-iodo-*N*-methylbenzamide (1a)

The residue was dissolved in $CHCl_3$ and was subjected to column chromatography on silica gel. Elution with $CHCl_3$:hexane:AcOEt (5:3:1) gave 5-methyl-[1,3]dioxolo[4,5-*a*]phenanthridin-6(5*H*)-one (**2a**) and successive elution with the same solvent gave 5-methyl-[1,3]dioxolo[4,5-*b*]phenanthridin-6(5*H*)-one (**3a**).

5-Methyl-[1,3]dioxolo[4,5-*a*]phenanthridin-6(5*H*)-one (2a): colorless needles (from AcOEt), mp 200-202 ˚C. IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.77 (3H, s), 6.21 (2H, s), 6.88(1H, d, J = 8.5 Hz), 7.04 (1H, d, J = 8.5 Hz), 7.59 (1H, ddd, J = 8.0, 7.5, 1.0 Hz), 7.74 (1H, ddd, J = 8.0, 7.5, 1.0 Hz), 8.55 (1H, dd, J = 8.0, 1.5 Hz), 8.68 (1H, dd, J = 8.5, 1.0 Hz). *Anal.* Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N,5.53. Found: C, 71.29; H, 4.52; N, 5.50.

5-Methyl-[1,3]dioxolo[4,5-*b*]phenanthridin-6(5*H*)-one (3a): colorless needles (from AcOEt), mp 240-243 ˚C. IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.78 (3H, s), 6.08 (2H, s), 6.95 (1H, s),

7.52 (1H, dd, *J* = 7.5, 7.5 Hz), 7.67 (1H, s), 7.72 (1H, ddd, *J* = 7.5, 7.5, 1.5 Hz), 8.06 (1H, d, *J* = 8.0 Hz), 8.52 (1H, dd, *J* = 8.0, 1.5 Hz). *Anal.* Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N,5.53. Found: C, 71.12; H, 4.51; N, 5.68.

Biaryl Coupling Reaction of 2-Iodo-3'-methoxy-*N*-methylbenzamide (1b)

The residue was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel. Elution with hexane:*i*-Pr_2O (2:1) gave 5-methyl-1-methoxyphenanthridin-6(5*H*)-one (**2b**) and successive elution with the same solvent gave 5-methyl-3-methoxyphenanthridin-6(5*H*)-one (**3b**).

5-Methyl-1-methoxyphenanthridin-6(5*H*)-one (2b): colorless needles (from AcOEt), mp 156.5-158 ˚C. IR (KBr) cm^{-1}: 1645. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.81 (3H, s), 4.07 (3H, s), 6.90 (1H, d, *J* = 8.0 Hz), 7.09 (1H, d, *J* = 8.0 Hz), 7.47 (1H, dd, *J* = 8.0, 8.0 Hz), 7.56 (1H, ddd, *J* = 7.5, 7.5, 1.0 Hz), 7.72 (1H, ddd, *J* = 8.5, 7.5, 1.5 Hz), 8.60 (1H, ddd, *J* = 8.0, 1.5, 0.5 Hz), 9.22 (1H, dd, *J* = 8.5, 1.0 Hz). *Anal.* Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N,5.85. Found: C, 75.21; H, 5.65; N, 5.94.

5-Methyl-3-methoxyphenanthridin-6(5*H*)-one (3b): colorless needles (from $CHCl_3$-Et_2O), mp 91.5-93 ˚C. IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.77 (3H, s), 3.93 (3H, s), 6.86 (1H, d, *J* = 2.5 Hz), 6.89 (1H, dd, *J* = 8.5, 2.5 Hz), 7.50 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.70 (1H, ddd, *J* = 8.0, 7.0, 1.3 Hz), 8.13 (1H, dd, *J* = 8.0, 1.0 Hz), 8.16 (1H, d, *J* = 8.5 Hz), 8.94 (1H, ddd, *J* = 8.0, 1.5, 1.0 Hz). *Anal.* Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N,5.85. Found: C, 75.22; H, 5.49; N, 5.82.

Biaryl Coupling Reaction of 3-(2-iodo-*N*-methylbenzamido)phenyl acetate (1c)

Water (1 mL) was added to the reaction mixture and was stirred for 15 min under reflux. The reaction mixture was acidified with 10% HCl and extracted with AcOEt. The residue was dissolved in $CHCl_3$–EtOH and subjected to column chromatography on silica gel. Elution with $CHCl_3$:hexane:AcOEt (5:3:1) gave 1-hydroxy-5-methylphenanthridin-6(5*H*)-one (**2d**) and successive elution with the same solvent gave 3-hydroxy-5-methylyphenanthridin-6(5*H*)-one (**3d**).

1-Hydroxy-5-methylphenanthridin-6(5*H*)-one (2d): colorless needles (from EtOH), mp 285-289 ˚C. IR (KBr) cm^{-1}: 3150, 1605. ^{1}H-NMR (500 MHz, d_6-acetone) δ: 3.76 (3H, s), 6.93 (1H, d, *J* = 8.0 Hz), 7.10 (1H, d, *J* = 8.0 Hz), 7.39 (1H, dd, *J* = 8.0, 8.0 Hz), 7.56 (1H, dd, *J* = 8.0, 8.0 Hz), 7.72 (1H, ddd, *J* = 8.5, 7.5, 1.5 Hz), 8.50 (1H, dd, *J* = 8.0, 2.0 Hz), 9.43 (1H, d, *J* = 8.0 Hz). *Anal.* Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N,6.22. Found: C, 74.58; H, 4.78; N, 6.19.

3-Hydroxy-5-methylyphenanthridin-6(5*H*)-one (3d): colorless prisms (from EtOH), mp 218-221 ˚C. IR (KBr) cm^{-1}: 3150, 1610. ^{1}H-NMR (500 MHz, d_6-acetone) δ: 3.71 (3H, s), 6.87 (1H, dd, *J* = 8.0, 2.5 Hz), 6.97 (1H, d, *J* = 2.5 Hz), 7.50 (1H, ddd, *J* = 8.0, 8.0, 1.5 Hz), 7.75 (1H, ddd, *J* = 8.0, 8.0, 1.5 Hz), 8.27 (1H, d, *J* = 8.0 Hz), 8.31 (1H, d, *J* = 8.0 Hz), 8.38 (1H, dd, *J* = 8.0, 1.5 Hz). *Anal.* Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.55; H, 4.99; N, 6.26.

Biaryl Coupling Reaction of 3-(2'-iodo-*N*-methylbenzamido)phenol (1d)

The reaction mixture was acidified with 10% HCl and extracted with AcOEt. The residue was dissolved in $CHCl_3$–EtOH and subjected to column chromatography on silica gel. Elution with $CHCl_3$:hexane:AcOEt (5:3:1) gave gave 1-hydroxy-5-methylphenanthridin-6(5*H*)-one (**2d**) and successive elution with the same solvent gave 3-hydroxy-5-methylyphenanthridin-6(5*H*)-one (**3d**).

REFERENCES AND NOTES

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