JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo501822m • Publication Date (Web): 04 Nov 2014

Substituent Electronic Effects Govern Direct Intramolecular C-N Cyclization of *N*-(Biphenyl)pyridin-2-amines Induced by Hypervalent Iodine(III) Reagents

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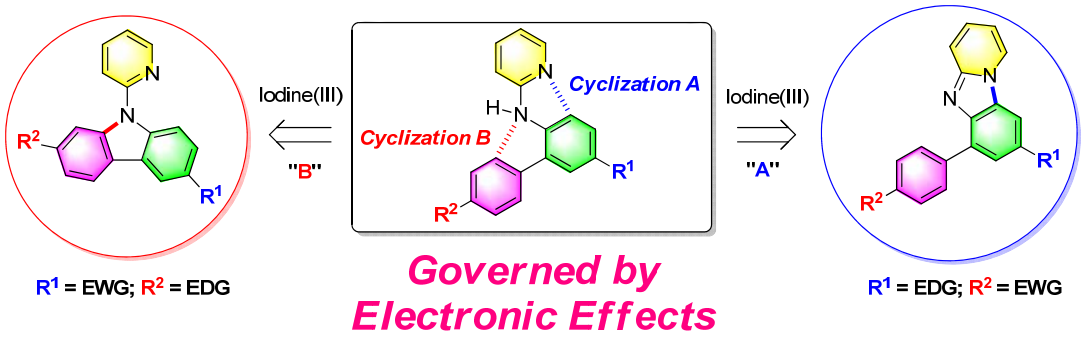


ABSTRACT: The hypervalent iodine(III) reagents induced the direct intramolecular C-N cyclization of *N*-(biphenyl)pyridin-2-amines to establish a variety of 6-arylbenzimidazoles and *N*-pyridinyl-9*H*-carbazoles is presented. The substituent electronic effects govern the formation of benzimidazoles and carbazoles from the reaction of *N*-(biphenyl)pyridin-2-amines with hypervalent iodine(III) reagents is investigated. Radical trapping and UV-Vis spectroscopic experiments on the detection of the cation radical are carried out. Rational mechanisms for these reactions are presented. The selective intramolecular C-N and C-O cyclization of *N*-(biphenyl)acetamides based on the substituent electronic effects is also presented.

INTRODUCTION

The aromatic C-N bond formation is of great importance in synthetic chemistry on constructing many natural products, pharmaceuticals, and optoelectronics.[1] Among various notable C-N coupling reactions,[2] the Buchwald-Hartwig amination remains outstanding due to the provided mild reaction conditions, extensive substrate scope, high functional group compatibility, and further applications.[3,4] Significant advances have been made on conventional C(Ar)-N coupling reactions, however, these methodologies used to employ prefunctionalized materials (e.g., aryl halides) with amines or amides.[2] The direct C-N coupling without using prefunctionalized materials therefore reveals its merit in organic synthesis.[5]

The direct intramolecular C-N coupling *via* C-H activation has been recognized as a very powerful and efficient method to establish various nitrogen heteroarenes, such as carbazoles, benzimidazoles, indoles and phenathridines.[6] A pioneering work on the direct intramolecular C-N cyclization of *N*-(biphenyl)acetamides to *N*-acetyl-9*H*-carbazoles *via* palladium(II)-catalyzed C-H activation had been reported by the Buchwald group in 2005.[6a] Gaunt,[6b] Driver,[6c] Youn,[6d] and Chu and Wu[6e,f] subsequently presented the direct intramolecular C-N cyclization of *N*-(benzyl)biphenyl-2-amines, 2-azido-1,1'-biphenyl, *N*-(tosyl)biphenyl-2-amines, and *N*-(biphenyl)pyridin-2-amines to *N*-benzyl-9*H*-carbazoles, 9*H*-carbazoles, *N*-tosyl-9*H*-carbazoles, and *N*-pyridinyl-9*H*-carbazoles, respectively, which were carried out by the palladium(II) and rhodium(II) catalysts. Very recently, the use of copper(II) catalyst for the direct intramolecular C-N

coupling of *N*-(biphenyl)picolinamides to 9*H*-carbazoles *via* the direct oxidation/coupling of C-H and N-H bonds was reported by Hirano and Miura.[6g] On the other hand, the Chang[6h] and Antonchick[6i] groups employed $PhI(OAc)_2$ as the oxidant into the direct intramolecular C-N cyclization of *N*-(biphenyl)benzenesulfonamides and *N*-biphenyl-4-methylbenzenesulfonamides to form *N*-phenylsulfonyl-9*H*-carbazoles and *N*-tosyl-9*H*-carbazoles, respectively. Moreover, Chang and co-workers found that the addition of $Cu(OTf)_2$ can facilitate the reaction, whereas the Antonchick group carried out the reaction by using a catalytic amount of $PhI(OAc)_2$ as the catalyst in the presence of 2,2'-diiodo-4,4',6,6'-tetramethylbiphenyl and peracetic acid.

In addition to carbazoles formation, Kutsumura and Saito,[6j] Maes,[6k] Zhu,[6l-o] Punniyamurthy,[6p] Das,[6q] and Antonchick[6r] presented the synthesis of benzimidazoles direct from either *N*-(phenyl)pyridin-2-amines or amidines *via* the intramolecular C-N bond formation using a stoichiometric amount of hypervalent iodine(III) reagents and a catalytic amount of $Cu(OAc)_2$, respectively. Kutsumura and Saito also used *N*-dihydrothiazin-2-yl and *N*-oxazin-2-yl anilines as the starting substrates. In the Maes group, they used the catalytic amount of $Cu(OAc)_2 \cdot H_2O$ with 3,4,5-trifluorobenzoic acid as a superior additive to achieve the synthesis of benzimidazoles in good product yields. Zhu and co-workers combined $Fe(NO_3)_3 \cdot 9H_2O$ with $Cu(OAc)_2$ to generate an active copper(III) species to catalyze the synthesis of benzimidazoles *via* an electrophilic aromatic substitution pathway. Furthermore, an *in situ* preparation of the hypervalent iodine(III) reagent was developed by the same group and able to catalyze the C-H cycloamination of

N-aryl-2-aminopyridines and *N*-arylamidines. They additionally utilized that $PhI(OPiv)_2$ in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and $PhI(OAc)_2$ combining Cs_2CO_3 as an additive in 2,2,2-trifluoroethanol (TFE) to perform the synthesis of benzimidazoles through the demethylenation/C-H cycloamination of *N*-benzyl-2-aminopyridines and the direct C-H imidation of *N*-arylamidines, respectively. On the other hand, the Punniyamurthy group used iodobenzene as a precatalyst to furnish the synthesis of benzimidazoles in the presence of *m*CPBA through the C-H amination of *N*-subsituted amidines. Das and co-workers also reported the synthesis of benzimidazoles catalyzed by $PhI(OAc)_2$ in water. Recently, the Antonchick group achieved the $PhI(OAc)_2$-catalyzed the annulation of arenes with 2-aminopyridines in HFIP to produce various benzimidazoles within a methyl group as a traceless non-chelating directing group.

From the above reports and our previous work,[6e,f] we were interested in a direct intramolecular C-N bond formation of the starting substrates bearing two feasible C-N coupling sites. Which coupling pathway does it prefer to take place in the situation? *N*-(Biphenyl)pyridin-2-amines were thus chosen as model molecules to investigate the site selectivity under the hypervalent iodine(III) reagent conditions, and we especially focused on the influence of the substituent electronic effects. Radical trapping and UV-Vis spectroscopic experiments were also applied to elucidate whether a cation radical intermediate was generated in the course of the reaction. Finally, the selective intramolecular C-N and C-O cyclization of *N*-(biphenyl)acetamides was studied based on the substituent electronic effects.

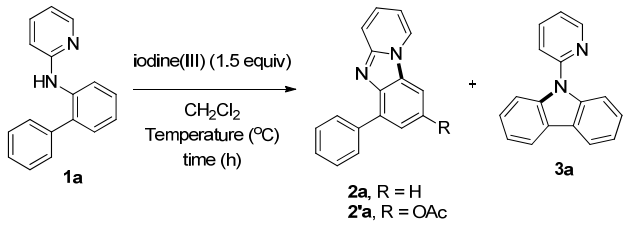
RESULTS AND DISCUSSION

Optimization for the Direct Intramolecular C-N Cyclization of *N*-(Biphenyl)pyridin-2-amines:

First, starting substrates **1** for the presented study were prepared by the reaction of *N*-phenylpyridin-2-amines (**8**) with a series of arylborane reagents **9** and **10** *via* palladium(II)-catalyzed direct C-H activation and arylation using copper(II) acetate and *p*-benzoquinone (BQ) as the oxidant and promotor, respectively, in *tert*-butyl alcohol[6e,f] (the detail synthetic procedure, please see the Experimental Section). Subsequently, the direct intramolecular C-N cyclization of *N*-(biphenyl)pyridin-2-amines **1** to 6-arylbenzimidazoles **2** and *N*-pyridinyl-9*H*-carbazoles **3** was examined by the reaction of *N*-([1,1'-biphenyl]-2-yl)pyridin-2-amine (**1a**) with iodobenzene diacetate ($PhI(OAc)_2$) and iodobenzene bis(trifluoroacetate) ($PhI(OTFA)_2$), respectively, in dichloromethane.[7] These experimental results are summarized in Table 1. First, the reaction was carried out at 0 ^oC to room temperature and traced by Thin-Layer Chromatography (TLC) and we found that substrate **1a** was almost consumed within 1-2 hours using either $PhI(OAc)_2$ or $PhI(OTFA)_2$ as the oxidant. In these two cases, 6-phenylbenzimidazole **2a** was generated as the major product (48% yield for both of $PhI(OAc)_2$ and $PhI(OTFA)_2$) while *N*-pyridinyl-9*H*-carbazole **3a** as the minor product (6% yield for $PhI(OAc)_2$ and 8% for $PhI(OTFA)_2$) (entry 1 and 5, Table 1). Herein, an additional product, 8-acetoxy-6-phenylbenzimidazole (**2'a**) was isolated in 11% yield by the use of $PhI(OAc)_2$, however, none of such product (i.e., **2'a**) was obtained when $PhI(OAc)_2$ was replaced by

$PhI(OTFA)_2$ in the reaction. In order to examine the influence of the reaction temperature, the reaction was subsequently proceeding at room temperature, 40-50, and 60-70 ^oC. According to experimental results, substrate **1a** was again consumed within 1-2, 0.5 hours, and 10 minutes, respectively, at these reaction temperatures and whatever $PhI(OAc)_2$ or $PhI(OTFA)_2$ was used (entries 2-4 and 6-8, Table 1). Although a higher reaction temperature can efficiently reduce the reaction time, the product yields and ratios of **2a**, **2'a**, and **3a** do not have much difference at these reaction temperatures (see Table 1). We therefore chose room temperature as the optimal reaction temperature for the direct intramolecular C-N cyclization of **1**.

Table 1. Optimization for the Direct Transformation of 1a to 2a, 2'a and 3a



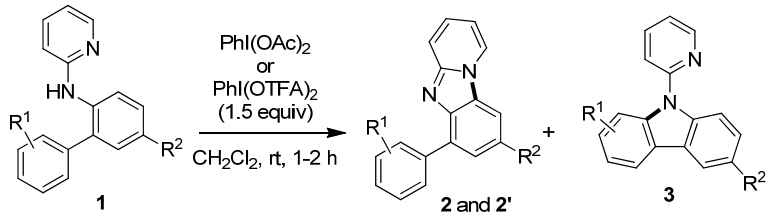
entry	iodine(III)	T (^oC)	*t* (h)	product ratio (**2a**:**2'a**:**3a**)[a]	total yield (%)[b]
1	$PhI(OAc)_2$	0-rt	2	74:17:9	65
2		rt	2	71:18:11	88
3		40-50	0.5	69:19:12	88
4		60-70	10 min	62:28:10	89
5	$PhI(OTFA)_2$	0-rt	1	85:0:15	56
6		rt	1	94:0:6	80
7		40-50	0.5	93:0:7	85
8		60-70	10 min	93:0:7	89

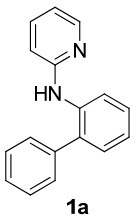
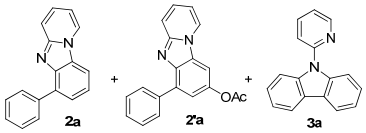
[a]Product ratio was determined by GC-FID for three runs. [b]Product yield was obtained as an average for three runs by GC-FID (using *n*-octadecane as the internal standard).

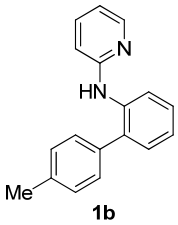
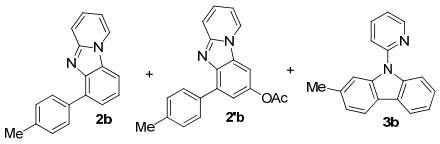
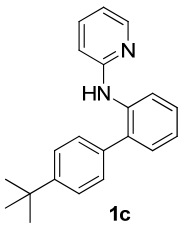
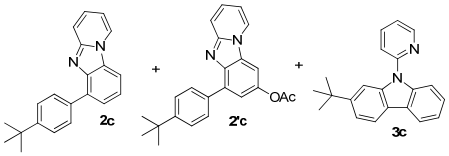
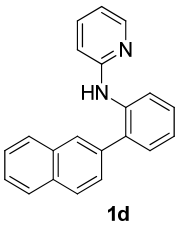
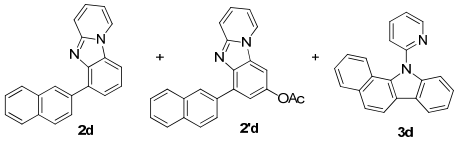
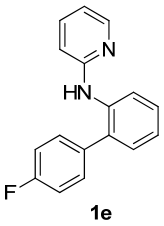
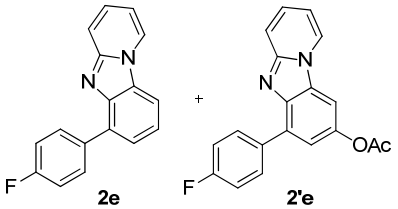
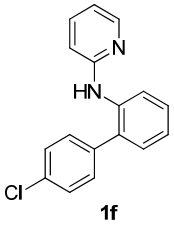
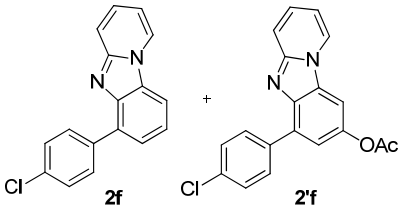
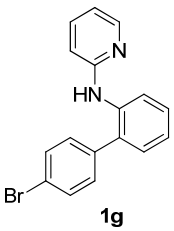
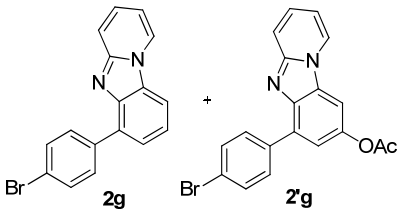
Substrate Scope: With the optimal reaction conditions in hand (1.5 equivalents of iodine(III) reagents in CH_2Cl_2 at room temperature for 1-2 hours), we subsequently carried out the reaction of **1** with either $PhI(OAc)_2$ or $PhI(OTFA)_2$ to give these following C-N coupling products, 6-arylbenzimidazoles **2**, 8-acetoxy-6-arylbenzimidazoles **2'** and *N*-pyridinyl-9*H*-carbazoles **3** in modest to excellent total yields (30-99%, Table 2). Substrates **1a-c** bearing a hydrogen, methyl, and *tert*-butyl substituent, respectively, by the treatment of $PhI(OAc)_2$ afforded 6-arylbenzimidazoles **2a-c** as major products (45-57% yields) and both of 8-acetoxy-6-arylbenzimidazoles **2'a-c** and *N*-pyridinyl-9*H*-carbazoles **3a-c** as minor products (43-55% yields) (entries 1-3, Table 2). Product ratios of **2a-c**, **2'a-c**, and **3a-c** were determined by GC-FID to be 71:18:11, 60:26:14, and 56:28:16, respectively. The reaction of **1d** bearing a naphthyl group with $PhI(OAc)_2$ produced *N*-pyridinyl-9*H*-carbazole **3d**[8] (65% yield) with two concomitant minor products, 6-naphthylbenzimidazole **2d** (13% yield) and 8-acetoxy-6-naphthylbenzimidazole **2'd** (7% yield) (entry 4, Table 2). Furthermore, substrates **1e-h** bearing a halogen group (F-, Cl, Br-, and I-) were also introduced into the reaction to give a mixture of benzimidazoles **2e-g** and 8-acetoxy-substituted benzimidazoles **2'e-g** in product ratios **2e**:**2'e** = 88:12, **2f**:**2'f** = 85:15, and **2g**:**2'g** = 72:28 by GC-FID with 87-90% total yields and none of *N*-pyridinyl-9*H*-carbazoles **3e-g** was isolated (entries 5-7, Table 2). However, only a single product, benzimidazole **2h** (80% yield) was isolated in the case of **1h** (entry 8, Table 2). In addition, we isolated benzimidazoles **2i-m** as a single product in 70-96% yields from the reaction of **1i-m** with $PhI(OAc)_2$ (entries 9-13, Table 2). In these cases of **1i**

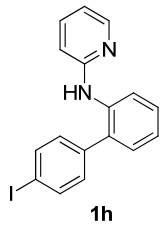
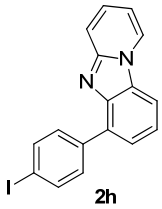
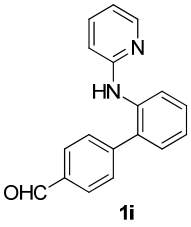
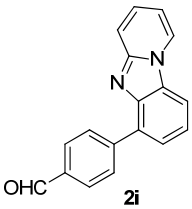
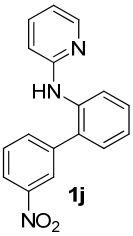
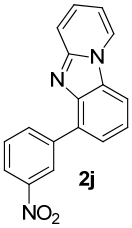
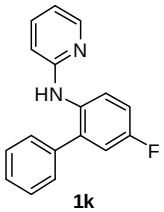
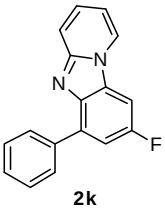
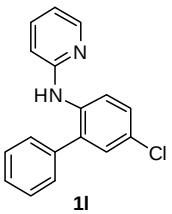
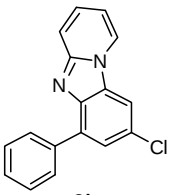
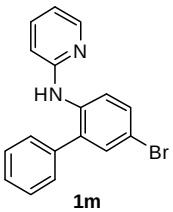
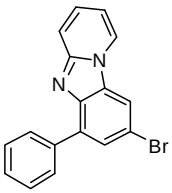
and **1j**, the electron-withdrawing group (-CHO and -NO_2) might disfavor the acetoxylation on the *N*-phenyl ring that eventually resulted in none of products **2'i-j** formed. On the other hand, the halogen substituent (F-, Cl-, and Br-) tagged at the *para* position of the *N*-phenyl ring in substrates **1k-m** prevented the acetoxylation by $PhI(OAc)_2$. In addition to $PhI(OAc)_2$, $PhI(OTFA)_2$ was also employed to substrates **1** under the aforementioned reaction conditions that eventually generated the alternative of benzimidazole **2** and carbazole **3** where none of acetoxylated products **2'** was formed (see Table 2). This might be due to the poor reactivity of the trifluoroacetate anion ($^-$OTFA). Other than that, the reaction of **1a-m** with $PhI(OTFA)_2$ showed similar results with that of $PhI(OAc)_2$ in terms of chemical yields and product ratios. These structures of benzimidazoles **2f** and **2'f** were finally secured by X-ray crystallography (see Figure S2, Supporting Information).[9]

Table 2. Direct Intramolecular C-N Cyclization of 1 to 2, 2', and 3 Induced by Either of $PhI(OAc)_2$ and $PhI(OTFA)_2$



entry	substrate **1**	product ratio (**2**:**2'**:**3**)[a]	total yield (%)[b]
1	 **1a**	 **2a** **2'a** **3a** 71:18:11 (97:0:3)	80 (75), 74 (70)

2	 1b	 2b + 2'b + 3b 56:28:16 (90:0:10)	82 (83), 76 (75)
3	 1c	 2c + 2'c + 3c 60:26:14 (97:0:3)	75 (84), 70 (79)
4	 1d	 2d + 2'd + 3d 15:8:77 (43:0:57)	30 (38), 24 (32)
5	 1e	 2e + 2'e 88:12	87 (88), 83 (85)
6	 1f	 2f + 2'f 85:15	88 (89), 85 (85)
7	 1g	 2g + 2'g 72:28	80 (54), 74 (50)

8	 **1h**	 **2h**	80 (90), 73 (85)
9	 **1i**	 **2i**	70 (80), 65 (76)
10	 **1j**	 **2j**	96 (99), 91 (95)
11	 **1k**	 **2k**	70 (79), 64 (74)
12	 **1l**	 **2l**	79 (73), 75 (70)
13	 **1m**	 **2m**	71 (74), 65 (70)

[a]Product ratio was determined by GC-FID for three runs and the ratio in the parentheses is from the treatment of $PhI(OTFA)_2$. [b]Product yield was determined as an average by GC-FID for three runs (using *n*-octadecane as the internal standard) and the value in the parentheses is from the treatment of $PhI(OTFA)_2$. The isolated yield was reported after the

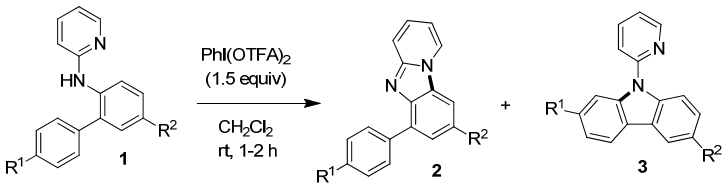
comma for both of $PhI(OAc)_2$ and $PhI(OTFA)_2$.

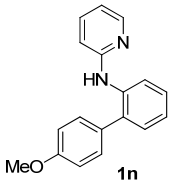
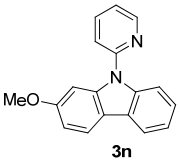
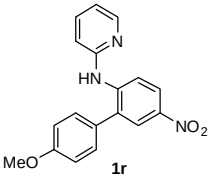
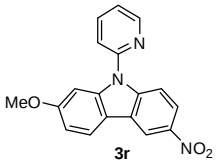
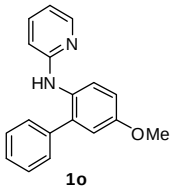
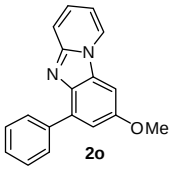
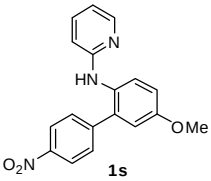
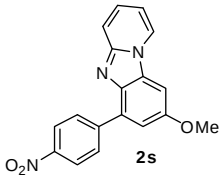
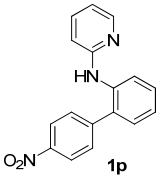
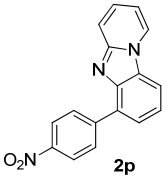
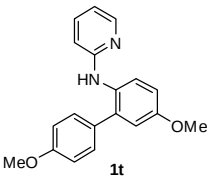
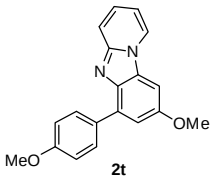
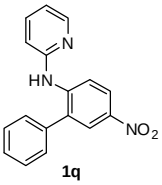
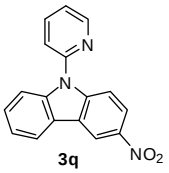
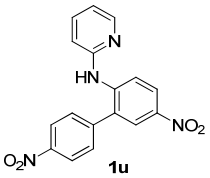
Based on the above experimental results, we found that the substituent electronic effects seem to play as an important factor for the formation of benzimidazole **2** and carbazole **3** in the direct intramolecular C-N cyclization of *N*-(biphenyl)pyridin-2-amines **1**.

Substituent Electronic Effects in the Direct Intramolecular C-N Cyclization of 1: In order to verify the influence of the substituent electronic effects in the direct intramolecular C-N cyclization of **1**, we employed substrates **1n-u** bearing the alternative of methoxy (-OMe, a strong electron-donating substituent) and nitro group ($-NO_2$, a strong electron-withdrawing substituent) to investigate the site selectivity of the direct intramolecular C-N cyclization of **1**. These experimental results are summarized in Table 3. We found that the reaction of substrates **1n-u** with $PhI(OTFA)_2$ only produced a single product, 6-arylbenzimidazole **2** or *N*-pyridinyl-9*H*-carbazole **3** (see Table 3).[10] First, substrate **1n** (R_1 = OMe/R_2 = H) was transformed to carbazole **3n** in 95% yield (entry 1, Table 3). By contrast, substrate **1o** (R_1 = H/R_2 = OMe) by the treatment of $PhI(OTFA)_2$ generated benzimidazole **2o** in 82% yield (entry 2, Table 3). We subsequently carried out the reaction of **1p** (R_1 = NO_2/R_2 = H) and **1q** (R_1 = H/R_2 = NO_2) with $PhI(OTFA)_2$ and found the anticipated benzimidazole **2p** and carbazole **3q** were produced in 90% and 80% yields, respectively (entry 3 and 4, Table 3).[11] On the basis of the above experimental results, the formation of benzimidazole **2** and carbazole **3** in the reaction of **1** with $PhIX_2$ (X = OAc and OTFA) can indeed selectively be

controlled not only by a strong electron-donating substituent (e.g., -OMe) but also a strong electron-withdrawing substituent (e.g., -NO_2). In addition to **1n-q** bearing a methoxy or -nitro substituent, substrates **1r-u** bearing a pair of methoxy and nitro substituents were also examined under the same reaction conditions. As expected, **1r** (R_1 = OMe/R_2 = NO_2) and **1s** (R_1 = NO_2/R_2 = OMe) were definitely transformed to carbazole **3r** and benzimidazole **2s** in 68% and 58% yields, respectively (entry 5 and 6, Table 3). Finally, a competitive experiment for the direct intramolecular C-N cyclization of **1** was carried out by the employment of di-methoxy and di-nitro substituted substrates **1t** (R_1 = OMe/R_2 = OMe) and **1u** (R_1 = NO_2/R_2 = NO_2). From the reaction of **1t** with PhI(OTFA)$_2$, only benzimidazole **2t** was isolated in 68% yield and none of carbazole **3t** was obtained (entry 7, Table 3). This might indicate that the amino group of **1t** also plays as an electron-donating role and thus prefer to generate benzimidazole **2t** as the single product. However, we did not observe any anticipated benzimidazole **2u** or carbazole **3u** was generated in the reaction of **1u** with PhI(OTFA)$_2$, and only recovered a large amount of starting material (entry 8, Table 3). This implies that a strong electron-withdrawing group (e.g., -NO_2) tagged on the certain aryl ring could deactivate the aryl rings and then prevents the intramolecular C-N bond coupling. Herein, the competitive experiment again elucidates that the substituent electronic effects govern the direct intramolecular C-N cyclization of **1**.

Table 3. The Influence of the Substituent Electronic Effects on $PhI(OTFA)_2$-Induced the Direct Intramolecular C-N Cylcyization of 1



entry	substrate **1**	product **2** or **3**	yield (%)[a]	entry	substrate **1**	product **2** or **3**	yield (%)[a]
1	 **1n**	 **3n**	95 (90)	5	 **1r**	 **3r**	58 (55)
2	 **1o**	 **2o**	82 (80)	6	 **1s**	 **2s**	68 (62)
3	 **1p**	 **2p**	90 (86)	7	 **1t**	 **2t**	68 (64)
4	 **1q**	 **3q**	80 (75)	8	 **1u**	--	0

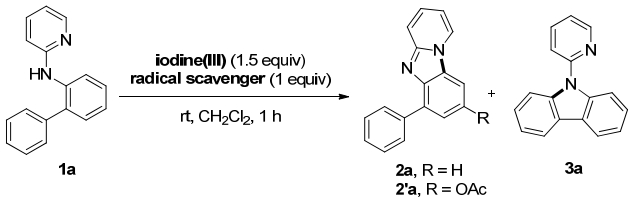
[a]Product yield was determined as an average by GC-FID using *n*-octadecane as the internal standard and the isolated yield was reported in the parenthesis.

The Cation Radical Detection and Radical Trapping Experiments: In the direct intramolecular C-N cyclization of **1** with both of $PhI(OAc)_2$ and $PhI(OTFA)_2$, we initially recognized the cation radical is the only key intermediate based on the Kita's pioneering work in 1994.[12] In their studies, UV-Vis and ESR spectroscopic technologies were employed to detect the cation radical. In view of this, we also attempted to detect the cation radical arose from the reaction of **1o** with either of $PhI(OTFA)_2$ and $PhI(OAc)_2$ in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$) by the UV-Vis spectroscopy (see Figure S3, Supporting Information). In the solution of **1o** with $PhI(OTFA)_2$, we observed that a broaden absorption band between 400 and 550 nm was arose (Figure S3a, Supporting Information) and that is suggested to be the characteristic of the cation radical ($\mathbf{1o}^{\bullet+}$) according to Kita's studies.[12] However, none of additional absorption bands was observed in the case of **1o** with $PhI(OAc)_2$ and its UV-Vis spectrum is almost the same with that of free substrate **1o** (Figure S3b, Supporting Information). This indicates that none of the cation radical is generated in the reaction of **1o** with $PhI(OAc)_2$.

In addition to UV-Vis spectroscopic experiments, we also carried out radical trapping experiments by using 1,1-diphenylethylene (DPE) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) as radical scavengers into the reaction of **1a** with $PhI(OAc)_2$ or $PhI(OTFA)_2$. These experimental results are summarized in Table 4. The total yield for the reaction of **1a** with $PhI(OAc)_2$ is slightly down to 65% and 45% from 80% (none of radical scavengers, entry 1, Table 4) by the addition of DPE and BHT (entry 3 and 5, Table 4). However, the total yield for the case of $PhI(OTFA)_2$ is

dramatically decreased to 15% and 6% from 75% (none of radical scavengers, entry 2, Table 4) in the presence of DPE and BHT (entry 4 and 6, Table 4). These experimental results are consistent with that of the cation radical detection of **1o** by UV-Vis spectroscopy (see Figure S3, Supporting Information).

Table 4. The Influence of Radical Scavengers on the Reaction of 1 with $PhI(OAc)_2$ and/or $PhI(OTFA)_2$

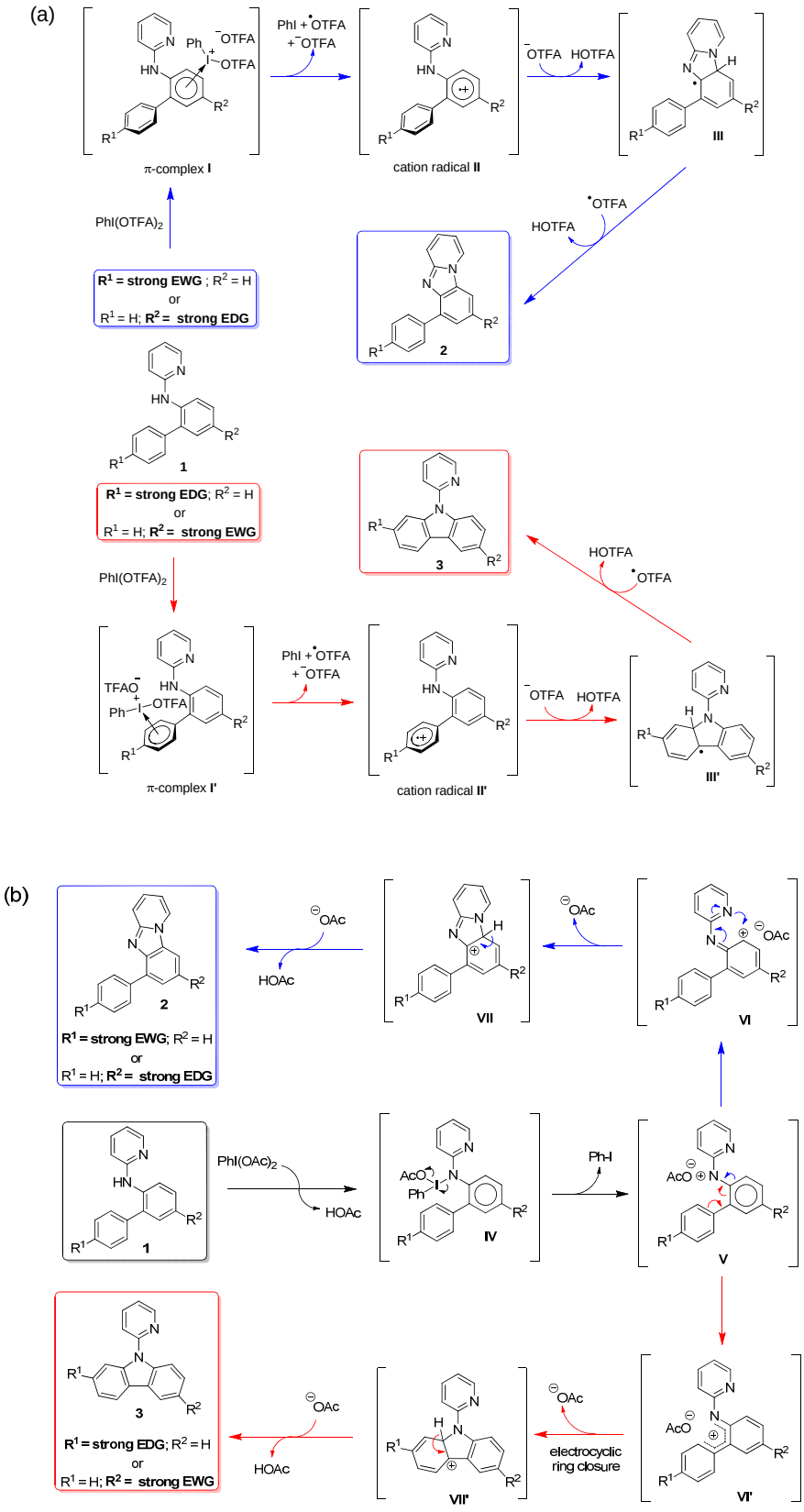


entry	radical scavenger	iodine(III)	product ratio (**2a**:**2'a**:**3a**)[a]	total yield (%)[b]
1	--	$PhI(OAc)_2$	71:18:11	80
2	--	$PhI(OTFA)_2$	97:0:3	75
3	DPE[c]	$PhI(OAc)_2$	80:12:8	65
4		$PhI(OTFA)_2$	91:0:9	15
5	BHT[c]	$PhI(OAc)_2$	87:0:13	45
6		$PhI(OTFA)_2$	100:0:0	6

[a]Product ratio was determined by GC-FID for three runs. [b]Product yield was determined as an average by GC-FID for three runs using *n*-octadecane as the internal standard. [c]DPE = 1,1-diphenylethylene; BHT = 2,6-di-*tert*-butyl-4-methylphenol.

Based on these UV-Vis spectroscopic and radical trapping experimental results, we believe that the cation radical (i.e., $\mathbf{1}^{\bullet+}$) is the key intermediate in the direct intramolecular C-N cyclization of **1** with $PhI(OTFA)_2$, but does not form in the case of $PhI(OAc)_2$. By contrast, the nitrenium ion (R_2N^+) is suggested to be the key intermediate in the reaction of **1** with $PhI(OAc)_2$.[13]

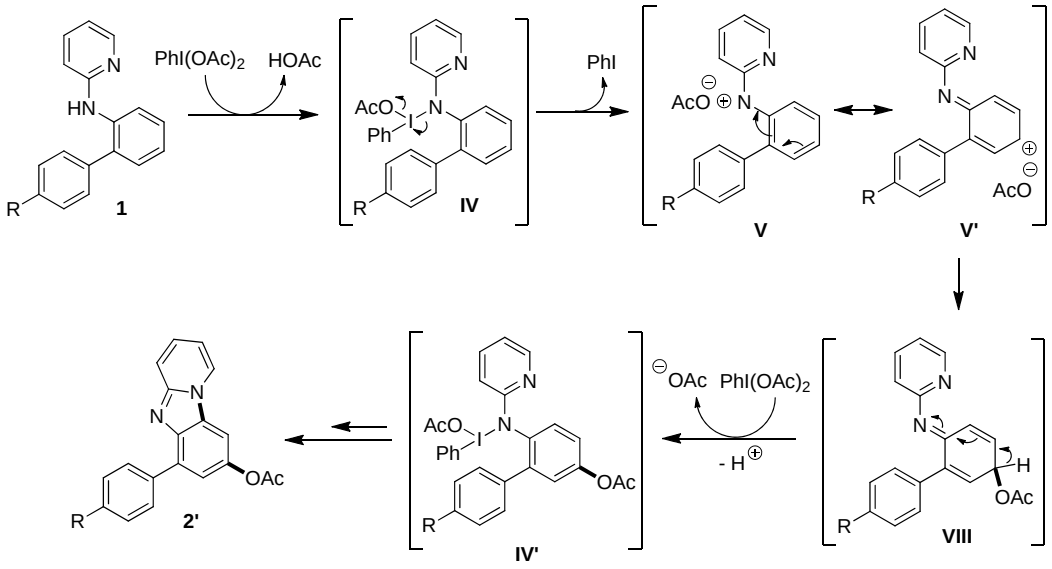
Proposed Mechanisms: Based on our studies, two possible reaction mechanisms *via* the cation radical and nitrenium ion for the direct intramolecular C-N cyclization of *N*-(biphenyl)pyridine-2-amines **1** to benzimidazoles **2** and carbazoles **3** by $PhI(OTFA)_2$ and $PhI(OAc)_2$ are presented in Scheme 1. In Scheme 1a, the binding of **1** with $PhI(OTFA)_2$ generates π-complex **I** (and/or **I'**) on the electron-richer phenyl ring. The π-complex **I** (and/or **I'**) is then transformed to the cation radical **II** (and/or **II'**) *via* one-electron abstraction by $PhI(OTFA)_2$. Subsequently, the cation radical **II** (and/or **II'**) is converted to a radical intermediate **III** (and/or **III'**) through the intramolecular C-N coupling. Finally, benzimidazole **2** and carbazole **3** are given through the re-aromatization of **III** and **III'**. In Scheme 1b, the amine nitrogen of **1** first attacks the iodine(III) center of $PhI(OAc)_2$ to generate the iodonium intermediate **IV** and subsequently converted to intermediate **V** by a release of iodobenzene. The intermediate **V** is then divided into the alternative of intermediates **VI**[14a] and **VI'**[14b] *via* the electron transfer process. Furthermore, the pyridinyl nitrogen of **VI** attacks the carbon cation to generate a C-N bond and undergoes the electron transfer process to give intermediate **VII**. On the other hand, the intermediate **VI'** is transformed to **VII'** *via* the electrocyclic ring closure and that eventually constructs a new C-N



Scheme 1. Proposed mechanism for the formation of benzimidazole **2** and carbazole **3** by the reaction of **1** with (a) $PhI(OTFA)_2$ and (b) $PhI(OAc)_2$.

bond. Finally, both of benzimidazole **2** and carbazole **3** are given by the re-aromatization of **VII** and **VII'**.

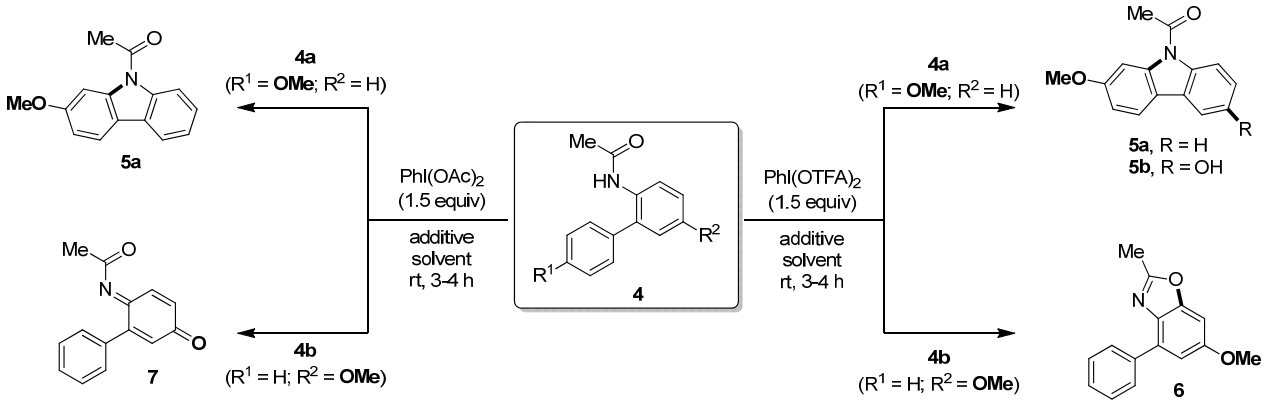
Regarding the formation of 8-acetoxy-6-arylbenzimidazole **2'**, we initially suspected that it is derived from the reaction of 6-arylbenzimidazole **2** with $PhI(OAc)_2$. To verify the hypothesis, we independently carried out the reaction of **2a** with $PhI(OAc)_2$ (1.5 equivalents) under the aforementioned reaction conditions, but none of anticipated product **2'a** was detected by ^1H NMR spectroscopy and GC-FID. In the reaction, only starting material (i.e., **2a**) was recovered even the reaction time was prolonged. Thus, we suppose the acetoxylation might first take place on starting substrate **1** and then undergo the direct intramolecular C-N coupling to give the acetoxylated product **2'**. A proposed mechanism for the formation of acetoxylated benzimidazole **2'** from **1** by the employment of $PhI(OAc)_2$ is presented in Sc heme 2. Initially, the nitrenium ion **V** is generated through the ligand exchange between **1** and $PhI(OAc)_2$ and the subsequent nitrogen-iodine bond cleavage of intermediate **IV** by a release of iodobenzene. Furthermore, the charge delocalized intermediate **V'** is attacked by the acetate anion to afford intermediate **VIII**. Then intermediate **VIII** is fast converted to **IV'** *via* re-aromatization process promoted by $PhI(OAc)_2$. The acetoxylated benzimidazole **2'** is eventually formed through the direct intramolecular C-N cyclization of **IV'**.



Scheme 2. Proposed mechanism for the formation of acetoxylated benzimidazole **2'** from **1** by the employment of $PhI(OAc)_2$.

The Selective Intramolecular C-N and C-O Cyclization of *N*-(Biphenyl)acetamides Governed by the Substituent Electronic Effects: In addition to *N*-(biphenyl)pyridin-2-amines **1**, we also introduced *N*-(biphenyl)acetamide **4** into the reaction by the treatment of $PhI(OTFA)_2$ and $PhI(OAc)_2$, respectively. These experimental results are summarized in Table 5. Herein, compounds **4a** and **4b**[15] were chose as model substrates (the detail synthetic procedure, please see the Experimental Section). Both of them were subsequently treated with $PhI(OTFA)_2$ in dichloromethane at room temperature, however, only 15% yield of carbazole **5b**[16] was isolated from the reaction of **4a** with $PhI(OTFA)_2$ (entry 1, Table 5), and none of anticipated benzoxazole **6** was obtained in the case of **4b** (entry 2, Table 5). However, 86% yield of carbazole **5a** and 90% yield of benzoxazole **6** were given when acetonitrile was used as the solvent in the reaction of **4a** and **4b**

Table 5. Direct Intramolecular C-N and C-O Cyclization of 4 in the Presence of $PhI(OAc)_2$ and/or $PhI(OTFA)_2$



entry	substrate	oxidant	additive	solvent	product	yield (%)[a]
1	**4a**	$PhI(OTFA)_2$	--	CH_2Cl_2	**5b**	14 (10)
2	**4b**	$PhI(OTFA)_2$	--	CH_2Cl_2	**6**	0
3	**4a**	$PhI(OTFA)_2$	--	CH_3CN	**5a**	86 (80)
4	**4b**	$PhI(OTFA)_2$	--	CH_3CN	**6**	90 (85)
5	**4a**	$PhI(OTFA)_2$	TMSOTf[b]	CH_3CN	**5a**	0
6	**4b**	$PhI(OTFA)_2$	TMSOTf[b]	CH_3CN	**6**	53 (47)
7	**4a**	$PhI(OAc)_2$	--	CH_2Cl_2	**5a**	47 (41)
8	**4b**	$PhI(OAc)_2$	--	CH_2Cl_2	**7**	10 (6)
9	**4a**	$PhI(OAc)_2$	--	CH_3CN	**5a**	89 (85)
10	**4b**	$PhI(OAc)_2$	--	CH_3CN	**7**	10 (5)
11	**4a**	$PhI(OAc)_2$	TMSOTf[b]	CH_3CN	**5a**	0
12	**4b**	$PhI(OAc)_2$	TMSOTf[b]	CH_3CN	**6**	42 (35)

[a]Product yield was determined as an average by GC-FID for three runs using *n*-octadecane as the internal standard and

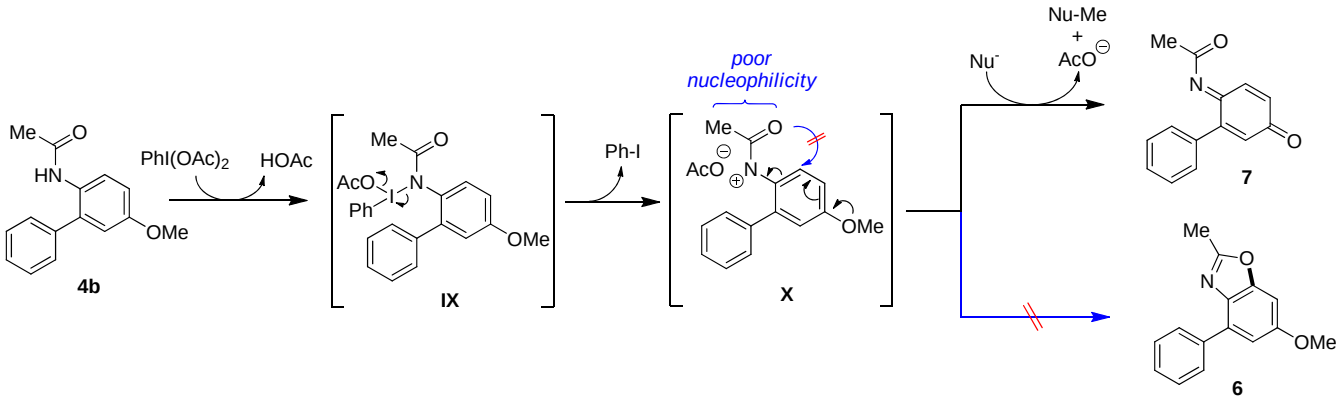
the isolated yield was reported in the parenthesis. [b]2 equivalents of TMSOTf was added.

with $PhI(OTFA)_2$ (entry 3 and 4, Table 5). In 2012, Yu and co-workers reported that $PhI(OTFA)_2$-mediated intramolecular C-O coupling of electron-richer *N*-(phenyl)benzamides to establish a variety of benzoxazoles.[17] Under their optimal reaction conditions (1.2 equiv $PhI(OTFA)_2$ and 2 equiv TMSOTf at room temperature in acetonitrile), a *N*-(biphenyl)acetamide analogue, *N*-(phenyl)acetamide was unable to afford 2-methylbenzo[*d*]oxazole. Based on their reaction conditions, TMSOTf was added into the reaction of **4a**,**b** with $PhIX_2$ (X = OTFA and OAc), but none of anticipated carbazole **5a** was generated (entry 5 and 11, Table 5) and concurrently the product yield of benzoxazole **6** was not obviously improved (42-53%, entry 6 and 12, Table 5). Finally, carbazole **5a** was generated in 47-89% yields from the reaction of **4a** with $PhI(OAc)_2$ in both of dichloromethane and acetonitrile (entry 7 and 9, Table 5).

On the other hand, the reaction of **4b** with $PhI(OAc)_2$ in dichoromethane or acetonitrile did not give the desired benzoxazole **6** (entry 8 and 10, Table 5), by contrast, approximate 10% yield of benzoquinoneimine **7** was isolated from the reaction.[18] A possible mechanism for the formation of **7** from **4b** by $PhI(OAc)_2$ is proposed in Scheme 3. The ligand exchange between **4b** and $PhI(OAc)_2$ produces intermediate **IX** which is subsequently converted to the nitrenium ion **X** by a release of iodobenzene. Compound **7** is then generated *via* the nucleophilic substitution (S_N2) of methoxy group and the electron transfer of intermediate **X**. Based on the finding of benzoquinoneimine **7**, it

again strongly support the proposal of nitrenium ion as a key intermediate in the reaction of **1** (even **4**) with $PhI(OAc)_2$ (see Scheme 1b). In addition, we did not isolate benzimidazole **6** in the reaction of **4b** with $PhI(OAc)_2$, and this might be due to the poor nucleophilicity of the acetamide group (see Scheme 3).

On the basis of the above studies, we found that $PhI(OTFA)_2$ can selectively induce the direct intramolecular C-N and C-O cyclization of *N*-(biphenyl)acetamides **4** based on the substituent electronic effects to afford the alternative of carbazole **5** and benzoxazole **6** in good yields (86-90%) in acetonitrile.



Scheme 3

CONCLUSION

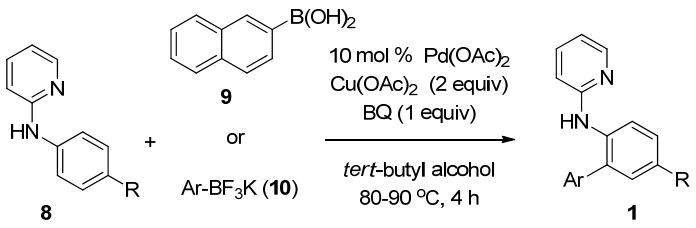
We have demonstrated the direct intramolecular C-N cyclization of *N*-(biphenyl)pyridin-2-amines governed by the substituent electronic effects to form either benzimidazoles or carbazoles with hypervalent iodine(III) reagents. Rational reaction mechanisms in the study were presented based on controlled experiments, radical intermediate detection, and the formation of the key product, in

which the cation radical was suggested to be the key intermediate for the reaction by $PhI(OTFA)_2$, whereas another intermediate is believed to be the nitrenium ion when $PhI(OAc)_2$ is used. In addition, the selective intramolecular C-N and C-O cyclization of *N*-(biphenyl)acetamides was achieved based on the substituent electronic effects. Finally, we believe our observation and investigation can provide an insight into related carbon-heteroatom coupling reactions *via* the cation radical or nitrenium ion and as a useful synthetic strategy in organic synthesis.

EXPERIMENTAL SECTION

General: Solvents and reagents were purchased from commercial suppliers and used without purification. ^{1}H NMR spectra were measured on 300 and 500 MHz NMR spectrometers. Natural abundance ^{13}C NMR spectra were measured by using 300 and 500 MHz NMR spectrometers operating at 75 and 125 MHz, respectively. Chemical shifts are given in parts per million (ppm) and coupling constant *J* in hertz (Hz) for both nuclei, with the solvent (usually $CDCl_3$) peak as an internal standard. The reference peak for ^{1}H is δ 7.26 of chloroform, and for ^{13}C it is the central peak at δ 77.0. Low- and high-resolution mass spectrometry was obtained by the following ionization method and mass analyzer type: EI-magnetic sector. Melting points were measured by using open capillary tubes and uncorrected.

General Procedure for the Synthesis of Starting Substrate 1:



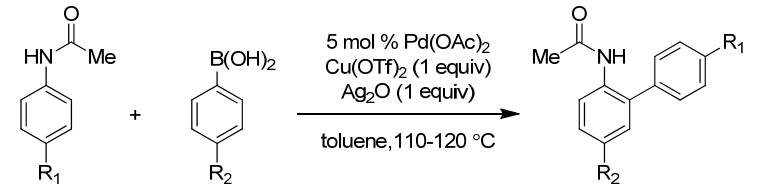
The synthesis of substrates **1a-c**, **e-g**, **i-j**, **n**, **p** had been reported, please see ref. 6e. A well-stirred solution of *N*-phenylpyridin-2-amines **8** (**8a**, R = H: 90 mg, 0.53 mmol for **1d** and **1h**; **8k**, R = F: 100 mg, 0.532 mmol for **1k**; **8l**, R = Cl: 109 mg, 0.534 mmol for **1l**; **8m**, R = Br: 132 mg, 0.530 mmol for **1m**; **8o**, R = OMe: 106 mg, 0.530 mmol for **1o**; **8q**, R = NO_2: 114 mg, 0.530 mmol for **1q**) with 2-naphthylboronic acid (**9**) (138 mg, 0.802 mmol for **1d**), potassium *p*-iodophenyltrifluoroborate (**10b**) (123 mg, 0.398 mmol for **1h**), potassium phenyltrifluoroborates (**10a**) (147 mg, 0.799 mmol for **1k-m**, **o**, **q**), potassium *p*-methoxyphenyltrifluoroborates (**10c**) (171 mg, 0.799 mmol for **1r** and **1t**), potassium *p*-nitrophenyltrifluoroborates (**10d**) (182 mg, 0.795 mmol for **1s** and **1u**), 10 mol % $Pd(OAc)_2$ (12 mg, 0.054 mmol), $Cu(OAc)_2$ (193 mg, 1.06 mmol), BQ (57 mg, 0.53 mmol) in *tert*-butyl alcohol (10 mL) was heated to 80-90 ^oC, and stirred at this temperature for 4 hours. After cooling down to room temperature, the solution was filtered through a pad of celite and then the filtrate was added to water (15 mL). The solution was further extracted with ethyl acetate (10 mL x 2). Finally, organic layers were combined, dried over $MgSO_4$, filtered, and evaporated *in vacuum*. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (60/1 to 10/1) as the eluent to give a series of compounds **1**. All product yields were determined by GC-FID using *n*-octadecane as the internal standard and shown as

follows: **1d**: 58% (92 mg, 0.31 mmol); **1h**: 22% (45 mg, 0.12 mmol); **1k**: 40% (55 mg, 0.21 mmol), **1l**: 46% (67 mg, 0.24 mmol); **1m**: 41% (72 mg, 0.22 mmol), **1o**: 62% (91 mg, 0.33 mmol); **1q**: 38% (49 mg, 0.17 mmol); **1r**: 22% (39 mg, 0.12 mmol); **1s**: 24% (42 mg, 0.13 mmol); **1t**: 18% (29 mg, 0.095 mmol); **1u**: 20% (37 mg, 0.11 mmol).

General Procedure for the Synthesis of Compounds 2, 2', and 3: A well-stirred solution of **1** with either of $PhI(OAc)_2$ (35 mg, 0.11 mmol) and $PhI(OTFA)_2$ (47 mg, 0.11 mmol) in dichloromethane (5 mL) was held at room temperature for 1-2 hours. The reaction solution was then washed by water (5 mL) and the aqueous layer was extracted by dichloromethane (5 mL x 2). Organic layers were combined, dried over $MgSO_4$, filtered, and evaporated *in vacuum*. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (5/1 to 1/1) as the eluent to give products **2**, **2'**, and **3**. The amounts of substrates **1** are listed as follows: **1a**: 18 mg, 0.072 mmol; **1b**: 19 mg, 0.072 mmol; **1c**: 22 mg, 0.072 mmol; **1d**: 21 mg, 0.072 mmol; **1e**: 19 mg, 0.072 mmol; **1f**: 20 mg, 0.072 mmol; **1g**: 23 mg, 0.072 mmol; **1h**: 27 mg, 0.072 mmol; **1i**: 20 mg, 0.072 mmol; **1j**: 21 mg, 0.072 mmol; **1k**: 19 mg, 0.072 mmol; **1l**: 20 mg, 0.072 mmol; **1m**: 23 mg, 0.072 mmol; **1n**: 20 mg, 0.072 mmol; **1o**: 20 mg, 0.072 mmol; **1p**: 21 mg, 0.072 mmol; **1q**: 21 mg, 0.072 mmol; **1r**: 23 mg, 0.072 mmol; **1s**: 23 mg, 0.072 mmol; **1t**: 22 mg, 0.072 mmol; **1u**: 24 mg, 0.072 mmol. All product yields were determined by GC-FID using *n*-octadecane as the internal standard and shown as follows: **2a**: 57% (10 mg, 0.041 mmol); **2b**: 46% (9 mg, 0 033 mmol); **2c**: 45% (10 mg, 0.032 mmol); **2d**: 5% (1 mg, 0.004 mmol); **2e**: 77% (15 mg, 0.055 mmol); **2f**: 75% (15 mg, 0.054

mmol); **2g**: 58% (13 mg, 0.042 mmol); **2h**: 80% (21 mg, 0.058 mmol); **2i**: 70% (14 mg, 0.050 mmol); **2j**: 96% (20 mg, 0.069 mmol); **2k**: 70% (13 mg, 0.050 mmol); **2l**: 79% (16 mg, 0.057 mmol); **2m**: 71% (17 mg, 0.051 mmol); **2o**: 82% (16 mg, 0.059 mmol); **2p**: 90% (19 mg, 0.065 mmol); **2s**: 68% (16 mg, 0.049 mmol); **2t**: 68% (15 mg, 0.049 mmol); **2'a**: 14% (3 mg, 0.01 mmol); **2'b**: 23% (5 mg, 0.017 mmol); **2'c**: 20% (5 mg, 0.014 mmol); **2'd**: 2% (0.4 mg, 0.001 mmol); **2'e**: 10% (2 mg, 0.007 mmol); **2'f**: 13% (3 mg, 0.009 mmol); **2'g**: 22% (6 mg, 0.02 mmol); **3a**: 9% (2 mg, 0.006 mmol); **3b**: 13% (2 mg, 0.009 mmol); **3c**: 11% (2 mg, 0.008 mmol); **3d**: 23% (5 mg, 0.017 mmol); **3n**: 95% (19 mg, 0.068 mmol); **3q**: 80% (17 mg, 0.058 mmol); **3r**: 58% (13 mg, 0.042 mmol).

Synthetic Procedure of Substrate 4:



8a, R_1 = H; **8b**, R_1 = OMe

9a, R_2 = OMe; **9b**, R_2 = H

4a, R_1 = H; R_2 = OMe; **4b**, R_1 = OMe; R_2 = H

A well-stirred solution of **8** (**8a**: 93 mg, 0.69 mmol for **4a**; **8b**: 114 mg, 0.691 mmol for **4b**) with boronic acid **9** (**9a**: 210 mg, 1.38 mmol for **4a**; **9b**: 168 mg, 1.38 mmol for **4b**), 5 mol % $Pd(OAc)_2$ (8 mg, 0.09 mmol), $Cu(OTf)_2$ (250 mg, 0.694 mmol), Ag_2O (160 mg, 0.693 mmol) in toluene (10 mL) was heated at 110-120 ^oC for 24 hours. After cooling down to room temperature, the reaction solution was filtered through a pad of celite. The filtrate was washed with water (20 mL) and the aqueous layer was extracted with ethyl acetate (15 mL x 3). Organic layers were combined, dried

over $MgSO_4$, filtered, and evaporated *in vacuum*. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (10/1 to 5/1) as the eluent to give product **4a** (25%, 41 mg, 0.17 mmol) and **4b** (66%, 109 mg, 0.452 mmol).

Synthesis of Compounds 5-7: The synthetic procedure is the same with that of **2**, **2'**, and **3**. The amounts of reaction reagents are listed as follows: **4a** and **4b** (50 mg, 0.21 mmol); $PhI(OTFA)_2$ (133 mg, 0.309 mmol); CH_3CN (5 mL); eluent (hexane/ethyl acetate = 30/1 to 10/1) to give carbazole **5a** (86%, 43 mg, 0.18 mmol) and benzoxazole **6** (90%, 45 mg, 0.19 mmol). $PhI(OAc)_2$ (100 mg, 0.311 mmol) instead of $PhI(OTFA)_2$ gave carbazole **5a** (89%, 45 mg, 0.19 mmol) and benzoquinoneimine **7** (10%, 5 mg, 0.021 mmol). The reaction was carried out in CH_2Cl_2 (5 mL, instead of CH_3CN) to give carbazole **5b** (14%, 8 mg, 0.029 mmol).

General Procedure for the Reaction of *N*-([1,1'-Biphenyl]-2-yl)pyridin-2-amine (1a) with $PhIX_2$ (X = OAc and OTFA) by the Addition of Radical Scavengers (DPE and BHT): A well-stirred solution of **1a** (15 mg, 0.061 mmol) with either of $PhI(OAc)_2$ (30 mg, 0.092 mmol) and $PhI(OTFA)_2$ (40 mg, 0.092 mmol) in dichloromethane (5 mL) was added by 1,1-diphenylethylene (DPE) (11 mg, 0.061 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (13 mg, 0.061 mmol), respectively, and kept at room temperature for 1 hour. The reaction solution was then washed by water (5 mL) and the aqueous layer was extracted by dichloromethane (5 mL x 2). Organic layers were combined, dried over $MgSO_4$, filtered, and evaporated *in vacuum*. Finally, the product ratio and yield of **2a**, **2'a**, and **3a** were determined by GC-FID (using *n*-octadecane as the internal

standard).

General Procedure for the Reaction of *N*-(Biphenyl)acetamides (4a and 4b) with $PhIX_2$ (X = OTFA and OAc) by the Addition of Lewis Acid (TMSOTf): A well-stirred solution of **4a** (50 mg, 0.21 mmol) and **4b** (50 mg, 0.21 mmol) with either of $PhI(OTFA)_2$ (107 mg, 0.250 mmol) and $PhI(OAc)_2$ (80 mg, 0.25 mmol) in acetonitrile (5 mL) was added by trimethylsilyl trifluoromethanesulfonate (TMSOTf) (92 mg, 0.42 mmol) and kept at room temperature for 3-4 hours. The reaction solution was then washed by water (5 mL) and the aqueous layer was extracted by dichloromethane (5 mL x 2). Organic layers were combined, dried over $MgSO_4$, filtered, and evaporated *in vacuum* to give carbazole **5** in 0% and benzoxazole **6** in 53% (26 mg, 0.11 mmol for $PhI(OTFA)_2$) and 42% (20 mg, 0.090 mmol for $PhI(OAc)_2$), respectively, in which the product yield was determined by GC-FID (using *n*-octadecane as the internal standard).

Characterization Data of Compounds 1-7:

Characterization data of compounds **3a-c** and **3n**, please see ref. 6e.

***N*-(2-(Naphthalen-2-yl)phenyl)pyridin-2-amine (1d):** Pale-yellow solid; mp 120-121 ^{o}C; R_f = 0.61 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (bs, 1 H), 6.71 (dd, *J* = 7.0, 5.5 Hz, 1 H), 6.79 (d, *J* = 8.5 Hz, 1 H), 7.16 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1 H), 7.37-7.41 (m, 2 H), 7.46 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1 H), 7.50-7.53 (m, 3 H), 7.83-7.89 (m, 5 H), 8.15 (d, *J* = 4.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.8 (CH), 115.1 (CH), 120.7 (CH), 123.0 (CH), 126.2 (CH), 126.3 (CH), 127.3 (CH), 127.7 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH x 2), 131.0 (CH), 132.6

(Cq), 133.3 (Cq), 133.6 (Cq), 136.3 (Cq), 137.6 (Cq), 137.7 (CH), 148.2 (CH), 155.8 (Cq); MS (EI, *m/z*) 296 (M^+, 100), 295 (100), 169 (87); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{21}H_{16}N_2$ 296.1313; Found 296.1314.

***N*-(4'-Iodo-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1h):** Pale-yellow solid; mp 145-146 ^oC; R_f = 0.69 (*n*-Hexane/ethyl acetate = 4/1); ^1H NMR (500 MHz, $CDCl_3$) δ 6.32 (bs, 1 H), 6.73 (dd, *J* = 5.0, 5.0 Hz, 1 H), 6.79 (d, *J* = 8.5 Hz, 1 H), 7.12-7.16 (m, 3 H), 7.27 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.36 (ddd, *J* = 8.3, 8.3, 1.5 Hz, 1 H), 7.47 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1 H), 7.34-7.76 (m, 3 H), 8.16 (d, *J* = 4.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 93.4 (Cq), 108.5 (CH), 115.2 (CH), 121.3 (CH), 123.4 (CH), 128.6 (CH), 130.5 (CH), 131.2 (CH x 2), 132.5 (Cq), 137.2 (Cq), 137.8 (CH), 137.9 (CH x 2), 138.3 (Cq), 148.3 (CH), 155.8 (Cq); MS (EI, *m/z*) 372 (M^+, 100), 371 (55), 244 (32), 169 (99), 71 (25); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{13}IN_2$ 372.0124; Found 372.0124.

***N*-(5-Fluoro-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1k):** Pale-yellow viscous liquid; R_f = 0.48 (*n*-hexane/ethyl acetate = 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 6.21 (bs, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 6.70 (dd, *J* = 6.2, 6.2 Hz, 1 H), 7.03-7.09 (m, 2 H), 7.36-7.47 (m, 6 H), 7.72-7.77 (m, 1 H), 8.15 (d, *J* = 4.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.5 (CH), 114.7 (CH), 114.9 (d, J_{C-F} = 21.9 Hz, CH), 117.3 (d, J_{C-F} = 22.8 Hz, CH), 124.3 (d, J_{C-F} = 8.3 Hz, CH), 128.0 (CH), 128.9 (CH x 2), 129.0 (CH x 2), 132.8 (Cq), 136.5 (d, J_{C-F} = 7.8 Hz, Cq), 137.7 (Cq), 138.3 (CH), 146.9 (CH), 156.0 (Cq), 159.2 (d, J_{C-F} = 242.5 Hz, Cq); MS (EI, *m/z*) 264 (M^+, 100), 263 (91), 248 (29), 187 (54), 71

(19), 57 (24); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{13}FN_2$ 264.1063; Found 264.1063.

***N*-(5-Chloro-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1l):** White solid; mp 98-99 °C; R_f = 0.59 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.33 (bs, 1 H), 6.69-6.75 (m, 2 H), 7.26-7.49 (m, 8 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 8.17 (d, *J* = 4.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.1 (CH), 115.4 (CH), 121.6 (CH), 127.4 (Cq), 128.0 (CH), 128.1 (CH), 129.0 (CH x 2), 129.1 (CH x 2), 130.3 (CH), 134.4 (Cq), 136.2 (Cq), 137.5 (Cq), 137.7 (CH), 148.3 (CH), 155.5 (Cq); MS (EI, *m/z*) 282 (M^+ + 2, 33), 280 (M^+, 100), 264 (27), 203 (57), 71 (28), 57 (37); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{13}{}^{35}ClN_2$ 280.0767; Found 280.0764.

***N*-(5-Bromo-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1m):** Pale-yellow solid; mp 84-85 °C; R_f = 0.59 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.33 (bs, 1 H), 6.70-6.76 (m, 2 H), 7.37-7.50 (m, 8 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 8.18 (d, *J* = 4.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.2 (CH), 114.9 (Cq), 115.5 (CH), 121.7 (CH), 128.1 (CH), 129.0 (CH x 2), 129.2 (CH x 2), 131.0 (CH), 133.2 (CH), 134.6 (Cq), 136.7 (Cq), 137.4 (Cq), 137.7 (CH), 148.3 (CH), 155.3 (Cq); MS (EI, *m/z*) 326 (M^+ + 2, 100), 324 (M^+, 99), 249 (45), 247 (47); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{13}{}^{79}BrN_2$ 324.0262; Found 324.0260.

***N*-(5-Methoxy-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1o):** White solid; mp 139-140 °C; R_f = 0.50 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3 H), 6.23 (bs, 1 H), 6.34 (m, 2 H), 6.90-6.94 (m, 2 H), 7.32-7.43 (m, 6 H), 7.55 (d, *J* = 8.1 Hz, 1 H), 8.10 (bs, 1 H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 55.6 (CH_3), 107.6 (CH), 113.9 (CH), 114.1 (CH), 125.3 (CH), 127.6 (CH), 128.6 (CH x 2), 129.0 (CH x 2), 130.0 (Cq), 137.0 (Cq), 137.8 (Cq), 138.8 (CH), 147.8 (CH), 156.4 (Cq), 157.1 (Cq); MS (EI, *m/z*) 276 (M^+, 100), 261 (47), 199 (29), 88 (45), 70 (52), 61 (58); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{18}H_{16}N_2O$ 276.1263; Found 276.1263.

***N*-(5-Nitro-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1q):** Yellow liquid; R_f = 0.59 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.5 Hz, 1 H), 6.86 (bs, 1 H), 6.91 (ddd, *J* = 7.0, 5.0, 0.5 Hz, 1 H), 7.45-7.59 (m, 6 H), 8.13 (d, *J* = 2.5 Hz, 1H), 8.22 (dd, *J* = 9.0, 2.5 Hz, 1 H), 8.31 (dd, *J* = 5.0, 1.0 Hz, 1 H), 8.44 (d, *J* = 9.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.9 (CH), 116.3 (CH), 117.4 (CH), 124.6 (CH), 126.1 (CH), 128.8 (CH), 129.3 (CH x 2), 129.6 (CH x 2), 130.3 (Cq), 136.4 (Cq), 138.0 (CH), 140.9 (Cq), 144.1 (Cq), 148.2 (CH), 153.6 (Cq); MS (EI, *m/z*) 291 (M^+, 83), 290 (60), 244 (38), 214 (46), 89 (100); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{13}N_3O_2$ 291.1008; Found 291.1010.

***N*-(4'-Methoxy-5-nitro-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1r):** Yellow liquid; R_f = 0.53 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 3 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.87 (bs, 1 H), 6.91 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1 H), 7.05 (d, *J* = 9.0 Hz, 2 H), 7.38 (d, *J* = 9.0 Hz, 2 H), 7.58 (ddd, *J* = 7.8, 7.8, 2.0 Hz, 1 H), 8.11 (d, *J* = 2.5 Hz, 1 H), 8.20 (dd, *J* = 9.0, 2.5 Hz, 1 H), 8.31 (dd, *J* = 5.0, 1.0 Hz, 1 H), 8.42 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4 (CH_3), 111.8 (CH), 115.0 (CH x 2), 116.1 (CH), 117.3 (CH), 124.4 (CH), 126.2 (CH), 128.4 (Cq), 130.1 (Cq), 130.6 (CH x 2), 137.9 (CH), 140.9 (Cq), 144.4 (Cq), 148.3 (CH), 153.7 (Cq), 159.9

(Cq); MS (EI, *m/z*) 321 (M^+, 22), 85 (23), 71 (41), 61 (100), 57 (74); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{18}H_{15}N_3O_3$ 321.1113; Found 321.1115.

***N*-(5-Methoxy-4'-nitro-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1s):** Yellow solid; mp 130-131 ^oC; R_f = 0.44 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3 H), 6.07 (bs, 1 H), 6.53 (d, *J* = 8.4 Hz, 1 H), 6.66 (dd, *J* = 6.6, 5.1 Hz, 1 H), 6.91 (d, *J* = 3.0 Hz, 1 H), 7.00 (dd, *J* = 8.7, 3.0 Hz, 1 H), 7.41 (dd, *J* = 8.7, 1.5 Hz, 1 H), 7.49 (d, *J* = 9.0 Hz, 1 H), 7.56 (d, *J* = 9.0 Hz, 2 H), 8.08 (d, *J* = 4.8 Hz, 1 H), 8.22 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.7 (CH_3), 107.2 (CH), 114.6 (CH), 115.2 (CH), 115.7 (CH), 123.8 (CH x 2), 127.1 (CH), 129.8 (Cq), 130.0 (CH x 2), 135.8 (Cq), 138.0 (CH), 145.8 (Cq), 147.1 (Cq), 148.0 (CH), 157.0 (Cq), 157.1 (Cq); MS (EI, *m/z*) 321 (M^+, 100), 306 (27), 199 (16), 71 (19), 57 (26); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{18}H_{15}N_3O_3$ 321.1113; Found 321.1110.

***N*-(4',5-Dimethoxy-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1t):** Yellow liquid; R_f = 0.55 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3 H), 3.83 (s, 3 H), 6.28 (bs, 1 H), 6.61-6.65 (m. 2 H), 6.88-6.92 (m, 4 H), 7.30 (d, *J* = 9.0 Hz, 2 H), 7.41 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 8.10 (d, *J* = 4.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3 (CH_3), 55.6 (CH_3), 107.5 (CH), 113.4 (CH), 114.1 (CH x 2), 115.8 (CH), 125.1 (CH), 130.1 (Cq), 130.2 (CH x 2), 131.0 (Cq), 136.6 (Cq), 137.8 (CH), 147.8 (CH), 156.3 (Cq), 157.1 (Cq), 159.1 (Cq); MS (EI, *m/z*) 306 (M^+, 100), 291 (26); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{19}H_{18}N_2O_2$ 306.1368; Found 306.1367.

***N*-(4',5-Dinitro-[1,1'-biphenyl]-2-yl)pyridin-2-amine (1u):** Yellow solid; mp 177-178 ^{o}C; R_f = 0.44 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (bs, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 6.96 (dd, *J* = 6.6, 5.4 Hz, 1 H), 7.62 (dd, *J* = 8.1, 8.1 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 8.15 (d, *J* = 2.4 Hz, 1 H), 8.27-8.41 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.8 (CH), 117.5 (CH), 117.9 (CH), 124.7 (CH x 2), 125.6 (CH), 126.1 (CH), 128.3 (Cq), 130.5 (CH x 2), 138.3 (CH), 141.4 (Cq), 143.3 (Cq), 143.9 (Cq), 148.0 (Cq), 148.3 (CH), 153.2 (Cq); MS (EI, *m/z*) 336 (M^+, 42), 85 (33), 71 (56), 57 (100); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{12}N_4O_4$ 336.0859; Found 336.0861.

6-Phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (2a): Pale-yellow liquid; R_f = 0.51 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 6.6, 6.6 Hz, 1 H), 7.37-7.56 (m, 5 H), 7.68 (dd, *J* = 7.2 Hz, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 7.88 (d, *J* = 8.1 Hz, 1 H), 8.07 (d, *J* = 7.8 Hz, 2 H), 8.49 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.3 (CH), 110.4 (CH), 118.4 (CH), 121.2 (CH), 125.0 (CH), 125.2 (CH), 127.4 (CH), 128.6 (CH x 2), 129.2 (CH), 129.3 (CH x 2), 132.8 (Cq), 138.5 (Cq), 142.5 (Cq), 148.5 (Cq); MS (EI, m/z) 244 (M^+, 100), 243 (M^+ - 1, 66); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{12}N_2$ 244.1000; Found 244.0997.

6-Phenylbenzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'a): Pale-yellow solid; mp 124-125 ^{o}C; R_f = 0.48 (*n*-hexane/ethyl acetate = 2/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 6.86 (dd, *J* = 6.6, 6.6 Hz, 1 H), 7.38-7.44 (m, 3 H), 7.50-7.55 (m, 2 H), 7.68 (d, *J* = 1.2 Hz, 1 H), 7.75 (d, *J* = 9.3 Hz, 1 H), 8.06 (d, *J* = 7.8 Hz, 1 H), 8.38 (d, *J* = 6.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2

(CH_3), 102.5 (CH), 110.7 (CH), 118.6 (CH), 119.0 (CH), 125.1 (CH), 127.8 (CH), 128.6 (CH x 2), 129.0 (Cq), 129.2 (CH), 129.3 (CH x 2), 133.4 (Cq), 137.6 (Cq), 140.3 (Cq), 145.1 (Cq), 149.1 (Cq), 170.0 (Cq); MS (EI, m/z) 302 (M^+, 22), 260 (100), 244 (28), 71 (31), 57 (33); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{19}H_{14}N_2O_2$ 302.1055; Found 302.1056.

6-(*p*-Tolyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2b): Pale-yellow solid; mp 135-136 ^oC; R_f = 0.56 (*n*-hexane/ethyl acetate = 1/1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 6.86 (dd, *J* = 6.5, 6.5 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.40-7.45 (m, 2 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.76 (d, *J* = 9.5 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 2 H), 8.48 (d, *J* = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3 (CH_3), 109.0 (CH), 110.3 (CH), 118.4 (CH), 121.2 (CH), 124.6 (CH), 125.2 (CH), 129.1 (CH), 129.2 (CH x 2), 129.3 (CH x 2), 132.9 (Cq), 135.6 (Cq), 137.1 (Cq), 142.5 (Cq), 148.4 (Cq); MS (EI, m/z) 258 (M^+, 100), 97 (34), 85 (36), 71 (41), 57 (47); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{18}H_{14}N_2$ 258.1157; Found 258.1158.

6-(*p*-Tolyl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'b): Pale-yellow solid; mp 135-136 ^oC; R_f = 0.43 (*n*-hexane/ethyl acetate = 1/1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3 H), 2.42 (s, 3 H), 6.85 (ddd, *J* = 6.5, 6.5, 1.0 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.38-7.42 (m, 2 H), 7.65 (d, *J* = 2.0 Hz, 1 H), 7.74 (d, *J* = 9.5 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 2 H), 8.37 (d, *J* = 7.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3), 21.3 (CH_3), 102.2 (CH), 110.6 (CH), 118.6 (CH), 118.7 (CH), 125.0 (CH), 128.9 (Cq), 129.1 (CH x 2), 129.3 (CH x 2), 133.5 (Cq), 134.7 (Cq), 137.6 (Cq),

140.3 (Cq), 145.1 (Cq), 149.0 (Cq), 170.0 (Cq); MS (EI, m/z) 316 (M^+, 36), 274 (100); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{20}H_{16}N_2O_2$ 316.1212; Found 316.1209.

6-(4-(*tert*-Butyl)phenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2c): Pale-yellow solid; mp 154-155 ^oC; R_f = 0.58 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 6.86 (dd, *J* = 6.6, 6.6 Hz, 1 H), 7.39-7.47 (m, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.77 (d, *J* = 9.3 Hz, 1 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 8.48 (d, *J* = 6.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4 (CH_3), 34.6 (Cq), 109.0 (CH), 110.3 (CH), 118.4 (CH), 121.2 (CH), 124.7 (CH), 125.1 (CH), 125.6 (CH x 2), 128.9 (CH x 2), 129.1 (CH), 129.3 (Cq), 132.8 (Cq), 135.6 (Cq), 124.5 (Cq), 148.4 (Cq), 150.2 (Cq); MS (EI, m/z) 300 (M^+, 54), 285 (100), 71 (40), 57 (39); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{21}H_{20}N_2$ 300.1626; Found 300.1627.

6-(4-(*tert*-Butyl)phenyl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'c): Pale-yellow solid; mp 63-64 ^oC; R_f = 0.58 (*n*-hexane/ethyl acetate = 1/1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 2.40 (s, 3 H), 6.86 (dd, *J* = 6.5, 6.5 Hz, 1 H), 7.39-7.43 (m, 2 H), 7.55 (d, *J* = 8.5 Hz, 2 H), 7.66 (d, *J* = 2.5 Hz, 1 H), 7.76 (d, *J* = 9.5 Hz, 1 H), 7.99 (d, *J* = 8.5 Hz, 2 H), 8.38 (d, *J* = 7.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3), 31.4 (CH_3), 34.6 (Cq), 102.2 (CH), 110.6 (CH), 118.6 (CH), 118.8 (CH), 125.0 (CH), 125.6 (CH x 2), 128.9 (CH x 2), 129.1 (CH), 133.5 (Cq), 134.7 (Cq), 145.1 (Cq), 149.0 (Cq), 150.7 (Cq), 170.0 (Cq); MS (EI, m/z) 358 (M^+, 17), 316 (37), 301 (34), 85 (66), 71 (100), 57 (90); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{23}H_{22}N_2O_2$ 358.1681; Found 358.1679.

6-(Naphthalen-2-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (2d): Yellow solid; mp 96-97 ^{o}C; R_f = 0.53 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (ddd, *J* = 7.0, 7.0, 1.0 Hz, 1 H), 7.43-7.52 (m, 4 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.88-7.93 (m, 2 H), 7.97-8.01 (m, 2 H), 8.22 (dd, *J* = 8.5, 1.5 Hz, 1 H), 8.52 (d, *J* = 7.0 Hz, 1 H), 8.55 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.4 (CH), 110.5 (CH), 118.4 (CH), 121.3 (CH), 125.2 (CH), 125.3 (CH), 125.8 (CH), 125.9 (CH), 127.5 (CH), 127.6 (CH), 128.0 (CH), 128.3 (CH), 128.5 (CH), 129.3 (CH + Cq), 132.7 (Cq), 132.9 (Cq), 133.7 (Cq), 136.0 (Cq), 142.6 (Cq), 148.5 (Cq); MS (EI, m/z) 294 (M^+, 100), 293 (M^+ - 1, 48); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{21}H_{14}N_2$ 294.1157; Found 294.1159.

6-(Naphthalen-2-yl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'd): Yellow viscous liquid; R_f = 0.41 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3 H), 6.88 (dd, *J* = 6.0, 6.0 Hz, 1 H), 7.43-7.54 (m, 4 H), 7.71 (d, *J* = 1.5 Hz, 1 H), 7.77 (d, *J* = 9.3 Hz, 1 H), 7.87-7.91 (m, 1 H), 7.96-8.00 (m, 2 H), 8.21 (d, *J* = 8.7 Hz, 1 H), 8.40 (d, *J* = 6.9 Hz, 1 H), 8.55 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.26 (CH_3), 102.6 (CH), 110.7 (CH), 118.6 (CH), 119.3 (CH), 125.1 (CH), 126.0 (CH), 126.1 (CH), 127.2 (CH), 127.6 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 129.1 (Cq), 129.3 (CH), 133.0 (Cq), 133.0 (Cq), 133.3 (Cq), 133.6 (Cq), 135.1 (Cq), 140.5 (Cq), 145.2 (Cq), 149.2 (Cq), 170.1 (Cq); MS (EI, m/z) 352 (M^+, 4), 310 (15), 111 (34), 97 (53), 85 (66), 71 (88), 57 (100); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{23}H_{16}N_2O_2$ 352.1212; Found 352.1209.

6-(4-Fluorophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2e): Pale-yellow solid; mp 86-87 ^{o}C; R_f = 0.64 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (ddd, *J* = 7.0, 7.0, 1.0 Hz, 1 H), 7.22 (dd, *J* = 9.0, 9.0 Hz, 2 H), 7.42-7.46 (m, 2 H), 7.63 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.76 (d, *J* = 9.5 Hz, 1 H), 7.88 (dd, *J* = 8.0, 1.0 Hz, 1 H), 8.06 (dd, *J* = 5.5, 2.0 Hz, 2 H), 8.49 (d, *J* = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.4 (CH), 110.5 (CH), 115.4 (d, $J_{C\text{-}F}$ = 21.4 Hz, CH x 2), 118.4 (CH), 121.2 (CH), 124.7 (CH), 125.2 (CH), 129.3 (CH), 130.9 (d, $J_{C\text{-}F}$ = 7.8 Hz, CH x 2), 131.7 (Cq), 134.5 (d, $J_{C\text{-}F}$ = 3.6 Hz, Cq), 142.4 (Cq), 148.5 (Cq), 162.4 (d, $J_{C\text{-}F}$ = 245.1 Hz, Cq); MS (EI, m/z) 262 (M^+, 100), 261 (M^+ - 1, 57); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{11}FN_2$ 262.0906; Found 262.0904.

6-(4-Fluorophenyl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'e): Pale-yellow solid; mp 84-85 ^{o}C; R_f = 0.41 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 6.87 (ddd, *J* = 7.0, 7.0, 0.5 Hz, 1 H), 7.21 (dd, *J* = 9.0, 9.0 Hz, 2 H), 7.36 (d, *J* = 2.5 Hz, 1 H), 7.42 (ddd, *J* = 9.0, 6.8, 1.0 Hz, 1 H), 7.67 (d, *J* = 2.5 Hz, 1 H), 7.74 (d, *J* = 9.0 Hz, 1 H), 8.05 (dd, *J* = 9.0, 5.5 Hz, 2 H), 8.38 (d, *J* = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3), 102.6 (CH), 110.7 (CH), 115.5 (d, $J_{C\text{-}F}$ = 21.4 Hz, CH x 2), 118.5 (CH), 118.8 (CH), 125.1 (CH), 129.0 (Cq), 129.4 (CH), 133.5 (d, $J_{C\text{-}F}$ = 8.3 Hz, CH x 2), 132.3 (Cq), 133.6 (d, *J* = 3.8 Hz, Cq), 140.2 (Cq), 145.1 (Cq), 149.2 (Cq), 162.7 (d, *J* = 245.5 Hz, Cq), 170.0 (Cq); MS (EI, m/z) 320 (M^+, 22), 278 (100); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{19}H_{13}FN_2O_2$ 320.0961; Found 320.0959.

6-(4-Chlorophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2f): Pale-yellow solid; mp 139-140 ^{o}C; R_f = 0.50 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (ddd, *J* = 7.0, 7.0, 1.0 Hz, 1 H), 7.43-7.47 (m, 2 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 7.64 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.73 (d, *J* = 9.5 Hz, 1 H), 7.90 (dd, *J* = 8.0, 0.5 Hz, 1 H), 8.04 (d, *J* = 8.5 Hz, 2 H), 8.49 (d, *J* = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.7 (CH), 110.6 (CH), 118.4 (CH), 121.2 (CH), 124.7 (CH), 125.2 (CH), 128.7 (CH x 2), 129.4 (Cq + CH), 130.6 (CH x 2), 131.4 (Cq), 133.4 (Cq), 137.0 (Cq), 142.4 (Cq), 148.6 (Cq); MS (EI, m/z) 280 (M^+ + 2, 34), 278 (M^+, 100), 242 (23); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{11}{}^{35}ClN_2$ 278.0611; Found 278.0610.

6-(4-Chlorophenyl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'f): Pale-yellow solid; mp 113-114 ^{o}C; R_f = 0.51 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 6.88 (dd, *J* = 6.5, 6.5 Hz, 1 H), 7.38 (d, *J* = 2.0 Hz, 1 H), 7.43 (ddd, *J* = 9.3, 6.5, 1.0 Hz, 1 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 7.69 (d, *J* = 2.0 Hz, 1 H), 7.75 (d, *J* = 9.0 Hz, 1 H), 8.02 (d, *J* = 8.5 Hz, 2 H), 8.39 (d, *J* = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3), 102.9 (CH), 110.8 (CH), 118.5 (CH), 118.8 (CH), 125.1 (CH), 128.8 (CH x 2), 129.0 (Cq), 129.5 (CH), 130.6 (CH x 2), 132.0 (Cq), 133.8 (Cq), 136.0 (Cq), 140.2 (Cq), 145.1 (Cq), 149.2 (Cq), 170.0 (Cq); MS (EI, m/z) 336 (M^+, 2), 85 (67), 71 (100), 57 (91); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{19}H_{13}{}^{35}ClN_2O_2$ 336.0666; Found 336.0664.

6-(4-Bromophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2g): Pale-yellow solid; mp 152-153 ^{o}C; R_f = 0.61 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 6.5, 6.5 Hz, 1

H), 7.31-7.46 (m, 2 H), 7.64-7.66 (m, 3 H), 7.76 (d, J = 9.5 Hz, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.97 (d, J = 8.5 Hz, 2 H), 7.49 (d, J = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.7 (CH), 110.6 (CH), 118.4 (CH), 121.2 (CH), 121.6 (Cq), 124.6 (CH), 125.2 (CH), 129.4 (Cq + CH), 130.9 (CH x 2), 131.4 (Cq), 131.7 (CH x 2), 137.4 (Cq), 142.4 (Cq), 148.6 (Cq); MS (EI, m/z) 324 (M^+ + 2, 29), 322 (M^+, 29), 111 (44), 97 (66), 85 (72), 71 (86), 57 (100); HRMS (EI-magnetic sector) m/z: [M^+] Calcd for $C_{17}H_{11}{}^{79}BrN_2$ 322.0106; Found 322.0105.

6-(4-Bromophenyl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl acetate (2'g): Pale-yellow solid; mp 128-129 ^{o}C; R_f = 0.46 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 6.88 (dd, J = 6.5, 6.5 Hz, 1 H), 7.38 (d, J = 1.5 Hz, 1 H), 7.44 (dd, J = 6.5, 6.5 Hz, 1 H), 7.65 (d, J = 8.0 Hz, 2 H), 7.69 (d, J = 1.5 Hz, 1 H), 7.74 (d, J = 9.0 Hz, 1 H), 7.96 (d, J = 8.0 Hz, 2 H), 8.39 (d, J = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3), 103.0 (CH), 110.8 (CH), 118.6 (CH), 118.7 (CH), 122.1 (Cq), 125.1 (CH), 129.1 (Cq), 129.5 (CH), 130.9 (CH x 2), 131.7 (CH x 2), 132.0 (Cq), 136.5 (Cq), 140.2 (Cq), 145.1 (Cq), 149.2 (Cq), 170.0 (Cq); MS (EI, m/z) 382 (M^+ + 2, 4), 380 (M^+, 4), 97 (55), 85 (78), 71 (90), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{19}H_{13}{}^{79}BrN_2O_2$ 380.0160; Found 380.0160.

6-(4-Iodophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2h): Pale-yellow solid; mp 112-113 ^{o}C; R_f = 0.60 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (ddd, J = 7.0, 7.0, 1.0 Hz, 1 H), 7.43-7.46 (m, 2 H), 7.64 (dd, J = 7.5, 1.0 Hz, 1 H), 7.76 (d, J = 9.5 Hz, 1 H),7.83 (d, J = 9.0 Hz, 2 H), 7.86 (d, J = 9.0 Hz, 2 H), 7.92 (dd, J = 8.0, 1.0 Hz, 1 H), 8.49 (d, J = 6.5 Hz, 1 H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 93.3 (Cq), 109.8 (CH), 110.6 (CH), 118.4 (CH), 121.2 (CH), 124.6 (CH), 125.2 (CH), 129.4 (Cq + CH), 131.1 (CH x 2), 131.5 (Cq), 137.6 (CH x 2), 138.0 (Cq), 142.4 (Cq), 148.6 (Cq); MS (EI, m/z) 370 (M^+, 100), 260 (39), 243 (91), 122 (44), 85 (51), 71 (65), 57 (64); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{17}H_{11}IN_2$ 369.9967; Found 369.9963.

6-(4-Formylphenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2i): Yellow solid; mp 62-63 ^oC; R_f = 0.44 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 6.5, 6.5 Hz, 1 H), 7.47-7.51 (m, 2 H), 7.75 (d, *J* = 7.5 Hz, 1 H), 7.80 (d, *J* = 9.5 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 8.05 (d, *J* = 8.5 Hz, 2 H), 8.29 (d, *J* = 8.5 Hz, 2 H), 8.52 (d, *J* = 7.0 Hz, 1 H), 10.10 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.6 (CH), 110.9 (CH), 118.4 (CH), 121.3 (CH), 125.2 (CH), 125.3 (CH), 129.5 (Cq), 129.8 (CH x 3), 130.1 (CH x 2), 131.0 (Cq), 135.2 (Cq), 142.3 (Cq), 144.8 (Cq), 148.7 (Cq), 192.2 (CH); MS (EI, *m/z*) 272 (M^+, 22), 111 (16), 95 (14), 85 (37), 71 (57), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{18}H_{12}N_2O$ 272.0950; Found 272.0947.

6-(3-Nitrophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2j): Yellow liquid; R_f = 0.59 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (ddd, *J* = 7.0, 7.0, 1.0 Hz, 1 H), 7.47-7.51 (m, 2 H), 7.70 (dd, *J* = 8.0, 8.0 Hz, 1 H), 7.74 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.78 (d, *J* = 9.5 Hz, 1 H), 7.97 (d, *J* = 8.0 Hz, 1H), 8.24 (ddd, *J* = 8.5, 2.0, 0.5 Hz, 1 H), 8.52 (d, *J* = 8.0 Hz, 2 H), 8.97 (dd, *J* = 2.0, 2.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 110.7 (CH), 110.9 (CH), 118.4 (CH), 121.2 (CH), 122.1 (CH), 124.0 (CH), 125.0 (CH), 125.2 (CH), 129.4 (CH), 129.5 (Cq), 129.7 (Cq), 129.8 (CH), 135.4 (CH), 140.2 (Cq), 142.3 (Cq), 148.6 (Cq), 148.8 (Cq); MS (EI, *m/z*) 289 (M^+, 22),

129 (24), 83 (27), 71 (55), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{17}H_{11}N_3O_2$ 289.0851; Found 289.0852.

8-Fluoro-6-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (2k): Yellow liquid; R_f = 0.51 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (ddd, *J* = 7.0, 7.0, 1.0 Hz, 1 H), 7.38-7.46 (m, 3 H), 7.52-7.55 (m, 3 H), 7.73 (d, *J* = 9.5 Hz, 1 H), 8.05 (d, *J* = 1.5 Hz, 1 H), 8.07 (d, *J* = 1.5 Hz, 1 H), 8.34 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 95.7 (d, $J_{C\text{-}F}$ = 27.4 Hz, CH), 110.6 (CH), 113.3 (d, $J_{C\text{-}F}$ = 25.5 Hz, CH), 118.6 (CH), 124.9 (CH), 128.0 (CH), 128.7 (CH x 2), 129.0 (CH), 129.3 (CH x 2), 133.9 (d, $J_{C\text{-}F}$ = 9.1 Hz, Cq), 137.4 (d, $J_{C\text{-}F}$ = 1.8 Hz, Cq), 138.9 (Cq), 149.0 (d, $J_{C\text{-}F}$ = 2.3 Hz, Cq), 158.3 (d, $J_{C\text{-}F}$ = 238.8 Hz, Cq); MS (EI, *m/z*) 262 (M^+, 80), 261 (45), 71 (65), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{17}H_{11}FN_2$ 262.0906; Found 262.0909.

8-Chloro-6-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (2l): Yellow liquid; R_f = 0.54 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (dd, *J* = 6.8, 6.8 Hz, 1 H), 7.38-7.43 (m, 2 H), 7.50-7.55 (m, 2 H), 7.63 (d, *J* = 1.8 Hz, 1 H), 7.73 (d, *J* = 9.3 Hz, 1 H), 7.83 (d, *J* = 1.8 Hz, 1 H), 8.03 (d, *J* = 7.5 Hz, 2 H), 8.35 (d, *J* = 6.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.2 (CH), 111.0 (CH), 118.5 (CH), 125.0 (CH), 125.4 (CH), 126.8 (Cq), 128.0 (CH), 128.6 (CH x 2), 129.2 (CH x 2), 129.6 (CH), 133.8 (Cq), 137.2 (Cq), 140.9 (Cq), 148.9 (Cq); MS (EI, *m/z*) 280 (M^+ + 2, 52), 278 (M^+, 100), 277 (82); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{17}H_{11}{}^{35}ClN_2$ 278.0611; Found 278.0609.

8-Bromo-6-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (2m): Yellow liquid; R_f = 0.53 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 6.5, 6.5 Hz, 1 H), 7.41-7.44 (m, 1 H), 7.49 (ddd, *J* = 9.0, 6.5, 1.0 Hz, 1 H), 7.53-7.56 (m, 2 H), 7.79 (d, *J* = 2.0 Hz, 1 H), 7.85 (d, *J* = 9.5 Hz, 1 H), 8.01-8.04 (m, 3 H), 8.43 (d, *J* = 7.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.4 (CH), 112.3 (CH), 114.4 (Cq), 118.4 (CH), 125.0 (CH), 128.1 (CH), 128.3 (CH), 128.8 (CH x 2), 129.3 (CH x 2), 129.9 (Cq), 130.2 (CH), 134.1 (Cq), 136.9 (Cq), 148.5 (Cq); MS (EI, *m/z*) 324 (M^+ + 2, 99), 322 (M^+, 100), 243 (17), 242 (31), 122 (20); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{17}H_{11}{}^{79}BrN_2$ 322.0106; Found 322.0108.

8-Methoxy-6-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (2o): Yellow liquid; R_f = 0.53 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (s, 3 H), 6.85 (dd, *J* = 6.5, 6.5 Hz, 1 H), 7.31 (d, *J* = 2.5 Hz, 1 H), 7.34 (d, *J* = 2.5 Hz, 1 H), 7.35-7.42 (m, 2 H), 7.53 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.78 (d, *J* = 9.0 Hz, 1 H), 8.04 (d, *J* = 7.5 Hz, 2 H), 8.38 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.1 (CH_3), 92.4 (CH), 110.5 (CH), 115.0 (CH), 118.4 (CH), 124.7 (CH), 127.7 (CH), 128.3 (CH), 128.6 (CH x 2), 129.2 (CH x 2), 129.4 (Cq), 133.4 (Cq), 136.7 (Cq), 138.0 (Cq), 147.8 (Cq), 155.5 (Cq); MS (EI, *m/z*) 274 (M^+, 100), 259 (76), 231 (21); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{18}H_{14}N_2O$ 274.1106; Found 274.1109.

6-(4-Nitrophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2p): Yellow liquid; R_f = 0.63 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 7.0, 7.0 Hz, 1 H), 7.48-7.51 (m, 2 H), 7.74 (dd, *J* = 7.5, 0.5 Hz, 1 H), 7.78 (d, *J* = 9.5 Hz, 1 H), 7.98 (d, *J* = 8.5 Hz, 1

H), 8.32 (d, *J* = 9.0 Hz, 2 H), 8.39 (d, *J* = 9.0 Hz, 2 H), 8.53 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.9 (CH), 111.0 (CH), 118.4 (CH), 121.2 (CH), 123.8 (CH x 2), 125.2 (CH x 2), 129.6 (Cq), 129.8 (Cq), 129.9 (CH x 2), 142.5 (Cq), 145.2 (Cq), 146.8 (Cq), 148.9 (Cq); MS (EI, *m/z*) 289 (M^+, 5), 129 (15), 97 (22), 73 (42), 71 (56), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{17}H_{11}N_3O_2$ 289.0851; Found 289.0854.

8-Methoxy-6-(4-nitrophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2s): Yellow liquid; R_f = 0.50 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 3 H), 6.86 (dd, *J* = 6.3, 6.3 Hz, 1 H), 7.37-7.41 (m, 3 H), 7.70 (d, *J* = 9.3 Hz, 1 H), 8.26-8.39 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.2 (CH_3), 94.0 (CH), 110.7 (CH), 115.2 (CH), 118.5 (CH), 123.8 (CH x 2), 124.8 (CH), 128.7 (CH), 129.8 (Cq), 130.0 (CH x 2), 130.5 (Cq), 137.3 (Cq), 144.8 (Cq), 147.0 (Cq), 148.4 (Cq), 155.3 (Cq); MS (EI, m/z) 319 (M^+, 100), 304 (77), 258 (41), 229(38), 71(32); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{18}H_{13}N_3O_3$ 319.0957; Found 319.0954.

8-Methoxy-6-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (2t): Pale-yellow solid; mp 104-105 ^{o}C; R_f = 0.40 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3 H), 3.98 (s, 3 H), 6.82 (dd, *J* = 6.9, 6.9 Hz, 1 H), 7.07 (d, *J* = 8.7 Hz, 1 H), 7.29-7.36 (m, 2 H), 7.73 (d, *J* = 9.3 Hz, 1 H), 8.03 (d, *J* = 8.7 Hz, 1 H), 8.36 (d, *J* = 6.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4 (CH_3), 56.1 (CH_3), 91.7 (CH), 110.1 (CH), 114.1 (CH x 2), 114.2 (CH), 118.5 (CH), 124.6 (CH), 127.8 (CH), 129.4 (Cq), 130.4 (CH x 2), 130.7 (Cq), 133.2 (Cq), 137.2 (Cq), 147.9 (Cq),

155.4 (Cq), 159.3 (Cq); MS (EI, m/z) 304 (M^+, 18), 284 (37), 111 (51), 97(74), 85 (75), 71(94), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{19}H_{16}N_2O_2$ 304.1212; Found 304.1214.

11-(Pyridin-2-yl)-11*H*-benzo[*a*]carbazole (3d): Yellow solid; mp 196-197 ^oC; R_f = 0.62 (*n*-hexane/ethyl acetate = 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 2 H), 7.35-7.54 (m, 6 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.96-8.00 (m, 2 H), 8.16-8.22 (m, 2 H), 8.83 (d, *J* = 3.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 110.7 (CH), 119.0 (CH), 119.7 (CH), 120.8 (Cq), 121.0 (CH), 121.9 (Cq), 122.2 (CH), 122.6 (CH), 122.9 (CH), 123.3 (CH), 124.3 (Cq), 124.8 (CH), 125.0 (CH), 125.4 (CH), 129.3 (CH), 133.5 (Cq), 135.1 (Cq), 138.9 (CH), 141.5 (Cq), 150.2 (CH), 153.4 (Cq); MS (EI, m/z) 294 (M^+, 15), 149 (100), 85 (44), 71 (65), 57 (76); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{21}H_{14}N_2$ 294.1157; Found 294.1154.

2-Methoxy-6-nitro-9-(pyridin-2-yl)-9*H*-carbazole (3r): Yellow liquid; R_f = 0.56 (*n*-hexane/ethyl acetate = 2/1); ^1H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 3 H), 7.02 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.25 (d, *J* = 2.5 Hz, 1 H), 7.43 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.76 (d, *J* = 9.0 Hz, 1 H), 8.02 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1 H), 8.05 (d, *J* = 8.5 Hz, 1 H), 8.27 (dd, *J* = 9.0, 2.5 Hz, 1 H), 8.78 (dd, *J* = 5.0, 1.0 Hz, 1 H), 8.91 (d, *J* = 2.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.8 (CH_3), 96.1 (CH), 110.6 (CH), 110.7 (CH), 115.9 (CH), 117.2 (Cq), 119.5 (CH), 120.7 (CH), 121.7 (CH), 122.6 (CH), 124.3 (Cq), 139.0 (CH), 142.2 (Cq), 142.3 (Cq), 143.0 (Cq), 150.0 (CH), 150.6 (Cq), 160.4 (Cq); MS (EI, m/z) 319 (M^+, 100), 71(24), 57 (23); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{18}H_{13}N_3O_3$ 319.0957; Found 319.0954.

***N*-(4'-Methoxy-[1,1'-biphenyl]-2-yl)acetamide (4a):** White solid; mp 90-91 ^{o}C; R_f = 0.50 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 3 H), 3.87 (s, 3 H), 7.00-7.37 (m, 7 H), 8.26 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3 (CH_3), 114.5 (CH x 2), 121.5 (CH), 124.3 (CH), 128.1 (CH), 130.2 (CH), 130.4 (CH x 2), 131.8 (Cq), 134.9 (Cq), 159.3 (Cq), 168.2 (Cq); MS (EI, m/z) 241 (M^+, 60), 199 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{15}H_{15}NO_2$ 241.1103; Found 241.1102.

***N*-(5-Methoxy-[1,1'-biphenyl]-2-yl)acetamide (4b):** White solid; mp 90-91 ^{o}C; R_f = 0.40 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 3.81 (s, 3 H), 6.90 (d, *J* = 3.0 Hz, 1 H), 6.92-6.93 (m, 2 H), 7.35-7.50 (m, 5 H), 8.01 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5 (CH_3), 113.4 (CH), 115.4 (CH), 124.2 (CH), 127.7 (Cq), 128.0 (CH), 129.0 (CH x 2), 129.1 (CH x 2), 134.6 (Cq), 138.3 (Cq), 156.5 (Cq), 168.4 (Cq); MS (EI, m/z) 241 (M^+, 84), 199 (85), 184 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{15}H_{15}NO_2$ 241.1103; Found 241.1101.

9-Acetyl-2-methoxy-9*H*-carbazole (5a): White solid; mp 69-70 ^{o}C; R_f = 0.50 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.87 (s, 3 H), 3.93 (s, 3 H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1 H), 7.34-7.42 (m, 2 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 7.90 (dd, *J* = 4.5, 1.0 Hz, 1 H), 7.92 (d, *J* = 1.5 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.7 (CH_3), 55.8 (CH_3), 102.0 (CH), 111.4 (CH), 115.7 (CH), 119.1 (CH), 119.7 (Cq), 120.2 (CH), 123.7 (CH), 125.9 (CH), 126.7 (Cq), 138.4 (Cq), 140.1 (Cq), 159.8 (Cq), 170.2 (Cq); MS (EI, m/z) 239 (M^+, 66), 197 (100), 182

(55), 154 (36); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{15}H_{13}NO_2$ 239.0946; Found 239.0944.

9-Acetyl-6-hydroxy-2-methoxy-9*H*-carbazole (5b): Pale-yellow solid; mp 168-169 ^{o}C; R_f = 0.7 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (500 MHz, d_6-acetone) δ 2.85 (s, 3 H), 3.90 (s, 3 H), 6.93 (dd, *J* = 9.0, 2.0 Hz, 1 H), 6.99 (dd, *J* = 9.0, 2.0 Hz, 1 H), 7.41 (d, *J* = 2.0 Hz, 1 H), 7.89-7.91 (m, 2 H), 8.02 (d, *J* = 9.0 Hz, 1 H), 8.52 (bs, 1 H); ^{13}C NMR (125 MHz, d_6-acetone) δ 27.6 (CH_3), 56.0 (CH_3), 102.8 (CH), 105.6 (CH), 11.8 (CH), 114.8 (CH), 117.8 (CH), 120.5 (Cq), 121.3 (CH), 128.6 (Cq), 133.2 (Cq), 141.5 (Cq), 155.2 (Cq), 160.9 (Cq), 170.6 (Cq); MS (EI, m/z) 255 (M^+, 8), 88 (60), 70 (71), 61 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{15}H_{13}NO_3$ 255.0895; Found 255.0894.

6-Methoxy-2-methyl-4-phenylbenzo[*d*]oxazole (6): Pale-yellow viscous liquid; R_f = 0.50 (*n*-hexane/ethyl acetate = 7/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (s, 3 H), 3.90 (s, 3 H), 7.00 (d, *J* = 2.5 Hz, 1 H), 7.07 (d, *J* = 2.5 Hz, 1 H), 7.39 (dd, *J* = 7.5, 7.5 Hz, 1 H), 7.50 (d, *J* = 7.5, 7.5 Hz, 2 H), 7.90 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5 (CH_3), 56.0 (CH_3), 94.3 (CH), 111.1 (CH), 127.9 (CH), 128.6 (CH x 2), 128.7 (CH x 2), 132.7 (Cq), 133.1 (Cq), 137.2 (Cq), 152.3 (Cq), 157.6 (Cq), 162.6 (Cq); MS (EI, m/z) 239 (M^+, 100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{15}H_{13}NO_2$ 239.0946; Found 239.0945.

***N*-Acetyl-2-pheylbenzoquinone imine (7):** Yellow viscous liquid; R_f = 0.70 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3 H), 6.66 (dd, *J* = 10.2, 2.4 Hz, 1 H), 6.74 (d,

J = 2.4 Hz, 1 H), 6.99 (d, *J* = 10.2 Hz, 1 H), 7.44-7.45 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.4 (CH_3), 128.2 (CH x 2), 129.5 (CH x 2), 129.7 (CH), 131.2 (CH), 132.8 (CH), 134.3 (Cq), 134.6 (CH), 149.4 (Cq), 152.7 (Cq), 185.1 (Cq), 186.2 (Cq); MS (EI, m/z) 227 (M^+ + 2, 20), 225 (M^+, 10), 185 (45), 85(64), 71 (74), 57 (100); HRMS (EI-magnetic sector) m/z: [M+] Calcd for $C_{14}H_{11}NO_2$ 225.0790; Found 225.0792.

ASSOCIATED CONTENT

Supporting Information

^{1}H-^{1}H COSY NMR spectrum of compound **3d**. Two X-ray crystal structures of **2f** and **2'f**, and their CIF files giving X-ray crystallographic data. UV-Vis spectra of the radical cation **1o**$^{\bullet+}$. ^{1}H, ^{13}C and DEPT NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

We thank the Ministry of Science and Technology of the Republic of China (NSC 101-2113-M-110-014-MY3 and NSC-100-2113-M-110-006-MY3) for financial support and Mr. Min-Yuan Hung for his technical supports and services in GC-MS, Center for Research Resources and Development of Kaohsiung Medical University (Taiwan).

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(7) The reaction of **1a** with $PhI(OAc)_2$ was initially examined in toluene, however, no reaction took place and most starting substrate **1a** was recovered. Then we turned to use dichoromethane as the reaction solvent and found that the total yield of products **2a**, **2'a**, and **3a** was dramatically increased to 88% in product ratio 71:18:11. In addition, acetonitrile was also employed to the reaction and similar results were observed compared with that of dichoromethane where the product ratio and yield of **2a**, **2'a**, and **3a** were determined to be 89:7:4 (by GC-FID) and 77%, respectively, by the use of $PhI(OAc)_2$. Meanwhile, the product ratio and yield of **2a** and **3a** were found to be 98:2

and 98%, respectively, by the use of $PhI(OTFA)_2$. Finally, we chose dichoromethane as the optimal solvent based on the operational convenience.

(8) The regiostructure of **3d** was confirmed by 500 MHz ^1H NMR spectroscopy, in which a pair of doublet patterns for proton-3 and proton-4 (δ 7.77, J = 8.5 Hz; δ 8.21, J = 8.5 Hz, see Page S-131, Supporting Information) located on the naphthyl moiety was observed and the independent ^1H-^1H coupling correlation between them was verified by ^1H-^1H COSY NMR spectroscopy (see Figure S1, Supporting Information).

(9) Copies of the deposited crystallographic data CCDC-1010807 (**2f**) and CCDC-1010808 (**2'f**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(10) In order to avoid the formation of 8-acetoxy-6-arylbenzimidazoles **2'** for the reaction, $PhI(OAc)_2$ was replaced by $PhI(OTFA)_2$.

(11) We also carried out the reaction of **1n** and **1p** with $PhIX_2$ (X = OTFA or OAc) in acetonitrile, in which carbazole **3n** and benzimidazole **2p** were generated in 75-90 and 89-99% yields, respectively.

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(14) The presented intermediates are supported by literature reports, see: (a) ref. 17 and (b) Samanta, R.; Kulikov, K.; Strohmann, C.; Antonchick, A. P. *Synthesis* **2012**, *44*, 2325-2332.

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(16) Product **5b** is believed to result from the hydrolysis of 9-acetyl-2-methoxy-6-trifluoroacetoxy-9*H*-carbazole.

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(18) An analogue, *N*-(benzoyl)benzoquinoneimine had been reported by the reaction of *N*-(4-ethoxyphenyl)benzamide with $PhI(OAc)_2$, see ref. 17.