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N-Arylation of Pyridin-2(1*H*)-ones with Pentavalent Organobismuth Reagents under Copper-Free Conditions

Kazuhiro Ikegai,[1,2] **Yuzo Nagata,**[1] **and Teruaki Mukaiyama***[1,3]

[1]The Kitasato Institute, Center for Basic Research, 6-15-5 (TCI) Toshima, Kita-ku, Tokyo 114-0003

[2]Astellas Pharma Inc., Miyukigaoka Research Center, 21 Miyukigaoka, Tsukuba 305-8585

[3]Kitasato Institute for Life Sciences, Kitasato University, 5-9-1 Shirokane, Minato-ku, Tokyo 108-8641

Received October 31, 2005; E-mail: mukaiyam@abeam.ocn.ne.jp

An efficient method for the *N*-arylation of pyridin-2(1*H*)-ones and the related heteroaromatic lactams has been established via ligand-coupling reactions using tri- or tetra-aryl organobismuth(V) reagents such as triarylbismuth dichlorides. Also, *N*-alkenylation of pyridin-2(1*H*)-one was achieved similarly by using alkenyltriarylbismuth(V) reagents.

N-Arylated derivatives of pyridin-2(1*H*)-ones and the related heterocyclic lactams such as quinolin-2(1*H*)-ones are important components in many active pharmaceuticals and are frequently employed for the investigation of their structure–activity relationships.[1]

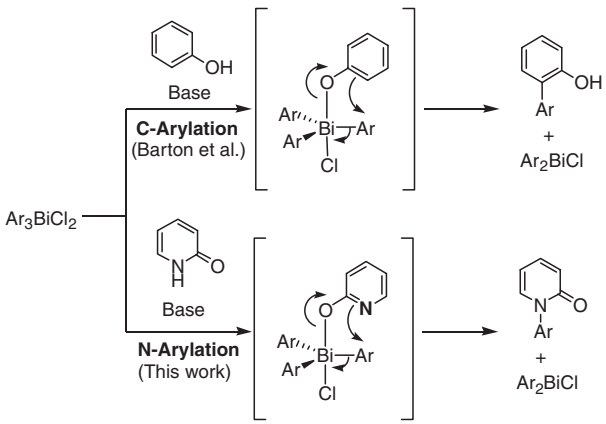
The development of direct *N*-arylation reactions of nitrogen-containing substrates such as primary or secondary amines, amides, and heterocycles is an important issue in organic synthesis. The classical copper-mediated Ullmann (or Goldberg-modified Ullmann) condensation reactions[2] were commonly carried out under harsh reaction conditions (high temperatures, use of strong bases and stoichiometric amounts of copper or copper salts, and long reaction times) and the *N*-arylation reactions of amides were usually sluggish compared to those of amines due to their lower nucleophilicities. Recently, Avendaño described the *N*-arylation of carbostyrils with catalytic copper(II) acetate ($Cu(OAc)_2$) and *p*-tolyllead triacetate at elevated temperatures.[3] Ukita et al.[4] and Renger[5] reported Goldberg–Ullmann condensation of various heteroaromatic lactams and aryl halides with copper(I) iodide (CuI) or copper on silica (Cu/SiO_2) at elevated temperatures. More recently, Chan and Lam reported on the modified Ullmann-arylation of a wide range of NH substrates, including poorly nucleophilic substrates such as heteroaromatic amides, by using arylboronic acids as aryl donors in the presence of $Cu(OAc)_2$ and either triethylamine or pyridine at room temperature.[6] Researchers at Merck applied the Chan–Lam's condition to direct *N*-arylation of pyridin-2(1*H*)-ones in a program for the discovery of novel and potent Factor Xa inhibitors.[7] Li and Dixon also reported that *N*-arylation of pyridin-2(1*H*)-ones with aryl halides proceeded smoothly by employing the Buchwald's CuI–diamine ligand system.[1a]

The arylation of organic substrates by pentavalent bismuth reagents[8] has been known since 1980.[9] Various poly-arylbismuth(V) compounds such as Ph_3BiCl_2, Ph_3BiCO_3, Ph_4BiOTs, and Ph_5Bi are efficient reagents for the regioselective *C*-arylation of phenols,[10] active methylene, or methine compounds,[11] metal–enolates,[12] and enones.[14] The *C*-arylation of phenols takes place preferentially at the *ortho* position.[10] The regioselectivity can be rationalized by assuming a mechanism that involves the formation of covalently bonded Ar_3XBi^V–OPh complexes that undergo ligand-coupling reactions via a concerted intramolecular aryl transfer (see Scheme 1). On the other hand, the facile *N*-arylation of amines and amides by bismuth reagents required the presence of copper catalysts such as metallic copper and $Cu(OAc)_2$ (Barton-modified Ullmann reaction).[2b,14,15] However, we expected that copper-free *N*-arylation of heteroaromatic lactams such as pyridin-2(1*H*)-one (or 2-hydroxypyridine) may proceed by ligand coupling via covalent bismuth(V)–OPy intermediates based on the analogy with *C*-arylation of phenols (Scheme 1).

In this article, we would like to report on a new and efficient method for copper-free *N*-arylation and -alkenylation of pyridin-2(1*H*)-ones by using pentavalent organobismuth reagents such as triarylbismuth dichlorides, providing various *N*-aryl (or -alkenyl) pyridin-2(1*H*)-ones in moderate-to-high yields.[16]

Results and Discussion

At first, pyridin-2(1*H*)-one (2.0 equiv) was treated successively with a base (2.0 equiv) and tri-*o*-tolylbismuth dichloride



Scheme 1. Working hypothesis for *N*-arylation of pyridin-2(1*H*)-ones.

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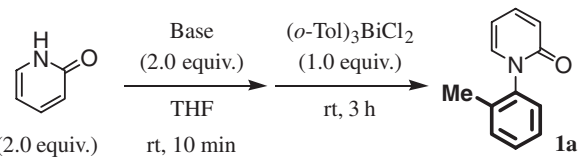
Table 1. Effect of Bases on *N*-*o*-Tolylation of Pyridin-2-one[a)]



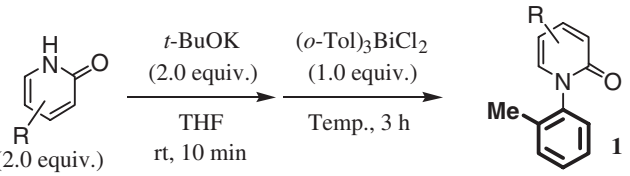
Entry	Base	Yield/%[b)]
1	*t*-BuOLi	ND[d)]
2	*n*-BuLi	ND[d)]
3	*t*-BuONa	72
4	NaH	75
5	*t*-BuOK	95 (40)[c)]
6	1,1,3,3-Tetramethylguanidine	69
7	Et_3N	ND[d)]

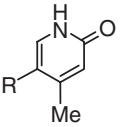
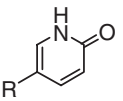
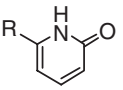
a) All reactions were carried out with pyridin-2(1*H*)-one (0.6 mmol), *t*-BuOK (0.6 mmol), and (*o*-Tol)$_3$BiCl$_2$ (0.3 mmol) in THF (3 mL) at rt. b) Isolated yields. c) The yield in the case when the reaction was carried out with equimolar amounts of the reagents (0.3 mmol) in THF (3 mL). d) Not detected.

(1.0 equiv) in tetrahydrofuran (THF) at room temperature in order to attempt the *N*-arylation reaction as shown in Table 1. The desired *N*-*o*-tolylated product **1a** was formed most effectively in the case when potassium *t*-butoxide (*t*-BuOK) was used (Table 1, Entry 5). The use of sodium hydride (NaH) or sodium *t*-butoxide (*t*-BuONa) was found moderately effective to give **1a** in 72–75% yields, while lithium bases did not afford the arylated product (Table 1, Entries 1–4). In the case when 1,1,3,3-tetramethylguanidine (TMG) was used as an organic base, **1a** was obtained in 69% yield (Table 1, Entry 6). Thus, we decided to use *t*-BuOK as the base in the following experiments. It is important to note that the yield of **1a** decreased to 40% when the reaction was carried out by using equimolar amounts of pyridin-2(1*H*)-one, *t*-BuOK, and (*o*-Tol)$_3$BiCl$_2$, and that the addition of *t*-BuOK (2.0 equiv) to the THF solution of pyridin-2(1*H*)-one (2.0 equiv) and (*o*-Tol)$_3$BiCl$_2$ (1.0 equiv) gave **1a** only in 70% yield.

Next, *o*-tolylation of substituted pyridin-2(1*H*)-ones was tried under the above-mentioned conditions of using (*o*-Tol)$_3$-BiCl$_2$ and *t*-BuOK (Table 2). Various 1-(2-methylphenyl)pyridin-2(1*H*)-one derivatives were successfully synthesized in moderate-to-high yields under mild and copper-free conditions. It should be noted that these *o*-tolylated products were not formed by the copper-catalyzed Ullmann reactions between pyridin-2(1*H*)-ones and 2-halotoluene because of the steric hindrance of the *o*-tolyl group.[1] *N*-*o*-Tolylation of 3- or 4-methylpyridin-2(1*H*)-one proceeded smoothly at room temperature (Table 2, Entries 1 and 4), although refluxing conditions were required when substrates having electron-withdrawing substituents such as halogen, carboxylic ester, and nitro groups were used (Table 2, Entries 2, 3, and 5–9). *N*-*o*-Tolylation of sterically hindered 6-methylpyridin-2(1*H*)-one gave **1k** in modest yield under refluxing conditions (Table 2, Entry 10), while the 6-chloro derivative never afforded the desired product (Table 2, Entry 11). Thus, the present condition showed broad substrate generality in the *o*-tolylation of substituted pyridin-2(1*H*)-ones. According to Li and Dixon's report,[1a] arylation of 5-nitropyridin-2(1*H*)-one and 6-methylpyridin-2(1*H*)-one with aryl halides afforded trace amounts of the desired products by the CuI–diamine system.

Table 2. *N*-*o*-Tolylation of Substituted Pyridin-2-ones[a)]



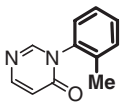
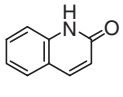
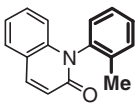
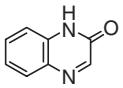
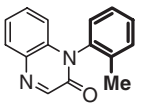
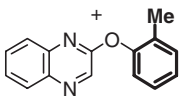
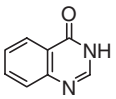
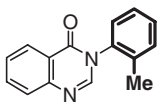
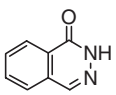
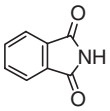
Entry	Substrate		Temp/°C	Yield/%[b)]	Product
1		R = Me	rt	95	**1b**
2		R = Br	reflux	93	**1c**
3		R = NO_2	reflux	78	**1d**
4		R = H	rt	90	**1e**
5		R = NO_2	reflux	89	**1f**
6		R = Cl	reflux	79	**1g**
7		R = Br	reflux	51	**1h**
8		R = CO_2Et	reflux	86	**1i**
9		R = NO_2	reflux	85	**1j**
10		R = Me	reflux	42	**1k**
11		R = Cl	reflux	ND[c)]	—

a) All reactions were carried out with a substrate (0.6 mmol), *t*-BuOK (0.6 mmol), and (*o*-Tol)$_3$BiCl$_2$ (0.3 mmol) in THF (3 mL). b) Isolated yields. c) Not detected.

N-*o*-Tolylation of various heteroaromatic lactams was also studied (see Table 3). Pyrimidin-4(3*H*)-one, quinolin-2(1*H*)-one, and quinazolin-4(3*H*)-one were arylated regioselectively and gave **1l**, **1m**, and **1o** in good yields (Table 3, Entries 1, 3, and 5). In the case of the reaction with quinoxalin-2(1*H*)-one (Table 3, Entry 4), the *N*-tolylated product **1n** was formed along with a small amount of the *O*-tolylated product **2n** (82 and 10%, respectively). The reactions with pyrimidin-2(1*H*)-one, phthalazin-1(2*H*)-one, and phthalimide did not afford the arylated products under the same conditions (Table 3, Entries 2, 6, and 7).

We next focused on the substituent effects on migratory aptitudes of aryl ligands attached to the bismuth(V) center[17] and the arylation of pyridin-2(1*H*)-one was examined by using various substituted triarylbismuth dichlorides (Table 4). *ortho*-Substituted phenyl groups as well as an unsubstituted phenyl one were transferred to the nitrogen atom of pyridin-2(1*H*)-one. Importantly, triphenylbismuth dichloride (Ph_3BiCl_2) and tri(*p*-Tol)bismuth dichloride ((*p*-Tol)$_3$BiCl$_2$) were less reactive in the aryl transfer in comparison with sterically congested (*o*-Tol)$_3$BiCl$_2$, and the *N*-arylated products **1p** and **1q** were produced only when the reactions were carried out under refluxing conditions (Table 4, Entries 1 and 2). The similar reactivity differences between Ph_3BiCl_2 and (*o*-Tol)$_3$BiCl$_2$ in the oxidation of alcohols were reported by Matano and co-workers.[18] They explained the reasons for the result by considering that the introduction of a methyl group to the *ortho* position may have weakened the C–Bi^V bonds in the transition states

Table 3. *N*-*o*-Tolylation of Various Heteroaromatic Lactams[a)]

Entry	Substrate	Product		Yield/%[b)]
1			**1l**	77
2		—	—	ND[c)]
3			**1m**	71
4			**1n**	82
			**2n**	10
5			**1o**	76
6		—	—	ND[c)]
7		—	—	ND[c)]

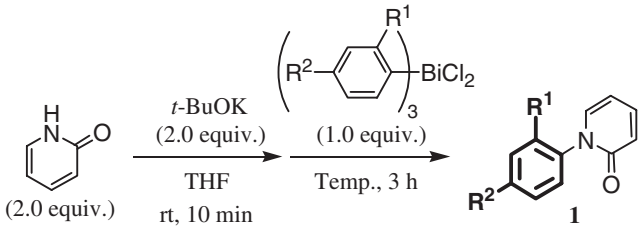
a) All reactions were carried out with a substrate (0.6 mmol), *t*-BuOK (0.6 mmol), and $(o\text{-Tol})_3BiCl_2$ (0.3 mmol) in refluxing THF (3 mL). b) Isolated yields. c) Not detected.

due to the steric hindrance, which increased the rate of the aryl migration. The use of $(p\text{-MeO-C}_6H_4)_3BiCl_2$ led to regioselective *N*-arylation to afford **1s** in 81% yield, while the use of sterically hindered $(o\text{-MeO-C}_6H_4)_3BiCl_2$ and $(4\text{-MeO-2-Me-C}_6H_3)_3BiCl_2$ afforded the desired products with modest *N*-/*O*-selectivities (Table 4, Entries 4, 7, and 9).

Next, *N*-phenylation of pyridin-2(1*H*)-one was investigated by using various tri- or tetra-phenylbismuth(V) reagents (see Table 5). Triphenylbismuth difluoride (Ph_3BiF_2) showed high reactivity comparable to that of Ph_3BiCl_2, affording **1p** in 73% yield (Table 5, Entry 2). The desired product was not formed with $Ph_3Bi(OAc)_2$ or Ph_3BiCO_3 (Table 5, Entries 3 and 4). This indicates that the leaving groups on the bismuth center influence the formation of the covalent Bi^V–OPy intermediate. When tetraphenylbismuth(V) reagents such as Ph_4BiF[12a] and $[Ph_4Bi^+][BF_4^-]$[19a] were allowed to react with an equimolar amount of the amide, **1p** was obtained in reasonable yields (68 and 51% yields, respectively) together with considerable amounts of triphenylbismuthane (Table 5, Entries 5 and 6).

As shown in Table 6, *N*-alkenylation of pyridin-2(1*H*)-one was next tried by using styryltri-*p*-tolylbismuth(V) reagents **4a**[19b] and **4b**,[12a] which were prepared from $(p\text{-Tol})_3BiF_2$ according to Matano and Maruoka's procedure. It was unanticipated that the use of the tetra-coordinated bismuthonium salt **4a**, which is a useful reagent for *C*-alkenylation of phenols and 1,3-dicarbonyl compounds,[19b] would give the *N*-styrylpyridin-2(1*H*)-one (**3**) only in 19% yield and the unreacted pyridin-2(1*H*)-one would be recovered. The decrease in yield compared to the *N*-phenylation with $[Ph_4Bi^+][BF_4^-]$ can be explained by considering the decomposition of **4a** via α-proton abstraction and subsequent vinylidene carbene generation.[20] Based on this consideration, the use of the un-ionized, penta-coordinated styryltri-*p*-tolylbismuth fluoride **4b** was then tried, and **3** and **1q** were produced in high total yield, but the selectivity of alkenyl vs aryl transfer was quite lower in the *N*-alkenylation

Table 4. Substituent Effects on Aryl Ligands[a)]



Entry	R^1	R^2	Temp/°C	Yield/%[b)]	Product
1	H	H	reflux	71	**1p**
2	H	Me	reflux	62	**1q**
3	H	Cl	rt	69	**1r**
4	H	OMe	reflux	81	**1s**
5	Me	H	rt	95	**1a**
6	Me	Cl	rt	91	**1t**
7	Me	OMe	rt	38 (47)[c)]	**1u** (**2u**)
8	CF_3	H	rt	71	**1v**
9	OMe	H	reflux	47 (9)[c)]	**1w** (**2w**)

a) All reactions were carried out with pyridin-2(1*H*)-one (0.6 mmol), *t*-BuOK (0.6 mmol), and a bismuth reagent (0.3 mmol) in THF (3 mL). b) Isolated yields. c) Yields of the corresponding *O*-arylated products **2**.

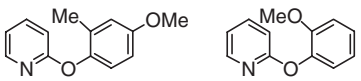
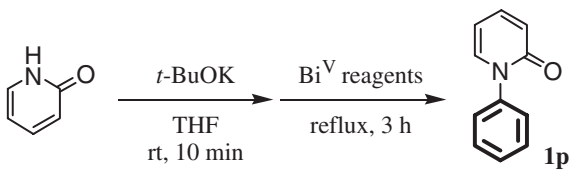


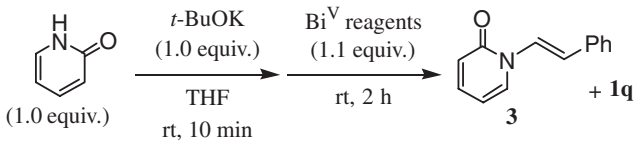
Table 5. Phenylation of Pyridin-2(1*H*)-one by Using Various Organobismuth(V) Reagents



Entry	Reagent	Yield/%	Entry	Reagent	Yield/%
1[a)]	Ph_3BiCl_2	71	4[a)]	Ph_3BiCO_3	0
2[a)]	Ph_3BiF_2	73	5[b)]	Ph_4BiF	68
3[a)]	$Ph_3Bi(OAc)_2$	0	6[b)]	$[Ph_4Bi^+][BF_4^-]$	51

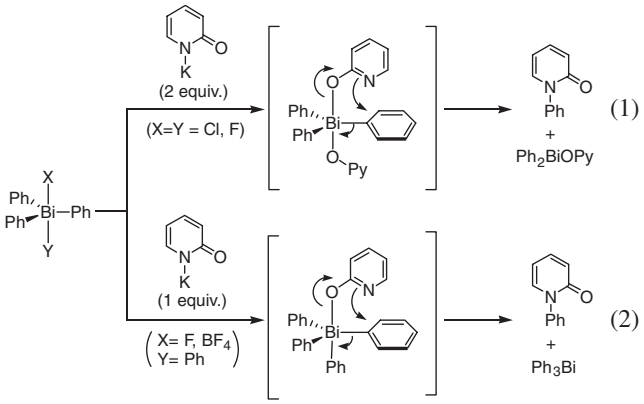
a) Reactions were carried out with pyridin-2(1*H*)-one (0.6 mmol), *t*-BuOK (0.6 mmol), and a bismuth reagent (0.3 mmol) in refluxing THF (3 mL). b) Reactions were carried out with equimolar amounts of pyridin-2(1*H*)-one, *t*-BuOK, and a bismuth reagent (0.3 mmol) in refluxing THF (3 mL).

Table 6. *N*-Alkenylation with Alkenyltriarylbismuth Reagents[a)]

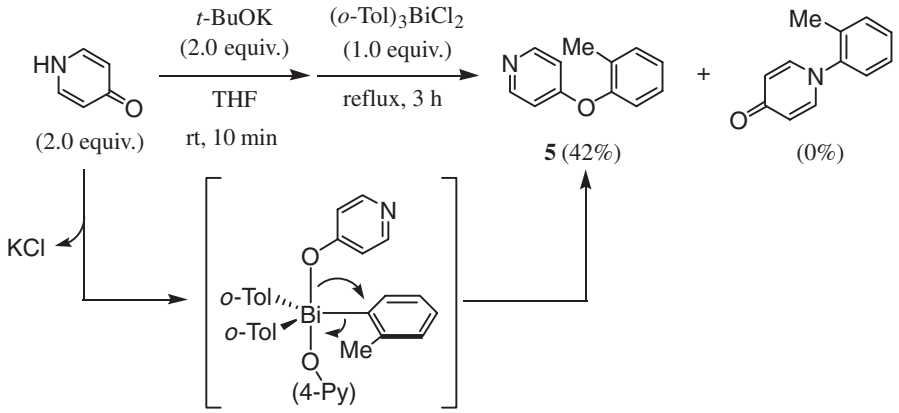


Entry	Reagent		Yield/% 3	1q
1	$[(p\text{-Tol})_3Bi^+CH{=}CHPh][BF_4^-]$	**4a**	19	trace
2	$(p\text{-Tol})_3Bi(F)CH{=}CHPh$	**4b**	44	42

a) Reactions were carried out with pyridin-2(1*H*)-one (0.2 mmol), *t*-BuOK (0.2 mmol), and a bismuth reagent (0.22 mmol) in THF (2 mL) at rt.



Scheme 2. Postulated mechanisms.



Scheme 3. *O*-Selective tolylation of pyridin-4(1*H*)-one.

of pyridin-2(1*H*)-one compared to the case of *C*-alkenylation of 1,3-dicarbonyl compounds[19b] and enol silyl ethers.[12a]

A postulated reaction mechanism of the present arylation reactions is described in Scheme 2. In the cases of the reactions with triarylbismuth dichlorides, two-fold amounts of the potassium salt of pyridin-2(1*H*)-one were needed so as to attain better results. Therefore, it is considered that the two molecules of the substrate were initially replaced at the bismuth(V) center and the corresponding adduct, namely $Ar_3Bi(OPy)_2$, was generated as a key intermediate. The adduct in turn thermally decomposed via the reductive elimination of trivalent bismuth derivatives, affording the desired *N*-arylated product (Scheme 2, Eq. 1). The *N*-phenylation with tetraphenylbismuth(V) reagents were analogously explained by considering the Ph_4Bi-(OPy) adduct, which was transformed into *N*-phenylpyridin-2(1*H*)-one and triphenylbismuthane (Scheme 2, Eq. 2).

In order to prove the importance of the postulated imidate-like structure of Bi^V–O–C(R)=N(R) in the above Bi^V complexes, the arylation of pyridin-4(1*H*)-one with $(o\text{-Tol})_3BiCl_2$ was then tried (Scheme 3). Surprisingly, *O*-selective arylation took place at elevated temperatures and 4-(2-methylphenoxy)-pyridine (**5**) was formed predominantly in 42% yield. The result was in contrast to facile *N*-arylation of pyridin-2(1*H*)-one at room temperature. The *O*-arylation proceeded probably via the ligand coupling from the (pyridin-4-yloxy)–bismuth(V) intermediate. A similar *O*-selective phenylation of *p*-nitrophenol by the thermal degradation of (*p*-nitrophenyloxy)tetraphenylbismuth was reported by Barton et al.[10a] It is considered, therefore, that the imidate-type structure of Bi^V–O–C(R)=N(R) in the above-mentioned (pyridin-2-yloxy)–Bi^V complexes are likely to induce *N*-arylation via a concerted reaction through a weakly polarized, cyclic transition state.

Conclusion

It was demonstrated here that copper-free, facile *N*-arylation of various types of structurally and electrically diverse pyridin-2(1*H*)-ones and the related heteroaromatic lactams such as pyrimidin-4(3*H*)-one, quinolin-2(1*H*)-one, quinazolin-4(3*H*)-one, and quinoxalin-2(1*H*)-one was accomplished by a novel arylation system using a combination of tri- or tetra-arylbismuth(V) reagents and potassium *t*-butoxide. The arylation reactions usually took place at a nitrogen atom of the amide moieties in a regioselective manner, and various functionalities such as halogen, carboxylic ester, and nitro groups on pyridin-2(1*H*)-one were tolerated under the mild conditions. In a similar fashion, *N*-alkenylation of pyridin-2(1*H*)-one with the alkenyltriarylbismuth fluoride **4b** was also achieved with a moderate selectivity of alkenyl vs aryl transfer. To the best of our knowledge, this is the first example of efficient *N*-arylation of amide substrates with pentavalent bismuth reagents under copper-free conditions.

Experimental

General. All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and remain uncorrected. Infrared (IR) spectra were recorded by an attenuated total reflection (ATR) method on a SensIR Technologies Travel*IR*™ spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM-EX270L (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; $\delta = 77.0$ ppm). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700T or a Thermo Electron Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analysis were performed on a vario EL III analyzer. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. All reactions were carried out under an argon atmosphere in dried glassware, unless otherwise noted. Triarylbismuth dichlorides[18] (or difluorides[21]), Ph_4BiBF_4,[19a] Ph_4BiF,[12a] **4a**,[19b] and **4b**[12a] were prepared according to the reported procedures. Ph_3BiCO_3, $Ph_3Bi(OAc)_2$, and *t*-BuOK were purchased from Tokyo Kasei Kogyo and used without any purification. Pyridin-2(1*H*)-one derivatives and other amides were purchased from Tokyo Kasei Kogyo or Aldrich, and used without any purification. Dehydrated THF was purchased from Kanto Chemical Co., Inc.

Typical Experimental Procedure for the Synthesis of *N*-Arylpyridin-2(1*H*)-ones Using Ar_3BiCl_2 and *t*-BuOK. To a solution of pyridin-2(1*H*)-one (57.1 mg, 0.6 mmol) in anhydrous THF (3.0 mL) was added potassium *t*-butoxide (67.3 mg, 0.6 mmol) at room temperature. After 10 min, triarylbismuth dichloride (0.3 mmol) was added to the resulting suspension and the solution was allowed to stand at the temperatures shown in Tables 1–5. After 2 h, the mixture was diluted with ethyl acetate and washed successively with 1 M HCl, 2 M NaOH, and brine, then dried over Na_2SO_4. After concentration, the crude was purified by preparative thin-layer chromatography (eluent: hexane/EtOAc, the range from 3/2 to 2/3) to afford the desired arylated product.

1-(2-Methylphenyl)pyridin-2(1*H*)-one (1a): White solid. mp 74–75 °C. IR (ATR, cm^{-1}) 1657, 1572, 1527, 1274, 1253, 1135, 759. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.48–7.24 (m, 4H), 7.23–7.12 (m, 2H), 6.65 (dd, $J = 9.5$, 0.7 Hz, 1H), 6.23 (ddd, $J = 6.8$, 6.6, 1.3 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 161.8, 139.9, 139.8, 137.7, 134.7, 130.8, 128.8, 126.9, 126.8, 121.5, 105.6, 17.5. Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56%. Found: C, 77.31; H, 6.00; N, 7.43%.

3-Methyl-1-(2-methylphenyl)pyridin-2(1*H*)-one (1b): White solid. mp 95–98 °C. IR (ATR, cm^{-1}) 1650, 1592, 1546, 1493, 1266, 764. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.36–7.22 (m, 4H), 7.16 (d, $J = 6.4$ Hz, 1H), 7.07 (dd, $J = 6.8$, 1.3 Hz, 1H), 6.15 (t, $J = 6.8$ Hz, 1H), 2.19 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.2, 140.3, 136.8, 135.1, 134.8, 130.8, 130.6, 128.6, 126.9, 126.8, 105.3, 17.6, 17.3. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%. Found: C, 78.34; H, 6.61; N, 6.89%.

3-Bromo-1-(2-methylphenyl)pyridin-2(1*H*)-one (1c): White solid. mp 85–87 °C. IR (ATR, cm^{-1}) 1650, 1596, 1578, 1492, 1260, 748. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.81 (d, $J = 7.1$ Hz, 1H), 7.40–7.08 (m, 5H), 6.15 (t, $J = 7.1$ Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 158.0, 141.8, 139.8, 137.4, 134.6, 130.9, 129.1, 126.9, 126.7, 117.1, 105.7, 17.5. Anal. Calcd for $C_{12}H_{10}BrNO$: C, 54.57; H, 3.82; N, 5.30; Br, 30.25%. Found: C, 54.43; H, 3.90; N, 5.24; Br, 30.00%.

3-Nitro-1-(2-methylphenyl)pyridin-2(1*H*)-one (1d): Yellow solid. mp 103–105 °C. IR (ATR, cm^{-1}) 1676, 1594, 1518, 1487, 1334, 1261, 1246, 768, 748. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.40 (dd, $J = 7.6$, 2.1 Hz, 1H), 7.61 (dd, $J = 6.6$, 2.1 Hz, 1H), 7.50–7.25 (m, 3H), 7.16 (d, $J = 6.8$ Hz, 1H), 6.41 (dd, $J = 7.6$, 6.6 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.7, 144.5, 139.2, 139.0, 138.6, 134.5, 131.1, 129.7, 127.1, 126.6, 103.3, 17.5. Anal. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17%. Found: C, 62.41; H, 4.36; N, 12.09%.

4-Methyl-1-(2-methylphenyl)pyridin-2(1*H*)-one (1e): White solid. mp 140–141 °C. IR (ATR, cm^{-1}) 1658, 1579, 1527, 1272, 848, 790, 776. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38–7.10 (m, 4H), 7.07 (d, $J = 6.9$ Hz, 1H), 6.46 (s, 1H), 6.08 (d, $J = 6.9$ Hz, 1H), 2.23 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 161.8, 151.4, 139.9, 136.6, 134.9, 130.8, 128.7, 127.0, 126.8, 119.8, 108.2, 21.3, 17.6. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%. Found: C, 78.07; H, 6.58; N, 6.91%.

4-Methyl-1-(2-methylphenyl)-5-nitropyridin-2(1*H*)-one (1f): Yellow solid. mp 140–143 °C. IR (ATR, cm^{-1}) 1677, 1607, 1530, 1490, 1433, 1341, 1315, 1272, 1240, 1214, 1091, 927, 882, 772, 722. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.48–7.11 (m, 4H), 6.47 (s, 1H), 2.60 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 160.0, 146.0, 140.6, 138.1, 134.6, 132.2, 131.2, 129.9, 127.3, 126.7, 120.8, 21.5, 17.6. Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47%. Found: C, 63.97; H, 5.05; N, 11.52%.

5-Chloro-1-(2-methylphenyl)pyridin-2(1*H*)-one (1g): White solid. mp 94–96 °C. IR (ATR, cm^{-1}) 1661, 1588, 1527, 1492, 1268, 824, 743. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41–7.23 (m, 5H), 7.17 (d, $J = 6.9$ Hz, 1H), 6.64 (d, $J = 9.7$ Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 160.3, 140.9, 139.3, 135.3, 134.8, 131.1, 129.3, 127.1, 126.8, 122.4, 112.2, 17.6. Anal. Calcd for $C_{12}H_{10}ClNO$: C, 65.61; H, 4.59; N, 6.38; Cl, 16.14%. Found: C, 65.40; H, 4.63; N, 6.28; Cl, 16.22%.

5-Bromo-1-(2-methylphenyl)pyridin-2(1*H*)-one (1h): White solid. mp 97–99 °C. IR (ATR, cm^{-1}) 1681, 1589, 1521, 1492, 1279, 822, 731. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.44 (d, $J = 9.7$ Hz, 1H), 7.40–7.24 (m, 4H), 7.16 (d, $J = 7.1$ Hz, 1H), 6.59 (d, $J = 9.7$ Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 160.3, 142.9, 139.2, 137.6, 134.8, 131.1, 129.3, 127.1, 126.8, 122.8, 97.8, 17.6. Anal. Calcd for $C_{12}H_{10}BrNO$: C, 54.57; H, 3.82; N, 5.30; Br, 30.25%. Found: C, 54.42; H, 3.91; N, 5.28; Br, 29.83%; HRMS (FAB$^+$): Calcd for $C_{12}H_{11}BrNO$: $[M + H]^+$ 264.0024. Found: m/z 264.0034.

Ethyl 1-(2-Methylphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (1i): Colorless oil. IR (ATR, cm^{-1}) 1712, 1667, 1538, 1438, 1262, 1239, 1098, 770, 727. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.10 (dd, $J = 2.6$, 0.5 Hz, 1H), 7.96 (dd, $J = 9.7$, 2.6 Hz, 1H), 7.43–7.28 (m, 3H), 7.20 (d, $J = 6.9$ Hz, 1H), 6.65 (d, $J = 9.6$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.16 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.9, 161.7, 143.0, 139.3, 138.9, 134.7, 131.1, 129.4, 127.1, 126.8, 120.3, 110.0, 61.0, 17.5, 14.3. HRMS (FAB$^+$): Calcd for $C_{15}H_{16}NO_3$: $[M + H]^+$ 258.1130. Found: m/z 258.1115.

1-(2-Methylphenyl)-5-nitropyridin-2(1*H*)-one (1j): Yellow oil. IR (ATR, cm^{-1}) 1677, 1616, 1555, 1500, 1336, 1271, 1241, 1102, 829, 732. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.54 (d, $J = 3.0$ Hz, 1H), 8.18 (dd, $J = 10.1$, 3.0 Hz, 1H), 7.48–7.30 (m, 3H), 7.20 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 10.2$ Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (68 MHz, $CDCl_3$) δ 160.6, 139.8, 138.4, 134.5, 133.5, 131.3, 130.6, 130.0, 127.4, 126.6, 120.2, 17.6. HRMS (FAB^+): Calcd for $C_{12}H_{11}N_2O_3$: $[M+H]^+$ 231.0770. Found: m/z 231.0753.

6-Methyl-1-(2-methylphenyl)pyridin-2(1*H*)-one (1k): White solid. mp 93–95 °C. IR (ATR, cm^{-1}) 1657, 1579, 1545, 813, 767, 722. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41–7.24 (m, 4H), 7.13–7.04 (m, 1H), 6.54 (d, $J = 9.2$ Hz, 1H), 6.12 (d, $J = 6.8$ Hz, 1H), 2.08 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.2, 146.1, 139.5, 137.8, 134.9, 131.2, 128.9, 127.5, 127.2, 118.4, 106.0, 21.1, 17.3. HRMS (FAB^+): Calcd for $C_{13}H_{14}NO$: $[M+H]^+$ 200.1075. Found: m/z 200.1087.

3-(2-Methylphenyl)pyrimidin-4(3*H*)-one (1l): Colorless oil. IR (ATR, cm^{-1}) 1670, 1521, 1246, 985, 835, 754. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.96 (d, $J = 6.6$ Hz, 1H), 7.48–7.28 (m, 3H), 7.18 (d, $J = 7.4$ Hz, 1H), 6.56 (d, $J = 6.6$ Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 160.0, 153.3, 151.0, 136.0, 135.2, 131.2, 129.8, 127.2 (×2), 116.5, 17.6. HRMS (FAB^+): Calcd for $C_{11}H_{11}N_2O$: $[M+H]^+$ 187.0871. Found: m/z 187.0859.

1-(2-Methylphenyl)quinolin-2(1*H*)-one (1m): White solid. mp 142–145 °C. IR (ATR, cm^{-1}) 1658, 1589, 1557, 1489, 1444, 1401, 1292, 1245, 828, 768. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.99 (d, $J = 9.4$ Hz, 1H), 7.60 (dd, $J = 7.7$, 1.3 Hz, 1H), 7.47–7.27 (m, 4H), 7.24–7.11 (m, 2H), 6.80 (d, $J = 9.4$ Hz, 1H), 6.55 (d, $J = 8.4$ Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 161.6, 140.2, 139.7, 136.3, 136.0, 131.4, 130.2, 129.1, 128.5, 128.2, 127.6, 122.2, 122.1, 120.2, 115.3, 17.3. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95%. Found: C, 81.30; H, 5.64; N, 5.87%.

1-(2-Methylphenyl)quinoxalin-2(1*H*)-one (1n): White solid. mp 114–116 °C. IR (ATR, cm^{-1}) 1653, 1586, 1458, 754, 741. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.51–7.25 (m, 5H), 7.17 (d, $J = 6.9$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 154.0, 150.8, 135.7, 134.1, 133.3, 133.1, 131.6, 130.8, 130.0, 129.7, 128.0, 127.7, 123.8, 115.1, 17.4. Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86%. Found: C, 76.36; H, 5.27; N, 11.99%.

2-(2-Methylphenoxy)quinoxaline (2n): White solid. mp 82–84 °C. IR (ATR, cm^{-1}) 1569, 1492, 1392, 1300, 1214, 1175, 750. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.11–8.00 (m, 1H), 7.79–7.53 (m, 3H), 7.38–7.10 (m, 4H), 2.21 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 156.7, 151.1, 140.1, 139.4, 138.7, 131.3, 130.5, 130.2, 128.8, 127.7, 127.2, 127.0, 125.6, 121.8, 16.6. HRMS (FAB^+): Calcd for $C_{15}H_{13}N_2O$: $[M+H]^+$ 237.1028. Found: m/z 237.1043.

3-(2-Methylphenyl)quinazolin-4(3*H*)-one (1o): Colorless oil. IR (ATR, cm^{-1}) 1670, 1607, 1602, 1469, 1295, 1264, 913, 769. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.37 (d, $J = 7.6$ Hz, 1H), 7.99 (s, 1H), 7.87–7.72 (m, 2H), 7.60–7.29 (m, 4H), 7.25 (d, $J = 7.1$ Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 160.2, 147.9, 146.2, 136.5, 135.6, 134.4, 131.2, 129.6, 127.7, 127.5, 127.4, 127.2, 127.0, 122.3, 17.8. HRMS (FAB^+): Calcd for $C_{15}H_{13}N_2O$: $[M+H]^+$ 237.1028. Found: m/z 237.1043.

1-Phenylpyridin-2(1*H*)-one[4,5] (1p): White solid. mp 126–128 °C (lit.[4] mp 129 °C). IR (ATR, cm^{-1}) 1654, 1579, 1526, 1491, 1276, 1255, 1139, 759, 690. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.53–7.28 (m, 7H), 6.65 (d, $J = 9.2$ Hz, 1H), 6.19 (dt, $J = 6.8$, 1.3 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.1, 140.7, 139.7, 137.8, 129.1, 128.3, 126.3, 121.7, 105.8.

1-(4-Methylphenyl)pyridin-2(1*H*)-one[7] (1q): White solid. mp 131–133 °C. IR (ATR, cm^{-1}) 1657, 1580, 1525, 1506, 1275, 816, 760. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41–7.20 (m, 6H), 6.64 (d, $J = 9.2$ Hz, 1H), 6.21 (t, $J = 6.6$ Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.3, 139.6, 138.2 (×2), 137.9, 129.7, 126.1, 121.6, 105.6, 21.1. HRMS (FAB^+): Calcd for $C_{12}H_{12}NO$: $[M+H]^+$ 186.0919. Found: m/z 186.0930.

1-(4-Chlorophenyl)pyridin-2(1*H*)-one (1r): White solid. mp 132–134 °C. IR (ATR, cm^{-1}) 1658, 1575, 1531, 1487, 1275, 1085, 997, 841, 820, 757, 732. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.53–7.22 (m, 6H), 6.64 (d, $J = 9.2$ Hz, 1H), 6.25 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.0, 139.9, 139.2, 137.4, 134.2, 129.4, 127.8, 121.9, 106.1. HRMS (FAB^+): Calcd for $C_{11}H_9ClNO$: $[M+H]^+$ 206.0373. Found: m/z 206.0379.

1-(4-Methoxyphenyl)pyridin-2(1*H*)-one (1s): White solid. mp 106–108 °C. IR (ATR, cm^{-1}) 1657, 1582, 1507, 1248, 827, 774, 763. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43–7.24 (m, 4H), 6.98 (d, $J = 8.7$ Hz, 2H), 6.64 (d, $J = 9.2$ Hz, 1H), 6.21 (t, $J = 6.6$ Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.5, 159.2, 139.6, 138.1, 133.7, 127.5, 121.7, 114.4, 105.6, 55.5. HRMS (FAB^+): Calcd for $C_{12}H_{12}NO_2$: $[M+H]^+$ 202.0868. Found: m/z 202.0869.

1-(4-Chloro-2-methylphenyl)pyridin-2(1*H*)-one (1t): White solid. mp 124–126 °C. IR (ATR, cm^{-1}) 1649, 1585, 1531, 1486, 1286, 1135, 998, 849, 835, 775. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (ddd, $J = 9.2$, 6.6, 2.0 Hz, 1H), 7.36–7.23 (m, 2H), 7.20–7.08 (m, 2H), 6.66 (ddd, $J = 9.2$, 1.3, 0.8 Hz, 1H), 6.26 (ddd, $J = 6.8$, 6.6, 1.3 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 161.8, 140.0, 138.5, 137.5, 136.9, 134.5, 130.8, 128.3, 127.1, 121.7, 106.0, 17.6. Anal. Calcd for $C_{12}H_{10}ClNO$: C, 65.61; H, 4.59; N, 6.38; Cl, 16.14%. Found: C, 65.49; H, 4.58; N, 6.30; Cl, 16.22%.

1-(4-Methoxy-2-methylphenyl)pyridin-2(1*H*)-one (1u): White solid. mp 116–117 °C. IR (ATR, cm^{-1}) 1649, 1579, 1500, 1236, 1053, 701. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41 (ddd, $J = 9.1$, 6.4, 2.0 Hz, 1H), 7.19 (ddd, $J = 6.8$, 2.0, 0.7 Hz, 1H), 7.10 (dd, $J = 7.7$, 1.3 Hz, 1H), 6.89–6.78 (m, 2H), 6.66 (ddd, $J = 9.1$, 1.3, 0.7 Hz, 1H), 6.22 (ddd, $J = 6.8$, 6.4, 1.3 Hz, 1H), 3.82 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.3, 159.5, 139.8, 138.3, 136.1, 133.0, 127.9, 121.7, 116.1, 112.2, 105.6, 55.4, 17.9. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51%. Found: C, 72.51; H, 6.08; N, 6.52%.

2-(4-Methoxy-2-methylphenoxy)pyridine (2u): Colorless oil. IR (ATR, cm^{-1}) 1592, 1498, 1464, 1426, 1238, 1197, 1041, 865, 776. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.20–8.12 (m, 1H), 7.63 (ddd, $J = 8.2$, 7.1, 2.0 Hz, 1H), 6.98 (d, $J = 8.6$ Hz, 1H), 6.95–6.88 (m, 1H), 6.86–6.72 (m, 3H), 3.79 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.9, 156.5, 147.6, 145.5, 139.1, 131.7, 122.6, 117.6, 116.3, 112.0, 110.2, 55.5, 16.7. HRMS (FAB^+): Calcd for $C_{13}H_{14}NO_2$: $[M+H]^+$ 216.1025. Found: m/z 216.1029.

1-[2-(Trifluoromethyl)phenyl]pyridin-2(1*H*)-one (1v): White solid. mp 100–102 °C. IR (ATR, cm^{-1}) 1663, 1583, 1530, 1316, 1161, 1114, 1061, 763. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87–7.54 (m, 3H), 7.48–7.33 (m, 2H), 7.18 (ddd, $J = 6.9$, 1.0, 0.8 Hz, 1H), 6.64 (ddd, $J = 9.2$, 1.3, 0.8 Hz, 1H), 6.23 (ddd, $J = 6.8$, 6.6, 1.3 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.3, 140.2, 138.3 (d, $J = 2$ Hz), 137.8, 133.1, 130.1, 129.4, 127.5 (q, $J = 31$ Hz), 127.3 (q, $J = 5$ Hz), 122.7 (q, $J = 273$ Hz), 121.5, 105.1. HRMS (FAB^+): Calcd for $C_{12}H_9F_3NO$: $[M+H]^+$ 240.0636. Found: m/z 240.0636.

1-(2-Methoxyphenyl)pyridin-2(1*H*)-one (1w): White solid. mp 127–129 °C. IR (ATR, cm^{-1}) 1658, 1580, 1524, 1503, 1291, 1270, 1236, 759. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46–7.33 (m, 2H), 7.31–7.15 (m, 2H), 7.11–6.98 (m, 2H), 6.65 (ddd, $J = 9.2$, 1.3, 0.8 Hz, 1H), 6.19 (ddd, $J = 6.8$, 6.6, 1.3 Hz, 1H), 3.81 (s,

3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.1, 154.0, 139.7, 138.8, 130.1, 129.5, 128.4, 121.6, 120.8, 112.3, 105.2, 55.9. Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96%. Found: C, 71.13; H, 5.61; N, 6.80%.

2-(2-Methoxyphenoxy)pyridine (2w): White solid. mp 89–90 °C. IR (ATR, cm^{-1}) 1595, 1569, 1496, 1467, 1427, 1270, 1241, 1174, 1109, 1023, 746. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.14 (ddd, $J = 4.9$, 2.0, 0.8 Hz, 1H), 7.65 (ddd, $J = 8.2$, 7.3, 2.0 Hz, 1H), 7.20 (ddd, $J = 8.4$, 7.3, 1.8 Hz, 1H), 7.14 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.06–6.88 (m, 4H), 3.77 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.5, 151.6, 147.3, 142.4, 138.9, 125.8, 122.9, 120.9, 117.8, 112.8, 110.5, 55.8. HRMS (FAB$^+$): Calcd for $C_{12}H_{12}NO_2$: $[M + H]^+$ 202.0868. Found: m/z 202.0872.

A Typical Procedure for the *N*-Alkenylation of Pyridine-2(1*H*)-one. Synthesis of 1-Styrylpyridin-2(1*H*)-one (3): To a solution of pyridine-2(1*H*)-one (19.0 mg, 0.2 mmol) in anhydrous THF (2.0 mL) was added potassium *t*-butoxide (22.4 mg, 0.2 mmol) and the mixture was stirred for 10 min at room temperature. The styryltri-*p*-tolylbismuth reagent **4a** or **4b** (0.22 mmol) was added to the mixture, and the mixture was stirred for an additional 2 h at rt. The reaction was quenched with 1 M HCl and the mixture was extracted with ethyl acetate, and the combined organic layer was dried over Na_2SO_4. The solution was concentrated in vacuo and the residue was subjected to thin-layer chromatography on silica gel (hexane/EtOAc = 1/1) to give **3** as a white solid. **3**; mp 135–137 °C. IR (ATR, cm^{-1}) 1657, 1585, 1530, 1264, 957, 751, 690. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.00 (d, $J = 14.8$ Hz, 1H), 7.63 (d, $J = 6.9$ Hz, 1H), 7.53–7.20 (m, 6H), 6.74–6.56 (m, 2H), 6.26 (t, $J = 6.8$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 161.3, 139.3, 134.6, 132.6, 128.7, 128.1, 126.6, 125.8, 121.5, 121.1, 106.7. HRMS (FAB$^+$): Calcd for $C_{13}H_{12}NO$: $[M + H]^+$ 198.0919. Found: m/z 198.0922.

4-(2-Methylphenoxy)pyridine (5): Colorless oil. IR (ATR, cm^{-1}) 1573, 1486, 1250, 1204, 1179, 1110, 881, 814, 775, 743, 714. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.43 (d, $J = 5.9$ Hz, 2H), 7.33–6.10 (m, 3H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 5.9$ Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.5, 151.7, 151.2, 131.7, 130.6, 127.5, 125.7, 121.2, 111.3, 16.0. HRMS (FAB$^+$): Calcd for $C_{12}H_{12}NO$: $[M + H]^+$ 186.0919. Found: m/z 186.0931.

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