ORGANOMETALLICS
Article
Cite This: Organometallics XXXX, XXX, XXX−XXX
pubs.acs.org/Organometallics

Palladium-Catalyzed Late-Stage *ortho*-C−H Bond Aroylation of Anilines Using 4-Methoxy-2-pyridinyl as a Removable Directing Group

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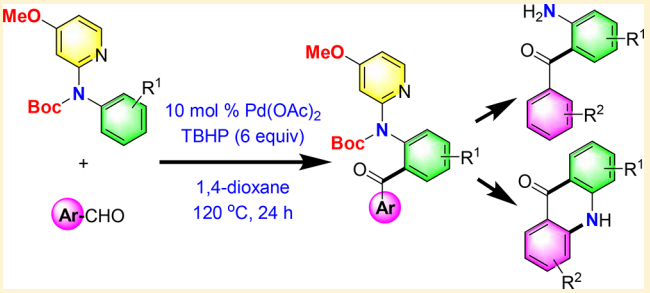
Supporting Information

ABSTRACT: A synthetic methodology for the late-stage *ortho*-C−H bond aroylation of anilines with aryl aldehydes led to a variety of *ortho*-aroylated anilines by the use of palladium(II) acetate, *tert*-butyl hydroperoxide, and 1,4-dioxane as the catalyst, oxidant, and solvent, respectively, is presented. An *N*-phenylpyridin-2-amine palladacycle was isolated and characterized by X-ray crystallography. Controlled experiments, radical trapping experiments, and the experiments of the kinetic isotope effect were undertaken to support the proposed reaction mechanism. Syntheses of 2-aminobenzophenone and 9(10*H*)-acridanone based on the developed methodology were successfully demonstrated.



INTRODUCTION

In the past decade, transition-metal-catalyzed C−H bond functionalization has seen an increased interest in organic synthesis.[1] In comparison with conventional methods, the synthetic strategy can efficiently reduce reaction steps and the formation of byproducts, and the preactivation of starting substrates is not required. Therefore, the way of C−H bond functionalization enables molecular synthesis to become more efficient and simpler. To date, a number of research works have been conducted in the literature.[2]

On the other hand, the so-called directing group often plays an important role in the transition-metal-catalyzed C−H bond functionalization.[3] It is not only able to promote the reactivity but also to control the regioselectivity for the type of reaction, such as the *ortho*-, *meta*-, and *para*-position of a phenyl ring.[4] The pyridinyl is believed to be the most common directing group due to its good affinity with transition metals, especially for the palladium ion. Therefore, it is often used in our studies with respect to the palladium-catalyzed selective *ortho*-C−H bond functionalization.[5]

In view of the importance of benzophenones in organic synthesis[6] and biological activity,[7] organic chemists are devoted to developing versatile synthetic methods to target this molecular skeleton. So far, numerous methodologies for the synthesis of benzophenones have been conducted in literature, especially for the *ortho* cross-dehydrogenative coupling (CDC) of arenes and aryl aldehydes.[5a,8] In these methods, the palladium ion and *tert*-butyl hydroperoxide (TBHP) have been examined to be the best metal catalyst and a radical initiator, respectively, in terms of the synthetic practicability. Moreover, various directing groups, such as the pyridinyl, acetyl, carbamate, isoxazole, and so on were involved in these reported reactions.

In 2015, we successfully demonstrated that the palladium-catalyzed *ortho*-C−H bond aroylation of phenols with aryl aldehydes using the pyridinyl as a directing group. The reaction was undertaken via the intermolecular C_{Ar}−H/$C_{Aldehyde}$−H bond cross-coupling to afford a variety of 2-hydroxybenzophenones followed by the removal of the pyridinyl group.[5a] Moreover, the synthesis of 1-hydroxy-9*H*-fluoren-9-ones[9] was achieved by the intramolecular C_{Ar}−H/C_{Ar}−H bond cross-coupling reaction of 2-hydroxybenzophenones. Finally, this work encouraged us to continuously study the palladium-catalyzed *ortho*-C−H bond aroylation of anilines.

In the presented study, the palladium-catalyzed *ortho*-C−H bond aroylation of 4-methoxy-*N*-arylpyridin-2-amines with aryl aldehydes in the presence of TBHP was undertaken to afford a variety of *ortho*-aroylated 4-methoxy-*N*-arylpyridin-2-amines in modest to good yields. Meanwhile, a possible reaction mechanism was presented based on the investigation of controlled and radical trapping experiments as well as the experiments of the kinetic isotope effect. Toward the synthetic application, 2-aminobenzophenone can be given by removing the pyridinyl group of *ortho*-phenylated 4-methoxy-*N*-phenyl-

Received: February 22, 2019

DOI: 10.1021/acs.organomet.9b00119
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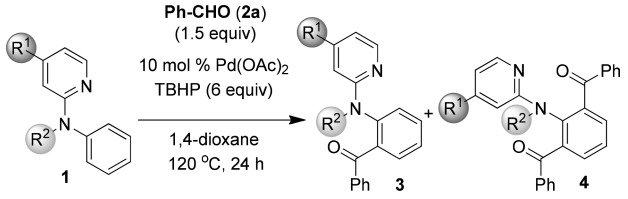
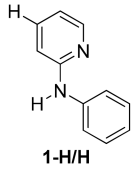
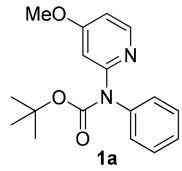
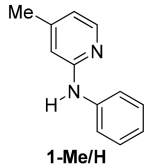
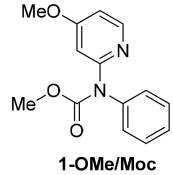
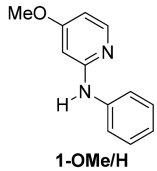
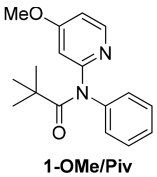
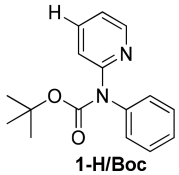
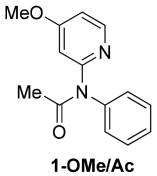
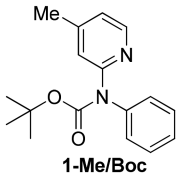
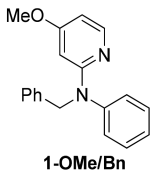
Table 1. Reactivity Investigation of the Pyridinyl and *N*-Protecting Groups in the Palladium-Catalyzed *ortho*-C−H Bond Aroylation of 1



entry	substrate	Product **3**,**4** (ratio)[a]	yield (%)[b]	entry	substrate	Product **3**,**4** (ratio)[a]	yield (%)[b]
1	 **1-H/H**	**3-H/H**, R^1 = H; R^2 = H	0	6	 **1a**	**3a** + **4a** (67:33), R^1 = OMe; R^2 = Boc	87
2	 **1-Me/H**	**3-Me/H**, R^1 = Me; R^2 = H	0	7	 **1-OMe/Moc**	**3-OMe/Moc** + **4-OMe/Moc** (65:35), R^1 = OMe; R^2 = Moc	88
3	 **1-OMe/H**	**3-OMe/H**, R^1 = OMe; R^2 = H	0	8	 **1-OMe/Piv**	**3-OMe/Piv** + **4-OMe/Piv** (77:23), R^1 = OMe; R^2 = Pivaloyl	45
4	 **1-H/Boc**	**3-H/Boc**, R^1 = H; R^2 = Boc	trace	9	 **1-OMe/Ac**	**3-OMe/Ac**, R^1 = OMe; R^2 = Acetyl	33
5	 **1-Me/Boc**	**3-Me/Boc**, R^1 = Me; R^2 = Boc	40	10	 **1-OMe/Bn**	**3-OMe/Bn**, R^1 = OMe; R^2 = Bn	28

[a]Product ratio was determined as an average of three runs by GC-FID. [b]Product yield was determined as an average of three runs by the isolation.

pyridin-2-amine. In addition, 9(10*H*)-acridanone[10] can be directly synthesized through the palladium-catalyzed intramolecular C−H/N−H bond cross-coupling of 2-aminobenzophenone or *ortho*-phenylated 4-methoxy-*N*-phenylpyridin-2-amine followed by the removal of the pyridinyl group.

RESULTS AND DISCUSSION

Reactivity Investigation of the Directing Group and *N*-Protecting Group for the Palladium-Catalyzed *ortho*-C−H Bond Aroylation of 1. At the beginning of this study, we first carried out the reaction of *N*-phenylpyridin-2-amine (**1-H/H**) with benzaldehyde (**2a**) in the presence of palladium(II) acetate and TBHP as the catalyst and a radical initiator, respectively. 1,4-Dioxane was the solvent and the reaction was held at 120 °C for 24 h. However, none of the desired product **3-H/H** was found under the above reaction conditions (entry 1, Table 1). On the basis of our previous experience, the directing group bearing an electron-donating group (e.g., methyl or methoxy) can significantly promote the reactivity of the palladium-catalyzed site-selective (e.g., *ortho*) C−H bond activation.[5b] Therefore, we turned to employ compounds **1-Me/H** and **1-OMe/H** as new starting substrates by using 4-methyl and 4-methoxy as the directing group, respectively. However, there was still none of the desired *ortho*-aroylated products **3-Me/H** and **3-OMe/H** obtained from the reaction of **1-Me/H** or **1-OMe/H** with **2a**, and the starting substrate (i.e., **1-Me/H** or **1-OMe/H**) was recovered (entries 2−3, Table 1). These results made us consider the role of the free amino group of **1** in the reaction. Thus, we tagged a protecting group, *tert*-butyloxycarbonyl (Boc) on the secon-

DOI: 10.1021/acs.organomet.9b00119
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dary amino groups of **1-H/H**, **1-Me/H**, and **1-OMe/H** led to **1-H/Boc**, **1-Me/Boc**, and **1-OMe/Boc**. The subsequent *ortho*-C−H bond aroylation of *N*-Boc protected substrates **1-H/Boc**, **1-Me/Boc**, and **1-OMe/Boc** with **2a** was carried out under the aforementioned reaction conditions. The experimental results showed that the desired *ortho*-benzoylated products **3-H/Boc**, **3-Me/Boc**, and **3a** (accompanied dibenzoylated product **4a**) were generated in the trace, 40%, and 87% yield, respectively (entries 4−6, Table 1). In other words, the electronic property of the directing group (i.e., pyridinyl) is important for the reaction, whereas the *N*-protecting group (e.g., Boc) is also critical for this case.

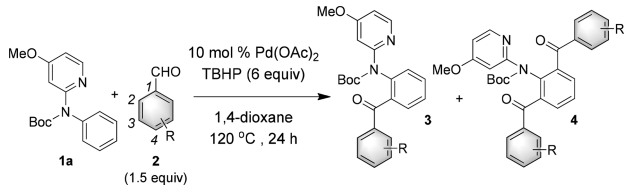
On the basis of these above results, we attempted to understand the influence of the *N*-protecting group of **1** in the presented reaction. Therefore, a series of *N*-protecting groups, such as methyloxycarbonyl (Moc), *tert*-butylcarbonyl (Piv), acetyl (Ac), and benzyl (Bn) were introduced to **1-OMe/H**. Then, various *N*-protecting substrates **1-OMe/Moc**, **1-OMe/Piv**, **1-OMe/Ac**, and **1-OMe/Bn** was generated and further examined under the aforementioned reaction conditions. Experimental results addressed that the yield of *ortho*-benzoylated products **3-OMe/Moc**, **3-OMe/Piv**, **3-OMe/Ac**, and **3-OMe/Bn** accompanied dibenzoylated products **4-OMe/Moc**, **4-OMe/Piv**, and **4-OMe/Ac** was determined to be 88%, 45%, 33%, and 28% yields, respectively (entries 7−10, Table 1). Herein, we chose Boc as the optimal *N*-protecting group for the palladium-catalyzed *ortho*-C−H bond aroylation of **1** with **2**. This is because Boc is relatively easy to remove compared to Moc. By varying the *N*-protecting group of **1-OMe/H**, the oxygen atom (not the one on the carbonyl group) of Boc or Moc is critical for the reaction. This might be due to the electrostatic repulsion between the oxygen atom of the *N*-protecting group and the nitrogen atom of the pyridinyl group. The phenomenon forces the coordination of the palladium ion and pyridine to orient to the *ortho*-C−H bond as well as prevents the interaction between the amine and TBHP. These two factors might eventually result in the occurrence of the *ortho*-C−H bond aroylation of **1-OMe/Boc** in good yields. Moreover, the steric effect of the *N*-protecting group might also potentially provide the influence in the reaction (see entries 8−10, Table 1).

Optimization of the Reaction Conditions. According to the reactivity investigation of the directing group and *N*-protecting group, both of Boc and 4-methoxy-2-pyridinyl group were eventually chosen as the optimal *N*-protecting group and directing group for the palladium-catalyzed *ortho*-C−H bond aroylation of anilines **1** with aryl aldehyde **2**. Next, the reaction of **1a** with **2a** in the presence of palladium(II) acetate was examined by the variation of the oxidant, solvent, the amount of reagents, and the reaction temperature (see Table S1).

First of all, a variety of oxidants (6 equiv) were screened in the presence of 10 mol % $Pd(OAc)_2$ using 1,4-dioxane as the reaction solvent in which these reactions were heated at 120 °C for 24 h (entries 1−10 and 18, Table S1). The screening results showed that the anticipated product **3a** was generated only by the use of TBPB (*tert*-butyl peroxybenzoate) and TBHP as the oxidant. The product ratio (yield) of **3a** and **4a** was determined to be >99:1 (35%) and 67:33 (87%), respectively (entries 1 and 18, Table S1). In addition to the oxidant, we also evaluated the solvent effect in the presence of 10 mol % $Pd(OAc)_2$ and 6 equiv TBHP (entries 11−21, Table S1). The results of solvent screening showed that 1,4-dioxane still acted as the best solvent for the reaction. Then, the reaction temperature was varied from 80 to 140 °C to give 120 °C as the best temperature (entry 18 and 22−24, Table S1). Finally, the equivalent of TBHP was examined from 0 to 7 (entries 25−29, Table S1) to indicate 6 equiv as the optimal amount in which a mixture of **3a** and **4a** was isolated in 87% total yield with product ratio 67:33 (entry 18, Table S1). On the basis of the optimized experiments, we finally decided to use the following reaction conditions for the *ortho*-C−H bond aroylation of **1**: 10 mol % $Pd(OAc)_2$, 6 equiv TBHP, and 1.5 equiv aryl aldehyde **2** in 1,4-dioxane heated at 120 °C for 24 h.

Substrate Scope. With the optimized reaction conditions in hand, we subsequently carried out the demonstration of substrates for the palladium-catalyzed *ortho*-C−H bond aroylation of **1a** with a variety of aryl aldehyde **2** (Table 2).

Table 2. *ortho*-C−H Bond Aroylation of 1a with 2



entry	aldehyde (**2**)	product **3**, **4** (ratio)[a]	yield (%)[b]
1	R = H (**2a**)	**3a** + **4a** (68:32)	87
2	R = 4-OMe (**2b**)	**3b** + **4b** (67:33)	89
3	R = 4-NO_2 (**2c**)	not detected	0
4	R = 4-CF_3 (**2d**)	**3d**	24
5	R = 4-Ac (**2e**)	**3e**	44
6	R = 2-F (**2f**)	**3f** + **4f** (98:2)	58
7	R = 3-F (**2g**)	**3g** + **4g** (88:12)	84
8	R = 4-F (**2h**)	**3h** + **4h** (90:10)	86
9	R = 2-Cl (**2i**)	**3i**	39
10	R = 3-Cl (**2j**)	**3j** + **4j** (98:2)	57
11	R = 4-Cl (**2k**)	**3k** + **4k** (95:5)	62
12	R = 3-Br (**2l**)	**3l**	31
13	R = 4-Br (**2m**)	**3m**	37
14	R = 3,5-diMe (**2n**)	**3n** + **4n** (78:22)	88
15	R = 2,4-diMe (**2o**)	**3o** + **4o** (88:12)	61
16	R = 3,5-diOMe (**2p**)	**3p**	35
17	R = 2,4-diOMe (**2q**)	**3q** + **4q** (90:10)	29
18	R = 3-CHO (**2r**)	**3r**	45

[a]Product ratio was determined as an average of three runs by GC-FID. [b]Product yield was determined as an average of three runs by the isolation.

A series of *ortho* monoaroylated products **3a,b,f−h,j,k,n,o,q** (major) as well as diaroylated products **3a,b,f−h,j,k,n,o,q** (minor) were obtained as following product ratios and yields **3a**:**4a** = 68:32 (87%), **3b**:**4b** = 67:33 (89%), **3f**:**4f** = 98:2 (58%), **3g**:**4g** = 88:12 (84%), **3h**:**4h** = 90:10 (86%), **3j**:**4j** = 98:2 (57%), **3k**:**4k** = 95:5 (64%), **3n**:**4n** = 78:22 (88%), **3o**:**4o** = 88:12 (61%), and **3q**:**4q** = 90:10 (29%) (entries 1−2, 5−8, 10−11, 14−15, and 17, Table 2). On the other hand, only monoaroylated products **3d,e,i,l,m,p,r** were isolated in 24−45% yields by the reaction of **1a** with **2d,e,i,l,m,p,r** (entries 4−5, 9, 12−13, 16, and 18, Table 2), whereas none of the anticipated product **3d** was generated (entry 3, Table 2). These experimental results show that aryl aldehyde **2** bearing an electron-donating group (e.g., OMe) usually exhibits better reactivity than that of the electron-withdrawing group (e.g.,

DOI: 10.1021/acs.organomet.9b00119
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NO_2) in the presented reaction. This might be due to the electronic donating effect of the aroyl group could stabilize the palladium intermediate (see Figure 3). By contrast, the electronic withdrawing effect may destabilize it. Moreover, the steric hindrance of aryl aldehydes **2** seems to potentially offer the influence on the reactivity, which resulted in low product yields. For instance, *ortho*-substituted aryl aldehydes **2f**, **2i**, **2o**, and **2q** (see entries 6, 9, 15 and 17, Table 2).[11] In addition, when isophthalaldehyde (**2r**) which contains two formyl groups at C1 and C3-position of benzene ring was used, none of the dual C−H/C−H bond coupling product was given. Only monoaroylated product **3r** was isolated in 45% yield (entry 18, Table 2). Finally, the structure of dibenzoylated *N*-Boc protected 4-methoxy-*N*-phenylpyridin-2-amine (**4a**) was secured by X-ray crystallography as shown as Figure 1a.[12]

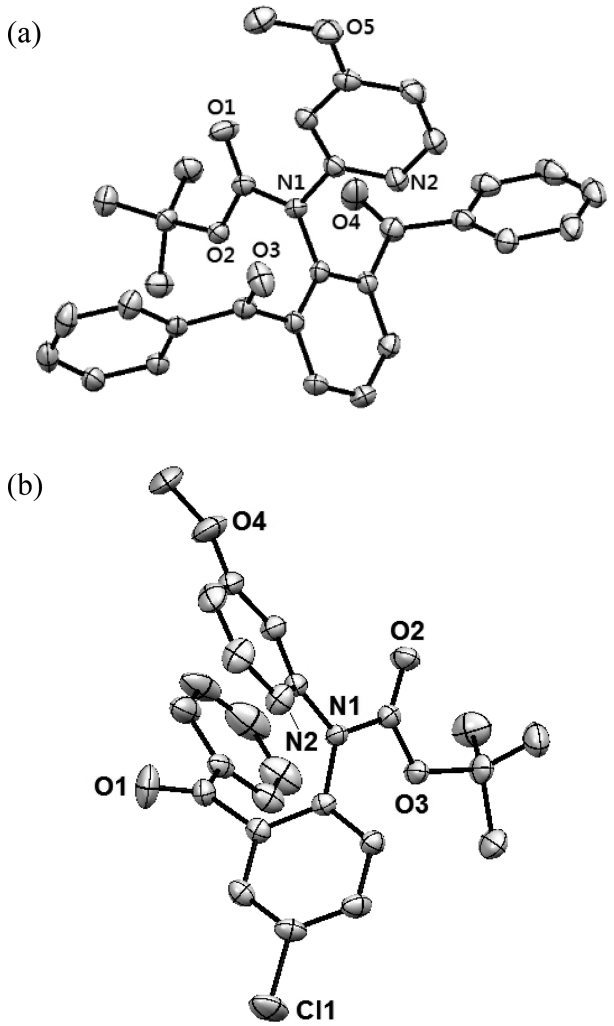
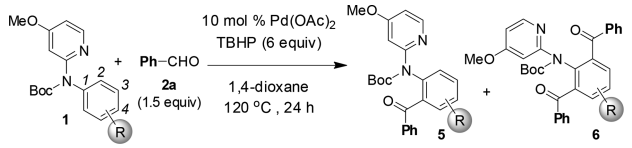


Figure 1. An ORTEP drawing of (a) compound **4a** and (b) compound **5h**.[12] All hydrogen atoms are omitted for clarity.

In addition to substrate **1a**, we also conducted the reaction of **1b**−**i** with **2a** under the optimized reaction conditions to afford a variety of *ortho* monobenzoylated *N*-Boc protected 4-methoxy-*N*-arylpyridin-2-amine **5** (a major product) and dibenzoylated products **6** (a minor product was produced in some cases) in 39−94% yields. These experimental results are summarized in Table 3. On the basis of the comparison of

Table 3. *ortho*-C−H Bond Benzoylation of 1 with 2a



entry	substrate (**1**)	product **5**, **6** (ratio)[a]	yield (%)[b]
1	R = 2-OMe (**1b**)	**5b**	91
2	R = 3-OMe (**1c**)	**5c**	83
3	R = 4-OMe (**1d**)	**5d** + **6d** (61:39)	93
4	R = 4-F (**1e**)	**5e** + **6e** (71:29)	74
5	R = 3-F (**1f**)	**5f**	57
6	R = 2-F (**1g**)	**5g**	94
7	R = 4-Cl (**1h**)	**5h** + **6h** (92:8)	79
8	R = 4-Br (**1i**)	**5i**	39

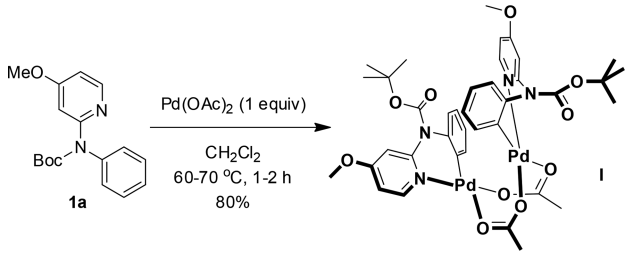
[a]Product ratio was determined as an average of three runs by GC-FID. [b]Product yield was determined as an average of three runs by the isolation.

product yields, the substituent electronic effect in the *ortho*-C−H bond aroylation of substrates **1b**−**i** seems not to apparently influence the reactivity. The structure of *ortho* monobenzoylated product **5h** was eventually secured by X-ray crystallography as shown as Figure 1b.[12] In addition, *ortho* dibenzoylated products **6d**, **6e**, and **6h** were isolated in 39%, 29%, and 8% product ratios, respectively (entries 3−4, and 7, Table 3).

Mechanistic Investigation. In order to gain an insight of the reaction, we subsequently carried out a series of experiments that include the preparation of a palladacycle, controlled experiments, radical trapping experiments, and the experiments of kinetic isotope effect to support the proposed catalytic mechanism.

1. Preparation and Characterization of the Palladacycle **I.** The palladacycle **I** was prepared by the stoichiometric reaction of **1a** with palladium(II) acetate in dichloromethane (see the Supporting Information). The reaction was heated at 60−70 °C for 1−2 h to afford palladacycle **I** in 80% yield (Scheme 1).

Scheme 1. Preparation of Palladacycle I



The structure of **I** was secured by X-ray crystallography as shown as Figure 2.[12] On the basis of the structural analysis of **I**, we further confirm that the pyridinyl group of **1a** is the directing group, but not the Boc group. In other words, the pyridinyl group coordinates with the palladium(II) ion, which enables the *ortho*-C−H bond activation of aniline to generate **I**. By contrast, the Boc group herein plays only as a protecting group for the secondary amine of **1a**. It does not participate in the coordination of the palladium(II) ion. The conformation of **I** looks like a U-shape geometry, as well as the two ligands (i.e., **1a**) are aligned as a head-to-tail form. Finally, the reaction of **I** with **2a** in the presence of TBHP (6 equiv) was done; however, none of the anticipated *ortho*-benzoylated product **3a**

DOI: 10.1021/acs.organomet.9b00119
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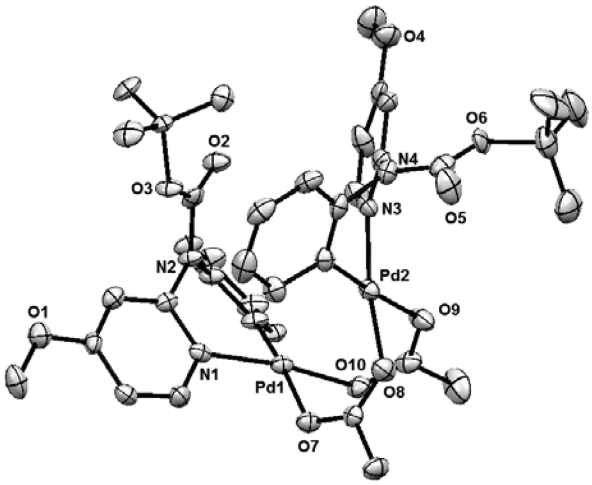
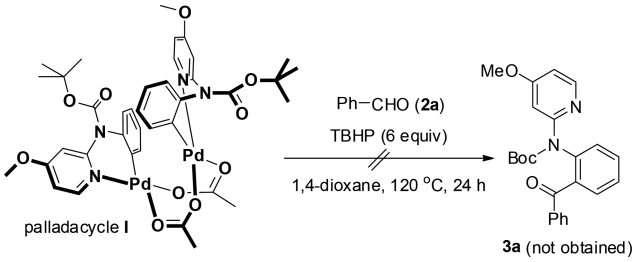


Figure 2. An ORTEP drawing of palladacycle **I**.[12] All hydrogen atoms are omitted for clarity.

was observed (Scheme 2). This result implies that the palladacycle **I** might not be the key intermediate for the palladium-catalyzed *ortho*-C−H bond aroylation of **1** with **2**.

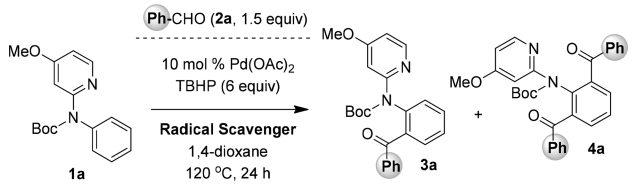
Scheme 2. Controlled Experiment by the Stoichiometric Reaction of I with 2a



2. Radical Trapping Experiment. To examine whether the presented reaction occurs via a radical process, the reaction of **1a** with **2a** in the presence of BHT, DPE, and TEMPO, respectively, was undertaken (see Table 4) (BHT = butylated hydroxytoluene, DPE = 1,1-diphenylethylene, and TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl). The experimental results showed that the total yield of products **3a** and **4a** dramatically decreased down to 17%, 27%, and the trace amount from 87% (in the absence of a radical scavenger) when 3 equiv of BHT, DPE, and TEMPO was added to the reaction, respectively. This study indicates that a radical species at least could be involved in the course of the reaction.

3. Investigation of the Kinetic Isotope Effect. To evaluate the *ortho*-C−H bond cleavage of **1** in the presented reaction is whether a rate-determining step, the intra- and intermolecular kinetic isotope effect (KIE) experiments as well as the KIE from two parallel reactions were done by the use of **1a-D$_1$**, **1a**, and **1a-D$_5$** as starting substrates. Next, we carried out the reaction of **1a-D$_1$**, **1a**, and **1a-D$_5$** with 4-methoxybenzaldehyde (**2b**) under the optimized reaction conditions. Basically, the determination of KIE was undertaken on the basis of the ^{1}H NMR spectroscopy (see Scheme 3 and Supporting Information). The value of $(k_H/k_D)_{intra}$, $(k_H/k_D)_{inter}$, and $(k_H/k_D)_{parallel}$ was determined to be 5.4, 1.0, and 0.9, respectively.[13] The analysis of experimental results indicates that the palladium-catalyzed *ortho*-C−H bond cleavage of **1** is not involved in the rate-determining steps of the presented reaction. By contrast, the binding of **1** with the palladium ion is strongly suggested to be the key rate-determining step in the reaction.[14]

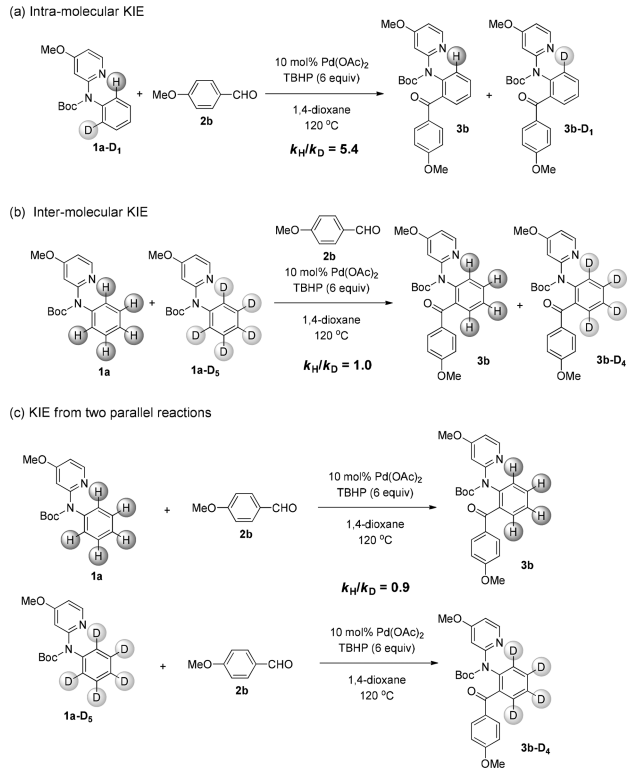
Table 4. Radical Trapping Experiments for the Palladium-Catalyzed *ortho*-C−H Bond Benzoylation of 1a with 2a



entry	radical scavenger (equiv)	product ratio (**3a**:**4a**)[a]	yield (%)[b]
1	–	68:32	87
2	BHT (1)	67:33	65
3	BHT (2)	93:7	25
4	BHT (3)	95:5	17
5	DPE (1)	90:10	70
6	DPE (2)	95:5	54
7	DPE (3)	95:5	27
8	TEMPO (1)	90:10	52
9	TEMPO (2)	90:10	20
10	TEMPO (3)	100:0	trace

[a]Product ratio was determined as an average of three runs by GC-FID. [b]Product yield was determined as an average of three runs by the isolation.

Scheme 3. Investigation of the Kinetic Isotope Effect for Palladium-Catalyzed *ortho*-C−H Bond Aroylation of 1



Proposed Mechanism. On the basis of the above mechanistic studies, a possible catalytic process for the palladium-catalyzed *ortho*-C−H bond aroylation of **1** with **2** is presented as shown as Figure 3. In the beginning, the binding of substrate **1** and palladium(II) acetate enables the formation of π-complex **II** by release of acetate anion. The π-

DOI: 10.1021/acs.organomet.9b00119
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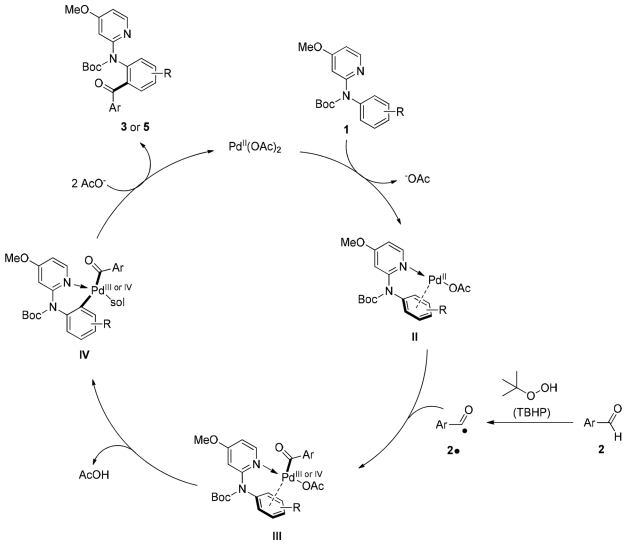
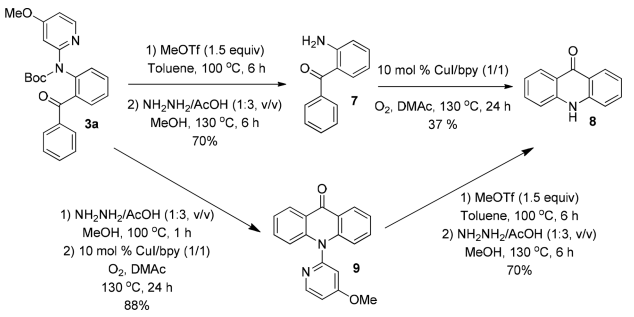


Figure 3. A proposed catalytic mechanism for the palladium-catalyzed *ortho*-C−H bond aroylation of **1** with **2**.

complex **II** is then transformed to the key aroyl palladium(III or IV) π-complex **III** by the redox reaction of the π-complex **II** and the aroyl radical **2•** (generated from aryl aldehydes **2** by the treatment of TBHP via one electron abstraction). Next, the π-complex **III** is fast transformed to intermediate **IV** via the palladium(III or IV) insertion at the *ortho*-C−H bond of aniline ring accompanied the release of acetic acid. Finally, the desired product **3** or **5** is generated through the reductive elimination of the intermediate **IV**. Meanwhile, the palladium-(II) acetate is regenerated from the intermediate **IV** to continue the catalytic cycle.

Synthetic Applications. The synthetic extension for a developed methodology is important. To demonstrate the merit of *ortho*-aroylated *N*-Boc protected 4-methoxy-*N*-arylpyridin-2-amines **3** and **5** in organic synthesis, we herein chose compound **3a** as a modeling substrate to approach the syntheses of 2-aminobenzophenone (**7**), 9(10*H*)-acridanone (**8**), and *N*-(4-methoxy-2-pyridinyl)-9(10*H*)-acridanone (**9**) (see Scheme 4). First, the pyridinyl and Boc groups of **3a** were

Scheme 4. Synthetic Applications of Compound 3a



concurrently removed by the treatment of methyl trifluoromethanesulfonate (MeOTf) in toluene heated at 100 °C for 6 h and followed by the addition of hydrazine/acetic acid (3/1, v/v)[5c] in methanol heated at 130 °C for 6 h to afford 2-aminobenzophenone (**7**) in 70% yield. Afterward, compound **7** was directly transformed to 9(10*H*)-acridanone (**8**) in 37% yield under the reaction conditions as shown as follows: 10 mol % CuI/bipyridine (1/1, equiv/equiv) in the presence of oxygen gas in dimethylacetamide (DMAC) heated at 130 °C for 24 h.[15] On the other hand, the synthesis of **8** can be obviously improved by another synthetic route. That is, the treatment of **3a** by a solution of hydrazine/acetic acid (3/1, v/v) in methanol heated at 100 °C for 1 h, and then conducted to the same reaction conditions with the synthesis of **8** from **7**, which underwent the intramolecular C−H/N−H bond coupling to give *N*-pyridinyl-9(10*H*)-acridanone (**9**) in 88% yield. Finally, the pyridinyl group of **9** was again removed to afford **8** in 70% yield by employing the same reaction conditions with the transformation of **3a** to **7**.

CONCLUSION

We have developed a simple and efficient methodology for the synthesis of *ortho*-aroylated *N*-Boc protected *N*-arylpyridin-2-amines using palladium(II) acetate and aryl aldehyde as the catalyst and coupling reagent, respectively, in the presence of a key oxidant, *tert*-butyl hydroperoxide. The *ortho*-aroylated *N*-arylpyridin-2-amines are easily transformed to the alternative of 2-aminobenzophenones and 9(10*H*)-acridanones. In addition, we present a possible catalytic mechanism to explain the reaction through the studies of the palladacycle, controlled experiments, radical trapping experiments, and kinetic isotope effects. The methodology provides a facile route to synthesize *ortho*-aroylated anilines directed from anilines and aryl aldehydes. It can serve as a useful tool to target 2-aminobenzophenone and 9(10*H*)-acridanone analogue. Finally, we believe that the developed methodology is able to play an important role in the synthetic field of pharmaceuticals and materials.

EXPERIMENTAL SECTION

General Methods. Solvents and reagents were purchased from commercial suppliers, and used without purification. ^{1}H NMR spectra were measured on 300, 400, and 500 MHz NMR spectrometers. Natural abundance ^{13}C NMR spectra were measured by using 300, 400, and 500 MHz NMR spectrometers operating at 75, 100, 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 for most of the compounds: EI-magnetic sector. Melting points were measured by using open capillary tubes and uncorrected.

General Procedure for the Synthesis of Compounds 3−6. A well-stirred solution of substrate **1** with aryl aldehydes **2** by the addition of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), TBHP (108 mg, 1.2 mmol) in 1,4-dioxane (3 mL) was heated at 120 °C for 24 h. After cooling down to room temperature, the reaction solution was washed by water (20 mL). The solution was then extracted by ethyl acetate (15 mL × 3). Organic layers were combined, dried over $MgSO_4$, filtered through a pad of Celite, and evaporated in a vacuum. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (30/1 to 10/1) as the eluent to afford products **3-6**. The amounts of **1** and **2** are listed as follows. **1-H/H**: 27 mg, 0.20 mmol for **3-H/H**; **1-Me/H**: 37 mg, 0.20 mmol for **3-Me/H**; **1-OMe/H**: 48 mg, 0.20 mmol for **3-OMe/H**; **1-H/Boc**: 54 mg, 0.20 mmol for **3-H/Boc**; **1-Me/Boc**: 57 mg, 0.20 mmol for **3-Me/Boc**; **1-OMe/Moc**: 52 mg, 0.20 mmol for **3-OMe/Moc** and **3-OMe/Moc**; **1-OMe/Piv**: 57 mg, 0.20 mmol for **3-OMe/Piv** and **3-OMe/Piv**; **1-OMe/Ac**: 49 mg, 0.02 mmol for **3-OMe/Ac** and **3-OMe/Ac**; **1-OMe/Bn**: 58 mg, 0.20 mmol for **3-OMe/Bn** and **3-OMe/Bn**; **1a**: 60 mg, 0.20 mmol for **3-4**; **1b**: 66 mg, 0.20 mmol for **5b**; **1c**: 66 mg, 0.20 mmol for **5c**; **1d**: 66 mg, 0.2 mmol for **5d** and **6d**; **1e**: 64 mg, 0.20 mmol for **5e** and **6e**: **1f**: 64 mg, 0.20 mmol for **5f**; **1g**: 64 mg, 0.20 mmol for **5g**; **1h**: 64 mg,

DOI: 10.1021/acs.organomet.9b00119
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0.20 mmol for **5h** and **6h**; **1i**: 76 mg, 0.20 mmol for **5i**; **2a**: 32 mg, 0.30 mmol for **3a** and **4a**; **2b**: 41 mg, 0.30 mmol for **3b** and **4b**; **2c**: 45 mg, 0.30 mmol for **3c**; **2d**: 52 mg, 0.30 mmol for **3d**; **2e**: 45 mg, 0.30 mmol for **3e**; **2f**: 37 mg, 0.30 mmol for **3f** and **4f**; **2g**: 37 mg, 0.30 mmol for **3g** and **4g**; **2h**: 37 mg, 0.30 mmol for **3h** and **4h**; **2i**: 42 mg, 0.30 mmol for **3i**; **2j**: 42 mg, 0.30 mmol for **3j** and **4j**; **2k**: 42 mg, 0.30 mmol for **3k** and **4k**; **2l**: 56 mg, 0.30 mmol for **3l**; **2m**: 56 mg, 0.30 mmol for **3m**; **2n**: 40 mg, 0.30 mmol for **3n** and **4n**; **2o**: 40 mg, 0.30 mmol for **3o** and **4o**; **2p**: 50 mg, 0.30 mmol for **3p**; **2q**: 50 mg, 0.30 mmol for **3q** and **4q**; **2r**: 40 mg, 0.30 mmol for **3r**. All product yields were determined by the isolation and shown as follows: **3-H/H**: 0% (0 mg, 0 mmol); **3-Me/H**: 0% (0 mg, 0 mmol); **3-OMe/H**: 0% (0 mg, 0 mmol); **3-H/Boc**: trace; **3-Me/Boc**: 40% (31 mg, 0.080 mmol); **3-OMe/Moc**: 57% (41 mg, 0.11 mmol); **3-OMe/Piv**: 35% (27 mg, 0.070 mmol); **3-OMe/Ac**: 33% (23 mg, 0.070 mmol); **3-OMe/Bn**: 28% (22 mg, 0.060 mmol); **3a**: 59% (49 mg, 0.12 mmol); **3b**: 60% (52 mg, 0.12 mmol); **3c**: 0% (0 mg, 0 mmol); **3d**: 24% (24 mg, 0.050 mmol); **3e**: 44% (40 mg, 0.090 mmol); **3f**: 57% (47 mg, 0.11 mmol); **3g**: 74% (63 mg, 0.15 mmol); **3h**: 77% (65 mg, 0.15 mmol); **3i**: 39% (34 mg, 0.080 mmol); **3j**: 56% (49 mg, 0.11 mmol); **3k**: 61% (54 mg, 0.12 mmol); **3l**: 30% (29 mg, 0.060 mmol); **3m**: 37% (36 mg, 0.070 mmol); **3n**: 69% (60 mg, 0.14 mmol); **3o**: 54% (47 mg, 0.11 mmol); **3p**: 35% (33 mg, 0.070 mmol); **3q**: 26% (24 mg, 0.050 mmol); **3r**: 45% (39 mg, 0.090 mmol); **4-OMe/Moc**: 31% (32 mg, 0.070 mmol); **4-OMe/Piv**: 10% (10 mg, 0.020 mmol); **4a**: 28% (29 mg, 0.060 mmol); **4b**: 29% (33 mg, 0.060 mmol); **4f**: 1% (1 mg, 0.002 mmol); **4g**: 10% (11 mg, 0.020 mmol); **4h**: 9% (10 mg, 0.020 mmol); **4j**: 1% (1 mg, 0.002 mmol); **4k**: 3% (4 mg, 0.006 mmol); **4n**: 19% (22 mg, 0.040 mmol); **4o**: 7% (8 mg, 0.01 mmol); **4q**: 3% (4 mg, 0.006 mmol); **5b**: 91% (79 mg, 0.18 mmol); **5c**: 83% (72 mg, 0.17 mmol); **5d**: 57% (50 mg, 0.11 mmol); **5e**: 53% (45 mg, 0.11 mmol); **5f**: 57% (48 mg, 0.11 mmol); **5g**: 94% (79 mg, 0.19 mmol); **5h**: 73% (64 mg, 0.15 mmol); **5i**: 39% (38 mg, 0.080 mmol); **6d**: 36% (39 mg, 0.070 mmol); **6e**: 21% (22 mg, 0.040 mmol); **6h**: 6% (7 mg, 0.01 mmol).

Synthesis of Compound 7. A well-stirred solution of **3a** (81 mg, 0.20 mmol) in toluene (2 mL) by the addition of MeOTf (45 μL, 0.4 mmol) was heated at 100 °C under nitrogen gas for 6 h. After cooling down to room temperature, the reaction solution was evaporated in a vacuum. The residue was dissolved in methanol (2 mL) and then the mixed solution of hydrazine (0.3 mL) and acetic acid (0.9 mL) (1:3, v/v) was added to the above solution, which was further heated at 130 °C for 6 h. After cooling down to room temperature, water (20 mL) was added to the solution, which was further extracted by ethyl acetate (15 mL × 3). Organic layers were combined, dried over $MgSO_4$, filtered through a pad of Celite, and evaporated in a vacuum. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (30/1 to 10/1) as the eluent to give product **7** in 70% (28 mg, 0.14 mmol).

Synthesis of Compound 8. A well-stirred solution of **7** (500 mg, 2.50 mmol), copper(II) iodide (9.5 mg, 0.050 mmol), 2,2′-bipyridine (8 mg, 0.05 mmol) in dimethylacetamide (10 mL) was heated at 130 °C for 24 h. After cooling down to room temperature, water (20 mL) was added to the above solution that was further extracted by ethyl acetate (15 mL × 3). Organic layers were combined, dried over $MgSO_4$, filtered through a pad of Celite, and evaporated in a vacuum. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (30/1 to 10/1) as the eluent to give product **8** in 37% (447 mg, 0.98 mmol).

Synthesis of (a) Compound 9 transformed to (b) Compound 8. (a) A well-stirred solution of **3a** (500 mg, 2.50 mmol) in methanol (10 mL) was added by the mixed solution of hydrazine (1.8 mL) and acetic acid (5.4 mL) (1:3, v/v), which was heated at 100 °C for 3 h. After cooling down to room temperature, 15 mL of water was added to the above solution, which was extracted by ethyl acetate (15 mL × 2). Organic layers were combined, dried over $MgSO_4$, filtered through a pad of Celite, and evaporated in vacuum. Next, the residue was dissolved in dimethylacetamide (5 mL) without purification, and subsequently, copper(II) iodide (9.5 mg, 0.050 mmol) and 2,2′-bipyridine (8 mg, 0.05 mmol) were added to the above solution, which was heated at 130 °C for 24 h. After cooling down to room temperature, 20 mL of water was added to the above solution that was further extracted by ethyl acetate (15 mL × 3). Organic layers were combined, dried over $MgSO_4$, filtered through a pad of Celite, and evaporated in a vacuum. The residue was purified by silica gel chromatography using *n*-hexane/ethyl acetate (30/1 to 10/1) as the eluent to give product **9** in 88% (447 mg, 0.98 mmol). (b) The operating procedure for the synthesis of **8** from **9** was the same as that of **7** to **8**, and the yield of **8** is 70% (133 mg, 0.69 mmol).

Characterization Data of Compounds 3–9.[16] *tert-Butyl phenyl(pyridin-2-yl)carbamate (1-H/Boc).* White solid; mp 64–65 °C; R_f = 0.53 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 7.07 (ddd, J = 5.6, 4.8, 0.8 Hz, 1 H), 7.20–7.25 (m, 3 H), 7.32–7.37 (m, 2 H), 7.50 (d, J = 8.0 Hz, 1 H), 7.70 (ddd, J = 8.6, 7, 2.0 Hz, 1 H), 8.38 (dd, J = 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.2 (CH_3), 81.6 (C_q), 120.5 (CH), 121.0 (CH), 126.3 (CH), 127.6 (CH × 2), 128.8 (CH × 2), 137.5 (CH), 141.8 (C_q), 148.6 (CH), 153.6 (C_q), 155.4 (C_q); MS (EI, m/z) 270 (M^+, 3), 169 (100), 57 (45); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{16}H_{18}N_2O_2$ 270.1368, found 270.1369.

tert-Butyl (4-methylpyridin-2-yl)(phenyl)carbamate (1-Me/Boc). White solid; mp 64–65 °C; R_f = 0.53 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9 H), 2.36 (s, 3 H), 6.91 (dd, J = 5.2, 0.8 Hz, 1 H), 7.19–7.23 (m, 3 H), 7.30–7.36 (m, 3 H), 8.24 (d, J = 5.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.0 (CH_3), 28.2 (CH_3 × 3), 81.5 (C_q), 121.6 (CH), 121.9 (CH), 126.1 (CH), 127.5 (CH × 2), 128.7 (CH × 2), 141.9 (C_q), 148.2 (CH), 148.9 (C_q), 153.7 (C_q), 155.4 (C_q); MS (EI, m/z) 284 (M^+, 4), 183 (100), 57 (46); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{17}H_{20}N_2O_2$ 284.1525, found 284.1534.

Methyl (4-methoxypyridin-2-yl)(phenyl)carbamate (1-OMe/Moc). White solid; mp 64–65 °C; R_f = 0.53 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3 H), 3.85 (s, 3 H), 6.66 (dd, J = 5.6, 2.4 Hz, 1 H), 7.07 (d, J = 2.0 Hz, 1 H), 7.26 (m, 3 H), 7.35–7.37 (m, 2 H), 8.20 (d, J = 5.6, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.2 (CH_3), 55.3 (CH_3), 106.2 (CH), 108.0 (CH), 126.8 (CH), 127.5 (CH × 2), 128.9 (CH × 2), 141.1 (C_q), 149.4 (CH), 155.1 (C_q), 156.4 (C_q), 167.1 (C_q); MS (EI, m/z) 258 (M^+, 1), 257 (21), 177 (100), 164 (30), 161 (48); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{14}H_{14}N_2O_3$ 258.1004, found 258.1005.

N-(4-Methoxypyridin-2-yl)-N-phenylpivalamide (1-OMe/Piv). White solid; mp 66–67 °C; R_f = 0.52 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.17 (s, 9 H), 3.80 (s, 3 H), 6.63 (d, J = 2.4 Hz, 1 H), 6.70 (dd, J = 6.0, 2.4 Hz, 1 H), 7.23–7.30 (m, 3 H), 7.33–7.37 (m, 2 H), 8.27 (d, J = 5.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.3 (CH_3 × 3), 42.1 (C_q), 55.3 (CH_3), 107.7 (CH), 108.6 (CH), 127.1 (CH), 128.5 (CH × 2), 129.1 (CH × 2), 143.4 (C_q), 149.6 (CH), 158.6 (C_q), 167.3 (C_q), 181.1 (C_q); MS (EI, m/z) 284 (M^+, 1), 199 (100), 200 (17), 283 (14); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{17}H_{20}N_2O_2$ 284.1525, found 284.1524.

N-(4-Methoxypyridin-2-yl)-N-phenylacetamide (1-OMe/Ac). White solid; mp 58–59 °C; R_f = 0.43 (*n*-hexane/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3 H), 3.84 (s, 3 H), 6.69 (dd, J = 5.6, 2.4 Hz, 1 H), 6.99 (d, J = 1.2 Hz, 1 H), 7.29–7.33 (m, 3 H), 7.38–7.43 (m, 2 H), 8.24 (d, J = 5.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2 (C_q), 55.4 (CH_3), 106.9 (CH), 108.5 (CH × 2), 127.5 (CH), 128.1 (CH), 129.4 (CH × 2), 142.0 (C_q), 149.6 (CH), 156.7 (C_q), 167.1 (C_q), 170.9 (C_q); MS (EI, m/z) 242 (M^+, 1), 199 (100), 200 (47); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{14}H_{14}N_2O_2$ 242.1055, found 242.1056.

N-Benzyl-4-methoxy-N-phenylpyridin-2-amine (1-OMe/Bn). White solid; mp 81–82 °C; R_f = 0.63 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3 H), 5.25 (s, 2 H), 5.99 (d, J = 2.0 Hz, 1 H), 6.27 (dd, J = 6.0, 2.0 Hz, 1 H), 7.14–7.35 (m, 10 H), 8.05 (d, J = 5.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7 (C_q), 160.6 (C_q), 148.9 (CH), 145.4 (C_q), 139.4 (C_q), 129.6 (CH × 2), 128.2 (CH × 2), 127.5 (CH × 2), 126.9 (CH × 2), 126.6 (CH), 125.6 (CH), 101.8 (CH), 93.5 (CH), 54.8 (CH_3), 53.7 (CH_2); MS (EI, m/z) 290 (M^+, 1), 289 (48), 213 (65), 182 (45); HRMS (EI-

DOI: 10.1021/acs.organomet.9b00119
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magnetic sector) m/z [M^+] calcd for $C_{19}H_{18}N_2O$ 290.1419, found 290.1421.

*tert-Butyl (4-methoxypyridin-2-yl)(phenyl)carbamate (**1a**).* White solid; mp 66−67 °C; R_f = 0.40 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 3.86 (s, 3 H), 6.63 (dd, J = 5.5, 2.5 Hz, 1 H), 7.04 (d, J = 2.5 Hz, 1 H), 7.20−7.25 (m, 3 H), 7.36 (t, J = 8.0 Hz, 2 H), 8.19 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2 (CH_3 × 3), 55.3 (CH_3), 81.5 (C_q), 106.4 (CH), 107.6 (CH), 126.2 (CH), 127.5 (CH × 2), 128.7 (CH × 2), 141.8 (C_q), 149.3 (CH), 153.5 (C_q), 156.9 (C_q), 166.8 (C_q); MS (EI, m/z) 300 (M^+, 4); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{17}H_{20}N_2O_3$ 300.1474, found 300.1476.

*tert-Butyl (2-methoxyphenyl)(4-methoxypyridin-2-yl)carbamate (**1b**).* Yellow solid; mp 72−73 °C; R_f = 0.59 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 9 H), 3.80 (s, 3 H), 3.85 (s, 3 H), 6.55 (dd, J = 5.7, 2.1 Hz, 1 H), 6.93−6.97 (m, 2 H), 7.16−7.30 (m, 3 H), 8.10 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 55.6 (CH_3), 81.0 (C_q), 104.1 (CH), 107.0 (CH), 111.7 (CH), 120.6 (CH), 128.4 (CH), 129.7 (CH), 130.7 (C_q), 148.8 (CH), 153.7 (C_q), 155.4 (C_q), 156.8 (C_q), 166.5 (C_q); MS (EI, m/z) 330 (M^+, 1), 299 (100), 243 (76), 199 (97), 89 (62), 57 (70); HRMS m/z calcd for $C_{18}H_{22}N_2O_4$ 330.1580, found 330.1579.

*tert-Butyl (3-methoxyphenyl)(4-methoxypyridin-2-yl)carbamate (**1c**).* Brown solid; mp 50−51 °C; R_f = 0.56 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 3.77 (s, 3 H), 3.85 (s, 3 H), 6.64 (dd, J = 5.4, 1.8 Hz, 1 H), 6.79 (t, J = 7.8 Hz, 3 H), 7.00 (s, 1 H), 7.22 (d, J = 9.0 Hz, 1 H), 8.21 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2 (CH_3 × 3), 55.2 (CH_3), 55.3 (CH_3), 81.6 (C_q), 106.6 (CH), 107.7 (CH), 111.8 (CH), 113.3 (CH), 119.8 (CH), 129.2 (CH), 142.8 (C_q), 149.4 (CH), 153.4 (C_q), 156.8 (C_q), 159.8 (C_q), 166.8 (C_q); MS (EI, m/z) 330 (M^+, 22), 230 (100), 215 (55), 57 (100); HRMS m/z calcd for $C_{18}H_{22}N_2O_4$ 330.1580, found 330.1578.

*tert-Butyl (4-methoxyphenyl)(4-methoxypyridin-2-yl)carbamate (**1d**).* White solid; mp 108−109 °C; R_f = 0.55 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9 H), 3.80 (s, 3 H), 3.85 (s, 3 H), 6.60 (dd, J = 5.7, 2.4 Hz, 1 H), 6.88 (d, J = 6.9 Hz, 2 H), 7.06 (d, J = 2.1 Hz, 1 H), 7.14 (d, J = 8.7 Hz, 2 H), 8.18 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2 (CH_3 × 3), 55.3 (CH_3), 55.4 (CH_3), 81.4 (C_q), 105.9 (CH), 107.4 (CH), 114.0 (CH × 2), 128.9 (CH × 2), 134.7 (C_q), 149.2 (CH), 153.8 (C_q), 157.0 (C_q), 157.8 (C_q), 166.8 (C_q); MS (EI, m/z) 330 (M^+, 8), 230 (100), 215 (60); HRMS m/z calcd for $C_{18}H_{22}N_2O_4$ 330.1580, found 330.1582.

*tert-Butyl (4-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**1e**).* Yellow solid; mp 58−59 °C; R_f = 0.31 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9 H), 3.87 (s, 3 H), 6.63 (dd, J = 6.0, 2.4 Hz, 1 H), 7.00−7.10 (m, 3 H), 7.17−7.21 (m, 2 H), 8.17 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2 (CH_3 × 3), 55.3 (CH_3), 81.8 (C_q), 106.0 (CH), 107.6 (CH), 115.6 (d, J_{C-F} = 22.8 Hz, CH), 129.4 (d, J_{C-F} = 8.3 Hz, CH), 137.7 (d, J_{C-F} = 2.8 Hz, C_q), 149.2 (CH), 153.5 (C_q), 156.6 (C_q), 160.9 (d, J_{C-F} = 244.0 Hz, C_q), 166.9 (C_q); MS (EI, m/z) 318 (M^+, 4), 230 (48), 217 (100), 57 (54); HRMS m/z calcd for $C_{17}H_{19}FN_2O_3$ 318.1380, found 318.1377.

*tert-Butyl (3-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**1f**).* Yellow solid; mp 68−69 °C; R_f = 0.28 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 3.87 (s, 3 H), 6.67 (dd, J = 6.0, 2.4 Hz, 1 H), 6.89−7.03 (m, 4 H), 7.24−7.32 (m, 1 H), 8.21 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.4 (CH_3), 82.0 (C_q), 106.7 (CH), 108.0 (CH), 113.0 (d, J_{C-F} = 21.0 Hz, CH), 114.6 (d, J_{C-F} = 23.8 Hz, CH), 122.9 (d, J_{C-F} = 2.8 Hz, CH), 129.6 (d, J_{C-F} = 9.1 Hz, CH), 143.2 (d, J_{C-F} = 10.0 Hz, C_q), 149.5 (CH), 153.1 (C_q), 156.4 (C_q), 162.6 (d, J_{C-F} = 245.1 Hz, C_q), 167.0 (C_q); MS (EI, m/z) 318 (M^+, 3), 217 (100), 57 (50); HRMS m/z calcd for $C_{17}H_{19}FN_2O_3$ 318.1380, found 318.1377.

*tert-Butyl (2-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**1g**).* White solid; mp 61−62 °C; R_f = 0.30 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9 H), 3.87 (s, 3 H), 6.59 (dd, J = 5.7, 2.1 Hz, 1 H), 7.10−7.16 (m, 2 H), 7.22−7.30 (m, 3 H), 8.10 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.3 (CH_3), 81.9 (C_q), 104.3 (CH), 107.5 (CH), 116.0 (d, J_{C-F} = 20.0 Hz, CH), 124.1 (d, J_{C-F} = 3.6 Hz, CH), 128.6 (d, J_{C-F} = 7.8 Hz, CH), 129.4 (d, J_{C-F} = 12.8 Hz, C_q), 130.3 (d, J_{C-F} = 0.9 Hz, CH), 148.8 (CH), 153.0 (C_q), 156.0 (C_q), 158.3 (d, J_{C-F} = 247.9 Hz, C_q), 166.7 (C_q); MS (EI, m/z) 318 (M^+, 2), 217 (22), 199 (100), 57 (38); HRMS m/z calcd for $C_{17}H_{19}FN_2O_3$ 318.1380, found 318.1380.

*tert-Butyl (4-chlorophenyl)(4-methoxypyridin-2-yl)carbamate (**1h**).* Yellow solid; mp 74−75 °C; R_f = 0.50 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 3.86 (s, 3 H), 6.64 (dd, J = 5.5, 2.5 Hz, 1 H), 7.07 (d, J = 2.5 Hz, 1 H), 7.15 (d, J = 6.5 Hz, 2 H), 7.30 (d, J = 8.5 Hz, 2 H), 8.18 (d, J = 5.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.3 (CH_3), 81.9 (C_q), 106.3 (CH), 107.8 (CH), 128.8 (CH × 2), 128.9 (CH × 2), 131.8 (C_q), 140.3 (C_q), 149.3 (CH), 153.2 (C_q), 156.5 (C_q), 166.9 (C_q); MS (EI, m/z) 334 (M^+, 3), 233 (65), 57 (100); HRMS m/z calcd for $C_{17}H_{19}ClN_2O_3$ 334.1084, found 334.1086.

*tert-Butyl (4-bromophenyl)(4-methoxypyridin-2-yl)carbamate (**1i**).* Orange solid; mp 120−121 °C; R_f = 0.50 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9 H), 3.87 (s, 3 H), 6.65 (dd, J = 5.7, 2.1 Hz, 1 H), 7.05−7.10 (m, 3 H), 7.45 (d, J = 8.7 Hz, 2 H), 8.18 (d, J = 5.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2 (CH_3 × 3), 55.4 (CH_3), 82.0 (C_q), 106.3 (CH), 107.8 (CH), 119.7 (C_q), 129.1 (CH × 2), 131.8 (CH × 2), 140.9 (C_q), 149.3 (CH), 153.2 (C_q), 156.4 (C_q), 166.9 (C_q); MS (EI, m/z) 378 (M^+, 5), 279 (100), 277 (90), 57 (57); HRMS m/z calcd for $C_{17}H_{19}BrN_2O_3$ 378.0579, found 378.0580.

tert-Butyl (2-benzoylphenyl)(4-methylpyridin-2-yl)carbamate (3-Me/Boc). White oil; R_f = 0.53 (*n*-hexane/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 2.21 (s, 3 H), 6.71 (dd, J = 5.2, 0.4 Hz, 1 H), 7.09 (s, 1 H), 7.33−7.57 (m, 8 H), 7.70 (dd, J = 8.0, 0.8 Hz, 1 H), 8.03 (d, J = 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (CH_3), 28.1 (CH_3), 81.8 (C_q), 120.6 (CH), 121.1 (CH), 126.5 (CH), 127.9 (CH × 2), 129.5 (CH), 130.0 (CH × 2), 130.7 (CH), 130.9 (CH), 132.7 (CH), 136.9 (C_q), 137.2 (C_q), 139.8 (C_q), 147.2 (CH), 148.2 (C_q), 153.2 (C_q), 154.6 (C_q), 195.7 (C_q); MS (ESI+, m/z) 389 (M^+, 100); HRMS (ESI+) m/z [M + H] calcd for $C_{24}H_{25}N_2O_3$ 389.1860, found 389.1865.

Methyl (2-benzoylphenyl)(4-methoxypyridin-2-yl)carbamate (3-OMe/Moc). White oil; R_f = 0.59 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3 H), 3.77 (s, 3 H), 6.50 (dd, J = 5.6, 2.4 Hz, 1 H), 7.16 (d, J = 2.0 Hz, 1 H), 7.36−7.45 (m, 5 H), 7.50−7.57 (m, 2 H), 7.75 (td, J = 7.6, 2.0 Hz,, 2 H), 8.01 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.2 (CH_3), 55.2 (CH_3), 104.6 (CH), 108.2 (CH), 126.7 (CH), 128.0 (CH × 2), 129.6 (CH), 130.2 (CH × 2), 131.2 (CH), 132.9 (CH), 139.3(C_q), 148.4 (CH), 154.7(C_q), 155.9(C_q), 166.8(C_q), 166.4(C_q), 195.6(C_q); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{21}H_{18}N_2O_4$ 362.1267, found 362.1267.

N-(2-Benzoylphenyl)-N-(4-methoxypyridin-2-yl)pivalamide (3-OMe/Piv). White oil; R_f = 0.63 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9 H), 3.79 (s, 3 H), 6.71 (dd, J = 6.0, 2.4 Hz, 1 H), 7.08 (d, J = 2.4 Hz, 1 H), 7.24−7.33 (m, 3 H), 7.44 (t, J = 7.6 Hz, 3 H), 7.56 (tt, J = 9.2, 1.2 Hz, 1 H), 7.85 (dd, J = 8.0, 0.8 Hz, 2 H), 8.22 (d, J = 5.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6 (CH_3× 3), 41.7 (C_q), 55.4 (CH_3), 107.8 (CH), 109.9 (CH), 126.0 (CH), 128.2 (CH × 2), 128.7 (CH), 129.5 (CH), 130.6 (CH × 2), 131.1 (CH), 133.1 (CH), 136.8 (C_q), 137.7 (C_q), 148.7 (CH), 158.3 (C_q), 167.4 (C_q), 180.7 (C_q), 196.2 (C_q); MS (ESI, m/z) 411 (M^+23, 1), 397 (80), 389 (100), 381 (90); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{24}H_{24}N_2O_3$ 388.1787, found 388.1786.

N-(2-Benzoylphenyl)-N-(4-methoxypyridin-2-yl)acetamide (3-OMe/Ac). White oil; R_f = 0.53 (*n*-hexane/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 3 H), 3.76 (s, 3 H), 6.57 (bs, 1 H), 7.19 (d, J = 2.4 Hz, 1 H), 7.38−7.40 (m, 4 H), 7.49−7.57 (m, 3 H), 7.78 (d, J = 2.8 Hz, 2 H), 8.10 (bs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7 (CH_3), 55.2 (CH_3), 109.0 (CH), 126.9 (CH), 128.1 (CH × 2), 128.2 (CH), 129.3(CH), 130.4 (CH × 2), 131.3 (CH), 132.9 (CH), 134.4 (C_q), 136.7 (C_q), 137.8 (C_q), 140.1 (C_q), 148.6

DOI: 10.1021/acs.organomet.9b00119
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(CH), 167.0 (C_q), 171.1 (C_q), 195.6 (Cq); MS (EI, *m/z*) 361 (M^+, 1), 340 (30), 177 (41), 86 (58), 84 (100), 70 (28), 61 (44); HRMS (EI-magnetic sector) *m/z* [M^+] calcd for $C_{21}H_{18}N_2O_3$ 346.1317, found 346.1318.

(2-(Benzyl(4-methoxypyridin-2-yl)amino)phenyl)(phenyl)-methanone (3-OMe/Bn). White oil; R_f = 0.56 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3 H), 4.95 (s, 2 H), 5.78 (s, 1 H), 6.13 (d, *J* = 5.8 Hz, 1 H), 7.16−7.25 (m, 7 H), 7.30−7.35 (m, 3 H), 7.44−7.51 (m, 3 H), 7.63 (dd, *J* = 9.2, 0.8 Hz, 1 H), 7.74 (d, *J* = 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1 (C_q), 166.6 (C_q), 159.6 (C_q), 148.6 (CH), 144.4 (C_q), 138.8(C_q), 137.4 (C_q), 132.6 (CH), 131.9 (CH), 130.2 (CH), 129.6 (CH), 128.3 (CH × 2), 127.9 (CH × 2), 127.3 (CH × 2), 126.8 (CH), 125.8 (CH), 101.8 (C_q), 93.5 (CH), 54.8 (CH2), 54.7 (CH_3); MS (EI, *m/z*) 394 (M^+, 1), 289 (100), 213 (20); HRMS (EI-magnetic sector) *m/z* [M^+] calcd for $C_{26}H_{22}N_2O_2$ 394.1681, found 394.1681.

*tert-Butyl (2-benzoylphenyl)(4-methoxypyridin-2-)carbamate (**3a**).* Yellow solid; mp 76−77 °C; R_f = 0.40 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.74 (s, 3 H), 6.45 (dd, *J* = 6.0, 2.4 Hz, 1 H), 6.92 (d, *J* = 2.1 Hz, 1 H), 7.32−7.58 (m, 7 H), 7.72 (d, *J* = 7.2 Hz, 2 H), 7.97 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.1 (CH_3), 81.9 (C_q), 104.6 (CH), 107.6 (CH), 126.6 (CH), 127.9 (CH × 2), 129.5 (CH), 130.1 (CH × 2), 130.7 (CH), 131.0 (CH), 132.7 (CH), 137.0 (C_q), 137.3 (C_q), 139.8 (C_q), 148.2 (CH), 153.1 (C_q), 156.1 (C_q), 166.4 (C_q), 195.7 (C_q); MS (EI, *m/z*) 405 (M^+,1), 275 (43), 243 (64), 227 (53), 99 (100); HRMS *m/z* calcd for $C_{24}H_{24}N_2O_4$ 404.1736, found 404.1735.

*tert-Butyl (2-(4-methoxybenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**3b**).* Yellow solid; mp 122−123 °C; R_f = 0.51 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.74 (s, 3 H), 3.84 (s, 3 H), 6.45 (dd, *J* = 5.7, 2.4 Hz, 1 H), 6.82 (d, *J* = 9.0 Hz, 2 H), 6.93 (d, *J* = 2.1 Hz, 1 H), 7.33−7.56 (m, 4 H), 7.70 (d, *J* = 8.7 Hz, 2 H), 7.98 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.1 (CH_3), 55.4 (CH_3), 81.8 (C_q), 104.8 (CH), 107.6 (CH), 113.2 (CH × 2), 126.6 (CH), 129.2 (CH), 130.2 (C_q), 130.6 (CH), 130.7 (CH), 132.4 (CH × 2), 137.4 (C_q), 139.6 (C_q), 148.2 (CH), 153.1 (C_q), 156.2 (C_q), 163.3 (C_q), 166.4 (C_q), 194.4 (C_q); MS (EI, *m/z*) 434 (M^+, 1), 243 (40), 199 (100), 57 (66); HRMS *m/z* calcd for $C_{25}H_{26}N_2O_5$ 434.1842, found 434.1844.

*tert-Butyl (4-methoxypyridin-2-yl)(2-(4-(trifluoromethyl)-benzoyl)phenyl)carbamate (**3d**).* Yellow solid; mp 148−149 °C; R_f = 0.48 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.76 (s, 3 H), 6.47 (dd, *J* = 5.7, 1.8 Hz, 1 H), 6.99 (s, 1 H), 7.36−7.43 (m, 3 H), 7.56−7.62 (m, 3 H), 7.83 (d, *J* = 8.1 Hz, 2 H), 7.95 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.1 (CH_3), 82.1 (C_q), 104.3 (CH), 107.4 (CH), 124.9 (q, J_{C-F} = 4.8 Hz, CH × 2), 126.7 (CH), 129.4 (CH), 130.2 (CH × 2), 130.7 (CH), 131.5 (CH), 133.8 (C_q), 136.5 (C_q), 139.9 (C_q), 140.3 (C_q), 148.2 (CH), 153.1 (C_q), 155.9 (C_q), 166.5 (C_q), 194.7 (C_q); MS (EI, *m/z*) 472 (M^+, 1), 343 (26), 227 (43), 199 (100); HRMS *m/z* calcd for $C_{25}H_{23}F_3N_2O_4$ 472.1610, found 472.1611.

*tert-Butyl (2-(4-acetylbenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3e**).* Yellow solid; mp 118−119 °C; R_f = 0.50 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 2.62 (s, 3 H), 3.75 (s, 3 H), 6.46 (dd, *J* = 6.0, 2.4 Hz, 1 H), 6.99 (d, *J* = 2.4 Hz, 1 H), 7.38−7.44 (m, 3 H), 7.58 (td, *J* = 6.9, 1.8 Hz, 1 H), 7.79 (d, *J* = 8.1, 2 H), 7.89−7.97 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8 (CH_3), 28.0 (CH_3 × 3), 55.1 (CH_3), 82.0 (C_q), 104.3 (CH), 107.4 (CH), 126.7 (CH), 127.8 (CH × 2), 129.4 (CH), 130.1 (CH × 2), 130.7 (CH), 131.4 (CH), 136.7 (C_q), 139.6 (C_q), 139.9 (C_q), 140.9 (C_q), 148.1 (CH), 153.1 (C_q), 155.9 (C_q), 166.5 (C_q), 195.1 (C_q), 197.5 (C_q); MS (EI, *m/z*) 446 (M^+, 1), 345 (61), 317 (81), 243 (92), 227 (88), 199 (100), 147 (76); HRMS *m/z* calcd for $C_{26}H_{26}N_2O_5$ 446.1842, found 446.1840.

*tert-Butyl (2-(2-fluorobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3f**).* Yellow solid; mp 166−167 °C; R_f = 0.54 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.79 (s, 3 H), 6.48 (dd, *J* = 5.7, 2.4 Hz, 1 H), 7.00−7.12 (m, 3 H), 7.34−7.59 (m, 6 H), 7.99 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.2 (CH_3), 81.9 (C_q), 103.8 (CH), 107.4 (CH), 116.3 (d, J_{C-F} = 21.5 Hz, CH), 123.6 (d, J_{C-F} = 3.6 Hz, CH), 126.9 (CH), 127.0 (d, J_{C-F} = 11.4 Hz, C_q), 129.9 (CH), 130.9 (CH), 131.8 (d, J_{C-F} = 11.0 Hz, CH), 133.6 (d, J_{C-F} = 8.8 Hz, CH), 137.1 (C_q), 139.8 (C_q), 148.1 (CH), 153.1 (C_q), 156.1 (C_q), 160.8 (d, J_{C-F} = 256.0 Hz, C_q), 166.5 (C_q), 192.5 (C_q); MS (EI, *m/z*) 422 (M^+, 1), 301 (65), 243 (90), 227 (55), 199 (100), 123 (71); HRMS *m/z* calcd for $C_{24}H_{23}FN_2O_4$ 422.1642, found 422.1642.

*tert-Butyl (2-(3-fluorobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3g**).* Yellow solid; mp 76−77 °C; R_f = 0.43 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.77 (s, 3 H), 6.46 (dd, *J* = 3.9, 1.8 Hz, 1 H), 6.98 (s, 1 H), 7.20−7.44 (m, 6 H), 7.50−7.57 (m, 2 H), 7.97 (d, *J* = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.2 (CH_3), 82.0 (C_q), 104.4 (CH), 107.6 (CH), 116.6 (d, J_{C-F} = 22.8 Hz, CH), 119.7 (d, J_{C-F} = 21.9 Hz, CH), 125.8 (d, J_{C-F} = 3.6 Hz, CH), 126.6 (CH), 129.3 (CH), 129.6 (d, J_{C-F} = 8.1 Hz, CH), 130.6 (CH), 131.3 (CH), 136.6 (C_q), 139.5 (d, J_{C-F} = 6.4 Hz, C_q), 139.9 (C_q), 148.2 (CH), 153.1 (C_q), 156.0 (C_q), 162.3 (d, J_{C-F} = 246.1 Hz, C_q), 166.5 (C_q), 194.4 (C_q); MS (EI, *m/z*) 422 (M^+, 1), 340 (44), 177 (65), 61 (94), 57 (100); HRMS *m/z* calcd for $C_{24}H_{23}FN_2O_4$ 422.1642, found 422.1640.

*tert-Butyl (2-(4-fluorobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3h**).* Yellow solid; mp 84−85 °C; R_f = 0.60 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.76 (s, 3 H), 6.46 (dd, *J* = 5.7, 2.4 Hz, 1 H), 6.98−7.05 (m, 3 H), 7.37−7.43 (m, 3 H), 7.63 (td, *J* = 8.4, 2.1 Hz, 1 H), 7.76 (t, *J* = 5.4 Hz, 2 H), 7.96 (d, *J* = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.0 (C_q), 104.6 (CH), 107.5 (CH), 115.1 (d, J_{C-F} = 21.9 Hz, CH), 126.6 (CH), 129.2 (CH), 130.6 (CH), 131.1 (CH), 133.6 (d, J_{C-F} = 2.8 Hz, C_q), 136.9 (C_q), 139.8 (C_q), 148.2 (CH), 153.1 (C_q), 156.0 (C_q), 164.5 (C_q), 165.5 (d, J_{C-F} = 242.2 Hz, C_q), 166.5 (C_q), 194.2 (C_q); MS (EI, *m/z*) 422 (M^+, 1), 243 (43), 199 (100), 85 (44), 71 (42), 57 (41); HRMS *m/z* calcd for $C_{24}H_{23}FN_2O_4$ 422.1642, found 422.1645.

*tert-Butyl (2-(2-chlorobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3i**).* Yellow solid; mp 94−95 °C; R_f = 0.40 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 9 H), 3.81 (s, 3 H), 6.49 (dd, *J* = 6.0, 2.1 Hz, 1 H), 7.15−7.19 (m, 2 H), 7.29−7.41 (m, 5 H), 7.49 (d, *J* = 7.2 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.98 (d, *J* = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 81.9 (C_q), 103.5 (CH), 107.4 (CH), 126.2 (CH), 127.1 (CH), 130.2 (CH), 130.7 (CH), 131.3 (CH), 131.4 (CH), 131.5 (CH), 132.1 (C_q), 132.4 (CH), 136.1 (C_q), 138.2 (C_q), 140.3 (C_q), 147.9 (CH), 153.2 (C_q), 156.0 (C_q), 166.5 (C_q), 194.2 (C_q); MS (EI, *m/z*) 438 (M^+, 1), 340 (61), 275 (65), 243 (97), 199 (100), 177 (99), 161 (74); HRMS *m/z* calcd for $C_{24}H_{23}ClN_2O_4$ 438.1346, found 438.1347.

*tert-Butyl (2-(3-chlorobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3j**).* Yellow solid; mp 88−89 °C; R_f = 0.45 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.77 (s, 3 H), 6.46 (dd, *J* = 5.7, 2.1 Hz, 1 H), 6.99 (d, J= 1.8 Hz, 1 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 7.38−7.48 (m, 4 H), 7.54−7.62 (m, 2 H), 7.70 (s, 1 H), 7.96 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.1 (C_q), 104.3 (CH), 107.6 (CH), 126.7 (CH), 128.1 (CH), 129.3 (CH), 129.9 (CH), 130.6 (CH), 131.3 (CH), 132.6 (CH), 134.0 (C_q), 136.6 (C_q), 139.0 (C_q), 139.8 (C_q), 148.2 (CH), 153.1 (C_q), 155.9 (C_q), 166.5 (C_q), 194.5 (C_q); MS (EI, *m/z*) 438 (M^+, 1), 309 (40), 227 (78), 199 (100); HRMS *m/z* calcd for $C_{24}H_{23}ClN_2O_4$ 438.1346, found 438.1345.

*tert-Butyl (2-(4-chlorobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3k**).* Yellow solid; mp 106−107 °C; R_f = 0.48 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.78 (s, 3 H), 6.47 (dd, *J* = 5.7, 1.8 Hz, 1 H), 6.98 (d, *J* = 1.8 Hz, 1 H), 7.30−7.43 (m, 5 H), 7.56 (td, *J* = 7.2, 1.8 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.0 (C_q), 104.5 (CH), 107.5 (CH), 126.6 (CH), 128.3 (CH × 2), 129.2 (CH), 130.7 (CH), 131.2 (CH), 131.4 (CH × 2), 135.7 (C_q), 136.8 (C_q), 139.1 (C_q), 139.8 (C_q), 148.2 (CH), 153.1 (C_q), 156.0 (C_q), 166.5 (C_q), 194.5 (C_q);

DOI: 10.1021/acs.organomet.9b00119
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MS (EI, m/z) 438 (M^+, 1), 309 (49), 243 (81), 227 (64), 199 (100); HRMS m/z calcd for $C_{24}H_{23}{}^{35}ClN_2O_4$ 438.1346, found 438.1343.

*tert-Butyl (2-(3-bromobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3l**).* Yellow solid; mp 78−79 °C; R_f = 0.43 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.77 (s, 3 H), 6.46 (dd, J = 5.7, 2.1 Hz, 1 H), 6.99 (s, 1 H), 7.23−7.25 (t, J = 7.8 Hz, 1 H), 7.38−7.43 (m, 3 H), 7.54−7.66 (m, 3 H), 7.84 (s, 1 H), 7.96 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.1 (C_q), 104.3 (CH), 107.6 (CH), 126.7 (CH), 128.5 (CH), 129.5 (CH), 130.6 (CH), 131.3 (CH), 132.8 (CH), 135.5 (CH), 136.6 (C_q), 139.2 (C_q), 139.8 (C_q), 148.2 (CH), 153.1 (C_q), 155.9 (C_q), 166.5 (C_q), 194.4 (C_q); MS (EI, m/z) 482 (M^+, 1), 353 (39), 299 (37), 243 (87), 227 (87), 199 (100); HRMS m/z calcd for $C_{24}H_{23}BrN_2O_4$ 482.0841, found 482.0843.

*tert-Butyl (2-(4-bromobenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3m**).* Yellow solid; mp 82−83 °C; R_f = 0.48 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.77 (s, 3 H), 6.47 (dd, J = 5.4, 1.8 Hz, 1 H), 6.98 (s, 1 H), 7.37−7.60 (m, 8 H), 7.95 (d, J = 5.7, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.0 (C_q), 104.5 (CH), 107.5 (CH), 126.7 (CH), 127.8 (C_q), 129.3 (CH), 130.7 (CH), 131.2 (CH × 2), 131.5 (CH × 2), 136.1 (C_q), 136.7 (C_q), 139.8 (C_q), 148.2 (CH), 153.1 (C_q), 156.0 (C_q), 166.5 (C_q), 194.7 (C_q); MS (EI, m/z) 482 (M^+, 1), 355 (27), 227 (52), 199 (100). HRMS m/z calcd for $C_{24}H_{23}BrN_2O_4$ 482.0841, found 482.0844.

*tert-Butyl (2-(3,5-dimethylbenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**3n**).* Yellow solid; mp 132−133 °C; R_f = 0.63 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 2.26 (s, 6 H), 3.74 (s, 3 H), 6.44 (dd, J = 5.4, 2.1 Hz, 1 H), 6.95 (d, J = 2.4 Hz, 1 H), 7.12 (s, 1 H), 7.29 (s, 2 H), 7.34−7.46 (m, 3 H), 7.52−7.58 (m, 1 H), 7.98 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1 (CH_3 × 2), 28.0 (CH_3 × 3), 55.1 (CH_3), 81.8 (C_q), 104.6 (CH), 107.6 (CH), 126.6 (CH), 127.8 (CH × 2), 129.4 (CH), 130.7 (CH), 130.8 (CH), 134.5 (CH), 137.4 (C_q), 137.5 (C_q), 137.6 (C_q), 139.6 (C_q), 148.1 (CH), 153.1 (C_q), 156.2 (C_q), 166.3 (C_q), 196.2 (C_q); MS (EI, m/z) 432 (M^+, 1), 303 (63), 243 (88), 227 (89), 199 (100); HRMS m/z calcd for $C_{26}H_{28}N_2O_4$ 432.2049, found 432.2047.

*tert-Butyl (2-(2,4-dimethylbenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**3o**).* Yellow solid; mp 90−91 °C; R_f = 0.48 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 2.29 (s, 3 H), 2.31 (s, 3 H), 3.77 (s, 3 H), 6.46 (dd, J = 5.7, 2.1 Hz, 1 H), 6.84−6.90 (m, 2 H), 6.98 (s, 1 H), 7.34 (d, J = 6.6 Hz 1 H), 7.32−7.46 (m, 3 H), 7.51 (td, J = 7.2, 1.5 Hz 1 H), 7.98 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7 (CH_3), 21.3 (CH_3), 28.1 (CH_3 × 3), 55.1 (CH_3), 81.8 (C_q), 104.1 (CH), 107.2 (CH), 125.6 (CH), 126.9 (CH), 130.3 (CH), 131.1 (CH), 131.2 (CH), 131.9 (CH), 132.0 (CH), 134.8 (C_q), 138.1 (C_q), 138.9 (C_q), 139.7 (C_q), 141.6 (C_q), 148.0 (CH), 153.1 (C_q), 156.1 (C_q), 166.3 (C_q), 197.3 (C_q); MS (EI, m/z) 432 (M^+, 1), 303 (41), 243 (88), 199 (100), 124 (37); HRMS m/z calcd for $C_{26}H_{28}N_2O_4$ 432.2049, found 432.2046.

*tert-Butyl (2-(3,5-dimethoxybenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**3p**).* Yellow solid; mp 86−87 °C; R_f = 0.63 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.75 (s, 9 H), 6.46 (dd, J = 5.7, 1.8 Hz, 1 H), 6.59 (s, 1 H), 6.82 (d, J = 1.8 Hz, 2 H), 6.92 (s, 1 H), 7.37−7.56 (m, 4 H), 7.98 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.1 (CH_3), 55.5 (CH_3 × 2), 81.9 (C_q), 104.7 (CH), 105.5 (CH), 107.5 (CH), 107.6 (CH × 2), 126.6 (CH), 129.5 (CH), 130.8 (CH), 131.0 (CH), 137.0 (C_q), 139.4 (C_q), 139.8 (C_q), 148.1 (CH2), 153.1 (C_q), 156.1 (C_q), 160.3 (C_q × 2), 166.3 (C_q), 195.5 (C_q); MS (EI, m/z) 464 (M^+, 1), 335 (38), 227 (100), 199 (91); HRMS m/z calcd for $C_{26}H_{28}N_2O_6$ 464.1947, found 464.1950.

*tert-Butyl (2-(2,4-dimethoxybenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**3q**).* White solid; mp 68−69 °C; R_f = 0.47 (*n*-hexane/ethyl acetate = 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.59 (s, 3 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 6.30−6.34 (m, 2 H), 6.46 (dd, J = 5.7, 2.1 Hz, 1 H), 6.96 (d, J = 2.1 Hz,1 H), 7.33 (t, J = 8.1 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 7.51 (td, J = 6.8, 1.5 Hz, 1 H), 8.00 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.0 (CH_3), 55.4 (CH_3 × 2), 81.6 (C_q), 98.3 (CH), 107.3 (CH), 121.2 (C_q), 126.7 (CH), 129.6 (CH), 130.5 (CH), 131.1 (CH), 134.0 (CH), 139.1 (C_q), 139.2 (C_q), 147.9 (CH), 153.2 (C_q), 156.1 (C_q), 160.5 (C_q), 163.8 (C_q), 166.2 (C_q), 194.0 (C_q); MS (EI, m/z) 464 (M^+, 1), 305 (42), 243 (85), 199 (100), 165 (47), 57 (70); HRMS m/z calcd for $C_{26}H_{28}N_2O_6$ 464.1947, found 464.1949.

*tert-Butyl (2-(3-formylbenzoyl)phenyl)(4-methoxypyridin-2-yl)-carbamate (**3r**).* Yellow solid; mp 88−89 °C; R_f = 0.63 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 3.75 (s, 3 H), 6.45 (dd, J = 5.7, 2.4 Hz, 1 H), 6.98 (d, J = 2.1 Hz, 1 H), 7.38−7.48 (m, 3 H), 7.55−7.61 (m, 2 H), 7.95 (d, J = 6.0 Hz, 1 H), 8.03 (dd, J = 7.5, 1.5 Hz, 2 H), 8.19 (s, 1 H), 9.98 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.2 (CH_3), 82.2 (Cq), 104.5 (CH), 107.4 (CH), 126.8 (CH), 128.8 (CH), 129.3 (CH), 130.6 (CH), 131.5 (CH), 132.2 (CH), 132.3 (CH), 135.4 (CH), 136.1 (C_q), 136.5 (C_q), 138.2 (C_q), 139.9 (C_q), 148.2 (CH), 153.1 (C_q), 155.9 (C_q), 166.5 (C_q), 191.5 (CH), 194.6 (C_q); MS (EI, m/z) 432 (M^+, 1), 303 (27), 227 (66), 199 (100), 184 (28); HRMS m/z calcd for $C_{25}H_{24}N_2O_5$ 432.1685, found 432.1683.

Methyl (2,6-dibenzoylphenyl)(4-methoxypyridin-2-yl)carbamate (4-OMe/Moc). White oil; R_f = 0.63 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.62 (s, 3 H), 3.67 (s, 3 H), 6.32 (dd, J = 4.4, 2.4 Hz, 1 H), 6.99 (bs, 1 H), 7.35 (td, J = 7.6, 1.2 Hz, 4 H), 7.51 (td, J = 8.4, 1.2 Hz, 3 H), 7.62 (dd, J = 7.2, 0.8 Hz, 2 H), 7.71 (d, J = 5.6 Hz, 1 H), 7.74−7.77 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 53.2 (CH_3), 55.0 (CH_3), 102.1 (C_q), 107.7 (CH), 126.5 (CH), 127.9 (CH × 4), 130.0 (CH × 4), 131.2 (CH × 2), 132.9 (CH × 2), 137.1(C_q × 2), 139.3(C_q × 2), 147.1 (CH), 154.4 (C_q), 154.9 (C_q), 166.4 (C_q × 2), 195.2 (C_q); MS (EI, m/z) 466 (M^+, 1), 362 (58), 361 (100), 317 (51); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{28}H_{22}N_2O_5$ 466.1529, found 466.1530.

N-(2,6-Dibenzoylphenyl)-N-(4-methoxypyridin-2-yl)pivalamide (4-OMe/Piv). White oil; R_f = 0.66 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.76 (9 H), 3.73 (3 H), 6.52 (dd, J = 3.6, 1.6 Hz, 1 H), 7.01 (d, J = 1.2 Hz, 1 H), 7.39−7.47 (m, 7 H), 7.54 (t, J = 5.2 Hz, 2 H), 7.83 (d, J = 4.4 Hz, 4 H), 7.90 (d, J = 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.1 (CH_3× 3), 41.3 (C_q), 55.2 (CH_3), 107.9 (CH), 109.2 (CH), 126.1 (CH), 128.1 (CH × 4), 130.5 (CH × 4), 130.9 (CH × 2), 133.0 (CH × 2), 136.9 (C_q × 2), 139.4 (C_q × 2), 140.2 (C_q), 147.9 (CH), 157.2 (C_q), 167.0 (C_q), 179.7 (C_q), 195.5 (C_q × 2); MS (EI, m/z) 492 (M^+, 1), 369 (90), 353 (51), 347 (100), 305 (43); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{31}H_{28}N_2O_4$ 492.2049, found.492.2051.

*tert-Butyl (2,6-dibenzoylphenyl)(4-methoxypyridin-2-yl)-carbamate (**4a**).* White solid; mp 126−127 °C; R_f = 0.48 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 3.64 (s, 3 H), 6.28 (dd, J = 5.7, 2.1 Hz, 1 H), 6.81 (bs, 1 H), 7.32 (t, J = 7.5 Hz, 4 H), 7.48 (t, J = 7.8 Hz, 3 H), 7.62 (d, J = 7.5 Hz, 2 H), 7.66 (d, J = 5.7 Hz, 1 H), 7.76 (d, J = 7.2 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 54.9 (CH_3), 82.2 (C_q), 101.8 (C_q), 107.2 (CH), 126.3 (CH), 127.9 (CH × 4), 130.0 (CH × 4), 131.2 (CH), 132.6 (CH × 2), 137.3 (C_q × 2), 139.2 (C_q × 2), 146.8 (CH), 152.6 (C_q), 155.1 (C_q), 166.1 (C_q), 195.2 (C_q × 2); MS (EI, m/z) 508 (M^+, 1), 331 (39), 303 (100), 213 (21), 105 (22); HRMS m/z calcd for $C_{31}H_{28}N_2O_5$ 508.1998, found 508.2000.

*tert-Butyl (2,6-bis(4-methoxybenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4b**).* Yellow solid; mp 138−139 °C; R_f = 0.49 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9 H), 3.66 (s, 3 H), 3.83 (s, 6 H), 6.28 (dd, J = 5.7, 2.1 Hz, 1 H), 6.80 (d, J = 8.7 Hz, 4 H), 6.85−6.93 (m, 1 H), 7.45 (t, J = 6.6 Hz, 1 H), 7.57 (d, J = 7.5 Hz, 2 H), 7.68 (d, J = 7.5 Hz, 1 H), 7.74 (d, J = 8.7 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 54.9 (CH_3), 55.4 (CH_3 × 2), 82.0 (C_q), 102.0 (CH), 107.1 (CH), 113.1 (CH × 4), 126.1 (CH), 130.2 (C_q × 2), 130.7 (CH × 2), 132.4 (CH × 4), 137.4 (C_q), 139.5 (C_q × 2), 147.0 (CH), 152.6 (C_q), 155.4 (C_q), 163.2 (C_q × 2), 166.1 (C_q), 193.9 (C_q × 2); MS (EI, m/z) 568 (M^+, 1), 361 (93), 333 (100), 225 (94), 135 (93); HRMS m/z calcd for $C_{33}H_{32}N_2O_7$ 568.2210, found 568.2209.

DOI: 10.1021/acs.organomet.9b00119
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*tert-Butyl (2,6-bis(2-fluorobenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4f**).* Yellow solid; mp 140−141 °C; R_f = 0.61 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.68 (s, 3 H), 6.31 (dd, J = 5.7, 2.1 Hz, 1 H), 6.87 (s, 1 H), 6.95−7.08 (m, 4 H), 7.35−7.43 (m, 2 H), 7.46−7.56 (m, 3 H), 7.67−7.73 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.3 (C_q), 107.1 (CH), 116.3 (d, J_{C-F} = 21.5 Hz, CH × 2), 123.6 (d, J_{C-F} = 3.6 Hz, CH × 2), 126.7 (d, J_{C-F} = 11.5 Hz, C_q × 2), 127.0 (CH), 131.6 (CH × 2), 131.9 (CH × 2), 133.5 (d, J_{C-F} = 8.6 Hz, CH × 2), 137.3 (C_q), 139.5 (C_q × 2), 146.7 (CH), 152.5 (C_q), 154.6 (C_q), 160.8 (d, J_{C-F} = 256.0 Hz, C_q), 166.1 (C_q × 2), 192.1 (C_q × 2); MS (EI, m/z) 544 (M^+, 1), 321 (78), 264 (31), 158 (100); HRMS m/z calcd for $C_{31}H_{26}F_2N_2O_5$ 544.1810, found 544.1808.

*tert-Butyl (2,6-bis(3-fluorobenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4g**).* Yellow solid; mp 128−129 °C; R_f = 0.55 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 3.67 (s, 3 H), 6.30 (dd, J = 5.7, 1.2 Hz, 1 H), 6.85 (s, 1 H), 7.17 (t, J = 4.5 Hz, 2 H), 7.26−7.33 (m, 2 H), 7.45 (d, J = 9.0 Hz, 2 H), 7.52−7.54 (m, 3 H), 7.61−7.67 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.5 (C_q), 101.8 (CH), 107.3 (CH × 2), 116.6 (d, J_{C-F} = 21.9 Hz, CH × 2), 119.7 (d, J_{C-F} = 21.9 Hz, CH × 2), 125.7 (d, J_{C-F} = 2.8 Hz, CH × 2), 126.6 (CH), 129.6 (d, J_{C-F} = 7.3 Hz, CH × 2), 131.1 (CH × 2), 137.6 (C_q), 138.9 (C_q × 2), 139.4 (d, J_{C-F} = 6.4 Hz, C_q × 2), 146.9 (CH), 152.5 (C_q), 154.8 (C_q), 162.3 (d, J_{C-F} = 246.1 Hz, C_q × 2), 166.3 (C_q), 193.8 (d, J_{C-F} = 1.9 Hz, C_q × 2); MS (EI, m/z) 544 (M^+, 1), 340 (62), 177 (100), 161 (72), 57 (61); HRMS m/z calcd for $C_{31}H_{26}F_2N_2O_5$ 544.1810, found 544.1808.

*tert-Butyl (2,6-bis(4-fluorobenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4h**).* Yellow solid; mp 132−133 °C; R_f = 0.53 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 3.67 (s, 3 H), 6.31 (dd, J = 5.4, 1.5 Hz, 1 H), 6.85 (s, 1 H), 6.99 (t, J = 8.4 Hz, 4 H), 7.45 (t, J = 8.1 Hz, 1 H), 7.58−7.61 (m, 2 H), 7.65 (d, J = 5.7 Hz, 1 H), 7.79 (td, J = 5.7, 2.4 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.4 (C_q), 107.1 (CH), 115.0 (d, J_{C-F} = 21.9 Hz, CH × 4), 126.5 (CH), 131.0 (CH × 2), 132.6 (d, J_{C-F} = 9.1 Hz, CH × 4), 133.5 (d, J_{C-F} = 2.8 Hz, C_q × 2), 137.6 (C_q), 139.1 (C_q × 2), 146.9 (CH), 152.5 (C_q), 155.0 (C_q), 164.5 (C_q), 166.4 (J_{C-F} = 24.6 Hz, C_q × 2), 193.6 (C_q × 2); MS (EI, m/z) 544 (M^+, 1), 349 (49), 321 (100), 123 (36); HRMS m/z calcd for $C_{31}H_{26}F_2N_2O_5$ 544.1810, found 544.1811.

*tert-Butyl (2,6-bis(3-chlorobenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4j**).* Yellow solid; mp 138−139 °C; R_f = 0.55 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.67 (s, 3 H), 6.31 (dd, J = 5.7, 2.1 Hz, 1 H), 6.83 (s,1 H), 7.27 (t, J = 7.8 Hz, 2 H), 7.43 (dd, J = 2.1, 1.2 Hz, 2 H), 7.45−7.54 (m, 1 H), 7.60−7.67 (m, 5 H), 7.73 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.5 (C_q), 101.6 (C_q), 107.4 (CH), 126.7 (CH), 127.9 (CH × 2), 129.3 (CH × 2), 129.9 (CH × 2), 131.3 (CH), 132.6 (CH × 2), 134.3 (C_q × 2), 137.6 (C_q), 138.9 (C_q × 2), 146.9 (CH), 152.5 (C_q), 154.7 (C_q), 166.3 (C_q), 193.8 (C_q × 2); MS (EI, m/z) 576 (M^+, 1), 365 (100), 337 (98), 225 (32); HRMS m/z calcd for $C_{31}H_{26}C_{l2}N_2O_5$ 576.1219, found 576.1217.

*tert-Butyl (2,6-bis(4-chlorobenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4k**).* Yellow solid; mp 180−181 °C; R_f = 0.65 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 3.68 (s, 3 H), 6.32 (dd, J = 6.0, 2.1 Hz, 1 H), 6.79 (s, 1 H), 7.29 (d, J = 8.7 Hz, 4 H), 7.50 (t, J = 6.9 Hz, 1 H), 7.62−7.70 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.4 (C_q), 107.1 (CH), 126.6 (CH), 128.2 (CH × 4), 131.0 (CH), 131.3 (CH × 4), 135.6 (C_q × 2), 139.0 (C_q × 2), 139.1 (C_q × 2), 146.8 (CH), 152.5 (C_q), 154.7 (C_q), 166.4 (C_q), 194.0 (C_q × 2); MS (EI, m/z) 576 (M^+, 1), 365 (67), 337 (100), 139 (43); HRMS m/z calcd for $C_{31}H_{26}C_{l2}N_2O_5$ 576.1219, found 576.1216.

*tert-Butyl (2,6-bis(3,5-dimethylbenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4n**).* Yellow solid; mp 154−155 °C; R_f = 0.60 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 2.26 (s, 12 H), 3.65 (s, 3 H), 6.27 (dd, J = 5.7, 2.1 Hz, 1 H), 6.90 (m, 1 H), 7.10 (m, 2 H), 7.39 (m, 4 H), 7.46 (t, J = 7.2 Hz, 1 H), 7.60 (d, J = 7.2 Hz, 2 H), 7.66 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1 (CH_3 × 4), 27.9 (CH_3 × 3), 54.9 (CH_3), 81.9 (C_q), 107.2 (CH), 126.1 (CH), 127.8 (CH × 4), 131.0 (CH), 134.3 (CH × 2), 137.4 (C_q × 2), 137.5 (C_q × 4), 139.5 (C_q × 2), 146.7 (CH), 152.6 (C_q), 155.2 (C_q), 166.1 (C_q), 195.6 (C_q × 2); MS (EI, m/z) 564 (M^+, 1), 331 (34), 242 (84), 133 (100); HRMS m/z calcd for $C_{35}H_{36}N_2O_5$ 564.2624, found 564.2626.

*tert-Butyl (2,6-bis(2,4-dimethylbenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4o**).* White solid; mp 156−157 °C; R_f = 0.65 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 2.28 (s, 6 H), 2.40 (s, 6H), 3.67 (s, 3 H), 6.29 (dd, J = 5.7, 2.1 Hz, 1 H), 6.74−6.80 (m, 3 H), 6.97 (s, 2 H), 7.27 (d, J = 8.7 Hz, 2 H), 7.40 (t, J = 7.8 Hz, 1 H), 7.57 (d, J = 7.5 Hz, 2 H), 7.73 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3 × 2), 21.3 (CH_3 × 2), 28.0 (CH_3 × 3), 54.8 (CH_3), 81.9 (C_q), 106.8 (CH), 125.3 (CH × 2), 126.6 (CH × 2), 131.6 (CH), 131.9 (CH × 4), 132.0 (CH), 134.9 (C_q × 2), 137.7 (C_q), 138.7 (C_q), 140.3 (C_q), 141.3 (C_q × 2), 146.7 (CH), 152.9 (C_q), 155.0 (C_q), 166.0 (C_q × 2), 196.9 (C_q × 2); MS (EI, m/z) 564 (M^+, 1), 359 (38), 331 (100), 225 (52), 133 (60); HRMS m/z calcd for $C_{35}H_{36}N_2O_5$ 564.2624, found 564.2626.

*tert-Butyl (2,6-bis(2,4-dimethoxybenzoyl)phenyl)(4-methoxypyridin-2-yl)carbamate (**4q**).* Yellow solid; mp 96−97 °C; R_f = 0.30 (*n*-hexane/ethyl acetate = 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.61 (s, 6 H), 3.67 (s, 3 H), 3.79 (s, 6 H), 6.26−6.34 (m, 5 H), 6.83 (s, 1 H), 7.37 (t, J = 7.8 Hz, 1 H), 7.46 (d, J = 8.7 Hz, 2 H), 7.56 (d, J = 7.8 Hz, 2 H), 7.67 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 54.8 (CH_3), 55.3 (CH_3 × 2), 55.4 (CH_3 × 2), 81.7 (C_q), 98.2 (CH × 2), 101.4 (CH), 103.8 (CH × 2), 106.7 (CH), 121.2 (C_q), 126.2 (CH), 131.1 (CH × 2), 134.1 (CH × 2), 136.5 (C_q), 141.0 (C_q × 2), 146.3 (CH), 152.6 (C_q), 155.0 (C_q), 160.5 (C_q × 2), 163.6 (C_q × 2), 165.8 (C_q), 193.5 (C_q × 2); MS (EI, m/z) 628 (M^+, 1), 363 (100), 225 (96), 165 (32); HRMS m/z calcd for $C_{35}H_{36}N_2O_9$ 628.2421, found 628.2421.

*tert-Butyl (2-benzoyl-6-methoxyphenyl)(4-methoxypyridin-2-yl)-carbamate (**5b**).* White solid; mp 112−113 °C; R_f = 0.45 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 3.72 (s, 3 H), 3.89 (s, 3 H), 6.38 (dd, J = 5.7, 1.8 Hz, 1 H), 6.92 (s, 1 H), 7.00 (d, J = 7.5 Hz, 1 H), 7.13 (d, J = 8.1 Hz, 1 H), 7.30−7.40 (m, 3 H), 7.48 (t, J = 7.2 Hz, 1 H), 7.67 (d, J = 7.5 Hz, 2 H), 7.90 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (CH_3 × 3), 55.0 (CH_3), 56.0 (CH_3), 81.2 (C_q), 102.8 (CH), 107.0 (CH), 113.5 (CH), 120.8 (CH), 127.8 (CH × 2), 127.9 (CH), 128.8 (C_q), 129.9 (CH × 2), 132.7 (CH), 137.4 (C_q), 138.4 (C_q), 148.1 (CH), 152.9 (C_q), 155.9 (Cq), 156.1 (C_q), 166.1 (C_q), 195.8 (C_q); MS (EI, m/z) 434 (M^+, 1), 329 (36), 273 (100), 257 (31), 229 (100); HRMS m/z calcd for $C_{25}H_{26}N_2O_5$ 434.1842, found 434.1844.

*tert-Butyl (2-benzoyl-5-methoxyphenyl)(4-methoxypyridin-2-yl)-carbamate (**5c**).* Yellow solid; mp 68−69 °C; R_f = 0.54 (*n*-hexane/ethyl acetate = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.76 (s, 3 H), 3.87 (s, 3 H), 6.48 (dd, J = 5.7, 2.1 Hz, 1 H), 6.87 (dd, J = 8.4, 2.4 Hz, 1 H), 6.97 (dd, J = 5.7, 2.1 Hz, 2 H), 7.33−7.43 (m, 3 H), 7.50 (t, J = 7.2 Hz, 1 H), 7.70 (d, J = 7.2 Hz, 2 H), 8.01 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.1 (CH_3), 55.5 (CH_3), 81.8 (C_q), 104.7 (CH), 107.7 (CH), 112.0 (CH), 116.1 (CH), 127.9 (CH × 2), 129.3 (C_q), 130.0 (CH × 2), 131.8 (CH), 132.3 (CH), 138.1 (C_q), 142.0 (C_q), 148.3 (CH), 153.0 (C_q), 156.2 (C_q), 161.8 (C_q), 166.4 (C_q), 195.0 (C_q); MS (EI, m/z) 434 (M^+, 1), 303 (100), 229 (47), 105 (39); HRMS m/z calcd for $C_{25}H_{26}N_2O_5$ 434.1842, found 434.1843.

*tert-Butyl (2-benzoyl-4-methoxyphenyl)(4-methoxypyridin-2-yl)-carbamate (**5d**).* Yellow solid; mp 128−129 °C; R_f = 0.30 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 6.44 (dd, J = 5.7, 1.8 Hz, 1 H), 6.84 (d, J = 1.8 Hz, 1 H), 6.93 (d, J = 2.7 Hz, 1 H), 7.08 (dd, J = 8.7, 3.0 Hz, 1 H), 7.32−7.37 (m, 3 H), 7.48 (t, J = 7.2 Hz, 1 H), 7.72 (d, J = 7.2 Hz, 2 H), 7.98 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.1 (CH_3), 55.6 (CH_3), 81.7 (C_q), 104.5 (CH), 107.5 (CH), 114.2 (CH), 116.6 (CH), 128.0 (CH × 2), 130.0 (CH × 2), 131.9 (CH), 132.4 (C_q), 132.8 (CH), 137.1 (C_q), 137.9 (C_q), 148.2 (CH), 153.3 (C_q), 156.2 (C_q), 157.8 (C_q), 166.3 (C_q), 195.6 (C_q);

DOI: 10.1021/acs.organomet.9b00119
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MS (EI, m/z) 434 (M^+, 1), 273 (39), 257 (23), 229 (100), 105 (26), 57 (37); HRMS m/z calcd for $C_{25}H_{26}N_2O_5$ 434.1842, found 434.1844.

*tert-Butyl (2-benzoyl-4-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**5e**).* Yellow solid; mp 132−133 °C; R_f = 0.50 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 3.73 (s, 3 H), 6.45 (dd, J = 5.7, 1.8 Hz, 1 H), 6.93 (d, J = 1.2 Hz, 1 H), 7.13 (dd, J = 8.1, 2.7 Hz, 1 H), 7.24−7.25 (m, 1 H), 7.33−7.43 (m, 3 H), 7.51 (t, J = 4.5 Hz, 1 H), 7.70 (d, J = 7.8 Hz, 2 H), 7.94 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.1 (CH_3), 82.1 (C_q), 104.3 (CH), 107.6 (CH), 116.1 (d, J_{C-F} = 23.6 Hz, CH), 117.8 (d, J_{C-F} = 22.4 Hz, CH), 128.1 (CH × 2), 130.0 (CH × 2), 132.6 (d, J_{C-F} = 8.1 Hz, CH), 133.0 (CH), 135.6 (d, J_{C-F} = 3.3 Hz, C_q), 136.7 (C_q), 138.7 (d, J_{C-F} = 6.9 Hz, C_q), 148.1 (CH), 153.0 (C_q), 155.8 (C_q), 160.1 (d, J_{C-F} = 247.4 Hz, C_q), 166.4 (C_q), 194.3 (C_q); MS (EI, m/z) 422 (M^+, 1), 293 (35), 261 (45), 245 (44), 217 (100), 57 (44); HRMS m/z calcd for $C_{24}H_{23}FN_2O_4$ 422.1642, found 422.1642.

*tert-Butyl (2-benzoyl-5-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**5f**).* Yellow solid; mp 132−133 °C; R_f = 0.53 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.75 (s, 3 H), 6.47 (dd, J = 5.7, 2.4 Hz, 1 H), 6.93 (d, J = 2.4 Hz, 1 H), 7.07 (td, J = 8.1, 2.4 Hz, 1 H), 7.17 (dd, J = 9.3, 2.4 Hz, 1 H), 7.33−7.54 (m, 4 H), 7.69 (d, J = 7.2 Hz, 2 H), 7.97 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.3 (C_q), 104.6 (CH), 107.8 (CH), 113.8 (d, J_{C-F} = 21.1 Hz, CH), 118.0 (d, J_{C-F} = 21.9 Hz, CH), 128.0 (CH × 2), 130.0 (CH × 2), 131.3 (d, J_{C-F} = 9.1 Hz, CH), 132.8 (CH), 133.2 (d, J_{C-F} = 3.6 Hz, C_q), 137.3 (C_q), 142.0 (d, J_{C-F} = 11.0 Hz, C_q), 148.2 (CH), 152.7 (C_q), 155.7 (C_q), 163.7 (d, J_{C-F} = 250.0 Hz, C_q), 166.5 (C_q), 194.6 (C_q); MS (EI, m/z) 422 (M^+, 2), 217 (100); HRMS m/z calcd for $C_{24}H_{23}FN_2O_4$ 422.1642, found 422.1643.

*tert-Butyl (2-benzoyl-6-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**5g**).* Yellow solid; mp 78−79 °C; R_f = 0.48 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9 H), 3.73 (s, 3 H), 6.41 (dd, J = 6, 2.4 Hz, 1 H), 6.99 (d, J = 1.5 Hz, 1 H), 7.24 (t, J = 6.9 Hz, 1 H), 7.26−7.43 (m, 4 H), 7.50 (t, J = 7.2 Hz, 1 H), 7.67 (d, J = 7.5 Hz, 2 H), 7.89 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.1 (CH_3), 82.2 (C_q), 102.9 (CH), 107.4 (CH), 117.9 (d, J_{C-F} = 21.0 Hz, CH), 124.5 (d, J_{C-F} = 3.6 Hz, CH), 127.9 (CH), 128.3 (d, J_{C-F} = 8.1 Hz, CH × 2), 129.8 (CH × 2), 132.9 (CH), 137.0 (C_q), 139.0 (C_q), 148.0 (CH), 152.3 (C_q), 155.2 (C_q), 159.0 (d, J_{C-F} = 249.3 Hz, C_q), 166.3 (C_q), 194.6 (d, J_{C-F} = 2.8 Hz, C_q); MS (EI, m/z) 422 (M^+, 2), 303 (71), 245 (69), 217 (100); HRMS m/z calcd for $C_{24}H_{23}FN_2O_4$ 422.1642, found 422.1642.

*tert-Butyl (2-benzoyl-4-chlorophenyl)(4-methoxypyridin-2-yl)carbamate (**5h**).* Yellow solid; mp 130−131 °C; R_f = 0.60 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.74 (s, 3 H), 6.45 (dd, J = 5.7, 2.1 Hz, 1 H), 6.90 (d, J = 1.5 Hz, 1 H), 7.34−7.40 (m, 4 H), 7.51 (d, J = 8.1 Hz, 2 H), 7.70 (d, J = 7.5 Hz, 2 H), 7.95 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.1 (CH_3), 82.3 (C_q), 104.4 (CH), 107.7 (CH), 128.1 (CH × 2), 129.2 (CH), 130.0 (CH × 2), 130.9 (CH), 132.1 (CH), 132.4 (C_q), 133.1 (CH), 136.6 (C_q), 138.3 (C_q), 138.4 (C_q), 148.2 (CH), 155.8 (C_q), 155.7 (C_q), 166.4 (C_q), 194.2 (C_q); MS (EI, m/z) 309 (M^+, 1), 277 (62), 261 (63), 105 (54), 57 (73); HRMS m/z calcd for $C_{24}H_{23}ClN_2O_4$ 438.1346, found 438.1345.

*tert-Butyl (2-benzoyl-4-bromophenyl)(4-methoxypyridin-2-yl)carbamate (**5i**).* Yellow solid; mp 125−126 °C; R_f = 0.60 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9 H), 3.74 (s, 3 H), 6.45 (d, J = 5.1 Hz, 1 H), 6.90 (s, 1 H), 7.30−7.39 (m, 3 H), 7.52−7.55 (m, 2 H), 7.65−7.71 (m, 3 H), 7.95 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (CH_3 × 3), 55.2 (CH_3), 82.3 (C_q), 104.5 (CH), 107.7 (CH), 120.3 (C_q), 128.1 (CH × 2), 130.0 (CH × 2), 132.1 (CH), 132.4 (CH), 133.1 (CH), 133.9 (CH), 136.6 (C_q), 138.7 (C_q), 138.8 (C_q), 148.2 (CH), 152.8 (C_q), 155.7 (C_q), 166.5 (C_q), 194.1 (C_q); MS (EI, m/z) 482 (M^+, 1), 353 (53), 321 (51), 305 (43), 277 (96), 105 (75), 57 (100); HRMS m/z calcd for $C_{24}H_{23}BrN_2O_4$ 482.0841, found 482.0841.

*tert-Butyl (2,6-dibenzoyl-4-methoxyphenyl)(4-methoxypyridin-2-yl)carbamate (**6d**).* Yellow solid; mp 164−165 °C; R_f = 0.40 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 3.62 (s, 3 H), 3.84 (s, 3 H), 6.27 (dd, J = 5.7, 2.1 Hz, 1 H), 6.72 (s, 1 H), 7.12 (s, 2 H), 7.32 (t, J = 7.5 Hz, 4 H), 7.47 (t, J = 7.5 Hz, 2 H),7.66 (d, J = 5.7 Hz, 1 H), 7.77 (d, J = 7.2 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 54.9 (CH_3), 55.8 (CH_3), 82.0 (C_q), 102.0 (C_q), 107.1 (CH), 116.4 (CH × 2), 127.9 (CH × 4), 130.0 (CH × 4), 132.6 (CH × 2), 137.2 (C_q × 2), 140.2 (C_q × 2), 146.8 (CH), 152.9 (C_q), 155.2 (C_q), 157.3 (C_q), 166.1 (C_q), 195.0 (C_q × 2); MS (EI, m/z) 538 (M^+, 1), 333 (100), 105 (39), 77 (30), 57 (32); HRMS m/z calcd for $C_{32}H_{30}N_2O_6$ 538.2104, found 538.2101.

*tert-Butyl (2,6-dibenzoyl-4-fluorophenyl)(4-methoxypyridin-2-yl)carbamate (**6e**).* White solid; mp 148−149 °C; R_f = 0.60 (*n*-hexane/ethyl acetate = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 3.65 (s, 3 H), 6.30 (d, J = 4.2 Hz, 1 H), 6.79 (s, 1 H), 7.35 (t, J = 7.2 Hz, 6 H), 7.51 (t, J = 7.2 Hz, 2 H), 7.67 (d, J = 5.4 Hz, 1 H), 7.78 (d, J = 7.5 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.4 (C_q), 107.3 (CH), 117.9 (d, J_{C-F} = 23.8 Hz, CH), 128.0 (CH × 4), 129.9 (CH × 4), 132.9 (CH × 2), 136.7 (C_q × 2), 141.1 (d, J_{C-F} = 6.0 Hz, C_q), 146.7 (CH), 152.6 (C_q), 154.8 (C_q), 159.9 (d, J_{C-F} = 249.6 Hz, C_q), 166.2 (C_q × 2), 193.8 (C_q × 2); MS (EI, m/z) 526 (M^+, 1), 349 (41), 321 (100), 57 (36); HRMS m/z calcd for $C_{31}H_{27}FN_2O_5$ 526.1904, found 526.1902.

*tert-Butyl (2,6-dibenzoyl-4-chlorophenyl)(4-methoxypyridin-2-yl)carbamate (**6h**).* Yellow solid; mp 121−122 °C; R_f = 0.68 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9 H), 3.62 (s, 3 H), 6.29 (dd, J = 5.7, 2.1 Hz, 1 H), 6.76 (s, 1 H), 7.33 (t, J = 7.5 Hz, 4 H), 7.49 (t, J = 7.2 Hz, 2 H), 7.58 (s, 2 H), 7.65 (d, J = 5.7 Hz, 1 H), 7.75 (d, J = 7.5 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9 (CH_3 × 3), 55.0 (CH_3), 82.6 (C_q), 101.8 (C_q), 107.3 (CH), 128.1 (CH × 5), 129.9 (CH × 5), 130.8 (CH), 132.4 (C_q), 132.9 (CH × 2), 136.7 (C_q × 2), 140.7 (C_q × 2), 146.8 (CH), 152.3 (C_q), 154.7 (C_q), 166.2 (C_q), 193.7 (C_q × 2); MS (EI, m/z) 542 (M^+, 1), 365 (84), 337 (100), 105 (82), 77 (49), 57 (71); HRMS m/z calcd for $C_{31}H_{27}ClN_2O_5$ 542.1608, found 542.1607.

*(2-Aminophenyl)(phenyl)methanone (**7**).* Yellow solid; R_f = 0.63 (*n*-hexane/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (bs, 2 H), 6.60 (td, J = 4.8, 0.8 Hz, 1 H), 6.73 (dd, J = 5.6, 0.8 Hz, 1 H), 7.29 (td, J = 4.8, 0.8 Hz, 1 H), 7.44 (tt, J = 4.4, 0.8 Hz, 3 H), 7.51 (tt, J = 4.4, 0.8 Hz, 1 H), 7.62−7.64 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.5 (CH), 117.0 (CH), 118.2 (C_q), 128.1 (CH × 2), 129.1 (CH × 2), 131.0 (CH), 134.2 (CH), 134.5 (CH), 140.1 (C_q), 150.9 (C_q), 199.0 (C_q); MS (EI, m/z) 197 (M^+, 1), 196 (100), 120 (21); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{13}H_{11}NO$ 197.0841, found 197.0840.

*9(10H)-Acridanone (**8**).* Yellow solid; R_f = 0.43 (*n*-hexane/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.25 (td, J = 6.8, 1.2 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.73 (td, J = 7.2, 1.6 Hz, 2 H), 8.23 (dd, J = 8.0, 1.6 Hz, 2 H), 11.73 (d, J = 0.4 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 117.3 (CH × 2), 120.5 (C_q × 2), 121.0 (CH × 2), 126.0 (CH × 2), 133.4 (CH × 2), 140.9 (C_q × 2), 176.8 (C_q); MS (EI, m/z) 196 (M^+, 1); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{13}H_9NO$ 195.0684, found 195.0686.

*10-(4-Methoxypyridin-2-yl)acridin-9(10H)-one (**9**).* White oil; R_f = 0.43 (*n*-hexane/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3 H), 6.69 (d, J = 5.6 Hz, 2 H), 6.97 (d, J = 1.2 Hz, 1 H), 7.12 (dd, J = 4.0, 1.6 Hz, 1 H), 7.29 (td, J = 4.8, 0.8 Hz, 2 H), 7.52 (td, J = 4.4, 0.8 Hz, 2 H), 8.58 (dd, J = 5.2, 0.8 Hz, 2 H), 8.68 (d, J = 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9 (CH_3), 111.2 (CH), 116.2 (CH × 2), 121.8 (CH × 2), 127.5 (CH × 2), 130.0 (CH), 133.3 (CH × 2), 152.3 (CH), 142.2 (C_q × 2), 153.9 (C_q), 169.1 (C_q), 173.2 (C_q × 2), 178.2 (C_q); MS (EI, m/z) 302 (M^+, 1), 88 (43), 70 (64), 61 (100); HRMS (EI-magnetic sector) m/z [M^+] calcd for $C_{19}H_{14}N_2O_2$ 302.1055, found 302.1054.

DOI: 10.1021/acs.organomet.9b00119
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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00119.

Optimization of reaction conditions, synthesis and characterization of starting substrates, preparation of deuterium-labeled substrates **1a-D$_1$** and **1a-D$_5$**, and KIEs operation and calculation, ^{1}H, ^{13}C and DEPT (90° and 135°) NMR spectra of new and known compounds (PDF)

Accession Codes

CCDC 1897991−1897993 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Ministry of Science and Technology of the Republic of China (MOST 104-2113-M-143-002-MY2 and MOST 106-2113-M-143-001-MY2) for financial support and Mr. Min-Yuan Hung for his technical support and services in GC−MS, Center for Research Resources and Development of Kaohsiung Medical University (Taiwan).

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DOI: 10.1021/acs.organomet.9b00119
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reacts with the palladium center, the *ortho* steric hindrance might suppress the reactivity. By contrast, the starting substrates **1b** and **1g** bearing an *ortho*-substituent might cause the steric hindrance between the pyridine and aniline to form an orthogonal molecular geometry, which might promote the ease of the formation of the palladium complex **I** or **II**. The phenomenon may eventually result in the observation of the excellent yield.

(12) Copies of the deposited crystallographic data CCDC-1897993 (**4a**), CCDC-1897992 (**5h**), and CCDC-1897991 (**I**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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DOI: 10.1021/acs.organomet.9b00119
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