Synlett S. L. Yedage, B. M. Bhanage Letter

Amides and Ethers as Chemoselective Surrogates for Copper(II)-Catalyzed *ortho* Benzoyloxylation of 2-Phenylpyridines

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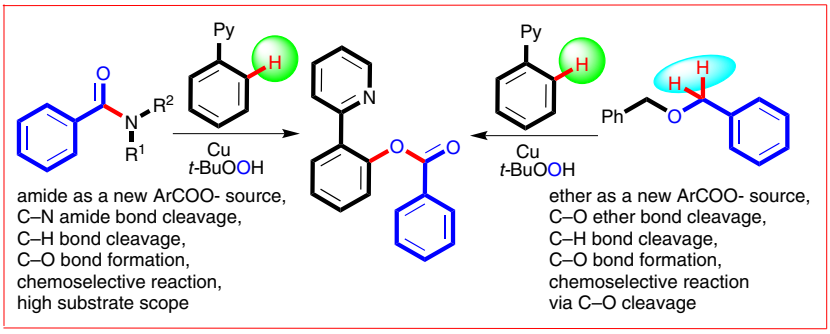

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Abstract Chemoselective *ortho* benzoyloxylation of 2-phenylpyridine derivatives using amides and ethers as novel arylcarboxy sources using a Cu(II)/TBHP catalytic system has been reported. It is a simple protocol for *ortho* benzoyloxylation using amides and ethers as surrogates. A broad range of amides and ethers was found to be compatible under optimized reaction conditions to provide the corresponding products in good to excellent yield. The reaction proceeds through the cleavage of C–N, C–O, and C–H bonds and the formation of a new C–O bond via C–H functionalization.

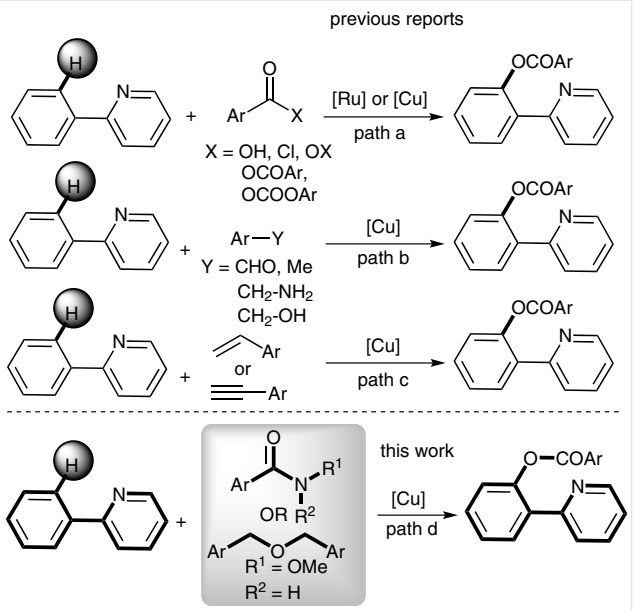
Key words C–H activation, amide, ether, copper acetate, benzoyloxylation

Combinations of transition-metal catalysts and chelating groups have brought about a resurgence in organic chemistry.[1] Several transition metals have explored for the functionalization of the unreactive C–H bond.[2] Thus, C–H bond activation is one of the most attractive approaches for reducing the number of synthetic steps in organic synthesis leading towards the development of atom economical protocols.[3] Recently, our group has studied several C–C, C–O, and C–N bond formation reactions via cleavage of C–C, C–N, and C–H bonds using transition-metal catalysts.[4]

Acylation of substrates possessing directing groups has been successfully achieved using expensive metal catalysts such as ruthenium, rhodium, and palladium with various acylating agents.[5] Clearly, it is desirable if the same conversion could be achieved using an inexpensive catalyst with an amide as a new acyl source. To the best of our knowledge, the use of a copper–amide combination has not been reported for acylation through C–H functionalization.

We explored the efficiency of a copper catalyst for radically induced acylation of 2-phenylpyridine (**1a**) with *N*-methoxybenzamide (**2a**). The reaction was performed using **2a** as an acyl source in the presence of CuI catalyst (5 mol%) and TBHP (3 equiv) as an oxidant in chlorobenzene solvent at 100 °C. Interestingly, the reaction gave *ortho*-benzoyloxylated product **3aa** in 41% yield instead of the expected *ortho*-acylated product (Table 1, entry 1). This result is rather surprising as benzamides are not known to act as synthetic equivalents of the benzoyloxy (ArCOO) group for such a reaction. In this regard, other research groups have previously reported the oxidation of *N*-methoxyamides for the synthesis of biaryl imino/keto carboxylic acids as well as deamidative arylation of azoles.[6] However, *ortho* benzoyloxylation of 2-phenylpyridine (**1a**) from *N*-methoxybenzamide (**2a**) as an ArCOO surrogate via HERON rearrangement[7] has not been reported in the literature. Most of the protocols report hydroxylation and acetoxylation of 2-phenylpyridine. In other words hydroxylation and acetoxylation are two general forms for C–O bond formation via C–H bond activation.[8] However; there are few reports in the literature pertaining to *ortho* benzoyloxylation.

Prior to the protocol reported herein, *ortho* benzoyloxylation of 2-phenylpyridine (**1a**) has been carried out using benzoic acids/chlorides/salts, anhydrides, and peroxides as arylcarboxy surrogates using ruthenium, palladium, and copper catalysts (Scheme 1, path a).[9] Additionally, aromatic aldehydes (ArCHO), alkylbenzenes (ArMe), benzylamines ($ArCH_2NH_2$), and benzyl alcohols ($ArCH_2OH$) have been used as alternative sources of the ArCOO group for *ortho* benzoyloxylation of 2-phenylpyridines (Scheme 1, path b).[10] In addition, Patel and co-workers have reported terminal styrenes and arylalkynes as ArCOO sources for *ortho* benzoyloxylation (Scheme 1, path c).[11] However, as far as we are aware, the present methodology, using arylamides as benzoyloxy surrogates, is novel and unparalleled in the literature (Scheme 1, path d). This protocol potentially provides an opportunity to use amides as new benzoyloxy equivalents for catalytic benzoyloxylation reactions.

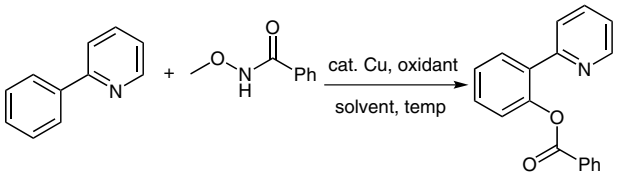


Scheme 1 Various approaches for *ortho* benzoyloxylation via C–H activation

To optimize the reaction conditions, 2-phenylpyridine (**1a**) and *N*-methoxybenzamide (**2a**) were chosen as model substrates for the *ortho* benzoyloxylation reaction.

A series of experiments was carried out to study the effect of various reaction parameters such as different copper catalysts, oxidants, catalyst loading, solvents, temperature, and reaction time on the yield of the desired products. The results are displayed in Table 1. Initially, various copper precursors were screened. Copper(I) salts such as CuI, CuBr, Cu_2O, CuCl, and copper(II) salts such as $CuSO_4{\cdot}5H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(OAc)_2{\cdot}H_2O$, and $Cu(OAc)_2$ were studied using TBHP (5–6 M in decane; Table 1, entries 1–8). It was observed that $Cu(OAc)_2$ provided a good yield of the desired product **3aa** (Table 1, entry 8). However, other copper catalysts provided **3aa** in moderate to poor yields. Subsequently, by changing the quantity of TBHP (5–6 M in decane) from three to five equivalents the product yield was improved to 59% (Table 1, entries 8 and 9). With further increase in TBHP quantity to 6 mmol, the yield of **3aa** decreased (Table 1, entry 10). It was also observed that increasing the $Cu(OAc)_2$ loading to 10 mol% increased the yield of desired product **3aa** to 81% at 120 °C (Table 1, entry 11). However, when the reaction was carried out without copper catalyst, the formation of **3aa** was not observed (Table 1, entry 12). It was also observed that the reaction did not proceed in the absence of TBHP (5–6 M in decane; Table 1, entry 13). Furthermore, various oxidants such as TBHP (aq 70%), H_2O_2, and MCPBA were studied for the reaction, but failed to give the desired product indicating the uniqueness of TBHP (5–6 M in decane) as the oxidant for this reaction (Table 1, entries 14–16). A 10 mol% $Cu(OAc)_2$ loading was found to be optimum as far as product yield is concerned. Any increase or decrease in $Cu(OAc)_2$ loading lowered the yield of the product (Table 1, entries 17 and 18). Increasing the reaction temperature to 130 °C or decreasing the reaction temperature to 100 °C led to a decrease in the yield of **3aa** (Table 1, entries 19–21). It was also observed that the optimized reaction time is 24 hours. A decrease in reaction time to 12 hours and 6 hours reduced the yield of the product. The effect of solvent was also significant. Various solvents were screened for the reaction. Among these,

Table 1 Optimization of Reaction Parameters[a]



1a **2a** **3aa**

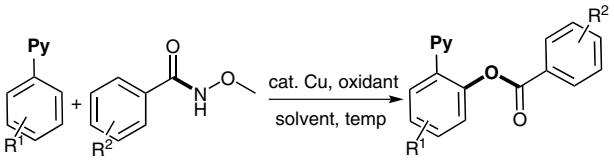
Entry	Catalyst (mol%)	Oxidant (equiv)	Solvent	Temp (°C)	Yield (%)[b]
1	CuI (5)	TBHP (3)	PhCl	120	41
2	CuBr (5)	TBHP (3)	PhCl	120	trace
3	CuCl (5)	TBHP (3)	PhCl	120	trace
4	$CuSO_4{\cdot}5H_2O$ (5)	TBHP (3)	PhCl	120	trace
5	$Cu(NO_3)_2{\cdot}3H_2O$ (5)	TBHP (3)	PhCl	120	32
6	$Cu(OAc)_2{\cdot}H_2O$ (5)	TBHP (3)	PhCl	120	30
7	Cu_2O (5)	TBHP (3)	PhCl	120	45
8	$Cu(OAc)_2$ (5)	TBHP (3)	PhCl	120	52
9	$Cu(OAc)_2$ (5)	TBHP (5)	PhCl	120	59
10	$Cu(OAc)_2$ (5)	TBHP (6)	PhCl	120	54
11	$Cu(OAc)_2$ (10)	TBHP (5)	PhCl	120	81
12	–	TBHP (5)	PhCl	120	n.r.
13	$Cu(OAc)_2$ (10)	–	PhCl	120	n.r.
14	$Cu(OAc)_2$ (10)	TBHP (aq 70%) (5)	PhCl	120	trace
15	$Cu(OAc)_2$ (10)	H_2O_2	PhCl	120	n.r.
16	$Cu(OAc)_2$ (10)	MCPBA (5)	PhCl	120	n.r.
17	$Cu(OAc)_2$ (20)	TBHP (5)	PhCl	120	62
18	$Cu(OAc)_2$ (5)	TBHP (5)	PhCl	120	39
19	$Cu(OAc)_2$ (10)	TBHP (5)	PhCl	130	51
20	$Cu(OAc)_2$ (10)	TBHP (5)	PhCl	100	57
21	$Cu(OAc)_2$ (10)	TBHP (5)	PhCl	R.T	n.r.
22	$Cu(OAc)_2$ (10)	TBHP (5)	DCE	120	47
23	$Cu(OAc)_2$ (10)	TBHP (5)	DMF	120	trace
24	$Cu(OAc)_2$ (10)	TBHP (5)	xylene	120	27
25	$Cu(OAc)_2$ (10)	TBHP (5)	toluene	120	30

[a] Reaction conditions: 2-phenylpyridine (**1a**, 0.5 mmol), *N*-methoxybenzamide (**2a**, 0.5 mmol), chlorobenzene (0.5 mL), time 24 h.
[b] GC yield.

chlorobenzene was superior to 1,2-dichloroethane, DMF, xylene, and toluene (Table 1, entries 22–25). Thus, the optimized reaction conditions were established as: **1a** (0.5 mmol), **2a** (0.5 mmol), $Cu(OAc)_2$ (10 mol%), TBHP (5 mmol), and chlorobenzene (0.5 mL) at 120 °C for 24 h.

Under the optimized reaction conditions, the scope of the protocol was studied for a wide range of *N*-methoxyamide derivatives containing different functional groups at the 2-, 3-, and 4-positions. The results are summarized in Table 2. In general, **2a** reacts with **1a** to give **3aa** in 78% yield. It was observed that reactions of 2-phenylpyridine with *N*-methoxybenzamide derivatives with electron-donating substituents such as Me, OMe, and *t*-Bu result in good yields of **3ab**–**af**. It was noted that 2-methyl *N*-methoxybenzamide provided a lower yield of **3ad** as compared to **3ac** (3-Me) and **3ab** (4-Me) presumably due to steric effects. Next, *N*-methoxy-2-naphthamide gave higher yields than *N*-methoxy-1-naphthamide, and this was again attributed to steric effects (**3ag**–**ah**). Weakly electron-withdrawing groups such as Cl and Br on the aromatic ring of amides resulted in moderate to good yields.

Table 2 Substrate Scope of 2-Phenylpyridine and *N*-Methoxybenzamide[a,b]



1a **2a–k** **3aa–bk**

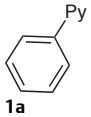
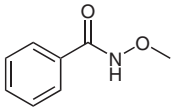
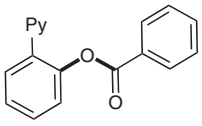
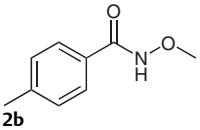
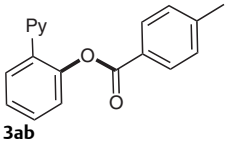
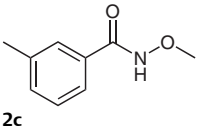
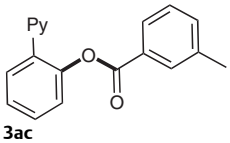
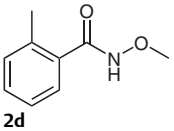
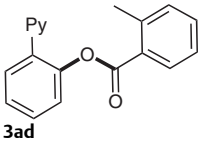
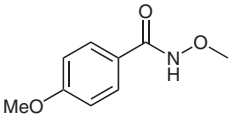
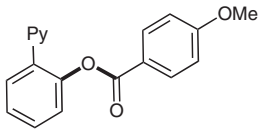
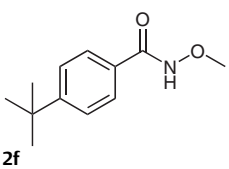
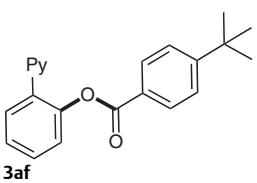
Entry	2-Arylpyridine	*N*-Methoxybenzamide	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **3aa**	78
2	**1a**	 **2b**	 **3ab**	79
3	**1a**	 **2c**	 **3ac**	79
4	**1a**	 **2d**	 **3ad**	53
5	**1a**	 **2e**	 **3ae**	74
6	**1a**	 **2f**	 **3af**	77

Table 2 (continued)

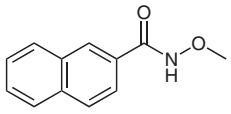
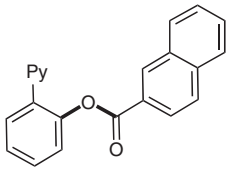
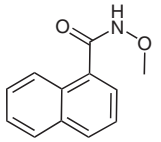
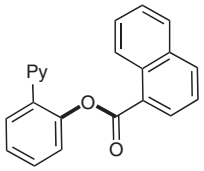
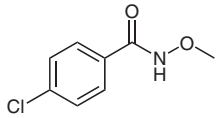
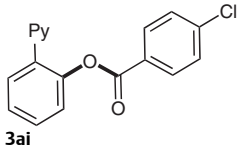
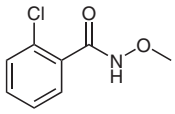
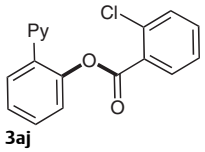
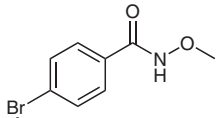
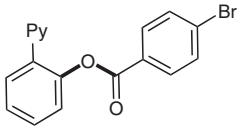
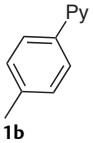
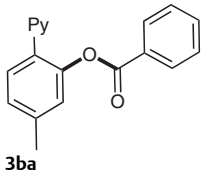
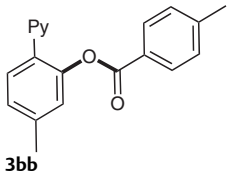
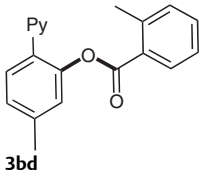
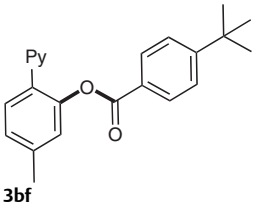
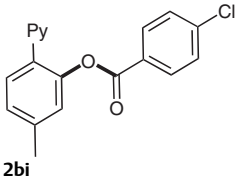
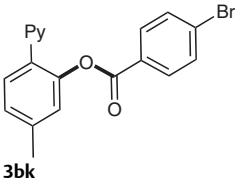
Entry	2-Arylpyridine	*N*-Methoxybenzamide	Product	Yield (%)[b]
7	**1a**	 **2g**	 **3ag**	71
8	**1a**	 **2h**	 **3ah**	69
9	**1a**	 **2i**	 **3ai**	67
10	**1a**	 **2j**	 **3aj**	47
11	**1a**	 **2k**	 **3ak**	63
12	 **1b**	**2a**	 **3ba**	76
13	**1b**	**2b**	 **3bb**	77
14	**1b**	**2d**	 **3bd**	54

Table 2 (continued)

Entry	2-Arylpyridine	*N*-Methoxybenzamide	Product	Yield (%)[b]
15	**1b**	**2f**	 **3bf**	77
16	**1b**	**2i**	 **2bi**	67
17	**1b**	**2k**	 **3bk**	63

[a] Reaction conditions: 2-phenylpyridine derivatives **1a**,**b** (0.5 mmol), *N*-methoxybenzamide derivatives **2a–l** (0.5 mmol), $Cu(OAc)_2$ (10 mol%), TBHP (5–6 M in decane; 5 mmol), chlorobenzene (0.5 mL), 120 °C, 24 h.
[b] Yield of isolated pure product.

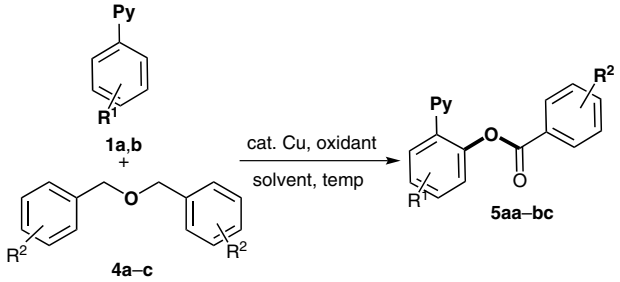
Similarly to the methyl-substituted benzamides, 2-chloro-*N*-methoxybenzamide gave a lower yield of **3aj** compared to 4-substituted substrates **3ai**–**ak**. Benzoyloxylation of 2-(*p*-tolyl)pyridine (**1b**) was also explored with a variety of *N*-methoxybenzamides under the optimized reaction conditions and the results obtained are summarized in Table 2. It was observed that **1b** showed almost the same pattern of reactivity as observed for **1a**. It can be seen that 2-(*p*-tolyl)pyridine with various *N*-methoxybenzamides containing Me, Cl, and Br substituents also provided moderate to good yields of **3ba**–**bk**. Benzoic acid derivatives were synthesized from dibenzyl ethers.[12]

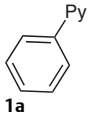
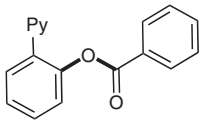
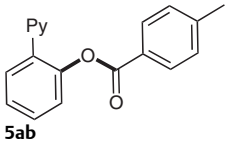
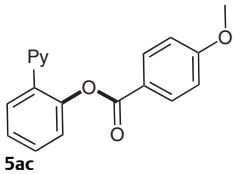
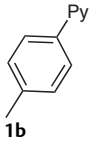
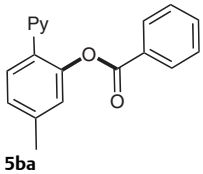
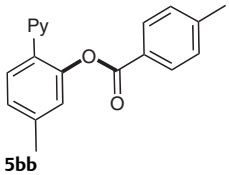
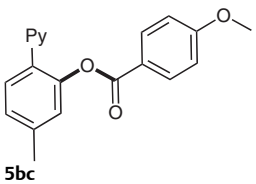
Encouraged by these results, we tried to extend the scope of our protocol to dibenzyl ethers as new sources of ArCOO. To explore their utility in C–H activation processes we aimed to investigate whether dibenzyl ether can act as a possible benzoyloxy source similar to *N*-methoxybenzamide. We carried out the reaction using the previously optimized parameters with dibenzyl ether instead of *N*-methoxybenzamide. It was observed that the desired product **5aa** was obtained in 71% after 24 hours (Table 3). To explore the substrate scope, symmetrical dibenzyl ethers as benzoyloxylation sources were also studied under the optimized reaction conditions. It was observed that 2-phenylpyridine reacted with different substituted symmetrical dibenzyl ethers to furnish the respective products **5aa**–**ac** in good yields. In addition, 2-(*p*-tolyl)pyridine also reacted with substituted dibenzyl ethers possessing Me and OMe substituents to deliver the corresponding *ortho*-benzoyloxylation products **5ba**–**bc** in good yields.

Additional experiments were performed to develop a better understanding of the *ortho*-benzoyloxylation reaction mechanism. Product **3aa** was not observed when the reaction of 2-phenylpyridine and benzamide was carried out under standard reaction conditions for 24 hours (Scheme 2, eq. a). When the same reaction was carried out using *N*-hydroxybenzamide, a trace amount of product **3aa** was observed (Scheme 2, eq. b). Next, *N*-methoxybenzamide was reacted with 2-phenylpyridine under standard reaction conditions in the presence of 1 mmol TEMPO, and product **3aa** was observed in trace amounts (Scheme 2, eq. c). When the reaction was carried out using *N*-methoxy-*N*-methyl benzamide (Weinreb amide), no product was observed (Scheme 2, eq. d).

N-Methoxybenzamide was converted into benzoic acid (94%) and methyl benzoate (6%) under the optimized reaction conditions. From these control experiments, we can conclude that the *N*-MeO group and the N–H bond are essential in the same molecule for the *ortho* benzoyloxylation of 2-phenylpyridine using amides as a carboxy surrogate. Dibenzyl ether was used for the acylation of sp^2 C–H bonds under oxidative conditions.[13]

Table 3 Substrate Scope of 2-Phenylpyridine and Substituted Dibenzyl Ether[a,b]



Entry	2-Aryl pyridine	Dibenzyl ether	Product	Yield (%)[b]
1	 **1a**	Bn_2O **4a**	 **5aa**	71
2	**1a**	$(4\text{-}MeC_6H_4CH_2)_2O$ **4b**	 **5ab**	73
3	**1a**	$(4\text{-}MeOC_6H_4CH_2)_2O$ **4c**	 **5ac**	71
4	 **1b**	**4a**	 **5ba**	71
5	**1b**	**4b**	 **5bb**	74
6	**1b**	**4c**	 **5bc**	70

[a] Reaction conditions: 2-phenylpyridine **1a**,**b** (1 mmol), dibenzyl ether **4a**–**c** (0.5 mmol), $Cu(OAc)_2$ (10 mol%), TBHP (5–6 M; 5 mmol), chlorobenzene (0.5 mL), 120 °C, 24 h.
[b] Yield of isolated pure product.

On the basis of these experimental observations (Scheme 2) and previous reports, a plausible mechanism for the copper-catalyzed *ortho* benzoyloxylation of 2-arylpyridine with *N*-methoxyamide and dibenzyl ether via direct C–H bond activation as well as C–N and C–O bond cleavage in the presence of TBHP is depicted in Scheme 3. Cleavage of the C–N and C–O bonds of *N*-methoxybenzamide and dibenzyl ether has been reported in the literature.[6,12] *ortho* Benzoyloxylation of 2-phenylpyridine can occur via three pathways. The prominent pathways are path A, from *N*-methoxybenzamide, and path B from dibenzyl ether. In path A, the copper catalyst and oxidant react with **2a** to form an alkoxyamidyl radical **a**.[7d] Subsequently, TBHP attacks at nitrogen and forms intermediate **b**. From this intermediate there are two possibilities; (i) formation of methyl benzoate **c** and (ii) *tert*-butyl peroxyester **d** with removal of alkoxynitrene **e** by HERON rearrangement.[7] In our case, there is a possibility that *tert*-butyl perester **d** forms as a major intermediate that undergoes further reaction to form the desired product. As with path B, the dibenzyl ether **4a** is transformed into **a′** in the presence of copper catalyst and TBHP oxidant.[12] Then **a′** is converted into the oxonium ion **b′** via abstraction of a hydrogen atom at the benzylic position of **a′**. Next, intermediate **c′** is formed by the hydration of **b′**. Furthermore, hemiacetal **c′** cleaved into the aldehyde **d′** and benzyl alcohol **e′**. Under oxidative conditions benzyl alcohol **e′** is converted into the benzaldehyde **d′**. Then, the aldehyde **d′** transformed into peroxyester **d** via the reaction of aldehyde **d′** with *tert*-butylperoxy radical.[10b] Homolytic cleavage of **d** provides benzoyloxy radical **f** along with *tert*-butoxyl radical.[10b,11] As with path C, copper(II) undergoes chelation with **1a** to give complex **g** that reacts with benzoyloxy radical **f** to provide a copper(III) intermediate **h**, which undergoes reductive elimination to give the desired product **3aa**/**5aa** and generates a copper(I) species. The copper(I) species is then oxidized to copper(II) to enter the next catalytic cycle.

To conclude, our protocol[14] reveals various amides and dibenzyl ethers as arylcarbonyloxy sources for substrate-directed chemoselective *ortho* benzoyloxylation of 2-phenylpyridine in the presence of a Cu(II)/TBHP system. From the results obtained, it can be concluded that this reaction proceeds via HERON rearrangement of *N*-methoxyamide. The present protocol reports the cleavage of C–H, C–N, and C–O bonds and the synthesis of new C–O bond via sp^2 C–H bond activation.

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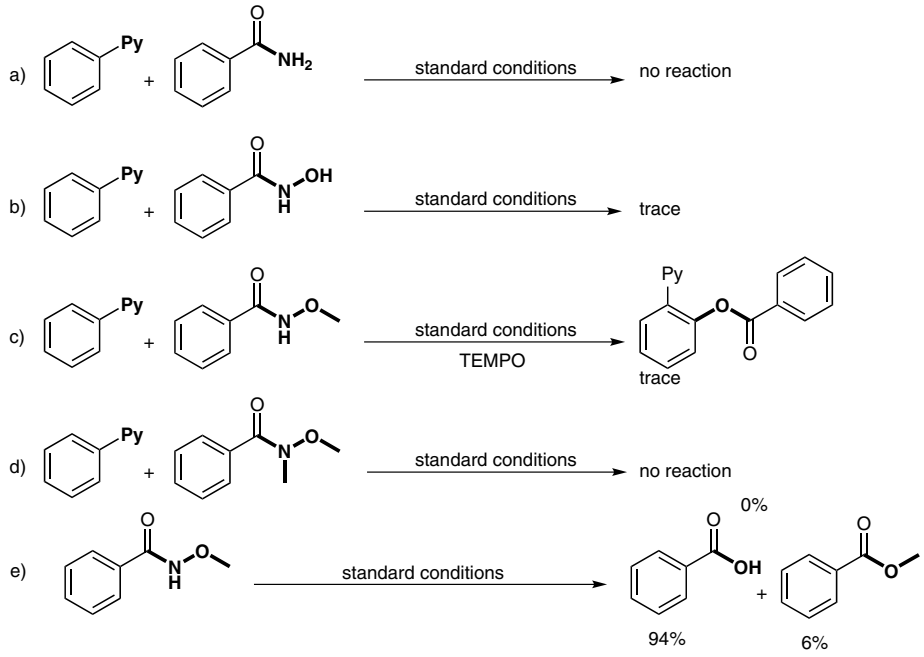
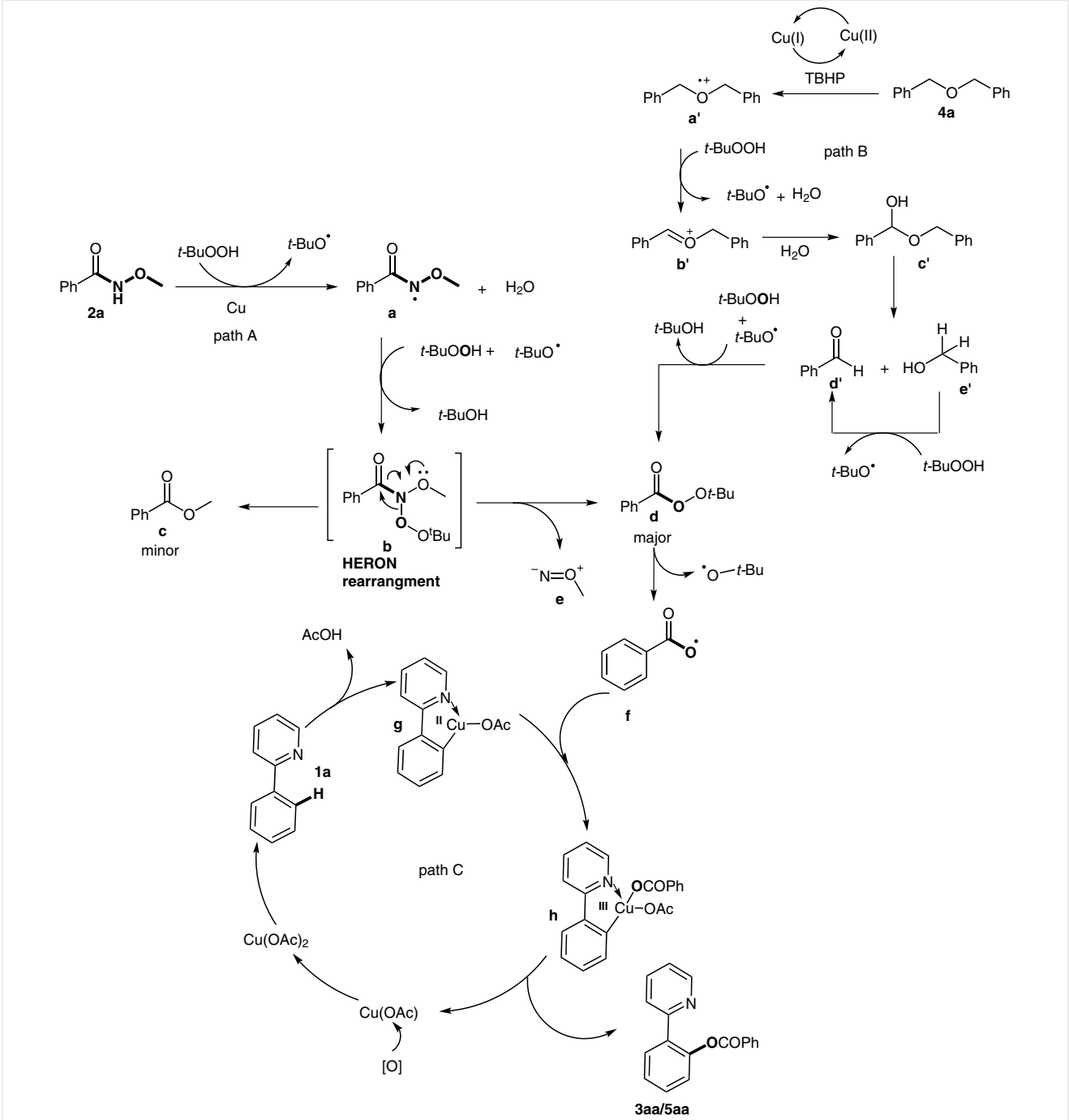
Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378830.



Scheme 2 Control experiments



Scheme 3 Proposed mechanism for *ortho* benzoyloxylation

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(14) **Representative Experimental Procedure for the Oxidative Benzoyloxylation of 2-Phenylpyridine with *N*-Methoxybenzamide**

2-Phenylpyridine (**1a**, 0.5 mmol, 77 mg), *o*-methoxybenzamide (**2a**, 0.5 mmol, 75 mg), and $Cu(OAc)_2$ (5 mol%, 18 mg) in chlorobenzene (0.5 mL) were charged in an oven-dried 10 mL single-necked round-bottom flask. At r.t. TBHP (5–6 M in decane, 5 mmol. 0.5 mL) was added dropwise to the reaction flask with stirring. The flask was then equipped with a condenser, and the reaction mixture was stirred at 120 °C for 24 h open to the atmosphere, and the progress of reaction was monitored by TLC and/or GC. After completion, the reaction mixture was allowed to cool to r.t., diluted with EtOAc (10 mL), and the organic phase was washed with 5% aq $NaHCO_3$ (2 × 5 mL) followed by H_2O (2 × 5 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was evaporated by rotary evaporation to obtain the crude product that was then purified by column chromatography (silica gel, 100–200 mesh), with PE–EtOAc as the eluent to afford the pure product. The products structure and purity were confirmed by GC–MS spectrometry and ^1H and ^{13}C NMR spectroscopic analysis.

Representative Analytical Data

2-(Pyridin-2-yl)phenyl 4-Methylbenzoate (3ab)[10]

Yield: 114 mg (79%); yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 4 Hz, 1 H), 7.95 (d, *J* = 8 Hz, 2 H), 7.78–7.75 (m, 1 H), 7.60–7.58 (m, 1 H), 7.54 (d, *J* = 8 Hz, 1 H), 7.46–7.44 (m, 1 H), 7.40–7.36 (m, 1 H), 7.29–7.23 (m, 3 H), 7.16–7.13 (m, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.21, 155.55, 149.62, 148.33, 144.31, 136.13, 133.34, 130.92, 130.24, 129.71, 129.23, 126.69, 126.33, 123.77, 123.37, 122.12, 21.76 ppm. GC–MS (EI, 70 eV): *m/z* (%) = 289 (10.3) [M^+], 119 (100), 91 (28.6), 65 (8.7), 40 (31.0).