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Synthesis of *N*-acetoxy-*N*-arylamides via Diacetoxyiodobenzene Promoted Double Acylation Reaction of Hydroxylamines with Aldehydes†

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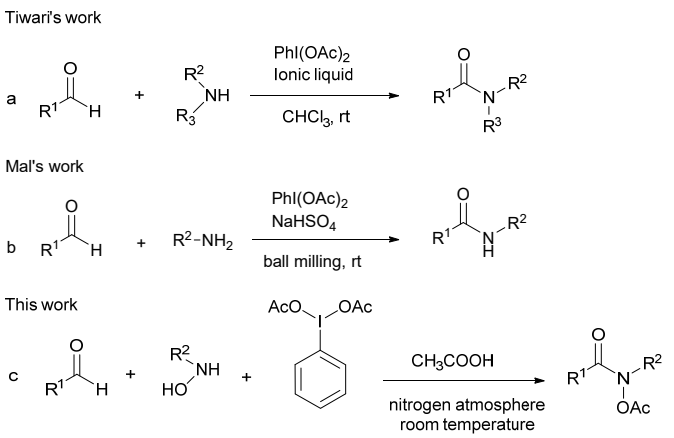
Huaiyuan Zhang,[a] Yingpeng Su,[a] Ke-Hu Wang,[a] Danfeng Huang,[a] Jun Li,[a] Yulai Hu*[a,b]

A facile and efficient synthesis of *N*-acetoxy-*N*-arylamides through double acylations of hydroxylamines with aldehydes and diacetoxyiodobenzene is reported. The yields of the products are good to excellent.

Introduction

Amides are prevalent structural motifs that are found in proteins, natural products, polymers, pharmaceuticals and materials.[1] For example, more than 25% of drugs on the market contain amide groups.[2] Thus, methods for synthesis of amides have received extensive attention. To date, many synthetic approaches have been developed for the synthesis of amides. The conventional methods are based on the condensation of carboxylic acids and amines.[3] These methods usually suffered from very harsh conditions such as high temperature above 100 °C or poor atom economy. To overcome these limitations, alternative methods are developed, such as the Schmidt reaction,[4] the Ritter reaction,[5] the Ugi-type multicomponent reactions,[6] the Beckmann rearrangement,[7] aminocarbonylation of aryl halides,[8] catalytic amidation of carboxylic acids with amines[9] or their surrogates[10], amidation of carboxylic acid surrogates such as aldehydes, ketones, alcohols, esters, thioacids, alkenes, alkynes, etc.[11] Within these emerging amide formation methods, oxidative amidation of aldehydes with different kinds of amines is a very attractive and efficient method because of easy availability and cheap price of aldehydes and amines in industry. These reactions were usually carried out in the presence of transition-metal catalysts.[12] In recent years, several metal-free procedures have also been reported. For instance, *N*-heterocyclic carbenes,[13a-13c] iodine[13d] and Bu_4NI catalyzed[13e-13f] amidation of aldehydes provided efficient protocols for synthesis of amides.

On the other hand, $PhI(OAc)_2$ has emerged as versatile and environmentally benign reagents for organic chemistry in recent years.[14] First of all, $PhI(OAc)_2$ has showed diverse oxidative transformations such as halogenation,[15] rearrangement,[16] allylation,[17] azidation,[18] dearomatization,[19] spirocyclization,[20] thiocyanation,[21] selenylation,[22] and oxidative coupling[23] reaction resulting in the formation of new C-C, C-N and other C-heteroatom or heteroatom-heteroatom bonds.[24] In addition, $PhI(OAc)_2$ has showed a particularly important application as selective reagents in the total synthesis of natural products.[25] Meanwhile, $PhI(OAc)_2$ can be used in the amidation of aldehydes with amines (Scheme 1). In 2012, Tiwari's group reported the amidation of aldehydes using $PhI(OAc)_2$ in the presence of ionic liquid (Scheme 1, a).[26] In 2015, Mal's group also reported coupling of aldehydes with primary amines into amides via C–H activation using diacetoxyiodobenzene (Scheme 1, b).[27] Furthermore, *N*-acetoxy-*N*-arylamides, derivatives of hydroxamic acids, are important synthetic intermediates,[28] which were usually obtained from the lead tetraacetate mediated oxidative rearrangement of nitrones.[28a,29] Herein, we would like to report a convenient method for the preparation of *N*-acetoxy-*N*-arylamides from $PhI(OAc)_2$-promoted double acylation reaction of hydroxylamines with aldehydes (Scheme 1, c).



Scheme 1. Amidation of aldehydes mediated by diacetoxyiodobenzene.

[a] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070.
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China.
E-mail: huyl@nwnu.edu.cn.

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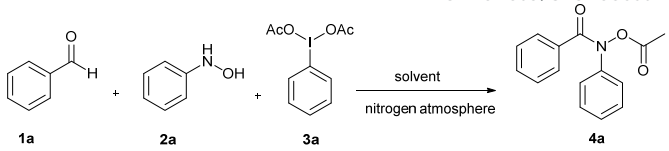
Results and discussion

At the outset of the study, mixture of benzaldehyde **1a** (1 equiv) and *N*-phenylhydroxylamine **2a** (1 equiv) in DCM was stirred at room temperature for 10 hours. After removing the solvent under vacuum, the residue was dissolved in dry acetonitrile, and diacetoxyiodobenzene **3a** (1 equiv) was added under nitrogen atmosphere. After stirring the mixture at room temperature for one hour, the double acylated product **4a** was obtained in 45% yield (Table 1, entry 1). In order to improve the yield, the reaction conditions were examined in detail. Firstly, the mole ratio of the substrate **3a** was screened when **1a** and **2a** was fixed to 1:1[30]. As mole ratio of **3a** was gradually increased, the yield of **4a** was slightly improved. The 1:1:2 mole ratio of **1a**:**2a**:**3a** was finally determined to be the best one, and used to optimize other conditions (Table 1, entry 3). Next, various solvents were investigated. As shown in Table 1, both of aprotic and protic solvents could give desired product **4a**, but the product yields in most of aprotic solvents were lower than those in protic solvents. The best result was obtained in acetic acid with the yield of **4a** going up to 75% (Table 1, entries 5-12). Then, the effect of temperature on the reaction was also checked. It was found that the room temperature was the most suitable temperature (Table 1, entries 12-14). Finally, other commercially available hypervalent iodine compounds such as phenyliodine bis(trifluoroacetate) (PIFA) and [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent) were applied in the reactions. However, no corresponding products were obtained when PIFA or HTIB was used in the reaction. Thus, the best reaction condition was treatment of aldehydes with 1 equiv of hydroxylamines in CH_2Cl_2 at room temperature overnight. After removing the solvent, the residue was dissolved in acetic acid, and diacetoxyiodobenzene **3a** (2 equiv) was added under nitrogen atmosphere to give the target products.

The scope and generality of the process was next explored under the optimized conditions. Firstly, a variety of aromatic aldehydes were employed to react with *N*-phenylhydroxylamine **2a**. As shown in Table 2, most of aromatic aldehydes could give desired products regardless of whether the substituents on the phenyl ring were electron-donating or electron-withdrawing groups. In some cases, the position of substituents on phenyl rings of aromatic aldehydes had great influence on the reactions. For instance, the *p*-nitrobenzaldehyde could make the reaction occurred smoothly to afford the product **4l** in 73% yield, but the *o*-nitrobenzaldehyde could not produce the product **4j** in the same reaction (Table 2, **4l** and **4j**). Heterocyclic aromatic aldehydes such as 2-furaldehyde and 2-pyridinecarboxaldehyde provided the corresponding products in good yields (Table 2, **4n** and **4o**). Unfortunately, aliphatic aldehydes, such as *n*-butyraldehyde and heptanal, could not give the corresponding products (Table 2, **4p** and **4q**).

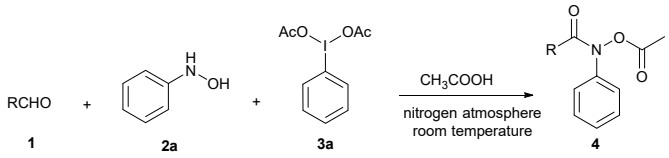
Table 1. Optimization of the reaction conditions.[a]

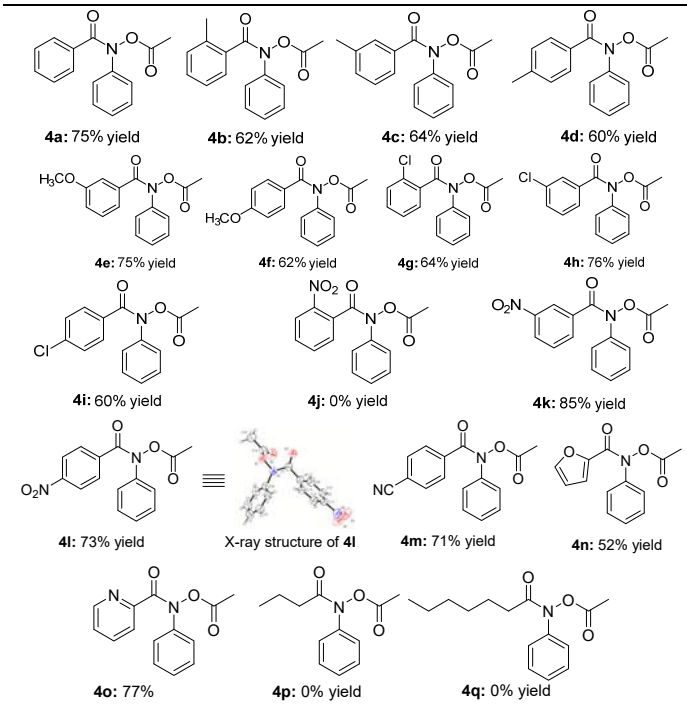


Entry	Mole Ratio of **1a**/**2a**/**3a**	Temp. (°C)	Solvent	Isolated yield (%)
1	1/1/1	rt	MeCN	45
2	1/1/1.5	rt	MeCN	43
3	1/1/2	rt	MeCN	51
4	1/1/2.5	rt	MeCN	46
5	1/1/2	rt	CH_2Cl_2	62
6	1/1/2	rt	PhMe	38
7	1/1/2	rt	THF	40
8	1/1/2	rt	DMF	25
9	1/1/2	rt	$MeNO_2$	71
10	1/1/2	rt	CH_3OH	49
11	1/1/2	rt	CH_3CH_2OH	71
12	1/1/2	rt	CH_3COOH	75
13	1/1/2	0	CH_3COOH	67
14	1/1/2	reflux	CH_3COOH	48

[a]Reactions were carried out on a 0.47 mmol scale of **1a** and **2a** in 5 mL of DCM. After formation of nitrone, DCM was removed and 4 mL of new solvent and **3a** were added.

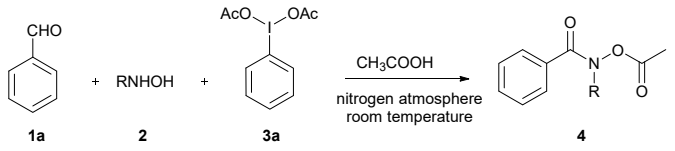
Table 2. Scope of the aldehydes.[a]

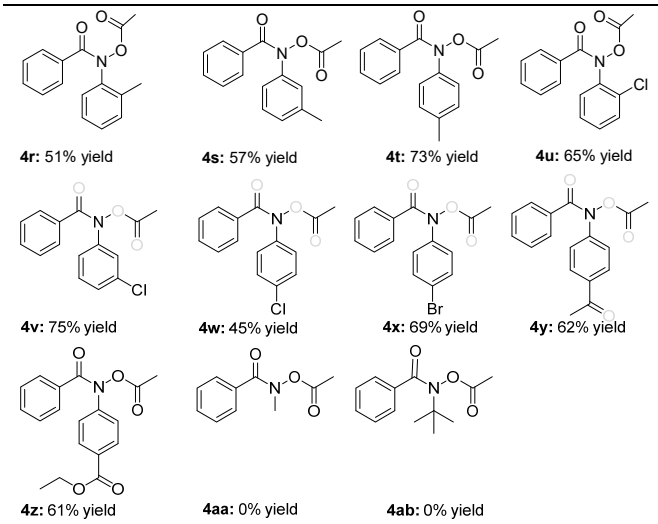




[a]Reactions were carried out on a 0.47 mmol scale of **1** and **2a** in 5 mL of DCM. After formation of nitrones, DCM was removed and 4 mL of AcOH and 0.94 mmol of **3a** were added. Isolated yield (SiO_2).

Table 3. Scope of the hydroxylamines.[a]



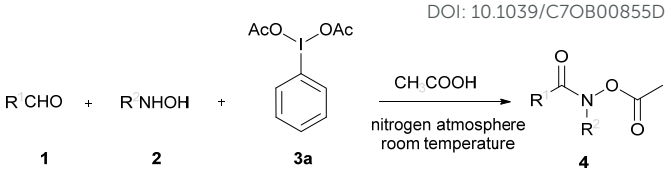


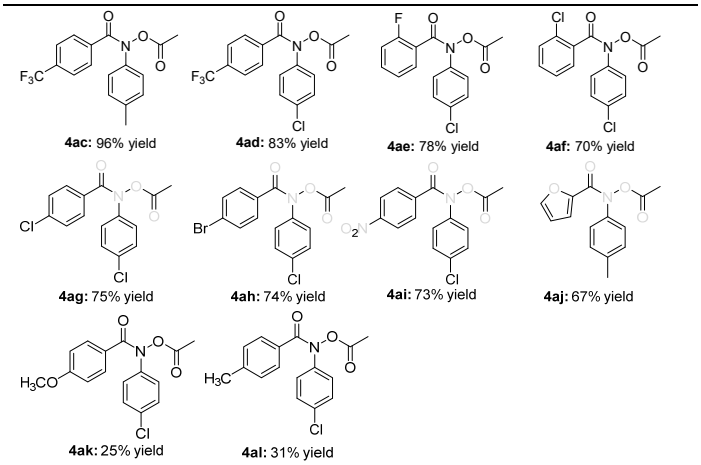
[a]Reactions were carried out on a 0.47 mmol scale of **1a** and **2** in 5 mL of DCM. After formation of nitrone, DCM was removed and 4 mL of AcOH and 0.94 mmol of **3a** were added. Isolated yield (SiO_2).

Then, the substrate scope of hydroxylamines **2** was examined. Various *N*-aromatic hydroxylamines containing methyl, chloro, bromo, acetyl and ester groups reacted with benzaldehyde **1a** smoothly to afford the corresponding products in 45-75% yields (Table 3, **4r** to **4z**). However, aliphatic hydroxylamines such as *N*-methylhydroxylamine and *N*-(*t*-butyl)hydroxylamine could not provide the desired products **4aa** and **4ab** (Table 3, **4aa** and **4ab**).

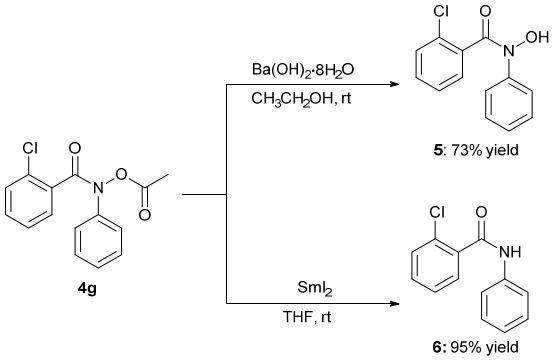
Next, compatibility of the substituents on aromatic aldehydes and aromatic hydroxylamines was also investigated as showed in Table 4. The products would be obtained in higher yields when more electron-withdrawing groups were attached on aromatic aldehydes. In contrast, if the electron-donating groups were attached on the aldehydes, the yields of the products would decrease. For example, product **4ac**, which came from 4-trifluoromethylbenzaldehyde, was obtained in 96% yield, but product **4ak**, which came from 4-methoxybenzaldehyde, was produced only in 25% yield. The same results could be observed between product **4ad** and product **4al**. On the other hand, when the aldehydes were the same, the aromatic hydroxylamines with electron-donating groups on their phenyl rings would give the products in higher yields than those with electron-withdrawing groups. For instance, the product **4ac** was produced in higher yield than the product **4ad**. At last, if the aromatic ketones, such as acetophenone or 4-bromoacetophenone, were used in the reactions instead of aldehydes, no corresponding products would be formed.

Table 4. Scope of various aldehydes and hydroxylamines.[a]





[a]Reactions were carried out on a 0.47 mmol scale of **1** and **2** in 5 mL of DCM. After formation of nitrone, DCM was removed and 4 mL of AcOH and 0.94 mmol of **3a** were added. Isolated yield (SiO_2).

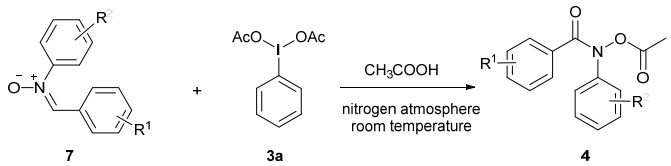


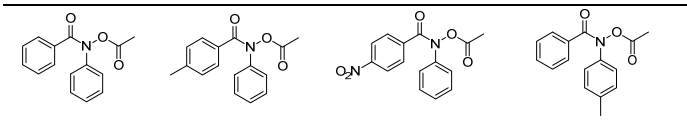
Scheme 2. Transformation of product **4g**.

To explore the application of the products **4** in organic synthesis, the compound **4g** was chose for further transformations. It could be easily hydrolyzed to *N*-hydroxyl amide **5** in 73% yield when the compound **4g** was exposed to $Ba(OH)_2{\cdot}8H_2O$ in ethanol. If **4g** was treated with SmI_2 in THF, acetoxyl group would be removed to afford amide **6** in 95% yield (Scheme 2).

To investigate the reaction mechanism, nitrones were assumed to be the intermediates in the reactions. Thus, some nitrones were prepared firstly, and then reacted with $PhI(OAc)_2$ under the optimized reaction conditions. It was found that the corresponding products were also obtained in about the same yields as above (Table 5). These indicated that nitrones were formed at the beginning of the reactions.

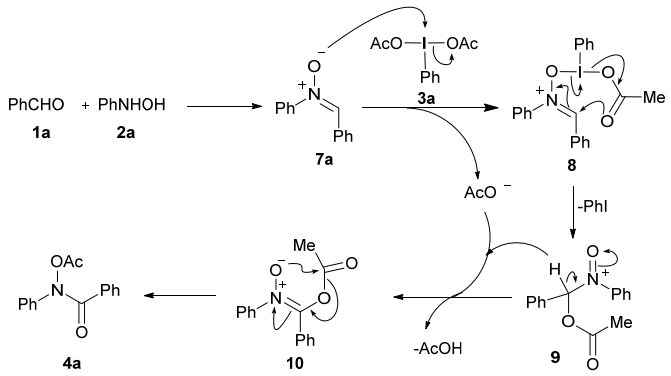
Table 5. Reactions of nitrones with diacetoxyiodobenzene for the synthesis of *N*-acetoxy-*N*-arylamides.[a]





[a]Reactions were carried out on a scale of 0.25 mmol scale of **7** and 0.50 mmol of **3a** in 4 mL of AcOH. Isolated yield (SiO_2).

Based on the above experimental results and literature reports[29b, 31], a plausible mechanism for this reaction was proposed in scheme 3. At the beginning, aldehyde **1a** reacted with hydroxylamine **2a** to form nitrone **7a**. The ligand exchange of **7a** and PIDA **3a** produced intermediate **8**, which conducted intramolecular rearrangement to produce intermediate **9**. Deprotonation of intermediate **9** by acetate afforded intermediate **10**, which gave the final product **4a** after migration of acyl group and isomerization.



Scheme 3. Plausible mechanism.

Conclusions

In summary, an efficient double acylation protocol for the preparation of *N*-acetoxy-*N*-arylamides has been developed. The method couples the aromatic aldehydes and hydroxylamines directly in the presence of diacetoxyiodobenzene to afford the *N*-acetoxy-*N*-arylamides in good to excellent yields. One advantage of the method is double acylation between *N*-acylation and *O*-acylation of hydroxylamines. The nitrogen atoms in hydroxylamines are only acylated by acyl groups of aldehydes, but the oxygen atoms in hydroxylamines are acylated by acetyl group of diacetoxyiodobenzene. Another advantage is that the two acyl groups were introduced into the same amide molecules at the same time.

Experimental Section

General Procedure for the Synthesis of Compounds 4 from 1, 2 and 3a

The aldehyde **1** (0.47 mmol, 1 equiv) and hydroxylamine **2** (0.47 mmol, 1 equiv) was put in a dried round-bottom flask (50 mL) fitted with a magnetic bar. Then dichloromethane (5 mL) was added. The mixture was stirred at room temperature and the reaction was monitored by TLC. After complete generation of nitrones, the reaction mixture was concentrated under reduced pressure, and diacetoxyiodobenzene **3a** (0.94 mmol, 2 equiv) in acetic acid (4 mL) were added into the flask. The resulting mixture was stirred at room temperature under nitrogen atmosphere for 1 h, and then the saturated Na_2CO_3 solution (10 mL) was poured into the flask. After stirring for 10 min, the mixture was extracted with EtOAc (3 × 10 mL). The organic layer were combined, dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using PE : EA (10:1) as eluent to afford the product **4**.

General Procedure for the Synthesis of Compounds 4 from 7 and 3a

The nitrone **7** (0.25 mmol, 1 equiv) and diacetoxyiodobenzene **3a** (0.50 mmol, 2 equiv) were put in a dried round-bottom flask (50 mL) fitted with a magnetic bar. Then acetic acid (4 mL) was added under nitrogen atmosphere. The mixture was stirred at room temperature for 1 h, and then the saturated Na_2CO_3 solution was poured into the flask. After stirring for 10 min, the mixture was extracted with EtOAc (3 × 10 mL). The organic layer were combined, dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using PE : EA (10:1) as eluent to afford the product **4**.

***N*-acetoxy-*N*-phenylbenzamide (4a).**[29b] White solid, 90.0 mg, yield 75%. m.p. 47–48 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.53–7.52 (m, 2H), 7.38–7.35 (m, 1H), 7.31–7.25 (m, 7H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 166.8, 140.6, 133.2, 131.0, 129.2, 128.8, 128.4, 128.1, 126.9, 18.4; HRMS (ESI) M/Z calcd for $C_{15}H_{14}NO_3$ [M+H$^+$] 256.0968, found: 256.0970.

***N*-acetoxy-2-methyl-*N*-phenylbenzamide (4b).** White solid, 78.5 mg, yield 62%. m.p. 61–62 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.30–7.19 (m, 7H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 139.4, 135.9, 133.9, 130.5, 129.8, 129.0, 128.3, 127.5, 126.1, 125.3, 19.3, 18.2; HRMS (ESI) M/Z calcd for $C_{16}H_{16}NO_3$ [M+H$^+$] 270.1125, found: 270.1123.

***N*-acetoxy-3-methyl-*N*-phenylbenzamide (4c).** White solid, 81.0 mg, yield 64%. m.p. 90–91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 1H), 7.31–7.29 (m, 4H), 7.27–7.25 (m, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 2.28 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 167.0, 140.6, 138.0, 133.1, 131.8, 129.3, 129.1, 128.3, 127.8, 126.8, 125.8, 21.2, 18.4; HRMS (ESI) M/Z calcd for $C_{16}H_{16}NO_3$ [M+H$^+$] 270.1125, found: 270.1122.

***N*-acetoxy-4-methyl-*N*-phenylbenzamide (4d).**[32] White solid, 75.9 mg, yield 60%. m.p. 88–89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42 (d, *J* = 7.8 Hz, 2H), 7.30–7.25 (m, 5H), 7.06 (d, *J* =

7.8 Hz, 2H), 2.30 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 166.8, 141.5, 140.8, 130.2, 129.1, 128.9, 128.7, 128.3, 126.9, 21.4, 18.4; HRMS (ESI) M/Z calcd for $C_{16}H_{16}NO_3$ [M+H$^+$] 270.1125, found: 270.1123.

***N*-acetoxy-3-methoxy-*N*-phenylbenzamide (4e).** White solid, 100.6 mg, yield 75%. m.p. 68−69 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.31−7.28 (m, 4H), 7.27−7.24 (m, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.07−7.05 (m, 2H), 6.89−6.88 (m, 1H), 3.69 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 166.4, 159.1, 140.5, 134.3, 129.1, 129.0, 128.4, 126.8, 121.0, 117.4, 113.5, 55.2, 18.3; HRMS (ESI) M/Z calcd for $C_{16}H_{15}NO_4Na$ [M+Na$^+$] 308.0893, found: 308.0889.

***N*-acetoxy-4-methoxy-*N*-phenylbenzamide (4f).** White solid, 83.1 mg, yield 62%. m.p. 74−75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.51 (d, *J* = 9.0 Hz, 2H), 7.33−7.27 (m, 5H), 6.76 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 168.0, 166.5, 161.8, 141.2, 131.0, 129.2, 128.3, 127.0, 125.1, 113.4, 55.3, 18.5; HRMS (ESI) M/Z calcd for $C_{16}H_{15}NO_4Na$ [M+Na$^+$] 308.0893, found: 308.0889.

***N*-acetoxy-2-chloro-*N*-phenylbenzamide (4g).** White solid, 87.1 mg, yield 64%. m.p. 88−89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.38−7.26 (m, 9H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.6, 162.8, 138.8, 134.0, 131.1, 130.9, 129.7, 129.0, 127.6, 126.5, 110.0, 18.1; HRMS (ESI) M/Z calcd for $C_{15}H_{12}ClNO_3Na$ [M+Na$^+$] 312.0398, found: 312.0399.

***N*-acetoxy-3-chloro-*N*-phenylbenzamide (4h).** White solid, 104.3 mg, yield 76%. m.p. 102−103 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.55 (s, 1H), 7.37−7.28 (m, 7H), 7.20 (t, *J* = 7.8 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 165.3, 140.1, 135.0, 134.2, 131.1, 129.4, 129.3, 128.9, 128.8, 127.0, 126.8, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{12}ClNO_3Na$ [M+Na$^+$] 312.0398, found: 312.0401.

***N*-acetoxy-4-chloro-*N*-phenylbenzamide (4i).**[32] White solid, 81.7 mg, yield 60%. m.p. 105−107 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.47 (d, *J* = 7.8 Hz, 2H), 7.34−7.27 (m, 5H), 7.25 (d, *J* = 8.4 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 165.6, 140.2, 137.2, 131.6, 130.2, 129.3, 128.6, 128.4, 126.9, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{13}ClNO_3$ [M+H$^+$] 290.0578, found: 290.0576.

***N*-acetoxy-3-nitro-*N*-phenylbenzamide (4k).** Yellow oil, 119.9 mg, yield 85%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.38 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 6.0 Hz, 1H), 7.36−7.32 (m, 5H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.6, 147.7, 139.6, 134.9, 134.5, 129.6, 129.4, 129.3, 127.3, 125.6, 123.9, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{12}N_2O_5Na$ [M+Na$^+$] 323.0638, found: 323.0635.

***N*-acetoxy-4-nitro-*N*-phenylbenzamide (4l).**[33] White solid, 103.0 mg, yield 73%. m.p. 157−158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.14 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.35−7.32 (m, 5H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.6, 148.9, 139.4, 129.7, 129.5, 129.3, 127.1, 123.4, 110.0, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{12}N_2O_5Na$ [M+Na$^+$] 323.0638, found: 323.0634.

***N*-acetoxy-4-cyano-*N*-phenylbenzamide (4m).** White solid, 93.5 mg, yield 71%. m.p. 105−106 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.61 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.35−7.29 (m, 5H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.6, 164.6, 139.6, 137.5, 131.9, 129.5, 129.2, 129.1, 127.0, 117.8, 114.6, 18.2; HRMS (ESI) M/Z calcd for $C_{16}H_{12}N_2O_3Na$ [M+Na$^+$] 303.0740, found: 303.0737.

***N*-acetoxy-*N*-phenylfuran-2-carboxamide (4n).** White solid, 59.9 mg, yield 52%. m.p. 70−71 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.50−7.48 (m, 2H), 7.44−7.40 (m, 4H), 6.66 (d, *J* = 3.0 Hz, 1H), 6.38 (dd, *J* = 3.6, 1.8 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 164.6, 151.7, 148.5, 140.1, 136.6, 128.9, 128.2, 125.2, 124.4, 18.3; HRMS (ESI) M/Z calcd for $C_{13}H_{12}NO_4$ [M+H$^+$] 246.0761, found: 246.0758.

***N*-acetoxy-*N*-phenylpicolinamide (4o).** White solid, 92.7 mg, yield 77%. m.p. 75−76 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1H), 7.79−7.72 (m, 2H), 7.39−7.25 (m, 6H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 156.2, 145.4, 145.3, 140.0, 129.3, 129.2, 127.4, 118.2, 111.5, 18.4; HRMS (ESI) M/Z calcd for $C_{14}H_{13}N_2O_3$ [M+H$^+$] 257.0921, found: 257.0918.

***N*-acetoxy-*N*-(o-tolyl)benzamide (4r).** White solid, 64.6 mg, yield 51%. m.p. 65−66 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.49 (d, *J* = 7.2 Hz, 2H), 7.35−7.32 (m, 2H), 7.25−7.22 (m, 4H), 7.12 (d, *J* = 4.8 Hz, 1H), 2.38 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.5, 139.0, 137.0, 133.0, 131.1, 131.0, 129.9, 129.7, 128.4, 127.9, 126.7, 18.3, 17.9; HRMS (ESI) M/Z calcd for $C_{16}H_{15}NO_3Na$ [M+Na$^+$] 292.0944, found: 292.0950.

***N*-acetoxy-*N*-(m-tolyl)benzamide (4s).** White solid, 72.1 mg, yield 57%. m.p. 70−71 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.53 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 10.2 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 166.8, 140.4, 139.2, 133.3, 130.9, 129.2, 128.8, 128.6, 128.0, 127.3, 124.0, 21.1, 18.3; HRMS (ESI) M/Z calcd for $C_{16}H_{15}NO_3Na$ [M+Na$^+$] 292.0944, found: 292.0952.

***N*-acetoxy-*N*-(p-tolyl)benzamide (4t).**[29b] White solid, 92.4 mg, yield 73%. m.p. 88−89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 166.7, 138.8, 138.0, 133.3, 130.9, 129.8, 128.7, 128.0, 127.2, 21.1, 18.3; HRMS (ESI) M/Z calcd for $C_{16}H_{16}NO_3$ [M+H$^+$] 270.1125, found: 270.1122.

***N*-acetoxy-*N*-(2-chlorophenyl)benzamide (4u).** White solid, 88.5 mg, yield 65%. m.p. 80−81 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.56 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.29−7.26 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 137.9, 133.8, 132.9, 132.2, 131.2, 131.0, 130.6, 128.5, 128.1, 127.6, 18.4; HRMS (ESI) M/Z calcd for $C_{15}H_{13}ClNO_3$ [M+H$^+$] 290.0578, found: 290.0580.

***N*-acetoxy-*N*-(3-chlorophenyl)benzamide (4v).** Yellow liquid, 102.1 mg, yield 75%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.55−7.53 (m, 2H), 7.42−7.39 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.24−7.19 (m, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 166.9, 141.5, 134.6, 132.9, 131.3, 129.9, 128.5, 128.2, 128.1, 125.9, 124.3, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{13}ClNO_3$ [M+H$^+$] 290.0578, found: 290.0577.

***N*-acetoxy-*N*-(4-chlorophenyl)benzamide (4w).**[29b] White solid, 61.3 mg, yield 45%. m.p. 108−109 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.53−7.52 (m, 2H), 7.41−7.38 (m, 1H), 7.32−7.26 (m,

6H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 166.8, 139.0, 134.0, 133.0, 131.2, 129.3, 128.6, 128.2, 127.8, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{12}ClNO_3Na$ [M+Na$^+$] 312.0398, found: 312.0403.

***N*-acetoxy-*N*-(4-bromophenyl)benzamide (4x).** White solid, 108.4 mg, yield 69%. m.p. 66−67 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.2 Hz, 2H), 7.44−7.39 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.8, 166.8, 139.5, 132.9, 132.3, 131.3, 128.6, 128.2, 128.0, 122.0, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{12}BrNO_3Na$ [M+Na$^+$] 355.9893, found: 355.9905.

***N*-acetoxy-*N*-(4-acetylphenyl)benzamide (4y).** White solid, 86.6 mg, yield 62%. m.p. 116−117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.45−7.39 (m, 3H), 7.34 (t, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 196.6, 167.8, 166.9, 144.1, 135.4, 133.0, 131.5, 129.2, 128.5, 128.3, 124.2, 26.5, 18.2; HRMS (ESI) M/Z calcd for $C_{17}H_{15}NO_4Na$ [M+Na$^+$] 320.0893, found: 320.0901.

Ethyl 4-(*N*-acetoxybenzamido)benzoate (4z). White solid, 93.8 mg, yield 61%. m.p. 72−73 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 166.8, 165.5, 144.1, 133.1, 131.4, 130.4, 129.2, 128.6, 128.3, 124.4, 61.2, 18.2, 14.2; HRMS (ESI) M/Z calcd for $C_{18}H_{18}NO_5$ [M+H$^+$] 328.1179, found: 328.1176.

***N*-acetoxy-*N*-(p-tolyl)-4-(trifluoromethyl)benzamide (4ac).** White solid, 152.2 mg, yield 96%. m.p. 67−68 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.63 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 165.3, 139.4, 137.3, 136.9, 132.5 (q, $J_{C\text{-}F}$ = 33.0 Hz), 130.0, 129.1, 127.3, 125.1 (q, $J_{C\text{-}F}$ = 3.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 271.5 Hz), 21.1, 18.3; HRMS (ESI) M/Z calcd for $C_{17}H_{15}F_3NO_3$ [M+H$^+$] 338.0999, found: 338.0998.

***N*-acetoxy-*N*-(4-chlorophenyl)-4-(trifluoromethyl)benzamide (4ad).** Yellow oil, 139.3 mg, yield 83%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.65 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.33−7.27 (m, 4H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 165.5, 138.3, 136.5, 134.6, 132.9 (q, $J_{C\text{-}F}$ = 33.0 Hz), 129.6, 129.0, 127.9, 125.3 (q, $J_{C\text{-}F}$ = 4.5 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.5 Hz), 18.2; HRMS (ESI) M/Z calcd for $C_{16}H_{11}ClF_3NO_3Na$ [M+Na$^+$] 380.0272, found: 380.0278.

***N*-acetoxy-*N*-(4-chlorophenyl)-2-fluorobenzamide (4ae).** White solid, 112.8 mg, yield 78%. m.p. 98−99 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.48 (t, *J* = 7.2 Hz, 1H), 7.37−7.27 (m, 5H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.98 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.5, 158.4 (d, $J_{C\text{-}F}$ = 250.5 Hz), 137.5, 134.3, 132.5 (d, $J_{C\text{-}F}$ = 7.5 Hz), 129.6, 129.1, 127.9, 124.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 122.3 (d, $J_{C\text{-}F}$ = 15.0 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 18.0; HRMS (ESI) M/Z calcd for $C_{15}H_{11}ClFNO_3Na$ [M+Na$^+$] 330.0304, found: 330.0303.

***N*-acetoxy-2-chloro-*N*-(4-chlorophenyl)benzamide (4af).** White solid, 106.6 mg, yield 70%. m.p. 72−73 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.38−7.27 (m, 8H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.6, 137.3, 133.8, 131.1, 129.7, 129.3, 126.7, 18.1; HRMS (ESI) M/Z calcd for $C_{15}H_{15}Cl_2N_2O_3$ [M+NH$_4^+$] 341.0454, found: 341.0453.

***N*-acetoxy-4-chloro-*N*-(4-chlorophenyl)benzamide (4ag).** White solid, 114.27 mg, yield 75%. m.p. 75−77 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.47 (d, *J* = 7.8 Hz, 2H), 7.31−7.25 (m, 6H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 166.8, 140.6, 133.2, 131.0, 129.2, 128.8, 128.4, 128.1, 126.9, 18.4; HRMS (ESI) M/Z calcd for $C_{15}H_{11}Cl_2NO_3Na$ [M+Na$^+$] 346.0008, found: 346.0012.

***N*-acetoxy-4-bromo-*N*-(4-chlorophenyl)benzamide (4ah).** White solid, 128.2 mg, yield 74%. m.p. 70−71 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 165.9, 138.7, 134.4, 131.8, 131.5, 130.2, 129.5, 127.9, 126.0, 18.3; HRMS (ESI) M/Z calcd for $C_{15}H_{11}BrClNO_3Na$ [M+Na$^+$] 389.9503, found: 389.9499.

***N*-acetoxy-*N*-(4-chlorophenyl)-4-nitrobenzamide (4ai).**[33] White solid, 114.8 mg, yield 73%. m.p. 166−167 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.18 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.34−7.27 (m, 4H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.6, 149.1, 139.0, 137.9, 135.0, 129.7, 128.0, 123.5, 109.9, 18.2; HRMS (ESI) M/Z calcd for $C_{15}H_{11}ClN_2O_5Na$ [M+Na$^+$] 357.0249, found: 357.0246.

***N*-acetoxy-*N*-(p-tolyl)furan-2-carboxamide (4aj).** White solid, 81.6 mg, yield 67%. m.p. 107−108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 6.36 (dd, *J* = 3.6, 1.2 Hz, 1H), 2.40 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 156.2, 145.4, 145.2, 139.8, 137.3, 130.0, 127.8, 118.0, 111.4, 21.3, 18.5; HRMS (ESI) M/Z calcd for $C_{14}H_{14}NO_4$ [M+H$^+$] 260.0917, found: 260.0914.

***N*-acetoxy-*N*-(4-chlorophenyl)-4-methoxybenzamide (4ak).** Yellow oil, 37.5 mg, yield 25%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 9.0 Hz, 2H), 7.30−7.28 (m, 2H), 7.25−7.24 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 162.1, 134.0, 131.0, 129.4, 128.0, 124.7, 113.5, 110.0, 55.3, 18.4; HRMS (ESI) M/Z calcd for $C_{16}H_{14}ClNO_4Na$ [M+Na$^+$] 342.0604, found: 342.0608.

***N*-acetoxy-*N*-(4-chlorophenyl)-4-methylbenzamide (4al).** yellow oil, 44.1 mg, yield 31%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42 (d, *J* = 8.4 Hz, 2H), 7.29−7.24 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 2.33 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.9, 166.9, 141.9, 139.4, 134.0, 130.0, 129.4, 128.9, 128.8, 128.0, 21.5, 18.4; HRMS (ESI) M/Z calcd for $C_{16}H_{14}ClNO_3Na$ [M+Na$^+$] 326.0554, found: 326.0558.

General Procedure for the Synthesis of Compounds 5

Hydrated barium hydroxide (1.47 mmol, 7 equiv) was added to a solution of the *N*-acetoxy-2-chloro-*N*-phenylbenzamide **4g** in ethanol (7 ml) under nitrogen atmosphere and the mixture was stirred at room temperature for 1.5 h. Then, hydrochloric acid was added to acidify the mixture to pH 1. The resulting mixture was extracted with EtOAc (3 × 10 mL). The organic layer were combined, dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using PE : EA (5:3) as eluent to afford the product **5**.

2-chloro-*N*-hydroxy-*N*-phenylbenzamide (5).[34] White solid, 38.0 mg, yield 73%. m.p. 103−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.46 (s, 1H), 7.29−7.21 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 162.5, 137.8, 133.1, 131.6, 131.2, 129.9, 129.4, 128.8, 128.2, 126.7, 125.1.

General Procedure for the Synthesis of Com.p.ounds 6

To a stirring solution of the *N*-acetoxy-2-chloro-*N*-phenylbenzamide **4g** (0.21 mmol, 1 equiv) in dry THF (5 mL), maintained under nitrogen atmosphere at room temperature, was added a freshly prepared solution of SmI_2 in THF dropwise. After TLC analysis indicated complete reaction, the mixture was diluted with CH_2Cl_2 (10 mL), then quenched with 10 ml of 10% aqueous sodium thiosulfate solution. The resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer were combined, dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using PE : EA (100:1) as eluent to afford the product **6**.

2-chloro-*N*-phenylbenzamide (6).[35] White solid, 46.2 mg, yield 95%. m.p. 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.44−7.32 (m, 5H), 7.17 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 164.5, 137.5, 135.2, 131.6, 130.6, 130.3, 130.2, 129.1, 127.2, 124.8, 120.1.

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ARTICLE

Synthesis of *N*-acetoxy-*N*-arylamidesvia Diacetoxyiodobenzene Promoted Double Acylation Reaction of Hydroxylamines with Aldehydes

Huaiyuan Zhang, Yingpeng Su, Ke-Hu Wang, Danfeng Huang, Jun Li, Yulai Hu*

A facile and efficient synthesis of *N*-acetoxy-*N*-arylamides through double acylations of hydroxylamines with aldehydes and diacetoxyiodobenzene is reported. The yields of the products are good to excellent.