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# Metal-free regioselective C-3 acetoxylation of *N*-substituted indoles: Crucial impact of nitrogen-substituent†

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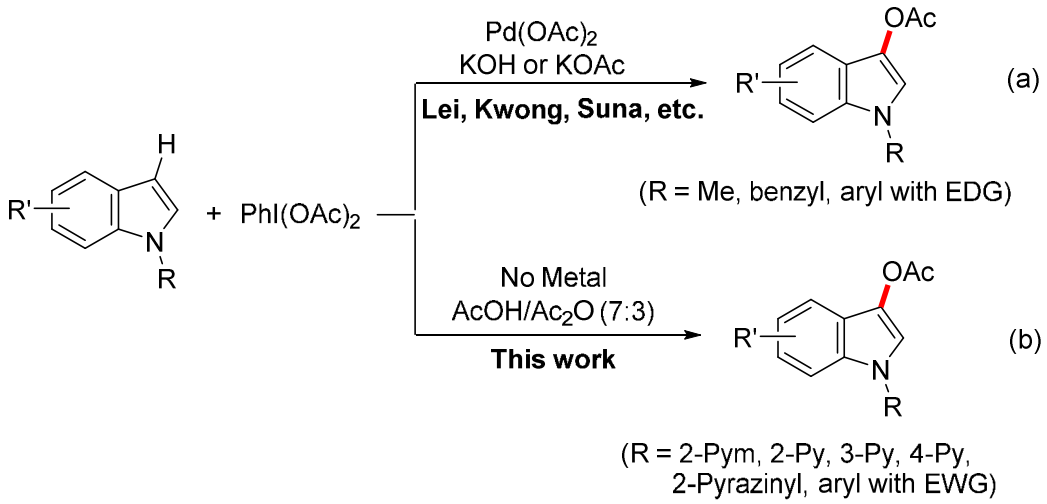
**Abstract:** A metal-free method for the regioselective C-3 acetoxylation of the *N*-substituted indoles with $PhI(OAc)_2$ is described under mild reaction conditions. This method tolerates a broad range of functional groups with moderate to good yields. The π-electron-deficient aryl-substituents on the *N*-atom of indoles and the acidic reaction medium remarkably favor the C-3 acetoxylation.

† Electronic supplementary information (ESI) available.

## Introduction

Direct functionalization of C–H bond to form C–O bond is among the most demanding chemical reaction in synthetic organic chemistry.[1] The C–O bond formation in arenes to obtain hydroxylated-,[2] alkoxylated-[3] or acetoxylated-arenes[4] are considerably explored, and the regioselectivity has been successfully achieved by the installation of a Lewis-base directing group. In contrast to many reports on the acetoxylation of arenes, the synthesis of the regioselectively acetoxylated heteroarenes is relatively scarce.[5] Among the heteroarenes, the indole derivatives are very important building blocks, found in many pharmaceuticals as well as in the biologically active compounds. In particular, 3-acetoxyindoles are potential materials, applied for the detection of acetylcholinesterase in tissue slices[6] and they could also be used as a starting precursors for the synthesis of potential 5-hydroxytryptamine$_6$ (5-HT$_6$) receptor ligand scafolds.[7] Hence, the efficient synthesis of 3-acetoxyindoles through the regioselective C-3 acetoxylation of indole derivatives is highly desirable. The groups of Lei,[8] Kwong[7] and Suna[9] have independently reported the C-3 acetoxylation of *N*-substituted indoles using Pd(OAc)$_2$ catalyst, and PhI(OAc)$_2$ as an external oxidant (Scheme 1a). This palladium-catalyzed regioselective acetoxylation process is applicable to the various indole substrates containing methyl, benzyl, aryl or arenesulfonyl group as the nitrogen-substituents. However, the employment of the precious metal catalysts for the functionalization of probable pharmacological indole derivatives, limit the advancement of these metal-catalyzed acetoxylation processes.



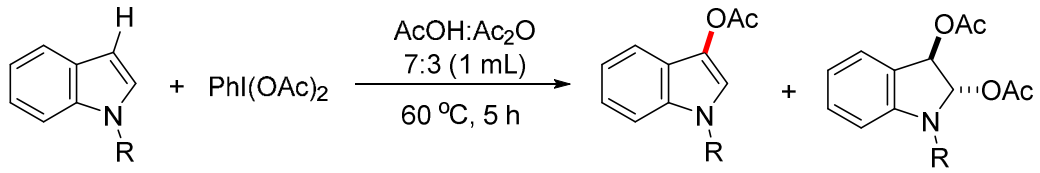

**Scheme 1** Regioselective C-3 acetoxylation of substituted-Indoles: (a) palladium-catalyzed acetoxylation of *N*-methyl, *N*-benzyl- or *N*-aryl Indoles, (b) this work demonstrates: metal-free acetoxylation of *N*-(hetero)aryl indoles.

In recent years, numerous reports have been described for the C–H bond functionalization under the transition-metal-free conditions.[10] A transition-metal-free C-3 acetoxylation of the free *NH*-indole has been described under the strong basic condition by Huang and co-workers.[11] However, this method is not applicable to the *N*-substituted indole substrates and has limited scope. The C-3 acetoxylation of *N*-Boc-protected indole has been observed by Lei *et.al.* during their studies directed toward the synthesis of diacetoxylated indolines.[12] To our knowledge, a comprehensive approach for the metal-free C-3 acetoxylation of the *N*-substituted indoles with high regioselectivity is not known. Herein, we present the regioselective C-3 acetoxylation of the *N*-substituted indoles with $PhI(OAc)_2$ as an oxidant under the metal-free and mild reaction conditions. Moreover, we have demonstrated the effect of the *N*-substituents on reactivity and selectivity of the indole acetoxylations.

## Results and discussion

During the investigation of a less expensive first-row transition metal catalyst for the acetoxylation of the *N*-substituted indoles employing $PhI(OAc)_2$ in acetic acid solvent, we observed that the C-3 acetoxylation of indole occurred in the absence of metal catalysts, when a suitable substituent on the nitrogen atom of indole was installed. For example, the reaction of 1-pyrimidinyl indole (**1a**) with $PhI(OAc)_2$ in $AcOH/Ac_2O$ solvent at 60 $^oC$, exclusively produced 1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (**2a**) in 93% isolated yield (Table 1, entry 1). The 1-arylindoles, like 1-phenylindole (**3a**) reacted with $PhI(OAc)_2$ under the metal-free condition to afford the corresponding C-3 acetoxylated indole **4a** in 50% yield; whereas the reaction of 1-(4-methoxypheny)indole (**3b**) with $PhI(OAc)_2$ under the same condition produced only 37% of the acetoxylated compound **4b**. Surprisingly, the free *NH*-indole or indoles having electron-rich substituents at the nitrogen-center, such as 1-methylindole, were decomposed to the unknown compounds at room temperature. However, the indoles bearing strong electron-withdrawing substituents at the nitrogen-atom, such as 1-(acetyl)indole and 1-(tosyl)indole produced the diacetoxylated indolines in 91% and 28% yields, respectively (Table 1, entries 6, 7).[12] These studies on the effect of *N*-substituents towards the acetoxylation of indoles suggested that a $\pi$-electron-deficient (hetero)arene-substituent on the nitrogen atom of indole greatly enhances the selective C-3 acetoxylation reaction.

**Table 1** Effect of nitrogen-substituents on C-3 acetoxylation of indoles[a]




**1**; R = heteroaryl
**3**; R = H, alkyl, aryl, acyl, tosyl

**2**; R = heteroaryl
**4**; R = H, alkyl, aryl, acyl, tosyl

**5**

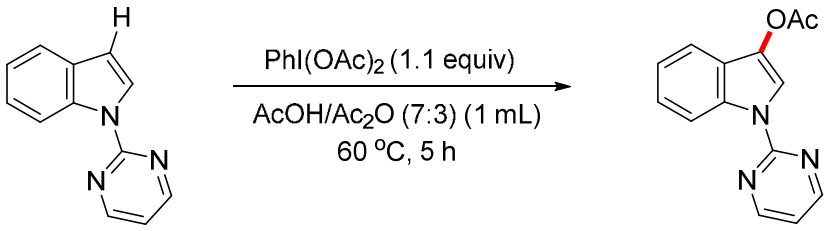
| Entry | R | % Yield (**2** or **4**) | **5** | Recovered (**1** or **3**) |
|---|---|---|---|---|
| 1 | 2-Pym | 93 (**2a**) | - | - |
| 2 | Ph | 50 (**4a**) | - | 35 (**3a**) |
| 3 | 4-MeO-$C_6H_4$ | 37 (**4b**) | - | -[b] |
| 4 | H | - | - | -[c] |
| 5 | $CH_3$ | - | - | -[c] |
| 6 | $C(O)CH_3$ | - | 91 | 5 |
| 7 | Tosyl | - | 28 | 70 |

[a] Reaction conditions: Compound **1** or **3** (0.30 mmol), $PhI(OAc)_2$ (0.106 g, 0.33 mmol), $AcOH/Ac_2O$ (1.0 mL), yields of isolated compounds. [b] Starting compound was not recovered. [c] Decomposed into intractable products at room temperature.

After optimizing the effect of *N*-substituent's on the metal-free acetoxylation of indoles, we have tested the impact of various solvents and oxidants on the acetoxylation reaction (Table 2). The use of glacial acetic acid as solvent instead of $AcOH/Ac_2O$, produced the desired acetoxylated product **2a** in 76% isolated yield (entry 2). However, the complete decomposition of **1a** was observed in TFA/TFAA under the reaction conditions (entry 3). The employment of non-acid solvent 2,2,2-trifluoroethanol (TFE) gave

only 20% of product **2a**, whereas the reactions in $CH_3CN$ or 1,2-dichloroethane (DCE) did not produce any acetoxylated products (entry 4, 5). The presence of strong oxidant $PhI(TFA)_2$ resulted in the decomposition of **1a**; however, other organic oxidants, such as *m*-CPBA, *tert*-BuOOH or inorganic oxidants like $K_2S_2O_8$ and oxone were ineffective, and most of the starting material was recovered (entry 6-8).

**Table 2** Optimization of reaction parameters for C-3 acetoxylation of **1a**[a]

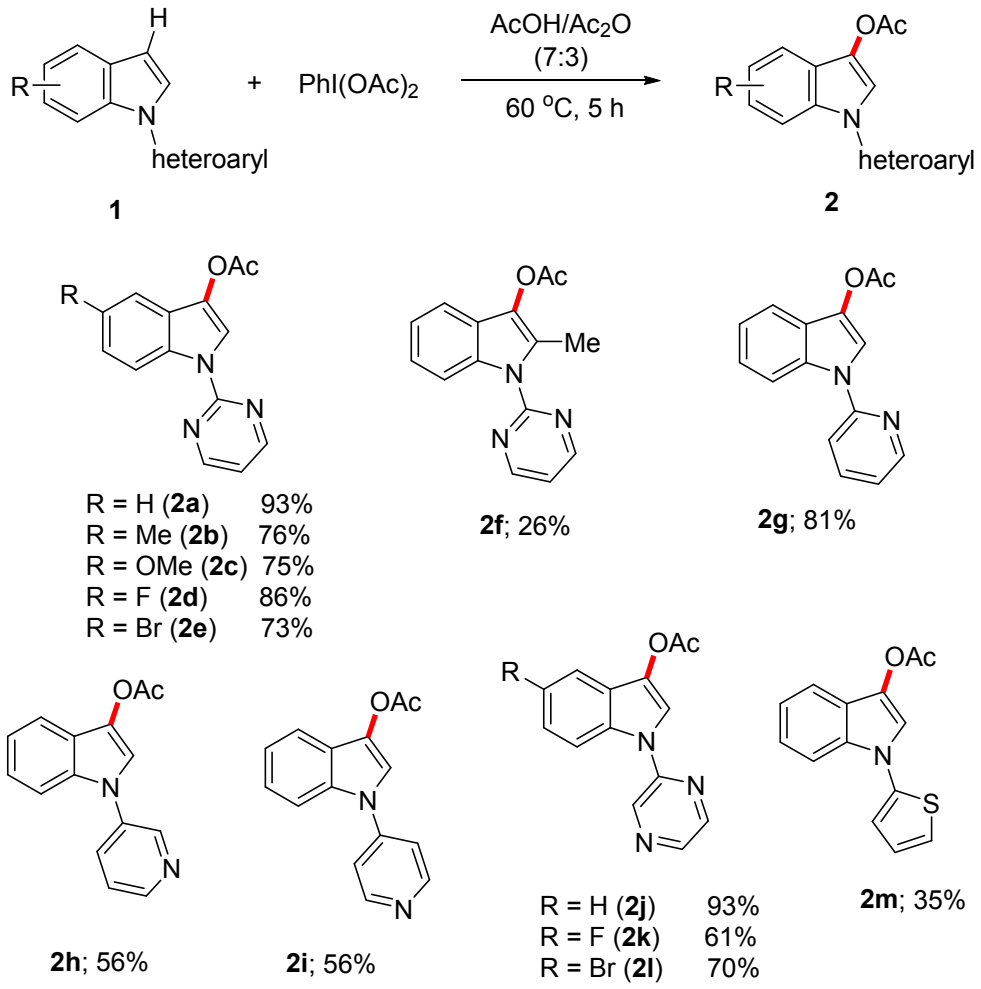



**1a** **2a**

| Entry | Variation from "standard condition" | Yield (%)[b] |
|---|---|---|
| 1 | - | 93 |
| 2 | AcOH instead of $AcOH/Ac_2O$ | 76 |
| 3 | TFA/TFAA instead of $AcOH/Ac_2O$ | -[c] |
| 4 | TFE instead of $AcOH/Ac_2O$ | 20 |
| 5 | $CH_3CN$, DCE instead of $AcOH/Ac_2O$ | NR |
| 6 | $PhI(TFA)_2$ instead of $PhI(OAc)_2$ | -[c] |
| 7 | *m*-CPBA instead of $PhI(OAc)_2$ | trace |
| 8 | $K_2S_2O_8$, Oxone or *t*-BuOOH instead of $PhI(OAc)_2$ | NR |
| 9 | 25 °C instead of 60 °C | 15 |

[a] Reaction conditions: **1a** (0.059 g, 0.30 mmol), $PhI(OAc)_2$ (0.106 g, 0.33 mmol), $AcOH/Ac_2O$ (1.0 mL). TFE (2,2,2-Trifluoroethanol), TFA (Trifluoroacetic acid), TFAA (Trifluoroacetic anhydride), NR = No reaction. [b] Yields of isolated compounds. [c] Decomposed into intractable compounds.

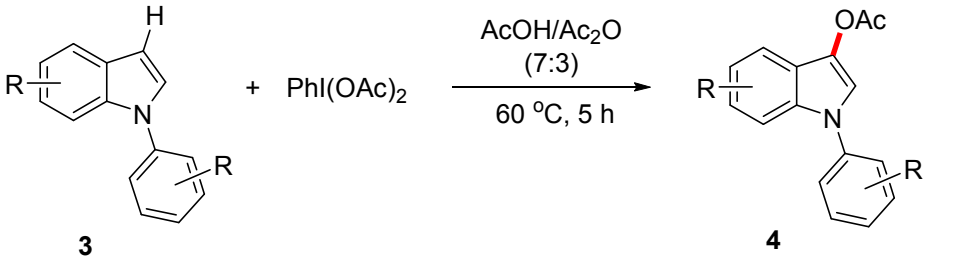
Having the optimized reaction conditions in hand, we probed the scope of the metal-free C-3 acetoxylation of the *N*-heteroaryl-substituted indoles **1** employing $PhI(OAc)_2$ as the oxidant in $AcOH/Ac_2O$ solvent (Scheme 2). Notably, the *N*-pyrimidinyl indoles containing electronically different functional groups reacted smoothly to produce the desired acetoxylated products (**2a**-**2e**) in good yields. The tolerability of the functional groups such as –F, –Br is significant, as they can be further functionalized into important compounds. It is noteworthy that the direct acetoxylation of indoles **1** occurred with excellent regioselectivity to predominantly produce C-3 acetoxylated indoles. Particularly, by employing 2-pyrimidinyl as the *N*-substituent on indoles, neither the starting compounds nor the acetoxylated products were decomposed. More hindered 2-substituted indole **1f** reacted with low efficacy to produced **2f** in 26% yield. In addition to the *N*-pyrimidinyl indoles, the indoles containing 2-pyridinyl and 2-pyrazinyl as nitrogen-substituents reacted efficiently to give the desired acetoxylated products in good yields. The pyridinyl-substituted indoles, **1h** and **1i** reacted moderately to yield the corresponding acetoxylated compounds **2h** and **2i**, respectively. Evidently, the $\pi$-electron-rich 2-thiophenyl substituted indole **1m** produced the acetoxylated compound **2m** in low yield.

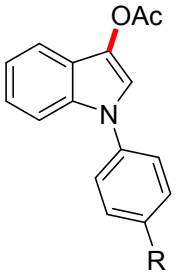



**Scheme 2** Scope of C-3 acetoxylation of *N*-heteroaryl substituted indoles.

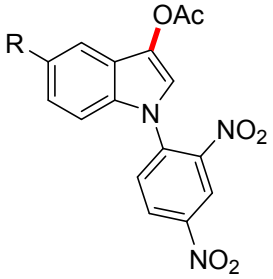
We further extended the metal-free acetoxylation method for the selective acetoxylation of the *N*-aryl substituted indoles. Hence, the different substituted *N*-aryl indoles **3** undergo acetoxylations at C-3 position to give the desired products in moderate yields (Scheme 3). Interestingly, a number of important functional groups like –F, $–CF_3$, –C(O)Me, –C(O)OMe, –CN and $–NO_2$ are well tolerated under the reaction conditions. To our surprise, the 2,4-dinitrophenyl substituted indoles **3i** and **3j** produced the acetoxylated products in good yields. The indoles containing *N*-aryl substituents with electron-

withdrawing groups on the aryl backbone were found to produce improved yields of the C-3 acetoxylation, than the *N*-aryl substituents bearing electron-donating groups. Unlike free-*NH*-indole or indoles bearing electron-rich *N*-protecting groups, the *N*-aryl substituted indoles does not impart decomposition; however they produced 1-aryl-indolin-3-one and 2-oxo-1-aryl-indolin-3-yl acetate as the side products in different scale, which accounts for the low yields of the C-3 acetoxylated products.[13] Most likely, these side products are formed from the hydrolysis of C-3 acetoxylated and diacetoxylated indoles.

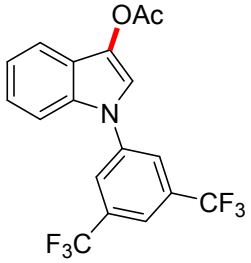



R = H (**4a**) 50%
R = OMe (**4b**) 37%
R = F (**4c**) 40%
R = $CF_3$ (**4d**) 45%
R = COMe (**4e**) 35%
R = COOMe (**4f**) 41%
R = CN (**4g**) 56%
R = $NO_2$ (**4h**) 53%

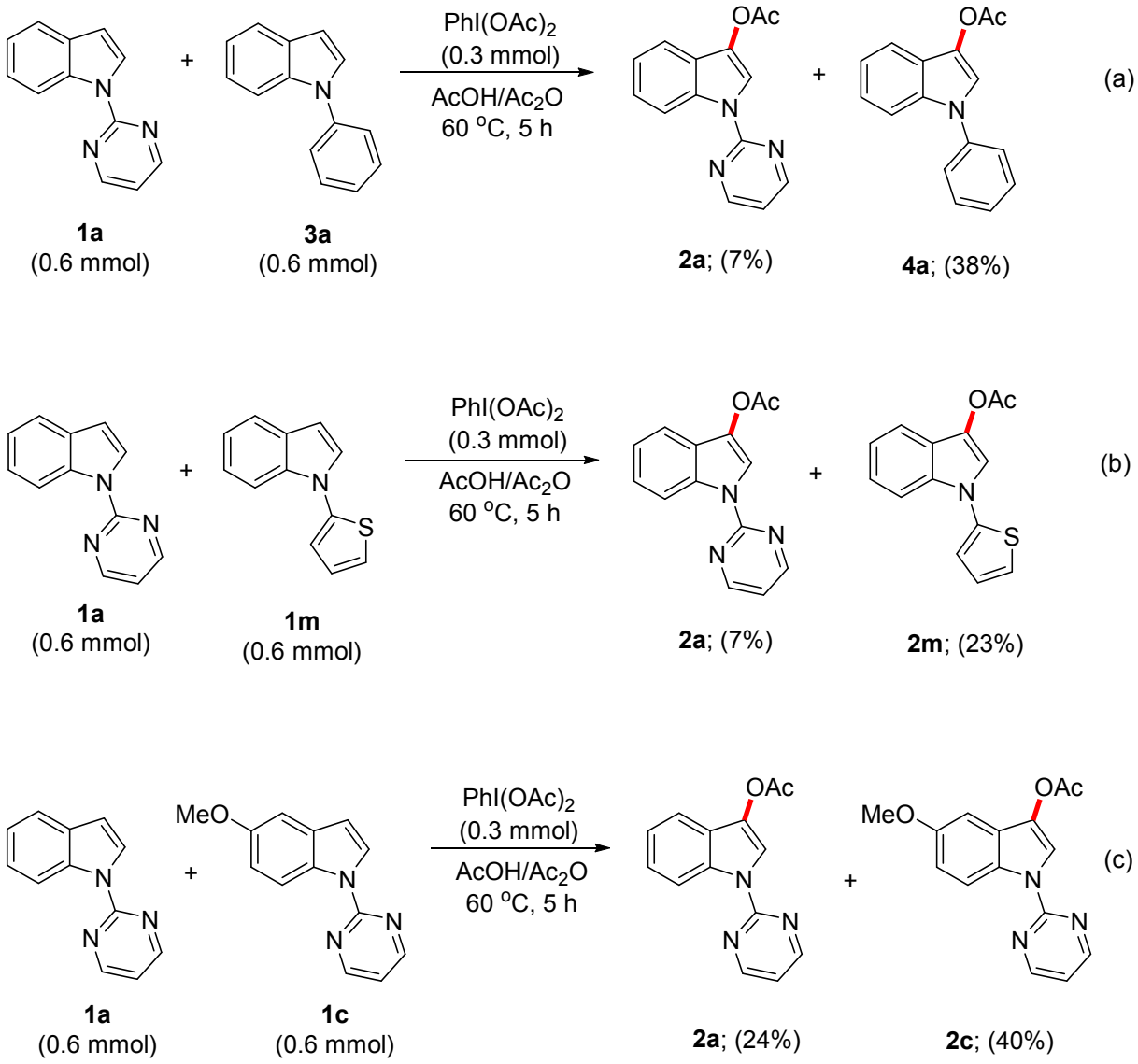



R = H (**4i**) 76%
R = F (**4j**) 61%




**4k**; 54%

**Scheme 3** Scope of C-3 acetoxylation of *N*-aryl substituted indoles.

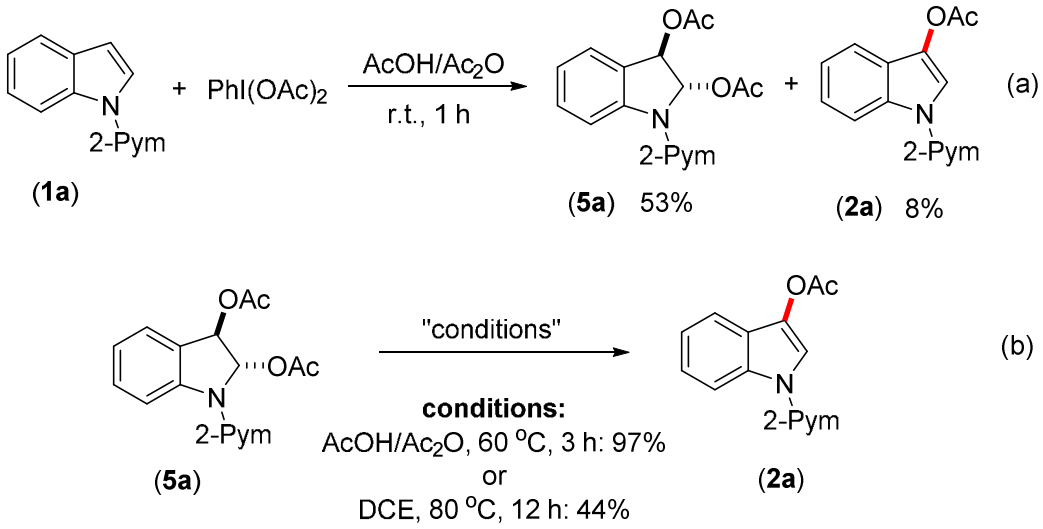



**Scheme 4** Intermolecular competition experiments.

In order to obtain the mechanistic insight, the intermolecular competition experiments between the indoles **1a** and **3a** as well as between **1a** and **1m**, were conducted (Scheme 4a, 4b); which highlighted that the indoles bearing π-electron-rich arene substituents were acetoxylated predominantly, though the yields were unsatisfactory. Further, an additional experiment between the different substituted *N*-

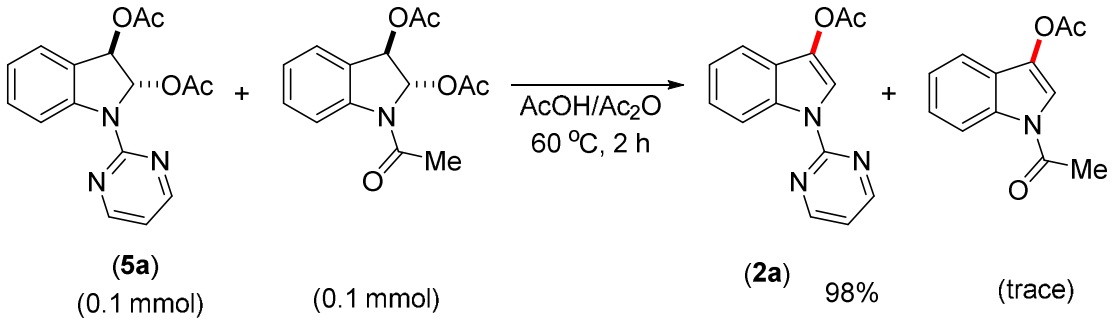
pyrimidinyl-indoles **1a** and **1c** (Scheme 4c) clearly demonstrated that the electron-rich indole was preferentially acetoxylated, which revealed the nucleophilicity parameter[14] of indoles for the acetoxylation process.

Further, to isolate the probable intermediate species, an experiment of **1a** with $PhI(OAc)_2$ was carried out at room temperature, which produced the diacetoxylated indoline **5a** in 53% yield after 1 h (Scheme 5a). The formation of **5a** might follow the pathway proposed for the similar compounds.[12] Compound **5a** led to the complete conversion into the acetoxylated product **2a** upon heating in $AcOH/Ac_2O$ solvent for 3 h (Scheme 5b). This clearly demonstrated that the formation of **2a** from **1a** occurred *via* the intermediacy of **5a**. The dehydroacetoxylation of **5a** to **2a** also occurred under non-acidic condition, however with low efficacy. Similar to the indoline **5a**, the intermediate species for the indole **1m** could not be observed; instead the direct formation of **2m** was accomplished, including the intractable decomposed products.




**Scheme 5** Synthesis and reactivity of intermediate species.

To understand the dehydroacetoxylation process of the different *N*-substituted diacetoxyindolines, the compound **5a** and 1-acetylindoline-2,3-diyl diacetate were heated in a single pot at 60 $^{o}$C (Scheme 6). The compound **5a** was completely converted into the C-3 acetoxylated product **2a** in 2 h, whereas a trace amount of the C-3 acetoxylated product was formed from the 1-acetylindoline-2,3-diyl diacetate; suggesting that the dehydroacetoxylation of diacetoxylated indoline is significant in the presence of 2-pyrimidinyl as the *N*-substituent. Further, looking into the excellent reactivities of the indoles containing 2-Py, 2-Pym, 2-pyrazinyl or 2-nitroarene as the *N*-substituents (**1a**-**1g**, **1i**-**1l**, **3i** and **3j**); we assume that the N-atom or N-group at the *ortho*-position of the substituents might have some additional influence on the dehydroacetoxylation reaction, in addition to the electronics of the substituents.




**Scheme 6** Dehydroacetoxylation of diacetoxylated compounds.

## Conclusions

In summary, we have reported an efficient and regioselective method for the C-3 acetoxylation of the *N*-substituted indoles in the absence of metal-catalysts, wherein a broad range of functional groups are tolerated. The indoles containing π-electron-deficient arene substituents on the *N*-atom are acetoxylated efficiently than the one bearing strong

sigma electron-donating or sigma electron-withdrawing substituents. The diacetoxylated indoline is proposed to be the active intermediate for the acetoxylation of the *N*-substituted indoles, where the dehydroacetoxylation is facilitated in the presence of a $\pi$-deficient arene substituents on the *N*-atom of indoles.

## Experimental section

**General information.** All manipulations were conducted in an argon atmosphere using standard Schlenk techniques in pre-dried glassware. Liquid reagents were flushed with argon prior to use. The starting compounds, *N*-acyl-1*H*-indole,[12] *N*-tosyl-1*H*-indole,[12] *N*-benzyl-1*H*-indole,[7] *N*-aryl-1*H*-indoles,[15] *N*-pyridinyl-1*H*-indole,[16] *N*-pyrimidinyl-1*H*-indole[15a,17] and 1-acetylindoline-2,3-diyl diacetate[12] were synthesized according to the previously described procedures. All other chemicals were obtained from commercial sources and were used without further purification. Representative starting compounds **1** and **3** as well as $PhI(OAc)_2$ were analyzed by ICP-AES, which showed only trace amount of transition metals (< 0.1 ppm Fe, Co, Ni, Cu, Pd, Rh and Ru). The yields refer to isolated compounds, estimated to be > 95% pure as determined by $^1$H NMR. The $^1$H and $^{13}$C NMR spectra are referenced to the residual solvent signals ($CDCl_3$: $\delta$H = 7.26 ppm, $\delta$C = 77.2 ppm).

**Representative procedures for the preparation of *N*-substituted indoles**

**Representative procedure A:** To a stirred solution of 1*H*-indole (0.120 g, 1.00 mmol) in DMF (15 mL) at 0 $^o$C was added NaH (0.027 g, 1.10 mmol). After stirring the reaction mixture at 0 $^o$C for 30 min, (hetero)aryl halide (1.20 mmol) was added and the reaction mixture was heated at 130 $^o$C for 24 h. Then the reaction mixture was cooled to ambient temperature, poured into $H_2O$ (20 mL) and extracted with EtOAc (15 mL x 3). The

combined organic phase was washed with $H_2O$ (15 mL x 3) and dried over $Na_2SO_4$. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel.

**Representative procedure B:** A mixture of 1*H*-indole (0.328 g, 2.80 mmol), (hetero)aryl halide (2.00 mmol), CuI (0.076 g, 0.40 mmol) and $Cs_2CO_3$ (1.30 g, 4.00 mmol) were taken in a flask and DMF (15 mL) was added into it. The reaction mixture was vigorously stirred at 120 $^oC$ under argon atmosphere for 40 h. Then the reaction mixture was cooled to ambient temperature, poured into $H_2O$ (20 mL) and extracted with EtOAc (15 mL x 3). The combined organic phase was washed with $H_2O$ (15 mL x 3) and dried over $Na_2SO_4$. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel.

**2-Methyl-1-(pyrimidin-2-yl)-1*H*-indole (1f).**[18] The representative procedure **A** was followed using, 2-methyl-1*H*-indole (0.40 g, 3.05 mmol), 2-chloropyrimidine (0.489 g, 4.27 mmol), and NaH (0.095 g, 3.96 mmol). Purification by column chromatography on silica gel (hexane/EtOAc/$Et_3N$: 20/1/0.5) yielded **1f** (0.153 g, 24%) as a brown solid. M. p. = 48-50 $^oC$. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.79 (d, *J* = 4.9 Hz, 2H), 8.37 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.31-7.24 (m, 2H), 7.11 (t, *J* = 4.9 Hz, 1H), 6.50 (s, 1H), 2.78 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 158.5, 158.1, 137.9, 137.0, 129.6, 122.5, 121.9, 119.6, 117.0, 114.1, 106.8, 16.7. IR (neat): $\nu_{max}/cm^{-1}$ 3032, 2962, 2853, 1562, 1417, 1305, 1205, 785, 733. HRMS (ESI) *m/z* Calcd for $C_{13}H_{11}N_3+H^+$ $[M+H]^+$ 210.1026; Found 210.1024.

**1-(Pyrazin-2-yl)-1*H*-indole (1j).**[19] The representative procedure **A** was followed, using 1*H*-indole (0.120 g, 1.00 mmol), NaH (0.027 g, 1.10 mmol) and 2-iodopyrazine

(0.246 g, 1.20 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **1j** (0.186 g, 95%) as a brown solid. M. p. = 77-79 $^{o}$C. $^{1}$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.85 (s, 1H), 8.44 (d, *J* = 2.1 Hz, 1H), 8.36 (d, *J* = 2.1 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 3.4 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.23 (dd, *J* = 7.9, 7.0 Hz, 1H), 6.74 (d, *J* = 3.4 Hz, 1H). $^{13}$C{$^{1}$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 149.2, 142.8, 140.0, 136.4, 135.2, 130.7, 125.0, 123.9, 122.2, 121.4, 113.5, 107.3. IR (neat): $\nu_{max}$/cm$^{-1}$ 3108, 3053, 1450, 1360, 839, 739. HRMS (ESI) *m/z* Calcd for $C_{12}H_9N_3$+$H^+$ $[M+H]^+$ 196.0869; Found 196.0869.

**5-Fluoro-1-(pyrazin-2-yl)-1*H*-indole (1k)**: The representative procedure **A** was followed, using 5-fluoro-1*H*-indole (0.23 g, 1.70 mmol), NaH (0.045 g, 1.87 mmol) and 2-iodopyrazine (0.420 g, 2.04 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **1k** (0.33 g, 91%) as a brown solid. M. p. = 112-114 $^{o}$C. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.84 (d, *J* = 1.2 Hz, 1H), 8.47-8.46 (m, 1H), 8.41 (d, *J* = 2.7 Hz, 1H), 8.30 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.72 (d, *J* = 3.7 Hz, 1H), 7.29 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.06 (td, *J* = 9.1, 2.5 Hz, 1H), 6.71 (d, *J* = 3.4 Hz, 1H). $^{13}$C{$^{1}$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 159.0 (d, $J_{C-F}$ = 239.0 Hz), 149.1, 142.6, 140.2, 136.0, 131.8, 131.4 (d, $J_{C-F}$ = 10.0 Hz), 126.3, 114.9 (d, $J_{C-F}$ = 9.3 Hz), 111.9 (d, $J_{C-F}$ = 25.4 Hz), 107.2 (d, $J_{C-F}$ = 3.8 Hz), 106.5 (d, $J_{C-F}$ = 23.9 Hz). $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −121.6 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 2921, 1469, 1443, 1353, 809, 753, 714, 616. HRMS (ESI) *m/z* Calcd for $C_{12}H_8FN_3$+$H^+$ $[M+H]^+$ 214.0775; Found 214.0775.

**5-Bromo-1-(pyrazin-2-yl)-1*H*-indole (1l).** The representative procedure **A** was followed, using 5-bromo-1*H*-indole (0.330 g, 1.70 mmol), NaH (0.045 g, 1.87 mmol) and 2-iodopyrazine (0.420 g, 2.04 mmol). Purification by column chromatography on silica gel

(hexane/EtOAc: 2/1) yielded **1l** (0.44 g, 95%) as off-white solid. M. p. = 98-100 $^{o}$C. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.84 (d, *J* = 1.2 Hz, 1H), 8.49-8.48 (m, 1H), 8.43 (d, *J* = 2.7 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 3.4 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.69 (d, *J* = 3.2 Hz, 1H). $^{13}$C{$^{1}$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 149.0, 142.8, 140.5, 136.2, 134.0, 132.3, 126.7, 126.0, 123.9, 115.4, 115.3, 106.7. IR (neat): $\nu_{max}$/cm$^{-1}$ 2921, 1519, 1482, 1416, 1198, 1136, 1054, 1004, 957, 752, 709. HRMS (ESI) *m/z* Calcd for $C_{12}H_8BrN_3$+H$^+$ [M+H]$^+$ 273.9974, 275.9954; Found 273.9974, 275.9953.

**1-(Thiophen-2-yl)-1*H*-indole (1m).**[15c] The representative procedure **B** was followed, using 1*H*-indole (0.328 g, 2.80 mmol), 2-bromothiophene (0.326 g, 2.00 mmol), CuI ( 0.076 g, 0.40 mmol) and $Cs_2CO_3$ (1.30 g, 4.00 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 100/1) yielded **1m** (0.286 g, 72%) as a green liquid. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.64 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.27-7.22 (m, 2H), 7.17 (dd, *J* = 7.1, 6.9 Hz, 1H), 7.12 (dd, *J* = 5.6, 1.5 Hz, 1H), 7.03 (dd, *J* = 3.7, 1.5 Hz, 1H), 7.01-6.99 (m, 1H), 6.63 (d, *J* = 3.2 Hz, 1H). $^{13}$C{$^{1}$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 141.8, 137.2, 129.5, 129.2, 126.2, 123.0, 121.8, 121.2, 121.0, 120.6, 110.8, 104.3. IR (neat): $\nu_{max}$/cm$^{-1}$ 3108, 3009, 1611, 1550, 1459, 1312, 1226, 1201, 1013, 903, 842. HRMS (ESI) *m/z* Calcd for $C_{12}H_9NS$+H$^+$ [M+H]$^+$ 200.0528; Found 200.0526.

**1-(4-(Trifluoromethyl)phenyl)-1*H*-indole (3d).**[20] The representative procedure **B** was followed, using 1*H*-indole (0.302 g, 2.58 mmol), 1-iodo-4-(trifluoromethyl)benzene (0.50 g, 1.84 mmol), CuI (0.070 g, 0.368 mmol) and $Cs_2CO_3$ (1.20 g, 3.68 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 20/1) yielded **3d** (0.408 g, 85%) as a brown solid. M. p. = 50-52 $^{o}$C. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.75

(d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.60-7.56 (m, 3H), 7.31 (d, *J* = 3.4 Hz, 1H), 7.24-7.17 (m, 2H), 6.70 (d, *J* = 3.2 Hz, 1H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): $\delta$ = 143.0, 135.7, 129.9, 128.3 (q, $J_{C-F}$ = 32.4 Hz), 127.6, 127.1 (q, $J_{C-F}$ = 3.8 Hz), 124.2 (q, $J_{C-F}$ = 171.8 Hz), 124.1, 123.1, 121.6, 121.2, 110.5, 105.1. $^{19}F$-NMR (377 MHz, $CDCl_3$): $\delta$ = −62.2 (s). IR (neat): $\nu_{max}/cm^{-1}$ 3058, 2962, 1607, 1521, 1455, 1318, 1158, 1061, 1013, 840. HRMS (ESI) *m/z* Calcd for $C_{15}H_{10}F_3N+H^+$ $[M+H]^+$ 262.0838; Found 262.0837.

**Methyl 4-(1*H*-indol-1-yl)benzoate (3f).**[15c] The representative procedure **B** was followed, using 1*H*-indole (0.328 g, 2.80 mmol), methyl 4-iodobenzoate (0.524 g, 2.00 mmol ), CuI (0.076 g, 0.40 mmol) and $K_2CO_3$ (0.553 g, 4.00 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 10/1) yielded **3f** (0.231 g, 46%) as a grey solid. M. p. = 55-57 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.18 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 3.4 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 3.4 Hz, 1H), 3.95 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 166.6, 143.9, 135.6, 131.4, 130.0, 127.8, 127.6, 123.4, 123.0, 121.5, 121.1, 110.7, 105.1, 52.4. IR (neat): $\nu_{max}/cm^{-1}$ 3106, 3049, 2947, 1707, 1602, 1509, 1455, 1433, 1281, 1117, 1097, 720. HRMS (ESI) *m/z* Calcd for $C_{16}H_{13}NO_2+H^+$ $[M+H]^+$ 252.1019; Found 252.1012.

**1-(4-Nitrophenyl)-1*H*-indole (3h).**[19,20] The representative procedure **B** was followed, using 1*H*-indole (0.328 g, 2.80 mmol), 1-iodo-4-nitrobenzene (0.50 g, 2.00 mmol), CuI (0.076 g, 0.40 mmol) and $K_2CO_3$ (0.553 g, 4.00 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 20/1) yielded **3h** (0.224 g, 47%) as a yellow solid. M. p. = 132-134 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.33 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.62-7.60 (m, 3H), 7.33 (d, *J* = 3.1 Hz, 1H), 7.27 (dd, *J* = 7.6, 7.3 Hz,

1H), 7.21 (dd, *J* = 7.6, 7.3 Hz, 1H), 6.75 (d, *J* = 3.0 Hz, 1H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 145.3, 145.1, 135.4, 130.2, 127.2, 125.6, 123.5, 123.4, 121.8, 121.7, 110.6, 106.3. IR (neat): $\nu_{max}/cm^{-1}$ 3109, 1592, 1503, 1455, 1317, 1100, 882, 852, 690. HRMS (ESI) *m/z* Calcd for $C_{14}H_{10}N_2O_2+H^+$ $[M+H]^+$ 239.0815; Found 239.0811.

**1-(2,4-Ninitrophenyl)-1*H*-indole (3i).**[21] The representative procedure **B** was followed, using 1*H*-indole (0.351 g, 3.00 mmol), 1-chloro-2,4-dinitrobenzene (0.73 g, 3.60 mmol), CuI (0.114 g, 0.60 mmol), $K_2CO_3$ (0.830 g, 6.00 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **3i** (0.424 g, 50%) as an orange solid. M. p. = 96-98 $^oC$. $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.89 (d, *J* = 2.5 Hz, 1H), 8.54 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 6.6 Hz, 1H), 7.30-7.21 (m, 3H), 7.15 (d, *J* = 3.4 Hz, 1H), 6.83 (d, *J* = 3.2 Hz, 1H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): $\delta$ = 145.4, 144.6, 138.0, 135.8, 129.7, 129.6, 128.1, 127.2, 123.9, 122.2, 121.9, 121.8, 109.4, 107.5. IR (neat): $\nu_{max}/cm^{-1}$ 3103, 1601, 1539, 1493, 1453, 1339, 1231, 1200, 844, 769, 752. HRMS (ESI) *m/z* Calcd for $C_{14}H_9N_3O_4+H^+$ $[M+H]^+$ 284.0666; Found 284.0668.

**1-(2,4-Ninitrophenyl)-5-fluoro-1H-indole** (**3j**).[22] The representative procedure **B** was followed, using 5-fluoro-1*H*-indole (0.203 g, 1.50 mmol), 1-chloro-2,4-dinitrobenzene (0.365 g, 1.80 mmol), CuI (0.057 g, 0.30 mmol), $K_2CO_3$ (0.415 g, 3.00 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **3j** (0.138g, 31%) as a yellow solid. M. p. = 151-153 $^oC$. $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.90 (d, *J* = 2.2 Hz, 1H), 8.60 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.34 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.17 (d, *J* = 3.4 Hz, 1H), 7.13-7.10 (m, 1H), 7.00 (td, *J* = 8.8, 2.2 Hz, 1H), 6.77 (d, *J* = 2.9 Hz, 1H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): $\delta$ = 159.1 (d, $J_{C-F}$ = 238.1 Hz), 145.8, 145.0, 138.0, 132.6, 130.5 (d, $J_{C-F}$ = 10.0 Hz), 129.9, 128.9, 128.4, 122.0, 112.3 (d, $J_{C-F}$ = 27.0

Hz), 110.3 (d, $J_{C–F}$ = 9.2 Hz), 107.5 (d, $J_{C–F}$ = 4.6 Hz), 107.3 (d, $J_{C–F}$ = 23.9 Hz). $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −121.5 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 3147, 3117, 3100, 1601, 1524, 1339, 1135, 908, 729. MS (EI) *m/z*: 301 $[M]^+$, 281, 256, 226, 208, 181, 135.

**1-(3,5-Bis(trifluoromethyl)phenyl)-1H-indole** (**3k**).[22] The representative procedure **B** was followed, using 1*H*-indole (0.328 g, 2.80 mmol), 1-bromo-3,5-bis(trifluoromethyl)benzene (0.586 g, 2.00 mmol), CuI (0.076 g, 0.40 mmol) and $Cs_2CO_3$ (1.30 g, 4.00 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 10/1) yielded **3k** (0.222 g, 34%) as a light yellow liquid. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.97 (s, 2H), 7.84 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 3.4 Hz, 1H), 7.29 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.22 (dd, *J* = 7.6, 7.3 Hz, 1H), 6.75 (d, *J* = 3.2 Hz, 1H). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 141.5, 135.6, 133.6 (q, $J_{C–F}$ = 34.0 Hz), 130.0, 127.3, 124.0 (q, $J_{C–F}$ = 3.0 Hz), 123.7, 123.1 (q, $J_{C–F}$ = 272.6 Hz), 121.9, 121.7, 119.8 (q, $J_{C–F}$ = 3.8 Hz), 109.9, 106.1. $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −63.0 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 3284, 3062, 2963, 1477, 1402, 1275, 1115, 1103, 890, 847, 702. MS (EI) *m/z*: 329 $[M]^+$, 310, 233, 213, 116.

**Representative procedure for C-3 acetoxylation of *N*-substituted indoles**

**Synthesis of 1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (2a).** To a flame-dried Schlenk tube equipped with magnetic stir bar was introduced $PhI(OAc)_2$ (0.106 g, 0.33 mmol) and 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (0.059 g, 0.30 mmol) under argon. The Schlenk tube with the mixture was evacuated and refilled with argon. To the above mixture was added acetic acid and acetic anhydride (7:3) solvent mixture (1.0 mL). The resultant reaction mixture was then degassed, refilled with argon and stirred at 60 $^o$C in a pre-heated oil bath for 5 h. At ambient temperature, $H_2O$ (5 mL) and saturated $NaHCO_3$

solution (15 mL) were added and the reaction mixture was extracted with ethyl acetate (15 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and the solvent was evaporated *in vacuo*. The resultant residue was purified by column chromatography on silica gel (hexane/EtOAc: 5/1) to yielded acetoxylated compound **2a** (0.071 g, 93%) as off-white solid. M. p. = 117-119 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.81 (d, *J* = 8.6 Hz, 1H), 8.66 (d, *J* = 4.7 Hz, 2H), 8.43 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.01 (t, *J* = 4.7 Hz, 1H), 2.40 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.3, 158.3, 157.9, 133.7, 133.0, 124.8, 124.2, 122.3, 117.6, 116.6, 116.2, 114.7, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 3195, 2926, 1744, 1455, 1430, 1368, 1208, 809, 787. HRMS (ESI) *m/z* Calcd for $C_{14}H_{11}N_3O_2$+$Na^+$ $[M+Na]^+$ 276.0743; Found 276.0738.

**5-Methyl-1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (2b).** The representative procedure was followed, using 5-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1b**) (0.063 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **2b** (0.061 g, 76%) as a brown solid. M. p. = 161-163 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.66 (d, *J* = 8.6 Hz, 1H), 8.62 (d, *J* = 4.9 Hz, 2H), 8.37 (s, 1H), 7.34 (s, 1H), 7.19 (d, *J* = 8.6, 1H), 6.95 (t, *J* = 4.7 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.3, 158.1, 157.8, 133.4, 131.8, 131.3, 126.2, 124.3, 117.3, 116.3, 115.9, 114.7, 21.5, 21.1. IR (neat): $\nu_{max}/cm^{-1}$ 3202, 2917, 2851, 1747, 1579, 1451, 1430, 1206, 908, 785, 711. HRMS (ESI) *m/z* Calcd for $C_{15}H_{13}N_3O_2$+$Na^+$ $[M+Na]^+$ 290.0900; Found 290.0894.

**5-Methoxy-1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (2c).** The representative procedure was followed, using 5-methoxy-1-(pyrimidin-2-yl)-1*H*-indole (**1c**) (0.068 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on

silica gel (hexane/EtOAc: 2/1) yielded **2c** (0.064 g, 75%) as a light brown crystalline solid. M. p. = 166-168 $^{o}$C. $^{1}$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.69 (d, *J* = 9.5 Hz, 1H), 8.61 (d, *J* = 4.7 Hz, 2H), 8.39 (s, 1H), 6.99-6.95 (m, 3H), 3.89 (s, 3H), 2.40 (s, 3H). $^{13}$C{$^{1}$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.2, 158.2, 157.7, 155.7, 133.5, 127.9, 124.8, 117.7, 116.0, 115.2, 114.1, 99.5, 55.8, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 3209, 2923, 1745, 1435, 1222, 1204, 911, 821, 776. HRMS (ESI) *m/z* Calcd for $C_{15}H_{13}N_3O_3$+Na$^{+}$ [M+Na]$^{+}$ 306.0849; Found 306.0844.

**5-Fluoro-1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (2d).** The representative procedure was followed, using 5-fluoro-1-(pyrimidin-2-yl)-1*H*-indole (**1d**) (0.064 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 3/1) yielded **2d** (0.070 g, 86%) as an off-white solid. M. p. = 173-175 $^{o}$C. $^{1}$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.77 (dd, *J* = 9.2, 4.6 Hz, 1H), 8.66 (d, *J* = 4.9 Hz, 2H), 8.46 (s, 1H), 7.20 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.09 (td, *J* = 9.2, 1.8 Hz, 1H), 7.03 (t, *J* = 4.9 Hz, 1H), 2.39 (s, 3H). $^{13}$C{$^{1}$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.2, 159.1 (d, $J_{C-F}$ = 239.4 Hz), 158.3, 157.7, 133.4, 129.4, 124.9 (d, $J_{C-F}$ = 9.5 Hz), 117.9 (d, $J_{C-F}$ = 9.5 Hz), 116.4, 116.3, 112.7 (d, $J_{C-F}$ = 24.8 Hz), 103.2 (d, $J_{C-F}$ = 24.8 Hz), 21.1. $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −121.0 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 3208, 2921, 2852, 1745, 1449, 1197, 792, 786, 588. HRMS (ESI) *m/z* Calcd for $C_{14}H_{10}FN_3O_2$+Na$^{+}$ [M+Na]$^{+}$ 294.0649; Found 294.0647.

**5-Bromo-1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (2e).** The representative procedure was followed, using 5-bromo-1-(pyrimidin-2-yl)-1*H*-indole (**1e**) (0.082 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 3/1) yielded **2e** (0.073 g, 73%) as a light brown solid. M. p. = 178-179 $^{o}$C.

$^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.68-8.65 (m, 3H), 8.42 (s, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.04 (t, *J* = 4.9 Hz, 1H), 2.39 (s, 3H). $^{13}$C{$^1$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.1, 158.3, 157.6, 132.6, 131.6, 127.6, 125.8, 120.3, 118.2, 116.5, 115.9, 115.7, 21.1. IR (neat): $\nu_{max}$/cm$^{-1}$ 3205, 2923, 1758, 1456, 1433, 1204, 956, 867, 784. HRMS (ESI) *m/z* Calcd for $C_{14}H_{10}BrN_3O_2$+Na$^+$ [M+Na]$^+$ 353.9849, 355.9828; Found 353.9848, 355.9824.

**2-Methyl-1-(pyrimidin-2-yl)-1*H*-indol-3-yl acetate (2f).** The representative procedure was followed, using 2-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1f**) (0.075 g, 0.358 mmol) and $PhI(OAc)_2$ (0.127 g, 0.394 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 2/1) yielded **2f** (0.025 g, 26%) as a yellow solid. M. p. = 54-56 $^o$C. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.75 (d, *J* = 4.9 Hz, 2H), 8.42 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 7.6, 1H), 7.27-7.19 (m, 2H), 7.11 (t, *J* = 4.9 Hz, 1H), 2.59 (s, 3H), 2.42 (s, 3H). $^{13}$C{$^1$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 169.2, 158.5, 158.2, 134.1, 131.4, 127.0, 123.5, 123.1, 122.2, 117.1, 116.6, 114.8, 20.8, 12.8. IR (neat): $\nu_{max}$/cm$^{-1}$ 2923, 2852, 1756, 1575, 1559, 1421, 1366, 1205, 733. HRMS (ESI) *m/z* Calcd for $C_{15}H_{13}N_3O_2$+Na$^+$ [M+Na$^+$] 290.0900; Found 290.0896.

**1-(Pyridin-2-yl)-1*H*-indol-3-yl acetate (2g).** The representative procedure was followed, using 1-(pyridin-2-yl)-1*H*-indole (**1g**) (0.058 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by preparative TLC (hexane/EtOAc: 5/1) and extraction in $CH_2Cl_2$ (15 mL x 3) yielded **2g** (0.061 g, 81%) as a yellow liquid. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.54 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 7.95 (s, 1H), 7.79 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.33 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.24 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.14 (dd, *J* = 7.3, 4.9 Hz, 1H),

2.40 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.4, 152.6, 149.0, 138.6 133.0, 132.5, 124.3, 122.8, 121.5, 120.1, 117.8, 114.8, 114.4, 113.7, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 3178, 2962, 1752, 1449, 1435, 1357, 1207, 1009, 990, 799, 782. HR-MS (ESI) *m/z* Calcd for $C_{15}H_{12}N_2O_2+H^+$ $[M+H]^+$ 253.0972; Found 253.0969.

**1-(Pyridin-3-yl)-1*H*-indol-3-yl acetate (2h).** The representative procedure was followed, using 1-(pyridin-3-yl)-1*H*-indole (**1h**) (0.058 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by preparative TLC (hexane/EtOAc: 5/1) and extraction in $CH_2Cl_2$ (15 mL x 3) yielded **2h** (0.042 g, 56%) as a yellow liquid. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.84 (d, *J* = 1.8 Hz, 1H), 8.60 (d, *J* = 4.6 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.59 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 7.9, 4.6 Hz, 1H), 7.28 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.22 (dd, *J* = 7.6, 7.3 Hz, 1H), 2.40 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.5, 147.5, 145.7, 136.3, 133.0, 132.5, 131.7, 124.4, 124.0, 121.8, 121.2, 118.3, 116.6, 110.2, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 3019, 3011, 1745, 1214, 746, 667. HRMS (ESI) *m/z* Calcd for $C_{15}H_{12}N_2O_2+H^+$ $[M+H]^+$ 253.0972; Found 253.0969.

**1-(Pyridin-4-yl)-1*H*-indol-3-yl acetate (2i).** The representative procedure was followed, using 1-(pyridin-4-yl)-1*H*-indole (**1i**) (0.058 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by preparative TLC (hexane/EtOAc: 5/1) and extraction in $CH_2Cl_2$ (15 mL x 3) yielded **2i** (0.042 g, 56%) as a yellow liquid. $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.73 (d, *J* = 4.7 Hz, 2H), 7.75-7.66 (m, 3H), 7.49 (d, *J* = 4.9 Hz, 2H), 7.35 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 2.43 (s, 3H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): $\delta$ = 168.3, 151.4, 146.7, 133.4, 132.2, 124.5, 122.7, 121.7, 118.5, 117.4, 115.6, 111.0, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 2928, 2855, 1730, 1586, 1512, 1456, 1367, 1161, 993,

943, 807, 659. HRMS (ESI) *m/z* Calcd for $C_{15}H_{12}N_2O_2$+$H^+$ $[M+H]^+$ 253.0972; Found 253.0971.

**1-(Pyrazin-2-yl)-1*H*-indol-3-yl acetate (2j).** The representative procedure was followed, using 1-(pyrazin-2-yl)-1*H*-indole (**1j**) (0.059 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by preparative TLC (hexane/EtOAc: 5/1) and extraction in $CH_2Cl_2$ (15 mL x 3) yielded **2j** (0.071 g, 93%) as a brown solid. M. p. = 145-147 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.86 (d, *J* = 1.0 Hz, 1H), 8.48 (dd, *J* = 2.5, 1.7 Hz, 1H), 8.40 (d, *J* = 2.5 Hz, 1H), 8.34 (d, *J* = 8.6 Hz, 1H), 8.01 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.37 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.28 (dd, *J* = 8.3, 7.8 Hz, 1H), 2.41 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.3, 149.3, 142.7, 140.0, 136.3, 134.1, 132.6, 125.0, 123.2, 122.3, 118.1, 114.0, 113.7, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 3021, 2961, 1737, 1449, 1425, 1365, 1210, 1123, 1013, 839, 729. HRMS (ESI) *m/z* Calcd for $C_{14}H_{11}N_3O_2$+$Na^+$ $[M+Na]^+$ 276.0743; Found 276.0741.

**5-Fluoro-1-(pyrazin-2-yl)-1*H*-indol-3-yl acetate (2k).** The representative procedure was followed, using 5-fluoro-1-(pyrazin-2-yl)-1*H*-indole (**1k**) (0.064 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel ($CH_2Cl_2$/EtOAc: 15/1) yielded **2k** (0.050 g, 61%) as an off-white solid. M. p. = 166-168 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.81 (s, 1H), 8.47 (s, 1H), 8.41 (s, 1H), 8.37 (dd, *J* = 9.2, 4.3 Hz, 1H), 8.03 (s, 1H), 7.27-7.25 (m, 1H), 7.10 (td, *J* = 9.2, 2.4 Hz, 1H), 2.40 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.1, 159.0 (d, $J_{C-F}$ = 240.3 Hz), 149.1, 142.6, 140.1, 135.8, 133.9, 129.1, 123.9 (d, $J_{C-F}$ = 9.5 Hz), 115.7 (d, $J_{C-F}$ = 9.5 Hz), 115.0, 113.2 (d, $J_{C-F}$ = 24.8 Hz), 103.5 (d, $J_{C-F}$ = 24.8 Hz), 21.2. $^{19}F$-NMR (377 MHz, $CDCl_3$): $\delta$ =

−121.6 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 2924, 1748, 1480, 1446, 1201, 1007, 911, 839, 764. HRMS (ESI) *m/z* Calcd for $C_{14}H_{10}FN_3O_2$+$H^+$ $[M+H]^+$ 272.0830; Found 272.0828.

**5-Bromo-1-(pyrazin-2-yl)-1*H*-indol-3-yl acetate (2l).** The representative procedure was followed, using 5-bromo-1-(pyrazin-2-yl)-1*H*-indole (**1l**) (0.082 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel ($CH_2Cl_2$/EtOAc: 20/1) yielded **2l** (0.069 g, 70%) as a light brown solid. M. p. = 162-164 $^oC$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.81 (s, 1H), 8.48 (s, 1H), 8.42 (d, *J* = 2.5 Hz, 1H), 8.27 (d, *J* = 9.1 Hz, 1H), 8.00 (s, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.44 (dd, *J* = 8.8, 1.7 Hz, 1H), 2.40 (s, 3H). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 168.1, 149.0, 142.6, 140.4, 136.0, 133.2, 131.2, 127.9, 124.8, 120.8, 115.9, 115.6, 114.6, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 3170, 2923, 1759, 1446, 1422, 1243, 1061, 1006, 835, 735. HRMS (ESI) *m/z* Calcd for $C_{14}H_{10}BrN_3O_2$+$H^+$ $[M+H]^+$ 332.0029, 334.0009; Found 332.0030, 334.0008.

**1-(Thiophen-2-yl)-1*H*-indol-3-yl acetate (2m).** The representative procedure was followed, using 1-(thiophen-2-yl)-1*H*-indole (**1m**) (0.043 g, 0.22 mmol) and $PhI(OAc)_2$ (0.077 g, 0.24 mmol). Purification by preparative TLC (hexane/EtOAc: 5/1) and extraction in $CH_2Cl_2$ (15 mL x 3) yielded **2m** (0.020 g, 35%) as a liquid. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.60-7.54 (m, 3H), 7.29-7.25 (m, 1H), 7.22-7.16 (m, 2H), 7.08-7.02 (m, 2H), 2.38 (s, 3H). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 168.4, 141.4, 134.4, 131.9, 126.2, 124.0, 122.0, 121.4, 121.1, 120.9, 118.5, 118.0, 110.9, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 3010, 2962, 2854, 1747, 1613, 1547, 1460, 1366, 1225, 1010, 692. HRMS (ESI) *m/z* Calcd for $C_{14}H_{11}NO_2S$+$Na^+$ $[M+Na]^+$ 280.0403; Found 280.0398.

**1-Phenyl-1*H*-indol-3-yl acetate (4a).**[7] The representative procedure was followed, using 1-phenyl-1*H*-indole (**3a**) (0.058 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol).

Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **4a** (0.038 g, 50%) as a liquid. $^{1}$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 7.61 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.51-7.48 (m, 4H), 7.35-7.31 (m, 1H), 7.23 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.18 (dd, *J* = 7.6, 7.3 Hz, 1H), 2.38 (s, 3H). $^{13}$C{$^{1}$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.6, 139.6, 133.0, 131.7, 129.8, 126.6, 124.6, 123.4, 121.4, 120.6, 118.0, 117.2, 110.8, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 3007, 2978, 2873, 1745, 1712, 1501, 1457, 1367, 1223, 1110, 696. HRMS (ESI) *m/z* Calcd for $C_{16}H_{13}NO_2$+Na$^+$ [M+Na]$^+$ 274.0838; Found 274.0833.

**1-(4-Methoxyphenyl)-1*H*-indol-3-yl acetate (4b).**[7] The representative procedure was followed, using 1-(4-methoxyphenyl)-1*H*-indole (**3b**) (0.067 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 4/1) yielded **4b** (0.031 g, 37%) as a liquid. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.60 (d, *J* = 7.6 Hz, 1H), 7.49 (s, 1H), 7.43-7.37 (m, 3H), 7.24-7.14 (m, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 2.38 (s, 3H). $^{13}$C{$^{1}$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 168.7, 158.5, 133.5, 132.5, 131.2, 126.2, 123.2, 120.9, 120.3, 117.9, 117.6, 114.9, 110.6, 55.8, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 3176, 2966, 2840, 1747, 1548, 1510, 1370, 1207, 1029, 739, 588. HRMS (ESI) *m/z* Calcd for $C_{17}H_{15}NO_3$+Na$^+$ [M+Na]$^+$ 304.0944; Found 304.0935.

**1-(4-Fluorophenyl)-1*H*-indol-3-yl acetate (4c).** The representative procedure was followed, using 1-(4-fluorophenyl)-1*H*-indole (**3c**) (0.076 g, 0.36 mmol) and $PhI(OAc)_2$ (0.127 g, 0.39 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 15/1) yielded **4c** (0.039 g, 40%) as a yellow liquid. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.67 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.49-7.46 (m, 3H), 7.30-7.21 (m, 4H), 2.43 (s, 3H). $^{13}$C{$^{1}$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.6, 161.2 (d, $J_{C-F}$ = 246.6 Hz), 135.6 (d, $J_{C-F}$ = 2.3 Hz),

133.3, 131.7, 126.4 (d, $J_{C-F}$ = 8.5 Hz), 123.5, 121.3, 120.6, 118.0, 117.2, 116.6 (d, $J_{C-F}$ = 23.1 Hz), 110.4, 21.2. $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −115.1 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 3160, 2927, 2854, 1745, 1509, 1366, 1202, 1128, 819, 738, 558. HRMS (ESI) *m/z* Calcd for $C_{16}H_{12}FNO_2$+Na$^+$ [M+Na]$^+$ 292.0744; Found 292.0739.

**1-(4-(Trifluoromethyl)phenyl)-1*H*-indol-3-yl acetate (4d).** The representative procedure was followed, using 1-(4-(trifluoromethyl)phenyl)-1*H*-indole (**3d**) (0.078 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 10/1) yielded **4d** (0.043 g, 45%) as a brown solid. M. p. = 99-101 $^o$C. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.79-7.76 (m, 2H), 7.66-7.61 (m, 4H), 7.58 (dd, *J* = 8.3, 4.9 Hz, 1H), 7.30-7.20 (m, 2H), 2.40 (s, 3H). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 168.5, 142.7, 132.8, 132.6, 128.4 (q, $J_{C-F}$ = 33.1 Hz), 127.1 (q, $J_{C-F}$ = 3.1 Hz), 124.2 (q, $J_{C-F}$ = 272.0 Hz), 124.1, 124.0, 122.0, 121.2, 118.3, 116.6, 110.6, 21.2. $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −62.3 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 3163, 2926, 1746, 1369, 1333, 1106, 1065, 841, 763, 736. HRMS (ESI) *m/z* Calcd for $C_{17}H_{12}F_3NO_2$+Na$^+$ [M+Na]$^+$ 342.0712; Found 342.0706.

**1-(4-Acetylphenyl)-1*H*-indol-3-yl acetate (4e).** The representative procedure was followed, using 1-(4-(1*H*-indol-1-yl)phenyl)ethan-1-one (**3e**) (0.071 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 3/1) yielded **4e** (0.031 g, 35%) as a light yellow liquid. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.10 (d, *J* = 8.5 Hz, 2H), 7.64-7.58 (m, 5H), 7.28 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.22 (dd, *J* = 7.6, 7.3 Hz, 1H), 2.64 (s, 3H), 2.40 (s, 3H). $^{13}$C{$^1$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 197.0, 168.5, 143.6, 134.7, 132.7, 132.6, 130.2, 124.0, 123.5, 122.1, 121.3, 118.3, 116.5,

110.8, 26.8, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 2962, 2931, 2861, 1717, 1265, 1128, 1074, 736. HRMS (ESI) *m/z* Calcd for $C_{18}H_{15}NO_3$+Na$^+$ [M+Na]$^+$ 316.0944; Found 316.0938.

**Methyl 4-(3-acetoxy-1*H*-indol-1-yl)benzoate (4f).** The representative procedure was followed, using methyl 4-(1*H*-indol-1-yl)benzoate (**3f**) (0.075 g, 0.30 mmol) and PhI(OAc)$_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **4f** (0.038 g, 41%) as a liquid. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.18 (d, *J* = 8.5 Hz, 2H), 7.64-7.60 (m, 3H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.28 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.22 (dd, *J* = 7.6, 7.3 Hz, 1H), 3.96 (s, 3H), 2.40 (s, 3H). $^{13}$C{$^1$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.5, 166.5, 143.5, 132.7, 132.6, 131.4, 127.7, 124.0, 123.4, 122.0, 121.2, 118.2, 116.5, 110.8, 52.4, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 3028, 3012, 2954, 1717, 1605, 1515, 1457, 1437, 1365, 1280, 1206, 738, 664. HRMS (ESI) *m/z* Calcd for $C_{18}H_{15}NO_4$+Na$^+$ [M+Na]$^+$ 332.0893; Found 332.0887.

**1-(4-Cynophenyl)-1*H*-indol-3-yl acetate (4g).** The representative procedure was followed, using 4-(1*H*-indol-1-yl)benzonitrile (**3g**) (0.066 g, 0.30 mmol) and PhI(OAc)$_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **4g** (0.046 g, 56%) as a light brown solid. M. p. = 110-112 $^o$C. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ = 7.81 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.63-7.60 (m, 3H), 7.33 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.27 (dd, *J* = 8.2, 7.0 Hz, 1H), 2.43 (s, 3H). $^{13}$C{$^1$H}-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.4, 143.4, 133.9, 133.1, 132.4, 124.3, 124.0, 122.3, 121.6, 118.5, 118.4, 116.1, 110.6, 109.4, 21.2. IR (neat): $\nu_{max}$/cm$^{-1}$ 2921, 2851, 2225, 1776, 1562, 1509, 1366, 1211, 1126, 1012, 845, 743. HRMS (ESI) *m/z* Calcd for $C_{17}H_{12}N_2O_2$+Na$^+$ [M+Na]$^+$ 299.0791; Found 299.0787.

**1-(4-Nitrophenyl)-1*H*-indol-3-yl acetate (4h).** The representative procedure was followed, using 1-(4-nitrophenyl)-1*H*-indole (**3h**) (0.071 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 5/1) yielded **4h** (0.047 g, 53%) as a yellow solid. M. p. = 142-144 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.38 (d, *J* = 8.9 Hz, 2H), 7.68-7.62 (m, 5H), 7.33 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.24 (dd, *J* = 7.6, 7.3 Hz, 1H), 2.41 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.4, 145.2, 145.1, 133.5, 132.5, 125.7, 124.6, 123.5, 122.5, 121.8, 118.6, 116.2, 110.7, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 2923, 2852, 1746, 1592, 1524, 1222, 1129, 865, 748, 695, 528. HRMS (ESI) *m/z* Calcd for $C_{16}H_{12}N_2O_4+Na^+$ $[M+Na]^+$ 319.0689; Found 319.0688.

**1-(2,4-Dinitrophenyl)-1*H*-indol-3-yl acetate (4i).** The representative procedure was followed, using 1-(2,4-dinitrophenyl)-1*H*-indole (**3i**) (0.085 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 4:1) yielded **4i** (0.078 g, 76%) as an orange solid. M. p. = 147-148 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.92 (d, *J* = 2.4 Hz, 1H), 8.57 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 1H), 7.33-7.27 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 168.0, 145.5, 144.7, 138.0, 134.3, 133.1, 130.0, 128.3, 125.0, 122.3, 122.2, 122.1, 118.8, 116.2, 109.5, 21.2. IR (neat): $\nu_{max}/cm^{-1}$ 3158, 3084, 2852, 1751, 1601, 1527, 1366, 1224, 1128, 748, 702, 569. HRMS (ESI) *m/z* Calcd for $C_{16}H_{11}N_3O_6+Na^+$ $[M+Na]^+$ 364.0540; Found 364.0533.

**1-(2,4-Dinitrophenyl)-5-fluoro-1*H*-indol-3-yl acetate (4j).** The representative procedure was followed, using 1-(2,4-dinitrophenyl)-5-fluoro-1*H*-indole (**3j**) (0.09 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 4:1) yielded **4j** (0.066 g, 61%) as an orange solid. M. p. = 120-

122 °C. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.90 (d, *J* = 2.4 Hz, 1H), 8.57 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.55 (s, 1H), 7.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.08-6.99 (m, 2H), 2.39 (s, 3H). $^{13}$C{$^{1}$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 167.9, 159.0 (d, $J_{C-F}$ = 239.7 Hz), 145.8, 144.9, 137.7, 134.0 (d, $J_{C-F}$ = 4.6 Hz), 130.1, 129.6, 128.4, 122.9 (d, $J_{C-F}$ = 10.8 Hz), 122.1, 117.9, 113.5 (d, $J_{C-F}$ = 26.2 Hz), 110.7 (d, $J_{C-F}$ = 9.3 Hz), 104.4 (d, $J_{C-F}$ = 25.4 Hz), 21.1. $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −120.4 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 2922, 2852, 1754, 1452, 1338, 1202, 1188, 769, 729, 521. HRMS (ESI) *m/z* Calcd for $C_{16}H_{10}FN_3O_6$+Na$^+$ [M+Na]$^+$ 382.0446; Found 382.0445.

**1-(3,5-Bis(trifluoromethyl)phenyl)-1*H*-indol-3-yl acetate (4k).** The representative procedure was followed, using 1-(3,5-bis(trifluoromethyl)phenyl)-1*H*-indole (**3k**) (0.099 g, 0.30 mmol) and $PhI(OAc)_2$ (0.106 g, 0.33 mmol). Purification by column chromatography on silica gel (hexane/EtOAc: 20/1) yielded **4k** (0.063 g, 54%) as a light brown solid. M. p. = 68-70 °C. $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.96 (s, 2H), 7.83 (s, 1H), 7.66-7.64 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.32 (dd, *J* = 7.3, 7.1 Hz, 1H), 7.24 (dd, *J* = 7.6, 7.3 Hz, 1H), 2.40 (s, 3H). $^{13}$C{$^{1}$H}-NMR (100 MHz, $CDCl_3$): $\delta$ = 168.4, 141.1, 133.5 (q, *J* = 33.3 Hz), 133.2, 132.7, 124.6, 124.0 (q, *J* = 2.9 Hz), 123.1 (q, *J* = 272.8 Hz), 122.2, 121.7, 119.7, 118.6, 116.2, 110.0, 21.1. $^{19}$F-NMR (377 MHz, $CDCl_3$): $\delta$ = −63.0 (s). IR (neat): $\nu_{max}$/cm$^{-1}$ 3185, 3066, 2927, 1750, 1279, 1216, 1202, 1168, 1085, 888, 737, 682. HRMS (ESI) *m/z* Calcd for $C_{18}H_{11}F_6NO_2$+H$^+$ [M+H]$^+$ 388.0767; Found 388.0762.

**Synthesis of 1-(pyrimidin-2-yl)indoline-2,3-diyl diacetate (5a).** To a flame-dried Schlenk tube equipped with magnetic stir bar was introduced phenyl-$\lambda^3$-iodanediyl diacetate, $PhI(OAc)_2$ (0.354 g, 1.1 mmol) and 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (0.195 g, 1.0 mmol) under argon. The Schlenk tube with reaction mixture was evacuated and

refilled with argon. To the above mixture was added acetic acid and acetic anhydride (7:3) solvent mixture (1.0 mL). The resultant reaction mixture was then degassed, refilled with argon and stirred at room temperature for 1 h. Then the reaction mixture was quenched with $H_2O$ (5 mL) and saturated $NaHCO_3$ solution (15 mL) and the reaction mixture was extracted with ethyl acetate (15 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and the solvent was evaporated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexane/EtOAc: 2/1) to yielded diacyloxylated compound **5a** (0.165 g, 53%) as an off-white solid. M. p. = 143-145 $^oC$. $^1H$-NMR (500 MHz, $CDCl_3$): $\delta$ = 8.54 (d, *J* = 4.6 Hz, 2H), 8.45 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.22 (s, 1H), 7.06 (dd, *J* = 7.6, 7.3 Hz, 1H), 6.85 (t, *J* = 4.6 Hz, 1H), 6.01 (s, 1H), 2.07 (s, 3H), 2.05 (s, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta$ = 170.2, 170.1, 158.4, 158.0, 144.4, 131.0, 127.6, 127.4, 122.9, 116.2, 114.0, 87.9, 75.6, 21.1. IR (neat): $\nu_{max}/cm^{-1}$ 3735, 3015, 1734, 1730, 1585, 1488, 1444, 1227, 1014, 761, 617. HRMS (ESI) *m/z* Calcd for $C_{16}H_{15}N_3O_4+Na^+$ $[M+Na]^+$ 336.0955; Found 336.0952.

**Representative procedure for the competition experiments.** To a flame-dried Schlenk tube equipped with magnetic stir bar was introduced compound **1a** (0.117 g, 0.6 mmol), compound **3a** (0.116 g, 0.6 mmol) and $PhI(OAc)_2$ (0.097 g, 0.30 mmol) under argon. The Schlenk tube with the mixture was evacuated and refilled with argon. To the above mixture was added acetic acid and acetic anhydride (7:3) solvent mixture (2.0 mL). The resultant reaction mixture was then degassed, refilled with argon and stirred at 60 $^oC$ in a pre-heated oil bath for 5 h. At ambient temperature, $H_2O$ (5 mL) and saturated $NaHCO_3$ solution (15 mL) were added and the reaction mixture was extracted with ethyl acetate (15 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and the solvent was

evaporated *in vacuo*. To the resultant residue, acetone (5 mL) and *p*-xylene (0.3 mmol) were added and injected into Gas Chromatograph. The GC yield was calculated with respect to internal standard *p*-xylene.

**Procedure for the dehydroacetoxylation reaction.** To a flame-dried Schlenk tube equipped with magnetic stir bar was introduced compound **5a** (0.031 g, 0.1 mmol) and 1-acetylindoline-2,3-diyl diacetate (0.028 g, 0.1 mmol). To the above mixture was added acetic acid and acetic anhydride (7:3) solvent mixture (1.0 mL). The resultant reaction mixture was then degassed, refilled with argon and stirred at 60 $^{o}$C in a pre-heated oil bath for 2 h. At ambient temperature, $H_2O$ (3 mL) and saturated $NaHCO_3$ solution (10 mL) were added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and the solvent was evaporated *in vacuo*. To the resultant residue, acetone (5 mL) and *p*-xylene (0.2 mmol) were added and injected into Gas Chromatograph. The GC yield was calculated with respect to internal standard *p*-xylene.

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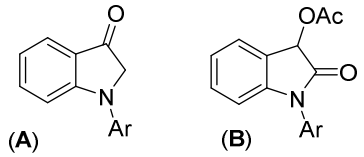


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