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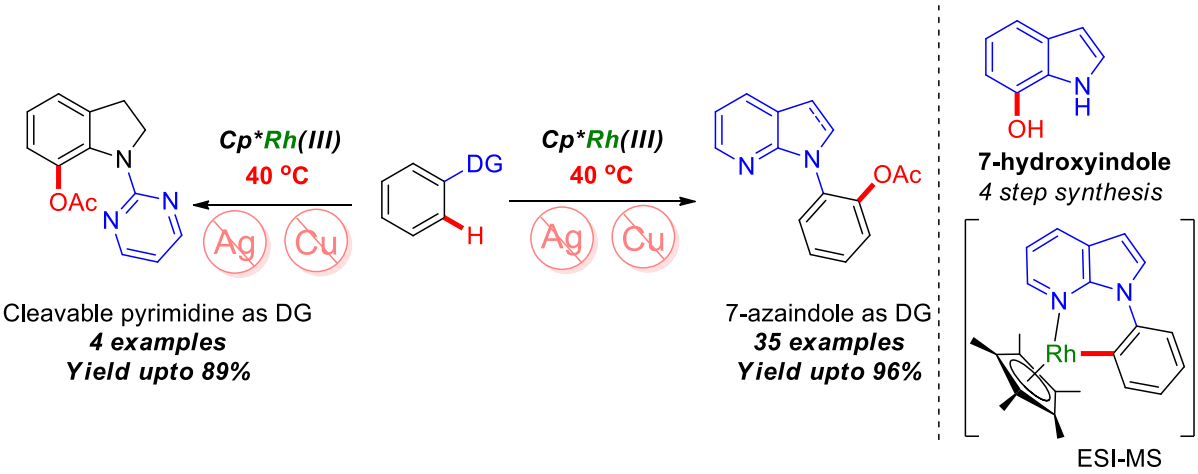
Rhodium Catalyzed sp^2 C-H Acetoxylation of *N*-Aryl Azaindoles/ *N*-Heteroaryl Indolines

Aniket Mishra,[†] Tripta Kumari Vats,[†] Mahesh P. Nair, Arindam Das and Indubhusan Deb*

Organic and Medicinal Chemistry Division, Indian Institute of Chemical Biology, 4-Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India

Supporting Information Placeholder



Abstract:

A silver and copper free rhodium catalyzed C–H acetoxylation reaction of azaindoles has been achieved at near ambient temperature employing PIDA as a non-metallic acetoxy source. The method is highly selective, efficient, scalable and requires acetic anhydride as the sole additive. The scope of the reaction has been successfully tested with a wide array of medicinally important heterocyclic scaffolds with diverse functional group tolerance. A series of kinetic experiments was conducted to gain a detailed insight into the reaction mechanism. The methodology developed could be successfully expanded for C7-acetoxylation of indoline derivatives using pyrimidine as a detachable directing group for the synthesis of 7-hydroxyindole.

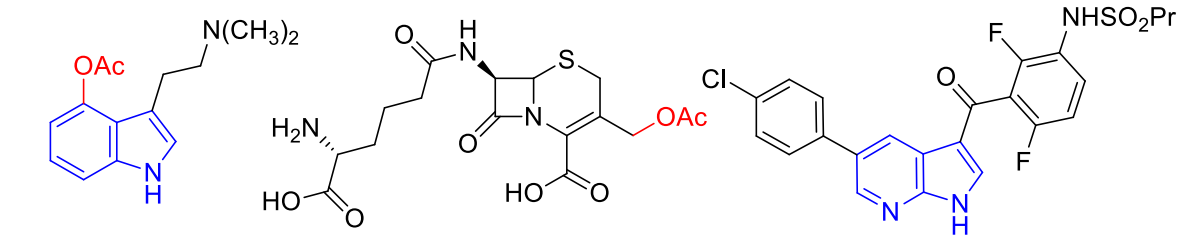
Introduction:

During the last decade C–H bond functionalization of an organic molecule via the aid of a suitable transition metal catalyst has seen a sudden expansion due to the easy accessibility of inert C–H bonds of diverse molecular systems. Various transition metals such as Pd, Cu, Rh, Ru, Co, Fe, Ni and Ir have been extensively exploited in a plethora of synthetic

transformations *via* C–H bond activation. Recently, the direct formation of C–O bond has been attracted much attention in organic synthesis. Acetoxy group has the properties like the ability to induce polar nature, unique H-bond donor accepting capacity and can also be used as an alcohol or phenol group introducing functional group modifier and as a consequence pharmaceutical importance of acetoxy group is well reflected in its application as a proper pro-drug tool,[1a-1b] anti-microbial[1c] and herbicidal[1d] activities. Additionally acetoxy group also forms part of many marketed drugs[1g] and natural products (Figure 1).[1h–1j]

In this context, a number of direct sp^2 and sp^3 C–H bond acetoxylation has been accomplished using palladium[2] and less commonly with copper[3] and ruthenium[4] catalysis. But most of these methods suffer from the drawback of excessive use of metallic acetoxy source and/or toxic silver oxidants. Further, the methods often require high temperature, strong acids as additive or a solvent such as acetic acid, which limit their application towards substrates bearing various sensitive functional groups and complex moieties. In stark contrast, high valent rhodium catalysis, which follows entirely different mechanistic pathway and has become popular only very recently, is often more selective, milder and well tolerant of various functional groups, while requiring low catalyst loading.[5] However, a milder approach employing rhodium catalysis for direct and selective C–H acetoxylation for directing arenes is yet to be explored.[6]

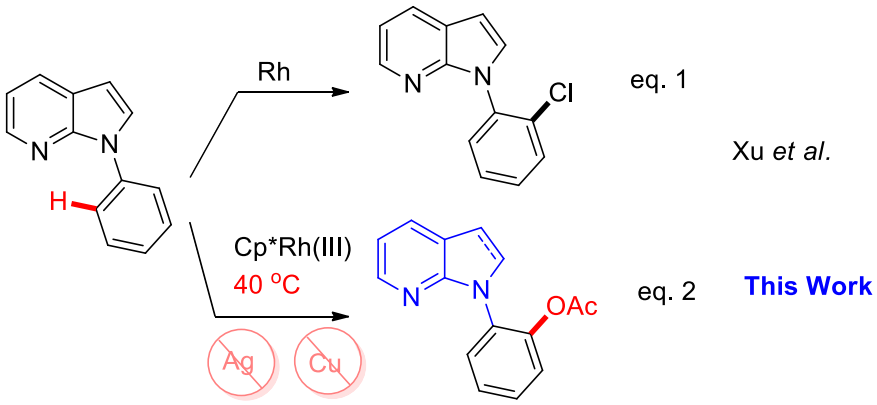
Figure 1.Representative Bio-active molecules



We noticed that 7-azaindole is a unique heterocyclic moiety present in a number of natural products,[7a] two marketed drugs (vemurafenib,[7b] venetoclax[7c]), other bio-active molecules[7d-7g] and useful materials (Figure 1).[7h-7i] In spite of these numerous applications, it is only very recently that this has been introduced in metal catalyzed transformations.[8] However, carbon-heteroatom bond formation utilizing 7-azaindole moiety as directing group is confined to C–Cl bond only (Scheme 1, eq. 1).[8a] Hence, the selective introduction of acetoxy group *via* direct C–O bond formation in 7-azaindole framework could be highly solicited. Continuing

our research interest in 7-azaindoles,[8e] herein we wish to report a mild silver/copper free rhodium (III) catalyzed direct mono and *ortho*-selective acetoxylation of *N*-aryl-7-azaindoles using PIDA as a non-metallic acetoxy source in presence of Ac_2O as sole organo-additive in 1,2-dichloroethane at 40 °C (Scheme 1, eq. 2).

Scheme 1. Azaindole directed carbon-heteroatom bond formation

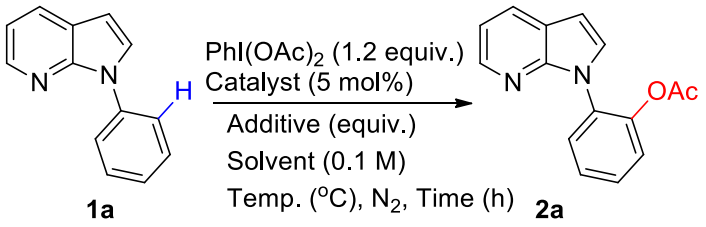


Results and discussion:

We commenced the study by using *N*-phenyl-7-azaindole (**1a**) as model substrate and $PhI(OAc)_2$ (PIDA) as non metallic acetoxy source. Realizing that this can be challenging due to the electrophilic nature of PIDA and more reactive C3 position of 7-azaindole,[9] we selected a highly reactive and air stable cationic complex $[Cp^*Rh(MeCN)_3](SbF_6)_2$ to overcome this problem. To our delight, the desired product 2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (**2a**) was obtained in 42% yield in presence of 5 mol% of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ complex as catalyst and 1.0 equiv. of PIDA in toluene at 110 °C for 24 h under N_2 (Table 1, entry 1). No formation of bis or 3-acetoxylated product was observed. A seriesof solvents were screened (Table 1, entries 2-5) and 1,2-dichloroethane was found to be the solvent of choice (Table 1, entry 2). In order to improve the yield, various inorganic and organic acetate sources as additive were tested (Table 1, entries 6-9) but all of these (NaOAc, CsOAc and AcOH) were found to have extremely detrimental effect on the yield of **2a** except Ac_2O which gave the desired product in moderate (50%) yield (Table 1, entry 9). Surprisingly, when the loading of Ac_2O was increased to 16.0 equiv., **2a** was obtained in 75% yield (Table 1, entry 10). However, further increase in amount of Ac_2O was not beneficial (Table 1, entry 11). In order to improve the efficacy of the reaction, loading of $PhI(OAc)_2$ was increased to 1.2 equiv. and a marginal improvement was observed (Table 1, entry 12). Interestingly, when the loading of $PhI(OAc)_2$ was increased to 3.0 equiv., the bis acetoxylated

product was obtained in 35% yield along with trace amount of desired product (Table 1, entry 13).

Table 1. Optimization of reaction condition for acetoxylation of *N*-aryl-7-azaindole[a]



Entry	Catalyst (5 mol%)	Additive (equiv.)	Solvent (0.1 M)	Temp (°C)	Time (h)	Yield of **2a**[b] (%)
1[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	-	toluene	110	24	42
2[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	-	DCE	110	24	65
3[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	-	PhCl	110	24	42
4[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	-	1,4-dioxane	110	24	nr
5[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	-	MeCN	100	24	trace
6[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	NaOAc (1.0)	DCE	110	24	24
7[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	CsOAc (1.0)	DCE	110	24	8
8[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	AcOH (1.0)	DCE	110	24	24
9[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (1.0)	DCE	110	24	50
10[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	110	24	75
11[c]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (26.0)	DCE	110	24	71
12	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	110	24	77
13[d]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	90	24	- (35)[e]
14	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	90	24	81
15	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	90	1	89
16	**$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$**	**Ac_2O (16.0)**	**DCE**	**40**	**6**	**91**
17[f]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	40	6	87
18[g]	$[Cp^*RhCl_2]_2/AgSbF_6$	Ac_2O (16.0)	DCE	40	6	65
19[g]	$[Cp^*IrCl_2]_2/AgSbF_6$	Ac_2O (16.0)	DCE	40	6	- (18)[h]
20[g]	$Cp^*Co(CO)I_2/AgSbF_6$	Ac_2O (16.0)	DCE	40	6	- (34)[h]
21[g]	$[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$	Ac_2O (16.0)	DCE	40	6	- (22)[h]
22[i]	$[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$	Ac_2O (16.0)	DCE	40	6	nr

[a]Reaction condition: Unless otherwise mentioned, **1** (0.2 mmol), $PhI(OAc)_2$ (1.2 equiv.), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol%), Ac_2O (16.0 equiv.), DCE (2.0 mL, 0.1 M), 40 °C, N_2. [b]All yields refer to isolated yields, yields within parenthesis refer to isolated yields of unwanted side products, and "nr" refers to "no reaction". [c]1.0 equiv. of $PhI(OAc)_2$ was used. [d]3.0 equiv. of $PhI(OAc)_2$ was used. [e]Bis acetoxylation at both of the *ortho* positions was observed exclusively. [f]3 mol% $[Cp^*Rh(MeCN)_3](SbF_6)_2$ was used. [g]$AgSbF_6$ (30 mol%) was used. [h]Acetoxylation was observed at 3-position of 7-azaindole ring exclusively. [i]$PhI(OAc)_2$ was omitted.

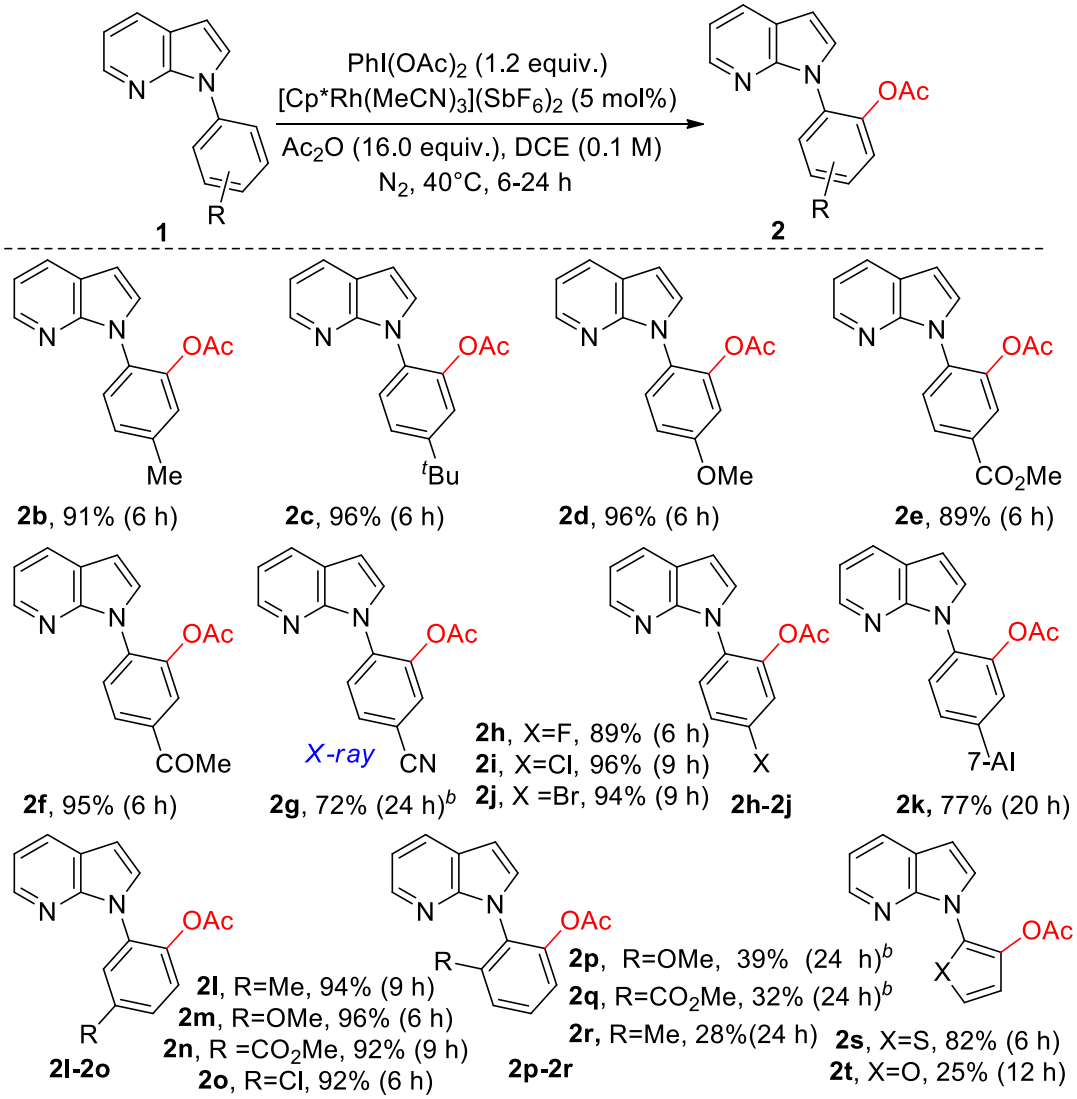
Further, careful tuning of the reaction condition revealed that lesser temperature (Table 1, entry 14) and lesser time (Table 1, entry 15) increased the yield of **2a** dramatically. This is not unexpected as the decomposition of product may take place under more harsh condition. Finally, 40 °C as temperature and 6 h as time were found to be best at which the desired product was obtained at an excellent yield of 91% (Table 1, entry 16).

When the catalyst loading was decreased to 3 mol%, a comparable yield was observed (Table 1, entry 17). But the more popular $[Cp^*RhCl_2]_2/AgSbF_6$ catalytic combination proved to be less effective (Table 1, entry 18). Other transition metals catalysts such as $[Cp^*IrCl_2]_2$, $Cp^*Co(CO)I_2$ and $[Ru(p\text{-cymene})Cl_2]_2$ were found to be completely ineffective and in all cases acetoxylation was observed at 3-position of 7-azaindole ring (Table 1, entries 19-21). In absence of $PhI(OAc)_2$ the reaction was shut down completely (Table 1, entry 22). Hence, for the present reaction both $[Cp^*Rh(MeCN)_3]$ $(SbF_6)_2$ and $PhI(OAc)_2$ play crucial roles.

After establishing the optimal condition, we set out to explore the scope of acetoxylation with an array of *N*-aryl-7-azaindole derivatives (Scheme 2). We found that 3 mol% of catalyst is less effective than 5 mol% of the same for various substrates (**2d**, **2i**, **2m**, **2o** and **2s**, see table S1 in SI for details), so 5 mol% of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ was chosen as optimal loading for the catalyst. Both electron-donating (**1b**-**1d**) and electron-withdrawing (**1e**-**1j**) groups at *para* position of aryl ring were compatible and afforded the acetoxylated products **2b**-**2j** in good to excellent yields. Notably, the halide groups fluoro, chloro and bromo were well tolerated (**2h**-**2j**). Interestingly, when *N*-phenyl-7-azaindole substrate with 7-azaindole itself as substitution on its para position was subjected to acetoxylation under the standard condition, the monoacetoxylated product **2k** was formed exclusively in good yield (77%).

We next investigated the substituent effect at *meta* position of aryl group. To our delight, both electron-donating and electron-withdrawing group containing substrates **1l**-**1o** gave the desired products **2l**-**2o** with excellent yields and excellent regio selectivity. However, *ortho* substituted substrates **1p**-**1r** showed moderate conversion which can be attributed to steric effect. Pleasingly, the thiophene containing substrate **1s** underwent the reaction smoothly and furnished the desired product **2s** in excellent yield. However, the conversion of furan tethered **1t** to **2t** was moderate.

Scheme 2. Scope of acetoxylation of *N*-aryl-7-azaindoles[a]

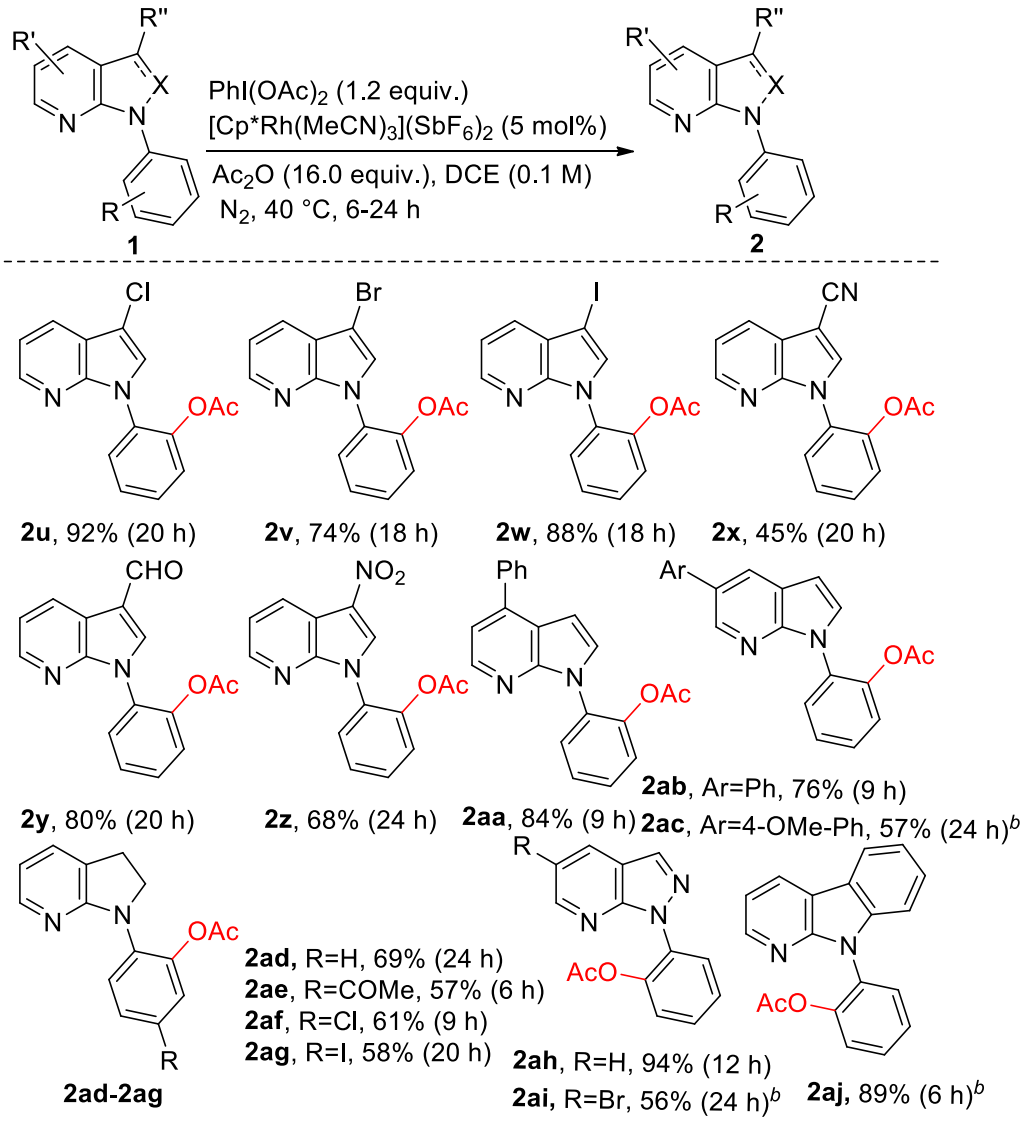


[a]Reaction condition: Unless otherwise mentioned, **1** (0.2 mmol), $PhI(OAc)_2$ (1.2 equiv.), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol%), Ac_2O (16.0 equiv.), DCE (2.0 mL), 40 °C, N_2. [b]Reaction temperature 90 °C. 7-AI: 7-azaindole.

Next we focused on various substitutions on 7-azaindole ring and found that they have minor influence on reaction condition (Scheme 3). Chloro, bromo and iodo groups at 3-position showed good to excellent conversion and gave the desired products **2u**-**2w**. Gratifyingly, cyano, formyl and nitro, all synthetically useful functional groups, were tolerated at 3-position and gave the compounds **2x**-**2z** in moderate to good yields. Different aryl groups at 4 and 5-position were also successful (**2aa**-**2ac**).

To the best of our knowledge, *N*-aryl-7-azaindolines have not been explored in TM catalyzed direct C–H functionalizations and therefore we thought of using this class of substrates for the present acetoxylation reaction.

Scheme 3. Scope of acetoxylation of *N*-aryl-7-azaindoles and related compounds[a]



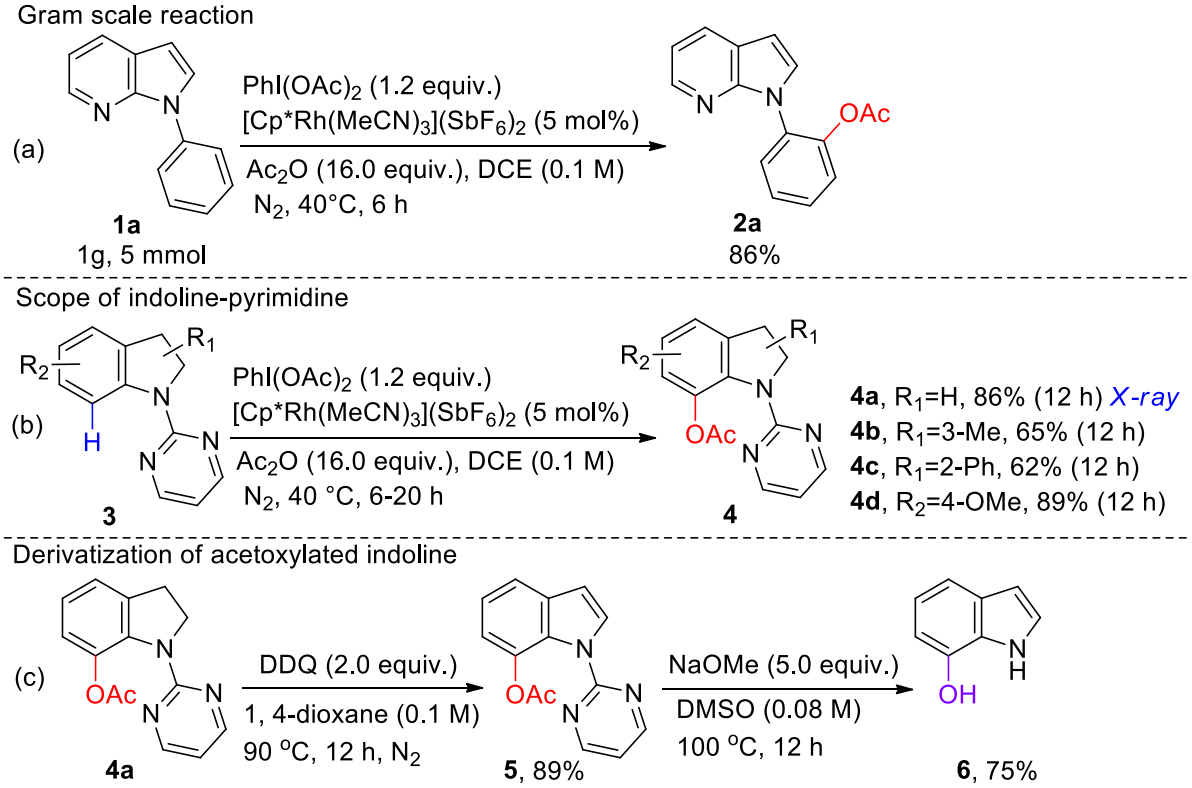
[a]Reaction condition: Unless otherwise mentioned, **1** (0.2 mmol), $PhI(OAc)_2$ (1.2 equiv.), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol%), Ac_2O (16.0 equiv.), DCE (2.0 mL), 40 °C, N_2. [b]Reaction temperature 90 °C.

A series of *N*-aryl-7-azaindoline derivatives **1ad**-**1ag** underwent reaction under standard conditions smoothly and acetoxylation occurred selectively at *ortho* position to give expected products **2ad**-**2ag** in moderate to good yields. The methodology was also compatible with *N*-aryl-7-azaindazoles and the substrates **1ah** and **1ai** afforded desired products **2ah** and **2ai** in

94% and 56% yields respectively. α-carboline containing substrate **1aj** also gave the desired product **2aj** in excellent yield of 89%.

In order to broaden the synthetic utility of the methodology, we conducted a gram scale experiment under standard condition and the desired product **2a** was obtained in 86% yield (Scheme 4a). When we subjected pyrimidine-tethered indoline derivatives[10] **3a-3d** under standard condition, acetoxylation occurred at C7 position exclusively and the desired products **4a-4d** were obtained in moderate to good yields (Scheme 4b). To illustrate the synthetic utility of C7 acetoxylated indoline, **4a** was oxidized by DDQ to give indole **5**. Furthermore, the pyrimidine group could be successfully cleaved by treating with sodium methoxide to obtain 7-hydroxyindole **6** (Scheme 4c).

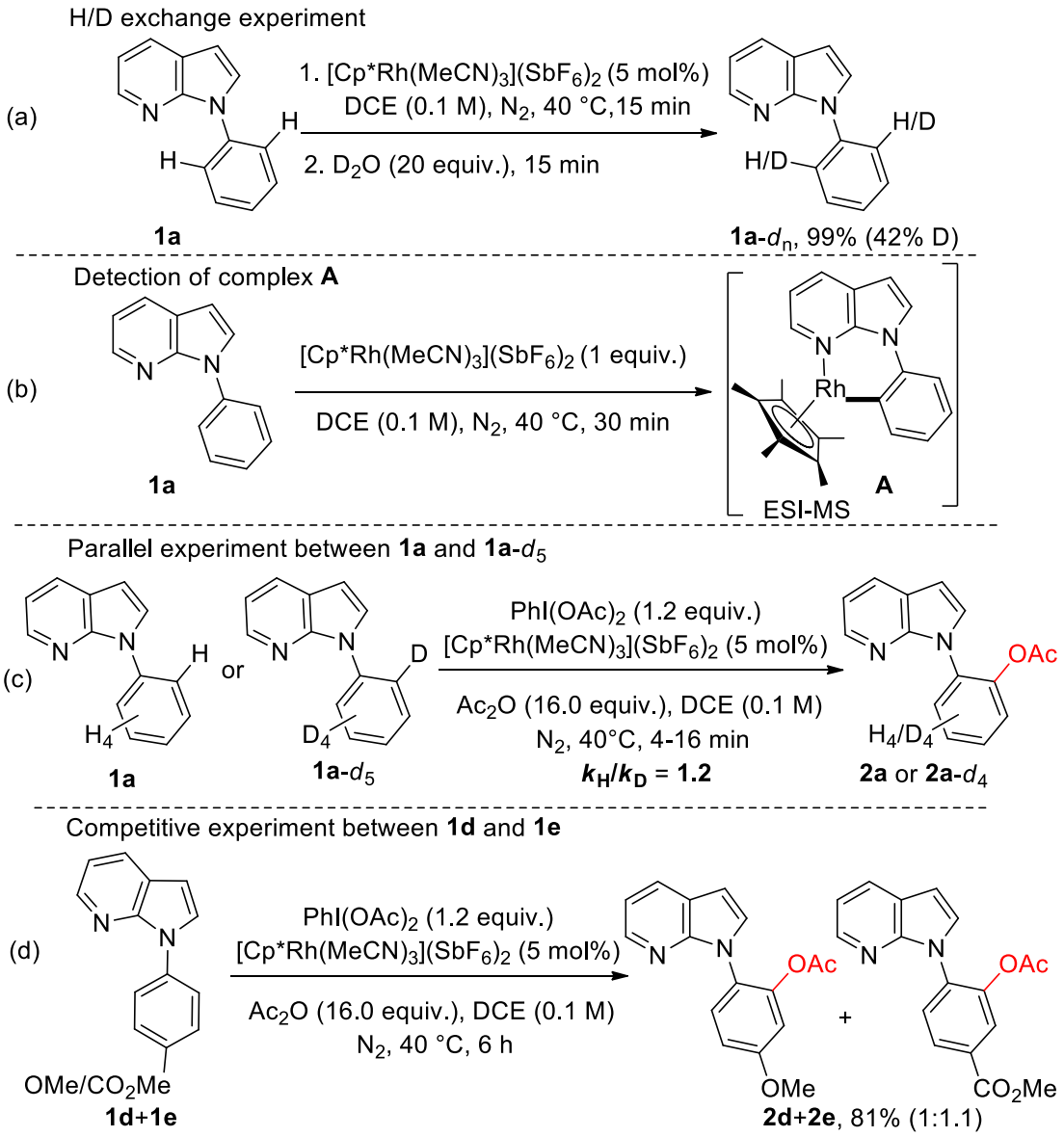
Scheme 4. Gram scale reaction, scope of acetoxylation for indoline-pyrimidine and derivatization of acetoxylated indoline[a]



In order to gain some insight into the reaction mechanism, a few experiments were conducted (Scheme 5). When the reaction was performed with **1a** in absence of PIDA and Ac_2O and quenched with excess D_2O, 42% deuterium incorporation was observed in the recovered starting material (Scheme 5a and SI). When a stoichiometric reaction was carried out between substrate**1a** and rhodium catalyst, the formation of complex **A** was confirmed by ESI-MS

(Scheme 5b and SI). These experiments prove that a reversible C–H bond cleavage may be involved in the acetoxylation process. A low kinetic isotopic effect value (k_H/k_D) of 1.2 was observed when two different sets of parallel experiments were performed in separate reaction vessels with **1a** and **1a**-d_5, which suggests that C–H bond cleavage may not be involved in the rate determining step of the reaction (Scheme 5c and SI). Intermolecular competition experiments between **1d** and **1e** indicates that there is no significant substituent effect on the reaction (Scheme 5d and SI).

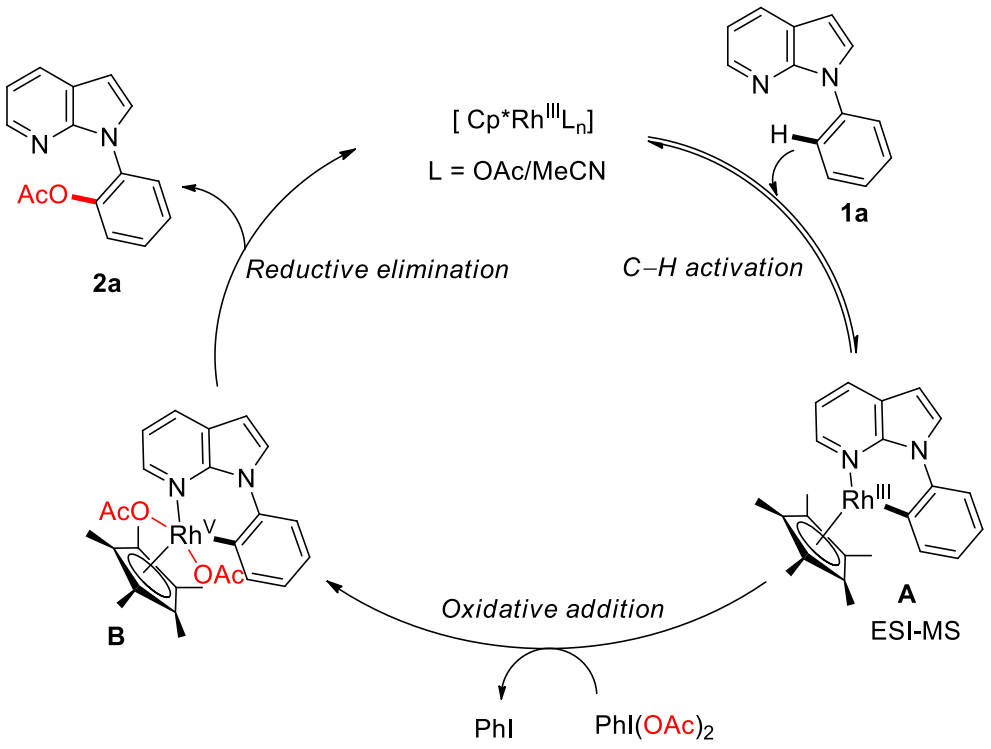
Scheme 5. Mechanistic Experiments



Based on the mechanistic studies performed and prior reports,[6] a plausible catalytic cycle has been drawn (Scheme 6). Cationic complex [Cp*RhL$_n$] (where n=OAc and/or MeCN) may

undergo reversible C–H bond cleavage in presence of **1a** and produce a rhodacycle intermediate **A**, which undergoes oxidative addition in presence of PIDA to form a rhodium (V) complex **B**. Then reductive elimination takes place to give the desired product **3a** along with the regenerated Rh (III) catalyst. Although the role of acetic anhydride is not fully understood at present, it may provide acetate ions which can help to form more reactive rhodium species to act as the effective catalyst and/or to provide extra acetate source which has been previously described as sole additive in acetoxylation reactions catalyzed by palladium in presence of PIDA.[2g, 2i]

Scheme 6. Plausible mechanism



Summary:

In conclusion, we have demonstrated a rhodium catalyzed highly efficient and *ortho* selective acetoxylation of *N*-aryl-7-azaindoles and related moieties. The method developed is stoichiometric heavy-metal free and does not require harsh conditions. The proof of chelation assistance was supported by conducting kinetic experiments.

Experimental section:

General Information:

All reactions were carried out in oven-dried reaction vessels under nitrogen atmosphere unless otherwise mentioned. TLC analysis was performed on silica gel TLC plates. Column chromatography was done using 230−400 mesh silica gel by applying pressure through an air pump. ^{1}H and ^{13}C NMR spectra were recorded on 300 and 600 MHz spectrometers and are reported as chemical shifts (δ) in parts per million (ppm), and multiplicities are abbreviated as s= singlet, d = doublet, t = triplet, sex = sextet, m = multiplet, comp = complex. Internal standards or residual solvent signals were used as reference. HRMS (m/z) was recorded using ESI (Q-Tof and Orbitrap, positive ion) and EI (magnetic sector, positive ion) mode. Melting points were determined in a capillary melting point apparatus and are uncorrected. GC analysis was done on a GC system with a flame ionizing detector (FID). Single-crystal X-ray data were recorded in a diffractometer with Mo Kα radiation. The CIF files were submitted to CCDC (1567757&1571959) and can be obtained at https://summary.ccdc.cam.ac.uk/structure-summary-form. *N*-aryl 7-azaindoles/indolines/indazoles (**1a**-**1ah**)[8a] and indolinyl pyrimidines (**3a**-**3c**)[10c] were prepared by literature method.

General procedure for acetoxylation:

Small (milligram) scale:

An oven dried 10 mL schlenk tube was charged with *N*-phenyl-7-azaindole (**1a**) (0.2 mmol, 38.8 mg), PIDA (1.2 equiv., 77.3 mg) and catalyst $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5.0 mol%, 8.3 mg). The tube was evacuated and backfilled with nitrogen and to it were added freshly distilled acetic anhydride (16.0 equiv., 0.30 ml) and anhydrous DCE (2.0 mL, 0.1 M) under nitrogen atmosphere. The reaction mixture was degassed and backfilled with nitrogen 3 times. It was then closed with teflon-lined cap and kept for stirring at 40 °C (pre heated oil bath temperature) for 6 h. After the completion of the reaction, reaction mixture was filtered through a short pad of celite and the solvent was removed under reduced pressure. Saturated sodium bicarbonate solution was added to the reaction mixture followed by extraction with ethylacetate and water. The combined organic layers were concentrated and purified through column chromatography on silica gel using ethyl acetate/pet ether as eluent to obtain 2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (**2a**) in 91% yield (45.9 mg).

Large (gram) scale:

An oven dried 100 mL round-bottom flask equipped with reflux condenser was charged with *N*-phenyl-7-azaindole (**1a**) (5.1 mmol, 1.0 g), PIDA (1.2 equiv., 1.99 g) and catalyst

$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5.0 mol%, 214 mg). The RB was evacuated and backfilled with nitrogen and to it were added freshly distilled acetic anhydride (16.0 equiv., 7.7 ml) and anhydrous DCE (51.0 mL, 0.1 M) under nitrogen atmosphere. The reaction mixture was degassed and backfilled with nitrogen 3 times. It was kept for stirring at 40 °C (pre heated oil bath temperature) for 6 h. After the completion of the reaction, reaction mixture was filtered through a short pad of celite and the solvent was removed under reduced pressure. Saturated sodium bicarbonate aqsolution was added to the reaction mixture followed by extraction with ethylacetate and water. The combined organic layers were concentrated and purified through column chromatography on silica gel using ethyl acetate/pet ether as eluent to obtain 2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (**2a**) in 86% yield (1.1 g).

Characterization data of acetoxylated products:

2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2a):

Yield 91% (45.9 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.90 (s, 3 H), 6.62 (d, *J* = 3.6 Hz, 1 H), 7.12 (dd, *J* = 7.8 Hz, 4.6 Hz, 1 H), 7.30 – 7.33 (comp,2 H), 7.38 – 7.49 (comp, 2 H), 7.60 (dd, *J* = 7.5 Hz, 2.0 Hz, 1 H), 7.96 (dd, *J* = 7.8 Hz, 1.7 Hz, 1 H), 8.34 (dd, *J* = 4.6 Hz, 1.7 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.5, 101.5, 116.5, 120.6, 123.8, 126.7, 128.6, 128.7, 128.9 (x 2), 130.6, 143.7, 145.8, 147.8, 168.7; **HRMS** (EI, m/z) calcd for $C_{15}H_{12}N_2O_2$ $[M]^+$ 252.0899, found 252.0894.

5-methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2b):

Yield 91% (48.5 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.91 (s, 3 H), 2.46 (s, 3 H), 6.62 (d, *J* = 3.6 Hz, 1 H), 7.12 – 7.14 (comp, 2 H), 7.23 – 7.24 (m, 1 H), 7.30 (d, *J* = 3.6 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.97 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 8.36 (dd, *J* = 4.2 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$)δ 20.6, 21.2, 101.3, 116.5, 120.5, 124.2, 127.5, 127.9, 128.4, 128.9, 129.1, 139.4, 143.7, 145.7, 148.1, 169.0; **HRMS** (ESI, m/z) calcd. for $C_{16}H_{14}N_2NaO_2$ $[M+Na]^+$ 289.0953, found 289.0945.

5-(tert-butyl)-2-(1H-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2c):

Yield 96% (59.4 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 9:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 1.92 (s, 3 H), 6.62 (d, *J* = 3.6 Hz, 1H), 7.14 (dd,

J = 7.8 Hz, 4.8 Hz, 1 H), 7.31 – 7.32 (comp, 2 H), 7.45 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 7.54 (app d, *J* = 8.4 Hz, 1 H), 7.98 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.38 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H);**^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 31.3, 34.9, 101.3, 116.5, 120.6, 120.9, 123.9, 127.8, 128.0, 129.0, 129.1, 143.7, 145.5, 147.9, 152.4, 168.9; **HRMS** (EI, m/z) calcd for $C_{19}H_{20}N_2O_2$ $[M]^+$ 308.1525, found 308.1521.

5-methoxy-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2d):

Yield 96% (54.2 mg); yellow solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 40 – 42 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.89 (s, 3 H), 3.88 (s, 3 H), 6.61 (d, *J* = 3.6 Hz, 1 H), 6.87 (d, *J* = 2.4 Hz, 1 H), 6.97 (dd, *J* = 9.0 Hz, 2.7 Hz, 1 H), 7.13 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.27 (d, *J* = 3.0 Hz, 1 H), 7.49 (d, *J* = 9.0 Hz, 1 H), 7.97 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 8.35 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.5, 55.8, 101.1, 109.4, 112.4, 116.4, 120.5, 123.4, 128.9, 129.3, 129.4, 143.7, 147.0, 148.2, 159.8, 168.8; **HRMS** (ESI, m/z) calcd for $C_{16}H_{15}N_2O_3$ $[M+H]^+$ 283.1083, found 283.1089.

Methyl 3-acetoxy-4-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)benzoate (2e):

Yield 89% (55.2 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.89 (s, 3 H), 3.88 (s, 3 H), 6.61 (d, *J* = 3.6 Hz, 1 H), 6.87 (d, *J* = 2.4 Hz, 1 H), 6.96 (dd, *J* = 8.4 Hz, 2.7 Hz, 1 H), 7.12 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.27 (d, *J* = 3.6 Hz, 1 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.97 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 8.35 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 52.5, 102.5, 117.0, 120.9, 125.4, 127.9, 128.3, 128.4, 129.2, 130.1, 134.7, 143.9, 145.1, 147.7, 165.6, 168.4; **HRMS** (ESI, m/z) calcd for $C_{17}H_{15}N_2O_4$ $[M+H]^+$ 311.1032, found 311.1035.

5-acetyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2f):

Yield 95% (55.9 mg); brown solid; the eluent composition: petroleum ether/ethyl acetate = 3:2; **mp** 60 – 62 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 2.66 (s, 3 H), 6.68 (d, *J* = 3.6 Hz, 1 H), 7.17 (dd, *J* = 7.2 Hz, 4.2 Hz, 1 H), 7.37 (d, *J* = 3.6 Hz, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.93 (d, *J* = 1.8 Hz, 1 H), 7.99 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.01 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.36 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 26.7, 102.6, 117.1, 120.9, 124.1, 126.6, 128.3, 128.4, 129.3, 134.7, 136.8, 143.9, 145.3, 147.7, 168.4, 196.2; **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}N_2O_3Na$ $[M+Na]^+$ 317.0902, found 317.0908.

5-cyano-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2g):

Yield 72% (39.9 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 68 – 70 °C (crystallization from DCM and hexane); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.02 (s, 3 H), 6.71 (d, *J* = 3.6 Hz, 1 H), 7.20 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.36 (d, *J* = 3.6 Hz, 1 H), 7.67 (d, *J* = 1.8 Hz, 1 H), 7.72 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 7.85 (d, *J* = 7.8 Hz, 1 H), 8.01 (dd, *J* = 7.8 Hz, 1.8 Hz, 1 H), 8.36 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 103.2, 111.6, 117.4, 117.6, 121.0, 128.0, 128.1, 129.2, 129.4, 130.4, 135.0, 144.0, 145.2, 147.6, 168.0; **HRMS** (ESI, m/z) calcd for $C_{16}H_{11}N_3O_2Na$ $[M+Na]^+$ 300.0749, found 300.0746.

5-fluoro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2h):

Yield 89% (48.1 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 7:3; **mp** 86 – 89 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.91 (s, 3 H), 6.64 (d, *J* = 3.6 Hz, 1 H), 7.11 (dd, *J* = 9.0 Hz, 2.7 Hz, 1 H), 7.13 – 7.17 (comp, 2 H), 7.28 (d, *J* = 3.6 Hz, 1 H), 7.58 (dd, *J* = 9.0 Hz, 6.0 Hz, 1 H), 7.99 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.36 (dd, *J* = 4.2 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.5, 101.7, 111.7 (d, $^2J_{F–C}$ = 25.5 Hz), 113.7 (d, $^2J_{F–C}$ = 22.5 Hz), 116.7, 120.6, 126.9 (d, $^4J_{F–C}$ = 4.5 Hz), 128.9, 129.1, 129.7 (d, $^3J_{F–C}$ = 10.5 Hz), 143.8, 146.8 (d, $^3J_{F–C}$ = 12.0 Hz), 148.0, 161.7 (d, $^1J_{F–C}$ = 247.5 Hz), 168.3; **HRMS** (EI, m/z) calcd for $C_{15}H_{11}FN_2O_2$ $[M]^+$ 270.0805, found 270.0812.

5-chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2i):

Yield 96% (55.1 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 59 – 60 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.94 (s, 3 H), 6.65 (d, *J* = 3.6 Hz, 1 H), 7.15 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.29 (d, *J* = 3.6 Hz, 1 H), 7.37 (d, *J* = 2.4 Hz, 1 H), 7.41 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 1 H), 7.98 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.35 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.5, 102.0, 116.8, 120.6, 124.4, 127.0, 128.6, 129.2, 129.4 (2 C), 133.8, 143.9, 146.2, 147.9, 168.3; **HRMS** (ESI, m/z) calcd for $C_{15}H_{11}ClN_2O_2Na$ $[M+Na]^+$ 309.0407, found 309.0418.

5-bromo-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2j):

Yield 94% (62.2 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **NMR** (600 MHz, $CDCl_3$) δ 1.94 (s, 3 H), 6.65 (d, *J* = 3.6 Hz, 1 H), 7.16 (dd, *J* = 7.8 Hz, 4.5 Hz, 1 H), 7.30 (d, *J* = 3.6 Hz, 1 H), 7.50 - 7.52 (comp, 2 H), 7.56 (dd, *J* = 8.4 Hz, 1.8 Hz, 1

H), 7.98 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H) , 8.35 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.5, 102.0, 116.8, 120.7, 121.3, 127.3, 128.6, 129.2, 129.7, 129.9 (2 C), 143.9, 146.2, 147.8, 168.3; **HRMS** (ESI, m/z) calcd for $C_{15}H_{11}BrN_2O_2Na$ $[M+Na]^+$ 352.9902, found 352.9902.

2,5-bis(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2k):

Yield 77% (56.7 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 46 – 48°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.96 (s, 3 H), 6.67 – 6.70 (comp, 2 H), 7.15 – 7.20 (comp, 2 H), 7.38 (d, *J* = 3.6 Hz, 1 H), 7.60 (d, *J* = 3.6 Hz, 1 H), 7.77 – 7.78 (m, 1 H), 7.89 – 7.91 (comp, 2 H), 7.99 – 8.02 (comp, 2 H), 8.38 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H), 8.42 (dd, *J* = 4.2 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 101.8, 102.6, 116.7, 117.1, 119.2, 120.7, 121.5, 121.8, 127.4, 128.3, 128.9, 129.1, 129.2, 129.3, 138.5, 143.8 (2 C), 146.2, 147.5, 148.0, 168.4; **HRMS** (ESI, m/z) calcd for $C_{22}H_{17}N_4O_2$ $[M+H]^+$ 369.1352, found 369.1347.

4-methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2l):

Yield 94% (50.1 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.91 (s, 3 H), 2.45 (s, 3 H), 6.62 (d, *J* = 3.6 Hz, 1 H), 7.14 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.21 (d, *J* = 8.4 Hz, 1 H), 7.28 (dd, *J* = 7.8 Hz, 2.4 Hz, 1 H), 7.30 (d, *J* = 3.6 Hz, 1 H), 7.41 (d, *J* = 2.4 Hz, 1 H), 7.98 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 8.37 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.5, 21.0, 101.4, 116.5, 120.6, 123.4, 129.0, 129.1, 129.2, 129.5, 130.2, 136.8, 143.7 (2 C), 148.0, 169.1; **HRMS** (ESI, m/z) calcd for $C_{16}H_{14}N_2O_2Na$ $[M+Na]^+$ 289.0953, found 289.0945.

4-methoxy-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2m):

Yield 96% (54.2 mg); colourless oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.91 (s, 3 H), 3.86 (s, 3 H), 6.63 (d, *J* = 3.6 Hz, 1 H), 7.01 (dd, *J* = 9.0 Hz, 3.3 Hz, 1 H), 7.13 – 7.15 (comp, 2 H), 7.23 (d, *J* = 9.0 Hz, 1 H), 7.32 (d, *J* = 3.6 Hz, 1 H), 7.98 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 8.37 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.5, 55.8, 101.6, 113.8, 114.3, 116.6, 120.6, 124.3, 128.9, 129.0, 131.1, 139.3, 143.8, 147.9, 157.7, 169.2; **HRMS** (ESI, m/z) calcd for $C_{16}H_{14}N_2O_3Na$ $[M+Na]^+$ 305.0902, found 305.0909.

Methyl 4-acetoxy-3-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)benzoate (2n):

Yield 92% (57.1 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.94 (s, 3 H), 3.95 (s, 3 H), 6.67 (d, *J* = 3.6 Hz, 1 H), 7.16 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.34 (d, *J* = 3.6 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 8.00 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.16 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.30 (d, *J* = 1.8 Hz, 1 H), 8.36 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 52.4, 102.1, 116.8, 120.7, 124.1, 128.7 (2 C), 129.2, 130.0, 130.2, 130.8, 143.9, 147.8, 149.4, 165.7, 168.1; **HRMS** (EI, m/z) calcd for $C_{17}H_{14}N_2O_4$ $[M]^+$ 310.0954, found 310.0937.

4-chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2o):

Yield 92% (52.8 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 9:1; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.93 (s, 3 H), 6.66 (d, *J* = 3.6 Hz, 1 H), 7.16 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.27 – 7.31 (comp, 2 H), 7.44 (dd, *J* = 9.0 Hz, 2.7 Hz, 1 H), 7.64 (d, *J* = 2.4 Hz, 1 H), 7.99 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 8.37 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 102.2, 116.9, 120.7, 125.0, 128.5, 128.7 (2 C), 129.2, 131.6, 131.7, 143.9, 144.4, 147.8, 168.5; **HRMS** (ESI, m/z) calcd for $C_{15}H_{11}N_2ClO_2Na$ $[M+Na]^+$ 309.0407, found 309.0408.

3-methoxy-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2p):

Yield 39% (22.0 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 48 – 50 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.78 (s, 3 H), 3.78 (s, 3 H), 6.64 (d, *J* = 3.6 Hz, 1 H), 6.94 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 7.01 (dd, *J* = 8.4 Hz, 0.9 Hz, 1 H), 7.12 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.23 (d, *J* = 3.6 Hz, 1 H), 7.46 (app t, *J* = 8.4 Hz, 1 H), 7.98 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.34 (dd, *J* = 4.8 Hz, 1.2 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.4, 56.2, 101.2, 109.8, 115.4, 116.2, 119.8, 120.4, 128.9, 129.5, 130.0, 143.5, 148.0, 148.3, 156.8, 168.9; **HRMS** (ESI, m/z) calcd for $C_{16}H_{15}N_2O_3$ $[M+H]^+$ 283.1083, found 283.1083.

Methyl 3-acetoxy-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)benzoate (2q):

Yield 32% (19.9 mg); yellow solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 68 – 70 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.91 (s, 3 H), 3.49 (s, 3 H), 6.66 (d, *J* = 3.6 Hz, 1 H), 7.12 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.24 (d, *J* = 3.6 Hz, 1 H), 7.50 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.59 (app t, *J* = 8.1 Hz, 1 H), 7.97 – 7.99 (comp, 2 H), 8.30 (dd, *J* = 4.8 Hz, 1.2 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 21.0, 52.2, 113.5, 116.5, 117.8, 126.6, 127.7,

128.2, 128.8, 129.3, 131.3, 132.9, 136.6, 144.4, 144.7, 166.6, 168.3; **HRMS** (EI, m/z) calcd for $C_{17}H_{14}N_2O_4$ $[M]^+$ 310.0954, found 310.0955.

3-methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2r):

Yield 28% (14.9 mg); yellow solid; the eluent composition: petroleum ether/ethyl acetate = 9:1; **mp** 79 – 80 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.83 (s, 3 H), 2.10 (s, 3 H), 6.65 (d, *J* = 3.6 Hz, 1 H), 7.12 – 7.14 (comp, 2 H), 7.18 (d, *J* = 3.6 Hz, 1 H), 7.31 (app d, *J* = 7.8 Hz, 1H), 7.42 (app t, *J* = 7.8 Hz, 1H), 8.00 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1 H), 8.35 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 17.8, 20.4, 101.3, 116.3, 120.2, 121.0, 128.5, 129.0, 129.1, 129.3, 129.8, 139.0, 143.8, 147.7, 148.0, 169.3; **HRMS** (EI, m/z) calcd for $C_{16}H_{14}N_2O_2$ $[M]^+$ 266.1055, found 266.1047.

2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)thiophen-3-yl acetate (2s):

Yield 82% (42.4 mg); brown oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 6.64 (d, *J* = 3.6 Hz, 1 H), 7.03 (d, *J* = 6.0 Hz, 1 H), 7.17 (dd, *J* = 7.8 Hz, 4.8 Hz, 1 H), 7.25 (d, *J* = 6.0 Hz, 1 H), 7.38 (d, *J* = 3.6 Hz, 1 H), 7.96 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.40 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.7, 102.6, 117.1, 120.8 (2 C), 121.4, 125.1, 129.2, 129.3, 140.2, 144.0, 148.4, 168.4; **HRMS** (ESI, m/z) calcd for $C_{13}H_{10}N_2O_2SNa$ $[M+Na]^+$ 281.0361, found 281.0357.

2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)furan-3-yl acetate (2t):

Yield 25% (12.1 mg); brown oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.14 (s, 3 H), 6.62 – 6.65 (comp, 2 H), 7.15 (dd, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.32 – 7.34 (comp, 2 H), 7.94 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 8.36 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.6, 103.1, 108.3, 117.3, 120.7, 128.1, 129.2, 129.4, 133.1, 138.5, 144.2, 148.5, 168.0; **HRMS** (ESI, m/z) calcd for $C_{13}H_{11}N_2O_3$ $[M+H]^+$ 243.0770, found 243.0768.

2-(3-chloro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate(2u):

Yield 92% (52.8 mg); brown oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.96 (s, 3 H), 7.23 (dd, *J* = 8.4 Hz, 4.5 Hz, 1 H), 7.33 (s, 1 H), 7.35 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.43 (app td, *J* = 7.8 Hz, 1.6 Hz, 1 H), 7.50 (app td, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.59 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.02 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 8.41

(dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 105.7, 117.1, 118.6, 124.0, 125.4, 126.8, 127.0, 128.6, 129.2, 129.8, 145.0, 145.8, 146.4, 168.6; **HRMS** (ESI, m/z) calcd for $C_{15}H_{11}ClN_2O_2Na$ $[M+Na]^+$ 309.0407, found 309.0403.

2-(3-bromo-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2v):

Yield 74% (49.0 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 76 – 78 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.96 (s, 3 H), 7.23 (dd, *J* = 8.4 Hz, 4.5 Hz, 1 H) 7.35 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.39 (s, 1 H), 7.43 (app td, *J* = 7.5 Hz, 1.6 Hz, 1 H), 7.50 (app td, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.59 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 7.95 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 8.40 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 90.6, 117.3, 120.1, 124.0, 126.8, 127.8, 127.9, 128.6, 129.2, 129.8, 145.0, 145.7, 146.9, 168.6; **HRMS** (ESI, m/z) calcd for $C_{15}H_{11}BrN_2O_2Na$ $[M+Na]^+$ 352.9902, found 352.9899.

2-(3-iodo-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2w):

Yield 88% (66.6 mg); yellow solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 90 – 91 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.96 (s, 3 H), 7.23 (dd, *J* = 8.4 Hz, 4.5 Hz, 1 H), 7.35 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.43 (app td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.45 (s, 1 H), 7.50 (app td, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.59 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.81 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 8.38 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 56.2, 117.5, 123.2, 124.0, 126.8, 128.6, 129.2, 129.6, 129.8, 132.7, 145.0, 145.7, 147.5, 168.6; **HRMS** (ESI, m/z) calcd for $C_{15}H_{11}IN_2O_2Na$ $[M+Na]^+$ 400.9763, found 400.9767.

2-(3-cyano-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2x):

Yield 88%(48.8 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 72 – 74 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.94 (s, 3 H), 7.31 – 7.38 (comp, 2 H), 7.43 – 7.48 (m, 1 H), 7.53 – 7.59 (comp, 2 H), 7.85 (s, 1 H), 8.16 (dd, *J* = 7.8 Hz, 1.6 Hz, 1 H), 8.47 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.5, 86.6, 114.5, 118.8, 119.5, 124.1, 126.9, 128.5 (2 C), 128.7, 130.2, 135.9, 145.7, 146.2, 146.9, 168.3; **HRMS** (EI, m/z) calcd for $C_{16}H_{11}N_3O_2$ $[M]^+$ 277.0851, found 277.0850.

2-(3-formyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2y):

Yield 80% (44.8 mg); yellow solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 70 – 72 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.93 (s, 3 H), 7.34 (dd, *J* = 8.4 Hz, 4.5

Hz, 1 H), 7.40 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 7.48 (app td, *J* = 7.8 Hz, 1.4 Hz, 1 H), 7.58 (app td, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.62 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 7.97 (s, 1 H), 8.46 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H), 8.67 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 10.08 (s, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 117.4, 117.9, 119.5, 124.1, 127.0, 128.6, 129.2, 130.2, 131.0, 139.0, 145.9 (2 C), 148.8, 168.6, 185.0; **HRMS** (EI, m/z) calcd for $C_{16}H_{12}N_2O_3$ $[M]^+$ 280.0848, found 280.0853.

2-(3-nitro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2z):

Yield 68%(40.4 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 152 – 153°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.98 (s, 3 H), 7.42 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 7.44 (dd, *J* = 9.0 Hz, 4.8 Hz, 1 H), 7.49 (app td, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.59 – 7.62 (m, 1 H), 7.63 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 8.34 (s, 1 H), 8.50 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H), 8.66 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.6, 113.4, 120.4, 124.2, 127.0, 128.2, 128.5, 128.6, 129.6, 130.6 (x 2), 145.7, 146.2, 146.5, 168.2; **HRMS** (EI, m/z) calcd for $C_{15}H_{11}N_3O_4$ $[M]^+$ 297.0750, found 297.0746.

2-(4-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2aa):

Yield 84% (55.2 mg); yellow solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 104 – 106°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.98 (s, 3 H), 6.86 (d, *J* = 3.0 Hz, 1 H), 7.26 (d, *J* = 4.8 Hz, 1 H), 7.37 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 7.39 (d, *J* = 3.6 Hz, 1 H), 7.44 – 7.47 (m, 1 H), 7.48 – 7.52 (comp, 2 H), 7.56 – 7.59 (comp, 2 H), 7.67 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 7.80 – 7.82 (comp, 2 H), 8.44 (d, *J* = 4.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.7, 101.1, 115.8, 118.7, 123.9, 126.8, 128.5, 128.6, 128.8, 128.9, 129.2, 130.7, 137.5, 138.7, 142.4, 144.1, 145.9, 148.6, 168.9; **HRMS** (EI, m/z) calcd for $C_{21}H_{16}N_2O_2$ $[M]^+$ 328.1212, found 328.1205.

2-(5-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2ab):

Yield 76% (49.9 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 69 – 71°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.99 (s, 3 H), 6.71 (d, *J* = 3.6 Hz, 1 H), 7.37 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 7.38 (d, *J* = 3.6 Hz, 1 H), 7.40 – 7.42 (m, 1 H), 7.47 (app td, *J* = 7.5 Hz, 1.6 Hz, 1 H), 7.49 – 7.53 (comp, 3 H), 7.66 – 7.68 (comp, 3 H), 8.18 (d, *J* = 2.4 Hz, 1 H), 8.63 (d, *J* = 2.4 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.7, 101.8, 120.7,

123.9, 126.8, 127.2, 127.4, 127.5, 128.7, 128.9, 129.0, 129.8, 130.4, 130.6, 139.4, 143.1, 145.8, 147.5, 168.8; **HRMS** (EI, m/z) calcd for $C_{21}H_{16}N_2O_2$ $[M]^+$ 328.1212, found 328.1212.

2-(5-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2ac):

Yield 57% (40.8 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.95 (s, 3 H), 3.87 (s, 3 H), 6.65 (d, *J* = 3.6 Hz, 1 H), 7.00 – 7.04 (comp, 2 H), 7.31 – 7.34 (comp, 2 H), 7.42 – 7.48 (comp, 2 H), 7.54 – 7.57 (comp, 2 H), 7.63 (dd, *J* = 7.5 Hz, 2.0 Hz, 1 H), 8.09 (d, *J* = 2.1 Hz, 1 H), 8.54 (d, *J* = 2.1 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.6, 55.3, 101.7, 114.4, 120.6, 123.8, 126.7, 126.9, 128.4, 128.6, 128.7, 129.6, 130.0, 130.5, 131.8, 142.8, 145.8, 147.1, 159.0, 168.8; **HRMS** (ESI, m/z) calcd for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1396, found 359.1397.

2-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2ad):

Yield 69% (35.1 mg); brown oil; the eluent composition: petroleum ether/ethyl acetate = 7:3; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.05 (s, 3 H), 3.15 (t, *J* = 8.4 Hz, 2 H), 3.97 (t, *J* = 8.4 Hz, 2 H), 6.57 (dd, *J* = 7.2 Hz, 5.1 Hz, 1 H), 7.22 (dd, *J* = 7.8 Hz, 2.1 Hz, 1 H), 7.24 (app td, *J* = 7.8 Hz, 1.6 Hz, 1 H), 7.28 (app td, *J* = 7.5 Hz, 1.8 Hz, 1 H), 7.31 – 7.33 (m, 1 H), 7.45 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.91 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.9, 26.3, 51.1, 113.6, 123.2, 123.8, 125.6, 126.0, 126.5, 131.6, 134.2, 145.7, 146.0, 160.7, 169.0; **HRMS** (EI, m/z) calcd for $C_{15}H_{14}N_2O_2$ $[M]^+$ 254.1055, found 254.1058.

5-acetyl-2-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate(2ae):

Yield 57% (33.8 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 7:3; **mp** 74 – 76°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.10 (s, 3 H), 2.59 (s, 3 H), 3.18 (t, *J* = 8.4 Hz, 2 H), 4.05 (t, *J* = 8.4 Hz, 2 H), 6.65 – 6.67 (m, 1 H), 7.37 – 7.39 (m, 1 H), 7.60 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 7.80 (s, 1 H), 7.86 (app dt, *J* = 8.4 Hz, 1.8 Hz, 1 H), 7.95 (d, *J* = 5.4 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 21.0, 26.4, 26.5, 50.7, 114.8, 123.2, 123.8, 124.4, 126.5, 132.0, 133.4, 138.8, 143.7, 145.9, 159.5, 168.8, 196.2; **HRMS** (ESI, m/z) calcd for $C_{17}H_{16}N_2O_3Na$ $[M+Na]^+$ 319.1059, found 319.1056.

5-chloro-2-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl acetate (2af):

Yield 61% (35.2 mg); brown oil; the eluent composition: petroleum ether/ethyl acetate = 7:3; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.02 (s, 3 H), 3.13 (t, *J* = 8.4 Hz, 2 H), 3.91 (t, *J* = 8.4 Hz, 2

H), 6.56 (dd, *J* = 7.2 Hz, 5.2 Hz, 1 H), 7.20 – 7.24 (comp, 2 H), 7.29 – 7.32 (m, 1 H), 7.34 – 7.38 (m, 1 H), 7.87 (dd, *J* = 5.4 Hz, 1.2 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.8, 26.2, 50.9, 113.9, 123.1, 124.2, 126.2, 126.6, 130.5, 131.7, 133.0, 145.8, 145.9, 160.4, 168.5; **HRMS** (EI, m/z) calcd for $C_{15}H_{13}ClN_2O_2$ $[M]^+$ 288.0666, found 288.0670.

2-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)-5-iodophenyl acetate (2ag):

Yield 58% (44.1 mg); brown oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.04 (s, 3 H), 3.15 (t, *J* = 8.4 Hz, 2 H), 3.94 (t, *J* = 8.4 Hz, 2 H), 6.59 (dd, *J* = 6.6 Hz, 5.1 Hz, 1 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 7.33 (dd, *J* = 7.2 Hz, 1.2 Hz, 1 H), 7.55 (d, *J* = 1.8 Hz, 1 H), 7.56 – 7.58 (m, 1 H), 7.90 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H);**^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.9, 26.3, 50.8, 88.1, 114.0, 123.2, 126.7, 131.8, 132.8, 134.3, 135.5, 145.8, 145.9, 160.2, 168.6; **HRMS** (EI, m/z) calcd for $C_{15}H_{13}IN_2O_2$ $[M]^+$ 380.0022, found 380.0022.

2-(1*H*-pyrazolo[3,4-*b*]pyridin-1-yl)phenyl acetate (2ah):

Yield 94% (47.6 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 7:3; 39 – 40 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.04 (s, 3 H), 7.23 (dd, *J* = 7.8 Hz, 4.5 Hz, 1 H), 7.37 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 7.45 (app td, *J* = 7.5 Hz, 1.6 Hz, 1 H), 7.49 (app td, *J* = 1.8 Hz, 7.2 Hz, 1 H), 7.80 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 8.16 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 8.24 (s, 1 H), 8.60 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.9, 116.1, 117.6, 124.3, 126.4, 127.6, 128.9, 130.2, 130.5, 134.4, 144.9, 149.4, 150.6, 168.8; **HRMS** (EI, m/z) calcd for $C_{14}H_{11}N_3O_2$ $[M]^+$ 253.0851, found 253.0847.

2-(5-bromo-1*H*-pyrazolo[3,4-*b*]pyridin-1-yl)phenyl acetate (2ai):

Yield 56% (37.2 mg); yellow oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.06 (s, 3 H), 7.38 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 7.45 (app td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.52 (app td, *J* = 7.8 Hz, 1.4 Hz, 1 H), 7.76 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H), 8.20 (s, 1 H), 8.29 (d, *J* = 2.4 Hz, 1 H), 8.62 (d, *J* = 2.4 Hz, 1 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 20.9, 113.4, 117.5, 124.3, 126.5, 127.6, 129.3, 130.1, 132.0, 133.6, 144.8, 149.0, 150.2, 168.6; **HRMS** (ESI, m/z) calcd for $C_{14}H_{10}BrN_3O_2Na$ $[M+Na]^+$ 353.9854, found 353.9856.

2-(9*H*-pyrido[2,3-*b*]indol-9-yl)phenyl acetate (2aj):

Yield 89% (53.8 mg); viscous oil; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 132 – 134°C **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.62 (s, 3 H), 7.22 – 7.29 (comp, 2 H), 7.33 (app t, *J* = 7.5 Hz, 1 H), 7.42 – 7.50 (comp, 3 H), 7.55 (app td, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.64 (dd, *J* = 7.8 Hz, 1.8 Hz, 1 H), 8.11 (app d, *J* = 7.5 Hz, 1 H), 8.38 (dd, *J* = 7.5 Hz, 1.8 Hz, 1 H), 8.49 (dd, *J* = 4.8 Hz, 1.8 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.3, 110.6, 116.1, 116.2, 120.8 (3 C), 124.2, 126.7, 127.0, 128.2, 128.3, 129.2, 129.9, 139.8, 146.5, 147.1, 151.8, 168.2; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}N_2O_2Na$ $[M+Na]^+$ 325.0953, found 325.0957.

1-(pyrimidin-2-yl)indolin-7-yl acetate (4a):

Yield 86% (43.9 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 132 – 134°C (crystallization from chloroform and hexane); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 3.15 (t, *J* = 8.1 Hz, 2 H), 4.42 (t, *J* = 7.8 Hz, 2 H), 6.73 (t, *J* = 4.8 Hz, 1 H), 7.02 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 7.13 (dd, *J* = 1.2 Hz, 6.6 Hz, 1 H), 8.43 (d, *J* = 4.8 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 21.4, 29.2, 52.3, 112.3, 122.0, 122.8, 123.8, 134.9, 136.8, 139.1, 157.5, 160.0, 168.8; **HRMS** (ESI, m/z) calcd for $C_{14}H_{13}N_3O_2Na$ $[M+Na]^+$ 278.0905 found 278.0903.

3-methyl-1-(pyrimidin-2-yl)indolin-7-yl acetate (4b):

Yield 65% (35.0 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 7:3; **mp** 78 – 80°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.32 (d, *J* = 6.9 Hz, 3 H), 2.09 (s, 3 H), 3.45 (sex, *J* = 7.2 Hz, 1 H), 3.88 (dd, *J* = 11.4 Hz, 7.5 Hz, 1 H), 4.59 (dd, *J* = 11.4 Hz, 8.4 Hz, 1 H), 6.69 (t, *J* = 4.8 Hz, 1 H), 6.98 – 7.08 (comp, 3 H), 8.39 (d, *J* = 4.8 Hz, 2 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 18.7, 21.4, 35.8, 60.0, 112.2, 120.8, 122.9, 124.0, 134.5, 139.0, 141.8, 157.5, 160.0, 168.8; **HRMS** (ESI, m/z) calcd for $C_{15}H_{15}N_3O_2Na$ $[M+Na]^+$ 292.1062, found 292.1064.

2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl acetate (4c):

Yield 62% (41.1 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 4:1; **mp** 119 – 121°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.18 (s, 3 H), 3.04 (dd, *J* = 15.6 Hz, 1.8 Hz, 1 H), 3.89 (dd, *J* = 15.6 Hz, 9.6 Hz, 1 H), 5.97 (*J* = 9.0 Hz, 1 H), 6.75 (t, *J* = 4.8 Hz, 1 H), 7.07 – 7.09 (comp, 3 H), 7.25 – 7.27 (comp, 1 H), 7.33 – 7.36 (comp, 2 H), 7.43 – 7.44 (comp, 2 H), 8.42 (d, *J* = 4.8 Hz, 2 H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 21.5, 38.7, 66.4,

112.8, 122.3, 123.1, 124.3, 125.5, 127.2, 128.6, 134.8, 135.0, 139.4, 143.2, 157.6, 160.1, 169.0; **HRMS** (ESI, m/z) calcd for $C_{20}H_{17}N_3O_2Na$ $[M+Na]^+$ 354.1218, found 354.1214.

4-methoxy-1-(pyrimidin-2-yl)indolin-7-yl acetate (4d):

Yield 89% (50.8 mg); colourless solid; the eluent composition: petroleum ether/ethyl acetate = 3:1; **mp** 76 – 78°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.08 (s, 3 H), 3.04 (t, *J* = 8.1 Hz, 2 H), 3.84 (s, 3 H), 4.39 (t, *J* = 8.0 Hz, 2 H), 6.59 (d, *J* = 9.0 Hz, 1 H), 6.70 (t, *J* = 4.8 Hz, 1 H), 6.96 (d, *J* = 9.0 Hz, 1 H), 8.40 (d, *J* = 4.5 Hz, 2 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 21.2, 26.0, 52.5, 55.6, 106.0, 112.2, 122.9, 123.4, 133.0, 135.9, 153.2, 157.3, 160.0, 169.2; **HRMS** (EI, m/z) calcd for $C_{15}H_{15}N_3O_3$ $[M]^+$ 285.1113, found 285.1102.

Derivatization of acetoxylated indoline 4a:

Synthesis of 1-(pyrimidin-2-yl)-1*H*-indol-7-yl acetate (5):

Following a literature procedure,[10c] a mixture of **4a** (160.0 mg, 0.6 mmol) and DDQ (356.0 mg, 2.0 equiv.) was placed in an oven dried 20 mL schlenk tube and to it was added anhydrous 1, 4-dioxane (7.8 mL) under nitrogen. Then it was slowly heated to 90 °C (oil bath temperature) while stirring for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified through column chromatography on silica gel using ethyl acetate/pet ether (1:9) as eluent to obtain 1-(pyrimidin-2-yl)-1*H*-indol-7-yl acetate (5) in 89% yield (142.0 mg). Brown solid; **mp** 74 – 76 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.19 (s, 3 H), 6.73 (d, *J* = 3.6 Hz, 1 H), 7.03 (dd, *J* = 7.5 Hz, 1.2 Hz, 1 H), 7.12 (t, *J* = 4.8 Hz, 1 H), 7.23 (app t, *J* = 7.8 Hz, 1 H), 7.52 (dd, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.99 (d, *J* = 3.6 Hz, 1 H), 8.70 (d, *J* = 4.8 Hz, 2 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 21.4, 107.0, 117.1, 118.3, 119.0, 122.5, 126.6, 129.6, 134.6, 137.5, 157.4, 158.2, 169.1; **HRMS** (EI, m/z) calcd for $C_{14}H_{11}N_3O_2Na$ $[M+Na]^+$ 276.0749, found 276.0745.

Synthesis of 1*H*-indol-7-ol (6):

A mixture of **5** (43.0 mg, 0.17 mmol) and sodium methoxide (45.9 mg, 5.0 equiv.) was placed in an 10 mL oven dried schlenk tube and it was evacuated and backfilled with nitrogen (3 times). To it was added anhydrous DMSO (2.0 mL) under nitrogen and the tube was evacuated and backfilled with nitrogen (3 times) again. Next it was slowly heated to 100 °C (oil bath temperature) while stirring for 12 h. After cooling to room temperature, the reaction mixture was extracted with ethylacetate and water. The combined organic layers were

concentrated under reduced pressure and the residue was purified through column chromatography on silica gel using ethyl acetate/pet ether (1:4) as eluent to obtain 1*H*-indol-7-ol (6) in 73% yield (16.5 mg). Colourless solid; **mp** 78 – 79 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.23 (br s, 1 H), 6.55 (app t, *J* = 2.7 Hz, 1 H), 6.58 (d, *J* = 7.2 Hz, 1 H), 6.96 (app t, *J* = 7.8 Hz, 1 H), 7.21 (app t, *J* = 2.7 Hz, 1 H), 7.26 (d, *J* = 7.8 Hz, 1 H), 8.41 (br s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 102.9, 106.4, 113.7, 120.1, 124.2, 125.7, 130.1, 141.4. **MS** (EI, m/z) calcd for C_8H_7NO 133, found 133 (100%), 104 (80%), 77 (60%). The data is in good agreement with literature.[11]

1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl acetate (7):

(Obtained as side product during optimization, Table 1, entry 19-21): Yellow solid; **mp** 42 – 44°C; the eluent composition: petroleum ether/ethyl acetate = 7:3; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.42 (s, 3 H), 7.19 (dd, *J* = 7.8 Hz, 4.5 Hz, 1 H), 7.34 – 7.37 (m, 1 H), 7.54 (app t, *J* = 8.1 Hz, 2 H), 7.73 (s, 1 H), 7.77 (app d, *J* = 7.2 Hz, 2 H), 7.96 (dd, *J* = 8.4 Hz, 1.5 Hz, 1 H), 8.43 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR**(150 MHz, $CDCl_3$) δ 21.0, 114.1, 116.7, 116.9, 124.1, 126.4, 126.6, 129.4 (2 C), 138.0, 143.8, 144.5, 168.4; **HRMS** (EI, m/z) calcd for $C_{15}H_{12}N_2O_2$ $[M]^+$ 252.0899, found 252.0900.

2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)-1,3-phenylene diacetate (8):

(Obtained as side product during optimization, Table 1, entry 13): Yellow oil; the eluent composition: petroleum ether/ethyl acetate = 3:1; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.85 (s, 6 H), 6.61 (d, *J* =3.6 Hz, 1 H), 7.10 – 7.16 (comp, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 7.50 (t, *J* = 8.4 Hz, 1 H), 7.95 (dd, *J* = 7.8 Hz, 1.8 Hz, 1 H), 8.33 (dd, *J* = 4.8 Hz, 1.5 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.3, 101.9, 116.6, 120.2, 121.0, 123.2, 124.1, 128.9, 129.0, 143.8, 147.9, 148.0, 168.4; **HRMS** (ESI, m/z) calcd for $C_{17}H_{15}N_2O_4$ $[M+H]^+$ 311.1032, found 311.1029.

Mechanistic experiments:

(a) Procedure for H/D exchange experiment:

An oven dried 10 mL schlenk tube was charged with *N*-phenyl-7-azaindole (**1a**) (0.2 mmol, 38.8 mg) and catalyst $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5.0 mol%, 8.3 mg). The tube was evacuated and backfilled with nitrogen and to it was added anhydrous DCE (2.0 mL, 0.1 M) under nitrogen atmosphere. The reaction mixture was degassed and backfilled with nitrogen 3

times. It was then closed with teflon-lined cap and kept for stirring at 40 °C (pre heated oil bath temperature) for 15 min. Then reaction mixture was cooled to ambient temperature and under nitrogen D_2O (1.0 mL, 20 equiv.) was added and stirred at 40 °C for another 15 min. After that reaction mixture was filtered through a short pad of celite and the solvent was removed under reduced pressure. Saturated sodium bicarbonate solution was added to the reaction mixture followed by extraction with ethyl acetate and water. The combined organic layers were concentrated and the starting material (**1a**-d_n) was recovered (38.4 mg, 99%) by purifying through column chromatography on silica gel using ethyl acetate/pet ether as eluent. The deuterium incorporation (42%) was determined by ^{1}H NMR spectroscopy (See SI for details).

(b) Procedure for identification of rhodacycle A:

An ovendried 10 mL schlenk tube was charged with *N*-phenyl-7-azaindole (**1a**) (0.1 mmol, 19.4 mg) and catalyst $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.1 mmol, 83.3 mg). The tube was evacuated and backfilled with nitrogen and to it was added anhydrous DCE (1.0 mL, 0.1 M) under nitrogen atmosphere. The reaction mixture was degassed and backfilled with nitrogen 3 times. It was then closed with teflon-lined cap and kept for stirring at 40 °C (pre heated oil bath temperature) for 30 min. Then reaction mixture was cooled to ambient temperature and filtered through celite. Then the solvent was removed under reduced pressure and the crude reaction mixture was subjected for mass analysis (ESI, m/z). Strong peaks at 431(M^+) and 432 ($M+H^+$) clearly indicated the formation of desired complex **A**. However, attempts for isolation of the same were failed (See SI for details).

(c) Procedure for parallel experiment between 1a and 1a-d_5:

Two sets of parallel reactions (four each) of **1a** and **1a**-d_5 (all 0.2 mmol scale) were subjected under standard condition in 10 mL oven dried schlenk tubes. The reactions were quenched with ethyl acetate by putting in an ice-bath at four different time intervals. 0.2 mmol of tridecane (internal standard) was added in each reaction mixture and the percentage conversion was monitored by GC analysis. Primary kineic isotopic effect (KIE) was found to be 1.2 (See SI for details).

(d) Procedure for competitive experiment between 1d and 1e:

To an oven dried 10 mL schlenk tube a mixture of **1d** (22.4 mg, 0.1 mmol) and **1e** (25.2 mg, 0.1 mmol) were subjected under standard condition. After 6 h, the reaction was stopped and

cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. Saturated sodium bicarbonate solution was added to the reaction mixture followed by extraction with ethylacetate and water. The combined organic layers were concentrated and purified through column chromatography on silica gel using ethyl acetate/pet ether as eluent to obtain a mixture of **2d** and **2e** (48.0 mg, 81% combined yield). The ratio of both the products (**2d**:**2e**=1:1.1) was determined by ^{1}H NMR spectroscopy (See SI for details).

AUTHOR CONTRIBUTION

† A. M. and T. K. V. contributed equally.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. http://pubs.acs.org.

Additional screening data, mechanistic experimentaldetails, single crystal X-ray structure of **2g** and **4a**, as well as ^{1}H and ^{13}CNMR spectra of all new compounds (PDF).

Single crystal X-ray diffraction data for compounds **2g** and **4a** (CIF).

AUTHOR INFORMATION

Corresponding Author

*E-mail: indubhusandeb@iicb.res.in, indubhusandeb@gmail.com

Notes

The authors declare no competing financial interest.

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