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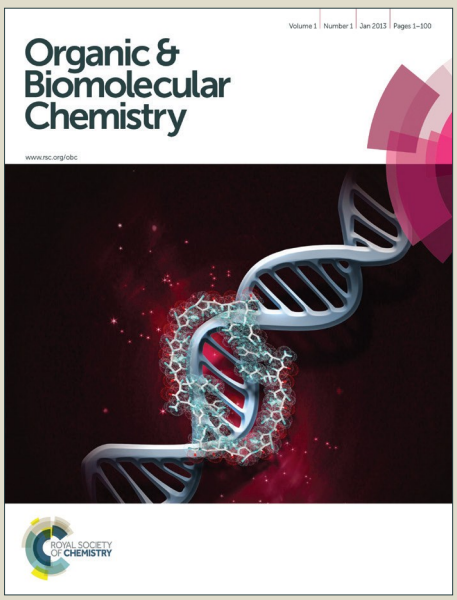

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ARTICLE TYPE

Rhodium(III)-catalyzed C–C coupling of 7-azaindoles with vinyl acetates and allyl acetates

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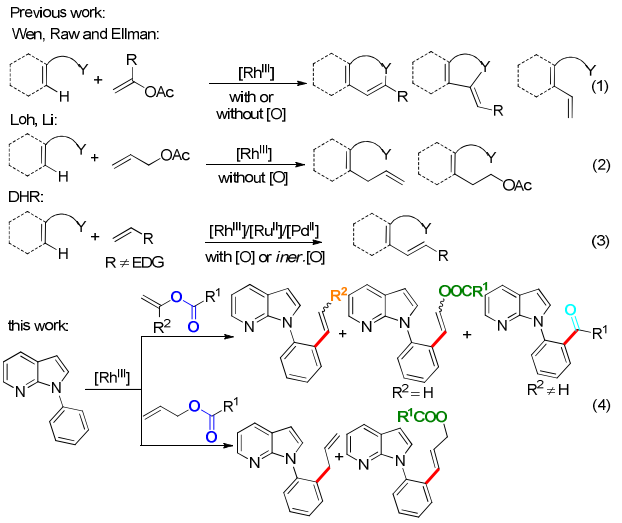
The behaviour of electron-rich alkenes with 7-azaindoles in rhodium(III)-catalyzed C–H activation is investigated. Various substituted vinyl acetates and allyl acetates as coupling partners reacted smoothly providing a wide variety of 7-azaindole derivatives, and the selectivity of the coupling reaction is alkene-dependent. In addition, the approaches of rhodium(III)-catalyzed dehydrogenative Heck-type reaction (DHR) and carbonylation reaction were quite novel and simple.

The azaindole ring system, particularly the structural moiety of 7-azaindoles, is one of the most valuable units present in many biologically active natural products.[1-4] However, only limited methods were developed in functional group modifications of 7-azaindoles with the aid of transition metals.[5,6] Given the unique structure of 7-azaindoles, the development of new protocols for efficient utilities of the motif could be highly desirable.

Recently, a number of methodologies were established to generate the diversity of heterocyclic scaffolds via rhodium-catalyzed C–C coupling between arenes and alkenes.[7-9] However, reports on rhodium(III)-catalyzed C–H activation of substituted vinyl acetates mostly afforded functionalized olefinated products, in which vinyl acetate serves as an acetylene equivalent (Scheme 1, eq 1).[8] While, it was also found that allyl acteates generally provided allylated or alkylated products (Scheme 1, eq 2).[9] To our knowledge, transition-metal-catalyzed dehydrogenative Heck-type reactions (DHR) (Scheme 1, eq 3) are usually the oxidative coupling of sp^2 C–H and reactive electron-withdrawing olefins or ethylene by using external oxidants,[10] while only few examples through internal oxidants.[11] Therefore, there is increased interest in investigating DHR of electron-rich alkenes and 7-azaindoles owing to its usability and accessibility.

Herein, we describe a novel rhodium(III)-catalyzed C–H activation of 7-azaindoles with less-reactive electron-rich alkenyl esters and allyl acetates to provide unexpected DHR and carbonyl products besides other 7-azaindole derivatives, that the selectivity of the coupling reaction is depended on alkenes (Scheme 1, eq 4).



Scheme 1 Rhodium(III)-catalyzed C–H bonds activation.

Results and Discussion

We began our study by examining the potential reaction of 7-azaindole **1a** and vinyl acetate **2a** (Table 1). Only trace amount of olefinated product **3aa** and unexpected DHR product **4aa** were detected when the reaction was carried out under $[Cp^*RhCl_2]_2/AgSbF_6$ catalyst system, which was reported by Ellman for the preparation of styrene derivatives (entry 1).[8c] To our delight, the highly efficient preformed cationic $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ catalyst could increase the yields of each product (entry 2). Indeed, the solvent was very essential for producing products selectively, in which dioxane was the optimal solvent (entries 3-5). Satisfyingly, the yield of **4aa** was improved enormously when we increased the loading of **2a** as co-solvent (entry 6). In addition, the reaction gave the best total yields in 98% even when the catalyst loading was reduced to 3 mol % (entry 7). However, no better results were obtained with the attempt to further lower the loading of catalyst (entries 8 and 9).

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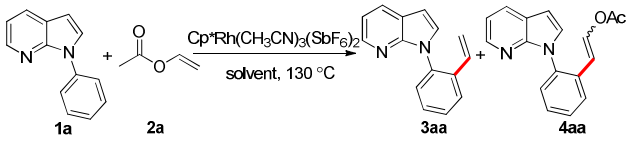
Table 1 Optimization of the reaction conditions[a]



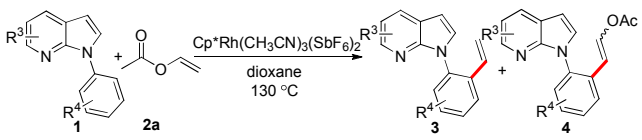
Entry	Catalyst/[equiv]	Additive	Solvent	Yield[b] [%] 3aa	4aa
1[c]	$[Cp^*RhCl_2]_2$/0.05	$AgSbF_6$	MeOH	8	7
2	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.05	–	toluene	10	32
3	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.05	–	dioxane	15	35
4	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.05	–	DMF	8	10
5	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.05	–	*t*AmOH	22	20
6[d]	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.05	–	dioxane	25	70
7[d]	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.03	–	dioxane	38	60
8[d]	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.02	–	dioxane	22	40
9[d]	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$/0.01	–	dioxane	10	25

[a] Reaction conditions unless otherwise specified: 0.1 mmol of **1a**, 1.0 mmol of **2a**, 1.0 mL of solvent, 130 °C, Ar atmosphere. [b] Isolated yield. [c] The same conditions as reported: 5 mol % of $[Cp^*RhCl_2]_2$, 20 mol % of $AgSbF_6$, 0.5 mL of **2a**, 0.5 mL of MeOH, 24 h. [d] 0.5 mL of **2a**.

With the optimized conditions in hand, we first examined the scope of substituted 7-azaindoles. As shown in Table 2, a range of 7-azaindoles with diverse *N*-aryl groups were explored. The substrates with halogen on pyridine ring (**1b** and **1c**) reacted smoothly with vinyl acetate **2a** delivering corresponding products in excellent total yields, and giving DHR products and olefinated products in better ratios. In addition, the dialkenylation product **5** was obtained in the reaction. Moreover, the functionalized alkene substituted substrate **1d** and alkyl substituted substrate **1e** also showed good reactivity. In contrast, azaindole fused with an array of diversely substituted phenyl rings (**1f**, **1g** and **1h**) underwent the optimized conditions to deliver the corresponding products in excellent total yields (entries 5-7).

To further highlight the applicability of this procedure, we explored the scope with respect to various substituted electron-rich alkenyl esters (Table 3). The present process showed wide substrate tolerance with alkenyl esters. Due to other alkenyl esters were less active than vinyl acetate, we raised the catalyst loading up to 5 mol %. Vinyl butyrate **2b** and vinyl pivalate **2c** both reacted without incident under the reaction conditions to give the same olefinated product **3aa** in 46% and 40% yields, respectively. In contrast, the DHR products **4ab** and **4ac** were also formed in moderate yields. In addition, vinyl aromatic esters **2d** and **2e** also have the similar high reactivity, providing two kinds of products with total yields up to 98%. Importantly, methyl and phenyl substituents on vinyl (**2f** and **2g**) were well tolerated, and the corresponding *ortho*-olefination products (**3af** and **3ag**) were constructed effectively. Particularly, acetyl substituted 7-azaindole **6** was generated under this reaction system.[12,13]

Table 2 Reaction scope of 7-azaindole derivatives[a]



Entry	7-Azaindole **1**	Yield[b] [%]
1	**1b**	**3ba**, 25; **4ba**, 68 (*Z*:*E* = 1:9)
2	**1c**	**3ca**, 14; **4ca**, 70 (*Z*:*E* = 2:1); **5**, 8 (*Z*:*E* = 1:2)
3	**1d**	**3da**, 20; **4da**, 75 (*Z*:*E* = 1:1.1)
4	**1e**	**3ea**, 20; **4ea**, 32 (*Z*:*E* = 1:2)
5	**1f**	**3fa**, 40; **4fa**, 50 (*Z*:*E* = 1:1.5)
6	**1g**	**3ga**, 43; **4ga**, 50 (*Z*:*E* = 1:2)
7	**1h**	**3ha**, 25; **4ha**, 66 (*Z*:*E* = 1:1.2)

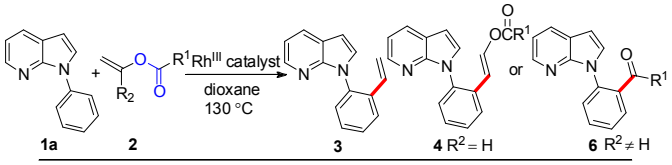
[a] General reaction conditions unless otherwise specified: 0.1 mmol of **1**, 0.5 mL of **2a**, 3 mol % of $Cp^*Rh(CH_3CN)_3(SbF_6)_2$, 1.0 mL of dioxane, 130 °C, Ar atmosphere. [b] Isolated yield. Ratios of Z/E are given within parentheses and were determined by ^1H NMR analysis.

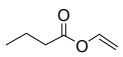
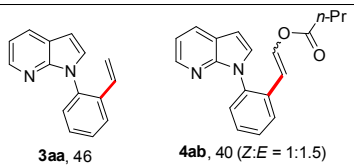
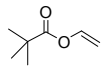
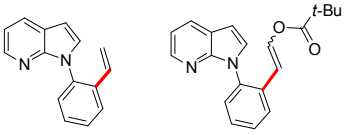
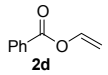
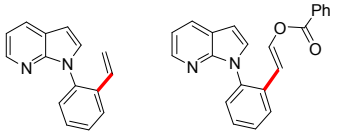
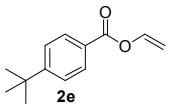
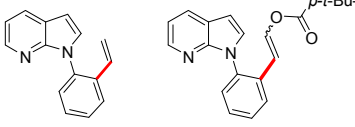
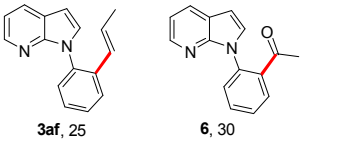
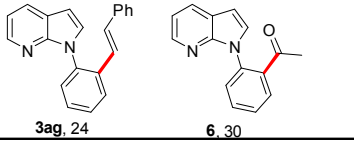
To our delight, allyl electrophiles **7a** and **7b** were tolerated in this reaction giving the allylation product **8** (which can be transformed to more stable olefinated product **3af**) both in 70% yield (Table 4). It's worth mentioning that the DHR products (**4ah** and **4ai**) were also observed in the reactions.

In order to better illustrate the synthetic utility of the DHR products, further transformations were conducted (Scheme 2). Surprisingly, benzaldehyde derivative **9** was formed when DHR product **4aa** was treated with NaOH under air, while enol tautomerism product phenylacet-aldehyde was not observed (eq 5). However, only a trace amount of product **9** and a mixture of unidentified products were observed when the reaction was performed under Ar atmosphere. In contrast, DHR products **4ah** reacted smoothly under the same conditions to give the corresponding hydrolysis product **10** in 99% yield (eq 6). These evidences indicate that the enol as the hydrolysis product from **4aa** is just an unstable intermediate which could be further oxidized by oxygen to provide benzaldehyde **9**.[13,14]

Moreover, to figure out the relationship of the DHR and olefinated products, some experiments were conducted (Scheme 3). When **3aa** was explored as a substrate under the standard conditions in the presence or absence of vinyl acetate **2a**, **4aa** was

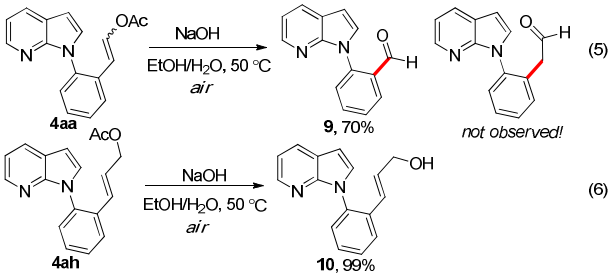
Table 3 Scope of electron-rich alkenyl esters[a]



Entry	Alkene **2**	Yield[b] [%]
1.	 **2b**	 **3aa**, 46 **4ab**, 40 (*Z*:*E* = 1:1.5)
2.	 **2c**	 **3aa**, 40 **4ac**, 37 (*Z*:*E* = 1:5)
3.	 **2d**	 **3aa**, 48 **4ad**, 50
4.	 **2e**	 **3aa**, 35 **4ae**, 45 (*Z*:*E* = 1:6)
5.	 **2f**	 **3af**, 25 **6**, 30
6.	 **2g**	 **3ag**, 24 **6**, 30

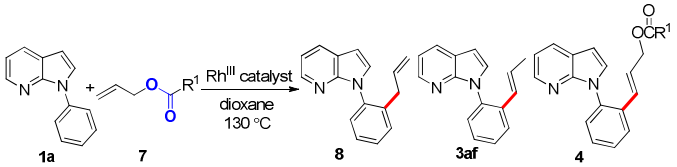
[a] General reaction conditions unless otherwise specified: 0.1 mmol of **1a**, 10 equiv of **2**, 5 mol % of Cp*Rh(CH$_3$CN)$_3$(SbF$_6$)$_2$, 1.4 mL of dioxane, 130 °C, Ar atmosphere, Rh^{III} = Cp*Rh(CH$_3$CN)$_3$(SbF$_6$)$_2$. [b] Isolated yield. Ratios of Z/E are given within parentheses and were determined by ^{1}H NMR analysis.

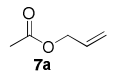
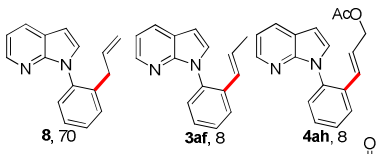
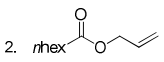
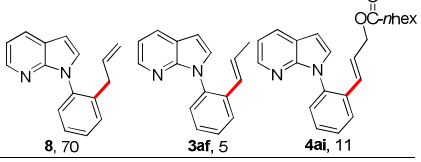
not observed (eqs 7 and 8). In contrast, the reaction did not take place at all when using **4aa** as a substrate (eq 9). These indicate that **3aa** and **4aa** have no relationship in this catalytic system.



Scheme 2 Synthetic applications of the DHR products. Reaction conditions: NaOH (2 equiv), EtOH/H$_2$O (1:1), 50 °C, under air, 3 h.

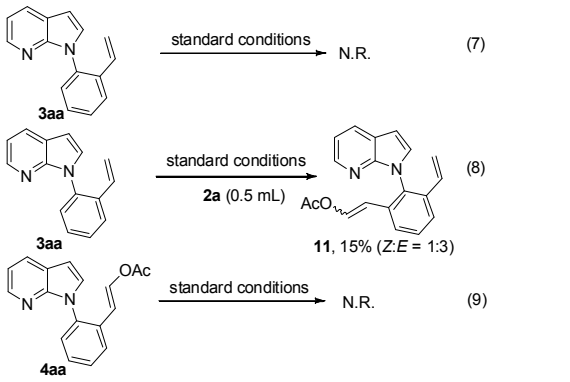
Table 4 Scope of allyl acetates[a]



Entry	Allyl acetate **7**	Yield[b] [%]
1.	 **7a**	 **8**, 70 **3af**, 8 **4ah**, 8
2.	 **7b**	 **8**, 70 **3af**, 5 **4ai**, 11

[a] General reaction conditions unless otherwise specified: 0.1 mmol of **1a**, 10 equiv of **7**, 5 mol % of Cp*Rh(CH$_3$CN)$_3$(SbF$_6$)$_2$, 1.4 mL of dioxane, 130 °C, Ar atmosphere, Rh^{III} = Cp*Rh(CH$_3$CN)$_3$(SbF$_6$)$_2$. [b] Isolated yield.

We proposed a plausible mechanism based on these results (Scheme 4).[8c,12,13,15] The pathway begins with C–H activation to form a six-membered rhodacycle species **I**. Then, the vinyl acetate coordinates to rhodacycle species **I** to form intermediate **II**. Regioselective insertion of vinyl acetate into the Rh–C bond from intermediate **II** gives rhodacycle species **III**, which undergoes *β*–H elimination to give rhodium-hydride **IV**. Reinsertion of the Rh-H bond provides more stable seven-membered metallacycle **V**. Elimination of acetate affords styrene product **3aa** (path A). Intermediate **V** might undergo *β*–H elimination to afford **4aa** and Rh(I) species, and the latter can be reoxidized to rhodium(III) catalyst to allow the reaction cycle to continue (path B). However, the oxidant is still unclear right now, and further mechanistic studies will be required to elucidate the mechanism for oxidation. In addition, although the mechanistic details of producing of the product **6** are not clear, we proposed a plausible mechanism in the supporting information.[13]

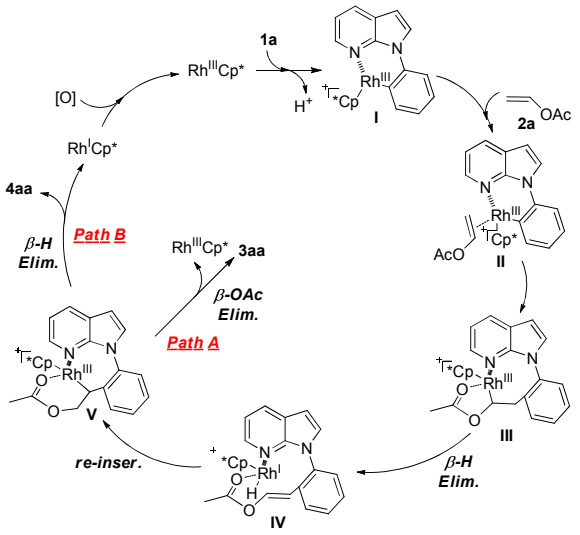


Scheme 3 Studies on the relationship of the DHR and olefinated products.

Conclusion

In summary, we have developed the novel rhodium(III)-catalyzed C–H activation of 7-azaindoles and various electron-

donating olefins. Furthermore, diverse substituted alkenyl esters and allyl acetates are well tolerated, meanwhile giving access to a range of different 7-azaindole derivatives. In this way, we have extended the scope of DHR and carbonyl reaction. We anticipate that this approach will find applications in the selective diversification of heterocyclic frameworks. Further investigation of the catalytic mechanism is underway in our laboratory.



Scheme 4 Plausible reaction mechanism.

Acknowledgments

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Experimental

General remarks

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ or DMSO-d_6 solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether.

General procedure for the preparation of the 7-azaindole derivatives: 1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), vinyl acetate **2a** (0.5 mL) and Cp*Rh$(CH_3CN)_3(SbF_6)_2$ (2.5 mg, 3.0 mol %) were stirred in dioxane (1.0 mL) in seal tube at 130 °C for 30 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:50) to give the product **3aa** as colorless oil (8.3 mg, 38%), ethyl acetate and petroleum ether (1:10) to give the product **4aa** as colorless oil (16.6 mg, 60%).

1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (3aa). 30 h, 48% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 – 8.31 (m, 1H), 7.99 (dd, J = 7.8, 1.0 Hz, 1H), 7.76 (d, J = 6.9 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.30 (d, J = 3.5 Hz, 1H), 7.12 (dd, J = 7.8, 4.7 Hz, 1H), 6.63 (d, J = 3.5 Hz, 1H), 6.33 (dd, J = 17.5, 11.0 Hz, 1H), 5.72 (d, J = 17.5 Hz, 1H), 5.18 (d, J = 11.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 143.8, 135.8, 135.1, 132.2, 129.9, 128.9, 128.6, 128.5, 128.4, 126.3, 120.5, 116.4, 116.3, 100.8 ppm. ESI HRMS: calcd. for $C_{15}H_{12}N_2$+H 221.1079, found 221.1086.

(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4aa); **(Z)-2-(1H-pyrrolo[2,3-b] pyridin-1-yl)styryl acetate (4aa')**; (**4aa**:**4aa'** = **5**:**4**). 30 h, 60% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (t, J = 3.8 Hz, 2H), 8.03 – 7.96 (m, 3H), 7.77 (d, J = 12.7 Hz, 1H), 7.66 (d, J = 6.2 Hz, 1H), 7.46 (dd, J = 11.0, 7.5 Hz, 2H), 7.41 (dd, J = 15.7, 6.0 Hz, 4H), 7.28 (t, J = 3.1 Hz, 2H), 7.13 (dt, J = 11.0, 6.9 Hz, 3H), 6.63 (dd, J = 20.7, 3.4 Hz, 2H), 6.01 (d, J = 12.7 Hz, 1H), 5.35 (d, J = 7.4 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{14}N_2O_2$+H 279.1134, found 279.1124.

4-chloro-1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (3ba). 30 h, 25% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (d, J = 5.1 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.46 (dd, J = 10.8, 4.3 Hz, 1H), 7.43 (td, J = 7.5, 1.4 Hz, 1H), 7.38 (dd, J = 7.7, 1.1 Hz, 1H), 7.33 (d, J = 3.5 Hz, 1H), 7.15 (d, J = 5.1 Hz, 1H), 6.74 (d, J = 3.5 Hz, 1H), 6.27 (dd, J = 17.5, 11.0 Hz, 1H), 5.72 (d, J = 17.5 Hz, 1H), 5.19 (d, J = 11.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 144.2, 136.2, 135.4, 135.2, 131.9, 130.4, 128.8, 128.6, 128.4, 126.4, 119.8, 116.7, 116.5, 99.4 ppm. ESI HRMS: calcd. for $C_{15}H_{11}ClN_2$+H 255.0689, found 255.0693.

(E)-2-(4-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ba); **(Z)-2-(4-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ba')**; (**4ba:4ba' = 9:1**). 30 h, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 5.1 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.48 (dd, J = 7.8, 4.0 Hz, 1H), 7.44 (s, 2H), 7.33 (d, J = 3.2 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.73 (d, J = 3.2 Hz, 1H), 5.30 (d, J = 7.4 Hz, 1H), 2.22 (s, 1H), 2.12 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+Na 335.0563, found 335.0558, 337.0560.

5-bromo-1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (3ca). 24 h, 14% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 1.5 Hz, 1H), 8.11 (d, J = 1.7 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H), 7.44 (dt, J = 14.5, 7.2 Hz, 2H), 7.37 (d, J = 6.9 Hz, 1H), 7.30 (d, J = 3.4 Hz, 1H), 6.58 (d, J = 3.4 Hz, 1H), 6.26 (dd, J = 17.5, 11.0 Hz, 1H), 5.72 (d, J = 17.5 Hz, 1H), 5.19 (d, J = 11.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 135.3, 135.1, 131.9, 131.3, 131.0, 128.7, 128.6, 128.3, 126.4, 122.1, 116.6, 112.3, 100.4 ppm. ESI HRMS: calcd. for $C_{15}H_{11}BrN_2$+H 299.0184, found 299.0174, 301.0181.

(E)-2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ca); **(Z)-2-(5-bro mo-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ca')**; (**4ca:4ca' = 1:2**). 24 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.10 (d, J = 6.5 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 12.8 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.42 (d, J = 4.0 Hz, 3H), 7.38 (dd, J = 13.5, 7.0 Hz, 1H), 7.29 (s, 2H), 7.16 (d, J = 7.4 Hz, 1H), 6.60 (d, J = 3.3 Hz, 1H), 6.56 (d, J = 3.3 Hz, 1H), 5.94 (d, J = 12.7 Hz, 1H), 5.29 (d, J = 7.3 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 2H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}BrN_2O_2$+Na 379.0058, found 379.0066, 381.0049.

(1E,1'E)-(2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)-1,3-phenylene)bis(ethene-2,1-diyl) diacetate (5); **(1Z,1'Z)-(2-(5-bromo-1H-pyrrolo[2,3-b]pyridine-1-yl)-1,3-phenylene)bis(ethene-2,1-diyl) diacetate (5')**; (**5:5' = 2:1**). 24 h,

8% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 2H), 7.99 (t, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 12.8 Hz, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 7.49 – 7.37 (m, 6H), 7.28 (s, 2H), 7.13 (dd, *J* = 10.7, 6.9 Hz, 3H), 6.65 (d, *J* = 3.2 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 6.01 (d, *J* = 12.8 Hz, 1H), 5.35 (d, *J* = 7.3 Hz, 1H), 2.09 (s, 2H), 2.08 (s, 4H) ppm. ESI HRMS: calcd. for $C_{21}H_{17}BrN_2O_4$+Na 463.0269, found 463.0279, 465.0264.

(E)-methyl3-(1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)acrylate (3da). 12 h, 20% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.17 (s, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.33 (d, *J* = 3.2 Hz, 1H), 6.67 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.73 (d, *J* = 17.4 Hz, 1H), 5.20 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 149.2, 144.8, 143.1, 135.3, 135.0, 131.9, 131.3, 128.7, 128.6, 128.3, 127.7, 126.4, 123.3, 120.6, 116.6, 116.3, 101.5, 51.6 ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O_2$+H 305.1290, found 305.1281.

(2E)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H pyrrolo[2,3-b]pyridin-5-yl)acrylate (4da); **(2Z)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)acrylate (4da')**; **(4da:4da' = 1.1:1)**. 12 h, 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (s, 2H), 8.17 (dd, *J* = 9.4, 1.3 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.78 (d, *J* = 12.7 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.48 (dd, *J* = 11.2, 4.9 Hz, 1H), 7.43 (dd, *J* = 16.7, 9.1 Hz, 4H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 3.4 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H), 6.51 (d, *J* = 3.3 Hz, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 5.97 (d, *J* = 12.8 Hz, 1H), 5.32 (d, *J* = 7.4 Hz, 1H), 3.82 (s, 6H), 2.11 (s, 3H), 2.09 (s, 3H) ppm. ESI HRMS: calcd. for $C_{21}H_{18}N_2O_4$+ H 363.1345, found 363.1354.

Methyl3-(1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)propanoate (3ea). 12 h, 20% yield; ^{1}H NMR (600 MHz,$CDCl_3$): δ 8.19 (d, *J* = 1.0 Hz, 1H), 7.82 (s, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.42 (ddd, *J* = 21.7, 11.9, 4.4 Hz, 3H), 7.28 – 7.25 (m, 1H), 6.57 (d, *J* = 3.4 Hz, 1H), 6.32 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 11.1 Hz, 1H), 3.68 (s, 3H), 3.07 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 147.6, 144.2, 135.8, 135.0, 132.2, 130.2, 128.5, 128.4, 128.3, 128.3, 126.3, 120.4, 116.2, 100.4, 51.6, 36.2, 28.2 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2$+H 307.1447, found 307.1440.

(E)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)propanoate (4ea); **(Z)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)propanoate (4ea')**; **(4ea:4ea' = 2:1)**. 12 h, 32% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H), 8.02 – 7.98 (m, 1H), 7.85 – 7.80 (m, 2H), 7.78 (d, *J* = 12.8 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.43 (ddd, *J* = 15.5, 10.4, 6.7 Hz, 6H), 7.26 (d, *J* = 3.2 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 6.55 (d, *J* = 3.5 Hz, 1H), 6.01 (d, *J* = 12.8 Hz, 1H), 5.35 (d, *J* = 7.4 Hz, 1H), 3.68 (s, 6H), 3.07 (td, *J* = 7.7, 2.5 Hz, 4H), 2.69 (td, *J* = 7.7, 3.1 Hz, 4H), 2.10 (s, 3H), 2.09 (s, 3H) ppm. ESI HRMS: calcd. for $C_{21}H_{20}N_2O_4$+H 365.1501, found 365.1501.

1-(4-chloro-2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (3fa). 24 h, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 7.37 (q, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.13 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 6.26 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.73 (d, *J* = 17.5 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 135.7, 133.3, 130.2, 128.7, 128.5, 128.0, 127.5, 125.3, 119.5, 116.5, 115.6, 100.2 ppm. ESI HRMS: calcd. for $C_{15}H_{11}ClN_2$+H 255.0689, found 255.0683, 257.0665.

(E)-5-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4fa); **(Z)-5-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4fa')**; **(4fa:4fa' = 1.5:1)**. 24 h, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 2H), 7.98 (t, *J* = 7.5 Hz, 3H), 7.78 (d, *J* = 12.8 Hz, 1H), 7.63 (s, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 5.94 (d, *J* = 12.8 Hz, 1H), 5.28 (d, *J* = 7.4 Hz, 1H), 2.14 (s, 2H), 2.09 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+Na 335.0563, found 335.0558, 337.0592.

1-(5-chloro-2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (3ga). 30 h, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 4.2 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 11.8 Hz, 2H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.13 (dd, *J* = 7.5, 4.8 Hz, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 6.27 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.70 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 11.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 144.0, 136.7, 133.7, 133.7, 131.4, 129.5, 129.1, 128.7, 128.6, 127.4, 120.5, 116.7, 116.7, 101.4 ppm. ESI HRMS: calcd. for $C_{15}H_{11}ClN_2$+H 255.0689, found 255.0684, 257.0638.

(E)-4-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ga); (Z)-4-chloro- 2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ga'**); (**4ga**:**4ga'** = **2**:**1**). 30 h, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 3.0 Hz, 2H), 7.98 (t, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 12.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.40 (dd, *J* = 13.9, 9.1 Hz, 3H), 7.24 (d, *J* = 3.9 Hz, 2H), 7.14 (dt, *J* = 12.2, 4.0 Hz, 3H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.61 (d, *J* = 3.4 Hz, 1H), 5.95 (d, *J* = 12.8 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 2.09 (s, 2H), 2.07 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+ Na 335.0563, found 335.0557.

1-(4-methoxy-2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (3ha). 24 h, 25% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (d, *J* = 4.0 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 3.7 Hz, 1H), 7.23 (d, *J* = 2.7 Hz, 1H), 7.10 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.23 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.69 (d, *J* = 17.5 Hz, 1H), 5.16 (d, *J* = 11.0 Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 148.8, 143.8, 136.4, 132.1, 130.1, 129.6, 129.0, 128.9, 120.4, 116.4, 116.2, 114.3, 110.9, 100.5, 55.6 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2O$+H 251.1184, found 251.1174.

(E)-5-methoxy-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ha); **(Z)-5-methoxy-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (4ha')**; **(4ha:4ha' = 1.2:1)**. 24 h, 66% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 – 8.31 (m, 2H), 8.00 – 7.96 (m, 2H), 7.75 (d, *J* = 12.7 Hz, 1H), 7.58 (d, *J* = 2.9 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.13 (dd, *J* = 7.5, 4.9 Hz, 2H), 7.12 – 7.09 (m, 2H), 6.97 (d, *J* = 2.9 Hz, 1H), 6.94 (d, *J* = 2.9 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.62 (d, *J* = 3.5 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 5.92 (d, *J* = 12.8 Hz, 1H), 5.25 (d, *J* = 7.4 Hz, 1H), 3.89 (s, 2H), 3.88 (s, 3H), 2.13 (s, 2H), 2.07 (s, 3H) ppm. ESI HRMS: calcd. for $C_{18}H_{16}N_2O_3$+H 309.1239, found 309.1229.

(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styrylbutyrate (4ab). 36 h, 24% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (d, *J* = 3.8 Hz,

1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 12.7 Hz, 1H), 7.66 (d, *J* = 6.8 Hz, 1H), 7.41 (dt, *J* = 12.0, 4.3 Hz, 3H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.13 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.00 (d, *J* = 12.8 Hz, 1H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.64 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 148.4, 143.9, 137.6, 135.9, 132.1, 129.7, 129.0, 128.8, 128.6, 128.2, 126.4, 120.5, 116.4, 110.6, 101.1, 35.7, 18.0, 13.5 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2$+H 307.1447, found 307.1440.

(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl butyrate (**4ab'**). 36 h, 16% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.4 Hz, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.44 (dt, *J* = 8.6, 4.9 Hz, 3H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 5.33 (d, *J* = 7.4 Hz, 1H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.69 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 148.3, 143.8, 136.1, 135.1, 131.3, 130.5, 129.8, 129.0, 128.4, 128.1, 128.0, 120.6, 116.4, 106.7, 100.9, 35.8, 18.0, 13.6 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2$+H 307.1447, found 307.1437.

(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl pivalate (**4ac**). 48 h, 31% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 4.5 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 12.8 Hz, 1H), 7.67 (d, *J* = 6.2 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.13 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.66 (d, *J* = 3.4 Hz, 1H), 6.04 (d, *J* = 12.8 Hz, 1H), 1.19 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 148.4, 143.9, 138.1, 135.7, 132.1, 129.7, 128.9, 128.8, 128.5, 128.1, 126.4, 120.5, 116.4, 110.4, 101.04, 38.6, 26.8 ppm. ESI HRMS: calcd. for $C_{20}H_{20}N_2O_2$+Na 343.1422, found 343.1418.

(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl pivalate (4ac'). 48 h, 6% yield; ^{1}H NMR (600 MHz,$CDCl_3$): δ 8.33 (d, *J* = 4.3 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 14.7, 7.1 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.63 (d, *J* = 3.4 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 1.32 (s, 9H) ppm. ESI HRMS: calcd. for $C_{20}H_{20}N_2O_2$+Na 343.1422, found 343.1418.

(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl benzoate (**4ad**). 48 h, 50% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.17 (dd, *J* = 8.1, 0.9 Hz, 2H), 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.54 (m, 4H), 7.53 – 7.50 (m, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 7.17 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H), 5.53 (d, *J* = 7.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 143.9, 136.3, 135.4, 133.8, 131.4, 130.7, 130.1, 129.9, 129.0, 128.7, 128.5, 128.2, 128.1, 120.6, 116.5, 107.9, 101.0 ppm. ESI HRMS: calcd. for $C_{22}H_{16}N_2O_2$+H 341.1290, found 341.1282.

(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl-4-(tert-butyl)benzoate (**4ae**). 48 h, 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 4.2 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 6.9 Hz, 1H), 7.46 – 7.40 (m, 5H), 7.32 (d, *J* = 3.4 Hz, 1H), 7.14 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.19 (d, *J* = 12.7 Hz, 1H), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 157.5, 148.4, 143.9, 138.0, 135.9, 132.1, 129.9, 129.8, 129.0, 128.8, 128.6, 128.2, 126.5, 125.7, 125.4, 120.5, 116.4, 111.1, 101.1 ppm. ESI HRMS: calcd. for $C_{26}H_{24}N_2O_2$+H 397.1916, found 397.1909.

(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl-4-(tert-butyl)benzoate (**4ae'**). 48 h, 6% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.6 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.98 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.53 (t, *J* = 8.3 Hz, 3H), 7.49 (d, *J* = 7.1 Hz, 1H), 7.44 (dd, *J* = 13.5, 7.3 Hz, 2H), 7.33 (d, *J* = 3.5 Hz, 1H), 7.11 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.63 (d, *J* = 3.5 Hz, 1H), 5.45 (d, *J* = 7.3 Hz, 1H), 1.37 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 157.6, 148.3, 143.8, 136.1, 135.5, 131.5, 130.7, 130.0, 129.9, 128.9, 128.4, 128.1, 128.1, 125.8, 125.7, 120.5, 116.4, 107.4, 100.9, 35.2, 31.0 ppm. ESI HRMS: calcd. for $C_{26}H_{24}N_2O_2$+H 397.1916, found 397.1909.

(E)-1-(2-(prop-1-en-1-yl)phenyl)-1H-pyrrolo[2,3-b]pyridine (**3af**). 24 h, 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.38 (dd, *J* = 13.4, 5.7 Hz, 3H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.11 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 6.26 – 6.14 (m, 1H), 5.98 (d, *J* = 15.7 Hz, 1H), 1.71 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.8, 134.4, 134.1, 129.0, 127.8, 127.4, 127.3, 127.3, 126.4, 125.3, 125.1, 119.4, 115.2, 99.6, 17.7 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2$+H 235.1235, found 235.1240.

1-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)ethanone (**6**). 48 h, 30% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 4.6 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 3.5 Hz, 1H), 7.13 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.68 (d, *J* = 3.5 Hz, 1H), 1.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 148.0, 143.9, 137.6, 135.7, 132.2, 129.3, 129.0, 128.8, 128.0, 127.8, 120.9, 116.9, 102.2, 28.4 ppm. ESI HRMS: calcd. for $C_{15}H_{12}N_2O$+Na 259.0847, found 259.0845.

(E)-1-(2-styrylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3ag**). 48 h, 24% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (d, *J* = 4.2 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.25 (s, 4H), 7.19 (dd, *J* = 8.5, 4.0 Hz, 1H), 7.13 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.07 (d, *J* = 16.3 Hz, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 143.9, 137.0, 136.0, 134.7, 130.8, 130.1, 129.0, 128.5, 128.3, 128.2, 127.7, 126.5, 126.4, 123.9, 120.6, 116.4, 100.9, 29.6 ppm. ESI HRMS: calcd. for $C_{21}H_{16}N_2$+H 297.1392, found 297.1398.

(E)-3-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)allyl acetate (**4ah**). 24 h, 8% yield ; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.5 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.45 – 7.41 (m, 3H), 7.28 (d, *J* = 3.5 Hz, 1H), 7.13 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.64 (d, *J* = 3.5 Hz, 1H), 6.24 (s, 2H), 4.53 (d, *J* = 2.5 Hz, 2H), 1.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 148.5, 143.9, 136.0, 133.7, 129.9, 129.0, 129.0, 128.5, 128.4, 126.7, 125.6, 120.5, 116.4, 101.0, 64.7, 20.8 ppm. ESI HRMS: calcd. for $C_{18}H_{16}N_2O_2$+Na 315.1109, found 315.1118.

(E)-3-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl -allylheptanoate (**4ai**). 24 h, 11% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.3 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 4.4 Hz, 1H), 7.43 (d, *J* = 9.4 Hz, 3H), 7.28 (d, *J* = 3.3 Hz, 1H), 7.12 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 6.24 (s, 2H), 4.54 (s, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.52 (dd, *J* = 13.9, 6.8 Hz, 2H), 1.25 (s, 6H), 0.87 (t, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 148.1, 143.9, 129.9, 129.0, 128.7, 128.6, 128.5, 128.4, 126.7, 125.8, 116.4, 101.0, 64.5, 34.2, 31.4,

28.7, 24.8, 22.4, 14.0 ppm. ESI HRMS: calcd. for $C_{23}H_{26}N_2O_2$+H 363.2073, found 363.2071.

1-(2-allylphenyl)-1H-pyrrolo[2,3-b]pyridine (**8**). 24 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.35 (s, 2H), 7.29 – 7.22 (m, 1H), 7.10 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.61 (d, *J* = 3.4 Hz, 1H), 5.82 – 5.69 (m, 1H), 4.92 (d, *J* = 9 .8 Hz, 1H), 4.80 (d, *J* = 17.0 Hz, 1H), 3.18 (d, *J* = 6.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 143.7, 137.8, 136.8, 136.3, 130.4, 129.5, 128.7, 128.6, 127.2, 120.4, 116.2, 100.6, 35.9 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2$+H 235.1235, found 235.1228.

2-(1H-pyrrolo[2,3-b]pyridin-1-yl)benzaldehyde (**9**). 2 h, 70% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.72 (s, 1H), 8.32 (d, *J* = 3.8 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.19 – 7.15 (m, 1H), 6.73 (d, *J* = 2.8 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 189.3, 148.9, 144.2, 140.0, 134.7, 131.6, 129.4, 129.2, 128.6, 128.0, 127.6, 120.7, 117.3, 102.6 ppm. ESI HRMS: calcd. for $C_{14}H_{10}N_2O$+H 223.0871, found 223.0873.

(E)-3-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)prop-2-en-1-ol (**10**). 2 h, 99% yield; ^{1}H NMR (400 MHz, $CDCL_3$): δ 8.31 (d, *J* = 4.3 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 1H), 7.47 – 7.36 (m, 4H), 7.28 (d, *J* = 3.1 Hz, 1H), 7.12 (dd, *J* = 7.3, 4.7 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.35 – 6.26 (m, 1H), 6.21 (d, *J* = 16.1 Hz, 1H), 4.11 (d, *J* = 4.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.8, 135.8, 134.2, 131.1, 129.8, 129.0, 128.6, 128.4, 128.4, 126.7, 126.2, 120.5, 116.4, 101.0, 63.5 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2O$+H 251.1184, found 251.1174.

(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-3-vinylstyryl acetate (**11**); **(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-3-vinylstyryl acetate** (**11'**); (**11**:**11'** = 3:1). 48 h, 15% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (d, *J* = 3.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.73 (d, *J* = 12.7 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 7.15 – 7.11 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 13.5 Hz, 1H), 6.05 – 5.94 (m, 1H), 5.76 – 5.64 (m, 2H), 5.10 (d, *J* = 11.0 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H), 2.21 (s, 1H), 2.05 (s, 3H) ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O_2$+H 305.1290, found 305.1288.

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