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Rhodium(II)-Catalyzed Regioselective C3-Alkylation of 2-Arylimidazo[1,2-a]pyridines with Aryl Diazoesters

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Abstract. A regioselective C3-alkylation based on the reaction of 2-arylimidazo[1,2-a]pyridines with a wide range of aryl α-diazoesters in the presence of a Rh(II) catalyst in dichloroethane at room temperature was developed. This method could be applied in the synthesis of benzoimidazoquinolizinone and cycloheptaimidazopyridinone, which are novel heterocyclic scaffolds.

Keywords: Imidazopyridine; Regioselective; Aryl diazoester; Rhodium; C3-Alkylation

Introduction

Imidazo[1,2-a]pyridines are significant privileged scaffolds in azaheterocycle chemistry,[1] and they are commonly found in natural products, pharmaceuticals, and biologically active compounds (Figure 1).[2] Among azaheterocycles, imidazopyridines and especially 3-alkyl-2-arylimidazo[1,2-a]pyridines are not only essential pharmacophores but also practical synthetic intermediates that can be easily converted into valuable molecules.[3] Although a variety of streamlined approaches for synthesizing 3-alkyl-2-arylimidazo[1,2-a]pyridines, including Cu-catalyzed nucleophilic addition to *N*-acyliminium ions derived

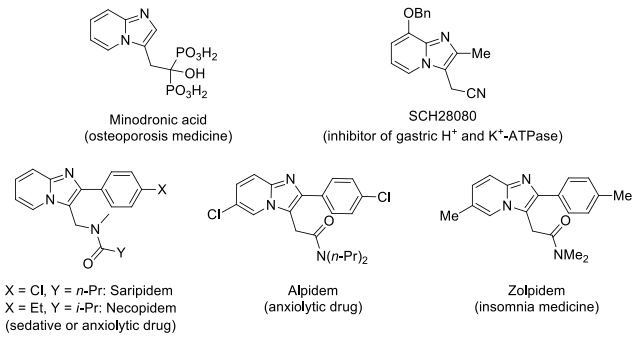

Figure 1. Bioactive Imidazo[1,2-a]pyridines.

from *N*-benzyloxycarbonylamino sulfones (eq 1);[4] Friedel-Crafts alkylation of imidazo[1,2-a]pyridines with β-nitrostyrenes (eq 2);[5] and Yb-catalyzed three-component reaction of aldehydes, acetamides, and imidazo[1,2-a]pyridines (eq 3),[6] have been reported,[7] these methods often suffer from a narrow substrate scope, requiring harsh reaction conditions, and poor regioselectivity (Scheme 1). In addition, Li and coworkers reported that Ir(III) and Rh(III) complexes could catalyze the carbocyclization between 2-phenylimidazo[1,2-a]pyridine and α-diazo esters (eqs 4 and 5).[8] The reaction occurs through C–H activation and monoalkylation or dialkylation of the arene followed by an intramolecular electrophilic aromatic substitution. Iridium(III) and rhodium(III) catalysts showed complementary scopes of the α diazo substrate. However, since they utilize C–H activation, only one or two reactive species derived from the diazo compound can be introduced at the *ortho*-positions of the 2-phenyl group of 2-phenylimidazo[1,2-a]pyridine. Hence, functional groups could not be introduced at the C3-position of 2-arylimidazo[1,2-a]pyridine. Recently, we attempted to introduce various functional groups onto 2-arylimidazo[1,2-a]pyridine to construct a library based on the imidazo[1,2-a]pyridine skeleton.[9] Because a highly reactive electrophilic carbene was generated from the Rh(II) catalysts and diazo

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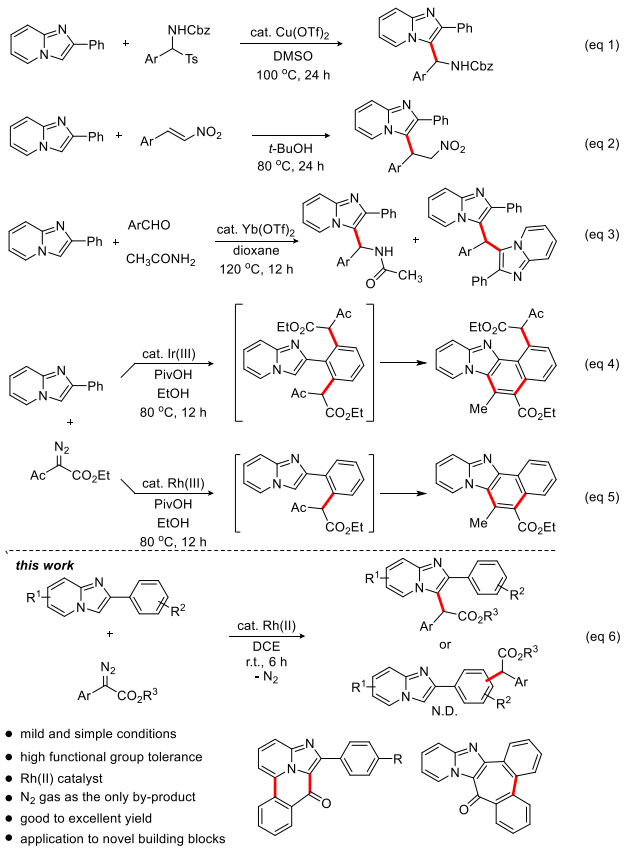


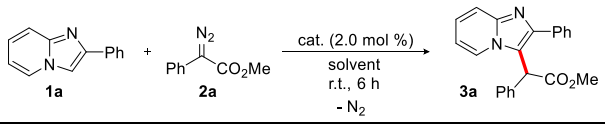
Scheme 1. 3-Alkylation of 2-Arylimidazo[1,2-a]pyridines.

compounds, we were very curious about the introduction of carbene moieties derived from diazo compounds in the presence of a transition metal catalyst into the aryl or the imidazopyridine ring upon treatment with 2-arylimidazo[1,2-a]pyridine. Herein, we report a regioselective C3-alkylation based on the reaction of 2-arylimidazo[1,2-a]pyridines with a wide range of aryl α-diazoesters in the presence of a Rh(II) catalyst at room temperature (eq 6). No mono- or di-alkylation of the aryl ring of the 2-arylimidazo[1,2-a]pyridine was observed. Additional cyclizations using C3-alkylated 2-arylimidazo[1,2-a]pyridines were conducted to provide benzoimidazoquinolizinone and cycloheptaimidazopyridinone, which are novel heterocyclic scaffolds.

Results and Discussion

First, we examined the reaction of 2-phenylimidazo[1,2-a]pyridine (**1a**) (0.2 mmol, 1.0 equiv) with methyl 2-phenyl-2-diazoacetate (**2a**) (0.3 mmol, 1.5 equiv) using a variety of catalysts and solvents (Table 1). CuCl (2.0 mol %) was not effective (entry 1). However, when $Cu(OAc)_2$ and $Cu(OTf)_2$ (each at 2.0 mol %) were used in dichloroethane (DCE) at room temperature for 6 h, the desired C3-alkylated 2-phenylimidazo[1,2-a]pyridine (**3a**) was gratifyingly produced in yields of 11% and 63%, respectively (entries 2 and 3). Next, a

Table 1. Reaction Optimization [a]



Entry	Catalyst	Solvent	Yield [%][b]
1	CuCl	DCE	0
2	$Cu(OAc)_2$	DCE	11
3	$Cu(OTf)_2$	DCE	63
4	$Rh_2(TPA)_4$	DCE	72
5	$Rh_2(Opiv)_4$	DCE	84
6	$Rh_2(OAc)_4$	DCE	83
7	$Rh_2(oct)_4$	DCE	98 (97)[c]
8	$Rh_2(oct)_4$	CH_2Cl_2	89
9	$Rh_2(oct)_4$	THF	30
10	$Rh_2(oct)_4$	Toluene	91
11	$Rh_2(oct)_4$	DCE	85[d]
12	$Rh_2(oct)_4$	DCE	85[e]

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv) was reacted with **2a** (1.5 equiv) in the presence of catalyst (2.0 mol %) in solvent (2.0 mL) under a N_2 atmosphere.
[b] NMR yield using dibromomethane as an internal standard.
[c] Isolated yield.
[d] **2a** (1.2 equiv) was used.
[e] DCE (1.0 mL) was used.

number of rhodium(II) catalysts, including $Rh_2(TPA)_4$, $Rh_2(OPiv)_4$, $Rh_2(OAc)_4$, and $Rh_2(oct)_4$ (each at 2.0 mol %), were tested in DCE at room temperature, and these experiments revealed that $Rh_2(oct)_4$ performed the best, providing **3a** in quantitative yield (entries 4-7). Dichloromethane, tetrahydrofuran, and toluene gave inferior results compared to that achieved with DCE (entries 8-10). The reaction of **2a** (1.2 equiv) in DCE at room temperature for 6 h gave rise to **3a** in 85% yield (entry 11). Concentrations of substrate from 0.1 M to 0.2 M furnished **3a** in 85% yield (entry 12). No alkylation of the aryl ring of 2-arylimidazo[1,2-a]pyridine was observed.

The solid-state structure of **3a** was confirmed by single-crystal X-ray diffraction (Figure 2 and the Supporting Information). Importantly, X-ray analyses revealed that the phenyl rings at the 2- and 3-positions are distorted with respect to the plane of the imidazopyridine, and they show dihedral angles of 47.8° and 74.1°, respectively. Although the solid-state structure suggests that electron delocalization between each phenyl group and the imidazopyridine moiety is unfavorable, these moieties can interact with each other electronically through the free rotation of the phenyl groups in solution.

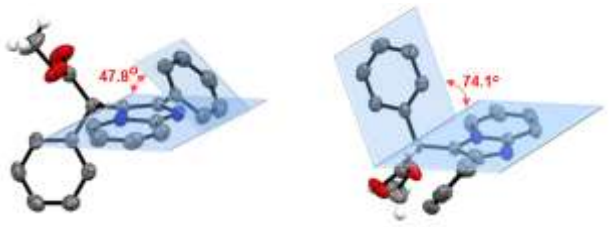
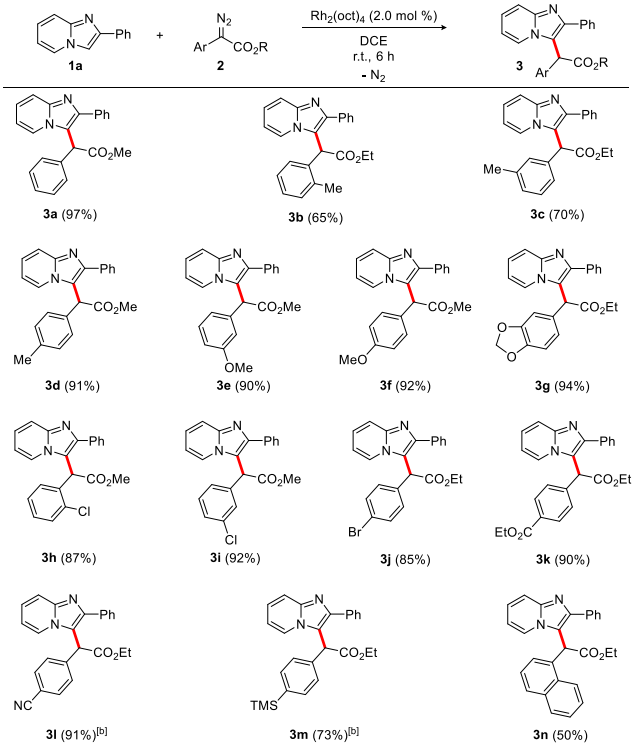


Figure 2. Molecular Structure of Imidazo[1,2-a]pyridine **3a**.

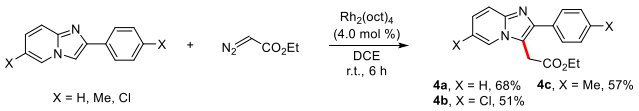
Inspired by these results, we investigated the scope of alkyl 2-aryl-2-diazoacetates (**2**) in the reaction with 2-phenylimidazo[1,2-a]pyridine (**1a**) (Table 2). Electronic variation of the substituents on the aryl group of 2-aryl-2-diazoacetate (**2**) slightly influenced the reaction efficiency. Electron-donating 2-methyl, 3-methyl, and 4-methyl groups afforded the corresponding C3-alkylated 2-phenylimidazo[1,2-a]pyridines (**3b**, **3c**, and **3d**) in good to excellent yields (65% to 91%). Strongly electron-donating 3- and 4-methoxy groups did not affect the efficiency of the C3-alkylation reaction. Methylenedioxy-substituted ethyl 2-aryl-2-diazoacetate efficiently underwent the C3-alkylation, producing desired imidazo[1,2-a]pyridine **3g** in 94% yield. The conditions of the C3-alkylation reaction were compatible with electron-withdrawing groups, including 2-chloro, 3-chloro, and 4-bromo groups,

Table 2. Scope of Alkyl 2-Aryl-2-diazoacetates[a]

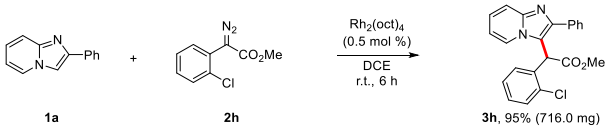


[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv) was reacted with **2** (1.5 equiv) and $Rh_2(oct)_4$ (2.0 mol %) in DCE (2.0 mL) under N_2 atmosphere.
[b] 60 °C, 2 h.

and these substrates provided the desired imidazo[1,2-a]pyridines (**3h**, **3i**, and **3j**) in high yields (85% to 92%). 4-Ethoxycarbonyl- and 4-cyano-substituted 2-aryl-2-diazoesters are tolerated in the present transformation, providing corresponding products **3k** (90%) and **3l** (91%). Notably, a diazoacetate bearing a labile trimethylsilyl group efficiently underwent C3-alkylation with **1a** at 60 °C in 2 h, producing desired product **3m** in 73% yield. Ethyl 1-naphthyl-2-diazoacetate was C3-alkylated product (**3n**) in 50% yield due to steric effects. The tolerance of a variety of substituents, including chloro, bromo, ester, cyano, and trimethylsilyl groups, is important, as these functional groups can be further transformed. However, methyl 2-diazo-3-oxobutanoate, methyl 2-diazo-4-phenylbutanoate, ethyl 2-diazo-3-oxo-3-phenylpropanoat, and dimethyl 2-diazomalonate were not effective. In addition, the present method worked equally well even with unstable ethyl diazoacetates at room temperature and afforded the desired compounds (**4a-4c**) in good yields.



To demonstrate the applicability of the present method to larger scale processes, 2.0 mmol of 2-phenylimidazo[1,2-a]pyridine (**1a**, 0.39 g) was treated with methyl 2-(2-chlorophenyl)-2-diazoacetate (**2h**, 1.5 equiv) with 0.5 mol % catalyst loading in DCE at room temperature for 6 h, and the reaction afforded corresponding compound **3h** (0.72 g, 95%).



Next, imidazo[1,2-a]pyridine derivatives (**1**) with a wide range of substituents on the pyridine moiety were examined in the C3-alkylation reaction with methyl 2-phenyl-2-diazoacetate (**2a**) (Table 3). Electronic modification of the substituents on the pyridine ring did not affect the reaction efficiency. The Rh-catalyzed C3-alkylation with methyl 2-phenyl-2-diazoacetate occurred regioselectively at the C3-position of the imidazopyridine ring of 8-, 7-, and 6-methyl-2-phenylimidzo[1,2-a]pyridines and provided the desired products (**5a** **5b**, and **5c**) in good to excellent yields (73% to 98%). A substrate having an electron-donating 7-ethyl group was converted to the corresponding imidazo[1,2-a]pyridine (**5d**) in 91% yield. C3-Alkylation product **5e** was obtained in 98% yield despite the presence of a strong electron-donating methoxy group. The conditions of the C3-alkylation reaction were compatible with 7- and 6-chloro groups, and **5f** and **5g** were produced in 90% and 75% yields, respectively. Encouraged by these

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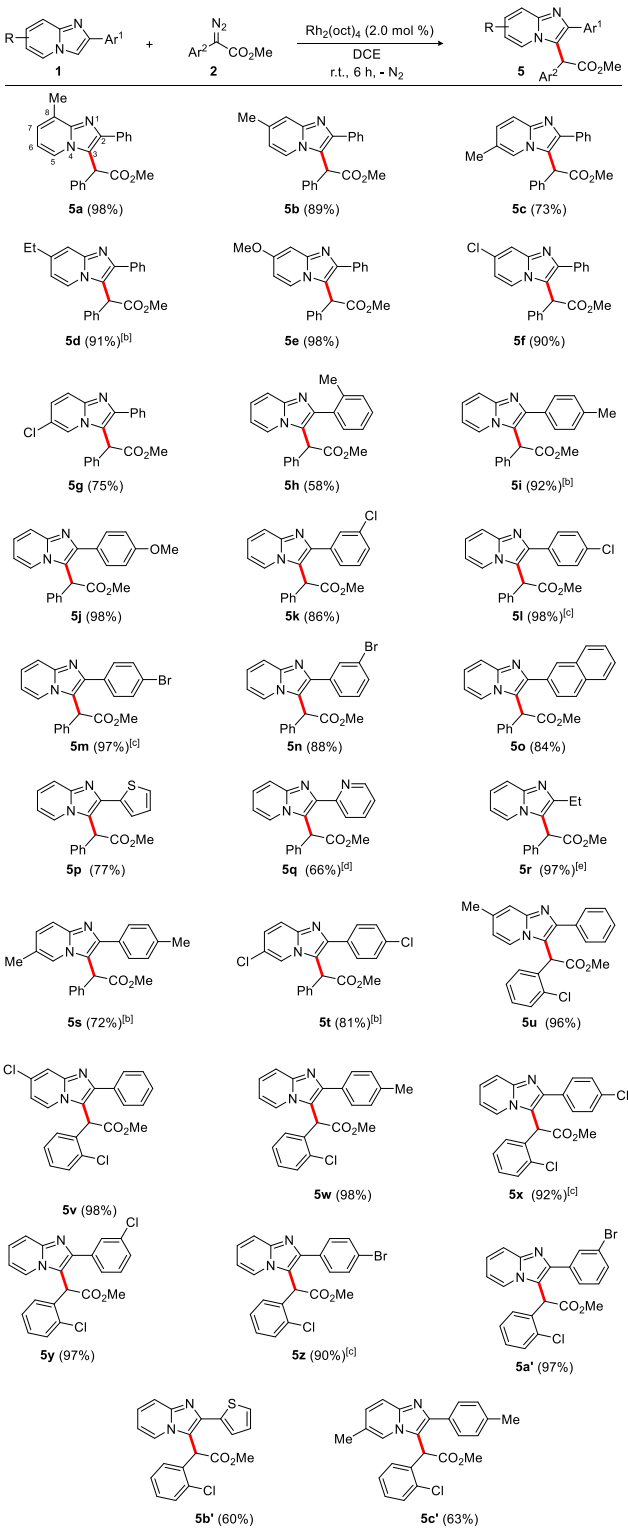
Table 3. Scope of 2-Arylimidazo[1,2-a]pyridines[a]



[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv) was reacted with **2a** (1.5 equiv) and $Rh_2(oct)_4$ (2.0 mol %) in DCE (2.0 mL) under a N_2 atmosphere.
[b] Reaction time 18 h.
[c] 60 °C, 2 h.
[d] $Rh_2(oct)_4$ (4.0 mol %) was used at 100 °C for 4 h.
[e] 100 °C, 4 h.

results, we applied this catalytic system to a number of 2-arylimidazo[1,2-a]pyridines to demonstrate the scope of the developed method. Although imidazo[1,2-a]pyridine with an *ortho*-tolyl group at the C2-position was C3-alkylated to produce **5h** in 58% yield due to steric effects, *para*-tolyl-substituted imidazopyridine smoothly underwent the Rh-catalyzed C3-alkylation reaction to afford **5i** in 92% yield. Likewise, imidazo[1,2-a]pyridine, with a 4-methoxyphenyl group, efficiently afforded corresponding C3-alkylated compound **5j** in 98% yield. The present method worked equally well with the electron-poor 3-chloro- and 3-bromophenyl-substituted imidazopyridines, which allowed the facile construction of C3-alkylimidazo[1,2-a]pyridines **5k** (86%) and **5n** (88%). Because the reactivities of imidazopyridines with 4-chloro- and 4-bromophenyl moieties were low due to the inductive and resonance effects, the C3-alkylation was conducted under slightly modified conditions (DCE, 60 °C, 2 h) but still produced **5l** and **5m** in quantitative yields, respectively. 2-Naphthyl-substituted imidazo[1,2-a]pyridine underwent the Rh-catalyzed C3-alkylation, affording the desired compound (**5o**) in 84% yield. An imidazo[1,2-a]pyridine bearing a thiophen-2-yl and pyridin-2-yl moieties also provided the corresponding imidazopyridines **5p** and **5q** in 77% and 66% yields, respectively. Replacement of phenyl to ethyl group (**5r**) expanded diversity of the present method and increased substrate scope. The substrate having a methyl group on the pyridine as well as on the phenyl ring of 2-phenylimidazo[1,2-a]pyridine furnished desired imidazopyridine **5s** in 72% yield. Two chloro-substituted 2-phenylimidazo[1,2-a]pyridine was also reacted with **2a** to produce **5t** in 81% yield. When 2-(2-chlorophenyl)-2-diazoacetate **(2h)** was reacted with imidazopyridines (**1**) with a wide range of substituents, including methyl, chloro, and bromo groups, on the pyridine as well as on the phenyl ring of 2-phenylimidazo[1,2-a]pyridine, the corresponding products were obtained in high yields. Thiophen-2-yl-substituted imidazo[1,2-a]pyridine was easily converted to the desired product (**5b'**) in 60% yield.

Next, various methods using C3-alkylated imidazopyridines have been developed to synthesize novel heterocyclic scaffolds (Scheme 2). When C3-alkylated imidazopyridine (**3a**) was treated again with methyl 2-phenyl-2-diazoacetate (**2a**) in the presence of $Rh_2(oct)_4$ (2.0 mol %) in DCE at room temperature for 6 h, the desired dialkylated compound from the electrophilic aromatic substitution reaction on the 2-phenyl ring was not observed (eq 7). This reaction was carried out with $[Cp^*RhCl_2]_2$ (4.0 mol %) and $AgSbF_6$ (16.0 mol %), and it afforded *ortho*-alkylated product **6** in 56% yield (*dr* = 1:1.3) through a C–H activation (eq 8). C3-Alkylated substrate **3h**, generated from 2-phenylimidazo[1,2-a]pyridine (**1a**) and methyl 2-(2-chlorophenyl)-2-diazoacetate (**2h**), was treated with $Pd(OAc)_2$ (5.0 mol %), $PCy_3{\cdot}HBF_4$ (10.0 mol %), and K_2CO_3 (1.5 equiv) in DMA at 130 °C for 12 h under a nitrogen atmosphere,

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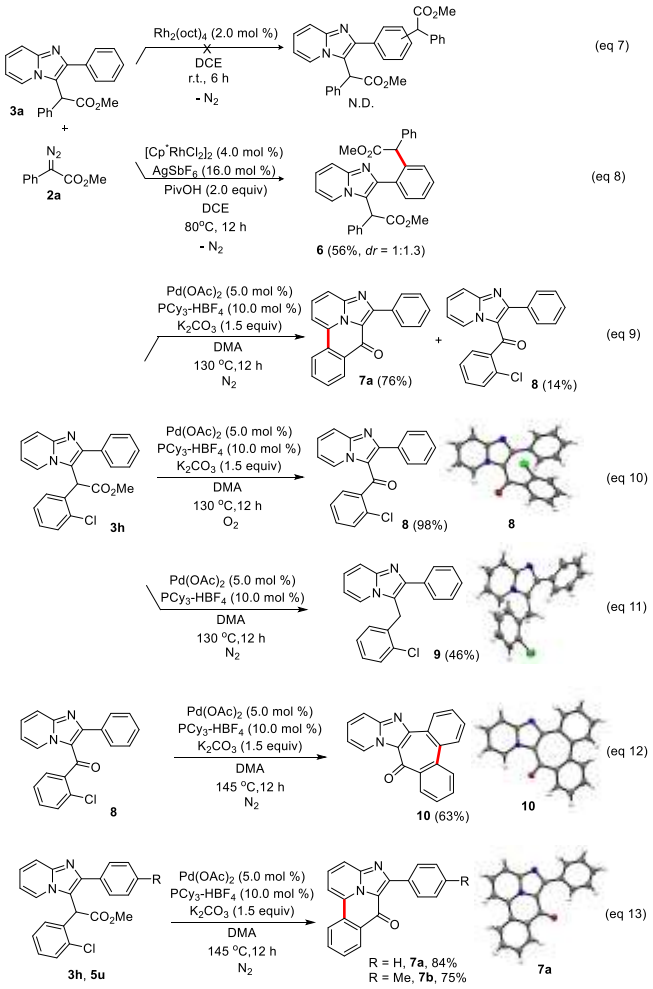
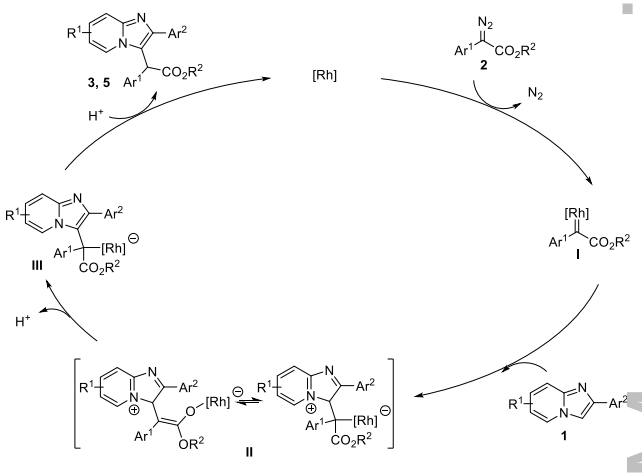
providing benzoimida-zoquinolizinone **7a** (76%) and *ortho*-chlorobenzoyl imidazopyridine **8** (14%) (eq 9). The structure of **7a** and **8** was unambiguously determined by X-ray crystallography (see the Supporting Information). When the reaction was conducted under an oxygen atmosphere, imidazopyridine **8** was produced in 98% yield (eq 10). In addition, when the reaction was carried out without K_2CO_3 in DMA at 130 ºC for 12 h under a nitrogen atmosphere, *ortho*-chlorobenzyl imidazopyridine (**9**) was obtained in 46% yield (eq 11). The structure of **9** was unambiguously determined by X-ray crystallography (see the Supporting Information). We were pleased to obtain cyclohepta-imidazopyridinone (**10**) in 63% yield from **8** in the presence of $Pd(OAc)_2$ (5.0 mol %), $PCy_3{\cdot}HBF_4$ (10.0 mol %), and K_2CO_3 (1.5 equiv) in DMA at 145 °C in 12 h under a nitrogen atmosphere, indicating that **8** is not an intermediate in the formation of benzoimidazoquinolizinone (**7a**) (eq 12). The obtained cyclic compound was confirmed to be cycloheptaimidazopyridinone (**10**) by NMR spectroscopy and single-crystal X-ray analysis (see the Supporting Information). The C3-alkylated compounds (**3h** and **5u**) were smoothly converted to **7a** (84%) and **7b** (75%), respectively, under the same reaction conditions (eq 13).



Scheme 2. Second Alkylation and Application Using C3-Alkylation Products.

A possible mechanism for the production of the C3-alkylated imidazopyridines (**3** and **5**) from the 2-arylimidazo[1,2-a]pyridines (**1**) and alkyl 2-aryl-2-diazoacetates (**2**) is described in Scheme 3. First, the diazoester (**2**) was converted into a rhodium-carbenoid[10] in the presence of the rhodium(II) catalyst with the release of N_2 as the only byproduct. The nucleophilic attack[7] of the C3-carbon atom of the imidazopyridine onto the electrophilic carbene carbon of **I** affords rhodium-bound zwitterionic intermediate **II**, which is aromatized by deprotonation to furnish intermediate **III**. Finally, protoderhodation of **III** provides C3-alkylated imidazopyridine (**3** and **5**) and regenerates the Rh(II) catalyst.



Scheme 3. A Possible Mechanism.

Conclusion

In summary, we have developed a regioselective C3-alkylation of 2-arylimidazo[1,2-a]pyridines with aryl α-diazoesters in the presence of a Rh(II) catalyst in dichloroethane at room temperature. This method was applied in the synthesis of benzoimidazoquinolizinone and cycloheptaimidazopyridinone, which are novel heterocyclic scaffolds.

Experimental Section

General: Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230-400 mesh). ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^{1}H

(chloroform-*d*) and δ 77.2 for $^{13}C\{^1H\}$ (chloroform-*d*)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) were obtained by electron impact (EI) ionization technique (magnetic sector - electric sector double focusing mass analyzer) from the KBSI (Korea Basic Science Institute Daegu Center). Melting points were determined in open capillary tube. CCDC-1845635, 1884733, 1885361, 1892633, and 1887335 contains the supplementary crystallographic data of **3a**, **7a**, **8**, **9** and **10** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Procedure of the Rh-Catalyzed C3-Alkylation of Imidazo[1,2-*a*]pyridine with Aryl Diazoester: A dried test tube equipped with a magnetic stirring bar was charged with imidazo[1,2-a]pyridine **1** (0.2 mmol, 1.0 equiv), $Rh_2(oct)_4$ (3.2 mg, 0.004 mmol, 2.0 mol %), diazoester **2** (0.3 mmol, 1.5 equiv), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at room temperature for 6 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by Silica gel column chromatography with EtOAc and hexane to give the corresponding alkylated products **3**, and **4**.

Methyl 2-phenyl-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3a): Yield: 66.4 mg (97%); R_f = 0.3 (EtOAc: Hexane = 1:1); Ivory solid; Melting point: 129-131 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, *J* = 6.9 Hz, *J* = 1.1 Hz, 1H), 7.79-7.76 (m, 2H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42-7.37 (m, 1H), 7.33-7.27 (m, 3H), 7.20 (ddd, *J* = 9.0 Hz, *J* = 6.8 Hz, *J* = 1.2 Hz 1H), 7.08-7.05 (m, 2H), 6.63 (td, *J* = 10.3 Hz, *J* = 1.1 Hz, 1H), 5.90 (s, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.3, 146.3, 145.8, 134.5, 134.2, 129.1, 129.0, 128.8, 128.2, 127.7, 127.5, 126.3, 124.9, 117.7, 115.5, 111.9, 52.8, 47.3; IR (film): 3366, 3059, 2951, 1736, 1602, 1384, 1073, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{18}N_2O_2$ 342.1368; Found 342.1366.

Ethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(o-tolyl)acetate (3b): Yield: 48.2 mg (65%); R_f = 0.3 (EtOAc: Hexane = 1:1); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 3H), 7.47-7.43 (m, 2H), 7.40-7.36 (m, 1H), 7.23-7.12 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.68 (td, *J* = 10.3 Hz, *J* = 1.0 Hz, 1H), 5.73 (s, 1H), 4.25-4.10 (m, 2H), 2.03 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.6, 145.9, 145.5, 137.2, 134.4, 133.4, 131.5, 129.0, 128.7, 128.13, 128.08, 127.6, 126.4, 125.5, 124.7, 117.8, 115.7, 112.2, 61.9, 46.6, 19.7, 14.2; IR (film): 3397, 3063, 2978, 1731, 1604, 1383, 1073, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{22}N_2O_2$ 370.1681; Found 370.1684.

Ethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(m-tolyl)acetate (3c): Yield: 51.9 mg (70%); R_f = 0.3 (EtOAc: Hexane = 1:1); Ivory solid; Melting point: 75-77 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.81-7.78 (m, 2H), 7.67 (dt, *J* = 9.1 Hz, *J* = 1.1 Hz, 1H), 7.49-7.45 (m, 2H), 7.41-7.37 (m, 1H), 7.21-7.16 (m, 2H), 7.08 (dd, *J* = 7.5 Hz, *J* = 0.4 Hz, 1H), 6.86 (t, *J* = 8.6 Hz, 2H), 6.62 (td, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 5.83 (s, 1H), 4.31-4.19 (m, 2H), 2.27 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.0, 146.2, 145.8, 138.8, 134.5, 134.3, 129.1, 128.9, 128.7, 128.5, 128.2, 126.5, 124.9, 124.5, 117.6, 115.8, 111.7, 61.9, 47.5, 21.6, 14.3; IR (film): 3052, 2979, 1732, 1606, 1383, 1186, 1073, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{22}N_2O_2$ 370.1681; Found 370.1684.

Methyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(p-tolyl)acetate (3d): Yield: 64.9 mg (91%); R_f = 0.3 (EtOAc: Hexane = 1:1); Ivory solid; Melting point: 137-139 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.67 (dt, *J* = 9.0 Hz, *J* = 1.1 Hz, 1H), 7.49-7.45 (m, 2H), 7.41-7.37 (m, 1H), 7.21-7.17 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.63 (td, *J* = 10.3 Hz, *J* = 1.0 Hz, 1H), 5.85 (s, 1H), 3.76 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 146.2, 145.8, 137.5, 134.3, 131.4, 129.1, 128.8, 128.2, 127.5, 126.4, 124.9, 117.7, 115.7, 111.9, 52.7, 47.0, 21.1; IR (film): 3397, 3051, 2950, 1736, 1605, 1383, 1073, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_2$ 356.1525; Found 356.1526.

Methyl 2-(3-methoxyphenyl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3e): Yield: 67.0 mg (90%); R_f = 0.3 (EtOAc:Hexane = 1:1); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dt, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.26-7.17 (m, 2H), 6.81 (dd, *J* = 8.2 Hz, *J* = 1.9 Hz, 1H), 6.67-6.62 (m, 3H), 5.86 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 160.2, 146.3, 145.8, 136.1, 134.3, 130.1, 129.1, 128.8, 128.2, 126.4, 125.0, 119.8, 117.7, 115.5, 113.9, 112.7, 111.9, 55.4, 52.8, 47.3; IR (film): 3366, 3053, 2951, 1736, 1600, 1383, 1073, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_3$ 372.1474; Found 372.1470.

Methyl 2-(4-methoxyphenyl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3f): Yield: 68.5 mg (92%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 70-72 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.41-7.37 (m, 1H), 7.22-7.13 (m, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.84-6.80 (m, 2H), 6.64 (t, *J* = 10.3 Hz, *J* = 1.0 Hz, 1H), 5.83 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.6, 159.1, 146.1, 145.7, 134.3, 129.1, 128.8, 128.7, 128.2, 126.31, 126.29, 125.0, 117.7, 115.8, 114.4, 112.0, 55.4, 52.8, 46.6; IR (film): 3375, 2952, 2928, 1736, 1610, 1383, 1074, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_3$ 372.1474; Found 372.1476.

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(2-phenylimidazo-[1,2-a]pyridin-3-yl)acetate (3g): Yield: 75.3 mg (94%); R_f = 0.3 (EtOAc:Hexane = 1:1); Pink oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.8 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.66 (t, *J* = 6.7 Hz, 1H), 6.55-6.52 (m, 2H), 5.91 (s,

2H), 5.74 (s, 1H), 4.28-4.15 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 148.3, 147.1, 146.1, 145.7, 134.2, 129.1, 128.7, 128.21, 128.18, 126.3, 125.0, 120.7, 117.6, 115.8, 111.9, 108.5, 108.2, 101.3, 61.9, 47.1, 14.2; IR (film): 3566, 2979, 1730, 1501, 1488, 1235, 1037, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{20}N_2O_4$ 400.1420; Found 400.1423.

Methyl 2-(2-chlorophenyl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3h): Yield: 65.6 mg (87%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 64-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dt, *J* = 6.8 Hz, *J* = 1.0 Hz, 1H), 7.73 (dt, *J* = 9.1 Hz, *J* = 1.0 Hz, 1H), 7.66-7.63 (m, 2H), 7.49-7.42 (m, 3H), 7.40-7.35 (m, 1H), 7.31-7.24 (m, 2H), 7.18-7.14 (m, 1H), 6.87 (dd, *J* = 7.7 Hz, *J* = 0.9 Hz, 1H), 6.78 (td, *J* = 10.3 Hz, *J* = 1.0 Hz, 1H), 5.95 (s, 1H), 3.61 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 146.4, 145.7, 134.7, 134.2, 133.3, 130.4, 129.6, 129.3, 129.0, 128.7, 128.3, 127.3, 125.1, 124.9, 118.1, 114.6, 112.8, 53.0, 46.4; IR (film): 3398, 3061, 2950, 1736, 1383, 1072, 751, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}ClN_2O_2$ 376.0979; Found 376.0981.

Methyl 2-(3-chlorophenyl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3i): Yield: 69.3 mg (92%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.0 Hz, 1H), 7.77-7.74 (m, 2H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.28-7.20 (m, 3H), 7.10 (s, 1H), 6.92 (dd, *J* = 7.5 Hz, *J* = 0.7 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H), 5.85 (s, 1H), 3.78 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 146.6, 145.9, 136.6, 135.1, 134.1, 130.3, 129.1, 128.9, 128.4, 128.2, 127.9, 126.0, 125.8, 125.2, 117.9, 114.8, 112.3, 53.0, 47.0; IR (film): 3397, 3055, 2951, 1737, 1595, 1383, 1074, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}ClN_2O_2$ 376.0979; Found 376.0977.

Ethyl 2-(4-bromophenyl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3j): Yield: 74.0 mg (85%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 7.0 Hz, *J* = 1.2 Hz, 1H), 7.78-7.75 (m, 2H), 7.69 (dt, *J* = 9.1 Hz, *J* = 1.2 Hz, 1H), 7.49-7.46 (m, 2H), 7.44-7.38 (m, 3H), 7.23-7.19 (m, 1H), 6.96-6.93 (m, 2H), 6.69-6.65 (m, 1H), 5.77 (s, 1H), 4.30-4.17 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 146.5, 145.8, 134.1, 133.6, 132.1, 129.4, 129.1, 128.8, 128.3, 126.1, 125.1, 121.8, 117.8, 115.1, 112.1, 62.1, 47.0, 14.2; IR (film): 3366, 3052, 1732, 1605, 1382, 1074, 700, 604 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{19}{}^{79}BrN_2O_2$ 434.0630, $C_{23}H_{19}{}^{81}BrN_2O_2$ 436.0612; Found 434.0632, 436.0617.

Ethyl 4-(2-ethoxy-2-oxo-1-(2-phenylimidazo[1,2-a]pyridin-3-yl)ethyl)benzoate (3k): Yield: 77.1 mg (90%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 8.4 Hz, *J* = 1.9 Hz, 2H), 7.93 (dt, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.80-7.77 (m, 2H), 7.69 (dt, *J* = 9.1 Hz, *J* = 1.0 Hz, 1H), 7.51-7.46 (m, 2H), 7.43-7.39 (m, 1H), 7.21 (ddd, *J* = 9.0 Hz, *J* = 6.8 Hz, 2H), 7.16-7.13 (m, 2H), 6.63 (td, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 5.88 (s, 1H), 4.35 (q, *J* = 7.6 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 166.2, 146.9, 139.7, 134.1, 130.2, 130.1, 129.1, 128.8, 128.4, 127.7, 126.1, 125.1, 117.8, 115.1, 112.1, 62.2, 61.2, 47.6, 14.4, 14.3; IR (film): 3412, 3055, 2981, 1730, 1610, 1384, 1074, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{24}N_2O_4$ 428.1736; Found 428.1738.

Ethyl 2-(4-cyanophenyl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3l): Yield: 69.4 mg (91%); R_f = 0.3 (EtOAc:Hexane = 1:1); Pink oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.71 (dt, *J* = 9.1 Hz, *J* = 1.0 Hz, 1H), 7.61-7.58 (m, 2H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 1H), 7.24 (ddd, *J* = 9.1 Hz, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.21-7.18 (m, 1H), 6.68 (td, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 5.86 (s, 1H), 4.33-4.20 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9, 146.8, 145.9, 140.0, 133.9, 132.7, 129.0, 128.9, 128.6, 128.5, 125.6, 125.3, 118.4, 118.0, 114.3, 112.4, 111.9, 62.4, 47.4, 14.2; IR (film): 3054, 2981, 2229, 1732, 1607, 1383, 1073, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{19}N_3O_2$ 381.1479; Found 381.1477.

Ethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(4-(trimethylsilyl)phenyl)acetate (3m): Yield: 62.6 mg (73%); R_f = 0.3 (EtOAc:Hexane = 2:1); Ivory solid; Melting point: 67-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.79-7.76 (m, 2H), 7.68 (dt, *J* = 9.0 Hz, *J* = 1.1 Hz, 1H), 7.48-7.43 (m, 4H), 7.40-7.36 (m, 1H), 7.19 (ddd, *J* = 9.1 Hz, *J* = 6.7 Hz, *J* = 1.2 Hz, 1H), 7.05 (dd, *J* = 8.2 Hz, *J* = 0.9 Hz, 2H), 6.64 (td, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 5.85 (s, 1H), 4.31-4.18 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.23 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.2, 147.7, 147.0, 141.3, 136.4, 135.6, 135.3, 130.4, 130.0, 129.4, 128.1, 127.8, 126.2, 118.9, 116.9, 113.1, 63.2, 48.7, 15.5, 0.2; IR (film): 3446, 3055, 2955, 1731, 1382, 1248, 1073, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{28}N_2O_2Si$ 428.1924; Found 428.1920.

Ethyl 2-(naphthalen-1-yl)-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3n): Yield: 40.6 mg (50%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 187-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.0 Hz, 1H), 7.84 (q, *J* = 8.2 Hz, 2H), 7.74-7.71 (m, 2H), 7.66 (t, *J* = 9.0 Hz, 2H), 7.47-7.42 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 3H), 7.25 (s, 1H), 7.19-7.15 (m, 1H), 6.66 (t, *J* = 6.9 Hz, 1H), 6.33 (s, 1H), 4.26-4.10 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7,145.9, 145.8, 134.4, 134.3, 131.7, 130.7, 129.22, 129.17, 129.1, 128.8, 128.3, 126.8, 126.1, 125.8, 125.7, 125.2, 124.7, 123.1, 117.8, 116.0, 112.2, 62.1, 46.2, 14.2; IR (film): 3052, 2979, 1732, 1598, 1385, 1186, 1072, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{22}N_2O_2$ 370.1681; Found 370.1684.

Methyl 2-(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5a): Yield: 69.6 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 58-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.77-7.75 (m, 2H), 7.48-7.44 (m, 2H), 7.40-7.35 (m, 1H),

7.31-7.24 (m, 3H), 7.07-7.05 (m, 2H), 6.98 (dt, *J* = 6.8 Hz, *J* = 1.0 Hz, 1H), 6.55 (t, 1H), 5.84 (s, 1H), 3.76 (s, 3H), 2.68 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 146.2, 145.9, 134.7, 134.5, 129.3, 129.0, 128.8, 128.1, 127.7, 127.5, 124.0, 123.7, 115.9, 112.0, 52.7, 47.4, 17.3; IR (film): 3387, 3058, 2951, 1736, 1603, 1380, 1073, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_2$ 356.1525; Found 356.1521.

Methyl 2-(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5b): Yield: 63.4 mg (89%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 90-92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.1 Hz, 1H), 7.77-7.75 (m, 2H), 7.48-7.44 (m, 2H), 7.42 (t, *J* = 0.8 Hz, 1H), 7.39-7.36 (m, 1H), 7.32-7.26 (m, 3H), 7.07-7.04 (m, 2H), 6.46 (dd, *J* = 7.1 Hz, *J* = 1.7 Hz, 1H), 5.86 (s, 1H), 3.78 (s, 3H), 5.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 146.3, 146.0, 136.0, 134.7, 134.4, 129.0, 128.8, 128.1, 127.7, 127.6, 125.5, 116.0, 114.9, 114.6, 52.8, 21.4; IR (film): 3058, 2950, 1736, 1604, 1381, 1156, 1073, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_2$ 356.1523; Found 356.1525.

Methyl 2-(6-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5c): Yield: 52.0 mg (73%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 148-150 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.1 Hz, 1H), 7.77-7.74 (m, 2H), 7.48-7.44 (m, 2H), 7.85 (t, *J* = 7.1 Hz, 1H), 7.40-7.36 (m, 1H), 7.32-7.27 (m, 3H), 7.07-7.04 (m, 2H), 6.47 (dd, *J* = 7.1 Hz, *J* = 1.7 Hz, 1H), 5.86 (s, 1H), 3.78 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 146.3, 146.1, 136.0, 134.7, 134.4, 129.0, 128.8, 128.1, 127.7, 127.6, 125.5, 116.1, 114.9, 114.6, 52.8, 47.3, 21.4; IR (film): 3367, 3059, 2951, 1736, 1604, 1381, 1073, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_2$ 356.1525; Found 356.1527.

Methyl 2-(7-ethyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5d): Yield: 67.4 mg (91%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 108-110 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.1 Hz, *J* = 0.7 Hz, 1H), 7.78-7.75 (m, 2H), 7.48-7.44 (m, 3H), 7.40-7.36 (m, 1H), 7.32-7.27 (m, 3H), 7.08-7.05 (m, 2H), 6.50 (dd, *J* = 7.1 Hz, *J* = 1.7 Hz, 1H), 5.87 (s, 1H), 3.78 (s, 3H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 146.4, 146.1, 142.1, 134.7, 134.4, 129.0, 128.8, 128.1, 127.7, 127.6, 125.7, 114.9, 114.6, 113.6, 52.8, 47.3, 28.5, 14.4; IR (film): 3375, 3059, 2965, 1737, 1604, 1382, 1073, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{22}N_2O_2$ 370.1681; Found 370.1678.

Methyl 2-(7-methoxy-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5e): Yield: 73.0 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 120-122 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.78-7.75 (m, 2H), 7.48-7.45 (m, 2H), 7.40-7.36 (m, 1H), 7.32-7.27 (m, 3H), 7.07-7.05 (m, 2H), 6.97 (s, 1H), 6.35 (dd, *J* = 7.6 Hz, *J* = 2.6 Hz, 1H), 5.84 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.6, 158.3, 147.3, 145.7, 134.8, 134.2, 129.1, 128.9, 128.8, 128.1, 127.7, 127.5, 126.9, 114.4, 106.9, 94.8, 55.6, 52.8, 47.3; IR (film): 3366, 3060, 2953, 1736, 1604, 1214, 1071, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_3$ 372.1474; Found 372.1476.

Methyl 2-(7-chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5f): Yield: 67.8 mg (90%); R_f = 0.3 (EtOAc:Hexane = 1:3); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.4 Hz, *J* = 0.4 Hz, 1H), 7.77-7.75 (m, 2H), 7.66 (dd, *J* = 2.0 Hz, *J* = 0.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42-7.38 (m, 1H), 7.32-7.27 (m, 3H), 7.04 (dd, *J* = 7.1 Hz, *J* = 1.4 Hz, 2H), 6.60 (dd, *J* = 7.4 Hz, *J* = 2.1 Hz, 1H), 5.89 (s, 1H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 147.1, 145.6, 134.1, 133.7, 131.6, 129.1, 129.0, 128.8, 128.4, 127.9, 127.3, 126.7, 116.4, 115.9, 113.5, 52.8, 47.2; IR (film): 3366, 3061, 2951, 1736, 1383, 1155, 1070, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}N_2O_2$ 376.0978; Found 376.0979.

Methyl 2-(6-chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5g): Yield: 56.5 mg (75%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 120-122 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 1.9 Hz, *J* = 0.7 Hz, 1H), 7.75-7.73 (m, 2H), 7.61 (dd, *J* = 9.5 Hz, *J* = 0.6 Hz, 1H), 7.50-7.46 (m, 2H), 7.35-7.28 (m, 3H), 7.16 (dd, *J* = 9.5 Hz, *J* = 1.9 Hz, 1H), 7.06-7.04 (m, 2H), 5.87 (s, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.1, 147.2, 144.2, 133.9, 133.8, 129.3, 129.0, 128.9, 128.5, 128.0, 127.4, 126.4, 124.1, 120.1, 118.0, 116.4, 52.9, 47.3; IR (film): 3060, 2951, 1736, 1603, 1382, 1197, 1075, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}ClN_2O_2$ 376.0978; Found 376.0979.

Methyl 2-phenyl-2-(2-(o-tolyl)imidazo[1,2-a]pyridin-3-yl)acetate (5h): Yield: 41.3 mg (58%); R_f = 0.3 (EtOAc: Hexane = 1:3); Ivory solid; Melting point: 114-116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.9 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.34-7.28 (m, 6H), 7.25-7.18 (m, 2H), 7.05 (d, *J* = 6.7 Hz, 2H), 6.66 (t, *J* = 6.8 Hz, 1H), 5.46 (s, 1H), 3.72 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 146.7, 145.5, 138.3, 134.6, 133.5, 130.7, 130.4, 129.0, 128.6, 127.7, 127.6, 126.1, 125.6, 124.7, 117.9, 116.7, 111.9, 52.6, 47.3, 20.3; IR (film): 3059, 3028, 2951, 1736, 1602, 1381, 734, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_2$ 356.1527; Found 356.1525.

Methyl 2-phenyl-2-(2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)acetate (5i): Yield: 65.6 mg (92%); R_f = 0.3 (EtOAc: Hexane = 1:3); Ivory solid; Melting point: 160-162 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 3H), 7.32-7.27 (m, 5H), 7.18 (ddd, *J* = 8.9 Hz, *J* = 6.7 Hz, *J* = 1.1 Hz, 1H), 7.07-7.05 (m, 2H), 7.97 (td, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 5.89 (s, 1H), 3.78 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 146.4, 145.8, 138.1, 134.6, 131.3, 129.5, 129.1, 129.0, 127.7, 127.6, 126.3, 124.9, 117.6, 115.3, 111.9, 52.8, 47.4, 21.4; IR (film): 2950, 1736, 1601, 1380, 1361, 1067, 731, 697 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_2$ 356.1525; Found 356.1524.

Methyl 2-(2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5j): Yield: 73.0 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 189-

191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 3.5 Hz, 1H), 7.73-7.70 (m, 2H), 7.67-7.64 (m, 1H), 7.31-7.27 (m, 3H), 7.16 (ddd, J = 9.0 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.07-7.05 (m, 2H), 7.03-6.99 (m, 2H), 6.60 (td, J = 10.3 Hz, J = 1.2 Hz, 1H), 5.87 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 159.7, 146.2, 145.7, 134.5, 130.2, 129.0, 127.7, 127.5, 126.7, 126.2, 124.8, 117.5, 115.0, 114.2, 111.8, 55.4, 52.7, 47.3; IR (film): 3367, 2951, 1736, 1499, 1384, 1249, 1175, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{20}N_2O_3$ 372.1474; Found 372.1474.

Methyl 2-(2-(3-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5k): Yield: 64.8mg (86%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.0 Hz, 1H), 7.83 (s, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.63 (td, J = 6.8 Hz, J = 1.8 Hz, 1H), 7.42-7.35 (m, 2H), 7.34-7.28 (m, 3H), 7.22 (ddd, J = 9.1 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.06-7.04 (m, 2H), 6.65 (td, J = 10.3 Hz, J = 1.1 Hz, 1H), 5.85 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 145.8, 144.9, 136.1, 134.8, 134.2, 130.0, 129.2, 129.1, 128.3, 127.9, 127.5, 127.0, 126.3, 125.3, 117.7, 115.9, 112.2, 52.9, 47.3; IR (film): 2951, 1736, 1600, 1362, 1197, 1078, 739, 696 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}ClN_2O_2$ 376.0976; Found 376.0979.

Methyl 2-(2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5l): Yield: 73.9 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.0 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 9.1 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.33-7.29 (m, 3H), 7.21 (ddd, J = 8.8 Hz, J = 6.9 Hz, J = 0.8 Hz, 1H), 7.06-7.04 (m, 2H), 6.65 (td, J = 6.8 Hz, J = 0.7 Hz, 1H), 5.83 (s, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 145.9, 145.2, 134.3, 134.2, 132.8, 130.3, 129.1, 129.0, 127.9, 127.5, 126.3, 125.3, 117.7, 115.7, 112.1, 52.9, 47.3; IR (film): 3060, 2951, 1736, 1599, 1380, 1092, 698, 604 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}ClN_2O_2$ 376.0978; Found 376.0979.

Methyl 2-(2-(4-bromophenyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5m): Yield: 81.7 mg (97%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dt, J = 7.0 Hz, J = 1.1 Hz, 1H), 7.68-7.64 (m, 3H), 7.62-7.58 (m, 2H), 7.33-7.28 (m, 3H), 7.20 (ddd, J = 9.1 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.06-7.03 (m, 2H), 6.64 (td, J = 10.3 Hz, J = 1.2 Hz, 1H), 5.83 (s, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 145.9, 145.1, 134.2, 133.2, 132.0, 130.7, 129.1, 127.9, 127.5, 126.3, 125.3, 122.6, 117.7, 115.7, 112.1, 52.9, 47.3; IR (film): 3060, 2951, 1736, 1599, 1361, 1072, 1010, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}{}^{79}BrN_2O_2$ 420.0475, $C_{22}H_{17}{}^{81}BrN_2O_2$ 422.0466; Found 420.0473, 420.0456.

Methyl 2-(2-(3-bromophenyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5n): Yield: 74.1 mg (88%); R_f = 0.3 (EtOAc:Hexane = 1:3); White solid; Melting point: 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.53 (ddd, J = 8.0 Hz, J = 1.9 Hz, J = 1.0 Hz, 1H), 7.35-7.27 (m, 4H), 7.21 (ddd, J = 9.1 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.06-7.04 (m, 2H), 6.65 (td, J = 10.3 Hz, J = 1.1 Hz, 1H), 5.85 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2. 145.8. 144.8. 136.3. 134.2. 132.2. 131.3. 130.3. 129.1. 127.9. 127.51. 127.47. 126.4. 125.3. 123.0. 117.8. 115.9. 112.2. 52.9. 47.3; IR (film): 3060, 2950, 1737, 1362, 1198, 996, 696, 607 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}{}^{79}BrN_2O_2$ 420.0473 $C_{22}H_{17}{}^{81}BrN_2O_2$ 422.0456; Found 420.0475, 422.0453.

Methyl 2-(2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5o): Yield: 65.9 mg (84%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.02 (d, J = 7.0 Hz, 1H), 7.97-7.92 (m, 2H), 7.91-7.85 (m, 2H), 7.91-7.85 (m, 2H), 7.71 (d, J = 9.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.33-7.27 (m, 3H), 7.21 (ddd, J = 9.0 Hz, J = 6.8 Hz, J = 0.9 Hz, 1H), 7.10-7.08 (m, 2H), 6.65 (td, J = 6.9 Hz, J = 0.8 Hz, 1H) 6.01 (s, 1H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 146.3, 145.9, 134.5, 133.5, 133.1, 131.7, 129.1, 128.5, 128.2, 127.84, 127.79, 127.6, 126.9, 126.4, 126.3, 125.1, 117.7, 115.9, 112.0, 52.8, 47.5; IR (film): 3057, 2950, 1736, 1602, 1359, 1159, 732, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{20}N_2O_2$ 392.1525; Found 392.1521.

Methyl 2-phenyl-2-(2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl)acetate (5p): Yield: 53.7 mg (77%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.46 (dd, J = 3.5 Hz, J = 0.7 Hz, 1H), 7.42 (dd, J = 5.1 Hz, J = 0.7 Hz, 1H), 7.34-7.28 (m, 3H), 7.18 (ddd, J = 8.8 Hz, J = 7.1 Hz, J = 0.8 Hz, 1H), 7.15-7.13 (m, 1H), 7.10-7.08 (m, 2H), 6.60 (td, J = 10.2 Hz, J = 0.7 Hz, 1H), 6.06 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.1, 145.8, 140.2, 137.0, 134.1, 129.1, 127.9, 127.8, 127.5, 126.6, 126.2, 125.8, 125.3, 117.5, 115.2, 112.1, 52.8, 47.3; IR (film): 3063, 2950, 1736, 1601, 1360, 1079, 735, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{16}N_2O_2S$ 348.0930; Found 348.0932.

Methyl 2-phenyl-2-(2-(pyridin-2-yl)imidazo[1,2-a] pyridin-3-yl)acetate (5q): Yield: 45.3 mg (66%); R_f = 0.3 (EtOAc:Hexane = 1:1); Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dq, J = 4.8 Hz, J = 0.8 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.0 Hz, 1H), 7.78 (td, J = 11.6 Hz, J = 1.9 Hz, 1H), 7.67 (s, 1H), 7.64 (dt, J = 9.1 Hz, J = 1.1 Hz, 1H), 7.32-7.15 (m, 8H), 6.62 (td, J = 10.3 Hz, J = 1.2 Hz, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 154.4, 148.8, 145.3, 141.9, 136.6, 135.4, 128.8, 127.7, 127.3, 126.0, 125.1, 122.3, 122.2, 119.2, 117.7, 112.0, 52.4, 46.4; IR (film): 3042, 1621, 1488, 1427, 1226, 1201, 1011, 988, 751 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{17}N_3O_2$ 343.1321; Found 343.1325.

Methyl 2-(2-ethylimidazo[1,2-a]pyridin-3-yl)-2-phenyl acetate (5r): Yield: 57.1 mg (97%); R_f = 0.3 (EtOAc:Hexane = 3:1); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.0 Hz, 1H), 7.57 (d, J = 9.0 Hz, 1H), 7.37-7.26 (m, 3H), 7.13-7.09 (m, 3H), 6.56 (td, J = 10.3 Hz,

J = 1.1 Hz, 1H), 5.59 (s, 1H), 3.78 (s, 3H), 2.85 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.3, 148.3, 145.3, 134.5, 128.9, 127.6, 127.5, 125.4, 124.1, 117.0, 114.7, 111.4, 52.6, 46.7, 21.2, 14.5; IR (film): 3072, 2898, 1718, 1647, 1426, 1321, 1226, 978, 751 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{18}N_2O_2$ 294.1368; Found 294.1370.

Methyl 2-(6-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5s): Yield: 53.3 mg (72%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 129-131 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.32-7.25 (m, 5H), 7.07-7.02 (m, 3H), 5.85 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 2.18 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 146.1, 144.8, 137.9, 134.7, 131.5, 129.5, 129.0, 128.9, 128.0, 127.7, 123.7, 121.5, 116.9, 115.0, 52.7, 47.3, 21.4, 18.6; IR (film): 3367, 2950, 1736, 1603, 1496, 1382, 1164, 697 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{22}N_2O_2$ 370.1681; Found 370.1679.

Methyl 2-(6-chloro-2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)-2-phenylacetate (5t): Yield: 66.6 mg (81%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 127-129 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.2 Hz, 1H), 7.70-7.67 (m, 2H), 7.60 (dd, *J* = 9.5 Hz, *J* = 0.4 Hz, 1H), 7.47-7.43 (m, 2H), 7.36-7.30 (m, 3H), 7.17 (dd, *J* = 9.5 Hz, *J* = 2.0 Hz, 1H), 7.05-7.03 (m, 2H), 5.80 (s, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 146.0, 144.2, 134.6, 132.3, 130.3, 129.3, 129.1, 128.1, 127.4, 126.7, 124.1, 120.3, 118.0, 116.5, 53.0, 47.3; IR (film): 3061, 2952, 1736, 1602, 1484, 1380, 1102, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{16}Cl_2N_2O_2$ 410.0586; Found 410.0589.

Methyl 2-(2-chlorophenyl)-2-(7-methyl-2-phenyl imidazo[1,2-a]pyridin-3-yl)acetate (5u): Yield: 75.0 mg (96%); R_f = 0.3 (EtOAc:Hexane = 1:1); Ivory solid; Melting point: 166-168 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.1Hz, 1H), 7.48-7.46 (m, 2H), 7.45-7.41 (m, 2H), 7.38-7.34 (m, 1H), 7.30-7.26 (m, 1H), 6.86 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 1H), 6.61 (dd, *J* = 7.1 Hz, *J* = 1.7 Hz, 1H), 5.92 (s, 1H), 3.61 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9, 146.1, 135.9, 134.7, 134.3, 133.5, 130.4, 129.5, 129.3, 128.9, 128.7, 128.2, 127.3, 124.3, 116.4, 115.4, 113.9, 52.9, 46.4, 21.4; IR (film): 3397, 3061, 2950, 1738, 1380, 1200, 1072, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{19}ClN_2O_2$ 390.1136; Found 390.1135.

Methyl 2-(7-chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(2-chlorophenyl)acetate (5v): Yield: 80.6 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 147-149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.4 Hz, *J* = 0.7 Hz, 1H), 7.71 (dd, *J* = 2.1 Hz, *J* = 0.8 Hz, 1H), 7.65-7.62 (m, 2H), 7.48-7.42 (m, 3H), 7.41-7.37 (m, 1H), 7.29 (td, *J* = 7.7 Hz, *J* = 1.6 Hz, 1H), 7.16 (td, *J* = 11.4 Hz, *J* = 1.3 Hz, 2H), 6.85 (dd, *J* = 7.8 Hz, *J* = 0.8 Hz, 1H), 6.76 (dd, *J* = 7.4 Hz, *J* = 2.1 Hz, 1H), 5.92 (s, 1H), 3.64 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.7, 147.3, 145.5, 134.7, 133.7, 132.9, 131.6, 130.6, 129.7, 129.1, 128.9, 128.8, 128.5, 127.4, 125.6, 116.8, 114.8, 114.3, 53.1, 46.3; IR (film): 3062, 2951, 1738, 1445, 1382, 1201, 1066, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{16}Cl_2N_2O_2$ 410.5087; Found 410.0589.

Methyl 2-(2-chlorophenyl)-2-(2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)acetate (5w): Yield: 76.6 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:10); White solid; Melting point: 147-149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dt, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.72 (dt, *J* = 9.1 Hz, *J* = 0.6 Hz, 1H), 7.55-7.52 (m, 2H), 7.48 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.30-7.22 (m, 4H), 7.14 (td, *J* = 11.4 Hz, *J* = 1.2 Hz, 1H), 6.86 (dd, *J* = 7.8 Hz, *J* = 0.9 Hz, 1H), 6.76 (td, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 5.95 (s, 1H), 3.62 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9, 146.5, 145.6, 138.1, 134.7, 133.3, 131.2, 130.4, 129.51, 129.45, 129.3, 128.8, 127.3, 125.0, 124.8, 118.0, 114.3, 112.7, 53.0, 46.4, 21.4; IR (film): 3389, 2950, 1737, 1502, 1360, 1200, 909, 732 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{19}ClN_2O_2$ 390.1131; Found 390.1135.

Methyl 2-(2-chlorophenyl)-2-(2-(4-chlorophenyl) imidazo[1,2-a]pyridin-3-yl)acetate (5x): Yield: 75.7 mg (92%); R_f = 0.3 (EtOAc:Hexane = 1:3); Purple solid; Melting point: 163-165 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.69 (dt, *J* = 9.1 Hz, *J* = 1.1 Hz, 1H), 7.60-7.57 (m, 2H), 7.45 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.41-7.37 (m, 2H), 7.27-7.20 (m, 2H), 7.13 (td, *J* = 11.4 Hz, *J* = 1.2 Hz, 1H), 6.89 (dd, *J* = 7.8 Hz, *J* = 1.1 Hz, 1H), 6.75 (td, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 5.89 (s, 1H), 3.63 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 145.7, 145.3, 134.7, 134.4, 133.1, 132.8, 130.4, 130.2, 129.6, 129.2, 128.8, 127.3, 125.0, 124.9, 118.1, 114.9, 112.8, 52.9, 46.4; IR (film): 3388, 3054, 2950, 1738, 1380, 1361, 1201, 703 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{16}Cl_2N_2O_2$ 410.0586; Found 410.0589.

Methyl 2-(2-chlorophenyl)-2-(2-(3-chlorophenyl)-imidazo[1,2-a]pyridin-3-yl)acetate (5y): Yield: 79.8 mg (97%); R_f = 0.3 (EtOAc:Hexane = 1:3); Ivory solid; Melting point: 138-140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.0 Hz, 1H), 7.74-7.70 (m, 2H), 7.49-7.46 (m, 2H), 7.37-7.32 (m, 2H), 7.31-7.25 (m, 2H), 7.16 (td, *J* = 7.6 Hz, *J* = 0.9 Hz, 1H), 6.88 (d, *J* = 7.0 Hz, 1H), 6.80 (td, *J* = 10.3 Hz, *J* = 0.9 Hz, 1H), 5.91 (s, 1H), 3.65 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 145.6, 144.9, 135.9, 134.68, 134.65, 132.9, 130.4, 129.9, 129.7, 129.2, 128.4, 127.3, 126.9, 125.2, 125.0, 118.1, 115.03, 115.02, 113.0, 53.1, 46.2; IR (film): 3397, 3063, 2951, 1739, 1601, 1201, 1078, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{16}Cl_2N_2O_2$ 410.0591; Found 410.0589.

Methyl 2-(2-(4-bromophenyl)imidazo[1,2-a]pyridin-3-yl)-2-(2-chlorophenyl)acetate (5z): Yield: 82.0 mg (90%); R_f = 0.3 (EtOAc:Hexane = 1:3); Purple solid; Melting point: 174-176 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.56-7.20 (m, 4H), 7.45 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.28-7.21 (m, 2H), 7.13 (td, *J* = 11.4 Hz, *J* = 1.1 Hz, 1H), 6.89 (dd, *J* = 7.7 Hz, *J* = 0.8 Hz, 1H), 6.76 (td, *J* = 10.3 Hz, *J* = 1.1 Hz, 1H), 5.89 (s, 1H), 3.63 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 145.7, 145.3, 134.7, 133.3, 133.1, 131.8, 130.5, 130.4, 129.6, 129.2, 127.36, 125.02, 124.96,

122.6, 118.1, 114.9, 112.8, 52.9, 46.4; IR (film): 3053, 2950, 1737, 1361, 1201, 1073, 752, 703 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{16}{}^{79}BrClN_2O_2$ 454.0084 $C_{22}H_{16}{}^{81}BrClN_2O_2$ 456.0063; Found 454.0084, 456.0063.

Methyl 2-(2-(3-bromophenyl)imidazo[1,2-a]pyridin-3-yl)-2-(2-chlorophenyl)acetate (5a'): Yield: 88.4 mg (97%); R_f = 0.3 (EtOAc:Hexane = 1:3); Brown solid; Melting point: 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 1H), 7.86 (t, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 9.1 Hz, 1H), 7.53-7.46 (m, 3H), 7.30-7.24 (m, 3H), 7.14 (td, *J* = 11.4 Hz, *J* = 1.0 Hz, 1H), 6.88 (dd, *J* = 7.7 Hz, *J* = 0.7 Hz, 1H), 6.80 (td, *J* = 6.9 Hz, *J* = 0.9 Hz, 1H), 5.91 (s, 1H), 3.65 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.6, 145.6, 144.7, 136.2, 134.6, 132.9, 132.0, 131.2, 130.4, 130.1, 129.6, 129.1, 127.29, 127.26, 125.2, 124.9, 122.8, 118.1, 115.1, 113.0, 53.0, 46.2; IR (film): 3389, 3058, 2951, 1737, 1599, 1470, 1201, 700 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{16}{}^{79}BrClN_2O_2$ 454.0081 $C_{22}H_{16}{}^{81}BrClN_2O_2$ 456.0070; Found 454.0084, 456.0063.

Methyl 2-(2-chlorophenyl)-2-(2-(thiophen-2-yl)imidazo [1,2-a]pyridin-3-yl)acetate (5b'): Yield: 45.9 mg (60%); R_f = 0.3 (EtOAc:Hexane = 1:3); White solid; Melting point: 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.47 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 2H), 7.39 (dd, *J* = 5.1 Hz, *J* = 0.6 Hz, 1H), 7.29-7.21 (m, 3H), 7.14 (td, *J* = 7.6 Hz, *J* = 0.7 Hz, 1H), 7.09 (dd, *J* = 5.0 Hz, *J* = 3.7 Hz, 1H), 6.87 (dd, *J* = 7.7 Hz, *J* = 0.5 Hz, 1H), 6.75 (td, *J* = 10.2 Hz, *J* = 0.8 Hz, 1H), 6.11 (s, 1H), 3.68 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 145.6, 140.3, 136.7, 134.7, 132.8, 130.4, 129.6, 129.1, 127.8, 127.3, 126.7, 125.8, 125.2, 124.8, 117.9, 114.2, 112.9, 53.0, 46.2; IR (film): 3069, 2950, 1737, 1380, 1213, 1081, 751, 702 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{15}ClN_2O_2S$ 382.0545; Found 382.0543.

Methyl 2-(2-chlorophenyl)-2-(6-methyl-2-(p-tolyl) imidazo[1,2-a]pyridin-3-yl)acetate (5c'): Yield: 51.0 mg (63%); R_f = 0.3 (EtOAc:Hexane = 1:3); Purple solid; Melting point: 69-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.52-7.47 (m, 3H), 7.28 (td, *J* = 11.5 Hz, *J* = 1.3 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.15 (td, *J* = 11.4 Hz, *J* = 1.2 Hz, 1H), 7.10 (dd, *J* = 9.2 Hz, *J* = 1.6 Hz, 1H), 6.85 (dd, *J* = 7.8 Hz, *J* = 0.9 Hz, 1H), 5.91 (s, 1H), 3.61 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 146.2, 144.7, 138.0, 134.7, 133.5, 131.3, 130.3, 129.5, 129.4, 128.7, 128.0, 127.3, 122.5, 122.4, 117.3, 114.0, 52.9, 46.4, 21.4, 18.6; IR (film): 3025, 2950, 1738, 1442, 1382, 1168, 1042, 702 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{21}ClN_2O_2$ 404.1294; Found 404.1292.

Procedure for the Preparation of Alpidem and Zolpidem Precursors: A dried test tube equipped with a magnetic stirring bar was charged with imidazo[1,2-*a*]pyridine **1** (0.2 mmol, 1.0 equiv), $Rh_2(oct)_4$ (2.3 mg, 0.004 mmol, 2.0 mol %), ethyl diazoacetate (15% in toluene, 0.3 mmol, 1.5 equiv), and DCE (2.0 mL). The resulting mixture was stirred at room temperature for 3 h under a nitrogen atmosphere, and then another batch of $Rh_2(oct)_4$ (2.0 mol %) and ethyldiazoacetate (1.5 equiv) were added. After being stirred at room temperature for 3 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give the corresponding drug precursors.

Ethyl 2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (4a)[7h]**:** Yield: 38.1 mg (68%); R_f = 0.3 (EtOAc:Hexane = 1:2); Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.9 Hz, 1H), 7.86-7.84 (m, 2H), 7.67 (d, *J* = 6.9 Hz, 1H), 7.50-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.23 (ddd, *J* = 9.1 Hz, *J* = 6.7 Hz, *J* = 1.2 Hz, 1H), 6.86 (td, *J* = 10.2 Hz, *J* = 1.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.6, 145.2, 144.8, 134.2, 128.8, 128.7, 128.0, 124.6, 123.8, 117.8, 113.1, 112.5, 61.8, 31.0, 14.3.

Ethyl 2-(6-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)acetate (4b)[7h]**:** Yield: 31.5 mg (51%); R_f = 0.3 (EtOAc: Hexane = 1:2); Ivory solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.29-7.26 (m, 2H), 7.06 (dd, *J* = 9.2 Hz, *J* = 1.5 Hz, 1H), 4.22 (dd, *J* = 7.1 Hz, 2H), 4.01 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 1.28 (t, *J* = 7.1 Hz,, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 144.6, 144.2, 137.6, 131.5, 129.4, 128.5, 127.6, 122.0, 121.4, 116.9, 112.5, 61.6, 31.0, 21.4.

Ethyl 2-(6-chloro-2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)acetate (4c)[7h]**:** Yield: 39.8 mg (57%); R_f = 0.3 (EtOAc:Hexane = 1:2); Ivory solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 1.9 Hz, *J* = 0.7 Hz, 1H) 7.79-7.75 (m, 2H), 7.59 (dd, *J* = 9.5 Hz, *J* = 0.6 Hz, 1H), 7.47-7.44 (m, 2H), 7.21 (dd, *J* = 9.5 Hz, *J* = 1.9 Hz, 1H). 4.25 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.0, 144.6, 143.6, 134.4, 132.3, 129.9, 129.1, 126.3, 121.9, 121.0, 118.1, 113.8, 62.0, 30.9, 14.3.

Procedure of Rh (III)-Catalyzed Alkylation of C3-Alkylated Imidazopyridine: A dried test tube equipped with a magnetic stirring bar was charged with C3-alkylated imidazo[1,2-*a*]pyridine **3a** (0.2 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol, 4.0 mol %), $AgSbF_6$ (11 mg, 0.032 mmol, 16.0 mol %), PivOH (46 μL, 0.4 mmol, 2.0 equiv), diazoester **2a** (0.4 mmol, 2.0 equiv), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give **6** (1:1.3 ratio).

Methyl 2-(2-(3-(2-methoxy-2-oxo-1-phenylethyl) imidazo[1,2-a]pyridin-2-yl)phenyl)-2-phenylacetate (6): Yield: 54.9 mg (56%); R_f = 0.3 (EtOAc:Hexane = 1:2); Orange oil; inseparable mixture of diasteromers (1:1.3 ratio); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 0.6H), 7.96 (d, *J* = 7.0 Hz, 0.4H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.41-7.34 (m, 2H), 7.33-7.25 (m, 6H), 7.23-7.16 (m, 4H), 7.11-7.06 (m, 2H), 6.65 (td, *J* = 10.3 Hz, *J* = 1.1 Hz, 0.6H), 6.60 (td, *J* = 10.3 Hz, *J* = 1.1 Hz, 0.4H), 6.02 (s, 0.3H), 5.75 (s, 0.6H), 5.52 (s, 0.6H), 5.45 (s, 0.3H), 3.77 (s, 1H), 3.667 (s, 1.7H) 3.666 (s, 1H),

3.52 (s, 1.7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.7, 173.4, 171.5, 171.3, 145.9, 145.6, 145.5, 139.3, 139.1, 139.0. 138.8. 134.6. 134.4. 133.5. 133.4. 131.1. 130.9. 130.0, 129.5, 129.05, 129.03, 128.98, 128.91, 128.87, 128.8, 128.6, 128.5, 127.7, 127.6, 127.5, 127.3, 127.10, 127.07, 127.02, 126.96, 126.4, 126.3, 124.89, 124.86, 117.9, 117.8, 117.4, 117.2, 111.9, 111.8, 53.1, 52.9, 52.7, 52.3, 52.1, 47.30, 47.27; IR (film): 3366, 3059, 2951, 1736, 1602, 1384, 1073, 699 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{31}H_{26}N_2O_4$ 490.1895; Found 490.1893.

Application of C3-Alkylated Imidazopyridine

1) Synthetic procedure for 7a and 8 (eq 11): A dried test tube equipped with a magnetic stirring bar was charged with C3-alkylated imidazo[1,2-*a*]pyridine **3h** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol %), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 10.0 mol %), K_2CO_3 (41.5 mg, 0.3 mmol, 1.5 equiv), and DMA (1.0 mL) under a nitrogen atmosphere. After being stirred at 130 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give the corresponding Cyclization products **7a** and **8**.

2) Synthetic procedure for 8 (eq 12): A dried test tube equipped with a magnetic stirring bar was charged with C3-alkylated imidazo[1,2-*a*]pyridine **3h** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol %), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 10.0 mol %), K_2CO_3 (41.5 mg, 0.3 mmol, 1.5 equiv), and DMA (1.0 mL) under an oxygen atmosphere. After being stirred at 130 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give the corresponding products **8**.

3) Synthetic procedure for 9 (eq 13): A dried test tube equipped with a magnetic stirring bar was charged with C3-alkylated imidazo[1,2-*a*]pyridine **3h** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol %), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 10.0 mol %), and DMA (1.0 mL) under a nitrogen atmosphere. After being stirred at 130 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give the corresponding products **9**.

4) Synthetic procedure for 10 (eq 14): A dried test tube equipped with a magnetic stirring bar was charged with 3-Acylated imidazo[1,2-*a*]pyridine **8** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol %), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 10.0 mol %), K_2CO_3 (41.5 mg, 0.3 mmol, 1.5 equiv), and DMA (1.0 mL) under a nitrogen atmosphere. After being stirred at 130 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give the corresponding Cyclization products **10**.

5) Synthetic procedure for 7a, and 7b (eq 15): A dried test tube equipped with a magnetic stirring bar was charged with C3-alkylated imidazo[1,2-*a*]pyridine **3h or 5u** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol %), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 10.0 mol %), K_2CO_3 (41.5 mg, 0.3 mmol, 1.5 equiv), and DMA (1.0 mL) under a nitrogen atmosphere. After being stirred at 145 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with EtOAc and hexane to give the corresponding Cyclization products **7a** or **7b**.

5-Phenyl-6H-benzo[a]imidazo[5,1,2-de]quinolizin-6-one (7a): Yield: 49.8 mg (84%); R_f = 0.3 (EtOAc:Hexane = 1:1); Yellow solid; Melting point: 197-199 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74-8.69 (m, 3H), 8.43 (d, *J* = 7.4 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.86 (q, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 7.3 Hz, 1H), 7.61-7.57 (m, 2H), 7.55-7.50 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 155.5, 145.0, 134.0, 132.9, 132.5, 130.91, 130.88, 130.4, 130.1, 128.5, 128.4, 128.3, 127.6, 123.5, 119.6, 116.7, 110.9; IR (film): 3069, 1630, 1478, 1331, 1235, 921, 754, 691 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{12}N_2O$ 296.0947; Found 296.0950.

5-(*p*-tolyl)-6H-benzo[a]imidazo[5,1,2-de]quinolizin-6-one (7b): Yield: 46.6 mg (75%); R_f = 0.3 (EtOAc:Hexane = 1:1); Yellow solid; Melting point: 187-189 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 2H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.04 (dd, *J* = 8.7 Hz, *J* = 0.6 Hz, 1H), 7.88-7.82 (m, 2H), 7.78 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7, 155.7, 145.1, 140.7, 134.1, 132.5, 130.9, 130.1, 130.0, 129.2, 128.5, 128.3, 127.6, 123.5, 119.6, 116.5, 110.7, 21.8; IR (film): 3073, 2918, 1631, 1599, 1480, 1332, 1232, 757 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{14}N_2O$ 310.1102; Found 310.1106.

(2-Chlorophenyl)(2-phenylimidazo[1,2-a]pyridin-3-yl)methanone (8): Yield: 65.2 mg (98%); R_f = 0.3 (EtOAc: Hexane = 1:4); Yellow solid; Melting point: 136-138 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.89 (dt, *J* = 6.9 Hz, *J* = 1.1 Hz, 1H), 7.82 (dt, *J* = 8.9 Hz, *J* = 1.0 Hz, 1H), 7.63-7.58 (m, 1H), 7.28-7.25 (m, 2H), 7.18 (td, *J* = 10.4 Hz, *J* = 1.2 Hz, 1H), 7.13-7.03 (m, 6H), 6.90 (td, *J* = 11.1 Hz, *J* = 1.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 184.6, 157.5, 147.9, 139.0, 133.8, 131.9, 131.0, 130.3, 130.0, 129.8, 129.7, 129.3, 128.3, 127.5, 126.2, 120.7, 117.6, 115.4; IR (film): 3062, 1612, 1393, 1327, 1221, 898, 753, 645 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{13}ClN_2O$ 332.0718; Found 332.0716.

3-(2-Chlorobenzyl)-2-phenylimidazo[1,2-a]pyridine (9): Yield: 29.3 mg (46%); R_f = 0.3 (EtOAc:Hexane = 1:4); Yellow solid; Melting point: 66-68 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 3H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.47 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.43-7.39 (m, 2H), 7.35-7.31 (m, 1H), 7.21-7.16 (m, 2H), 7.05 (td, *J* = 11.5 Hz, *J* = 1.1 Hz, 1H), 6.73-6.70 (m, 2H), 4.52 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 144.7, 134.4, 134.3, 134.2, 129.8, 128.7, 128.5, 128.4, 128.1, 127.9, 127.4, 124.4, 123.3, 117.7, 116.6, 112.4, 27.8; IR (film): 3059, 1678, 1504, 1444, 1359, 1073, 749, 699 cm^{-1}; HRMS (EI)

m/z: $[M]^+$ Calcd for $C_{20}H_{15}ClN_2$ 318.0921; Found 318.0924.

9H-Dibenzo[4',5':6',7']cyclohepta[1',2':4,5]imidazo[1,2-a]pyridin-9-one (10): Yield: 37.3 mg (63%); R_f = 0.3 (EtOAc:Hexane = 1:5); Ivory solid; Melting point: 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, J = 7.0 Hz, 1H), 8.72 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 8.38 (dd, J = 7.8 Hz, J = 1.6 Hz, 2H), 7.95 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H), 7.89 (dd, J = 7.9 Hz, J = 1.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.63 (td, J = 11.1 Hz, J = 1.5 Hz, 1H), 7.60-7.52 (m, 3H), 7.51-7.47 (m, 1H), 7.02 (td, J = 10.4 Hz, J = 1.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 181.1, 149.3, 147.6, 138.9, 136.9, 136.2, 131.8, 131.7, 131.4, 130.4, 129.7, 129.4, 129.23, 129.17, 128.54, 128.45, 128.1, 124.2, 117.2, 114.2; IR (film): 3073, 2918, 1631, 1599, 1480, 1332, 1232, 757 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{12}N_2O$ 296.0954; Found 296.0950.

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References

[1] a) A. R. Katritzky, *Comprehensive heterocyclic chemistry III*, 1st ed., Elsevier, Amsterdam, **2008**; b) E. S. Hand, W. W. Paudler, *J. Org. Chem.* **1978**, *43*, 658-663; c) E. S. Hand, W. W. Paudler, *J. Org. Chem.* **1978**, *43*, 2900-2906.

[2] a) S. Hegde, M. Schmidt, *Annual Reports in Medicinal Chemistry* **2010**, *45*, 467–537; b) D. J. Keeling, S. M. Laing, J. Senn-Bilfinger, *Biochemical Pharmacology* **1988**, *37*, 2231-2236; c) D. J. Sanger, *Behav. Pharmacol*. **1995**, *6*, 116-126; d) G.-Y. Duan, Y.-J. Zhang, B.-Q. Hao, *Acta Cryst.* **2010**, *E66*, o3272; e) B. Zivkovic, E. Morel, D. Joly, Gh. Perrault, D. J. Sanger, K. G. Lloyd, *Pharmacopsychiatry* **1990**, *23*, 108-113; f) B. Du, A. Shan, Y. Zhang, X. Zhong, D. Chen, K. Cai, *Am. J. Med. Sci.* **2014**, *347*, 178-182.

[3] a) Y. Maruyama, K. Anami, M. Terasawa, K. Goto, T. Imayoshi, Y. Kadobe, Y. Mizushima, *Arzneim.-Forsch.* **1981**, *31*, 1111-1118; b) D. Belohlavek, P. Malfertheiner, *J. Scand. Gastroenterol. Suppl.* **1979**, *54*, 44; c) C. Parisio, F. Clementi, *Lab. Invest.* **1976**, *35*, 484-495; d) Y. Uemura, S. Tanaka, S. Ida, T. Yuzuriha, *J. Pharm. Pharmacol.* **1993**, *45*, 1077-1081; e) L. Almirante, L. Polo, A. Mugnaini, E. Provinciali, P. Rugarli, A. Biancotti, A. Gamba, W. Murmann, *J. Med. Chem.* **1965**, *8*, 305-312; f) K. Mizushige, T. Ueda, K. Yukiiri, H. Suzuki, *Cardiovasc. Drug Rev.* **2002**, *20*, 163-174.

[4] H. J. Park, J.-G. Jun, *Bull. Korean Chem. Soc.* **2017**, *38*, 1123-1128.

[5] K. Li, X. Zhu, S. Lu, X.-Y. Zhou, Y. Xu, X.-Q. Hao, M.-P. Song, *Synlett* **2016**, *27*, 387-390.

[6] K. Pericherla, B. Khungar, A. Kumar, *Tetrahedron Lett*. **2012**, *53*, 1253-1257.

[7] a) J. Koubachi, S. El Kazzouli, S. Berteina-Raboin, A. Mouaddib, G. Guillaumet, *Synthesis* **2008**, *16*, 2537-2542; b) J. Koubachi, S. Berteina-Raboin, A. Mouaddib, G. Guillaumet, *Synthesis* **2009**, *2*, 271-276; c) H. Cao, S. Lei, J. Liao, J. Huang, H. Qiu, Q. Chen, S. Qiu, Y. Chen, *RSC Adv*. **2014**, *4*, 50137-50140; d) S. Wang, X. Huang, Z. Ge, X. Wang, R. Li, *RSC Adv*. **2016**, *6*, 63532-63535; e) M. Zhu, X. Han, W. Fu, Z. Wang, B. Ji, X.-Q. Hao, M.-P. Song, C. Xu, *J. Org. Chem.* **2016**, *81*, 7282-7287; f) H. Su, L. Wang, H. Rao, H. Xu, *Org. Lett*. **2017**, 19, 2226-2229; g) Q. Chang, Z. Liu, P. Liu, L. Yu, P. Sun, *J. Org. Chem.* **2017**, *82*, 5391-5397; h) N. Chernyak, V. Gevorgyan, *Angew. Chem.* **2010**, 122, 2803-2806; *Angew. Chem. Int. Ed*. **2010**, *49*, 2743-2746; i) L. C. Rao, N. S. Kumar, H. M. Meshram, *RSC Adv.* **2015**, *5*, 70949-70957; j) M. Ghosh, A. Naskar, S. Mishra, A. Hajra, *Tetrahedron Lett.* **2015**, *56*, 4101-4104; k) S. Mondal, S. Samanta, S. Santra, A. K. Bagdi, A. Hajra, *Adv. Synth. Catal.* **2016**, *358*, 3633-3641; l) F. Liu, Z. Shen, Y. Yuan, P. Sun, *Org. Biomol. Chem.* **2016**, *14*, 6523-6530; m) V. M. Pérez, D. Fregoso López, L. D. Miranda, *Tetrahedron Lett.* **2017**, *58*, 1326-1329.

[8] Y. Li, F. Wang, S. Yu, X. Li, *Adv. Synth. Catal.* **2016**, *358*, 880-886.

[9] S. Park, H. Kim, J.-Y. Son, K. Um, S. Lee, Y. Beak, B. Seo, P. H. Lee, *J. Org. Chem.* **2017**, *82*, 10209-10218.

[10] M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911-936.

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FULL PAPER

Rhodium(II)-Catalyzed Regioselective C3-Alkylation of 2-Arylimidazo[1,2-a]pyridines with Aryl Diazoesters

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