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Rh(III)-Catalyzed Oxidative Annulation of 2-Phenylimidazo[1,2-*a*]pyridines with Alkynes: Mono versus Double C−H Activation

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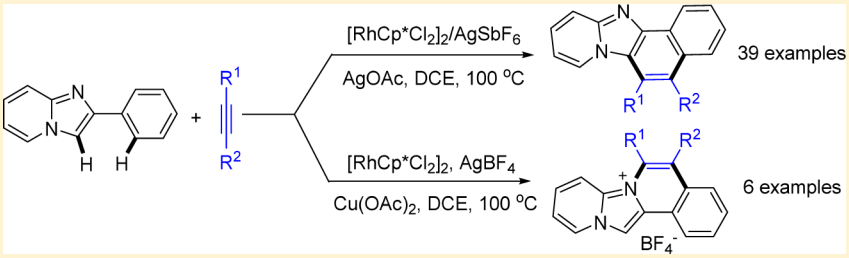
Supporting Information



ABSTRACT: Rh(III)-catalyzed C−H activation of 2-phenylimidazo[1,2-*a*]pyridines in divergent oxidative coupling with alkynes has been achieved. Selective mono versus 2-fold C−H activation has been attained under condition control. When AgOAc was used as an oxidant, the coupling afforded 5,6-disubstituted naphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridines as a result of initial nitrogen chelation-assisted C−H activation at the benzene ring followed by rollover C−H activation. In contrast, the reaction afforded a fused isoquinolinium salt as a result of C−C and C−N coupling when $AgBF_4$ was employed as a co-oxidant. A rhodacyclic intermediate has been isolated.

INTRODUCTION

Arenes and heteroarenes with extended conjugated π-systems have received considerable attention owing to their potential utility as organic electronic materials.[1] Therefore, many future applications require the improvement of existing synthetic methods for extended π-systems. Transition metal-catalyzed C−H bond activation has received increasing attention as a powerful strategy in synthetic chemistry in the past decades.[2] In particular, Rh(III)-catalyzed functionalization of C(aryl)−H bonds has experienced tremendous progress owing to their high efficiency, broad scope, and high functional group tolerance.[3] Significantly, preparation of heterocycles via rhodium(III)-catalyzed C−H activation of arenes and oxidative coupling with alkynes has been established as an important method by many research groups.[4] The group of Miura and Satoh demonstrated the rhodium(III)-catalyzed synthesis of polyarylated naphthyl-/anthrylazole,[5] acene,[6] indolo[2,1-*a*]-isoquinoline,[7] and naphthothiophene derivatives.[8] Cramer and co-workers reported the synthesis of anthracenes via oxidative annulations of naphthalenes.[9] Very recently, Rh(III)-catalyzed efficient syntheses of aza-fused polycyclic quinolines,[10] naphthapyrans,[11] phenanthroimidazoles,[12] and naphthyridines[13] have also been described. Hua and co-workers reported synthesis of multisubstituted 2-aminoquinolines via Rh(III)-catalyzed coupling between tetrazoles and internal alkynes.[14]

As a continuation of our interest in Rh(III)-catalyzed double C−H activation of arenes,[15] we aim to explore the synthesis of fused heteroaromatics through double C−H bond activation resulting in oxidative annulations. We reasoned that the coupling of 2-phenylimidazo[1,2-*a*]pyridines with alkynes may follow this reaction pattern. This is because, in addition to chelation-assisted C−H activation in the benzene ring, the 3-position of this heterocycle is also very reactive. Thus, the expected 2-fold C−H activation process may involve either N-chelation-assisted C−H activation followed by subsequent rollover C−H bond activation[16] or C(3)-chelation-assisted cyclometalation. We now report a convenient condition-controlled approach to access 5,6-disubstituted naphtho[1′,2′:4,5]imidazo-[1,2-*a*]pyridines and a fused isoquinolinium via rhodium(III)-catalyzed C−H activation of 2-phenylimidazo[1,2-*a*]pyridines.

RESULTS AND DISSCUSSION

The coupling of 2-phenylimidazo[1,2-*a*]pyridine (**1a**) with diphenylacetylene (**2a**) was selected as a model reaction for the screening of the reaction parameters (Table 1). The initial reaction of **1a** with **2a** was carried out in the presence of 4 mol % of $[RhCp^*Cl_2]_2$ (Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl) and 16 mol % of $AgSbF_6$ as the catalyst at 100 °C in DCE. While no product was detected when Ag_2CO_3 was used as an oxidant (Table 1, entry 1), switching the oxidant to AgOAc and $Cu(OAc)_2$ resulted in the isolation of the desired product **3aa** in 87% and 44% yield, respectively (entries 2 and 3), as a result of formal 2-fold C−H activation. Further examination of the solvent revealed that 1,4-dioxane, toluene, THF, and EtOAc all gave inferior results (entries 4−7). In a control experiment, omitting $AgSbF_6$ led to the product **3aa** in a low yield (entry 8) and no reaction was observed when neither $AgSbF_6$ nor

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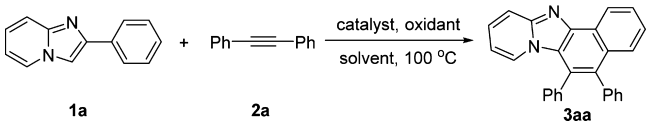
Table 1. Optimization Studies[a]



1a 2a 3aa

entry	catalyst	oxidant	solvent	yield (%)[b]
1	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3	DCE	nd
2	$[RhCp^*Cl_2]_2/AgSbF_6$	AgOAc	DCE	87
3	$[RhCp^*Cl_2]_2/AgSbF_6$	$Cu(OAc)_2$	DCE	44
4	$[RhCp^*Cl_2]_2/AgSbF_6$	AgOAc	1,4-dioxane	56
5	$[RhCp^*Cl_2]_2/AgSbF_6$	AgOAc	toluene	38
6	$[RhCp^*Cl_2]_2/AgSbF_6$	AgOAc	THF	42
7	$[RhCp^*Cl_2]_2/AgSbF_6$	AgOAc	EtOAc	35
8	$[RhCp^*Cl_2]_2$	AgOAc	DCE	75
9	–	AgOAc	DCE	nd

[a]Reaction conditions: $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), oxidant (2.2 equiv), **1a** (0.20 mmol), and **2a** (0.24 mmol) in solvent (2 mL) at 100 °C for 12 h. [b]Yield of isolated product.

$[RhCp^*Cl_2]_2$ was used (entry 9). Thus, the following conditions were eventually chosen for subsequent studies: $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (2.2 equiv) in DCE (2 mL) at 100 °C for 12 h.

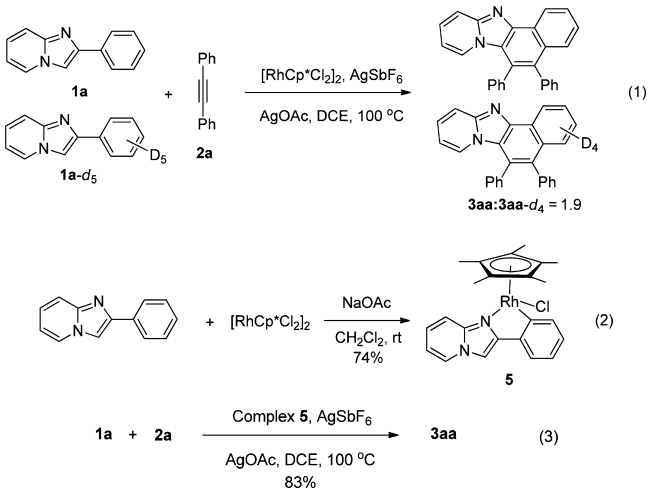
Under the standard reaction conditions, we first examined the scope of the 2-arylimidazo[1,2-*a*]pyridine substrates (**1a**–**y**) in the coupling with diphenylacetylene (**2a**) (Scheme 1). 2-Arylimidazo[1,2-*a*]pyridines bearing electron-donating, electron-withdrawing, and halogen groups at the para position of benzene ring were generally well-tolerated and afforded products **3aa**–**ha** in moderate to good isolated yields. Moreover, a larger-scale (5 mmol) synthesis of **3aa** resulted in somewhat lower isolation (60%). An exception was observed for the substrate bearing a *p*-nitro group, where only low isolated yield was obtained (**3ia**). It was observed that substrate bearing a *m*-chloro group underwent selective C–H activation at the less hindered site to afford the desired product **3ja** in 83% yield. However, the *m*-methoxy-substituted substrate afforded two regioisomeric products that could be chromatographically separated (**3ka** and **3k′a**), and the identity of **3k′a** has been confirmed by X-ray crystallography.[17] The desired products were isolated in 70–80% yield when a methyl or halogen group was introduced to the imidazo[1,2-*a*]pyridine ring (**3la**–**oa**). Substrates bearing methyl, methoxy, halo, and even cyano on both the benzene and pyridine ring also reacted smoothly to afford products in good yields (**3pa**–**wa**). However, the 8-methyl-substituted substrate exhibited lower reactivity and formed **3xa** in 39% yield, implying that the reaction is strongly affected by the steric effect at this position and that the C–H activation might be assisted by N-coordination. Importantly, the arene ring in the substrate is not limited to a benzene system. When 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine was employed under the standard conditions, product **3ya** was isolated in 93% yield.

We next explored the scope and limitations of alkyne substrate in this coupling (Scheme 2). Symmetric diarylacetylenes bearing various substituents such as methyl, methoxy, halogen, and trifluoromethyl at the 4-position all coupled smoothly with **1a** in 67–89% yields (**3ab**–**af**). Diarylacetylene bearing a *m*-methyl provided **3ag** in low yield, and two rotational isomers were observed as indicated by ^1H and ^{13}C NMR spectroscopy. This reaction is also compatible with *o*-fluoro-substituted diarylacetylene, from which product **3ah** was isolated in 43% yield.

The annulative coupling between bis(2-thiophenyl)acetylene and **1a** took place to afford **3ai** in only 33% yield, indicative of limitation of the alkyne. It should be noted that diethyl acetylenedicarboxylate displayed good reactivity and afforded product **3aj** in 85% yield. Unsymmetrical alkynes such as 1-phenyl-1-propyne were also applicable. Although the efficiency of this reaction is limited (**3ak**, 33%), the regioselectivity with respect to alkyne insertion is high. Aside from **2k**, other unsymmetrical diarylacetylenes or alkyl phenylpropiolate also coupled with **1a** in high efficiency, but a mixture of two regioisomeric products was isolated in approximately 2:1 ratio (**3al** and **3al′**, **3am** and **3am′**, **3an** and **3an′**), and they failed to be chromatographically separated. All the above results seem to indicate that more electron-poor alkynes are more reactive. In contrast, both 3-hexyne and phenylacetylene failed to undergo the desired reaction.

To further extend the usage of the arene substrates and encouraged by the reports by Cheng,[18] You,[19] and others,[20] we applied the imidazo[1,2-*a*]pyridines to an alternative oxidative C–C/C–N coupling reaction. Thus, **1a** and **2a** were treated under modified conditions reported by You, and the reaction afforded a fused isoquinolinium **4a** in 88% yield. The scope of the arenes and alkynes was next briefly explored (Scheme 3). It was found that substrates bearing methyl, methoxy, and chloro groups were fully tolerated in this transformation, and the salt products were isolated in consistently good to high yields (**4a**–**f**).

To further understand the physical properties of these products, we measured the absorption and emission spectra of a few products in CH_2Cl_2. **3aa**, **3ca**, and **3ya** showed strong absorption bands between 240 and 300 nm and showed strong emissions of violet light between 410 and 480 nm when irradiated by light at 260 nm wavelength. In contrast, **3ia** only showed relatively weak emissions at 393 and 618 nm when irradiated by light of 310 nm wavelength (see Supporting Information).



Several experiments have been performed to investigate the reaction mechanism. A competitive reaction has been conducted using an equimolar mixture of **1a** and 2-([D_5]-phenyl)imidazo[1,2-*a*]pyridine (**1a**-d_5) in the coupling with **2a**. ^1H NMR spectroscopic analysis of the product mixture revealed a kinetic isotope effect (KIE) of 1.9 at a low conversion (eq 1). A stoichiometric reaction between **1a** and $[RhCp^*Cl_2]_2$ was performed in the presence of NaOAc, from which the cyclometalated product **5** was isolated in 74% yield. Complex

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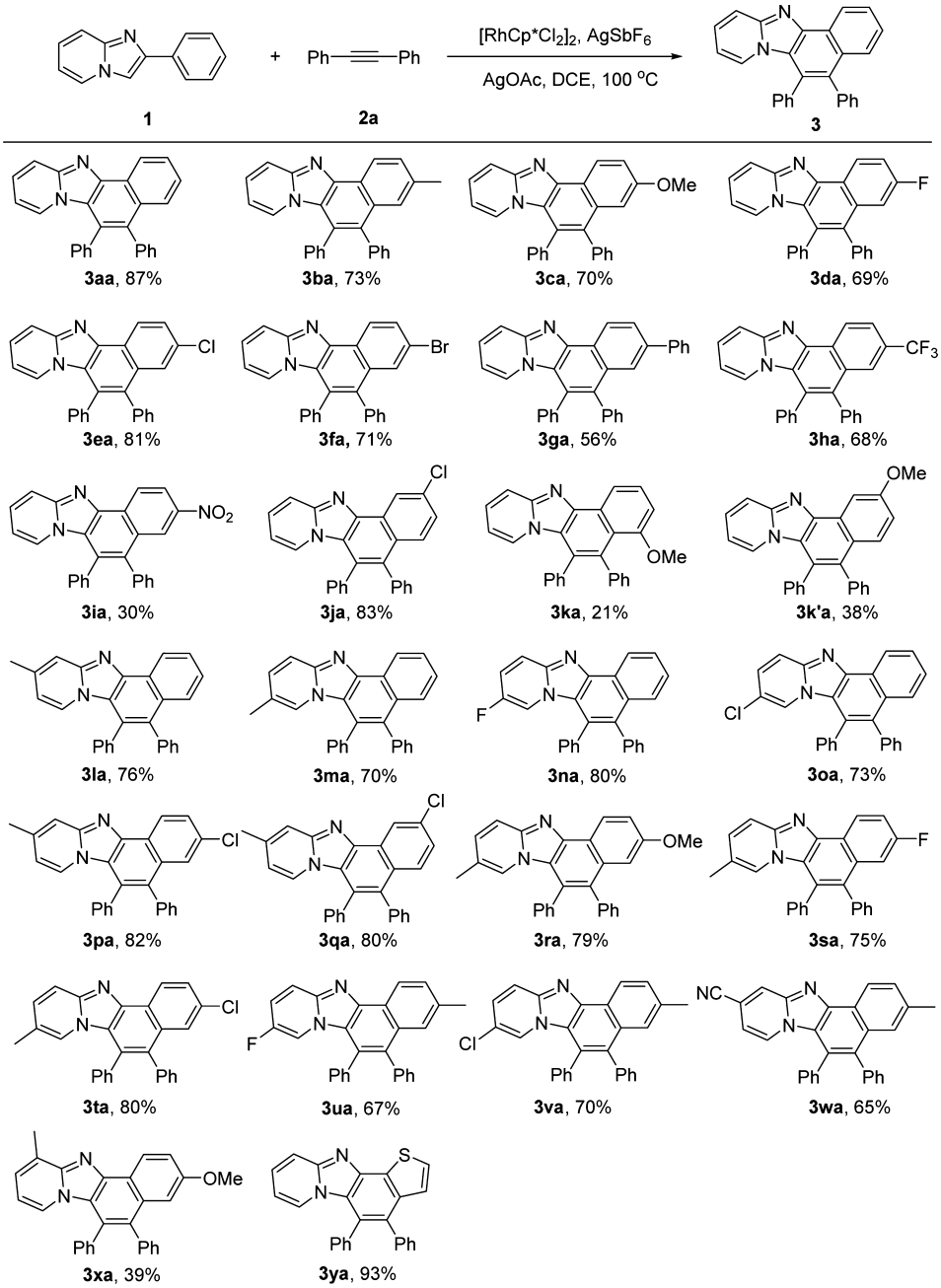
Scheme 1. Substrate Scope of 2-Phenylimidazo[1,2-*a*]pyridines[a]



[a]Reaction conditions: $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (2.2 equiv), **1** (0.20 mmol), and **2a** (0.24 mmol) in DCE (2 mL) at 100 °C for 12 h. Yield of isolated product.

5 has been fully characterized by ^1H and ^{13}C NMR spectroscopy. In particular, the Rh−C resonates as a doublet at δ 174.4 (J_{Rh-C} = 31.2 Hz) in the ^{13}C NMR spectrum (100 MHz, $CDCl_3$). Complex **5** proved to be an active catalyst because when it was designated as a catalyst (7 mol %) in the presence of $AgSbF_6$ for the coupling between **1a** and **2a**, product **3aa** was isolated in a comparable yield (eq 3). In addition to this coupling reaction, **5** also proved to be an active catalyst for the C−C/C−N coupling between **1a** and **2a** to afford **4a** in 82% yield. These results indicated that in both coupling systems, the C−H activation is initially assisted by N-coordination, and in the formation of **3aa**, subsequent rollover C−H activation[16] to the C(3) position of the heterocycle is likely involved (see Scheme 4).

Based on these observations and literature precedents,[16a,19] a proposed reaction mechanism is given in Scheme 4. First, coordination of **1a** to rhodium and subsequent cyclometalation generates rhodacyclic intermediate **5**. Insertion of an incoming alkyne gives seven-membered rhodacycle **6**. This intermediate is proposed to undergo nitrogen decoordination and rollover C−H activation[16] to afford intermediate **7**, which is proposed to undergo reductive elimination to afford product **3aa** and a Rh(I) species. The Rh(I) is reoxidized by AgOAc to regenerate the rhodium(III) active catalyst for the next catalytic cycle. Alternatively, C−N bond reductive elimination of the rhodacycle **6** followed by anion exchange gives the fused isoquinolinium salt **4a** and a Rh(I) species, which was oxidized by $Cu(OAc)_2$ to regenerate the Rh(III) active catalyst.

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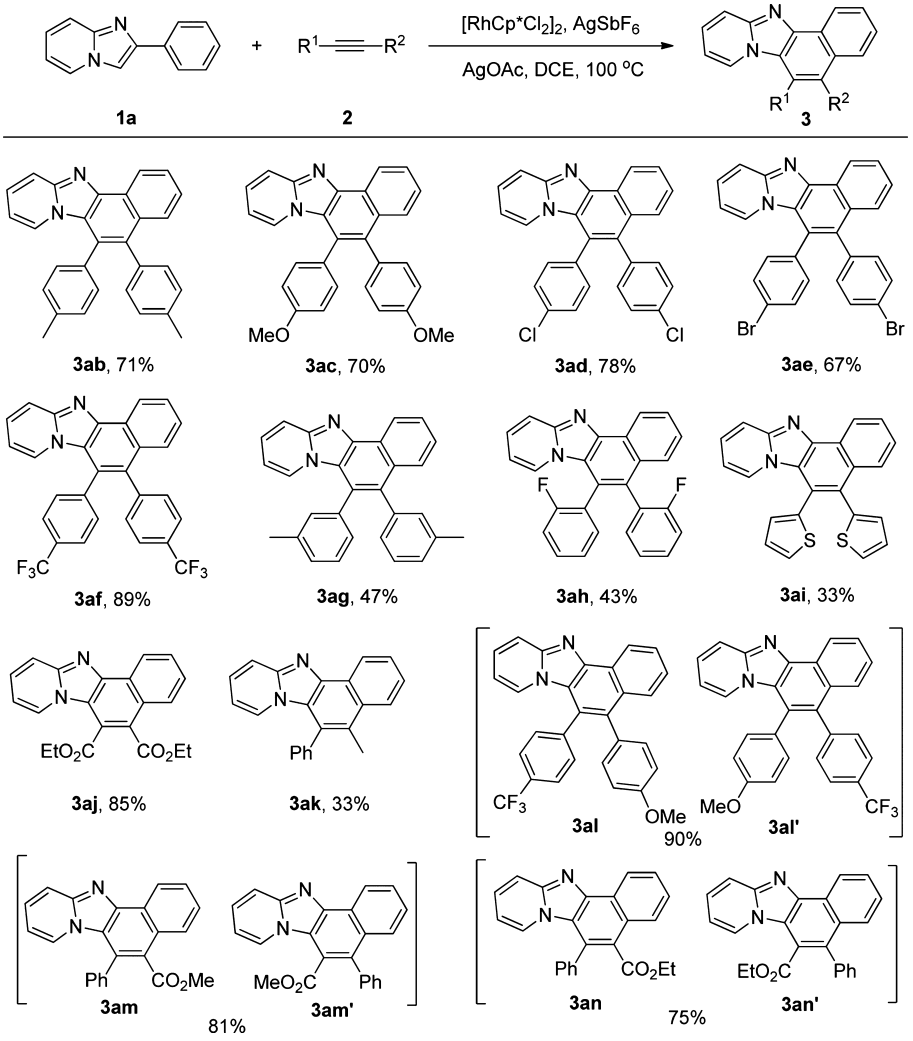
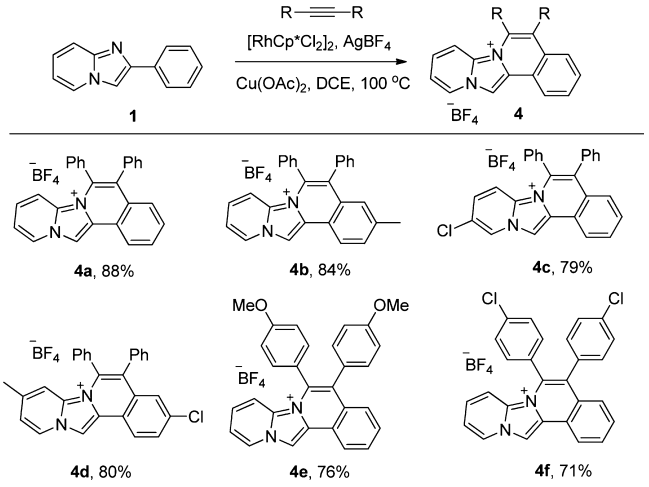
Scheme 2. Scope of the Alkyne Substrate[a]



Scheme 3. Synthesis of Fused Isoquinolinium Tetrafluoroborates[a]



[a]Reaction conditions: $[RhCp^*Cl_2]_2$ (4 mol %), $AgBF_4$ (1.0 equiv), $Cu(OAc)_2$ (1.0 equiv), **1** (0.20 mmol), and **2** (0.20 mmol) in DCE (3 mL) at 100 °C for 24 h. Yield of isolated product.

CONCLUSION

We have developed Rh(III)-catalyzed divergent C−H activation of 2-phenylimidazo[1,2-*a*]pyridines in the oxidative coupling with alkynes. Selective mono versus 2-fold C−H activation has been attained under condition control. When AgOAc was used as an oxidant, this coupling afforded 5,6-disubstituted naphtho-[1′,2′:4,5]imidazo[1,2-*a*]pyridines as a result of initial chelation-assisted C−H activation at the benzene ring followed by rollover C−H activation at the heterocycle. In contrast, the reaction afforded a fused isoquinolinium as a result of C−C and C−N coupling while $AgBF_4$ was employed as a co-oxidant. In both cases, the initial C−H activation is assisted by nitrogen coordination. A rhodacyle complex has been isolated and has been established as a reactive intermediate. This work expanded the scope of rhodium-catalyzed C−H activation of arenes for the synthesis of extended π-systems.

EXPERIMENTAL SECTION

General Information. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Diarylacetylenes[21] other than diphenylacetylene and 2-phenylimidazo[1,2-*a*]pyridines[22] were prepared by following literature

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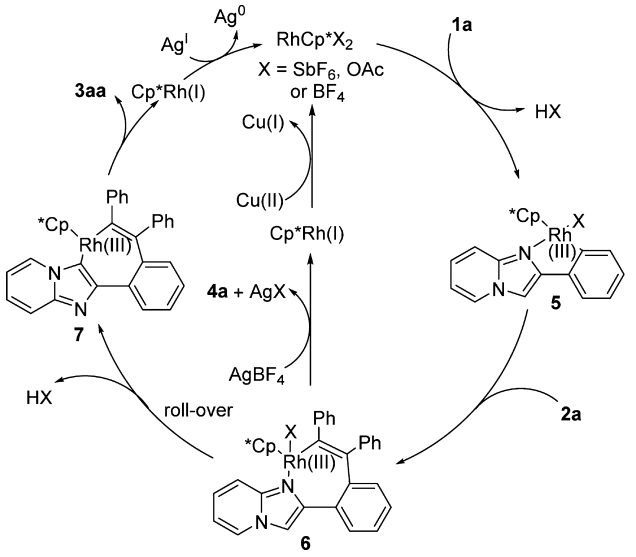
Scheme 4. Proposed Reaction Mechanism



reports. $[RhCp^*Cl_2]_2$ was prepared from $RhCl_3 \cdot xH_2O$ according to a literature procedure.[23] All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. HRMS data were obtained via ESI mode with a TOF mass analyzer. Column chromatography was performed on silica gel (300−400 mesh) using ethyl acetate (EA)/petroleum ether (PE) or MeOH/CH_2Cl_2.

General Procedures for Synthesis of 3. 2-Phenylimidazo[1,2-*a*]-pyridines (0.20 mmol), alkynes (0.24 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), AgOAc (2.2 equiv), and DCE (2 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product **3**.

5,6-Diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3aa***). white solid (64.4 mg, 87%); mp 299−300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.70 (ddd, J = 8.1, 6.9, 1.0 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.49 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.35−7.17 (m, 12H), 6.48 (td, J = 7.0, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.1, 138.8, 137.1, 133.7, 131.8, 131.7, 130.6, 128.7, 127.9, 127.8, 127.7, 127.4, 126.80, 126.77, 126.7, 126.4, 126.34, 126.32, 123.2, 122.8, 118.0, 110.8; HRMS: $[M + H]^+$ calculated for $C_{27}H_{19}N_2$: 371.1543, found 371.1542.

3-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ba***). white solid (56.1 mg, 73%); mp 292−293 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.54 (dd, J = 8.3, 1.2 Hz, 1H), 7.37 (s, 1H), 7.34−7.16 (m, 12H), 6.46 (td, J = 7.0, 1.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.2, 138.9, 137.3, 136.1, 133.3, 131.82, 131.81, 130.6, 128.6, 128.4, 127.8, 127.7, 127.2, 127.0, 126.8, 126.7, 126.6, 124.3, 123.1, 122.4, 117.9, 110.6, 22.2; HRMS: $[M + H]^+$ calculated for $C_{28}H_{21}N_2$: 385.1699, found 385.1703.

3-Methoxy-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ca***). pale yellow solid (56.1 mg, 70%); mp 244−246 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 8.9 Hz, 1H), 7.79 (d, J = 9.1 Hz, 1H), 7.36 (dd, J = 8.9, 2.5 Hz, 1H), 7.33−7.15 (m, 12H), 6.96 (d, J = 2.5 Hz, 1H), 6.45 (td, J = 7.0, 1.1 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 148.3, 141.3, 138.9, 137.2, 133.1, 132.8, 131.7, 130.5, 128.6, 127.8, 127.8, 127.3, 127.2, 126.8, 126.6, 124.7, 121.8, 121.1, 117.8, 117.1, 110.6, 108.3, 55.3; HRMS: $[M + H]^+$ calculated for $C_{28}H_{21}N_2O$: 401.1648, found 401.1650.

3-Fluoro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3da***). pale yellow solid (53.5 mg, 69%); mp 279−280 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 8.9, 5.9 Hz, 1H), 7.82 (d, J = 9.1 Hz, 1H), 7.44 (td, J = 8.6, 2.5 Hz, 1H), 7.37−7.20 (m, 11H), 7.18−7.15 (m, 2H), 6.50 (dd, J = 10.0, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 242.7 Hz), 148.4, 141.2, 138.3, 136.9, 133.1 (d, J = 7.5 Hz), 133.0 (d, J = 3.3 Hz), 131.6, 130.4, 128.7, 128.04, 127.99, 127.91, 127.6, 127.0, 126.7, 125.5 (d, J = 9.1 Hz), 123.1, 122.5, 118.0, 115.8 (d, J = 24.5 Hz), 111.9 (d, J = 22.3 Hz), 110.9; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}FN_2$: 389.1449, found 389.1447.

3-Chloro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ea***). white solid (65.5 mg, 81%); mp 300−301 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.64 (dd, J = 8.7, 2.0 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.38−7.29 (m, 4H), 7.29−7.20 (m, 6H), 7.19−7.13 (m, 2H), 6.50 (td, J = 7.0, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 141.0, 138.0, 136.8, 132.9, 132.7, 132.4, 131.7, 130.4, 128.8, 128.1, 128.0, 127.9, 127.8, 127.1, 127.0, 126.8, 126.7, 124.8, 124.6, 123.0, 118.0, 111.0; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}ClN_2$: 405.1153, found 405.1154.

3-Bromo-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3fa***). pale yellow solid (63.7 mg, 71%); mp 302−303 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 8.6 Hz, 1H), 7.92−7.68 (m, 3H), 7.43−7.10 (m, 12H), 6.51 (t, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 141.0, 138.0, 136.7, 133.0, 132.8, 131.7, 130.4, 129.9, 129.6, 128.8, 128.1, 128.0, 127.9, 127.8, 127.1, 126.7, 125.0, 124.8, 123.0, 120.8, 118.1, 111.0; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}BrN_2$: 449.0648, found 449.0644.

3,5,6-Triphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ga***). white solid (49.9 mg, 56%); mp >300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 8.5 Hz, 1H), 7.98 (dd, J = 8.5, 1.7 Hz, 1H), 7.90−7.81 (m, 2H), 7.61−7.54 (m, 2H), 7.43−7.37 (m, 2H), 7.36−7.19 (m, 13H), 6.50 (td, J = 6.9, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 141.7, 139.1, 138.7, 137.2, 134.1, 132.0, 131.8, 130.6, 128.9, 128.7, 127.9, 127.8, 127.7, 127.5, 127.33, 127.29, 126.9, 126.7, 125.98, 125.95, 125.4, 123.8, 118.1, 110.8. Two carbons are not visible due to overlapping peaks; HRMS: $[M + H]^+$ calculated for $C_{33}H_{23}N_2$: 447.1856, found 447.1856.

5,6-Diphenyl-3-(trifluoromethyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ha***). white solid (59.6 mg, 68%); mp 261−262 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 8.5 Hz, 1H), 7.92 (s, 1H), 7.88 (dd, J = 8.6, 1.3 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.38−7.21 (m, 10H), 7.20−7.14 (m, 2H), 6.51 (td, J = 7.1, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 140.6, 137.7, 136.6, 134.1, 131.7, 130.8, 130.4, 128.8, 128.3, 128.23, 128.18, 128.0, 127.94, 127.89, 127.3, 126.7, 125.2 (q, J = 4.5 Hz), 124.7 (q, J = 270.6 Hz), 124.2, 123.9, 122.0 (q, J = 3.2 Hz), 118.2, 111.2; HRMS: $[M + H]^+$ calculated for $C_{28}H_{18}F_3N_2$: 439.1417, found 439.1418.

3-Nitro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ia***). yellow solid (25.0 mg, 30%); mp >300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 9.0 Hz, 1H), 8.56 (d, J = 2.1 Hz, 1H), 8.44 (dd, J = 9.0, 2.2 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.43−7.35 (m, 4H), 7.33−7.23 (m, 6H), 7.23−7.17 (m, 2H), 6.57 (t, J = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.1, 140.5, 137.2, 136.2, 134.9, 131.7, 130.8, 130.3, 129.4, 129.1, 129.0, 128.5, 128.4, 128.1, 127.6, 126.8, 124.9, 124.7, 124.4, 119.9, 118.4, 111.6; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}N_3O_2$: 416.1394, found 416.1395.

2-Chloro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ja***). pale white solid (67.1 mg, 83%); mp 277−278 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 1.9 Hz, 1H), 7.78 (d, J = 9.1 Hz, 1H), 7.51 (d, J = 8.9 Hz, 1H), 7.37 (dd, J = 9.0, 2.0 Hz, 1H), 7.35−7.26 (m, 4H), 7.26−7.18 (m, 6H), 7.17−7.11 (m, 2H), 6.47 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 140.2, 138.3, 136.7, 133.4, 132.5, 131.6, 130.4, 129.8, 129.4, 128.7, 128.0, 127.8, 127.7, 127.04, 127.00, 126.9, 126.8, 126.6, 123.3, 122.3, 118.0, 110.9; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}ClN_2$: 405.1153, found 405.1154.

4-Methoxy-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (***3ka***). pale yellow solid (16.8 mg, 21%); mp 239−240 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.32−7.24 (m, 4H), 7.21−7.15 (m, 2H), 7.12−7.06 (m, 5H), 7.04 (dd, J = 8.8, 4.5 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 6.45 (t, J = 6.8 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 148.3, 143.0, 141.0, 137.3, 131.9, 130.8, 130.4, 128.4, 128.3, 127.6, 127.5, 127.1, 126.7, 126.2, 125.1, 123.1, 122.5, 118.0,

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116.2, 110.7, 108.4, 100.2, 56.0; HRMS: $[M + H]^+$ calculated for $C_{28}H_{21}N_2O$: 401.1648, found 401.1651.

*2-Methoxy-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3k′a**).* pale white solid (30.4 mg, 38%); mp 279−280 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 2.6 Hz, 1H), 7.84 (d, J = 9.4 Hz, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.34−7.27 (m, 5H), 7.26−7.20 (m, 5H), 7.19−7.16 (m, 2H), 7.13 (dd, J = 9.2, 2.7 Hz, 1H), 6.47 (t, J = 6.9 Hz, 1H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 148.0, 140.5, 138.9, 137.2, 133.8, 131.7, 130.8, 129.5, 128.6, 127.8, 127.64, 127.62, 127.3, 126.74, 126.72, 126.5, 124.1, 123.3, 118.3, 118.0, 110.7, 102.1, 56.0; HRMS: $[M + H]^+$ calculated for $C_{28}H_{21}N_2O$: 401.1648, found 401.1648.

*10-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3la**).* pale yellow solid (58.4 mg, 76%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.62−7.56 (m, 2H), 7.47 (ddd, J = 8.3, 6.9, 1.1 Hz, 1H), 7.34−7.28 (m, 3H), 7.26−7.16 (m, 7H), 7.13 (d, J = 7.2 Hz, 1H), 6.32 (dd, J = 7.2, 1.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.2, 138.9, 138.6, 137.2, 133.1, 131.8, 131.5, 130.6, 128.6, 127.8, 127.68, 127.66, 126.7, 126.24, 126.16, 126.1, 125.7, 123.1, 122.7, 116.2, 113.5, 21.7. One carbon is not visible due to overlapping peaks; HRMS: $[M + H]^+$ calculated for $C_{28}H_{21}N_2$: 385.1699, found 385.1698.

*9-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ma**).* white solid (53.8 mg, 70%); mp 288−289 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 9.3 Hz, 1H), 7.71−7.66 (m, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.51−7.45 (m, 1H), 7.36−7.29 (m, 3H), 7.28−7.18 (m, 7H), 7.15 (dd, J = 9.3, 1.4 Hz, 1H), 6.96 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 141.1, 138.9, 137.3, 133.3, 131.8, 131.5, 130.6, 130.5, 128.6, 127.8, 127.74, 127.68, 126.9, 126.7, 126.4, 126.3, 126.2, 124.4, 123.1, 122.7, 120.1, 117.3, 18.6; HRMS: $[M + H]^+$ calculated for $C_{28}H_{21}N_2$: 385.1699, found 385.1699.

*9-Fluoro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3na**).* yellow solid (62.1 mg, 80%); mp 295−297 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.1 Hz, 1H), 7.81 (dd, J = 9.9, 5.3 Hz, 1H), 7.71 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.51 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.39−7.32 (m, 3H), 7.28−7.18 (m, 8H), 7.13 (dd, J = 5.1, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6 (d, J = 234.0 Hz), 145.8, 142.0, 138.6, 136.4 (d, J = 19.6 Hz), 134.3, 131.72, 131.69, 130.5, 128.8, 128.2, 127.9, 127.8, 126.9, 126.61, 126.58, 126.5, 123.6 (d, J = 2.0 Hz), 123.0, 119.5 (d, J = 26.0 Hz), 118.3 (d, J = 8.8 Hz), 113.6, 113.1; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}FN_2$: 389.1449, found 389.1446.

*9-Chloro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3oa**).* yellow solid (58.9 mg, 73%); mp 295−296 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 9.6 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.40−7.33 (m, 3H), 7.29−7.17 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 141.6, 138.5, 136.5, 134.5, 131.8, 131.7, 130.4, 128.9, 128.5, 128.2, 127.9, 127.8, 126.9, 126.7, 126.6, 126.3, 124.6, 123.1, 122.9, 118.7, 118.2. One carbon is not visible due to overlapping peaks; HRMS: $[M + H]^+$ calculated for $C_{27}H_{18}ClN_2$: 405.1153, found 405.1150.

*3-Chloro-10-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3pa**).* pale yellow solid (68.5 mg, 82%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.7 Hz, 1H), 7.62 (dd, J = 8.7, 2.0 Hz, 1H), 7.57 (d, J = 1.8 Hz, 2H), 7.36−7.29 (m, 3H), 7.28−7.20 (m, 5H), 7.18−7.14 (m, 2H), 7.12 (d, J = 7.2 Hz, 1H), 6.35 (dd, J = 7.2, 1.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 141.0, 139.1, 138.1, 136.9, 132.5, 132.3, 132.2, 131.8, 130.4, 128.7, 128.0, 127.93, 127.89, 127.0, 126.8, 126.7, 125.8, 124.8, 124.5, 122.9, 116.2, 113.8, 21.8; HRMS: $[M + H]^+$ calculated for $C_{28}H_{20}ClN_2$: 419.1310, found 419.1312.

*2-Chloro-10-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3qa**).* pale yellow solid (66.9 mg, 80%); mp 279−280 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 2.1 Hz, 1H), 7.53 (s, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.36 (dd, J = 9.0, 2.3 Hz, 1H), 7.33−7.29 (m, 3H), 7.26−7.19 (m, 5H), 7.16−7.13 (m, 2H), 7.11 (d, J = 7.2 Hz, 1H), 6.32 (dd, J = 7.2, 1.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 140.3, 139.0, 138.4, 136.8, 132.8, 132.3, 131.7, 130.5, 129.7, 129.3, 128.7, 127.9, 127.8, 127.0, 126.92, 126.89, 126.7, 125.7, 123.2, 122.3, 116.2, 113.8, 21.7; HRMS: $[M + H]^+$ calculated for $C_{28}H_{20}ClN_2$: 419.1314, found 419.1312.

*3-Methoxy-9-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ra**).* pale yellow solid (65.4 mg, 79%); mp 233−234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 8.9 Hz, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.36−7.29 (m, 4H), 7.26−7.16 (m, 7H), 7.11 (dd, J = 9.3, 1.6 Hz, 1H), 6.96 (d, J = 2.5 Hz, 1H), 6.93 (s, 1H), 3.70 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 147.4, 141.3, 138.9, 137.3, 132.9, 132.4, 131.7, 130.5, 130.3, 128.5, 127.8, 127.7, 127.3, 126.7, 124.6, 124.4, 121.7, 121.1, 119.8, 117.0, 116.9, 108.2, 55.3, 18.5; HRMS: $[M + H]^+$ calculated for $C_{29}H_{23}N_2O$: 415.1805, found 415.1810.

*3-Fluoro-9-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3sa**).* pale yellow solid (60.3 mg, 75%); mp 287−289 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 9.0, 5.9 Hz, 1H), 7.70 (d, J = 9.3 Hz, 1H), 7.42 (td, J = 8.6, 2.5 Hz, 1H), 7.37−7.30 (m, 3H), 7.28−7.12 (m, 9H), 6.94 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 254.6 Hz), 147.5, 141.1, 138.4, 137.0, 132.9 (d, J = 9.0 Hz), 132.5 (d, J = 4.5 Hz), 131.7, 130.7, 130.4, 128.6, 128.1, 127.89, 127.88, 127.0, 125.4 (d, J = 9.0 Hz), 124.4, 123.1, 122.3, 120.2, 117.1, 115.7 (d, J = 24.5 Hz), 111.8 (d, J = 22.4 Hz), 18.5; HRMS: $[M + H]^+$ calculated for $C_{28}H_{20}FN_2$: 403.1605, found 403.1606.

*3-Chloro-9-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ta**).* pale yellow solid (66.9 mg, 80%); mp 263−264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 9.3 Hz, 1H), 7.62 (dd, J = 8.7, 2.0 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.37−7.31 (m, 3H), 7.29−7.21 (m, 5H), 7.20−7.12 (m, 3H), 6.94 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 141.0, 138.1, 136.9, 132.5, 132.4, 132.2, 131.7, 130.9, 130.4, 128.6, 128.1, 127.94, 127.89, 127.1, 126.9, 126.7, 124.7, 124.6, 124.4, 122.9, 120.3, 117.2, 18.6; HRMS: $[M + H]^+$ calculated for $C_{28}H_{20}ClN_2$: 419.1310, found 419.1306.

*9-Fluoro-3-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3ua**).* pale yellow solid (53.9 mg, 67%); mp 291−292 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 8.3 Hz, 1H), 7.77 (dd, J = 9.8, 5.3 Hz, 1H), 7.54 (dd, J = 8.3, 1.2 Hz, 1H), 7.37 (s, 1H), 7.36−7.30 (m, 3H), 7.28−7.16 (m, 8H), 7.09 (dd, J = 5.1, 2.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6 (d, J = 233.8 Hz), 145.7, 142.1, 138.7, 136.6, 136.4, 133.9, 131.9, 131.7, 130.5, 128.8, 128.6, 128.1, 127.7, 127.2, 126.8, 126.6, 124.4, 123.2 (d, J = 2.2 Hz), 122.9, 119.2 (d, J = 26.0 Hz), 118.1 (d, J = 8.8 Hz), 113.3, 113.1, 22.2; HRMS: $[M + H]^+$ calculated for $C_{28}H_{20}FN_2$: 403.1605, found 403.1602.

*9-Chloro-3-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3va**).* yellow solid (58.5 mg, 70%); mp 282−283 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.3 Hz, 1H), 7.73 (d, J = 9.6 Hz, 1H), 7.54 (dd, J = 8.3, 1.1 Hz, 1H), 7.39−7.32 (m, 4H), 7.29−7.16 (m, 8H), 7.15 (d, J = 1.7 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 141.6, 138.6, 136.6, 136.4, 134.0, 131.9, 131.7, 130.4, 128.8, 128.6, 128.3, 128.1, 127.7, 127.1, 126.8, 126.6, 124.5, 124.3, 123.0, 122.5, 118.5, 118.1, 22.2; HRMS: $[M + H]^+$ calculated for $C_{28}H_{20}ClN_2$: 419.1310, found 419.1313.

*3-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine-10-carbonitrile (**3wa**).* yellow solid (53.2 mg, 65%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 8.3 Hz, 1H), 8.19 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.40−7.33 (m, 4H), 7.30−7.21 (m, 6H), 7.20−7.16 (m, 2H), 6.58 (dd, J = 7.3, 1.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 142.8, 138.2, 137.3, 136.4, 136.0, 132.3, 131.5, 130.5, 129.1, 128.9, 128.3, 127.8, 127.4, 127.2, 127.1, 126.4, 124.2, 124.1, 123.3, 123.1, 117.7, 110.4, 109.4, 22.3; HRMS: $[M + H]^+$ calculated for $C_{29}H_{20}N_3$: 410.1652, found 410.1656.

*3-Methoxy-11-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo-[1,2-a]pyridine (**3xa**).* yellow solid (32.3 mg, 39%); mp 216−218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.9 Hz, 1H), 7.34 (dd, J = 8.9, 2.5 Hz, 1H), 7.32−7.27 (m, 3H), 7.26−7.16 (m, 7H), 7.13 (d, J = 7.0 Hz, 1H), 7.07 (d, J = 6.7 Hz, 1H), 6.95 (d, J = 2.4 Hz, 1H), 6.38 (t, J = 6.9 Hz, 1H), 3.71 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 148.8, 141.1, 139.0, 137.3, 132.9, 132.7, 131.8, 130.6, 128.6, 127.8, 127.7, 127.5, 127.4, 126.7, 125.8, 125.0, 124.4, 122.3,

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121.3, 116.9, 110.5, 108.1, 55.3, 17.9; HRMS: $[M + H]^+$ calculated for $C_{29}H_{23}N_2O$: 415.1805, found 415.1808.

*4,5-Diphenylthieno[3″,2″:5′,6′]benzo[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ya**).* white solid (70.0 mg, 93%); mp 266−267 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 9.1 Hz, 1H), 7.46 (d, J = 5.3 Hz, 1H), 7.36−7.31 (m, 4H), 7.31−7.18 (m, 8H), 7.16 (d, J = 5.3 Hz, 1H), 6.46 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 139.4, 139.2, 138.4, 136.7, 131.18, 131.16, 131.0, 129.1, 128.7, 128.3, 128.0, 127.7, 127.2, 126.7, 125.54, 125.46, 124.5, 123.4, 117.9, 110.5; HRMS: $[M + H]^+$ calculated for $C_{25}H_{17}N_2S$: 377.1107, found 377.1108.

*5,6-Di-p-tolylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ab**).* white solid (56.5 mg, 71%); mp 286−287 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 7.68 (ddd, J = 8.0, 6.8, 0.9 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.47 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.32−7.26 (m, 2H), 7.12 (d, J = 8.6 Hz, 4H), 7.09−7.03 (m, 4H), 6.49 (td, J = 6.9, 1.1 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.0, 137.4, 136.1, 135.8, 134.1, 133.9, 131.9, 131.6, 130.4, 129.4, 128.4, 127.8, 127.2, 126.9, 126.8, 126.3, 126.2, 123.1, 118.0, 110.6, 21.5, 21.4. DEPT 135 analysis revealed that a quaternary carbon signal overlaps with the δ 126.8 signal and a tertiary carbon signal overlaps with the δ 126.2 signal. HRMS: $[M + H]^+$ calculated for $C_{29}H_{23}N_2$: 399.1856, found 399.1855.

*5,6-Bis(4-methoxyphenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ac**).* white solid (60.2 mg, 70%); mp 285−287 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 9.1 Hz, 1H), 7.69 (t, J = 7.3 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 6.8 Hz, 1H), 7.33−7.28 (m, 1H), 7.14 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.1 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 6.52 (t, J = 6.8 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.3, 133.9, 132.8, 132.1, 131.6, 131.2, 129.4, 127.8, 127.3, 126.83, 126.78, 126.31, 126.25, 123.1, 118.0, 114.2, 113.3, 110.7, 55.4, 55.3. Four carbons are not visible due to signal overlapping. HRMS: $[M + H]^+$ calculated for $C_{29}H_{23}N_2O_2$: 431.1754, found 431.1759.

*5,6-Bis(4-chlorophenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ad**).* white solid (68.5 mg, 78%); mp 281−282 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.71 (t, J = 7.0 Hz, 1H), 7.57−7.47 (m, 2H), 7.39−7.29 (m, 4H), 7.25 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.56 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.4, 137.0, 135.4, 134.2, 133.1, 133.0, 132.5, 131.8, 131.3, 129.2, 128.2, 127.6, 127.4, 126.7, 126.6, 126.4, 126.3, 125.6, 123.3, 122.4, 118.2, 111.1; HRMS: $[M + H]^+$ calculated for $C_{27}H_{17}Cl_2N_2$: 439.0763, found 439.0767.

*5,6-Bis(4-bromophenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ae**).* pale yellow solid (70.7 mg, 67%); mp 292−294 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.3 Hz, 1H), 7.70 (ddd, J = 8.0, 6.3, 1.7 Hz, 1H), 7.56−7.46 (m, 4H), 7.41 (d, J = 8.3 Hz, 2H), 7.35−7.30 (m, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 6.57 (t, J = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.4, 137.5, 135.8, 133.3, 132.4, 132.1, 131.24, 131.17, 127.6, 127.4, 126.7, 126.6, 126.4, 126.3, 125.5, 123.3, 122.4, 122.3, 121.3, 118.2, 111.2. One carbon is not visible due to overlapping peaks; HRMS: $[M + H]^+$ calculated for $C_{27}H_{17}Br_2N_2$: 526.9753, found 526.9756.

*5,6-Bis(4-(trifluoromethyl)phenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3af**).* white solid (90.0 mg, 89%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.74 (ddd, J = 8.1, 6.7, 1.3 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.56−7.46 (m, 4H), 7.40 (d, J = 8.0 Hz, 2H), 7.35 (ddd, J = 9.1, 6.7, 1.0 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 7.1 Hz, 1H), 6.57 (td, J = 7.0, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.4, 141.7, 140.6, 132.2, 132.1, 131.0, 130.6 (q, J = 32.5 Hz), 129.5 (q, J = 32.4 Hz), 127.8, 127.3, 127.0, 126.9, 126.6, 126.1, 125.9 (q, J = 3.7 Hz), 125.3, 124.9 (q, J = 270.4 Hz), 124.3 (q, J = 3.7 Hz), 124.0 (q, J = 270.7 Hz), 123.4, 122.1, 118.4, 111.4. One carbon is not visible due to overlapping peaks; HRMS: $[M + H]^+$ calculated for $C_{29}H_{17}F_6N_2$: 507.1290, found 507.1292.

*5,6-Di-m-tolylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ag**).* pale yellow solid (37.5 mg, 47%); mp 245−247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.49 (ddd, J = 8.1, 6.8, 1.0 Hz, 1H), 7.33−7.27 (m, 2H), 7.24−7.18 (m, 1H), 7.17−7.09 (m, 2H), 7.09−6.97 (m, 5H), 6.50 (t, J = 6.8 Hz, 1H), 2.29 (d, J = 4.2 Hz, 3H), 2.27 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.0, 138.7, 138.3, 138.2, 137.1, 137.03, 136.98, 133.84, 133.81, 132.6, 132.5, 131.7, 131.3, 131.2, 128.9, 128.8, 128.54, 128.52, 128.5, 128.4, 127.9, 127.59, 127.56, 127.5, 127.4, 127.3, 126.9, 126.8, 126.2, 123.1, 118.0, 110.7, 21.57, 21.56, 21.52, 21.51; HRMS: $[M + H]^+$ calculated for $C_{29}H_{23}N_2$: 399.1856, found 399.1860.

*5,6-Bis(2-fluorophenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ah**).* pale yellow solid (34.9 mg, 43%); mp 276−277 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.73 (ddd, J = 8.1, 5.2, 2.8 Hz, 1H), 7.58−7.50 (m, 2H), 7.42 (d, J = 6.6 Hz, 1H), 7.39−7.29 (m, 3H), 7.29−7.21 (m, 2H), 7.17−6.98 (m, 4H), 6.57 (td, J = 7.0, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 243.2 Hz), 159.9 (d, J = 244.6 Hz), 148.3, 141.8, 132.8 (d, J = 2.8 Hz), 131.7 (d, J = 1.2 Hz), 131.3, 130.8 (d, J = 7.7 Hz), 129.7 (d, J = 7.9 Hz), 128.3, 127.6, 127.0, 126.8, 126.69, 126.65, 126.4 (d, J = 17.2 Hz), 125.9, 124.73 (d, J = 3.6 Hz), 124.72 (d, J = 16.9 Hz), 123.9 (d, J = 3.6 Hz), 123.4, 122.8, 121.0, 118.2, 115.7 (d, J = 21.5 Hz), 115.1 (d, J = 22.1 Hz), 111.4; HRMS: $[M + H]^+$ calculated for $C_{27}H_{17}F_2N_2$: 407.1354, found 407.1356.

*5,6-Di(thiophen-2-yl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ai**).* pale yellow solid (25.2 mg, 33%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 8.2 Hz, 1H), 7.87−7.83 (m, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 5.1 Hz, 1H), 7.41−7.32 (m, 3H), 7.13−6.94 (m, 4H), 6.62 (t, J = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.8, 138.9, 137.0, 132.4, 130.1, 129.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.1, 126.8, 126.72, 126.67, 126.53, 126.50, 123.3, 123.2, 121.2, 118.1, 111.3; HRMS: $[M + H]^+$ calculated for $C_{23}H_{15}N_2S_2$: 383.0671, found 383.0676.

*Diethyl naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine-5,6-dicarboxylate (**3aj**).* pale yellow solid (61.5 mg, 85%); mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.1 Hz, 1H), 8.75 (d, J = 7.1 Hz, 1H), 8.32 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 9.1 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.45 (dd, J = 8.8, 7.0 Hz, 1H), 6.90 (t, J = 6.9 Hz, 1H), 4.62−4.48 (m, 4H), 1.47 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.0, 149.6, 143.8, 129.0, 128.2, 128.0, 127.7, 127.6, 127.5, 126.6, 125.3, 123.6, 119.5, 119.3, 118.2, 111.9, 62.7, 62.1, 14.4, 14.2; HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_4$: 363.1339, found 363.1340.

*5-Methyl-6-phenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3ak**).* pale yellow solid (20.3 mg, 33%); mp 179−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.74 (t, J = 7.4 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.64−7.56 (m, 3H), 7.44−7.38 (m, 2H), 7.25 (t, J = 7.9 Hz, 1H), 7.17 (d, J = 7.1 Hz, 1H), 6.46 (t, J = 6.9 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 140.2, 138.2, 131.5, 130.1, 129.5, 128.5, 126.9, 126.7, 126.53, 126.49, 126.4, 126.3, 125.3, 123.7, 123.1, 118.0, 110.6, 16.0. One carbon is not visible due to overlapping peaks; HRMS: $[M + H]^+$ calculated for $C_{22}H_{17}N_2$: 309.1386, found 309.1390.

*5-(4-Methoxyphenyl)-6-(4-(trifluoromethyl)phenyl)naphtho-[1′,2′:4,5]imidazo[1,2-a]pyridine (**3al**) and 6-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3al′**).* pale yellow solid (84.2 mg, 90% in total). Selected signals: Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.73−7.66 (m, 1H), 7.61 (t, J = 9.2 Hz, 2H), 7.53−7.46 (m, 2H), 7.36 (d, J = 7.7 Hz, 2H), 7.30 (dd, J = 11.1, 5.7 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.52 (t, J = 6.8 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 148.2, 132.6, 131.1, 125.6 (q, J = 3.7 Hz), 118.2, 113.4, 111.1, 55.3. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.73−7.66 (m, 1H), 7.61 (t, J = 9.2 Hz, 2H), 7.53−7.46 (m, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.30 (dd, J = 11.1, 5.7 Hz, 1H), 7.22 (d, J = 7.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.52 (t, J = 6.8 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR

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(100 MHz, $CDCl_3$) δ 159.3, 148.3, 124.7 (d, J = 3.8 Hz), 118.0, 114.3, 111.0, 55.4; HRMS: $[M + H]^+$ calculated for $C_{29}H_{20}F_3N_2O$: 469.1522, found 469.1522.

*Methyl 6-phenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine-5-carboxylate (**3am**) and methyl 5-phenylnaphtho[1′,2′:4,5]imidazo-[1,2-a]pyridine-6-carboxylate (**3am′**).* pale yellow solid (57.0 mg, 81% in total). Selected signals: Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.1 Hz, 1H), 8.47 (d, J = 7.0 Hz, 1H), 7.88 (d, J = 9.1 Hz, 1H), 6.88 (t, J = 6.8 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 148.4, 141.7, 138.3, 133.7, 130.8, 129.7, 129.1, 128.2, 127.9, 127.6, 126.7, 126.4, 123.3, 118.2, 111.7, 52.5. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 9.1 Hz, 1H), 7.37−7.30 (m, 1H), 6.54 (t, J = 6.9 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 149.0, 142.5, 135.9, 130.7, 129.0, 128.4, 128.3, 126.9, 126.8, 126.2, 126.0, 125.8, 123.5, 121.8, 119.9, 111.3, 52.1; HRMS: $[M + H]^+$ calculated for $C_{23}H_{17}N_2O_2$: 353.1285, found 353.1289.

*Ethyl 6-phenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine-5-carboxylate (**3an**) and ethyl 5-phenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine-6-carboxylate (**3an′**).* pale yellow solid (54.9 mg, 75% in total). Selected signals: Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 7.3 Hz, 1H), 8.54 (d, J = 7.0 Hz, 1H), 7.89 (d, J = 9.1 Hz, 1H), 6.88 (t, J = 6.8 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.4, 133.5, 131.0, 129.9, 129.0, 128.2, 128.0, 127.9, 127.6, 126.7, 123.3, 118.2, 111.6, 62.0, 13.6. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 7.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.37−7.29 (m, 1H), 6.53 (t, J = 6.8 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 135.9, 130.8, 128.5, 127.4, 127.3, 126.6, 126.23, 126.19, 123.5, 118.9, 118.2, 111.2, 61.3, 13.9; HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}N_2O_2$: 367.1441, found 367.1438.

General procedures for synthesis of 4. 2-Phenylimidazo[1,2-*a*]pyridines (0.20 mmol), alkynes (0.20 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgBF_4$ (1.0 equiv), $Cu(OAc)_2$ (1.0 equiv) and DCE (3 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 24 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using CH_2Cl_2/MeOH to afford the desired product **4**.

*5,6-Diphenylpyrido[2′,1′:2,3]imidazo[5,1-a]isoquinolin-7-ium tetrafluoroborate (**4a**).* brown solid (80.6 mg, 88%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.63 (s, 1H), 9.21 (d, J = 5.4 Hz, 1H), 8.66 (d, J = 7.9 Hz, 1H), 7.87 (t, J = 7.5 Hz, 1H), 7.80−7.67 (m, 3H), 7.63−7.47 (m, 5H), 7.42−7.26 (m, 5H), 7.21 (d, J = 8.1 Hz, 1H), 6.04 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 134.5, 134.1, 132.1, 131.7, 131.3, 131.22, 131.19, 130.8, 130.6, 130.4, 129.9, 129.61, 129.56, 129.2, 128.2, 127.9, 127.6, 126.6, 124.5, 120.5, 119.0, 113.1. One carbon is not visible due to overlapping peaks; ^{19}F NMR (376 MHz, DMSO-d_6) δ −148.35, −148.41. The two signals in the ^{19}F NMR spectrum are due to presence of ^{10}B and ^{11}B isotopes. However, no fine coupling was detected. HRMS: $[M - BF_4]$ calculated for $C_{27}H_{19}N_2$: 371.1543, found 371.1542.

*3-Methyl-5,6-diphenylpyrido[2′,1′:2,3]imidazo[5,1-a]isoquinolin-7-ium tetrafluoroborate (**4b**).* brown solid (79.3 mg, 84%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 1H), 9.19 (d, J = 4.2 Hz, 1H), 8.54 (d, J = 8.1 Hz, 1H), 7.69 (s, 3H), 7.62−7.46 (m, 5H), 7.41−7.26 (m, 5H), 6.99 (s, 1H), 6.10−5.95 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.3, 134.3, 134.1, 132.1, 131.8, 131.3, 131.0, 130.81, 130.75, 130.6, 130.4, 130.0, 129.5, 129.2, 128.2, 127.9, 127.6, 126.3, 124.4, 118.9, 118.1, 113.0, 107.2, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ −148.33, −148.38. The two signals in the ^{19}F NMR spectrum are due to presence of ^{10}B and ^{11}B isotopes. However, no fine coupling was detected. HRMS: $[M - BF_4]$ calculated for $C_{28}H_{21}N_2$: 385.1699, found 385.1703.

*10-Chloro-5,6-diphenylpyrido[2′,1′:2,3]imidazo[5,1-a]-isoquinolin-7-ium tetrafluoroborate (**4c**).* brown solid (77.7 mg, 79%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.55 (s, 2H), 8.74 (d, J = 7.5 Hz, 1H), 7.96−7.81 (m, 2H), 7.77 (t, J = 7.0 Hz, 1H), 7.63−7.47 (m, 5H), 7.41−7.20 (m, 6H), 6.01 (d, J = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 133.9, 133.2, 132.0, 131.9, 131.5, 131.42, 131.35, 130.8, 130.6, 130.0, 129.7, 129.3, 128.3, 127.9, 127.5, 126.7, 125.5, 124.7, 120.3, 113.8, 108.0. Two carbons are not visible due to overlapping peaks; ^{19}F NMR (376 MHz, DMSO) δ −148.41, −148.46. The two signals in the ^{19}F NMR spectrum are due to presence of ^{10}B and ^{11}B isotopes. However, no fine coupling was detected. HRMS: $[M - BF_4]$ calculated for $C_{27}H_{18}ClN_2$: 405.1153, found 405.1157.

*3-Chloro-9-methyl-5,6-diphenylpyrido[2′,1′:2,3]imidazo[5,1-a]-isoquinolin-7-ium tetrafluoroborate (**4d**).* brown solid (80.9 mg, 80%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 9.12 (d, J = 6.7 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.66−7.49 (m, 6H), 7.44−7.29 (m, 5H), 7.06 (s, 1H), 5.62 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.4, 135.5, 134.8, 133.5, 133.4, 131.6, 131.5, 130.73, 130.65, 130.4, 130.3, 129.5, 129.2, 128.9, 128.5, 128.2, 126.6, 126.0, 125.5, 121.0, 119.5, 112.0, 107.8, 21.8; ^{19}F NMR (376 MHz, DMSO-d_6) δ −148.33, −148.39. The two signals in the ^{19}F NMR spectrum are due to presence of ^{10}B and ^{11}B isotopes. However, no fine coupling was detected. HRMS: $[M - BF_4]$ calculated for $C_{28}H_{20}ClN_2$: 419.1310, found 419.1311.

*5,6-Bis(4-methoxyphenyl)pyrido[2′,1′:2,3]imidazo[5,1-a]-isoquinolin-7-ium tetrafluoroborate (**4e**).* brown solid (78.7 mg, 76%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.60 (s, 1H), 9.20 (d, J = 4.2 Hz, 1H), 8.62 (d, J = 6.8 Hz, 1H), 7.90−7.65 (m, 4H), 7.50 (d, J = 7.2 Hz, 2H), 7.31−7.16 (m, 3H), 7.10 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 7.0 Hz, 2H), 6.18 (d, J = 8.6 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.2, 158.5, 134.5, 132.3, 132.2, 131.8, 131.3, 131.0, 130.4, 129.5, 129.3, 127.70, 126.65, 126.3, 124.3, 123.9, 120.4, 118.9, 114.6, 113.7, 113.3, 107.6, 55.2, 55.0. One carbon is not visible due to overlapping peaks; ^{19}F NMR (376 MHz, DMSO-d_6) δ −148.34, −148.39. The two signals in the ^{19}F NMR spectrum are due to presence of ^{10}B and ^{11}B isotopes. However, no fine coupling was detected. HRMS: $[M - BF_4]$ calculated for $C_{29}H_{23}N_2O_2$: 431.1754, found 431.1757.

*5,6-Bis(4-chlorophenyl)pyrido[2′,1′:2,3]imidazo[5,1-a]-isoquinolin-7-ium tetrafluoroborate (**4f**).* brown solid (74.8 mg, 71%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 9.23 (d, J = 6.0 Hz, 1H), 8.67 (d, J = 7.5 Hz, 1H), 7.96−7.80 (m, 2H), 7.75 (d, J = 6.4 Hz, 2H), 7.62 (s, 4H), 7.46 (d, J = 7.7 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.21 (d, J = 7.8 Hz, 1H), 6.30 (d, J = 9.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.3, 134.5, 132.9, 132.8, 132.7, 132.5, 131.9, 131.3, 131.2, 131.1, 130.4, 129.8, 129.7, 129.6, 129.5, 128.5, 127.0, 126.6, 124.5, 120.6, 119.1, 113.1, 107.8. The two signals in the ^{19}F NMR spectrum are due to presence of ^{10}B and ^{11}B isotopes. However, no fine coupling was detected. ^{19}F NMR (376 MHz, DMSO-d_6) δ −148.34, −148.39; HRMS: $[M - BF_4]$ calculated for $C_{27}H_{17}Cl_2N_2$: 439.0763, found 439.0762.

Procedure for Synthesis of Complex 5. 2-Phenylimidazo[1,2-*a*]pyridine (0.15 mmol, 29.1 mg), $[RhCp^*Cl_2]_2$ (0.07 mmol, 43.3 mg), NaOAc (6 equiv, 34.3 mg), and CH_2Cl_2 (4 mL) were charged into the sealed tube. The reaction mixture was stirred at room temperature for 12 h. After filtration, the solvent was removed under reduced pressure and the residue was washed with Et_2O five times to afford complex **5** (48.3 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.82 (s, 1H), 7.56 (d, J = 32.3 Hz, 2H), 7.36−7.12 (m, 3H), 6.98 (s, 1H), 6.67 (s, 1H), 1.64 (s, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4 (d, J_{Rh-C} = 31.2 Hz), 152.3, 143.8, 139.0, 137.1, 128.4, 127.9, 125.9, 122.7, 121.9, 114.2, 112.8, 105.7, 95.1 (d, J_{Rh-C} = 6.2 Hz), 9.8. HRMS: $[M - Cl]^+$ calculated for $C_{23}H_{24}N_2Rh$: 431.0995, found 431.1006.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all new products and crystallographic data of **3ka′** (including CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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