JOC The Journal of Organic Chemistry

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Synthesis of Naphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridines and Imidazo[5,1,2-*cd*]indolizines Through Pd-Catalyzed Cycloaromatization of 2-Phenylimidazo[1,2-*a*]pyridines with Alkynes

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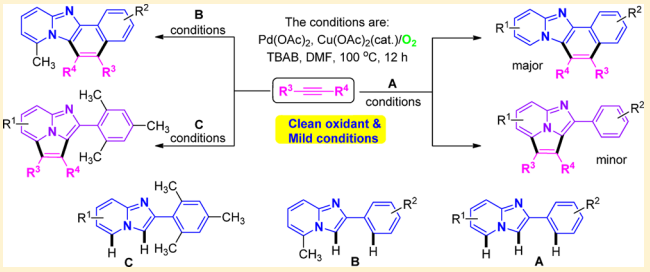
Supporting Information

ABSTRACT: In this paper, palladium-catalyzed oxidative cycloaromatization of 2-phenylimidazo[1,2-*a*]pyridine (PIP) with internal alkyne is studied. From this reaction, two classes of fused *N*-heterocycle, naphtho[1′,2′:4,5]imidazo[1,2-*a*]-pyridine (NIP) and imidazo[5,1,2-*cd*]indolizine (IID), were formed through dehydrogenative coupling featured with cleavage of the C−H bonds located on different moiety of the PIP substrates. Moreover, when 5-methyl-2-phenylimidazo [1,2-*a*]pyridine or 2-mesitylimidazo[1,2-*a*]pyridine was used, either NIP or IID could be obtained as an exclusive product with good efficiency. Intriguingly, Pd(II) showed different action mode in promoting this reaction compared with Rh(III) and led to the formation of NIP with reversed regio-selectivity for the reaction of asymmetrical alkyne.



INTRODUCTION

Nitrogen-containing heterocyclic frameworks have been found in a large number of naturally occurring and synthetic compounds with interesting biological activities and functional properties.[1,2] Among them, the imidazo[1,2-*a*]pyridine scaffold serves as a core structure in a plethora of pharmaceutically active compounds and a number of commercial drugs.[3−5] Due to its importance, the construction and functionalization of the imidazo[1,2-*a*]pyridine framework have attracted considerable attention.[6] In this aspect, Cossio[7a] and Gryko[7b] have reported an efficient construction of benzo[*a*]imidazo[5,1,2-*cd*]-indolizines with interesting photophysical properties through tandem [8 + 2] cycloaddition-[2 + 6 + 2] dehydrogenation of imidazo[1,2-*a*]pyridines with benzynes. While this strategy is of solid reliability and has been frequently used, the highly reactive benzyne intermediate needed therein is formed *in situ* through the elimination reaction of complex precursors such as 2-(trimethylsilyl)phenyl triflates.

Meanwhile, C−H bond activation has emerged as a valuable tool in searching for greener and more sustainable synthetic methodologies as this strategy usually means obviation of prior functionalization of substrates and minimization of waste formation.[8] Among various versions of C−H bond activation and their following application, transition-metal-catalyzed annulation of alkyne with arene to afford fused aromatics is rapidly prevailing.[9] In this regard, Miura reported that benzene ring could be efficiently constructed through Rh-catalyzed annulation of phenylazoles with internal alkynes via dual cleavage of C−H bonds by using $Cu(OAc)_2$ as an oxidant.[10] Following this pioneering work, Jiao developed a Pd-catalyzed cycloaromatization of 2- and 3-arylindoles with internal alkynes in the presence of molecular oxygen.[11] Chen developed an efficient construction of aza-fused polycyclic quinolines from *N*-arylazoles and alkynes under the catalysis of Rh-complex.[12] Interestingly, Jin reported a Pd-catalyzed alkyne-directed C−H cleavage of bis-biaryl alkynes to produce 9,9′-bifluorenylidene derivatives with MnO_2 as an oxidant and PivOH as an additive.[13] In addition, Hu developed a dehydrogenative Heck annulation reaction of indolizine with diaryl acetylene with oxygen gas as a clean oxidant.[14] During the preparation of this manuscript, Li reported a Rh(III)-catalyzed oxidative coupling of 2-phenylimidazo[1,2-*a*]pyridine (PIP) with alkyne to give naphtho[1′,2′:4,5]imidazo[1,2-*a*] pyridine (NIP) or isoquino-linium salt (IQS) (Scheme 1a).[15a] Inspired by these elegant pioneering studies, we herein wish to report a novel synthesis of NIP and imidazo[5,1,2-*cd*]indolizines (IID) through Pd-catalyzed triple C−H bonds activation of PIP and their cycloaromatization with internal alkynes (Scheme 1b). It is worth noting that in promoting the oxidative coupling of PIP with internal alkyne, Pd(II) showed a different action mode compared with Rh(III)-complex in that Pd(II) catalyst gave PIP and IID, while Rh(III)-complex led to the formation of PIP or IQS. Moreover, when asymmetrical internal alkyne was used as the substrate, different regio-selectivity in the formation of NIP was observed under the promotion of Rh(III) or Pd(II) (Scheme 1).

Received: May 15, 2015
Published: July 13, 2015

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

Scheme 1. Oxidative Annulations of PIP with Inner Alkyne Promoted by Rh(III) or Pd(II) Catalyst

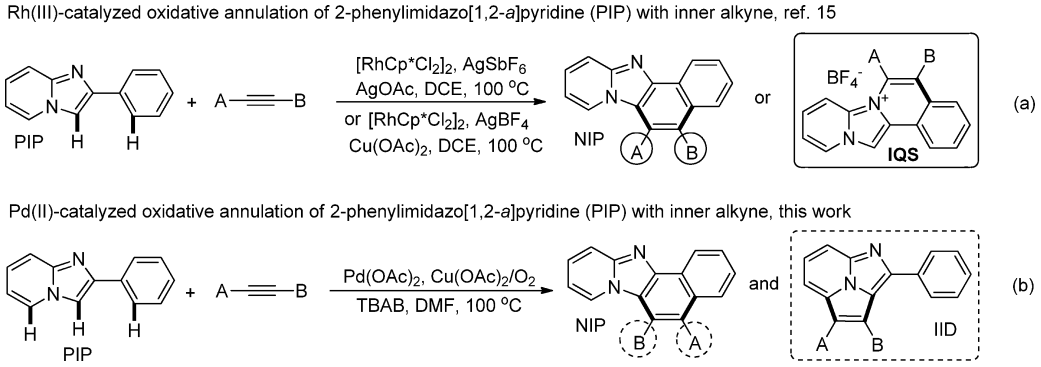
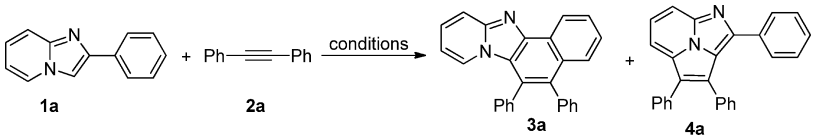


Table 1. Optimization on the Reaction Conditions[a]



					yield (%)[b]	
entry	catalyst	oxidant	additive	solvent	**3a**	**4a**
1	$Pd(OAc)_2$	air	–	DMF	25	8
2	$Pd(OAc)_2$	O_2	–	DMF	32	14
3	$Pd(OAc)_2$	$Cu(OAc)_2$ (1 equiv)	–	DMF	43	16
4	$Pd(OAc)_2$	$PhI(OAc)_2$ (1 equiv)	–	DMF	25	trace
5	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	–	DMF	41	15
6	$PdCl_2$	$Cu(OAc)_2/O_2$	–	DMF	trace	trace
7	$PdCl_2(PPh_3)_2$	$Cu(OAc)_2/O_2$	–	DMF	trace	trace
8	$Pd(dba)_2$	$Cu(OAc)_2/O_2$	–	DMF	25	9
9	$Pd(PPh_3)_4$	$Cu(OAc)_2/O_2$	–	DMF	19	trace
10	–	$Cu(OAc)_2/O_2$	–	DMF	–	–
11	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAB	DMF	65	18
12	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAF	DMF	58	17
13	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	PivOH	DMF	54	16
14	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	PivOH + TBAB	DMF	60	15
15	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAB	DMSO	63	16
16	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAB	AcOH	21	8
17	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAB	DMA	45	18
18	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAB	dioxane	50	13
19	$Pd(OAc)_2$	$Cu(OAc)_2/O_2$	TBAB	toluene	19	6
20	$Pd(OAc)_2$	–[c]	TBAB	DMF	trace	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (0.02 mmol), and $Cu(OAc)_2$ (0.04 mmol) unless otherwise noted, O_2 (balloon), additive (0.2 mmol), solvent (2 mL), 100 °C, 12 h. [b]Isolated yield. [c]The reaction was carried out under nitrogen.

RESULTS AND DISCUSSION

Our study was initiated by treating 2-phenylimidazo[1,2-*a*]pyridine (**1a**) with 1,2-diphenyl ethyne (**2a**) in the presence of $Pd(OAc)_2$ in DMF at 100 °C under air for 12 h. It was then found that this reaction could afford a NIP derivative, 5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridine (**3a**), and an IID derivative, 2,3,4-triphenylimidazo[5,1,2-*cd*]indolizine (**4a**), in yields of 25% and 8%, respectively (Table 1, entry 1). To improve the efficiency, some oxidants frequently used in the annulations of internal alkynes with arenes, including molecular oxygen, $Cu(OAc)_2$, and $PhI(OAc)_2$, were used to assist the dehydrogenative process (entries 2–4). Among the oxidants, $Cu(OAc)_2$ gave the best result (entry 3). Gratifyingly, our following study showed that a combination of catalytic amount of $Cu(OAc)_2$ (0.2 equiv) with O_2 (balloon) gave a similar result as that obtained with stoichiometric amount of $Cu(OAc)_2$ (entries 5 and 3). Next, different palladium catalysts were tried, but no increase in the yield of **3a** or **4a** was observed (entries 6–9). In the absence of Pd catalyst, no reaction took place (entry 10). Then, some additives were tested. The reaction could be significantly improved in the presence of tetrabutylammonium bromide (TBAB), tetrabutylammonium fluoride (TBAF), pivalic acid (PivOH), or a combination of TBAB with PivOH (entries 11–14). Among the additives, TBAB turned out to be the most efficient (entry 11).[16] Different solvents were tried as possible reaction media (entries 15–19). It was observed that while DMSO gave a similar result as that of DMF, other solvents were less effective. In the absence of any oxidant, only trace amount of **3a** and **4a** was formed (entry 20). In summary of our optimization, treatment of **1a** with **2a** in the presence of 0.1 equiv of $Pd(OAc)_2$, 0.2 equiv of $Cu(OAc)_2$, and 1 equiv of TBAB in DMF under an oxygen atmosphere at 100

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508–7518

°C for 12 h afforded **3a** in a yield of 65% together with **4a** in a yield of 18% (entry 11).

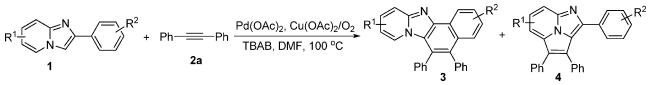
With the optimized reaction conditions in hand, we then explored the scope of this reaction. First, **2a** was used as a model substrate to react with different PIPs (**1**). The results listed in Table 2 indicated that while all the substrates took part in this reaction smoothly, the yields of **3** and **4** were affected obviously by the electronic nature of the imidazo[1,2-*a*]pyridine scaffold as well as the 2-phenyl unit. Compared with **1a**, substrates with an electron-rich 2-phenyl moiety gave NIP derivatives (**3**) in increased yields and IID derivatives (**4**) in decreased yields (entries 2, 3, and 7). On the other hand, substrates with an electron-deficient 2-phenyl moiety gave **3** in decreased yields and **4** in increased yields (entries 4 and 5). As for the imidazo[1,2-*a*]pyridine scaffold, the opposite is the case in that substrates with electron-withdrawing group afforded **3** in higher yields and **4** in lower yields (entries 11 and 12), while those bearing electron-donating group gave **4** in higher yields and **3** in lower yields (entries 9 and 10). It is also worth noting that 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (**1j**), exhibiting low reactivity under the catalysis of Rh(III),[15a] could efficiently participate in this reaction under the catalysis of Pd(II) (entry 10). Notably, in addition to PIPs, 2-(thiophen-2-yl) and 2-(naphthalene-1-yl)imidazo[1,2-*a*]pyridines (**1g** and **1h**) were also suitable substrates for this reaction (entries 7 and 8).

Second, **1a** was used as a model substrate to react with different inner alkynes (**2**). It was found that diaryl-substituted alkynes (Table 3, **2b**–**2e**) with different functional groups attached on the phenyl ring could undergo this reaction smoothly to give the corresponding products in good yields (Table 3, entries 1–4). Notably, the electronic nature of the phenyl moiety in **2** did not have obvious effect on the efficiency of this reaction as either electron-poor or electron-rich phenyl-substituted alkynes gave similar yields of **3** and **4**. Interestingly, diethyl but-2-ynedioate (**2f**) could act as a suitable substrate (entry 5). When the reaction was extended to prop-1-yn-1-ylbenzene (**2g**) and pent-1-yn-1-ylbenzene (**2h**), two asymmetrically disubstituted alkynes with an aryl and an alkyl group, the reaction preceded smoothly and showed good regioselectivity as only one of the two possible regio-isomers was obtained in the formation of **3r**, **4r**, **3s**, and **4s** (entries 6 and 7). More interestingly, it has been reported that under the catalysis of Rh(III), 5-methyl-6-phenylnaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridine (5-M-6-P-NIP) was obtained from the reaction of **1a** and **2g**.[15a] Under the catalysis of Pd(II) as revealed in this work, on the other hand, 6-methyl-5-phenylnaphtho[1′,2′:4,5]-imidazo[1,2-*a*]pyridine (6-M-5-P-NIP, **3r**) was obtained from the same substrates (entry 6).[18]

Third, with **2a** as a model substrate, several PIP derivatives (**1**) with a methyl group attached on the 5-position of the imidazo[1,2-*a*]pyridine scaffold were tested. As one of the reaction sites needed for the formation of IID (**4**) was blocked, the reactions exclusively afforded NIPs (**3**) (Table 4, entries 1–6). In general, substrates having an electron-donating group on the 2-phenyl moiety showed higher efficiency (entries 2 and 6) than substrates with an electron-withdrawing group (entries 3 and 4).

Fourthly, with **2a** as a model substrate, the reaction of some PIP substrates (**1**) bearing 2,4,6-trimethyl groups on the 2-phenyl unit was studied. As the reaction sites needed for the formation of NIP derivatives (**3**) were blocked by methyl groups, the reactions exclusively afforded IID derivatives (**4**) in good yields (Table 5, entries 1–6).

Table 2. Studies on the Scope of 2-Phenylimidazo[1,2-*a*]pyridines (1)[a]



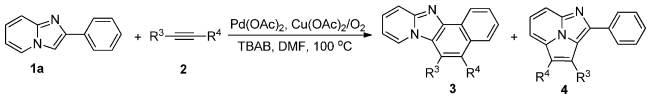
Entry	1	3 [b]	4 [b]
1	**1a**	**3a**, 65%	**4a**, 18%
2	**1b**	**3b**[17], 72%	**4b**, 15%
3	**1c**	**3c**, 75%	**4c**, 13%
4	**1d**	**3d**, 50%	**4d**, 33%
5	**1e**	**3e**, 39%	**4e**, 42%
6	**1f**	**3f**, 40%	**4f**, 45%
7	**1g**	**3g**, 80%	**4g**, 9%
8	**1h**	**3h**, 43%	**4h**, 35%
9	**1i**	**3i**, 55%	**4i**, 29%
10	**1j**	**3j**, 60%	**4j**, 26%
11	**1k**	**3k**, 69%	**4k**, 7%
12	**1l**	**3l**, 77%	**4l**, -

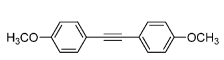
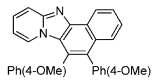
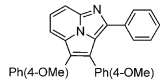
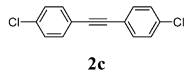
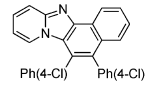
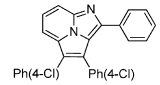
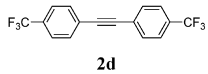
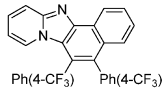
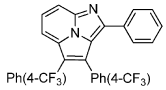
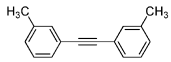
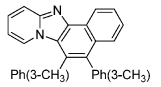
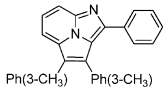
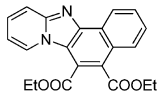
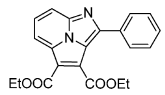
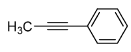
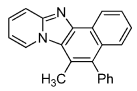
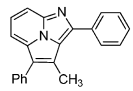
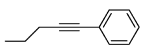
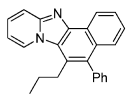
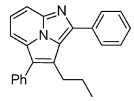
[a]Raction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2$ (0.04 mmol), O_2 (balloon), TBAB (0.2 mmol), and DMF (2 mL), 100 °C, 12 h. [b]Isolated yield.

Based on the above results and previous reports,[14,15] plausible mechanisms for the formation of **3a** and **4a** are

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508–7518

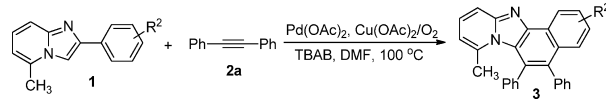
Table 3. Studies on the Scope of Inner Alkynes (2)[a]

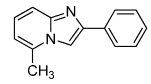
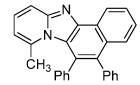
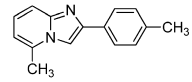
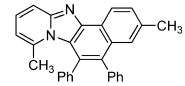
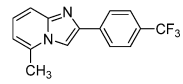
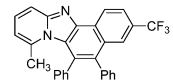
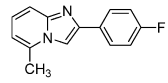
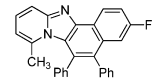
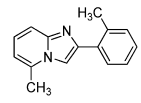
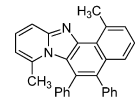
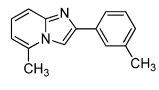
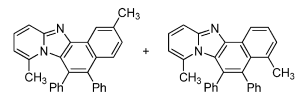


Entry	2	3[b]	4[b]
1	 2b	 **3m**, 61%	 **4m**[19], 16%
2	 2c	 **3n**, 60%	 **4n**, 20%
3	 2d	 **3o**, 63%	 **4o**, 15%
4	 2e	 **3p**, 66%	 **4p**, 20%
5	2f	 **3q**, 53%	 **4q**, 14%
6	 2g	 **3r**, 56%	 **4r**, 14%
7	 2h	 **3s**, 47%	 **4s**, 16%

[a]Raction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2$ (0.04 mmol), O_2 (balloon), TBAB (0.2 mmol), and DMF (2 mL), 100 °C, 12 h. [b]Isolated yield.

Table 4. Studies on the Scope of 1 for the Exclusive Formation of 3[a]



Entry	1	3[b]
1	 1m	 **3t**, 60%
2	 1n	 **3u**, 65%
3	 1o	 **3v**, 53%
4	 1p	 **3w**, 56%
5	 1q	 **3x**, 52%
6	 1r	 **3y** + **3y′**, 68%[c]

[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2$ (0.04 mmol), O_2 (balloon), TBAB (0.2 mmol), and DMF (2 mL), 100 °C, 12 h. [b]Isolated yield. [c]**3y**:**3y′** = 3:2, the ratio of the regioisomers was determined by ^1H NMR.

proposed in Scheme 2. Initially, electrophilic aromatic palladation on the 3-position of **1a** by the cleavage of C−H(1) bond affords intermediate **A**. Then, the C−C triple bond of **2a** inserts into the C−Pd bond in **A** to produce intermediate **B**. The following cleavage of C−H(2) bond affords a seven-membered palladacycle intermediate **C**. In the next stage, reductive elimination occurs with **C** to generate **3a** together with Pd(0), which is reoxidized into the Pd(II) species by $Cu(OAc)_2$(cat.)/O_2. On the other hand, the formation of **4a** should also involve the formation of intermediate **A** and **B** from **1a**. Then, cleavage of C−H(3) bond of intermediate **B** would give a six-membered palladacycle intermediate **D**, and the following reductive elimination of **D** will eventually produce **4a**.

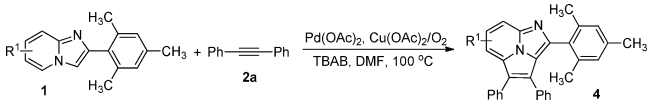
In order to get some insight into the relative potential for the formation of **3a** or **4a** from the reaction of **1a** and **2a**, a quantum chemical calculation was performed. The geometries of **3a** and **4a** were fully optimized at the B3LYP/6-31G(d) level by using Gaussian 09 program, and the optimizations were followed by the frequency calculation of the normal modes of vibration to check the ground-state nature of the optimized structures. The calculated results (Figure 1) show that **3a** is 10.39 kcal/mol more stable than **4a**. This difference in energy may be a possible reason to explain the fact that the formation of **3a** is more favorable than that of **4a** (see Table 2, entry 1).

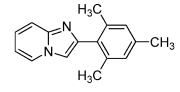
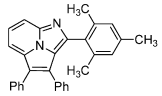
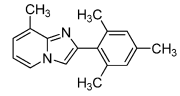
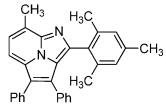
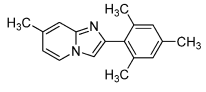
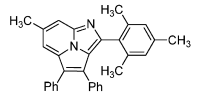
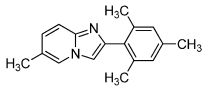
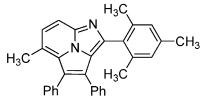
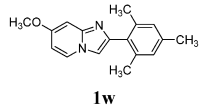
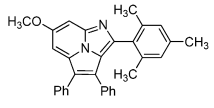
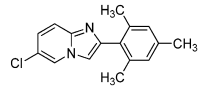
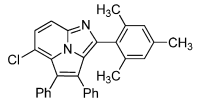
Furthermore, the yields of substituted **3** and **4** were also affected by the electronic nature of the imidazo[1,2-*a*]pyridine scaffold and the 2-phenyl unit of **1** in that higher selectivity for **3** was obtained from **1** with an electron-rich 2-phenyl moiety or with an electron-withdrawing group on the imidazo[1,2-*a*]pyridine unit. On the other hand, higher selectivity for **4** was obtained from **1** with an electron-poor 2-phenyl moiety or with an electron-donating group on the imidazo[1,2-*a*]pyridine unit. These results implied that the cleavage of C−H2 bond and C−H3 bond as shown in Scheme 2 might be one of the rate-limiting steps for this dehydrogenative coupling reaction and that the cleavage of the C−H bond could be significantly facilitated by higher electronic density of the aromatic ring upon which the C−H bond is embedded.

Finally, it is worth noting that the action mode of Pd(II) in promoting the reaction of **1** with **2** is different from that of Rh(III) (Scheme 3).[15a] To be specific, the initiating step for Rh(III)-catalyzed procedure is the activation and cleavage of C−H(a) bond on the 2-phenyl unit assisted by N-coordination

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

Table 5. Studies on the Scope of 1 for the exclusive formation of 4[a]



Entry	1	4[b]
1	 1s	 4t, 77%
2	 1t	 4u, 81%
3	 1u	 4v, 79%
4	 1v	 4w, 77%
5	 1w	 4x, 86%
6	 1x	 4y, 65%

[a]Raction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2$ (0.04 mmol), O_2 (balloon), TBAB (0.2 mmol), and DMF (2 mL), 100 °C, 12 h. [b]Isolated yield.

to give intermediate **I**, while with Pd(II) as a catalyst the initiating step is the activation and cleavage of C−H(b) bond attached on the heterocycle moiety to give intermediate **A**. This difference in action mode can account for the different regioselectivity shown in the reaction of **1a** with **2g** under the catalysis of Rh(III) or Pd(II) (Table 3, entry 6). With Rh(III)-complex as a catalyst, the insertion of the C−C triple bond of **2g** into the C−Rh bond of intermediate **I** from the less steric side of the triple bond affords the more stable seven-membered rhodacycle **II** with longer conjugation system (compare intermediate **II** with **II′**), from which 5-M-6-P-NIP is formed through nitrogen decoordination, rollover C−H activation, and reductive elimination. On the other hand, when Pd(II) was used, the insertion of the C−C triple bond of **2g** into the C−Pd bond of intermediate **A** from the less steric side of the triple bond of **2g** gives the more stable intermediate **B** with longer conjugation system (compare intermediate **B** with **B′**) and eventually results in the formation of 6-M-5-P-NIP.

To further verify the proposed reaction mechanism as shown in Schemes 2 and 3, some control experiments were carried out. First, 2-phenylimidazo[1,2-*a*]pyridine (**1a**) was treated with D_2O in DMF at 100 °C for 12 h (Scheme 4, (1)). It turned out that under these conditions 18% H/D exchange for the H atom attached to the imidazolyl ring of **1a** could occur in DMF in the absence of any catalyst. Second, in the presence of $Pd(OAc)_2$/$Cu(OAc)_2$/TBAB, treating the mixture of **1a** and D_2O in DMF at 100 °C for 12 h resulted in 88% H/D exchange for the H atom attached to the imidazolyl ring and 4% H/D exchange for the H atoms attached to the 2-phenyl ring of **1a**. The fact that the presence of palladium catalyst could significantly facilitate the H/D exchange for the H atom attached on the imidazolyl ring supports the proposed reaction mechanism in which palladium complexes are considered as key intermediates, and this cross coupling reaction should start with the palladium-assisted cleavage of H atom attached to imidazolyl ring rather than those attached to the 2-phenyl ring.

CONCLUSION

In this study, PIP was found to be able to take part in two kinds of cycloaromatization reactions with inner alkyne to give NIP and IID simultaneously, while the former was in most cases formed as a dominating product. Substrate scope studies with different PIPs and internal alkynes told that the reactions could tolerate a number of functional groups to give products with structural diversity. Interestingly, when 5-methyl-2-phenylimidazo[1,2-*a*]pyridine or 2-mesitylimidazo[1,2-*a*] pyridine, with the hydrogen atoms on specific locations replaced by methyl groups, was used as substrate, either NIP or IID could be obtained exclusively with good efficiency. It is also notable that for this Pd(II)-catalyzed dehydrogenative coupling, molecular oxygen could act as an efficient and clean oxidant. Compared with literature procedures for the preparation of fused N-heterocylcles, the method developed in this paper showed advantages such as commercially available or easily obtainable starting materials, obviated prefunctionalization of substrates, and minimized generation of waste chemicals.

EXPERIMENTAL SECTION

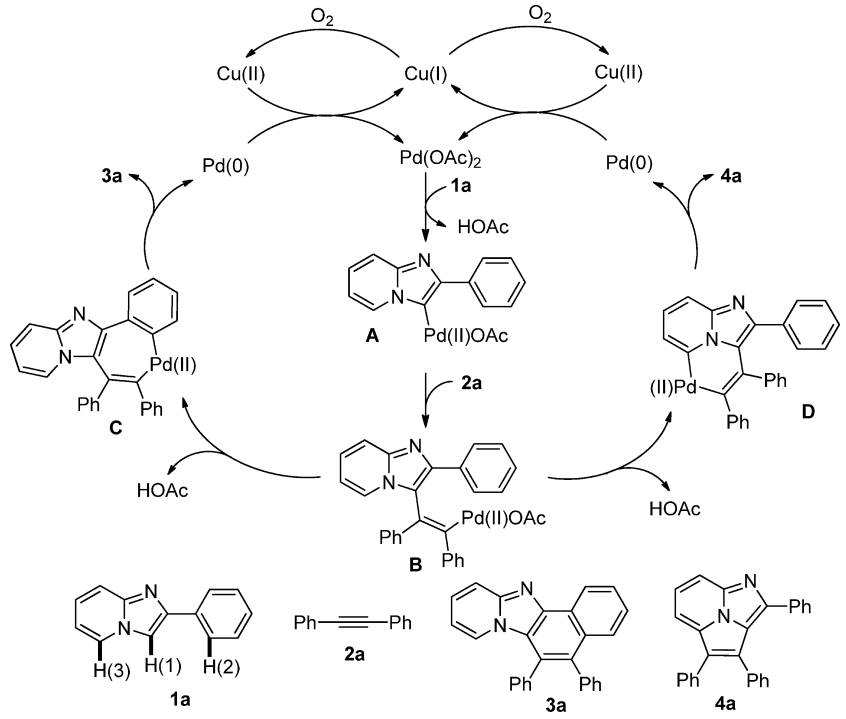
2-Phenylimidazo[1,2-*a*]pyridines (PIPs, **1**) were synthesized from 2-aminopyridines and 2-bromoacetophenones.[6b] Melting points were recorded with a micro melting point apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm from tetramethylsilane (TMS) as internal standard in $CDCl_3$ solutions. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc., and coupling constants are given in Hz. High-resolution mass spectra (HRMS) were obtained via ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F_{254} 0.25 mm).

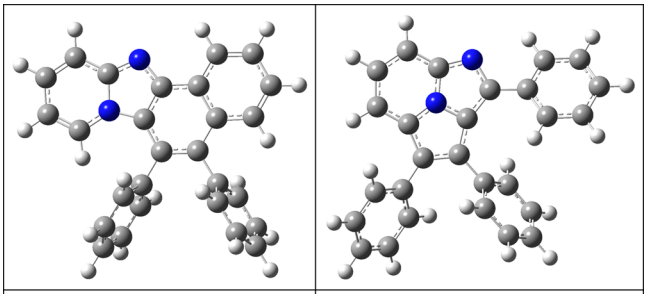
Typical procedure for the synthesis of 3a and spectroscopic data of 3a−3y, 4a−4k, 4m−4y. To a flask containing 2-phenylimidazo[1,2-*a*]pyridine (**1a**, 0.2 mmol) and 1,2-diphenylethyne (**2a**, 0.3 mmol) in DMF (2 mL) were added $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2$ (0.04 mmol), and TBAB (0.2 mmol). After the mixture was stirred under an oxygen atmosphere (balloon) at 100 °C for 12 h, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum, and the crude product was purified by chromatography on silica-gel to afford **3a** and **4a**. **3b−3y**, **4b−4k**, and **4m−4y** were obtained in a similar manner.

5,6-Diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3a**).[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.24); yellow solid (48.1 mg, 65%); mp: 298−299 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 6.50 (t, J = 6.8 Hz, 1H), 7.20−7.34 (m, 12H), 7.51 (t, J = 7.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 8.99 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ:

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

Scheme 2. Plausible Mechanisms for the Formation of 3a and 4a





3a, 0 kcal/mol	**4a**, 10.39 kcal/mol

Figure 1. Geometry structure and relative energy of **3a** and **4a**.

110.6, 117.8, 122.6, 123.0, 126.1, 126.16, 126.18, 126.5, 126.58, 126.61, 127.2, 127.5, 127.6, 127.7, 128.5, 130.4, 131.5, 131.6, 133.5, 136.9, 138.6, 140.9, 148.0. MS: m/z 371 $[MH]^+$.

*3-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3b**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.25); yellow solid (55.3 mg, 72%); mp: 297−299 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 6.48 (t, J = 6.8 Hz, 1H), 7.18−7.33 (m, 12H), 7.39 (s, 1H), 7.56 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 8.88 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.1, 110.5, 117.7, 122.2, 122.9, 124.0, 126.4, 126.5, 126.6, 126.8, 127.1, 127.5, 127.6, 128.2, 128.4, 130.4, 131.6, 133.1, 135.9, 137.0, 138.7, 140.9, 148.0. One carbon is not visible due to overlapping peaks; MS: m/z 385 $[MH]^+$.

*3-Methoxy-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3c**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.22); yellow solid (60.0 mg, 75%); mp: 242−243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.13 (s, 3H), 6.49 (t, J = 6.8 Hz, 1H), 6.97 (s, 1H), 7.19−7.39 (m, 13H), 7.84 (d, J = 9.6 Hz, 1H), 8.89 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.1, 108.1, 110.5, 116.9, 117.6, 120.8, 121.6, 124.6, 126.4, 126.6, 127.1, 127.2, 127.6, 127.7, 128.5, 130.3, 131.5, 132.7, 132.9, 137.0, 138.6, 141.0, 148.1, 158.0. MS: m/z 401 $[MH]^+$.

*3-Fluoro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3d**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.25); yellow solid (38.8 mg, 50%); mp: 282−283 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.50 (t, J = 6.8 Hz, 1H), 7.16−7.34 (m, 13H), 7.42−7.47 (m, 1H), 7.83 (d, J = 8.4 Hz, 1H), 8.94−8.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.7, 111.6, 111.8, 115.7 (d, J_{C-F} = 24.5 Hz), 117.7, 122.2, 122.8, 125.3, 125.4, 126.5, 126.8, 127.5, 127.7, 127.8 (d, J_{C-F} = 6.5 Hz), 128.5, 130.2, 131.4, 132.8 (d, J_{C-F} = 9.2 Hz), 136.6, 138.1, 140.9, 148.2, 161.2 (d, J_{C-F} = 243.0 Hz). MS: m/z 389 $[MH]^+$.

*5,6-Diphenyl-3-(trifluoromethyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3e**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.23); yellow solid (34.2 mg, 39%); mp: 265−266 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.54 (t, J = 6.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.24−7.30 (m, 6H), 7.33−7.37 (m, 4H), 7.84−7.90 (m, 2H), 7.92 (s, 1H), 9.08 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.1, 118.0, 121.9 (q, J_{C-F} = 2.6 Hz), 123.7, 124.0, 124.8 (q, J_{C-F} = 270.2 Hz), 125.0 (q, J_{C-F} = 4.6 Hz), 126.6, 127.1, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.6, 130.2, 130.5, 131.5, 133.9, 136.3, 137.5, 140.4, 148.4. MS: m/z 439 $[MH]^+$.

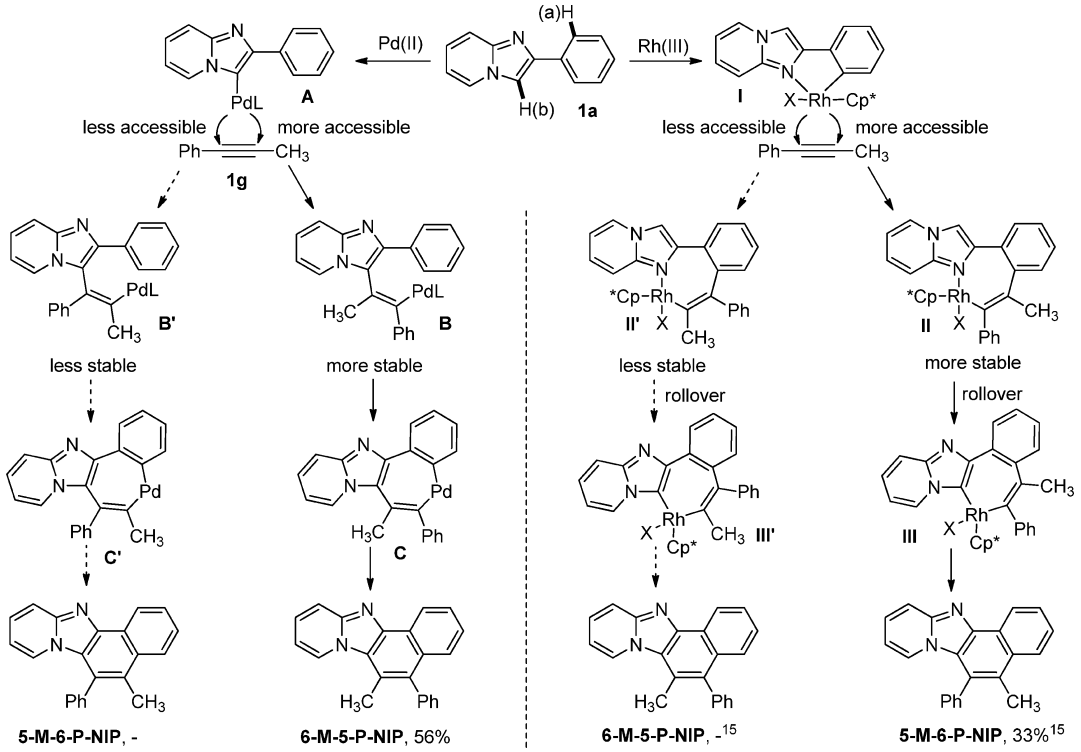
*1-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3f**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.27); yellow solid (30.7 mg, 40%); mp: 274−275 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.48 (s, 3H), 6.48 (t, J = 7.2 Hz, 1H), 7.19−7.40 (m, 13H), 7.50 (t, J = 8.0 Hz, 2H), 7.87 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.5, 110.4, 118.2, 123.4, 125.35, 125.38, 125.7, 126.2, 126.46, 126.55, 127.5, 127.6, 128.4, 128.5, 130.4, 131.6, 132.5, 134.1, 136.3, 137.2, 139.4, 142.0, 146.9. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 $[M + H]^+$, found: 385.1709.

*4,5-Diphenylthieno[3″,2″:5′,6′]benzo[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3g**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.3); yellow solid (60.2 mg, 80%); mp: 265−266 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.47 (t, J = 6.8 Hz, 1H); 7.16−7.35 (m, 13H), 7.46 (d, J = 5.6 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.4, 117.7, 123.2, 124.4, 125.36, 125.42, 126.6, 127.0, 127.6, 127.9, 128.2, 128.6, 128.8, 130.8, 131.0, 136.5, 138.2, 139.0, 139.1, 148.9. One carbon is not visible due to overlapping peaks; MS: m/z 377 $[MH]^+$.

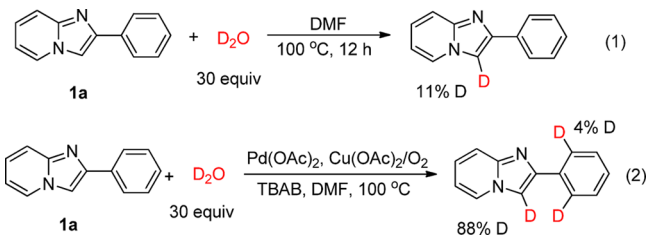
*7,8-Diphenylphenanthro[4′,3′:4,5]imidazo[1,2-a]pyridine (**3h**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.24); yellow solid (36.1 mg, 43%); mp: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.99 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.34−7.45 (m, 5H), 7.54 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 7.2 Hz, 1H), 7.89 (t, J = 8.8 Hz, 2H), 8.03 (d, J = 4.0

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

Scheme 3. Different Action Mode of Pd(II) and Rh(III) on the C−H Bond Activation of PIP



Scheme 4. Control Experiments to Verify the Proposed Reaction Mechanism



Hz, 2H), 8.15 (t, J = 4.0 Hz, 1H), 8.59 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.7, 112.8, 125.0, 125.9, 126.2, 126.5, 126.7, 127.0, 127.2, 127.7, 128.0, 128.1, 128.8, 129.6, 130.3, 130.5, 130.7, 131.1, 131.4, 131.6, 132.1, 133.1, 133.7, 134.1, 140.0, 150.3. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{31}H_{21}N_2$: 421.1704 [M + H] $^+$, found: 421.1712.

*10-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3i**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.32); yellow solid (42.3 mg, 55%); mp: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 6.34 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.19−7.26 (m, 7H), 7.31−7.34 (m, 3H), 7.48 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 8.95 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 113.4, 116.0, 122.5, 122.9, 125.5, 125.97, 126.03, 126.5, 127.49, 127.52, 127.6, 128.4, 128.8, 130.4, 131.3, 131.6, 133.0, 137.0, 138.5, 138.7, 140.9, 148.6. One carbon is not visible due to overlapping peaks; MS: m/z 385 [MH]$^+$.

*11-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3j**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.28); yellow solid (46.1 mg, 60%); mp: 248−249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.83 (s, 3H), 6.43 (t, J = 6.8 Hz, 1H), 7.12 (d, J = 6.4 Hz, 1H), 7.17−7.34 (m, 11H), 7.50 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 9.06 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.7, 110.6, 119.8, 123.1, 123.2, 124.3, 125.9, 126.0, 126.2, 126.6, 126.7, 127.5, 127.60, 127.65, 128.5, 128.7, 130.5, 131.4, 131.7, 133.5, 137.0, 138.7, 140.5, 148.5. HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 [M + H]$^+$, found: 385.1716.

*9-Chloro-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3k**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.26); yellow solid (55.8 mg, 69%); mp: 296−297 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20−7.29 (m, 9H), 7.37−7.38 (m, 3H), 7.53 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.81 (d, J = 9.6 Hz, 1H), 8.95 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 118.0, 118.6, 122.7, 122.9, 124.4, 126.0, 126.4, 126.5, 126.8, 127.6, 127.7, 128.0, 128.5, 128.7, 128.8, 130.2, 130.9, 131.5, 131.6, 134.4, 136.2, 138.2, 146.0. MS: m/z 405 [MH]$^+$.

*5,6-Diphenyl-9-(trifluoromethyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3l**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.25); yellow solid (67.5 mg, 77%); mp: 279−280 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24−7.32 (m, 7H), 7.40−7.46 (m, 4H), 7.58 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 9.6 Hz, 1H), 8.98 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 114.5, 114.9, 118.4, 122.8 (q, J_{C-F} = 4.6 Hz), 123.1, 124.4 (q, J_{C-F} = 269.3 Hz), 125.7, 126.1, 126.4, 126.7, 126.8, 126.9, 127.7, 127.8, 128.2, 128.9, 130.2, 131.4, 131.8, 134.9, 136.0, 138.1, 141.7, 147.3. HRMS calcd for $C_{28}H_{18}F_3N_2$: 439.1422 [M + H]$^+$, found: 439.1423.

*5,6-Bis(4-methoxyphenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3m**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.22); yellow solid (52.5 mg, 61%); mp: 290−291 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 3.84 (s, 3H), 6.53 (t, J = 6.4 Hz, 1H), 6.81 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.85 (d, J = 9.6 Hz, 1H), 8.96 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.15, 55.20, 110.8, 113.1, 114.0, 117.7, 123.0, 125.9, 126.2, 126.6, 127.4, 127.6, 129.1, 130.9, 131.4, 131.9, 132.6, 133.9, 140.4, 147.8, 158.1, 158.9. Three carbons are not visible due to overlapping peaks; MS: m/z 431 [MH]$^+$.

*5,6-Bis(4-chlorophenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3n**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.25); yellow solid (52.6 mg, 60%); mp: 277−278 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.54 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.30−7.34 (m, 4H), 7.46−7.53 (m, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.81 (d, J = 9.6 Hz, 1H), 8.95 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.0, 117.9, 122.2, 123.1,

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

125.4, 126.1, 126.2, 126.4, 126.5, 127.2, 127.5, 128.0, 129.0, 131.1, 131.6, 132.3, 132.76, 132.84, 134.0, 135.1, 136.8, 141.1, 148.1. MS: *m/z* 439 $[MH]^+$.

*5,6-Bis(4-(trifluoromethyl)phenyl)naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3o**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.25); yellow solid (63.8 mg, 63%); mp: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.60 (t, J = 6.8 Hz, 1H), 7.25 (d, J = 6.8 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.35−7.42 (m, 3H), 7.49−7.56 (m, 4H), 7.65 (d, J = 8.0 Hz, 2H), 7.76 (t, J = 7.2 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 9.01 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 118.1, 121.9, 123.2, 123.9 (q, J_{C-F} = 270.8 Hz), 124.1 (q, J_{C-F} = 270.3 Hz), 124.8 (q, J_{C-F} = 3.8 Hz), 125.1, 125.7 (q, J_{C-F} = 2.8 Hz), 125.9, 126.3, 126.7, 126.8, 127.1, 127.7, 129.3 (q, J_{C-F} = 32.2 Hz), 130.4 (q, J_{C-F} = 32.5 Hz), 130.9, 131.9, 132.0, 140.4, 141.5, 142.2, 148.3. MS: *m/z* 507 $[MH]^+$.

*5,6-Di-m-tolylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3p**).*[15] Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.26); yellow solid (52.6 mg, 66%); mp: 249−250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.27 (s, 3H), 2.30 (s, 3H), 6.51 (t, J = 6.8 Hz, 1H), 7.00−7.16 (m, 7H), 7.20−7.32 (m, 3H), 7.50 (t, J = 7.2 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.85 (d, J = 9.2 Hz, 1H), 8.98 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 21.4, 110.5, 117.8, 122.7, 122.9, 126.1, 126.6, 127.1, 127.25, 127.31, 127.4, 127.7, 128.2, 128.3, 128.4, 128.6, 128.7, 130.97, 131.02, 131.5, 132.3, 132.4, 133.6, 136.8, 138.1, 138.5, 140.8, 148.0. MS: *m/z* 399 $[MH]^+$.

*Diethyl naphtho[1′,2′:4,5]imidazo[1,2-a]pyridine-5,6-dicarboxylate (**3q**).*[15] Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.3); yellow solid (38.4 mg, 53%); mp: 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46−1.50 (m, 6H), 4.51−4.60 (m, 4H), 6.97 (t, J = 7.2 Hz, 1H), 7.51−7.55 (m, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.79 (d, J = 6.8 Hz, 1H), 8.93 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 14.3, 62.0, 62.7, 112.0, 118.0, 119.2, 119.4, 123.5, 126.5, 127.3, 127.5, 127.7, 127.8, 128.2, 128.9, 143.5, 149.5, 150.3, 166.9, 168.1. MS: *m/z* 363 $[MH]^+$.

*6-Methyl-5-phenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3r**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.28); yellow solid (34.5 mg, 56%); mp: 233−234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.76 (s, 3H), 6.96 (t, J = 6.8 Hz, 1H), 7.34−7.36 (m, 2H), 7.45−7.58 (m, 6H), 7.64−7.68 (m, 1H), 7.97 (d, J = 9.2 Hz, 1H), 8.93 (d, J = 8.0 Hz, 1H), 9.00 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.7, 111.7, 117.9, 120.7, 123.0, 124.2, 124.8, 125.7, 126.2, 127.0, 127.27, 127.31, 127.5, 128.5, 131.0, 131.9, 134.0, 139.5, 147.2. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{22}H_{17}N_2$: 309.1391 $[M + H]^+$, found: 309.1398.

*5-Phenyl-6-propylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3s**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.28); yellow solid (31.6 mg, 47%); mp: 187−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (t, J = 7.6 Hz, 3H), 1.65−1.75 (m, 2H), 2.99 (t, J = 8.4 Hz, 2H), 6.97 (t, J = 6.4 Hz, 1H), 7.35−7.40 (m, 3H), 7.43−7.47 (m, 2H), 7.50−7.55 (m, 3H), 7.65 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 8.67 (d, J = 7.2 Hz, 1H), 8.92 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 23.8, 32.0, 111.5, 118.4, 122.8, 123.7, 125.4, 125.6, 125.8, 126.0, 126.7, 127.3, 127.4, 128.3, 131.0, 131.9, 133.4, 139.6, 141.4, 147.8. HRMS calcd for $C_{24}H_{21}N_2$: 337.1704 $[M + H]^+$, found: 337.1715.

*8-Methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3t**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.27); yellow solid (46.1 mg, 60%); mp: 273−274 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.71 (s, 3H), 6.54 (d, J = 6.4 Hz, 1H), 7.07−7.27 (m, 10H), 7.35−7.41 (m, 1H), 7.48−7.54 (m, 2H), 7.72 (t, J = 8.0 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 9.06 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.1, 114.4, 114.6, 123.4, 124.3, 126.60, 126.62, 126.9, 127.1, 127.4, 127.7, 127.8, 127.9, 128.3, 128.6, 128.9, 129.1, 131.3, 131.6, 131.7, 139.5, 140.49, 140.53, 149.3. HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 $[M + H]^+$, found: 385.1712.

*3,8-Dimethyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]pyridine (**3u**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.29); yellow solid (51.8 mg, 65%); mp: 287−288 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.69 (s, 3H), 2.45 (s, 3H), 6.44 (d, J = 6.8 Hz, 1H), 7.02−7.04 (m, 2H), 7.09−7.14 (m, 2H), 7.16−7.20 (m, 3H), 7.27−7.32 (m, 5H), 7.55 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 8.91 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.1, 23.1, 113.2, 115.3, 123.0, 124.0, 124.2, 126.4, 126.6, 126.8, 127.6, 127.68, 127.73, 128.0, 128.2, 131.3, 131.7, 131.8, 133.1, 136.2, 139.9, 140.1, 141.1, 142.9, 150.4. HRMS calcd for $C_{29}H_{23}N_2$: 399.1861 $[M + H]^+$, found: 399.1855.

*8-Methyl-5,6-diphenyl-3-(trifluoromethyl)naphtho[1′,2′:4,5]-imidazo[1,2-a]pyridine (**3v**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.26); yellow solid (47.9 mg, 53%); mp: 263−264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.67 (s, 3H), 6.47 (d, J = 6.8 Hz, 1H), 7.01−7.07(m, 4H), 7.13−7.18 (m, 3H), 7.26−7.27 (m, 3H), 7.32 (t, J = 8.0 Hz, 1H), 7.76 (d, J = 9.2 Hz, 1H), 7.83 (s, 1H), 7.86 (d, J = 8.8 Hz, 1H), 9.10 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.1, 113.8, 115.5, 121.8 (q, J_{C-F} = 3.3 Hz), 124.1, 124.5 (q, J_{C-F} = 270.2 Hz), 124.8 (q, J_{C-F} = 4.5 Hz), 125.7, 126.9, 127.2, 127.5, 127.8, 127.9, 128.2, 128.4, 129.5, 130.7, 131.2, 131.6, 133.7, 138.7, 140.2, 140.4, 142.4, 150.8. HRMS calcd for $C_{29}H_{20}F_3N_2$: 453.1578 $[M + H]^+$, found: 453.1589.

*3-Fluoro-8-methyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3w**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.27); yellow solid (45.0 mg, 56%); mp: 241−242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.69 (s, 3H), 6.47 (d, J = 6.8 Hz, 1H), 7.03−7.09 (m, 4H), 7.15−7.19 (m, 4H), 7.27−7.28 (m, 3H), 7.33 (t, J = 8.0 Hz, 1H), 7.42−7.46 (m, 1H), 7.76 (d, J = 9.2 Hz, 1H), 8.98−9.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.1, 111.3, 111.5, 113.4, 115.3, 115.6 (d, J_{C-F} = 25.3 Hz), 122.7, 124.2, 125.5 (d, J_{C-F} = 9.4 Hz), 126.7, 127.1, 127.8, 128.1, 129.2, 131.2, 131.6, 132.7, 132.9 (d, J_{C-F} = 8.8 Hz), 139.3, 140.2, 140.7, 142.9, 150.6, 161.3 (d, J_{C-F} = 235.9 Hz). HRMS calcd for $C_{28}H_{20}FN_2$: 403.1610 $[M + H]^+$, found: 403.1601.

*1,8-Dimethyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3x**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.28); yellow solid (41.4 mg, 52%); mp: 280−281 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.66 (s, 3H), 3.45 (s, 3H), 6.43 (d, J = 6.8 Hz, 1H), 6.99 (d, J = 6.4 Hz, 2H), 7.09−7.15 (m, 5H), 7.26−7.39 (m, 4H), 7.43 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 8.4 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.1, 24.7, 113.2, 115.7, 125.1, 125.5, 125.6, 126.4, 126.7, 127.1, 127.6, 127.8, 127.9, 128.6, 128.7, 131.2, 131.8, 132.7, 133.8, 136.3, 139.9, 140.5, 141.0, 149.1. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{29}H_{23}N_2$: 399.1861 $[M + H]^+$, found: 399.1868.

*4,8-Dimethyl-5,6-diphenylnaphtho[1′,2′:4,5]imidazo[1,2-a]-pyridine (**3y**) and 2,8-Dimethyl-5,6-diphenylnaphtho[1′,2′:4,5]-imidazo[1,2-a]pyridine (**3y′**).* Eluent: petroleum ether/ethyl acetate = 3:1 (R_f = 0.3); yellow solid (54.2 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.66 (s, 3H), 1.70 (s, 2H), 1.92 (s, 3H), 2.65 (s, 2H), 6.42−6.46 (m, 1.61H), 6.98−7.15 (m, 10H), 7.28−7.36 (m, 10H), 7.43 (d, J = 8.4 Hz, 0.7 H) 7.55−7.61 (m, 3H), 7.77 (d, J = 8.8 Hz, 1H), 8.81 (s, 0.6H), 9.02 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 23.1, 25.4, 113.0, 113.3, 115.29, 115.32, 122.2, 122.4, 126.0, 126.35, 126.45, 126.6, 126.7, 126.8, 127.3, 127.4, 127.6, 127.68, 127.74, 128.3, 128.36, 128.39, 129.5, 130.3, 131.28, 131.34, 131.6, 131.7, 131.8, 132.8, 133.6, 136.2, 136.5, 140.0, 140.1, 140.96, 141.02, 142.6, 150.4. HRMS calcd for $C_{29}H_{23}N_2$: 399.1861 $[M + H]^+$, found: 399.1851.

*2,3,4-Triphenylimidazo[5,1,2-cd]indolizine (**4a**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.28);yellow solid (13.3 mg, 18%); mp: 210−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27−7.48 (m,13H), 7.83 (d, J = 7.2 Hz, 2H), 7.97−7.98 (m, 2H), 8.05−8.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 112.8, 124.2, 127.0, 127.3, 128.1, 128.3, 128.5, 128.6, 129.4, 129.7, 130.2, 131.0, 131.6, 131.7, 133.5, 133.9, 134.0, 140.0, 151.0. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{27}H_{19}N_2$: 371.1548 $[M + H]^+$, found: 371.1551.

*3,4-Diphenyl-2-(p-tolyl)imidazo[5,1,2-cd]indolizine (**4b**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.26); yellow solid (11.5 mg, 15%); mp: 225−226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 7.09 (d, J = 7.6 Hz, 2H), 7.29−7.47 (m, 10H), 7.73 (d, J = 8.8 Hz, 2H), 7.93−7.97 (m, 2H), 8.01−8.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 111.0, 112.5, 124.1, 126.88, 126.94, 127.1, 128.1, 128.5, 128.6, 129.1, 129.6, 130.1, 130.7, 131.0, 131.5, 133.9,

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

134.1, 139.6, 140.0, 151.2. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 $[M + H]^+$, found: 385.1709.

2-(4-Methoxyphenyl)-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4c**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.25); yellow solid (10.4 mg, 13%); mp: 200−201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.83 (s, 3H), 6.81 (d, J = 8.8 Hz, 2H), 7.31−7.47 (m, 10H), 7.78 (d, J = 8.8 Hz, 2H), 7.94−7.97 (m, 2H), 7.98−7.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3, 110.6, 112.4, 113.8, 123.8, 126.1, 126.9, 127.0, 128.1, 128.3, 128.5, 128.6, 130.1, 131.0, 131.1, 131.4, 131.6, 134.0, 134.1, 140.0, 151.1, 160.8. HRMS calcd for $C_{28}H_{21}N_2O$: 401.1654 $[M + H]^+$, found: 401.1642.

2-(4-Fluorophenyl)-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4d**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.28); yellow solid (25.6 mg, 33%); mp: 202−203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (t, J = 9.2 Hz, 2H), 7.30−7.47 (m, 10H), 7.78−7.81 (m, 2H), 7.93−7.98 (m, 2H), 8.01−8.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 112.8, 115.4 (d, J_{C-F} = 22.2 Hz), 124.0, 127.1, 127.4, 128.3, 128.59, 128.63, 129.8 (d, J_{C-F} = 3.1 Hz), 130.1, 130.9, 131.4 (d, J_{C-F} = 3.5 Hz), 131.5, 131.7, 133.8, 133.9, 139.9, 149.8, 163.6 (d, J_{C-F} = 247.8 Hz). One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{27}H_{18}FN_2$: 389.1454 $[M + H]^+$, found: 389.1442.

3,4-Diphenyl-2-(4-(trifluoromethyl)phenyl)imidazo[5,1,2-cd]-indolizine (**4e**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.27); yellow solid (36.8 mg, 42%); mp: 243−244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31−7.47 (m, 10H), 7.52 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.97−8.02 (m, 2H), 8.06−8.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.1, 113.3, 124.1 (q, J_{C-F} = 270.8 Hz), 124.7, 125.2 (q, J_{C-F} = 3.6 Hz), 127.2, 127.4, 128.1, 128.5, 128.7, 129.7, 130.1, 130.6, 130.8, 131.0, 131.5, 131.9, 133.6 (q, J_{C-F} = 21.5 Hz), 137.0, 139.8, 148.6. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{28}H_{18}F_3N_2$: 439.1422 $[M + H]^+$, found: 439.1408.

3,4-Diphenyl-2-(o-tolyl)imidazo[5,1,2-cd]indolizine (**4f**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.3); yellow solid (34.6 mg, 45%); mp: 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 7.12−7.16 (m, 3H), 7.20−7.48 (m, 9H), 7.53 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 4.4 Hz, 2H), 8.05−8.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 111.4, 112.6, 125.0, 125.5, 126.2, 126.7, 127.2, 127.8, 128.2, 128.8, 128.9, 130.2, 130.5, 131.3, 131.5, 132.0, 133.3, 133.6, 134.1, 137.3, 139.7, 151.2. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 $[M + H]^+$, found: 385.1691.

3,4-Diphenyl-2-(thiophen-2-yl)imidazo[5,1,2-cd]indolizine (**4g**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.33); yellow solid (6.8 mg, 9%); mp: 211−212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.92 (t, J = 4.4 Hz, 1H), 6.98 (d, J = 3.2 Hz, 1H), 7.29−7.53 (m, 11H), 7.94−8.00 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.0, 112.9, 127.1, 127.3, 127.5, 128.0, 128.36, 128.42, 128.5, 128.65, 128.70, 129.1, 130.1, 130.8, 131.5, 131.6, 133.8, 134.1, 137.7, 140.0, 144.9. HRMS calcd for $C_{25}H_{17}N_2S$: 377.1112 $[M + H]^+$, found: 377.1116.

2-(Naphthalen-1-yl)-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4h**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.25); yellow solid (29.4 mg, 35%); mp: 226−227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.49 (t, J = 7.2 Hz, 1H), 7.22−7.36 (m, 12H), 7.63 (d, J = 8.8 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.91−7.99 (m, 3H), 11.13 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.5, 118.2, 121.9, 124.7, 125.9, 126.4, 126.6, 126.7, 126.99, 127.05, 127.6, 127.76, 127.78, 127.8, 128.6, 129.3, 130.0, 130.4, 130.9, 131.7, 132.1, 134.2, 137.1, 139.4, 142.0, 148.1. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{31}H_{21}N_2$: 421.1704 $[M + H]^+$, found: 421.1716.

6-Methyl-2,3,4-triphenylimidazo[5,1,2-cd]indolizine (**4i**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.30); yellow solid (22.3 mg, 29%); mp: 199−200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.84 (s, 3H), 7.29−7.48 (m, 13H), 7.81−7.87 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.9, 111.9, 113.8, 126.6, 126.9, 128.1, 128.2, 128.3, 128.5, 128.6, 129.2, 129.6, 130.2, 131.0, 131.2, 131.8, 133.8, 134.1, 138.5, 140.0, 150.9. HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 $[M + H]^+$, found: 385.1712.

7-Methyl-2,3,4-triphenylimidazo[5,1,2-cd]indolizine (**4j**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.29); yellow solid (20.0 mg, 26%); mp: 221−222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.05 (s, 3H), 7.26−7.41 (m, 11H), 7.46 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 112.9, 122.9, 124.5, 126.9, 127.2, 128.0, 128.2, 128.3, 128.5, 128.6, 129.1, 129.7, 130.1, 130.2, 130.6, 131.1, 133.8, 134.1, 140.5, 150.6. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{28}H_{21}N_2$: 385.1704 $[M + H]^+$, found: 385.1702.

5-Chloro-2,3,4-triphenylimidazo[5,1,2-cd]indolizine (**4k**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.28); yellow solid (5.7 mg, 7%); mp: 224−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28−7.38 (m, 11H), 7.42−7.44 (m, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 120.7, 124.5, 126.3, 127.5, 127.7, 127.8, 128.1, 128.3, 128.4, 129.7, 131.0, 131.9, 132.6, 133.1, 133.2, 133.3, 138.9, 151.9. Two carbons are not visible due to overlapping peaks; HRMS calcd for $C_{27}H_{18}ClN_2$: 405.1158 $[M + H]^+$, found: 405.1151.

3,4-Bis(4-methoxyphenyl)-2-phenylimidazo[5,1,2-cd]indolizine (**4m**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.26); yellow solid (13.8 mg, 16%); mp: 207−208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 3.87 (s, 3H), 6.89 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 6.0 Hz, 5H), 7.39 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 7.2 Hz, 2H), 7.90−7.96 (m, 2H), 8.02 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.2, 55.3, 110.1, 112.3, 113.9, 114.1, 126.2, 126.4, 126.8, 128.3, 129.2, 129.7, 131.0, 131.2, 132.0, 132.3, 133.8, 146.3, 150.6, 158.7, 159.5. Two carbons are not visible due to overlapping peaks; HRMS calcd for $C_{29}H_{23}N_2O_2$: 431.1759 $[M + H]^+$, found: 431.1746.

3,4-Bis(4-chlorophenyl)-2-phenylimidazo[5,1,2-cd]indolizine (**4n**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.27); yellow solid (17.5 mg, 20%); mp: 204−205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30−7.37 (m, 11H), 7.80 (d, J = 6.8 Hz, 2H), 7.88−7.96 (m, 2H), 8.03 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.7, 112.7,123.8, 126.0, 127.2, 128.5, 128.9, 129.0, 129.6, 130.1, 131.2, 131.3, 132.0, 132.3, 133.30, 133.34, 134.5, 140.0, 151.3. Two carbons are not visible due to overlapping peaks; HRMS calcd for $C_{27}H_{17}Cl_2N_2$: 439.0769 $[M + H]^+$, found: 439.0766.

2-Phenyl-3,4-bis(4-(trifluoromethyl)phenyl)imidazo[5,1,2-cd]-indolizine (**4o**). Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.25); yellow solid (15.2 mg, 15%); mp: 191−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29−7.33 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 4H), 7.67 (t, J = 7.6 Hz, 4H), 7.76 (d, J = 7.6 Hz, 2H), 8.00−8.06 (m, 2H), 8.12 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.1, 113.1, 123.97, 124.0 (q, J_{C-F} = 270.5 Hz), 124.1 (q, J_{C-F} = 270.6 Hz), 125.7 (q, J_{C-F} = 3.9 Hz), 125.8 (q, J_{C-F} = 4.1 Hz), 127.6, 128.5, 129.4 (q, J_{C-F} = 31.5 Hz), 129.6, 129.9, 130.1, 130.3, 130.6 (q, J_{C-F} = 32.6 Hz), 131.1, 131.4, 133.2, 137.2, 137.4, 140.2, 151.9. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{29}H_{17}F_6N_2$: 507.1296 $[M + H]^+$, found: 507.1308.

2-Phenyl-3,4-di-m-tolylimidazo[5,1,2-cd]indolizine (**4p**). Eluent: Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.29); yellow solid (15.9 mg, 20%); mp: 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 2.36 (s, 3H), 7.14−7.35 (m, 11H), 7.85 (d, J = 7.2 Hz, 2H), 7.96 (d, J = 6.0 Hz, 2H), 8.03−8.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 21.5, 111.2, 112.7, 124.3, 126.9, 127.2, 127.3, 127.8, 127.9, 128.2, 128.3, 128.5, 128.8, 129.3, 129.7, 130.8, 131.8, 133.66, 133.74, 133.9, 138.0, 138.1, 139.9, 150.9. Two carbons are not visible due to overlapping peaks; HRMS calcd for $C_{29}H_{23}N_2$: 399.1861 $[M + H]^+$, found: 399.1852.

Diethyl 2-phenylimidazo[5,1,2-cd]indolizine-3,4-dicarboxylate (**4q**). Eluent: petroleum ether/ethyl acetate = 10:1 (R_f = 0.3); yellow solid (10.1 mg, 14%); mp: 121−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.42 (t, J = 7.2 Hz, 3H), 1.48 (t, J = 7.2 Hz, 3H), 4.50 (q, J = 7.2 Hz, 2H), 4.58 (q, J = 7.2 Hz, 2H), 7.51−7.56 (m, 3H), 8.07−8.09 (m, 2H), 8.22 (d, J = 6.8 Hz, 2H), 8.33−8.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 14.4, 61.1, 62.7, 112.8, 116.1, 116.4, 121.9, 123.2, 126.6, 129.1, 129.5, 130.0, 130.8, 132.8, 140.8, 154.5, 163.3,

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518

165.6. HRMS calcd for $C_{21}H_{19}N_2O_4$: 363.1345 $[M + H]^+$, found: 363.1349.

*3-Methyl-2,4-diphenylimidazo[5,1,2-cd]indolizine (**4r**).* Eluent: petroleum ether/ethyl acetate = 10:1 (R_f = 0.25); yellow solid (8.6 mg, 14%); mp: 118−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.94 (s, 3H), 7.44−7.54 (m, 2H), 7.57−7.63 (m, 4H), 7.68 (d, J = 6.8 Hz, 2H), 7.85 (d, J = 7.6 Hz, 1H), 7.93 (t, J = 7.6 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 110.6, 111.3, 126.7, 127.2, 127.4, 128.3, 128.5, 128.9, 129.0, 129.1, 129.4, 130.0, 132.1, 134.1, 134.5, 139.8, 150.3. HRMS calcd for $C_{22}H_{17}N_2$: 309.1391 $[M + H]^+$, found: 309.1382.

*2,4-Diphenyl-3-propylimidazo[5,1,2-cd]indolizine (**4s**).* Eluent: petroleum ether/ethyl acetate = 10:1 (R_f = 0.25); yellow solid (10.8 mg, 16%); mp: 103−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.6 Hz, 3H), 1.68−1.74 (m, 2H), 3.27 (t, J = 8.0 Hz, 2H), 7.45−7.53 (m, 2H), 7.56−7.65 (m, 6H), 7.80 (d, J = 8.0 Hz, 1H), 7.92 (t, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 8.26 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 25.0, 29.2, 110.7, 111.4, 125.0, 126.6, 127.3, 128.4, 128.8, 128.9, 129.0, 129.4, 130.2, 132.1, 133.3, 134.2, 134.7, 139.9, 150.2. HRMS calcd for $C_{24}H_{21}N_2$: 337.1704 $[M + H]^+$, found: 337.1695.

*2-Mesityl-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4t**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.31); yellow solid (63.5 mg, 77%); mp: 55−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (s, 6H), 2.36 (s, 3H), 6.92 (s, 2H), 7.06 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.92−7.96 (m, 2H), 8.06 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 21.3, 111.3, 112.5, 125.5, 125.7, 126.5, 127.3, 127.8, 128.2, 128.3, 128.9, 130.0, 130.2, 131.0, 131.1, 132.2, 133.1, 134.3, 137.2, 138.2, 139.9, 150.7. HRMS calcd for $C_{30}H_{25}N_2$: 413.2017 $[M + H]^+$, found: 413.2009.

*2-Mesityl-7-methyl-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4u**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.32); yellow solid (69.0 mg, 81%); mp: 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.00 (s, 6H), 2.35 (s, 3H), 2.97 (s, 3H), 6.90 (s, 2H), 7.03 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 7.31−7.41 (m, 3H), 7.56 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.3, 20.6, 21.3, 112.8, 123.1, 125.4, 126.1, 127.3, 127.7, 128.2, 128.4, 128.9, 129.9, 130.2, 130.4, 130.7, 130.8, 133.1, 134.2, 137.3, 138.3, 139.0, 148.3. One carbon is not visible due to overlapping peaks; HRMS calcd for $C_{31}H_{27}N_2$: 427.2174 $[M + H]^+$, found: 427.2162.

*2-Mesityl-6-methyl-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4v**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.3); yellow solid (67.4 mg, 79%); mp: 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.01 (s, 6H), 2.36 (s, 3H), 2.85, (s, 3H), 6.91, (s, 2H), 7.06 (t, J = 7.2 Hz, 2H), 7.16−7.21 (m, 3H), 7.38 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.81 (s, 1H), 7.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.2, 21.2, 22.8, 111.9, 113.4, 124.9, 127.2, 127.7, 128.1, 128.2, 128.9, 129.9, 130.2, 131.2, 131.3, 131.8, 133.2, 134.5, 137.1, 137.9, 138.0, 140.0. Two carbons are not visible due to overlapping peaks; HRMS calcd for $C_{31}H_{27}N_2$: 427.2174 $[M + H]^+$, found: 427.2160.

*2-Mesityl-5-methyl-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4w**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.33); yellow solid (65.6 mg, 77%); mp: 195−196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.04 (s, 6H), 2.37 (s, 3H), 2.57 (s, 3H), 6.92 (s, 2H), 6.99 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.2 Hz, 1H), 7.42−7.46 (m, 3H), 7.51−7.54 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.8, 20.5, 21.3, 111.1, 125.00, 125.04, 126.7, 127.4, 127.6, 127.9, 128.3, 128.4, 129.0, 129.9, 130.2, 131.1, 131.2, 131.5, 133.2, 135.0, 137.2, 138.0, 138.7, 149.5. HRMS calcd for $C_{31}H_{27}N_2$: 427.2174 $[M + H]^+$, found: 427.2166.

*2-Mesityl-6-methoxy-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4x**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.29); yellow solid (76.1 mg, 86%); mp: 209−210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.02 (s, 6H), 2.36 (s, 3H), 4.08 (s, 3H), 6.91 (s, 2H), 7.06 (t, J = 7.6 Hz, 2H), 7.16−7.20 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.56−7.58 (m, 3H), 7.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.3, 56.7, 96.9, 101.1, 124.2, 125.0, 127.2, 127.8, 128.1, 128.2, 128.9, 129.9, 130.1, 131.0, 132.0, 132.3, 133.1, 134.3, 137.1, 138.0, 140.3, 150.7, 161.1. HRMS calcd for $C_{31}H_{27}N_2O$: 443.2123 $[M + H]^+$, found: 443.2125.

*5-Chloro-2-mesityl-3,4-diphenylimidazo[5,1,2-cd]indolizine (**4y**).* Eluent: petroleum ether/ethyl acetate = 5:1 (R_f = 0.28); yellow solid (58.0 mg, 65%): mp 165−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.02 (s, 6H), 2.36 (s, 3H), 6.92 (s, 2H), 7.00 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 7.2 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.41−7.42 (m, 3H), 7.54−7.56 (m, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.3, 111.4, 120.6, 125.9, 126.4, 127.7, 127.88, 127.93, 128.1, 128.2, 128.3, 128.4, 130.0, 130.7, 131.9, 132.6, 132.7, 133.2, 137.1, 138.4, 138.9, 151.7. HRMS calcd for $C_{30}H_{24}ClN_2$: 447.1628 $[M + H]^+$, found: 447.1622.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra, X-ray crystal structures of **3b** and **4m**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01092.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (NSFC) (grant numbers 21272058, 21172057), Program for Innovative Research Team in Science and Technology in University of Henan Province (15IRTSTHN 003), Program for Science and Technology Innovation Talents in Universities of Henan Province (15HASTIT005), and PCSIRT (IRT 1061) for financial support.

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(17) The structure of **3b** was confirmed by X-ray diffraction analysis, see SI for the details.
(18) The structure of **3r** was established based on its NMR data and by comparing its NMR data with those of its regio-isomer as reported in reference 15, see SI for the details.
(19) The structure of **4m** was confirmed by X-ray diffraction analysis, see SI for the details.

DOI: 10.1021/acs.joc.5b01092
J. Org. Chem. 2015, 80, 7508−7518