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1-Alkynyl- and 1-Alkenyl-3-arylimidazo[1,5-*a*]pyridines: Synthesis, Photophysical Properties, and Observation of a Linear Correlation between the Fluorescent Wavelength and Hammett Substituent Constants

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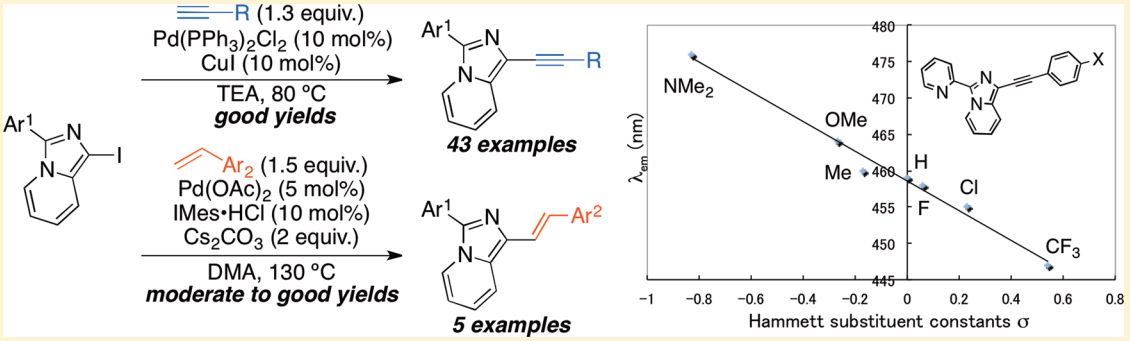
Supporting Information

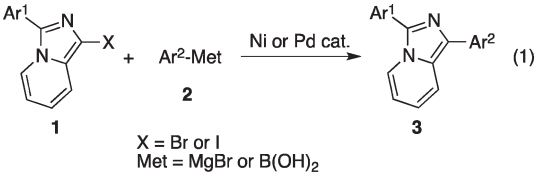
ABSTRACT:



1-Alkynyl- and 1-alkenyl-3-arylimidazo[1,5-*a*]pyridines were synthesized. The Sonogashira coupling of 3-aryl-1-iodoimidazo[1,5-*a*]-pyridines and various terminal alkynes with $Pd(PPh_3)_2Cl_2$ (10 mol %) and CuI (10 mol %) in triethylamine at 80 °C for 12 h afforded the corresponding 1-alkenyl-3-arylimidazo[1,5-*a*]pyridines in good to excellent yields. The Mizoroki−Heck reaction of 3-aryl-1-iodoimidazo[1,5-*a*]pyridines and various styrene derivatives proceeded smoothly with $Pd(OAc)_2$ (5 mol %), IMes·HCl (10 mol %), and Cs_2CO_3 (2 equiv) in DMA at 130 °C for 20 h to give the alkenylated imidazo[1,5-*a*]pyridines in moderate to high yields. The fluorescence maxima and fluorescence quantum yields of the alkynylated products were 458−560 nm and Φ_F = 0.08−0.26 in chloroform solution, and those of the alkenylated imidazopyridines were 479−537 nm and Φ_F = 0.03−0.13. The absorption behaviors of the obtained alkynylated and alkenylated imidazo[1,5-*a*]pyridines showed a good fit to the values predicted by TDDFT calculations at the B3LYP/6-311++G(d,p) level. In addition, the alkynylated imidazo[1,5-*a*]pyridines obtained showed linear correlations between the Hammett substituent constants of the substituents on the arylalkynyl group and their fluorescence wavelengths.

INTRODUCTION

Imidazo[1,5-*a*]pyridines are an important class of compounds that have potential as functional materials[1,2] and bioactive compounds.[3] Therefore, the development of methods for the synthesis of imidazo[1,5-*a*]pyridine derivatives has recently attracted considerable attention.[4−6] As part of our investigation of the synthesis and photophysical properties of multifunctional imidazo[1,5-*a*]-pyridines, we recently reported a synthesis of diverse 1,3-diarylated imidazo[1,5-*a*]pyridine derivatives **3** using cross-coupling reactions of 1-halogenated 3-aryl-imidazo[1,5-*a*]pyridines **1** and organometallic reagents **2** (eq 1).[7]



The obtained diarylated imidazopyridines showed fluorescent emission in a wavelength range of 454−526 nm. In addition, the quantum yields of 1,3-diarylated imidazopyridines were improved compared to those of the parent 3-arylated imidazopyridines. Meanwhile, there is likely no correlation between the photophysical properties of these imidazopyridines and the electronic properties of their substituents. In this context, most biaryl moieties have twisted structures due to steric repulsion between their substituents, and this results in the formation of a distorted π-conjugated system. As a result, the electronic properties of the substituents do not strongly influence their photophysical properties. In common with such biaryls, most 1,3-diarylated imidazo-[1,5-*a*]pyridines **3** also form distorted π-conjugated systems due to steric repulsion between the hydrogen atoms at the 4- or 7-positions of imidazo[1,5-*a*]pyridines and substituted aromatic

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rings, as suggested by X-ray analyses[7,8] and DFT calculations[9] (Figure 1, left). Our subsequent interest in the substituent effects on the photophysical properties of imidazo[1,5-*a*]pyridines led us to further investigate the formation of undistorted π-conjugated systems with two aryl groups on imidazopyridines (Figure 1). For this purpose, π-conjugated spacers, such as ethynylene and ethenylene groups, have usually been introduced into Ar−Ar moieties.[10]

Meanwhile, straightforward methods for obtaining alkynylated and alkenylated imidazo[1,5-*a*]pyridines have not been well-established. Transition-metal-catalyzed cross-coupling reactions of aryl halides with terminal alkynes (Sonogashira coupling)[11] and alkenes (Mizoroki−Heck reaction)[12] are some of the most versatile methods for introducing alkynyl and alkenyl moieties, respectively, into aromatic compounds. Many reviews regarding these reactions are available. However, there are few examples of the use of electron-rich nitrogen-containing heteroarenes as one or both of the substrates in cross-coupling reactions,[13] since electron-rich heteroaryl metal species, even heteroaryl−transition metal intermediates in these processes, are often unstable and readily undergo protonolysis or decomposition under the reaction conditions.[14] Therefore, further optimization of the reaction conditions is essential if we wish to use these reactions to synthesize alkynyl- and alkenylimidazopyridines. In this report, we describe the synthesis of imidazo[1,5-*a*]pyridines that contain alkynyl or alkenyl groups to establish tunable photofunctional materials by means of Sonogashira coupling and Mizoroki−Heck reaction. The photophysical properties of the resulting imidazo[1,5-*a*]pyridine derivatives were also investigated. During our investigations, we found a linear correlation between the Hammett substituent constants of introduced substituents on arylalkynyl groups and the emission wavelength.

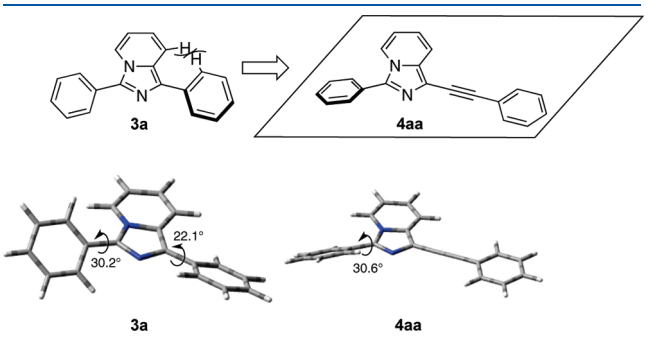


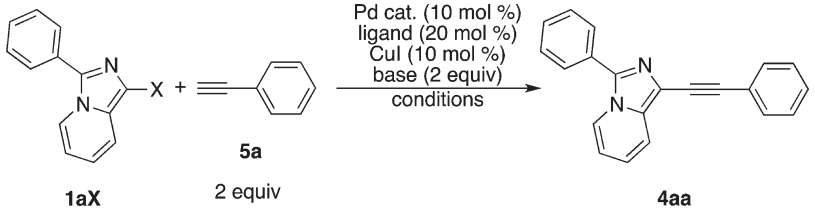
Figure 1. Steric repulsion in **3a** and the planar structure of **4aa** and the optimized structures of **3a** and **4aa** calculated at the B3LYP/6-31G level.

RESULTS AND DISCUSSION

Synthesis of 1-Alkynylated Imidazo[1,5-*a*]pyridines by Sonogashira Coupling Reaction. The results of the initial screening of the reaction conditions for the Sonogashira coupling of halogenated imidazopyridines **1a** and phenylacetylene **5a** are shown in Table 1. The reaction of 1-bromo-3-phenylimidazo[1,5-*a*]pyridine **1aBr** with phenylacetylene (**5a**) (2 equiv), $HN(i\text{-}Pr)_2$ (2 equiv) and a catalytic amount of $Pd(PPh_3)_2Cl_2$ (10 mol %) and CuI (10 mol %) in dioxane did not give any products at all (entry 1).[15] The use of $P(t\text{-}Bu)_3$ as a ligand, which effectively facilitated the Suzuki−Miyaura coupling reaction of a series of imidazopyridyl halides, perhaps due to acceleration of the oxidative addition of such electron-rich halides, was not effective (entry 2).[7b] The desired alkynylated product **4aa** was obtained when $Pd(PPh_3)_4$ was used as a catalyst (entry 3), and the use of acetonitrile as a solvent slightly improved the yield of **4aa** (entry 4). The reaction of **1aI** with $Pd(PPh_3)_2Cl_2$ as a catalyst in Et_3N gave **4aa** in better yield (entry 5), and thus we chose these reaction conditions for further investigations.

The scope of suitable substrates in the Sonogashira coupling of **1** was then examined. The results are summarized in Table 2. The reaction tolerated a variety of substituents on the terminal alkynes, such as 4-methoxyphenyl (PMP) (**5b**), 4-trifluoromethylphenyl (**5c**), 2-pyridyl (**5d**), 1-naphthyl (**5e**), silyl (**5f** and **5g**), alkenyl (**5h**), and alkyl (**5i**) groups, to give the coupling products in moderate to high yields (entries 1−9). In addition, a prolonged reaction time improved the yield of the products in some of the reactions (e.g., entry 5). The reaction of electron-donating 4-methoxyphenyl substituted iodoimidazo[1,5-*a*]pyridines **1bI** and terminal alkynes **5** gave the corresponding products **4b** in good yields (entries 10−14). The reaction also proceeded with the use of electron-deficient substrates such as trifluoromethylphenyl- (**1cI**) and fluorophenyl- (**1dI**) imidazopyridines (entries 15−22). The coupling

Table 1. Optimization of the Sonogashira Coupling of 1a and 5a



entry	X	cat.	ligand	base	conditions	**4aa** yield (%)[a]
1	Br	$Pd(PPh_3)_2Cl_2$	none	$HN(i\text{-}Pr)_2$	dioxane, rt, 17 h	no reaction
2	Br	$Pd(MeCN)_2Cl_2$	$P(t\text{-}Bu)_3 \cdot HBPh_4$	$HN(i\text{-}Pr)_2$	dioxane, rt, 24 h	no reaction
3	Br	$Pd(PPh_3)_4$	none	$EtN(i\text{-}Pr)_2$	dioxane, 60 °C, 20 h	53
4	Br	$Pd(PPh_3)_4$	none	$EtN(i\text{-}Pr)_2$	MeCN, 60 °C, 20 h	60
5	I	$Pd(PPh_3)_2Cl_2$	none	none	Et_3N, 80 °C, 12 h	65[b]

[a] Isolated yield. [b] The reaction was carried out with 1.3 equiv of **5a**.

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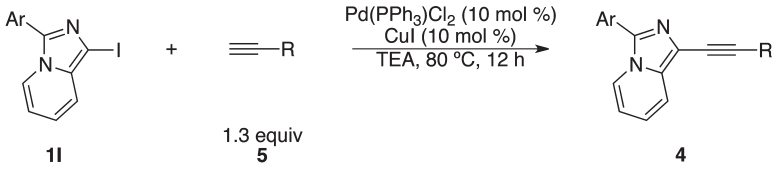
Table 2. Reaction of Various Terminal Alkynes 5 with Halogenated Imidazopyridine Derivatives 1[a]



1l **5** **4**

1: Ar = Ph(**1al**), 4-MeOC$_6$H$_4$(**1bl**), 4-CF$_3$C$_6$H$_4$(**1cl**), 4-FC$_6$H$_4$(**1dl**), 2-pyridyl(**1el**), 2-thienyl(**1fl**)

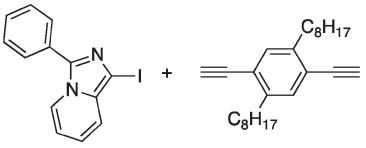
5: R = Ph(**5a**), 4-MeOC$_6$H$_4$(**5b**), 4-CF$_3$C$_6$H$_4$(**5c**), 2-pyridyl(**5d**), 1-naphtyl(**5e**), Me$_3$Si(**5f**), Et$_3$Si(**5g**), 1-cyclohexenyl(**5h**), 1-pentyl(**5i**), 4-FC$_6$H$_4$(**5j**), 4-ClC$_6$H$_4$(**5k**), 4-MeC$_6$H$_4$(**5l**), 4-NMe$_2$C$_6$H$_4$(**5m**), 2-HC(O)C$_6$H$_4$(**5n**), 2-MeOC$_6$H$_4$(**5o**), 2-MeSC$_6$H$_4$(**5p**)

entry	Ar	R	product	yield (%)	entry	Ar	R	product	yield (%)
1	Ph	Ph	**4aa**	65	21	4-FC$_6$H$_4$	2-pyridyl	**4dd**	72
2		PMP	**4ab**	64	22		1-Naph	**4de**	90
3		4-CF$_3$C$_6$H$_4$	**4ac**	99	23	2-pyridyl	Ph	**4ea**	86
4		2-pyridyl	**4ad**	84	24		PMP	**4eb**	84
5		1-Naph	**4ae**	69 (85)[b]	25		4-CF$_3$C$_6$H$_4$	**4ec**	91
6		TMS	**4af**	88	26		2-pyridyl	**4ed**	91
7		TES	**4ag**	80	27		1-naphtyl	**4ef**	59
8		1-cyclohexenyl	**4ah**	73	28		4-FC$_6$H$_4$	**4ej**	99
9		C$_5$H$_{11}$	**4ai**	81	29		4-ClC$_6$H$_4$	**4ek**	99
10	PMP	Ph	**4ba**	79	30		4-MeC$_6$H$_4$	**4el**	99[c]
11		PMP	**4bb**	77	31		4-NMe$_2$C$_6$H$_4$	**4em**	87
12		2-pyridyl	**4bd**	69	32		2-HC(O)C$_6$H$_4$	**4en**	87[d]
13		1-Naph	**4be**	80	33		2-MeOC$_6$H$_4$	**4eo**	63[c]
14		TMS	**4bf**	99	34		2-MeSC$_6$H$_4$	**4ep**	83
15	4-CF$_3$C$_4$H$_4$	Ph	**4ca**	82	35	2-thienyl	Ph	**4fa**	81
16		PMP	**4cb**	74	36		4-CF$_3$C$_6$H$_4$	**4 fc**	76
17		2-pyridyl	**4 cd**	71	37		4-FC$_6$H$_4$	**4fj**	77
18		1-Naph	**4ce**	99	38		4-ClC$_6$H$_4$	**4fk**	73
19	4-FC$_6$H$_4$	Ph	**4da**	99	39		4-MeC$_6$H$_4$	**4fl**	70
20		PMP	**4db**	75					

[a] Isolated yields. [b] The reaction was performed for 14 h. [c] The reaction was performed at 60 °C for 4 h. [d] The reaction was performed at 60 °C for 5 h.

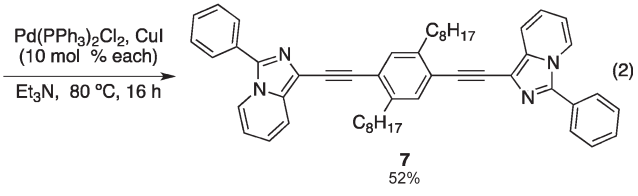
reaction was not disturbed by the use of 2-pyridylimidazopyridine **1eI** as a substrate, which may act as a bidentate ligand for the catalyst and could not be used in Kumada−Tamao−Corriu couplings.[7b] As a result, the reaction of **1eI** and various terminal alkynes **5** took place to give **4** in good to high yields (entries 23−34), even with an arylacetylene bearing a formyl group (**5h**). The coupling reaction of imidazopyridines bearing electron-rich heteroaromatics such as 2-thienylimidazopyridine **1fI** also proceeded to give the corresponding products **4f** in good yields (entries 35−39).

We then focused on the synthesis of bis-imidazo[1,5-*a*]-pyridines linked by a π-conjugated spacer such as benzene- and fluorine-based bis-ethynylene.[16] Under the optimized reaction conditions, the reactions of **1aI** and diethynylbenzene **6** or diethynylfluorene **8** gave the corresponding bis-imidazopyridine **7** and **9** in respective yields of 52% and 48% (eqs 2 and 3). Additionally, the synthesis of direct ethynylene-bridged unsymmetric bis-imidazopyridines, which are expected to form a donor−acceptor system, was carried out as follows (eq 4). First, the treatment of **4af** and **4bf** with tetrabutylammonium fluoride (TBAF) in THF at room temperature led to the desilylated products **10a** and **10b** in respective yields of 74% and 88%. Next, **10a** and **10b** were treated with iodoimidazopyridine **1cI** in the presence of a catalytic amount of Pd(PPh$_3$)$_2$Cl$_2$ and CuI in Et$_3$N at 80 °C for 16 h to give the unsymmetric bis-imidazopyridines **11a** and **11b** in moderate yields.



1aI **6**

2.2 equiv



7

52%

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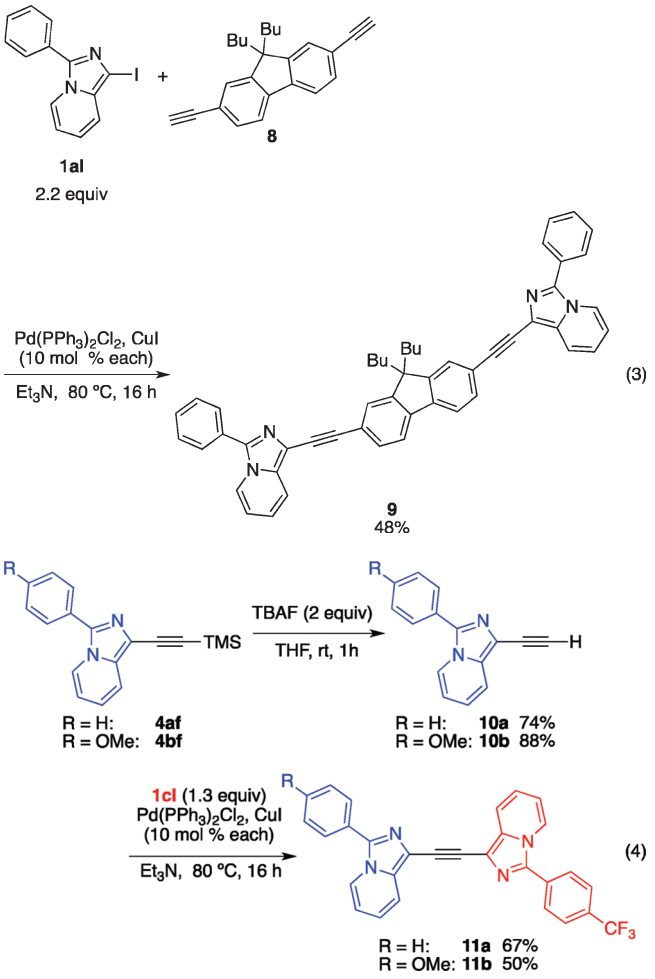
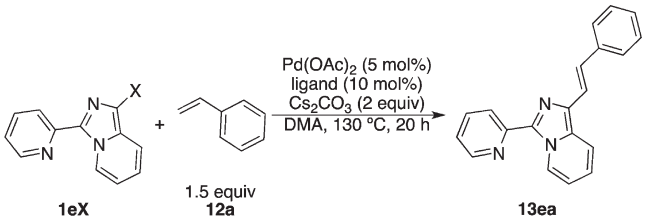
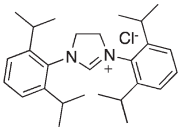
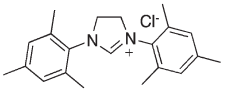


Synthesis of 1-Alkenylated Imidazo[1,5-*a*]pyridines by the Mizoroki−Heck Reaction. To introduce arylalkenyl groups into imidazopyridines, the Mizoroki−Heck reaction of **1** and terminal alkene **12** was examined. The optimization of the reaction conditions is displayed in Table 3. The reaction of **1eBr** with styrene **12a**, Cs_2CO_3, and a catalytic amount of $Pd(OAc)_2$ in DMA at 100 °C for 20 h did not give the product at all (entry 1).[12] In contrast, the reaction took place with the use of **1eI** instead of bromide **1eBr** and PPh_3 as a ligand to give the product **13ea** in 56% yield (entry 2). The use of an electron-rich ligand such as P(*t*-Bu)$_3$ improved the yield of **13ea** (entry 3). Use of the *N*-heterocyclic carbene (NHC) precursor IPr·HCl (**14a**) also promoted the reaction, but the yield was moderate (entry 4),[17] whereas the precursor bearing mesityl groups IMes·HCl (**14b**) served as a suitable ligand for the reaction and gave the corresponding product **13ea** in high yield (entry 5).

With the conditions in hand, the reactions of iodinated imidazo[1,5-*a*]pyridines **1I** and a series of styrene derivatives **12** were carried out. The results are listed in Table 4. The reaction of 3-phenyl-1-iodoimidazo[1,5-*a*]pyridine and styrene derivatives (**12a** and **12b**) under the optimized conditions gave the alkenylated products **13aa** and **13ac** in respective yields of 55% and 54%. The reaction of electron-rich heteroaryl iodide **1bI** and **12a** gave the corresponding product **13ba** in moderate yield. Meanwhile, the treatment of both iodoimidazopyridines bearing electron-deficient groups **1cI** and a heteroarene **1eI** with **12a** afforded the coupling products **13ca** and **13ea** in good yields.

Table 3. Optimization of the Mizoroki−Heck Reaction with 1 and 12



entry	X	ligand	yield (%)[a]
1[b]	Br	none	N. R.
2	I	PPh_3[c]	56
3	I	P(*t*-Bu)$_3$•HBPh$_4$	76
4	I	 **14a**(IPr·HCl)	58
5	I	 **14b**(IMes·HCl)	85

[a] Isolated yield. [b] The reaction was carried out with 2 equiv of styrene. [c] The reaction was carried out with 20 mol % of PPh_3.

Photophysical Properties of Imidazo[1,5-*a*]pyridine Derivatives. UV−vis and fluorescence spectra of the obtained imidazopyridine derivatives were measured. Selected results are listed in Table 5.[18] The photophysical properties of the alkynylated imidazo[1,5-*a*]pyridines indicated that the arylalkynyl groups clearly influence the absorption and emission maxima (λ_{abs} and λ_{em}) and fluorescence quantum yields (entries 3−21). As expected, in a series of 3-phenylimidazopyridines such as **14a**, **3a**, and **4aa**, the longest λ_{abs} values of 1-phenylethynyl-3-phenylimidazopyridine **4aa** were red-shifted (**14a** 317 nm, **3a** 388 nm vs **4aa** 397 nm, entries 1 and 2 vs 3), since the formation of the extended planar π-conjugated system leads to a smaller HOMO−LUMO band gap. The absorption and emission of alkenylated imidazopyridine **13aa** were also significantly red-shifted (λ_{abs} 425 nm, λ_{em} 536 nm) compared to those of the parent **14a** and **3a** (entry 26). To understand this observation, DFT and TDDFT calculations were performed for a series of imidazopyridines at the B3LYP level with a 6-311++G(d,p) basis set. As a result, the HOMO−LUMO band gaps narrowed and the predicted absorption wavelength increased in the order **14a**, **3a**, **4aa**, and **13aa** (Figure 2, left).[19] These results are consistent with the experimental observations. Aryl groups at the C3 position of **4** had less of an effect on their absorptions, emissions, and quantum yields (entries 3, and 6—9) as in **14** and **3**. In contrast, the electronic properties of the substituents on the arylalkynyl groups of **4** clearly influence their photophysical properties. For instance, 2-pyridylimidazopyridines **4e** bearing electron-rich alkynes show red-shifted emissions based on **4ea** (entries 9 vs 10, 14 and 15). On the other hand, electron-poor alkynes show blue-shifted emissions (entries 9 vs 11, 12, and 13).

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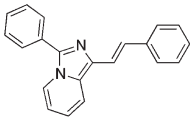
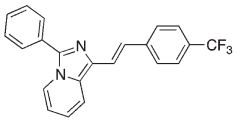
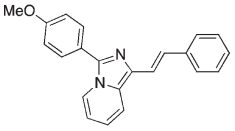
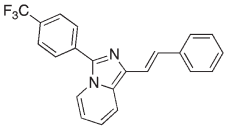
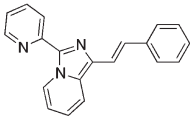
Table 4. Reactions of Various Styrenes 12 and Imidazopyridine Derivatives 1

entry	product	yield (%)[a]
1		**13aa**: 55
2		**13ac**: 54
3		**13ba**: 54
4		**13ca**: 90
5		**13ea**: 85

[a] Isolated yield.

Dramatically red-shifted emission was observed with imidazopyridines bearing a 2-formyl-phenylethynyl group **4en** (560 nm, entry 16). During our investigation of the electronic influences of the alkynyl substituents at the 1-position, we found that the λ_{em} values of 3-phenylimidazopyridine derivatives **4a** have a linear correlation with the Hammett substituent constants of the substituents on the arylalkynyl group, as shown in Figure 3.[20] Similar correlations were also found with 3-(2-pyridyl)- **4e** and 3-(2-thienyl)imidazopyridine **4f** derivatives. In contrast, 1,3-diarylated imidazopyridines **3** likely showed no trend in the emission wavelength (Figure 3, lower right).[21] These observations imply that the electronic influence of the substituents on arylalkynyl groups directly affected the imidazopyridine ring of **4** via an undistorted planar π-conjugated system, which efficiently resulted in a linear correlation between emission and the substituent constants.[22] Futhermore, the photophysical properties such as absorption and emission behaviors are consistent with the results regarding HOMO−LUMO gaps calculated by DFT calculations and the absorption behaviors predicted by TDDFT calculations, which should also be related to emission behavior (e.g., Figure 2, right).[24] Meanwhile, most of the peak tops of the longest UV−vis absorptions of alkynylated imidazopyridines **4** were indistinct, since the peaks are immersed in adjacent larger absorptions, and this is probably why the series of alkynylated imidazopyridines **4** did not show an ordered correlation between the observed longest UV−vis absorptions and the substituents (e.g., Figure S2 in Supporting Information).

Imidazopyridine dimers bearing benzene- and fluorene-based spacers **7** and **9** had a similar λ_{em} as **4aa**, while stronger UV absorption and slightly improved Φ_F were observed (entries 3 vs 22 and 23). Ethynylene-bridged dimers **11a** and **11b** show a similar UV absorption wavelength (329 and 330 nm) but a red-shifted fluorescent emission wavelength (501 and 506 nm) compared with **4aa** (entries 3 vs 24 and 25).

CONCLUSION

In conclusion, we have synthesized 1-alkynyl- and 1-alkenylimidazo[1,5-*a*]pyridines by means of Sonogashira coupling and Mizoroki−Heck reaction and investigated their photophysical properties. All of the imidazopyridine derivatives obtained exhibited fluorescence in solution. The fluorescence maxima and fluorescence quantum yields of the alkynylated products were 458−560 nm and Φ_F = 0.08−0.26 in chloroform solution. Furthermore, the fluorescence maxima and fluorescence quantum yields of the alkenylated imidazopyridines were 479−537 nm and Φ_F = 0.03−0.13, respectively. The alkynylated imidazopyridines **4** obtained show linear correlations between the Hammett substituent constants of the substituents on the arylalkynyl group and their fluorescence wavelength. On the basis of this predictable property, a series of alkynylated imidazopyridines may have potential as tunable fluorescent materials. Further investigations of the properties and applications of imidazo[1,5-*a*]pyridine derivatives are underway.

EXPERIMENTAL SECTION

General. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded in $CDCl_3$. Chemical shifts of ^{1}H and ^{13}C were reported in δ values referenced to tetramethylsilane and $CDCl_3$ as internal standards, respectively. The ^{19}F chemical shifts are expressed in δ values deshielded with respect to CF_3COOH as an external standard. The mass spectra (MS) and high resolution mass spectra (HRMS) were obtained by ionizing samples via electron ionization (70 eV).

Materials. Unless otherwise noted, reagents were obtained commercially and used without purification. Terminal alkynes **5k**,[25] **5l**,[26] **8**,[27] and imidazo[1,5-*a*]pyridine derivatives **1**[7b] were prepared according to the literature. Compound **6** was prepared according to a modified procedure in the literature.[27] Silica gel 60N (spherical, neutral, 40−50 mm) from Kanto Chemical Co., Inc. was used in flash column chromatography.

Synthesis of 1-Iodoimidazo[1,5-*a*]pyridine (1).

1-Iodo-3-(2-thienyl)imidazo[1,5-*a*]pyridine (1fl). To a solution of 3-(2-thienyl)imidazo[1,5-*a*]pyridine (0.30 g, 1.5 mmol) in THF (3 mL) was added iodine (0.42 g, 1.7 mmol, 1.1 equiv) at room temperature under an Ar atmosphere. The resulting mixture was stirred

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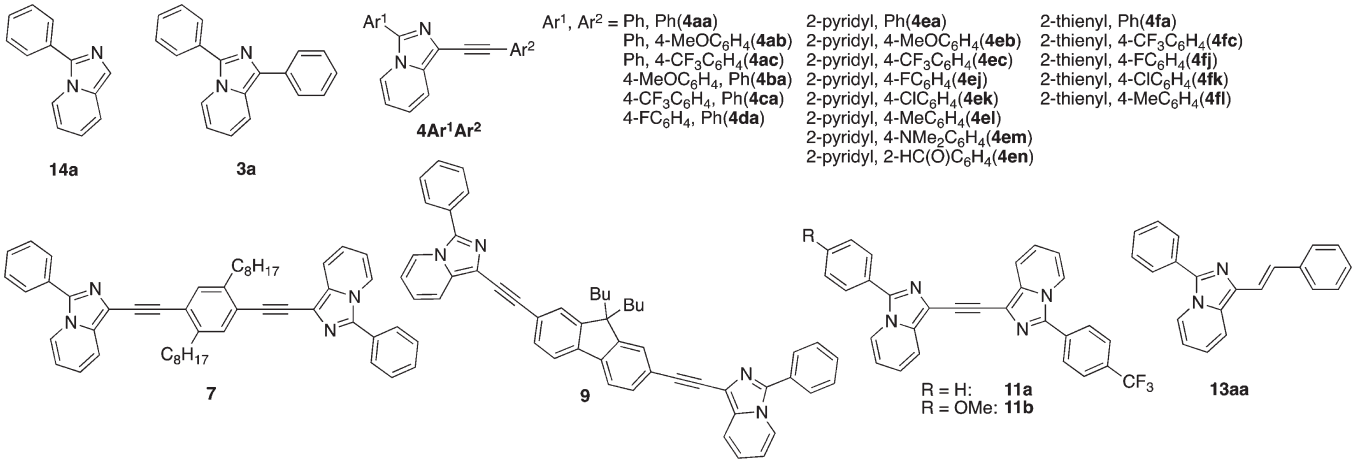
Table 5. Selected Photophysical Properties of the Obtained Imidazo[1,5-*a*]pyridines

		UV−vis[a]		fluorescence[a]				UV−vis[a]		fluorescence[a]	
entry		λ_{abs} (nm)	log ε	λ_{em} (nm)	Φ_F[b]	entry		λ_{abs} (nm)	log ε	λ_{em} (nm)	Φ_F[b]
1	**14a**	317	4.25	461	0.07	14	**4el**	407	4.01	460	0.19
								370	4.42		
								332	4.42		
2	**3a**	388	3.45	477	0.16	15	**4em**	410	4.09	476	0.07
		345	3.88					379	4.37		
		306	4.14					339	4.43		
3	**4aa**	397	3.78	478	0.23	16	**4en**	420	4.20	560	0.20
		333	4.41					398	4.30		
		320	4.40					371	4.40		
								287	3.43		
4	**4ab**	387	3.91	485	0.23	17	**4fa**	405	3.91	490	0.06
		331	4.56					369	4.30		
		315	4.60					337	4.50		
5	**4ac**	416	3.70	465	0.21	18	**4 fc**	399	4.16	483	0.08
		373	4.26					363	4.44		
		344	4.49					348	4.52		
6	**4ba**	398	3.81	488	0.20	19	**4fj**	399	3.97	489	0.07
		335	4.43					370	4.29		
		321	4.45					333	4.43		
7	**4ca**	411	3.50	473	0.16	20	**4fk**	397	3.96	487	0.07
		355	4.32					343	4.41		
		330	4.43								
		317	4.36								
8	**4da**	377	3.93	478	0.25	21	**4fl**	402	3.74	493	0.08
		332	4.40								
		318	4.41					371	4.05		
								335	4.28		
9	**4ea**	410	3.93	459	0.15	22	**7**	405	4.62	479	0.26
		368	4.55					342	4.64		
		331	4.36								
10	**4eb**	410	3.88	464	0.15	23	**9**	409	4.80	476	0.26
		370	4.44								
		330	4.36					379	4.77		
11	**4ec**	410	4.18	447	0.19	24	**11a**	407	4.21	501	0.15
		387	4.52					329	4.45		
		369	4.60					318	4.42		
								295	4.34		
12	**4ej**	409	3.90	458	0.19	25	**11b**	405	4.19	506	0.16
		367	4.48					330	4.45		
		330	4.48					318	4.45		
								298	4.40		
13	**4ek**	410	4.04	455	0.07	26	**13aa**	425	3.73	536	0.03
		389	4.42					346	4.42		
		367	4.53								
		336	4.47								

[a] Measured in $CHCl_3$ (10^{-5} M). [b] Quantum yields (Φ_F) were determined with reference to quinine sulfate in 0.1 M aqueous sulfuric acid (excited at 350 nm).



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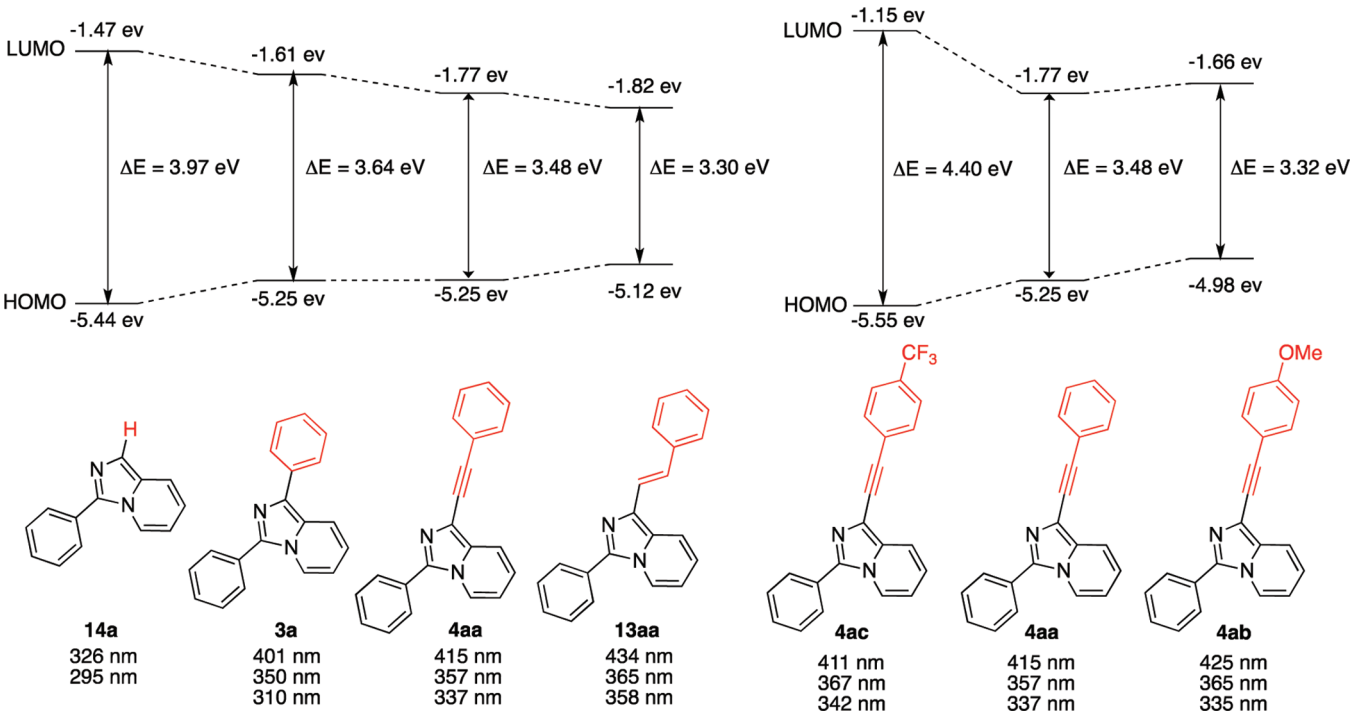

Figure 2. Energy levels of the HOMO and LUMO and the absorption wavelength predicted by TDDFT calculations of compounds **14a**, **3a**, **4**, and **13aa** at the B3LYP/6-311++G(d,p) level.

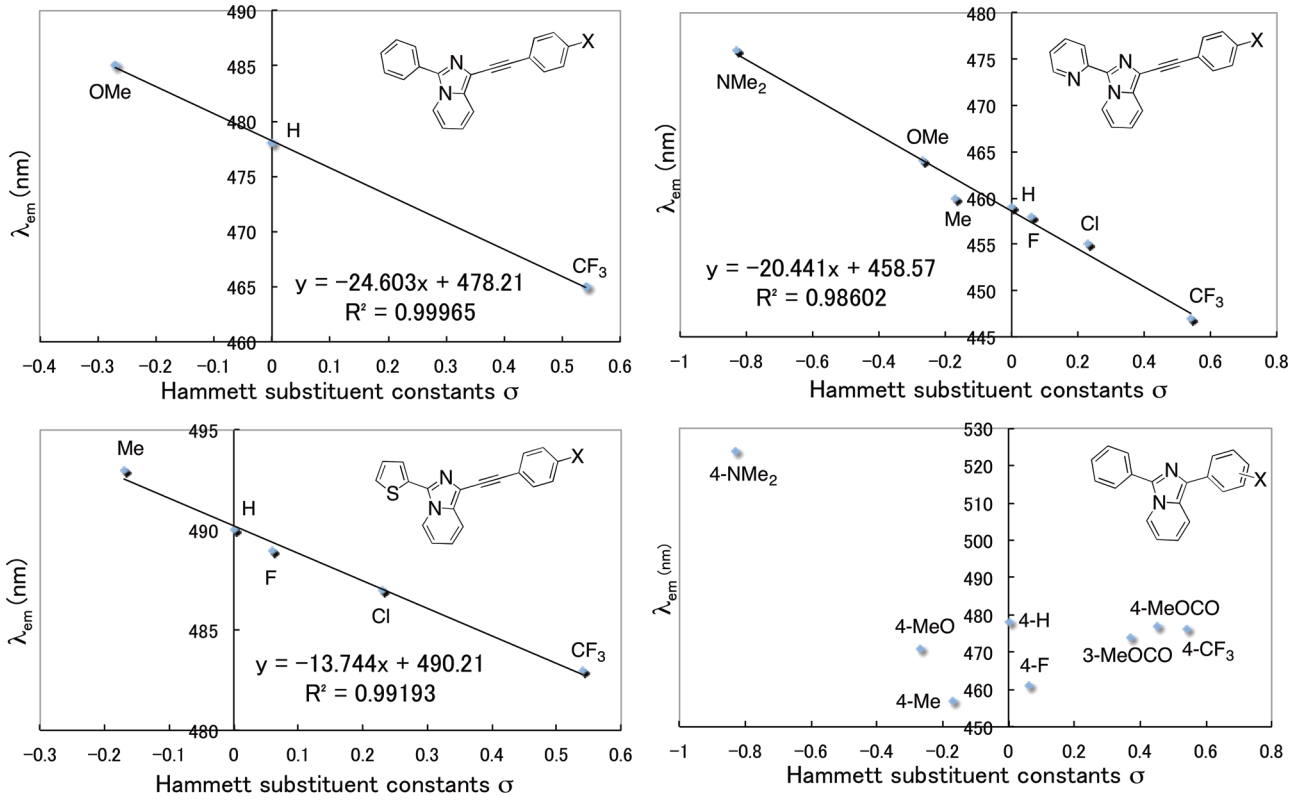

Figure 3. Correlations between λ_{em} and Hammett substituent constants[23] of **4a**, **4e**, **4f**, and **3a**.

at 40 °C for 15 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ aq, neutralized with $NaHCO_3$ aq, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash

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column chromatography on silica gel (*n*-hexane/EtOAc = 4:1) to give 1-iodo-3-(2-thienyl)imidazo[1,5-*a*]pyridine (0.25 g, 52%) as a yellow solid. Mp 104−105 °C, R_f = 0.43 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3096, 2916, 1738, 1628, 1498, 1401, 1359, 1262 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.67 (dd, J = 7.3, 6.8 Hz, 1H), 6.80 (dd, J = 8.8, 6.8 Hz, 1H), 7.16 (dd, J = 4.9, 3.4 Hz, 1H), 7.34 (d, J = 9.3 Hz, 1H), 7.41 (d, J = 4.9 Hz, 1H), 7.48 (d, J = 3.4 Hz, 1H), 8.26 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 74.3, 114.5, 118.9, 120.2, 122.1, 125.3, 126.4, 127.6, 131.1, 133.5, 135.1. MS (EI) *m*/*z* 326 (M^+); HRMS (EI) calcd for $C_{11}H_7IN_2S$ (M^+) 325.9375, found 325.9371.

General Procedure for Sonogashira Coupling of 1 and 5. Into an oven-dried screw-capped reaction tube were placed $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (10 mol %), 1-iodo-3-arylimidazo[1,5-*a*]pyridine **1** (0.25 mmol), terminal alkyne **5** (1.3 equiv) and triethylamine (1 mL). The reaction tube was flushed with Ar, and the resulting solution was then heated at 80 °C and stirred for the reaction period. The mixture was cooled at room temperature and purified by flash column chromatography on silica gel (*n*-hexane/EtOAc) to give the coupling product **4**.

1-Phenylethynyl-3-phenylimidazo[1,5-*a*]pyridine (4aa). Yellow solid. Mp 156−158 °C, R_f = 0.35 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2203, 1597, 1522, 1487, 1352, 1212, 1126, 756, 693 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.59 (dd, J = 7.2, 6.3 Hz, 1H), 6.83 (dd, J = 8.8, 6.3 Hz, 1H), 7.24−7.30 (m, 3H), 7.37−7.48 (m, 3H), 7.53 (d, J = 7.1 Hz, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 8.21 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.7, 92.7, 114.1, 115.0, 118.9, 120.8, 122.1, 123.6, 127.9, 128.2, 128.3, 129.1, 129.2, 129.6, 131.4, 134.3, 138.4. MS (EI) *m*/*z* 294 (M^+); HRMS (EI) calcd for $C_{21}H_{14}N_2$ (M^+) 294.1157, found 294.1158.

1-(4-Methoxyphenyl)ethynyl-3-phenylimidazo[1,5-*a*]pyridine (4ab). Yellow solid. Mp 129−130 °C, R_f = 0.25 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2834, 2359, 2203, 1602, 1521, 1502, 1439, 1245, 1171, 1125, 836, 746, 694 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H), 6.63 (dd, J = 7.3, 6.3 Hz, 1H), 6.86 (dd, J = 9.3, 6.3 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.43−7.55 (m, 5H), 7.69 (d, J = 9.3 Hz, 1H), 7.82 (d, J = 6.8 Hz, 2H), 8.26 (dd, J = 7.3 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ 55.5, 81.4, 92.8, 114.3, 115.6, 116.0, 119.2, 120.8, 122.3, 128.5, 129.3 (two carbon atoms were overlapped), 129.4, 129.9, 133.2, 134.3, 138.5, 159.8. MS (EI) *m*/*z* 324 (M^+); HRMS (EI) calcd for $C_{22}H_{16}N_2O$ (M^+) 324.1263, found 324.1263.

1-(4-Trifluoromethylphenyl)ethynyl-3-phenylimidazo-[1,5-*a*]pyridine (4ac). Yellow solid. Mp 187−189 °C, R_f = 0.50 (*n*-hexane/EtOAc = 1:1); IR (KBr) 2976, 2960, 2201, 1609, 1562, 1325 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.67 (dd, J = 7.3, 6.3 Hz, 1H), 6.92 (dd, J = 9.0, 6.3 Hz, 1H), 7.47 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.3 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.67−7.71 (m, 3H), 7.81 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 85.5, 91.6, 114.2, 118.6, 121.4, 122.2, 124.0 (q, J_{C-F} = 272.1 Hz), 125.2 (q, J_{C-F} = 3.3 Hz), 127.5, 128.2, 129.1, 129.3, 129.4 (q, J_{C-F} = 33.3 Hz), 131.3, 133.6, 133.8, 134.9, 138.7. ^{19}F NMR ($CDCl_3$) δ −63.0. MS (EI) *m*/*z* 362 (M^+). HRMS (EI) calcd for $C_{22}H_{22}F_3N_2$ (M^+) 362.1031, found 362.1028.

1-(2-Pyridyl)ethynyl-3-phenylimidazo[1,5-*a*]pyridine (4ad). Yellow solid. Mp 132−134 °C, R_f = 0.22 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2359, 2341, 2202, 1580, 1558, 1508, 1465, 1428, 1350, 1126, 1068, 775, 695 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.60 (dd, J = 7.8, 7.3 Hz, 1H), 6.93 (dd, J = 9.3, 7.3 Hz, 1H), 7.21 (dd, J = 7.8, 4.9 Hz, 1H), 7.44−7.69 (m, 5H), 7.80−7.83 (m, 3H), 8.29 (d, J = 7.3 Hz, 1H), 8.60 (d, J = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 83.2, 92.3, 113.5, 113.9, 118.6, 121.2, 121.8, 121.9, 126.7, 127.9, 128.1, 128.7, 128.9, 135.0, 135.8, 136.4, 143.5, 149.5. MS (EI) *m*/*z* 295 (M^+); HRMS (EI) calcd for $C_{20}H_{13}N_3$ (M^+) 295.1109, found 295.1104.

1-(1-Naphthyl)ethynyl-3-phenyl-imidazo[1,5-*a*]pyridine (4ae). Yellow solid. Mp 129−130.5 °C, R_f = 0.30 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2359, 2341, 1558, 1506, 1457, 1247, 1029, 803, 743, 689 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.65 (dd, J = 7.2, 6.8 Hz, 1H), 6.92 (dd, J = 8.8, 6.8 Hz, 1H), 7.44−7.62 (m, 6H), 7.77−7.87 (m, 6H), 8.26 (d, J = 7.3 Hz, 1H), 8.58 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 87.6, 90.9, 114.1, 115.1, 118.8, 121.0, 121.3, 122.1, 125.4, 126.4, 126.5, 126.7, 128.3, 128.3, 129.1, 129.2, 129.5, 130.1, 132.1, 133.0, 133.2, 134.5, 138.5. MS (EI) *m*/*z* 344 (M^+); HRMS (EI) calcd for $C_{25}H_{16}N_2$ (M^+) 344.1313, found 344.1321.

1-(Trimethylsilyl)ethynyl-3-phenylimidazo[1,5-*a*]pyridine (4af). Brown oil. R_f = 0.50 (*n*-hexane/EtOAc = 4:1); IR (neat) 2943, 2863, 2145, 1604, 1510, 1461, 1407, 1353, 1317, 1129, 1075, 997, 694 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.29 (s, 9H), 6.63 (dd, J = 7.3, 6.8 Hz, 1H), 6.67 (dd, J = 9.3, 6.8 Hz, 1H), 7.44−7.53 (m, 3H), 7.63 (d, J = 9.3 Hz, 1H), 7.79 (d, J = 7.3 Hz, 2H), 8.24 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ −0.03, 97.8, 97.9, 114.0, 114.9, 118.8, 120.9, 122.0, 128.2, 129.0, 129.1, 129.5, 134.8, 138.0. MS (EI) *m*/*z* 290 (M^+); HRMS (EI) calcd for $C_{18}H_{18}N_2Si$ (M^+) 290.1239, found 290.1246.

1-(Triethylsilyl)ethynyl-3-phenylimidazo[1,5-*a*]pyridine (4ag). Brown oil. R_f = 0.50 (*n*-hexane/EtOAc = 4:1); IR (neat) 2957, 2360, 2145, 1629, 1518, 1350, 1246, 1126, 1073, 843, 748 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.11 (s, 15H), 6.63 (dd, J = 7.8, 6.3 Hz, 1H), 6.87 (dd, J = 9.3, 6.3 Hz, 1H), 7.45−7.53 (m, 3H), 7.61 (d, J = 9.3 Hz, 1H), 7.78 (d, J = 7.3 Hz, 2H), 8.23 (d, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 11.3, 18.7, 94.1, 99.6, 113.9, 115.3, 118.8, 120.8, 121.9, 128.3, 128.9, 129.1, 129.5, 135.2, 137.8. MS (EI) *m*/*z* 332 (M^+); HRMS (EI) calcd for $C_{21}H_{24}N_2Si$ (M^+) 332.1709, found 332.1716.

1(1-Cyclohexyenyl)ethynyl-3-phenylimidazo[1,5-*a*]pyridine (4ah). Brown oil. R_f = 0.55 (*n*-hexane/EtOAc = 4:1); IR (neat) 2927, 2362, 2169, 1633, 1509, 1445, 1354, 1301, 1172, 1124, 1075, 951, 916, 771, 728, 695 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.60−1.72 (m, 4H), 2.13−2.19 (m, 2H), 2.27−2.32 (m, 2H), 6.26 (tt, J = 4.2, 2.0 Hz, 1H), 6.60 (dd, J = 7.3, 6.3 Hz, 1H), 6.82 (dd, J = 9.0, 6.3 Hz, 1H), 7.4−7.53 (m, 3H), 7.61 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 7.1 Hz, 2H), 8.23 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.5, 22.3, 25.7, 29.2, 79.6, 94.4, 113.8, 115.4, 118.8, 120.2, 120.8, 121.8, 128.1, 128.9, 128,9, 129.5, 133.7, 134.4, 138.0. MS (EI) *m*/*z* 298 (M^+); HRMS (EI) calcd for $C_{21}H_{18}N_2$ (M^+) 298.1470, found 298.1483.

1-(1-Heptynyl)-3-phenylimidazo[1,5-*a*]pyridine (4ai). Brown oil. R_f = 0.90 (*n*-hexane/EtOAc = 4:1); IR (neat) 3065, 2932, 2858, 2361, 2329, 1602, 1461, 1358, 1300, 1189, 957, 773, 745, 696 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 1.36 (quint, J = 6.8 Hz, 2H), 1.48 (tq, J = 7.3, 6.8 Hz, 2H), 1.66 (quint, J = 6.8 Hz, 2H), 2.51 (t, J = 6.8 Hz, 2H), 6.59 (d, J = 7.3, 6.3 Hz, 1H), 6.80 (d, J = 8.3, 6.3 Hz, 1H), 7.1−7.52 (m, 3H), 7.59 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 19.7, 22.2, 28.5, 31.1, 73.1, 93.6, 113.7, 115.7, 118.8, 119.9, 121.7, 128.1, 128.8, 128.9, 129.6, 133.5, 137.5. MS (EI) *m*/*z* 288 (M^+); HRMS (EI) calcd for $C_{20}H_{20}N_2$ (M^+) 288.1626, found 288.1622.

1-Phenylethynyl-3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (4ba). Yellow solid. Mp 181−182 °C, R_f = 0.40 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2360, 2199, 1607, 1528, 1510, 1486, 1464, 1257, 1182, 1020, 835, 744, 688 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.60 (dd, J = 7.3, 6.3 Hz, 1H), 6.84 (dd, J = 8.3, 6.3 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 7.30−7.37 (m, 3H), 7.59 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 8.3 Hz, 1H), 7.73 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.3, 82.8, 92.6, 113.8, 114.4, 114.5, 118.7, 120.5, 121.9, 122.0, 123.6, 127.8, 128.3, 129.6, 131.3, 134.1, 138.4, 160.0. MS (EI) *m*/*z* 324 (M^+); HRMS (EI) calcd for $C_{22}H_{16}N_2O$ (M^+) 324.1263, found 324.1264.

1-(4-Methoxyphenyl)ethynyl-3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (4bb). Yellow solid. Mp 177−178 °C, R_f = 0.15 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2833, 2360, 2201, 1603, 1528, 1503, 1461, 1351, 1288, 1245, 1181, 1105, 835 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 3.86 (s, 3H), 6.59 (dd, J = 7.3, 6.8 Hz, 1H), 6.81 (dd, J = 9.3, 6.8 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 9.3 Hz, 1H), 7.73 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.2, 55.3, 81.3, 92.4, 113.7,

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113.9, 114.4, 114.8, 115.8, 118.8, 120.2, 121.9, 122.0, 129.6, 132.8, 133.7, 138.2, 159.4, 160.2. MS (EI) *m*/*z* 354 (M^+); HRMS (EI) calcd for $C_{23}H_{18}N_2O_2$ (M^+) 354.1368, found 354.1366.

1-(2-Pyridyl)ethynyl-3-(4-methoxyphenyl)imidazo[1,5-*a*]-pyridine (4bd). Yellow solid. Mp 166−167 °C, R_f = 0.10 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2975, 2360, 2199, 1608, 1580, 1529, 1509, 1462, 1255, 1182, 1143, 1021, 839, 778, 742 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H), 6.61 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.86 (dd, *J* = 9.0, 6.3 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 7.8, 4.9 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.63 (dd, *J* = 7.8, 7.0 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 1H), 8.17 (d, *J* = 7.0 Hz, 1H), 8.60 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.3, 83.3, 92.3, 113.4, 113.9, 114.3, 118.8, 121.2, 121.6, 122.0, 122.1, 126.8, 129.6, 135.0, 136.0, 138.6, 143.8, 149.7, 160.2. MS (EI) *m*/*z* 325 (M^+); HRMS (EI) calcd for $C_{21}H_{15}N_3O$ (M^+) 325.1215, found 325.1222.

1-(1-Naphthyl)ethynyl-3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (4be). Yellow solid. Mp 163−164 °C, R_f = 0.35 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2360, 2199, 1608, 1576, 1558, 1539, 1458, 1353, 1311, 1244, 1171, 1033, 797, 774, 743 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H), 6.64 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.89 (dd, *J* = 9.0, 6.3 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.47 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.54 (dd, *J* = 8.1, 6.8 Hz, 1H), 7.60 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.75−7.78 (m, 3H), 7.81−7.85 (m, 2H), 7.87 (dd, *J* = 7.3, 6.3 Hz, 1H), 8.20 (d, *J* = 7.3 Hz, 1H), 8.59 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.3, 87.8, 90.8, 113.9, 114.4, 114.7 (two carbon atoms were overlapped), 118.8, 120.8, 121.3, 121.9, 122.1, 125.4, 126.4, 126.5, 126.7, 128.2, 129.7, 130.0, 133.0, 133.2, 134.3, 138.6, 160.3. MS (EI) *m*/*z* 374 (M^+); HRMS (EI) calcd for $C_{26}H_{18}N_2O$ (M^+) 374.1419, found 374.1416.

1-(Trimethylsilyl)ethynyl-3-phenylimidazo[1,5-*a*]pyridine (4bf). Brown oil. R_f = 0.30 (*n*-hexane/EtOAc = 4:1); IR (neat) 2957, 2898, 2836, 3243, 1611, 1249, 839 cm^{-1}. ^1H NMR ($CDCl_3$) δ −0.27 (s, 9H), 3.87 (s, 3H), 6.62 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.85 (dd, *J* = 9.3, 6.3 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 8.17 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ −0.01, 55.3, 97.7, 97.8, 113.8, 114.4, 114.5, 118.8, 120.6, 121.9, 122.0, 129.7, 134.6, 138.1, 160.3. MS (EI) *m*/*z* 320 (M^+); HRMS (EI) calcd for $C_{16}H_{12}N_2O$ (M^+) 320.1345, found 320.1342.

1-Phenylethynyl-3-(4-trifluoromethylphenyl)imidazo[1,5-*a*]-pyridine (4ca). Yellow solid. Mp 157−159 °C, R_f = 0.40 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3087, 2925, 2360, 2206, 1616, 1517, 1486, 1410, 1330, 1172, 1126, 1107, 1070, 856, 758, 745, 692 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.72 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.93 (dd, *J* = 9.3, 6.8 Hz, 1H), 7.33−7.39 (m, 3H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 9.3 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 8.29 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.1, 92.8, 114.7, 119.0, 121.3, 121.7, 123.3, 123.5 (q, J_{C-F} = 272.1 Hz), 126.0 (q, J_{C-F} = 3.3 Hz), 128.2, 128.4, 128.6, 130.7 (q, J_{C-F} = 33.1 Hz), 130.8, 131.4, 133.0, 134.8, 136.7. ^{19}F NMR ($CDCl_3$) δ −63.1. MS (EI) *m*/*z* 362 (M^+); HRMS (EI) calcd for $C_{22}H_{13}F_3N_2$ (M^+) 362.1031, found 362.1035.

1-(4-Methoxyphenyl)ethynyl-3-(4-trifluoromethylphenyl)-imidazo[1,5-*a*]pyridine (4cb). Yellow solid. Mp 163−164 °C, R_f = 0.20 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2360, 1604, 1519, 1504, 1464, 1411, 1326, 1288, 1250, 1172, 1131, 1106, 1066, 1029, 854 835 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.69 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.90- 6.92 (m, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 9.3 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 8.27 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.2, 80.7, 92.8, 114.0, 114.7, 115.4, 118.1, 119.0, 121.0, 121.7, 123.8 (q, J_{C-F} = 272.1 Hz), 125.9 (q, J_{C-F} = 4.4 Hz), 128.1, 130.5 (q, J_{C-F} = 32.6 Hz), 132.9, 133.0, 134.4, 136.4, 159.6. ^{19}F NMR ($CDCl_3$) δ −63.0. MS (EI) *m*/*z* 392 (M^+); HRMS (EI) calcd for $C_{23}H_{15}F_3N_2O$ (M^+) 392.1136, found 392.1130.

1-(2-Pyridyl)ethynyl-3-(4-trifluoromethylphenyl)imidazo-[1,5-*a*]pyridine (4cd). Yellow solid. Mp 129−130 °C, R_f = 0.35 (*n*-hexaneEtOAc = 4:1); IR (KBr) 2360, 2341, 2199, 1616, 1582, 1514, 1411, 1324, 1159, 1123, 1066, 924, 851 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.76 (dd, *J* = 7.8, 6.8 Hz, 1H), 6.97 (dd, *J* = 9.3, 6.8 Hz, 1H), 7.23 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 9.3 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 8.31 (d, *J* = 7.3 Hz, 1H), 8.64 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.5, 92.5, 114.7, 114.9, 119.0, 121.9, 121.9, 122.4, 123.6 (q, J_{C-F} = 272.1 Hz), 126.0 (q, J_{C-F} = 4.4 Hz), 127.0, 128.2, 130.8 (q, J_{C-F} = 33.0 Hz), 132.8, 135.7, 136.1, 137.0, 143.6, 150.0. ^{19}F NMR ($CDCl_3$) δ −63.1. MS (EI) *m*/*z* 363 (M^+); HRMS (EI) calcd for $C_{21}H_{12}F_3N_3$ (M^+) 363.0983, found 363.0968.

1-(1-Naphthyl)ethynyl-3-(4-trifluoromethylphenyl)imidazo[1,5-*a*]pyridine (4ce). Yellow solid. Mp 177−178 °C, R_f = 0.22 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2359, 2202, 1615, 1505, 1460, 1410, 1386, 1326, 1166, 1124, 1068, 957, 852, 799, 744 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.69 (dd, *J* = 7.3, 6.8 Hz, 1H), 6.94 (dd, *J* = 8.8, 6.8 Hz, 1H), 7.45 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.52 (dd, *J* = 8.3, 7.8 Hz, 1H), 7.60 (dd, *J* = 7.8, 6.8 Hz, 1H), 7.76−7.78 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 8.26 (d, *J* = 7.3 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 87.2, 91.2, 114.8, 115.9, 118.9, 121.0, 121.5, 121.8, 123.8 (q, J_{C-F} = 271.1 Hz), 125.3, 126.0 (q, J_{C-F} = 3.3 Hz), 126.4, 126.4, 126.7, 128.2, 128.3, 128.5, 130.2, 130.7 (q, J_{C-F} = 33.1 Hz), 132.9, 133.0, 133.2, 134.9, 136.8. ^{19}F NMR ($CDCl_3$) δ −63.0. MS (EI) *m*/*z* 412 (M^+); HRMS (EI) calcd for $C_{26}H_{15}F_3N_2$ (M^+) 412.1187, found 412.1197.

1-Phenylethynyl-3-(4-fluorophenyl)imidazo[1,5-*a*]pyridine (4da). Yellow solid. Mp 157−159 °C, R_f = 0.40 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3560, 2359, 2204, 1633, 1529, 1514, 1351, 1313, 1224, 1126, 1065, 1006, 958, 845, 755, 691 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.65 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.88 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.21 (t, *J* = 8.8 Hz, 2H), 7.31−7.37 (m, 3H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.77−7.80 (m, 2H), 8.27 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.5, 92.7, 114.2, 114.9, 116.1 (d, J_{C-F} = 22.3 Hz), 118.8, 120.8, 121.8, 123.5, 125.7 (d, J_{C-F} = 4.1 Hz), 127.9, 128.3, 130.1 (d, J_{C-F} = 8.3 Hz), 131.3, 134.3, 137.8, 163.1 (d, J_{C-F} = 249.8 Hz). ^{19}F NMR ($CDCl_3$) δ −111.4. MS (EI) *m*/*z* 312 (M^+); HRMS (EI) calcd for $C_{21}H_{13}FN_2$ (M^+) 312.1063, found 312.1059.

1-(4-Methoxyphenyl)ethynyl-3-(4-fluorophenyl)imidazo-[1,5-*a*]pyridine (4db). Yellow solid. Mp 144−145 °C, R_f = 0.30 (*n*-hexane/EtOAc = 2:1); IR (KBr) 3090, 2360, 2202, 1603, 1529, 1283, 1248, 1223, 838, 745 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.64 (dd, *J* = 7.8, 6.3 Hz, 1H), 6.66 (dd, *J* = 8.8, 6.3 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.77−7.80 (m, 2H), 8.18 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.2, 81.0, 92.5, 114.0, 114.1, 115.3, 115.6, 116.1 (d, J_{C-F} = 21.5 Hz), 118.9, 120.5, 121.7, 125.8 (d, J_{C-F} = 3.3 Hz), 130.5 (d, J_{C-F} = 8.3 Hz), 132.9, 133.9, 137.2, 159.5, 163.0 (d, J_{C-F} = 249.8 Hz). ^{19}F NMR δ −111.5. MS (EI) *m*/*z* 342 (M^+); HRMS (EI) calcd for $C_{22}H_{15}FN_2O$ (M^+) 342.1168, found 342.1164.

1-(2-Pyridyl)ethynyl-3-(4-fluorophenyl)imidazo[1,5-*a*]-pyridine (4dd). Yellow solid. Mp 132−133 °C, R_f = 0.30 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2359, 2342, 2200, 1579, 1524, 1510, 1224, 851, 777, 745 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.70 (dd, *J* = 7.3, 6.8 Hz, 1H), 6.93 (dd, *J* = 9.3, 7.3 Hz, 1H), 7.20−7.25 (m, 3H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.67 (dd, *J* = 9.3, 7.8 Hz, 1H), 7.78−7.82 (m, 3H), 8.21 (d, *J* = 6.3 Hz, 1H), 8.63 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.9, 92.4, 113.9, 114.4, 116.2 (d, J_{C-F} = 21.5 Hz), 119.0, 121.5, 121.9, 122.3, 125.5 (d, J_{C-F} = 3.3 Hz), 126.9, 130.2 (d, J_{C-F} = 8.3 Hz), 135.3, 136.1, 137.7, 143.8, 149.9, 163.2 (d, J_{C-F} = 250.6 Hz). ^{19}F NMR ($CDCl_3$) d −111.2. MS (EI) *m*/*z* 313 (M^+); HRMS (EI) calcd for $C_{20}H_{12}FN_3$ (M^+) 313.1015, found 313.1014.

1-(1-Naphthyl)ethynyl-3-(4-fluorophenyl)imidazo[1,5-*a*]-pyridine (4de). Yellow solid. Mp 196−197 °C, R_f = 0.40 (*n*-hexane/

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EtOAc = 4:1); IR (KBr) 2359, 2197, 1531, 1515, 1505, 1351, 1311, 1220, 1157, 1009, 956, 846, 813, 776 cm^{-1}. ^1H NMR ($CDCl_3$)δ 6.65 (dd, J = 7.8, 6.3 Hz, 1H), 6.90 (dd, J = 9.3, 6.3 Hz, 1H), 7.20−7.26 (m, 2H), 7.46 (dd, J = 8.3, 7.1 Hz, 1H), 7.52 (dd, J = 8.3, 6.8 Hz, 1H), 7.60 (dd, J = 8.3, 6.8 Hz, 1H), 7.77 (d, J = 9.3 Hz, 1H), 7.80−7.83 (m, 4H), 7.86 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.1 Hz, 1H), 8.56 (d, J = 8.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 87.5, 90.9, 114.3, 115.1, 116.2 (d, J_{C-F} = 21.5 Hz), 118.8, 121.0, 121.2, 125.3, 125.7 (d, J_{C-F} = 3.3 Hz), 126.4, 126.4, 126.7, 128.3, 128.4, 128.6, 130.2 (d, J_{C-F} = 8.3 Hz), 130.3, 133.0, 133.2, 134.5, 137.5, 163.2 (d, J_{C-F} = 249.8 Hz). ^{19}F NMR ($CDCl_3$) d −111.3. MS (EI) m/z 362 (M^+); HRMS (EI) calcd for $C_{25}H_{15}FN_2$ (M^+) 362.1219, found 362.1221.

1-Phenylethynyl-3-(2-pyridyl)imidazo[1,5-*a*]pyridine (4ea). Yellow solid. Mp 109−110 °C, R_f = 0.40 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3040, 2360, 2207, 1586, 1562, 1487, 1428, 1356, 1328, 1312, 1275, 1066, 1002, 781, 746, 689 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.78 (dd, J = 7.3, 6.8 Hz, 1H), 7.00 (dd, J = 9.8, 6.8 Hz, 1H), 7.21 (dd, J = 7.3, 4.9 Hz, 1H), 7.32−7.39 (m, 3H), 7.63 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 9.3 Hz, 1H), 7.77 (d, J = 8.1, 7.3 Hz, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.61 (d, J = 4.9 Hz, 1H), 9.99 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.5, 92.6, 114.3, 115.0, 117.8, 122.0, 122.0, 122.1, 123.4, 126.7, 127.9, 128.2, 131.4, 135.1, 135.5, 136.5, 148.0, 150.3. MS (EI) m/z 295 (M^+); HRMS (EI) calcd for $C_{20}H_{13}N_3$ (M^+) 295.1109, found 295.1110.

1-(4-Methoxyphenyl)ethynyl-3-(2-pyridyl)imidazo[1,5-*a*]-pyridine (4eb). Yellow solid. Mp 161−163 °C, R_f = 0.25 (*n*-hexane/EtOAc = 2:1); IR (KBr) 2359, 2341, 1607, 1587, 1517, 1504, 1427, 1294, 1254, 1169, 1067, 1022, 757 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H), 6.79 (dd, J = 8.3, 7.3 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.98 (dd, J = 8.8, 7.3 Hz, 1H), 7.20 (dd, J = 7.8, 5.3 Hz, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.77 (dd, J = 7.8, 7.3 Hz, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.63 (d, J = 5.3 Hz, 1H), 10.00 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.2, 81.0, 92.5, 114.0, 114.3, 115.4, 115.5, 118.0, 121.8, 122.0, 122.2, 126.7, 133.0, 135.0, 135.3, 136.6, 148.1, 150.5, 159.5. MS (EI) m/z 325 (M^+); HRMS (EI) calcd for $C_{21}H_{15}N_3O$ (M^+) 325.1215, found 325.1221.

1-(4-Trifluoromethylphenylethynyl)-3-(2-pyridyl)imidazo[1,5-*a*]pyridine (4ec). Yellow solid. Mp 132−134 °C, R_f = 0.26 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2050, 2918, 2200, 1611, 1588, 1502, 1315 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.84 (dd, J = 7.8, 6.8 Hz, 1H), 7.06 (dd, J = 9.3, 6.8 Hz, 1H), 7.24 (dd, J = 7.8, 5.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 9.3 Hz, 1H), 7.80 (dd, J = 8.3, 7.8 Hz, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.65 (d, J = 5.8 Hz, 1H), 10.04 (d, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 85.3, 91.6, 114.3, 114.5, 117.8, 122.3, 122.4, 122.6, 125.3 (q, J_{C-F} = 4.1 Hz), 126.8 (q, J_{C-F} = 272.1 Hz), 127.0, 127.3, 129.3 (q, J_{C-F} = 32.3 Hz), 131.5, 135.6, 136.1, 136.7, 148.2, 150.3. ^{19}F NMR ($CDCl_3$) d −63.1. MS (EI) m/z 363 (M^+); HRMS (EI) calcd for $C_{21}H_{12}F_3N_3$ (M^+) 363.0983, found 363.0971.

1-(2-Pyridyl)ethynyl-3-(2-pyridyl)imidazo[1,5-*a*]pyridine (4ed). Yellow solid. Mp 155−157 °C, R_f = 0.30 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3047, 2360, 2209, 1581, 1560, 1513, 1467, 1426, 1324, 1314, 1277, 1247, 1187, 1145, 1124, 1005, 960, 781, 689 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.84 (dd, J = 7.8, 6.8 Hz, 1H), 7.05 (dd, J = 9.3, 6.8 Hz, 1H), 7.21−7.24 (m, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.69 (dd, J = 7.8, 7.3 Hz, 1H), 7.79 (dd, J = 9.0, 8.3 Hz, 1H), 7.86 (d, J = 9.3 Hz, 1H), 8.41 (d, J = 7.3 Hz, 1H), 8.62−8.64 (m, 2H), 10.01 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 83.0, 92.3, 114.5, 118.0, 122.2, 122.3, 122.7, 126.9, 126.9, 132.0, 132.1, 135.3, 136.1, 136.5, 136.6, 143.7, 148.1, 139.9, 150.3. MS (EI) m/z 296 (M^+); HRMS (EI) calcd for $C_{19}H_{12}N_4$ (M^+) 296.1062, found 296.1060.

1-(1-Naphthyl)ethynyl-3-(2-pyridyl)imidazo[1,5-*a*]pyridine (4ee). Yellow solid. Mp 157−159 °C, R_f = 0.30 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3116, 2359, 2342, 2192, 1584, 1560, 1502, 1427, 1313, 1276, 1187, 1145, 1098, 795, 766 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.78 (dd, J = 7.3, 6.8 Hz, 1H), 7.01 (dd, J = 9.3, 6.8 Hz, 1H), 7.19 (dd, J = 7.8, 4.9 Hz, 1H), 7.46 (dd, J = 7.8, 7.6 Hz, 1H), 7.52 (dd, J = 7.6, 6.8 Hz, 1H), 7.61 (dd, J = 8.3, 6.8 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.79−7.86 (m, 4H), 8.43 (d, J = 8.3 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.62 (d, J = 4.9 Hz, 1H), 10.00 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 87.5, 90.9, 114.4, 115.2, 117.9, 121.1, 112.2, 122.3, 125.3, 126.3, 126.4, 126.7, 126.8, 128.3, 128.4, 130.2, 133.0, 133.2, 135.3, 135.7, 136.6, 148.2, 150.4. MS (EI) m/z 345 (M^+); HRMS (EI) calcd for $C_{24}H_{15}N_3$ (M^+) 345.1266, found 345.1263.

1-(4-Fluorophenylethynyl)-3-(2-pyridyl)imidazo[1,5-*a*]-pyridine (4ej). Yellow solid. Mp 168−170 °C, R_f = 0.27 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3056, 2208, 1589, 1498, 1428, 1227, 1149 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.81 (dd, J = 7.3, 6.8 Hz, 1H), 6.99−7.08 (m, 3H), 7.22 (dd, J = 8.8, 4.9 Hz, 1H), 7.60 (dd, J = 8.8, 5.8 Hz, 2H), 7.73 (d, J = 9.3 Hz, 1H), 7.79 (dd, J = 8.3, 7.3 Hz, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.64 (d, J = 4.9 Hz, 1H), 10.01 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.6, 91.9, 114.4, 114.9, 115.6 (d, J_{C-F} = 22.3 Hz), 117.9, 119.5, 122.1, 122.2, 122.2, 126.8, 133.3 (d, J_{C-F} = 8.3 Hz), 135.3, 135.6, 136.6, 148.2, 150.4, 163.2 (d, J_{C-F} = 250.6 Hz). ^{19}F NMR ($CDCl_3$) δ −112.5. MS (EI) m/z 313 (M^+); HRMS (EI) calcd for $C_{20}H_{12}FN_3$ (M^+) 313.1015, found 313.1013.

1-(4-Chlorophenylethynyl)-3-(2-pyridyl)imidazo[1,5-*a*]-pyridine (4ek). Yellow solid. Mp 162−164 °C, R_f = 0.38 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3059, 2205, 1588, 1513, 1428, 1090 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.81 (dd, J = 7.3, 6.3 Hz, 1H), 7.02 (dd, J = 9.0, 6.3 Hz, 1H), 7.22 (dd, J = 7.6, 4.9 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 9.0 Hz, 1H), 7.79 (dd, J = 7.6, 7.3 Hz, 1H), 8.41 (d, J = 7.3 Hz, 1H), 8.53 (d, J = 4.9 Hz, 1H), 10.01 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 83.6, 91.6, 114.5, 114.7, 117.8, 122.0, 122.2, 122.3, 126.9, 128.7, 132.6, 133.9, 135.4, 135.7, 136.6, 136.7, 148.1, 150.4. MS (EI) m/z 329 (M^+); HRMS (EI) calcd for $C_{20}H_{12}ClN_3$ (M^+) 329.0720, found 329.0719.

1-(4-Methylphenylethynyl)-3-(2-pyridyl)imidazo[1,5-*a*]-pyridine (4el). Yellow solid. Mp 173−174 °C, R_f = 0.30 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2812, 1586, 1516, 1503, 1428, 1249, 1189 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H), 6.80 (dd, J = 7.8, 6.8 Hz, 1H), 7.00 (dd, J = 9.3, 6.8 Hz, 1H), 7.17 (d, J = 8.8 Hz, 2H), 7.23 (dd, J = 7.3, 6.3 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.73−7.80 (m, 2H), 8.43 (d, J = 7.8 Hz, 1H), 8.63 (d, J = 4.9 Hz, 1H), 10.01 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.7, 82.1, 93.1, 114.7, 115.7, 118.4, 120.7, 122.2, 122.4, 122.6, 127.1, 129.4, 131.7, 135.5, 135.8, 136.9, 138.5, 148.5, 150.8. MS (EI) m/z 309 (M^+); HRMS (EI) calcd for $C_{21}H_{15}N_3$ (M^+) 309.1266, found 309.1243.

1-(4-*N*,*N*′-Dimethylphenylethynyl)-3-(2-pyridyl)-imidazo-[1,5-*a*]pyridine (4em). Yellow solid. Mp 185−186 °C, R_f = 0.12 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2909, 2200, 1605, 1585, 1536, 1372, 1189 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.98 (s, 6H), 6.68 (d, J = 8.8 Hz, 2H), 6.77 (dd, J = 7.3, 6.8 Hz, 1H), 6.95 (dd, J = 9.8, 6.8 Hz, 1H), 7.20 (dd, J = 7.8, 4.9 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.73−7.79 (m, 2H), 8.43 (d, J = 8.3 Hz, 1H), 8.61 (d, J = 4.9 Hz, 1H), 9.98 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 40.1, 80.0, 93.6, 110.2, 111.8, 114.3, 116.1, 118.1, 121.4, 121.9, 122.1, 126.5, 130.6, 132.7, 134.9, 136.5, 148.1, 150.0, 150.5. MS (EI) m/z 338 (M^+); HRMS (EI) calcd for $C_{22}H_{18}N_4$ (M^+) 338.1531, found 338.1518.

1-(2-Pyridyl)-3-(2-formyl-phenyl)imidazo[1,5-*a*]pyridine (4en). Yellow solid. Mp 153−154 °C, R_f = 0.20 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2195, 1687, 1590, 1517, 1505, 1268, 1189, 752, 689 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.89 (dd, J = 7.4, 6.8 Hz, 1H), 7.12 (dd, J = 9.3, 6.8 Hz, 1H), 7.27−7.30 (m, 1H), 7.46 (dd, J = 7.8, 7.3 Hz, 1H), 7.62 (dd, J = 7.8, 7.3 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.78−7.84 (m, 2H), 7.98 (d, J = 7.8 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H), 8.68 (d, J = 4.8 Hz, 1H), 10.09 (d, J = 7.4 Hz, 1H), 10.77 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 88.9, 90.1, 114.7, 117.9, 122.4, 122.5, 123.0, 127.1, 127.8, 128.2, 130.6, 133.2, 133.9, 134.2, 135.4, 136.5, 136.8, 141.5, 148.3, 150.3, 191.2. MS (EI) m/z

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323 (M^+). HRMS (EI) calcd for $C_{21}H_{13}N_3O$ (M^+) 323.1059, found 323.1056.

1-[2-(Methoxy)phenyl]ethynyl]-3-(2-pyridyl)imidazo[1,5-*a*]-pyridine (4eo). Yellow solid. Mp 169−171 °C, R_f = 0.23 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3113, 3040, 3002, 2969, 2935, 2207, 1531, 1515, 1250, 746 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.97 (s, 3H), 6.83 (dd, J = 7.3, 6.3 Hz, 1H), 6.92−6.98 (m, 2H), 7.04 (dd, J = 8.8, 6.3 Hz, 1H), 7.22−7.27 (m, 1H), 7.32 (dd, J = 8.3, 7.3 Hz, 1H), 7.60 (J = 7.3 Hz, 1H), 7.78−7.82 (m, 2H), 8.44 (d, J = 8.8 Hz, 1H), 8.65 (d, J = 4.8 Hz, 1H), 10.00 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.8, 88.5, 89.2, 110.6, 112.7, 114.5, 115.6, 118.2, 120.5, 121.9, 122.1, 122.2, 126.6, 129.5, 133.2, 135.1, 135.6, 136.6, 148.2, 150.4, 159.9. MS (EI) m/z 325 (M^+). HRMS (EI) calcd for $C_{21}H_{15}N_3O$ (M^+) 325.1215, found 325.1218.

1-[2-(Methylthio)phenyl]ethynyl]-3-(2-pyridyl)imidazo-[1,5-*a*]pyridine (4ep). Yellow solid. Mp 161−162 °C, R_f = 0.03 (*n*-hexane/EtOAc = 10:1); IR (KBr) 3077, 1582, 1505, 1429, 1343, 1248, 1016 cm^{-1}. ^1H NMR ($CDCl_3$) d 2.53 (s, 3H), 6.79 (t, J = 6.8 Hz, 1H), 7.01 (dd, J = 8.3, 6.8 Hz, 1H), 7.11 (dd, J = 7.8, 7.3 Hz, 1H), 7.17−7.21 (m, 2H), 7.23−7.29 (m, 1H), 7.56 (d, J = 7.3 Hz, 1H), 7.76 (dd, J = 9.3, 7.8 Hz, 1H), 7.89 (d, J = 9.3 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H), 9.99 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 15.2, 89.3, 90.2, 114.5, 115.0, 118.3, 121.6, 122.1, 122.2, 122.3, 124.1, 124.3, 126.7, 128.3, 131.9, 135.2, 136.0, 136.5, 140.8, 148.0, 150.3. MS (EI) m/z 341. HRMS (EI) calcd for $C_{21}H_{15}N_3S$ (M^+) 341.0987, found 341.0977.

1-Phenylethynyl-3-(2-thienyl)imidazo[1,5-*a*]pyridine (4fa). Yellow solid. Mp 174−175 °C, R_f = 0.38 (*n*-hexane/EtOAc = 3:1); IR (KBr) 2931, 1652, 1558, 1509, 1487, 1249, 1047 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.75 (dd, J = 6.8, 6.3 Hz, 1H), 6.91 (dd, J = 8.8, 6.3 Hz, 1H), 7.19 (dd, J = 4.9, 3.4 Hz, 1H), 7.32−7.38 (m, 3H), 7.45 (d, J = 4.9 Hz, 1H), 7.57−7.61 (m, 3H), 7.72 (d, J = 8.8 Hz, 1H), 8.36 (d, J = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.3, 92.9, 114.6, 115.2, 118.9, 120.8, 122.3, 123.4, 125.4, 126.5, 127.6, 127.9, 128.3, 131.3, 131.4, 133.0, 134.3. MS (EI) m/z 300 (M^+) calcd for $C_{19}H_{12}N_2S$ (M^+) 300.0721, found 300.0721.

1-(4-Trifluoromethylphenylethynyl)-3-(2-thienyl)imidazo[1,5-*a*]pyridine (4 fc). Yellow solid. Mp 144−146 °C, R_f = 0.25 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3076, 2201, 1635, 1560, 1537, 1227, 1210 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.78 (dd, J = 6.8, 6.3 Hz, 1H), 6.97 (dd, J = 8.8, 6.8 Hz, 1H), 7.21 (t, J = 4.4 Hz, 1H), 7.48 (d, J = 4.4 Hz, 1H), 7.60−7.74 (m, 6H), 8.40 (d, J = 6.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.5, 85.4, 92.1, 114.8, 115.1, 119.1, 121.7, 122.8, 124.4 (q, J = 272.1 Hz, $\underline{C}F_3$), 125.6 (q, J = 3.3 Hz, $CF_3-C{=}\underline{C}$), 126.0, 127.2, 128.0, 129.8 (q, J = 32.6 Hz, CF_3-$\underline{C}$), 131.6, 131.7, 133.8, 135.2. ^{19}F NMR ($CDCl_3$) δ −63.0. MS (EI) m/z 368 (M^+); HRMS (EI) calcd for $C_{20}H_{11}F_3N_2S$ (M^+) 368.0595, found 368.0605.

1-(4-Fluorophenylethynyl)-3-(2-thienyl)imidazo[1,5-*a*]-pyridine (4fj). Yellow solid. Mp 144−146 °C, R_f = 0.25 (*n*-hexane/EtOAc = 4:1); IR (KBr) 3071, 2210, 1595, 1498, 1402, 1311, 1249, 1229 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.65 (dd, J = 7.4, 6.3 Hz, 1H), 6.82 (dd, J = 8.8, 6.3 Hz, 1H), 6.92 (t, J = 8.8 Hz, 2H), 7.10 (dd, J = 5.0, 3.6 Hz, 1H), 7.36 (d, J = 5.0 Hz, 1H), 7.46−7.49 (m, 3H), 7.60 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 82.0, 91.7, 114.5, 114.9, 115.6 (d, J = 21.5 Hz, $F-C{=}\underline{C}$), 118.7, 119.5 (d, J = 3.3 Hz, $F-C{=}C-C{=}\underline{C}$), 120.8, 122.3, 125.4, 126.5, 127.6, 131.4, 133.1, 133.1 (d, J = 8.3 Hz, $F-C{=}C-\underline{C}$), 134.3, 162.3 (d, J = 249.8 Hz, F-$\underline{C}$). ^{19}F NMR ($CDCl_3$) d −111.6. MS (EI) m/z 318 (M^+); HRMS (EI) calcd for $C_{19}H_{11}FN_2S$ (M^+) 318.0627, found 318.0621.

1-(4-Chlorophenylethynyl)-3-(2-thienyl)imidazo[1,5-*a*]-pyridine (4fk). Yellow solid. Mp 107−109 °C, R_f = 0.40 (*n*-hexane/EtOAc = 3:1); IR (KBr) 2925, 2201, 1652, 1512 m 1487, 1309, 1253, 1089 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.77 (dd, J = 6.8, 6.3 Hz, 1H), 6.94 (dd, J = 8.8, 6.3 Hz, 1H), 7.20 (dd, J = 4.8, 3.4 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 4.8 Hz, 1H), 7.52 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 3.4 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 8.40 (d, J = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 83.4, 91.8, 114.7, 114.8, 118.8, 121.0, 121.9, 122.4, 125.5, 126.6, 127.6, 128.6, 131.4, 132.5, 133.9, 134.5, 135.7. MS (EI) m/z 334 (M^+); HRMS (EI) calcd for $C_{19}H_{11}ClN_2S$ (M^+) 334.0331, found 334.0337.

1-(4-Methylphenylethynyl)-3-(2-thienyl)imidazo[1,5-*a*]pyridine (4fl). Yellow solid. Mp 161−162 °C, R_f = 0.45 (*n*-hexane/EtOAc = 3:1); IR (KBr) 2945, 2203, 1652, 1558, 1497, 1306, 1256 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 6.70 (dd, J = 6.8, 6.3 Hz, 1H), 6.86 (dd, J = 8.8, 6.8 Hz, 1H), 7.14−7.16 (m, 3H), 7.42 (d, J = 4.9 Hz, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 8.8 HZ, 1H), 8.31 (d, J = 6.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.5, 81.7, 92.8, 114.5, 115.4, 118.7, 120.3, 120.6, 122.2, 125.2, 126.4, 127.6, 129.0, 131.2, 131.5, 132.9, 134.2, 138.1. MS (EI) m/z 314 (M^+); HRMS (EI) calcd for $C_{20}H_{14}N_2S$ (M^+) 314.0878, found 314.0882.

9,9-Dibutyl-2,7-bis(3-phenylimidazo[1,5-*a*]pyrid-1-yl)-ethynyl-9*H*-fluorene (7). Brown solid. Mp 126−127.5 °C, R_f = 0.15 (*n*-hexane/EtOAc = 4:1); IR (KBr) 1601, 1509, 1467, 1352, 1300, 1126 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.61−0.67 (m, 4H), 0.70 (t, J = 7.3 Hz, 6H), 1.11 (quint, J = 7.3 Hz, 4H), 1.99−2.03 (m, 4H), 6.65 (dd, J = 7.3, 6.3 Hz, 2H), 6.90 (dd, J = 9.3, 6.3 Hz, 2H), 7.46 (t, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 4H), 7.61 (d, J = 7.3 Hz, 2H), 7.62 (s, 2H), 7.68 (d, J = 7.3 Hz, 2H), 7.77 (d, J = 9.3 Hz, 2H), 7.84 (d, J = 7.3 Hz, 4H), 8.28 (d, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 13.7, 22.9, 25.8, 40.1, 55.0, 83.1, 93.8, 114.0, 115.1, 118.9, 119.8, 120.8, 122.0, 122.1, 125.9, 128.2, 129.0, 129.1, 129.5, 130.3, 134.2, 138.4, 140.4, 151.1. MS (EI) m/z 710 (M^+); HRMS (EI) calcd for $C_{51}H_{42}N_4$ (M^+) 710.3409, found 710.3410.

1,4-Dioctyl-2,5-bis(3-phenylimidazo[1,5-*a*]pyrid-1-yl)-ethynylbenzene (9). Brown solid. Mp 116−117 °C, R_f = 0.13 (*n*-hexane/EtOAc = 4:1); IR (KBr) 1911, 1698, 1349, 1124, 1064 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 6H), 1.20−1.48 (m, 20H), 1.77 (quint, J = 6.8 Hz, 4H), 2.91 (t, J = 6.8 Hz, 4H), 6.66 (dd, J = 6.8, 6.3 Hz, 2H), 6.90 (dd, J = 9.3, 6.3 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.48 (s, 2H), 7.53 (t, J = 7.8 Hz, 4H), 7.68 (d, J = 9.3 Hz, 2H), 7.83 (d, J = 7.8 Hz, 4H), 8.28 (d, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 29.2, 29.48, 29.50, 30.4, 31.8, 34.1, 87.1, 91.9, 114.0, 115.3, 118.7, 120.8, 122.1, 122.4, 128.2, 129.0, 129.1, 129.5, 132.1, 134.4, 138.4, 141.4. MS (EI) m/z 734 (M^+); HRMS (EI) calcd for $C_{52}H_{54}N_4$ (M^+) 734.4348, found 734.4338.

1-(3-Phenylimidazo[1,5-*a*]pyrid-1-yl)ethynyl-3-phenyl-imidazo[1,5-*a*]pyridine (11a). Brown solid. Mp 188−190 °C, R_f = 0.49 (*n*-hexane/EtOAc = 1:1); IR (KBr) 2923, 2364, 1614, 1511, 1322, 1133, 1103, 1063, 695 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.63 (dd, J = 7.3, 6.3 Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H), 6.83−6.90 (m, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.51 (dd, J = 7.8, 7.3 Hz, 2H), 7.74−7.82 (m, 6H), 7.97 (d, J = 8.3 Hz, 2H), 8.24−8.28 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 85.1, 86.0, 114.1, 114.7, 115.0, 116.1, 119.0, 119.2, 120.8, 121.1, 121.6, 121.9, 123.7 (q, J = 272.1 Hz, $\underline{C}F_3$), 125.9 (q, J = 3.3 Hz, $CF_3-C{=}\underline{C}$), 128.1, 129.0, 129.1, 129.5, 130.0, 130.3 (q, J = 33.1 Hz, CF_3-$\underline{C}$), 133.1, 134.4, 134.7, 136.4, 138.2 (Ar). ^{19}F NMR ($CDCl_3$) δ −63.0. MS (EI) m/z 478 (100, M^+). HRMS (EI) calcd for $C_{29}H_{17}F_3N_4$ (M^+) 478.1405, found 478.1403.

1-{3-(4-Trifluoromethylphenylimidazo[1,5-*a*]pyridin-1-yl)-ethynyl-3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (11b). Brown solid. Mp 198−200 °C, R_f = 0.13 (*n*-hexane/EtOAc = 4:1); IR (KBr) 2922, 1631, 1613, 1530, 1514, 1415, 1351, 1324, 1286, 1246, 1163, 1064, 835 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H), 6.62 (dd, J = 7.2, 6.6 Hz, 1H), 6.71 (dd, J = 7.2, 6.6 Hz, 1H), 6.83 (dd, J = 9.1, 6.6 Hz, 1H), 6.88 (dd, J = 9.1, 6.6 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 7.73−7.82 (m, 6H), 7.96 (d, J = 8.3 Hz, 2H), 8.19 (d, J = 7.2 Hz, 1H), 8.28 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.3, 85.1, 86.1, 113.9, 114.4, 114.6, 114.7, 119.0, 119.4, 120.5, 121.1, 121.6, 121.9, 122.0, 124.0 (q, J = 272.1 Hz, $\underline{C}F_3$), 126.0 (q, J = 3.3 Hz, $CF_3-C{=}\underline{C}$), 128.3, 129.7, 130.5 (q, J = 33.1 Hz, CF_3-$\underline{C}$), 133.1, 134.2, 134.8, 135.2, 136.4, 138.3, 160.2. ^{19}F NMR ($CDCl_3$) d−63.0. MS (EI) m/z 508 (M^+). HRMS (EI) calcd for $C_{30}H_{19}F_3N_4O$ (M^+) 508.1511, found 508.1510.

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Synthesis of 1-Ethynyl-imidazo[1,5-*a*]pyridines 10. To a solution of corresponding **4** (0.5 mmol) in THF was added TBAF in THF (2 equiv), and the mixture was stirred for 1 h at room temperature. The mixture was diluted with water (5 mL), extracted with DCM (10 mL × 3), washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc) to give the desilylated product **10**.

1-Ethynyl-3-phenylimidazo[1,5-*a*]pyridine (10a). Brown oil. R_f = 0.35 (*n*-hexane/EtOAc = 4:1); IR (neat) 3289, 3062, 2102, 1509, 774 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.39 (s, 1H), 6.54 (dd, *J* = 8.8, 6.6 Hz, 1H), 6.78 (dd, *J* = 8.3, 6.6 Hz, 1H), 7.34−7.38 (m, 1H), 7.44 (t, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 77.0, 80.4, 113.5, 113.7, 118.0, 120.9, 121.7, 127.8, 128.7, 128.8, 129.1, 134.7, 137.7. MS (EI) *m*/*z* 218 (M^+); HRMS (EI) calcd for $C_{15}H_{10}N_2$ (M^+) 218.0844, found 218.0842.

1-Ethynyl-3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (10b). Brown oil. R_f = 0.24 (*n*-hexane/EtOAc = 4:1); IR (neat) 3292, 3003, 2097, 1611, 1257, 835, 697 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.40 (s, 1H), 3.84 (s, 3H), 6.57 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.82 (dd, *J* = 9.1, 6.3 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 9.1 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 55.2, 77.2, 80.4, 113.3, 113.7, 113.8, 118.3, 120.8, 121.8, 122.0, 129.6, 134.7, 138.1, 160.2. MS (EI) *m*/*z* 248 (M^+). HRMS (EI) calcd for $C_{16}H_{12}N_2O$ (M^+) 248.0950, found 248.0954.

General Procedure for the Heck Reaction of 1. To a screw-capped test tube was added Cs_2CO_3 (1.5 equiv). The test tube was dried at 150 °C in vacuo for 3 h. To the test tube were added $Pd(OAc)_2$ (5 mol %), IPr·HCl (10 mol %), 1-iodo-3-arylimidazo[1,5-*a*]pyridine **1** (0.25 mmol), freshly distilled styrene (1.1 equiv), and DMA (1 mL). The resulting mixture was stirred under an Ar atmosphere at 130 °C for 20 h. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc) to give the coupling product **13**.

3-Phenyl-1-styrylimidazo[1,5-*a*]pyridine (13aa). Yellow solid. Mp 114.5−115.5 °C, R_f = 0.30 (*n*-hexane/EtOAc = 10:1); IR (KBr) 3025, 1623, 1595, 1299, 737 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.61 (dd, *J* = 7.3,6.3 Hz, 1H), 6.83 (dd, *J* = 9.3, 6.3 Hz, 1H), 7.27−7.32 (m, 1H), 7.40−7.45 (m, 3H), 7.50−7.65 (m, 6H), 7.71 (d, *J* = 9.3 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 2H), 8.23 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 113.4, 118.1, 118.4, 119.5, 121.9, 126.2, 126.9, 128.3, 128.5, 128.6, 129.0, 129.1, 129.3, 129.9, 130.5, 138.1, 138.7. MS (EI) *m*/*z* 296 (M^+); HRMS (EI) calcd for $C_{21}H_{16}N_2$ (M^+) 296.1313, found 296.1312.

3-Phenyl-1-{(4-trifluoromethylphenyl)ethenyl}imidazo-[1,5-*a*]pyridine (13ac). Yellow solid. Mp 145−147 °C, R_f = 0.28 (*n*-hexane/EtOAc = 10:1); IR (KBr) 3028, 2933, 1617, 1596, 1574, 1322 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.61 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.84 (dd, *J* = 9.3, 6.3 Hz, 1H), 7.43−7.69 (m, 10H), 7.84 (d, *J* = 7.3 Hz, 2H), 8.21 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 113.4, 117.6, 119.9, 120.3, 121.8, 124.0, 124.1 (q, *J* = 272.1 Hz, $\underline{C}F_3$), 125.3 (q, *J* = 3.3 Hz, $\underline{C}$=C−CF_3), 125.8, 128.0 (q, *J* = 33.1 Hz, $\underline{C}$−CF_3), 128.1, 128.8, 128.9, 129.4, 129.6, 129.6, 138.9, 141.3. ^{19}F NMR ($CDCl_3$) δ −62.8. MS (EI) *m*/*z* 364 (M^+); HRMS (EI) calcd for $C_{22}H_{15}F_3N_2$ (M^+) 364.1187. Found 364.1189.

3-(4-Methoxyphenyl)-1-styrylimidazo[1,5-*a*]pyridine (13ba). Yellow solid. Mp 163−164 °C, R_f = 0.20 (*n*-hexane/EtOAc = 10:1); IR (KBr) 3028, 1623, 1609, 1593, 1254, 733 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.51 (dd, *J* = 7.3, 6.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 6.8 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.34−7.38 (m, 3H), 7.52 (d, *J* = 16.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.3, 113.2, 114.5, 118.1, 118.4, 119.3, 121.8, 122.4, 125.9, 126.1, 126.8, 128.6, 129.0, 129.8, 130.1, 138.2, 138.8, 160.2. MS (EI) *m*/*z* 326 (M^+); HRMS (EI) calcd for $C_{22}H_{18}N_2O$ (M^+) 326.1419, found 326.1418.

1-Styryl-3-(4-trifluoromethylphenyl)imidazo[1,5-*a*]pyridine (13ca). Yellow solid. Mp 143−145 °C, R_f = 0.28 (*n*-hexane/EtOAc = 10:1); IR (KBr) 3029, 2926, 1635, 1625, 1607, 1572, 1325 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.62 (dd, *J* = 7.3, 6.3 Hz, 1H), 6.84 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.35 (d, *J* = 16.1 Hz, 1H), 7.54 (d, *J* = 16.1 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H), 8.20 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 114.2, 118.1, 118.3, 119.9, 121.6, 124.0 (q, *J* = 272.1 Hz, $\underline{C}F_3$), 126.0 (q, *J* = 3.3 Hz, $\underline{C}$=C−CF_3), 126.3, 126.8, 127.1, 128.3, 128.3, 128.7, 129.8, 130.5 (q, *J* = 33.1 Hz, $\underline{C}$−CF_3), 131.3, 133.5, 137.9. ^{19}F NMR ($CDCl_3$) δ −62.8. MS (EI) *m*/*z* 364 (M^+). HRMS (EI) calcd for $C_{22}H_{15}F_3N_2$ (M^+) 364.1187, found 364.1180.

3-(2-Pyridyl)-1-styrylimidazo[1,5-*a*]pyridine (13ea). Yellow solid. Mp 168−170 °C, R_f = 0.20 (*n*-hexane/EtOAc = 10:1); IR (KBr) 3047, 1621, 1585, 1560, 743 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.56 (dd, *J* = 7.3, 6.5 Hz, 1H), 6.75 (d, *J* = 8.8, 6.5 Hz, 1H), 7.03 (dd, *J* = 7.3, 4.4 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 16.1 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 16.1 Hz, 1H), 7.43 (d, 7.3 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 7.8, 7.3 Hz, 1H), 8.3 (d, *J* = 7.8 Hz, 1H), 8.47 (d, *J* = 4.4 Hz, 1H), 9.77 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 113.9, 117.3, 118.5, 120.8, 121.9, 122.3, 126.3, 126.6, 126.6, 127.0, 128.7, 130.7, 130.7, 135.5, 136.5, 138.0, 148.2, 150.8. MS (EI) *m*/*z* 297 (M^+); HRMS (EI) calcd for $C_{20}H_{15}N_3$ (M^+) 297.1266, found 297.1266.

■ ASSOCIATED CONTENT

Supporting Information. X-ray analyses of **4ea** and **4fa**, Figures S1−7, Tables S1−12, and copies of ^1H and ^{13}C NMR for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) See Supporting Information for details of the photophysical properties of **3** (Table S10). One of the referees pointed out that respective linear correlations seem to exist at the positive and negative regions of σ value on the plot. In fact, as shown in Figure S1, acceptable approximate lines could be drawn at those regions, respectively, without the value of **3a**. The observation probably suggested that the absorption and/or emission mechanisms on **3** are totally switched by polarity of those substituents, and at least it is different from the mechanisms on **4**. Further theoretical and structural investigations are underway to discuss the correlations.

(22) X-ray crystallographic analyses of **4ea** and **4fa** indicated that the phenyl group on the alkynyl group and imidazo[1,5-*a*]pyridyl group form twisted structures in the solid state due to the formation of strong π-stacking between imidazopyridine rings and the resulting tightly packed crystal system. See Supporting Information (Figures S3−6, Table S11).

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(24) Because the calculations only simulate ground-state energy and localized electronic absorptions and the σ value only correlates ground-state electron-donor/acceptor properties, fluorescent emission normally cannot be understood with DFT and/or TD-DFT calculations and the σ value directly, in particular with the absorption and emission that occur via charge-transfer (CT)-type transition in excitation−relaxation mechanism. Meanwhile, it is obvious from Figure 3 that the energy band gaps in relaxation processes along with fluorescent emission from excited **4** are strongly correlated to electron-donor/acceptor properties of substituents and likely to the result of DFT and TD-DFT calculations (i.e., HOMO−LUMO energy gaps of grand-state orbitals) as well. Also, if the absorption and emission occur with a CT-type transition mechanism, these spectra should be changed by polarity of the solvent owing to stabilization of the excited states, but no recognizable changes of the peak positions were observed in preliminary solvent-dependent UV−vis and fluorescent studies (in *c*-hexane, chloroform, acetonitrile, and DMSO) of **4aa**−**ac** (Table S12 in Supporting Information) though the shapes slightly changed in *c*-hexane (Figure S7 in Supporting Information). The result probably suggested that at least the relaxation processes along with fluorescent emission does not occur with CT type transition as a main factor. At any rate, further investigations are needed to understand the mechanism.

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