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C–H Activation

Microwave-Assisted C-2 Direct Alkenylation of Imidazo[4,5-*b*]pyridines: Access to Fluorescent Purine Isosteres with Remarkably Large Stokes Shifts

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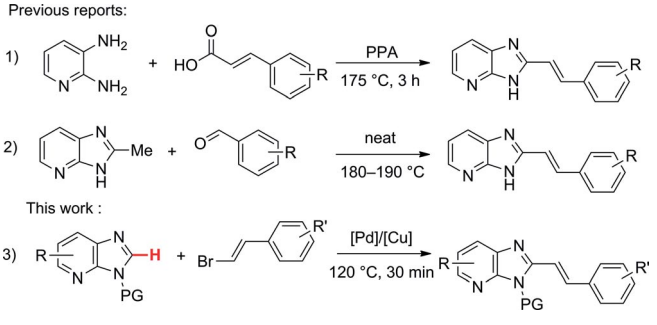
Abstract: We describe herein the first C-2 direct alkenylation of the valuable 3*H*-imidazo[4,5-*b*]pyridine promoted by microwave-assisted Pd/Cu co-catalysis. The reaction is rapid and compatible with a wide range of functional groups either on the imidazo[4,5-*b*]pyridine ring or on the styryl bromides thereby leading to the isolation of 23 compounds with moderate to good yields. The relevance of this method is demonstrated by its application to the synthesis of new cross-conjugated push–pull 2-vinyl- and 2-alkynylimidazo[4,5-*b*]pyridines characterized by satisfactory fluorescence quantum yields and remarkable solvatofluorochromic properties.

Introduction

Direct C–H functionalization allows the formation of C–C and C–heteroatom bonds directly on hydrogenated positions, without prior conversion of one of the coupling partners into an organometallic species as is the case for traditional transition-metal-catalyzed cross-couplings. This time-saving, atom-efficient synthetic method has been studied on an extensive range of heterocycles in the last decade and represents a major step forward in organic chemistry.[1]

In the context of our medicinal chemistry program, we were interested in generating C-2 alkenylated 3*H*-imidazo[4,5-*b*]pyridine derivatives. These are purine isosteres that can be found in increasing numbers of molecules designed for diverse biological applications and have been applied in the treatment of cancers,[2] neurodegenerative diseases,[3] diabetes,[4] and hypertension.[5] Additionally, the 3*H*-imidazo[4,5-*b*]pyridine core has been used as an unnatural base pair template for site-specific insertion of nucleotide analogues into DNA and RNA and has been applied to local structural analyses of nucleic acids thanks to its fluorescent properties.[6] However, this was not the first example of a fluorescent imidazo[4,5-*b*]pyridine; both the ground- and excited-state of 2-(2′-hydroxyphenyl)-imidazo[4,5-*b*]pyridine were extensively studied between 2000 and 2013.[7] More recently, Krishnamoorthy et al. have studied the fluorescence properties of 2-(2′-dimethylaminophenyl)imidazo[4,5-*b*]pyridine,[8] and the effect of introducing a double bond between the heterocyclic core and the *p*-(dimethylamino)phenyl moiety.[9]

The introduction of a styryl motif at position 2 of the imidazo[4,5-*b*]pyridine was first described by Komlossy et al. in 1964 on three examples using the condensation of 2,3-diaminopyridine with cinnamic acids in the presence of polyphosphoric acid [PPA, Scheme 1, Equation (1)].[10] However, this method requires harsh conditions and affords the expected products in understandably poor yields. In 1979, Ratnam et al. reported the condensation of various substituted benzaldehydes in large excess with 2-methylimidazo[4,5-*b*]pyridines at high temperature to give the styrylimidazo[4,5-*b*]pyridine in moderate to good yields [Scheme 1, Equation (2)].[11]



Scheme 1. Synthesis of 2-vinylimidazo[4,5-*b*]pyridines.

To date, no direct C-2 alkenylation conditions for the generation of 2-vinylimidazo[4,5-*b*]pyridines have been described [Scheme 1; Equation (3)], and only C-2 direct arylation methodologies can be found in the literature. Dominguez and co-workers have reported the copper-catalyzed intramolecular direct arylation of an *o*-iodobenzyl-protected imidazo[4,5-*b*]pyridine.[12] Similar palladium-catalyzed intramolecular arylations have been described by the Iaroshenko group using *o*-halogenated aryl groups with a wider scope.[13] However, in all these

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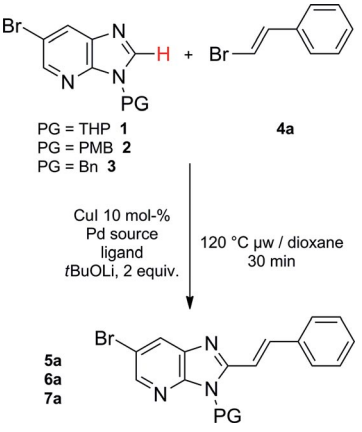
examples, starting materials were functionalized at position 7 with an electron-withdrawing group, mainly a trifluoromethyl moiety. The same group then published intermolecular nickel-catalyzed direct arylation conditions that afford several 2-aryl-7-(trifluoromethyl)imidazo[4,5-*b*]pyridines in high yields.[14] In 2013, various 2-arylimidazo[4,5-*b*]pyridines were obtained using a palladium/copper co-catalysis system; this approach is compatible with a number of substitutions on the heterocycle.[15] Accordingly, we have envisaged the direct C-2 alkenylation of 3*H*-imidazo[4,5-*b*]pyridines based on our previous work involving Pd/Cu-catalyzed C-8 direct functionalization of purines using styryl bromides.[16] Herein, we report a rapid, regioselective and functional group-tolerant methodology for C-2 alkenylation of 3*H*-imidazo[4,5-*b*]pyridines and its use in the synthesis of two novel fluorescent derivatives.

Results and Discussion

Optimization

We chose as starting material 6-bromoimidazo[4,5-*b*]pyridine which would eventually allow us to introduce molecular diversity at position 6 thus enabling us to generate a library of 6-substituted-2-alkenyl-imidazo[4,5-*b*]pyridines. Since direct C-2 alkenylation of the unprotected 6-bromoimidazo[4,5-*b*]pyridine failed, we subsequently investigated the reaction between 3-THP-imidazo[4,5-*b*]pyridine **1** (THP = tetrahydropyranyl) and *E*-β-bromostyrene **4a** using a Pd/Cu co-catalyst system under microwave irradiation conditions.[16] Unfortunately, the yield of alkenylated imidazo[4,5-*b*]pyridine **5a** did not exceed 40 % (Table 1, Entries 1 and 2). Changing the protecting group from THP to *p*-methoxybenzyl (PMB) had a positive effect on the reaction, giving **6a** in a 52 % yield (Table 1, Entry 3). Utilization of other palladium sources such as $PdCl_2$(dppf) or $Pd(PPh_3)_4$ resulted in lower yields (Table 1, Entries 4 and 5). Finally, regarding our work on related *N*-9-benzylpurines, we applied the tentatively optimal conditions (Entry 3) to *N*-3-benzyl (Bn) protected imidazo[4,5-*b*]pyridine **3**. Indeed, target 3-benzyl-2-styrylimidazo[4,5-*b*]pyridine **7a** was isolated in 66 % yield as a single *E*-stereoisomer (Table 1, Entry 6). Subsequently, a brief examination of the importance of ligand structures on reaction efficiency revealed that when ligands were changed to XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl), XantPhos [4,5-bis(diphenylphosphanyl)-9,9-dimethylxanthene] or terpyridine (Table 1, Entries 8–10) product yields suffered. Importantly, a 1:2 ratio Pd to CuI proved to be crucial to maintain the highest yield (Table 1, Entry 6). In control experiments, where the copper or the palladium was left out, only trace amounts of **7a** were formed (not shown). Furthermore, for comparison, the same reaction carried out overnight using traditional oil bath heating afforded alkenylated imidazo[4,5-*b*]pyridine **7a** in only 8 % yield. Replacing dioxane with a less polar solvent such as fluorobenzene resulted in a lower yield of direct alkenylation product (Table 1, Entry 6). Finally, when the reaction was scaled up to 2.6 mmol, alkenylated product **7a** was obtained in 70 % yield (Table 1, Entry 6). It appears that the N-3 protecting group has a significant effect on the outcome of the reaction by either modifying the acidity of the C–H bond or by inducing an extra potential coordination site for the catalyst. Since *N*-3-benzylimidazo[4,5-*b*]pyridine **3** gave the best result in direct alkenylation reactions, it was chosen as the substrate by which to access the scope of the reaction with various readily accessible *E*-β-bromostyrenes.

Table 1. Optimization of the microwave-assisted direct alkenylation conditions.[a]



Entry	PG	Pd source (5 mol-%)	Ligand (20 mol-%)	Yield [%]
1	THP	$Pd(OAc)_2$	phenanthroline	37
2	THP	$Pd(OAc)_2$	phenanthroline	26[b]
3	PMB	$Pd(OAc)_2$	phenanthroline	52
4	PMB	$PdCl_2$(dppf)	phenanthroline	3
5	PMB	$Pd(PPh_3)_4$	phenanthroline	25
6	Bn	$Pd(OAc)_2$	phenanthroline	66/41[c]/37[d]/70[e]
7	Bn	$PdCl_2(MeCN)_2$	phenanthroline	55
8	Bn	$Pd(OAc)_2$	XPhos	3
9	Bn	$Pd(OAc)_2$	XantPhos	20
10	Bn	$Pd(OAc)_2$	terpyridine	37

[a] All reactions were duplicated and performed in a sealed tube with 0.33–0.35 mmol of substrate (1 equiv.), styryl bromide (2 equiv.), CuI (10 mol-%), *t*BuOLi (2 equiv.) under microwave irradiation at 120 °C for 30 min, yields are calculated on the basis of isolated products (average of two runs). [b] 10 equiv. of β-bromostyrene were used. [c] 10 mol-% of $Pd(OAc)_2$. [d] Distilled fluorobenzene was used as solvent. [e] The reaction was performed with 2.6 mmol of substrate.

Reaction Scope

By using $Pd(OAc)_2$ (5 mol-%), CuI (10 mol-%), phenanthroline (20 mol-%), *t*BuOLi (2 equiv.) in dioxane under microwave irradiation conditons at 120 °C for 30 min, both electron-rich and electron-deficient β-bromostyrenes reacted at the C-2 position of imidazo[4,5-*b*]pyridine **3** in moderate to good yields (Scheme 2). A variety of functional groups including halides, acetals, ethers and cyano moieties were well tolerated under the reaction conditions; importantly, such groups can be used for further chemical transformations. The reaction proceeded equally well with a heteroaryl-substituted alkene (Scheme 2, **7o**, 59 %), although the presence of an alkyl substituent hindered direct alkenylation and simply returned unreacted starting material. The incorporation of a nitro group in the styrene sub-

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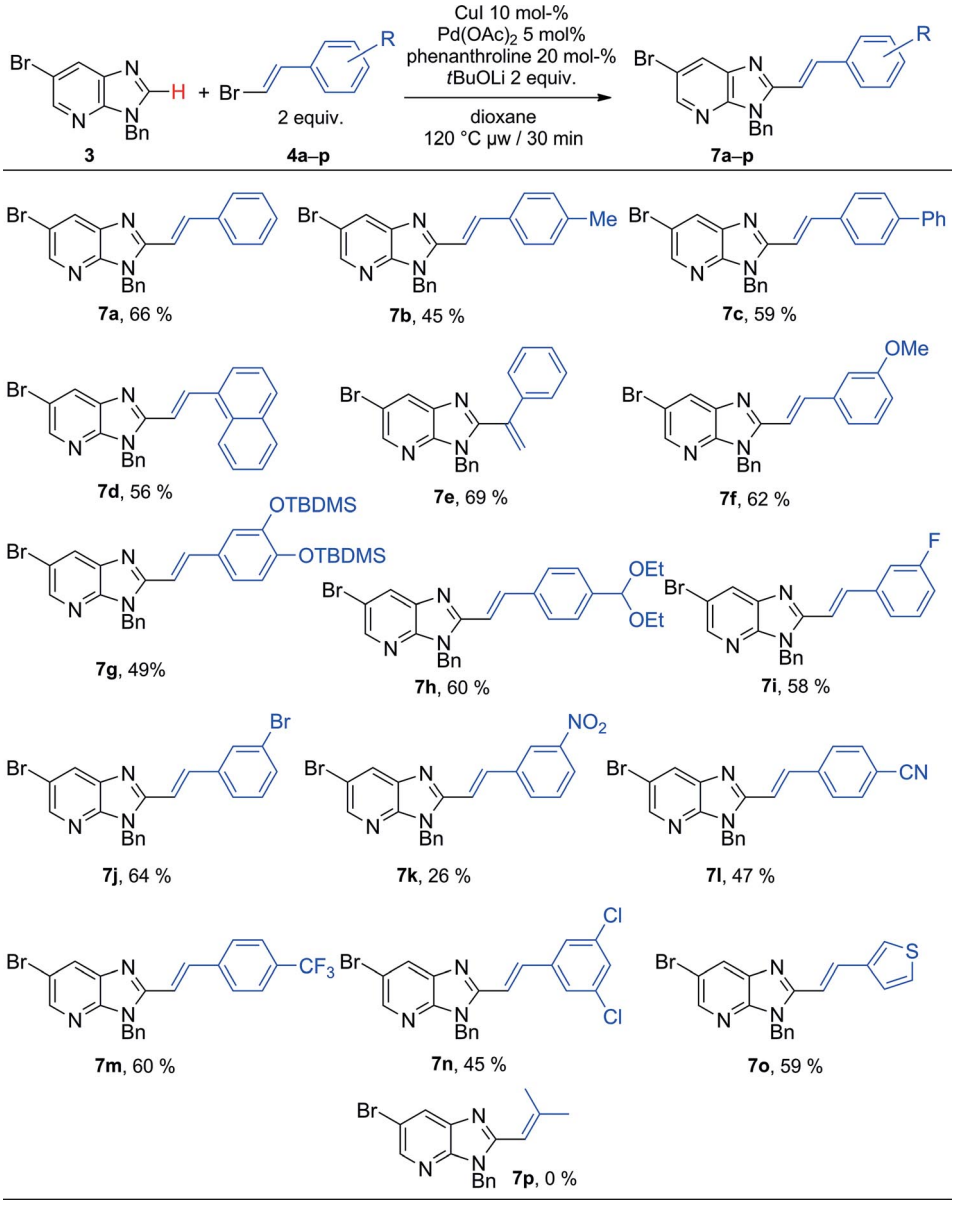

Scheme 2. Scope of direct alkenylation of imidazo[4,5-*b*]pyridines with alkenyl bromides.

strate translated to a disappointing yield of only 26 % (Scheme 2, **7k**).

Next, the reaction scope was investigated with respect to the substitution pattern of the heterocycle (Scheme 3). Substrates representing 5-, 6- and 7-halogenated imidazo[4,5-*b*]pyridines were successfully alkenylated in good yields at the C-2 position, leaving the halide moiety unchanged and available for subsequent functionalizations *en route* to polysubstituted imidazo[4,5-*b*]pyridines. *N*-3-Benzylimidazo[4,5-*b*]pyridine (**11**) itself underwent C-2 alkenylation, albeit in moderate yield (Scheme 3, **11a**, 42 %). 6-Arylimidazo[4,5-*b*]pyridines were also compatible with the microwave-assisted catalytic direct alkenylation conditions although to varying extents based on the precise substituents. The presence of a methoxy substituent was deleterious to the reaction since alkenylated product **12a** was isolated in only 9 % yield. By contrast, the presence of electron-withdrawing groups did not affect the outcome of the reaction, since fluorocyano derivative **14a** was obtained in good yield (Scheme 3, 68 %).

Synthesis of Donor–Acceptor Fluorophores

With the aim of preparing new fluorescent probes, our methodology was applied to the synthesis of a novel push–pull imidazo[4,5-*b*]pyridine bearing a 4-(dimethylamino)phenyl substituent as an electron donor in position 6 and a styryl group bearing an electron-withdrawing function (CF_3) at position 2 of the imidazo[4,5-*b*]pyridine core (Scheme 4). Starting from *N*-3-benzylimidazo[4,5-*b*]pyridine (**3**), Suzuki conditions were applied to give 6-(4-dimethylaminophenyl)imidazo[4,5-*b*]pyridine (**15**) in a non-optimized yield of 34 %. Then, the 4-(trifluoromethyl)phen-

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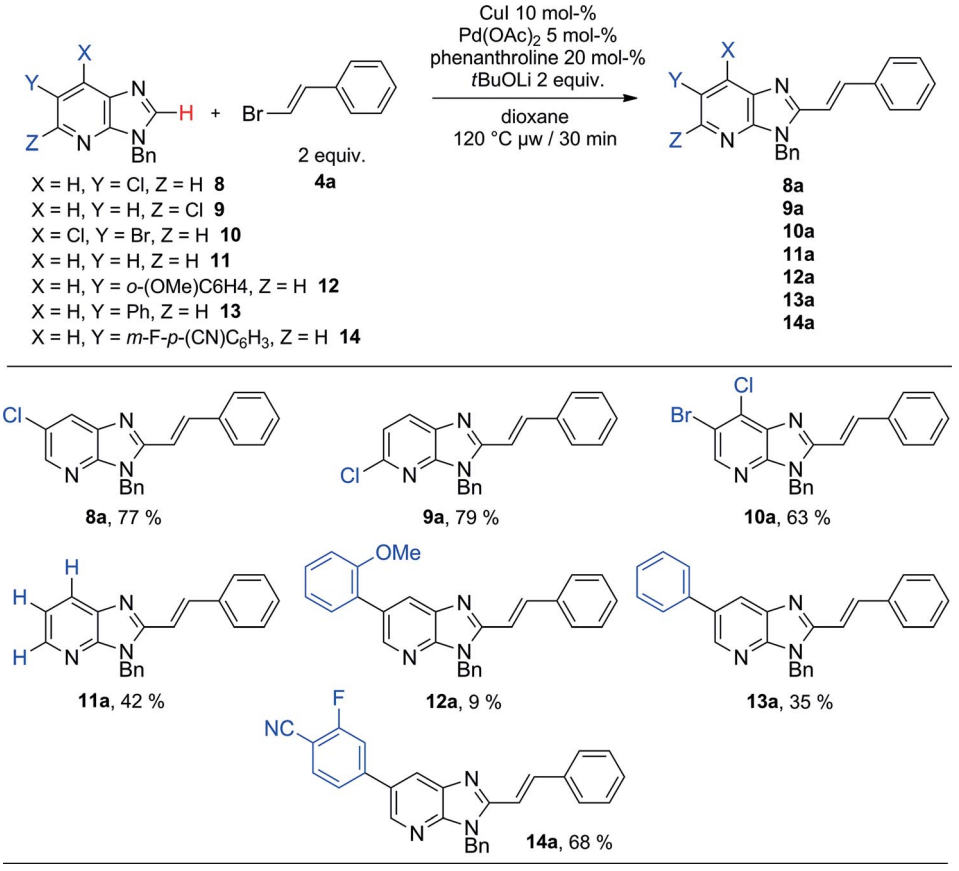
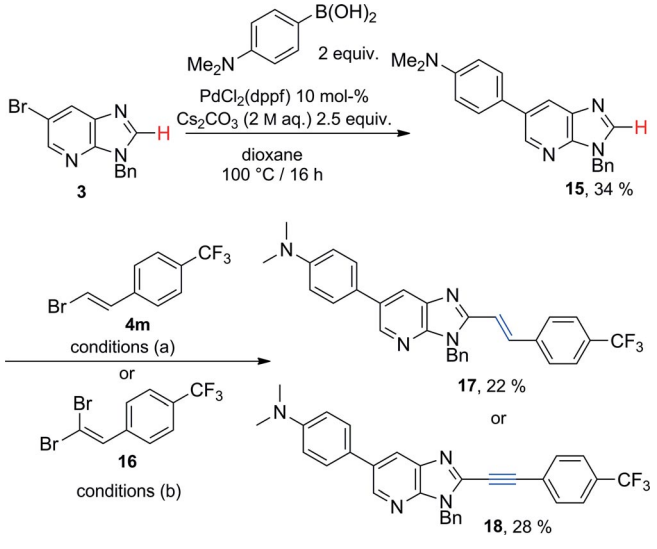


Scheme 3. Scope of direct alkenylation with various substituted imidazo[4,5-*b*]pyridines.

ylvinyl moiety was introduced through the direct C-2 alkenylation process. Pleasingly, compound **17** was isolated in a significantly better yield (22 %) than had been the case for **12a** (9 %, Scheme 3). For the sake of comparison, we also examined the effect on fluorescence capabilities of introducing a triple C–C bond between the donor and acceptor. The ethynyl spacer in **18** was introduced at position 2 of imidazo[4,5-*b*]pyridine via a direct alkynylation reaction using 1,1-dibromo-1-alkene **16** as a coupling partner under catalytic copper conditions in the presence of *t*BuOLi in dioxane at 120 °C (Scheme 4).[17]



Scheme 4. Synthesis of two novel fluorescent 2-vinyl and 2-alkynyl imidazo[4,5-*b*]pyridines. (a) CuI (10 mol-%), 1,10-phenanthroline (20 mol-%), $Pd(OAc)_2$ (5 mol-%), *t*BuOLi (2 equiv.), dioxane, microwave irradiation, 120 °C, 30 min. (b) $CuBr{\cdot}SMe_2$ (10 mol-%), DPEPhos (20 mol-%), *t*BuOLi (6 equiv.), dioxane, reflux, 4 h.

Photophysical Properties

The photophysical properties of compounds **17**, **18** and their precursors **7m** and **15** in various solvents are summarized in Table 2. Derivatives **17** and **18** absorb in the near-UV spectral region (**17**: λ_{max} = 386 nm, **18**: λ_{max} = 375 nm in toluene, Figure 1), displaying rather broad spectra with a clear long-wavelength shoulder (**17**) or maximum (**18**), and exhibit almost no solvatochromism. The blueshift of the absorption spectrum of the ethynyl derivative **18**, compared with vinyl analogue **17**, is in agreement with the data for analogous donor–acceptor systems.[18] Remarkably, both **17** and **18** are fluorescent and display strong solvatofluorochromism (Figure 1), with emission maxima ranging, for **17**, from 459 nm in cyclohexane to 654 nm in MeCN (for **18**: from 438 to 612 nm in these solvents). This behavior leads to solvent-dependent Stokes shifts reaching

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rather high values (**17**: from 4800 cm^{-1} in cyclohexane to 11000 cm^{-1} in MeCN, **18**: from 4600 cm^{-1} in cyclohexane to 10900 cm^{-1} in MeCN). It is worth noting that the Stokes shift values of **17** and **18** are quite close in the same solvents, whereas in most reported systems, the ethynyl derivatives usually display larger Stokes shifts.[18b,18c] A similar situation was observed in the series of π-conjugated oxazole dyes.[18d] The fluorescence quantum yields of compounds **17** and **18** are high in cyclohexane and toluene (ϕ = 60–66 %) but decrease in polar solvents (ϕ < 1 % in MeCN). In a fashion similar to that for **17** and **18**, their precursor **15** displays essentially solvent-independent absorption, albeit at lower wavelengths (λ_{max} = 315 nm in toluene), together with a rather strong solvatofluorochromism, with emission maxima ranging from 379 nm (in cyclohexane) to 515 nm (in MeOH). In contrast to **17** and **18**, the fluorescence quantum yield of **15** remains significant even in polar aprotic solvents (ϕ = 46 % in MeCN). Finally, derivative **7m**, devoid of the electron-donor substituent, shows essentially solvent-independent emission spectra (λ_{em} = 405–411 nm) with a rather small Stokes shift of 2400–3000 cm^{-1}.

To further investigate the effect of donor–acceptor interplay in the ground and excited states of compounds **17** and **18**, we studied changes in their absorption and emission spectra upon protonation with trifluoroacetic acid (TFA) in toluene. The protonation of both molecules is expected to take place at the dimethylamino group, leading to loss of the electron-donor character of the phenyl substituent. Addition of TFA leads to a relatively small blueshift of the absorption bands of both compounds (**17**: from 386 to 355 nm, **18**: from 375 to 347 nm, Figure 2), indicating a moderate decrease in the intramolecular charge transfer in the ground state. At the same time, protonation leads to a nearly complete suppression of the long-wavelength emission of both compounds. Altogether, these observations indicate a weak coupling of electron-donor and -acceptor substituents in the ground state of unprotonated **17** and **18**, along with an efficient charge separation in the excited state and emission from a charge-transfer state;[19] the formation of the charge-transfer state is hindered upon protonation of the molecule. The charge-transfer character of the emissive state is much less pronounced in model compounds **15**, and particularly **7m**, whose photophysical properties resemble those of an apolar chromophore.

Finally, since photostability is very important for fluorescent dyes, the stability of compounds **7m**, **15**, **17** and **18** was assessed by monitoring their absorption spectra upon continuous white-light irradiation (Supporting Information, Figure S1). Under these conditions, the spectra of derivatives **7m** and **17** bearing a vinylene linker, demonstrate significant changes, as ex-

Table 2. Photophysical properties of compounds **7m**, **15**, **17** and **18**.

	Solvent	λ_{abs} [nm] [a]	ε_{abs} [cm^{-1} M^{-1}] [a]	λ_{em} [nm] [b]	Quantum yield φ_F [%]	Stokes shift [cm^{-1}]
15[c]	cyclohexane	308	18300	**379**; 390	63	6000; 6800
	toluene	315	19300	408	67	7200
	dioxane	313	21300	413	62	7700
	AcOEt	312	21400	430	52	8800
	DCM	313	21000	444	61	9400
	THF	310	22600	433	55	9200
	ACN	313	21600	468	46	10600
	MeOH	311	22300	515	2	12700
7m[d]	cyclohexane	371	29000	386; **405**; 431	12	1047; 2300; 3800
	toluene	373	27700	389; **409**; 434	16	1100; 2400; 3800
	dioxane	371	29300	392; **411**; 431	12	1400; 2600; 3800
	AcOEt	368	30800	386; **408**; 427	9	1300; 2700; 3800
	DCM	371	28300	391; **410**; 430	10	1400; 2600; 3700
	THF	369	32900	391; **410**; 431	11	1500; 2700; 3900
	ACN	365	33500	388; **409**; 428	5	1600; 2900; 4000
	MeOH	365	25500	385; **404**; 425	5	1400; 2600; 3900
17[e]	cyclohexane	376	26300	459; **484**	63	4800; 5900
	toluene	386	23600	521	59	6700
	dioxane	385	24700	538	36	7400
	AcOEt	380	27200	603	2	9700
	DCM	382	25900	606	3	9700
	THF	385	25700	607	2	9500
	ACN	380	24300	654	<1 %	11000
	MeOH	378	24200	–	n.d.[g]	–
18[f]	cyclohexane	365	20000	**438**; 458	63	4600; 5600
	toluene	375	18100	490	66	6300
	dioxane	378	18100	511	61	6900
	DCM	372	16800	565	10	9200
	AcOEt	370	20000	568	4	9400
	THF	374	17500	572	3	9300
	ACN	368	18300	612	<1 %	10900
	MeOH	373	17700	–	n.d.	–

[a] Long-wavelength absorption peak or shoulder (as marked with an asterisk in Figure 1). [b] In case of multiple peaks, the strongest one is indicated in bold typeface. [c] λ_{ex} = 315 nm. [d] λ_{ex} = 350 nm. [e] λ_{ex} = 400 nm. [f] λ_{ex} = 380 nm. [g] Not detectable.

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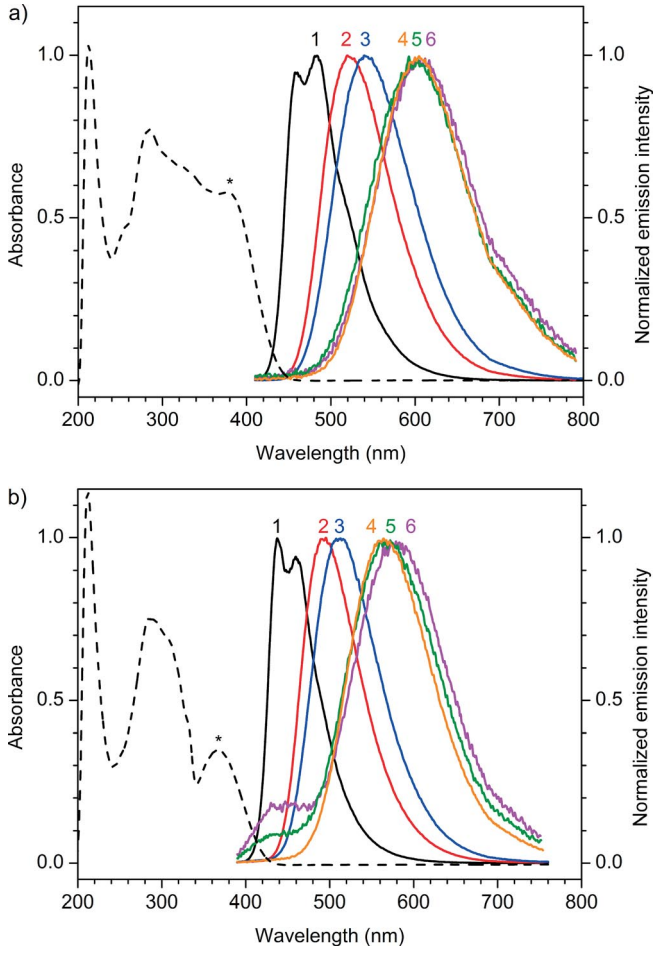

Figure 1. Absorption (dashed lines, c = 20 μM in cyclohexane) and normalized fluorescence emission spectra (solid lines, c = 20 μM) of **17** (a, λ_{ex} = 400 nm) and **18** (b, λ_{ex} = 380 nm) in different solvents: (1) cyclohexane, (2) toluene, (3) 1,4-dioxane, (4) DCM, (5) AcOEt, (6) THF. The long-wavelength absorption peak (or shoulder) is labeled with an asterisk.

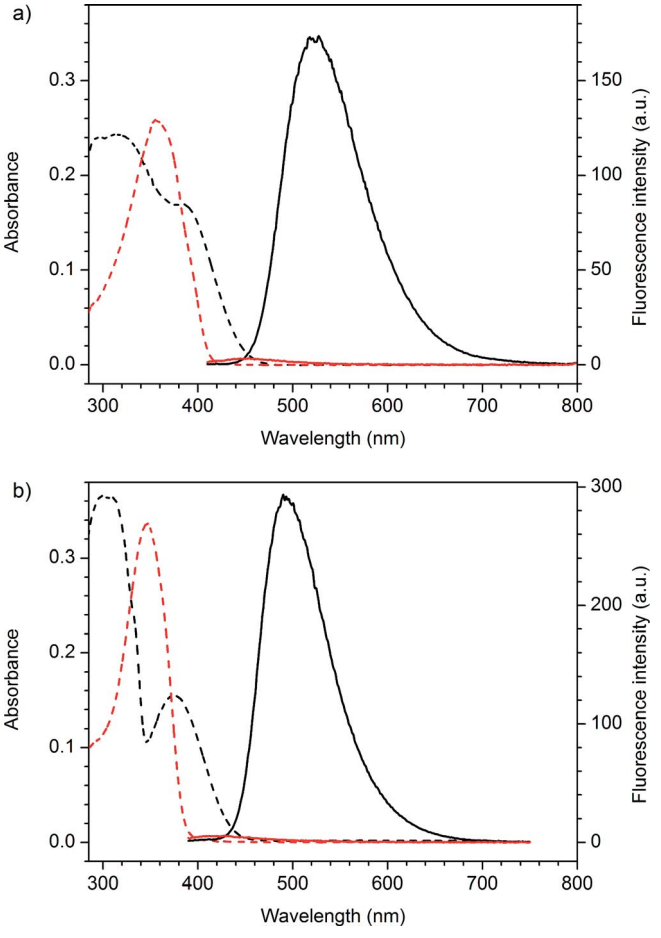

Figure 2. Absorption (dashed lines) and fluorescence emission (solid lines) spectra of a) **17** and b) **18** in the absence (black) and in the presence of 0.1 M TFA (red); c = 10 μM in toluene, λ_{ex} = 400 nm (a) or 380 nm (b).

pected for compounds that undergo an *E–Z* photoisomerization of the double bond.[9,20] The isosbestic points observed in both cases suggest that this photoisomerization process is not accompanied by other degradation reactions. In contrast, the spectra of derivatives **15** and **18** do not show noticeable changes, thus demonstrating the photostability of the donor-substituted imidazo[4,5-*b*]pyridine core and the ethynyl derivative.

Computational Studies

To understand the redshifted emission of compounds **17** and **18**, we analyzed the solvatochromism data using Lippert–Mataga plots (Supporting Information, Figure S2).[21] The slopes extracted from these plots indicate a significant increase of dipole moments upon excitation (**17**: $\Delta\mu$ = 18.9 D, **18**: $\Delta\mu$ = 19.4 D), confirming the charge-transfer character of the emission.

Further, we performed DFT calculations using a hybrid CAM-B3LYP functional with a D95V basis set (Supporting Information, Table S1) in order to understand the nature of electronic transitions. The results demonstrate that, in both **17** and **18**, HOMO and LUMO are, to a great extent, spatially separated (Figure 3); thus, the HOMO is located mostly at the donor-substituted phenyl ring, whereas the LUMO is situated on the acceptor-substituted alkenyl (alkynyl) branch, with a partial overlap of orbitals at the imidazo[4,5-*b*]pyridine core. The spatial separation of HOMO and LUMO is a typical feature of cross-conjugated

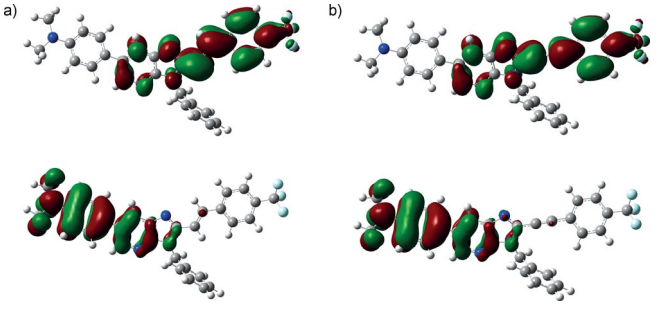

Figure 3. Frontier molecular orbital plots (bottom: HOMO, top: LUMO, isovalue = 0.02) for molecules of a) **17** and b) **18** at ground-state geometries. See Supporting Information for calculation details.

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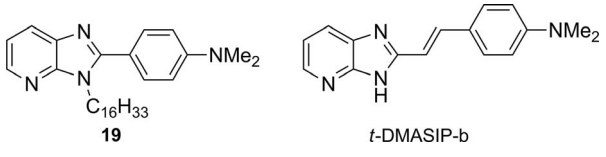
π systems[22] which, in our case, is due to the substitution pattern (2,6) of the imidazo[4,5-*b*]pyridine core. According to TD-DFT calculations, the HOMO → LUMO transition is predominant in the lowest-energy transitions (Supporting Information, Table S2), confirming their charge-transfer character. The experimentally observed blueshift of the absorption maximum for ethynyl derivative **18** with respect to that of the vinylene analogue **17** was correctly reproduced by TD-DFT calculations, although the absolute energies of vertical transitions were less satisfactory (Supporting Information, Table S1). Furthermore, DFT calculations also predict a strong increase in dipole moments upon excitation from the ground state to the first excited state (**17**: μ_g = 6.8 D, μ_e = 23.8 D, **18**: μ_g = 6.8 D, μ_e = 26.6 D), in excellent agreement with experimental data.

Thus, it may be assumed that the long-wavelength emission of 6-donor-2-acceptor-substituted imidazo[4,5-*b*]pyridines **17** and **18** originates from a charge-transfer state (e.g. a TICT state whose geometry is different from the ground state), as it was shown for similar systems.[19,23] The photophysical properties of novel derivatives **17** and **18** may be compared with the prototype imidazo[4,5-*b*]pyridines lacking the acceptor group, namely 1-hexadecyl-2-[4-(dimethylamino)phenyl]imidazo[4,5-*b*]-pyridine **19**[8] and *t*-DMASIP-b (Scheme 5) studied by the Krishnamoorthy group.[9] Whereas all these derivatives absorb in the near-UV region of spectrum, the fluorescence emission of derivatives **17** and **18** is significantly redshifted compared to those of **19** (λ_{max} = 361–431 nm) and *t*-DMASIP-b (λ_{max} = 415–513 nm), leading to significantly higher Stokes shift values (**17** and **18**: up to 11000 cm^{-1}; *t*-DMASIP-b: up to 5720 cm^{-1} in MeCN). Also, the fluorosolvatochromism of **17** and **18** is significantly stronger than in **19**, *t*-DMASIP-b, as well as simpler donor–π–acceptor systems.[18c,24] This highlights the efficiency of the cross-conjugated donor–acceptor scaffold in the design of "mega-Stokes", highly fluorosolvatochromic fluorophores. Remarkably, molecules with spatially separated HOMO and LUMO are attracting increasing levels of interest as scaffolds for the design of fluorescent probes, since they allow the energy levels of these orbitals to be independently modulated.[22b,23a]



Scheme 5. Fluorescent imidazo[4,5-*b*]pyridine derivatives studied in other works.

Conclusions

In summary, we have demonstrated that microwave-assisted direct C-2 alkenylation represents an efficient method for broadly applicable regioselective functionalization of imidazo[4,5-*b*]pyridines. This approach is useful for the synthesis of push–pull-type fluorophores. The large Stokes shift, together with pronounced solvatofluorochromic properties, renders the donor–acceptor substituted imidazo[4,5-*b*]pyridine scaffold a promising platform for the development of fluorescent probes.

Experimental Section

General: Commercially available reagents and solvents were used without further purification, yields refer to isolated and purified products. Reactions were monitored by TLC carried out on 60F-254 silica gel plates and visualized under UV light at 254 and 365 nm. Column chromatography was performed with a Teledyne ISCO Combiflash Companion using pre-packed silica 60 columns. Chemical shifts (δ) of ^{1}H and ^{13}C NMR are reported in ppm and residual non deuterated solvents were used as references. Multiplicities are designated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, br. s = broad singlet, m = multiplet. All indicated high-resolution masses for bromine-containing derivatives correspond to the ^{79}Br isotope. Microwave irradiations were performed with a CEM explorer and temperature measurement of reaction mixtures was achieved using an IR sensor. The method was set with maximum power of 150 W (without Powermax) and maximum pressure of 16 bar. Reaction times refer to the hold time at the desired temperature. Reactions were cooled by compressed air after the heating period was over. Melting points were measured with a Stuart SMP30. Absorption spectra were recorded with an Agilent Cary 300 Bio double-beam spectrophotometer in quartz cells (path length 1 cm), using slit widths of 2 nm and a scan rate of 150 nm min^{-1}. Extinction coefficients were determined using linear Beer–Lambert plots on a range of solution concentrations from 10–30 μM. Fluorescence spectra were recorded with an Agilent Cary Eclipse Bio or Horiba Jobin Yvon Fluoromax 3 fluorimeter in quartz cells with a cross-section of 1 × 0.5 cm, using slit widths of 2.5 or 5 nm. Fluorescence quantum yields were determined by comparative method on 1–3 μM solutions using Quinine sulfate as a reference (φ = 0.54 in 0.5 M H_2SO_4).[25] The photostabilities of compounds **7m**, **15**, **17** and **18** were evaluated in quartz cells using solutions in dioxane (c = 20 μM), upon continuous white light irradiation (150 W lamp, illuminance: 1530 lx).

General Procedure A for the Preparation of Vinyl Bromides:[16] To a solution of the corresponding dibromovinyl derivative (1 equiv.) in diethyl phosphite (3 equiv.) was added triethylamine (3 equiv.). The reaction was stirred at room temperature for 2 h. Diethyl ether was added and the salts were removed by filtration. The filtrate was then concentrated under reduced pressure and the residue was purified by column chromatography in cyclohexane to give the desired product.

(*E*)-{[4-(2-Bromovinyl)-1,2-phenylene]bis(oxy)}bis(*tert*-butyldimethylsilane) (4g): The reaction was carried out following General Procedure A using {[4-(2,2-dibromovinyl)-1,2-phenylene]bis-(oxy)}bis(*tert*-butyldimethylsilane) (1.4 g, 2.6 mmol) to render the desired product as a yellow oil (760 mg, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96 (d, $^3J_{H,H}$ = 13.9 Hz, 1 H), 6.76 (s, 3 H), 6.54 (d, $^3J_{H,H}$ = 13.9 Hz, 1 H), 0.99 (s, 9 H), 0.97 (s, 9 H), 0.19 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 147.2, 136.9, 129.7, 121.3, 119.8, 118.9, 104.2, 26.1, 18.5, 18.6, –4.0 ppm. MS (ES^+): m/z (%) = 442.1 (40) [M + H]$^+$. HRMS (ESI) calcd. for $C_{20}H_{35}BrO_2Si_2$ 442.1359, found 442.1362.

(*E*)-1-(2-Bromovinyl)-3,5-dichlorobenzene (4n): The reaction was carried out following General Procedure A using 1,3-dichloro-5-(2,2-dibromovinyl)benzene (1.2 g, 3.6 mmol) to afford the desired product as a yellow oil (591 g, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (t, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.17 (d, $^4J_{H,H}$ = 1.5 Hz, 2 H), 6.99 (d, $^3J_{H,H}$ = 14.1 Hz, 1 H), 6. 85 (d, $^3J_{H,H}$ = 14.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 135.6, 134.9, 128.2, 124.6, 110.0 ppm. HRMS (APPI) calcd. for $C_8H_5BrCl_2$ 249.8952, found 249.8939.

Compounds **4a**, **4e** and **4p** are commercially available. Compounds **4b**,[26] **4c**,[27] **4d**,[28] **4f**,[27] **4h**,[27] **4i**,[28] **4j**,[29] **4k**,[28] **4l**,[30] **4m**,[31] and

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4o[32] all showed satisfactory spectroscopic data in agreement with those reported in the literature.

General Procedure B for the synthesis of 3*H*-imidazo[4,5-*b*]pyridines and General Procedure C for the benzyl protection of 3*H*-imidazo[4,5-*b*]pyridines.

General Procedure B: To a mixture of the 2,3-diaminopyridine (1 equiv.) in methyl-orthoformate was added dropwise a 10 M HCl aqueous solution (2 equiv.). The reaction was stirred overnight at room temp. Subsequently, the reaction mixture was dissolved in H_2O, neutralized by addition of a 3 M NaOH aqueous solution and extracted with AcOEt. The combined organic layers were dried with anhydrous $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure afforded the desired products with no further purification.

General Procedure C: To a mixture of the 3*H*-imidazo[4,5-*b*]pyridine substrate (1 equiv.) in dry DMF at 0 °C under an argon atmosphere was added NaH (1.1 equiv.) portionwise. The mixture was left stirring at 0 °C for 30 min under an argon atmosphere then BnBr (1.1 equiv.) was added dropwise. The reaction mixture was then warmed up to room temp. and stirred under argon overnight. Subsequently, the DMF was evaporated under reduced pressure and the resulting residue was taken in H_2O and extracted with AcOEt. The combined organic layers were dried on $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a gradient of cyclohexane to AcOEt 40:60 cyclohexane to give the corresponding product.

6-Bromo-3-(tetrahydro-2*H*-pyran-2-yl)-3*H*-imidazo[4,5-*b*]pyridine (1): The first step was carried out following General Procedure B with commercially available 2,3-diamino-5-bromopyridine (12 g, 63.8 mmol) in methyl orthoformate (200 mL) to give the desired 6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**a**) as a dark grey solid (12 g, 95 %), m.p. 223–225 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.47 (s, 1 H), 8.41 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 8.27 (d, $^4J_{H,H}$ = 1.2 Hz, 1 H) ppm. MS (ES$^+$): *m/z* (%) = 198.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_6H_5N_3Br$ 197.9667, found 197.9669. Compound **a** generated in this fashion showed satisfactory spectroscopic data in agreement with those reported in the literature.[33]

To a mixture of 6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**a**) (1.1 g, 5.6 mmol) in AcOEt (15 mL) was added *p*-toluenesulfonic acid monohydrate (106 mg, 0. 56 mmol) and the reaction was heated to 65 °C under an argon atmosphere for 30 min. Subsequently, DHP (1.5 mL, 16.7 mmol) was added and the reaction mixture was refluxed under an argon atmosphere overnight. The mixture was then taken in H_2O and pH was adjusted to 7 with a 3 M NaOH aqueous solution. The aqueous layer was extracted with AcOEt and the combined organic layers were dried on anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a gradient of cyclohexane to 40:60 AcOEt/cyclohexane to give **1** as a yellow oil (1.05 g, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (d, $^4J_{H,H}$ = 1.7 Hz, 1 H), 8.26 (s, 1 H), 8.20 (d, $^4J_{H,H}$ = 1.7 Hz, 1 H), 5.80 (dd, $^3J_{H,H}$ = 9.6, $^4J_{H,H}$ = 2.5 Hz), 4.17 (dd, $^3J_{H,H}$ = 12.3, $^4J_{H,H}$ = 2.5 Hz, 1 H), 3.79 (td, $^3J_{H,H}$ = 11.2, $^4J_{H,H}$ = 2.7 Hz, 1 H), 2.20–1.98 (m, 3 H), 1.87–1.57 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 144.9, 143.1, 136.7, 130.6, 114.3, 81.9, 68.9, 31.9, 25.0, 23.0 ppm. MS (ES$^+$): *m/z* (%) = 198.0 (100) [M – THP + H]$^+$, 282.0 (30) [M + H]$^+$, 585.0 (30) [2M + Na]$^+$. HRMS (ESI) calcd. for $C_{11}H_{13}N_3OBr$ 282.0242, found 282.0245.

6-Bromo-3-(4-methoxybenzyl)-3*H*-imidazo[4,5-*b*]pyridine (2): To a mixture of 6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**a**) (4 g, 20.2 mmol) in dry DMF (58 mL) at 0 °C under an argon atmosphere was added NaH (890 mg, 22.2 mmol) portionwise. The mixture was left stirring at 0 °C for 30 min under argon and then *p*-methoxybenzyl bromide (3.2 mL, 22.2 mmol) was added dropwise. The reaction mixture was then warmed up to room temp. and stirred under an argon atmosphere overnight. Subsequently, the DMF was evaporated under reduced pressure and the resulting residue was taken in H_2O and extracted with AcOEt. The combined organic layers were dried on $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a gradient of cyclohexane to 50:50 AcOEt/cyclohexane to give the corresponding product as a green solid (2.5 g, 39 %), m.p. 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.20 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.99 (s, 1 H), 7.26 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 6.87 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 5.37 (s, 2 H), 3.79 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 145.7, 145.2, 144.9, 136.5, 130.4, 129.4, 127.4, 114.4, 114.0, 55.3, 46.9 ppm. MS (ES$^+$): *m/z* (%) = 318.0 (100) [M + H]$^+$, 359.0 (10) [M + CH_3CN + H]$^+$. HRMS (ESI) calcd. for $C_{14}H_{13}N_3OBr$ 318.0242, found 318.0237.

3-Benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (3): The protection was carried out using 6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**a**) (6 g, 30.3 mmol) in DMF (80 mL) following General Procedure C. Chromatography using a gradient of cyclohexane to 40:60 AcOEt/cyclohexane gave a beige solid (3.4 g, 39 %), m.p. 106–108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, $^4J_{H,H}$ = 1.7 Hz, 1 H), 8.21 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 8.02 (s, 1 H), 7.41–7.26 (m, 5 H), 5.44 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 145.5, 145.2, 136.5, 135.5, 130.5, 129.2, 128.6, 127.9, 114.2, 47.4 ppm. MS (ES$^+$): *m/z* (%) = 288.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{13}H_{11}N_3Br$ 288.0136, found 288.0150.

3-Benzyl-6-chloro-3*H*-imidazo[4,5-*b*]pyridine (8): The first step was carried out following General Procedure B with commercially available 2,3-diamino-5-chloropyridine (6 g, 41.8 mmol) in methyl-orthoformate (137 mL) to give the desired 6-chloro-3*H*-imidazo-[4,5-*b*]pyridine (**b**) as a grey solid (5.9 g, 92 %), m.p. 233–235 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.50 (s, 1 H), 8.34 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H), 8.15 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 149.8, 145.7, 142.1, 131.2, 124.4, 123.4 ppm. MS (ES$^+$): *m/z* (%) = 154.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_6H_5N_3Cl$ 154.0172, found 154.0175.

The cyclization was carried out using 6-chloro-3*H*-imidazo[4,5-*b*]pyridine (**b**) (4 g, 26.1 mmol) in DMF (64 mL) following General Procedure C. Chromatography using a gradient of cyclohexane to 40:60 AcOEt/cyclohexane gave **8** as a beige solid (2.35 g, 37 %), m.p. 104–106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.06 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 8.04 (s, 1 H), 7.35–7.28 (m, 5 H), 5.44 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 145.3, 143.4, 135.8, 135.5, 129.1, 128.5, 127.8, 127.5, 126.3, 47.3 ppm. MS (ES$^+$): *m/z* (%) = 244.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{13}H_{11}N_3Cl$ 244.0642, found 244.0646.

3-Benzyl-5-chloro-3*H*-imidazo[4,5-*b*]pyridine (9): To a mixture of 10 M HCl aqueous solution (28.5 mL, 285 mmol, 3.3 equiv.) in EtOH (170 mL), was added commercially available 2-amino-6-chloro-3-nitropyridine (15 g, 86.4 mmol, 1 equiv.). Iron (14.8 g, 265 mmol, 3 equiv.) was then added portionwise and the medium was heated at reflux for 3 h. Subsequently, the reaction mixture was cooled down to room temp. taken in EtOH and filtered through Celite. The filtrate was concentrated under reduced pressure and the resulting residue was taken in AcOEt and neutralized with a 3 M NaOH aqueous solution. After a novel filtration through Celite, the aqueous layer was extracted with AcOEt. The combined organic layers were dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the desired 2,3-diamino-6-chloropyridine (**c**)

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as a dark brown solid with no further purification (8.6 g, 69 %), m.p. 121–122 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 6.67 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H), 6.33 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 5.77 (s, 2 H), 4.74 (s, 2 H) ppm. Compound **c** generated in this way showed spectroscopic data in agreement with those reported in the literature.[34]

The cyclization was subsequently carried out following General Procedure B with 2,3-diamino-6-chloropyridine (**c**) (8.6 g, 60 mmol) in methyl-orthoformate (195 mL) to give the desired 5-chloro-3*H*-imidazo[4,5-*b*]pyridine (**d**) as a grey solid (9 g, 98 %), m.p. 224–226 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.50 (s, 1 H), 8.07 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.29 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 151.6, 145.2, 143.7, 128.4, 126.1, 117.6 ppm. MS (ES$^+$): *m*/*z* (%) = 154.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_6H_5N_3Cl$ 154.0172, found 154.0172.

The protection was then carried out using 6-chloro-3*H*-imidazo-[4,5-*b*]pyridine (**d**) (6 g, 39.1 mmol) in DMF (112 mL) following General Procedure C. Chromatography using a gradient of cyclohexane to 40:60 AcOEt/cyclohexane gave **9** a light pink solid (3.2 g, 34 %), m.p. 101–103 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.02 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.98 (s, 1 H), 7.36–7.3 (m, 5 H), 7.27 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 5.43 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 146.5, 146.1, 144.2, 135.4, 134.2, 130.5, 129.2, 128.6, 128.1, 118.9, 47.3 ppm. MS (ES$^+$): *m*/*z* (%) = 244.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{13}H_{11}N_3Cl$ 244.0642, found 244.0638.

3-Benzyl-6-bromo-7-chloro-3*H*-imidazo[4,5-*b*]pyridine (10): To a mixture of 6-bromo-3*H*-imidazo[4,5-*b*]pyridine (1 g, 5.1 mmol) in AcOH (5 mL) was added *m*-chloroperbenzoic acid (2.5 g, 10.1 mmol, 2 equiv.). The reaction mixture was stirred at room temp. for 3 d then filtered through a sintered glass disk to afford a first fraction of 6-bromo-3*H*-imidazo[4,5-*b*]pyridine 4-oxide. The filtrate was concentrated under reduced pressure, taken in AcOEt and filtered again to render a second fraction of the *N*-oxide. Both fractions of 6-bromo-3*H*-imidazo[4,5-*b*]pyridine 4-oxide were taken in AcOEt and the resulting suspension was refluxed for 1 h. Subsequent filtration through sintered glass disk afforded 6-bromo-3*H*-imidazo[4,5-*b*]pyridine 4-oxide with no trace of benzoic acid. The solid was distributed in microwave tubes in 250 mg portions and $POCl_3$ (1.5 mL) was added in each tube. The reaction mixture was heated under microwave irradiation at 80 °C for 10 min. Subsequently, the crude materials were poured on ice and neutralized with a 3 M NaOH aqueous solution and the aqueous layer was extracted with AcOEt. The combined organic layers were dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to give the desired product as a beige solid **e** in inseparable mixture (ratio 85:15) with the 6-bromo-5-chloro-3*H*-imidazo[4,5-*b*]pyridine isomer (620 mg, 53 %), m.p. 199–201 °C. ^{1}H NMR (300 mHz, CD$_3$OD): δ = 8.51 (s, 2 H), 8.46 (s, 0.33 H, 5-Cl isomer) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 146.6, 145.8, 145.5, 142.3, 133.7, 133.2, 132.3, 130.4, 128.8, 127.8, 113.1, 111.1 ppm. MS (ES$^+$): *m*/*z* (%) = 231.9 (100) [M + H]$^+$, 273.0 (20) [M + CH$_3$CN + H]$^+$. HRMS (ESI) calcd. for $C_6H_4N_3ClBr$ 231.9277, found 231.9287.

The inseparable mixture (**e**) of 6-bromo-7-chloro-3*H*-imidazo[4,5-*b*]pyridine and 6-bromo-5-chloro-3*H*-imidazo[4,5-*b*]pyridine (600 mg, 2.6 mmol) was used in DMF (9 mL) with NaH (186 mg, 1.8 equiv.) and BnBr (430 µL, 1.4 equiv.). Chromatography using a gradient of cyclohexane to AcOEt 40:60 cyclohexane gave the isolated desired regioisomer **10** as a yellow oil (200 mg, 23 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.52 (s, 1 H), 8.04 (s, 1 H), 7.31 (s, 5 H), 5.43 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 146.6, 146.2, 145.0, 135.1, 135.0, 134.4, 129.2, 128.6, 127.8, 115.0, 47.7 ppm. MS (ES$^+$): *m*/*z* (%) = 322.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{13}H_{10}N_3ClBr$ 321.9747, found 321.9738.

3-Benzyl-3*H*-imidazo[4,5-*b*]pyridine (11): To a mixture of 6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**a**) (1 g, 5.1 mmol) in MeOH (20 mL) was added 10 % palladium on carbon (537 mg, 0.5 mmol, 10 mol-%). The reaction mixture was flushed with argon then purged twice before flushing with hydrogen. The medium was stirred at room temp. overnight. Subsequently, filtration of the reaction mixture on Celite and concentration of the filtrate under reduced pressure rendered 3*H*-imidazo[4,5-*b*]pyridine (**f**) as a grey solid with no further purification (540 mg, 90 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.43 (s, 1 H), 8.34 (dd, $^3J_{H,H}$ = 4.5, $^4J_{H,H}$ = 1.0 Hz, 1 H), 8.01 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.0 Hz, 1 H), 7.21 (dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 4.5 Hz, 1 H) ppm. Compound **f** generated in this fashion showed spectroscopic data in agreement with those reported in the literature.[33]

The protection was subsequently carried out using 3*H*-imidazo[4,5-*b*]pyridine (**f**) (500 mg, 4.2 mmol) in DMF (9 mL) with NaH (300 mg, 1.8 equiv.) and BnBr (700 µL, 1.4 equiv.). Chromatography using a cyclohexane to 40:60 AcOEt/cyclohexane gradient elution gave **11** as a light brown solid (200 mg, 23 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.43 (dd, $^3J_{H,H}$ = 4.7, $^4J_{H,H}$ = 1.3 Hz, 1 H), 8.09 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.3 Hz, 1 H), 8.03 (s, 1 H), 7.36–7.27 (m, 5 H), 7.24 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H), 5.48 (s, 2 H) ppm. Compound **11** generated in this fashion showed satisfactory spectroscopic data in agreement with those reported in the literature.[35]

General Procedure D for Suzuki Coupling: To a mixture of 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (1 equiv.), $PdCl_2$-(dppf) (5 mol-%) and the corresponding boronic acid (1.5 equiv.) in dioxane was added a 2 M aqueous solution of Cs_2CO_3 (2 equiv.). The reaction mixture was heated at 100 °C under an argon atmosphere overnight. Subsequently, H_2O is added and the mixture is extracted with AcOEt. The combined organic layers were dried on anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a gradient of cyclohexane to 60:40 AcOEt/cyclohexane to give the corresponding product.

3-Benzyl-6-(2-methoxyphenyl)-3*H*-imidazo[4,5-*b*]pyridine (12): The reaction was performed following General Procedure D on 150 mg of substrate using (2-methoxyphenyl)boronic acid (119 mg, 0.8 mmol) to afford the desired product as a yellow oil (120 mg, 73 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.59 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.26 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.04 (s, 1 H), 7.41–7.33 (m, 7 H), 7.09 (d, *J* = 7.3 Hz, 1 H), 7.03 (d, *J* = 9.0 Hz, 1 H), 5.51 (s, 2 H), 3.84 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 156.6, 146.0, 145.8, 144.1, 135.9, 135.0, 131.2, 129.4, 129.1, 129.0, 128.9, 128.3, 127.8, 127.8, 121.1, 111.2, 55.5, 47.1 ppm. MS (ES$^+$): *m*/*z* (%) = 316.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{20}H_{18}N_3O$ 316.1450, found 316.1451.

3-Benzyl-6-phenyl-3*H*-imidazo[4,5-*b*]pyridine (13): The reaction was performed following General Procedure D on 300 mg of substrate, using phenylboronic acid (190 mg, 1.6 mmol) to afford the desired product as a beige solid (242 mg, 81 %), m.p. 134–136 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.67 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.26 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.07 (s, 1 H), 7.63 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H), 7.50 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H), 7.41 (d, *J* = 7.4 Hz, 1 H), 7.34 (s, 5 H), 5.51 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 146.6, 144.6, 144.0, 138.8, 135.8, 135.5, 132.6, 129.1, 128.4, 127.8, 127.6, 127.5, 126.4, 47.2 ppm. MS (ES$^+$): *m*/*z* (%) = 286.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{19}H_{16}N_3$ 286.1344, found 286.1331.

4-(3-Benzyl-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-2-fluorobenzonitrile (14): The reaction was performed following General Procedure D on 300 mg of substrate using (4-cyano-3-fluorophenyl)boronic acid (258 mg, 1.6 mmol) to afford the desired product as a beige solid

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(290 mg, 85 %), m.p. 201–203 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.25 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.13 (s, 1 H), 7.74 (dd, *J* = 8.1, 6.7 Hz, 1 H), 7.53 (dd, *J* = 8.1, 1.8 Hz, 1 H), 7.48 (dd, *J* = 10.2, 1.5 Hz, 1 H), 7.35 (m, 5 H), 5.52 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 161.8, 147.7, 146.3 (d, $J_{F,C}$ = 8.2 Hz), 145.5, 143.6, 135.5, 134.1, 129.4, 129.1, 128.5, 127.8, 126.5, 123.7 (d, $J_{F,C}$ = 3.2 Hz), 115.2 (d, $J_{F,C}$ = 20.5 Hz), 113.9, 100.1 (d, $J_{F,C}$ = 15.8 Hz), 47.4 ppm. MS (ES$^+$): *m/z* (%) = 329.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{20}H_{14}N_4F$ 329.1202, found 329.1198.

4-(3-Benzyl-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-*N*,*N*-dimethylaniline (15): The reaction was performed following General Procedure D on 300 mg of substrate using (4-dimethylaminophenyl)boronic acid (515 mg, 3.1 mmol) and doubling the quantities of catalyst and base to afford the desired product as a grey solid (100 mg, 34 %), m.p. 199–201 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H), 8.19 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H), 8.06 (s, 1 H), 7.53 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.33 (s, 5 H), 6.85 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 5.50 (s, 2 H), 3.01 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 144.9, 143.3, 142.5, 134.9, 134.6, 131.7, 128.0, 127.2, 127.1, 126.7, 125.6, 124.3, 111.9, 46.1, 39.5 ppm. MS (ES$^+$): *m/z* (%) = 239.1 (40) [M – Bn + H]$^+$, 329.2 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{21}N_4$ 329.1766, found 329.1770.

General Procedure E for Direct Alkenylation of Imidazo[4,5-*b*]-pyridines: In a microwave tube under an argon atmosphere were introduced the imidazo[4,5-*b*]pyridine substrate (1 equiv.), CuI (10 mol-%), 1,10-phenanthroline (20 mol-%), $Pd(OAc)_2$ (5 mol-%) and lithium *tert*-butoxide (2 equiv.), followed by the desired vinyl bromide (2 equiv.) as a solution in dioxane (2 mL). The tube was flushed with argon, sealed and heated under microwave irradiation at 120 °C for 30 min. Subsequently, the mixture was taken in water and extracted with AcOEt. The combined organic layers were dried on anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a gradient of cyclohexane to 40:60 AcOEt/cyclohexane to give the corresponding product.

(*E*)-6-Bromo-2-styryl-3-(tetrahydro-2*H*-pyran-2-yl)-3*H*-imidazo[4,5-*b*]pyridine (5a): The reaction was performed following General Procedure E on 6-bromo-3-(tetrahydro-2*H*-pyran-2-yl)-3*H*-imidazo[4,5-*b*]pyridine (**1**) (90 mg, 0.3 mmol) using β-bromostyrene (117 mg, 0.6 mmol) to afford the desired product as a light yellow solid (45 mg, 37 %), m.p. 139–141 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H), 8.10 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.96 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H), 7.62 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H), 7.54 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H), 7.45–7.35 (m, 3 H), 6.05 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H), 4.31 (d, $^3J_{H,H}$ = 10.6 Hz, 1 H), 3.81 (t, $^3J_{H,H}$ = 10.8 Hz, 1 H), 2.32–2.24 (m, 1 H), 2.11–2.08 (m, 1 H), 1.94–1.71 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 146.0, 143.9, 138.3, 136.3, 135.8, 129.5, 129.0, 128.8, 127.6, 115.5, 114.4, 82.5, 69.4, 31.8, 25.3, 23.3 ppm. MS (ES$^+$): *m/z* (%) = 302.0 (80) [M – THP + H]$^+$, 384.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{19}H_{19}N_3OBr$ 384.0711, found 384.0717.

(*E*)-6-Bromo-3-(4-methoxybenzyl)-2-styryl-3*H*-imidazo[4,5-*b*]-pyridine (6a): The reaction was performed following General Procedure E on 6-bromo-3-(4-methoxybenzyl)-3*H*-imidazo[4,5-*b*]pyridine (**2**) (90 mg, 0.3 mmol) using β-bromostyrene (104 mg, 0.6 mmol) to afford the desired product as a beige solid (62 mg, 52 %), m.p. 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1 H), 8.13 (s, 1 H), 7.99 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 7.52 (s, 2 H), 7.38 (s, 3 H), 7.18 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H), 7.05 (d, $^3J_{H,H}$ = 14.9 Hz, 1 H), 6.84 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H), 5.53 (s, 2 H), 3.76 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 153.3, 147.0, 144.4, 139.0, 136.6, 135.4, 129.7, 129.0, 128.7, 128.3, 128.1, 127.6, 115.6, 114.4, 112.9, 55.3, 45.1 ppm. MS (ES$^+$): *m/z* (%) = 420.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{22}H_{19}N_3OBr$ 420.0711, found 420.0721.

(*E*)-3-Benzyl-6-bromo-2-styryl-3*H*-imidazo[4,5-*b*]pyridine (7a): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using β-bromostyrene (127 mg, 0.7 mmol) to afford the desired product as a beige solid (91 mg, 66 %), m.p. 154–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.14 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.98 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.50 (m, 2 H), 7.38–7.21 (m, 8 H), 7.01 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 5.59 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 147.0, 144.5, 139.1, 136.6, 136.0, 135.4, 129.7, 129.1, 129.0, 128.7, 128.2, 127.6, 126.8, 114.5, 112.8, 45.5 ppm. MS (ES$^+$): *m/z* (%) = 390.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{17}N_3Br$ 390.0606, found 390.0612.

(*E*)-3-Benzyl-6-bromo-2-(4-methylstyryl)-3*H*-imidazo[4,5-*b*]pyridine (7b): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-4-methylbenzene (137 mg, 0.7 mmol) to afford the desired product as a light yellow solid (65 mg, 45 %), m.p. 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 8.13 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.96 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 7.41 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.32–7.26 (m, 3 H), 7.23–7.17 (m, 4 H), 6.96 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 5.58 (s, 2 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 147.1, 144.3, 140.1, 139.2, 136.6, 136.0, 132.7, 129.7, 129.0, 128.6, 128.1, 127.5, 126.8, 114.4, 111.7, 45.5, 21.5 ppm. MS (ES$^+$): *m/z* (%) = 404.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{22}H_{19}N_3Br$ 404.0762, found 404.0762.

(*E*)-2-{2-[(1,1′-Biphenyl)-4-yl]vinyl}-3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (7c): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-4-(2-bromovinyl)-1,1′-biphenyl (180 mg, 0.7 mmol) to afford the desired product as a light yellow solid (90 mg, 59 %), m.p. 253–255 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H), 8.16 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.03 (d, $^3J_{H,H}$ = 15.7 Hz, 1 H), 7.64–7.57 (m, 6 H), 7.48–7.43 (m, 2 H), 7.40–7.27 (m, 5 H), 7.23 (s, 1 H), 7.05 (d, $^3J_{H,H}$ = 15.7 Hz, 1 H), 5.61 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 147.1, 144.5, 142.5, 140.2, 138.6, 136.6, 136.0, 134.4, 129.1, 128.9, 128.7, 128.2, 128.1, 127.8, 127.6, 127.0, 126.8, 114.5, 112.6, 45.5 ppm. MS (ES$^+$): *m/z* (%) = 466.1 (100) [M + H]$^+$, 931.2 (10) [2M + H]$^+$. HRMS (ESI) calcd. for $C_{27}H_{21}N_3Br$ 466.0919, found 466.0927.

(*E*)-3-Benzyl-6-bromo-2-[2-(naphthalen-1-yl)vinyl]-3*H*-imidazo[4,5-*b*]pyridine (7d): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)naphthalene (162 mg, 0.7 mmol) to afford the desired product as a yellow solid (88 mg, 56 %), m.p. 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.77 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H), 8.42 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H), 8.23–8.20 (m, 2 H), 7.87 (d, *J* = 8.7 Hz, 2 H), 7.67 (d, *J* = 6.7 Hz, 1 H), 7.62–7.43 (m, 4 H), 7.36–7.29 (m, 3 H), 7.23 (s, 1 H), 7.10 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H), 5.63 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 146.0, 143.5, 135.5, 135.0, 135.0, 132.6, 131.9, 130.3, 128.9, 128.0, 127.8, 127.6, 127.1, 125.7, 125.7, 125.2, 124.4, 123.3, 122.6, 114.6, 113.4, 44.5 ppm. MS (ES$^+$): *m/z* (%) = 440.1 (100) [M + H]$^+$, 879.1 (10) [2M + H]$^+$. HRMS (ESI) calcd. for $C_{25}H_{19}N_3Br$ 440.0762, found 440.0759.

3-Benzyl-6-bromo-2-(1-phenylvinyl)-3*H*-imidazo[4,5-*b*]pyridine (7e): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine **3** (100 mg, 0.4 mmol) using α-bromostyrene (127 mg, 0.7 mmol) to afford the desired product as a brownish oil (94 mg, 69 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.22 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 7.32 (d,

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$^3J_{H,H}$ = 5.1 Hz, 3 H), 7.26 (s, 2 H), 7.22–7.15 (m, 3 H), 6.97 (d, $^3J_{H,H}$ = 3.6 Hz, 2 H), 5.97 (s, 1 H), 5.73 (s, 1 H), 5.19 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 147.2, 145.1, 139.2, 137.3, 136.1, 135.9, 129.9, 129.0, 128.9, 128.6, 127.8, 127.2, 126.9, 122.6, 114.2, 46.6 ppm. MS (ES^+): *m/z* (%) = 390.1 (100) $[M + H]^+$. HRMS (ESI) calcd. for $C_{21}H_{17}N_3Br$ 390.0606, found 390.0602.

(*E*)-3-Benzyl-6-bromo-2-(3-methoxystyryl)-3*H*-imidazo[4,5-*b*]pyridine (7f): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-3-methoxybenzene (148 mg, 0.7 mmol) to afford the desired product as a yellow solid (87 mg, 62 %), m.p. 141–143 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 8.14 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.94 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.30 (t, $^3J_{H,H}$ = 7.8 Hz, 4 H), 7.21 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.11 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H), 7.02 (s, 1 H), 6.94 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 6.90 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.8 Hz, 1 H), 5.59 (s, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 153.2, 147.0, 144.5, 139.0, 136.8, 136.6, 136.0, 130.0, 129.1, 128.8, 128.2, 126.8, 120.1, 115.2, 114.5, 113.2, 112.9, 55.3, 45.5 ppm. MS (ES^+): *m/z* (%) = 420.1 (100) $[M + H]^+$. HRMS (ESI) calcd. for $C_{22}H_{19}N_3OBr$ 420.0711, found 420.0718.

(*E*)-3-Benzyl-2-{3,4-bis[(*tert*-butyldimethylsilyl)oxy]styryl}-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (7g): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-{[4-(2-bromovinyl)-1,2-phenylene]bis(oxy)}bis(*tert*-butyldimethylsilane) (308 mg, 0.7 mmol) to afford the desired product as a light yellow solid (120 mg, 49 %), m.p. 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H), 8.11 (s, 1 H), 7.85 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 7.31–7.15 (m, 5 H), 7.03–6.93 (m, 2 H), 6.81 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H), 6.76 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 5.57 (s, 2 H), 0.99 (s, 9 H), 0.98 (s, 9 H), 0.21 (d, *J* = 2.9 Hz, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 148.9, 147.2, 147.1, 144.1, 138.9, 136.6, 136.1, 129.1, 129.0, 128.4, 128.1, 126.8, 121.3, 121.3, 120.1, 114.3, 110.5, 108.2, 45.5, 25.9, 25.9, 18.5, –4.1 ppm. MS (ES^+): *m/z* (%) = 650.2 (100) $[M + H]^+$, 1299.4 (10) $[2M + H]^+$. HRMS (ESI) calcd. for $C_{33}H_{45}N_3O_2BrSi_2$ 650.2234, found 650.2226.

(*E*)-3-Benzyl-6-bromo-2-[4-(diethoxymethyl)styryl]-3*H*-imidazo[4,5-*b*]pyridine (7h): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-4-(diethoxymethyl)benzene (198 mg, 0.7 mmol) to afford the desired product as a yellow solid (110 mg, 60 %), m.p. 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.14 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 7.98 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.50 (s, 4 H), 7.36–7.27 (m, 3 H), 7.24–7.18 (m, 2 H), 7.01 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.59 (s, 2 H), 5.50 (s, 1 H), 3.81–3.28 (m, 4 H), 1.24 (t, *J* = 7.0 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 147.0, 144.5, 140.7, 138.7, 136.6, 136.0, 135.4, 129.1, 128.8, 128.2, 127.4, 127.3, 126.8, 114.5, 113.0, 101.1, 61.1, 45.5, 26.9, 15.2 ppm. MS (ES^+): *m/z* (%) = 418.1 (30) [deprotected aldehyde + H]$^+$, 492.1 (100) $[M + H]^+$. HRMS (ESI) calcd. for $C_{26}H_{27}N_3O_2Br$ 492.1287, found 492.1266.

(*E*)-3-Benzyl-6-bromo-2-(3-fluorostyryl)-3*H*-imidazo[4,5-*b*]pyridine (7i): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-3-fluorobenzene (140 mg, 0.7 mmol) to afford the desired product as a beige solid (85 mg, 58 %), m.p. 141–143 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1 H), 8.15 (s, 1 H), 7.93 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 7.38–7.26 (m, 5 H), 7.23–7.14 (m, 3 H), 7.09–7.03 (m, 1 H), 6.99 (d, $^3J_{H,H}$ = 15.7 Hz, 1 H), 5.60 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4 (d, $J_{F,C}$ = 245 Hz), 152.8, 147.0, 144.8, 137.7, 137.6 (d, $J_{F,C}$ = 4.4 Hz), 136.5, 135.9, 130.4 (d, $J_{F,C}$ = 8.3 Hz), 129.1, 128.9, 128.2, 126.8, 123.7 (d, $J_{F,C}$ = 2.6 Hz), 116.4 (d, $J_{F,C}$ = 21.4 Hz), 114.6, 114.1, 113.5 (d, $J_{F,C}$ = 21.9 Hz), 45.56 ppm. MS (ES^+): *m/z* (%) = 408.0 (100) $[M + H]^+$. HRMS (ESI) calcd. for $C_{21}H_{16}N_3BrF$ 408.0512, found 408.0499.

(*E*)-3-Benzyl-6-bromo-2-(3-bromostyryl)-3*H*-imidazo[4,5-*b*]pyridine (7j): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-bromo-3-(2-bromovinyl)benzene (182 mg, 0.7 mmol) to afford the desired product as a beige solid (104 mg, 64 %), m.p. 177–179 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.15 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 7.89 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.62 (s, 1 H), 7.47 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H), 7.41 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H), 7.35–7.26 (m, 3 H), 7.25–7.15 (m, 3 H), 6.99 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.60 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.7, 147.0, 144.8, 137.5, 137.3, 136.5, 135.9, 132.4, 130.5, 130.0, 129.2, 129.0, 128.2, 126.8, 126.4, 123.1, 114.6, 114.2, 45.6 ppm. MS (ES^+): *m/z* (%) = 468.0 (100) $[M + H]^+$. HRMS (ESI) calcd. for $C_{21}H_{16}N_3Br_2$ 467.9711, found 467.9712.

(*E*)-3-Benzyl-6-bromo-2-(3-nitrostyryl)-3*H*-imidazo[4,5-*b*]pyridine (7k): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-3-nitrobenzene (158 mg, 0.7 mmol) to afford the desired product as a brown solid (40 mg, 26 %), m.p. 210–212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (s, 1 H), 8.34 (s, 1 H), 8.17 (s, 2 H), 8.00 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.75 (d, *J* = 6.9 Hz, 1 H), 7.56 (t, *J* = 7.8 Hz, 1 H), 7.38–7.28 (m, 2 H), 7.28–7.19 (m, 3 H), 7.12 (d, $^3J_{H,H}$ = 16.4 Hz, 1 H), 5.64 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 148.8, 147.0, 145.2, 137.2, 136.4, 136.0, 135.8, 133.5, 130.0, 129.2, 129.2, 128.4, 126.8, 123.9, 121.4, 115.9, 114.8, 45.7 ppm. MS (ES^+): *m/z* (%) = 435.0 (100) $[M + H]^+$, 476.1 (10) $[M + CH_3CN + H]^+$. HRMS (ESI) calcd. for $C_{21}H_{16}N_4O_2Br$ 435.0457, found 435.0462.

(*E*)-4-[2-(3-Benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridin-2-yl)vinyl]benzonitrile (7l): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (90 mg, 0.3 mmol) using (*E*)-4-(2-bromovinyl)benzonitrile (130 mg, 0.6 mmol) to afford the desired product as a light yellow solid (60 mg, 47 %), m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.18 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 7.97 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 7.67 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 7.57 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.33 (m, 2 H), 7.22 (m, 3 H), 7.08 (d, $^3J_{H,H}$ = 15.7 Hz, 1 H), 5.62 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 147.0, 145.3, 139.7, 136.6, 136.5, 135.9, 132.7, 129.2, 129.2, 128.3, 127.8, 126.7, 118.5, 116.3, 114.8, 112.6, 45.6 ppm. MS (ES^+): *m/z* (%) = 415.1 (50) $[M + H]^+$. HRMS (ESI) calcd. for $C_{22}H_{16}N_4Br$ 415.0558, found 415.0552.

(*E*)-3-Benzyl-6-bromo-2-[4-(trifluoromethyl)styryl]-3*H*-imidazo[4,5-*b*]pyridine (7m): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene (174 mg, 0.7 mmol) to afford the desired product as a beige solid (90 mg, 60 %), m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.16 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 7.98 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.63 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.58 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.40–7.28 (m, 3 H), 7.24–7.17 (m, 2 H), 7.07 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.62 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 147.0, 145.0, 138.7, 137.1, 136.5, 135.9, 129.2, 129.1, 128.3, 127.6, 126.8, 126.0, 122.1, 118.5, 115.3, 114.7, 45.6 ppm. MS (ES^+): *m/z* (%) = 458.0 (100) $[M + H]^+$. HRMS (ESI) calcd. for $C_{22}H_{16}N_3BrF_3$ 458.0480, found 458.0481.

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(*E*)-3-Benzyl-6-bromo-2-(3,5-dichlorostyryl)-3*H*-imidazo[4,5-*b*]-pyridine (7n): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-1-(2-bromovinyl)-3,5-dichlorobenzene (175 mg, 0.7 mmol) to afford the desired product as a beige solid (74 mg, 45 %), m.p. 191–193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.16 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 7.83 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.37–7.28 (m, 6 H), 7.20 (d, $^3J_{H,H}$ = 6.3 Hz, 2 H), 6.98 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.61 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 147.0, 146.9, 145.1, 138.4, 136.4, 135.9, 135.8, 135.6, 129.2, 129.1, 128.3, 126.8, 125.7, 115.6, 114.8, 45.6 ppm. MS (ES$^+$): *m/z* (%) = 458.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{15}N_3Cl_2Br$ 457.9826, found 457.9819.

(*E*)-3-Benzyl-6-bromo-2-[2-(thiophen-3-yl)vinyl]-3*H*-imidazo[4,5-*b*]pyridine (7o): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-3*H*-imidazo[4,5-*b*]pyridine (**3**) (100 mg, 0.4 mmol) using (*E*)-3-(2-bromovinyl)thiophene (131 mg, 0.7 mmol) to render the desired product as a brown solid (75 mg, 59 %), m.p. 154–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H), 8.12 (s, 1 H), 7.97 (d, $^3J_{H,H}$ = 15.4 Hz, 1 H), 7.45 (s, 1 H), 7.35–7.26 (m, 5 H), 7.21 (m, 2 H), 6.81 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 5.57 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5, 147.1, 144.3, 138.5, 136.6, 136.0, 132.9, 129.1, 128.6, 128.1, 127.0, 127.0, 126.8, 124.7, 114.4, 112.5, 45.5 ppm. MS (ES$^+$): *m/z* (%) = 396.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{19}H_{15}N_3SBr$ 396.0170, found 396.0166.

(*E*)-3-Benzyl-6-chloro-2-styryl-3*H*-imidazo[4,5-*b*]pyridine (8a): The reaction was performed following General Procedure E on 3-benzyl-6-chloro-3*H*-imidazo[4,5-*b*]pyridine (**8**) (100 mg, 0.4 mmol) using styryl bromide (150 mg, 0.8 mmol) to afford the desired product as a beige solid (110 mg, 77 %), m.p. 166–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H), 8.00 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.00 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 7.51 (m, 2 H), 7.41–7.27 (m, 6 H), 7.25–7.19 (m, 2 H), 7.02 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.60 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5, 146.8, 142.5, 139.1, 136.1, 135.9, 135.4, 129.7, 129.1, 129.0, 128.2, 127.6, 126.8, 126.7, 125.9, 112.8, 45.5 ppm. MS (ES$^+$): *m/z* (%) = 346.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{17}N_3Cl$ 346.1111, found 346.1112.

(*E*)-3-Benzyl-5-chloro-2-styryl-3*H*-imidazo[4,5-*b*]pyridine (9a): The reaction was performed following General Procedure E on 3-benzyl-5-chloro-3*H*-imidazo[4,5-*b*]pyridine (**9**) (100 mg, 0.4 mmol) using styryl bromide (150 mg, 0.8 mmol) to afford the desired product as a beige solid (114 mg, 79 %), m.p. 149–151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.96 (d, $^3J_{H,H}$ = 15.3 Hz, 1 H), 7.52–7.46 (m, 2 H), 7.39–7.27 (m, 6 H), 7.25–7.15 (m, 3 H), 6.99 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 5.60 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 147.7, 145.2, 138.6, 136.0, 135.5, 134.3, 129.6, 129.1, 128.9, 128.7, 128.1, 127.5, 126.9, 119.3, 112.9, 45.5 ppm. MS (ES$^+$): *m/z* (%) = 346.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{17}N_3Cl$ 346.1111, found 346.1104.

(*E*)-3-Benzyl-6-bromo-7-chloro-2-styryl-3*H*-imidazo[4,5-*b*]pyridine (10a): The reaction was performed following General Procedure E on 3-benzyl-6-bromo-7-chloro-3*H*-imidazo[4,5-*b*]pyridine (**10**) (100 mg, 0.3 mmol) using β-bromostyrene (114 mg, 0.6 mmol) to afford the desired product as a yellow solid (80 mg, 63 %), m.p. 191–193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 8.10 (d, $^3J_{H,H}$ = 15.4 Hz, 1 H), 7.51 (s, 2 H), 7.36–7.22 (m, 8 H), 7.00 (d, $^3J_{H,H}$ = 14.7 Hz, 1 H), 5.59 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 147.5, 145.4, 140.0, 135.7, 135.3, 134.6, 133.1, 129.8, 129.1, 128.9, 128.2, 127.6, 126.8, 115.1, 112.3, 45.9 ppm. MS (ES$^+$): *m/z* (%) = 424.0 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{16}N_3ClBr$ 424.0216, found 424.0204.

(*E*)-3-Benzyl-2-styryl-3*H*-imidazo[4,5-*b*]pyridine (11a): The reaction was performed following General Procedure E on 3-benzyl-3*H*-imidazo[4,5-*b*]pyridine (**11**) (100 mg, 0.5 mmol) using β-bromostyrene (175 mg, 1 mmol) to afford the desired product as a light brown solid (58 mg, 42 %), m.p. 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H), 8.04 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.96 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 7.50 (m, 2 H), 7.41–7.21 (m, 9 H), 7.04 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H), 5.65 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 148.4, 143.9, 138.2, 136.4, 135.6, 135.5, 129.5, 129.0, 128.9, 128.0, 127.5, 126.8, 126.5, 119.0, 113.2, 45.3 ppm. MS (ES$^+$): *m/z* (%) = 312.1 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{21}H_{18}N_3$ 312.1501, found 312.1506.

(*E*)-3-Benzyl-6-(2-methoxyphenyl)-2-styryl-3*H*-imidazo[4,5-*b*]-pyridine (12a): The reaction was performed following General Procedure E on 3-benzyl-6-(2-methoxyphenyl)-3*H*-imidazo[4,5-*b*]-pyridine (**12**) (100 mg, 0.3 mmol) using β-bromostyrene (116 mg, 0.6 mmol) to afford the desired product as a yellow oil (12 mg, 9 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.24 (s, 1 H), 8.01 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H), 7.52 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H), 7.44–7.24 (m, 10 H), 7.13–7.00 (m, 3 H), 5.67 (s, 2 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5, 147.1, 144.3, 138.5, 136.6, 136.0, 133.3, 132.9, 129.1, 128.6, 128.1, 127.0, 126.9, 126.8, 124.7, 114.4, 112.5, 45.5, 26.9 ppm. MS (ES$^+$): *m/z* (%) = 418.2 (100) [M + H]$^+$, 835.4 (10) [2M + H]$^+$. HRMS (ESI) calcd. for $C_{28}H_{24}N_3O$ 418.1919, found 418.1909.

(*E*)-3-Benzyl-6-phenyl-2-styryl-3*H*-imidazo[4,5-*b*]pyridine (13a): The reaction was performed following General Procedure E on 3-benzyl-6-phenyl-3*H*-imidazo[4,5-*b*]pyridine (**13**) (100 mg, 0.4 mmol) using β-bromostyrene (104 mg, 0.6 mmol) to afford the desired product as a beige solid (42 mg, 35 %), m.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (s, 1 H), 8.21 (s, 1 H), 8.02 (d, $^3J_{H,H}$ = 16.3 Hz, 1 H), 7.65 (d, $^3J_{H,H}$ = 5.7 Hz, 2 H), 7.56–7.46 (m, 4 H), 7.44–7.26 (m, 9 H), 7.06 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.67 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 147.9, 143.3, 139.0, 138.4, 136.4, 135.5, 135.6, 133.1, 129.5, 129.0, 129.1, 128.9, 128.1, 127.6, 127.5, 126.8, 124.8, 113.2, 45.5 ppm. MS (ES$^+$): *m/z* (%) = 388.2 (100) [M + H]$^+$, 775.4 (10) [2M + H]$^+$. HRMS (ESI) calcd. for $C_{27}H_{22}N_3$ 388.1814, found 388.1796.

(*E*)-4-(3-Benzyl-2-styryl-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-2-fluorobenzonitrile (14a): The reaction was performed following General Procedure E on 4-(3-benzyl-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-2-fluorobenzonitrile (**14**) (120 mg, 0.4 mmol) using styryl bromide (134 mg, 0.7 mmol) to afford the desired product as a light yellow solid (106 mg, 68 %), m.p. 197–199 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 8.18 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.04 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 7.74 (dd, $^3J_{H,H}$ = 7.7, 6.8 Hz, 1 H), 7.57–7.47 (m, 4 H), 7.44–7.25 (m, 8 H), 7.06 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H), 5.67 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 161.8, 153.8, 149.0, 146.5, 142.8, 139.3, 136.0, 135.6, 135.4, 134.1, 129.9, 129.8, 129.1, 129.0, 128.2, 127.6, 126.8, 124.7, 123.7, 114.0, 112.7, 45.6 ppm. MS (ES$^+$): *m/z* (%) = 431.2 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{28}H_{20}N_4F$ 431.1672, found 431.1664.

(*E*)-4-{3-Benzyl-2-[4-(trifluoromethyl)styryl]-3*H*-imidazo[4,5-*b*]-pyridin-6-yl}-*N*,*N*-dimethylaniline (17): The reaction was performed following General Procedure E on 4-(3-benzyl-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-*N*,*N*-dimethylaniline (**15**) (85 mg, 0.3 mmol) using (*E*)-1-(2-bromovinyl)-4-(trifluoromethyl)benzene (**4m**) (130 mg, 0.5 mmol) to afford the desired product as a bright orange solid (28 mg, 22 %). Compound **17** was additionally purified by re-

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crystallization in EtOH/dioxane prior to photophysical analysis, m.p. 184–186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (d, $^4J_{H,H}$ = 1.7 Hz, 1 H), 8.18 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.99 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H), 7.61–7.54 (m, 7 H), 7.34–7.24 (m, 4 H), 7.10 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H), 6.86 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 5.66 (s, 2 H), 3.01 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.5, 150.1, 147.1, 143.5, 139.1, 136.4, 136.0, 135.6, 133.5, 131.0, 130.6, 129.1, 128.1, 127.5, 126.7, 126.6, 125.8, 124.0, 122.12, 115.8, 113.0, 45.5, 40.6 ppm. MS (ES$^+$): *m/z* (%) = 499.2 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{30}H_{26}N_4F_3$ 499.2110, found 499.2100.

(*E*)-4-(3-Benzyl-2-{[4-(trifluoromethyl)phenyl]ethynyl}-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-*N*,*N*-dimethylaniline (18): 4-(3-benzyl-3*H*-imidazo[4,5-*b*]pyridin-6-yl)-*N*,*N*-dimethylaniline (**15**) (100 mg, 0.3 mmol) was introduced in a round-bottom flask along with $CuBr{\cdot}SMe_2$ (6 mg, 10 mol-%) and DPEPhos (33 mg, 20 mol-%) in dioxane (2 mL) at room temperature under an argon atmosphere. Stirring was maintained for 5 min. Then, LiO*t*Bu (146 mg, 6 equiv.) was added, followed by 1-(2,2-dibromoethenyl)-4-(trifluoromethyl)benzene[36] (**16**) (200 mg, 2 equiv.) and the mixture was heated at reflux for 4 h. Subsequent filtration of the medium on Celite and purification by column chromatography using a gradient of cyclohexane to AcOEt afforded the desired product as a yellow solid (43 mg, 28 %). Compound **18** was additionally purified by recrystallization in EtOH/dioxane prior to photophysical analysis, m.p. 215–217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 8.16 (s, 1 H), 7.67 (s, 3 H), 7.53 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.43–7.40 (m, 2 H), 7.36–7.29 (m, 4 H), 6.85 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 5.66 (s, 2 H), 3.02 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 145.2, 136.2, 135.5, 134.3, 134.2, 133.7, 132.4, 131.7, 131.3, 130.0, 128.8, 128.6, 128.1, 127.8, 126.2, 125.5, 125.6, 125.0, 124.7, 121.8, 112.9, 94.3, 47.0, 40.5 ppm. MS (ES$^+$): *m/z* (%) = 497.2 (100) [M + H]$^+$. HRMS (ESI) calcd. for $C_{30}H_{24}N_4F_3$ 497.1953, found 497.1947.

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