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Synthesis of Polysubstituted Imidazoles and Pyridines *via* Samarium(III) Triflate-Catalyzed [2+2+1] and [4+2] Annulations of Unactivated Aromatic Alkenes with Azides

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Abstract: Samarium(III) triflate-catalyzed [2+2+1] and [4+2] annulations have been identified for the preparation of fully substituted imidazoles and 2,3,5-trisubstituted pyridines from the readily available unactivated aromatic alkenes and azidomethyl aromatics. These reactions proceeded smoothly with one- or two-nitrogen synthons to afford a range of two types of skeletally distinct N-heterocycles in good yields. Mechanistic studies revealed that the annulation reaction proceed *via* an initial samarium(III) triflate-induced 1,3 dipolar cycloaddition followed by 1,2-migration to form an enamine as the key intermediate. Density functional theory (DFT) calculations suggested that the selectivity of 1,2-H and 1,2-aryl migration depends on the structure of the alkenes.

Keywords: aromatic alkenes; benzyl azides; cascade reactions; fully substituted imidazoles; 2,3,5-trisubstituted pyridines

Introduction

Intermolecular cascade reactions can allow for the straightforward and selective construction of complicated molecules in a one-pot manner from relatively simple building blocks.[1] Organic azide-alkene cycloadditions have been proven to be powerful synthetic tools for the ready access to diverse azaheterocycles. For example, the uncatalyzed thermal cycloaddition of organic azides with alkenes, especially the intramolecular azide-alkene cycloaddition reaction, has allowed many successful syntheses of complex molecules.[2] The transition metal-catalyzed annulation of alkenes with aryl azides or sulfonyl azides ("C_2+N_1" addition) represents a general approach for the direct synthesis of aziridines, and different transition metal catalysts for this reaction such as Fe, Co, Mn, Cu, Rh and Ru based compounds have been developed.[3] Although extensive efforts have been devoted to the utilization of organic azides and alkenes as cyclization partners in heterocycle syntheses, the rare earth metal-catalyzed intermolecular cascade annulations of unactivated aromatic alkenes and azidomethyl aromatics are rare.

On the other hand, polysubstituted imidazoles and pyridines are privileged scaffolds in many natural products and biologically active molecules.[4] Highly substituted imidazoles also play important roles in materials chemistry due to their excellent photophysical properties.[5] However, only a limited number of typical methodologies exist for the assembly of highly substituted imidazoles and polysubstituted pyridines.[6] Thus, it is still challenging and highly desirable to develop novel and efficient synthetic methods for these azaheterocycles from simple and readily accessible building blocks.

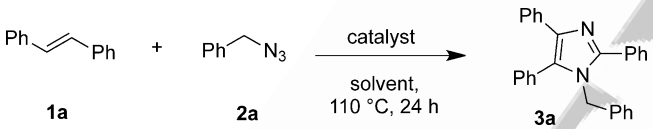
Our group has previously reported the rare earth metal-catalyzed [3+2] cycloaddition of organic azides with electron-deficient olefins to produce 1,2,3-triazoles or enamines.[7] In this paper, we wish to present

our findings on the rare earth metal-catalyzed intermolecular [2+2+1] and [4+2] annulation reactions between unactivated aromatic alkenes and azidomethyl aromatics. In the presence of a catalytic amount of $Sm(OTf)_3$ and atmospheric pressure oxygen, the readily available azidomethyl aromatics were successfully applied as two- or one-nitrogen synthons to prepare 1,2,4,5-tetrasubstituted imidazoles and 2,3,5-trisubstituted pyridines by the reactions with stilbenes and aromatic 1,3-dienes, respectively. Preliminary mechanistic evidence for the bifurcated reaction pathway will also be presented to highlight key aspects of these transformations.

Results and Discussion

To initiate our investigations, we examined the reactions of stilbenes with azidomethyl aromatics. Table 1 presents the results of screening for appropriate reaction conditions for the model reaction between **1a** and **2a**. We first attempted the reaction in the absence of any metal catalyst in toluene at 110 °C for 24 h, and TLC analysis indicated no product formation (Table 1, entry 1). When a mixture of **1a** and benzyl azide (1:1.2 mol ratio) was treated with 5 mol% $Sc(OTf)_3$ in toluene at 110 °C for 24 h, tetrasubstituted imidazole **3a** was isolated in 30% yield. Doubling the loading amount of benzyl azide enhanced the yield to 45%. Interestingly, simply subjecting the reaction mixture to an atmosphere of oxygen resulted in further improvement of the yield to 61% (Table 1, entry 2). It was noted that other metal catalysts, such as $Cu(OTf)_2$, $In(OTf)_3$, $[Rh(COD)Cl]_2$, $Pd(TFA)_2$, or $AuCl_3$, were not suitable for this transformation (Table 1, entries 8–12). $Sm(OTf)_3$ was found to be more effective than other rare earth metal triflates (Table 1, entry 3 *vs.* entry 2 and entries 4–7). Among various solvents examined, toluene and PhCl turned out to be the best (Table 1, entries 13–17). Additionally, 5 mol% of the $Sm(OTf)_3$ was sufficient to promote the reaction effectively. Increasing the catalyst loading amount to 10 mol% did not facilitate the reaction or improve the yield (Table 1, entry 3 *vs.* entry 18). Finally, the optimal conditions were identified as the following: reaction of **1a** and **2a** in toluene with 5 mol% of $Sm(OTf)_3$ and atmospheric pressure oxygen at 110 °C for 24 h. Under these conditions, 1,2,4,5-tetrasubstituted imidazole **3a** was obtained in 75% yield (Table 1, entry 3).

Table 1. Optimization of the synthesis of 1,2,4,5-tetrasubstituted imidazoles.[a]

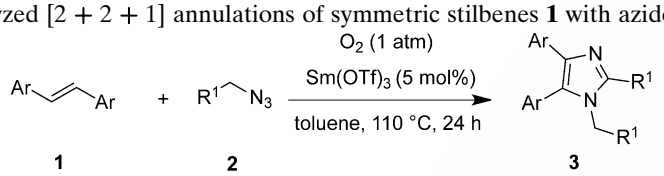


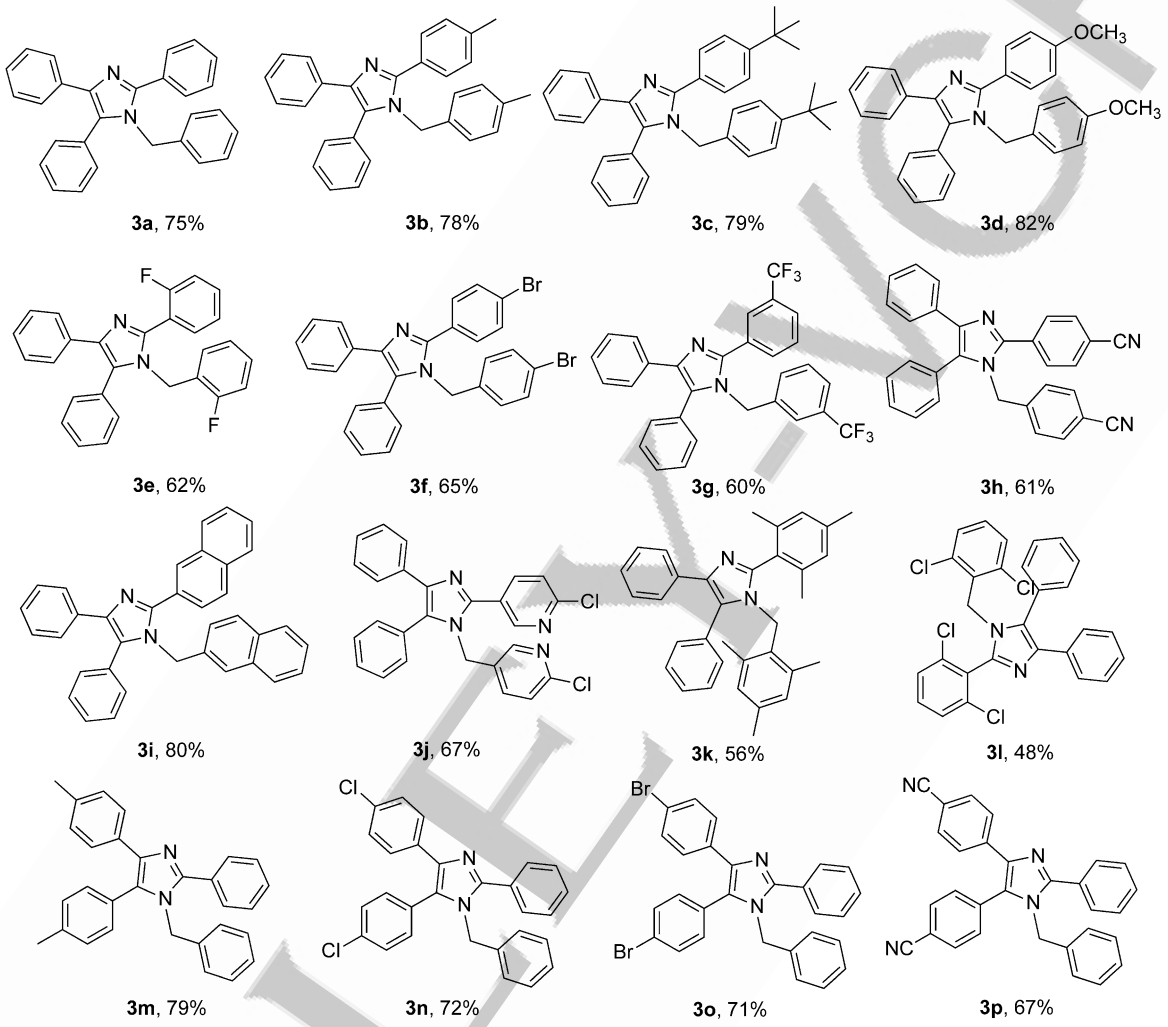
Entry	Catalyst	Solvent	Yield [%][b] of **3a**
1	none	toluene	0
2	$Sc(OTf)_3$ (5 mol%)	toluene	61
3	**$Sm(OTf)_3$ (5 mol%)**	**toluene**	**75**
4	$Ce(OTf)_3$ (5 mol%)	toluene	57
5	$Yb(OTf)_3$ (5 mol%)	toluene	42
6	$Pr(OTf)_3$ (5 mol%)	toluene	47
7	$La(OTf)_3$ (5 mol%)	toluene	45
8	$Cu(OTf)_2$ (5 mol%)	toluene	0
9	$In(OTf)_3$ (5 mol%)	toluene	0
10	$[Rh(COD)Cl]_2$ (5 mol%)	toluene	0
11	$Pd(TFA)_2$ (5 mol%)	toluene	0
12	$AuCl_3$ (5 mol%)	toluene	0
13	$Sm(OTf)_3$ (5 mol%)	PhCl	72
14[c]	$Sm(OTf)_3$ (5 mol%)	DCE	0
15[c]	$Sm(OTf)_3$ (5 mol%)	CH_3CN	0
16	$Sm(OTf)_3$ (5 mol%)	DMF	0
17	$Sm(OTf)_3$ (5 mol%)	DMSO	0
18	$Sm(OTf)_3$ (10 mol%)	toluene	73

[a] Carried out with 0.5 mmol of stilbene **1a** and 1.1 mmol of benzyl azide **2a** in the presence of catalyst and atmospheric-pressure oxygen in solvent (4 mL) at 110 °C for 24 h (except for entry 1).
[b] Isolated yield of pure product based on **1a**.
[c] The reaction mixture of stilbene **1a** (0.5 mmol), benzyl azide **2a** (1.1 mmol), $Sm(OTf)_3$ (0.025 mmol) and solvent (4 mL) in a 20 mL sealed tube was stirred at 110 °C for 24 h.

Having identified the optimal conditions for the synthesis of tetrasubstituted imidazoles, we next explored the substrate scope of this [2+2+1] annulation reaction. The results are summarized in Table 2. A variety of benzyl azides substituted with alkyl (**3b**, **3c**), methoxy (**3d**), halogen (**3e**, **3f**), trifluoromethyl (**3g**) and cyano (**3h**) groups at the *ortho*, *meta*, or *para* position underwent the [2+2+1] annulation readily, providing the anticipated tetrasubstituted imidazoles **3** in good yields. In general, benzyl azides possessing electron-donating groups on the phenyl ring provided the cyclization products in higher yields than those bearing electron-withdrawing groups (**3b–d** *vs.* **3e–h**). The structure of a representative product **3f**[8] was unambiguously confirmed by X-ray crystallographic analysis (Figure 1). In addition, azides bearing 2-naphthyl (**3i**) and 3-pyridyl (**3j**) groups also reacted smoothly and afforded the corresponding imidazoles in good yields. Noteworthy, substrates with steric hindrance (**3k** and **3l**) could be employed in [2+2+1] annulations with the stilbene **1a**, although in moderate yields. Both electron-neutral and electron-poor stilbenes were found to be suitable for this transformation while electron-poor stilbenes afforded the products in lower yields (**3n–q** *vs.* **3m**). In the case of asymmetric stilbene **1q**, tetrasubstituted imidazoles **3q** and **3q′** were isolated in 32% and 37% yield, respectively (Scheme 1). Stilbene **1r** possessing a strongly electron-donating group (OCH_3) at the *meta* position

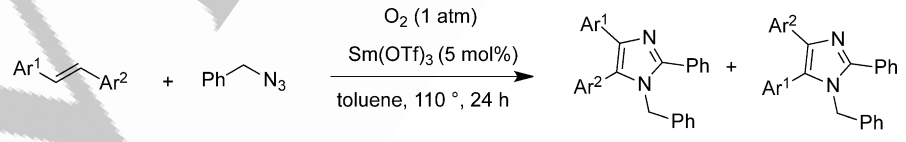
Table 2. $Sm(OTf)_3$-catalyzed [2 + 2 + 1] annulations of symmetric stilbenes **1** with azidomethyl aromatics **2**.[a,b]





[a] *Reaction conditions:* 0.5 mmol of **1** and 1.1 mmol of azidomethyl aromatics in the presence of $Sm(OTf)_3$ (5 mol%) and atmospheric-pressure oxygen in 4 mL of toluene at 110 °C for 24 h.

[b] Isolated yield of pure product based on **1**.



1q: Ar^1 = 4-Br-C_6H_4, Ar^2 = C_6H_5 — **3q, 32%** — **3q', 37%**

1r: Ar^1 = 3-OMe-C_6H_4, Ar^2 = 3-Cl-C_6H_4 — **3r, 63%** — **3r', 15%**

1s: Ar^1 = 4-OMe-C_6H_4, Ar^2 = 4-F-C_6H_4 — **3s, 77%**

Scheme 1. $Sm(OTf)_3$-catalyzed [2+2+1] annulations of asymmetric stilbenes **1** with benzyl azide **2a**.

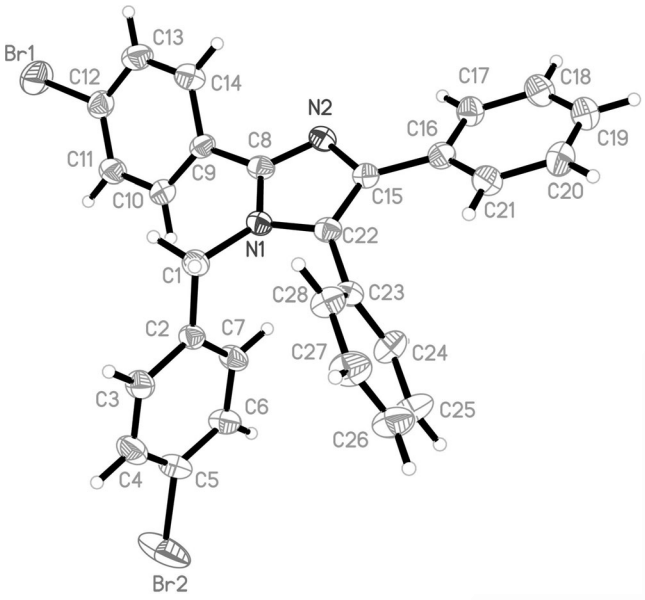


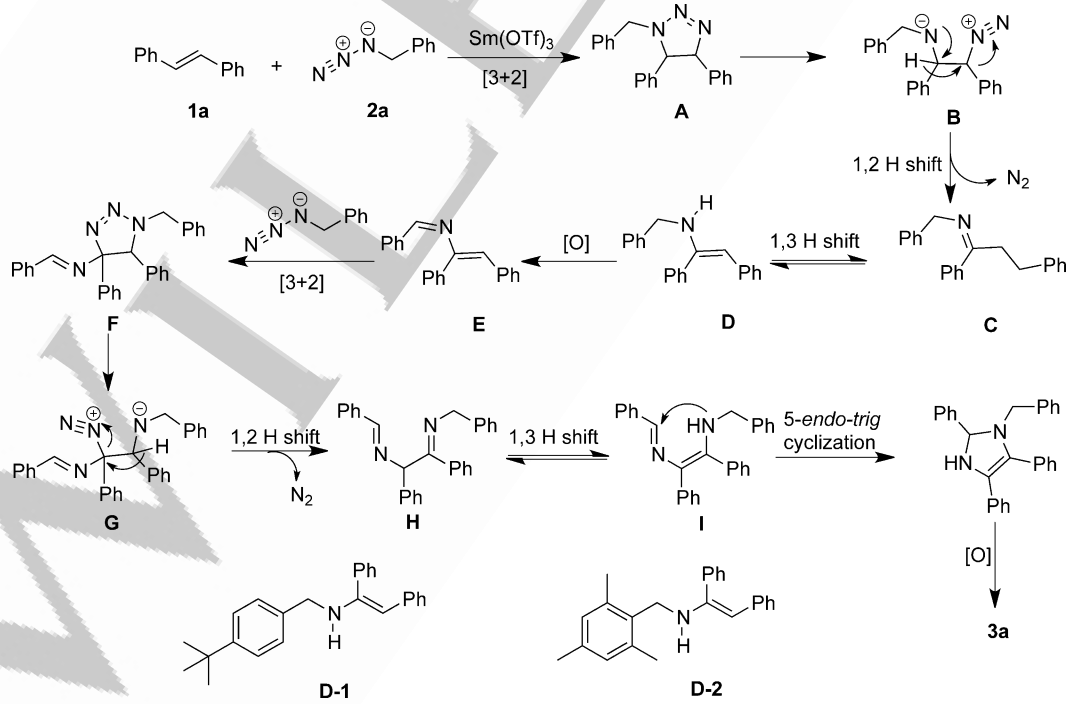
Figure 1. X-ray crystal structure of 1,2,4,5-tetrasubstituted imidazole **3f**.

afforded imidazole **3r** in 63% yield along with its isomer **3r′** in 15% yield. However, 4-methoxy-4′-fluoro-substituted stilbene **1s** provided imidazole **3s** as the only isolated product (77% yield).

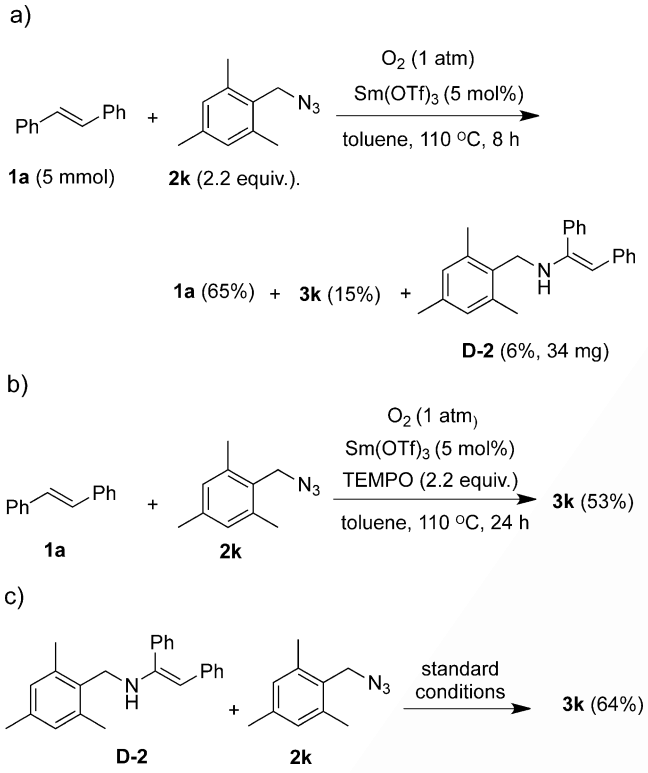
Although the azidomethyl aromatics **2** have been extensively studied for the synthesis of nitrogen-containing heterocycles,[9] the incorporation of two molecules of azidomethyl aromatics into a five-membered ring product has not been reported, which represents a new application of this versatile class of molecules under rare earth metal catalysis.

On the basis of the reported mechanistic studies of azides and alkenes,[7,10] we proposed a plausible pathway for the stilbene-azide [2+2+1] annulation reaction, as depicted in Scheme 2. Under $Sm(OTf)_3$ activation, 1,3-dipolar cycloaddition of benzyl azide **2a** with the stilbene **1a** occurs first to form the unstable triazoline intermediate **A**. Subsequently, **A** decomposes to a zwitterionic species **B**, which undergoes 1,2 H-shift with the loss of nitrogen and 1,3 H-shift to give the enamine **D**. This rationale was supported by the isolation of enamines **D-1** and **D-2** from the reaction mixtures. Oxidation of **D** delivers the α,β-unsaturated imine **E**, which undergoes a second intermolecular 1,3-dipolar cycloaddition, followed by 1,2 H-shift with the loss of nitrogen and 1,3 H-shift to form intermediate **I**. Ultimately, intermediate **I** generates the final tetrasubstituted imidazole **3a** *via* 5-*endo-trig* cyclization[11] and oxidation.

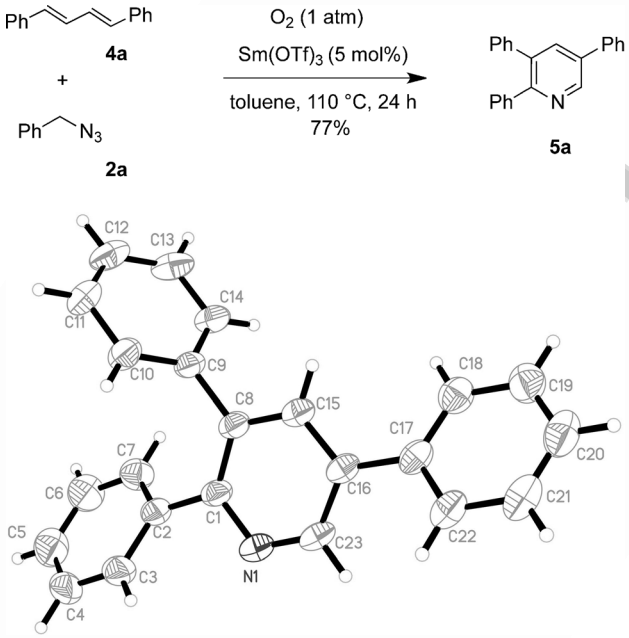
Under the standard reaction conditions, enamine **D** did not accumulate even for the [2+2+1] annulation reaction of stilbene **1a** with sterically hindered benzyl azide **2k**. When a mixture of **1a** (0.5 mmol) and **2k** (1.1 mmol) was treated with 5 mol% $Sm(OTf)_3$ and atmospheric pressure oxygen in toluene at 110 °C for 24 h, only a trace amount of **D** was detected by ^{1}H NMR and LC-MS analyses. However, when these substrates were allowed to react at 110 °C for 8 h on a 5 mmol scale, chromatography resulted in the isola-



Scheme 2. A plausible reaction mechanism for the stilbene-azide [2+2+1] annulation reaction.



Scheme 3. Control experiments.



Scheme 4. Synthesis of 2,3,5-trisubstituted **5a** and X-ray crystal structure of **5a**.

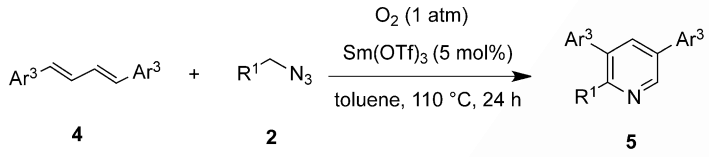
tion of 65% of the starting material **1a** along with 15% yield of imidazole **3k** and 6% enamine **D-2** (Scheme 3, a).To further support the proposed reaction pathway, additional two control experiments were carried out. It was observed that the presence of 2.2 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) did not suppress the annulation of stilbene **1a** with benzyl azide **2k** under optimized conditions (Scheme 3, b), suggesting that a radical mechanism was not likely involved. Furthermore, when the enamine **D-2** was employed to react with benzyl azide **2k** under standard reaction conditions, the desired product **3k** was obtained in 64% yield (Scheme 3, c), which further supported that the imidazole product could be derived from the intermediate enamine **D** in the annulation reaction.

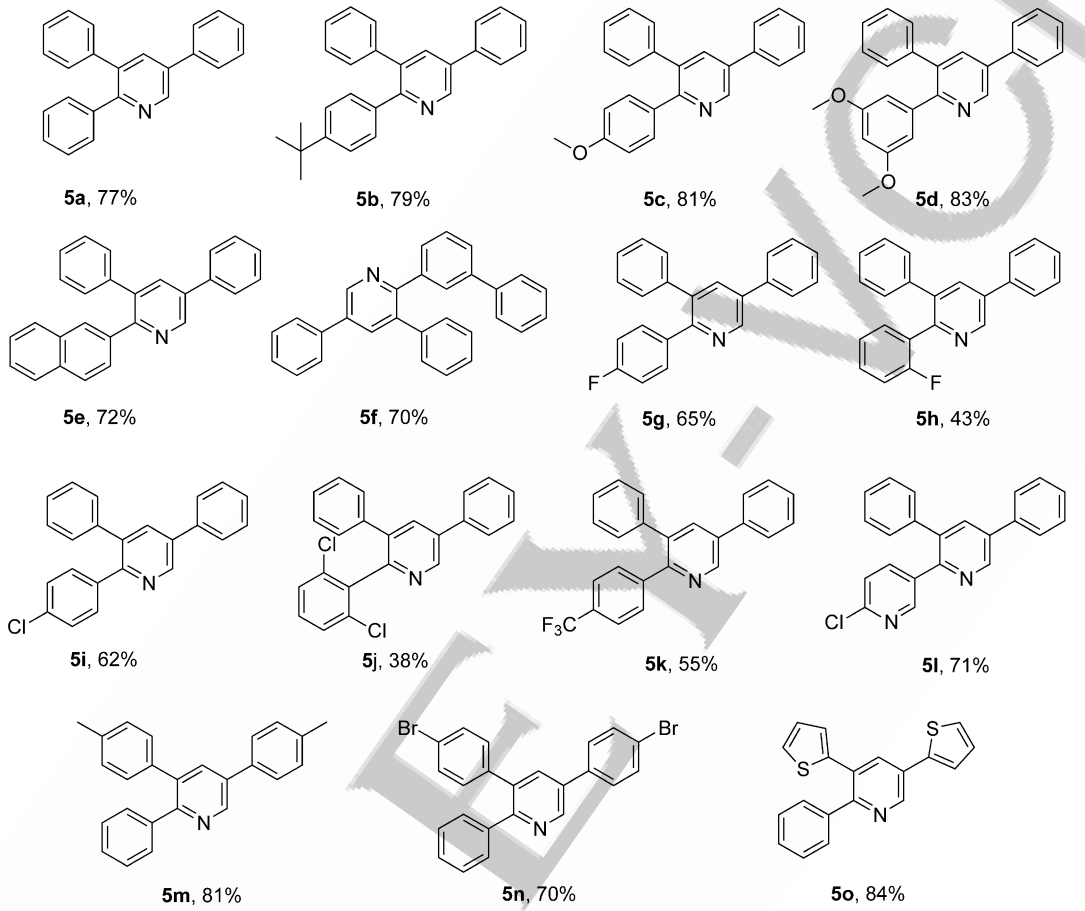
Encouraged by the successful incorporation of the stilbenes **1** as annulation reaction partners, we investigated the reaction of 1,4-diphenylbuta-1,3-dienes **4a** with benzyl azide **2a**. We envisaged that the 1,4-diphenylbuta-1,3-diene **4a** would function as a four-carbon synthon for [4+*N*] annulation with the azide. To our delight, under identical conditions as described for stilbenes **1**, the reaction of **4a** and **2a** proceeded readily to produce 2,3,5-triphenylpyridine **5a** as the sole product *via* a formal [4+2] cycloaddition in 77% isolated yield (Scheme 4). The structure of **5a**[12] was further confirmed by X-ray crystallography analysis, as described in Scheme 4.

The substrate scope was explored with a diverse set of azidomethyl aromatics and aromatic 1,3-dienes (Table 3). Consistent with the results of fully substituted imidazole synthesis, good functional group compatibility was observed, as products with tertiary butyl (**5b**), methoxy (**5c**, **5d**), phenyl (**5f**), fluoro (**5g**, **5h**), chloro (**5i**, **5j**), and trifluoromethyl (**5k**) substituents were obtained. Moreover, the substituent at the *para* (**5c**) and *meta* (**5d**) positions were not detrimental to the reaction yield. In analogy to the electronic effects observed for the reactions with stilbenes **1**, electron-donating groups (**5c**, **5d**) resulted in higher yields than electron-withdrawing groups (**5g**–**k**). The azides bearing 2-naphthyl (**5e**) and 3-pyridyl (**5l**) also readily underwent cycloadditions with **4a**, affording the corresponding 2,3,5-trisubstituted pyridines in good yields. While *ortho* substituents on the benzyl azide resulted in low yields (**5h**, **5j**), both electron-neutral (**5m**) and electron-deficient (**5n**) 1,4-diphenylbuta-1,3-dienes were effective annulation reaction partners, and furnished the 2,3,5-trisubstituted pyridines in good yields. Especially, a heterocyclic 1,3-diene afforded **5o** in high yield.

The proposed mechanistic pathway for the 1,3-diene-azide [4+2] annulation reaction is shown in Scheme 5. The key event is the formation of the triazoline intermediate **J**, generated *via* 1,3-dipolar cycloaddition of benzyl azide **2a** with an olefinic double bond of 1,3-diene **4a**. The decomposition of intermediate **J** leads to 1,2-phenyl migration with the elimination of molecular nitrogen and 1,3 H-shift to form enamine **M**. Oxidation of **M** provides the aza-triene intermediate **N**, which subsequently undergoes 6π-

Table 3. $Sm(OTf)_3$-catalyzed [4+2] annulations of aromatic 1,3-dienes **4** with azidomethyl aromatics **2**.[a,b]

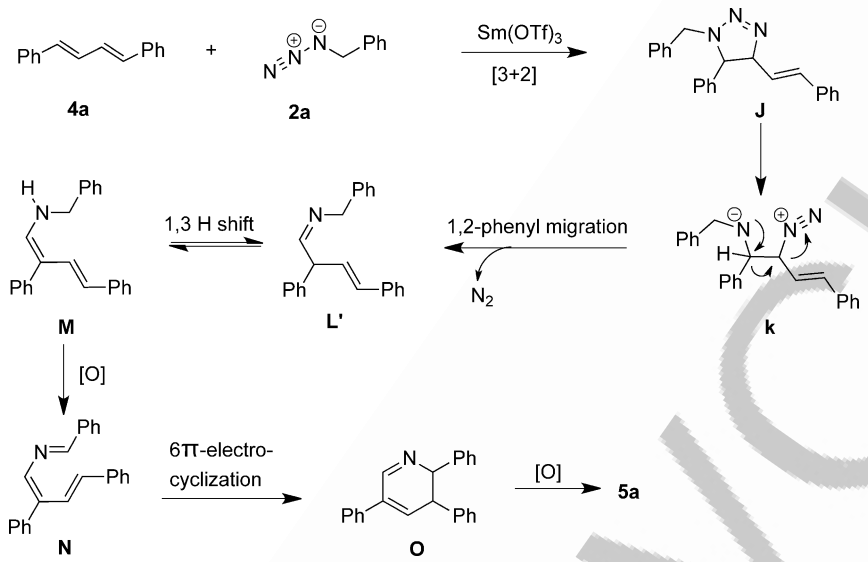




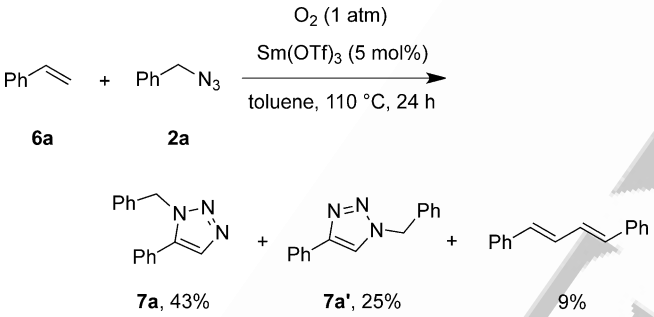
[a] *Reaction conditions:* 0.5 mmol of **4** and 0.6 mmol of azidomethyl aromatics in the presence of $Sm(OTf)_3$ (5 mol%) and atmospheric-pressure oxygen in 4 mL of toluene at 110 °C for 24 h.
[b] Isolated yield of pure product based on **4**.

electrocyclization to yield a transient dihydropyridine **O**.[13] Rapid aerobic oxidation generates the final 2,3,5-trisubstituted pyridine **5a**.

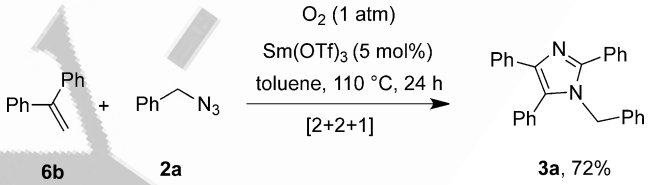
We also investigated the possibility of extending the substrate scope to aromatic terminal alkenes. Our anticipation was that the aromatic terminal alkenes would undergo regioselective 1,3-dipolar cycloaddition with azidomethyl aromatics to yield imidazoles *via* a cascade process. However, under the same reaction conditions, the reaction of styrene **6a** with benzyl azide **2a** gave the [3+2] cycloaddition products **7a** and **7a′** in 43% and 25% isolated yields, respectively, along with homo-coupling side product 1,4-diphenylbuta-1,3-dienes (9%). The expected imidazole product was not generated at all (Scheme 6). Evidently, the products of **7a** and **7a′** were obtained *via* $Sm(OTf)_3$-mediated 1,3-dipolar cycloaddition to form triazolines, followed by oxygen oxidation. A range of reaction conditions (catalysts, solvents, temperatures) for the above transformation were screened, but we only obtained mixtures of several other products (data not shown). Intriguingly, the reaction of 1,1-diphenylethylene **6b** with the benzyl azide **2a** exclusively provided the [2+2+1] annulation product, tetrasubstituted imidazole **3a** in 72% yield, whereas the [3+2] adduct was not detected (Scheme 7). Scheme 8 presents a mechanistic rationale for the [2+2+1] annulation of **6b** and **2a** to form **3a**. This reaction pro-



Scheme 5. A plausible reaction mechanism for the 1,3-diene-azide [4+2] annulation reaction.

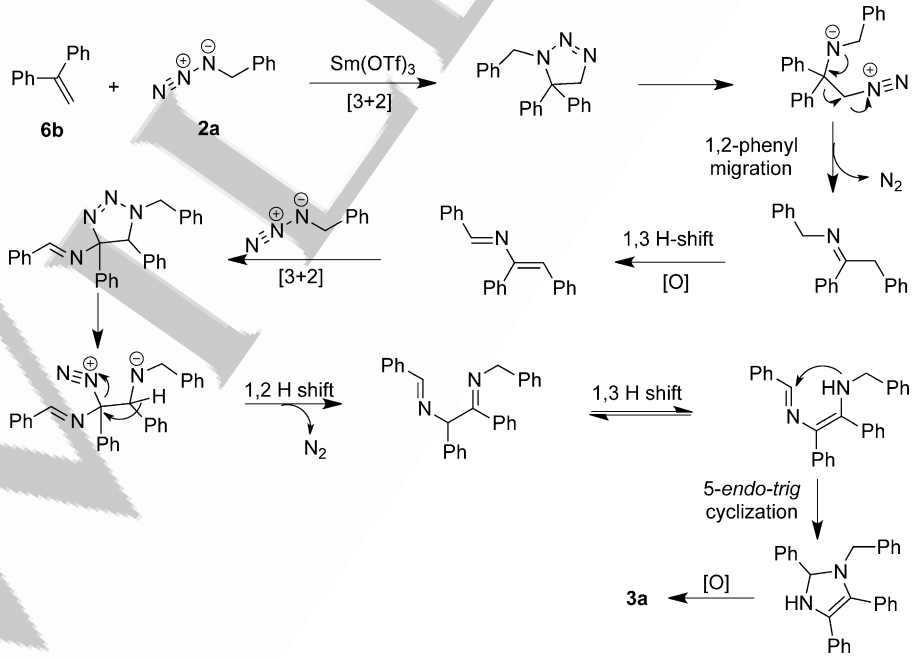


Scheme 6. $Sm(OTf)_3$-catalyzed [3+2] cycloaddition of styrene **6a** with benzyl azide **2a**.



Scheme 7. $Sm(OTf)_3$-catalyzed [2+2+1] annulation of 1,1-diphenylethylene **6b** with benzyl azide **2a**.

ceeds *via* an initial $Sm(OTf)_3$-induced 1,3 dipolar cycloaddition followed by a series of rearrangements, cyclizations, and oxidations to furnish the final compound **3a**.



Scheme 8. Proposed mechanistic pathway for the formation of imidazole **3a** from **6b** and **2a**.

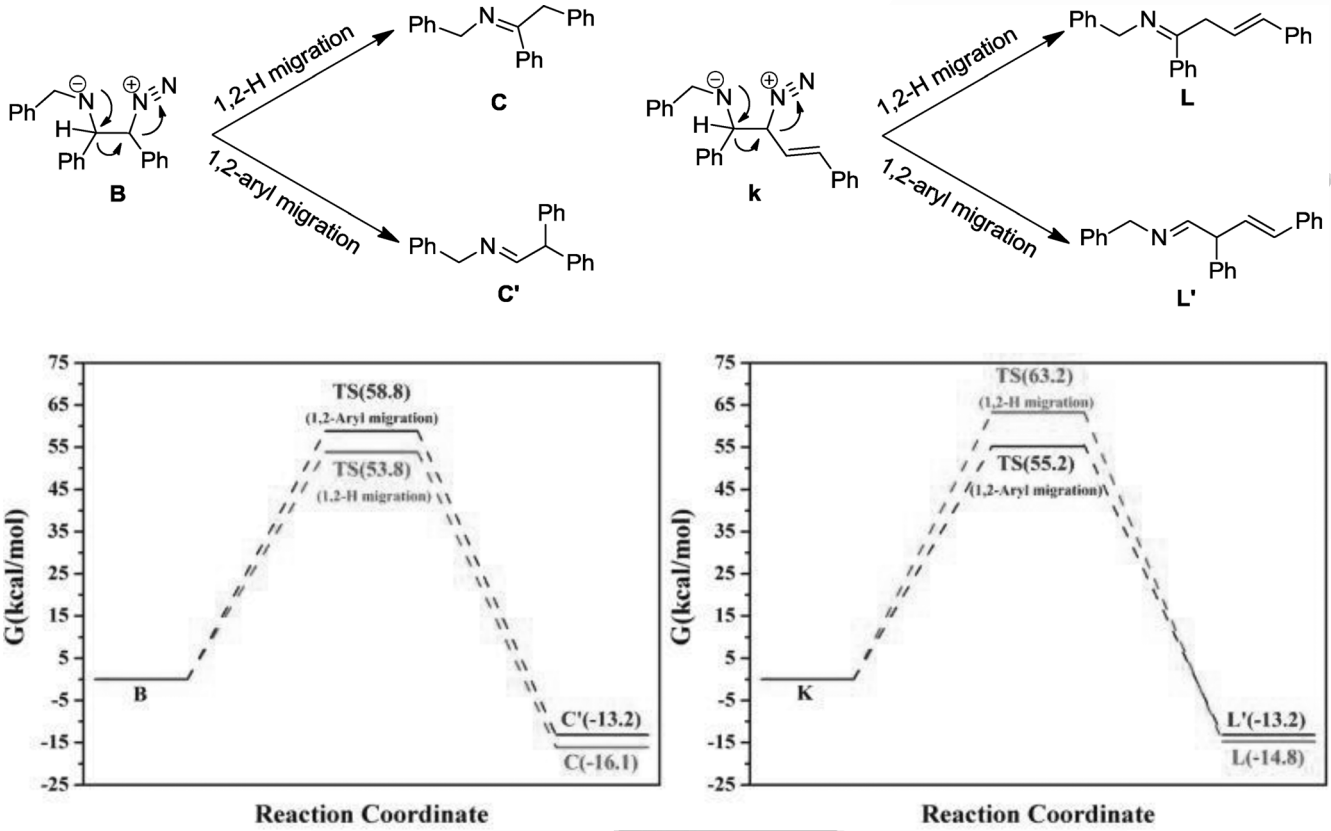


Figure 2. Comparison of the transition state energy between the 1,2-H migration and the 1,2-aryl migration mechanism.

The above experimental results revealed that the zwitterionic intermediates could undergo the 1,2-H or 1,2-aryl migration with the elimination of N_2, which is dependent on the structure of the alkene. Density functional theory (DFT) calculations [B3LYP with the 6-31+G (d, p) basis set] were performed on 1,2-H and 1,2-aryl migration (Figure 2). Evidently, in the stilbene-azide [2+2+1] annulation reaction, the activation energy difference between 1,2-H and 1,2-aryl migrations is *ca.* 5 kcal mol^{-1}, suggesting that 1,2-H migration is 4.6×10^3-fold faster than 1,2-aryl migration according to the Arrhenius equation. And the thermodynamic energy from **B** to **C** was found to be 3 kcal mol^{-1} lower than that from **B** to **C′**. These results are in good agreement with the experimental observations. In addition, the molecular orbital surfaces and energy levels of corresponding reaction state were also calculated (see Figure S1 in the Supporting Information). The transition state energy of 1,2-H migration is about 0.64 eV higher than that of 1,2-aryl migration (2.27 eV *vs.* 1.63 eV), indicating that the transition state of 1,2-H migration is more favorable than that of 1,2-aryl migration. Similar computations and analyses were also performed for the 1,3-diene-azide [4+2] annulation reaction, and the results in Figure 2 and Figure S2 (in the Supporting Information) indicate that the 1,3-diene-azide [4+2] annulation reaction is less favorable than the 1,2-aryl migration, consistent with the experimental results.

Conclusions

We have developed a new cascade process for the $Sm(OTf)_3$-catalyzed [2+2+1] and [4+2] annulations of unactivated aromatic alkenes with azidomethyl aromatics to prepare fully substituted imidazoles and 2,3,5-trisubstituted pyridines in good yields. This substrate-controlled bifurcated cascade process not only provides an approach to access a range of skeletally distinct N-heterocycles but also represents a new strategy to develop cascade reactions from organic azides. Notably, the incorporation of two molecules of azidomethyl aromatics into a five-membered ring product is a new application for this versatile class of molecules under rare earth metal catalysis conditions.

Experimental Section

General Experimental Details

Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were

recorded at 500 MHz and 125 MHz, respectively, using $CDCl_3$ as a reference standard ($\delta = 7.26$ ppm) for ^1H NMR and ($\delta = 77.04$ ppm) for ^{13}C NMR. HR-MS (ion trap) were recorded using APCI or ESI. Melting points were uncorrected. Precoated silica gel plates F-254 were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (300–400 mesh). Starting azidomethyl aromatics were readily prepared according to literature procedures. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

General Experimental Procedure for the Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles 3

Under an oxygen atmosphere, a mixture of stilbene **1** (1.0 equiv., 0.5 mmol), azidomethyl aromatics **2** (2.2 equiv., 1.1 mmol), $Sm(OTf)_3$ (0.05 equiv., 0.025 mmol), and 4 mL of toluene was refluxed at 110 °C for 24 h. The progress of the reaction was monitored by thin-layer chromatography. After cooling down the reaction mixture, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford 1,2,4,5-tetrasubstituted imidazoles **3**.

1-Benzyl-2,4,5-triphenyl-1*H*-imidazole (3a): white solid; mp 167–169 °C (lit.[14] 165–167 °C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.69$–7.63 (m, 2H), 7.62–7.55 (m, 2H), 7.42–7.38 (m, 3H), 7.37–7.30 (m, 3H), 7.24–7.18 (m, 7H), 7.17–7.13 (m, 1H), 6.82–6.80 (m, 2H), 5.12 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 148.1$, 138.2, 137.6, 134.5, 131.1, 131.2, 130.1, 129.1, 128.9, 128.8, 128.7, 128.6, 128.6, 128.1, 127.4, 126.8, 126.4, 126.1, 48.3; HR-MS (ESI): $m/z =$ 387.1857, calcd. for $C_{28}H_{23}N_2$ 387.1861 $[M+H^+]$.

1-(4-Methylbenzyl)-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (3b): white solid; mp 135–137 °C (lit.[15] 132–135 °C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.58$–7.54 (m, 4H), 7.36–7.29 (m, 3H), 7.24–7.18 (m, 6H), 7.15–7.12 (m, 1H), 7.01 (d, $J = 7.9$ Hz, 2H), 6.70 (d, $J = 8.0$ Hz, 2H), 5.06 (s, 2H), 2.37 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 148.2, 138.8, 137.9, 136.9, 134.7, 134.6, 131.2, 131.1, 130.9, 129.9, 129.3, 129.3, 128.9, 128.8, 128.6, 128.1, 126.9, 126.3, 125.9, 48.0, 21.4, 21.1; HR-MS (ESI-ion trap): $m/z =$ 415.2181, calcd. for $C_{30}H_{27}N_2$: 415.2174 $[M+H]^+$.

1-(4-*tert*-bButylbenzyl)-2-(4-*tert*-butylphenyl)-4,5-diphenyl-1*H*-imidazole (3c): white solid; mp 167–169 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.64$–7.59 (m, 4H), 7.46–7.42 (m, 2H), 7.36–7.33 (m, 1H), 7.32–7.28 (m, 2H), 7.21 (dd, $J = 7.8$, 5.9 Hz, 6H), 7.15–7.12 (m, 1H), 6.74 (d, $J = 8.3$ Hz, 2H), 5.09 (s, 2H), 1.35 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 151.9$, 150.3, 148.2, 137.9, 134.7, 131.3, 131.2, 130.9, 129.9, 128.8, 128.7, 128.5, 128.1, 128.0, 126.8, 126.2, 125.9, 125.5, 125.4, 48.1, 34.7, 34.5, 31.5, 31.3; HR-MS (ESI-ion trap): $m/z = 499.3112$, calcd. for $C_{36}H_{39}N_2$: 499.3113 $[M+H]^+$.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (3d): white solid; mp 145–146 °C (lit.[15] 152–154 °C); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.59$–7.54 (m, 4H), 7.35–7.32 (m, 2H), 7.23–7.17 (m, 5H), 7.15–7.11 (m, 1H), 6.94–6.90 (m, 2H), 6.74–6.89 (m, 4H), 5.02 (s, 2H), 3.82 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 160.1$, 158.8, 147.9, 131.2, 131.1, 130.5, 129.8, 129.7, 129.6, 129.4, 128.8, 128.6, 128.4, 128.1, 127.3, 126.8, 126.3, 114.0, 113.9, 55.3, 55.2, 47.7; HRMS (ESI-ion trap): $m/z = 447.2070$, calcd. for $C_{30}H_{27}N_2O_2$ $[M+H]^+$: 447.2073.

1-(2-Fluorobenzyl)-2-(2-fluorophenyl)-4,5-diphenyl-1*H*-imidazole (3e): white solid; mp 169–171 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.63$–7.58 (m, 2H), 7.56–7.54 (m, 2H), 7.39–7.33 (m, 3H), 7.23–7.19 (m, 4H), 7.17–7.13 (m, 1H), 7.12–7.08 (m, 2H), 6.92–6.85 (m, 2H), 6.72 (dd, $J = 8.7$, 5.2 Hz, 2H), 5.04 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 163.2 (d, $^1J_{C,F} = 247.8$ Hz), 162.0 (d, $^1J_{C,F} = 245.0$ Hz), 147.1, 138.2, 134.2, 133.0 (d, $^4J_{C,F} = 3.1$ Hz), 132.9, 131.0, 131.0, 130.9, 130.8, 130.0, 129.0, 128.8, 128.2, 127.7 (d, $^3J_{C,F} =$ 8.1 Hz), 127.6, 127.1 (d, $^4J_{C,F} = 3.3$ Hz), 127.0, 126.8, 126.6, 115.8 (d, $^2J_{C,F} = 21.8$ Hz), 115.6 (d, $^2J_{C,F} = 21.8$ Hz), 47.63; HR-MS (ESI-ion trap): $m/z = 423.1667$, calcd. for $C_{23}H_{18}N$: 423.1673 $[M+H]^+$.

1-(4-Bromobenzyl)-2-(4-bromophenyl)-4,5-diphenyl-1*H*-imidazole (3f): white solid; mp 183–185 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.56$–7.48 (m, 6H), 7.39–7.33 (m, 5H), 7.23–7.20 (m, 4H), 7.16 (t, $J = 7.2$ Hz, 1H), 6.66 (d, $J =$ 8.2 Hz, 2H), 5.03 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 146.9, 138.5, 136.3, 134.1, 131.9, 131.9, 131.0, 130.6, 130.4, 130.3, 129.6, 129.0, 129.0, 128.2, 127.6, 126.8, 126.7, 123.5, 121.5, 47.9; HR-MS (ESI-ion trap): $m/z = 545.0046$, 543.0066, calcd. for $C_{28}H_{21}Br_2N_2$: 545.0051, 543.0071 $[M+H]^+$.

4,5-Diphenyl-1-[3-(trifluoromethyl)benzyl]-2-[3-(trifluoromethyl)phenyl]-1*H*-imidazole (3g): light yellow solid; mp 128–130 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.89$ (s, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.59–7.53 (m, 3H), 7.45 (d, $J = 7.7$ Hz, 1H), 7.41–7.32 (m, 4H), 7.27–7.22 (m, 4H), 7.19–7.16 (m, 1H), 6.97 (d, $J = 6.0$ Hz, 2H), 5.15 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 146.5$, 138.7, 137.9, 133.9, 132.1, 131.6, 131.2 (q, $J_{CF} = 32.5$ Hz), 131.0, 130.8 (q, $J_{CF} = 32.5$ Hz), 130.5, 130.4, 129.4, 129.3, 129.3, 129.2, 129.1, 128.2, 126.8, 126.7, 126.0 (q, $J = 3.9$ Hz), 125.8 (q, $J = 3.6$ Hz), 123.7 (q, $J_{C,F} = 271.0$ Hz), 123.6 (q, $J_{C,F} =$ 271.0 Hz), 124.6 (q, $J = 3.8$ Hz), 123.2 (q, $J = 3.8$ Hz), 48.07; HR-MS (ESI-ion trap): $m/z = 523.1600$, calcd. for $C_{30}H_{21}F_6N_2$: 523.1609 $[M+H]^+$.

4-[1-(4-Cyanobenzyl)-4,5-diphenyl-1*H*-imidazol-2-yl]benzonitrile (3h): light yellow solid; mp 176–177 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.79$–7.77 (m, 2H), 7.74–7.70 (m, 2H), 7.57–7.54 (m, 4H), 7.44–7.40 (m, 1H), 7.40–7.36 (m, 2H), 7.26–7.18 (m, 5H), 6.95–6.91 (m, 2H), 5.21 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 145.8$, 142.0, 139.4, 134.8, 133.5, 132.7, 132.6, 131.1, 130.8, 130.0, 129.3, 129.2, 129.2, 128.3, 127.1, 126.8, 126.6, 118.3, 118.1, 112.7, 112.0, 48.3; HR-MS (ESI-ion trap): $m/z = 437.1759$, calcd. for $C_{30}H_{21}N_4$: 437.1766 $[M+H]^+$.

2-(Naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-4,5-diphenyl-1*H*-imidazole (3i): light yellow solid; mp 149–151 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.17$ (s, 1H), 7.90–7.80 (m, 4H), 7.77–7.66 (m, 5H), 7.52–7.44 (m, 4H), 7.38–7.26 (m, 8H), 7.20 (t, $J = 7.1$ Hz, 1H), 7.03 (d, $J = 8.4$ Hz, 1H), 5.36 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 148.1$, 138.5, 135.2, 134.5, 133.3, 133.3, 133.1, 132.7, 131.1, 131.0, 130.9, 130.5, 128.9, 128.8, 128.7, 128.5, 128.4, 128.4, 128.2, 128.2, 127.9, 127.7, 126.9, 126.7, 126.5, 126.4, 126.1, 125.0, 123.9, 48.7; HR-MS (ESI-ion trap): $m/z = 487.2172$, calcd. for $C_{36}H_{27}N_2$: 487.2174 $[M+H]^+$.

2-Chloro-5-{[2-(6-chloropyridin-3-yl)-4,5-diphenyl-1*H*-imidazol-1-yl]methyl}pyridine (3j): light yellow solid; mp 181–

182 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71–8.55 (m, 1H), 7.97 (dd, J = 8.3, 2.5 Hz, 1H), 7.76 (d, J = 2.1 Hz, 1H), 7.51 (dd, J = 8.3, 1.3 Hz, 2H), 7.44–7.37 (m, 4H), 7.24–7.16 (m, 6H), 7.00 (dd, J = 8.3, 2.6 Hz, 1H), 5.11 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.1, 151.2, 148.9, 147.5, 143.7, 139.5, 139.1, 136.4, 133.5, 131.1, 130.8, 130.0, 129.5, 129.4, 128.3, 127.1, 126.8, 125.8, 124.6, 124.4, 45.6; HR-MS (ESI-ion trap): m/z = 457.0993, calcd. for $C_{26}H_{19}Cl_2N_4$: 457.0987 $[M+H]^+$.

2-Mesityl-4,5-diphenyl-1-(2,4,6-trimethylbenzyl)-1*H*-imidazole (3k): white solid; mp 175–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.4 Hz, 2H), 7.41–7.36 (m, 3H), 7.32 (dd, J = 6.5, 3.0 Hz, 2H), 7.18 (t, J = 7.5 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.75 (s, 2H), 6.48 (s, 2H), 4.85 (s, 2H), 2.27 (s, 3H), 2.14 (s, 3H), 1.94 (s, 6H), 1.75 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.2, 138.8, 138.5, 137.4, 137.0, 131.6, 130.9, 129.8, 129.4, 128.9, 128.6, 128.3, 128.0, 127.9, 126.8, 126.6, 126.0, 124.5, 124.0, 43.9, 21.2, 20.7, 20.0, 19.6; HR-MS (ESI-ion trap): m/z = 471.2804, calcd. for $C_{34}H_{35}N_2$: 471.2800 $[M+H]^+$.

1-(2,6-Dichlorobenzyl)-2-(2,6-dichlorophenyl)-4,5-diphenyl-1*H*-imidazole (3l): light yellow solid; mp 179–181 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 2H), 7.48–7.43 (m, 5H), 7.22–7.17 (m, 5H), 7.15–7.12 (m, 1H), 7.01–6.95 (m, 3H), 5.25 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.8, 137.4, 137.3, 136.5, 134.5, 131.6, 131.1, 130.9, 130.7, 130.6, 130.2, 129.3, 128.9, 128.7, 128.4, 128.0, 127.9, 126.9, 126.3, 44.8; HR-MS (ESI-ion trap): m/z = 525.0278, calcd. for $C_{28}H_{19}N_2Cl_4$; 525.0273 $[M+H]^+$.

1-Benzyl-2-phenyl-4,5-di-*p*-tolyl-1*H*-imidazole (3m): white solid; mp 74–76 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.62 (m, 2H), 7.49–7.46 (m, 2H), 7.39–7.35 (m, 3H), 7.21–7.18 (m, 3H), 7.12–7.09 (m, 4H), 7.03 (d, J = 8.0 Hz, 2H), 6.83–6.81 (m, 2H), 5.09 (s, 2H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.8, 138.4, 138. 1, 137.8, 135.8, 131.8, 131.2, 131.0, 130.2, 129.7, 129.5, 129.1, 128.8, 128.5, 128.4, 128.1, 127.3, 126.7, 126.0, 48.2, 21.3, 21.1; HR-MS (ESI-ion trap): m/z = 415.2181, calcd. for $C_{30}H_{27}N_2$: 415.2174 $[M+H]^+$.

1-Benzyl-4,5-bis(4-chlorophenyl)-2-phenyl-1*H*-imidazole (3n): white solid; mp 123–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65–7.63 (m, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.42–7.39 (m, 3H), 7.29 (d, J = 8.4 Hz, 2H), 7.23–7.17 (m, 5H), 7.10 (d, J = 8.4 Hz, 2H), 6.84–6.76 (m, 2H), 5.09 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.6, 137.5, 137.2, 135.0, 132.7, 132.3, 132.3, 130.5, 129.2, 129.2, 129.2, 129.0, 128.9, 128.7, 128.7, 128.4, 128.1, 127.6, 125.9, 48.4; HR-MS (ESI-ion trap): m/z = 455.1084, calcd. for $C_{28}H_{21}Cl_2N_2$: 455.1082 $[M+H]^+$.

1-Benzyl-4,5-bis(4-bromophenyl)-2-phenyl-1*H*-imidazole (3o): white solid; mp 132–133 °C (lit.[15] 128–131 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65–7.61 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.42–7.40 (m, 5H), 7.34 (d, J = 8.6 Hz, 2H), 7.24–7.21 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 6.82–6.76 (m, 2H), 5.09 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.66, 137.5, 137.1, 133.1, 132.5, 132.2, 131.3, 130.5, 129.7, 129.2, 129.0, 128.9, 128.8, 128.7, 128.4, 127.6, 125.9, 123.3, 120.5, 48.5; HR-MS (ESI-ion trap): m/z = 545.0056, 543.0078, calcd. for $C_{28}H_{21}Br_2N_2$, 545.0051, 543.0071 $[M+H]^+$.

4,4′-(1-Benzyl-2-phenyl-1*H*-imidazole-4,5-diyl)dibenzonitrile (3p): yellow solid; mp 205–207 °C; ^{1}H NMR (500 MHz, DMSO): δ = 7.89 (d, J = 8.5 Hz, 2H), 7.72–7.67 (m, 4H), 7.58–7.56 (m, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.50–7.48 (m, 3H), 7.20–7.14 (m, 3H), 6.73 (d, J = 7.3 Hz, 2H), 5.21 (s, 2H); ^{13}C NMR (125 MHz, DMSO): δ = 149.2, 139.1, 137.1, 136.5, 135.4, 133.4, 133.2, 132.8, 132.1, 130.8, 130.5, 129.2, 129.2, 129.1, 128.1, 127.2, 126.2, 119.4, 118.9, 112.3, 109.3, 48.6; HR-MS (APCI-ion trap): m/z = 437.1747, calcd. for $C_{30}H_{21}N_4$: 437.1766.

1-Benzyl-4-(4-bromophenyl)-2,5-diphenyl-1*H*-imidazole (3q): white solid; mp 154–156 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 2H), 7.46–7.42 (m, 2H), 7.42–7.35 (m, 4H), 7.35–7.30 (m, 4H), 7.22–7.16 (m, 5H), 6.79–6.78 (m, 2H), 5.10 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.2, 137.3, 136.9, 133.2, 132.0, 131.2, 131.0, 130.6, 130.4, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 127.5, 126.0, 120.4, 48.4; HR-MS (ESI-ion trap): m/z = 465.0956, 467.0934, calcd. for $C_{28}H_{22}BrN_2$; 465.0966, 467.0946 $[M+H]^+$.

1-Benzyl-5-(4-bromophenyl)-2,4-diphenyl-1*H*-imidazole (3q′): white solid; mp 135–137 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.65 (m, 2H), 7.57–7.55 (m, 2H), 7.46–7.39 (m, 5H), 7.25–7.20 (m, 5H), 7.19–7.16 (m, 1H), 7.08–7.04 (m, 2H), 6.81–6.80 (dd, J = 7.3, 2.2 Hz, 2H), 5.10 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.4, 137.2, 132.7, 132.1, 132.0, 129.9, 129.2, 129.1, 129.0, 128.7, 128.7, 128.6, 128.2, 127.6, 127.3, 127.0, 126.7, 125.9, 123.1, 48.4; HR-MS (ESI-ion trap): m/z = 465.0951, 467.0930, calcd. for $C_{28}H_{22}BrN_2$: 465.0966, 467.0946 $[M+H]^+$.

1-Benzyl-5-(3-chlorophenyl)-4-(3-methoxyphenyl)-2-phenyl-1*H*-imidazole (3r): light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 1.8 Hz, 1H), 7.66 (dd, J = 6.6, 2.9 Hz, 2H), 7.42–7.38 (m, 3H), 7.36 (d, J = 6.8 Hz, 1H), 7.26–7.19 (m, 4H), 7.13–7.08 (m, 2H), 6.92 (dd, J = 8.3, 2.6 Hz, 1H), 6.83 (t, J = 7.0 Hz, 3H), 6.68–6.65 (m, 1H), 5.11 (s, 2H), 3.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.8, 148.2, 137.6, 134.2, 131.7, 130.6, 130.0, 129.4, 129.3, 129.1, 129.0, 128.7, 128.6, 127.5, 126.8, 126.4, 126.1, 126.0, 125.8, 124.7, 123.4, 115.6, 115.4, 55.1, 48.4; HR-MS (ESI-ion trap): m/z = 451.1562, calcd. for $C_{29}H_{24}ClN_2O$: 451.1577 $[M+H]^+$.

1-Benzyl-4-(3-chlorophenyl)-5-(3-methoxyphenyl)-2-phenyl-1*H*-imidazole (3r′): light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (dd, J = 6.1, 2.7 Hz, 2H), 7.44–7.40 (m, 3H), 7.34–7.32 (m, 1H), 7.24–7.21 (m, 4H), 7.19–7.14 (m, 2H), 7.13–7.12 (m, 2H), 7.09 (d, J = 7.7 Hz, 1H), 6.82–6.77 (m, 2H), 6.76–6.71 (m, 1H), 5.11 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.5, 148.3, 137.1, 134.6, 131.5, 131.1, 130.0, 129.9, 129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.0, 127.6, 126.0, 119.4, 113.4, 111.6, 55.1, 48.6; HR-MS (ESI-ion trap): m/z = 451.1582, calcd. for $C_{29}H_{24}ClN_2O$: 451.1577 $[M+H]^+$.

1-Benzyl-5-(4-fluorophenyl)-4-(4-methoxyphenyl)-2-phenyl-1*H*-imidazole (3s): light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.7 Hz, 1H), 7.60–7.57 (m, 2H), 7.43 (d, J = 8.8 Hz, 1H), 7.38–7.25 (m, 5H), 7.21–7.09 (m, 7H), 6.94–6.89 (m, 1H), 6.87 (dd, J = 8.7, 2.3 Hz, 1H), 6.78 (d, J = 2.2 Hz, 1H), 5.30 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.4 (d, $^1J_{C,F}$ = 242.5 Hz), 156.6, 137.9, 137.1, 131.6 (d, $^4J_{C,F}$ = 2.5 Hz), 128.9, 128.6 (d, $^3J_{C,F}$ = 7.8 Hz), 127.8, 127.4, 126.9, 126.2, 124.5, 124.4, 120.8, 120.5, 116.5, 115.4 (d, $^2J_{C,F}$ = 21.2 Hz), 114.1, 109.9, 55.7, 50.1; HR-MS (ESI-ion trap): m/z = 435.1865, calcd. for $C_{29}H_{24}FN_2O$: 435.1873 $[M+H]^+$.

(*E*)-*N*-(4-*tert*-Butylbenzyl)-1,2-diphenylethenamine (D-1): yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.44–7.39 (m, 4H), 7.30 (d, J = 6.8 Hz, 2H), 7.20–7.18 (m, 4H), 6.69 (d, J = 8.3 Hz, 2H), 5.08 (s, 2H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.2, 130.9, 130.1, 129.3, 128.8, 128.6, 128.5, 128.3, 128.1, 127.3, 126.9, 126.0, 125.6, 125.4, 48.2, 31.4, 31.3.

(*E*)-1,2-Diphenyl-*N*-(2,4,6-trimethylbenzyl)ethenamine (D-2): light yellow solid; mp 103–105 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57–7.46 (m, 6H), 7.44 (dd, J = 7.7, 1.7 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 7.01 (s, 1H), 6.90 (s, 2H), 4.79 (s, 2H), 2.30 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.5, 138.2, 137.6, 135.5, 134.7, 131.2, 130.9, 129.5, 129.1, 128.8, 128.1, 127.9, 126.6, 126.2, 44.1, 21.0, 19.5; HR-MS (APCI-ion trap): m/z = 328.2069, calcd. for $C_{24}H_{26}N$: 328.2065 $[M+H]^+$.

General Experimental Procedure for the Synthesis of 2,3,5-Trisubstituted Pyridines 5

Under an oxygen atmosphere, a mixture of aromatic 1,3-diene **4** (1.0 equiv., 0.5 mmol), azidomethyl aromatics **2** (1.2 equiv., 0.6 mmol), $Sm(OTf)_3$ (0.05 equiv., 0.025 mmol), and 4 mL of toluene was refluxed at 110 °C for 24 h. The progress of the reaction was monitored by thin-layer chromatography. After cooling down the reaction mixture, the solvent was evaporated under reduced pressure. The target product **5** was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether.

2,3,5-Triphenylpyridine (5a): light yellow solid; mp 120–121 °C (lit.[16] 121–122 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.95 (d, J = 2.2 Hz, 1H), 7.94 (d, J = 2.2 Hz, 1H), 7.72–7.67 (m, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.46–7.41 (m, 3H), 7.33–7.25 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9, 146.7, 139.9, 139.9, 137.4, 137.0, 136.0, 135.0, 129.9, 129.6, 129.2, 128.4, 128.2, 128.0, 127.9, 127.4, 127.2; HR-MS (ESI-ion trap): m/z = 308.1434, calcd. for $C_{23}H_{18}N$: 308.1439.

2-(4-*tert*-Butylphenyl)-3,5-diphenylpyridine (5b): light yellow solid; mp 140–142 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.91 (d, J = 1.2 Hz, 1H), 7.91 (d, J = 1.2 Hz, 1H), 7.68 (d, J = 7.9 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.36–7.27 (m, 9H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.8, 150.9, 146.6, 140.1, 137.5, 137.0, 136.8, 135.8, 134.7, 129.6, 129.5, 129.1, 128.4, 128.1, 127.3, 127.1, 124.9, 34.57, 31.28; HR-MS (ESI-ion trap): m/z = 364.2043, calcd. for $C_{27}H_{26}N$: 364.2065 $[M+H]^+$.

2-(4-Methoxyphenyl)-3,5-diphenylpyridine (5c): white solid; mp 180–181 °C (lit.[17] 179.6–181.0 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.93 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 2.2 Hz, 1H), 7.69–7.67 (m, 2H), 7.53–7.49 (m, 2H), 7.44–7.38 (m, 3H), 7.37–7.27 (m, 5H), 6.81 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4, 155.5, 146.6, 140.3, 137.5, 137.0, 135.6, 134.5, 132.3, 131.3, 129.6, 129.2, 128.5, 128.1, 127.3, 127.1, 113.4, 55.2; HR-MS (ESI-ion trap): m/z = 338.1542, calcd. for $C_{24}H_{20}N$: 338.1545 $[M+H]^+$.

2-(3,5-Dimethoxyphenyl)-3,5-diphenylpyridine (5d): yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.93 (d, J = 2.1 Hz, 1H), 7.93 (d, J = 2.1 Hz, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 6.8 Hz, 2H), 7.45–7.41 (m, 1H), 7.35–7.26 (m, 5H), 6.58 (d, J = 2.2 Hz, 2H), 6.39 (d, J = 2.2 Hz, 1H), 3.62 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.2, 155.6, 146.6, 141.5, 140.0, 137.4, 136.9, 136.1, 135.2, 129.5, 129.2, 128.4, 128.2, 127.4, 127.1, 107.9, 106.6, 101.2, 55.3; HR-MS (ESI-ion trap): m/z = 368,1665, calcd. for $C_{25}H_{22}NO_2$: 368.1651 $[M+H]^+$.

2-(Naphthalen-2-yl)-3,5-diphenylpyridine (5e): yellow solid; mp 183–185 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.05–8.96 (m, 1H), 8.04 (s, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.80–7.76 (m, 2H), 7.72–7.69 (m, 3H), 7.53 (t, J = 7.5 Hz, 2H), 7.47–7.42 (m, 4H), 7.33–7.29 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.6, 146.8, 139.9, 137.4, 137.3, 137.1, 136.2, 135.1, 133.2, 132.9, 129.6, 129.6, 129.2, 128.5, 128.5, 128.2, 127.6, 127.5, 127.4, 127.3, 127.2, 126.3, 125.9; HR-MS (ESI-ion trap): m/z = 358.1582, calcd. for $C_{27}H_{20}N$: 358.1596 $[M+H]^+$.

2-(Biphenyl-3-yl)-3,5-diphenylpyridine (5f): yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.98 (s, 1H), 7.98 (s, 1H), 7.70 (t, J = 7.2 Hz, 2H), 7.62 (s, 1H), 7.54–7.50 (m, 4H), 7.45–7.42 (m, 1H), 7.41–7.24 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.7, 146.8, 141.0, 140.6, 137.4, 137.0, 136.2, 135.1, 130.05, 129.7, 129.6, 129.2, 128.8, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 127.4, 127.2, 127.1, 126.7; HR-MS (ESI-ion trap): m/z = 384.1720, calcd. for $C_{29}H_{22}N$: 384.1752 $[M+H]^+$.

2-(4-Fluorophenyl)-3,5-diphenylpyridine (5g): light yellow solid; mp 128–130 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.91 (s, 1H), 7.92 (s, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.45–7.36 (m, 3H), 7.33–7.32 (m, 3H), 7.25–7.24 (m, 2H), 6.95 (t, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6 (d, $^1J_{C,F}$ = 246.3 Hz), 154.8, 146.7, 139.7, 137.3, 137.1, 135.9, 135.8 (d, $^4J_{C,F}$ = 2.5 Hz), 135.2, 131.7 (d, $^3J_{C,F}$ = 7.5 Hz), 129.6, 129.2, 128.6, 128.3, 127.5, 127.1, 114.9 (d, $^2J_{C,F}$ = 21.2 Hz); HR-MS (ESI-ion trap): m/z = 326.1310, calcd. for $C_{23}H_{17}NF$: 326.1345 $[M+H]^+$.

2-(2-Fluorophenyl)-3,5-diphenylpyridine (5h): yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.95 (d, J = 2.2 Hz, 1H), 7.97 (d, J = 2.2 Hz, 1H), 7.71–7.67 (m, 2H), 7.54–7.42 (m, 5H), 7.29–7.27 (m, 3H), 7.25–7.23 (m, 2H), 7.18–7.15 (m, 1H), 6.94–6.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.6 (d, $^1J_{C,F}$ = 247.5 Hz), 146.3, 139.1, 137.8, 137.2, 136.5, 136.0, 131.8, 131.7, 130.2 (d, $^3J_{C,F}$ = 8.1 Hz), 129.9, 129.2, 128.9, 128.4, 128.2, 127.5, 127.2, 124.1 (d, $^4J_{C,F}$ = 3.5 Hz), 115.6 (d, $^2J_{C,F}$ = 21.2 Hz); HR-MS (APCI-ion trap): m/z = 320.1323, calcd. for $C_{23}H_{17}NF$: 326.1345 $[M+H]^+$.

2-(4-Chlorophenyl)-3,5-diphenylpyridine (5i): light yellow solid; mp 176–177 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 7.92 (s, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.38–7.29 (m, 5H), 7.29–7.25 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.5, 146.7, 139.5, 138.2, 137.2, 137.1, 136.0, 135.3, 134.0, 131.3, 129.5, 129.2, 128.6, 128.3, 128.2, 127.6, 127.1; HR-MS (ESI-ion trap): m/z = 342.1039, calcd. for $C_{23}H_{17}NCl$: 342.1050 $[M+H]^+$.

2-(2,6-Dichlorophenyl)-3,5-diphenylpyridine (5j): white solid; mp 90–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.97 (d, J = 2.2 Hz, 1H), 7.98 (d, J = 2.2 Hz, 1H), 7.73–7.70 (m, 2H), 7.53–7.50 (m, 2H), 7.45–7.42 (m, 1H), 7.32–7.29 (m, 3H), 7.28–7.26 (m, 2H), 7.28–7.25 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9, 146.7, 139.9, 139.9, 137.4, 136.9, 136.0, 135.0, 129.9, 129.6, 129.2, 128.4, 128.2, 127.9, 127.8, 127.4, 127.1; HR-MS (APCI-ion trap): m/z = 376.0637, calcd. for $C_{23}H_{16}Cl_2N$: 376.0660 $[M+H]^+$.

3,5-Diphenyl-2-[4-(trifluoromethyl)phenyl]pyridine (5k): light yellow solid; mp 163–165 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.97 (d, J = 1.3 Hz, 1H), 7.97 (d, J = 1.3 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.57–7.50 (m, 6H), 7.45 (t, J = 7.3 Hz, 1H), 7.38–7.36 (m, 3H), 7.28–7.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.2, 146.9, 143.5, 139.3, 137.1, 137.1, 136.4, 135.7, 130.3, 129.8 (q, $J_{C,F}$ = 32.1 Hz), 129.6, 129.2, 128.7, 128.4, 127.8, 127.2, 124.9 (q, J = 3.8 Hz), 124.2 (q, $J_{C,F}$ = 270.9 Hz); HR-MS (ESI-ion trap): m/z = 376.1308, calcd. for $C_{24}H_{17}NF_3$: 376.1313 $[M+H]^+$.

6′-Chloro-3,5-diphenyl-2,3′-bipyridine (5l): light yellow solid; mp 175–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.94 (d, J = 2.2 Hz, 1H), 8.42 (d, J = 2.1 Hz, 1H), 7.93 (d, J = 2.2 Hz, 1H), 7.70 (dd, J = 8.3, 2.5 Hz, 1H), 7.67–7.64 (m, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.37–7.32 (m, 3H), 7.25–7.22 (m, 2H), 7.20 (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.3, 150.8, 150.6, 147.1, 139.9, 138.9, 137.1, 136.9, 136.5, 135.9, 134.5, 129.5, 129.3, 128.9, 128.5, 128.1, 127.2, 123.4; HRMS (ESI-ion trap): m/z = 343.1005, calcd. for $C_{22}H_{16}NCl$: 343.1002 $[M+H]^+$.

2-Phenyl-3,5-di-*p*-tolylpyridine (5m):[18] light yellow solid; mp 101–102 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.90 (d, J = 2.2 Hz, 1H), 7.90 (d, J = 2.3 Hz, 1H), 7.58–7.56 (m, 2H), 7.43–7.40 (m, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.28–7.26 (m, 3H), 7.15–7.09 (m, 5H), 2.43 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.6, 146.3, 140.1, 138.1, 137.1, 137.0, 136.7, 135.9, 134.9, 134.6, 129.9, 129.8, 129.5, 129.1, 127.9, 127.7, 127.0, 21.2, 21.1; HR-MS (APCI-ion trap): m/z = 336.1730, calcd. for $C_{25}H_{22}N$: 336.1752 $[M+H]^+$.

3,5-Bis(4-bromophenyl)-2-phenylpyridine (5n): yellow solid; mp 154–155 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.91 (d, J = 2.2 Hz, 1H), 7.86 (d, J = 2.3 Hz, 1H), 7.68–7.64 (m, 2H), 7.57–7.53 (m, 2H), 7.48–7.44 (m, 2H), 7.42–7.38 (m, 2H), 7.34–7.29 (m, 3H), 7.15–7.09 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2, 146.6, 139.3, 138.6, 136.5, 136.1, 134.9, 134.0, 132.4, 131.7, 131.2, 129.8, 128.7, 128.2, 128.2, 122.8, 121.9; HR-MS (ESI-ion trap): m/z = 465.9621, 463.9642, calcd. for $C_{23}H_{16}NBr_2$: 465.9629, 463.9649 $[M+H]^+$.

2-Phenyl-3,5-di(thiophen-2-yl)pyridine (5o): brown oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.94 (d, J = 2.2 Hz, 1H), 8.02 (d, J = 2.3 Hz, 1H), 7.52–7.48 (m, 2H), 7.46 (dd, J = 3.6, 1.1 Hz, 1H), 7.41 (dd, J = 5.1, 1.1 Hz, 1H), 7.38–7.35 (m, 3H), 7.32 (dd, J = 5.1, 1.2 Hz, 1H), 7.17 (dd, J = 5.1, 3.6 Hz, 1H), 6.98 (dd, J = 5.1, 3.6 Hz, 1H), 6.89 (dd, J = 3.6, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2, 145.5, 140.8, 139.8, 139.7, 135.4, 129.5, 129.2, 129.0, 128.4, 128.3, 128.1, 127.7, 127.4, 126.7, 126.3, 124.6; HR-MS (APCI-ion trap): m/z = 320.0546, calcd. for $C_{19}H_{14}NS_2$; 320.0568 $[M+H]^+$.

1-Benzyl-5-phenyl-1*H*-1,2,3-triazole (7a):[19] white solid; mp 68–70 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (s, 1H), 7.44–7.38 (m, 3H), 7.29–7.23 (m, 5H), 7.09–7.05 (m, 2H), 5.54 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.2, 135.5, 133.2, 129.5, 129.0, 128.9, 128.8, 128.1, 127.2, 126.9, 51.8; HR-MS (ESI-ion trap): m/z = 236.1185, calcd. for $C_{15}H_{14}N_3$: 236.1188 $[M+H]^+$.

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (7a′): white solid; mp 130–132 °C (lit.[20] 129–131 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 2H), 7.70 (s, 1H), 7.44–7.37 (m, 5H), 7.36–7.31 (m, 3H), 5.57 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.2, 134.8, 130.6, 129.2, 128.8, 128.8, 128.2, 128.1, 125.7, 119.6, 54.2; HR-MS (APCI-ion trap): m/z = 236.1173, calcd. for $C_{15}H_{14}N_3$: 236.1188 $[M+H]^+$.

CAUTION*: Sufficient care has to be exercised while handling organic azides because of their explosive nature.*

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References

[1] For reviews of cascade reactions, see: a) K. C. Nicolaou, J. S. Chen, *Chem. Soc. Rev.* **2009**, *38*, 2993; b) F.-Z. Peng, Z.-H. Shao, *Curr. Org. Chem.* **2011**, *15*, 4144; c) L.-Q. Lu, J.-R. Chen, W.-J. Xiao, *Acc. Chem. Res.* **2012**, *45*, 1278.

[2] For representative examples, see: a) R. Ducray, M. A. Ciufolini, *Angew. Chem.* **2002**, *114*, 4882; *Angew. Chem. Int. Ed.* **2002**, *41*, 4688; b) S. Kim, Y. M. Lee, J. Lee, T. Lee, Y. Fu, Y. Song, J. Cho, D. Kim, *J. Org. Chem.* **2007**, *72*, 4886; c) Y. Zhou, P. V. Murphy, *Org. Lett.* **2008**, *10*, 3777; d) B. W.-Q. Hui, S. Chiba, *Org. Lett.* **2009**, *11*, 729; e) I. de Miguel, M. Velado, B. Herradón, E. Mann, *Adv. Synth. Catal.* **2013**, *355*, 1237.

[3] For recent representative examples, see: a) H. Han, S. B. Park, S. K. Kim, S. Chang, *J. Org. Chem.* **2008**, *73*, 2862; b) V. Subbarayan, J. V. Ruppel, S. Zhu, J. A. Perman, X. P. Zhang, *Chem. Commun.* **2009**, 4266; c) S. A. Cramer, D. M. Jenkins, *J. Am. Chem. Soc.* **2011**, *133*, 19342; d) C. Kim, T. Uchida, T. Katsuki, *Chem. Commun.* **2012**, *48*, 7188; e) L.-M. Jin, X. Xu, H. Lu, X. Cui, L. Wojtas, X. P. Zhang, *Angew. Chem.* **2013**, *125*, ####; *Angew. Chem. Int. Ed.* **2013**, *52*, 5309.

[4] Selected recent reviews of imidazoles with biological activities: a) N. Rani, A. Sharma, G. K. Gupta, R. Singh, *Mini Rev. Med. Chem.* **2013**, *11*, 1626; b) S. N. Riduan, Y. Zhang, *Chem. Soc. Rev.* **2013**, *42*, 9055; selected examples of pyridines with biological activities: c) L. Olbe, E. Carlsson, P. Lindberg, ~~*Nature*~~ **2003**, ~~**421–426**~~, 132; d) J. P. Michael, *Nat. Prod. Rep.* **2005**, *22*, 627; e) S. D. Roughley, A. M. Jordan, *J. Med. Chem.* **2011**, *54*, 3451.

[5] a) P. Abhishek, C. J. Kulkarni, A. B. Tonzola, A. Samson, *J. Mater. Chem.* **2004**, *16*, 4556; b) Z. Wang, P. Lu, S. Chen, Z. Gao, F. Shen, W. Zhang, Y. Xu, H. S. Kwok, Y. Ma, *J. Mater. Chem.* **2011**, *21*, 5451.

[6] For representative recently reported methods on synthesis of fully substituted imidazoles, see: a) B. Hu, Z. Wang, N. Ai, J. Zheng, X.-H. Liu, S. Shan, Z. Wang, *Org. Lett.* **2011**, *13*, 6362; b) Y.-B. Nie, L. Wang, M.-W. Ding, *J. Org. Chem.* **2012**, *77*, 696; c) K. Rajaguru, R.

Suresh, A. Mariappan, S. Muthusubramanian, N. Bhuvanesh, *Org. Lett.* **2014**, *16*, 744; d) S. Pusch, T. Opatz, *Org. Lett.* **2014**, *16*, 5430; e) S. Samanta, D. Roy, S. Khamarui, D. K. Maiti, *Chem. Commun.* **2014**, *50*, 2477; for representative recently reported methods on synthesis of polysubstituted pyridines, see: f) Y.-F. Wang, K. K. Toh, E. P. J. Ng, S. Chiba, *J. Am. Chem. Soc.* **2011**, *133*, 6411; g) J. M. Neely, T. Rovis, *J. Am. Chem. Soc.* **2014**, *136*, 2735; h) X. Qi, H. Xiang, Q. He, C. Yang, *Org. Lett.* **2014**, *16*, 4186; i) M.-N. Zhao, R.-R. Hui, Z.-H. Ren, Y.-Y. Wang, Z.-H. Guan, *Org. Lett.* **2014**, *16*, 3082.

[7] a) Y.-C. Wang, Y.-Y. Xie, H.-E. Qu, H.-S. Wang, Y.-M. Pan, F.-P. Huang, *J. Org. Chem.* **2014**, *79*, 4463; b) Y.-Y. Xie, Y.-C. Wang, H.-E. Qu, X.-C. Tan, H.-S. Wang, Y.-M. Pan, *Adv. Synth. Catal.* **2014**, *356*, 3347.

[8] CCDC 1023041 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[9] For representative examples, see: a) D. Fischer, H. Tomeba, N. K. Pahadi, N. T. Patil, Y. Yamamoto, *Angew. Chem.* **2007**, *119*, 4848; *Angew. Chem. Int. Ed.* **2007**, *46*, 4764; b) D. Fischer, H. Tomeba, N. K. Pahadi, N. T. Patil, Z. Huo, Y. Yamamoto, *J. Am. Chem. Soc.* **2008**, *130*, 15720; c) Z. Song, Y.-M. Zhao, H. Zhai, *Org. Lett.* **2011**, *13*, 6331; d) N. Gigant, I. Gillaizeau, *Org. Lett.* **2012**, *14*, 4622; e) S. Gupta, J. Han, Y. Kim, S. W. Lee, Y. H. Rhee, J. Park, *J. Org. Chem.* **2014**, *79*, 9094; f) K. Suman, L. Srinu, S. Thennarasu, *Org. Lett.* **2014**, *16*, 3732.

[10] D. S. Reddy, W. R. Judd, J. Aubé, *Org. Lett.* **2003**, *5*, 3899.

[11] L. Xiang, Y. Niu, X. Pang, X. Yang, R. Yan, *Chem. Commun.* **2015**, *51*, 6598.

[12] CCDC 1023042 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[13] For preparation of pyridines by 6π-electrocyclization of aza-triene derivatives, see: a) K. Tanaka, H. Mori, M. Yamamoto, S. Katsumura, *J. Org. Chem.* **2001**, *66*, 3099; b) J. R. Manning, H. M. L. Davies, *J. Am. Chem. Soc.* **2008**, *130*, 8602; c) D. A. Colby, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 3645; d) S. Liu, L. S. Liebeskind, *J. Am. Chem. Soc.* **2008**, *130*, 6918; e) Y. Jiang, C.-M. Park, T.-P. Loh, *Org. Lett.* **2014**, *16*, 3432.

[14] S. Kantevari, S. V. N. Vuppalapati, D. O. Biradar, L. Nagarapu, *J. Mol. Catal. A: Chem.* **2007**, *266*, 109.

[15] S. Samanta, D. Roy, S. Khamarui, D. K. Maiti, *Chem. Commun.* **2014**, *50*, 2477.

[16] D.-S. Kim, J.-W. Park, C.-H. Jun, *Chem. Commun.* **2012**, *48*, 11334.

[17] J. Barluenga, A. Jiménez-Aquino, M. A. Fernández, F. Aznar, C. Valdés, *Tetrahedron* **2008**, *64*, 778.

[18] Q. Wang, C. Wan, Y. Gu, J. Zhang, L. Gao, Z. Wang, *Green Chem.* **2011**, *13*, 578.

[19] D. Wang, L. Salmon, J. Ruiz, D. Astruc, *Chem. Commun.* **2013**, *49*, 6956.

[20] H. Hiroki, K. Ogata, S.-I. Fukuzawa, *Synlett* **2013**, *24*, 843.