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Base-Promoted β-C(sp^3)–H Functionalization of Enaminones: An Approach to Polysubstituted Pyridines

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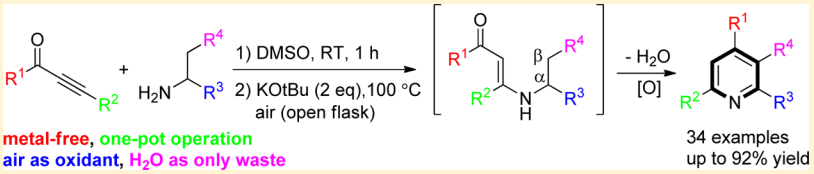
Supporting Information



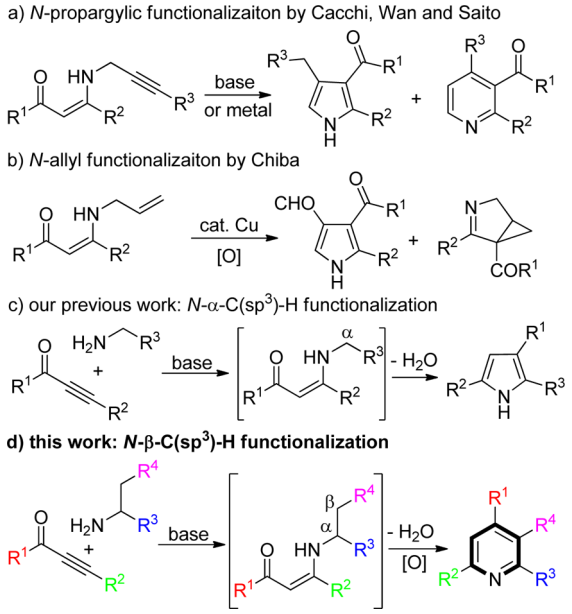
ABSTRACT: A convenient "one-pot" base-promoted synthesis of polysubstituted pyridines from 1-arylethylamines and ynones through the direct β-C(sp^3)–H functionalization of enaminones under metal-free conditions has been developed. An intermolecular Michael addition reaction and an intramolecular condensation were involved in this procedure, which features high regioselectivity, high efficiency, and environmental friendliness. Various polysubstituted pyridines were provided in up to 92% yield for 34 examples.

INTRODUCTION

Pyridine represents one of the most prevalent structural heterocycles in natural products, pharmaceuticals, and advanced materials.[1] Consequently, extensive research has focused on building this motif.[2] Among which, the condensation of carbonyl compounds with ammonia is well-documented as the traditional method.[3] Recently, transition-metal-catalyzed C–H functionalization and cycloaddition reactions[4] and metal-free pyridine synthesis[5] have provided complementary pathways. Despite these advances, the development of a more flexible and operationally simple method using readily available starting materials with broad functional group tolerability is still highly desirable.

β-Enaminones are gaining increased interest as attracting building blocks due to the ambident nucleophilicity of enamines and the ambident eletrophilicity of enones.[6] Among which, *N*-propargyl β-enaminones have been used as intermediates for the synthesis of polysubstituted pyrroles and pyridines in the present of base or transition metal by the groups of Cacchi,[7] Wan,[8] and Saito[9] (Scheme 1, a). *N*-Allyl β-enaminones have been employed in the copper-mediated aerobic synthesis of 3-azabicyclo[3.1.0]hex-2-enes and 4-carbonylpyrroles by the Chiba group (Scheme 1, b).[10] Recently, we reported a base-promoted intramolecular condensation of *N*-benzyl β-enaminones for the synthesis of substituted pyrroles through a direct activation of the sp^3 C–H bond adjacent to nitrogen (Scheme 1, c).[11] In 2011, the Knochel group reported a novel substrate-controlled regioselective arylation of substituted Boc-piperidines,[12] in which, when the α-C of the nitrogen atom was occupied by a methyl group (2-methylpiperidine), the arylation unexpectedly occurred at the β-C position. In our continuing efforts in enaminone chemistry,[11,13] we explore the possibility of direct β-C(sp^3)–H functionalization of *N*-(α-substituted)-benzyl-β-enaminones. As a result, a novel protocol to build polysubstituted pyridines from simple 1-arylethylamines and ynones under mild reaction conditions has been established (Scheme 1, d).

Scheme 1. Synthesis of *N*-Heterocycles from Enaminones



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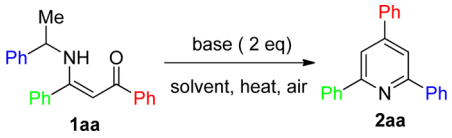
RESULTS AND DISCUSSION

Initially, (*Z*)-1,3-diphenyl-3-((1-phenylethyl)amino)prop-2-en-1-one **1aa** was chosen as a model substrate to optimize the reaction parameters. A series of DMSO-tailored heterogeneous base systems were tested first. As seen from Table 1, all the base/DMSO systems could promote the formation of 2,4,6-triphenylpyridine **2aa** (entries 1−6). The combination of KO^{t}Bu/DMSO was found to be the most effective (yield of **2aa** being 61%, entry 1). Organic base, such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), also worked, albeit in a low yield (32%, entry 7). Further screening solvents showed that this reaction was highly solvent-dependent. Moderate to good yields were achieved in DMSO, DMF, and NMP (entries 2, 8, 9). Toluene, CH_3CN, and dioxane, however, led to no reaction or low yields (entries 10−12). A 78% yield of the desired product was achieved when the temperature was raised to 100 °C (entry 14). Further increasing the reaction temperature accelerated this transformation, but the yield was not improved (entry 15). O_2 atmosphere and decreasing the amount of KO^{t}Bu from 2 equiv to 1 equiv resulted in lower yields (entries 16 and 17). Finally, the optimal condition was identified as 2 equiv of KO^{t}Bu in DMSO at 100 °C under an air atmosphere.

Since the enaminones **1** could be readily prepared from ynones **3** and 1-arylethylamines **4** via Michael addition reaction, a straightforward "one-pot" strategy was adopted to directly synthesize the polysubstituted pyridines **2** from ynones **3** and 1-arylethylamines **4**, avoiding isolation of the intermediate enaminones **1** (Scheme 2). To our delight, 2,4,6-triphenylpyridine **2aa** was obtained from this one-pot strategy in a similar isolated yield as that from enaminone **1aa** (76% vs 77%). Next,

Table 1. Optimization of the Reaction Conditions for the Cyclization of Compound 1aa to 2aa[a]

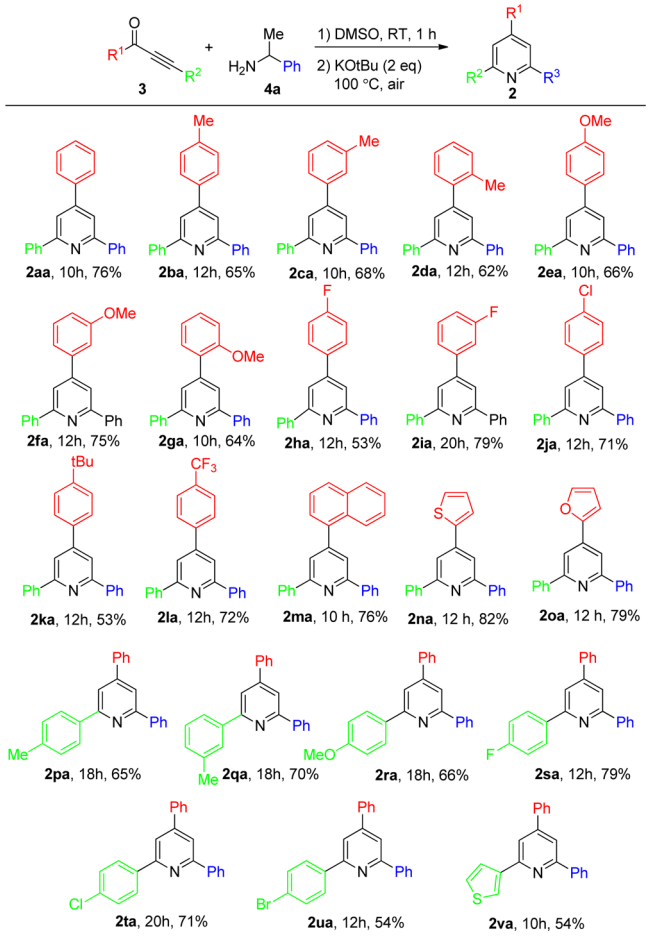


1aa **2aa**

entry	base	solvent	temp (°C)	*t* (h)	yield (%)[b]
1	KO^{t}Bu	DMSO	80	12	61
2	NaO^{t}Bu	DMSO	80	12	53
3	LiO^{t}Bu	DMSO	80	18	37
4	NaOMe	DMSO	80	36	36
5	KOH	DMSO	80	12	59
6	NaOH	DMSO	80	36	56
7	DBU	DMSO	80	36	32
8	KO^{t}Bu	DMF	80	36	38
9	KO^{t}Bu	NMP	80	12	45
10	KO^{t}Bu	toluene	80	36	NR
11	KO^{t}Bu	CH_3CN	80	36	trace
12	KO^{t}Bu	dioxane	80	36	NR
13	KO^{t}Bu	DMSO	90	12	73
14	**KO^{t}Bu**	**DMSO**	**100**	**10**	**78** (77)
15	KO^{t}Bu	DMSO	110	8	73
16[c]	KO^{t}Bu	DMSO	100	4	65
17[d]	KO^{t}Bu	DMSO	100	36	71

[a]Reaction conditions: **1a** (0.25 mmol), base (0.5 mmol), 1 mL of solvent under air. [b]Yields were determined by GC, isolated yield in parentheses. NR = no reaction. [c]Under O_2. [d]0.25 mmol of base. DMF = *N*,*N*-dimethylformamide. NMP = *N*-methyl-2-pyrrolidone. DMSO = dimethyl sulfoxide.

Scheme 2. Reactions of 1-Phenylethylamine 4a with Various Ynones 3



the scope of yonones was explored. The results showed that both electron-withdrawing and electron-donating substituents on R^1 and R^2 were well-tolerated. 1,3-Diarylynones containing electrodonating groups, such as −Me (**2ba**−**2da**, **2pa**−**2qa**), −OMe (**2ea**−**2ga**, **2ra**), and −^{t}Bu (**2ka**), provided the corresponding pyridines in good yields (53−75%). The reactions of 1,3-diarylynones with electrowithdrawing groups (−F and $-CF_3$) also took place efficiently (72−79%, Scheme 2, **2ha**−**2ia**, **2la**, and **2sa**). On the other hand, the steric hindrance did not influence the transformation obviously. The *ortho* substituents on R^1 (**2da** and **2ga**) gave similar yields to the corresponding substrates with *para* and *meta* substituents (**2da** vs **2ba**, **2ca** and **2ga** vs **2ea**, **2fa**). Halogen, including F, Cl, and Br, were all well-tolerated (**2ha**−**2ja** and **2sa**−**2ua**, 53−79% yield), which makes this reaction particularly attractive for increasing the molecular complexity by plenty of transition-metal-catalyzed coupling reactions. The fused aryl and heteroaryl groups, such as naphthyl, thienyl, and furanyl, were also suitable substrates and provided the corresponding pyridines (**2ma**−**2oa**, **2va**) in 54−82% yields. When R^1 or R^2 was an alkyl group, no desired product was obtained.

The scope of 1-arylethylamines **4** was investigated as well (Scheme 3). 1-Phenylethylamines with both electron-withdrawing and electron-donating as well as halogen substitutents, such as methyl, methoxy, fluoro, chloro, and bromo, afforded the corresponding 2,4,6-triarylpyridines in appreciable yields (58−86%, **2ab**−**2af**). 1-(Naphthalen-2-yl)ethylamine and 1-

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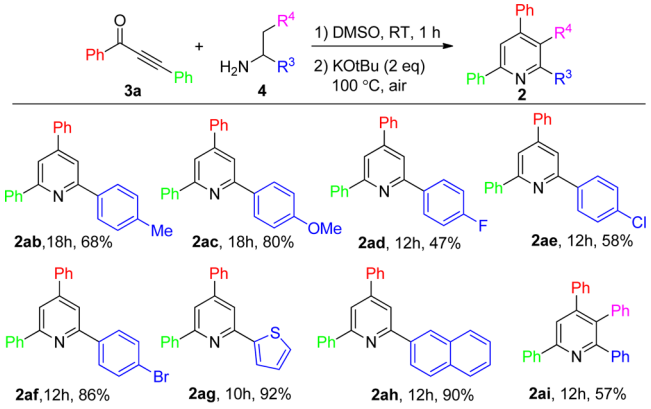
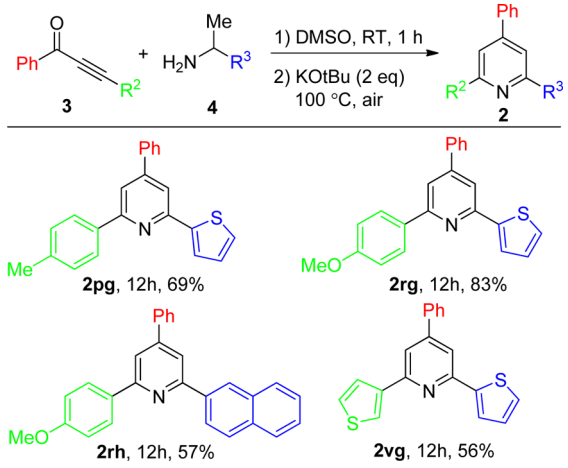
Scheme 3. Reaction of 1,3-Diphenylprop-2-yn-1-one 3a with Various 1-Arylethylamines 4



(thiophen-2-yl)ethylamine proceeded smoothly and produced the desired pyridines **2ag** and **2ah** in excellent yields (92% and 90%, respectively). In terms of the R^4 group, the aryl group worked well under the optimized reaction conditions (57%, Scheme 2, **2ai**). The alkyl group (1-phenylpropan-1-amine, for example) remained inert; only the enaminone intermediate was obtained.

2,4,6-Triarylpyridines (TAPs, Kröhnke pyridines) are useful intermediates in the synthesis of drugs, herbicides, insecticides, and desiccants and are also widely used in supramolecular chemistry.[14] However, unsymmetrical 2,4,6-triarylpyridines are challenging targets for most reported methods.[15] To further the extensive application of our methodology, the synthesis of unsymmetrical 2,4,6-triarylpyridine has been explored as well (Scheme 4). As seen in Scheme 4, four unsymmetrical 2,4,6-

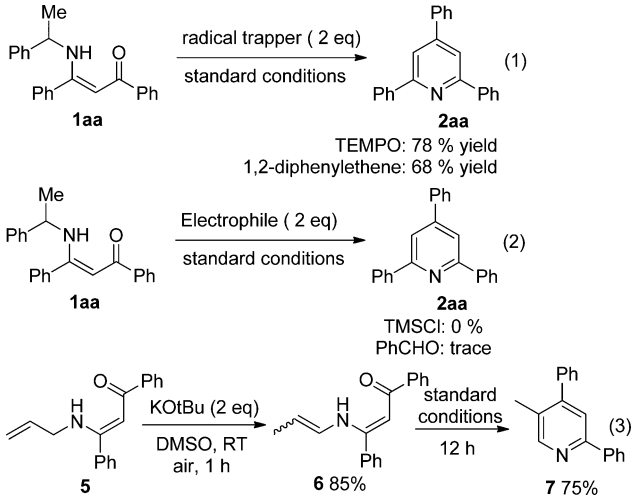
Scheme 4. One-Pot Synthesis of Unsymmetrical 2,4,6-Triarylpyridines



triarylpyridines were obtained in moderated to good isolated yields (56−83%), suggesting that this protocol could be used for preparation of unsymmetrical pyridines directly from simple amines and ynones.

To gain further insight into the possible reaction mechanism, some controlled experiments were carried out (Scheme 5). The radical scavengers, TEMPO (2,2,6,6-tetramethylpiperidinooxy) and 1,1-diphenylethylene, did not inhibited this transformation (eq 1), which indicated that a radical pathway might not be involved in this reaction. When enaminone **1aa** was treated

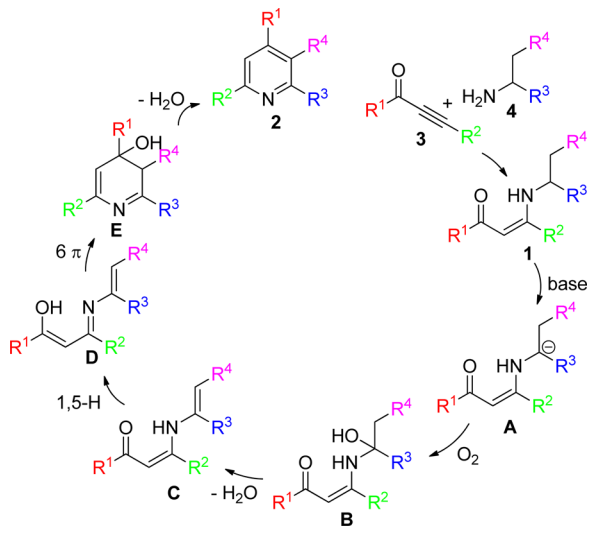
Scheme 5. Controlled Experiments



with 2 equiv of electrophiles (TMSCl and benzaldehyde) under the standard reaction conditions, the desired product **2aa** was not detected (eq 2). These results indicated that this KO^{t}Bu-mediated reaction might be an anion-initiated reaction to the target products. When *N*-propenyl enaminone **6**, prepared from base-promoted alkene isomerization of *N*-allyl enaminone **5**,[16] was treated under the standard conditions for 12 h (eq 3), the desired pyridine product **7** was obtained in 75% yield. This result indicated that an *N*-alkenyl enaminone intermediate might be involved in this reaction.

On the basis of the literatures and aforementioned observations, a tentative reaction mechanism for the formation of functionalized pyridines **2** was proposed, as depicted in Scheme 6. The initial Michael addition reaction of 1-

Scheme 6. Proposed Reaction Mechanism



arylethylamines **3** and ynones **4** provided the enaminones **1**. Deprotonation of **1** by KO^{t}Bu generated the anion intermediates **A**.[11,17] Subsequently, a base-promoted hydroxylation gave the α-hydroxy enaninones **B**.[18] Intermediate **B** then underwent dehydration to give *N*-alkenyl enaminone **C**. Base-promoted 1,5-H shift led to intermediate **D**, which further gave the intermediate **E** by intramolecular electrocyclization.

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Finally, the desired product **2** was formed spontaneously by dehydration of **E**.

CONCLUSION

In conclusion, an efficient approach to polysubstituted pyridines in moderate to excellent yields from readily available 1-arylethylamines and ynones has been developed. The novel direct *N*-β-C(sp^3)−H functionalization of enaminones was applied in this reaction. This protocol only required 2 equiv of KO^{t}Bu as an additive, used air as an oxidant, and generated 2 equiv of H_2O as sole byproduct, which made this process environmentally friendly. This highly practical and modular synthesis represents an alternative method to synthesize pyridine with a broad substrate scope, high atom efficiency, and important synthetic potential of the products.

EXPERIMENTAL SECTION

Unless otherwise stated, all commerical materials and solvents were used directly without further purification. Melting points were determined in open glass capillaries and were uncorrected. ^{1}H NMR spectra were recorded on 400 MHz spectrometers, and ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard at room temperature. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70−230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4 × 15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). The α,β-ynones **3** were prepared according to the literatures.[19]

General Procedure for Synthesis of Polysubstituted Pyridines 2. 1-Arylethylamines **4** (0.5 mmol), α,β-ynones **3** (0.5 mmol), and 2 mL of DMSO were added to a 5 mL Schlenk tube equipped with magnetic stirring. The mixture was stirred at ambient temperature. After completion of Michael addition (monitored by TLC), 2 equiv of KO^{t}Bu was added, and the mixture was heated to 100 °C, and stirred under air atmosphere. After completing reaction, the mixture was diluted with ethyl acetate (10 mL) and washed with brine (3 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvents were evaporated, and the residue was purified by silica gel column chromatography with EA/petroleum ether (1:10) as the eluent to afford the products **2**.

*2,4,6-Triphenylpyridine (**2aa**).*[15c] White crystalline solid (116.7 mg, 76%), mp: 140−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.17 (m, 4H), 7.87 (s, 2H), 7.76−7.71 (m, 2H), 7.53−7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 150.2, 139.6, 139.0, 129.1, 129.0, 128.9, 128.7, 127.2, 127.1, 117.1.

*2,6-Diphenyl-4-(p-tolyl)pyridine (**2ba**).*[15c] Pale yellow solid (104.3 mg, 65%), mp: 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.5 Hz, 4H), 7.85 (s, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.5 Hz, 4H), 7.43 (d, J = 7.3 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 150.0, 139.6, 139.0, 136.0, 129.8, 128.9, 128.6, 127.1, 126.9, 116.8, 21.2.

*2,6-Diphenyl-4-(m-tolyl)pyridine (**2ca**).*[15b] Pale yellow solid (109.1 mg, 68%), mp: 100−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, J = 3.3, 2.7, 1.8 Hz, 4H), 7.88 (d, J = 2.4 Hz, 2H), 7.56−7.48 (m, 6H), 7.47−7.39 (m, 3H), 7.29 (dd, J = 4.3, 3.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 150.3, 139.6, 139.0, 138.8, 129.7, 129.0, 128.7, 127.9, 127.1, 124.3, 117.1, 21.5.

*2,6-Diphenyl-4-(o-tolyl)pyridine (**2da**).*[20] Pale yellow solid (99.5 mg, 62%), mp: 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.3 Hz, 4H), 7.66 (s, 2H), 7.49 (t, J = 7.5 Hz, 4H), 7.42 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 5.3 Hz, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 151.3, 139.8, 139.5, 135.1, 130.7, 129.2, 129.0, 128.7, 128.3, 127.1, 126.1, 119.3, 20.4.

*4-(4-Methoxyphenyl)-2,6-diphenylpyridine (**2ea**).*[15c] Pale yellow solid (111.2 mg, 66%), mp: 99−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.15 (m, 4H), 7.84 (s, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.53−7.46 (m, 4H), 7.44 (d, J = 7.2 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.4, 149.6, 139.7, 131.3, 128.9, 128.6, 128.3, 127.1, 116.6, 114.5, 55.4.

*4-(3-Methoxyphenyl)-2,6-diphenylpyridine (**2fa**).* Yellow oil (126.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.2 Hz, 4H), 7.87 (s, 2H), 7.58−7.39 (m, 7H), 7.32 (d, J = 7.6 Hz, 1H), 7.24 (d, J = 10.0 Hz, 1H), 7.00 (dd, J = 8.1, 2.2 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 157.5, 150.1, 140.6, 139.6, 130.2, 129.0, 128.7, 127.1, 119.6, 117.1, 114.5, 113.0, 55.4; HRMS (ESI) m/z calcd for $C_{24}H_{20}NO$ (MH^+) 338.1545, found 338.1541.

*4-(2-Methoxyphenyl)-2,6-diphenylpyridine (**2ga**).* Pale yellow solid (107.8 mg, 64%), mp: 120−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.5 Hz, 4H), 7.85 (s, 2H), 7.49 (t, J = 7.5 Hz, 4H), 7.41 (dt, J = 12.5, 6.2 Hz, 4H), 7.11−7.01 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.6, 147.9, 139.8, 130.5, 130.0, 128.8, 128.6, 128.4, 127.1, 121.0, 119.7, 111.4, 55.6; HRMS (ESI) m/z calcd for $C_{24}H_{20}NO$ (MH^+) 338.1545, found 338.1543.

*4-(4-Fluorophenyl)-2,6-diphenylpyridine (**2ha**).*[15c] Pale yellow solid (86.1 mg, 53%), mp: 127−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.5 Hz, 4H), 7.82 (s, 2H), 7.71 (dd, J = 8.5, 5.4 Hz, 2H), 7.51 (t, J = 7.5 Hz, 4H), 7.44 (t, J = 7.1 Hz, 2H), 7.22 (dd, J = 15.0, 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, J = 249.1 Hz), 157.6, 149.2, 139.5, 135.2 (d, J = 3.2 Hz), 129.2, 129.0 (d, J = 8.3 Hz), 128.8, 127.2, 116.9, 116.1 (d, J = 21.7 Hz).

*4-(3-Fluorophenyl)-2,6-diphenylpyridine (**2ia**).* Pale yellow solid (128.4 mg, 79%), mp: 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.4 Hz, 4H), 7.87 (s, 2H), 7.50 (dt, J = 27.3, 7.3 Hz, 9H), 7.19 (t, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.27 (d, J = 246.9 Hz), 157.7, 148.9, 141.3 (d, J = 7.6 Hz), 139.7, 130.7 (d, J = 8.3 Hz), 129.2, 128.7, 127.1, 122.9 (d, J = 2.8 Hz), 116.9, 115.8 (d, J = 21.1 Hz), 114.2 (d, J = 22.3 Hz); HRMS (ESI) m/z calcd for $C_{23}H_{17}FN$ (MH^+) 326.1345, found 326.1345.

*4-(4-Chlorophenyl)-2,6-diphenylpyridine (**2ja**).*[15c] White crystalline solid (121.1 mg, 71%), mp: 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.14 (m, 4H), 7.81 (s, 2H), 7.65 (dd, J = 8.8, 2.1 Hz, 2H), 7.55−7.40 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 148.9, 139.4, 137.5, 135.2, 129.3, 129.1, 128.7, 128.4, 127.1, 116.8.

*4-(4-(tert-Butyl)phenyl)-2,6-diphenylpyridine (**2ka**).* Yellow oil (96.2 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 4H), 7.88 (s, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.56−7.48 (m, 6H), 7.43 (t, J = 7.2 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 152.3, 150.0, 139.7, 136.1, 129.0, 128.7, 127.1, 126.8, 126.1, 117.0, 34.7, 31.3; HRMS (ESI) m/z calcd for $C_{27}H_{26}N$ (MH^+) 364.2065, found 364.2062.

*2,6-Diphenyl-4-(4-(trifluoromethyl)phenyl)pyridine (**2la**).* White crystalline solid (135.0 mg, 72%), mp: 137−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 4H), 7.85 (dd, J = 12.2, 5.9 Hz, 4H), 7.78 (d, J = 8.3 Hz, 2H), 7.49 (dt, J = 26.3, 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.8, 139.2, 129.3, 128.8, 128.7, 127.6, 127.1, 126.1 (dd, J = 7.0, 3.4 Hz), 117.0; HRMS (ESI) m/z calcd for $C_{24}H_{17}F_3N$ (MH^+) 376.1313, found 376.1310.

*4-(Naphthalen-1-yl)-2,6-diphenylpyridine (**2ma**).* Pale yellow solid (135.7 mg, 76%), mp: 134−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−8.17 (m, 5H), 8.03−7.93 (m, 4H), 7.93−7.88 (m, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.54 (dd, J = 12.5, 5.6 Hz, 6H), 7.46 (t, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.1, 139.6, 136.3, 133.5, 133.4, 129.1, 129.0, 128.7, 128.4, 127.8, 127.2, 126.8, 126.7, 126.5, 124.8 117.3; HRMS (ESI) m/z calcd for $C_{27}H_{20}N$ (MH^+) 358.1596, found 358.1594.

*2,6-Diphenyl-4-(thiophen-2-yl)pyridine (**2na**).*[15c] Pale yellow solid (128.3 mg, 82%), mp: 163−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.3 Hz, 4H), 7.84 (s, 2H), 7.58 (d, J = 3.5 Hz, 1H), 7.45 (ddd, J = 15.2, 11.0, 6.1 Hz, 7H), 7.16−7.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 142.9, 141.9, 139.3, 129.1, 128.7, 128.3, 127.1, 126.9, 125.2, 115.3.

*4-(Furan-2-yl)-2,6-diphenylpyridine (**2oa**).*[20] White crystalline solid (117.3 mg, 79%), mp: 170−171 °C. ^{1}H NMR (400 MHz,

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CDCl3) δ 8.22−8.17 (m, 4H), 7.93 (s, 2H), 7.59 (dd, J = 1.8, 0.6 Hz, 1H), 7.54−7.48 (m, 4H), 7.47−7.41 (m, 2H), 6.98 (dd, J = 3.5, 0.5 Hz, 1H), 6.57 (dd, J = 3.4, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 152.0, 143.6, 139.5, 139.1, 129.1, 128.7, 127.1, 113.0, 112.1, 108.5.

*2,4-Diphenyl-6-(p-tolyl)pyridine (**2pa** and **2ab**).*[21] Pale yellow solid (**2pa**: 104.3 mg, 65%; **2ab**: 109.1 mg, 68%), mp: 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 5.3, 3.3 Hz, 2H), 8.11 (d, J = 8.2 Hz, 2H), 7.86 (s, 2H), 7.75 (dd, J = 5.2, 3.2 Hz, 2H), 7.55−7.41 (m, 6H), 7.32 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 157.4, 150.1, 139.7, 139.2, 139.0, 136.8, 129.4, 129.1, 129.0, 128.9, 128.7, 127.2, 127.1, 127.0, 116.8, 116.8, 21.3.

*2,4-Diphenyl-6-(m-tolyl)pyridine (**2qa**).* White crystalline solid (112.4 mg, 70%), mp: 106−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.3 Hz, 2H), 8.02 (s, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.86 (s, 2H), 7.76−7.71 (m, 2H), 7.54−7.36 (m, 7H), 7.25 (d, J = 7.7 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.5, 150.1, 139.7, 139.6, 139.1, 138.3, 129.8, 129.1, 129.0, 128.9, 128.7, 128.6, 127.8, 127.7, 127.2, 124.3, 117.2, 117.1, 21.6; HRMS (ESI) m/z calcd for $C_{24}H_{20}N$ (MH^+) 322.1596, found 322.1592.

*2-(4-Methoxyphenyl)-4,6-diphenylpyridine (**2ra** and **2ac**).*[22] White crystalline solid (**2ra**: 111.2 mg, 66%; **2ac**: 134.8 mg, 80%), mp: 106−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23−8.14 (m, 4H), 7.82 (dd, J = 3.3, 1.3 Hz, 2H), 7.76−7.70 (m, 2H), 7.55−7.40 (m, 6H), 7.07−7.00 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.3, 157.1, 150.1, 139.7, 139.2, 132.2, 129.1, 128.9, 128.9, 128.7, 128.4, 127.2, 127.1, 116.5, 116.3, 114.1, 55.4.

*2-(4-Fluorophenyl)-4,6-diphenylpyridine (**2sa** and **2ad**).*[23] White crystalline solid (**2sa**: 128.4 mg, 79%; **2ad**: 76.4 mg, 47%), mp: 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23−8.16 (m, 4H), 7.88 (d, J = 1.3 Hz, 1H), 7.83 (d, J = 1.3 Hz, 1H), 7.74 (dd, J = 5.2, 3.2 Hz, 2H), 7.56−7.44 (m, 6H), 7.24−7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, J = 248.4 Hz), 157.6, 156.5, 150.3, 139.5, 139.0, 135.7 (d, J = 3.1 Hz), 129.1, 129.1, 129.0, 128.9 (d, J = 8.3 Hz), 128.7, 127.8, 127.1, 117.1, 116.8, 115.59 (d, J = 21.6 Hz).

*2-(4-Chlorophenyl)-4,6-diphenylpyridine (**2ta** and **2ae**).*[21] Pale yellow solid (**2ta**: 121.1 mg, 71%; **2ae**: 98.9 mg, 58%), mp: 120−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ8.26−8.16 (m, 4H), 7.88 (s, 2H), 7.73 (d, J = 7.2 Hz, 2H), 7.54−7.48 (m, 6H), 7.45 (d, J = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 150.2, 139.6, 139.0, 129.1, 129.0, 128.9, 128.8, 128.7, 128.4, 127.2, 127.1, 117.1.

*2-(4-Bromophenyl)-4,6-diphenylpyridine (**2ua** and **2af**).*[23] Pale yellow solid (**2ua**: 104.1 mg, 76%; **2af**: 165.6 mg, 86%), mp: 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 4H), 7.88 (s, 2H), 7.77−7.71 (m, 2H), 7.54−7.48 (m, 6H), 7.47−7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 150.2, 139.6, 139.1, 129.1, 129.0, 129.0, 128.7, 127.2, 127.1, 117.1.

*2,4-Diphenyl-6-(thiophen-3-yl)pyridine (**2va**).* Pale yellow solid (84.5 mg, 54%), mp: 110−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.4 Hz, 2H), 8.06 (d, J = 3.0 Hz, 1H), 7.86−7.78 (m, 2H), 7.73 (dd, J = 11.4, 3.9 Hz, 3H), 7.54−7.40 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.6, 150.1, 142.5, 139.5, 139.0, 129.1, 129.0, 128.9, 128.7, 127.1, 127.1, 126.5, 126.1, 123.8, 116.8, 116.8; HRMS (ESI) m/z calcd for $C_{21}H_{16}NS$ (MH^+) 314.1003, found 314.1001.

*2,4-Diphenyl-6-(thiophen-2-yl)pyridine (**2ag**).* Pale yellow solid (144.0 mg, 92%), mp: 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.12 (m, 2H), 7.82−7.68 (m, 5H), 7.56−7.39 (m, 7H), 7.18−7.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 152.7, 150.2, 145.4, 139.0, 138.8, 129.1, 129.1, 129.0, 128.7, 127.9, 127.7, 127.1, 127.0, 124.6, 116.8, 115.3; HRMS (ESI) m/z calcd for $C_{21}H_{16}NS$ (MH^+) 314.1003, found 314.1003.

*2-(Naphthalen-2-yl)-4,6-diphenylpyridine (**2ah**).* White crystalline solid (160.6 mg, 90%), mp: 126−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.42 (dd, J = 8.6, 1.8 Hz, 1H), 8.29 (dd, J = 5.2, 3.4 Hz, 2H), 8.06 (d, J = 1.3 Hz, 1H), 8.02 (dd, J = 8.9, 5.9 Hz, 2H), 7.93 (dd, J = 8.9, 2.8 Hz, 2H), 7.85−7.77 (m, 2H), 7.62−7.48 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 157.4, 150.3, 139.7, 139.1, 137.0, 133.8, 133.6, 129.2, 129.1, 129.1, 128.8, 128.4, 127.8, 127.3, 127.3, 126.5, 126.5, 126.3, 125.0, 117.4, 117.2; HRMS (ESI) m/z calcd for $C_{27}H_{20}N$ (MH^+) 358.1596, found 358.1595.

*2,3,4,6-Tetraphenylpyridine (**2ai**).*[24] Pale yellow solid (109.2 mg, 57%), mp: 178−181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.4 Hz, 2H), 7.80 (s, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.46−7.38 (m, 3H), 7.26−7.20 (m, 6H), 7.18−7.05 (m, 5H), 6.94 (d, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 155.6, 150.6, 141.0, 139.8, 139.1, 137.9, 132.8, 131.4, 130.2, 129.3, 129,0, 128.7, 127.9, 127.7, 127.5, 127.3, 127.3, 127.0, 126.6, 120.3.

*4-Phenyl-2-(thiophen-2-yl)-6-(p-tolyl)pyridine (**2pg**).* Yellow oil (112.8 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 2H), 7.81−7.65 (m, 5H), 7.53−7.42 (m, 3H), 7.39 (dd, J = 5.0, 1.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 5.0, 3.7 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 152.6, 150.0, 145.6, 139.1, 138.9, 136.2, 129.4, 129.0, 128.9, 127.9, 127.5, 127.1, 126.9, 124.5, 116.4 115.0, 21.3; HRMS (ESI) m/z calcd for $C_{22}H_{18}NS$ (MH^+) 328.1160, found 328.1158.

*2-(4-Methoxyphenyl)-4-phenyl-6-(thiophen-2-yl)pyridine (**2rg**).* Pale yellow solid (142.3 mg, 83%), mp: 103−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.10 (m, 2H), 7.78−7.67 (m, 5H), 7.55−7.44 (m, 3H), 7.41 (dd, J = 5.0, 1.0 Hz, 1H), 7.14 (dd, J = 5.0, 3.7 Hz, 1H), 7.06−7.00 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 156.9, 152.6, 150.1, 145.6, 139.0, 131.7, 129.1, 129.0, 128.3, 127.9, 127.5, 127.1, 124.5, 116.0, 114.6, 114.1, 55.4; HRMS (ESI) m/z calcd for $C_{22}H_{18}NOS$ (MH^+) 344.1109, found 344.1107.

*2-(4-Methoxyphenyl)-6-(naphthalen-2-yl)-4-phenylpyridine (**2rh**).* Pale yellow solid (110.3 mg, 57%), mp: 123−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 1.2 Hz, 1H), 8.37 (dd, J = 8.6, 1.8 Hz, 1H), 8.26−8.17 (m, 2H), 7.99 (d, J = 1.4 Hz, 3H), 7.93−7.88 (m, 1H), 7.86 (d, J = 1.3 Hz, 1H), 7.79 (d, J = 6.9 Hz, 2H), 7.60−7.44 (m, 5H), 7.07 (d, J = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.3, 157.2, 150.2, 139.3, 137.0, 133.7, 133.5, 132.3, 129.1, 128.9, 128.7, 128.5, 128.3, 127.7, 127.2, 126.4, 126.4, 126.2, 124.9, 116.8, 116.5, 114.1, 55.4; HRMS (ESI) m/z calcd for $C_{28}H_{22}NO$ (MH^+) 388.1707, found 388.1705.

*4-Phenyl-2-(thiophen-2-yl)-6-(thiophen-3-yl)pyridine (**2vg**).* Pale yellow solid (89.3 mg, 56%), mp: 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 3.0, 1.2 Hz, 1H), 7.79 (dd, J = 5.0, 1.2 Hz, 1H), 7.72−7.68 (m, 4H), 7.66 (d, J = 1.4 Hz, 1H), 7.55−7.45 (m, 3H), 7.44−7.36 (m, 2H), 7.13 (dd, J = 5.0, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 152.7, 150.1, 145.3, 142.1, 138.7, 129.1, 129.0, 127.9, 127.7, 127.1, 126.4, 126.2, 124.6, 124.0, 116.6, 115.0; HRMS (ESI) m/z calcd for $C_{19}H_{14}NS_2$ (MH^+) 320.0568, found 320.0564.

*5-Methyl-2,4-diphenylpyridine (**7**).*[25] Pale yellow solid (91.9 mg, 75%), mp: 78−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 0.4 Hz, 1H), 8.01 (dd, J = 8.4, 1.1 Hz, 2H), 7.61 (s, 1H), 7.51−7.35 (m, 8H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.2, 149.9, 139.4, 139.3, 129.1, 128.6, 128.6, 128.5, 128.4, 127.9, 126.7, 120.9, 16.9.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00635.

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Author Contributions

The authors declare no competing financial interest.

Notes

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