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TMSOTf-mediated Kröhnke pyridine synthesis using HMDS as the nitrogen source under microwave irradiation†

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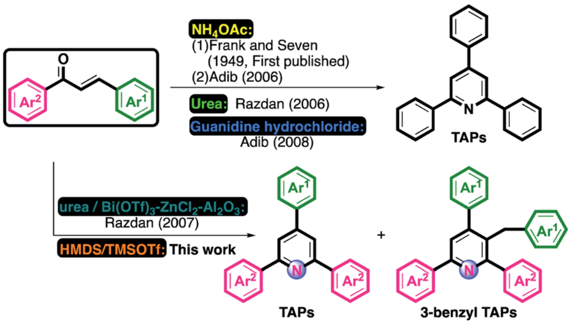
An efficient protocol for the preparation of pyridine skeletons has been successfully developed involving the TMSOTf/HMDS (trifluoromethanesulfonic acid/hexamethyldisilane) system for the intermolecular cyclization of chalcones under MW (microwave) irradiation conditions. This method provides a facile approach to synthesize 2,4,6-triaryl or 3-benzyl-2,4,6-triarylpyridines in good to excellent yields. Interestingly, the 2,6-diazabicyclo[2.2.2]oct-2-ene core was obtained by changing the acid additive to $Sn(OTf)_2$, and the desired product was also confirmed using X-ray single-crystal diffraction analysis.

Pyridines serve as an essential framework, and their derivatives have gained considerable interest in organic chemistry owing to their presence in a wide range of natural products such as NAD (nicotinamide adenine dinucleotide) nucleotides, pyridoxine (vitamin B_6), pyridine alkaloids,[1] pharmaceuticals (as antimalarial, vasodilatory, anaesthetic, anticonvulsant and antiepileptic drugs),[2] agrochemicals (as fungicides, pesticides, and herbicides),[3] electrochemical,[4] functionalized materials,[5] organocatalysts,[6] and synthetic ligands.[7] Among them, 2,4,6-triarylpyridines (TAPs, known as Kröhnke pyridines) are practical intermediates in the synthesis of drugs, herbicides, insecticides, desiccants, and surfactants.[8] Due to their excellent π-stacking ability and thermal stability, these substituted pyridines can be used in fluorescent small molecules, polymers, supramolecules, and for asymmetric catalysis and coordination.[9] They are also recognized as useful precursors as they are structurally related to symmetrical triaryl-thiopyrylium, triaryl-selenopyrylium, and triaryl-telluropyrylium photosensitizers, and have been investigated for photodynamic cell-specific cancer therapeutic agents.[10] These chalcogenopyrylium analogues are also applied in achieving nucleophilic displacement,[11] *C*-alkylation of β-diketones *via* a radical pathway,[12] electrophilic aminations,[13] and for the preparation of substituted azepines.[14] Considering the versatile functions of TAPs in the fields of organic synthesis and medicinal chemistry, the synthetic protocols of TAPs are still of great interest.[15]

TAPs were first prepared *via* the thermal condensation of aldehydes with ammonia by the Russian chemist Aleksey Chichibabin in 1906.[17] This reaction was then modified as the condensation of aldehydes and enolizable ketones with various nitrogen sources, and has become the most popular protocol for the construction of symmetrical scaffolds, which contain identical substituents at the 2- and 6-positions of the pyridine ring.[18]

Most Chichibabin-type TAP synthetic approaches start from acetophenones with benzaldehydes in the presence of ammonium acetate and are catalyzed by a variety of catalysts.[15,16,19] Among these, the synthetic routes for the synthesis of symmetrical TAPs not only involve the Chichibabin reaction but also methods with fixed nitrogen on starting materials such as benzylamines[20] or oxime acetates.[21] For the preparation of symmetrical TAPs, chalcones are usually applied as the starting material or paired with condensable synthons from various ammonia sources.[22] As shown in Scheme 1, Frank and Seven reported the revised Chichibabin reaction for the preparation of pyridines.[18] In 2006, Adib described a revised method involving the solvent-free synthesis of TAPs.[23] Meanwhile, Razdan developed a solid-supported synthesis of TAPs using urea as an ammonia source.[24] Later, Adib substituted guanidine hydrochloride for urea to prepare TAPs under neat and MW



Scheme 1 Synthesis of 2,4,6-triarylpyridines (TAPs).

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† Electronic supplementary information (ESI) available: Experimental procedures, characterisation data, copies of ^{1}H and ^{13}C NMR spectra, and crystallographic data for **2q** and **4**. CCDC 2085356 and 2085361. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d2ra00084a

conditions.[25] Interestingly, Razdan's group reported a synthetic route for the synthesis of TAPs and 3-benzyl TAPs using immobilized metal catalysts and urea as an ammonia source.[26]

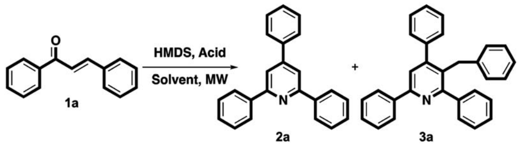
In continuation of our efforts in the synthesis of diversified heterocyclic skeletons under microwave (MW) conditions,[27] we recently developed a series of synthetic protocols for the synthesis of substituted nitrogen-containing compounds involving the HMDS/TMSOTf system under MW conditions.[27a–c] On the basis of our previous successful experiments, HMDS serves as a useful N source in this synthetic routes. Only one method for one-pot synthesis of TAPs and 3-benzyl TAPs from chalcones, using urea as the N source, and the immobilized metal catalysts, have been reported.[26] Therefore, we applied such metal-free conditions to synthesize substituted TAPs and 3-benzyl TAPs. Although the synthetic protocols for TAPs are well documented, the development of facile methodologies is of great interest. In this work, we describe a facile synthetic route for the synthesis of TAPs and rare 3-benzyl TAPs under MW with modest to good yields.

First, the chalcone compound **1a** was selected as a model substrate to react with HMDS as a nitrogen source by using acidic additives under MW to optimize this Kröhnke reaction conditions, as shown in Table 1. Based on the basis of our previous work, we believe that TMSOTf is an appropriate acidic additive to catalyze HMDS in heterocyclic compound synthesis.[27a–c] In entry 1, the reaction was conducted in DCM and HMDS and catalyzed by TMSOTf under MW at 150 °C in 0.5 h, 50% yield of **2a** and 44% yield of **3a** were obtained. When the reaction solvent was changed to other nonpolar solvents such as toluene and THF, no obvious yield changes were detected (entries 2–3), but MeCN affected the decreasing yield and only a trace amount of **3a** was isolated (entry 4). Surprisingly, $(CuOTf)_2\cdot$toluene did not favor the reaction, while AgOTf and $Cu(OTf)_2$ provided modest yields (entries 5–7). Some metal(III) triflates were also investigated in this synthesis route, including $Sc(OTf)_3$, $Bi(OTf)_3$, $Fe(OTf)_3$, and $In(OTf)_3$; similar yields of **2a** and lower yields of **3a** were detected (entries 8–11). $In(OTf)_3$ showed a higher tendency for the formation of **2a** than for **3a**. Other Lewis acids were also chosen to test the reaction, and the results suggest that non-triflate-type Lewis acids give poor results (entries 12–14). In entries, 15–17, Brønsted acids, AcOH, TfOH and *p*-TsOH were also investigated in this reaction. AcOH and TfOH could successfully promote this reaction and provide modest yields, but *p*-TsOH did not work. Notably, only one literature report has discussed the preparation of 3-benzyl TAPs. According to the results for entries 1 to 17, we confirmed that entry 1 shows the best conditions for this intermolecular cyclization for the preparation of substituted TAPs and 3-benzyl TAPs in totally high yields.

With the optimal conditions in hand, we initially examined the scope and generality of functionalized chalcones **1b–1q** for this intermolecular cyclization. As shown in Table 2, we first investigated the electron-withdrawing substituents on the Ar^1 ring, including the 4-halogenated substituent **1b–1d** and 4-nitro group **1e**. The corresponding TAPs **2b–2e** and 3-benzyl TAPs **3b–3e** were obtained in modest to good yields. Some electron-donating substituents on *para*-position of the Ar^1 ring, such as methyl **1f**, methoxy **1g**, and phenyl **1h** were also examined under optimized conditions and the desired TAPs **2f–2h** and 3-benzyl TAPs **3f–3h** were isolated in good yields. Other functionalized groups on the Ar^1 ring, including 1-naphthalene **1i**, 2-methyl **1j**, 2-methoxy **1k**, 3-methyl **1l**, 3-methoxy **1m**, 3,4-dimethoxy **1n** also reacted smoothly under optimal conditions and provided the relevant TAPs **2i–2n** and 3-benzyl TAPs **3i–3n** in totally good to excellent yields. Notably, when the Ar^1 ring was 2-naphthalene **1o**, anthracene **1p**, or piperonal **1q**, only corresponding TAPs **2o–2q** were obtained. This may be because the steric hindrance effect causes the unsuccessful formation of 3-benzyl TAPs **3o–3q**. The structure of **2q** was also confirmed from X-ray single-crystal crystallography.[28]

Then, we tested a variety of chalcones with various functional groups on the Ar^2 ring to extend the scope of the reaction and generality of this intermolecular cyclization. The results showed high generality and broad functional group tolerance. The corresponding compound structures and related yields are illustrated in Table 3. The *para*-substituted group of the Ar^2 ring was first examined; when the Ar^1 ring was benzene, including **1r** ($Ar^2 = 4\text{-}FC_6H_4$), **1s** ($Ar^2 = 4\text{-}FC_6H_4$), **1t** ($Ar^2 = 4\text{-}MeC_6H_4$), **1u** ($Ar^2 = 4\text{-}OMeC_6H_4$) and **1v** ($Ar^2 = 4\text{-}PhC_6H_4$), total yields of corresponding TAPs **2r–2v** and 3-benzyl TAPs **3r–3v** were between 76% and 95% yields. Some *meta*- and *ortho*-substituents on Ar^2 ring, such as **1w** ($Ar^2 = 3\text{-}FC_6H_4$), **1x** ($Ar^2 = 2\text{-}MeC_6H_4$) and **1y** ($Ar^2 = 2\text{-}BrC_6H_4$), and heterocyclic ring **1z** (Ar^2 = 3-thiophene)

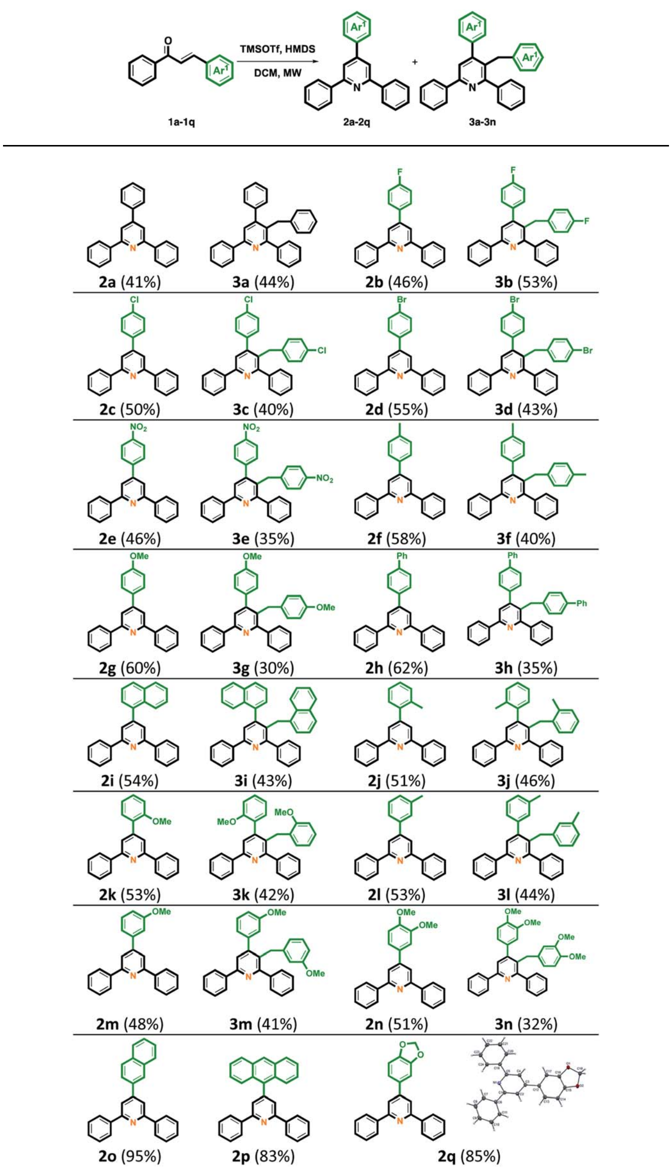
Table 1 Optimization of the reaction conditions[a]



Entry	Acid	Solvent	Yields[b] (%) 2a	Yields[b] (%) 3a
1	TMSOTf	DCM	50	44
2	TMSOTf	Toluene	48	43
3	TMSOTf	THF	56	33
4	TMSOTf	MeCN	44	<5
5	AgOTf	DCM	44	17
6[c]	$(CuOTf)_2\cdot$toluene	DCM	N.R.	N.R.
7	$Cu(OTf)_2$	DCM	58	15
8	$Sc(OTf)_3$	DCM	52	24
9	$Bi(OTf)_3$	DCM	47	30
10	$Fe(OTf)_3$	DCM	52	30
11	$In(OTf)_3$	DCM	62	20
12	Ac_2O	DCM	N.R.	N.R.
13	$AlCl_3$	DCM	23	—[d]
14	$BF_3\cdot OEt_2$	DCM	31	20
15	AcOH	DCM	52	20
16	TfOH	DCM	50	23
17[c]	*p*-TsOH	DCM	N.R.	N.R.

[a] Reaction conditions: **1a** (1.0 mmol), HMDS (0.5 mL, 2.4 mmol), acid (0.5 mmol), solvent (2 mL), MW (150 °C), 0.5 h. [b] Isolated yields. [c] No reaction occurred. [d] Unknown products were obtained.

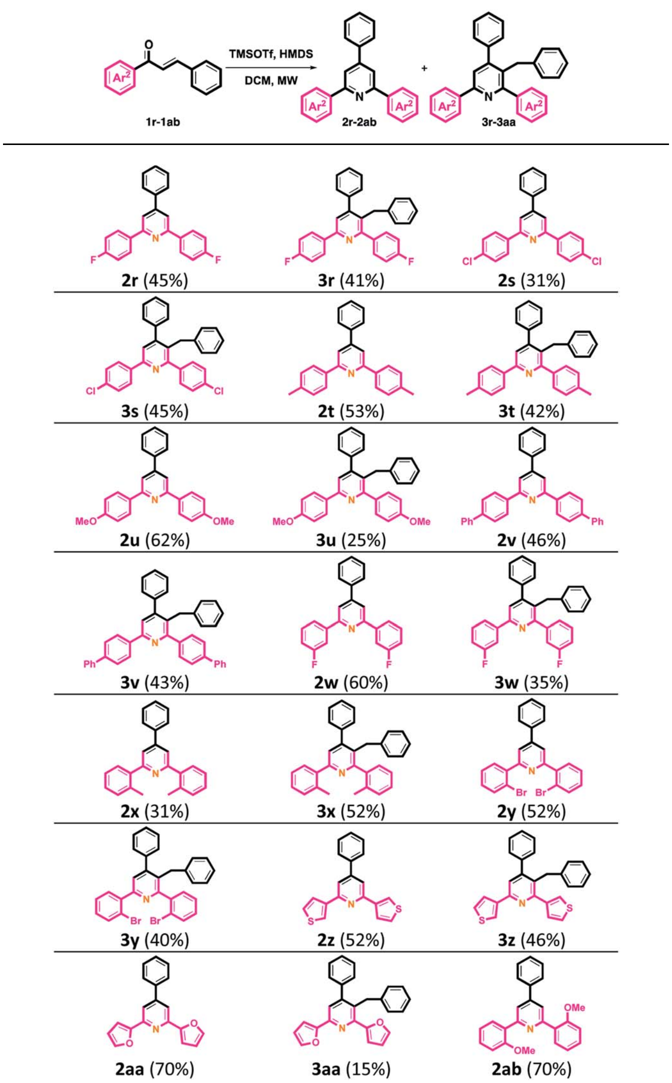
Table 2 Synthesis of **2a–2q** and **3a–3n**[a,b]



2a (41%) **3a** (44%) **2b** (46%) **3b** (53%)
2c (50%) **3c** (40%) **2d** (55%) **3d** (43%)
2e (46%) **3e** (35%) **2f** (58%) **3f** (40%)
2g (60%) **3g** (30%) **2h** (62%) **3h** (35%)
2i (54%) **3i** (43%) **2j** (51%) **3j** (46%)
2k (53%) **3k** (42%) **2l** (53%) **3l** (44%)
2m (48%) **3m** (41%) **2n** (51%) **3n** (32%)
2o (95%) **2p** (83%) **2q** (85%)

[a] Reaction conditions: **1a–1q** (1.0 mmol), HMDS (0.5 mL, 2.4 mmol), TMSOTf (0.1 mL, 0.5 mmol), DCM (2 mL), MW (150 °C), 0.5 h. [b] Isolated yields.

Table 3 Synthesis of **2r–2ab** and **3r–3aa**[a,b]

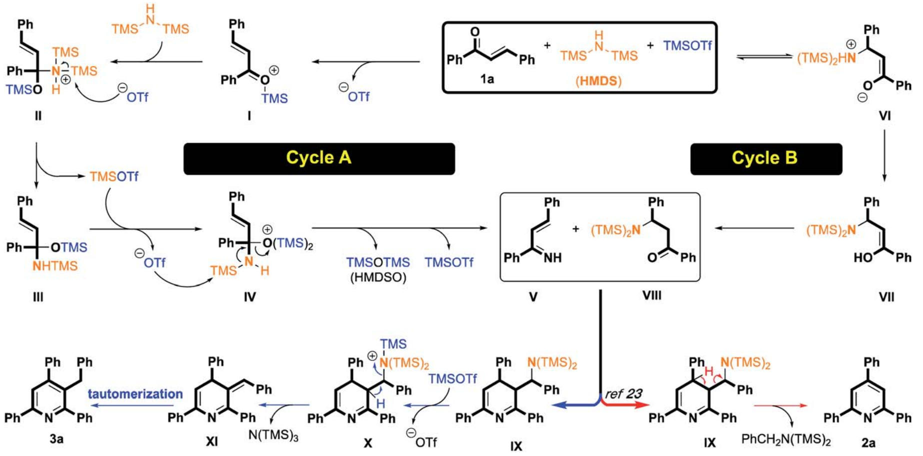


2r (45%) **3r** (41%) **2s** (31%)
3s (45%) **2t** (53%) **3t** (42%)
2u (62%) **3u** (25%) **2v** (46%)
3v (43%) **2w** (60%) **3w** (35%)
2x (31%) **3x** (52%) **2y** (52%)
3y (40%) **2z** (52%) **3z** (46%)
2aa (70%) **3aa** (15%) **2ab** (70%)

[a] Reaction conditions: **1r–1ab** (1.0 mmol), HMDS (0.5 mL, 2.4 mmol), TMSOTf (0.1 mL, 0.5 mmol), DCM (2 mL), MW (150 °C), 0.5 h. [b] Isolated yields.

and **1aa** (Ar^2 = 2-furan) provided the desired products **2w–2aa** and **3w–3aa** in totally good to excellent yields. We assume that the steric hindrance is the reason for the selective formation of product 2 ab from 1 ab at 70% yield.

Based on the above-mentioned results and our previous work,[27] a plausible pathway for the selective synthesis of TAPs and 3-benzyl TAPs is illustrated as shown in Scheme 2. In cycle A, compound **1a** was first activated using TMSOTf to generate intermediate **I** with the release of the triflate anion. HMDS was added to intermediate **I** through nucleophilic addition to give intermediate **II**, which was then attacked by the triflate anion to form intermediate **III** along with recycling of TMSOTf. TMSOTf activated the oxygen of intermediate **III** again to give intermediate **IV**, which was also attacked by the triflate anion to afford intermediate **V** together with HMDSO (hexamethyldisiloxane) and recycle TMSOTf. In cycle B, the 1,4-addition of HMDS with compound **1a** occurred to generate derivative **VI**, followed by proton exchange to give intermediate **VII**. Intermediate **VIII** was formed *via* keto–enol tautomerization. After the formation of intermediate **V** from cycle A and the generation of intermediate **VIII** from cycle B, the intermolecular cyclization occurred smoothly, yielding intermediate **IX**. For the red arrow, the oxidative aromatization with the release of *N*,*N*-di(trimethylsilyl)-benzylamine would yield TAPs product **2a.**[23] Considering the blue arrow, TMSOTf activated benzylamine fragment to obtain intermediate **X**, and then aromatization occurred with the removal of tris(trimethylsilyl)amine to form 3-benzylidiene-3,4-

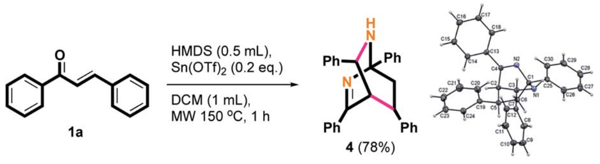


Scheme 2 Proposed mechanism for the synthesis of TAPs.

dihydropyridine **XI**, which is spontaneously converted to the corresponding 3- benzyl TAPs **3a** by tautomerism.

Surprisingly, an unexpected product **4** was obtained in 78% yield when the acidic additive was changed from TMSOTf to $Sn(OTf)_2$ under this condition. Interestingly, one C–C bond and two C–N bonds were established in one step to generate a new diazobicyclo[2.2.2]octene product. This is the first report of the synthesis of 2,6-diazabicyclo[2.2.2]oct-2-ene core. Considering the novelty of the structure, the mechanism will be proposed with the scope on various substrates. Based on these intriguing chemical aspects, further possible applications should also be investigated from a future perspective. As shown in Scheme 3, the structure of **4** was also confirmed using X-ray single-crystal crystallography.[28]

This intermolecular cyclization in the same reagents and equivalents was heated by using a normal hot plate as a heating source that was also studied in some control experiments, as shown in Scheme 4. No reaction occurred when the reaction was conducted at room temperature (eqn (a)). Owing to the low boiling point of dichloromethane, changing evaporable dichloromethane to high boiling point toluene in a hot plate at reflux is necessary for the investigation. In eqn (b) and (c), although the total yields are similar to the optimized condition, a lower yield of **3a** was obtained. No obvious yield change was observed while increasing the reaction temperature to 200 °C under the MW system (eqn (d)). According to these control experiments, we think that the MW system is a better heating source than a normal hot plate.



Scheme 3 Synthesis of product **4**.

(a) $$\mathbf{1a} \xrightarrow[\text{CH}_2\text{Cl}_2,\ \textbf{rt},\ 1\text{ h}]{\text{HMDS , TMSOTf}} \mathbf{2a}\ (0\%) + \mathbf{3a}\ (0\%)$$

(b) $$\mathbf{1a} \xrightarrow[\textbf{Toluene},\ \text{reflux},\ 1\text{ h}]{\text{HMDS , TMSOTf}} \mathbf{2a}\ (70\%) + \mathbf{3a}\ (15\%)$$

(c) $$\mathbf{1a} \xrightarrow[\text{DCM, MW } \mathbf{100}\ ^{\circ}\text{C, 1 h}]{\text{HMDS , TMSOTf}} \mathbf{2a}\ (60\%) + \mathbf{3a}\ (25\%)$$

(d) $$\mathbf{1a} \xrightarrow[\text{DCM, MW } \mathbf{200}\ ^{\circ}\text{C, 1 h}]{\text{HMDS , TMSOTf}} \mathbf{2a}\ (49\%) + \mathbf{3a}\ (44\%)$$

Scheme 4 The control experiments.

Conclusions

In conclusion, we have described an efficient protocol for the synthesis of pyridine skeleton, including TAPs and 3-benzyl TAPs, from simple chalcones with functional group tolerance in good to excellent yields. This intermolecular annulation involved the combination of TMSOTf/HMDS and was conducted in a microwave irradiation system. By changing the acidic additive to $Sn(OTf)_2$ in the reaction, a new 2,6-diazabicyclo[2.2.2]oct-2-ene core was obtained in moderate yield. The structures of some products were confirmed by X-ray single-crystal diffraction analysis. Considering the importance of the pyridine skeleton, biological and medicinal activities will be further examined and published in due course.

Experimental section

General information

All used reagents and solvents were commercially available and used without further purification. Reactions were routinely performed using the Discover SP system (CEM) in the sealed reaction vessels in a standard mode with the temperature monitored using a vertically focused IR sensor. All reactions were monitored using thin-layer chromatography on silica gel 60 F254 (Merck) with detection by UV light. Column chromatography was performed using silica gel (200–300 mesh).

Products in organic solvents were dried with anhydrous magnesium sulfate before concentration *in vacuo*. Melting points were determined using an MP-2D melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVIII 500 spectrometer operating at 500 and 125 MHz, respectively. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz) and integration. HRMS were obtained on a Waters LCT Premier XE (Waters Corp., Manchester, UK) instrument equipped with an electrospray source. The X-ray intensity data were measured at a low temperature of 100 K using a Mo Kα radiation diffractometer equipped with a kappa geometry goniometer and corrected for absorption effects using the numerical method (SADABS).

General procedure for the synthesis of skeletons 2 and 3

A mixture of chalcone **1** (1.0 mmol), hexamethyldisilane (0.5 mL, 2.4 mmol), trimethylsilyl trifluoromethanesulfonate (0.1 mL, 0.5 mmol) in dichloromethane (2 mL), in a dried 35 mL microwave vial at 25 °C. The mixture was treated in a microwave irradiation instrument and stirred at 150 °C for 0.5 h. The consumption of the starting materials was confirmed by TLC. The reaction was cooled to 25 °C, the mixture of crude products was transferred to a 100 mL round bottom flask, and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford the crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1–1/1) afforded compounds **2a–2ab**, **3a–3n** and **3r–3aa**.

2,4,6-Triphenylpyridine (2a).[20c] Yield = 41% (63 mg); colorless solid; mp = 138–139 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{18}N$ 308.1439, found 308.1447; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35–8.31 (m, 4H), 7.96 (s, 2H), 7.82–7.80 (m, 2H), 7.66–7.57 (m, 6H), 7.57–7.51 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.32 (2x), 149.99, 139.45 (2x), 138.87, 128.96 (2x), 128.93 (2x), 128.83, 128.58 (4x), 127.03 (6x), 116.93 (2x).

3-Benzyl-2,4,6-triphenylpyridine (3a).[26] Yield = 44% (87 mg); white solid; mp = 134–135 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{24}N$ 398.1909, found 398.1914; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21–8.12 (m, 2H), 7.73–7.67 (m, 1H), 7.61–7.54 (m, 2H), 7.53–7.47 (m, 2H), 7.46–7.35 (m, 7H), 7.33–7.27 (m, 2H), 7.14–7.05 (m, 3H), 6.74–6.66 (m, 2H), 4.16 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.28, 154.49, 152.31, 141.27, 140.90, 139.96, 138.99, 129.83, 129.10 (2x), 128.78, 128.58 (2x), 128.48 (2x), 128.17 (2x), 128.13 (2x), 127.94 (2x), 127.85 (2x), 127.72, 127.65, 126.92 (2x), 125.44, 120.59, 35.02.

4-(4-Fluorophenyl)-2,6-diphenylpyridine (2b).[20c] Yield = 46% (75 mg); colorless solid; mp = 141–142 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{17}FN$ 326.1340, found 326.1337; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.0 Hz, 4H), 7.84 (s, 2H), 7.74–7.71 (m, 2H), 7.54 (t, J = 8.0 Hz, 4H), 7.49–7.46 (m, 2H), 7.23 (t, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.31 (d, J = 247.25 Hz), 157.49 (2x), 149.04, 139.36 (2x), 135.03 (d, J = 3.0 Hz), 129.08 (2x), 128.87 (d, J = 8.25 Hz, 2x), 128.68 (4x), 127.06 (4x), 116.83 (2x), 116.06 (d, J = 21.375 Hz, 2x).

3-(4-Fluorobenzyl)-4-(4-fluorophenyl)-2,6-diphenylpyridine (3b).[26] Yield = 53% (115 mg); white solid; mp = 166–167 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}F_2N$ 434.1720, found 434.1716; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 9.0 Hz, 2H), 7.60 (s, 1H), 7.54–7.35 (m, 8H), 7.21–7.13 (m, 2H), 7.04 (t, J = 9.0 Hz, 2H), 6.74 (t, J = 8.0 Hz, 2H), 6.61–6.52 (m, 2H), 4.04 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.34 (d, J = 245.875 Hz), 160.93 (d, J = 242.375 Hz), 160.26, 154.78, 151.31, 141.00, 138.77, 136.32 (d, J = 2.875 Hz), 135.80 (d, J = 3.25 Hz), 130.11 (d, J = 8.0 Hz, 2x), 129.85, 129.41 (d, J = 7.625 Hz, 2x), 129.05 (2x), 128.97, 128.67 (2x), 128.10 (2x), 127.95, 126.94 (2x), 120.73, 115.24 (d, J = 21.25 Hz, 2x), 114.73 (d, J = 21.0 Hz, 2x), 34.27.

4-(4-Chlorophenyl)-2,6-diphenylpyridine (2c).[20c] Yield = 50% (85 mg); yellow solid; mp = 119–120 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{17}ClN$ 342.1044, found 342.1048; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.0 Hz, 4H), 7.84 (s, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.56–7.49 (m, 6H), 7.48–7.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.66 (2x), 148.92, 139.38 (2x), 137.46, 135.17, 139.31 (2x), 129.15 (2x), 128.72 (4x), 128.43 (2x), 127.10 (4x), 116.79 (2x).

3-(4-Chlorobenzyl)-4-(4-chlorophenyl)-2,6-diphenylpyridine (3c).[26] Yield = 40% (92 mg); white solid; mp = 179–180 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}Cl_2N$ 466.1124, found 466.1120; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 7.5 Hz, 2H), 7.59 (s, 1H), 7.52–7.47 (m, 4H), 7.43–7.36 (m, 4H), 7.33 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.0 Hz, 2H), 4.02 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.39, 154.95, 151.13, 140.92, 139.15, 138.72, 138.21, 134.04, 131.48, 129.79 (2x), 129.40 (2x), 129.20, 129.03 (2x), 128.69 (2x), 128.51 (2x), 128.12 (4x), 128.01 (2x), 126.96 (2x), 120.48, 34.47.

4-(4-Bromophenyl)-2,6-diphenylpyridine (2d).[21a] Yield = 55% (106 mg); white solid; mp = 128–129 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{17}BrN$ 386.0539, found 386.0533; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 7.5 Hz, 4H), 7.84 (s, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.53 (t, J = 8.0 Hz, 4H), 7.49–7.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.68 (2x), 148.93, 139.37 (2x), 137.95, 132.25 (2x), 129.12 (2x), 128.68 (6x), 127.09 (4x), 123.36, 116.67 (2x).

3-(4-Bromobenzyl)-4-(4-bromophenyl)-2,6-diphenylpyridine (3d).[26] Yield = 43% (119 mg); white solid; mp = 180–181 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}BrN$ 554.0114, found 554.0109; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 7.5 Hz, 2H), 7.58 (s, 1H), 7.52–7.43 (m, 6H), 7.42–7.34 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.0 Hz, 2H), 4.00 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.43, 154.97, 151.11, 140.93, 139.67, 138.71, 131.47 (2x), 131.07 (2x), 130.09 (2x), 129.79 (2x), 129.02 (5x), 128.66 (2x), 128.10 (2x), 127.99, 126.95 (2x), 122.20, 120.32, 119.55, 34.54.

4-(4-Nitrophenyl)-2,6-diphenylpyridine (2e).[26] Yield = 46% (81 mg); white solid; mp = 174–175 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{17}N_2O_2$ 353.1290, found 353.1290; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, J = 8.5 Hz, 2H), 8.24–8.18 (m, 4H), 7.90 (d, J = 8.5 Hz, 2H), 7.88 (s, 2H), 7.56–7.51 (m, 4H), 7.51–7.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.96 (2x), 148.14, 147.83, 145.44, 139.00 (2x), 129.42 (2x), 128.81 (4x), 128.16 (2x), 127.11 (4x), 124.35 (2x), 116.93 (2x).

3-(4-Nitrobenzyl)-4-(4-nitrophenyl)-2,6-diphenylpyridine (3e).[26] Yield = 35% (112 mg); yellow solid; mp = 206–207 °C; HRMS (ESI, M^+ + H) calcd for $C_{30}H_{22}N_3O_4$ 488.1605, found 488.1603; ^1H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.5 Hz, 2H), 8.13–8.06 (m, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.62 (s, 1H), 7.51–7.35 (m, 10H), 6.78 (d, J = 8.5 Hz, 2H), 4.17 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.80, 155.70, 150.06, 147.77, 147.62, 146.22, 146.10, 140.35, 138.18, 129.50 (2x), 128.88 (2x), 128.83 (2x), 128.73 (2x), 128.42, 128.39 (2x), 127.64, 127.01 (2x), 123.73 (2x), 123.38 (2x), 119.92, 35.15.

2,6-Diphenyl-4-(*p*-tolyl)pyridine (2f).[20c] Yield = 58% (93 mg); white solid; mp = 117–118 °C; HRMS (ESI, M^+ + H) calcd for $C_{24}H_{20}N$ 322.1590, found 322.1588; ^1H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.5 Hz, 4H), 7.90 (s, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.54 (t, J = 8.0 Hz, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.42 (2x), 150.00, 139.64 (2x), 139.03, 136.03, 129.79 (2x), 128.95 (2x), 128.65 (4x), 127.10 (4x), 126.96 (2x), 116.85 (2x), 21.22.

3-(4-Methylbenzyl)-2,6-diphenyl-4-(*p*-tolyl)pyridine (3f).[26] Yield = 40% (85 mg); white solid; mp = 153–154 °C; HRMS (ESI, M^+ + H) calcd for $C_{32}H_{28}N$ 426.2216, found 426.2215; ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz, 2H), 7.64 (s, 1H), 7.54–7.43 (m, 4H), 7.42–7.33 (m, 4H), 7.17 (s, 4H), 6.89 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 8.0 Hz, 2H), 4.06 (s, 2H), 2.39 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.28, 154.39, 152.29, 141.41, 139.16, 138.03, 137.47, 137.15, 134.85, 130.03, 129.14 (2x), 128.86 (2x), 128.72, 128.60 (4x), 128.50 (2x), 128.04 (2x), 127.89 (2x), 127.68, 126.95 (2x), 120.78, 34.55, 21.18, 20.92.

4-(4-Methoxyphenyl)-2,6-diphenylpyridine (2g).[21a] Yield = 60% (101 mg); white solid; mp = 101–102 °C; HRMS (ESI, M^+ + H) calcd for $C_{24}H_{20}NO$ 338.1545, found 338.1541; ^1H NMR (500 MHz, $CDCl_3$): 8.22 (d, J = 7.5 Hz, 4H), 7.87 (s, 2H), 7.72 (d, J = 9.0 Hz, 2H), 7.57–7.50 (m, 4H), 7.49–7.43 (m, 2H), 7.06 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.43, 157.41 (2x), 149.59, 139.68 (2x), 131.24, 128.93 (2x), 128.64 (4x), 128.28 (2x), 127.09 (4x), 116.57 (2x), 114.49 (2x), 55.38.

3-(4-Methoxybenzyl)-4-(4-methoxyphenyl)-2,6-diphenylpyridine (3g).[26] Yield = 30% (69 mg); yellow solid; mp = 147–148 °C; HRMS (ESI, M^+ + H) calcd for $C_{32}H_{28}NO_2$ 458.2115, found 458.2112; ^1H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 2H), 7.62 (s, 1H), 7.52–7.47 (m, 2H), 7.46–7.42 (m, 2H), 7.41–7.33 (m, 4H), 7.18 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 6.57 (d, J = 9.0 Hz, 2H), 4.02 (s, 2H), 3.83 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.20, 159.15, 157.38, 154.41, 151.90, 141.35, 139.11, 133.25, 132.36, 130.35, 129.77 (2x), 129.11 (2x), 129.07 (2x), 128.72, 128.60 (2x), 127.93 (2x), 127.71, 126.93 (2x), 120.93, 113.59 (2x), 113.31 (2x), 55.28, 55.12, 34.09.

4-([1,1′-Biphenyl]-4-yl)-2,6-diphenylpyridine (2h).[20d] Yield = 62% (119 mg); white solid; mp = 136–137 °C; HRMS (ESI, M^+ + H) calcd for $C_{29}H_{22}N$ 384.1747, found 384.1744; ^1H NMR (500 MHz, $CDCl_3$): δ 8.29–8.19 (m, 4H), 7.95 (s, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.59–7.44 (m, 8H), 7.43–7.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.54 (2x), 149.62, 141.86, 140.28, 139.56 (2x), 137.78, 129.04 (2x), 128.90 (2x), 128.69 (4x), 127.78 (2x), 127.69, 127.54 (2x), 127.12 (4x), 127.10 (2x), 116.89 (2x).

4-([1,1′-Biphenyl]-4-yl)-3-([1,1′-biphenyl]-4-ylmethyl)-2,6-diphenylpyridine (3h). Yield = 35% (96 mg); yellow solid; mp = 87–88 °C; HRMS (ESI, M^+ + H) calcd for $C_{42}H_{32}N$ 550.2529, found 550.2523; ^1H NMR (500 MHz, $CDCl_3$): δ 8.16–8.08 (m, 2H), 7.70 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.55–7.49 (m, 4H), 7.46 (t, J = 8.0 Hz, 4H), 7.42–7.28 (m, 12H), 6.73 (d, J = 8.5 Hz, 2H), 4.17 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.41, 154.68, 152.03, 141.29, 140.83, 140.65, 140.49, 140.18, 139.04, 138.98, 138.34, 129.90, 129.18 (2x), 129.06 (2x), 128.87, 128.85 (2x), 128.68 (6x), 128.04 (2x), 127.84, 127.52, 127.08 (2x), 127.01 (3x), 126.92 (2x), 126.84 (2x), 126.59, 120.68 (2x), 34.86.

4-(Naphthalen-1-yl)-2,6-diphenylpyridine (2i).[19g] Yield = 54% (96 mg); white solid; mp = 251–252 °C; HRMS (ESI, M^+ + H) calcd for $C_{27}H_{20}N$ 358.1590, found 358.1587; ^1H NMR (500 MHz, $CDCl_3$): δ 8.26–8.21 (m, 4H), 8.00–7.94 (m, 3H), 7.86 (s, 2H), 7.63–7.43 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.94 (2x), 150.24, 139.39 (2x), 138.05, 133.79, 130.97, 129.08 (2x), 128.77, 128.71 (4x), 128.50, 127.12 (4x), 126.72, 126.67, 126.17, 125.38 (2x), 120.14 (2x).

4-(Naphthalen-1-yl)-3-(naphthalen-1-ylmethyl)-2,6-diphenylpyridine (3i). Yield = 43% (107 mg); yellow solid; mp = 208–209 °C; HRMS (ESI, M^+ + H) calcd for $C_{38}H_{28}N$ 498.2216, found 498.2209; ^1H NMR (500 MHz, $CDCl_3$): δ 8.20–8.13 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.69–7.61 (m, 4H), 7.53–7.27 (m, 12H), 7.19–7.07 (m, 4H), 6.81 (d, J = 8.0 Hz, 1H), 4.46 (d, J = 16.0 Hz, 1H), 4.18 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.25, 154.65, 151.05, 141.00, 138.92, 136.86 (2x), 133.30, 133.23, 131.22, 131.02, 130.96, 129.14 (2x), 128.93, 128.67 (2x), 128.24 (2x), 128.03, 128.01 (2x), 127.92, 126.98 (2x), 126.29, 126.25 (2x), 126.10, 125.77, 125.32, 125.23, 125.09, 124.95, 124.78, 123.02, 121.56, 32.76.

2,6-Diphenyl-4-(*o*-tolyl)pyridine (2j).[20c] Yield = 51% (82 mg); white solid; mp = 119–120 °C; HRMS (ESI, M^+ + H) calcd for $C_{24}H_{20}N$ 322.1590, found 322.1592; ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.0 Hz, 4H), 7.68 (s, 2H), 7.52 (t, J = 8.0 Hz, 4H), 7.48–7.42 (m, 2H), 7.35 (d, J = 8.0 Hz, 4H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.79 (2x), 151.33, 139.80, 139.47 (2x), 135.14, 130.66, 129.23, 129.01 (2x), 128.69 (4x), 128.34, 127.07 (4x), 126.10, 119.35 (2x), 20.37.

3-(2-Methylbenzyl)-2,6-diphenyl-4-(*o*-tolyl)pyridine (3j). Yield = 46% (98 mg); yellow solid; mp = 127–128 °C; HRMS (ESI, M^+ + H) calcd for $C_{32}H_{28}N$ 426.2216, found 426.2210; ^1H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, J = 7.5 Hz, 2H), 7.57 (dd, J = 1.5, 7.5 Hz, 2H), 7.56 (s, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.42–7.33 (m, 4H), 7.20 (t, J = 7.5 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.98–6.91 (m, 3H), 6.89–6.84 (m, 1H), 6.72–6.66 (m, 1H), 3.97 (d, J = 16.0 Hz, 1H), 3.73 (d, J = 16.0 Hz, 1H), 1.97 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.27, 154.48, 152.11, 141.16, 139.09, 139.05, 138.90, 135.83, 135.13, 130.60, 129.94, 129.38, 129.13 (2x), 128.82, 128.67, 128.64 (2x), 128.52, 127.98 (2x), 127.80 (2x), 126.93 (2x), 125.52, 125.47, 125.35, 120.47, 32.17, 19.73, 19.26.

4-(2-Methoxyphenyl)-2,6-diphenylpyridine (2k).[19a] Yield = 53% (89 mg); yellow gum; HRMS (ESI, M^+ + H) calcd for $C_{24}H_{20}NO$ 338.1545, found 338.1541; ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 7.5 Hz, 4H), 7.88 (s, 2H), 7.55–7.49 (m, 4H), 7.48–7.41 (m, 4H), 7.14–7.09 (m, 1H), 7.07 (d, J = 8.5 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.74 (2x), 156.60, 147.87, 139.85 (2x), 130.50, 130.02, 128.78 (2x), 128.60 (4x), 128.46, 127.13 (4x), 121.06, 119.70 (2x), 111.44, 55.67.

3-(2-Methoxybenzyl)-4-(2-methoxyphenyl)-2,6-diphenylpyridine (3k). Yield = 42% (96 mg); yellow gum; HRMS (ESI, $M^+ + H$) calcd for $C_{32}H_{28}NO_2$ 458.2115, found 458.2114; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz, 2H), 7.59 (s, 1H), 7.57–7.53 (m, 2H), 7.47–7.41 (m, 2H), 7.40–7.30 (m, 4H), 7.28–7.23 (m, 1H), 7.02–6.95 (m, 2H), 6.87–6.81 (m, 2H), 6.66 (s, 1H), 6.65 (s, 1H), 6.51 (d, J = 8.0 Hz, 1H), 4.00 (d, J = 15.0 Hz, 1H), 3.95 (d, J = 15.0 Hz, 1H), 3.67 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.94 (2x), 156.50, 156.01, 154.09, 149.44, 141.55, 139.39, 131.65, 130.28, 129.43 (2x), 129.16 (2x), 128.97, 128.76, 128.52 (3x), 127.74 (2x), 127.43, 126.96 (2x), 126.32, 121.24, 120.12, 119.82, 110.40, 109.43, 55.18, 54.96, 28.80.

2,6-Diphenyl-4-(*m*-tolyl)pyridine (2l).[20c] Yield = 53% (85 mg); yellow solid; mp = 84–85 °C; HRMS (ESI, $M^+ + H$) calcd for $C_{24}H_{20}N$ 322.1590, found 322.1588; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26–8.20 (m, 4H), 7.90 (s, 2H), 7.5–7.51 (m, 6H), 7.49–7.41 (m, 3H), 7.31 (d, J = 7.5 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.42 (2x), 150.30, 139.61 (2x), 139.02, 138.80, 129.70, 128.99 (2x), 128.67 (5x), 127.86, 127.11 (4x), 124.27, 117.13 (2x), 21.52.

3-(3-Methylbenzyl)-2,6-diphenyl-4-(*m*-tolyl)pyridine (3l). Yield = 44% (94 mg); white gum; HRMS (ESI, $M^+ + H$) calcd for $C_{32}H_{28}N$ 426.2216, found 426.2209; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 2H), 7.65 (s, 1H), 7.59–7.51 (m, 2H), 7.51–7.44 (m, 2H), 7.44–7.34 (m, 4H), 7.29–7.23 (m, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.01 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 7.0 Hz, 1H), 6.48 (d, J = 7.5 Hz, 1H), 6.42 (s, 1H), 4.06 (s, 2H), 2.33 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.15, 154.35, 152.44, 141.38, 140.96, 139.96, 139.09, 137.74, 137.25, 130.13, 129.45, 129.20 (4x), 128.74, 128.59 (2x), 128.31, 128.00, 127.94 (2x), 127.70, 126.93 (2x), 126.13, 125.55, 125.32, 120.59, 35.01, 21.30, 21.20.

4-(3-Methoxyphenyl)-2,6-diphenylpyridine (2m).[20c] Yield = 48% (81 mg); white solid; mp = 124–125 °C; HRMS (ESI, $M^+ + H$) calcd for $C_{24}H_{20}NO$ 338.1539, found 338.1538; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 7.5 Hz, 4H), 7.90 (s, 2H), 7.54 (t, J = 7.5 Hz, 4H), 7.50–7.43 (m, 3H), 7.35 (d, J = 7.5 Hz, 1H), 7.28 (t, J = 2.0 Hz, 1H), 7.03 (dd, J = 2.0, 8.0 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.14 157.46 (2x), 150.06, 140.53, 139.53 (2x), 130.14, 129.02 (2x), 128.67 (4x), 127.10 (4x), 119.57, 117.13 (2x), 114.17, 112.99, 55.40.

3-(3-Methoxybenzyl)-4-(3-methoxyphenyl)-2,6-diphenylpyridine (3m). Yield = 41% (94 mg); yellow gum; HRMS (ESI, $M^+ + H$) calcd for $C_{32}H_{28}NO_2$ 458.2115, found 458.2114; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 7.5 Hz, 2H), 7.65 (s, 1H), 7.54 (d, J = 7.0 Hz, 2H), 7.46 (t, J = 7.0 Hz, 2H), 7.43–7.33 (m, 4H), 7.28 (t, J = 8.0 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.90 (dd, J = 2.0, 8.0 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.74 (s, 1H), 6.61 (dd, J = 1.0, 8.0 Hz, 1H), 6.31 (d, J = 7.5 Hz, 1H), 6.24 (s, 1H), 4.07 (s, 2H), 3.66 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.22, 159.30, 159.23, 154.59, 152.20, 142.83, 141.28, 139.02, 129.56, 129.28, 129.17 (2x), 128.87 (2x), 128.82, 128.62 (2x), 127.99 (2x), 127.79, 126.97 (2x), 120.92, 120.81, 120.52, 113.90 (2x), 113.79, 111.19, 55.06, 55.02, 35.14.

4-(3,4-Dimethoxyphenyl)-2,6-diphenylpyridine (2n).[22e] Yield = 51% (92 mg); yellow gum; HRMS (ESI, $M^+ + H$) calcd for $C_{25}H_{22}NO_2$ 368.1645, found 368.1641; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24–8.17 (m, 4H), 7.85 (s, 2H), 7.56–7.50 (m, 4H), 7.48–7.43 (m, 2H), 7.33 (dd, J = 2.5, 8.5 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 8.5 Hz, 1H), 4.01 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.46 (2x), 149.94 (2x), 149.43, 139.64 (2x), 131.78, 128.98 (2x), 128.66 (4x), 127.10 (4x), 119.78, 116.79 (2x), 111.54, 110.15, 56.10, 56.01.

3-(3,4-Dimethoxybenzyl)-4-(3,4-dimethoxyphenyl)-2,6-diphenylpyridine (3n).[26] Yield = 32% (83 mg); yellow gum; HRMS (ESI, $M^+ + H$) calcd for $C_{34}H_{32}NO_4$ 518.2326, found 518.2328; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 7.5 Hz, 2H), 7.65 (s, 1H), 7.59–7.50 (m, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.41–7.33 (m, 4H), 6.88 (d, J = 8.0 Hz, 1H), 6.84 (dd, J = 2.0, 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.26 (dd, J = 2.0, 8.0 Hz, 1H), 6.23 (d, J = 2.0 Hz, 1H), 4.03 (s, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.67 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.12, 154.57, 152.05, 148.63, 148.51, 148.40, 146.97, 141.36, 139.05, 134.17, 132.65, 130.00, 129.19 (2x), 128.82, 128.63 (2x), 127.99 (2x), 127.81, 126.94 (2x), 121.00, 120.83, 120.31, 111.98, 111.61, 110.86 (2x), 55.90, 55.84, 55.65, 55.61, 34.68.

4-(Naphthalen-2-yl)-2,6-diphenylpyridine (2o).[22e] Yield = 95% (170 mg); white solid; mp = 128–129 °C; HRMS (ESI, $M^+ + H$) calcd for $C_{27}H_{20}N$ 358.1590, found 358.1590; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30–8.21 (m, 5H), 8.05–7.96 (m, 4H), 7.95–7.90 (m, 1H), 7.87 (dd, J = 1.5, 8.0 Hz, 1H), 7.60–7.52 (m, 6H), 7.51–7.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.56 (2x), 150.07, 139.59 (2x), 136.27, 133.49, 133.40, 129.05 (2x), 128.91, 128.70 (4x), 128.42, 127.74, 127.15 (4x), 126.74, 126.68, 126.45, 124.81, 117.28 (2x).

4-(Anthracen-9-yl)-2,6-diphenylpyridine (2p). Yield = 83% (169 mg); yellow solid; mp = 222–223 °C; HRMS (ESI, $M^+ + H$) calcd for $C_{31}H_{22}N$ 408.1747, found 408.1745; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.28–8.22 (m, 4H), 8.10 (d, J = 8.5 Hz, 2H), 7.84 (s, 2H), 7.75 (d, J = 9.0 Hz, 2H), 7.54–7.48 (m, 6H), 7.47–7.43 (m, 2H), 7.42–7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.03 (2x), 148.90, 139.23 (2x), 134.30, 131.29 (2x), 129.53 (2x), 129.20 (2x), 128.74 (4x), 128.53 (2x), 127.48, 127.13 (4x), 126.15 (2x), 126.07 (2x), 125.35 (2x), 121.39 (2x).

4-(Benzo[*d*][1,3]dioxol-5-yl)-2,6-diphenylpyridine (2q).[20d] Yield = 85% (149 mg); white solid; mp = 152–153 °C; HRMS (ESI, $M^+ + H$) calcd for $C_{24}H_{18}NO_2$ 352.1332, found 352.1333; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20–8.18 (m, 4H), 7.82 (s, 2H), 7.55–7.48 (m, 4H), 7.47–7.42 (m, 2H), 7.28–7.21 (m, 2H), 6.96 (d, J = 8.0 Hz, 1H), 6.06 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.46 (2x), 149.71, 148.47, 148.44, 139.55 (2x), 133.12, 129.02 (2x), 128.69 (4x), 127.09 (4x), 121.06, 116.76 (2x), 108.86, 107.45, 101.49. Single-crystal X-ray diagram: crystal of **2q** was grown by slow diffusion of EtOAc into a solution of **2q** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P21/n$, a = 6.4058(2) Å, b = 12.1092(3) Å, c = 21.6453(7) Å, V = 1677.71(9) Å^3, Z = 4, d_{calcd} =

1.391 mg m^{-3}, $F(000) = 736$, 2θ range 1.927–27.102, R indices (all data) $R1 = 0.0412$, w$R2 = 0.0956$. CCDC number is 2085356.

2,6-Bis(4-fluorophenyl)-4-phenylpyridine (2r).[20c] Yield = 45% (77 mg); white solid; mp = 175–176 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{16}F_2N$ 344.1245, found 344.1242; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.20–8.16 (m, 4H), 7.82 (d, $J = 6.0$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.57–7.52 (m, 2H), 7.51–7.47 (m, 1H), 7.20 (t, $J = 8.5$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.64 (d, $J =$ 247.125 Hz, 2x), 156.46 (2x), 150.44, 138.84 (2x), 135.57 (d, $J =$ 2.75 Hz, 2x), 129.15 (2x), 129.11, 128.89 (d, $J = 8.2$ Hz, 4x), 127.14 (2x), 116.67, 115.62 (d, $J = 21.3625$ Hz, 4x).

3-Benzyl-2,6-bis(4-fluorophenyl)-4-phenylpyridine (3r). Yield = 41% (89 mg); colorless gum; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}F_2N$ 434.1715, found 434.1710; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.10–8.03 (m, 2H), 7.59 (s, 1H), 7.47–7.40 (m, 2H), 7.38–7.31 (m, 3H), 7.25–7.21 (m, 2H), 7.16–7.10 (m, 2H), 7.08–7.00 (m, 5H), 6.66–6.61 (m, 2H), 4.06 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.51 (d, $J = 246.75$ Hz), 162.54 (d, $J = 245.5$ Hz), 159.40, 153.59, 152.60, 140.70, 139.75, 137.24 (d, $J = 3.125$ Hz), 135.07 (d, $J = 2.75$ Hz), 130.82 (d, $J = 8.0$ Hz, 2x), 129.88, 128.74 (d, $J = 8.25$ Hz, 2x), 128.48 (2x), 128.27 (2x), 128.13 (2x), 128.01 (2x), 127.86, 125.65, 120.43, 115.57 (d, $J = 21.5$ Hz, 2x), 114.92 (d, $J = 21.375$ Hz, 2x), 35.04.

2,6-Bis(4-chlorophenyl)-4-phenylpyridine (2s).[20c] Yield = 31% (58 mg); colorless solid; mp = 186–187 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{16}Cl_2N$ 376.0654, found 376.0654; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.12 (d, $J = 8.5$ Hz, 4H), 7.84 (s, 2H), 7.73–7.71 (m, 2H), 7.56–7.49 (m, 7H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 156.31 (2x), 150.54, 138.67, 137.75 (2x), 135.27 (2x), 129.17 (3x), 128.90 (4x), 128.33 (4x), 127.14 (2x), 117.06 (2x).

3-Benzyl-2,6-bis(4-chlorophenyl)-4-phenylpyridine (3s). Yield = 45% (47 mg); white solid; mp = 169–170 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}Cl_2N$ 466.1124, found 466.1120; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.02 (d, $J = 8.5$ Hz, 2H), 7.61 (s, 1H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.35–7.31 (m, 5H), 7.24–7.21 (m, 2H), 7.08–7.04 (m, 3H), 6.68–6.59 (m, 2H), 4.05 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 159.28, 153.43, 152.70, 140.57, 139.59, 139.54, 137.26, 135.07, 133.99, 130.44 (2x), 130.23, 128.85 (2x), 128.46 (2x), 128.29 (2x), 128.21 (2x), 128.19 (2x), 128.13 (2x), 128.06 (2x), 127.93, 125.71, 120.63, 35.02.

4-Phenyl-2,6-di-*p*-tolylpyridine (2t).[20c] Yield = 53% (89 mg); colorless solid; mp = 159–160 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{25}H_{22}N$ 336.1747, found 336.1744; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.12 (d, $J = 8.0$ Hz, 4H), 7.85 (s, 2H), 7.76–7.74 (m, 2H), 7.55–7.52 (m, 2H), 7.49–7.47 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 4H), 2.45 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 157.38 (2x), 149.99, 139.26, 138.93 (2x), 136.88 (2x), 129.38 (4x), 129.04 (2x), 128.83, 127.16 (2x), 126.97 (4x), 116.49 (2x), 21.30 (2x).

3-Benzyl-4-phenyl-2,6-di-*p*-tolylpyridine (3t). Yield = 42% (89 mg); white solid; mp = 149–150 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{32}H_{28}N$ 426.2216, found 426.2219; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.99 (d, $J = 7.5$ Hz, 2H), 7.57 (s, 1H), 7.40 (d, $J = 7.5$ Hz, 2H), 7.34–7.28 (m, 3H), 7.24 (d, $J = 7.5$ Hz, 2H), 7.21–7.18 (m, 2H), 7.17 (d, $J = 7.5$ Hz, 2H), 7.07–6.99 (m, 3H), 6.68–6.61 (m, 2H), 4.07 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 160.17, 154.48, 152.24, 141.17, 140.19, 138.71, 138.54, 137.44, 136.31, 129.43, 129.32 (2x), 129.08 (2x), 128.66 (2x), 128.52 (2x), 128.24 (2x), 128.10 (2x), 127.85 (2x), 127.58, 126.82 (2x), 125.41, 120.16, 35.10, 21.27, 21.24.

2,6-Bis(4-methoxyphenyl)-4-phenylpyridine (2u).[21a] Yield = 62% (114 mg); white solid; mp = 131–132 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{25}H_{22}NO_2$ 368.1645, found 368.1645; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.20 (d, $J = 9.0$ Hz, 4H), 7.79 (s, 2H), 7.75 (d, $J =$ 7.5 Hz, 2H), 7.58.7.52 (m, 2H), 7.51–7.46 (m, 1H), 7.07 (d, $J =$ 8.0 Hz, 4H), 3.89 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 160.40 (2x), 156.81 (2x), 149.84, 139.21, 132.23 (2x), 128.94 (2x), 128.72, 128.27 (4x), 127.05 (2x), 115.53 (2x), 113.93 (4x), 55.24 (2x).

3-Benzyl-2,6-bis(4-methoxyphenyl)-4-phenylpyridine (3u). Yield = 25% (57 mg); white solid; mp = 117–118 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{32}H_{28}NO_2$ 458.2115, found 458.2119; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.12 (d, $J = 8.5$ Hz, 2H), 7.60 (s, 1H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.39–7.33 (m, 3H), 7.30–7.23 (m, 2H), 7.15–7.06 (m, 3H), 7.02 (d, $J = 9.0$ Hz, 2H), 6.95 (d, $J = 9.0$ Hz, 2H), 6.77–6.70 (m, 2H), 4.14 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 160.28, 159.65, 159.22, 154.04, 152.22, 141.15, 140.14, 133.92, 131.68, 130.39 (2x), 128.87, 128.44 (2x), 128.14 (4x), 128.03 (2x), 127.84 (2x), 127.51, 125.39, 119.51, 113.89 (2x), 113.33 (2x), 55.20, 55.18, 35.06.

2,6-Di([1,1′-biphenyl]-4-yl)-4-phenylpyridine (2v).[20c] Yield = 46% (106 mg); white solid; mp = 180–181 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{35}H_{26}N$ 460.2060, found 460.2058; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.32 (d, $J = 8.0$ Hz, 4H), 7.95 (s, 2H), 7.82–7.75 (m, 6H), 7.70 (d, $J = 8.0$ Hz, 4H), 7.59–7.53 (m, 2H), 7.53–7.46 (m, 5H), 7.43–7.37 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 157.12 (2x), 150.23 (2x), 141.81 (2x), 140.68 (2x), 139.06, 138.47 (2x), 129.13 (2x), 129.00 (2x), 128.83 (4x), 127.52 (4x), 127.43 (4x), 127.20 (2x), 127.12 (4x), 117.04 (2x).

2,6-Di([1,1′-biphenyl]-4-yl)-3-benzyl-4-phenylpyridine (3v). Yield = 43% (118 mg); white solid; mp = 182–183 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{42}H_{32}N$ 550.2529, found 550.2537; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.21 (d, $J = 8.5$ Hz, 2H), 7.73–7.69 (m, 3H), 7.68–7.62 (m, 4H), 7.61 (s, 4H), 7.49–7.43 (m, 4H), 7.39–7.33 (m, 5H), 7.29–7.23 (m, 2H), 7.10–7.04 (m, 3H), 6.73–0.6.66 (m, 2H), 4.15 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 160.03, 154.19, 152.44, 141.55, 140.99, 140.91, 140.66, 140.62, 140.27, 139.99, 137.94, 130.00, 129.60 (2x), 128.78 (2x), 128.75 (2x), 128.54 (2x), 128.27 (2x), 128.20 (2x), 127.95 (2x), 127.73, 127.44, 127.36 (2x), 127.34 (2x), 127.30, 127.14 (2x), 127.07 (2x), 126.79 (2x), 125.53, 120.58, 35.17.

2,6-Bis(3-fluorophenyl)-4-phenylpyridine (2w).[16c] Yield = 60% (103 mg); white solid; mp = 147–148 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{16}F_2N$ 344.1245, found 344.1254; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.98–7.92 (m, 4H), 7.89 (s, 2H), 7.77–7.72 (m, 2H), 7.58–7.53 (m, 2H), 7.52–7.45 (m, 3H), 7.18–7.13 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.35 (d, $J = 243.75$ Hz, 2x), 156.19 (d, $J = 2.25$ Hz, 2x), 150.62, 141.62 (d, $J = 7.375$ Hz, 2x), 138.59, 130.20 (d, $J = 8.125$ Hz, 2x), 129.22, 129.20 (2x), 127.15 (2x), 122.56 (d, $J = 2.375$ Hz, 2x), 117.62 (2x), 116.00 (d, $J =$ 21.125 Hz, 2x), 114.06 (d, $J = 22.75$ Hz, 2x).

3-Benzyl-2,6-bis(3-fluorophenyl)-4-phenylpyridine (3w). Yield = 35% (76 mg); white solid; mp = 102–103 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}NF_2$ 434.1715, found 434.1724; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86–7.80 (m, 2H), 7.63 (s, 1H), 7.44–7.38 (m, 1H), 7.37–7.33 (m, 3H), 7.32–7.28 (m, 1H), 7.25–7.21 (m, 3H), 7.19–7.15 (m, 1H), 7.11–7.02 (m, 5H), 6.65–6.59 (m, 2H), 4.08 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.32 (d, J = 243.875 Hz), 162.48 (d, J = 244.375 Hz), 159.12, 153.29, 152.74, 143.17 (d, J = 7.5 Hz), 141.19 (d, J = 7.375 Hz), 140.49, 139.56, 130.63, 130.15 (d, J = 8.125 Hz), 129.53 (d, J = 8.125 Hz), 128.48 (2x), 128.31 (2x), 128.14 (2x), 128.03 (2x), 127.95, 125.71, 124.78 (d, J = 2.625 Hz), 122.42 (d, J = 2.375 Hz), 121.03, 116.32 (d, J = 22.0 Hz), 115.80 (d, J = 21.375 Hz), 114.84 (d, J = 21.0 Hz), 113.92 (d, J = 22.75 Hz), 35.01.

4-Phenyl-2,6-di-*o*-tolylpyridine (2x).[21a] Yield = 31% (52 mg); white solid; mp = 133–134 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{25}H_{22}N$ 336.1747, found 336.1747; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74–7.72 (m, 2H), 7.60 (s, 2H), 7.54–7.49 (m, 4H), 7.48–7.43 (m, 1H), 7.34–7.27 (m, 6H), 2.49 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.09 (2x), 148.79, 140.72 (2x), 138.49, 135.90 (2x), 130.68 (2x), 129.83 (2x), 129.13 (2x), 129.02, 128.24 (2x), 127.12 (2x), 125.83 (2x), 120.11 (2x), 20.62 (2x).

3-Benzyl-4-phenyl-2,6-di-*o*-tolylpyridine (3x). Yield = 52% (111 mg); colorless gum; HRMS (ESI, M$^+$ + H) calcd for $C_{32}H_{28}N$ 426.2216, found 426.2220; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51–7.46 (m, 1H), 7.43–7.32 (m, 6H), 7.29–7.18 (m, 5H), 7.17–7.02 (m, 2H), 7.04–6.97 (m, 3H), 6.56–6.48 (m, 2H), 4.00 (d, J = 15.0 Hz, 1H), 3.97 (d, J = 15.0 Hz, 1H), 2.45 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.42, 157.27, 151.27, 140.34, 140.21, 140.19, 139.86, 136.06, 135.93, 30.66, 130.20, 130.06, 129.78, 128.98, 128.76 (2x), 128.38 (2x), 128.33 (2x), 128.08, 127.77 (2x), 127.71 (2x), 125.75, 125.47, 125.32, 124.02, 34.78, 20.60, 19.54.

2,6-Bis(2-bromophenyl)-4-phenylpyridine (2y).[19g] Yield = 52% (120 mg); white solid; mp = 150–151 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{23}H_{16}Br_2N$ 463.9644, found 463.9644; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.78–7.75 (m, 2H), 7.74–7.70 (m, 4H), 7.55–7.50 (m, 2H), 7.49–7.46 (m, 1H), 7.45–7.41 (m, 2H), 7.27 (td, J = 2.0, 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.39 (2x), 148.20, 141.18 (2x), 138.11, 133.29 (2x), 131.75 (2x), 129.76 (2x), 129.13 (3x), 127.58 (2x), 127.21 (2x), 121.94 (2x), 121.41 (2x).

3-Benzyl-2,6-bis(2-bromophenyl)-4-phenylpyridine (3y). Yield = 40% (111 mg); yellow gum; HRMS (ESI, M$^+$ + H) calcd for $C_{30}H_{22}Br_2N$ 554.0114, found 554.0108; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dd, J = 2.0, 7.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.42–7.31 (m, 6H), 7.25–7.13 (m, 4H), 7.05–6.99 (m, 3H), 6.63–6.56 (m, 2H), 4.13 (d, J = 16.0 Hz, 1H), 3.88 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.31, 155.56, 151.08, 141.27, 140.83, 140.06, 139.41, 133.21, 132.49, 131.78, 131.19, 131.12, 129.61, 129.30, 128.70 (2x), 128.34 (2x), 128.28 (2x), 127.89, 127.84 (2x), 127.53, 127.03, 125.55, 125.26, 122.95, 121.98, 35.03.

4-Phenyl-2,6-di(thiophen-3-yl)pyridine (2z).[20c] Yield = 52% (83 mg); yellow solid; mp = 135–136 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{19}H_{14}NS_2$ 320.0562, found 320.0561; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (dd, J = 1.5, 3.0 Hz, 2H), 7.84 (dd, J = 1.5, 5.0 Hz, 2H), 7.76–7.72 (m, 4H), 7.59–7.54 (m, 2H), 7.52–7.48 (m, 1H), 7.45 (dd, J = 3.0, 5.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.64 (2x), 150.15, 142.44 (2x), 138.90, 129.09 (2x), 128.98, 127.10 (2x), 126.45 (2x), 126.14 (2x), 123.78 (2x), 116.60 (2x).

3-Benzyl-4-phenyl-2,6-di(thiophen-3-yl)pyridine (3z). Yield = 46% (94 mg); yellow solid; mp = 138–139 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{26}H_{20}NS_2$ 410.1032, found 410.1024; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (dd, J = 1.5, 3.0 Hz, 1H), 7.73 (dd, J = 1.5, 5.0 Hz, 1H), 7.49 (s, 1H), 7.43–7.36 (m, 3H), 7.35–7.28 (m, 4H), 7.21–7.08 (m, 5H), 6.81 (d, J = 7.0 Hz, 2H), 4.12 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.17, 152.65, 150.95, 142.01, 141.77, 141.19, 139.81, 129.47, 129.00, 128.40 (2x), 128.26 (2x), 128.14 (2x), 128.12, 127.77 (2x), 126.35, 126.11, 125.75, 124.83, 124.70, 123.59, 120.34, 35.40.

2,6-Di(furan-2-yl)-4-phenylpyridine (2aa).[21a] Yield = 70% (100 mg); brown solid; mp = 118–119 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{19}H_{14}NO_2$ 288.1025, found 288.1033; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (s, 2H), 7.78–7.74 (m, 2H), 7.58–7.55 (m, 2H), 7.54–7.50 (m, 2H), 7.49–7.44 (m, 1H), 7.20 (dd, J = 1.0, 3.0 Hz, 2H), 6.58–6.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.77 (2x), 149.77, 149.69 (2x), 143.28 (2x), 138.38, 129.11, 129.04 (2x), 127.03 (2x), 114.80 (2x), 112.05 (2x), 109.09 (2x).

3-Benzyl-2,6-di(furan-2-yl)-4-phenylpyridine (3aa). Yield = 15% (28 mg); brown gum; HRMS (ESI, M$^+$ + H) calcd for $C_{26}H_{20}NO_2$ 378.1494, found 378.1489; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.54–7.52 (m, 1H), 7.49–7.47 (m, 1H), 7.36–7.30 (m, 3H), 7.20–7.16 (m, 2H), 7.16–7.07 (m, 4H), 6.87–6.82 (m, 3H), 6.56–6.53 (m, 1H), 6.44–6.41 (m, 1H), 4.29 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.50 (2x), 153.14, 149.22, 147.05, 143.27, 142.98, 140.98, 139.50, 128.50 (2x), 128.38, 128.18 (2x), 128.15 (2x), 128.03 (2x), 127.90, 125.62, 118.78, 111.98, 111.83, 111.40, 108.85, 34.92.

2,6-Bis(2-methoxyphenyl)-4-phenylpyridine (2ab).[21c] Yield = 44% (129 mg); white solid; mp = 133–134 °C; HRMS (ESI, M$^+$ + H) calcd for $C_{25}H_{22}NO_2$ 368.1651, found 368.1642; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.96 (dd, J = 1.5, 7.5 Hz, 2H), 7.76–7.72 (m, 2H), 7.54–7.49 (m, 2H), 7.47–7.42 (m, 1H), 7.42–7.36 (m, 2H), 7.14–7.09 (m, 2H), 7.04 (d, J = 8.5 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.08 (2x), 155.97 (2x), 147.66, 139.48, 131.56 (2x), 129.72 (2x), 129.62, 128.91 (2x), 128.51 (2x), 127.34 (2x), 121.41 (2x), 121.05 (2x), 111.41 (2x), 55.72 (2x).

1,3,5,8-Tetraphenyl-2,6-diazabicyclo[2.2.2]oct-2-ene (4). A mixture of chalcone 1 (1.0 mmol), hexamethyldisilane (0.5 mL, 2.4 mmol), tin(II) trifluoromethanesulfonate (0.2 mmol) in dichloromethane (2 mL) was taken in a dried 35 mL microwave vial at 25 °C. The mixture was treated in a microwave irradiation instrument and stirred at 150 °C for 1 h. The consumption of starting materials were confirmed by TLC. The reaction was cooled to 25 °C, the mixture of crude product was transferred to a 100 mL round bottom flask, and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1–1/1) afforded compound **4**. Yield = 78% (162 mg); colorless solid; mp = 176–177 °C; HRMS (ESI, M$^+$ + Na) calcd for $C_{30}H_{26}N_2Na$ 437.1988, found 437.1980; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.58–7.47 (m, 4H), 7.46–7.32 (m, 5H), 7.16–7.04 (m, 3H), 6.96–6.83 (m, 2H), 4.16 (d, J =

1.5 Hz, 1H), 3.64 (d, $J = 1.5$ Hz, 1H), 3.29 (dd, $J = 5.5$, 10.0 Hz, 1H), 2.76 (dd, $J = 10.0$, 13.0 Hz, 1H), 1.97 (br s, 1H), 1.89 (dd, $J = 5.5$, 13.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.82, 145.40, 144.05, 142.35, 137.50, 130.21, 128.47 (2x), 128.35 (2x), 128.29 (2x), 128.20 (2x), 127.49 (2x), 127.38, 127.07 (3x), 126.87 (2x), 126.54 (2x), 126.29, 75.05, 57.69, 47.42, 42.91, 34.98. Single-crystal X-ray analysis: crystals of **4** were grown by slow diffusion of EtOAc into a solution of **4** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*cmb.$\bar{\text{m}}$acr1, $a = 9.8179(3)$ Å, $b = 10.4973(3)$ Å, $c = 11.9206(3)$ Å, $V = 1094.83(5)$ Å^3, $Z = 2$, $d_{\text{calcd}} = 1.257$ mg m^{-3}, $F(000) = 440$, 2θ range 1.761–30.034, R indices (all data) $R1 = 0.0529$, w$R2 = 0.1131$. CCDC number is 2085361.

Conflicts of interest

The authors declare no conflicts of interest.

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28 CCDC 2085356 (**2q**) and 2085361 (**4**), contain the supplementary crystallographic data for this paper.