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# Regiocontrolled synthesis of 2,4,6-triarylpyridines from methyl ketones, electron-deficient acetylenes and ammonium acetate†

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A novel one-pot two-step approach for the synthesis of 2,4,6-triarylpyridines *via* *t*-BuOK/DMSO-promoted *C*-vinylation of a variety of methyl ketones with electron-deficient acetylenes (alkynones) followed by a cyclization of the *in situ* generated unsaturated 1,5-dicarbonyl species with ammonium acetate has been developed. This approach possesses competitive advantages such as high regioselectivity, available starting materials and the absence of transition-metal catalysts, oxidants and undesirable byproducts. A wide synthetic utility of the developed approach was demonstrated by the synthesis of trisubstituted, tetrasubstituted and fused pyridines.

## Introduction

2,4,6-Triarylpyridines (TAPs, Kröhnke pyridines) and their bench-stable salts (Katritzky salts) are valuable building blocks in synthetic[1] and supramolecular[2] chemistry as well as in the design of advanced devices. In particular, they are exploited as components of OLEDs,[3] hole-transporting materials for solar cells,[4] and optical sensors.[5] Recently, TAPs-based metal–organic frameworks have been synthesized and used for highly selective detection of ions[6] and small molecules[7] and for separation of gas mixtures.[8] Moreover, TAPs demonstrate a great potential for the treatment of cancer acting as topoisomerase inhibitors[9] or G-quadruplex binding ligands.[10]

Many synthetic approaches to the 2,4,6-triarylpyridine core have been established to date.[11] However, the development of convenient regiocontrolled syntheses of unsymmetrical TAPs ($R^1 \neq R^2 \neq R^3$, Scheme 1) still remains a challenge. The most frequently employed in applied sciences approach to unsymmetrical 2,4,6-triarylpyridines is known to be the Kröhnke pyridine synthesis[3a,11c,12] comprising the nucleophilic addition of pyridinium ylide to an α,β-enone (Scheme 1A). In this case, the formation of aromatic pyridine ring occurs through the elimination of a pyridinium salt. Other, much less common, methods are based on the reactions of diverse unsaturated three carbon substrates with 1-arylethylamines (Scheme 1B),[13] ethyl nitroacetate/boronic acids (Scheme 1C),[14] enaminones (Scheme 1D),[15] cyclic sulfamidate imines (Scheme 1E)[16] *etc.*

The recent trends of organic synthesis, raised by green chemistry and pot-atom-step-economy (PASE)[17] paradigms, have encouraged synthetic community to modify existing and to find new methods for the assembly of well-known molecular architectures in order to mitigate negative environmental impacts. In this context, there is a perfect field for researches on the regiocontrolled synthesis of TAPs with a special focus on minimizing the formation of undesirable byproducts and excluding the use of transition-metal catalysts, oxidants and hardly-accessible starting materials.

Acetylenes having highly reactive carbon–carbon triple bond represent an ideal structural unit for atom-economic and energy-saving processes *via* diverse addition and cycloaddition reactions.[18] As a part of our long-standing research interest in the chemistry of acetylenes, we have recently reported the first example of direct *C*-vinylation of weakly nucleophilic ketones with terminal alkyl- and arylacetylenes[19] to afford β,γ-unsaturated ketones, which further have been successfully applied as a platform for diverse cascade assemblies of valuable carbo- and heterocyclic compounds.[18d] Building on our experience, in the present work we propose a novel synthetic approach toward 2,4,6-triarylpyridines, which relies on the *in situ* generation of unsaturated 1,5-dicarbonyl intermediates through base-promoted *C*-vinylation of methyl ketones with electron-deficient acetylenes (alkynones) (Scheme 2A). The proposed method has a number of obvious benefits in comparison with previously reported synthetic protocols toward

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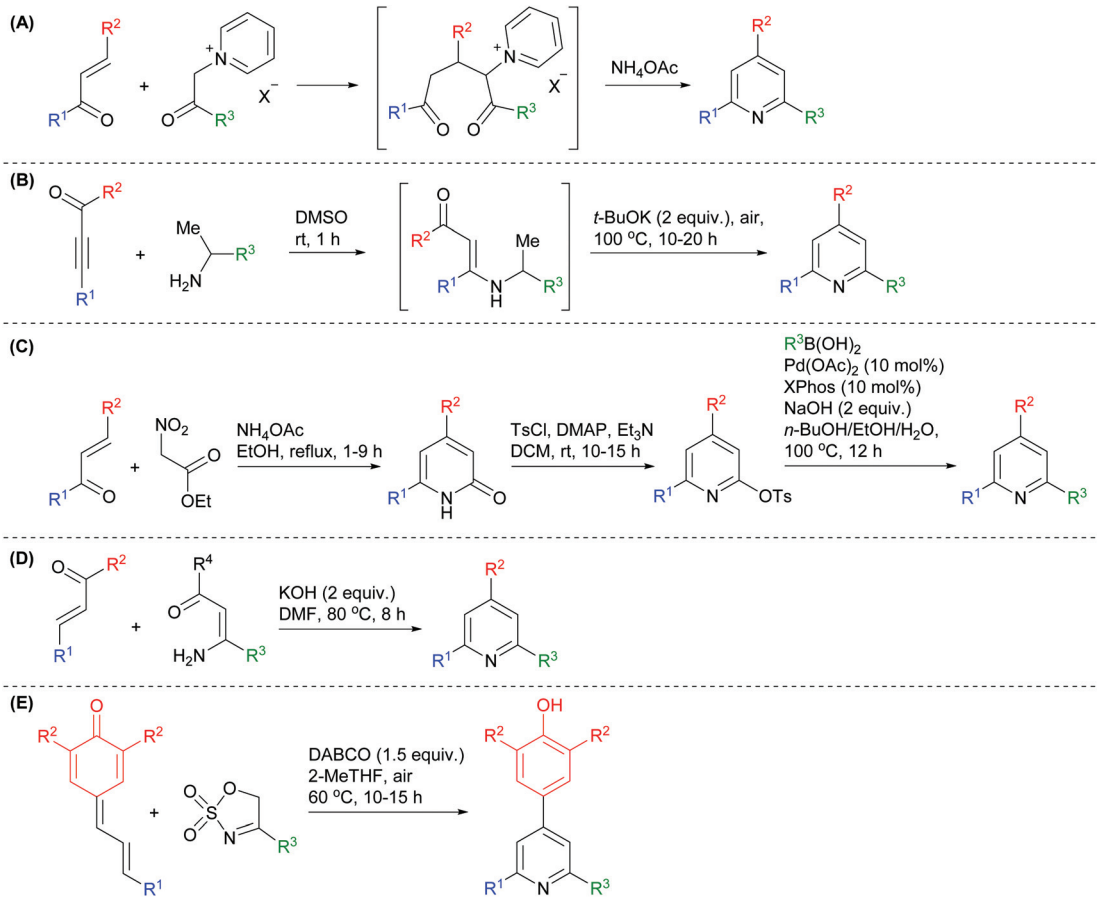
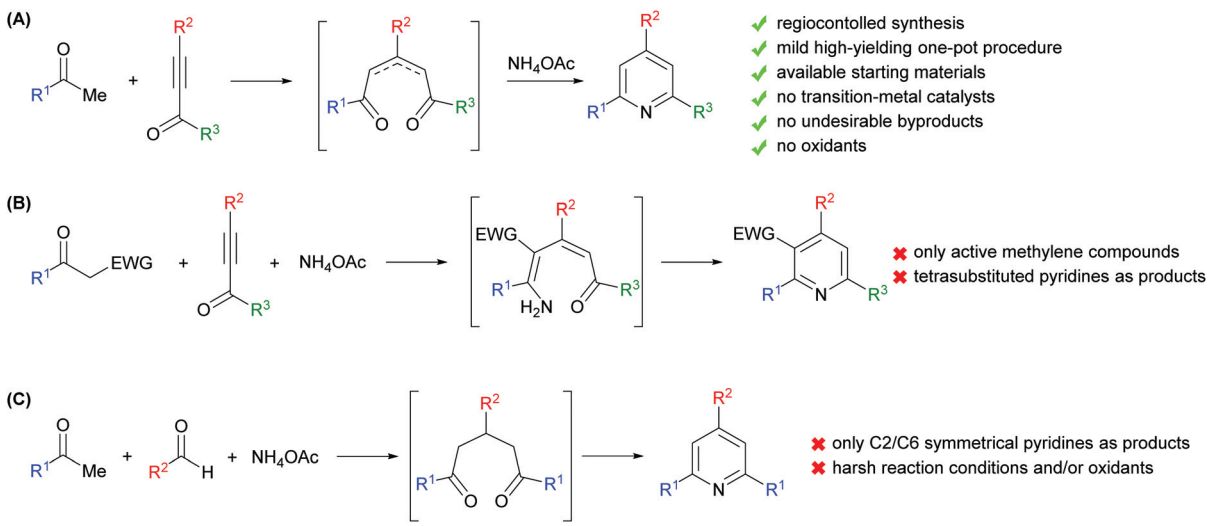



**Scheme 1** Selected examples of regiocontrolled syntheses of TAPs.




**Scheme 2** One-pot two-step regiocontrolled synthesis of TAPs from methyl ketones, electron-deficient acetylenes and ammonium acetate.

unsymmetrical TAPs (*cf.* Scheme 1), being only partly related to the Bohlmann–Rahtz pyridine synthesis (Scheme 2B)[11c,20] from substrate point of view and to the Chichibabin reaction (Scheme 2C)[11c,21] from mechanistic point of view.

## Results and discussion

The conventional way to convert methyl ketones to *C*-anionic nucleophilic species comprises their treatment with strong

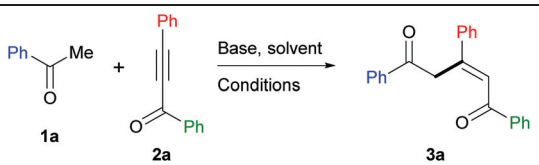
 

bases such as lithium diisopropylamide, alkali metals hydroxides and alkoxides *etc*. At the same time, it is well known that alkynones as highly reactive compounds[22] are susceptible to hydrolytic cleavage and anionic polymerization under similar conditions.[23] We have assumed that one possibility to solve this dilemma is the use of non-nucleophilic superbasic systems capable of ensuring the high concentration of anionic species even at room temperature.[24] As a matter of fact, the model reaction between equimolar amounts of acetophenone (**1a**) and 1,3-diphenylprop-2-yn-1-one (**2a**) in the presence of superbasic system potassium *tert*-butoxide/dimethylsulfoxide at room temperature for 0.5 h afforded the desired unsaturated 1,5-diketone **3a** exclusively as *E*-isomer in 68% yield (Table 1, entry 1). Although the studied range of the reaction time and temperature had no remarkable effect on the reaction outcome (entries 2–4) the addition of *t*-BuOK to the mixture of reactants in DMSO was found to be slightly exothermic that should be taken into account for gram-scale syntheses. The decrease in the amount of *t*-BuOK to 0.5 equiv. per **1a** resulted in the formation of diketone **3a** in a low yield (12%, entry 5) probably because of deactivation of the base through the side reactions with CH-acidic **3a** and reactive acetylene **2a**. Among the bases tested, only *t*-BuOK and *t*-BuONa showed a good catalytic activity (entries 1 and 6–8). The choice of the solvent (in this case, a ligand toward alkali metal cation) was pivotal; DMF, NMP, MeCN, and toluene were tested and gave the significantly lower yields of diketone **3a** (entries 9–12). Next, the ratio and concentration of the reactants were varied (entries 13–17). Finally, the desired unsaturated 1,5-diketone **3a** was obtained in 83% isolated yield, when acetophenone (**1a**), 1,3-diphenylprop-2-yn-1-one (**2a**), and *t*-BuOK in a molar ratio of 1 : 2 : 2 were reacted in DMSO (0.125 M per **1a**) at room temperature for 0.5 h.

Next, 2,4,6-triphenylpyridine (**4a**) was easily synthesized in 76% isolated yield *via* a one-pot two-step approach consisting of *t*-BuOK/DMSO-promoted addition of acetophenone (**1a**) to 1,3-diphenylprop-2-yn-1-one (**2a**, Table 1, entry 17) followed by the treatment of resulting reaction mixture with ammonium acetate (5.0 equiv. per **1a**) at 60 °C for 5 h. Further, the substrate scope of the novel synthetic approach to 2,4,6-triarylpyridines was studied.

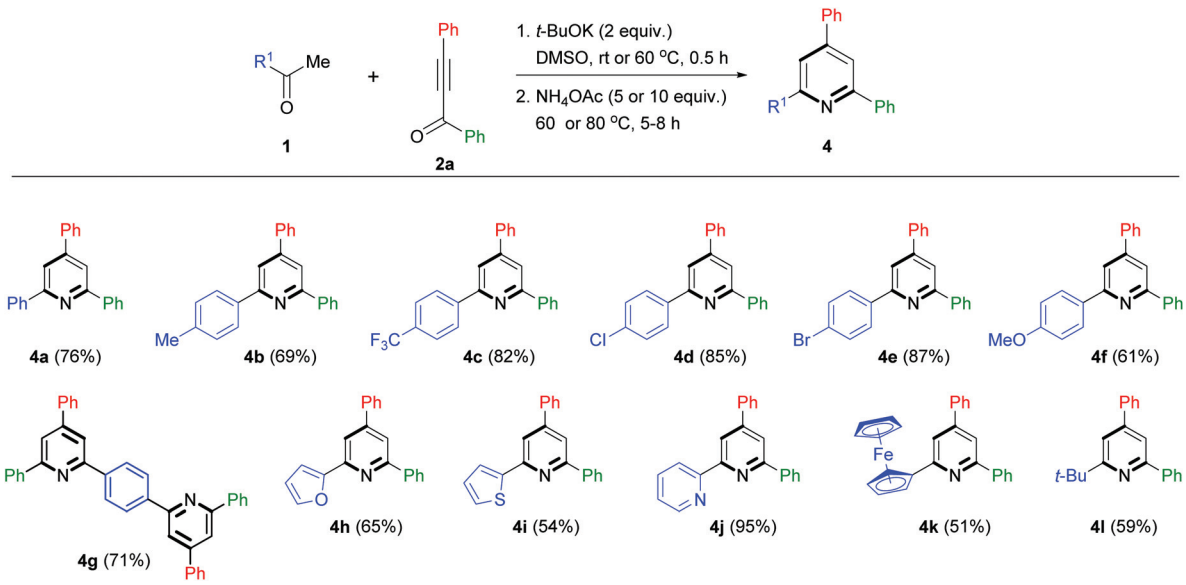
As follows from Scheme 3 and Table S1 (see ESI†), acetophenones bearing trifluoromethyl, bromo and chloro substituents at the *para*-position of the benzene ring smoothly reacted with 1,3-diphenylprop-2-yn-1-one (**2a**) under the same conditions to afford the pyridines **4c–e** in good yields (82–87%). The presence of electron-donating groups as exemplified by the reactivity of 4-methyl and 4-methoxyacetophenones required somewhat harsher reaction conditions on the second stage (a longer reaction time and a greater excess of ammonium acetate) to provide a full conversion of the intermediate 1,5-dicarbonyl compounds to pyridines **4b** and **4f** (in 69% and 61% yields, respectively). Interestingly, the best yields of pyridines **4h** and **4i** (65% and 54%, respectively, Scheme 3) were achieved when the first stage, the reaction of 2-acetylfuran or 2-acetylthiophene with 1,3-diphenylprop-2-yn-1-one

**Table 1** Optimization of the C-vinylation of acetophenone (**1a**) with 1,3-diphenylprop-2-yn-1-one (**2a**)[a]




| Entry | Base | Solvent | Conditions | Conversion of **1a**,[b] [%] | Yield of **3a**,[b] [%] |
|---|---|---|---|---|---|
| 1 | *t*-BuOK (1.0 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 93 | 68 |
| 2 | *t*-BuOK (1.0 equiv.) | DMSO (0.25 M) | rt, 0.25 h | 90 | 56 |
| 3 | *t*-BuOK (1.0 equiv.) | DMSO (0.25 M) | 40 °C, 0.5 h | 90 | 50 |
| 4[c] | *t*-BuOK (1.0 equiv.) | DMSO/THF (0.25 M) | 15 °C, 0.5 h | 83 | 68 |
| 5 | *t*-BuOK (0.5 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 67 | 12 |
| 6 | *t*-BuONa (1.0 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 95 | 54 |
| 7 | KOH·0.5$H_2O$ (1.0 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 55 | 8 |
| 8 | DBU (1.0 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 50 | 6 |
| 9 | *t*-BuOK (1.0 equiv.) | DMF (0.25 M) | rt, 0.5 h | 55 | 23 |
| 10 | *t*-BuOK (1.0 equiv.) | NMP (0.25 M) | rt, 0.5 h | 62 | 35 |
| 11 | *t*-BuOK (1.0 equiv.) | MeCN (0.25 M) | rt, 0.5 h | 35 | 4 |
| 12 | *t*-BuOK (1.0 equiv.) | toluene (0.25 M) | rt, 0.5 h | 83 | 25 |
| 13[d] | *t*-BuOK (1.0 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 85 | 45 |
| 14[d] | *t*-BuOK (1.5 equiv.) | DMSO (0.25 M) | rt, 0.5 h | 100 | 77 |
| 15[d] | *t*-BuOK (1.5 equiv.) | DMSO (0.5 M) | rt, 0.5 h | 100 | 77 (73)[e] |
| 16[d] | *t*-BuOK (1.5 equiv.) | DMSO (0.125 M) | rt, 0.5 h | 100 | 80 |
| **17**[f] | ***t*-BuOK (2.0 equiv.)** | **DMSO (0.125 M)** | **rt, 0.5 h** | **100** | **88 (83)**[g] |

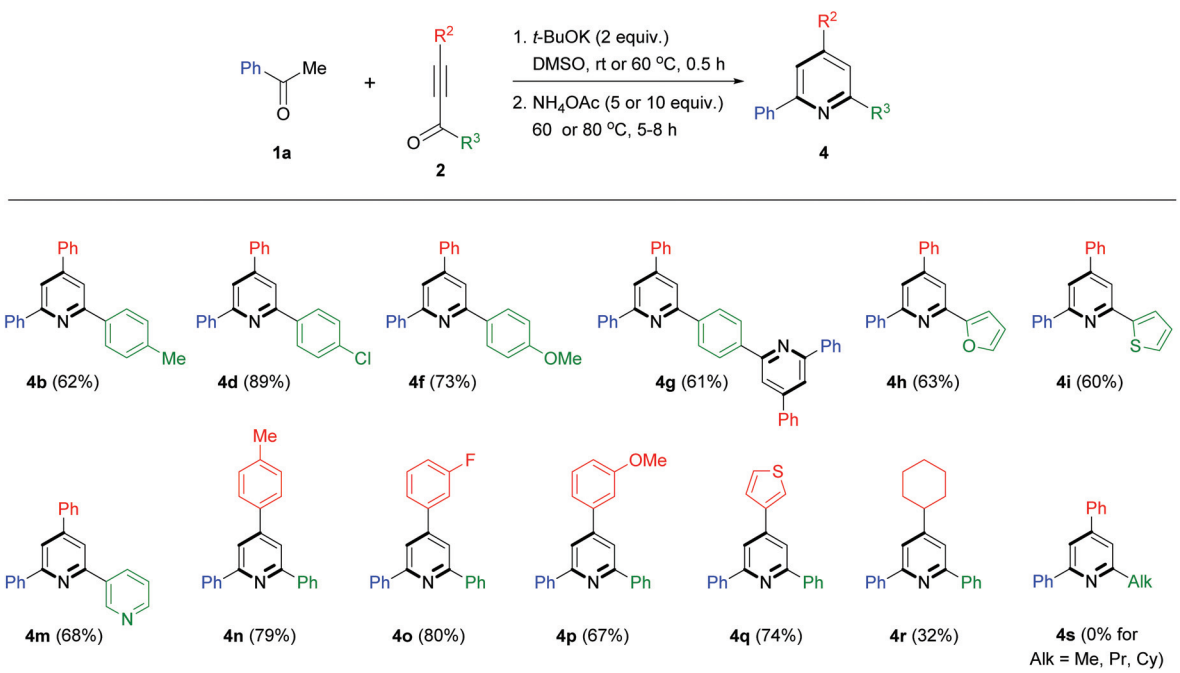
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), the amount of base and solvent was calculated per **1a** in accordance with the equivalent ratios and molarities given in the Table 1. [b] Yields determined by $^1$H NMR using durene as an internal standard. [c] The mixture of DMSO/THF (10 : 1 v/v ratio) was used. [d] Molar ratio of **1a** : **2a** = 1 : 1.5. [e] In parentheses isolated yield is given for reaction on 10.0 mmol scale. [f] Molar ratio of **1a** : **2a** = 1 : 2, unreacted **2a** was registered by IR spectroscopy in a crude after reaction completion. [g] In parentheses isolated yield is given for reaction on 0.5 mmol scale.




**Scheme 3** The methyl ketones scope of the one-pot two-step regiocontrolled approach to TAPs. Reaction conditions: ketone **1** (0.375 mmol), 1,3-diphenylprop-2-yn-1-one **2a** (0.75 mmol), *t*-BuOK (0.75 mmol), DMSO (3 mL). Pyridine **4j** was synthesized on 2.5 mmol scale. Isolated yields are given.

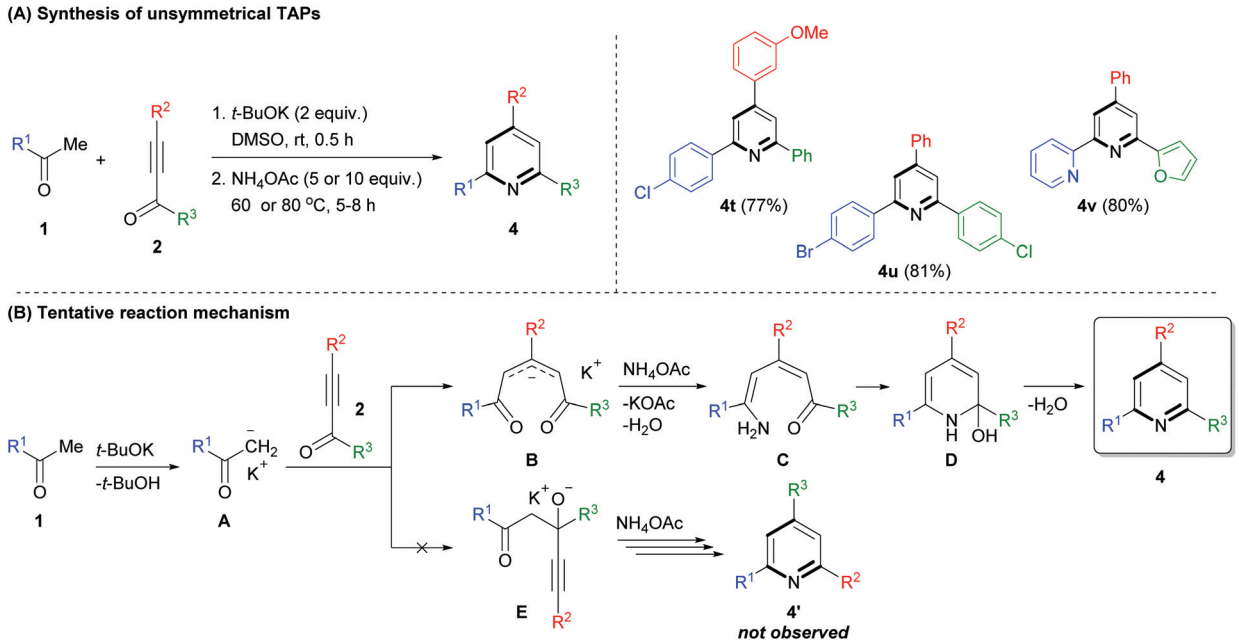
(**2a**), was conducted at elevated temperature (60 °C). To test the scalability of the one-pot two-step protocol we performed the reaction of 2-acetylpyridine with 1,3-diphenylprop-2-yn-1-one (**2a**) in 2.5 mmol scale and obtained 2,2′-bipyridine **4j** in excellent 95% isolated yield. Moreover, several more exotic methyl ketones, namely 1,4-diacetylbenzene, acetylferrocene and 3,3-dimethylbutan-2-one were successfully transformed into the corresponding dipyridine **4g**, ferrocenylpyridine **4k** and *tert*-butylpyridine **4l**, respectively (Scheme 3).

Next, a set of alkynones was subjected to a similar reaction using acetophenone (**1a**) as a model methyl ketone (Scheme 4). The corresponding pyridines were synthesized in good yields (60–89%) from alkynones having aryl and hetaryl substituents both at the carbon–carbon triple bond and the




**Scheme 4** The alkynones scope of the one-pot two-step regiocontrolled approach to TAPs. Reaction conditions: ketone **1** (0.375 mmol), alkynone **2** (0.75 mmol), *t*-BuOK (0.75 mmol), DMSO (3 mL). Isolated yields are given.



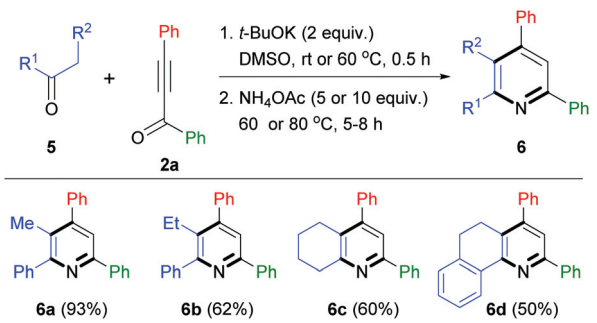

**Scheme 5** Tentative reaction mechanism of the one-pot two-step regiocontrolled synthesis of unsymmetrical TAPs. Reaction conditions: ketone **1** (0.375 mmol), alkynone **2** (0.75 mmol), *t*-BuOK (0.75 mmol), DMSO (3 mL). Isolated yields are given.

carbonyl function (Scheme 4). However, the alkynones having at least one alkyl substituent were less effective in the studied reaction. Thus, 3-cyclohexyl-1-phenylprop-2-yn-1-one was converted to 4-cyclohexyl-2,6-diphenylpyridine **4r** in only 32% yield, while the reactions of acetophenone (**1a**) with 3-phenyl-1-alkylprop-2-yn-1-ones (examples of alkyl groups were methyl, propyl and cyclohexyl) failed to yield pyridines and led to the complex reaction mixtures apparently due to side reactions initiated by competing deprotonation of alkyl moieties on the first stage.

To examine the regioselectivity, the synthesis of unsymmetrical TAPs has been explored as well (Scheme 5A). As outlined in Scheme 5A, three representatives of unsymmetrical TAPs were obtained in good yields (77–81%) with total regiocontrol, confirming that this approach could be used for the synthesis of unsymmetrical TAPs from available methyl ketones and electron-deficient acetylenes (alkynones).

Summarizing the results obtained, the following tentative mechanism can be suggested (Scheme 5B). The reaction starts from the formation of potassium enolate **A** from methyl ketone **1** and *t*-BuOK, which further attacks the carbon–carbon triple bond of alkynone **2** to afford potassium salt of unsaturated 1,5-diketone **B**. The addition of ammonium acetate on the second stage leads to neutralization of salt **B** with simultaneous nucleophilic addition of ammonia to the carbonyl function. Intramolecular cyclization of the obtained amine **C** followed by water molecule elimination from dihydropyridine **D** completes the assembly of TAP. It is worth noting that no product of competing addition of potassium enolate to the carbon–oxygen double bond of alkynone **2** was detected (total regiocontrol), although arylpropynals ($R^3$ = H) are known to give aldol type products **E** under similar basic conditions.[25]

Once the main goal of our study had been reached, we proposed that the developed synthetic approach has a greater scope and may be extended to the design of more substituted pyridines (Scheme 6). Thus, when propiophenone and butyrophenone as acetophenone homologues were employed in the reaction with 1,3-diphenylprop-2-yn-1-one (**2a**), the corresponding 3-methyl-(**6a**) and 3-ethyl-(**6b**) 2,4,6-triphenylpyridines were formed in 93% and 62% yields, respectively. The use of cyclohexanone and α-tetralone delivered the fused pyridines, namely tetrahydroquinoline **6c** and dihydrobenzo[*h*]quinoline **6d**, in 60% and 50% yields, respectively. Obviously, the above mentioned transformations are just an illustration of a much




**Scheme 6** The extension of the one-pot two-step approach to the synthesis of tetrasubstituted and fused pyridines. Reaction conditions: ketone **5** (0.375 mmol), 1,3-diphenylprop-2-yn-1-one **2a** (0.75 mmol), *t*-BuOK (0.75 mmol), DMSO (3 mL). Isolated yields are given.

broader range of potential manipulations to construct the desired pyridine derivatives.

## Conclusions

In summary, we have disclosed a novel one-pot two-step regiocontrolled synthetic approach toward 2,4,6-triarylpyridines based on the *C*-vinylation of methyl ketones with electron-deficient acetylenes (alkynones) followed by cyclization of *in situ* generated unsaturated 1,5-dicarbonyl intermediates under treatment with ammonium acetate. The amenability of the proposed reaction sequence to diversely decorated methyl ketones and alkynones was evaluated, making it possible to synthesize a number of 2,4,6-triarylpyridines in good-to-excellent yields. Furthermore, tetrasubstituted and fused pyridines were shown to be accessible through our method using methyl ketones homologues.

## Experimental

All chemicals and solvents were purchased from commercial sources. Starting alkynones were synthesized according to the published method.[26] Thin layer chromatography was carried out on Merck silica gel 60 F254 pre-coated aluminium foil sheets and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel ($SiO_2$), 70–230 mesh, pore size 60 Å. NMR spectra were recorded from solutions in $CDCl_3$ on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for $^1H$ and 100.6 MHz for $^{13}C$). Chemical shifts ($\delta$) are quoted in parts per million (ppm). The residual solvent peak, $\delta_H$ 7.26 and $\delta_C$ 77.10, was used as a reference. Coupling constants ($J$) are reported in Hertz (Hz). The multiplicity abbreviations used are: s singlet, d doublet, dd doublet of doublet, t triplet, m multiplet, br broad signal. High-resolution mass spectra were recorded from acetonitrile solution with 0.1% HFBA on HPLC Agilent 1200/Agilent 6210 TOF instrument equipped with electrospray ionization (ESI) source. Melting points (uncorrected) were measured on a digital melting point apparatus Electrothermal IA 9200.

### Procedure for the synthesis of diketone 3a

A 10 mL round-bottom flask with stir bar was sequentially charged with acetophenone (**1a**, 60 mg, 0.5 mmol), 1,3-diphenylprop-2-yn-1-one (**2a**, 206 mg, 1.0 mmol) and DMSO (4 mL). Then *t*-BuOK (112 mg, 1.0 mmol) was added, the reaction flask was capped with a glass stopper, and the reaction mixture was stirred at room temperature (20–24 °C) for 0.5 h. The reaction mixture was then quenched with water (20 mL), neutralized with 10% HCl(aq), and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with water (2 × 5 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography over silica gel using hexane-diethyl ether (gradient from 1/0 to 0/1, v/v) as an eluent to afford the desired diketone **3a**.

### (*E*)-1,3,5-Triphenylpent-2-ene-1,5-dione (3a)

A cream solid (136 mg, 83% yield), mp 99–101 °C (lit.[27] 97–99 °C), $R_f$ = 0.36 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.08 (d, $J$ = 7.4 Hz, 2H, Ph), 7.99 (d, $J$ = 7.4 Hz, 2H, Ph), 7.61–7.53 (m, 4H, Ph), 7.51–7.44 (m, 4H, Ph, 1H, =CH), 7.43–7.40 (m, 3H, Ph), 4.87 (s, 2H, $CH_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 196.2, 191.0, 152.9, 142.2, 139.2, 137.2, 133.2, 132.8, 129.5, 128.9, 128.8, 128.7, 128.4, 128.4, 127.0, 123.8, 43.1. HRMS (ESI-TOF) calcd for $[C_{23}H_{18}O_2 + H]^+$ 327.1385, found 327.1383.

### General procedure for the synthesis of pyridines 4 and 6

A 10 mL round-bottom flask with stir bar was sequentially charged with ketone (0.375 mmol), alkynone (0.75 mmol) and DMSO (3 mL). Then *t*-BuOK (84 mg, 0.75 mmol) was added, the reaction flask was capped with a glass stopper, and the reaction mixture was stirred at room temperature (20–24 °C) or at 60 °C for 0.5 h. Then $NH_4OAc$ (144 mg, 1.875 mmol, 5 equiv.) was added to the flask, a glass stopper was replaced by a reflux condenser, and the reaction mixture was stirred at 60 °C or 80 °C for 5–8 h. In some cases the addition of $NH_4OAc$ (144 mg, 1.875 mmol, 5 equiv.) was repeated after the first 4 h (see Table S1† for detailed reaction conditions). The reaction mixture was then quenched with water (20 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with water (2 × 5 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography over silica gel using hexane-diethyl ether (gradient from 1/0 to 0/1, v/v) as an eluent to afford the desired pyridine **4** and **6**.

### 2,4,6-Triphenylpyridine (4a)

Following the general procedure, **4a** was prepared from acetophenone (45 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (88 mg, 76% yield), mp 135–137 °C (lit.[13] 140–141 °C), $R_f$ = 0.64 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.22 (d, $J$ = 7.4 Hz, 4H), 7.90 (s, 2H), 7.76 (d, $J$ = 7.4 Hz, 2H), 7.54–7.44 (m, 9H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.6, 150.6, 139.7, 139.2, 129.2, 129.1, 129.1, 128.8, 127.3, 127.3, 117.2. HRMS (ESI-TOF) calcd for $[C_{23}H_{17}N + H]^+$ 308.1439, found 308.1437.

### 2,4-Diphenyl-6-(*p*-tolyl)pyridine (4b)

Following the general procedure, **4b** was prepared from 4′-methylacetophenone (50 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol) and isolated as a light yellow solid (83 mg, 69% yield) **OR 4b** was prepared from acetophenone (45 mg, 0.375 mmol) and 3-phenyl-1-(*p*-tolyl)prop-2-yn-1-one (165 mg, 0.75 mmol) and isolated as a light yellow solid (75 mg, 62% yield), mp 120–121 °C (lit.[13] 119–120 °C), $R_f$ = 0.73 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.21 (d, $J$ = 7.3 Hz, 2H), 8.12 (d, $J$ = 8.1 Hz, 2H),

7.87 (s, 2H), 7.75 (d, $J$ = 7.0 Hz, 2H), 7.55–7.43 (m, 6H), 7.33 (d, $J$ = 8.1 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.6, 157.5, 150.2, 139.8, 139.3, 139.1, 136.9, 129.5, 129.2, 129.1, 129.0, 128.8, 127.3, 127.3, 127.1, 116.9, 116.9, 21.4. HRMS (ESI-TOF) calcd for $[C_{24}H_{19}N + H]^+$ 322.1596, found 322.1593.

### 2,4-Diphenyl-6-(4-(trifluoromethyl)phenyl)pyridine (4c)

Following the general procedure, **4c** was prepared from 4′-(trifluoromethyl)acetophenone (71 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (116 mg, 82% yield), mp 136–137 °C (lit.[28] 135–137 °C), $R_f$ = 0.65 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.32 (d, $J$ = 8.3 Hz, 2H), 8.21 (d, $J$ = 7.0 Hz, 2H), 7.95 (s, 1H), 7.92 (s, 1H), 7.79–7.75 (m, 4H), 7.58–7.46 (m, 6H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.8, 155.9, 150.5, 143.0, 139.3, 138.8, 130.9 (q, $J$ = 32.3), 129.4, 129.3, 129.3, 128.9, 127.5, 127.3, 127.2, 125.7 (q, $J$ = 3.8 Hz), 124.4 (q, $J$ = 272.0 Hz), 117.9, 117.4. HRMS (ESI-TOF) calcd for $[C_{24}H_{16}F_3N + H]^+$ 376.1313, found 376.1313.

### 2-(4-Chlorophenyl)-4,6-diphenylpyridine (4d)

Following the general procedure, **4d** was prepared from 4′-chloroacetophenone (58 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol) and isolated as a light yellow solid (109 mg, 85% yield), **OR 4d** was prepared from acetophenone (45 mg, 0.375 mmol) and 1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (181 mg, 0.75 mmol) and isolated as a light yellow solid (114 mg, 89% yield), mp 133–134 °C (lit.[13] 120–122 °C), $R_f$ = 0.70 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.20 (d, $J$ = 7.3 Hz, 2H), 8.16 (d, $J$ = 8.5 Hz, 2H), 7.90 (s, 1H), 7.86 (s, 1H), 7.75 (d, $J$ = 7.1 Hz, 2H), 7.56–7.45 (m, 8H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.6, 156.2, 150.4, 139.4, 138.9, 138.0, 135.2, 129.2, 129.2, 129.1, 128.9, 128.8, 128.5, 127.2, 127.2, 117.4, 116.8. HRMS (ESI-TOF) calcd for $[C_{23}H_{16}ClN + H]^+$ 342.1050, found 342.1048.

### 2-(4-Bromophenyl)-4,6-diphenylpyridine (4e)

Following the general procedure, **4e** was prepared from 4′-bromoacetophenone (75 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (126 mg, 87% yield), mp 153–155 °C (lit.[28] 151–153 °C), $R_f$ = 0.68 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.19 (d, $J$ = 7.1 Hz, 2H), 8.10 (d, $J$ = 8.6 Hz, 2H), 7.91 (s, 1H), 7.86 (s, 1H), 7.74 (d, $J$ = 6.9 Hz, 2H), 7.64 (d, $J$ = 8.6 Hz, 2H), 7.56–7.44 (m, 6H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.7, 156.3, 150.4, 139.5, 138.9, 138.5, 131.9, 129.3, 129.2, 129.2, 128.8, 128.8, 127.3, 127.2, 123.6, 117.5, 116.8. HRMS (ESI-TOF) calcd for $[C_{23}H_{16}BrN + H]^+$ 386.0544, found 386.0546.

### 2-(4-Methoxyphenyl)-4,6-diphenylpyridine (4f)

Following the general procedure, **4f** was prepared from 4′-methoxyacetophenone (56 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol) and isolated as a light yellow solid (77 mg, 61% yield) **OR 4f** was prepared from acetophenone (45 mg, 0.375 mmol) and 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (177 mg, 0.75 mmol) and isolated as a light yellow solid (92 mg, 73% yield), mp 99–101 °C (lit.[13] 106–108 °C), $R_f$ = 0.57 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.22 (d, $J$ = 7.8 Hz, 2H), 8.20 (d, $J$ = 8.8 Hz, 2H), 7.85 (s, 1H), 7.85 (s, 1H), 7.76 (d, $J$ = 7.2 Hz, 2H), 7.56–7.44 (m, 6H), 7.06 (d, $J$ = 8.8 Hz, 2H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 160.7, 157.5, 157.2, 150.2, 139.8, 139.3, 132.4, 129.2, 129.1, 129.0, 128.8, 128.5, 127.3, 127.2, 116.6, 116.4, 114.2, 55.5. HRMS (ESI-TOF) calcd for $[C_{24}H_{19}NO + H]^+$ 338.1544, found 338.1544.

### 1,4-Bis(4,6-diphenylpyridin-2-yl)benzene (4g)

Following the general procedure, **4g** was prepared from 1,4-diacetylbenzene (61 mg, 0.375 mmol), 1,3-diphenylprop-2-yn-1-one (310 mg, 1.5 mmol), potassium *tert*-butoxide (168 mg, 1.5 mmol) and ammonium acetate (288 mg, 3.75 mmol) in DMSO (3 mL) **OR 4g** was prepared from acetophenone (90 mg, 0.75 mmol), 1,1′-(1,4-phenylene)bis(3-phenylprop-2-yn-1-one) (125 mg, 0.375 mmol), potassium *tert*-butoxide (112 mg, 0.75 mmol) and ammonium acetate (288 mg, 3.75 mmol) in DMSO (3 mL). The reaction mixture after cooling to room temperature was diluted with water (15 mL), and extracted with DCM (3 × 10 mL). The combined organic extracts were washed with water (2 × 5 mL) and dried ($CaCl_2$). After removal of the solvent, the residue was treated with diethyl ether and **4g** was isolated as a brown solid (143 mg, 71% yield **OR** 122 mg, 61% yield), mp 292–294 °C (lit.[29] 302–304 °C). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.38 (s, 4H), 8.25 (d, $J$ = 7.6 Hz, 4H), 7.99 (s, 2H), 7.93 (s, 2H), 7.79 (d, $J$ = 7.3 Hz, 4H), 7.58–7.46 (m, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.8, 157.2, 150.5, 140.3, 139.8, 139.3, 129.3, 129.3, 129.2, 128.9, 127.6, 127.4, 127.3, 117.5, 117.4. HRMS (ESI-TOF) calcd for $[C_{40}H_{28}N_2 + H]^+$ 537.2331, found 537.2334.

### 2-(Furan-2-yl)-4,6-diphenylpyridine (4h)

Following the general procedure, **4h** was prepared from 2-acetylfuran (41 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol) and isolated as a light yellow solid (72 mg, 65% yield) **OR 4h** was prepared from acetophenone (45 mg, 0.375 mmol) and 1-(furan-2-yl)-3-phenylprop-2-yn-1-one (147 mg, 0.75 mmol) and isolated as a light yellow solid (70 mg, 63% yield), mp 87–88 °C (lit.[28] 90–92 °C), $R_f$ = 0.68 (hexane-diethyl ether, 3/1, v/v). $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.17 (d, $J$ = 7.2 Hz, 2H), 7.90 (s, 1H), 7.83 (s, 1H), 7.77 (d, $J$ = 7.0 Hz, 2H), 7.59–7.44 (m, 7H), 7.27 (d, $J$ = 3.3 Hz, 1H), 6.59 (dd, $J$ = 1.5 Hz, $J$ = 3.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.8, 154.3, 150.1, 149.9, 143.3, 139.5, 138.9, 129.2, 129.2, 128.8, 127.3, 127.2, 117.0, 115.2, 112.2, 109.2. HRMS (ESI-TOF) calcd for $[C_{21}H_{15}NO + H]^+$ 298.1232, found 298.1230.

### 2,4-Diphenyl-6-(thiophen-2-yl)pyridine (4i)

Following the general procedure, **4i** was prepared from 2-acetylthiophene (47 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-

one (155 mg, 0.75 mmol) and isolated as a light yellow solid (63 mg, 54% yield) **OR 4i** was prepared from acetophenone (45 mg, 0.375 mmol) and 3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (159 mg, 0.75 mmol) and isolated as a light yellow solid (70 mg, 60% yield), mp 105–106 °C (lit.[28] 112–114 °C), $R_f$ = 0.66 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.20 (d, $J$ = 7.1 Hz, 2H), 7.82 (s, 1H), 7.80 (s, 1H), 7.75–7.74 (m, 3H), 7.56–7.44 (m, 7H), 7.17–7.15 (m, 1H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.5, 152.9, 150.3, 145.6, 139.2, 139.0, 129.3, 129.3, 129.2, 128.9, 128.1, 127.8, 127.3, 127.2, 124.8, 116.9, 115.5. HRMS (ESI-TOF) calcd for $[C_{21}H_{15}NS + H]^+$ 314.1003, found 314.1002.

### 4,6-Diphenyl-2,2′-bipyridine (4j)

Following the general procedure, **4j** was prepared from 2-acetylpyridine (303 mg, 2.5 mmol), 1,3-diphenylprop-2-yn-1-one (1030 mg, 5.0 mmol), potassium *tert*-butoxide (560 mg, 2.5 mmol) and ammonium acetate (963 mg, 12.5 mmol) in DMSO (10 mL, 0.25 M) and isolated as a white solid (732 mg, 95% yield), mp 156–158 °C (lit.[30] 157–158 °C), $R_f$ = 0.24 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.74–8.70 (m, 2H), 8.68 (s, 1H), 8.23 (d, $J$ = 7.3 Hz, 2H), 8.00 (s, 1H), 7.89–7.83 (m, 3H), 7.57–7.51 (m, 4H), 7.49–7.46 (m, 2H), 7.35–7.33 (m, 1H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.3, 156.5, 156.4, 150.4, 149.2, 139.6, 138.9, 137.0, 129.2, 129.1, 129.1, 128.9, 127.4, 127.2, 123.9, 121.6, 118.6, 117.7. HRMS (ESI-TOF) calcd for $[C_{22}H_{16}N_2 + H]^+$ 309.1392, found 309.1393.

### 2-Ferrocenyl-4,6-diphenylpyridine (4k)

Following the general procedure, **4k** was prepared from acetylferrocene (86 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as an orange oil (80 mg, 51% yield), $R_f$ = 0.66 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.22 (d, $J$ = 7.1 Hz, 2H), 7.77–7.75 (m, 3H), 7.58–7.45 (m, 7H), 5.12–5.11 (m, 2H), 4.46–4.45 (m, 2H), 4.12 (s, 5H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 160.0, 157.1, 149.3, 139.9, 139.4, 129.2, 129.0, 129.0, 128.8, 127.3, 127.2, 116.7, 115.7, 84.5, 70.0, 69.8, 67.8. HRMS (ESI-TOF) calcd for $[C_{27}H_{21}FeN + H]^+$ 416.1102, found 416.1101.

### 2-(*tert*-Butyl)-4,6-diphenylpyridine (4l)

Following the general procedure, **4l** was prepared from 3,3-dimethylbutan-2-one (38 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light pink solid (64 mg, 59% yield), mp 88–90 °C (lit.[28] 87–89 °C), $R_f$ = 0.83 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.23 (d, $J$ = 7.2 Hz, 2H), 7.82 (s, 1H), 7.74 (d, $J$ = 7.1 Hz, 2H), 7.57–7.44 (m, 7H), 1.56 (s, 9H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 169.7, 156.2, 149.6, 140.1, 139.9, 129.1, 128.9, 128.7, 128.7, 127.4, 127.1, 115.9, 115.6, 38.0, 30.5. HRMS (ESI-TOF) calcd for $[C_{21}H_{21}N + H]^+$ 288.1752, found 288.1752.

### 4,6-Diphenyl-2,3′-bipyridine (4m)

Following the general procedure, **4m** was prepared from acetophenone (45 mg, 0.375 mmol) and 3-phenyl-1-(pyridin-3-yl) prop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a white solid (79 mg, 68% yield), mp 153–155 °C (lit.[31] 161 °C), $R_f$ = 0.60 (diethyl ether). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 9.40 (s, 1H), 8.69 (d, $J$ = 3.7 Hz, 1H), 8.51 (d, $J$ = 7.9 Hz, 1H), 8.20 (d, $J$ = 7.2 Hz, 2H), 7.93 (s, 1H), 7.88 (s, 1H), 7.74 (d, $J$ = 6.9 Hz, 2H), 7.56–7.42 (m, 7H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 158.0, 155.0, 150.6, 150.1, 148.6, 139.2, 138.7, 135.1, 134.6, 129.4, 129.3, 128.9, 127.2, 127.2, 123.6, 117.8, 117.1. HRMS (ESI-TOF) calcd for $[C_{22}H_{16}N_2 + H]^+$ 309.1392, found 309.1390.

### 2,6-Diphenyl-4-(*p*-tolyl)pyridine (4n)

Following the general procedure, **4n** was prepared from acetophenone (45 mg, 0.375 mmol) and 1-phenyl-3-(*p*-tolyl)prop-2-yn-1-one (165 mg, 0.75 mmol), isolated as a light yellow solid (95 mg, 79% yield), mp 117–118 °C (lit.[13] 118–120 °C), $R_f$ = 0.71 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.27 (d, $J$ = 7.5 Hz, 4H), 7.92 (s, 2H), 7.69 (d, $J$ = 7.7 Hz, 2H), 7.59–7.56 (m, 4H), 7.52–7.48 (m, 2H), 7.37 (d, $J$ = 7.7 Hz, 2H), 2.48 (s, 3H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.5, 150.1, 139.8, 139.1, 136.2, 129.9, 129.1, 128.8, 127.2, 127.1, 117.0, 21.3. HRMS (ESI-TOF) calcd for $[C_{24}H_{19}N + H]^+$ 322.1596, found 322.1593.

### 4-(3-Fluorophenyl)-2,6-diphenylpyridine (4o)

Following the general procedure, **4o** was prepared from acetophenone (45 mg, 0.375 mmol) and 3-(3-fluorophenyl)-1-phenylprop-2-yn-1-one (168 mg, 0.75 mmol), isolated as a light yellow solid (98 mg, 80% yield), mp 128–130 °C (lit.[13] 138–139 °C), $R_f$ = 0.65 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.22 (d, $J$ = 7.4 Hz, 4H), 7.87 (s, 2H), 7.56–7.45 (m, 9H), 7.20–7.17 (m, 1H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 163.4 (d, $J$ = 246.9 Hz), 157.8, 149.0 (d, $J$ = 2.0 Hz), 141.5 (d, $J$ = 7.8 Hz), 139.5, 130.8 (d, $J$ = 8.3 Hz), 129.3, 128.9, 127.3, 123.0 (d, $J$ = 2.8 Hz), 117.0, 116.0 (d, $J$ = 21.1 Hz), 114.3 (d, $J$ = 22.4 Hz). HRMS (ESI-TOF) calcd for $[C_{23}H_{16}FN + H]^+$ 326.1345, found 326.1343.

### 4-(3-Methoxyphenyl)-2,6-diphenylpyridine (4p)

Following the general procedure, **4p** was prepared from acetophenone (45 mg, 0.375 mmol) and 3-(3-methoxyphenyl)-1-phenylprop-2-yn-1-one (177 mg, 0.75 mmol), isolated as a light beige solid (85 mg, 67% yield), mp 122–124 °C (lit.[32] 121–122 °C), $R_f$ = 0.57 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.21 (d, $J$ = 7.4 Hz, 4H), 7.89 (s, 2H), 7.54–7.51 (m, 4H), 7.47–7.44 (m, 3H), 7.34 (d, $J$ = 7.6 Hz, 1H), 7.27–7.26 (m, 1H), 7.02 (d, $J$ = 8.1 Hz, 1H), 3.91 (s, 3H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 160.3, 157.6, 150.1, 140.6, 139.7, 130.3, 129.1, 128.8, 127.2, 119.7, 117.2, 114.3, 113.1, 55.5. HRMS (ESI-TOF) calcd for $[C_{24}H_{19}NO + H]^+$ 338.1545, found 338.1545.

### 2,6-Diphenyl-4-(thiophen-3-yl)pyridine (4q)

Following the general procedure, **4q** was prepared from acetophenone (45 mg, 0.375 mmol) and 1-phenyl-3-(thiophen-3-yl) prop-2-yn-1-one (159 mg, 0.75 mmol), isolated as a light yellow solid (87 mg, 74% yield), mp 143–145 °C, $R_f$ = 0.66 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.23 (d, $J$ = 7.2 Hz, 4H), 7.89 (s, 2H), 7.77 (s, 1H), 7.58–7.47 (m, 8H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.7, 144.5, 140.4, 139.7, 129.2, 128.8, 127.2, 127.1, 126.1, 123.1, 116.3. HRMS (ESI-TOF) calcd for $[C_{21}H_{15}NS + H]^+$ 314.1003, found 314.1001.

### 4-Cyclohexyl-2,6-diphenylpyridine (4r)

Following the general procedure, **4r** was prepared from acetophenone (45 mg, 0.375 mmol) and 3-cyclohexyl-1-phenylprop-2-yn-1-one (159 mg, 0.75 mmol), isolated as a white solid (38 mg, 32% yield), mp 102–104 °C (lit.[33] 97–99 °C), $R_f$ = 0.77 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.18 (d, $J$ = 7.2 Hz, 4H), 7.57 (s, 2H), 7.54–7.51 (m, 4H), 7.46–7.43 (m, 2H), 2.70–2.63 (m, 1H), 2.02–1.99 (m, 2H), 1.95–1.92 (m, 2H), 1.85–1.82 (m, 1H), 1.62–1.42 (m, 4H), 1.39–1.29 (m, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 158.1, 157.1, 140.0, 128.9, 128.7, 127.2, 117.8, 44.5, 33.8, 26.8, 26.1. HRMS (ESI-TOF) calcd for $[C_{23}H_{23}N + H]^+$ 314.1909, found 314.1910.

### 2-(4-Chlorophenyl)-4-(3-methoxyphenyl)-6-phenylpyridine (4t)

Following the general procedure, **4t** was prepared from 4′-chloroacetophenone (58 mg, 0.375 mmol) and 3-(3-methoxyphenyl)-1-phenylprop-2-yn-1-one (177 mg, 0.75 mmol), isolated as a white solid (108 mg, 77% yield), mp 107–108 °C, $R_f$ = 0.56 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.19–8.15 (m, 4H), 7.89 (s, 1H), 7.84 (s, 1H), 7.55–7.44 (m, 6H), 7.32 (d, $J$ = 7.5 Hz, 1H), 7.27–7.26 (m, 1H, overlaped), 7.01 (d, $J$ = 8.2 Hz, 1H), 3.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 160.3, 157.6, 156.2, 150.2, 140.4, 139.4, 138.0, 135.2, 130.3, 129.2, 128.9, 128.8, 128.4, 127.2, 119.6, 117.4, 116.9, 114.3, 113.2, 55.5. HRMS (ESI-TOF) calcd for $[C_{24}H_{18}ClNO + H]^+$ 372.1155, found 372.1154.

### 2-(4-Bromophenyl)-6-(4-chlorophenyl)-4-phenylpyridine (4u)

Following the general procedure, **4u** was prepared from 4′-bromoacetophenone (75 mg, 0.375 mmol) and 1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (181 mg, 0.75 mmol), isolated as a light yellow solid (128 mg, 81% yield), mp 188–190 °C, $R_f$ = 0.77 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.13 (d, $J$ = 8.6 Hz, 2H), 8.07 (d, $J$ = 8.6 Hz, 2H), 7.86 (s, 2H), 7.73 (d, $J$ = 6.9 Hz, 2H), 7.64 (d, $J$ = 8.6 Hz, 2H), 7.56–7.48 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 156.6, 156.5, 150.8, 138.8, 138.4, 137.9, 135.5, 132.0, 129.4, 129.3, 129.1, 128.8, 128.5, 127.3, 123.8, 117.3, 117.2. HRMS (ESI-TOF) calcd for $[C_{23}H_{15}BrClN + H]^+$ 422.0134, found 422.0144.

### 6-(Furan-2-yl)-4-phenyl-2,2′-bipyridine (4v)

Following the general procedure, **4v** was prepared from 2-acetylpyridine (45 mg, 0.375 mmol) and 1-(furan-2-yl)-3-phenylprop-2-yn-1-one (147 mg, 0.75 mmol), isolated as a light yellow solid (89 mg, 80% yield), mp 145–147 °C, $R_f$ = 0.16 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.72 (d, $J$ = 4.0 Hz, 1H), 8.61–8.59 (m, 2H), 7.97–7.96 (m, 1H), 7.87–7.82 (m, 3H), 7.58 (s, 1H), 7.53–7.44 (m, 3H), 7.32 (dd, $J$ = 5.0 Hz, $J$ = 6.5 Hz, 1H), 7.26 (d, $J$ = 3.3 Hz, 1H), 6.59 (dd, $J$ = 1.7 Hz, $J$ = 3.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 156.4, 156.1, 154.2, 150.1, 149.4, 149.1, 143.3, 138.5, 136.9, 129.1, 129.0, 127.2, 123.9, 121.5, 117.3, 116.4, 112.2, 109.0. HRMS (ESI-TOF) calcd for $[C_{20}H_{14}N_2O + H]^+$ 299.1184, found 299.1186.

### 3-Methyl-2,4,6-triphenylpyridine (6a)

Following the general procedure, **6a** was prepared from propiophenone (50 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (112 mg, 93% yield), mp 135–137 °C (lit.[28] 141–143 °C), $R_f$ = 0.53 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.13 (d, $J$ = 7.6 Hz, 2H), 7.73–7.71 (m, 2H), 7.66 (s, 1H), 7.54–7.40 (m, 11H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 159.6, 154.2, 151.7, 141.6, 140.4, 139.5, 129.6, 128.9, 128.7, 128.7, 128.6, 128.2, 128.0, 128.0, 127.1, 127.0, 120.1, 18.1. HRMS (ESI-TOF) calcd for $[C_{24}H_{19}N + H]^+$ 322.1596, found 322.1594.

### 3-Ethyl-2,4,6-triphenylpyridine (6b)

Following the general procedure, **6b** was prepared from butyrophenone (56 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (78 mg, 62% yield), mp 91–93 °C (lit.[34] 99–100 °C), $R_f$ = 0.61 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.12 (d, $J$ = 7.5 Hz, 2H), 7.68 (d, $J$ = 7.5 Hz, 2H), 7.63 (s, 1H), 7.55–7.40 (m, 11H), 2.77 (q, $J$ = 7.4 Hz, 2H), 0.84 (t, $J$ = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 159.7, 153.8, 151.4, 141.8, 140.5, 139.3, 133.5, 129.1, 128.7, 128.6, 128.6, 128.6, 128.4, 128.1, 127.7, 127.0, 120.7, 22.2, 14.9. HRMS (ESI-TOF) calcd for $[C_{25}H_{21}N + H]^+$ 336.1752, found 336.1754.

### 2,4-Diphenyl-5,6,7,8-tetrahydroquinoline (6c)

Following the general procedure, **6c** was prepared from cyclohexanone (37 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (64 mg, 60% yield), mp 100–102 °C (lit.[28] 102–104 °C), $R_f$ = 0.53 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 7.99 (d, $J$ = 7.1 Hz, 2H), 7.48–7.35 (m, 9H), 3.11 (t, $J$ = 6.5 Hz, 2H), 2.67 (t, $J$ = 6.2 Hz, 2H), 1.99–1.93 (m, 2H), 1.80–1.74 (m, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 157.8, 154.4, 150.3, 139.9, 139.9, 128.7, 128.7, 128.7, 128.5, 128.4, 127.8, 127.0, 119.2, 33.5, 27.4, 23.2, 23.2. HRMS (ESI-TOF) calcd for $[C_{21}H_{19}N + H]^+$ 286.1596, found 286.1593.

**2,4-Diphenyl-5,6-dihydrobenzo[*h*]quinoline (6d)**

Following the general procedure, **6d** was prepared from 1-tetralone (55 mg, 0.375 mmol) and 1,3-diphenylprop-2-yn-1-one (155 mg, 0.75 mmol), isolated as a light yellow solid (63 mg, 50% yield), mp 124–126 °C (lit.[28] 126–128 °C), $R_f$ = 0.74 (hexane-diethyl ether, 3/1, v/v). $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 8.61 (d, $J$ = 7.7 Hz, 1H), 8.21 (d, $J$ = 8.3 Hz, 2H), 7.62 (s, 1H), 7.53–7.42 (m, 9H), 7.36 (t, $J$ = 7.4 Hz, 1H), 7.25 (d, $J$ = 8.5 Hz, 1H), 2.98–2.94 (m, 2H), 2.90–2.86 (m, 2H). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 154.6, 152.7, 149.4, 139.7, 139.5, 138.3, 135.4, 129.2, 128.9, 128.8, 128.8, 128.6, 128.1, 128.0, 127.6, 127.2, 126.9, 125.9, 120.0, 28.3, 25.4. HRMS (ESI-TOF) calcd for $[C_{25}H_{19}N + H]^+$ 334.1596, found 334.1593.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

1 (*a*) A. R. Katritzky and C. M. Marson, Pyrylium Mediated Transformations of Primary Amino Groups into Other Functional Groups. New Synthetic Methods (41), *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 420–429; (*b*) F.-S. He, S. Ye and J. Wu, Recent Advances in Pyridinium Salts as Radical Reservoirs in Organic Synthesis, *ACS Catal.*, 2019, **9**, 8943–8960; (*c*) H. Yue, C. Zhu, L. Shen, Q. Geng, K. J. Hock, T. Yuan, L. Cavallo and M. Rueping, Nickel-Catalyzed C-N Bond Activation: Activated Primary Amines as Alkylating Reagents in Reductive Cross-Coupling, *Chem. Sci.*, 2019, **10**, 4430–4435; (*d*) S. L. Rössler, B. J. Jelier, E. Magnier, G. Dagousset, E. M. Carreira and A. Togni, Pyridinium Salts as Redox–Active Functional Group Transfer Reagents, *Angew. Chem.*, 2020, **59**, 9264–9280.

2 (*a*) E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder and Y. Zimmermann, Development of Supramolecular Structure through Alkylation of Pendant Pyridyl Functionality, *J. Chem. Soc., Dalton Trans.*, 2000, 2219–2228; (*b*) G. W. V. Cave, M. J. Hardie, B. A. Roberts and C. L. Raston, Versatile Six–Component Molecular Capsule Based on Benign Synthons - Selective Confinement of a Heterogeneous Molecular Aggregate, *Eur. J. Org. Chem.*, 2001, 3227–3231; (*c*) Y.-M. Zhang, M. Han, H.-Z. Chen, Y. Zhang and Y. Liu, Reversible Molecular Switch of Acridine Red by Triarylpyridine-Modified Cyclodextrin, *Org. Lett.*, 2013, **15**, 124–127; (*d*) H. Wang, C.-H. Liu, K. Wang, M. Wang, H. Yu, S. Kandapal, R. Brzozowski, B. Xu, M. Wang, S. Lu, X.-Q. Hao, P. Eswara, M.-P. Nieh, J. Cai and X. Li, Assembling Pentatopic Terpyridine Ligands with Three Types of Coordination Moieties into a Giant Supramolecular Hexagonal Prism: Synthesis, Self-Assembly, Characterization, and Antimicrobial Study, *J. Am. Chem. Soc.*, 2019, **141**, 16108–16116.

3 (*a*) I. Sasaki, Recent Uses of Kröhnke Methodology: a Short Survey, *Synthesis*, 2016, **48**, 1974–1992; (*b*) L. F. B. Fontes, R. N. da Silva, A. M. S. Silva and S. Guieu, Unsymmetrical 2,4,6−Triarylpyridines as Versatile Scaffolds for Deep–Blue and Dual–Emission Fluorophores, *ChemPhotoChem*, 2020, **4**, 5312–5317.

4 L. Duan, Y. Chen, J. Jia, X. Zong, Z. Sun, Q. Wu and S. Xue, Dopant-Free Hole-Transport Materials Based on 2,4,6-Triarylpyridine for Inverted Planar Perovskite Solar Cells, *ACS Appl. Energy Mater.*, 2020, **3**, 1672–1683.

5 (*a*) B. Tang, F. Yu, P. Li, L. Tong, X. Duan, T. Xie and X. Wang, A Near-Infrared Neutral pH Fluorescent Probe for Monitoring Minor pH Changes: Imaging in Living HepG2 and HL-7702 Cells, *J. Am. Chem. Soc.*, 2009, **131**, 3016–3023; (*b*) H. Muraoka, T. Obara and S. Ogawa, Synthesis and Optical Properties, Including Fluorosolvatochromic and ICT-Based Protonsensing Behaviors of a Series of 2,4,6-Tris (5-aryl-2-thienyl)pyridines, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 2019, **194**, 726–730.

6 (*a*) Y. Zhang, X. Yang and H.-C. Zhou, Direct Synthesis of Functionalized PCN-333 via Linker Design for $Fe^{3+}$ Detection in Aqueous Media, *Dalton Trans.*, 2018, **47**, 11806–11811; (*b*) H. Chen, L. Fan, H. Lv and X. Zhang, Robust Anionic $Ln^{III}$-Organic Frameworks: Chemical Fixation of $CO_2$, Tunable Light Emission, and Fluorescence Recognition of $Fe^{3+}$, *Inorg. Chem.*, 2020, **59**, 13407–13415.

7 (*a*) Z. H. Fard, Y. Kalinovskyy, D. M. Spasyuk, B. A. Blight and G. K. H. Shimizu, Alkaline-Earth Phosphonate MOFs with Reversible Hydration-Dependent Fluorescence, *Chem. Commun.*, 2016, **52**, 12865–12868; (*b*) S.-L. Hou, J. Dong, X.-L. Jiang, Z.-H. Jiao, C.-M. Wang and B. Zhao, Interpenetration-Dependent Luminescent Probe in Indium-Organic Frameworks for Selectively Detecting Nitrofurazone in Water, *Anal. Chem.*, 2018, **90**, 1516–1519; (*c*) J. H. Carter, X. Han, F. Y. Moreau, I. da Silva, A. Nevin, H. G. W. Godfrey, C. C. Tang, S. Yang and M. Schröder, Exceptional Adsorption and Binding of Sulfur Dioxide in a Robust Zirconium-Based Metal-Organic Framework, *J. Am. Chem. Soc.*, 2018, **140**, 15564–15567; (*d*) D. Wang, Z. Hu, S. Xu, D. Li, Q. Zhang, W. Ma, H. Zhou, J. Wu and Y. Tian, Fluorescent Metal-Organic Frameworks Based on Mixed Organic Ligands: New Candidates for Highly Sensitive Detection of TNP, *Dalton Trans.*, 2019, **48**, 1900–1905; (*e*) Z.-H. Jiao, X.-L. Jiang, S.-L. Hou, M.-H. Tang and B. Zhao, Highly Sensitive and Selective Luminescence Sensor Based on Two-fold Interpenetrated MOFs for

 

Detecting Glutamate in Serum, *Inorg. Chem.*, 2020, **59**, 2171–2177; (*f*) B. Wang, R. He, L.-H. Xie, Z.-J. Lin, X. Zhang, J. Wang, H. Huang, Z. Zhang, K. S. Schanze, J. Zhang, S. Xiang and B. Chen, Microporous Hydrogen-Bonded Organic Framework for Highly Efficient Turn-Up Fluorescent Sensing of Aniline, *J. Am. Chem. Soc.*, 2020, **142**, 12478–12485; (*g*) C.-Y. Zhu, Z. Wang, J.-T. Mo, Y.-N. Fan and M. Pan, A Long Persistent Phosphorescent Metal-Organic Framework for Multi-Level Sensing of Oxygen, *J. Mater. Chem. C*, 2020, **8**, 9916–9922.

8 (*a*) L. Liu, Z. Yao, Y. Ye, L. Chen, Q. Lin, Y. Yang, Z. Zhang and S. Xiang, Robustness, Selective Gas Separation, and Nitrobenzene Sensing on Two Isomers of Cadmium Metal-Organic Frameworks Containing Various Metal-O-Metal Chains, *Inorg. Chem.*, 2018, **57**, 12961–12968; (*b*) H. Chen, G.-L. Zhuang, L. Fan, X. Zhang, L.-N. Gao and D. Sun, A Highly Robust Heterometallic $Tb^{III}/Ni^{II}$-Organic Framework for $C_2$ Hydrocarbon Separation and Capture, *Chem. Commun.*, 2020, **56**, 2047–2050; (*c*) P. Guo, Q. Chu, N. Gong, X. Yan and B. Liu, High $C_2$ Hydrocarbons Capture and Selective $C_2/C_1$ Separation in A Tb(III)-Organic Framework, *J. Solid State Chem.*, 2020, **287**, 121345.

9 (*a*) R. Karki, P. Thapa, H. Y. Yoo, T. M. Kadayat, P.-H. Park, Y. Na, E. Lee, K.-H. Jeon, W.-J. Cho, H. Choi, Y. Kwon and E.-S. Lee, Dihydroxylated 2,4,6-Triphenyl Pyridines: Synthesis, Topoisomerase I and II Inhibitory Activity, Cytotoxicity, and Structure-Activity Relationship Study, *Eur. J. Med. Chem.*, 2012, **49**, 219–228; (*b*) P. Thapa, R. Karki, M. Yun, T. M. Kadayat, E. Lee, H. B. Kwon, Y. Na, W.-J. Cho, N. D. Kim, B.-S. Jeong, Y. Kwon and E.-S. Lee, Synthesis, and Antitumor Evaluation of 2,4,6-Triaryl Pyridines Containing Chlorophenyl and Phenolic Moiety, *Eur. J. Med. Chem.*, 2012, **52**, 123–136; (*c*) R. Karki, C. Park, K.-Y. Jun, J.-G. Jee, J.-H. Lee, P. Thapa, T. M. Kadayat, Y. Kwon and E.-S. Lee, Synthesis, Antitumor Activity, and Structure-Activity Relationship Study of Trihydroxylated 2,4,6-Triphenyl Pyridines as Potent and Selective Topoisomerase II Inhibitors, *Eur. J. Med. Chem.*, 2014, **84**, 555–565; (*d*) A. Shrestha, S. Park, S. Shin, T. M. Kadayat, G. Bist, P. Katila, Y. Kwon and E.-S. Lee, Design, Synthesis, Biological Evaluation, Structure-Activity Relationship Study, and Mode of Action of 2-Phenol-4,6-Dichlorophenyl-Pyridines, *Bioorg. Chem.*, 2018, **79**, 1–18; (*e*) B. A. Baloutaki, M. H. Sayahi, M. Nikpassand and H. Kefayati, An Efficient Method for the Synthesis of New Derivatives of 2,4,6-Triarylpyridines as Cytotoxic Agents, *Res. Chem. Intermed.*, 2020, **46**, 1153–1163.

10 (*a*) Z. A. E. Waller, P. S. Shirude, R. Rodriguez and S. Balasubramanian, Triarylpyridines: a Versatile Small Molecule Scaffold for G-Quadruplex Recognition, *Chem. Commun.*, 2008, 1467–1469; (*b*) N. M. Smith, G. Labrunie, B. Corry, P. L. T. Tran, M. Norret, M. Djavaheri-Mergny, C. L. Raston and J.-L. Mergny, Unraveling the Relationship Between Structure and Stabilization of Triarylpyridines as G-Quadruplex Binding Ligands, *Org. Biomol. Chem.*, 2011, **9**, 6154–6162; (*c*) J. Beauvarlet, R. Nath Das, K. Alvarez-Valadez, I. Martins, A. Muller, E. Darbo, E. Richard, P. Soubeyran, G. Kroemer, J. Guillon, J.-L. Mergny and M. Djavaheri-Mergny, Triarylpyridine Compounds and Chloroquine Act in Concert to Trigger Lysosomal Membrane Permeabilization and Cell Death in Cancer Cells, *Cancers*, 2020, **12**, 1621.

11 (*a*) A. R. Katritzky, A. A. A. Abdel-Fattah, D. O. Tymoshenko and S. A. Essawy, A Novel and Efficient 2,4,6-Trisubstituted Pyridine Ring Synthesis via α-Benzotriazolyl Ketones, *Synthesis*, 1999, 2114–2118; (*b*) B. Heller and M. Hapke, The Fascinating Construction of Pyridine Ring Systems by Transition Metal-Catalysed [2 + 2 + 2] Cycloaddition Reactions, *Chem. Soc. Rev.*, 2007, **36**, 1085–1094; (*c*) C. Allais, J.-M. Grassot, J. Rodriguez and T. Constantieux, Metal-Free Multicomponent Syntheses of Pyridines, *Chem. Rev.*, 2014, **114**, 10829–10868; (*d*) E. Vessally, A. Hosseinian, L. Edjlali, A. Bekhradnia and M. D. Esrafili, New Page to Access Pyridine Derivatives: Synthesis from N-Propargylamines, *RSC Adv.*, 2016, **6**, 71662–71675; (*e*) J. S. S. Neto and G. Zeni, Ten Years of Progress in the Synthesis of Six-Membered N-Heterocycles from Alkynes and Nitrogen Sources, *Tetrahedron*, 2020, **76**, 130876.

12 Z. Wang, Kröhnke Pyridine Synthesis, in *Comprehensive Organic Name Reactions and Reagents*, John Wiley & Sons, 2010, pp. 1695–1698.

13 J. Shen, D. Cai, C. Kuai, Y. Liu, M. Wei, G. Cheng and X. Cui, Base-Promoted β-C($sp^3$)-H Functionalization of Enaminones: An Approach to Polysubstituted Pyridines, *J. Org. Chem.*, 2015, **80**, 6584–6589.

14 R. Khajuria, P. Kannaboina, K. K. Kapoor, A. Gupta, G. Raina, A. K. Jassal, L. K. Rana, M. S. Hundal and P. Das, Divergent Synthesis of 4,6-Diarylated Pyridin-2(1H)-ones from Chalcones: Novel Access to 2,4,6-Triarylpyridines, *Org. Biomol. Chem.*, 2015, **13**, 5944–5954.

15 H. Zhang, J. Shen, G. Cheng, B. Wu and X. Cui, Base–Promoted Synthesis of 2,4,6–Triarylpyridines from Enaminones and Chalcones, *Asian J. Org. Chem.*, 2018, **7**, 1089–1092.

16 S. Guin, S. K. Gudimella and S. Samanta, 1,6-Addition of Vinyl p-Quinone Methides with Cyclic Sulfamidate Imines: Access to 4-Hydroxyaryl-2,6-Diarylpyridines, *Org. Biomol. Chem.*, 2020, **18**, 1337–1342.

17 (*a*) P. A. Clarke, S. Santos and W. H. C. Martin, Combining Pot, Atom and Step Economy (PASE) in Organic Synthesis. Synthesis of Tetrahydropyran-4-ones, *Green Chem.*, 2007, **9**, 438–440; (*b*) W. Zhang and W. B. Yi, in *Pot, Atom, and Step Economy (PASE) Synthesis*, Springer, Cham, 2019.

18 (*a*) K. I. Galkin and V. P. Ananikov, Alkynes as a Versatile Platform for Construction of Chemical Molecular Complexity and Realization of Molecular 3D Printing, *Russ. Chem. Rev.*, 2016, **85**, 226; (*b*) I. V. Alabugin and E. Gonzalez-Rodriguez, Alkyne Origami: Folding Oligoalkynes into Polyaromatics, *Acc. Chem. Res.*, 2018, **51**, 1206; (*c*) S. B. Alyabyev and I. P. Beletskaya, Gold as a Catalyst. Part II. Alkynes in the Reactions of Carbon-

Carbon Bond Formation, *Russ. Chem. Rev.*, 2018, **87**, 984; (*d*) B. A. Trofimov and E. Yu, Schmidt, Acetylenes in the Superbase-Promoted Assembly of Carbocycles and Heterocycles, *Acc. Chem. Res.*, 2018, **51**, 1117; (*e*) I. V. Alabugin, E. Gonzalez-Rodriguez, R. K. Kawade, A. A. Stepanov and S. F. Vasilevsky, Alkynes as Synthetic Equivalents of Ketones and Aldehydes: a Hidden Entry into Carbonyl Chemistry, *Molecules*, 2019, **24**, 1036.

19 (*a*) B. A. Trofimov, E. Y. Schmidt, I. A. Ushakov, N. V. Zorina, E. V. Skital'tseva, N. I. Protsuk and A. I. Mikhaleva, Base–Catalyzed Stereoselective Vinylation of Ketones with Arylacetylenes: A New C(sp3)-C(sp2) Bond–Forming Reaction, *Chem. – Eur. J.*, 2010, **16**, 8516; (*b*) B. A. Trofimov, E. Y. Schmidt, N. V. Zorina, E. V. Ivanova and I. A. Ushakov, Transition-Metal-Free Superbase-Promoted Stereoselective α-Vinylation of Ketones with Arylacetylenes: a General Strategy for Synthesis of β,γ-Unsaturated Ketones, *J. Org. Chem.*, 2012, **77**, 6880.

20 (*a*) M. C. Bagley, C. Brace, J. W. Dale, M. Ohnesorge, N. G. Phillips, X. Xiong and J. Bower, Synthesis of Tetrasubstituted Pyridines by the Acid-Catalysed Bohlmann-Rahtz Reaction, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1663–1671; (*b*) X. Xiong, M. C. Bagley and K. Chapaneri, A New Mild Method for the One-Pot Synthesis of Pyridines, *Tetrahedron Lett.*, 2004, **45**, 6121–6124; (*c*) M. C. Bagley, K. Chapaneri, J. W. Dale, X. Xiong and J. Bower, One-Pot Multistep Bohlmann-Rahtz Heteroannulation Reactions: Synthesis of Dimethyl Sulfomycinamate, *J. Org. Chem.*, 2005, **70**, 1389–1399.

21 (*a*) E. Tabrizian, A. Amoozadeh, S. Rahmani, E. Imanifar, S. Azhari and M. Malmir, One-Pot, Solvent-Free and Efficient Synthesis of 2,4,6-Triarylpyridines Catalyzed by Nano-Titania-Supported Sulfonic Acid as a Novel Heterogeneous Nanocatalyst, *Chin. Chem. Lett.*, 2015, **26**, 1278–1282; (*b*) M. A. Zolfigol, M. Safaiee, F. Afsharnadery, N. Bahrami-Nejad, S. Baghery, S. Salehzadeh and F. Maleki, Silica Vanadic Acid $[SiO_2\text{-}VO(OH)_2]$ as an Efficient Heterogeneous Catalyst for the Synthesis of 1,2-Dihydro-1-Aryl-3H-Naphth[1,2-e][1,3]oxazin-3-one and 2,4,6-Triarylpyridine Derivatives via Anomeric Based Oxidation, *RSC Adv.*, 2015, **5**, 100546–100559; (*c*) M. B. Boroujeni, A. Hashemzadeh, M.-T. Faroughi, A. Shaabani and M. M. Amini, Magnetic MIL-101-SO3H: a Highly Efficient Bifunctional Nanocatalyst for the Synthesis of 1,3,5-Triarylbenzenes and 2,4,6-Triarylpyridines, *RSC Adv.*, 2016, **6**, 100195–100202; (*d*) M. Safaiee, B. Ebrahimghasri, M. Ali Zolfigol, S. Baghery, A. Khoshnood and D. A. Alonso, Synthesis and Application of Chitosan Supported Vanadium Oxo in the Synthesis of 1,4-Dihydropyridines and 2,4,6-Triarylpyridines via Anomeric Based Oxidation, *New J. Chem.*, 2018, **42**, 12539–12548; (*e*) H. Wang, W. Zhao, J. Du, F. Wei, Q. Chen and X. Wang, Cationic Organotin Cluster $[t\text{–}Bu_2Sn(OH)(H_2O)]_2^{2+}2OTf^-$–Catalyzed One–Pot Three–Component Syntheses of 5–Substituted 1H–Tetrazoles and 2,4,6–Triarylpyridines in Water, *Appl. Organomet. Chem.*, 2019, **33**, e5132; (*f*) J. Chen, H. Meng, F. Zhang, F. Xiao and G.-J. Deng, Transition-Metal-Free Selective Pyrimidines and Pyridines Formation from Aromatic Ketones, Aldehydes and Ammonium Salts, *Green Chem.*, 2019, **21**, 5201–5206.

22 (*a*) Y. Li, J. Yu, Y. Bi, G. Yan and D. Huang, Tandem Reactions of Ynones: via Conjugate Addition of Nitrogen–, Carbon–, Oxygen–, Boron–, Silicon–, Phosphorus–, and Sulfur–Containing Nucleophiles, *Adv. Synth. Catal.*, 2019, **361**, 4839–4881; (*b*) C. Nájera, L. K. Sydnes and M. Yus, Conjugated Ynones in Organic Synthesis, *Chem. Rev.*, 2019, **119**, 11110–11244.

23 (*a*) L. G. Fedenok and M. S. Shvartsberg, A Method for the Preparation of Terminal Acetylenes, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2376–2377; (*b*) M. P. Davydova, S. F. Vasilevsky and V. G. Nenajdenko, Reaction of Trifluoroacetyl Acetylenes with β-Amino Alcohols. Synthesis of Enaminoketones and Unusual Fragmentation, *J. Fluor. Chem.*, 2016, **190**, 61–67; (*c*) S. F. Vasilevsky, M. P. Davydova, V. I. Mamatyuk, N. Tsvetkov, A. Hughes, D. S. Baranov and I. V. Alabugin, Full Cleavage of C≡C Bond in Electron-Deficient Alkynes via Reaction with Ethylenediamine, *Aust. J. Chem.*, 2017, **70**, 421–429; (*d*) K. V. Belyaeva, L. P. Nikitina, A. V. Afonin, A. V. Vashchenko and B. A. Trofimov, Synthesis of N-(Z)-Acylethenyl-6-Hydroxydihydrophenanthridines via the Stereoselective Functionalization of Phenanthridine with Acylacetylenes and Water, *Tetrahedron Lett.*, 2020, **61**, 151553.

24 (*a*) B. A. Trofimov, Chalcogenation in Multiphase Superbase Systems, *Sulfur Rep.*, 1992, **11**, 207–227; (*b*) P. Caubère, Unimetal Super Bases, *Chem. Rev.*, 1993, **93**, 2317–2334; (*c*) N. M. Vitkovskaya, V. B. Orel, V. B. Kobychev, A. S. Bobkov, D. Z. Absalyamov and B. A. Trofimov, Quantum–Chemical Models of $KOH(KOBu^t)$/DMSO Superbasic Systems and Mechanisms of Base–Promoted Acetylene Reactions, *Int. J. Quantum Chem.*, 2020, **120**, e26158.

25 (*a*) H. Stetter and A. Reischl, Notiz über eine neue Methode zur Herstellung von 2.6—Diphenyl–pyrylium–perchlorat, *Chem. Ber.*, 1960, **93**, 1253–1256; (*b*) A. A. Golovanov, D. R. Latypova, V. V. Bekin, V. S. Pisareva, A. V. Vologzhanina and V. A. Dokichev, Synthesis of 1,5-Disubstituted (E)-Pent-2-en-4-yn-1-ones, *Russ. J. Org. Chem.*, 2013, **49**, 1264–1269; (*c*) J. Wang, C. Shen, T. Wang, S. Mo, X. Li and Z. Zhang, Synthesis of 3-Formylfurans via a Silver(I)-Catalyzed Epoxide Ring-Opening/1,2-Acyl Migration/Cyclization Cascade, *Adv. Synth. Catal.*, 2016, **358**, 3943–3948.

26 R. J. Cox, D. J. Ritson, T. A. Dane, J. Berge, J. P. H. Charmant and A. Kantacha, Room Temperature Palladium Catalysed Coupling of Acyl Chlorides with Terminal Alkynes, *Chem. Commun.*, 2005, 1037–1039.

27 M. Borthakur, M. Dutta, S. Gogoi and R. C. Boruah, Microwave Promoted and Lewis Acid Catalysed Synthesis of 2,4,6-Triarylpyridines Using Urea as Benign Source of Ammonia, *Synlett*, 2008, 3125–3128.

28 W. W. Tan, Y. J. Ong and N. Yoshikai, Synthesis of Highly Substituted Pyridines through Copper–Catalyzed

 

Condensation of Oximes and α,β–Unsaturated Imines, *Angew. Chem., Int. Ed.*, 2017, **56**, 8240–8244.

29 A. Kurfuerst, P. Lhotak, M. Petru and J. Kuthan, Oligophenylene 2,4,6-Triarylpyridines and Analogous Diaza-p-Terphenyls, Diaza-p-Quaterphenyls and Diaza-p-Quinquephenyls with Luminiscent Activity, *Collect. Czech. Chem. Commun.*, 1989, **54**, 462–472.

30 A. R. Katritzky, E. M. Elisseou, R. C. Patel and B. Plau, Preparation and Reactions of Pyrylium Salts Containing α-Pyridyl Groups, *J. Chem. Soc., Perkin Trans. 1*, 1982, 125–130.

31 F. Kröhnke, The Specific Synthesis of Pyridines and Oligopyridines, *Synthesis*, 1976, 1–24.

32 Q. Yang, Y. Zhang, W. Zeng, Z.-C. Duan, X. Sang and D. Wang, Merrifield Resin-Supported Quinone as An Efficient Biomimetic Catalyst for Metal-Free, Base-Free, Chemoselective Synthesis of 2,4,6-Trisubstituted Pyridines, *Green Chem.*, 2019, **21**, 5683–5690.

33 Z.-Y. Mao, X.-Y. Liao, H.-S. Wang, C.-G. Wang, K.-B. Huang and Y.-M. Pan, Acid-Catalyzed Tandem Reaction for the Synthesis of Pyridine Derivatives via C=C/C(sp3)-N Bond Cleavage of Enones and Primary Amines, *RSC Adv.*, 2017, **7**, 13123–13129.

34 N. S. Prostakov, A. V. Varlamov and G. A. Vasil'ev, Synthesis of Pyridine Bases from Piperidine Derivatives, *Chem. Heterocycl. Compd.*, 1977, **13**, 639–642.