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Palladium-catalyzed one-pot synthesis of benzo[*b*][1,6] naphthyridines via Sonogashira coupling and annulation reactions from 2-chloroquinoline-3-carbonitriles

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ABSTRACT

Palladium-catalyzed one-pot synthesis of 1,3-disubstituted benzo[*b*][1,6]naphthyridines and [1,6]naphthyridines has been described from easily accessible precursors, 2-chloroquinoline-3-carbonitriles and 2-chloropyrido-3-carbonitrile via sequential additions of palladium-catalyst for Sonogashira-coupling and the following annulations in good to excellent yields. A plausible mechanism for annulation is discussed.

1. Introduction

[1,6]Naphthyridine and their benzo-fused analogues are present in numerous products of marine alkaloids (Fig. 1)[1] and display wide range of physiological activities, such as anti-tumour and anti-inflammatory activities,[2] HIV-1 integrase inhibitors containing metal binding motif,[3] AKt1 and AKt2 inhibitors,[4] cytotoxic activity.[5] Consequently, various synthetic routes have been developed for the synthesis of [1,6]naphthyridines and their benzo analogues.[1,3a,6] Kozlowski and Larock et al. have reported [1,6]naphthyridines from 4-aminopyridine and allyl alcohol using palladium methodology.[7] Rudys et al. have reported three component reactions to benzo[*b*][1,6]naphthyridines.[8] Sakamoto et al. have reported the synthesis of [1,6]naphthyridines from *o*-alkynylpyridinecarboxaldehydes with ammonia.[9] We have also reported benzo[*b*][1,6]naphthyridines from the corresponding quinoline-3-carboxaldehyde analogues using similar reaction.[10]

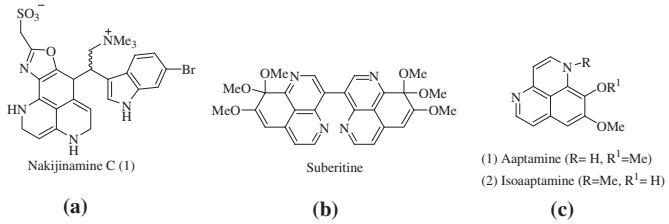

Fig. 1. Significant examples of marine alkaloids containing [1,6]naphthyridine skeletons.

In recent years, inter- and intramolecular palladium-catalyzed annulation reactions of internal and terminal alkynes with aryl or heteroaryl halides possessing nucleophilic functional group next to halide have emerged as a versatile and efficient route to the synthesis of various heterocycles and fused-heterocycles.[11] The palladium-catalyzed annulations of *N*-*tert*-butyl *o*-iodobenzaldimine and *N*-*tert*-butyl *o*-iodoindolealdimine with internal and terminal alkynes have been reported to isoquinolines and pyrido-fused indoles, respectively.[12] However, similar Pd-catalyzed annulations with *o*-halo aryl/heteroaryl carbonitriles have been less studied. Larock et al. have reported Pd-catalyzed annulation of 2-iodobenzonitrile with internal alkynes to 2,3-diarylindenones (Scheme 1A).[13] Wei et al. have reported Pd-catalyzed intramolecular annulation of *o*-phenylethynyl benzonitriles with aryl iodide to isoindoles in low yields (Scheme 1B).[14] However, Pd-catalyzed intramolecular annulations of corresponding hetero analogues have not been studied. Recently, we have reported Pd-catalyzed intramolecular cyclization/annulation of

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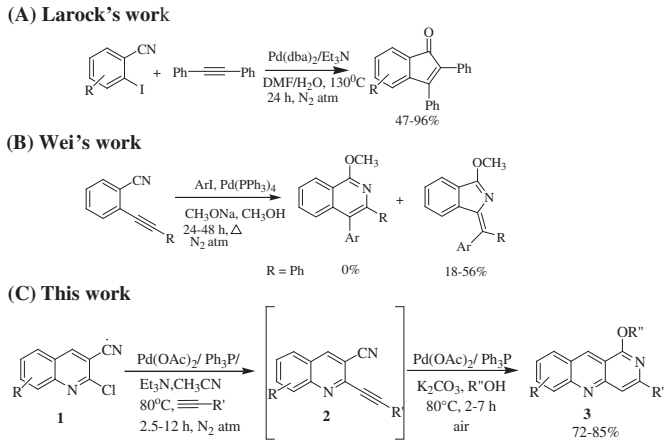
alkene and alkyne to the synthesis of cyclopenta- and pyrano-fused quinolines, respectively.[15] Since Sonogashira coupling reaction proceeded with the aid of Pd-catalyst, we envisioned that two-step Pd-catalyzed Sonogashira coupling and annulation process could proceed in one-pot from 2-chloroquinoline-3-carbonitriles and pyridine analogues to afford benzo[*b*][1,6]naphthyridines and [1,6]naphthyridines. Thus, we herein report Pd-catalyzed one-pot synthesis of benzo[*b*][1,6]naphthyridines and [1,6]naphthyridines from 2-chloroquinoline-3-carbonitriles and their pyridine-analogues with terminal alkynes by sequential addition of palladium-catalyst in the Sonogashira-coupling and annulation reaction, respectively.



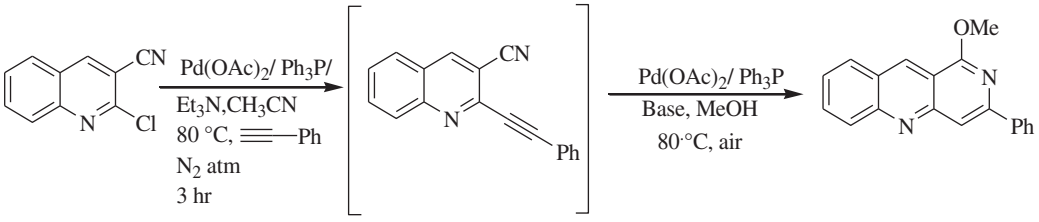
Scheme 1. Reactions on carbonitriles.

2. Results and discussion

Initially, we examined the reaction of 2-chloroquinoline-3-carbonitriles **1** with terminal alkynes using our earlier reported palladium-catalyzed annulation conditions[15b] with a view to synthesize benzo[*b*][1,6]naphthyridines **3** (Scheme 1). The reaction of **1a** (0.25 mmol) with phenylacetylene (0.26 mmol) using 10 mol % of $Pd(OAc)_2$, 20 mol % of PPh_3 and 2 equiv Et_3N in acetonitrile at 80 °C under N_2 for Sonogashira coupling and subsequent annulation by addition of methanol as nucleophile and solvent at same temperature in aerobic atmosphere for overnight, failed to provide the cyclized product **3a** (Table 1, entry 1). However, adding 1.5 equiv of K_2CO_3 along with methanol in annulation step under similar conditions afforded the cyclized product **3a** in 75% yield. This result could be explained by considering that methoxide ion acts as nucleophile in annulation process (entry 2). Encouraged by this observation, we further examined the sequential reaction using 5 mol % of $Pd(OAc)_2$, 10 mol % of PPh_3 and 2 equiv of Et_3N in acetonitrile at 80 °C under N_2 atm for Sonogashira coupling and 5 mol % of $Pd(OAc)_2$, 10 mol % of PPh_3 and 1.5 equiv K_2CO_3 in methanol at same temperature in aerobic conditions for annulation step. The reaction proceeded smoothly and provided the cyclized product **3a** in 80% yield (entry 3). Thus, considering sequential additions of palladium-catalyst as our reaction conditions, we next examined other parameters, such as other available palladium-catalysts and bases to find an optimal reaction conditions for annulation step (entries 4–10). The available palladium catalysts $PdCl_2$ and $Pd(dba)_2$ were found less effective (entries 4 and 5). Using $PdCl_2$ in Sonogashira coupling and $Pd(OAc)_2$ or $PdCl_2$ for annulations, adversely affected the yield as well as the rate of reaction (entries 6 and 7). Among the inorganic bases, K_3PO_4 and Cs_2CO_3 were tested. K_3PO_4 afforded the product **3a** in same yield (entry 8) whereas Cs_2CO_3 was found ineffective (entry 9). Further on increasing the amount of K_2CO_3 to 2 equiv did not improve the yield of **3a** (entry 10). The annulation reaction using Sonogashira coupling product **2a** did not show significant variation in the yield of **3a** (entry 11).

Based on the sequential additions using 5 mol % of $Pd(OAc)_2$, 10 mol % of PPh_3 and 2 equiv of Et_3N in acetonitrile at 80 °C under N_2 atm for Sonogashira coupling followed by further addition of 5 mol % of $Pd(OAc)_2$, 10 mol % of PPh_3 and 1.5 equiv K_2CO_3 in methanol under aerobic conditions for 0.25 mmol of **1a** with

Table 1
Optimization table for one-pot sequential Sonogashira coupling and intramolecular cyclization of 2-chloroquinoline-3-carbonitrile



Entry	Sonogashira coupling[a]			Annulation reaction			Time (h)[b]	Yield[c] (%) (**4a**)
	Catalyst (mol %)	Ligand (mol %)	Base (equiv)	Catalyst (mol %)	Ligand (mol %)	Base (equiv)		
1	$Pd(OAc)_2$ (10)	Ph_3P (20)	Et_3N (2)	—	—	—	Overnight	Nr[d]
2	$Pd(OAc)_2$ (10)	Ph_3P (20)	Et_3N (2)	—	—	K_2CO_3 (1.5)	3.5	75
3	**$Pd(OAc)_2$ (5)**	**Ph_3P (10)**	**Et_3N (2)**	**$Pd(OAc)_2$ (5)**	**Ph_3P (10)**	**K_2CO_3 (1.5)**	**3**	**80**
4	$Pd(OAc)_2$ (10)	Ph_3P (20)	Et_3N (2)	$PdCl_2$ (5)	Ph_3P (10)	K_2CO_3 (1.5)	5	65
5	$Pd(OAc)_2$ (5)	Ph_3P (10)	Et_3N (2)	$Pd(dba)_2$ (5)	Ph_3P (10)	K_2CO_3 (1.5)	7	45
6	$PdCl_2$ (5)	Ph_3P (10)	Et_3N (2)	$Pd(OAc)_2$ (5)	Ph_3P (10)	K_2CO_3 (1.5)	3.5	80
7	$PdCl_2$ (5)	Ph_3P (10)	Et_3N (2)	$PdCl_2$ (5)	Ph_3P (10)	K_2CO_3 (1.5)	6	60
8	$Pd(OAc)_2$ (5)	Ph_3P (10)	Et_3N (2)	$Pd(OAc)_2$ (5)	Ph_3P (10)	K_3PO_4 (1.5)	3	80
9	$Pd(OAc)_2$ (5)	Ph_3P (10)	Et_3N (2)	$Pd(OAc)_2$ (5)	Ph_3P (10)	Cs_2CO_3 (1.5)	21	Trace
10	$Pd(OAc)_2$ (5)	Ph_3P (10)	Et_3N (2)	$Pd(OAc)_2$ (5)	Ph_3P (10)	K_2CO_3 (2)	3	79
11	—	—	—	$Pd(OAc)_2$ (5)	Ph_3P (10)	K_2CO_3 (1.5)	3.5	82

The bold value signifies the optimized condition in the reaction.
[a] Time for Sonogashira coupling is 3 h.
[b] Annulation time.
[c] Isolated yields.
[d] Nr=no reaction.

0.26 mmol of phenylacetylene gave the best yield of the annulated product **3a** and this is used as our optimized reaction conditions (entry 3).

To explore the generality and scope of this coupling-annulation processes, the reactions of **1a** with phenylacetylenes bearing different substituents on phenyl ring were examined under optimized reaction conditions. The reactions proceeded smoothly and afforded the annulated products **3**(**ab**–**ae**) in good yields. Results are summarized in Table 2 (entries 1–5). No significant variations in the yields were found with phenylacetylene ring bearing electron donating (entries 2–4) or electron withdrawing group (entry 5). However, rate was higher with phenylacetylene bearing electron withdrawing group (as monitored by TLC at regular intervals of 30 min). Further annulation with acetylene bearing alkyl group afforded the lower yield in less time (entry 6). To further explore the scope of annulations, the reaction of compound **4** with phenylacetylene and phenylacetylene bearing electron donating and withdrawing groups were examined under optimized conditions and afforded [1,6] naphthyridines **5**(**a**–**c**) in good yields (Table 2, entries 7–9). The effects of electron donating and electron withdrawing groups on the rate and yields were similar to quinoline analogues (entries 8 and 9).

To further explore the generality and scope of the annulation reactions, we examined the reaction of various substituted 2-chloroquinoline-3-carbonitriles **1**(**b**–**h**) with phenylacetylene. The reactions proceeded smoothly and afforded the annulated products, 1-methoxy-3-phenylbenzo[*b*][1,6]naphthyridines **3**(**b**–**h**) in good yields (Table 2, entries 10–16). An electron-donating groups on phenyl ring in quinolines are less reactive than electron withdrawing groups, however no significant variations are found in the yields of the annulated products (entries 10–16).

To further explore the generality and scope of this annulation, various alcohols as nucleophiles and solvents were tested with substrate **1a** using optimized conditions. Primary alcohols, such as EtOH and *n*-BuOH, reacted well and provided good yields of desired benzo[*b*][1,6]naphthyridines (entries 17 and 18). It is noteworthy that annulation of **2a** failed with *i*-PrOH and *t*-BuOH, which could be attributed to steric hindrance or dehydration of alcohols (entries 19 and 20). Further, phenol was also tested for annulation, the rate of reaction was slower and afforded cyclized product **3ai** in 72% (entry 21) and could be attributed to weak nucleophilicity of phenoxide ion.

A single X-ray crystallographic analysis of **3ac** was performed to establish the structure of annulated products.[16] An ORTEP representation of the molecule **3ac** is given in Fig. 2.

A plausible mechanism for Pd-catalyzed cyclization is illustrated in Scheme 2. In this reaction $Pd(OAc)_2$ plays dual role:[11d] (1) as a Lewis acid, which forms complex **A** with the nitrogen atom of the cyano group, facilitating the nucleophilic attack of methoxide ion on carbon atom of cyano group and (2) as a transition metal catalyst, which forms complex **B** with π-electrons of alkyne. Complex **B** undergoes cyclization to give organopalladium intermediate **C**, which on protonation with AcOH gives cyclized product **3a**.

3. Conclusions

In conclusion, we have developed a novel Pd-catalyzed one-pot synthesis of benzo[*b*][1,6]naphthyridines and [1,6]naphthyridines via C–C, C–N and C–O bonds formation from 2-chloroquinoline-3-carbonitriles and 2-chloro-5-phenylpyrido-3-carbonitrile, respectively. Further, the annulations are facile with the acetylene bearing either alkyl group or phenyl ring with electron withdrawing group. The reaction conditions avoided purification of intermediates, which saves time and solvents.

4. Experimental section

4.1. General

Unless otherwise stated, all reactions were performed under nitrogen and air successively. Solvents were purified following standard literature procedures. Melting points were measured in an open capillary tube and are uncorrected. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded 300 MHz spectrometer. Multiplicities are given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The chemical shifts (δ parts per million) and coupling constants (J Hertz) are reported in the standard fashion with reference to either internal tetramethylsilane (for ^1H) or the central line (77.0 ppm) of $CDCl_3$ (for ^{13}C). Moisture and residual peak of $CDCl_3$ appear at δ 1.5 and 7.2, respectively, in ^1H NMR. High resolution mass spectra (HRMS) were obtained on micro TOF QII high-resolution mass spectrometer (ESI) and 6200 series TOF/6500 SRIES QTOF B.05.00 (B5042.0). 2-chloroquinoline-3-carbonitrile **1**(**a**–**g**) was synthesized by our previously reported method.[17] Single-crystal X-ray data was collected for compound **3ac**.

4.2. General procedure for synthesis of benzo[*b*][1,6] naphthyridines

A mixture of substituted 2-chloroquinoline-3-carbonitriles **1**(**a**–**h**) (0.25 mmol), phenylacetylene (0.26 mmol), $Pd(OAc)_2$ (5 mol %) and PPh_3 (10 mol %) in CH_3CN (2 mL) and TEA (2 equiv) were stirred under N_2 at 80 °C, after completion of reaction (as monitored by TLC), solvent was evaporated and further $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), K_2CO_3 (1.5 equiv) and 4 mL of methanol were added under aerobic condition at 80 °C upto completion. The mixture was concentrated in vacuo and residue was purified by column chromatography on silica gel using EtOAc/hexane as eluent.

*4.2.1. 1-Methoxy-3-phenyl-benzo[b][1,6]naphthyridine (**3a**).* Light green solid; yield: 57.2 mg (80%); mp 106–107 °C; R_f=0.35 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ=4.33 (s, 3H), 7.43–7.59 (m, 3H), 7.86 (t, J=7.5 Hz, 1H), 8.04 (d, J=7.8 Hz, 2H), 8.18–8.32 (m, 3H), 9.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=54.1, 110.9, 113.9, 125.8, 126.6, 126.8, 128.5, 128.7, 129.0, 129.2, 132.2, 134.3, 138.7, 151.1, 151.5, 152.8, 161.1; IR (KBr, cm^{-1}): 2926; HRMS calcd for $C_{19}H_{15}N_2O$ $[M+H]^+$ 287.1184, found 287.1174.

*4.2.2. 1-Methoxy-3-(3-methylphenyl)benzo[b][1,6]naphthyridine (**3ab**).* White solid; isolated yield: 61.5 mg (82%); mp 111–112 °C; R_f=0.28 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 4.32 (s, 3H), 7.32 (d, J=8.1 Hz, 1H), 7.52–7.58 (m, 2H), 7.79–7.87 (m, 2H), 8.01 (d, J=8.4 Hz, 2H), 8.14–8.20 (m, 3H), 9.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 55.9, 120.1, 121.4, 126.4, 126.8, 127.9, 128.4, 128.7, 129.4, 129.7, 130.7, 132.2, 135.5, 137.9, 143.5, 148.9, 160.3; IR (KBr cm^{-1}): 2928, 3450. HRMS calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1335.

*4.2.3. 1-Methoxy-3-(4-methylphenyl)-benzo[b][1,6]naphthyridine (**3ac**).* White solid; isolated yield: 61.5 mg 82%; mp 114–115 °C; R_f=0.28 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 4.32 (s, 3H), 7.32 (d, J=7.5 Hz, 1H), 7.56 (d, J=6.6 Hz, 1H), 7.85 (t, J=8.1 Hz, 2H), 8.01 (d, J=9.6 Hz, 2H), 8.14–8.20 (m, 3H), 9.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 54.2, 109.5, 113.9, 125.9, 126.4, 126.9, 128.5, 129.2, 129.4, 132.3, 132.6, 135.0, 135.8, 139.4, 142.5, 150.8, 161; IR (KBr cm^{-1}): 3437, 2924; HRMS calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1335.

*4.2.4. 1-Methoxy-3-(4-methoxyphenyl)benzo[b][1,6]naphthyridine (**3ad**).* Yellow solid; isolated yield: 67.0 mg (85%); mp 119–120 °C;

Table 2
Palladium-catalyzed one-pot synthesis of 1,3-disubstituted benzo[*b*][1,6]naphthyridines[a]

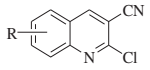
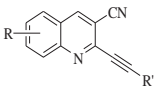
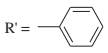
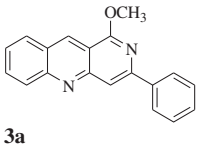
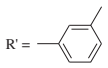
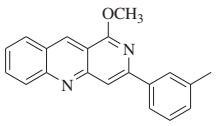
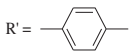
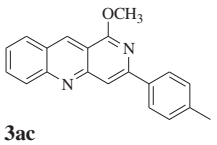
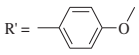
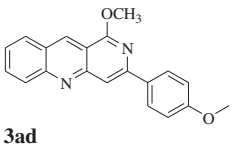
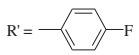
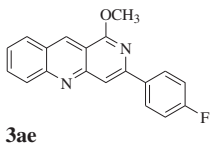
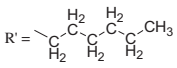
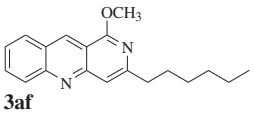
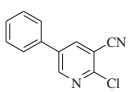
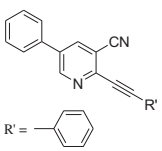
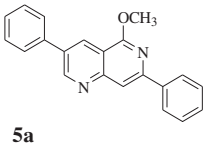
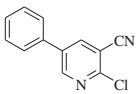
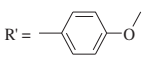
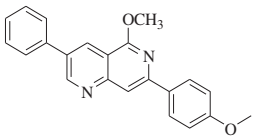
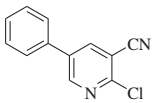
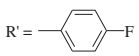
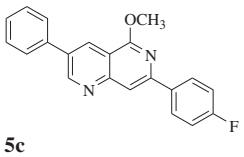
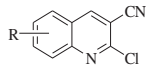
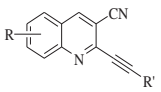
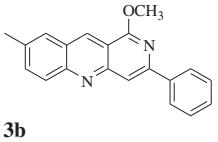
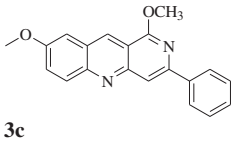
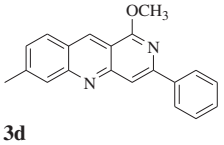
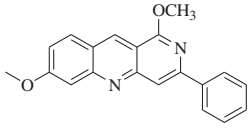
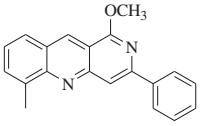
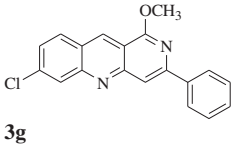
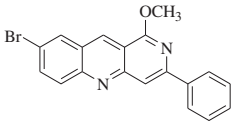
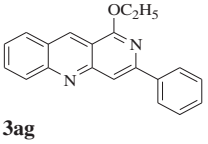
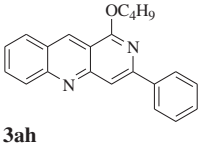
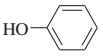
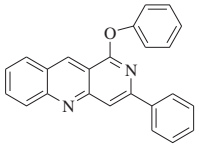
Entry	Substrate	Intermediate	Sonogashira coupling time (h)	Nucleo-/solvent	Product	Annulation time (h)	Yield[b] (%)
	 **(1)**	 **(2)**					
1	R=H **1a**		3	MeOH	 **3a**	3	80
2	R=H **1a**		3.5	MeOH	 **3ab**	4	82
3	R=H **1a**		3.5	MeOH	 **3ac**	4	82
4	R=H **1a**		4	MeOH	 **3ad**	4	85
5	R=H **1a**		2.5	MeOH	 **3ae**	2.5	80
6	R=H **1a**		12	MeOH	 **3af**	2	72[c]
7	 **4**		3	MeOH	 **5a**	4	76
8	 **4**		4	MeOH	 **5b**	5	80
9	 **4**		2.5	MeOH	 **5c**	2	76

Table 2 (*continued*)

Entry	Substrate  **(1)**	Intermediate  **(2)**	Sonogashira coupling time (h)	Nucleo-/solvent	Product	Annulation time (h)	Yield[b] (%)
10	R=6-Me **1b**	R' = 	3	MeOH	 **3b**	4	77
11	R=6-OMe **1c**	R' = 	4	MeOH	 **3c**	4.5	79
12	R=7-Me **1d**	R' = 	4.5	MeOH	 **3d**	4	78
13	R=7-OMe **1e**	R' = 	5	MeOH	 **3e**	4	80
14	R=8-Me **1f**	R' = 	5	MeOH	 **3f**	5	74
15	R=7-Cl **1g**	R' = 	3	MeOH	 **3g**	2	75
16	R=6-Br **1h**	R' = 	3	MeOH	 **3h**	2	75
17	R=H **1a**	R' = 	3	EtOH	 **3ag**	5	78
18	R=H **1a**	R' = 	3	*n*-BuOH	 **3ah**	7	75

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate (1)	Intermediate (2)	Sonogashira coupling time (h)	Nucleo-/solvent	Product	Annulation time (h)	Yield[b] (%)
19	R=H **1a**	R' = 	3	*i*-PrOH	S.M.	21	S.M.[d]
20	R=H **1a**	R' = 	3	*t*-BuOH	S.M.	21	S.M.
21	R=H **1a**	R' = 	3	HO 		12	72

Conditions:
[a] (i) 5 mol % $Pd(OAc)_2$, 10 mol % Ph_3P, 2 equiv Et_3N, CH_3CN, 80 °C, N_2 atm; (ii) 5 mol % $Pd(OAc)_2$, 10 mol % Ph_3P, 1.5 equiv K_2CO_3, 4 mL MeOH, 80 °C, air.
[b] Isolated yields.
[c] 5 mol % $Pd(OAc)_2$, 10 mol % Ph_3P, 15 mol % CuI, 2 equiv Et_3N, CH_3CN, 80 °C, N_2 atmosphere for Sonogashira coupling and cyclization was performed on isolated product.
[d] S.M.=starting material.

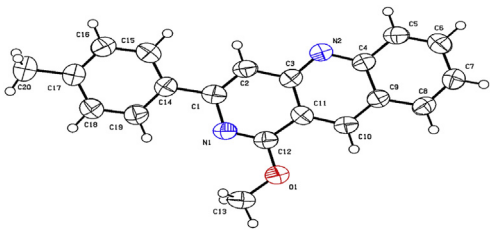
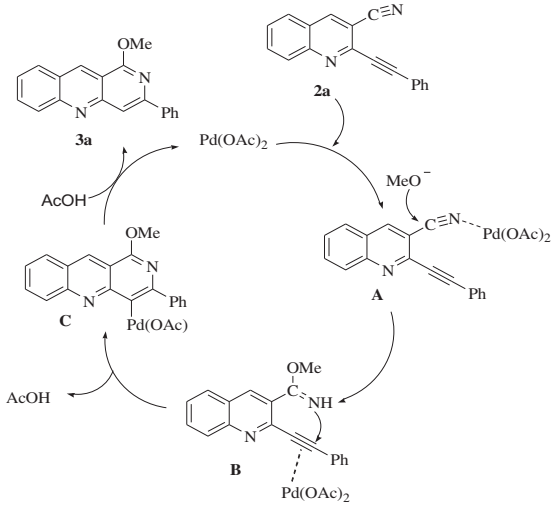


Fig. 2. ORTEP drawing of the X-ray structure of **3ac**.



Scheme 2. Plausible mechanism.

R_f=0.15 (05:95 EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H), 4.32 (s, 3H), 7.04 (d, *J*=8.7 Hz, 2H), 7.54 (t, 1H), 7.85 (t, 1H), 7.95 (s, 1H), 8.03 (d, *J*=8.4 Hz, 1H), 8.16–8.24 (m, 3H), 9.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.0, 55.3, 109.3, 113.6, 114.0, 125.5, 126.3, 128.2, 128.9, 129.2, 131.3, 132.0, 134.2, 150.8, 151.4, 152.9, 160.5, 160.9; IR (KBr cm^{-1}): 2925; HRMS calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290, found 317.1285.

*4.2.5. 3-(4-Fluorophenyl)-1-methoxy-benzo[b][1,6]naphthyridine (**3ae**).* Yellow solid; isolated yield: 61.0 mg (80%); mp 118–119 °C; R_f=0.25 (05:95 EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.32 (s, 3H), 7.18 (d, *J*=8.7 Hz, 1H), 7.58 (d, *J*=8.1 Hz, 1H), 7.87 (t, *J*=8.1 Hz, 1H), 7.98 (s, 1H), 8.04 (d, *J*=8.1 Hz, 1H), 8.18–8.24 (m, 3H), 9.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.3, 109.2, 109.5, 113.8, 115.5, 115.8, 126.1, 126.5, 128.2, 128.7, 128.8, 129.2, 132.8, 132.7, 135.3, 139.1, 161.1; IR (KBr cm^{-1}): 2961, 3056; HRMS calcd for $C_{19}H_{14}FN_2O$ $[M+H]^+$ 305.1090, found 305.1085.

*4.2.6. 3-Hexyl-1-methoxy-benzo[b][1,6]naphthyridine (**3af**).* Yellow liquid; isolated yield: 53.0 mg (72%); R_f=0.40 (05:95 EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, *J*=6.3 Hz, 3H), 1.34–1.42 (m, 6H), 1.84 (t, 2H), 2.84 (t, *J*=7.5 Hz, 2H), 4.20 (s, 3H), 7.34 (s, 1H), 7.52 (t, *J*=7.2 Hz, 1H), 7.83 (t, *J*=7.5 Hz, 1H), 8.01 (d, *J*=8.1 Hz, 1H), 8.16 (d, *J*=8.7 Hz, 1H), 9.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 28.6, 28.9, 31.7, 38.2, 53.9, 112.3, 113.2, 125.3, 126.2, 128.9, 129.1, 131.8, 134.2, 151.1, 152.6, 157.0, 160.8; IR (KBr cm^{-1}): 2927; HRMS calcd for $C_{19}H_{23}N_2O$ $[M+H]^+$ 295.1810, found 295.1805.

*4.2.7. 5-Methoxy-3,7-diphenyl-[1,6]naphthyridine (**5a**).* White solid; isolated yield: 59.2 mg (76%); mp 101–102 °C; R_f=0.30 (05:95 EtOAc/hexane); 101 °C ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.28 (s, 3H), 7.42–7.56 (m, 6H), 7.73 (d, *J*=7.2 Hz, 2H), 7.98 (s, 1H), 8.22 (d, *J*=7.5 Hz, 2H), 8.68 (s, 1H), 9.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.0, 111.3, 114.0, 126.8, 127.2, 128.2, 128.5, 128.6, 129.0, 129.2, 129.7, 134.1, 137.3, 138.7, 151.4, 153.7, 160.6; IR (KBr cm^{-1}): 2923; HRMS calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1341, found 313.1335.

*4.2.8. 5-Methoxy-7-(4-methoxy-phenyl)-3-phenyl[1,6]naphthyridine (**5b**).* White solid; isolated yield: 68.5 mg (80%); mp 129–130 °C; R_f=0.30 (05:95 EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H), 4.26 (s, 3H), 7.03 (d, *J*=9.0 Hz, 2H), 7.43–7.55 (m, 3H), 7.72 (d, *J*=7.5 Hz, 2H), 7.89 (s, 1H), 8.18 (d, *J*=9.0 Hz, 2H), 8.66 (s, 1H), 9.25 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.8, 55.2, 110.0, 113.6, 114.0, 127.1, 127.2, 128.1, 129.1, 129.6, 131.3, 133.4, 133.7, 137.4, 151.2, 152.8, 153.6,

160.5; IR (KBr cm^{-1}): 2925; HRMS calcd for $C_{22}H_{19}N_2O_2$ $[M+H]^+$ 343.1447, found 343.1420.

*4.2.9. 7-(4-Fluoro-phenyl)-5-methoxy-3-phenyl-[1,6]naphthyridine (**5c**).* White solid; isolated yield: 62.7 mg (76%); mp 121–122 °C; R_f=0.40 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 4.27 (s, 3H), 7.19 (d, J=8.7 Hz, 1H), 7.51–7.58 (m, 4H), 7.73 (d, J=7.2 Hz, 2H), 7.91 (s, 1H), 8.19 (d, J=8.1 Hz, 2H), 8.68 (s, 1H), 9.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.09, 111.01, 113.98, 115.74, 127.24, 128.64, 129.23, 129.74, 134.23, 137.30, 150.41, 151.30, 152.73, 153.80, 160.68, 161.85, 165.74; IR (KBr cm^{-1}): 2923; HRMS calcd for $C_{21}H_{16}FN_2O$ $[M+H]^+$ 331.1247, found 331.1221.

*4.2.10. 1-Methoxy-8-methyl-3-phenyl-benzo[b][1,6]naphthyridine (**3b**).* Yellow solid; isolated yield: 57.7 mg (77%); mp 95–96 °C; R_f=0.30 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 2.59 (s, 3H), 4.32 (s, 3H), 7.43 (d, J=6.9 Hz, 1H), 7.48–7.56 (m, 2H), 7.69 (d, J=8.7 Hz, 1H), 7.77 (s, 1H), 8.03–8.11 (m, 2H), 8.26 (d, J=7.2 Hz, 2H), 9.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 54.1, 110.7, 114.0, 126.8, 127.3, 128.6, 129.8, 132.3, 133.2, 135.1, 135.7, 138.8, 145.6, 146.0, 148.0, 160.3, 164.0; IR (KBr cm^{-1}): 2924; HRMS calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1335.

*4.2.11. 1,8-Dimethoxy-3-phenyl-benzo[b][1,6]naphthyridine (**3c**).* Yellow solid; isolated yield: 62.50 mg (79%); mp 108–109 °C; R_f=0.28 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 3.98 (s, 3H), 4.32 (s, 3H), 7.41 (d, J=6.9 Hz, 1H), 7.48–7.56 (m, 3H), 8.02 (s, 1H), 8.08 (d, J=9.6 Hz, 1H), 8.25 (d, J=7.5 Hz, 3H), 9.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.0, 55.5, 104.4, 110.8, 114.0, 126.7, 126.9, 127.5, 128.6, 128.8, 130.4, 131.7, 138.8, 148.4, 149.8, 151.1, 157.1, 160.6; IR (KBr cm^{-1}): 2924; HRMS calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290, found 317.1285.

*4.2.12. 1-Methoxy-7-methyl-3-phenyl-benzo[b][1,6]naphthyridine (**3d**).* Light yellow solid; isolated yield: 58.5 mg (78%); mp 98–99 °C; R_f=0.30 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 2.66 (s, 3H), 4.32 (s, 3H), 7.38–7.45 (m, 2H), 7.51 (t, J=7.5 Hz, 2H), 7.92 (m, 2H), 8.02 (s, 1H), 8.26 (d, J=7.5 Hz, 2H), 9.11 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.5, 54.2, 106.4, 127.0, 127.3, 127.5, 127.8, 128.1, 128.5, 128.7, 128.9, 129.1, 129.3, 129.7, 142.0, 143.5, 154.5, 162.8; IR (KBr cm^{-1}): 2924; HRMS calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1335.

*4.2.13. 1,7-Dimethoxy-3-phenyl-benzo[b][1,6]naphthyridine(**3e**).* - Light green solid; isolated yield: 63.5 mg (80%); mp 115–116 °C; R_f=0.28 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 3.98 (s, 3H), 4.32 (s, 3H), 7.41–7.55 (m, 5H), 8.02 (s, 1H), 8.07 (d, J=9.6 Hz, 1H), 8.24 (d, J=7.5 Hz, 2H), 9.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.0, 55.5, 104.3, 110.8, 113.9, 126.6, 126.9, 127.4, 128.6, 128.8, 130.4, 131.7, 138.8, 148.3, 149.8, 151.0, 157.0, 160.5; IR (KBr cm^{-1}): 2925; HRMS calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290, found 317.1278.

*4.2.14. 1-Methoxy-6-methyl-3-phenyl-benzo[b][1,6]naphthyridine (**3f**).* Light yellow solid; isolated yield: 55.5 mg 74%; mp 123–124 °C; R_f=0.40 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 2.93 (s, 3H), 4.33 (s, 3H), 7.42–7.51 (m, 3H), 7.57–7.68 (m, 2H), 7.77–7.89 (m, 1H), 8.10 (s, 1H), 8.26–8.30 (m, 2H), 9.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3, 54.0, 111.4, 119.3, 125.5, 126.8, 127.1, 127.8, 128.6, 128.8, 131.4, 132.9, 134.0, 138.8, 142.7, 145.4, 152.0, 160.9; IR (KBr cm^{-1}): 2919; HRMS calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1335.

*4.2.15. 7-Chloro-1-methoxy-3-phenyl-benzo[b][1,6]naphthyridine (**3g**).* Green solid; isolated yield: 60.0 mg (75%); mp 79–80 °C; R_f=0.25 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 4.33 (s, 3H), 7.42–7.54 (m, 2H), 7.69 (d, J=8.4 Hz, 1H), 7.88 (d, J=8.4 Hz, 1H), 7.96–8.32 (m, 3H), 8.37 (s, 1H), 9.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.6, 110.6, 120.5, 121.5, 126.5, 126.9, 127.2, 127.7, 128.5, 128.7, 129.0, 130.4, 131.6, 134.4, 144.8, 148.0, 160.4; IR (KBr cm^{-1}): 2925; HRMS calcd for $C_{19}H_{14}ClN_2O$ $[M+H]^+$ 321.0795, found 321.0789.

*4.2.16. 8-Bromo-1-methoxy-3-phenyl-benzo[b][1,6]naphthyridine (**3h**).* Yellow solid; isolated yield: 68.0 mg (75%); mp 92–93 °C; R_f=0.22 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 4.33 (s, 3H), 7.43–7.58 (m, 4H), 7.86 (t, J=7.8 Hz, 1H), 8.03 (d, J=8.4 Hz, 2H), 8.20 (d, J=8.7 Hz, 1H), 8.26 (d, J=7.5 Hz, 2H), 9.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.1, 110.8, 113.9, 125.8, 126.8, 128.5, 128.7, 129.1, 129.2, 132.2, 132.6, 134.4, 138.7, 142.0, 142.4, 152.7, 161.1; IR (KBr cm^{-1}): 2924. HRMS calcd for $C_{19}H_{14}BrN_2O$ $[M+H]^+$ 365.0289, found 365.0263.

*4.2.17. 1-Ethoxy-3-phenyl-benzo[b][1,6]naphthyridine (**3ag**).* Yellow solid; isolated yield: 58.5 mg (78%); mp 90–91 °C; R_f=0.33 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 1.62 (t, J=6.9 Hz, 3H), 4.81 (q, 2H), 7.40–7.58 (m, 4H), 7.85 (t, J=7.5 Hz, 1H), 8.05 (d, J=7.8 Hz, 2H), 8.18–8.26 (m, 3H), 9.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.5, 62.6, 110.5, 114.3, 125.7, 126.5, 126.8, 128.4, 128.6, 129.0, 129.1, 132.0, 134.2, 138.8, 151.1, 151.4, 152.8, 160.7; IR (KBr cm^{-1}): 2926, 3432; HRMS calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1341, found 301.1322.

*4.2.18. 1-Butoxy-3-phenyl-benzo[b][1,6]naphthyridine (**3ah**).* Yellow solid; isolated yield: 61.5 mg (75%); mp 74–75 °C; R_f=0.30 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 1.08 (t, J=7.5 Hz, 3H), 1.53–1.69 (m, 2H), 2.00 (t, J=7.8 Hz, 2H), 4.75 (t, J=6.3 Hz, 2H), 7.42–7.58 (m, 4H), 7.85 (t, J=7.8 Hz, 1H), 8.03 (d, J=9.6 Hz, 2H), 8.18–8.26 (m, 3H), 9.16 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 19.5, 31.0, 66.6, 110.6, 114.1, 125.7, 126.5, 126.8, 128.3, 128.6, 129.0, 129.1, 132.0, 134.2, 138.8, 151.1, 151.4, 152.8, 160.9; IR (KBr cm^{-1}): 2927; HRMS calcd for $C_{22}H_{21}N_2O$ $[M+H]^+$ 329.1654, found 329.1648.

*4.2.19. 1-Phenoxy-3-phenyl-benzo[b][1,6]naphthyridine (**4ai**).* Yellow liquid; isolated yield: 62.5 mg (72%); R_f=0.10 (05:95 EtOAc/hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 6.84 (t, J=8.7 Hz, 1H), 6.94 (t, J=7.2 Hz, 1H), 7.41–7.52 (m, 6H), 7.83 (t, J=8.1 Hz, 1H), 7.97 (t, J=7.8 Hz, 3H), 8.15 (d, J=8.7 Hz, 1H), 8.25 (d, J=6.9 Hz, 2H), 9.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.3, 114.5, 125.4, 125.5, 126.4, 126.9, 128.5, 128.6, 128.9, 129.0, 129.5, 136.0, 139.2, 150.6, 151.5, 153.7, 154.4, 161.4; IR (KBr cm^{-1}): 2927; HRMS calcd for $C_{24}H_{17}N_2O$ $[M+H]^+$ 349.1341, found 349.1335.

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16. Crystal data for **3ac**: empirical formula, $C_{20}H_{16}N_2O$; formula weight, 300.35; crystal colour, habit: light yellow, block; crystal system, triclinic; lattice parameters, a=8.9724(12), b=9.7978(14), c=10.2831(13), α=89.148° (11), β=67.507° (13), γ=68.453° (13), space group $P\bar{1}$; Z=2; D_{calcd}=1.293 g/cm^3; R (int.)=0.0178; reflections collected/unique 5525/4109; refinement method full-matrix least-squares on F^2; melting point 114–115 °C; R indices (index ranges) $-11\leq h\leq 11$, $-12\leq k\leq 13$, $-12\leq l\leq 12$; *GoF* 1.024; R_1 0.0649; wR_2 0.1896; largest diff. peak and hole (e A^{-3}) 0.27 and −0.22. Crystallographic data (excluding structure factors) for the structures in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 908156. Copies of the data can be obtained free of charge on an application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk].
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