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Chemoselective Azidation of *o*-Alkynylaldehydes over [3 + 2] Cycloaddition and Subsequent Staudinger Reaction: Access to Benzonaphthyridines/Naphthyridines

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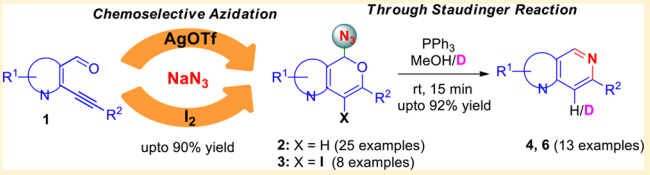
Supporting Information

ABSTRACT: An efficient tandem approach for the chemoselective synthesis of functionalized azido-pyranoquinolines and azido-iodo-pyranoquinolines via electrophilic cyclization of *o*-alkynylaldehydes in the presence of sodium azide under mild reaction conditions is described. Mechanistic studies confirm the formation of azido-pyranoquinolines through nucleophilic attack of azide on pyrilium intermediate over [3 + 2] cycloaddition of the azide on the alkyne. The synthesized azido-pyranoquinolines were transformed into benzonaphthyridines via Staudinger reaction. The mechanistic pathway was supported by deuterium labeling experiment and X-ray crystallographic studies.



INTRODUCTION

In recent times, new perspectives have been developed for organic azides, and their synthesis has gained considerable attention due to their versatile use as an intermediate for the construction of *N*-containing molecules.[1] Synthetic utility of azides has been explicitly demonstrated by their implementation in azide−alkyne Huisgen cycloaddition[2a] and Staudinger ligation[2b] for chemical biology and drug discovery. Moreover, incorporation of the azide moiety in lead organic compounds accelerates their biological activities.[3] Despite ample azidation reactions,[4] the strategy for selective azidation at the carbonyl center remains challenging. Triazole formation via [3 + 2] cycloaddition of azide with alkynes[5] and alkynyl aldehydes[6] has been well-established (Schemes 1i and ii). Electrophilic cyclization using metal catalysts and nucleophiles has emerged as an efficient tool for the construction of heterocycles (Scheme 1iii).[7] However, implication of azide as an external nucleophile in the cyclization of *o*-alkynylaldehydes remains elusive.

Notably, the napthyridine core is associated with a wide range of biological activities, including anticancer,[8a] anti-HIV-1,[8b] antimicrobial,[8c] and adrenoceptor blocking activities.[8d] Naphthyridines are also known for use as luminescence materials because of their structural properties.[8e] Previously, naphthyridine[9] derivatives were synthesized using metal-catalyzed tandem cyclization.[10a] Recently, Singh[10b] and our group[10c] described the synthesis of benzonapthyridines using Pd-catalyzed arylation and cyclization, respectively (Scheme 1iv). Owing to the pharmacological importance and in continuation of our ongoing research,[11] herein we developed a facile chemoselective strategy for the synthesis of pyranoquinolines and benzonaphthyridines. We initiated our reaction with readily accessible *o*-alkynylaldehydes and sodium azide via electrophilic cyclization followed by concomitant Staudinger reaction to afford the substituted napthyridines (Scheme 1v).

RESULTS AND DISCUSSION

We begin our preliminary observations with 2-(phenylethynyl)-quinoline-3-carbaldehyde **1a** along with NaN_3 by using our previously reported conditions[11b] (10 mol % of $AgNO_3$ as a catalyst in H_2O at 80 °C); however, no progress in the reaction was observed after 1 h (Table 1, entry 1). Other solvents such as DCE and toluene (entries 2 and 3) failed to provide the desired product. When MeOH was used as a solvent at 70 °C, it acted as a strong nucleophile and formed 1-methoxy-3-phenyl-1*H*-isochromene exclusively in 70% yield instead of product **2a** (entry 4); however, MeCN failed to provide desired product with $AgNO_3$ (entry 5). The reaction with other silver salts such as AgTFA and AgOAc (10 mol %) in MeCN afforded the desired product **2a** in lower yield (entries 6 and 7). Use of AgOTf afforded the desired product **2a** in 76% yield in 6 h (entry 8). The yield of the product remained the same when the reaction was run for 4 h (entry 9). Longer reaction time afforded the product in slightly lower yield (entry 10), while 5 mol % of AgOTf provided the product **2a** in 56% yield (entry 11). Use of $TMSN_3$ as an azide source gave product **2a** in diminished yield (entry 12), whereas TsN_3 was found incompatible for the reaction (entry 13). When the amount of NaN_3 was decreased to 0.5 mmol, product **2a** was obtained in 58% yield (entry 14). Other metal salts such as cobalt(II), copper(II), palladium(II), gold(I), and gold(III) with different counterions were found inadequate (entries 12−19). When the reaction was performed in the absence of catalyst and solvent,

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Scheme 1. Previous Reports versus Present Work

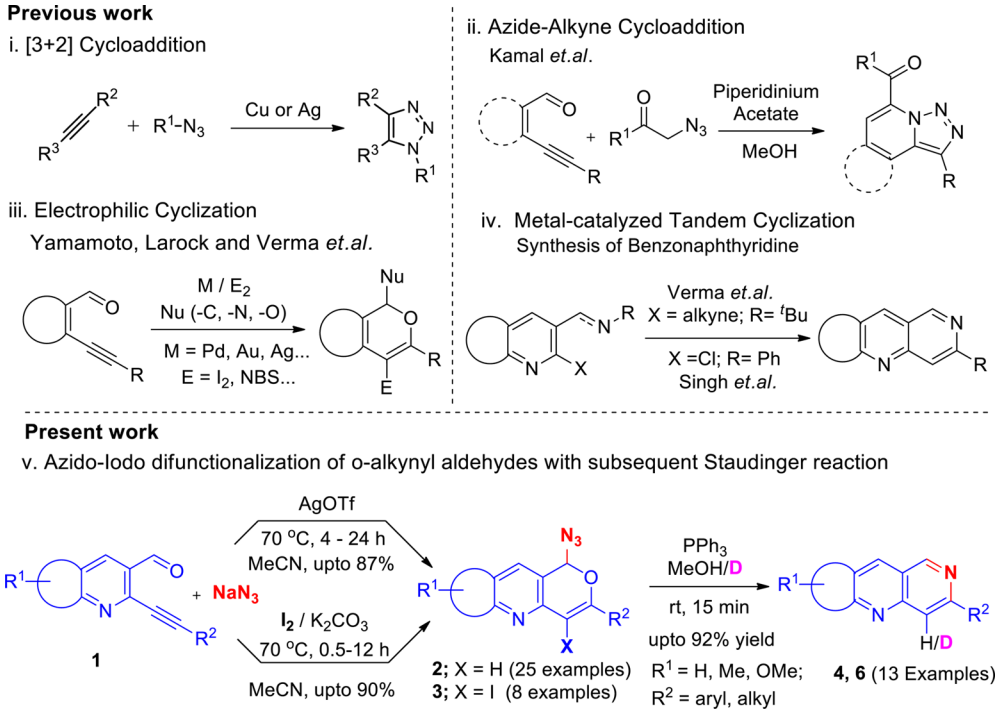
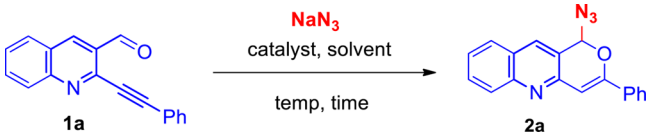


Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	solvent	temp (°C)/time (h)	**2a** yield (%)[b]
1[11b]	$AgNO_3$ (10)	H_2O	80/1	NR
2	$AgNO_3$ (10)	DCE	80/6	NR
3	$AgNO_3$ (10)	toluene	80/6	NR
4	$AgNO_3$ (10)	MeOH	70/6	NR[c]
5	$AgNO_3$ (10)	MeCN	70/6	NR
6	AgTFA (10)	MeCN	70/6	46
7	AgOAc (10)	MeCN	70/6	35
8	AgOTf (10)	MeCN	70/6	76
9	**AgOTf (10)**	**MeCN**	**70/4**	**76**
10	AgOTf (10)	MeCN	70/12	72
11	AgOTf (5)	MeCN	70/4	56
12	AgOTf (10)	MeCN	70/4	68[d]
13	AgOTf (10)	MeCN	70/4	NR[e]
14	AgOTf (10)	MeCN	70/24	58[f]
15	$COCl_2$ (10)	MeCN	70/6	26
16	CuOAc (10)	MeCN	70/6	31
17	$PdCl_2$ (10)	MeCN	70/6	20
18	AuCl (10)	MeCN	70/6	35
19	$AuCl_3$ (10)	MeCN	70/6	28
20			70/24	NR

[a]Reactions were carried out using **1a** (0.5 mmol) and NaN_3 (1.0 mmol) in 2.0 mL of solvent. NR: no reaction. [b]Isolated yield. [c]Isochromene was obtained in 70% yield. [d]Using $TMSN_3$ (1.0 mmol). [e]Using TsN_3 (1.0 mmol). [f]Using 0.5 mmol of NaN_3.

the desired product **2a** was not obtained in 24 h (entry 20). After screening various solvents and catalysts, it was found that the solvent and choice of silver salts was crucial for the formation of desired azido products.

With the optimal reaction conditions, we next extended the scope of the reaction by utilizing a variety of substituted *o*-alkynylaldehydes having an electron-releasing, electron-withdrawing, heteroaromatic, and aliphatic groups (Table 2). When phenyl substituted substrate **1a** was reacted under standard conditions, 76% yield of desired product **2a** was obtained. Electron-releasing groups such as -Me, -Et, and -OMe at a distal end of the phenyl ring of alkyne afforded the corresponding products **2b–e** in 74–84% yields; however, 2-(*o*-tolylethynyl)-quinoline-3-carbaldehyde **1f** provided the desired product **2f** in slightly lower yield, which might be due to the steric congestion. The substrate **1g** bearing an electron-withdrawing −CF3 group on the para position of the phenyl ring provided the products **2g** in 67% yield, whereas thienyl substituted *o*-alkynylaldehyde **1h** provided the desired product **2h** in 72% yield. The reaction was successful with substrates having aliphatic alkynes **1i** and terminal alkyne **1j**. Further, the optimal protocol was utilized for substrates having 6-methyl and 6-methoxy-substituted alkynyl quinoline-3-carbaldehydes **1k–w** having a variety of electron-rich and electron-poor alkynes, the corresponding products **2k–w** were obtained in 65–84% yields. The reaction was also compatible with substrate 2-((3,5-dimethoxyphenyl)ethynyl)-6-methoxy quinoline-3-carbaldehyde **1x** and afforded the desired product **2x** in 82% yield. The formations of desired azido-pyranoquinolines were confirmed by spectroscopic studies and X-ray crystallographic data of product **2b**.

After obtaining successful results with metal-catalyzed cyclization, we next explored iodine-induced ring closure for the synthesis of substituted azido-iodo-pyranoquinolines **3a–f** from corresponding *o*-alkynyl aldehydes (Scheme 2). The reaction was preceded through the iodonium intermediate **1′**, which subsequently cyclized through 6-*endo dig* cyclization in the presence of sodium azide, and molecular iodine afforded the desired product **3**. The phenyl and electron-rich substituted arenes afforded the substituted azido-iodo products **3a–e** in

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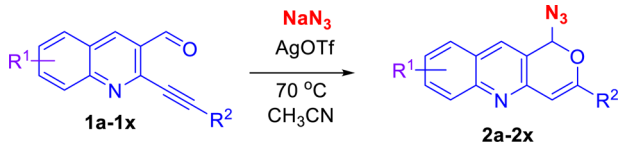
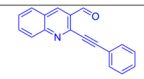
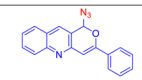
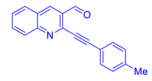
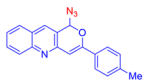
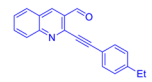
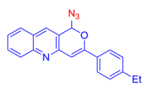
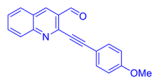
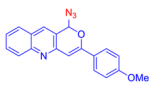
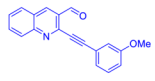
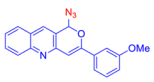
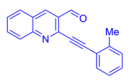
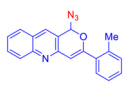
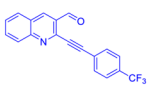
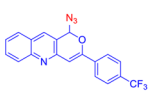
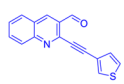
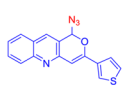
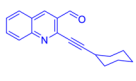
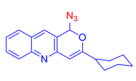
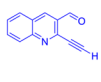
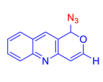
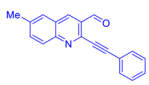
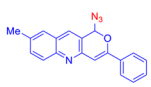
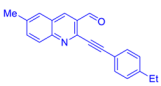
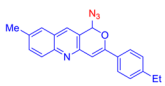
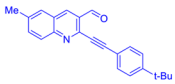
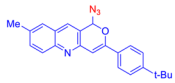
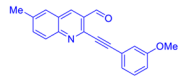
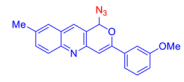
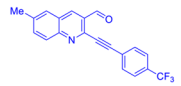
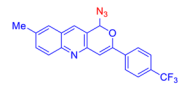
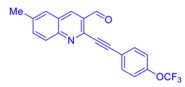
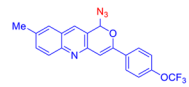
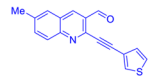
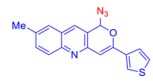
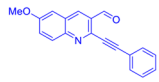
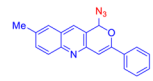
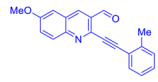
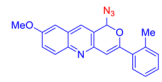
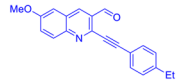
Table 2. Synthesis of Azido-pyranoquinolines[a]



entry	*o*-alkynylaldehyde (**1**)		product (**2**)		yield (%)
1		**1a**		**2a**	76
2		**1b**		**2b**	80
3		**1c**		**2c**	80
4		**1d**		**2d**	84
5		**1e**		**2e**	74
6		**1f**		**2f**	64[b]
7		**1g**		**2g**	67
8		**1h**		**2h**	72
9		**1i**		**2i**	65[c]
10		**1j**		**2j**	60[c]
11		**1k**		**2k**	80
12		**1l**		**2l**	82
13		**1m**		**2m**	83
14		**1n**		**2n**	78
15		**1o**		**2o**	70
16		**1p**		**2p**	68
17		**1q**		**2q**	75
18		**1r**		**2r**	81
19		**1s**		**2s**	65[b]
20		**1t**		**2t**	84
21		**1u**		**2u**	87
22		**1v**		**2v**	72
23		**1w**		**2w**	79
24		**1x**		**2x**	82

[a]Reactions were carried out using optimal reaction conditions (Table 1 entry 11). [b]Reaction completed in 18 h. [c]Reaction completed in 24 h.

76–90% yield. The alkyl substituted **1y** was well-tolerated and provided the product **3f** in moderate yield.

Next, we extended the utility of synthesized azido-pyranoquinolines/azido-iodopyrano quinolines via Staudinger reaction[12] (Table 3). When substrates **2** or **3** were treated with PPh_3 in MeOH at room temperature, interestingly, we obtained benzonapthyridines **4** exclusively instead of amino-pyranoquinolines **5**/iodo-benzonapthyridines **4′**. We successfully explored the Staudinger reaction for the construction of biologically important functionalized benzonaphthyridines **4a–j** in good to excellent yield. The reaction proceeded smoothly with various electron-donating as well as electron-deficient substrates. The substrate **3f** having aliphatic substitution provided the targeted benzonapthyridine **4j** in 88% yield.

The scope of chemoselective azidation was next investigated with alkynyl-nicotinaldehyde **1z** and **1aa** for the synthesis of napthyridines 6. The reaction proceeded well and provided the desired 1,6 and 2,6 napthyridines **6a** and **6b** via electrophilic iodocyclization followed by Staudinger reaction in good yields (Scheme 3).

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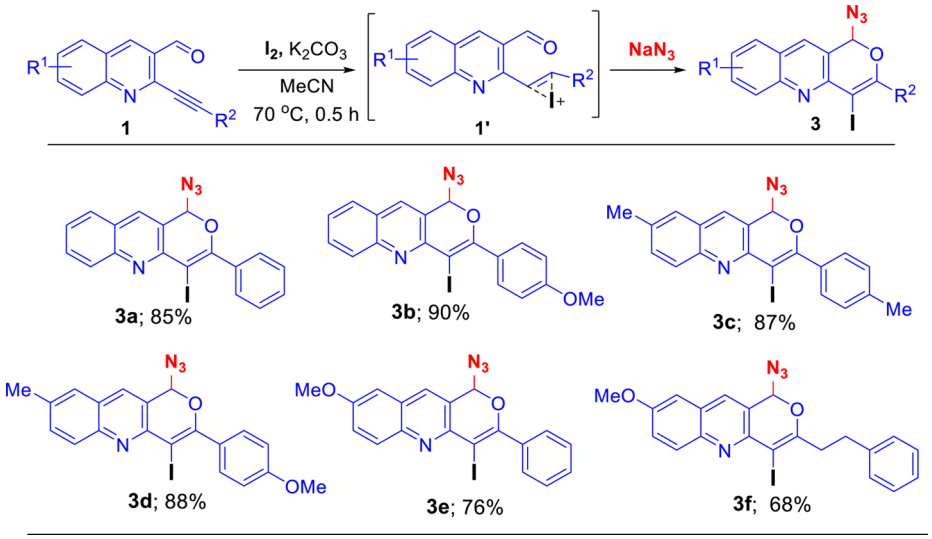
Scheme 2. Synthesis of Azido-iodo-pyrano Quinolines



Further, we performed the deuterium labeling studies of azido-substrate **2l** by using MeOD as a solvent, which showed that the deuterium was incorporated at the C-4 position in the benzonaphthyridine **4f**-D1 (Scheme 4). This result supports the involvement of a tautomerization step (v and vi) as described in the plausible mechanism (Scheme 5) for the synthesis of benzonapthyridine.

On the basis of the above observations, we proposed a mechanistic pathway for the reaction as described in Scheme 5. It includes two steps: the first step involves the formation of azido-pyranoquinolines **2**, and the second step shows the direct conversion of azidopyrano quinolines **2** into benzonaphthyridines **4**. The first step of the mechanistic cycle is initiated by the coordination of silver metal to the alkyne triple bond,[13] which triggers the attack of carbonyl oxygen to form oxonium ion via electrophilic cyclization **i**. Consequently, nucleophilic attack of azide followed by demetalation afforded the azidated product **2**.

Next, the synthesis of benzonapthyridine was demonstrated in step 2 via formation of aza-ylide species[12] **iii** by using triphenylphosphine, which subsequently forms unstable intermediate **iv** in the presence of MeOD. The instability and presence of the nitrogen lone pair trigger the opening of the pyran ring, which immediately tautomerizes to give species **vi**.[14] Rapid intramolecular cyclization of species **vi** followed by aromatization leads to the generation of desired product **4**.

It was interesting to note that when the reaction was performed with substrate **1l** in DMSO at 120 °C under the metal-free condition, the triazole substituted aldehyde **7** was formed exclusively in 74% yields instead of azido-pyranoquinolines **2l** (Scheme 6). This was probably due to the preferential [3 + 2] cycloaddition over alkyne activation in the absence of a metal catalyst.

Next, we demonstrated the synthetic utility of the azido-pyranoquinolines for the synthesis of trizolo-pyranoquinolines via [3 + 2] cycloaddition (Scheme 7). The analogues of these compounds have been used to tag azide installation within virus particles,[15a] nucleic acids,[15b] and proteins from complex tissue lysates[15c] with virtually no background labeling. The trizolo-pyranoquinolines **8a–c** were synthesized in 96–98% yield using $CuSO_4 \cdot 5H_2O$ as a catalyst.

CONCLUSION

In summary, we have demonstrated chemoselective azidation of *o*-alkynyl aldehydes via 6-*endo dig* electrophilic cyclization over [3 + 2] cycloaddition reaction using the silver catalyst as well as inexpensive iodine. Further, the synthesized azido-pyranoquinolines were elucidated under Staudinger reaction conditions for the generation of benznaphthyridines and napthyridines via breaking of the C–O bond and successive intramolecular N–C bond formation. On the contrary, the metal-free conditions afforded the trizolo-pyranoquinolines through [3 + 2] cycloaddition reaction. The deuterium incorporation in benzonaphthyridines confirmed the proposed mechanistic pathway. This chemistry is general and expected to find application in a variety of organic syntheses.

EXPERIMENTAL SECTION

The starting materials 2-alkynylaldehydes required for synthesis were prepared by using our reported methodology. The structure and purity of known starting materials were confirmed by comparison of their physical and spectral data (^{1}H NMR and ^{13}C NMR) with those reported in literature.[16]

Characterization. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$/DMSO-d_6. Chemical shifts for protons and carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constants in Hertz, and integration. High-resolution mass spectra were recorded on an electrospray mass spectrometer. Crystal structure analysis was accomplished on a single-needle X-ray diffractometer. TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates and visualized by either UV irradiation or by staining with I_2. All purchased chemicals were used as received. All melting points are uncorrected. All HRMS were measured using a Q-TOF B.05.01 (B5125) instrument.

General Procedure for the Synthesis of Azido-pyranoquinolines (2a–x). In an oven-dried reaction vial, 2-alkynyl-quinoline3-carbaldehyde (0.5 mmol) was dissolved in acetonitrile (2 mL), and then NaN_3 (1.0 mmol) was added. Then, AgOTf (10 mol %) was added to the reaction mixture. The resulting reaction mixture was heated at 70 °C for 4–24 h. Progression of the reaction was monitored by TLC and, when complete consumption of 2-alkynyl-quinoline-3-carbaldehyde occured, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with water (15 mL),

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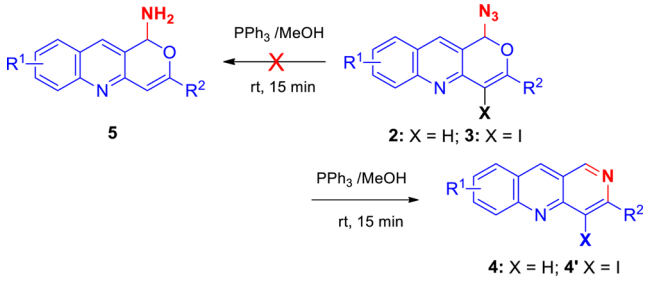
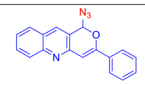
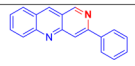
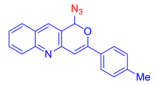
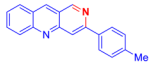
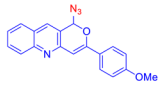
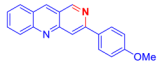
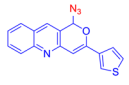
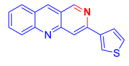
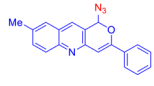
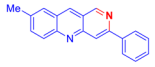
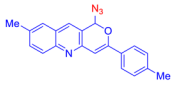
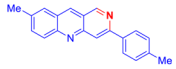
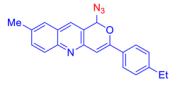
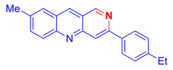
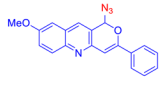
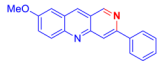
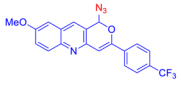
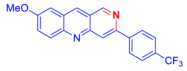
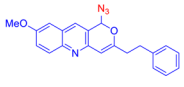
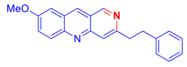
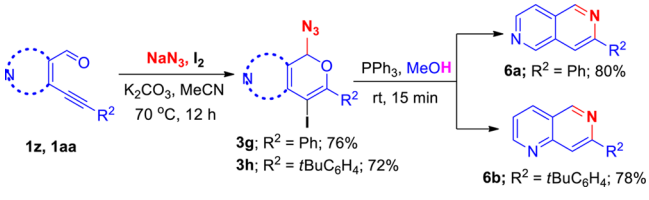
Table 3. Synthesis of Benzo-Naphthyridines via Staudinger Reaction[a]



Entry	Substrate 2/ 3	Product 4	Yield %
1	 2a	 4a	90
2	 2b	 4b	88
3	 2d/3b	 4c	84/ 82[b]
4	 2h	 4d	90
5	 2k	 4e	90
6	 3c	 4f	87
7	 2l	 4g	87
8	 2r	 4h	90/ 89[b]
9	 2v	 4i	92
10	 3f	 4j	88

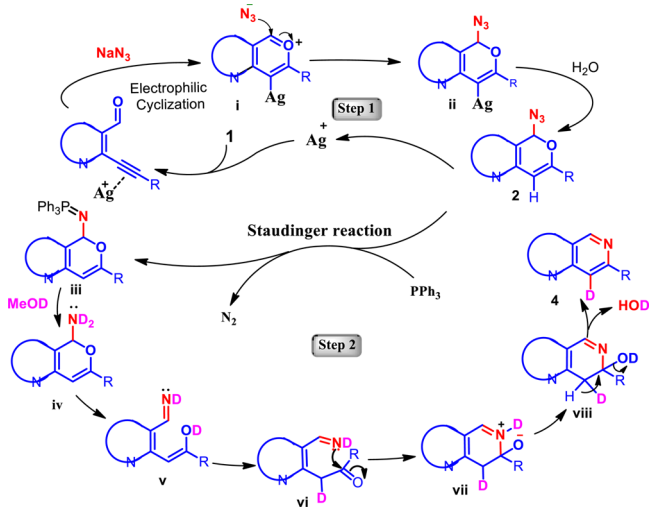
[a]Reactions were carried out using **2**/**3** (0.5 mmol) and PPh_3 (1.2 equiv) in 2.0 mL of MeOH at rt for 15 min. [b]Using **3** as substrate.

Scheme 3. Synthesis of 1,6 and 2,6-Naphthyridines from Azido-iodo-pyranopyridines



Scheme 4. Deuterium Labeling Studies

Scheme 5. Proposed Reaction Mechanism



washed with aqueous saturated brine solution, and then extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography (hexane:ethyl acetate 90:10) to afford the corresponding product. All compounds were crystallized in DCM−hexane.

1-Azido-3-phenyl-1H-pyrano[4,3-b]quinoline (***2a***). The product was obtained as light yellow crystals (114.0 mg, 76% yield), mp 102−104 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 1H), 7.93 (s, 1H), 7.81−7.77 (m, 2H), 7.73 (d, J = 8.3 Hz, 1H), 7.67−7.63 (m, 1H), 7.44−7.35 (m, 4H), 6.89 (s, 1H), 6.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.11, 149.06, 133.0, 132.6, 130.7, 130.3, 128.8, 128.7, 128.0, 126.9, 126.1, 125.6, 120.8, 102.8, 88.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{12}N_4O$ 301.1089; found 301.1088.

1-Azido-3-(p-tolyl)-1H-pyrano[4,3-b]quinoline (***2b***). The product was obtained as pale white needles (122.46 mg, 78% yield), mp 120−122 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.3 Hz, 1H), 7.96 (s, 1H), 7.78−7.68 (m, 4H), 7.48−7.44 (m, 1H), 7.24 (d, J = 7.6 Hz, 2H), 6.90 (s, 1H), 6.75 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 149.3, 149.1, 140.7, 132.5, 130.6, 130.2, 129.4, 128.7, 128.0, 126.8, 126.0, 125.6, 120.8, 102.1, 88.3, 21.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_4O$ 315.1246; found 315.1238.

1-Azido-3-(4-ethylphenyl)-1H-pyrano[4,3-b]quinolines (***2c***). The product was obtained as pale yellow crystals (131.20 mg, 80% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 1H), 7.95 (s, 1H), 7.75−7.72 (m, 3H), 7.68−7.64 (m, 1H), 7.44−7.41 7.43 (m, 1H), 7.23 (d, J = 7.6 Hz, 2H), 6.87 (s, 1H), 6.73 (s, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 149.3, 149.1, 147.0, 132.5, 130.7, 130.4, 128.8, 128.3, 128.0, 126.8, 126.0, 125.7, 120.8, 102.1, 88.3, 28.8, 15.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_4O$ 329.1402; found 329.1402.

1-Azido-3-(4-methoxyphenyl)-1H-pyrano[4,3-b]quinolines (***2d***). The product was obtained as light brown needles (138.60 mg, 84% yield), mp 150−152 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 1H), 7.93 (s, 1H), 7.76−7.73 (m, 3H), 7.67−7.63 (m, 1H), 7.44−7.40 (m, 1H), 6.92 (dd, J = 8.7 and 1.8 Hz, 2H), 6.79 (s, 1H), 6.71 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 155.0, 146.9, 145.1, 133.1, 131.3, 130.2, 130.1, 128.7, 127.9, 125.5, 123.3, 121.0, 105.7, 102.8, 88.3, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_4O_2$ 331.1195; found 331.1189.

1-Azido-3-(3-methoxyphenyl)-1H-pyrano[4,3-b]quinolines (***2e***). The product was obtained as yellow crystals (122.10 mg, 74%

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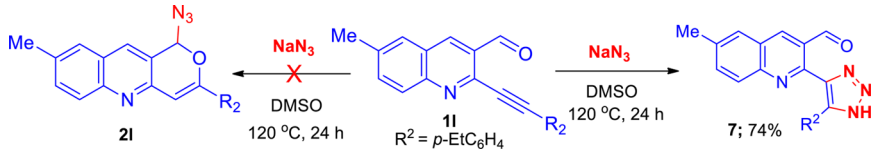
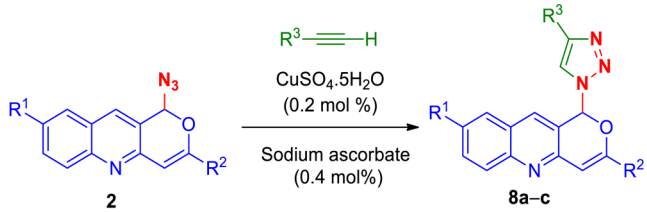
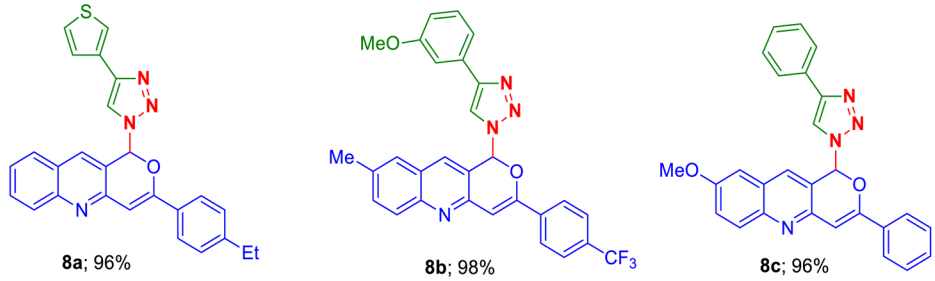
Scheme 6. Reaction of an Alkyne with Azide



Scheme 7. Synthesis of Trizolo-pyranoquinolines





yield), mp 140–142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 1H), 8.00 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.74–7.69 (m, 1H), 7.50–7.44 (m, 2H), 7.35–7.33 (m, 2H), 6.98 (dd, J = 8.3 and 2.2 Hz, 1H), 6.94 (s, 1H), 6.78 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 155.6, 148.3, 147.6, 136.2, 134.5, 133.0, 131.9, 128.5, 126.9, 120.8, 118.2, 116.4, 110.6, 103.2, 88.4, 55.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{19}H_{14}N_4O_2$ 331.1195; found 331.1203.

1-Azido-3-(o-tolyl)-1H-pyrano[4,3-b]quinolines (**2f**). The product was obtained as light yellow needles (100.48 mg, 64% yield), mp 115–117 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.00 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.71–7.67 (m, 1H), 7.50–7.44 (m, 2H), 7.31–7.26 (m, 1H), 7.22 (d, J = 6.8 Hz, 2H), 6.70 (s, 1H), 6.54 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 150.2, 149.0, 141.0, 132.6, 131.1, 130.7, 129.8, 129.7, 129.6, 129.3, 128.1, 126.1, 125.9, 125.8, 121.2, 106.8, 88.7, 20.8; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{19}H_{14}N_4O$ 315.1246; found 315.1238.

1-Azido-3-(4-(trifluoromethyl)phenyl)-1H-pyrano[4,3-b]quinoline (**2g**). The product was obtained as light yellow needles (125.0 mg, 67% yield), mp 160–162 °C, ^{1}H NMR (400 MHz, CDC_{l3}) δ 7.98 (d, J = 8.3 Hz, 1H), 7.95 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.69–7.58 (m, 3H), 7.46–7.42 (m, 1H), 6.96 (s, 1H), 6.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 149.1, 148.5, 136.3, 132.8, 130.9, 128.9, 128.0, 127.0, 126.5, 125.7 (q, J = 3.8 Hz, 1C), 120.8, 104.6, 88.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{19}H_{11}F_3N_4O$ 369.0963; found 369.0962.

1-Azido-3-(thiophen-3-yl)-1H-pyrano[4,3-b]quinoline (**2h**). The product was obtained as pale yellow crystals (110.16 mg, 72% yield), mp 140–142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 1H), 7.96 (s, 1H), 7.80–7.76 (m, 2H), 7.72–7.68 (m, 1H), 7.48–7.47 (m, 1H), 7.45–7.42 (m, 1H), 7.38–7.36 (m, 1H), 6.78 (s, 1H), 6.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 149.1, 135.5, 132.6, 130.7, 128.8, 128.0, 126.8, 126.0, 124.9, 124.6, 120.8, 102.6, 88.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{10}N_4OS$ 307.0654; found 307.0648.

1-Azido-3-cyclohexyl-1H-pyrano[4,3-b]quinolines (**2i**). The product was obtained as light orange crystals (99.45 mg, 65% yield), mp 140–142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 1H), 7.86 (s, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.64–7.61 (m, 1H), 7.41–7.37 (m, 1H), 6.51 (s, 1H), 6.12 (s, 1H), 2.25–2.19 (m, 1H), 1.98–1.93 (m, 2H), 1.79–1.76 (m, 2H), 1.37–1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 149.2, 148.8, 132.6, 130.5, 128.6, 127.9, 126.7, 125.7, 120.4, 101.5, 88.0, 42.4, 30.4, 26.0, 25.9; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{18}H_{18}N_4O$ 307.1559; found 307.1565.

1-Azido-1H-pyrano[4,3-b]quinoline (**2j**). The product was obtained as light yellow crystals (67.20 mg, 60% yield), mp 122–124 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 1H), 7.91 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.68–7.64 (m, 1H), 7.46–7.42 (m, 1H), 6.94 (d, J = 6.1 Hz, 1H), 6.55 (s, 1H), 6.29 (d, J = 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 133.1, 130.7, 128.9, 128.0, 127.0, 126.3, 107.6, 87.9; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_8N_4O$ 225.0776; found 225.0784.

1-Azido-8-methyl-3-phenyl-1H-pyrano[4,3-b]quinoline (**2k**). The product was obtained as dark yellow crystals (125.60 mg, 80% yield), mp 130–132 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.81–7.78 (m, 2H), 7.51–7.48 (m, 2H), 7.41–7.35 (m, 3H), 6.88 (s, 1H), 6.71 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 148.3, 147.7, 136.2, 133.1, 133.0, 131.9, 130.2, 128.7, 128.5, 127.0, 125.6, 120.8, 102.9, 88.4, 21.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{19}H_{14}N_4O$ 315.1246; found 315.1238.

1-Azido-3-(4-ethylphenyl)-8-methoxy-1H-pyrano[4,3-b]quinoline (**2l**). The product was obtained as white crystals (140.22 mg, 82% yield), mp 158–160 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 9.1 Hz, 1H), 7.82 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.48–7.47 (m, 2H), 7.21 (d, J = 7.6 Hz, 2H), 6.83 (s, 1H), 6.68 (s, 1H), 2.63 (q, J = 7.6 Hz, 2H), 2.45 (s, 3H), 1.19 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.5, 147.6, 146.8, 136.0, 132.9, 131.9, 130.5, 128.4, 128.2, 126.9, 126.8, 125.6, 120.8, 102.2, 88.3, 28.8, 21.5, 15.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{18}N_4O$ 343.1559; found 343.1573.

1-Azido-3-(4-(tert-butyl)phenyl)-8-methyl-1H-pyrano[4,3-b]-quinolines (**2m**). The product was obtained as light yellow needles (153.55 mg, 83% yield), mp 168–170 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.89 (m, 2H), 7.78 (d, J = 9.1 Hz, 2H), 7.55–7.53 (m, 2H), 7.47 (d, J = 8.3 Hz, 2H), 6.90 (s, 1H), 6.75 (s, 1H), 2.51 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.7, 148.5,

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147.6, 136.0, 132.9, 131.9, 128.4, 126.9, 125.7, 125.4, 120.8, 102.2, 88.4, 22.6, 21.5, 14.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}N_4O$ 371.1872; found 371.1869.

*1-Azido-3-(3-methoxyphenyl)-8-methyl-1H-pyrano[4,3-b]-quinoline (**2n**).* The product was obtained as light yellow crystals (134.16 mg, 78% yield), mp 138−140 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 4H), 7.65 (d, J = 8.4 Hz, 2H), 7.53−7.51 (m, 2H), 6.96 (s, 1H), 6.75 (s, 1H), 3.90 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 155.6, 148.3, 147.6, 136.2, 134.5, 133.0, 131.9, 129.7, 128.5, 126.9, 120.8, 118.2, 116.4, 110.6, 103.2, 88.4, 55.2, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_4O_2$ 345.1352; found 345.1352.

*1-Azido-8-methyl-3-(4-(trifluoromethoxy)phenyl)-1H-pyrano[4,3-b]quinolines (**2o**).* The product was obtained as yellow crystals (139.30 mg, 70% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.87 (m, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.52−7.50 (m, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.87 (s, 1H), 6.72 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 150.3, 147.8, 147.5, 136.4, 133.1, 132.0, 131.6, 128.4, 127.1, 126.9, 121.6, 120.9, 120.5, 119.1, 103.3, 88.3, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_3N_4O_2$ 399.1069; found 399.1077.

*1-Azido-8-methyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrano[4,3-b]quinolines (**2p**).* The product was obtained as pale yellow crystals (129.88 mg, 68% yield), mp 170−172 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 4H), 7.65 (d, J = 8.3 Hz, 2H), 7.53−7.51 (m, 2H), 6.96 (s, 1H), 6.75 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.7, 147.6, 136.6, 136.4, 133.2, 132.1, 128.6, 127.1, 127.0, 125.7 (q, J = 3.8 Hz, 1C), 120.7, 104.6, 88.4, 21.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_3N_4O$ 383.1120; found 383.1132.

*1-Azido-8-methyl-3-(thiophen-3-yl)-1H-pyrano[4,3-b]quinoline (**2q**).* The product was obtained as pale white crystals (120.0 mg, 75% yield), mp 135−137 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 1H), 7.89 (s, 1H), 7.797−7.790 (m, 1H), 7.55−7.53 (m, 2H), 7.44−7.43 (m, 1H), 7.39−7.37 (m, 1H), 6.78 (s, 1H), 6.72 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 148.2, 147.5, 136.1, 135.6, 133.0, 132.0, 128.3, 126.9, 126.7, 124.9, 124.5, 120.7, 102.5, 88.2, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{12}N_4OS$ 321.0810; found 321.0808.

*1-Azido-8-methoxy-3-phenyl-1H-pyrano[4,3-b]quinolines (**2r**).* The product was obtained as yellow crystals (133.78 mg, 81% yield), mp 95−97 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 9.1 Hz, 1H), 7.88 (s, 1H). 7.84 (dd, J = 8.3 and 2.2 Hz, 2H), 7.46−7.41 (m, 3H), 7.37 (dd, J = 9.1 and 2.2 Hz, 1H), 7.07−7.06 (m, 1H), 6.92 (s, 1H), 6.75 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 155.0, 146.9, 145.1, 133.1, 131.3, 130.2, 130.1, 128.7, 127.9, 125.5, 123.3, 121.0, 105.7, 102.8, 88.3, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_4O_2$ 331.1195; found 331.1189.

*1-Azido-8-methoxy-3-(o-tolyl)-1H-pyrano[4,3-b]quinoline) (**2s**).* The product was obtained as yellow needles (111.8 mg, 65% yield), mp 98−100 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.87 (m, 2H), 7.52−7.49 (m, 2H), 7.40−7.38 (m, 1H), 7.32−7.28 (m, 2H), 6.93−6.90 (m, 2H), 6.72 (s, 1H), 3.81 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 155.6, 148.3, 147.6, 136.2, 134.5, 133.0, 131.9, 129.7, 128.5, 126.9, 120.8, 118.2, 116.4, 110.6, 103.2, 88.4, 55.2, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_4O_2$ 345.1352; found 345.1352.

*1-Azido-3-(4-ethylphenyl)-8-methoxy-1H-pyrano[4,3-b]-quinolines (**2t**).* The product was obtained as light yellow crystals (150.36 mg, 84% yield), mp 106−108 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 9.1 Hz, 1H), 7.83 (s, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 9.1 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.01 (s, 1H), 6.84 (s, 1H), 6.69 (s, 1H), 3.86 (s, 3H), 2.63 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 155.4, 147.0, 146.8, 131.4, 130.5, 130.0, 128.2, 127.8, 125.6, 123.3, 121.0, 105.8, 101.9, 88.3, 55.6, 28.8, 15.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_4O_2$ 359.1508; found 359.1506.

*1-Azido-8-methoxy-3-(4-methoxyphenyl)-1H-pyrano[4,3-b] quinolines (**2u**).* The product was obtained as light yellow crystals (156.6 mg, 87% yield), mp 115−117 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 9.1 Hz, 1H), 7.83 (s, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.31 (dd, J = 9.1 and 2.2 Hz, 1H), 7.01 (d, J = 3.0 Hz, 1H), 6.90 (d, J = 9.1 Hz, 2H), 6.79 (s, 1H), 6.68 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 157.4, 155.2, 147.2, 132.2, 131.3, 129.9, 127.7, 127.2, 125.6, 123.3, 121.0, 114.1, 105.8, 100.9, 88.3, 55.6, 55.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_4O_3$ 361.1301; found 361.1292.

*1-Azido-8-methoxy-3-(4-(trifluoromethyl)phenyl)-1H-pyrano[4,3-b]quinolone (**2v**).* The product was obtained as pale white crystals (143.2 mg, 72% yield), mp 118−120 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.93 (m, 2H), 7.91−7.89 (m, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.39 (dd, J = 9.1 and 3.0 Hz, 1H), 7.07 (d, J = 2.2 Hz, 1H), 6.98 (s, 1H), 6.76 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.3, 146.2, 145.2, 136.5, 131.3, 130.4, 128.1, 125.6 (q, J = 3.8 Hz, 1C), 123.6, 121.0, 105.7, 104.6, 88.4, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_3N_4O_2$ 399.1069; found 399.1077.

*1-Azido-8-methoxy-3-(thiophen-3-yl)-1H-pyrano[4,3-b]-quinolines (**2w**).* The product was obtained as light yellow needles (132.7 mg, 79% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 9.1 Hz, 1H), 7.81 (s, 1H), 7.71 (s, 1H), 7.37−7.36 (m, 1H), 7.32−7.30 (m, 2H), 7.01 (d, J = 2.2 Hz, 1H), 6.70 (s, 1H), 6.65 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 151.6, 146.8, 145.0, 135.6, 131.3, 130.1, 127.8, 126.7, 124.8, 124.2, 123.3, 121.0, 105.8, 102.5, 88.2, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{12}N_4O_2S$ 337.0759; found 337.0753.

*1-Azido-3-(3,5-dimethoxyphenyl)-8-methoxy-1H-pyrano[4,3-b]-quinolines (**2x**).* The product was obtained as light yellow crystals (159.89 mg, 82% yield), mp 102−104 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 9.1 Hz, 1H), 7.90 (s, 1H), 7.40 (dd, J = 9.1 and 2.7 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 7.01 (d, J = 2.2 Hz, 2H), 6.92 (s, 1H), 6.76 (s, 1H), 6.55−6.54 (m, 1H), 3.93 (s, 3H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 157.6, 154.8, 146.7, 145.1, 135.0, 131.3, 130.2, 127.9, 123.4, 121.1, 105.7, 103.4, 103.3, 102.7, 88.3, 55.6, 55.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_4O_4$ 391.1406; found 391.1403.

General Procedure for the Synthesis of Azido-iodo-pyranoquinolines (3a−h). In an oven-dried reaction vial, 2-alkynyl-quinoline-3-carbaldehyde (0.5 mmol) was taken in acetonitrile (2 mL), and then NaN_3 (2.0 equiv), K_2CO_3 (2.5 equiv), and molecular iodine (2.5 equiv) were added. The resulting reaction mixture was heated at 70 °C for 0.5 h. Progression of the reaction was monitored by TLC, and when complete consumption of 2-alkynyl-quinoline-3-carbaldehyde occurred, the reaction mixture was cooled to room temperature. The solution was washed with a saturated solution of $Na_2S_2O_3$ and then extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography (hexane:ethyl acetate 98:2) to afford the corresponding product.

*1-Azido-4-iodo-3-phenyl-1H-pyrano[4,3-b]quinoline (**3a**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (180.62 mg, 85% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 1H), 7.89 (s, 1H), 7.78 (d, J = 8.3 Hz 1H), 7.72−7.68 (m, 3H), 7.50−7.46 (m, 1H), 7.42−7.40 (m, 3H), 6.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 148.9, 147.4, 135.8, 132.5, 130.7, 130.3, 130.2, 129.6, 128.0, 127.6, 127.3, 126.9, 120.2, 88.4, 78.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}IN_4O$ 427.0056; found 427.0029.

*1-Azido-4-iodo-3-(4-methoxyphenyl)-1H-pyrano[4,3-b]quinoline (**3b**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (205.20 mg, 90% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.3 Hz, 1H), 7.93 (s, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.79−7.74 (m, 3H), 7.55−7.51 (m, 1H), 6.98 (d, J = 8.3 Hz, 2H), 6.68 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 157.0, 148.9, 147.8, 132.3, 132.1, 130.7, 129.5, 127.9, 127.6, 127.2, 126.7, 120.3, 113.3, 88.3, 77.3, 55.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{13}IN_4O_2$ 457.0161; found 457.0158.

*1-Azido-4-iodo-8-methyl-3-(p-tolyl)-1H-pyrano[4,3-b]quinoline (**3c**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (197.49 mg, 87% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 9.16 Hz, 1H), 7.75 (s, 1H),

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7.60 (d, J = 8.3 Hz 2H), 7.51−7.49 (m, 2H), 7.20 (d, J = 7.6 Hz, 2H), 6.58 (s, 1H), 2.45 (s, 3H), 2.4 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 147.5, 146.7, 140.5, 136.9, 132.95, 132.89, 131.7, 130.1, 129.2, 128.6, 127.2, 126.4, 120.1, 88.4, 78.0, 21.6, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}IN_4O$ 454.0369; found 455.0365.

*1-Azido-4-iodo-3-(4-methoxyphenyl)-8-methyl-1H-pyrano[4,3-b] quinoline (**3d**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (220.90 mg, 88% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 9.16 Hz, 1H), 7.77 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.53−7.51 (m, 2H), 6.91 (d, J = 8.3 Hz, 2H), 6.59 (s, 1H), 3.80 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 156.5, 147.5, 147.0, 136.8, 133.0, 132.0, 131.7, 129.2, 127.9, 127.2, 126.5, 120.2, 113.2, 88.4, 76.7, 55.4, 21.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}IN_4O_2$ 471.0318; found 471.0310.

*1-Azido-4-iodo-8-methoxy-3-phenyl-1H-pyrano[4,3-b]quinoline (**3e**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (173.28 mg, 76% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 9.1 Hz, 1H), 7.74 (s, 1H), 7.70−7.68 (m, 2H), 7.39−7.38 (m, 3H), 7.33 (dd, 9.5 and 3.0 Hz, 1H), 7.02−7.01 (m, 1H), 6.58 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.1, 145.2, 145.0, 135.8, 131.1, 131.0, 130.2, 130.1, 128.4, 127.9, 123.4, 120.4, 105.1, 88.4, 78.5, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{13}IN_4O_2$ 457.0161; found 457.0158.

*1-Azido-4-iodo-8-methoxy-3-phenethyl-1H-pyrano[4,3-b]-quinoline (**3f**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (164.56 mg, 68% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 9.1 Hz, 1H), 7.64 (s, 1H), 7.28 (dd, 9.1 and 3.0 Hz, 1H), 7.23−7.22 (m, 4H), 7.15−7.13 (m, 1H), 6.96−6.95 (m, 1H), 6.38 (s, 1H), 381 (s, 3H), 3.08−2.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.8, 144.8, 144.3, 140.3, 130.93, 130.86, 128.5, 128.4, 128.1, 126.3, 123.2, 119.9, 105.2, 88.0, 78.9, 55.5, 39.7, 32.9, 29.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}IN_4O_2$ 485.0474; found 485.0467.

*1-Azido-4-iodo-3-phenyl-1H-pyrano[4,3-c]pyridine (**3g**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (142.50 mg, 76% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75−8.73 (m, 1H), 7.75 (d, 9.1 Hz, 2H), 7.51 (d, 6.8 Hz, 1H), 7.28−7.25 (m, 1H), 6.98 (d, 8.3 Hz, 2H), 6.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 155.4, 151.2, 148.5, 132.6, 132.0, 127.4, 122.5, 120.8, 113.3, 88.2, 75.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_9IN_4O$ 376.9899; found 376.9908.

*5-Azido-7-(4-(tert-butyl)phenyl)-8-iodo-5H-pyrano[4,3-b]pyridine (**3h**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (155.52 mg, 72% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74−8.72 (m, 1H), 7.73−7.70 (m, 2H), 7.51−7.47 (m, 3H), 7.26−7.24 (m, 1H), 6.55 (s, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.6, 151.2, 148.3, 132.6, 132.4, 130.0, 124.9, 122.6, 120.8, 88.2, 76.2, 34.9, 31.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}IN_4O$ 433.0525; found 433.0540.

General Procedure for the Synthesis of 3-Phenylbenzo[*b*]-[1,6]naphthyridine (4a−j). The 3-substituted benzonaphthyridines were prepared from azido-pyrano[4,3-*b*]quinoline **2** (0.50 mmol) in 2 mL of methanol in reaction vial. Then, 1.2 equiv of PPh_3 was added to the reaction mixture and stirred for 0.5 h. The solid compound precipitated and settled. Completion of the reaction was monitored by TLC, and after completion, the precipitate was filtered under vacuum and washed with hexane. Then, the final compounds were crystallized from chloroform.

*3-Phenylbenzo[b][1,6]naphthyridine (**4a**).* The product was obtained as yellow crystals (115.20 mg, 90% yield), mp 190−192 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.89 (s, 1H), 8.36 (s, 1H), 8.18−8.16 (m, 3H), 8.00 (d, J = 8.3 Hz, 1H), 7.84−7.81 (m, 1H), 7.69−7.66 (m, 1H), 7.55−7.51 (m, 1H), 7.41−7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 138.8, 137.3, 133.4, 133.3 132.6, 130.5, 130.4, 129.2, 129.03, 128.9, 128.5, 128.4, 127.2, 126.4, 121.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{12}N_2$ 257.1079; found 257.1076.

*3-(p-Tolyl)benzo[b][1,6]naphthyridine (**4b**).* The product was obtained as light yellow crystals (118.80 mg, 88% yield), mp 195−197 °C, ^{1}H NMR (400 MHz, $CDCl_3$) 9.59 (s, 1H), 8.96 (s, 1H), 8.41 (s, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 7.6 Hz, 2H), 8.08 (d, J = 8.3 Hz, 1H), 77.50−7.46 (m, 1H), 7.62−7.58 (m, 1H), 7.36 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 150.8, 150.3, 139.3, 137.3, 136.1, 135.2, 133.3, 132.5, 130.4, 129.7, 129.0, 128.6, 127.1, 126.3, 115.9, 22.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_2$ 271.1235; found 271.1235.

*3-(4-Methoxyphenyl)benzo[b][1,6]naphthyridine (**4c**).* The product was obtained as pale yellow crystals (120.12 mg, 84% yield), mp 188−190 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.92 (s, 1H), 8.34 (s, 1H), 8.23−8.19 (m, 3H), 8.05 (d, J = 8.3 Hz, 1H), 7.90−7.86 (m, 1H), 7.60−7.56 (m, 1H), 7.07 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 154.6, 153.6, 152.1, 150.5, 137.3, 133.3, 132.5, 131.4, 130.5, 129.3, 129.0, 128.5, 126.1, 120.9, 114.3, 55.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_2O$ 287.1184; found 287.1179.

*3-(Thiophen-3-yl)benzo[b][1,6]naphthyridine (**4d**).* The product was obtained as pale white crystals (115.28 mg, 88% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.93 (s, 1H), 8.29 (s, 1H), 8.23 (d, J = 8.3 Hz, 1H), 8.20−8.19 (m, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.91−7.87 (m, 1H), 7.82−7.80 (m, 1H), 7.61−7.58 (m, 1H), 7.48−7.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.1, 150.4, 150.0, 141.7, 137.4, 132.7, 129.3, 129.1, 126.9, 126.8, 126.3, 126.0, 124.8, 121.1, 115.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{10}N_2S$ 263.0643; found 263.0635.

*8-Methyl-3-phenylbenzo[b][1,6]naphthyridine (**4e**).* The product was obtained as yellow crystals (121.50 mg, 90% yield), mp 220−222 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.77 (s, 1H), 8.35 (s, 1H), 8.17−8.15 (m, 2H), 8.08 (d, J = 9.1 Hz, 1H), 7.74 (s, 1H), 7.68−7.65 (m, 1H), 7.49−7.45 (m, 2H), 7.40−7.37 (m, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 153.5, 151.0, 149.9, 139.0, 136.4, 136.0, 135.6, 129.1, 129.0, 128.9, 127.2, 127.0, 121.3, 116.7, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_2$ 271.1235; found 271.1235.

*8-Methyl-3-(p-tolyl)benzo[b][1,6]naphthyridine (**4f**).* The product was obtained as yellow crystals (123.54 mg, 87% yield), mp 202−204 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.80 (s, 1H), 8.38 (s, 1H), 8.14−8.12 (m, 3H), 7.78 (s, 1H), 7.48−7.45 (m, 1H), 7.34 (d, J = 7.6 Hz, 2H), 2.59 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 150.9, 149.8, 139.2, 136.3, 136.1, 135.6, 132.1, 132.0, 129.7, 128.9, 128.5, 128.4, 127.1, 121.2, 115.9, 21.7, 21.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_2$ 285.1392; found 285.1385.

*3-(4-Ethylphenyl)-8-methylbenzo[b][1,6]naphthyridine (**4g**).* The product was obtained as light yellow crystals (129.63 mg, 87% yield), mp 190−192 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.76 (s, 1H), 8.33 (s, 1H), 8.10−8.06 (m, 3H), 7.74 (s, 1H), 7.66 (dd, J = 8.3 and 1.5 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 2.53 (s, 3H). 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 150.0, 148.6, 145.5, 143.2, 136.4, 136.3, 136.1, 135.6, 129.0, 128.5, 127.2, 127.1, 127.0, 118.9, 116.0, 28.7, 21.8, 15.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_2$ 299.1548; found 299.1541.

*8-Methyl-3-(p-tolyl)benzo[b][1,6]naphthyridine (**4h**).* The product was obtained as light yellow crystals (128.70 mg, 90% yield), mp 98−100 °C,^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.79 (s, 1H), 8.42 (s, 1H), 8.22 (d, J = 7.6 Hz, 2H), 8.14 (d, J = 9.1 Hz, 1H), 7.60−7.53 (m, 3H), 7.46 (d, J = 6.8 Hz, 1H), 7.22 (d, J = 2.3 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.0, 153.0, 149.3, 148.8, 138.9, 134.5, 130.8, 128.9, 128.07, 127.96, 127.1, 121.4, 116.9, 103.7, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_2O$ 287.1184; found 287.1179.

*8-Methoxy-3-(4-(trifluoromethyl)phenyl)benzo[b][1,6]-naphthyridine (**4i**).* The product was obtained as pale white crystals (162.84 mg, 92% yield), mp 140−142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.72 (s, 1H), 8.38 (s, 1H), 8.26 (d, J = 8.3 Hz, 2H), 8.08 (d, J = 9.1 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.53 (dd, J = 9.5 and 2.3 Hz, 1H), 7.15 (d, J = 3.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 154.2, 151.2, 149.4, 148.5, 142.3, 134.5, 130.9, 128.4, 128.2, 127.3, 125.8 (q, J = 3.8 Hz, 1C), 122.2, 121.7,

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117.7, 103.6, 55.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_3N_2O$ 355.1058; found 355.1047.

*8-Methoxy-3-phenethylbenzo[b][1,6]naphthyridine (**4j**).* The product was obtained as light yellow crystals (138.1 mg, 88% yield), mp 195−197 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.68 (s, 1H), 8.03 (d, J = 9.9 Hz, 1H), 7.69 (s, 1H), 7.49 (dd, J = 9.5 and 3.0 Hz, 1H), 7.21−7.19 (m, 5H), 7.13 (d, J = 3.0 Hz, 1H), 3.93 (s, 3H), 3.28−3.25 (m, 2H), 315−3.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 156.7, 153.8, 148.9, 148.4, 141.4, 134.7, 132.9, 130.6, 129.7, 129.6, 127.9, 127.8, 125.9, 120.7, 118.7, 103.7, 55.7, 33.9, 35.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_2O$ 315.1497; found 315.1489.

General Procedure for the Synthesis of 4g-D1. 3-(4-Ethylphenyl)-8-methylbenzo[b][1,6]naphthyridine(**4g-D1**) was prepared from azido-pyrano[4,3-b]quinoline **3l** (0.50 mmol) in 2 mL of deuterated methanol MeOD in a reaction vial. Then, 1.2 equiv of PPh_3 was added to the reaction mixture, which was stirred for 0.5 h. The solid compound was precipitated and settled. After completion of the reaction, the precipitate was filtered under vacuum and washed with hexane. Then, the final compound was crystallized from chloroform.

*3-(4-Ethylphenyl)-8-methylbenzo[b][1,6]naphthyridine (**4g-D1**).* The product was obtained as yellow crystals (112.12 mg, 75% yield), mp 192−194 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56−9.55 (m, 1H), 8.83 (s, 1H), 8.17−8.12 (m, 3H), 7.80 (s, 1H), 7.75−7.72 (m, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.26 (s, 1H), 2.74 (q, J = 7.6 Hz, 2H), 2.60 (s, 3H), 1.30 (dt, J = 7.6 and 2.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 151.2, 151.0, 145.5, 136.6, 136.34, 136.26, 135.6, 129.0, 128.5, 127.4, 127.14, 127.08, 127.0, 119.6, 28.7, 21.8, 15.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}DN_2$ 300.1611; found 300.1611.

*General Procedure for the Synthesis of Naphthyridines from Azido-iodo-pyranopyridines (**6a** and **b**).* The 3-substituted naphthyridines were prepared from azido-pyranopyridine **3** (0.50 mmol) in 2 mL of methanol in a reaction vial. Then, 1.2 equiv of PPh_3 was added to the reaction mixture and stirred for 0.5 h. The solid compound was precipitated and settled. Completion of the reaction was monitored by TLC and, after completion, the precipitate was filtered under vacuum and washed with hexane. Then, the final compounds were crystallized from chloroform.

*3-Phenyl-2,6-naphthyridine (**6a**).* The product was obtained as light yellow crystals (82.40 mg, 80% yield), mp 195−197 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.69 (s, 1H), 8.03 (d, J = 9.1 Hz, 1H), 7.69 (s, 1H), 7.49 (dd, J = 9.5 and 2.2 Hz, 1H), 7.20−7.19 (m, 3H), 7.14−7.13 (m, 1H), 7.12−7.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 153.8, 144.5, 141.5, 134.6, 130.8, 128.5, 128.4, 127.83, 127.78, 126.0, 122.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{10}N_2$ 207.0922; found 207.0933.

*7-(4-(tert-Butyl)phenyl)-1,6-naphthyridine (**6b**).* The product was obtained as yellow crystals (102.18 mg, 78%), mp 165−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 9.05−9.04 (m, 1H), 8.31 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.45−7.42 (m, 1H), 1.36 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 154.8, 152.5, 152.3, 151.2, 135.8, 135.4, 126.8, 125.8, 122.4, 121.8, 117.1, 34.6, 31.2; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{18}N_2$ 262.1470; found 262.1470.

General Procedure for the Synthesis of 1*H*-1,2,3-Triazolyl Aldehydes 7. 1*H*-1,2,3-Triazolyl aldehydes **7** were prepared by using 0.5 mmol of **1l** and 1.0 mmol of NaN_3in 2 mL of DMSO in an oven-dried vial and stirring the reaction at 120 °C for 24 h. Progression of the reaction was monitored by TLC, and when complete consumption of substrate occurred, the reaction mixture was cooled to room temperature. After completion, the reaction mixture was diluted with H_2O, extracted with ethyl acetate (15 mL × 3), and dried over $NaSO_4$. The compound was purified by column chromatography in 10% ethyl acetate/hexane.

*2-(5-(4-Ethylphenyl)-1H-1,2,3-triazol-4-yl)-6-methylquinoline-3-carbaldehyde (**7**).* The product was crystallized in DCM/hexane and obtained as a yellow solid (126.54 mg, 74% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.70 (s, 1H), 8.08 (d, J = 9.1 Hz, 1H), 7.74 (s, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 2.61−2.55 (m, 5H), 1.17 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 148.1, 145.2, 138.5, 137.5, 135.3, 129.0, 128.22, 128.16, 128.07, 128.0, 127.2, 127.0, 126.1, 28.6, 21.6, 15.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_4O$ 343.1559; found 343.1529.

General Procedure for the Synthesis of Trizolo-pyranoquinolines (8a−c). The triazolo-pyranoquinolines were prepared from 0.50 mmol of **3,** 1.2 equiv of alkynes, 0.2 mol % $CuSO_4{\cdot}5H_2O$, and 0.4 mol % of sodium ascorbate in 2 mL of THF:H_2O (3:1) in a oven-dried vial and stirred at room temperature for 24 h. Reaction completion was monitored by TLC. After completion, the reaction mixture was extracted with ethyl acetate (15 mL × 3) and dried over $NaSO_4$. The compound was purified by column chromatography in 10% ethyl acetate/hexane. The highly fluorescent solid compound was obtained.

*3-(4-Ethylphenyl)-1-(4-(thiophen-3-yl)-1H-1,2,3-triazol-1-yl)-1H-pyrano[4,3-b]quinoline (**8a**).* The product was obtained as light brown crystals (209.28 mg, 96% yield), mp 202−204 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.3 Hz, 1H), 7.97 (s, 1H), 7.91 (s, 1H), 7.72−7.68 (m, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.528−7.524 (m, 1H), 7.46−7.42 (m, 1H), 7.41−7.40 (m, 1H), 7.24−7.16 (m, 4H), 6.96 (s, 1H), 2.59 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.4, 149.2, 147.5, 146.8, 144.7, 134.1, 131.4, 131.1, 130.3, 129.8, 128.7, 128.3, 128.2, 126.9, 126.5, 126.4, 125.9, 125.6, 121.7, 119.4, 117.8, 101.4, 84.7, 28.8, 15.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{20}N_4OS$ 437.1436; found 437.1438.

*1-(4-(3-Methoxyphenyl)-1H-1,2,3-triazol-1-yl)-8-methyl-3-(4-(trifluoromethoxy)phenyl)-1H-pyrano[4,3-b]quinoline (**8b**).* The product was obtained as light yellow crystals (259.70 mg, 98% yield), mp 168−170 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.91 (m, 3H), 7.70 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 1H), 7.48 (s, 1H), 7.44 (s, 1H), 7.18−7.14 (m, 4H), 6.94 (s, 1H), 6.76−6.73 (m, 1H), 3.72 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.5, 150.6, 148.4, 148.0, 147.7, 137.0, 133.8, 133.5, 131.0, 129.8, 128.6, 127.4, 127.1, 127.0, 121.0, 119.0, 118.2, 118.1, 114.7, 110.6, 102.8, 84.7, 55.3, 21.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{29}H_{21}F_3N_4O_3$ 531.1644; found 531.1661.

*8-Methoxy-3-phenyl-1-(4-phenyl-1H-1,2,3-triazol-1-yl)-1H-pyrano[4,3-b]quinoline (**8c**).* The product was crystallized in DCM/hexane and obtained as light yellow crystals (205.20 mg, 95% yield), mp 168−170 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.92 (m, 3H), 7.73−7.68 (m, 4H), 7.57 (s, 1H), 7.43−7.37 (m, 4H), 7.33−7.29 (m, 1H), 7.72−7.24 (m, 1H), 7.03−7.02 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 155.3, 148.5, 146.6, 145.4, 132.6, 132.4, 130.4, 130.2, 129.7, 128.8, 128.7, 128.4, 128.0, 125.72, 125.66, 124.2, 119.6, 118.0, 105.6, 102.2, 84.8, 55.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{20}N_4O_2$ 433.1665; found 433.1659.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01016.

Data and copies of ^{1}H, ^{13}C NMR, and HRMS spectra for target compounds (PDF)

Crystallographic information file for compound **3b** (CCDC reference number 1520520) (CIF)

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The authors declare no competing financial interest.

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