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Green Protocol for the Novel Synthesis of Thiochromeno[4,3-*b*]pyridine and Chromeno[4,3-*b*]pyridine Derivatives Utilizing a High-Pressure System

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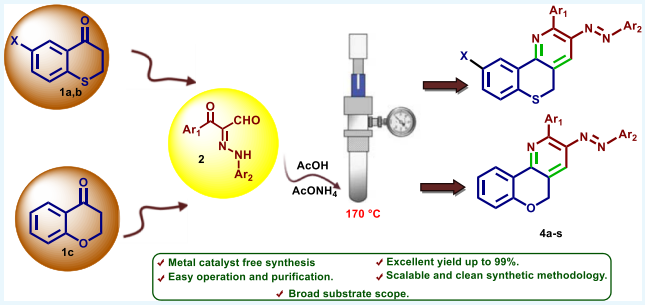
ABSTRACT: A suitable and effective Q-tube-assisted strategy for the synthesis of novel, unrivalled thiochromeno[4,3-*b*]pyridine and chromeno[4,3-*b*]pyridine derivatives has been sophisticated, which includes ammonium acetate-mediated cyclocondensation reactions between 3-oxo-2-arylhydrazonopropanals and heterobenzocyclic ketones such as thiochroman-4-one and chroman-4-one, respectively. The high-pressure Q-tube reactor was shown to be superior to conventional heating. Furthermore, this Q-tube reactor-assisted protocol is safe owing to facile pressing and sealing, a broad substrate scope, and simple work-up and purification processes, as well as being scalable and having a high atom economy. The proposed mechanistic route includes two sequential dehydrative stages. In this investigation, X-ray crystallographic analysis was performed to authenticate the targeted products.



INTRODUCTION

Fusion of chromene with pyridine can form two interesting classes of tricyclic systems such as chromeno[2,3-*b*]pyridines and chromeno[4,3-*b*]pyridines. The chromeno[2,3-*b*]pyridines had a wide range of pharmacological potentialities and were found in two anti-inflammatory commercial drugs: amlexanox[1,2] and pranoprofen (Figure 1).[3] Chromeno[4,3-*b*]-pyridine derivatives are also an interesting class of three-fused heterocycles with broad medicinal and biological importance.[4] Some chromeno[4,3-*b*]pyridine derivatives were reported to have potential anticancer,[5−9] anti-inflammatory,[10] antimicrobial,[11,12] and antifibrotic activities[13] and estrogen receptor β-selective ligands[14] as well as TNF-α inhibitors.[15] Four naturally occurring chromeno[4,3-*b*]pyridine derivatives (**A**−**D**) were isolated from a fungus *Phomopsis sp.* and exhibited good antioxidant activity (Figure 1).[16] Moreover, the thiochromeno-containing compounds demonstrated potent biological properties,[17] for example, and, not for all, they can act as antibacterial,[18−20] antioxidant,[20] antifungal,[21,22] antiviral,[23] antitumor,[24] and anticancer agents.[25] Furthermore, some members exhibited herbicidal[26,27] and insecticidal[28] activity.

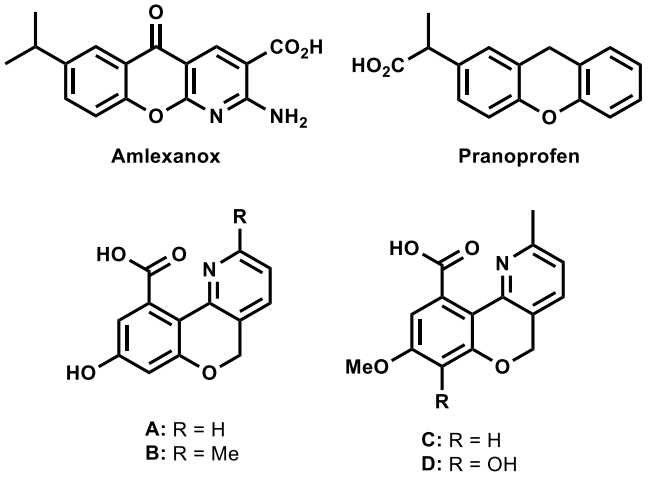


Figure 1. Some biologically active chromanone-containing compounds.

Due to their high biological activity, various synthetic approaches were examined by researchers for the preparation of the chromeno[4,3-*b*]pyridine skeletons. The reported synthetic routes included: (1) reaction of 3-arylidene-4-chromanone acyl pyridinium iodide salts,[5,8,9] (2) intramolecular heterocyclization of *O*-propargylated aromatic hydroxyaldehydes,[29] and (3) intramolecular Diels−Alder cycloadditions of *O*-propargylated azadienyl benzene[30] or 3-

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Scheme 1. Reactions of Thiochroman-4-one 1a and Arylhydrazonal 2a

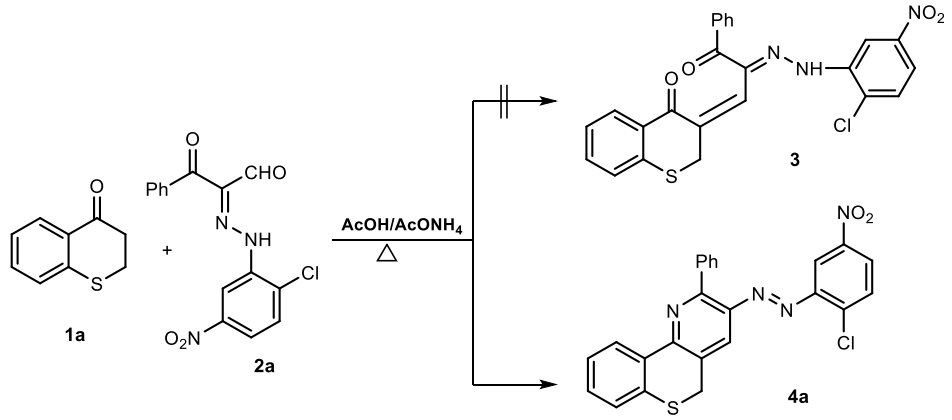
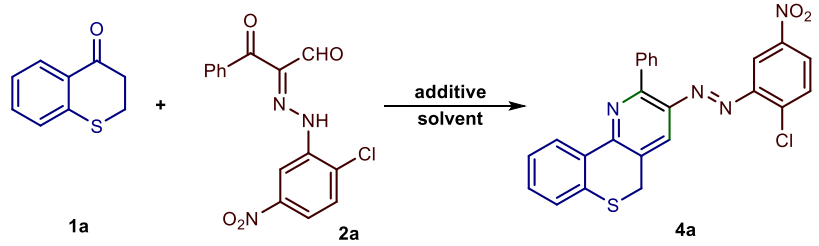


Table 1. Optimization of the Reaction between Thiochroman-4-one 1a and Arylhydrazonal 2a[a]



entry	solvent	additive	T (°C)	time	product (% yield)[c]
1	1,4-dioxane	$AcONH_4$	reflux	18 h	
2	DMF	$AcONH_4$	reflux	18 h	
3	CH_3CN	$AcONH_4$	reflux	18 h	
4	EtOH	$AcONH_4$	reflux	18 h	
5	propanol	$AcONH_4$	reflux	18 h	
6	AcOH	$AcONH_4$	reflux	6 h	45[a]
7	AcOH	$AcONH_4$	Q-tube (155 °C)[b]	45 min	82[a]
8	AcOH	$AcONH_4$	Q-tube (160 °C)	45 min	86
9	AcOH	$AcONH_4$	Q-tube (165 °C)	45 min	91
10	**AcOH**	**$AcONH_4$**	**Q-tube (170 °C)**	**45 min**	**93**

[a]Reaction conditions: thiochroman-4-one **1a** (5 mmol), arylhydrazonal **2a** (5 mmol), and ammonium acetate (10 mmol) in acetic acid (15 mL). [b]Temperature of the oil bath. [c]Isolated yield.

(*O*-propynyloxyphenyl)-triazine.[31] A little attention has been paid toward the biologically active thiochromeno[2,3-*b*]-pyridine derivatives[32,33] where few synthetic routes for some examples of thiochromeno[2,3-*b*]pyridines were published.[34−37] Apart from this, only one publication for the synthesis of the thiochromeno[4,3-*b*]pyridine skeleton was reported via a multicomponent reaction of thiochromanone with dimethylformamide-dimethylacetal and ethyl acetoacetate in the presence of ammonium acetate.[38] In continuation to our work which aimed at developing new synthetic routes for new heterocyclic compounds,[39−47] herein the Q-tube reactor was used in this study. In comparison with conventional heating, the Q-tube reactor has several characteristics and features[48−55] including (1) better yield and performance, (2) a cleaner product profile that means light color and less impurities and byproducts, (3) energy savings, lower reaction time, and higher reproducibility, and (4) cheaper and safer because the sealing and pressing are easy. Such promising unique features have encouraged us to utilize the Q-tube in our research to explore the impact of the high pressure on the reaction profile conducted in this study that aimed at synthesizing two very significant classes of compounds, namely, thiochromeno[4,3-*b*]pyridine and chromeno[4,3-*b*]pyridine derivatives.

RESULTS AND DISCUSSION

In an effort to develop a new greener strategy for synthesizing distinctive classes of thiochromeno[4,3-*b*]pyridine and chromeno[4,3-*b*]pyridine derivatives, we report herein an ammonium acetate-induced Q-tube-assisted system that efficiently provides these targeted compounds from easily obtainable precursors: 3-oxo-2-arylhydrazonopropanals and the heterobenzocyclic ketones (thiochroman-4-one and chroman-4-one) in a single-step reaction (Scheme 1). Our research began with an investigation of the reaction between the thiochroman-4-one (**1a**) and 2-[2-(2-chloro-5-nitrophenyl)-hydrazineylidene]-3-oxo-3-phenylpropanal (**2a**) as a model reaction (Table 1). Initially, it was observed that refluxing an equimolar mixture of thiochroman-4-one (**1a**) and arylhydrazonal **2a** in the presence of two equivalents of ammonium acetate in different solvents, such as dioxane, dimethylformamide (DMF), acetonitrile, ethanol, or propanol at atmospheric pressure for 18 h, did not give any products (Table 1, entries

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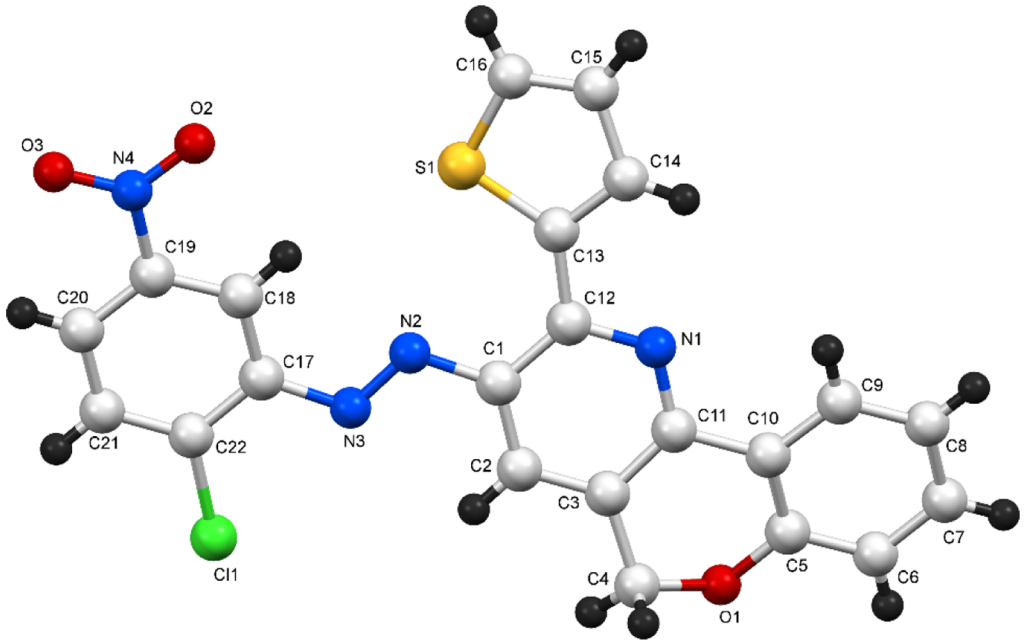

Figure 2. X-ray plot of single crystallographic data collected for **4s**.

1−5). However, conducting this model reaction in acetic acid as a solvent at reflux for 6 h afforded a product identified as 3-[(2-chloro-5-nitrophenyl)diazenyl]-2-phenyl-5*H*-thiochromeno[4,3-*b*]pyridine (**4a**) in 45% yield (Table 1, entry 6), but not the acyclic product **3** based on its spectroscopic data (Scheme 1). For example, the mass spectrometry (MS) and high-resolution MS (HRMS) spectrometric analyses of **4a** showed a molecular ion peak at 458 and an exact mass of *m*/*z* 458.0599 in complete agreement with the molecular composition of $C_{24}H_{15}ClN_4O_2S$ corresponding to **4a**. The ^{1}H NMR spectrum of **4a** in TFA-d revealed a set of resonance peaks in the region of 7.32−8.22 ppm due to 13 aromatic protons in addition to two singlet signals at 8.76 and 4.08 ppm corresponding to the pyridine H-4 and CH_2 protons, respectively. Moreover, the ^{13}C NMR spectra of **4a** showed 22 signals and were free of any C═O signals. The skeletal structure of this class of compounds was also confirmed by obtaining an X-ray single crystal structure of one member of this family, as shown in Figure 2.

The obtained results encouraged us to investigate the factors influencing the optimization of this reaction in order to synthesize the target compounds in a sustainable and green manner, as well as to highlight the benefits of the Q-tube pressure reactor as an affordable, cost-effective alternative to the expensive microwave reactor. Because of its simple sealing and pressure release features, the Q-tube pressure reactor enables a specific chemical reaction to be carried out safely under high pressure. This eliminates inadvertent explosions caused by abrupt increases in pressure when using a typical sealed-pressure tube. Thus, for comparison purposes, we carried out the abovementioned model reaction utilizing the Q-tube reactor by mixing equimolar amounts of thiochroman-4-one (**1a**) and arylhydrazonal **2a** and double equivalents of ammonium acetate in acetic acid using a 35 mL borosilicate-glass tube of the high-pressure Q-tube reactor with heating at 160 °C for 45 min to produce the same product **4a** in better yield (86%) (Table 1, entry 8). It is worthy to mention that doubling the quantities of the reactants also provided **4a** in a very comparable yield. Elongation of the reaction time did not improve the reaction yield. After the clear emphasis on the efficiency of Q-tube and acetic acid-ammonium acetate buffer system to conduct the targeted reaction (Table 1, entries 7−10), we studied the effect of temperature on the reaction course where temperature plays a vital role in determining the efficacy of reactions. Therefore, when the reaction was performed at 155 °C, the reaction yield was found to be 82% (Table 1, entry 7), and upon increasing the temperature to 165 °C and then to 170 °C, compound **4a** was obtained in 91 and 93% yields, respectively (Table 1, entries 9 and 10). Thus, the best temperature for conducting this reaction was 170 °C.

For diversity, further investigations have been conducted to assess the scope and limitations of the above reaction under the optimum condition obtained from the model experiment (entry 10, Table 1). For this target, an assortment of arylhydrazonals **2b−g** was synthesized to carry out their reactions with (thio)chroman-4-ones **1a−c**. Thus, heating an equimolar mixture of (thio)chroman-4-ones **1a,b** and arylhydrazonals **2** in the presence of a double equivalent of ammonium acetate in acetic acid at high pressure by using Q-tube at 170 °C led to the formation of the corresponding (thio)chromeno[4,3-*b*]pyridine derivatives **4**. During this study, it was observed that the nature of substituents on the *N*-aryl moiety of the arylhydrazonals has an influence on the reaction yields, where arylhydrazonals having an *N*-aryl moiety substituted with two electron-withdrawal substituents such as halogens (Cl and Br) and NO_2 provided the corresponding thiochromeno[4,3-*b*]pyridine products in excellent yields (Table 2). While for *N*-aryl moieties having one electron-withdrawal substituent (such as Cl or Br), the desired thiochromeno[4,3-*b*]pyridine derivatives were produced in a little bit lower yields. Furthermore, reaction of the arylhydrazonals **2** with the 6-chlorothiochroman-4-one **1c** afforded the corresponding thiochromeno[4,3-*b*]pyridine derivatives in very high yields (Table 2, entries 2,5,8,11, and 18). The exact structure of the chromeno[4,3-*b*]pyridine products and their

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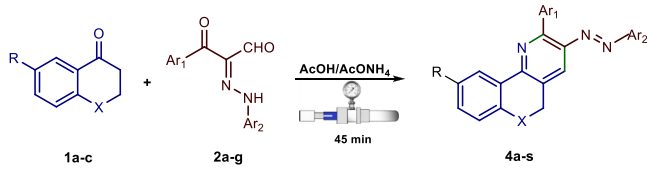
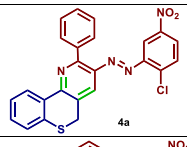
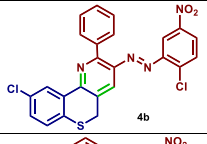
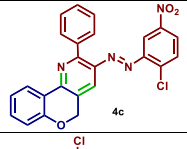
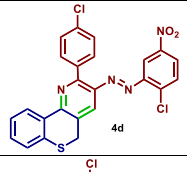
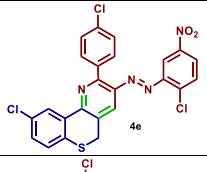
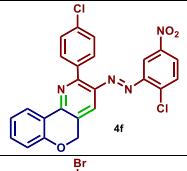
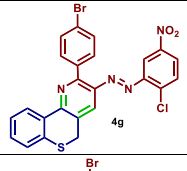
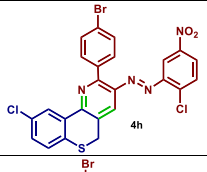
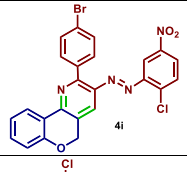
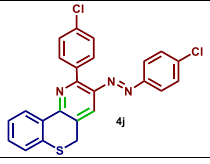
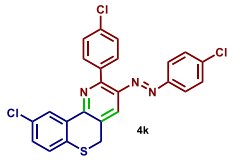
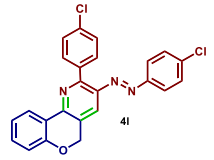
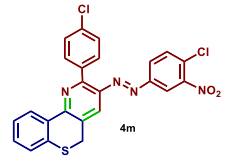
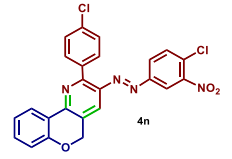
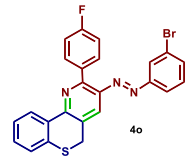
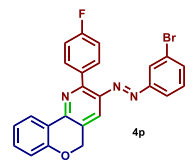
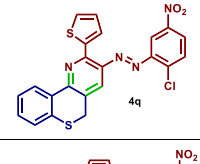
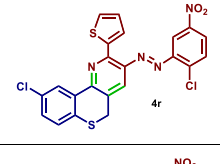
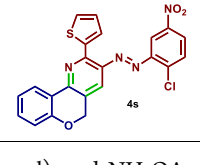
Table 2. Reactions of (Thio)chroman-4-ones 1a−c with Arylhydrazonals 2a−g Using Q-Tube[a]



1a-c 2a-g 4a-s

Entry	Ar_1	Ar_2	Product	Yield (%)[b]
1	Ph	2-Cl-5-NO_2-Ph	 4a	93
2	Ph	2-Cl-5-NO_2-Ph	 4b	89
3	Ph	2-Cl-5-NO_2-Ph	 4c	91
4	4-Cl-Ph	2-Cl-5-NO_2-Ph	 4d	94
5	4-Cl-Ph	2-Cl-5-NO_2-Ph	 4e	93
6	4-Cl-Ph	2-Cl-5-NO_2-Ph	 4f	90
7	4-Br-Ph	2-Cl-5-NO_2-Ph	 4g	95
8	4-Br-Ph	2-Cl-5-NO_2-Ph	 4h	91
9	4-Br-Ph	2-Cl-5-NO_2-Ph	 4i	92
10	4-Cl-Ph	4-Cl-Ph	 4j	88
11	4-Cl-Ph	4-Cl-Ph	 4k	85
12	4-Cl-Ph	4-Cl-Ph	 4l	87
13	4-Cl-Ph	4-Cl-3-NO_2-Ph	 4m	94
14	4-Cl-Ph	4-Cl-3-NO_2-Ph	 4n	91
15	4-F-Ph	3-Br-Ph	 4o	85
16	4-F-Ph	3-Br-Ph	 4p	84
17	C_4H_3S	2-Cl-5-NO_2-Ph	 4q	90
18	C_4H_3S	2-Cl-5-NO_2-Ph	 4r	88
19	C_4H_3S	2-Cl-5-NO_2-Ph	 4s	90

[a]Reaction conditions: a mixture of thiochroman-4-one and chroman-4-one (5 mmol), arylhydrazonals (5 mmol), and NH_4OAc (10 mmol) in AcOH (15 mL) was charged in the Q-tube reactor's 35 mL glass tube and heated for 45 min at 170 °C (oil bath). [b]Isolated yield.

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regioselectivities were unequivocally confirmed by measuring the X-ray single crystal of an exemplified compound, compound **4s**, as depicted in Figure 2 and Table 3.

Table 3. Some of the Selected Bond Angles and Bond Lengths for 4s

bond	bond length (Å)	bond	bond angle (°)
C1−C2	1.395 (4)	C3−C2−C1	119.8 (3)
C2−C3	1.366 (4)	C5−C10−C11	118.6 (3)
N3−C17	1.417 (3)	C11−N1−C12	118.7 (2)
N2−C1	1.407 (3)	C5−C10−C11	118.6 (3)
N1−C11	1.335 (3)	C1−C12−C13	125.2 (2)
N1−C12	1.330 (3)	N2−N3−C17	114.1 (2)
N2−N3	1.254 (3)	N3−N2−C1	114.3 (2)
C5−O1	1.374 (4)	C18−C19−N4	117.7 (3)
C4−O1	1.437 (4)	C5−O1−C4	116.2 (2)

Scheme 2 depicts the mechanistic approach for this Q-tube cyclocondensation process, which consists of two successive condensation reactions. In this manner, the enol form of thiochroman-4-one or chroman-4-one (**1**) generated by AcOH-driven enolization was nucleophilically added to the arylhydrazonal aldehyde carbonyl-carbon to create the adduct **A**, which forms the alkylidene intermediate **B** by losing one water molecule. This intermediate was then transformed to the nonisolable intermediate **C** in the presence of ammonium acetate. The NH_2 moiety targeted thiochroman-4-one or chroman-4-one (1) carbonyl carbon in the second nucleophilic addition to generate the adduct **D**, which lost the second water molecule to produce the targeted compound **4**.

CONCLUSIONS

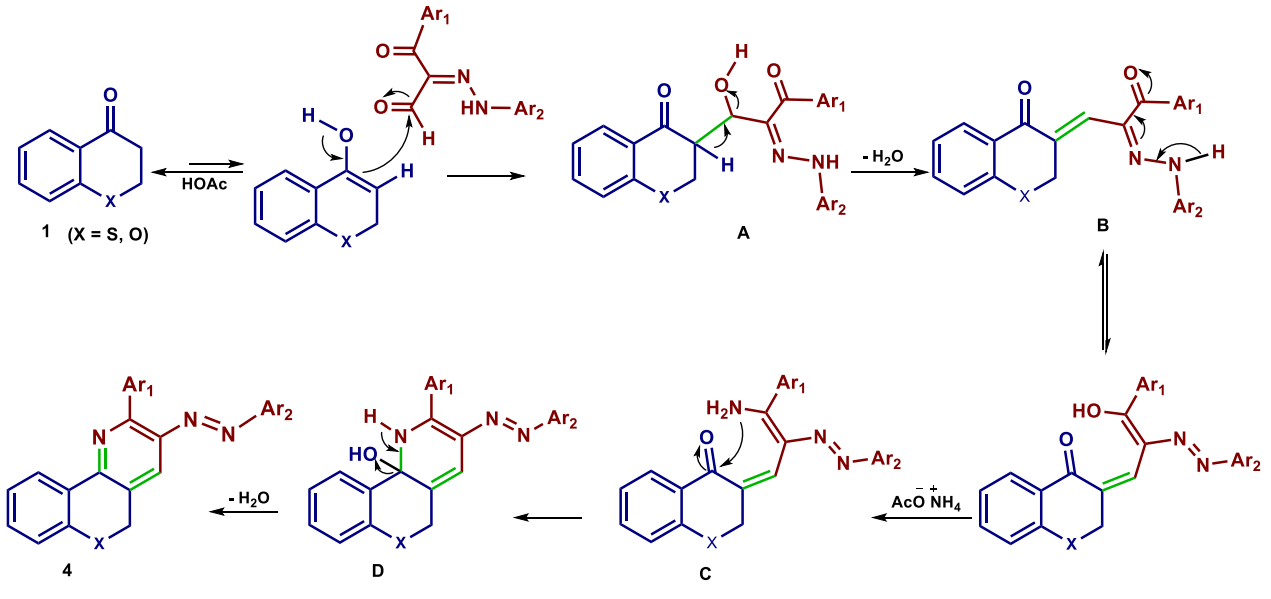
In conclusion, the abovementioned research study developed an efficient high-pressure Q-tube-assisted methodology for synthesizing an unparalleled series of thiochromeno[4,3-*b*]pyridine and chromeno[4,3-*b*]pyridine derivatives through ammonium acetate-mediated cyclocondensation reactions of 3-oxo-2-arylhydrazonopropanals with thiochroman-4-one and chroman-4-one precursors, respectively, by using the high-pressure Q-tube reactor as a secure, efficient, and environmentally benign tool.

EXPERIMENTAL SECTION

General. Melting points were measured using an uncorrected Griffin melting point equipment. KBr discs and a Jasco FTIR-6300 spectrophotometer were used to record IR spectra. On a Bruker DPX 600 superconducting NMR spectrometer, 1H NMR (600 MHz) and 13C NMR (150 MHz) spectra were recorded at 25 °C using TFA-d as the solvent and TMS as an internal standard. Chemical shifts () were reported in parts per million (ppm). A high-resolution gas chromatography (GC)−MS (DFS) thermos spectrometer at 70.1 eV and a magnetic sector mass analyzer were used to record low-resolution electron impact mass spectra [MS (EI)] and high-resolution electron impact mass spectra [HRMS (EI)]. Thin-layer chromatography (TLC) was used to track the progress of the reactions and assess the homogeneity of the products. The reactions were carried out with the help of a Q-tube kit from Q Labtech (distributed by Sigma-Aldrich), which included a stainless-steel adapter with a pressure gauge (300 psi), a needle adapter, a borosilicate glass pressure tube (35 mL), a Teflon sleeve, PTFE-faced silicone septa, and a catch bottle. A Bruker X8 Prospector diffractometer was used to acquire X-ray crystallographic data.

Cyclocondensation Reactions between (Thio)-chroman-4-ones 1a−c and Arylhydrazonals 4a−s. *General Procedure.* A mixture of (thio)chroman-4-ones **1a−c** (5 mmol), arylhydrazonals **2a−g** (5 mmol), NH_4OAc (10 mmol), and glacial AcOH (15 mL) was charged in the glass tube (35 mL) of the Q-tube reactor, and then, a septa was mounted on the top of each tube and the required cap and pressure adapter were utilized. The mixture was heated for 45 min at 170 °C (oil bath). The progress of each reaction was tracked utilizing GC−MS and TLC. After cooling to room temperature, the formed solid products were filtered off, washed with EtOH, and re-crystallized from the proper solvent (as shown below) to provide the thiochromeno[4,3-*b*]pyridine and chromeno[4,3-*b*]pyridine systems as pure products.

Scheme 2. Mechanistic Approach for the Formation of Compound 4



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*(E)-3-[(2-Chloro-5-nitrophenyl)diazenyl]-2-phenyl-5H-thiochromeno[4,3-b]pyridine (**4a**).* Recrystallized from the EtOH/DMF mixture (1:2) as orange crystals, yield: 2.10 g (93%), m.p. 246−247 °C; IR (KBr): ν/cm^{-1} 1593 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.08 (s, 2H, CH_2), 7.32 (td, J = 7.8, 1.8 Hz, 1H, Ar−H), 7.45−7.50 (m, 2H, Ar−H), 7.54 (t, J = 7.8 Hz, 2H, Ar−H), 7.63 (t, J = 7.8 Hz, 1H, Ar−H), 7.64−7.70 (m, 3H Ar−H), 8.05 (d, J = 7.8 Hz, 1H, Ar−H), 8.17−8.22 (m, 2H, Ar−H), 8.76 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.93 (CH_2), 115.53, 127.53, 129.58, 129.98, 130.45, 130.48, 131.74, 132.28, 133.42, 134.36, 135.19, 135.81, 136.46, 137.65, 143.35, 147.26, 147.85, 149.45, 151.21, 152.39, 156.03; MS (EI): m/z (%) 460 (M^+ + 2, 26.10), 459 (M^++1, 33.08), 458 (M^+, 63.14), 457 (M^+ − 1, 45.91). HRMS (EI): m/z calcd for $C_{24}H_{15}ClN_4O_2S$ (M^+), 458.0599; found, 458.0599.

*(E)-9-Chloro-3-[(2-chloro-5-nitrophenyl)diazenyl]-2-phenyl-5H-thiochromeno[4,3-b]pyridine (**4b**).* Recrystallized from the dioxane/DMF mixture (1:1) as orange crystals, yield: 2.17 g (89%), m.p. 249−250 °C; IR (KBr): ν/cm^{-1} 1595 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.22 (s, 2H, CH_2), 7.56−7.58 (m, 2H, Ar−H), 7.68 (t, J = 7.8 Hz, 2H, Ar−H), 7.77−7.79 (m, 3H, Ar−H), 7.83 (dd, J = 7.8, 1.2 Hz, 1H, Ar−H), 8.21 (d, J = 1.2 Hz, 1H, Ar−H), 8.34−8.36 (m, 2H Ar−H), 8.90 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 32.31 (CH_2), 115.90, 129.04, 129.85, 130.49, 130.55, 132.08, 133.63, 133.77, 134.95, 135.57, 136.82, 137.28, 137.63, 141.94, 147.73, 148.68, 149.82, 151.54, 151.56, 156.88; MS (EI): m/z (%) 494 (M^++2, 79.68), 493 (M^+ + 1, 86.11), 492 (M^+, 100.00), 491 (M^+ − 1, 85.94). HRMS (EI): m/z calcd for $C_{24}H_{14}Cl_2N_4O_2S$ (M^+), 492.0209; found, 492.0210.

*(E)-3-[(2-Chloro-5-nitrophenyl)diazenyl]-2-phenyl-5H-chromeno[4,3-b]pyridine (**4c**).* Recrystallized from the EtOH/DMF mixture (1:1) as orange crystals, yield: 2.00 g (91%), m.p. 276−277 °C; IR (KBr): ν/cm^{-1} 1589 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 5.44 (s, 2H, CH_2), 7.14 (d, J = 8.4 Hz, 1H, Ar−H), 7.20 (t, J = 8.4 Hz, 1H, Ar−H), 7.59−7.63 (m, 3H, Ar−H), 7.68−7.70 (m, 3H Ar−H), 7.74 (d, J = 8.4 Hz, 1H, Ar−H), 8.05 (dd, J = 7.8, 1.8 Hz, 1H, Ar−H), 8.24−8.26 (m, 2H, Ar−H), 8.71 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 68.80 (CH_2), 115.34, 115.90, 121.69, 126.77, 126.79, 129.71, 130.22, 131.48, 132.38, 133.15, 133.17, 134.96, 135.64, 141.05, 147.02, 147.50, 149.25, 149.69, 150.97, 156.19, 161.78; MS (EI): m/z (%) 444 (M^+ + 2, 30.05), 443 (M^++1, 46.39), 442 (M^+, 94.02), 441 (M^+ − 1, 85.79). HRMS (EI): m/z calcd for $C_{24}H_{15}ClN_4O_3$ (M^+), 442.0827; found, 442.0822.

*(E)-3-[(2-Chloro-5-nitrophenyl)diazenyl]-2-(4-chlorophenyl)-5H-thiochromeno[4,3-b]pyridine (**4d**).* Recrystallized from the dioxane/DMF mixture (2:1) as orange crystals, yield: 2.30 g (94%), m.p. 253−254 °C; IR (KBr): ν/cm^{-1} 1595 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.42 (s, 2H, CH_2), 7.67 (td, J = 7.8, 1.8 Hz, 1H, Ar−H), 7.80−7.86 (m, 4H, Ar−H), 7.96 (d, J = 8.4 Hz, 2H, Ar−H), 8.04 (d, J = 7.8 Hz, 1H, Ar−H), 8.37 (d, J = 7.8 Hz, 1H, Ar−H), 8.53−8.55 (m, 2H, Ar−H), 9.10 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.99 (CH_2), 115.43, 127.47, 128.78, 129.64, 130.12, 130.47, 132.12, 132.33, 134.45, 134.74, 135.29, 136.85, 137.79, 143.26, 143.50, 147.40, 147.83, 149.44, 151.18, 152.69, 154.81; MS (EI): m/z (%) 494 (M^+ + 2, 68.59), 493 (M^++1, 73.04), 492 (M^+, 100.00), 491 (M^+ − 1, 67.89). HRMS (EI): m/z calcd for $C_{24}H_{14}Cl_2N_4O_2S$ (M^+), 492.0209; found, 492.0209.

*(E)-9-Chloro-3-[(2-chloro-5-nitrophenyl)diazenyl]-2-(4-chlorophenyl)-5H-thiochromeno-[4,3-b]pyridine (**4e**).* Recrystallized from the dioxane/DMF mixture (1:1) as orange crystals, yield: 2.41 g (93%), m.p. 262−263 °C; IR (KBr): ν/cm^{-1} 1593 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.15 (s, 2H, CH_2), 7.49−7.50 (m, 2H, Ar−H), 7.59 (d, J = 8.4 Hz, 2H, Ar−H), 7.69 (d, J = 8.4 Hz, 2H, Ar−H), 7.78 (d, J = 9.0 Hz, 1H, Ar−H), 8.14 (d, J = 1.8 Hz, 1H, Ar−H), 8.28−8.31 (m, 2H, Ar−H), 8.84 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.51 (CH_2), 114.97, 127.96, 128.15, 129.07, 129.77, 131.65, 132.82, 134.20, 134.22, 134.80, 136.33, 136.47, 136.90, 141.23, 143.06, 146.99, 147.82, 148.99, 150.69, 150.98, 154.85; MS (EI): m/z (%) 528 (M^++2, 98.92), 527 (M^+ + 1, 86.23), 526 (M^+, 92.04), 525 (M^+ − 1, 100.00). HRMS (EI): m/z calcd for $C_{24}H_{13}Cl_3N_4O_2S$ (M^+), 525.9819; found, 525.9818.

*(E)-3-[(2-Chloro-5-nitrophenyl)diazenyl]-2-(4-chlorophenyl)-5H-chromeno[4,3-b]pyridine (**4f**).* Recrystallized from the dioxane/DMF mixture (1:1) as orange crystals, yield: 2.12 g (90%), m.p. 260−261 °C; IR (KBr): ν/cm^{-1} 1590 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 5.73 (s, 2H, CH_2), 7.43 (d, J = 7.8 Hz, 1H, Ar−H), 7.49 (t, J = 7.8 Hz, 1H, Ar−H), 7.86 (d, J = 8.4 Hz, 2H, Ar−H), 7.91 (t, J = 7.8 Hz, 1H, Ar−H), 7.95 (d, J = 8.4 Hz, 2H, Ar−H), 8.04 (d, J = 9.0 Hz, 1H, Ar−H), 8.33 (dd, J = 7.8, 1.8 Hz, 1H, Ar−H), 8.52−8.55 (m, 2H, Ar−H), 9.00 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 69.00 (CH_2), 115.42, 116.04, 121.93, 126.98, 127.05, 128.74, 130.00, 132.04, 132.68, 133.74, 134.69, 135.23, 141.40, 143.24, 147.31, 147.66, 149.41, 150.16, 151.12, 155.11, 162.08; MS (EI): m/z (%) 478 (M^+ + 2, 58.90), 477 (M^++1, 76.05), 476 (M^+, 94.01), 475 (M^+ − 1, 84.02). HRMS (EI): m/z calcd for $C_{24}H_{14}Cl_2N_4O_3$ (M^+), 476.0437; found, 476.0436.

*(E)-2-(4-Bromophenyl)-3-[(2-chloro-5-nitrophenyl)-diazenyl]-5H-thiochromeno[4,3-b]pyridine (**4g**).* Recrystallized from the dioxane/DMF mixture (1:1) as orange crystals, yield: 2.50 g (95%), m.p. 248−249 °C; IR (KBr): ν/cm^{-1} 1593 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.14 (s, 2H, CH_2), 7.41 (t, J = 7.8 Hz, 1H, Ar−H), 7.56−7.61 (m, 4H, Ar−H), 7.73−7.78 (m, 3H, Ar−H), 8.10 (d, J = 7.8 Hz, 1H, Ar−H), 8.26−8.28 (m, 2H, Ar−H), 8.83 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.57 (CH_2), 115.03, 127.02, 128.77, 129.21, 129.69, 130.04, 130.90, 131.90, 133.99, 134.30, 134.77, 134.85, 136.43, 137.37, 143.07, 146.99, 147.35, 149.01, 150.76, 152.28, 154.49; MS (EI): m/z (%) 538 (M^++2, 100.00), 537 (M^+ + 1, 77.05), 536 (M^+, 66.28), 535 (M^+ − 1, 39.07). HRMS (EI): m/z calcd for $C_{24}H_{14}BrClN_4O_2S$ (M^+), 535.9704; found, 535.9703.

*(E)-2-(4-Bromophenyl)-9-chloro-3-[(2-chloro-5-nitrophenyl)diazenyl]-5H-thiochromeno-[4,3-b]pyridine (**4h**).* Recrystallized from the dioxane/DMF mixture (1:1) as orange crystals, yield: 2.50 g (91%), m.p. 261−262 °C; IR (KBr): ν/cm^{-1} 1592 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.17 (s, 2H, CH_2), 7.51−7.52 (m, 2H, Ar−H), 7.61 (d, J = 9.0 Hz, 2H, Ar−H), 7.76−7.81 (m, 3H, Ar−H), 8.16 (s, 1H, Ar−H), 8.29−8.30 (m, 2H, Ar−H), 8.86 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.54 (CH_2), 115.00, 128.17, 128.45, 129.09, 129.14, 129.79, 131.06, 132.83, 134.25, 134.73, 134.82, 136.37, 136.48, 136.93, 141.25, 147.02, 147.77, 148.99, 150.71, 151.02, 154.93; MS (EI): m/z (%) 572 (M^++2, 100), 571 (M^+ + 1, 72.09), 570 (M^+, 54.78), 569 (M^+ − 1,

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32.05). HRMS (EI): m/z calcd for $C_{24}H_{13}BrCl_2N_4O_2S$ (M^+), 569.9314; found, 569.9309.

(E)-2-(4-Bromophenyl)-3-[(2-chloro-5-nitrophenyl)-diazenyl]-5H-chromeno[4,3-b]pyridine (**4i**). Recrystallized from the EtOH/DMF mixture (1:1) as orange crystals, yield: 2.37 g (92%), m.p. 252−253 °C; IR (KBr): ν/cm^{-1} 1588 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 6.07 (s, 2H, CH_2), 7.79 (d, J = 8.4 Hz, 1H, Ar−H), 7.84 (t, J = 8.4 Hz, 1H, Ar−H), 8.21 (d, J = 7.8 Hz, 2H, Ar−H), 8.26 (t, J = 8.4 Hz, 1H, Ar−H), 8.38−8.40 (m, 3H, Ar−H), 8.67 (dd, J = 8.4, 1.8 Hz, 1H, Ar−H), 8.87−8.91 (m, 2H, Ar−H), 9.35 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 68.95 (CH_2), 115.38, 115.96, 121.90, 126.95, 126.96, 129.10, 130.00, 131.27, 132.64, 133.70, 134.61, 135.10, 135.20, 141.41, 147.29, 147.57, 149.36, 150.14, 151.07, 155.16, 162.04; MS (EI): m/z (%) 522 (M^+ + 2, 97.81), 521 (M^+ + 1, 100.00), 520 (M^+, 72.14), 519 (M^+ − 1, 60.98). HRMS (EI): m/z calcd for $C_{24}H_{14}BrClN_4O_3$ (M^+), 519.9932; found 519.9936.

(E)-2-(4-Chlorophenyl)-3-[(4-chlorophenyl)diazenyl]-5H-thiochromeno[4,3-b]pyridine (**4j**). Recrystallized from dioxane as orange crystals, yield: 1.95 g (88%), m.p. 202−203 °C; IR (KBr): ν/cm^{-1} 1591 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.07 (s, 2H, CH_2), 7.33−7.37 (m, 3H, Ar−H), 7.45−7.53 (m, 4H, Ar−H), 7.60 (d, J = 8.4 Hz, 2H, Ar−H), 7.71 (d, J = 7.8 Hz, 2H, Ar−H), 8.01 (d, J = 7.8 Hz, 1H, Ar−H), 8.69 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.45 (CH_2), 127.06, 127.34, 128.55, 128.75, 129.90, 131.51, 131.80, 131.99, 133.74, 134.07, 134.10, 136.15, 136.85, 142.39, 142.50, 143.29, 147.92, 150.77, 153.12; MS (EI): m/z (%) 449 (M^++2, 44.53), 448 (M^+ + 1, 53.94), 447 (M^+, 63.09), 446 (M^+ − 1, 54.61). HRMS (EI): m/z calcd for $C_{24}H_{15}Cl_2N_3S$ (M^+), 447.0358; found, 447.0359.

(E)-9-Chloro-2-(4-chlorophenyl)-3-[(4-chlorophenyl)-diazenyl]-5H-thiochromeno[4,3-b]pyridine (**4k**). Recrystallized from the dioxane/DMF mixture (2:1) as orange crystals, yield: 2.00 g (85%), m.p. 191−192 °C; IR (KBr): ν/cm^{-1} 1593 (C═N); ^{1}H NMR (TFA-*d*, 400 MHz): δ 4.17 (s, 2H, CH_2), 7.42−7.47 (m, 2H, Ar−H), 7.60 (d, J = 8.4 Hz, 2H, Ar−H), 7.69 (d, J = 8.4 Hz, 2H, Ar−H), 7.75 (d, J = 8.4 Hz, 2H, Ar−H), 7.93 (d, J = 8.4 Hz, 2H, Ar−H), 8.14 (s, 1H, Ar−H), 8.79 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.42 (CH_2), 127.34, 127.67, 128.70, 130.83, 131.44, 131.97, 132.23, 132.61, 134.01, 134.09, 134.87, 136.11, 136.43, 140.58, 142.62, 143.49, 148.39, 149.49, 153.09; MS (EI): m/z (%) 483 (M^+ + 2, 91.97), 482 (M^+ + 1, 100.00), 481 (M^+, 87.12), 480 (M^+ − 1, 75.68). HRMS (EI): m/z calcd for $C_{24}H_{14}Cl_3N_3S$ (M^+), 480.9969; found, 480.9952.

(E)-2-(4-Chlorophenyl)-3-[(4-chlorophenyl)diazenyl]-5H-chromeno[4,3-b]pyridine (**4l**). Recrystallized from dioxane as orange crystals, yield: 1.85 g (87%), m.p. 228−229 °C; IR (KBr): ν/cm^{-1} 1591 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 6.10 (s, 2H, CH_2), 9.33 (d, J = 7.8 Hz, 1H, Ar−H), 9.39 (t, J = 7.8 Hz, 1H, Ar−H), 9.57 (d, J = 8.4 Hz, 2H, Ar−H), 9.75 (d, J = 8.4 Hz, 2H, Ar−H), 9.78−9.81 (m, 3H, Ar−H), 9.90 (d, J = 9.0 Hz, 2H, Ar−H), 10.17 (d, J = 7.8 Hz, 1H, Ar−H), 10.81 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 69.41 (CH_2), 116.57, 122.26, 127.06, 127.31, 128.22, 129.51, 132.35, 132.83, 133.00, 133.98, 134.99, 141.21, 143.22, 143.82, 148.67, 149.11, 153.97, 154.19, 161.97; MS (EI): m/z (%) 433 (M^+ + 2, 34.96), 432 (M^+ + 1, 50.04), 431 (M^+, 51.23), 430 (M^+ − 1, 58.12). HRMS (EI): m/z calcd for $C_{24}H_{15}Cl_2N_3O$ (M^+), 431.0587; found, 431.0584.

(E)-3-[(4-Chloro-3-nitrophenyl)diazenyl]-2-(4-chlorophenyl)-5H-thiochromeno[4,3-b]pyridine (**4m**). Recrystallized from the dioxane/DMF mixture (2:1) as orange crystals, yield: 2.30 g (94%), m.p. 214−215 °C; IR (KBr): ν/cm^{-1} 1594 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 4.70 (s, 2H, CH_2), 8.07−7.13 (m, 3H, Ar−H), 8.16 (d, J = 8.4 Hz, 2H, Ar−H), 8.21−8.26 (m, 2H, Ar−H), 8.35 (d, J = 8.4 Hz, 2H, Ar−H), 8.63 (d, J = 8.4 Hz, 1H, Ar−H), 8.93 (d, J = 2.4 Hz, 1H, Ar−H), 9.35 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.49 (CH2), 115.78, 127.96, 128.97, 130.04, 130.85, 131.52, 131.75, 133.38, 133.66, 133.96, 134.13, 135.70, 136.30, 137.36, 142.95, 142.95, 147.33, 150.63, 151.92, 152.92, 154.08; MS (EI): m/z (%) 494 (M^+ + 2, 68.61), 493 (M^+ + 1, 71.18), 492 (M^+, 100.00), 491 (M^+ − 1, 65.90). HRMS (EI): m/z calcd for $C_{24}H_{14}Cl_2N_4O_2S$ (M^+), 492.0209; found, 492.0209.

(E)-3-[(4-Chloro-3-nitrophenyl)diazenyl]-2-(4-chlorophenyl)-5H-chromeno[4,3-b]pyridine (**4n**). Recrystallized from the dioxane/DMF mixture (1:1) as orange crystals, yield: 2.15 g (91%), m.p. 241−242 °C; IR (KBr): ν/cm^{-1} 1591 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 5.46 (s, 2H, CH_2), 7.17 (d, J = 7.8 Hz, 1H, Ar−H), 7.23 (t, J = 7.8 Hz, 1H, Ar−H), 7.58 (d, J = 8.4 Hz, 2H, Ar−H), 7.63−766 (m, 3H, Ar−H), 7.69 (d, J = 8.4 Hz, 1H, Ar−H), 8.00 (dd, J = 8.4, 1.8 Hz, 1H, Ar−H), 8.06 (d, J = 7.8 Hz, 1H, Ar−H), 8.32 (d, J = 1.2 Hz, 1H, Ar−H), 8.70 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 68.74 (CH_2), 115.81, 121.68, 123.11, 126.74, 128.54, 130.37, 131.78, 132.12, 133.44, 134.38, 134.83, 135.81, 141.04, 142.97, 147.35, 149.60, 150.72, 153.09, 154.55, 161.72, 164.78; MS (EI): m/z (%) 478 (M^+ + 2, 61.04), 477 (M^+ + 1, 85.97), 476 (M^+, 100.00), 475 (M^+ − 1, 96.07). HRMS (EI): m/z calcd for $C_{24}H_{14}Cl_2N_4O_3$ (M^+) 476.0437, found 476.0431.

(E)-3-[(3-Bromophenyl)diazenyl]-2-(4-fluorophenyl)-5H-thiochromeno[4,3-b]pyridine (**4o**). Recrystallized from dioxane as orange crystals, yield: 2.00 g (85%), m.p. 212−213 °C; IR (KBr): ν/cm^{-1} 1590 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 5.10 (s, 2H, CH_2), 7.24−7.33 (m, 3H, Ar−H), 7.38 (t, J = 7.6 Hz, 1H, Ar−H), 7.49−7.60 (m, 3H, Ar−H), 7.70−7.73 (m, 2H, Ar−H), 7.77 (d, J = 8.0 Hz, 1H, Ar−H), 7.88 (s, 1H, Ar−H), 8.05 (d, J = 8.0 Hz, 1H, Ar−H), 8.70 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 31.45 (CH_2), (118.45, 118.67) (d^2, J_{CF} = 22.0 Hz), 125.59, 125.94, (126.26, 126.29) (d^4, J_{CF} = 3.0 Hz), 127.07, 128.04, 128.83, 129.93, 131.83, 132.88, 133.72, (135.37, 135.46) (d^3, J_{CF} = 9.0 Hz), 135.98, 136.92, 138.81, 142.47, 147.69, 150.99, 153.52, 155.49, (167.00, 169.54) (d^1, J_{CF} = 254.0 Hz); MS (EI): m/z (%) 477 (M^+ + 2, 96.03), 476 (M^+ + 1, 100.00), 475 (M^+, 90.15), 474 (M^+ − 1, 69.34). HRMS (EI): m/z calcd for $C_{24}H_{15}BrFN_3S$ (M^+), 475.0149; found, 475.0147.

(E)-3-[(3-Bromophenyl)diazenyl]-2-(4-fluorophenyl)-5H-chromeno[4,3-b]pyridine (**4p**). Recrystallized from dioxane as orange crystals, yield: 1.90 g (84%), m.p. 229−230 °C; IR (KBr): ν/cm^{-1} 1593 (C═N); ^{1}H NMR (TFA-*d*, 600 MHz): δ 5.40 (s, 2H, CH_2), 7.14 (d, J = 8.4 Hz, 1H, Ar−H), 7.19 (t, J = 8.4 Hz, 1H, Ar−H), 7.25−7.27 (m, 2H, Ar−H), 7.30 (t, J = 7.8 Hz, 1H, Ar−H), 7.58−7.61 (m, 2H, Ar−H), 7.69−7.71 (m, 2H, Ar−H), 7.75 (d, J = 8.4 Hz, 1H, Ar−H), 7.85 (t, J = 1.8 Hz, 1H, Ar−H), 8.00 (dd, J = 8.4, 1.8 Hz, 1H, Ar−H), 8.60 (s, 1H, pyridine H-4); ^{13}C{^{1}H} NMR (TFA-*d*, 150 MHz): δ 68.48 (CH_2), 115.64, (118.38, 118.53) (d^2, J_{CF} = 22.5 Hz), 121.34, 125.54, 125.83, 126.20, 126.23, 126.27, 126.41, 127.97, 132.00, (132.81, 132.83) (d^4, J_{CF} = 3.0 Hz), (135.33, 135.39)

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(d^3, J_{CF} = 9.0 Hz), 138.70, 140.34, 147.54, 148.38, 153.73, 155.40, 161.12, (167.39, 169.10) (d^1, J_{CF} = 256.5 Hz); MS (EI): m/z (%) 461 (M^+ + 2, 69.12), 460 (M^+ + 1, 100.00), 459 (M^+, 70.08), 458 (M^+ − 1, 80.26). HRMS (EI): m/z calcd for $C_{24}H_{15}BrFN_3O$ (M^+), 459.0377; found, 459.0377.

*(E)-3-[(2-Chloro-5-nitrophenyl)diazenyl]-2-(thiophen-2-yl)-5H-thiochromeno[4,3-b]pyridine (**4q**).* Recrystallized from dioxane as deep orange crystals, yield: 2.10 g (90%), m.p. 238−239 °C; IR (KBr): ν/cm^{-1} 1619 (C═N); ^1H NMR (TFA-*d*, 600 MHz): δ 4.10 (s, 2H, CH_2), 7.35 (t, J = 5.6 Hz, 1H, Ar−H), 7.46 (t, J = 7.2 Hz, 1H, Ar−H), 7.56−7.58 (m, 2H, Ar−H), 7.82 (d, J = 7.2 Hz, 1H, Ar−H), 8.05−8.14 (m, 4H, Ar−H), 8.35 (d, J = 7.2 Hz, 1H, Ar−H), 8.76 (s, 1H, pyridine H-4); $^{13}C\{^1H\}$ NMR (TFA-*d*, 150 MHz): δ 31.19, 126.89, 128.84, 129.76, 129.99, 130.24, 130.75, 131.90, 133.45, 134.26, 134.85, 135.31, 137.30, 137.74, 141.38, 143.05, 145.37, 147.24, 148.26, 149.14, 150.84, 151.73; MS (EI): m/z (%) 466 (M^++2, 40.21), 465 (M^+ + 1, 41.16), 464 (M^+, 100.00), 463 (M^+ − 1, 47.05); HRMS (EI): m/z calcd for $C_{22}H_{13}O_2N_4ClS_2$ (M^+), 464.0163; found ,464.0166.

*(E)-9-Chloro-3-[(2-chloro-5-nitrophenyl)diazenyl]-2-(thiophen-2-yl)-5H-thiochromeno[4,3-b]pyridine (**4r**).* Recrystallized from dioxane as deep orange crystals, yield: 2.15 g (88%), m.p. 250−251 °C; IR (KBr): ν/cm^{-1} 1616 (C═N); ^1H NMR (TFA-*d*, 600 MHz): δ 4.11 (s, 2H, CH_2), 7.34 (t, J = 4.8 Hz, 1H, Ar−H), 7.51−7.52 (m, 2H, Ar−H), 7.82 (d, J = 8.4 Hz, 1H, Ar−H), 8.06 (d, J = 4.8 Hz, 1H, Ar−H), 8.13 (s, 1H, Ar−H), 8.17 (d, J = 4.8 Hz, 1H, Ar−H), 8.36 (dd, J = 9.0, 2.4 Hz, 1H, Ar−H), 8.74 (d, J = 3.0 Hz, 1H, Ar−H),, 8.77 (s, 1H, pyridine H-4); $^{13}C\{^1H\}$ NMR (TFA-*d*, 150 MHz): δ 31.39, 128.26, 128.95, 129.69, 130.00, 130.89, 133.02, 133.85, 134.51, 135.01, 135.93, 136.58, 137.02, 141.42, 141.69, 146.04, 147.46, 148.90, 149.29, 150.71, 150.99; MS (EI): m/z (%) 500 (M^+ + 2, 71.98), 499 (M^+ + 1, 63.01), 498 (M^+, 100.00), 497 (M^+ − 1, 53.21); HRMS (EI): m/z calcd for $C_{22}H_{12}Cl_2N_4O_2S_2$ (M^+), 497.9773; found, 497.9776.

*(E)-3-[(2-Chloro-5-nitrophenyl)diazenyl]-2-(thiophen-2-yl)-5H-chromeno[4,3-b]pyridine (**4s**).* Recrystallized from dioxane as orange crystals, yield: 2.00 g (90%), m.p. 269−270 °C; IR (KBr): ν/cm^{-1} 1610 (C═N); ^1H NMR (TFA-*d*, 600 MHz): δ 5.42 (s, 2H, CH_2), 7.18 (d, J = 8.4 Hz, 1H, Ar-H), 7.28 (t, J = 8.4 Hz, 1H, Ar-H), 7.37 (d, J = 5.4 Hz, 1H, Ar-H), 7.68 (t, J = 8.4 Hz, 1H, Ar-H), 7.84 (d, J = 8.4 Hz, 1H, Ar-H), 8.07-8.09 (m, 2H, Ar-H), 8.13 (d, J = 5.4 Hz, 1H, Ar-H), 8.37 (d, J = 8.4 Hz, 1H, Ar-H), 8.68 (s, 1H, pyridine H-4), 8.77 (d, J = 2.4 Hz, 1H, Ar-H); $^{13}C\{^1H\}$ NMR (TFA-*d*, 150 MHz): δ 68.25, 115.29, 121.36, 126.21, 126.34, 129.57, 129.62, 130.53, 131.55, 134.71, 135.32, 140.80, 141.38, 145.13, 147.09, 148.44, 148.99, 149.14, 150.70, 152.25, 152.57, 161.46; MS (EI): m/z (%) 450 (M^++2, 37.12), 449 (M^+ + 1, 44.09), 448 (M^+, 95.18), 447 (M^+ − 1, 57.32); HRMS (EI): m/z calcd for $C_{22}H_{13}O_3N_4ClS$ (M^+), 448.0391; found, 448.0391. Crystal Data, moiety formula: $C_{22}H_{13}O_3N_4ClS$, M = 448.87, monoclinic, a = 7.4390(4) Å, b = 25.3934(11) Å, c = 10.4929(4) Å, V = 1962.88(16) Å^3, $\alpha = \gamma = 90°$, β = 97.990(3) °, space group: $P2_1/c$ (#14), Z = 4, D_{calc} = 1.519 g·cm^{-3}, No. of reflection measured: 3296, unique: 2483, θ_{max} = 66.06°, R1 = 0.0578 (CCDC 2110964).[56]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05347.

MS, HRMS, ^1H NMR, and ^{13}C NMR spectra for the reported compounds (PDF)

Crystallographic data for compound **4s** (CIF)

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Notes

The authors declare no competing financial interest.

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