Microwave-Assisted Expeditious Synthesis of Novel Benzo[*b*][1,8]-naphthyridine-3-carbonitriles

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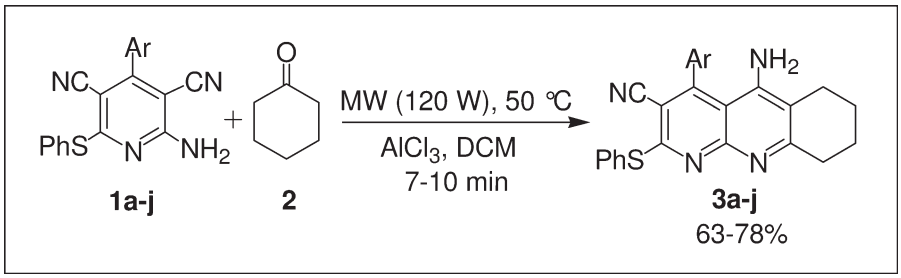

A rapid and facile method for the synthesis of novel 5-amino-2-sulfanyl tetrahydrobenzo[*b*][1,8]-naphthyridine-3-carbonitrile derivatives has been developed by the treatment of 2-amino-3,5-dicarbonitrile-6-sulfanyl pyridines with cyclohexanone in the presence of anhydrous aluminium chloride in dry dichloromethane under controlled microwave irradiation.

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INTRODUCTION

Naphthyridine derivatives are compounds of current interest due to their diverse biological activities including anti-tumor [1], anti-inflammatory [1d,2,3], antifungal [3], antibacterial [4], anticonvulsant [5], antihypertensive [6], and antiproliferative [7]. They also act as potential inhibitors of platelet aggregation, protein tyrosine kinases, topoisomerase I, and human immunodeficiency virus-1 (HIV-1) integrase [8–11] and are used for the diagnosis and treatment of human diseases such as acquired immune deficiency syndrome (AIDS) and allergies [12]. Recently, naphthyridines have been reported as label-free aptamer-based sensor using abasic site-containing DNA and nucleobase-specific fluorescence ligands [13]. 1,8-Naphthyridine-3-carbonitriles have been particularly identified as a new class of serotonin 5-HT_3 receptor antagonists [14]. Because of their biological and pharmacological importance, the synthesis of naphthyridine derivatives has attracted a great deal of current attention and a number of reports for the synthesis of such systems have appeared [14,15]. However, to the best of our knowledge, there exists no report on the synthesis of 5-amino-2-sulfanyl tetrahydrobenzo[*b*][1,8]-naphthyridine-3-carbonitriles, which may be much potent and useful products for further synthetic as well as biological studies.

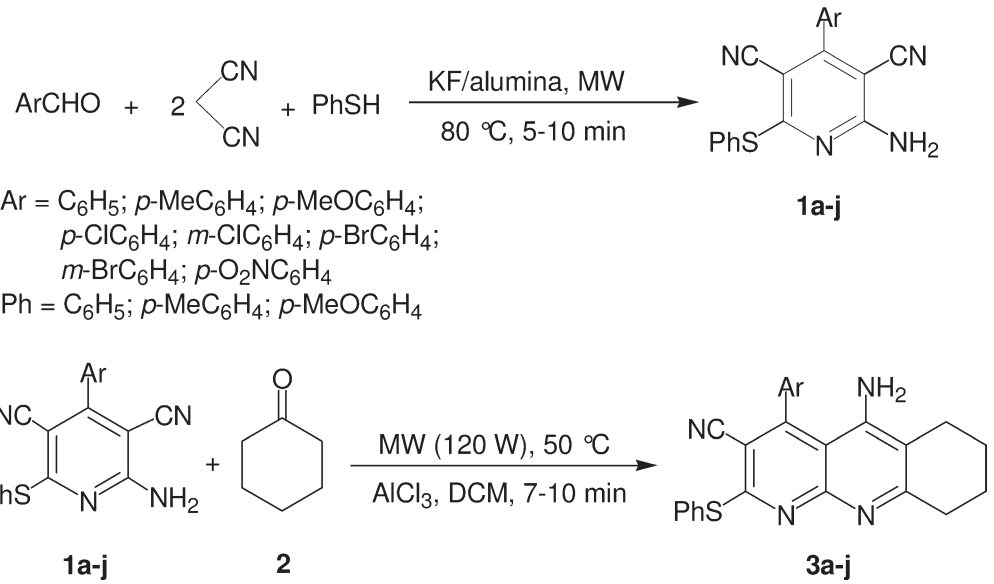
Microwave (MW) irradiation has evolved as a powerful method to perform organic synthesis with great success, particularly in the light of the current paradigm shift to ''Green Chemistry.'' It provides chemical processes with special attributes, such as enhanced reaction rates, higher yields of pure products, better selectivity, improved ease of manipulation, rapid optimization of reactions, and several eco-friendly advantages [16].

RESULTS AND DISCUSSION

Because of our interest on MW-assisted synthesis of heterocyclic compounds [17], we report herein an aluminum chloride catalyzed, expeditious procedure for the construction of novel 5-amino-2-sulfanyl tetrahydrobenzo[*b*][1,8]-naphthyridine-3-carbonitrile derivatives **3a–j** by the reaction of 2-amino-3,5-dicarbonitrile-6-sulfanyl pyridines **1a–j** with cyclohexanone **2** in dichloromethane under MW irradiation in reasonably good yield (63–78%; Scheme 1). The starting substrates, 2-amino-3,5-dicarbonitrile-6-sulfanyl pyridines **1a–j**, were prepared *via* a three-component reaction of aromatic aldehyde, malononitrile, and thiophenol using KF/alumina as catalyst in ethanol under controlled MW conditions [17a].

To screen the experimental conditions, a model reaction of 2-amino-4-phenyl-6-phenylsulfanylpyridine-3,5-dicarbonitrile **1a** with cyclohexanone **2** was carried out using various Lewis acids under conventional heating as well as under MW irradiation. The results are summarized in Table 1. When the reaction was carried out using anhydrous $AlCl_3$ (1.5 equiv) in DCM (2 mL), the desired naphthyridine **3a** was formed in 56% yield under conventional heating at reflux in 1.0 h and 74% yield under

Scheme 1



MW at 50°C in 7 min (Table 1, entry 5). Decreasing the molar proportion of $AlCl_3$ decreases the yield of the product considerably (Table 1, entries 1-4); however, an increase in the molar proportion (2.0 equiv) of $AlCl_3$ does not improve the product yield further (Table 1, entry 6). Switching to other Lewis acids such as $FeCl_3$, $ZnCl_2$, I_2, $InCl_3$, $Yb(OTf)_3$, $Sc(OTf)_3$, and Montmorillonite K 10 gave rise to very low yield or no formation of the product (Table 1, entries 10–16). It is worthwhile to mention that no anticipated product is formed in solvents such as ethanol, methanol, and acetonitrile (Table 1, entries 7–9).

Thus, it is concluded from the Table 1 that $AlCl_3$ in DCM (2 mL) under MW irradiation (120 W, 50°C) affords the optimum yield of the product with considerable reduction in reaction time. Further, increase of MW power and temperature did not improve the product yield.

Table 1

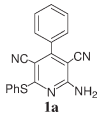
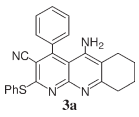
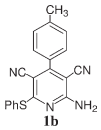
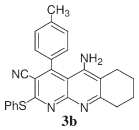
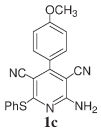
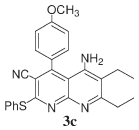
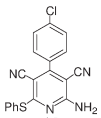
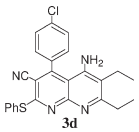
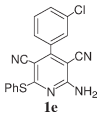
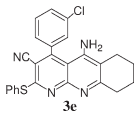
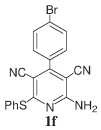
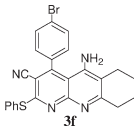
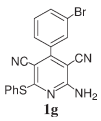
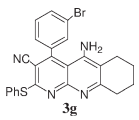
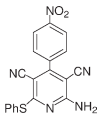
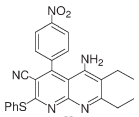
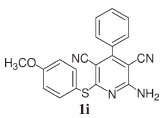
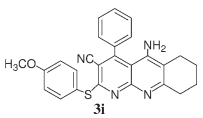
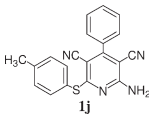
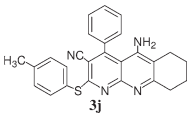
Optimization of reaction conditions for **3a**.

		Reaction conditions			
		Reflux		MW	
Entry	Lewis acid	Time (h)	Yield (%)	Time (min)	Yield (%)
1	$AlCl_3$ (0.5 equiv)	1.5	Trace	10	17
2	$AlCl_3$ (1.0 equiv)	1.5	20	10	42
3	$AlCl_3$ (1.1 equiv)	1.0	25	10	47
4	$AlCl_3$ (1.3 equiv)	1.0	41	7	63
5	$AlCl_3$ (1.5 equiv)	1.0	56	7	74
6	$AlCl_3$ (2.0 equiv)	1.0	55	7	74
7	$AlCl_3$ (1.5 equiv)[a]	2.0	–	10	–
8	$AlCl_3$ (1.5 equiv)[b]	2.0	–	10	–
9	$AlCl_3$ (1.5 equiv)[c]	2.0	–	10	–
10	$FeCl_3$(1.5 equiv)	1.5	30	8	53
11	$ZnCl_2$(2.0 equiv)	2.0	23	10	47
12	I_2 (1.0 equiv)	2.0	–	10	–
13	$InCl_3$ (20 mol %)	2.0	–	10	–
14	$Yb(OTf)_3$ (20 mol %)	1.5	–	10	–
15	$Sc(OTf)_3$ (20 mol %)	1.5	–	10	–
16	Montmorillonite K 10 (1.5 equiv)	2.0	–	10	–

[a] Reaction carried out in ethanol.
[b] Reaction carried out in methanol.
[c] Reaction carried out in acetonitrile.

Table 2

MW-assisted synthesis[a] of 5-amino-2-sulfanyl tetrahydrobenzo[*b*][1,8]-naphthyridine-3-carbonitriles.

Entry	Pyridine derivatives	Product	Time (min)	Yield[b] (%)	Mp (°C)
1	 **1a**	 **3a**	7	74	243–244
2	 **1b**	 **3b**	7	77	295–296
3	 **1c**	 **3c**	7	78	274–275
4	 **1d**	 **3d**	8	74	264–265
5	 **1e**	 **3e**	10	70	234–235
6	 **1f**	 **3f**	8	71	267–268
7	 **1g**	 **3g**	10	68	228–230
8	 **1h**	 **3h**	10	63	216–217
9	 **1i**	 **3i**	7	76	240–241
10	 **1j**	 **3j**	7	75	257–258

[a] MW heating (120 W, 50°C) using substituted pyridines (1 mmol) and cyclohexanone (1.2 mmol).
[b] Isolated yield based on recrystallization.

Under the optimized set of reaction conditions (Table 1, entry 5), various substituted pyridines **1** were allowed to undergo reaction with cyclohexanone **2** in a molar ratio of 1:1.2 with $AlCl_3$ (1.5 equiv) in dry DCM (2 mL) using safe pressure regulation 10-mL pressurized vial with ''snap-on'' cap under MW (120 W, 50°C) heating for 7–10 min. The results are given in Table 2. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of reaction, the mixture was poured into an ice-cold water contained in

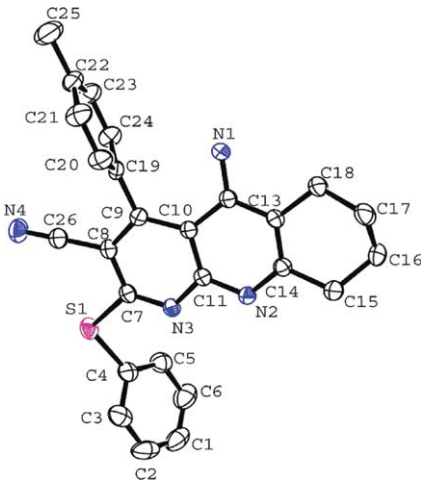


Figure 1. ORTEP diagram of compound **3b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a beaker and was extracted with DCM (3× 10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The resultant solid was purified by recrystallization from ethanol to obtain pure product **3** in moderate to good yield.

All the products **3a–j** are new and have been fully characterized on the basis of their IR, ^{1}H-NMR, ^{13}C-NMR, and elemental analyses. Single crystal X-ray analysis of one product, **3b**, conclusively confirmed the structures of these compounds. An Oak Ridge thermal ellipsoid plot (ORTEP) diagram of **3b** is shown in Figure 1 [18].

From the molecular structure, it is clear that the condensation of substituted pyridine derivatives and cyclohexanone results in the formation of products with three fused rings. Two of them are heteroaromatics having bond lengths 1.308–1.443 Å, which is in conformity with the reported range; whereas the third one is aliphatic having bond length 1.509–1.527 Å, corresponding to C—C single bond.

A mechanistic rationalization for this reaction is provided in Scheme 2. The reaction is initiated by the nucleophilic addition of NH_2 at the electrophilic carbonyl carbon followed by loss of water to give imine. Thus, the imine formed undergoes tautomerism to enamine, which then nucleophilically attacks at the cyano group with subsequent aromatization to provide the product **3**. The role of $AlCl_3$ is assumed to enhance the elecrtophilicity of the carbonyl and cyano carbons.

CONCLUSIONS

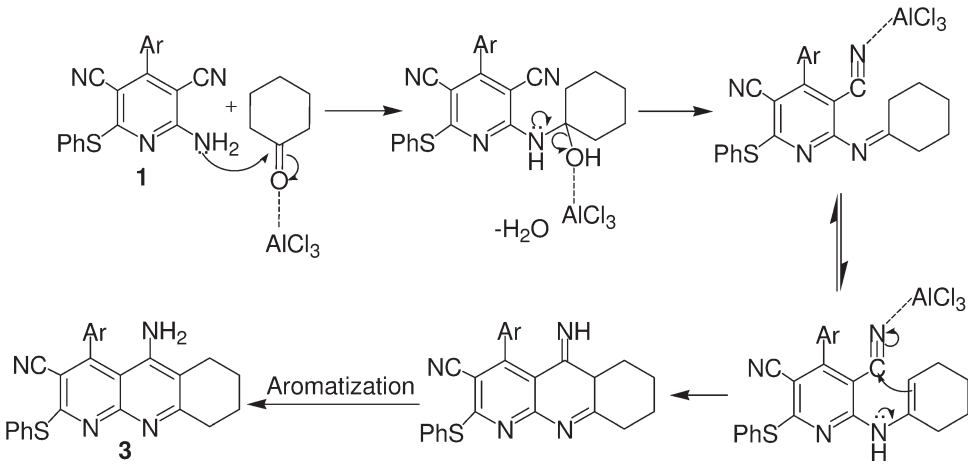
In conclusion, an expeditious synthesis of novel 5-amino-2-sulfanyl tetrahydrobenzo[*b*][1,8]-naphthyridine-3-carbonitriles in high purity and in good yields has been developed *via* cyclocondensation of 2-amino-3,5-dicarbonitrile-6-sulfanyl pyridines with cyclohexanone in dichloromethane using anhydrous $AlCl_3$ as catalyst under MW irradiation.

EXPERIMENTAL

Aluminum chloride (powder) and cyclohexanone were procured from E. Merck, Germany. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. NMR spectra were run on a JEOL AL300 FT-NMR spectrometer; chemical shifts are given in δ ppm, relative to tetramethylsilane (TMS) as internal standard. Elemental microanalysis was performed on Exeter Analytical Inc., Model CE-440 CHN Analyzer. Melting points were measured in open capillaries and are uncorrected. The X-ray diffraction measurements were carried out at 293 K on a CrysAlispro Oxford Diffractometer equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). The MW irradiation was effected using the CEM's Discover BenchMate single-mode MW synthesis system using safe pressure regulation 10-mL pressurized vials with ''snap-on'' cap.

General procedure for the synthesis of 3a–j. Substituted pyridine **1** (1 mmol), cyclohexanone **2** (1.2 mmol), anhydrous

Scheme 2



$AlCl_3$ (1.5 mmol), and dry DCM (2 mL) were mixed in a sealed pressure regulation 10-mL pressurized vial with ''snap-on'' cap. The mixture was irradiated in a single-mode MW synthesis system at 120 W power and 50°C temperature for 7–10 min. After completion of reaction (TLC), the mixture was poured into a beaker containing ice cold water and was extracted with DCM (3× 10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The resultant solid was recrystallized from ethanol to yield pure product **3a–j**.

5-Amino-4-phenyl-2-phenylsulfanyl-6,7,8,9-tetrahydrobenzo-[b][1,8]-naphthyridine-3-carbonitrile (3a). Yellow solid; IR (KBr): 3432, 3350, 2928, 2210, 1617, 1531 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.45–7.71 (m, 10H, ArH), 4.39 (s, 2H, NH_2), 2.97 (t, *J* = 5.4 Hz, 2H, CH_2), 2.30 (t, *J* = 5.4 Hz, 2H, CH_2), 1.84–1.86 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.3, 161.4, 154.7, 154.3, 149.6, 136.1, 135.6, 130.4, 129.8, 129.5, 127.9, 115.0, 112.1, 105.9, 104.3, 34.0, 23.4, 22.2, 18.4; Anal. Calcd. for $C_{25}H_{20}N_4S$: C, 73.50; H, 4.93; N, 13.71; Found: C, 73.41; H, 4.98; N, 13.75.

5-Amino-4-(4-methylphenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3b). Yellow solid; IR (KBr): 3467, 3346, 2921, 2217, 1621, 1539, 1510 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.69–7.72 (m, 2H, ArH), 7.40–7.47 (m, 5H, ArH), 7.31–7.34 (m, 2H, ArH), 4.45 (s, 2H, NH_2), 2.95 (t, *J* = 5.7 Hz, 2H, CH_2), 2.48 (s, 3H, CH_3), 2.30 (t, *J* = 5.7 Hz, 2H, CH_2), 1.83–1.85 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.3 (C), 161.2 (C), 154.9 (C), 154.6 (C), 149.6 (C), 140.6 (C), 135.4 (CH), 133.1 (C), 130.5 (CH), 129.4 (CH), 128.1 (C), 127.8 (CH), 115.2 (C), 112.0 (C), 106.3 (C), 104.6 (C), 34.2 (CH_2), 23.4 (CH_2), 22.4 (CH_2), 22.2 (CH_2), 21.5 (CH_3); Anal. Calcd. for $C_{26}H_{22}N_4S$: C, 73.90; H, 5.25; N, 13.26; Found: C, 74.01; H, 5.16; N, 13.32.

5-Amino-4-(4-methoxyphenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3c). Light yellow solid; IR (KBr): 3478, 3339, 2920, 2218, 1630, 1548, 1507 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.69–7.71 (m, 2H, ArH), 7.45–7.47 (m, 3H, ArH), 7.36 (d, *J* = 8.4 Hz, 2H, ArH), 7.11 (d, *J* = 8.4 Hz, 2H, ArH), 4.49 (s, 2H, NH_2), 3.91 (s, 3H, OCH_3), 2.95 (t, *J* = 5.4 Hz, 2H, CH_2), 2.31 (t, *J* = 5.4 Hz, 2H, CH_2), 1.84–1.86 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.1 (C), 161.5 (C), 154.6 (C), 154.3 (C), 148.7 (C), 140.3 (C), 135.2 (CH), 133.2 (C), 130.7 (CH), 129.3 (CH), 128.3 (C), 127.5 (CH), 115.1 (C), 112.0 (C), 109.5 (C), 106.4 (C), 55.1 (CH_3), 34.0 (CH_2), 24.1 (CH_2), 23.5 (CH_2), 22.1 (CH_2); Anal. Calcd. for $C_{26}H_{22}N_4OS$: C, 71.21; H, 5.06; N, 12.78; Found: C, 71.32; H, 5.13; N, 12.71.

5-Amino-4-(4-chlorophenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3d). Yellow solid; IR (KBr): 3470, 3343, 2951, 2221, 1628, 1544, 1492 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.59–7.71 (m, 4H, ArH), 7.39–7.48 (m, 5H, ArH), 4.34 (s, 2H, NH_2), 2.96 (t, *J* = 5.7 Hz, 2H, CH_2), 2.32 (t, *J* = 5.7 Hz, 2H, CH_2), 1.86 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.7, 159.9, 154.1, 152.6, 149.2, 135.8, 134.6, 133.9, 129.4, 129.0, 128.8, 114.4, 112.0, 105.4, 38.6, 33.6, 22.9, 21.6; Anal. Calcd. for $C_{25}H_{19}ClN_4S$: C, 67.79; H, 4.32; N, 12.65; Found: C, 67.66; H, 4.39; N, 12.60.

5-Amino-4-(3-chlorophenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3e). Light yellow solid; IR (KBr): 3438, 3341, 3036, 2219, 1628, 1547, 1522 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56–7.70 (m, 3H, ArH), 7.54 (s, 1H, ArH), 7.36–7.47 (m, 5H, ArH), 4.39 (s, 2H, NH_2), 2.96 (t, *J* = 5.7 Hz, 2H, CH_2), 2.33 (t, *J* = 5.7 Hz, 2H, CH_2), 1.84–1.86 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.8, 161.3, 154.8, 152.4, 149.2, 137.9, 135.9, 135.3, 131.1, 130.6, 129.5, 128.2, 127.8, 126.2, 114.9, 112.4, 105.8, 104.3, 34.3, 23.5, 22.3, 22.2; Anal. Calcd. for $C_{25}H_{19}ClN_4S$: C, 67.79; H, 4.32; N, 12.65; Found: C, 67.91; H, 4.24; N, 12.69.

5-Amino-4-(4-bromophenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3f). Brown solid; IR (KBr): 3468, 3348, 3216, 2988, 2215, 1628, 1536, 1501 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.68–7.77 (m, 4H, ArH), 7.32–7.47 (m, 5H, ArH), 4.38 (s, 2H, NH_2), 2.95 (m, 2H, CH_2), 2.57 (m, 2H, CH_2), 2.30–2.32 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.5, 158.7, 155.2, 152.2, 148.7, 135.5, 134.8, 132.7, 129.6, 128.5, 115.1, 112.8, 104.9, 34.8, 33.7, 22.7, 22.1; Anal. Calcd. for $C_{25}H_{19}BrN_4S$: C, 61.60; H, 3.93; N, 11.49; Found: C, 61.68; H, 3.98; N, 11.45.

5-Amino-4-(3-bromophenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3g). Light yellow solid; IR (KBr): 3438, 3336, 2218, 1623, 1547, 1488 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.67–7.76 (m, 3H, ArH), 7.59 (s, 1H, ArH), 7.41–7.52 (m, 5H, ArH), 4.41 (s, 2H, NH_2), 2.94 (t, *J* = 5.4 Hz, 2H, CH_2), 2.31 (t, *J* = 5.4 Hz, 2H, CH_2), 1.84-1.86 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.8, 161.4, 154.8, 152.3, 149.2, 138.1, 133.6, 131.3, 129.5, 127.8, 126.6, 123.9, 114.8, 112.4, 105.8, 34.2, 33.5, 23.5, 22.2; Anal. Calcd. for $C_{25}H_{19}BrN_4S$: C, 61.60; H, 3.93; N, 11.49; Found: C, 61.47; H, 3.85; N, 11.55.

5-Amino-4-(4-nitrophenyl)-2-phenylsulfanyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3h). Yellow solid; IR (KBr): 3426, 3318, 3076, 2222, 1637, 1541, 1518 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.41–8.50 (m, 4H, ArH), 7.46–7.57 (m, 5H, ArH), 5.55 (s, 2H, NH_2), 2.98 (m, 2H, CH_2), 2.32 (m, 2H, CH_2), 1.86 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 162.3, 161.1, 154.5, 152.6, 148.7, 135.8, 135.5, 129.8, 129.6, 129.3, 124.9, 124.4, 112.2, 105.7, 104.7, 33.8, 22.6, 22.4, 18.5; Anal. Calcd. for $C_{25}H_{19}N_5O_2S$: C, 66.21; H, 4.22; N, 15.44; Found: C, 66.29; H, 4.15; N, 15.49.

5-Amino-2-(4-methoxyphenylsulfanyl)-4-phenyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3i). Yellow solid; IR (KBr): 3434, 3330, 3048, 2209, 1628, 1551, 1437 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44–7.62 (m, 5H, ArH), 6.95–7.01 (m, 4H, ArH), 4.38 (s, 2H, NH_2), 3.86 (s, 3H, OCH_3), 2.95 (t, *J* = 5.7 Hz, 2H, CH_2), 2.29 (t, *J* = 5.7 Hz, 2H, CH_2), 1.83–1.85 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.7 (C), 158.9 (C), 155.1 (C), 154.6 (C), 148.4 (C), 141.0 (C), 136.3 (CH), 133.5 (C), 130.2 (CH), 129.6 (CH), 127.9 (C), 126.7 (CH), 115.6 (C), 111.9 (C), 109.7 (C), 105.1 (C), 55.4 (CH_3), 34.1 (CH_2), 23.9 (CH_2), 23.3 (CH_2), 22.3 (CH_2); Anal. Calcd. for $C_{26}H_{22}N_4OS$: C, 71.21; H, 5.06; N, 12.78; Found: C, 71.10; H, 4.98; N, 12.84.

5-Amino-2-(4-methylphenylsulfanyl)-4-phenyl-6,7,8,9-tetra-hydrobenzo[b][1,8]-naphthyridine-3-carbonitrile (3j). Orange solid; IR (KBr): 3450, 3326, 3047, 2921, 2214, 1617, 1547, 1463 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56–7.61 (m, 5H, ArH), 7.26–7.44 (m, 4H, ArH), 4.40 (s, 2H, NH_2), 2.93 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.29 (m, 2H, CH_2), 1.84 (m, 4H, 2× CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.1 (C),

159.8 (C), 155.1 (C), 153.3 (C), 149.4 (C), 141.2 (C), 136.7 (CH), 133.8 (C), 130.4 (CH), 129.7 (CH), 129.1 (C), 128.8 (CH), 115.5 (C), 111.7 (C), 109.6 (C), 106.4 (C), 34.6 (CH_2), 24.5 (CH_2), 23.7 (CH_2), 22.1 (CH_2), 20.8 (CH_3); Anal. Calcd. for $C_{26}H_{22}N_4S$: C, 73.90; H, 5.25; N, 13.26; Found: C, 73.81; H, 5.32; N, 13.31.

X-ray crystallographic data for compound 3b. Empirical formula, $C_{26}H_{22}N_4S$; formula weight, 422.54; crystal color, yellow color; crystal dimensions, 0.25 × 0.23 × 0.22 mm^3; monoclinic space group = P 21/c, a = 11.4944(18) Å, b = 14.559(2) Å, c = 13.214(4) Å, $\alpha = 90°$, $\beta = 95.261(17)$, $\gamma = 90°$, V = 2202.2(8) $Å^3$, T = 293(2) K, Z = 4, d = 1.274 Mg/m^{-3}, $\mu = 0.168$ mm^{-1}, 12929 observed reflections, final R_1 = 0.0576, wR_2 = 0.1485 and for all data R_1 = 0.0883, wR_2 = 0.1631 [18].

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[18] Detailed X-ray crystallographic data are available from the CCDC, 12 union road, Cambridge CB2 1EZ, UK; for compound **3b** (CCDC 756224). These data can be obtained from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.