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Synthesis and Photophysical Properties of 3-Amino-4-arylpyridin-2(1*H*)-ones

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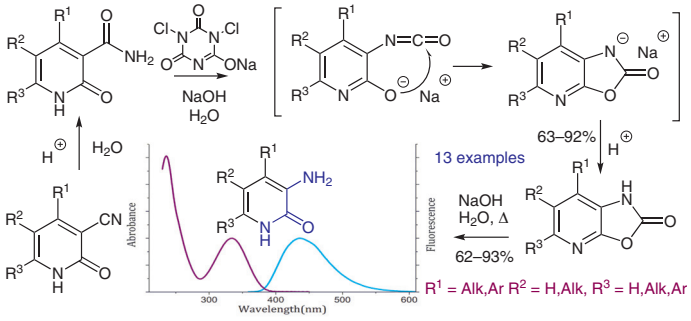

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Abstract A method has been developed for the preparation of oxazolo[5,4-*b*]pyridin-2(1*H*)-ones based on the Hoffmann reaction of 2-oxo-1,2-dihydropyridine-3-carboxamides. Hydrolysis of oxazolo[5,4-*b*]pyridin-2(1*H*)-ones and the Hoffmann reaction of 2-oxo-1,2-dihydropyridine-3-carboxamides yielded 3-aminopyridin-2(1*H*)-ones, including 4-aryl substituted derivatives in the series, for which effective phosphors with a quantum yield of up to 0.78 were detected. Photophysical properties of 3-aminopyridin-2(1*H*)-ones were studied by UV and luminescence spectroscopy methods, and the relationship between their structure and photophysical properties was revealed.

Key words oxazolo[5,4-*b*]pyridin-2(1*H*)-one, Hofmann reaction, 3-aminopyridin-2(1*H*)-ones, luminophores, electronic spectra

3-Aminopyridin-2(1*H*)-ones are widely used as scaffolds for constructing biologically active compounds.[1] Among these compounds, the cardiotonic preparation amrinone is used in clinical practice.[2] The presence of an 'embedded' amino acid fragment makes them attractive building blocks for the synthesis of peptidomimetics.[3] They are also used to produce more complex heterocyclic compounds.[4] 3-Aminopyridin-(1*H*)-ones containing a hydrogen atom or an alkyl group at the C-4 position are well known. Such compounds are usually obtained from 3-functionally substituted 2-pyridones.[5] However, data on 4-aryl-substituted 3-aminopyridin-2(1*H*)-ones are scarce.

Previously, we developed a method for the preparation of 3-functionally substituted pyridin-2(1*H*)-ones[6] by the intramolecular cyclization of *N*-(3-oxoalkenyl)amides. Among the compounds obtained, 3-amino-4-arylpyridin-2(1*H*)-ones[7] were found to be efficient phosphors and to possess antioxidant activity,[4b,7b] and therefore were of interest as cell probes to record the generation of reactive oxygen species. However, the proposed method had some limitations associated with the availability of the starting compounds and scaling of the synthesis.

Herein, we reported an alternative approach to the synthesis of 3-amino-4-arylpyridin-2(1*H*)-ones based on oxazolo[5,4-*b*]pyridin-2(1*H*)-ones, and describe their optical properties. It should be noted that oxazolo[5,4-*b*]pyridin-2(1*H*)-ones are also biologically active compounds. Among them were found substances suitable for the treatment of inflammatory and cardiovascular diseases, cancer, allergies, rheumatoid arthritis, multiple sclerosis,[8] type II diabetes,[9] and neurological or psychiatric disorders etc.[10] Their derivatives are antagonists of TRPM8 channel[11] and analgesics.[12] Most methods for the preparation of oxazolo[5,4-*b*]pyridin-2(1*H*)-ones include the reaction of 3-aminopyridin-2(1*H*)-ones with toxic reagents such as phosgene,[13] triphosgene,[9,11,12c] or carbonyldiimidazole.[8,10,12c]

Available 4-aryl-3-cyanopyridin-2(1*H*)-ones were used as starting compounds for the synthesis of oxazolo[5,4-*b*]pyridin-2(1*H*)-ones. The former were obtained by known methods, such as condensation of 1,3-diketones with cyanoacetamide (**1a**,**b**),[14] the reaction of α,β-unsaturated ketones with cyanoacetamide in air (**1c–h**),[15] and the three-component condensation of aromatic aldehydes, ketones, and cyanoacetamide (**1i–m**),[16] with yields of 49–92% (Scheme 1).

Hydrolysis of the obtained nitriles in polyphosphoric acid (PPA) (**1c–f**,**j**,**m**) or sulfuric acid (**1a–c**,**g–i**,**k**,**l**) led to the formation of the corresponding amides **2a–m** with yields of 60–92%. The reaction of nitriles with PPA proceeded more slowly (24–48 h) than with sulfuric acid (4 h); however, the yields of the products bearing donor substituents (**2d–f**) were slightly higher (Scheme 1).

N-Methyl-3-cyanopyridin-2(1*H*)-one **1n** was obtained by reacting compound **1c** with methyl iodide in the presence of K_2CO_3. Subsequent hydrolysis of the cyano group

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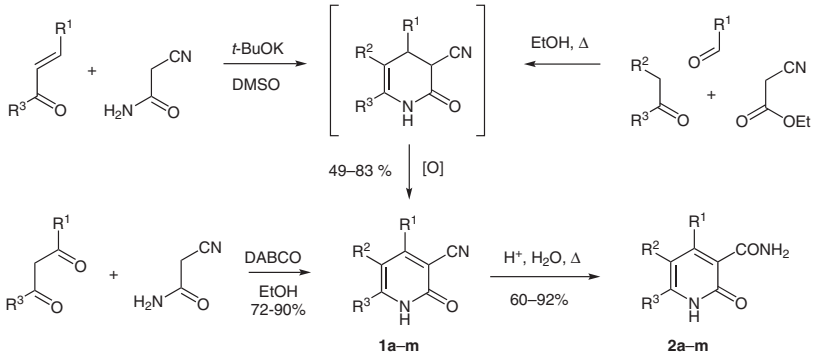
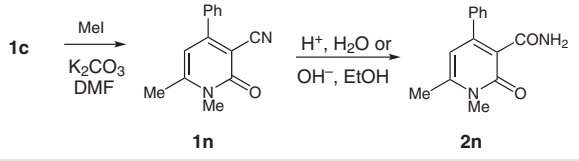


a. $R^1 = R^3 = Me$, $R^2 = H$; **b.** $R^1 = Me$, $R^2 = H$, $R^3 = Ph$; **c.** $R^1 = Ph$, $R^2 = H$, $R^3 = Me$; **d.** $R^1 = C_6H_4$-4-OMe, $R^2 = H$, $R^3 = Me$; **e.** $R^1 = C_6H_3$-3,4-$(OMe)_2$, $R^2 = H$, $R^3 = Me$; **f.** R^1 = 2-Th, $R^2 = H$, $R^3 = Me$; **g.** $R^1 = C_6H_4$-4-NMe_2, $R^2 = H$, $R^3 = Me$; **h.** $R^1 = Ph$, $R^2 = R^3 = H$; **i.** $R^1 = R^3 = Ph$, $R^2 = H$; **j.** $R^1 = Ph$, $R^2 = H$, $R^3 = C_6H_3$-2,3-$(OMe)_2$; **k.** $R^1 = Ph$, $R^2 = H$, R^3 = 2-Py; **l.** $R^1 = Ph$, $R^2 + R^3 = CH_2CH_2$-2-C_6H_4; **m.** $R^1 = Ph$, $R^2 + R^3 = CH_2O$-2-C_6H_4

Scheme 1 Synthesis of 2-oxo-1,2-dihydropyridine-3-carboxamides

resulted in amide **2n** (Scheme 2). Unlike the N-unsubstituted 3-cyanopyridin-2(1*H*)-one **1c**, the presence of an alkyl substituent at the nitrogen atom blocking the pyridone–pyridol tautomerism makes it possible to perform the reaction in an alkaline medium (Scheme 2).

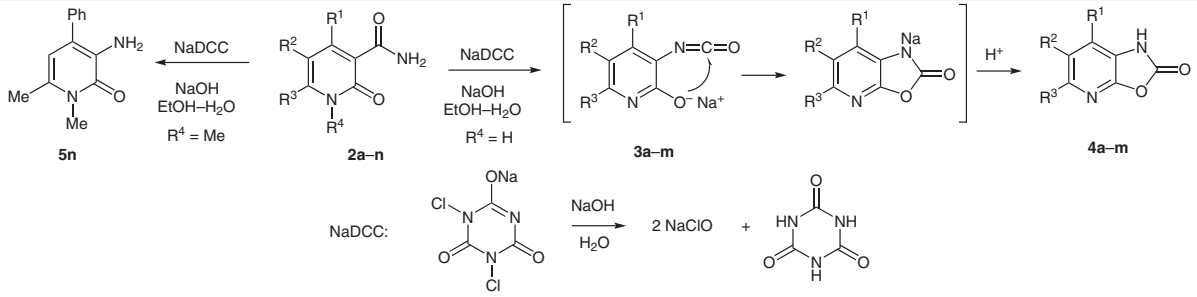


Scheme 2 Synthesis of 1,6-dimethyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carboxamide (**2n**)

It was previously shown that alkyl-substituted 2-oxo-1,2-dihydropyridine-3-carboxamides react with sodium hypobromite in the Hoffmann reaction.[17] The isocyanates formed undergo cyclization at room temperature to give oxazolo[5,4-*b*]pyridin-2(1*H*)-ones. In contrast, a mixture of 3-aminopyridin-2(1*H*)-ones and oxazolo[5,4-*b*]pyridin-2(1*H*)-ones was formed when the reaction temperature was raised to 80 °C. An attempt to apply this approach for the synthesis of 4-aryl-substituted 3-aminopyridin-2(1*H*)-ones was unsuccessful.[18] The reaction of 6-methyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carboxamide (**2c**) even with a lack of sodium hypobromite led to the formation of a mixture of 3-amino-4-phenylpyridin-2(1*H*)-one and its 5-bromo derivative.[18] At the same time, 5-methyl-7-phenyloxazolo[5,4-*b*]pyridin-2(1*H*)-one (**4c**) was obtained at room temperature by reacting amide **2c** with calcium hypochlorite. Compound **4c** was converted into 3-amino-6-methyl-4-phenylpyridin-2(1*H*)-one (**5c**) (see Scheme 4), when heated with alkali.

The low stability of hypochlorites and hypobromites upon storage stimulated repeated attempts to modify the Hoffmann reaction by replacing them with other reagents such as NBS/MeONa,[19a] NBS/DBU,[19b] $TsNBr_2$/DBU,[19c] trichloroisocyanuric acid (TCCA)/DBU,[19d] or 1,3-dichloro-5,5-dimethylhydantoin (DCDMH)/base (MeONa or DBU).[19e] Recently, the surface-stable, soluble sodium salt of dichloroisocyanuric acid (NaDCC)[20] has been widely used to disinfect surfaces and water. Sodium dichloroisocyanurate can also be used in the Hoffmann reaction to generate sodium hypochlorite.[21]

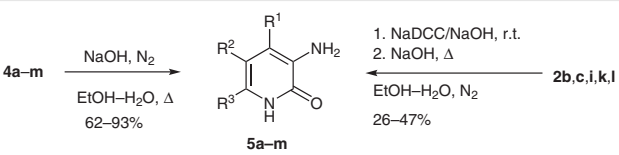
The reaction of amides **2a–m** with 2 equivalents of sodium dichloroisocyanurate in the presence of NaOH afforded oxazolo[5,4-*b*]pyridin-2(1*H*)-ones **4a–m** with yields of 63–92% (Scheme 3, Table 1) as a result of intramolecular cyclization of the intermediate isocyanates **3a–m**. Pyridin-



Scheme 3 Synthesis of 2-oxo-1,2-dihydropyridine-3-carboxamides **4a–m**

2(1*H*)-one **2n** was converted into 3-amino-1,6-dimethyl-4-phenylpyridin-2(1*H*)-one (**5n**) with 79% yield under similar conditions (Scheme 3, Table 1).

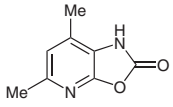
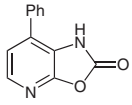
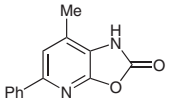
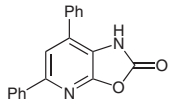
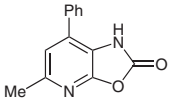
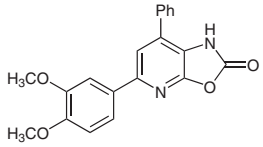
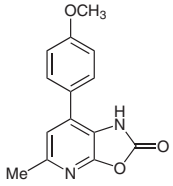
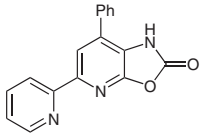
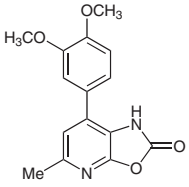
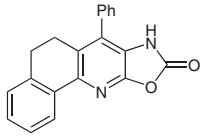
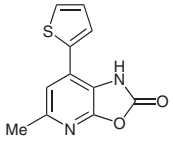
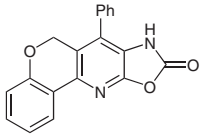
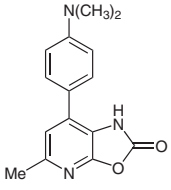
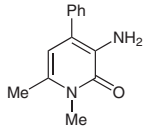
Since hydrolysis in an alkaline medium proceeded more easily and with a high yield of the target product, 3-amino-4-arylpyridin-2(1*H*)-ones **5a–m** were obtained in 62–87% yields by heating compounds **4a–m** in ethanol in the presence of alkali. 3-Amino-4-arylpyridines **5** could be prepared in one step without isolating oxazolo[5,4-*b*]pyridin-2(1*H*)-ones **4** starting from amides **2**. However, in this case, the yields of compounds **5** were found to be lower (Scheme 4).



Scheme 4 Synthesis of 3-aminopyrimidin-2(1*H*)-ones **5a–m**

To our knowledge, neither the optical properties of 3-amino-4-arylpyridin-2(1*H*)-ones nor data on the luminescence properties of these compounds have been reported. We therefore recorded the absorption and fluorescence

Table 1 Hoffman Reaction Products **4a–m** and **5n**

Entry	Structure	Yield (%)	Entry	Structure	Yield (%)
4a		87	**4h**		82
4b		71	**4i**		73
4c		92	**4j**		63
4d		83	**4k**		64
4e		88	**4l**		69
4f		72	**4m**		71
4g		72	**5n**		79

spectra of dilute solutions of these compounds in ethanol, established the light absorption coefficient, and calculated the fluorescence quantum yields (Table 2). As an example, Figure 1 shows the absorption and luminescence spectra of compound **5c**.

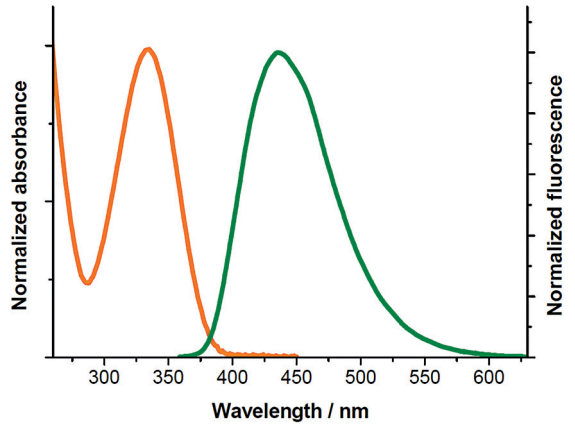


Figure 1 Normalized absorption and luminescence spectra of a solution of **5c** in EtOH

In the UV spectra of all 3-amino-4-arylpyridin-2(1*H*)-ones **5a–n**, two main absorption bands corresponding to π–π* (less than 267 nm) and n–π* (329–352 nm) transitions are observed. The emission maxima lie in the range 409–451 nm.

Table 2 UV and Luminescence Data for Compounds **5a–n**

Compd	UV/Vis[a]		Photoluminescence[a]		
	$^{max}\lambda_{abs}$ [nm]	ε, 10^3 [$M^{-1}\cdot cm^{-1}$]	λ_{ex} [nm]	$^{max}\lambda_{em}$ [nm]	Quantum yield Φ_{fl}[b]
5a	311	4.5	310	–	0.00±0.00
5b	337	17.6	330, 340	409	0.03±0.00
5c	334	8.9	335, 350	435	0.76±0.03
5d	335	7.7	335, 355	444	0.48±0.02
5e	334	9.8	335, 350	437	0.50±0.02
5f	351	8.3	350, 355	451	0.37±0.01
5g	339	12.1	345, 350	438	0.24±0.01
5h	329	7.4	320, 330	420	0.70±0.03
5i	364	16.4	345, 350	430	0.22±0.01
5j	353	15.9	350, 355	442	0.18±0.01
5k	364	21.1	355, 365	430	0.03±0.00
5l	364	18.0	355, 364	424	0.32±0.02
5m	372	23.0	355, 372	432	0.36±0.02
5n	335	7.5	330, 340	438	0.52±0.02

[a] EtOH (**5b–n**) and water (**5a**) were used as solvents (10^{-7} to 10^{-5} mol/L).
[b] The fluorescence quantum yield was calculated relative to the standard (quinine sulfate in 0.5 M. H_2SO_4, Φ_{fl} = 0.546).

The fluorescence quantum yield reached 0.76 (**5c**). Comparison of compound **5c** and **5i–m** shows that replacing the methyl group in position C(6) with an aryl (hetaryl) substituent leads to a significant decrease in the quantum yield (Φ_{fl} = 0.03–0.36) and a slight increase in the light absorption coefficient. The quantum yield also decreases with the introduction of a methyl group on the nitrogen atom of the pyridone ring (**5n**) (Φ_{fl} = 0.52), as well as donor substituents on the benzene ring (**5c–e**,**g**) (Φ_{fl} = 0.24–0.50) or its replacement with a thiophene cycle (**5f**) (Φ_{fl} = 0.37).

It should be noted that alkyl substituted 3-amino-4,6-alkylpyridin-2(1*H*)-one **5a** does not possess luminescent properties. The introduction of a phenyl substituent at position C(6) leads to insignificant luminescence (Φ_{fl} = 0.03) of 3-aminopyridone **5b** and a hypsochromic shift of the luminescence maximum (409 nm) as compared to the 4-phenyl substituted 3-aminopyridin-2(1*H*)-one **5c** (435 nm).

In conclusion, a method was developed for the preparation of oxazolo[5,4-*b*]pyridin-2(1*H*)-ones based on the reaction of 2-oxo-1,2-dihydropyridine-3-carboxamides with sodium dichloroisocyanurate in an aqueous alcoholic medium. Available and stable sodium dichloroisocyanurate was found to be an effective reagent for the Hoffmann reaction. A simple method was proposed for the synthesis of 3-aminopyridin-2(1*H*)-ones, including 4-aryl-substituted ones, by hydrolysis of oxazolo[5,4-*b*]pyridin-2(1*H*)-ones or by the Hoffmann reaction of 2-oxo-1,2-dihydropyridine-3-carboxamides. For the first time, the photophysical properties of 3-amino-4-arylpyridin-2(1*H*)-ones were studied and structure–properties relationships were revealed. Effective phosphors with a high fluorescence quantum yield were found in the series of 3-amino-4-arylpyridin-2(1*H*)-ones obtained.

The IR spectra were recorded with an Infralum FT-801 spectrophotometer from KBr pellets. Crude products were purified by column chromatography with silica gel (100–200 mesh) or by recrystallization.

The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance Instrument operating at 400 MHz and 100 MHz for ^1H and ^{13}C nuclei, respectively. Chemical shifts are referenced relative to TMS or the residual signals of protonated solvents as an internal standard: chloroform (δ = 7.25(1) ppm in ^1H NMR, δ = 77.00(3) ppm in ^{13}C NMR), DMSO-d_6 (δ = 2.49(5) ppm in ^1H NMR, δ = 39.5(7) ppm in ^{13}C NMR). The ^{13}C NMR spectra were obtained in the J-modulation mode unless noted otherwise. The elemental analyses were carried out with a Carlo Erba 1106 CHN analyzer. The melting points were determined with a Reach devices RD-MP. UV/Vis spectra were recorded in EtOH (10^{-7} to 10^{-5} mol/L) with a UV/Vis/NIR Spectrometer Lambda 750 (Perkin Elmer), while fluorescence spectra were recorded with a Cary Eclipse (Agilent) fluorescence spectrometer. Fluorescence excitation spectra were recorded to determine the excitation wavelength at which the maximum fluorescent response is observed. Subsequent fluorescence emission spectra were recorded at excitation wavelengths determined in this manner. The quantum yield of examined compounds was determined relative to quinine sulfate in 0.5 M H_2SO_4, Φ_{fl} = 0.546, by using the comparative method.[22]

The progress of the reaction and purity of the products were monitored by thin-layer chromatography on Sorbfil UV-254 plates, which were visualized with UV light (254, 365 nm). All chemicals were of analytical grade and purchased from Sigma–Aldrich Chemical Co.

4-Methyl-2-oxo-1,2-dihydropyridine-3-carbonitriles 1a,b; General Procedure

A mixture of a 1,3-diketone (50 mmol), cyanoacetamide (4.20 g, 50 mmol), and DABCO (0.5 mol, 56.0 mg) in EtOH (50 mL) was heated at reflux for 1–1.5 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was cooled. The precipitate formed was filtered off and recrystallized from ethanol.[14]

4,6-Dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (1a)[14]

Yield: 6.62 g (90%); white crystals; mp >250 °C (ethanol) (Lit.[23] 288–289 °C).

IR (KBr): 3302, 3139, 2218, 1662 cm^{-1}.

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.90; H, 5.52; N, 19.02.

4-Methyl-2-oxo-6-phenyl-1,2-dihydropyridine-3-carbonitrile (1b)

Yield: 7.60 g (72%); white crystals; mp >250 °C (ethanol) (Lit.[24] 272–273 °C).

IR (KBr): 3270, 3138, 2222, 1627 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.41 (s, 3 H), 6.73 (s, 1 H), 7.49–7.55 (m, 3 H), 7.78 (dd, J = 7.8, 1.8 Hz, 2 H), 12.46 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.8, 107.1, 115.9, 127.5 (2C), 128.9 (2C), 131.0, 132.1, 150.4, 160.2, 161.4.

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.32; H, 4.74; N, 13.29.

4-Aryl-2-oxo-1,2-dihydropyridine-3-carbonitriles 1c–h; General Procedure

Potassium *tert*-butoxide (9.24 g, 0.11 mol) was added to a cooled solution of α,β-unsaturated ketone or cinnamaldehyde (0.10 mol) and 2-cyanoacetamide (9.24 g, 0.11 mol) in DMSO (100 mL). Cooling was stopped after 30 min and the reaction mixture was stirred at r.t. for 1 day with bubbling of dry air (reaction monitored by TLC). Then the reaction mixture was poured into water (500 mL) and neutralized with 2 N HCl solution. The precipitate formed was filtered off, washed with water, and recrystallized from EtOH or EtOAc–AcOH.[15]

6-Methyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (1c)[18]

Yield: 16.80 g (80%); white powder; mp >250 °C (ethanol) (Lit.[25] 265–270 °C).

IR (KBr): 3293, 3197, 2234, 1669 cm^{-1}.

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.23; H, 4.82; N, 13.36.

4-(4-Methoxyphenyl)-6-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (1d)

Yield: 19.92 g (83%); yellow powder; mp >250 °C (EtOAc–AcOH) (Lit.[25] 242 °C).

IR (KBr): 3294, 3138, 2220, 1664, 1629 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.28 (s, 3 H), 3.81 (s, 3H), 6.26 (s, 1 H), 7.06 (d, J = 8.6 Hz, 2 H), 7.57 (d, J = 8.6 Hz, 2 H), 12.37 (br s,1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.0, 55.3, 96.5, 106.2, 114.1 (2C), 116.8, 128.0, 129.6 (2C), 151.5, 159.5, 160.9, 161.5.

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.18; H, 4.99; N, 11.69.

4-(3,4-Dimethoxyphenyl)-6-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (1e)

Yield: 21.33 g (79%); yellow powder; mp >250 °C (EtOAc–AcOH) (Lit.[25] >280 °C).

IR (KBr): 3288, 2997, 2219, 1691, 1636 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.30 (s, 3 H), 3.83 (s, 3H), 3.84 (s, 3H), 6.28 (s, 1 H), 7.09 (d, J = 8.6 Hz, 1 H), 7.18–7.25 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.8, 55.5, 55.6, 96.3, 105.8, 112.0, 112.2, 116.5, 120.9, 128.2, 148.6, 150.6, 151.2 (2C), 159.1, 161.4.

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.87; H, 5.18 N, 10.42.

6-Methyl-2-oxo-4-(2-thienyl)-1,2-dihydropyridine-3-carbonitrile (1f)

Yield: 15.55 g (72%); yellow powder; mp >250 °C (ethanol).

IR (KBr): 3300, 3123, 2213, 1656, 1623 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.27 (s, 3 H), 6.46 (s 1 H), 7.27 (dd, J = 4.9, 3.9 Hz, 1 H), 7.90 (d, J = 3.9 Hz, 1 H), 7.93 (d, J = 4.1 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.0, 94.2, 104.8, 117.1, 128.6, 130.7, 131.6, 136.8, 150.8, 151.8, 161.6.

Anal. Calcd for $C_{11}H_8N_2OS$: C, 61.09; H, 3.73; N, 12.95. Found: C, 61.24; H, 3.76; N, 12.90.

4-[4-(Dimethylamino)phenyl]-6-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (1g)

Yield: 13.66 g (54%); orange powder; mp >250 °C (EtOAc–AcOH).

IR (KBr): 3341, 3177, 2216, 1698, 1648 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.27 (s, 3 H), 2.99 (s, 6 H), 6.25 (s, 1 H), 7.80 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.8 Hz, 2 H), 12.03 (br s,1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.7, 39.7 (2C, overlapped with DMSO-d_6 signal), 94.8, 105.3, 111.3 (2C), 117.0, 122.0, 128.9 (2C), 150.2, 151.5, 159.3, 161.5.

Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 70.99; H, 5.95; N, 16.62.

2-Oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (1h)

Yield: 10.58 g (54%); white crystals; mp 235–236 °C (ethanol) (Lit.[15] 237–238 °C).

IR (KBr): 3095, 2220, 1667 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.34 (d, J = 6.7 Hz, 1 H), 7.51–7.64 (m, 5 H), 7.79 (d, J = 6.7 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 100.9, 106.7, 116.3, 128.0 (2C), 128.9 (2C), 130.5, 135.9, 140.3, 160.6, 160.7.

Anal. Calcd for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.28; H, 4.16; N, 14.32.

4,6-Diaryl-2-oxo-1,2-dihydropyridine-3-carbonitriles 1i–m; General Procedure

A solution of benzaldehyde (5.1 mL, 0.05 mol), aromatic ketone (0.06 mol), ethyl cyanoacetate (6.4 mL, 0.06 mol) and ammonium acetate (30.8 g, 0.4 mol) in absolute EtOH (80 mL) was heated at reflux for 16–20 h. After cooling, the precipitate formed was filtered off, washed with cold EtOH and H_2O, and dried.

2-Oxo-4,6-diphenyl-1,2-dihydropyridine-3-carbonitrile (1i)

Yield: 9.52 g (70%); green powder; mp >250 °C (ethanol) (Lit.[15] >300 °C).

IR (KBr): 3156, 2699, 1654 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 6.78 (s, 1 H), 7.47–7.52 (m, 3 H), 7.52–7.55 (m, 3 H), 7.69 (dd, J = 6.7, 2.9 Hz, 2 H), 7.90 (dd, J = 7.6, 2.0 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 97.1, 105.7, 117.4, 127.7 (2C), 128.8 (2C), 128.3 (2C), 128.9 (2C), 130.1, 130.8, 133.8, 136.7, 153.0, 158.9, 164.1.

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.55; H, 4.51; N, 10.36.

6-(3,4-Dmethoxyphenyl)-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (1j)

Yield: 8.80 g (53%); green powder; mp >250 °C (ethanol) (Lit.[26] 255–257 °C).

IR (KBr): 3291, 3004, 2222, 1643, 1631 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.83 (s, 3 H), 3.86 (s, 3 H), 6.79 (s, 1 H), 7.07 (d, ^3J = 8.4 Hz, 1 H), 7.48 (d, J = 2.4 Hz, 1 H), 7.52 (dd, J = 8.4 Hz, ^4J = 2.4 Hz, 1 H), 7.54–7.57 (m, 3 H), 7.70 (dd, J = 6.7, J = 2.9 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.7, 55.8, 97.4, 105.1, 110.8, 111.8, 116.8, 121.2, 124.2, 128.2 (2C), 128.8 (2C), 130.3, 136.3, 148.8, 151.1, 151.5, 159.9, 162.1.

Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.43; H, 4.92; N, 8.49.

6-Oxo-4-phenyl-1,6-dihydro-2,2′-bipyridine-5-carbonitrile (1k)

Yield: 7.92 g (58%); dark-green powder; mp >250 °C (ethanol).

IR (KBr): 3279, 3066, 2220, 1647, 1620 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.34 (s, 1 H), 7.54–7.62 (m, 4 H), 7.69–7.76 (m, 2H), 7.98–8.05 (m, 1 H), 8.31 (d, J = 8.0 Hz, 1 H), 8.72–8.79 (m, 1 H), 12.12 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 99.8, 105.7, 115.3, 121.7, 125.2, 127.5 (2C), 128.3 (2C), 129.8, 135.7, 137.2, 147.9 (br s, 2C), 149.1, 159.4, 160.5.

Anal. Calcd for $C_{17}H_{11}N_3O$: C, 74.71; H, 4.06; N, 15.38. Found: C, 74.89; H, 4.00; N, 15.33.

2-Oxo-4-phenyl-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile (1l)

Yield: 8.46 g (54%); green powder; mp >250 °C (ethanol) (Lit.[27] 312–314 °C).

IR (KBr): 3126, 3068, 2222, 1632, 1609 cm^{-1}.

^1H NMR (400 MHz, CF_3CO_2D): δ = 2.70–2.78 (m, 2 H), 2.88–2.97 (m, 2 H), 7.41–7.45 (m, 3 H), 7.55 (dd, J = 7.1, 7.4 Hz, 1 H), 7.58–7.65 (m, 4 H), 7.43 (d, J = 7.4 Hz, 1 H).

^{13}C NMR (100 MHz, CF_3CO_2D): δ = 25.6, 29.1, 101.1, 114.9 (overlapped with CF_3CO_2D signal), 123.3, 126.1, 127.6, 129.3 (2C), 130.2, 131.0, 131.2 (2C), 132.8, 135.7, 135.8, 142.6, 149.4, 165.3, 167.3.

Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.33; H, 4.81; N, 9.30.

2-Oxo-4-phenyl-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridine-3-carbonitrile (1m)

Yield: 8.55 g (57%); green powder; mp >250 °C (ethanol).

IR (KBr): 3296, 3072, 2219, 1656, 1631 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.77 (s, 2 H), 7.00 (dd, J = 8.2, 1.0 Hz, 1 H), 7.14 (ddd, J = 8.6, 7.9, 1.0 Hz, 1 H, H-9), 7.41–7.48 (m, 3 H), 7.53–7.58 (m, 3 H), 8.10 (dd, J = 7.9, 1.5 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 64.5, 99.3, 109.4, 115.9, 117.3, 122.4, 124.1, 127.8 (2C), 128.9 (2C), 129.9, 133.5, 133.8, 143.2 (br. s., 2C); 156.3, 156.8, 161.4.

Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33. Found: C, 75.81; H, 4.09; N, 9.39.

1,6-Dimethyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (1n)

A mixture of pyridin-2(1*H*)-one **1c** (2.1 g, 0.01 mol), methyl iodide (0.75 mL, 0.012 mol), K_2CO_3 (2.76 g, 0.02 mol) in anhydrous DMF (10 mL) was stirred at r.t. for 4 h. After the reaction completed, the mixture was poured into water (100 mL). The precipitate formed was filtered off, washed with water, and recrystallized from EtOH.

Yield: 1.95 g (87%); white crystals; mp 141–142 °C (ethanol) (Lit.[28] 143–144 °C).

IR (KBr): 2222, 1650 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.48 (s, 3 H overlapped with DMSO-d_6 signal), 3.50 (s, 3 H), 6.49 (s, 1 H), 7.51–7.56 (m, 3 H), 7.56–7.62 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.0, 31.4, 96.4, 107.6, 116.7, 127.9 (2C), 128.8 (2C), 130.3, 135.7, 154.2, 157.5, 161.0.

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 75.06; H, 5.44; N, 12.56.

2-Oxo-1,2-dihydropyridine-3-carboxamides 2a–n; General Procedures

General Procedure A

A solution of nitrile **1a–c**, **1g–i**, **1k**, **1l**, or **1n** (0.01 mol) in concd H_2SO_4 (3 mL) was heated at 95 °C for 4 h. After cooling, the reaction mixture was poured into ice (50 g) and neutralized with aqueous ammonia. The solid formed was filtered off, washed with water, and recrystallized from EtOH or EtOAc–AcOH.

General Procedure B

A solution of nitrile **1c–f**, **1j**, **1m**, **1n** (0.01 mol) in PPA, prepared from P_2O_5 (3 mL) and 80% H_3PO_4 (3 mL), was heated at 95 °C for 4 h. After cooling, the reaction mixture was poured into ice (50 g) and neutralized with aqueous ammonia. The solid formed was filtered off, washed with water, and recrystallized from EtOH or EtOAc–AcOH.

4,6-Dimethyl-2-oxo-1,2-dihydropyridine-3-carboxamide (2a)

Yield: 1.35 g (Method A, 92%); white crystals; mp 230–231 °C (ethanol) (Lit.[29] 214–215 °C).

IR (KBr): 3319, 3154, 1658, 1645 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.15 (s, 3 H), 2.34 (s, 3 H), 5.98 (s, 1 H), 7.16 (s, 1 H), 8.64 (s, 1 H), 11.88 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.2, 21.6, 109.5, 118.4, 146.1, 154.8, 162.5, 167.5.

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.94; H, 5.97; N, 16.88.

4-Methyl-2-oxo-6-phenyl-1,2-dihydropyridine-3-carboxamide (2b)

Yield: 1.46 g (Method A, 70%); white crystals; mp >250 °C (ethanol).

IR (KBr): 3363, 3200, 1695, 1640 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.39 (s, 3 H), 6.57 (s, 1 H), 7.30 (s, 1 H), 7.46–7.51 (m, 3 H), 7.76 (dd, J = 6.6, 3.0 Hz, 2 H), 8.39 (s, 1 H), 10.83 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.1, 108.6, 121.3, 127.0 (2C), 128.8 (2C), 130.1, 132.8, 146.1, 152.8, 162.1, 167.4.

Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.36; H, 5.37; N, 12.23.

6-Methyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carboxamide (2c)[18]

Yield: 1.96 g (Method A, 86%), 1.69 g (Method B, 74%); white crystals; mp 255–257 °C (ethanol) (Lit.[30] 253–255 °C).

IR (KBr): 3436, 3313, 1677, 1658 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.44; H, 5.33; N, 12.35.

4-(4-Methoxyphenyl)-6-methyl-2-oxo-1,2-dihydropyridine-3-carboxamide (2d)

Yield: 1.64 g (Method B, 64%); pale-yellow powder; mp 234–235 °C (decomp.) (EtOAc–AcOH).

IR (KBr): 3341, 3175, 1633, 1610 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.18 (d, J = 0.8 Hz, 3 H), 3.77 (s, 3 H), 6.26 (d, J = 0.8 Hz, 1 H), 6.93 (d, J = 8.8 Hz, 2 H), 7.10 (s, 1 H), 7.39 (d, J = 8.8 Hz, 2 H), 7.60 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.4, 55.1, 106.2, 113.5 (2C), 122.8, 129.0 (2C), 131.0, 144.9, 150.0, 159.3, 161.3, 167.7.

Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.58. Found: C, 65.34; H, 5.32; N, 10.66.

4-(3,4-Dimethoxyphenyl)-6-methyl-2-oxo-1,2-dihydropyridine-3-carboxamide (2e)

Yield: 2.13 g (Method B, 79%); pale-yellow powder; mp 199–201 °C (decomp.) (EtOAc–AcOH).

IR (KBr): 3432, 3304, 1664, 1608 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.19 (s, 3 H); 3.73 (s, 3 H), 3.76 (s, 3 H), 6.05 (s, 1 H), 6.95 (d, J = 8.4 Hz, 1 H), 7.01 (d, J = 8.0 Hz, 1 H), 7.09 (s, 1 H), 7.17 (s, 1 H), 7.60 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.5, 55.5, 55.6, 106.2, 111.5, 111.8 (2C), 120.4, 123.2, 131.1, 144.9, 148.2, 149.1, 149.9, 161.3, 168.2.

Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.63; H, 5.54; N, 9.62.

6-Methyl-2-oxo-4-(2-thienyl)-1,2-dihydropyridine-3-carboxamide (2f)

Yield: 1.76 g (Method B, 75%); pale-yellow powder; mp 236–237 °C (ethanol).

IR (KBr): 3459, 3343, 1670, 1630 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.18 (s, 3 H), 6.16 (s, 1 H), 7.12 (dd, J = 5.1, 3.7 Hz, 1 H), 7.33 (s, 1 H), 7.51 (d, J = 3.5 Hz, 1 H), 7.76 (s, 1 H), 7.68 (d, J = 5.1 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.4, 104.5, 122.8, 127.9, 128.3, 128.6, 139.0, 140.7, 144.9, 161.0, 168.1.

Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 56.36; H, 4.30; N, 11.96. Found: C, 56.19; H, 4.39; N, 12.04.

4-[4-(Dimethylamino)phenyl]-6-methyl-2-oxo-1,2-dihydropyridine-3-carboxamide (2g)

Yield: 1.78 g (Method A, 66%); orange powder; mp 251–252 °C (EtOAc–AcOH).

IR (KBr): 3341, 3177, 2216, 1698, 1648 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.17 (s, 3 H), 2.91 (s, 6 H), 6.01 (s, 1 H), 6.99 (d, J = 8.9 Hz, 2 H), 7.10 (s, 1 H), 7.35 (d, ^3J = 8.9 Hz, 2 H), 7.52 (s, 1 H), 11.69 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.5, 39.7 (2C, overlapped with DMSO-d_6 signal), 106.0, 111.6 (2C), 122.1, 125.7, 128.7 (2C), 144.4, 150.0, 150.4, 161.5, 168.4.

Anal. Calcd for $C_{15}H_{17}N_3O_2$: C, 66.40; H, 6.32; N, 15.49. Found: C, 66.59; H, 6.25; N, 15.56.

2-Oxo-4-phenyl-1,2-dihydropyridine-3-carboxamide (2h)

Yield: 1.63 g (Method A, 75%); white crystals; mp 235–236 °C (ethanol) (Lit.[31] 237–238 °C).

IR (KBr): 3431, 3153, 1667, 1645 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 6.85 (d, J = 6.9 Hz, 1 H), 7.18 (s, 1 H), 7.36–7.47 (m, 6 H), 7.65 (s, 1 H), 11.68 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 107.5, 126.9, 127.7 (2C), 128.3 (2C), 128.5, 134.7, 138.4, 149.8, 160.5, 167.3.

Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.40; H, 4.65; N, 13.16.

2-Oxo-4,6-diphenyl-1,2-dihydropyridine-3-carboxamide (2i)

Yield: 2.46 g (Method A, 85%); white powder; mp 252 °C (ethanol) (Lit.[30] 254–256 °C).

IR (KBr): 3403, 3353, 3125, 1660, 1630 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 6.62 (s, 1 H), 7.24 (s, 1 H), 7.38–7.45 (m, 3 H), 7.47–7.52 (m, 3 H), 7.56–7.59 (m, 2 H), 7.69 (s, 1 H), 7.80–7.86 (m, 2 H), 11.99 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 105.7, 122.6, 127.0 (2C), 127.8 (2C), 128.4, 128.2 (2C), 128.7 (2C), 129.8, 138.5 (2C), 145.7, 149.6, 161.2, 167.3.

Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.39; H, 4.86; N, 9.65. Found: C, 74.60; H, 4.80; N, 9.72.

6-(3,4-Dimethoxyphenyl)-2-oxo-4-phenyl-1,2-dihydropyridine-3-carboxamide (2j)

Yield: 2.10 g (Method B, 60%); pale-yellow powder; mp 172–173 °C (ethanol).

IR (KBr): 3402, 3271, 1673, 1630 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.80 (s, 3 H), 3.84 (s, 3 H), 6.58 (s, 1 H), 7.03 (d, J = 8.4 Hz, 1 H), 7.24–7.29 (m, 1 H), 7.38–7.46 (m, 5 H), 7.53–7.57 (m, 2 H), 7.73 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.7, 57.0, 105.7, 110.3, 111.8 (2C), 119.9, 123.5, 125.6, 127.8 (2C), 128.2 (2C), 128.4, 138.8, 146.3, 148.8, 150.3, 150.4, 161.4, 167.5.

Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.80. Found: C, 68.39; H, 5.16; N, 8.92.

6-Oxo-4-phenyl-1,6-dihydro-2,2′-bipyridine-5-carboxamide (2k)

Yield: 2.38 g (Method A, 82%); yellow powder; mp 223–224 °C (ethanol).

IR (KBr): 3305, 3172, 1662, 1638 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.21 (s, 1 H), 7.24 (s, 1 H), 7.41–7.51 (m, 4 H), 7.54–7.62 (m, 2H), 7.68 (s, 1 H), 7.92–8.00 (m, *J* = 7.7, 1.9 Hz, 1 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.70 (d, *J* = 4.3 Hz, 1 H), 11.38 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 107.3, 121.0, 124.8, 125.9, 127.8 (2C), 128.3 (2C), 128.5, 137.7, 138.2, 149.4, 149.4, 149.6, 160.2, 167.2.

Anal. Calcd for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.24. Found: C, 70.30; H, 4.46; N, 14.16.

2-Oxo-4-phenyl-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carboxamide (2l)

Yield: 2.62 g (Method A, 83%); pale-yellow powder; mp >250 °C (EtOAc–AcOH).

IR (KBr): 3381, 3188, 1668, 1629 cm^{-1}.

^{1}H NMR (400 MHz, CF_3CO_2D): δ = 2.63 (t, *J* = 7.4 Hz, 2 H), 3.00 (t, *J* = 7.3 Hz, 2 H), 7.41–7.49 (m, 3 H), 7.59 (dd, *J* = 7.8, 7.4 Hz, 1 H), 7.70 (dd, *J* = 7.4, 7.4 Hz, 1 H), 7.77–7.85 (m, 3 H), 8.10 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, CF_3CO_2D): δ = 25.7, 28.6, 109.1, 126.5, 126.8, 128.2, 128.3 (2C), 130.6, 131.4, 133.1 (2C), 133.8, 135.4, 137.4, 143.5, 150.4, 163.5 (overlapped with CF_3CO_2D signal), 165.4, 173.5.

Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 76.11; H, 5.05; N, 8.93.

2-Oxo-4-phenyl-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridine-3-carboxamide (2m)

Yield: 2.32 g (Method B, 73%); yellow powder; mp >250 °C (EtOAc–AcOH).

IR (KBr): 3388, 3183, 1679, 1627 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.89 (s, 2 H), 7.16 (d, *J* = 6.2 Hz, 1 H), 7.29–7.39 (m, 1 H), 7.29–7.39 (m, 2 H), 7.66–7.75 (m, 1 H), 7.78–7.90 (m, 3 H), 8.07 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 66.3, 108.7, 115.5 (overlapped with CF_3CO_2D signal), 120.3, 120.8 (overlapped with CF_3CO_2D signal), 126.3 (br s, 2C), 128.1 (2C), 133.3 (2C), 133.7, 134.3, 140.3, 147.3, 160.9, 161.0, 166.7, 173.7.

Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.90; H, 4.38; N, 8.87.

1,6-Dimethyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carboxamide (2n)

A mixture of nitrile **1n** (2.24 g, 0.01 mol), NaOH (4.00 g, 0.1 mmol), EtOH (50 mL), and H_2O (10 mL) was heated at reflux for 8 h. After cooling, the mixture was neutralized with 1N HCl solution. The solid formed was filtered off, washed with water, and recrystallized from EtOH.

Yield: 1.48 g (61%), 1.98 g (Method A, 82%), 1.62 g (Method B, 67%); pale-yellow crystals; mp 182–184 °C.

IR (KBr): 3433, 3198, 1673, 1632 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.39 (s, 3 H), 3.46 (s, 3 H), 6.18 (s, 1 H), 7.10 (s, 1 H), 7.36–7.42 (m, 3 H), 7.43–7.47 (m, 2 H), 7.56 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.3, 30.8, 107.2, 122.7, 127.6, 128.1, 128.2, 138.4, 147.0, 147.7, 160.5, 167.5.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.30; H, 5.91; N, 11.62.

[1,3]Oxazolo[5,4-*b*]pyridin-2(1*H*)-ones (4a–m); General Procedure

Sodium dichloroisocyanurate (1.10 g, 5 mmol) was added to a suspension of amide **2a–m** (5 mmol) in 2 N NaOH solution (20 mL). The mixture was vigorously stirred at r.t. for 2–3 h, and then neutralized with 2N HCl solution. The precipitate was filtered off, washed with water, and recrystallized from acetone or toluene.

5,7-Dimethyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4a)

Yield: 0.72 g (87%); white powder; mp 210–211 °C (acetone).

IR (KBr): 3476, 3294, 1777 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.23 (s, 3 H), 2.33 (s, 3 H), 6.84 (s, 1 H), 11.36 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 15.6, 23.0, 120.6, 120.8, 128.9, 148.4, 149.9, 151.3.

Anal. Calcd for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.03. Found: C, 58.68; H, 4.79; N, 17.12.

7-Methyl-5-phenyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4b)

Yield: 0.80 g (71%); pale-yellow powder; mp 226–228 °C (toluene).

IR (KBr): 3424, 3084, 1748 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3 H), 7.34–7.38 (m, 1 H), 7.42–7.46 (m, 2 H), 7.64 (s, 1 H), 7.93–7.98 (m, 2 H), 12.04 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 15.9, 118.8, 122.6, 125.9 (2C), 128.4, 128.7 (2C), 129.4, 137.9, 147.2, 152.5, 152.7.

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 68.89; H, 4.37; N, 12.44.

5-Methyl-7-phenyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4c)[18]

Yield: 1.04 g (92%); white powder; mp 225–228 °C (decomp.) (acetone).

IR (KBr): 3122, 1798, 1642 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.34 (s, 3 H), 6.99 (s, 1 H), 7.27 (t, *J* = 7.4 Hz, 1 H), 7.40 (dd, *J* = 8.2, 7.4 Hz, 2 H), 8.16 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.4, 113.6, 126.8, 127.2, 127.9 (2C), 128.4 (2C), 135.1, 137.2, 141.6, 158.6, 163.4.

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 68.89; H, 4.53; N, 12.52.

7-(4-Methoxyphenyl)-5-methyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4d)

Yield: 1.06 g (83%); white powder; mp 205–206 °C (acetone).

IR (KBr): 3211, 1791, 1634 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.42 (s, 3 H), 3.81 (s, 3 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 7.13 (s, 1 H), 7.56 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 55.4, 114.5 (2C), 117.9, 118.3, 126.2, 129.4 (2C), 130.8, 149.1, 152.7, 153.0, 160.0.

Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.38; H, 4.83; N, 10.77.

7-(3,4-Dimethoxyphenyl)-5-methyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4e)

Yield: 1.33 g (88%); white powder; mp 214–215 °C (acetone).

IR (KBr): 3207, 1787, 1635 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.43 (s, 3 H), 3.81 (s, 3 H), 3.85 (s, 3 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 7.14–7.16 (m, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 55.6, 55.7, 111.4, 112.1, 118.2, 118.5, 120.7, 126.6, 131.3, 149.0 (2C), 149.7, 152.8, 153.1.

Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.68; H, 4.99; N, 10.01.

5-Methyl-7-(2-thienyl)[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4f)

Yield: 0.84 g (72%); white powder; mp >250 °C (acetone).

IR (KBr): 3206, 1763, 1627 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.42 (s, 3 H), 7.14 (d, *J* = 3.5 Hz, 1 H), 7.23 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.69–7.72 (m, 1 H), 7.74 (d, *J* = 5.1 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.8, 116.1, 117.8, 124.0, 128.0, 128.1, 128.5, 135.9, 148.7, 153.1, 153.2.

Anal. Calcd for $C_{11}H_8N_2O_2S$: C, 55.88; H, 3.47; N, 12.06. Found: C, 56.06; H, 3.61; N, 12.23.

7-[4-(Dimethylamino)phenyl]-5-methyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4g)

Yield: 0.97 g (72%); pale-yellow powder; mp >250 °C (acetone).

IR (KBr): 3229, 1753, 1605 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.40 (s, 3 H), 2.95 (s, 6 H), 6.77 (d, *J* = 9.0 Hz, 2 H), 7.10 (s, 1 H), 7.46 (d, ^3J = 9.0 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.2, 39.8 (2C, overlapped with DMSO-d_6 signal), 112.2 (2C), 117.3, 117.7, 120.8, 128.8 (2C), 131.7, 149.0, 150.8, 152.8, 153.0.

Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60. Found: C, 67.12; H, 5.49; N, 15.43.

7-Phenyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4h)

Yield: 1.04 g (82%); white powder; mp 229–230 °C (acetone).

IR (KBr): 3507, 1808, 1793 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.31 (d, *J* = 5.5 Hz, 1 H), 7.47–7.55 (m, 3 H), 7.63–7.66 (m, 2 H), 7.98 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 119.6, 121.7, 128.1 (2C), 129.1 (2C), 129.3, 130.6, 133.8, 140.0, 153.1, 153.4.

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 68.26; H, 3.67; N, 13.40.

5,7-Diphenyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4i)

Yield: 1.05 g (73%); white powder; mp 224–225 °C (acetone).

IR (KBr): 3106, 1756, 1631 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.36–7.56 (m, 6 H), 7.74 (d, *J* = 6.7 Hz, 2 H), 7.87 (s, 1 H), 8.06 (d, *J* = 7.2 Hz, 2 H), 12.12 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 115.9, 120.7, 126.2 (2C), 128.3 (2C), 128.5, 128.7 (2C), 129.0 (2C), 129.2, 131.4, 134.0, 137.8, 147.9, 153.1, 153.3.

Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 74.72; H, 4.31; N, 9.92.

5-(3,4-Dimethoxyphenyl)-7-phenyl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4j)

Yield: 1.09 g (63%); white powder; mp >250 °C (acetone).

IR (KBr): 3208, 1777, 1636 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.80 (s, 3 H), 3.85 (s, 3 H), 7.02 (d, *J* = 9.0 Hz, 1 H), 7.48–7.57 (m, 3 H), 7.61–7.64 (m, 2 H), 7.72–7.77 (m, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.5, 55.6, 110.0, 112.0, 115.0, 118.9, 120.0, 128.1 (2C), 128.8 (2C), 129.0, 130.6, 131.4, 134.0, 147.9, 149.0, 149.6, 152.9, 153.1.

Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.73; H, 4.78; N, 8.16.

7-Phenyl-5-pyridin-2-yl[1,3]oxazolo[5,4-*b*]pyridin-2(1*H*)-one (4k)

Yield: 0.95 g (64%); white powder; mp 224 °C (acetone).

IR (KBr): 3202, 1784, 1633 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.39 (dd, *J* = 7.8, 4.4 Hz, 1 H), 7.49–7.59 (m, 3 H), 7.62–7.72 (m, 2 H), 7.88–7.94 (ddd, *J* = 8.0, 7.8, 1.7 Hz, 1 H); 8.23 (d, *J* = 8.0 Hz, 1 H), 8.31 (s, 1 H), 8.63 (d, *J* = 4.4 Hz, 1 H), 12.19 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 116.3, 119.7, 121.1, 123.6, 128.0 (2C), 129.1 (2C), 129.2, 131.1, 133.9, 137.2, 146.7, 149.1, 152.9, 153.0, 154.3.

Anal. Calcd for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.53. Found: C, 70.32; H, 3.96; N, 14.41.

7-Phenyl-5,8-dihydrobenzo[*h*][1,3]oxazolo[5,4-*b*]quinolin-9(6*H*)-one (4l)

Yield: 1.11 g (71%); white powder; mp >250 °C (acetone).

IR (KBr): 3179, 1767, 1624 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.67–2.78 (m, 4 H), 7.22–7.33 (m, 3 H), 7.42 (d, *J* = 6.7 Hz, 1 H), 7.49–7.58 (m, 3 H), 8.06 (d, *J* = 7.2 Hz, 1 H), 11.78 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 24.6, 27.2, 122.1, 124.1, 126.3, 126.8, 127.5, 128.4, 128.7, 128.8 (2C), 129.2 (2C), 130.7, 132.7, 134.0, 137.0, 143.1, 151.3, 153.0.

Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 74.42; H, 4.49; N, 8.91. Found: C, 74.20; H, 4.49; N, 8.91.

7-Phenyl-6*H*-chromeno[4,3-*b*][1,3]oxazolo[4,5-*e*]pyridin-9(8*H*)-one (4m)

Yield: 1.09 g (69%); yellow powder; mp >250 °C (acetone).

IR (KBr): 3185, 1772, 1629 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 5.07 (s, 2 H), 6.93 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.10 (ddd, *J* = 7.7, 7.6, 1.0 Hz, 1 H), 7.29 (ddd, *J* = 8.0, 7.6, 1.5 Hz, 1 H), 7.41 (dd, *J* = 7.7, 1.5 Hz, 2 H), 7.53–7.58 (m, 3 H), 8.00 (dd, *J* = 7.7, 1.7 Hz, 1 H), 11.04 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 65.1, 116.4, 120.4, 122.3, 122.8, 123.9, 128.7, 128.9 (2C), 130.0 (2C), 129.2, 130.5, 131.1, 139.4, 149.6, 152.5, 152.6, 154.9.

Anal. Calcd for $C_{19}H_{12}N_2O_3$: C, 72.15; H, 3.82; N, 8.86. Found: C, 72.42; H, 3.90; N, 8.74.

3-Aminopyridin-2(1*H*)-ones 5a–m; General Procedure

Method A

Solid NaOH (0.32 g, 8 mmol) was added to a suspension of oxazolone **4a–m** (2 mmol) in EtOH (2 mL) and H_2O (2 mL for **4b–m** or 4 mL for **4a**). The mixture was heated at reflux for 2–4 h under nitrogen atmosphere. After cooling, the mixture was diluted with water (6 mL) and acidified with 2N HCl solution to pH 8–9. The precipitate formed was filtered off and recrystallized from EtOH, H_2O or EtOH–H_2O (1:1).

Method B

Sodium dichloroisocyanurate (0.44 g, 2 mmol) and NaOH (0.64 g, 16 mmol) were added to a cooled suspension of amide **2b**, **2c**, **2i**, **2k**, **2l** (2 mmol) in H_2O (10 mL). The mixture was stirred for 2–3 h at r.t., EtOH (5 mL) was added and the mixture was heated at reflux under nitrogen for 2–4 h. After cooling, the mixture was diluted with water (6 mL) and acidified with 2N HCl solution to pH 8–9. The precipitate formed was filtered off, purified by column chromatography with silica gel ($CHCl_3$–MeCOOEt, 1:1) and recrystallized from EtOH or EtOH–H_2O (1:1).

3-Amino-4,6-dimethylpyridin-2(1*H*)-one (5a)

Yield: 0.257 g (Method A, 93%); white crystals; mp 202–203 °C (water) (Lit.[32] 201–202 °C).

IR (KBr): 3441, 3327, 1641 cm^{-1}.

UV (H_2O): λ_{max} (log ε) = 249 (3.33), 311 nm (3.65).

Anal. Calcd for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 60.93; H, 7.27; N, 20.34.

3-Amino-4-methyl-6-phenylpyridin-2(1*H*)-one (5b)

Yield: 0.332 g (Method A, 83%), 0.132 g (Method B, 33%); white crystals; mp 186–187 °C (ethanol).

IR (KBr): 3412, 3320, 1643 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 337 nm (4.24).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 3.85 (br s, 2 H), 7.33 (t, *J* = 7.3 Hz, 1 H), 7.41 (dd, *J* = 7.4, 7.3 Hz, 2 H), 7.63 (d, *J* = 7.4 Hz, 2 H), 11.68 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0, 109.0, 124.7, 125.6 (2C), 128.3, 128.9, 133.0, 133.5, 134.1, 158.7.

Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.96; H, 6.00; N, 14.05.

3-Amino-6-methyl-4-phenylpyridin-2(1*H*)-one (5c)[7a]

Yield: 0.348 g (Method A, 87%), 0.188 g (Method B, 47%); white crystals; mp 194–195 °C (ethanol–water).

IR (KBr): 3448, 3350, 1632 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 239 (4.30), 334 nm (3.95).

Anal. Calcd for $C_{12}H_{12}N_2O$: C, 72.10; H, 6.13; N, 13.91. Found: C, 71.98; H, 6.04; N, 13.99.

3-Amino-4-(4-methoxyphenyl)-6-methylpyridin-2(1*H*)-one (5d)[7b]

Yield: 0.377 g (Method A, 82%); white crystals; mp 206–208 °C (decomp.) (ethanol–water).

IR (KBr): 3452, 3354, 1634 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 249 (4.27), 335 nm (3.89).

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.94; H, 6.07; N, 12.25.

3-Amino-4-(3,4-dimethoxyphenyl)-6-methylpyridin-2(1*H*)-one (5e)[7b]

Yield: 0.437 g (Method A, 84%); pale-yellow crystals; mp 216–217 °C (ethanol–water).

IR (KBr): 3438, 3337, 1637 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 252 (4.26), 293 (3.87), 334 nm (3.99).

Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.82; H, 6.13; N, 10.88.

3-Amino-6-methyl-4-(2-thienyl)pyridin-2(1*H*)-one (5f)[7b]

Yield: 0.313 g (Method A, 79%); pale-yellow crystals; mp 189–191 °C (ethanol–water).

IR (KBr): 3390, 3314, 1656 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 255 (4.20), 351 nm (3.92).

Anal. Calcd for $C_{10}H_{10}N_2OS$: C, 58.23; H, 4.89; N, 13.58. Found: C, 58.46; H, 4.99; N, 13.67.

3-Amino-4-[4-(dimethylamino)phenyl]-6-methylpyridin-2(1*H*)-one (5g)

Yield: 0.290 g (Method A, 62%); pale-yellow crystals; mp 244–245 °C (ethanol).

IR (KBr): 3476, 3361, 1632 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 263 (4.16), 311 (4.13), 339 nm (4.08).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.10 (s, 3 H), 2.92 (s, 6 H), 4.35 (br s, 2 H), 5.80 (s, 1 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 7.32 (d, *J* = 8.8 Hz, 2 H), 11.21 (br s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 17.6, 39.7 (2C, overlapped with DMSO-d_6 signal), 106.0, 112.2 (2C), 124.8, 125.3, 128.2 (2C), 129.4, 130.5, 149.4, 158.64.

Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.29; H, 6.96; N, 17.44.

3-Amino-4-phenylpyridin-2(1*H*)-one (5h)

Yield: 0.296 g (Method A, 80%); white crystals; mp 227–228 °C (ethanol–water).

IR (KBr): 3418, 3321, 1618 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 235 (4.26), 329 nm (3.87).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.37 (br s, 2 H), 6.21 (d, *J* = 6.9 Hz, 1 H), 6.86 (d, *J* = 6.9 Hz, 1 H), 7.34–7.38 (m, 4 H), 11.94 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.8, 120.7, 126.7, 128.0, 128.1 (2C), 129.1 (2C), 134.2, 137.7, 159.3.

Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.18; H, 5.50; N, 15.04.

3-Amino-4,6-diphenylpyridin-2(1*H*)-one (5i)

Yield: 0.393 g (Method A, 75%), 0.204 g (Method B, 39%); yellow crystals; mp 208 °C (ethanol).

IR (KBr): 3445, 3348, 1632 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 237 (4.30), 260 (4.23), 364 nm (4.21).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.47 (br s, 2 H), 6.49 (s, 1 H), 7.33–7.34 (m, 4 H), 7.47–7.49 (m, 2 H), 7.55 (d, *J* = 7.2 Hz, 2 H), 7.71 (d, *J* = 7.6 Hz, 2 H), 12.23 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.8, 125.7 (2C), 128.7, 127.9, 128.1 (2C), 128.2, 128.8 (2C), 129.1 (2C), 133.0, 133.1, 134.1, 137.9, 159.4.

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 78.06; H, 5.45; N, 10.79.

3-Amino-6-(3,4-dimethoxyphenyl)-4-phenylpyridin-(1*H*)-one (5j)

Yield: 0.387 g (Method A, 60%); yellow crystals; mp 218–219 °C (ethanol).

IR (KBr): 3435, 3342, 1633 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 266 (4.20), 303 (4.09), 353 nm (4.20).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H), 4.00 (s, 3 H), 4.39 (br s, 2 H), 6.43 (s, 1 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 7.24–7.29 (m, 2 H), 7.41 (t, *J* = 7.2 Hz, 1 H), 7.54–7.58 (m, 2 H), 7.54–7.58 (m, 2 H), 11.95 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.0, 56.2, 107.1, 109.5, 111.6, 118.5, 127.2, 127.3, 128.0, 128.2 (2C), 129.1 (2C), 132.5, 133.3, 138.0, 149.4, 149.5, 159.5.

Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.58; H, 5.52; N, 8.80.

5-Amino-4-phenyl-2,2′-bipyridin-6(1*H*)-one (5k)

Yield: 0.368 g (Method A, 70%), 0.138 g (Method B, 26%); yellow crystals; mp 98 °C (ethanol).

IR (KBr): 3478, 3358, 1638 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 267 (4.12), 364 nm (4.32).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65 (br s, 2 H), 6.80 (s, 1 H), 7.15–7.21 (m, 1 H), 7.36–7.42 (m, 1 H), 7.46–7.53 (m, 4 H), 7.64–7.71 (m, 2 H), 8.55 (d, *J* = 4.7 Hz, 1 H), 10.66 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.5, 117.8, 122.4, 123.4, 128.0, 128.1 (2C), 129.2 (2C), 128.8, 135.8, 136.8, 137.7, 148.8, 149.0, 157.5.

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 73.17; H, 5.06; N, 15.83.

3-Amino-4-phenyl-5,6-dihydrobenzo[*h*]quinolin-2(1*H*)-one (5l)

Yield: 0.420 g (Method A, 73%), 0.242 g (Method B, 42%); pale-yellow crystals; mp 167–169 °C (ethanol).

IR (KBr): 3478, 3358, 1638 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 239 (4.25), 364 nm (4.26).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (t, *J* = 7.4 Hz, 2 H), 2.70 (t, *J* = 7.4 Hz, 2 H), 4.23 (br s, 2 H), 7.13–7.20 (m, 2 H), 7.26–7.34 (m, 3 H), 7.40 (d, *J* = 7.4 Hz, 1 H), 7.47–7.53 (m, 2 H), 7.93 (d, *J* = 7.8 Hz, 1 H), 12.05 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 28.6, 116.1, 121.5, 126.9, 127.0, 127.3, 127.8, 128.0, 129.0 (2C), 129.3 (2C), 129.4, 134.0, 135.9, 136.2 (2C), 158.2.

Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 79.36; H, 5.67; N, 9.60.

3-Amino-4-phenyl-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-2-one (5m)

Yield: 0.371 g (Method A, 64%); yellow crystals; mp >250 °C (ethanol).

IR (KBr): 3463, 3351, 1641 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 236 (4.34), 317 (3.91), 372 nm (4.36).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.33 (br s, 2 H), 4.72 (s, 2 H), 6.87 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.04 (ddd, *J* = 7.7, 7.6, 1.1 Hz, 1 H), 7.16 (ddd, *J* = 7.9, 7.6, 1.4 Hz, 1 H), 7.29 (d, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 7.4 Hz, 1 H), 7.51 (dd, *J* = 7.4, 7.4 Hz, 2 H), 8.03 (dd, *J* = 7.7, 1.4 Hz, 1 H), 12.85 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.4, 110.4, 116.7, 118.4, 121.8, 122.1, 123.7, 124.9, 128.5, 128.7 (2C), 129.5 (2C), 129.3, 134.1, 134.3, 154.1, 158.7.

Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.69; H, 4.73; N, 9.45.

3-Amino-1,6-dimethyl-4-phenylpyridin-2(1*H*)-one (5n)

Sodium dichloroisocyanurate (0.220 g, 1 mmol) was added to a mixture of amide **2n** (0.240 g, 1 mmol) and NaOH (0.32 g, 8 mmol) in EtOH (4 mL) and water (2 mL). The mixture was vigorously stirred at r.t. for 1 h, and then neutralized with 2N HCl solution. The precipitate was filtered off, washed with water, and recrystallized from ethanol.

Yield: 0.170 g (79%); pale-yellow crystals; mp 150–152 °C (ethanol).

IR (KBr): 3457, 3316, 1642 cm^{-1}.

UV (EtOH): λ_{max} (log ε) = 237 (4.32), 335 nm (3.88).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (d, *J* = 0.8 Hz, 3 H), 3.59 (s, 3 H), 4.22 (br s, 2 H), 5.97 (d, *J* = 0.8 Hz, 1 H), 7.29–7.34 (m, 1 H), 7.40–7.47 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 31.6, 108.3, 124.5, 127.7, 128.0 (2C), 128.9 (2C), 131.3, 131.9, 137.9, 158.9.

Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.90; H, 6.53; N, 13.14.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690231.

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