HETEROCYCLES, Vol. 89, No. 3, 2014, pp. 739 - 746. © 2014 The Japan Institute of Heterocyclic Chemistry
Received, 20th December, 2013, Accepted, 24th January, 2014, Published online, 29th January, 2014
DOI: 10.3987/COM-13-12919

SYNTHESIS OF 10-SUBSTITUTED BENZO[*b*][1,8]NAPHTHYRIDIN-5(10*H*)-ONES BASED ON THE REACTION OF (2-CHLOROPYRIDIN-3-YL)(2-HALOPHENYL)METHANONES WITH PRIMARY AMINES

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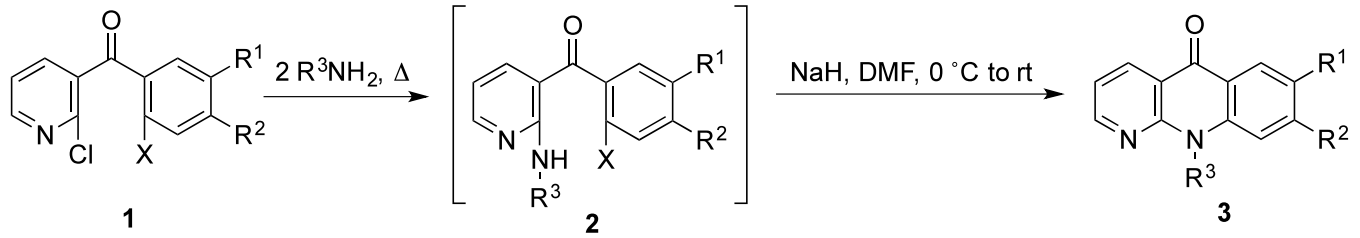
Abstract – The reaction of (2-chloropyridin-3-yl)(2-halophenyl)methanones, derived from 2-chloropyridine and 2-halobenzaldehydes, with two equivalents of benzenamines or arylmethanamines followed by treatment of the resulting (2-aryl(or arylmethyl)aminopyridin-2-yl)(2-halophenyl)methanones with sodium hydride in DMF at 0 ˚C to room temperature have proven to provide an efficient method for the preparation of 10-aryl(or arylmethyl)benzo[*b*][1,8]naphthyridin-5(10*H*)-ones. This methodology is shown to be applicable for the preparation benzo[*b*][1,7]naphthyridin-5(10*H*)-one derivatives by using 3-chloropyridine as a starting material in place of 2-chloropyridine.

Benzo[*b*][1,8]naphthyridin-5(10*H*)-ones have attracted much attention because some of these derivatives have recently been reported to exhibit biological activity.[1] Moreover, a compound having this heterocyclic structure has been found in nature.[2] The construction of benzo[*b*][1,8]naphthyridin-5(10*H*)-one structure commonly relies upon intramolecular Friedel-Crafts acylation of 2-(phenylamino)pyridine-3-carboxylic acid.[3] However, this synthesis suffers from the harsh reaction conditions and the limited scope of substrates. Therefore, new synthetic approaches to this class of heterocycles have recently reported.[4] On the other hand, we previously demonstrated a synthesis of 10-substituted acridin-9(10*H*)-ones by the reaction of (2-fluorophenyl)(2-halophenyl)methanones with primary amines and the subsequent treatment with sodium hydride.[5] We envisioned that similar treatment of (2-chloropyridin-3-yl)(2- halophenyl)methanones with primary amines and then sodium hydride could result in the formation of 10-substituted benzo[*b*][1,8]naphthyridin-5(10*H*)-ones. In this manuscript, we present a novel methodology that allows the facile synthesis of 10-aryl(or

arylmethyl)benzo[*b*][1,8]naphthyridin-5(10*H*)-ones (**3**) starting from the reaction of 2-chloro-3-lithiopyridine, generated from 2-chloropyridine,[6] with 2-halobenzaldehydes.[7] We also report a similar preparation of 10-substituted benzo[*b*][1,7]naphthyridin-5(10*H*)-ones (**6**) starting from 3-chloropyridine. Benzo[*b*][1,7]naphthyridin-5(10*H*)-one derivatives are also of biological interest.[8]

Our synthesis of 10-substituted benzo[*b*][1,8]naphthyridin-5(10*H*)-ones (**3**) from (2-chloropyridin-3-yl)(2-halophenyl)methanones (**1**) was conducted by following the procedure illustrated in Scheme 1. The precursors (**1**) were easily prepared in satisfactory yields from commercially available 2-chloropyridine and 2-halobenzaldehydes according to the procedure previously reported by us.[9] These precursors were then heated with two equivalents of benzenamines or arylmethanamines at the temperature indicted in Table 1 without any solvents. After removal of the respective ammonium chlorides (see Experimental section), the resulting crude (2-aryl(or arylmethyl)aminopyridin-3-yl)(2-halophenyl)methanones (**2**) were treated with sodium hydride in DMF at 0 ˚C to room temperature to give, after workup with water and purification of the resulting precipitate by recrystallization, the desired products **3**. As can be seen from Table 1, good yields were obtained independent of the substituent on the benzene ring of the amines. For the first step of the procedure, somewhat higher temperature was required for the synthesis of 10-aryl derivatives compared to that for the synthesis of 10-arylmethyl derivatives. This can be reasonably explained by the lower nucleophilicity of benzenamines than that of arylmethanamines. For the subsequent ring closure step, the halogen ortho to the carbonyl (X = Cl or Br) did not give marked influence on the progress of the reaction. The unambiguous assignments of the intermediate **2** were not achieved. However, the single product was observed in each case by TLC analyses of the crude reaction mixtures, and the selective substitution of amines with the 2-chloro on the pyridine ring is reasonable.



Scheme 1

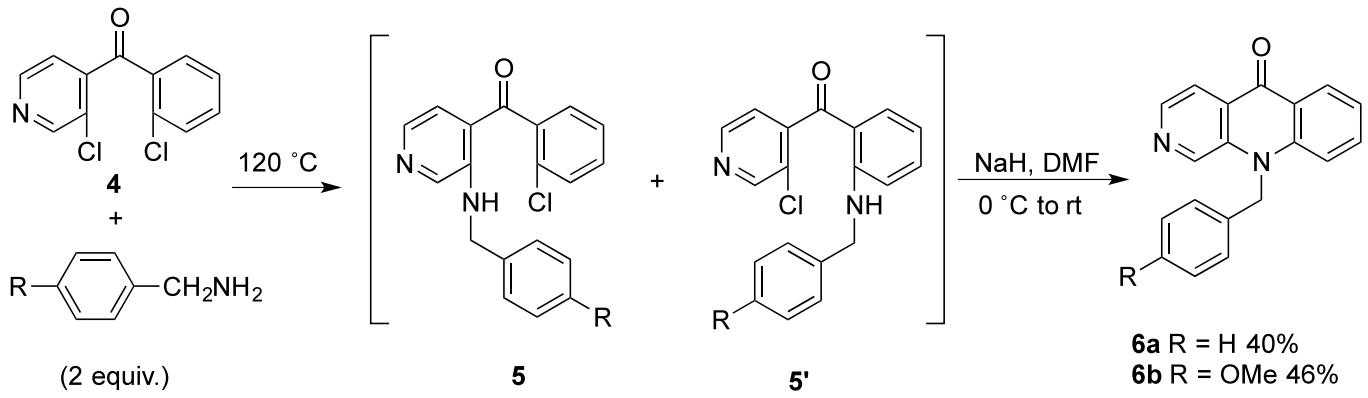
Subsequently, the present procedure proved to be applicable to the synthesis of 10-substituted benzo[*b*][1,7]naphthyridin-5(10*H*)-ones (**6**). (2-Chlorophenyl)(3-chloropyridin-4-yl)methanones (**4**)[5] was first subjected to the reaction with benzenamine. However, it proceeded very sluggishly and uncleanly to give a considerably complex mixture of products and only a trace amount of the desired 10-phenylbenzo[*b*][1,7]naphthyridin-5(10*H*)-one was obtained after treatment with sodium hydride as

described above. Fortunately, arylmethanamines performed better than benzenamine. When compound (**4**) was allowed to react with phenylmethanamine and (4-methoxyphenyl)methanamine, substitution of one of the chloro groups of **4** with these amines proceeded rather slowly. However, the resulting crude intermediates (**5**) and (**5'**) were treated with sodium hydride to afford the corresponding desired products, 10-(arylmethyl)benzo[*b*][1,7]naphthyridin-5(10*H*)-ones (**6a**) and (**6b**), respectively, in moderate yields, as shown in Scheme 2.

Table 1. Preparation of benzo[*b*][1,8]naphthyridin-5(10*H*)-ones (**3**)

Entry	**1**	R^3	Temp./°C	**3**	Yield/%[a]
1	**1a** ($R^1 = R^2 = H$, X = Cl)	Ph	120	**3a**	93
2	**1a**	4-$MeOC_6H_4$	120	**3b**	94
3	**1a**	Bn	100	**3c**	85
4	**1a**	4-$MeOC_6H_4CH_2$	100	**3d**	88
5	**1b** (R^1 = Cl, R^2 = H, X = Br)	4-ClC_6H_4	120	**3e**	88
6	**1b**	4-$MeC_6H_4CH_2$	100	**3f**	92
7	**1c** (R^1 = OMe, R^2 = H, X = Br)	4-MeC_6H_4	120	**3g**	82
8	**1c**	Bn	100	**3h**	89
9	**1d** ($R^1 = R^2$ = OMe, X = Br)	Ph	120	**3i**	84
10	**1d**	Bn	100	**3j**	90

[a] Yields of isolated products.



Scheme 2

It is important to note that the present procedure could not be applied to the synthesis of 5-substituted benzo[*b*][1,6]naphthyridin-10(5*H*)-ones, because (2-chlorophenyl)(4-chloro-3-pyridin-3-yl)methanone was too unstable to be isolated in enough pure form to use in the next step.

In conclusion, we have developed a facile method for the synthesis of 10-substituted benzo[*b*][1,8]naphthyridin-5(10*H*)-ones from readily available starting materials, 2-chloropyridine, 2-halobenzaldehydes, and primary amines using easy operations. We also have present the method can be applied to the synthesis of 10-(arylmethyl)benzo[*b*][1,7]naphthyridin-5(10*H*)-ones, though the yields is

not so high compared to those of benzo[*b*][1,8]naphthyridin-5(10*H*)-ones.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum65 FTIR spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400FT NMR spectrometer operating at 400 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low- (EI, 70 eV) or high-resolution MS spectra (DART, positive) were measured by a JEOL JMS AX505 HA spectrometer or a Thermo Scientific Exactive spectrometer, respectively. TLC was carried out on Merck Kieselgel 60 PF_{254}. Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. *n*-BuLi was supplied by Asia Lithium Corporation. All other chemicals used in this study were commercially available.

(2-Chloropyridin-3-yl)(2-halophenyl)methanones (1) and (2-chlorophenyl)(3-chloropyridin-4-yl)methanone (4): prepared from the respective chloropyridines and 2-halobenzaldehydes, *via* oxidation of the corresponding (2-chloropyridin-3-yl)(2-halophenyl)methanols, according to the reported procedure.[9] The physical, spectral, and analytical data for new compounds follow.

(2-Bromo-5-chlorophenyl)(2-chloropyridin-3-yl)methanol: yield: 77%; a yellow solid; mp 142–144 °C (hexane/CH_2Cl_2); IR (KBr) 3385 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.82 (br s, 1H), 6.38 (s, 1H), 7.22 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.28 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 2.0 Hz, 1H), 8.38 (dd, *J* = 4.9, 2.0 Hz, 1H). Anal. Calcd for $C_{12}H_8BrCl_2NO$: C, 43.28; H, 2.42; N, 4.21. Found: C, 43.20; H, 2.43; N, 4.18.

(2-Bromo-5-chlorophenyl)(2-chloropyridin-3-yl)methanone (1b): yield: 74%; a yellow oil; R_f 0.47 (AcOEt/hexane 1:5); IR (neat) 1688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.42 (m, 2H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.94 (dd, *J* = 7.8, 2.0 Hz, 1H), 8.58 (dd, *J* = 4.9, 2.0 Hz, 1H). Anal. Calcd for $C_{12}H_6BrCl_2NO$: C, 43.54; H, 1.83; N, 4.23. Found: C, 43.26; H, 2.01; N, 4.11.

(2-Bromo-4,5-dimethoxyphenyl)(2-chloropyridin-3-yl)methanol: yield: 72%; a beige oil; R_f 0.38 (AcOEt/hexane 1:3); IR (neat) 3382, 1602 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.77 (br s, 1H), 3.79 (s, 3H), 3.89 (s, 3H), 6.34 (s, 1H), 6.87 (s, 1H), 7.05 (s, 1H), 7.26 (dd, *J* = 8.4, 5.1 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.35 (dd, *J* = 5.1, 1.7 Hz, 1H). Anal. Calcd for $C_{14}H_{13}BrClNO_3$: C, 46.89; H, 3.65; N, 3.91. Found: C, 46.94; H, 3.50; N, 3.61.

(2-Bromo-4,5-dimethoxyphenyl)(2-chloropyridin-3-yl)methanone (1d): yield: 74%; a white solid; mp

123–125 °C (hexane/CH_2Cl_2); IR (KBr) 1668 cm^{-1}; ^1H NMR (400 MHz) δ 3.90 (s, 3H), 3.95 (s, 3H), 7.05 (s, 1H), 7.20 (s, 1H), 7.37 (dd, *J* = 8.4, 5.1 Hz, 1H), 7.84 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.53 (dd, *J* = 5.1, 1.7 Hz, 1H). Anal. Calcd for $C_{14}H_{11}BrClNO_3$: C, 47.15; H, 3.11; N, 3.93. Found: C, 45.85; H, 3.06; N, 3.76.

Typical Procedure for the Preparation of Benzo[*b*][1,8]naphthyridin-5(10*H*)-ones (3) and Benzo[*b*][1,7]naphthyridin-5(10*H*)-ones (6). 10-Phenylbenzo[*b*][1,8]naphthyridin-5(10*H*)-one (3a). A mixture of **1a** (0.20 g, 0.79 mmol) and $PhNH_2$ (0.15 g, 1.6 mmol) was heated at 120 °C under stirring until complete consumption of **1a** had been confirmed by TLC analysis on SiO_2 (*ca*. 3.5 h). After cooling to rt, Et_2O (20 mL) was added and the precipitate was filtered off. The filtrate was concentrated by evaporation to give a residue, which was dissolved in DMF (3 mL). To this solution NaH (60% in oil; 38 mg, 0.95 mmol) was added at 0 °C under stirring and it was continued at rt overnight. Water (20 mL) was added and the precipitate was collected by filtration and recrystallized from hexane/CH_2Cl_2 to give **3a** (0.20 g, 93%); a white solid; mp 267–269 °C; IR (KBr) 1649, 1607 cm^{-1}; ^1H NMR (500 MHz) δ 6.86 (d, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 7.8, 4.6 Hz, 1H), 7.33 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1H), 7.55 (dd, *J* = 7.8, 7.3, 1.4 Hz, 1H), 7.62 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.68 (dd, *J* = 7.8, 7.3 Hz, 2H), 8.56 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.63 (dd, *J* = 4.6, 2.3 Hz, 1H), 8.85 (dd, *J* = 7.8, 2.3 Hz, 1H); ^{13}C NMR δ 116.75, 117.45, 117.92, 122.16, 122.25, 127.21, 129.09, 129.86, 130.38, 133.89, 136.53, 138.74, 143.33, 152.15, 153.80, 178.66; MS *m*/*z* 272 (M^+, 100). Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.40; H, 4.48; N, 10.04.

10-(4-Methoxyphenyl)benzo[*b*][1,8]naphthyridin-5(10*H*)-one (3b): a white solid; mp 243–245 °C (hexane/CH_2Cl_2); IR (KBr) 1649, 1607 cm^{-1}; ^1H NMR (500 MHz) δ 3.93 (s, 3H), 6.92 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.24 (dd, *J* = 7.8, 4.6 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.31 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1H), 7.55 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1H), 8.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.66 (dd, *J* = 4.6, 1.8 Hz, 1H), 8.84 (dd, *J* = 7.8, 1.8 Hz, 1H); ^{13}C NMR δ 55.50, 115.59, 116.82, 117.53, 117.84, 122.17, 122.19, 127.16, 130.71, 131.12, 133.86, 136.53, 143.69, 152.38, 153.83, 159.72, 178.66; MS *m*/*z* 302 (M^+, 100). Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.44; H, 4.69; N, 9.16.

10-(Phenylmethyl)benzo[*b*][1,8]naphthyridin-5(10*H*)-one (3c): a pale-yellow solid; mp 166–168 °C (hexane–CH_2Cl_2) (lit.,[10] mp 166–168 °C). The IR and ^1H NMR data for this product were identical to those reported previously.[10]

10-[(4-Methoxyphenyl)methyl]benzo[*b*][1,8]naphthyridin-5(10*H*)-one (3d): a pale-yellow solid; mp 185–187 °C (hexane/CH_2Cl_2); IR (KBr) 1640, 1608 cm^{-1}; ^1H NMR (500 MHz) δ 3.76 (s, 3H), 6.02 (br, 2H), 6.83 (d, *J* = 9.2 Hz, 2H), 7.12 (d, *J* = 9.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.29–7.33 (m, 2H), 7.65 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 8.56 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.78 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.86 (dd, *J* = 8.0, 1.7 Hz, 1H); ^{13}C NMR δ 46.49, 55.20, 114.23, 116.27, 116.87, 117.90, 122.05, 122.76, 127.31, 127.59, 128.65, 134.39, 136.81, 141.84, 151.16, 153.74, 158.80, 178.50; MS *m*/*z* 316 (M^+, 100). Anal.

Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.86; H, 5.19; N, 8.74.

7-Chloro-10-(4-chlorophenyl)-10*H*-benzo[*b*][1,8]naphthyridin-5-one (3e): a pale-yellow solid; mp 238–240 ˚C (hexane/CH_2Cl_2); IR (KBr) 1639 cm^{-1}; ^1H NMR (500 MHz) δ 6.83 (d, *J* = 9.2 Hz, 1H), 7.27–7.31 (m, 3H), 7.49 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 8.50 (d, *J* = 2.3 Hz, 1H), 8.63 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.81 (dd, *J* = 8.0, 1.7 Hz, 1H); ^{13}C NMR δ 116.62, 118.46, 118.93, 123.02, 126.49, 128.58, 130.85, 131.15, 134.15, 135.37, 136.71, 136.81, 141.41, 151.88, 154.02, 177.44; MS *m/z* 340 (M^+, 100). Anal. Calcd for $C_{18}H_{10}Cl_2N_2O$: C, 63.36; H, 2.95; N, 8.21. Found: C, 63.46; H, 3.05; N, 8.35.

7-Chloro-10-[(4-methylphenyl)methyl]-10*H*-benzo[*b*][1,8]naphthyridin-5-one (3f): a pale-yellow solid; mp 252–254 ˚C (hexane/CH_2Cl_2); IR (KBr) 1635, 1600 cm^{-1}; ^1H NMR (500 MHz) δ 2.30 (s, 3H), 6.02 (br s, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 7.4, 4.6 Hz, 1H), 7.45 (d, *J* = 9.2 Hz, 1H), 7.55 (dd, *J* = 9.1, 2.9 Hz, 1H), 8.50 (d, *J* = 2.9 Hz, 1H), 8.77 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.84 (dd, *J* = 7.4, 1.7 Hz, 1H); ^{13}C NMR δ 21.03, 46.96, 116.76, 118.12, 118.23, 123.68, 125.92, 126.75, 128.14, 129.60, 133.25, 134.45, 136.91, 137.18, 140.27, 151.03, 154.05, 177.40; MS *m/z* 334 (M^+, 100). Anal. Calcd for $C_{20}H_{16}ClN_2O$: C, 71.75; H, 4.52; N, 8.37. Found: C, 71.70; H, 4.80; N, 8.21.

7-Methoxy-10-(4-methylphenyl)-10*H*-benzo[*b*][1,8]naphthyridin-5-one (3g): a yellow solid; mp 223–225 ˚C (hexane/$CHCl_3$); IR (KBr) 1638, 1615 cm^{-1}; ^1H NMR (500 MHz) δ 2.52 (s, 3H), 3.95 (s, 3H), 6.86 (d, *J* = 9.7 Hz, 1H), 7.18 (dd, *J* = 9.7, 3.4 Hz, 1H), 7.22–7.24 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 3.4 Hz, 1H), 8.65 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.85 (dd, *J* = 8.0, 1.7 Hz, 1H); ^{13}C NMR δ 21.42, 55.83, 100.03, 105.96, 115.96, 117.58, 119.31, 122.83, 124.61, 129.47, 131.06, 136.16, 138.26, 139.07, 151.60, 153.77, 155.18, 178.07; MS *m/z* 316 (M^+, 100). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.85; H, 5.24; N, 8.77.

7-Methoxy-10-phenylmethyl-10*H*-benzo[*b*][1,8]naphthyridin-5-one (3h): a yellow solid; mp 175–177 ˚C (hexane/CH_2Cl_2); IR (KBr) 1634, 1614 cm^{-1}; ^1H NMR (500 MHz) δ 3.92 (s, 3H), 6.10 (br s, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.23–7.30 (m, 5H), 7.44 (d, *J* = 9.6 Hz, 1H), 7.96 (d, *J* = 3.2 Hz, 1H), 8.76 (dd, *J* = 4.6, 1.8 Hz, 1H), 8.87 (dd, *J* = 7.8, 1.8 Hz, 1H); ^{13}C NMR δ 47.10, 55.76, 196.69, 116.08, 117.66, 118.01, 121.06, 123.59, 124.98, 126.02, 127.30, 128.86, 136.54, 136.88, 150.64, 153.67, 155.01, 177.93; MS *m/z* 316 (M^+, 100). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.79; H, 5.10; N, 8.86.

7,8-Dimethoxy-10-phenyl-10*H*-benzo[*b*][1,8]naphthyridin-5-one (3i): a yellow solid; mp 222–224 ˚C (hexane/CH_2Cl_2); IR (KBr) 1637, 1616 cm^{-1}; ^1H NMR (500 MHz) δ 3.66 (s, 3H), 4.03 (s, 3H), 6.21 (s, 1H), 7.25 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.69 (dd, *J* = 8.0, 7.4 Hz, 2H), 7.92 (s, 1H), 8.60 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.85 (dd, *J* = 8.0, 1.7 Hz, 1H); ^{13}C NMR δ 55.79, 56.29, 96.10, 99.00, 106.26, 115.94, 116.29, 117.73, 129.18, 129.81, 130.36, 136.31, 138.90, 139.63, 146.00, 153.04, 154.80, 174.50; MS *m/z* 332 (M^+, 100). Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N,

8.43. Found: C, 72.79; H, 4.94; N, 8.24.

7,8-Dimethoxy-10-phenylmethyl-10*H*-benzo[*b*][1,8]naphthyridin-5-one (3j): a yellow solid; mp 209–211 ˚C (hexane/CH_2Cl_2); IR (KBr) 1637, 1614 cm^{-1}; ^1H NMR (500 MHz,) δ 3.79 (s, 3H), 4.00 (s, 3H), 6.10 (br s, 2H), 6.86 (s, 1H), 7.19 (d, *J* = 6.9 Hz, 2H), 7.26 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.29–7.32 (m, 3H), 7.92 (s, 1H), 8.75 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.88 (dd, *J* = 8.0, 1.7 Hz, 1H); ^{13}C NMR δ 47.35, 56.00, 56.19, 98.37, 106.72, 116.48, 116.63, 117.80, 126.13, 127.45, 128.96, 136.66, 137.06, 138.02, 145.77, 150.78, 152.88, 155.02, 176.70; MS *m/z* 346 (M^+, 100). Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.65; H, 5.45; N, 8.04.

10-(Phenylmethyl)benzo[*b*][1,7]naphthyridin-5(10*H*)-one (6a): a yellow solid; mp 170–172 ˚C (hexane/CH_2Cl_2); IR (KBr) 1643, 1607 cm^{-1}; ^1H NMR (500 MHz) δ 5.71 (s, 2H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.34–7.40 (m, 4H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.72 (ddd, *J* = 8.6, 6.8, 1.7 Hz, 1H), 8.32 (d, *J* = 5.2 Hz, 1H), 8.55 (d, *J* = 5.2 Hz, 1H), 8.58 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR δ 50.34, 115.39, 118.76, 122.45, 122.88, 125.54, 126.17, 127.80, 128.15, 129.39, 134.70, 135.03, 137.13, 139.56, 141.45, 142.41, 177.61. HR MS. Calcd for $C_{19}H_{15}N_2O$ (M+H): 287.1184. Found: *m/z* 287.1167. Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.69; H, 5.03; N, 9.74.

10-(4-Methoxyphenylmethyl)benzo[*b*][1,7]naphthyridin-5(10*H*)-one (6b): a yellow solid; mp 184–186 ˚C (hexane/CH_2Cl_2); IR (KBr) 1643, 1595 cm^{-1}; ^1H NMR (500 MHz) δ 3.79 (s, 3H), 5.65 (s, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.73 (ddd, *J* = 8.6, 7.4, 1.7 Hz, 1H), 8.31 (d, *J* = 5.2 Hz, 1H), 8.54 (d, *J* = 5.2 Hz, 1H), 8.58 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.99 (s, 1H); ^{13}C NMR δ 49.85, 55.32, 114.78, 115.45, 118.77, 122.42, 122.86, 126.13, 126.45, 126.78, 127.78, 135.03, 137.11, 139.64, 141.37, 142.40, 159.42, 177.64. HR MS. Calcd for $C_{20}H_{17}N_2O_2$ (M+H): 317.1290. Found: *m/z* 317.1284. Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.74; H, 5.12; N, 8.66.

ACKNOWLEDGEMENTS

We are grateful to Mrs. Miyuki Tanmatsu of our university for recording mass spectra and performing combustion analyses.

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