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ONE-POT SYNTHESIS OF THREE TYPES OF 2,3-DISUBSTITUTED THIENOPYRIDINES FROM HALOPYRIDINYL KETONES

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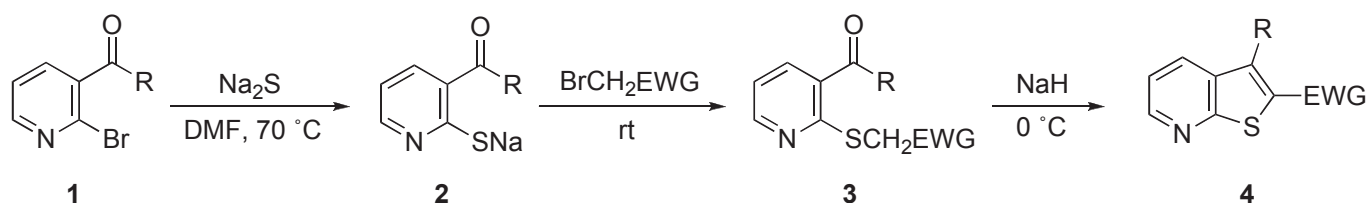
Abstract – This report describes a one-pot synthesis of three types of thienopyridine derivatives from the respective halopyridinyl ketones. Thus, the reaction of 2-bromopyridin-3-yl ketones, derived from 2-bromopyridine, with sodium sulfide followed by successive treatment BrCH₂EWG's and sodium hydride afforded 2,3-disubstituted thieno[2,3-*b*]pyridines. Similar one-pot sequences starting from aryl 3-bromopyridin-4-yl ketones and aryl 4-chloropyridin-3-yl ketones could also be readily performed to afford 2,3-disubstituted thieno[2,3-*c*]pyridines and 2,3-disubstituted thieno[3,2-*c*]pyridines, respectively.

INTRODUCTION

Thienopyridines are present in a large number of molecules of pharmaceutical and biological interest.^{1,2,3} Although several efficient methods for the preparation of thieno[2,3-*b*]pyridine derivatives have been reported,⁴ there have been only a few reports on the synthesis of thieno[2,3-*c*]pyridine and thieno[3,2-*c*]pyridine derivatives.⁵ For example, 2-substituted thieno[2,3-*c*]pyridines have been prepared by cyclization of the Schiff bases between thiophene-2-carboxaldehydes and aminoacetaldehyde dimethyl acetal.^{5a} Recently, two routes to 3-substituted 4-aminothieno[3,2-*c*]pyridines from 4-bromothiophene-3-carboxylic acid have been reported by Engstrom and co-workers.^{5d} We therefore embarked on the research for developing a procedure which is applicable to the synthesis of all these thienopyridine systems. In this paper we disclose a one-pot sequence using the respective halopyridinyl ketones, sodium sulfide, and BrCH₂EWG's (EWG = electron withdrawing group; CN, CO₂*t*-Bu, C(=O)Ph) that provides a new entry for the synthesis of 2,3-disubstituted thieno[2,3-*b*]pyridine, thieno[2,3-*c*]pyridine, and thieno[3,2-*c*]pyridine derivatives.

RESULTS AND DISCUSSION

First, we investigated conditions for the one-pot synthesis of 2,3-substituted thieno[2,3-*b*]pyridines (**4**) from 2-bromopyridin-3-yl ketones (**1**), which could be easily prepared from commercially available 2-bromopyridine via 2-bromo-3-lithiopyridine⁶ (see Experimental section). We found that the synthesis of 2,3-substituted thieno[2,3-*b*]pyridines (**4**) could be conducted as illustrated in Scheme 1. The starting materials (**1**) were allowed to react with sodium sulfide nonahydrate in DMF at 70 °C, and the resulting sodium thiolate intermediates (**2**) were treated with BrCH₂EWG's at room temperature to give 2-sulfenylated pyridin-3-yl ketones (**3**), which were then treated with sodium hydride at 0 °C to give, after the usual workup and subsequent purification by recrystallization or column chromatography on silica gel, the desired thieno[2,3-*b*]pyridine derivatives (**4**). It is notable that sodium hydride works well in the presence of water derived from disodium sulfide nonahydrate. The results are summarized in Table 1, which indicates that the yields of the products were fair-to-good in general.



Scheme 1

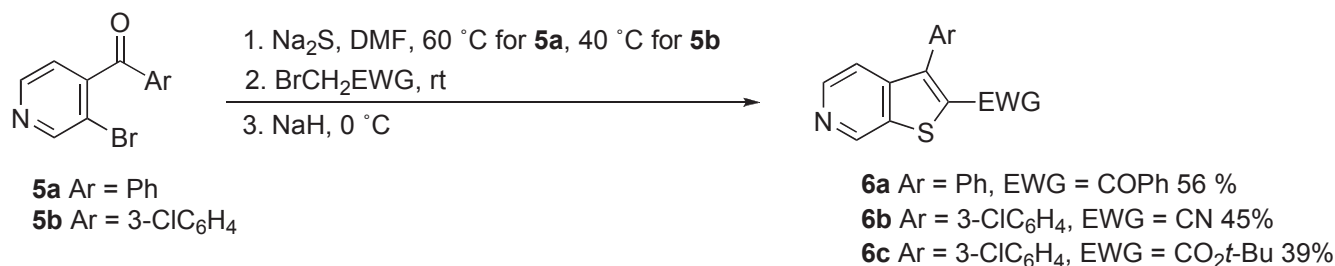
Table 1. One-pot preparation of thieno[2,3-*b*]pyridines (**4**) from 2-bromopyridin-3-yl ketones (**1**)

Entry	1	EWG	4 (Yield/%) ^a
1	1a (R = Et)	CN	4a (60)
2	1b (R = Ph)	CN	4b (73)
3	1b	CO ₂ <i>t</i> -Bu	4c (65)
4	1b	COPh	4d (61)
5	1c (R = 4-MeOC ₆ H ₄)	CN	4e (67)
6	1c	CO ₂ <i>t</i> -Bu	4f (63)

^aIsolated yields of pure products after recrystallization or column chromatography.

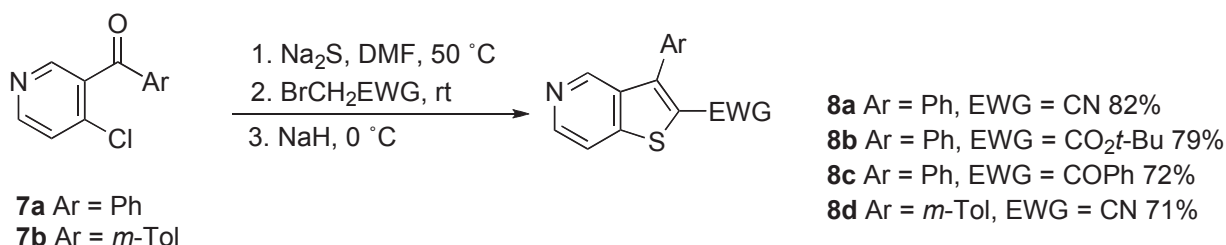
To demonstrate the generality of the present one-pot transformation, we decided to prepare 2,3-disubstituted thieno[2,3-*c*]pyridine derivatives (**6**) from aryl 3-bromopyridin-4-yl ketones (**5**), which was readily prepared from commercially available 3-bromopyridine via a reaction of 3-bromo-4-lithiopyridine⁶ with *N,N*-dimethylbenzamides. We found that when compounds **5** was successively treated with disodium sulfide, BrCH₂EWG's, and sodium hydride under conditions similar to those for the preparation of **4**, the corresponding desired products (**6**) were obtained, as shown in Scheme 2. The reaction of **5** with sodium sulfide proceeded more smoothly at lower reaction temperature

than those of **1**. Unfortunately, however, rather complicated mixtures of the products were formed after addition of sodium hydride and we were unable to obtain **6** in satisfactory yields. This may be ascribed to the formation of the products arising from bispyridinylation of disodium sulfide in the first step.



Scheme 2

Thereafter, we tried to prepare 2,3-disubstituted thieno[3,2-*c*]pyridine derivatives (**8**) from aryl 4-chloropyridin-3-yl ketones (**7**), which was readily prepared from commercially available 4-chloropyridine via a reaction of 4-chloro-3-lithiopyridine⁶ with *N,N*-dimethylbenzamides, using similar one-pot conditions. The one-pot sequence starting with **7** under conditions as described above proceeded more cleanly and smoothly compared to those for the preparation of products (**4**) and (**6**) to result in the formation of the corresponding products (**8**) in relatively good yields, as shown in Scheme 3.



Scheme 3

In conclusion, we have demonstrated that the one-pot sequence from halopyridinyl ketones provides a new and facile entry to three types of 2,3-disubstituted thienopyridine derivatives. Because the methodology starts with readily available and inexpensive materials and was performed under operationally simple conditions, it may be of value in organic synthesis. Further research addressing the applicability of this methodology to the synthesis of related heterocycles is currently under investigation in our laboratory.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Shimadzu FTIR-8300 spectrophotometer. The ¹H NMR

spectra were determined in CDCl_3 using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400 FT NMR spectrometer operating at 400 MHz. The ^{13}C NMR spectra were determined in CDCl_3 using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were measured by a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 PF_{254} . Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 1-(2-Bromopyridin-3-yl)propan-1-one (**1a**)⁷ and (2-bromopyridin-3-yl)-phenylmethanone (**1b**)^{4b} were prepared according to the reported methods. *N,N*-Dimethylbenzamides were prepared from the respective benzoyl chloride and dimethylamine. All other chemicals used in this study were commercially available.

Aryl Halopyridinyl Ketones (1c), (5a), (5b), (7a), and (7b). These compounds were prepared by the reaction of 2-bromo-3-lithiopyridine, 3-bromo-4-lithiopyridines, or 4-chloro-3-lithiopyridine, generated by treating the respective halopyridines with LDA according to the previously reported procedure,⁶ with *N,N*-dimethylbenzamides in THF at -78°C .

(2-Bromopyridin-3-yl)(4-methoxyphenyl)methanone (1c): in 56% yield; a yellow oil; R_f 0.25 (2:5 THF–hexane); IR (neat) 1668 cm^{-1} ; ^1H NMR (500 MHz) δ 3.90 (s, 3H), 6.97 (d, $J = 8.7\text{ Hz}$, 2H), 7.40 (dd, $J = 7.3, 4.6\text{ Hz}$, 1H), 7.64 (dd, $J = 7.3, 1.8\text{ Hz}$, 1H), 7.79 (d, $J = 8.7\text{ Hz}$, 2H), 8.51 (dd, $J = 4.6, 1.8\text{ Hz}$, 1H). Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{BrNO}_2$: C, 53.45; H, 3.45; N, 4.79. Found: C, 53.49; H, 3.58; N, 4.66.

(3-Bromopyridin-4-yl)phenylmethanone (5a): in 52% yield; a pale-yellow solid; mp $70\text{--}71^\circ\text{C}$ (hexane– Et_2O); IR (KBr) 1676 cm^{-1} ; ^1H NMR (500 MHz) δ 7.27 (d, $J = 5.0\text{ Hz}$, 1H), 7.51 (t, $J = 7.3\text{ Hz}$, 2H), 7.66 (t, $J = 7.3\text{ Hz}$, 1H), 7.80 (d, $J = 7.3\text{ Hz}$, 2H), 8.67 (d, $J = 5.0\text{ Hz}$, 1H), 8.85 (s, 1H). Anal. Calcd for $\text{C}_{12}\text{H}_8\text{BrNO}$: C, 54.99; H, 3.08; N, 5.34. Found: C, 54.83; H, 3.17; N, 5.24.

(3-Bromopyridin-4-yl)(3-chlorophenyl)methanone (5b): in 60% yield; a pale-yellow solid; mp $79\text{--}80^\circ\text{C}$ (hexane); IR (KBr) 1682 cm^{-1} ; ^1H NMR (500 MHz) δ 7.26 (d, $J = 4.6\text{ Hz}$, 1H), 7.45 (t, $J = 7.8\text{ Hz}$, 1H), 7.63 (dd, $J = 7.8, 1.8\text{ Hz}$, 2H), 7.79 (t, $J = 1.8\text{ Hz}$, 1H), 8.70 (d, $J = 4.6\text{ Hz}$, 1H), 8.86 (s, 1H). Anal. Calcd for $\text{C}_{12}\text{H}_7\text{BrClNO}$: C, 48.60; H, 2.38; N, 4.72. Found: C, 48.59; H, 2.41; N, 4.63.

(4-Chloropyridin-3-yl)phenylmethanone (7a):⁸ in 69% yield; a pale-yellow oil; R_f 0.29 (1:3 THF–hexane). The spectral (IR and ^1H NMR) data for this compound were identical those reported previously.⁸

(4-Chloropyridin-3-yl)(3-methylphenyl)methanone (7b): in 59% yield; a pale-yellow oil; R_f 0.33 (1:5 THF–hexane); IR (neat) $1668, 1603\text{ cm}^{-1}$; ^1H NMR (500 MHz) δ 2.42 (s, 3H), 7.38 (dd, $J = 7.8, 7.3\text{ Hz}$, 1H), 7.45 (d, $J = 5.5\text{ Hz}$, 1H), 7.46 (d, $J = 7.3\text{ Hz}$, 1H), 7.57 (d, $J = 7.8\text{ Hz}$, 1H), 7.65 (s, 1H), 8.60 (s, 1H), 8.64 (d, $J = 5.5\text{ Hz}$, 1H). Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{ClNO}$: 67.39; H, 4.35; N, 6.05. Found: C, 67.34; H, 4.31; N, 6.01.

Typical Procedure for the Preparation of Thieno[2,3-*b*]pyridines (4). 3-Ethylthieno[2,3-*b*]pyridine-2-carbonitrile (4a). A stirred mixture of **1a** (0.21 g, 0.96 mmol) and Na₂S nonahydrate (0.23 g, 0.96 mmol) in DMF (3.5 mL) was heated at 70 °C for 1 h. After cooling to rt, 2-bromoacetonitrile (0.12 g, 0.96 mmol) was added and the mixture was stirred for 10 min at the same temperature. Then NaH (60% in oil; 38 mg, 0.96 mmol) was added at 0 °C, and stirring was continued for an additional 10 min at the same temperature before water (15 mL) was added. The organic materials were extracted with AcOEt three times (10 mL each), and the combined extracts were washed with water and then brine, and then dried over anhydrous Na₂SO₄. After evaporation of the solvent, the resulting residual solid was recrystallized from hexane–CH₂Cl₂ to give **4a** (0.11g, 60%); a pale-yellow solid; mp 108–109 °C; IR (KBr) 2218 cm⁻¹; ¹H NMR (500 MHz) δ 1.37 (t, *J* = 7.3 Hz, 3H), 3.09 (q, *J* = 7.3 Hz, 2H), 7.44 (dd, *J* = 7.8, 4.6 Hz, 1H), 8.14 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.74 (dd, *J* = 4.6, 1.8 Hz, 1H); ¹³C NMR δ 14.46, 22.04, 105.45, 113.73, 120.29, 130.30, 131.18, 149.15, 150.09, 162.25; MS *m/z* 188 (M⁺, 43), 173 (100). Anal. Calcd for C₁₀H₈N₂S: C, 63.80; H, 4.28; N, 14.88. Found: C, 63.71; H, 4.11; N, 14.66.

3-Phenylthieno[2,3-*b*]pyridine-2-carbonitrile (4b): a pale-yellow solid; mp 137–138 °C (hexane–Et₂O); IR (KBr) 2218 cm⁻¹; ¹H NMR (500 MHz) δ 7.44 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.54–7.63 (m, 5H), 8.16 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.78 (dd, *J* = 4.6, 1.4 Hz, 1H); MS *m/z* 236 (M⁺, 100). Anal. Calcd for C₁₄H₈N₂S: C, 71.16; H, 3.41; N, 11.86. Found: C, 71.02; H, 3.42; N, 11.63.

1,1-Dimethylethyl 3-Phenylthieno[2,3-*b*]pyridine-2-carboxylate (4c): a white solid; mp 115–116 °C (hexane); IR (KBr) 1693 cm⁻¹; ¹H NMR (500 MHz) δ 1.37 (s, 9H), 7.28 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.36 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.43–7.50 (m, 3H), 7.78 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.68 (dd, *J* = 4.6, 1.4 Hz, 1H); MS *m/z* 311 (M⁺, 22), 255 (100). Anal. Calcd for C₁₈H₁₇NO₂S: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.36; H, 5.52; N, 4.50.

Phenyl(3-phenylthieno[2,3-*b*]pyridin-2-yl)methanone (4d): pale-yellow needles; mp 130–131 °C (hexane–CH₂Cl₂); IR (KBr) 1653 cm⁻¹; ¹H NMR (500 MHz) δ 7.20 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.21–7.28 (m, 6H), 7.36 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.38 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.4 Hz, 2H), 8.07 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.73 (dd, *J* = 4.6, 1.4 Hz, 1H); MS *m/z* 315 (M⁺, 93), 314 (100). Anal. Calcd for C₂₀H₁₃NOS: C, 76.16; H, 4.15; N, 4.44. Found: C, 76.15; H, 4.17; N, 4.47.

3-(4-Methoxyphenyl)thieno[2,3-*b*]pyridine-2-carbonitrile (4e): a white solid; mp 182–184 °C (hexane–CH₂Cl₂); IR (KBr) 2214, 1616 cm⁻¹; ¹H NMR (500 MHz) δ 3.91 (s, 3H), 7.10 (d, *J* = 8.7 Hz, 2H), 7.43 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 8.16 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.76 (dd, *J* = 4.6, 1.8 Hz, 1H); ¹³C NMR δ 55.47, 105.07, 114.45, 114.81, 120.72, 123.93, 130.44 (2C), 132.80, 146.05, 150.28, 160.77, 161.99; MS *m/z* 266 (M⁺, 100). Anal. Calcd for C₁₅H₁₀N₂OS: C, 67.65; H, 3.78; N, 10.52. Found: C, 67.42; H, 3.77; N, 10.43.

1,1-Dimethylethyl 3-(4-Methoxyphenyl)thieno[2,3-*b*]pyridine-2-carboxylate (4f): a pale-yellow solid; mp 183–184 °C (hexane–CH₂Cl₂); IR (KBr) 1715, 1609 cm⁻¹; ¹H NMR (500 MHz) δ 1.43 (s, 9H), 3.88 (s,

3H), 7.02 (d, $J = 8.7$ Hz, 2H), 7.28 (dd, $J = 8.2, 4.6$ Hz, 1H), 7.31 (d, $J = 8.7$ Hz, 2H), 7.82 (dd, $J = 8.2, 1.4$ Hz, 1H), 8.67 (dd, $J = 4.6, 1.4$ Hz, 1H); MS m/z 341 (M^+ , 27), 285 (100). Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10. Found: C, 66.91; H, 5.63; N, 4.01.

Typical Procedure for the Preparation of Thieno[2,3-*c*]pyridines (6). 3-(3-Chlorophenyl)thieno[2,3-*c*]pyridine-2-carbonitrile (6b). A stirred mixture of **5b** (0.25 g, 0.83 mmol) and Na_2S nonahydrate (0.22 g, 0.91 mmol) in DMF (3.5 mL) was heated at 40 °C for 30 min. After cooling to rt, 2-bromoacetonitrile (0.11 g, 0.91 mmol) was added and the mixture was stirred for 20 min at the same temperature. Then NaH (60% in oil; 36 mg, 0.91 mmol) was added 0 °C and stirring was continued for an additional 15 min at the same temperature. After workup similar to that described for the preparation of **4a**, the crude product was purified by column chromatography on silica gel to afford **6b** (0.10 g, 45%); a pale-yellow solid; mp 187–189 °C (hexane– CH_2Cl_2); IR (KBr) 2222 cm^{-1} ; 1H NMR (400 MHz) δ 7.50–7.56 (m, 3H), 7.60 (t, $J = 1.5$ Hz, 1H), 7.72 (dd, $J = 5.5, 1.1$ Hz, 1H), 8.67 (d, $J = 5.5$ Hz, 1H), 9.26 (d, $J = 1.1$ Hz, 1H); ^{13}C NMR δ 111.64, 113.42, 118.15, 127.39, 129.05, 130.16, 130.76, 132.56, 135.39, 136.85, 141.64, 144.81, 145.38, 145.61; MS m/z 270 (M^+ , 100). Anal. Calcd for $C_{14}H_7ClN_2S$: C, 62.11; H, 2.61; N, 10.35. Found: C, 61.97; H, 2.75; N, 10.58.

Phenyl(3-phenylthieno[2,3-*c*]pyridin-2-yl)methanone (6a): colorless crystals; mp 143–145 °C (hexane– CH_2Cl_2); IR (KBr) 1647 cm^{-1} ; 1H NMR (500 MHz) δ 7.20–7.31 (m, 7H), 7.39 (t, $J = 7.3$ Hz, 1H), 7.66 (d, $J = 7.3$ Hz, 2H), 7.69 (d, $J = 5.5$ Hz, 1H), 8.59 (d, $J = 5.5$ Hz, 1H), 9.27 (s, 1H); MS m/z 315 (M^+ , 100). Anal. Calcd for $C_{20}H_{13}NOS$: C, 76.16; H, 4.15; N, 4.44. Found: C, 76.08; H, 4.18; N, 4.60.

1,1-Dimethylethyl 3-(3-Chlorophenyl)thieno[2,3-*c*]pyridine-2-carboxylate (6c): a pale-yellow solid; mp 97–99 °C (hexane); IR (KBr) 1695 cm^{-1} ; 1H NMR (400 MHz) δ 1.40 (s, 9H), 7.25 (ddd, $J = 7.8, 7.3, 1.5$ Hz, 1H), 7.37 (s, 1H), 7.38 (dd, $J = 5.9, 1.1$ Hz, 1H), 7.43–7.45 (m, 2H), 8.51 (d, $J = 5.9$ Hz, 1H), 9.20 (d, $J = 1.1$ Hz, 1H); MS m/z 345 (M^+ , 19), 289 (100). Anal. Calcd for $C_{18}H_{16}ClNO_2S$: C, 62.51; H, 4.66; N, 4.05. Found: C, 62.32; H, 4.76; N, 4.01.

Typical Procedure for the Preparation of Thieno[3,2-*c*]pyridines (8). 3-Phenylthieno[3,2-*c*]pyridine-2-carbonitrile (8a). A stirred mixture of **7a** (0.27 g, 1.3 mmol) and Na_2S nonahydrate (0.33 g, 1.4 mmol) in DMF (3.5 mL) was heated at 50 °C for 2 h. After cooling to rt, 2-bromoacetonitrile (0.17 g, 1.4 mmol) was added and the mixture was stirred for 5 min at the same temperature. Then NaH (60% in oil; 55 mg, 1.4 mmol) was added at 0 °C and stirring was continued for an additional 5 min at the same temperature. After workup similar to that described for the preparation of **4a**, the crude product was purified by recrystallization from hexane– CH_2Cl_2 to afford **8a** (0.24 g, 82%); a pale-yellow solid; mp 172–173 °C (hexane– CH_2Cl_2); IR (KBr) 2214 cm^{-1} ; 1H NMR (500 MHz) δ 7.56–7.63 (m, 3H), 7.67 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.85 (dd, $J = 5.5, 0.9$ Hz, 1H), 8.67 (d, $J = 5.5$ Hz, 1H), 9.17 (d, $J = 0.9$ Hz, 1H); MS m/z 236 (M^+ , 100). Anal. Calcd for $C_{14}H_8N_2S$: C, 71.16; H, 3.41; N, 11.86. Found: C, 70.93; H, 3.52; N, 11.83.

1,1-Dimethylethyl 3-Phenylthieno[3,2-*c*]pyridine-2-carboxylate (8b): pale-yellow crystals; mp 92–93

°C (hexane); IR (KBr) 1694 cm^{-1} ; ^1H NMR (500 MHz) δ 1.36 (s, 9H), 7.41 (dd, $J = 7.8, 0.9$ Hz, 2H), 7.45–7.52 (m, 3H), 7.79 (d, $J = 5.9$ Hz, 1H), 8.54 (d, $J = 5.9$ Hz, 1H), 8.78 (s, 1H); MS m/z 311 (M^+ , 54), 255 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{S}$: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.27; H, 5.55; N, 4.42.

Phenyl(3-phenylthieno[3,2-*c*]pyridin-2-yl)methanone (8c): pale-yellow crystals; mp 117–118 °C (hexane– CH_2Cl_2); IR (KBr) 1630 cm^{-1} ; ^1H NMR (500 MHz) δ 7.18 (dd, $J = 7.8, 7.3$ Hz, 2H), 7.23–7.27 (m, 3H), 7.30–7.32 (m, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 7.61 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.87 (dd, $J = 5.5, 0.9$ Hz, 1H), 8.60 (d, $J = 5.5$ Hz, 1H), 9.05 (d, $J = 0.9$ Hz, 1H); ^{13}C NMR δ 117.13, 127.96, 128.50, 128.57, 129.61, 130.21, 132.80, 132.82, 135.36, 136.84, 138.37, 140.34, 144.65, 147.64, 147.82, 191.06; MS m/z 315 (M^+ , 95), 314 (100). Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{NOS}$: C, 76.16; H, 4.15; N, 4.44. Found: C, 76.15; H, 4.20; N, 4.34.

3-(3-Methylphenyl)thieno[3,2-*c*]pyridine-2-carbonitrile (8d): a pale-yellow solid; mp 135–137 °C (hexane– CH_2Cl_2); IR (KBr) 2218 cm^{-1} ; ^1H NMR (500 MHz) δ 2.49 (s, 3H), 7.38 (d, $J = 7.3$ Hz, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.47 (s, 1H), 7.50 (dd, $J = 7.8, 7.3$ Hz, 1H), 7.84 (dd, $J = 6.0, 0.9$ Hz, 1H), 8.66 (d, $J = 6.0$ Hz, 1H), 9.17 (d, $J = 0.9$ Hz, 1H); MS m/z 250 (M^+ , 100). Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{N}_2\text{S}$: C, 71.97; H, 4.03; N, 11.19. Found: C, 72.04; H, 4.15; N, 11.15.

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