Synthesis of 3-Arylthieno[2,3-*b*]-, -[2,3-*c*]- or -[3,2-*c*]pyridines Utilizing an Interrupted Pummerer Reaction

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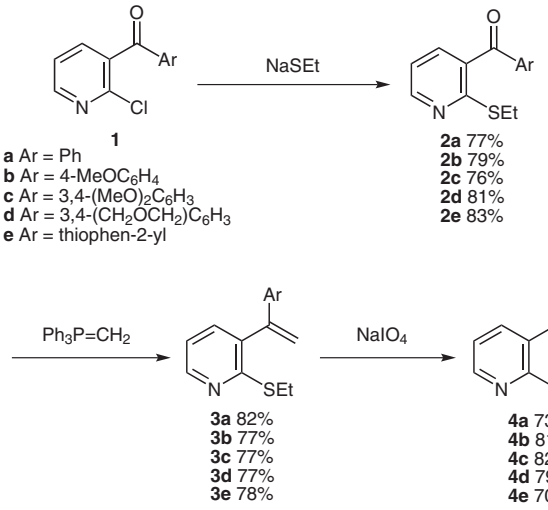
Abstract: An efficient procedure for the synthesis of three types of thienopyridines has been developed. Thus, 3-(1-arylethenyl)-2-(ethylsulfinyl)pyridines, 4-(1-arylethenyl)-3-(ethylsulfinyl)pyridines, and 3-(1-arylethenyl)-4-(ethylsulfinyl)pyridines, which can be easily prepared from the respective aryl chloropyridinyl ketones in a three-step sequence, undergo an interrupted Pummerer reaction on treatment with excess acetic anhydride at temperatures ranging from 100 to 130 °C to give 3-arylthieno[2,3-*b*]pyridines, 3-arylthieno[2,3-*c*]pyridines, and 3-arylthieno[3,2-*c*]pyridines, respectively.

Key words: thieno[2,3-*b*]pyridines, thieno[2,3-*c*]pyridines, thieno[3,2-*c*]pyridines, interrupted Pummerer reaction, acetic anhydride

Some derivatives having the thieno[2,3-*b*]pyridine, thieno[2,3-*c*]pyridine, or thieno[3,2-*c*]pyridine skeleton have been reported to exhibit various biological activity.[1–4] A number of efficient syntheses of thieno[2,3-*b*]pyridine derivatives have been reported.[1e,g,5] Surprisingly, however, there have been only a few efficient methods for the preparation of thieno[2,3-*c*]- or -[3,2-*c*]pyridines in the literature.[2e,6] On the other hand, we have recently reported a synthesis of 3-arylbenzo[*b*]thiophenes by means of an interrupted Pummerer reaction of 1-(arylethenyl)-2-(ethylsulfinyl)benzenes.[7] Hence, we were interested in developing a new method applicable to the preparation of all of these three types of thienopyridine derivatives by applying this procedure to the respective pyridine substrates. The results of our study, which provide a convenient and common approach to these thienopyridines, are reported here. We found that the interrupted Pummerer reaction of 3-(1-arylethenyl)-2-(ethylsulfinyl)pyridines, 4-(1-arylethenyl)-3-(ethylsulfinyl)pyridines, and 3-(1-arylethenyl)-4-(ethylsulfinyl)pyridines, which could be prepared from the respective aryl chloropyridinyl ketones in an easy three-step sequence, gave 3-arylthieno[2,3-*b*]pyridines, 3-arylthieno[2,3-*c*]pyridines, and 3-arylthieno[3,2-*c*]pyridines, respectively.

Our study on the synthesis of thienopyridines began by preparing (2-chloropyridin-3-yl)phenylmethanone (**1a**). This compound has previously been prepared by the reaction of 2-chloro-3-lithiopyridine,[8] generated from commercially available 2-chloropyridine and lithium diisopropylamide, with benzaldehyde followed by oxidation of the resulting alcohol with activated manganese(VI) oxide.[9] We found that the ketone **1a** could be prepared directly by treatment of 2-chloro-3-lithiopyridine with *N*,*N*-dimethylbenzamide (see experimental section). Ketone **1a** was transformed into 2-(ethylsulfinyl)-3-(1-phenylethenyl)pyridine (**4a**) (Scheme 1). Thus, substitution of the 2-chloro group with sodium ethanethiolate afforded [(2-(ethylsulfanyl)pyridin-3-yl]phenylmethanone (**2a**), which was allowed to react with methylenetriphenylphosphorane to give 2-(ethylsulfanyl)-3-(1-phenylethenyl)pyridine (**3a**); oxidation of this sulfide with sodium metaperiodate in aqueous methanol gave **4a**.



Scheme 1 Preparation of 3-(1-arylethenyl)-2-(ethylsulfinyl)pyridines **4**

The precursor **4a** was then subjected to treatment with acetic anhydride under the conditions for the preparation of 3-arylbenzo[*b*]thiophenes reported previously by us.[7] Thus, **4a** was dissolved in excess acetic anhydride and the solution was heated at 100 °C until complete consumption of the starting material **4a** (TLC analyses). The reaction was, however, complicated by the competing normal Pummerer reaction and reduction of the sulfoxide moiety to give a complex mixture containing the desired 3-phenylthieno[2,3-*b*]pyridine (**5a**) (interrupted Pummerer product, via **A**), 1-{[3-(1-phenylethenyl)pyridin-2-yl]sulfanyl}ethyl acetate (**6**) (normal Pummerer product, via **B**),

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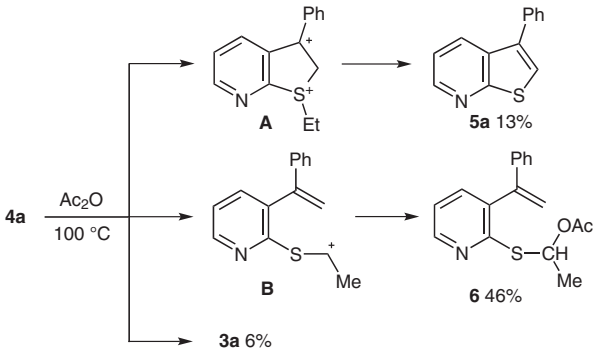
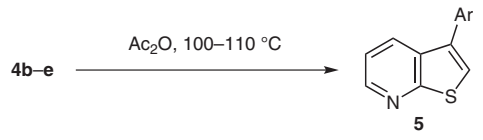
and **3a** (reduction product) (Scheme 2). This disappointing result may be ascribed to the lower stability of the cationic intermediate **A** due to the nitrogen of pyridine ring compared to the corresponding intermediate for 3-phenylbenzo[*b*]thiophene previously prepared by us.[7]



Scheme 2 Products from 2-(ethylsulfinyl)-3-(1-phenylethenyl)pyridine (**4a**)

This result led us to investigate the reaction of the substrate carrying electron-rich (hetero)aryl groups **4b–e**. (2-Chloropyridin-3-yl)(4-methoxyphenyl)methanone (**1b**) was prepared as described for the preparation of **1a**. However, this direct approach to aryl(2-chloropyridin-3-yl)methanones could not be applied to 3,4-dimethoxyphenyl **1c**, 3,4-(methylenedioxy)phenyl **1d**, and thiophen-2-yl derivatives **1e**. These ketones were prepared by the reaction of 2-chloro-3-lithiopyridine with the respective aldehydes followed by oxidation with manganese(IV) oxide. Aryl(2-chloropyridin-3-yl)methanones **1b–e** were converted into **4b–e** in a manner similar to that for the preparation of **4a** from **1a**. All of the reactions proceeded uneventfully providing the corresponding 3-(1-arylethenyl)-2-(ethylsulfinyl)pyridines **4b–e** in good yields (Scheme 1).

As expected, the interrupted Pummerer reaction of **4b–e** proved to proceed relatively cleanly on treatment with acetic anhydride at 100–110 °C to give, after simply removing acetic anhydride under reduced pressure followed by purification by preparative TLC or column chromatography on silica gel, the desired corresponding 3-arylthieno[2,3-*b*]pyridines **5b–e** (Scheme 3). The yields of the products were fair-to-good as summarized in Table 1 (entries 2–5). As can be seen from entry 5, this transformation also works well with thiophen-2-yl precursor **4e** to afford the corresponding product, 3-(thiophen-2-yl)thieno[2,3-*b*]pyridine (**5e**), in a yield almost equivalent to those of **5b–d**, though a considerably extended reaction time was needed.



Scheme 3 Preparation of 3-arylthieno[2,3-*b*]pyridines **5**

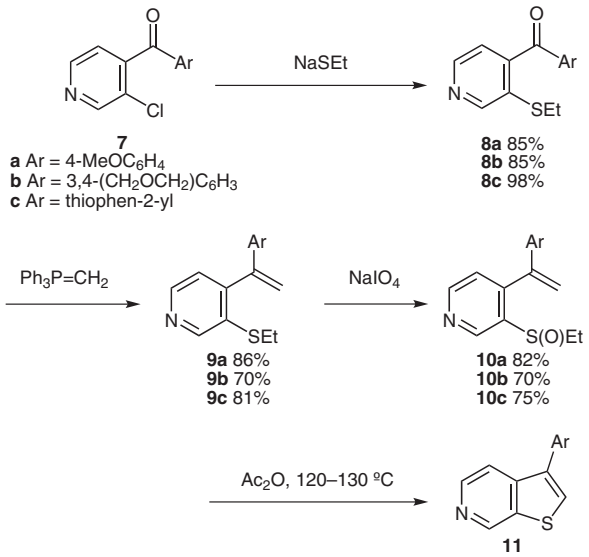
Table 1 Acetic Anhydride Mediated Synthesis of Thienopyridines **5**, **11**, and **16**

Entry	Sulfoxide **4**, **10**, or **15**	Temp (°C)	Time (h)	Product	Yield[a] (%)
1	**4a**	100	31	**5a**	13
2	**4b**	100	6	**5b**	79
3	**4c**	110	9	**5c**	71
4	**4d**	100	4	**5d**	76
5	**4e**	100	23	**5e**	72
6	**10a**	120	24	**11a**	46
7	**10b**	120	22	**11b**	40
8	**10c**	130	26	**11c**	42
9	**15a**	120	10	**16a**	62
10	**15b**	120	10	**16b**	63
11	**15c**	110	10	**16c**	63
12	**15d**	120	28	**16d**	64

[a] Isolated yields.

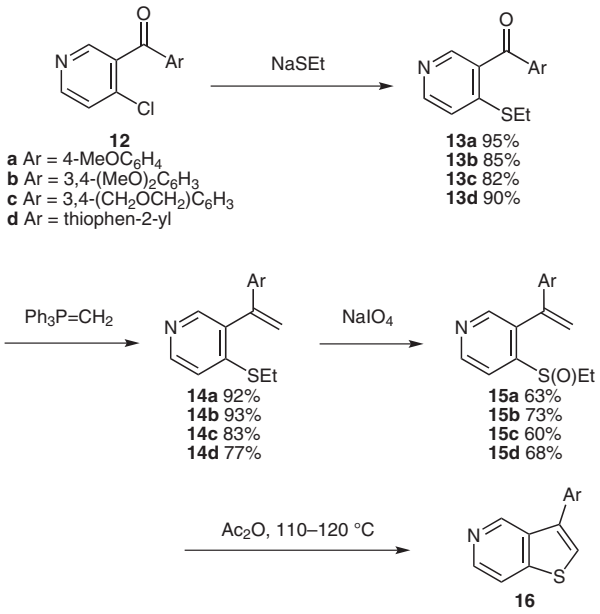
In order to examine the generality of the present sequence, attempts to synthesize 3-arylthieno[2,3-*c*]pyridines **11** from aryl(3-chloropyridin-4-yl)methanones **7** were carried out (Scheme 4). Three ketones **7a–c** were prepared from commercially available 3-chloropyridine in a manner similar to that described for the preparation of **1** and transformed into the corresponding 4-(1-arylethenyl)-3-(ethylsulfinyl)pyridines **10a–c** by the same three-step sequence used for the preparation of **4**. The reactions of **10** with acetic anhydride required higher reaction temperatures and longer reaction times compared to those for the preparation of **5** from **4**, and gave rather complicated mixtures of products, from which only moderate yields of the desired products **11** were obtained (Table 1, entries 6–8). We reasoned that these somewhat disappointing results may be ascribed to the lower electron density of 4-(1-arylethenyl) groups compared to that of 3-(1-arylethenyl) groups due to conjugation with the pyridine C=N moiety.

The present sequence could also be applied to the synthesis of 3-arylthieno[3,2-*c*]pyridines **16** (Scheme 5). Four aryl(4-chloropyridin-3-yl)methanones **12a–d** were easily prepared from commercially available 4-chloropyridine as described for the preparation of **1** and **7**, and the conversion of **12a–d** into 3-(1-arylethenyl)-4-(ethylsulfinyl)pyridines **15a–d** was carried out as described above. These four sulfoxides **15a–d** were then exposed to treatment with acetic anhydride at the temperatures indicated in Table 1, which were slightly higher than those for the preparation of **5** and slightly lower than those for the preparation of **11**. The desired 3-arylthieno[3,2-*c*]pyridines **16a–d** were obtained in acceptable yields (Table 1, entries 9–12). Thiophen-2-yl substrate **15d** reacted sluggishly



Scheme 4 Preparation of 3-arylthieno[2,3-*c*]pyridines **11**

with acetic anhydride to complete the reaction in a much longer reaction time comparable to that of **5e** (entry 12). However, the yield of the corresponding product **16d** was nearly equal to those of the other products **16a–c**.



Scheme 5 Preparation of 3-arylthieno[3,2-*c*]pyridines **16**

In conclusion, we have developed a convenient procedure for the synthesis of three types of 3-arylthienopyridines utilizing an interrupted Pummerer reaction of the respective (1-arylethenyl)(ethylsulfinyl)pyridines. Although the 3-substituents in the products are limited to electron-rich aryl groups, the present method may find value in organic synthesis because of its notable advantages: (i) Thienopyridines synthesized in the present study, especially 3-arylthieno[2,3-*c*]pyridines and 3-arylthieno[3,2-*c*]pyridines, are very difficult to prepare by previous methods.[2e,6] (ii) The precursors for the last step of the present sequence can be easily prepared from commercially available and inexpensive chloropyridines using conventional organic reactions. (iii) The last step of the present synthesis can be operated easily.

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined as with a Shimadzu FTIR-8300 spectrophotometer. The ^{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. 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 Wako Gel C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use. 4-Methoxy-*N*,*N*-dimethylbenzamide was prepared by a previously reported procedure.[10] All other chemicals used in this study were commercially available.

Aryl(2-chloropyridin-3-yl)methanones 1a,b, (3-Chloropyridin-4-yl)(4-methoxyphenyl)methanone (7a), and (4-Chloropyridin-3-yl)(4-methoxyphenyl)methanone (12a)

These compounds were prepared by treating 2-chloro-3-lithiopyridine, 3-chloro-4-lithiopyridine, or 4-chloro-3-lithiopyridine with appropriate *N*,*N*-dimethylbenzamides in THF at –78 °C under the same conditions for the reaction of these chlorolithiopyridine with benzaldehydes.[8]

(2-Chloropyridin-3-yl)phenylmethanone (1a)[9]

Yellow oil; yield: 66%; R_f = 0.26 (THF–hexane, 1:4). The spectral data (IR and ^{1}H NMR) were identical to those reported previously.[9]

(2-Chloropyridin-3-yl)(4-methoxyphenyl)methanone (1b)

Yellow solid; yield: 56%; mp 75–77 °C (Et_2O).

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

^{1}H NMR: δ = 3.89 (s, 3 H), 6.96 (d, *J* = 9.2 Hz, 2 H), 7.38 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.72 (dd, *J* = 7.3, 1.8 Hz, 1 H), 7.78 (d, *J* = 9.2 Hz, 2 H), 8.54 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 62.96; H, 4.33; N, 5.49.

(3-Chloropyridin-4-yl)(4-methoxyphenyl)methanone (7a)

White solid; yield: 70%; mp 94–97 °C (hexane–Et_2O).

IR (KBr): 1655 cm^{-1}.

^{1}H NMR: δ = 3.90 (s, 3 H), 6.97 (d, *J* = 9.2 Hz, 2 H), 7.27 (d, *J* = 5.0 Hz, 1 H), 7.77 (d, *J* = 9.2 Hz, 2 H), 8.62 (d, *J* = 5.0 Hz, 1 H), 8.71 (s, 1 H).

Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 62.96; H, 4.09; N, 5.49.

(4-Chloropyridin-3-yl)(4-methoxyphenyl)methanone (12a)

Yellow solid; yield: 56%; mp 86–89 °C (hexane–Et_2O).

IR (KBr): 1649 cm^{-1}.

^{1}H NMR: δ = 3.90 (s, 3 H), 6.97 (d, *J* = 9.2 Hz, 2 H), 7.44 (d, *J* = 5.5 Hz, 1 H), 7.79 (d, *J* = 9.2 Hz, 2 H), 8.58 (s, 1 H), 8.62 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 62.97; H, 4.28; N, 5.37.

Aryl(2-chloropyridin-3-yl)methanones 1c–e, Aryl(3-chloropyridin-4-yl)methanones 7b,c, and Aryl(4-chloropyridin-3-yl)methanones 12

These compounds were prepared by treating 2-chloro-2-lithiopyridine with appropriate aldehydes in THF at –78 °C,[8] followed by oxidation of the resulting alcohols with MnO_2 under the reported conditions.[9]

(2-Chloropyridin-3-yl)(3,4-dimethoxyphenyl)methanol

Yellow oil; yield: 60%; R_f = 0.19 (THF–hexane, 1:2).

IR (neat): 3381, 1604 cm^{-1}.

^1H NMR: δ = 2.43 (d, *J* = 3.7 Hz, 1 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 6.10 (d, *J* = 3.7 Hz, 1 H), 6.82–6.94 (m, 3 H), 7.31 (dd, *J* = 7.8, 4.6 Hz, 1 H), 8.01 (dd, *J* = 7.8, 1.8 Hz, 1 H), 8.32 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04; N, 5.01. Found: C, 59.95; H, 5.23; N, 4.76.

(2-Chloropyridin-3-yl)(3,4-dimethoxyphenyl)methanone (1c)

White solid; yield: 57%; mp 185–187 °C (hexane–CH_2Cl_2).

IR (KBr): 1655 cm^{-1}.

^1H NMR: δ = 3.96 (s, 6 H), 6.86 (d, *J* = 7.8 Hz, 1 H), 7.19 (dd, *J* = 7.3, 1.8 Hz, 1 H), 7.38 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.58 (d, *J* = 2.3 Hz, 1 H), 7.72 (dd, *J* = 7.8, 2.3 Hz, 1 H), 8.54 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{14}H_{12}ClNO_3$: C, 60.55; H, 4.36; N, 5.04. Found: C, 60.71; H, 4.60; N, 4.90.

(1,3-Benzodioxol-5-yl)(2-chloropyridin-3-yl)methanol

White solid; yield: 68%; mp 113–115 °C (THF).

IR (KBr): 3343 cm^{-1}.

^1H NMR: δ = 2.35 (d, *J* = 3.2 Hz, 1 H), 5.95 (d, *J* = 1.4 Hz, 1 H), 5.96 (d, *J* = 1.4 Hz, 1 H), 6.05 (d, *J* = 3.2 Hz, 1 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 6.83 (d, *J* = 1.8 Hz, 1 H), 6.87 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.31 (dd, *J* = 7.8, 4.6 Hz, 1 H), 8.04 (dd, *J* = 7.8, 1.8 Hz, 1 H), 8.32 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{13}H_{10}ClNO_3$: C, 59.22; H, 3.82; N, 5.31. Found: C, 58.94; H, 3.85; N, 5.23.

(1,3-Benzodioxol-5-yl)(2-chloropyridin-3-yl)methanone (1d)

Yellow oil; yield: 62%; R_f = 0.32 (THF–hexane, 1:2).

IR (neat): 1661, 1603 cm^{-1}.

^1H NMR: δ = 6.09 (s, 2 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 7.26 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.37 (dd, *J* = 7.3, 4.6 Hz, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H), 7.71 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.54 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{13}H_8ClNO_3$: C, 59.67; H, 3.08; N, 5.35. Found: C, 59.53; H, 3.29; N, 5.07.

(2-Chloropyridin-3-yl)(thiophen-2-yl)methanol

Pale-yellow oil; yield: 56%; R_f = 0.33 (THF–hexane, 1:3).

IR (neat): 3334 cm^{-1}.

^1H NMR: δ = 2.67 (d, *J* = 3.7 Hz, 1 H), 6.39 (d, *J* = 3.7 Hz, 1 H), 6.95–6.97 (m, 2 H), 7.29 (dd, *J* = 5.0, 1.4 Hz, 1 H), 7.33 (dd, *J* = 7.3, 4.6 Hz, 1 H), 8.10 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.35 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{10}H_8ClNOS$: C, 53.22; H, 3.57; N, 6.21. Found: C, 53.13; H, 3.75; N, 6.09.

(2-Chloropyridin-3-yl)(thiophen-2-yl)methanone (1e)

Yellow oil; yield: 70%; R_f = 0.24 (THF–hexane, 2:5).

IR (neat): 1647, 1609 cm^{-1}.

^1H NMR: δ = 7.16 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.38 (dd, *J* = 7.3, 4.6 Hz, 1 H), 7.43 (dd, *J* = 3.7, 0.9 Hz, 1 H), 7.80 (dd, *J* = 7.3, 1.8 Hz, 1 H), 7.82 (dd, *J* = 5.0, 0.9 Hz, 1 H), 8.56 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{10}H_6ClNOS$: C, 53.70; H, 2.70; N, 6.26. Found: C, 53.83; H, 2.70; N, 6.19.

(1,3-Benzodioxol-5-yl)(3-chloropyridin-4-yl)methanol

White solid; yield: 67%; mp 168–171 °C (hexane–CH_2Cl_2).

IR (KBr): 3154 cm^{-1}.

^1H NMR: δ = 2.36 (d, *J* = 3.2 Hz, 1 H), 5.94 (d, *J* = 1.4 Hz, 1 H), 5.96 (d, *J* = 1.4 Hz, 1 H), 6.02 (d, *J* = 3.2 Hz, 1 H), 6.77 (d, *J* = 7.8 Hz, 1 H), 6.82 (d, *J* = 1.4 Hz, 1 H), 6.86 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.68 (d, *J* = 5.0 Hz, 1 H), 8.50 (s, 1 H), 8.54 (d, *J* = 5.0 Hz, 1 H).

Anal. Calcd for $C_{13}H_{10}ClNO_3$: C, 59.22; H, 3.82; N, 5.31. Found: C, 58.94; H, 3.54; N, 5.13.

(1,3-Benzodioxol-5-yl)(3-chloropyridin-4-yl)methanone (7b)

Yellow oil; yield: 67%; R_f = 0.40 (EtOAc–hexane, 1:3).

IR (neat): 1667, 1603 cm^{-1}.

^1H NMR: δ = 6.10 (s, 2 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 7.23 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.26 (d, *J* = 4.6 Hz, 1 H), 7.38 (d, *J* = 1.8 Hz, 1 H), 8.62 (d, *J* = 4.6 Hz, 1 H), 8.70 (s, 1 H).

Anal. Calcd for $C_{13}H_8ClNO_3$: C, 59.67; H, 3.08; N, 5.35. Found: C, 59.78; H, 3.19; N, 5.09.

(3-Chloropyridin-4-yl)(thiophen-2-yl)methanol

White solid; yield: 72%; mp 116–118 °C (hexane–Et_2O).

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

^1H NMR: δ = 2.77 (d, *J* = 3.9 Hz, 1 H), 6.37 (d, *J* = 3.9 Hz, 1 H), 6.92–7.00 (m, 2 H), 7.31 (dd, *J* = 4.9, 1.4 Hz, 1 H), 7.72 (d, *J* = 4.9 Hz, 1 H), 8.52 (s, 1 H), 8.55 (d, *J* = 4.9 Hz, 1 H).

Anal. Calcd for $C_{10}H_8ClNOS$: C, 53.22; H, 3.57; N, 6.21. Found: C, 53.28; H, 3.75; N, 6.04.

(3-Chloropyridin-4-yl)(thiophen-2-yl)methanone (7c)

Yellow oil; yield: 66%; R_f = 0.44 (EtOAc–hexane, 1:2).

IR (neat): 1651 cm^{-1}.

^1H NMR: δ = 7.17 (dd, *J* = 4.6, 3.6 Hz, 1 H), 7.35 (d, *J* = 5.0 Hz, 1 H), 7.42 (dd, *J* = 3.6, 1.4 Hz, 1 H), 7.84 (dd, *J* = 4.6, 1.4 Hz, 1 H), 8.64 (d, *J* = 5.0 Hz, 1 H), 8.74 (s, 1 H).

Anal. Calcd for $C_{10}H_6ClNOS$: C, 53.70; H, 2.70; N, 6.26. Found: C, 53.54; H, 2.75; N, 6.04.

(4-Chloropyridin-3-yl)(3,4-dimethoxyphenyl)methanol

White solid; yield: 62%; mp 108–111 °C (hexane–Et_2O).

IR (KBr): 3133 cm^{-1}.

^1H NMR: δ = 2.51 (d, *J* = 3.7 Hz, 1 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 6.15 (d, *J* = 3.7 Hz, 1 H), 6.83 (d, *J* = 8.2 Hz, 1 H), 6.90 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.94 (d, *J* = 1.8 Hz, 1 H), 7.28 (d, *J* = 5.5 Hz, 1 H), 8.43 (d, *J* = 5.5 Hz, 1 H), 8.88 (s, 1 H).

Anal. Calcd for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04; N, 5.01. Found: C, 60.01; H, 5.13; N, 5.05.

(4-Chloropyridin-3-yl)(3,4-dimethoxyphenyl)methanone (12b)

White solid; yield: 72%; mp 173–176 °C (hexane–Et_2O).

IR (KBr): 1651 cm^{-1}.

^1H NMR: δ = 3.96 (s, 6 H), 6.87 (d, *J* = 8.7 Hz, 1 H), 7.21 (dd, *J* = 8.7, 2.3 Hz, 1 H), 7.45 (d, *J* = 5.5 Hz, 1 H), 7.58 (d, *J* = 2.3 Hz, 1 H), 8.59 (s, 1 H), 8.63 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{14}H_{12}ClNO_3$: C, 60.55; H, 4.36; N, 5.04. Found: C, 60.57; H, 4.41; N, 4.81.

(1,3-Benzodioxol-5-yl)(4-chloropyridin-3-yl)methanol
Pale-yellow solid; yield: 60%; mp 126–128 °C (hexane–CH_2Cl_2).

IR (KBr): 3177 cm^{-1}.

^1H NMR: δ = 2.59 (d, *J* = 3.7 Hz, 1 H), 5.95 (d, *J* = 1.4 Hz, 1 H), 5.96 (d, *J* = 1.4 Hz, 1 H), 6.11 (d, *J* = 3.7 Hz, 1 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 6.86–6.88 (m, 2 H), 7.27 (d, *J* = 5.0 Hz, 1 H), 8.42 (d, *J* = 5.0 Hz, 1 H), 8.87 (s, 1 H).

Anal. Calcd for $C_{13}H_{10}ClNO_3$: C, 59.22; H, 3.82; N, 5.31. Found: C, 59.16; H, 3.89; N, 5.19.

(1,3-Benzodioxol-5-yl)(4-chloropyridin-3-yl)methanone (12c)
Yellow oil; yield: 57%; R_f = 0.43 (THF–hexane, 1:2).

IR (neat): 1661, 1603 cm^{-1}.

^1H NMR: δ = 6.09 (s, 2 H), 8.85 (d, *J* = 8.2 Hz, 1 H), 7.27 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.40 (d, *J* = 1.8 Hz, 1 H), 7.43 (d, *J* = 5.5 Hz, 1 H), 8.57 (s, 1 H), 8.62 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{13}H_8ClNO_3$: C, 59.67; H, 3.08; N, 5.35. Found: C, 59.37; H, 3.19; N, 5.27.

(4-Chloropyridin-3-yl)(thiophen-2-yl)methanol
Pale-yellow solid; yield: 78%; mp 104–106 °C (hexane–Et_2O).

IR (KBr): 3300 cm^{-1}.

^1H NMR: δ = 2.86 (d, *J* = 4.1 Hz, 1 H), 6.43 (d, *J* = 4.1 Hz, 1 H), 6.95–6.97 (m, 2 H), 7.29–7.31 (m, 2 H), 8.45 (d, *J* = 5.5 Hz, 1 H), 8.92 (s, 1 H).

Anal. Calcd for $C_{10}H_8ClNOS$: C, 53.22; H, 3.57; N, 6.21. Found: C, 53.04; H, 3.68; N, 6.07.

(4-Chloropyridin-3-yl)(thiophen-2-yl)methanone (12d)
Yellow oil; yield: 56%; R_f = 0.57 (EtOAc–hexane, 1:1).

IR (neat): 1648 cm^{-1}.

^1H NMR: δ = 7.17 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.45–7.47 (m, 2 H), 7.83 (dd, *J* = 5.0, 1.4 Hz, 1 H), 8.64 (d, *J* = 5.5 Hz, 1 H), 8.69 (s, 1 H).

Anal. Calcd for $C_{10}H_6ClNOS$: C, 53.70; H, 2.70; N, 6.26. Found: C, 53.53; H, 2.89; N, 6.04.

3-Aroyl-2-(ethylsulfanyl)pyridines 2, 4-Aroyl-3-(ethylsulfanyl)pyridines 8, and 3-Aroyl-4-(ethylsulfanyl)pyridines 13
These compounds were prepared by treating **1**, **7**, and **12** with NaSEt, generated from EtSH and NaH, in DMF at 0 °C under the conditions reported previously.[7]

[2-(Ethylsulfanyl)pyridin-3-yl]phenylmethanone (2a)
Pale-yellow solid; mp 61–62 °C (hexane).

IR (KBr): 1649 cm^{-1}.

^1H NMR: δ = 1.33 (t, *J* = 7.3 Hz, 3 H), 3.20 (q, *J* = 7.3 Hz, 2 H), 7.07 (dd, *J* = 7.3, 4.6 Hz, 1 H), 7.49 (dd, *J* = 7.8, 7.3 Hz, 2 H), 7.61 (tt, *J* = 7.3, 1.4 Hz, 1 H), 7.62 (dd, *J* = 7.3, 1.8 Hz, 1 H), 7.78 (dd, *J* = 7.8, 1.4 Hz, 2 H), 8.57 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.11; H, 5.39; N, 5.76. Found: C, 68.92; H, 5.32; N, 5.71.

[2-(Ethylsulfanyl)pyridin-3-yl](4-methoxyphenyl)methanone (2b)
Yellow oil; R_f = 0.29 (THF–hexane, 1:4).

IR (neat): 1651 cm^{-1}.

^1H NMR: δ = 1.31 (t, *J* = 7.3 Hz, 3 H), 3.18 (q, *J* = 7.3 Hz, 2 H), 3.88 (s, 3 H), 6.94 (d, *J* = 8.7 Hz, 2 H), 7.06 (dd, *J* = 7.3, 4.6 Hz, 1 H), 7.56 (dd, *J* = 7.3, 1.4 Hz, 1 H), 7.77 (d, *J* = 8.7 Hz, 2 H), 8.54 (dd, *J* = 4.6, 1.4 Hz, 1 H).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.79; H, 5.43; N, 5.02.

[2-(Ethylsulfanyl)pyridin-3-yl](3,4-dimethoxyphenyl)methanone (2c)
White solid; mp 101–103 °C (hexane–Et_2O).

IR (KBr): 1645 cm^{-1}.

^1H NMR: δ = 1.32 (t, *J* = 7.3 Hz, 3 H), 3.19 (q, *J* = 7.3 Hz, 2 H), 3.949 (s, 3 H), 3.954 (s, 3 H), 6.86 (d, *J* = 8.2 Hz, 1 H), 7.08 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.25 (dd, *J* = 7.3, 1.8 Hz, 1 H), 7.54 (s, 1 H), 7.57 (d, *J* = 7.3 Hz, 1 H), 8.56 (d, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.28; H, 5.79; N, 4.89.

(1,3-Benzodioxol-5-yl)[2-(ethylsulfanyl)pyridin-3-yl]methanone (2d)
Yellow oil; R_f = 0.42 (Et_2O–hexane, 1:1).

IR (neat): 1651, 1603 cm^{-1}.

^1H NMR: δ = 1.32 (t, *J* = 7.3 Hz, 3 H), 3.19 (q, *J* = 7.3 Hz, 2 H), 6.08 (s, 2 H), 6.84 (d, *J* = 8.2 Hz, 1 H), 7.07 (dd, *J* = 7.3, 4.6 Hz, 1 H), 7.29 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.37 (d, *J* = 1.8 Hz, 1 H), 7.55 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.55 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87. Found: C, 62.81; H, 4.50; N, 4.70.

[2-(Ethylsulfanyl)pyridin-3-yl](thiophen-2-yl)methanone (2e)
Yellow oil; R_f = 0.52 (Et_2O–hexane, 1:1).

IR (neat): 1651 cm^{-1}.

^1H NMR: δ = 1.33 (t, *J* = 7.3 Hz, 3 H), 3.20 (q, *J* = 7.3 Hz, 2 H), 7.08 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.14 (dd, *J* = 5.0, 4.1 Hz, 1 H), 7.48 (dd, *J* = 4.1, 1.8 Hz, 1 H), 7.73 (dd, *J* = 7.3, 1.4 Hz, 1 H), 7.76 (dd, *J* = 5.0, 1.4 Hz, 1 H), 8.57 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{12}H_{11}NOS_2$: C, 57.80; H, 4.45; N, 5.62. Found: C, 57.80; H, 4.48; N, 5.61.

[3-(Ethylsulfanyl)pyridin-4-yl](4-methoxyphenyl)methanone (8a)
Yellow oil; R_f = 0.35 (THF–hexane, 1:2).

IR (neat): 1661 cm^{-1}.

^1H NMR: δ = 1.24 (t, *J* = 7.3 Hz, 3 H), 2.91 (q, *J* = 7.3 Hz, 2 H), 3.89 (s, 3 H), 6.95 (d, *J* = 9.2 Hz, 2 H), 7.19 (d, *J* = 4.6 Hz, 1 H), 7.75 (d, *J* = 9.2 Hz, 2 H), 8.56 (d, *J* = 4.6 Hz, 1 H), 8.73 (s, 1 H).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.88; H, 5.54; N, 5.04.

(1,3-Benzodioxol-5-yl)[3-(ethylsulfanyl)pyridin-4-yl]methanone (8b)
Yellow oil; R_f = 0.37 (THF–hexane, 1:3).

IR (neat): 1661 cm^{-1}.

^1H NMR: δ = 1.24 (t, *J* = 7.3 Hz, 3 H), 2.91 (q, *J* = 7.3 Hz, 2 H), 6.09 (s, 2 H), 6.83 (d, *J* = 8.2 Hz, 1 H), 7.18 (dd, *J* = 4.6 Hz, 1 H), 7.21 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.38 (d, *J* = 1.4 Hz, 1 H), 8.56 (d, *J* = 4.6 Hz, 1 H), 8.72 (s, 1 H).

Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87. Found: C, 62.50; H, 4.78; N, 4.83.

[3-(Ethylsulfanyl)pyridin-4-yl](thiophen-2-yl)methanone (8c)
Yellow oil; R_f = 0.43 (THF–hexane, 1:2).

IR (neat): 1645 cm^{-1}.

^1H NMR: δ = 1.27 (t, *J* = 7.3 Hz, 3 H), 2.96 (q, *J* = 7.3 Hz, 2 H), 7.15 (dd, *J* = 5.0, 3.6 Hz, 1 H), 7.31 (d, *J* = 5.0 Hz, 1 H), 7.40 (dd, *J* = 3.6, 0.9 Hz, 1 H), 7.80 (dd, *J* = 5.0, 0.9 Hz, 1 H), 8.57 (d, *J* = 5.0 Hz, 1 H), 8.75 (s, 1 H).

Anal. Calcd for $C_{12}H_{11}NOS_2$: C, 57.80; H, 4.45; N, 5.62. Found: C, 58.01; H, 4.54; N, 5.43.

[4-(Ethylsulfanyl)pyridin-3-yl](4-methoxyphenyl)methanone (13a)
Yellow oil; R_f = 0.50 (THF–hexane, 1:2).

IR (neat): 1651 cm^{-1}.

^1H NMR: δ = 1.37 (t, *J* = 7.3 Hz, 3 H), 2.98 (q, *J* = 7.3 Hz, 2 H), 3.90 (s, 3 H), 6.96 (d, *J* = 8.7 Hz, 2 H), 7.27 (d, *J* = 5.5 Hz, 1 H), 7.81 (d, *J* = 8.7 Hz, 2 H), 8.50 (s, 1 H), 8.51 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.72; H, 5.59; N, 5.04.

(3,4-Dimethoxyphenyl)[4-(ethylsulfanyl)pyridin-3-yl]methanone (13b)
White solid; mp 107–109 °C (hexane–Et_2O).

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

^1H NMR: δ = 1.37 (t, *J* = 7.3 Hz, 3 H), 2.99 (q, *J* = 7.3 Hz, 2 H), 3.955 (s, 3 H), 3.964 (s, 3 H), 6.87 (d, *J* = 8.7 Hz, 1 H), 7.27 (d, *J* = 5.5 Hz, 1 H), 7.29 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.55 (d, *J* = 1.8 Hz, 1 H), 8.51 (s, 1 H), 8.52 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.27; H, 5.67; N, 4.61.

(1,3-Benzodioxol-5-yl)[4-(ethylsulfanyl)pyridin-3-yl]methanone (13c)
Yellow oil; R_f = 0.33 (Et_2O–hexane, 1:4).

IR (neat): 1645 cm^{-1}.

^1H NMR: δ = 1.36 (t, *J* = 7.3 Hz, 3 H), 2.98 (q, *J* = 7.3 Hz, 2 H), 6.08 (s, 2 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 7.26 (d, *J* = 5.5 Hz, 1 H), 7.31 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.38 (d, *J* = 1.4 Hz, 1 H), 8.49 (s, 1 H), 8.51 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87. Found: C, 62.91; H, 4.80; N, 4.82.

[4-(Ethylsulfanyl)pyridin-3-yl](thiophen-2-yl)methanone (13d)
Yellow oil; R_f = 0.50 (THF–hexane, 1:1).

IR (neat): 1634 cm^{-1}.

^1H NMR: δ = 1.38 (t, *J* = 7.3 Hz, 3 H), 3.00 (q, *J* = 7.3 Hz, 2 H), 7.17 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.28 (d, *J* = 5.5 Hz, 1 H), 7.55 (dd, *J* = 3.7, 0.9 Hz, 1 H), 7.79 (dd, *J* = 5.0, 0.9 Hz, 1 H), 8.53 (d, *J* = 5.5 Hz, 1 H), 8.70 (s, 1 H).

Anal. Calcd for $C_{12}H_{11}NOS_2$: C, 57.80; H, 4.45; N, 5.62. Found: C, 57.79; H, 4.29; N, 5.61.

3-(1-Arylethenyl)-2-(ethylsulfanyl)pyridines 3, 4-(1-Arylethenyl)-3-(ethylsulfanyl)pyridines 9, and 3-(1-Arylethenyl)-4-(ethylsulfanyl)pyridines 14
These compounds were prepared by treating **2**, **8**, and **13** with $Ph_3P{=}CH_2$ in THF at 0 °C under conditions reported previously.[11]

2-(Ethylsulfanyl)-3-(1-phenylethenyl)pyridine (3a)
Pale-yellow oil; R_f = 0.62 (THF–hexane, 1:4).

IR (neat): 1615 cm^{-1}.

^1H NMR: δ = 1.27 (t, *J* = 7.3 Hz, 3 H), 3.10 (q, *J* = 7.3 Hz, 2 H), 5.34 (s, 1 H), 6.86 (d, *J* = 0.9 Hz, 1 H), 7.02 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.26–7.33 (m, 5 H), 7.37 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.44 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80. Found: C, 74.50; H, 6.29; N, 5.71.

2-(Ethylsulfanyl)-3-[1-(4-methoxyphenyl)ethenyl]pyridine (3b)
Pale-yellow oil; R_f = 0.60 (THF–hexane, 1:5).

IR (neat): 1605 cm^{-1}.

^1H NMR: δ = 1.28 (t, *J* = 7.3 Hz, 3 H), 3.10 (q, *J* = 7.3 Hz, 2 H), 3.80 (s, 3 H), 5.21 (d, *J* = 0.9 Hz, 1 H), 5.76 (d, *J* = 0.9 Hz, 1 H), 6.84 (d, *J* = 9.2 Hz, 2 H), 7.02 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.21 (d, *J* = 9.2 Hz, 2 H), 7.37 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.43 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.80; H, 6.32; N, 5.19.

2-(Ethylsulfanyl)-3-[1-(3,4-dimethoxyphenyl)ethenyl]pyridine (3c)
Colorless oil; R_f = 0.45 (EtOAc–hexane, 1:5).

IR (neat): 1601 cm^{-1}.

^1H NMR: δ = 1.28 (t, *J* = 7.3 Hz, 3 H), 3.12 (q, *J* = 7.3 Hz, 2 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 5.24 (s, 1 H), 5.78 (s, 1 H), 6.72 (dd, *J* = 8.2, 1.4 Hz, 1 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 6.91 (d, *J* = 1.4 Hz, 1 H), 7.03 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.38 (dd, *J* = 7.3, 1.4 Hz, 1 H), 8.44 (dd, *J* = 5.0, 1.4 Hz, 1 H).

Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.48; H, 6.19; N, 4.89.

3-[1-(1,3-Benzodioxol-5-yl)ethenyl]-2-(ethylsulfanyl)pyridine (3d)
White solid; mp 63–64 °C (hexane–Et_2O).

IR (KBr): 1601 cm^{-1}.

^1H NMR: δ = 1.28 (t, *J* = 7.3 Hz, 3 H), 3.11 (q, *J* = 7.3 Hz, 2 H), 5.22 (s, 1 H), 5.74 (s, 1 H), 5.96 (s, 2 H), 6.68 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.73 (d, *J* = 8.2 Hz, 1 H), 6.84 (d, *J* = 1.8 Hz, 1 H), 7.02 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.36 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.43 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.21; H, 5.31; N, 4.62.

2-(Ethylsulfanyl)-3-[1-(thiophen-2-yl)ethenyl]pyridine (3e)
Pale-yellow oil; R_f = 0.47 °C_6H_6–hexane, 1:5).

IR (neat): 1608 cm^{-1}.

^1H NMR: δ = 1.30 (t, *J* = 7.3 Hz, 3 H), 3.14 (q, *J* = 7.3 Hz, 2 H), 5.18 (s, 1 H), 5.83 (s, 1 H), 6.68 (dd, *J* = 3.7, 0.9 Hz, 1 H), 6.93 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.03 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.22 (d, *J* = 5.0 Hz, 1 H), 7.42 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.45 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{13}H_{13}NS_2$: C, 63.12; H, 5.30; N, 5.66. Found: C, 63.02; H, 5.41; N, 5.88.

3-(Ethylsulfanyl)-4-[1-(4-methoxyphenyl)ethenyl]pyridine (9a)
Colorless crystals; mp 49–51 °C (hexane).

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

^1H NMR: δ = 1.22 (t, *J* = 7.3 Hz, 3 H), 2.87 (q, *J* = 7.3 Hz, 2 H), 3.80 (s, 3 H), 5.18 (s, 1 H), 5.76 (s, 1 H), 6.84 (d., *J* = 8.7 Hz, 2 H), 7.13 (d, *J* = 5.0 Hz, 1 H), 7.17 (d, *J* = 8.7 Hz, 2 H), 8.42 (d, *J* = 5.0 Hz, 1 H), 8.55 (s, 1 H).

Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.79; H, 6.60; N, 5.18.

4-[1-(1,3-Benzodioxol-5-yl)ethenyl]-3-(ethylsulfanyl)pyridine (9b)
Pale-yellow oil; R_f = 0.38 (EtOAc–hexane, 1:5).

IR (neat): 1602 cm^{-1}.

^1H NMR: δ = 1.24 (t, *J* = 7.3 Hz, 3 H), 2.89 (q, *J* = 7.3 Hz, 2 H), 5.18 (s, 1 H), 5.74 (s, 1 H), 5.97 (s, 2 H), 6.61 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.72 (d, *J* = 8.2 Hz, 1 H), 6.81 (d, *J* = 1.8 Hz, 1 H), 7.12 (d, *J* = 5.0 Hz, 1 H), 8.42 (d, *J* = 5.0 Hz, 1 H), 8.54 (s, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.28; H 5.45; N, 4.89.

3-(Ethylsulfanyl)-4-[1-(thiophen-2-yl)ethenyl]pyridine (9c)
Pale-yellow oil; R_f = 0.50 (EtOAc–hexane, 1:2).

IR (neat): 1607 cm^{-1}.

^1H NMR: δ = 1.25 (t, *J* = 7.3 Hz, 3 H), 2.91 (q, *J* = 7.3 Hz, 2 H), 5.12 (s, 1 H), 5.82 (s, 1 H), 6.62 (dd, *J* = 3.6, 1.4 Hz, 1 H), 6.92 (dd, *J* = 5.1, 3.6 Hz, 1 H), 7.17 (dd, *J* = 5.1, 0.7 Hz, 1 H), 7.23 (dd, *J* = 5.1, 1.4 Hz, 1 H), 8.44 (d, *J* = 5.1 Hz, 1 H), 8.59 (s, 1 H).

Anal. Calcd for $C_{13}H_{13}NS_2$: C, 63.12; H, 5.30; N, 5.66. Found: C, 63.05; H, 5.41; N, 5.65.

4-(Ethylsulfanyl)-3-[1-(4-methoxyphenyl)ethenyl]pyridine (14a)
Colorless oil; R_f = 0.59 (EtOAc–hexane, 1:2).

IR (neat): 1605 cm^{-1}.

^1H NMR: δ = 1.29 (t, *J* = 7.3 Hz, 3 H), 2.89 (q, *J* = 7.3 Hz, 2 H), 3.81 (s, 3 H), 5.22 (s, 1 H), 5.78 (s, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 7.11 (d, *J* = 5.5 Hz, 1 H), 7.21 (d, *J* = 8.7 Hz, 2 H), 8.29 (s, 1 H), 8.42 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.69; H, 6.19; N, 5.10.

3-[1-(3,4-Dimethoxyphenyl)ethenyl]-4-(ethylsulfanyl)pyridine (14b)
Colorless oil; R_f = 0.28 (EtOAc–hexane, 1:10).

IR (neat): 1601 cm^{-1}.

^1H NMR: δ = 1.30 (t, *J* = 7.3 Hz, 3 H), 2.90 (q, *J* = 7.3 Hz, 2 H), 3.85 (s, 3 H), 3.88 (s, 3 H), 5.24 (s, 1 H), 5.79 (s, 1 H), 6.72 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 6.90 (d, *J* = 1.8 Hz, 1 H), 7.12 (d, *J* = 5.5 Hz, 1 H), 8.31 (s, 1 H), 8.43 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.68; H, 6.42; N, 4.77.

3-[1-(1,3-Benzodioxol-5-yl)ethenyl]-4-(ethylsulfanyl)pyridine (14c)
Pale-yellow oil; R_f = 0.47 (EtOAc–hexane, 1:2).

IR (neat): 1603 cm^{-1}.

^1H NMR: δ = 1.31 (t, *J* = 7.3 Hz, 3 H), 2.90 (q, *J* = 7.3 Hz, 2 H), 5.22 (s, 1 H), 5.75 (s, 1 H), 5.96 (s, 2 H), 6.68 (dd, *J* = 8.2, 1.4 Hz, 1 H), 6.73 (d, *J* = 8.2 Hz, 1 H), 6.84 (d, *J* = 1.4 Hz, 1 H), 7.11 (d, *J* = 5.5 Hz, 1 H), 8.28 (s, 1 H), 8.42 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.16; H 5.40; N, 4.65.

4-(Ethylsulfanyl)-3-[1-(thiophen-2-yl)ethenyl]pyridine (14d)
Yellow oil; R_f = 0.49 (EtOAc–hexane, 1:1).

IR (neat): 1604 cm^{-1}.

^1H NMR: δ = 1.32 (t, *J* = 7.3 Hz, 3 H), 2.93 (q, *J* = 7.3 Hz, 2 H), 5.17 (s, 1 H), 5.86 (s, 1 H), 6.68 (d, *J* = 3.7 Hz, 1 H), 6.93 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.14 (d, *J* = 5.5 Hz, 1 H), 7.23 (d, *J* = 5.0 Hz, 1 H), 8.23 (s, 1 H), 8.44 (d, *J* = 5.5 Hz, 1 H).

Anal. Calcd for $C_{13}H_{13}NS_2$: C, 63.12; H, 5.30; N, 5.66. Found: C, 63.07; H, 5.41; N, 5.54.

3-(1-Arylethenyl)-2-(ethylsulfinyl)pyridines 4, 4-(1-Arylethenyl)-3-(ethylsulfinyl)pyridines 10, and 3-(1-Arylethenyl)-4-(ethylsulfinyl)pyridines 15
These compounds were prepared by treating **3**, **9**, and **14** with $NaIO_4$ in aq MeOH at r.t.[7]

2-(Ethylsulfinyl)-3-(1-phenylethenyl)pyridine (4a)
Pale-yellow oil; R_f = 0.36 (THF–hexane, 4:1).

IR (neat): 1614, 1045 cm^{-1}.

^1H NMR: δ = 1.11 (t, *J* = 7.3 Hz, 3 H), 2.74–2.81 (m, 1 H), 2.92–2.99 (m, 1 H), 5.36 (s, 1 H), 5.93 (s, 1 H), 7.22–7.24 (m, 2 H), 7.33–7.35 (m, 3 H), 7.46 (dd, *J* = 7.8, 4.6 Hz, 1 H), 7.67 (dd, *J* = 7.8, 1.8 Hz, 1 H), 8.82 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44. Found: C, 69.75; H, 5.81; N, 5.30.

2-(Ethylsulfinyl)-3-[1-(4-methoxyphenyl)ethenyl]pyridine (4b)
Pale-yellow oil; R_f = 0.51 (THF–hexane, 5:1).

IR (neat): 1607, 1028 cm^{-1}.

^1H NMR: δ = 1.13 (t, *J* = 7.3 Hz, 3 H), 2.77–2.84 (m, 1 H), 2.93–3.00 (m, 1 H), 3.81 (s, 3 H), 5.23 (s, 1 H), 5.83 (s, 1 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 7.16 (d, *J* = 8.7 Hz, 2 H), 7.45 (dd, *J* = 7.8, 4.6 Hz, 1 H), 7.66 (dd, *J* = 7.8, 1.8 Hz, 1 H), 8.82 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.71; H, 6.01; N, 4.66.

2-(Ethylsulfinyl)-3-[1-(3,4-dimethoxyphenyl)ethenyl]pyridine (4c)
Colorless oil; R_f = 0.45 (EtOAc–hexane, 5:1).

IR (neat): 1601, 1022 cm^{-1}.

^1H NMR: δ = 1.13 (t, *J* = 7.3 Hz, 3 H), 2.79–2.88 (m, 1 H), 2.95–3.03 (m, 1 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 5.25 (s, 1 H), 5.84 (s, 1 H), 6.61 (dd, *J* = 8.0, 2.2 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.88 (d, *J* = 2.2 Hz, 1 H), 7.46 (dd, *J* = 7.6, 4.8 Hz, 1 H), 7.66 (dd, *J* = 7.6, 1.8 Hz, 1 H), 8.82 (dd, *J* = 4.8, 1.8 Hz, 1 H).

Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.21; H, 6.01; N, 4.36.

3-[1-(1,3-Benzodioxol-5-yl)ethenyl]-2-(ethylsulfinyl)pyridine (4d)
Pale-yellow oil; R_f = 0.19 (THF–hexane, 2:1).

IR (neat): 1603, 1038 cm^{-1}.

^1H NMR: δ = 1.14 (t, *J* = 7.3 Hz, 3 H), 2.80–2.87 (m, 1 H), 2.95–3.02 (m, 1 H), 5.24 (s, 1 H), 5.81 (s, 1 H), 5.99 (s, 2 H), 6.57 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.73 (d, *J* = 8.2 Hz, 1 H), 6.82 (d, *J* = 1.8 Hz, 1 H), 7.45 (dd, *J* = 7.8, 4.6 Hz, 1 H), 7.65 (dd, *J* = 7.8, 1.8 Hz, 1 H), 8.82 (dd, *J* = 4.6, 1.8 Hz, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.70; H, 5.00; N, 4.54.

2-(Ethylsulfinyl)-3-[1-(thiophen-2-yl)ethenyl]pyridine (4e)
Yellow oil; R_f = 0.38 (THF–hexane, 4:1).

IR (neat): 1607, 1045 cm^{-1}.

^1H NMR: δ = 1.14 (t, *J* = 7.3 Hz, 3 H), 2.85–2.94 (m, 1 H), 2.97–3.05 (m, 1 H), 5.18 (s, 1 H), 5.87 (s, 1 H), 6.62 (dd, *J* = 3.6, 1.1 Hz,

1 H), 6.93 (dd, *J* = 4.7, 3.6 Hz, 1 H), 7.26 (dd, *J* = 4.7, 1.1 Hz, 1 H), 7.44 (dd, *J* = 7.7, 4.7 Hz, 1 H), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1 H), 8.82 (dd, *J* = 4.7, 1.5 Hz, 1 H).

Anal. Calcd for $C_{13}H_{13}NOS_2$: C, 59.28; H, 4.98; N, 5.32. Found: C, 59.25; H, 4.93; N, 5.34.

3-(Ethylsulfinyl)-4-[1-(4-methoxyphenyl)ethenyl]pyridine (10a)
Colorless oil; R_f = 0.43 (THF–hexane, 2:1).

IR (neat): 1607, 1045 cm^{-1}.

^1H NMR: δ = 1.14 (t, *J* = 7.3 Hz, 3 H), 2.59–2.67 (m, 1 H), 2.75–2.82 (m, 1 H), 3.82 (s, 3 H), 5.27 (s, 1 H), 5.77 (s, 1 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 7.13 (d, *J* = 8.7 Hz, 2 H), 7.23 (d, *J* = 5.0 Hz, 1 H), 8.75 (d, *J* = 5.0 Hz, 1 H), 9.13 (s, 1 H).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.61; H, 6.01; N, 5.02.

4-[1-(1,3-Benzodioxol-5-yl)ethenyl]-3-(ethylsulfinyl)pyridine (10b)
Yellow oil; R_f = 0.36 (EtOAc–hexane, 3:1).

IR (neat): 1603, 1040 cm^{-1}.

^1H NMR: δ = 1.16 (t, *J* = 7.3 Hz, 3 H), 2.61–2.69 (m, 1 H), 2.78–2.85 (m, 1 H), 5.28 (s, 1 H), 5.75 (s, 1 H), 6.00 (s, 2 H), 6.59 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 6.76 (d, *J* = 1.8 Hz, 1 H), 7.23 (d, *J* = 5.0 Hz, 1 H), 8.76 (d, *J* = 5.0 Hz, 1 H), 9.13 (s, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.49; H, 5.09; N, 4.43.

4-[1-(Thiophen-2-yl)ethenyl]-3-(ethylsulfinyl)pyridine (10c)
Yellow oil; R_f = 0.28 (EtOAc–hexane, 4:1).

IR (neat): 1607, 1045 cm^{-1}.

^1H NMR: δ = 1.17 (t, *J* = 7.3 Hz, 3 H), 2.64–2.72 (m, 1 H), 2.83–2.90 (m, 1 H), 5.23 (s, 1 H), 5.84 (s, 1 H), 6.67 (d, *J* = 2.7 Hz, 1 H), 6.96 (dd, *J* = 5.0, 1.4 Hz, 1 H), 7.26–7.31 (m, 2 H), 8.78 (d, *J* = 4.6 Hz, 1 H), 9.16 (s, 1 H).

Anal. Calcd for $C_{13}H_{13}NOS_2$: C, 59.28; H, 4.98; N, 5.32. Found: C, 59.06; H, 4.84; N, 5.48.

4-(Ethylsulfinyl)-3-[1-(4-methoxyphenyl)ethenyl]pyridine (15a)
Yellow oil; R_f = 0.28 (EtOAc–hexane, 2:1).

IR (neat): 1607, 1030 cm^{-1}.

^1H NMR: δ = 1.81 (t, *J* = 7.3 Hz, 3 H), 2.53–2.60 (m, 1 H), 2.77–2.84 (m, 1 H), 3.82 (s, 3 H), 5.31 (s, 1 H), 5.77 (s, 1 H), 6.86 (d, *J* = 9.2 Hz, 2 H), 7.15 (d, *J* = 9.2 Hz, 2 H), 7.93 (dd, *J* = 5.0, 0.9 Hz, 1 H), 8.57 (s, 1 H), 8.84 (d, *J* = 5.0 Hz, 1 H).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.74; H, 6.04; N, 4.92.

3-[1-(3,4-Dimethoxyphenyl)ethenyl]-4-(ethylsulfinyl)pyridine (15b)
Pale-yellow oil; R_f = 0.44 (EtOAc–hexane, 5:1).

IR (neat): 1601, 1024 cm^{-1}.

^1H NMR: δ = 1.09 (t, *J* = 7.3 Hz, 3 H), 2.54–2.61 (m, 1 H), 2.77–2.85 (m, 1 H), 3.84 (s, 3 H), 3.89 (s, 3 H), 5.33 (s, 1 H), 5.79 (s, 1 H), 6.68 (dd, *J* = 8.2, 2.3 Hz, 1 H), 6.79–6.81 (m, 2 H), 7.94 (d, *J* = 5.0 Hz, 1 H), 8.58 (s, 1 H), 8.84 (d, *J* = 5.0 Hz, 1 H).

Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.09; H, 6.07; N, 4.29.

3-[1-(1,3-Benzodioxol-5-yl)ethenyl]-4-(ethylsulfinyl)pyridine (15c)
Pale-yellow oil; R_f = 0.21 (EtOAc–hexane, 1:2).

IR (neat): 1603, 1032 cm^{-1}.

^1H NMR: δ = 1.10 (t, *J* = 7.3 Hz, 3 H), 2.54–2.62 (m, 1 H), 2.79–2.86 (m, 1 H), 5.32 (s, 1 H), 5.75 (s, 1 H), 6.00 (s, 2 H), 6.61 (d, *J* = 8.2 Hz, 1 H), 6.74–6.76 (m, 2 H), 7.93 (d, *J* = 5.0 Hz, 1 H), 8.56 (s, 1 H), 8.84 (d, *J* = 5.0 Hz, 1 H).

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.55; H, 5.18; N, 4.62.

4-(Ethylsulfinyl)-3-[2-(thiophen-2-yl)ethenyl]pyridine (15d)
Yellow oil; R_f = 0.22 (EtOAc–hexane, 1:1).

IR (neat): 1605, 1062 cm^{-1}.

^1H NMR: δ = 1.11 (t, *J* = 7.3 Hz, 3 H), 2.58–2.65 (m, 1 H), 2.84–2.91 (m, 1 H), 5.26 (s, 1 H), 5.86 (s, 1 H), 6.70 (dd, *J* = 3.7, 0.9 Hz, 1 H), 6.96 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.30 (dd, *J* = 5.0, 0.9 Hz, 1 H), 7.96 (d, *J* = 5.0 Hz, 1 H), 8.59 (s, 1 H), 8.86 (d, *J* = 5.0 Hz, 1 H).

Anal. Calcd for $C_{13}H_{13}NOS_2$: C, 59.28; H, 4.98; N, 5.32. Found: C, 59.03; H, 4.86; N, 5.37.

3-Arylthienopyridines 5, 11, and 16; General Procedure
A soln of **4**, **10**, or **15** (1.0 mmol) in Ac_2O (2 mL) was heated at 100–130 °C under stirring until the starting material had disappeared. After removal of excess Ac_2O under reduced pressure, the residue was purified by preparative TLC or column chromatography (silica gel), or recrystallization to afford product(s).

3-Phenylthieno[2,3-*b*]pyridine (5a)[11]
This compound was obtained in 13% yield along with 1-{[3-(1-phenylethenyl)pyridin-2-yl]sulfanyl}ethyl acetate (**6**) (46%) and **3a** (6%).

Thieno[2,3-*b*]pyridine 5a
R_f = 0.25 (THF–hexane, 1:20).

The spectral (IR, ^1H and ^{13}C NMR) of this product were identical to those reported previously.[11]

Acetate 6
Pale yellow oil; R_f = 0.25 (THF–hexane, 1:20).

IR (neat): 1744, 1616 cm^{-1}.

^1H NMR: δ = 1.60 (d, *J* = 6.9 Hz, 3 H), 1.99 (s, 3 H), 5.33 (s, 1 H), 5.87 (s, 1 H), 6.94 (q, *J* = 6.9 Hz, 1 H), 7.07 (dd, *J* = 7.3, 5.0 Hz, 1 H), 7.26 (dd, *J* = 7.8, 1.8 Hz, 2 H), 7.29–7.33 (m, 3 H), 7.40 (dd, *J* = 7.3, 1.8 Hz, 1 H), 8.44 (dd, *J* = 5.0, 1.8 Hz, 1 H).

Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.12; H, 5.92; N, 4.42.

3-(4-Methoxyphenyl)thieno[2,3-*b*]pyridine (5b)
Pale-yellow solid; mp 95–97 °C (Et_2O).

IR (KBr): 3101, 1521, 1241, 1035 cm^{-1}.

^1H NMR: δ = 3.88 (s, 3 H), 7.03 (d, *J* = 8.7 Hz, 2 H), 7.33 (dd, *J* = 8.2, 4.6 Hz, 1 H), 7.43 (s, 1 H), 7.49 (d, *J* = 8.7 Hz, 2 H), 8.16 (dd, *J* = 8.2, 1.4 Hz, 1 H), 8.61 (dd, *J* = 4.6, 1.4 Hz, 1 H).

^{13}C NMR: δ = 55.4, 114.4, 119.3, 122.4, 127.8, 129.5, 130.5, 131.4, 135.3, 146.6, 159.4, 162.5.

MS: *m*/*z* = 241 (100%, $[M^+]$).

Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.61; H, 4.74; N, 5.59.

3-(3,4-Dimethoxyphenyl)thieno[2,3-*b*]pyridine (5c)
Pale-yellow solid; mp 104–106 °C (hexane–CH_2Cl_2).

IR (KBr): 3068, 1605, 1524, 1261, 1022 cm^{-1}.

^1H NMR: δ = 3.94 (s, 3 H), 3.96 (s, 3 H), 7.00 (d, *J* = 8.2 Hz, 1 H), 7.06 (d, *J* = 1.8 Hz, 1 H), 7.11 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.34 (dd, *J* = 7.8, 4.6 Hz, 1 H), 7.46 (s, 1 H), 8.18 (dd, *J* = 7.8, 1.4 Hz, 1 H), 8.61 (dd, *J* = 4.6, 1.4 Hz, 1 H).

^{13}C NMR: δ = 56.02, 56.04, 111.6, 111.7, 119.4, 120.8, 122.6, 128.6, 130.5, 131.4, 135.5, 146.7, 149.0, 149.3, 162.5.

MS: *m*/*z* = 271 (100%, $[M^+]$).

Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.56; H, 5.07; N, 5.05.

3-(1,3-Benzodioxol-5-yl)thieno[2,3-*b*]pyridine (5d)
White solid; mp 121–124 °C (hexane–Et_2O).

IR (KBr): 3101, 1518, 1236, 1031 cm^{-1}.

^1H NMR: δ = 6.04 (s, 2 H), 6.94 (d, *J* = 8.2 Hz, 1 H), 7.02–7.03 (m, 2 H), 7.34 (dd, *J* = 8.2, 4.6 Hz, 1 H), 7.43 (s, 1 H), 8.17 (dd, *J* = 8.2, 1.4 Hz, 1 H), 8.61 (dd, *J* = 4.6, 1.4 Hz, 1 H).

^{13}C NMR: δ = 101.3, 108.7, 108.8, 119.4, 121.9, 122.8, 129.2, 130.4, 131.2, 135.2, 146.7, 147.4, 148.1, 162.4.

MS: *m*/*z* = 255 (100%, $[M^+]$).

Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.79; H, 3.56; N, 5.31.

3-(Thiophen-2-yl)thieno[2,3-*b*]pyridine (5e)
Yellow oil; R_f = 0.35 (THF–hexane, 1:50).

IR (neat): 3113, 1519, 1238, 1028 cm^{-1}.

^1H NMR: δ = 7.17 (d, *J* = 5.1, 3.7 Hz, 1 H), 7.32 (dd, *J* = 3.7, 1.4 Hz, 1 H), 7.36–7.39 (m, 2 H), 7.60 (s, 1 H), 8.38 (dd, *J* = 8.4, 1.4 Hz, 1 H), 8.62 (dd, *J* = 4.5, 1.4 Hz, 1 H).

^{13}C NMR: δ = 119.7, 123.7, 125.17, 125.22, 127.8, 128.4, 130.7, 130.8, 136.8, 147.0, 162.3.

MS: *m*/*z* = 217 (100%, $[M^+]$).

Anal. Calcd for $C_{11}H_7NS_2$: C, 60.80; H, 3.25; N, 6.45. Found: C, 60.69; H, 3.39; N, 6.40.

3-(4-Methoxyphenyl)thieno[2,3-*c*]pyridine (11a)
Pale-yellow solid; mp 78.5–81 °C (hexane–Et_2O).

IR (KBr): 3088, 1612, 1491, 1248, 1030 cm^{-1}.

^1H NMR: δ = 3.88 (s, 3 H), 7.04 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 7.78 (dd, *J* = 6.0, 0.9 Hz, 1 H), 7.60 (s, 1 H), 8.53 (d, *J* = 6.0 Hz, 1 H), 9.18 (d, *J* = 0.9 Hz, 1 H).

^{13}C NMR: δ = 55.3, 114.4, 117.1, 127.0, 127.6, 129.6, 137.2, 137.3, 143.2, 143.2, 145.2, 159.5.

MS: *m*/*z* = 241 (100%, $[M^+]$).

Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.91; H, 4.51; N, 6.01.

3-(1,3-Benzodioxol-5-yl)thieno[2,3-*c*]pyridine (11b)
Pale-yellow solid; mp 134–136 °C (hexane–CH_2Cl_2).

IR (KBr): 3091, 1487, 1248, 1030 cm^{-1}.

^1H NMR: δ = 6.05 (s, 2 H), 6.95 (d, *J* = 8.7 Hz, 1 H), 7.03–7.05 (m, 2 H), 7.60 (s, 1 H), 7.79 (dd, *J* = 5.5, 0.9 Hz, 1 H), 8.53 (d, *J* = 5.5 Hz, 1 H), 9.18 (s, 1 H).

^{13}C NMR: δ = 101.3, 108.8, 108.9, 117.1, 122.1, 128.0, 128.4, 137.2, 137.3, 143.1, 143.3, 145.2, 147.6, 148.1.

MS: *m*/*z* = 255 (100%, $[M^+]$).

Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.83; H, 3.62; N, 5.40.

3-(Thiophen-2-yl)thieno[2,3-*c*]pyridine (11c)
Pale-yellow oil; R_f = 0.26 (EtOAc–hexane, 1:5).

IR (neat): 3084, 1578, 1275, 1031 cm^{-1}.

^1H NMR: δ = 7.18 (dd, *J* = 5.0, 3.6 Hz, 1 H), 7.36 (dd, *J* = 3.6, 1.4 Hz, 1 H), 7.41 (d, *J* = 5.0, 1.4 Hz, 1 H), 7.75 (s, 1 H), 7.99 (dd, *J* = 5.0, 0.9 Hz, 1 H), 8.58 (d, *J* = 5.0 Hz, 1 H), 9.18 (d, *J* = 0.9 Hz, 1 H).

^{13}C NMR: δ = 117.2, 125.5, 125.6, 127.8, 128.7, 130.3, 135.8, 137.2, 142.6, 143.6, 145.2.

MS: *m*/*z* = 217 (100%, $[M^+]$).

Anal. Calcd for $C_{11}H_7NS_2$: C, 60.80; H, 3.25; N, 6.45. Found: C, 60.80; H, 3.18; N, 6.50.

3-(4-Methoxyphenyl)thieno[3,2-*c*]pyridine (16a)
White solid; mp 102–105 °C (hexane–CH_2Cl_2).

IR (KBr): 3084, 1611, 1497, 1250, 1030 cm^{-1}.

^1H NMR: δ = 3.88 (s, 3 H), 7.04 (d, *J* = 8.7 Hz, 2 H), 7.35 (s, 1 H), 7.53 (d, *J* = 8.7 Hz, 2 H), 7.83 (dd, *J* = 5.4, 0.9 Hz, 1 H), 8.49 (d, *J* = 5.4 Hz, 1 H), 9.19 (s, 1 H).

^{13}C NMR: δ = 55.4, 114.4, 117.6, 122.9, 127.0, 129.7, 134.2, 137.2, 142.6, 145.5, 148.1, 159.6.

MS: *m*/*z* = 241 (100%, $[M^+]$).

Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.51; H, 4.73; N, 5.89.

3-(3,4-Dimethoxyphenyl)thieno[3,2-*c*]pyridine (16b)
White solid; mp 142–144 °C (hexane–CH_2Cl_2).

IR (KBr): 3092, 1501, 1234, 1032 cm^{-1}.

^1H NMR: δ = 3.95 (s, 3 H), 3.97 (s, 3 H), 7.02 (d, *J* = 8.2 Hz, 1 H), 7.12 (d, *J* = 1.8 Hz, 1 H), 7.17 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.39 (s, 1 H), 7.85 (d, *J* = 5.5 Hz, 1 H), 8.51 (d, *J* = 5.5 Hz, 1 H), 9.22 (s, 1 H).

^{13}C NMR: δ = 56.0 (2 C), 111.5, 111.8, 117.6, 121.1, 123.1, 127.3, 134.2, 137.4, 142.7, 145.6, 148.2, 149.1, 149.2.

MS: *m*/*z* = 271 (100%, $[M^+]$).

Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.33; H, 5.01; N, 5.17.

3-(1,3-Benzodioxol-5-yl)thieno[3,2-*c*]pyridine (16c)
Colorless crystals; mp 119–121 °C (hexane–Et_2O).

IR (KBr): 3094, 1489, 1248, 1047 cm^{-1}.

^1H NMR: δ = 6.06 (s, 2 H), 6.95 (d, *J* = 7.3 Hz, 1 H), 7.07 (s, 1 H), 7.08 (d, *J* = 7.8 Hz, 1 H), 7.36 (s, 1 H), 7.83 (d, *J* = 5.5 Hz, 1 H), 8.50 (d, *J* = 5.5 Hz, 1 H), 9.19 (s, 1 H).

^{13}C NMR: δ = 101.4, 108.8, 109.1, 117.6, 122.3, 123.3, 128.4, 134.1, 137.3, 142.8, 145.5, 147.7, 148.1, 148.2.

MS: *m*/*z* = 255 (100%, $[M^+]$).

Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.82; H, 3.72; N, 5.30.

3-(Thiophen-2-yl)thieno[3,2-*c*]pyridine (16d)
Yellow oil; R_f = 0.50 (EtOAc–hexane, 1:2).

IR (neat): 3088, 1574, 1435, 1281 cm^{-1}.

^1H NMR: δ = 7.20 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.39–7.42 (m, 2 H), 7.54 (s, 1 H), 7.84 (dd, *J* = 5.5, 0.9 Hz, 1 H), 8.53 (d, *J* = 5.5 Hz, 1 H), 9.42 (s, 1 H).

^{13}C NMR: δ = 117.7, 124.2, 125.6, 125.8, 127.9, 130.2, 133.5, 135.7, 142.6, 145.3, 148.3.

MS: *m*/*z* = 217 (100%, $[M^+]$).

Anal. Calcd for $C_{11}H_7NS_2$: C, 60.80; H, 3.25; N, 6.45. Found: C, 60.78; H, 3.16; N, 6.28.

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