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# *N*-(3-Benzo[*b*]thienyl)iminophosphoranes toward the Synthesis of Benzo[*b*]thieno[3,2-*b*]pyridines: Reactivity and Alternative Regioselectivity with α,β-unsaturated Ketones and Aldehydes

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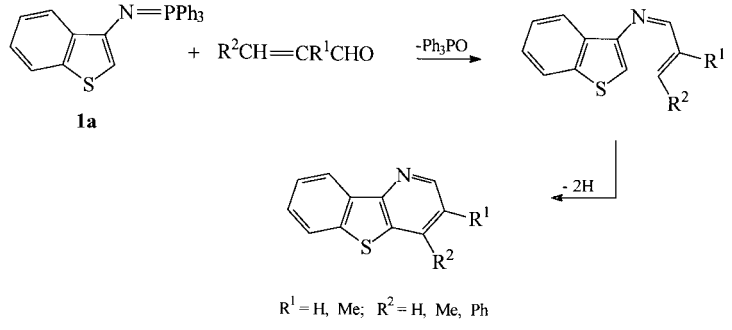
**Abstract**—The novel *N*-(3-benzo[*b*]thienyl)iminophosphoranes **1b**–**d** react with α,β-unsaturated aldehydes and ketones **2a**–**e** to give varying mixtures of the regioisomeric benzothieno[3,2-*b*]pyridines **3a**–**d** and **4a**–**d** as a result of preferential attack of either imino nitrogen or α-thienyl carbon at the enone carbonyl group. The findings indicate that the progressive replacement of phenyl with methyl P-substituent greatly enhances the reactivity of the phosphorane **1** and concomitantly enhances the propensity of the phosphorane itself for addition to the enone by the α-thienyl carbon. 

## Introduction

Iminophosphoranes are important intermediates which have found extensive use in the production of acyclic and, especially, heterocyclic nitrogen-containing compounds.[1] *N*-aryl- and certain *N*-heteroaryl-iminophosphoranes have been largely investigated; instead, those derived from five-membered heteroarenes containing one heteroatom remain virtually unexplored, despite the fact that their preparation from readily available azido precursors is now feasible.[2]

In previous work we first prepared *N*-(3-benzo[*b*]thienyl)-iminotriphenylphosphorane **1a** and its *N*-(2-benzo[*b*]thienyl)-substituted analogue by Staudinger reaction of 3-azido- and 2-azido-benzothiophene with triphenylphosphine.[2] Both phosphorane compounds proved to be useful nitrogen intermediates for the construction of benzothieno[*b*]pyridines, which represent a class of pharmacological bioactive compounds of special interest as isosters with indolopyridines[3] and as annelated NADH models.[4] In fact, mild thermal reaction of the phosphorane **1a** (and its positional isomer) with α,β-unsaturated aldehydes directly yielded moderate yields of corresponding benzothienopyridines that were considered to form through electrocyclization and eventual dehydrogenation of the initial aza Wittig imine products (Scheme 1).

Strong support to the postulated aza Wittig-electrocyclization mechanism arose from successful detection of certain azahexatriene intermediates. Moreover, consistent with the




**Scheme 1.**

*Keywords*: azides; iminophosphoranes; annulation reactions; fused pyridines.
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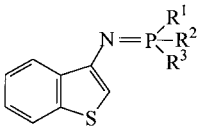
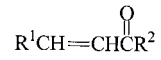
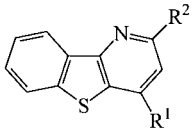


**1b** : $R^1 = R^2 = Ph$, $R^3 = Me$
**1c** : $R^1 = Ph$, $R^2 = R^3 = Me$
**1d** : $R^1 = R^2 = R^3 = Me$



**2a** : $R^1 = H$, $R^2 = Me$
**2b** : $R^1 = Ph$, $R^2 = Me$
**2c** : $R^1 = COOMe$, $R^2 = Me$
**2d** : $R^1 = Ph$, $R^2 = H$
**2e** : $R^1 = Me$, $R^2 = H$



**3a** : $R^1 = H$, $R^2 = Me$
**3b** : $R^1 = Ph$, $R^2 = Me$
**3c** : $R^1 = COOMe$, $R^2 = Me$
**3d** : $R^1 = Ph$, $R^2 = H$

**4a** : $R^1 = Me$, $R^2 = H$
**4b** : $R^1 = Me$, $R^2 = Ph$
**4c** : $R^1 = Me$, $R^2 = COOMe$
**4d** : $R^1 = H$, $R^2 = Ph$

**Figure 1.**

postulated mechanism, the reactions with cinnamaldehyde, crotonaldehyde and methacrylaldehyde occurred in a regiospecific fashion to give a single 4- or 3-substituted benzothienopyridine.[2] However, our subsequent efforts to enlarge the scope of these novel annulation reactions by using but-3-en-2-one as the carbonyl substrate showed that both triphenylphosphoranes were virtually inert with the ketone. We were therefore led to prepare the mono-, di-, and trimethyl-P-substituted (3-benzothienylimino)phosphoranes **1b**–**d** (Fig. 1) and thence to examine their possible use with α,β-unsaturated ketones and aldehydes. Compounds **1b**–**d** were predicted to be more reactive than the triphenyl counterpart **1a** since the electron-donating methyl group(s) should decrease the positive charge on the phosphorus and concomitantly increase the negative charge on the imino nitrogen.[1a]

Herein we report the results of our study on the reactions of the phosphoranes **1b**–**d** (and **1a**) with the enones **2a**–**e** shown in Fig. 1.

## Results and Discussion

The phosphoranes **1b**–**d** were readily prepared by Staudinger reaction of 3-azidobenzothiophene with the appropriate phosphine, following an analogous procedure to that previously employed for the triphenyl derivative **1a**. The mono- and dimethyl-phosphoranes **1b**,**c** were isolated as fairly stable solid compounds, whereas the trimethyl analogue **1c** was obtained as a crude oil which showed a tendency to decompose and thence was directly used without purification.

In contrast with the previous triphenylphosphorane **1a**, the methylphosphorane **1b** succeeded in reacting with but-3-en-2-one **2a**, in toluene solution at 70°C, to furnish, in moderate overall yield, equal amounts of 2-methylbenzo-[*b*]thieno[3,2-*b*]pyridine **3a** (the expected aza Wittig-electrocyclization pyridine product) and the 4-methyl positional isomer **4a** (Fig. 1 and Table 1; entry 1). Under comparable conditions the dimethylphosphorane **1c** with **2a** similarly furnished both isomeric pyridines **3a** and **4a**, but in this case their overall yield was significantly higher and, additionally, the proportion of the isomer **4a** was greatly enhanced (Table 1; entry 2). Like the phosphorane **1c**, in the presence of **2a** the rather unstable trimethyl derivative **1d** also yielded the pyridine **4a** in preference to the isomer **3a**, although in a less efficient fashion (Table 1; entry 3). With *trans*-4-phenyl-3-buten-2-one **2b** the compound **1b** reacted to give a modest yield of the sole disubstituted pyridine **3b** (Fig. 1 and Table 1; entry 4), whereas the more reactive dimethyl analogue **1c** could afford, besides the above pyridine **3b**, significant amounts of its regioisomer **4b** (Table 1; entry 5). Moreover, with

**Table 1.** Reactions of the phosphoranes **1a**–**d** with the α,β-unsaturated ketones **2a**–**c** and aldehydes **2d**, **e** (reactions were normally carried out in PhMe at 70°C by using equimolar amounts of phosphorane **1** and enone **2**)

| Entry | Phosphorane | Enone | Benzothienopyridine(s) (% yield)[a] |
|---|---|---|---|
| 1 | **1b** | **2a** | **3a** (25)+**4a** (25) |
| 2 | **1c** | **2a** | **3a** (15)+**4a** (60) |
| 3 | **1d** | **2a** | **3a** (10)+**4a** (40) |
| 4 | **1b** | **2b** | **3b** (26) |
| 5 | **1c** | **2b** | **3b** (33)+**4b** (15) |
| 6 | **1a** | **2c** | **3c** (30) |
| 7 | **1b** | **2c** | **3c** (46)+**4c** (27) |
| 8 | **1c** | **2c** | **3c** (47)+**4c** (42) |
| 9 | **1a** | **2d** | **3d** (45)[b] |
| 10 | **1b** | **2d** | **3d** (30)+**4d** (25) |
| 11 | **1c** | **2d** | **3d** (15)+**4d** (40) |
| 12 | **1a** | **2e** | **4a** (62)[b] |
| 13 | **1b** | **2e** | **4a** (41)+**3a** (30) |
| 14 | **1c** | **2e** | **4a** (20)+**3a** (51) |
| 15 | **1d**[c] | **2e** | **4a** (16)+**3a** (30) |

[a] Yield isolated by column chromatography.
[b] See Ref. 2.
[c] Reaction carried out at 45°C.

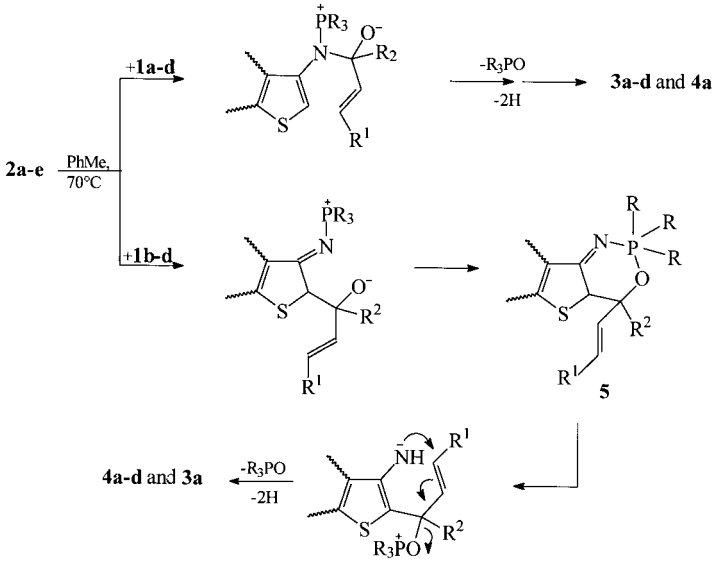
methyl *trans*-4-oxo-2-pentenoate **2c** both methylated phosphoranes **1b,c** led, in high yields, to the corresponding disubstituted pyridines **3c** and **4c**, which isomers occurred in a ratio of ca. 2:1 and 1:1 on passing respectively from **1b** to **1c** (Fig. 1 and Table 1; entries 7 and 8).

In the present work the triphenylphosphorane **1a** was found to fail to react with the ketone **2b**, while, in the presence of the (activated) keto ester **2c**, it could successfully afford only the aza Wittig-electrocyclization pyridine **3c**, albeit in modest yield (Table 1; entry 6). When the benzothienyl phosphoranes **1b**–**d** were reacted with *trans*-cinnamaldehyde **2d** and *trans*-crotonaldeyde **2e**, interestingly, the ensuing chemical trend was strictly comparable with that displayed by the corresponding reactions with the ketones **2a**–**c**. Indeed, with the aldehydes **2d,e** the methylated derivatives **1b**–**d,** unlike the triphenylphosphorane **1a**,[2] similarly furnished varying mixtures of the respective 4-substituted-, **3d** and **4a**, and 2-substituted-benzothienopyridines, **4d** and **3a**, in relative ratios reversing on going from **1b** to **1c**,**d** (Fig. 1 and Table 1; entries 9–15). Structural assignment to the previously known benzothienopyridines **3a**,**d**,**4a** and to those hitherto unknown **3b**,**c**,**4b**–**d** was generally performed on the basis of elemental analysis in addition to $^{1}H$ and $^{13}C$ NMR spectral data. In particular, $^{1}H$ NMR spectroscopy clearly showed that the the hydrogen and/or methyl substituents attached at the α-position of the pyridine moiety absorb at a significantly lower field than when they are attached at the γ-position. Moreover, the values of the coupling constant of the vicinal α- and β-hydrogens in the compounds **3d**,**4a** ($J$=ca. 6 Hz) were found to be expectedly lower than that observed for the β- and γ-hydrogens in the compound **3a** ($J$=8.5 Hz).

Thus, our present and previous findings revealed that the progressive replacement of phenyl with methyl P-substituent can greatly enhance the reactivity of benzothienylphosphorane **1** towards enones **2**, concomitantly enhancing the propensity of **1** to behave like the *N*-vinyl congeners[5] by adopting the β-(α-thienyl-)carbon instead of the imino nitrogen. In fact, with all the enones **2a**–**e** the methylated phosphoranes **1b** and, especially, **1c**,**d** showed a fair tendency to produce the respective benzothienopyridines **4a**–**d** (and **3a**) at the expense of the isomeric aza Wittig-electrocyclization ones **3a**–**d** (and **4a**). The compounds **1b**–**d** presumably led to the pyridines **4a**–**d** and **3a** through the reaction sequences outlined in Scheme 2. These involve primary addition of the α-thienyl carbon of **1b**–**d** to the carbonyl carbon of the enones **2a**–**e** leading to an intermediate phosphorane **5**, which, upon subsequent fragmentation, undergoes cyclization to pyridine with eventual dehydrogenation. Analogous type of reaction sequences have already been invoked in the reaction of certain (vinylimino)phosphoranes with cinnamaldehydes similarly leading to cyclized pyridines.[6,7]

However, it is worth noting that in the presence of enones **2** the vinyl phosphoranes are normally envisaged to yield pyridines as a result of (frontier orbital-controlled) addition to the enone β-vinyl carbon rather than of alternative (charge-controlled) addition to the carbonyl one.[6] On this basis, in the observed production of the pyridines **4a**–**d** and **3a** the compounds **1b**–**d** would be generally entitled to add to the enones **2a**–**e** in a mode unusual for the vinyl counterparts. At this stage we have no clear explanation of the actual reasons that might cause a different addition mode by those types of related compounds, but it is possible that kinetic and thermodynamic factors in the addition of those phosphoranes at either enone carbonyl or vinyl carbon can play a relative role to a different extent.

Regardless of mechanistic implications, our overall results now indicate that the thermal reactions of the phosphoranes **1** with unsaturated aldehydes and ketones can offer a convenient, general protocol for the production of benzothieno[3,2-*b*]pyridines, for which compounds the few literature methods are rather difficult and/or give (very) low yields.[3,4,8] Such a protocol, in principle, should be of wide utility for achieving *b*-fusion[9] of a pyridine ring onto five-membered heteroarenes by using the α- and β-azido derivatives as the nitrogen precursors.[10,11] Of special interest is our present observation that the




**Scheme 2.**

regiochemistry of the outcoming substituted pyridines can be largely governed by a proper choice of the phosphorane **1** reagent since phenyl substituents on the phosphorus can favor attack of the imino nitrogen on the enone carbonyl group and instead methyl substituents favor alternative attack of the α-thienyl carbon. This observation will be useful in the future planning of the synthesis of benzothieno[*b*]pyridines bearing specific substituents at the 2-, 3- and/or 4-positions of the pyridine moiety.

## Experimental

The enones **2a**–**e** were commercially available. 3-Azidobenzo[*b*]thiophene was prepared according to a literature method.[12] Column chromatography was carried out on Merck silica gel (0.063–0.200 mm particle size) by progressive elution with hexane–ethyl acetate mixtures. $^1$H and $^{13}$C NMR spectra were normally carried out in $CDCl_3$ solutions, using tetramethylsilane as the internal standard. Massa spectra were obtained with a Hewlett-Packard 5971 mass-selective detector on a Hewlett-Packard 5890 gas chromatograph [OV-1 capillary column between 70–250°C (20°C min$^{-1}$)].

The methylphosphoranes **1b**–**d** were prepared from 3-azidobenzothiophene (350 mg, 2 mmol) and the appropriate phosphine (2 mmol) by following the same procedure as previously described for the triphenyl analogue **1a**.[2]

Chromatographic purification gave *N-(3-benzo[b]thienyl)-methyldiphenylphosphorane* (**1b**) (555 mg, 80%) as an orange solid, mp 105–107°C [$^1$H NMR (300 MHz) $\delta$ 8.18–8.10 (m, 1H), 7.92–7.81 (m, 5H), 7.78–7.70 (m, 1H), 7.60–7.48 (m, 5H), 7.40–7.27 (m, 2H), 5.64 (s, 1H), 2.20 (d, 3H, $^2J_{PH}$=15.8 Hz); IR (Nujol) $\nu_{max}$ 1520, 1340, 1250, 970, 880 cm$^{-1}$. Anal. Calcd for $C_{21}H_{18}NPS$: C, 72.60; H, 5.22; N, 4.03; S, 9.23. Found: C, 72.32; H, 5.20; N, 4.10; S, 9.13%].

Chromatographic purification gave *N-(3-benzo[b]thienyl)-dimethylphenylphosphorane* (**1c**) (445 mg, 78%) as an orange solid, mp 145–147°C [$^1$H NMR (300 MHz) $\delta$ 8.04–7.98 (m, 1H), 7.76–7.70 (m, 1H), 7.60–7.48 (m, 5H), 7.40–7.27 (m, 2H), 5.71 (s, 1H), 1.98 (d, 6H, $^2J_{PH}$= 17.6 Hz); IR (Nujol) $\nu_{max}$ 1570, 1320, 1230, 970, 930, 880 cm$^{-1}$. Anal. Calcd for $C_{16}H_{16}NPS$: C, 67.35; H, 5.65; N, 4.91; S, 11.24. Found: C, 67.30; H, 5.67; N, 4.98; S, 11.18%].

The crude *N-(3-benzo[b]thienyl)trimethylphosphorane* (**1d**) (334 mg, 75%) was obtained as a viscous oil which showed a tendency to decompose under work-up conditions and was thence directly employed without purification [$^1$H NMR (300 MHz) $\delta$.7.90–7.86 (m, 1H), 7.28–7.22 (m, 1H), 7.40–7.27 (m, 2H), 6.08 (s, 1H), 1.71 (d, 6H, $^2J_{PH}$=13 Hz), 1.54 (d, 3H, $^2J_{PH}$=15 Hz)].

### Thermal reactions of the phosphoranes 1a–d with the enones 2a–e.

**General procedure.** A mixture of the appropriate iminophosphorane **1** (0.12 mmol) and enone **2** (0.12 mmol) in dry toluene (3 ml) was stirred at 70°C for 16–24 h, after which time the starting reagents were normally shown by TLC to be largely absent (but the essayed mixture of **1a** and **2b** was shown to remain virtually unchanged). The excess of solvent was removed under vacuum and the residual material chromatographed. The reaction of the most reactive phosphorane **1d** with the aldehyde **2e** was carried out in a similar fashion but using a lower temperature (45°C) and a reduced time (1.5 h). Yields of the isolated benzo[*b*]thieno[3,2-*b*]pyridines **3a**–**d**, **4a**–**d** are given in Table 1. Physical and analytical data for every compound **3**,**4** were as follows.

**2-Methylbenzo[*b*]thieno[3,2-*b*]pyridine (3a).**[13] Thick oil [$^1$H NMR (300 MHz) 8.59–8.51 (m, 1H), 8.08 (d, 1H, *J*=8.5 Hz), 7.90–7.82 (m, 1H), 7.60–7.51 (m, 2H), 7.26 (d, 1H, *J*=8.5 Hz), 2.79 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 155.1, 140.0, 134.8, 132.1, 128.4, 125.1, 124.8, 123.2, 122.9, 122.5, 121.0, 28.5; MS *m*/*z* 199 (M$^+$, 100). Anal. Calcd for $C_{12}H_9NS$: C, 72.33; H, 4.55; N, 7.03; S, 16.09. Found: C, 72.11; H, 4.58; N, 7.06; S, 16.05%].

**4-Methylbenzo[*b*]thieno[3,2-*b*]pyridine (4a).**[13] Thick oil [$^1$H NMR (300 MHz) $\delta$ 8.64 (d, 1H, *J*=5.6 Hz), 8.52–8.44 (m, 1H), 7.92–7.82 (m, 1H), 7.61–7.50 (m, 2H), 7.20 (d, 1H, *J*=5.6 Hz), 2.61 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 146.8, 143.9, 141.3, 136.2, 134.8, 132.0, 128.4, 125.0, 123.2, 122.9, 121.5, 30.1; MS *m*/*z* 199 (M$^+$, 100). Anal. Calcd for $C_{12}H_9NS$: C, 72.33; H, 4.55; N, 7.03; S, 16.09. Found: C, 72.21; H, 4.55; N, 7.11; S, 16.15%].

**2-Methyl-4-phenylbenzo[*b*]thieno[3,2-*b*]pyridine (3b).** Yellow solid, mp 75–78°C [$^1$H NMR (300 MHz) $\delta$ 8.62–8.52 (m, 1H), 7.89–7.74 (m, 3H), 7.68–7.48 (m, 5H), 7.35 (s, 1H), 2.85 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 156.0, 144.1, 143.1, 139.0, 137.5, 131.5, 129.1, 128.5, 128.1, 127.5, 127.3, 127.0, 126.8, 122.5, 121.0, 31.1; MS *m*/*z* 275 (M$^+$, 100). Anal. Calcd for $C_{18}H_{13}NS$: C, 78.51; H, 4.76; N, 5.09; S, 11.64. Found: C, 78.48, H, 4.81; N, 5.03; S, 11.70%].

**4-Methyl-2-phenylbenzo[*b*]thieno[3,2-*b*]pyridine (4b).** Yellow solid, mp 82–85°C [$^1$H NMR (300 MHz) $\delta$ 8.62–8.55 (m, 1H), 7.92–7.85 (m, 1H), 7.67 (s, 1H), 7.65–7.40 (m, 7H), 2.69 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 154.9, 152.9, 141.8, 139.9, 134.8, 131.0, 130.6, 129.0, 128.5, 128.3, 128.1, 126.9, 124.0, 123.3, 122.7, 118.7, 118.6, 29.3; MS *m*/*z* 275 (M$^+$, 100). Anal. Calcd for $C_{18}H_{13}NS$ requires C, 78.51; H, 4.76; N, 5.09; S, 11.64. Found: C, 78.55; H, 4.78; N, 5.13; S, 11.68].

**Methyl 2-methylbenzo[*b*]thieno[3,2-*b*]pyridine-4-carboxylate (3c).** Yellow solid, mp 120–122°C [$^1$H NMR (300 MHz) $\delta$ 8.54–8.48 (m, 1H), 7.94–7.88 (m, 1H), 7.86 (s, 1H), 7.62–7.5 (m, 2H), 4.09 (s, 3H), 2.84 (s, 3H); $^{13}$C NMR (75 MHz) 166.0, 156.1, 154.0, 141.5, 134.5, 131.5, 131.0, 129.1, 125.0, 122.0, 121.5, 120.5, 53.1, 29.0; MS *m*/*z* 257 (M$^+$, 100). Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; S, 12.46. Found: C, 65.30; H, 4.38; N, 5.42; S, 12.55%].

**Methyl 4-methylbenzo[*b*]thieno[3,2-*b*]pyridine-2-carboxylate (4c).** Bright yellow solid, mp 105–107°C [$^1$H NMR (300 MHz) $\delta$ 8.58–8.51 (m, 1H), 8.09 (s, 1H), 7.94–7.86 (m, 1H), 7.76–7.51 (m, 2H), 4.09 (s, 3H), 2.68 (s, 3H); $^{13}$C

NMR (75 MHz) $\delta$ 167.0, 152.0, 146.1, 143.1, 135.0, 131.0, 129.1, 128.5, 125.1, 124.0, 122.6, 122.1, 53.0, 29.0; MS *m*/*z* 257 ($M^+$, 100). Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; S, 12.46. Found: C, 65.38; H, 4.35; N, 5.43; S, 12.48%].

**4-Phenylbenzo[*b*]thieno[3,2-*b*]pyridine (3d).**[14] Yellow solid, mp 73–75°C [$^1$H NMR (300 MHz) $\delta$ 8.84 (d, 1H, *J*=6.0 Hz), 8.58–8.53 (m, 1H), 7.90–7.87 (m, 1H), 7.83–7.79 (m, 2H), 7.62–7.54 (m, 5H), 7.45 (d, 1H, *J*=6.0 Hz); $^{13}$C NMR (75 MHz) $\delta$ 147.5, 144.5, 140.2, 139.2, 138.7, 137.0, 134.5, 129.6, 129.3, 128.5, 128.1, 125.4, 125.2, 123.2, 122.5, 121.0; MS *m*/*z* 261 ($M^+$, 100). Anal. Calcd for $C_{17}H_{11}NS$: C, 78.13; H, 4.24; N, 5.36; S, 12.27. Found: C, 78.20; H, 4.26; N, 5.29; S, 12.25%].

**2-Phenylbenzo[*b*]thieno[3,2-*b*]pyridine (4d).** Pale yellow solid, mp 85–87°C [$^1$H NMR (300 MHz) $\delta$ 8.66–8.61 (m, 1H), 8.25–8.18 (m, 3H), 7.94–7.82 (m, 2H), 7.62–7.42 (m, 5H); $^{13}$C NMR (75 MHz) $\delta$ 153.8, 152.7, 140.5, 139.8, 134.9, 132.3, 130.9, 129.0, 128.8, 128.4, 128.0, 127.1, 124.9, 123.3, 123.1, 122.9, 118.1; MS *m*/*z* 261 ($M^+$, 100). Anal. Calcd for $C_{17}H_{11}NS$: C, 78.13; H, 4.24; N, 5.36; S, 12.27. Found: C, 78.26; H, 4.28; N, 5.32; S, 12.35%].

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14. The benzothienopyridine **3d** had been previously prepared, but no analytical data had been provided (Ref. 2).