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Novel *N*-(2-benzo[*b*]thienyl)iminophosphoranes and their use in the synthesis of benzo[*b*]thieno[2,3-*b*]pyridines

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Dedicated to Professor Piero Spagnolo on the occasion of his 60th birthday

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Abstract—Novel *N*-(2-benzo[*b*]thienyl)iminophosphoranes react with α,β-unsaturated aldehydes and ketones to give benzo[*b*]thieno[2,3-*b*]pyridines in an aza-Wittig/electrocyclic-ring closure process. The diphenylmethyliminophosphorane reacts with aromatic and heteroaromatic aldehydes to give iminic products: upon UV irradiation, two imines furnish cyclization products in acceptable yields. © 2002 Elsevier Science Ltd. All rights reserved.

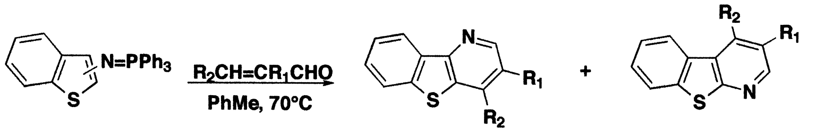
1. Introduction

In the last 20 years, the chemistry of iminophosphoranes has been largely expanded mainly due to its use in the synthesis of nitrogen heterocycles via inter- and intramolecular aza-Wittig reactions.[1,2] However, *N*-(heteroaryl)iminophosphoranes have so been far poorly utilized, despite the fact that they are now readily available from azido precursors.[3]

In a previous work,[3] we described the first examples of 3- and 2-benzothienyliminotriphenylphosphoranes derived from 3-azido and 2-azido-benzothiophene, respectively, and their use in the regiospecific synthesis of 3- and/or 4-substituted benzothieno[*b*]pyridines through aza-Wittig reaction with α,β-unsaturated aldehydes followed by in situ electrocyclization of the resultant imines (Scheme 1). However, the attempted use of α,β-unsaturated ketones in this protocol proved to be unsuccessful owing to the apparent inertness of the triphenylphosphorane.

Benzothieno[*b*]pyridines represent a class of compounds of pharmacological interest either as isosteres of indolopyridines[4] or as potential antiallergics;[5] moreover, a study of their antinflammatory effects has also been recently reported.[6] Since all the previously known syntheses normally occurred in many steps and/or in low yields, we were subsequently led to investigate the reactions of (more reactive) mono-, di- and trimethyl-P-substituted (3-benzothienyl)iminophosphoranes with both α,β-unsaturated aldehydes and ketones as a general route to benzo[*b*]thieno[3,2-*b*]pyridines.[7] These reactions were interestingly found to afford regioisomeric benzothieno[3,2-*b*]pyridines as a result of preferential attack of either imino nitrogen or α-thienyl carbon at the enone carbonyl group.[7] Iminophosphoranes obtained from reaction with mono- and dialkyl aryl phosphines are less known then the triphenyl derivatives, but they are more useful since the electron-donating methyl group should increase the nucleophilicity of imino nitrogen. In this way it was possible to obtain preferentially one of the two regioisomeric benzothieno[3,2-*b*]pyridines

As an extension of this work we now report the preparation of two novel *N*-(2-benzo[*b*]thienyl)iminophosphoranes **1b** and **1c** and their employment, together with the already known **1a**,[3] in the synthesis of benzo[*b*]thieno[2,3-*b*]-



a $R_1=R_2=H$ 70%; **b** $R_1=H$, $R_2=Ph$ 45%; **c** $R_1=H$, $R_2=Me$ 50%; **d** $R_1=Me$, $R_2=H$ 60%

Scheme 1.

Keywords: azide; iminophosphorane; aza-Wittig reaction; benzothienopyridines.

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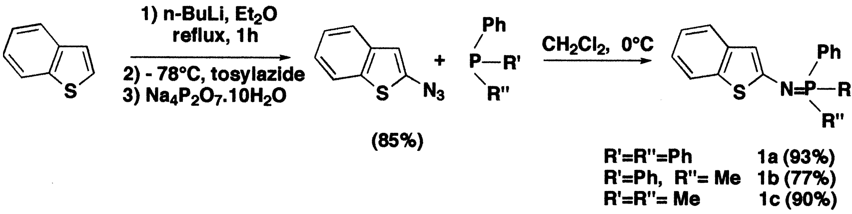
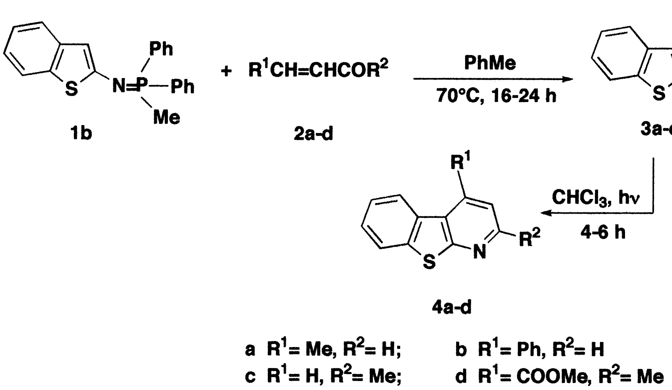


Scheme 2.



Scheme 3.

pyridines using an analogous aza-Wittig/electrocyclization reaction.

2. Results and discussion

The diphenylmethyl-**1b** and the dimethylphenylphosphorane **1c** were prepared by Staudinger reaction of 2-azidobenzo[*b*]thiophene with diphenylmethyl- and dimethylphenyl phosphine, following a procedure analogous to that we had employed for the corresponding triphenyl derivative **1a**.[3] (Scheme 2).

These new iminophosphoranes **1b** and **1c** were isolated as stable solid compounds, although the dimethylphenylphosphorane **1c** appears rather sensitive to light, as is **1a**.

The 2-benzothienyl phosphoranes **1a**–**c** were first reacted with crotonaldehyde **2a** and but-3-en-2-one **2c** in order to verify if the reaction might lead to benzothieno[2,3-*b*]pyridines as regioisomeric mixtures, similar to that previously observed and reported with 3-benzothienyl compounds.[7]

The obtained results were different from those of the 3-derivatives: in fact, the present reactions only furnished isolable aza-Wittig iminic products showing that the reactivity of the three phosphoranes was substantially similar. In such cases, the final benzo[*b*]thieno[2,3;*b*]pyridines could be obtained only after UV irradiation of the iminic products in chloroform solution.

In Scheme 3, the reaction pattern for compound **1b** and enones **2a**–**d** is reported, while in Table 1 a complete set of reaction products **3a**–**d** and **4a**–**d** is reported.

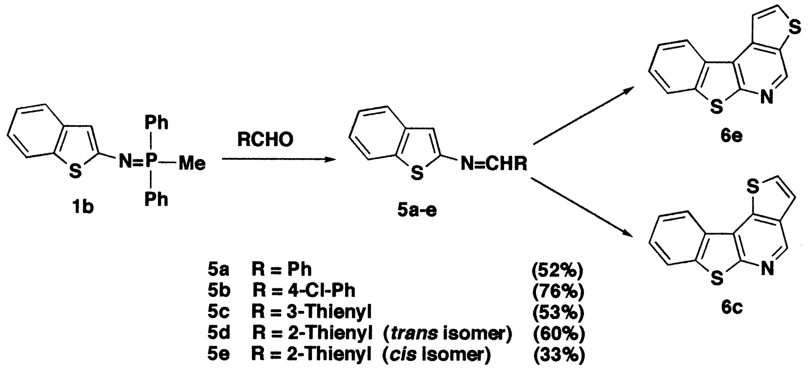
Due to the apparent feasibility of this reaction, and the acceptable yields of tricyclic compounds, we decided to

Table 1. Reactions of the phosphoranes **1a**–**c** with the α,β-unsaturated aldehydes **2a**,**b** and ketones **2c**,**d**

Entry	Phosphorane	Enone **2**			Imine **3** (%)[a]	Benzothienopyridine **4** (%)[a]
		R^1	R^2			
1	**1a**	Me	H	**a**	–	40
2	**1a**	H	Me	**c**	–	38
3	**1c**	Me	H	**a**	–	43
4	**1c**	H	Me	**c**	–	40
5	**1b**	Me	H	**a**	50	Quant.
6	**1b**	Ph	H	**b**	42	Quant.
7	**1b**	H	Me	**c**	46	Quant.
8	**1b**	CO_2Me	Me	**d**	65	Quant.

Reactions were normally carried out in PhMe at 70°C using equimolar amounts of phosphorane **1** and enone **2**.

[a] Yield after purification by column chromatography.



Scheme 4.

extend the heterocyclization to aromatic and heteroaromatic aldehydes, in order to obtain interesting tetracyclic structures.

On the basis of the previous reported data (Table 1) we investigated mainly the reactivity of phosphorane **1b**[8] towards other enones, including aromatic/heteroaromatic aldehydes.

The phosphorane **1b** was reacted with the benzaldehyde and 4-chloro-benzaldehyde affording in few hours the iminic products **5a** and **5b** which were isolated and purified on a silica gel column with petroleum ether/ethyl acetate 8:2 as eluent.

The same reaction was then tested with a less aromatic aldehyde, 3-thiophencarboxaldehyde, affording the imine **5c** in acceptable yield (Scheme 4).

While the reaction was performed with the 2-thiophencarboxaldehyde, both isomeric imines (*trans*/*cis*) **5d** and **5e** were isolated and identified by NMR spectroscopy.

Then the cyclization was tried on all the obtained iminic products **5a–e** firstly under usual conditions with a low power UV lamp and then using an UV lamp with higher power (see Section 4).

As reported in Scheme 4, cyclization occurred with imine **5c** with the obtaining of the tetracyclic compound **6c**, while for imines **5a** and **5b** we obtained only polymeric materials or reduction products. Also the *cis* imine **5e** gave cyclization product **6e**, while the **5d** imine (*trans* isomer) was recovered unchanged from reaction mixture.

Considering these final reported results, the different reactivities of heterocyclic imines (reacting) and aromatic one (non-reacting) deserve a deeper discussion.

First, since the cyclization reaction is a reaction with a low quantum yield, the change of the UV source was fundamental to induce faster kinetics in this slow reaction, although degradation products are also obtained with this powerful UV source.

The cyclizations of imines derived from aromatic aldehydes and aromatic amines have been reported but only in the presence of strong acid.[9] Other Schiff bases were observed to undergo smooth photocyclization in neutral solution containing an oxidant. However, in our experiments, we performed the cyclization reaction without the presence of either acid or oxidant. Therefore, probably, the observed behaviour can be due to the presence of heteroaromatic structures. In fact, since evidently this reaction should require a loss of aromaticity in the probable mechanism of intramolecular cyclization, the reaction of heteroaromatic structures should be favoured, in comparison with that of aromatic compounds.

This behaviour depends on the different transition state energies for the cyclization reaction. We calculated the transition state energy for the reaction of **5a** and **5c** by using semiempirical methods (PM3) on HyperChem™. This way we obtained $\Delta H^{\neq}$ for the described reactions: for **5a**, we obtained a value of 38 kcal mol^{-1}, while, in the case of the cyclization reaction of **5c**, we obtained 34 kcal mol^{-1}. These results are in agreement with the experimental results, considering that the higher activation energy observed in the case of **5a** could prevent the reaction to occur.

3. Conclusions

In this work we describe a useful protocol for the regiospecific preparation of benzothieno[2,3-*b*]pyridines based on the aza-Wittig reaction of the phosphorane **1b** (and **1a**,**c**) with a variety of unsaturated aldehydes and ketones including heteroaromatic and aromatic aldehydes. This methodology is quite interesting since it can be easily performed and requires readily available starting materials and mild reaction conditions, even if the yields in fused pyridines are moderate. Further work is currently under investigation to better explain the behaviour of the aromatic and heteroaromatic imines in order to obtain improved results also in this cyclization reaction.

4. Experimental

Column chromatography was carried out on Merck silica gel (0.063–0.200 mm particle size) by progressive elution with petroleum ether/ethyl acetate mixtures. ^{1}H and ^{13}C NMR spectra were normally carried out in CDCl$_3$ solutions on a Bruker AM 300 MHz. For UV irradiation a mercuric lamp Helios-Italquartz was used (Power: 125 W). Mass 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 enones and aromatic/heteroaromatic aldehydes used were commercially available.

The solvents were dried with P_2O_5 for dichloromethane and with sodium/benzophenone for toluene and diethyl ether. 2-Azidobenzo[*b*]thiophene was prepared by modifying the known procedure[10] in the following way: an aqueous solution of sodium pirophosphate decahydrate was added to a triazene salt; then 2-azidobenzo[*b*]thiophene was extracted with ethyl acetate until to the total dissolution of the solid residue. Then the organic phase was dried over sodium sulphate, concentrated in vacuum and filtered through florisil to give the desired product in 85% yield

4.1. Synthesis of compounds 1a–c: general procedure

2-Azidobenzothiophene (350 mg, 2 mmol) in dry dichloromethane (5 ml) was added dropwise to a solution of appropriate phosphine (2 mmol) in dry dichloromethane (5 ml) at 0°C, in a nitrogen atmosphere.

After 2 h, the reaction mixture was taken to room temperature for another hour and, after TLC evaluation in EP/AcOEt 7:3, was concentrated under vacuum: the residual material was crystallized from diethyl ether and characterized by ^{1}H and ^{13}C NMR. Physical and analytical data for every iminophosphorane are as follows.

4.1.1. *N*-(2-Benzo[*b*]thienyl)triphenylphosphorane (1a). The title compound was reported in literature.[3]

4.1.2. *N*-(2-Benzo[*b*]thienyl)methyldiphenylphosphorane (1b). The title compound (535 mg, 77%) was obtained as a yellow solid. Mp 120–123°C (^{1}H NMR (300 MHz) δ 7.83–7.76 (m, 6H); 7.61–7.45 (m, 6H); 7.44–7.41 (m, 1H); 7.27–7.24 (m, 1H); 7.12– 7.09 (m, 1H); 6.97–6.95 (m, 1H); 6.01 (s, 1H); 2.21 (d, 3H, $^2J_{PH}$=12.8 Hz); ^{13}C NMR (75 MHz) δ 158.22, 141.88, 140.89, 134.55, 132.90, 132.50, 132.03, 131.50, 131.00, 129.60, 129.00, 128.82, 124.00, 121.55, 120.05, 119.15, 105.05, 15.03; IR (Nujol) ν_{max} 1520, 1440, 1230, 960, 870, 760 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%].

4.1.3. *N*-(2-Benzo[*b*]thienyl)dimethylphenylphosphorane (1c). The title compound (513 mg 90%) was obtained as a dark yellow solid. Mp 130–133°C (^{1}H NMR (300 MHz) δ 7.82–7.72 (m, 2H); 7.61–7.43 (m, 3H); 7.32–7.28 (m, 2H); 7.12–7.09 (m, 1H); 6.97–6.77 (m, 1H); 6.00 (s, 1H); 1.99–1.96 (d, 6H, J_{PH}=16 Hz); ^{13}C NMR (75 MHz) δ 158.22, 141.55, 133.82, 132.34, 130.51, 129.22, 129.02, 123.77, 121.15, 120.55, 119.60, 104.33, 15.50, 14.80; IR (Nujol) ν_{max} 1570, 1520, 1470, 1250, 1110, 970, 890, 750 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%.

4.2. Thermal reactions: general procedure

A mixture of the appropriate iminophosphorane (0.12 mmol) and aldehyde or ketone (0.12 mmol) in dry toluene (3 ml) was stirred at 70°C for 16–24 h, after which time the starting materials were normally shown by TLC to be largely absent, except for the reaction of **1a** with benzaldehyde and 3-thiophencarboxaldeyde.

The solvent was removed under vacuum and residual material was chromatographed to furnish imines **3a–d** and **5a–e**, respectively. Yields and physical and analytical data for every compound are as follows: compounds **5a** and **5b** were known, but is reported only melting points, so we furnished spectroscopic data.

4.2.1. 2-[*N*-(*E*)-But-2-enylideneamino]benzo[*b*]thiophene (3a). Thick oil, 12 mg 50%, (^{1}H NMR (300 MHz) δ 8.0–7.92 (m, 1H); 7.72–7.64 (m, 2H); 7.34–7.24 (m, 2H); 7.22–7.15 (m, 1H); 6.54–6.38 (m, 2H); 2.23 (s, 3H); ^{13}C NMR (75 MHz) δ 161.13, 143.40, 139.50, 133.33, 132.85, 127.15, 126.86, 125.50, 122.20, 120.25, 115.50, 18.30. Anal. calcd for $C_{12}H_{11}NS$: C, 71.61; H, 5.51; N, 6.96; S, 15.93%. Found: C, 71.58; H, 5.49; N, 6.98; S, 15.96%

4.2.2. 2-[*N*-(*E*)-(3-Phenyl)-prop-2-enylideneamino]benzo[*b*]thiophene (3b). Thick oil, 13 mg 42% (^{1}H NMR δ 8.32–8.29 (m, 1H), 7.76–7.70 (m, 2H), 7.59–7.55 (m, 2H) 7.46–7.39 (m, 3H), 7.36–7.30 (m, 2H), 7.23–7.20 (m, 1H), 7.14–7.10 (m, 1H); ^{13}C NMR (75 MHz) δ 163.20, 150.60, 145.75, 143.45, 141.50, 138.85, 137.55, 134.50, 133.60, 130.35, 128.55, 126.20, 125.70, 124.35, 123.75, 122.20, 121.40. Anal. calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.92; S, 12.17%. Found: C, 77.51; H, 5.01; N, 5.95; S, 12.15%.

4.2.3. 2-[*N*-(1-Methyl)-prop-2-enylideneamino]benzo-[*b*]thiophene (3c). Thick oil, 9 mg 46%(^{1}H NMR (300 MHz) δ 7.72–7.64 (m, 2H), 7.22–7.15 (s, 1H), 7.10–7.05 (m, 2H), 6.54–6.50 (m, 1H), 6.37–6.31 (m, 1H), 6.25–620 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz) δ 161.50, 150,.35 144.70, 143.55, 139.00, 133.25, 127.45, 126.50, 122.30, 120.15, 117.75, 25.15. Anal. calcd for $C_{12}H_{11}NS$: C, 71.61; H, 5.51; N, 6.96; S, 15.93%. Found: C, 71.60; H, 5.49; N, 6.98; S, 15.94%.

4.2.4. 2-[*N*-(*E*)-(1-Methyl)-(3-carboxymethyl)-prop-2-enylideneamino]benzo[*b*]thiophene (3d). Thick oil, 20 mg 65% (^{1}H NMR (300 MHz) δ 7.79–7.71 (m, 1H), 7.55–7.48 (m, 2H), 7.35–7.29 (m, 1H), 7.12 (s,1H), 6.52–6.49 (m, 1H), 6.46–6.44 (m, 1H), 3.91 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz) δ 170.50, 167.15, 143.35, 138.30, 133.40, 132.25, 128.60, 126.45, 125.50, 122.35, 120.15, 115.50, 55.30, 24.85. Anal. calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; S, 12.36%. Found: C, 64.80; H, 5.07, N.5.38; S, 12.40%.

4.2.5. 2-[*N*-Benzylideneamino]benzo[*b*]thiophene[11] (5a). Yellow solid, mp 142–144°C (lit. 143–145°C), 14.8 mg 52%[^{1}H NMR (300 MHz) δ 8.52 (s, 1H), 7.99–7.90 (m, 2H), 7.82–7.72 (m, 2H), 7.57–7.45 (m, 3H), 7.40 (s, 1H) 7.38–7.32 (m, 2H); ^{13}C NMR (75 MHZ) δ 167.50, 158.25, 152.33, 139.00, 137.50, 136.25, 132.36, 131.75, 128.00, 127.10, 125.35, 124.15, 123.05, 121.50, 120.00. Anal. calcd for $C_{14}H_{13}NS$: C, 75.92; H, 4.67; N, 5.90; S, 13.51%. Found: C, 75.90; H, 4.62; N, 5.95; S, 13.53%.

4.2.6. 2-[*N*-(4-Chlorobenzylideneamino](benzo[*b*]thiophene[11] (5b). Yellow solid, mp 196–197°C (lit. 194–195°C), 24 mg 76% [^{1}H NMR (300 MHz) δ 8.45 (s, 1H), 7.88–7.84 (m, 2H), 7.76–7.73 (m, 2H), 7.50–7.46 (m, 2H), 7.40–7.36 (m, 3H); ^{13}C NMR (75 MHz) δ 165.40, 158.25, 155.15, 152.20, 138.44, 137.25, 133.00, 131.15, 127.30, 126.45, 125.60, 123.15, 122.05, 121.00, 120.50. Anal. calcd for $C_{15}H_{10}ClNS$: C, 66.29; H, 3.71; N, 5.15; S, 11.80%. Found: C, 66.25; H, 3.73; N, 5.13; S, 11.85%.

4.2.7. 2-[*N*-(3-Thienylideneamino)]benzo[*b*]thiophene (5c). Yellow solid, mp 123–126°C, 15.3 mg 53% [^{1}H NMR (300 MHz) δ 8.51 (s, 1H), 7.86–7.81 (m, 1H), 7.75–7.68 (m, 4H), 7.55–7.51 (m, 1H), 7.42–7.38 (m, 2H); ^{13}C NMR (75 MHZ) δ 153.05, 140.50, 139.20, 136.25, 131.20, 130.85, 127.00, 126.50, 125.38, 124.25, 123.62, 122.50, 120.00. Anal. calcd for $C_{13}H_9NS_2$: C, 64.17; H, 3.73; N, 5.76; S, 26.35. Found: C, 64.18; H, 3.70; N, 5.77; S, 26.38%.

4.2.8. *trans*-2-[*N*-(2-Thienylideneamino)]benzo[*b*]thiophene (5d). Bright yellow solid, mp 135–138°C, 17.5 mg 60% [^{1}H NMR (300 MHz) δ 8.6 (s, 1H), 7.73–7.67 (m, 2H), 7.5–7.58 (m, 2H), 7.38–7.31 (m, 3H), 7.18–7.14 (m, 1H); ^{13}C NMR (75 MHz) δ 153.30, 143.25, 133.50, 132.77, 131.00, 130.40, 128.55, 127.20, 125.85, 124.43, 123.02, 122.75, 120.50. Anal. calcd for $C_{13}H_9NS_2$: C, 64.17; H, 3.73; N, 5.76; S, 26.35. Found: C, 64.15; H, 3.70; N, 5.78; S, 26.38%.

4.2.9. *cis*-2-[*N*-(2-Thienylideneamino)]benzo[*b*]thiophene (5e). Yellow solid, mp 112–115°C, 9.6 mg 33% [^{1}H NMR (300 MHz) δ 8.56 (s, 1H), 8.31–8.27 (m, 1H) 7.61–7.56 (m, 1H) 7.5–7.38 (m, 2H), 7.22–7.10 (m, 3H), 6.80–6.66 (m, 1H); ^{13}C NMR (75 MHz) δ 152.50, 148.75, 143.20, 139.40, 136.00, 131.15, 130.58, 127.35, 126.44, 125.00, 124.35, 123.55, 122.44, 120.00; Anal. calcd for $C_{13}H_9NS_2$: C, 64.17; H, 3.73; N, 5.76; S, 26.35. Found: C, 64.20; H, 3.70; N, 5.78; S, 26.40%.

4.3. Photochemical reactions: general procedure

A chloroform solution of the isolated imines was irradiated for 6 h with a low power lamp: generally, after this time, by TLC the imine's absence was clear: the reaction products were purified, when it was necessary, by preparative chromatography to give the cyclization products **4a–d**. For compounds **5a–e** a higher power lamp was needed (125 W) to obtain the cyclization products **6c** and **6e**, characterized by ^{1}H-, ^{13}C NMR. The data are as follows: compounds **4a** and **4c** were reported,[12] so we give only spectroscopic data

4.3.1. 4-Methylbenzo[*b*]thieno[2,3-*b*]pyridine (4a). Dark yellow solid $T_{\text{dec.}}$ 143°C, 12 mg [^{1}H NMR (300 MHz) δ 8.51–8.48 (m, 1H), 8.32–8.28 (m, 1H), 7.96–7.90 (m, 1H), 7.56–7.50 (m, 2H), 7.20–7.17 (m, 1H), 2.9 (s, 3H); ^{13}C NMR (75 MHz) δ 160.13, 147.80, 145.18, 136.25, 134.80, 133.00, 128.40, 126.05, 124.88, 123.00, 122.55, 21.15; 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%.

4.3.2. 4-Phenylbenzo[*b*]thieno[2,3-*b*]pyridine (4b). Thick oil, 13.3 mg [^{1}H NMR (300 MHz) δ 8.44–8.42 (m, 1H), 8.16–8.12 (m, 2H), 7.92–7.89 (m, 1H), 7.80–7.77 (m, 1H), 7.74–7.70 (m, 1H) 7.54–7.48 (m, 5H); ^{13}C NMR (75 MHz) δ 161.18, 153.55, 148.00, 147.33, 144.50, 140.22, 138.74, 134.88, 133.80, 129.60, 128.55, 127.40, 126.25, 125.44, 123.20, 122.50, 117.00; 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%.

4.3.3. 2-Methylbenzo[*b*]thieno[2,3-*b*]pyridine (4c). Brown solid, mp 88–90°C, 11 mg [^{1}H NMR (300 MHz) δ 8.6–8.57 (m, 1H), 8.10–8.06 (m, 1H), 7.88–7.84 (m, 1H), 7.50–7.44 (m, 2H), 7.26–7.23 (m, 1H), 2.72 (s, 3H); ^{13}C NMR (75 MHz) δ 162.00, 157.85, 139.50, 137.44, 136.25, 129.50, 127.34, 125.00, 123.20, 121.10, 119.50, 25.40; 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%.

4.3.4. Methyl 2-methylbenzo[*b*]thieno[2,3-*b*]pyridine-4-carboxylate (4d). Pale yellow solid, mp 75–77°C, 18.4 mg [^{1}H NMR (300 MHz) δ 8.4–8.32 (m,1H), 7.92–7.85 (m, 1H), 7.57–7.42 (m, 3H), 4.12 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (75 MHz) δ 170.12, 157.50, 140.40, 136.70, 132.33, 131.55, 128.90, 126.33, 125.50, 123.20, 122.85, 118.50, 53.15, 26.35; 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%.

4.3.5. Thieno[3,2-*c*]pyridino[2,3-*d*]benzo[*b*]thiophene (6c). Thick oil, 6 mg [^{1}H NMR (300 MHz) δ 9.88 (s, 1H), 8.9 (s, 1H), 7.9–7.87 (m, 1H), 7.84–7.79 (m, 1H), 7.65–7.60 (m, 1H), 7.50–7.44 (m, 2H); ^{13}C NMR (75 MHz) δ 168.50, 149.75, 141.60, 138.00, 134.44, 131.37, 128.10, 127.05, 125.55, 123.50, 122.24, 121.65, 120.33; MS *m/z* 241 (M^+, 100). Anal. calcd for $C_{13}H_7NS_2$: C, 64.70; H, 2.92; N, 5.80, S, 26.57%. Found: C, 64.65; H, 2.95; N, 5.83; S, 26.59%.

4.3.6. Thieno[2,3-*c*]pyridino[2,3-*d*]benzo[*b*]thiophene (6e). Thick oil, 3 mg [^{1}H NMR (300 MHz) δ 8.83 (s, 1H), 8.2–8.15 (m, 1H), 7.9–7.85 (m, 1H), 7.6–7.35 (m, 4H); ^{13}C NMR (75 MHz) δ 167.00, 147.32, 143.50, 142.20, 138.35, 137.44, 134.78, 133.55, 132.00, 130.25, 127.30, 125.60, 122.88; MS *m/z* 241 (M^+, 100). Anal. calcd for $C_{13}H_7NS_2$: C, 64.70; H, 2.92; N, 5.80, S, 26.57%. Found: C, 64.68; H, 2.90; N, 5.85; S, 26.57%.

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