From *N*-Substituted Thioamides to Symmetrical and Unsymmetrical 3,4,5-Trisubstituted 4*H*-1,2,4-Triazoles: Synthesis and Characterisation of New Chelating Ligands

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An improved protocol for the synthesis of *N*-substituted pyridine-2-thiocarboxamides under the conditions of the Willgerodt–Kindler reaction, employing a catalytic amount of sodium sulfide nonahydrate, has been developed. Following this protocol, eight thioamides carrying aromatic or aliphatic *N*-substituents have been prepared in good to excellent yields. Condensation of these thioamides or their *S*-alkylated congeners with hydrazides in refluxing 1-butanol has afforded eight unfused 3,4,5-trisubstituted 4*H*-1,2,4-triazoles in good yields, including four examples of the otherwise not easily obtainable 4-alkyl-3,5-diaryl-4*H*-1,2,4-triazoles.

Introduction

Over the last three decades coordination chemists have developed an ever-increasing interest in 1,2,4-triazole derivatives due to the versatile coordination chemistry of these ligands[1−3] and the intriguing magnetic properties of the resulting transition metal complexes.[4−7] In the course of our ongoing investigation of the coordination chemistry of 1,2,4-triazole-based ligands carrying 2-pyridyl groups in the 3- and/or 5-position,[2,8,9] a straightforward and general synthetic strategy was needed that would make unfused 3,4,5-trisubstituted 4*H*-1,2,4-triazoles easily accessible and, at the same time, would allow for the variation of all three substituents. A survey of the literature[10] revealed that most of the known compounds of this type have been prepared by methods involving, as the key step, the cyclisation of N^3-substituted N^1-acyl amidrazones.[11−15] Since such compounds are accessible by a variety of methods (Scheme 1), the synthesis of 3,4,5-trisubstituted 4*H*-1,2,4-triazoles via these intermediates can be considered the most general and versatile approach. Of all of the possible routes to N^3-substituted N^1-acyl amidrazones, the condensation of *N*-substituted thioamides with hydrazides was the most appealing for the following reasons: (a) thioamides are stable and relatively nonhazardous compounds which can be synthesised in a variety of ways,[16−20] and whose potential and usefulness for the synthesis of heterocyclic systems is well established;[21,22] (b) hydrazides are easily accessible from the corresponding esters;[23] (c) there are no obvious restrictions with regard to the substitution pattern of the desired 1,2,4-triazoles, and all three substituents can potentially be varied over a wide range of choices; (d) the desired 1,2,4-triazole can be prepared from either of two possible combinations of an *N*-substituted thioamide and a hydrazide, i.e. from either the R^3/R^4-thioamide and the R^5-hydrazide, or the R^5/R^4-thioamide and the R^3-hydrazide. Santus[24] and subsequently Reiter and Berg[25] have already demonstrated the convenience and versatility of this method. Of particular interest to us were the hitherto unknown 4-alkyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles with their electron-donating alkyl groups.[2,10,26] Since the alkylation of *N*-unsubstituted 1,2,4-triazoles usually occurs at one of the nitrogen atoms of the N_2 unit,[27] the alkylation of 3,5-di(2-pyridyl)-1*H*-1,2,4-triazole[28] is not a viable route for accessing 4-alkyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles.[29−31] It was anticipated that the thioamide−hydrazide condensation could provide a solution to these synthetic difficulties. In this paper we report the synthesis and characterisation of some *N*-substituted pyridine-2-thiocarboxamides and unfused 3,4,5-trisubstituted 4*H*-1,2,4-triazoles.

Results and Discussion

Preparation of the Hydrazides

The known hydrazides used in this work, namely benzohydrazide (**1**) and pyridine-2-carbohydrazide (**2**), were most conveniently prepared by the reaction of the corresponding esters with hydrazine monohydrate.[23] Thus, hydrazide **1** was obtained from methyl benzoate and a slight excess of hydrazine monohydrate in 79% yield after recrystallisation from benzene/ethanol (5:1). This solvent mixture was used since the solubility of hydrazide **1** in ethanol was too high, while it was poorly soluble in benzene alone. The reaction

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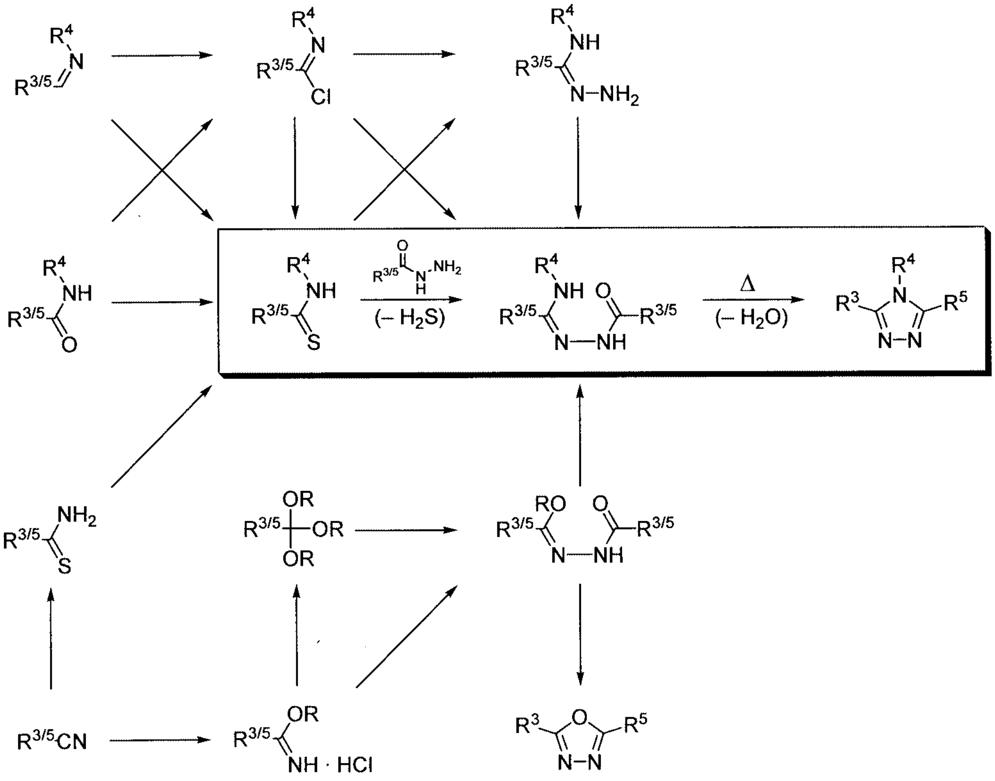
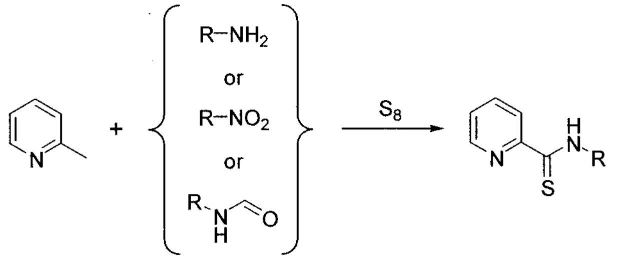


Scheme 1. Possible routes to N^3-substituted N^1-acyl amidrazones as intermediates in the synthesis of unfused 3,4,5-trisubstituted 4*H*-1,2,4-triazoles; the box highlights the route described in this work

of ethyl pyridine-2-carboxylate with a twofold excess of hydrazine monohydrate similarly gave, after evaporation of the reaction mixture and recrystallisation of the residue from ethanol, hydrazide **2** in 83% yield.

Preparation of the *N*-Substituted Thioamides

A convenient method for the preparation of *N*-substituted thioamides is the Willgerodt−Kindler reaction, which usually employs aromatic ketones as starting materials.[32,33] However, it has been shown that this reaction can also be applied to 2-methylpyridine.[34,35] Thus, *N*-substituted pyridine-2-thiocarboxamides have been prepared by reaction of 2-methylpyridine with primary amines,[34,35] nitro compounds,[34] or *N*-substituted formamides[16,36] as amine sources in the presence of sulfur at elevated temperatures (Scheme 2). Under these standard conditions the yields are usually only poor to moderate (Table 1). In the search for an improved protocol, the use of a catalytic amount of sodium sulfide nonahydrate, as mentioned in a Soviet patent,[37] appeared promising and was therefore further investigated.



Scheme 2. Possible amine sources for the synthesis of *N*-substituted pyridine-2-thiocarboxamides under the conditions of the Willgerodt−Kindler reaction

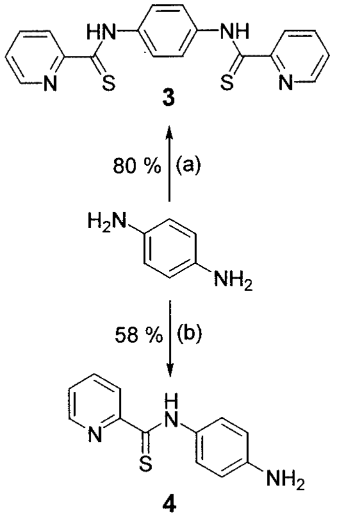
The reaction of a 6:1 molar ratio of sulfur and 1,4-phenylenediamine in the presence of 5 mol % of sodium sulfide nonahydrate and a large excess of refluxing 2-methylpyridine afforded *N*,*N*′-(1,4-phenylene)bis(pyridine-2-thiocarboxamide (**3**)[34,37–39] after 72 h in 80% yield (Scheme 3). The yield was much higher than those previously reported (Table 1). Interestingly, using similar reaction conditions but with only two equivalents rather than a large excess of 2-methylpyridine, Martin[40] had failed to obtain thioamide **3**, instead isolating 2,6-di(2-pyridyl)benzo[1,2-*d*;4,5-*d*′]bis(thiazole), formed by the oxidative cyclisation of thioamide **3**. Reducing the amount of sulfur and 2-methylpyridine in the reaction mixture relative to 1,4-phenylenediamine to 2.4:2:1 afforded a different product, which was identified as the hitherto unknown *N*-(4-aminophenyl)pyridine-2-thiocarboxamide (**4**), with a yield of 58% (Scheme 3).

The conditions successfully employed for the synthesis of thioamide **3** were then adapted for the preparation of *N*-(4-pyridyl)pyridine-2-thiocarboxamide (**5**).[41] This compound had previously only been obtained in an acceptable yield of 57% from the reaction of 2-methylpyridine, sulfur and 4-aminopyridine in a pressure vessel at 200 °C, while carrying

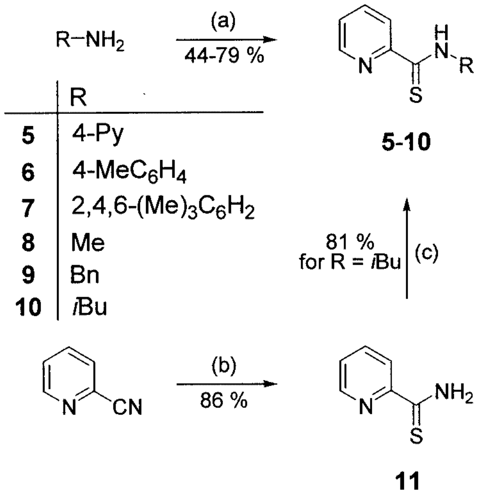
Table 1. Comparison of literature yields with the yields obtained in this work for *N*-substituted pyridine-2-thiocarboxamides synthesised under the conditions of the Willgerodt−Kindler reaction

N-Substituent	Literature yield	This work[a]
1,4-phenylene (**3**)	19%[b] (from 4-nitroaniline)[34]	
	21%[b] (from 4-nitroaniline)[38]	
	40%[b] (from 4-nitroaniline)[39]	
	47%[a] (from 1,4-phenylenediamine)[37]	80%
4-pyridyl (**5**)	14%[b] (from 4-aminopyridine)[41]	
	57%[c] (from 4-aminopyridine)[41]	77%
4-methylphenyl (**6**)	30%[b] (from 4-nitrotoluene)[34]	
	55%[b] (from 4-methylaniline)[42]	
	14%[b] (from 4-methylaniline)[43]	79%
2,4,6-trimethylphenyl (**7**)	65%[b] (from 2,4,6-trimethylaniline)[44]	74%
methyl (**8**)	17%[b] (from methylamine hydrochloride)[45]	
	50%[b] (from *N*-methylformamide)[36]	
	34%[d] (from *N*-methylformamide)[46]	69%

[a] Reaction carried out in the presence of a catalytic amount of sodium sulfide nonahydrate with the appropriate amine. [b] Reaction carried out under standard conditions. [c] Reaction carried out in a pressure vessel. [d] Reaction carried out in the presence of a catalytic amount of iodine.



Scheme 3. Synthesis of thioamides **3** and **4**; reagents and conditions: (a) 6 equiv. S_8, 5 mol % $Na_2S{\cdot}9H_2O$, large excess 2-methylpyridine, reflux; (b) 2.4 equiv. S_8, 5 mol % $Na_2S{\cdot}9H_2O$, 2 equiv. 2-methylpyridine, 150 °C



Scheme 4. Synthesis of thioamides **5**−**11**; reagents and conditions: (a) S_8, cat. $Na_2S{\cdot}9H_2O$, 2-methylpyridine, reflux; (b) NH_3, H_2S, EtOH, room temperature; (c) isobutylamine, reflux

out the same reaction at ambient pressure at reflux reportedly only yielded 14% of the desired product.[41] In contrast, we obtained a 77% yield of thioamide **5** at ambient pressure with 2 mol % of sodium sulfide nonahydrate as a catalyst. To test the general applicability and efficiency of these modified reaction conditions (i.e. sulfur/amine ratio of 3:1, large excess of 2-methylpyridine, 2 mol % sodium sulfide nonahydrate, reflux at ambient pressure), the synthesis of another two *N*-arylpyridine-2-thiocarboxamides, namely *N*-(4-methylphenyl)pyridine-2-thiocarboxamide (**6**)[34,42,43] and *N*-(2,4,6-trimethylphenyl)pyridine-2-thiocarboxamide (**7**),[44] was carried out (Scheme 4). In these two cases the modified reaction conditions also proved to be superior to earlier protocols, the yields of the recrystallised products being 79 and 74%, respectively (Table 1).

While in principle not only aromatic but also aliphatic amines can be used in the Willgerodt−Kindler reaction, in practice, this is simple only for high-boiling amines since the lower alkylamines, especially, are very volatile substances. Thus, reactions involving the lower alkylamines can only be carried out in pressure vessels. However, Schäfer and Wegler[45] have reported that not only free amines but also their hydrochloride salts can be reacted under the conditions of the Willgerodt−Kindler reaction. The possibility of preparing *N*-methylpyridine-2-thiocarboxamide (**8**)[36,45−47] from methylamine hydrochloride was therefore examined next. Initially, the original protocol,[45] that is without the addition of sodium sulfide nonahydrate, was followed exactly, albeit on only one tenth of the scale. Thus, the reaction of sulfur, methylamine hydrochloride and 2-

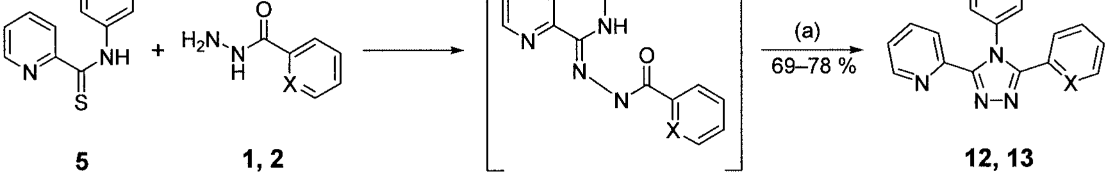
methylpyridine in a 3:1:1 molar ratio at 170 °C gave, after workup, a 19% yield of pure thioamide **8**, which is in good agreement with the literature.[45] Subsequently, the reaction was carried out with the modified reaction conditions, i.e. using an excess of 2-methylpyridine in the presence of 2 mol % of sodium sulfide nonahydrate. After workup and recrystallisation of the crude product, thioamide **8** was obtained in a much better yield of 69% (Scheme 4). In the case of *N*-benzylpyridine-2-thiocarboxamide (**9**),[47,48] which to the best of our knowledge has never been prepared before under the conditions of the Willgerodt−Kindler reaction, the yield was only moderate (44%). For the preparation of *N*-isobutylpyridine-2-thiocarboxamide (**10**),[47,48] a different approach was taken. First, pyridine-2-thiocarboxamide **(11)** was synthesised in 86% yield by the hydrosulfanylation of pyridine-2-carbonitrile.[49] Thioamide **11** was then reacted with an excess of isobutylamine at reflux to give thioamide **10** in 81% yield as a golden liquid (Scheme 4). Interestingly, Kluiber[47] has also found thioamide **10** to be a liquid at room temperature, while Rukhadze[48] has characterised it as a low-melting solid.

Preparation of the 1,2,4-Triazoles

After the successful condensation of thioamide **3** with hydrazide **1** in 1-butanol to give 3,3′-diphenyl-5,5′-di(2-pyridyl)-4,4′-(1,4-phenylene)bis(4*H*-1,2,4-triazole) in 48% yield,[8] the use of this reaction in the synthesis of other unfused 3,4,5-trisubstituted 4*H*-1,2,4-triazoles was examined. Thus, when thioamide **5** was allowed to react with hydrazide **1** in ethanol at room temperature,[24] evolution of hydrogen sulfide was noticeable, and the appearance of the yellow-orange suspension changed, thus indicating the formation of a new solid. Analysis of an impure sample of this initial product by ^{1}H and ^{13}C NMR spectroscopy revealed that it was not the desired 1,2,4-triazole but the intermediate N^3-substituted N^1-acyl amidrazone (Scheme 5). This is in agreement with the findings by Santus.[24] On heating the initially obtained suspension, a clear orange solution was obtained which was refluxed for several hours. Monitoring of the reaction by TLC showed the formation of a second product, which was subsequently identified as pyppt (**12**). However, when ethanol was used as the solvent, the reaction could not be driven to completion even with prolonged heating, use of a large excess of hydrazide **1** or removal of the hydrogen sulfide formed in the reaction by bubbling a steady stream of nitrogen through the reaction mixture. As the separation of the relatively small amount of the desired product from the much larger amounts of unchanged starting materials and intermediates proved to be difficult, pyridine[24] was tried next as the reaction solvent in the hope of achieving higher conversion rates due to higher reaction temperatures. In this solvent, however, the reaction of thioamide **5** with hydrazide **1** was much more sluggish, and practically no hydrogen sulfide evolved at room temperature, presumably due to the lower solubility of hydrazide **1** in this solvent. Here too, the reaction did not go to completion, although conversion seemed to be higher than in ethanol. The best results were obtained when thioamide **5** was treated with a slight excess of hydrazide **1** in refluxing 1-butanol,[25] the solvent which has also been used in the synthesis of 3,3′-diphenyl-5,5′-di(2-pyridyl)-4,4′-(1,4-phenylene)bis(4*H*-1,2,4-triazole).[8] Under these conditions, triazole **12** crystallised in analytically pure form and in 78% yield upon cooling. The reaction of thioamide **5** with hydrazide **2** under identical conditions gave pydpt (**13**) in 69% yield (Scheme 5).

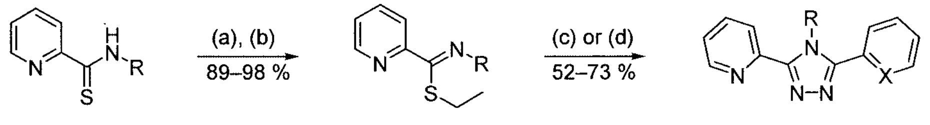
The conversion of thioamide **6** into the new compound pmppt (**15**) and its known but previously uncharacterised congener pmdpt (**16**)[50−53] was explored next. When thioamide **6** reacted with hydrazide **1** under the conditions described above for the preparation of triazoles **12** and **13**, only a small amount of triazole **15** was formed, and mainly unchanged starting materials were recovered. Subsequently, acetic acid and 1,2-ethandiol were tested as alternative solvents for this reaction but without success. Toluene and xylene were also employed under both normal reflux conditions and in the presence of a catalytic amount of toluene-4-sulfonic acid monohydrate in a Dean−Stark apparatus. However, significant improvements were not achieved under any of these conditions. In agreement with the observation that almost no hydrogen sulfide was produced, it seemed plausible that it was not the dehydrative cyclisation of the intermediate N^3-substituted N^1-acyl amidrazone that was hampered, but rather the formation of the latter by the reaction of thioamide **6** with hydrazide **1**.

A common way to increase the susceptibility of thioamides to nucleophilic attack is *S*-alkylation.[22] Most thioamides can be readily *S*-alkylated by simply heating them with an excess of the alkylating agent. In the present case, however, the use of these conditions was expected to lead to unwanted overalkylation and quaternisation of the pyridine ring. Deprotonation of the thioamide prior to alkylation



	X
1	CH
2	N
12	CH
13	N

Scheme 5. Synthesis of triazoles **12** and **13**; reagents and conditions: (a) BuOH, reflux

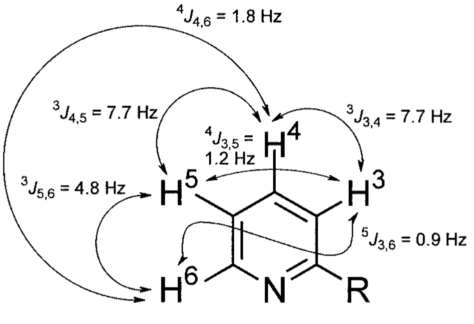


6, 8, 10 **14, 17, 20** **15, 16, 18, 19, 21, 22**

	6, 14	**8,17**	**10, 20**	**15**	**16**	**18**	**19**	**21**	**22**
R	4-MeC$_6$H$_4$	Me	*i*Bu	4-MeC$_6$H$_4$	4-MeC$_6$H$_4$	Me	Me	*i*Bu	*i*Bu
X				CH	N	CH	N	CH	N

Scheme 6. Synthesis of triazoles **15**, **16**, **18**, **19**, **21** and **22**; reagents and conditions: (a) NaOEt, EtOH, room temperature; (b) EtBr, EtOH, 50 °C; (c) hydrazide **1**, BuOH, reflux; (d) hydrazide **2**, BuOH, reflux

and the use of only a slight excess of the alkylating agent therefore seemed advisable. A search of the literature revealed that *S*-alkylation of pyridine-derived thioamides has been reported only once; the reaction conditions involve the use of iodomethane and potassium *tert*-butoxide in tetrahydrofuran.[54] With the use of slightly different conditions, *S*-alkylation of thioamide **6** was achieved by its reaction with sodium ethoxide in ethanol at room temperature, followed by the addition of bromoethane and refluxing of the reaction mixture. This afforded impure ethyl *N*-(4-methylphenyl)pyridine-2-carboximidothioate (**14**) in almost quantitative yield as an orange oil. This material, as well as the other *S*-alkylated thioamides that were subsequently prepared, have a very unpleasant odour reminiscent of rotten garlic. Condensation of this crude material with hydrazides **1** and **2** readily occurred in 1-butanol at reflux and afforded triazoles **15** and **16** in 65 and 71% yield, respectively. Using this *S*-alkylation−condensation sequence the compounds meppt (**18**) and medpt (**19**), as well as ibppt (**21**) and ibdpt (**22**), all hitherto unknown and carrying alkyl groups on N^4, were similarly prepared in moderate to good yields via ethyl *N*-methylpyridine-2-carboximidothioate (**17**) and ethyl *N*-isobutylpyridine-2-carboximidothioate (**20**), respectively (Scheme 6). Thioamides **8** and **10** could not be converted into triazoles **18**, **19**, **21** and **22** directly without prior *S*-alkylation. The latter compounds exhibited very good solubility in all organic solvents, which resulted in losses during their purification by recrystallisation. In the case of triazoles **21** and **22** recrystallisation was particularly unsatisfactory, and purification was instead best achieved by column chromatography.



3-Py*H*: ddd, $^3J_{3,4}$ = 7.7 Hz, $^4J_{3,5}$ = 1.2 Hz, $^5J_{3,6}$ = 0.9 Hz
4-Py*H*: dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7 Hz, $^4J_{4,6}$ = 1.8 Hz
5-Py*H*: ddd, $^3J_{4,5}$ = 7.7 Hz, $^3J_{5,6}$ = 4.8 Hz, $^4J_{3,5}$ = 1.2 Hz
6-Py*H*: ddd, $^3J_{5,6}$ = 4.8 Hz, $^4J_{4,6}$ = 1.8 Hz, $^5J_{3,6}$ = 0.9 Hz

Figure 1. Coupling constants observed for the 2-pyridyl groups in the ^{1}H NMR spectra (CDCl$_3$) of compounds **2**−**22**

NMR Spectroscopy

In 2-substituted pyridines each of the four protons couples with the other three. Consequently, four doublets of doublets of doublets (ddd) should be observed in the ^{1}H NMR spectra of these systems. In the present work the spectra of all compounds incorporating such a moiety show the expected four resonances, three of which were indeed doublets of doublets of doublets, while the signal for 4-Py*H* appears as a doublet of triplets (dt) due to the magnitude of the coupling constants $^3J_{3,4}$ and $^3J_{4,5}$ (Figure 1).

The chemical shifts for the individual pyridine protons of the *N*-substituted thioamides **3**−**10** differ only very slightly from one another and were practically unaffected by the nature of the *N*-substituent. In the case of the *N*-benzyl-substituted thioamide **9**, the signal for 4-Py*H* coincides with the multiplet observed for the five protons of the phenyl ring; this prevented the exact determination of the chemical shift of this proton. The pyridine resonances for the parent thioamide **11** are all observed within the narrow ranges given in Figure 2. In contrast, as might be expected, the chemical shifts for the protons of the thioamido groups in compounds **3**−**11** vary over a wide range. No concentration dependence of these signals was observed. For the *N*-alkyl-substituted thioamides **8**−**10**, the resonance for the CSN*H* proton appears at δ = 10.21−10.38 ppm, while for the *N*-aryl-substituted thioamides **3**−**6** this signal is observed at δ = 11.91−12.23 ppm. This downfield shift on changing the substituent from an electron-donating alkyl group to an electron-withdrawing aryl group was taken to be a direct consequence of the electronic effect of the respective substituent. Thioamide **7**, with its 2,4,6-trimethylphenyl group, shows an intermediate chemical shift of δ = 11.29 ppm for its CSN*H* proton, presumably due to some cancellation of the electron-withdrawing effect of the phenyl group by the three electron-donating methyl groups. The presence of two thioamido protons in the parent thioamide **11** gives rise to two CSN*H* resonances, which are observed as broad singlets at δ = 7.90 and 9.54 ppm. The former signal is assigned to the proton *trans* to the pyridine nitrogen atom, while the latter is assigned to the *cis* proton, its relative downfield shift is a result of a hydrogen bond interaction with the pyridine nitrogen atom in solution.

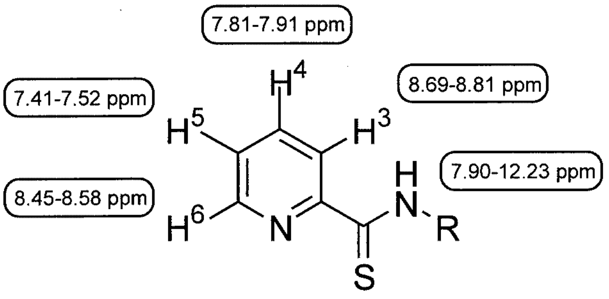


Figure 2. Chemical shifts observed in the ^{1}H NMR spectra ($CDCl_3$) of thioamides **3−11**

Figure 3 shows the chemical shift ranges for the pyridine and thioamido carbon atoms observed in the ^{13}C NMR spectra of thioamides **3−11**. Apart from the chemical shifts for the *C*SNH carbon atoms, which vary over a range of almost 10 ppm, the resonances for the 6-Py*C* atoms show the largest variation, ranging over about 2 ppm, while the signals for the remaining carbon atoms are influenced by the nature of the *N*-substituent to a lesser extent.

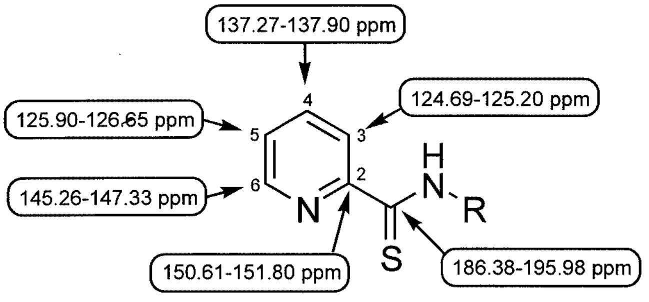


Figure 3. Chemical shifts observed in the ^{13}C NMR spectra ($CDCl_3$) of thioamides **3−11**

In comparison with the chemical shifts observed for the pyridine protons in the ^{1}H NMR spectra of thioamides **3−11**, the signals of the corresponding protons in the spectra of triazoles **12**, **13**, **15**, **16**, **18**, **19**, **21** and **22** (Figure 4) are shifted upfield. This shift is rather small and is practically negligible for the signals for 4-, 5- and 6-Py*H*, whereas it is quite significant for the 3-Py*H* resonance. As a result of this, the positions of the 3- and 6-Py*H* signals relative to each other in the spectra of the triazoles are inverted with respect to their positions in the spectra of the thioamides.

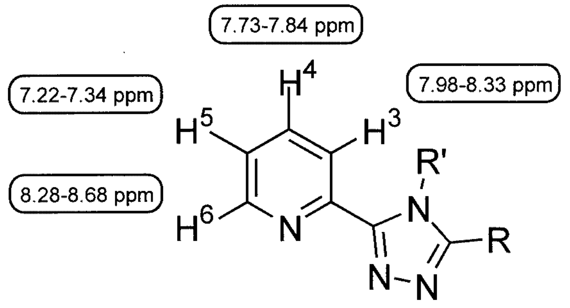


Figure 4. Chemical shifts observed in the ^{1}H NMR spectra ($CDCl_3$) of triazoles **12**, **13**, **15**, **16**, **18**, **19**, **21** and **22**

In the ^{13}C NMR spectra of the triazoles **12**, **13**, **15**, **16**, **18**, **19**, **21** and **22** (Figure 5), the resonances for 2-, 3-, 4- and 5-Py*C* are shifted slightly upfield relative to the corresponding signals in the spectra of thioamides **3−11**; the signal for 3-Py*C* displays the largest shift. In contrast, the signal for 6-Py*C* in the triazole spectra is shifted downfield quite significantly relative to that in the thioamide spectra. The chemical shift of the signal for the triazole carbon atom that carries the 2-pyridyl group is in the same range for both the 4-substituted 3-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazoles **12**, **15**, **18** and **21** and the 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles **13**, **16**, **19** and **22**. There is, however, a noticeable tendency for this signal to appear at the slightly higher values of δ = 153.99−154.63 ppm for the symmetrical triazoles, while in the spectra of their unsymmetrical congeners it is observed at δ = 153.15−154.04 ppm. Within the latter group of compounds, in all cases the triazole carbon atom adjacent to the phenyl group resonates downfield (δ = 155.43−157.25 ppm) from the triazole carbon atom that carries the 2-pyridyl group. In general terms it was found that in both the ^{1}H and ^{13}C NMR spectra, the chemical shifts of the pyridine system are not affected by the nature of the N^4-substituent of the triazole. This is also true for the triazole carbon atoms whose chemical shifts are influenced by the substituent directly attached to them only.

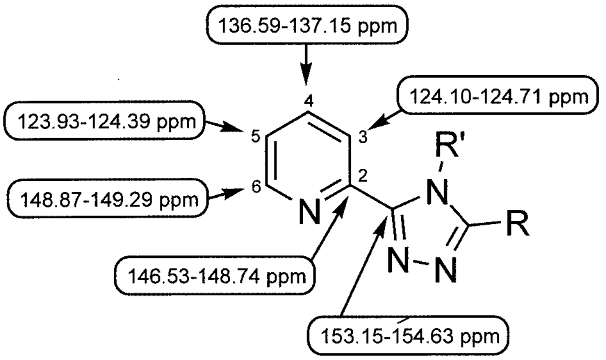


Figure 5. Chemical shifts observed in the ^{13}C NMR spectra ($CDCl_3$) of triazoles **12**, **13**, **15**, **16**, **18**, **19**, **21** and **22**

X-ray Diffraction

Single crystals of ibdpt (**22**) were grown by slow evaporation of a solution of this compound in ethyl acetate/cyclohexane (2:1). A specimen was studied by X-ray diffraction, which unambiguously confirmed the structural assignment made on the basis of the spectroscopic data. The molecular structure of ibdpt (**22**) is shown in Figure 6. As in the structures of all other 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles,[2] the pyridine−triazole−pyridine moiety is not planar, but the N(1)- and N(4)-pyridine rings are tilted with respect to the triazole mean plane by 39.9(1) and 26.5(1)°, respectively. Here too, the two pyridine rings adopt the usual conformation; the pyridine nitrogen atoms point away from the N_2 unit of the central triazole ring and are on opposite sides of the triazole mean plane.

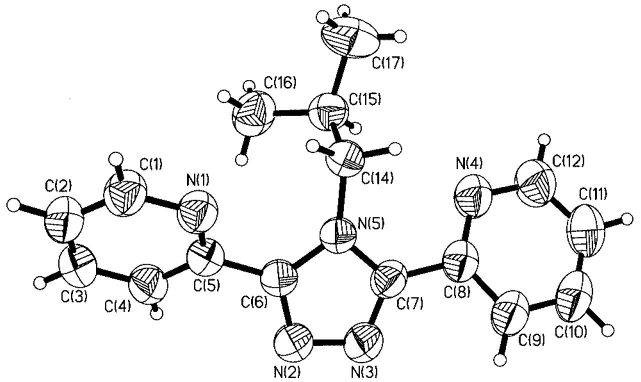


Figure 6. View of the molecular structure of triazole **22** (50% thermal ellipsoids)

Conclusion

The use of a catalytic amount of sodium sulfide nonahydrate in combination with an excess of 2-methylpyridine provides a convenient, efficient and widely applicable protocol for the preparation of *N*-substituted pyridine-2-thiocarboxamides by means of the Willgerodt−Kindler reaction. Since the excess 2-methylpyridine can be recovered during workup, this process is also economical. Low-boiling volatile amines can be used in this reaction as their hydrochloride salts, which removes the need to use a pressure vessel for the preparation of the respective thioamides. This protocol is therefore an efficient way to conveniently prepare these lower alkyl-substituted compounds in particular. With this method it has been possible to increase the yields of the respective thioamides significantly relative to previously reported protocols. The condensation of *N*-substituted pyridine-2-thiocarboxamides, or in some cases preferably the corresponding ethyl carboximidothioates, i.e. their *S*-ethylated congeners, with hydrazides has afforded a range of new unfused 3,4,5-trisubstituted 4*H*-1,2,4-triazoles in good yields. Along with the findings by other authors, these results demonstrate that the thioamide−hydrazide condensation is a very versatile and efficient method for the preparation of 3,4,5-trisubstituted 4*H*-1,2,4-triazoles in particular, but also for other substituted 1,2,4-triazoles that carry any type of substituent. It seems that the only limitation of this method is the availability of suitably substituted precursors. The investigation of the coordination chemistry of these new chelating ligands will be reported in due course.[9,10,26]

Experimental Section

General Remarks: All reagents were commercially available and were used as received. Unless stated otherwise, all solvents used were laboratory reagent grade. Dry ethanol required for some reactions was obtained by distillation from magnesium turnings. Column chromatography was carried out under gravity on Merck silica gel 60 (200−400 mesh, 40−63 μm). For thin-layer chromatographic analyses Macherey−Nagel Alugram SIL G/UV_{254} aluminium sheets were used. Visualisation was achieved with ultraviolet light (254 nm). Melting points were determined with a Gallenkamp melting point apparatus in open glass capillaries and are uncorrected. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded with a Varian INOVA-500 spectrometer at 25 °C. Chemical shifts are given relative to tetramethylsilane with the residual solvent signals as secondary reference (chloroform: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; dimethyl sulfoxide: $\delta_H = 2.50$ ppm, $\delta_C = 39.52$ ppm).[55] Peak assignments were made on the basis of chemical shifts, integration patterns and coupling constants, as well as two-dimensional correlation experiments where necessary. Infrared spectra were recorded with a Perkin−Elmer Spectrum BX FT-IR spectrophotometer over the range 4000−400 cm^{-1}. All solid samples were measured as potassium bromide pellets, while liquid samples were measured as films between sodium chloride plates. Mass spectra were run on a Shimadzu LCMS-QP8000α spectrometer with acetonitrile as the solvent. X-ray data were collected with a STOE IPDS diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SHELXS-97[56,57] and refined against F^2 by full-matrix least-squares techniques with SHELXL-97.[58]

Benzohydrazide (1): A heterogeneous mixture of methyl benzoate (34.1 g, 0.25 mol) and hydrazine monohydrate (15.0 g, 0.30 mol) was refluxed for 18 h during which time a clear colourless solution was obtained. After cooling, all volatiles were evaporated under reduced pressure, and the resulting colourless crystalline solid was dried in vacuo. Recrystallisation from benzene/ethanol (5:1) gave 27.1 g (79%) of analytically pure benzohydrazide (**1**) as colourless needles. M.p. 111−113 °C. $C_7H_8N_2O$ (136.15): calcd. C 61.75, H 5.92, N 20.57; found C 61.66, H 6.12, N 20.38. ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 4.56$ (br. s, 2 H, CONHN*H*$_2$), 7.42−7.46 (m, 2 H, 3- and 5-Ph*H*), 7.48−7.52 (m, 1 H, 4-Ph*H*), 7.82−7.84 (m, 2 H, 2- and 6-Ph*H*), 9.78 (br. s, 1 H, CON*H*NH$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): $\delta = 126.96$ (2- and 6-Ph*C*), 128.31 (3- and 5-Ph*C*), 131.06 (4-Ph*C*), 133.33 (1-Ph*C*), 165.94 (*C*ONHNH$_2$) ppm. IR (KBr): $\tilde{\nu} = 3299$, 3206, 3019, 2874, 1661, 1616, 1566, 1487, 1446, 1349, 1289, 1121, 1004, 992, 919, 884, 802, 685, 674, 517, 414 cm^{-1}. APCI-MS (pos., MeCN): $m/z = 137$ [M + H]$^+$. TLC (SiO$_2$, EtOAc): $R_f = 0.23$.

Pyridine-2-carbohydrazide (2): Hydrazine monohydrate (10.0 g, 0.20 mol) was added dropwise to ethyl pyridine-2-carboxylate (15.1 g, 0.10 mol). A moderately exothermic reaction took place. The resulting clear solution was refluxed for 18 h. After cooling, all volatiles were evaporated under reduced pressure, and the colourless crystalline solid thus obtained was dried in vacuo. Recrystallisation from ethanol gave 11.4 g (83%) of analytically pure pyridine-2-carbohydrazide (**2**) as colourless needles. M.p. 100−102 °C. $C_6H_7N_3O$ (137.14): calcd. C 52.55, H 5.14, N 30.64; found C 52.49, H 5.18, N 30.71. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.53 (br. s, 2 H, CONHN*H*$_2$), 7.56 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.94−8.00 (m, 2 H, 3- and 4-Py*H*), 8.60 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*), 9.87 (br. s, 1 H, CON*H*NH$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): δ = 121.73 (3-Py*C*), 126.24 (5-Py*C*), 137.64 (4-Py*C*), 148.50 (6-Py*C*), 149.85 (2-Py*C*), 162.65 (*C*ONHNH$_2$) ppm. IR (KBr): ṽ = 3308, 3212, 1675, 1651, 1594, 1570, 1522, 1473, 1434, 1338, 1303, 1247, 1149, 1125, 1085, 1046, 999, 975, 819, 751, 703, 643, 621, 485, 446, 410 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 138 [M + H]$^+$. TLC (SiO$_2$, EtOAc): R_f = 0.19.

***N*,*N*′-(1,4-Phenylene)bis(pyridine-2-thiocarboxamide) (3):** A mixture of 1,4-phenylenediamine (2.70 g, 25.0 mmol), sulfur (4.81 g, 0.15 mol) and sodium sulfide nonahydrate (0.30 g, 5 mol %) in 2-methylpyridine (25 mL) was refluxed for 72 h. After cooling, all volatiles were removed in vacuo. The dark solid residue was suspended in ethanol (50 mL), and the mixture was refluxed for 1 hour. The resulting suspension was filtered whilst hot. The orange microcrystalline solid thus obtained was washed with ethanol and dissolved in refluxing 2 M aqueous sodium hydroxide (150 mL). The dark solution was filtered whilst hot and, after cooling, was acidified to pH 5 by dropwise addition of concd. hydrochloric acid. The resulting yellow precipitate was filtered off and washed thoroughly with water. Drying in vacuo gave 7.04 g (80%) of essentially pure *N*,*N*′-(1,4-phenylene)bis(pyridine-2-thiocarboxamide) (**3**) as a bright yellow powder. This material could be used for subsequent reactions without further purification. An analytically pure sample was obtained as brown lustrous needles by recrystallisation from 1,4-dioxane. M.p. 213−215 °C. $C_{18}H_{14}N_4S_2$ (350.47): calcd. C 61.68, H 4.03, N 15.99, S 18.30; found C 61.59, H 3.97, N 15.99, S 18.00. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.49 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 2 H, 2 × 5-Py*H*), 7.90 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 2 H, 2 × 4-Py*H*), 8.25 (s, 4 H, 4 × Ph*H*), 8.57 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 6-Py*H*), 8.81 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 3-Py*H*), 12.18 (br. s, 2 H, 2 × CSN*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 122.99 (4 × PhC_H), 124.95 (2 × 3-Py*C*), 126.24 (2 × 5-Py*C*), 136.84 (2 × PhC_q), 137.72 (2 × 4-Py*C*), 146.72 (2 × 6-Py*C*), 151.58 (2 × 2-Py*C*), 187.60 (2 × *C*SNH) ppm. IR (KBr): ṽ = 3122, 1583, 1545, 1510, 1453, 1434, 1417, 1391, 1362, 1315, 1280, 1195, 1089, 1040, 992, 839, 779, 740, 718, 617, 523 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 351 [M + H]$^+$. APCI-MS (neg., MeCN): *m*/*z* = 349 [M − H]$^-$. TLC (SiO$_2$, EtOAc): R_f = 0.66.

***N*-(4-Aminophenyl)pyridine-2-thiocarboxamide (4):** A mixture of 1,4-phenylenediamine (2.70 g, 25.0 mmol), sulfur (1.92 g, 60.0 mmol), 2-methylpyridine (4.66 g, 50.0 mmol) and sodium sulfide nonahydrate (0.30 g, 5 mol %) was heated at 150 °C for 18 h. After cooling, 2 M aqueous sodium hydroxide (50 mL) was added, and the mixture was filtered. The filtrate was acidified to pH 5 by dropwise addition of concd. hydrochloric acid, and the resulting yellow precipitate was filtered off and washed thoroughly with water. Drying in vacuo gave 3.35 g (58%) of essentially pure *N*-(4-aminophenyl)pyridine-2-thiocarboxamide (**4**) as a yellow powder. An analytically pure sample was obtained as orange-brown blocks by recrystallisation from acetonitrile. M.p. 145−147 °C. $C_{12}H_{11}N_3S$ (229.31): calcd. C 62.86, H 4.84, N 18.32, S 13.98; found C 62.69, H 4.97, N 18.53, S 13.72. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.79 (br. s, 2 H, PhN*H*$_2$), 6.75 (d, ^3J = 8.5 Hz, 2 H, 3- and 5-Ph*H*), 7.44 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.84 (d, ^3J = 8.5 Hz, 2 H, 2- and 6-Ph*H*), 7.87 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.53 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*), 8.81 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 11.91 (br. s, 1 H, CSN*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 115.06 (3- and 5-Ph*C*), 124.44 (2- and 6-Ph*C*), 124.92 (3-Py*C*), 125.90, (5-Py*C*), 130.27 (1-Ph*C*), 137.55 (4-Py*C*), 145.26 (6-Py*C*), 146.66 (4-Ph*C*), 151.80 (2-Py*C*), 186.38 (*C*SNH) ppm. IR (KBr): ṽ = 3384, 3300, 3088, 1619, 1585, 1524, 1501, 1460, 1434, 1356, 1280, 1266, 1210, 1171, 1095, 1050, 1003, 995, 924, 831, 775, 734, 701, 617, 498 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 230 [M + H]$^+$. APCI-MS (neg., MeCN): *m*/*z* = 228 [M − H]$^-$. TLC (SiO$_2$, EtOAc): R_f = 0.62.

***N*-(4-Pyridyl)pyridine-2-thiocarboxamide (5):** A mixture of 4-aminopyridine (9.31 g, 0.10 mol), sulfur (9.62 g, 0.30 mol) and sodium sulfide nonahydrate (0.48 g, 2 mol %) in 2-methylpyridine (60 mL) was refluxed for 48 h. After cooling and removal of all volatiles in vacuo, the dark solid residue was taken up in 2 M aqueous sodium hydroxide (200 mL), and the mixture was filtered. The filtrate was diluted with water (400 mL) and acidified to pH 5 by dropwise addition of concd. hydrochloric acid. The resulting very voluminous yellow precipitate was filtered off and washed thoroughly with water. Drying in vacuo gave 16.7 g (77%) of analytically pure *N*-(4-pyridyl)pyridine-2-thiocarboxamide (**5**) as a yellow powder. M.p. 130−132 °C. $C_{11}H_9N_3S$ (215.27): calcd. C 61.37, H 4.21, N 19.52, S 14.89; found C 61.37, H 4.18, N 19.61, S 14.71. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.52 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.91 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.15−8.17 (m, 2 H, 3′- and 5′-Py*H*), 8.56 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*), 8.66−8.68 (m, 2 H, 2′- and 6′-Py*H*), 8.73 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 12.23 (br. s, 1 H, CSN*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 115.47 (3′- and 5′-Py*C*), 124.90 (3-Py*C*), 126.65 (5-Py*C*), 137.90 (4-Py*C*), 145.58 (4′-Py*C*), 146.72 (6-Py*C*), 150.96 (2′- and 6′-Py*C*), 151.13 (2-Py*C*), 189.66 (*C*SNH) ppm. IR (KBr): ṽ = 3170, 1598, 1576, 1519, 1462, 1441, 1408, 1358, 1330, 1301, 1256, 1227, 1158, 1100, 1043, 998, 989, 841, 815, 778, 737, 622, 562, 529 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 216 [M + H]$^+$. APCI-MS (neg., MeCN): *m*/*z* = 214 [M − H]$^-$. TLC (SiO$_2$, EtOAc): R_f = 0.28.

***N*-(4-Methylphenyl)pyridine-2-thiocarboxamide (6):** A mixture of 4-methylaniline (10.7 g, 0.10 mol), sulfur (9.62 g, 0.30 mol) and sodium sulfide nonahydrate (0.48 g, 2 mol %) in 2-methylpyridine (60 mL) was refluxed for 48 h. After cooling and removal of all volatiles in vacuo, the dark solid residue was taken up in dichloromethane (200 mL), and the mixture was filtered through a column of silica gel. The filtrate was evaporated under reduced pressure, and the resulting solid was dried in vacuo. Recrystallisation from ethanol gave 18.1 g (79%) of analytically pure *N*-(4-methylphenyl)pyridine-2-thiocarboxamide (**6**) as a yellow crystalline solid. M.p. 99−101 °C. $C_{13}H_{12}N_2S$ (228.31): calcd. C 68.39, H 5.30, N 12.27, S 14.04; found C 68.10, H 5.58, N 12.40, S 13.88. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.38 (s, 3 H, PhC*H*$_3$), 7.26 (d, ^3J = 8.4 Hz, 2 H, 3- and 5-Ph*H*), 7.46 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.87 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 7.93 (d, ^3J = 8.4 Hz, 2 H, 2- and 6-Ph*H*), 8.54 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*), 8.80 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 11.99 (br. s, 1 H, CSN*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 21.29 (Ph*C*H$_3$), 122.87 (2- and 6-Ph*C*), 124.93 (3-Py*C*), 126.05 (5-Py*C*), 129.54 (3- and 5-Ph*C*), 136.35 (1-Ph*C*), 136.63 (4-Ph*C*), 137.54 (4-Py*C*), 146.64 (6-Py*C*), 151.60 (2-Py*C*), 187.66 (*C*SNH) ppm. IR

(KBr): ṽ = 3197, 1586, 1535, 1512, 1458, 1435, 1380, 1197, 1147, 1093, 1038, 993, 829, 808, 792, 757, 736, 666, 618, 507 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 229 $[M + H]^+$. APCI-MS (neg., MeCN): *m*/*z* = 227 $[M - H]^-$. TLC (SiO_2, EtOAc): $R_f = 0.69$.

***N*-(2,4,6-Trimethylphenyl)pyridine-2-thiocarboxamide (7):** The reaction of 2,4,6-trimethylaniline (13.5 g, 0.10 mol), sulfur (9.62 g, 0.30 mol), sodium sulfide nonahydrate (0.48 g, 2 mol %) and 2-methylpyridine (60 mL), following the procedure described above for the preparation of *N*-(4-methylphenyl)-2-pyrdinethiocarboxamide (**6**), gave 19.1 g (74%) of analytically pure *N*-(2,4,6-trimethylphenyl)pyridine-2-thiocarboxamide (**7**) as yellow-brown lustrous flakes. M.p. 117−119 °C. $C_{15}H_{16}N_2S$ (256.37): calcd. C 70.28, H 6.29, N 10.93, S 12.51; found C 70.21, H 6.41, N 11.22, S 12.27. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.22 (s, 6 H, 2- and 6-PhC*H*$_3$), 2.33 (s, 3 H, 4-PhC*H*$_3$), 6.99 (s, 2 H, 3- and 5-Ph*H*), 7.50 (ddd, $^3J_{4,5} = 7.7$, $^3J_{5,6} = 4.8$, $^4J_{3,5} = 1.2$ Hz, 1 H, 5-Py*H*), 7.89 (dt, $^3J_{3,4} = {}^3J_{4,5} = 7.7$, $^4J_{4,6} = 1.8$ Hz, 1 H, 4-Py*H*), 8.58 (ddd, $^3J_{5,6} = 4.8$, $^4J_{4,6} = 1.8$, $^5J_{3,6} = 0.9$ Hz, 1 H, 6-Py*H*), 8.80 (ddd, $^3J_{3,4} = 7.7$, $^4J_{3,5} = 1.2$, $^5J_{3,6} = 0.9$ Hz, 1 H, 3-Py*H*), 11.29 (br. s, 1 H, CSN*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 18.19 (2- and 6-Ph*C*H_3), 21.23 (4-Ph*C*H_3), 125.02 (3-Py*C*), 126.27 (5-Py*C*), 129.19 (3- and 5-Ph*C*), 133.84 (1-Ph*C*), 135.10 (2- and 6-Ph*C*), 137.43 (4-Py*C*), 137.98 (4-Ph*C*), 147.09 (6-Py*C*), 151.14 (2-Py*C*), 191.27 (*C*SNH) ppm. IR (KBr): ṽ = 3268, 2975, 2947, 2908, 2852, 1585, 1565, 1499, 1460, 1431, 1422, 1366, 1259, 1212, 1139, 1093, 1044, 1006, 992, 853, 805, 790, 757, 743, 701, 661, 648, 617, 601, 574, 505, 407 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 257 $[M + H]^+$. APCI-MS (neg., MeCN): *m*/*z* = 255 $[M - H]^-$. TLC (SiO_2, EtOAc): R_f = 0.72.

***N*-Methylpyridine-2-thiocarboxamide (8):** A mixture of methylamine hydrochloride (13.5 g, 0.20 mol), sulfur (19.2 g, 0.60 mol) and sodium sulfide nonahydrate (0.96 g, 2 mol %) in 2-methylpyridine (80 mL) was refluxed for 24 h. After cooling, all volatiles were removed in vacuo. The dark residue was taken up in 6 M hydrochloric acid (200 mL), and the mixture was filtered. Solid sodium hydroxide (48.0 g, 1.20 mol) was added to the filtrate in portions at 0 °C, followed by 2 M aqueous sodium hydroxide until the aqueous phase was neutral. The resulting heterogeneous mixture was extracted with dichloromethane (5 × 100 mL). The combined organic layers were dried with anhydrous sodium sulfate and filtered through a column of silica gel. The filtrate was evaporated under reduced pressure, and the brown crystalline solid thus obtained was dried in vacuo. Recrystallisation from cyclohexane/ethyl acetate (5:1) gave 21.1 g (69%) of analytically pure *N*-methylpyridine-2-thiocarboxamide (**8**) as yellow prisms. M.p. 75−77 °C. $C_7H_8N_2S$ (152.21): calcd. C 55.24, H 5.30, N 18.40, S 21.06; found C 55.29, H 5.26, N 18.29, S 20.86. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.39 (d, $^3J = 5.1$ Hz, 3 H, C*H*$_3$), 7.41 (ddd, $^3J_{4,5} = 7.7$, $^3J_{5,6} = 4.8$, $^4J_{3,5} = 1.2$ Hz, 1 H, 5-Py*H*), 7.81 (dt, $^3J_{3,4} = {}^3J_{4,5} = 7.7$, $^4J_{4,6} = 1.8$ Hz, 1 H, 4-Py*H*), 8.47 (ddd, $^3J_{5,6} = 4.8$, $^4J_{4,6} = 1.8$, $^5J_{3,6} = 0.9$ Hz, 1 H, 6-Py*H*), 8.69 (ddd, $^3J_{3,4} = 7.7$, $^4J_{3,5} = 1.2$, $^5J_{3,6} = 0.9$ Hz, 1 H, 3-Py*H*), 10.21 (br. s, 1 H, CSN*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 32.72 (*C*H_3), 124.69 (3-Py*C*), 126.09 (5-Py*C*), 137.34 (4-Py*C*), 147.00 (6-Py*C*), 151.15 (2-Py*C*), 191.85 (*C*SNH) ppm. IR (KBr): ṽ = 3272, 1585, 1533, 1438, 1351, 1271, 1224, 1163, 1100, 1045, 993, 956, 796, 743, 702, 604 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 153 $[M + H]^+$. APCI-MS (neg., MeCN): *m*/*z* = 151 $[M - H]^-$. TLC (SiO_2, EtOAc): R_f = 0.68.

***N*-Benzylpyridine-2-thiocarboxamide (9):** A mixture of benzylamine (10.7 g, 0.10 mol), sulfur (9.62 g, 0.30 mol) and sodium sulfide nonahydrate (0.48 g, 2 mol %) in 2-methylpyridine (60 mL) was refluxed for 48 h. After cooling, all volatiles were removed in vacuo. The resulting dark oily residue solidified with difficulty. It was taken up in dichloromethane (200 mL), and the solution was washed with 2 M hydrochloric acid (50 mL) and water (50 mL), and dried with anhydrous sodium sulfate. The solution was then filtered through a column of silica gel. The filtrate was evaporated under reduced pressure, and the resulting orange solid was dried in vacuo. Recrystallisation from ethanol gave 10.2 g (44%) of analytically pure *N*-benzylpyridine-2-thiocarboxamide (**9**) as a yellow crystalline solid. M.p. 75−77 °C. $C_{13}H_{12}N_2S$ (228.31): calcd. C 68.39, H 5.30, N 12.27, S 14.04; found C 68.64, H 5.21, N 12.45, S 13.90. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.07 (d, $^3J = 5.5$ Hz, 2 H, PhC*H*$_2$), 7.32−7.44 (m, 6 H, 5-Py*H* and 5 × Ph*H*), 7.84 (dt, $^3J_{3,4} = {}^3J_{4,5} = 7.7$, $^4J_{4,6} = 1.8$ Hz, 1 H, 4-Py*H*), 8.45 (ddd, $^3J_{5,6} = 4.8$, $^4J_{4,6} = 1.8$, $^5J_{3,6} = 0.9$ Hz, 1 H, 6-Py*H*), 8.73 (ddd, $^3J_{3,4} = 7.7$, $^4J_{3,5} = 1.2$, $^5J_{3,6} = 0.9$ Hz, 1 H, 3-Py*H*), 10.38 (br. s, 1 H, CSN*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 50.03 (Ph*C*H_2), 125.09 (3-Py*C*), 126.20 (5-Py*C*), 128.09 (4-Ph*C*), 128.41 (2- and 6-Ph*C*), 129.03 (3- and 5-Ph*C*), 136.52 (1-Ph*C*), 137.38 (4-Py*C*), 147.06 (6-Py*C*), 151.11 (2-Py*C*), 191.02 (*C*SNH) ppm. IR (KBr): ṽ = 3237, 1514, 1453, 1435, 1377, 1337, 1326, 1278, 1242, 1197, 1073, 996, 944, 794, 751, 734, 698, 497 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 229 $[M + H]^+$. APCI-MS (neg., MeCN): *m*/*z* = 227 $[M - H]^-$. TLC (SiO_2, EtOAc): R_f = 0.71.

***N*-Isobutylpyridine-2-thiocarboxamide (10):** A mixture of pyridine-2-thiocarboxamide (**11**) (9.67 g, 70.0 mmol) and isobutylamine (35 mL) was refluxed for 2 h. All volatiles were then evaporated under reduced pressure, and the residue was dissolved in dichloromethane (100 mL). The solution was washed with water (50 mL) and sat. aqueous sodium chloride (50 mL), and dried with anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure, and distillation of the residue in vacuo gave 11.1 g (81%) of analytically pure *N*-isobutylpyridine-2-thiocarboxamide (**10**) as a golden liquid. $C_{10}H_{14}N_2S$ (194.29): calcd. C 61.82, H 7.26, N 14.42, S 16.50; found C 62.10, H 7.47, N 14.23, S 16.33. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 [d, $^3J = 6.8$ Hz, 6 H, $CH_2CH(CH_3)_2$], 2.16 [non, $^3J = 6.8$ Hz, 1 H, $CH_2CH(CH_3)_2$], 3.70 [dd, $^3J_{C,H,CH} = 6.8$, $^3J_{C,H,NH} = 5.8$ Hz, 2 H, $CH_2CH(CH_3)_2$], 7.41 (ddd, $^3J_{4,5} = 7.7$, $^3J_{5,6} = 4.8$, $^4J_{3,5} = 1.2$ Hz, 1 H, 5-Py*H*), 7.82 (dt, $^3J_{3,4} = {}^3J_{4,5} = 7.7$, $^4J_{4,6} = 1.8$ Hz, 1 H, 4-Py*H*), 8.48 (ddd, $^3J_{5,6} = 4.8$, $^4J_{4,6} = 1.8$, $^5J_{3,6} = 0.9$ Hz, 1 H, 6-Py*H*), 8.70 (ddd, $^3J_{3,4} = 7.7$, $^4J_{3,5} = 1.2$, $^5J_{3,6} = 0.9$ Hz, 1 H, 3-Py*H*), 10.26 (br. s, 1 H, CSN*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.60 [$CH_2CH(CH_3)_2$], 27.78 [$CH_2CH(CH_3)_2$], 53.24 [$CH_2CH(CH_3)_2$], 124.93 (3-Py*C*), 126.05 (5-Py*C*), 137.33 (4-Py*C*), 147.00 (6-Py*C*), 151.23 (2-Py*C*), 190.80 (*C*SNH) ppm. IR (neat): ṽ = 3290, 2957, 1586, 1519, 1461, 1434, 1332, 1282, 1257, 1214, 1097, 1067, 1043, 999, 970, 795, 742 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 195 $[M + H]^+$. APCI-MS (neg., MeCN): *m*/*z* = 193 $[M - H]^-$. TLC (SiO_2, EtOAc): R_f = 0.72.

Pyridine-2-thiocarboxamide (11): A solution of pyridine-2-carbonitrile (15.6 g, 0.15 mol) in dry ethanol (150 mL) was saturated with gaseous ammonia, and a slow stream of hydrogen sulfide was then passed through the solution for 1 h. The resulting yellow suspension was stirred at room temperature for 2 h and was then evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (500 mL), and the solution was washed with water (100 mL) and sat. aqueous sodium chloride (100 mL), and dried with anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure, and drying of the residue in vacuo gave 18.0 g (86%) of essentially pure pyridine-2-thiocarboxamide (**11**) as yellow prisms. This material could be used for subsequent reactions without further purification. An analytically pure sample was obtained as large yellow needles by recrystallisation from cyclohexane/ethyl acetate (5:1). M.p. 138−140 °C. $C_6H_6N_2S$ (138.19): calcd. C 52.15, H 4.38, N 20.27, S 23.20; found C 51.97, H 4.25, N 20.26, S 23.02. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.83 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 7.90 (br. s, 1 H, *cis*-CSN*H*), 8.51 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*), 8.69 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 9.54 (br. s, 1 H, *trans*-CSN*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 125.20 (3-Py*C*), 126.51 (5-Py*C*), 137.27 (4-Py*C*), 147.33 (6-Py*C*), 150.61 (2-Py*C*), 195.98 (*C*SNH_2) ppm. IR (KBr): ṽ = 3346, 3235, 3147, 1600, 1582, 1565, 1441, 1397, 1305, 1275, 1256, 1046, 994, 901, 795, 725, 671, 526, 438 cm^{-1}. APCI-MS (pos., MeCN): *m*/*z* = 139 $[M + H]^+$. APCI-MS (neg., MeCN): *m*/*z* = 137 $[M - H]^-$. TLC (SiO_2, EtOAc): R_f = 0.68.

3-Phenyl-5-(2-pyridyl)-4-(4-pyridyl)-4*H*-1,2,4-triazole (pyppt, 12): A mixture of *N*-(4-pyridyl)pyridine-2-thiocarboxamide (**5**) (4.30 g, 20.0 mmol) and benzohydrazide (**1**) (3.27 g, 24.0 mmol) in 1-butanol (80 mL) was refluxed for 24 h. On cooling, the product crystallised from the orange reaction mixture. It was filtered off, washed with ethanol and dried in vacuo to give 4.71 g (78%) of analytically pure pyppt (**12**) as fine colourless needles. M.p. 251−253 °C. $C_{18}H_{13}N_5$ (299.33): calcd. C 72.23, H 4.38, N 23.40; found C 72.25, H 4.44, N 23.67. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15−7.17 (m, 2 H, 3′- and 5′-Py*H*), 7.25 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.30−7.34 (m, 2 H, 3- and 5-Ph*H*), 7.38−7.42 (m, 3 H, 2-, 4- and 6-Ph*H*), 7.81 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.26 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 8.28 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*), 8.65−8.67 (m, 2 H, 2′- and 6′-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 123.03 (3′- and 5′-Py*C*), 124.30 (3-Py*C*), 124.38 (5-Py*C*), 126.31 (1-Ph*C*), 128.80 (3- and 5-Ph*C*), 129.12 (2- and 6-Ph*C*), 130.31 (4-Ph*C*), 137.04 (4-Py*C*), 144.05 (4′-Py*C*), 146.62 (2-Py*C*), 148.89 (6-Py*C*), 151.12 (2′- and 6′-Py*C*), 153.21 (5-Tz*C*), 155.43 (3-Tz*C*) ppm. IR (KBr): ṽ = 3055, 3035, 1591, 1569, 1508, 1469, 1451, 1419, 1217, 1165, 1087, 1074, 989, 846, 789, 771, 739, 712, 693, 631, 608, 500 cm^{-1}. ESI-MS (pos., MeCN): *m*/*z* = 300 $[M + H]^+$, 322 $[M + Na]^+$, 338 $[M + K]^+$. TLC (SiO_2, EtOAc): R_f = 0.12.

3,5-Di(2-pyridyl)-4-(4-pyridyl)-4*H*-1,2,4-triazole (pydpt, 13): The reaction of *N*-(4-pyridyl)pyridine-2-thiocarboxamide (**5**) (4.30 g, 20.0 mmol) and pyridine-2-carbohydrazide (**2**) (3.29 g, 24.0 mmol) in 1-butanol (80 mL), following the procedure described above for the preparation of pyppt (**12**), gave 4.20 g (69%) of analytically pure pydpt (**13**) as fine colourless needles. M.p. 264−266 °C. $C_{17}H_{12}N_6$ (300.32): calcd. C 67.99, H 4.03, N 27.98; found C 67.92, H 3.86, N 28.14. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20−7.22 (m, 2 H, 3′- and 5′-Py*H*), 7.24 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 2 H, 2 × 5-Py*H*), 7.79 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 2 H, 2 × 4-Py*H*), 8.21 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 3-Py*H*), 8.28 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 6-Py*H*), 8.62−8.64 (m, 2 H, 2′- and 6′-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 123.28 (3′- and 5′-Py*C*), 124.39 (2 × 5-Py*C*), 124.49 (2 × 3-Py*C*), 136.94 (2 × 4-Py*C*), 144.90 (4′-Py*C*), 146.53 (2 × 2-Py*C*), 148.99 (2 × 6-Py*C*), 150.41 (2′- and 6′-Py*C*), 153.99 (3- and 5-Tz*C*) ppm. IR (KBr): ṽ = 3060, 3037, 1595, 1586, 1573, 1509, 1464, 1445, 1431, 1421, 1174, 1148, 1087, 844, 791, 744, 714, 686, 637, 606 cm^{-1}. ESI-MS (pos., MeCN): *m*/*z* = 301 $[M + H]^+$, 323 $[M + Na]^+$, 339 $[M + K]^+$. TLC (SiO_2, EtOAc): R_f = 0.06.

Ethyl *N*-(4-Methylphenyl)pyridine-2-carboximidothioate (14): *N*-(4-Methylphenyl)pyridine-2-thiocarboxamide (**6**) (11.4 g, 50.0 mmol) was added to a solution of sodium ethoxide, prepared by dissolving sodium (1.15 g, 50.0 mmol) in dry ethanol (200 mL), and the reaction mixture was stirred at room temperature for 30 minutes. Bromoethane (5.45 g, 50.0 mmol) was then added to the resulting orange-brown solution, and the reaction mixture was heated at 50 °C for 6 h during which time some sodium bromide precipitated. After allowing the suspension to cool to room temperature, it was filtered, and the filtrate was evaporated under reduced pressure. The residue was taken up in dichloromethane (150 mL), and the mixture was washed with water (3 × 50 mL), sat. aqueous sodium carbonate (50 mL) and sat. aqueous sodium chloride (50 mL), and dried with anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure, and drying of the residue in vacuo gave 12.6 g (98%) of crude ethyl *N*-(4-methylphenyl)pyridine-2-carboximidothioate (**14**) as an orange oil. This material could be used in subsequent reactions without further purification. $C_{15}H_{16}N_2S$ (256.37). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.31 (s, 3 H, $PhCH_3$), 2.70 (q, ^3J = 7.4 Hz, 2 H, SCH_2CH_3), 6.60 (d, ^3J = 8.4 Hz, 2- and 6-Ph*H*), 6.92 (d, ^3J = 8.4 Hz, 3- and 5-Ph*H*), 7.17 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.45 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 7.81 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.65 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 15.03 (SCH_2CH_3), 21.00 ($PhCH_3$), 27.22 (SCH_2CH_3), 121.67 (2- and 6-Ph*C*), 123.16 (3-Py*C*), 124.39 (5-Py*C*), 129.51 (3- and 5-Ph*C*), 137.06 (4-Py*C*), 149.60 (6-Py*C*), 156.13 (2-Py*C*), 164.29 (*C*NS) ppm. ESI-MS (pos., MeCN): *m*/*z* = 257 $[M + H]^+$.

4-(4-Methylphenyl)-3-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazole (pmppt, 15): A mixture of crude ethyl *N*-(4-methylphenyl)pyridine-2-carboximidothioate (**14**) (5.13 g, 20.0 mmol) and benzohydrazide (**1**) (3.27 g, 24.0 mmol) in 1-butanol (50 mL) was refluxed for 24 h. On cooling, the product crystallised from the orange reaction mixture. It was filtered off and washed with ethanol. Drying in vacuo gave 3.28 g (52%) of analytically pure pmppt (**15**) as very fine colourless needles. Evaporation of the filtrate and recrystallisation of the solid residue from 2-propanol gave another 0.87 g (13%) of analytically pure material. M.p. 241−243 °C. $C_{20}H_{16}N_4$ (312.37): calcd. C 76.90, H 5.16, N 17.94; found C 76.62, H 5.20, N 17.85. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 7.08 (d, ^3J = 8.4 Hz, 2 H, 2- and 6-$Ph_{Me}H$), 7.16 (d, ^3J = 8.4 Hz, 2 H, 3- and 5-$Ph_{Me}H$), 7.22 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.27−7.31 (m, 2 H, 3- and 5-Ph*H*), 7.33−7.37 (m, 1 H, 4-Ph*H*), 7.44−7.47 (m, 2 H, 2- and 6-Ph*H*), 7.74 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.05 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 8.37 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 21.42 (CH_3), 123.93 (5-Py*C*), 124.55 (3-Py*C*), 127.15 (1-Ph*C*), 127.82 (2- and 6-$Ph_{Me}C$), 128.49 (3- and 5-Ph*C*), 129.01 (2- and 6-Ph*C*), 129.75 (4-Ph*C*), 129.91 (3- and 5-$Ph_{Me}C$), 133.31 (1-$Ph_{Me}C$), 136.65 (4-Py*C*), 139.19 (4-$Ph_{Me}C$), 147.34 (2-Py*C*), 149.14 (6-Py*C*), 154.04 (5-Tz*C*), 155.75 (3-Tz*C*) ppm. IR (KBr): ṽ = 1583, 1566, 1537, 1513, 1469, 1451, 1433, 1407, 1275, 1165, 1050, 999, 975, 849, 823, 796, 774, 743, 718, 709, 693, 622, 603 cm^{-1}. ESI-MS (pos., MeCN): *m*/*z* = 313 $[M + H]^+$, 335 $[M + Na]^+$, 351 $[M + K]^+$. TLC (SiO_2, EtOAc): R_f = 0.21.

4-(4-Methylphenyl)-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (pmdpt, 16): The reaction of crude ethyl *N*-(4-methylphenyl)pyridine-2-carboximidothioate (**14**) (5.13 g, 20.0 mmol) and pyridine-2-carbohydrazide (**2**) (3.29 g, 24.0 mmol) in 1-butanol (50 mL), following the procedure described above for the preparation of pmppt (**15**), gave 3.18 g (50%) of analytically pure pmdpt (**16**) as very fine colourless needles. Evaporation of the filtrate, and recrystallisation of the solid residue from 2-propanol gave another 1.35 g (21%) of analytically pure material. M.p. 204−206 °C. $C_{19}H_{15}N_5$ (313.36): calcd. C 72.84, H 4.80, N 22.47; found C 72.82, H 4.76, N 22.56. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, C*H*$_3$), 7.09−7.14 (m, 4 H, 2-, 3-, 5- and 6-Ph$_{Me}$*H*), 7.22 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 2 H, 2 × 5-Py*H*), 7.73 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 2 H, 2 × 4-Py*H*), 7.98 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 3-Py*H*), 8.40 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 21.40 (*C*H$_3$), 124.00 (2 × 5-Py*C*), 124.71 (2 × 3-Py*C*), 127.76 (2- and 6-Ph$_{Me}$*C*), 129.31 (3- and 5-Ph$_{Me}$*C*), 133.67 (1-Ph$_{Me}$*C*), 136.59 (2 × 4-Py*C*), 138.60 (4-Ph$_{Me}$*C*), 147.20 (2 × 2-Py*C*), 149.29 (2 × 6-Py*C*), 154.63 (3- and 5-Tz*C*) ppm. IR (KBr): ṽ = 1582, 1568, 1541, 1514, 1460, 1444, 1428, 1244, 1173, 1093, 1045, 995, 844, 821, 799, 787, 742, 642, 625, 602 cm^{-1}. ESI-MS (pos., MeCN): *m*/*z* = 314 [M + H]$^+$, 336 [M + Na]$^+$, 352 [M + K]$^+$. TLC (SiO_2, EtOAc): R_f = 0.13.

Ethyl *N*-Methylpyridine-2-carboximidothioate (17): The reaction of *N*-methylpyridine-2-thiocarboxamide (**9**) (7.91 g, 50.0 mmol) and bromoethane (5.45 g, 50.0 mmol) in the presence of sodium ethoxide, prepared by dissolving sodium (1.15 g, 50.0 mmol) in dry ethanol (200 mL), following the procedure described above for the preparation of ethyl *N*-(4-methylphenyl)pyridine-2-carboximidothioate (**14**) gave 8.39 g (93%) of crude ethyl *N*-methylpyridine-2-carboximidothioate (**17**) as an orange oil. This material could be used in subsequent reactions without further purification. $C_9H_{12}N_2S$ (180.27). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (t, ^3J = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$), 2.77 (q, ^3J = 7.4 Hz, 2 H, SC*H*$_2$CH$_3$), 3.43 (s, 3 H, NC*H*$_3$), 7.27 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.55 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 7.72 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.60 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 15.51 (SCH$_2$*C*H$_3$), 26.80 (S*C*H$_2$CH$_3$), 41.27 (N*C*H$_3$), 122.91 (3-Py*C*), 123.95 (5-Py*C*), 136.99 (4-Py*C*), 148.77 (6-Py*C*), 156.21 (2-Py*C*), 165.32 (*C*NS) ppm. ESI-MS (pos., MeCN): *m*/*z* = 181 [M + H]$^+$.

4-Methyl-3-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazole (meppt, 18): A mixture of crude ethyl *N*-methylpyridine-2-carboximidothioate (**17**) (3.61 g, 20.0 mmol) and benzohydrazide (**1**) (3.27 g, 24.0 mmol) in 1-butanol (50 mL) was refluxed for 24 h. Evaporation of the reaction mixture, and recrystallisation of the solid residue from ethyl acetate gave 2.81 g (59%) of analytically pure meppt (**18**) as colourless needles. M.p. 147−149 °C. $C_{14}H_{12}N_4$ (236.28): calcd. C 71.17, H 5.12, N 23.71; found C 71.03, H 5.07, N 23.67. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.05 (s, 3 H, C*H*$_3$), 7.34 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.48−7.53 (m, 3 H, 3-, 4- and 5-Ph*H*), 7.66−7.71 (m, 2 H, 2- and 6-Ph*H*), 7.83 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.33 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 8.66 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 34.34 (*C*H$_3$), 124.05 (5-Py*C*), 124.10 (3-Py*C*), 127.24 (1-Ph*C*), 128.97 (3- and 5-Ph*C*), 129.31 (2- and 6-Ph*C*), 130.21 (4-Ph*C*), 137.12 (4-Py*C*), 148.22 (2-Py*C*), 148.87 (6-Py*C*), 153.46 (5-Tz*C*), 157.00 (3-Tz*C*) ppm. IR (KBr): ṽ = 3047, 1588, 1569, 1517, 1485, 1470, 1443, 1430, 1278, 1150, 1096, 1076, 991, 927, 889, 789, 779, 773, 737, 722, 706, 699, 668, 623, 578, 485 cm^{-1}. ESI-MS (pos., MeCN): *m*/*z* = 237 [M + H]$^+$, 259 [M + Na]$^+$, 275 [M + K]$^+$. TLC (SiO_2, EtOAc): R_f = 0.15.

4-Methyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (medpt, 19): The reaction of crude ethyl *N*-methylpyridine-2-carboximidothioate (**17**) (3.61 g, 20.0 mmol) and pyridine-2-carbohydrazide (**2**) (3.29 g, 24.0 mmol) in 1-butanol (50 mL), following the procedure described above for the preparation of meppt (**18**), gave 2.49 g (52%) of analytically pure medpt (**19**) as colourless flakes. M.p. 175−177 °C. $C_{13}H_{11}N_5$ (237.26): calcd. C 65.81, H 4.67, N 29.52; found C 65.81, H 4.64, N 29.58. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.43 (s, 3 H, C*H*$_3$), 7.33 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 2 H, 2 × 5-Py*H*), 7.82 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 2 H, 2 × 4-Py*H*), 8.28 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 3-Py*H*), 8.67 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 34.97 (*C*H$_3$), 124.03 (2 × 5-Py*C*), 124.48 (2 × 3-Py*C*), 137.00 (2 × 4-Py*C*), 148.22 (2 × 2-Py*C*), 148.89 (2 × 6-Py*C*), 154.22 (3- and 5-Tz*C*) ppm. IR (KBr): ṽ = 3041, 1586, 1571, 1512, 1485, 1458, 1431, 1283, 1251, 1146, 1094, 992, 889, 793, 735, 724, 706, 674, 620, 567, 490 cm^{-1}. ESI-MS (pos., MeCN): *m*/*z* = 238 [M + H]$^+$, 260 [M + Na]$^+$, 276 [M + K]$^+$. TLC (SiO_2, EtOAc): R_f = 0.12.

Ethyl *N*-Isobutylpyridine-2-carboximidothioate (20): The reaction of *N*-(isobutyl)pyridine-2-thiocarboxamide (**11**) (9.72 g, 50.0 mmol) and bromoethane (5.45 g, 50.0 mmol) in the presence of sodium ethoxide, prepared by dissolving sodium (1.15 g, 50.0 mmol) in dry ethanol (200 mL), following the procedure described above for the preparation of ethyl *N*-(4-methylphenyl)pyridine-2-carboximidothioate (**14**) gave 10.0 g (89%) of crude ethyl *N*-(isobutyl)pyridine-2-carboximidothioate (**20**) as an orange oil. This material could be used in subsequent reactions without further purification. $C_{12}H_{18}N_2S$ (222.35). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 [d, ^3J = 6.8 Hz, 6 H, NCH$_2$CH(C*H*$_3$)$_2$], 1.07 (t, ^3J = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$), 2.08 [non, ^3J = 6.8 Hz, 1 H, NCH$_2$C*H*(CH$_3$)$_2$], 2.75 (q, ^3J = 7.4 Hz, 2 H, SC*H*$_2$CH$_3$), 3.42 [d, ^3J = 6.8 Hz, 2 H, NC*H*$_2$CH(CH$_3$)$_2$], 7.27 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.59 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 7.73 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.61 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 15.51 (SCH$_2$*C*H$_3$), 21.58 [NCH$_2$CH(*C*H$_3$)$_2$], 26.91 (S*C*H$_2$CH$_3$), 29.82 [NCH$_2$*C*H(CH$_3$)$_2$], 62.08 [N*C*H$_2$CH(CH$_3$)$_2$], 123.08 (3-Py*C*), 123.87 (5-Py*C*), 137.01 (4-Py*C*), 148.68 (6-Py*C*), 156.35 (2-Py*C*), 163.06 (*C*NS) ppm. ESI-MS (pos., MeCN): *m*/*z* = 223 [M + H]$^+$.

4-Isobutyl-3-phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazole (ibppt, 21): A mixture of crude ethyl *N*-(isobutyl)pyridine-2-carboximidothioate (**20**) (8.89 g, 40.0 mmol) and benzohydrazide (**1**) (6.13 g, 45.0 mmol) in 1-butanol (100 mL) was refluxed for 24 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (100 mL). The solution was washed with 2 M aqueous sodium hydroxide (3 × 50 mL), water (50 mL) and sat. aqueous sodium chloride (50 mL), and dried with anhydrous sodium sulfate. Column chromatography on silica gel eluting with ethyl acetate/cyclohexane (2:1) gave 7.56 g (67%) of analytically pure ibppt (**21**) as a colourless crystalline solid. M.p. 131−133 °C. $C_{17}H_{18}N_4$ (278.36): calcd. C 73.35, H 6.52, N 20.13; found C 73.21, H 6.31, N 20.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.59 [d, ^3J = 6.8 Hz, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.71 [non, ^3J = 6.8 Hz, 1 H, CH$_2$C*H*(CH$_3$)$_2$], 4.51 [d, ^3J = 6.8 Hz, 2 H, C*H*$_2$CH(CH$_3$)$_2$], 7.34 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 1 H, 5-Py*H*), 7.49−7.54 (m, 3 H, 3-, 4- and 5-Ph*H*), 7.61−7.65 (m, 2 H, 2- and 6-Ph*H*), 7.84 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 1 H, 4-Py*H*), 8.33 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 1 H, 3-Py*H*), 8.65 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 1 H, 6-Py*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 19.59 [CH$_2$CH(*C*H$_3$)$_2$], 29.74 [CH$_2$*C*H(CH$_3$)$_2$], 52.46 [*C*H$_2$CH(CH$_3$)$_2$], 124.06 (5-Py*C*), 124.12 (3-Py*C*), 128.06 (1-Ph*C*), 128.97 (3- and 5-Ph*C*), 129.59 (2- and 6-Ph*C*), 130.06 (4-Ph*C*), 137.15 (4-Py*C*), 148.63 (2-Py*C*), 148.88 (6-Py*C*), 153.15 (5-Tz*C*), 157.25 (3-Tz*C*) ppm. IR (KBr): $\tilde{\nu}$ = 2968, 2950, 2868, 1587, 1568, 1511, 1473, 1457, 1446, 1389, 1280, 1249, 1149, 1102, 991, 975, 923, 792, 772, 741, 729, 722, 698, 575 cm^{-1}. ESI-MS (pos., MeCN): *m/z* = 279 $[M + H]^+$, 301 $[M + Na]^+$, 317 $[M + K]^+$. TLC (SiO_2, EtOAc): $R_f = 0.30$.

4-Isobutyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (ibdpt, 22): The reaction of crude ethyl *N*-(isobutyl)pyridine-2-carboximidothioate (**20**) (8.89 g, 40.0 mmol) and pyridine-2-carbohydrazide (**2**) (6.17 g, 45.0 mmol) in 1-butanol (100 mL), following the procedure described above for the preparation of ibppt (**21**), gave 8.17 g (73%) of analytically pure ibdpt (**22**) as a colourless crystalline solid. M.p. 91–93 °C. $C_{16}H_{17}N_5$ (279.34): calcd. C 68.80, H 6.13, N 25.07; found C 68.91, H 6.18, N 25.30. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.69 [d, ^3J = 6.8 Hz, 6 H, $CH_2CH(CH_3)_2$], 1.90 [non, ^3J = 6.8 Hz, 1 H, $CH_2CH(CH_3)_2$], 5.20 [d, ^3J = 6.8 Hz, 2 H, $CH_2CH(CH_3)_2$], 7.34 (ddd, $^3J_{4,5}$ = 7.7, $^3J_{5,6}$ = 4.8, $^4J_{3,5}$ = 1.2 Hz, 2 H, 2 × 5-Py*H*), 7.84 (dt, $^3J_{3,4}$ = $^3J_{4,5}$ = 7.7, $^4J_{4,6}$ = 1.8 Hz, 2 H, 2 × 4-Py*H*), 8.31 (ddd, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.2, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 3-Py*H*), 8.68 (ddd, $^3J_{5,6}$ = 4.8, $^4J_{4,6}$ = 1.8, $^5J_{3,6}$ = 0.9 Hz, 2 H, 2 × 6-Py*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.63 [$CH_2CH(CH_3)_2$], 30.25 [$CH_2CH(CH_3)_2$], 52.18 [$CH_2CH(CH_3)_2$], 124.04 (2 × 5-Py*C*), 124.61 (2 × 3-Py*C*), 137.05 (2 × 4-Py*C*), 148.74 (2 × 2-Py*C*), 148.88 (2 × 6-Py*C*), 154.15 (3- and 5-Tz*C*) ppm. IR (KBr): $\tilde{\nu}$ = 2962, 2868, 1586, 1571, 1514, 1477, 1451, 1429, 1386, 1364, 1279, 1250, 1153, 1109, 1096, 996, 893, 809, 793, 742, 726, 713, 625, 620, 574 cm^{-1}. ESI-MS (pos., MeCN): *m/z* = 280 $[M + H]^+$, 302 $[M + Na]^+$, 318 $[M + K]^+$. TLC (SiO_2, EtOAc): $R_f = 0.26$.

Crystal Data for ibdpt (22): $C_{16}H_{17}N_5$, M = 279.35 g mol^{-1}, colourless block, 0.35 × 0.32 × 0.26 mm, monoclinic, space group $P2_1$, a = 8.1813(16) Å, b = 10.571(2) Å, c = 8.7214(17) Å, β = 98.41(3)°, V = 746.2(3) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.243 g cm^{-3}, T = 293(2) K, μ = 0.078 mm^{-1}, $F(000)$ = 296, 4918 reflections collected [2.36° < Θ < 26.23°], 2509 independent reflections [R(int) = 0.0180], $R1$ = 0.0288 [$I > 2\sigma(I)$], $wR2$ = 0.0724 (all data), GOF = 1.005, absolute structure factor −1(2), max./min. residual electron density 0.088/−0.080 e·$Å^{-3}$. CCDC-233197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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