Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 11862–11877

Regioselectivity, scope, and limitations of the addition of organolithium and allylmagnesium reagents to 1*H*-pyridine-2-thiones; access to 3,4-, 3,6-, and 5,6-dihydropyridine-2-thiones

Jacek G. Sośnicki*

Szczecin University of Technology, Institute of Chemistry and Environmental Protection, Al. Piastów 42, PL-71065 Szczecin, Poland

Received 14 July 2007; revised 31 August 2007; accepted 13 September 2007
Available online 22 September 2007

Abstract—Organolithium and lithium allyldibutylmagnesate reagents add to readily available NH, NMe, NBn, and NPh substituted pyridine-2-thiones yielding 4- and/or 6-substituted 3,4- or 3,6-dihydropyridine-2-thiones, respectively. The regioselectivity of the addition is dependent on the solvent, temperature, substituent at the nitrogen, and the type or organometallic reactant used, and allows tailoring of both systems. A simple conversion of 6-substituted β,γ-unsaturated δ-thiolactams into their α,β-unsaturated isomers makes the above processes a highly versatile synthetic methodology to access 6-substituted 5,6-dihydropyridine-2-thiones—valuable Michael acceptors.

1. Introduction

The piperidine ring occurs in a number of pharmaceuticals and natural products. Due to the wide range of biological activities[1] associated with the piperidine moiety, the synthesis of multifunctionalized piperidines is still an attractive synthetic enterprise.[2] In the functionalization of the piperidine ring, 1,4-nucleophilic addition is often used to introduce a new functionality. This synthetic approach is readily employed in α,β-unsaturated 2-,[3] 3-[4] or 4-piperidinones.[5] Amongst the reactions leading to unsaturated piperidinones from the derivatives of pyridine, those using nucleophilic addition of organometallics to *N*-acyl activated 4-alkoxypyridines yielding unsaturated 4-piperidinones have been the most commonly undertaken,[6] while the straightforward nucleophilic addition of organometallic reagents to pyridones has enjoyed less interest. The addition of organolithium reagents to NH 2-pyridone (2-hydroxypyridine) has been described,[7] while an example of the addition of tertiary lithium compound to *N*-benzyl 2-pyridone is also known.[8] In both cases, different regioselectivities, respectively, 1,6- and 1,4-addition, were observed. Regioselective 1,4-addition of Grignard reagents to *N*-galactosyl-2-pyridone was performed after activation of the latter using triisopropylsilyltrifluoromethanesulfonate (TIPSOTF).[9] The intramolecular version of the 1,6-addition to 2-pyridone ring was also applied in the synthesis of (+)-cytisine and (±)-anagyrine.[10]

Recently, regioselective 1,6-allylation of nonactivated *N*-allyl 2-pyridones by using lithium allydibutylmagnesium 'ate' complex was described as the first step in the synthesis in quinolizidines.[11]

In the last decade, α,β-unsaturated piperidine-2-thiones have been recognized as Michael acceptors and several 1,4-addition reactions of C-, N- and S-nucleophiles, affording 4-substituted δ-thiolactams were reported.[12] Moreover, the interest in thiolactams still grows as their synthetic potential lies in the highly convertible character of the C=S group, which opens up possibilities of further functionalizations,[13] also after the Michael addition step.[12b,c]

Exploring the concept of functionalization of the piperidine ring via unsaturated δ-thiolactams, we have recently published two preliminary reports on the addition of organometallics to 1*H*-pyridine-2-thiones as simple precursors. One concerned the addition of *n*-BuLi to NH-substituted pyridine-2-thione (commercially available as 2-mercaptopyridine).[14] The addition product—3,6-dihydropyridine-2-thione—was further submitted to stereoselective synthesis of bicyclic 2-piperidinones, in which the DBU-catalyzed Michael addition of 2-nitro-propane was the key step and was performed without isolation of the intermediate 5,6-dihydropyridine-2-thione. The second communication reported the synthesis of unsaturated 4- and 6-allyl substituted δ-thiolactams by addition of lithium allyldibutylmagnesate to NH- and NMe substituted pyridine-2-thiones, respectively.[15]

In continuation of our ongoing program aimed at the development of a general approach to polysubstituted piperidines

Keywords: Pyridine-2-thiones; Dihydropyridine-2-thiones; Organolithium reagents; Lithium allyldibutylmagnesates; Regioselectivity; Addition.
* Tel.: +48 91 4494798; fax: +48 91 4494639; e-mail: sosnicki@ps.pl

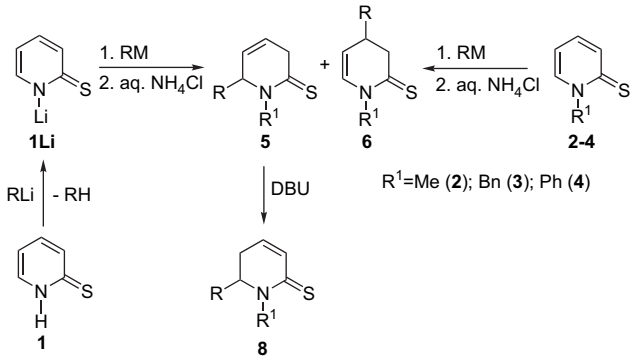
0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.09.029

from readily available starting materials, we now report a detailed study on the application of NH (**1**), NMe (**2**), NBn (**3**), and NPh (**4**) substituted derivatives of 1*H*-pyridine-2-thiones in the reaction with a broad spectrum of organolithium reagents (alkyl- allyl- and phenyl derivatives). The investigation of the allylation reaction was extended by the application of allyl-, 2-methylallyl-, and 3,3-dimethylallylmagnesium reagents comprising standard Grignard reagents and lithium allyldibutylmagnesates.[15] The application of the allylmagnesates aimed at checking their further usefulness in allylation reactions in comparison to standard allylmagnesium and allyllithium derivatives. Finally, as the double bond in β,γ-unsaturated thioamides was recognized to be easily moved from β,γ- to α,β-position[12b,16]and α,β-unsaturated δ-thiolactam (5,6-dihydropyridine-2-thiones) were proved to be valuable substrates in the 1,4-nucleophilic additions reactions, we present a simple synthesis of 6-substituted α,β-unsaturated precursors by simple isomerization of obtained 3,6-dihydropyridine-2-thiones, using DBU as base. So far, 5,6-dihydropyridine-2-thiones were obtained from acyclic ketothioamides,[17a,b] by thionation of appropriate 5,6-dihydropyridine-2-ones[12a] or by dehydration of saturated δ-thiolactams.[14,17c]

2. Results and discussion

2.1. Addition of organometallics to NH pyridine-2-thione (1)

At the first stage of our study, we investigated the NH-substituted 1*H*-pyridine-2-thione (**1**) in reaction with alkyl-, allyl- and phenyllithium reagents (Scheme 1). The results and conditions are presented in Table 1. RLi of 2–3 equiv, with respect to NH pyridine-2-thione (**1**), was required in order to obtain product **5** and/or **6** in optimum yields. The first equivalent of RLi converted **1** into the lithiated salt **1Li** and the second one induced the addition yielding 6- (**5**) or 4-addition products (**6**) (Scheme 1, Table 1). The lithium salt **1Li**, formed in THF, is colorless and the appearance of yellow color indicated that an excess of RLi was added and that the complete conversion of **1** into salt **1Li** took place. This titration-like effect allowed the use of the available (or the cheapest) organolithium reagent—mostly *n*-BuLi—as the first lithium reagent and thus minimized the use of the more expensive organolithium reagents. This operation was applied in the addition of ethyllithium and allyllithium derivatives (Table 1, entries 2 and 16–21, respectively).



Scheme 1.

Moreover, the color change was used to determine the molarity of the organolithium solutions.

Lithium reagents applied in this study exhibited various activities toward addition to NLi pyridine-2-thione (**1Li**). Amongst them, *t*-BuLi in pentane was the most reactive and due to its relatively short lifetime in ether at 0 °C[18] the reaction was initiated at a low temperature before subsequently raising the temperature. In the remaining cases the reactions were conducted at temperatures ranging from 0 to 20 °C and were quenched after few hours. The prolonged reaction time and the use of more than 3-fold excess of RLi reagent led to lower yields. With PhLi, the reaction required 18 h of stirring at 20 °C in Bu_2O as a solvent (Table 1, entry 15). The use of Et_2O resulted in lower yields (Table 1, entry 14). Surprisingly, MeLi was not reactive at all even when the reagent was used in a 6-fold excess (Table 1, entry 1). The allylation reactions proceeded easily upon treatment of **1Li** with allyllithiums or lithium allyldibutylmagnesates, providing 4-substituted isomers **6** in good yields (Table 1, entry 16, 18–21). (Lithium allyldibutylmagnesates were prepared simply by mixing 1 equiv of allylMgCl in THF and 2 equiv of *n*-BuLi in alkane.)[15] Allylmagnesium chloride was not reactive (Table 1, entry 17).

As far as regioselectivity is concerned the investigated reactions could be divided into three groups: the first group comprised the reactions with alkyllithium reagents (except isobutyllithium), which gave regioselectively 6-substituted addition products **5**, especially when the reactions were conducted in THF; the second group included the reactions with *t*-BuLi, PhLi, and isobutyllithium, performed in Et_2O or Bu_2O, which gave a mixture of 4- (**6**) and 6-substituted adducts (**5**). Allylation reactions belonging to the third group gave 4-allyl substituted adducts regioselectively. The different regioselectivity of allylation with respect to alkylation, observed in the case of lithium allyl- and 2-methylallyldibutylmagnesate reagents was proved to be the effect of Cope rearrangement (Scheme 2).[15] According to this process, the more thermodynamically stable 4-allyl substituted product forms from the primarily formed but less stable 6-allyl isomer. The evidence of the above was achieved by monitoring the reaction progress and by determination of the ratio of isomers **5/6** at several time intervals. Quenching the reaction after 0.5 h allowed the isolation of **5i** in 13% yield (Table 1, entry 18) and permitted a full spectroscopic analysis. The same effect seemed to be true for applications of allyllithiums. The formation of 6-substituted product was not observed when using 3,3-dimethylallyldibutylmagnesate, suggesting that the formation of 4-(1,1-dimethylallyl)-3,4-dihydropyridine-2-thione as a sole product (**6j**) was caused by steric effects (Table 1, entry 20).

As mentioned earlier, solvent was another factor affecting the regioselectivity. In general, the reactions performed in THF were the most regioselective, providing more amounts of 6-adducts, while those performed in Et_2O (Table 1, entry 5, 7, 9, and 10) and the one in toluene (Table 1, entry 6) were less selective.

In the case of *sec*-BuLi, the addition was not diastereoselective and provided products in 1:1 ratio of diastereoisomers (Table 1, entry 11).

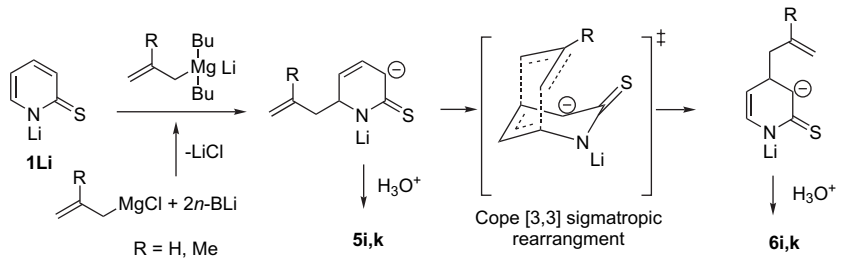
Table 1. Reaction conditions, ratios, and yields of **5/6** obtained in addition reactions of **1** with organolithium and organomagnesium reagents

Entry	RM		RM (equiv)	Solvent	Temp [°C]	Time [h]	Ratio of **5/6** in the crude mixture[a]	Ratio of **5/6** isolated	Conversion of **1**[a] [%]	Total yields of **5** and **6** [%]
1.	—Li		3–6	THF/cumene	20	24	—	—	0	0
2.	Li	**a**	1 BuLi 1.4	THF/Bu_2O/hexane	−5	2.5	99:1	99:1	>99	73
3.	Li		2.5	Bu_2O	0	1.5	94:6	95[d]:5	>99	61
4.	Li		3	THF/hexane	0–2	2	>99:1	98:2	95	73
5.	Li	**b**	2	Et_2O/hexane	0–2	2	90:10	92:8	93	63
6.	Li		2.3	Toluene	0 20	0.5 2	81:19	80:20	82	42
7.	Li[b]	**c**	2.8	Et_2O/hexane	0–2 20	0.25 2	75:25	78:22	69	37
8.	Li	**d**	3	THF/hexane	0–2	2.5	97:3	98:2	95	55
9.	Li		3	Et_2O/hexane	0–2	3	91: 9	90:10	71	37
10.	Li[b]	**e**	2.5	Et_2O/pentane	20	1	67:33	51:49	100	29
11.	Li[c]	**f**	3	THF/C_6H_{12}	0–2	1	98:2	>99:1	70	57
12.	Li	**g**	2.2	THF/pentane	−60 −60 to 0	0.3 1.25	97:3	98:2	86	50
13.	Li		2.2	Et_2O/pentane	−78 −78 to 20	1 1	63:37	65:35	100	83
14.	Li	**h**	2.1	Et_2O/Bu_2O	20	24	ca. 74:26	60:40	100	19
15.	Li		2	Bu_2O	20	18	ca. 54:46	48:52	58	31
16.	Li[e]		1 BuLi 1.3 AllylLi	THF/hexane	0–2	2	0:100	0:100	98	72
17.	MgCl	**i**	1 BuLi 1.3 AllylMgCl	THF/hexane	0 rt	5 24	—	—	0	0
18.	$MgBu_2Li$		1 BuLi 1.3 Allyl-$MgBu_2Li$	THF/hexane	0 0 rt rt rt	0.2 0.5 0.5 1.0 3.5	73:27 49:51 22:78 5:95 0:100	41:59 0:100	ca. 35 >99	31 80
19.	Li[e,f]	**j**	1 BuLi 1.3 3,3-dimethylallylLi	THF/hexane	0–2	2.5	0:100	0:100	100	60
20.	$MgBu_2Li$[f]		1 BuLi 1.3 3,3-dimethyl-allylMgBu$_2$Li	THF/hexane	0 rt	0.2 0.5	>1:99 >1:99	0:100	>99	65
21.	$MgBu_2Li$	**k**	1 BuLi 1.3 2-methyl-allylMgBu$_2$Li	THF/hexane	0 0 rt rt	0.2 1.0 2.0 3.0	90:10 70:30 6:94 0:100	0:100	>99	74

[a] Estimated using ^{1}H NMR spectroscopy.
[b] RLi obtained in the reaction of RI with 2 *t*-BuLi.[22]
[c] 1:1 mixture of diastereomers.
[d] Partly converted to α,β-unsaturated isomer.
[e] Allyllithium prepared from $AllylBu_3Sn$ (see Section 4).
[f] 1,1-Dimethylallyl substituent is in the product.

2.2. Addition of organometallics to *N*-substituted pyridine-2-thione 2–4

In general, the *N*-substituted 1*H*-pyridine-2-thiones **2**–**4** were characterized by a different type of reactivity and regioselectivity toward the organometallics tested in comparison than NH- substituted pyridine-2-thione **1** (Table 2, Scheme 1). Primary and secondary alkyllithium, and phenyllithium reagents were not sufficiently reactive to produce adducts. Only *n*-BuLi gave a 4-adduct in moderate yield in the



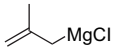
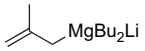
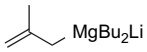
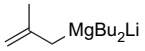
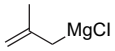
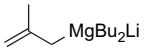
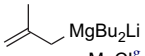
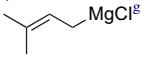
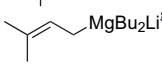
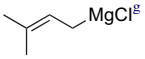
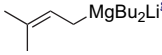
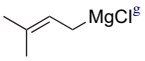
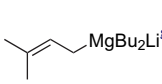
Scheme 2.

Table 2. Reaction conditions, ratios, and yields of **5/6** obtained in addition reaction of **2–4** with organolithium and organomagnesium reagents

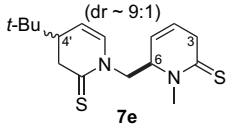
Entry	R^1	RM		RM (equiv)	Solvent	Temp [°C]	Time [min]	Ratio of **5/6** in the crude mixture[a]	Ratio of **5/6** isolated	Conversion **2–4**[a] [%]	Total yields of **5** and **6** [%]
1.	Bn	—Li		1.3	THF/Et_2O	−60 to rt	1.5	—	—	~10	0
2.	Me	Li		1.2	THF/hexane	0	60	Complex mixture	—	80	0
3.		Li		1.3	THF/hexane	−60	60	[b]	—	30	Traces
4.	Bn	Li	**l**	1.5	THF/hexane	0	30	20:80	0[c]:100	99	15
5.	Ph	Li	**m**	1.1	THF/hexane	0	30	>1:99	0:100	95	37
6.	Me[d]	Li	**n**	1.2	THF/hexane	−60	0.25	[b]	2:98	~80	35
7.	Bn	Li	**o**	1.2	THF/hexane	−60	0.25	1:99	0:100	>99	81
8.	Ph	Li	**p**	1.2	THF/hexane	−60	0.25	12:88	11:89	>99	83
9.	Bn	Li		1.3	Bu_2O/THF	−60	0.5	—	—	5	0
10.		Li[e]		1.2	THF/hexane	0	30	72:28	71:29	81	45
11.		Li[e]		1.2	THF/hexane	−70	30	95:5	95:5	95	86
12.	Me	MgCl	**q**	1.6	THF	0	40	96:4	94:6	88	64
13.		$MgBu_2Li$		1.05	THF/hexane	0	30	85:15	84:16	100	80
14.		$MgBu_2Li$		1.05	THF/hexane	−72	30	>99:1	100:0	85	75
15.		Li[e]		1.2	THF/hexane	0	15	56:44	56:44	>99	75
16.		Li		1.2	THF/hexane	−70	15	96:4	97:3	>99	87
17.	Bn	MgCl	**r**	1.6	THF	0	40	69:31	70:30	85	70
18.		$MgBu_2Li$		1.30	THF/hexane	0	30	68:32	67:33	100	79
19.		$MgBu_2Li$		1.10	THF/hexane	−72	30	97:3	96:4	100	88
20.		Li[e]		1.3	THF/hexane	0	30	15:85	14:86	92	69
21.		Li[e]		1.2	THF/hexane	−70	30	52:48	53:47	>99	91
22.	Ph	MgCl	**s**	1.5	THF	0	40	27:73[f]	30:70	98	68
23.		$MgBu_2Li$		1.1	THF/hexane	0	40	20:80[f]	28:72	99	85
24.		$MgBu_2Li$		1.25	THF/hexane	−72	30	71:24	73:27	99	96
25.		MgCl		1.5	THF	0	40	65:35	64:36	99	75
26.	Me	$MgBu_2Li$	**t**	1.2	THF/hexane	0	30	77:23	77:23	99	74
27.		$MgBu_2Li$		1.15	THF/hexane	−72	60	98:2	98:2	91	80

(*continued*)

Table 2. (*continued*)

Entry	R^1	RM		RM (equiv)	Solvent	Temp [°C]	Time [min]	Ratio of **5/6** in the crude mixture[a]	Ratio of **5/6** isolated	Conversion **2–4**[a] [%]	Total yields of **5** and **6** [%]
28.				1.4	THF	0	30	39:61	38:62	86	67
29.				1.05	THF/hexane	0	20	58:42	57:43	91	76
30.	Bn		**u**	1.1	THF/hexane	−45	45	84:16	84:16	100	90
31.				1.05	THF/hexane	−72	60	95:5	96:4	95	87
32.				1.5	THF	0	20	17:83	18:82	100	87
33.	Ph		**v**	1.05	THF/hexane	0	20	36:64	39:61	99	82
34.				1.1	THF/hexane	−72	30	66:34	68:32	91	76
35.				1.3	THF	0	60	3:97	3:97	87	79
36.	Me		**w**	1.2	THF/hexane	−72	30	4:96	4:96	90	80
37.				1.3	THF	0	60	>1:99	0:100	90	72
38.	Bn		**x**	1.3	THF/hexane	−72	15	>1:99	0:100	99	78
39.				1.3	THF	0	30	>1:99	0:100	>99	92
40.	Ph		**y**	1.2	THF/hexane	−72	15	>1:99	0:100	86	74

[a] Estimated using ^{1}H NMR spectroscopy.
[b] Traces of the dimeric product was detected by GC–MS.
[c] Product is present but could not be isolated in the pure state.
[d] By-product **7e** was isolated in 20% yield.



7e

[e] Allyllithium was prepared from AllylBu_3Sn (see Section 4).
[f] Could not be estimated with sufficient accuracy.
[g] 1,1-Dimethylallyl substituent is in the product.

reaction with NPh derivative **4** (Table 2, entry 5). *tert*-Butyllithium and all applied allylation reagents afforded products in satisfactory yield. However, amongst them, the NMe derivative gave lower yields in some cases (allyllithium 0 °C, Table 2, entry 10; *t*-BuLi −60 °C Table 2, entry 6) presumably due to the acidic character of the NCH_2 protons, which led to undesired side-reactions in the presence of strong bases (Table 2, entry 3, footnote b). In support of this, small amounts of dimer with an introduced *t*-Bu group were isolated from the products formed in the reaction between **2** and *t*-BuLi (Table 2, footnote, **7e**). High acidity of $CHsp^3$ group, adjacent to nitrogen was observed earlier when *N*-methyl 2-pyridone was treated with *n*-BuLi[19] and was also applied in functionalization of (−)-cytisine at NCH.[20]

Allylmagnesium chloride gave a positive result but only at 0 °C. At a lower temperature (ca. −40 °C) reaction did not occur. Allyllithium and lithium allyldibutylmagnesates exhibited similar reactivity and reacted well also at low temperatures, to give products **5** and **6** in good or very good yields, in general. It should be noted that lithium allyldibutylmagnesates exhibited lower basicity than allyllithum because it provided products **5q** and **6q** in good yield for NMe derivative **2** at 0 °C (Table 2, entry 13).

With respect to regioselectivity, the product distribution is opposite to that observed for NH- substituted pyridine-2-thione (**1**). The alkylation of *N*(alkyl, phenyl) substituted derivatives led mainly to 4-substituted adduct **6**, while their allylation led mostly to a greater amount of 6-substituted product **5**. The quantity of the latter increased in the sequence of NPh, NBn, NMe substituted derivatives and with decreasing temperature. Similarly to the reaction with NH pyridine-2-thione (**1**) the reaction of 3,3-dimethylallylmagnesiumchloride and the corresponding magnesate with **2–4** gave mainly 4-(1,1-dimethylallyl) substituted isomers

Table 3. Synthesis of 5,6-dihydropyridine-2-thiones **8**

Entry		R^1	R	DBU [equiv]	Time [h]	Yield **8** [%]
1.	**a**	H	Ethyl	0.1	0.5	81
2.	**b**	H	*n*-Butyl	0.3	1	80
3.	**c**	H	*n*-Pentyl	0.2	1	69
4.	**d**	H	*n*-Hexyl	0.3	1	66
5.	**e**	H	Isobutyl	0.1	0.7	71
6.	**f**	H	*sec*-Butyl[a]	0.2	2	72
7.	**g**	H	*tert*-Butyl	0.2	2.5	76
8.	**h**	H	Phenyl	0.2	0.5	70
9.	**i**	Me	Allyl	0.3	0.5	92
10.	**j**	Bn	Allyl	0.3	0.5	92
11.	**k**	Ph	Allyl	0.3	0.3	85
12.	**l**	Me	2-Methylallyl	0.3	0.5	83
13.	**m**	Bn	2-Methylallyl	0.3	0.5	95
14.	**n**	Ph	2-Methylallyl	0.3	0.3	93

[a] 1:1 mixture of diastereomers.

6w–y. This regioselectivity, caused probably by the steric effect, is independent of temperature and substituents at nitrogen.

Finally, we converted the obtained 6-substituted β,γ-unsaturated δ-thiolactams **5** into their α,β-unsaturated isomers **8**, using catalytic DBU in acetonitrile at rt (Table 3, Scheme 1). In contrast to the reactions of the analogous lactams, in which the equilibrium between the β,γ and α,β-unsaturated isomers does not permit exclusive isolation of the α,β-unsaturated isomer,[21] the isomerization of thiolactams **5** is complete after a few hours and gives the products **8** in good yield.

The structures of **8** and all regioisomeric products **5** and **6** separated easily by column chromatography were determined on the basis of 1D NMR (^{1}H, ^{13}C, and ^{13}C-DEPT) and 2D NMR (^{1}H, ^{1}H COSY, ^{13}C, and ^{1}H COSY) spectroscopy. ^{1}H NMR spectroscopy made it possible to differentiate both regioisomers. The chemical shifts (δ) of =CH protons were the main identification criteria. In the ^{1}H NMR spectra of 4-substituted regioisomers (**6**) signals for protons =CH-5 and =CH-6 appeared at separate chemical shifts ca. 5.4 ppm (as dd) and ca. 6.1 ppm (mainly as ddd), respectively, while in the ^{1}H NMR spectra of 6-substituted derivatives (**5**) protons =CH-4 and =CH-5 gave overlapped multiplets in the region of ca. 5.7–6.1 ppm.

3. Conclusion

We have described an efficient access to 6-substituted β,γ- and 4-substituted γ,δ-unsaturated piperidine-2-thiones obtained in the reaction between organolithium regents and NH, NMe, NBn, and NPh substituted pyridine-2-thiones. Although in some reactions the yields are not very high the reactions can be performed on a multigram scale and **1** as well as the majority of the lithium and allylmagnesium Grignard reagents used are commercially available. Allyllithium and especially the lithium allyldibutylmagnesate reagent were found to be the most useful.

In the field of allylation reactions the present study has illustrated the unprecedented worth of allyldibutylmagnesate as allylation reagents. Due to their simple preparation, availability, and reactivity similar to that of allyllithiums, it can be used instead of allyllithium, whose application is limited by less availability, higher cost, and toxicity of their often used precursors—allyltin compounds.

The regioselectivity of the addition, being dependent on the solvent, temperature, and substituent at the nitrogen, can be slightly tuned by changing these factors. As the regioselectivity depends on the type of organolithium reagent, the target synthesis of either 3,4- (**6**) or 3,6-dihydropyridine-2-thione (**5**) systems is also possible by the choice of the appropriate organolithium reactant.

Since organometallic reagents and pyridine-2-thiones **1–4** used in this synthetic procedure are readily available and the conversion of 6-substituted β,γ-unsaturated δ-thiolactams **5** into its α,β-unsaturated isomers **8** can be easily realized, the process described stands as a highly versatile synthetic methodology to access the 6-substituted δ-thiolactams being valuable Michael acceptors.

4. Experimental

4.1. General

Melting points were determined on a Boetius hot stage apparatus. ^{1}H and ^{13}C NMR spectroscopic measurements were performed on a Bruker DPX 400 spectrometer equipped with an 5 mm ^{1}H/BB—inverse probehead operating at 400.13 and 100.62 MHz. TMS was used as internal reference. Two-dimensional spectra were acquired using standard Bruker software. Mass spectra (70 eV) were recorded on an HP 6890 (Hewlett–Packard) GC–MS spectrometer equipped with a mass detector HP 5973. Silica gel (0.04–0.063 mm) purchased from Merck was used for preparative column chromatography. Elemental analyses were performed on EuroEA 3000 series, EuroVector CHNS-O Elemental Analyzer.

4.2. Compounds

Pyridine-2-thione **1**, *n*-BuLi (2.5 M in hexane), sec-BuLi (1.4 M in cyclohexane), *t*-BuLi (1.7 M in pentane), PhLi (2.0 M in Bu_2O), *n*-hexyllithium (2.3 M in hexane), allylMgCl (2.0 M in THF), and 2-methylallylMgCl (0.5 M in THF) were purchased from Aldrich. EtLi (1.7 M in Et_2O), MeLi (1.6 M in Et_2O), and *n*-BuLi (2.6 M in toluene) were purchased from Acros Organics. Not commercially available alkyllithiums were prepared from appropriate iodoalkanes and *t*-BuLi.[22] 3,3-Dimethylallylmagnesiumbromide was prepared as described earlier.[23] Solvents (THF, Et_2O, and toluene) were purified over sodium in argon atmosphere according to a standard procedure prior to use.

4.3. Synthesis of NMe (2), NBn (3), and NPh (4) derivatives of 1*H*-pyridine-2-thione (starting materials)

1*H*-Pyridine-2-thiones (**2–4**) were prepared from the corresponding 1*H*-pyridine-2-ones according to a standard procedure using Lawesson reagent in refluxing toluene (230 mL) in the molar ratio of 14.9:27.0 mmol (Lawesson reagent/pyridine-2-one). The oxygen–sulfur exchange was completed

after 0.5 h (established by TLC). Most of the solvent was distilled off in vacuo and the remaining mixture was twice chromatographed on silica gel: one run was performed using *n*-hexane/ethyl acetate (7:3) and the second run using $CHCl_3$/MeOH (98:2) as eluent. The obtained solids were crystallized from appropriate solvents.

4.3.1. 1-Methyl-1*H*-pyridine-2-thione (2). Yellow solid (3.14 g, 93%), mp 88–90 °C from *n*-hexane/ethyl acetate. IR (KBr pellet): ν=3064, 3044, 3008, 1620, 1538, 1486, 1424, 1410, 1188, 1144, 1124, 1114, 1056, 1024, 804, 756 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=3.99 (3H, s, NCH_3), 6.65 (1H, td, *J* 7.0, 1.5 Hz, CH-5), 7.21 (1H, ddd, *J* 8.6, 7.0, 1.5 Hz, CH-4), 7.67–7.72 (2H, m, CH-3, CH-6); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=46.0 (NCH_3), 113.4 (CH-5), 134.1 (CH-4), 136.1 (CH-2), 140.8 (CH-6), 180.4 (C-2); GC–MS (EI, 70 eV): *m*/*z*=125 (100, $M^{+\bullet}$), 97 (8), 81 (39), 80 (36). Found: C, 57.45; H, 5.62; N, 11.14; S, 25.72. C_6H_7NS requires: C, 57.56; H, 5.64; N, 11.19; S, 25.61%.

4.3.2. 1-Benzyl-1*H*-pyridine-2-thione (3). Yellow solid (5.33 g, 98%), mp 93–95 °C from *n*-hexane/ethyl acetate [lit. 85–87 °C benzene].[24] IR (KBr pellet): ν=3030, 2968, 1620, 1530, 1494, 1466, 1415, 1358, 1334, 1250, 1182, 1156, 1114, 1084, 1028, 824, 752, 738, 724, 697 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=5.81 (2H, s, NCH_2), 6.60 (1H, td, *J* 6.7, 1.5 Hz, CH-5), 7.15 (1H, ddd, *J* 8.7, 6.7, 1.7 Hz, CH-4), 7.29–7.40 (5H, m, C_6H_5), 7.56 (1H, dd, *J* 6.7, 1.7 Hz, CH-6), 7.75 (1H, d, *J* 8.7 Hz, CH-3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=58.7 (NCH_2), 113.6 (CH-5), 128.3, 129.0, 129.0, 135.1 (C_6H_5), 133.7 (CH-4), 136.4 (CH-2), 139.9 (CH-6), 181.0 (C-2); GC–MS (EI, 70 eV): *m*/*z*=201 (73, $M^{+\bullet}$), 168 (78), 124 (9), 91 (100), 79 (13), 65 (26). Found: C, 71.53; H, 5.58; N, 7.00; S, 16.00. $C_{12}H_{11}NS$ requires: C, 71.60; H, 5.51; N, 6.96; S, 15.93%.

4.3.3. 1-Phenyl-1*H*-pyridine-2-thione (4). Yellow solid (4.70 g, 93%), mp 103–105 °C from *n*-hexane/ethyl acetate [lit. 102–104 °C].[25] IR (KBr pellet): ν=3088, 3064, 3016, 1616, 1526, 1448, 1404, 1264, 1148, 768, 748, 694 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=6.70 (1H, td, *J* 6.8, 1.5 Hz, CH-5), 7.26 (1H, ddd, *J* 8.8, 6.8, 1.9 Hz, CH-4), 7.34 (2H, dd, *J* 7.8, 1.5 Hz, C_6H_5), 7.46–7.57 (3H, m, C_6H_5), 7.60 (1H, dd, *J* 6.8, 1.9 Hz, CH-6), 7.76 (1H, d, *J* 8.8 Hz, CH-3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=111.8 (CH-5), 125.6, 128.2, 128.7, 143.8 (C_6H_5), 133.4 (CH-4), 135.6 (CH-2), 139.8 (CH-6), 181.2 (C-2); GC–MS (EI, 70 eV): *m*/*z*=187 (46, $M^{+\bullet}$), 186 (100), 115 (6), 93 (6), 77 (10), 51 (12). Found: C, 70.53; H, 4.59; N, 7.60; S, 17.00. $C_{11}H_9NS$ requires: C, 70.55; H, 4.84; N, 7.48; S, 17.12%.

4.4. Procedure of addition of organolithium compounds to 1–4

To a cooled and stirred solution of 0.059 mol of 1*H*-pyridine-2-thiones (**1**–**4**) in dry solvent (see Tables 1 and 2) (100 mL) a portion of 0.059–0.177 mol of RLi solution (see Tables 1 and 2) was added via syringe over 5 min under argon (Notes 1 and 2). The mixture was stirred at the temperature and in the period indicated in Tables 1 and 2. After quenching with aqueous saturated NH_4Cl (25 mL), the water layer was extracted with ethyl acetate (2×150 mL) and the combined organic layers were dried over $MgSO_4$. Filtration, concentration in vacuo, and purification by flash column chromatography (silica gel, *n*-hexane/ethyl acetate) yielded **5** and **6**. Note 1: in the case of **1**, 0.059 mol of *n*-BuLi can be used instead of the first equivalent of RLi when THF was applied as solvent (Table 1). Note 2: allyllithiums were prepared by stirring the appropriate allyltributyltin compounds (1.0 equiv) with 1.0 equiv of *n*-BuLi at rt under argon over 30 min and were prepared prior to use.

4.5. Procedure of allylation of 1 by using lithium allyldibutylmagnesates

To a cooled and stirred solution of **1** (3.33 g, 0.03 mol) in dry THF (70 mL) at 0 °C a portion of 0.03 mol of *n*-BuLi solution in alkane was added via syringe over 5 min under argon. Simultaneously, in another Schlenk flask, 0.039 mol of allylMgCl or their allylic derivative in 20 cm^3 THF was kept under argon. *n*-BuLi (0.078 mol) was added via syringe at 0 °C over 5 min and the white suspension formed was stirred for 5 min. Subsequently, the suspension containing the lithium allyldibutylmagnesate was transferred to the solution of lithiated pyridine-2-thione via syringe. The resulting brown-orange solution was stirred for an appropriate temperature and time (Table 1). After quenching with aqueous saturated NH_4Cl (10 mL), the water layer was extracted with ethyl acetate (2×100 mL) and the combined organic layers were dried over $MgSO_4$. Filtration, concentration in vacuo, and purification by flash column chromatography (silica gel, *n*-hexane/ethyl acetate=8:2) yielded **6i**–**k** as a yellow solid, which was recrystallized from *n*-hexane.

4.6. Procedure of allylation of 2–4 by using lithium allyldibutylmagnesates

The procedure is the same as above but initial addition of *n*-BuLi is omitted. It means that pure pyridine-2-thiones **2**–**4** are applied for allylation.

4.7. Procedure of allylation of 2–4 by using standard allyl Grignard reagents

The procedure is the same as above but instead of lithium allyldibutylmagnesate a standard Grignard reagent is used.

4.7.1. 6-Ethyl-3,6-dihydro-1*H*-pyridine-2-thione (5a). Pale yellow solid, mp 72–74 °C from *n*-hexane. IR (KBr pellet): ν=3176 br, 3064 br, 2968, 2936, 2876, 1676, 1570, 1396, 1388, 1340, 1296, 1142, 1092, 958, 864, 812, 728, 690 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.95 (3H, t, *J* 7.5 Hz, CH_2CH_3), 1.61–1.80 (2H, m, CH_2CH_3), 3.46 (2H, ddd, *J* 4.9, 3.2, 1.7 Hz, CH_2-3), 4.00–4.08 (1H, m, CH-6), 5.72 (1H, dm, *J* 10.3 Hz, =CH-4), 5.79 (1H, dtd, *J* 10.3, 3.2, 1.7 Hz, =CH-5), 9.07 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=8.6 (CH_2CH_3), 28.9 (CH_2CH_3), 39.1 (CH_2-3), 56.2 (CH-6), 122.0, 123.4 (=CH-4, =CH-5), 198.8 (C-2); GC–MS (EI, 70 eV): *m*/*z*=141 (84, $M^{+\bullet}$), 112 (100), 78 (60), 67 (18). Found: C, 59.67; H, 7.96; N, 9.90; S, 22.83. $C_7H_{11}NS$ requires: C, 59.53; H, 7.85; N, 9.92; S, 22.70%.

4.7.2. 4-Ethyl-3,4-dihydro-1*H*-pyridine-2-thione (6a). Yellow oil. IR (film): ν=3204 br, 2964, 2924, 1500 br,

1320, 1144 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.94 (3H, t, J 7.3 Hz, CH_2CH_3), 1.37–1.50 (2H, m, CH_2CH_3), 2.28–2.39 (1H, m, CH-4), 2.75 (1H, dd, J 17.1, 9.8 Hz, CHH-3), 3.05 (1H, dd, J 17.1, 6.8 Hz, CHH-3), 5.42 (1H, dd, J 7.8, 3.9 Hz, =CH-5), 6.07 (1H, ddd, J 7.8, 4.4, 1.9 Hz, =CH-6), 9.23 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=10.9 (CH_2CH_3), 27.0 (CH_2CH_3), 32.1 (CH-4), 44.1 (CH_2-3), 115.5 (=CH-5), 123.6 (=CH-6), 200.4 (C-2); GC–MS (EI, 70 eV): m/z=141 (70, $M^{+\bullet}$), 112 (100), 78 (40), 67 (7); HRMS (EI) for $C_7H_{11}NS$: calculated 141.0612; found 141.0625.

4.7.3. 6-Butyl-3,6-dihydro-1*H*-pyridine-2-thione (5b). Pale yellow solid, mp 50–51 °C from *n*-hexane. IR (KBr pellet): ν=3156, 3044, 2956, 2940, 2860, 1562, 1390, 1328, 1148, 1116, 1096, 1076 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.85–0.95 (3H, m, CH_3), 1.28–1.40 (4H, m, 2×CH_2), 1.59–1.72 (2H, m CH_2), 3.43–3.47 (2H, m, CH_2-3), 4.00–4.06 (1H, m, CH-6), 5.70–5.79 (2H, m, =CH-4, =CH-5), 9.08 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=13.95 (CH_3), 22.5 (CH_2), 26.5 (CH_2), 35.7 (CH_2), 38.9 (CH_2-3), 55.4 (CH-6), 121.6, 123.9 (=CH-4, =CH-5), 198.8 (C-2); GC–MS (EI, 70 eV): m/z =169 (35, $M^{+\bullet}$), 136 (4), 112 (100), 78 (32). Found: C, 63.72; H, 8.90; N, 8.22; S, 19.03. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.7.4. 4-Butyl-3,4-dihydro-1*H*-pyridine-2-thione (6b). Pale yellow solid, mp 50–53 °C from *n*-hexane. IR (KBr pellet): ν=3192, 3140, 3000, 2952, 2920, 2856, 1522, 1364, 1336, 1300, 1144, 812, 740, 704 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.90 (3H, t, J ca. 7 Hz, CH_3), 1.25–1.46 (6H, m, 3×CH_2), 2.33–2.45 (1H, m, CH-4), 2.74 (1H, dd, J 16.9, 9.3 Hz, CHH-3), 3.03 (1H, dd, J 16.9, 6.9 Hz, CHH-3), 5.42 (1H, dd, J 7.6, 4.0 Hz, =CH-5), 6.06 (1H, ddd, J 7.6, 4.2, 1.7 Hz, =CH-6), 9.46 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.6, 28.5, 33.7 (3×CH_2), 30.5 (CH-4), 44.4 (CH_2-3), 115.9 (=CH-5), 123.5 (=CH-6), 200.2 (C-2); GC–MS (EI, 70 eV): m/z=169 (32, $M^{+\bullet}$), 136 (4), 126 (5), 112 (100), 78 (26). Found: C, 63.72; H, 8.90; N, 8.22; S, 19.03. $C_9H_{15}NS$ requires: C, 63.71; H, 8.79; N, 8.33; S, 19.11%.

4.7.5. 6-Pentyl-3,6-dihydro-1*H*-pyridine-2-thione (5c). Yellow oil. IR (film): ν=3172, 3052, 2924, 2856, 1672, 1556, 1462, 1396, 1334, 1136, 1114 cm^{-1}; ^1H NMR (300.1 MHz, $CDCl_3$): δ=0.76 (3H, t, J 6.4 Hz, CH_3), 1.17 (6H, br s, 3×CH_2), 1.45–1.57 (2H, m, CH_2), 3.29–3.36 (2H, br s, CH_2-3), 5.61 (2H, br s, =CH-4, =CH-5), 9.00 (1H, br s, NH); ^{13}C NMR (60.1 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.5, 24.1, 31.5, 35.9 (4×CH_2), 38.9 (CH_2-3), 55.4 (CH-6), 121.5, 123.9 (=CH-4, =CH-5), 198.7 (C-2); GC–MS (EI, 70 eV): m/z=183 (33, $M^{+\bullet}$), 182 (21), 150 (19), 124 (6), 112 (100), 78 (29);. HRMS (EI) for $C_{10}H_{17}NS$: calculated 183.1082; found 141.1089.

4.7.6. 4-Pentyl-3,4-dihydro-1*H*-pyridine-2-thione (6c). Yellow oil. IR (Nujol): ν=3188, 3136, 2928, 2852, 1656, 1522, 1414, 1366, 1320, 1144, 808, 736, 704 cm^{-1}; ^1H NMR (300.1 MHz, $CDCl_3$): δ=0.81 (3H, t, J 7.1 Hz, CH_3), 1.12–1.39 (8H, m, 4×CH_2), 2.23–2.39 (1H, m, CH-4), 2.66 (1H, dd, J 16.9, 6.9 Hz, CHH-3), 2.96 (1H, dd, J 16.9, 6.9 Hz, CHH-3), 5.34 (1H, dd, J 7.6, 4.0 Hz, =CH-5), 5.99 (1H, ddd, J 7.6, 4.3, 1.8 Hz, =CH-6), 9.58 (1H, br s, NH); ^{13}C NMR (60.1 MHz, $CDCl_3$): δ=14.0 (CH_3), 24.1, 30.5, 31.7, 33.9 (4×CH_2), 31.5 (CH-4), 44.4 (CH_2-3), 115.9 (=CH-5), 123.5 (=CH-6), 200.1 (C-2); GC–MS (EI, 70 eV): m/z=183 (50, $M^{+\bullet}$), 150 (14), 112 (100), 78 (43); HRMS (EI) for $C_{10}H_{17}NS$: calculated 183.1082; found 141.1079.

4.7.7. 6-Hexyl-3,6-dihydro-1*H*-pyridine-2-thione (5d). Yellow oil. IR (film): ν=3180, 3044, 2924, 2856, 1672, 1560, 1464, 1396, 1334, 1114 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.88 (3H, t, J 6.9 Hz, CH_3), 1.24–1.41 (m, 8H, 4×CH_2), 1.56–1.72 (2H, m, CH_2), 3.42–3.47 (2H, m, CH_2-3), 4.00–4.11 (1H, m, CH-6), 5.70–5.80 (2H, m, =CH-4, =CH-5), 9.19 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.5, 24.3, 29.0, 31.6, 36.0 (5×CH_2), 38.4 (CH_2-3), 55.3 (CH-6), 121.5 (=CH-4), 123.9 (=CH-5), 198.6 (C-2); GC–MS (EI, 70 eV): m/z=197 (61, $M^{+\bullet}$), 196 (53), 164 (52), 126 (12), 112 (100), 78 (41), 67 (9), 41 (11). Found: C, 67.08; H, 9.90; N, 7.20; S, 16.03. $C_9H_{15}NS$ requires: C, 66.95; H, 9.70; N, 7.10; S, 16.25%.

4.7.8. 4-Hexyl-3,4-dihydro-1*H*-pyridine-2-thione (6d). Pale yellow solid, mp 54–57 °C from *n*-hexane. IR (KBr pellet): ν=3196, 3144, 3000, 2956, 2924, 2856, 1522, 1360, 1144, 812, 736 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.88 (3H, t, J 7.0 Hz, CH_3), 1.22–1.46 (10H, m, 5×CH_2), 2.33–2.44 (1H, m, CH-4), 2.74 (1H, dd, J 16.9, 9.4 Hz, CHH-3), 3.03 (1H, dd, J 16.9, 6.9 Hz, CHH-3), 5.41 (1H, dd, J 7.5, 4.0 Hz, =CH-5), 6.06 (1H, ddd, J 7.5, 4.1, 1.6 Hz, =CH-6), 9.41 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.6, 26.3, 29.2, 31.7, 34.0 (5×CH_2), 30.5 (CH-4), 44.4 (CH_2-3), 115.9 (=CH-5), 123.5 (=CH-6), 200.3 (C-2); GC–MS (EI, 70 eV): m/z=197 (61), 196 (53), 164 (52), 126 (12), 112 (100), 78 (41), 67 (9), 41 (11). Found: C, 66.79; H, 9.90; N, 7.12; S, 16.30. $C_9H_{15}NS$ requires: C, 66.95; H, 9.70; N, 7.10; S, 16.25%.

4.7.9. 6-Isobutyl-3,6-dihydro-1*H*-pyridin-2-thione (5e). Pale yellow solid, mp 41–43 °C from *n*-hexane. IR (KBr pellet): ν=3156, 2952, 2916, 2868, 1672, 1558, 1396, 1320, 1176, 1140, 846, 820, 720, 712 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.96 (6H, d, J 6.6 Hz, 2×CH_3), 1.42–1.59 (2H, m, 6-CH_2), 1.79 (1H, heptet, J 6.6 Hz, $CH(CH_3)_2$), 3.44–3.48 (2H, m, CH_2-3), 4.00–4.10 (1H, m, CH-6), 5.71–5.80 (2H, m, =CH-4, =CH-5), 8.84 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.4, 22.8 (2×CH_3), 24.3 ($CH(CH_3)_2$), 38.9 (CH_2-3), 45.4 (6-CH_2), 53.7 (CH-6), 121.2, 124.2 (=CH-4, =CH-5), 198.7 (C-2); GC–MS (EI, 70 eV): m/z=169 (52, $M^{+\bullet}$), 112 (100), 78 (26). Found: C, 63.80; H, 8.90; N, 8.20; S, 19.06. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.7.10. 4-Isobutyl-3,4-dihydro-1*H*-pyridine-2-thione (6e). Pale yellow solid, mp 52–53 °C from *n*-hexane. IR (KBr pellet): ν=3200, 3148, 2956, 2896, 1516, 1368, 1350, 1308, 1142, 918, 740, 706 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.89 (3H, d, J 6.5 Hz, CH_3), 0.90 (3H, d, J 6.5 Hz, CH_3), 1.21 (1H, dt, J 13.6, 7.4 Hz, 3-CHH), 1.31 (1H, dt, J 13.6, 7.2 Hz, 3-CHH), 1.69 (1H,

heptet, *J* 6.8 Hz, $CH(CH_3)_2$), 2.41–2.53 (1H, m, CH-4), 2.71 (1H, dd, *J* 16.8, 9.2 Hz, C*H*H-3), 3.02 (1H, dd, *J* 16.8, 6.7 Hz, CH*H*-3), 5.42 (1H, dd, *J* 7.5, 4.0 Hz, =CH-5), 6.06 (1H, ddd, *J* 7.5, 4.2, 1.5 Hz, =CH-6), 9.43 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.5, 22.5 (2×CH_3), 24.7 (*C*H$(CH_3)_2$), 28.2 (CH-4), 43.0 (4-CH_2), 44.6 (CH_2-3), 116.0 (=CH-5), 123.5 (=CH-6), 200.1 (C-2); GC–MS (EI, 70 eV): *m*/*z*=169 (42, $M^{+\bullet}$), 112 (100), 78 (30). Found: C, 63.69; H, 8.99; N, 8.19; S, 19.00. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.7.11. 6-*sec*-Butyl-3,6-dihydro-1*H*-pyridine-2-thione (5f). Mixture of diastereomers=1:1, yellow oil. IR (film): ν=3184 br, 3052, 2960, 2932, 2876, 1672, 1564, 1460, 1398, 1328, 1116 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=0.88 (3H, d, *J* 6.8 Hz, C*H*$_3$CH), 0.91 (3H, d, *J* 6.9 Hz, C*H*$_3$CH), 0.94 (3H, t, *J* 7.4 Hz, C*H*$_3$CH$_2$), 0.95 (3H, t, *J* 7.4 Hz, C*H*$_3$CH$_2$), 1.15–1.29 (2H, m, 2×C*H*HCH$_3$), 1.40–1.53 (2H, m, 2×CH*H*CH$_3$), 1.64–1.81 (2H, m, 2×C*H*CH$_3$), 3.42–3.48 (4H, m, 2×CH_2-3), 3.99–4.07 (2H, br s, 2×CH-6), 5.67–5.86 (4H, m, 2×=CH-4, 2×=CH-5), 9.05 (1H, br s, NH), 9.22 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=11.9, 11.9 (2×*C*H$_3$CH$_2$), 14.0, 14.1 (2×*C*H$_3$CH), 24.9 25.1 (2×*C*H$_2$CH$_3$), 39.2, 39.3 (2×CH_2-3), 40.4, 40.6 (2×*C*HCH$_3$), 59.7, 59.7 (2×CH-6), 121.3, 122.4, 122.5, 122.9 (2×=CH-4, 2×=CH-5), 198.9, 199.4 (2×C-2); GC–MS (EI, 70 eV): *m*/*z*=169 (54), 112 (100), 78 (38). Found: C, 63.76; H, 8.99; N, 8.40; S, 19.03. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.7.12. 6-*tert*-Butyl-3,6-dihydro-1*H*-pyridine-2-thione (5g). Pale yellow solid, mp 136–138 °C from *n*-hexane/ethyl acetate. IR (KBr pellet): ν =3140, 3004, 2960, 1526, 1360, 1140, 914, 812, 762, 732, 688 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=0.98 (9H, s, 3×CH_3), 3.38 (1H, ddd, *J* 23.2, 4.7, 0.7 Hz, C*H*H-3), 3.53 (1H, ddd, *J* 23.3, 3.9, 2.8 Hz, CH*H*-3), 3.64–3.68 (1H, m, CH-6), 5.81–5.90 (2H, m, =CH-4, =CH-5), 8.47 (br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=25.6 (C(*C*H$_3$)$_3$), 37.4 (*C*(CH$_3$)$_3$), 39.3 (CH_2-3), 64.7 (CH-6), 121.7, 123.2 (=CH-4, =CH-5), 199.9 (C-2); GC–MS (EI, 70 eV): *m*/*z*=169 (54, M^+), 113 (35), 112 (100), 80 (22), 78 (32), 57 (12), 41 (11). Found: C, 63.81; H, 8.79; N, 8.21; S, 18.88. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.7.13. 4-*tert*-Butyl-3,4-dihydro-1*H*-pyridine-2-thione (6g). Pale yellow solid, mp 66–68 °C from *n*-hexane/ethyl acetate. IR (KBr pellet): ν=3180, 3060, 2964, 2872, 1668, 1554, 1394, 1334, 1112, 972, 922, 818, 784, 734 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=0.92 (9H, s, 3×CH_3), 2.17 (1H, dddd, *J* 9.0, 7.9, 4.1, 2.0 Hz, CH-4), 2.92 (1H, dd, *J* 17.3, 9.0 Hz, C*H*H-3), 3.01 (1H, dd, *J* 17.3, 7.9 Hz, CH*H*-3), 5.44 (1H, dd, *J* 7.8, 4.1 Hz, =CH-5), 6.14 (1H, ddd, *J* 7.8, 4.3, 2.0 Hz, =CH-6), 9.44 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=26.8 (C(*C*H$_3$)$_3$), 33.4 (*C*(CH$_3$)$_3$), 40.5 (CH_2-3), 41.1 (CH-4), 112.8 (=CH-5), 124.2 (=CH-6), 201.0 (C-2); GC–MS (EI, 70 eV): *m*/*z*=169 (50, M^+), 113 (40), 112 (100), 80 (24), 78 (28), 57 (12), 41 (11). Found: C, 63.78; H, 9.01; N, 8.26; S, 19.00. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.7.14. 6-Phenyl-3,6-dihydro-1*H*-pyridine-2-thione (5h). Pale yellow solid, mp 125–128 °C from *n*-hexane/ethyl acetate. IR (KBr pellet): ν=3144 br, 3056, 2968, 1672, 1564, 1328, 1124, 840, 740, 704, 684 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=3.44–3.63 (2H, m, CH_2-3), 5.02–5.07 (1H, m, CH-6), 5.78–5.87 (2H, m, =CH-4, =CH-5), 7.22–7.28 (2H, m, C_6H_5), 7.31–7.44 (3H, m C_6H_5), 8.99 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=38.6 (CH_2-3), 59.6 (CH-6), 121.1 (=CH-4), 123.8 (=CH-5), 127.2, 128.7, 129.2, 139.2 (C_6H_5), 197.9 (C-2); GC–MS (EI, 70 eV): *m*/*z*=189 (100), 188 (33), 156 (23), 147 (16), 130 (39), 129 (60), 128 (34), 115 (37), 112 (33), 104 (11), 91 (11), 78 (16), 77 (21), 51 (13). Found: C, 69.89; H, 5.70; N, 7.45; S, 17.01. $C_{11}H_{11}NS$ requires: C, 69.80; H, 5.86; N, 7.40; S, 16.94%.

4.7.15. 4-Phenyl-3,4-dihydro-1*H*-pyridine-2-thione (6h). Orange semi-solid. IR (KBr pellet): ν=3200 br, 1646, 1494, 1320, 1138, 760, 698 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=3.06 (1H, dd, *J* 17.1, 9.8 Hz, C*H*H-3), 3.29 (1H, dd, *J* 17.1, 7.3 Hz, CH*H*-3), 3.65–3.72 (1H, m, CH-4), 5.55 (1H, dd, *J* 7.6, 4.5 Hz,=CH-5), 6.22 (1H, ddd, *J* 7.6, 4.4, 1.9 Hz, =CH-6), 7.19–7.23 (2H, m, C_6H_5), 7.30–7.35 (2H, t, *J* 7.6 Hz, C_6H_5), 7.45 (1H, t, *J* 7.5 Hz, C_6H_5), 9.63 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=36.9 (CH-4), 46.4 (CH_2-3), 114.2 (=CH-5), 124.4 (=CH-6), 127.1, 128.9, 129.6, 142.2 (C_6H_5), 199.1 (C-2); GC–MS (EI, 70 eV): *m*/*z*=189 (100, $M^{+\bullet}$), 188 (65), 156 (21), 130 (68), 115 (25), 103 (12), 91 (10), 78 (13), 77 (15), 51 (8). Found: C, 69.77; H, 5.79; N, 7.33; S, 16.99. $C_{11}H_{11}NS$ requires: C, 69.80; H, 5.86; N, 7.40; S, 16.94%.

4.7.16. 6-Allyl-3,6-dihydro-1*H*-pyridine-2-thione (5i). Yellow oil. IR (film): ν=3168, 3048, 1558, 1392, 1332, 1128, 922 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=2.34 (1H, dt, *J* 14.0, 7.1 Hz, C*H*H-3), 2.42–2.50 (1H, m, CH*H*-3), 3.44–3.48 (2H, m, 6-CH_2), 4.42–4.12 (1H, m, CH-6), 5.18–5.26 (2H, m, =CH_2), 5.70–5.82 (3H, m, =CH-4, =CH-5, =CH), 8.84 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=39.0 (6-CH_2), 40.4 (CH_2-3), 54.5 (CH-6), 120.3 (=CH_2), 122.0, 123.3, 131.9 (=CH-4, =CH-5, =CH), 199.04 (C-2); GC–MS (EI, 70 eV): *m*/*z*=153 (M^+, 49), 112 (100), 78 (46). Found: C, 62.79; H, 7.09; N, 9.25; S, 21.14. $C_8H_{11}NS$ requires: C, 62.70; H, 7.24; N, 9.14; S, 20.92%.

4.7.17. 4-Allyl-3,4-dihydro-1*H*-pyridine-2-thione (6i). Pale yellow solid, mp 53–55 °C from *n*-hexane. IR (KBr pellet): ν=3188 br, 3144 br, 2996, 1640, 1522, 1436, 1404, 1364, 1324, 1300, 1140, 1106, 1056, 992, 976, 936, 914, 812, 742, 708 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=2.15 (2H, t, *J* 7.1 Hz, 4-CH_2), 2.44–2.56 (1H, m, CH-4), 2.77 (1H, dd, *J* 17.0, 9.7 Hz, C*H*H-3), 3.02 (1H, dd, *J* 17.0, 6.9 Hz, CH*H*-3), 5.06–5.13 (2H, m, =CH_2), 5.41 (1H, dd, *J* 7.5, 3.8 Hz, =CH-5), 5.66–5.79 (1H, m, =CH), 6.09 (1H, ddd, *J* 7.5, 4.3, 1.8 Hz, CH-6), 9.72 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=30.2 (CH-4), 38.1 (4-CH_2), 43.9 (CH_2-3), 114.9 (=CH-5), 117.8 (=CH_2), 123.8 (=CH-6), 134.6 (=CH), 199.9 (C-2); GC–MS (EI, 70 eV): *m*/*z*=153 (33, M+$^{\bullet}$), 112 (100), 78 (46). Found: C, 62.64; H, 7.40; N, 9.05; S, 21.35. $C_8H_{11}NS$ requires: C, 62.70; H, 7.24; N, 9.14; S, 20.92%.

4.7.18. 4-(1,1-Dimethylallyl)-3,4-dihydro-1*H*-pyridine-2-thione (6j). Pale yellow solid, mp 58–60 °C from *n*-hexane.

IR (KBr pellet): ν=3152 br, 3004, 2964, 1526, 1412, 1366, 1324, 1138, 912, 766 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.01 (6H, s, 2×CH_3), 2.24–2.32 (1H, m CH-4), 2.88 (1H, dd, *J* 17.4, 9.2 Hz, C*H*H-3), 2.98 (1H, dd, *J* 17.4, 7.9 Hz, CH*H*-3), 4.98–5.08 (2H, m, =CH_2), 5.41 (1H, dd, *J* 7.8, 4.0 Hz, =CH-5), 5.71 (1H, dd, *J* 17.4, 10.8 Hz, =CH), 6.13 (1H, ddd, *J* 7.7, 4.3, 1.9 Hz, =CH-6), 9.44 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=23.6, 23.7 (2×CH_3), 39.5 (CH-4), 40.0 (C(*C*H_3)$_3$), 40.4 (CH_2-3), 112.1 (=CH-5), 112.9 (=CH_2), 124.4 (=CH-6), 145.4 (=CH), 200.7 (C-2); GC–MS (EI, 70 eV): *m*/*z*=181 (18, M^+), 112 (100), 78 (30). Found: C, 66.19; H, 8.40; N, 7.75; S, 17.71. $C_{10}H_{15}NS$ requires: C, 66.25; H, 8.34; N, 7.73; S, 17.69%.

4.7.19. 4-(2-Methyl-allyl)-3,4-dihydro-1*H*-pyridine-2-thione (6k). Pale yellow solid, mp 51–53 °C from *n*-hexane. IR (KBr pellet): ν=3148 br, 3000, 1648, 1526, 1436, 1362, 1324, 1140, 932, 976, 896, 812, 742, 720 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.71 (3H, s, CH_3), 2.03–2.15 (2H, m, 4-CH_2), 2.55–2.66 (1H, m, CH-4), 2.73 (1H, dd, *J* 16.8, 9.7 Hz, C*H*H-3), 3.00 (1H, dd, *J* 16.8, 6.6 Hz, CH*H*-3), 4.74 (1H, br s, =C*H*H), 4.85 (1H, br s, =CH*H*), 5.41 (1H, dd, *J* 7.6, 3.8 Hz, =CH-5), 6.08 (1H, ddd, *J* 7.6, 4.3, 1.8 Hz, =CH-6), 9.52 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.1 (CH_3), 28.4 (CH-4), 42.0 (4-CH_2), 44.0 (CH_2-3), 113.4 (=CH-5), 115.3 (=CH_2), 123.7 (=CH-6), 141.7 (=*C*CH_3), 199.9 (C-2); GC–MS (EI, 70 eV): *m*/*z*=167 (M^+, 17); 112 (100), 78 (58). Found: C, 64.49; H, 7.69; N, 8.44; S, 19.04. $C_9H_{13}NS$ requires: C, 64.62; H, 7.83; N, 8.37; S, 19.17%.

4.7.20. 1-Benzyl-4-butyl-3,4-dihydro-1*H*-pyridine-2-thione (6l). Yellow oil. IR (KBr pellet): ν=3060, 2924, 1496, 1450, 1424, 1384, 1156, 1106, 948, 726, 696 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.88 (3H, t, *J* 7.1 Hz, CH_3), 1.24–1.41 (6H, m, 3×CH_2), 2.32–2.43 (1H, m, CH-4), 2.92 (1H, dd, *J* 16.4, 9.5 Hz, C*H*H-3), 3.22 (1H, dd, *J* 16.4, 6.6 Hz, CH*H*-3), 5.32 (1H, d, *J* 14.9 Hz, NC*H*H), 5.37 (1H, d, *J* 14.9 Hz, NCH*H*), 5.45 (1H, dd, *J* 7.7, 4.2 Hz, =CH-5), 6.13 (1H, dd, *J* 7.7, 5.7 Hz, =CH-6), 7.25–7.36 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.6, 28.5, 33.4 (3×CH_2), 30.6 (CH-4), 47.2 (CH_2-3), 55.4 (NCH_2), 118.0 (=CH-5), 127.6, 127.8, 128.7, 135.6 (C_6H_5), 128.0 (=CH-6), 198.6 (C-2); GC–MS (EI, 70 eV): *m*/*z*=259 (37, $M^{+\bullet}$), 226 (11), 202 (45), 168 (22), 91 (100), 65 (9). Found: C, 73.98; H, 8.35; N, 5.29; S, 12.29. $C_{16}H_{21}NS$ requires: C, 74.08; H, 8.16; N, 5.40; S, 12.36%.

4.7.21. 4-Butyl-1-phenyl-3,4-dihydro-1*H*-pyridine-2-thione (6m). Yellow oil. IR (film): ν=2956, 2924, 2868, 2856, 1596, 1492, 1404, 1356, 1152, 764, 692 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.92 (3H, t, *J* 7.2 Hz, CH_3), 1.30–1.52 (6H, m, 3×CH_2), 2.45–2.55 (1H, m, CH-4), 3.03 (1H, dd, *J* 16.3, 9.3 Hz, C*H*H-3), 3.30 (1H, ddd, *J* 16.3, 6.3, 0.8 Hz, CH*H*-3), 5.54 (1H, dd, *J* 7.6, 4.1 Hz, =CH-5), 6.25 (1H, dd, *J* 7.6, 1.2 Hz, =CH-6), 7.26 (2H, dd, *J* 8.3, 1.3 Hz, C_6H_5), 7.37 (1H, tt, *J* 7.5, 1.3 Hz, C_6H_5), 7.45 (2H, tt, *J* 7.3, ca. 1.5 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.7, 28.6, 33.0 (3×CH_2), 30.8 (CH-4), 47.7 (CH_2-3), 116.6 (=CH-5), 126.9, 129.5, 130.0, 144.5 (C_6H_5), 128.3 (=CH-6), 200.1 (C-2); GC–MS (EI, 70 eV): *m*/*z*=245 (24, $M^{+\bullet}$), 244 (30), 188 (100), 156 (7), 130 (8), 104 (8), 77 (28), 51 (9). Found: C, 73.35; H, 7.92; N, 5.82; S, 12.93. $C_{15}H_{19}NS$ requires: C, 73.42; H, 7.80; N, 5.71; S, 13.07%.

4.7.22. 4-*tert*-Butyl-1-methyl-3,4-dihydro-1*H*-pyridine-2-thione (6n). Yellow oil. IR (film): ν=2960, 1476, 1378, 1126, 1138, 1026 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.91 (9H, s, C(C*H*$_3$)$_3$), 3.01 (1H, dd, *J* 16.8, 9.5 Hz, C*H*H-3), 3.12 (1H, dd, *J* 16.8, 7.4 Hz, CH*H*-3), 3.48 (3H, s, NCH_3), 5.48 (1H, dd, *J* 12.0, 7.8 Hz, =CH-5), 6.22 (1H, dd, *J* 7.8, 1.9 Hz, =CH-6); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=26.8 (C(*C*H_3)$_3$), 32.9 (*C*(CH$_3$)$_3$), 41.2 (CH-4), 41.7 (NCH_3), 42.8 (CH_2-3), 114.6 (=CH-5), 130.4 (=CH-6), 198.4 (C-2); GC–MS (EI, 70 eV): *m*/*z*=183 (M^+, 41), 126 (100), 111 (10), 94 (30). Found: C, 65.55; H, 9.30; N, 7.51; S, 17.54%. $C_{10}H_{17}NS$ requires: C, 65.52; H, 9.35; N, 7.64; S, 17.49%.

4.7.23. 1-Benzyl-4-*tert*-butyl-3,4-dihydro-1*H*-pyridine-2-thione (6o). Yellow oil. IR (film): ν=3064, 2960, 1460, 1452, 1384, 1156, 1108, 944 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.89 (9H, s, C(C*H*$_3$)$_3$), 2.12–2.19 (1H, m, CH-4), 3.07 (1H, dd, *J* 16.8, 9.6 Hz, C*H*H-3), 3.20 (1H, dd, *J* 16.8, 7.3 Hz, CH*H*-3), 5.27 (1H, d, *J* 14.8 Hz, NC*H*H), 5.39 (1H, d, *J* 14.8 Hz, NCH*H*), 5.47 (1H, dd, *J* 8.0, 3.7 Hz, =CH-5), 6.20 (1H, ddd, *J* 8.0, 2.1, 0.5 Hz, =CH-6), 7.25–7.37 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=26.9 (C(*C*H_3)$_3$), 33.0 (*C*(CH$_3$)$_3$), 41.2 (CH-4), 43.3 (CH_2-3), 55.4 (NCH_2), 115.0 (=CH-5), 127.8, 127.9, 128.7, 135.5 (C_6H_5), 128.7 (=CH-6), 199.2 (C-2); GC–MS (EI, 70 eV): *m*/*z*=259 (M^+, 36), 202 (48), 170 (16), 112 (7), 91 (100), 65 (8). Found: C, 74.16; H, 8.00; N, 5.31; S, 12.54. $C_{15}H_{17}NS$ requires: C, 74.08; H, 8.16; N, 5.40; S, 12.36%.

4.7.24. 4-*tert*-Butyl-1-phenyl-3,4-dihydro-1*H*-pyridine-2-thione (6p). Yellow solid, mp 57–58 °C from *n*-hexane. IR (KBr pellet): ν=2960, 2816, 1646, 1596, 1492, 1418, 1360, 1154, 760, 736, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.99 (9H, s, C(C*H*$_3$)$_3$), 2.27 (1H, tdd, *J* 7.8, 4.5, 1.8 Hz, CH-4), 3.26 (2H, d, *J* 7.8 Hz, CH_2-3), 5.56 (1H, ddt, *J* 7.8, 4.5, ca. 0.6 Hz, =CH-5), 6.34 (1H, dd, *J* 7.8, 1.8 Hz, =CH-6), 7.24 (2H, dd, *J* 8.7, 1.6 Hz, C_6H_5), 7.37 (1H, tt, *J* 7.6, 1.2 Hz, C_6H_5), 7.43–7.48 (2H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=27.0 (C(*C*H_3)$_3$), 33.4 (*C*(CH$_3$)$_3$), 41.4 (CH-4), 43.8 (CH_2-3), 113.4 (=CH-5), 126.8, 128.3, 129.5, 144.5 (C_6H_5), 130.7 (=CH-6), 200.7 (C-2); GC–MS (EI, 70 eV): *m*/*z*=245 (M^+, 63), 189 (57), 188 (100), 186 (33), 156 (42), 130 (12), 77 (26). Found: C, 73.46; H, 7.88; N, 5.67; S, 12.99. $C_{15}H_{19}NS$ requires: C, 73.42; H, 7.80; N, 5.71; S, 13.07%.

4.7.25. 6-Allyl-1-methyl-3,6-dihydro-1*H*-pyridine-2-thione (5q). Pale yellow oil. IR (film): ν=3076, 3044, 2976, 2932, 1678, 1640, 1516, 1432, 1392, 1350, 1328, 1230, 1128, 1082, 996, 922 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=2.42–2.58 (2H, m, 6-CH_2), 3.46 (1H, br d, *J* ca. 22.7 Hz, C*H*H-3), 3.53 (3H, s, NCH_3), 3.72 (1H, dt, *J* 22.7, ca. 3.6 Hz, CH*H*-3), 4.16 (1H, septet, *J* 3.5 Hz, CH-6), 5.13–5.21 (2H, m, =CH_2), 5.64–5.7 (1H, m, =CH), 5.79–5.89 (2H, m, =CH-4, =CH-5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=38.1 (6-CH_2), 41.7 (CH_2-3), 41.8

(NCH_3), 62.6 (CH-6), 120.0 (=CH_2), 123.1, 124.0, 131.2 (=CH-4, =CH-5, =CH), 196.7 (C-2); GC–MS (EI, 70 eV): *m*/*z*=167 (M^+, 57), 134 (9), 126 (100), 111 (20). Found: C, 64.87; H, 7.79; N, 8.33; S, 19.11. $C_9H_{13}NS$ requires: C, 64.62; H, 7.83; N, 8.37; S, 19.17%.

4.7.26. 4-Allyl-1-methyl-3,4-dihydro-1*H*-pyridine-2-thione (6q). Pale yellow oil. IR (film): ν=3076, 2976, 2924, 1640, 1480, 1378, 1252, 1136, 1052, 996, 920, 728 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=2.12 (2H, t, *J* 7.1 Hz, 4-CH_2), 2.41–2.52 (1H, m, CH-4), 2.85 (1H, dd, *J* 16.5, 10.1 Hz, C*H*H-3), 3.13 (1H, dd, *J* 16.5, 6.5 Hz, CH*H*-3), 3.50 (3H, s, NCH_3), 5.04–5.12 (2H, m, =CH_2), 5.45 (1H, dd, *J* 7.6, 3.9 Hz, =CH-5), 5.66–5.79 (1H, m, =CH), 6.18 (1H, dd, *J* 7.6, 1.9 Hz, =CH-6); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=30.4 (CH-4), 37.9 (4-CH_2), 41.8 (N-CH_3), 46.2 (CH_2-3), 116.5 (=CH-5), 117.6 (=CH_2), 130.0 (=CH-6), 134.7 (=CH), 197.5 (C-2); GC–MS (EI, 70 eV): *m*/*z*=167 (M^+, 73), 126 (100), 111 (22), 94 (8), 85 (7), 70 (13). Found: C, 64.66; H, 7.85; N, 8.51; S, 19.22. $C_9H_{13}NS$ requires: C, 64.62; H, 7.83; N, 8.37; S, 19.17%.

4.7.27. 6-Allyl-1-benzyl-3,6-dihydro-1*H*-pyridine-2-thione (5r). White solid, mp 78–80 °C from *n*-hexane/ethyl acetate. IR (KBr pellet): ν=1500, 1448, 1394, 1350, 1328, 1180, 1166, 926, 732 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=2.36–2.54 (2H, m, 6-CH_2), 3.51 (1H, dm, *J* 22.2 Hz, C*H*H-3), 3.88 (1H, ddd, *J* 22.2, 4.9, 1.9 Hz, CH*H*-3), 4.02–4.09 (1H, m, CH-6), 4.40 (1H, d, *J* 15.0 Hz, NC*H*H), 5.10–5.18 (2H, m, =CH_2), 5.64–5.77 (1H, m, =CH), 5.79 (1H, ddd, *J* 9.7, 4.6, 3.1 Hz, =CH-5), 5.86 (1H, ddd, *J* 9.7, 5.0, 1.9 Hz, =CH-4), 6.55 (1H, d, *J* 15.0 Hz, NCH*H*), 7.24–7.37 (5H, m C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=37.8 (6-CH_2), 42.6 (CH_2-3), 54.3 (NCH_2), 58.7 (CH-6), 119.8 (=CH_2), 123.4 (=CH-4), 125.0 (=CH-5), 127.5, 127.7, 128.8, 135.1 (C_6H_5), 131.7 (=CH), 198.6 (C-2); GC–MS (EI, 70 eV): *m*/*z*=243 (M^+, 38), 242 (41), 210 (16), 202 (18), 168 (14), 152 (8), 149 (7), 148 (15), 132 (17), 112 (12), 91 (100), 65 (9). Found: C, 74.16; H, 7.05; N, 5.56; S, 13.22. $C_{15}H_{17}NS$ requires: C, 74.03; H, 7.04; N, 5.76; S, 13.18%.

4.7.28. 4-Allyl-1-benzyl-3,4-dihydro-1*H*-pyridine-2-thione (6r). Yellow oil. IR (film): ν=3064, 2924, 1640, 1496, 1448, 1382, 1352, 1252, 1206, 1156, 1102, 996, 950, 920, 726, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=2.12 (2H, t, *J* 7.1 Hz, 4-CH_2), 2.43–2.54 (1H, m, CH-4), 2.94 (1H, dd, *J* 16.5, 9.9 Hz, C*H*H-3), 3.21 (1H, dd, *J* 16.5, 6.3 Hz, CH*H*-3), 5.03–5.10 (2H, m, =CH_2), 5.30–5.39 (2H, m, NCH_2), 5.44 (1H, dd, *J* 7.7, 3.9 Hz, =CH-5), 5.65–5.78 (1H, m, =CH), 6.16 (1H, dd, *J* 7.7, 1.9 Hz, =CH-6), 7.25–7.37 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=30.4 (CH-4), 37.8 (4-CH_2), 46.7 (CH_2-3), 55.4 (NCH_2), 116.9 (=CH-5), 117.7 (=CH_2), 127.6, 127.8, 128.7, 135.5 (C_6H_5), 128.4 (=CH-6), 134.7 (=CH), 198.3 (C-2); GC–MS (EI, 70 eV): *m*/*z*=243 (M^+, 28), 202 (48), 168 (5), 124 (4), 91 (100), 65 (6). Found: C, 74.16; H, 7.00; N, 5.70; S, 13.05. $C_{15}H_{17}NS$ requires: C, 74.03; H, 7.04; N, 5.76; S, 13.18%.

4.7.29. 6-Allyl-1-phenyl-3,6-dihydro-1*H*-pyridine-2-thione (5s). Pale yellow oil. IR (film): ν=3080, 2932, 1640, 1596, 1492, 1462, 1404, 1388, 1310, 1240, 1144, 926, 754, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=2.41 (2H, dd, *J* 13.8, 7.4 Hz, 6-CH_2), 3.64 (1H, dm, *J* ca. 23 Hz, C*H*H-3), 3.86 (1H, ddd, *J* 23.2, 4.0, 2.7 Hz, CH*H*-3), 4.42 (1H, m, CH-6), 5.12–5.21 (2H, m, =CH_2), 5.70–5.82 (1H, m, =CH), 5.90–6.01 (2H, m, =CH-4, =CH-5), 7.24 (2H, d, *J* 7.5 Hz, C_6H_5), 7.40 (1H, tt, *J* 7.4, 1.1 Hz, C_6H_5), 7.50 (2H, t, *J* 7.5 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=34.9 (6-CH_2), 42.6 (CH_2-3), 63.9 (CH-6), 119.9 (=CH_2), 123.1, 124.4 (=CH-4, =CH-5), 127.5 br, 128.0, 129.6 br, 144.7 (C_6H_5), 131.5 (=CH), 199.6 (C-2); GC–MS (EI, 70 eV): *m*/*z*=229 (M^+, 65), 228 (25), 189 (31), 188 (100), 186 (44), 173 (10), 154 (14), 130 (13), 109 (16), 104 (15), 78 (21), 77 (43), 51 (13). Found: C, 73.16; H, 6.67; N, 6.01; S, 13.85. $C_{14}H_{15}NS$ requires: C, 73.32; H, 6.59; N, 6.11; S, 13.98%.

4.7.30. 4-Allyl-1-phenyl-3,4-dihydro-1*H*-pyridine-2-thione (6s). Pale yellow oil. IR (film): ν=3072, 2920, 1640, 1594, 1492, 1404, 1364, 1150, 920, 694 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=2.23 (2H, t, *J* 7.2 Hz, 4-CH_2), 2.56–2.67 (1H, m, CH-4), 3.06 (1H, dd, *J* 16.4, 9.6 Hz, C*H*H-3), 3.30 (1H, dd, *J* 16.4, 6.4 Hz, CH*H*-3), 5.10–5.17 (2H, m, =CH_2), 5.52 (1H, dd, *J* 7.6, 4.0 Hz, =CH-5), 5.74–5.86 (1H, m, =CH), 6.28 (1H, dd, *J* 7.6, 1.8 Hz, =CH-6), 7.25 (2H, d, *J* 7.2 Hz, C_6H_5), 7.37 (1H, tt, *J* 7.5, 1.2 Hz, C_6H_5), 7.46 (2H, tt, *J* 7.5, 1.7 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=30.6 (CH-4), 38.1 (4-CH_2), 47.3 (CH_2-3), 115.4 (=CH-5), 117.8 (=CH_2), 126.8, 128.3, 129.5, 144.5 (C_6H_5), 130.4 (=CH-6), 134.7 (=CH), 199.7 (C-2). GC–MS (EI, 70 eV): *m*/*z*=229 (M^+, 55), 189 (35), 188 (100), 173 (10), 154 (17), 130 (19), 109 (13), 104 (13), 93 (8), 78 (22), 77 (43), 51 (14). Found: C, 73.40; H, 6.66; N, 5.99; S, 14.04. $C_{14}H_{15}NS$ requires: C, 73.32; H, 6.59; N, 6.11; S, 13.98%.

4.7.31. 1-Methyl-6-(2-methyl-allyl)-3,6-dihydro-1*H*-pyridine-2-thione (5t). Pale yellow oil. IR (film): ν=3076, 2964, 2936, 1646, 1520, 1392, 1348, 1328, 1228, 1124, 1084, 898 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.79 (3H, s, =CCH_3), 2.28 (1H, dd, *J* 13.4, 8.5 Hz, 6-C*H*H), 2.49 (1H, dd, *J* 13.4, 4.2 Hz, 6-CH*H*), 3.45 (1H, br d, *J* ca. 22.6 Hz, C*H*H-3), 3.52 (3H, s, NCH_3), 3.74 (1H, ddd, *J* 22.6, 4.6, 2.6 Hz, CH*H*-3), 4.13–4.22 (1H, m, CH-6), 4.76 (1H, s, =C*H*H), 4.90 (1H, t, *J* 1.5 Hz, =CH*H*), 5.77–5.87 (2H, m, =CH-4, =CH-5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=23.0 (=C*C*H_3), 41.7 (CH_2-3), 42.3 (N-CH_3), 42.3 (6-CH_2), 62.1 (CH-6), 115.1 (=CH_2), 122.7, 124.8 (=CH-4, =CH-5), 140.0 (=*C*CH_3), 196.6 (C-2); GC–MS (EI, 70 eV): *m*/*z*=181 (M^+, 23), 148 (14), 126 (100), 111 (9), 42 (19). Found: C, 66.19; H, 8.44; N, 7.82; S, 17.80. $C_{10}H_{15}NS$ requires: C, 66.25; H, 8.34; N, 7.73; S, 17.69%.

4.7.32. 1-Methyl-4-(2-methyl-allyl)-3,4-dihydro-1*H*-pyridine-2-thione (6t). Pale yellow oil. IR (film): ν=3076, 2964, 2924, 1648, 1476, 1378, 1136, 892, 728 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.70 (3H, br s, =C*C*H_3), 2.05 (2H, d, *J* 7.6 Hz, 4-CH_2), 2.80 (1H, dd, *J* 16.5, 10.4 Hz, C*H*H-3), 3.12 (1H, dd, *J* 16.5, 6.3 Hz, CH*H*-3), 3.51 (3H, s, N-CH_3), 4.72 (1H, br s, =C*H*H), 4.84 (1H, br s, =CH*H*), 5.45 (1H, dd, *J* 7.6, 3.7 Hz, =CH-5), 6.17 (1H, dd, *J* 7.6, 1.9 Hz, =CH-6); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.2 (=C*C*H_3), 28.6 (CH-4), 41.8 (N-CH_3), 41.9 (4-CH_2), 46.4 (CH_2-3), 113.2 (=CH_2), 116.8 (=CH-5),

129.9 (=CH-6), 141.8 (=*C*CH_3), 197.5 (C-2); GC–MS (EI, 70 eV): *m*/*z*=181 (M^+, 93), 148 (11), 127 (30), 126 (100), 111 (36), 94 (14), 78 (24), 42 (19). Found: C, 66.38; H, 8.39; N, 7.66; S, 17.70. $C_{10}H_{15}NS$ requires: C, 66.25; H, 8.34; N, 7.73; S, 17.69%.

4.7.33. 1-Benzyl-6-(2-methyl-allyl)-3,6-dihydro-1*H*-pyridine-2-thione (5u). Pale yellow oil. IR (film): ν=3072, 3028, 2963, 1646, 1452, 1348, 1192, 1068, 898, 730, 700 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.74 (3H, br s, =CCH_3), 2.26 (1H, dd, *J* 13.3, 8.9 Hz, 6-C*H*H), 2.46 (1H, dd, *J* 13.3, 4.5 Hz, 6-CH*H*), 3.52 (1H, dm, *J* ca. 21 Hz, 3-C*H*H), 3.92 (1H, dm, *J* ca. 21 Hz, 3-CH*H*), 4.07–4.14 (1H, m, CH-6), 4.37 (1H, d, *J* 15.0 Hz, NC*H*H), 4.75 (1H, s, =C*H*H), 4.87 (1H, quintet, *J* 1.5 Hz, =CH*H*), 5.82–5.88 (2H, m, =CH-4, =CH-5), 6.55 (1H, d, *J* 15.0 Hz, NCH*H*), 7.24–7.37 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.8 (=C*C*H_3), 41.9 (6-CH_2), 42.5 (CH-3), 54.7 (NCH_2), 58.0 (6-CH), 115.0 (=CH_2), 123.2 (=CH-4), 125.9 (=CH-5), 127.5, 127.8, 128.8, 135.1 (C_6H_5), 140.2 (=*C*CH_3), 198.3 (C-2); GC–MS (EI, 70 eV): *m*/*z*=257 (M^+, 12), 256 (12), 224 (12), 202 (14), 148 (11), 112 (7), 91 (100), 65 (13). Found: C, 74.65; H, 7.58; N, 5.21; S, 12.33. $C_{16}H_{19}NS$ requires: C, 74.66; H, 7.44; N, 5.44; S, 12.46%.

4.7.34. 1-Benzyl-4-(2-methyl-allyl)-3,4-dihydro-1*H*-pyridine-2-thione (6u). Pale yellow oil. IR (film): ν=3068, 3028, 2932, 1648, 1496, 1458, 1424, 1384, 1352, 1158, 1104, 948, 894, 728, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.70 (3H, s, =CCH_3), 2.06 (2H, d, *J* 7.6 Hz, 4-CH_2), 2.54–2.65 (1H, m, CH-4), 2.90 (1H, dd, *J* 16.5, 10.0 Hz, C*H*H-3), 3.19 (1H, dd, *J* 16.5, 6.2 Hz, CH*H*-3), 4.70 (1H, quartet, *J* 0.8 Hz, =C*H*H), 4.83 (1H, s, =CH*H*), 5.32 (1H, d, *J* 14.8 Hz, NC*H*H), 5.39 (1H, d, *J* 14.8 Hz, NCH*H*), 5.45 (1H, dd, *J* 7.6, 3.8 Hz, =CH-5), 6.15 (1H, dd, *J* 7.6, 1.8 Hz), 7.27–7.37 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.2 (=C*C*H_3), 28.6 (CH-4), 41.8 (4-CH_2), 46.9 (CH_2-3), 55.4 (NCH_2), 113.3 (=CH_2), 117.3 (=CH-5), 127.6, 127.8, 128.7, 135.6 (C_6H_5), 128.3 (=CH-6), 141.7 (=CCH_3), 198.3 (C-2); GC–MS (EI, 70 eV): *m*/*z*=257 (M^+, 52), 224 (9), 202 (75), 168 (11), 124 (11), 91 (100), 65 (18). Found: C, 74.71; H, 7.51; N, 5.45; S, 12.49. $C_{16}H_{19}NS$ requires: C, 74.66; H, 7.44; N, 5.44; S, 12.46%.

4.7.35. 6-(2-Methyl-allyl)-1-phenyl-3,6-dihydro-1*H*-pyridine-2-thione (5v). Pale yellow oil. IR (film): ν=3052, 2968, 2936, 1646, 1596, 1492, 1462, 1406, 1342, 1316, 1242, 1142, 896, 746, 730, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.61 (3H, s, =CCH_3), 2.24 (1H, dd, *J* 13.2, 10.0 Hz, 6-C*H*H), 2.56 (1H, dd, *J* 13.2, 4.1 Hz, 6-CH*H*), 3.66 (1H, dm, *J* 22.3 Hz, C*H*H-3), 3.90 (1H, ddd, *J* 22.3, 4.8, 2.7 Hz, CH*H*-3), 4.39–4.52 (1H, m, CH-6), 4.73 (1H, s, =C*H*H), 4.84 (1H, br s, =CH*H*), 5.91 (1H, ddd, *J* 10.1, 4.2, 3.0 Hz, =CH-4), 6.01 (1H, ddd, *J* 10.1, 4.2, 3.0 Hz, =CH-5), 7.24 (2H, d, *J* 7.8 Hz, C_6H_5), 7.40 (1H, tt, *J* 7.5, 1.2 Hz, C_6H_5), 7.50 (2H, t, *J* 7.7 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.6 (=C*C*H_3), 42.3 (6-CH_2), 42.5 (CH_2-3), 63.1 (CH-6), 114.4 (=CH_2), 122.4 (=CH-4), 125.0 (=CH-5), 127.6 br, 128.1, 129.6, 140.1 (C_6H_5), 144.8 (=*C*CH_3), 199.3 (C-2); GC–MS (EI, 70 eV): *m*/*z*=243 (M^+, 20), 188 (100), 186 (30), 104 (13), 77 (33). Found: C, 73.91; H, 7.19; N, 5.49; S, 13.23. $C_{15}H_{17}NS$ requires: C, 74.03; H, 7.04; N, 5.76; S, 13.18%.

4.7.36. 4-(2-Methyl-allyl)-1-phenyl-3,4-dihydro-1*H*-pyridine-2-thione (6v). Pale yellow oil. IR (film): ν=3072, 2968, 2928, 1648, 1596, 1492, 1348, 1152, 894, 748, 726, 694 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.75 (3H, br s, =CCH_3), 2.16 (2H, d, *J* 7.6 Hz, 4-CH_2), 2.67–2.79 (1H, m, CH-4), 3.00 (1H, dd, *J* 16.3, 10.0 Hz, C*H*H-3), 3.28 (1H, ddd, *J* 16.3, 6.2, 0.6 Hz, CH*H*-3), 4.78 (1H, br s, =C*H*H), 4.87 (1H, br s, =CH*H*), 5.52 (1H, dd, *J* 7.6, 3.8 Hz, =CH-5), 6.27 (1H, dd, *J* 7.6, 1.8 Hz, =CH-6), 7.26 (2H, dd, *J* 6.7, 1.4 Hz, C_6H_5), 7.37 (1H, tt, *J* 7.4, 1.2 Hz, C_6H_5), 7.46 (2H, t, *J* 7.4 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.3 (=C*C*H_3), 28.8 (CH-4), 42.0 (N-CH_2), 47.4 (CH_2-3), 113.4 (=CH_2), 115.9 (=CH-5), 126.9, 128.3, 129.5, 144.4 (C_6H_5), 130.2 (=CH-6), 141.7 (=*C*CH_3), 199.7 (C-2); GC–MS (EI, 70 eV): *m*/*z*=243 (M^+, 65), 210 (13), 190 (18), 189 (42), 188 (100), 186 (46), 173 (13), 156 (13), 155 (14), 154 (19), 132 (14), 130 (20), 109 (14), 104 (14), 78 (24), 77 (44); HRMS (EI) for $C_7H_{11}NS$: calculated 243.1082; found 243.1072.

4.7.37. 4-(1,1-Dimethyl-allyl)-1-methyl-3,4-dihydro-1*H*-pyridine-2-thione (6w). Pale yellow oil. IR (film): ν=3080, 2968, 1478, 1376, 1132, 1004, 916 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.00 (6H, s, 2×CH_3), 2.25 (1H, dddd, *J* 9.6, 7.3, 4.0, 2.1 Hz, CH-4), 2.97 (1H, dd, *J* 16.8, 9.6 Hz, C*H*H-3), 3.10 (1H, dd, *J* 16.8, 7.3 Hz, CH*H*-3), 3.47 (3H, s, NCH_3), 4.99 (1H, dd, *J* 17.3, 1.2 Hz, =C*H*H), 5.03 (1H, dd, *J* 10.7, 1.2 Hz, =CH*H*), 5.44 (1H, dd, *J* 7.8, 4.0 Hz, =CH-5), 5.70 (1H, dd, *J* 17.3, 10.7 Hz, =CH), 6.21 (1H, dd, *J* 7.8, 2.1 Hz, =CH-6); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=23.6, 23.8 (2×CH_3), 39.0 ($(CH_3)_2C$), 40.2 (CH-4), 41.7 (NCH_3), 42.6 (CH_2-3), 112.7 (=CH_2), 113.9 (=CH-5), 130.6 (=CH-6), 145.4 (=CH), 198.1 (C-2); GC–MS (EI, 70 eV): *m*/*z*=195 (M^+, 15), 126 (100). 111 (10), 78 (7), 42 (7); HRMS (EI) for $C_{11}H_{17}NS$: calculated 195.1082; found 195.1087.

4.7.38. 1-Benzyl-4-(1,1-dimethyl-allyl)-3,4-dihydro-1*H*-pyridine-2-thione (6x). Pale yellow oil. IR (film): ν=3084, 2964, 2928, 2876, 1650, 1496, 1452, 1412, 1388, 1164, 1100, 920, 752, 698 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.99 (6H, s, 2×CH_3), 2.23–2.29 (1H, m, CH-4), 3.04 (1H, dd, *J* 16.9, 9.8 Hz, C*H*H-3), 3.18 (1H, dd, *J* 16.9, 7.2 Hz, CH*H*-3), 4.98 (1H, dd, *J* 17.4, 1.1 Hz, =C*H*H), 5.01 (1H, dd, *J* 10.8, 1.1 Hz, =CH*H*), 5.27 (1H, d, *J* 14.7 Hz, NC*H*H), 5.36 (1H, d, *J* 14.7 Hz, NCH*H*), 5.43 (1H, dd, *J* 7.9, 3.9 Hz, =CH-5), 5.69 (1H, dd, *J* 17.4, 10.8 Hz, =CH), 6.20 (1H, dd, *J* 7.9, 2.1 Hz, =CH-6), 7.26–7.36 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=23.7, 23.8 (2×CH_3), 39.2 ($(CH_3)_2C$), 40.2 (CH-4), 43.2 (CH_2-3), 55.5 (NCH_2), 112.9 (=CH_2), 114.4 (=CH-5), 127.9, 127.9, 128.7, 135.48 (C_6H_5), 128.9 (=CH-6), 145.4 (=CH), 198.9 (C-2). GC–MS (EI, 70 eV): *m*/*z*=271 (M^+, 17), 202 (71). 168 (7), 124 (11), 91 (100), 65 (15), 41 (10); HRMS (EI) for $C_{17}H_{21}NS$: calculated 271.1395; found 271.1416.

4.7.39. 4-(1,1-Dimethyl-allyl)-1-phenyl-3,4-dihydro-1*H*-pyridine-2-thione (6y). Pale yellow solid, mp 57–59 °C from *n*-hexane. IR (KBr pellet): ν=2968, 2924, 1648,

1640, 1596, 1494, 1412, 1364, 1310, 1156, 920, 764, 742, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.09 (3H, s, CH_3), 1.10 (3H, s, CH_3), 2.37 (1H, tdd, *J* 7.9, 4.4, 1.9 Hz, CH-4), 3.23 (2H, dd, *J* 7.9, 0.5 Hz, CH_2-3), 5.05 (1H, dd, *J* 17.3, 1.1 Hz, =C*H*H), 5.08 (1H, dd, *J* 10.7, 1.1 Hz, =CH*H*), 5.51 (1H, dd, *J* 7.8, 4.4 Hz, =CH-5), 5.80 (1H, dd, *J* 17.3, 10.7 Hz, =CH), 6.33 (1H, dd, *J* 7.8, 1.9 Hz, =CH-6), 7.22–7.26 (2H, m, C_6H_5), 7.34–7.39 (1H, m, C_6H_5), 7.42–7.48 (2H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=23.7, 24.0 (2×CH_3), 39.5 ($C(CH_3)_2$), 40.4 (CH-4), 43.6 (CH_2-3), 112.7 (=CH-5), 113.0 (=CH_2), 126.7, 128.3, 129.5, 144.5 (C_6H_5), 130.9 (=CH-6), 145.4 (=CH), 200.3 (C-2); GC–MS (EI, 70 eV): *m*/*z* =257 (29, M^+), 189 (39), 188 (100), 173 (9), 154 (13), 130 (13), 77 (26). Found: C, 74.82; H, 7.56; N, 5.45; S, 12.59. $C_{16}H_{19}NS$ requires: C, 74.66; H, 7.44; N, 5.44; S, 12.46%.

4.7.40. 6-(4-*tert*-Butyl-2-thioxo-3,4-dihydro-2*H*-pyridin-1-ylmethyl)-1-methyl-3,6-dihydro-1*H*-pyridine-2-thione (7e). Pale red oil. IR (film): ν=2960, 2872, 1648, 1512, 1458, 1384, 1348, 1156, 1116, 914, 732 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.92 (9H, s, $C(CH_3)_3$), 2.11–2.18 (1H, m, CH-4′), 3.04 (1H, dd, *J* 16.7, 8.9 Hz, C*H*H-3′), 3.12 (1H, dd, *J* 16.7, 7.6 Hz, CH*H*-3′), 3.48 (1H, dm, *J* 23.3 Hz, C*H*H-3), 3.56 (3H, s, NCH_3), 3.78 (1H, dd, *J* 13.1, 2.5 Hz, NC*H*H), 3.83 (1H, ddd, *J* 23.2, 4.8, 1.7 Hz, CH*H*-3), 4.40 (1H, dd, *J* 13.1, 6.0 Hz, NCH*H*), 4.78–4.85 (1H, br m, CH-6), 5.51 (1H, dd, *J* 7.9, 4.3 Hz, =CH-5′), 5.90 (1H, ddd, *J* 9.9, 4.8, 3.2 Hz, =CH-4 or =CH-5), 5.96 (1H, ddd, *J* 9.9, 5.0, 1.8 Hz, =CH-4 or =CH-5), 6.12 (1H, dd, *J* 7.9, 1.9 Hz, =CH-6′); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=25.9 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 39.9 (CH-4′), 41.0 (CH_2-3), 41.8 (NCH_3), 42.2 (CH_2-3′), 55.9 (NCH_2), 57.8 (CH-6), 113.7 (=CH-5′), 122.2, 124.1 (=CH-4, =CH-5), 129.2 (=CH-6′), 195.7, 199.0 (C-2, C-2′); GC–MS (EI, 70 eV): *m*/*z*=308 (M^+, 1), 275 (4). 251 (19), 167 (11), 139 (31), 126 (100), 112 (7), 94 (7), 42 (8); HRMS (EI) for $C_{16}H_{24}N_2S_2$: calculated 308.1381; found 308.1383.

4.8. Synthesis of 5,6-dihydropyridine-2-thiones 8

The mixture of **5** (2.14 mmol) and catalytic amount of DBU (Table 3) in acetonitrile (5 mL) was stirred at rt for an appropriate time (Table 3). After addition of aqueous saturated NH_4Cl (5 mL), the water layer was extracted with ethyl acetate (2×50 mL) and the combined organic layers were dried over $MgSO_4$. Filtration, concentration in vacuo, and purification by column chromatography (silica gel, *n*-hexane/ethyl acetate=8:2 to 7:3) afforded **7** as yellow product.

4.8.1. 6-Ethyl-5,6-dihydro-1*H*-pyridine-2-thione (8a). Yellow oil (245 mg, 81%). IR (film): ν=3196, 2936, 2876, 1622, 1524, 1348, 1154, 1140 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.00 (3H, t, *J* 7.3 Hz, CH_3), 1.64 (1H, septet, *J* 7.4 Hz, 6-C*H*H), 1.73 (1H, septet, *J* 7.4 Hz, 6-CH*H*), 2.14 (1H, ddt, *J* 18.1, 11.7, 2.4 Hz, C*H*H-5), 2.41 (1H, dt, *J* 18.1, 5.4 Hz, CH*H*-5), 3.50 (1H, sextet, *J* ca. 6 Hz, CH-6), 6.36 (1H, ddd, *J* 9.3, 5.4, 2.9 Hz, =CH-4), 6.41 (1H, dm, *J* 9.3 Hz, =CH-3), 7.98 (1H, s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=9.77 (CH_3), 27.4 (6-CH_2), 28.2 (CH_2-5), 53.7 (CH-6), 130.7 (=CH-3), 133.4 (=CH-4), 192.3 (C-2); GC–MS (EI, 70 eV): *m*/*z*=141 (75, M^+), 112 (100), 84 (28), 78 (57), 67 (8), 58 (22), 45 (12), 39 (15). Found: C, 59.51; H, 8.00; N, 10.04; S, 22.55. $C_7H_{11}NS$ requires: C, 59.53; H, 7.85; N, 9.92; S, 22.70%.

4.8.2. 6-Butyl-5,6-dihydro-1*H*-pyridine-2-thione (8b). Yellow solid (289 mg, 80%), mp 55–57 °C from *n*-hexane. IR (KBr pellet): ν=3196 br, 3024, 2956, 2928, 2856, 1626, 1530, 1376, 1352, 1308, 1148, 1112, 1060 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.90 (3H, t, *J* 8.3 Hz, CH_3), 1.30–1.45 (4H, m 2×CH_2), 1.52–1.77 (2H, m, CH_2), 2.14 (1H, ddt, *J* 11.5, 2.0 Hz, C*H*H-5), 2.40 (1H, dt, *J* 18.0, 5.4 Hz, CH*H*-5), 3.55 (1H, sextetd, *J* 6.4, 1.8 Hz, CH-6), 6.32–6.42 (2H, m, CH-3, CH-4), 8.32 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=13.8 (CH_3), 22.4 (CH_2), 27.3 (CH_2), 28.4 (CH_2-5), 33.9 (CH_2), 52.2 (CH-6), 130.2 (CH-4), 133.3 (CH-3), 192.0 (C-2); GC–MS (EI, 70 eV): *m*/*z*=169 (28, $M^{+\bullet}$), 136 (2), 126 (4), 112 (100), 87 (7), 78 (21). Found: C, 63.99; H, 8.86; N, 8.11; S, 19.11. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.8.3. 6-Pentyl-5,6-dihydro-1*H*-pyridine-2-thione (8c). Yellow oil (270 mg, 69%). IR (film): ν=3192 br, 2932, 2856, 1620, 1524 br, 1326, 1150 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.90 (3H, t, *J* 6.8 Hz, CH_3), 1.24–1.41 (6H, m, 3×CH_2), 1.56–1.73 (2H, m, CH_2), 2.14 (1H, dddd, *J* 18.1, 11.8, 2.6, 2.3 Hz, C*H*H-5), 2.39 (1H, dt, *J* 18.1, 5.6 Hz, CH*H*-5), 3.50–3.59 (1H, m, CH-6), 6.34 (1H, ddd, *J* 9.5, 5.3, 2.8 Hz, =CH-4), 6.41 (1H, dm, *J* 9.5 Hz, =CH-3), 7.88 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.5 (CH_2), 25.0 (CH_2), 28.7 (CH_2-5), 31.5 (CH_2), 34.5 (CH_2), 52.4 (CH-6), 130.4 (=CH-3), 133.3 (=CH-4), 192.5 (C-2); GC–MS (EI, 70 eV): *m*/*z*=183 (33, M^+), 182 (31), 150 (6), 126 (7), 112 (100), 84 (9), 78 (25). Found: C, 65.49; H, 9.40; N, 7.75; S, 17.60. $C_{10}H_{17}NS$ requires: C, 65.52; H, 9.35; N, 7.64; S, 17.49%.

4.8.4. 6-Hexyl-5,6-dihydro-1*H*-pyridine-2-thione (8d). Yellow oil (278 mg, 66%). IR (film): ν=3188 br, 2924, 2856, 1622, 1522, 1328, 1152, 1110, 760 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.89 (3H, t, *J* ca. 7.0 Hz, CH_3), 1.23–1.45 (8H, 4×CH_2), 1.51–1.73 (2H, m, CH_2), 2.14 (1H, ddt, *J* 18.0, 11.8, 2.6 Hz, C*H*H-5), 2.39 (1H, dt, *J* 18.0, 11.8, 2.6 Hz, CH*H*-5), 3.55 (1H, sextetd, *J* 6.7, 1.7 Hz, CH-6), 6.35 (1H, ddd, *J* 9.7, 5.2, 2.8 Hz, =CH-4), 6.40 (1H, br d, *J* 9.7 Hz, =CH-3), 7.92 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.5, 25.3, 28.7, 29.0, 31.6, 34.5 (6×CH_2), 52.4 (CH-6), 130.4, 133.3 (=CH-3, =CH-4), 192.4 (C-2); GC–MS (EI, 70 eV): *m*/*z*=197 (36, $M^{+\bullet}$), 196 (42), 164 (8), 126 (9), 112 (100), 84 (8), 78 (24). Found: C, 66.99; H, 9.90; N, 7.15; S, 16.25. $C_{11}H_{19}NS$ requires: C, 66.95; H, 9.70; N, 7.10; S, 16.25%.

4.8.5. 6-Isobutyl-5,6-dihydro-1*H*-pyridine-2-thione (8e). Yellow oil (257 mg, 71%). IR (KBr pellet): ν=3450 v br, 3188 br, 2952, 1624, 1526, 1464, 1428, 1416, 1382, 1312, 1160, 1138, 1112, 1048, 762 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=0.94 (6H, d, *J* 6.5 Hz, 2×CH_3), 1.40 (1H, ddd, *J* 14.0, 7.6, 6.6 Hz, 6-C*H*H), 1.59 (1H, dt, *J* 14.0, ca. 6.9 Hz, 6-CH*H*), 1.74 (1H, sepd, *J* 6.6, 0.8 Hz, $CH(CH_3)_2$), 2.11 (1H, ddt, *J* 18.0, 11.7, ca. 2.9 Hz, C*H*H-5), 2.39 (1H, dt, *J* 18.0, 5.7 Hz, CH*H*-5), 3.58–3.68 (1H, m, CH-6), 6.35 (1H, ddd, *J* 9.5, 5.2, 2.9 Hz, =CH-4), 6.41 (1H, br d, *J* ca.

9.7 Hz, =CH-3), 7.80 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.4 (CH_3), 22.6 (CH_3), 24.3 ($CH(CH_3)_2$), 29.1 (CH_2-5), 43.5 (6-CH_2), 50.4 (CH-6), 130.5 (=CH-3), 133.3 (=CH-4), 192.5 (C-2); GC–MS (EI, 70 eV): m/z=169 (51, $M^{+\bullet}$), 112 (100), 78 (28). Found: C, 63.99; H, 9.00; N, 8.35; S, 18.71. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.8.6. 6-*sec*-Butyl-5,6-dihydro-1*H*-pyridine-2-thione (8f). Mixture of diastereomers=1:1. Yellow solid (261 mg, 72%). IR (KBr pellet): ν=3176, 2960, 2872, 1622, 1530, 1460, 1416, 1378, 1352, 1152, 754 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=0.91–1.01 (12H, m, 4×CH_3), 1.12–1.35 (2H, m, 2×C*H*H), 1.40–1.60 (2H, m, 2×CH*H*), 1.60–1.78 (2H, m, 2×6-CH), 2.18–2.32 (4H, m, 2×CH_2-5), 3.47–3.57 (2H, m, 2×CH-6), 6.32–6.43 (4H, m, 2×=CH-3, 2×=CH-4), 7.87, 7.95 (two br s, 2×NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=11.5, 11.7, 14.6, 15.0 (4×CH_3), 24.4 (CH_2-5), 25.1 (CH_2), 25.6 (CH_2, CH_2-5), 37.9, 38.1 (2×6-CH), 56.3, 56.6 (2×CH-6), 130.3 (2×=CH-3), 133.6, 133.6 (2×=CH-4), 192.8, 192.9 (2×C-2); GC–MS (EI, 70 eV): m/z=169 (43, $M^{+\bullet}$), 112 (100), 78 (31). Found: C, 63.75; H, 8.99; N, 8.29; S, 18.98. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.8.7. 6-*tert*-Butyl-5,6-dihydro-1*H*-pyridine-2-thione (8g). Yellow solid (275 mg, 76%), mp 68–70 °C from *n*-hexane. IR (KBr pellet): ν=3244 br, 2960, 2868, 1624, 1506, 1376, 1318, 1134, 1094, 1116, 760, 710 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=1.00 (9H, s, $C(CH_3)_3$), 2.23 (1H, ddt, J 18.2, 12.9, 2.0 Hz, C*H*H-5), 2.30–2.39 (1H, m, CH*H*-5), 3.29 (1H, ddd, J 12.9, 6.2, 1.5 Hz, CH-6), 6.37 (1H, ddd, J 9.6, 5.5, 2.7 Hz, =CH-4), 6.42 (1H, dm, J 9.6 Hz, =CH-3), 7.53 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=24.1 (CH_2-5), 25.8 ($C(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.3 (CH-6), 130.0 (=CH-3), 133.7 (=CH-4), 193.3 (C-2); GC–MS (EI, 70 eV): m/z=169 (43, $M^{+\bullet}$), 112 (100), 78 (26), 41 (6). Found: C, 63.99; H, 8.95; N, 8.34; S, 19.11. $C_9H_{15}NS$ requires: C, 63.85; H, 8.93; N, 8.27; S, 18.94%.

4.8.8. 6-Phenyl-5,6-dihydro-1*H*-pyridine-2-thione (8h). Yellow solid (283 mg, 70%), mp 127–130 °C from *n*-hexane/ethyl acetate. IR (KBr pellet): ν=3450 v br, 3168 br, 2984, 1620, 1512 br, 1452, 1416, 1376, 1332, 1304, 1134, 762, 700 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=2.53–2.61 (2H, m, CH_2-5), 4.67 (1H, ddd, J 11.6, 6.6, 1.5 Hz, CH-6), 6.38 (1H, ddd, J 9.5, 5.3, 3.2 Hz, =CH-4), 6.51 (1H, dm, J ca. 9.6 Hz, =CH-3), 7.33–7.44 (5H, m, C_6H_5), 7.76 (1H, br s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=31.6 (CH_2-5), 57.1 (CH-6), 126.8, 128.9, 129.2, 139.6 (C_6H_5), 130.4 (=CH-3), 132.6 (=CH-4), 193.2 (C-2); GC–MS (EI, 70 eV): m/z=189 (100, $M^{+\bullet}$), 154 (5), 128 (11), 112 (10), 106 (36), 84 (52), 77 (15), 58 (11). Found: C, 69.89; H, 5.80; N, 7.45; S, 17.01. $C_{11}H_{11}NS$ requires: C 69.80; H, 5.86; N, 7.40; S, 16.94%.

4.8.9. 6-Allyl-1-methyl-5,6-dihydro-1*H*-pyridine-2-thione (8i). Yellow oil (329 mg, 92%). IR (film): ν=3072, 2924, 1624, 1502, 1346, 1320, 1240, 1112, 922 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=2.30–2.47 (3H, m, 6-CH_2, C*H*H-5), 2.64 (1H, ddt, J 18.4, 7.5, 2.7 Hz, CH*H*-5), 3.49 (3H, s, N-CH_3), 3.67 (1H, quartet, J 7.4 Hz, CH-6), 5.08–5.17 (2H, m, =CH_2), 5.64–5.77 (1H, m, =CH), 6.05–6.12 (1H, m, =CH-4), 6.50 (1H, dd, J 9.5, 3.0 Hz, =CH-3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=26.7 (CH_2-5), 35.1 (6-CH_2), 42.6 (N-CH_3), 59.7 (CH-6), 119.1 (=CH_2), 127.7 (=CH-4), 132.0 (=CH-3), 133.5 (=CH), 188.9 (C-2); GC–MS (EI, 70 eV): m/z=167 (M^+, 48), 166 (28), 134 (23), 126 (100), 111 (30), 97 (10), 85 (13), 42 (39). Found: C, 64.86; H, 7.82; N, 8.25; S, 18.99. $C_9H_{13}NS$ requires: C, 64.62; H, 7.83; N, 8.37; S, 19.17%.

4.8.10. 6-Allyl-1-benzyl-5,6-dihydro-1*H*-pyridine-2-thione (8j). Yellow oil (479 mg, 92%). IR (film): ν=3072, 2936, 1620, 1484, 1452, 1348, 1320, 1190, 1152, 756, 732, 698 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=2.30 (1H, dd, J 18.4, 6.4 Hz, C*H*H-5), 2.30–2.50 (3H, m, 6-CH_2, CHH-5), 3.56–3.65 (1H, m, CH-6), 4.28 (1H, d, J 14.9 Hz, NC*H*H), 5.05–5.15 (2H, m, =CH_2), 5.59–5.71 (1H, m, =CH), 6.05–6.10 (1H, m, =CH-4), 6.33 (1H, d, J 14.9 Hz, NCH*H*), 6.62 (1H, dd, J 9.5, 2.8 Hz, =CH-3), 7.25–7.39 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=26.9 (CH_2-5), 34.5 (6-CH_2), 55.2 (NCH_2), 55.3 (CH-6), 119.1 (=CH_2), 127.7, 127.8, 128.8, 136.5 (C_6H_5), 127.8 (=CH-4), 132.3 (=CH-3), 133.6 (=CH), 189.7 (C-2); GC–MS (EI, 70 eV): m/z=243 (M^+, 11), 242 (18), 202 (7), 168 (11), 152 (8), 132 (30), 112 (19), 97 (14), 91 (100), 65 (14). Found: C, 74.11; H, 6.88; N, 5.88; S, 13.25. $C_{15}H_{17}NS$ requires: C, 74.03; H, 7.04; N, 5.76; S, 13.18%.

4.8.11. 6-Allyl-1-phenyl-5,6-dihydro-1*H*-pyridine-2-thione (8k). Yellow oil (417 mg, 85%). IR (film): ν=3072, 2940, 1622, 1596, 1492, 1440, 1388, 1388, 1338, 1312, 1166, 922, 760, 698 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=2.44–2.62 (3H, m, C*H*H-5, 6-CH_2), 2.77 (1H, ddt, J 18.3, 7.2, 2.6 Hz, CH*H*-5), 3.88–3.96 (1H, m, CH-6), 5.04–5.12 (2H, m, =CH_2), 5.50–5.63 (1H, m, =CH), 6.22 (1H, dddd, J 9.6, 6.3, 2.6, 1.0 Hz, =CH-4), 6.67 (1H, ddd, J 9.6, 2.8, 0.7 Hz, =CH-3), 7.30 (2H, dd, J 7.9, 1.3 Hz, C_6H_5), 7.38 (1H, tt, J 7.5, 1.2 Hz, C_6H_5), 7.48 (2H, t, J 7.8 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=26.9 (CH_2-5), 35.0 (6-CH_2), 60.2 (CH-6), 119.1 (=CH_2), 127.8, 128.1, 129.6, 145.2 (C_6H_5), 128.5 (=CH-4), 132.7 (=CH-3), 133.4 (=CH), 191.0 (C-2); GC–MS (EI, 70 eV): m/z=229 (M^+, 50), 228 (42), 188 (100), 186 (89), 173 (13), 109 (10), 104 (69), 85 (13), 77 (90), 51 (25). Found: C, 73.30; H, 6.70; N, 6.22; S, 13.99. $C_{14}H_{15}NS$ requires: C, 73.32; H, 6.59; N, 6.11; S, 13.98%.

4.8.12. 1-Methyl-6-(2-methyl-allyl)-5,6-dihydro-1*H*-pyridine-2-thione (8l). Pale yellow oil (322 mg, 83%). IR (film): ν=3072, 2932, 1624, 1500, 1398, 1346, 1324, 1240, 1124, 896, 746 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ=1.75 (3H, s, =C*C*H$_3$), 2.27–2.41 (3H, m, 6-CH_2, C*H*H-5), 2.61 (1H, ddt, J 18.3, 7.4, 2.6 Hz, CH*H*-5), 3.49 (3H, s, N-CH_3), 3.77 (1H, quartet, J 7.4 Hz, CH-6), 4.74 (1H, s, =C*H*H), 4.89 (1H, s, =CH*H*), 6.04–6.11 (1H, m, =CH-4), 6.51 (1H, dd, J 9.5, 3.0 Hz, =CH-3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.2 (=C*C*H$_3$), 26.4 (CH_2-5), 38.3 (6-CH_2), 42.3 (N-CH_3), 58.2 (CH-6), 114.9 (=CH_2), 127.7 (=CH-4), 132.0 (=CH-3), 140.9 (=*C*CH$_3$), 188.8 (C-2); GC–MS (EI, 70 eV): m/z=181 (M^+, 24), 148 (12), 126 (100), 85 (8), 78 (24), 42 (38). Found: C, 66.30; H, 8.38; N, 7.77; S, 17.81. $C_{10}H_{15}NS$ requires: C, 66.25; H, 8.34; N, 7.73; S, 17.69%.

4.8.13. 1-Benzyl-6-(2-methyl-allyl)-5,6-dihydro-1*H*-pyridine-2-thione (8m). Yellow oil (523 mg, 95%). IR (film): ν=3072, 3028, 2936, 1622, 1482, 1452, 1386, 1348, 1322, 1194, 1152, 1096, 950, 896, 758, 734, 700 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.68 (3H, s, =CCH_3), 2.22–2.34 (2H, m, C*H*H-5, 6-C*H*H), 2.35–2.43 (1H, m, CH*H*-5), 2.43 (1H, dd, *J* 13.6, 10.2 Hz, 6-CH*H*), 3.66–3.74 (1H, m, CH-6), 4.26 (1H, d, *J* 14.8 Hz, NC*H*H), 4.71 (1H, s, =C*H*H), 4.86 (1H, t, *J* 1.4 Hz, =CH*H*), 6.08 (1H, dddd, *J* 9.5, 6.4, 2.3, 1.2 Hz, =CH-4), 6.33 (1H, d, *J* 14.8 Hz, NCH*H*), 6.62 (1H, dd, *J* 9.5, 2.6 Hz, =CH-3), 7.27–7.40 (5H, m, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=22.2 (=C*C*H_3), 26.8 (CH_2-5), 38.0 (6-CH_2), 53.7 (CH-6), 55.1 (NCH_2), 114.8 (=CH_2), 127.8, 127.9, 128.8, 136.6 (C_6H_5), 132.2 (=CH-3), 140.9 (=*C*CH_3), 189.6 (C-2); GC–MS (EI, 70 eV): *m*/*z*=257 (M^+, 34), 256 (31), 224 (12), 202 (21), 200 (12), 168 (16), 166 (13), 112 (28), 97 (15), 91 (100), 65 (15). Found: C, 74.49; H, 7.33; N, 5.23; S, 12.44. $C_{16}H_{19}NS$ requires: C, 74.66; H, 7.44; N, 5.44; S, 12.46%.

4.8.14. 6-(2-Methyl-allyl)-1-phenyl-5,6-dihydro-1*H*-pyridine-2-thione (8n). Yellow oil (484 mg, 93%). IR (film): ν=3072, 2936, 1646, 1622, 1596, 1492, 1440, 1388, 1338, 1316, 1166, 898, 760, 732, 696 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ=1.54 (3H, br s, =CCH_3), 2.41 (1H, dd, *J* 13.5, 4.0 Hz, 6-C*H*H), 5.50 (1H, ddd, *J* 18.3, 6.4, 1.2 Hz, C*H*H-5), 2.58 (1H, dd, *J* 13.5, 11.0 Hz, 6-CH*H*), 2.75 (1H, ddt, *J* 18.3, 7.1, 2.4 Hz, CH*H*-5), 3.97–4.06 (1H, m, CH-6), 4.71 (1H, br s, =C*H*H), 4.84 (1H, br s, =CH*H*), 6.21 (1H, dddd, *J* 9.6, 6.4, 2.5, 1.2 Hz, =CH-4), 6.68 (1H, ddd, *J* 9.6, 2.9, 0.6 Hz, =CH-3), 7.31 (2H, dd, *J* 8.5, 1.4 Hz, C_6H_5), 7.38 (1H, tt, *J* 7.4, 1.2 Hz, C_6H_5), 7.48 (2H, br t, *J* 7.4 Hz, C_6H_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=21.8 (=C*C*H_3), 26.7 (CH_2-5), 38.4 (6-CH_2), 58.9 (CH-6), 114.6 (=CH_2), 127.7, 128.0, 129.6, 145.3 (C_6H_5), 128.5 (=CH-4), 132.7 (=CH-3), 141.0 (=*C*CH_3), 190.8 (C-2); GC–MS (EI, 70 eV): *m*/*z*=243 (M^+, 34), 242 (20), 188 (100), 186 (72), 173 (11), 104 (45), 77 (48), 51 (11). Found: C, 73.99; H, 7.05; N, 5.70; S, 13.11. $C_{15}H_{17}NS$ requires: C, 74.03; H, 7.04; N, 5.76; S, 13.18%.

Acknowledgements

The support by the National Committee for Scientific Research (KBN, Grant No. 3 T09A 106 28) is gratefully acknowledged.

References and notes

1. For selected examples see: (a) Leung, D.; Abbenante, G.; Fairlie, D. P. *J. Med. Chem.* **2000**, *43*, 305–341; (b) Vacher, B.; Bonnaud, B.; Funes, P.; Jubault, N.; Koek, W.; Assie, M. B.; Cosi, C.; Kleven, M. *J. Med. Chem.* **1999**, *42*, 1648–1660; (c) Webber, R. K.; Metz, S.; Moore, W. M.; Connor, J. R.; Currie, M. G.; Fok, K. F.; Hagen, T. J.; Hansen, D. W., Jr.; Jerome, G. M.; Manning, P. T.; Pitzele, B. S.; Toth, M. V.; Trivedi, M.; Zupec, M. E.; Tjoeng, F. S. *J. Med. Chem.* **1998**, *41*, 96–101; (d) Babine, R. E.; Bender, S. L. *Chem. Rev.* **1997**, *97*, 1359–1472.
2. Rubiralta, M.; Giralt, E.; Diez, A. *Piperidines. Structure, Preparation, Reactivity and Synthetic Application of Piperidines and its Derivatives*; Elsevier: Amsterdam, 1991; For selected reviews on piperidines see: (a) Buffat, M. G. P. *Tetrahedron* **2004**, *60*, 1701–1729; (b) Laschat, S.; Dickner, T. *Synthesis* **2000**, 1781–1813; (c) Sardina, F. J.; Rapoport, H. *Chem. Rev.* **1996**, *96*, 1825–1849 and references cited therein.
3. (a) Pineschi, M.; Moro, F. D.; Gini, F.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun.* **2004**, 1244–1246; (b) Ecija, M.; Diez, A.; Rubiralta, M.; Casamitjana, N.; Kogan, M. J.; Giralt, E. *J. Org. Chem.* **2003**, *68*, 9541–9553; (c) Casamitjana, N.; Jorge, A.; Perez, C. G.; Bosch, J.; Espinosa, E.; Molins, E. *Tetrahedron Lett.* **1997**, *38*, 2295–2298.
4. (a) Harris, J. M.; Padwa, A. *J. Org. Chem.* **2003**, *68*, 4371–4381; (b) Gil, L.; Compere, D.; Guilloteau-Bertin, B.; Chiaroni, A.; Marazano, C. *Synthesis* **2000**, *14*, 2117–2126; (c) Harris, J. M.; Padwa, A. *Org. Lett.* **2002**, *12*, 2029–2032; (d) Imanishi, T.; Yagi, N.; Hanaoka, M. *Chem. Pharm. Bull.* **1983**, *31*, 1243–1253; (e) Imanishi, T.; Shin, H.; Yagi, N.; Nakai, A.; Hanaoka, M. *Chem. Pharm. Bull.* **1983**, *31*, 1183–1190; (f) Imanishi, T.; Shin, H.; Hanaoka, M.; Momose, T.; Imanishi, I. *Chem. Pharm. Bull.* **1982**, *30*, 4037–4045; (g) Imanishi, T.; Yagi, N.; Shin, H.; Hanaoka, M. *Chem. Pharm. Bull.* **1982**, *30*, 4052–4059.
5. (a) Donohoe, T. J.; Johnson, D. J.; Mace, L. H.; Bamford, M. J.; Ichihara, O. *Org. Lett.* **2005**, *7*, 435–438; (b) Sebesta, R.; Pizzuti, M. G.; Boersma, A. J.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun.* **2005**, 1711–1713; (c) Klegraf, E.; Follmann, M.; Schollmeyer, D.; Kunz, H. *Eur. J. Org. Chem.* **2004**, *15*, 3346–3360; (d) Neipp, C. E.; Martin, S. F. *J. Org. Chem.* **2003**, *68*, 8867–8878; (e) Comins, D. L.; Killpack, M. O.; Despagnet, E.; Zeller, E. *Heterocycles* **2002**, *58*, 505–520; (f) Heintzelman, G.; Fang, W.-K.; Keen, S. P.; Wallace, G. A.; Weinreb, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 8851–8853; (g) Xie, C.; Runnegar, M. T. C.; Snider, B. B. *J. Am. Chem. Soc.* **2000**, *122*, 5017–5024; (h) Comins, D. L.; LaMunyon, D. H.; Chen, X. *J. Org. Chem.* **1997**, *62*, 8182–8187; (i) Heintzelman, G. R.; Weinreb, S. M.; Parvez, M. *J. Org. Chem.* **1996**, *61*, 4594–4599; (j) Comins, D. L.; Killpack, M. O. *J. Am. Chem. Soc.* **1992**, *114*, 10972–10974; (k) Comins, D. L.; Dehghani, A. *J. Org. Chem.* **1995**, *60*, 794–795; (l) Comins, D. L.; Dehghani, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1838–1839; (m) Dodd, D. S.; Oehlschlager, A. C. *J. Org. Chem.* **1992**, *57*, 2794–2803.
6. Comins, D. L. *J. Heterocycl. Chem.* **1999**, *36*, 1491–1500.
7. Thomas, E. W. *J. Org. Chem.* **1986**, *51*, 2184–2191.
8. Seebach, D.; Boes, M.; Naef, R.; Schweizer, B. *J. Am. Chem. Soc.* **1983**, *105*, 5390–5398.
9. (a) See Ref. 5c; (b) Klegraf, E.; Knauer, S.; Kunz, H. *Angew. Chem., Ind. Ed.* **2006**, *45*, 2623–2626.
10. Gray, D.; Gallagher, T. *Angew. Chem., Ind. Ed.* **2006**, *45*, 2419–2423.
11. Sośnicki, J. G. *Tetrahedron Lett.* **2006**, *47*, 6809–6812.
12. (a) Sośnicki, J. G.; Jagodziński, T. S.; Liebscher, J. *J. Heterocycl. Chem.* **1997**, *34*, 643–648; (b) Sośnicki, J. G.; Liebscher, J. *Synlett* **1996**, 1117–1118; (c) Sośnicki, J. G.; Westerlich, S. *Tetrahedron Lett.* **2002**, *43*, 1325–1328; (d) Sośnicki, J. G.; Jagodziński, T. S.; Hansen, P. E. *Tetrahedron* **2001**, *57*, 8705–8718.
13. Jagodziński, T. S. *Chem. Rev.* **2003**, *103*, 197–227.
14. Sośnicki, J. G. *Synlett* **2003**, 1673–1677.
15. Sośnicki, J. G. *Tetrahedron Lett.* **2005**, *46*, 4295–4298.
16. Tamaru, Y.; Kagotani, M.; Yoshida, Z.-i. *Tetrahedron Lett.* **1981**, *22*, 3409–3412.

17. (a) Fisyuk, A. S.; Vorontsova, M. A. *Khim. Getreotsikl. Soedin.* **1998**, 73–76; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1998**, *34*, 65–68; (b) Fisyuk, A. S.; Berdovich, L. V.; Temnikov, D. V.; Knyaz'kova, L. N. *Khim. Getreotsikl. Soedin.* **1997**, 921–927; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1997**, *33*, 805–810; (c) Cardwell, K.; Hewitt, B.; Ladlow, M.; Magnus, P. *J. Am. Chem. Soc.* **1988**, *110*, 2242–2248 and references cited therein.
18. Stanetty, P.; Koller, H.; Mihovilovic, M. *J. Org. Chem.* **1992**, *57*, 6833–6837.
19. Meghani, P.; Joule, A. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1–8 and references cited therein.
20. Houllier, N.; Gouault, S.; Lasne, M.-C.; Rouden, J. *Tetrahedron* **2006**, *62*, 11679–11686.
21. Tinarelli, A.; Paolucci, C. *J. Org. Chem.* **2006**, *71*, 6630–6633.
22. (a) Negishi, E.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* **1990**, *55*, 5406–5409; (b) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404–5406.
23. Lipshutz, B. H.; Hackmann, C. *J. Org. Chem.* **1994**, *59*, 7437–7444.
24. Jones, R. A.; Katritzky, A. R. *J. Chem. Soc.* **1960**, 2942–2946.
25. Becher, J.; Frandsen, E. G. *Acta Chem. Scand. Ser. B* **1976**, *30*, 839–866.