SELECTIVE THIOPHILIC ADDITION OF ALKYL- AND ARYLLITHIUMS TO DITHIO ESTERS AND A SULFINE IN THE PYRIDINE SERIES

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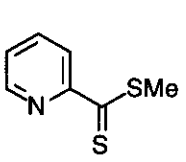
Abstract - Reaction of two dithio esters and a new sulfine (*S*-thiocarbonyl oxide) with various aryl- and alkyllithiums at –78°C afforded dithio acetals or their oxides, arising from a thiophilic addition. The intermediate carbanions can be trapped by alkyl halides or an aldehyde. This provides a new entry to pyridyl acyl anions, *"Umpolung"* synthons.

Thiocarbonyl compounds often behave in a specific manner.[1] Due to relatively poor overlap between 2p and 3p orbitals of carbon and sulfur atoms, they exhibit a higher reactivity than carbonyl compounds. The sense of addition of nucleophiles can be reversed in relation with the small difference of electronegativity between sulfur and carbon atoms. The high polarisability of sulfur also makes that the mode of addition of a nucleophile to a C=S bond may be balanced subtly according to a variety of parameters: the nature of the nucleophile, the thiocarbonyl compound, the solvent... Various reactions have been evidenced: thiophilic and carbophilic addition, reduction, enethiolisation, double addition, coupling reactions.[1] Most of the synthetic developments of these reactions have concentrated on the selective thiophilic addition of Grignard reagents to dithio esters from the Thuillier-Masson-Saquet[2-4] and Meyers groups,[5,6] and on carbophilic addition of alkyllithiums to thione esters, a reaction pioneered by Swenton[7] and extended by Nicolaou.[8,9]

To our knowledge the behaviour of heteroaromatic thiocarbonyl compounds with organolithiums or Grignards has not been reported. In the context of studies on the metalation of π-deficient aromatic derivatives, we investigated pyridines bearing a dithio ester group linked to the position 2 or 3 of the ring. We report that these two cases indeed lead to clean thiophilic addition. Moreover, the use a thiocarbonyl oxide moiety on the 3 position allowed us to achieve a similar selective reaction.

SYNTHESIS OF PYRIDYLDITHIOCARBOXYLATES AND A SULFINE

Methyl 2-pyridyldithiocarboxylate (**1**) and 3-pyridyldithiocarboxylate (**2**) were prepared according to a general method by Mayer and his group:[10] reaction of picolyl chloride with octasulfur and triethylamine, and subsequent alkylation with iodomethane. However we had to adapt the stoichiometry of the reagents (picolyl chloride : sulfur : triethylamine = 1 : 3 : 3) and optimise the reaction time to attain yields up to 60%.



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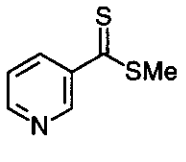
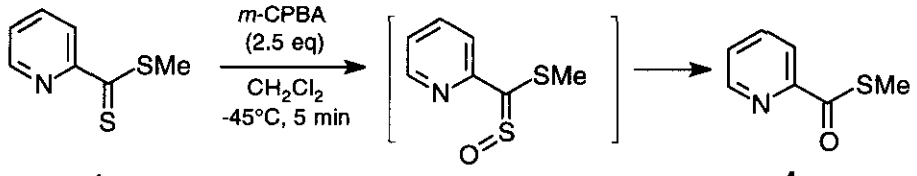


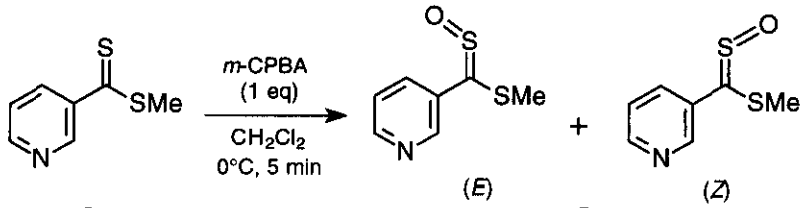
2

We also intended to use the corresponding sulfines (*S*-oxides) (**3**) and (**5**). Though a number of aromatic sulfines are known and rather stable molecules,[11-14] these heteroaromatic examples have not been reported. We attempted their preparation by the direct oxidation of thiocarbonyl compounds (**1**) and (**2**) with one equivalent of *meta*-chloroperoxybenzoic acid (*m*-CPBA). To our surprise for dithio ester (**1**) we were not able to detect the formation of the awaited sulfine (**3**) under a variety of conditions. Instead the corresponding thiol ester (**4**) was formed in a 40% yield when 2.5 equivalents of oxidising agent were used. This arises either from the unstability of sulfine (**3**) or by a rapid second oxidation leading to **4**.



1 **3** **4**

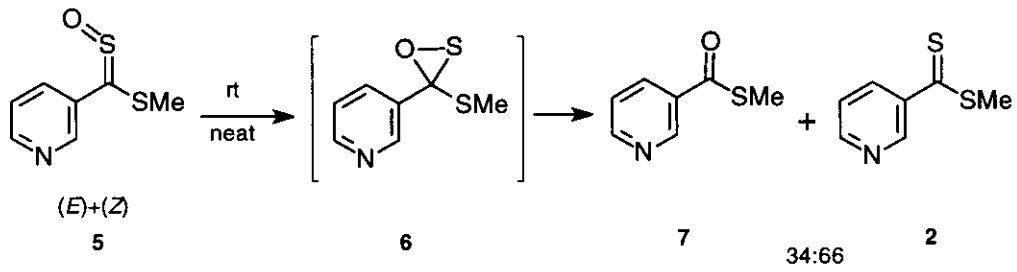
In contrast we were glad to obtain a sulfine (**5**) in 79% yield by reaction of dithio ester (**2**) and one equivalent of *m*-CPBA. It could be chromatographed on silica gel. It is a mixture of (*E*) and (*Z*) isomers in a 79:21 ratio, as shown[13,15] by NMR (^{1}H: SMe at 2.35 for *E* and 2.57 ppm for *Z* ; ^{13}C = SMe at 19.3 for *E* and 16.3 ppm for Z, C=S=O at 184.1 for *E* and 189.5 ppm for Z). This *S*-oxide (**5**) is moderately stable: its half life time was estimated to 20 days at room temperature.



2 **5** 79%

NMR analysis of a sample left at room temperature has shown that it first equilibrated into mixtures richer in the (*Z*) isomer, and subsequently was transformed into a 34:66 mixture of *S*-methyl 2-pyridylthioester (**7**) and, unexpectedly, dithio ester (**2**). Formation of a thiocarbonyl compound by thermal rearrangement of a sulfine has indeed very few precedents.[11,16] We assume that a 2 electron electrocyclisation leads[11,17] to

an intermediate oxathiirane (**6**) which undergoes one of two possible rearrangement pathways with extrusion either of sulfur or oxygen atoms.



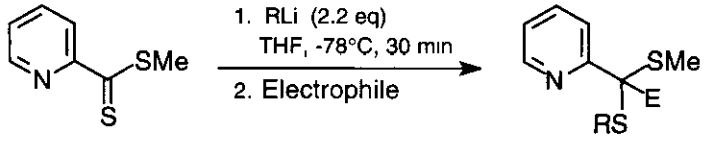
The structure under which the sulfur or the oxygen species are eliminated is intriguing. Adam's group has very recently published[18,19] the first trapping of sulfur from a sulfine under photochemical irradiation and by using the highly strained *trans*-cyclooctene.

The transformation of a sulfine into a carbonyl derivative, here a carboxylic thiol ester, has a number of precedents.[11,16] It must be stressed however that not much is reported about the thermal stability of aromatic dithio ester oxides.[11,13] In contrast we have shown in a previous study that aliphatic dithio ester oxides are moderately stable and afford essentially dithioperoxyesters, arising by an original rearrangement.[20-22]

The consequence of these observations is that, for synthetic purposes, the sulfine (**5**) can indeed be used provided it is freshly prepared.

THIOPHILIC ADDITION OF ORGANOLITHIUMS TO PYRIDYL DITHIO ESTERS

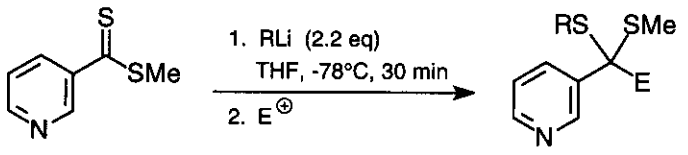
2-Pyridyl dithio ester (**1**) was submitted to various alkyl- and aryllithiums at –78°C in THF. After water quench dithio acetals (**8**) were isolated in 30-88 % yields (Table 1). The best results were obtained with 2.2 equivalents of base and 30 min for the reaction time. It is remarkable that all reagents which we tried led to thiophilic addition: alkyllithiums, phenyllithium and substituted pyridyl- or diazinyllithium. No product of carbophilic attack was observed. It could be noticed that aryllithiums led to better yields than alkyllithiums.



1 8

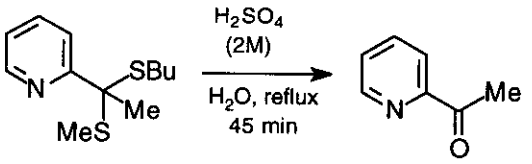
The intermediate anion could be trapped by other electrophiles: iodomethane, allyl or benzyl bromide and ethanal.

Analogous results were obtained with compound (**2**) bearing the dithio ester on the 3 position of the pyridine nucleus. Various electrophiles were used. Yields of dithio acetals (**9**) range from 18 to 85%.



2 **9**

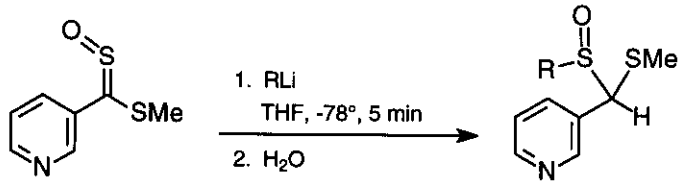
The products (**8**) and (**9**) are masked aldehydes or ketones. The pyridine ring facilitates the conversion to a carbonyl compound as shown by the conversion to methyl pyridyl ketone (**11**) achieved by treatment with aqueous sulfuric acid. It is noteworthy that salts of soft metal such as mercury, silver or copper are not necessary for this transformation.[23-25]



8c **11**
67%

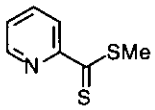
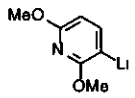
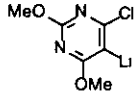
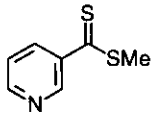
THIOPHILIC ADDITION TO A SULFINE

According to reports by Zwanenburg[11,26,27] and to our recent results,[28,29] dithioester oxides are very reactive towards organolithiums and the sense of addition is thiophilic. We wanted to use a sulfine in the pyridine series for this purpose. Addition of methyllithium or *n*-butyllithium to sulfine (**5**) proceeded smoothly to afford dithio acetal oxides (**10**). Yields of 55-75% were obtained with one equivalent of nucleophile and increased to 68-90% with two equivalents (Table 2). Products are formed as mixtures of diastereoisomers in a 53/47 ratio, and it can be mentioned that the major one was easily separated by crystallisation with pentane.



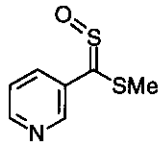
5 **10**

Table 1. Thiophilic addition of organolithiums to dithio esters (1) and (2)

Compound		Organolithium[a]	Electrophile	Temp ℃	Time min	Product	Yield %
	**1**	MeLi	H_2O	–78	15	**8a**	63
		n-BuLi	H_2O	–78	15	**8b**	76
		n-BuLi	MeI	–78	90	**8c**	70
		n-BuLi	AllylBr	rt	75	**8d**	59
		n-BuLi	BenzylBr	–78	30	**8e**	46
		n-BuLi	MeCHO	–78	120	**8f**	49
		s-BuLi	H_2O	–78	15	**8g**	50
		t-BuLi	H_2O	–78	15	**8h**	30
		PhLi	H_2O	–78	15	**8i**	88
			MeI	–78	90	**8j**	82
			MeI	–78	90	**8k**	49
	**2**	n-BuLi	H_2O	–78	15	**9a**	21
		n-BuLi	MeI	–78	90	**9b**	18
		t-BuLi	H_2O	–78	15	**9c**	27
		PhLi	H_2O	–78	15	**9d**	85
		PhLi	MeI	–78	90	**9e**	77
		PhLi	AllylBr	rt	90	**9f**	78
		PhLi	BenzylBr	–78 then rt	60 120	**9g**	61
		PhLi	MeCHO	–78 then 0	60 60	**9h**	41

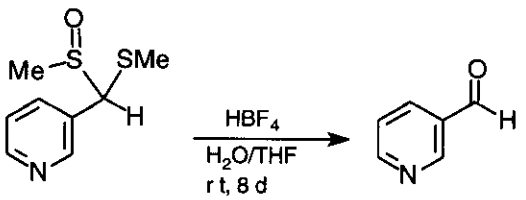
[a] Addition of the organolithium was carried out at –78°C and the mixture was stirred at the same temperature for 30 min in all cases.

Table 2. Thiophilic addition of organolithiums to sulfine (5)

Compound		Organolithium Addition at –78°C for 5 min		Electrophile		Product	
			Equiv RLi		Temp ℃		Yield %
	**5**	MeLi	1	H_2O	–78	**10aa**	55[a]
		MeLi	2	H_2O	–78	**10aa**	68[a]
		n-BuLi	1	H_2O	–78	**10ba**	75[a]
		n-BuLi	2	H_2O	–78	**10ba**	90[a]
		n-BuLi	2	MeI	–78 then rt[b]	**10bb**	63

a) Mixture of diastereoisomers in a 53:47 ratio for both cases.
b) Addition of iodomethane was carried out at –78°C and the mixture was stirred at room temperature for 42 h.

Dithio acetal oxides are easier to convert to carbonyl compounds than dithio acetals.[30-32] Treatment of **10aa** with a mineral acid, HBF_4, at room temperature gave 3-pyridylcarboxaldehyde (**12**) in 78% yield.



10aa **12**

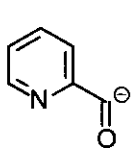
DISCUSSION

Our study has dealt with two pyridyl dithio esters (**1**) and (**2**) and one corresponding sulfine (**5**), which could be prepared by *m*-CPBA oxidation and exhibited moderate stability, requiring fresh preparation for synthetic purposes.

We were able to achieve a selective thiophilic addition to dithio esters (**1**) and (**2**) with a variety of organolithiums. This adds further examples to the rather limited possibilities of this original reaction in the aromatic series and brings the first examples in the heteroaromatic series. No *ortho*-metalation[33-35] or nucleophilic addition (1,2- or 1,4-) to the pyridine ring[36-39] has been observed.

The thiophilic addition brings a supplementary entry to carbanions being stabilized by two sulfur groups such as those obtained from dithianes in the *"Umpolung"* chemistry.[25,40] A noteworthy difference is that the intermediate anions here arise from an addition instead of a deprotonation reaction. An other difference with previous reports on the thiophilic addition is that here the nucleophilic agents are organolithiums instead of Grignard reagents. Though the latter reagents react nicely with aliphatic dithio esters[1,2] (see also some rare examples[3] of aromatic dithio esters), the intermediate anions have an halogenomagnesium counterion and are thus less reactive than the lithium carbanions formed in the present work. Addition of organolithiums to aromatic dithio esters has very few precedents.[41]

Thiophilic addition was also achieved selectively with the new sulfine (**5**). The present results demonstrate that the sulfur compounds (**1**), (**2**) and (**5**) can be used as acyl anion synthons (**13**) and (**14**).



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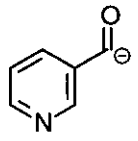

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EXPERIMENTAL

Methyl 2-pyridyldithiocarboxylate (1)

Prepared by modification of a procedure of the literature.[10] To a mixture of 2-picolyl chloride hydrochloride (4 g, 24.4 mmol), dichloromethane (25 mL) and water (25 mL), was added a saturated aqueous solution of sodium hydrogen carbonate until neutralisation. Dichloromethane (25 mL) was added and the organic phase was washed with a saturated aqueous solution of sodium hydrogen carbonate, and dried over magnesium sulfate. The free amine was isolated by evaporation of the solvent and introduced into a two neck flask. Sulfur (2.35 g, 73 mmol), dimethylformamide (12 mL) and triethylamine (10.2 mL, 73 mmol) were added. The mixture was stirred and heated to 25-30°C for 6.5 h. It was cooled with an ice water bath and iodomethane (13.6 mL, 219 mmol) was added dropwise. The mixture was stirred at rt for 20 min. Ether (10 mL) was added until a homogeneous mixture was isolated. It was washed with brine. The deep red aqueous phase was extracted by ether until it became yellow. The combined organic layers were washed

with brine, dried over magnesium sulfate and were concentrated by evaporation. The dithio ester (**1**) was isolated by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 1:1 as burgundy red crystals (mp 52-53°C, pentane)in 62% yield (2.578 g); ^{1}H NMR ($CDCl_3$): δ 2.75 (s, 3H, SCH_3), 7.47 (ddd, $J_{5,6}$= 4.9, $J_{5,4}$= 7.6 and $J_{5,3}$ = 0.9 Hz, 1H, H_5), 7.78 (td, $J_{4,5}$= $J_{4,3}$= 7.6 and $J_{4,6}$= 1.8 Hz , 1H, H_4), 8.32 (d_{app}, J_{app} = 8.5 Hz, 1H, H_3), 8.62 (d, $J_{5,6}$= 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 20.2 (SCH_3), 122.3 (C_3), 126.8 (C_5), 136.9 (C_4), 148.1 (C_6), 156.6 (C_2), 227.9 (C=S); MS: 169 (M^+, 48), 122 (M^+ - SCH_3, 77), 105 (75), 91 (CH_3S-C=S^+, 31), 78 (M^+ - S=C-SCH_3,100), 69 (47); IR (KBr): ν 782, 1068 cm^{-1}. Anal. Calcd for $C_7H_7NS_2$: C, 49.67; H, 4.17; N, 8.28; S, 37.88. Found: C, 50.02; H, 4.08; N, 7.78; S, 38.12.

Methyl 3-pyridyldithiocarboxylate (2)

Prepared by modification of a method of the literature[10] according to our procedure for the synthesis of (**3**). It was carried out with 3-picolyl chloride hydrochloride (12 g, 73 mmol), sulfur (7.036 g, 219 mmol), dimethylformamide (40 mL) and triethylamine (30.5 mL, 219 mmol). The reaction mixture was stirred at 25-30°C for 27 h. Iodomethane (13.7 mL, 219 mmol) was added and the mixture was stirred at rt for 20 min. After workup, methyl 3-pyridyldithiocarboxylate (**2**) was isolated by distillation ($bp_{0.03}$ 81-82°C) as burgundy red oil in 50% yield (6.2 g) ; ^{1}H NMR ($CDCl_3$): δ 2.81 (s, 3H, SCH_3), 7.34 (ddd, $J_{5,6}$= 4.9, $J_{4,5}$= 7.9 and $J_{2,5}$= 0.6 Hz, 1H, H_5), 8.23 (dt, $J_{4,5}$= 7.9 and $J_{4,6}$= 1.5 Hz, 1H, H_4), 8.74 (dd, $J_{4,6}$= 1.5 and $J_{5,6}$= 4.9 Hz, 1H, H_6), 9.17 (d_{app}, J_{app} = 1.8 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$): δ 20.8 (SCH_3), 123.3 (C_5), 134.2 (C_4), 140.5 (C_3), 147.0 (C_6), 152.7 (C_2), 225.7 (C=S); MS: 169 (M^+, 60), 122 (M^+ - SCH_3, 60), 106 (19), 95 (19), 78 (M^+ - S=C-SCH_3, 44) ; 69 (21), 51 (32), 45 (29); IR (NaCl): ν 1576, 1412, 1242, 1064, 1038, 1020 cm^{-1}. Anal. Calcd for $C_7H_7NS_2$: C, 49.67; H, 4.17; N, 8.28; S, 37.88. Found: C, 49.52; H, 4.32; N, 8.02; S, 38.14.

S-Methyl 2-pyridylthiocarboxylate (4)

To a solution of methyl 2-pyridyldithiocarboxylate (**1**) (500 mg, 2.95 mmol) in dichloromethane (20 mL) cooled between –40°C and –45°C, 60% *m*-CPBA (2.12 g, 7.37 mmol) was added. The mixture was stirred during 5 min. The solution was washed with a saturated aqueous solution of sodium hydrogen carbonate (3 x 20 mL), then with brine (20 mL). The organic phase was dried over magnesium sulfate and concentrated by evaporation. The thiol ester (**4**) was isolated by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 7:3 as pink cristals (mp 53-54°C) in 40% yield (181 mg); ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 3H, SCH_3), 7.52 (ddd, $J_{5,6}$ = 4.9, $J_{4,5}$= 7.6 and $J_{5,3}$= 1.2 Hz, 1H, H_5), 7.86 (td, $J_{4,5}$= 7.6 and $J_{4,6}$= 1.8 Hz, 1H, H_4), 7.97 (dapp, J_{app}= 7.9 Hz, 1H, H_3), 8.70 (d_{app}, J_{app} = 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 11.7 (SCH_3), 120.3, 127.9, 137.3, 149.2, 151.9, 194.2 (C=O); MS: 153 (M^+, 64), 136 (35), 107 (54), 106 (49), 89 (57), 78 (M^+ - O=C-SCH_3, 100), 77 (98); IR (KBr): ν 1672 cm^{-1} (C=O) . Anal. Calcd for C_7H_7NOS: C, 54.88; H, 4.61; N, 9.14; O, 10.44; S, 20.93. Found: C, 54.72; H, 4.71; N, 9.19; O, 10.68; S, 20.54.

3-[(Methylthio)sulfinylmethyl]pyridine (5)

To a solution of methyl 2-pyridyldithiocarboxylate (**2**) (2 g, 11.8 mmol) in dichloromethane (80 mL) cooled at 0°C, 60% *m*-CPBA (2.51 g, 10 mmol) was added. The mixture was stirred at 0°C during 5 min. The solution was washed with a saturated aqueous solution of sodium hydrogen carbonate (3 x 50 mL), then with brine (50 mL). The organic phase was dried over magnesium sulfate and concentrated by evaporation. The sulfine (**5**) was isolated by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 4:1 as an orange oil (1.72 g) in 79% yield; ^{1}H NMR ($CDCl_3$) isomer *(E)*: δ 2.35 (s, 3H, SCH_3), 7.40-7.47 (m, 1H, $H_{pyridyl}$), 8.53 (dt, J_1 = 2.1 and J_2 = 7.9 Hz, 1H, $H_{pyridyl}$), 8.71 (dd, J_3 = 1.5 and J_4 = 4.9 Hz, 1H, $H_{pyridyl}$), 9.22 (d_{app}, J_{app} = 2.2 Hz, 1H, $H_{pyridyl}$); Isomer *(Z)*: 2.58 (s, 3H, SCH_3), 7.40-7.47 (m, 1H, $H_{pyridyl}$), 7.76 (dt, J_1 = 2.1 and J_2 = 7.9 Hz, 1H, $H_{pyridyl}$), 8.66 (d_{app}, J_{app} = 1.5 Hz, 1H, $H_{pyridyl}$), 8.76 (dd, J_3 = 1.8 and J_4 = 4.9 Hz, 1H, $H_{pyridyl}$); ^{13}C NMR ($CDCl_3$) isomer *(E)*: δ 19.3 (SCH_3), 123.9, 135.9, 148.9, 152.0, 184.1 (C=S=O); Isomer *(Z)*: 16.3 (SCH_3), 124.0, 128.9, 136.2,

148.3, 152.7, 189.5 (C=S=O); MS: 185 (M^+, 22), 168 (30), 153 (M^+ - S, 42), 136 (37), 122 (Py-C=S^+, 100), 106 (43), 89 (41), 78 (Py^+, 39), 77 (100).

S-Methyl 3-pyridylthiocarboxylate (7)

A sample of sulfine (**5**) (208 mg, 1.23 mmol) was left at rt for 57 days. NMR revealed the transformation to a mixture of thiol ester (**7**) and dithio ester (**2**) in a 66:34 ratio. These two products could not be separated but the structure of compound (**7**) could be deduced by analogy with compound (**4**); ^{1}H NMR ($CDCl_3$): δ 2.52 (s, 3H, SCH_3), 7.41 (ddd_{app}, J_{app} = 4.9, J'_{app} = 8 and J''_{app} = 0.8 Hz, 1H, H_5), 8.19-8.26 (m, 1H, H_4), 8.79 (dd, J = 1.7 and J' = 4.9 Hz, 1H, H_6), 9.17 (m, 1H, H_2); ^{13}C NMR ($CDCl_3$): δ 11.8 (SCH_3), 123.7, 134.2, 134.5, 148.5, 153.8, 191.1 (C=O); IR (NaCl): ν 1664 cm^{-1} (C=O).

General Procedure A for Addition of Alkyllithiums to Dithio Esters

A solution of 1.3 mmol of alkyllithium (0.81 mL of methyllithium/1.6 M in ether or 0.52 mL of *n*-butyllithium/2.5 M in hexane or 1 mL of *sec*-butyllithium/1.3 M in hexane-pentane or 0.865 mL of *tert*-butyllithium/1.5 M in pentane - 2.2 eq) was added to anhydrous tetrahydrofuran (25 mL) at –78°C under an atmosphere of dry argon. A solution of methyl 2- or 3-pyridyldithiocarboxylate (100 mg, 0.59 mmol) in 5 mL of anhydrous tetrahydrofuran was added and the mixture was stirred for 30 min at –78°C. The electrophile was then added except for products (**8a-b**), (**8g-h**) and (**9a**), (**9c**), for which the reaction mixture was directly submitted to hydrolysis. The hydrolysis was carried out using a mixture of 35% aqueous hydrochloric acid (1 mL), ethanol (2 mL) and tetrahydrofuran (2 mL). The solution was gently warmed to rt and made slightly basic with a saturated sodium hydrogen carbonate solution (15 mL). The aqueous layer was extracted with dichloromethane (3x25 mL) and then the combined organic layers were dried over magnesium sulfate and were concentrated by evaporation. The product was isolated by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 13:2.

2-[Bis(methylsulfanyl)methyl]pyridine (8a)

Dithio ester (**1**) was reacted with methyllithium according to the procedure A. Hydrolysis was carried out at –78°C. Compound (**8a**) was isolated as a colorless oil in 63% yield (69 mg); ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 6H, $(SCH_3)_2$), 4.88 (s, 1H, $CH(SCH_3)_2$), 7.13 (dd, $J_{5,6}$ = 4.9 and $J_{5,4}$ = 7.8 Hz, 1H, H_5), 7.42 (d, $J_{3,4}$ = 7.8 Hz, 1H, H_3), 7.64 (td, $J_{4,3}$ = $J_{4,5}$ = 7.8 and $J_{4,6}$ = 1.8 Hz, 1H, H_4), 8.48 (dd, $J_{6,4}$ = 1.8 and $J_{6,5}$ = 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 15.0 ($(SCH_3)_2$), 58.7 ($\underline{C}H(SCH_3)_2$), 122.4, 123.1 (C_3, C_5), 137.5 (C_4), 149.3 (C_6), 159.9 (C_2); IR (KBr): ν 3047, 3004, 2914, 749 cm^{-1}. Anal. Calcd for $C_8H_{11}NS_2$: C, 51.85; H, 5.98; N, 7.56. Found: C, 51.85; H, 6.13; N, 7.76.

2-[(Butylsulfanyl)(methylsulfanyl)methyl]pyridine (8b)

Dithio ester (**1**) was reacted with *n*-butyllithium according to the procedure A. Hydrolysis was carried out at –78°C. Compound (**8b**) was isolated as a colorless oil in 76% yield (102 mg); ^{1}H NMR ($CDCl_3$): δ 0.82 (t, $J_{CH_2CH_3}$ = 7.2 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.35 (m, 2H, $SC_2H_4C\underline{H}_2CH_3$), 1.51 (m, 2H, $SCH_2C\underline{H}_2C_2H_5$), 2.07 (s, 3H, SCH_3), 2.60 (m, 2H, $SC\underline{H}_2C_3H_7$), 4.93 (s, 1H, $C\underline{H}(SCH_3)(SC_4H_9)$), 7.13 (ddd, $J_{5,3}$ = 1.0, $J_{5,6}$ = 4.9 and $J_{5,4}$ = 7.7 Hz, 1H, H_5), 7.46 (dd, $J_{3,5}$ = 1.0 and $J_{3,4}$ = 7.7 Hz, 1H, H_3), 7.64 (td, $J_{4,3}$ = $J_{4,5}$ = 7.7 and $J_{4,6}$ = 1.8 Hz, 1H, H_4), 8.47 (dd, $J_{6,5}$ = 4.9 and $J_{6,4}$ = 1.8 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 14.2, 14.9 (SCH_3, $S(C_3H_6)\underline{C}H_3$), 21.1 ($SC_2H_4\underline{C}H_2CH_3$), 31.7, 32.0 ($S\underline{C}_2H_4C_2H_5$), 57.1 ($\underline{C}H(SCH_3)(SC_4H_9)$), 122.4, 123.0 ($C_3$, C_5), 137.4 (C_4), 149.3 (C_6), 160.3 (C_2); IR (KBr): ν 3047, 2956, 2925, 748 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NS_2$: C, 58.10; H, 7.54; N, 6.16. Found: C, 58.34; H, 7.64; N, 6.07.

2-[1-Butylsulfanyl-1-(methylsulfanyl)ethyl]pyridine (8c)

Dithio ester (**1**) was reacted with *n*-butyllithium according to the procedure A. Iodomethane (0.13 mL, 2.1 mmol) was then added and the mixture was stirred for 90 min at –78°C. Hydrolysis was carried out at –78°C. Compound (**8c**) was isolated as a colorless oil in 70% yield (100 mg); ^{1}H NMR ($CDCl_3$): δ 0.82 (t,

$J_{CH_2CH_3}$ = 7.1 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.40 (m, 4H, $SCH_2C_2\underline{H}_4CH_3$), 1.98, 2.00 (2xs, 2x3H, $C(C\underline{H}_3)(SC\underline{H}_3)(SC_4H_9)$), 2.45 (m, 2H, $SC\underline{H}_2C_3H_7$), 7.13 (ddd, $J_{5,3}$ = 1.1, $J_{5,6}$ = 4.9 and $J_{5,4}$ = 7.8 Hz, 1H, H_5), 7.66 (td, $J_{4,3}$ = $J_{4,5}$ = 7.8 and $J_{4,6}$ = 1.8 Hz, 1H, H_4), 7.77 (dd, $J_{3,5}$ = 1.1 and $J_{3,4}$ = 7.8 Hz, 1H, H_3), 8.53 (dd, $J_{6,4}$ = 1.8 and $J_{6,5}$ = 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 14.3, 14.8 (SCH_3, $S(C_3H_6)\underline{C}H_3$), 22.9 ($SC_2H_4\underline{C}H_2CH_3$), 28.9 ($C(\underline{C}H_3)(SCH_3)(SC_4H_9)$), 31.5, 30.5 ($S\underline{C}_2H_4C_2H_5$), 61.5 ($\underline{C}(CH_3)(SCH_3)(SC_4H_9)$), 122.1, 122.7 ($C_3$, C_5), 137.2 (C_4), 148.8 (C_6), 161.4 (C_2); IR (KBr): ν 3047, 3002, 2979, 761, 741 cm^{-1}. Anal. Calcd for $C_{12}H_{19}NS_2$: C, 59.70; H, 7.93; N, 5.80. Found: C, 59.59; H, 7.96; N, 5.66.

2-[1-Butylsulfanyl-1-(methylsulfanyl)but-3-enyl]pyridine (8d)

Dithio ester (**1**) was reacted with *n*-butyllithium according to the procedure A. Allyl bromide (0.18 mL, 2.1 mmol) was then added and the mixture was warmed to rt and stirred for 75 min. Hydrolysis was carried out at rt. Compound (**8d**) was isolated as a yellow oil in 59% yield (93 mg); ^{1}H NMR ($CDCl_3$): δ 0.79 (t, $J_{CH_2CH_3}$ = 7.3 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.20-1.45 (m, 4H, $SCH_2C_2\underline{H}_4CH_3$), 1.94 (s, 3H, SCH_3), 2.40 (m, 2H, $SC\underline{H}_2C_3H_7$), 2.93 (d, J_{CH_2CH} = 6.7 Hz, 2H, $C(SCH_3)(SC_4H_9)(C\underline{H}_2CHCH_2)$), 5.00 (m, 2H, $C(SCH_3)(SC_4H_9)(CH_2CHC\underline{H}_2)$), 5.60 (m, 1H, $C(SCH_3)(SC_4H_9)(CH_2C\underline{H}CH_2)$), 7.09 (ddd, $J_{5,3}$ = 1.1, $J_{5,6}$ = 4.8 and $J_{5,4}$ = 7.8 Hz, 1H, H_5), 7.67 (m, 2H, H_3,H_4), 8.50 (dd, $J_{6,5}$ = 4.8 and $J_{6,4}$ = 1.8 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 12.9, 14.3 (SCH_3, $SC_3H_6\underline{C}H_3$), 22.9 ($SC_2H_4\underline{C}H_2CH_3$), 29.6, 31.2 ($S\underline{C}_2H_4CH_2CH_3$), 43.8 ($C(SCH_3)(SC_4H_9)(\underline{C}H_2CHCH_2)$), 68.2 ($\underline{C}(SCH_3)(SC_4H_9)(C_3H_5)$), 118.3 ($C(SCH_3)(SC_4H_9)(CH_2CH\underline{C}H_2)$), 122.6, 122.7 ($C_3$, C_5), 133.5 ($C(SCH_3)(SC_4H_9)(CH_2\underline{C}HCH_2)$), 136.9 ($C_4$), 148.7 ($C_6$), 161.5 ($C_2$); IR (KBr): ν 2870, 1956, 1926, 748 cm^{-1}. Anal. Calcd for $C_{14}H_{21}NS_2$: C, 62.87; H, 7.91; N, 5.24. Found: C, 63.08; H, 7.81; N, 5.29.

2-(1-Butylsulfanyl-1-methylsulfanyl-2-phenylethyl)pyridine (8e)

Dithio ester (**1**) was reacted with *n*-butyllithium according to the procedure A. Benzyl bromide (0.25 mL, 2.1 mmol) was then added and the mixture was stirred at –78°C for 30 min. Hydrolysis was carried out at –78°C. Compound (**8e**) was isolated as a colorless oil in 46% yield (86 mg); ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J_{CH_2CH_3}$ = 7.4 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.25-1.50 (m, 4H, $SCH_2C_2\underline{H}_4CH_3$), 2.03 (s, 3H, SCH_3), 2.40-2.50 (m, 2H, $SC\underline{H}_2C_3H_7$), 3.49 (s, 2H, CH_2Ph), 6.81 (m, 2H, H'$_3$), 7.1 (m, 4H, H_5, H'$_2$, H'$_4$), 7.55 (td, $J_{4,5}$ = $J_{4,3}$ = 8.1 and $J_{4,6}$ = 1.8 Hz, 1H, H_4), 7.61 (dd, $J_{3,5}$ = 1.0 and $J_{3,4}$ = 8.1 Hz, 1H, H_3), 8.55 (dd, $J_{6,4}$ = 1.8 and $J_{6,5}$ = 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 13.4, 14.3 (SCH_3, $SC_3H_6\underline{C}H_3$), 22.9 ($SC_2H_4\underline{C}H_2CH_3$), 30.1, 31.2 ($S\underline{C}_2H_4C_2H_5$), 70.4 ($\underline{C}(SCH_3)(SC_4H_9)$), 122.6, 123.5 ($C_3$, C_5), 127.2, 128.1 ($C_{2'}$, $C_{4'}$), 131.0 ($C_{3'}$), 135.8 ($C_{1'}$), 135.9 (C_4), 149.0 (C_6), 160.9 (C_2); IR (KBr): ν 3057, 3045, 2920, 748 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NS_2$: C, 68.09; H, 7.30; N, 4.41. Found: C, 67.87; H, 7.47; N, 4.27.

1-Butylsulfanyl-1-methylsulfanyl-1-(2-pyridyl)-2-propanol (8f)

Dithio ester (**1**) was reacted with *n*-butyllithium according to the procedure A. Acetaldehyde (0.4 mL, 7 mmol) was then added and the mixture was stirred at –78°C for 2 h. Hydrolysis was carried out at –78°C. Compound (**8f**) was isolated as a yellow oil in 49% yield (78 mg); ^{1}H NMR ($CDCl_3$): δ 0.83 (t, $J_{CH_2CH_3}$ = 7.2 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.25-1.50 (m, 7H, $CH(OH)(C\underline{H}_3)$), $SCH_2C_2\underline{H}_4CH_3$), 2.00 (s, 3H, SCH_3), 2.25-2.75 (m, 2H, $SC\underline{H}_2C_3H_7$), 4.35 (m, 1H, $C\underline{H}(OH)(CH_3)$), 5.35 (s, 1H, OH), 7.18 (dd, $J_{5,6}$ = 4.7 and $J_{5,4}$ = 8.0 Hz, 1H, H_5), 7.69 (td, $J_{4,5}$ = $J_{4,3}$ = 8.0 and $J_{4,6}$ = 1.7 Hz, 1H, H_4), 7.81 (d, $J_{3,4}$ = 8.0 Hz, 1H, H_3), 8.51 (dd, $J_{6,5}$ = 4.7 and $J_{6,4}$ = 1.7 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 13.4, 14.3 (SCH_3, $SC_3H_6\underline{C}H_3$), 19.5 ($CH(OH)(\underline{C}H_3)$), 22.9 ($SC_2H_4\underline{C}H_2CH_3$), 30.4, 31.6 ($S\underline{C}H_2\underline{C}H_2C_2H_5$), 70.8 ($\underline{C}(SCH_3)(SC_4H_9)$), 73.2 ($\underline{C}H(OH)(CH_3)$), 123.0, 124.2 ($C_3$, C_5), 137.3 (C_4), 148.6 (C_6), 160.8 (C_2); IR (KBr): ν 3373, 2956, 2927, 2870, 757 cm^{-1}. Anal. Calcd for $C_{13}H_{21}NOS_2$: C, 57.52; H, 7.80; N, 5.16. Found: C, 57.76; H, 7.69; N, 5.06.

2-[(1-Methylpropylsulfanyl)(methylsulfanyl)methyl]pyridine (8g)

Dithio ester (**1**) was reacted with *sec*-butyllithium according to the procedure A. Hydrolysis was carried out at –78°C. Compound (**8g**) was isolated as a yellow oil in 50% yield (67 mg); ^{1}H NMR ($CDCl_3$): δ 0.93 (m, 3H, $SCH(CH_3)(CH_2C\underline{H}_3)$), 1.25 (m, 3H, $SCH(C\underline{H}_3)(C_2H_5)$), 1.60 (m, 2H, $SCH(CH_3)(C\underline{H}_2CH_3)$), 2.10 (s, 3H, SCH_3), 2.90 (m, 1H, $SC\underline{H}(CH_3)(C_2H_5)$), 5.00 (s, 1H, $C\underline{H}(SCH_3)(SC_4H_9)$), 7.16 (ddd, $J_{5,3}$ = 1.2, $J_{5,6}$ = 4.9 and $J_{5,4}$ = 7.5 Hz, 1H, H_5), 7.54 (dd, $J_{3,5}$ = 1.2 and $J_{3,4}$ = 7.5 Hz, 1H, H_3), 7.68 (td, $J_{4,5}$ = $J_{4,3}$ = 7.5 and $J_{4,6}$ = 1.8 Hz, 1H, H_4), 8.50 (dd, $J_{6,4}$ = 1.8 and $J_{6,5}$ = 4.9 Hz, 1H, H_6); IR (KBr): ν 3049, 2947, 2941, 741 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NS_2$: C, 58.10; H, 7.54; N, 6.16. Found: C, 58.87; H, 7.56; N, 6.29.

2-[(1,1-Dimethylethylsulfanyl)(methylsulfanyl)methyl]pyridine (8h)

Dithio ester (**1**) was reacted with *tert*-butyllithium according to the procedure A. Hydrolysis was carried out at –78°C. Compound (**8h**) was isolated as a yellow oil in 30% yield (40 mg); ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 9H, $SC(CH_3)_3$), 2.12 (s, 3H, SCH_3), 4.97 (s, 1H, $C\underline{H}(SCH_3)(SC_4H_9)$), 7.14 (ddd, $J_{5,3}$ = 1.2, $J_{5,6}$ = 4.9 and $J_{5,4}$ = 7.8 Hz, 1H, H_5), 7.59 (dd, $J_{3,5}$ = 1.2 and $J_{3,4}$ = 7.8 Hz, 1H, H_3), 7.67 (td, $J_{4,5}$ = $J_{4,3}$ = 7.8 and $J_{4,6}$ = 1.7 Hz, 1H, H_4), 8.47 (dd, $J_{6,4}$ = 1.7 and $J_{6,5}$ = 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 16.6 (SCH_3), 31.8 ($SC(\underline{C}H_3)_3$), 46.0 ($S\underline{C}(CH_3)_3$), 54.1 ($\underline{C}H(SCH_3)(SC_4H_9)$), 123.0, 123.1 ($C_3$, C_5), 137.7 (C_4), 149.2 (C_6), 162.4 (C_2); IR (KBr): ν 3049, 2947, 2861, 746 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NS_2$: C, 58.10; H, 7.54; N, 6.16. Found: C, 58.50; H, 7.39; N, 6.26.

3-[(Butylsulfanyl)(methylsulfanyl)methyl]pyridine (9a)

Dithio ester (**2**) was reacted with *n*-butyllithium according to the procedure A. Hydrolysis was carried out at –78°C. Compound (**9a**) was isolated as a colorless oil in 21% yield (28 mg); ^{1}H NMR ($CDCl_3$): δ 0.96 (t, $J_{CH_2CH_3}$ = 7.1 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.20-1.60 (m, 4H, $SCH_2C_2\underline{H}_4CH_3$), 2.15 (s, 3H, SCH_3), 2.48 (m, 2H, $SC\underline{H}_2C_3H_7$), 4.82 (s, 1H, $C\underline{H}(SCH_3)(SC_4H_9)$), 7.23 (dd, $J_{5,6}$ = 4.8 and $J_{5,4}$ = 8.0 Hz, 1H, H_5), 7.81 (ddd, $J_{4,6}$ = 1.5, $J_{4,2}$ = 2.2 and $J_{4,5}$ = 8.0 Hz, 1H, H_4), 8.56 (dd, $J_{6,5}$ = 4.8 and $J_{6,4}$ = 1.5 Hz, 1H, H_6), 8.62 (d, $J_{2,4}$ = 2.2 Hz, 1H, H_2). Anal. Calcd for $C_{11}H_{17}NS_2$: C, 58.10; H, 7.54; N, 6.16. Found: C, 58.18; H, 7.66; N, 6.26.

3-[1-Butylsulfanyl-1-(methylsulfanyl)ethyl]pyridine (9b)

Dithio ester (**2**) was reacted with *n*-butyllithium according to the procedure A. Iodomethane (0.13 mL, 2.1 mmol) was then added and the mixture was stirred at –78°C for 90 min. Hydrolysis was carried out at –78°C. Compound (**9b**) was isolated as a colorless oil in 18% yield (26 mg); ^{1}H NMR ($CDCl_3$): δ 0.87 (t, $J_{CH_2CH_3}$ = 7.4 Hz, 3H, $SC_3H_6C\underline{H}_3$), 1.25-1.50 (m, 4H, $SCH_2C_2\underline{H}_4CH_3$), 2.00, 2.03 (2xs, 2x3H, SCH_3, $C(C\underline{H}_3)(SCH_3)(SC_4H_9)$), 2.48 (m, 2H, $SC\underline{H}_2C_3H_7$), 7.27 (ddd, $J_{5,2}$ = 0.8, $J_{5,6}$ = 4.7 and $J_{5,4}$ = 8.1 Hz, 1H, H_5), 8.02 (ddd, $J_{4,6}$ = 1.5, $J_{4,2}$ = 2.2 and $J_{4,5}$ = 8.1 Hz, 1H, H_4), 8.48 (dd, $J_{6,5}$ = 4.7 and $J_{6,4}$ = 1.5 Hz, 1H, H_6), 8.92 (dd, $J_{2,5}$ = 0.8 and $J_{2,4}$ = 2.2 Hz, 1H, H_2); IR (KBr): ν 3050, 2979, 2965, 747 cm^{-1}. Anal. Calcd for $C_{12}H_{19}NS_2$: C, 59.70; H, 7.93; N, 5.80. Found: C, 59.55; H, 7.81; N, 5.93.

3-[(1,1-Dimethylethylsulfanyl)(methylsulfanyl)methyl]pyridine (9c)

Dithio ester (**2**) was reacted with *tert*-butyllithium according to the procedure A. Hydrolysis was carried out at –78°C. Compound (**9c**) was isolated as a yellow oil in 27% yield (36 mg); ^{1}H NMR ($CDCl_3$): 1.28 (s, 3H, $SC(CH_3)_3$), 2.07 (s, 3H, SCH_3), 4.80 (s, 1H, $C\underline{H}(SCH_3)(SC_4H_9)$), 7.24 (dd, $J_{5,6}$ = 4.7 and $J_{5,4}$ = 7.9 Hz, 1H, H_5), 7.82 (ddd, $J_{4,6}$ = 1.5, $J_{4,2}$ = 2.0 and $J_{4,5}$ = 7.9 Hz, 1H, H_4), 8.45 (dd, $J_{6,5}$ = 4.7 and $J_{6,4}$ = 1.5 Hz, 1H, H_6), 8.58 (d, $J_{2,4}$ = 2.2 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$): δ 17.0 (SCH_3), 31.9 ($SC(\underline{C}H_3)_3$), 46.2 ($S\underline{C}(CH_3)_3$), 50.0 ($\underline{C}H(SCH_3)(SC_4H_9)$), 124.4 ($C_5$), 136.1 ($C_4$), 138.6 ($C_3$), 149.4, 149.5 ($C_2$ and C_6); IR (KBr): ν 3012, 2948, 2937, 751, 747 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NS_2$: C, 58.10; H, 7.54; N, 6.16. Found: C, 58.17; H, 7.69; N, 6.08.

General Procedure B for Addition of Phenyllithium to Dithio Esters

Iodobenzene (0.155 mL, 1.4 mmol) was added to a solution of *n*-butyllithium (2.5 M in hexane, 1.1 mL, 2.75 mmol) in anhydrous tetrahydrofuran (25 mL) at –78°C under an atmosphere of dry argon. The mixture was stirred for 30 min and a solution of methyl 2- or 3-pyridyldithiocarboxylate (107 mg, 0.63 mmol) in 5 mL of anhydrous tetrahydrofuran was added. The mixture was stirred for 30 min at –78°C. The electrophile was then added except for products (**8i**) and (**9d**), which were directly submitted to hydrolysis. The hydrolysis was carried out using a mixture of 35% aqueous hydrochloric acid (1 mL), ethanol (2 mL) and tetrahydrofuran (2 mL). The solution was gently warmed to rt and made slightly basic with a saturated sodium hydrogen carbonate solution (15 mL). The aqueous layer was extracted with dichloromethane (3x25 mL) and then the combined organic layers were dried over magnesium sulfate and concentrated by evaporation. The product was isolated by column chromatography on silica gel with a mixture of petroleum ether, ethyl acetate 13:2.

2-[(Methylsulfanyl)(phenylsulfanyl)methyl]pyridine (8i)

Dithio ester (**1**) was reacted with phenyllithium according to the procedure B. Hydrolysis was carried out at –78°C. Compound (**8i**) was isolated as a yellow oil in 88% yield (137 mg); ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 3H, SCH_3), 5.28 (s, 1H, $CH(SCH_3)(SPh)$), 7.13 (ddd, $J_{5,3}$ = 1.1, $J_{5,6}$ = 4.9 and $J_{5,4}$ = 7.7 Hz, 1H, H_5), 7.22 (m, 3H, H_{phenyl}), 7.40 (m, 3H, H_3, 2 H_{phenyl}), 7.61 (td, $J_{4,5}$ = $J_{4,3}$ = 7.7 and $J_{4,6}$ = 1.8 Hz, 1H, H_4), 8.51 (ddd, $J_{6,3}$ = 0.9, $J_{6,4}$ = 1.8 and $J_{6,5}$ = 4.9 Hz, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 15.8 (SCH_3), 60.7 ($\underline{C}H(SCH_3)(SPh)$), 122.7, 123.3 ($C_3$, C_5), 128.4, 129.5 ($C_{2'}$, $C_{4'}$), 133.2 ($C_{3'}$), 134.9 ($C_{1'}$), 137.7 (C_4), 149.7 (C_6), 159.6 (C_2); IR: ν 3052, 3004, 2915, 744 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NS_2$: C, 63.13; H, 5.30; N, 5.64. Found: C, 63.41; H, 5.25; N, 5.48.

3-[(Methylsulfanyl)(phenylsulfanyl)methyl]pyridine (9d)

Dithio ester (**2**) was reacted with phenyllithium according to the procedure B. Hydrolysis was carried out at –78°C. Compound (**9d**) was isolated as a yellow oil in 85% yield (132 mg); ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, SCH_3), 5.08 (s, 1H, $C\underline{H}(SCH_3)(SPh)$), 7.20 (m, 4H, H_5, 4 H_{phenyl}), 7.30 (m, 2H, H_{phenyl}), 7.68 (dd, $J_{4,2}$ = 1.8 and $J_{4,5}$ = 7.9 Hz, 1H, H_4), 8.45 (d, $J_{6,5}$ = 4.4 Hz, 1H, H_6), 8.48 (d, $J_{2,4}$ = 1.8 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$): δ 16.6 (SCH_3), 56.9 ($\underline{C}H(SCH_3)(SPh)$), 124.1 ($C_5$), 128.9, 129.6 ($C_{2'}$, $C_{4'}$), 133.8 ($C_{1'}$), 134.0 ($C_{3'}$), 135.8 (C_4), 136.4 (C_3), 149.5, 149.7 (C_2, C_6); IR (KBr): ν 3047, 2957, 2942, 756 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NS_2$: C, 63.13; H, 5.30; N, 5.64. Found: C, 63.42; H, 5.31; N, 5.79.

3-[1-Methylsulfanyl-1-(phenylsulfanyl)ethyl]pyridine (9e)

Dithio ester (**2**) was reacted with phenyllithium according to the procedure B. Iodomethane (0.14 mL, 2.25 mmol) was then added and the mixture was stirred at –78°C for 90 min. Hydrolysis was carried out at –78°C. Compound (**9e**) was isolated as a yellow oil in 77% yield (127 mg); ^{1}H NMR ($CDCl_3$): 1.95, 2.10 (2xs, 2x3H, SCH_3, $C(C\underline{H}_3)(SCH_3)(SPh)$), 7.25 (m, 6H, H_5, H_{phenyl}), 7.89 (ddd, $J_{4,6}$ = 1.4, $J_{4,2}$ = 2.2 and $J_{4,5}$ = 8.0 Hz, 1H, H_4), 8.48 (dd, $J_{6,4}$ = 1.4 and $J_{6,5}$ = 4.8 Hz, 1H, H_6), 8.76 (dd, $J_{2,5}$ = 0.8 and $J_{2,4}$ = 2.2 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$): δ 14.7 (SCH_3), 28.2 ($C(\underline{C}H_3)(SCH_3)(SPh)$), 60.7 ($\underline{C}(CH_3)(SCH_3)(SPh)$), 123.5 ($C_5$), 129.2, 130.1 ($C_{2'}$, $C_{4'}$), 132.0 ($C_{1'}$), 135.8 ($C_{3'}$), 137.4 (C_4), 139.5 (C_3), 149.1, 149.2 (C_2, C_6); IR (KBr): ν 3053, 2970, 2917, 751 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NS_2$: C, 64.32; H, 5.78; N, 5.36. Found: C, 63.21; H, 5.88; N, 5.56.

3-[1-Methylsulfanyl-1-(phenylsulfanyl)but-3-enyl]pyridine (9f)

Dithio ester (**2**) was reacted with phenyllithium according to the procedure B. Allyl bromide (0.19 mL, 2.2 mmol) was then added and the mixture was warmed up to rt and stirred for 90 min. Hydrolysis was carried out at rt. Compound (**9f**) was isolated as a yellow oil in 78% yield (141 mg); ^{1}H NMR ($CDCl_3$): δ 2.99 (d, J_{CH_2CH} = 6.9 Hz, 2H, $C(SPh)(SCH_3)(C\underline{H}_2CHCH_2)$), 5.10 (m, 2H, $C(SPh)(SCH_3)(CH_2CHC\underline{H}_2)$), 5.76 (m, 1H, $C(SPh)(SCH_3)(CH_2C\underline{H}CH_2)$), 2.11 (s, 3H, SCH_3), 7.21 (m, 6H, H_5, H_{phenyl}), 7.80 (ddd, $J_{4,6}$ = 1.4, $J_{4,2}$ = 2.0 and $J_{4,5}$ = 8.0 Hz, 1H, H_4), 8.45 (dd, $J_{6,4}$ = 1.4 and $J_{6,5}$ = 4.8 Hz, 1H, H_6), 8.76 (d,

$J_{2,4}$ = 2.0 Hz, 1H, H_2); IR (KBr): ν 3052, 2958, 2950, 749 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NS_2$: C, 66.86; H, 5.96; N, 4.87. Found: C, 66.12; H, 5.90; N, 4.81.

3-(1-Methylsulfanyl-1-phenylsulfanyl-2-phenylethyl)pyridine (9g)

Dithio ester (**2**) was reacted with phenyllithium according to the procedure B. Benzyl bromide (0.26 mL, 2.2 mmol) was then added. The mixture was stirred for 1 h at –78°C then warmed up to rt and stirred for 2 h. Hydrolysis was carried out at rt. Compound (**9g**) was isolated as a yellow oil in 61% yield (130 mg); ^1H NMR ($CDCl_3$): δ 2.10 (s, 3H, SCH_3), 3.52 (m, 2H, CH_2Ph) 6.85-7.30 (m, 11H, H_5, H_{phenyl}), 7.75 (d, $J_{4,5}$ = 8.1 Hz, 1H, H_4), 8.47 (d, $J_{6,5}$ = 4.6 Hz, 1H, H_6), 8.52 (s, 1H, H_2); IR (KBr): ν 3021, 2997, 748 cm^{-1}. Anal. Calcd for $C_{20}H_{19}NS_2$: C, 71.18; H, 5.67; N, 4.15. Found: C, 69.9; H, 5.64; N, 4.09.

1-Methylsulfanyl-1-phenylsulfanyl-1-(3-pyridyl)-2-propanol (9h)

Dithio ester (**2**) was reacted with phenyllithium according to the procedure B. Acetaldehyde (0.4 mL, 7 mmol) was then added. The mixture was stirred at –78°C for 1 h then warmed to 0°C and stirred for 1 h. Hydrolysis was carried out at 0°C. Compound (**9h**) was isolated as a yellow oil in 41% yield (75 mg); ^1H NMR ($CDCl_3$): δ 1.32 (m, 3H, $CH(C\underline{H}_3)(OH)$), 2.00 (s, 3H, SCH_3), 4.38 (m, 1H, $C\underline{H}(CH_3)(OH)$), 5.30 (s, 1H, OH), 7.30 (m, 6H, H_5, H_{phenyl}), 7.90 (dd, $J_{4,2}$ = 2.1 and $J_{4,5}$ = 7.9 Hz, 1H, H_4), 8.49 (d, $J_{6,5}$ = 4.9 Hz, 1H, H_6), 8.70 (d, $J_{2,4}$ = 2.1 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$): δ 20.2 (SCH_3), 29.2 ($CH(\underline{C}H_3)(OH)$), 69.1 ($\underline{C}(C_2H_4OH)(SCH_3)(SPh)$), 72.5 ($\underline{C}H(CH_3)(OH)$), 123.9 ($C_5$), 129.1, 131.0 ($C_{2'}$, $C_{4'}$), 132.5 ($C_{1'}$), 134.6 ($C_{3'}$), 137.3 (C_4), 140.1 (C_3), 149.8, 150.1 (C_2, C_6); IR (KBr): ν 3365, 3011, 2972, 749 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NOS_2$: C, 61.82; H, 5.88; N, 4.81. Found: C, 61.71; H, 5.88; N, 4.89.

2,6-Dimethoxy-3-[1-methylsulfanyl-1-(2-pyridyl)ethyl]pyridine (8j)

A solution of *n*-butyllithium (2.5M in hexane, 0.59 mL, 1.47 mmol) was added dropwise to a solution of 2,6-dimethoxypyridine (186 mg, 1.34 mmol) in 25 mL of anhydrous tetrahydrofuran at –78°C under an atmosphere of dry argon. The mixture was warmed to rt and stirred for 30 min. The mixture was then cooled to –78°C and a solution of methyl 2-pyridyldithiocarboxylate (102 mg, 0.6 mmol) in 5 mL of tetrahydrofuran was added. After 30 min, iodomethane (0.12 mL, 1.9 mmol) was added and the mixture was stirred for 90 min at –78°C. Hydrolysis was carried out using a mixture of 35% aqueous hydrochloric acid (1 mL), ethanol (2 mL) and tetrahydrofuran (2 mL). The solution was gently warmed to rt and made slightly basic with a saturated sodium hydrogen carbonate solution (15 mL). The aqueous layer was extracted with dichloromethane (3x25 mL) and the combined organic layers were dried over magnesium sulfate and concentrated by evaporation. The dithio acetal (**8j**) was isolated by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 13:2 as a yellow oil which crystallized as an amorphous solid in 82% yield (159 mg); ^1H NMR ($CDCl_3$): δ 1.92, 2.07 (2xs, 2x3H, SCH_3, $C(C\underline{H}_3)(SCH_3)(SPyr)$), 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.19 (d, $J_{5,4}$ = 8.1 Hz, 1H, H_5), 7.08 (dd, $J_{5',6'}$ = 4.8 and $J_{5',4'}$ = 7.9 Hz, 1H, $H_{5'}$), 7.39 (d, $J_{4,5}$ = 8.1 Hz, 1H, H_4), 7.56 (m, 2H, $H_{3'}$, $H_{4'}$), 8.47 (d, $J_{6',5'}$ = 4.8 Hz, 1H, $H_{6'}$); ^{13}C NMR ($CDCl_3$): δ 14.1 (SCH_3), 27.0 ($C(SCH_3)(Spyr)(\underline{C}H_3)$), 54.1 (2x$OCH_3$), 65.9 ($\underline{C}(SCH_3)(SPyr)(CH_3)$), 102.0 ($C_5$), 103.6 ($C_3$), 122.2, 122.5 ($C_{3'}$, $C_{5'}$), 136.6 ($C_{4'}$), 148.4, 151.2 (C_4, $C_{6'}$), 162.2 ($C_{2'}$), 164.6, 164.9 (C_2, C_6); IR (KBr): ν 3365, 3011, 2972, 749 cm^{-1}. Anal. Calcd for $C_{15}H_{18}N_2O_2S_2$: C, 55.87; H, 5.63; N, 8.69. Found: C, 55.59; H, 5.72; N, 8.78.

6-Chloro-2,4-dimethoxy-5-[1-methylsulfanyl-1-(2-pyridyl)ethyl]pyridine (8k)

A solution of *n*-butyllithium (2.5 M in hexane, 0.47 mL, 1.17 mmol) was added dropwise to a solution of 6-chloro-2,4-dimethoxypyridine (196 mg, 1.1 mmol) in anhydrous tetrahydrofuran (25 mL) at –78°C under an atmosphere of dry argon. The mixture was stirred for 10 min and a solution of methyl 2-pyridyldithiocarboxylate (85 mg, 0.51 mmol) in 5 mL of tetrahydrofuran was added. After 30 min, iodomethane (0.08 mL, 1.28 mmol) was added and the mixture was stirred for 90 min at –78°C. Hydrolysis was carried out using a mixture of 35% aqueous hydrochloric acid (1 mL), ethanol (2 mL) and

tetrahydrofuran (2 mL). The solution was gently warmed to rt and made slightly basic with a saturated sodium hydrogen carbonate solution (15 mL). The aqueous layer was extracted with dichloromethane (3x25 mL) and the combined organic layers were dried over magnesium sulfate and concentrated by evaporation. The dithio acetal (**8k**) was isolated by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 13:2 as yellow oil in 49% yield (89 mg); ^{1}H NMR ($CDCl_3$): δ 1.99, 2.18 (2xs, 2x3H, SCH_3, $C(C\underline{H}_3)(SCH_3)(SPyr)$), 3.70 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 7.17 (dd, $J_{5',6'}$ = 4.8 and $J_{5',4'}$ = 8.1 Hz, 1H, $H_{5'}$), 7.64 (m, 2H, $H_{3'}$, $H_{4'}$), 8.50 (d, $J_{6',5'}$ = 4.8 Hz, 1H, $H_{6'}$); ^{13}C NMR ($CDCl_3$): δ 14.7 (SCH_3), 26.8 ($C(SCH_3)(SPyr)(\underline{C}H_3)$), 55.7, 56.2 ($2xOCH_3$), 67.5 ($\underline{C}(SCH_3)(SPyr)(CH_3)$), 105.8 ($C_5$), 122.0, 123.0 ($C_{3'}$, $C_{5'}$), 137.1 ($C_{4'}$), 148.4 ($C_{6'}$), 162.1 ($C_{2'}$), 164.6, 169.6, 174.0 (C_2, C_4, C_6); IR (KBr): ν 2946, 2995, 1027, 789 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_3O_2ClS_2$: C, 46.99; H, 4.51; N, 7.83. Found: C, 46.69; H, 4.59; N, 8.96.

2-Acetylpyridine (11)

2-[1-Butylsulfanyl-1-(methylsulfanyl)ethyl]pyridine (**8c**) (118 mg, 0.49 mmol) was added to 40 mL of sulfuric acid (2 M in water). The mixture was refluxed for 45 min and then cooled to rt. It was made slightly basic with a concentrated solution of ammonia. The aqueous layer was extracted with dichloromethane (3x30 mL) and the combined organic layers were dried over magnesium sulfate and concentrated by evaporation. The ketone (**11**) was isolated by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate 14:1 as a colorless oil in 67% yield (40 mg). This product has been identified with an authentic commercial sample. ^{1}H NMR ($CDCl_3$): δ 2.74 (s, 3H, CH_3), 7.48 (dd, $J_{5,4}$= 7.9 and $J_{5,6}$= 3.6 Hz, 1H, H_5), 7.84 (t, $J_{4,5}$= $J_{4,3}$= 7.9 Hz, 1H, H_4), 8.05 (d, $J_{3,4}$= 7.9 Hz, 1H, H_3), 8.69 (d, $J_{6,5}$= 3.6 Hz, 1H, H_6). Anal. Calcd for C_7H_7NO: C, 69.40; H, 5.82; N, 11.56. Found: C, 70.69; H, 5.82; N, 11.56.

3-[(Methylsulfinyl)(methylsulfanyl)methyl]pyridine (10aa)

A solution of methyllithium (1.6 M in ether, 1.26 mL, 2 mmol) was added to a solution of sulfine (**5**) (186 mg, 1 mmol) in anhydrous THF (15 mL) at –78°C. After stirring for 10 min at –78°C, the mixture was quenched by addition of a 1:4 solution of water in THF. The organic layer was extracted with dichloromethane (10 mL), washed with brine (2x10 ml), dried over magnesium sulfate. After concentration under vacuum, the compound (**10aa**) was isolated in 68% yield (137 mg). A 53:47 diastereoisomeric ratio was determined by ^{1}H NMR. The dithio acetals could not be purified by chromatography because of their decomposition on silica gel; ^{1}H NMR ($CDCl_3$) major isomer: δ 2.29 (s, 3H, SCH_3), 2.43 (s, 3H, CH_3S=O), 4.75 (s, 1H, $CHSCH_3$), 7.38-7.39 (m, 1H, H_2), 7.68 (dt_{app}, J_{app} = 1.8 and 7.8 Hz, 1H, H_6), 8.58-8.61 (m, 2H, H_4 and H_5); minor isomer: 2.34 (s, 3H, SCH_3), 2.49 (s, 3H, CH_3S=O), 4.70 (s, 1H, $CHSCH_3$), 7.34-7.36 (m, 1H, H_2), 7.80 (dt_{app}, J_{app} = 1.8 and J_{app} = 7.9 Hz, 1H, H_6), 8.76-8.79 (m, 2H, H_4 and H_5); ^{13}C NMR ($CDCl_3$) major isomer: δ 17.0 (SCH_3), 33.8 ($O{=}SCH_3$), 68.2 ($\underline{C}HSCH_3$), 123.4, 127.3, 136.2, 149.5, 150.2; minor isomer: 16.3 (SCH_3), 35.7 ($O{=}SCH_3$), 69.1 ($\underline{C}HSCH_3$), 123.6, 128.4, 132.3, 136.4, 149.9; IR (NaCl): ν 1050 (S=O), 1420, 2920, 3414 cm^{-1}. Anal. Calcd for $C_8H_{11}NOS_2$: C, 47.73; H, 5.51; N, 6.96; S, 31.85. Found: C, 47.16; H, 5.34; N,7.05; S, 31.56.

3-[(Butylsulfinyl)(methylsulfanyl)methyl]pyridine (10ba)

A solution of *n*-butyllithium (1.6 M in hexane, 3.83 mL, 6.12 mmol) was added to a solution of sulfine (**5**) (566 mg, 3.06 mmol) in anhydrous THF (40 mL) at –78°C. After stirring for 10 min at –78°C, the mixture was quenched by addition of a 1:4 solution of water in THF . The organic layer was extracted with dichloromethane (20 mL), washed with brine (2x20 mL), dried over magnesium sulfate. After concentration under vacuum, the compound (**10ba**) was isolated in 96% yield (714 mg). A 53:47 diastereoisomeric ratio was determined by ^{1}H NMR. The dithio acetals could not be purified by chromatography because of their decomposition on silica gel; ^{1}H NMR ($CDCl_3$) major isomer: δ 0.93 (t, J = 7.3 Hz, 3H, $C\underline{H}_3CH_2$), 1.45 (sex_{app}, J_{app} = 7.0 Hz, 2H, $C\underline{H}_2CH_3$), 1.73 (m, 2H, $C\underline{H}_2CH_2S$=O), 2.29 (s, 3H, SCH_3), 2.62 (m, 2H, CH_2S=O), 4.67 (s, 1H, $C\underline{H}SCH_3$), 7.38 (m, 1H, H_5), 7.81-7.84 (m, 1H,

H_4), 8.59-8.61 (m, 2H, H_2 and H_6); minor isomer: 0.89 (t, J = 7.3 Hz, 3H, $C\underline{H}_3CH_2$), 1.24-1.51 (m, 2H, $C\underline{H}_2CH_3$), 1.62-1.80 (m, 2H, $C\underline{H}_2CH_2S{=}O$), 2.53-2.69 (m, 2H, $CH_2S{=}O$), 4.70 (s, 1H, $C\underline{H}SCH_3$), 7.29-7.40 (m, 1H, H_5), 7.67-7.74 (m, 1H, H_4), 8.58-8.65 (m, 2H, H_2 and H_6); ^{13}C NMR ($CDCl_3$) major isomer: δ 14.0 ($\underline{C}H_3CH_2$), 15.6 (SCH_3), 22.4 ($\underline{C}H_2CH_3$), 25.2 ($\underline{C}H_2CH_2S{=}O$), 50.3 ($CH_2S{=}O$), 67.5 ($\underline{C}HSCH_3$), 124.0 ($CH\underline{C}{=}C$), 137.1, 150.3, 150.5; minor isomer: 13.7 ($\underline{C}H_3CH_2$), 17.0 (SCH_3), 22.0 ($\underline{C}H_2CH_3$), 24.8 ($\underline{C}H_2CH_2S{=}O$), 48.1 ($CH_2S{=}O$), 67.6 ($\underline{C}HSCH_3$), 123.5 ($CH\underline{C}{=}C$), 128.3, 136.7, 149.1, 150.2; IR (KBr): ν 2932, 2912, 1422, 1028 (S=O), 716 cm^{-1}; MS: 138 (M^+ - *n*-BuSOH, 97), 106 ($CH_3(CH_2)SOH^+$, 100), 78 (Py^+, 55), 51 (52).

3-[1-Butylsulfinyl-1-(methylsulfanyl)ethyl]pyridine (10bb)

A solution of *n*-butyllithium (1.6 M in hexane, 0.88 mL, 1.4 mmol) was added to a solution of sulfine (**5**) (130 mg, 0.70 mmol) in anhydrous THF (15 mL) at –78°C. After stirring for 10 min at –78°C, iodomethane (0.18 mL, 2.88 mmol) was added and the mixture was stirred at rt for 4 days. Then the solution was hydrolysed and the organic layer was extracted with dichloromethane (10 mL), washed with brine (2x10 mL), dried over magnesium sulfate. After concentration under vacuum, the compound (**10bb**) was isolated in 63% yield (114 mg). A 57/43 ratio was determined by NMR. The dithio acetal could not be purified by chromatography because of its decomposition on silica gel; ^1H NMR ($CDCl_3$) major isomer: δ 0.97 (t, J = 7.3 Hz, 3H, $C\underline{H}_3CH_2$), 1.44-1.52 (m, 2H, $CH_3C\underline{H}_2$), 1.55-1.82 (m, 2H, $CH_3CH_2C\underline{H}_2$), 2.31 (s, 3H, SCH_3), 2.57 (s, 3H, ($C\underline{H}_3$)C(SCH_3)), 2.60-2.78 (m, 2H, $CH_2S{=}O$), 7.33 (dd, $J_{5,4}$ = 8.1 and $J_{5,6}$ = 4.7 Hz, 1H, H_5), 7.87 (dt_{app}, $J_{4,5}$ = 8.1 and J_{app} = 1.7 Hz, 1H, H_4), 8.59 (d_{app}, J_{app} = 4.7 Hz, 1H, H_6), 8.78 (d_{app}, J_{app} = 1.9 Hz, 1H, H_2); minor isomer: 0.85 (t, J = 7.3 Hz, 3H, $C\underline{H}_3CH_2$), 1.30-1.37 (m, 2H, $CH_3C\underline{H}_2$), 1.55-1.82 (m, 2H, $CH_2S{=}O$), 2.08 (s, 3H, SCH_3), 2.57 (s, 3H, ($C\underline{H}_3$)C(SCH_3)), 2.60-2.78 (m, 2H, $CH_3CH_2C\underline{H}_2$), 7.33 (dd, $J_{5,4}$ = 8.1 and $J_{5,6}$ = 4.7 Hz, 1H, H_5), 7.87 (dt_{app}, $J_{4,5}$ = 8.1 and J_{app} = 1.7 Hz, 1H, H_4), 8.59 (d_{app}, J_{app} = 4.7 Hz, 1H, H_6), 8.78 (d_{app}, J_{app} = 1.9 Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$) major isomer: δ 12.6 (SCH_3), 13.9 ($\underline{C}H_3CH_2$), 21.9 ($CH_3\underline{C}H_2$), 24.5 ($CH_3CH_2\underline{C}H_2$), 38.5 (($\underline{C}H_3$)C(SCH_3)), 54.4 ($CH_2S{=}O$), 65.9 ((CH_3)$\underline{C}$(SCH_3)), 123.2 (C_5), 132.3 (C_3), 134.8 (C_4), 148.1 (C_6), 149.6 (C_2); minor isomer: 13.6 ($\underline{C}H_3CH_2$), 19.3 (SCH_3), 22.1 ($CH_3\underline{C}H_2$), 24.6 ($CH_3CH_2\underline{C}H_2$), 38.5 (($\underline{C}H_3$)C(SCH_3)), 51.3 ($CH_2S{=}O$), 65.9 ((CH_3)$\underline{C}$(SCH_3)), 123.2 (C_5), 132.3 (C_3), 134.8 (C_4), 148.1 (C_6), 149.6 (C_2); IR (NaCl): ν 3442, 2960, 2932, 1030 (S=O) cm^{-1}.

3-Pyridylcarboxaldehyde (12)

To a solution of dithio acetal (**10ba**) (182 mg, 0.75 mmol) in THF (3 mL) was added an aqueous solution of 50% HBF_4 in THF (1.4 mL). The mixture was stirred at rt during 8 days. A saturated aqueous solution of sodium hydrogen carbonate (10 mL) was used to neutralize the acid and to wash the mixture (3x10 mL). The aqueous phase was extracted by ether (15 mL). The organic layer was dried over magnesium sulfate and concentrated by evaporation. NMR spectrum showed a mixture (142 mg) of aldehyde (**12**) and butyl methyl disulfide with a respective 63:37 ratio. These two products could not be isolated. The purity was estimated about 90%, in comparaison with an authentic commercial sample. ^1H NMR ($CDCl_3$): δ 7.37-7.44 (m, 1H, H_5), 8.20 (d_{app}, J_{app} = 8.1 Hz, 1H, H_4), 8.77-8.80 (m, 1H, H_6), 9.18 (br s, 1H, H_2), 10.1 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ 125.1, 132.3, 136.8, 153.5, 156.7, 192.0 (C=O); IR (NaCl): ν 1666 cm^{-1} (C=O).

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