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REACTIONS OF POLYHALOPYRIDINES. 17*. SYNTHESIS OF 2-, 3-, AND 4-PERFLUORO-ALKYLTHIOPOLYCHLOROPYRIDINES

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2-, 3-, and 4-Perfluoroalkylthiopolychloropyridines have been synthesized using perfluoroalkylated thiol and disulfide derivatives of polychloropyridines via the thermal decomposition of Xe(II) bisperfluoroalkylcarboxylates. It was shown that their formation takes place from the starting thiols only through the formation of the disulfides. It was found that 3,4,5,6-tetrachloro-2-trifluoromethylthiopyridine reacts with potassium p-tolylthiolate with retention of the fluorine containing fragment and substitution of the chlorine atom in position 4 of the pyridine ring by the tolythio group.

Keywords: 2,3,4-perfluoroalkylthiopolychloropyridines, perfluoroalkylation of heterocyclic thiols and disulfides, nucleophilic substitution reactions.

We have recently developed a method for the perfluoroalkylation of aromatic and heterocyclic thiols and disulfides based on the thermolytic reactions with bisperfluoroalkylcarboxylates of divalent xenon [2, 3]. The generation of the latter can be brought about either initially by mixing equimolar amounts of XeF_2 and the perfluorocarboxylic acid with cooling in a suitable solvent (e.g. CH_2Cl_2, MeCN) and with subsequent introduction into the reaction mixture of the sulfur containing compound or by an in situ addition of XeF_2 to a mixture of the sulfur containing substrate with an excess of the perfluorocarboxylic acid (which, moreover, fulfils a further role as solvent).

We have already reported the perfluoroalkylation of a series of 4-mercaptopolychloropyridines to form 4-perfluoroalkylthiopolychloropyridines [4] and suggest that the perfluoroalkylation process takes place as a result of the recombination of polychloropyridylthiyl and perfluoroalkyl radicals:

$$Xe(OCOR_F)_2 \longrightarrow Xe + 2CO_2 + 2R_F$$

$$PySH + R_F^{\bullet} \longrightarrow PyS^{\bullet} + R_FH$$

$$PyS^{\bullet} + R_F^{\bullet} \longrightarrow PySR_F$$

Py = polychloropyrid-4-yl

* For Communication 16 see [1].

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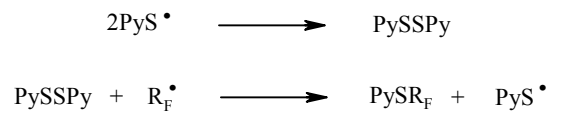
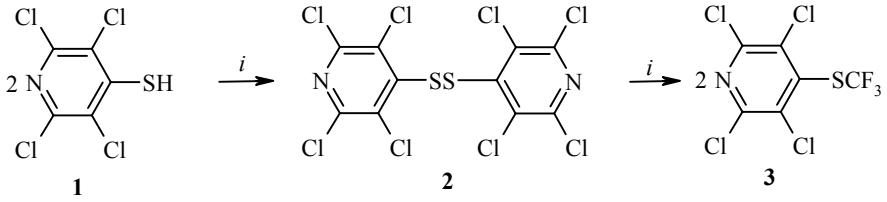
or *via* an intermediate formation of bis(polychloropyrid-4-yl) disulfides:



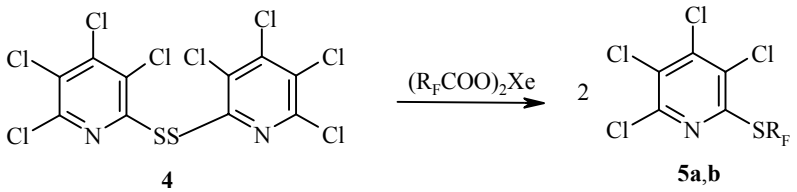
In this work we have used TLC to study the reaction of the starting 2,3,5,6-tetrachloro-4-mercaptopyridine (**1**) to the perfluoroalkylation product 2,3,5,6-tetrachloro-4-trifluoromethylthiopyridine (**3**) and shown that the formation of the latter occurs only *via* the intermediate disulfide **2**, the latter being generated in the reaction medium from thiol **1** in the presence of the Xe bisperfluoroalkylcarboxylate, prepared from 1 equivalent of XeF_2. The subsequent addition of a further 2-3 equivalents of this reagent ensures a complete reaction of **2** to the expected compound **3**. Separate experiments with the trifluoromethylation of the disulfide **2** (prepared by method [5]) led to 2,3,5,6-tetrachloro-4-trifluoromethylthiopyridine (**3**), the physicochemical and spectroscopic properties and the yields of which were identical to those obtained before in the case of the thiol **1** [2].



i = $(CF_3COO)_2Xe$

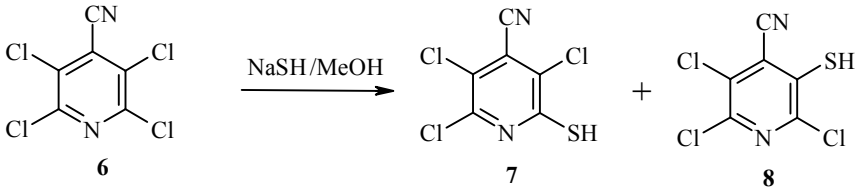
The sole difference consists only in the lower consumption (in fact one equivalent) of XeF_2. Hence, for the given perfluoroalkylation process, there can be used as starting materials both the thiols and the disulfides of the polychloropyridines. It was also shown that the yields are the same for all of the perfluoroalkylation methods and this is related to the adequate solubility of the starting compounds **1** and **2** in both CH_2Cl_2 and in the perfluorocarboxylic acids.

In this work we have attempted to synthesized other isomers of the perfluoroalkylthiopolychloropyridines with perfluoroalkylthio groups at the 2 and 3 positions of the pyridine ring. The main problem in the preparation of such compounds is connected with the poor availability of the starting substituted thiols and disulfides of the polychloropyridines **2** and **3**. For the latter, the most typical are the formation of derivatives at position 4 of the pyridine ring *via* nucleophilic substitution reactions with sulfur containing agents [6]. There is a single report in the literature of the preparation of 3,4,5,6-tetrachloro-2-mercaptopyridine [7] and bis(3,4,5,6-tetrachloropyrid-2-yl) disulfide (**4**) [8]. The disulfide **4** underwent perfluoroalkylation in CH_2Cl_2 solution using method A because of the poor solubility in perfluorocarboxylic acids (trifluoroacetic and perfluoropropionic). With molar reagent ratios of disulfide **4**:XeF_2:CF_3COOH of 1:3:7 and disulfide **4**:XeF_2:C_2H_5COOH of 1:3:9 the 3,4,5,6-tetrachloro-2-trifluoromethylthiopyridine (**5a**) and 3,4,5,6-tetrachloro-2-pentafluoroethylthiopyridine (**5b**) were formed in 69% and 17% yield respectively.



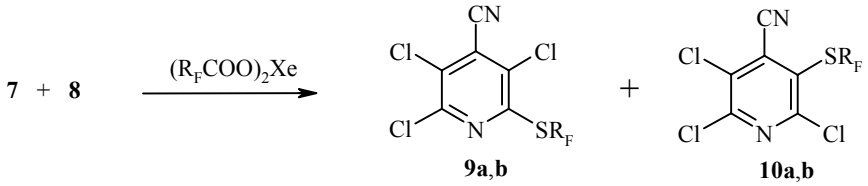
5 a $R_F = CF_3$, **b** $R_F = C_2F_5$

Another possible synthesis of 2-mercaptopolychloropyridines might be the use of polychloropyridines which are substituted at position 4 of the pyridine ring by e.g. CN, COOAlk, CF_3 and other poor leaving groups in standard reactions with alkali metal hydrosulfides. Hence the reaction of 2,3,5,6-tetrachloroisonicotinonitrile (**6**) with sodium hydrosulfide gave a mixture, the chromato-mass spectrometric analysis of which showed the presence of two isomeric trichloromercaptoisonicotinonitriles in the ratio 3:1, evidently with the thiol groups at the 2 and 3 positions of the pyridine ring. According to the mass spectrometric data of both isomers the main reaction product can be assigned as 3,5,6-trichloro-4-cyano-2-mercaptopyridine (**7**) and the second as 2,5,6-trichloro-4-cyano-3-mercaptopyridine (**8**).



6 **7** **8**

Attempts to separate compounds **7** and **8** chromatographically were unsuccessful hence the mixture was subjected to perfluoroalkylation with XeF_2 in perfluorocarboxylic acids (trifluoroacetic and perfluoropropionic). As a result, a mixture of the isomeric trifluoromethylthio- and trichloropentafluoroethylthio-4-cyanopyridines was obtained and this was separated into the pure compounds using column chromatography to give the isomers in the same ratio of 3:1.

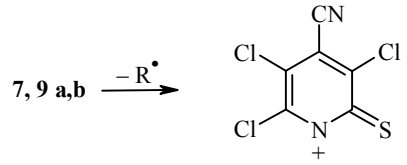


9a,**b** **10a**,**b**

9, **10 a** $R_F = CF_3$, **b** $R_F = C_2F_5$

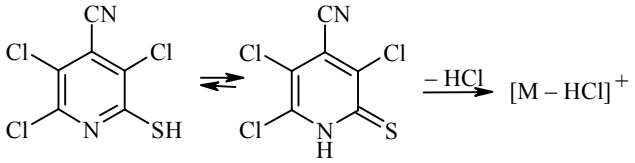
A comparison of the ^{13}C NMR spectra of the starting thiol **1** [9] and the trifluoromethylthio derivative **3** (Table 1) shows a significant shift in the spectrum of the signals of the latter to high field: by 12.7 ppm for the $C_{(4)}$ atom bound to the sulfur containing group and to low field by 11.3 ppm for the two neighboring $C_{(3)}$ and $C_{(5)}$ atoms whereas the position of the signals for $C_{(2)}$ and $C_{(6)}$ are changed much less (a low field shift of 1.5 ppm). The calculated effects of substituting the Cl atom in position 4 of the pyridine ring by an SCF_3 group are overall for the pyridine C atoms in pentachloropyridine: $C_{(2)}$, $C_{(6)}$ = +0.9; $C_{(3)}$, $C_{(5)}$ = +7.7, and $C_{(4)}$ = -7.6 ppm (this data is needed for comparison with the spectrum of compound **5a**). Localization of the SCF_3 group in position 2 of the pyridine ring leads to an even more marked shift of the carbon atom signals, both for the directly bound $C_{(2)}$ and the neighboring $C_{(3)}$ (-16.4 and +18.7 ppm respectively) whereas the effect of the substitution for the $C_{(4)}$, $C_{(5)}$, and $C_{(6)}$ atoms are -0.6, +1.8, and +2.2 ppm (compound **5a**). In the spectra of the isomers **9a** and **10a** which contain a trifluoromethyl group in positions 2 and 3 a significant difference is seen. While the 3-SCF_3 group in derivative **10a** is characterized by a shift of the signals for the $C_{(3)}$ atom of -7.3 ppm and for the neighboring atoms $C_{(2)}$ and $C_{(4)}$ of +3.0 and +5.5 ppm relative to the resonances of the corresponding carbon atoms in the spectrum of tetrachloroisonicotinonitrile [10], the 2-SCF_3 isomer **9a** is typified by a marked shift of the signals for the $C_{(2)}$ atom to high field by 15.3 and for the neighboring $C_{(3)}$ atom to low field by 21.2 ppm. In addition, in the latter case a significant shift is observed to low field for the $C_{(6)}$ atom resonance. It should be noted that the spectroscopic parameters (^{13}C NMR spectra of the pyridine fragments) of compounds **9b, 10b** agree to a significant extent with those for the fluorine homologs **9a, 10a**.

The isomeric pairs of pyridine thio derivatives **7, 8, 9a,b** and **10a,b** can be positively identified from their mass spectra. The existence of a sulfur atom in position 2 of the pyridine ring leads to the appearance of a dominant route for the decomposition of M^+ linked with the formation of a thionium ion.

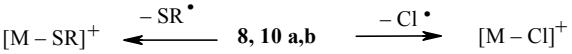


R = H, CF_3, C_2F_5

In the case of the thiol **7** itself the M^+ ion can occur in the thione form and lose a molecule of HCl.



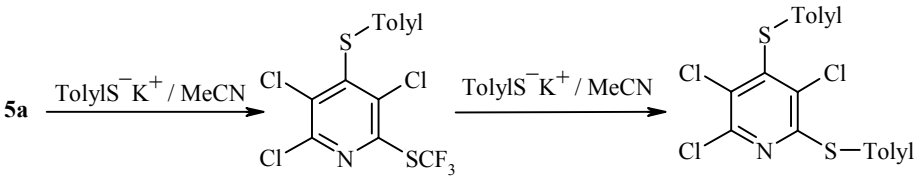
A change of the sulfur containing substituent to position 3 completely changes the fragmentation pattern. The maximum in the mass spectra of all of the studied compounds of this type is the $[M\text{-}Cl]^+$ ion which is totally absent in the spectra of the corresponding isomers. In addition to this process a fission of an SR radical is observed.



R = H, CF_3, C_2F_5

Hence from the main [M-Cl], [M-SR], and [M-R] peaks it is possible to make unambiguous deductions regarding the structure of the isomeric compounds.

The polychloropyridines **5, 9, 10** contain atoms of chlorine active towards nucleophilic substitution and can be used as synthons in the preparation of a series of novel compounds containing "superlipophilic" perfluoroalkylthio groups. In contrast to the 4-substituted derivatives (previously obtained by us) which readily lose the perfluoroalkylthio group in reactions with sulfur containing nucleophilic reagents like alkali metals hydrosulfides N,N-dimethyldithiocarbamates, methanethiolates, and phenylthiolates [11], the compounds **5a,b** with the fluorine containing group localized in position 2 might be expected to form substitution products with retention of the latter. Hence, the reaction of compound **5a** with one equivalent of potassium tolylthiolate in acetonitrile solution gives compound **11**, the ^{19}F NMR spectrum of which shows a singlet at -39.9 ppm. This confirms the presence of the trifluoromethylthio group in the molecule and the ^1H NMR spectrum shows a singlet at 2.41 ppm for the methyl group and a double doublet for the phenyl protons at 7.23 ppm thus confirming the presence in the molecule of both the trifluoromethylthio- and the tolylthio groups. With a second equivalent of the sulfur containing reagent there occurs a substitution of the fluorine containing fragment to give the 3,5,6-trichloro-2,4-bis(*p*-tolylthio)pyridine (**12**).



11 **12**

TABLE 1. ^{19}F and ^{1}H NMR Spectra of Compounds **3, 5a,b, 9a,b**, and **10a,b**

Compound	^{19}F NMR spectrum, δ, ppm (*J*, Hz)	^{13}C NMR spectrum, δ, ppm (*J*, Hz)					
		$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	Other atoms C
3	-38.03 (3F, s, SCF_3)	147.1	137.4	137.2	137.4	147.1	128.2 (q, J_{CF} = 313.0, CF_3)
5a	-40.49 (3F, s, SCF_3)	129.8	148.4	144.1	131.5	148.4	128.4 (q, J_{CF} = 308.3, CF_3)
5b	-90.91 (2F, q, *J* = 2.8, SCF_2), -82.00 (3F, t, *J* = 2.8, CF_3)	132.1	146.6	144.6	131.4	148.4	119.0 (qt, J_{CF} = 285.1, $^2J_{CF}$ = 35.0, CF_3); 120.7 (tq, J_{CF} = 294.9, $^2J_{CF}$ = 41.0, SCF_2)
9a	-39.09 (3F, s, SCF_3)	131.9	153.2	122.9	133.5	155.5	128.1 (q, J_{CF} = 311.1, CF_3); 111.5 (CN)
9b	-89.86 (2F, q, *J* = 2.8, SCF_2), -83.82 (3F, t, *J* = 2.8, CF_3)	132.6	154.0	122.5	133.8	156.6	119.0 (qt, J_{CF} = 258.2, $^2J_{CF}$ = 35.1, CF_3); 121.1 (tq, J_{CF} =296.4, $^2J_{CF}$ = 42.1,CF_3); 112.2 (CN)
10a	-38.87 (3F, s, SCF_3)	150.2	124.9	131.0	132.2	149.0	128.1 (q, J_{CF} = 308.6, CF_3); 111.5 (CN)
10b	-91.89 (2F, q, *J* = 2.7, SCF_2), -83.23 (3F, t, *J* = 2.7, CF_3)	148.3	124.7	133.2	133.4	147.3	118.3 (qt, J_{CF} = 287.6, $^2J_{CF}$ = 36.9, SCF_2); 120.0 (tq, J_{CF} = 292.5, $^2J_{CF}$ = 43.0, CF_3); 110.8 (CN)

TABLE 2. Characteristics of Compounds **3, 5a,b, 9a,b**, and **10a,b**

Compound	Mass spectrum, *m*/*z* (I_{rel}, %)	High resolution mass spectrum			mp, °C	Yield, %
		found: $[M]^+$	empirical formula	calculated: M		
3	315 ($[M]^+$, 100), 296 ($[M–F]^+$, 4), 280 ($[M–Cl]^+$, 6), 246 ($[M–CF_3]^+$, 6), 211 ($[M–CF_3,–Cl]^+$, 66), 69 ($[CF_3]^+$, 75)	314.8454	$C_6Cl_4F_3NS$	314.8458		87
5a	315 ($[M]^+$, 79), 296 ($[M–F]^+$, 3), 280 ($[M–Cl]^+$, 90), 246 ($[M–CF_3]^+$, 13), 214 ($[M–SCF_3]^+$, 10), 211 ($[M–Cl,–CF_3]^+$, 43), 202 ($[M–CSCF_3]^+$, 18), 176 ($[M–2Cl, –CF_3]^+$, 8), 141 ($[M–3Cl,–CF_3]^+$, 18), 106 ($[M–4Cl, –CF_3]^+$, 25), 69 ($[CF_3]^+$, 81)	314.8452	$C_6Cl_4F_3NS$	314.8458		69
5b	365 ($[M]^+$, 100), 330 ($[M–Cl]^+$, 23), 296 ($[M–CF_3]^+$, 61), 246 ($[M–C_2F_5]^+$, 38), 214 ($[M–SC_2F_5]^+$, 27), 211 ($[M–Cl,–C_2F_5]^+$, 81), 151 ($[SC_2F_5]^+$, 1), 119 ($[C_2F_5]^+$, 42), 69 ($[CF_3]^+$, 92)	364.8433	$C_7Cl_4F_5NS$	364.8426	44-45	18
9a	306 ($[M]^+$, 29), 287 ($[M–F]^+$, 2), 271 ($[M–Cl]^+$, 1), 237 ($[M–CF_3]^+$, 12), 202 ($[M–CF_3,–Cl]^+$, 17), 176 ($[M–CF_3,–CN,–Cl]^+$, 14), 167 ($[M–CF_3, –2Cl]^+$, 1), 141 ($[M–CF_3,–2Cl,–CN]^+$, 7), 132 ($[M–CF_3,–3Cl]^+$, 12), 106 ($[M–3Cl,–CF_3,–CN]^+$, 7), 69 ($[CF_3]^+$, 100)	305.8788	$C_7Cl_3F_3NS$	305.8800	38-39	50
9b	356 ($[M]^+$, 86), 337 ($[M–F]^+$, 9), 287 ($[M–CF_3]^+$, 34), 237 ($[M–C_2F_5]^+$, 100), 202 ($[M–C_2F_5,–Cl]^+$, 62), 176 ($[M–C_2F_5,–Cl,–CN]^+$, 22), 132 ($[M–C_2F_5,–3Cl]^+$, 35), 119 ($[C_2F_5]^+$, 40), 106 ($[M–C_2F_5,–Cl,–CN]^+$, 100)	355.8742	$C_8Cl_3F_5N_2S$	355.8768	43-44	54
10a	306 ($[M]^+$, 96), 271 ($[M–Cl]^+$, 80), 202 ($[M–CF_3,–Cl]^+$, 28), 132 ($[M–CF_3, –3Cl]^+$, 20), 106 ($[M–3Cl, –CF_3, –CN]^+$, 12), 69 ($[CF_3]^+$, 100)	307.8752	$C_7{}^{35}Cl_2{}^{37}ClF_3N_2S$	307.8770	40-41	22
10b	356 ($[M]^+$, 58), 337 ($[M–F]^+$, 6), 321 ($[M–Cl]^+$, 19), 287 ($[M–CF_3]^+$, 46), 237 ($[M–C_2F_5]^+$, 20), 202 ($[M–C_2F_5,–Cl]^+$, 56), 176 ($[M–C_2F_5,–Cl,–CN]^+$, 12), 144 ($[M–SC_2F_5,–Cl,–CN]^+$, 17), 119 ($[C_2F_5]^+$, 57), 69 ($[CF_3]^+$, 100)	355.8742	$C_8Cl_3F_5N_2S$	355.8768	43-44	18

Hence the obtained results for the reactivity of compound **5a**, in which the perfluoroalkylthio group occurs in position 2 of the pyridine ring allows one to increase markedly the scope of the nucleophilic substitution reaction occurring with retention of "superlipophilic" fluorine containing groups and, therefore, to broaden the synthetic possibilities of this class of polychloropyridine derivatives.

EXPERIMENTAL

Column chromatography was carried out using Merck silica gel 60 (230-400 mesh) and TLC using Merck 60 F_{254} silica gel plates. ^1H, ^{13}C, and ^{19}F NMR spectra were obtained on Bruker AC 200, Bruker AM 360, or Bruker AM 500 instruments (200, 360, or 500 MHz) using $CDCl_3$ solvent and TMS or $CFCl_3$ internal standards. GLC-MS analysis was carried out on a Hewlett-Packard 5890 instrument (70 eV) with a 30 m capillary column covered with HP1 phase. High resolution mass spectra were taken on a VG Autospec spectrometer.

The physicochemical and spectroscopic parameters for the synthesized compounds are given in Tables 1 and 2.

Perfluoroalkylation of Polychloropyridine Thiols and Disulfides. Synthesis of 2-, 3-, and 4-Perfluoroalkylthiopolychloropyridines. (General Method). A. The starting thiol or disulfide (0.8 mmol) was added with stirring at -20°C to a suspension of the xenon bisperfluoroalkylcarboxylate (prepared by mixing XeF_2 (0.4 g, 2.4 mmol) and the corresponding perfluorocarboxylic acid (0.6-1.2 ml, 7.2 mmol) in CH_2Cl_2 (25 ml)). The reaction mixture was stirred with spontaneous heating to +5°C. The end of the reaction was indicated by the cessation of evolution of gas.

B. XeF_2 (1.0 g, 6.0 mmol) was added to a suspension of the starting disulfide or thiol (2.0 mmol) in the corresponding perfluorocarboxylic acid (3.6-5.2 ml, 48.0 mmol) which was stirred at 30°C. The end of the reaction was indicated by the cessation of evolution of gas.

The reaction mixture obtained by methods A or B was neutralized with Na_2CO_3 solution, extracted with chloroform, dried over Na_2SO_4, and evaporated in vacuo. The residue was chromatographed on a silica gel column using hexane (compounds **5a,b**) or a 1:4 mixture of benzene–hexane (**9a,b** and **10a,b**).

Reaction of Compound 4a with Potassium *p*-Tolylthiolate. (General Method). A solution of *p*-tolylthiolate, prepared from *p*-thiocresol (0.080 g, 0.6 mmol) and KOH (85%, 0.047 g, 0.6 mmol) (experiment A) or from *p*-thiocresol (0.16 g, 1.2 mmol) and KOH (85%, 0.094 g, 1.2 mmol) (experiment B), in MeOH was added dropwise with stirring to compound **5a** (0.19 g, 0.6 mmol) in MeCN (6 ml) at room temperature and then dried in vacuo. Stirring was continued for 5 h, solvent was distilled off, and the residue was chromatographed on a silica gel column using a mixture of heptane benzene eluent (2:1 for experiment A or 1:1 for experiment B).

3,5,6-Trichloro-4-(*p*-tolylthio)-2-trifluoromethylpyridine ($C_{13}H_7Cl_3F_3NS_2$) (11). Experiment A. According to GLC data the obtained sample contains about 90-92% of the main material in 60% yield as a light yellow oil. The principal contaminant which amounts to several percent is 3,5,6-trichloro-4-methoxy-2-trifluoromethylthiopyridine. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 7.23 (4H, dd, J = 9.0, Ar). ^{19}F NMR spectrum, δ, ppm: -39.87 (3F, s, SCF_3). Mass spectrum, *m/z* (*I*, %): 403 ($[M]^+$, 100), 384 ($[M\text{-}F]^+$, 3), 368 ($[M\text{-}Cl]^+$, 7), 348 ($[M\text{-}F, \text{-}HCl]^+$, 18), 332 ($[M\text{-}HCl, \text{-}Cl]^+$, 26), 299 ($[M\text{-}Cl, \text{-}CF_3]^+$, 5), 267 ($[M\text{-}Cl, \text{-}SCF_3]^+$, 36), 263 ($[M\text{-}HCl, \text{-}Cl, \text{-}CF_3]^+$, 1), 231 (12), 123 ($[C_7H_7S]^+$, 11), 91 ($[C_7H_7]^+$, 19), 69 ($[CF_3]^+$, 23).

3,5,6-Trichloro-4-methoxy-2-trifluoromethylthiopyridine ($C_7H_3Cl_3F_3NOS$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.10 (3H, s, OMe). Mass spectrum, *m/z* (*I*, %): 311 ($[M]^+$, 100), 292 ($[M\text{-}F]^+$, 4), 276 ($[M\text{-}Cl]^+$, 56), 242 ($[M\text{-}CF_3]^+$, 11), 207 ($[M\text{-}Cl, \text{-}CF_3]^+$, 15).

3,5,6-Trichloro-2,4-bis(*p*-tolylthio)pyridine ($C_{19}H_{14}Cl_3NS_2$) (12). Experiment B. Yield 58%, white crystals; mp 74-75°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 (3H, s, CH_3); 2.42 (3H, s, CH_3); 7.04-7.42 (8H, m, Ar). Mass spectrum, *m/z* (*I*, %): 425 ($[M]^+$, 100), 390 ($[M-Cl]^+$, 30), 354 ($[M-Cl. -HCl]^+$, 45), 319 ($[M-HCl, -2Cl]^+$, 15), 298 ($[M-HCl, -C_7H_7]^+$, 17), 263 ($[M-Cl, -HCl, -C_7H_7]^+$, 20), 231 ($[M-Cl, -HCl, -C_7H_7S]^+$, 10), 123 ($[C_7H_7S]^+$, 56), 91 ($[C_7H_7]^+$, 43). Found: *m/z* 424.9635 $[M]^+$. $C_{19}H_{14}Cl_3NS_2$. Calculated: M 424.9633.

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