Modelling nucleophilic substitution at silicon in solution using hypervalent silicon compounds based on 2-thiopyridones

Alan R. Bassindale,* David J. Parker and Peter G. Taylor *

The Chemistry Department, The Open University, Walton Hall, Milton Keynes, UK MK7 6AA

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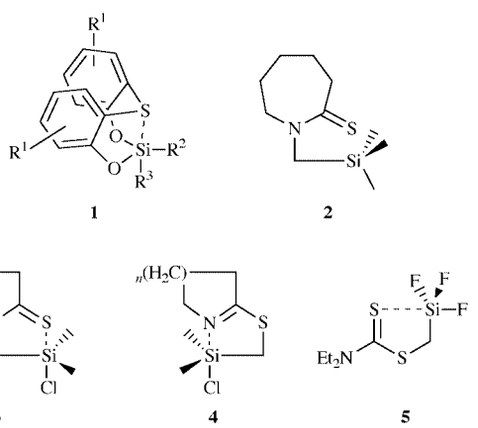
Halodimethylsilylmethyl derivatives of 2-thiopyridones have been prepared. The N–CH_2 isomer is favoured with the 6-methylthiopyridone. ^{13}C and ^{29}Si chemical shifts have been used to calculate the extent of sulfur–silicon bond formation and the extent of pentacoordination. The results are consistent with the oxygen analogues and reveal that as expected sulfur is a poorer nucleophile than oxygen. The unsubstituted thiopyridone and the 5-trifluoromethyl derivative favour the S–CH_2 isomer. Again the mapping of nucleophilic substitution by nitrogen is in line with sulfur and oxygen nucleophiles, but in this series nitrogen is a poorer nucleophile than expected. The results are discussed in terms of steric strain, the preferences for alkylation of the pyridones and the bond strength of coordination to silicon.

Introduction

We have recently mapped the reaction coordinate for substitution at silicon in solution using an NMR technique.[1–3] This involved synthesising a range of structurally similar pentavalent silicon compounds that provide a picture of how the geometry around silicon changes as the extent of nucleophile–silicon bond formation increases and the silicon leaving group bond breaks. Thus, each individual structure represents a snapshot of the reaction at a particular point on the modelled reaction profile. The minimum requirement for studying the progress of such a reaction is two parameters that measure the extent of bond formation or breaking and/or the change in geometry around a key site. The extent of nucleophile–silicon bond formation is measured by examining how the chemical shift of other atoms attached to the nucleophilic atom, change with the coordination number of the nucleophilic atom. Our previous study employed substituted pyridones, where the ^{13}C chemical shifts of the ring carbons change in a concerted fashion as the pyridone oxygen becomes progressively coordinated to a silicon. The degree of pentacoordination at silicon was measured using the ^{29}Si chemical shift. Both the extent of pentacoordination and nucleophile–silicon bond formation are expressed as a percentage and thus require model compounds to define the tetracoordinate and pentacoordinate limiting cases.

Our results demonstrated that as the extent of reaction increases the nucleophile–silicon bond is formed at the expense of the leaving group forming a genuine pentacoordinate species followed by loss of the leaving group. A similar picture has emerged in the solid state, where several groups have shown that formation of the nucleophile–silicon bond is accompanied by lengthening of the silicon–leaving group bond.[4–7] The tetrahedral reactants are converted into a trigonal bipyramidal structure with the non-participating groups equatorial, followed by reversion to a tetrahedral structure. To test the generality of this technique we have been examining a series of related aromatic ligands. In particular we have been interested in how the change to a sulfur nucleophile would modify the reaction profile.

Previous studies have shown that hypervalent silicon compounds involving sulfur can be formed, albeit less readily than with oxygen nucleophiles. Holmes has examined a series of cyclic silanes of the type **1**, where there is the possibility of S–Si transannular interactions.[8–10] Even when R^2 and R^3 are alkyl groups, substantial S–Si coordination was observed by X-ray crystallography. The Si–S bond length varies between 2.98 and 3.29 Å compared to the sum of the van der Waals radii (3.90 Å) and the sum of the covalent radii (2.20 Å). The geometry at silicon is displaced from the tetrahedral to the trigonal bipyrimidal by between 36% and 54%, depending upon the substituents on the aromatic rings and the silicon.[10] Pentacoordination is confirmed in the solid state and in solution by the ^{29}Si NMR spectra which demonstrate a 7–8 ppm upfield shift from that expected for a corresponding tetrahedral silicon. Ovchinnikov has shown that the thiolactam **2** exhibits no S–Si coordination.[11] This is perhaps not surprising, since no electronegative groups are present at silicon and unlike **1**, the trimethylsilyl group is conformationally free. The X-ray structure reveals a S–Si bond length of 4.03 Å. Calculations suggested that to achieve S–Si bond lengths of between 3.05 and 3.60 Å would involve a destabilising interaction between one of the hydrogen of the $SiCH_2$ and one of the hydrogens on the ring CH_2 adjacent to the nitrogen. This conclusion is reinforced by the observation that the reaction of chloromethyldimethylchlorosilane with thiolactams leads to structures of the type **4** rather than **3**.[12,13] Whereas, the corresponding oxygen systems involve a planar chelate ring, the longer S–Si distance leads to non-planarity in **3** and thus unfavourable interactions. A substantial S–Si coordination has been observed in the dithio-



1 **2** **3** **4** **5**

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Table 1 % Si–Nu bond formation of compounds **6a–d** and **9a–d**

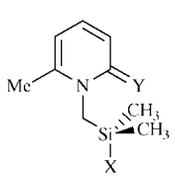
Compound	% Si–S	δ^{29}Si	% Pentacoordination	Compound	% Si–O	% Pentacoordination
6a	5	27.0	2	**9a**	50	93
6b	21	−0.1	42	**9b**	70	81
6c	34	—	—	**9c**	70	77
6d	91	26.7	13	**9d**	90	21

carbamate **5**.[14] The S–Si bond length is 2.70 Å, 1.2 Å shorter than the sum of the van der Waals radii. The geometry at silicon is displaced from the tetrahedral to the trigonal bipyrimidal by 77%.

To examine the extent of S–Si bond formation in solution we have prepared a range of hypervalent silicon compounds of the type **6** with 2(1*H*)-thiopyridone as the ligand. The 2(1*H*)-thiopyridone ligand has a rich coordination chemistry, being used with elements such as nickel,[15] antimony,[16] platinum,[17] aluminium,[18] silver[19] and tin.[20] However, we have been unable to find any reported complexes between thiopyridones and silicon.

Results and discussion

We prepared a range of 6-methyl-2-thiopyridone complexes, **6a–d**. Treatment of 6-methyl-2(1*H*)-pyridone with phosphorus pentasulfide gave the thiopyridone which was converted into the trimethylsilyl derivative with diethylaminotrimethylsilane.[21] Reaction of this with chloromethyldimethylchlorosilane gave the chloro derivative **6b**, whereas treatment with chloromethyldimethylsilyltriflate gave the triflato derivatives **6d**. The bromo derivative, **6c**, was prepared by treating the 6-methyl-2-trimethylsilylthiopyridine with bromomethyldimethylchlorosilane. The fluoro derivative, **6a**, was prepared by treating the chloro derivatives, **6b**, with antimony trifluoride.

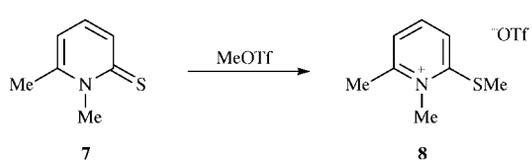


6a Y = S, X = F
6b Y = S, X = Cl
6c Y = S, X = Br
6d Y = S, X = OSO_2CF_3

9a Y = O, X = F
9b Y = O, X = Cl
9c Y = O, X = Br
9d Y = O, X = OSO_2CF_3

As expected, the ^{13}C chemical shifts of the thiopyridine ring changed in a concerted fashion as the extent of Si–S bond formation increased in the order **6a**, **6b**, **6c** and **6d**. The ^{29}Si chemical shift first decreased then increased. However, it was not possible to observe a ^{29}Si resonance for **6c**, despite varying the solvent and pulse delays. To convert this chemical shift data into % Si–S bond formation and % pentacoordination, they need to be compared with model compounds representing 0 and 100% Si–S bond formation and 0 and 100% pentacoordination. 1,6-Dimethyl-2-thiopyridone was used as a model for 0% Si–S bond formation. This was prepared by desilylation of **6a** with fluoride ion.

Treatment of **7** with methyl triflate, as shown in Scheme 1,

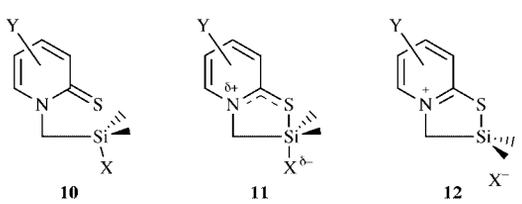


7 **8**

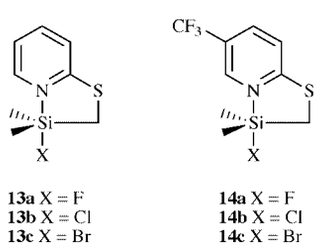
Scheme 1

gave **8** which was used as the model for 100% Si–S bond formation. Although neither of these compounds contain a silicon they nevertheless reveal how the ^{13}C chemical shifts of the ring carbons change on coordination at sulfur. Table 1 lists the % Si–S bond formation of compounds **6a–d**, based on a comparison of the chemical shifts of their ring carbons with those of **7** and **8**. Data for the oxygen analogue **9a–d** are also given.[3]

The variation of the ring carbon ^{13}C and the ^{29}Si chemical shifts with the leaving group X in the series **6a–d**, clearly demonstrates the formation of hypervalent silicon species involving sulfur donation in solution. Comparison with **9a–d** shows that in agreement with previous studies, the sulfur ligand is less nucleophilic towards silicon than the corresponding oxygen ligand. In fact, the fluoro compound **6a** has the lowest extent of nucleophile–silicon bond formation measured in any pyridone series, even lower than the 3-nitropyridone derivative. This behaviour is also reflected with the chloro and bromo derivatives, **6b** and **6c**. However, the triflate is such a strong leaving group that even with such a poor nucleophile, the sulfur–silicon bond formation is extensive. Thus, of all the compounds studied, this series shows the biggest change in the % Si–nucleophile bond formation with the leaving group. For compounds that exhibited a % Si–S bond formation between 0 and 50% the extent of pentacoordination was calculated, as before, based on the predicted ^{29}Si chemical shifts of the limiting cases **10** and **11**, that is +28 and −40 ppm respectively. For



10 **11** **12**



13a X = F
13b X = Cl
13c X = Br
13d X = OTf

14a X = F
14b X = Cl
14c X = Br
14d X = OTf

compounds that exhibited a % Si–S bond formation between 50 and 100% the extent of pentacoordination was calculated using the predicted ^{29}Si chemical shifts of the limiting cases **11** and **12**, that is −40 and +36 ppm respectively.[3] Table 1 shows the % pentacoordination of compounds **6a–d**.

As observed in the pyridone series, as the extent of S–Si bond formation increases the % pentacoordination first increases then, after 50% S–Si bond formation which involves the optimal pentacoordinate state, the % pentacoordination decreases. Thus, as the Si–X bond lengthens, the silicon reverts to its tetrahedral geometry. Fig. 1 demonstrates that these thiopyridone data fit well on the curve established for pyridones, suggesting that the extent of pentacoordination depends solely upon the % silicon–nucleophile bond formation rather than on the nature of the nucleophile itself. We also examined the % Si–nucleophile bond formation for the unsubstituted thiopyridone and 5-trifluoromethylthiopyridone. The derivatives were prepared in the same way as for the 6-methylthiopyridones. However, in these cases the *S*-methylene compounds, **13** and **14**,

Table 2 The % Si–Nu bond formation of compounds **13a–d** and **14a–d**

Compound	% Si–Nu	δ^{29}Si	% Pentacoordination	Compound	% Si–Nu	δ^{29}Si	% Pentacoordination
13a	8	17.0	17	**14a**	7	26.0	3
13b	36	−19.4	75	**14b**	16	19.2	14
13c	69	−0.8	55	**14c**	24	7.3	33
13d	92	40.6	0	**14d**	77	7.6	44

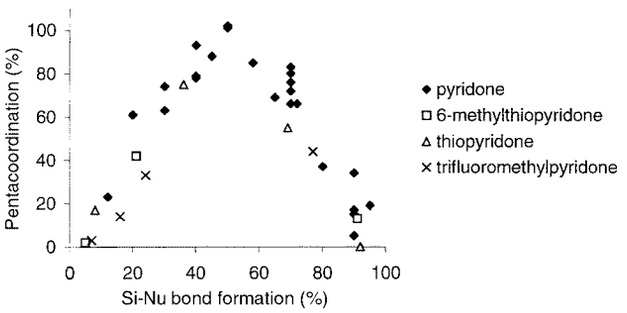
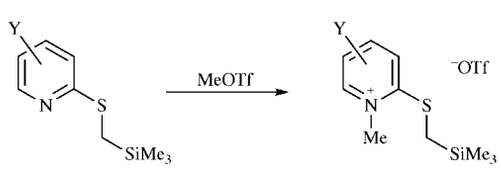


Fig. 1 Plot of % pentacoordination against % Si–Nu bond formation

rather than *N*-methylene ones were formed. All the spectral data were consistent with an S–CH_2 linkage rather than a N–CH_2 linkage. For example, the ^{13}C chemical shifts of C2 in **13** and **14** were all around 160 ppm, very similar to that of 2-methylthiopyridine (160.4 ppm) and very different from that of *N*-methylpyridone, (181.1 ppm).

Within the two series, the ^{13}C chemical shifts of the pyridine ring changed in a concerted fashion as the extent of Si–N bond formation increased in the order X = F, Cl, Br, OTf, and the ^{29}Si chemical shift first decreased then increased. Compounds **15** and **16** were used as models for 0 and 100% Si–N bond formation, Scheme 2.



15 **16**

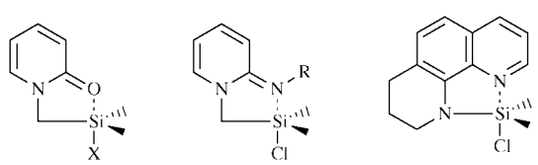
Scheme 2

Table 2 lists the % Si–Nu bond formation of compounds **13a–d** and **14a–d**, based on a comparison of the chemical shifts of their ring carbons with those of **15** and **16**. Unfortunately the variation in the ^{13}C chemical shifts of the ring carbons on going from 0% Si–Nu to 100% Si–Nu bond formation was not as large as has been observed in other series, thus are more prone to experimental error.

Again, the variation of the ring carbon ^{13}C and the ^{29}Si chemical shifts with the leaving group X in both series clearly demonstrates the formation of hypervalent silicon species involving nitrogen donation in solution. As before the % pentacoordination was calculated using model compounds. 0% pentacoordination could be modelled as before using trialkylhalosilanes. The value of the ^{29}Si chemical shift for 100% pentacoordination was obtained using a variable temperature NMR study on compound **13b**. As has been observed by Kummer, as the temperature of a solution of a pentacoordinate species is changed so the ^{29}Si chemical shift can go through a minimum as the structure of the complex first becomes more pentacoordinate and then less pentacoordinate. The minimum value corresponds to 100% pentacoordination.[22] This gave a value of −35 ppm for the ^{29}Si chemical shift of a purely pentacoordinate species involving a pyridinium nitrogen. Unfortunately we do not have a model for 0% pentacoordination involving 100% N–Si bond formation, however, the triflate **13d** suggests that a value around −40 ppm would be suitable. Table 2 shows the % pentacoordination of compounds **13a–d** and **14a–d**, and these values are also plotted in Fig. 1. The data cover the full range of nucleophile–silicon bond formation and exhibit the same pattern of formation of the pentavalent species followed by loss of the leaving group and reversion to the tetrahedral compound. Within experimental error, the data correspond well with the data for oxygen and sulfur nucleophiles, suggesting that the extent of bond formation is the primary factor in determining the extent of pentacoordination. This corroborates the use of different leaving groups to create each series since the extent of pentacoordination will be predominantly determined by the extent of silicon–leaving group bond formation irrespective of the nature of the group.

As expected the electron withdrawing trifluoromethyl group reduces the nucleophilicity of the nitrogen such that the extent of N–Si bond formation in the series **14a–d** is less than in the series **13a–d**. This is particularly apparent with **14d** which has the smallest extent of silicon–nucleophile bond formation that we have measured for a triflate leaving group.

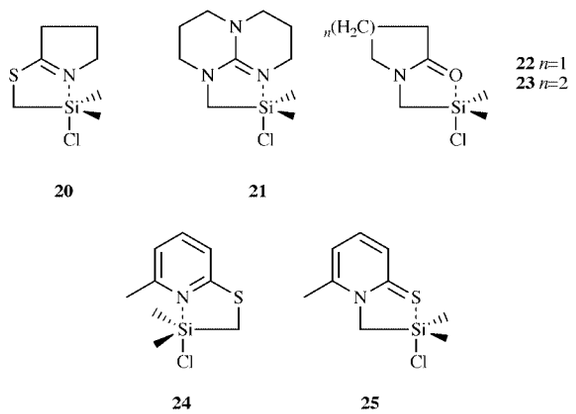
Comparison of the extent of bond formation and pentacoordination for the series **13a–d** with the corresponding unsubstituted pyridones, **17a–d**, suggests that the pyridinium



17 **18** **19**

nitrogen in **13a–d** is a poorer nucleophile than the oxygen in **17a–d**.[3] The crystal structures have been reported of a number of pentavalent alkylchlorosilicon compounds involving an sp^2 nitrogen as the donor atom in a five membered ring, **18**,[23] **19**,[24] **20**[13] and **21**.[25] Examination of the silicon–nitrogen bond lengths and the silicon–chlorine bond lengths suggest that an sp^2 nitrogen has a similar, if not greater, nucleophilicity than an sp^2 oxygen. For example, the Si–N and Si–Cl bond lengths in compound **18** are 1.90 and 2.60 Å respectively, whereas the Si–O and Si–Cl bond lengths in the 2-quinolinone analogue of compound **17** are 1.94 and 2.32 Å respectively.[26] Similarly, the Si–N and Si–Cl bond lengths in compound **20** are 1.95 and 2.42 Å respectively and in **21** are 1.85 and 2.68 Å. However, the Si–O and Si–Cl bond lengths in compound **23** are 1.95 and 2.31 Å respectively, again showing poorer oxygen–silicon bond formation and/or more extensive Si–Cl breaking.[27] This pattern is reinforced by the ^{29}Si chemical shifts. Compound **17b** has a ^{29}Si chemical shift of −41.1 ppm whereas that of **18** is +6.4 ppm. Variable temperature studies have shown that the downfield shift for **18** is due to more extensive Si–N bond formation leading to a less pentacoordinate species. Similarly **20** has a ^{29}Si chemical shift of −38.1 ppm[12] whereas that in **22** is −9.7 ppm.[28a] In this case the high field shift of **20** is due to greater Si–N bond formation. Examination of the mechanism of formation of O–Si chelates by Pestunovich has shown the formation of an intermediate N–Si chelate which has a more negative ^{29}Si chemical shift than the corresponding O–Si chelate.[28b] The ^{29}Si chemical shifts of **13b** and **17b** are −19.4 and −41.1 ppm respectively, and variable temperature studies confirm that this is the

result of less Si–N bond formation in **13b**. This apparent reversal in behaviour between the oxygen and nitrogen donors may be a result of the dependence of the extent of nucleophile bond formation on other factors such as the geometry of the chelate ring. This has been demonstrated to be a factor in the lactam series where the ^{29}Si chemical shifts of compounds **22** and **23**, which only differ in the ring size, are −9.7 and −38.5



20 **21**

24 **25**

respectively. In compound **13** the problems of including long bonds to sulfur in the chelate ring may be further exacerbated by the planarity of the pyridone ring. The geometry of the chelate ring and the strength of nucleophile–silicon bonds also play an important role in determining which isomeric chelate predominates. In the pyridone series only the N–CH_2 isomer with a coordinate Si–O bond is observed. However, with the corresponding thiopyridone the S–CH_2 isomer with a coordinate N–CH_2 bond predominates. This reflects previous work on amides and thioamides where **4** predominates over **3**.[11,12,13] Similarly we have observed that with ureas the O–Si chelate is formed but with thioureas the N–Si chelate is observed.[29] Assuming that the observed isomers represent the thermodynamically favoured forms, in the absence of silicon coordination, the pattern reflects that observed with methylpyridones and amides. Beak has shown that in the liquid phase the *N*-methylpyridone form is favoured over the methoxypyridine form by 52 kJ mol^{-1}.[30] However, the *S*-methylthiopyridine is favoured over the *N*-methylthiopyridone by 10 kJ mol^{-1}.[31] With cyclic lactams the *N*-methylamide form is favoured over the *O*-methylimidate form by 72 kJ mol^{-1} and this preference is retained in the sulfur analogue by 19 kJ mol^{-1}.[32] The equilibrium between the isomeric chelated forms will reflect this preference for alkylation together with a contribution for X–Si bond formation and the geometry of the ring. In the amide and pyridone series the preference for the N–CH_2 isomer with a coordinate Si–O bond is enhanced by the greater molar bond enthalpy of the Si–O bond (445 kJ mol^{-1}) over the Si–N bond (333 kJ mol^{-1}).[33] With the thiopyridone the S–CH_2 isomer with a coordinate N–CH_2 is preferred. In this case the N–Si bond has a greater molar bond enthalpy than the S–Si bond (299 kJ mol^{-1})[33] and thus, this reinforces the inherent preference for S alkylation in thiopyridones. This behaviour is also reflected in the greater basicity of *S*-methylthiopyridine compared to *N*-methylthiopyridone.[34] Interestingly, trimethylsilylation of the thiopyridones always gave the trimethylsilylmercapto derivative, whereas with simple thioamides N-trimethylsilylation is observed.[13] With the aromatic system the inherent balance between the mercaptopyridine and the thiopyridone overcomes the difference in Si–N and Si–S bond strengths. The preference for the S–CH_2 isomer **4** over the N–CH_2 isomer **3** in the thiolactam series must be a result of the stronger N–Si bond formation overcoming the reduced inherent preference for *N*-alkylation of thioamides. This is confirmed by **2** where, in the absence of substantial silicon coordination, the normal pattern is observed.

The delicate balance between *N*- and *S*-alkylation is revealed by the reversal of isomer preference on changing the substituent on the thiopyridine ring.The *S*-alkylated isomer predominates in **13** and **14** whereas **6** favours the *N*-alkylated isomer. This may arise as a result of a steric and/or electronic effect of the substituent on the position of the equilibrium. To test the origin of the substituent effect we prepared the corresponding chlorodimethylsilylmethyl derivative of 4-methyl-2(1*H*)-thiopyridone, which should have a similar electronic effect to the 6-methyl isomer but no steric effect. With this compound the natural preference for *S*-alkylation was observed, suggesting the predominance of the *N*-alkyl isomer with 6-methylthiopyridone arises from a steric effect. Theoretical calculations were performed on the isomers **24** and **25** to calculate the nearest non-bonded interactions of the 6-methyl group. The 4-methyl-2(1*H*)-thiopyridinone derivative has a ^{29}Si chemical shift of −26.9 suggesting it is 87% pentacoordinate. This indicates about 40% N–Si bond formation based on Fig. 1. This corresponds to a Si–N bond distance of about 2.05 Å based on the relationship between O–Si bond formation and Si–O bond length determined in the 2-quinolinone series, scaled to the standard Si–N bond length.[26] This seems reasonable based on the Si–N bond distance in **20** (1.95 Å) which has a more negative ^{29}Si chemical shift. For **25** a fixed Si–S bond distance of 2.1 Å was employed based on the observed 21% Si–S bond formation, again scaled to the standard Si–S bond length. Both molecular mechanics and semi-empirical calculations show **24** to involve at least one hydrogen from the 6-methyl group being a distance of less than two van der Waals radii from the hydrogens of the methyl group attached to silicon. Such interactions are not present in isomer **25**, which leads to it being the favoured form. As a result of the longer bonds to sulfur, both isomers **24** and **25** involve either non-planar chelate rings or acute angle strain. As suggested earlier, this possibly explains the reduced nitrogen coordination observed in **13** and **14** compared to other 5-membered ring sp^2 nitrogen coordinated chelates.

Experimental

Melting points were determined on a Buchi 510 melting point apparatus and are uncorrected. Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates or as KBr discs on a Pye Unicam SP 1050 or a Nicolet 205 FT-IR spectrometer. NMR spectra were recorded as solutions in deuteriochloroform with tetramethylsilane as internal standard on a JEOL FX 90Q or a JEOL EX 400 NMR spectrometer (*J* values are given in Hz). Mass spectra were obtained using a Cresta MS 30 instrument or a VG20-250 quadrupole instrument.

General procedure for the preparation of 2-thiopyridones

The 2(1*H*)-pyridone precursor (140 mmol) and phosphorous pentasulfide (61.40 g, 140 mmol) in the form of powders were shaken vigorously together in a 250 cm^3 stoppered, round-bottomed flask. Under a gentle flow of nitrogen, the flask was heated in an oil bath at a temperature close to the melting point of the 2-pyridone for 5 hours. The fused mixture was allowed to cool to room temperature and hydrolysed by concentrated aqueous sodium hydroxide (150 cm^3). The resulting suspension was stirred for a further 18 hours to allow hydrolysis to reach completion, after which the pH was adjusted to approximately 8 with concentrated hydrochloric acid (5 cm^3). The product was extracted into chloroform (4 × 50 cm^3) and the washings combined and dried over magnesium sulfate. Removal of solvent by rotary evaporation afforded a solid brown residue. This was recrystallised from 3 : 1 ethyl acetate–chloroform giving yellow/orange plate-like crystals of the 2-thiopyridone compound.

(i) 6-Methyl-2(1*H*)-thiopyridone. Yield 12.03 g (70%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 2.48 (3H, s, CH_3), 6.55 (1H, d, $^3J_{H5\text{-}H4}$

8.4, H5), 7.31 (1H, dd, $^3J_{H4-H5}$ and $^3J_{H4-H3}$ 8.4, H4), 7.37 (1H, d, $^3J_{H3-H4}$, H3) and 13.8 (1H, b, NH); δ_C(100 MHz, $CDCl_3$ Me_4Si) 18.9 (CH_3), 114.1 (C5), 130.7 (C3), 138.7 (C4), 148.8 C(6) and 176.4 (C2); *m*/*z*(EI) 125 (M^+), 110.80 (Found: C, 57.31; H, 5.59; N, 11.07. C_6H_7NS requires C, 57.57; H, 5.64; N, 11.19%).

(ii) 4-Methyl-2(1*H*)-thiopyridone. Yield 5.76 g (63%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 2.27 (3H, s, CH_3), 6.64 (1H, dd, $^3J_{H5-H6}$ 6.4, $^4J_{H5-H3}$ 2.0, H5), 7.41 (1H, s, H3), 7.53 (1H, d, $^3J_{H6-H5}$ 6.4, H6) and 13.0 (1H, b, NH); δ_C(100 MHz, $CDCl_3$, Me_4Si) 21.4 (CH_3), 116.3 (C5), 132.9 (C3), 136.2 (C6), 150.5 (C4) and 174.9 (C2); *m*/*z*(EI) 125 (M^+), 110.80 (Found: C, 57.46; H, 5.61; N, 11.13. C_6H_7NS requires C, 57.57; H, 5.64; N, 11.19%).

General procedure for the synthesis of trimethylsilylated 2-thiopyridines from 2-thiopyridones

To a solution of the appropriate 2-thiopyridone compound (56 mmol) in toluene was added trimethylsilyldiethylamine (9.01 g, 62 mmol). The solution was refluxed under nitrogen for 5 hours. The solvent was removed by distillation under nitrogen leaving a dark brown liquid. This liquid was distilled under high vacuum conditions and yielded the silylated derivative as a bright yellow distillate.

(i) 2-(Trimethylsilylmercapto)pyridine. Yield 9.21 g (90%); bp 35 °C (0.03 mmHg) δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.36 (9H, s, $Si(CH_3)_3$), 6.80 (1H, ddd, $^3J_{H5-H4}$ 7.6, $^3J_{H5-H6}$ 4.8, $^4J_{H5-H3}$ 0.8, H5), 7.14 (1H, ddd, $^3J_{H3-H4}$, 7.6, $^4J_{H3-H5}$ and $^5J_{H3-H6}$ 0.8, H3), 7.26 (1H, ddd, $^3J_{H4-H3}$ and $^3J_{H4-H5}$ 7.6, $^4J_{H4-H6}$ 2.0, H4) and 8.21 (1H, d, $^3J_{H6-H5}$ 4.8, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 1.1 ($Si(CH_3)_3$), 119.0 (C5), 125.8 (C3), 135.5 (C4), 148.5 (C6) and 158.4 (C2); δ_{Si}(79 MHz, $CDCl_3$, Me_4Si) 16.6; *m*/*z*(EI) 183 (M^+), 168, 153, 138, 78.

(ii) 5-Trifluoromethyl-2-(trimethylsilylmercapto)pyridine. Yield 3.13 g (75%); bp 50 °C (0.05 mmHg); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.48 (9H, s, $Si(CH_3)_3$), 7.36 (1H, d, $^3J_{H3-H4}$ 8.4, H3), 7.62 (1H, dd, $^3J_{H4-H3}$ 8.4, $^4J_{H4-H6}$ 2.4, H4) and 8.79 (1H, d, $^4J_{H6-H4}$ 2.4, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 1.2 ($Si(CH_3)_3$), 122.4 (q, $^2J_{C-F}$ 33.1, C5), 124.0 (q, $^1J_{C-F}$ 270.2, CF_3), 125.2 (C3), 132.7 (C4), 145.8 (C6) and 164.5 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −64.1; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 18.0; *m*/*z*(EI) 251 (M^+), 236, 232, 73 (Found: C, 42.77; H, 4.80; N, 5.71. $C_9H_{12}F_3NSSi$ requires C, 43.01; H, 4.81; N, 5.57%).

(iii) 6-Methyl-2-(trimethylsilylmercapto)pyridine. Yield 8.89 g (94%); bp 52 °C (0.03 mmHg); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.44 (9H, s, $Si(CH_3)_3$), 2.43 (3H, s, 6-CH_3), 6.79 (1H, d, $^3J_{H5-H4}$ 7.8, H5), 7.05 (1H, d, $^3J_{H3-H4}$ 7.8, H3) and 7.28 (1H, dd, $^3J_{H4-H3}$ and $^3J_{H4-H5}$ 7.8, H4); δ_C(100 MHz, $CDCl_3$, Me_4Si) 1.4 ($Si(CH_3)_3$), 24.0 (6-CH_3), 118.8 (C5), 122.7 (C3), 136.3 (C4), 157.4 (C6) and 157.8 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 16.2; *m*/*z*(EI) 197 (M^+) (Found: MH^+, 197.0694 (EI) $C_9H_{15}NSSi$ requires M_r, 197.0695), 182, 167, 152, 92, 73.

(iv) 4-Methyl-2-(trimethylsilylmercapto)pyridine. Yield 2.26 g (82%); bp 60 °C (0.06 mmHg). (After 5 days the liquid crystallised—giving yellow plate-like crystals (mp 42 °C); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.44 (9H, s, $Si(CH_3)_3$), 2.22 (3H, s, 4-CH_3), 6.77 (1H, d, $^3J_{H5-H6}$ 4.9, H5), 7.14 (1H, s, H3) and 8.14 (1H, d, $^3J_{H6-H5}$ 4.9, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 1.4 ($Si(CH_3)_3$), 20.7 (4-CH_3), 120.6 (C5), 127.6 (C3), 147.1 (C6), 148.2 (C4) and 158.7 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 17.0; *m*/*z*(Ei) 197 (M^+) (Found: M^+, 197.0694 (EI), $C_9H_{15}NSSi$ requires M_r, 197.0695), 182, 92, 73.

General procedure for the synthesis of chlorodimethylsilylmethylthiopyridones from trimethylsilylated thiopyridones and chloro(chloromethyl)dimethylsilane

A solution of the trimethylsilylated thiopyridone (5.45 mmol) was prepared in benzene under a nitrogen atmosphere. Chloro(chloromethyl)dimethylsilane (0.78 g, 5.45 mmol) was added drop-wise with stirring and the solution allowed to stand for 30 minutes at room temperature. Upon crystallisation, the solvent was decanted off, the solid washed twice with diethyl ether and dried for 1 hour under high vacuum.

(i) 2-(Chlorodimethylsilylmethylmercapto)pyridine 13b. Yellow crystalline solid (0.98 g, 83%); δ(400 MHz, $CDCl_3$, Me_4Si) 0.76 (6H, s, $Si(CH_3)_2$), 2.65 (2H, s, S-CH_2), 7.20 (1H, dd, $^3J_{H5-H4}$ 7.6, $^3J_{H5-H6}$ 4.8, H5), 7.32 (1H, d, $^3J_{H3-H4}$ 8.4, H3), 7.70 (1H, dd, $^3J_{H4-H3}$ 8.4, $^3J_{H4-H5}$ 7.6, H4) and 8.28 (1H, d, $^3J_{H6-H5}$ 4.8, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 8.8 ($Si(CH_3)_2$), 16.7 (S-CH_2), 120.1 (C5), 122.3 (C3), 138.6 (C4), 144.5 (C6) and 159.6 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) −19.4; *m*/*z*(EI) 217/219 (3 : 1) (M^+), 202/204 (3 : 1) (M^+ − Me), 182, 124, 78 (Found: C, 44.12; H, 5.52; N, 6.34; Cl, 14.30. $C_8H_{12}ClNSSi$ requires C, 44.12; H, 5.55; N, 6.43; Cl, 14.72%).

(ii) 2-(Chlorodimethylsilylmethylmercapto)-5-trifluoromethylpyridine 14b. A bright yellow liquid after distillation (0.55 g, 55%) bp 60 °C (0.03 mmHg); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.58 (6H, s, $Si(CH_3)_2$), 2.70 (2H, s, S-CH_2), 7.34 (1H, d, $^3J_{H3-H4}$ 8.8, H3), 7.69 (1H, dd, $^3J_{H4-H3}$ 8.8, $^4J_{H4-H6}$ 2.4, H4) and 8.61 (1H, s, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 2.7 ($Si(CH_3)_2$), 17.0 (S-CH_2), 121.6 (C3), 122.6 (q, $^2J_{C-F}$ 33.0, C5), 123.7 (q, $^1J_{C-F}$ 270.2, CF_3), 132.9 (C4), 145.2 (C6) and 164.3 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −64.2; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 19.2; *m*/*z*(EI) 285/287 (3 : 1) (M^+) (Found: M^+, ^{35}Cl, 285.0021. $C_9H_{11}{}^{35}ClF_3NSSi$ requires M_r, 285.0022). 270/272 (3 : 1) (M^+ − Me), 250, 192, 93.

(iii) 1-(Chlorodimethylsilylmethyl)-6-methyl-2-thiopyridone 6b. Pale yellow crystalline solid (1.16 g, 8.11 mmol); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.72 (6H, s, $Si(CH_3)_2$), 2.63 (3H, s, 6-CH_3), 4.34 (2H, s, N-CH_2), 6.70 (1H, d, $^3J_{H5-H4}$ 7.6, H5), 7.22 (1H, m, H4) and 7.57 (1H, d, $^3J_{H3-H4}$ 8.8, H3); δ_C(100 MHz, $CDCl_3$, Me_4Si) 5.9 ($Si(CH_3)_2$), 23.0 (6-CH_3), 49.9 (N-CH_2), 116.6 (C5), 130.5 (C3), 134.6 (C4), 149.9 (C6) and 176.4 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) −0.1; *m*/*z*(EI) 231/233 (3 : 1) (M^+) (Found: M^+, ^{35}Cl, 231.0305. $C_9H_{14}{}^{35}ClNSSi$ requires M_r, 231.0305), 216/218 (3 : 1) (M^+ − Me), 196, 138.

(iv) 2-(Chlorodimethylsilylmethylmercapto)-4-methylpyridine. Yellow crystalline solid (0.58 g, 81%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.77 (6H, s, $Si(CH_3)_2$), 2.39 (3H, s, 4-CH_3), 2.70 (2H, s, S-CH_2), 7.00 (1H, d, $^3J_{H5-H6}$ 6.0, H5), 7.12 (1H, s, H3) and 8.08 (1H, d, $^3J_{H6-H5}$ 6.0, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si), 8.4 ($Si(CH_3)_2$), 16.6 (S-CH_2), 21.2 (4-CH_3), 121.7 (C5), 122.0 (C3), 143.2 (C6), 151.2 (C4) and 159.7 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) −26.9; *m*/*z*(EI) 231/233 (3 : 1) (M^+) (Found: M^+, ^{35}Cl, 231.0305. $C_9H_{14}{}^{35}ClNSSi$ requires M_r, 231.0305), 216/218 (3 : 1) (M^+ − Me), 196, 138.

General procedure for the synthesis of fluorodimethylsilylmethylthiopyridones from chlorodimethylsilylmethylthiopyridones using antimony trifluoride

The appropriate chlorodimethylsilylmethylthiopyridone (5.45 mmol) was either dissolved or suspended in benzene under a nitrogen atmosphere. Granular antimony trifluoride (0.33 g, 1.85 mmol) was introduced and the reagents stirred together for 1 hour at room temperature. The organic phase was decanted from the oily antimony-containing by-products and hydrolysed by shaking with distilled water (50 cm^3). The organic phase was extracted into dichloromethane (3 × 50 cm^3).The extracts were combined and dried over magnesium sulfate and the solvents removed by rotary evaporation. The remaining residue, either an oily liquid or crystalline solid, was either vacuum distilled or recrystallised from an appropriate solvent.

(i) 2-(Fluorodimethylsilylmethylmercapto)pyridine 13a. Pale yellow oil (0.42 g, 39%); bp 47 °C (0.05 mmHg); δ_H(400 MHz,

$CDCl_3$, Me_4Si) 0.33 (6H, d, $^3J_{H\text{-}F}$ 7.3, $Si(CH_3)_2$), 2.37 (2H, d, $^3J_{H\text{-}F}$ 4.8, S-CH_2), 6.93 (1H, ddd, $^3J_{H5\text{-}H4}$ 7.2, $^3J_{H5\text{-}H6}$ 5.6, $^4J_{H5\text{-}H3}$ 0.8, H5), 7.17 (1H, d, $^3J_{H3\text{-}H4}$ 8.4, H3), 7.41 (1H, ddd, $^3J_{H4\text{-}H3}$ 8.4 and $^3J_{H4\text{-}H5}$ 7.2, $^4J_{H4\text{-}H6}$ 2.0, H4) and 8.30 (1H, d, $^3J_{H6\text{-}H5}$ 5.6, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) −0.4 (d, $^2J_{C\text{-}F}$ 16.5, $Si(CH_3)_2$), 14.0 (d, $^2J_{C\text{-}F}$ 22.0, S-CH_2), 119.3 (C5), 121.5 (C3), 136.1 (C4), 147.7 (C6) and 159.2 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −142.5; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 17.0 (d, $^1J_{Si\text{-}F}$ 275.8); *m*/*z*(EI) 202 (MH^+), 186, 182, 124, 78, 77 (Found: C, 48.15; H, 6.10; N, 6.93. $C_8H_{12}FNSSi$ requires C, 47.73; H, 6.01; N, 6.96%).

(ii) 2-(Fluorodimethylsilylmethylmercapto)-5-trifluoromethylpyridine 14a. Pale yellow oil (0.11 g, 23%), bp 52 °C (0.06 mmHg); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.36 (6H, d, $^3J_{H\text{-}F}$ 7.2, $Si(CH_3)_2$), 2.51 (2H, d, $^3J_{H\text{-}F}$ 5.2, S-CH_2), 7.31 (1H, d, $^3J_{H3\text{-}H4}$ 8.4, H3), 7.67 (1H, dd, $^3J_{H4\text{-}H3}$ 8.4, $^4J_{H4\text{-}H6}$ 2.4, H4) and 8.63 (1H, s, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) −1.1 (d, $^2J_{C\text{-}F}$ 14.7, $Si(CH_3)_2$), 14.4 (d, $^2J_{C\text{-}F}$ 18.4, S-CH_2), 121.3 (C3), 122.3 (q, $^2J_{C\text{-}F}$ 33.1, C5), 123.8 (q, $^1J_{C\text{-}F}$ 270.2, CF_3), 132.5 (C4), 145.6 (C6) and 164.5 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −155.5; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 26.0 (d, $^1J_{Si\text{-}F}$ 280.3); *m*/*z*(Ei) 270 (MH^+), 254, 250, 192, 77 (Found: C, 40.42; H, 4.29; N, 5.38. $C_9H_{11}F_4NSSi$ requires C, 40.14; H, 4.12; N, 5.20%).

(iii) 1-(Fluorodimethylsilylmethyl)-6-methyl-2-thiopyridone 6a. From 1-(chlorodimethylsilylmethyl)-6-methyl-2-thiopyridone (1.76 g, 7.59 mmol). Pale yellow oil (1.02 g, 62%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.38 (6H, d, $^3J_{H\text{-}F}$ 8.0, $Si(CH_3)_2$), 2.54 (3H, s, $6CH_3$), 4.38 (2H, d, $^3J_{H\text{-}F}$ 6.8, N-CH_2), 6.60 (1H, d, $^3J_{H5\text{-}H4}$ 7.2, H5), 7.10 (m, 1H, H4) and 7.63 (1H, d, $^3J_{H3\text{-}H4}$ 8.8, H3); δ_C(100 MHz, $CDCl_3$, Me_4Si) −1.0 (d, $^2J_{C\text{-}F}$ 14.6, $Si(CH_3)_2$), 22.8 (6-CH_3), 46.4 (d, $^2J_{C\text{-}F}$ 23.7, N-CH_2), 115.5 (C5), 132.7 (C3), 133.0 (C4), 148.7 (C6) and 179.1 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −150.2; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 27.0 (d, $^1J_{Si\text{-}F}$ 281.3); *m*/*z*(EI) 215 (M^+) (Found: M^+, 215.0600. $C_9H_{14}FNSSi$ requires M_r, 215.0600), 200, 196, 138, 78.

General procedure for the synthesis of bromodimethylsilylmethyl thiopyridones from trimethylsilylated thiopyridones and bromo(chloromethyl)dimethylsilane

A solution of the trimethylsilylated thiopyridone (2.77 mmol) was prepared in benzene under a nitrogen atmosphere. (Bromomethyl)chlorodimethylsilane (0.52 g, 2.77 mmol) was added drop-wise with stirring and the solution allowed to stand for 30 minutes at room temperature. After crystallisation the solvent was decanted off, the material washed twice with diethyl ether and dried for 1 hour under high vacuum.

(i) 2-(Bromodimethylsilylmethylmercapto)pyridine 13c. White crystalline solid (0.55 g, 93%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 1.07 (6H, s, $Si(CH_3)_2$), 3.01 (2H, s, S-CH_2), 7.44 (1H, m, H5), 7.51 (1H, d, $^3J_{H3\text{-}H4}$ 8.8, H3), 7.96 (1H, m, H4) and 8.49 (1H, d, $^3J_{H6\text{-}H5}$ 5.6, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 7.9 ($Si(CH_3)_2$), 16.5 (S-CH_2), 121.2 (C5), 123.3 (C3), 141.2 (C4), 143.6 (C6) and 162.7 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) −0.8; *m*/*z*(FAB) 182 (M^+ − Br) (Found: C, 36.22; H, 4.74; N, 5.34. $C_8H_{12}BrNSSi$ requires C, 36.64; H, 4.61; N, 5.34%).

(ii) 2-(Bromodimethylsilylmethylmercapto)-5-trifluoromethylpyridine 14c. Yellow crystalline solid (0.70 g, 63%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.66 (6H, s, $Si(CH_3)_2$), 2.74 (2H, s, S-CH_2), 7.35 (1H, d, $^3J_{H3\text{-}H4}$ 7.8, H3), 7.72 (1H, d, $^3J_{H4\text{-}H3}$ 7.8, H4) and 8.51 (1H, s, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 4.7 ($Si(CH_3)_2$), 17.3 (S-CH_2), 122.0 (C3), 122.7 (q, $^2J_{C\text{-}F}$ 34.9, C5), 123.0 (q, $^1J_{C\text{-}F}$ 272.1, CF_3), 133.7 (C4), 143.5 (C6) and 164.5 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −64.2; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 7.3; *m*/*z*(FAB) 250 (M^+ − Br) (Found: C, 32.51; H, 3.33; N, 4.21. $C_9H_{11}BrF_3NSSi$ requires C, 32.73; H, 3.36; N, 4.24%).

(iii) 1-(Bromodimethylsilylmethyl)-6-methyl-2-thiopyridone 6c. White crystalline solid (1.66 g, 97%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.32 (6H, s, $Si(CH_3)_2$), 2.66 (3H, s, 6-CH_3), 4.47 (2H, s, N-CH_2), 6.99 (1H, d, $^3J_{H5\text{-}H4}$ 7.2, H5), 7.40 (1H, m, H4) and 7.65 (1H, d, $^3J_{H3\text{-}H4}$ 8.4, H3); δ_C(100 MHz, $CDCl_3$, Me_4Si) −1.5 ($Si(CH_3)_2$), 22.8 (6-CH_3), 47.4 (N-CH_2), 119.4 (C5), 131.5 (C3), 136.7 (C4), 153.1 (C6) and 174.8 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si); *m*/*z*(EI) 196 (M^+ − Br) (Found: M^+ − Br, 196.0616. $C_9H_{14}NSSi$ requires M_r, 196.0616); (FAB$^-$) 79/81 (1 : 1) (Br^-).

General procedure for the synthesis of trifluoromethylsulfonyldimethylsilylmethylthiopyridones from chlorodimethylsilylmethylthiopyridones using trimethylsilyl trifluoromethanesulfonate

To a solution or suspension of the appropriate chlorodimethylsilylmethylthiopyridone (1.20 mmol) (usually freshly prepared) under a nitrogen atmosphere, was added trimethylsilyl trifluoromethanesulfonate (trimethylsilyltriflate) (0.20 g, 1.22 mmol) by syringe, drop-wise, with stirring. Within 30 minutes the product formed as a suspension and the solvent was decanted off. The isolated material was washed with diethyl ether (2 × 5 cm^3) and dried under high vacuum for 2 hours.

(i) 2-(Dimethyltrifluoromethylsulfonylsilylmethylmercapto)-pyridine 13d. White crystalline solid (0.29 g, 80%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.87 (6H, s, $Si(CH_3)_2$), 2.80 (2H, s, S-CH_2), 7.55 (1H, m, H5), 7.63 (1H, d, $^3J_{H3\text{-}H4}$ 8.8, H3), 8.07 (1H, m, H4) and 8.61 (1H, d, $^3J_{H6\text{-}H5}$ 6.0, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 0.8 ($Si(CH_3)_2$), 12.5 (S-CH_2), 120.5 (q, $^1J_{C\text{-}F}$ 327.3, SO_3CF_3), 122.3 (C5), 123.6 (C3), 143.3 (C4), 143.9 (C6) and 164.4 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −80.1; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 40.6; *m*/*z*(EI) 182 (M^+ − OTf) (Found: M^+ − OTf, 182.0459. $C_8H_{12}NSSi$ requires M_r, 182.0459); (FAB$^-$) 149 ($^-$OTf), 80, 69.

(ii) 2-(Dimethyltrifluoromethylsulfonylsilylmethylmercapto)-5-trifluoromethylpyridine 14d. Yellow crystalline solid (0.54 g, 77%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.82 (6H, s, $Si(CH_3)_2$), 2.77 (2H, s, S-CH_2), 7.77 (1H, d, $^3J_{H3\text{-}H4}$ 8.8, H3), 8.13 (1H, dd, $^3J_{H4\text{-}H3}$ 8.8, $^4J_{H4\text{-}H6}$ 2.0, H4) and 8.62 (1H, s, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) 3.2 ($Si(CH_3)_2$), 13.3 (S-CH_2), 119.2 (q, $^1J_{C\text{-}F}$ 316.3, SO_3CF_3), 122.0 (q, $^1J_{C\text{-}F}$ 270.6, 5-CF_3), 123.7 (C3), 124.6 (q, $^2J_{C\text{-}F}$ 34.8, C5), 137.3 (C4), 140.5 (C6) and 167.2 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −64.5 (5-CF_3), −80.0 (SO_3CF_3); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 7.6; *m*/*z*(EI) 250 (M^+ − OTf); (FAB$^-$) 149 ($^-$OTf), 80, 69 (Found: C, 30.34; H, 2.82; N, 3.86. $C_{10}H_{11}F_6NO_3S_2Si$ requires C, 30.07; H, 2.78; N, 3.51%).

(iii) 1-(Dimethyltrifluoromethylsulfonylsilylmethyl)-6-methyl-2-thiopyridone 6d. White crystalline solid (0.21 g, 84%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.75 (6H, s, $Si(CH_3)_2$), 2.70 (3H, s, 6-CH_3), 4.24 (2H, s, N-CH_2), 7.43 (1H, d, $^3J_{H5\text{-}H4}$ 8.0, H5), 7.72 (1H, d, $^3J_{H3\text{-}H4}$ 8.4, H3) and 7.94 (1H, m, H4); δ_C(100 MHz, $CDCl_3$, Me_4Si) 1.2 ($Si(CH_3)_2$), 22.9 (6-CH_3), 50.4 (N-CH_2), 122.0 (q, $^1J_{C\text{-}F}$ 318.2, SO_3CF_3), 124.6 (C5), 126.4 (C3), 143.4 (C4), 158.4 (C6) and 163.9 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −75.8; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 26.7; *m*/*z*(EI) 196 (M^+ − OTf) (Found: M^+ − OTf 196.0616. $C_9H_{14}NSSi$ requires M_r, 196.0616); (FAB$^-$) 149 ($^-$OTf), 80, 69.

General procedure for the synthesis of trimethylsilylmethylmercaptopyridines

To a solution of the appropriate trimethylsilylated thiopyridone (4.67 mmol) in toluene (20 cm^3) was added (iodomethyl)-trimethylsilane (1.00 g, 4.67 mmol). The mixture was refluxed for 3 days under a nitrogen atmosphere and allowed to cool to room temperature. The solution was hydrolysed by stirring vigorously with aqueous sodium hydroxide (0.1 M, 10 cm^3)

overnight. The organic phase was extracted into dichloromethane (3 × 30 cm^3) and the extracts combined and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator afforded a brown oil. Vacuum distillation (0.05 mmHg) of this oil gave the required compounds as pale yellow liquids.

(i) 2-(Trimethylsilylmethylmercapto)pyridine. Yield 0.83 g (91%); bp 50 °C (0.05 mmHg); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.15 (9H, s, $Si(CH_3)_3$), 2.37 (2H, s, S-CH_2), 6.91 (1H, ddd, $^3J_{H5\text{-}H4}$ 7.2, $^3J_{H5\text{-}H6}$ 4.9, $^4J_{H5\text{-}H3}$ 1.2, H5), 7.17 (1H, ddd, $^3J_{H3\text{-}H4}$ 8.2, $^4J_{H3\text{-}H5}$ 1.2, $^5J_{H3\text{-}H6}$ 0.9, H3), 7.43 (1H, ddd, $^3J_{H4\text{-}H3}$ 8.2, $^3J_{H4\text{-}H5}$ 7.2, $^4J_{H4\text{-}H6}$ 1.8, H4) and 8.41 (1H, ddd, $^3J_{H6\text{-}H5}$ 4.9, $^4J_{H6\text{-}H4}$ 1.8, $^5J_{H6\text{-}H3}$ 0.9, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) −1.6 ($Si(CH_3)_3$), 15.4 (S-CH_2), 118.9 (C5), 121.3 (C3), 135.6 (C4), 149.2 (C6) and 161.4 (C2); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 1.9; *m*/*z*(EI) 197 (M^+), 182, 167, 124, 78, 73 (Found: C, 54.35; H, 7.48; N, 6.98. $C_9H_{15}NSSi$ requires C, 54.77; H, 7.66; N, 7.10%).

(ii) 5-Trifluoromethyl-2-(trimethylsilylmethylmercapto)-pyridine. Yield 0.53 g (46%); bp 52 °C (0.05 mmHg); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.16 (9H, s, $Si(CH_3)_3$), 2.41 (2H, s, S-CH_2), 7.27 (1H, d, $^3J_{H3\text{-}H4}$ 8.5, H3), 7.63 (1H, dd, $^3J_{H4\text{-}H3}$ 8.5, $^4J_{H4\text{-}H6}$ 2.5, H4) and 8.67 (1H, s, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) −1.7 ($Si(CH_3)_3$), 15.4 (S-CH_2), 120.9 (C3), 122.0 (q, $^2J_{C\text{-}F}$ 33.6, C5), 124.1 (q, $^1J_{C\text{-}F}$ 271.9, CF_3), 132.2 (C4), 146.2 (C6) and 166.5 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −64.0; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 2.1; *m*/*z*(EI) 265 (M^+), 250, 246, 73 (Found: C, 45.43; H, 5.02; N, 5.44. $C_{10}H_{14}F_3NSSi$ requires C, 45.26; H, 5.32; N, 5.28%).

1,6-Dimethyl-2-thiopyridone

The synthesis proceeded as in the preparation of 1-(fluorodimethylsilylmethyl)-6-methyl-2-thiopyridone, **6a** (2.39 g, 10.29 mmol) but using half an equivalent of antimony trifluoride (0.92 g, 5.15 mmol). The product was purified by recrystallisation from 1:1 diethyl ether–ethyl acetate yielding a pale yellow crystalline solid (1.17 g, 82%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 2.47 (3H, s, 6-CH_3), 4.04 (3H, s, N-CH_3), 6.50 (1H, d, $^3J_{H5\text{-}H4}$ 6.8, H5), 7.04 (1H, m, H4) and 7.64 (1H, d, $^3J_{H3\text{-}H4}$ 8.6, H3); δ_C(100 MHz, $CDCl_3$, Me_4Si) 22.5 (6-CH_3), 40.0 (N-CH_3), 115.1 (C5), 133.4 (C4), 133.6 (C3), 149.4 (C6) and 181.4 (C2); *m*/*z*(EI) 139 (M^+), 124, 94 (Found: C, 59.97; H, 6.47; N, 9.93. C_7H_9NS requires C, 60.39; H, 6.52; N, 10.06%).

General procedure for the synthesis of pyridinium trifluoromethanesulfonate(triflate) salts from trimethylsilylmethylmercaptopyridines

A solution of the appropriate 2-(trimethylsilylmethylmercapto)-pyridine compound (1.32 mmol) in benzene (5 cm^3) was prepared and methyl trifluoromethanesulfonate (0.22 g, 1.32 mmol) added drop-wise by syringe. A white precipitate of the product formed within 5 minutes and was isolated by decanting off the solvent and washing the residue with diethyl ether (2 × 1 cm^3) before drying it under high vacuum for 1 hour.

(i) 1-Methyl-2-(trimethylsilylmethylmercapto)pyridinium trifluoromethanesulfonate. Yield 0.45 g (93%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.27 (9H, s, $Si(CH_3)_3$), 2.46 (2H, s, S-CH_2), 4.25 (3H, s, N-CH_3), 7.61 (1H, m, H5), 8.07 (1H, d, $^3J_{H3\text{-}H4}$ 8.4, H3), 8.33 (1H, m, H4) and 8.88 (1H, d, $^3J_{H6\text{-}H5}$ 5.6, H6); δ_C(100 MHz, $CDCl_3$ Me_4Si) −1.8 ($Si(CH_3)_3$), 17.9 (S-CH_2), 45.8 (N-CH_3), 120.7 (q, $^1J_{C\text{-}F}$ 321.7, SO_3CF_3), 122.0 (C5), 124.6 (C3), 143.5 (C4), 146.7 (C6) and 163.1 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −80.1; δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 3.5; *m*/*z*(EI) 212 (M^+ − OTf), 73; (FAB^-) 149 ($^-$OTf), 80, 69 (Found: C, 36.12; H, 4.93; N, 3.78. $C_{11}H_{18}F_3NO_3S_2Si$ requires C, 36.55; H, 5.01; N, 3.87%).

(ii) 1-Methyl-5-trifluoromethyl-2-(trimethylsilylmethylmercapto)pyridinium trifluoromethanesulfonate. Yield 0.63 g, (97%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.26 (9H, s, $Si(CH_3)_3$), 2.53 (2H, s, S-CH_2), 4.28 (3H, s, N-CH_3), 8.37–8.32 (2H, m, H3/H4) and 9.13 (1H, s, H6); δ_C(100 MHz, $CDCl_3$, Me_4Si) −1.9 ($Si(CH_3)_3$), 18.2 (S-CH_2), 46.5 (N-CH_3), 120.8 (q, $^1J_{C\text{-}F}$ 323.3, SO_3CF_3), 121.8 (q, $^1J_{C\text{-}F}$ 270.1, 5-CF_3), 124.6 (q, $^2J_{C\text{-}F}$ 37.5, C5), 125.8 (C3), 139.1 (C4), 144.5 (C6) and 168.3 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −64.6 (5-CF_3), −80.4 (SO_3CF_3); δ_{Si}(17.8 MHz, $CDCl_3$, Me_4Si) 3.7; *m*/*z*(FAB^+) 280 (M^+ − OTf), 73; (FAB^-) 149 ($^-$OTf), 80, 69 (Found: C, 33.44; H, 3.82; N, 3.38. $C_{12}H_{17}F_6NO_3S_2Si$ requires C, 33.56; H, 3.99, N, 3.26%).

1.6-Dimethyl-2-(methylmercapto)pyridinium trifluoromethanesulfonate

1,6-Dimethyl-2-thiopyridone (0.18 g, 1.29 mmol) was dissolved in toluene (7 cm^3) under a nitrogen atmosphere. Methyl triflate (0.23 g, 1.40 mmol) was added drop-wise with stirring. The solution momentarily turned cloudy before the product precipitated as a yellow crystalline solid. The solvent was decanted off, the crystals washed with diethyl ether (3 × 5 cm^3) and dried on a high vacuum line for 2 hours (0.22 g, 52%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 2.78 (3H, s, S-CH_3), 2.81 (3H, s, 6-CH_3), 4.09 (3H, s, N-CH_3), 7.57 (1H, d, $^3J_{H5\text{-}H4}$ 8.1, H5), 7.73 (1H, d, $^3J_{H3\text{-}H4}$ 8.6, H3) and 8.13 (1H, m, H4); δ_C(100 MHz, $CDCl_3$, Me_4Si) 16.4 (S-CH_3), 21.8 (6-CH_3), 40.7 (N-CH_3), 120.8 (q, $^1J_{C\text{-}F}$ 319.8, SO_3CF_3), 122.4 (C3), 124.1 (C5), 142.8 (C4), 156.4 (C6) and 161.7 (C2); δ_F(90 MHz, $CDCl_3$, Me_4Si) −80.1; *m*/*z*(EI) 154 (M^+ − OTf), 139, 107, 92; (FAB^-) 149 ($^-$OTf), 80, 69 (Found: C, 35.20; H, 4.01; N, 4.55. $C_9H_{12}F_3NO_3S_2$ requires C, 35.64; H, 3.99; N, 4.62%).

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