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

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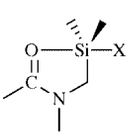
A novel method for performing structure correlations in solution is described. Examination of how the ^{13}C chemical shifts of the ring carbons of substituted 2-pyridones change on complexation of the oxygen with silicon has enabled the % Si–O bond formation to be determined in solution for a number of pentacoordinate silicon species with 2-pyridones as ligands. The % pentacoordination in these complexes has been determined from the ^{29}Si chemical shift using model compounds for the tetracoordinate and pentacoordinate limiting cases. Correlation of the % Si–O bond formation with % pentacoordination enables the pathway for substitution at silicon to be mapped in solution. The generality of these techniques is examined using a series of related aromatic ligands.

Introduction

X-Ray crystallographic studies have been used by Dunitz, Bürgi[1] and others[2–6] to determine the molecular pathways of a variety of reactions. Such crystal structure correlations involve collecting together the crystal structures of a range of structurally similar compounds and then sequencing them on the basis of key crystal data (usually inter-atom distances). Thus, a picture of the gradual molecular deformation on going from reactants to products is built up. Each individual structure represents a snapshot of the reaction at a particular point on the modelled reaction profile. This methodology has been applied to nucleophilic substitution at silicon by a number of groups.[3–6] The general picture that has emerged involves formation of the nucleophile–silicon bond accompanied by lengthening of the silicon–leaving group bond. The tetrahedral reactants are converted into a trigonal bipyramidal structure with the non-participating groups equatorial followed by reversion to a tetrahedral structure. For example, Baukov[4] and Pestunovich[5] separately examined the crystal structures of a range of related amidomethylhalosilanes (**1**). The resulting trajectory for nucleophilic substitution at silicon exhibited a hyperbolic relationship between the Si–O and Si–X bond lengths and a regular variation of the position of the silicon atom relative to the plane of the three equatorial carbon atoms.



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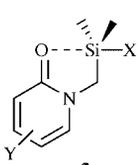

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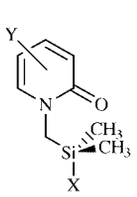


3a Y = H, X = F
3b Y = H, X = Cl
3c Y = H, X = Br
3d Y = H, X = OSO_2CF_3

4a Y = 5Cl, X = F
4b Y = 5Cl, X = Cl
4c Y = 5Cl, X = Br
4d Y = 5Cl, X = OSO_2CF_3

5a Y = 6Cl, X = F
5b Y = 6Cl, X = Cl
5c Y = 6Cl, X = Br
5d Y = 6Cl, X = OSO_2CF_3

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

7a Y = 3OMe, X = F
7b Y = 3OMe, X = Cl
7c Y = 3OMe, X = Br
7d Y = 3OMe, X = OSO_2CF_3

8a Y = $3NO_2$, X = F
8b Y = $3NO_2$, X = Cl
8c Y = $3NO_2$, X = Br
8d Y = $3NO_2$, X = OSO_2CF_3

We sought to develop a method that would enable similar structure correlations to be obtained in the solution phase, using ^{13}C and ^{29}Si NMR spectroscopy as the monitoring tools. Initial results have been published[7,8] and this paper provides a detailed description of the technique.

Unlike X-ray crystallography, which gives detailed information on the bond lengths and spacial arrangement of atoms, NMR only provides an insight into the connectivity and localised environment around particular nuclei.[9] Furthermore quantitative molecular coordinates can usually only be obtained through the use of model compounds. Thus, structural correlations using NMR require careful design of appropriate systems. The minimum requirement for studying the progress of a reaction is two parameters that measure the extent of bond formation or breaking and/or the change in geometry around a key site. NMR chemical shifts are sensitive to a number of parameters such as bond order, coordination number and localised electronic environment. Thus deconvolution of NMR data to provide the required information to construct a reaction profile is potentially very difficult. Clearly the task is made much easier if the system is designed so that particular chemical shifts essentially depend upon only one of the variables.

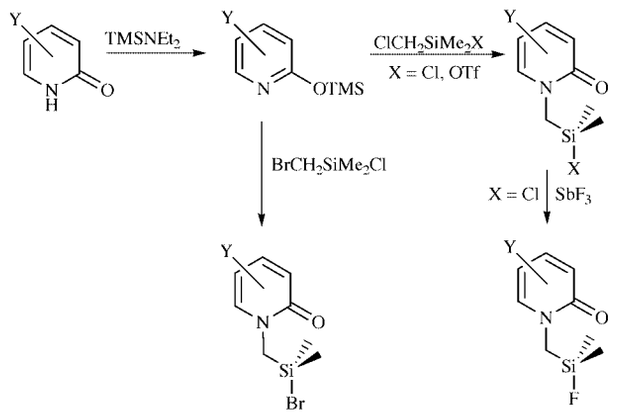
The ^{29}Si chemical shift is particularly susceptible to the coordination number around the silicon, having a value of between +24 ppm and −76 ppm for four coordinate silicon, −47 ppm and −110 ppm for five coordinate silicon[10] and −142 ppm and −220 ppm for six coordinate silicon.[11] Although the regions overlap for four and five coordination, the addition of an extra ligand to a four coordinate silicon leads to a substantial upfield shift. Thus, within a series of structurally similar compounds, the ^{29}Si chemical shift can be used as an indicator of the gradual change in coordination number.[12]

The extent of bond formation or breaking is a little more difficult to measure. For example, the attacking or leaving atom may not be NMR active or its chemical shift may depend upon a number of factors. One alternative is to monitor the chemical shifts of atoms attached to the attacking atoms. However, this may lead to a smaller variation in the chemical shifts and there is still no guarantee that the chemical shift will only depend upon the extent of bond formation or breaking. A better strategy is to use conjugated systems where bonding changes at the nucleophilic atom are relayed to more distant atoms that are not affected by other changes at the reaction centre. Furthermore the chemical shift change in such conjugated systems is often substantial. We chose to base our initial studies on the

substituted 2-pyridones (**2**). Judicious choice of substituent Y and leaving group X leads to a series of compounds with differing extents of O–Si bond formation and Si–X bond cleavage enabling us to model the pathway for substitution at silicon.

Results and discussion

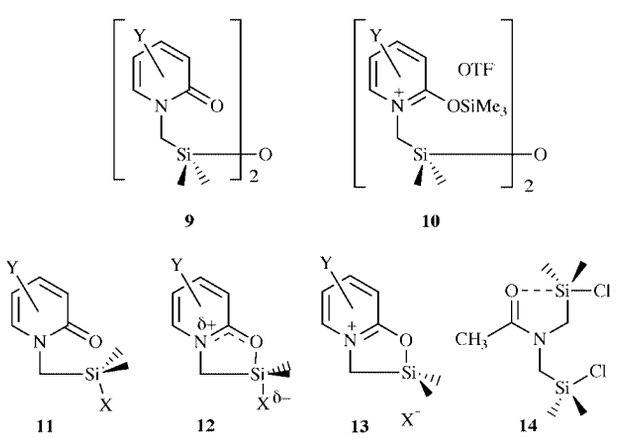
The model compounds **3a–d**, **4a–d**, **5a–d**, **6a–d**, **7a–d** and **8a–d** were prepared from the commercially available 2-pyridones, as shown in Scheme 1. Treatment of the substituted 2-pyridone



Scheme 1 Synthesis of model compounds.

with diethylaminotrimethylsilane gave the corresponding 2-trimethylsiloxypyridine.[13] Reaction of this with chloromethyldimethylchlorosilane gave the chloro derivatives **3b–8b**,[14] whereas treatment with chloromethyldimethylsilyl triflate gave the triflato derivatives **3d–8d**. The bromo derivatives were prepared by treating the substituted 2-trimethylsiloxypyridine with bromomethyldimethylchlorosilane. Reaction using chloromethyldimethylfluorosilane gave the chloro derivative, thus the fluoro derivatives were prepared by treating the chloro derivatives with antimony trifluoride.

The ^{13}C spectra of these pentacoordinate compounds showed that as predicted the chemical shift of the ring carbons changed systematically with leaving group, a similar pattern being observed for each substituted 2-pyridone. However, in order to carry out a structure correlation, the extent of bond formation or breaking needs to be calculated from this chemical shift data. This is achieved using the corresponding model compounds **9** and **10** that represent 0 and 100% O–Si bond formation



respectively. Since these two compounds are the limiting cases that provide the anchor for the calculation of the % Si–O bond formation, it is important that they are chosen with care. Compound **9** was employed, rather than the simpler *N*-methyl-2-pyridone, to ensure that the electronic effects of the N-substituent on the chemical shifts of the ring carbons were

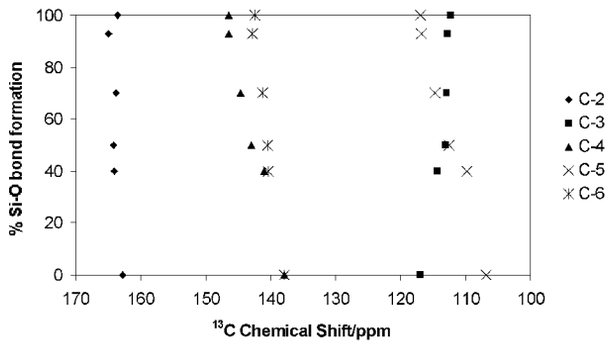


Fig. 1 The change in chemical shift as a function of Si–O bond formation for compounds **5a–d**.

similar to those expected of compound **2** with 0% O–Si bond formation. There is the possibility of some Si–O bond formation with compound **9**, but this was shown to be negligible by the ^{29}Si chemical shifts, which are consistent with a four coordinate disiloxane.[15] Similarly, the ^{13}C chemical shifts of the ring carbons are equivalent to those of non-silicon containing *N*-alkyl-2-pyridones. X-Ray crystal structures of amidomethylhalosilanes **1**, where X is phenoxide, have a PhO–Si bond length very close to that of a covalent O–Si bond and little distortion of the tetrahedral arrangement around silicon.[6] Compound **10** provides a good model for 100% O–Si bond formation. The ^{13}C chemical shifts of the ring carbons are similar to those of 2-methoxypyridinium salts.[16] The only drawback with using **10** as the limiting case is that compound **2** with 100% Si–O bond formation involves formation of a five membered ring. This may lead to geometry changes in the aromatic ring that are not present in compound **10**.

We have previously shown that when a 10% w/w solution of *N*-methyl-2-pyridone in $CDCl_3$ is titrated with successive amounts of trimethylsilyl trifluoromethanesulfonate, silylation is complete and exchange between the 2-pyridone to the pyridinium forms is fast on the NMR time scale.[7] There is a good linear correlation between the ^{13}C chemical shifts of each ring carbon and the mole fraction of the pyridinium form. However, the direction and extent of the change of the chemical shift varies greatly from one carbon to another. In calculating the extent of Si–O bond formation in compounds of the type **2,** we have assumed that the ^{13}C chemical shifts of the ring carbons vary in a linear fashion with the extent of Si–O bond formation between the two extremes of 0% bond formation, as represented by compound **9**, and 100% bond formation, as represented by compound **10**. The justification for this assumption is best demonstrated in the 6-chloro-2-pyridone system. Fig. 1 shows a plot of the extent of bond formation against the ^{13}C chemical shifts of the ring carbons. The data show that on going from the 2-pyridone to the pyridinium forms the chemical shift of each position changes in a coherent fashion and can increase or decrease. In general for all the simple 2-pyridones studied, the chemical shifts of carbons 4, 5 and 6 increase with Si–O bond formation whereas that of carbon 3 often decreases. The increase arises from the shift in π electron density away from the ring towards the exocyclic oxygen on Si–O bond formation. The decrease at carbon 3 is not easy to explain. However, compared to the 1-alkyl-2-pyridone, a similar pattern is observed when boron trifluoride complexes with 2-methoxypyridine.[16]

Small deviations from the line are observed which may arise from experimental error, specific interactions within the model compound or a non-linear response of the chemical shift to the extent of bond formation. In each case the % Si–O bond formation has been estimated to give the best fit to the complete set of data. This can either be achieved visually or by calculating the % Si–O bond formation for each ^{13}C resonance based on those observed with the limiting cases **9** and **10**. The weighted

Table 1 % Si–O bond formation for each of the model compounds **3**–**8** as calculated from the ^{13}C chemical shifts of the ring carbons, together with the % pentacoordination calculated from the ^{29}Si chemical shifts

Compound	Y	X	% Si–O bond formation	% Penta-coordination
3a	H	F	30	74
3b	H	Cl	50	102
3c	H	Br	70	73
3d	H	OTf	90	10
4a	5-Cl	F	30	63
4b	5-Cl	Cl	65	71
4c	5-Cl	Br	70	66
4d	5-Cl	OTf	90	19
5a	6-Cl	F	40	79
5b	6-Cl	Cl	50	101
5c	6-Cl	Br	70	84
5d	6-Cl	OTf	90	37
6a	6-Me	F	50	93
6b	6-Me	Cl	70	81
6c	6-Me	Br	70	77
6d	6-Me	OTf	90	21
7a	3-OMe	F	20	61
7b	3-OMe	Cl	45	88
7c	3-OMe	Br	72	68
7d	3-OMe	OTf	95	23
8a	3-NO_2	F	12	23
8b	3-NO_2	Cl	40	78
8c	3-NO_2	Br	58	85
8d	3-NO_2	OTf	80	44

average % Si–O bond formation is then calculated with weightings proportional to the size of the variation in the chemical shift. Using such techniques the uncertainty in the % Si–O bond formation is estimated to be approximately ±5%.

The % Si–O bond formation for each of the model compounds **3**–**8** are given in Table 1. The extent of bond formation for each substituted 2-pyridone follows the expected order with the leaving group ability TfO > Br > Cl > F.[17,18] However, the % Si–O bond formation for each leaving group is modified by the substituent. Structures **11**, **12** and **13** represent the various structural extremes. Structure **11** involves no O–Si bond formation and **13** complete O–Si bond formation with loss of the leaving group. In this latter structure there will be some build up of charge at the oxygen, but most of the charge will be located around the nitrogen. Structure **12** involves a pentacoordinate silicon with partial O–Si bond formation and Si–X bond cleavage. In this latter structure there is partial build up of positive charge on the nitrogen. Thus, substituents that stabilise the build up of positive charge at the nitrogen will favour O–Si bond formation. The 3-nitro group is strongly electron withdrawing, thus will resist the build up of positive charge at the nitrogen and thus, of all the substituents it has the lowest extent of bond formation for each leaving group. The 6-methyl group will stabilise the adjacent build up of positive charge and thus has the greater extent of bond formation. The orders of the extents of bond formation for each leaving group do vary a little, but the trend is 6-Me > 5-Cl > 6-Cl > H > 3-OMe > $3NO_2$.

Interestingly the size of the variation in the % Si–O bond formation with leaving group decreases as the substituent changes from nitro through hydrogen to methyl. A similar picture emerges if one focuses on each leaving group and calculates the variation of the % Si–O bond formation with substituent. The triflate leaving group has the largest extent of bond formation and thus a relatively small change in the % Si–O bond formation is observed with substituent. On the other hand the fluoro leaving group has the smallest extent of bond formation and this leads to a larger range of % Si–O bond formation with substituent.

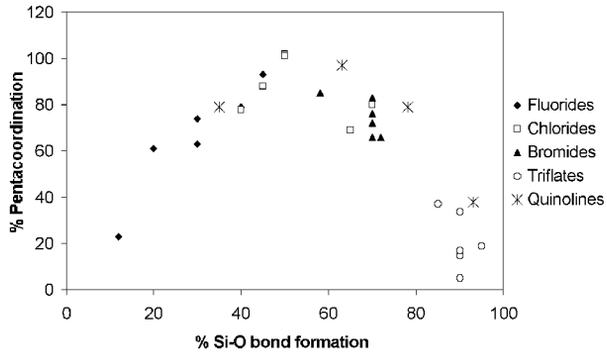


Fig. 2 % Pentacoordination *versus* the % Si–O bond formation.

In order to carry out a structural correlation it is necessary to have some measure of the coordination state of the silicon. This is measured using the ^{29}Si chemical shift. Again the conversion from chemical shift information to % pentacoordination requires the use of model compounds. In this instance three anchor points are required. One to model 0% pentacoordination involving 0% Si–O bond formation, compound **11**, one to model 0% pentacoordination involving 100% Si–O bond formation, compound **13** and one to model 100% pentacordination, compound **12**. The ^{29}Si NMR chemical shifts of Me_3SiCl, Me_3SiF and Me_3SiBr all appear within ±2 ppm of +28 ppm and so this value was used to anchor the scale at 0% pentacoordination with 0% O–Si bond formation.[15] The small variation of the chemical shift with leaving group confirms that the major arbiter of the ^{29}Si chemical shift is the coordination state at silicon. The X-ray crystal structure of **14** has been reported and shows one silicon to be tetracoordinated and the other completely pentacoordinated.[4,19] We have measured the ^{29}Si chemical shifts in $CDCl_3$ and found that the tetracoordinate silicon gives rise to a resonance at 26.8 ppm whereas the pentacoordinate silicon gives rise to a resonance at −39.9 ppm. The value for the tetracoordinate silicon is within experimental error of the limiting value of 28 ppm. We have used the chemical shift of the pentacoordinate silicon to define 100% pentacoordination as a chemical shift of −40 ppm.[20] Formation of a fully pentacoordinate silicon in compound **12** should involve 50% Si–O bond formation. Compounds **3b** and **5b** both exhibit 50% Si–O bond formation and their ^{29}Si chemical shifts are both within 2 ppm of this proposed limiting value for a pentacoordinate silicon. The second tetrahedral limiting value, corresponding to compound **13**, was set to +36 ppm based on the ^{29}Si chemical shift of *O*-trimethylsilylated *N*-methyl-2-hydroxypyridine. For compounds that exhibited a % Si–O bond formation between 0 and 50% the extent of pentacoordination was calculated using the limiting cases **11** and **12**, that is +28 and −40 ppm respectively. For compounds that exhibited a % Si–O bond formation between 50 and 100%, the extent of pentacoordination was calculated using the limiting cases **12** and **13**, that is −40 and +36 ppm respectively. Table 1 shows the % pentacoordination of compounds **3**–**8**.

For each substituent, as the leaving group ability improves in the order fluoro, chloro, bromo and triflate, the % pentacoordination first increases then decreases. This change occurs earlier for substituents that stabilise the positive charge on nitrogen, that is those that favour Si–O bond formation. Fig. 2 shows how the % pentacoordination varies as a function of % Si–O bond formation. At first, as the extent of bond formation increases, the % pentacoordination gets larger as the compound moves from resembling **11** to resembling **12**. At 50% Si–O bond formation the maximum pentacoordination is observed. This is associated with the most negative ^{29}Si chemical shifts. As the extent of bond formation increases from this point, the leaving group becomes more detached and thus the % pentacoordination decreases. Eventually, the Si–O bond is completely

formed and the leaving group lost with the silicon reverting to a completely tetrahedral structure, **13**. As expected the compounds with the poorest leaving group, the fluoro derivatives, lie on the left of the graph and show only an increase in % pentacoordination. The chloro derivatives are clustered around the point of full pentacoordination and the bromides exhibit about 70% Si–O bond formation with decreasing pentacoordination. Finally the triflates, which contain the best leaving group, show almost complete Si–O bond formation with little pentacoordination.

An alternative explanation is that rather than a continuum of structures from **11** through **12** to **13**, the reaction mixture contains only **11**, **12** and **13** in equilibrium. As the substituent and leaving group changes so the equilibrium position first moves from favouring **11** to favouring **12** and then **13**. Such a series of equilibria would have to be rapid on the NMR timescale in order to give single sets of resonances in the NMR spectra of each nucleus. X-Ray crystallography demonstrates that a continuum of structures is possible in the solid state and thus we would assume that a similar variety is possible in the solution phase.[4–6] This is supported by conductivity studies on solutions of the 2-pyridones in acetonitrile. If the equilibria hypothesis were correct, compounds with about 75% Si–O bond formation should conduct electricity since they will contain equal amounts of covalent **12** and ionic **13**. However, none of the bromides studied exhibited any conductivity.

Kummer has recently shown that the ^{29}Si, ^{13}C and ^{1}H NMR chemical shifts of the 2-pyridone derivatives **3b** and **3c** are dependent upon the temperature, solvent and concentration.[21] For example, with **3c** in $CDCl_3$, the ^{29}Si chemical shift changes from −27.3 ppm at 80 °C to +3.3 ppm at −55 °C. Similarly, at 25 °C, the ^{29}Si chemical shift of **3c** is about −10 ppm in $CDCl_3$ and CD_3CN but −28 ppm in C_6D_5CN and −39.2 in C_6D_6. In $CDCl_3$ a ten-fold change in the concentration can lead to an 8 ppm shift in the ^{29}Si resonance. This variation in chemical shift was explained in terms of a change in solvent parameters which disturbs the balance of **11**, **12** and **13** between the various equilibria.

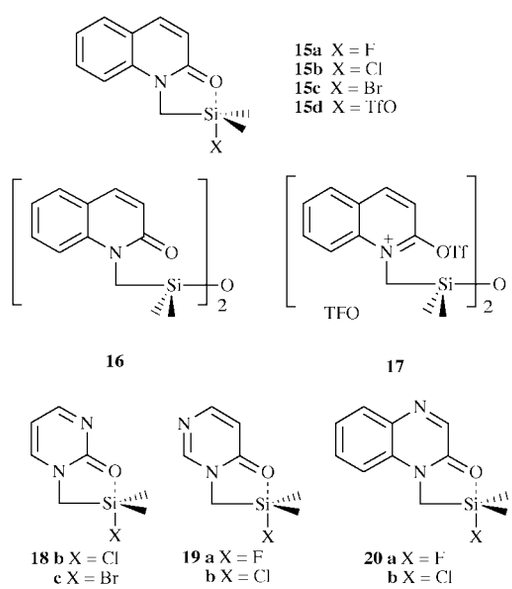
Throughout this study we have carried out all NMR measurements at 25 °C and at constant concentration. As a result of solubility problems we were forced to use a range of solvents and solvent mixtures. However, the main solvents employed, $CDCl_3$ and CD_3CN, had similar solvent parameters such that the variation was kept to a minimum. For example, at 25 °C, Kummer has shown that **3b** had a ^{29}Si chemical shift of −39.0 in $CDCl_3$ and −42.1 in CD_3CN, whereas **3b** had a ^{29}Si resonance in $CDCl_3$ of −11.1 and in CD_3CN of −9.5. Thus any variation in the chemical shifts measured, and thus the % pentacoordination or Si–O bond formation, is relatively small and within the experimental error of the method (±5%). As evidence for this, the fluorides **3a–8a** were measured in $CDCl_3$, yet the plot of % pentacoordination against % Si–O bond formation shows a similar scatter for the fluorides as for the other halogens, even though these latter compounds were measured in a range of solvents or solvent mixtures.

Just as specific interactions in the crystal lead to changes in bond lengths and bond angles so variations of the solvent parameters will be accompanied by changes in the bond lengths and bond angles of the pentacoordinate species in solution. For example, Kummer argues that variation in the acceptor properties of the solvent will disturb the equilibria through changes in the coordination of the solvent with the 'leaving group'. Such varying coordination will also affect the Si–X bond length and other geometric parameters. Thus, if variation of the solvent, concentration and temperature affect the solvent parameters such that the equilibria are disturbed, these must be accompanied by wholesale changes in the structure. If these changes in structure result in a coherent variation of the ^{13}C and ^{29}Si chemical shifts, they remain valid models for use in our solution phase mapping technique. Using a range of measuring conditions only becomes a problem if the data is correlated with other inherent parameters such as Hammett sigma values and this may explain the variation in the magnitude and/or order with respect to the various substituents.

Voronkov has measured the IR stretching frequencies of (aroyloxymethyl)trifluorosilanes and shown that whilst the medium has a large effect on the frequencies, suggesting a change in bond orders, non-coordinated species could only be observed in the gas phase.[22,23] Non-coordinated species could be observed in organic solvents with the mono- and di-fluoro analogues suggesting that the equilibrium between coordinated and non-coordinated species becomes important for compounds with low % pentacoordination.[24] IR studies on the corresponding lactams revealed the absence of uncoordinated species in solution as would be expected from the stronger coordination, however, the frequency was less susceptible to changes in the solvent. Nevertheless the warning suggested by Kummer is worth heeding and all further comparisons have been carried out at constant temperature, concentration and solvent.

Assuming **3**–**8** are discrete compounds, Fig. 2 represents a solution phase structure correlation for substitution at silicon. 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 nucleophile. A similar picture has emerged in the solid state. However, this is the first time that such a process has been demonstrated in solution.

We were interested in extending the series to include related 2-pyridone structures. We thus prepared the 2-quinolone series **15a–d** using a similar methodology to that employed for



the 2-pyridones. However, the triflate derivative was prepared by reaction of the chloro derivative **15b** with trimethylsily trifluoromethanesulfonate. We have found that pentacoordinate silicon species Si^1–X^1 undergo exchange with tetracoordinate silicon species Si^2–X^2 to give pentacoordinate Si^1–X^2 when X^1 is below X^2 in the series Cl < Br < TfO. Thus this provides an easier route to triflate derivatives than the use of chloromethyldimethylsilyl triflate. 8-Hydroxyquinoline has been used as a bidentate ligand for silicon,[25] tin[26] and antimony.[27] However, the 2 isomer has only been used as a ligand for rhenium.[28] Compounds **16** and **17** were used as model compounds to anchor the calculation of the % Si–O bond formation. Titration of **16** with aliquots of trimethylsilyl triflate gave a linear relationship between the ring ^{13}C chemical shifts and the proportion of trimethylsilyl triflate added. After two equivalents of the triflate had been added, no further chemical shift change

Table 2 % Si–O bond formation and % pentacoordination for the 2-quinolones **15a–d**

Compound	Leaving group	% Si–O bond formation	% Penta-coordination
15a	F	35	79
15b	Cl	63	97
15c	Br	78	79
15d	OTf	93	38

occurred and the NMR data were consistent with **17**. For compounds **15a–d** all of the aromatic ^{13}C chemical shifts were used to calculate the % Si–O bond formation, however, in this compound the variation of the chemical shift was generally smaller than that observed with the 2-pyridones. The extent of Si–O bond formation is given in Table 2. To determine the extent of pentacoordination, values of 28 and −40 ppm were used to anchor the chemical shift scale to a tetrahedral silicon with no Si–O interaction and a fully pentacoordinate silicon respectively. *O*-Trimethylsilylated *N*-methyl-2-hydroxyquinoline has a ^{29}Si chemical shift of 12.2 ppm and this was used to anchor the scale to a tetrahedral silicon with 100% Si–O bond formation. Values for the % pentacoordination of **15a–d** are also given in Table 2. Again, the same ordering of leaving groups is observed and as the % Si–O bond formation increases, the extent of pentacoordination first increases to a maximum and then decreases. The % Si–O bond formation for the 2-quinolones is consistently higher than those of the corresponding unsubstituted 2-pyridones. This is the result of further delocalisation of the positive charge on formation of the quinolinium species. This data overlaps well with that shown in Fig. 1 for the simple 2-pyridones. However, above 50% Si–O bond formation, the extent of pentacoordination is consistently a little higher than that obtained with the 2-pyridone system. This may be a result of differences between the two series in the relationship between the chemical shift and the extent of Si–O bond formation. Alternatively, a 'tighter' pentacoordinate species may be formed in the 2-quinolone series where the loss of the leaving group is less advanced. To extend the series further we examined the diaza derivatives **18**, **19** and **20**. The electron withdrawing effect of an aza group is similar to that of a nitro group in the same position.[29] We might therefore expect **18b** and **c** to have a similar structure to **8b** and **c** respectively. Compound **18b** has a ^{29}Si resonance at −33.7 ppm similar to that of **8b** at −25 ppm. Compound **18c** has a ^{29}Si resonance at −27.6 ppm very close to that of **8c**, −27.9 ppm, confirming the similarity between the two series. The ^{29}Si chemical shift of **19b**, the corresponding 5 isomer, is −16.7 ppm suggesting that in this position the nitrogen has a larger electron withdrawing influence. The ^{29}Si chemical shift of **20a** (−6.1 ppm) and **20b** (−27.1 ppm) are both less negative than the corresponding 2-quinolones (**15a**, −25.4 ppm and **15b**, −38.3 ppm). This again suggests that electron withdrawal by the aza group at the 4 position decreases the extent of O–Si bond formation and pentacoordination. Comparison of the ^{29}Si chemical shifts suggests that electron withdrawal is not as great in **20a** and **b** as in **19a** and **b**. In this instance, the order of O–Si bond formation reflects that of O protonation.[30]

We prepared the corresponding disiloxanes to use as model compounds for 0% Si–O bond formation. However, we were unable to titrate these compounds with trimethylsilyl triflate to form the *O*-trimethylsilylated derivatives, which were to act as models for 100% Si–O bond formation. In all cases the presence of the second aza group led to exchange of the trimethylsilyl group between the oxygen and the nitrogen leading to line broadening of the ring carbon signals or multiple peaks. Without an appropriate anchor for the ^{13}C resonances of the ring carbons it was not possible to calculate the precise % Si–O bond formation.

In conclusion we have successfully mapped substitution at silicon in solution using model compounds. We have examined the strengths and weaknesses of this NMR technique for a range of 2-pyridone ligands. In future publications we will explore the applicability of this technique to other ligands and nucleophilic systems.

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 SP1050 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 and the precision of the chemical shifts is appropriate for the subsequent calculations). All NMR Mass spectra were obtained using a Cresta MS 30 instrument or a VG20-250 quadrupole instrument.

Conductivity measurements

Conductivity measurements were carried out using a PTI-10 digital conductivity meter (quoted ±0.5%, repeatability ±1 digit). All experiments were perfomed under nitrogen. Calibration of the meter was checked by using a standard solution of potassium chloride. The compound whose conductivity was to be determined was dissolved in acetonitrile and introduced into the cell by a syringe. The conductivity of the following solutions were measured: $^{n}Bu_4NBr$ (0.23 g, 7 ml, CH_3CN, 0.1 M solution) 182 μS cm^{-1}; **3c** (X = Br, Y = H) (0.17 g, 7 ml, CH_3CN, 0.1 M solution) 8 μS cm^{-1}; **3d** (X = OTf, Y = H) (0.22 g, 7 ml, CH_3CN, 0.1 M solution) 29 μS cm^{-1}.

General procedure for the silylation of 2-pyridones with diethylaminotrimethylsilane[13]

2-Pyridone (25 mmol) was dissolved in 10 ml of benzene. Diethylaminotrimethylsilane (25 mmol) was added to the reaction mixture and refluxed for 5 h under nitrogen. The volatile materials were removed under reduced pressure and the product isolated by distillation. The siloxypyridines were used for the synthesis of silyl-2-pyridones without any characterisation other than NMR.

The following siloxypyridines were obtained:

2-Trimethylsiloxypyridine. 3.0 g, 72%, bp 37 °C/1 mmHg; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.35 (9H, s, $SiMe_3$) and 6.6–8.1 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.52 ($SiMe_3$), 112.3 (C3), 116.2 (C 5), 138.3 (C4), 146.7 (C6) and 162.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 19.9.

6-Methyl-2-trimethylsiloxypyridine. 2.9 g, 65%, bp 45 °C /0.2 mmHg; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.34 (9H, s, $SiMe_3$), 2.33 (3H, s, Me) and 6.4–7.4 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.57 ($SiMe_3$), 24.0 (Me), 109.2 (C3), 115.6 (C5), 139.0 (C4), 156.2 (C6) and 162.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 19.3.

3-Methoxy-2-trimethylsiloxypyridine. 3.9 g, 80%, bp 66 °C/ 0.5 mmHg; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.36 (9H, s, $SiMe_3$), 3.75 (3H, s, OMe) and 6.8–7.7 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) −0.57 ($SiMe_3$), 55.0 (OMe), 116.6 (C5), 117.8 (C4), 137.0 (C6), 144.4 (C3) and 152.5 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 20.7.

5-Chloro-2-trimethylsiloxypyridine. 4.2 g, 84%, bp 60 °C/2 mmHg; δ_H (90 MHz, CD_3CN, Me_4Si) 0.34 (9H, s, $SiMe_3$) and 6.5–8.1 (3H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) −0.23

($SiMe_3$), 110.6 (C3), 116.2 (C4), 140.7 (C6), 147.9 (C5) and 161.8 (C2); δ_{Si} (17.8 MHz, CD_3CN, Me_4Si) 21.4.

3-Nitro-2-trimethylsiloxypyridine. 4.2 g, 79%, bp 92 °C/0.5 mmHg; δ_H (90 MHz, CD_3CN, Me_4Si) 0.40 (9H, s, $SiMe_3$) and 7.0–8.3 (3H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) −0.34 ($SiMe_3$), 116.9 (C5), 134.8 (C4), 142.5 (C3), 151.6 (C6) and 154.7 (C2); δ_{Si} (17.8 MHz, CD_3CN, Me_4Si) 25.5.

6-Chloro-2-trimethylsiloxypyridine. 4.3 g, 85%, bp 67 °C/3 mmHg; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.36 (9H, s, $SiMe_3$) and 6.5–7.6 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) −0.29, 113.5 (C3), 123.8 (C4), 138.4 (C5), 145.3 (C6) and 160.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 22.4.

General procedure for the synthesis of chlorodimethylsilylmethyl-2-pyridones

Chloromethyldimethylchlorosilane, (0.3 g, 2.5 mmol) in dry diethyl ether was added slowly to a stirred solution of 2-trimethylsiloxypyridine (2.5 mmol) in dry diethyl ether under nitrogen. The reaction mixture was stirred for 1 h. The solid was filtered under nitrogen and dried under vacuum.

The following chlorodimethylsilylmethyl-2-pyridones were obtained:

1-(Chlorodimethylsilylmethyl)-2-pyridone 3b. 0.43 g, 87%, mp 91–94 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.64 (6H, s, $SiMe_2$), 3.7 (2H, s, NCH_2) and 6.8–7.9 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 7.5 ($SiMe_2$), 42.2 ($SiCH_2$), 113.6 (C5), 115.8 (C3), 140.0 (C4), 143.3 (C6) and 160.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −41.1 (Found: C, 47.79; H, 6.06; N, 6.78; Cl, 17.14. $C_8H_{12}NOClSi$ requires C, 47.63; H, 6.01; N, 6.94; Cl, 17.57%).

1-(Chlorodimethylsilylmethyl)-6-methyl-2-pyridone 6b. 0.40 g, 84%, mp 99–104 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.53 (6H, s, $SiMe_2$), 2.7 (3H, s, Me) 3.7 (2H, s, NCH_2) and 6.8–8.0 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.21 ($SiMe_2$), 20.6 (Me), 37.8 ($SiCH_2$), 111.3 (C5), 115.6 C3), 144.8 (C6), 151.0 (C4) and 163.4 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −24.7 (Found: C, 49.90; H, 6.46; N, 6.42; Cl, 16.50. $C_9H_{14}NOClSi$ requires C, 50.10; H, 6.54; N, 6.49; Cl, 16.43%).

1-(Chlorodimethylsilylmethyl)-3-methoxy-2-pyridone 7b. 0.31 g, 88%, mp 96–99 °C; δ_H (90 MHz, CD_3CN, Me_4Si) 0.62 (6H, s, $SiMe_2$), 3.7 (2H, s, NCH_2), 3.9 (3H, s, OMe) and 6.7–7.6 (3H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) 6.4 ($SiMe_2$), 43.6 ($SiCH_2$), 56.6 (OMe), 110.9 (C5), 118.0 (C3), 129.5 (C6), 147.2 (C4) and 157.6 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −32.0; *m/z* (EI) 231/233 (3 : 1, M^+), 216/218 (3 : 1, $M^+ - Me$), 200/202 (3 : 1, $M^+ - OMe$), 196 ($M^+ - Cl$), 181 ($M^+ - MeCl$).

1-(Chlorodimethylsilylmethyl)-5-chloro-2-pyridone 4b. 0.56 g, 88%, mp 99–106 °C; δ_H (90 MHz, CD_3OD, Me_4Si) 0.46 (6H, s, $SiMe_2$), 4.0 (2H, s, NCH_2) and 7.2–8.4 (3H, m, arom); δ_C (22.5 MHz, CD_3OD, Me_4Si) 1.2 ($SiMe_2$), 43.0 ($SiCH_2$), 116.2 (C5), 120.8 (C3), 138.2 (C6), 144.7 (C4) and 160.9 (C2); δ_{Si} (17.8 MHz, CD_3OD, Me_4Si) −17.1; *m/z* (EI) 235/237/239 (10 : 6 : 1, M^+), 220/222/224 (10 : 6 : 1, $M^+ - Me$), 200/202 (3 : 1, $M^+ - Cl$), 165 ($M^+ - 2Cl$) (Found: C, 40.54; H, 4.72; N, 5.92 $C_8H_{11}NOCl_2Si$ requires C, 40.69; H, 4.69; N, 5.93%).

1-(Chlorodimethylsilylmethyl)-3-nitro-2-pyridone 8b. 0.51 g, 77%, mp 96–100 °C; δ_H (90 MHz, CD_3CN, Me_4Si) 0.50 (6H, s, $SiMe_2$), 3.7 (2H, s, NCH_2) and 6.7–8.4 (3H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) 0.57 ($SiMe_2$), 43.8 ($SiCH_2$), 105.9 (C5), 136.7 (C3), 140.1 (C6), 146.4 (C4) and 156.6 (C2); δ_{Si} (17.8 MHz, CD_3CN, Me_4Si) −25.0; *m/z* (EI) 246/248 (3 : 1, M^+), 231/233 (3 : 1, $M^+ - Me$), 211, 185/187 (3 : 1, $M^+ - NO_2$), 165 ($M^+ - ClNO_2$) (Found: C, 39.21; H, 4.52; N, 11.39. $C_8H_{11}N_2O_3ClSi$ requires 38.95; H, 4.49; N, 11.35%).

1-(Chlorodimethylsilylmethyl)-6-chloro-2-pyridone 5b. 0.47 g, 85%, mp 99–101 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.67 (6H, s, $SiMe_2$), 3.7 (2H, s, NCH_2) and 6.8–7.8 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 7.3 ($SiMe_2$), 42.3 ($SiCH_2$), 112.5 (C5), 113.1 (C3), 140.5 (C4), 143.0 (C6) and 164.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −40.9; *m/z* (EI) 235/237/239 (10 : 6 : 1, M^+), 220/222/224 (10 : 6 : 1, $M^+ - Me$), 202/204 (3 : 1, $M^+ - Cl$), 165 ($M^+ - 2Cl$) (Found: C, 40.80; H, 4.63; N, 6.27. $C_8H_{11}NOCl_2Si$ requires C, 40.69; H, 4.69; N, 5.93%).

General procedure for the synthesis of bromodimethylsilylmethyl-2-pyridones

The synthesis was identical to that for the synthesis of chlorodimethylsilylmethyl-2-pyridones except that chloromethyldimethylchlorosilane was replaced by bromomethyldimethylchlorosilane (0.32 g, 2.5 mmol).

The following bromodimethylsilylmethyl-2-pyridones were obtained:

1-(Bromodimethylsilyl)methyl-2-pyridone 3c. 0.44 g, 86%, mp 102–104 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.72 (6H, s, $SiMe_2$), 3.9 (2H, s, NCH_2) and 6.9–8.1 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.9 ($SiMe_2$), 44.8 ($SiCH_2$), 115.0 (C3), 115.7 (C5), 141.0 (C4), 146.1 (C6) and 163.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −18.4; *m/z* (EI) 166 ($M^+ - Br$), 136 ($M^+ - BrMe_2$), 106, 78 (Found: C, 38.95; H, 4.76; N, 5.51. $C_8H_{12}NOBrSi$ requires C, 39.01; H, 4.92; N, 5.69%).

1-(Bromodimethylsilylmethyl)-6-methyl-2-pyridone 6c. 0.54 g, 87%, bp 108–111 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.45 (6H, s, $SiMe_2$), 2.7 (3H, s, Me), 3.7 (2H, s, NCH_2) and 6.8–8.0 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.7 ($SiMe_2$), 20.7 (Me), 37.9 ($SiCH_2$), 111.5 (C5), 115.2 (C3), 144.8 (C6), 151.6 (C4) and 163.7 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −21.3 (Found: C, 41.67; H, 5.37; N, 5.40. $C_9H_{14}NOBrSi$ requires C, 41.54; H, 5.42; N, 5.38%).

1-(Bromodimethylsilylmethyl)-3-methoxy-2-pyridone 7c. 0.45 g, 90%, mp 105–108 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.73 (6H, s, $SiMe_2$), 4.0 (3H, s, OMe), 4.2 (2H, s, NCH_2) and 7.1–7.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) −0.63 ($SiMe_2$), 44.9 (Me), 58.0 ($SiCH_2$), 116.1 (C5), 122.1 (C3), 132.1 (C6), 147.3 (C4) and 154.9 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −14.3.

1-(Bromodimethylsilylmethyl)-5-chloro-2-pyridone 4c. 0.65 g, 88%, mp 107–112 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.44 (6H, s, $SiMe_2$), 4.4 (2H, s, NCH_2) and 7.4–8.6 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) −0.34 ($SiMe_2$), 42.9 ($SiCH_2$), 115.8 (C5), 122.0 (C3), 138.9 (C6), 145.4 (C4) and 160.3 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −12.7; *m/z* (EI) 279/281/283 (3 : 4 : 1, M^+), 264/266/268 (3 : 4 : 1, $M^+ - Me$), 200/202 (3 : 1, $M^+ - Br$), 186/188 (3 : 1, $M^+ - MeBr$) (Found: C, 34.00; H, 4.09; N, 4.99. $C_8H_{11}NOClBrSi$ requires C, 34.24; H, 3.95; N, 4.99%).

1-(Bromodimethylsilylmethyl)-3-nitro-2-pyridone 8c. 0.69 g, 90%, mp 110–112 °C; δ_H (90 MHz, CD_3CN, Me_4Si) 0.76 (6H, s, $SiMe_2$), 3.9 (2H, s, NCH_2) and 7.1–8.7 (3H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) 1.5 ($SiMe_2$), 45.0 ($SiCH_2$), 111.2 (C5), 135.7 (C3), 141.4 (C6), 146.5 (C4) and 157.(C2); δ_{Si} (17.8 MHz, CD_3CN, Me_4Si) −27.9; *m/z* (EI) 292/290 (1 : 1, M^+), 211 ($M^+ - Br$), 181 ($M^+ - BrMe_2$).

1-(Bromodimethylsilylmethyl)-6-chloro-2-pyridone 5c. 0.60 g, 88%, mp 105–109 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.55 (6H, s, $SiMe_2$), 3.9 (2H, s, NCH_2) and 6.8–8.1 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.7 (SiMe), 40.1 ($SiCH_2$), 113.0 (C5),

114.7 (C3), 141.3 (C4), 144.7 (C6) and 163.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −27.4; *m/z* (EI) 279/281/283 (3:4:1, M^+), 264/266/268 (3:4:1), 200/202 (3:1), 186/188 (3:1) (Found: C, 34.58; H, 4.22; N, 4.99. $C_8H_{11}NOClBrSi$ requires C, 34.24; H, 3.95; N, 4.99%).

General procedure for the synthesis of fluorodimethylsilylmethyl-2-pyridones

Chloromodimethylsilylmethyl-2-pyridone (5 mmol) was dissolved (or suspended) in 5 ml dry benzene under nitrogen. Antimony trifluoride (0.30 g, 1.7 mmol) was added and the reaction mixture was stirred for 0.5 h. The reaction mixture was then diluted with excess water and extracted with chloroform (3 × 75 ml). The washed extract was dried over anhydrous magnesium sulfate and the solvent removed using a rotary evaporator to obtain a colourless crystalline solid, which was dried under vacuum.

The following fluorodimethylsilylmethyl-2-pyridones were obtained:

1-(Fluorodimethylsilylmethyl)-2-pyridone 3a. 0.57 g, 92%, mp 82–86 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.32 (6H, d, $^3J_{HSiF}$ 6.8, $SiMe_2$), 3.2 (2H, s, NCH_2) and 6.5–7.7 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.8 (d, $^2J_{CSiF}$ 25, SiMe), 39.5 (d, $^2J_{CSiF}$ 44.0, $SiCH_2$), 109.2 (C5), 116.8 (C3), 139.1 (C4), 141.4 (C6) and 163.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −22.3 (d, $^1J_{SiF}$ 256.8); *m/z* (EI) 185 (M^+), 184, 170, 166 (Found: C, 51.60; H, 6.51; N, 7.45. $C_8H_{12}NOFSi$ requires C, 51.86; H, 6.53; N, 7.56%).

1-(Fluorodimethylsilylmethyl)-6-methyl-2-pyridone 6a. 0.61 g, 91%, mp 87–89 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.28 (6H, d, $^3J_{HSiF}$ 5.9, $SiMe_2$), 2.5 (3H, s, Me), 3.0 (2H, s, NCH_2) and 6.5–7.5 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 2.4 (d, $^2J_{CSiF}$ 27.2, SiMe), 20.9, 35.8 (d, $^2J_{CSiF}$ 50.5, $SiCH_2$), 110.2 (C5), 112.5 (C3), 141.2 (C6), 148.6 (C4) and 163.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −35.5 (d, $^1J_{SiF}$ 252.9) (Found: C, 54.26; H, 7.11; N, 6.96. $C_9H_{14}NOFSi$ requires C, 54.24; H, 7.08; N, 7.03%).

1-(Fluorodimethylsilylmethyl)-3-methoxy-2-pyridone 7a. 0.66 g, 92%, mp 88–92 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.35 (6H, d, $^3J_{HSiF}$ 5.1, $SiMe_2$), 3.3 (2H, s, NCH_2), 3.9 (3H, s, OMe) and 6.2–6.4 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.4 (d, $^2J_{CSiF}$ 23.3, SiMe), 40.2 (d, $^2J_{CSiF}$ 40.2, $SiCH_2$), 56.1 (OMe), 107.7 (C5), 114.6 (C3), 129.7 (C6), 148.3 (C4) and 158.3 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −13.5 (d, $^1J_{SiF}$ 258.8) (Found: C, 50.02; H, 6.64; N, 6.39. $C_9H_{14}NO_2FSi$ requires C, 50.21; H, 6.55; N, 6.51%).

1-(Fluorodimethylsilylmethyl)-5-chloro-2-pyridone 4a. 0.66 g, 90%, mp 91–95 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.31 (6H, d, $^3J_{CSiF}$ 7.8, $SiMe_2$), 3.2 (2H, s, NCH_2) and 6.7–7.7 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.2 (d, $^2J_{CSiF}$ 19.4, SiMe), 40.4 (d, $^2J_{CSiF}$ 41.4, $SiCH_2$), 115.0 (C5), 118.0 (C3), 137.0 (C6), 142.1 (C4) and 161.9 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −14.6 (d, $^1J_{SiF}$ 259.8); *m/z* (EI) 219/221 (3:1, M^+), 218/220 (3:1, $M^+ - H$), 204/206 (3:1, $M^+ - Me$), 184 ($M^+ - MeF$) (Found: C, 43.26; H, 5.00; N, 6.07. $C_8H_{11}NOFClSi$ requires C, 43.73; H, 5.05; N, 6.37%).

1-(Fluorodimethylsilylmethyl)-3-nitro-2-pyridone 8a. 0.69 g, 90%, mp 87–90 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.38 (6H, d, $^3J_{CSiF}$ 7.8, $SiMe_2$), 3.6 (2H, s, NCH_2) and 6.4–8.4 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) −0.52 (d, $^2J_{CSiF}$ 18.1, SiMe), 42.7 (d, $^2J_{CSiF}$ 29.8, $SiCH_2$), 105.1 (C5), 137.4 (C3), 145.9 (C4) and 155.6 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 12.5 (d, $^1J_{SiF}$ 272.5) (Found: C, 42.01; H, 4.95: N, 11.83. $C_8H_{11}N_2O_3FSi$ requires C, 41.72;H, 4.82; N, 12.17%).

1-(Fluorodimethylsilylmethyl)-6-chloro-2-pyridone 5a. 0.68 g, 92%, mp 90–95 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.31 (6H, br s, $SiMe_2$), 3.2 (2H, s, NCH_2) and 6.6–7.6 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.9 (d, $^2J_{CSiF}$ 19.4, SiMe), 38.0 (d, $^2J_{CSiF}$ 46.6 Hz, $SiCH_2$), 109.8 (C5), 114.3 (C3), 140.4 (C6), 141.0 (C4) and 164.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −26.0 (d, $^1J_{SiF}$ 257.8); *m/z* (EI) 219/221 (3:1, M^+), 218/220 (3:1, $M^+ - H$), 204/206 (3:1, $M^+ - Me$), 184 ($M^+ - FMe$) (Found: C, 43.10; H, 5.00; N, 6.21. $C_8H_{11}NOClFSi$ requires C, 43.73; H, 5.05; N, 6.37%).

General procedure for the synthesis of trifluoromethylsulfonyloxydimethylsilylmethyl-2-pyridone

The synthesis was identical to that for the synthesis of chlorodimethylsilylmethyl-2-pyridones except that chloromethyldimethylchlorosilane was replaced by chloromethyldimethylsilyl triflate (0.62 g, 2.5 mmol).

Chloromethyldimethylsilyl triflate. Trifluoromethanesulfonic acid (5 ml, 37.8 mmol) was added to 3.34 ml (37.8 mmol) chloromethyldimethylchlorosilane, with stirring under nitrogen. The reaction mixture was heated at 60 °C for 5 h. The product was isolated by distillation. (8.6 g, 89%), bp 62 °C/8 mmHg; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.60 (6H, s, $SiMe_2$) and 3.0 (2H, s, CH_2); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) −3.0 ($SiMe_2$), 27.6 ($SiCH_2$) and 118.9 (q, $^1J_{CF}$ 317.1, CF_3); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 31.7; *m/z* (EI) 256/258 (3:1, M^+), 207 ($M^+ - MeCl$), 191 ($M^+ - ClMe_2$) (Found: C, 18.95; H, 3.13. $C_4H_8O_3C1F_3SSi$ requires C, 18.71; H, 3.15%).

The following dimethylsilylmethyl-2-pyridone triflates were obtained:

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-2-pyridone 3d. 0.63 g, 88%, mp 120–123 °C; δ_H (90 MHz, CD_3CN, Me_4Si) 0.66 (6H, s, $SiMe_2$), 4.0 (2H, s, NCH_2) and 7.2–8.3 (4H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) 0.17 ($SiMe_2$), 42.8 ($SiCH_2$), 115.2 (C5), 118.3 (C3), 142.3 (C4), 147.5 (C6) and 162.9 (C2); δ_{Si} (17.8 MHz, CD_3CN, Me_4Si) 32.3.

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-6-methyl-2-pyridone 6d. 0.69 g, 90%, mp 128–132 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.64 (6H, s, $SiMe_2$), 2.6 (3H, s, Me), 3.8 (2H, s, NCH_2) and 7.0–8.1 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 3.2 ($SiMe_2$), 20.5 (Me), 39.8 ($SiCH_2$), 111.5 (C5), 117.9 (C3), 121.0 (q, $^1J_{CF}$ 321.0, CF_3), 146.1 (C6), 152.7 (C4) and 163.0 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 23.0 (Found: C, 36.52; H, 4.48; N, 4.80. $C_{10}H_{14}NSF_3O_4Si$ requires C, 36.46; H, 4.28; N, 4.25%).

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-3-methoxy-2-pyridone 7d. 1.1 g, 85%, mp 127–130 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.69 (6H, s, $SiMe_2$), 3.9 (3H, s, OMe), 4.0 (2H, s, NCH_2) and 7.1–7.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 3.1 ($SiMe_2$), 42.9 ($SiCH_2$), 57.2 (OMe), 116.9 (C5), 120.3 (q, $^1J_{CF}$ 319.2, CF_3), 123.5 (C3), 131.3 (C6), 146.5 (C4) and 155.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 21.3 (Found: C, 34.92; H, 3.92; N, 4.10. $C_{10}H_{14}NSF_3O_5Si$ requires C, 34.78; H, 4.09; N, 4.06%).

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-5-chloro-2-pyridone 4d. 0.74 g, 88%, mp 136–139 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.67 (6H, s, $SiMe_2$), 4.0 (2H, s, NCH_2) and 7.1–8.3 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.7 ($SiMe_2$), 41.5 ($SiCH_2$), 115.8 (C5), 118.8 (q, $^1J_{CF}$ 319.7, CF_3), 123.9 (C3), 139.6 (C6), 147.0 (C4) and 61.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 25.2; *m/z* (EI) 349/351 (3:1, M^+), 334/336 (3:1, $M^+ - Me$), 200/202 ($M^+ - CF_3SO_3$) (Found: C, 31.02; H, 3.32; N, 4.27. $C_9H_{11}O_4F_3CINSSi$ requires C, 30.90; H, 3.17; N, 4.00%)

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-3-nitro-2-pyridone 8d. 0.80 g, 89%, mp 129–131 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.66 (6H, s, $SiMe_2$), 4.0 (2H, s, NCH_2) and 7.2–8.8 (3H,

m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 3.2 ($SiMe_2$), 42.1 ($SiCH_2$), 114.8 (C5), 120.3 (q, $^1J_{CF}$ 319.4, CF_3), 135.5 (C3), 142.4 (C6), 147.4 (C4) and 158.0 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 4.5 (Found: C, 29.96; H, 3.64; N, 8.86. $C_9H_{11}OF_3N_2SSi$ requires C, 30.0; H, 3.08; N, 7.78%).

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-6-chloro-2-pyridone 5d. 1.3 g, 92%, mp 135–140 °C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.65 (6H, s, $SiMe_2$), 3.9 (2H, s, NCH_2) and 7.2–8.0 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.7 ($SiMe_2$), 41.8 (CH_2), 112.8 (C5), 116.8 (C3), 120.3 (q, $^1J_{CF}$ 319.7, CF_3), 142.8 (C6) 146.4, (C4) and 165.0 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 10.7; *m/z* (EI) 349/351 (3:1, M^+), 334/336 (3:1, $M^+ - Me$) and 200/202 (3:1, $M^+ - Tf$) (Found: C, 31.56; H, 3.21; N, 4.49. $C_9H_{11}O_4F_3ClNSSi$ requires C, 30.90; H, 3.17; N, 4.00%).

General procedure for the synthesis of 1,1,3,3-tetramethyl-1,3-bis(2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane

The corresponding chlorodimethylsilylmethyl-2-pyridone (0.5 g) was added to 1 ml of distilled water. The reaction mixture was stirred for 1 h and then extracted with chloroform (3 × 75 ml). The washed extract was dried over anhydrous magnesium sulfate and distilled under reduced pressure and dried under vacuum.

The following disiloxanes were obtained:

1,1,3,3-Tetramethyl-1,3-bis(2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.16 (6H, s, $SiMe_2$) 3.4 (2H, s, NCH_2) and 6.0–7.2 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.63 ($SiMe_2$), 42.4 ($SiCH_2$), 105.6 (C5), 119.7 (C3), 138.3 (C4), 138.6 (C6) and 162.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 4.2.

1,1,3,3-Tetramethyl-1,3-bis(6-methyl-2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.29 (6H, s, $SiMe_2$), 2.5 (3H, s, Me), 3.5 (2H, s, NCH_2) and 6.3 −7.4 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 2.20 ($SiMe_2$), 21.4 (Me), 38.2, ($SiCH_2$), 109.6 (C5), 114.2 (C3), 139.9 (C6), 147.5 (C4) and 163.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 4.2.

1,1,3,3-Tetramethyl-1,3-bis(3-methoxy-2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.20 (6H, s, $SiMe_2$), 3.6 (2H, s, NCH_2) 3.8 (3H, s, OMe) and 6.1–6.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.40 ($SiMe_2$), 55.8 (OMe), 42.7 ($SiCH_2$), 105.1 (C5), 112.2 (C3), 129.3 (C6), 149.7 (C4) and 157.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 3.4.

1,1,3,3-Tetramethyl-1,3-bis(5-chloro-2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.20 (6H, s, $SiMe_2$), 3.8 (2H, s, NCH_2) and 6.2–7.2 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.51 ($SiMe_2$), 43.1, ($SiCH_2$), 112.4 (C5), 120.5 (C3), 136.0 (C6), 139.9 (C4) and 160.9 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 3.5.

1,1,3,3-Tetramethyl-1,3-bis(3-nitro-2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.15 (6H, s, $SiMe_2$), 3.7 (2H, s, NCH_2) and 6.3–8.3 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.57 ($SiMe_2$), 44.5, ($SiCH_2$), 103.7 (C5), 138.2 (C3), 138.2 (C6), 146.1 (C4) and 154.9 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 5.0.

1,1,3,3-Tetramethyl-1,3-bis(6-chloro-2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.20 (6H, s, $SiMe_2$), 3.8 (2H, s, NCH_2) and 6.4–7.2 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.92 ($SiMe_2$), 39.8, ($SiCH_2$), 106.9 (C5), 117.0 (C3), 137.9 (C6), 137.9 (C4) and 162.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 3.5.

General procedure for the synthesis of 1,1,3,3-tetramethyl-1,3-bis(2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate

The corresponding 1,1,3,3-tetramethyl-1,3-bis(2-oxo-1,2-dihydro-1-pyridylmethyl)disiloxane (2.0 mmol) was dissolved in 2.0 ml of deuterochloroform in a 5 mm NMR tube. Aliquots of trimethylsilyl triflate were added and the NMR spectra obtained. The NMR spectrum did not significantly change after addition of 1 equiv. of trimethylsilyl triflate.

The following disiloxanes were obtained:

1,1,3,3-Tetramethyl-1,3-bis(2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.21 (6H, s, $SiMe_2$) 4.0 (2H, s, NCH_2) and 7.2–8.3 (4H, m, arom); δ_C (22.5, $CDCl_3$, Me_4Si) 0.40 ($SiMe_2$), 42.5, ($SiCH_2$), 115.1 (C5), 117.8 (C3), 119.0 ($^1J_{CF}$ 317.0, CF_3), 141.5 (C4), 146.9 (C6) and 162.5 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 2.5.

1,1,3,3-Tetramethyl-1,3-bis(6-methyl-2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.20 (6H, s, $SiMe_2$), 2.6 (3H, s, Me), 3.8 (2H, s, NCH_2) and 7.0–7.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 2.00 ($SiMe_2$), 20.8 (Me), 39.9, ($SiCH_2$), 111.6 (C5), 116.9 (C3), 119 ($^1J_{CF}$ 318.1, CF_3), 145.1 (C6), 151.3 (C4) and 162.7 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 7.4.

1,1,3,3-Tetramethyl-1,3-bis(3-methoxy-2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.20 (6H, s, $SiMe_2$), 4.0 (2H, s, NCH_2), 4.0 (3H, s, OMe) and 7.2–7.7 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.98 ($SiMe_2$), 42.8, ($SiCH_2$), 57.2 (OMe), 116.6 (C5), 119.5 ($^1J_{CF}$ 318.4, CF_3), 122.7 (C3), 130.8 (C6), 146.6 (C4) and 156.0 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 9.5.

1,1,3,3-Tetramethyl-1,3-bis(5-chloro-2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.10 (6H, s, $SiMe_2$), 4.1 (2H, s, NCH_2) and 7.1–8.2 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.80 ($SiMe_2$), 42.9, ($SiCH_2$), 115.5 (C5), 119.0 ($^1J_{CF}$ 318.0, CF_3), 123.5 (C3), 139.0 (C6), 146.4 (C4) and 161.6 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 7.2.

1,1,3,3-Tetramethyl-1,3-bis(3-nitro-2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.10 (6H, s, $SiMe_2$), 3.9 (2H, s, NCH_2) and 7.2–8.8 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 42.4, ($SiCH_2$), 114.3 (C5), 120.0 ($^1J_{CF}$ 318.4, CF_3), 135.8 (C3), 142.4 (C6), 146.9 (C4) and 158.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 2.6.

1,1,3,3-Tetramethyl-1,3-bis(6-chloro-2-trimethylsiloxypyridiniomethyl)disiloxane ditriflate. δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.10 (6H, s, $SiMe_2$), 3.9 (2H, s, NCH_2) and 7.1–8.1 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.61 ($SiMe_2$), 41.5, ($SiCH_2$), 113.3 (C5), 116.3 (C3), 119.0 ($^1J_{CF}$ 318.0, CF_3), 141.8 (C6), 145.8 (C4) and 161.0 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 7.2.

1-(Fluorodimethylsilylmethyl)-2-quinolone 15a

1-(Chlorodimethylsilylmethyl)-2-quinolone (**15b**) (0.75 g, 2.98 mmol) was dissolved in benzene (4 cm^3) under a nitrogen atmosphere. Granular antimony trifluoride (0.18 g, 1.01 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 solid was recrystallised from chloroform to give the pure product (0.40 g, 57%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.38 [6H, d, *J* 6.4,

$Si(CH_3)_2$], 3.18 (2H, s, N-CH_2), 6.82 (1H, d, *J* 9.4, H3), 7.38 (1H, m, H6), 7.73–7.64 (3H, m, H5/H7/H8) and 7.95 (1H, d, *J* 9.4, H4); δ_C (100 MHz, $CDCl_3$, Me_4Si) 2.0 [d, *J* 23.8, $Si(CH_3)_2$], 33.9 (d, *J* 47.5, N-CH_2), 115.9 (C8), 117.1 (C3), 121.4 (C4a), 123.6 (C6), 129.0 (C5), 131.8 (C7), 139.3 (C8a), 141.4 (C4) and 162.9 (C2); δ_F (90 MHz, $CDCl_3$) −114.2; δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) 25.4 (d, *J* 254.3); *m/z* 235 (M^+, 35%), 234 ($M^+ - H$, 100), 220 ($M^+ - CH_3$, 99) (Found: C, 60.83; H, 5.98; N, 5.86. $C_{12}H_{14}FNOSi$ requires C, 61.25; H, 6.00; N, 5.95%).

1-(Chlorodimethylsilylmethyl)-2-quinolone 15b

A solution of 2-(trimethylsiloxy)quinoline[31] (0.65 g, 2.99 mmol) was prepared in benzene (4 cm^3) under a nitrogen atmosphere. Chloro(chloromethyl)dimethylsilane (0.44 g, 2.66 mmol) was added drop-wise with stirring and the solution allowed to stand for 30 minutes at room temperature. After removal of the solvent the product was recrystallised from acetonitrile to give colourless needle-like crystals (0.67 g, 89%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.75 [6H, s, $Si(CH_3)_2$], 3.65 (2H, s, N-CH_2), 6.93 (1H, d, *J* 9.2, H3), 7.49 (1H, m, H6), 7.83–7.77 (3H, m, H5/H7/H8) and 8.09 (1H, d, *J* 9.2, H4); δ_C (100 MHz, $CDCl_3$, Me_4Si) 7.4 [$Si(CH_3)_2$], 38.6 (N-CH_2), 115.4 (C3), 116.5 (C8), 121.9 (C4a), 124.8 (C6), 129.3 (C5), 132.7 (C7) , 138.1 (C8a), 143.1 (C4) and 163.4 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −38.4 ; *m/z* 253 (M^+, 13), 252 ($M^+ - H$, 40), 251 (M^+, 37), 250 ($M^+ - H$, 100), 238 ($M^+ - CH_3$, 31), 236 ($M^+ - CH_3$, 76) (Found: C, 57.15; H, 5.86; N, 5.35. $C_{12}H_{14}ClNOSi$ requires C, 57.24; H, 5.60; N, 5.56%).

1-(Bromodimethylsilylmethyl)-2-quinolone 15c

A solution of 2-(trimethylsiloxy)quinoline[31] (0.65 g, 2.99 mmol) was prepared in benzene (5 cm^3) under a nitrogen atmosphere. (Bromomethyl)chlorodimethylsilane (0.56 g, 2.99 mmol) was added drop-wise with stirring and the solution allowed to stand for 30 minutes at room temperature. After removal of the solvent the product was recrystallised from acetonitrile to give colourless cubic crystals (0.74 g, 84%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.81 [6H, s, $Si(CH_3)_2$], 3.94 (2H, s, N-CH_2), 7.04 (1H, d, *J* 8.5, H3), 7.55 (1H, m, H6), 7.91–7.84 (3H, m, H5/H7/H8) and 8.22 (1H, d, *J* 8.5, H4); δ_C (100 MHz, $CDCl_3$, Me_4Si) 6.1 [$Si(CH_3)_2$], 39.0 (N-CH_2), 114.6 (C3), 117.1 (C8), 122.3 (C4a), 125.5 (C6), 129.4 (C5), 133.3 (C7), 137.8 (C8a), 144.1 (C4) and 163.4 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −28.9. *m/z* 297 (M^+, 4%), 296 ($M^+ - H$, 9), 295 (M^+, 4), 294 ($M^+ - H$, 9), 282 ($M^+ - CH_3$, 1), 280 ($M^+ - CH_3$, 6), 216 ($M^+ - Br$, 100), 128 [$M^+ - CH_2Si(CH_3)_2Br$, 31] (Found: C, 49.37; H, 4.88; N, 4.79. $C_{12}H_{14}BrNOSi$ requires C, 48.65; H, 4.76; N, 4.73%).

1-(Trifluoromethylsulfonyloxydimethylsilylmethyl)-2-quinolone 15d

To a solution of **15b** (0.37 g, 1.47 mmol) under a nitrogen atmosphere, was added trimethylsilyl triflate (0.34 g, 1.53 mmol) by syringe, drop-wise, with stirring. After 30 minutes the solvent was removed by distillation at atmospheric pressure under nitrogen followed by pumping at high vacuum. The crude product was washed with diethyl ether (2 × 5 cm^3) and dried under high vacuum for 2 hours. Recrystallisation from benzene gave colourless cubic crystals (0.48 g, 89%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.69 [6H, s, $Si(CH_3)_2$], 3.88 (2H, s, N-CH_2), 7.11 (lH, d, *J* 9.2, H3), 7.64 (1H, m, H6), 7.95–7.88 (3H, m, H5/H7/H8) and 8.36 (lH, d, *J* 9.2, H4); δ_C (100 MHz, $CDCl_3$, Me_4Si) 2.7 [$Si(CH_3)_2$], 37.2 (N-CH_2), 113.8 (C3), 117.2 (C8), 119.8 (q, $^1J_{CF}$ 316.4, SO_3CF_3), 122.8 (C4a), 126.4 (C6), 129.7 (C5), 133.9 (C7), 137.7 (C8a), 145.5 (C4) and 163.4 (C2); δ_F (90 MHz, $CDCl_3$) −79.9; δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −8.1; *m/z* 365 (M^+, 20%), 364 ($M^+ - H$, 27), 350 ($M^+ - CH_3$, 18), 216 ($M^+ - SO_3CF_3$, 100), 128 [$M^+ - CH_2Si(CH_3)_2SO_3CF_3$, 49] (Found: C, 42.24; H, 3.99; N, 3.77. $C_{13}H_{14}F_3NO_4Si$ requires C, 42.73; H, 3.86; N, 3.83%).

1,1,3,3-Tetramethyl-1,3-bis(2-oxo-1,2-dihydro-1-quinolylmethyl)disiloxane 16

1-(Chlorodimethylsilylmethyl)-2-quinolone **15b** (4.54 g, 15.33 mmol) was dissolved in acetone (20 cm^3) with stirring. Distilled water (20 cm^3) was added and stirring continued for a further 16 hours at room temperature. The solution was extracted with chloroform (3 × 50 cm^3) and the aqueous phase discarded. The extracts were combined and dried over magnesium sulfate. Removal of the solvent initially by rotary evaporation and latterly by high vacuum pumping afforded **16** as a colourless, highly viscous oil (5.2 g, 76%); δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.13 [12H, s, $Si(CH_3)_2$], 3.66 (4H, s, N-CR_2), 6.72 (2H, d, *J* 9.2, H3), 7.20 (2H, m, H6), 7.39 (2H, m, H8), 7.57 (4H, m, H5/H7) and 7.66 (2H, d, *J* 9.2, H4); δ_C (100 MHz, $CDCl_3$, Me_4Si) 1.1 [$Si(CH_3)_2$], 35.4 (N-CR_2), 115.3 (C8), 120.8 (C4a), 120.9 (C3), 121.8 (C6), 128.7 (C5), 130.3 (C7), 138.4 (C4), 139.9 (C8a) and 161.8 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) 1.5; *m/z* (EI) 433 ($M^+ - CH_3$, 3%), 290 ($M^+ - C_9H_6NO$, 100), 216 ($M^+ - C_{11}H_{12}NOSi$, 97) [Found: $M^+ - CH_3$, 433.1404. $C_{23}H_{25}N_2O_3Si_2$ requires 433.1404; Found $M^+ - C_9H_6NO$, 290.1033 (EI). $C_{14}H_{20}NO_2Si_2$ requires 290.1033].

1,1,3,3-Tetramethyl-1,3-bis(2-trimethylsiloxyquinoliniomethyl)-disiloxane ditriflate 17

In a 10 mm NMR tube capped by a rubber septum was prepared a solution of **16** (0.45 g, 1.00 mmol) in deuteriochoroform (2.5 cm^3). To the solution was added, by syringe, trimethylsilyl triflate (0.45 g, 2.02 mmol) and the reagents shaken briefly together. Compound **17** could only be observed in solution and is characterised by its NMR spectra; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.08 [18H, s, $Si(CH_3)_3$], 0.73 [12H, s, $Si(CH_3)_2$], 3.96 (4H, s, N-CH_2), 7.22 (2H, d, *J* 9.4, H3), 7.67 (2H, m, H6), 7.88 (2H, m, H8), 7.95 (2H, m, H7), 8.03 (2H, m, H5) and 8.56 (2H, d, *J* 9.4, H4); δ_C (100 MHz, $CDCl_3$, Me_4Si) 1.6 [$Si(CH_3)_2$], 2.0 [$Si(CH_3)_3$], 37.1 (N-CR_2), 113.7 (C3), 117.1 (C8), 120.9 (q, $^1J_{CF}$ 320.0, SO_3CF_3), 123.2 (C4a), 126.5 (C6), 130.1 (C5), 133.9 (C7), 137.6 (C8a), 146.3 (C4) and 163.3 (C2); δ_F (90 MHz, $CDCl_3$) −80.0; δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −0.8 [$Si(CH_3)_2$] and 11.7 [$Si(CH_3)_3$].

2-(Trimethylsiloxy)pyrimidine

Dried 2-hydroxypyrimidine hydrochloride (3.0 g, 23 mmol) was suspended in dry benzene (20 ml) under nitrogen. *N*,*N*-Diethyltrimethylsilylamine (4.6 g, 32 mmol) was then added and the mixture stirred under reflux for three hours, during which time the 2-hydroxypyrimidine hydrochloride dissolved and a solid (diethylamine hydrochloride) sublimed into the condenser. After cooling, the solvent was removed under vacuum, and the product purified by vacuum distillation to give 2-(trimethylsilyloxy)pyrimidine as a yellow liquid in a yield of 3.3 g (85%); ν_{max}(neat)/cm^{-1} 850, 939, 1253, 1350, 1560, 1429 and 2960; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.39 [9H, s, $Si(CH_3)_3$], 6.90 (1H, t, *J* 4.8, H4) and 8.47 (2H, d, *J* 4.8, H3, H5); δ_C (100 MHz, $CDCl_3$, Me_4Si) 0.0 ($SiMe_3$), 114.8 (C5), 159.2 (C4 and 6) and 163.7 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) 23.2.

N-(Chlorodimethylsilylmethyl)-2-pyrimidone 18b

2-(Trimethylsiloxy)pyrimidine was dissolved in dry diethyl ether under nitrogen. Chloro(chloromethyl)dimethylsilane was then added, the flask agitated briefly to mix the reactants, and then left for three hours. After this time a yellow precipitate had formed. The solvent was removed and the precipitate washed with further dry diethyl ether before being dried under vacuum. ν_{max}(neat)/cm^{-1} 836, 1564, 1634 and 1743; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.62 [6H, s, $Si(CH_3)_2$], 3.65 (2H, s, NCH_2), 6.73 (1H, dd,

J 6.5, 4.0, H5), 8.14 (1H, dd, *J* 6.5, 2.4, H4) and 8.60 (1H, dd, *J* 4.0, 2.4, H6); δ_C (100 MHz, $CDCl_3$, Me_4Si) 7.4 ($SiMe_2$), 44.9 ($SiCH_2$), 109.8 (C5), 149.6 (C4), 160.9 (C6) and 167.3 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −33.7; *m/z* (EI) 204, 202 (M^+), 189, 187 ($M^+ - Me$), 164 ($M^+ - Cl$) (Found: M^+, 202.033. $C_7H_{11}N_2OSiCl$ requires 202.033).

N-(Bromodimethylsilylmethyl)-2-pyrimidone 18c

2-(Trimethylsiloxy)pyrimidine was dissolved in dry diethyl ether. (Bromomethyl)chlorodimethylsilane was then added and the flask briefly agitated to mix the reactants. After standing for two hours, a white precipitate had formed. The solvent was removed and the precipitate dried under vacuum; ν_{max}(neat)/cm^{-1} 839, 1101, 1215, 1583, 1734 and 2960; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.84 [6H, s, $Si(CH_3)_2$], 4.02 (2H, s, NCH_2), 7.20 (1H, dd, 1H, *J* 6.3, 4.7, H5), 8.61 (1H, dd, *J* 6.3, 2.4, H4) and 8.89 (1H, dd, *J* 4.7, 2.4, H6); δ_C (100 MHz, $CDCl_3$, Me_4Si) 7.5 ($SiMe_2$), 45.4 ($SiCH_2$), 111.9 (C5), 151.3 (C4), 161.2 (C6) and 167.5 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −27.6 [Found: $M^+ - Me$, 167.0641 (EI). $C_7H_{11}N_2OSi$ requires 167.0641].

3-(Fluorodimethylsilylmethyl)-4-pyrimidone 19a

As a result of competing desilylation, the proportion of antimony trifluoride was reduced to approximately 0.25 equivalents. Thus, using a similar procedure to that above, 3-(chlorodimethylsilylmethyl)-4-pyrimidone **19b** (4.95 g, 24.43 mmol) was suspended in 20 cm^3 benzene and reacted with antimony trifluoride (1.09 g, 6.10 mmol). This gave 3-(fluorodimethylsilylmethyl)-4-pyrimidone as a pale yellow oil (1.9 g, 42%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.37 [6H, d, $^3J_{HF}$ 7.6, $Si(CH_3)_2$], 3.32 (2H, s, $N\text{-}CH_2$), 6.51 (1H, d, $^3J_{H5H6}$ 7.2, H5), 7.98 (1H, d, $^3J_{H6H5}$ 7.2, H6), 8.27 (1H, s, H2); δ_C (100 MHz, $CDCl_3$, Me_4Si) −0.2 [d, $^2J_{CF}$ 18.3, $Si(CH_3)_2$], 37.3 (d, $^2J_{CF}$ 32.9, $N\text{-}CH_2$), 114.0 (C5), 151.8 (C2), 154.6 (C6) and 162.3 (C4); δ_F (90 MHz, $CDCl_3$, Me_4Si) −141.6; δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) 8.8 (d, $^1J_{SiF}$ 269.0) [Found: MH^+, 187.0703 (FAB). $C_7H_{12}FN_2OSi$ requires 187.0703].

3-(Chlorodimethylsilylmethyl)-4-pyrimidone 19b

Using a similar procedure to that above, chloro(chloromethyl)-dimethylsilane (1.48 g, 10.35 mmol) was reacted with 4-(trimethylsiloxy)pyrimidine (1.74 g, 10.34 mmol) in 5 ml of benzene. This gave 3-(chlorodimethylsilylmethyl)-4-pyrimidone as a white crystalline solid (1.8 g, 86%) δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.68 [6H, s, $Si(CH_3)_2$], 3.53 (2H, s, $N\text{-}CH_2$), 6.63 (1H, d, $^3J_{H5H6}$ 6.4, H5), 8.13 (1H, d, $^3J_{H6H5}$ 6.4, H6) and 8.38 (1H, s, H2); δ_C (100 MHz, $CDCl_3$, Me_4Si) 5.7 [$Si(CH_3)_2$], 39.4 ($N\text{-}CH_2$), 112.7 (C5) 150.9 (C2), 156.0 (C6) and 163.3 (C4); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −16.7; *m/z* (EI) 202/204 (3:1) (M^+) (Found: M^+, 202.0329. $C_7H_{11}{}^{35}ClN_2OSi$ requires 202.0329), 167 ($M^+ - Cl$) (Found: $M^+ - Cl$, 167.0641. $C_7H_{11}N_2OSi$ requires 167.0641).

1-(Fluorodimethylsilylmethyl)quinoxalin-2-one 20a

1-(Chlorodimethylsilylmethyl)quinoxalin-2-one **20b** (11.02 g, 43.60 mmol) was suspended in benzene (40 ml) under a nitrogen atmosphere. Granular antimony trifluoride (2.60 g, 14.55 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 residue was recrystallised from acetonitrile to give 1-(fluorodimethylsilylmethyl)quinoxalin-2-one as a white crystalline solid (5.4 g, 53%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.43 [6H, d, $^3J_{HF}$ 7.8, $Si(CH_3)_2$], 3.23 (2H, s, $N\text{-}CH_2$), 7.47 (1H, m, H6), 7.56 (1H, d, $^3J_{H8H7}$ 8.4, H8), 7.71 (1H, m, H7), 7.96 (1H, d, $^3J_{H5H6}$ 8.0, H5) and 8.40 (1H, s, H3); δ_C (100 MHz, $CDCl_3$, Me_4Si) 1.3 [d, $^2J_{CF}$ 22.1, $Si(CH_3)_2$], 33.4 (d, $^2J_{CF}$ 40.5, $N\text{-}CH_2$), 115.1 (C8), 124.8 (C6), 130.6 (C5), 131.9 (C7), 132.9 (C4a), 134.4 (C8a), 146.9 (C3) and 155.5 (C2); δ_F (90 MHz, $CDCl_3$, Me_4Si) −128.7; δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −6.1 (d, $^1J_{SiF}$ 260.3); *m/z* (EI) 236 (M^+), 235 ($M^+ - H$), 221, 158, 77 (Found C, 56.40; H, 5.49; N, 12.30. $C_{11}H_{13}FN_2OSi$ requires C, 55.91; H, 5.54; N, 11.85%).

1-(Chlorodimethylsilylmethyl)quinoxalin-2-one 20b

Chloro(chloromethyl)dimethylsilane (0.56 g, 3.90 mmol) was added drop-wise with stirring to a solution of 2-(trimethylsiloxy)quinoxaline (0.85 g, 3.89 mmol) in 10 ml of benzene under a nitrogen atmosphere. The solution was allowed to stand for 30 minutes at room temperature. The solvent was removed by distillation under nitrogen and latterly by high vacuum pumping. By washing the resulting brown solid residue with diethyl ether (2 × 2 cm^3) and drying under high vacuum for 1 hour, a creamy white powder was obtained (0.80 g, 81%); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.76 [6H, s, $Si(CH_3)_2$], 3.54 (2H, s, $N\text{-}CH_2$), 7.58 (1H, ddd, $^3J_{H6\text{-}H5}$ 8.4, $^3J_{H6\text{-}H7}$ 7.6, $^4J_{H6\text{-}H8}$ 1.1, H6), 7.67 (1H, dd, $^3J_{H8\text{-}H7}$ 8.8, $^4J_{H8\text{-}H6}$ 1.1, H8), 7.80 (1H, ddd, $^3J_{H7\text{-}H8}$ 8.8, $^3J_{H7\text{-}H6}$ 7.6, $^4J_{H7\text{-}H5}$ 1.6, H7), 8.05 (1H, dd, $^3J_{H5\text{-}H6}$ 8.4, $^4J_{H5\text{-}H7}$ 1.6, H5) and 8.53 (1H, s, H3); δ_C (100 MHz, $CDCl_3$, Me_4Si) 6.9 [$Si(CH_3)_2$], 37.3 ($N\text{-}CH_2$), 115.7 (C8), 126.0 (C6), 130.9 (C5), 131.5 (C4a), 132.7 (C7), 135.1 (C8a), 144.3 (C3) and 155.8 (C2); δ_{Si} (79 MHz, $CDCl_3$, Me_4Si) −27.1; *m/z* (EI) 252/254 (3:1) (M^+) , 251/253 (3:1) ($M^+ - H$) 237/239 (3:1) ($M^+ - Me$), 217, 129 [Found: M^+, 252.0486 (EI). $C_{11}H_{13}{}^{35}ClN_2OSi$ requires 252.0486].

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