Quinoline-based Silylium ions. Synthesis, Structure and Lewis Acidity

Nivesh Kumar, Claire Laye, Frederic Robert, Yannick Landais

Quinoline-based Silylium ions. Synthesis, Structure and Lewis Acidity.

Nivesh Kumar,[†[a]] Claire Laye,[†[a]] Frédéric Robert*[a] and Yannick Landais*[a]

Dr. N. Kumar, Dr. C. Laye, Dr. F. Robert, Prof. Dr. Y. Landais
Univ. Bordeaux, CNRS, Institut des Sciences Moléculaires (ISM), UMR-5255, F-33400, Talence, France
E-mail: yannick.landais@u-bordeaux.fr; frederic.robert@u-bordeaux.fr
Web page : http://ylandais-chemistry.info/

Abstract: Heteroarylsilyl cations elaborated from a quinoline skeleton have been prepared from the corresponding silanes and their structures studied by ^{1}H, ^{29}Si, and ^{15}N NMR. DOSY experiments and DFT calculations were also carried out showing that the silyl cation center is stabilized intramolecularly by the quinoline nitrogen atom (N1), forming a highly strained and quasi planar 4-membered ring. Oxygenated and nitrogenated substituents at the C4 position on the quinoline ring were shown to reinforce the Si-N1 interaction through a p-π conjugation. The Lewis acidity of this class of silylium was finally determined using Müller's nitrilium method.

Introduction

Silylium ions have been of growing interest for several years in organic catalysis due to their exceptional Lewis acidity.[1] They have thus been used as Lewis acids for example in Diels-Alder or Mukaiyama reactions, but also to activate small molecules such as CO, H_2 or in defluorination processes.[1,2] Their synthesis has however been a long-standing problem due to their high reactivity and instability in the presence of all types of nucleophiles present in condensed phase, whether solvents or counter-anions. These electronically deficient species can be classified in different categories, depending on whether they are free (*i.e.* I, Figure 1), thus tricoordinated and perfectly planar, or coordinated by internal or external Lewis base donors. The latter exhibit pyramidal geometries as shown by XRDS, and can be distinguished as σ or π-stabilized silyl cations II and III respectively.[1] Free silyl ions signals in ^{29}Si NMR generally appear at chemical shifts higher than 200 ppm, while inter- and intramolecularly stabilized silyl ions exhibit chemical shifts in the 40-120 ppm range. Several acidity scales have appeared over time to evaluate their Lewis acidity. These include the Gutmann-Beckett method,[3] the fluoride ion affinity (FIA) scale,[4] and more recently the scale developed by Müller,[5] addressing the specific case of the intramolecularly stabilized silyl cations.

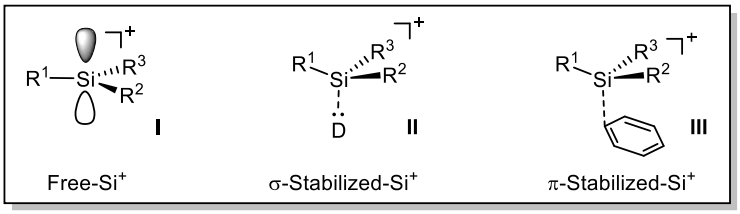


Figure 1. Free- and stabilized silylium cations.

In this context, our laboratory has recently shown an interest toward Si-centered chirality in intramolecularly stabilized silylated cations.[6] We first developed a series of chiral silylium ions 1, in which the chirality was centered both on the ligand (a chiral axis in a binaphthyl moiety) and on the silicon center (Figure 2).[7] It was shown that abstraction of the Si-H hydrogen atom by a trityl cation (J. Y. Corey reaction),[8] proceeded with inversion of configuration at silicon. Similarly, hydride delivery onto the silyl cation also proceeded through inversion. The net retentive process was rationalized by the participation of the neighboring Lewis basic substituent. More recently, the study was completed with an investigation of the chiral memory at silicon using a quinoline-silane 3 bearing a unique Si-centered chirality.[9] As in the binaphthyl model, a retention of configuration was observed. Extensive NMR studies along with XRDS allowed to determine unambiguously the structure of the quinoline-silylium cation 2, in which the silicon center was coordinated to the heterocyclic nitrogen center through a strained four-membered ring system. As in 1, anchimeric assistance of the Lewis basic sp^2 nitrogen center was shown to be determinant for the retention of the configuration at the silicon center.[10]

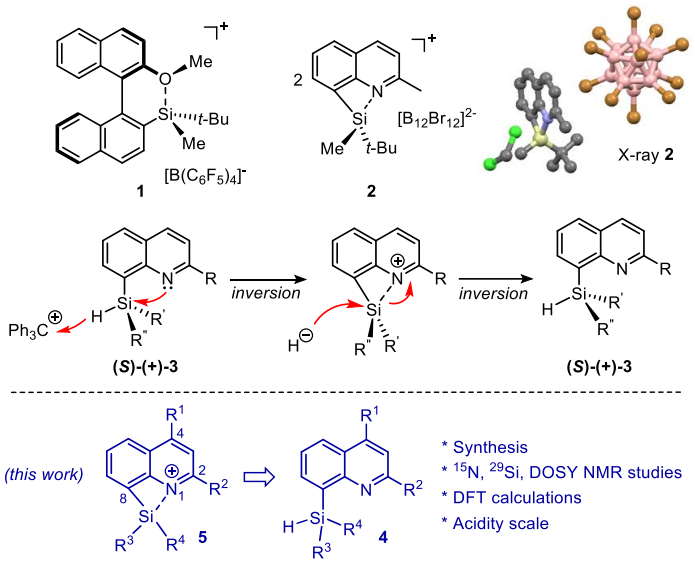
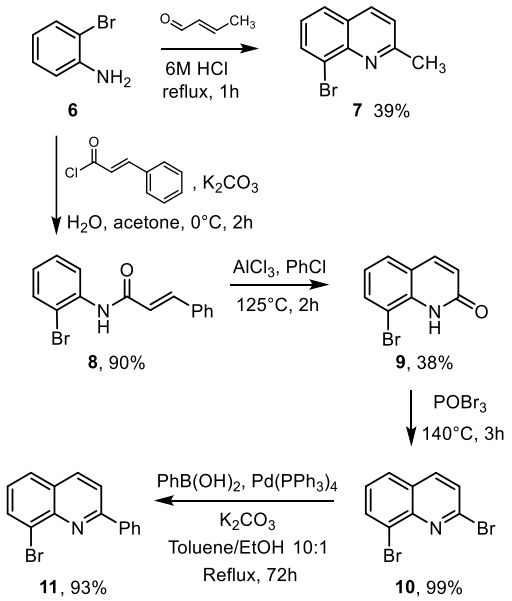


Figure 2. Chiral silylium cations and retention of chirality at silicon.

We report here an extension of this study to the synthesis of a series of substituted quinoline-silyliums 5 bearing various substituents (C2, C4) on the quinoline ring. Silylium cations 5 were prepared from the corresponding silanes 4 using the J. Y. Corey reaction (Figure 2). ^{1}H, ^{13}C, ^{15}N and ^{29}Si NMR studies, supported by DFT calculations, are reported, allowing a determination of their structure when XRDS is not available. Their Lewis acidity was finally evaluated and compared with that of related silyliums from the literature.

Results and Discussion

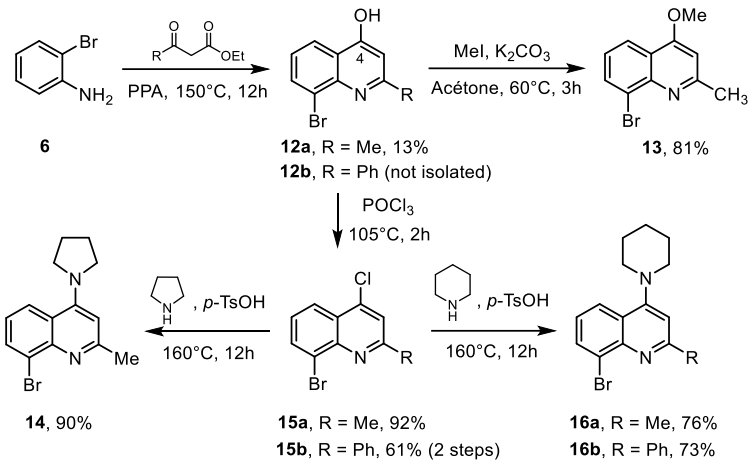
The above silanes **4** were prepared through silylation of the corresponding 8-bromoquinolines (Scheme 1). **7** was thus available in a single step, albeit in modest yield, through a Doebner-Miller reaction between 2-bromoaniline **6** and but-2-enal.[11] The 8-bromoquinoline **11** having a Ph substituent was obtained through treatment of amide **8** prepared from 2-bromoaniline **6** and cinnamyl chloride, using $AlCl_3$. This led to the desired bromoquinolinone **9** in 38% yield along with the debrominated product (in 28%, not shown). Bromination of **9** with $POBr_3$ then afforded the dibrominated quinoline **10**, which upon Suzuki coupling led to the 8-bromo-2-phenylquinoline **11** in excellent yield.



Scheme 1. Preparation of bromoquinoline precursors.

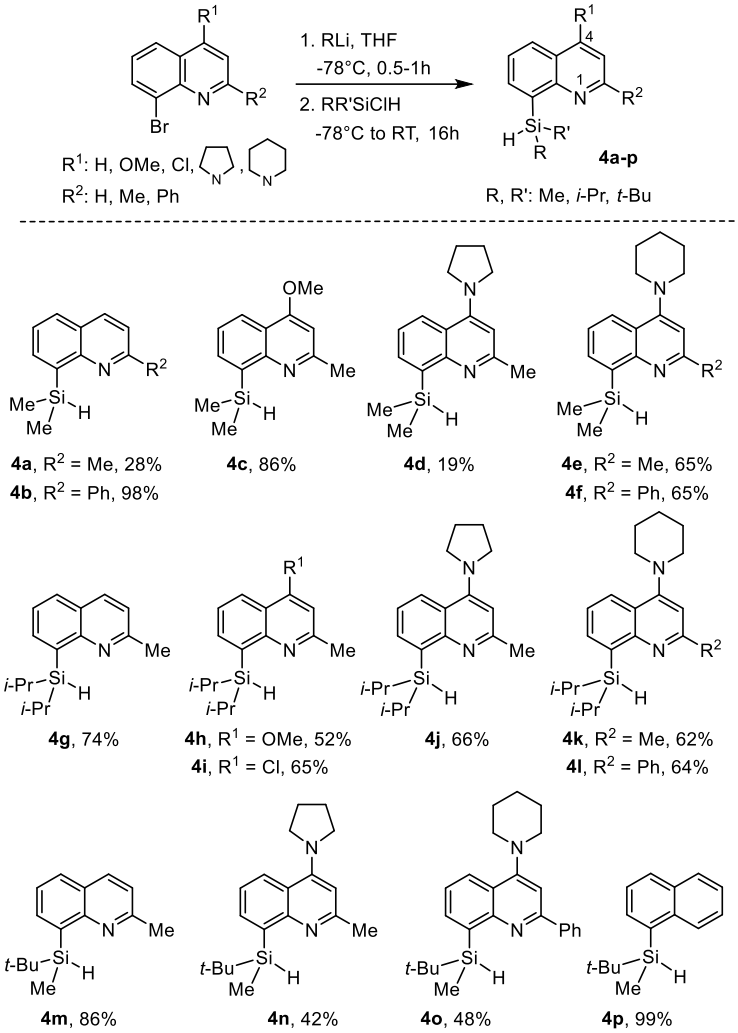
The 4-substituted quinolines were prepared starting from the 4-hydroxyquinolines **12a-b**, available through reaction between 2-bromoaniline **6** and the suitable β-ketoesters (Scheme 2).[12] **12a** was thus isolated, albeit in a poor yield, and was then converted into the corresponding ether **13** and chloride **15a** through treatment with

$POCl_3$. In a similar way, **12b** which was not isolated was directly converted into **15b** in satisfying overall yield. Finally, 4-aminoquinolines **14** and **16a-b** were accessible in good yields through amination of the corresponding chlorides.



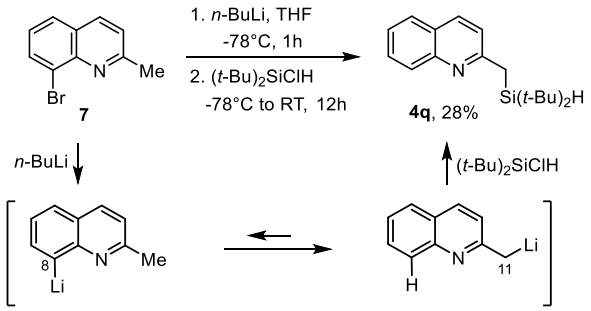
Scheme 2. Preparation of 4-substituted quinoline precursors.

The ensuing silylation of 8-bromoquinolines proved more difficult than expected, as intermediate lithiated species undergo the migration of the negative charge through the aromatic nucleus making them very unstable. This phenomenon is favored by the electrostatic repulsion between the carbanionic center at C8 and the sp^2 nitrogen lone pair.[13] Various silanes were nevertheless made available, after some experimentations, through bromine-lithium exchange with a suitable organo-lithium at low temperature, followed by addition of the chlorosilane. With unhindered chlorosilanes (Me_2SiClH), the Br-Li exchange was carried out at -78°C, followed by the addition of the chlorosilane at low temperature. Then, the mixture was allowed to warm up to room temperature overnight to afford the corresponding silylquinolines **4a-f** in low to excellent yields (Method A, see exp. Section) (Scheme 3). With the sterically more hindered *i*-Pr_2SiH moiety, an alternative strategy was devised, mixing first the bromide and the chlorosilane, before adding the *n*-BuLi at -78°C (Internal quench, Method B).[14] Using this procedure, compound **4g** was thus obtained in 74% yield as compared with 13% using the conventional protocol A. Finally, the *t*-BuMeSiH fragment was introduced using 2 equivalents of *t*-BuLi at -78°C before the addition of the corresponding chlorosilane, leading to silylquinolines **4m-p** in moderate to high yields (Method C). It is worth noticing that the desired silanes **4a-p** are obtained after purification by chromatography using deactivated silica, in order to avoid the high amount of silanol and the corresponding siloxanes thus generated (see ESI). Finally, the amount of organolithium used should be carefully monitored to avoid further alkylation (with *n*-BuBr or *t*-BuBr) at C11 (see ESI).



Scheme 3. Preparation of silyl-substituted quinoline **4a-o**. Naphthylsilane **4p**.

Incorporation of the highly hindered $(t\text{-Bu})_2$SiH fragment was also studied, but lithiation of **7** did not afford the desired 8-silylquinoline but instead the 11-isomer **4q** resulting from a slow silylation at C8, favoring the anionic translocation and formation of the thermodynamically more stable benzylic anion at C11 (Scheme 4).[14,15]



Scheme 4. Silylation of 8-bromoquinoline with $(t\text{-Bu})_2$SiClH.

Silanes **4a-p** were characterized by multinuclear NMR spectrometry, FT-IR and HRMS. These silanes show expected chemical shifts for the Si-H hydrogen atom with δ^1H ranging between 4.04 and 4.84 ppm and δ^{29}Si between 12.1 and -18.1 ppm. It is however worth noticing that δ^{29}Si chemical shifts in the Me_2Si series (**4a-f**) greatly differ from those of their *t*-BuMeSi analogues **4m-p**, with respectively δ^{29}Si between -17.4 and -18.1 ppm for the former and δ^{29}Si at lower fields ranging from 2.6 to -6.4 ppm for the latter. This effect of the *t*-Bu substituent has been documented previously.[9,10a] Similarly, δ^{29}Si signals in silanes **4g-l** bearing a $(i\text{-Pr})_2$Si group are deshielded with chemical shifts in the 11.7-12.2 ppm region further substantiating the sensitivity of ^{29}Si NMR chemical shifts toward the nature of substituents attached to silicon. In contrast, substituents at C2 and more

importantly at C4 do not influence significantly chemical shifts in the hydrosilane **4a-f** series in which $\delta^1H_{(Si\text{-}H)}$, $\delta\ ^1H_{(Si\text{-}Me)}$ and $\delta\ ^{13}C_{(Si\text{-}Me)}$ are roughly identical (Table S1). Finally, with respect to the IR absorption bands corresponding to the Si-H bond vibration, silanes **4a-p** show absorptions between 2073-2116 cm^{-1}, in good agreement with literature data (2080-2280 cm^{-1}).[9]

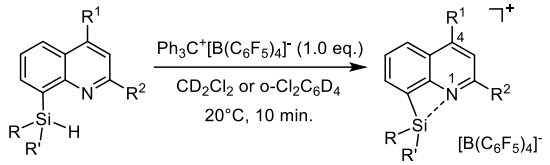
Silylium cations **5a-o** were prepared through abstraction of the Si-H hydrogen of the corresponding silanes **4a-o** using commercially available $Ph_3C^+[B(C_6F_5)_4]^-$.[8] Due to their high reactivity, silylium cations were not purified and their yields were therefore estimated using, as an internal standard, triphenylmethane, a by-product produced in stoichiometric amount. Yields of cations **5a-o** ranged between 51 and 80% (Table 1), except for quinolinedimethylsilyl **4a** and **4b**, which led to complex mixtures. ^{29}Si NMR chemical shifts of silylium ions were found in the 45-70 ppm region and thus, much higher than their corresponding silane precursors as expected due to their ionization, leading to $\Delta\delta^{29}Si$ ranging between 40 and 90 ppm. The ^{29}Si NMR chemical shifts in **5a-o** was found to be independent of the solvent used. For instance, for cation **5m**, a $\delta^{29}Si$ of 64.3 ppm was obtained in CD_2Cl_2, 63.8 ppm in o-$C_6D_4Cl_2$, and 63.7 ppm in C_6D_5Cl, ruling out a possible interaction between the positively charged silicon center and the solvent.[9] In order to evaluate the effect of the quinoline nitrogen atom (N1) on the stabilization of the silicon center, we also prepared silylium ion **5p** from naphthylsilane **4p**. **5p** is lacking the nitrogen stabilization and is therefore a much stronger Lewis acid as indicated by the degradation of the $[B(C_6F_5)_4]^-$ anion, which can be detected from the ^{19}F NMR of the crude reaction mixture in o-dichlorobenzene (see ESI). A ^{29}Si NMR chemical shift for the silicon center of **5p** at 81.6 ppm was however observed when it was prepared in d_8-toluene. This signal is consistent with the formation of a silyl cation stabilised by the aromatic solvent.[16]

The influence of substituents on the silicon center, at C2 and C4 was then looked at. The variation of the nature of substituents on the silicon center has only a minimal effect, as suggested by the closely related chemical shifts between **5e** bearing a small $SiMe_2$ group and **5k** and **5o** for instance having sterically more hindered *i*-Pr and *t*-Bu substituents (Table 1, entries 5, 11 and 15).[17] The difference of chemical shifts in ^{29}Si NMR ($\Delta\delta_{Si}$) between **5e** and **5k** is also reduced to 4.5 ppm in the cationic series as compared to 30 ppm in the silane counterpart, suggesting a reduced effect of the steric hindrance around silicon after ionisation. The trend observed for the silanes nevertheless appears to be the same as for their cationic counterparts with: $\delta^{29}Si(Me_2Si^+) < \delta^{29}Si(t\text{-}BuMeSi^+) < \delta^{29}Si(i\text{-}Pr_2Si^+)$.

The substituent at C4 appears as the most influential with noticeable effect on the ^{29}Si chemical shift. For instance, silyl cations bearing a piperidinyl group (*i.e.* **5e-f**, **5k-l** and **5o**) at C4 exhibit ^{29}Si NMR chemical shifts between 49.8 and 54.6 ppm, slightly lower than their unsubstituted analogues **5a-b**, **5g** and **5m**, showing $\delta^{29}Si$ NMR shifts above 60 ppm. A similar trend is observed with the pyrrolidinyl substituent at C4 with ^{29}Si chemical shifts around 46-52 ppm in **5d**, **5j** and **5n**, as well as with the OMe group in **5c** and **5h**, albeit with lower intensity ($\delta^{29}Si$ = 56-61 ppm). In contrast, quinoline **5i** bearing a chloro substituent displays slightly higher $\delta^{29}Si$ chemical shift (67.3 ppm), close to that of **5g** having no substituent at C4 (66.8 ppm). Chemical shift in ^{29}Si NMR is recognized as a reliable indicator of the silylium character of an R_3Si^+ species.[1] The accumulation of positive charge on the silicon atom is reflected by an increase in its chemical shift. Free triarylsilylium ions have thus ^{29}Si NMR resonances above 210-230 ppm,[1,18] while solvent-stabilized silyl cations have chemical shifts close to $\delta^{29}Si$ = 80-100 ppm.[17] Therefore, the lower chemical shift in silylium ions **5e-f**, **5k-l**, **5o**, or **5d**, **5j** and **5n** possessing an amino substituent at C4, albeit moderate, indicates a stronger interaction between silicon and the quinoline nitrogen center (N1), the basicity of which is enhanced by the conjugation with the amino substituents at C4 (*vide infra*).[19] The same effect, yet weaker, is observed with the OMe substituent. In contrast, the electron-withdrawing chlorine atom leads to a slight weakening of the Si-N1 interaction. In line with this, the chemical shift in **5p** (81.6 ppm), lacking such an interaction is as expected higher than those of silylium ions **5a-o**. Finally, it is worth noticing that while **5a-b** are highly unstable, their analogues **5c-f** possessing an electron-donating group at C4 can be observed, suggesting that the increased Lewis basicity at N1 in these cases compensate for the lack of kinetic protection by the bulky substituents on the silicon center.

The substituent at C2 displays a weaker effect on the silicon environment as indicated by the small difference in chemical shift in ^{29}Si NMR for instance between **5e** and **5f** ($\Delta\delta^{29}Si$ = 0.8 ppm) or **5k** and **5l** ($\Delta\delta^{29}Si$ = 0.3 ppm)(Table 1). These observations are not restricted to the piperidinyl series, but are consistent for all silyl cations.

Table 1. Chemical shifts of silyliums **5a-p** in ^{29}Si and ^{15}N NMR.



4a-p **5a-p**

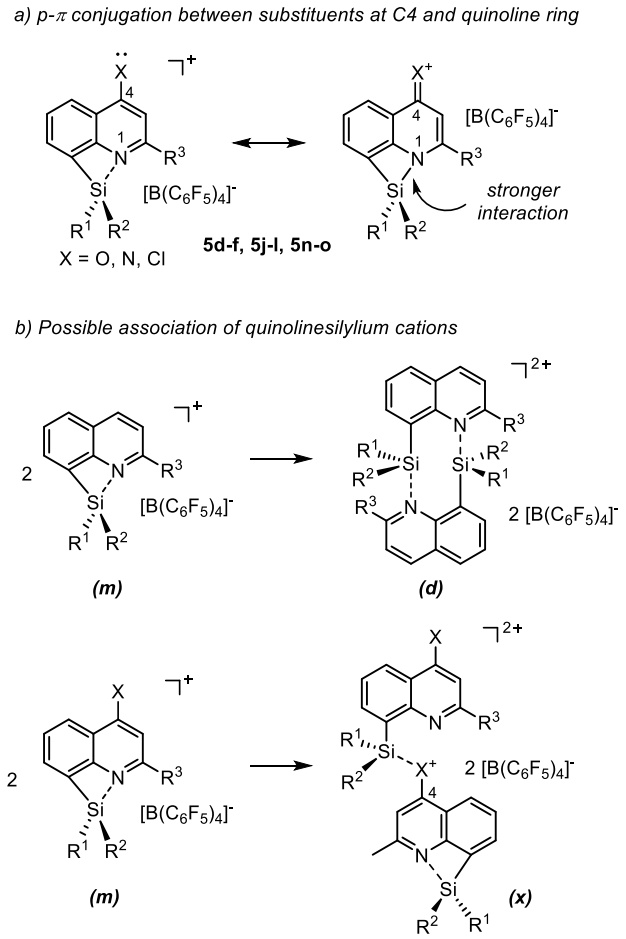
Entry	Silylium	Yield	δ_{Si}[a]	$\Delta\delta_{Si}$[b]	δ_{N1}[c]	$\Delta\delta_{N1}$[d]	δ_{N4}[e]	$\Delta\delta_{N4}$[f]
1	**5a**	-	60.2	77.7	216.6	-94		
2	**5b**	-	63.7	81.1				
3	**5c**	71	56.1	73.7	196.3	-93.4		
4	**5d**	19	46.4	64.5	173.3	-106.7	125.8	42.6
5	**5e**	72	49.8	67.9	178.9	-114.1	110.3	43.3
6	**5f**	74	50.6	68.2	175.5	-117.5	114.2	45.9
7	**5g**	72	66.8	55.1	214.2	-98		
8	**5h**	70	61.4	49.6	190.4	-101.4		
9	**5i**	75	67.3	55.2	210.2	-99.4		
10	**5j**	61	52.1	39.9	169.3	-113.9	126.0	44.5
11	**5k**	61	54.3	42.4	174.9	-120.6	110.2	43.7
12	**5l**	75	54.6	42.5	171.8	-118.2	115.4	47.8
13	**5m**	80	64.3	62.1	215.4	-98.1		
14	**5n**	76	49.1	46.5	171.5	-111.8	126.4	44.4
15	**5o**	51	51.6	50.6	172.2	-119.6	113.6	45.9
16	**5p**	-	81.6	88.0				

[a] ^{29}Si NMR chemical shift of the Si center in **5**. [b] Chemical shift difference in ^{29}Si NMR between Si centers in **4** and **5**. [c] ^{15}N NMR chemical shift of the N1 center in **5**. [d] Chemical shift difference in ^{15}N NMR between N1 centers in **4** and **5**. [e] ^{15}N NMR chemical shift of the N4 center in **5**. [f] Chemical shift difference in ^{15}N NMR between N4 centers in **4** and **5**.

These data, along with our previous XRDS on silyl cation **5m** having a carborane counter-anion[9] point toward a stabilization of the positive silicon center by the quinoline nitrogen atom in the above cations **5a-o**. However, the limited access to structural data in the series above, due to the low crystallinity of silyl cations **5a-o** having a $[B(C_6F_5)_4]^-$ anion, prompted us to perform additional NMR studies, including ^1H-^{15}N HMBC and DOSY experiments.

^1H-^{15}N HMBC experiments thus allowed us to access to the useful ^{15}N chemical shifts of silanes **4a-o** and the corresponding silylium ions **5a-o**. These values are particularly interesting as they provide information on the electronic environment of the nitrogen N1 and also that of the amino substituents at C4. These chemical shifts along with the corresponding $\Delta\delta_{N1}$ and $\Delta\delta_{N4}$ are summarized in Table 1. As an example, **4m** N1 exhibits a $\delta^{15}N$ at 313.5 ppm while the silyl cation **5m** shows a $\delta^{15}N$ of 215.4 ppm. ^1H-^{15}N HMBC experiments reveal a correlation between N1 and the methyl substituent on the silicon, showing an interaction between this nitrogen center and the positive silyl ion (see ESI). The difference in ^{15}N chemical shift between silanes and silylium ions is estimated around -94.0 to -100.1 ppm for the series lacking substituent at C4 (**5a-b**, **5g**, **5m**).[9] For the C-4 substituted analogues, the difference of chemical shift becomes more significant. For instance, for compounds bearing a piperidinyl group in position 4, the quinoline nitrogen undergoes a $\Delta\delta_{N1}$ ranging between -114.4 to -120.6 ppm (entries 5-6, 11-12 and 15). This deshielding effect indicates a stronger interaction between the nitrogen N1 and silicon. The heterocyclic nitrogen thus behaves as a silylpyridinium.[20] This is also consistent with lower chemical shifts in ^{29}Si NMR for these silylium ions. ^{15}N NMR also provides information on the

conjugation of nitrogenated substituents at C4 in models **5d-f**, **5j-l**, and **5n-o**. This conjugation is assessed by a clear change in the chemical shift of the nitrogen atom on the C4 center between silanes and the corresponding silyl cation (*vide infra*) (Scheme 5a). For instance, the piperidinyl nitrogen at C4 in silane **4k** exhibits a $\delta^{15}N$ chemical shift (δ_{N4}) at 66.5 ppm, while the corresponding silyl cation **5k** displays a signal at 110.2 ppm.



Scheme 5. Si-N interactions in quinolinesilylium cations **5**. ***(m)*** : monomeric form ; ***(d)*** : dimeric form; ***(x)***: dimeric form with Si-X interactions.

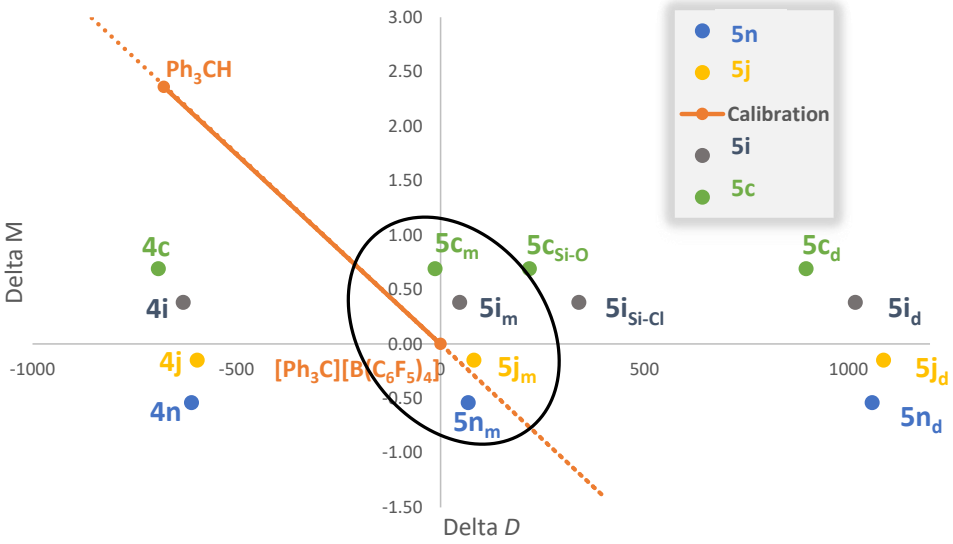
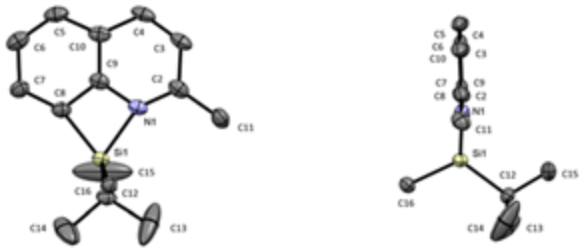


Figure 3. DOSY experiments for silyl cations **5a-o**. ΔD = f(ΔM).

Finally, DOSY experiments were also performed as to rule out the possible intermolecular interaction between the quinolinyl nitrogen center of one silyl cation and the silicon center of a second silylium species. It was also of interest to investigate the possible intermolecular interaction between the more basic sp^3 nitrogen centers of pyrrolidinyl and piperidinyl substituents of silanes **5d-f**, **5j-l**, and **5n-o** with cationic silicon centers (Scheme 5b). The DOSY ^{1}H (Diffusion Ordered SpectroscopY) technique, allows to differentiate compounds in a mixture through their molecular weight. Two compounds diffuse differently in deuterated solvent due to their unique relaxations, which is dependent on their molecular weight and three-dimensional shape. Thus, the diffusion coefficient *D* obtained for each compound provides information about its structure. We thus applied the DOSY technique to the crude mixtures obtained after conversion of silanes **4c-n** into silylium ions **5c-n** (Table 1). Here, species appear in the form of ionic pairs despite the use of a weakly coordinating anion.[21] The following diffusion coefficients values were obtained for instance in the case of **5m**. Triphenylmethane generated as a by-product thus showed a diffusion coefficient D_{Ph3CH} = 13.8 e^{-10} $m^2.s^{-1}$ for a molecular weight of 244.34 $g.mol^{-1}$. Silyl cation **5m** showed a $D_{\mathbf{5m}}$ = 9.82 e^{-10} $m^2.s^{-1}$, a value close to that obtained for $Ph_3C^+[B(C_6F_5)_4]^-$ $D_{Ph3C.TPFPB}$ = 9.81 e^{-10} $m^2.s^{-1}$ having a molecular weight such as $M_{PH3C.TPFPB}$ = 922.37 $g.mol^{-1}$. This suggests that **5m** with a molar weight of 921.46 $g.mol^{-1}$ is in monomeric form in solution. The dimeric form (Scheme 5b), which implies a molar mass twice as high, would have a very different diffusion coefficient from that of $Ph_3C^+[B(C_6F_5)_4]^-$. DOSY experiments were also applied to the other silyl cations and the results summarized in Figure 3. The calibration straight line (orange) was generated from the molecular weights and diffusion coefficients *D* of the known Ph_3CH and $Ph_3C^+[B(C_6F_5)_4]^-$. $\Delta D = f(\Delta M)$ in Figure 3 was thus elaborated, with ΔD as the difference between the diffusion coefficient of a given silyl cation (monomeric and dimeric forms) and that of known $Ph_3C^+[B(C_6F_5)_4]^-$ and ΔM their differences of molecular weight.[22] Each silylium ion was represented on the graph as a monomer ***(m***) or as a dimer ***(d)***. Dimers resulting from interaction between the silicon center of the silyl cation and the heteroatom (Cl, O or N) of substituents at C4 of a second monomer were noted as ***(x)*** (Scheme 5). Graph in Figure 3 clearly shows that monomers **5(*m*)** are closer to the calibration line that any dimer **5(*d*)** or **5(*x*)**, further supporting the intramolecular stabilization of the silylium ion in solution by the nitrogen atom N1, as shown in Scheme 5, ruling out the dimeric forms **5(*d*)** and **5(*x*)**. The absence of signals resulting from the formation of diastereomeric pairs in the ^{1}H and ^{29}Si NMR of silylium **5m** (having $R^1 \neq R^2$) also supports the unique formation of a monomeric system.

Computational investigations were finally carried out, first calculating ^{29}Si NMR chemical shifts for some silylium ions **5c-p** (see ESI). Table 2 summarizes the calculated values (performed at the M06-2X/Def2-TZVPP level), which fit well with experimental ones, thereby validating the method. Geometries of the different cations, substituted or not at C4 were thus calculated and were all shown to be stabilized intramolecularly by the quinoline N1 nitrogen, in good agreement with experimental data. Their structures are constrained, as it was assumed with respect to the chemical shift in ^{15}N NMR. In addition, calculated C9C8Si and C9N1Si angles for **5m** of 88.46°, and 87.88° respectively (instead of 120°) and N1-Si distance ($d_{N\text{-}Si}$) of 1.889 Å are well in line with experimental values obtained through XRDS of **5m** having a carborane anion.[9] Interestingly, as the C9NSi angle becomes larger, the C9C8Si angle becomes smaller as a result of the shortening of the N1-Si bond. Values obtained for the other silyl cations summarized in Table 2 also deserve a comment. As a general trend, the shortest $d_{N\text{-}Si}$ is observed for compounds having a substituent at C4 capable of π-conjugation, (Scheme 5a) in good agreement with experimental data obtained for silylium cations **5d-f**, **5j-l**, **5n-o** and notably their lower ^{29}Si NMR chemical shifts. This conjugation is further supported by the short C4-X bond in these silyliums. For instance, in cation **5c**, the calculated bond distance $d_{C4\text{-}O}$ is 1.314 Å, in-between a C-O (1.43 Å) and a C=O (1.22 Å) bond, consistent with the donating nature of the OMe substituent. The effect is even larger for nitrogenated pyrrolidinyl and piperidinyl substituents, in which, the C4-N bond (1.331 to 1.346 Å) is much closer to a C=N bond than a C-N bond (1.30 *vs* 1.47 Å respectively), indicating an efficient p–π orbital interaction. Interestingly, the $d_{C4\text{-}N}$ distance is significantly shorter for the pyrrolidinyl group ($d_{C4\text{-}N}$ = 1,331 Å in **5n**) than for the piperidinyl one ($d_{C4\text{-}N}$ = 1,346 Å in **5o**), in line with the well-known almost perfect sp^2 nitrogen hybridization which is more easily accommodated in a 5-membered ring free from angle strain.[23] Chloroquinoline model **5i** shows a $d_{N\text{-}Si}$ equivalent to that of unsubstituted system **5g**. However, chemical shift in ^{29}Si for **5i** is the highest in the whole series, which may result from an inductive effect of the chloro substituent, resulting in a slightly more Lewis acidic silicon center. Finally, all these silyliums are little pyramidalized according to DFT calculations, the sum of the angles around the silicon ($\Sigma\alpha(Si)$) ranging between 350.12° and 352.73° (for a theoretical value of 360°C for a "free" silylium ion). For the naphthylsilyl cation **5p**, a computed structure with a complexation of the silylium on toluene is in good agreement with observed ^{29}Si NMR chemical shift.

Table 2. Calculated ^{29}Si NMR and structural data for some silyl cations.



Entry	Silylium	$\delta_{Si\ (exp)}$[a]	$\delta_{Si\ (calc)}$[b]	$d_{N1\text{-}Si}$[c]	$d_{C4\text{-}X}$[d]	Angle C9C8Si[e]	Angle C9N1Si[f]	$\Sigma\alpha$(Si)
1	**5c**	56.1	57.6	1.867	1.314	87.88	89.06	352.54
2	**5d**	46.3	51.3	1.840	1.330	88.02	90.34	351.62
3	**5g**	66.8	67.6	1.890	-	88.43	88.90	352.67
4	**5h**	61.4	63.6	1.875	1.315	88.05	89.04	352.34
5	**5i**	67.3	68.0	1.888	1.703	88.40	89.07	352.73
6	**5k**	54.3	58.5	1.853	1.343	88.02	90.01	351.62
7	**5l**	54.6	54.4	1.853	1.347	87.94	89.95	350.59
8	**5m**	64.3	63.0	1.889	-	88.46	87.88	352.48
9	**5n**	49.1	50.6	1.846	1.331	87.13	90.25	351.52
10	**5o**	51.6	53.5	1.856	1.346	88.08	90.05	350.12
11	**5p**	81.6	75.2	-	-	126.3	-	341.14

[a] ^{29}Si NMR experimental chemical shift of the Si center in **5**. [b] ^{29}Si NMR calculated chemical shift of the Si center in **5** (GIAO M06L/Def2-TZVPP). [c] Bond length between Si and N1. [d] Bond length between C4 and C4 substituent heteroatom X. [e] C8-C9 and C8-Si bonds angle. [f] C9-N1 and N1-Si bonds angle.

Interestingly, the calculation of molecular orbitals of some complexes shows that Si orbitals are involved in the LUMO for the naphthylsilylium-toluene complex **5p** whereas the LUMO is located only on the quinoline part for the others. With 4-substituted silyl cations **5h** and **5n**, the LUMO is clearly located also on the heteroatom at C4, supporting a greater delocalization of the positive charge (Figure 4).

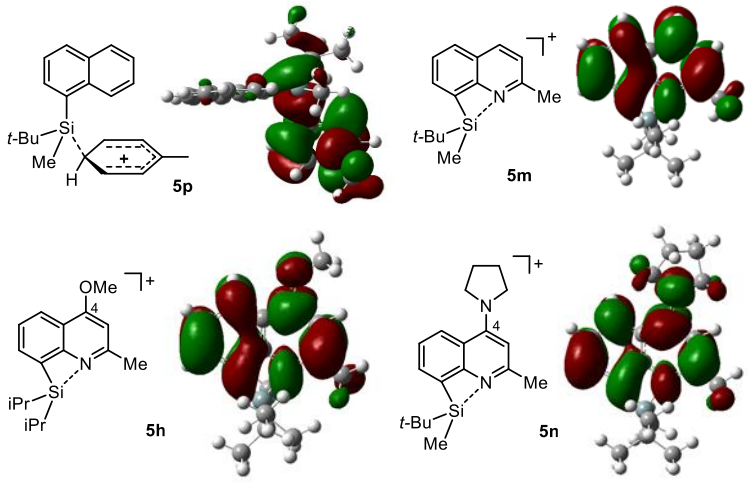


Figure 4. Calculated structures for silyl cations and LUMO plots.

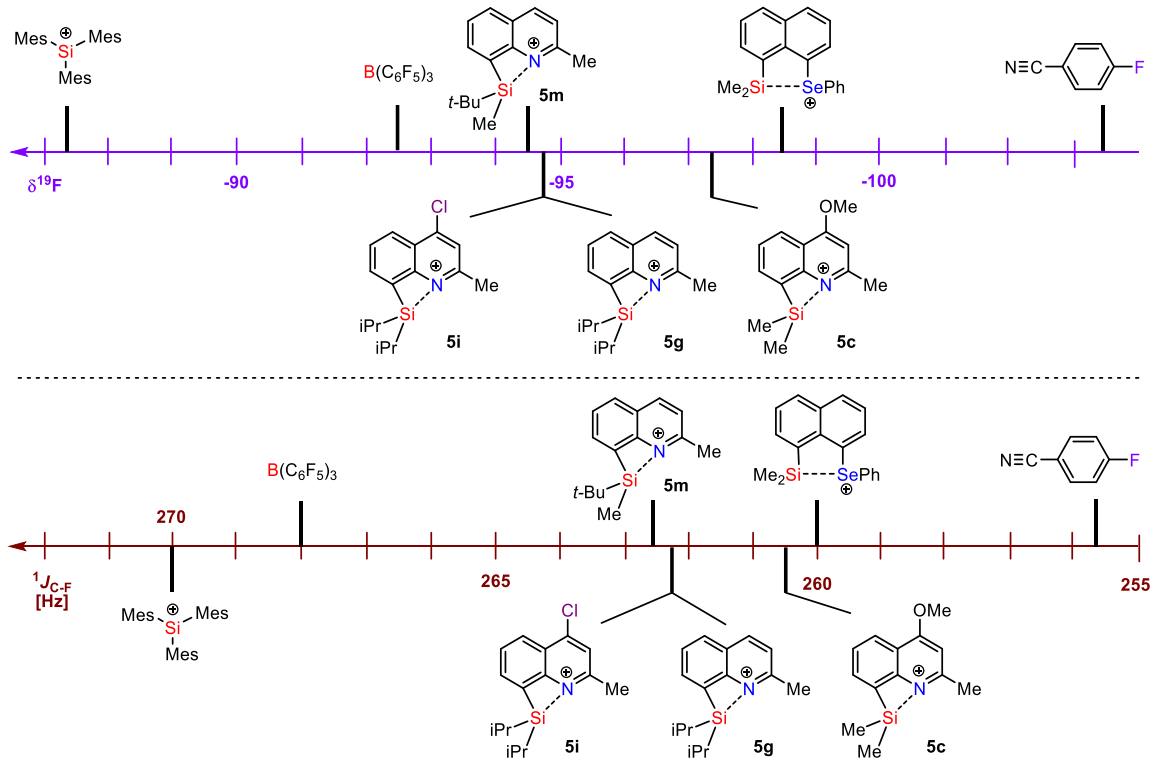
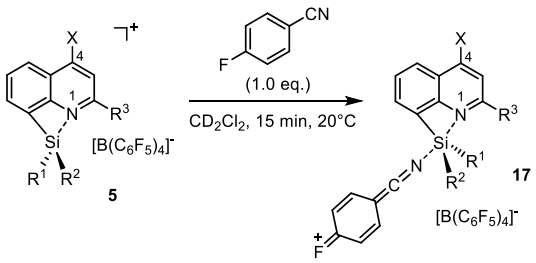


Figure 5. Lewis acidity scale according to Müller *et al.*'s method.

The Lewis acidity of some of the silylium ions above was finally assessed using a method recently disclosed by Müller *et al.*[5] Their approach is based on the complexation of silylium cations by the nitrogen center of the weak Lewis basic *p*-fluorobenzonitrile and the measurement of the fluorine chemical shift as well as the $^{1}J_{C\text{-}F}$ coupling constant in the Lewis adduct complex through ^{19}F NMR (Scheme 6). This acidity scale is particularly well suited for Lewis-base stabilized silyl cation as the nitrile-Si interaction should not disrupt the intramolecular LB-Si interaction within the silylium ion and thus provides a realistic measurement of the Lewis acidity of the silicon center in these cations. Silyl cations **5c**, **5i**, **5g** and **5m** reacted well with *p*-fluorobenzonitrile and led to consistent results, while their analogues bearing nitrogenated substituents at C4 led surprisingly to no reaction, leaving the nitrile unchanged. For instance, the nitrilium adduct of silyl cation **5m** was characterized by a chemical shift in ^{29}Si NMR at 23.6 ppm, in good agreement with silyl-nitrilium chemical shifts described in literature (in the range 6-40 ppm).[1] ^{19}F NMR of the nitrilium complex of **5m** has been shifted toward low field with a $\Delta\delta^{19}F$ = 8.9 ppm. Both this shift and the increase in the coupling constant $^{1}J_{C\text{-}F}$ are indicative of the importance of the quinoid resonance structure **17** (Scheme 6).



Scheme 6. Lewis acidity of some silyl cations based on Müller's scale.

The chemical shift in ^{15}N NMR of the nitrilium nitrogen atom of **17m** (issued from silyl cation **5m**) is observed at 292.7 ppm, thus lying between that of the silane precursor **4m** (δ^{15}N = 315.5 ppm) and that of the silyl cation **5m** (δ ^{15}N = 215.4 ppm), indicating a lengthening of the intramolecular Si-N1 bond, consistent with the formation of a pentavalent complex such as **17**. Similar results were observed with silyl cations **5c**, **5i**, and **5g** (see nitrilium salts **17c**, **17i** and **17g** respectively, ESI), allowing their incorporation into Müller's Lewis acidity scale.[5] Our compounds appear within the range of silyl cations stabilized intramolecularly by a Lewis base. Interestingly, the acidity order remains the same whether they are ranked according to their chemical shift in ^{19}F NMR or by their coupling constant $^{1}J_{C\text{-}F}$. Their Lewis acidity are very close and follows the order **5m** > **5g** ~ **5i** > **5c** suggesting a weak effect of the substituents at C4 (Figure 5).

Conclusion

As a summary, we described a series of quinoline silylium cations bearing various substituents, on the silicon center, at C2 and more importantly at C4. Although we do not have access to XRDS for most silyl cations (except for **5m** having a carborane anion), a thorough ^{1}N, ^{13}C, ^{15}N and ^{29}Si NMR study along with DOSY experiments provided important information about their monomeric structure. These data, along with DFT calculations support silylium cations in which the cationic silicon center is stabilized intramolecularly by the quinoline nitrogen center at position 1 within a constrained four membered ring. π-Donating substituents at C4 reinforce this stabilization as shown by the smaller distances calculated between N1 and Si and also by the shortest bond length between the heteroatom (O, N) and the quinoline C4 carbon. These DFT calculations, validated earlier by XRDS on silyl cation **5m**,[9] are in excellent agreement with the NMR data and constitute a reliable tool to establish the geometry of these Lewis basic stabilized silylium cations. This work shows that basic substituents on the aromatic core do not necessarily quench the Lewis acidity of the silylium species providing that an intramolecular interaction is present and bypass such interactions. Finally, the various LB-stabilized silyl cations were incorporated in a Lewis acidic scale using the Müller acidity scale, indicating a modest Lewis acidity as compared to free silyliums, but similar to closely related silyl cations such as naphthylsilyl cations stabilized by chalcogen.[5] All these studies demonstrate that the incorporation of various substituents at C4 allows a high degree of tunability with this quinoline skeleton, that could be useful for further studies in catalysis.

Experimental Section

General procedure A for the dimethylsilylation reaction. In a flame-dried flask equipped with a magnetic stirrer, the 8-bromoquinoline derivative (1.0 eq.) was diluted in dry THF (0.5 M) under an inert atmosphere. Freshly titrated *n*-BuLi in hexanes (1-1.5 eq.) was then added dropwise at -78°C, followed after 1 h at -78°C by Me_2SiClH (1-1.5 eq.). The mixture was stirred for 15 min at -78°C, then slowly warmed up to room temperature and stirred overnight. To the crude mixture, CH_2Cl_2 and H_2O were then added. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (3 x). The combined organic layers were washed with brine then dried over Na_2SO_4 and the solvents removed under reduced pressure. Purification was carried out through column chromatography over silica gel (deactivated with Et_3N), with petroleum ether as an eluent, affording the desired silanes **4a-f**.

General procedure B for the diisopropylsilylation reaction. A flame-dried flask equipped with a magnetic stirrer was charged with the 8-bromo-quinoline derivative (1.0 eq.) and *i*-Pr_2SiClH (1.2-1.3 eq.) in dry Et_2O or THF (0.3-1 M) under an inert atmosphere. Then, freshly titrated *n*-BuLi in hexanes (1.1-1.2 eq.) was added dropwise at -78°C over 1h using a syringe pump. The resulting mixture was then slowly warmed up to room temperature and stirred for 16h. To the crude mixture Et_2O and H_2O were added. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (3 x). The combined organic layers were washed with brine then dried over Na_2SO_4 and the solvents removed under reduced pressure. Purification was carried out through column chromatography over silica gel (deactivated with Et_3N), with petroleum ether as an eluent, affording the desired silanes **4g-l**.

General procedure C for the tert-butyl(methyl)silylation reaction. A flame-dried flask equipped with a magnetic stirrer was charged with the 8-bromoquinoline derivative (1.0 eq.) in dry THF (0.2-0.6 M) under an inert atmosphere. Then, freshly titrated *t*-BuLi in hexanes (2-2.1 eq.) was added carefully (but with a "fast" dropwise) at -78°C, and the mixture stirred for 20 min at -78°C. Then, *t*-BuMeSiClH (2-2.1 eq.) was added at -78°C and the resulting mixture slowly warmed up to room temperature and stirred for 18h. To the crude mixture Et_2O and H_2O were added. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (3 x). The combined organic layers were washed with brine then dried over Na_2SO_4 and the solvents removed under reduced pressure. Purification was carried out through column chromatography over silica gel (deactivated with Et_3N), with petroleum ether as an eluent, affording the desired silanes **4m-p**.

General procedure D for the synthesis of silylium ions 5. In a glovebox under an argon or nitrogen atmosphere, a solution of $Ph_3C^+[B(C_6F_5)_4]^-$ (1.0-1.05 eq.) in deuterated solvent (0.3 mL), was added to the silane **4** (1.0 eq.) and then injected into a dry J-Young NMR tube. Deuterated solvent (0.2 mL) was used to wash the vials and complete the tube at room temperature. The tube was tightly closed, shaken, and then NMR spectroscopies of the reaction mixture were recorded.

[1] For reviews on silylium ions chemistry, see: a) R. J. P. Corriu, M. Henner, *J. Organomet. Chem.* **1974**, *74*, 1-28; b) T. Müller, *Silylium ions and stabilized silylium ions* in Science of Synthesis, Knowledge updates 2013/3, Vol. Ed.: M. Oestreich, G. Thieme Verlag KG, Stuttgart, **2013**, pp. 1-42; c) H. F. T. Klare, M. Oestreich, *Dalton Trans* **2010**, *39*, 9176-9184; d) A. Sekiguchi, V. Y. Lee, *Organometallic compounds of low-coordinate Si, Ge, Sn and Pb*, Wiley, Chichester, **2010**; e) V. Y. Lee, *Russ. Chem. Rev.* **2019**, *88*, 351–369; f) Q. Wu, E. Irran, R. Müller, M. Kaupp, H. F. T. Klare, M. Oestreich, *Science* **2019**, *365*, 168-172; g) J. C. L. Walker, H. F. T. Klare, M. Oestreich, *Nat. Rev. Chem.* **2020**, *4*, 54-62; h) J. S. Siegel, *Nat. Rev. Chem.*, **2020**, *4*, 4-5; i) H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, M. Oestreich, *Chem. Rev.* **2021**, *121*, doi.org/10.1021/acs.chemrev.0c00855.

[2] a) K. Hara, R. Akiyama, M. Sawamura, *Org. Lett.* **2005**, *7*, 5621-5623; b) R. K. Schmidt, K. Müther, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2012**, *134*, 4421-4428; c) H. F. T. Klare, K. Bergander, M. Oestreich, *Angew. Chem. Int. Ed.* **2009**, *48*, 9077-9079. *Angew. Chem.* **2009**, *121*, 9241-9243; d) A. R. Nödling, K. Müther, V. H. G. Rohde, G. Hilt, M. Oestreich, *Organometallics* **2014**, *33*, 302-308; e) A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 12636-12638. *Angew. Chem.* **2011**, *123*, 12845-12848; f) M. Reißmann, A. Schäfer, S. Jung, T. Müller, *Organometallics* **2013**, *32*, 6736-6744; g) L. Omann, Z.-W. Qu, E. Irran, H. F. T. Klare, S. Grimme, M. Oestreich, *Angew. Chem. Int. Ed.* **2018**, *57*, 8301-

8305. *Angew. Chem.* **2018**, *130*, 8433-8437; h) M. Devillard, B. de Bruin, M. A. Siegler, J. I. van der Vlugt, *Chem. Eur. J.* **2017**, *23*, 13628-13632 ; i) V. J. Scott, Ç.-Ç. Remle, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 2852-2853; j) C. Douvris, O. V. Ozerov, *Science*, **2008**, *321*, 1188-1190; k) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946-4953; l) N. Lühmann, H. Hirao, S. Shaik, T. Müller, *Organometallics* **2011**, *30*, 4087-4096; m) N. Lühmann, R. Panisch, T. Müller, *Appl. Organomet. Chem.* **2010**, *24*, 533-537; n) O. Allemann, S. Duttwyler, K. K.; Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574-577; o) T. Stahl, H. F. T. Klare, M. Oestreich, *ACS Catal.* **2013**, *3*, 1578-1587; p) N. Kordts, S. Künzler, S. Rathjen, T. Sieling, H. Großekappenberg, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2017**, *23*, 10068-10079; q) I. Mallov, A. J. Ruddy, H. Zhu, S. Grimme, D. W. Stephan, *Chem. Eur. J.* **2017**, *23*, 17692-17696; r) M. Reißmann, A. Schäfer, S. Jung, T. Müller, *Organometallics* **2013**, *32*, 6736-6744; s) Q.-A. Chen, H. F. T. Klare, M. Oestreich, *J. Am. Chem. Soc.* **2016**, *138*, 7868-7871; t) H. Arii, Y. Yano, K. Nakabayashi, S. Yamaguchi, M. Yamamura, K. Mochida, T. Kawashima, *J. Org. Chem.* **2016**, *81*, 6314-6319.

[3] a) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Für Chem.* **1975**, *106*, 1235–1257. b) M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530–533.

[4] a) L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881–17896; b) J. C. Haartz, D. H. McDaniel, *J. Am. Chem. Soc.* **1973**, *95*, 8562–8565.

[5] S. Künzler, S. Rathjen, A. Merk, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2019**, *25*, 15123–15130.

[6] For an early study, see: V. H. G. Tohde, P. Pommerening, H. F. T. Klare, M. Oestreich, *Organometallics*, **2014**, *33*, 3618-3628.

[7] P. Ducos, V. Liautard, F. Robert, Y. Landais, *Chem. Eur. J.* **2015**, *21*, 11573-11578.

[8] J. Y. Corey, *J. Am. Chem. Soc.* **1975**, *97*, 3237-3238.

[9] A. Fernandes, C. Laye, S. Pramanik, D. Palmeira, Ö. Ö. Pekel, S. Massip, M. Schmidtmann, T. Müller, F. Robert, Y. Landais, *J. Am. Chem. Soc.* **2020**, *142*, 564–572.

[10] For recent examples of anchimeric assistance in derivatives with Si-centered chirality, see: a) T. Müller, S. Künzler, S. Rathjen, K. Rüger, M. S. Würdemann, M. Wernke, P. Tholen, C. Girschik, M. Schmidtmann, Y. Landais, *Chem. Eur. J.* **2020**, *26*, 16441-16449; b) N. Fontana, N. A. Espinosa-Jalapa, M. Seidl, J. O. Bauer, *Chem. Eur. J.* **2021**, *27*, 2649-2653.

[11] A.-M. Lord, M. F. Mahon, M. D. Lloyd, M. D. Threadgill, *J. Med. Chem.* **2009**, *52*, 868–877.

[12] C. Zang, Y. Liu, Z.-J. Xu, C.-W. Tse, X. Guan, J. Wei, J.-S. Huang, C.-M. Che, *Angew. Chem. Int. Ed.* **2016**, *55*, 10253–10257. *Angew. Chem.* **2016**, *128*, 10409-10413.

[13] J. A. Joule, K. Mills, Heterocyclic Chemistry, Wiley, Hoboken, N.J, 2009.

[14] J. Clayden, *Organolithiums: Selectivity for Synthesis*, Tetrahedron Organic Chemistry Series, Pergamon, Oxford, **2002**, Vol 23.

[15] T.E. Harmon, D. A. Shirley, *J. Org. Chem.* **1974**, *21*, 3164-3165.

[16] J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917-1918.

[17] W. Huynh, M. Conley, *Dalton Trans.* **2020**, *49*, 16453-16463.

[18] K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, *Science* **2002**, *297*, 825-827.

[19] G. Höfle, W. Steglich, H. Vorbrüggen, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 569-583. *Angew. Chem.* **1978**, *90*, 602-615.

[20] K. Hensen, T. Zengerly, P. Pickel, G. Klebe, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 725–726. *Angew. Chem.* **1983**, *95*, 739-739.

[21] P. S. Pregosin, *Prog. Nucl. Magn. Reson. Spectrosc.* **2006**, *49*, 261-288.

[22] D. P. Valencia, F. J. González, *Electrochem. Commun.* **2011**, *13*, 129-132.

[23] Enamines from pyrrolidines are known to possess nitrogen lone pair having higher p-character than those from piperidines, thus showing higher reactivity towards electrophiles, see: a) B. Kempf, N. Hampel, A. R. Ofial, H. Mayr, *Chem. Eur. J.* **2003**, *9*, 2209-2218; b) S. Lakhdar, B. Maji, H. Mayr, *Angew. Chem., Int. Ed.* **2012**, *51*, 5739-5742. *Angew. Chem.* **2012**, *124*, 5837-5840.