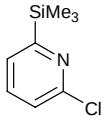
Electronic Supporting Information

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a JEOL EX 400 NMR and JEOL lambda 300 NMR spectrometer operating at a frequency of 300 MHz for ^{1}H, ^{13}C and 400 MHz for ^{29}Si. 1H NMR spectra were referenced to the $CDCl_3$ (7.26 ppm) signal, ^{13}C NMR spectra were referenced to the $CDCl_3$ (77.67 ppm) signal and ^{29}Si NMR spectra were referenced to TMS (0.0 ppm). Melting points were taken on a Gallenkamp heating block and are uncorrected. Micro-analysis of the samples was performed by MEDAC Ltd. of Brunel University. All reactions were carried out under nitrogen atmosphere. Toluene dried, distilled over sodium wire and and stored over Linde 4Å molecular sieve. Chloroform dried, distilled over calcium hydride powder.

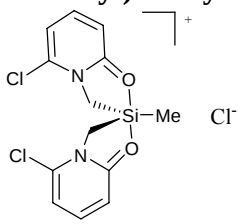
6-Chloro-2-trimethylsiloxypyridine.



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 analysis.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ= 0.36 (9H, s, $SiMe_3$) and 6.5–7.6 (3H, m, arom); **^{13}C NMR** (300 MHz, $CDCl_3$, Me_4Si) δ=0.29, 113.5 (C3), 123.8 (C4), 138.4 (C5), 145.3 (C6) and 160.8 (C2); **^{29}Si NMR** (400 MHz, $CDCl_3$, Me_4Si): δ=22.4.
4.3 g, 85%, bp 67 ^{o}C/3 mmHg;

Synthesis of Bis(6-chloropyridonemethyl)methylsilicon chloride(4)



Bis-Chloromethylmethylchlorosilane, (0.23 g, 1.3 mmol) was added slowly to a stirred solution of 2-trimethylsiloxypyridine (0.5g, 2.6 mmol) in dry toluene under nitrogen. The reaction mixture was stirred for 1 h and than heated with a hot-air gun. The solid was filtered under nitrogen and dried under vacuum to afford 0.9g, 90% yield and crystallized for X-ray analysis from hot chloroform to get colourless crystals. In the elemental analysis we consistently find that the found % for the C analysis is approximately 2% lower than the calculated value despite the use of combustion aids. This is presumably due to silicon carbide formation.

NMR: ^{1}H (300 MHz, $CDCl_3$, Me_4Si): δ=0.50 (3H, s, SiMe), 3.56, 4.19 (4H, dd, J_{ab}= 16.8Hz, 2 x NCH_aH_b), and 6.6–7.9 (6H, m, arom); ^{13}C (300 MHz, $CDCl_3$, Me_4Si): δ= 1.4 (SiMe), 37.9 (NCH2), 112.3 (C5), 115.2 (C3), 142.1 (C6), 144.8 (C4) and 163.8 (C2); ^{29}Si (400 MHz, $CDCl_3$, Me_4Si): δ= -47.5. m.p. 91–94 ^{o}C. Elemental analysis: Calculated for $C_{16}H_{20}Cl_3N_2O_2Si$: C, 47.24; H, 4.96; Cl, 26.15; N, 6.89; Found: C, 45.50; H, 4.73; Cl, 25.58; N, 7.58.

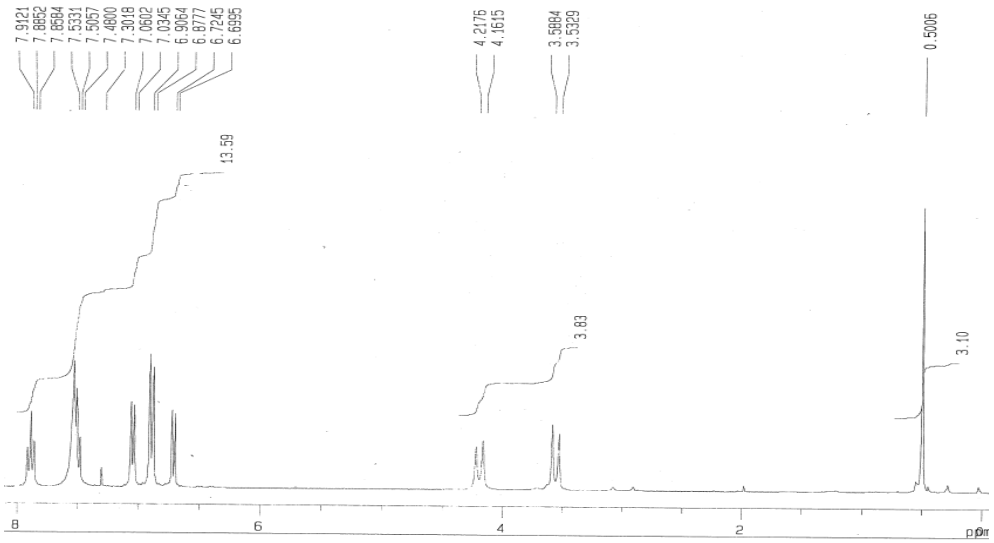


Fig. S1 ^{1}H (300.40 MHz) NMR spectrum of **4** in $CDCl_3$ solution at 22.7^{o}C.

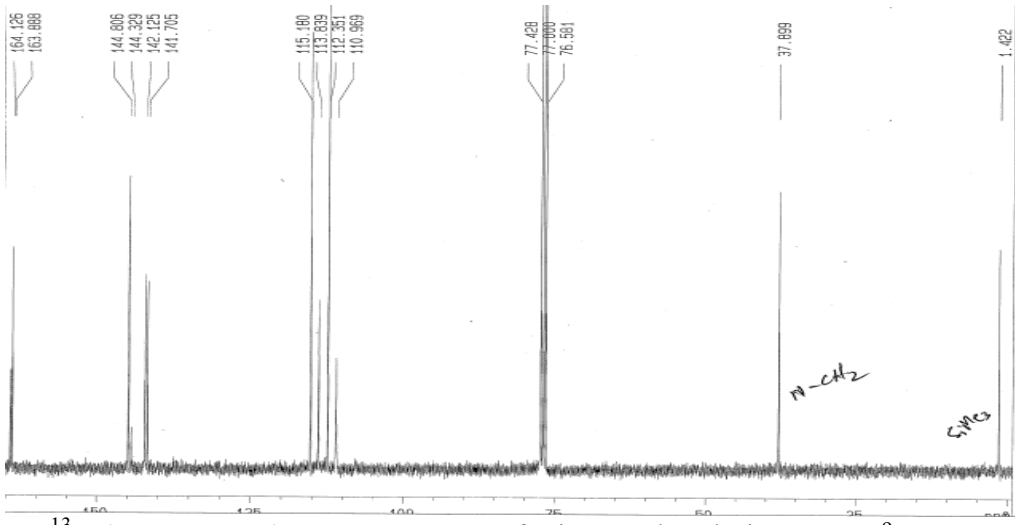


Fig.S2 ^{13}C (300.40 MHz) NMR spectrum of **4** in $CDCl_3$ solution at 23.3^{o}C

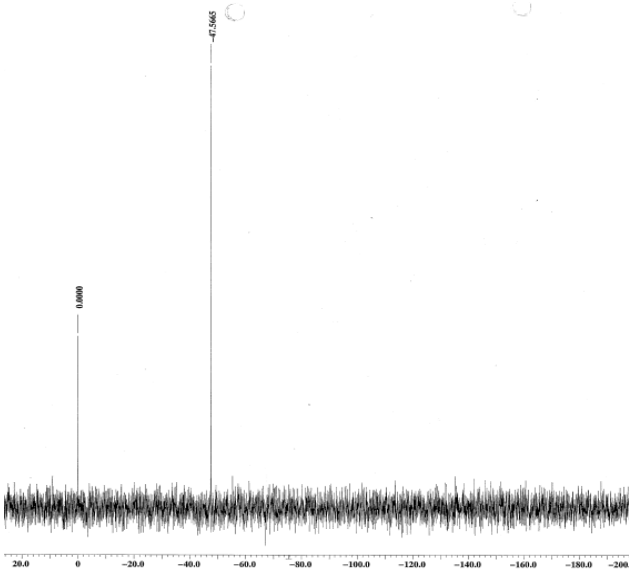


Fig.S3 ^{29}Si (400.00 MHz) NMR spectrum of **4** in $CDCl_3$ (TMS as an internal reference) solution at 20.3°C

The experimental details of X-ray structural studies.

Crystals of $C_{18}H_{19}Cl_4N_3O_4Si$ are monoclinic, space group $P2_1/n$, a = 7.6414(8) Å, b = 21.915(2) Å, c = 12.8697(14) Å, β = 96.267(2)° V = 2142.3(4) Å^3, Z = 4, M = 511.25, d_{calc} = 1.585 g cm^{-3}, μ(MoKα) = 6.40 cm^{-1}, F(000) = 1048. The single crystal of studied was small colorless prism with dimensions 0.20 × 0.15 × 0.12 mm. Intensities of 26805 reflections were measured with a Smart APEX II diffractometer at 100K [λ(MoKα) = 0.71073 Å, ω-scans, θ < 30.03°, 3 runs with 5 s exposition per frame]. 6212 independent reflections (R_{int} = 0.0325) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation. Hydrogen atoms were located from the difference Fourier map and refined in isotropic approximation. The refinement converged to wR_2 = 0.0958 and GOF = 1.014 for all independent reflections [R_1 = 0.0374 was calculated against F for 5481 observed reflections with $I > 2\sigma(I)$]. Main structural parameters are summarized in Table 1s.

Crystals of $C_{44}H_{49}Cl_{12}N_7O_9Si_3$ are triclinic, space group $P\text{-}1$, a = 13.549(5) Å, b = 15.753(6) Å, c = 16.005(7) Å, α = 67.998(8)°, β = 74.146(9)°, γ = 66.783(7)°, V = 2879(2) Å^3, Z = 2, M = 1329.57, d_{calc} = 1.534 g cm^{-3}, μ(MoKα) = 6.97 cm^{-1}, F(000) = 1360. The single crystal studied was small colorless prism with dimension 0.23 × 0.20 × 0.08. Intensities of 12355 reflections were measured with a Smart APEX II diffractometer at 100K [λ(MoKα) = 0.71073 Å, ω-scans, θ < 27.10°, 3 runs with 10 s exposition per frame]. The single crystal of 1 was a twin. The integral intensities of measured reflections were treated as superposition of two domains in 1:1 ratio. The second domain was rotated from first domain by 180.0 degrees about reciprocal axis 0.000 -0.002 1.000 and real axis -0.176 -0.317 1.000. 12463 independent reflections were used in further refinement. Separate scale factors for reflections from both domains (HKLF 5 and BASF instructions). The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation. Hydrogen atoms were located from the difference Fourier map and

refined in isotropic approximation. The refinement converged to wR_2 = 0.1408 and GOF = 1.003 for all independent reflections [R_1 = 0.0536 was calculated against F for 9987 observed reflections with $I > 2\sigma(I)$]. Main structural parameters are summarized in Table 1s.

Table 1s. Selected bond lengths [pm] and angles [°]: *(except cation the Si…Cl distances also included)*

TBP-model notation (ideal value)	4a		4b	4c		4d	
Si–1	Si(1)-O(1)	184.71(12)	186.4(3)	Si(1A)-O(1A)	186.6(3)	Si(1B)-O(1B)	187.1(3)
Si–2	Si(1)-C(2)	189.28(16)	188.5(5)	Si(1A)-C(2A)	189.0(4)	Si(1B)-C(2B)	189.3(4)
Si–3	Si(1)-C(1)	184.75(17)	184.2(4)	Si(1A)-C(1A)	185.3(4)	Si(1B)-C(1B)	186.1(4)
Si–4	Si(1)-C(8)	189.55(16)	191.3(5)	Si(1A)-C(8A)	189.4(4)	Si(1B)-C(8B)	189.6(4)
Si–5	Si(1)-O(2)	187.37(12)	185.8(3)	Si(1A)-O(2A)	185.8(3)	Si(1B)-O(2B)	185.9(3)
	Si(1)…Cl(3)	410.49(7)	354.1(2)	Si(1A)…Cl(3A)	396.5(2)	Si(1B)…Cl(3B)	390.5(2)
	O(1)-C(3)	129.01(19)	127.6(5)	O(1A)-C(3A)	128.9(5)	O(1B)-C(3B)	128.5(5)
	C(3)-N(1)	136.69(19)	137.1(6)	C(3A)-N(1A)	136.3(5)	C(3B)-N(1B)	136.5(5)
	N(1)-C(2)	147.38(19)	147.1(5)	N(1A)-C(2A)	148.3(5)	N(1B)-C(2B)	148.6(5)
	C(3)-C(4)	140.7(2)	141.0(6)	C(3A)-C(4A)	140.2(6)	C(3B)-C(4B)	140.9(6)
	C(4)-C(5)	137.1(2)	136.8(7)	C(4A)-C(5A)	136.6(6)	C(4B)-C(5B)	135.2(6)
	C(5)-C(6)	140.1(2)	139.3(7)	C(5A)-C(6A)	140.2(6)	C(5B)-C(6B)	141.1(6)
	C(6)-C(7)	136.5(2)	136.0(6)	C(6A)-C(7A)	136.3(6)	C(6B)-C(7B)	136.8(6)
	C(7)-N(1)	136.1(2)	136.0(6)	C(7A)-N(1A)	137.0(5)	C(7B)-N(1B)	136.7(5)
	C(7)-Cl(1)	171.06(16)	172.2(5)	C(7A)-Cl(1A)	170.8(4)	C(7B)-Cl(1B)	171.3(4)
	O(2)-C(9)	128.93(19)	129.1(5)	O(2A)-C(9A)	128.9(5)	O(2B)-C(9B)	128.5(5)
	C(9)-N(2)	137.0(2)	136.8(5)	N(2A)-C(9A)	136.8(5)	N(2B)-C(9B)	136.9(5)
	N(2)-C(8)	147.25(19)	146.5(5)	N(2A)-C(8A)	147.0(5)	N(2B)-C(8B)	148.3(5)
	C(9)-C(10)	140.3(2)	139.9(6)	C(9A)-C(10A)	140.0(6)	C(9B)-C(10B)	140.8(6)
	C(10)-C(11)	137.4(3)	136.1(6)	C(10A)-C(11A)	137.0(6)	C(10B)-C(11B)	137.2(6)
	C(11)-C(12)	140.1(3)	141.0(6)	C(11A)-C(12A)	139.4(6)	C(11B)-C(12B)	139.3(6)
	C(12)-C(13)	136.4(2)	135.5(6)	C(12A)-C(13A)	136.5(6)	C(12B)-C(13B)	134.5(6)
	C(13)-N(2)	136.6(2)	136.5(5)	C(13A)-N(2A)	136.0(5)	C(13B)-N(2B)	136.3(5)
	C(13)-Cl(2)	170.73(18)	171.4(4)	C(13A)-Cl(2A)	171.9(4)	C(13B)-Cl(2B)	172.0(4)
θ_{12} (90)	O(1)-Si(1)-C(2)	86.38(6)	85.77(17)	O(1A)-Si(1A)-C(2A)	85.84(15)	O(1B)-Si(1B)-C(2B)	85.57(15)
θ_{13} (90)	O(1)-Si(1)-C(1)	95.53(7)	97.11(17)	O(1A)-Si(1A)-C(1A)	96.99(17)	O(1B)-Si(1B)-C(1B)	95.21(17)
θ_{14} (90)	O(1)-Si(1)-C(8)	88.35(6)	88.51(16)	O(1A)-Si(1A)-C(8A)	89.86(15)	O(1B)-Si(1B)-C(8B)	88.39(15)
θ_{15} (180)	O(1)-Si(1)-O(2)	168.98(6)	165.72(15)	O(2A)-Si(1A)-O(1A)	167.04(14)	O(2B)-Si(1B)-O(1B)	169.30(15)

θ_{23} (120)	C(2)-Si(1)-C(1)	117.42(8)	112.3(2)	C(1A)-Si(1A)-C(2A)	119.33(19)	C(1B)-Si(1B)-C(2B)	116.4(2)
θ_{24} (120)	C(2)-Si(1)-C(8)	122.74(7)	132.67(19)	C(2A)-Si(1A)-C(8A)	128.66(19)	C(2B)-Si(1B)-C(8B)	125.77(19)
θ_{25} (90)	C(2)-Si(1)-O(2)	89.44(6)	89.11(17)	O(2A)-Si(1A)-C(2A)	86.99(15)	O(2B)-Si(1B)-C(2B)	89.76(15)
θ_{34} (120)	C(1)-Si(1)-C(8)	119.84(8)	115.0(2)	C(1A)-Si(1A)-C(8A)	111.98(19)	C(1B)-Si(1B)-C(8B)	117.77(19)
θ_{35} (90)	C(1)-Si(1)-O(2)	95.45(7)	97.17(17)	C(1A)-Si(1A)-O(2A)	95.93(17)	C(1B)-Si(1B)-O(2B)	95.48(17)
θ_{45} (90)	C(8)-Si(1)-O(2)	85.34(6)	85.18(16)	C(8A)-Si(1A)-O(2A)	86.21(15)	C(8B)-Si(1B)-O(2B)	86.54(15)
	Si(1)-O(1)-C(3)	115.15(10)	115.0(3)	Si(1A)-O(1A)-C(3A)	114.9(3)	Si(1B)-O(1B)-C(3B)	114.4(2)
	O(1)-C(3)-N(1)	116.44(13)	116.7(4)	O(1A)-C(3A)-N(1A)	116.3(4)	O(1B)-C(3B)-N(1B)	116.6(4)
	C(3)-N(1)-C(2)	114.52(12)	114.0(4)	C(3A)-N(1A)-C(2A)	114.6(3)	C(3B)-N(1B)-C(2B)	114.2(3)
	N(1)-C(2)-Si(1)	107.27(10)	107.9(3)	N(1A)-C(2A)-Si(1A)	107.1(2)	N(1B)-C(2B)-Si(1B)	106.9(3)
	N(1)-C(3)-C(4)	119.52(14)	119.0(4)	N(1A)-C(3A)-C(4A)	119.1(4)	N(1B)-C(3B)-C(4B)	118.8(4)
	C(3)-C(4)-C(5)	118.89(15)	118.9(5)	C(3A)-C(4A)-C(5A)	119.3(4)	C(3B)-C(4B)-C(5B)	119.7(4)
	C(4)-C(5)-C(6)	120.93(15)	121.5(4)	C(4A)-C(5A)-C(6A)	121.0(4)	C(4B)-C(5B)-C(6B)	121.1(4)
	C(5)-C(6)-C(7)	118.50(15)	118.2(5)	C(5A)-C(6A)-C(7A)	118.6(4)	C(5B)-C(6B)-C(7B)	118.1(4)
	C(6)-C(7)-N(1)	121.36(14)	121.8(5)	C(6A)-C(7A)-N(1A)	120.7(4)	C(6B)-C(7B)-N(1B)	121.0(4)
	C(7)-N(1)-C(3)	120.77(13)	120.7(4)	C(7A)-N(1A)-C(3A)	121.3(3)	C(7B)-N(1B)-C(3B)	121.3(4)
	O(1)-C(3)-C(4)	124.04(14)	124.3(4)	O(1A)-C(3A)-C(4A)	124.6(4)	O(1B)-C(3B)-C(4B)	124.6(4)
	C(2)-N(1)-C(7)	124.70(13)	125.2(4)	C(2A)-N(1A)-C(7A)	124.1(3)	C(2B)-N(1B)-C(7B)	124.5(3)
	N(1)-C(7)-Cl(1)	116.82(11)	116.2(3)	N(1A)-C(7A)-Cl(1A)	116.6(3)	N(1B)-C(7B)-Cl(1B)	117.1(3)
	C(6)-C(7)-Cl(1)	121.81(13)	122.0(4)	C(6A)-C(7A)-Cl(1A)	122.6(3)	C(6B)-C(7B)-Cl(1B)	121.9(3)
	Si(1)-O(2)-C(9)	115.16(10)	114.7(3)	Si(1A)-O(2A)-C(9A)	114.9(3)	Si(1B)-O(2B)-C(9B)	115.1(3)
	O(2)-C(9)-N(2)	116.16(13)	116.2(3)	O(2A)-C(9A)-N(2A)	116.1(4)	O(2B)-C(9B)-N(2B)	116.7(4)
	C(9)-N(2)-C(8)	114.42(13)	114.4(3)	C(9A)-N(2A)-C(8A)	115.0(3)	C(9B)-N(2B)-C(8B)	114.7(3)
	N(2)-C(8)-Si(1)	108.10(10)	107.3(3)	N(2A)-C(8A)-Si(1A)	106.8(3)	N(2B)-C(8B)-Si(1B)	107.0(2)
	N(2)-C(9)-C(10)	119.60(15)	119.9(4)	N(2A)-C(9A)-C(10A)	119.7(4)	N(2B)-C(9B)-C(10B)	119.3(4)
	C(9)-C(10)-C(11)	118.64(16)	118.9(4)	C(9A)-C(10A)-C(11A)	119.0(4)	C(9B)-C(10B)-C(11B)	118.7(4)
	C(10)-C(11)-C(12)	121.35(16)	121.3(4)	C(10A)-C(11A)-C(12A)	121.1(4)	C(10B)-C(11B)-C(12B)	120.9(4)
	C(11)-C(12)-C(13)	118.28(16)	117.8(4)	C(11A)-C(12A)-C(13A)	118.1(4)	C(11B)-C(12B)-C(13B)	118.9(4)
	C(12)-C(13)-N(2)	121.33(16)	122.1(4)	C(12A)-C(13A)-N(2A)	122.0(4)	C(12B)-C(13B)-N(2B)	121.7(4)
	C(13)-N(2)-C(9)	120.73(14)	120.0(3)	C(13A)-N(2A)-C(9A)	120.1(4)	C(13B)-N(2B)-C(9B)	120.4(3)
	O(2)-C(9)-C(10)	124.24(15)	123.9(4)	O(2A)-C(9A)-C(10A)	124.1(4)	O(2B)-C(9B)-C(10B)	124.1(4)
	C(8)-N(2)-C(13)	124.84(13)	125.5(4)	C(8A)-N(2A)-C(13A)	124.9(3)	C(8B)-N(2B)-C(13B)	124.9(3)
	C(12)-C(13)-Cl(2)	121.76(13)	121.7(4)	C(12A)-C(13A)-Cl(2A)	122.0(3)	C(12B)-C(13B)-Cl(2B)	122.0(3)
	N(2)-C(13)-Cl(2)	116.91(12)	116.1(3)	N(2A)-C(13A)-Cl(2A)	116.0(3)	N(2B)-C(13B)-Cl(2B)	116.2(3)

Hydrogen bonds for structure containing cation 4a

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (º)
O1L—H1LA…Cl2	0.85	2.10	2.9478 (14)	174
O1W—H1WA…N1L	0.85	2.13	2.980 (2)	178

Hydrogen bonds for structure containing cations 4b-d

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (º)
O1W—H1WA...Cl3A	0.85	2.08	2.916 (3)	166
O1W—H1WB...Cl4	0.85	2.01	2.861 (5)	174
O1W—H1WC...N1L	0.85	1.76	2.611 (6)	179
O2W—H2WA...Cl3B	0.85	2.09	2.883 (3)	154
O2W—H2WB...Cl5	0.85	2.14	2.958 (4)	161
O2W—H2WC...Cl3	0.85	1.99	2.834 (5)	172