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Full Paper

Si-Functionalised Pyridines

Sequential Synthesis of Organosilicon-Linked 2-Methoxypyridines by Non-Cryogenic *ortho*-Metallation Using the *n*Bu$_2$TMPMg·Li Reagent and Hydrosilylation

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Abstract: The non-cryogenic synthesis of 5/6- and/or 3-silyl-functionalised 2-methoxypyridines by a 5-Br/Mg exchange process using *n*Bu$_2$*i*PrMg Li and LiCl and involving C-3 metallation using a novel *n*Bu$_2$TMPMg Li reagent is described. Furthermore, the usefulness of *n*Bu$_2$TMPMg Li in the functionalisation of 2-methoxypyridine at the 3-position with a wide range of electrophiles was successfully tested. The above achievements have allowed the construction of organosilicon-linked 2-methoxypyridines composed of two, three and four rings by the hydrosilylation of 5- and/or 3-SiH(or alkenyl) derivatives using the hitherto rarely applied [Pt(cod)Me$_2$] catalyst. Additionally, the synthesis of a one-chain oligomer consisting of eight 2-methoxypyridines obtained by the hydrosilylation/polymerisation approach, followed by protodesilylation of the SiHMe$_2$ group was also achieved by manipulating the amount of catalyst in the reactions.

Introduction

Organosilicon compounds[1] are of great importance in modern organic chemistry because of their usefulness in the protection of functional groups[2] and their broad application in, for example, asymmetric synthesis,[3] cross-coupling reactions[4] and natural product synthesis.[5] This class of compounds and related siloxanes are the subject of continuously growing interest due to their ability to form oligomers,[6] dendrimers[7] and polymers[8] and because of their unique properties, which have resulted in certain pivotal developments in the fields of silica-supported catalysis,[9] biosensors[10] and material[11] and nano sciences.[12] Moreover, the recognition of the silicon atom as a bio-isosteric unit[13] and its successful use in bioengineering[14] also indicate their great value in medicinal applications.[15]

Of numerous substituted pyridines, which form a class of versatile and most useful heterocycles (because of their utility in general synthesis,[16] the synthesis of biologically important compounds and their broad applicability in coordination[17] and supramolecular[18] chemistry as well as in material sciences), pyridylsilanes are recognised as a particularly practical combination. They have been applied, for example, in nicotine[19] and dihydrosilole[20] synthesis, in a variety of synthetic approaches based on the strong directing effect of silicon[21] and in the synthesis of new ligands[22] and materials.[23] The synthesis and synthetic applications of 2-methoxypyridylsilanes have been less studied, although the presence of a 2-methoxy group allows many synthetic transformations, for example, into NR and NH 2-pyridones, 2-chloro-substituted derivatives[24] or cross-coupled products obtained by the direct replacement of the 2-MeO group by aryl rings.[25]

Previously, 6-,[26] 5-,[27] 4-[28] or 3-functionalised[26b,28b,29] 2-methoxypyridines equipped with silicon-containing moieties were obtained by the halogen/lithium exchange method or *ortho*-metallation. In both procedures, organolithium reagents and cryogenic conditions are usually required.

However, recently we reported the synthesis of functionalised 2-methoxypyridines by a method based on a halogen/magnesium exchange process performed under non-cryogenic conditions (at 0 °C).[30] The starting substrates were 3-iodo-, 5-bromo- or 6-bromo-substituted 2-methoxypyridine derivatives, and the halogen/magnesium exchange agent was lithium di-*n*-butyl(isopropyl)magnesate (*n*Bu$_2$*i*PrMg Li + LiCl), which belongs to the relatively new and useful family of bimetallic "ate" complexes.[31] By applying this method we were able to obtain 3-, 5- or 6-trimethylsilyl-substituted 2-methoxypyridines at around 0 °C.[30]

Continuing our research program aimed at the development of new synthetic methods that do not require cryogenic conditions, also inspired by the potentially large number of applications of pyridylsilanes in materials sciences and coordination chemistry, we propose now a sequential, non-cryogenic synthesis of organosilicon-linked 2-methoxypyridine compounds (Scheme 1). The essential concept is based on the introduction of substituents containing alkenylSi and/or HSi groups, first at C-5 (or C-6) and subsequently at C-3, followed by the connection of the functionalised pyridine rings by hydrosilylation.[32] However, although we planned to achieve the initial functional-

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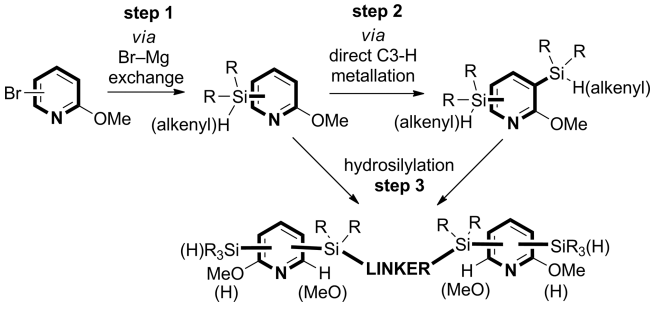
isations at C-5 or C-6 (Scheme 1, step 1) by using the previously described non-cryogenic bromine/magnesium exchange method,[30] we intended to accomplish the functionalisation at C-3 by a novel non-cryogenic direct metallation using organomagnesium "ate" complexes (Scheme 1, step 2).



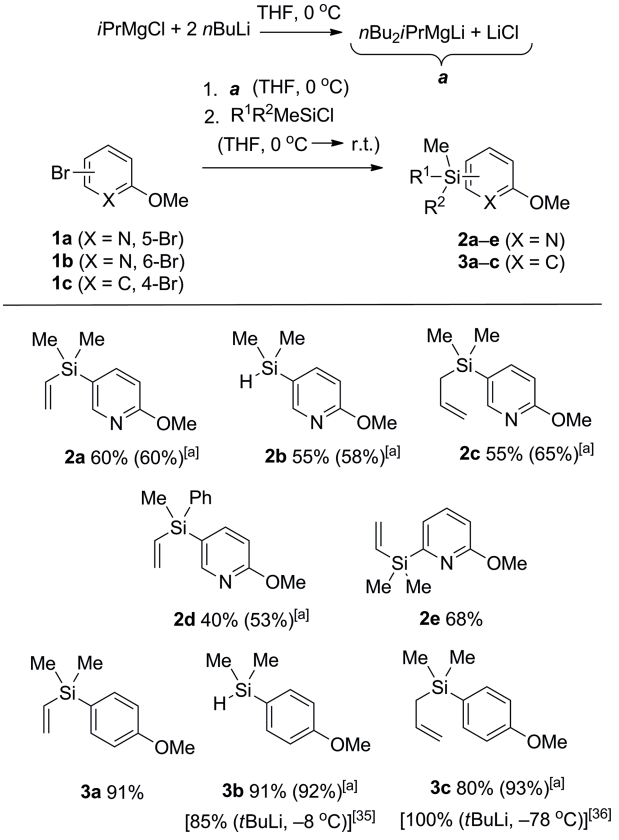
Scheme 1. Proposed strategy for the synthesis of organosilicon-linked 2-methoxypyridines.

Functionalisation at C-3 of 2-methoxypyridines by direct metallation, which is the original and key achievement of these studies, could offer a very effective alternative to functionalisation by the halide/metal exchange process and thus could attract widespread interest. It should be noted that although magnesates have been used previously for the direct CH metallation of a variety of heterocycles,[33] the *ortho*-metallation of 2-alkoxypyridine derivatives has been hitherto unreported. Furthermore, apart from this extension, the synthesis of linked 2-methoxypyridines seemed to be an interesting final synthetic objective, not only because of the potentially wide-ranging use of 2-methoxypyridylsilanes in materials and coordination chemistry, but also because of their possible further transformation into linked 2-pyridones, which could also be applied as ligands.[34]

Results and Discussion

In the first stage of our study, 5- and 6-silyl-functionalised 2-methoxypyridines were obtained according to the method mentioned above[30] by using commercially available HSi- or alkenylSi-functionalised chlorosilanes as electrophiles and in situ generated magnesate (nBu$_2$*i*PrMg Li + LiCl) as exchange reagent (Scheme 2). 2-Methoxypyridine products **2a**–**2e** were obtained on a few-gram scale in moderate or good yields and were purified mainly by distillation. By using the same protocol, anisole derivatives **3a**–**c** were also obtained for comparison by using 4-bromoanisole as substrate. The yields of these reactions were higher than those of the corresponding pyridine derivatives **2a**–**c** and comparable to that of **3b** and **3c** synthesised at low temperatures[35,36] (Scheme 2).

Next, we investigated the optimal conditions for the introduction of Si-functionalised moieties at C-3 of the 5-functionalised 2-methoxypyridines **2a**–**2e** by metallation at C-3 (*ortho*-metallation). For our first tests, we used the earlier obtained vinyl derivative **2a** and (chloro)dimethylsilane, varying the amount of deprotonating magnesate used (Table 1) and using a reaction temperature not lower than –5 °C. During the search for an efficient method for the *ortho*-metallation, we found that

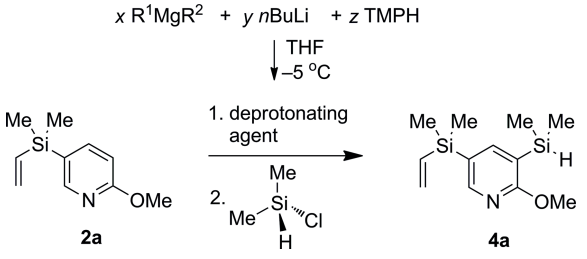


Scheme 2. Synthesis of 5-silyl-functionalised 2-methoxypyridines **2a**–**2e** and 4-silyl-functionalised anisoles **3a**–**3c**. [a] Yields estimated by ^{1}H NMR spectroscopy using an internal reference are given in the parentheses.

the use of magnesate, nBu$_2$*i*Pr(or nBu$_3$)Mg Li + LiCl, prepared simply by mixing organolithium and Grignard reagents, gave no positive results (Table 1, entries 1 and 2). Subsequently we used 2,2,6,6-tetramethylpiperidine (TMPH) because it had been successfully employed to prepare bimetallic magnesates with high deprotonative properties.[37] The use of the TMP-ligated magnesate nBu$_2$TMPMg Li + LiCl (or nBuTMP$_2$Mg Li + LiCl or TMP$_3$Mg Li + LiCl), obtained by mixing nBu$_2$*i*PrMg Li + LiCl and TMPH in a molar ratio of 1:1 (or 1:2 or 1:3, Table 1, entries 4–6) gave positive results. However, the best results (73 % yield) were achieved by the use of nBu$_2$TMPMg Li, with no LiCl in the reaction medium, despite an incomplete conversion (ca. 90 %; Table 1, entry 7). The latter reaction system was obtained by mixing equimolar amounts of nBu$_2$Mg, nBuLi and TMPH. Attempts to improve the reaction yields by extending the reaction time and raising the temperature were unsuccessful (Table 1, entries 8 and 10, respectively). Employment of the nBu$_3$Mg Li + 2LiBr and nBuTMP$_2$Mg Li + 2LiBr systems (at 22 °C), developed by Marsais and co-workers[33d], was also found to be less effective (Table 1, entries 11 and 12), similarly the use of TMPLi (Table 1, entries 13 and 14).

The results show that the application of the TMP ligand is crucial for the success of the synthesis by deprotonation and that the presence of the LiCl salt in the reaction media had a negative influence on the yield of **4a**. It should be noted that the negative effect of LiCl on deprotonation contrasts with

Table 1. Optimisation of the reaction conditions for the synthesis of **4a** by direct metallation at C-3 by using various organomagnesate and organolithium reagents prepared in situ.

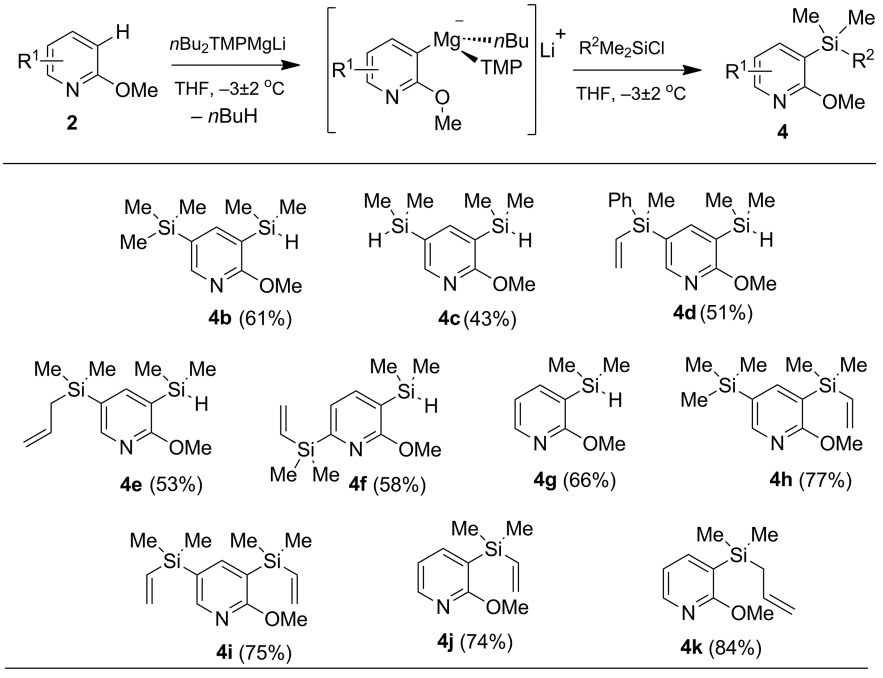


Entry[a]	R^1MgR^2 (amount [equiv.]) (*x*)	*n*BuLi [equiv.] (*y*)	TMPH [equiv.] (*z*)	Expected deprotonating agent[b,c]	*T* [°C]	Conv. of **2a** [%][d]	Yield of **4a** [%][e]
1	*n*BuMgCl (1.2) (1)	2.4 (2)	–	nBu_3Mg Li + LiCl	–5	–[f]	(0)
2	*i*PrMgCl (1.2) (1)	2.4 (2)	–	nBu_2iPrMg Li + LiCl	–5	–[f]	(0)
3	*n*BuMgCl (1.2) (1)	2.4 (2)	1.2 (1)	nBu_2TMPMg Li + LiCl	–5	–[f]	(29)
4	*i*PrMgCl (1.2) (1)	2.4 (2)	1.2 (1)	nBu_2TMPMg Li + LiCl	–5	79	(60)
5	*i*PrMgCl (1.2) (1)	2.4 (2)	2,4 (2)	$nBuTMP_2Mg$ Li + LiCl	–5	–[f]	(58)
6	*i*PrMgCl (1.2) (1)	2.4 (2)	3.6 (3)	TMP_3Mg Li + LiCl	–5	80	(42)
7	*n*BuMg*n*Bu (1.2) (1)	1.2 (1)	1.2 (1)	nBu_2TMPMg Li	–5	90	73 (73)
8	*n*BuMg*n*Bu (1.2) (1)	1.2 (1)	1.2 (1)	nBu_2TMPMg Li	–5	96	(65)[g]
9	*n*BuMg*n*Bu (1.2) (1)	1.2 (1)	2,4 (2)	$nBuTMP_2Mg$ Li	–5	–[f]	(25)
10	*n*BuMg*n*Bu (1.2) (1)	1.2 (1)	1.2 (1)	nBu_2TMPMg Li	22	–[f]	(53)
11	$MgBr_2$ (1.1) (1)	3.3 (3)	–	nBu_3Mg Li + 2LiBr	22	–[f]	(38)[h]
12	$MgBr_2$ (1.1) (1)	3.3 (3)	2.2 (2)	$nBuTMP_2Mg$ Li + 2LiBr	22	–[f]	(53)[h]
13	–	1.2 (1)	1.1 (0.9)	TMPLi[i]	–55	70	(40)
14	–	1.2 (1)	1.2 (1)	TMPLi[j]	–5	61	(40)

[a] Metallation was conducted over 1 h and 1.5 equiv. of Me_2HSiCl was used unless stated otherwise. [b] Proposed composition of deprotonating agent. [c] TMPH was added to the magnesium "ate" complex unless stated otherwise. [d] Conversions estimated by ^1H NMR spectroscopy. [e] Yields estimated by ^1H NMR spectroscopy using an internal reference are given in parentheses. [f] Not assigned. [g] Reaction was prolonged overnight. [h] 3.3 equiv. of Me_2HSiCl was used. [i] TMPLi was prepared at –30 °C. [j] Metallation was conducted over 1.5 h.

its positive influence on the Br/Mg exchange process (Scheme 2).[30] The dual, positive or negative, influence of the LiCl salt on the reaction course is an increasingly observed phenomenon.[38]

Having determined the optimised reaction conditions, we next extended 3-silyl functionalisation to the 5-silyl- and 6-silyl-substituted 2-methoxypyridine substrates **2a**–**2f** obtained in the former step as well as to unsubstituted 2-methoxypyridine

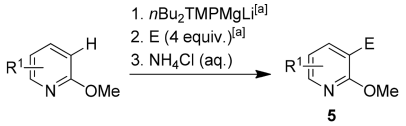


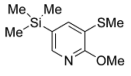
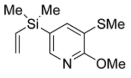
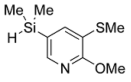
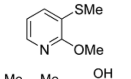
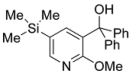
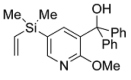
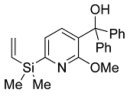
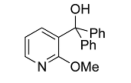
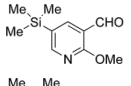
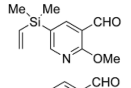
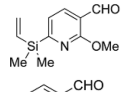
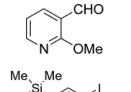
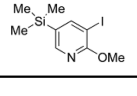
Scheme 3. 3-Silyl-functionalised 2-methoxypyridines obtained by *ortho*-metallation using the novel nBu_2TMPMg Li.

(Scheme 3) to identify substituent effects, if any. As a result, 3-functionalised products were obtained in moderate-to-good yields with no significant substituent effect of the 5- or 6-silyl-containing groups observed in comparison with unsubstituted 2-methoxypyridine.

Our next objective was to determine whether or not other 3-functionalised 2-methoxypyridines equipped with other substituents could be prepared by using the above optimised conditions for metallation at C-3. Thus, the 3-metallated intermediates were quenched with electrophiles such as $(MeS)_2$, DMF, Ph_2CO and I_2 (Table 2). As a result, 3-SMe (**5a**–**5d**), 3-$COHPh_2$ (**5e**–**5h**), 3-CHO (**5i**–**5l**) and 3-I (**5m**) substituted products were obtained, generally in good yields, except for the 3-CHO species, which were isolated in modest yields.

Table 2. 3-Functionalised 2-methoxypyridines obtained by *ortho*-metallation using the novel nBu_2TMPMg Li.



Entry	E	Product **5**	**5**	Isolated yield [%]
1	MeSSMe		**5a**	71
2	MeSSMe		**5b**	77
3	MeSSMe		**5c**	74
4	MeSSMe		**5d**	70
5	Ph_2CO		**5e**	68
6	Ph_2CO		**5f**	62
7	Ph_2CO		**5g**	73
8	Ph_2CO		**5h**	49
9	DMF		**5i**	41
10	DMF		**5j**	35
11	DMF		**5k**	57
12	DMF		**5l**	23
13	I_2		**5m**	60

[a] THF, −3 ± 2 °C.

Following the excellent structural studies of bimetallic complexes conducted by Mulvey and Robertson,[39] we proposed a structure for the intermediate magnesate (*n*Bu[2-MeO-3-pyridyl]TMPMg Li) optimised at the semi-empirical PM3 level of theory[40] (Figure 1). Because one THF solvent molecule usually takes part in the coordination to the lithium atom,[41] we calculated the proposed structure with one molecule of THF. The results show relatively short distances between Li and the surrounding atoms in the vicinity of the reactive site.

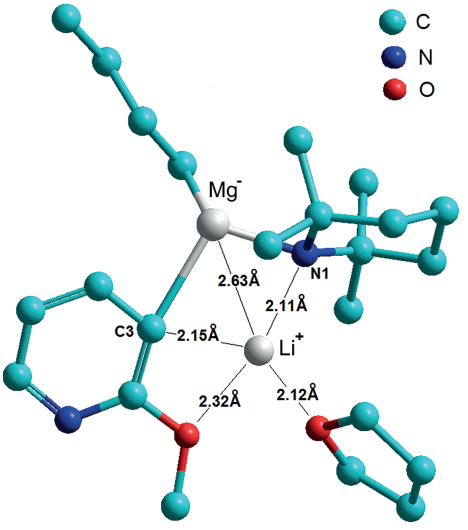


Figure 1. Proposed structure of the intermediate 2-methoxypyridine lithium–magnesium "ate" complex optimised at the semi-empirical PM3 level of theory with selected distances between Li and the surrounding atoms. Additional important bond lengths are: C3–Mg 2.37 Å; Mg–N1 1.89 Å (hydrogen atoms have been omitted for clarity).

The successful introduction of hydrosilyl and alkenylsilyl moieties into the 2-methoxypyridine ring has opened up further functionalisation possibilities. Numerous examples of modifications with hydrosilyl[42] and alkenylsilyl[43] groups have been described in the literature, and their conversions into other functional groups. Among them, the most important is the ability to produce covalent Si–C bonds by the insertion of an alkene into an Si–H bond.

The latter process, called hydrosilylation, is an ideal approach to the synthesis of a well-defined linkage between organic molecules.[32,44] Thus, in the next stage of this work we synthesised organosilicon-linked 2-methoxypyridine chains by hydrosilylation. Although hydrosilylation reactions can be carried out easily by using the most popular Karstedt or Speier catalysts due to their well-recognised high activity, we decided to check the applicability of $[Pt(cod)Me_2]$ (cod = cycloocta-1,5-diene; Figure 2). This commercially available catalyst has been used previously in certain cascade reactions,[45] however, to the best of our knowledge, there is only one article in the literature on its use in hydrosilylation.[46]

Before synthesising the linked-pyridine, we evaluated the activity of $[Pt(cod)Me_2]$ in toluene by monitoring by GC–MS the progress of the reaction between **2a** and **2b**, varying the amount of catalyst first at room temperature and then at 60 °C (see the Supporting Information). The optimisation revealed the

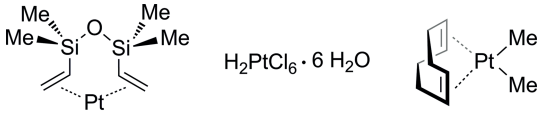
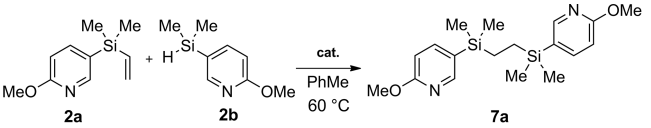


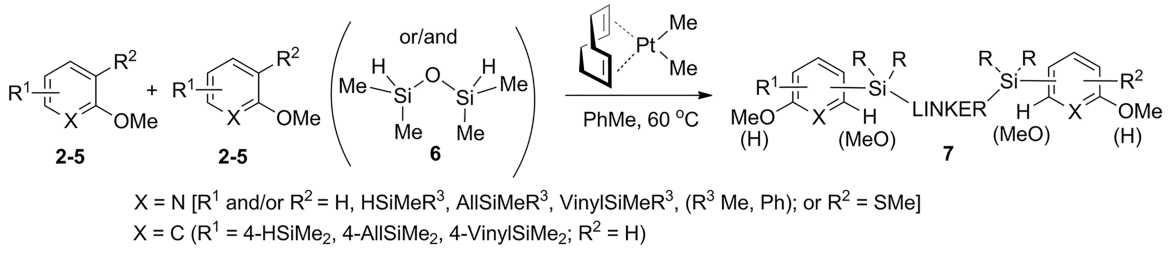
Figure 2. Karstedt [Pt^0], Speier [Pt^{IV}] and [Pt(cod)Me_2] [Pt^{II}] hydrosilylation catalysts.

completion of the reaction at 60 °C after 24 h by using 0.0425 mol-% of the catalyst, whereas at room temperature the reaction was completed after 6.5 days by using 0.125 mol-% of the catalyst. Repeating the reaction on the 5 mmol scale under the conditions assumed as optimal (60 °C, 24 h, 0.048 mol-% catalyst) gave product **7a** in an isolated yield of 88 %. These data allowed the maximum turnovers to be calculated: TON_{max} = 2083, actual turnover: TON = TON_{max} × 0.88 = 1833 and turnover frequency: TOF = 76 h^{-1} (Scheme 4). These results are similar to the data obtained by using the Karstedt catalyst under the same conditions, except for the fact that the latter reaction was faster (it was completed within 4 h, Scheme 4). TON_{actual} and TOF values of 1798 and 450 h^{-1}, respectively, were calculated for the reaction with the Karstedt catalyst. It should be noted that dry and deoxygenated toluene was not required.

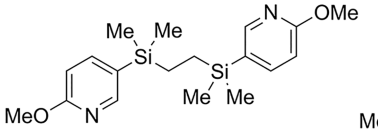


cat.	Time [h]	Yield **7a** [%]	TON_{max}	TON_{actual}	TOF [h^{-1}]
Pt(COD)Me$_2$ (0.048 mol-%)	24	88	2083	1833	76
Karstedt catalyst (0.040 mol-%)	4	72	2497	1798	450

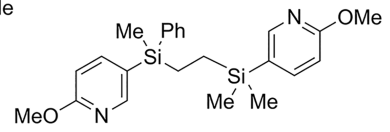
Scheme 4. Hydrosilylation of **2a** and **2b** using [Pt(cod)Me_2] and Karstedt catalysts.



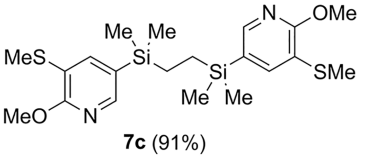
X = N [R^1 and/or R^2 = H, HSiMeR^3, AllSiMeR^3, VinylSiMeR^3, (R^3 Me, Ph); or R^2 = SMe]
X = C (R^1 = 4-HSiMe$_2$, 4-AllSiMe$_2$, 4-VinylSiMe$_2$; R^2 = H)



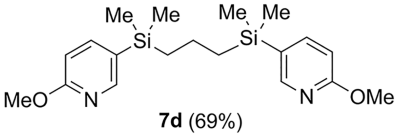
7a (88%)
(from **2a**, **2b**)



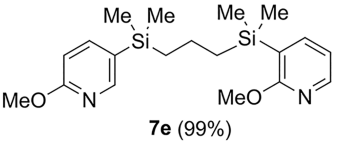
7b (98%)
(from **2b**, **2d**)



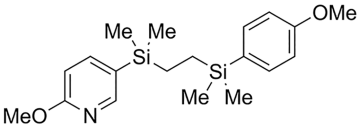
7c (91%)
(from **5b**, **5c**)



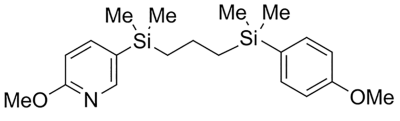
7d (69%)
(from **2b**, **2c**)



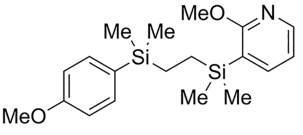
7e (99%)
(from **2c**, **4f**)



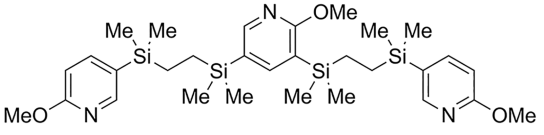
7f (77%)
(from **2a**, **3b**)



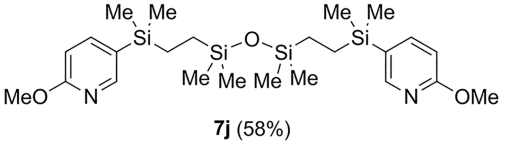
7g (63%)
(from **2c**, **3b**)



7h (46%)
(from **3a**, **4f**)



7i (63%)
(from **2b**, **4i**)

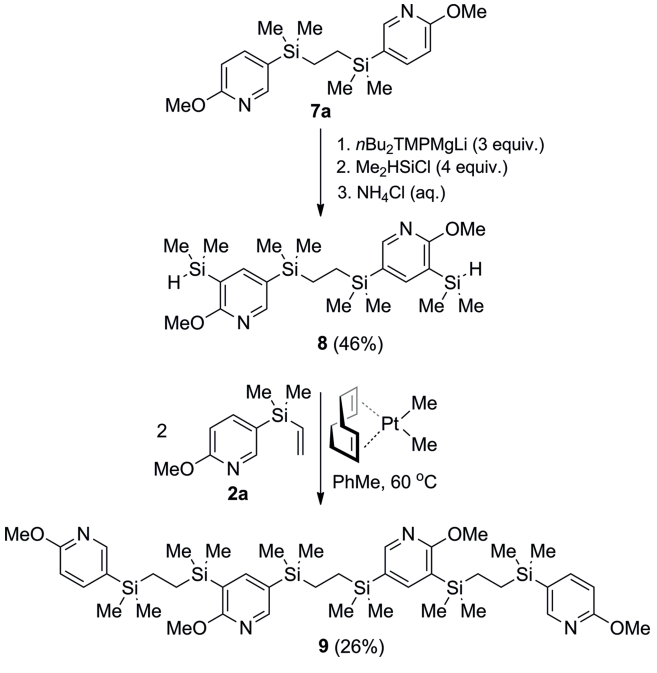


7j (58%)
(from **2a**, **6**)

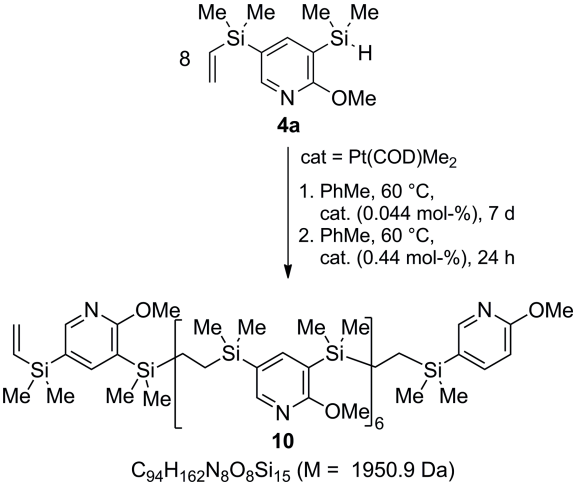
Scheme 5. Synthesis of organosilicon-linked 2-methoxypyridines by hydrosilylation using [Pt(cod)Me_2] as catalyst.

The above results and good product yields of the two-ring systems **7b**–**7h** in these reactions with [Pt(cod)Me_2] as catalyst showed that the functionalised 2-methoxypyridines and 4-functionalised anisole derivatives could be easily combined (Scheme 5). Furthermore, we found that by using this method, the three-ring system **7i** could be obtained by using bifunctional pyridine **4i**. In addition, the successful use of dihydrosiloxane **6** as a linker in the synthesis of **7j** indicates high prospects for the synthesis of similar linked bis-pyridine compounds because a large number or bifunctional SiH or Si(alkenyl) compounds are commercially available.

Encouraged by the successful synthesis of the three-ring system **7i**, we performed two additional preliminary experiments to explore whether it would be possible to obtain compounds with more than three connected 2-methoxypyridine rings. The first attempt was to obtain a four-ring system in a sequence of reactions comprising the introduction of two $SiMe_2H$ moieties by the bis-*ortho*-metallation of **7a** followed by hydrosilylation. The results presented in Scheme 6 show that this protocol was successful, however, although the double *ortho*-functionalisation led to the product **8** in 46 % yield, the hydrosilylation step gave a lower yield (26 %), which indicates the need for additional optimisation of the latter step. In a second attempt, the hydrosilylation/polymerisation of **4a** was performed by using [Pt(cod)Me_2] (Scheme 7). The reaction monitored by TLC showed that the substrate was very slowly consumed under the optimal conditions and that an additional portion of the catalyst, 10-fold bigger than that initially applied, was necessary to be added after 7 days. After an additional day of stirring, the reaction was complete (TLC indicated that the substrate was consumed). The results revealed, surprisingly, that the product **10**, which was isolated as a thick oil by precipitation from CH_2Cl_2 solution initiated by the addition of MeOH, as well as a number of other products of lower molecular weights (not isolated and assigned), did not contain a terminal $SiMe_2H$ group. The lack of this group was first identified by the absence of a Si–H band in the 2115–2103 cm^{-1} region of the IR spectra of the product **10** and the residue, whereas this band was present at 2120 cm^{-1} in the IR spectrum of substrate **4a**. Further structural analysis of **10** based on ^1H, ^{13}C, ^{13}C-DEPT-135 and ^{13}C–^1H correlation spectroscopy (see the Supporting Information) indicated eight interconnected rings of 2-methoxypyridine with a terminal dimethyl(vinyl)silyl group (located on one terminal 2-methoxypyridine ring) and the presence of a 3-H atom instead of a 3-Me_2SiH group on the second terminal ring (Scheme 6). MALDI-TOF analysis of the oligomer (see the Supporting Information) also supports the formation of eight-ring oligomer **10** as the average peak of the biggest *m/z* value appears at around 1933 (for the $[M + H]^+$ ion), which is close to the molar mass of **10** (1951 Da). It should be noted that repeated hydrosilylation/polymerisation of **4a** in dry and deoxygenated toluene gave the same result.



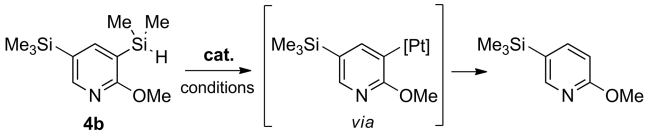
Scheme 6. Synthesis of organosilicon-linked 2-methoxypyridine **9** composed of four rings.



Scheme 7. Hydrosilylation/polymerisation of **4a**.

Obtaining the oligomerisation product **10** clearly indicates that apart from hydrosilylation, the [Pt(cod)Me_2] complex causes protodesilylation by cleavage of the C–Si bond between C-3 and $SiMe_2H$. To shed more light on this reaction, an additional experiment was performed to study the behaviour of the 3-$SiMe_2H$ group in **4a** by stirring in toluene in the presence of 0.044 mol-% of the catalyst [Pt(cod)Me_2] (which is the optimum amount used in the hydrosilylation reaction) and then in the presence of a 10-fold higher amount of the catalyst (0.44 mol-%). When a small amount of the catalyst was used, we observed only traces of the protodesilylation product (2-methoxy-5-(trimethylsilyl)pyridine, Scheme 8). On increasing the quantity of catalyst, 51 % yield of the desilylation product was obtained after 4 days. Almost the same results were observed with the Karstedt catalyst. These results indicate that protodesilylation as a side-reaction proceeds very slowly and only sparingly competes with hydrosilylation if a small amount of Pt catalyst is used, and that the desilylation process could be accelerated by increasing the quantity of the catalyst. This observation and the successful synthesis of the eight-ring oligomer **10** indicates that

manipulating the amount of the [Pt(cod)Me_2] catalyst could be potentially useful in the chain-length-controlled synthesis of linked poly-2-methoxypyridines by the hydrosilylation/polymerisation approach.



cat.	conditions	Yield [%][a]
Pt(COD)Me_2	PhMe, 60 °C, cat. (0.044 mol-%), 1 d	traces
Pt(COD)Me_2	PhMe, 60 °C, cat. (0.44 mol-%), 4 d	51
Karstedt catalyst	PhMe, 60 °C, cat. (0.44 mol-%), 4 d	49

[a] Assigned by GC-FID.

Scheme 8. Study of the influence of the quantity of Pt catalysts on the protodesilylation reaction.

Conclusions

We have extended the known synthesis of 2-methoxy-5-(trimethylsilyl)pyridines to other 5-silyl-functionalised derivatives by a Br/Mg exchange process using the *n*Bu_2*i*PrMg Li + LiCl reagent and developed a new method for the synthesis of 3-silyl-functionalised 2-methoxypyridines by a novel C3–H metallation using *n*Bu_2TMPMg Li as reagent. Both reactions were performed under non-cryogenic conditions. The successful installation of other substituents at the 3-position of 2-methoxypyridine using a wide range of electrophiles was also possible and indicated that the new *n*Bu_2TMPMg Li is a prospective reagent in *ortho*-metallation reactions. We have also demonstrated that the successful synthesis of HSi- and/or alkenylSi-functionalised 2-methoxypyridines opens up the possibility of synthesising pyridine-linked derivatives by hydrosilylation. In this field, the [Pt(cod)Me_2] catalyst, rarely used in hydrosilylation, was successfully employed in the synthesis of two- and three-ring systems. Four-pyridine- and eight-pyridine-ring systems were also constructed by combined double C-3 metallation/hydrosilylation and hydrosilylation/polymerisation, respectively. In the polymerisation approach, the effect of the amount of catalyst on the hydrosilylation and protodesilylation of the $SiHMe_2$ group has potential implications for controlling the chain length in oligomer synthesis. Further studies in this area are ongoing.

Experimental Section

General: See Supporting Information.

General Procedure for the Synthesis of 3-Functionalised 2-Methoxypyridines 4, 5 and 8 by *ortho*-Metallation: A 1.6 M solution of *n*BuLi in hexane (3.9 mL, 6.2 mmol) was added by syringe to a cooled (–4 ± 1 °C) and stirred mixture of 1.0 M *n*Bu_2Mg in heptane (6.2 mL, 6.2 mmol) and anhydrous THF (40 mL) in a Schlenk flask under argon. The mixture was stirred for 10 min at –4 ± 1 °C and anhydrous TMPH (1 mL; 6.2 mmol) was added by syringe and the mixture stirred for an additional 30 min. Subsequently, a precooled (–4 ± 1 °C) solution of the appropriate 2-methoxypyridine (5.2 mmol)* in anhydrous THF (5 mL) was added and the mixture stirred for 1 h at –4 ± 1 °C. Then the electrophile (20.8 mmol) was added and the mixture was continuously stirred for 1 h at 0 °C.** A saturated aq. solution of NH_4Cl was added, then extracted with EtOAc (2 × 75 mL) and the aqueous layer was separated. The combined organic layers were dried with $MgSO_4$, filtered, concentrated in vacuo and purified by distillation or flash column chromatography to give the corresponding products **4**, **5** and **8**. *In the synthesis of compound **8**, 2.07 mmol of substrate **7a** was used. **In the synthesis of compound **8**, the mixture was also stirred overnight.

3-(Dimethylsilyl)-5-[(ethenyl)dimethylsilyl]-2-methoxypyridine (4a): Yield 73 %. The crude product purified by distillation gave a colourless oil. B.p. 71–73 °C (4.0 mbar). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.33 (d, *J* = 3.7 Hz, 6 H, *Me*$_2$SiH), 0.34 (s, 6 H, Me_2Si), 3.95 (s, 3 H, OCH_3), 4.36 (sept, *J* = 3.7 Hz, 1 H, Si-H), 5.75 (dd, *J* = 20.1, 3.7 Hz, 1 H, =C*H*H), 6.06 (dd, *J* = 14.7, 3.7 Hz, 1 H, =CH*H*), 6.26 (dd, *J* = 20.1, 14.6 Hz, 1 H, =CH), 7.77 (d, *J* = 2.2 Hz, 1 H, 4-H), 8.26 (d, *J* = 2.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.31 [$Si(CH_3)_2$], –2.87 [$Si(CH_3)_2$], 53.19 (OCH_3), 118.56 (C-3), 124.08 (C-5), 133.18 (=CH_2), 137.49 (=CH), 150.58 (C-4), 153.59 (C-6), 168.40 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3052 (w), 3012 (w), 2956 (s), 2904 (w), 2120 (s), 1566 (s), 1548 (s), 1456 (s), 1400 (s), 1360 (m), 1350 (m), 1294 (s), 1248 (s), 1176 (w), 1122 (m), 1098 (m), 1020 (s), 956 (m), 900 (br. s), 838 (s), 814 (s), 792 (s), 776 (s), 700 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 251 (37) [M]$^{+\cdot}$, 250 (81), 237 (27), 236 (100), 224 (20), 210 (34), 206 (20), 192 (29), 177 (38), 162 (16), 89 (20), 59 (51). HRMS (ESI-TOF): calcd. for $C_{12}H_{22}NOSi_2$ 252.1240 [M + H]$^+$; found 252.1240.

3-(Dimethylsilyl)-2-methoxy-5-(trimethylsilyl)pyridine (4b): Yield 61 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.26 (s, 9 H, Me_3Si), 0.34 (d, *J* = 3.7 Hz, 6 H, *Me*$_2$SiH), 3.95 (s, 3 H, OCH_3), 4.37 (sept, *J* = 3.7 Hz, 1 H, Si-H), 7.78 (d, *J* = 2.1 Hz, 1 H, 4-H), 8.26 (d, *J* = 2.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.29 [$Si(CH_3)_2$], –1.08 [$Si(CH_3)_3$], 53.16 (OCH_3), 118.45 (C-3), 125.95 (C-5), 150.17 (C-4), 153.03 (C-6), 168.29 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3034 (w), 2956 (s), 2900 (w), 2120 (m), 1566 (s), 1548 (s), 1454 (s), 1398 (s), 1360 (m), 1348 (m), 1296 (s), 1264 (s), 1250 (s), 1176 (w), 1132 (s), 1100 (m), 1022 (s), 892 (s), 834 (s), 792 (s), 754 (m), 724 (w), 694 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 239 (21) [M]$^{+\cdot}$, 224 (100), 194 (12), 165 (32), 73 (17). HRMS (ESI-TOF): calcd. for $C_{11}H_{22}NOSi_2$ 240.1240 [M + H]$^+$; found 240.1237.

3,5-Bis(dimethylsilyl)-2-methoxypyridine (4c): Yield 43 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.34 [d, *J* = 3.7 Hz, 12 H, 2 × $Si(CH_3)_2$], 3.95 (s, 3 H, OCH_3), 4.37 (sept, *J* = 3.7 Hz, 1 H, SiH), 4.41 (sept, *J* = 3.7 Hz, 1 H, SiH), 7.80 (d, *J* = 2.0 Hz, 1 H, 4-H), 8.28 (d, *J* = 2.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.32, –3.74 [2 × $Si(CH_3)_2$], 53.22 (OCH_3), 118.71 (C-3), 123.16 (C-5), 150.74 (C-4), 153.64 (C-6), 168.53 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3008 (m), 2960 (s), 2904 (m), 2120 (s), 1566 (s), 1548 (s), 1454 (s), 1398 (s), 1360 (m), 1348 (m), 1296 (s), 1248 (s), 1176 (w), 1130 (s), 1098 (m), 1020 (s), 894 (s), 856 (s), 834 (s), 792 (s), 760 (m), 730 (m), 610 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%) = 225 (67) [M]$^{+\cdot}$, 224 (92), 210 (99), 195 (36), 194 (32), 180 (74), 166 (54), 151 (100), 136 (30), 89 (22), 59 (47). HRMS (ESI-TOF): calcd. for $C_{10}H_{20}NOSi_2$ 226.1083 [M + H]$^+$; found 226.1090.

3-(Dimethylsilyl)-5-[ethenyl(methyl)phenylsilyl]-2-methoxypyridine (4d): Yield 51 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.31 [d, *J* = 3.7 Hz, 6 H, $(CH_3)_2Si$], 0.62 (s, 3 H, SiMe), 3.95 (s, 3 H, OCH_3), 4.34 (sept, *J* = 3.6 Hz, 1 H, SiH), 5.79 (dd, *J* = 20.4, 3.8 Hz, 1 H, =C*H*H), 6.20 (dd, *J* = 14.7, 3.8 Hz, 1 H, =CH*H*), 6.45 (dd, *J* = 20.4, 14.7 Hz, 1 H, =CH), 7.34–7.40 (m, 3 H, C_6H_5), 7.50–

7.53 (m, 2 H, C_6H_5), 7.79 (d, *J* = 2.1 Hz, 1 H, 4-H), 8.26 (d, *J* = 2.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.52 [$Si(CH_3)_2$], –4.12 ($SiCH_3$), 53.22 (OCH_3), 118.69 (C-3), 122.13 (C-5), 127.93, 129.47, 134.68 (C_6H_5), 135.26 (=CH_2), 135.34 (=CH), 135.69 (C_6H_5), 151.32 (C-4), 154.67 (C-6), 168.53 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3052 (w), 3012 (w), 2948 (m), 2904 (w), 2124 (m), 1564 (s), 1548 (s), 1454 (s), 1428 (w), 1398 (s), 1360 (w), 1348 (w), 1296 (s), 1250 (s), 1176 (w), 1122 (s), 1020 (s), 958 (w), 886 (s), 836 (w), 792 (s), 732 (s), 700 (m), 634 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 313 (37) $[M]^{+\cdot}$, 312 (100), 298 (46), 286 (13), 254 (13), 239 (12), 121 (25). HRMS (ESI-TOF): calcd. for $C_{17}H_{24}NOSi_2$ 314.1396 $[M + H]^+$; found 314.1398.

5-[Dimethyl(prop-2-enyl)silyl]-3-(dimethysilyl)-2-methoxypyridine (4e): Yield 53 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.27 [s, 6 H, $Si(CH_3)_2$], 0.34 [d, *J* = 3.7 Hz, 6 H, $HSi(CH_3)_2$], 1.74 (dt, *J* = 8.1, 1.2 Hz, 2 H, CH_2), 3.95 (s, 3 H, OCH_3), 4.37 (sept, *J* = 3.7 Hz, 1 H, SiH), 4.84–4.90 (m, 2 H, =CH_2), 5.71–5.82 (m, 1 H, =CH), 7.77 (d, *J* = 2.2 Hz, 1 H, 4-H), 8.26 (d, *J* = 2.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.31 [$Si(CH_3)_2$], –3.40 [$Si(CH_3)_2$], 23.64 (CH_2), 53.19 (OCH_3), 113.73 (=CH_2), 118.49 (C-3), 124.28 (C-5), 134.25 (=CH), 150.42 (C-4), 153.33 (C-6), 168.39 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2960 (m), 2120 (m), 1630 (w), 1564 (m), 1548 (m), 1454 (m), 1400 (m), 1360 (w), 1296 (m), 1248 (m), 1132 (m), 1020 (w), 890 (s), 824 (m), 792 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 265 (3) $[M]^{+\cdot}$, 264 (7), 224 (100). HRMS (ESI-TOF): calcd. for $C_{13}H_{24}NOSi_2$ 266.1396 $[M + H]^+$; found 266.1389.

3-(Dimethylsilyl)-6-[(ethenyl)dimethylsilyl]-2-methoxypyridine (4f): Yield 58 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.32 [d, *J* = 3.7 Hz, 6 H, $HSi(CH_3)_2$], 0.37 [s, 6 H, $Si(CH_3)_2$], 3.96 (s, 3 H, OCH_3), 4.35 (sept, *J* = 3.7 Hz, 1 H, SiH), 5.82 (dd, *J* = 20.3, 3.8 Hz, 1 H, =CH*H*), 6.06 (dd, *J* = 14.7, 3.8 Hz, 1 H, =C*H*H), 6.33 (dd, *J* = 20.3, 14.7 Hz, 1 H, =CH), 7.07 (d, *J* = 6.8 Hz, 1 H, 5-H), 7.60 (d, *J* = 6.8 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.35 [$HSi(CH_3)_2$], –3.70 [$Si(CH_3)_2$], 52.91 (OCH_3), 118.37 (C-3), 122.83 (C-5), 132.94 (=CH_2), 137.40 (=CH), 143.38 (C-4), 164.98 (C-6), 166.80 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3048 (w), 3008 (w), 2960 (m), 2852 (w), 2120 (m), 1564 (s), 1538 (s), 1450 (s), 1404 (m), 1346 (s), 1292 (w), 1248 (s), 1194 (w), 1168 (w), 1066 (w), 1024 (m), 954 (w), 888 (s), 838 (s), 812 (s), 782 (s), 776 (s), 700 (w), 658 (w), 630 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 251 (63) $[M]^{+\cdot}$, 250 (100), 237 (22), 236 (91), 224 (25), 177 (40), 149 (34), 59 (42). HRMS (ESI-TOF): calcd. for $C_{12}H_{22}NOSi_2$ 252.1240 $[M + H]^+$; found 252.1243.

3-(Dimethylsilyl)-2-methoxypyridine (4g): Yield 66 %. The crude product purified by distillation gave a colorless oil; b.p. 85–87 °C (40.0 mbar). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.33 [d, *J* = 3.7 Hz, 6 H, $Si(CH_3)_2$], 3.95 (s, 3 H, OCH_3), 4.37 (sept, *J* = 3.7 Hz, 1 H, SiH), 6.85 (dd, *J* = 6.9, 5.1 Hz, 1 H, 5-H), 7.70 (dd, *J* = 6.9, 2.0 Hz, 1 H, 4-H), 8.18 (dd, *J* = 5.1, 2.0 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz $CDCl_3$): δ = –4.40 [$HSi(CH_3)_2$], 53.24 (OCH_3), 116.73 (C-5), 119.13 (C-3), 145.20 (C-4), 148.19 (C-6), 167.58 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3044 (w), 2956 (s), 2860 (w), 2124 (s), 1570 (s), 1532 (w), 1454 (s), 1386 (s),1296 (s), 1248 (s), 1084 (m), 1022 (s), 892 (s), 840 (m), 786 (s), 760 (w), 720 (w), 694 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 167 (28) $[M^{+\cdot}]$, 166 (55), 152 (30), 136 (30), 122 (100), 93 (26), 59 (28), 43 (17). HRMS (ESI-TOF): calcd. for $C_8H_{14}NOSi$ 168.0845 $[M + H]^+$; found 168.0841.

3-[(Ethenyl)dimethylsilyl]-2-methoxy-5-(trimethylsilyl)pyridine (4h): Yield 77 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.25 [s, 9 H, $Si(CH_3)_3$], 0.35 [s, 6 H, $Si(CH_3)_2$], 3.94 (s, 3 H, OCH_3), 5.77 (dd, *J* = 20.3, 3.7 Hz, 1 H, =C*H*H), 6.05 (dd, *J* = 14.7, 3.7 Hz, 1 H, =CH*H*), 6.35 (dd, *J* = 20.5, 14.7 Hz, 1 H, =CH), 7.72 (d, *J* = 2.1 Hz, 1 H, 4-H), 8.25 (d, *J* = 2.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.32 [$Si(CH_3)_2$], –1.08 [$Si(CH_3)_3$], 53.00 (OCH_3), 119.28 (C-3), 125.81 (C-5), 132.53 (=CH_2), 137.62 (=CH), 149.67 (C-4), 152.82 (C-6), 168.27 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3052 (w), 3008 (w), 2952 (s), 2900 (w), 1566 (s), 1548 (s), 1454 (s), 1398 (s), 1348 (m), 1296 (s), 1250 (s), 1176 (w), 1132 (m), 1096 (m), 1022 (s), 954 (m), 882 (s), 836 (s), 814 (s), 792 (m), 772 (m), 756 (m), 694 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 265 (13), 264 (22), 250 (100), 224 (21), 220 (43), 208 (13), 73 (19). HRMS (ESI-TOF): calcd. for $C_{13}H_{24}NOSi_2$ 266.1396 $[M + H]^+$; found 266.1388.

3,5-Bis[(ethenyl)dimethylsilyl]-2-methoxypyridine (4i): Yield 75 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.33 [s, 6 H, $Si(CH_3)_2$], 0.35 [s, 6 H, $Si(CH_3)_2$], 3.94 (s, 3 H, OCH_3), 5.73 (dd, *J* = 6.5, 3.7 Hz, 1 H, =C*H*H), 5.78 (dd, *J* = 6.5, 3.7 Hz, 1 H, =C*H*H), 6.03 (t, *J* = 3.9 Hz, 1 H, =CH*H*), 6.07 (t, *J* = 3.9 Hz, 1 H, =CH*H*), 6.25 (dd, *J* = 20.2, 14.6 Hz, 1 H, =CH), 6.34 (dd, *J* = 20.2, 14.6 Hz, 1 H, =CH), 7.72 (d, *J* = 2.1 Hz, 1 H, 4-H), 8.25 (d, *J* = 2.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.31 [$Si(CH_3)_2$], –3.9 [$Si(CH_3)_2$], 53.03 (OCH_3), 119.39 (C-3), 123.93 (C-5), 132.53 (=CH_2), 133.11 (=CH_2), 137.56 (=CH), 137.61 (=CH), 150.10 (C-4), 153.41 (C-6), 168.41 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3052 (w), 3012 (w), 2956 (m), 1564 (s), 1548 (m), 1454 (s), 1396 (s), 1350 (w), 1294 (m), 1250 (s), 1176 (w), 1124 (m), 1096 (w), 1022 (m), 954 (m), 878 (s), 838 (s), 810 (s), 774 (m), 694 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 277 (16) $[M]^{+\cdot}$, 276 (33), 263 (24), 262 (91), 232 (54), 220 (19), 89 (20), 85 (42), 59 (100), 43 (17). HRMS (ESI-TOF): calcd. for $C_{14}H_{24}NOSi_2$ 278.1396 $[M + H]^+$; found 278.1399.

3-[(Ethenyl)dimethylsilyl]-2-methoxypyridine (4j): Yield 74 %. The crude product purified by distillation gave a colourless oil. B.p. 63–64 °C (6.7 mbar). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.34 [s, 6 H, $Si(CH_3)_2$], 3.93 (s, 3 H, OCH_3), 5.76 (dd, *J* = 20.4, 3.7 Hz, 1 H, =C*H*H), 6.04 (dd, *J* = 14.7, 3.7 Hz, 1 H, =CH*H*), 6.34 (dd, *J* = 20.4, 14.7 Hz, 1 H, =CH), 6.84 (dd, *J* = 6.9, 5.1 Hz, 1 H, 5-H), 7.64 (dd, *J* = 6.9, 2.1 Hz, 1 H, 4-H), 8.16 (dd, *J* = 5.1, 2.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.36 [$Si(CH_3)_2$], 53.10 (OCH_3), 116.69 (C-5), 120.09 (C-3), 132.59 (=CH_2), 137.53 (=CH), 144.88 (C-4), 147.95 (C-6), 167.59 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3048 (w), 2948 (m), 1570 (s), 1454 (s), 1386 (s), 1296 (m), 1248 (s), 1086 (w), 1022 (s), 954 (m), 838 (s), 814 (m), 784 (s), 704 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 193 (11) $[M]^{+\cdot}$, 192 (32), 178 (100), 148 (93), 146 (35), 136 (50), 122 (25). HRMS (ESI-TOF): calcd. for $C_{10}H_{16}NOSi$ 194.1001 $[M + H]^+$; found 194.0991.

3-[Dimethyl(prop-2-enyl)silyl]-2-methoxypyridine (4k): Yield 84 %. The crude product purified by distillation gave a colourless oil. B.p. 53–55 °C (0.01 mbar). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.26 [s, 6 H, $Si(CH_3)_2$], 1.81 (dt, *J* = 8.1, 1.0 Hz, 2 H, CH_2), 3.93 (s, 3 H, OCH_3), 4.78–4.87 (m, 2 H, =CH_2), 5.69–5.80 (m, 1 H, =CH), 6.84 (dd, *J* = 6.9, 5.0 Hz, 1 H, 5-H), 7.62 (dd, *J* = 6.9, 2.0 Hz, 1 H, 4-H), 8.16 (dd, *J* = 5.0, 2.0 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.77 [$Si(CH_3)_2$], 22.71 (CH_2), 53.08 (OCH_3), 113.21 (=CH_2), 116.67 (C-5), 120.00 (C-3), 134.84 (=CH), 144.75 (C-4), 147.95 (C-6), 167.52 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3076 (w), 3044 (w), 2952 (m), 1628 (m), 1570 (s), 1454 (s), 1386 (s), 1294 (m), 1248 (s), 1192 (w), 1156 (m), 1084 (m), 1022 (s), 992 (w), 932 (w), 896 (m), 842 (s), 788 (s), 752 (w), 692 (w), 648 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 207 (<1) $[M]^{+\cdot}$, 166 (56), 136 (100). HRMS (ESI-TOF): calcd. for $C_{11}H_{18}NOSi$ 208.1158 $[M + H]^+$; found 208.1164.

2-Methoxy-3-(methylsulfanyl)-5-(trimethylsilyl)pyridine (5a): Yield 71 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C):

δ = 0.28 [s, 9 H, $Si(CH_3)_3$], 2.44 (s, 3 H, SMe), 4.02 (s, 3 H, OCH_3), 7.45 (d, *J* = 1.7 Hz, 1 H, 4-H), 8.02 (d, *J* = 1.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.09 [$Si(CH_3)_3$], 14.45 (SCH_3), 53.77 (OCH_3), 121.56 (C-3), 127.03 (C-5), 138.81 (C-4), 147.45 (C-6), 161.07 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (m), 1564 (s), 1462 (s), 1410 (s), 1360 (m), 1298 (m), 1262 (s), 1176 (w), 1124 (s), 1088 (s), 1018 (m), 882 (m), 834 (s), 766 (m), 694 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 227 (46) $[M]^{+\bullet}$, 212 (100). HRMS (ESI-TOF): calcd. for $C_{10}H_{18}NOSSi$ 228.0878 $[M + H]^+$; found 228.0869.

5-[(Ethenyl)dimethylsilyl]-2-methoxy-3-(methylsulfanyl)pyridine (5b): Yield 77 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.35 [s, 6 H, $Si(CH_3)_2$], 2.43 (s, 3 H, SCH_3), 4.02 (s, 3 H, OCH_3), 5.76 (dd, *J* = 20.2, 3.7 Hz, 1 H, =C*H*H), 6.07 (dd, *J* = 14.6, 3.7 Hz, 1 H, =CH*H*), 6.25 (dd, *J* = 20.2, 14.6 Hz, 1 H, =CH), 7.44 (d, *J* = 1.7 Hz, 1 H, 4-H), 8.02 (d, *J* = 1.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –2.87 [$Si(CH_3)_2$], 14.36 (SCH_3), 53.80 (OCH_3), 121.73 (C-3), 125.08 (C-5), 133.44 (=CH_2), 137.20 (=CH), 139.05 (C-4), 147.93 (C-6), 161.14 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3048 (w), 2952 (m), 2924 (w), 2856 (w), 1564 (s), 1462 (s), 1408 (s), 1362 (m), 1300 (m), 1260 (m), 1176 (w), 1124 (s), 1088 (s), 1016 (s), 956 (m), 874 (m), 838 (s), 814 (s), 778 (s), 700 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 239 (84) $[M]^{+\bullet}$, 238 (46), 224 (100), 212 (16), 198 (53). HRMS (ESI-TOF): calcd. for $C_{11}H_{18}NOSSi$ 240.0878 $[M + H]^+$; found 240.0873.

2-Methoxy-3-(methylsulfanyl)-5-(dimethylsilyl)pyridine (5c): Yield 74 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.35 [d, *J* = 3.7 Hz, 6 H, $Si(CH_3)_3$], 2.44 (s, 3 H, SCH_3), 4.02 (s, 3 H, OCH_3), 4.43 (sept, *J* = 3.7 Hz, 1 H, SiH), 7.46 (d, *J* = 1.7 Hz, 1 H, 4-H), 8.03 (d, *J* = 1.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.72 [$Si(CH_3)_3$], 14.31 (SCH_3), 53.86 (OCH_3), 121.98 (C-3), 124.16 (C-5), 138.91 (C-4), 147.86 (C-6), 161.20 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (m), 2920 (m), 2124 (s), 1564 (s), 1466 (s), 1408 (s), 1362 (m), 1298 (m), 1260 (s), 1176 (w), 1124 (s), 1088 (s), 1018 (s), 894 (s), 858 (m), 836 (m), 768 (m), 734 (w), 664 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 213 (86) $[M]^{+\bullet}$, 212 (20), 198 (100), 168 (13). HRMS (ESI-TOF): calcd. for $C_9H_{16}NOSSi$ 214.0722 $[M + H]^+$; found 214.0716.

2-Methoxy-3-(methylsulfanyl)pyridine (5d):[47] Yield 70 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless solid, m.p. 42–44 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 2.42 (s, 3 H, SCH_3), 4.02 (s, 3 H, OCH_3), 6.88 (dd, *J* = 7.4, 4.9 Hz, 1 H, 5-H), 7.37 (dd, *J* = 7.4, 1.7 Hz, 1 H, 4-H), 7.94 (dd, *J* = 4.9, 1.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.18 (SCH_3), 53.83 (OCH_3), 117.21 (C-5), 122.46 (C-3), 133.39 (C-4), 142.30 (C-6), 160.05 (C-2) ppm.

[2-Methoxy-5-(trimethylsilyl)-3-pyridyl]diphenylmethanol (5e): Yield 68 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless solid, m.p. 82–85 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.10 [s, 9 H, $Si(CH_3)_3$], 3.85 (s, 3 H, OCH_3), 5.01 (s, 1 H, OH), 6.83 (d, *J* = 1.8 Hz, 1 H, 4-H), 7.19–7.24 (m, 4 H, Ph-H), 7.25–7.34 (m, 6 H, Ph-H), 8.18 (d, *J* = 1.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.37 [$Si(CH_3)_3$], 53.45 (OCH_3), 80.97 (C-OH), 126.56 (C-5), 127.29 (C-Ar), 127.63 (C-Ar), 127.80 (C-Ar), 128.49 (C-3), 143.09 (C-4), 145.50 (C-Ar) 150.42 (C-6), 161.61 (C-2) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3548 (m), 3024 (w), 2952 (m), 1580 (m), 1556 (m), 1460 (s), 1448 (m), 1414 (m), 1364 (m), 1344 (m), 1296 (w), 1268 (s), 1246 (m), 1178 (m), 1120 (m), 1028 (m), 1004 (m), 964 (w), 918 (w), 840 (s), 784 (w), 764 (m), 756 (m), 700 (s), 644 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 363 (<1) $[M]^{+\bullet}$, 347 (6), 287 (100), 209 (33), 152 (11), 105 (13), 77 (13). HRMS (ESI-TOF): calcd. for $C_{22}H_{26}NO_2Si$ 364.1733 $[M + H]^+$; found 364.1725.

{2-Methoxy-5-[(ethenyl)dimethylsilyl]-3-pyridyl}diphenylmethanol (5f): Yield 62 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless solid, m.p. 56–61 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.18 [s, 6 H, $Si(CH_3)_2$], 3.85 (s, 3 H, OCH_3), 5.00 (s, 1 H, OH), 5.60 (dd, *J* = 20.0, 3.7 Hz, 1 H, =C*H*H), 5.95 (dd, *J* = 14.7, 3.7 Hz, 1 H, =CH*H*), 6.09 (dd, *J* = 20.0, 14.7 Hz, 1 H, =CH), 6.85 (d, *J* = 1.7 Hz, 1 H, 4-H), 7.18–7.34 (m, 10 H, 2 × C_6H_5), 8.18 (d, *J* = 1.7 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.10 [$Si(CH_3)_2$], 53.49 (OCH_3), 80.97 (C-OH), 124.64 (C-5), 127.29 (C-Ar), 127.62 (C-Ar), 127.81 (C-Ar), 128.66 (C-3), 133.24 (=CH_2), 136.93 (=CH), 143.58 (C-4), 145.47 (C-Ar), 151.00 (C-6), 161.74 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3540 (br. m), 3060 (w), 3028 (w), 2956 (m), 1582 (s), 1556 (m), 1492 (w), 1466 (s), 1448 (s), 1416 (s), 1364 (s), 1296 (w), 1274 (s), 1248 (w), 1180 (m), 1122 (s), 1014 (s), 964 (m), 916 (w), 838 (s), 812 (s), 776 (s), 758 (s), 702 (s), 664 (w), 646 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 375 (6) $[M]^{+\bullet}$, 360 (12), 298 (100), 192 (11), 105 (13), 85 (10), 77 (9). HRMS (ESI-TOF): calcd. for $C_{23}H_{26}NO_2Si$ 376.1733 $[M + H]^+$; found 376.1725.

{2-Methoxy-6-[(ethenyl)dimethylsilyl]-3-pyridyl}diphenylmethanol (5g): Yield 73 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.36 [s, 6 H, $Si(CH_3)_2$], 3.88 (s, 3 H, OCH_3), 5.21 (s, 1 H, OH), 5.81 (dd, *J* = 20.5, 3.8 Hz, 1 H, =CH*H*), 6.06 (dd, *J* = 14.7, 3.8 Hz, 1 H, =C*H*H), 6.32 (dd, *J* = 20.5, 14.7 Hz, 1 H, =CH), 6.69 (d, *J* = 7.3 Hz, 1 H, 5-H), 6.91 (d, *J* = 7.3 Hz, 1 H, 4-H), 7.10–7.27 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.62 [$Si(CH_3)_2$], 53.22 (OCH_3), 80.94 (C-OH), 123.04 (C-5), 127.23 (C-Ar), 127.73 (C-Ar), 127.83 (C-Ar), 128.53 (C-3), 133.10 (=CH_2), 136.53 (=CH), 137.23 (C-4), 145.67 (C-Ar), 160.18 (C-6), 162.54 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3536 (m), 3060 (w), 2952 (m), 2860 (w), 1690 (m), 1580 (m), 1556 (m), 1490 (w), 1454 (s), 1410 (w), 1364 (m), 1340 (m), 1236 (s), 1168 (w), 1130 (w), 1114 (w), 1016 (s), 954 (w), 866 (w), 834 (m), 812 (s), 778 (m), 760 (s), 702 (s), 664 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 375 (84) $[M]^{+\bullet}$, 360 (38), 298 (100), 284 (66), 270 (78), 256 (34), 192 (15), 105 (40), 77 (26), 59 (17). HRMS (ESI-TOF): calcd. for $C_{23}H_{26}NO_2Si$ 376.1733 $[M + H]^+$; found 376.1728.

(2-Methoxy-3-pyridyl)diphenylmethanol (5h):[48] Yield 49 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a white solid, m.p. 129–131 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 3.86 (s, 3 H, OCH_3), 5.10 (s, 1 H, OH), 6.78 (dd, *J* = 7.3, 4.9 Hz, 1 H, 2 H, 5-H), 6.81 (dd, *J* = 7.3, 2.2 Hz, 1 H, 4-H), 7.19–7.33 (m, 10 H, 2 × C_6H_5), 8.11 (dd, *J* = 4.9, 2.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 53.58 (OCH_3), 80.86 (C-OH) 116.73 (C-5), 127.32, 127.66, 127.90 (C-Ar), 129.31 (C-3), 138.42 (C-4), 145.53 (C-Ar), 145.83 (C-6), 160.94 (C-2) ppm. GC–MS (EI, 70 eV): *m/z* (%) = (13) $[M]^{+\bullet}$, 214 (100), 186 (13), 136 (33), 105 (21), 77 (21). HRMS (ESI-TOF): calcd. for $C_{19}H_{18}NO_2$ 292.1338 $[M + H]^+$; found 292.1344.

2-Methoxy-5-(trimethylsilyl)pyridine-3-carbaldehyde (5i): Yield 41 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless solid, m.p. 111–113 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.30 [s, 9 H, $Si(CH_3)_3$], 4.08 (s, 3 H, OCH_3), 8.20 (d, *J* = 2.0 Hz, 1 H, 4-H), 8.45 (d, *J* = 2.0 Hz, 1 H, 6-H), 10.39 (s, 1 H, CHO) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.22 [$Si(CH_3)_3$], 53.80 (OCH_3), 118.32 (C-3), 127.51 (C-5), 142.74 (C-4), 157.30 (C-6), 165.04 (C-2), 189.57 (CHO) ppm. IR (KBr pellet): $\tilde{\nu}$ = 2956 (m), 1676 (s), 1582 (s), 1556 (m), 1480 (s), 1442 (w), 1420 (w), 1392 (w), 1362 (w), 1324 (w), 1272 (m), 1248 (m), 1176 (w), 1104 (w), 1024 (m), 938 (m), 912 (m), 838 (s), 800 (w), 764 (w), 694 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 209 (14) $[M]^{+\bullet}$, 194 (100). HRMS (ESI-TOF): decomposition.

2-Methoxy-6-[(ethenyl)dimethylsilyl]pyridine-3-carbaldehyde (5k): Yield 57 %. The crude product purified by column chromatog-

raphy (silica gel, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.40 [s, 6 H, $Si(CH_3)_2$], 4.09 (s, 3 H, OCH_3), 5.84 (dd, J = 20.3, 3.7 Hz, 1 H, =CH*H*), 6.10 (dd, J = 14.7, 3.7 Hz, 1 H, =C*H*H), 6.31 (dd, J = 20.3, 14.7 Hz, 1 H, =CH), 7.23 (dd, J = 7.3, 0.7 Hz, 1 H, 4-H), 7.98 (d, J = 7.3 Hz, 1 H, 5-H), 10.37 (d, J = 0.7 Hz, 1 H, CHO) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.88 [$Si(CH_3)_2$], 53.51 (OCH_3), 117.75 (C-3), 123.09 (C-5), 133.79 (=CH_2), 135.19 (=CH), 136.30 (C-4), 163.20 (C-6), 173.10 (C-2), 189.92 (CHO) ppm. IR (film): $\tilde{\nu}$ = 3052 (w), 2952 (m), 2860 (w), 1690 (s), 1580 (s), 1456 (s), 1404 (w), 1388 (m), 1362 (s), 1264 (s), 1216 (w), 1128 (m), 1100 (m), 1018 (s), 956 (m), 814 (s), 782 (s), 706 (m), 676 (w), 638 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 221 (44) $[M]^{+\cdot}$, 220 (70), 206 (100), 194 (34), 193 (19), 180 (34), 178 (15), 165 (40), 136 (11), 59 (30). HRMS (ESI-TOF): calcd. for $C_{11}H_{16}NO_2Si$ 222.0950 $[M + H]^+$; found 222.0953.

2-Methoxypyridine-3-carbaldehyde (5l): The ^{1}H and ^{13}C NMR spectroscopic data for this product matched those reported previously.[30]

3-Iodo-2-methoxy-5-(trimethylsilyl)pyridine (5m): Yield 60 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 25:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.27 [s, 9 H, $Si(CH_3)_3$], 3.99 (s, 3 H, OCH_3), 8.07 (d, J = 1.6 Hz, 1 H, 4-H), 8.16 (d, J = 1.6 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.16 [$Si(CH_3)_3$], 54.57 (OCH_3), 80.84 (C-3), 129.50 (C-5), 151.06 (C-4), 152.69 (C-6), 162.31 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (m), 1566 (s), 1466 (s), 1412 (s), 1354 (m), 1294 (m), 1260 (m), 1172 (w), 1118 (m), 1052 (m), 1014 (m), 866 (m), 838 (s), 762 (m), 692 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 307 (48) $[M]^{+\cdot}$, 292 (100). HRMS (ESI-TOF): calcd. for $C_9H_{15}INOSi$ 307.9968 $[M + H]^+$; found 307.9963.

3-(Dimethylsilyl)-5-[(2-{[5-(dimethylsilyl)-6-methoxy-3-pyridyl]-dimethylsilyl}ethyl)dimethylsilyl]-2-methoxypyridine (8): Yield 46 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.23 [s, 12 H, $Si(CH_3)_2$], 0.33 [d, J = 3.7 Hz, 12 H, $SiH(CH_3)_2$], 0.63 [s, 4 H, $(CH_2)_2$], 3.94 (s, 6 H, OCH_3), 4.36 (sept, J = 3.7 Hz, 2 H, SiH), 7.73 (d, J = 2.1 Hz, 2 H, 2 × 4-H), 8.22 (d, J = 2.1 Hz, 2 H, 2 × 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –4.28 [2 × $Si(CH_3)_2$], –3.54 [2 × $SiH(CH_3)_2$], 7.88 (2 × CH_2), 53.16 (2 × OCH_3), 118.52 (2 × C-3), 124.75 (2 × C-5), 150.39 (2 × C-4), 153.32 (2 × C-6), 168.33 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 3004 (w), 2952 (s), 2904 (m), 2124 (s), 1566 (s), 1548 (s), 1454 (s), 1400 (s), 1360 (m), 1296 (s), 1250 (s), 1176 (m), 1132 (s), 1096 (m), 1020 (s), 896 (br. s), 834 (s), 808 (s), 790 (s), 724 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 475 (4) $[M]^{+\cdot}$, 463 (24), 462 (47), 418 (16), 417 (43), 225 (20), 224 (91), 150 (17), 89 (17), 73 (15), 59 (26). HRMS (ESI-TOF): calcd. for $C_{22}H_{41}N_2O_2Si_4$ 477.2245 $[M + H]^+$; found 477.2248.

General Procedure for the Synthesis of 7 and 9: The [Pt(cod)Me_2] catalyst (0.83 mg, 2.5 μmol) was added to a solution of the HSi (5.5 mmol)* and alkenylSi derivative (5.2 mmol) in toluene (25 mL), and the reaction mixture was stirred for 24 h at 60 °C.** After cooling, ethyl acetate (25 mL) was added and the solution was passed through a pad of Celite. Concentration in vacuo and purification by distillation or flash column chromatography yielded product **7** or **9**. *In the synthesis of **7i**, substrates **2b** and **4i** were used in a molar ratio of 2.2:1. In the synthesis of **7j**, substrates **2a** and **6** were used in a molar ratio of 2:1. In the synthesis of **9** substrates **2a** and **8** were used in a molar ratio of 2:1. **In the synthesis of **7e**, after stirring for 24 h at 60 °C, an additional portion (0.83 mg) of the [Pt(cod)Me_2] catalyst was added and the reaction mixture was stirred for 24 h at 60 °C.

2-Methoxy-5-({2-[(6-methoxy-3-pyridyl)dimethylsilyl]-ethyl}dimethylsilyl)pyridine (7a): Yield 88 %. The crude product purified by distillation gave a colourless oil. B.p. 141–145 °C (0.1 mbar). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.23 [s, 12 H, 2 × $Si(CH_3)_2$], 0.61 [s, 4 H, $(CH_2)_2$], 3.94 (s, 6 H, 2 × OCH_3), 6.73 (dd, J = 8.2, 0.7 Hz, 2 H, 2 × 3-H), 7.60 (dd, J = 8.2, 2.0 Hz, 2 H, 2 × 4-H), 8.20 (dd, J = 2.0, 0.7 Hz, 2 H, 2 × 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.61 [2 × $Si(CH_3)_2$], 7.83 (2 × CH_2), 53.22 (2 × OCH_3), 110.63 (2 × C-3), 124.95 (2 × C-5), 143.64 (2 × C-4), 151.85 (2 × C-6), 164.72 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 3020 (w), 3008 (w), 2952 (m), 2924 (w), 2876 (w), 2848 (w), 1582 (s), 1556 (m), 1486 (s), 1462 (m), 1432 (w), 1408 (w), 1384 (w), 1354 (s), 1336 (m), 1278 (s), 1250 (m), 1180 (w), 1136 (m), 1116 (s), 1076 (w), 1052 (m), 1012 (s), 834 (br. s), 778 (s), 756 (w), 702 (m), 610 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 360 (32) $[M]^{+\cdot}$, 332 (26), 331 (49), 317 (18), 240 (16), 167 (15), 166 (100). HRMS (ESI-TOF): calcd. for $C_{18}H_{28}N_2O_2Si_2$ 361.1768 $[M + H]^+$; found 316,1763.

2-Methoxy-5-[{2-[(6-methoxy-3-pyridyl)dimethylsilyl]ethyl}-(methyl)phenylsilyl]pyridine (7b): Yield 98 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.24 [s, 6 H, $Si(CH_3)_2$], 0.52 (s, 3 H, $SiCH_3$), 0.65–0.70 (m, 2 H, CH_2), 0.90–0.95 (m, 2 H, CH_2), 3.93, 3.94 (2 s, 6 H, 2 × OCH_3), 6.72 (dd, J = 8.2, 1.0 Hz, 1 H, 3-H), 6.72 (dd, J = 8.2, 1.0 Hz, 1 H, 3-H), 7.31–7.38 (m, 3 H, C_6H_5), 7.42–7.46 (m, 2 H, C_6H_5), 7.57 (dd, J = 8.2, 2.0 Hz, 1 H, 4-H), 7.58 (dd, J = 8.2, 2.0 Hz, 1 H, 4-H), 8.20 (dd, J = 2.0, 1.0 Hz, 1 H, 6-H), 8.22 (dd, J = 2.0, 1.0 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –5.11 ($SiCH_3$), –3.62 [$Si(CH_3)_2$], 6.27 (CH_2), 7.87 (CH_2), 53.22, 53.24 (2 × OCH_3), 110.63, 110.77, (2 × C-3), 123.09, 124.76 (2 × C-5), 127.93, 129.36, 134.35, 136.34 (C_6H_5), 143.63, 144.37 (2 × C-4), 151.88, 152.71 (2 × C-6), 164.75, 164.88 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 3080 (w), 2948 (m), 2908 (m), 1586 (s), 1556 (m), 1486 (s), 1462 (m), 1428 (w), 1406 (w), 1354 (s), 1282 (s), 1250 (m), 1176 (w), 1116 (s), 1052 (w), 1026 (s), 830 (s), 788 (s), 736 (m), 702 (m), 606 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 422 (55) $[M]^{+\cdot}$, 394 (51), 393 (58), 379 (19), 302 (12), 228 (100), 166 (32). HRMS (ESI-TOF): calcd. for $C_{23}H_{31}N_2O_2Si_2$ 423.1942 $[M + H]^+$; found 423.1907.

2-Methoxy-5-[(2-{[6-methoxy-5-(methylsulfanyl)-3-pyridyl]-dimethylsilyl}ethyl)dimethylsilyl]-3-(methylsulfanyl)pyridine (7c): Yield 91 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a white solid, m.p. 82–84 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.25 [s, 12 H, 2 × $Si(CH_3)_2$], 0.62 (s, 4 H, 2 × CH_2), 2.41 (s, 6 H, 2 × SCH_3), 4.02 (s, 6 H, 2 × OCH_3), 7.39 (d, J = 1.5 Hz, 2 × 4-H), 7.98 (d, J = 1.5 Hz, 2 H, 2 × 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.55 [2 × $Si(CH_3)_2$], 7.91 (2 × CH_2), 14.43 (2 × SCH_3), 53.80 (2 × OCH_3), 121.71 (2 × C-3), 125.69 (2 × C-5), 138.69 (2 × C-4), 147.69 (2 × C-6), 161.10 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 3036 (w), 3008 (w), 2992 (w), 2952 (m), 2908 (w), 1560 (s), 1468 (m), 1454 (s), 1408 (s), 1364 (m), 1316 (w), 1296 (m), 1252 (m), 1246 (m), 1176 (w), 1120 (s), 1086 (m), 1052 (w), 1016 (m), 966 (w), 872 (m), 836 (m), 808 (s), 780 (m), 760 (w), 708 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%) = 452 (46) $[M]^{+\cdot}$, 437(27), 409 (19), 405 (31), 286 (17), 212 (100), 169 (18). HRMS (ESI-TOF): calcd. for $C_{20}H_{33}N_2O_2S_2Si_2$ 453.1522 $[M + H]^+$; found 453.1508.

2-Methoxy-5-({3-[(6-methoxy-3-pyridyl)dimethylsilyl]propyl}-dimethylsilyl)pyridine (7d): Yield 69 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.22 [s, 12 H, 2 × $Si(CH_3)_2$], 0.76–0.82 (m, 4 H, 2 × CH_2), 1.32–1.41 (m, 2 H, CH_2), 3.94 (s, 6 H, 2 × OCH_3), 6.72 (dd, J = 8.3, 0.9 Hz, 1 H, 2 × 3-H), 7.59 (dd, J = 8.3, 2.0 Hz, 1 H, 2 × 4-H), 8.19–8.21 (m, 1 H, 2 × 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –2.91 [2 × $Si(CH_3)_2$], 18.26 (CH_2), 20.13 (2 ×

CH_2), 53.20 (2 × OCH_3), 110.59 (2 × C-3), 125.34 (2 × C-5), 143.56 (2 × C-4), 151.73 (2 × C-6), 164.69 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (m), 2916 (m), 1586 (s), 1556 (s), 1488 (s), 1462 (m), 1354 (s), 1286 (s), 1250 (m), 1178 (w), 1116 (s), 1026 (m), 904 (m), 830 (s), 772 (m), 698 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 374 (28) $[M]^{+\cdot}$, 345 (62), 166 (100). HRMS (ESI-TOF): calcd. for $C_{19}H_{31}N_2O_2Si_2$ 375.1924 $[M + H]^+$; found 375.1921.

2-Methoxy-5-({3-[(2-methoxy-3-pyridyl)dimethylsilyl]propyl}-dimethylsilyl)pyridine (7e): Yield 99 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz): δ = 0.21 [s, 12 H, 2 × $Si(CH_3)_2$], 0.76–0.87 (m, 4 H, 2 × CH_2), 1.31–1.40 (m, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 6.72 (d, *J* = 8.1 Hz, 1 H, 3′-H), 6.83 (d, *J* = 6.8, 5.1 Hz, 1 H, 5-H), 7.57–7.61 (m, 2 H, 4-H, 4′-H), 8.14 (dd, *J* = 5.1, 2.1 Hz, 1 H, 6-H), 8.20 (d, *J* = 2.1 Hz, 1 H, 6′-H) ppm. ^{13}C NMR (151.0 MHz, $CDCl_3$): δ = –3.19 [$Si(CH_3)_2$], –2.89 [$Si(CH_3)_2$], 18.39, 19.39, 20.08 (3 × CH_2), 53.01, 53.19 (2 × OCH_3), 110.56 (C-3′), 116.67 (C-5), 120.83 (C-3), 125.51 (C-5′), 143.57 (C-4′), 144.58 (C-4), 147.73 (C-6), 151.76 (C-6′), 164.69 (C-2′), 167.58 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3044 (w), 2952 (m), 2916 (m), 1586 (s), 1570 (s), 1556 (m), 1488 (s), 1454 (s), 1384 (s), 1354 (m), 1336 (w), 1286 (s), 1248 (s), 1116 (s), 1086 (w), 1024 (s), 944 (w), 904 (m), 834 (s), 786 (s), 696 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 374 (6) $[M]^{+\cdot}$, 359 (31), 278 (24), 166 (98), 136 (100). HRMS (ESI-TOF): calcd. for $C_{19}H_{31}N_2O_2Si_2$ 375.1924 $[M + H]^+$; found 375.1909.

2-Methoxy-5-({2-[(4-methoxyphenyl)dimethylsilyl]ethyl}-dimethylsilyl)pyridine (7f): Yield 77 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.21 [s, 6 H, $Si(CH_3)_2$], 0.22 [s, 6 H, $Si(CH_3)_2$], 0.61 (s, 4 H, 2 × CH_2), 3.81 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 6.72 (dd, *J* = 8.2, 0.9 Hz, 1 H, 3-H), 6.90 (dm, *J* = 8.5 Hz, 2 H, C_6H_4), 7.39 (dm, *J* = 8.5 Hz, 2 H, C_6H_4), 7.59 (dd, *J* = 8.2, 1.9 Hz, 1 H, 4-H), 8.2–8.22 (m, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.23 [$Si(CH_3)_2$], –3.11 [$Si(CH_3)_2$], 8.20 (CH_2), 8.32 (CH_2), 53.52 (OCH_3), 55.34 (OCH_3), 110.91 (C-3), 113.85 (Ar), 125.52 (C-5), 130.27 (Ar), 135.37 (Ar), 144.02 (C-4), 152.21 (C-6), 160.61 (Ar), 165.04 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3016 (w), 2952 (s), 2904 (m), 2840 (w), 1586 (s), 1556 (m), 1502 (s), 1486 (s),1462 (m), 1440 (w), 1408 (w), 1354 (s), 1320 (m), 1282 (s), 1246 (s), 1182 (m), 1132 (m), 1114 (s), 1052 (m), 1028 (s), 834 (br. s), 778 (s), 710 (m), 610 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 359 (41) $[M]^{+\cdot}$, 331 (48), 316 (26), 166 (53), 165 (100). HRMS (ESI-TOF): calcd. for $C_{19}H_{30}NO_2Si_2$ 360.1815 $[M + H]^+$; found 360.1813.

2-Methoxy-5-({3-[(4-methoxyphenyl)dimethylsilyl]propyl}-dimethylsilyl)pyridine (7g): Yield 63 %. The crude product purified by column chromatography (SiO_2, CH_2Cl_2) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.20 [s, 6 H, $Si(CH_3)_2$], 0.21 [s, 6 H, $Si(CH_3)_2$], 0.74–0.81 (m, 4 H, 2 × CH_2), 1.33–1.42 (m, 2 H, CH_2), 3.81 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 6.72 (dd, *J* = 8.2, 0.9 Hz, 1 H, 3-H), 6.88–6.91 (m, 2 H, C_6H_4), 7.37–7.41 (m, 2 H, C_6H_4), 7.59 (dd, *J* = 8.3, 2.0 Hz, 1 H, 4-H), 8.20–8.21 (m, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –2.88, –2.72 [2 × $Si(CH_3)_2$], 18.36, 20.12, 20.40 (3 × CH_2), 53.20, 55.00 (2 × OCH_3), 110.55 (C-3), 113.49 (Ar), 125.50 (C-5) 130.36 (Ar), 134.91 (Ar), 143.60 (C-4), 151.75 (C-6), 160.20 (Ar), 164.66 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (m), 2912 (m), 1586 (s), 1564 (w), 1556 (m), 1502 (m), 1486 (m), 1464 (w), 1354 (m), 1282 (s), 1248 (s), 1182 (m), 1138 (w), 1114 (s), 1028 (m), 904 (m), 828 (s), 770 (m), 694 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 373 (28) $[M]^{+\cdot}$, 344 (32), 264 (50), 165 (100). HRMS (ESI-TOF): calcd. for $C_{20}H_{32}NO_2Si_2$ 374.1972 $[M + H]^+$; found 374.1777.

2-Methoxy-3-({2-[(4-methoxyphenyl)dimethylsilyl]ethyl}dimethylsilyl)pyridine (7h): Yield 46 %. The crude product was purified by column chromatography (silica gel, DCM) to give a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.21, 0.22 (2 s, 12 H, 2 × $SiMe_2$), 0.53–0.60 (m, 2 H, CH_2), 0.67–0.73 (m, 2 H, CH_2), 3.81 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.83 (dd, *J* = 7.0, 5.0 Hz, 1 H, 5-H), 6.90 (d, *J* = 8.5 Hz, 2 H, C_6H_4), 7.40 (d, *J* = 8.5 Hz, 2 H, C_6H_4), 7.58 (dd, *J* = 7.0, 2.1 Hz, 1 H, 4-H), 8.14 (dd, *J* = 5.0, 2.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (151.0 MHz, $CDCl_3$): δ = –3.80 [$Si(CH_3)_2$], –3.39 [$Si(CH_3)_2$], 6.99, 8.06 (2 × CH_2), 53.00, 55.02 (2 × OCH_3), 113.50 (Ar), 116.67 (C-5), 120.64 (C-3), 130.26 (Ar), 135.06 (Ar), 144.86 (C-4), 147.72 (C-6), 160.25 (Ar), 167.63 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (s), 2928 (m), 2848 (w), 1594 (s), 1570 (s), 1502 (s), 1454 (s), 1384 (s), 1294 (m), 1278 (s), 1246 (s), 1182 (m), 1134 (m), 1112 (s), 1086 (w), 1054 (w), 1022 (m), 834 (s), 786 (s), 710 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 359 (9) $[M]^{+\cdot}$, 344 (32), 330 (22), 166 (100) 165 (89), 136 (92). HRMS (ESI-TOF): calcd. for $C_{19}H_{30}NO_2Si_2$ 360.1815 $[M + H]^+$; found 360.1807.

2-Methoxy-3,5-bis({2-[(6-methoxy-3-pyridyl)dimethylsilyl]ethyl}dimethylsilyl)pyridine (7i): Yield 63 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.2–0.25 [m, 24 H, 4 × $Si(CH_3)_2$], 0.54–0.74 (m, 8 H, 4 × CH_2), 3.89 (s, 3 H, $OCH_{3,A}$), 3.94 (s, 6 H, 2 × $OCH_{3,B}$), 6.72 (d, *J* = 8.2 Hz, 2 H, 2 × 3-H_B), 7.60 (dd, *J* = 8.2, 2.1 Hz, 1 H, 4-H_B), 7.61 (dd, *J* = 8.2, 2.1 Hz, 1 H, 4-H_B), 7.63 (d, *J* = 2.1 Hz, 1 H, 4-H_A), 8.20 (d, *J* = 2.2 Hz, 1 H, 6-H_A), 8.21–8.23 (m, 2 H, 2 × 6-H_B) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.83, [3 × $Si(CH_3)_2$], –3.11 [$Si(CH_3)_2$], 7.01, 7.84, 7.88, 7.93 (4 × CH_2), 52.91 ($OCH_{3,A}$), 53.19 (2 × $OCH_{3,B}$), 110.55, 110.62 (2 × C-3), 119.71, 124.48, 124.98, 125.21 (C-3, 3 × C-5), 142.61, 143.66 (2 × C-4_B), 149.83 (C-4_A), 151.86 (2 × C-6_B), 152.90 (C-6_A), 164.69, 164.72, 168.29 (3 × C-2) ppm. IR (film): $\tilde{\nu}$ = 3016 (w), 2952 (s), 2904 (m), 2840 (w), 1586 (s), 1556 (m), 1486 (s), 1462 (m), 1440 (w), 1396 (s), 1354 (s), 1282 (s), 1246 (s), 1182 (w), 1132 (m), 1114 (s), 1052 (m), 1028 (s), 880 (s), 834 (br. s), 778 (s), 710 (m), 610 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 612 (<1) $[M]^{+\cdot}$, 596 (2), 418 (39), 417 (100), 387 (10), 166 (35). HRMS (ESI-TOF): calcd. for $C_{30}H_{50}N_3O_3Si_4$ 612.2929 $[M + H]^+$; found 612.2935.

2-Methoxy-5-[10-(6-methoxy-3-pyridyl)-2,5,5,7,7,10-hexamethyl-6-oxa-2,5,7,10-tetrasilaundecan-2-yl]pyridine (7j): Yield 58 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = –0.04–0.04 [s, 12 H, 2 × $Si(CH_3)_2$], 0.22–0.29 [s, 12 H, 2 × $Si(CH_3)_2$], 0.35–0.41 (m, 4 H, 2 × CH_2), 0.59–0.65 (m, 4 H, 2 × CH_2), 3.95 (s, 6 H, 2 × OCH_3), 6.72–6.76 (m, 2 H, 2 × 5-H), 7.61–7.66 (m, 2 H, 2 × 4-H), 8.21–8.25 (m, 2 H, 2 × 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.31 [2 × $Si(CH_3)_2$], –0.05 [2 × $Si(CH_3)_2$], 7.49 (2 × CH_2), 10.51 (2 × CH_2), 53.41 (2 × OCH_3), 110.88 (2 × C-3), 125.45 (2 × C-5), 143.89 (2 × C-4), 152.12 (2 × C-6), 164.98 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 2956 (s), 2908 (m), 1586 (s), 1556 (m), 1486 (s), 1462 (w), 1432 (w), 1406 (w), 1384 (w), 1354 (m), 1284 (s), 1252 (s), 1178 (w), 1132 (m), 1116 (s), 1050 (br. s), 828 (br. s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 520 (4) $[M]^{+\cdot}$, 505 (25), 354 (11), 328 (16), 327 (33), 326 (100), 167 (22), 166 (90), 73 (17). HRMS (ESI-TOF): calcd. for $C_{42}H_{71}N_4O_4Si_6$ 521.2507 $[M + H]^+$; found 521.2525.

2-Methoxy-5-[(2-{[6-methoxy-5-({2-[(6-methoxy-3-pyridyl)dimethylsilyl]ethyl}dimethylsilyl)-3-pyridyl]dimethylsilyl}ethyl)dimethylsilyl]-3-({2-[(6-methoxy-3-pyridyl)dimethylsilyl]ethyl}dimethylsilyl)pyridine (9): Yield 26 %. The crude product purified by column chromatography (SiO_2, hexane/EtOAc, 20:1) gave a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.14 [s, 24 H, 4 × $Si(CH_3)_2$], 0.15 [s, 12 H, 2 × $Si(CH_3)_2$], 0.48–0.65 (m, 12 H, 6 × CH_2), 3.80 (s, 6 H, 2 × OCH_3), 3.84 (s, 6 H, 2 × OCH_3), 6.63 (dd, *J* = 8.2, 0.7 Hz, 2 H, 2 × 3-H), 7.52 (dd, *J* = 8.2, 2.0 Hz, 2 H, 2 × 4-H), 7.56 (d, *J* = 2.0 Hz, 2 H, 2 × 4-H), 8.12 (d, *J* = 2.0 Hz, 2 H, 2 × 6-H), 8.14 (dd, *J* = 2.0, 0.7 Hz, 2 H, 2 × 6-H) ppm. ^{13}C NMR

(100.6 MHz, $CDCl_3$): δ = –3.49 [2 × $Si(CH_3)_2$], –3.23 [4 × $Si(CH_3)_2$], 7.33 (2 × CH_2), 8.22 (2 × CH_2), 8.26 (2 × CH_2), 53.23 (2 × OCH_3), 53.46 (2 × OCH_3), 110.88 (2 × C-3), 119.99 (2 × C-3), 124.82 (2 × C-5), 125.47 (2 × C-5), 143.95 (2 × C-4), 150.15 (2 × C-4) 152.18 (2 × C-6), 153.23 (2 × C-6), 165.00 (2 × C-2), 168.59 (2 × C-2) ppm. IR (film): $\tilde{\nu}$ = 2952 (s), 2904 (m), 1586 (s), 1564 (s), 1548 (w), 1486 (m), 1454 (m), 1396 (s), 1352 (m), 1286 (s), 1248 (s), 1176 (w), 1132 (m), 1116 (s), 1096 (w), 1054 (m), 1024 (m), 880 (s), 830 (br. s), 710 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) = 862 (<1) $[M]^{+\cdot}$, 669 (29), 417 (100), 166 (50), 89 (12). HRMS (ESI-TOF): calcd. for $C_{42}H_{71}N_4O_4Si_6$ 863.4091 $[M + H]^+$; found 863.4097.

Synthesis of Oligomer 10: The $[Pt(cod)Me_2]$ catalyst (0.8 mg, 2.4 µmol) was added to a solution of compound **4a** (1.333 g, 5.3 mmol) in toluene (5 mL) and the reaction mixture was stirred at 60 °C for 7 d. After this time an additional portion of the catalyst (8 mg, 24 µmol) was added and the mixture was continuously stirred for an additional 24 h at 60 °C. After cooling, ethyl acetate (75 mL) was added and the solution was passed through a pad of Celite and washed with ethyl acetate (15 mL). After concentration in vacuo, 0.259 g (20 % yield) of product **10** was isolated as a thick oil by precipitation from CH_2Cl_2 solution initiated by adding MeOH.

5-{[2-({5-[(Ethenyl)dimethylsilyl]-2-methoxy-3-pyridyl}-dimethylsilyl)ethyl]dimethylsilyl}-2-methoxy-3-{[2-({6-methoxy-5-[(2-{[6-methoxy-5-({2-[(6-methoxy-5-)]2-})6-methoxy-5-]}2-)]6-methoxy-5-})2-]}-6-methoxy-3-pyridyldimethylsilyl]ethyl}dimethylsilyl)-3-pyridyl]dimethylsilyl}ethyl)-dimethylsilyl]-3-pyridyl}dimethylsilyl)ethyl]dimethylsilyl}-3-pyridyl)dimethylsilyl]ethyl}dimethylsilyl-3-pyridyl]dimethylsilyl}ethyl)dimethylsilyl]-3-pyridyl}dimethylsilyl)ethyl-dimethylsilylpyridine (10): ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 0.22 [s, 84 H, 14 × $Si(CH_3)_2$], 0.33 [s, 6 H, vinyl$Si(CH_3)_2$], 0.54–0.77 (m, 28 H, 14 × CH_2Si), 3.88 (s, 21 H, 7 × OCH_3), 3.93 (s, 3 H, OCH_3), 5.74 (dd, *J* = 20.1, 3.6 Hz, 1 H, =CH*H*), 6.05 (dd, *J* = 14.6, 3.6 Hz, 1 H, =C*H*H), 6.25 (dd, *J* = 20.1, 14.6 Hz, 1 H, =CH), 6.72 (d, *J* = 8.2 Hz, 1 H, 3-H), 7.57–7.74 (m, 8 H, 8 × 4-H), 8.17–8.29 (m, 8 H, 8 × 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.81 [7 × $Si(CH_3)_2$], –3.51 [7 × $Si(CH_3)_2$], –2.84 [vinyl$Si(CH_3)_2$], 7.08 (7 × CH_2), 7.94 (7 × CH_2), 52.94 (7 × OCH_3), 53.19 ($OCH_{3,A}$), 110.55 ($C\text{-}3_A$), 119.71, 119.80 (C-3), 123.83, 124.56, 124.77, 125.20 (C-5), 133.11 (=CH_2), 137.56 (=CH), 143.66 ($C\text{-}4_A$), 149.88, 150.06 (C-4), 151.85 ($C\text{-}6_A$), 152.85, 153.14 (C-6), 164.68 ($C\text{-}2_A$), 168.21, 168.36 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2950 (w), 2894 (w), 1584 (w), 1546 (m), 1490 (w), 1450 (m), 1394 (s), 1350 (w), 1244 (s), 1174 (w), 1132 (m), 1116 (m), 1094 (w), 1054 (w), 1020 (m), 876 (s), 800 (s), 772 (s), 704 (m), 620 (m) cm^{-1}.

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