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Towards Visible-Light Photocatalytic Reduction of Hypercoordinated Silicon Species

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Dedicated to Philippe Renaud in celebration of his 60th birthday and with all our friendship

Nowadays, the quest of new radical precursors based on heteroatom complexes occupies an increasingly important position in contemporary research. Herein, we investigated the behavior and the limitations of hexa- or pentacoordinated organochlorosilanes and related pentacoordinated silyliums as new families of complexes for the generation of radicals under photocatalytic reductive conditions. Particularly, treatment of chlorophenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) or the related silylium derivative with the *fac*-Ir(ppy)₃ (5 mol%)/NET₃ (1.5 equiv) system under blue LEDs irradiation generates a thiopyridyl radical which can participate in the formation of a carbon-sulfur bond by reaction with an allylsulfone. Computational studies supported this experimental finding, and particularly by showing that homolytic fragmentation of C-Ts bond is favored over the fragmentation of thiopyridyl radical.

Keywords: chlorosilane, silylium, hypercoordinated silicon compounds, photoreduction, radical, cyclic voltammetry, carbon-sulfur bond, allylation

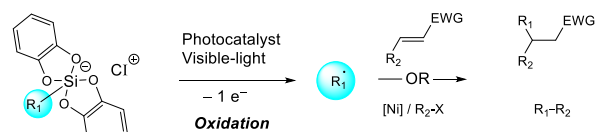
Introduction

Over the last few decades, organosilicon compounds have received a great deal of attention in organic synthesis,¹ and particularly radical synthetic chemistry, with the generation of transient silicon-centered radicals from silyl hydrides,^{2,3} behaving both as an effective mediator of radical reactions starting from a range of radical precursors (halides, chalcogens, xanthates, etc...) and as substrates for radical functionalization such as the hydrosilylation of unsaturated systems.^{2,3} The homolytic Si-H cleavage can be obtained for instance with the (TMS)₃SiH Chatgililoglu's reagent^{2,4} or the Et₃SiH/RSH system for polarity reversal catalysis introduced by Roberts.⁵ More anecdotal, silyl radicals can be generated by photolysis of a Si-B bond for the silylboration of olefins⁶ or by photocatalytic oxidation of the supersilanol (TMS)₃SiOH to perform halogen abstraction for Nickel/photoredox sp³-sp³ cross-coupling reactions.⁷ As another interesting property, organosilicons with an activated C-Si bond as well as hypercoordinated - penta- or hexacoordinated - silicon derivatives⁸ have revealed as a potential source of carbon-centered radicals under oxidative conditions, which can participate in further synthetic transformations.

A SET oxidation-desilylation of benzyltrimethylsilanes involving visible-light excited chiral iminium ions^{9a} or 9-mesityl-10-methylacridinium perchlorate salt^{9b} as a catalytic and strong photooxidant, allowed the formation of benzylic radicals which can be trapped by ground-state iminium ions or Michael-type acceptors respectively. In the same vein, α -alkoxymethyl radicals were successfully generated from the corresponding α -silyl ethers¹⁰ by photocatalyzed oxidation, as well as acyl radicals from acyl silanes.¹¹ But interestingly, what about the reactivity of hypercoordinated silicon derivatives under oxidative conditions? This question was first answered by Kumada who reported the oxidation of organopentafluorosilicates to provide organic radicals which can react

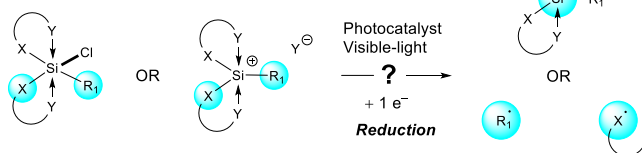
with a second equivalent of copper chloride and liberate the chlorinated product. However, this transformation required stoichiometric amount of copper salts and the low solubility of these substrates limits their use for synthesis.¹² In that context, Nishigaishi reported the photoallylation¹³ of benzyl-type derivatives and dicyanobenzene with the more soluble allyl bis-catecholato silicate¹⁴ but these studies were limited to the generation of allylic radical. Following our initial work on the oxidation of alkyltrifluoroborates in 2010,¹⁵ we prepared a series of bench stable alkyl biscatecholato silicates with a low oxidation potential (< 1V vs. SCE) and tested them under visible-light photooxidative condition^{16a} in order to generate functionalized alkyl radicals and particularly primary ones.^{16b,17} The scope of substrates for simple radical trapping and also for photoredox/nickel dual catalysis proved to be quite large from primary to tertiary radicals.^{16,18}

Previous studies



Cl[⊖] = K⁺[18-C-6] / NEt₄⁺

This study

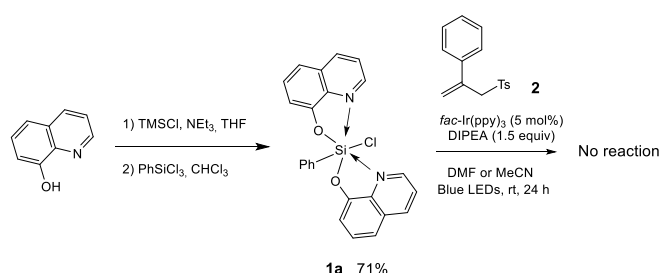


Scheme 1. Hypercoordinated silicon compounds as a source of radicals under photooxidative or photoreductive conditions

To date, the use of hypercoordinated silicon derivatives in radical synthesis has been limited to the generation of radicals under oxidative regimes and no attempt has been already made in a reductive manner. Herein, we reported the first results regarding the behavior of hypercoordinated chlorosilanes and the related cationic silicon derivatives under visible-light photoreductive conditions to generate radical species. We presumed that the presence of hypercoordinated ligands or the formation of silylium salts would favor the labilization of the Si-Cl bond during the reduction step to provide the formation of hypercoordinated silyl radicals. The latter may subsequently expel a carbon- or heteroatom-centered radical (R_1 or X , respectively) (Scheme 1).

Results and Discussion

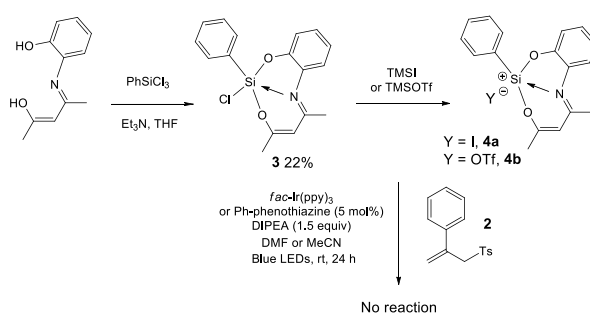
We thus tested the photoreduction of a set of hypercoordinated chlorosilanes whose synthesis has been already described in the literature. We started to investigate the reactivity of hexacoordinated silicons with bidentate N,O ligands such as 8-oxyquinolinato ligands. We first prepared compound **1a** from phenyltrichlorosilane and 8-hydroxyquinoline using the procedure developed by Wägler in 2014 (Scheme 2).¹⁹ We tried to evaluate the reduction potential of **1a** by cyclic voltammetry (CV) but, due to the insolubility of this organosilicon in acetonitrile and THF, it could not be determined. Nevertheless, we explored the photoreduction of **1a** using the highly reductant photocatalyst *fac*-Ir(ppy)₃ (5 mol%, E Ir(IV)/Ir(III)* = -1.7 V vs SCE) under blue LEDs irradiation in the presence 1.5 equiv. of allyl sulfone **2** as a radical acceptor and 1.5 equiv. of *N,N*-diisopropylethylamine (DIPEA) as sacrificial electron donor for the regeneration of the photocatalyst (Scheme 2). Whatever the nature of the solvent (0.1 mol/L), acetonitrile (CH₃CN) or dimethylformamide (DMF), no reaction occurred leaving the allylsulfone **1a** unchanged. *n*-Butyl and benzyl chlorosilanes were also efficiently synthesized (respectively 86% and 84% yield) and investigated but no appreciable improvement of the solubility was evident.



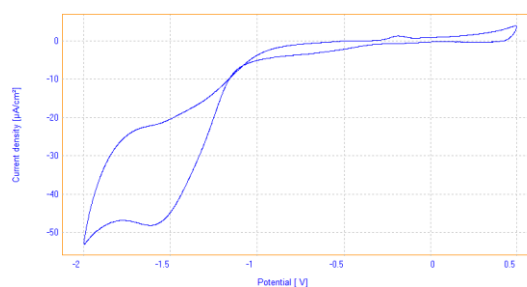
Scheme 2. Synthesis of hexavalent silicon compound **1a** with 8-oxyquinolinato ligands and reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions

In a second phase, we looked at more soluble silicon derivatives. In 2012, Tacke's group reported the formation of pentacoordinate chlorosilicon(IV)

complexes with tridentate dianionic O, N, O ligands such as the tridentate 2-((E)-((Z)-4-hydroxypent-3-en-2-ylidene)amino)phenol ligand.²⁰ We then synthesized the corresponding complex **3** as reported in scheme 3 and measured its reduction potential by CV. To our delight, we were pleased to see that the reduction potential of the hypercoordinated species **3** is higher than the tetravalent phenyl trichlorosilane (PhSiCl₃), i.e. -1.31 V vs SCE compared to -1.51 V vs SCE (see cyclic voltammogram of **3** and Si, scheme 4). This suggests that this tridentate ligand significantly increases the ability of the chlorosilane to be reduced. Compound **3** was then subjected to the same reaction conditions used for **1a**, but again no reaction was evidenced by TLC and confirmed by ¹H NMR (Scheme 3). Only starting materials were recovered. Even after addition of additives such as TMSI or TMSOTf in order to generate *in situ* the corresponding electron deficient silylium derivatives **4a** and **4b** (not characterized),²¹ no product was obtained and only degradation was observed. Switching from *fac*-Ir(ppy)₃ to a highly reducing organic photocatalyst such as *N*-phenylphenothiazine (Ph-PTZ) (E Ph-PTZ⁺ / P Ph-PTZ* = -2.5 V vs SCE),²² did not afford any product either.



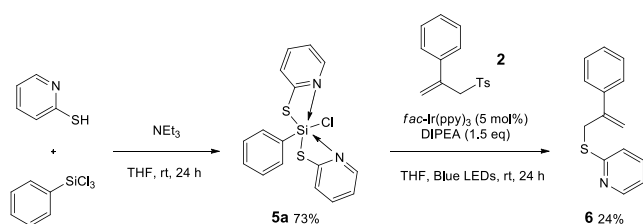
Scheme 3. Synthesis of pentavalent silicon compound **3**, using 2-((E)-((Z)-4-hydroxypent-3-en-2-ylidene)amino)phenol ligand, and the corresponding silylium derivatives **4a** and **4b** as well as their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions



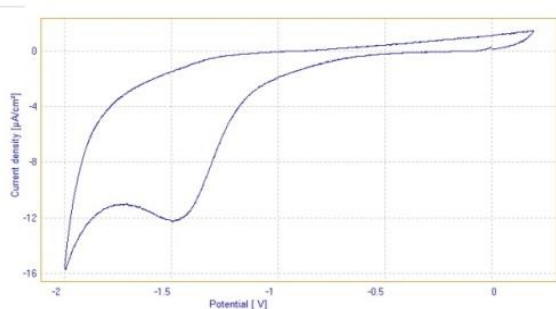
Scheme 4. Electrochemical studies: Cyclic voltammogram of **3** (10 mM) performed at 22°C in dried and degassed THF containing Bu₄NPF₆ (100 mM) as the supporting electrolyte at a scan rate of 0.1 V.s⁻¹. Glassy carbon, platinum plate and saturated calomel were used respectively as working, counter and reference electrodes respectively.

Thereafter, we were particularly interested in the photoreduction of hexacoordinated silicon complexes with two bidentate ligands N,S-

pyridine-2-thiolato.²³ In this case, we may benefit from the possible stabilization of the generated silyl radical by the sulfur atom as already observed in the disulfure bond.²³ Chlorophenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) (**5a**) was then synthesized following the protocol reported by Tacke in 2013 as outlined in **scheme 5**. Its reduction potential can be estimated by CV and showed a value of about -1.28 V vs SCE (**Scheme 6**), higher than the reduction potentials previously determined for the hypercoordinated silicon species **3** (*vide supra*). This increase of potential should facilitate the reduction of compound **5a** by the excited state of the photocatalyst *fac*-Ir(ppy)₃ (**Scheme 5**). This substrate was then treated under the same conditions as **1a** and **3**. Allylsulfide **6**, resulting from the addition of the ligand 2-thiopyridine to the allylsulfone **2**, was obtained in a 24% yield. We wondered if the yield in **6** can be improved and if this transformation involves a radical or an ionic pathway.



Scheme 5. Synthesis of pentavalent silicon compound **5a**, using N,S-pyridine-2-thiolato ligand followed by their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions. Formation of allylsulfide **6**



Scheme 6. Electrochemical studies: Cyclic voltammogram of **5a** (10 mM) performed at 22°C in dried and degassed THF containing Bu₄NPF₆ (100 mM) as the supporting electrolyte at a scan rate of 0.1 V.s⁻¹. Glassy carbon, platinum plate and saturated calomel were used respectively as working, counter and reference electrodes respectively.

Encouraged by these preliminary results, we first optimized the reaction conditions by screening the nature of the photocatalyst or the electron donor, by using different solvents and by modulating the reaction time or the ratio radical trap/hypercoordinated silicon (**2/5a**). Both DMF and CH₃CN proved beneficial solvents for the reaction, while the reaction was less effective in THF (**Table 1**, entries 1, 2, 3 and 9). With respect to the sacrificial electron donor, changing DIPEA to triethylamine gave a comparable yield whereas no reaction was observed with Hantzsch ester (**Table 1**, entries 2, 3 and 5). An extended irradiation time from 24h to 48h did not improve the photoreductive process (**Table 1**, entries 3 and 5). No more than 45% yield was reached with an excess of allylsulfone **2** (4 equiv, **Table 1**, entry 6). By contrast, if we consider allylsulfone **2** as the limiting

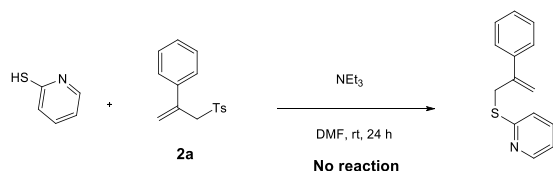
substrate, addition of 2 or 3 equiv of organochlorosilane **5a** led 66 or 78% of **6**, respectively (**Table 1**, entries 7 and 8). An organic dye such as fluorescein (F) (E (F[•]/F^{*}) = -1.61 V vs SCE) was investigated as an alternative to Ir(ppy)₃, but only 4% of **6** was obtained after 24h of irradiation (**Table 1**, entry 10).

Entry	Solvent	PCat	Equiv (2/5a)	Time (h)	Donor	Yield ^a
1	THF	Ir(ppy) ₃	1.5/1	24	DIPEA	24%
2	DMF	Ir(ppy) ₃	1.5/1	24	DIPEA	35%
3	DMF	Ir(ppy) ₃	1.5/1	24	Et ₃ N	36%
4	DMF	Ir(ppy) ₃	1.5/1	24	Hantzsch ester	0%
5	DMF	Ir(ppy) ₃	1.5/1	48	Et ₃ N	37%
6	DMF	Ir(ppy) ₃	4/1	24	DIPEA	45%
7	DMF	Ir(ppy) ₃	1/2	24	Et ₃ N	66%
8	DMF	Ir(ppy) ₃	1/3	24	Et ₃ N	78%
9	MeCN	Ir(ppy) ₃	1.5/1	24	Et ₃ N	32%
10	MeCN	Fluorescein	1.5/1	24	DIPEA	4%
11	DMF	-	1/3	24	Et ₃ N	33%
12	DMF	Ir(ppy) ₃	1/3	24	-	23%
13	DMF	Ir(ppy) ₃	1/3	24	Et ₃ N	0%

^a NMR yield using TMOP as internal standard

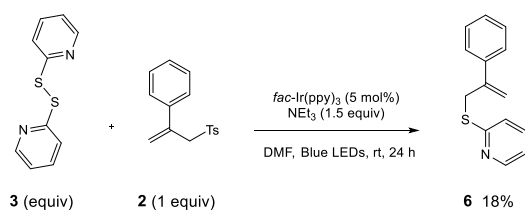
Table 1. Optimisation of the reaction conditions and control reactions

Control experiments have been performed in order to secure the role of the photocatalyst and exclude an ionic process (**Table 1**, entries 11, 12 and 13). In the absence of photocatalyst, we ran the reaction under blue LEDs irradiation and allylsulfide **6** was obtained in 33% yield. The formation of this small amount of **6** may arise from a photoinduced electron-transfer (PET) between NEt₃ and the organosilane **5a**. No reaction occurred without blue LEDs activation. Only 23% for **6** was obtained when NEt₃ was omitted. Even if we showed that the presence of the photocatalyst Ir(ppy)₃ is required to reach a good yield, we tested the reactivity between pyridine-2-thiol and acceptor allylsulfone **2** under basic conditions. As expected, no trace of **6** was formed showing that the formation of the allylation adduct does not involve an ionic pathway and a radical process is likely to occur (**Scheme 7**). Of note, addition of Ir(ppy)₃ (5 mol%) to this mixture led to only 9% yield of **6**. From these last studies, we can deduce that most of thiopyridyl radicals were generated by reduction of silane **5a** leading to adduct **6**, and not from the decomposition of **5a**.



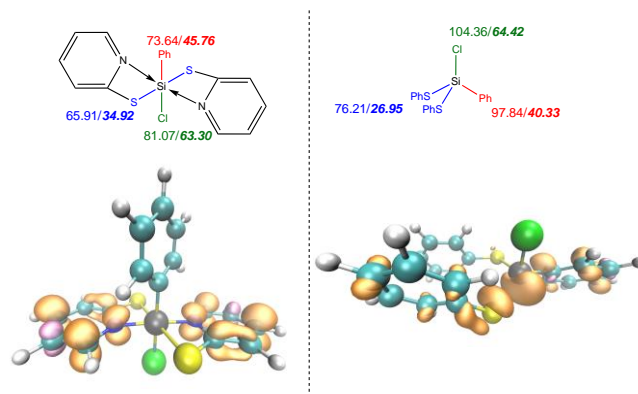
Scheme 7. Control experiment: reactivity between pyridine-2-thiol and acceptor allylsulfone **2** under basic conditions

In parallel, we examined the behavior of the commercially available aldrithiol™ under the same photocatalytic conditions, as a potential source of thiopyridyl radical. Starting from 3 equivalents of this compound, only a 18% yield of **6** was obtained compared to 78% from **5a**. This study showed all the interest of **5a** as an efficient precursor of thiopyridyl radical for synthetic transformations (**Scheme 8**).



Scheme 8. Photocatalytic reaction using aldrithiol™ as a radical precursor

Computational studies have been realized, namely at the B₃LYP-D₃/def2-SV(P) level with the TURBOMOLE suite of programs. Upon reduction, it was shown that the SET process is occurring on the π system of the pyridine moiety of **5a** (**Scheme 9**, lower part), in a similar manner to what have been observed with our biscatecholato silicates.^{18a} If we compare the various BDEs of the substrates before and after oxidation, this reduction strongly weakens all Si-X (X = C, S, Cl) bonds. Particularly, the energy of the Si-S bond (35 kcal/mol) is lower than the one of the Si-C bond (46 kcal/mol) and the Si-Cl bond (63 kcal/mol) and should favor the formation of the thiopyridyl radical (**Scheme 9**). We also investigated the non-hypercoordinated tetravalent species with two thiophenyl ligands, to compare directly the various BDE values with **5a**. This species is plotted on the right side of Scheme 9. The reduction process is taking place on the thiophenyl moiety but the energy of the Si-S bond before reduction (76 kcal/mol) is higher than for the hypervalent silane **5a** (66 kcal/mol). This comparison shows also that whereas **5a** has a positive electron affinity (10.35 kcal/mol), this is not the case for (PhS)₂Si(Cl)Ph (-1.96 kcal/mol), highlighting the ease of reduction of **5a**. As for **5a**, we also observed a small BDE of 27 kcal/mol after reduction. The other bonds are similarly affected by the reduction with the Si-Cl bond having a BDE of 64.5 kcal/mol and the Si-Ph being at 40 kcal/mol.



Scheme 9. Computational studies on **5a** and on phenylbis(phenylthio)chlorosilane. Upper part : bond dissociation energies before and after reduction. Lower part: spin density isosurfaces

Based on these experimental studies, DFT calculations and in accordance with the literature,²⁷ we can propose the following mechanism where the photoactivated catalyst under blue LEDs irradiation reduces hypercoordinated phenylchlorosilane **5a** at the pyridine moiety and promotes preferentially the homolytic cleavage of the Si-S bond between the thiopyridine ligand and silicon atom. The expelled thiopyridyl radical can be trapped by allylsulfone **2**. The photocatalyst is regenerated by action of NEt₃ (**Scheme 10**). It should be mentioned that formation of **6** involved sequential addition of the thiopyridine radical, generation of the transient radical intermediate **A** and homolytic fragmentation of the C-Ts bond. We were surprised by the fact that intermediate **A** is more prone to give the homolytic fragmentation of the C-Ts bond rather than the reversible extrusion of the thiopyridine radical moiety. It is indeed known in the literature that a thiophenyl radical is a good leaving group, presumably better than the phenylsulfonyl one.²⁴ To rationalize the observed selectivity, DFT calculations of β -fragmentation processes on intermediate **A** and on an analogous intermediate (**A'**) where the pyridine moiety is replaced by a phenyl were thus conducted, at the same level of theory (namely B₃LYP-D₃/def2-SV(P)). On **A'**, calculations indicate that departure of the tosyl radical is slightly favored over the thiophenyl radical fragmentation (barriers of 8.4 kcal/mol versus 9.3 kcal/mol). But the situation is totally different in the case of intermediate **A**: while the tosyl radical departure remains in the same energetic range with a barrier of 9 kcal/mol, the thiopyridyl radical extrusion proves to be unfeasible with an always increasing potential energy surface (see **Figure 1**), reaching value over 18 kcal/mol. It turns out that the thiopyridyl radical is particularly unstable and observation of the geometry highlights that this radical is trying to establish non-covalent interactions between the nitrogen of the pyridine moiety and the homobenzylic C-H to stabilize itself. Therefore, the mechanism proposed in **Scheme 10** is supported by this computational analysis.

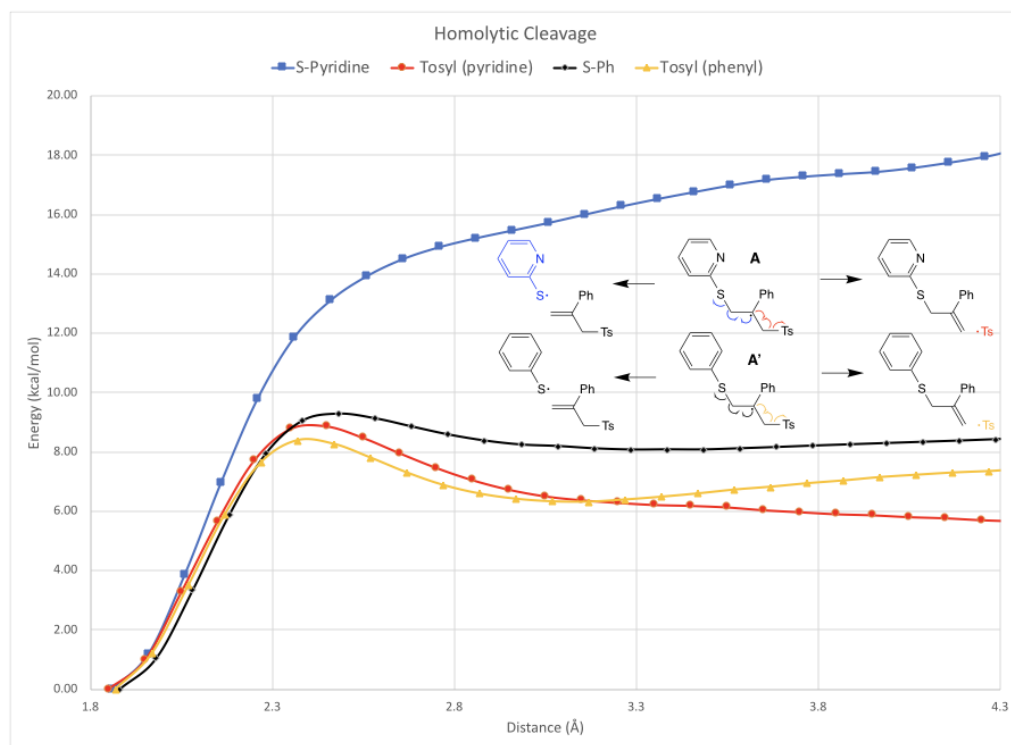
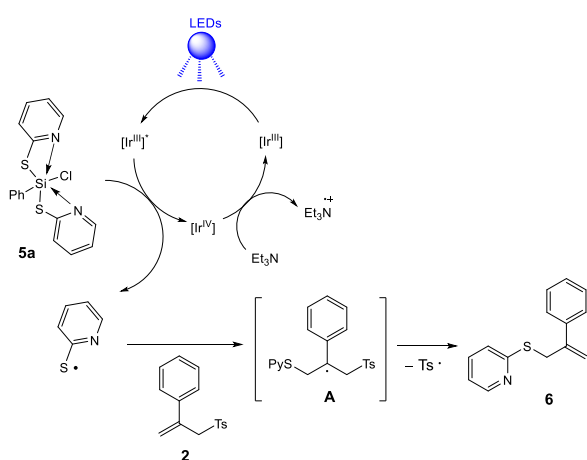
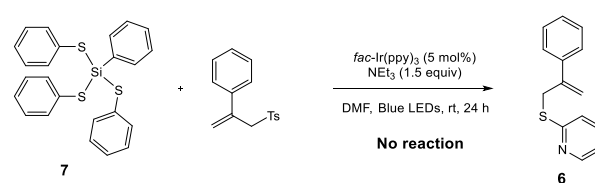


Figure 1. Calculated β -fragmentation processes for intermediate **A** and **A'**, at the B₃LYP-D₃/def2-SV(P) level.

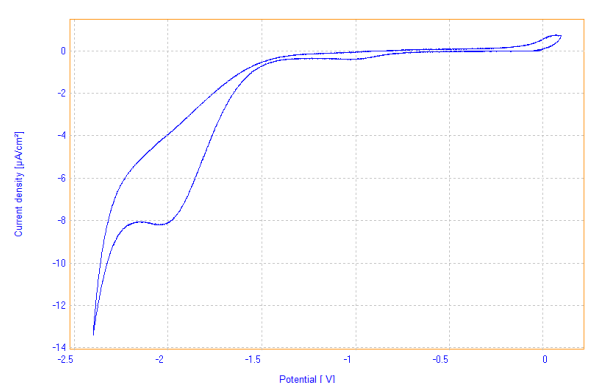


Scheme 10. Proposed mechanism for the formation of **6**

Due to the weakness of the Si-S bond and its ability to generate thiyl radicals under reductive conditions, we compared the reactivity of our previous system (**5a**) with the non-hypercoordinated tetravalent phenylsilane bearing three thiophenyl ligands **7** (Scheme 11). This one was synthesized from phenylsilane and thiophenol according to the literature procedure.²⁵ Its reduction potential was then measured. A value of -1.75 V vs SCE was obtained which appears to be lower than the reduction potential of **5a** (Scheme 12). This difference of potential may explain why no allylation adduct **6** was formed from **5a** under the same reductive conditions (Scheme 11).



Scheme 11. Photocatalytic reaction using phenyltris(phenylthio)silane as a radical precursor

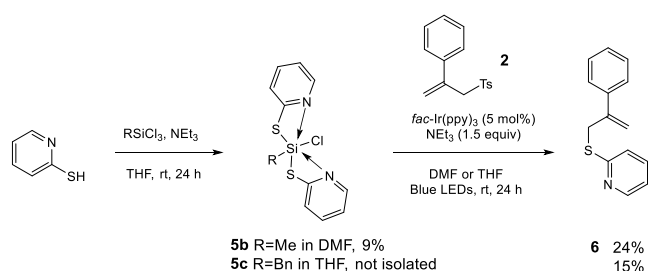


Scheme 12. Electrochemical studies: cyclic voltammetry of **7** (10 mM) performed at 22°C in dried and degassed THF containing Bu₄NPF₆ (100 mM) as the supporting electrolyte at a scan rate of 0.05 V.s⁻¹. Glassy carbon, platinum plate and saturated calomel were used respectively as working, counter and reference electrodes respectively.

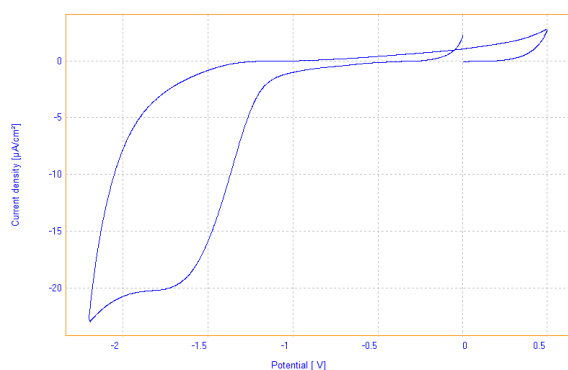
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We next evaluated the reactivity of the hypercoordinated methylchlorosilane **5b** under photocatalytic reductive conditions. We first prepared it by using the same procedure as for **5a** starting from methyltrichlorosilane and then we measured its reduction potential, which was estimated by CV at about -1.37 V (vs SCE). This value still suggests that the photo-excited photocatalyst *fac*-Ir(ppy)₃ (E Ir(IV)/Ir(III)* = -1.7 V vs SCE) can reduce this substrate. Treatment of **5b** (3 equiv) with **2** (1 equiv) in the presence of *fac*-Ir(ppy)₃ (5 mol%) and Et₃N (1.5 equiv) in DMF under blue LEDs irradiation gave **6** in 31% yield (**Scheme 13**). It should be noted that no addition of the methyl group was observed. For comparison, its benzyl analog **5c** has also been investigated. This compound was prepared *in-situ* from benzyltrichlorosilane but could not be isolated. Nevertheless, the photocatalytic reaction was carried on the crude reaction mixture and the allylsulfide **6** was obtained in 15% yield as the only product.

From those experiments, only the thiopyridyl radical was formed as evidenced by trapping experiments with allylsulfone **2**. The phenyl derivative was revealed to be the most reactive and provided the best yield in allylsulfide **6**. Interestingly, formation of phenyl, methyl or benzyl radical was never observed in these studies.

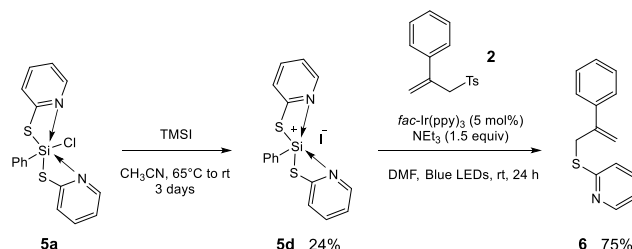


Scheme 13. Synthesis of pentavalent silicon compounds **5b** and **5c**, using N,S-pyridine-2-thiolato ligand followed by their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions. Formation of allylsulfide **6**.



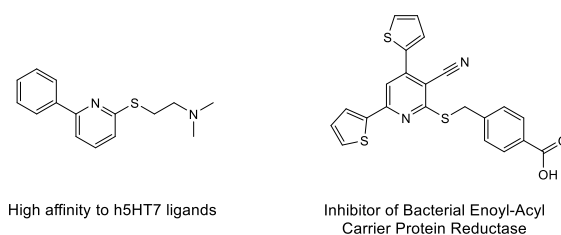
Scheme 14. Electrochemical studies: Cyclic voltammogram of **5b** (10 mM) performed at 22°C in dried and degassed THF containing Bu₄NPF₆ (100 mM) as the supporting electrolyte at a scan rate of 0.1 V.s⁻¹. Glassy carbon, platinum plate and saturated calomel were used respectively as working, counter and reference electrodes respectively.

Finally, we looked at the photoreduction of the highly electron deficient silylium derivative **5d** readily obtained by action of TMSI on the corresponding phenylchlorosilane **5a**.²¹ Under the optimized photocatalytic conditions determined for **5a**, **5d** provided **6** as the sole product with the same yield as **5a**. This result showed that silylium **5d** can be reduced as efficiently as phenylchlorosilane **5a** and participate in radical reactions (**Scheme 15**).



Scheme 15. Synthesis of silylium derivative **5d**, using N,S-pyridine-2-thiolato ligand followed by their reactivity in the presence of allylsulfone **2** under visible-light photoreductive conditions. Formation of allylsulfide **6**.

Interestingly, as the thiopyridine moiety is encountered in various bioactive molecules (**Scheme 16**),²⁶ efficient reactions allowing the synthesis of these compounds in mild conditions remains interesting.²⁷



Scheme 16. Bioactive molecules containing a thiopyridine scaffold

Conclusions

In conclusion, we have demonstrated that the modification of the ligands of hexacoordinated chlorosilane derivatives can efficiently modulate their reactivity towards photoreductive conditions. By using a thiopyridine ligand, the corresponding thiyl radical has been liberated and efficiently trapped by an allylsulfone as an acceptor. Even if these radicals could be formed through the oxidation of pyridine thiolate like phenyl thiolate,²⁸ no methodology has already been reported by using a reductive pathway. Experiments are currently ongoing in our laboratory for the formation of carbon-centered radicals by photoreduction of other types of hypercoordinated silicon species.

Experimental Section

To a Schlenk flask was added the silicon complex **5a-d**, Ir(ppy)₃ (5 mol %), and allyl sulfone **2**. The degassed solvent (0.1 mol/L or 0.067 mol/L) was then introduced followed by the amine (1.5 equiv) and the reaction mixture was irradiated with blue LEDs (470 nm) at room temperature for 24 h under an argon atmosphere. The reaction mixture was diluted with diethyl ether, washed with water (2 times), dried over MgSO₄ and evaporated under reduced pressure. The crude residue was purified by flash chromatography.

Supplementary Material ((optional))

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/MS-number>. ((Please delete this text if not appropriate))

Acknowledgements

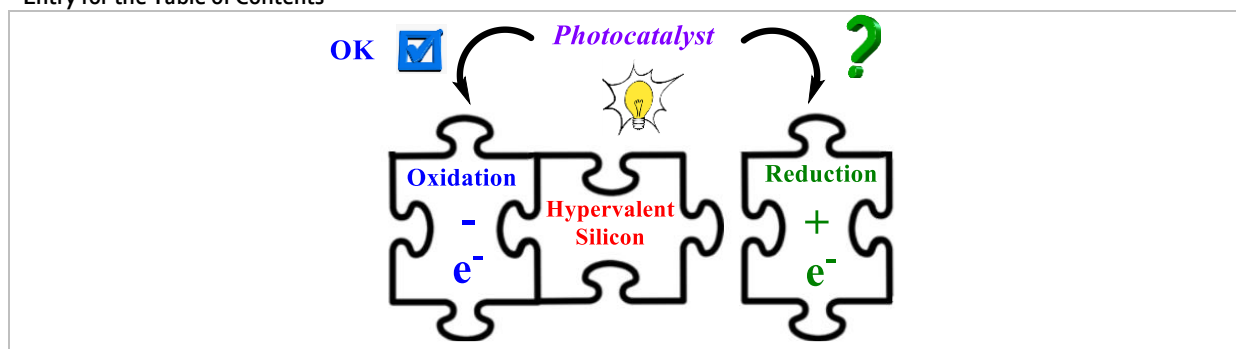
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Towards Visible-Light Photocatalytic Reduction of Hypercoordinated Silicon Species

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General informations

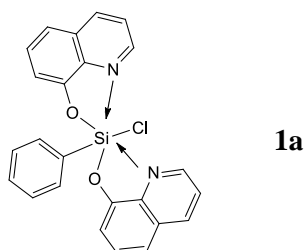
Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. THF, acetonitrile and diethyl ether were distilled over sodium/benzophenone, triethylamine over potassium hydroxide. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (ATR diamond) spectrophotometer. ^1H , ^{13}C NMR spectra were recorded at room temperature at 400, 377 and 100 MHz respectively, on a Bruker AVANCE 400 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet). Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a UV lamp ($\lambda = 254$ nm) and KMnO_4 staining. Flash Column Chromatographies were conducted on silica Geduran® Si 60 Å (40 – 63 μm). High resolution mass spectrometries were performed on a microTOF (ESI).

General procedures

1. Synthesis of the silicon complexes

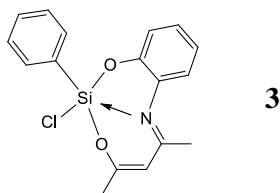
All these complexes were previously described by Tacke's, Yamamoto's or Wagler's group.

8,8'-((chloro(phenyl)silanediy)bis(oxy))diquinoline (**1a**)



To a dried Schlenck tube with 8-Oxyquinoline (2.00 g, 13.7 mmol) and triethylamine (2.89 mL, 20.7 mmol) in THF (50 mL) was added dropwise chlorotrimethylsilane (2.07 mL, 16.3 mmol) at 0°C. The triethylammonium salt was filtered off and washed with THF (2 x 10 mL). The residue was dissolved in chloroform (30 mL) and cooled to 0°C. At this temperature, phenyltrichlorosilane (1.1 mL, 6.86 mmol) was added and the solution was stored at room temperature. The yellow crystalline product was filtered off, washed with chloroform (2x5 mL) and dried in vacuo to afford 8,8'-((chloro(phenyl)silanediy)bis(oxy))diquinoline (**1a**) (2.1 g, 71%). No analysis could be done due to the very poor solubility of this compound.

2-chloro-4,6-dimethyl-2-phenylbenzo[d][1,3,6,2]dioxazasilonine (**3**)



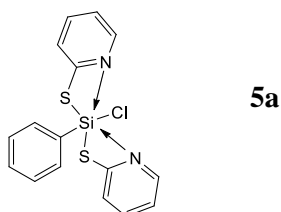
Triethylamine (40 mmol, 5.6 mL) and trichlorophenylsilane (20 mmol, 3.2 mL) were added at 0°C to a stirred suspension of 2-((E)-((Z)-4-hydroxypent-3-en-2-ylidene)amino)phenol (20.0 mmol, 3.82 g) in tetrahydrofuran (60 mL). After that, the resulting mixture was warmed to 20°C and was stirred at this temperature for 24h. The triethylammonium salt was filtered off and washed with tetrahydrofuran (2 x 10 mL). The solvent was removed under reduced pressure before addition of DCM (15 mL) and *n*-pentane (15 mL) on the residue. The resulting solution was kept undisturbed at room temperature for

24 h. The yellow crystalline product was isolated by filtration, washed with diethyl ether (15 mL), and dried in vacuo to afford 2-chloro-4,6-dimethyl-2-phenylbenzo[d][1,3,6,2]dioxazasilonine (**3**) (1.49 g, 22 %). The spectroscopic data are in agreement with those reported in the literature¹.

¹H NMR (400 MHz, CD₂Cl₂): δ 7.43-7.38 (dd, J = 8.0 Hz and 1.2 Hz, 1H), 7.37-7.32 (m, 2H), 7.31-7.24 (m, 2H), 7.24-7.15 (m, 3H), 7.01-6.93 (m, 1H), 5.73-5.71 (d, J = 0.4 Hz, 1H), 2.44 (s, 3H), 2.26 (s, 3H) ppm.

¹³C NMR (100 MHz, CD₂Cl₂): δ 172.1 (1C), 169.3 (1C), 151.6 (1C), 138.3 (1C), 132.6 (1C), 132.5 (2C), 129.8 (1C), 129.2 (1C), 127.9 (2C), 121.1 (1C), 120.7 (1C), 115.8 (1C), 107.0 (1C), 24.8 (1C), 24.3 (1C) ppm.

Chlorophenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) (**5a**)



To a Schlenk tube with a stirred solution of 2-pyridinethiol (14.2 mmol, 1.59 g) in tetrahydrofuran (30 mL) was added triethylamine (14.2 mmol, 1.44 g) and trichlorophenylsilane (7.09 mmol, 1.50 g). The reaction mixture was then stirred at room temperature for 16 h. The resulting triethylammonium salt was filtered off, washed with tetrahydrofuran (2×5 mL) and discarded. The solvent was concentrated *in vacuo*, then acetonitrile (20 mL) was added. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20°C then put in a freezer and kept undisturbed for 6 days. The resulting yellow crystalline solid was isolated by filtration and washed with diethyl ether (2×10 mL) before being dried in vacuo to afford chlorophenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) (**5a**) (1.87 g, 73%). The spectroscopic data are in agreement with those reported in the literature².

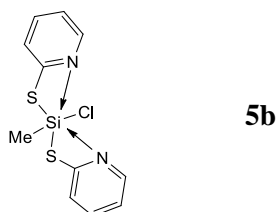
¹H NMR (400 MHz, CD₂Cl₂): δ 8.26-8.08 (brs, 2H), 7.77-7.70 (m, 2H), 7.66-7.60 (m, 2H), 7.48-7.43 (m, 2H), 7.24-7.18 (m, 3H), 7.12-7.05 (m, 2H) ppm.

¹³C NMR (100 MHz, CD₂Cl₂): δ 166.6 (2C), 152.7 (1C), 141.3 (2C), 140.9 (2C), 132.7 (2C), 127.9 (1C), 127.4 (2C), 125.6 (2C), 118.2 (2C) ppm.

¹ B. Theis, S. Metz, F. Back, C. Burschka, R. Tacke, *Z. Anorg. Allg. Chem.* **2009**, 635, 1306-1312

² J. A. Baus, C. Burschka, R. Bertemann, C. F. Guerra, F. M. Bickelhaupt, R. Tacke, *Inorg. Chem.* **2013**, 52, 10664-10676

Chloromethylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) (5b)

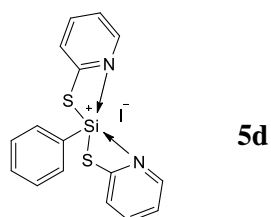


To a Schlenk tube with a solution of 2-pyridinethiol (13.7 mmol, 1.547 g) in tetrahydrofuran (27.8 mL) was added triethylamine (13.7 mmol, 1.81 mL) and methyltrichlorosilane (6.96 mmol, 0.817 mL). The reaction mixture was then stirred at room temperature for 16 h. The resulting precipitate was filtered off, washed with tetrahydrofuran (2×5 mL) and discarded. The solvent was concentrated *in vacuo*, followed by the addition of acetonitrile (15 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20°C then put in a freezer and kept undisturbed for 6 days. The resulting colorless crystalline solid was isolated by filtration and washed with diethyl ether (2×10 mL) before being dried *in vacuo* to afford chloromethylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) (**5b**) (180 mg, 9%). The spectroscopic data are in agreement with those reported in the literature².

¹H NMR (400 MHz, CD₂Cl₂): δ 8.10-7.99 (m, 2H), 7.77-7.67 (m, 2H), 7.50-7.42 (m, 2H), 7.11-6.98 (m, 2H), 1.16 (s, 3H) ppm.

¹³CNMR (100 MHz, CD₂Cl₂): δ 168.2 (2C), 141.0 (2C), 140.4 (2C), 125.4 (2C), 117.9 (2C), 26.0 (1C) ppm.

Phenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) Iodide (5d)

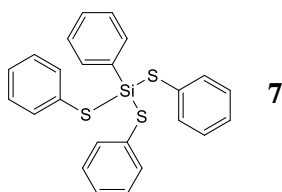


Iodotrimethylsilane (6.95 mmol, 1.39 g) was added in a single portion to a stirred solution of chlorophenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) (**6a**) (2.77 mmol, 1.00 g) in acetonitrile (30 mL). The resulting reaction mixture was then stirred at 65°C for 3 hours and at room temperature for 3 days. After that, the reaction mixture was concentrated *in vacuo*, then dissolved in acetonitrile (30 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to 20°C then put in a freezer and kept undisturbed at this temperature for 3 days. The resulting

colorless crystalline solid was isolated by filtration, washed with diethyl ether (2×5 mL), and dried in to afford phenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV) Iodide (**5d**) (300 mg, 24%). The spectroscopic data are in agreement with those reported in the literature.¹

¹H NMR (400 MHz, CD₂Cl₂): δ 8.46-8.22 (m, 2H), 8.06-7.82 (m, 2H), 7.73-7.57 (m, 4H), 7.43-7.24 (m, 5H) ppm.

Phenyltris(phenylthio)silane (7)



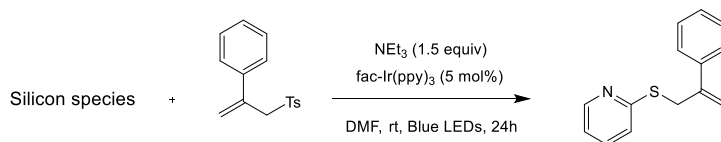
To a Schlenk flask was added the phenyl silane (4 mmol, 0.49 mL), the thiopyridine (12 mmol, 1.32 g) and RhCl(PPh₃)₃ (0.128 mmol, 120 mg) in 10 mL of hexane. The reaction mixture was stirred for 15 hours then filtrated, concentrated under vacuo and pentane was added. An oil appeared and this was taken out to give pure product phenyltris(phenylthio)silane (**7**) (600 mg, 35%). The spectroscopic data are in agreement with those reported in the literature³.

¹H NMR (400 MHz, CDCl₃): δ 7.65-7.09 (m, 20H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 135.1 (6C), 134.9 (3C), 132.0 (1C), 131.1 (1C), 128.9 (6C), 128.8 (2C), 128.0 (2C), 127.6 (3C) ppm.

2. Photocatalytic reaction

Standard procedure

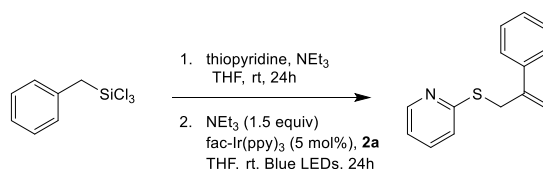


To a Schlenk flask was added the silicon complex **5a-d**, Ir(ppy)₃ (5 mol %), and allyl sulfone **2**. The degassed solvent (0.1 mol/L or 0.067 mol/L) was then introduced followed by the amine (1.5 eq.) and

³ J. B. Baruah, K. Osakada, T. Yamamoto, *Organometallics*. **1996**, 15, 456-459

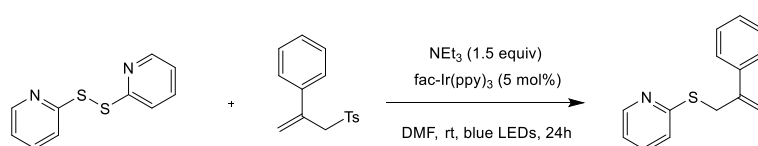
the reaction mixture was irradiated with blue LEDs (470 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether, washed with water (2 times), dried over MgSO₄ and evaporated under reduced pressure. The crude residue was purified by flash chromatography.

Photocatalytic reaction using Chlorobenzylbis[*N,S*-pyridine-2-thiolato(-)]silicon(IV) complex



To a dry Schlenk flask was added the benzyl trichlorosilane (2.0 mmol, 0.35 mL), triethylamine (4.0 mmol, 0.56 mL) and thiopyridine (4.0 mmol, 445 mg). The Schlenk flask was sealed with a rubber septum and evacuated / purged with vacuum / argon three times. Then 14 mL of dry and degazed THF were added and the solution was stirred for one day. The triethylammonium salt was filtrated off by canula then 7 mL of this solution were added to a dry Schlenk flask containing Irppy (0.0255 mmol, 14.73 mg) triethylamine (1 mmol, 0.14 mL) and allyl sulfone **2** (0.45 mmol, 122 mg). The reaction mixture was irradiated with blue LEDs (470 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether, washed with water (2 times), dried over MgSO₄ and evaporated under reduced pressure and analyzed by NMR using TMOP (1 equiv) as an internal standard.

Photocatalytic reaction using aldrithiolTM

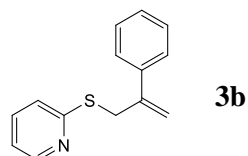


To a dry Schlenk flask was added aldrithiolTM (0.3 mmol, 66 mg), the Ir(ppy) (0.005 mol, 3.2 mg) and the allyl sulfone **2** (0.1 mmol, 27.2 mg). The Schlenk flask was sealed with a rubber septum and evacuated / purged with vacuum / argon three times. Then 1.5 mL of dry and degazed DMF was introduced followed by addition of the triethylamine (0.15 mmol, 0.021 mL) and the reaction mixture was irradiated with blue LEDs (470 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether, washed with water (2 times), dried over MgSO₄ and

evaporated under reduced pressure. The crude residue was analyzed by NMR using TMOP (1 equiv) as an internal standard.

Characterisation of the thiopyridine product

2-((2-phenylallyl)thio)pyridine (3b)



To a dried Schlenk flask was added the silicon complex (3 equiv), the acceptor (1 equiv), the Irppy (5 mol%), and the NEt_3 (1.5 equiv) in dried and degassed DMF (0.66M). The reaction mixture was irradiated with blue LEDs (477 nm) for 24h then diluted with diethyl ether washed with water (2 times) dried over MgSO_4 , filtered, evaporated under reduced pressure and analyzed by ^1H NMR CDCl_3 .

^1H NMR (400 MHz, CDCl_3): δ 8.53-8.41 (d, $J = 4.8$ Hz, 1H), 7.54-7.42 (m, 3H), 7.38-7.27 (m, 3H), 7.16-7.01 (m, 1H), 7.02-6.95 (m, 1H), 5.50-5.45 (s, 1H), 5.45-5.41 (s, 1H), 4.38-4.32 (s, 2H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 158.9 (1C), 149.6 (1C), 143.7 (1C), 139.7 (1C), 136.0 (1C), 128.5 (2C), 128.0 (1C), 126.4 (2C), 122.6 (1C), 119.7 (1C), 115.7 (1C), 34.7 (1C) ppm.

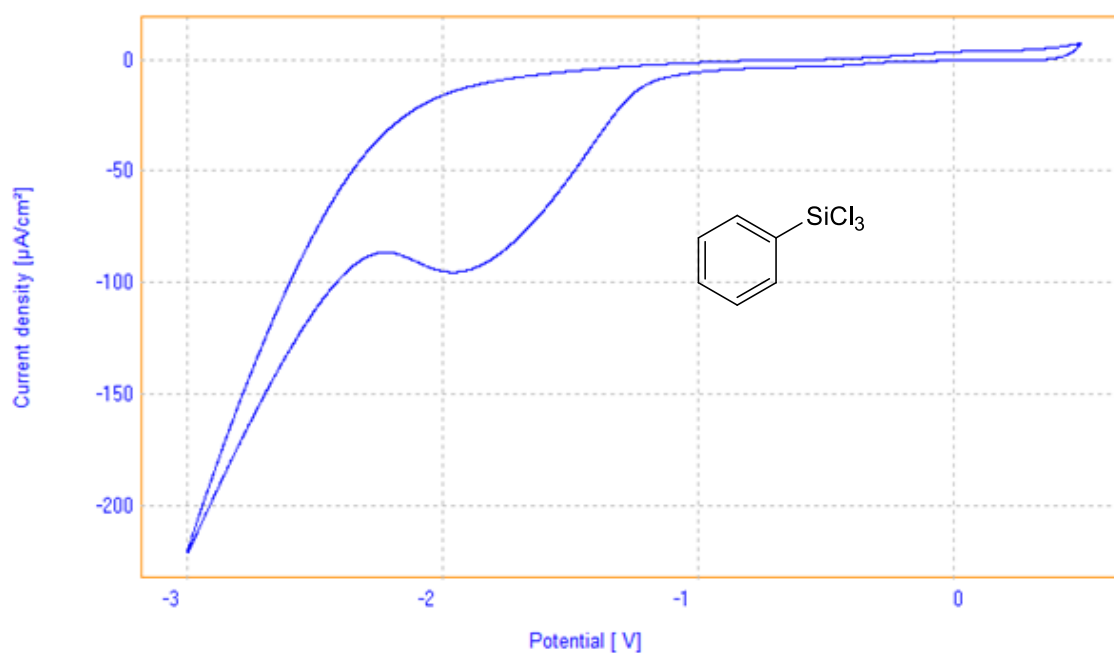
HRMS calc. for $[\text{C}_{14}\text{H}_{14}\text{NS}]$; 228.0841 found 228.0841.

IR (neat): 3051, 928, 1577, 1557, 1495, 1454, 1413, 1281, 1122 cm^{-1} .

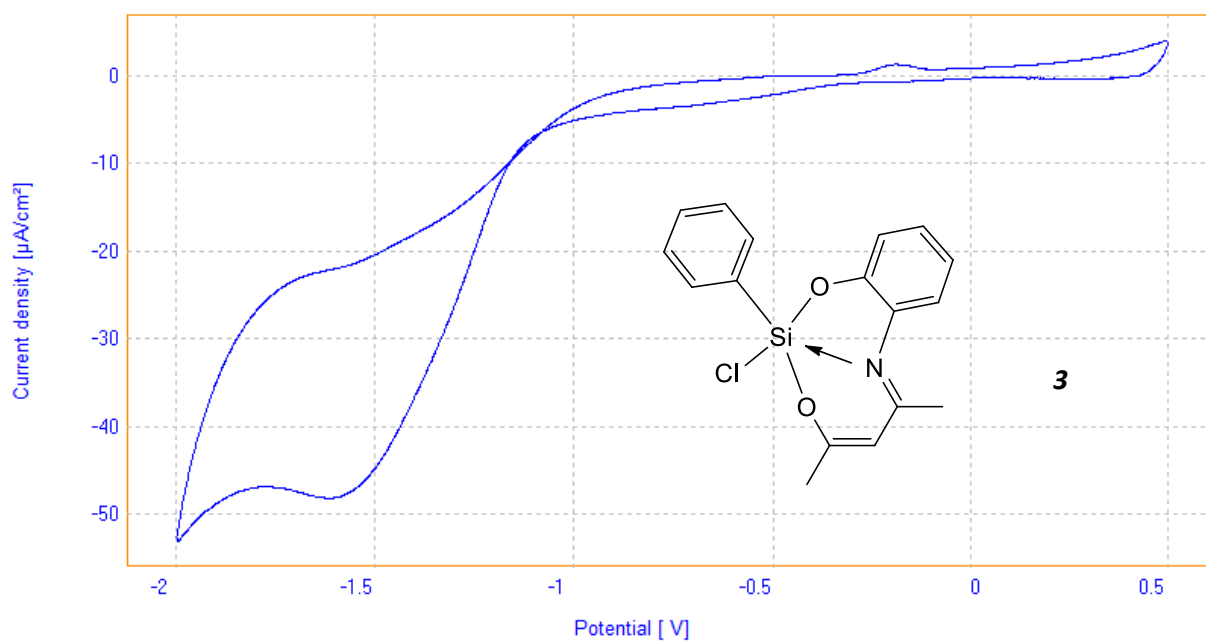
IV. Electrochemical measurement

The voltammetric measurement was recorded with a three electrodes apparatus in degassed THF with Bu_4NPF_6 (100 mM) as support electrolyte at 22°C. Measurements were monitored on an AutoLab PSTAT10 electrochemical workstation. Cyclic voltammetry (CV) was used to estimate the redox potential (half-wave potential). The CVs were obtained with a step potential of 0.009 V at a scan rate of 0.1 $\text{V}\cdot\text{s}^{-1}$ (0.05 $\text{V}\cdot\text{s}^{-1}$ for **7**). Glassy carbon, platinum plate, and saturated calomel were used as working, counter, and reference electrodes, respectively.

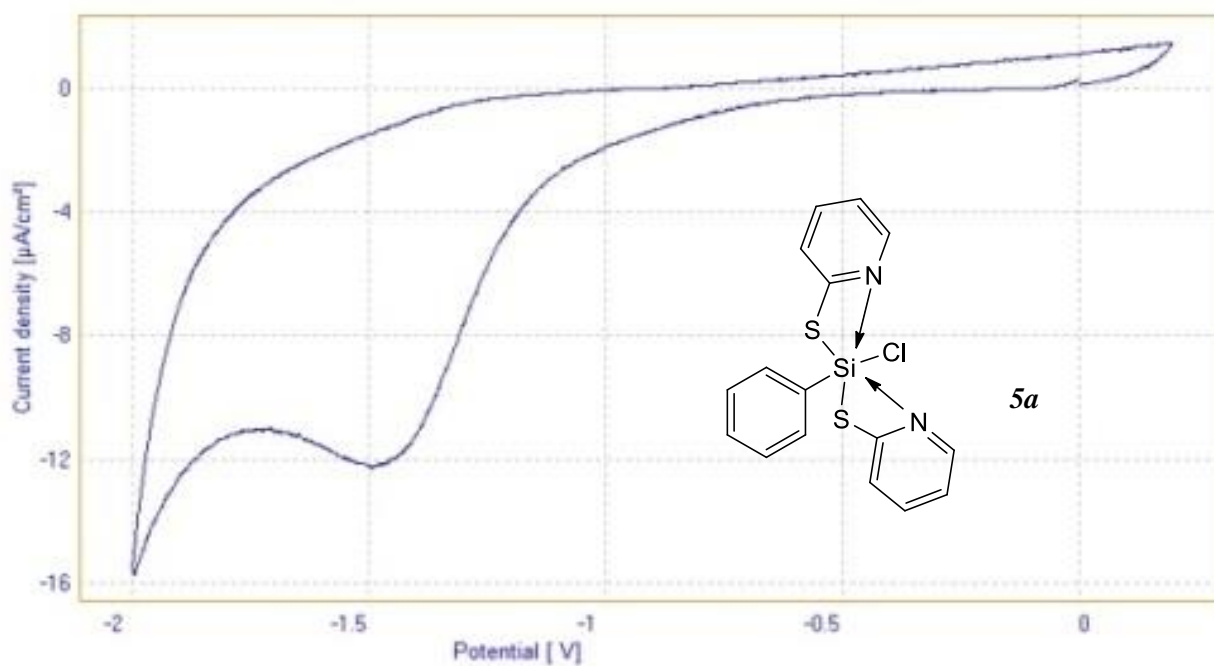
Voltammetry of phenyltrichlorosilane



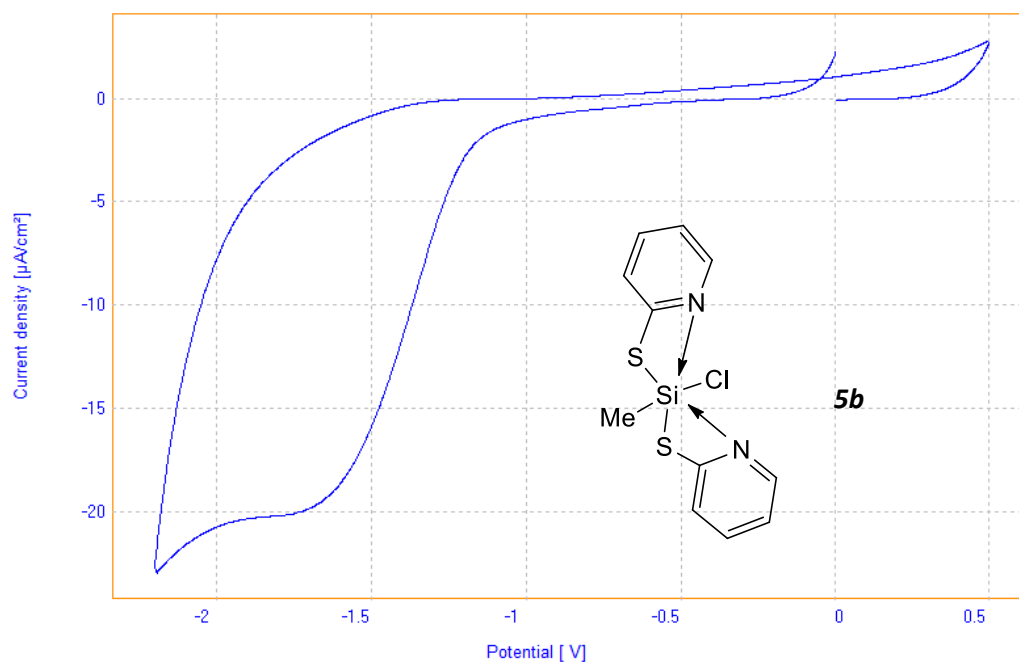
Voltammetry of 2-chloro-4,6-dimethyl-2-phenylbenzo[d][1,3,6,2]dioxazasilonine



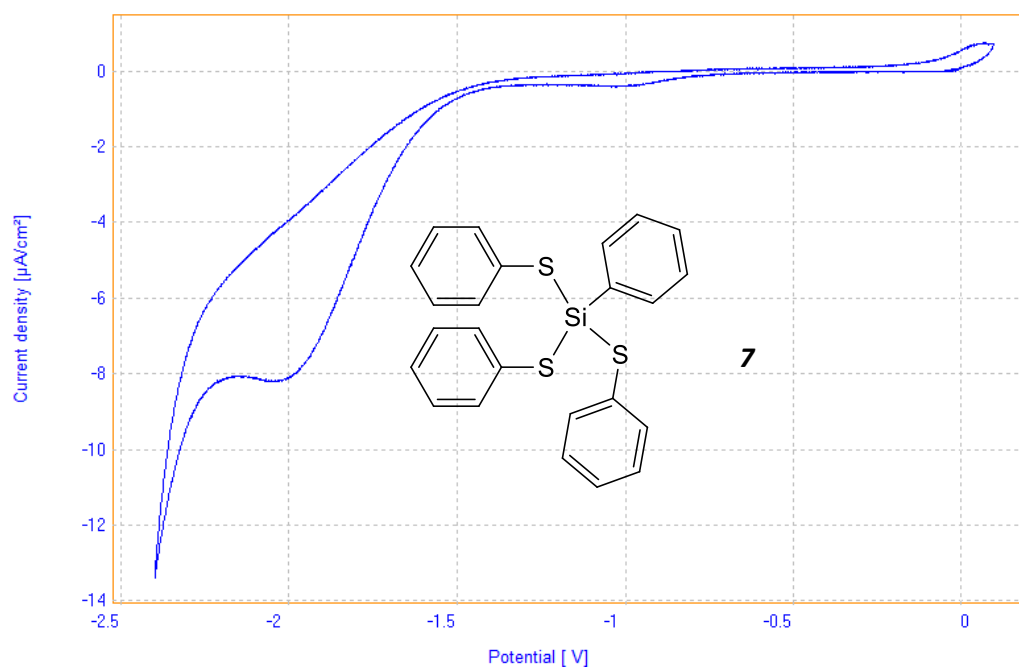
Voltammetry of Chlorophenylbis[N,S-pyridine-2-thiolato(-)]silicon(IV)



Voltammetry of 2,2'-((chloro(methyl)silanediy)bis(sulfanediyl)dipyridine



Voltammetry of phenyltris(phenylthio)silane



V. Coordinates of calculated species

Product 5a

35
Energy = -2271.578758134

Si	0.1339412	0.2623132	-0.1200367
S	-0.8499136	2.2294657	0.8308704
S	1.1129507	-1.7017118	-1.0832169
N	1.5482311	1.5428528	0.2086740
N	-1.2597695	-1.0644854	-0.3264308
C	2.8844381	1.5704412	0.0838227
C	3.6040984	2.7021672	0.4322368
C	2.8968594	3.8196105	0.9245919
C	1.5165523	3.7752736	1.0669684
C	0.8366116	2.5918252	0.7086980
C	-0.5635782	-2.0848213	-0.9014932
C	-1.2429127	-3.2732481	-1.2437341
C	-2.5967870	-3.3735682	-0.9534178
C	-3.2780342	-2.3077491	-0.3280679
C	-2.5645360	-1.1589665	-0.0261096
H	3.3550542	0.6588802	-0.2954389
H	4.6911659	2.7174820	0.3275170
H	3.4416002	4.7272870	1.2044682
H	0.9496361	4.6230131	1.4577966
H	-0.6920925	-4.0899536	-1.7152634
H	-3.1381678	-4.2917157	-1.2041045
H	-4.3396092	-2.3777261	-0.0808068
H	-3.0127189	-0.2918390	0.4674307
C	-0.1825354	0.9721625	-1.9067204
C	-1.4781956	1.2863731	-2.3518113
C	-1.7124543	1.7913603	-3.6353689
C	-0.6411425	2.0089779	-4.5080920
C	0.6585207	1.7095786	-4.0857659
C	0.8764063	1.1919520	-2.8045325
H	-2.3341756	1.1505124	-1.6809725
H	-2.7353494	2.0231923	-3.9515349
H	-0.8177957	2.4093783	-5.5120502
H	1.5069779	1.8717142	-4.7595500
H	1.9024301	0.9425993	-2.5110427
Cl	0.4931078	-0.5431913	1.9063140

Product 5a reduced

35
Energy = -2271.595248298

Si	0.1353387	0.2588526	-0.1053846
S	-0.8802060	2.2027725	0.8435756
S	1.1481203	-1.6829581	-1.0660396
N	1.5077421	1.5072028	0.2179211
N	-1.2162186	-1.0376558	-0.3102547
C	2.8652255	1.5322734	0.0854481
C	3.5817543	2.6713658	0.4123931
C	2.9013113	3.8084213	0.9008308
C	1.4965730	3.7549483	1.0649792
C	0.8191199	2.5865035	0.7268977
C	-0.5411045	-2.0871739	-0.8928430

C	-1.2209719	-3.2517867	-1.2400706
C	-2.6046178	-3.3495322	-0.9621321
C	-3.2584581	-2.2705490	-0.3279859
C	-2.5421522	-1.1299392	-0.0061425
H	3.3306963	0.6087616	-0.2687835
H	4.6701640	2.6736406	0.2957367
H	3.4530448	4.7175330	1.1605156
H	0.9331847	4.6036972	1.4612980
H	-0.6707924	-4.0720575	-1.7081489
H	-3.1573991	-4.2569758	-1.2251113
H	-4.3228494	-2.3253452	-0.0785870
H	-2.9773847	-0.2712100	0.5115846
C	-0.1837889	0.9755757	-1.9098701
C	-1.4815388	1.2584020	-2.3759276
C	-1.7165016	1.7621559	-3.6600614
C	-0.6444736	2.0125562	-4.5251406
C	0.6575438	1.7454221	-4.0846953
C	0.8748439	1.2311489	-2.8017429
H	-2.3394174	1.0908422	-1.7148409
H	-2.7441704	1.9652519	-3.9859453
H	-0.8213400	2.4113516	-5.5311657
H	1.5111670	1.9341991	-4.7475753
H	1.9036844	1.0138289	-2.4931567
Cl	0.5026853	-0.5720874	1.9742514

(PhS)₂Si(Cl)Ph

37

Energy = -2239.540640183

Si	-0.0767772	-0.7818033	0.7539276
Cl	0.1026238	1.2063706	0.0960718
S	1.6416238	-1.9035641	0.0935898
S	-2.0061521	-1.5744784	0.2032258
C	-0.0569185	-0.8434755	2.6217565
C	0.1553759	0.3042452	3.4076918
C	0.1845830	0.2155560	4.8030126
C	0.0044678	-1.0214801	5.4312438
C	-0.2075522	-2.1716256	4.6619601
C	-0.2395849	-2.0835776	3.2673369
C	-1.9415713	-1.8019299	-1.5831537
C	-1.7318463	-0.7274621	-2.4616352
C	-1.7633368	-0.9435647	-3.8414572
C	-2.0306988	-2.2175838	-4.3541951
C	-2.2531625	-3.2843928	-3.4780788
C	-2.2006666	-3.0824325	-2.0951675
C	1.6588731	-1.6506148	-1.6933658
C	2.1456606	-0.4510439	-2.2339282
C	2.2115526	-0.2914547	-3.6216669
C	1.8113847	-1.3290010	-4.4704064
C	1.3370521	-2.5279072	-3.9275194
C	1.2569767	-2.6912534	-2.5423654
H	0.2973312	1.2762500	2.9257072
H	0.3488922	1.1169733	5.4021806
H	0.0285417	-1.0903272	6.5238079
H	-0.3506275	-3.1409999	5.1505268
H	-0.4127245	-2.9901267	2.6774259
H	-1.5363951	0.2715158	-2.0658800
H	-1.5794847	-0.1053151	-4.5204366
H	-2.0607266	-2.3789357	-5.4363518
H	-2.4614683	-4.2851731	-3.8703618

H	-2.3607346	-3.9176928	-1.4072016
H	2.4620666	0.3542572	-1.5671732
H	2.5849546	0.6491218	-4.0396021
H	1.8658024	-1.2022508	-5.5563636
H	1.0108150	-3.3390898	-4.5851042
H	0.8685508	-3.6188951	-2.1157027

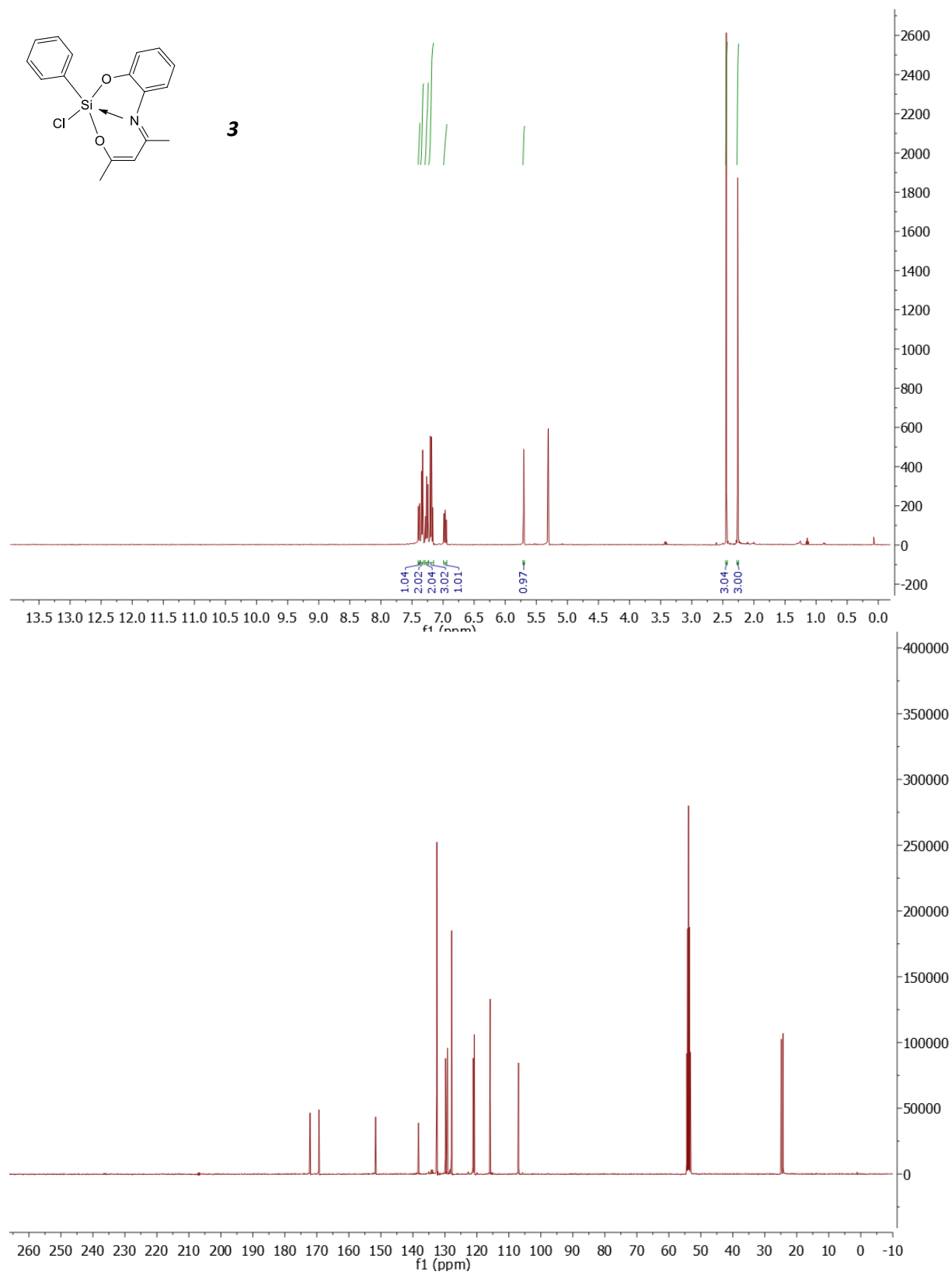
(PhS)₂Si(Cl)Ph reduced

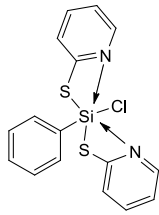
37

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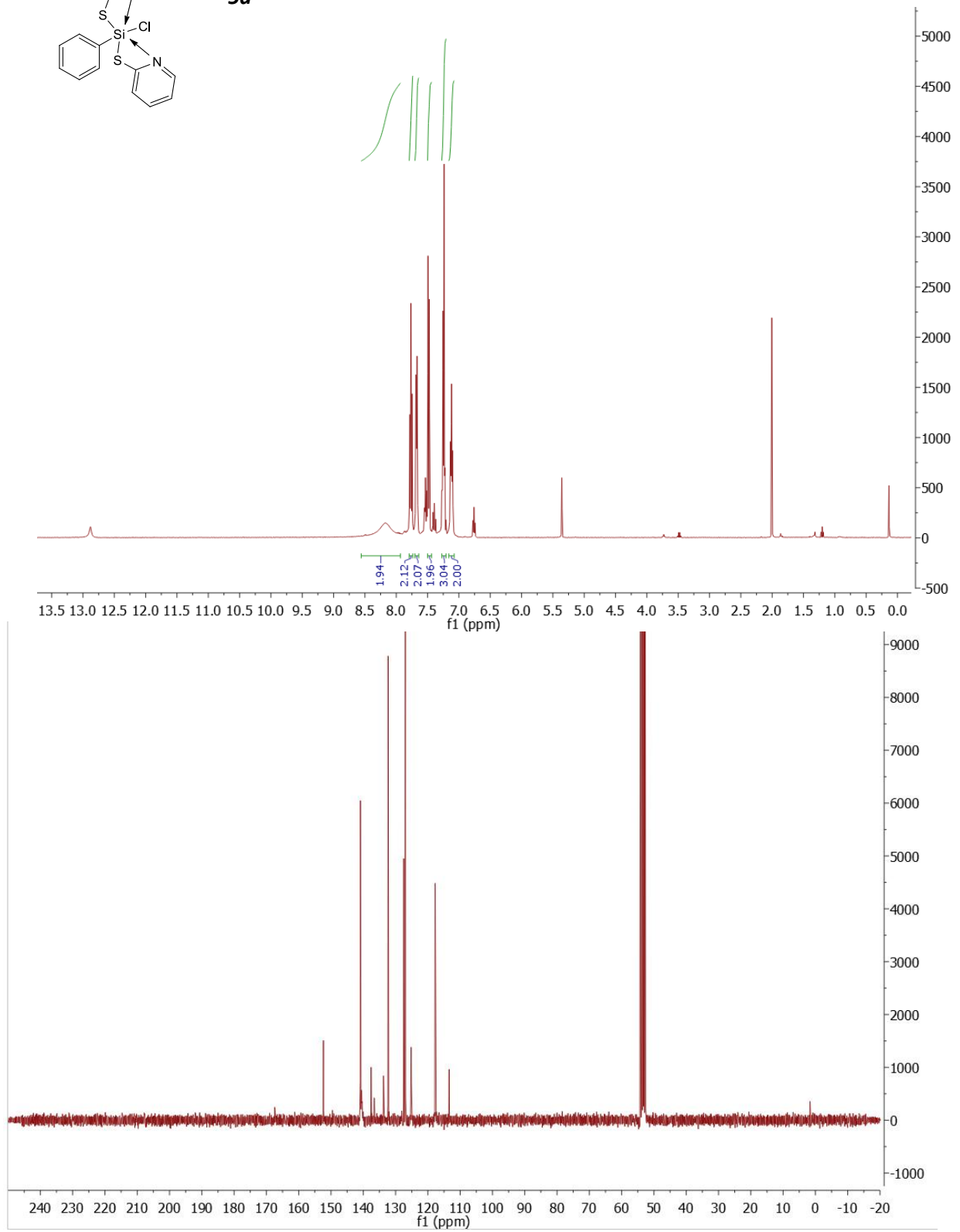
Si	-0.1500934	-1.1348488	0.9258758
Cl	-0.2545349	0.9019428	0.1951824
S	1.8529191	-1.8650776	0.3270731
S	-1.9114323	-2.1405851	-0.4439341
C	0.1426905	-0.8939630	2.7889075
C	-0.3981283	0.2095878	3.4999046
C	-0.3848425	0.2577576	4.8954507
C	0.1752492	-0.7885761	5.6431186
C	0.7195307	-1.8911308	4.9611503
C	0.6934262	-1.9469722	3.5685542
C	-2.0141081	-1.5186893	-2.1046336
C	-2.3609477	-0.1754113	-2.3787891
C	-2.4281557	0.2934392	-3.6921028
C	-2.1661056	-0.5612365	-4.7734909
C	-1.8211048	-1.8948139	-4.5134411
C	-1.7359604	-2.3647513	-3.2021836
C	1.6978524	-2.2254076	-1.4194790
C	1.4938297	-1.1965879	-2.3573767
C	1.4773107	-1.4817623	-3.7236960
C	1.6799317	-2.7900437	-4.1796180
C	1.8748571	-3.8185045	-3.2515653
C	1.8764461	-3.5413978	-1.8802171
H	-0.8220517	1.0486792	2.9378059
H	-0.8052995	1.1316200	5.4094072
H	0.1884600	-0.7481249	6.7381127
H	1.1731450	-2.7144010	5.5273141
H	1.1166685	-2.8236718	3.0633279
H	-2.5584911	0.4968665	-1.5402244
H	-2.6939625	1.3419150	-3.8756564
H	-2.2228317	-0.1904370	-5.8031727
H	-1.5940921	-2.5750430	-5.3433359
H	-1.4323766	-3.3973170	-3.0059016
H	1.3267785	-0.1763483	-2.0032153
H	1.2834452	-0.6752448	-4.4378982
H	1.6608146	-3.0090304	-5.2528079
H	2.0158873	-4.8499894	-3.5951552
H	2.0119767	-4.3456030	-1.1509425

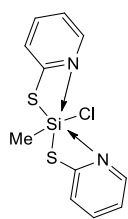
VI. ^1H , ^{13}C spectra



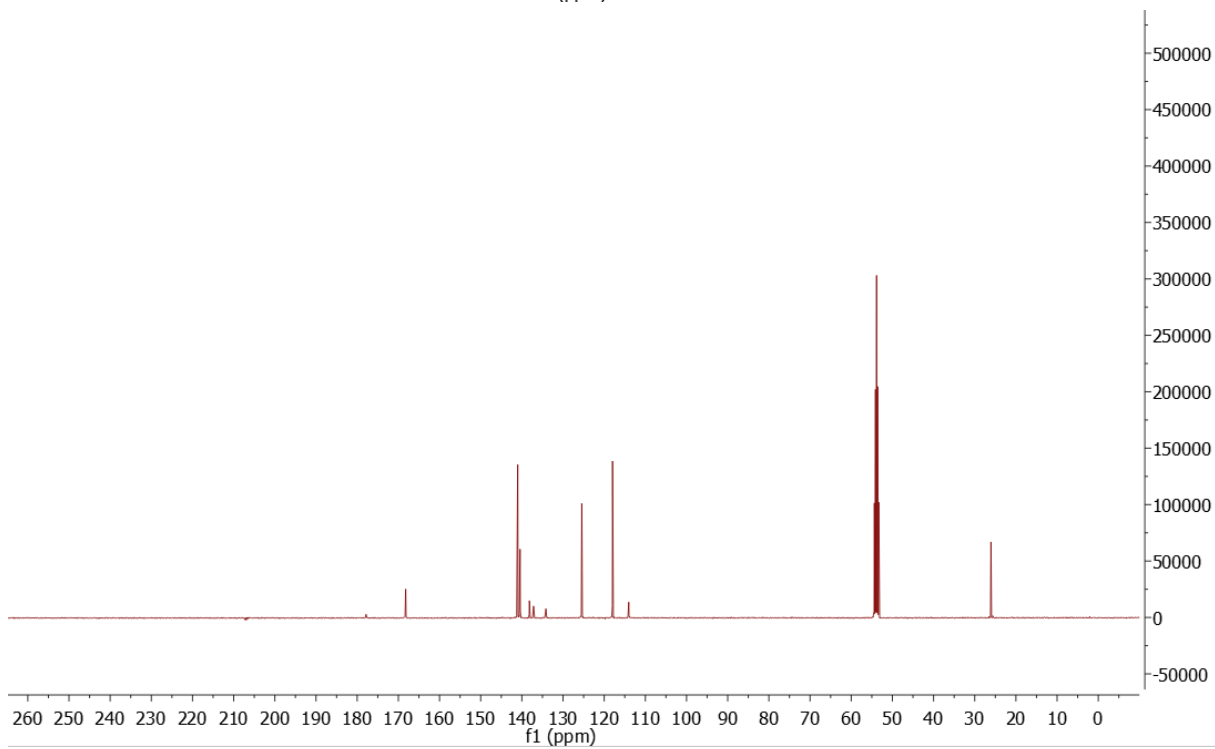
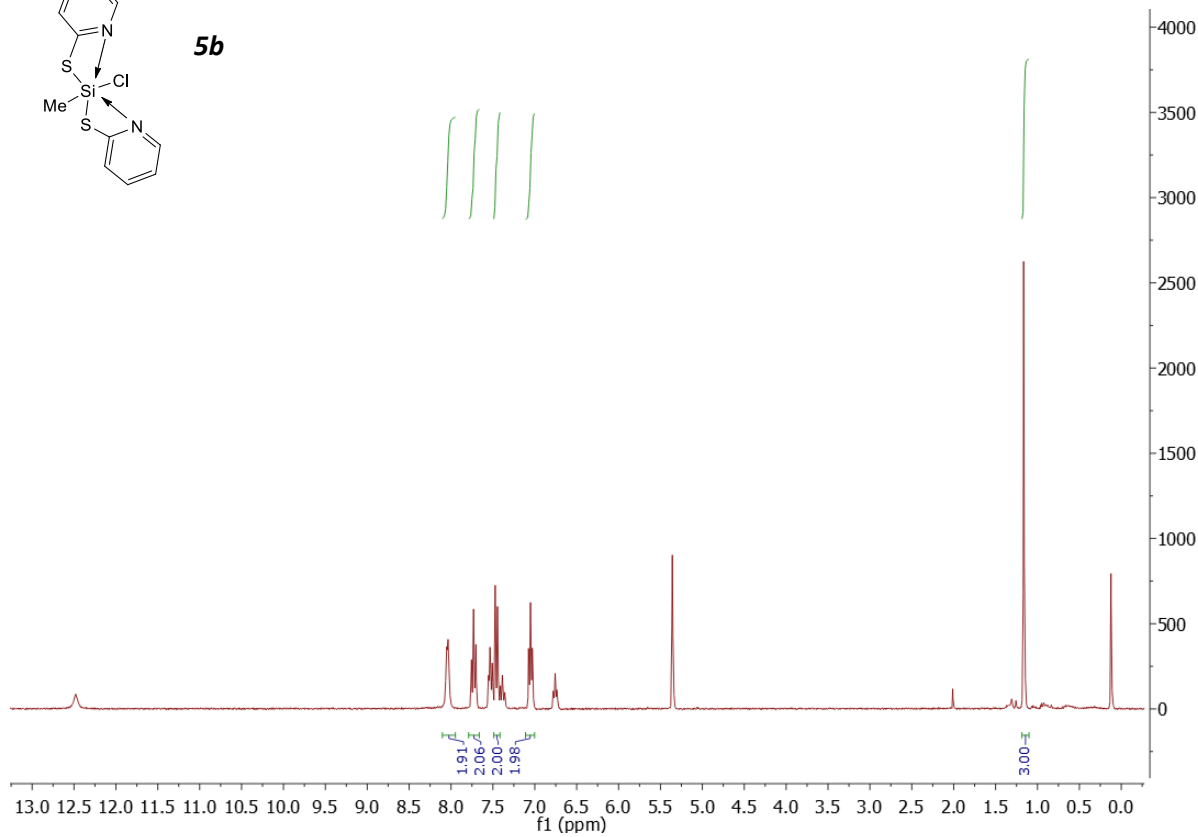


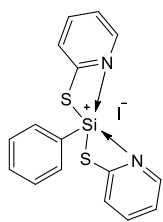
5a



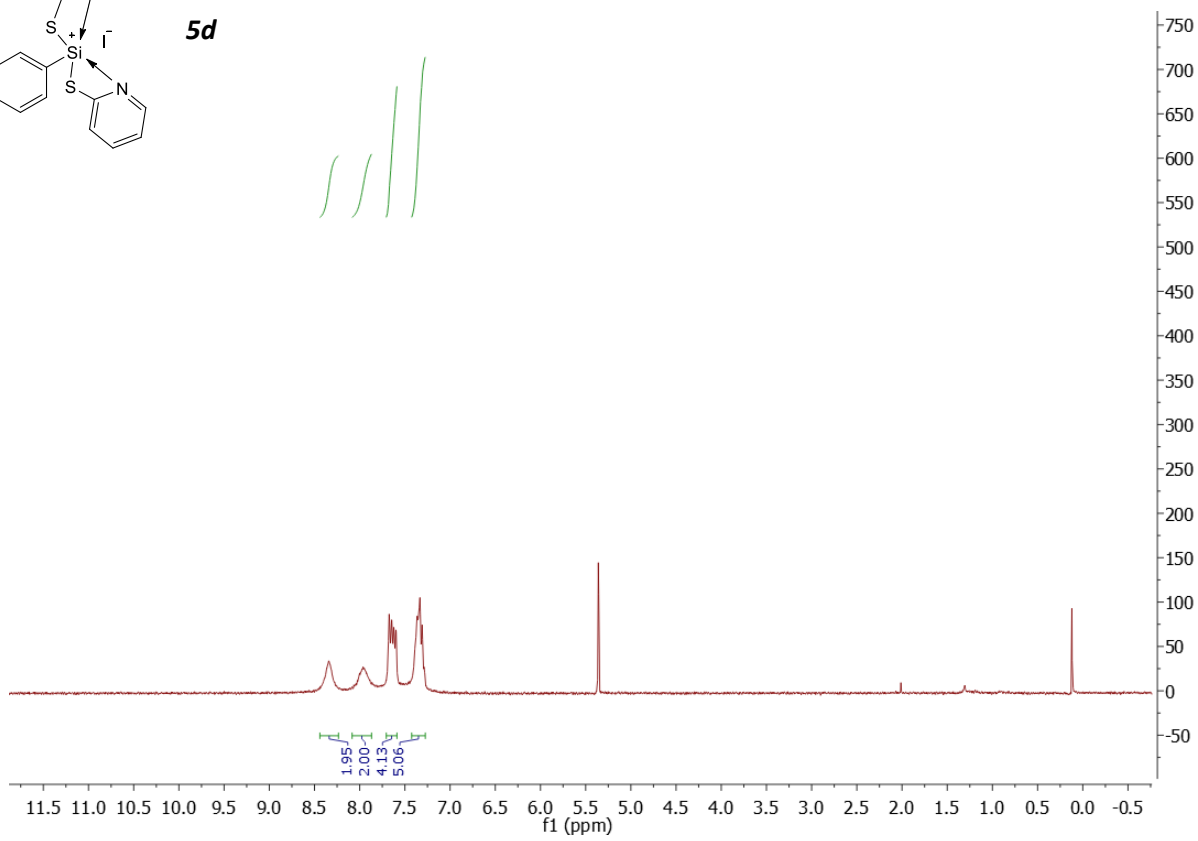


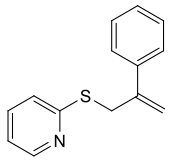
5b





5d





6

