

Synthesis and application of novel heteroaromatic alpha silanes

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Abstract

The present work focusses on heteroaromatic alpha silanes that have thus far not been described or studied in detail. Synthesis strategies through Grignard and palladium assisted reactions forming these silanes were explored and optimised. Additionally, previously not described intermediates of the catalytic reaction were studied.

The physicochemical properties of novel heteroaromatic alpha silanes were researched. The silanes were used in the formation of telechelic polymers and the targeted formation of resins. Their respective hydrolysis rates were assessed through time resolved rheologic measurements. Upscale reactions forming novel alpha silanes were conducted, followed by the use in industrially relevant one component room temperature vulcanising silicone formulations.

Zusammenfassung

Die vorliegende Arbeit konzentriert sich auf heteroaromatische Alphasilane, die bisher nicht im Detail untersucht wurden. Synthesestrategien durch Grignard- und Palladium- unterstützte Reaktionen zur Bildung dieser Silane wurden erforscht und optimiert. Zusätzlich wurden neue Intermediate, die während der Katalyse auftreten, erforscht.

Die neuen heteroaromatischen Alphasilane wurden auf ihre physikochemischen Eigenschaften hin untersucht. Die Silane wurden bei der Bildung von telechelischen Polymeren und der gezielten Bildung von Harzen eingesetzt. Ihre jeweiligen Hydrolyseraten wurden durch zeitaufgelöste, rheologische Messungen ermittelt. Es wurden Upscale-Reaktionen zur Bildung neuartiger Alphasilane durchgeführt, gefolgt von der Verwendung in industriell relevanten, bei Raumtemperatur vulkanisierenden, Einkomponenten-Silikonformulierungen.

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List of Abbreviations

[(dppf)PdCl₂]	(1,1'-Bis(diphenylphosphino)ferrocene) palladium(II) dichloride	GSK	GlaxoSmithKline
APC	Allylpalladium chloride dimer	HMBC	heteronuclear multiple bond correlation
Arg	Arginine	HPLC	high pressure liquid chromatography
AROP	anionic ring-opening polymerisation	HTV	high temperature vulcanising
ATR	attenuated total reflection	DIPEA	N,N-Diisopropylethylamine
bp	boiling point	<i>in situ</i>	in the original place
cataCXium A	Di-(1-adamantyl)- <i>n</i> -butylphosphin	IR	infrared
CROP	cationic ring-opening polymerisation	IUPAC	international union of pure and applied chemistry
D₄	Octamethylcyclotetrasiloxane	JohnPhos	(2-Biphenyl)-di- <i>tert</i> -butylphosphin
D₅	Decamethylcyclopentasiloxane	JosiPhos	1-[2-(Diphenylphosphino)-ferrocenyl]-ethylidicyclohexylphosphin
DavePhos	2-Dicyclohexylphosphino-2'-(N,N-dimethylamino)-biphenyl	K₂CO₃	Potassium Carbonate
DMSO	Dimethyl sulfoxide	K₃PO₄	Potassium Phosphate
Dppf	1,1'-Bis(diphenylphosphino)ferrocen	KOH	Potassium Hydroxide
Dppp	1,3-Bis(diphenylphosphino)propan	KOtBu	Potassium <i>tert</i> -butoxide
<i>e. g.</i>	exempli gratia (for the sake of example)	Mn	number average molecular weight
EI	electron ionization	MS	mass spectroscopy
ESI	electrospray ionization	Mw	weight average molecular weight
<i>et al.</i>	et alii (and others)	NMP	N-Methylpyrrolidone
FDA	food and drug administration	NMR	nuclear magnetic resonance
FT-IR	Fourier transform infrared spectroscopy	p.a.	pro analysis
GC	gas chromatography	PCy₃	Tricyclohexylphosphine
GPC	gel permeation chromatography	Pd / C	Palladium on carbon

Pd(acac)₂	Palladium(II)-bis(acetylacetonate)	ROMP	ring-opening metathesis polymerisation
Pd(dba)₂	Bis-(dibenzylidenacetone)-palladium(0)	rpm	revolutions per minute
Pd(OAc)₂	Palladium(II)-acetate	RTV-I	one component room temperature vulcanising
Pd(PPh₃)₄	Tetrakis(triphenylphosphine)palladium(0)	RTV-II	two component room temperature vulcanising
Pd₂(dba)₃	Tris(dibenzylideneacetone)dipalladium(0)	RuPhos	2-Dicyclohexylphosphino-2',6'-diisopropoxybiphenyl
PdCl₂	Palladium(II)-chloride	TBD	1,5,7-Triazabicyclo(4.4.0)dec-5-en
PDI	polydispersity index	THF	Tetrahydrofuran
PDMS	Polydimethylsiloxane	TIPT	Tetraisopropylorthotitanat
PdO	Palladium monoxide	TMDS	1,1,3,3-Tetramethyldisiloxane
ppm	parts per million	TMEDA	Tetramethylethylenediamine
Pyr	Pyridine	VTMO	Vinyltrimethoxysilane
REACH	registration, evaluation, authorisation and restriction of chemicals	Xphos	2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl
ROP	ring-opening polymerisation		

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1 Introduction

“There is only one thing that makes a dream impossible to achieve: the fear of failure.”

Paulo Coelho

1.1 Scope of this work

Reactive silicone monomers are key in one component curing of consumer and commercial grade sealants and adhesives due to their versatility, strength and low price. The ongoing research in this industrial highly important field has focused on less toxic and more environmentally benign compounds in recent years. Increasing monomer reactivity allows reducing and may eliminate the usage of catalysts, potentially reducing users' exposure to harmful substances. Consequently, industrial synthesis as well as intrinsic properties of the used compounds are of high interest.

Recent studies have highlighted the "alpha silicon effect", noting that introducing a heteroatom (an atom other than carbon, such as oxygen or nitrogen) in alpha position to a siloxane molecule with hydrolysable groups significantly increases their hydrolysis rate. The aim of this work is to exploit this effect, open a new substance class and explore its applicability in an industrial setting.

This thesis is divided into three main chapters. The first chapter will provide a theoretical background on the usage and chemistry of reactive silicones. The so-called alpha silicon effect and its high potential in commercial formulations is introduced. In chapter 2 a new class of compounds and different synthesis routes towards them are explored. First common strategies towards silanes are exploited proving feasibility of the proposed substance class. This is followed up by establishing a palladium catalysed carbon-silicon cross coupling for the target compounds. As no mechanistic data is available in literature extensive investigations are undertaken. The following chapter 3 describes the technical applicability of such newly synthesised compounds. This includes the downstream usage of silicones in polymers and resins as well as their application in commercial formulations and synthesis on an industrial scale. Finally, conclusions are summarized and an outlook for future research is provided.

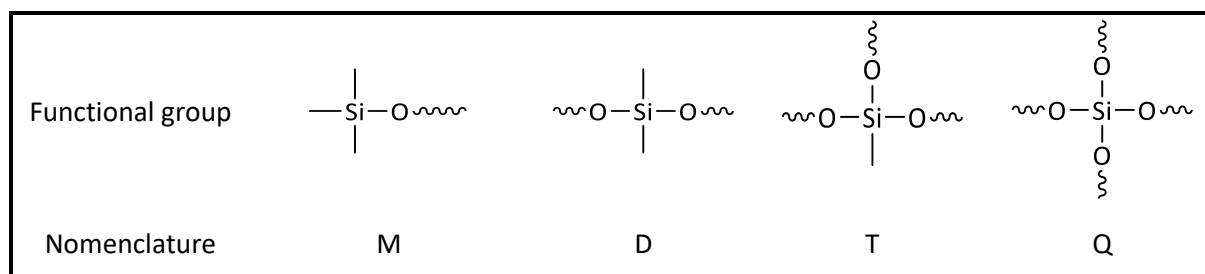
This thesis highlights the process from idea to application in an industrial environment, closely following each development step and tailoring towards commercial relevance.

1.2 Silicones

Silicones are a class of polymers made from the repeating unit $[R^1_{m^1}R^2_{m^2}Si(O)_{4-\frac{m^1+m^2}{2}}]_n$, where $m = 1 - 3$ and $n \geq 2$. The resulting compounds may be linear, branched or cyclic, exemplary structures are shown in Figure 1. The IUPAC definition specifies “silicone” as the linear or branched version of polyorganosiloxanes.¹

Silicone polymers have distinctive properties due to organic substituents on an inorganic chain, allowing them to be applied as emulsifiers, isolators, resins or elastomers in a broad range of applications.^{2,3} Various industrial applications are known from durable and waterproof adhesives and sealants⁴ to potting compounds in the electronics industry.⁵ Additionally its high biocompatibility⁶ makes it an excellent choice for on- or in-body applications. The unique properties of silicones and their resulting applications can be ascribed to the unique silicon-oxygen bond. It has increased bond lengths when compared to its carbon-oxygen analogue.⁷ The Si-O bonding is longer than the C-O bonding, which results in a wider Si-O-Si bond angle, allowing for easier rotation of the moieties attached to the silicon atoms, leading to the high flexibility of the silicone chains.⁸

To differentiate easily between silicones a nomenclature was established. M, D, T and Q indicate the number of silicon oxygen bonds present repeating unit within a polymeric chain. The functional group can have a significant impact on the physicochemical properties of the resulting molecule. The most common functional group in polysiloxanes is methyl, it is thus not indicated further in this nomenclature, any functional groups different from methyl are written behind the letter in suffix, such as H for hydrogen or Ph for phenyl. M refers to mono-siloxane ((CH₃)₃SiO_{0.5}), thus three functional groups are present, D for di-siloxane ((CH₃)₂SiO), T for tri-siloxane ((CH₃)SiO_{1.5}) and Q for quarternary siloxane (SiO₂).⁹ This nomenclature can be used for small molecules, polymers and three-dimensional networks such as resins. A practical example is M_HM_H describing 1,1,3,3-tetramethyldisiloxan, where one methyl in each M unit is replaced with a hydrogen.¹⁰



Scheme 1: Siloxane functional groups and their nomenclature from M to Q.

The versatility and range of silicone products can be attributed to the numerous possible combinations of building blocks and organic moieties. Silicone oils and fluids, specifically the common linear polyorganosiloxanes of the general structure MD_xM, are exemplified by polydimethylsiloxanes

Introduction

(PDMS). On the other hand, highly branched and viscous silicone resins consist of either MQ or DT combinations. Due to the bivalent nature of the D unit a cyclic siloxane can be noted according to the count of circularly repeating D units as shown in Figure 1. Additionally, this nomenclature allows the straightforward description of linear or branched siloxanes. MDM refers to a siloxane oligomer with a structure that includes two trimethyl-silyl (M) end groups and one dimethyl-siloxy (D) repeating unit.

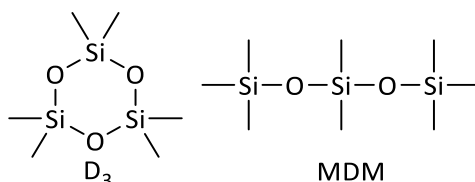
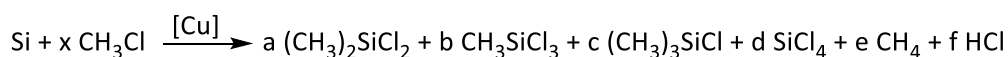


Figure 1: Exemplary silicone compounds, illustrating the use of MDTQ nomenclature: Hexamethylcyclotrisiloxane (D₃) and Octamethyltrisiloxane (MDM).

The term "silicone" was coined by Kipping¹¹ in the early 20th century during his studies of silicon and its compounds. Initially referred to as "silicon ketones" or "silicones", these materials were considered aggregates rather than polymers due to their limited variety and perceived inertness. Further research and characterisation by Kipping laid the foundations for silicon chemistry. In the 1940s, Rochow¹² and Müller¹³ independently reported the current state-of-the-art industrial synthesis of chloromethylsilanes, enabling the direct synthesis of organohalosilanes. The process is known as the direct process. This overcame the previously constrained access to silicone derivatives from silica. After a period of secrecy during World War II, these developments allowed the domain of silicones to grow. The combination of chloromethane and elemental silicon in the presence of copper at high temperatures yields a mixture of different chlorinated methylsilanes. Consecutive hydrolysis yields the corresponding silanols which condense to silicones.³ Alternative, less energy-intensive processes are the subject of ongoing research.^{14,15}

The primary reaction in the direct process involves the formation of dimethyldichlorosilane (Scheme 2). Other methylchlorosilanes are generated as by-products of side reactions, resulting in a mixture of silanes which requires purification through complex distillation procedures. Nevertheless, it is feasible to adjust the reaction temperature and use promoters to influence the composition of the various silanes. Despite these variables, dimethyldichlorosilane remains the main product of the direct process.¹⁶



Scheme 2: Basic reactions during the direct process where $x = a+b+c+d+e+f$. Main product formed depends on reaction conditions, usually a is formed as the main product.¹⁶

As the Müller-Rochow-process produces highly reactive methyl substituted chlorosilanes these are converted to higher value commodity and specialty chemicals. They undergo rapid condensation in the presence of water to form silanols. Silanols then condense with themselves, forming siloxanes (Figure

2). During this process polydimethyl siloxane, also referred to as PDMS, is formed. The resulting polymer bears hydroxy functionalisation on both ends. This is also referred to as α,ω -substituted as both the starting point “ α ” and end “ ω ” are functionalised with a hydroxy group. Alternatively, cyclic siloxanes, such as octamethylcyclotetrasiloxane, in accordance with the above-mentioned abbreviation convention referred to as D_4 are formed. Smaller cyclic siloxanes such as D_3 form in low quantities only, as the added ring strain makes them thermodynamically unfavored during the formation. Comparing polymeric chains and sterically less strained cyclic siloxanes their entropy is very similar.¹⁰ Higher rings have similar ring strains, however, are intrinsically unfavored by entropy. It is thus not surprising that during the condensation of methylchlorosilanes to siloxanes mainly D_4 is formed, when differently substituted chlorosilanes are used substituted cyclic siloxanes are obtained.

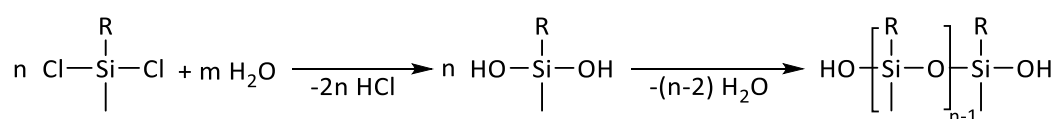


Figure 2: Condensation of dichlorosilanes with water forming disilanol, which undergo rapid condensation to form linear α,ω -hydroxy-substituted polydimethylsiloxane. Where R can be selected from a variety of organic substituents. When R is a methyl group the formed polymer can be referred to as polydimethylsiloxane (PDMS).

While silicones are comprised of the above-described substance class they bare unique properties making them versatile and important building blocks for industrial and consumer applications. A key property is their low thermal conductivity, at about one tenth that of most metals and one third that of common thermoplastics such as polyethylene, making them useful materials as insulators in e.g. electronics sealing.¹⁷ Furthermore, most silicones are classified as nontoxic¹⁸ and not releasing harmful chemicals when heated or burned.¹⁸ Combined with their high flexibility over a high temperature range, hydrophobic character and chemical resistance they are the go-to polymer in high demand consumer and professional construction applications.¹⁹ Depending on the application the final material properties can be fine-tuned by varying the polymers side group substitution and composition of the end product.

Ring-opening polymerisation (ROP) of cyclic siloxanes is a key approach for the synthesis of functional silicone polymers. The resulting polymers properties can be influenced by choice of polymerisation method, reactants and catalyst. Several ROP methods are common, each with their own set of reactants and catalysts, offering control over end- and side-group functionalised silicone polymers, as well as their key parameters, such as molecular weight and polydispersity index (PDI).²⁰

A common method is anionic ring-opening polymerisation (aROP) which typically involves monomers such as octamethylcyclotetrasiloxane (D_4). Cyclic siloxanes are polymerised using strong bases like butyllithium or potassium silanolate, serving as initiators by attacking the siloxane ring and opening it to form long chains. Functional monomers like 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane can be included in the polymerisation process to create block copolymers

with specific side group functionalisation, allowing post polymerisation modification of the polymer.²¹ The aROP results in polymers with narrow molecular weight distributions (low PDI) due to its “living” polymerisation nature. In this case “living” refers to the continuous chain growth without termination until all monomers are consumed. The precise control over PDI and ability to introduce well defined end groups makes aROP ideal for producing block copolymers. However, the method is restricted due to the need for strict reaction conditions, particularly moisture, which may lead to undesirable side reactions and chain termination.²²

In contrast cationic ring-opening polymerisation (cROP) offers a different approach to ROP, where the polymerisation is initiated by strong acids or Lewis acids, such as trifluoromethanesulfonic acid (TfOH) or boron trifluoride etherate ($\text{BF}_3\text{-OEt}_2$).²³ These catalyst work by protonating the oxygen atom of the cyclic siloxanes, leading to ring-opening and subsequent polymerisation of cycles. The cROP is preferred for production of functional polymers with well-defined end groups, allowing the selective introduction of end groups through choice of end-capping agent. However, the method can generate cyclic oligomers as side products which can be challenging in purification and reduces overall yield for polymer. Additionally, cROP lead to higher PDI when compared to aROP due to side reactions. Despite this the method is used for its control over molecular weight and end group functionalisation, making it suited to produce specialised silicone polymers.²⁴

Further functionalisation of silicone polymers can be achieved through hydrosilylation, modifying the side chains of pre-formed polymers.²⁵ This method uses vinyl-substituted cyclic siloxanes in polymerisation and introduces functional groups through hydrosilylation. Commonly platinum based catalysts such as Karstedt’s or Speier’s catalyst enable the addition of Si-H binds to the vinyl groups.²⁶ Due to the high yield of the reaction this method is efficient in the introduction of a wide range of functional groups. Depending on the introduced groups material properties of the final polymer such as hydrophobicity can be tailored. However, other material properties may be influenced such as thermal stability due to the added silicon-ethylene-silicone bridges introduced through hydrosilylation. Careful optimisation of the reaction conditions, such as catalyst concentration and temperature, is necessary to avoid incomplete reactions or unwanted side products, which can impact molecular weight and distribution.²⁷

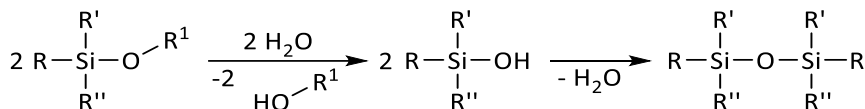
Selection of reactants and polymerisation mechanism can play a critical role in determining the key characteristics of a silicone polymer, including its molecular weight, polydispersity index and end group functionalisation. Anionic ring-opening polymerisation yields polymers with a narrow polydispersity and allows for precise control over end group functionalisation due to its “living” nature. In contrast cationic ring-opening polymerisation may result in broader polydispersity and formation of cyclic oligomers but offers greater flexibility in end group choice. Side-group modification can be achieved through hydrosilylation, allowing for the further introduction of diverse functionalities to the polymer,

changing its physicochemical properties, such as thermal, chemical, and mechanical performance. Overall, the strategic selection of reactants and polymerisation pathways is essential for tailoring the properties of silicone polymers.

1.3 Reactive silicones

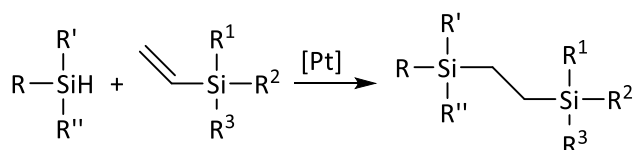
There are different subclasses of functional silanes differentiated through their substitution. There are two differentiations that can be made within the class of silanes: reactive and non-reactive substituted silanes. Non-reactive substitution describes a functionalisation that may not be easily functionalised further through reaction. Common substituents would be alkyl- or aryl-silanes. Here the strong carbon silicon bond, characterised through its low energy state, does not undergo further reaction easily. Reactive substituted silanes may be easily functionalised through chemical modification. Chlorosilanes are siloxane species where silicon is bonded to chlorine atoms (Si-Cl). Chlorosilanes are reactive intermediates used in the synthesis of silicone compounds. They serve as key precursors in the production of functional silanes and silicones. Chlorosilanes can undergo hydrolysis in the presence of water to form silanol groups (Si-OH), initiating subsequent condensation reactions (compare Figure 2). The choice of specific chlorosilane precursors can influence the final silicone properties and functionalities. Silanol, represented as (Si-OH), is a highly reactive siloxane species containing a hydroxyl functional group. Silanols can be found as terminal groups in linear silicones or as surface functionalities on silicone materials. They readily undergo condensation reactions with other silanol groups, leading to the formation of siloxane linkages (Si-O-Si) while releasing water. This condensation reaction is central to the cross-linking and curing of silicones. Siloxanes are the fundamental repeating unit of silicone polymers. They consist of silicon-oxygen-silicon (Si-O-Si) bonds, forming the backbone of silicone structures. They may form various structural varieties, including linear, cyclic, and branched forms. The nature and arrangement of siloxane linkages dictate the physical and chemical properties of silicone materials, an exemplary hydrolysis and condensation of pathway for reactive silanes is shown in Scheme 3. Oximosilanes feature oxime functional groups ($\text{N}=\text{C}(\text{Me})\text{OR}$) with R representing an organic moiety. These silanes are used as coupling agents and surface modifiers, especially in adhesives and sealants. Oxime groups can react with metal oxide surfaces, creating strong bonds and enhancing adhesion. The resulting oximosilane bonds contribute to improved durability and adhesion properties. Alkoxysilanes are siloxane species containing alkoxy functional groups (Si-OR) where R represents an organic group. Alkoxysilanes act as cross-linking agents and adhesion promoters. In the presence of moisture, alkoxy groups undergo hydrolysis, leading to the formation of silanol groups (Si-OH). Subsequent condensation reactions among silanol groups generate siloxane linkages, forming a silicone network with good mechanical properties as well as not exhibiting any unpleasant olfactory

characteristics. Acetoxysilanes feature acetoxy functional groups (Si-OOCCH_3) with each silicon atom bonded to an acetate group. These silanes are commonly employed as curing agents and cross-linkers in silicone sealants and adhesives. When exposed to moisture, acetoxysilanes undergo hydrolysis to form silanol groups (Si-OH) and acetic acid (CH_3COOH). Condensation reactions among silanol groups lead to the formation of a silicone elastomer network. An exemplary hydrolysis and condensation pathway using the reactive groups mentioned here is shown in Scheme 3.



Scheme 3: General hydrolysis and condensation of Silanes. Where R^1 can be hydrocarbon, aldehyde or imine.

Vinylsilanes are siloxane species where silicon is bonded to vinyl ($\text{CH}=\text{CH}_2$) functional groups. These silanes are notable for their ability to introduce unsaturation into silicone polymers. Vinylsilanes are used as cross-linkers in the synthesis of silicone elastomers.²⁸ The vinyl groups readily participate in hydrosilylation reactions where they react with silicon-hydrogen (Si-H) bonds in other silane or siloxane compounds (Scheme 4). This hydrosilylation process allows for the formation of stable carbon-silicon (C-Si) bonds and the creation of three-dimensional silicone networks, enhancing the mechanical properties and heat resistance of the resulting silicone materials. The regioselectivity of hydrosilylation, such as in the reaction of vinyltrimethoxysilane (VTMO) with hydridosilanes, results in the formation of alpha and beta addition products based on catalyst type, steric effects, and reaction conditions. The β -product, where the silicon adds to the carbon atom adjacent to the vinyl group, is generally favored under standard catalytic conditions, especially with platinum-based catalysts, due to a combination of electronic effects and the stabilizing interaction of the intermediate species. Alternatively, α -products, where silicon attaches to the terminal carbon of the vinyl group, can be selectively obtained using sterically hindered catalysts or under specific reaction conditions, such as higher temperatures or with catalysts that alter the electron density of the reactive sites. These variations highlight the influence of catalytic systems and molecular geometry on regioselectivity.^{29,30} The selective formation of these products is crucial for tailoring the properties of silicone-based materials which are widely used in applications ranging from adhesives to high-performance elastomers.³¹ Vinylsilanes play a crucial role in the development of silicone rubber and high-performance silicone products used in industries ranging from automotive to electronics.^{28,32,33}



Scheme 4: Hydrosilylation of a hydridosilane with a vinylsilane.

A combination of reactive and unreactive groups is common and often used to tailor the properties of the resulting compound, such as introducing non-reactive groups to polysiloxanes to form chemically stable polymers. Additionally, reactivity of the reactive groups may be influenced through all other substituents present on the silane centre. A common example is the increase of reactivity of alkoxysilanes when substituting with vinyl instead of methyl or ethyl.^{34–36}

1.4 Curing systems

In silicone curing systems a variety of methods and mechanisms can be used to cross-link organosilicon polymers. Generally, silicone systems can be differentiated into the underlying mechanism involved during curing. Curing, also referred to as vulcanising, being the formation of a three-dimensional network in a silicone mixture.³⁷ This enables their use in a broad range of industrial applications. These systems can be categorized based on the environmental conditions required during their curing process. Commonly literature differentiates between room temperature vulcanising (RTV) and high temperature vulcanising (HTV). The choice of curing method has a direct influence on the cured materials properties such as mechanical strength, chemical resistance and thermal stability.³⁸ Room temperature vulcanising silicone systems can be categorized into RTV-1 (one-part systems) and RTV-2 (two-part systems). RTV-1 systems are single component, cured through their reaction with moisture from ambient environment while not requiring heating or the addition of components. Contrary RTV-2 systems consist of two components that must be mixed prior to their application.

Free radical peroxide induced curing is a common mechanism involved in high temperature vulcanising (HTV) silicone. The process is based on the thermal decomposition of organic peroxides, generating free radicals *in situ*, leading to the vulcanisation of the silicone matrix. The process uses elevated temperatures to decompose organic peroxides into free radicals which then undergo reaction with unsaturated groups, such as vinyl, creating three dimensional networks. The temperature required depend on the organic peroxide used and can vary from 120 °C to 200 °C. Common peroxides used are benzoyl peroxide and dicumyl peroxide. The choice of peroxide is important as it can have influence on curing speed, cross-linking density and the final materials properties such as elasticity. As the activation process requires stability at high temperature common uses of peroxide cured silicones are in high temperature applications, such as gaskets and O-rings. Additionally, their high temperature resistance allows sterilisation, thus use in medical applications.^{38,39}

Silicones curing upon exposure to (ultraviolet) light are referred to as photoinitiated curing. This curing method has applications where rapid or highly localized curing is required. The mechanism of photoinitiated curing silicones relies on the absorption of UV light by a photo initiator, decomposition of which leads to reactive cations or radicals. These decomposition products then react with the polymer forming a cross-linked network. Radicals can be generated in a spatially limited area by

selective exposure to light and thus only local generation of reactive species. In this mechanism photo initiators are essential, deciding not only the reaction pathway (cation or radical) but also their quantum yield and peak absorption wavelength. The number of photons emitted at the photo initiators wavelength determines the rate of curing. This type of activation finds application in electronics encapsulation and coatings due to the rapid and externally triggered curing of such formulations.^{38,40}

Addition curing silicone systems use two components that can undergo addition reactions upon mixing, making them commonly applied in RTV-2 formulations. Most addition curing systems use hydrosilylation, the addition reaction between hydrosilanes with unsaturated double bonds in the presence of a platinum catalyst. The reactions commonly are active enough to proceed at room temperature but can be accelerated at elevated temperature. Due to the addition nature of this approach it is highly valued for its relative independence of ambient conditions and absence of volatile release. Common platinum-based catalysts are Speier's catalyst (chloroplatinic acid) and Karstedt's catalyst (Figure 3). The catalysts allow the controlled addition of hydrosilanes to vinyl functional silanes, vulcanising the mixture. Fine tuning of the process through the addition of inhibitors allows for tailor made products that find application in medical fields, electronics and mold making due to the absence of byproducts and precise control over the vulcanisation.^{38,41}

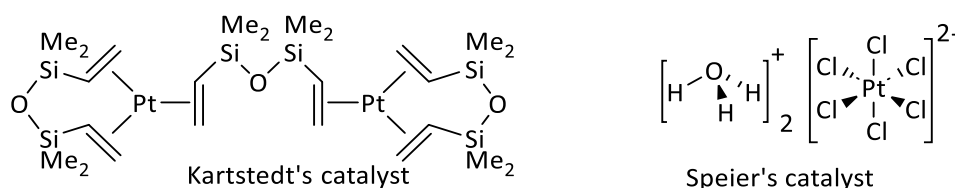


Figure 3: Karstedt's and Speier's catalyst, commonly used in hydrosilylation.

Condensation curing is a versatile process that involves a two-component system in which a hydroxyl-terminated silicone polymer reacts with a cross-linker, typically an alkoxy silane or acetoxy silane. This reaction is catalysed by metal complexes and it proceeds with the release of small molecules such as water, alcohols or acetic acid as by-products. The cross-linking reaction occurs between the hydroxyl groups of the silicone polymer and the alkoxy or acetoxy groups of the cross-linker. The reaction results in the formation of a siloxane network and the release of by-products. The curing process can occur at room temperature, although elevated temperatures can accelerate the reaction. If all end groups of polymers are functionalised with cross-linker water is required for an initial hydrolysis of the silane. In one component applications water is used as moisture from ambient conditions, while in two component applications water is directly added to the mixture. Tin-based catalysts such as dibutyltin dilaurate (DBTDL) are commonly used to promote condensation curing. In some formulations, titanium alkoxides may also be employed (see Figure 4). Other metal catalysts, such as platinum or palladium, can also be used in RTV-1 silicones but these are less common.^{42,43} The release of by-products must be

carefully managed as their presence can influence the final properties of the silicone elastomer. Common applications of condensation curing silicones are found in construction as sealants.^{38,44}

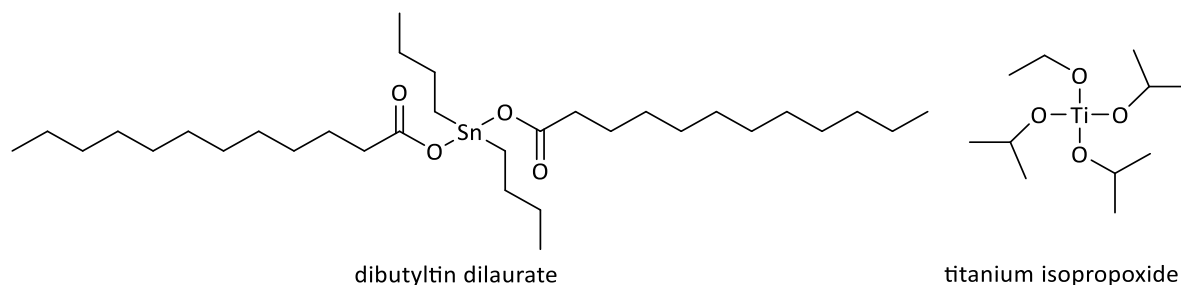


Figure 4: Catalysts dibutyltin dilaurate (DBTDL) and titanium isopropoxide (TIPT), commonly used in RTV-1 silicones.

1.5 Alpha silanes

In recent years a subclass of reactive organofunctional alkoxy silanes gained interest. Compounds bearing a heteroatom substituted methylene linker (α -siloxane, also referred to as α -silane) show a dramatic increase in hydrolysis speed for the alkoxy substituents when compared to similarly substituted β - or γ -siloxanes. This observed behaviour is referred to as α -effect or silicon α -effect with both terms used interchangeably. Due to their unique properties silanes of this structure are used in several polymers with cross-linking applications.^{45,46} The effect was first reported by Whitmore *et al.* in 1946⁴⁷, followed by a long dormant period as no particular interest in siloxanes and as described previously no commercially viable synthesis had been established. First usage of compounds of the general structure shown in Figure 5 appeared in patents filed in 1968 by Bayer AG^{48,49}, describing high reactivity of these compounds when used as moisture curing prepolymers. In 2003 new research activity was noted as Wacker AG^{50,51} and Henkel AG⁵² filed patents in the field. Interestingly only a limited amount of research has been undertaken to understand the α -effect while the cause of this effect has been a matter of debate for a long time.⁵³ Early publications attributed the effect to intramolecular donor-acceptor interactions between the heteroatom and silicon centre, attributing the increase in reactivity when compared to similarly substituted γ -siloxanes to a change in relative charge between silane and leaving groups. This assumption was first proven wrong by Mitzel *et al.*⁵⁴, showing that donor-acceptor behaviour of these compounds can only insufficiently describe the observed reactivity increase. While speculating that other factors such as pH, surrounding matrix and steric influences are involved in the effect no detailed investigation into their influence was published. The first comprehensive relation between theoretical modelling and experimental values was published by Berkefeld *et al.*^{55,56}, describing the discrepancy between theoretical modelling of hydrolysis speeds and the observed experimental data generated from synthesised compounds. No singular influence on the observed effect could be identified while the combination of several factors

such as pD-values* or hydrogen bonding between the functional groups contribute to the overall observed increase in reactivity.⁵⁵ More recent publications came to similar conclusions while using different base sets for calculation and additional or different silane derivatives than Berkefeld *et al.*^{55,57–}

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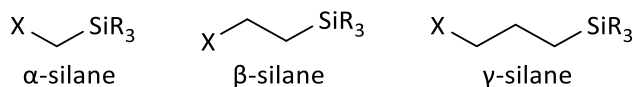


Figure 5: Comparison between alpha, beta and gamma substituted, functional silanes, where R can be alkoxy or other reactive and non-reactive substituents. X is a heteroatom substituent, such as sulphur or nitrogen.

Furthermore, industrial interest has been shown through the filing of several patents by different institutions over the last 30 years.^{60,61}

Notably, the α -effect in silanes must not be confused with the β -effect in silanes, as they involve distinct mechanistic phenomena and synthetic implications. The β -effect refers to a de-silylation process that occurs when an electron-donating heteroatom, such as oxygen or nitrogen, is located in the β -position relative to the silicon center. This interaction induces negative hyperconjugation, the lone pairs on the β -heteroatom interact with the antibonding orbital of the Si-C or Si-H bond.^{62–64} This weakens the silicon bond, allowing the elimination of the β -substituent. This effect is a cornerstone of synthetic strategies, such as the Peterson olefination, where the β -elimination of silane derivatives enables the formation of alkenes under acidic or basic conditions, offering control over syn- or anti-isomer formation depending on reaction conditions (see Figure 6).⁶⁵ For example, β -silyl alcohols can undergo elimination to yield stereoselective alkenes, demonstrating the synthetic utility of the β -effect.⁶⁶ In contrast, the α -effect in silanes, involving stabilization effects between a silicon atom and an adjacent α -position heteroatom, is less understood and significantly less explored in the context of synthetic applications. Due to its extensive use in the formation of C=C bonds and its clear mechanistic pathways, the β -effect in silanes is better characterised and applied in organic synthesis compared to the underexplored α -effect.⁶⁷

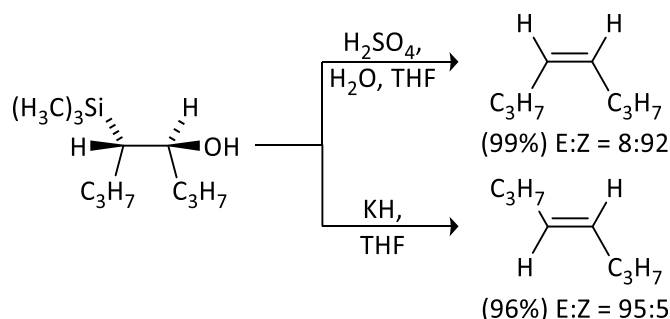


Figure 6: Use of β -silicon effect in the Peterson olefination and steering of reaction outcome through reaction condition choice.⁶⁵

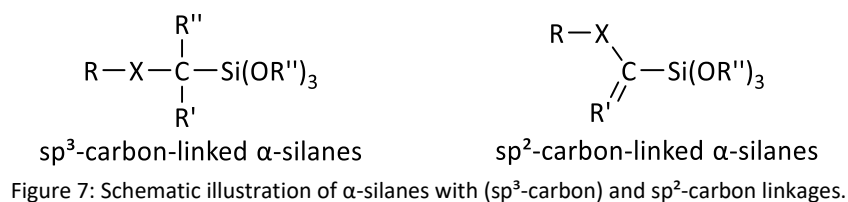
* pD values were recorded by Berkefeld *et al.* in deuterium oxide (“heavy water”), due to the slight differences in self-ionisation they are comparable to but not identical with pH values.

The main representatives of commercially available α -silanes are derivatives supplied by key chemical companies such as Wacker Chemie AG. Examples include trimethoxysilylmethyl derivatives, ethoxysilylmethyl derivatives and functionalised silanes with a nitrogen as heteroatom. Generally, commercial silanes are supplied with activity in moisture-curing systems and cross-linking reactions. For example, Wacker Chemie AG produces α -silanes under the product lines SILRES® and GENIOSIL®⁶⁸ which find wide application in adhesives, sealants and surface treatment applications. While such reactive compounds are at hand, the functional groups incorporated into commercially available α -silanes have remained limited, reflecting only limited scope of structure.^{68,69}

In conclusion, it is evident that there is a noticeable lack of structural diversity surrounding the α -silane scaffold, focussing on methylene linked α -substituted siloxanes, in the current landscape of chemical research. While α -silanes have proven to be valuable building blocks in various synthetic methodologies, most studies have focused on a limited range of structural variations. This lack of diversity has the potential to hinder the exploration of novel chemical space and limit the development of innovative applications. To advance our understanding of α -silane chemistry and unlock its full potential, it is imperative that future research endeavours embrace a more diverse approach to structural design, expanding and understanding boundaries of where and how α -effect plays a role.

1.6 Research question

Alpha substituted reactive silanes have long been recognized for their unique properties within the class of reactive silanes, playing a significant role in facilitating the room temperature vulcanisation of silicones and silane modified polymers worldwide. Historically, the use of α -silanes with special properties has been limited to methylene-linked compounds (sp^3 -carbon), constraining their substrate and substitution scope. This limitation may find resolution through the incorporation of sp^2 linked silanes, which opens exciting possibilities for heteroaromatic allyls, heteroaryls, or substituted heteroalkyls, a schematic illustration is shown in Figure 7. The inclusion of sp^2 centres into α -silanes represents a novel approach that offers a thrilling opportunity to explore new horizons within the established field of reactive silane-based adhesives and coatings.



The central objective of this thesis is to provide potential synthesis routes towards sp^2 α -silanes, given the absence of comprehensive descriptions of these compounds in the existing literature. Moreover,

the determination of physicochemical parameters for these compounds is of high importance, contributing significantly to academic knowledge and understanding of the α -silane class. This research effort also encompasses the investigation of mechanistic and material properties, which stand as the first of their kind due to the novelty of the group and partial synthesis pathways described. These endeavours aim to answer not only academically relevant but also industrially intriguing questions, such as the stability of sp^2 α -silanes when compared to commercially known silanes, their reactivity towards moisture, and ease of manufacturing.

The second chapter of this thesis shows a selection of sp^2 -carbon-linked α -silanes and a subclass of the same, the state of the art for these silanes, as well as their established synthesis routes. The chapter then shows two preferred synthesis routes, through a stoichiometric Grignard reaction and a palladium catalysed carbon silicon cross-coupling, optimises these reactions for the target α -silanes, shows their scope for the class of selected α -silanes and for the palladium route explores the mechanism.

Chapter three starts with the isolated α -silanes, uses them in downstream applications for polymer endcapping and in resin condensations and explores their physicochemical properties in a variety of application related experiments such as use of the silanes in industrially relevant silicone formulations. Additionally, the chapter shows the upscale of previously optimised synthesis.

All steps of this thesis are visualised in Figure 8. Starting with the identification of potential candidates (Chapter 2.3), followed by synthesis strategies via Grignard reaction (Step 1 in Figure 8, Chapter 2.4) and palladium-catalyzed coupling (Step 2 in Figure 8, Chapter 2.5), ultimately leading to the isolation of novel α -silanes. These silanes are subsequently applied (Chapters 3.1, 3.2, 3.3, and 3.5), and their scale-up synthesis is described in Chapter 3.4. The flowchart will be updated after each step is completed, with visual indicators highlighting the finished steps.

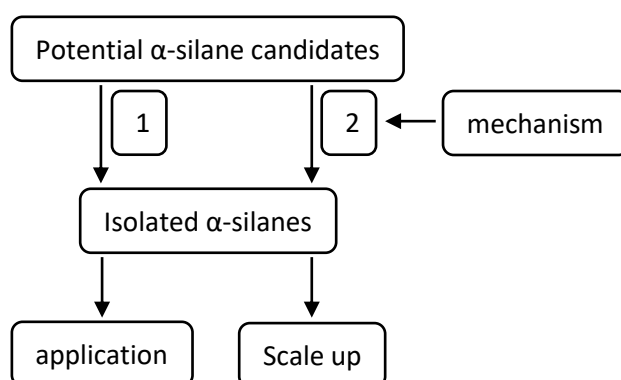


Figure 8: Flow chart presenting the general structure of this thesis.

2 Construction of silicon-carbon bonds towards α -silanes

2.1 Framework and objectives of the study

α -Silanes have been introduced in chapter 1.5. The silanes presented there and in the limited literature available on the topic derive from a methylene bridged silane. These silanes present a methylene group between the silicone and heteroatom. However, no references were found addressing a sp^2 -based carbon linker. This chapter will focus on the synthesis of such silanes from commonly available silanes. Different synthesis routes and approaches will be elaborated and shown. Both stoichiometric as well as catalytic approaches are considered and explored. The stoichiometric approach is based around established chemistry (chapter 2.4), showing the existence of the claimed structures from chapter 2.3. While chapter 2.5 shows the modification of a catalytic approach to forming carbon-silicon bonds, starting with feasibility and optimisation of the reaction and concluding with a mechanistic investigation and proposal of possible reaction mechanism.

A flowchart is presented in Figure 9. Starting from a sp^2 centre linked α -silanes either branched or cyclic derivatives can be drawn. When going for a carbon silicon bond formation route using heterocycles as the appropriate precursors would allow for more flexibility as their chemistry is well understood. Substituted derivatives are commercially available and they simplify the introduction of a sp^2 centre in alpha position to the silane greatly. Once heterocycles were selected, three common heteroatoms may be introduced: sulphur (S), nitrogen (N) and oxygen (O), resulting in thiophenes, pyrroles and furans respectively. These three heterocycles and their derivatives may be compared to cyclopentadienyl anions, resulting in compliance with Hückel's rule and exhibiting strong aromatic character. Hückel's rule states that a planar, cyclic molecule is aromatic and particularly stable if it contains a conjugated system with $(4n+2)$ π -electrons, where n is a non-negative integer. This rule helps predict aromaticity in organic compounds.⁷⁰ Their respective reactivity is influenced by the present heteroatom, with increasing electronegativity from furan to thiophene. Furans show typical diene reactivity while pyrrole and thiophene show more characteristic S_E type reactivity.⁷¹

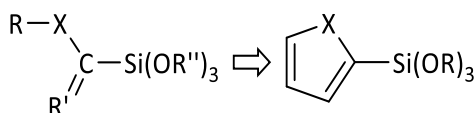


Figure 9: Identification of substructures previously not reported in literature.

2.2 Current state of the art

This chapter touches on the available strategies to synthesis functional silane compounds and elucidates the state of the art for silanes of the general structure shown in Figure 9. This will serve as a basis for the choice of potentially interesting α -silanes and synthesis strategies towards them.

2.2.1 State of the art for sp^2 linked α -silanes

Using lists of commercially available silanes, the heteroaryl structures derived from the compound shown in Figure 9 were reviewed. Literature known derivatives are described in the following. Manoso and DeShong⁷² showed the synthesis of different aryl-triethoxysilanes with a palladium (0) catalyst starting from aryl bromide and iodide (Figure 10). Their study reported the successful formation of the desired silane products along with the observation of an undesired hydration by-product. Commonly the treatment of silicon electrophiles with Grignard or lithium reagents is used for the generation of aryl-silanes. Either tetra-alkoxy, chloro-trialkoxo- or tetrachloro-silanes are treated with these species to yield the desired product. The authors optimise the Buchwald ligand and demonstrate that the oxidative addition of the catalyst into the silane bond is the key intermediate, from which either a carbon silicon or carbon hydrogen bond can be formed. The yields are affected by the electron properties of the aryl bromides used, with electron-rich aryl bromides yielding higher yields than electron-deficient aryl bromides. Additionally, the authors show that para substitution is preferred relative to the used halide, while ortho position diminished the yield significantly. Only two additional records of thiophene derived silanes are found in the literature, both of which use a Grignard reagent to generate the desired compound.^{72–74}

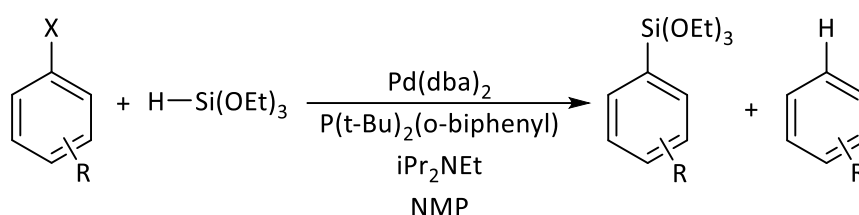


Figure 10: Synthesis of different aryl-triethoxysilanes with a palladium (0) catalyst starting from aryl bromide and iodide procedure according to.⁷²

Wolf and Lerebours⁷⁵ demonstrated the Hiyama type cross coupling of arylsiloxanes with aryl halides using a palladium-phosphine catalyst and sodium hydroxide, showing the reaction of furan and thiophene trimethoxysilane derivatives with 3-bromopyridine resulting in the appropriate cross coupling product. However, no source of the appropriate starting compounds has been disclosed. Han *et al.*⁷⁶ have shown cross-coupling reactions, using palladium as a catalyst (Hiyama coupling), of benzylic ammonium salts and a trimethoxy aryl compound. Here both furan- and thiophene-

trimethoxysilane were used to perform the cross-coupling reaction with ammonium benzonitrile (yielding 4-(furan-2-ylmethyl)benzonitrile and 4-(thiophen-2-ylmethyl)benzonitrile. However, no source of the appropriate starting compounds has been disclosed. Erchak *et al.*⁷⁷ showed the synthesis of alkoxy silanes from a hydridosilane-heterocycles via a methanolysis (Figure 11). Upon treatment with methanol hydrogen gas is released. By varying the molar ratio of methanol and starting the silane different substitutions on the silane could be achieved. The process itself is described to be autocatalytically, requiring no catalyst and only mild conditions.⁷⁷

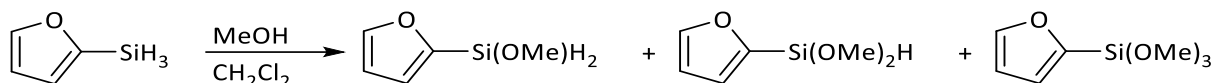


Figure 11: Methanolysis of furan-2-ylsilane in dichloromethane resulting in the formation of various furan-2-ylmethoxysilanes, as presented by Erchak *et al.*⁷⁷

Riedmiller *et al.*⁷⁴ showed the synthesis of furanyl-alkoxysilanes as an intermediate in the synthesis of hydride silanes. Here an unfunctionalised furan was treated with butyl lithium and tetramethyl orthosilicate in diethylether to yield di- and tri-substituted alkoxy silanes (Figure 12). Due to the simultaneous formation of several substitution products, they were separated through fractioned distillation.

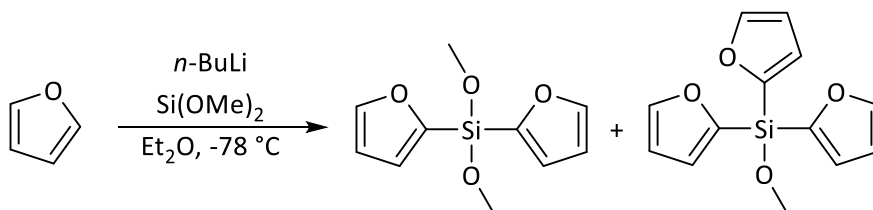


Figure 12: Treatment of unfunctionalised furan with butyl lithium and tetramethyl orthosilicate in diethyl ether to yield di- and tri-substituted furanyl-alkoxysilanes.⁷⁴

Fritzsche *et al.*⁷⁸ have shown the synthesis of N-methylpyrrolesilanes from N-methylpyrrole (Figure 13). Treatment with *n*-butyl lithium gave 2-lithium-N-methyl pyrrole which in turn was reacted with tetramethyl orthosilicate to yield the appropriate silane compounds. The concentration of tetramethyl orthosilicate had a direct influence on the substitution ratio, ranging from mono to tetra N-methylpyrrolesilanes. These in turn were converted to the hydridosilane species using lithium aluminum hydride, hoping to find suitable applications as hydrogenation agents and nanoparticle stabilizers, due to their thermal, hydrolytic and air stability (when substituted at least twice). It is reported that N-methylpyrrole-trimethoxysilane is highly susceptible to hydrolysis when exposed to air, indicating the effect anticipated by silanes described in this work.⁷⁸

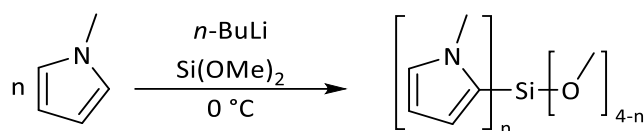


Figure 13: Treatment of N-methylpyrrole with butyllithium and tetramethyl orthosilicate results in the formation of mono ($n=1$), di ($n=2$) and tri ($n=3$) N-methylpyrrole-methoxy silanes as well as tetrapyrrolesilane ($n=4$). The equivalents, n , can range from 1 to 4.⁷⁸

No further records of heteroaromatic α -silanes were found in literature. As there are only a few examples of heteroaromatic α -silanes presented in literature and furthermore in majority of cases synthesised either as intermediate or as a Hiyama coupling substrate, little to no records on their physicochemical properties or presence of α -silane effect were systematically studied. This thesis provides synthesis strategies and a systematic approach in exploring this subclass of α -silanes.

2.2.2 Synthetic strategies targeting functional silanes

Simple silanes are commonly produced on large scale through e.g. direct process allowing the cheap and efficient generation of bulk material. Functionalised silanes such as reactive alkoxy silanes are prepared from them. The Grignard reaction is a powerful tool for synthesising functional silanes, see Figure 14.⁷⁹ In this approach an *in situ* generated organomagnesiumhalide (the Grignard reagent) is reacted with chloro or alkoxy silanes to form silicon carbon bonds. This method is particularly useful for the introduction of organic groups into low functional silanes.⁸⁰ For more elaborate or functionalised silanes both industry and academic literature reports the usage of either Grignard or lithium reagents with tetraalkoxy orthosilicate.⁷² While the reaction has been studied in detail and several tolerated groups are known no absolute control over the substitution pattern is reported when multi halogen substrates are used. Advantages of this approach are simplicity of the reaction setup, conversion of common silane substrates and formation of a wide range of carbon silicon bonds. Disadvantages are sensitivity towards moisture, side reactions with substrate or other functional groups⁸¹, as well as due to their radical intermediates present *in situ* certain substituents are unsuitable. This is an intrinsic limitation of the substrates commonly used in these reactions.⁸²

For Grignard reactions involving silanes and alkoxy silanes, the choice of organic substituents is crucial due to their impact on the formation and stability of radical intermediates during single electron transfer (SET) processes. Common substituents include alkyl groups such as methyl (Me), ethyl (Et), propyl (Pr) and butyl (Bu). Alkyls can stabilize radicals through hyperconjugation and inductive effect, with larger alkyl groups generally providing increased stability.⁸³ Aryl groups, such as phenyl (Ph) and substituted aryls like tolyl (Tol), stabilize radical intermediates through resonance delocalization, significantly enhancing their stability.⁸⁴ Alkoxy groups, including methoxy (OMe) and ethoxy (OEt), stabilize intermediates through electron-donating effects which is particularly important in

alkoxysilanes.⁸⁵ In alkoxysilanes, both the R group and the OR' groups influence the SET process. Aryl or bulky alkyl groups attached to silicon offer additional stabilization to silicon-centred radicals, promoting efficient product formation.⁸⁶ During the reaction of a Grignard reagent with an alkoxysilane-like, the Grignard reagent donates an electron to the silicon atom, forming a radical intermediate. The stability of this intermediate, determined by the substituents R, R', and OR'', is critical for the reaction's efficiency.⁶⁶ Therefore, the careful selection of substituents in silanes and alkoxysilanes is essential for optimising radical stability and achieving desired outcomes in Grignard reactions.⁸⁷

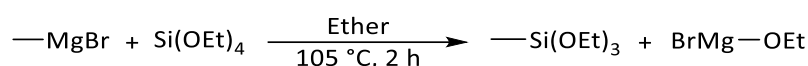


Figure 14: McBee *et al.*⁷⁹ reported the reaction of methylmagnesiumbromide with triethyl orthosilicate at 105 °C and 2 h forming methyl triethoxy silane and magnesium ethoxy bromide. They did not report which ether was used.

New fields of carbon silicon bond formation are photocatalytic silylation and base free coupling reactions. Photo-redox catalysis utilizes visible light to activate catalysts, forming carbon silicon bonds under mild conditions and enhancing functional group toleration.⁸⁸ Advantages of this approach are mild reaction conditions of the photocatalyst and reduced environmental impact, while their disadvantages include the need for specialised equipment and light sensitive catalysts. Base free strategies commonly use hypervalent iodine reagents or other organo-catalysts to achieve silylation without the need for a base or transition metal catalyst making their advantage align with green chemistry principles while being comparably simple. Disadvantages include potential substrate scope limitation and low reaction efficiency.⁸⁹

Particularly most of them use homogenous rare earth metal catalysts. This allows for the selective formation of novel carbon-silicon bonds. In the last two decades substantial progress has been made in the field, allowing for the introduction of highly functional groups and more atom economic access to compounds previously only accessed at low to no yield.⁹⁰ A plethora of different strategies has been successfully used in literature, most of which have their specific limitations. Most commonly and similarly to cross coupling in carbon ruthenium^{91,92}, rhodium^{82,93–97}, palladium^{72,98–107}, iridium^{108–112} and platinum^{113,114} complexes equipped with phosphine-based ligands are used to form novel carbon silicon bonds. An exemplary reaction using palladium is shown in Figure 15.

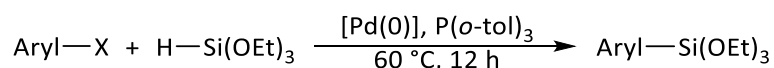


Figure 15: Manoso *et al.*⁷² showed the palladium catalysed carbon-silicon cross-coupling of aryl halides with triethoxysilane yielding an aryl-triethoxysilane. A palladium(0) precursor ([Pd(0)]) and tris(*o*-tolyl)phosphine (P(*o*-tol)₃) at 60 °C for 12 h were used.

Using ruthenium^{91,92} or rhodium^{82,93–97} complexes in cross-coupling reactions has been extensively explored. These catalysts are highly reactive with good selectivity, making them suitable for carbon-

silicon bond formation. Advantages include robustness of complexes and moderate reaction conditions, while disadvantages are high cost of metals, potential environmental implications and limitation to alkyl and arylsilanes. Palladium^{72,98–107} catalysed cross-coupling reactions such as Hiyama coupling are among the most studied and widely applied methods for carbon silicon bond formation. Palladium catalysts, in conjunction with fluoride ions, can enable the efficient coupling of aryl and vinyl halides with organosilanes. Advantages of palladium catalysis include high functional group tolerance, excellent yields and established reaction protocols.¹¹⁵ The disadvantages can be high cost of palladium and, if present, toxicity of fluoride. Iridium^{108–112} and platinum^{113,114} catalysts, although less common than palladium, also play a significant role in Si-C bond formation. These catalysts often allow for unique reactivity patterns and can be particularly useful for specific substrates. Advantages include their ability to catalyse reactions that are challenging with other metals, while disadvantages include their rarity and high cost, which limit their widespread use.

Additionally, several copper mediated synthesis strategies using different activation pathways, such as pre-functionalisation of a reactant with a highly active boron leaving group or activation of compounds due to intramolecular assisted coordination and directed C-H activation have been shown, most notably by the group of M. Oestreich.^{116–123} Copper catalysts are attractive due to their abundance and low cost. Advantages of copper catalysis include cost-effectiveness and the ability to employ mild reaction conditions. However, disadvantages include the need for pre-functionalisation of substrates, which can generate significant amounts of stoichiometric waste, and limited efficacy with certain substrates, such as siloxanes. A comprehensive review on recent advances in the field, including their specific limitations, has been published by Wilkinson *et al.*¹²² Different compounds can be accessed through silylation of various precursors, allowing the synthesis of highly functional compounds. Notably the substitution on the silane centre is limited to alkylsilanes with phenyldimethylsilanes most prominently used as it results in the highest yields for most procedures. Where different silanes are used extensive pre-functionalisation, mostly with boric acid derivatives, is employed, increasing the reactivity of the silane centre and raising yields to acceptable levels.

Silane substituted highly functional organic molecules are commonly used downstream in Hiyama cross couplings, allowing a carbon-carbon coupling between the silane functionalised compound and aryl, alkenyl or alkyl halides.¹²⁴

Another less common synthesis strategy relies on the *in situ* deprotonation of a carbon-substrate and activation of the silane by addition of fluoride sources. The complexation of fluorine with silanes is well known to yield pentavalent, highly reactive intermediates and thus significantly activates the silane, allowing a C-H activated carbon-silicon bond formation.^{125–129} Key work has been done by Nozawa-Kumada *et al.*¹²⁸ demonstrating the successful C-H bond activation in heteroarenes and benzenes by using trifluoromethyltrimethylsilane and catalytic amounts of fluoride. While direct

silylation was shown the publication heavily relies on the usage of rubidium and caesium fluoride and is limited to using a highly functional and polar silane substrate. Advantages of *in situ* deprotonation and fluoride activation include the high reactivity of intermediates and the ability to form Si-C bonds under mild conditions. However, disadvantages include the use of toxic and expensive fluoride sources and limitations in substrate scope, which require careful handling and may restrict the broader applicability of this method. According to recent publications nickel¹³⁰ and iron¹³¹ catalysts can also be highly effective for cross-coupling reactions, offering less environmentally impactful alternatives to palladium-based systems. These advances have paved the way for more sustainable and scalable processes in the synthesis of functional silanes, further broadening the scope of their applicability. Advantages of these newer catalytic systems may be lower cost and reduced environmental impact, as nickel and iron are more abundant and less toxic than palladium. However, yield, selectivity and substrate scope are not comparable to those of traditional palladium-based systems.

Cross coupling strategies are of highest importance as toxic reactive groups required in other strategies can be avoided. Additionally, comparably mild reaction conditions allow for a wide range of substituents. Most available synthesis strategies are limited to alkyl and aryl functional silanes when carbon silicon cross coupling is used, Murata *et al.*⁹⁴ where able to show a possible route for sp³ alkoxysilanes.

Overall, cross-coupling strategies for carbon-silicon bond-formation has significantly expanded the synthetic toolkit available to chemists. A variety of metal catalysts and activation strategies was shown, high levels of reactivity and selectivity are possible, enabling the synthesis of a wide range of functional silanes. The ongoing advancements in this field continue to address the challenges associated with each method, striving towards more efficient, economical and environmentally friendly processes for the production of these valuable compounds.

This is where chapter 2.5 starts out, establishing a reliable, mild and high- yield-method towards heteroaryl functionalised alkoxysilanes. Due to the complex nature of the used catalyst, publications by Murata *et al.*⁹⁹ and Manoso *et al.*⁷² were used a starting point. Not only establishing but optimising the method towards the generation of aforementioned silanes as well as investigating the underlying mechanism of the reaction at hand. As all structures are expected to be highly moisture sensitive all substance synthesis and storage was performed under strict exclusion of air and moisture. Inert argon gas was dried using phosphorus pentoxide. Common practice of thorough Schlenk technique was employed in all processing steps. When solids needed transfer between vessels an argon filled glove box was used. All liquid transfers were performed between sealed vessels using syringes with gas cushioning or inert syringes.

2.3 Identification of promising compounds for synthetic investigation

Building on the structural limitations imposed by the motif presented in Chapter 2.1, this chapter investigates derivatives of the proposed α -silane structure. These theoretical considerations draw on well-established findings about reactive alkoxy silanes and highlight potentially valuable derivatives, along with their possible applications.

For a first model study the thiophene derivative will be used as the precursor, it is expected to undergo common S_E type chemistry without any further complications such as derivatisation on furans. In industrial applications using alkoxy derived silanes for usage in curing or as adhesion promoters both methoxy and ethoxy groups are applied. While methoxy generally shows higher hydrolysis rates, quicker crosslinking and stronger networks, ethoxy produces harmless ethanol, which leaches from the cured polymer over time. In some applications methanol vapor can be undesirable. Nevertheless it is the most common alkoxy group used in this field.¹³² Due to its reactivity and abundance in industry, methoxy groups have been chosen as the cleavable alkoxy group, as it was possible to easily compare it to known compounds. When handling larger amounts (above 100 g) of substance, the use of methanol over ethanol derivatives will be reassessed (Chapter 3.4).

A selection within the group of novel sp^2 -linked α -silanes has been made exploring all relevant chemical properties with sample compounds, all target compounds are presented in Figure 16. The compounds will not only be fully characterised but will also be subjected to further experiments in Chapter 3. This will provide a broad database of trends in activity, allowing for the comparison of a wide variety of influences on the silane. This can help to tailor this class of silanes to a certain application.

Construction of silicon-carbon bonds towards α -silanes

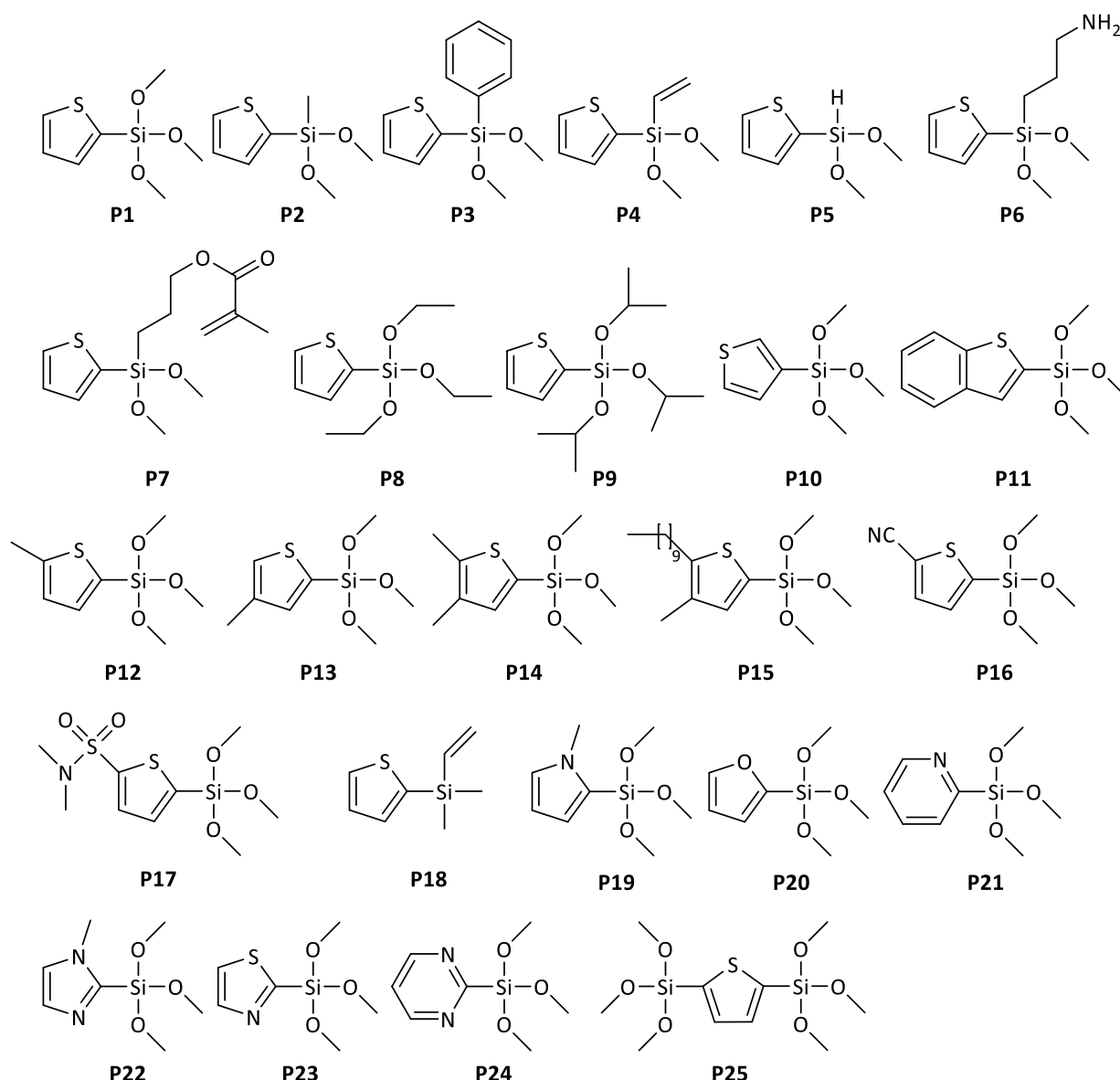


Figure 16: Overview of all target α -silanes **P1-P25**[†], accessed with varying synthetic approaches in this work.

Variation of the proposed structures may be made on the heterocycle or the silicon centre. Substitution is targeted on the most common substitutions used in industrially relevant silanes. A common substitution pattern in reactive silanes are trialkoxysilanes, while relevant they do not bear an extra substituent on the silicon, represented through **P1**. Other common substitutions are alkyl such as methyl (**P2**). Aryl will be represented by phenyl **P3**, vinyl by **P4**. Si-H bonds in silicon-containing compounds are polarized towards the hydride. This means that the bond has a partial negative charge on the hydrogen (making it hydride-like) and a partial positive charge on the silicon atom. This polarization occurs because silicon is less electronegative than hydrogen, resulting in a shift of electron density towards the hydrogen atom and changed reactivity, as explored in **P5**.¹³³ Two additional motifs

[†] The letter **P** is used to unambiguously describe the substances made in this work.

are proposed as they are common within commercial alkoxysilanes: propylamine (**P6**) and ethyl methacrylate (**P7**). A comparison between different alkoxy based leaving groups will provide insight into reactivity differences. From other publications it is known that a hydrolysis speed in alkoxysilanes of OMe > OEt > OiPr is generally observed.^{134,135} Therefore, an increase in the carbon chain length on the alkoxide reduces the reactivity. Compounds **P1**, **P8** and **P9** will be synthesised to verify this trend for the substances at hand. For an industrial application, the usage of ethoxy- and iso-propoxy-silanes is preferred when compared to their respective methoxy derivatives. The methanol released during the hydrolysis of such compounds can have a negative health and safety impact. Furthermore, the appropriate substrate may be significantly more toxic when comparing methoxy with ethoxy. Since the silanes shown in this work are based around the observed α -silane effect a comparison to a beta-silane derived compound is aspired. This compound may undergo elimination reactions due to overlap of the carbon-silicon and carbon- β -substituent orbital interactions. This is known to eliminate both silane and β -substituent as well as undergo silyl shifts via a three membered silyl heterocycle.^{62–64} This effect however is dependent in the tetrahedral angle.⁶³ Accordingly the observed strength for compound **P10** is strongly dependent on the heterocycle distortion. Additionally, 3-position substituted thiophenes are known to be highly toxic, thus far the specific toxicity has only been studied by theoretical calculation.¹³⁶ However, compound **P10** will be synthesised for comparison. It is advised against the usage on an industrial scale. An increased π -system, such as in **P11**, is expected to yield increased reactivity due to delocalization of electron density in the vicinity of the silane. Furthermore, a side reaction may occur due to the so-called beta-silicon effect. The steric influence on the heterocycle will be explored by the addition of alkyl substituents. The influence is expected to be primarily result from their steric nature, since there is only minor inductive effect expected. Compounds **P12** to **P15** will serve as sample compounds. Double substitution and elongated carbon chains are expected to further increase the observed effect, when comparing to a mono methyl substitution. Another major influence may be based around inductive effects on the heterocycle. A selection of substituents based on their electronic properties was made. The selected group must be inert to the chosen reaction conditions. Nitrile (**P16**) and sulfonamide (**P17**) substituents have been selected to represent a negative inductive effect. **P18** will serve as a comparative silane for hydrosilylation based polymer modifications in conjunction with **P4** exploring the differences between alkyl and alkoxy substitution. **P18** will not exhibit any α -silane effect. A positive inductive effect will be represented by methoxy (**P18**) substitution of the heterocycle.

All compounds shown thus far are thiophene based, however additional heteroatom substitution will be performed. The most common heterocycles furan (**P19**) and pyrrole (**P20**) are used. To inhibit downstream reactions and make the synthesis of the pyrrole derivative more streamlined it is advisable to use a methyl functionalised substrate, effectively surpassing any secondary reactions on

the nitrogen atom. Methyl substitution is used for its low steric bulk, little electronic and mesomeric implications. Of further interest may be the six membered pyridine substituted silanes (**P21**), as this would be the lightest six membered heterocycle substituted silane possible. As a further derivatization, common heteroaryl with more than one heteroatom will be used to study the influence and interaction of the two with the silane. N-methyl-imidazole (**P22**), thiazole (**P23**) and pyrimidine (**P24**) will be used as common bi-heteroatom aryls. Double substitution of the heterocycle will be performed as well, resulting in **P25**. The introduction of an additional silane centre will yield higher cross-linking density when hydrolysis is performed. This may also introduce interesting properties in a final application. The resulting compound is expected to have a higher boiling point compared to monosubstituted heterocycles, making downstream processing or workup such as distillation more challenging. No combination of silane and heteroaryl substitution was undertaken to simplify the resulting structures, as well as localize observed effects to one of the compounds substituents.

There are different synthesis strategies targeting functional alkoxysilanes. During synthesis it is important to work under water and moisture exclusion as depending on the alkoxysilane rapid hydrolysis may occur upon contact. A common source of functional silanes are mono to tetra chlorosilanes. Functional substitutions are either introduced during chlorosilane generation, such as the direct process, or via hydrosilylation of chloro-hydrogen-silanes with small molecules. As most chlorosilanes are highly corrosive, alcoholysis with the appropriate alcohol towards alkoxy-hydrogen silanes is performed, followed by functionalisation via hydrosilylation. A common example is the methanolysis of trichlorosilane to trimethoxysilane followed by the platinum catalysed hydrosilylation with allylamine forming 3-aminopropyltrimethoxysilane, which is used for a plethora of different industrial applications.¹³⁷ An alternative synthesis uses trimethoxysilane in hydrosilylation with allylchloride and subsequent amination with ammonia to form the described aminosilane.¹³⁸ A versatile approach for further functionalisation or introduction of bulky substituents to alkoxysilanes is a Grignard-type reaction.^{139,140} Several Grignard approaches are described: using alkoxy magnesium chloride on chlorosilanes, with and without subsequent alcoholysis.¹⁴¹ Also, tetra alkoxysilanes may be subjected to Grignard reagents. The substitution pattern of these reactions may be tailored via the used equivalents of Grignard reagent, from mono to tri functional siloxanes. When using chloro-alkoxysilanes a mixture of reaction products, substituting both chloro and alkoxy groups, are isolated. The usage of alkoxysilanes functionalised with bulky substituents has also been described in yields up to 84 % by Masaoka *et al.*¹⁴⁰ While alkoxysilanes are susceptible to hydrolysis they do not release gaseous hydrogen chloride during reaction and are thus easier and safer in handling. Furthermore, the commercial supply of functional alkoxysilanes is broad, while functional chlorosilanes are limited. This method may yield the targeted structures in a straightforward manner. There are more elaborate cross coupling strategies for carbon-silicon bond formation, however they are not as versatile as Grignard

reagents and require optimisation towards the targeted compounds, once the compounds are established catalytic approaches may use less harsh reaction conditions and produce fewer byproducts and waste when compared to Grignard reagents.

It must be noted that pyridines have unique radical stabilization properties.¹⁴² This affects the mechanism of Grignard reactions, since the formation of a reactive radical *in situ* is required. A publication by Rammal *et al.*¹¹² shows the specific formation of carbon silicon bonds between alkyl silanes and pyridines. While this is not optimised for siloxanes and is not mentioned in the paper it may pose an alternative route to this compound specifically. When approaches accessing other derivatives fail on this compound the method of Rammal *et al.*¹¹² will be employed and adapted, if necessary, for the desired structure **P21**.

This concludes the identification of potential α -silane candidates in this thesis. The initially presented flow chart is thus completed in its first step, the chart is shown below in Figure 17.

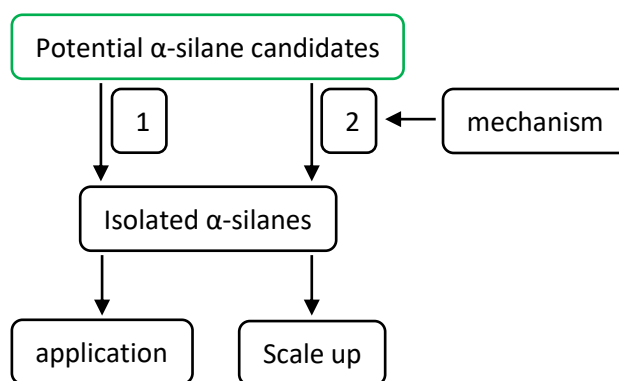


Figure 17: Flow chart presenting the general structure of this thesis, with the first step successfully finished.

2.4 Stoichiometric carbon-silicon bond formation

This chapter describes one of two ways to construct the α -silanes described in this work. It uses the Grignard reaction for the formation of the carbon-silicon bond, optimises reaction conditions and shows the scope of the optimised reaction for the target silanes disclosed in Chapter 2.3. The concentration of all changed parameters was calculated in gram per mol to guarantee comparability between all experiments rather than using a constant weight ratio. Additionally, all experiments in this chapter were run with minimum one repetition to exclude any outliers and confirm reproducibility of the shown results. The individual conversions are reported in appendix A3 while the conversions shown in this chapter are arithmetic means from all experiments to aid readability.

2.4.1 Feasibility of stoichiometric carbon-silicon bond formation

This chapter studies the synthesis of a new subclass of purpose made α -silanes, bearing a sp^2 centre in α -position. As there are only very few silanes of this structure known in literature, with none being

purpose made for applications in curing polymers, exploratory reactions targeting structure **P1** were conducted. Following the protocol provided by Riedmiller *et al.*⁷⁴ synthesis of compound **P1** was undertaken, establishing potential reaction conditions for further optimisation (Figure 18).

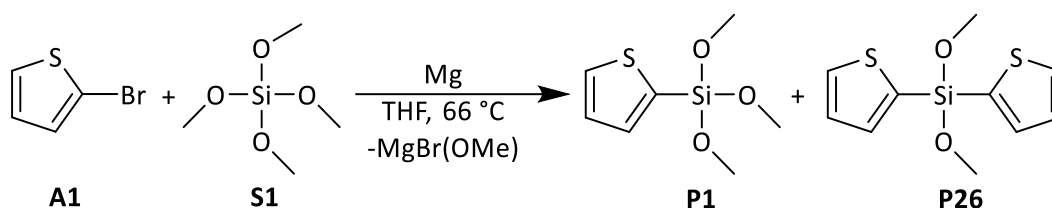


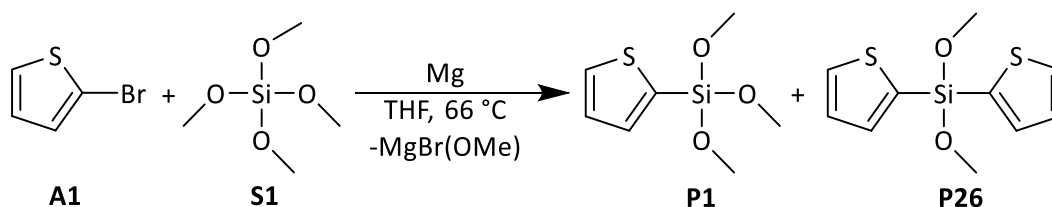
Figure 18: Grignard reaction between 2-bromothiophene and tetramethyl orthosilicate in THF at 66 °C forming mono (**P1**) and di (**P26**) thiophenyl-alkoxysilane. Procedure in accordance to Riedmiller *et al.*⁷⁴

2.4.2 Optimisation of stoichiometric carbon-silicon bond formation

While initial reactions showed the formation of the desired mono-thiophenylsilane (**P1**[‡]), significant formation of side product di-thiophenyl-dimethoxysilane (**P26**) were observed. Table 1 clearly shows the dominant formation of mono substituted product **P1** when adding silane to thiophene while reverse addition leads to a significant increase in bis substitution **P26**. A detailed investigation of conversion, yield and the isolated products such as **P1** are available in appendix A3.

Table 1: Grignard reaction of 2-bromothiophene with tetramethyl orthosilicate and magnesium powder in THF at 66 °C.

Varying the addition order of substrates to the reactor and recording resulting molar ratios between thiophenyl-trimethoxysilane (**P1**) and di-thiophenyl-dimethoxysilane (**P26**).



Addition sequence	Molar ratio P1 : P26
Silane to thiophene	97 : 3
Thiophene to silane	78 : 22

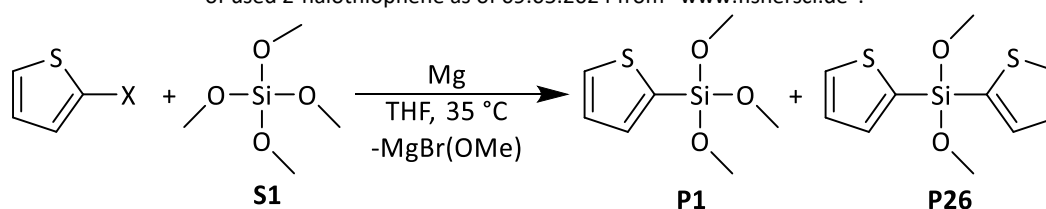
Classic Grignard reactions generate the active Grignard species in bulk prior to addition of the second substrate. As shown in Table 1 the order of addition of reactants to dried tetrahydrofuran (THF) with

[‡] The numbering system in this thesis is designed to provide a clear and consistent notation for the compounds used and synthesised. Target silanes are denoted as **P**, heteroaryls as **A**, and silanes used for synthesis as **S**. Each compound is assigned a specific number to enable straightforward identification. The numbering reflects the relationship between reactants and products, such that **A1** and **S1** lead to **P1**. While multiple combinations of **A** and **S** may result in the same product, the numbering ensures that one of the two reactants (**A** or **S**) always corresponds numerically with the product, maintaining clarity and consistency. Later chapters additionally use the letters **B** for base, **L** for ligand, **M** for metal precursor and **V** for solvent.

magnesium powder has a significant impact on product ratio. This is due to the *in situ* formation of active Grignard species through the reaction of 2-bromothiophene with magnesium. When thiophene is charged into the reactor first formation of significant amounts of active species is suspected. Addition of silane then leads to mono as well as multi substitution of alkoxides. When charging 2-bromothiophene to a reactor already containing the reactant silane formation of active species can be controlled through careful thiophene dosage. The active compound then reacts with the non-functionalised silane. After progression of addition a second reaction with a silane becomes more likely, with overall formation of bis substituted product stays low and less likely, while never reaching levels present addition of thiophene to silane. Through careful calculation and dosage of equimolar ratios significant formation of undesired multi-substituted silane can be minimised. This theoretical assessment was confirmed through experiments in Table 1.

For initial screening a bromo-functional heteroaryl was used. Subsequently all commercially available thiophene halides were screened, optimising for conversion, selectivity and cost of substrates. For comparison, reactions with commercially available derivatives containing a halide in 2-position of the thiophene were screened as presented in Table 2

Table 2: Grignard reaction of different 2-halothiophenes with tetramethyl orthosilicate and magnesium powder in THF at 35 °C. Recording the resulting conversions of 2-halothiophenes, selectivity for trimethoxy(thiophen-2-yl)silane and the cost of used 2-halothiophene as of 09.05.2024 from "www.fishersci.de".



2-Halothiophene	Conversion [%]	Selectivity [%]	Cost [€ / kg]
2-Chlorothiophen A26	24	87	412.00
2-Bromothiophen A1	52	97	283.00
2-Iodothiophen A27	57	96	1970.00

Seyferth¹⁴³ showed comparative conversions between different halide substitutions on alkyls and aryls. Highlighting the trend of increase reactivity of ethylene halide with increasing molecular weight of the halide, chlorides having significantly less conversion (15 %) than bromides (41 %) and iodides (43 %). As astatine is radioactive it does find no significant synthetic application. Fluoride-carbon bonds show significantly less reactivity than all other halogen-carbon bonds, making them less interesting for this application, while there are Grignard reactions using fluoride substituted substrates, they only find use in niche applications.¹⁴⁴ Comparing the conversions and selectivity for the desired structure **P1** presented in Table 2 it is evident that bromide **A1** and iodide **A27** substituted thiophenes are superior to chloride **A26** substituted. While pricing of chloride and bromide substituted thiophene is

comparable, a significant increase in price must be noted for iodide. This makes bromo substituted substrates the ideal choice for high yield and low-cost synthesis and is thus used in all further experiments if not indicated otherwise. Iodides may be used as fallback in case low yields are achieved with bromides.

During first experiments magnesium powder was used as a magnesium source for active Grignard species formation. During first screening temperatures rose by 1 K every two to five seconds, potentially leading to heating of the volatile ether and therefore handling of combustible and potentially explosive gases. When using all pre-dried substrates, magnesium and solvent, the commonly observed initiation times of Grignard reactions were on the scale of minutes. As the activity of powdered magnesium was established as too high, reduced activity was desirable to reduce rapid temperature increases after initiation. As shown in Figure 19 the use of magnesium shavings has less drastic temperature increases with comparable initiation times. While the overall released energy during Grignard reaction must be the same, slowed release of energy allows for easier dissipation of heat, more time to react to temperature changes by the operator and less drastic cooling. The faster temperature rise can be explained through the significantly larger surface of magnesium powder compared to shavings. For all subsequent experiments magnesium shavings were used. Additionally, a more controllable reaction process is desirable for upscaling the reaction, as shown in Chapter 3.4.

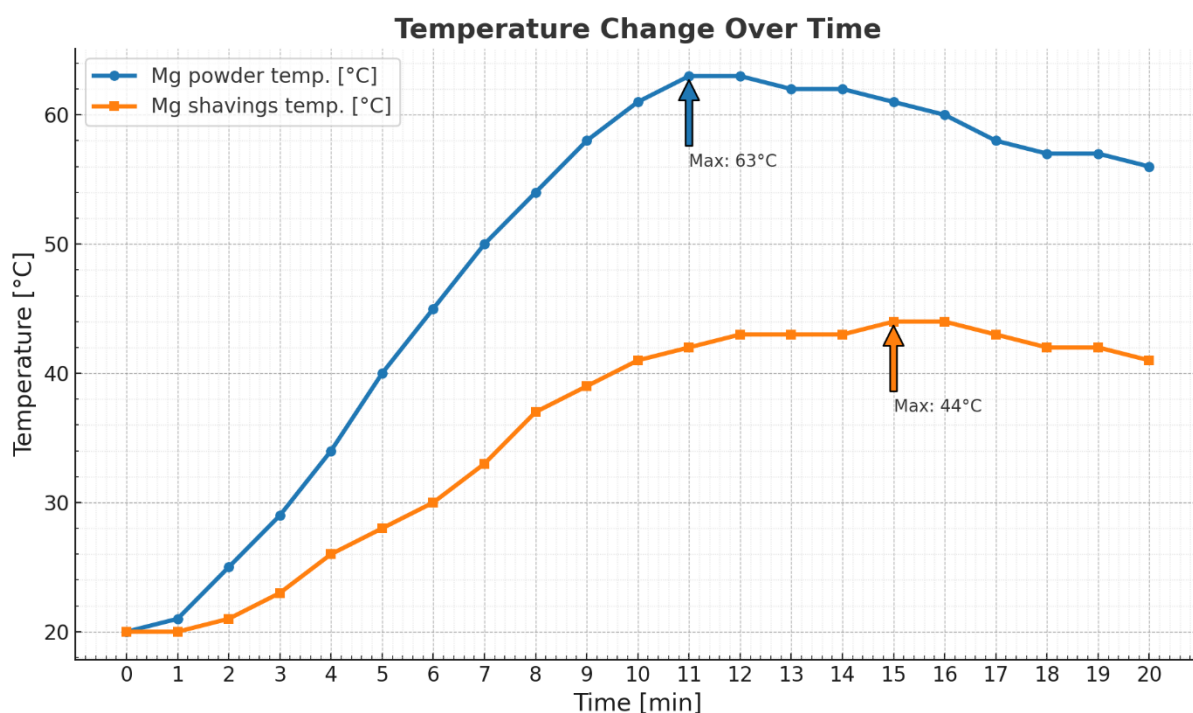
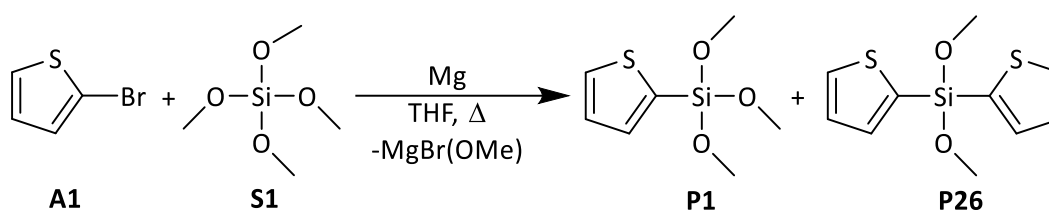


Figure 19: Time resolved temperature during initiation of Grignard reaction between 2-bromothiophene and tetramethyl orthosilicate in THF. Comparing magnesium powder and magnesium shavings.

After the addition sequence has been optimised the reaction temperature was screened with the same exemplary reaction between 2-bromothiophene and tetramethyl orthosilicate. During Grignard

reactions commonly a significant amount of energy is released during bond formation¹⁴⁵, indicated by a measurable increase in temperature. The reactions temperature was screened up to the boiling point (bp) of the used solvent ($\text{bp}_{\text{THF}} = 66\text{ }^{\circ}\text{C}$) as indicated in Table 3. The reaction reaches a maximum conversion at $45\text{ }^{\circ}\text{C}$ for the mono substituted product **P1** of 62 %. The reaction was monitored through nuclear magnetic resonance (NMR) At higher temperatures ^1H - and ^{29}Si -NMR spectra indicate the increasing formation of the double substitution product described during addition order optimisation. At lower temperatures remaining substrates were detected. All further experiments were conducted at $45\text{ }^{\circ}\text{C}$.

Table 3: Temperature screening of the Grignard reaction between 2-bromothiophene and tetramethyl orthosilicate in THF and in the presence of magnesium shavings.



Reaction temperature [$^{\circ}\text{C}$]	Crude conversion [%]
0	41
25	50
35	52
45	62
55	60
66	55

Lastly different filtration approaches to remove the stoichiometrically formed methoxy-magnesium-chloride were explored. Filtration under inert conditions is a straightforward process, involving either filtration elements in the flask containing contaminated products or an inert filtration frit, allowing for comparable filtration to common lab procedures transferred to an inert setup, without requiring the transfer of all reaction equipment into a glove box. When all low volatile compounds are removed, the target product, as well as substrates and potential side products are contaminated with the stoichiometrically formed magnesium salt described above, forming a highly viscous sludge. This sludge makes filtration unsatisfactory, reducing yields significantly. As the salt is barely soluble in hydrocarbons¹⁴⁶ pentane or heptane were used to extract all compounds from the sludge and consequently allowing easier filtration due to dilution of the sometimes viscous compounds. Hexane was excluded from these tests due to its toxicity.¹⁴⁷ The remaining sludge is then washed, further increasing yields (Table 4). As the used solvent for extraction does not significantly influence yields heptane was used for its higher boiling point and therefore easier and more safe handling.

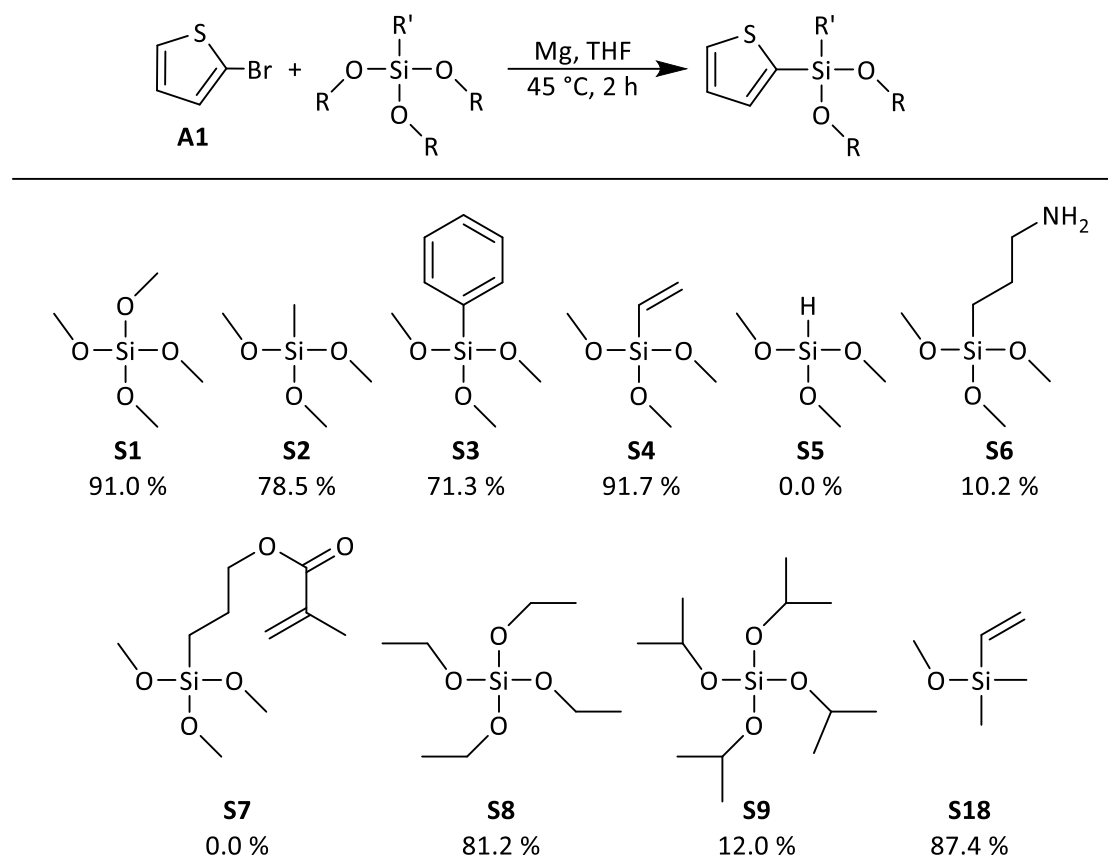
Table 4: Workup optimisation of the Grignard reaction between 2-bromothiophene and tetramethyl orthosilicate in THF and in the presence of magnesium shavings at 45 °C

Process optimisation	Crude yield [%]
None	21
Extracting sludge with pentane	53
Extracting sludge with heptane	56
Washing sludge with pentane	61
Washing sludge with heptane	62

2.4.3 Scope of optimised stoichiometric carbon-silicon bond formation

While optimizing the Grignard synthesis route in the previous chapter 2.4.2 the reproducible synthesis of compound **P1** was shown. Additional compounds were introduced in 2.3. Synthesis of these compounds was performed in accordance with the above optimised procedure. Exploring different limitations of the process and due to the unique nature of Grignard reaction converting an alkoxy silane to a newly formed carbon-silicon bond thiophene as heteroaryl was introduced to different functionalised silanes in Scheme 5. Furthermore, a variety of heteroaryls were converted with tetramethyl orthosilicate to the respective α -silanes, presented in Scheme 6. Previous screening of halides demonstrated that using iodide-substituted heteroaryls instead of bromide ones can result in minor improvements in conversion. To reduce variables in conversion efficiency and show more comparable results, trials involving iodide heteroaryls were not included in the summary but were added to appendix A3. All shown reactions are averaged from minimum one repetition. In total 53 experiments were conducted and fully worked up, describing and characterising the majority of compounds for the first time. All yields are reported after workup.

Construction of silicon-carbon bonds towards α -silanes



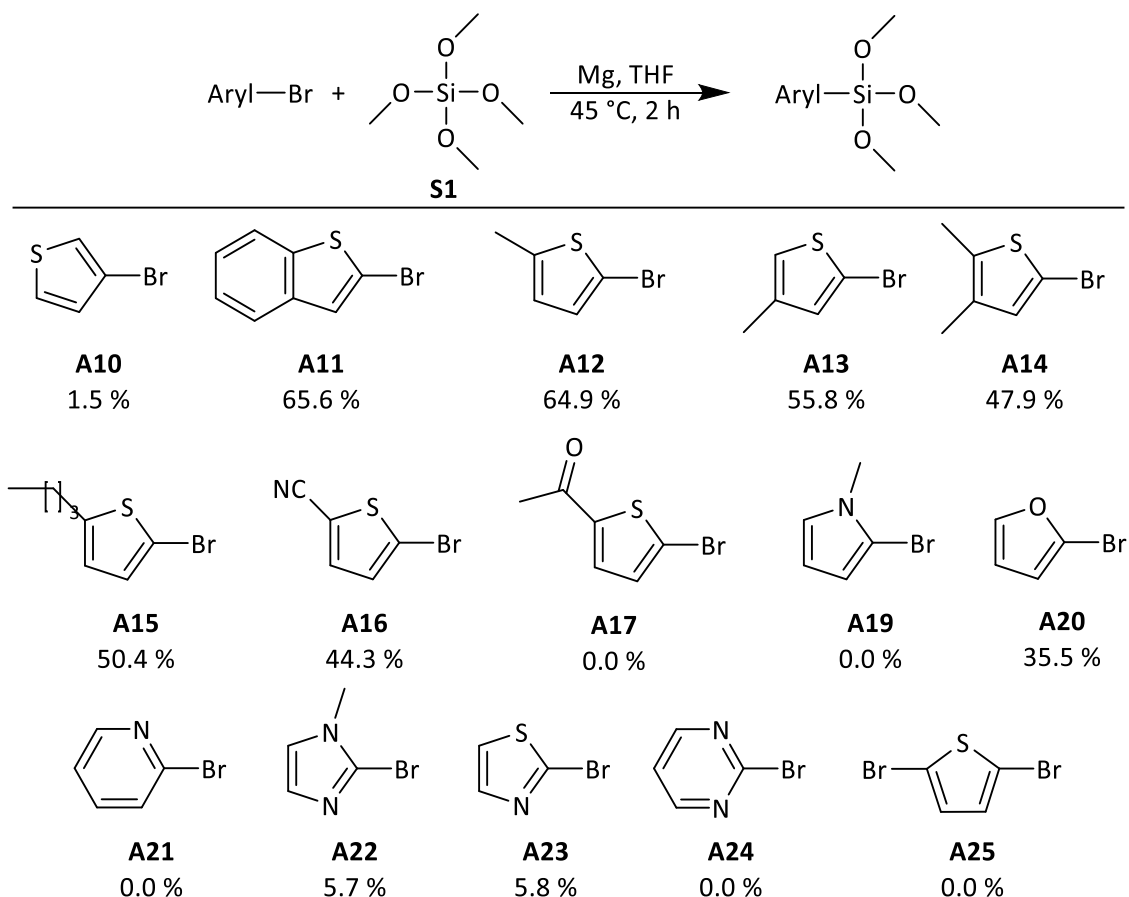
Scheme 5: Grignard reaction of **A1** with various silanes displayed below, including their respective yields. The reaction was run with magnesium in THF at 45 °C for 2 h. All yields stated are after workup and isolation for the target silane. Conversions and selectivity are reported in appendix A3.

Initially, the presented reaction was optimised for compound **P1**. Thus, high conversions and purity are expected when applying the optimised procedure to it. Furthermore, a high concentration of potential reactive alkoxides is present on the used tetramethyl orthosilicate, making the reaction statistically more likely. This also increases the chance of multiple substitution of the silane center. As previously elaborated, this was minimized through reaction condition optimisation and choice of substrate addition, suppressing multiple substitution though *in situ* generation of active Grignard species and excess silane used. Next several silane center substitutions were iterated, keeping thiophene and di-alkoxysilane unchanged. Replacing one alkoxy substituent with a non-reactive methyl (**P2**) substituent induces only minor changes to the electronic charge of the silane. However, this modification slightly reduces the conversion, likely due to a decrease in the number of reactive sites available. Similarly, phenyl (**P3**) and vinyl (**P4**) substitution diminish conversions slightly. Contrarily a hydrogen substituent (**P5**) significantly changes the silanes properties. For carbon hydrogen bonds a positive polarization of hydrogen can be expected. Due to the lower electronegativity of silicon (1.8) compared to carbon (2.5) polarization of bonds with hydrogen (2.1) result in a negative polarization of hydrogen, giving them hydride over proton characteristics. Their negative polarization makes them susceptible to attack from Grignard reagents, introducing potential for side reaction. It must be noted

that hydrides readily release hydrogen upon moisture contact, appropriate safety measures must be taken!¹⁴⁸

As there are no reaction rate comparisons between alkoxy and hydrogen substitution on silanes available reaction in accordance with Scheme 5 using **S5** targeting the formation of **P5** was undertaken. The conversion was not successful, resulting in a mixture of signals in NMR, likely resulting from competing reactions between alkoxy and hydrogen and subsequent polymerisation making further workup or analysis not possible. Rerunning the experiment targeting compound **P5** through the same method did not yield other results. Compound **P7** was not found after reaction, rather polymerisation of the silane was observed. This can be explained as methyl methacrylate or related structures have an activated double bond making them susceptible to nucleophilic attack and free-radical polymerisation. The active Grignard species can unintentionally act as free-radical initiators or may directly add to the double bond, leading to the polymerisation of methacrylate, rather than conversion of silane as observed here.¹⁴⁹ Comparing conversions of compound **P1** to compounds **P8** and **P9** a decrease in conversion is observed. This phenomenon can be readily elucidated by the progressive increase in steric bulk and changes in electron density imposed on the silane center by changing from methoxy to ethoxy and iso-propoxy substituents, respectively. This route also allows good access to **P18**, later used in chapter 3. With silane modification completed different substitutions patterns of thiophene and several heterocycles were iterated and proven stable as shown in Scheme 6.

Construction of silicon-carbon bonds towards α -silanes



Scheme 6: Grignard reaction of **S1** with various heteroaryl-bromides displayed below, including their respective yields. The reaction was run with magnesium in THF at 45 °C for 2 h. All yields stated are after workup and isolation for the target silane. Conversions and selectivity are reported in Appendix A3.

Synthesis of compound **P10** was approached through the previously described Grignard route with little success. The isolated compound readily decomposed under argon atmosphere, represented by a change in colour, as well as increasing noise in recorded NMR spectra. This behaviour can be attributed to the previously described beta-silicon effect, where an interaction of anti-binding orbitals leads to the rapid elimination of silane from the compound. While there were indications of desired silane formation found in NMR, decomposition made further analysis challenging. Compounds **P11** to **P17** were obtained from their respective substituted and halogenated thiophenes to the desired structures shown. Conversion differences can be attributed to changes of the electronic situation on the silane caused by thiophene substituents. As shown during screening of different halides using iodide rather than bromide substituted heteroaryls, small increases in conversion can be achieved. To aid in comparability of conversion efficiency trials with iodide heteroaryls were excluded from previous overview but included in data shown in the appendix. Again slight increase in conversion was detected, however again the prices for iodide heteroaryls is significantly higher than bromines, as exemplary shown in Table 2. Using heteroaryl halides with different heteroatoms (**A19** to **A24**) yielded the appropriate silanes **P19** to **P24**. The conversions when compared to thiophene derivatives are

diminished as shown in Scheme 6. However, where possible the silanes were fully worked up and characterised as they are described for the first time. The reduced conversions can be rationalized due to the changed electronic nature present in the heteroaryls, thus likely behaving differently than thiophene derivatives, for which the used procedure had been optimised. **P20** readily decomposes after NMR measurement, likely decomposition products are hydrolysis derivatives of the compound, appropriate spectra are presented in Appendix A4. This indicates high reactivity of this silane!

Compound **P25** was synthesised in a comparable process to all earlier compounds reported, equivalents of substrates were adjusted. Compound **P25** was isolated at reduced conversions when compared to synthesis of compound **P1**. As no other side reaction products were detected the synthesis was run for 72 h. While overall structure is comparable, electronic differences on the heteroaryl, as well as added steric bulk reduce the overall efficiency of the reaction. An exemplary characterisation by proton (^1H) and inverse gated silicone (^{29}Si -IG) nuclear magnetic resonance (NMR) spectroscopy with tailored NMR experiment is described in the following paragraph. The resulting spectra of all synthesised and described compounds were recorded and analysed by the same method. Their respective shifts and couplings are reported in appendix A3. All five membered mono-heteroaryls bare three hydrogen signals, each related to one proton on the heteroaryl. Due to the change from halogen to alkoxy silane substituent a shift in these signals is most notable and may be used for quick identification of reaction progress. All other present proton signals, such as substituents on the heteroaryl or alkoxy silane are present, but do not show significant changes during synthesis. It is known that electron rich aromatic systems such as heteroaryls increase the relaxation times of protons. Allowing for longer relaxation delays between measurements can solve this, however, short time between scans increases throughout. If the relaxation delay and respective excitations are chosen too short, protons cannot relax into the ground state before the next excitation takes place. When integrating such signals, they do not correlate linearly to the proton's concentration, showing a value smaller than present in the sample. Below a stack of two spectra of the same sample of compound **P2** at 2 seconds and 10 seconds is shown (Figure 20). As the sample had previously been distilled only signals related to **P2** are expected. With five distinct signals detected (three signals from thiophene, one from methoxy and one from methyl) the compounds appear pure. However, the observed signals are not integers. In cases where not all thiophene protons achieve full relaxation within shorter delays, comparing their integrations directly with methoxy signals provides a useful benchmark. However, heterogeneous relaxation among thiophene protons can complicate this comparison. By separately evaluating the integration of individual thiophene signals and using methoxy protons as a stable reference, deviations for specific thiophene protons at 2 second between scans were observed, which are corrected in spectra with 10 seconds between scans. Thus, not all thiophene protons were able to relax after two seconds. These findings validate the necessity for 10 seconds wait time between scans

for electron-rich aromatic systems to ensure accurate and consistent integration. All subsequent measurements of compounds in this work have thus been measured at 10 seconds. In all spectra, the signals related to protons 1 and 3 display consistent coupling with proton 2, resulting in identical hyperfine structure but distinct chemical shifts attributable to differences in their chemical environment. Signals 7.65 ppm and 7.30 ppm can be assigned to protons 1 and 3. Proton 2 exhibits coupling and appropriate hyperfine structure to both proton 1 and 3, resulting in signals around 7.45 ppm. The ratio of thiophene proton to methoxy protons 4 is 1 : 6, as the three protons in each methoxy group are chemically equivalent and the methoxy groups are magnetically equivalent, showing a singlet at 3.60 ppm in the absence of any nearby coupling partners. A second signal at 3.55 ppm is observed in some spectra due to residual methanol that is cleaved during the compound distillation process if small amounts of moisture enter the apparatus at low vacuum.

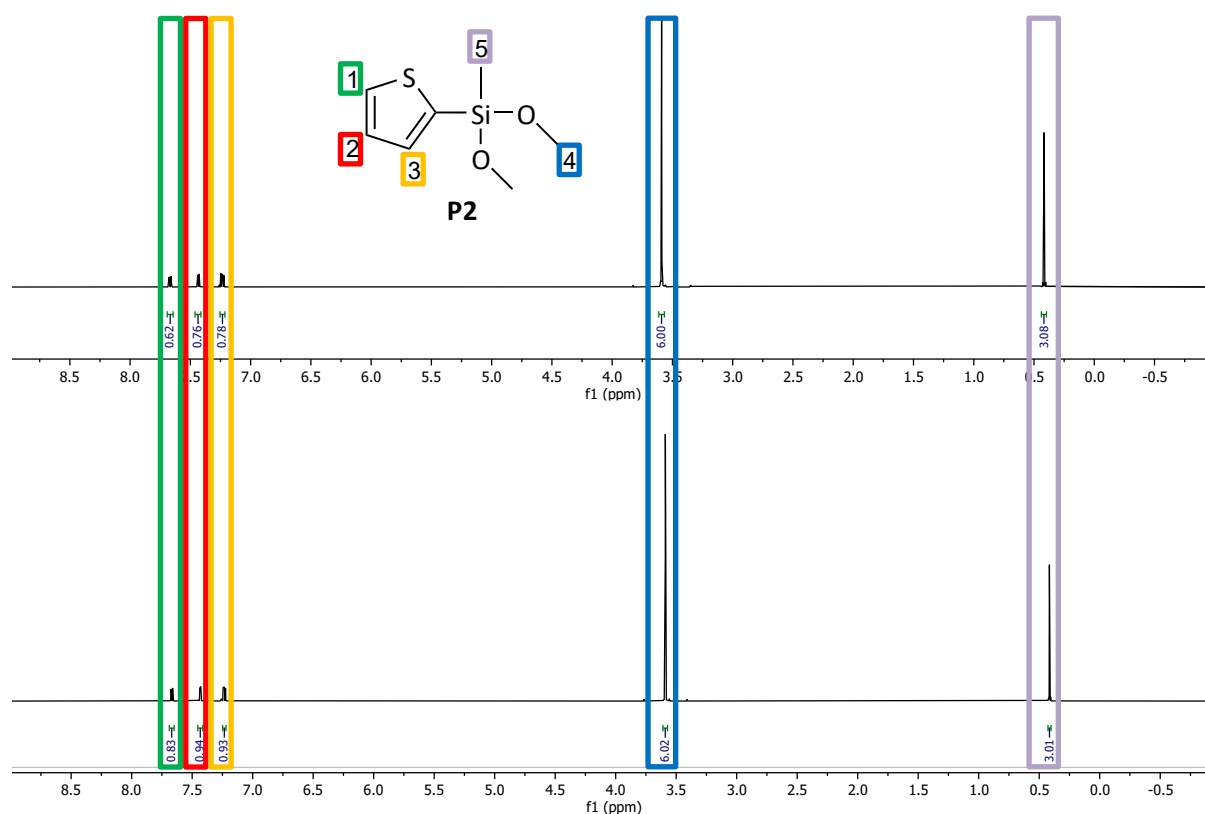


Figure 20: ^1H -NMR spectra stack of compound **P2** showing changes in relative integration between two seconds (top) and ten seconds (bottom) delay time between scans. Signal to proton correlation are illustrated through coloured contours.

The study was performed to explore the synthesis and reactivity of a number of silane compounds and in particular how structural changes impact reactivity and conversion rates of silanes in the range. Optimisation for compound **P1** was successful, but significant challenges met with the subsequent compounds, especially when dealing with sterically hindered or electronically different substituents on the silane centre. The study requires careful consideration of substituents on the silane compounds and their probable interaction with Grignard reagents. It remains for further work to find ways to avoid these reactivity problems with different reaction conditions, reagents or protective groups that hinder

polymerisation of the unwanted product to stabilize the intermediate or final products for analysis and use. It must be noted that the straightforward ability of Grignard reactions to use alkoxides as reactant groups allows for high degrees of functionalisation on silanes not accessible through many other chemical conversion processes! This concludes the first of two synthesis pathways of this thesis targeting α -silane. The initially presented flow chart is thus further completed, the chart is shown below in Figure 21.

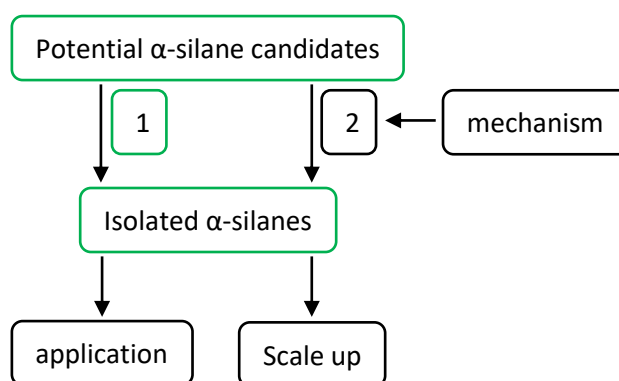


Figure 21: Flow chart presenting the general structure of this thesis, with the first of two synthesis routes completed.

2.5 Catalytic carbon-silicon bond formation

Catalytic bond formation is fundamental in modern synthetic chemistry. Catalysis can address environmental, economic and chemical challenges. By transforming stoichiometric conversions into catalytic processes, a general positive environmental impact can be achieved by reducing the amount of generated waste and lowering the required process heat. Catalysts can enable atom efficient transformations, potentially reducing the overall ecological footprint of the resulting compounds through improved resource utilization.¹⁵⁰ Economic benefits can be gained by running reactions at higher conversions and milder conditions. Streamlining synthesis, reducing energy consumption and allowing the use of less expensive substrates making the involved processes more cost effective.¹⁵¹ Catalysis offers greater chemical control and selectivity during the reaction, opening synthetic opportunities with increased efficiency or new strategies to previously inaccessible materials.^{150,151} The previous chapter (Chapter 2.4) described the synthesis of novel heteroaryl-silanes using Grignard-type chemistry. Earlier, Chapter 2.2 presented different strategies for generating the target silanes discussed in this work, concluding that carbon-silicon cross-coupling provides an efficient route to highly functional silanes, while also addressing the advantages and disadvantages of each approach. Building on these findings, this chapter examines the conversion of existing silanes into novel heteroaryl-substituted silanes by means of palladium-assisted carbon-silicon cross-coupling reactions. Because commercially relevant silanes often have limited functionalisation, the palladium-catalysed

methodology was selected for its high atom efficiency, favourable conversions, and compatibility with multiple silane substitutions, despite the added cost of using a palladium catalyst.

This chapter describes a second approach to constructing the α -silanes introduced in this work (complementary to the method discussed in Chapter 2.4). The formation of the target silanes via palladium-catalysed carbon–silicon cross-coupling is outlined, followed by reaction-condition optimization and an overview of the scope of the optimized reaction for the silanes disclosed in Chapter 2.3. The underlying catalytic mechanism is also investigated. To ensure consistent comparisons among experiments, the concentration of each parameter was calculated in moles per gram rather than by weight ratio. Moreover, every experiment was performed at least twice to rule out outliers and confirm reproducibility. Individual conversion values are reported in Appendix A3, while the conversions featured in this chapter represent arithmetic means to enhance clarity.

2.5.1 Feasibility of catalytic carbon-silicon bond formation

For a first feasibility study the approach reported by Murata *et al.*⁹⁹ was chosen. Here an iodine functionalised aryl is coupled to an alkoxy- hydridosilane using a palladium catalyst with a tris(2-methylphenyl)phosphane ($P(o\text{-tol})_3$) ligand in an amide solvent. The use of amide solvent is deemed essential as it was reported to significantly boost yields from 6 % when using toluene or 31 % when using dimethyl sulfoxide (DMSO) to 70 % when using N-methyl-2-pyrrolidone (NMP). Furthermore, they reported two competing reactions where either the cross-coupling product or the hydrogenated aryl is formed. Where instead of the cross-coupling proceeding between carbon and silicon, a hydride transfer from the silane to used aryl is observed, resulting also in the formation of hydrogenated aryl halide (Figure 22). Optimisation must be undertaken for the reaction at hand to preferably form the desired cross coupling product **P1**, while suppressing the formation of substitution between reactants. Previously, suggestions to the mechanism have been made^{72,99,152} but no mechanistic investigations have been reported. The reaction setup and all following reaction setups for catalytic carbon-silicon bond formation were performed under strict exclusion of air. All substrates, complexes, ligands, bases and solvents were thoroughly dried. Solids were weighted in an argon filled glove box and liquids were handled using common Schlenk or purging techniques with dry argon.

Construction of silicon-carbon bonds towards α -silanes

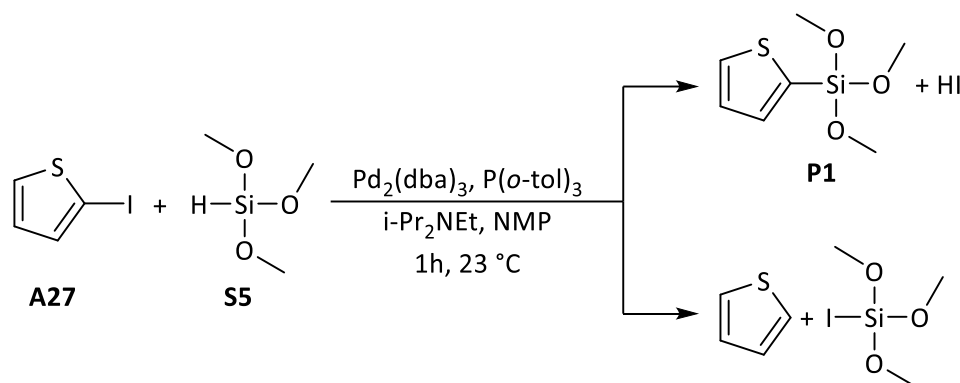


Figure 22: Competing reaction products during the palladium catalysed carbon-silicon cross coupling between 2-bromothiophene and trimethoxysilane. Formed products can be the intended cross coupling product **P1** and cleaved hydrogen bromide or the undesirable substitution of halide with hydride. Reaction was run with tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) as precursor, tri(*o*-tolyl) phosphine ($\text{P}(o\text{-tol})_3$) as ligand, N,N-diisopropylethylamine ($i\text{-Pr}_2\text{NEt}$) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 1 h at 23 °C.

The reaction shown in Figure 22 was run following the method reported by Murata *et al.*⁹⁹ and 65.1 % conversion of **A27** at a selectivity of 68 : 32 for the target silane **P1** was recorded. The analysis gathered shows the same formation of target silane **P1** as well as hydrogenated aryl as a side product as indicated by the referenced method, for a detailed description and results see Appendix A3. With these results the method was identified as promising but needs further optimisation for the catalytic formation of heteroaryl-silanes as investigated in this work.

The use of palladium in conjunction with a phosphine ligand has been commonly used over the last years for carbon-carbon cross-coupling. However, as previously shown the literature examples using it in carbon-silicon cross coupling are sparse. The need for an amide solvent is uncommon in such chemistry but as a significant boost in yield was shown an interaction with the catalyst either molecularly or by polarity is likely.¹⁵³

When working with either tri- or tetra-alkoxysilanes their respective toxicity must be noted.¹⁵⁴ Both silane compounds are marked with bare GHS sentence H330: "lethal if inhaled". When working with these substances appropriate protective equipment and measures must be in place. This is especially relevant when working on large scale with these compounds as described in section 3.5 in this work. Additionally, trialkoxysilanes bear a silicon hydrogen bond, which, when in contact with water reacts to alkoxy silanols, releasing one equivalent of hydrogen gas in the process.¹⁴⁶ It must be noted that the ignitable range of hydrogen air mixtures is broad, from 4 % to 75 % hydrogen in air, working below 4 % hydrogen concentration at any point must be assured through working at moisture free conditions elaborated above. Additionally, explosion protection measures such as inert gas atmosphere together with electric hydrogen sensors must be in place.¹⁵⁵

2.5.2 Optimisation of catalytic carbon-silicon bond formation

The work presented in chapter 2.5.1 has confirmed the potential application of palladium-based complexes in sp^2 -carbon-silane cross coupling the system is optimised iteratively with compound **P8** as a model structure. Potential influences such as substrates, ligands and solvents were investigated. Due to the toxicity differences comparing trimethoxy and triethoxysilane optimisation of the reaction was conducted with triethoxysilane as a model substrate, resulting in an optimisation of the reaction for compound **P8** over optimising for compound **P1** when compared to chapter 2.4.¹⁵⁴

The concentration of all changed parameters was calculated in mol per gram to guarantee comparability between all experiments rather than using a constant weight ratio. Additionally, all experiments in this chapter were run with minimum one repetition to exclude any outliers and confirm reproducibility of the shown results. The individual conversions are reported in appendix A3 while the conversions shown in this chapter are arithmetic means from all experiments to aid readability, while the majority of standard deviations is below 10 %, giving good reproducibility of the experiments.

The influence of halide was shown for the stoichiometric formation of the target compounds through Grignard reagents, appropriately halide screening was undertaken for this reaction. The same set of commercially available 2-halothiophenes was screened and presented in Figure 23.

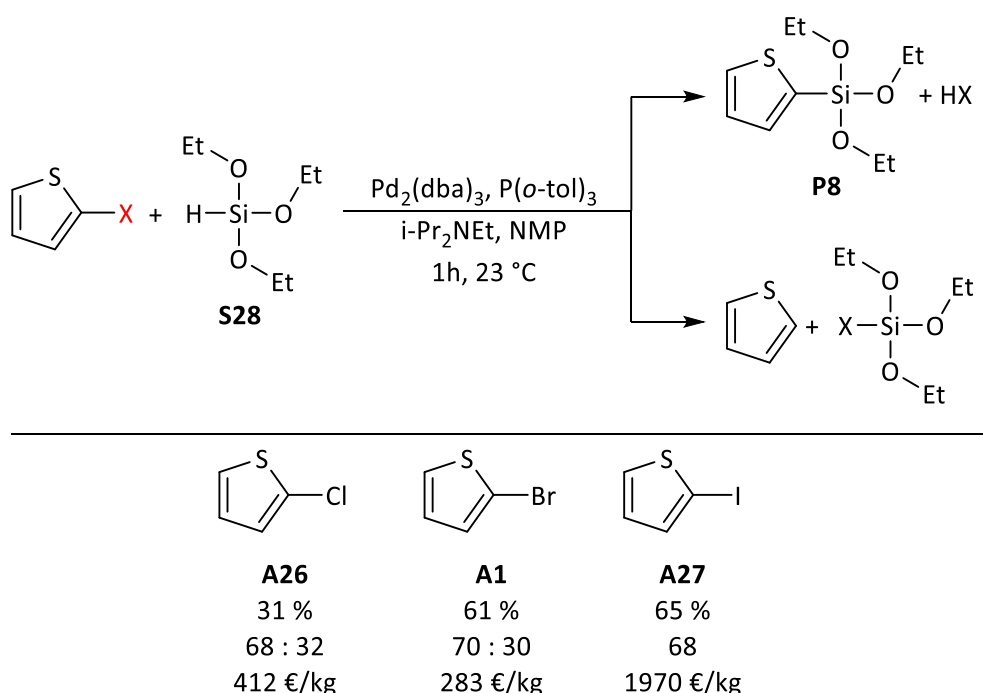


Figure 23: Catalytic carbon silicon cross coupling of different 2-halothiophenes with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) as precursor, tri(*o*-tolyl) phosphine ($P(o\text{-tol})_3$) as ligand, N,N-diisopropylethylamine (*i*- Pr_2NEt) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 1 hour at 23 °C. Recording the resulting conversions of 2-halothiophenes, selectivity for triethoxy(thiophen-2-yl)silane **P8** and the cost of used 2-halothiophene as of 09.05.2024 from "www.fishersci.de".

Chloro, bromo and iodo substitutions were chosen because fluoride-carbon bonds show significantly less reactivity than all other halogen-carbon bonds, making them less suitable for this application. Due to astatine's radioactive nature it does not find significant synthetic application.¹⁵⁶ Comparing the conversions and selectivity for the desired structure **P8** shown in Figure 23 it is evident that thiophenes substituted with bromide **A1** and iodide **A27** are superior to chloride **A26**. While pricing of chloride and bromide substituted thiophene is comparable, a significant increase in price is noted for iodide. This makes using bromo substituted substrates such as **A1** the ideal choice for high yield and low-cost synthesis. Iodides may be used as fallback in case low conversions are reached. Reports by Seyferth¹⁴³ support these findings, highlighting the trend of increased reactivity for ethylene halide with increasing molecular weight of the halide, chlorides reaching significantly less conversion than bromides and iodides.

Commercially relevant palladium sources contain palladium either in an atomically activated form as single atom or in complexes in either oxidation state zero or two. Alternatively, palladium zero is also available as elemental clusters on active carbon or silica, as well as palladium oxide. The usage of the required palladium phosphine complexes unfortunately is not possible for all phosphine ligands as these complexes commonly are highly air sensitive.

As an alternative more stable active palladium precursors are used which form the desired palladium complex *in situ*. Palladium sources reported herein were screened in Table 16, using 2-bromothiophene and triethoxysilane as substrates in N-methylpyrrolidone (NMP) and (2-biphenyl)di-tert-butylphosphine (JohnPhos) as phosphine ligand, with N,N-diisopropylethylamine (DIPEA) as base. The reaction mixtures were worked up and yields calculated from ¹H- and ²⁹Si-IG-NMR. A selection of palladium precursors was screened as shown in Figure 24.

Construction of silicon-carbon bonds towards α -silanes

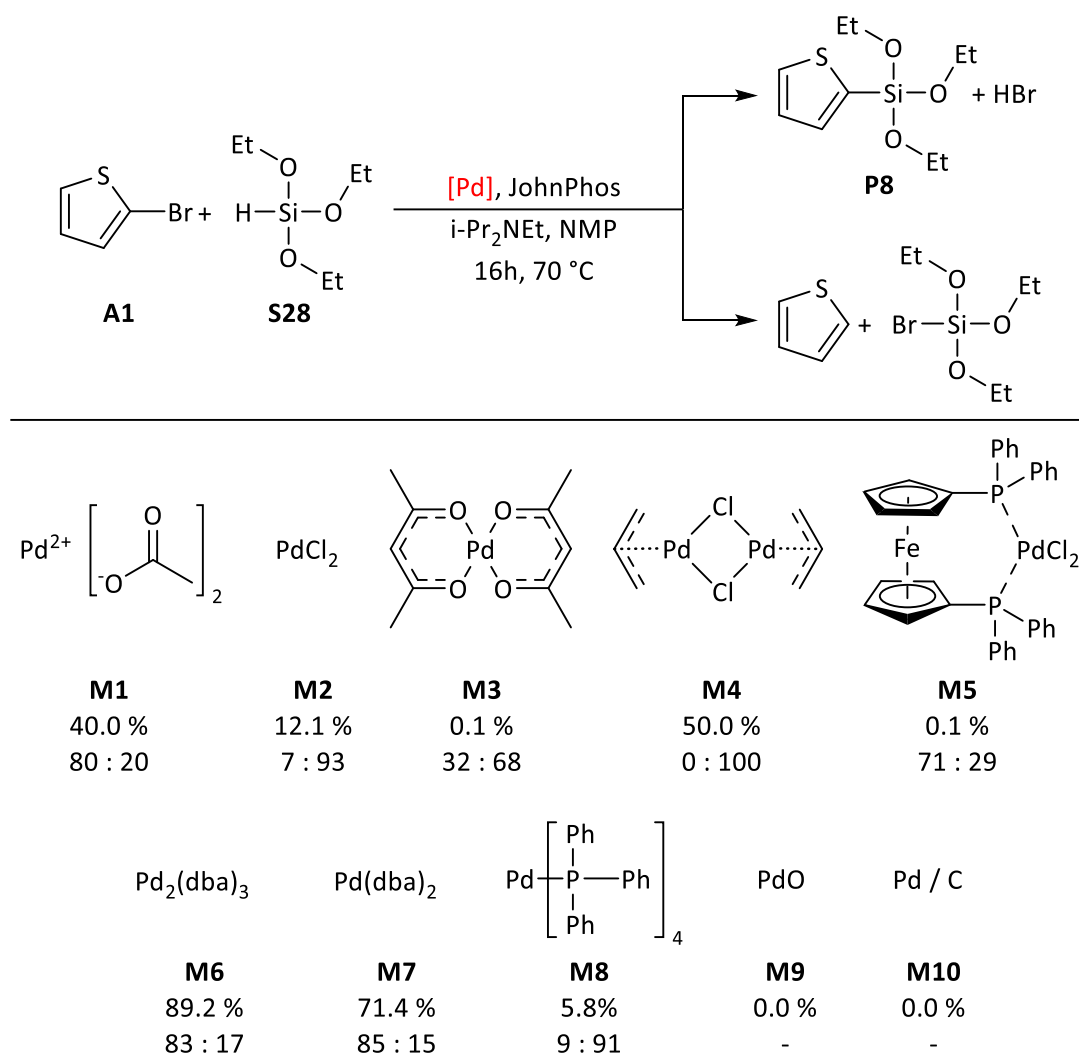


Figure 24: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride.

Reaction was run with various palladium precursors, (2-biphenyl)-di-*tert*-butylphosphine (JohnPhos) as ligand, N,N-diisopropylethylamine (*i*-Pr₂NEt) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.

The formation of the desired palladium complex is not only observed through analysis but also visible during the reaction, indicated by a colour change from yellow liquid and black and white solids to a clear, bright yellow to orange solution in the reaction flask. While the used palladium precursors in oxidation state zero show decent yield for the reaction at hand the yield is diminished when using palladium in oxidation state two. This may indicate the formation of the active complex in the catalytic cycle which is only possible in correct oxidation state. Additionally, an *in situ* formed dormant state is formed from the precursor, only forming from one oxidation state. The yield difference between Pd₂(dba)₃ and Pd(dba)₂ may be rationalized by absolute mass differences. The used amount of precursor for all shown yields was calculated for the mols palladium present in the compound, resulting in a lower weight of Pd₂(dba)₃ if during the complex formation process both palladium centres are not equally accessible. The amount of usable palladium may be diminished, potentially resulting in

lower yields during the same reaction time. Both clustered palladium sources did not form any desired catalyst and thus no yield is reported, indicated by analysis. Furthermore, no characteristic colour change to bright yellow orange was observed during the reaction. These findings hint that readily soluble palladium precursors are required to generate the intermediate complex present in the actual reaction. While Zaleskiy *et al.*¹⁵⁷ stated the potential involvement of palladium nanoparticles sourced from partially decomposed $\text{Pd}_2(\text{dba})_3$ the above findings suggest that such interactions can be ruled out due to the inefficiency of using common palladium nanoparticle sources such as Pd / C .^{158,159}

The silanes developed in this work are interesting not only from an academic but also commercial perspective for their properties. To aid potential upscale of the synthesis methods presented here factors such as cost must be taken into account as early as possible, e.g. as during screening of cost intensive palladium precursors. All costs already saved here do not need to be offset later through further optimisation. There are commercially available palladium precursors from which the eight most economic were screened for potential application in the investigated reaction. The price per palladium atom is calculated from the price of a sample, divided by its weight. Then multiplied by the compound's molecular weight, as stated in Table 5. The result is divided by the count of palladium atoms present in the compound, adjusting to the actual price per palladium atom. This results in $\text{€} / \text{mol Pd}$. When assuming all precursors can be used at similar molar loadings lower cost per mol palladium ($\text{€} / \text{mol Pd}$) is desirable.

Table 5: Overview of palladium precursor cost per mol palladium. Calculated based on prices fetched from sigmaaldrich.com on 21.01.2022.

Palladium precursor	Cost ($\text{€} / \text{g}$)	Molecular weight (g / mol)	Cost ($\text{€} / \text{mol Pd}$)
M1	125.00	224.51	28,063
M2	143.00	177.33	25,358
M3	61.50	304.64	18,735
M4	121.00	365.89	22,136
M5	87.70	731.71	64,170
M6	83.80	915.72	38,368
M7	61.00	575.00	35,075
M8	49.00	1155.56	56,622
M9	181.00	122.42	22,158
M10 (10 wt%)	52.00	106.42	-

A comparison of palladium precursors must be made based on a cost per mol palladium, as for all comparison/screening experiments the used amount of precursor was calculated on palladium equivalents level. Prices per palladium in this limited overview range from 18,735 $\text{€} / \text{mol Pd}$ to 64,170 $\text{€} / \text{mol Pd}$. Noteworthy is the small difference between $\text{Pd}_2(\text{dba})_3$ and $\text{Pd}(\text{dba})_2$ when comparing price per palladium. Furthermore, seemingly cheap compounds such as $\text{Pd}(\text{PPh}_3)_4$ are economically less favourable due to their high overall molecular weight.

The image displays four chemical structures of phosphine ligands used in cross-coupling reactions:

- Buchwald ligands:** A general structure showing a biphenyl core. The top phenyl ring has a phosphine group $-P(R^1)_2$ at the 2-position and a substituent R^2 at the 1-position. The bottom phenyl ring has substituents R^3 at the 3-position and R^4 at the 4-position.
- JohnPhos (L1):** A specific Buchwald ligand where the phosphine group is $-P(tBu)_2$ and the biphenyl core is unsubstituted.
- DavePhos (L2):** A specific Buchwald ligand where the phosphine group is $-P(Cy)_2$ and the biphenyl core has a dimethylamino group $-NMe_2$ at the 4-position of the bottom phenyl ring.
- XPhos (L3):** A specific Buchwald ligand where the phosphine group is $-P(Cy)_2$ and the biphenyl core has isopropyl groups $-iPr$ at the 3 and 4 positions of the bottom phenyl ring.

For example, **L3** has a sterically demanding biphenyl backbone which enhances its steric shielding and electron-donating ability. **L1** has bulky tert-butyl substituents which impart high stability and activity in a range of cross-coupling reactions. **L2** has a 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl backbone which provides high reactivity and selectivity in various palladium-catalysed cross-coupling reactions. This class of ligands has found widespread use in a variety of organic reactions, such as

palladium-catalysed cross coupling reactions and hydrogenation. In addition, asymmetric ligands are available allowing not only stereo- but also enantio-selective reactions.^{163–165}

The following ligands were screened in conjunction with the previously established palladium source $\text{Pd}(\text{dba})_2$ **M7**, 2-bromothiophene **A1** and triethoxysilane **S8** as substrates in NMP as solvent. Classic phosphine ligands and Buchwald type ligands were selected for screening, as previously palladium catalysed carbon-silicon cross-coupling has been reported for this class of ligands.⁷² The reaction was again worked up as described before and yields are reported from ^1H - and ^{29}Si -IG-NMR.

Construction of silicon-carbon bonds towards α -silanes

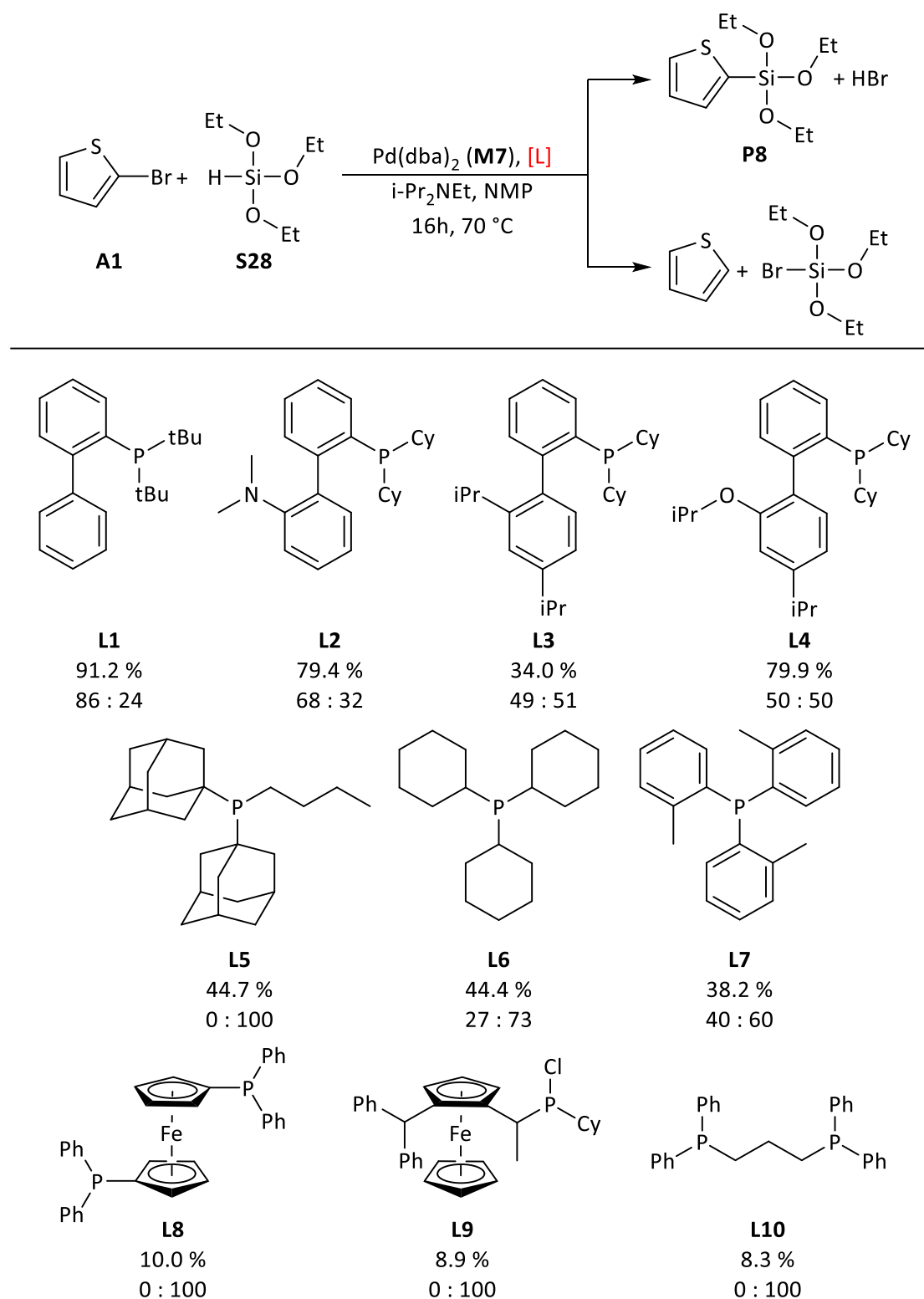


Figure 26: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with various phosphine ligands, **M7** as palladium precursor, N,N-diisopropylethylamine ($i\text{-Pr}_2\text{NEt}$) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(2-thienyl)silane **P8**.

While during the screening of palladium precursors a visual change could be observed when adding the precursors to the solution. This is not the case when screening ligands, as they may result in significantly different colours. Only the presence or absence of solids after initial solvation could be an indication of successful complexation of the palladium precursor. It was observed that without the presence of ligand little to no compound got dissolved and thus likely complexed. Observed differences between experiments compositions were not statistically relevant. Only analysis after the finished reaction measuring concentrations of substrates and product was thus used to determine the successful complexation and conversion of the substrates to the desired product.

From above shown ligands **L1**, **L2** and **L4** show good yield and selectivity for the target product. All three are Buchwald type phosphine ligands. It is thus likely that the underlying biaryl structure plays a critical role in the mechanism of the carbon-silicon cross coupling at hand! To our knowledge no mechanistic investigation on the palladium assisted carbon-silicon cross-coupling of an aryl-halide with a hydride-silane such as presented in the initially phosphines⁹⁹ catalysed publication has been reported before. Accordingly, the mechanism will be subject to investigation in chapter 2.5.3. There are publications on carbon-silicon cross couplings (see 2.2.2) but no reports on the combination aryl-halide with a hydride-silane and no reports involving alkoxy silanes.

Interestingly **L3** performed worse when compared to the other Buchwald ligands. There have been extensive studies comparing common derivatives. In Buchwald-Hartwig¹⁶⁶ Volcano plots of change in free energy and logarithmic rate constants of the reaction an optimum is established from theoretical calculations. The publication hints towards similar behaviour of **L3** and **L2**, though no studies on carbon-silicon cross couplings were made. For different reaction types the comparability is limited. It is likely, that **L3** limits the rate of a relevant reaction process and favours another, thus leading to the observed diminished yields when comparing the two. From this screening **L1** is selected for further optimisation due to its good commercial availability and slightly increased yield over the other well working ligands. **L5**, **L6** and **L7** showed high conversion of **A1**, however the formation of undesired hydrogenated aryl was favoured over the formation of target silane **P1**. This further showcases the importance of Buchwald type ligands in this reaction. Compounds **L8**, **L9** and **L10** showed some conversion of **A1**, but selectively led to the formation of undesired hydrogenated aryl, making them unsuitable for the application.

During the palladium catalysed reaction between halogen substituted heteroaryls and a silane one equivalent hydrogen halide is cleaved as side product. As Brønsted acids can act as hydrolysis catalysts for alkoxy silanes an appropriate base must be in place to quench the side product. Additionally, the base may not release stoichiometric amounts of water when in contact with the acid, as this would introduce significant amounts of moisture into the previously dried reactor, subsequently also hydrolysing the alkoxy silane. Nevertheless, such bases were tried as comparison experiments.

Additionally, arginine as an available basic amino acid was screened. Lastly, basic amines were tested. All used cations were chosen to be potassium limiting the differences in base to the anion, potentially reducing overall complexity of the system. All bases were thoroughly dried before use, solids were heated above the boiling point of water or the decomposition temperature of water of hydration. Liquids were subjected to inert vacuum distillation purifying the compound and removing all residual water in the process. This was confirmed for all used bases through Carl-Fischer titration, having water contents below 10 ppm.

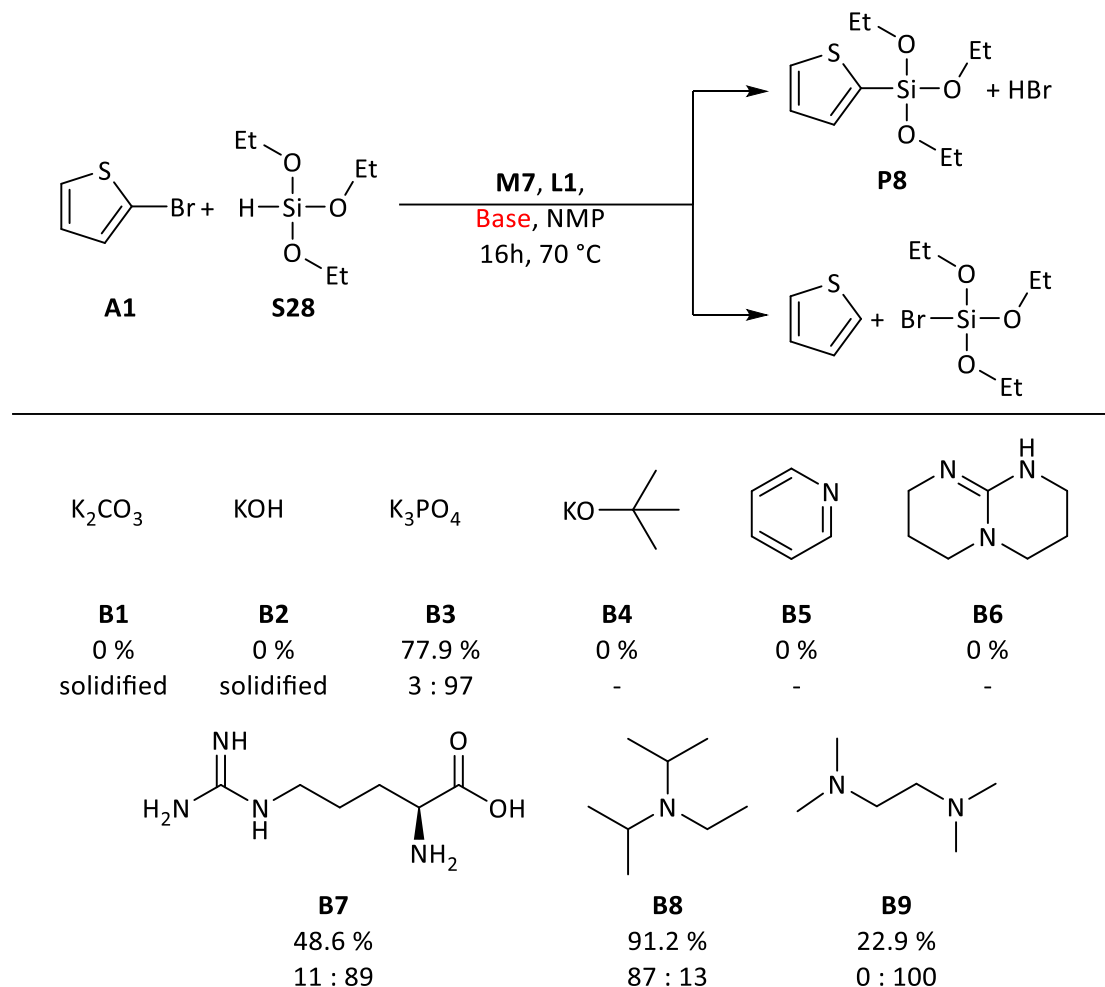


Figure 27: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with various bases, **M7** as palladium precursor, **L1** as ligand in N-methyl-2-pyrrolidone (NMP) as solvent for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.

First inorganic bases **B1** and **B2**, commonly found in synthetic labs, were screened. When in contact with protic acids both potassium carbonate and potassium hydroxide release water. This reflects not only in no yield but also during operation in the solidification of the solution. The release of water hydrolysis the alkoxysilanes, allowing them to undergo their intended reaction not during contact with moisture, but during their *in situ* formation. This forms a three dimensional, cured network in the reactor, destroying the targeted product. No studies on the solubility of **B3** in the used solvent were

conducted or literature known, however, suspended particles were present throughout the reactions progress, indicating little to no solubility. Interestingly it did perform well as a base in the intended application. However, a change in product formation was observed, as mainly the undesired hydrogenated aryl was formed. **B4** was used for its similarity to alkoxy functionalisation on the silane. If interactions of alkoxysilanes with the base were present during the reaction an exchange of methoxy or ethoxy used in the substrate for tert-butoxy was suspected. However, no such exchange, indicated by a shift in tert-butoxy signals in $^1\text{H-NMR}$, was detected. A selection of amine derived bases was screened. **B5** is readily available and potentially usable as a solvent but did not show satisfactory conversions. **B6** like arginine contains a guanidine structure motive. While commonly used for its high basicity no conversion was detected either. Interaction of guanidine with the used catalyst may play a role, when the base acts not only as a hydrogen halide scavenger but interacts with the catalyst itself. Next arginine (**B7**) as a representative basic amino acid containing a guanidine structure motive was screened. **B8** was used during previous optimisations and performed accordingly. The structurally similar **B9** contains two amine centres and is known to act as a ligand for some metal ions.¹⁶⁷ Observed discoloration and lacking yield indicate an interaction of **B9** with the catalyst, leading to an undesirable state and not forming the target product.

As described previously an amide is required in the reaction, with NMP being the most optimal one.⁷² While early publications could only speculate on the nature of its influence, Rudenko *et al.*¹⁶⁸ showed a significant impact of using various amide solvents in the palladium catalysed polymerisation of substituted 2-bromothiophenes. Most notably NMP and N,N-diisopropylformamide showed no polymerisation of the used compounds, suspecting that added bulk of amide solvents is only beneficial to a certain point, from which the palladium centre starts interacting less with the monomers π -system, thus reducing the observed proton activation. This effect might be beneficial in the stabilisation of a palladium thiophene intermediate, allowing a more efficient attack of the used silane. While only known for strictly carbon-based systems, the coordination mode between cyclic and acyclic amides is reported to differ, thus allowing other mechanistic availability of the palladium complex and resulting other mechanistic behaviour.^{168,169} Once an optimal solvent is established the mechanistic behaviour will be investigated in chapter 2.5.3.

Manoso *et al.*⁷² reported the need for an amide-based solvent during carbon-silicon cross couplings. However, they did not provide a conclusive explanation or investigations on why this would be the case. With the above optimised reaction parameters at hand solvent influence on the reaction was investigated. Common commercially available amides used as solvents were screened. The polar aprotic nature of amides allowed for speculation if other solvents with similar properties, such as acetonitrile or dimethyl sulfoxide, may be used instead. Thus, including them in the following screening shown in Figure 28.

Construction of silicon-carbon bonds towards α -silanes

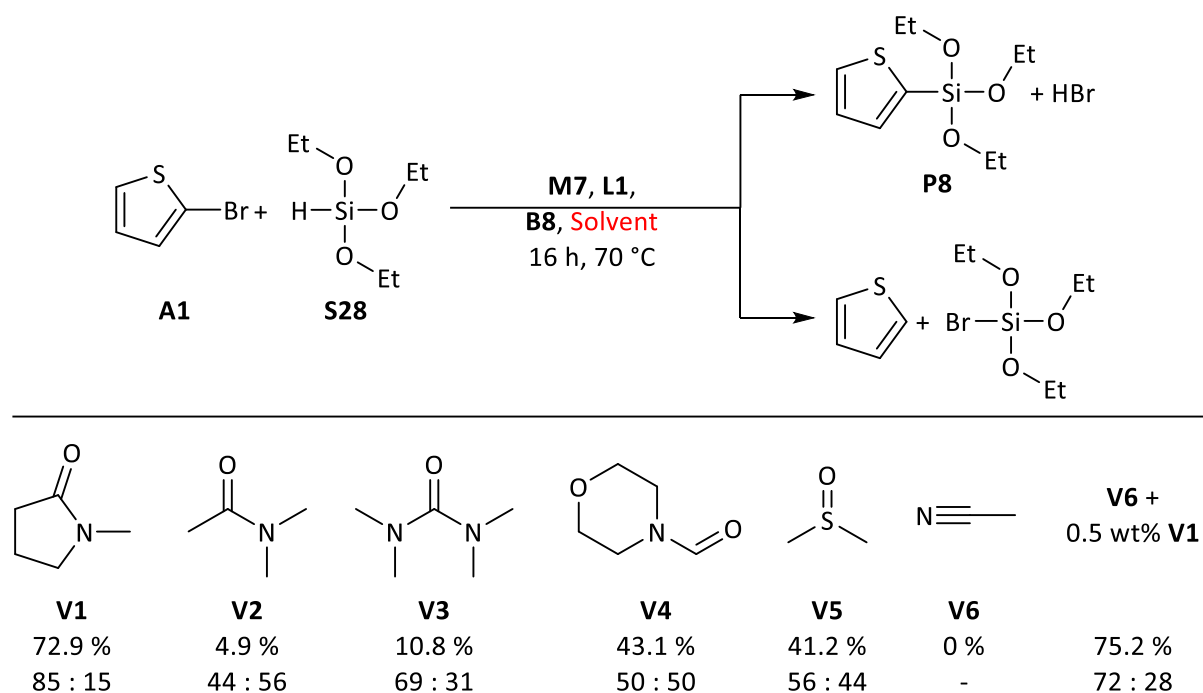


Figure 28: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with various solvents, **M7** as palladium precursor, **L1** as ligand and **B8** as base for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl) silane **P8**.

All previous screening experiments were conducted using **V1** and is listed here for reference. Yield is significantly diminished when using **V3**, residual signals of both substrates are found in the resulting products mixture. Gas release during workup hints towards the residual trimethoxysilane being converted to trimethoxy silanol, while releasing hydrogen gas, confirming the presence of substrate experimentally. **V4** forms the target product at 43.1 %, however, additionally hydration of 2-bromothiophene to thiophene is detected in NMR, while no residual **A1** was found. Combined with the observed change in colour during the reaction from orange to green indicates an interaction with the palladium complex, likely allowing for previously less relevant reaction pathways to take place. When using **V5** formation of 41.2 % product is detected. This finding suggests that strongly polar, aprotic solvents, rather than amide functionality, are crucial for the reaction. The results were supported by ^1H NMR analysis, indicating the desired target structure formed. Previous studies have proposed that the coordination of the solvent to a palladium complex could be achieved using **V5**. In this regard, Diao *et al.*¹⁷⁰ reported that **V5** can coordinate with open coordination spheres of palladium (II), forming complexes that are bound to both oxygen and sulphur. The authors observed changes in ^1H -NMR and IR spectra, with free **V5** at 2.53 ppm, sulphur-bound **V5** at 3.80 - 3.30 ppm, and oxygen-bound **V5** at 3.03 - 2.59 ppm. Interestingly, the degree of **V5** incorporation into the complex was directly related to its concentration, with mono-incorporation being prominent up to 1 eq. and double incorporation at 1.7 eq. This finding aligns with the assumed complexation of **V1** in the reaction,

suggesting that **V5** could replace **V1**. The use of **V5** over **V1** is also preferred due to environmental and health concerns raised by GlaxoSmithKline (GSK).^{170,171}

Acetonitrile (**V6**) was used as a polar aprotic solvent. While it is known that **V6** can coordinate to palladium complexes via its nitrogen atom, no significant interference or facilitation of the reaction mechanism by **V6** was observed under the tested conditions.^{172,173} However, this strong coordination can block critical steps in the catalytic cycle, such as substrate binding, oxidative addition, or trans metalation, potentially explaining the lack of reactivity. While the substrates, precatalyst, ligand and base were well soluble in **V6** under the tested conditions, no conversion of substrates was detected, suggesting that solubility alone does not account for the lack of reactivity. This further suggests that during the carbon-silicon cross-coupling of halogenated heteroaryls and alkoxysilanes the solvent is non-innocent, participating in parts of the reaction mechanism and allowing the desired product to be formed. Further investigations into the mechanism at hand will be shown in chapter 2.5.3 of this work. When assuming **V6** is not interacting with the complexes involved in the reaction, but its polar, aprotic nature is suited for the reaction small amounts of known working solvent may be added to the reaction mixture to form the desired intermediate. As previously mentioned, environmental and health concerns were raised for amide solvent, thus reducing their use while allowing the reaction at hand to still take place is desirable. Accordingly, 0.5 wt% **V1** were added to **V6** while keeping the rest of the reaction setup and workup procedure. From previously no conversion in pure **V6**, addition of catalytic amounts of **V1** conversion of 75.2 % was observed. This strongly indicates the involvement of **V1** during the reaction mechanism as activity of catalyst is not bound to polarity or non protic behaviour of the used solvent, but to the presence of amide solvent. This finding stands in contrast with previous reports⁷² indicating the inexplicable need for amides as solvent. To further elaborate on the likely interaction between solvent and intermediary complexes in the reaction mechanism, studies are described in chapter 2.5.3 of this work.

Compound omission studies were conducted, leaving out the individual reagents, but keeping the overall reaction setup and workup. Both substrates, catalyst precursor and ligand, base and solvent were left out individually.

Table 6: Compound omission study for the carbon silicon cross coupling reaction of 2-bromophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with **M7** as palladium precursor, **L1** as ligand and **B8** as base in **V1** for 16 h at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.

Omitted compound	Conversion of A1 [%]
Reference	91.2
M8	0.0
L1	0.0
B8	0.4
V1	0.0

When leaving out either substrate no product formation is anticipated. When either pre-catalyst or ligand are not present during the reaction, no product formation is observed either. Confirming the need for both palladium as well as the appropriate ligand. Small amounts of product are detected, when leaving out the base during reaction, though over time the reaction mixture solidified. This is likely due to high concentration of hydrogen bromide, acting as hydrolysis catalyst, leading to crosslinking of the silanes. When exposed to moisture the reactive alkoxysilane will react with itself forming three dimensional networks. This indicates some hydrogen bromide can be released from the catalytic intermediate without interfering with the catalytic cycle. When leaving out NMP, as it is used as solvent during the reaction, little to no stirring is possible, likely not mixing the setup thoroughly. Figure 28 showed that using incorrect or non-coordinating solvent no conversion is achieved either. In summary palladium precursor, ligand, base and solvent have been screened for the carbon-silicon cross coupling reaction of halogenated heteroaryls and trialkoxysilanes assisted by a palladium complex system. During these iterations several findings were reported, most noteworthy the previously unknown apparent participation of both base and solvent with the reaction mechanism. With the optimised reaction conditions at hand the intermediates, as well as complexation of substrates, base and solvent is subject of investigation in chapter 2.5.3.

2.5.3 Scope of optimised catalytic carbon-silicon bond formation

This chapter explores the scope of the palladium catalysed carbon-silicon cross-coupling of heteroaryl-halides and alkoxy silanes with the optimised reaction conditions from chapter 2.5.2. A similar approach as in chapter 2.4.3 is followed, here also the reaction conditions had been optimised to give good conversions and selectivity for a selected target silane and then expanding the scope to find the reactions limitations. Due to the unique nature of the silanes used for the palladium catalysed reaction presented in this chapter, only a limited scope of commercially available silanes is available, thus most silanes generated through this route have heteroaryl variations. Previous screening of halides demonstrated that using iodide-substituted heteroaryls instead of bromide ones can result in minor improvements in conversion. To aid in comparison of conversion efficiency, trials involving iodide heteroaryls were not included in the summary but were added to appendix A3. All yields are reported after workup.

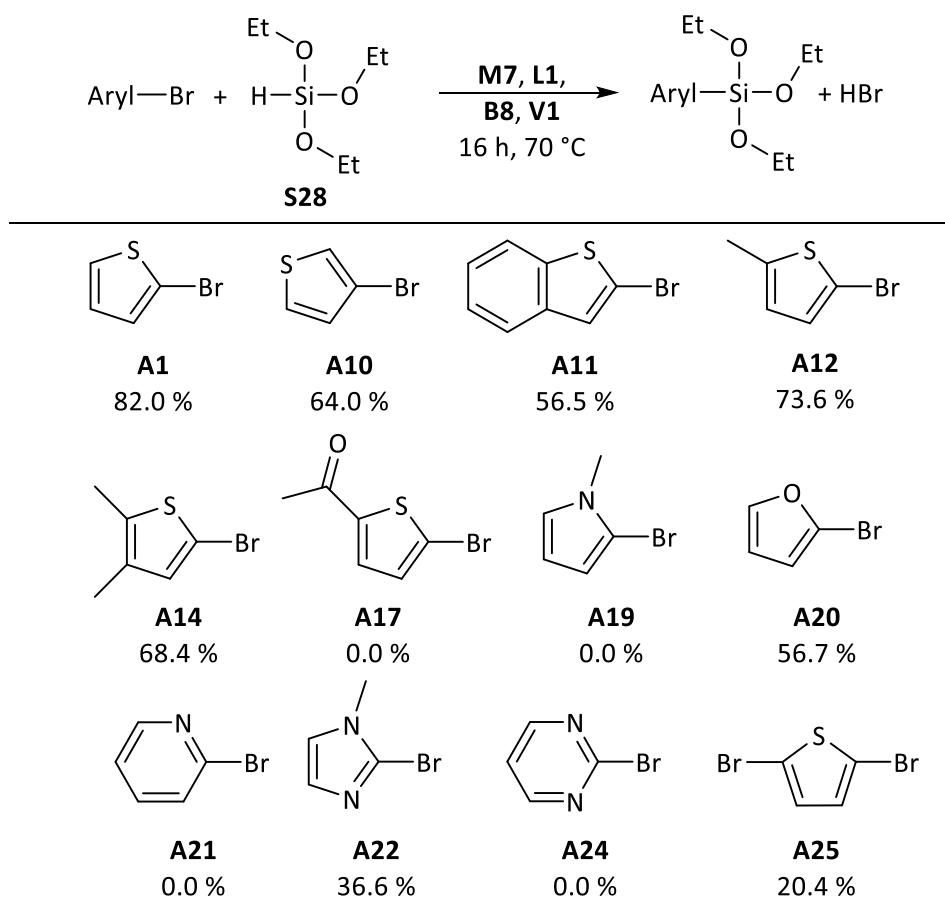


Figure 29: Palladium catalysed carbon-silicon cross-coupling reaction of various aryls with triethoxy silane, including their yields. The reaction was run with M7 (palladium precursor), L1 (Ligand), B8 (Base) and V1 (Solvent) for 16 h at 70 °C. All yields stated are after workup and isolation for the target silane. Conversions and selectivity are reported in Appendix A3.

Due to the limited selection of available hydrogen silanes all experiments were run with triethoxy silane. The formation of target silanes was monitored through NMR. For comparability of all reactions the reaction time and concentrations used were kept constant between all runs. While some reported

yields were diminished in all cases this is due to low conversion of the starting silane, likely due to an optimisation of the reaction for **P1**. This may be increased with longer reaction times. Interestingly for all reactions that formed the target silanes successfully the selectivity of the reaction reported through NMR is for all cases 75 % or higher, indicating a good selectivity between the possible reaction products for the target silane after the reaction had been optimised in 2.5.2. For comparability of all reactions the time and concentrations used were kept constant between all runs. It is evident from the results presented in Figure 29 that the palladium catalysed cross coupling of heteroaryls and silanes is possible, however, limitations may be imposed depending on the substrate used. While steric bulk (**A10-A12**, **A14**) does not impact the reaction significantly changes in heteroatom (**A19**, **A24**) do not lead to the desired cross-coupling product. This is likely to the changed electronic situation on the heteroaryl, leading to the preference of a different reaction pathway. Additional experiments with silanes **S5** and **S29** were run resulting in the formation of **P1** and **P2** (not shown here, see appendix A3). This concludes the second synthesis pathways of this thesis targeting α -silane. The initially presented flow chart is thus further completed, the chart is shown below in Figure 30.

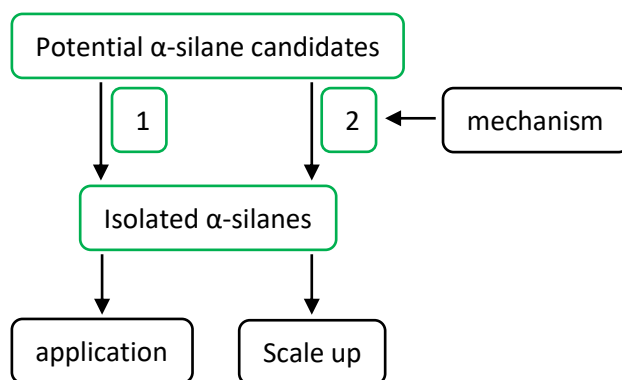


Figure 30: Flow chart presenting the general structure of this thesis, with the second synthesis route completed.

2.5.4 Mechanistic investigation of optimised catalytic carbon-silicon bond formation

Mechanistic investigations were undertaken as there currently are no comprehensive studies using palladium catalysts on siloxane carbon bond formation. Thus, the stepwise addition of catalyst precursors and substrates in optimised solvent is followed by both quantitative ^{31}P -NMR and direct injection electron spray ionisation (ESI) mass spectroscopy. Quantitative NMR at reaction temperature allows the assessment of relative complex concentrations equivalent to their presence in the studied reaction. Identification of catalytically relevant intermediates potentially allows the understanding of reaction mechanism and prediction of currently unknown optimisation potential. To prevent the potential isotopic exchange between substrates and the used deuterated solvent external standards were used, by adding sealed ampules filled with deuterated solvent to an NMR tube. This allows the shimming and locking of the NMR to the sample without contaminating the sample with deuterium.

This eliminates proton deuterium exchange between solvent and substrate, allowing following of potentially transferred hydrides. Due to the moisture sensitivity of the reactants sealed NMR tubes in Youngs style were used. Additionally, reaction solutions can be used directly in NMR and deuterated solvent does not need to be dried and degassed thoroughly before each measurement.^{174,175}

Specialised ^{31}P - ^1H -HMBC were recorded additionally, allowing the correlation and identification of different phosphine containing complex formed. All spectra in this chapter were recorded on an Agilent DD2 600 MHz. Mass spectroscopy allows the identification of intermediates independently of NMR, potentially confirming the presence of postulated intermediates. Direct injection ESI has been chosen as preliminary experiments showed the decomposition or re-equilibration between different intermediates during retention time in the high-pressure liquid chromatography connected upstream of the ESI. Injection in the ESI directly avoids this problem, while adding complexity to the resulting spectra as no separation of compounds before measurements occurs. The isotopic distribution of palladium allows the identification of complexes even without separating the intermediates from each other.¹⁷⁶ Additionally, ESI does not fragment the compounds like electron ionization (EI), further simplifying and defining the compound identification.

With all needed reaction compounds explored and optimised in previous chapters exploration of the reaction mechanism was started. A visual representation of the process is shown in Figure 31. The reaction sequence starts with the addition of **M7** ($\text{Pd}(\text{dba})_2$) and **L1** (JohnPhos) to **V1**, potentially forming the first complex either in NMP or in acetone with one equivalent of NMP as the need for NMP during the reaction was shown in the previous chapters. Addition of both substrates to the first complex is undertaken potentially forming two complex species with the oxidative addition of halo-heteroaryl to palladium agreeing best with literature.¹⁷⁷ If the halo-heteroaryl leads to complexation the complexes crystallisation may be facilitated using silver triflate, through the precipitation of silver halide.¹⁷⁸ Through the addition of base and reductive elimination of the target silane the generation of a new complex or the starting complex is anticipated. Furthermore, the formation of **C1** in acetonitrile (ACN) with stoichiometric amounts of **V1** is explored. Additionally, halide change using silver triflate and addition order of base are explored in the flowchart presented below.

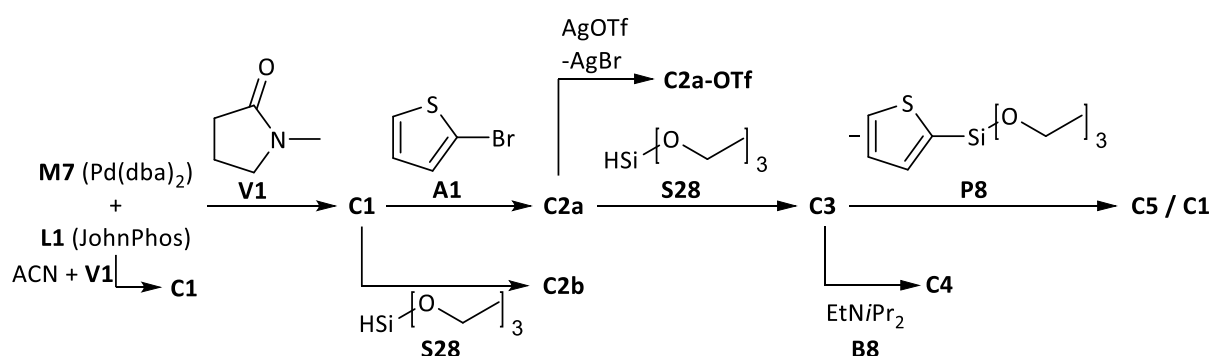


Figure 31: Flowchart of complex isolation steps. Identification and characterisation of each intermediate using NMR.

As previous chapters have shown the need for bis-(dibenzylidenacetone)-palladium(0) and JohnPhos both are mixed in the presence of NMP (as solvent or equimolar to palladium and ligand in acetonitrile), potentially forming the first complex. Figure 32 shows a ^{31}P -NMR stack of 1: $\text{Pd}(\text{dba})_2$ and JohnPhos in NMP; 2: $\text{Pd}(\text{dba})_2$ and JohnPhos in ACN and 1 eq NMP; 3: $\text{Pd}(\text{dba})_2$ and JohnPhos with triethoxysilane in NMP; 4: $\text{Pd}(\text{dba})_2$ and JohnPhos with 2-bromothiophene in NMP. Spectrum (1) shows the addition of $\text{Pd}(\text{dba})_2$ and JohnPhos to NMP.

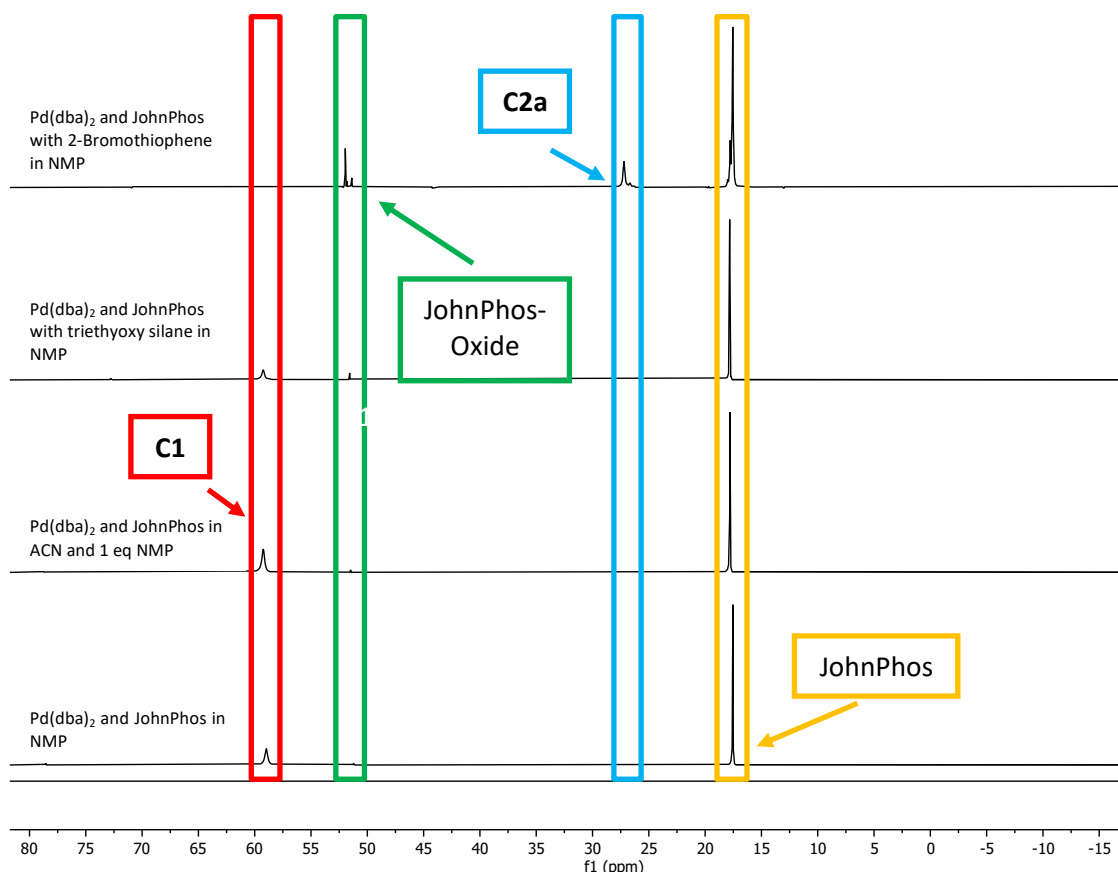


Figure 32: ^{31}P -NMR stack of 1: $\text{Pd}(\text{dba})_2$ and JohnPhos in NMP; $\text{Pd}(\text{dba})_2$ and JohnPhos in ACN and 1 eq NMP; $\text{Pd}(\text{dba})_2$ and JohnPhos with triethoxysilane in NMP; $\text{Pd}(\text{dba})_2$ and JohnPhos with 2-bromothiophene in NMP at reaction temperature.

The used amount of NMP was iteratively determined adding solvent until all compounds are solved and a clear liquid is obtained. Additionally, the solvation was indicated through visual colour change of the reaction mixture. The main signal observed in ^{31}P -NMR at 17.80 ppm closely matches literature known JohnPhos in deuterated chloroform at 18.334 ppm¹⁷⁹, the shift of signal is likely introduced by using nonstandard solvent as described above, slightly changing the chemical environment of the phosphine centre. An additional signal at 58.99 ppm hints towards the formation of a new phosphine species or a phosphine coordinated to palladium, suggesting the formation of a complex, from here on referred to as **C1**[§], a likely structure is shown in Figure 34. The formation of **C1** relative to free

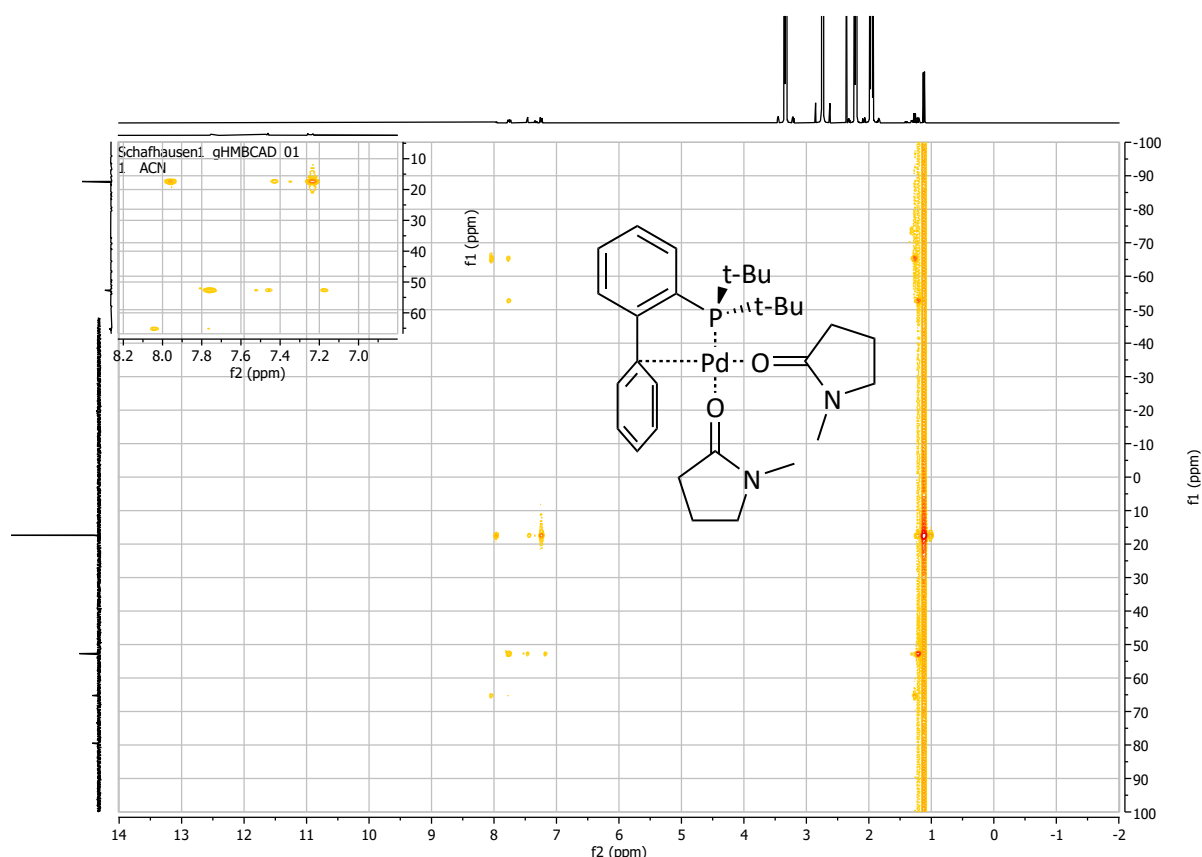
[§] This chapter uses the additional nomenclature **C** to refer to the suggested palladium complexes.

JohnPhos is low, further optimisation of reaction ligand and palladium ratios may resolve this. Alternatively, the use of other non-amide based, polar and aprotic solvents and addition of stoichiometric amounts of amide in relation to the palladium source were studied in spectrum 2 of Figure 32. As similar couplings are observed the formation of the same **C1** is likely, no changes were observed when adding palladium and ligand to pure acetonitrile, again proving the need for amide during the formation of **C1** and contributing to its likely structure. This observation agrees with the report by Scharf *et al.*¹⁸⁰ for CyJohnPhos forming a single palladium species complexed by one phosphine ligand and dba.

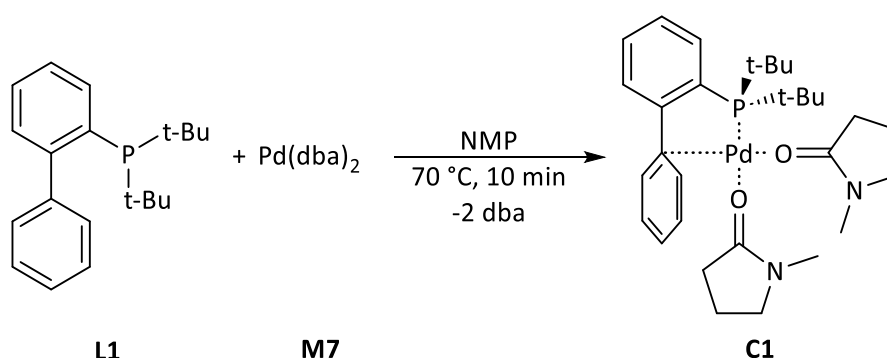
With the spectra of the target complex in hand a second experiment with changed solvent was set up. First both precursors were mixed and then dissolved in acetonitrile. Little to no solubility of the solids was noted and confirmed by NMR, only showing the presence of free JohnPhos in solution. When one equivalent NMP regarding the used precursors is added to the mixture all remaining solids dissolved. The formation of the target complex was confirmed by NMR (spectrum 2, Figure 32), showing the same shift previously reported when NMP was used as a solvent instead. Since the presence of NMP seems essential for the formation of the target complex it must interact with it in some way. This confirms the previous observations by Manoso *et al.*⁷² reporting the need for an amide solvent, as well as the solvent screening previously reported in this work.

To understand the interaction between palladium, ligand and solvent several crystallisation attempts were undertaken using varying counter solvents and temperatures while excluding moisture and air contamination.¹⁸¹ However, no crystals for X-ray measurements could be obtained.

For the identification and characterisation of the proposed complex **C1** 2D-NMR spectra were used (Figure 33). For the identification of free JohnPhos matching signals for both the aryl and alkyl substituents are found in the spectra. Similar signals are observed for the previously reported signal at 58.99 ppm with slightly shifted signals for the tert-butyl group. An additional signal is observed for the aryl system. Recently, complexation of the lower central carbon atom to palladium at 3.6 Å has been reported for CyJohnPhos.¹⁸⁰ Assuming similarity between CyJohnPhos and JohnPhos this signal can be attributed to the known complexation of the lower aryl ring with palladium and resulting symmetrical interaction with the lower aryl ring. The remaining signals are attributed to NMP. Little interaction between NMP and the phosphine is observed. Previously dependence of the formed complex was reported when using the complex substrates in acetonitrile with stoichiometric amounts of NMP. Since little correlation is seen in the ³¹P-¹H-HMBC (Figure 33) the interaction is suspected to be of solvation nature or only very weakly coordinating.

Figure 33: ^{31}P - ^1H -HMBC of **C1** in NMP.

The solution containing **C1** was subjected to direct injection ESI MS, however, no usable spectra were recorded, showing the individual substrates only. This is likely due to high bonding length and low stability of the intermediates, undergoing decomposition during ionization and in vacuum present during MS measurement. With experimental and spectroscopic confirmation for the need of amide during initial complex formation and the findings of Scharf *et al.*¹⁸⁰ a structure for **C1** is suggested in Figure 34, accommodating for both JohnPhos and amide complexation on the palladium centre.

Figure 34: Possible formation of **C1** during between JohnPhos (**L1**) and $\text{Pd}(\text{dba})_2$ (**M7**) in NMP.

To the reaction mixture of **C1** in NMP 2-bromothiophene and triethoxysilane are added separately, expecting the formation of a new complexes **C2a** or **C2b** intermediate with the substrate that reacts first during the catalytic cycle. A stack is presented in Figure 32 and their respective spectra are

presented in Appendix A4. One additional signal could be observed when adding triethoxysilane to **C1** at 51.55 ppm (spectrum 3, Figure 32), this would form **C2b**. The signal corresponds to the literature known JohnPhos-Oxide (52.4 ppm in deuterated chloroform),¹⁸² potentially formed in the mixture from residual oxygen gas dissolved in the substrate. No additional interactions are observed, thus the next complexation step in the catalytic cycle of the reaction at hand must not be the complexation of tri-alkoxysilane, thus **C2b** is not formed. However, when adding 2-bromothiophene to the complex additional signals at 18.13 ppm and 19.27 ppm are observed next to the previously reported signals with reduced intensity compared to before the addition (spectrum 4, Figure 32). Notably, the signal of the proposed **C1** disappears completely, indicating the full conversion of the complex to a newly formed complex, referred to as **C2a**. Additionally, the signal for JohnPhos-oxide at 51.55 ppm increases in intensity too, indicating the oxidation of JohnPhos, again likely from residual oxygen gas dissolved in 2-bromothiophene as it had not been degassed, but only dried prior to all experiments. Figure 32 spectrum 4 shows two additional signals, while one would expect the formation of one new complex if the oxidative addition of 2-bromothiophene is the next step in the catalytic cycle. The two observed signals can be attributed to two possible isomers formed *in situ*, as shown in Figure 35. The near equal intensity in ³¹P-NMR indicates the statistic formation of the two isomers, indicating that no steering effect of the ligand is present during this reaction step. To allow the elimination of the target product the substrates must coordinate in proximity, allowing its elimination. This is only possible when the next addition step is steered by the ligand. The open coordination sphere of the planar **C2a** is partially filled by coordinating the biaryl of JohnPhos, a specific property of Buchwald derived ligands. This has been reported for other substituted Buchwald ligand derivatives by Milner *et al.*¹²⁵ The high yield of Buchwald ligands reported in 2.5.2 for the reaction can thus be rationalized by the observed **C2a** allowing a stabilized but open coordination for the next substates complexation. The addition of base to **C2a** does not result in any change in NMR, thus likely is not interacting with either intermediate.

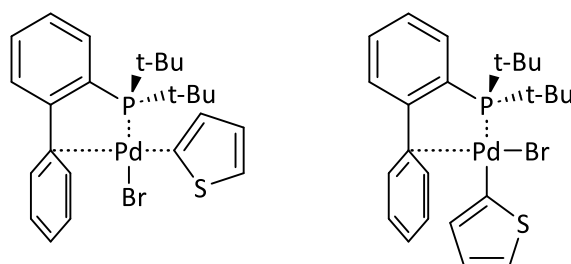


Figure 35: **C2a** isomers after the addition of 2-bromothiophene to a palladium(0)-JohnPhos complex (**C1**) in NMP.

Additionally, ³¹P-1H-HMBC NMR spectra of suspected **C2a** were recorded (Figure 36). The signals attributed to the formation of the two stereoisomers of **C2a** and the unknown signal were investigated. While the concentration of stereoisomers around -20 ppm is low there still is a correlation in the spectrum presented below. The 2-bromothiophene used in excess is well visible at 7.42, 7.26 and

7.06 ppm.¹⁸³ The signal at 7.06 ppm can be attributed to the CH α to the bridging carbon atom and is visible as a coupling in the spectrum shown below, confirming the presence of both phosphine and 2-bromothiophene on the palladium complex and thus the formation of either complex shown in Figure 35. Signals present in the ^{31}P - ^1H -HMBC at -53 ppm are suspected to be artifacts formed through aliasing of signals at 53 ppm.¹⁸⁴ This might have been caused by changing the spectral recording of ^{31}P component in HMBC from +50 - -50 ppm to +100 - -100 ppm.¹⁸⁵ The signals can thus be discarded but are shown here to not withhold this information. Additional signals present stem from **C1** and its formation.

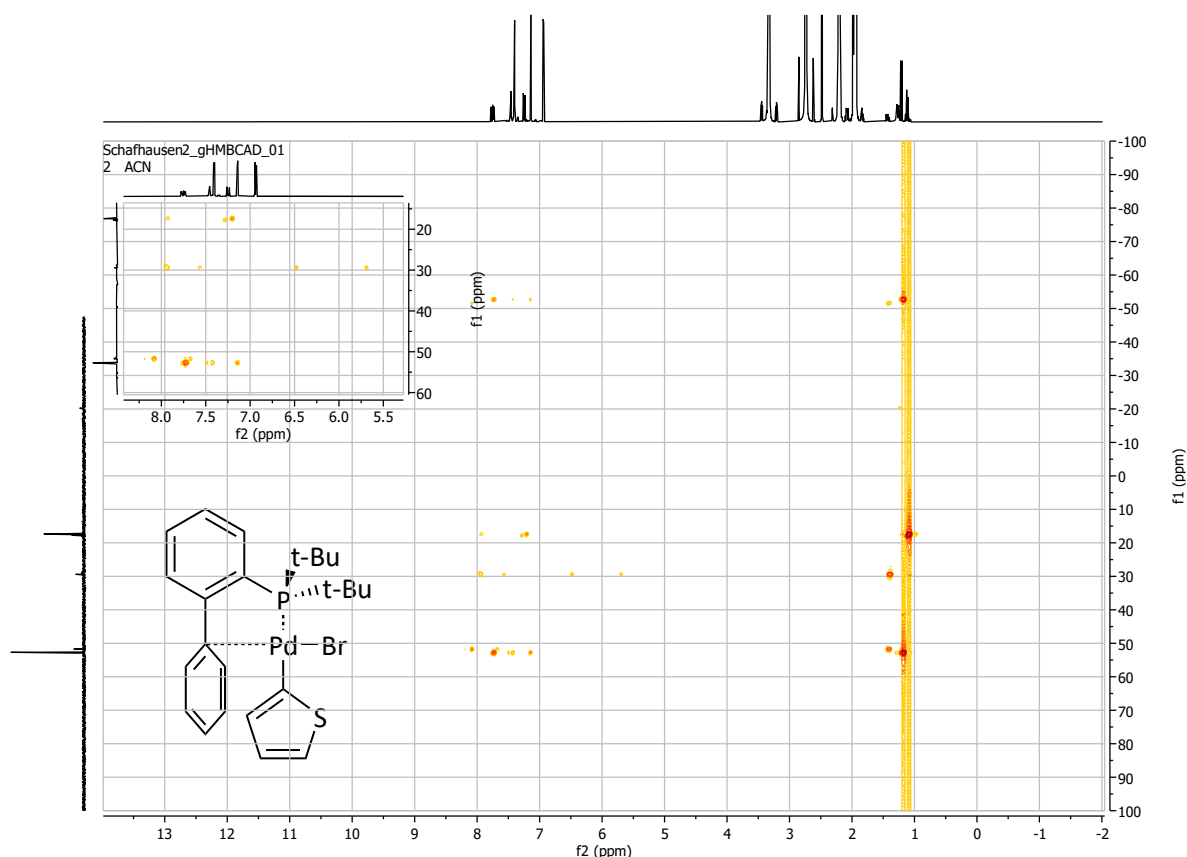


Figure 36: ^{31}P - ^1H -HMBC of **C2a** in NMP.

The formation of new phosphine complexes can be confirmed. Furthermore, the complexation of bromo-thiophene must be the first step in the catalytic cycle, equivalent of an oxidative addition in classic palladium catalysed cross-coupling reactions, further completing the flow chart of Figure 31 and confirming the structural suggestion of Figure 35.

^{31}P - ^1H -HMBC spectra were also recorded for the proposed complex **C3** (Figure 37). The signal observed at 29.38 ppm couples with the bis-aryl and alkyl system of JohnPhos and the protons from used thiophene but also shows two coupling signals with low intensity signals in ^1H -NMR at 5.69 and 6.47 ppm respectively. The signals cannot be attributed to any protons expected from structures thus far. All previously observed signals have been converted to the signal at 29.38 ppm, suggesting either full conversion to the compound or precipitation of a new compound. The latter however can be ruled out

as visual inspection of the sample did not show any precipitate formation. Commonly ^{31}P -NMR spectra are recorded in decoupled mode, suppressing any coupling between phosphorus and hydrogen. While this is beneficial for routine techniques it is not useful in this case. Especially ^1J coupling constants in phosphorus proton coupling are known to be high, such as diethyl phosphonate at $^1\text{J}_{^{31}\text{P},^1\text{H}}=691.3\text{ Hz}$. In 2020 Kahan *et al.*¹⁸⁶ described the formation of a stable palladium complex intermediate where two JohnPhos ligands are protonated, forming a cation and complex to a dimeric halogen containing palladium anion. While they were able to generate crystal structures of this complex similar crystals for the complex at hand could not be obtained. However, a similar behaviour is expected since in both cases JohnPhos is used. Additionally, they reported a chemical shift of 29.8 ppm for the phosphine, matching the observed shift from **C2a**. While the published structure is used as a stable complex in carbon-carbon cross couplings it may be a resting state in the mechanism investigated here, forming a stable intermediate during synthesis.

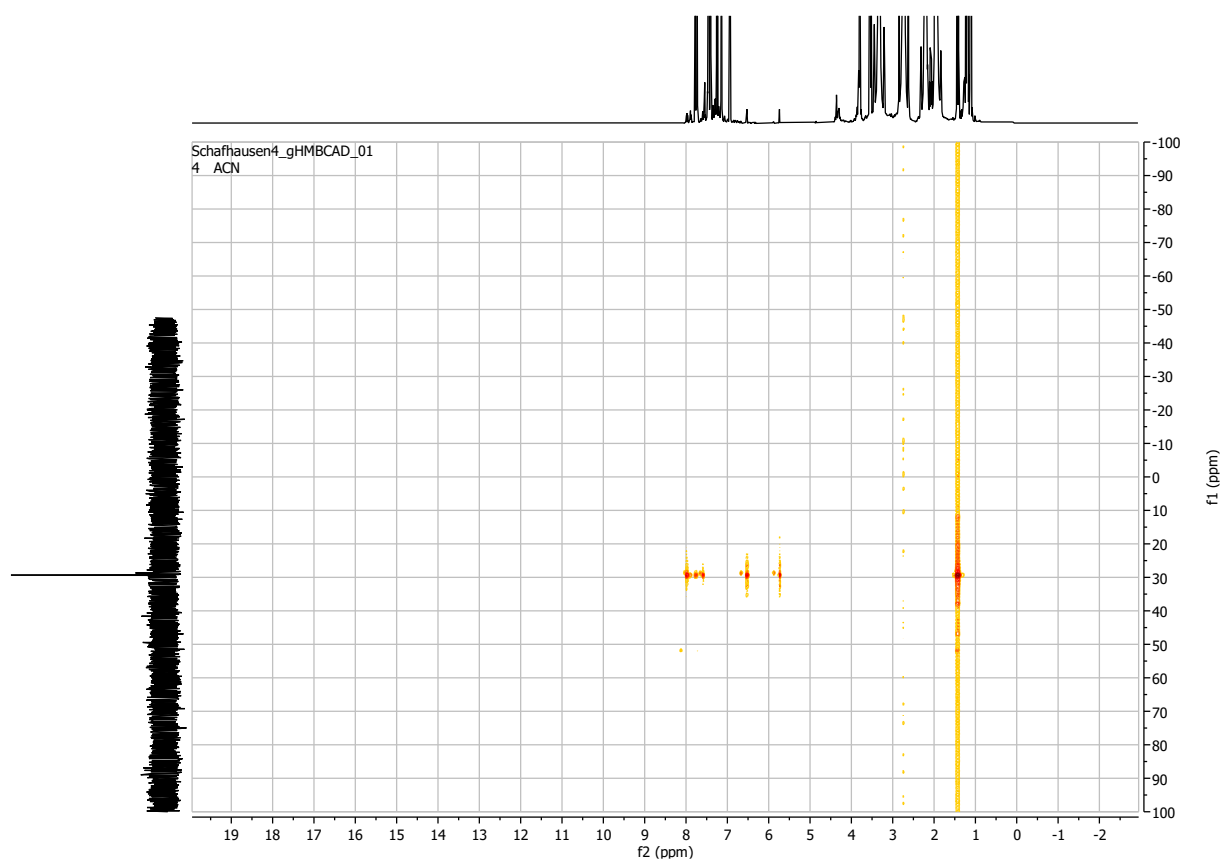


Figure 37: ^{31}P - ^1H -HMBC of **C3** in NMP.

When rerunning the phosphorus spectrum of **C3** in coupled mode, the previously observed singlet at 29.38 ppm split into a doublet, as shown in Figure 38. The coupling constant measured at $J(^{31}\text{P}) = 478\text{ Hz}$. The previously reported signals at 5.69 and 6.47 ppm were recorded at 243 MHz and yielded a $J(^1\text{H}) = 476\text{ Hz}$ coupling. This indicates that likely not two distinct signals are present, but one phosphorus-proton ^1J coupling and appropriately one phosphorus-proton bond. Whether the structure is essential in the mechanism or a byproduct through phosphine protonation due to the lack of base in the

experiment cannot be elucidated. Protonation of Buchwald ligands was reported before and may be the reason for the observed conversion improvement when using Buchwald ligands over other substituted phosphine ligands known to work in palladium-based carbon-carbon cross-couplings, needing this type of Ligand to stabilize the complex through hydrogen transfer. Alternatively, the ligand may shuttle the hydrogen halide away from the active complex, deprotonation in a second step through the interaction with base, similar to the findings by Ivančič *et al.*¹⁸⁷ and Chernyshev *et al.*¹⁸⁸ showing the organometallic nucleophile reformation through a hydrogen halide shuttle. Due to the ambiguous measurements, no definitive resulting structure can be provided.

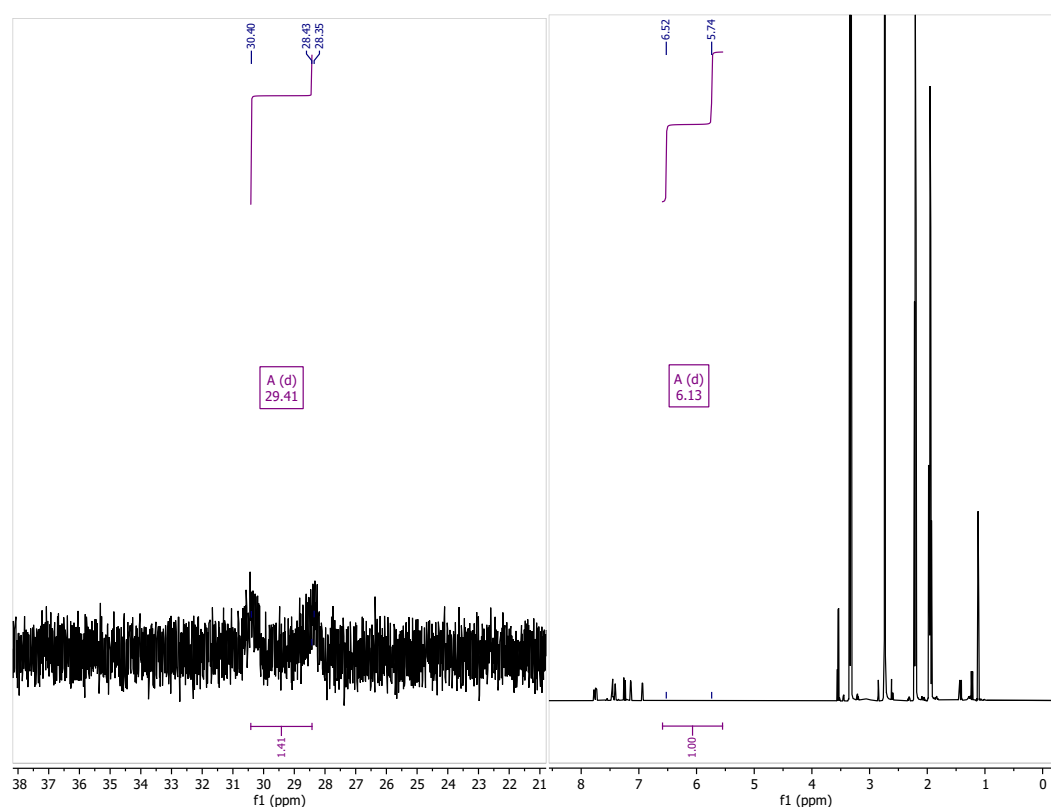


Figure 38: ^{31}P -NMR coupled mode (left) and ^1H NMR (right) of compound III. Each spectrum showing suspected 1J coupling at $J(^{31}\text{P}) = 478$ Hz and $J(^1\text{H}) = 476$ Hz.

With the formation of **C3** as the next catalytic intermediate it is not yet known at which point interaction with base needs to happen. Previous chapters have shown the need for a base during the formation of the target silane. Removal of bromide can either happen after 2-bromothiophene complexation (**C2a**) or during the addition of trialkoxysilane (**C3**). Both complexes were treated with **B8**, potentially forming further complexes (see Figure 31).

No changes can be seen during the addition of DIPEA to **C2a**, suggesting no interaction in the mechanism also, the formation of **C4** can thus be ruled out. Addition of DIPEA to **C3** causes significant changes to the complex and substrates. From the spectrum previously reported distinct signals of **C1** and a significant amount of JohnPhos-oxide can be correlated. Presence of **C1** suggests the regeneration of the initial complex after DIPEA addition to **C3**. This can be rationalized through both

the reductive elimination of the target silane, as well as interaction of base with stoichiometrically formed hydrogen bromide. JohnPhos-oxide again will be formed due to oxygen dissolved in the used substrates. Additionally signals previously attributed to compound **P8** are observed, indicating the release of the target silane. It is thus evident that hydrogen bromide must be fully formed before it can be removed from the catalyst as a reaction byproduct. These spectra unfortunately cannot differentiate if formation of hydrogen bromide or elimination of silane happen consecutively or in parallel. If a complex **C5** is formed during the process, it is too short lived to be detected through NMR. To elaborate on the results and provide additional data through X-ray diffraction analysis, complex crystallization was undertaken. There are various methods for this. All complex intermediates presented here have been subjected to vapor diffusion crystallization with no usable crystals after several attempts and methods such as slow solvent addition (see appendix A3). It is suspected that due to the unique amide interaction of the complex and thus changed solvation the method could not be applied here. Furthermore, due to the presence of bromine in some complex's reaction with silver triflate was run, precipitating highly insoluble silver bromide¹⁷⁸, and changing the counterion from bromide to triflate to aid in complex formation. Unfortunately, here also no crystals were obtained. No additional analysis methods were used to determine this intermediate step.

In summary **C1** formation was shown to require stoichiometric amounts of amide with regards to the complex, a new perspective compared to established literature previously speculating the need for amide as solvent.⁹⁹ From **C1** the addition of heteroaryl forms complex **C2a** through oxidative addition, two different signals were observed, stemming from two possible stereoisomers formed. Addition of silane to **C2a** forms complex **C3**. Here the previously not described formation of a protonated phosphine species was shown in NMR though its involvement in the catalytic cycle can only be speculated. The reductive elimination of the target heteroaryl silane is only observed upon base addition, likely due to the hindrance of the mechanism when excess hydrogen halide is present. The reductive elimination regenerates **C1** completing the catalytic cycle. With the used analysis method, no additional complex species could be detected. The flowchart presented in the beginning of this chapter has been adapted (Figure 39) highlighting the analytically detected complexes in green and those that could not be detected in red.

Construction of silicon-carbon bonds towards α -silanes

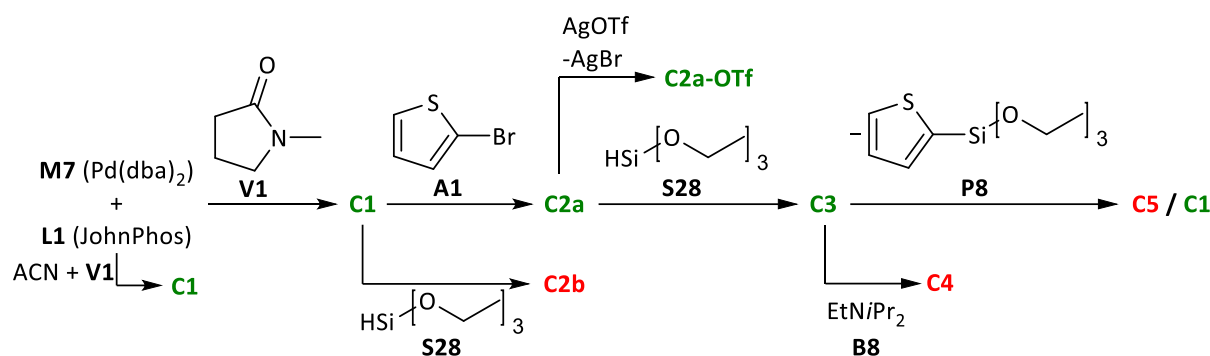


Figure 39: Flowchart of complex isolation steps, with experimental confirmations that were shown in this chapter highlighted in green and not confirmed complexes are highlighted red.

This concludes the mechanistic investigation of the palladium catalysed synthesis targeting α -silane.

The initially presented flow chart is thus further completed, the chart is shown below in Figure 40.

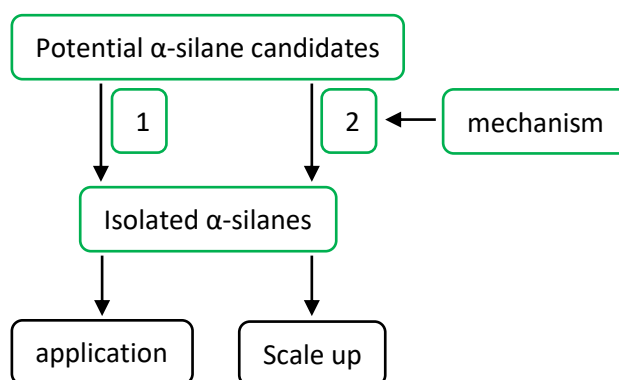


Figure 40: Flow chart presenting the general structure of this thesis, with the two synthesis routes and mechanistic investigation completed.

Through NMR measurements structural information on molecular level can be collected and analysed quantitatively, furthermore monitoring peak shift and intensity changes provides easy access to reaction rates, aiding in the kinetics studies. Potential downsides may be sample preparation, sensitivity problems when using common solvents due to overlapping of signals and access to equipment.^{189,190} The NMR core was heated to the previously established reaction temperature of 80 °C. Youngs NMR tubes were equipped with external deuterium references and equimolar ratios of reactants, added to and kept in the core continuously for 16 h. ^{31}P -NMR spectra are recorded once per hour to monitor changes in the complexes present. This setup replicated the laboratory reaction setup as close as possible, while allowing the continuous measurement of *in situ* NMR. A more detailed evaluation of the data and their integrals is shown in appendix A4. Unfortunately, after several runs no successful recordings of ^1H -NMR were possible, however are amended in the appendix.

Figure 41 shows the time resolved ^{31}P -NMR. Spectra are recorded one-hour apart, monitoring the changes to the complexes involved. Initially, major signals present in solution are **C1** (58.99 ppm) and free JohnPhos (**L1**, 17.80 ppm), as discussed before. Some minor signals can be observed at 51.55 ppm. These had been associated and referenced to JohnPhos-oxide. Over the course of the reaction, each

line indicating one hour at 80 °C. No product was allowed to evaporate during this time due to the sealed NMR tube. A reduction in signal intensity of **C1** with an increase in signal intensity of JohnPhos-oxide is observed. This may be rationalized through oxidation of the JohnPhos coordinated to palladium only, while non complexed JohnPhos is not subject to oxidation. As both signal intensity changes are equal, with constant intensity of free JohnPhos, it must be speculated that the palladium of **C1** also undergoes changes that prevents a re-complexation with free **L1**. The temperature of reaction may have an influence on the rate of JohnPhos oxidation, while the sealed nature of reaction setup prevents additional oxygen entering the system, stopping the ligands oxidations once fully used up. As these observed species only correlate to the state of catalyst deactivation, they cannot be used to determine the order in catalyst.

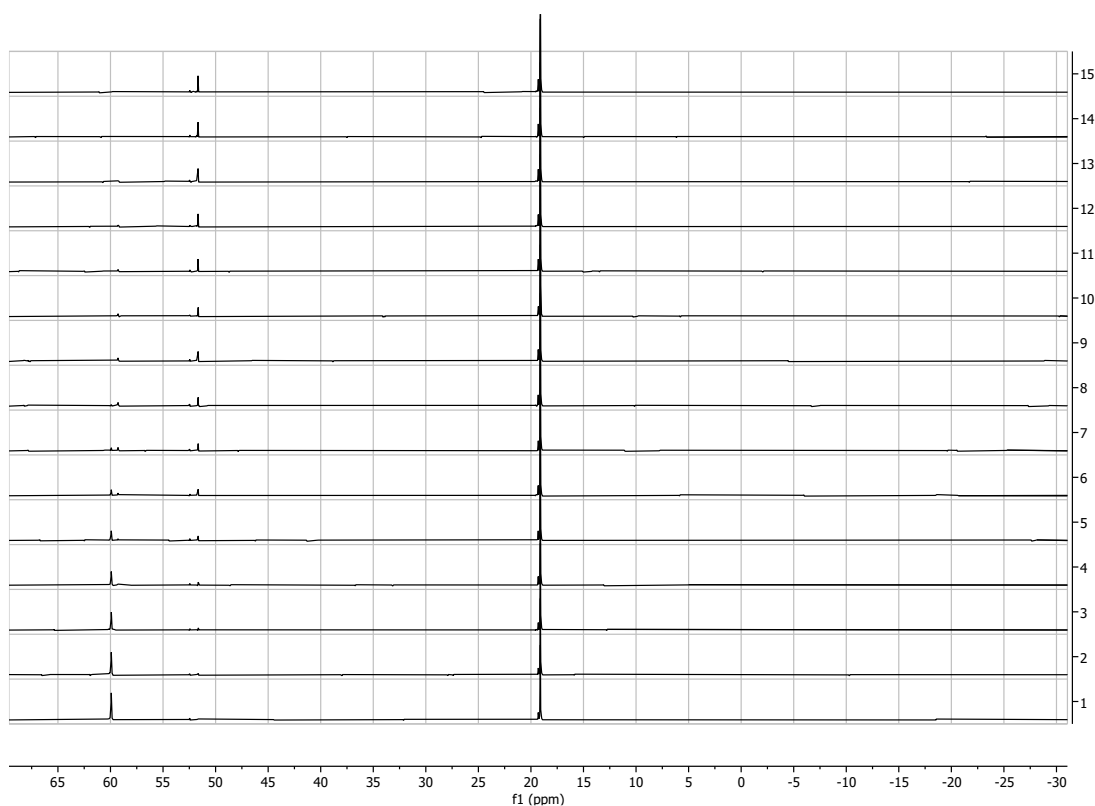


Figure 41: Time resolved ^{31}P -NMR of a reaction mixture as optimised in chapter 2.5.2 in this work. Containing equal amounts of trimethoxysilane and 2-bromothiophene in NMP. Additionally catalytic amounts of $\text{Pd}(\text{dba})_2$ and JohnPhos are added. The reaction mixture is kept at 80 °C for 14 h. With -1 starting at 0 h and recording subsequent spectra once per hour.

2.6 Summary

- This chapter presented the conceptualisation, state of the art and two synthesis routes of novel α substituted alkoxysilane.
- Reasoning and research question were presented for a target structure and its derivatives. Only two of the structures had previously been reported in literature, with little to no physicochemical data available.
- First exploration using Grignard reaction targeting thiophenyl-trimethoxysilane was shown, the reaction was optimised for the given structure varying temperature, stoichiometry, addition order of substrates and workup method. The optimised reaction was then used to synthesise a range of tri- and di-alkoxy thiophenyl silanes, bearing different alkoxides and additional functionalities on the silane centre. For all compounds characterisation, such as NMR, IR and MS was recorded for the first time in literature. This process is limited to using halogenated heteroaryls stable during SET steps of Grignard reactions and alkoxysilanes bearing one additional alkoxide over the target structure.
- To eliminate the structural limitations, stoichiometric by-product and precise handling of reaction conditions imposed by Grignard reactions the catalytic formation of carbon-silicon-bonds was explored. Reaction conditions were optimised, and several structure derivatives synthesised, showing the range of potential substrates of this reaction. Furthermore, mechanistic investigations were conducted, elucidating the sequence of substrate interaction with complex intermediates and substrate-complex interactions using 2D- ^{31}P - ^1H -NMR spectra, highlighting new findings for catalytic cycle of the palladium-based carbon-silicon-bond formation using Buchwald ligands and amide solvent.
- In total the first description of 23 novel α substituted alkoxysilanes was successfully reported.
- The findings presented in this chapter lead to one PCT patent application.¹⁹¹

3 Application of novel α -silanes in polymeric materials

While chapter 2 outlined the exploration and synthetic approaches for the preparation of heteroaryl derived α -silanes, chapter 3 focuses on potential applications, scalability, commercial relevance, and a comparison with commercially available alkoxysilanes. This chapter is divided into five main projects that fill in the gap between laboratory research and industrial application.

Project 1: Functionalisation of polydimethylsiloxanes (PDMS). This project focuses on functionalising PDMS at the α,ω -position using the heteroaryl derived α -silanes synthesised in the previous chapters. There are two major routes by which functionalisation could be carried out: condensation or hydrosilylation. Both methods were elaborately studied to find the most effective way the new compounds could be incorporated into PDMS structures. It involves addition reactions on silanol-terminated PDMS by silanes and condensation, in which Si-O-Si linkages are formed. Hydrosilylation involves the vinyl-end-capped PDMS, in which Si-C linkages are formed. Those modifications have been done to give the properties that are inherent in the PDMS a boost. These include thermal stability, mechanical strength, and chemical resistance.

Project 2: Partial condensation of silanes towards resins. The second project focuses on the well-defined, partial condensation of silanes to give rise to resins that may be used as an additive in commercial RTV-1 (room temperature vulcanising) silicone formulations. The target here is to achieve resins that pose unique characteristics in terms of performance to that of RTV-1 silicones, such as improved adhesion, durability, and cure speed. The level of condensation is monitored very closely for the control of the balance between reactivity and stability. The optimisation is done to the partial condensation process in such a way that there can be achieved consistent quality and performance in the resins resultant to make them useful for the industrial applications.

Project 3: Rheometer assisted time resolved condensation studies. The third project involved carrying out time-resolved condensation experiments on a rheometer under controlled temperature and humidity conditions. In doing so, these studies measure the transition of the substances from liquid to solid, which can give insight into curing behaviour and kinetics. This paper evaluates the performance of the new heteroaryl derived α -silanes by comparison of their kinetics with the commercially established reactive alkoxysilanes. This study is actually targeted at understanding how these new compounds react in different environmental conditions because this forms the basis for their applicability in practice.

Project 4: Synthesis process optimisation for scale-up. In this fourth project, we will consider optimisation of the synthesis process for scale-up. The previous project had the yield of up to a maximum of 1 gram per run in the synthesis of heteroaryl-derived α -silanes. After several iterations and optimisations, the process has been scaled up enormously. The last iteration has done using a steel

reactor of 20 litres for making compound **P4** and compound **P8**, with a capability of 2 kilograms. This scale-up is a crucial step toward industrial applicability, indicating that such compounds can be produced in the quantities needed for commercial usage. The production process cost-effectiveness and sustainability are also studied during the scalability study.

Project 5: Application in neutral RTV-1 silicone formulations. This final project will use the newly synthesised compounds in the formulation of, and as additives to, commercially important neutral RTV-1 silicone formulations. Neutral RTV-1 silicones are widely used in many industries because of their adhesion, excellent properties of durability, and easy way of application. These compositions further advance the performance of the formulations when the heteroaryl-derived α -silanes are included. This is pursued by general testing for comparing the characteristics of the RTV-1 silicones added with new additives, which are the cure speed, mechanical strengths, and environmental resistance.

3.1 PDMS end group functionalisation

Building on the α -silanes developed in Chapter 2, this chapter investigates their incorporation into polydimethylsiloxane (PDMS) as functional end groups. By leveraging the reactive sites of these silanes, PDMS chains can be modified to enhance the polymer's physical, chemical, or mechanical properties. There are different strategies available for the synthesis of PDMS derived polymers. In general end groups can be introduced before or after the formation of the polymer. By pre-functionalising an end-capping agent used during the polymerisation the desired end group is introduced quantitatively to each polymer chain in α - and ω -position. This approach is desirable as it provides for a reliable and quantitative introduction of the end group even at high molecular weights, however the synthesis of said end capping agent can be non-trivial and may require the use of less desirable functionalisation on the end group. Furthermore, the agent may require highly tuned properties not available when any end group is introduced, and the end group must be stable under polymerisation conditions. In contrast a functionalisation of a premade, terminated polymer is possible. Here the desired end group is introduced by reacting the polymer with the end group precursor. High selectivity and quantitative reactions are desired as specially in high molecular weight polymers as the weight concentration of end group is low and thus decreases the concentration available for further reactions. In contrast issues regarding reactivity and stability during polymerisation are avoided. Using either strategy requires the correct end group functional substrate, limiting to commercially available alkoxysilanes for condensation and double bond functional silanes for hydrosilylation. Furthermore, the presence of residual catalyst from the functionalisation reaction must be considered in downstream processing of the functionalised material, such as use in commercial silicone formulations.

Two high yield functionalisation strategies are known and are presented in section 1.2 of this work. Either condensation towards a silicon-oxygen-silicon bond or hydrosilylation result in almost quantitative yield, making them well suited for end group functionalisation. Both strategies can either be applied to the end-capping agent or the pre-functionalised PDMS. To aid in comparability of methods a polymerisation approach has been chosen that allows the introduction of either silane or siloxane end groups. By using tetramethyl-disiloxane and tetramethyl-disiloxanediol respectively in ring opening polymerisations of cyclic D_4 (Octamethylcyclotetrasiloxane) either end group can be introduced into the polymer.¹⁹² Both resulting silanes are available commercially, aiding in the potential large-scale applicability of the presented process. Alternatively, either tetramethyl-disiloxane or tetramethyl-disiloxanediol are functionalised with the end group and then subsequently used in polymerisation.^{192,193}

To establish hydrosilylation conditions preliminary experiments using tetramethyldisiloxane (TMDS) and vinyltrimethoxysilane (VTMO, **S4**) were conducted and later used for all follow up reaction. Both chemicals had good availability in the lab making them ideal screening substrates. The close structural relation of **S4** to compound **P4** is assumed sufficient to translate reaction conditions from **S4** to new silanes presented in this work and limit the amount needed for screening reactions. As highlighted in chapter 1.3 the reaction can lead to alpha or beta addition products, shown in Figure 42.

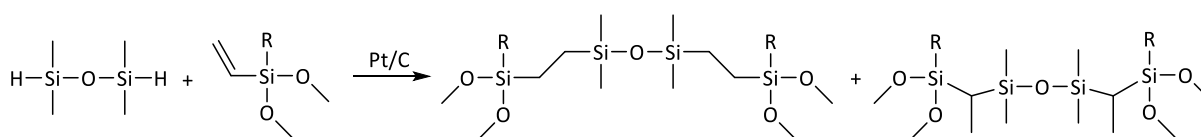


Figure 42: Hydrosilylation of Tetramethyldisiloxane with an alkoxy-vinyl-silane. Vinyltrimethoxysilane ($R = \text{OMe}$, **S4**) and Thiophenyl-vinyl-dimethoxysilane ($R = \text{Thiophenyl}$, **P4**) were used in this chapter. The reaction was optimised.

The reaction was optimised to yield the beta addition product, resulting in a linear linkage between the substrates. A detailed reaction optimisation is described in appendix A3.

Both shown hydrosilylation products were synthesised not only as example compounds, but also to be used in ring opening polymerisation (Figure 43), as well as additive in commercially relevant silicone formulations. With the required substrates for a functionalised PDMS via ring opening polymerisation (ROP) at hand again the **S4** product was used for condition exploration. The previously upscaled reactions material was used for this, as the precursors for hydrosilylation (**S4** and TMDS) both are commercially available, while compound **P4** was only scaled up at a later stage of this work, see chapter 3.4 for details.

For ring opening polymerisation several strategies are known in literature, with the main pathways introduced in 1.2 of this work. It must be noted that when working with compounds intended for hydrolysis upon moisture contact, such as **S4**, all handling must be performed under exclusion of water. This excludes all strategies involving water as a reactant or solvent. Furthermore, the substrates and

catalyst must be dry and not releasing water. This excluded catalysts such as ammonium hydroxide, making triflic acid catalysed anionic ring opening polymerisation (aROP) an ideal choice for the synthesis of alkoxy silane end group functionalised polydimethylsiloxanes.^{194,195}

The ^{29}Si -NMR shifts of the used cyclic siloxanes octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) are known at -19 ppm and repeating units in PDMS at -23 ppm allowing for differentiation between substrate and product in NMR.¹⁹⁶ Gel permeation chromatography (GPC) may be used to determine the weight average molecular weight (M_w) and number average molecular weight (M_n) with the associated polydispersity index (PDI). Due to the moisture sensitive end groups of the target polymer all measurements must be conducted under moisture exclusion, including the solvent for GPC measurements. Else partial polymerisation of the end groups cannot be ruled out.¹⁹⁷

Following aROP procedure according to Bezlepknia *et al.*¹⁹⁸ was tried with toluene and dimethyl sulfoxide as solvent and triflic acid as catalyst, measuring ^{29}Si -NMR after reaction to check for successful ring opening. In all synthesis attempts no significant ring opening of either D_4 or D_5 to the target structure was detected. Figure 43 b) shows the reaction ^{29}Si NMR spectrum of **S4** modified TMDS from this chapter with D_4 and catalytic amounts of triflic acid under inert conditions after 4 h. No conversion was detected, all additional signals in the spectrum stem from impurities in D_4 and prepared modified TMDS. The same reaction conditions result in 65 % conversion when using unmodified TMDS yielding Si-H terminated PDMS (Figure 43 a)).

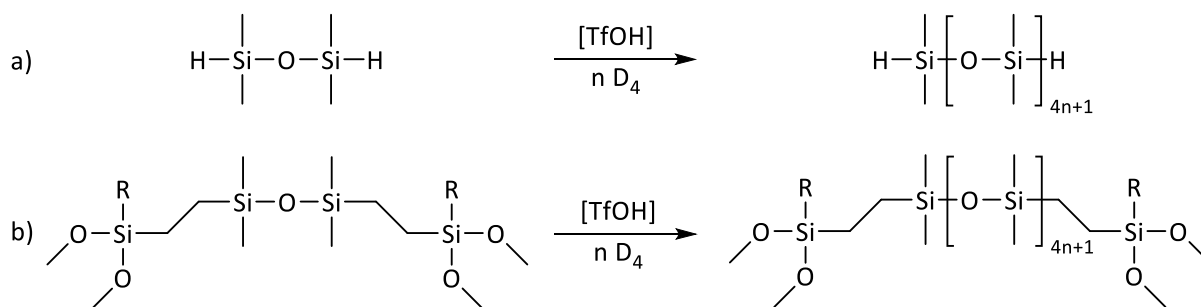


Figure 43: Ring opening polymerisation of a) tetramethyldisiloxane or b) hydrosilylation products from vinylsilanes and tetramethyldisiloxane using octamethylcyclotetrasiloxane (D_4) and triflic acid (TfOH) as catalyst. Trimethoxysilane ($\text{R} = \text{OME}$) and Thiophenyldimethoxysilane ($\text{R} = \text{Thiophenyl}$) functionalisation were used in this chapter.

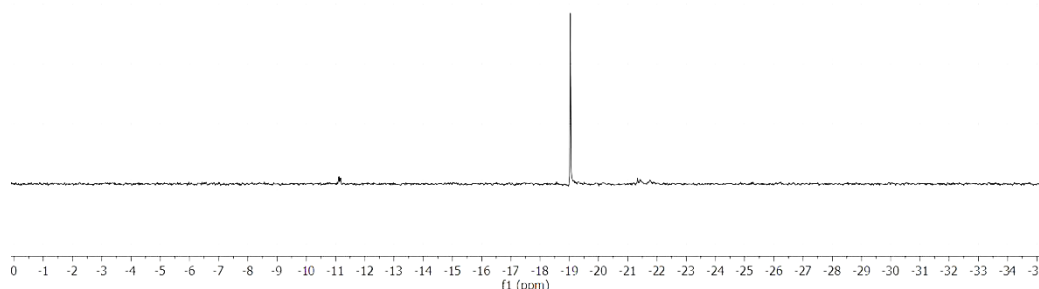


Figure 44: ^{29}Si -NMR spectrum after 4 h at aROP conditions using D_4 and TMDS modified with **S4** from this chapter.

Table 7: aROP of TMDS derivatives at 80 °C using different solvent conditions and triflic acid as catalyst. Conversion measured based on ^{29}Si -NMR shift comparing D_4 at -19 ppm and PDMS at -23 ppm.

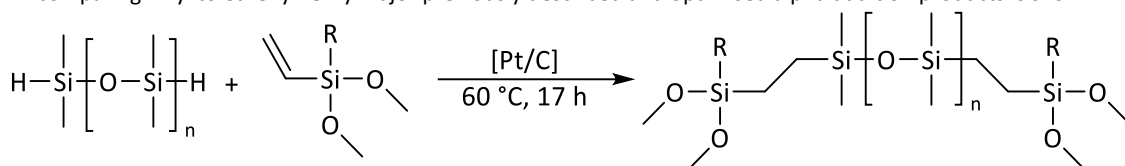
TMDS derivative	Solvent	Conversion [%]
TMDS	neat	65
TMDS	Toluene	63
TMDS	DMSO	52
TMDS- S4	neat	0
TMDS- S4	Toluene	0
TMDS- S4	DMSO	0
TMDS- P4	neat	0
TMDS- P4	Toluene	0
TMDS- P4	DMSO	0

When comparing conversions between modified and unmodified TMDS it is evident that either the modification or byproducts leftover from the modification hinder the use as a chain terminating agent in downstream ring opening polymerisation. TMDS could easily be removed through distillation, while used platinum-based catalysts remain in the product mixture. Platinum may have an interaction with the used triflic acid, potentially deactivating the ring opening polymerisation. During the hydrosilylation described in this chapter both alpha and beta products were detected, though their respective influence during ring opening polymerisations can be neglected, the overall change in polarity and mobility of the modified TMDS may have an influence on its effectiveness as a chain terminating agent, being sterically and electronically more challenged than in unmodified TMDS. Due to insufficient conversion reported in Table 7 of functionalised TMDS to end group modified PDMS reaction route per Figure 43 was abandoned, using the hydrosilylation intermediate products from vinylsilanes and TMDS as additives in later chapters only.

Alternatively to the functionalisation of chain termination agent used in ROP existing PDMS may be end group functionalised either through condensation of a silanol terminated PDMS with an alkoxy substituted silane e.g. compound **P1** in the presence of a condensation catalyst, such as in Figure 45 or through hydrosilylation of a silicon hydride terminated PDMS with a vinyl substituted alkoxy silane, such as compound **P4** in Table 8. It must be noted that theoretically an alkoxy substituted silicone hydride and vinyl terminated PDMS yield the same structure, though few alkoxy substituted silicone hydrides are commercially available and have not been successfully synthesised within the work presented here, thus limiting the scope to vinylsilanes. Using a trialkoxysilane for condensation and dialkoxysilane for hydrosilylation in both cases yields an α,ω -dialkoxy-silane-terminated polysiloxane, making the products more comparable in subsequent tests. The previously optimised reaction conditions for TMDS and **S4** were used for the functionalisation of PDMS through hydrosilylation as shown in Table 8. TMDS (tetramethyldisiloxane) is chemically similar to PDMS- H_2 (α,ω -hydrido-terminated polysiloxane) with the same chemical structure and a repeating unit $n = 1$. The longer chain

reduces the relative concentration of end group to repeating unit. To accommodate the vinylsilane equivalents were adapted to the end groups concentration and used at a molar ratio of 2.2 : 1. For all experiments commercially available α,ω -hydrido-terminated polysiloxane with $M_w = 2000 \frac{\text{g}}{\text{mol}}$ and $\text{PDI} = 1.1$ was used, as it has a low number of repeating units (n), thus high end group concentrations, aiding in potential conversions to the desired product.

Table 8: Platinum catalysed hydrosilylation of α,ω -hydrido-terminated polysiloxanes ($M_w = 2000 \frac{\text{g}}{\text{mol}}$, $\text{PDI} = 1.1$) with varying concentrations of vinylsilanes at 60°C , 17 h. Vinyltrimethoxysilane ($R = \text{OMe}$, **S4**) and Thiophenyl-vinyl-dimethoxysilane ($R = \text{Thiophenyl}$, **P4**) were used. Conversions based on ^{29}Si -NMR shift comparing hydride to alkylsilane, as well as ^1H -NMR shifts comparing vinyl to ethenyl. Only major previously described and optimised alpha addition products is shown.



Silane	Si-H : Vinyl equivalents	Conversion [%]
S4	1 : 1.1	0.0
S4	1 : 5	1.5
P4	1 : 1.1	0.0
P4	1 : 5	0.7

All used equivalents had been calculated for PDMS end groups present (determined through ^1H -NMR). This aids in comparability between PDMS and TMDS conversions, as well as ensure control over used equivalents between batches of PDMS and inherent small variations in molecular weight and end group concentration. This adaptation results in using significantly smaller weight percentages of silane when comparing the conversion of PDMS to previously presented conversions using TMDS. Dilution of the vinylsilanes in the polymers bulk and resulting reduction in absolute concentration may cause this. To accommodate the used equivalents had been drastically increased, though without significant increase in conversion as shown in Table 8. Due to the nature of this modification route classical work up procedures may not be used to remove substrates from the product, such as distillation (compounds with high boiling point and only small boiling point differences) or column purification (substrate PDMS and resulting modified PDMS with similar retention time differences). As shown in Table 8 none of the chosen, previously optimised hydrosilylation conditions resulted in conversions useful for further processing or specific analysis of the resulting polymer.

Lastly condensation of silanol terminated PDMS with trialkoxysilane was undertaken, this is the third process for high yielding synthesis of selectively end group modified PDMS with highly functionalised alkoxy silanes, such as compound **P1**, presented in Figure 45. **P1** is used here as after condensation with it two functional silanes will remain for further condensation. Using dialkoxide α -silanes would leave a monofunctional end-group termination, not able to undergo crosslinking through condensation. To

increase the processes conversion aminopropyl trimethoxysilane was used as condensation catalyst¹⁹⁸ and commercially available α,ω -hydroxy-terminated polysiloxane with $M_w = 10000$ g/mol and $PDI = 1.1$.

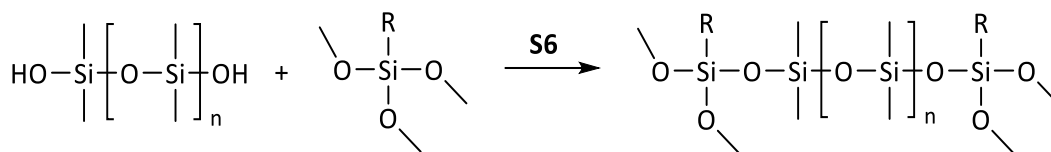


Figure 45: Condensation of vinyl-trialkoxysilane with α,ω -hydroxy-terminated polysiloxane using (3-Aminopropyl)trimethoxysilane (AMMO, **S6**) as catalyst. Vinyltrimethoxysilane ($R = \text{OMe}$, **S4**) and thiophenyl-trimethoxysilane ($R = \text{Thiophenyl}$, **P1**) were used.

NMR (shown in Appendix A4) shows successful condensation of both silanols with **S4** and **P4** after 2 h. No differences in GPC can be observed comparing before and after condensation. This is due to the minor differences in overall molecular weight of the polymer chain when adding the two silane units to the overall polymers chain length. This conversion shows the successful use of **S4** in polymer endcapping, which is known, but also the use of **P1** resulting in an exemplary α,ω -alpha-silane terminated PDMS. This polymer can then be used in condensation applications such as shown in chapter 3.5 of this work. While conversions have proven successful, showing the end group functionalisation of PDMS with alkoxysilanes this route is limited to substrate silanes bearing one alkoxide more than the target count of alkoxides on the final functionalised PDMS, as it is cleaved during the reaction. Additionally, a higher alkoxysilane loading is required for full conversion of all end groups due to their dilution with the polymer's backbone and thus resulting in reduced concentration. This may be beneficial when compared to using vinyl substituted silanes, as their choice may be more limited when compared to the variety of commercially available alkoxysilanes. This route does not allow to produce tailor-made end group functionalised PDMS, especially when compared to the pre-functionalisation of TMDS with subsequent ring opening polymerisation. If the route would work it would have allowed for tailor made molecular weights, while the end group functionalisation of PDMS either through condensation or hydrosilylation is limited to commercially available substrates.

To summarize successful and optimised hydrosilylation of 1,1,3,3-tetramethyldisiloxane (TMDS) with commercially available and novel vinylsilanes, using the Karstedt catalyst, achieved conversions up to 95%. Selectivity investigations of hydrosilylation were undertaken and optimised for alpha products. Ring-opening polymerisation was straightforward with TMDS, while unsuccessful with vinylsilane modified TMDS. Platinum-catalysed hydrosilylation of α,ω -hydrido-terminated polysiloxanes with vinylsilanes proved challenging, likely due to the dilution of end groups from the polymer backbone. The successful condensation of novel α -silanes with α,ω -hydroxy-terminated polysiloxanes was demonstrated. These findings were first published in the PCT patent application WO2023094197A1.¹⁹⁹

Their physicochemical properties and use in commercially relevant formulations will be further investigated in chapter 3.5.

3.2 Condensation towards resins

Following the methods for preparing and modifying α -silanes described in previous chapters, this chapter focuses on the condensation of these silanes to form resinous materials. The influence of different substituents, reaction conditions and catalysts on the resulting resins is explored.

Resins are a broad class of amorphous or semi-crystalline materials that can be natural or synthetic in origin. In the context of alkoxy-silanes, resins typically refer to the network polymers formed by the condensation of silane monomers. These resins can be thermoplastic, where they soften upon heating, or thermosetting, where they undergo an irreversible curing process to form a rigid network.²⁰⁰ The ability to tailor the chemical structure and network architecture of these resins makes them highly versatile for a wide range of applications.^{201,202}

In industrial terms, a resin is often defined by its end-use properties which include mechanical strength, thermal stability, chemical resistance, and adhesion.^{201,203} The specific properties of a resin depend on the monomeric units involved in its synthesis, the degree of cross-linking within the network and the nature of any functional groups present in the polymer chain. Thermoplastic resins are polymers that soften when heated and harden upon cooling, allowing them to be re-melted and reshaped multiple times. This property is due to the absence of cross-linking in their molecular structure which consists of linear or branched polymer chains. Common examples include polyethylene, polystyrene and polyvinyl chloride.³⁷ However, in the context of silane chemistry, thermoplastic resins are less relevant as silane-based systems tend to form cross-linked networks that exhibit thermosetting behaviour.²⁰⁴ Thermosetting resins, unlike thermoplastics, undergo an irreversible chemical reaction when cured, forming a three-dimensional network. This curing process can be initiated by heat or a catalyst. This leads to the formation of covalent bonds between polymer chains, resulting in a material that does not melt upon reheating. Examples include epoxy resins, phenolic resins, and certain polyurethanes. Silane-based resins typically fall into this category due to the cross-linking nature of siloxane bonds formed during condensation reactions.²⁰⁵

Silane-based resins are a specialised subclass of thermosetting resins, formed through the condensation of alkoxy-silanes. These resins are distinguished by the presence of silicon-oxygen (Si-O) bonds which form the backbone of the siloxane network. The properties of silane-based resins can be finely tuned by varying the types of siloxy units within the polymer, leading to materials with a wide range of mechanical, thermal and chemical properties.²⁰⁶ Silane-based resins are typically categorized based on the types of siloxy units present in their structure. The two most prominent types are MQ resins and DT resins, each offering distinct properties and applications. For MDTQ nomenclature

explanation see chapter 1.2 of this work. MQ resins are characterised by a combination of monofunctional M units ($R_3SiO_{0.5}$) and tetrafunctional Q units (SiO_2), resulting in a highly cross-linked three-dimensional siloxane network. The M units act as terminal groups that limit further cross-linking, while the Q units provide a robust and highly cross-linked siloxane network. This combination results in a resin that is rigid, thermally stable and highly resistant to environmental degradation, including UV radiation and oxidation. The extensive cross-linking provided by the Q units also imparts mechanical strength, making MQ resins suitable for high-performance applications where long-term durability is needed. Due to their robust structure, MQ resins are often employed in coatings, adhesives, and encapsulants, particularly in scenarios that demand high resistance to mechanical and chemical degradation.^{206,207} In contrast, DT resins are composed of difunctional D units (R_2SiO) and trifunctional T units ($RSiO_{1.5}$), which create a less densely cross-linked structure compared to MQ resins. The D units contribute to the formation of linear polymer chains, while the T units introduce some degree of cross-linking, also referred to as crosslinking density. As a result, DT resins are more flexible and exhibit lower viscosity, making them easier to process. These resins are needed in applications where elasticity, ease of application and reduced brittleness are desired such as flexible coatings, sealants and adhesives. The ability to adjust the ratio of D to T units allows for fine-tuning flexibility and mechanical strength, allowing DT resins to be tailor made. There are some examples of mixing the two classes, such as MTQ and MDQ resins.^{206,207} The extent of condensation and cross-linking determines the final properties of the resin.^{207,208} The condensation reactions can be catalysed by acids or bases and the rate of these reactions can be influenced by factors such as temperature, humidity and the presence of additives. Control over these parameters allows for the tailoring of the resin's properties to meet specific application requirements.^{206,207} DT resins are commonly used as coupling agents and adhesion promoters, as well as durability improvement and thus find application in adhesives, coatings and sealants.²⁰⁹ MQ resins are used for their silky texture, thermal stability and reinforcing properties in cosmetics and coatings.²¹⁰

The potential and various applications of silane derived resins have been shown for commercially available resins. As the alkoxysilanes presented in this work are novel and not available their behaviour and condensation towards resins and determination of their behaviour was explored in this chapter. There are known methods for the condensation of reactive silanes towards silanes. Following the method shown by Kuo *et al.*²¹¹ acid catalysed condensation of silanes in solvent and in neat conditions was undertaken. Neat conditions allow high concentrations of catalysts and used silanes. Solvent conditions allow for various concentrations and better heat transfer, while also distributing already formed resin nucleation sites. Precise addition of water to the silane is key during the formation of reactive resins, limiting further reaction forming an interconnected network. Aqueous hydrogen chloride is readily available and allows for different catalyst (HCl) and reactant (H_2O) concentrations to

be used. MQ and DT resins are common in literature and industry, due to their structural nature it is impossible to make thiophenyl substituted Q units, thus DT resins were chosen as condensation targets. Thiophenyl triethoxysilane (compound **P8**) and thiophenylvinyltrimethoxysilane (compound **P4**) were chosen as T_{het} and D_{het} units for subsequent condensations (Figure 46), denoting them with their heteroaryl substitution in this chapter. Due to their limited availability additional condensations were performed with dimethyldimethoxysilane as substitute D unit.

Characterisation of the formed resins is challenging due to their partial solid and potentially inhomogeneous nature of the formed resin. Several methods for the analysis of resins are used. Measurement of cross-linking density, directly influencing the mechanical properties of a resin, through swelling experiments is a common practice.²¹² The degree of a suited solvent uptake is inversely proportional to the density of the resins network. This however is also sensitive to the type of solvent and ambient conditions, making reproducibility challenging. Furthermore, gel permeation chromatography (GPC)²¹³ and dynamic viscosity measurements with a rheometer²¹³ can give further indications on the materials behaviour. Lastly end group analysis through NMR can aid in characterisation, however insolubility of resins can pose a challenge if no solid-state NMR is available.²¹⁴

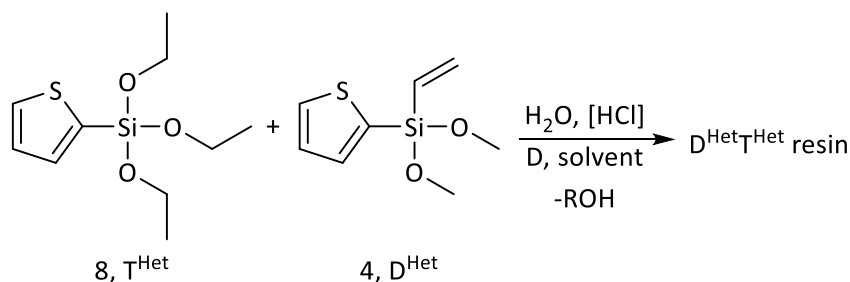


Figure 46: Condensation of compound **P8** (denoted as T^{Het}) with compound **P4** (denoted as D^{Het}) through the addition of water with catalytic amounts of hydrochloric acid at elevated temperature, resulting in the formation of $D^{\text{Het}}T^{\text{Het}}$ resin.

In accordance with the method presented by Kuo *et al.*²¹¹ a series of experiments were conducted to study the reactions of silanes under varying conditions. The experiments were divided into three main sets: The first set focused on varying the solvent while keeping the silane concentrations equimolar and reacting them with a constant amount of 1M hydrochloric acid at 70 °C for 24 hours. Here it is key when running a reaction in solvent instead of neat conditions that the solvent must be easy to remove, achieved by a low boiling point, to aid in the commercial relevance of the formed resin. In the second set, the ratio of silanes was varied while maintaining the same amount of water in THF, with the reaction conditions held constant at 60 °C for 24 h. The third set involved varying the amount of 1M hydrochloric acid used in the reaction with equimolar silanes in THF, under the same conditions of 60 °C for 24 h. For this third set, the equivalents were calculated based on the molar sum of reactive alkoxy groups to the molar amount of water in the 1M hydrochloric acid. A decrease in this ratio is expected to increase the conversion of silanes and thus form a higher molecular weight resin. The

results from these experiments, including the measured conversion rates and the molecular weights of the resulting products, were analysed to understand the effects of these variables on the reaction outcomes. Due to the size of the resulting table, it was moved to appendix A3 and can be viewed there as Table 26.

Initially the solvents influence on the formation of a resin is screened. Interestingly two opposing trends are measured. In ethyl acetate low conversion of the alkoxy silanes at high molecular weights is observed, while in tetrahydrofuran high conversion at low molecular weights is observed. This trend can be rationalised through different polarities of the solvents and resulting differences in water and hydrochloric acid solubility²¹⁵, directly influencing the formation of resins from the used silanes. The resulting changes in molecular weight are a direct consequence of this also, as it is likely that some silane is water soluble and thus reacts with a significant excess water forming higher molecular weight resins. While investigating the molar ratio of D to T units it is evident that the measured molecular weight is increased when more D units are present during condensation, while the crosslinking degree is reduced with more D units present. Both observations can be rationalized due to the incorporation of D units between cross-linking T units in the forming three-dimensional network, increasing the amount of repeating D units between each T unit, reducing the density of the formed network. Interestingly the changes are only visible in GPC and crosslinking density measurements, with the exposed end-groups of the resin remaining unchanged. During the same experiment, a difference in conversion can be observed where equimolar ratios of D and T units result in high conversions, while increasing amounts of D units reduce the conversion significantly. This can be a result from higher relative amounts of reactive alkoxy groups present on T units with different reactivity rates. Unsurprisingly the experiments with changed amounts of water showed that increasing the molar ratio of water to silanes reduces the amount of free alkoxy groups that can be detected in NM, increasing the overall conversion. The same effect is observed for increasing the temperature.

Through these factors it is straight forward to condense tailor made resins from the α -silane derivatives shown in this work with specific ratios of repeating (D) to crosslinking (T) units, molecular weights and degrees of unreacted alkoxy silanes depending on the resin's application. These findings were first published in the PCT patent application WO2023156602A1.²¹⁶

3.3 Rheological characterisation

Within the framework of this thesis chapter 2 provided an extensive discussion on the synthesis strategies on novel α -silanes. Chapters 3.1 and 3.2 focused on the further processing of said silanes. This chapter follows on from this work and focuses on the detailed rheological characterisation of the synthesised silanes, as well as the resulting polymers and resins. Rheology provides insights to

physicochemical and mechanical properties of these compounds on a macroscopic scale.²¹⁷ This is especially important regarding the condensation with water, leading to material property changes. A particular focus is placed on the observed changes in storage modulus (G') and loss modulus (G''), as they indicate the formation of three-dimensional networks. Due to these changes measurements were recorded over the span of 24 h, allowing for a tracking of the condensation reactions dynamics and the resulting changes in viscoelastic properties.^{217,218}

Rheology described the science of deformation and flow, providing a framework for understanding how materials may respond to applied forces. Rheology distinguishes between viscous behaviour, a state where material flows under stress and elastic behaviour, where material deforms but returns to its original state once the stress is removed. Key parameters in this field are shear stress and shear strain, additionally the frequently used parameter viscosity describes the materials resistance to flow. Many materials, including polymers, exhibit viscoelastic behaviour, a combination of both viscous and elastic material responses.²¹⁷ The central parameters to characterise this property are storage modulus (G') and loss modulus (G''). The storage modulus describes the energy stored in the material during its deformation, this corresponds to the materials elastic or “solid-like” properties. The loss modulus quantifies the energy dissipated during deformation, corresponding to its viscous or “liquid-like” properties. These parameters are not only measurement dependent, such as frequency or temperature, but are also intrinsic to a materials molecular structure. In siloxane condensation the transition from a predominantly viscous system to one that shows more elastic properties is of particular interest. As the silanes reacts with water the resulting condensation reaction forms additional siloxane bonds, progressively forming a three-dimensional network. This process is referred to as gelation and is typically marked by the crossover point where G' exceeds G'' , thus the material having more “solid-like” character than “liquid-like”. By monitoring the changes in G' and G'' in time resolved experiments it is possible to correlate chemical reaction of hydrolysis and condensation with changes in viscoelastic properties. The transition from a viscous to an elastic state was marked by the crossover of G' and G'' , indicating the formation of a fully developed network. This crossover serves as a direct marker of the gelation point, providing a quantifiable measure of the curing process.²¹⁹

From G' and G'' complex viscosities can be calculated. With the complex viscosity being calculated as shown in (1), where G^* is shown in (2) and ω is the angular frequency of oscilation that can be extracted from the oscilation frequency f set for the measurement through (3).

$$\eta^* = \frac{G^*}{\omega} \quad (1)$$

$$G^* = \sqrt{G'^2 + G''^2} \quad (2)$$

$$\omega = 2\pi f \quad (3)$$

The samples used in rheologic investigations were prepared in 2.4.3, 3.1 and 3.2 of this work. As all substances were handled under inert atmosphere so far no condensation was observed. The samples were transferred to the rheometer and measurements started immediately to capture the full range of viscoelastic behaviour. As the material is dependent on ambient conditions, especially humidity, all samples were handled under controlled ambient conditions to eliminate these variables. A chamber surrounding the measurement array, connected to a constant temperature and humidity source was used (fluctuations were $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ and $50\text{ \%} \pm 5\text{ \%}$). Previous studies have shown that fluctuations in ambient humidity (ranging from 15 % to 70 %) can significantly alter the curing rate of siloxane formulations, necessitating strict moisture control. Rheologic measurements were conducted using a HAAKE RheoStress 1 equipped with a plate-plate geometry with a diameter of 35 mm at 1 mm gap to minimise edge effects. Temperature was controlled using a Peltier system, ensuring constant local temperature of the measured material. Instead of a standard plate-plate or plate-cone geometry a specialised ring rotor was used. This allows an effective reduction in sample volume subjected to diffusion limits while maximising precision of forces recorded that may result from large surface of plate to gap ratio. The specialised ring rotor geometry was selected to minimize diffusion-related inconsistencies, which are particularly relevant for moisture-sensitive curing systems. This design reduces mass transport limitations and ensures a more homogeneous distribution of condensation effects. To reduce heat loss through the geometry a combination of high precision steel rotor and a ceramic rod with low thermal conductivity was used. The high level setup is shown in Figure 47.

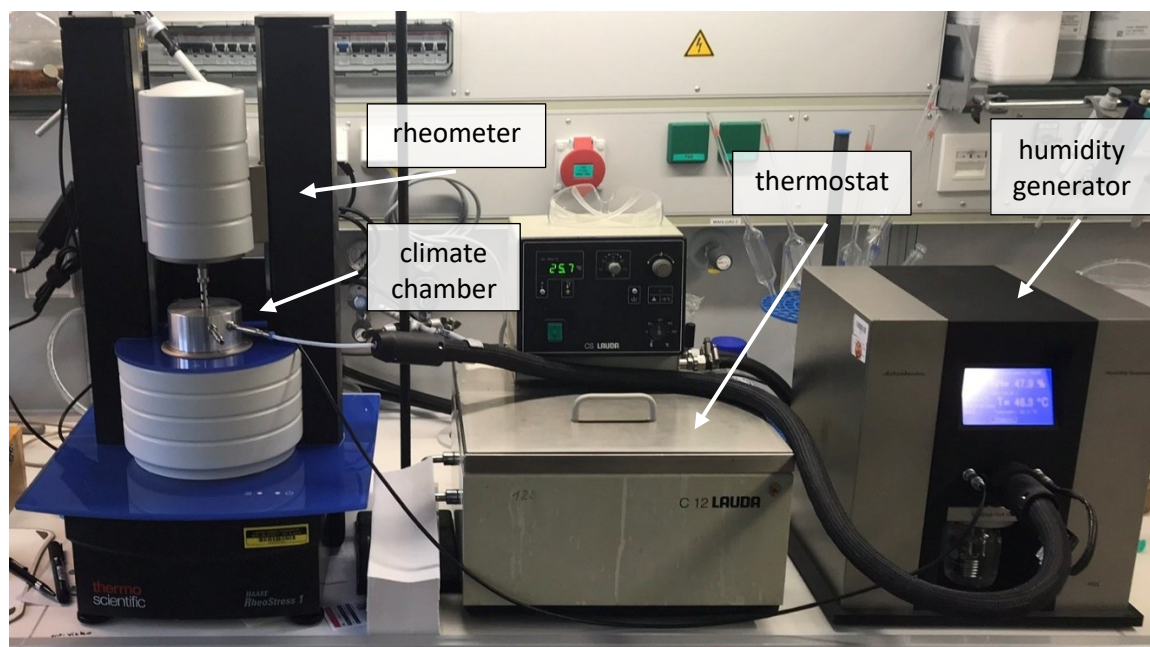


Figure 47: Measurement setup for time resolved rheology measurements using a HAAKE RheoStress 1 (rheometer) equipped with rotor and climate chamber (left) a Lauda C 12 (thermostat) connected to the RheoStress 1 peltier element (middle) and a dataphysics-instruments HGC 20 (humidity generator, right).

Before conducting the time-resolved measurements, a series of preliminary sweeps were performed to optimise the measurement parameters. These sweeps were essential to ensure that the selected frequency, strain amplitude, and temperature remained well within the linear viscoelastic range of the starting material while providing data with a satisfactory signal-to-noise ratio. For example, a strain amplitude sweep was carried out at a constant frequency to identify the plateau region where the storage (G') and loss (G'') moduli remained constant, confirming that the material's response was linear. Similarly, a frequency sweep was executed at a fixed, low strain to evaluate the materials behaviour over a range of frequencies, ensuring that the viscoelastic properties were stable and reproducible under the chosen conditions. A temperature of 23 °C was maintained during the experiments to guarantee controlled humidity levels, which is critical for accurate and consistent measurements. Representative examples of these preliminary sweeps, illustrating the identification of the linear viscoelastic range and the selection of optimal parameters, are presented and described in Appendix A3. At excessively high rotational speeds or frequencies, a non-linear increase in viscosity has been observed. At elevated deformation values, oscillatory measurements increasingly resemble rotational measurements. This occurs because, under such conditions, a significant portion of the measurement time is spent on the acceleration and deceleration phases of oscillation rather than within the steady oscillatory amplitude. As a result, the measured response is influenced by transient effects rather than the material's intrinsic viscoelastic properties.²²⁰

In the theoretical limit of infinitely increasing deformation, the oscillatory motion transitions into continuous rotation, effectively transforming the measurement into a shear flow experiment rather than an oscillatory test. This transition invalidates the fundamental assumptions of oscillatory rheology, where strain-controlled deformations should remain within the linear or weakly nonlinear viscoelastic regime. Consequently, only oscillatory experiments performed at sufficiently low deformation values are appropriate for tracking curing reactions.

Preliminary experiments identified an optimal parameter range for the subsequent curing studies, with deformations between $\gamma = 110$ and $\gamma = 3000$ and frequencies below 1 Hz. This range ensures that the material remains within the measurable viscoelastic regime while avoiding excessive shear-induced structural disruptions. Additionally, the sampling rate is reduced to every 30 seconds while averaging the measurements during this period so that any fluctuations induced during oscillation are removed. Due to the complex nature of the data, plots of each measurement are shown in Appendix A4. Here a summary of the plots is provided and key learning are interpreted. The time resolved measurements all show an initial induction period, dominated by fluctuations between each datapoint. The induction periods are not quantified here. This period is followed by a rapid increase of G' and G'' , as well as the associated complex viscosity η^* . While initially G' values are higher in all measurements a crossover point between the two can be seen. Table 9 lists the time between start and crossover point of G' and

G'' , as well as resulting viscosity for different silanes. Additionally, Figure 48 shows the viscosities of several silanes after fixed time intervals. In some instances a rapid reduction in values was observed, physically associated with the formation of gelled particles around the ring rotor, exemplary photos are shown in Appendix A3 (Figure 64 and Figure 65). Silanes **P1**, **P8**, **S2**, **S4** and **S6** were selected to provide a comparison of trialkoxy silanes with different substitution patterns. **P1** and **P8** represent the silanes presented in this work. **S2**, **S4** and **S6** bare different, common substitutions of trialkoxy silanes. Comparing tetraalkoxy silanes or dialkoxy silanes in this test is less ideal due to the different expected reactivities, additionally dialkoxy silane can undergo chain elongating, but not crosslinking.

Table 9: Time resolved rheology measurement of **P1**, **P8**, **S2**, **S4** and **S6** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions. Table shows the time until cross-over point and viscosity at crossover-point [Pas].

Silane	Time until crossover-point [min]	η^* at crossover-point [Pas]
P1	10	0.70
P8	35	0.73
S2	110	0.51
S4	40	0.71
S6	40	1.63

The data in Table 9 clearly shows differences in time until cross-over point between the different silanes. The difference can be correlated to how fast the silane forms a three-dimensional network and accordingly how high the hydrolysis rates of these silanes are. While the resolution of the measurement limits the significance slightly the general trends are still relevant. **S1** shows a significantly quicker crossover compared to all other measured silanes, indicative for its reactivity and fast formation of a gel-like substance once exposed to ambient conditions, highlighting its reactivity, likely induced through the α -effect. Crossover times for **P8**, **S4** and **S6** are comparable, this correlates with similar reactivity of the silanes, while **S2** shows a crossover only after 110 minutes, showing its comparatively low reactivity. Additionally, the viscosities at which the crossover occurs are constant throughout almost all silanes, with **S6** being the exception. The viscosity at crossover can thus not be used for a reliable determination of reactivity. The increased viscosity of **S6** can be attributed to partial hydrolysis of the compound prior to the conducted measurement.

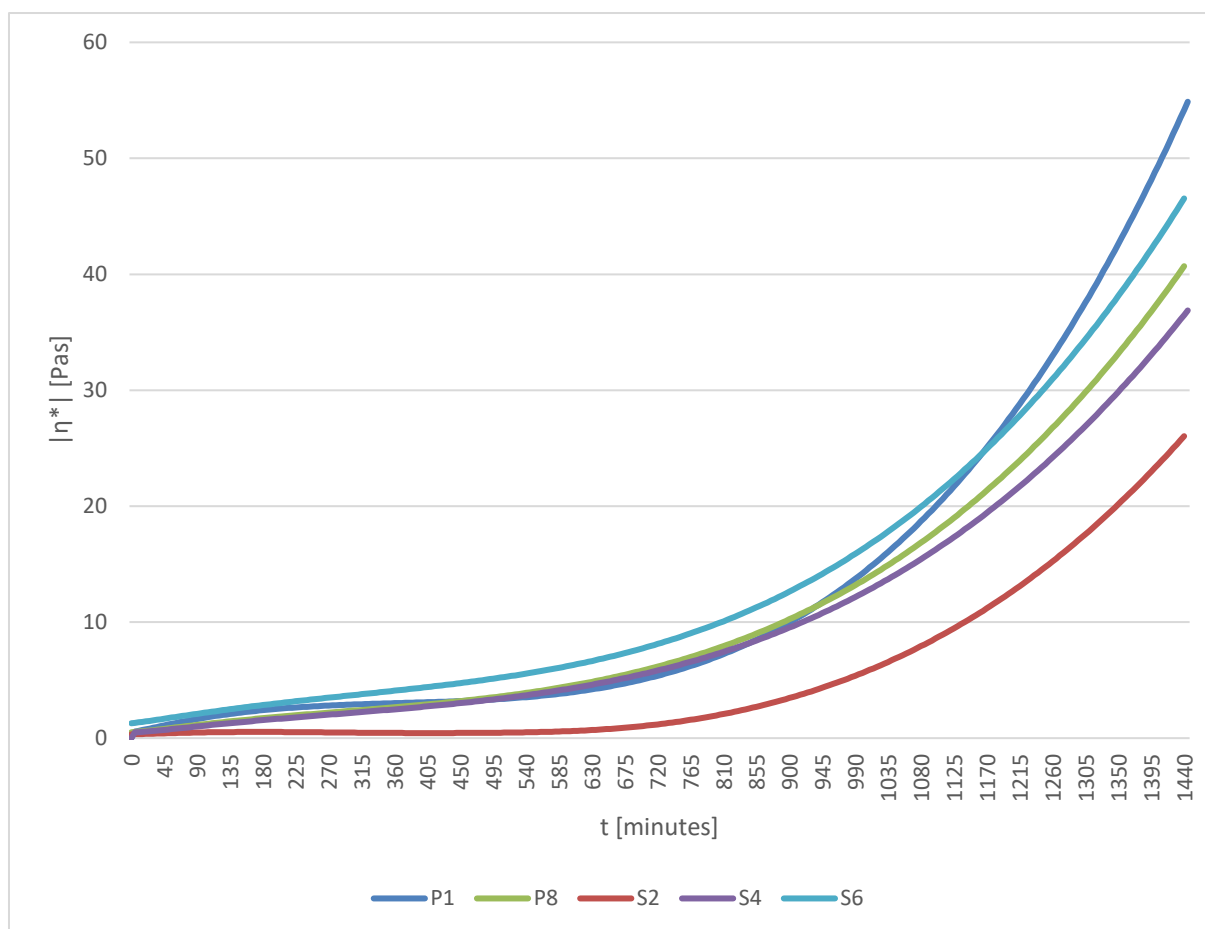


Figure 48: Time resolved rheology measurement of **P1**, **P8**, **S2**, **S4** and **S6** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions.

Figure 48 shows the time resolved changes in viscosity of all measured silanes (**P1**, **P8**, **S2**, **S4** and **S6**). All silanes show increases in viscosity, with **S2** viscosity significantly lower than the other silanes, this can be attributed to the fact that the methyl group substituent in **S2** does not contribute to its reactivity, thus it can be assumed as a baseline. **S4** shows increased reactivity over **S2**, but results in lower viscosity than the other silanes, likely due to a small contribution of the vinyl group to its reactivity. **S6** is known for its high hydrolysis rates and this phenomenon was confirmed through the measurements presented here. Compared to these established silanes, **P8** is of similar reactivity. However, it must be noted that it is not cleaving methanol, but ethanol. These measurements suggest a similar reactivity of **P8** as common methanol cleaving silanes, this is potentially interesting for applications where methanol free curing is required. Lastly, **P1** shows higher resulting viscosity than any other silane tested here, confirming the reactivity attributed to these silanes through the α -effect, even outperforming the industry standard **S4** while being amine free, this can be especially relevant for applications where amines cannot be applied, such as in systems using titanates as curing catalysts or very sensitive surfaces are contacted.²²¹ In this context, it is particularly relevant that all measurements were performed in the absence of a curing catalyst, thereby capturing the intrinsic

viscosity changes and corresponding reactivities. These parameters may be subject to variation depending on the specific catalyst used in an application-relevant system.

The study is limited by the gelation of the material under investigation. In some instances, the gelled material is expelled from the rotor as small chunks, rendering it unavailable for measurement. This phenomenon is visually observable as the expulsion of chunks. Additionally, the data reveal a rapid decrease in viscosity accompanied by erratic fluctuations in the signal, further indicating measurement disruptions. This phenomenon is inherent to the measurement and in most cases only evident at significant viscosities, usually in the area of high G'' where plastic deformation is predominant.

This chapter successfully demonstrated the correlation between the curing behaviour of selected novel α -silanes, as well as known reference silanes and their viscoelastic properties measured over a 24-hour period under standardised conditions. After an initial phase dominated by measurement oscillations, a clear increase in viscosity was observed. The evolution of the key parameters, G' (storage modulus) and G'' (loss modulus), revealed an initial predominance of viscous behaviour, followed by a transition to predominantly elastic behaviour as evidenced by the crossover point where G' exceeds G'' . By comparing the crossover points across the different silanes it was possible to assess their relative reactivities and curing characteristics. Notably, the α -silane derivatives from this work exhibited faster crossover points and more rapid increases in viscosity, while their initial viscosities remained comparable to those of the reference silanes. These results confirm the proposed α -effect in the silane curing process.

3.4 Large-scale synthesis

While the previous chapters focussed on the conception, synthesis and application of a novel class of reactive siloxanes this chapter focusses on the large-scale synthesis of the previously presented compounds. Screening experiments for both Grignard and catalyst-based reaction have been performed on 250 mg scale. For characterisation and application in the previous chapters selected compounds have been synthesised on 10 g scale. This was enough for physicochemical characterisations and application in e.g. resin formation. These results are satisfactory reactions on 10 g scale but are not industrially relevant. Thus, subsequent upscale experiments of the Grignard route described in chapter 2.4 were performed in close cooperation with Henkel AG. Substantial work on the large-scale safety of Grignard reactions has been published by Kryk *et al.*¹⁴⁵ While large scale Grignard reactions are frequently performed by students and in pharmaceutical synthesis²²² when not performed with proper preparation and precautions they can pose a substantial risk. Major problems occur when the reaction start is delayed due to trace impurities, such as water. Additionally, accumulation of organo-halide can lead to side reactions as well as unexpected consecutive

exothermic reactions.¹⁴⁵ While it is common in industrial synthesis to prepare a detailed operation procedure, with Grignard reaction it is vital to have applicable methods in case of a delayed reaction start or strong exothermic behaviour.²²³ Additionally, methods must be in place to safely interrupt the reaction at any point and if necessary, abort the setup. Online monitoring of the setup can aid in assessing the reactions behaviour *in situ*. It is advised to use a reflux condenser to allow an efficient and safe control of spontaneous exothermic bursts, however a process under reflux conditions requires monitoring of flow rates as conventional temperature measurements of the reactor do not give information over internal temperature increase. Additionally, cooling jacket inlet and outlet temperatures can be used to determine the heat balance of the reaction when a closed system is used. Since closed pressure systems make reaction setups more challenging the reaction at hand will be performed at atmospheric pressure using a reflux condenser but below the solvents boiling point, recording inlet and outlet temperatures. The condenser is thus used as a safety requisite rather than an active component in the process. The influence of water content on the initiation time has been investigated and found to be directly correlated.²²⁴ During processing, the water content of substrates, solvents and the reactor must be kept as low as possible. While substrates and solvents can be acquired dry or dried on preparative scale in a laboratory the reactor needs to be prepared separately. Tilstam and Weinmann²²⁵ reported water contents of 20 ppm after rinsing with solvent and blowing with dry inert gas, followed by keeping a slight positive pressure on the reactor to avoid any air leaking in. They furthermore reported different strategies on magnesium preparation. The usage of magnesium turnings is reported advantageous over powder as the reduced surface is oxidised less and can result in lower activity. While it may seem counterintuitive as reduced activity will increase reaction time, but also prevents so called runaway reactions.²²⁶ Furthermore turnings are less pyrophoric than powder, a relevant factor when handling considerable quantities of the substance. The oxide layer can be reduced by the addition of a mineral acid or pure iodine, else mechanical stress induced by stirring in the reactor can break the tunings and thus expose non oxidised surfaces when performed after reactor drying.²²⁵ A fall back strategy during large scale production can be the simultaneous preparation of a small batch reactor in a laboratory and transfer to the large scale reactor which immediately consumes all residual water and thus initiates the reaction. This is generally applied when the reactor batch won't start after a predefined period of time.²²⁵ It is important to note that there are significant toxicity differences between ethoxy and methoxysilanes and when handling large amounts (over 100 g) this must be factored in.¹⁵⁴ Thus, the following synthesis will be conducted with the slightly less reactive ethoxysilane. When no ethoxy based replacement is commercially available the methoxy derivative is used (see Figure 50).

With all precautions at hand an upscale of general reaction procedure A to 3 kg was planned and conducted in cooperation with Henkel AR. Synthesising compound **P1** and **P4** in a 20 L steel reactor in an upscale plant (Figure 49).

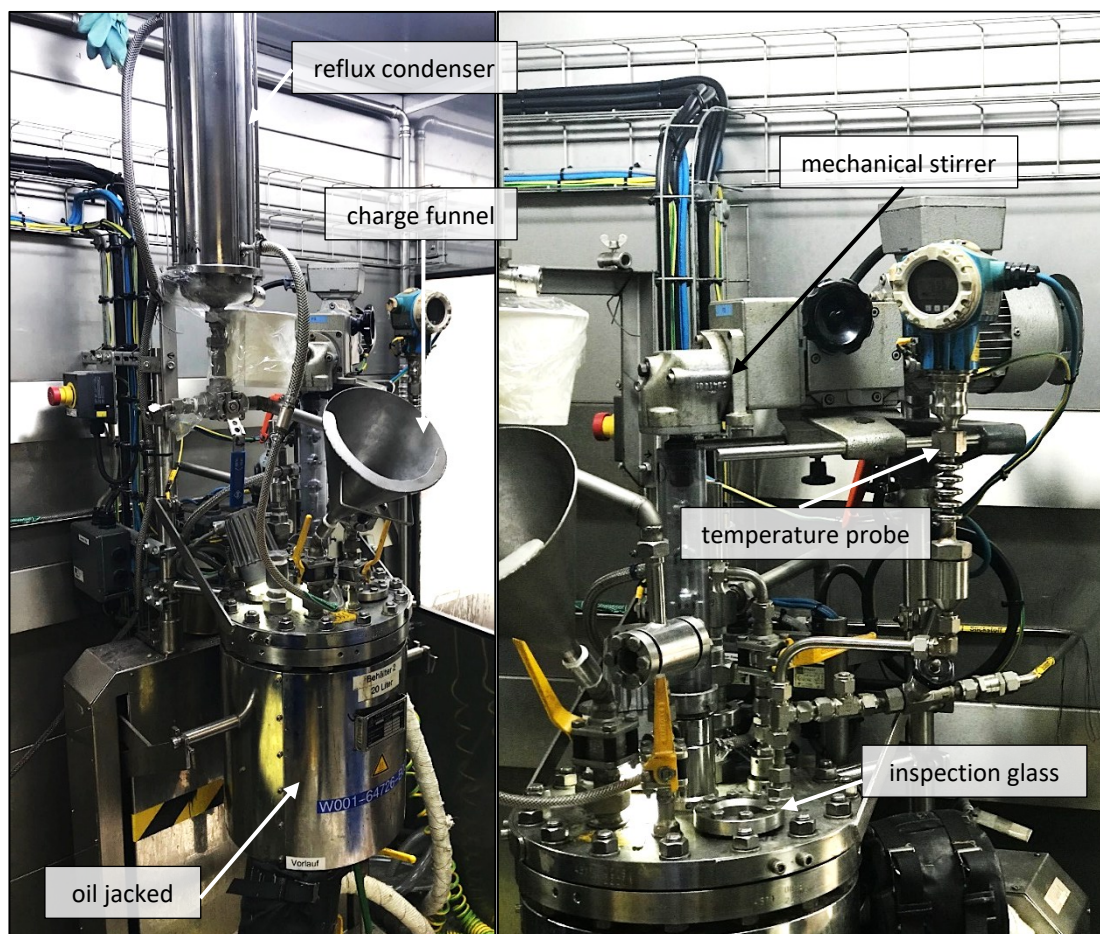


Figure 49: 20 L steel reactor at Henkel AG equipped with oil jacketed, mechanical stirring and reflux condenser. Several temperature probes and an inspection glass allow insights to the reactions progress.

Safety procedures and precautions were prepared and closely followed. The reaction apparatus was placed in a floor mounted fume hood and only entered wearing personal protective equipment, as well as a full-face gas mask equipped with AXBEKP3 filter. The steel reactor is equipped with an oil filled jacket cooler connected to a oil-water heat exchanger, a high efficiency water cooled reflux condenser and mechanical stirring. The reactor is pre-dried at 80 °C and 1.5 mbar for 4 h and then rinsed with acetone three times and blown dry with nitrogen gas. The appropriate amount of magnesium shavings was pre-dried at 280 °C and $1.0 \cdot 10^{-3}$ mbar for 1 h and transferred into the reactor, the setup was allowed to cool down to ambient temperature at a nitrogen pressure of 1.05 bar, preventing any moisture contamination. 600 mg Iodine were charged into the reactor and left to etch while stirring for 30 minutes, followed by 10 L THF. Tetra ethoxysilane was added to the reaction mixture and 7 vol% of the to be added 2-Bromothiophene are dosed using a peristaltic pump. After 34 minutes an increase in temperature from 26 °C to 46 °C is observed. This increase in

temperature is likely linked to the initiation of the reaction, however the temperature of circulating oil kept increasing to 37 °C, with no reduction in temperature after no further addition. This is likely due to the inefficient heat exchange between oil and water run in the setup, as it is designed to act as a thermostat rather than a cryostat. After this problem was resolved the reaction would not restart even after dosing a total of 4 vol% 2-Bromothiophene. Per previously defined code of conduct a previously prepared small-scale Grignard (10 g) setup was initiated and once active as indicated by a rise in temperature, transferred to the steel reactor. The remaining 2-bromothiophene was dosed at 5 ml per minute not exceeding 46 °C core temperature. After the addition was finished, the reactor was heated to 60 °C for 1 h. The reflux condenser is swapped for a Claisen bridge and THF is distilled off at 40 °C and 210 mbar, leaving a grey residue. A slurry was formed with the addition of 4 L dry n-Heptane and transferred to a dry flask under nitrogen. The slurry was filtered using a PALL high-pressure plate filter and POR3 equivalent plates²²⁷ at 6 bar nitrogen. The resulting liquid was distilled at 45 °C at 30 mbar. NMR signals are identical to previously reported signals in this work. The resulting product was isolated at a gross yield of **P8** at 81 % and at 76 % purity. An identical reaction setup and procedure was used in the large-scale synthesis of compound **P4**, resulting in a slightly yellow, clear liquid containing compound **P4** at of 87 % yield and at 79 % purity. In both cases the major impurity is the used silane.

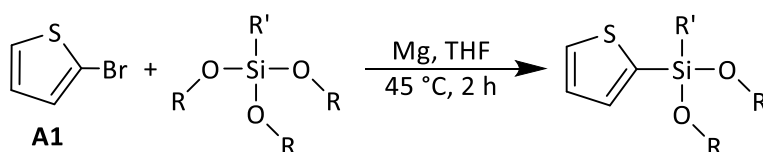


Figure 50: Grignard reaction of 2-bromothiophene and an alkoxy silane with magnesium shavings in tetrahydrofuran (THF) at 45 °C for 2 h at 3 kg scale. Silane **S8** (R = Ethyl, R' = Ethoxy) was used to yield **P8**, **S4** (R = Methyl, R' = Vinyl) was used to yield **P4**.

The increase in yield when performing the reactions on large scale when compared to the small batch setups used throughout this thesis at around 250 mg is attributed to less loss during the washing and filtration step, loosing less overall material in the filter material and a more efficient phase separation. To sum up the reported upscales the developed method is robust enough to be upscaled several powers and still yield satisfactory results. While chemically the reaction did work out well the added procedural overhead must not be neglected, as substantial preparations and 4 days of continuous work by at least two people in parallel is needed for smooth and safe processing. The preparation and running of upscales as presented here pose a great challenge but are equally rewarding especially when a compound that was first isolated on milligram scale less than six month ago is produced on kilogram scale. The successful upscale allowed for broad testing of different applications analogue to industrially relevant products, reported in section 3.5 of this work.

Like the Grignard based approach the previously reported and optimised catalytic setup was scaled up to 500 g in a double walled glass reactor. As prerinsing the reactor with acetone worked well this setup

was subjected to similar preparation as previously reported. Rinsing with acetone was followed by heating and vacuum, cooling down under nitrogen atmosphere. Workup has been performed in accordance with representative procedure B. The reaction proceeded as expected and formed the target compound at sufficient yield. The only challenge that must be overcome during reaction setup is the limited stability of the used palladium precursor when in contact with air, potentially limiting its applicability in bigger upscale reactions. The presented methods result in good yield and form the product at excellent selectivity. The reaction time and volume needed to produce comparable amount of pure compound is significantly lower, allowing for high turnover times and less running cost in commercial application. As per optimisation experiments and first scaleups batch reactors were used. For more industrially relevant applications a pilot plant using a more elaborate reactor setup may be used. While the experiments reported here have shown the feasibility and provided initial material for physical, application related testing a commercial application will require the large-scale production of the shown compounds.²²⁸

Panov *et al.* showed the beneficial use of methoxy and ethoxy cleaving alkoxy silanes in Grignard reactions, as the formed alkoxy magnesium halide complexes with the *in situ* formed Grignard reagent instead of the Grignard reagents with themselves, significantly increasing the reactivity. The effect is proposed to be caused by the electron donating nature and no steric hindrance of the two smallest alkyloxy derivatives.²²⁹

This concludes the successful scale up of the optimised reactions presented in chapter 2.4 and 2.5 from small laboratory to industrial scale. With the necessary precautions it was possible to transfer gained knowledge from laboratory to industrial scale and produce substantial amounts of novel α -silanes that can be used in downstream applications, such as presented in chapter 3 of this work. Furthermore, this concludes the flow chart presented in the beginning of this work as shown in Figure 51.

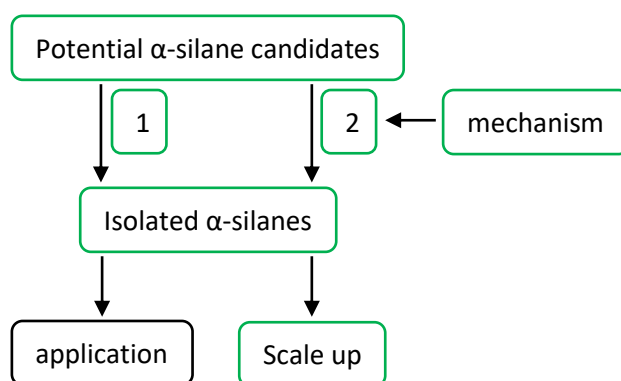


Figure 51: Flow chart presenting the general structure of this thesis with the upscale of both reaction routes completed.

3.5 Application of novel α -silane derivatives in commercial RTV-1 curing formulations

In this chapter all previously described silane derivatives were applied in commercially relevant silicone RTV-1 formulations. A formulation in the field of silicone adhesives and sealants is considered a mixture

of its components. The differences in silicone curing technology were established in chapter 1.4 of this work. The silicone used for this work is a RTV-1 system curing via the hydrolysis of alkoxysilanes to form a three dimensional network and thus curing the system. The system at hand is applied throughout a plethora of ambient conditions and surfaces. The system is made from a MW 100.000 g/mol bis hydroxide end capped PDMS, in this section referred to as “PDMS”. The PDMS is then end group functionalised through condensation with a trialkoxyvinylsilane. Most commonly vinyltrimethoxysilane is used, such compounds are referred to as “crosslinker”. These T units are reacted with the hydroxy end groups of PDMS to form polymer functionalised with reactive end groups that will undergo condensation in the presence of moisture eventually and in the presence of a curing catalyst. A common catalyst in the industry and used in the examples of this section is dioctyl-tin-dilaurate. A so-called “plasticiser” comprised of a variety of different bis-methyl end capped PDMS is added to the formulation making it more pliable once fully cured. In contrast to the PDMS plasticisers are not chemically bonded into the polymer matrix during curing. Lastly additional compounds are added to potentially increase the adhesion to different substrates. Such formulations are commonly sold in polyethylene cartridges, in some cases in coated aluminium foil bags or aluminium cartridges, giving them better shelf life due to higher moisture barrier properties of these materials. From these containers formulations are applied with a specialised cartridge gun, commonly available in home improvement stores, dispensing the material through a nozzle onto the to be sealed surface. A schematic depiction of a cartridge is shown in Figure 52.

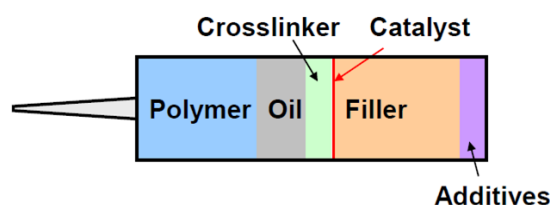


Figure 52: Exemplary schematic composition of a silicone cartridge composed of rough relative amounts of polymer, oil, crosslinker, catalyst, filler and additives.

The advantages of silicone-based formulations have been explained throughout this work. Their key benefits are broad temperature applicability, resistance to moisture and radiation. However, they also face challenges that are addressed in commercial formulations through the inclusion of additives and modification of the used polymers. A few exemplary challenges are shown here. High curing times can cause a vertically applied product to sag and leave an inhomogeneous seal, additionally high curing times leave the material susceptible to damage. Similarly, the time of material to form a “skin”, a first layer of material that has transitioned from pasty to flexible solid, is relevant. Before the formation of a skin the material can be worked, however is again susceptible to damage. Compatibility with other materials can be challenging dependent on the leaving group used in the formulation. Commonly acetoxo cleaving systems have good adhesion to surfaces, while the through condensation release

acetic acid can interact and subsequently damage pH sensitive surfaces such as copper²³⁰ or marble.²³¹ Other leaving groups while inert to substrates can have reduced adhesion to surfaces.

Lastly formulations, especially when sold as end-user or consumer products must comply the locally applicable standards, such as regulation concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH)²³² in Europe and United States Food and Drug Administration (FDA)²³³ in the US.

Any resulting physicochemical effects are recorded through a standardised testing regime. Tested parameters include skin over time (SOT), colour, tack free surface after 24 h, hardness after 1 day and 7 days and adhesion to various testing substrates through bead peel tests. Skin over time is measured in minutes after application of the composition to a surface. It represents the time required for the transition of the compositions surface from liquid to gel, visually shown through a change in material stringing when touched to forming a coherent film, not adhering when touched. Colour is assessed by measuring the materials surface colour in the CIELAB (L*a*b) colour space.²³⁴ When working on formulas intended for consumer applications often only the b component of colour is reported, as the b component is representative for yellow in the materials colour, directly correlating to the amount of yellowing a formula shows. Tack free refers to the absence of extractable or sticking compounds in a formula according to ASTM C679²³⁵, desirably after 24 hours, especially important for consumer products where dust and other particles may adhere to the materials surface. Shore A per ASTM D2240²³⁶ refers to the resistance of a materials surface to indentation or penetration by a standardised probe with defined shape and force, where the depth of indentation is anti-proportional to a unitless scale from 0 to 100, with full penetration at 0. Shore A is commonly used to refer to a material hardness, measured here after 1 day and 7 days to represent the materials initial hardness during curing and final hardness, assuming full curing after 7 days. Peel tests in accordance with ISO 11339²³⁷ are conducted to measure the cured formulas adherence to various substrates, indicating coherence failure of the formula or adherence failure to the surface, after applying increasing forces. Coherence failures at high required forces are desirable.²³⁸ For the purpose of comparison cohesion and adhesion failures are translated to numeric values 1-10. Where 1 indicates no adhesion, 5 indicates strong adhesion with beginning cohesion failure and 10 indicates adhesion failure with high force required.

To refine adhesion, skin formation and curing speed the base formulations are adapted and where necessary modified with additives. The compounds previously described in this work, as well as the modified PDMS and resins described in chapters 3.1 and 3.2, were incorporated in an exemplary formulation of the general composition shown in Table 10, more details available in Appendix A3. Targeting a reduction in skin formation times, improvement of adhesion and increase in curing speed.

Application of novel α -silanes in polymeric materials

Table 10: General composition of a representative formula used to assess the performance of silanes described in this work.

Compound	Relative amount
PDMS	80
Plasticiser	10
Silica	5
Crosslinker	4.9
Catalyst	0.1

The compounds are worked into readymade formulations through rapid contactless mixing, at the stated concentrations. To explore the impact of the novel silanes described in this work they were compared to the performance of the baseline formulation. To aid in comparability an additional experiment is shown with a commercially available silane at the same concentration. The silanes performance was evaluated in a formulation closely related to commercially available products to aid in industrially relevant applicability. Figure 53 shows the impact of adding 1 wt% of selected silanes from this work compared to the currently available baseline.

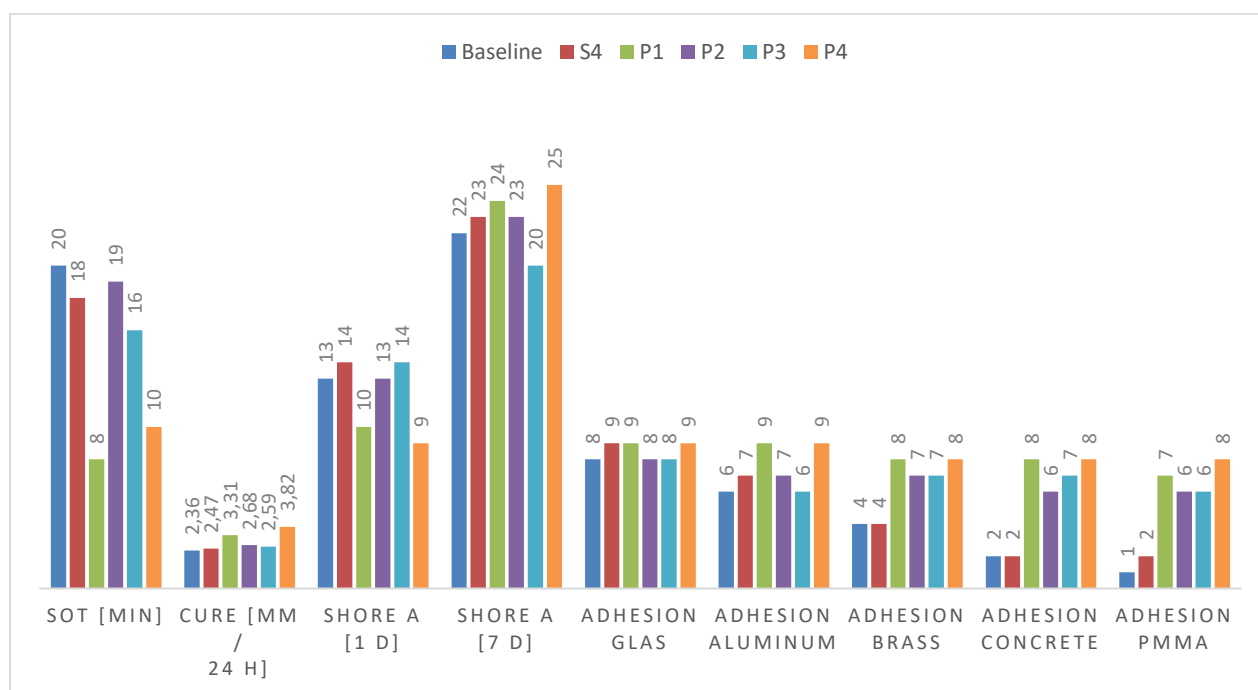


Figure 53: Use of a representative silicone formulation and measurement of associated physical parameters skin over time (SOT) (lower is better), cure through (higher is better), Shore A after one and seven days (higher is better), and adhesion on various substrates (higher is better) as baseline as well as stated silanes as additives.

With the baseline established comparison of various additives to the formula indicates several trends between the addition of a common vinylsilane **S4**, **P1** and **P4**, as well as **P2** and **P3**. In all instances adding **S4** slightly improves the performance of the baseline formula, indicating that through the addition of a reactive silane performance can be improved, however in most cases improvements are minor. Comparing the baseline performance and **S4** to values measured after the addition of 1 wt% **P1** or **P4** improved physical parameters are observed throughout the series with significant SOT

reductions indicating high reactivity and ability to rapidly form a skin and most notably significantly improved adhesion on the chosen model substrates especially on PMMA, a plastic where the baseline shows no adhesion. Compared to the high reactivity and improved adhesion of **P1** and **P4** the series using **P2** and **P3** shows minor changes in reactivity but results in a similar adhesion improvement compared to previously tested silanes. This test indicates that through the careful choice of heteroaryl silane from this work the material properties of a silicone formula can be tailored.

In a second iteration the functional PDMS described in 3.1 of this work end-group-functionalised with both **S4** (vinyltrimethoxysilane) and **P1** were incorporated into the baseline formula from Table 10 as 1 wt% additives with their respective performance shown in Figure 54.

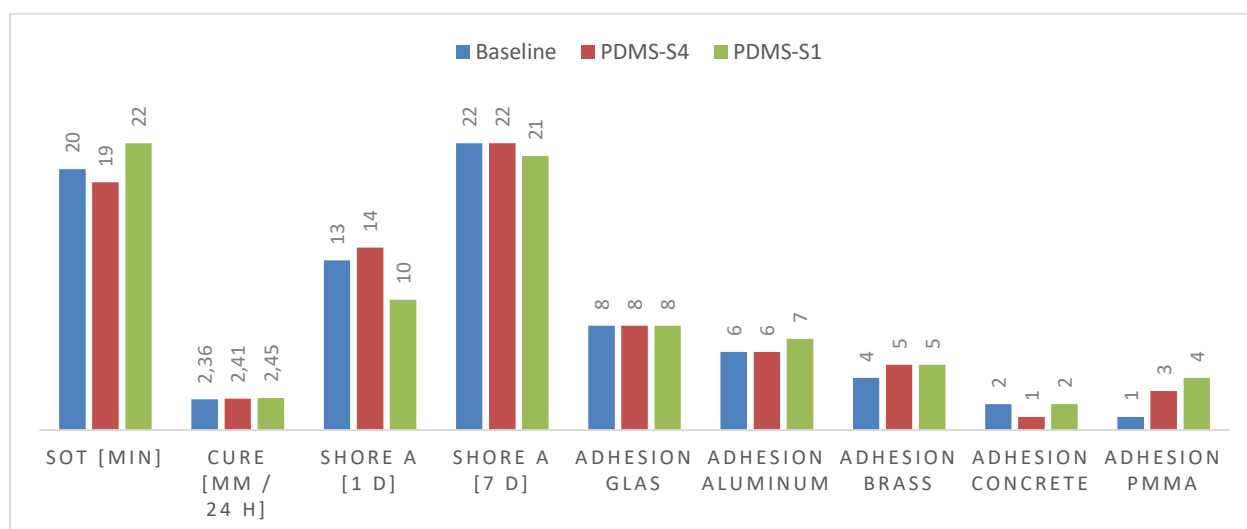


Figure 54: Use of a representative silicone formulation and measurement of associated physical parameters skin over time (SOT) (lower is better), cure through (higher is better), Shore A after one and seven days (higher is better), and adhesion on various substrates (higher is better) as baseline as well as PDMS functionalised with **S4** and **S1** from 3.1 of this work.

The assessment of using end-group functionalised PDMS in a reference formulation no significant differences between either the different PDMS derivatives nor to the baseline was observed. This might be associated to the low amount of material used in this study.

The tests above clearly indicate a positive influence of the silanes described in this work when added to an RTV-1 silicone formulation at 1 wt%, additionally this effect was shown to go beyond the use of a common commercially available silane. Interestingly reactivity differences between the silanes from this work had an influence on the time to form a skin and shore hardness, while all silanes showed a beneficial effect on the formulation's adhesion. The addition of an end group functionalised PDMS did not show significant improvement in these parameters. These findings were first published in the PCT patent application WO2023156603A1.²³⁹ Lastly this concludes the initially presented flowchart with the last step of this thesis, the application of novel α -silanes as shown in Figure 55.

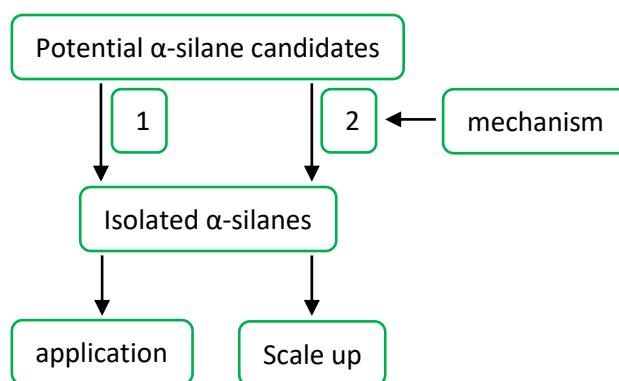


Figure 55: Flow chart presenting the general structure of this thesis, all steps completed.

3.6 Summary

- This chapter showed the use of novel alpha substituted alkoxy silane in a variety of applications highlighting the usability and suggested reactivity increasing effect associated with these silanes.
- End-group functionalisation of PDMS was successfully presented and polymers isolated.
- The silanes presented in chapter 2 of this work were successfully transferred to resins through controlled hydrolysis. Additionally, the silanes reactivity was studied through rheologic investigations, confirming the increased reactivity of the silanes when compared to structurally similar commercially used counterparts.
- Scalability of production using the route optimised in 2.4 was shown, including associated safety considerations. Showing the first large scale synthesis of compounds **P1** and **P4** introduced in this work.
- The use and effects of the isolated silanes, as well as the postprocessed compounds made through polymer modification and condensation in commercially relevant RTV-1 silicone formulations was shown. Confirming the positive impact of these silanes on reactivity and adhesion.
- The findings presented in this chapter lead to three PCT patent applications.^{199,216,239}

4 Conclusion and Outlook

α -Silanes are a relevant specialty class of reactive silanes, making use of the α -silane effect that significantly increases the reactivity and hydrolysis rate of reactive leaving group. This work is the first comprehensive study of sp^2 linked α -silanes. Due to the size of the substance class a preselection to the subclass of heteroaryl derived alkoxy silanes was made. This work comprehensively showed the design, synthesis and application of a novel class of α -silanes and confirmed the presence of an α -silane effect in their reactivity.

Chapter 2 showed the conceptualisation of this subclass, aiming to synthesise a variety of silanes, covering a broad range of likely material properties, as well as chemical derivatives to show the scope of this subclass. Two different synthesis strategies, stoichiometric Grignard reaction and palladium assisted carbon-silicon cross-couplings, were employed to synthesis the silanes in an efficient manner. Both reaction approaches were optimised for the target silanes and their respective scope was explored. Due to the wide variety of commercially available substrates and use of an alkoxy leaving group for the carbon-silicon bond-formation in the Grignard approach a broader scope could be achieved. Contrary, the catalysed approach uses Si-H containing substrates, limiting the approach to structural derivatives that are available with silane modification. Nevertheless, a high conversion, high selectivity catalysed approach allowed efficient access to a large variety of heteroaryl substituents. All α -silanes described herein were isolated through fractioned distillations and most were first described and characterised in this work.

Chapter 3 described the use of the silanes presented in chapter 2 in polymer end-group functionalisation, condensation towards resins and the use of the silanes, as well as these downstream products in commercially relevant formulations, resulting in increased reactivity and adhesion of the formulas. Furthermore, the reactivity of the silanes was confirmed through rheological investigations observing the increased hydrolysis rate when compared to chemically similar silanes. Moreover, given the demonstrated scalability and safety considerations, there is a clear pathway for industrial stakeholders to adopt these materials in large-scale manufacturing processes. Over time, these advances could contribute to more durable, higher-performance silicone-based products in sectors ranging from construction to electronics, reinforcing the significance of α -substituted alkoxysilanes as a versatile and impactful class of materials.

From the findings of this work a total of four PCT patent applications were filed.^{191,199,216,239}

Additional work extending the scope beyond heteroaryl derived sp^2 linked α -silanes may open up additional pathways and possibilities to new, reactive silanes. Mechanistic studies could benefit from advanced characterisation techniques, such as *in situ* spectroscopy and computational modelling, to

gain even deeper insights into reaction pathways and potentially identify entirely new transformation routes.

“And, when you want something, all the universe conspires in helping you to achieve it.”

Paulo Coelho

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Appendix

A1 Equipment and testing methods

Equipment:

All presented reaction were, if not indicated otherwise, performed under moisture free conditions and argon gas using Schlenk techniques for liquid and a glovebox for solid handling. All gasses were dried by passing them through a Sicapent® (phosphorus pentoxide with moisture indicator on inert carrier material) filled column. All equipment used was pre-heated in an oven to 80 °C, assembled hot and subjected to three vacuum (at least 1.0×10^{-2} mbar)-argon filling cycles.

Vacuum was measured using a CVC 3000 Vacuubrand directly attached to a Rettberg PTFE vacuum distributor and a Vacuubrand RZ 9 rotary vane pump. Highly moisture or air sensitive compounds were handled under argon in a MBraun LABmaster pro ECO glovebox, controlled by a Siemens Simatic HMI. Spedmixing is conducted using a Hauschild SpeedMixer® DAC 400.

NMR-Spectroscopy:

If not indicated otherwise NMR spectra were measured on a Bruker AV 300 (^1H = 300 MHz, ^{13}C = 75 MHz, ^{29}Si = 60 MHz) and AV 400 (^1H = 400 MHz, ^{13}C = 101 MHz, ^{29}Si = 79 MHz, ^{31}P = 162 MHz) instrument with deuterated solvents. All 2D spectra presented in this work were recorded on an Agilent DD2-600 MHz (^1H = 600 MHz, ^{13}C = 151 MHz, ^{29}Si = 119 MHz, ^{31}P = 243 MHz).

If not indicated otherwise all samples were measured at room temperature (297 K). Chemical shifts are reported in parts per million (ppm). All spectra were calibrated using the chemical shift of the used deuterated solvent and where applicable automatically calculated from the recorded ^1H spectra.

MS:

MS spectra were recorded using Agilent 6890/5973 (GC-MS), Agilent 7890/5977 (GC-MS), Agilent 1260/6130 Quadrupol (LC-MS) or Agilent 1200/6210 Time-of-Flight (LC-MS)

GPC:

Gel permeation chromatography was carried out on a HP1090 II with DAD detector at 40 °C using toluene as an eluent. The samples were passed through three PSS SDV gel columns with molecular weight ranges of 102, 103 and 104 g·mol⁻¹ at a flow rate of 0.9 ml·min⁻¹. The device was calibrated using polystyrene standards.

Elemental analysis:

All analysis was prepared and conducted by the analytics department at Leibnitz Institute for Catalysis e.V. A Leco TruSpec-932 was used for hydrogen, carbon, nitrogen and sulphur. Silicon and palladium were detected using a Perkin-Elmer Analyst 300 via atomic absorption spectroscopy.

Infrared Spectroscopy:

Infrared spectra were measured using ATR (attenuated total reflection) technique on a Bruker Alpha FT-IR-Spectrometer. All samples were directly applied to the diamond detector window. Absorption is reported in wave numbers cm^{-1} and measured in the range of 7000 – 375 cm^{-1} .

Viscosimetry:

Rheological measurements on samples were performed using a RheoStress 1. Either CR-Mode (controlled rate) at 25.00 °C or a self-developed method running time resolved CD-Mode (controlled deformation). The appropriate method is stated at each report. CR-Mode experiments were performed using a C35/1 ° Ti L cone-plate geometry from ThermoScientific. CD-Mode experiments were performed using a ring-rotor PR35-27 plate-plate geometry with circular cut-out eliminating mass transport limitations during time resolved experiments.

A2 Materials

If not indicated otherwise, all reagents were obtained from commercial suppliers and used without further purification. All solvents were obtained from commercial suppliers in p.a. or HPLC quality.

The following chemicals were obtained from Acros Organics; 1,1,3,3-Tetramethyldisiloxane, 1-Methyl-2-pyrrolidone (dried, under septum and over molecular sieves), Acetone, Chloroform, Dichloromethane, Dimethylformamide, Dimethylsulfoxide, Ethanol, Methanol, n-Heptane, n-Hexane, n-Pentane, Tetrahydrofuran (stabilized), Tetrahydrofuran (dried, stabilized, under septum and over molecular sieves), Toluene, Toluene (dried, under septum and over molecular sieves).

From Alfa Aesar Platinum on carbon was acquired.

The following chemicals were purchased from ChemPUR: 2-Iodothiophene, Chloromethyl(dimethyl)methoxysilane, Methoxydimethylvinylsilane, Thiophene.

All deuterated solvents were purchased from Deutero and Eurisotop; Acetic acid-d₄, Chloroform-d, Dichloromethane-d₂, Ethanol-d₆, Methanol-d₃, Methanol-d₄, Tetrahydrofuran-d₄, Toluene-d₈.

All chemicals listed below were acquired from fisher scientific: 2,5-Dibromo-3-methylpyridine, 2-Acetyl-5-bromothiophene, 2-Bromo-3-methylthiophene, 2-Bromo-3-thiophenecarboxylic acid, 3-Bromo-4-methylthiophene, 3-Bromofuran, 5-Chloro-2-furaldehyde, stabilized with 2% ethanol, 5-Chlorothiophene-2-sulfonamide, Methyl-diethoxysilane, N-Ethyl-diisopropylamine, Tetramethylammonium iodide, Tri(o-tolyl)phosphine, Triethoxy silane, trifluoromethanesulfonic acid.

The following chemicals were acquired from MilliporeSigma: [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane, 2,5-Dibromothieno[3,2-b]thiophene, 2,6-Dichloropyridine, 2-Iodo-1-methyl-1H-imidazole, 2-Bromo-1H-imidazole, 2-Bromo-3,5-dimethylthiophene, 2-Bromo-5-dodecylthiophene, 2-Bromobenzothiophene, 2-Bromopyrimidine, 2-Bromothiazole, 5-Chloro-2-thiophenecarbonitrile, 2-Thienyllithium, Allylpalladium(II) chloride dimer, Bis(triphenylphosphine)palladium(II) dichloride, Cyclopentadienyllithium, Isopropylmagnesium chloride solution, Palladium(II) chloride, Palladium(II) acetate, Platinum(IV) oxide, Tetrakis(triphenylphosphine)-palladium(0), Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Tetramethyl-orthosilicate, Trichlorosilane, Tris(dibenzylideneacetone)dipalladium(0), 2,5-Dibromo-3-methylthiophene.

The following chemicals were acquired from Tokyo Chemical Industry: 1,1'-Bis(diphenylphosphino)ferrocene 1-Methyl-2-pyrrolidone, 2-(Di-tert-butylphosphino)biphenyl, 2,3-Dihydrofuran, 2-Bromo-5-methylthiophene (stabilized with Copper chip + NaHCO₃), 2-Bromofuran (stabilized with CaO), 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl, 3,4-Dihydro-2H-pyran, 3-Sulfolene, 4-Formylmorpholine, Bis(dibenzylideneacetone)palladium(0), Chlorotriethoxysilane, N,N-Diisopropylethylamine, N,N-Dimethylacetamide, Silver trifluoromethanesulfonate, Tetramethylurea, Trichlorovinylsilane.

A3 Experiments and compound analysis.

If not stated otherwise all experiments have been repeated at least once, averaging the resulting yields from all experiments.

Synthesis of alpha heteroaryl substituted siloxanes

Representative procedure A:

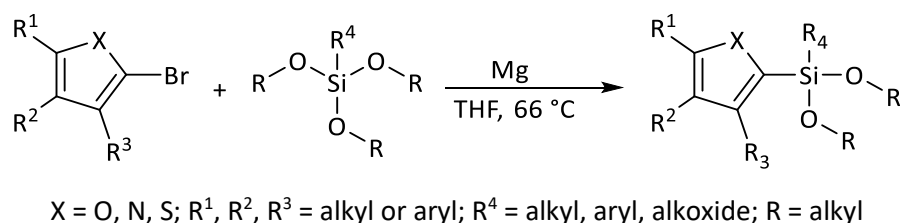
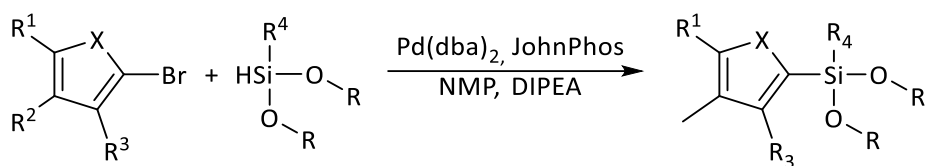


Figure S6: Reaction equation of representative procedure A. Reaction between a brominated, substituted heteroaryl with a substituted alkoxy silane in presence of magnesium in tetrahydrofuran (THF).

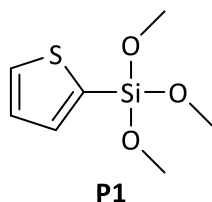
A three-neck round-bottom flask equipped with cooling condenser, dropping funnel, magnetic stir bar and a stopper is charged with magnesium chips (150 mmol, 1.5 eq, 3.6465 g) and flame-dried under reduced pressure and filled with dry argon. A crystal of iodine is added, etching the surface of the magnesium. Tetrahydrofuran (150 ml) followed by a silane of the general formula shown above is added to the flask (150 mmol, 1.5 eq). The stopper is swapped for a thermometer. To the dropping funnel 2-halogen heteroaryl (100 mmol, 1 eq) is added. While stirring, 10 vol% 2-bromothiophene is added to the flask in one portion. An increase in temperature is observed. Dropping is continued while maintaining a temperature between 40 °C and 50 °C. After the addition heating is turned on for 2 h. The tetrahydrofuran is distilled off, leaving a wet grey solid. Hexane (150 ml) is added to the flask and the solid is suspended, turning the colour from grey to white. The solids are filtered, and hexane is distilled off yielding a crude product at 10 – 75 %. Clean product is obtained by the means of vacuum distillation at 1.0 * 10⁻³ mbar at oil temperatures stated below.

Representative procedure B:

X = O, N, S; R¹, R², R³ = alkyl or aryl; R⁴ = alkyl, aryl, alkoxide; R = alkyl

Figure S7: Reaction equation of representative procedure B. Reaction between a brominated, substituted heteroaryl with a substituted alkoxy, hydro silane. Catalysed by Pd(dba)₂, JohnPhos and DIPEA in NMP.

A three-neck round-bottom flask is equipped with cooling condenser, two stoppers and a magnetic stir bar. The apparatus is flame dried under reduced pressure and filled with dry argon. Bis(dibenzylideneacetone)palladium(0) (Pd(dba)₂, 0.03 mmol, 3 mol%, 17.3 mg) and 2-(di-tert-butylphosphino)biphenyl (JohnPhos, 0.06 mmol, 6 mol%, 17.9 mg) are weighed into sample vials in a glovebox and subsequently transferred to the apparatus under air exclusion. One stopper is swapped for a septum. N-Methyl-2-pyrrolidone (99 mmol, 40 eq, 4.00 ml) is transferred from the storage container to the apparatus via an argon purged needle. Stirring is turned on, after a clear, dark red solution is obtained halogenated heteroaryl of the general formula shown above (1.00 mmol, 1 eq) is added, followed by N,N-diisopropylethylamine (3.00 mmol, 3 eq, 0.3877 g). To this an alkoxy silane (1.50 mmol, 1.5 eq) of the general formula shown above is added slowly. If applicable observations are reported for each compound. An oil-bath is added, and the reaction solution heated to 60 °C and stirred for 16 h. The flask contents are transferred to a separatory funnel and washed five times with pentane (5x 6 ml), washing the flask several times. The pentane phase is counter washed with deionized water. Any observations are reported for each compound. The pentane phase is dried over magnesium sulphate and low volatiles are removed on a rotary evaporator yielding a crude product at 35 – 95 °C. If necessary, vacuum distillation is performed identically with representative procedure A.

Synthesis of trimethoxy(thiophen-2-yl)silane (**P1**)

Compound **P1** was synthesised according to representative procedure A with 22.833 g **S1** and 16.303 g **A1**, distilling at 85 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 18.593 g of pure compound **P1** were isolated.

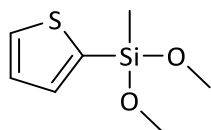
Compound **P1** was synthesised according to representative procedure B with 183.3 mg **S5** and 163.0 mg **A1**. 186.3 mg of **P1** at a purity of 89 % were isolated.

The analytical data were found to be identical within experimental between representative procedure A and B. This confirms that the same compound was obtained regardless of the synthetic route. Key characterisation data are summarized below.

¹H NMR (400 MHz, CDCl₃, 24 °C, ppm) δ = 7.77 (ddd, J = 12.2, 4.6, 0.9 Hz, 1H), 7.54 (dd, J = 3.4, 1.0 Hz, 1H), 7.31 (ddd, J = 4.6, 3.4, 1.0 Hz, 1H), 3.67 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, 24 °C, ppm) δ = 137.34, 132.39, 128.49, 128.46, 50.70. ²⁹Si NMR (79 MHz, CDCl₃, 24 °C, ppm) δ = -57.77. EA (% measured

(calculated)), C₇H₁₂O₃SSi: C 41.018 (41.15), H 5.9186 (5.92), S 15.92 (15.69), Si 8.02 (13.75). **MS (ESI-TOF)**: (*m/z* [M + H]⁺ measured (calculated)): 205.03; found: 205.0014.

Synthesis of dimethoxy(methyl)(thiophen-2-yl)silane (**P2**)



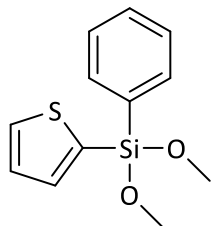
P2

Compound **P2** was synthesised according to representative procedure A with 20,433 g **S2** and 16.303 g **A1**, distilling at 63 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 14.783 g of pure compound **P2** were isolated.

Compound **P2** was synthesised according to representative procedure B with 106.2 mg **S29** and 163.0 mg **A1**. 148.2 mg of **P2** at a purity of 78 % were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.67 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.43 (dd, *J* = 3.4, 0.9 Hz, 1H), 7.23 (dd, *J* = 4.6, 3.4 Hz, 1H), 3.60 (s, 6H), 0.42 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 136.13, 132.62, 131.82, 128.32, 50.80, -3.93. **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -17.99. **EA** (% measured (calculated)), C₇H₁₂O₂SSi: C 44.703 (44.65), H 6.4246 (6.42), S 16.97 (17.02), Si 11.39 (14.91). **MS (ESI-TOF)**: (*m/z* [M + H]⁺ measured (calculated)): 189.03; found: 188.9976.

Synthesis of dimethoxy(phenyl)(thiophen-2-yl)silane (**P3**)

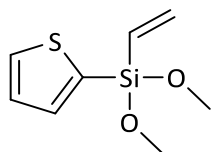


P3

Compound **P3** was synthesised according to representative procedure A with 29.744 g **S3** and 16.303 g **A1**, distilling at 142 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 17.853 g of pure compound **P3** were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.67 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.43 (dd, *J* = 3.4, 0.9 Hz, 1H), 7.23 (dd, *J* = 4.6, 3.4 Hz, 1H), 3.59 (s, 6H), 0.42 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 137.29, 134.78, 134.71, 132.33, 131.96, 130.88, 130.66, 128.29, 127.99, 51.12. **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -32.41. **EA** (% measured (calculated)), C₁₂H₁₄O₂SSi: C 57.62 (57.56), H 5.62 (5.64), S 12.82 (12.80), Si 11.41 (11.22). **MS (ESI-TOF)**: (*m/z* [M + H]⁺ measured (calculated)): 251.05; found: 250.8624.

Synthesis of dimethoxy(thiophen-2-yl)(vinyl)silane (**P4**)

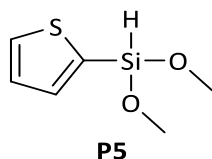


P4

Compound **P4** was synthesised according to representative procedure A with 22.235 g **S4** and 16.303 g **A1**, distilling at 116 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 22.971 g of pure compound **P4** were isolated.

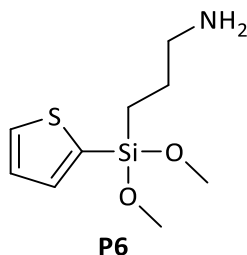
¹H NMR (400 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.69 (dd, J = 4.6, 1.0 Hz, 1H), 7.46 (dd, J = 3.4, 1.0 Hz, 1H), 7.25 (dd, J = 4.6, 3.4 Hz, 2H), 6.24 (dd, J = 14.7, 4.6 Hz, 1H), 6.15 (dd, J = 20.0, 14.7 Hz, 1H), 6.03 (dd, J = 20.0, 4.6 Hz, 1H), 3.62 (s, 6H). **¹³C NMR** (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 137.74, 136.88, 132.19, 130.88, 130.80, 128.25, 50.88. **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -33.17. **EA** (% measured (calculated)), C₈H₁₂O₂SSi: C 47.703 (47.97), H 6.0512 (6.04), S 15.76 (16.00), Si 11.39 (14.02). **MS (ESI-TOF)**: (m/z [M + H]⁺ measured (calculated)): 201.03; found: 200.4689.

Synthesis of dimethoxy(thiophen-2-yl)silane (**P5**)



Compound **P5** was not successfully synthesised via procedure A with 18.330 g **S5** and 16.303 g **A1**. Recorded NMR spectra are presented in the spectra section of appendix A4.

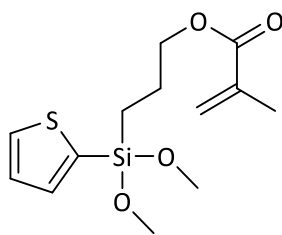
Synthesis of 3-(dimethoxy(thiophen-2-yl)silyl)propan-1-amine (**P6**)



Compound **P6** was synthesised according to representative procedure A with 26.894 g **S6** and 16,303 g **A1**, distilling at 160 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 2.360 g of pure compound **P6** were isolated.

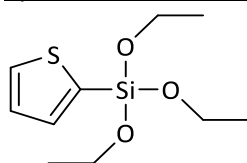
¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.41 (dd, J = 7.1, 1.6 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.08 (dd, J = 7.1, 4.8 Hz, 1H), 3.56 (s, 6H), 2.73 (p, J = 6.3 Hz, 2H), 1.60 (s, 2H), 1.15 (t, J = 6.2 Hz, 2H), 1.05 (t, J = 8.3 Hz, 2H). **¹³C NMR** (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 136.25, 132.13, 129.15, 127.11, 51.30, 44.23, 26.84, 9.14. **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -18.03. **EA** (% measured (calculated)), C₉H₁₇NO₂SSi: C, 46.20 (46.72), H 7.42 (7.41), N 3.14 (6.05), S 14.10 (13.86), Si 14.02 (12.14). **MS (ESI-TOF)**: (m/z [M + H]⁺ measured (calculated)): 232.07; found: 233.0023.

Synthesis of 3-(dimethoxy(thiophen-2-yl)silyl)propyl methacrylate (**P7**)

**P7**

Compound **P7** was not synthesised successfully. In both reaction runs the reaction mixture of **S7** and **A1** solidified and turned brown during the reaction. Spectra are presented in A4. No material containing signals in ^{29}Si NMR could be isolated after solidification.

Synthesis of triethoxy(thiophen-2-yl)silane (**P8**)

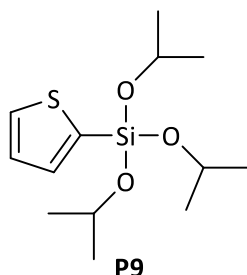
**P8**

Compound **P8** was synthesised according to representative procedure A with 31.250 g **S8** and 16.303 g **A1**, distilling at 106 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 20.008 g of pure compound **P8** were isolated.

Compound **P8** was synthesised according to representative procedure B with 246.3 mg **S28** and 163.0 mg **A1**. 222.0 mg of **P8** at a purity of 91 % were isolated.

^1H NMR (400 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 7.59 (dd, J = 4.6, 0.9 Hz, 1H), 7.38 (dd, J = 3.4, 0.9 Hz, 1H), 7.14 (dd, J = 4.6, 3.4 Hz, 1H), 3.78 (q, J = 7.0 Hz, 6H), 1.15 (t, J = 7.0 Hz, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 136.34, 133.37, 129.41, 127.19, 59.35, 18.34. ^{29}Si NMR (79 MHz, CD_2Cl_2 , 24 °C, ppm) δ = -61.44. **EA** (% measured (calculated)), $\text{C}_{10}\text{H}_{18}\text{O}_3\text{SSi}$: C 48.726 (48.75), H 7.3521(7.36), S 13.18 (13.01), Si 7.62 (11.40). **MS (ESI-TOF)**: (m/z [$\text{M} + \text{H}$] $^+$ measured (calculated)): 247.07; found: 247.0193.

Synthesis of triisopropoxy(thiophen-2-yl)silane (**P9**)

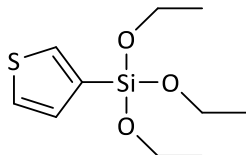
**P9**

Compound **P9** was synthesised according to representative procedure A with 39.816 g **S9** and 16.303 g **A1**, distilling at 155 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 3.462 g of pure compound **P9** were isolated.

^1H NMR (400 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 7.72 (dd, J = 4.6, 0.9 Hz, 1H), 7.51 (dd, J = 3.4, 0.9 Hz, 1H), 7.27 (dd, J = 4.6, 3.4 Hz, 1H), 3.81 (t, J = 6.6 Hz, 6H), 1.70 – 1.56 (m, 6H), 0.96 (t, J = 7.4 Hz, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 137.19, 132.27, 129.52, 128.17, 67.75, 22.34, 13.81. ^{29}Si NMR (79

MHz, CD₂Cl₂, 24 °C, ppm) δ = -61.61. **EA** (% measured (calculated)), C₁₃H₂₄O₃SSi: C 53.987 (54.13), H 8.4231 (8.39), S 10.87 (11.11), Si 6.61 (9.74). **MS (ESI-TOF)**: (m/z [M + H]⁺ measured (calculated)): 288.12; found: 288.0384.

Synthesis trimethoxy(thiophen-3-yl)silane (**P10**)



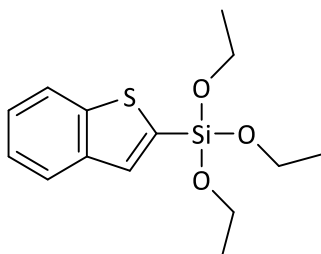
P10

Compound **P10** was synthesised according to representative procedure A with 3.125 g **S8** and 1.630 g **A10**, distilling at 102 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 0.306 g of compound **P10** were isolated. Rapidly decomposed after 72 h in a sealed ampule. (See listed NMR in A4 after decomposition)

Compound **P10** was synthesised according to representative procedure B with 246.3 mg **S28** and 163.0 mg **A10**. 149.4 mg of **P10** at a purity of 87.5 % were isolated. Rapidly decomposed after 72 h in a sealed ampule. (See listed NMR in A4 after decomposition)

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.24 (dd, J = 5.1, 3.2 Hz, 1H), 7.19 (dd, J = 3.2, 1.3 Hz, 1H), 6.96 (dd, J = 5.1, 1.4 Hz, 1H), 3.73 (q, J = 7.0 Hz, 6H), 1.13 (t, J = 7.0 Hz, 9H). **¹³C NMR** (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 129.86, 126.84, 122.82, 109.87, 58.99, 17.91. **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -81.91. **MS (ESI-TOF)**: (m/z [M + H]⁺ measured (calculated)): 247.07; found: 246.8681.

Synthesis of benzo[b]thiophen-2-yltrimethoxysilane (**P11**)

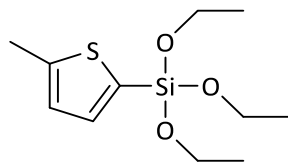


P11

Compound **P11** was synthesised according to representative procedure A with 3.125 g **S8** and 2.130 g **A11**, distilling at 180 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.669 g of 84 % pure compound **P11** were isolated.

Compound **P11** was synthesised according to representative procedure B with 246.3 mg **S28** and 213.0 mg **A11**. 174.0 mg of **P11** at a purity of 82.6 % were isolated.

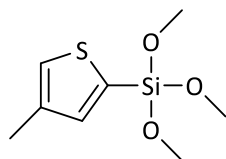
¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.88 – 7.72 (m, 2H), 7.63 (ddd, J = 20.4, 2.1, 1.0 Hz, 1H), 7.32 – 7.23 (m, 2H), 3.86 – 3.80 (m, 6H), 1.20 – 1.14 (m, 9H). **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = .40.17, -62.04. **EA** (% measured (calculated)), C₁₄H₂0O₃SSi: C 55.01 (56.72), H 6.91 (6.80), S 9.1 (10.81), Si 10.14 (9.47). **MS (ESI-TOF)**: (m/z [M + H]⁺ measured (calculated)): 297.09; found: 298.6387.

Synthesis of trimethoxy(5-methylthiophen-2-yl)silane (P12)**P12**

Compound P12 was synthesised according to representative procedure A with 3.125 g **S8** and 1.771 g **A12**, distilling at 89 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.417 g of 94 % pure compound **P12** were isolated.

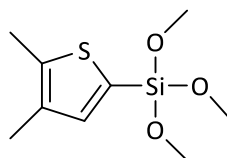
Compound **P12** was synthesised according to representative procedure B with 246.3 mg **S28** and 177.1 mg **A12**. 177.1 mg of **P12** at a purity of 90. % were isolated.

$^1\text{H NMR}$ (300 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 7.25 (d, J = 3.3 Hz, 1H), 6.88 (d, J = 3.2, 1H), 3.87 (q, J = 0.5 Hz, 6H), 2.54 (s, 3H), 1.24 (t, J = 0.5 Hz, 9H). $^{13}\text{C NMR}$ (101 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 141.54, 136.28, 130.29, 125.58, 59.35, 18.34, 15.75. $^{29}\text{Si NMR}$ (79 MHz, CD_2Cl_2 , 24 °C, ppm) δ = -88.89. **EA** (% measured (calculated)), $\text{C}_{11}\text{H}_{20}\text{O}_3\text{SSi}$: C 45.78 (50.73), H 7.73 (7.74), S 10.04 (12.31), Si 11.41 (10.78). **MS (ESI-TOF)**: (m/z [$\text{M} + \text{H}$]⁺ measured (calculated)): 261.09; found: 261.0006.

Synthesis of trimethoxy(4-methylthiophen-2-yl)silane (P13)**P13**

Compound P13 was synthesised according to representative procedure A with 2.283 g **S1** and 1.771 g **A1**, distilling at 105 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.218 g of pure compound **P13** were isolated.

$^1\text{H NMR}$ (300 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 7.13 – 7.08 (m, 1H), 6.72 – 6.68 (m, 1H), 3.57 (s, 9H), 2.25 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 135.65, 135.45, 128.13, 122.08, 50.89, 15.46. $^{29}\text{Si NMR}$ (79 MHz, CD_2Cl_2 , 24 °C, ppm) δ = -66.82. **EA** (% measured (calculated)), $\text{C}_8\text{H}_{14}\text{O}_3\text{SSi}$: C 45.3 (44.01), H 6.41 (6.46), S 12.70 (14.68), Si 14.05 (12.86). **MS (ESI-TOF)**: (m/z [$\text{M} + \text{H}$]⁺ measured (calculated)): 218.34; found: 217.9467.

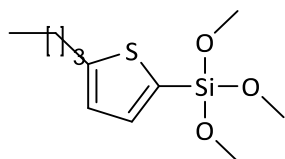
Synthesis of (4,5-dimethylthiophen-2-yl)trimethoxysilane (P14)**P14**

Compound P14 was synthesised according to representative procedure A with 2.283 g **S1** and 1.911 g **A14**, distilling at 150 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.113 g of pure compound **P14** were isolated.

Compound **P14** was synthesised according to representative procedure B with 183 mg **S5** and 111 mg **A4**. 184.5 mg of **P14** at a purity of 86.2 % were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 6.99 (s, 1H), 3.57 (s, 6H), 2.23 (s, 3H), 2.18 (s, 3H) ¹³C NMR (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 137.24, 133.57, 129.22, 123.63, 50.86, 13.21, 12.88. ²⁹Si NMR (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -72.15. EA (% measured (calculated)), C₉H₁₆O₃Si: C 45.84 (46.52), H 6.97 (6.94), S 15.09 (13.80), Si 14.04 (12.09). MS (ESI-TOF): (m/z [M + H]⁺ measured (calculated)): 234.06; found: 234.2583.

Synthesis of (5-(sec-butyl)thiophen-2-yl)trimethoxysilane (**P15**)

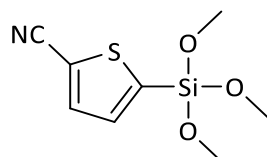


P15

Compound **P15** was synthesised according to representative procedure A with 2.283 g **S1** and 2.191 g **A15**, distilling at 105 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.312 g of pure compound **P15** were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.08 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.83 (m, 1H), 3.57 (s, 9H), 2.74 (td, *J* = 7.3, 0.9 Hz, 2H), 1.61 (tt, *J* = 7.3, 6.0 Hz, 2H), 1.38 (dtd, *J* = 13.4, 7.3, 6.1 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 145.80, 135.79, 127.90, 125.22, 50.88, 31.64, 31.34, 22.26, 13.78. ²⁹Si NMR (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -64.80.

Synthesis of 5-(trimethoxysilyl)thiophene-2-carbonitrile (**P16**)

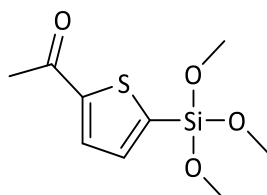


P16

Compound **P16** was synthesised according to representative procedure A with 2.833 g **S1** and 1.88 g **A16**, distilling at 100 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.016 g of pure compound **P16** were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.47 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.57 (s, 9H). ¹³C NMR (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 136.40, 133.79, 131.56, 114.84, 110.59, 50.87. ²⁹Si NMR (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -66.10.

Synthesis of 1-(5-(trimethoxysilyl)thiophen-2-yl)ethan-1-one (**P17**)



P17

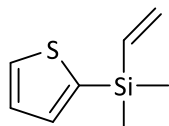
Compound **P17** could not be separated from the reaction mixture resulting from the representative procedure A with 2.293 g **S1** and 2.050 g **A17**.

Compound **P17** was synthesised according to representative procedure B with 183 mg **S5** and 205 mg **A17**.

Separation of **S1** or **S5** and **P17** through fractioned distillation was not successful. Likely NMR shifts are shown below. Furthermore, the appropriate spectra are shown in A4.

²⁹Si NMR (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -88.8.

Synthesis of dimethyl(thiophen-2-yl)(vinyl)silane (**P18**)

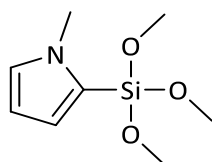


P18

Compound **P18** was synthesised according to representative procedure A with 1.743 g **S18** and 1.63 g **A1**, distilling at 75 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.683 g of pure compound **P18** were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.48 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.14 (dd, *J* = 3.4, 0.9 Hz, 1H), 7.05 (dd, *J* = 4.6, 3.3 Hz, 1H), 6.15 (dd, *J* = 20.2, 14.6 Hz, 1H), 5.97 – 5.84 (m, 1H), 5.64 (dd, *J* = 20.2, 3.7 Hz, 1H), 0.25 (s, 6H). ²⁹Si NMR (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -14.26. EA (% measured (calculated)), C₈H₁₂SSi: C 58.7 (57.08), H 6.98 (7.19), S 17.4 (19.05), Si 8.91 (16.7). MS (ESI-TOF): (*m/z* [M + H]⁺ measured (calculated)): 168.04; found: 168.0492.

Synthesis of 1-methyl-2-(trimethoxysilyl)-1H-pyrrole (**P19**)



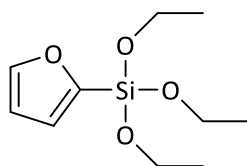
P19

Compound **P17** could not be separated from the reaction mixture resulting from the representative procedure A with 2.293 g **S1** and 1.600 g **A19**.

Compound **P17** was synthesised according to representative procedure B with 183 mg **S5** and 160 mg **A19**.

Separation of **S1** or **S5** and **P17** through fractioned distillation was not successful. Likely NMR shifts are shown below. Furthermore, the appropriate spectra are shown in A4.

Synthesis of furan-2-yltrimethoxysilane (**P20**)



P20

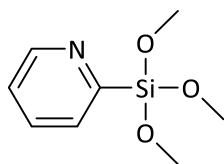
Compound **P20** was synthesised according to representative procedure A with 3.125 g **S8** and 1.771 g **A20**, distilling at 65 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 967 mg of 69 % pure compound **P12** were isolated.

Compound **P20** was synthesised according to representative procedure B with 246.3 mg **S28** and 177.7 mg **A20**. 143.6 mg of **P20** at a purity of 74.3 % were isolated.

The compound readily decomposed after synthesis, as shown in the NMR spectra presented in A4.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.69 (dd, J = 1.7, 0.6 Hz, 1H), 6.88 (dd, J = 3.3, 0.6 Hz, 1H), 6.43 (dd, J = 3.3, 1.6 Hz, 1H), 3.87 (q, J = 7.0 Hz, 6H), 1.28 – 1.16 (m, 9H). **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -66.79.

Synthesis of 2-(trimethoxysilyl)pyridine (**P21**)

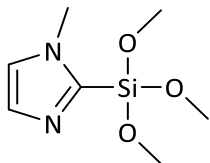


P21

Compound **P21** was not successfully synthesised according to representative procedure A. The reaction mixture solidified during reaction using 2.283 g **S1** and 1.580 g **A21**.

Compound **P21** was not successfully synthesised according to representative procedure B. The reaction mixture solidified during reaction using 183.3 mg **S5** and 158 mg **A21**.

Synthesis of 1-methyl-2-(trimethoxysilyl)-1H-imidazole (**P22**)



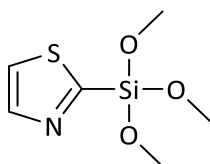
P22

Compound **P22** was synthesised according to representative procedure A with 2.283 g **S1** and 1.61 g **A22**, distilling at 96 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 1.153 g of pure compound **P22** were isolated.

Compound **P22** was synthesised according to representative procedure B with 183 mg **S5** and 161 mg **A22**. 93.1 mg of **P22** at a purity of 79.5 % were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.23 (d, J = 3.7 Hz, 1H), 7.19 (d, J = 3.7 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 9H). **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -64.94. **EA** (% measured (calculated)), C₇H₁₄N₂O₃Si: C 49.05 (41.56), H 5.99 (6.98), N 12.07 (13.85), Si 15.75 (13.88). **MS (ESI-TOF)**: (m/z [M + H]⁺ measured (calculated)): 203.08; found: 203.1071.

Synthesis of 2-(trimethoxysilyl)thiazole (**P23**)



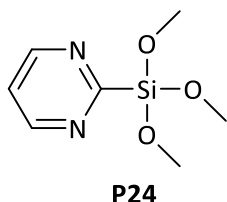
P23

Compound **P23** was synthesised according to representative procedure A with 2.283 g **S1** and 1.64 g **A23**, the compound did not distil at elevated temperature but decomposed. 312 mg of crude compound **P23** were at a purity of 38% were generated.

Compound **P23** was not successfully synthesised according to representative procedure B. The reaction was run using 183.3 mg **S5** and 164 mg **A24**. Only starting substrates are detected.

^1H and ^{29}Si NMR spectra were recorded. Due to the impurity of material no peaks are reported here. The corresponding spectra are presented in A4.

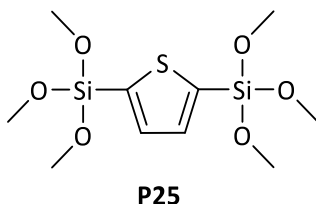
Synthesis of 2-(trimethoxysilyl)pyrimidine (**P24**)



Compound **P24** was not successfully synthesised according to representative procedure A. The reaction mixture solidified during reaction using 2.283 g **S1** and 1.589 g **A24**.

Compound **P24** was not successfully synthesised according to representative procedure B. The reaction mixture solidified during reaction using 183.3 mg **S5** and 158 mg **A24**.

Synthesis of 2,5-bis(trimethoxysilyl)thiophene (**P25**)

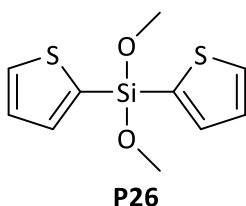


Compound **P25** was synthesised according to representative procedure A with 4.566 g **S1** and 2.419 g **A25** the reaction time was increased to 72 h, distilling at 195 °C oil bath and 1.0×10^{-3} mbar through a short path distillation apparatus. 922 mg of pure compound **P25** were isolated.

Compound **P25** was synthesised according to representative procedure B with 366.6 mg **S5** and 242 mg **A25**. 78.5 mg of **P25** at a purity of 84.1 % were isolated.

^1H NMR (300 MHz, CD_2Cl_2 , 24 °C, ppm) δ = 7.49 (s, 2H), 3.57 (s, 18H). ^{29}Si NMR (79 MHz, CD_2Cl_2 , 24 °C, ppm) δ = -59.89. EA (% measured (calculated)), $\text{C}_{10}\text{H}_{20}\text{O}_6\text{Si}_2$: C 32.1 (37.01), H 6.21 (6.21), S 7.45 (9.88), Si 12.43 (17.31). MS (ESI-TOF): (m/z [M + H]⁺ measured (calculated)): 324.05; found: 324.0506.

Synthesis of dimethoxydi(thiophen-2-yl)silane (**P26**)



P26 was not specifically synthesised but was isolated from **P1** through fractioned distillation after running procedure A targeting **P1**.

Appendix

¹H NMR (300 MHz, CD₂Cl₂, 24 °C, ppm) δ = 7.67 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.43 (dd, *J* = 3.4, 0.9 Hz, 1H), 7.23 (dd, *J* = 4.6, 3.4 Hz, 1H), 3.60 (s, 6H). **¹³C NMR** (101 MHz, CD₂Cl₂, 24 °C, ppm) δ = 136.13, 132.62, 131.82, 128.32, 50.80. **²⁹Si NMR** (79 MHz, CD₂Cl₂, 24 °C, ppm) δ = -17.99.

Table 11: Overview table of compounds P1 to P25 acquired through process A. Molecular weights were calculated using ChemDraw, isolated grams were measured, conversion calculated from expected over measured weight, selectivity assessed through NMR of the worked-up product. Yield is calculated as the product of conversions and selectivity.

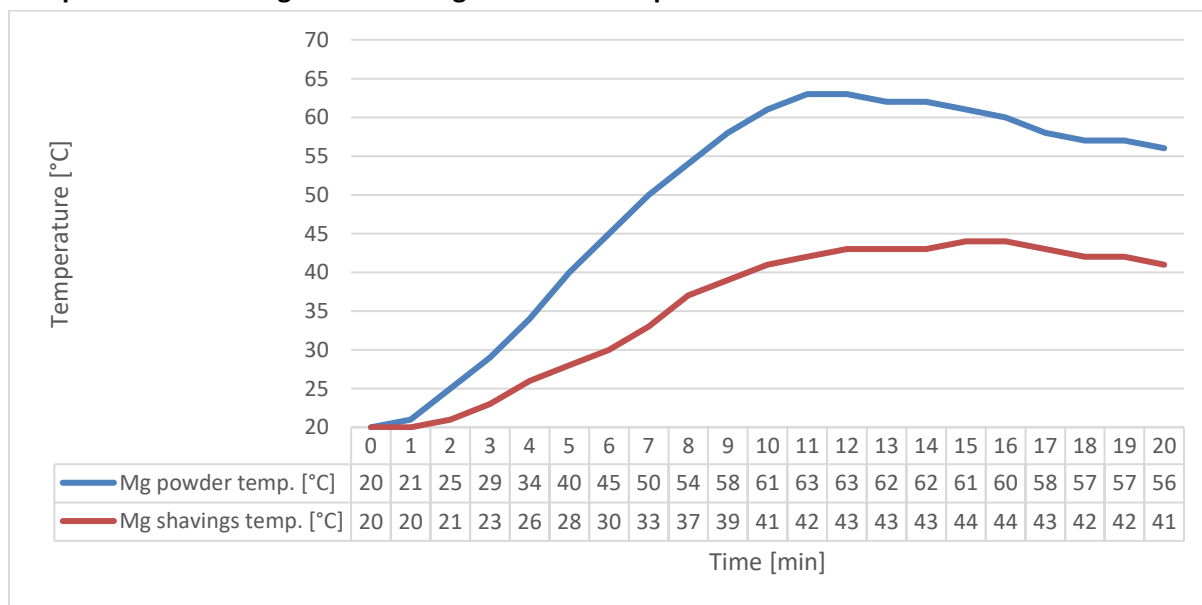
Compound	MW [g/mol]	compound after isolation [g]	Conversion [%]	Selectivity [%]	Yield [%]
P1	204.32	18.593	91.0	100	91.0
P2	188.32	14.783	78.5	100	78.5
P3	250.39	17.853	71.3	100	71.3
P4	200.33	18.370	91.7	100	91.7
P5	174.29	0.000	0.0	0	0.0
P6	231.39	2.360	10.2	100	10.2
P7	300.44	0.000	0.0	0	0.0
P8	246.40	20.008	81.2	100	81.2
P9	288.48	3.462	12.0	100	12.0
P10	204.32	0.306	1.5	100	1.5
P11	254.37	16.687	65.6	100	65.6
P12	218.34	14.170	64.9	100	64.9
P13	218.34	12.183	55.8	100	55.8
P14	232.37	11.131	47.9	100	47.9
P15	260.42	13.125	50.4	100	50.4
P16	229.33	10.159	44.3	100	44.3
P17	311.44	0.000	-	-	-
P18	168.33	14.712	87.4	100	87.4
P19	201.30	0.000	-	100	0.0
P20	188.25	9.676	51.4	69	35.5
P21	199.28	0.000	0.0	100	0.0
P22	202.29	1.153	5.7	100	5.7
P23	205.30	3.121	15.2	38	5.8
P24	200.27	0.000	0.0	100	0.0
P25	324.49	9.216	28.4	100	28.4

Appendix

Table 12: Overview table of compounds P1 to P25 acquired through process B. Molecular weights were calculated using ChemDraw, isolated grams were measured, conversion calculated from expected over measured weight, selectivity assessed through NMR of the worked-up product. Yield is calculated as the product of conversions and selectivity.

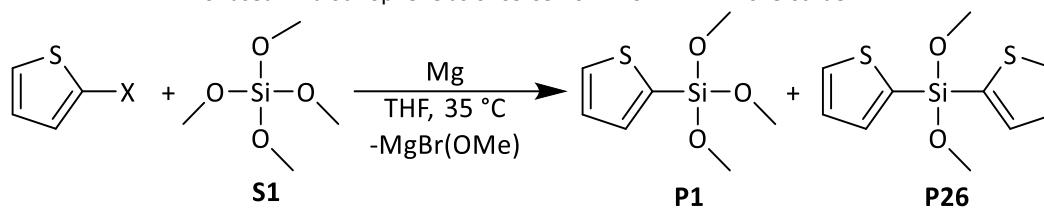
Compound	MW compound [g/mol]	after isolation [mg]	Conversion [%]	Selectivity [%]	Yield [%]
P1	204.32	186.3	91.2	92	83.9
P2	188.32	145.2	77.1	78	60.1
P8	246.40	222.0	90.1	91	82.0
P10	204.32	149.4	73.1	87.5	64.0
P11	254.37	174.0	68.4	82.6	56.5
P12	218.34	177.1	81.1	90.8	73.6
P14	232.37	184.5	79.4	86.2	68.4
P17	311.44	0.0	-	-	-
P19	201.30	0.0	0.0	100	0.0
P20	188.25	143.6	76.3	74.3	56.7
P21	199.28	0.0	0.0	0	0.0
P22	202.29	93.1	46.0	79.5	36.6
P24	200.27	0.0	0.0	0	0.0
P25	324.49	78.5	24.2	84.1	20.4

Temperature screening for initial Grignard reaction optimisation



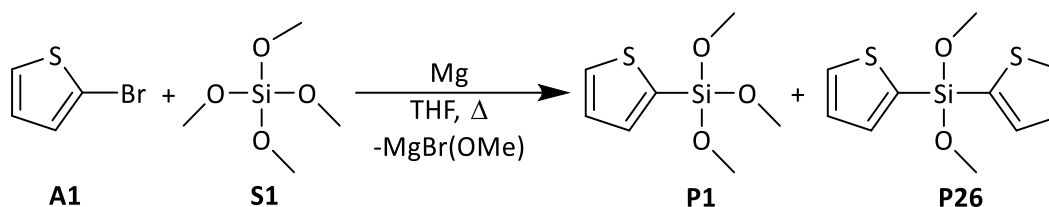
Appendix

Table 13: Grignard reaction of different 2-halothiophenes with tetramethyl orthosilicate and magnesium powder in THF at 35 °C. Recording the resulting conversions of 2-halothiophenes, selectivity for trimethoxy(thiophen-2-yl)silane and the cost of used 2-halothiophene as of 09.05.2024 from "www.fishersci.de".



2-Halothiophene	Conversion [%]	Selectivity [%]	Cost [€/kg]
2-Chlorothiophen A26	24	87	412.00
2-Bromothiophen A1	52	97	283.00
2-Iodothiophen A27	57	96	1970.00

Table 14: Temperature screening of the Grignard reaction between 2-bromothiophene and tetramethyl orthosilicate in THF and in the presence of magnesium shavings.



Reaction temperature [°C]	Crude conversion [%]
0 °C	41
25 °C	50
35 °C	52
45 °C	62
55 °C	60
66 °C	55

Table 15: Workup optimisation of the Grignard reaction between 2-bromothiophene and tetramethyl orthosilicate in THF and in the presence of magnesium shavings at 45 °C.

Process optimisation	Crude yield [%]
None	21
Extracting sludge with pentane	53
Extracting sludge with heptane	56
Washing sludge with pentane	61
Washing sludge with heptane	62

Procedure in agreement with Murata *et al.* for initial feasibility of palladium catalysed carbon-silicon cross coupling between a heteroarylhalide and a trialkoxysilane

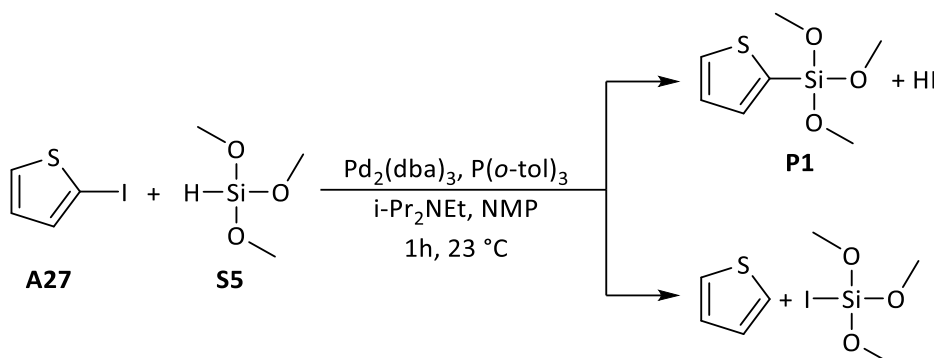


Figure 58: Competing reaction products during the palladium catalysed carbon-silicon cross coupling between 2-bromothiophene and trimethoxysilane. Formed products can be the intended cross coupling product **P1** and cleaved hydrogen bromide or the undesirable substitution of halide with hydride. Reaction was run with tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) as precursor, tri(*o*-tolyl) phosphine ($\text{P}(\text{o-tol})_3$) as ligand, N,N-diisopropylethylamine ($\text{i-Pr}_2\text{NEt}$) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 1 h our at 23 °C.

A three-neck round-bottom flask is equipped with cooling condenser, two stoppers and a magnetic stir bar. The apparatus is flame dried under reduced pressure and filled with dry argon. Tris(dibenzylideneacetone)dipalladium(0) **M6** (0.08 mmol, 80 mg) and tri(*o*-tolyl)phosphine **L7** (0.03 mmol, 91 mg) are weight into sample vials in a glovebox and subsequently transferred to the apparatus under air exclusion. One stopper is swapped for a septum. N-Methyl-2-pyrrolidone (20 ml) is transferred from the storage container to the apparatus via an argon purged needle. 2-iodothiophene **A27** (1.00 mmol, 1.00 g) is added, followed by N,N-diisopropylethylamine (15 mmol, 2.6 ml). To this trimethoxysilane **S5** (7.5 mmol, 1.24 g) is added slowly. The solution is stirred for 1 h at 23 °C. The flasks contents are transferred to a separatory funnel and washed five times with pentane (5x 6 ml), washing the flask several times. The pentane phase is counter washed with deionized water. The pentane phase is dried over magnesium sulphate and low volatiles are removed on a rotary evaporator. Conversion of **A27** is recorded at 65.1 % with a selectivity of the reaction for **P1** of 68 %. Furthermore, following the same procedure concentrations and weight ins of **M6**, **L7**, **V1**, **B8** and **S5** two additional halo-thiophenes were screened. 2-Bromothiophene **A1** (1.00 mmol, 210 mg) and 2-Chlorothiophene **A26** (1.00 mmol, 119 mg) were used. **A1** resulted in 150 mg **P1** (61 % conversion and 70 % selectivity), **A26** resulted in 76 mg **P1** (31 % conversion and 68 % selectivity)

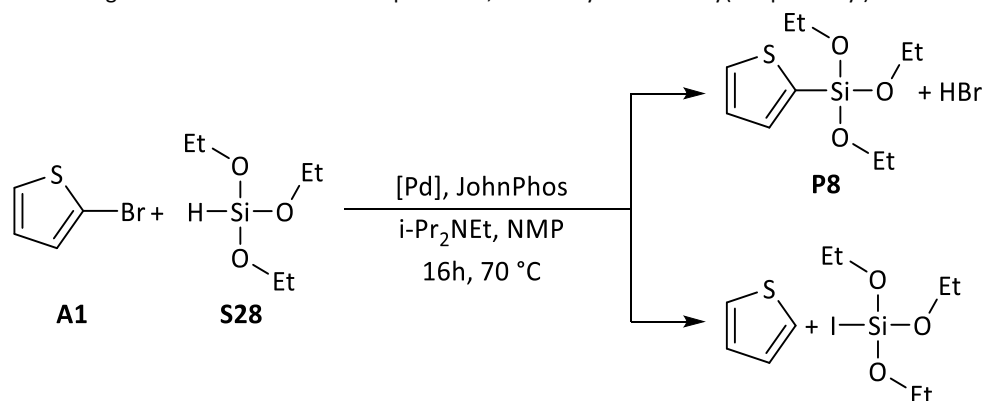
Representative procedure C

Palladium source screening was conducted according to general procedure B. Using different palladium precursors (0.03 mmol, 3 mol%) together with 2-(di-tert-butylphosphino)biphenyl (JohnPhos, 0.06 mmol, 6 mol%, 17.9 mg) dissolved in N-methyl-2-pyrrolidone (99 mmol, 40 eq, 4.00 ml). To this 2-bromothiophene (1.00 mmol, 1 eq, 163 mg), N,N-diisopropylethylamine (3.00 mmol, 3 eq, 0.3877 g) and triethoxysilane (1.00 mmol, 1 eq, 0.246 g) are added. From here general procedure B is resumed. The used palladium precursors and weighed samples are reported below.

Appendix

Table 16: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride.

Reaction was run with various palladiums precursors (2-biphenyl)-di-*tert*-butylphosphine (JohnPhos) as ligand, N,N-diisopropylethylamine (i-Pr₂NEt) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.

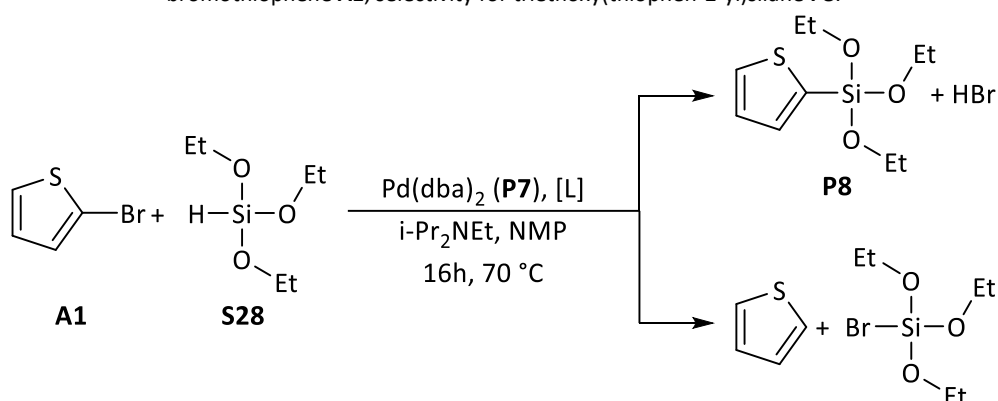


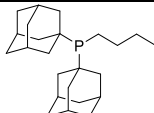
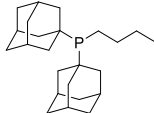
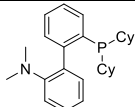
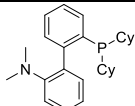
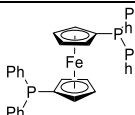
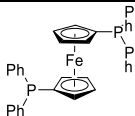
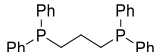
Palladium precursor IUPAC name		Weighed sample [mg]	Conversion of S28 [%]	Purity of P8
Palladium(II)-acetate	M1	6.74	41.3	82.6
Palladium(II)-acetate	M1	6.74	38.6	78.2
Palladium(II)-chloride	M2	5.32	10.5	6.1
Palladium(II)-chloride	M2	5.32	13.8	8.0
Palladium(II)-bis(acetylacetonate)	M3	3.14	-	30.4
Palladium(II)-bis(acetylacetonate)	M3	3.14	-	33.2
(1,1'-Bis(diphenylphosphino)ferrocene) palladium(II) dichloride	M4	22.0	57.0	0.0
(1,1'-Bis(diphenylphosphino)ferrocene) palladium(II) dichloride	M4	22.0	40.9	0.0
Allylpalladium chloride dimer	M5	5.49	-	69.2
Allylpalladium chloride dimer	M5	5.49	-	72.7
Tris(dibenzylideneacetone)dipalladium(0)	M6	27.5	89.1	79.0
Tris(dibenzylideneacetone)dipalladium(0)	M6	27.5	89.3	87.0
Bis-(dibenzylidenacetone)-palladium(0)	M7	17.3	74.6	91.2
Bis-(dibenzylidenacetone)-palladium(0)	M7	17.3	71.2	78.9
Tetrakis(triphenylphosphine)palladium(0)	M8	34.7	6.1	8.4
Tetrakis(triphenylphosphine)palladium(0)	M8	34.7	5.4	10.1
Palladium monoxide	M9	3.67	0.0	0.0
Palladium monoxide	M9	3.67	0.0	0.0
Palladium on carbon	M10	31.9	0.0	0.0
Palladium on carbon	M10	31.9	0.0	0.0

Representative procedure D

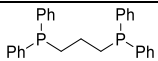
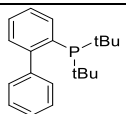
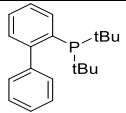
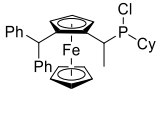
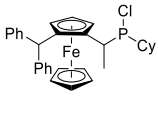
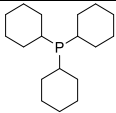
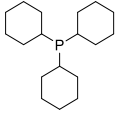
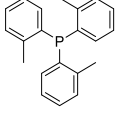
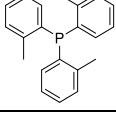
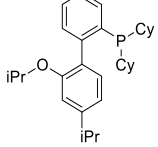
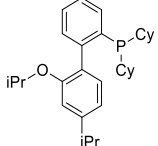
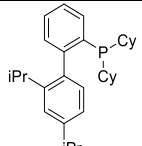
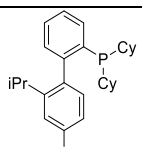
Representative experiments from procedure C established $\text{Pd}(\text{dba})_2$ as the best palladium precursor. Consequently, the used ligands were screened. Phosphor ligand screening was conducted according to general procedure B. Using bis(dibenzylideneacetone) palladium(0) together with different phosphor-based ligands (0.06 mmol, 6 mol%) dissolved in in N-methyl-2-pyrrolidone (99 mmol, 40 eq, 4.00 ml). To this 2-bromothiophene (1.00 mmol, 1 eq, 163 mg), N,N-diisopropylethylamine (3.00 mmol, 3 eq, 0.3877 g) and triethoxysilane (1.00 mmol, 1 eq, 0.246 g) are added. From here general procedure B is resumed. The used phosphor-based ligands and weighed samples are reported below.

Table 17: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with various phosphine ligands, $\text{Pd}(\text{dba})_2$ **P7** as palladium precursor, N,N-diisopropylethylamine (i-Pr₂NEt) as base in N-methyl-2-pyrrolidone (NMP) as solvent for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.



UIPAC Name		Abbreviation		Weighed sample [mg]	Conversion of A1 [%]	Selectivity for P8 [%]
Di-(1-adamantyl)- <i>n</i> -butylphosphin	L5	cataCXium A		21.5	44.3	0
Di-(1-adamantyl)- <i>n</i> -butylphosphin	L5	cataCXium A		21.5	45.1	0
2-Dicyclohexylphosphino-2'-(<i>N,N</i> -dimethylamino)-biphenyl	L2	DavePhos		23.6	77.6	68.9
2-Dicyclohexylphosphino-2'-(<i>N,N</i> -dimethylamino)-biphenyl	L2	DavePhos		23.6	81.2	66.8
1,1'-Bis(diphenylphosphino)ferrocen	L8	Dppf		33.3	10.3	0.0
1,1'-Bis(diphenylphosphino)ferrocen	L8	Dppf		33.3	9.6	0.0
1,3-Bis(diphenylphosphino)propan	L10	Dppp		24.7	8.5	0.0

Appendix

UIPAC Name	Abbreviation		Weighed sample [mg]	Conversion of A1 [%]	Selectivity for P8 [%]
1,3-Bis(diphenylphosphino)propan L10	Dppp		24.7	7.9	0.0
(2-Biphenyl)-di-tert-butylphosphin L1	JohnPhos		17.9	73.1	84.6
(2-Biphenyl)-di-tert-butylphosphin L1	JohnPhos		17.9	72.9	83.2
1-[2-(Diphenylphosphino)-ferrocenyl]-ethylidicyclohexylphosphin L9	JosiPhos		38.4	9.2	0.0
1-[2-(Diphenylphosphino)-ferrocenyl]-ethylidicyclohexylphosphin L9	JosiPhos		38.4	8.6	0.0
Tricyclohexylphosphine L6	PCy ₃		16.8	40.1	33.8
Tricyclohexylphosphine L6	PCy ₃		16.8	48.6	20.0
Tris(o-tolyl)phosphine L7	P(o-tol) ₃		28.0	38.7	41.2
Tris(o-tolyl)phosphine L7	P(o-tol) ₃		28.0	37.7	39.7
2-Dicyclohexylphosphino-2',6'-diisopropoxybiphenyl L4	RuPhos		28.6	80.2	50.0
2-Dicyclohexylphosphino-2',6'-diisopropoxybiphenyl L4	RuPhos		28.6	79.6	8.9
2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl L3	Xphos		38.4	13.2	0
2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl L3	Xphos		38.4	41.7	49.1

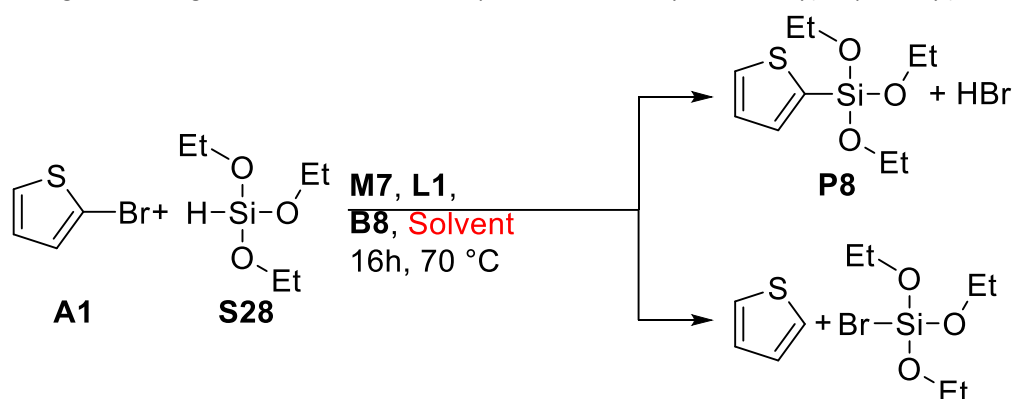
Representative procedure E

Representative experiments from procedures C and D established Pd(dba)₂ and JohnPhos. Solvent screening was conducted as follows. Bis(dibenzylideneacetone) palladium(0) (0.03 mmol, 3 mol%, 17.3 mg) together with (2-biphenyl)-di-tert-butylphosphin (0.06 mmol, 6 mol%, 17.9 mg) dissolved in different bipolar, aprotic solvents (99 mmol, 40 eq). To this 2-bromothiophene (1.00 mmol, 1 eq, 163 mg), N,N-diisopropylethylamine (3.00 mmol, 3 eq, 0.3877 g) and triethoxysilane (1.00 mmol, 1 eq, 0.246 g) are added. From here general procedure B is resumed. The used solvent and its volume are reported below.

Table 18: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride.

Reaction was run with various solvents, **M7** as palladium precursor, **L1** as ligand and **B8** as base for 16 hours at 70 °C.

Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.



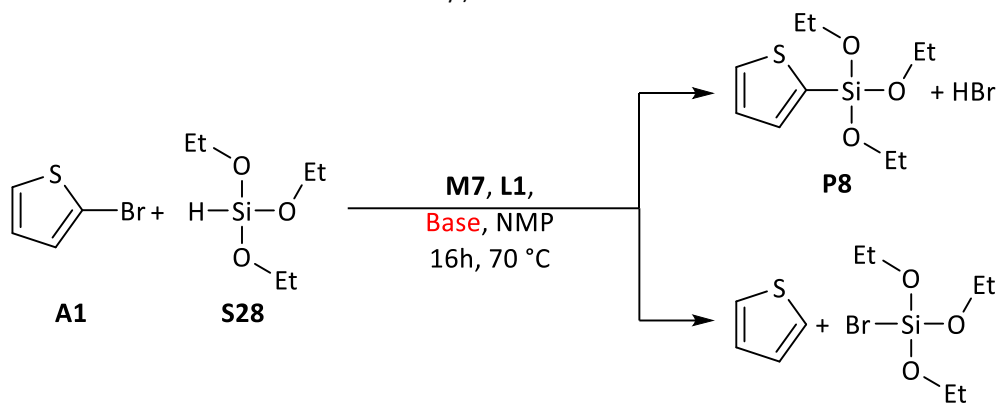
UIPAC Name		sample volume [ml]	Yield [%]	Purity [%]	Note
Dimethyl sulfoxide	V5	4.37	41.2	23.6	
Dimethyl sulfoxide	V5	4.37	45.8	87.6	
N,N-Dimethylacetamide	V2	5.70	1.2	27.7	
N,N-Dimethylacetamide	V2	5.70	8.5	59.8	
N-Formylmorpholine	V4	6.21	30.4	60.6	Green
N-Formylmorpholine	V4	6.21	55.8	40.2	Green
N-Methyl-2-pyrrolidone	V1	4.00	74.6	91.2	
N-Methyl-2-pyrrolidone	V1	4.00	71.2	78.9	
Tetramethylurea	V3	7.36	12.9	62.0	Gas release
Tetramethylurea	V3	7.36	8.7	75.2	Gas release
Acetonitrile	V6	5.17	0.0	0.0	
Acetonitrile	V6	5.17	0.0	0.0	
Acetonitrile + 0.5 wt% N-Methyl-2-pyrrolidone	V6 + 0.5 wt% V1	5.18	74.2	67	
Acetonitrile + 0.5 wt% N-Methyl-2-pyrrolidone	V6 + 0.5 wt% V1	5.18	76.2	77	

Representative procedure F

Representative experiments from procedures C, D and E established Pd(dba)₂, JohnPhos and NMP. Base screening was conducted as follows. Bis(dibenzylideneacetone) palladium(0) (0.03 mmol, 3 mol%, 17.3 mg) together with (2-biphenyl)-di-tert-butylphosphin (0.06 mmol, 6 mol%, 17.9 mg) dissolved

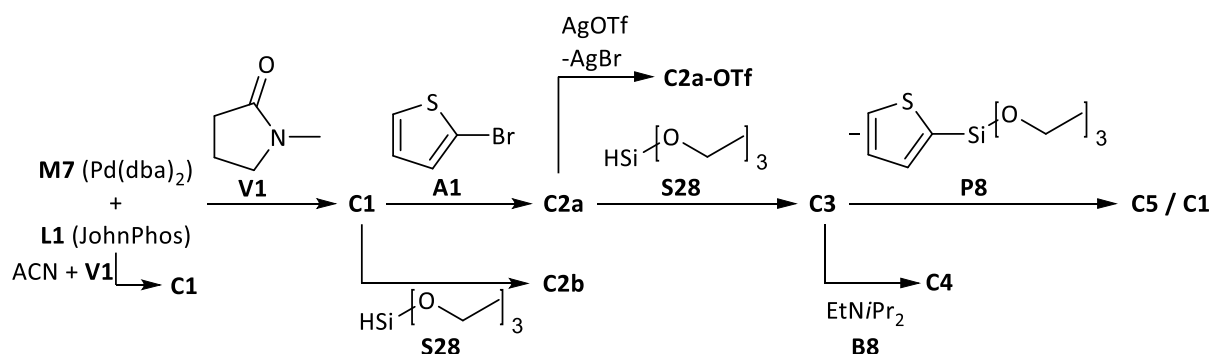
in in N-methyl-2-pyrrolidone (99 mmol, 40 eq, 4.00 ml). To this 2-bromothiophene (1.00 mmol, 1 eq, 163 mg), a base (3.00 mmol, 3 eq) and triethoxysilane (1.00 mmol, 1 eq, 0.246 g) are added. All bases were subjected to Carl-Fischer titration before they were used and water contents below 10 ppm were confirmed. From here general procedure B is resumed. The used base and weighed samples are reported below.

Table 19: Catalytic carbon silicon cross coupling of 2-bromothiophene **A1** with triethoxysilane **S28**. Formed products can be the intended cross coupling product **P8** and cleaved hydrogen halide or the undesirable substitution of halide with hydride. Reaction was run with various bases, **M7** as palladium precursor, L1 as ligand in N-methyl-2-pyrrolidone (NMP) as solvent for 16 hours at 70 °C. Recording the resulting conversions of 2-bromothiophene **A1**, selectivity for triethoxy(thiophen-2-yl)silane **P8**.



UIPAC Name		Weighed sample [mg]	Yield [%]	Purity [%]
1,5,7-triazabicyclo[4.4.0]dec-5-ene	B6	417.6	0.0	0.0
1,5,7-triazabicyclo[4.4.0]dec-5-ene	B6	417.6	0.0	0.0
Arginine	B7	522.6	50.2	10.0
Arginine	B7	522.6	46.9	11.2
N,N-Diisopropylethylamine	B8	387.7	91.7	86.1
N,N-Diisopropylethylamine	B8	387.7	90.7	87.8
Potassium carbonate	B1	414.6	0.0	0.0
Potassium carbonate	B1	414.6	0.0	0.0
Potassium hydroxide	B2	168.3	0.0	0.0
Potassium hydroxide	B2	168.3	0.0	0.0
Potassium tert-butoxide	B4	288.3	0.0	0.0
Potassium tert-butoxide	B4	288.3	0.0	0.0
Pyridine	B5	237.3	0.0	0.0
Pyridine	B5	237.3	0.0	0.0
Tetramethylethylenediamine	B9	348.6	21.0	0.0
Tetramethylethylenediamine	B9	348.6	24.8	0.0
Tripotassium phosphate	B3	690.8	80.2	2.4
Tripotassium phosphate	B3	690.8	75.6	3.1

Complex intermediate isolation and characterisation with reaction conditions established in representative procedures B to F.



Isolation of complex **C1** procedure A

Bis(dibenzylideneacetone)palladium(0) (0.06 mmol, 1 eq, 34.5 mg) and (2-biphenyl)-di-tert-butylphosphin (0.06 mmol, 1 eq, 17.9 mg) are added to an inert Schlenk tube. N-Methyl-2-pyrrolidone (6.46 mmol, 100 eq, 640 μl) is added resulting in a red solution. Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene- d_6 , sealed in a glass capillary, is added as an internal standard. Additionally direct injection ESI-MS is submitted. A vapor diffusion apparatus is prepared with dry, degassed diethyl ether. The remaining reaction volume is transferred into the freshly prepared apparatus and kept still for 2 weeks. Colorless needles were observed after 10 days. A ^1H -NMR measurement revealed pure JohnPhos as the main compound in the needle.

^{31}P NMR (121 MHz, CD_2Cl_2 , 80 $^\circ\text{C}$, ppm) δ = 58.99. **EA** no usable data could be generated through EA **MS (ESI-TOF)**: no usable data could be generated through MS.

Isolation of complex **C1** procedure B

Bis(dibenzylideneacetone) palladium(0) (0.06 mmol, 1 eq, 34.5 mg) and (2-biphenyl)-di-tert-butylphosphin (0.06 mmol, 1 eq, 17.9 mg) are added to an inert Schlenk tube. Acetonitrile (6.46 mmol, 100 eq, 206.8 μl) and N-methyl-2-pyrrolidone (0.06 mmol, 1 eq, 6.13 μl) are added resulting in a red solution. An NMR sample is prepared by sampling into an inert Young-NMR-tube. Benzene- d_6 , sealed in a glass capillary, is added as an internal standard. Resulting NMR shifts are identical with shifts resulting from isolation of complex **C1** procedure A. The remaining reaction volume is transferred into the freshly prepared apparatus and kept still for 2 weeks. After 14 days amorphous black solid precipitated from solution while discoloration was observed. No crystals were isolated.

Isolation of complex **C2a**

To the solution resulting from Isolation of **C1** procedure A 2-bromothiophene (0.06 mmol, 1 eq, 5.81 μl) is added and stirred at 60 $^\circ\text{C}$ for 30 minutes. Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene- d_6 , sealed in a glass capillary, is added as an internal standard. Additionally direct injection ESI-MS is submitted. The remaining reaction volume is transferred into the freshly prepared apparatus and kept still for 2 weeks. After 14 days amorphous black solid precipitated from solution while discoloration was observed. No crystals were isolated.

^{31}P NMR (121 MHz, CD_2Cl_2 , 80 $^\circ\text{C}$, ppm) δ = 19.27, 18.13. **EA** no usable data could be generated through EA **MS (ESI-TOF)**: no usable data could be generated through MS.

Isolation of complex **C2b**

To the solution resulting from Isolation of **C1** procedure A triethoxy silane (0.06 mmol, 1 eq, 11.1 μ l) is added and stirred at 60 °C for 30 minutes. Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene-d₆, sealed in a glass capillary, is added as in internal standard.

³¹P NMR (121 MHz, CD₂Cl₂, 80 °C, ppm) δ = 51.55 (JohnPhos Oxide¹⁸²). **EA** no usable data could be generated through EA **MS (ESI-TOF)**: no usable data could be generated through MS.

Isolation of complex **C2-OTf**

To the solution resulting from Isolation of **C2a** a silver salt (0.06 mmol, 1 eq) is added in the dark and stirred under light exclusion for 30 minutes. Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene-d₆, sealed in a glass capillary, is added as in internal standard. The remaining reaction volume is transferred into the freshly prepared apparatus and kept still for 2 weeks. After 14 days amorphous black solid precipitated from solution while discoloration was observed. No crystals were isolated.

Isolation of complex **C3**

To the solution resulting from Isolation of **C2a** triethoxy silane (0.06 mmol, 1 eq, 11.1 μ l) is added and stirred at 80 °C for 30 minutes. Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene-d₆, sealed in a glass capillary, is added as in internal standard. The remaining reaction volume is transferred into the freshly prepared apparatus and kept still for 2 weeks. After 14 days amorphous black solid precipitated from solution while discoloration was observed. No crystals were isolated.

¹H NMR (300 MHz, CD₂Cl₂, 80 °C, ppm) δ = 6.13 (d, J = 471.9 Hz, 1H). ³¹P NMR (121 MHz, CD₂Cl₂, 80 °C, ppm) δ = 29.41 (d, J = 477.8). **EA**: no usable data could be generated through EA. **MS (ESI-TOF)**: no usable data could be generated through MS.

Isolation of complex **C4**

To the solution resulting from Isolation of **C2a** N,N-diisopropylethylamine (0.18 mmol, 3 eq, 30.6 μ l) is added and stirred at 60 °C for 30 minutes. . Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene-d₆, sealed in a glass capillary, is added as in internal standard.

No changes compared to **C2a** signals can be observed in NMR.

Isolation of complex **C5**

To the solution resulting from Isolation of **C3** N,N-diisopropylethylamine (0.18 mmol, 3 eq, 30.6 μ l) is added and stirred at 60 °C for 30 minutes. . Analysis is prepared by sampling into an inert Young-NMR-tube. Benzene-d₆, sealed in a glass capillary, is added as in internal standard.

³¹P NMR (121 MHz, CD₂Cl₂, 80 °C, ppm) δ = 19.27, 18.13 **MS (ESI-TOF)**: no usable data could be generated through MS.

Detailed investigation on PDMS endgroup substitution

Detailed investigations on this reaction were run, identifying the reaction products, as well as optimising for best product formation. Time resolved experiments were conducted, sampling every 30 minutes, starting at t_0 with the addition of catalyst and followed using proton NMR. (Figure 59).

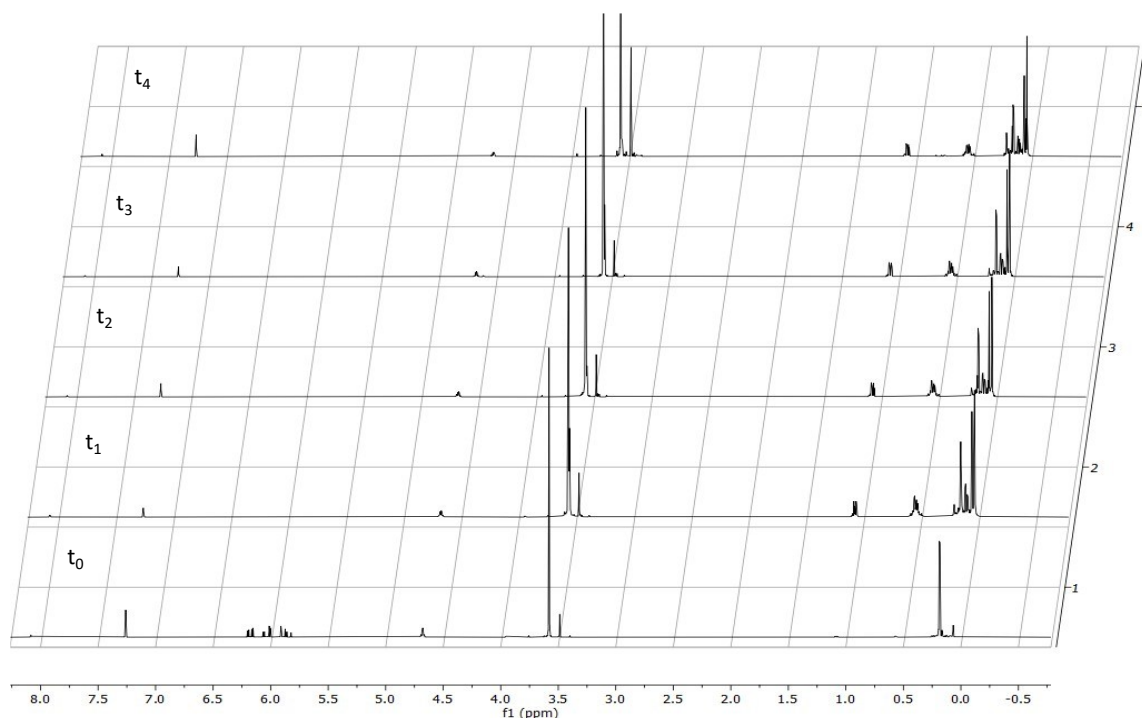


Figure 59: Stacked NMR spectra of hydrosilylation of **S4** with TMDS, recorded every 30 minutes (t₁-t₃) and after 17 h (t₄) after platinum on silica addition.

Experiments were conducted with equal amounts of **S4** to TMDS to attain mono substituted product. At t₀ the resulting spectrum is a mixture of substrate signals. Signals present at 0.19 ppm are attributed to methyl-silane-groups in TMDS showing doublet multiplicity due to its single proton-silicon bond. At t₄ additional signals are present between 0.03 ppm and 0.24 ppm are present as expected when a successful conversion to either α - or β -substituted product shown in Figure 42 is successful. As the conducted test were designed to yield mono substituted TMDS some double substitution may be present, explaining additional signals found in the same area. Due to broad peaks and limited resolution of the used device no differentiation between signals was undertaken. Signals at 3.58 ppm show methoxy substituted silane, presence of **S4**, with additional signals at 3.49 ppm relating to free methanol. During the reaction process integrals between both signals were recorded, while stating with 6 % methanol at t₀ 24 % methanol at t₄ were recorded. The evident reactivity of **S4** at the given conditions is high enough to react with moisture, partially hydrolysing the substrate on formed product. All reactions were performed under inert conditions, using dried argon as protecting gas. However, deuterated solvent used for NMR analysis was not dried and used as is, likely introducing moisture into the system, after a sample had been taken. This is further supported by the decrease in observed hydrolysis from t₂ to t₃. However, since this would involve a great deal of effort, it was not done due to the low impact during screening reactions. Lastly the consumption of **S4** is indicated by the reduction of integrals value of signals attributed to **S4** vinyl group at 5.82 - 5.91, 6.00 - 6.06 and 6.15 - 6.20 ppm.²⁴⁰ This corresponds to an increase in signal integrals attributed to the resulting carbon-silicon bond formed. To calculate the conversion the products integrals are summed and divided by the sum of integrals of product, vinyl and silane signals is multiplied by 100 yielding % conversion. Integrals from Figure 59 were taken and collected in Table 20.

Appendix

Table 20: Time resolved conversion of hydrosilylation of TMDS with **S4** using platinum on carbon.

Spectrum	Conversion [%]
t ₀	14.6
t ₁	98.1
t ₂	98.4
t ₃	98.7
t ₄	98.9

High conversion at 98.1 % after 30 minutes reaction time (t₁) is noted and used in downstream experiments as this is sufficient for further testing and streamlines reaction times significantly. Conversion at t₀ was expected to be 0.0 %. However, 14.6 % was recorded, this is attributed to the reaction progressing at room temperature until the NMR measurement is performed. While samples had been filtered using a syringe filter, residual platinum may further catalyse the reaction during waiting times. Samples had been taken after the addition of platinum on carbon to measure the reactions actual t₀ and not spectra before all additions are made as the presence of all chemicals present during the reaction may alter the resulting chemical shifts slightly. Else simple overlay of all substrates may be used.

Reaction conditions with and without solvent were compared. Reactions without solvent were run with all substrates and catalyst present. Toluene was chosen as solvent, as it was suspected to not interact with either catalyst or substrates during the reaction run, while allowing for a wide temperature range without the solvent evaporating. 20 equivalents of solvent were used relative to the substrates. With and without solvent reactions at room temperature (RT, 23 °C) and elevated temperature (60 °C) were conducted. The respective conversions after 17 h (t₄ spectrum for room temperature and no solvent from Figure 59 and Table 5) are listed in Table 21. All spectra show the above-described reduction in **S4** vinyl signal integral and subsequent increase of signals associated with the formed methylene groups.

Table 21: Conversions after 17 h of platinum catalysed hydrosilylation of TMDS with **S4** at different reaction conditions.

Conditions	Conversion [%]
RT, neat	98.9
RT, Toluene	91.4
60 °C, neat	99.4
60 °C, Toluene	87.0

The increased yield of reactions run in neat conditions makes these conditions more favourable, especially when the same setup is applied to higher molecular weight polymers, decreasing the concentration of reactive groups. Furthermore, neat conditions do not require the removal of solvent, but can be worked up by simple filtration, removing the catalyst. No further workup is required due to the almost stoichiometric conversion of substrates. Added workup steps for reactions run with toluene likely diminished the conversion further.

It must be noted that spectra taken from reactions run at 60 °C result in less differentiable signals after 17 h reaction time in ¹H-NMR between 0.00 ppm and 0.25 ppm (Figure 60). These signals are associated with TMDS methyl groups. As shown in Figure 42 two products may form during the reaction, resulting from alpha and beta hydrosilylation. The signals multiplicity and integration from reactions run at 60 °C, doublets integrating for 2H each, are attributed to the alpha product. It can be concluded that elevated temperatures lead to more selective alpha hydrosilylation for the given

substrates, making product identification easier. For all further reactions, if not indicated otherwise run in this chapter neat conditions at 60 °C for 17 h were chosen. The reaction was scaled up from 1 g to 25 g, gradually adding **S4** to TMDS, keeping the temperature below 60 °C. The reaction showed a conversion of 99.4 %, providing sufficient substrate for further reactions described in this chapter.

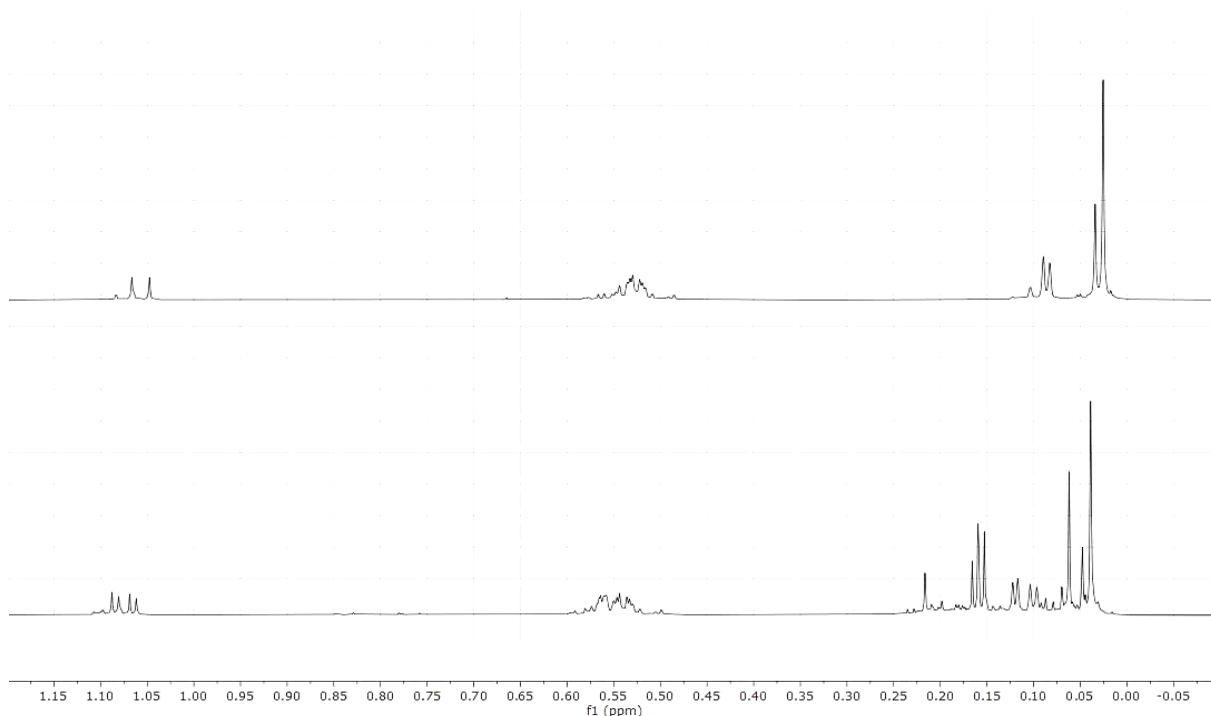


Figure 60: Platinum catalysed hydrosilylation of **S4** with TMDS after 17 h at 60 °C (top) and RT (bottom).

With the optimised reaction conditions at hand, hydrosilylation of compound **P4** with TMDS in accordance to Figure 42 was undertaken. Again, a decrease in vinyl and increase in signals associated to formed methylene groups in ^1H -NMR spectra is recorded. The conversion at 92.5 % is slightly diminished when compared to hydrosilylation of **S4** with TMDS. This is likely due to the added steric bulk of compound **P4**, with its rotation hindered thiophene compared to methoxy substituent in **S4**. Here again a differentiation of alpha and beta products could be seen in the ^1H -NMR spectra after the reaction both in the heteroaromatic region of thiophene, as well as the formed carbon-silicon bond. Interestingly the hydrosilylation lead to sufficient chemical shift differences to not only differentiate between substrate and product, but also between alpha and beta product, depicted in Figure 61, showing 87.3 % alpha and 12.6 % beta product. Hydrosilylation conditions were successfully established and reaction presented in Figure 42 was successfully shown.

Appendix

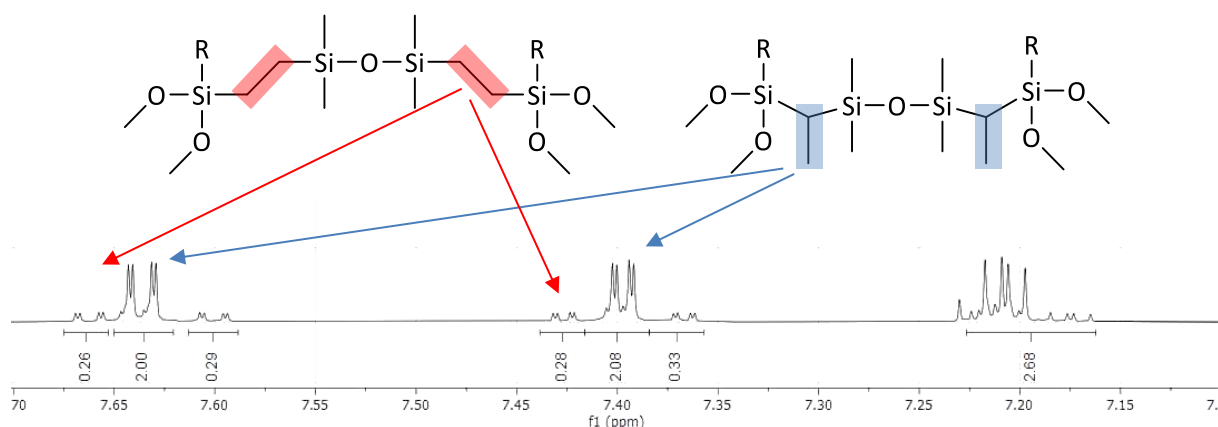


Figure 61: ^1H -NMR region 7.1-7.7 ppm of the reaction product between **P4** and TMDS.

The corresponding spectra are available in Appendix A4

Representative procedure G

A three-neck round-bottom flask equipped with cooling condenser, magnetic stir bar and a stopper is flame dried, filled with dry argon and charged with decamethylcyclopentasiloxane (D_5 , 168.57 mmol, 50.000 g). Optionally a solvent is added (100 ml). A chain termination agent according to the table below is added (49.45 mmol). The mixture is stirred and heated to 80 °C, trifluoromethanesulfonic acid (0.11 mmol, 10 μl) are added. The reaction is left to stir for 2 h and then quenched with sodium bicarbonate (19.05 mmol, 1.600 g). The mixture is filtered and subjected to distillation at 120 °C and 10 mbar. Resulting polymers analysis is listed in the table below.

Table 22: : aROP of TMDS derivatives at 80 °C using different solvent conditions and triflic acid as catalyst, stating the weighed samples for the TMDS-derivatives. Conversion measured based on ^{29}Si -NMR shift comparing D_4 at -19 ppm and PDMS at -23 ppm, Mn and PDI according to GPC measurement.

Entry	chain termination agent	solvent	Weighed sample [g]	Conversion [%]	Mn [g/mol]	PDI
1	TMDS	Neat	6.642	65	3429	1.14
2	TMDS	Toluene	6.642	63	3581	1.21
3	TMDS	DMSO	6.642	52	3492	1.18
4	TMDS- S4	Neat	21.302	0	-	-
5	TMDS- S4	Toluene	21.302	0	-	-
6	TMDS- S4	DMSO	21.302	0	-	-
7	TMDS- P4	Neat	26.454	0	-	-
8	TMDS- P4	Toluene	26.454	0	-	-
9	TMDS- P4	DMSO	26.454	0	-	-

Representative procedure H

To a reaction vial silanes **P4** and **P8** are consecutively added in the below stated amounts and equivalents (always summing to 2 mmol). Furthermore, 2 ml of the stated solvent is added. Lastly the stated amount of 1 M aqueous hydrochloric acid (HCl_{aq}) is added. The vials are closed, and the mixture is stirred at the stated temperature for 24 h. Lastly the vials are opened and further stirred at the same temperature for 2 h. Actual weights and resulting molar ratios are listed in Table 26. Samples are taken from the vials and subjected to analysis. Analysis results are listed in Table 26. Exemplary GPC and NMR spectra are shown in Appendix A4.

Amplitude sweep on a Thermo Scientific HAAKE RheoStress 1

A Thermo Scientific HAAKE RheoStress 1 equipped with a stainless-steel base and titanium ring-rotor (inner diameter 22 mm, outer diameter 30 mm) plate-plate geometry is equipped with a nitrogen purge chamber and is heated to 23 °C. The amplitude sweep mode was selected and conducted in the ranges stated below. After calibration a sample of compound **S1** is added to the plate and measurements are started. The resulting amplitude sweep is presented below with logarithmic axis.

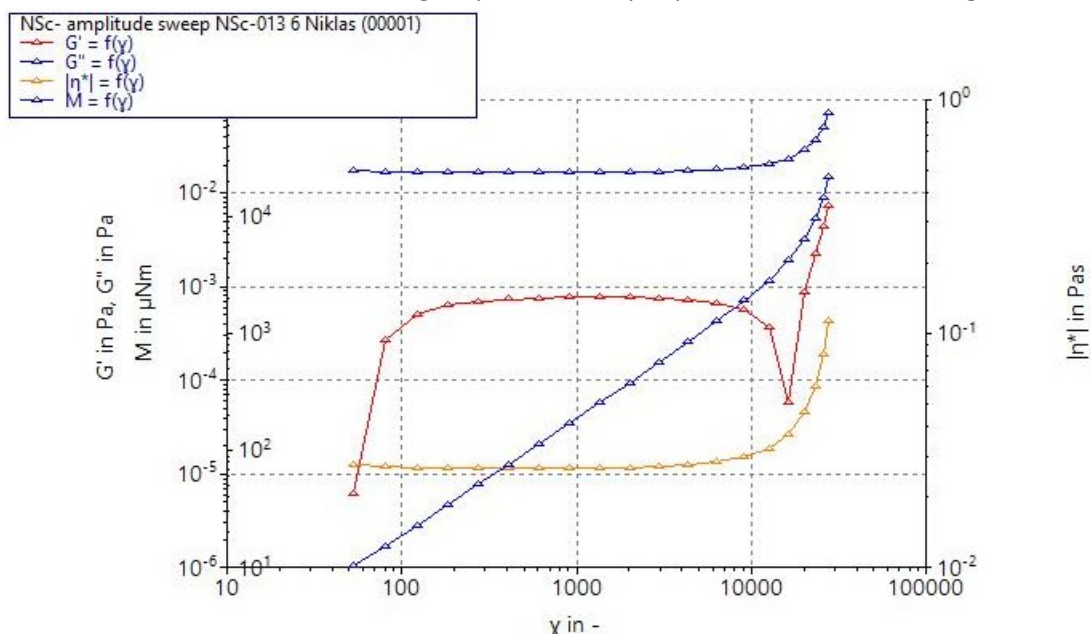


Figure 62: Amplitude sweep of **S1** at $\tau = 1\text{-}2000$ Pa, $f = 0,1$ Hz.

Table 23: Raw data of amplitude sweep of **S1** at $\tau = 1\text{-}2000$ Pa, $f = 0,1$ Hz.

SegIndex	τ in Pa	δ in °	G' in Pa	G'' in Pa	$ \eta^* $ in Pas
1	0.914	89.979	0.000006	0.0172	0.0274
2	1.369	89.082	0.000272	0.0170	0.0270
3	2.051	88.288	0.000502	0.0168	0.0267
4	3.066	87.803	0.000640	0.0167	0.0266
5	4.577	87.650	0.000683	0.0166	0.0265
6	6.837	87.461	0.000737	0.0166	0.0265
7	10.207	87.364	0.000765	0.0166	0.0265
8	15.240	87.292	0.000788	0.0167	0.0265
9	22.750	87.304	0.000788	0.0167	0.0267
10	33.973	87.324	0.000787	0.0168	0.0268
11	50.741	87.432	0.000764	0.0170	0.0272
12	75.828	87.578	0.000734	0.0173	0.0276
13	113.404	87.824	0.000678	0.0178	0.0284
14	169.860	88.223	0.000580	0.0187	0.0298
15	254.998	88.939	0.000377	0.0203	0.0324
16	383.684	89.857	0.000058	0.0234	0.0373
17	577.974	88.226	0.000893	0.0288	0.0459
18	870.464	86.519	0.002282	0.0375	0.0598
19	1309.692	85.086	0.004375	0.0509	0.0813
20	1967.747	84.135	0.007311	0.0712	0.1139

It can be assumed that significant deformations are not relevant for uncured systems such as the test substance investigated in this study. However, for curing polymeric systems, minimizing deformation is desirable to maintain structural integrity. At strain levels exceeding $\gamma = 3000$, a nonlinear response of the measured parameters becomes evident. Additionally, achieving high deformations requires correspondingly high oscillation amplitudes, as the oscillatory motion must be completed within the preset frequency. At higher deformation levels, the system transitions beyond the viscoelastic regime, making further analysis irrelevant for the intended application. Moreover, excessive deformation can lead to polymer chain disentanglement, thereby altering the material's response.²²⁰ Consequently, measurements at deformation levels exceeding this threshold were not conducted.

Frequency sweep on a Thermo Scientific HAAKE RheoStress 1

A Thermo Scientific HAAKE RheoStress 1 equipped with a stainless-steel base and titanium ring-rotor (inner diameter 22 mm, outer diameter 30 mm) plate-plate geometry is equipped with a nitrogen purge chamber and is heated to 23 °C. The frequency sweep mode was selected in the range $\tau = 26.74$ Pa, $f = 0.01 - 100$ Hz. After calibration a sample of compound **S1** is added to the plate and measurements are started. The resulting frequency sweep is presented below with logarithmic axis.

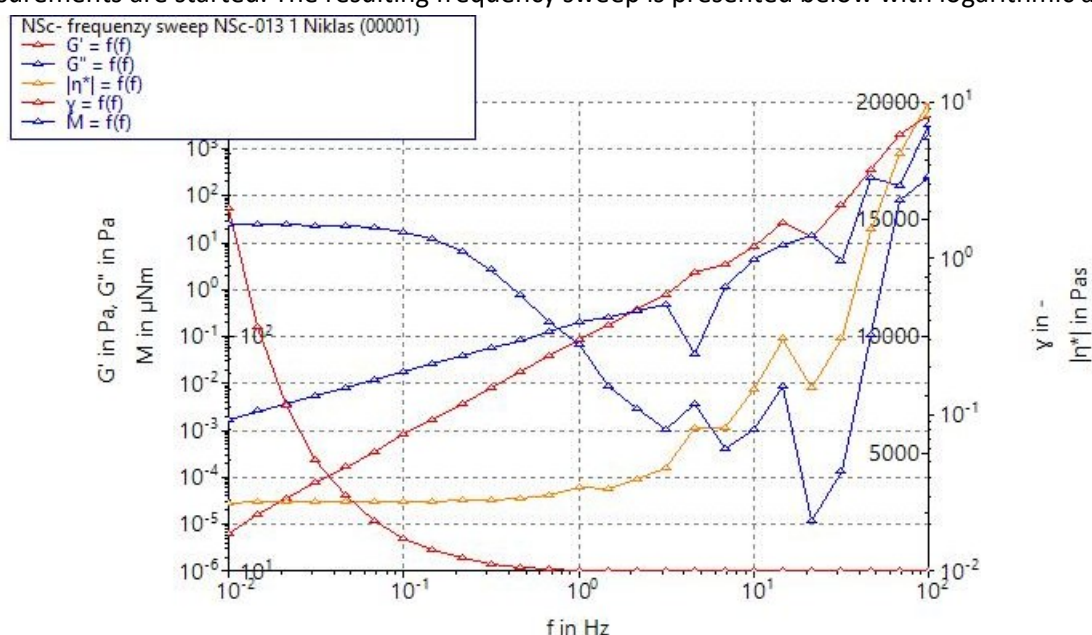


Figure 63: Frequency sweep of **S1** with $\tau = 26.74$ Pa, $f = 0.01 - 100$ Hz.

Appendix

Table 24: Raw data of frequency sweep of **S1** with $\tau = 26.74$ Pa, $f = 0.01 - 100$ Hz.

SegIndex	τ in Pa	δ in °	G' in Pa	G'' in Pa	$ \eta^* $ in Pas
1	26.717	89.798	0.000006	0.0017	0.0274
2	26.695	89.648	0.000016	0.0026	0.0279
3	26.646	89.483	0.000034	0.0038	0.0280
4	26.542	89.232	0.000075	0.0056	0.0281
5	26.321	88.853	0.000164	0.0082	0.0281
6	25.863	88.306	0.000355	0.0120	0.0281
7	24.968	87.426	0.000793	0.0176	0.0281
8	23.311	86.193	0.001722	0.0259	0.0281
9	20.656	84.364	0.003745	0.0379	0.0282
10	17.125	81.660	0.008156	0.0556	0.0283
11	13.426	77.667	0.017961	0.0821	0.0288
12	10.327	73.234	0.037809	0.1255	0.0306
13	8.282	67.126	0.084901	0.2012	0.0348
14	5.507	55.405	0.173866	0.2521	0.0332
15	4.420	42.516	0.385649	0.3536	0.0387
16	3.572	32.896	0.769091	0.4975	0.0461
17	4.568	1.002	2.391231	0.0418	0.0820
18	2.966	18.744	3.359406	1.1400	0.0829
19	3.551	29.329	7.911232	4.4449	0.1444
20	5.479	17.735	26.817980	8.5767	0.3053
21	1.463	47.131	13.677610	14.7348	0.1485
22	2.366	3.799	61.828609	4.1056	0.3119
23	9.100	34.396	365.905914	250.5058	1.5205
24	33.953	4.535	1985.224976	157.4758	4.6522
25	42.591	30.524	5380.075195	3172.1589	9.9402
26	43.232	19.066	4931.141113	1704.3140	8.3037

Frequency sweeps show stable and reproduceable results for 1 Hz and lower, this seems to be independent from the stress set for the measurement. The spectrum shown is a function of frequency. G' and G'' follow linear dependencies below 1 Hz and constant behavior of the resulting viscosity η . Therefore, measurements below 1 Hz are investigated further.

Representative procedure I

A Thermo Scientific HAAKE RheoStress 1 equipped with a stainless-steel base and titanium ring-rotor (inner diameter 22 mm, outer diameter 30 mm) plate-plate geometry is equipped with a nitrogen purge chamber and is heated to 23 °C. Continuous oscillation mode is selected based on the parameters established in representative procedures H and I and run at $\gamma = 150$, 0.1 Hz and 24 h. The sampling rate is set to average over 5 minutes (collecting several full oscillations each). Additionally, a humidity chamber and humidity generator and controller (dataphysics-instruments HGC 20) are used on the rotor contact area continuously generating a stream of 50 % humidity and 23 °C air.

Measurements are presented in Appendix A4 as graphs as there are several hundred datapoints collected per measurement, $|\eta^*|$ is calculated through (3). From the data polynomial fits correlating datapoint # with values are available and presented below:

P1:

$$G'(\mathbf{P1}) = 0.00000021 * \#^3 - 0.00006 * \#^2 + 0.0041 * \# + 0.2959; R^2 = 0.985$$

$$G''(\mathbf{P1}) = 0.00000315 * \#^3 - 0.0007 * \#^2 + 0.0579 * \# + 0.1428; R^2 = 0.992$$

P8:

$$G'(P8) = 0.0000002 * \omega^3 - 0.000048 * \omega^2 + 0.003798 * \omega + 0.29625; R^2 = 0.989$$

$$G''(P8) = 0.00000168 * \omega^3 - 0.0003 * \omega^2 + 0.0343 * \omega + 0.0661; R^2 = 0.995$$

S2:

$$G'(S2) = 0.00000013 * \omega^3 - 0.00002 * \omega^2 + 0.0015 * \omega + 0.1985; R^2 = 0.993$$

$$G''(S2) = 0.00000148 * \omega^3 - 0.000282 * \omega^2 + 0.0139 * \omega + 0.0364; R^2 = 0.989$$

S4:

$$G'(S4) = 0.00000002 * \omega^3 - 0.00004 * \omega^2 + 0.0019 * \omega + 0.2981; R^2 = 0.992$$

$$G''(S4) = 0.00000145 * \omega^3 - 0.000251 * \omega^2 + 0.031 * \omega + 0.0593; R^2 = 0.996$$

S6:

$$G'(S6) = 0.00000013 * \omega^3 - 0.00001 * \omega^2 + 0.0011 * \omega + 0.6989; R^2 = 0.993$$

$$G''(S6) = 0.00000195 * \omega^3 - 0.000379 * \omega^2 + 0.04596 * \omega + 0.3544; R^2 = 0.910$$

From this data the crossover-times of all silanes can be extracted through $G' = G''$ (See Table 26).

Table 25: Time resolved rheology measurement of **P1**, **P8**, **S2**, **S4** and **S6** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions. Table shows the time until cross-over point and viscosity at crossover-point [Pas].

Silane	Time until crossover-point [min]	η^* at crossover-point [Pas]
P1	10	0.70
P8	35	0.73
S2	110	0.51
S4	40	0.71
S6	40	1.63

In some instances, the formation of gelled particles under the ring rotor and the expulsion is observed. This is accompanied by fluctuations in data. An exemplary particle expulsion is shown in Figure 64. The corresponding rotor is shown in Figure 65.

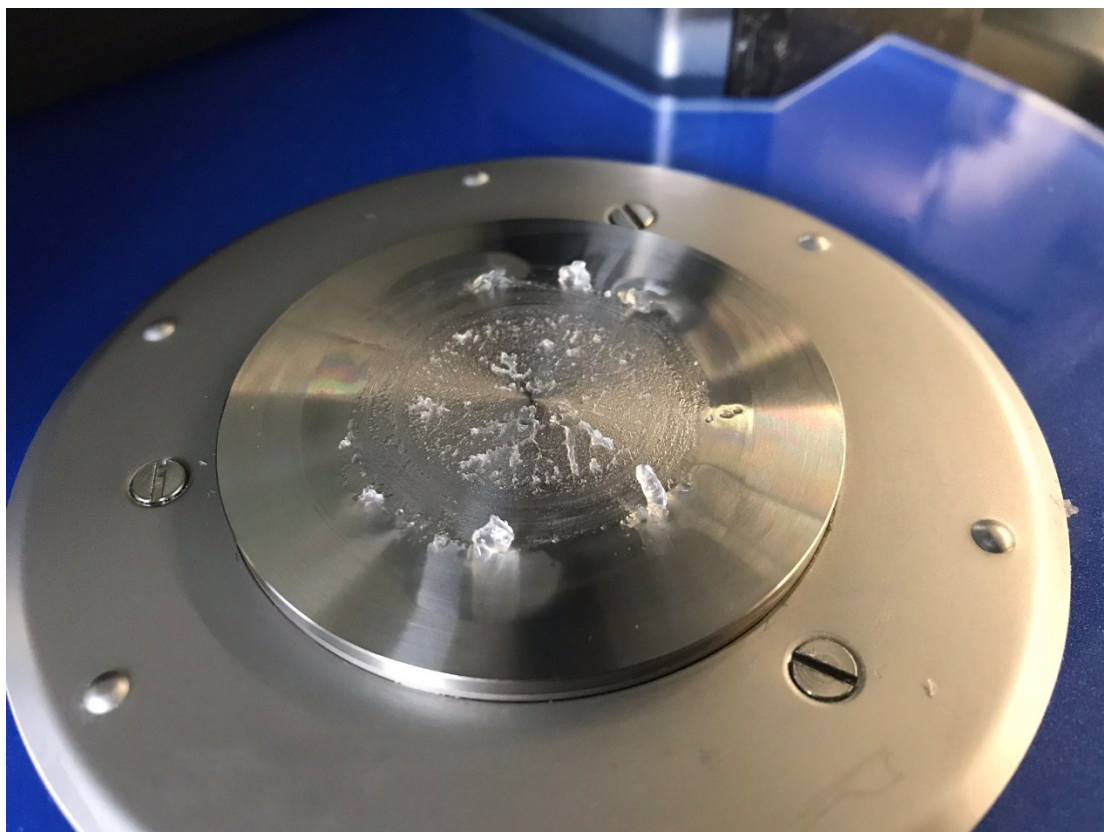


Figure 64: Thermo Scientific HAAKE RheoStress 1 peltier plate with particles expelled by the ring rotor (not shown).



Figure 65: Thermo Scientific titanium ring-rotor with gelled particles after 24 h measurement.

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Table 26: Overview table for representative procedure I listing weighed samples **P4** and **P8**, used solvent, amount of 1M hydrochloric acid, the molar ratio between P4, P8 and water, as well as the temperature of the reaction. Resulting GPC measurements, swelling degree as the quotient Q of the resins weight after and before swelling, as well as bound, residual methoxy content from NMR.

Entry	P4 [mg]	P8 [mg]	Solvent	HCl _{aq} [μl]	Molar ratio P4 : P8 : H ₂ O	Temperature [°C]	GPC		Swelling degree Q = W _{swollen} / W _{dry}	MeOSi content [%]
							Mn [g / mol]	PDI		
1	228.4	264.4	EtOAc	117	01:01:03	60	6083	2.84	1.42	85
2	228.4	264.4	EtOAc	117	01:01:03	60	6492	1.25	1.54	84
3	41.5	448.0	EtOAc	117	10:01:33	60	7195	2.40	1.64	74
4	41.5	448.0	EtOAc	117	10:01:33	60	3513	3.65	1.80	77
5	415.2	44.8	EtOAc	117	01:10:33	60	3878	1.76	1.26	76
6	415.2	44.8	EtOAc	117	01:10:33	60	4859	1.44	1.15	75
7	228.4	264.4	THF	117	01:01:03	60	1346	2.19	2.04	45
8	228.4	264.4	THF	117	01:01:03	60	1088	1.99	2.13	40
9	41.5	448.0	THF	117	10:01:33	60	1540	2.41	3.46	31
10	41.5	448.0	THF	117	10:01:33	60	1542	2.98	3.52	34
11	415.2	44.8	THF	117	01:10:33	60	1346	2.19	1.84	28
12	415.2	44.8	THF	117	01:10:33	60	1088	1.99	1.89	21
13	228.4	264.4	THF	29	01:01:01	60	1266	2.18	2.84	58
14	228.4	264.4	THF	29	01:01:01	60	1253	2.24	2.86	64
15	228.4	264.4	THF	468	01:01:10	60	1422	1.54	1.98	14
16	228.4	264.4	THF	468	01:01:10	60	1810	1.01	1.93	19
17	228.4	264.4	THF	117	01:01:03	23	261	1.45	4.21	34
18	228.4	264.4	THF	117	01:01:03	23	255	1.43	4.36	32
19	228.4	264.4	THF	117	01:01:03	100	1874	1.62	1.32	26
20	228.4	264.4	THF	117	01:01:03	100	1759	1.35	1.38	29

Upscale of reaction procedure A**Run 1**

The previously reported reaction procedure A has been upscaled as described in 3.4. The appropriate reaction procedure, including noted reaction temperatures is reported here.

A reaction setup as described per representative procedure A containing tetraethoxy-silane and 2-bromothiophene is prepared in a laboratory neighboring the scale-up plant. To a round bottom flask 243 g magnesium shavings are added and heated to 280 °C at 1.0×10^{-3} mbar for 1 h. In parallel a custom-made double wall stainless steel reactor is washed with acetone and then dried at 1.5 mbar and 80 °C jacket temperature for 4 h. The reactor is flushed with dry nitrogen and the above-described shavings transferred under a nitrogen blanket, followed by the addition of 10 L dry THF. 2.23 kg tetraethoxy silane are charged into the reactor. 644 ml 2-bromothiophene is prepared in a round bottom flask, connected to a variable speed peristaltic pump. Dosing is turned on to 50 ml per minute, adding a total of 45 ml. After 34 minutes an increase of reactor temperature from 26 °C to 46 °C is noted. The jacket temperature is noted to rise to maximum 37 °C. After 2 h no significant cooling of cooling fluid was noted. Dosing was continued at 10 ml per minute. No temperature increase is observed. The setup according to representative procedure A is initiated with 10 ml Thiophene, observing a temperature rise from 25 °C to 48 °C. The flask content was transferred under nitrogen to the steel reactor. Dosing into the reactor was continued at 5 ml per minute, noting a maximum temperature of 46 °C. After addition was finished the jacket temperature was increased to 60 °C for 1 h. Distillation from the reactor was carried out through a Claisen analogous bridge at 40 °C at 210 mbar, leaving a grey residue. The residue is transferred to a dry 6 L multi-neck round bottom flask. The reactor is washed with 4 L dry heptane. The resulting slurry is filtered through a dry 29.3 cm PALL high pressure filter equipped with a POR 3 filter disc. The resulting liquid is distilled at 45 °C and 30 mbar. Yielding 1.509 kg slightly yellow, clear liquid. The product is subjected to fractioned distillation and NMR results are equivalent to couplings reported for **P8**.

Run 2

An identical setup as described in run 1 was used, instead of tetraethoxy-silane 1.48 kg vinyl-trimethoxy-silane was used. Again 45 ml 2-bromothiophene were dosed to the reactor. The thermostat installed within the jacket loop of the reactor had been upgraded between the runs allowing for more efficient heat exchange. The reactor temperature is reported to rise from 28 °C to 35 °C initially, cooling to 30 °C within 4 minutes. The prepared reaction according to representative procedure A was not used. 2-bromothiophene addition was resumed, taking 2.5 h total. From here the workup reported in run 1 is continued. Yielding 1.135 kg (87 %) slightly yellow, clear liquid. NMR shows 79 % purity. The product is subjected to fractioned distillation and NMR results are equivalent to couplings reported for **P4**.

Addition of novel α -silanes to representative commercial formulation

To a 200 ml PP mix cup for a Hauschild SpeedMixer® 80 g 80.000 cSt α - ω -OH-polydimethylsiloxane followed by 10 g 1.000 cSt α - ω -methyl-polydimethylsiloxane, 5 g of fumed silica and 4.9 g vinyl-trimethoxy silane (**S4**) are added. The cup is closed and inserted into a Hauschild SpeedMixer® DAC 400. After 1 minute mixing at 2000 rpm the cup is opened, 0.1 g dioctyltin dilaurate as catalyst are added and the cup is subjected to mixing for 2 minutes at 100 mbar and 2000 rpm forming the reference sample. To this 1 wt% of material stated in the table below may be added. The resulting mixture is applied on a HDPE sheet at a thickness of 2 mm and left to cure for up to 7 days at 23 °C and 50 % humidity. The required time to form a skin is measured using a spatula. Tack free time is

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determined after 24 h through ASTM C679.²³⁵ Shore A values of the film are recorded according to ASTM D2240 after 1 and 7 days.²³⁶ Additionally, samples for peel tests were applied to the substrates stated below as a bead and left to cure for 7 days at 23 °C and 50 % humidity and measured according to ISO 11339.²³⁷ Additions of silanes from this work are listed in table and polymers formed in this work are added and measured according to table.

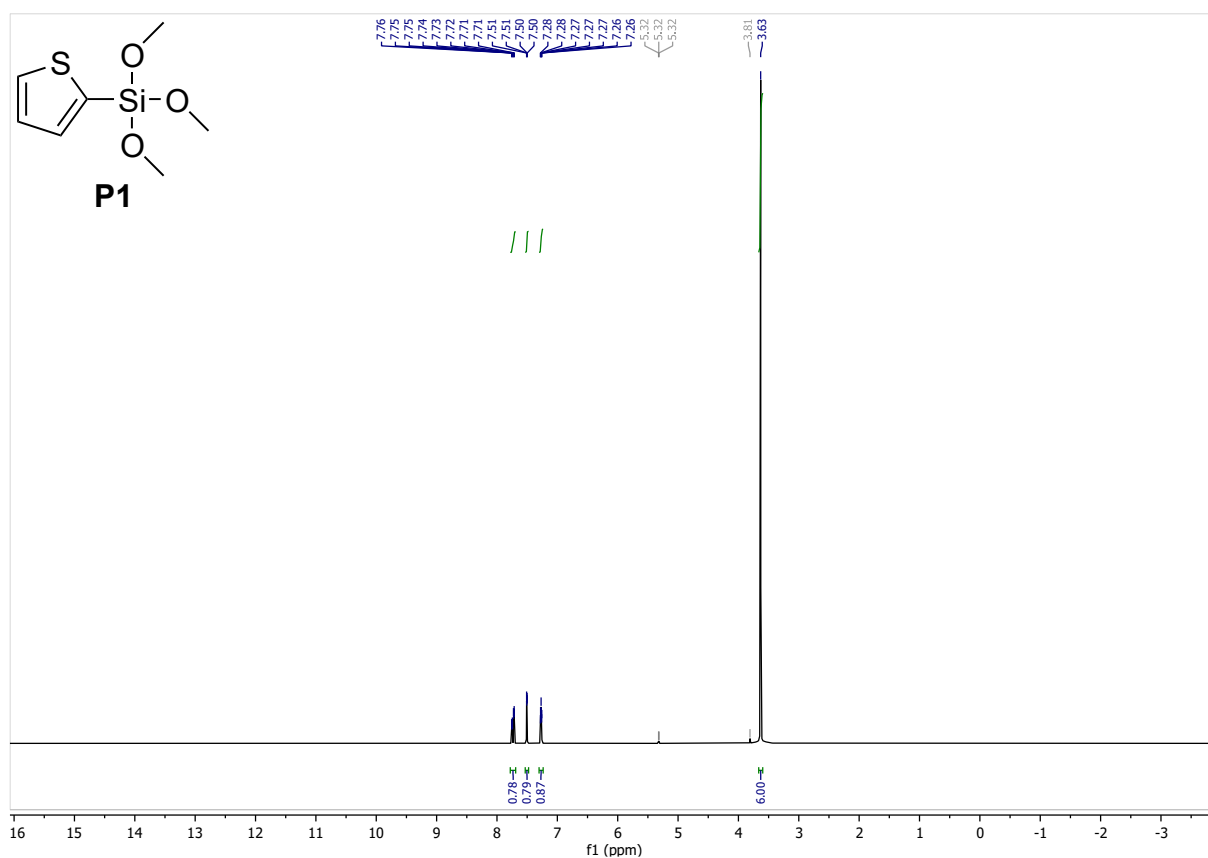
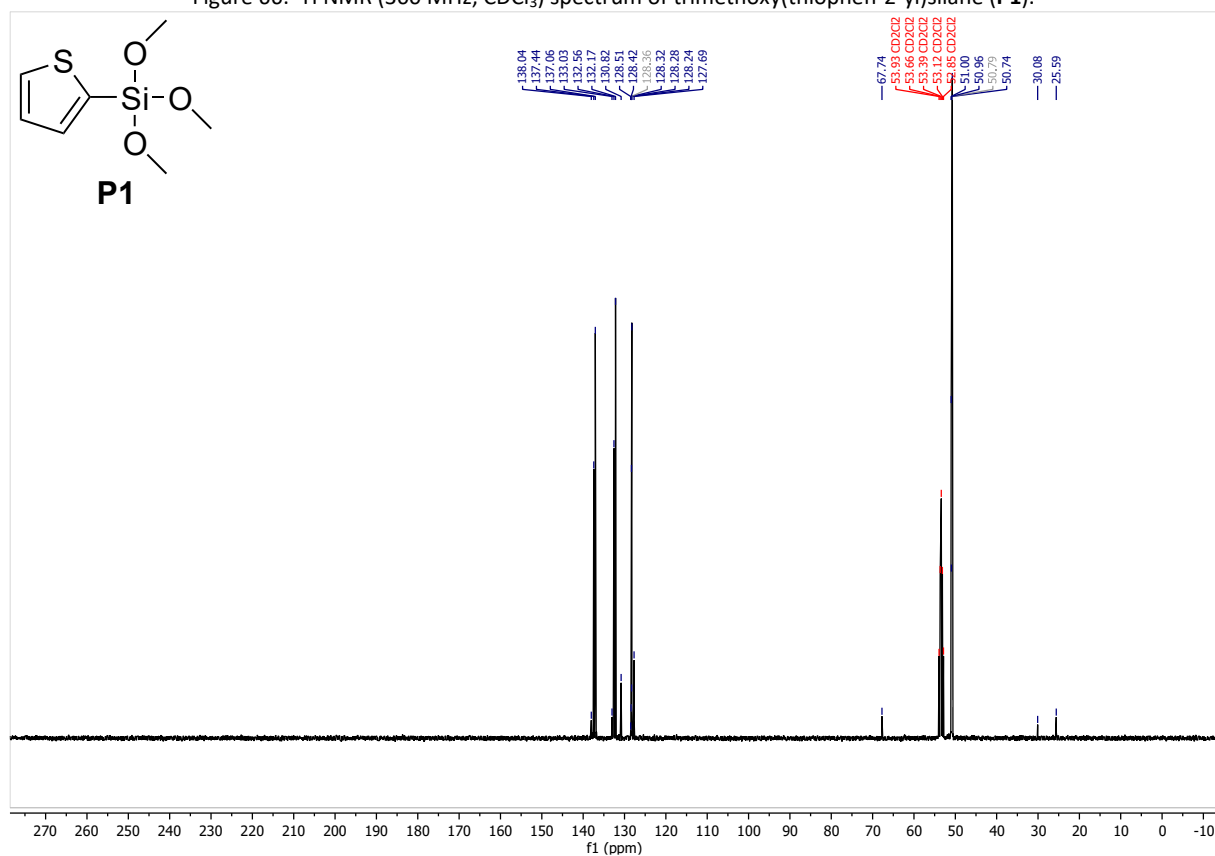
Table 27: To the representative mixture described above one weight percent of the stated silanes were added and tests conducted to the stated standards at controlled ambient conditions. The resulting measurement values are tabulated below.

Entry	Baseline	S4	P1	P2	P3	P4
SOT [min]	20	18	8	19	16	10
Cure through [mm / 24 h]	2.36	2.47	3.31	2.68	2.59	3.82
Shore A [1 d]	13	14	10	13	14	9
Shore A [7 d]	22	23	24	23	20	25
Adhesion Glas	8	9	9	8	8	9
Adhesion Aluminum	6	7	9	7	6	9
Adhesion Brass	4	4	8	7	7	8
Adhesion Concrete	2	2	8	6	7	8
Adhesion PMMA	1	2	7	6	6	8

Table 28: To the representative mixture described above one weight percent of a PDMS functionalised with the stated silane are added and tests conducted to the stated standards at controlled ambient conditions. The resulting measurement values are tabulated below.

Entry	Baseline	PDMS-S4	PDMS-S1
SOT [min]	20	19	22
Cure through [mm / 24 h]	2.36	2.41	2.45
Shore A [1 d]	13	14	10
Shore A [7 d]	22	22	21
Adhesion Glas	8	8	8
Adhesion Aluminium	6	6	7
Adhesion Brass	4	5	5
Adhesion Concrete	2	1	2
Adhesion PMMA	1	3	4

A4 Spectra

Figure 66: ¹H NMR (300 MHz, CDCl₃) spectrum of trimethoxy(thiophen-2-yl)silane (**P1**).Figure 67: ¹³C NMR (75 MHz, CDCl₃) spectrum of trimethoxy(thiophen-2-yl)silane (**P1**).

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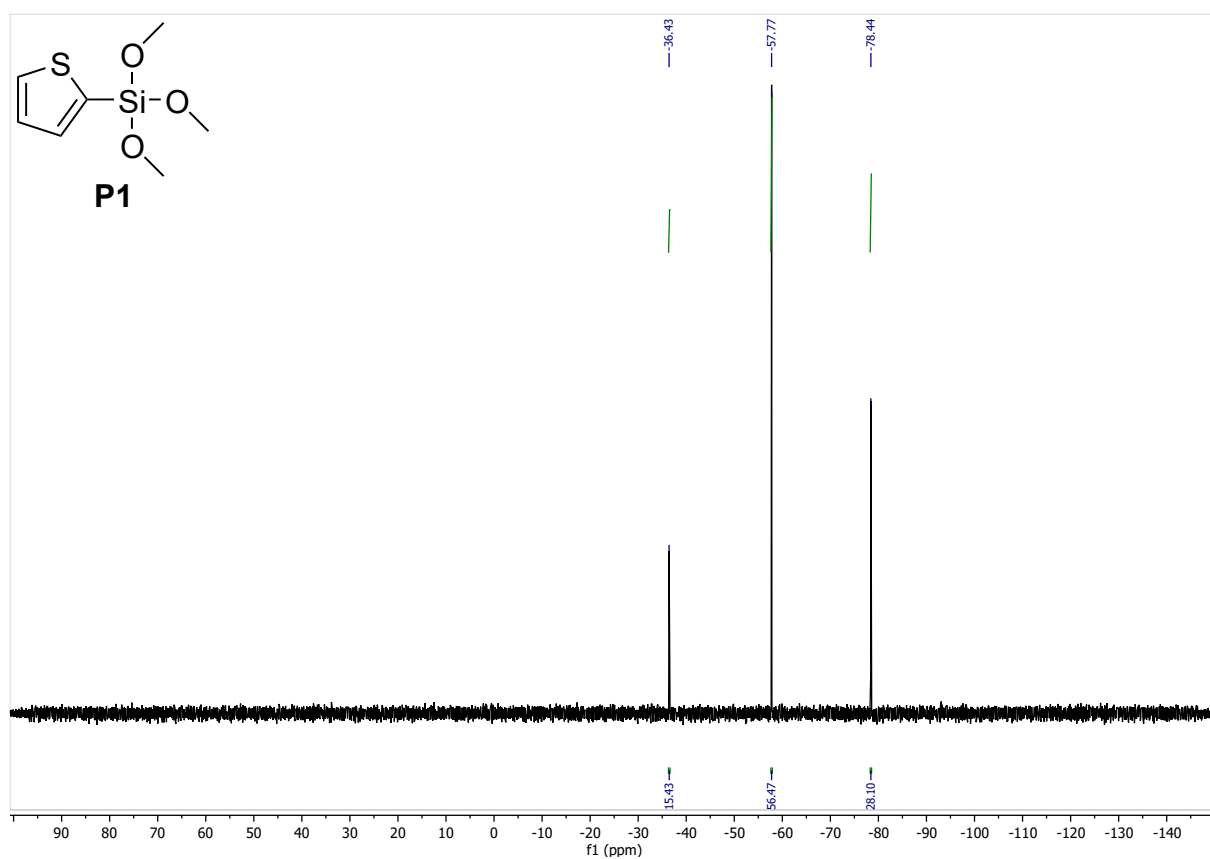


Figure 68: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of trimethoxy(thiophen-2-yl)silane (**P1**).

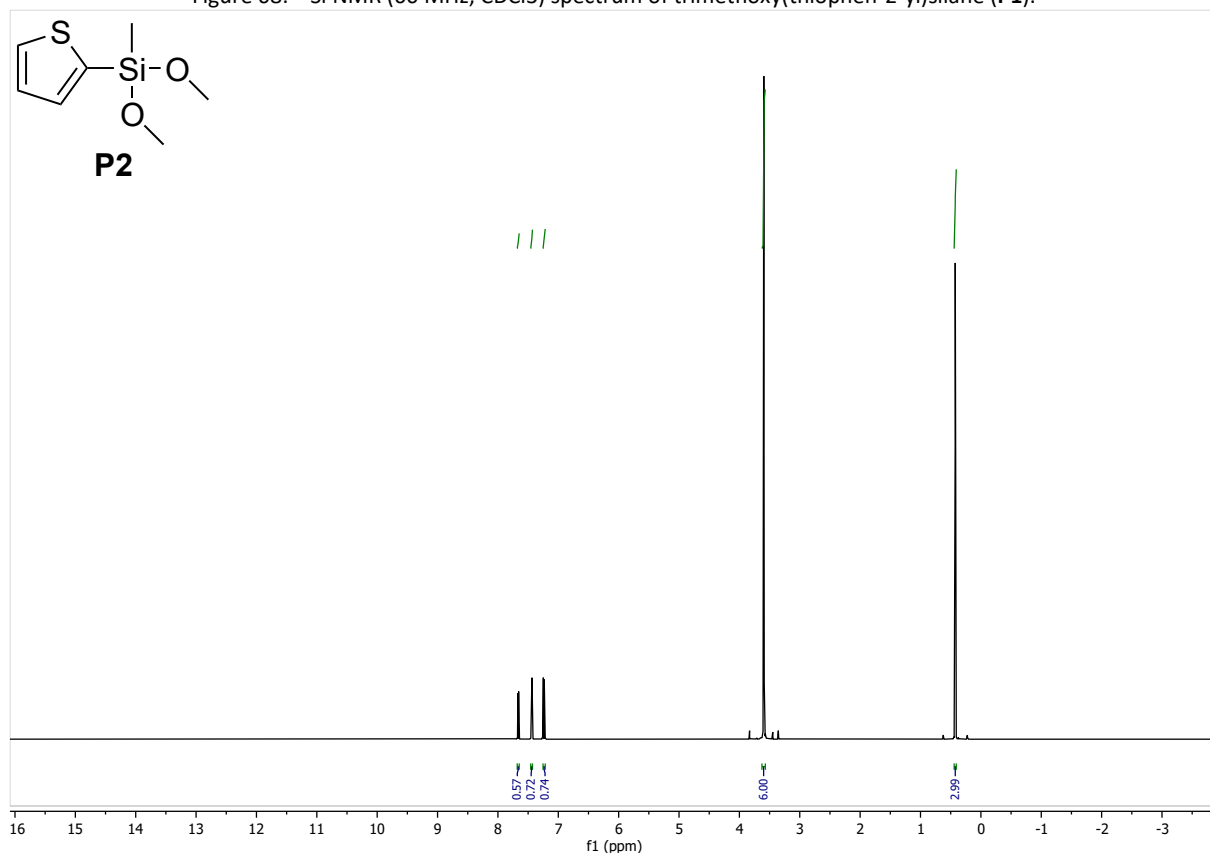


Figure 69: ¹H NMR (300 MHz, CDCl₃) spectrum of dimethoxy(methyl)(thiophen-2-yl)silane (**P2**).

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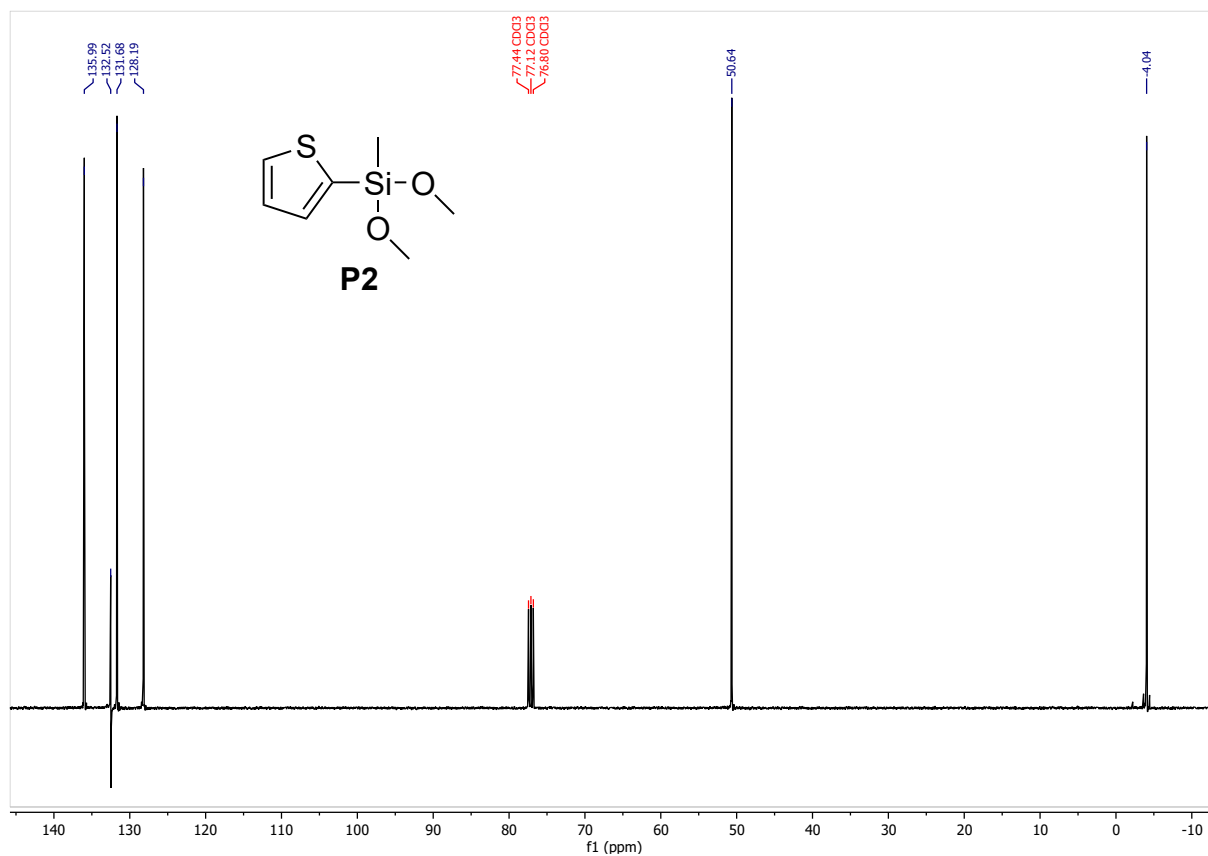


Figure 70: ^{13}C NMR (75 MHz, CDCl_3) spectrum of dimethoxy(methyl)(thiophen-2-yl)silane (**P2**).

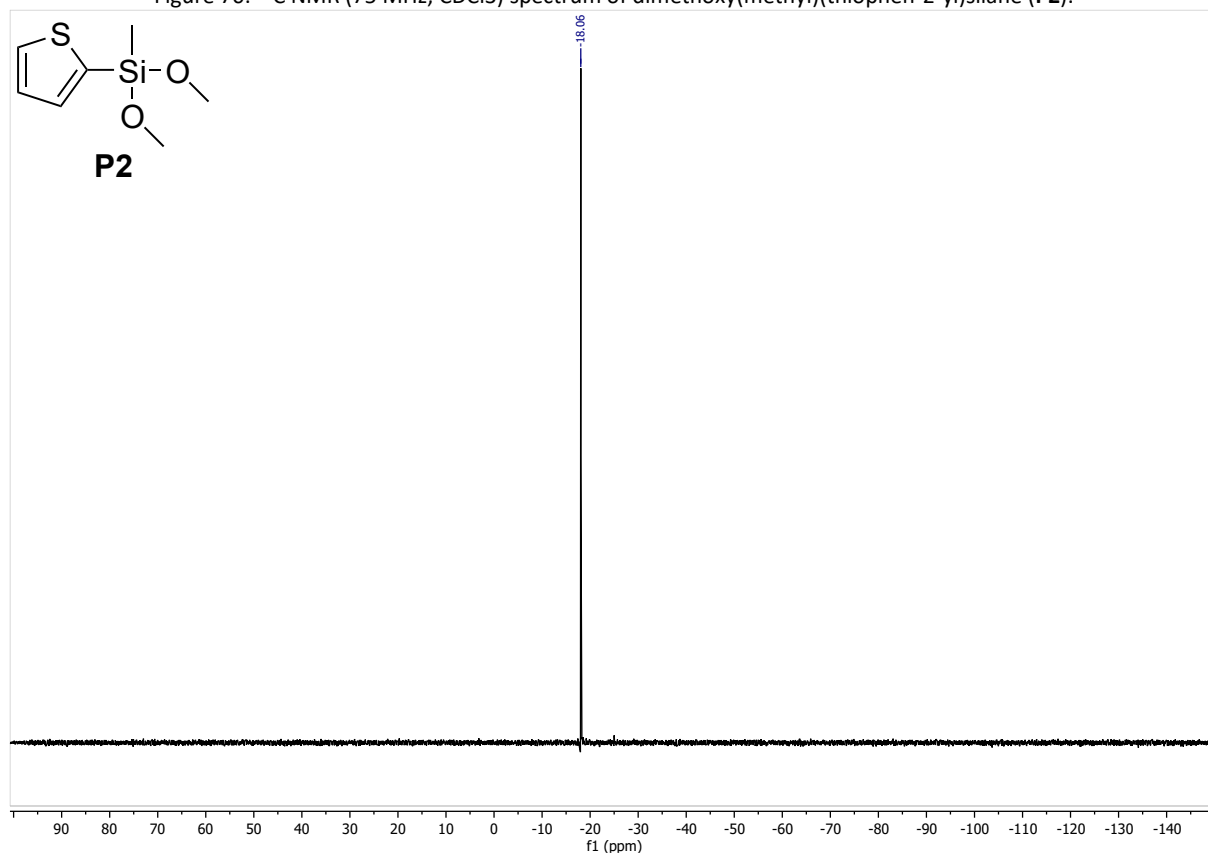
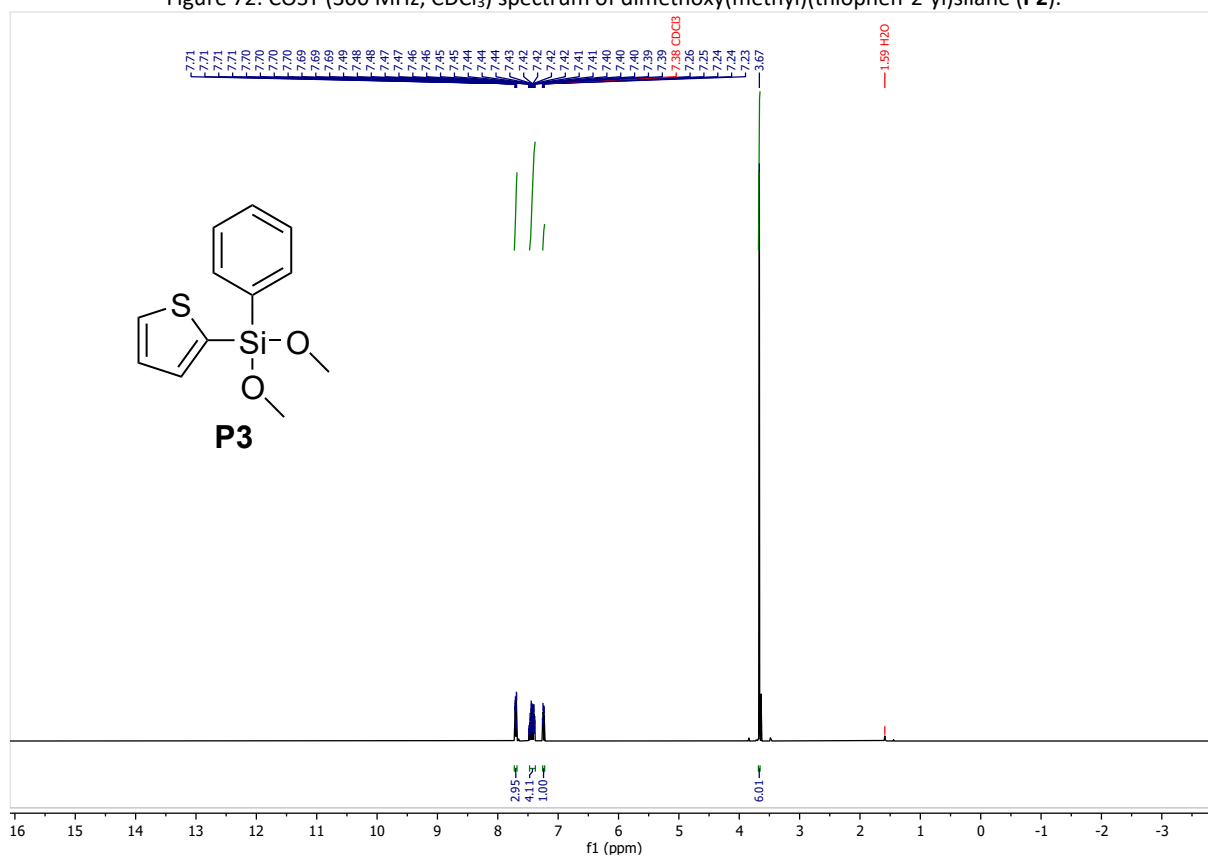
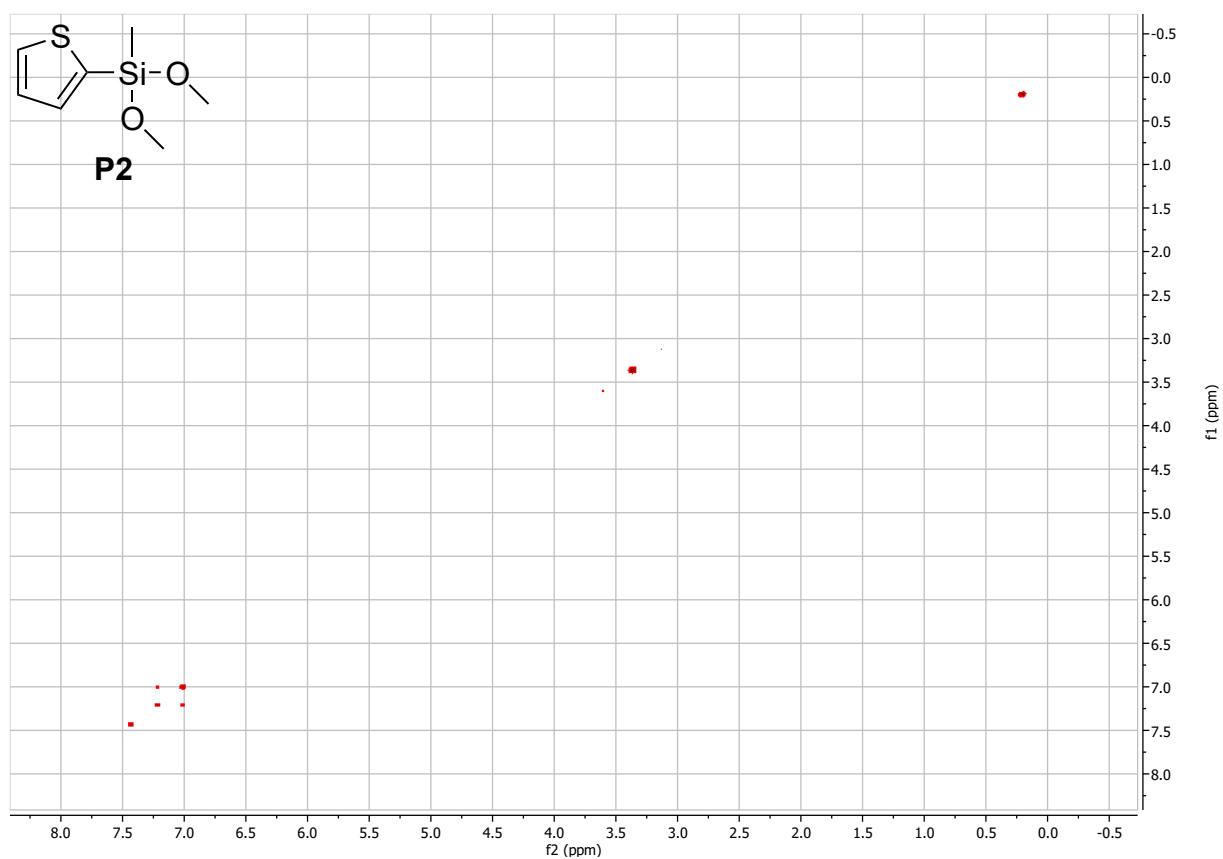


Figure 71: ^{29}Si NMR (60 MHz, CDCl_3) spectrum of dimethoxy(methyl)(thiophen-2-yl)silane (**P2**).

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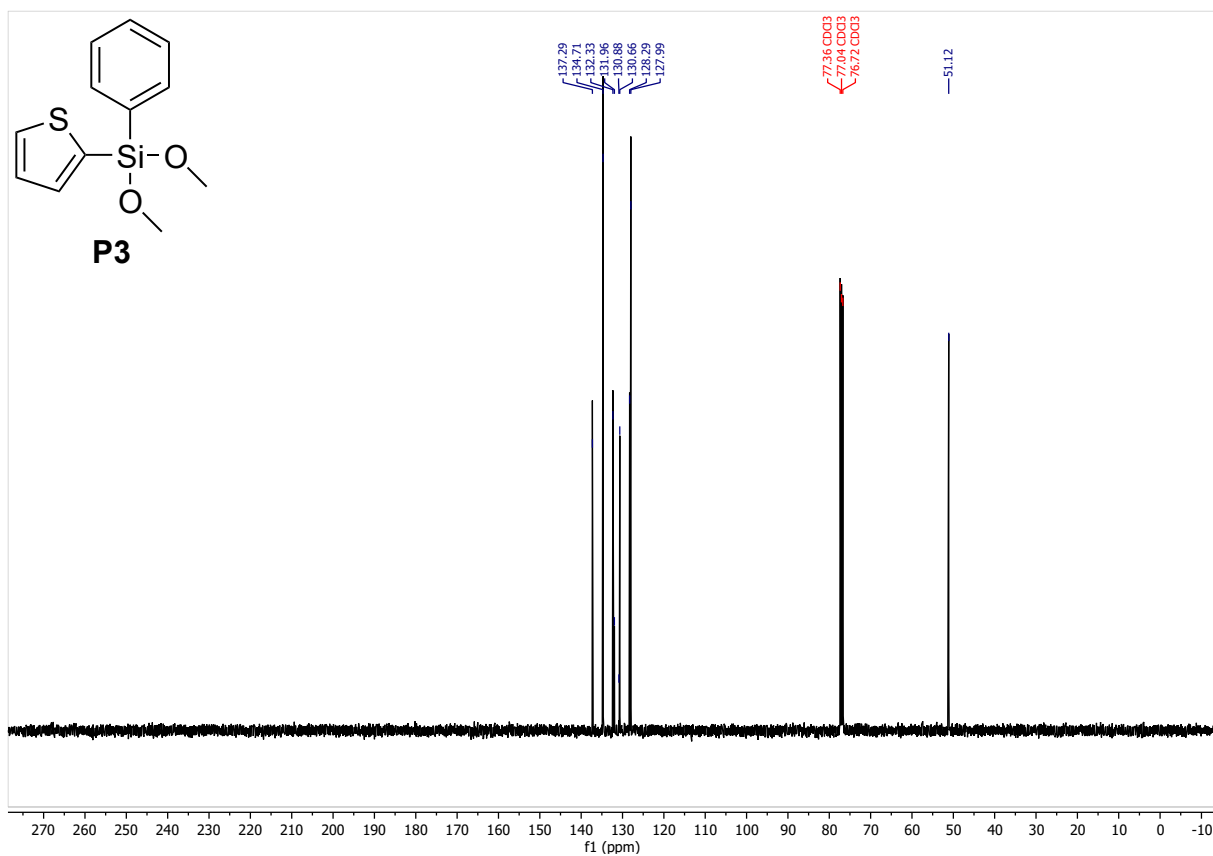


Figure 74: ^{13}C NMR (75 MHz, CDCl_3) spectrum of dimethoxy(phenyl)(thiophen-2-yl)silane (**P3**).

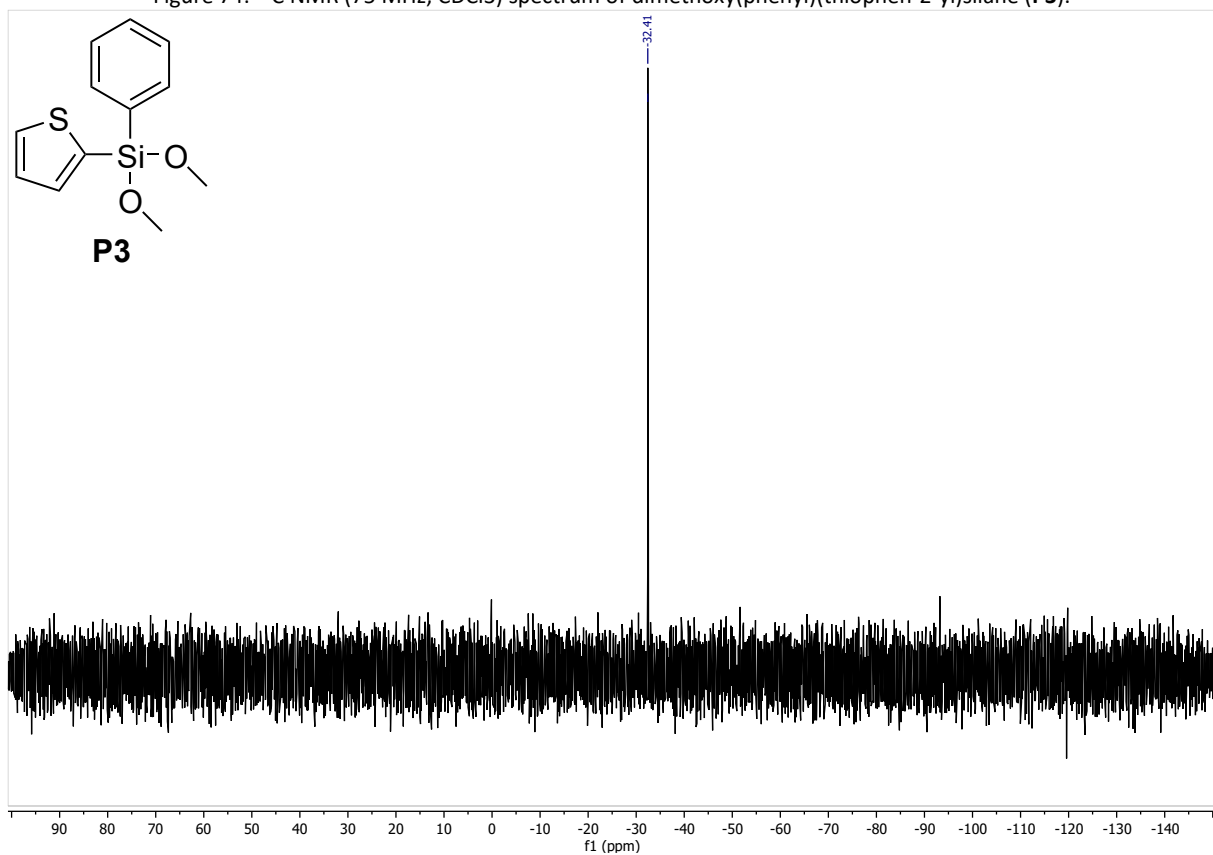
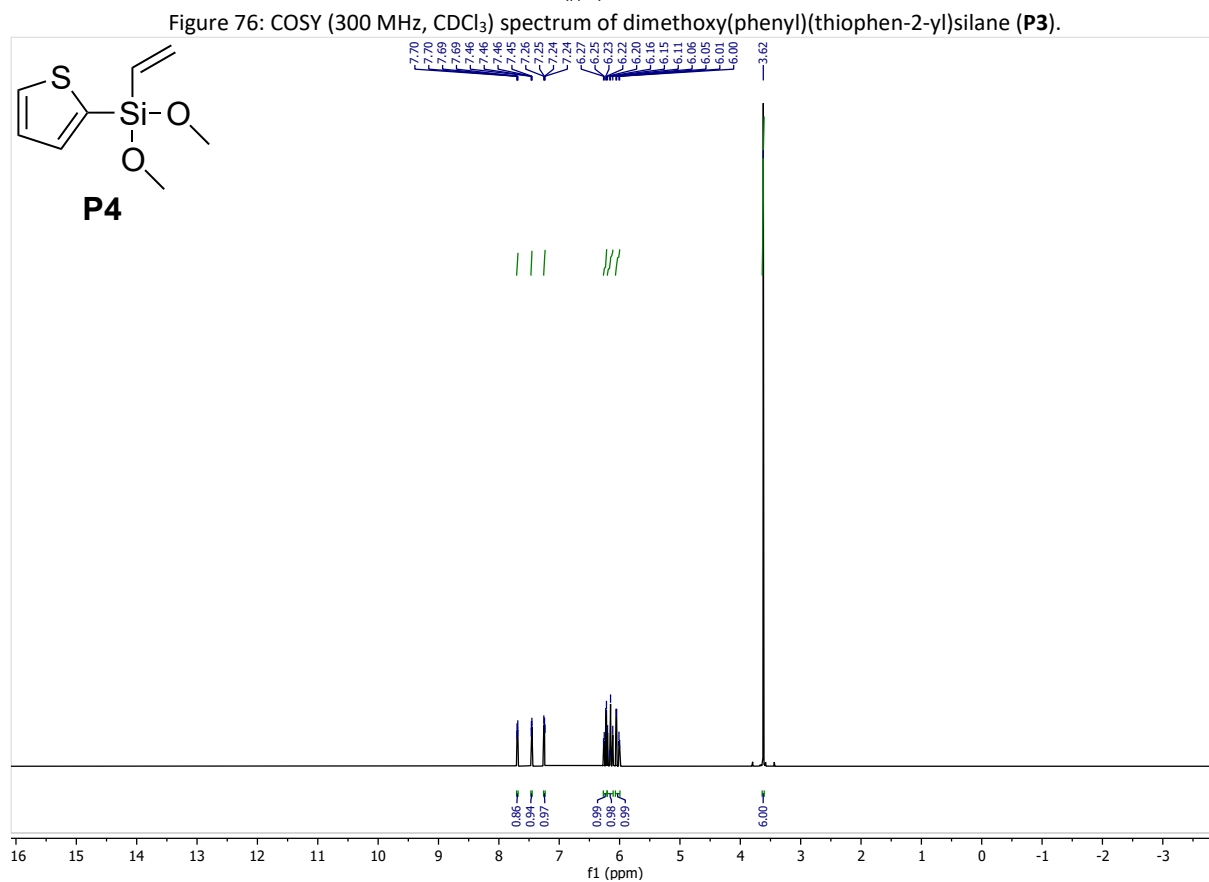
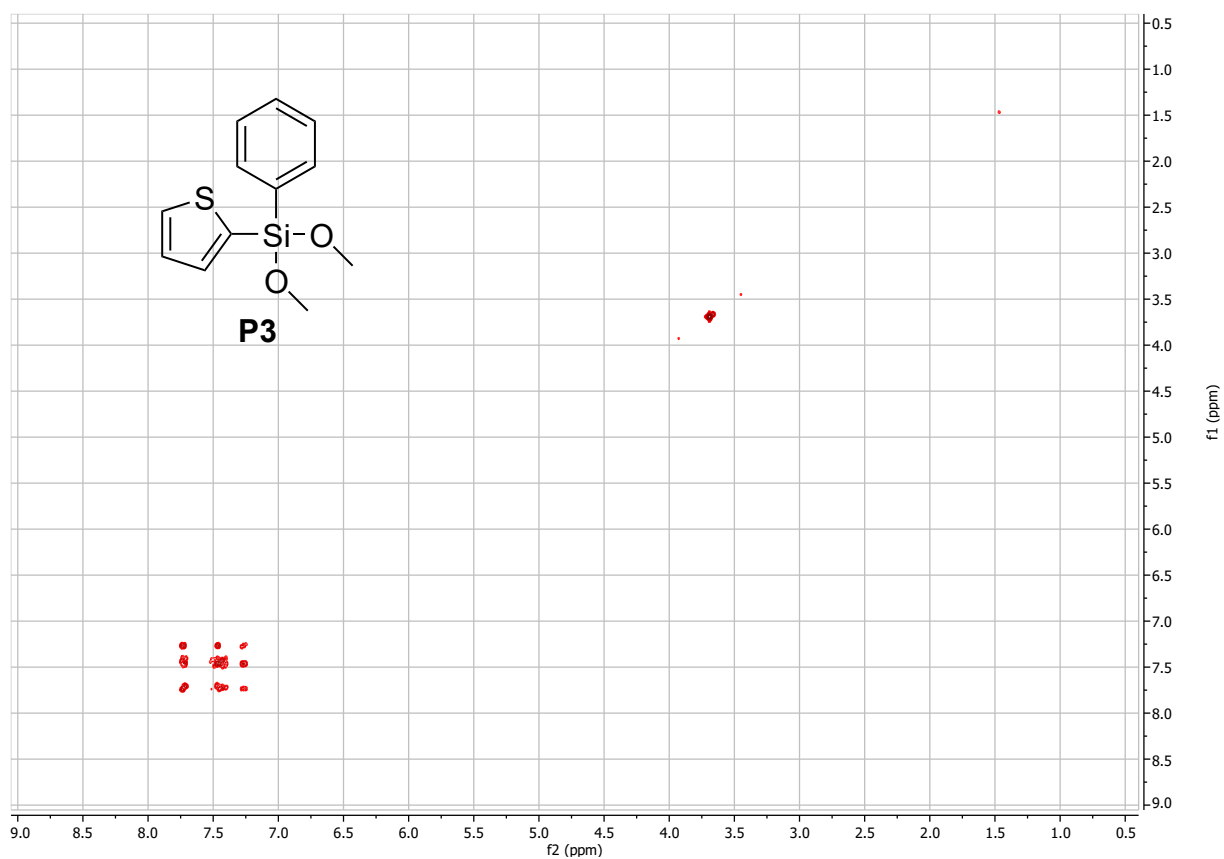


Figure 75: ^{29}Si NMR (60 MHz, CDCl_3) spectrum of dimethoxy(phenyl)(thiophen-2-yl)silane (**P3**).

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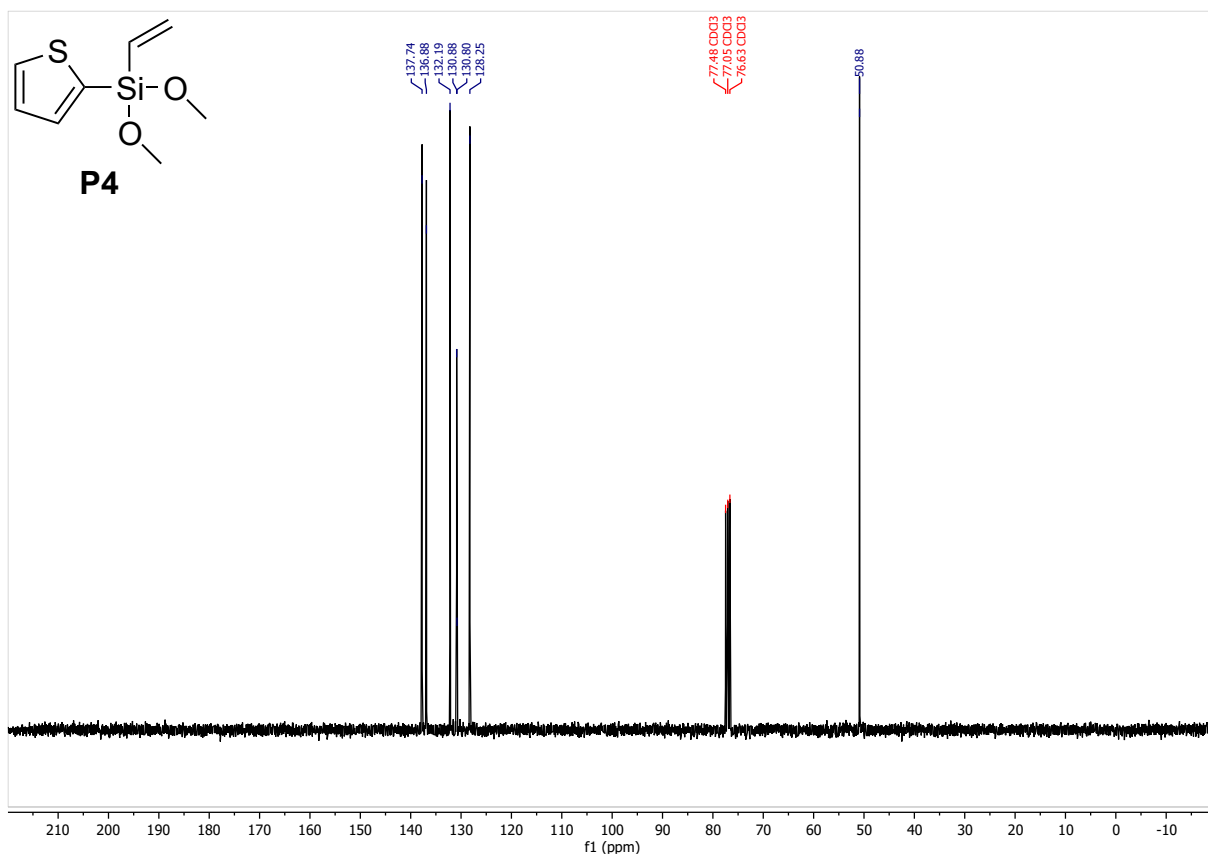


Figure 78: ¹³C NMR (75 MHz, CDCl₃) spectrum of dimethoxy(thiophen-2-yl)(vinyl)silane (**P4**).

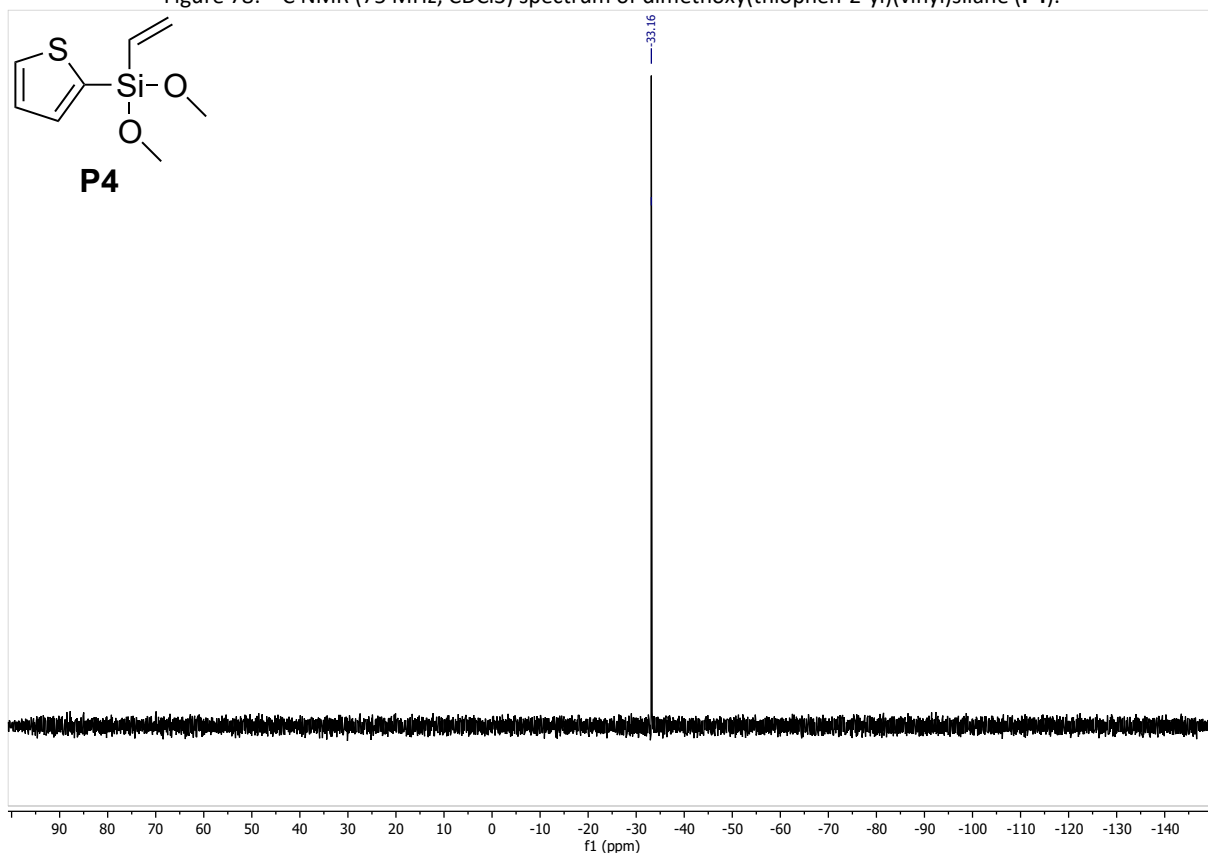
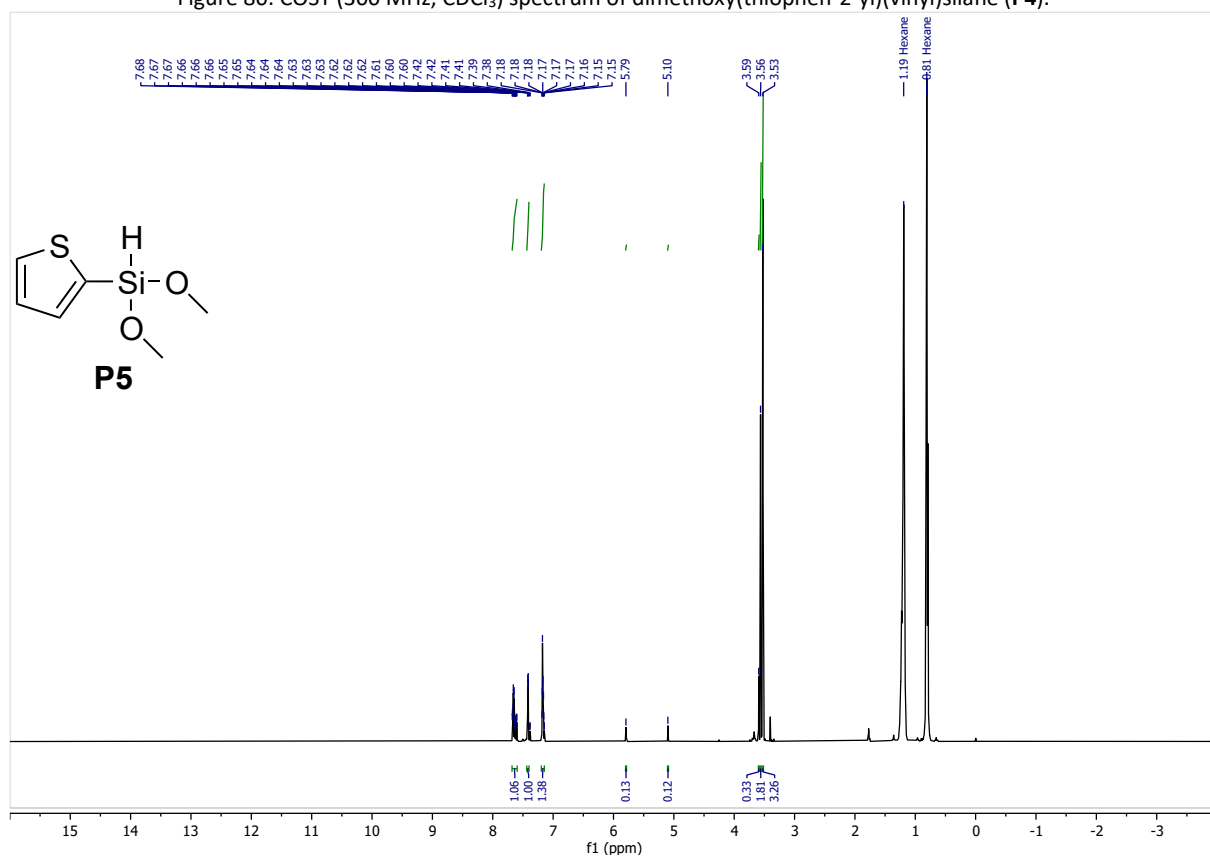
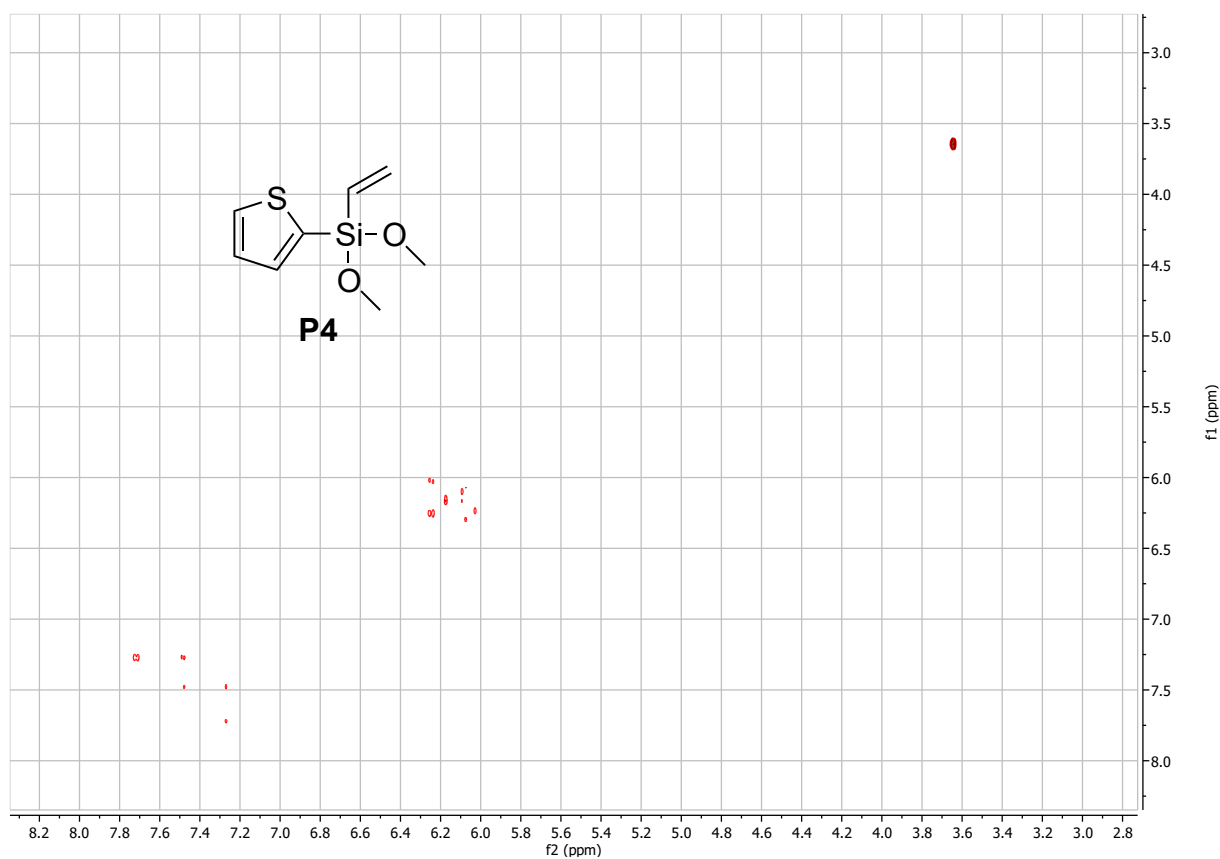


Figure 79: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of dimethoxy(thiophen-2-yl)(vinyl)silane (**P4**).



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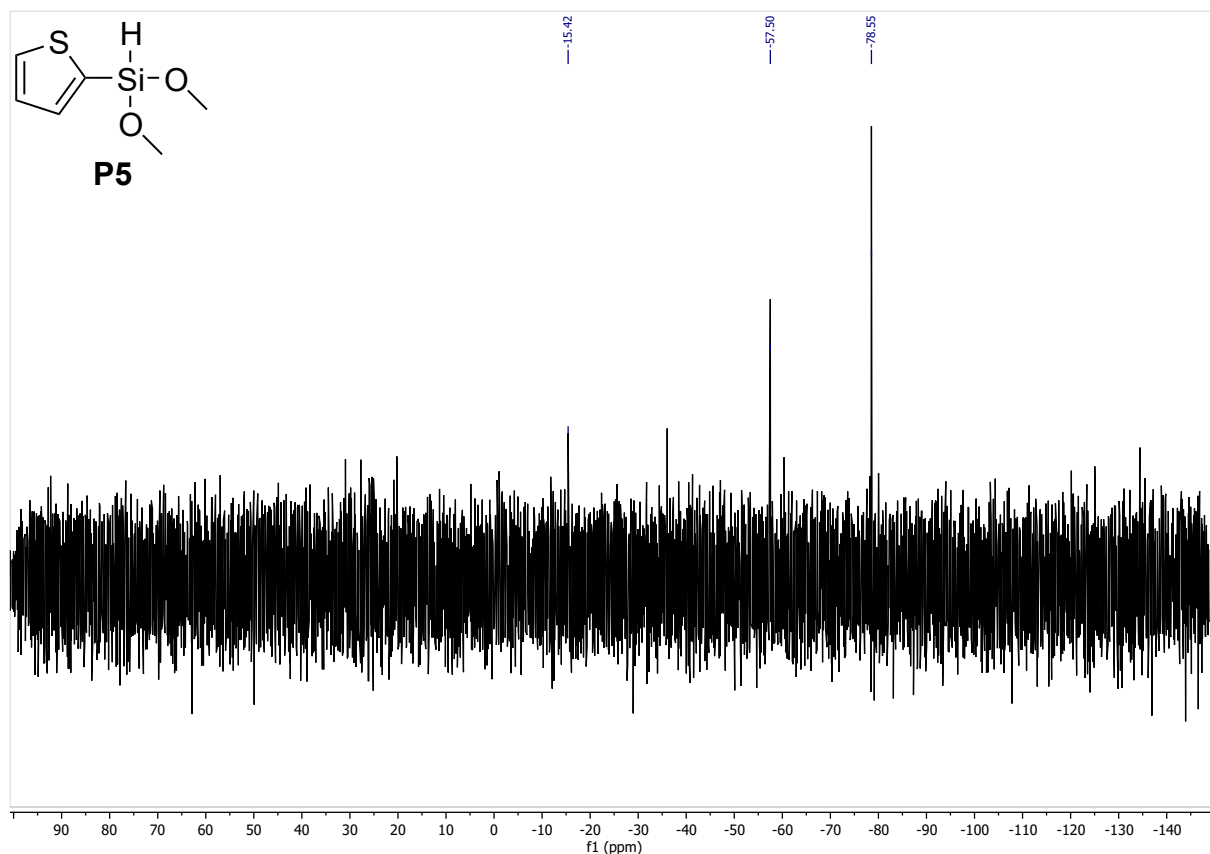


Figure 82: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of dimethoxy(thiophen-2-yl)silane (**P5**).

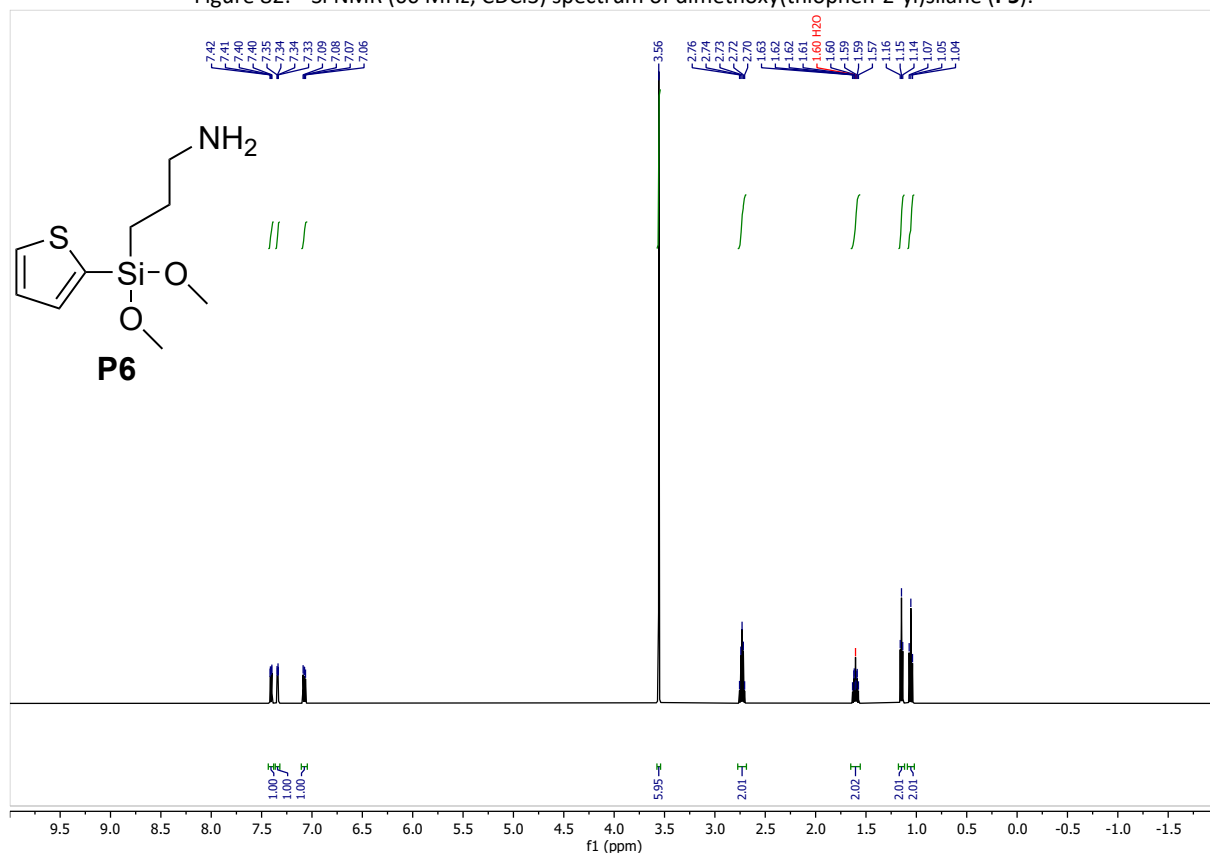


Figure 83: ¹H NMR (300 MHz, CDCl₃) spectrum of 3-(dimethoxy(thiophen-2-yl)silyl)propan-1-amine (**P6**).

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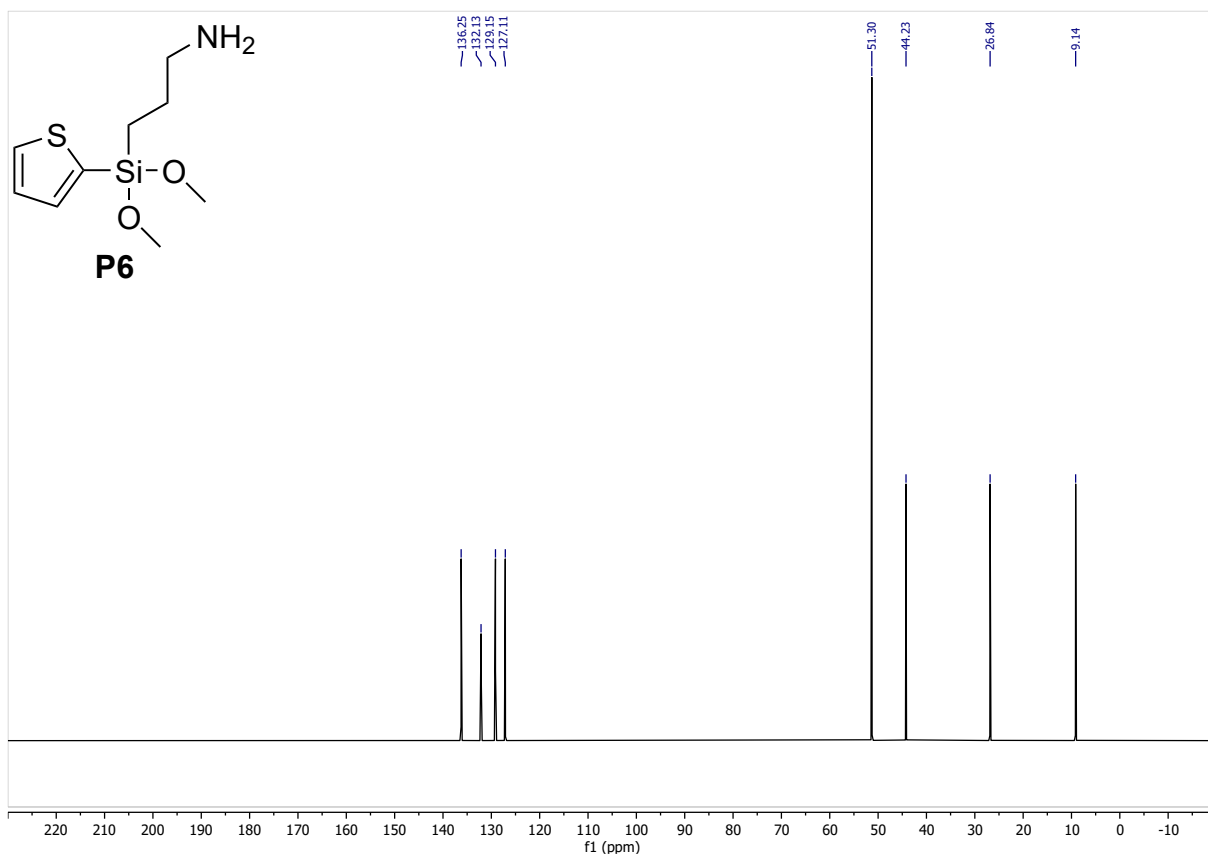


Figure 84: ¹³C NMR (75 MHz, CDCl₃) spectrum of 3-(dimethoxy(thiophen-2-yl)silyl)propan-1-amine (**P6**).

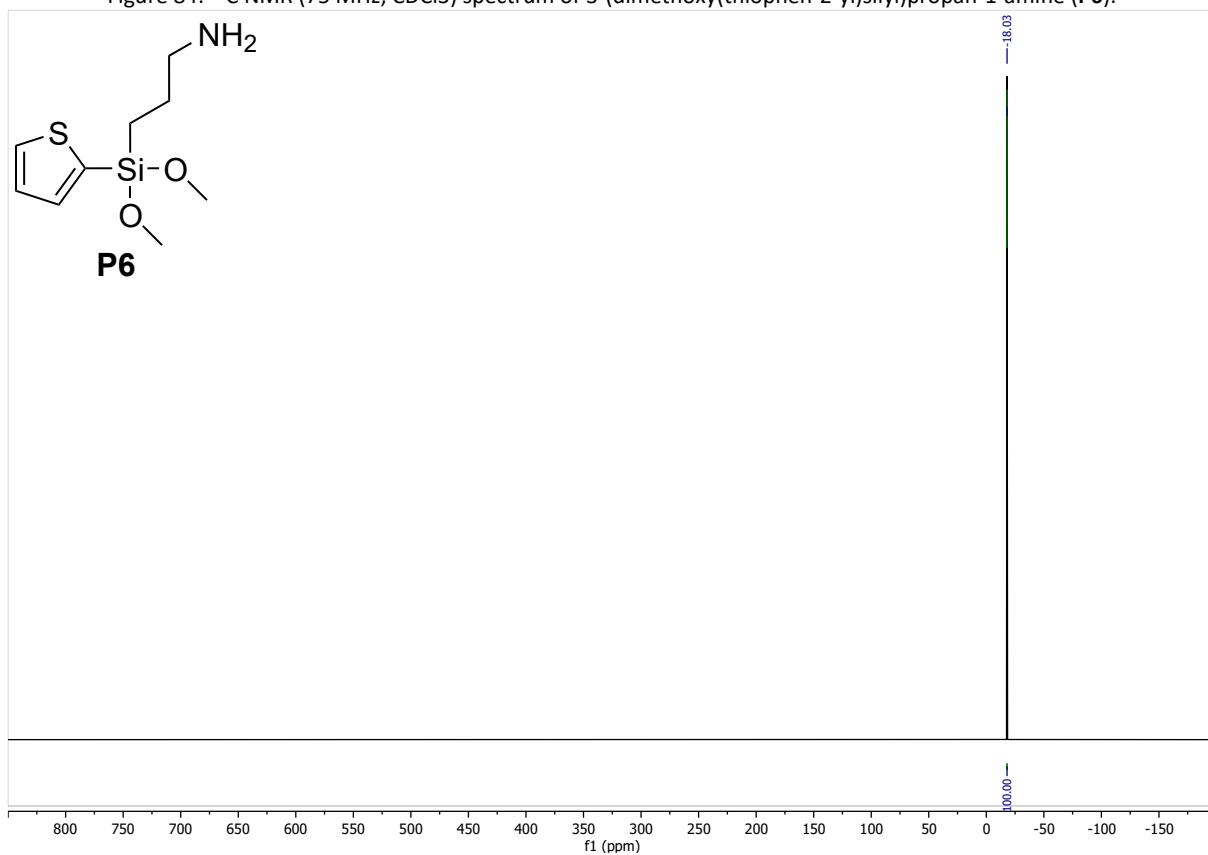
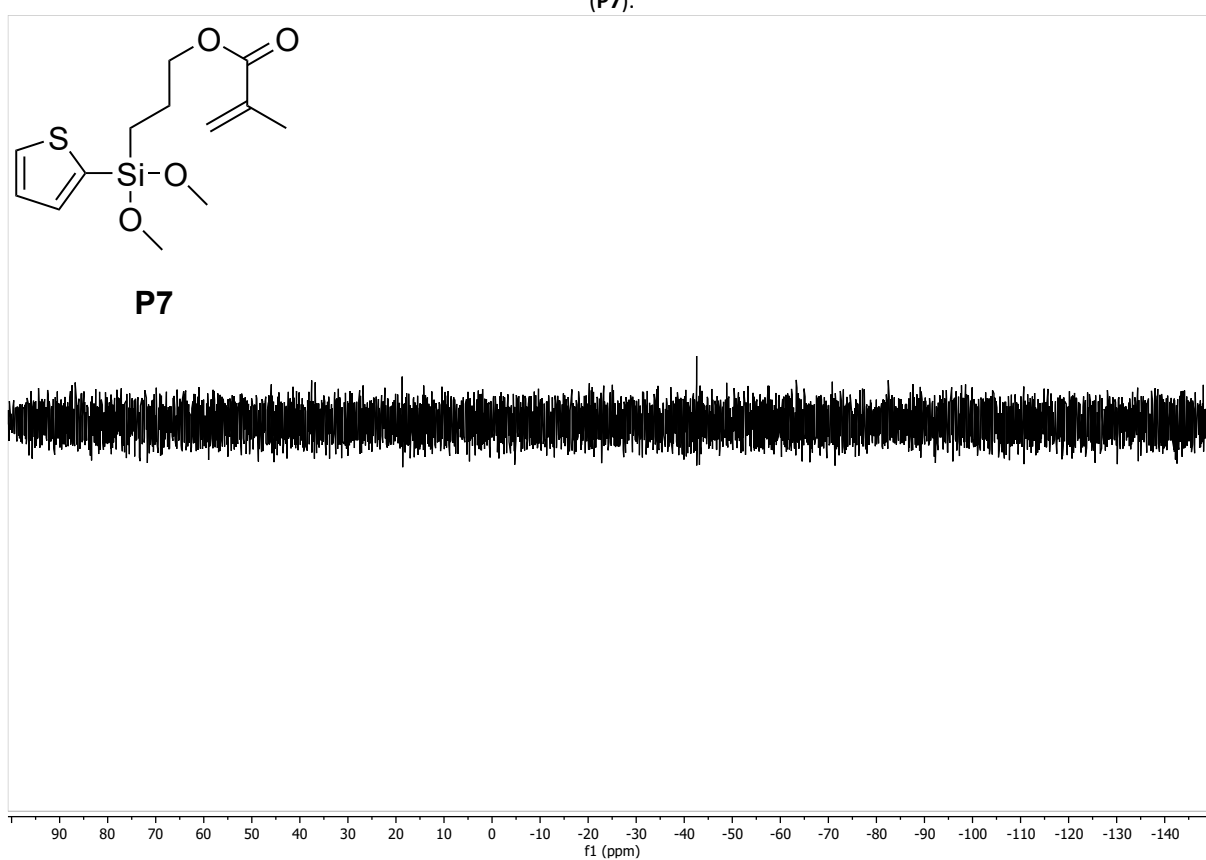
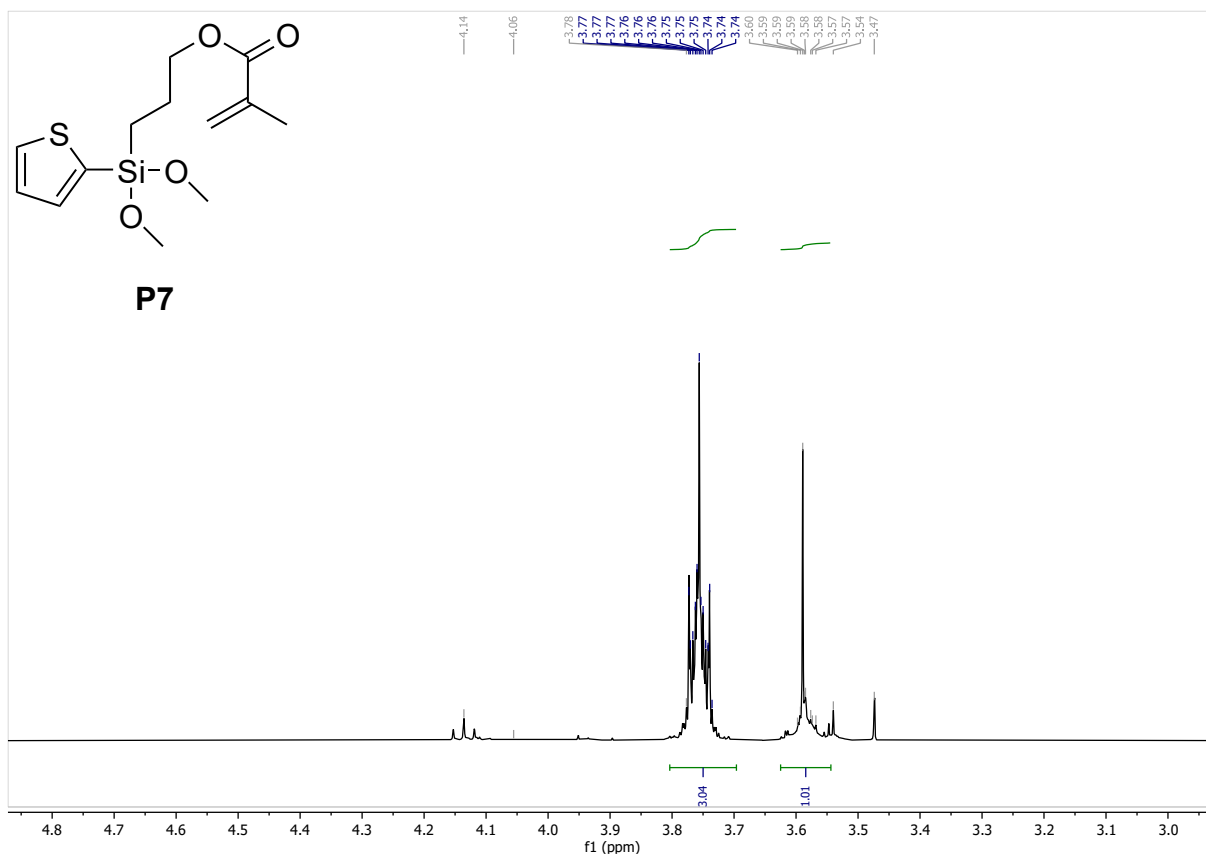


Figure 85: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of 3-(dimethoxy(thiophen-2-yl)silyl)propan-1-amine (**P6**).

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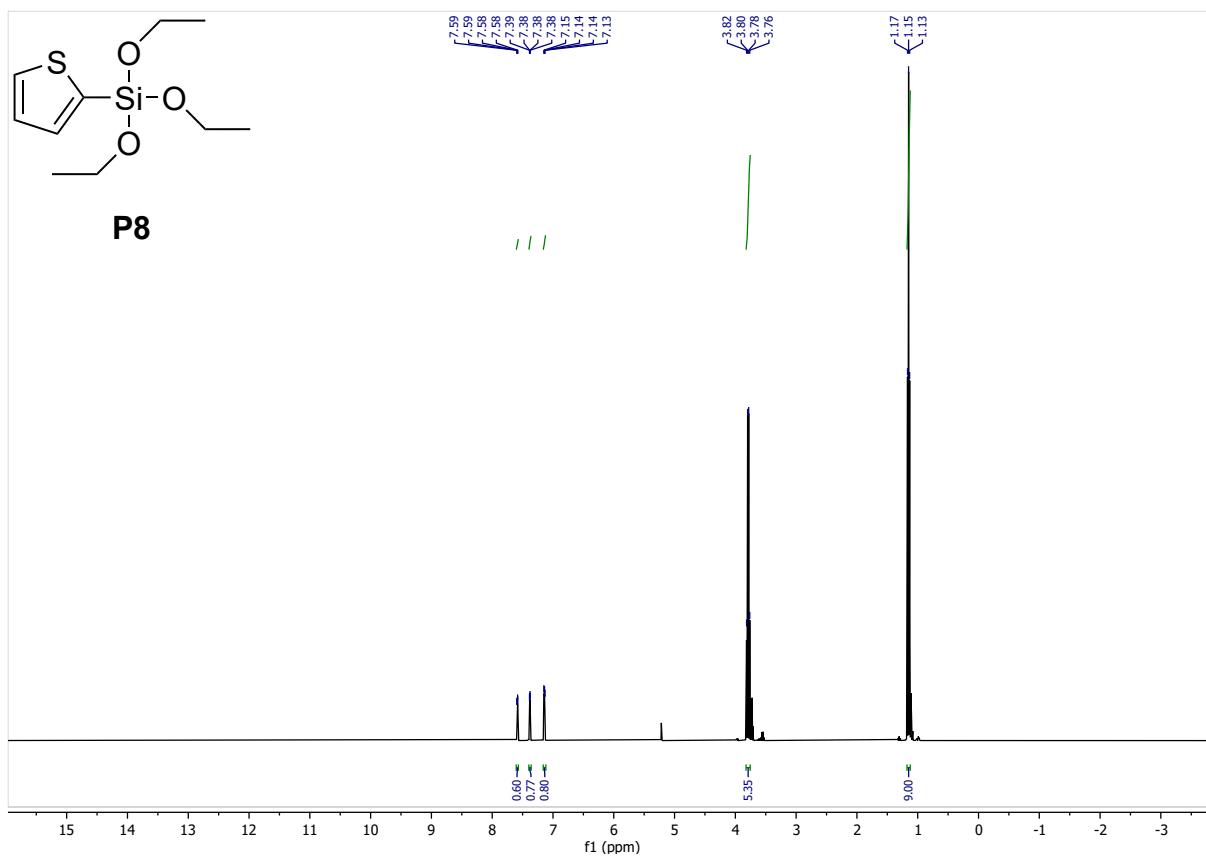


Figure 88: ¹H NMR (300 MHz, CDCl₃) spectrum of triethoxy(thiophen-2-yl)silane (**P8**).

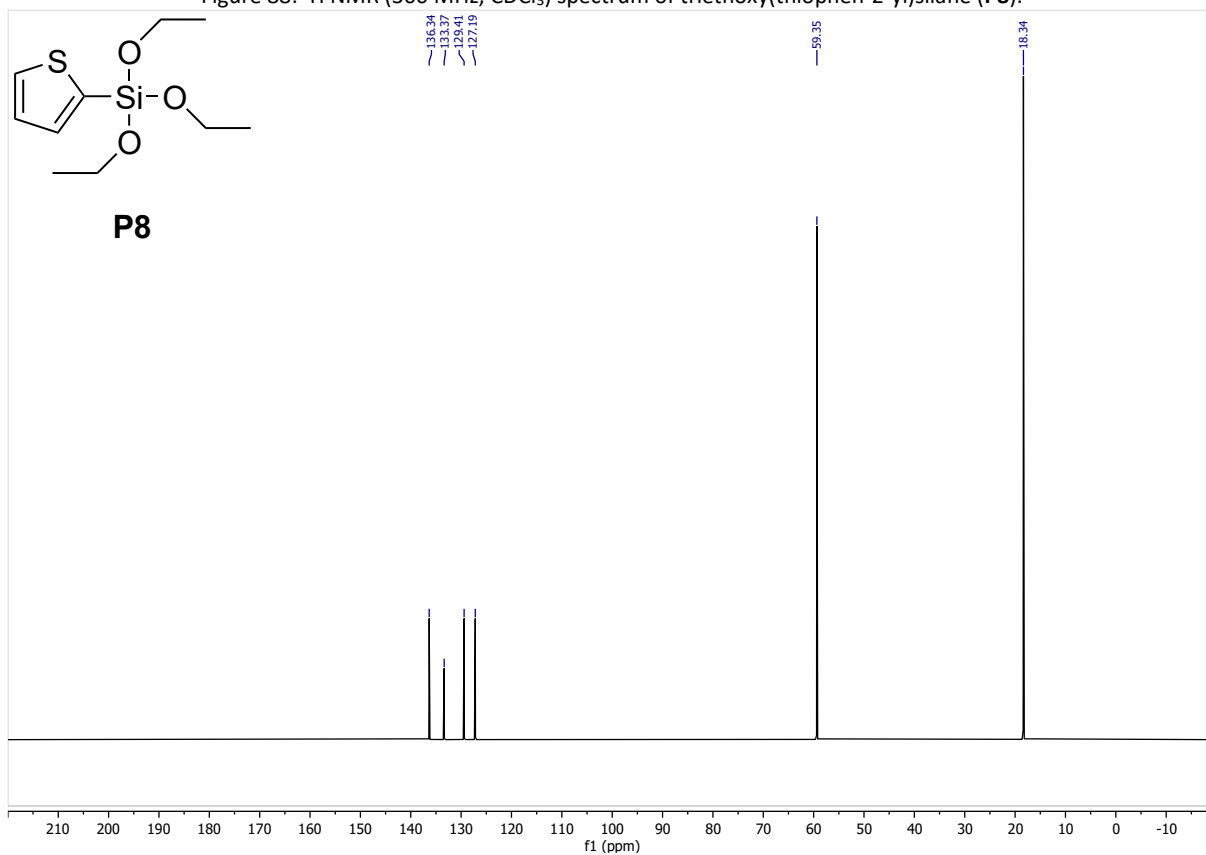


Figure 89 ¹³C NMR (75 MHz, CDCl₃) spectrum of triethoxy(thiophen-2-yl)silane (**P8**).

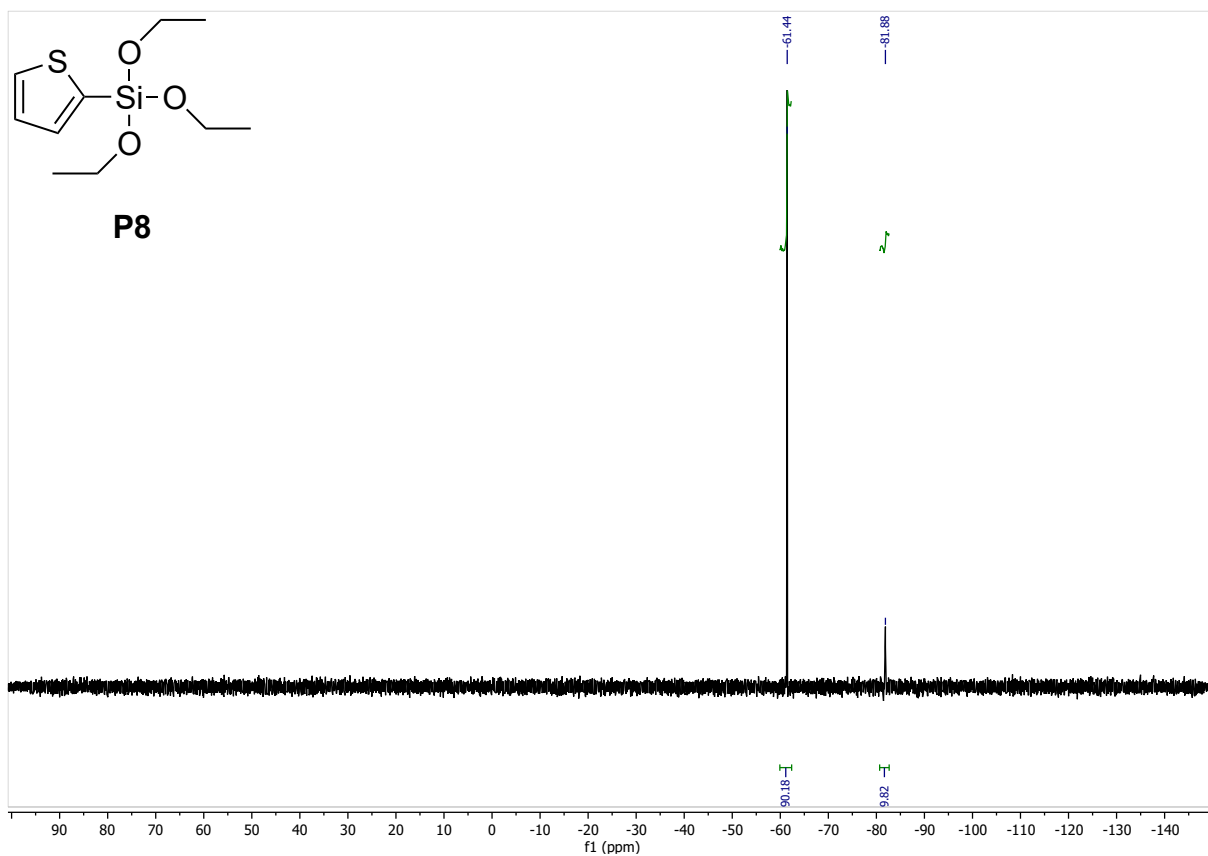


Figure 90: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of triethoxy(thiophen-2-yl)silane (P8).

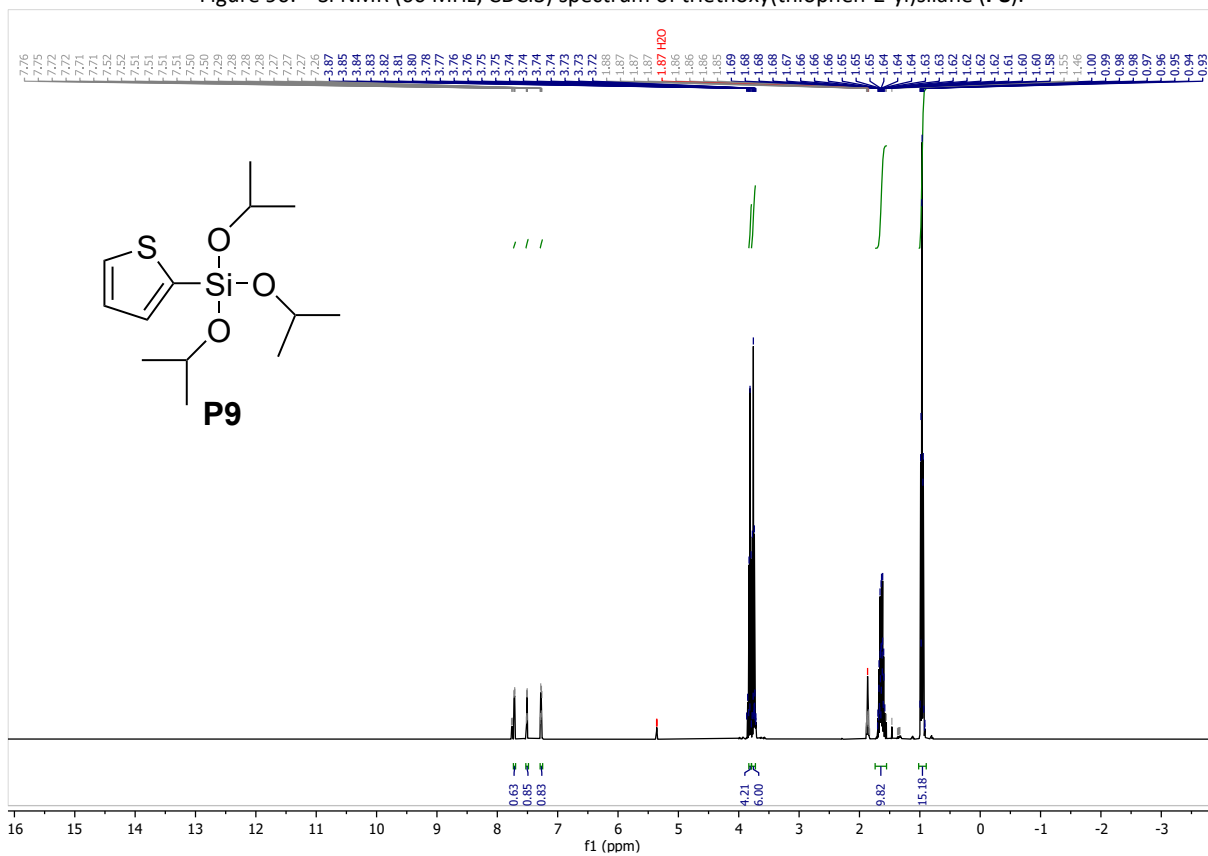


Figure 91: ¹H NMR (300 MHz, CDCl₃) spectrum of triisopropoxy(thiophen-2-yl)silane (P9).

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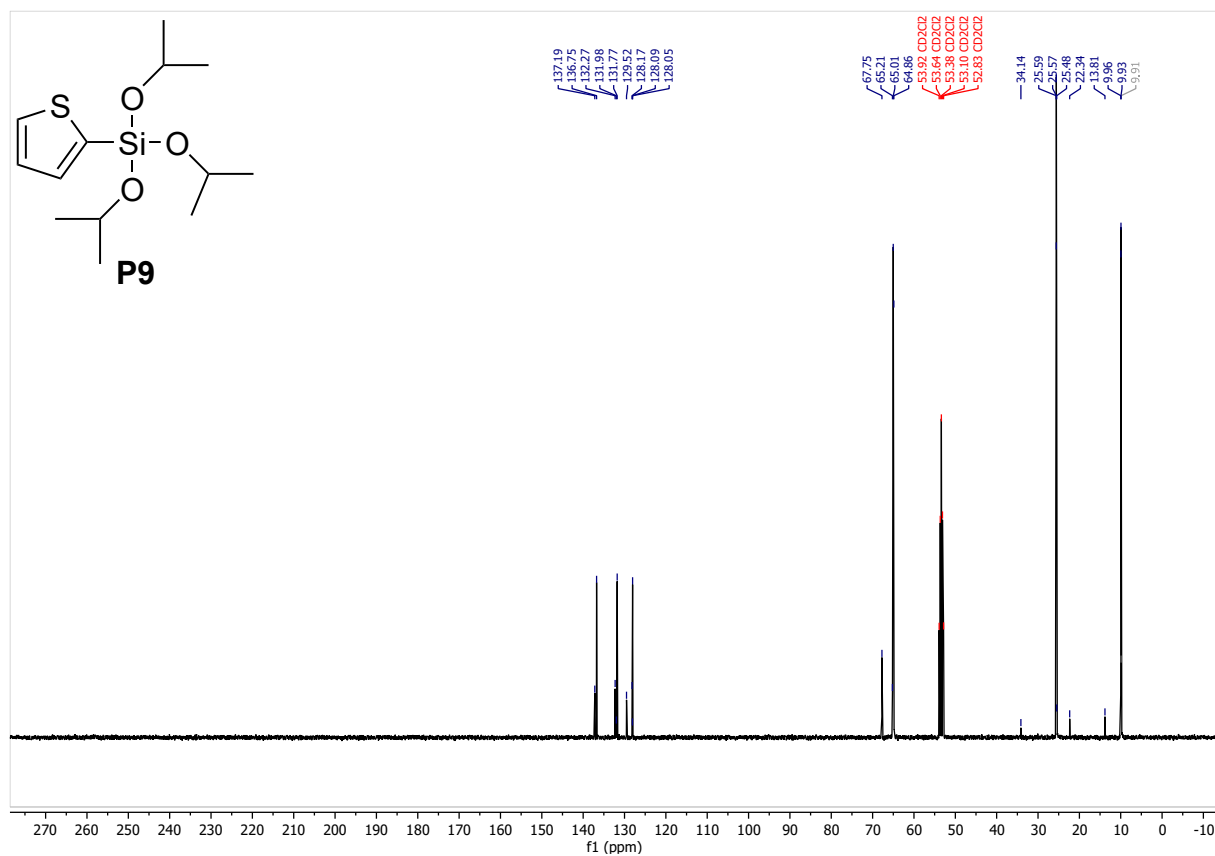


Figure 92: ¹³C NMR (75 MHz, CDCl₃) spectrum of triisopropoxy(thiophen-2-yl)silane (**P9**).

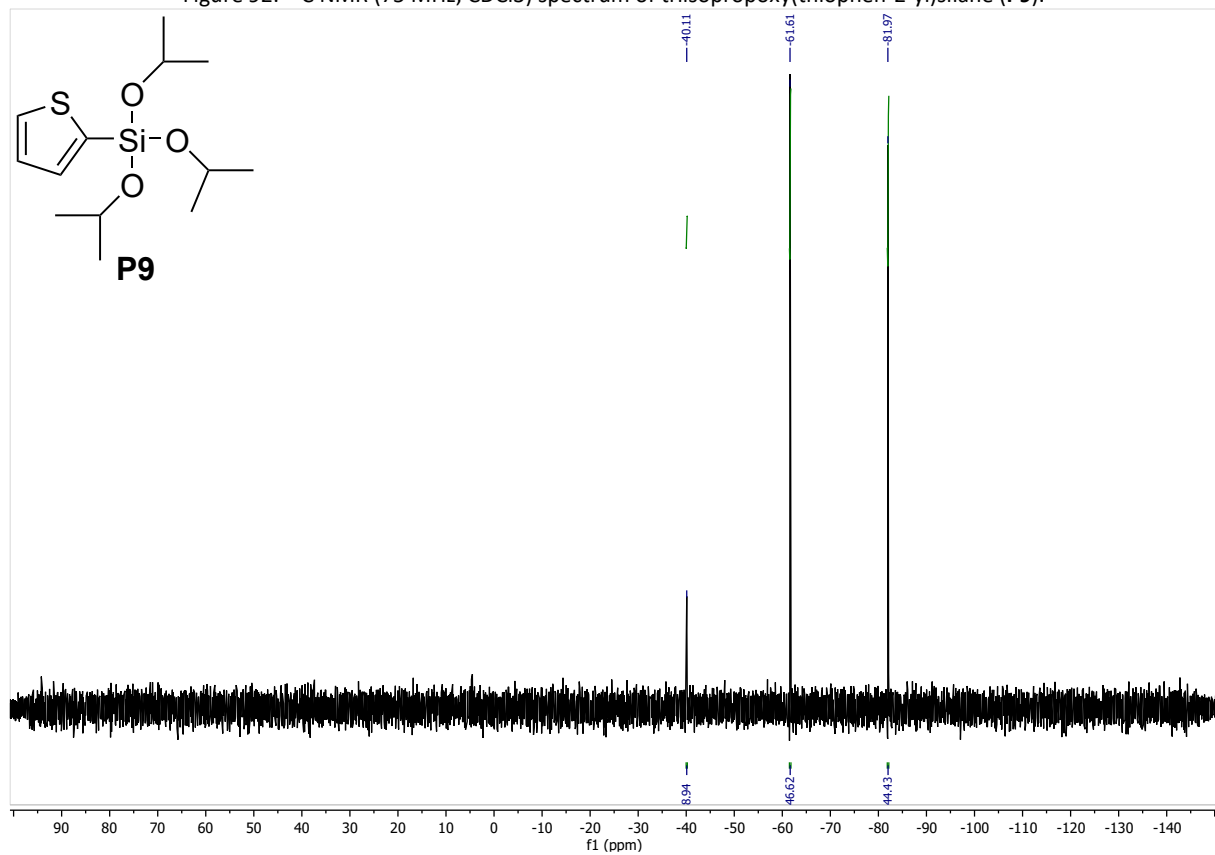


Figure 93: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of triisopropoxy(thiophen-2-yl)silane (**P9**).

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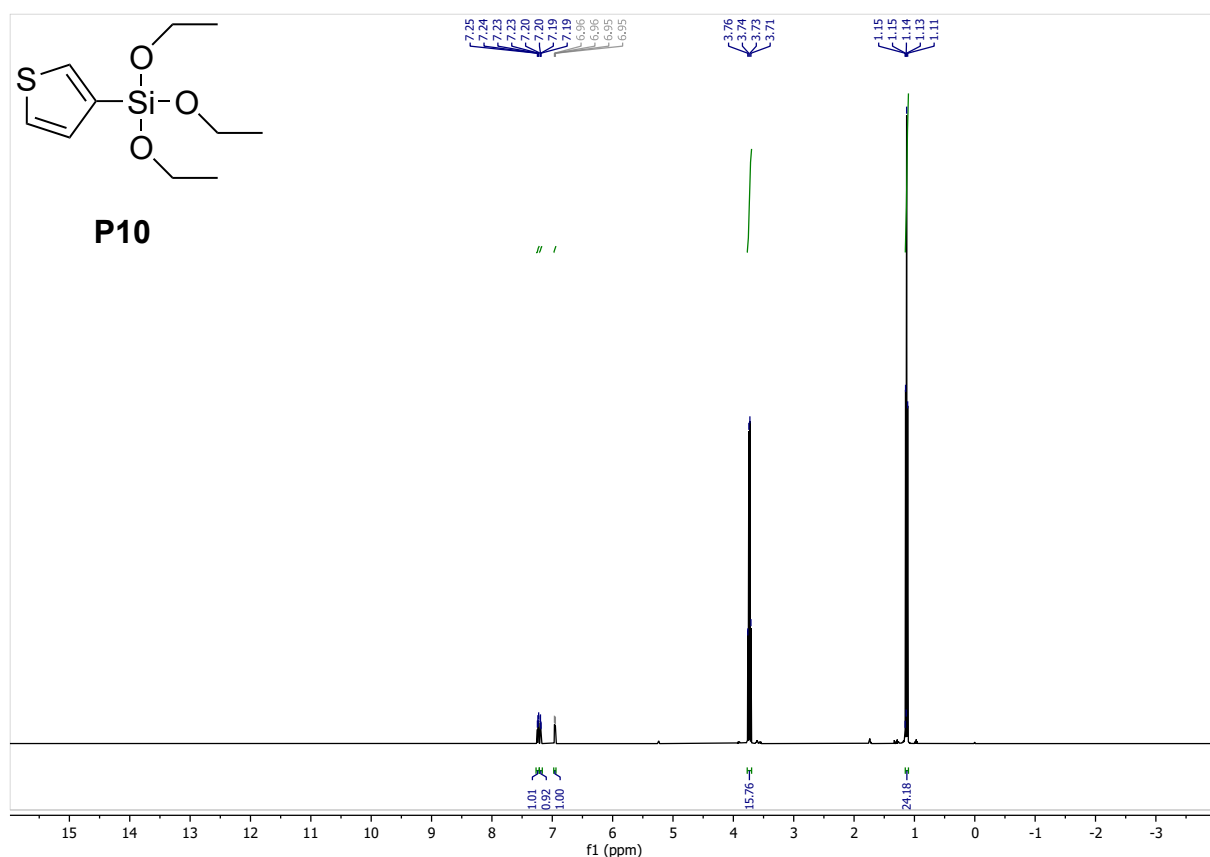


Figure 94: ¹H NMR (300 MHz, CDCl₃) spectrum of triethoxy(thiophen-3-yl)silane (**P10**).

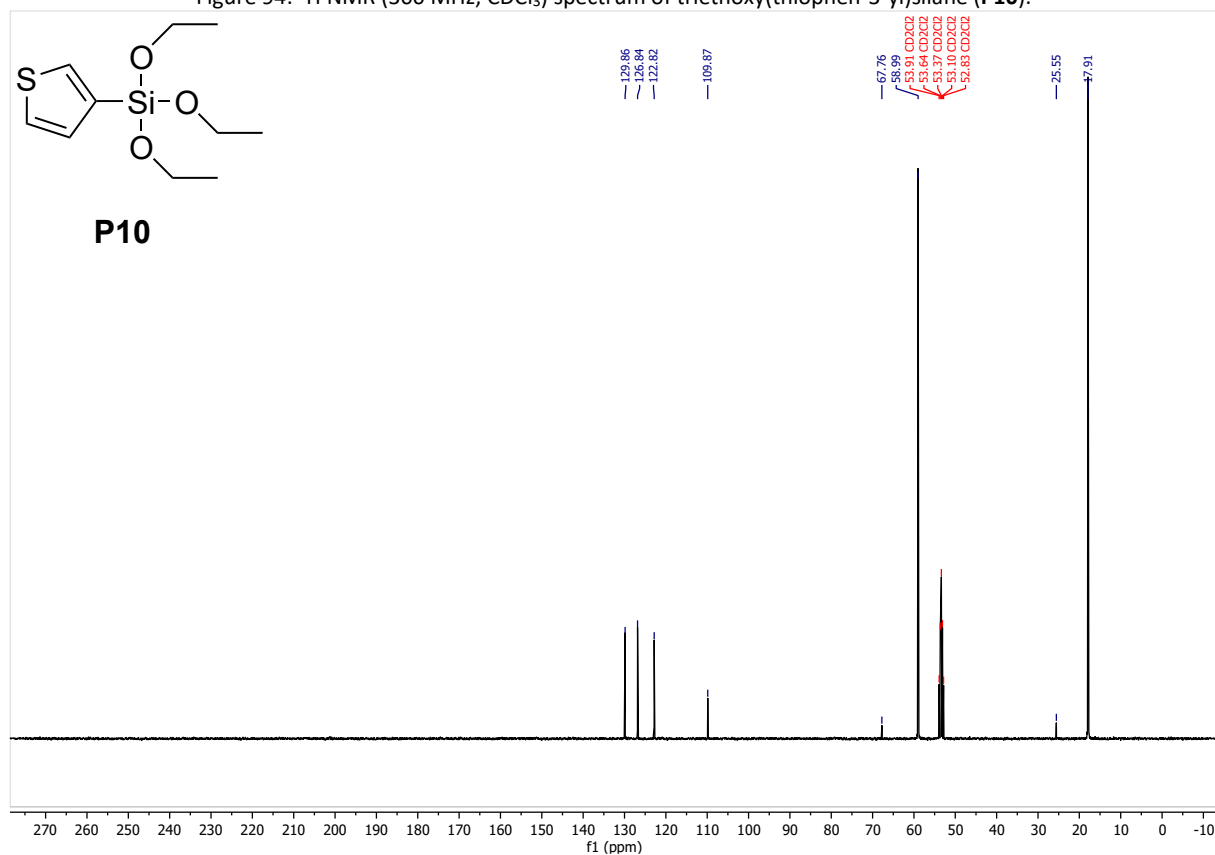


Figure 95: ¹³C NMR (75 MHz, CDCl₃) spectrum of triethoxy(thiophen-3-yl)silane (**P10**).

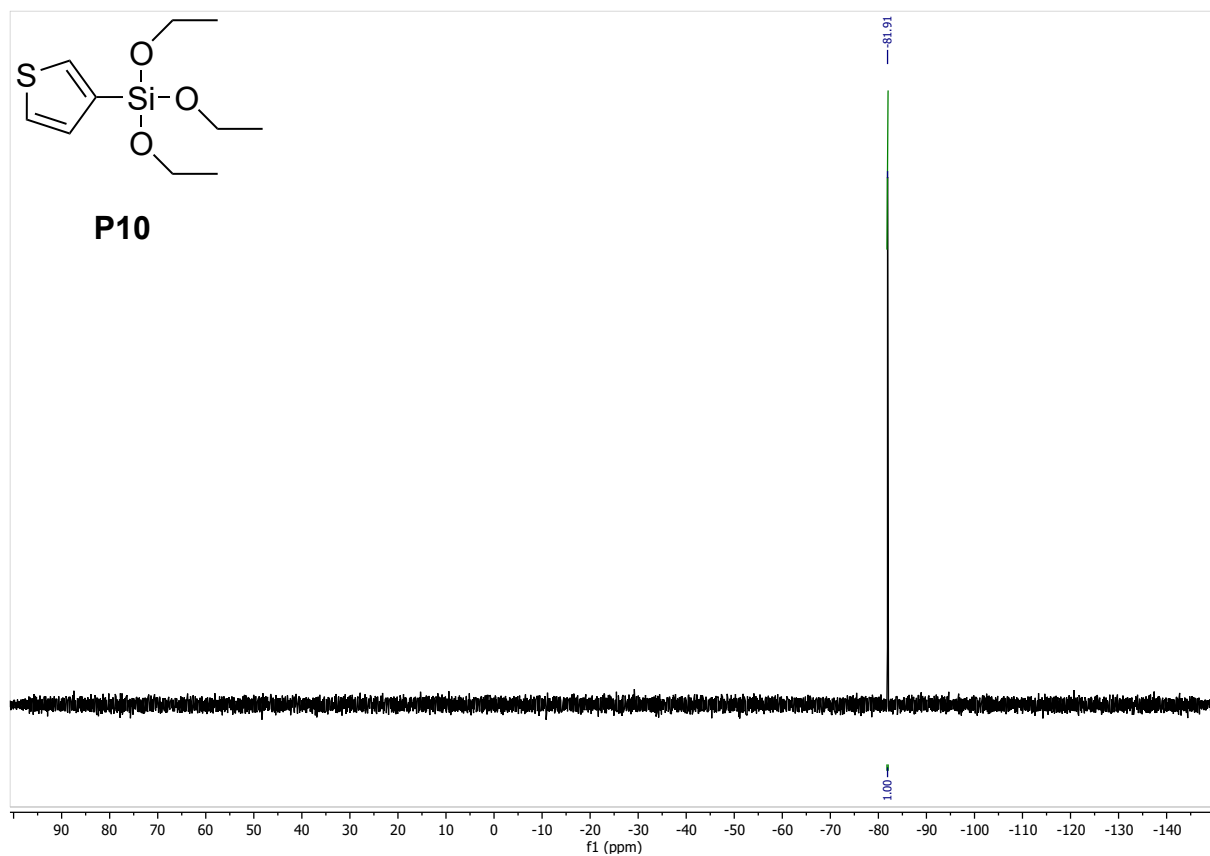


Figure 96: ^{29}Si NMR (60 MHz, CDCl_3) spectrum of triethoxy(thiophen-3-yl)silane (**P10**).

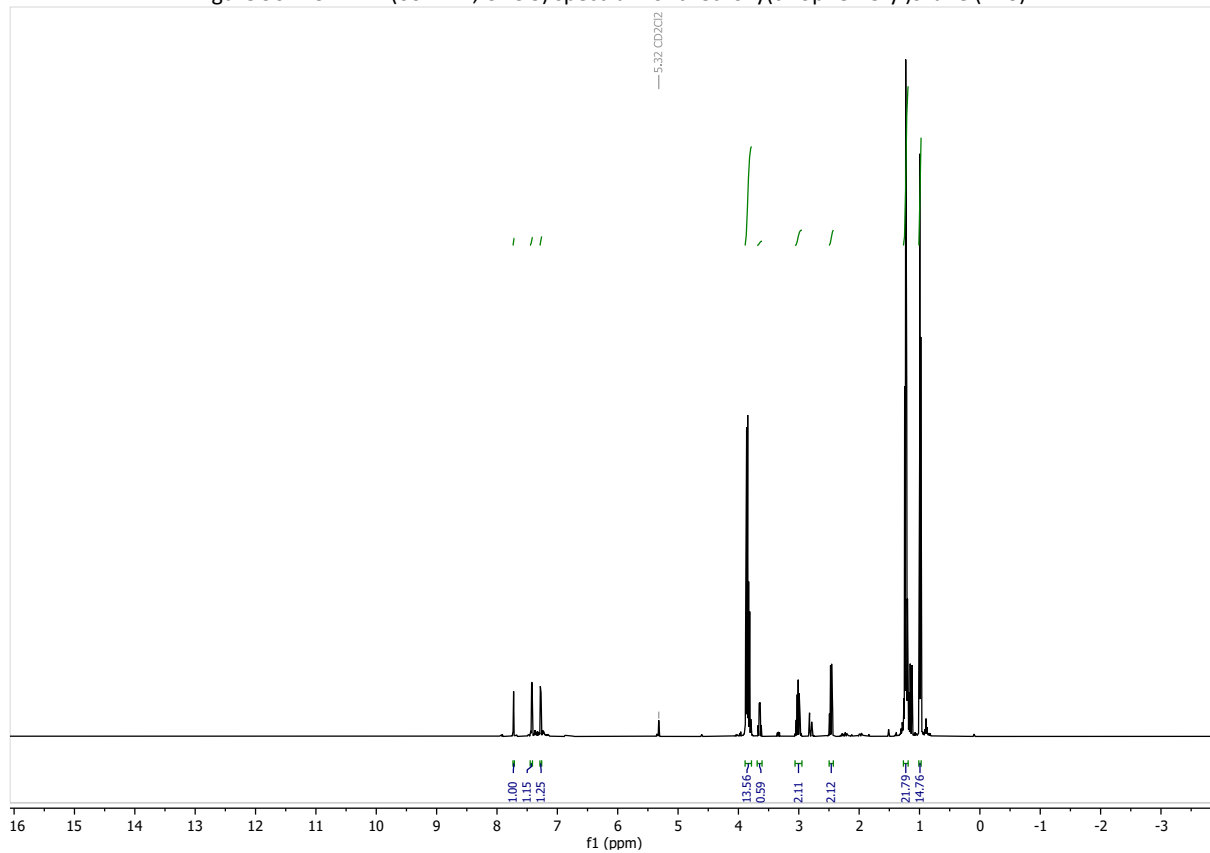


Figure 97: ^1H NMR (300 MHz, CDCl_3) spectrum of triethoxy(thiophen-3-yl)silane after 72 h in sealed ampule.

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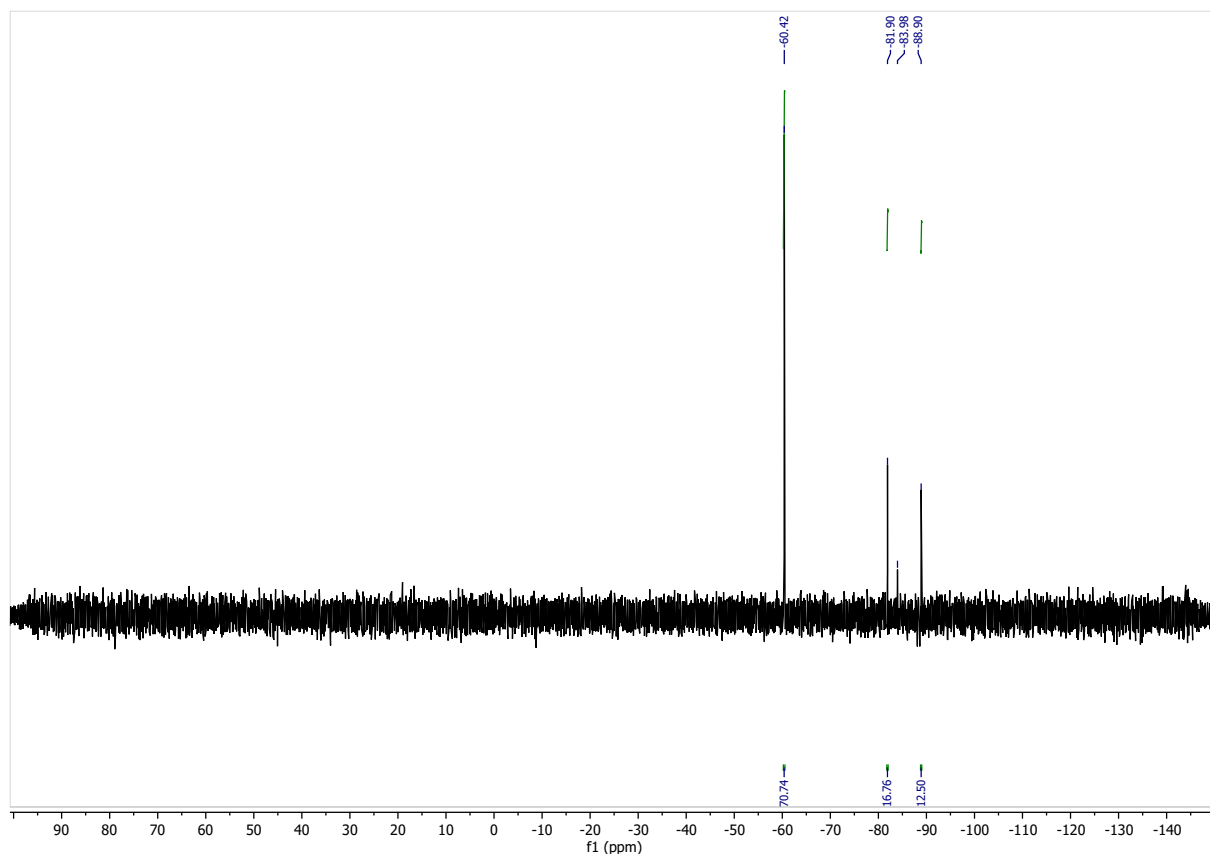


Figure 98: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of triethoxy(thiophen-3-yl)silane after 72 h in sealed ampule.

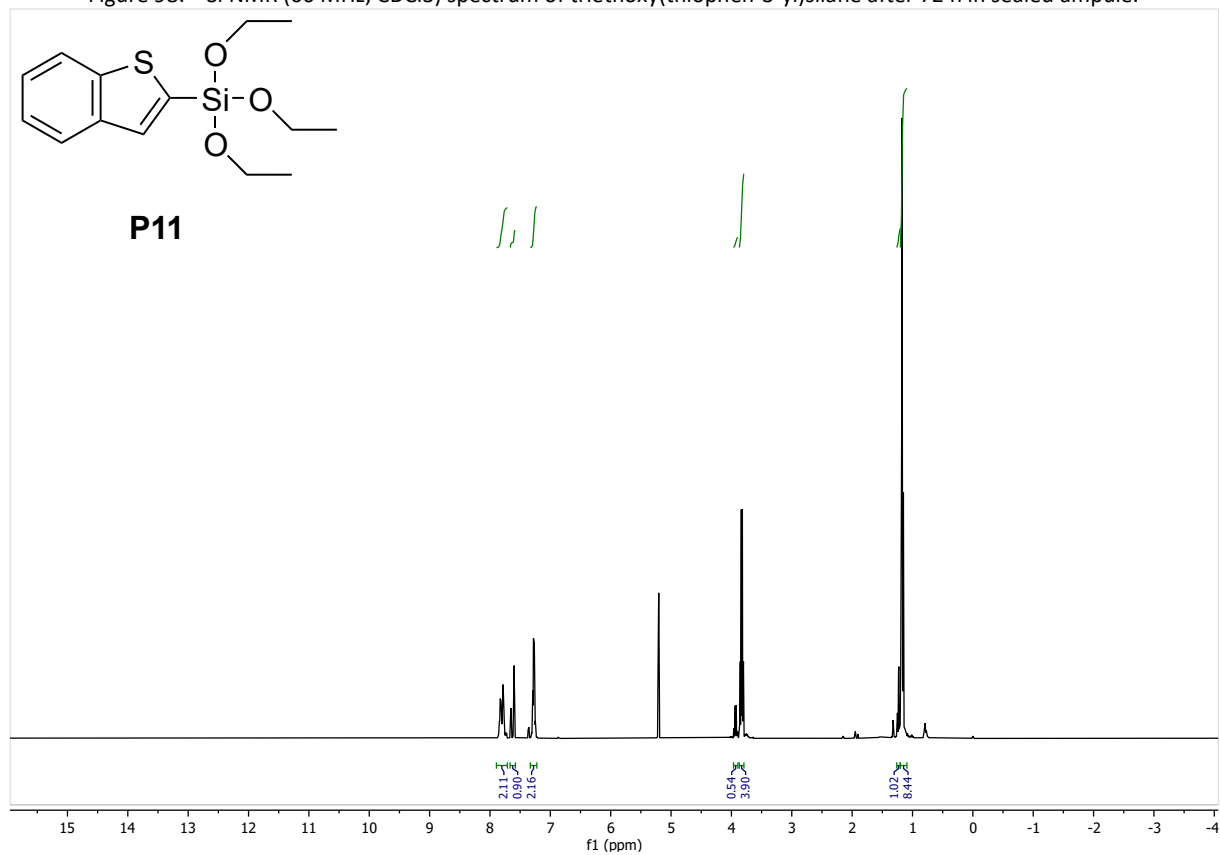
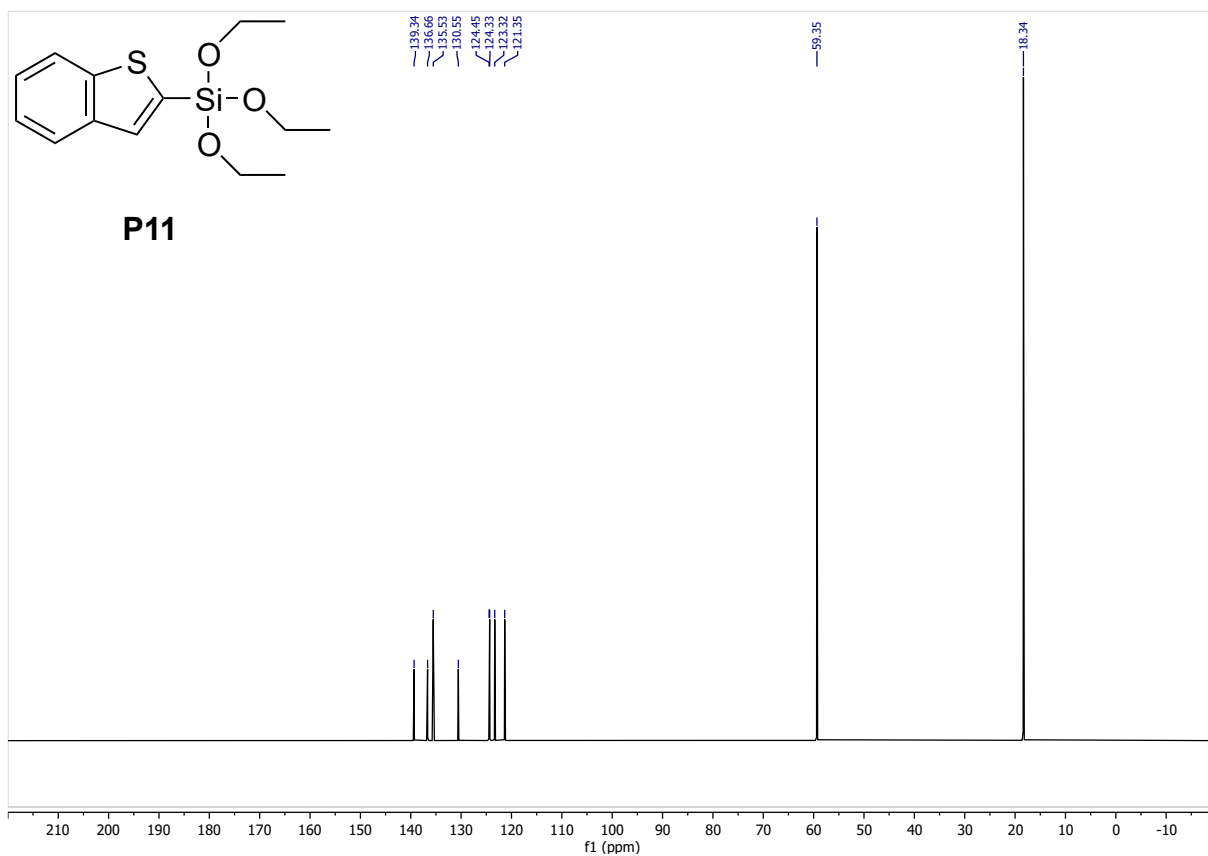
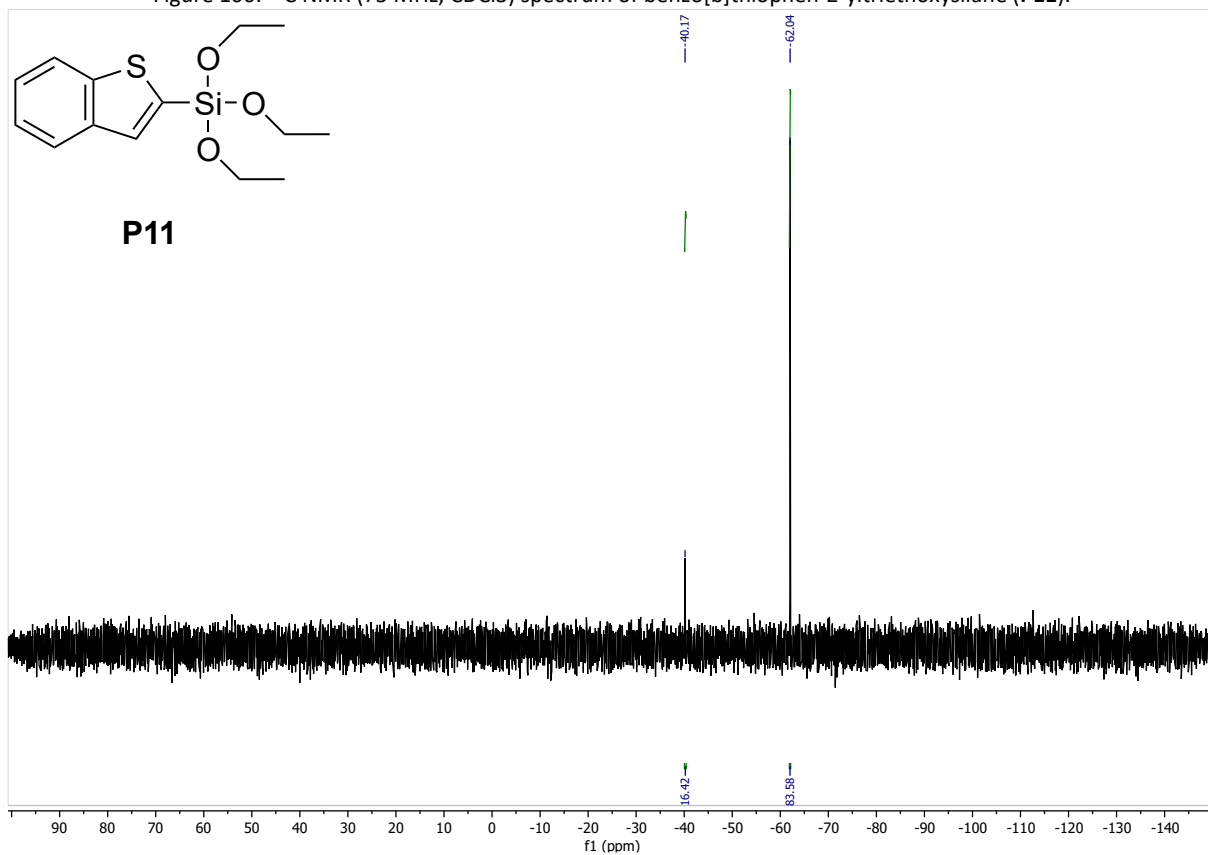
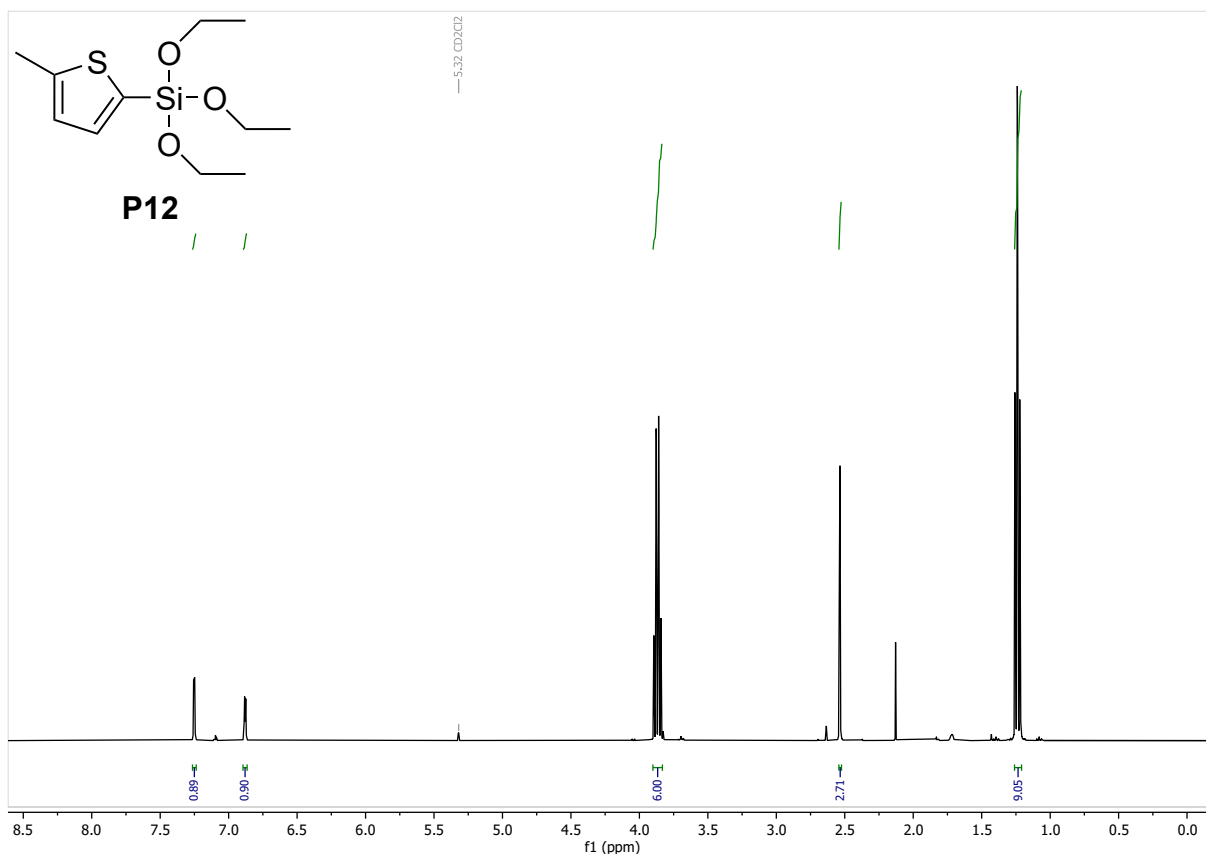
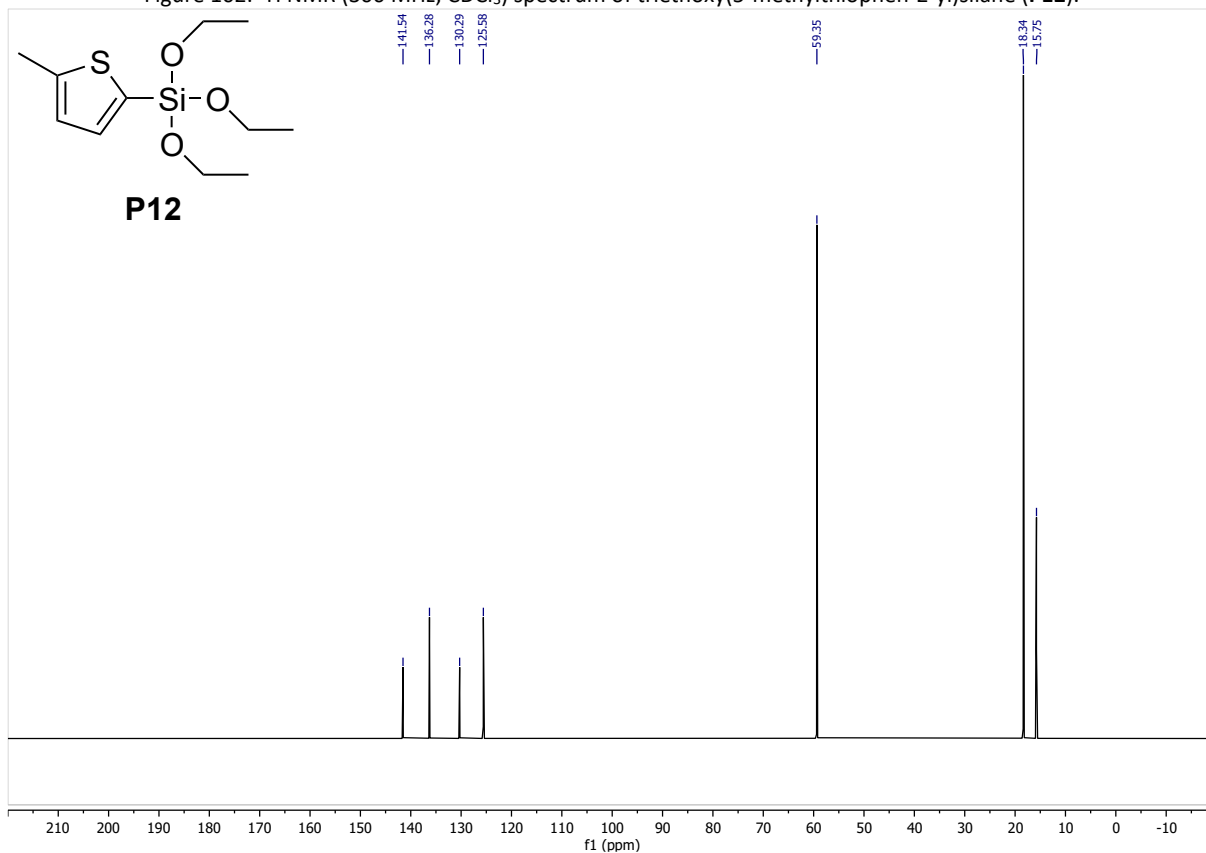
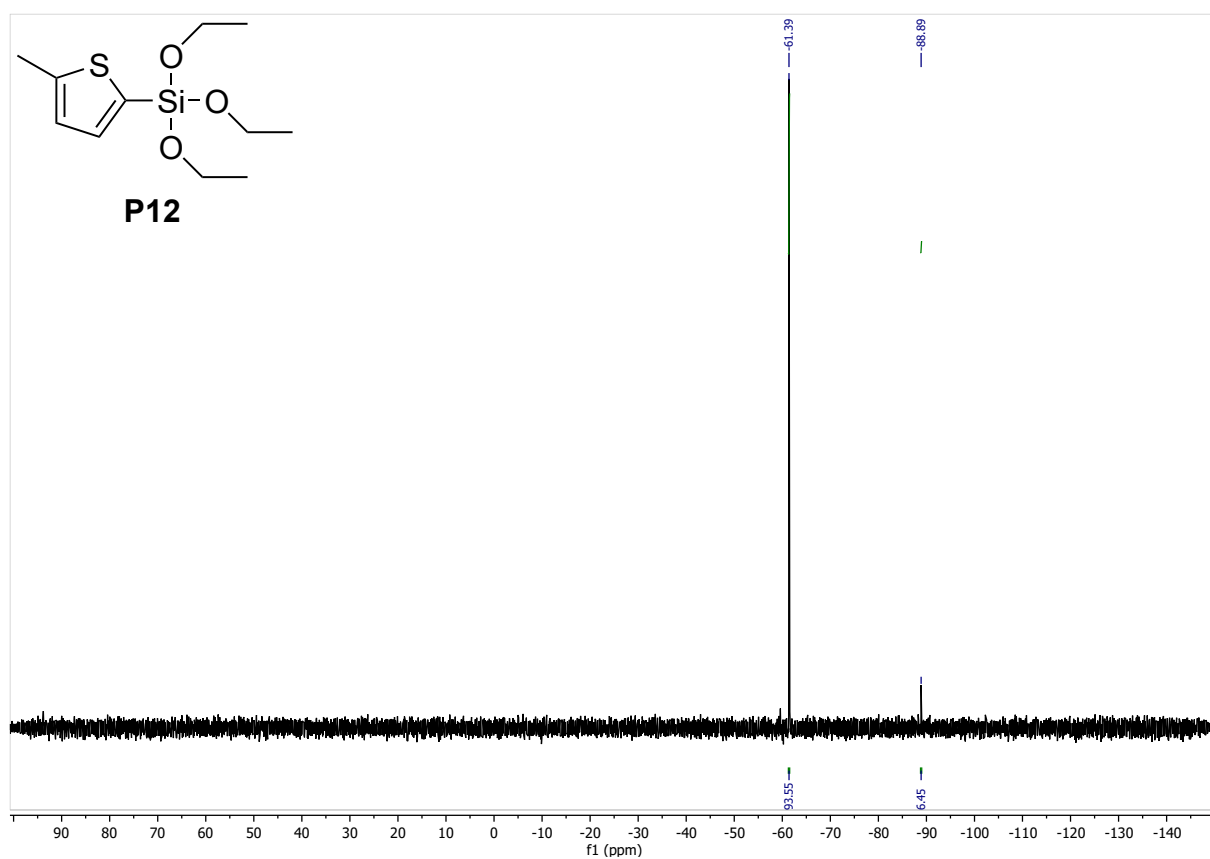
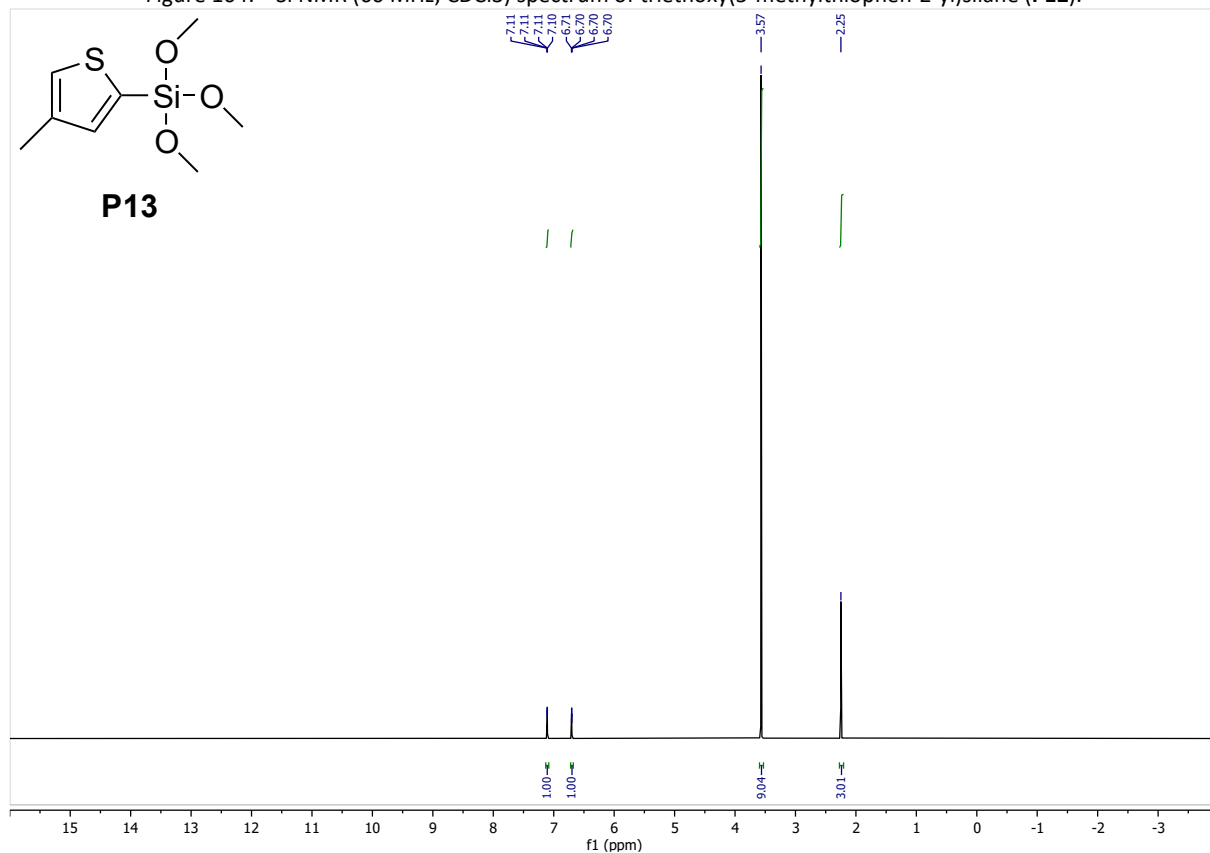


Figure 99: ¹H NMR (300 MHz, CDCl₃) spectrum of benzo[b]thiophen-2-yltriethoxysilane (**P11**).

Figure 100: ¹³C NMR (75 MHz, CDCl₃) spectrum of benzo[b]thiophen-2-yltriethoxysilane (**P11**).Figure 101: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of benzo[b]thiophen-2-yltriethoxysilane (**P11**).

Figure 102: ¹H NMR (300 MHz, CDCl₃) spectrum of triethoxy(5-methylthiophen-2-yl)silane (**P12**).Figure 103: ¹³C NMR (75 MHz, CDCl₃) spectrum of triethoxy(5-methylthiophen-2-yl)silane (**P12**).

Figure 104: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of triethoxy(5-methylthiophen-2-yl)silane (**P12**).Figure 105: ¹H NMR (300 MHz, CDCl₃) spectrum of trimethoxy(4-methylthiophen-2-yl)silane (**P13**).

Appendix

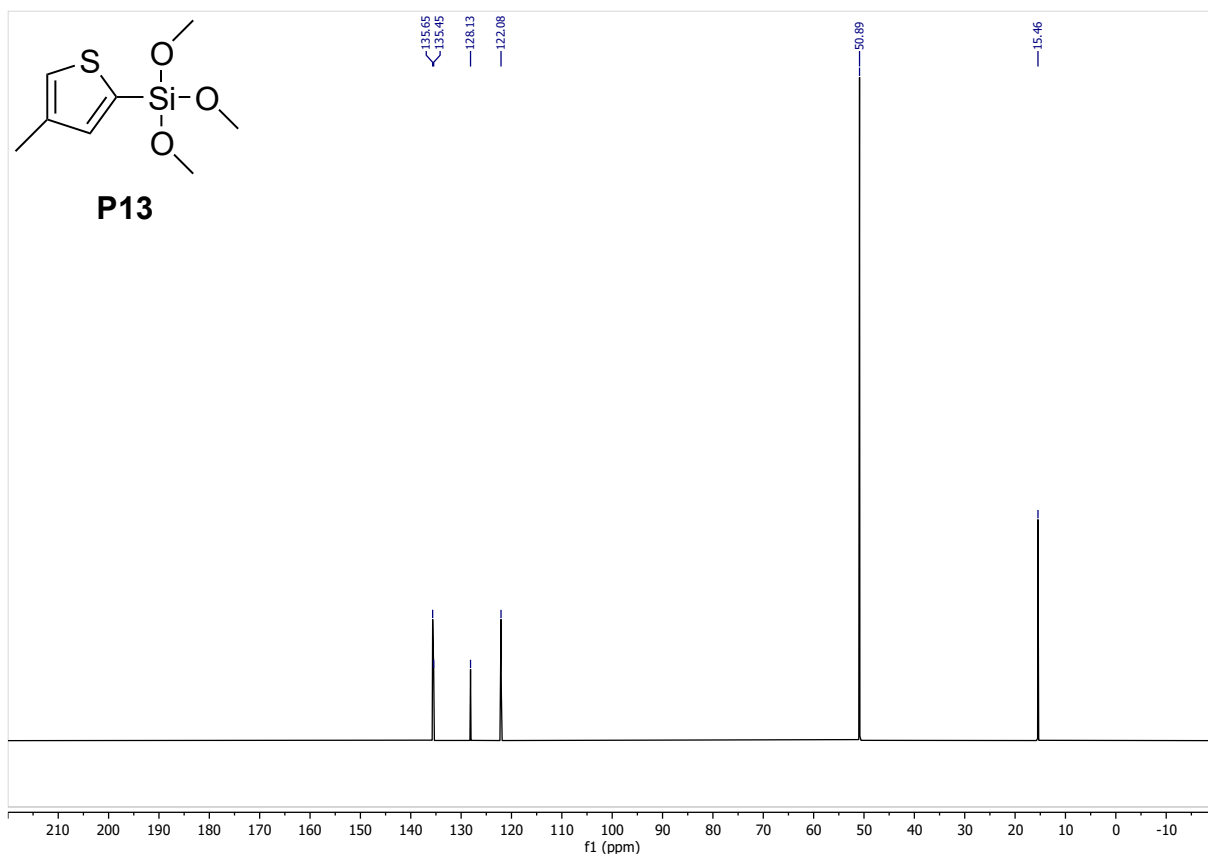


Figure 106: ¹³C NMR (75 MHz, CDCl₃) spectrum of trimethoxy(4-methylthiophen-2-yl)silane (**P13**).

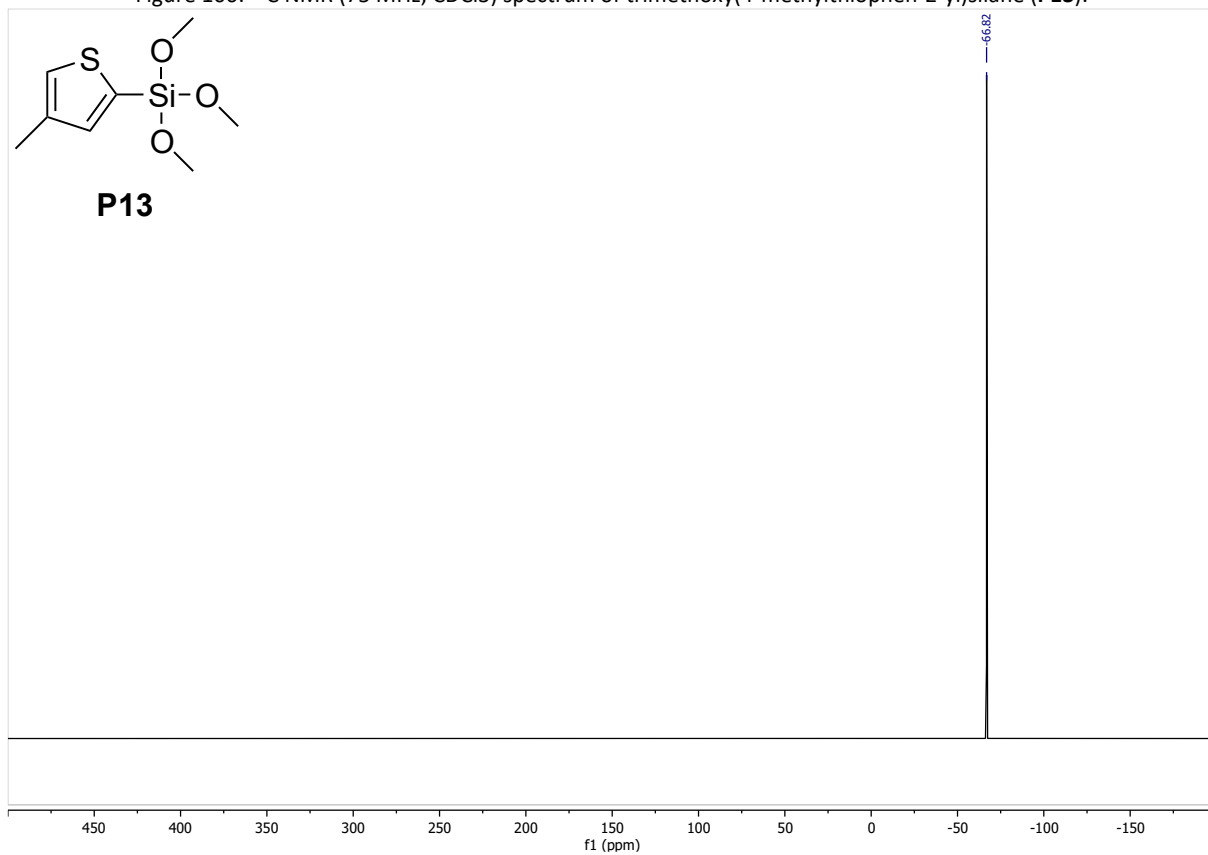
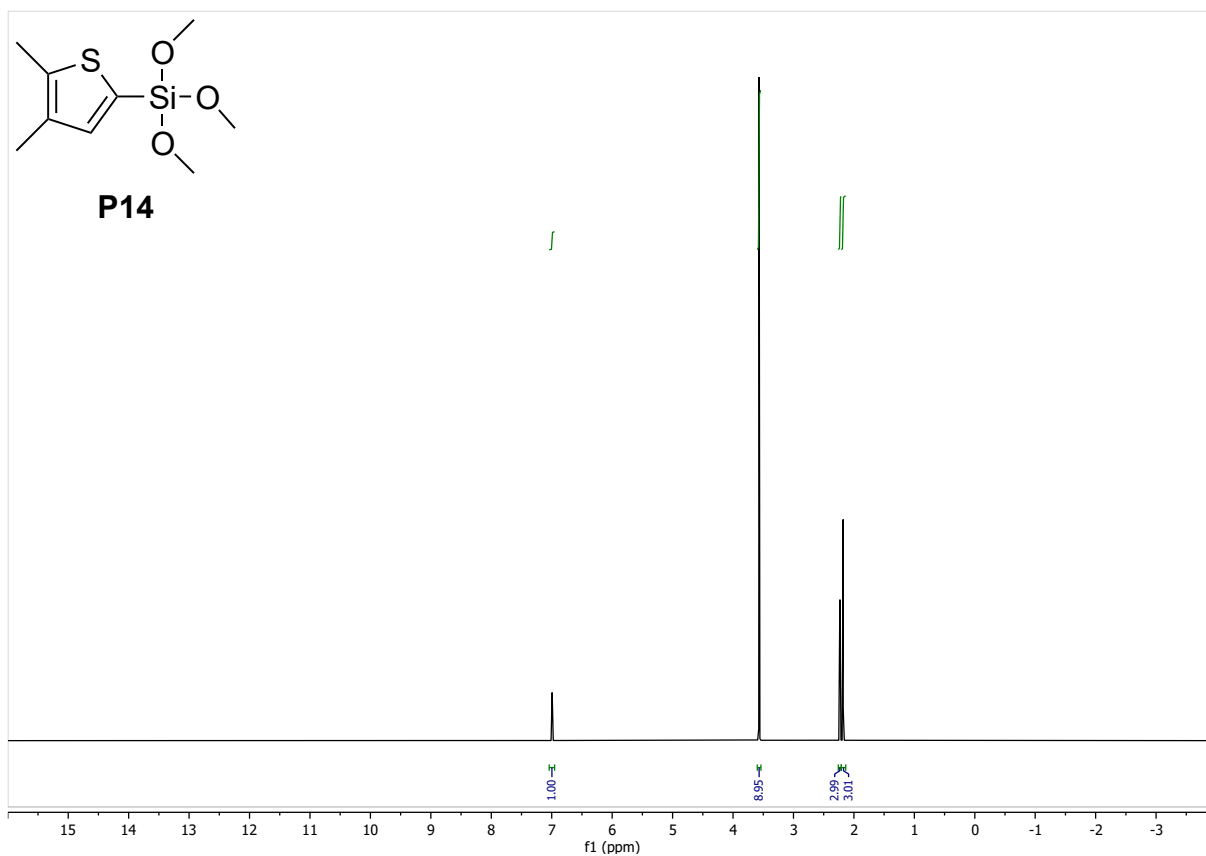
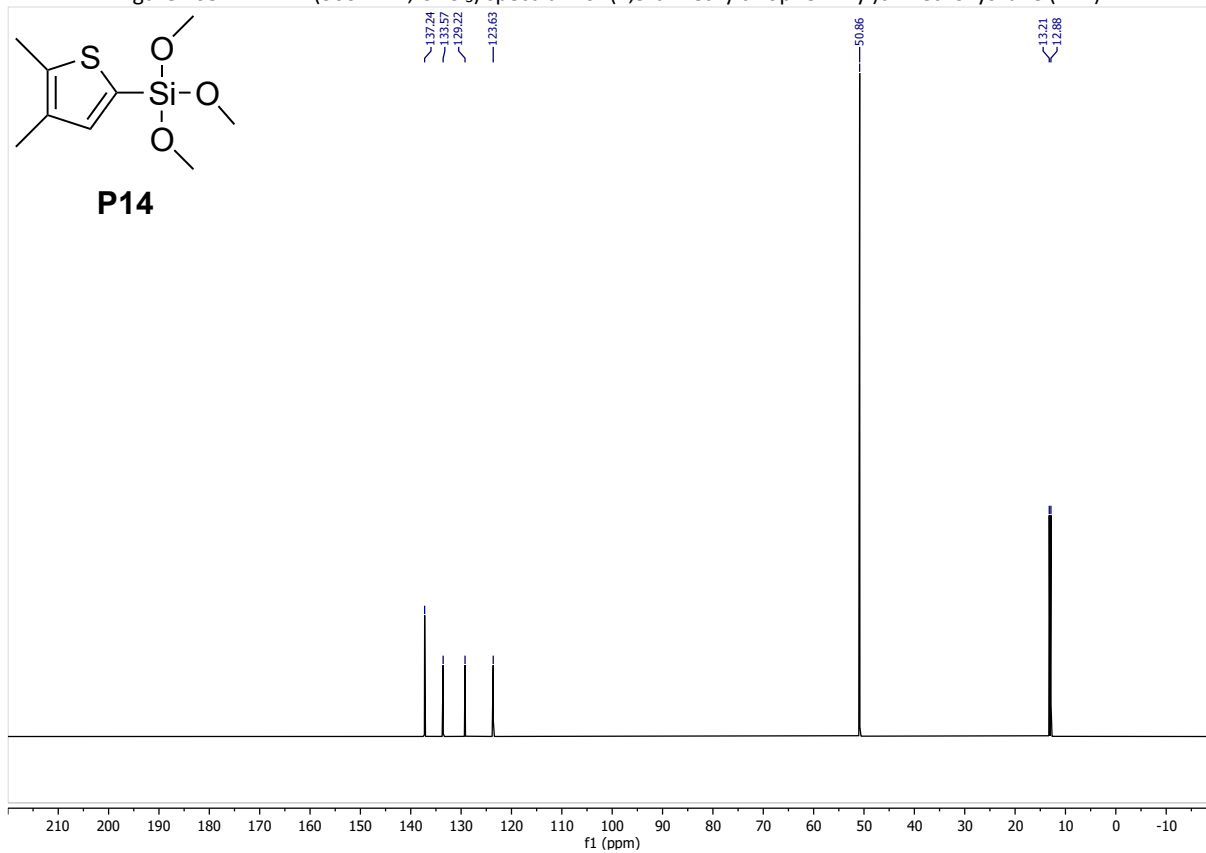
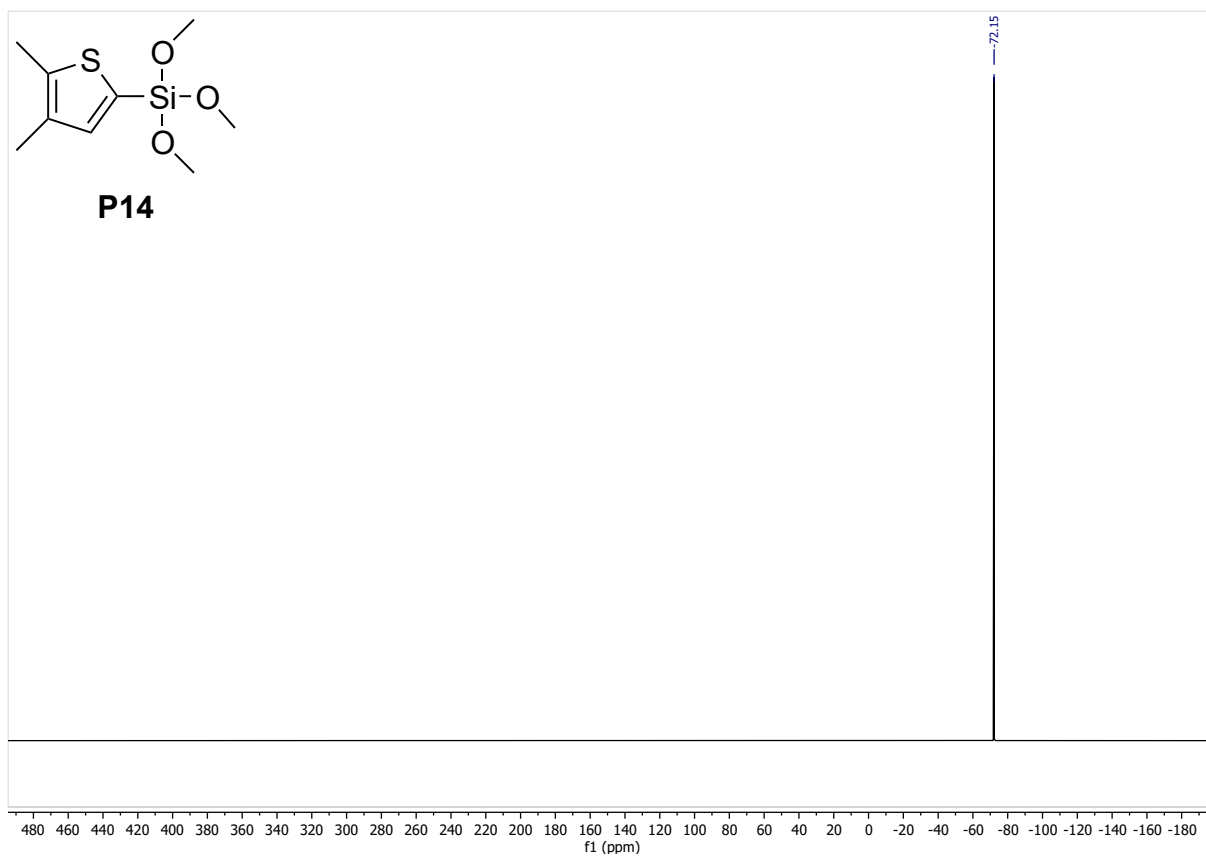
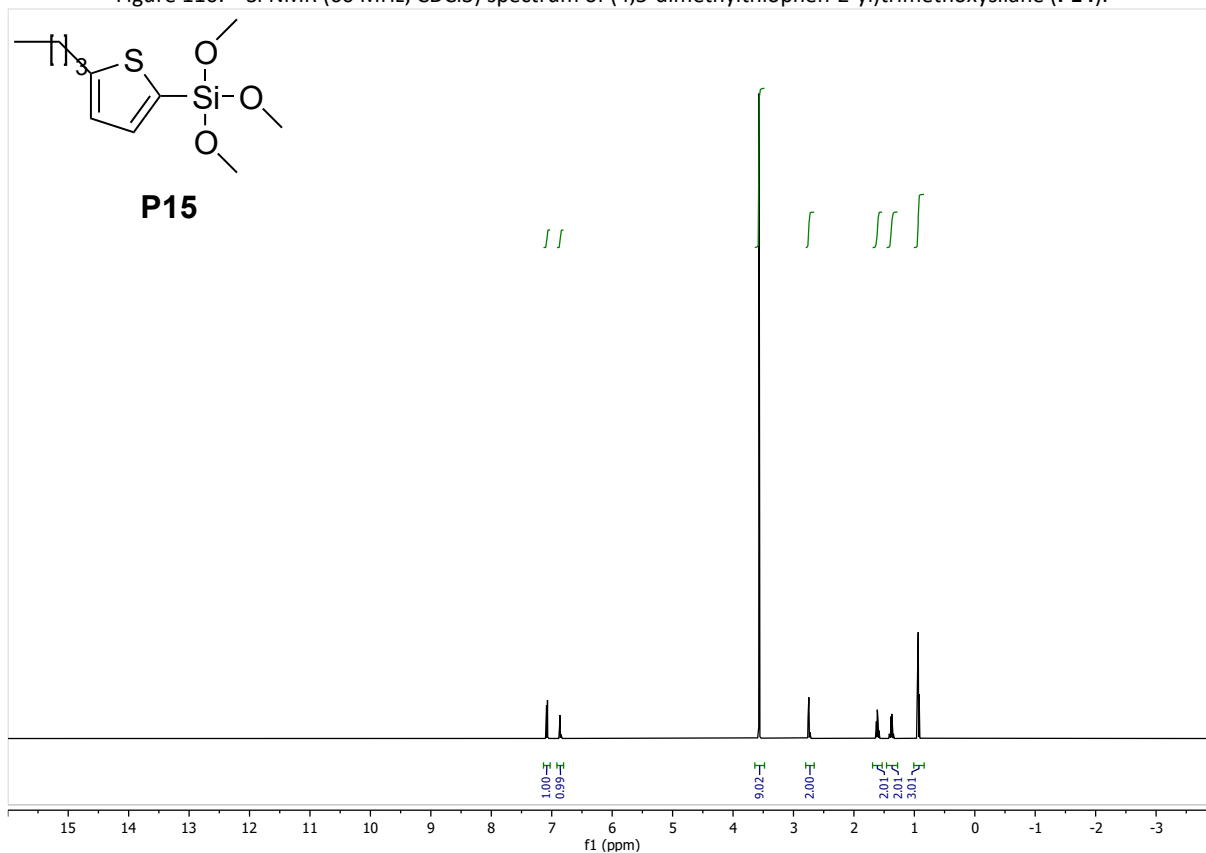


Figure 107: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of trimethoxy(4-methylthiophen-2-yl)silane (**P13**).

Figure 108: ¹H NMR (300 MHz, CDCl₃) spectrum of (4,5-dimethylthiophen-2-yl)trimethoxysilane (**P14**).Figure 109: ¹³C NMR (75 MHz, CDCl₃) spectrum of (4,5-dimethylthiophen-2-yl)trimethoxysilane (**P14**).

Figure 110: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of (4,5-dimethylthiophen-2-yl)trimethoxysilane (**P14**).Figure 111: ¹H NMR (300 MHz, CDCl₃) spectrum of (5-(sec-butyl)thiophen-2-yl)trimethoxysilane (**P15**).

Appendix

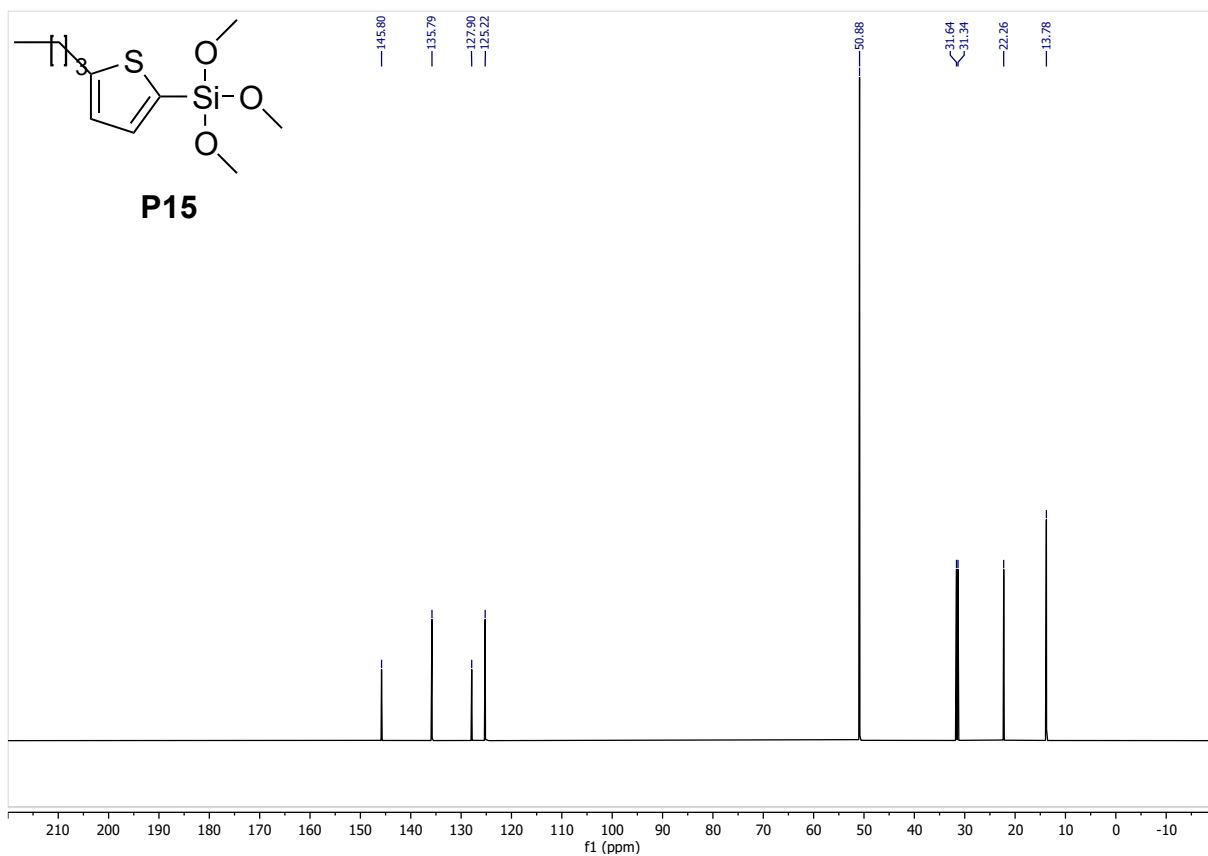


Figure 112: ¹³C NMR (75 MHz, CDCl₃) spectrum of (5-(sec-butyl)thiophen-2-yl)trimethoxysilane (**P15**).

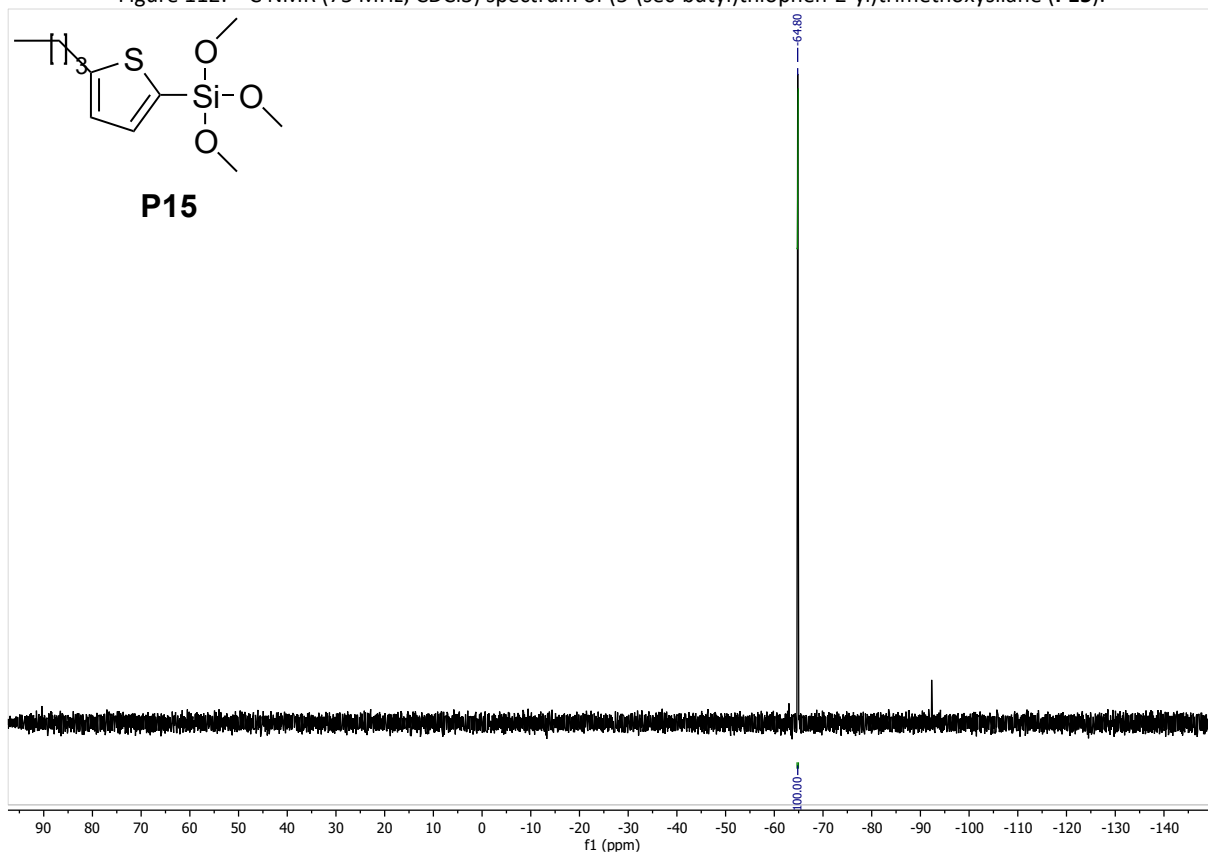


Figure 113: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of (5-(sec-butyl)thiophen-2-yl)trimethoxysilane (**P15**).

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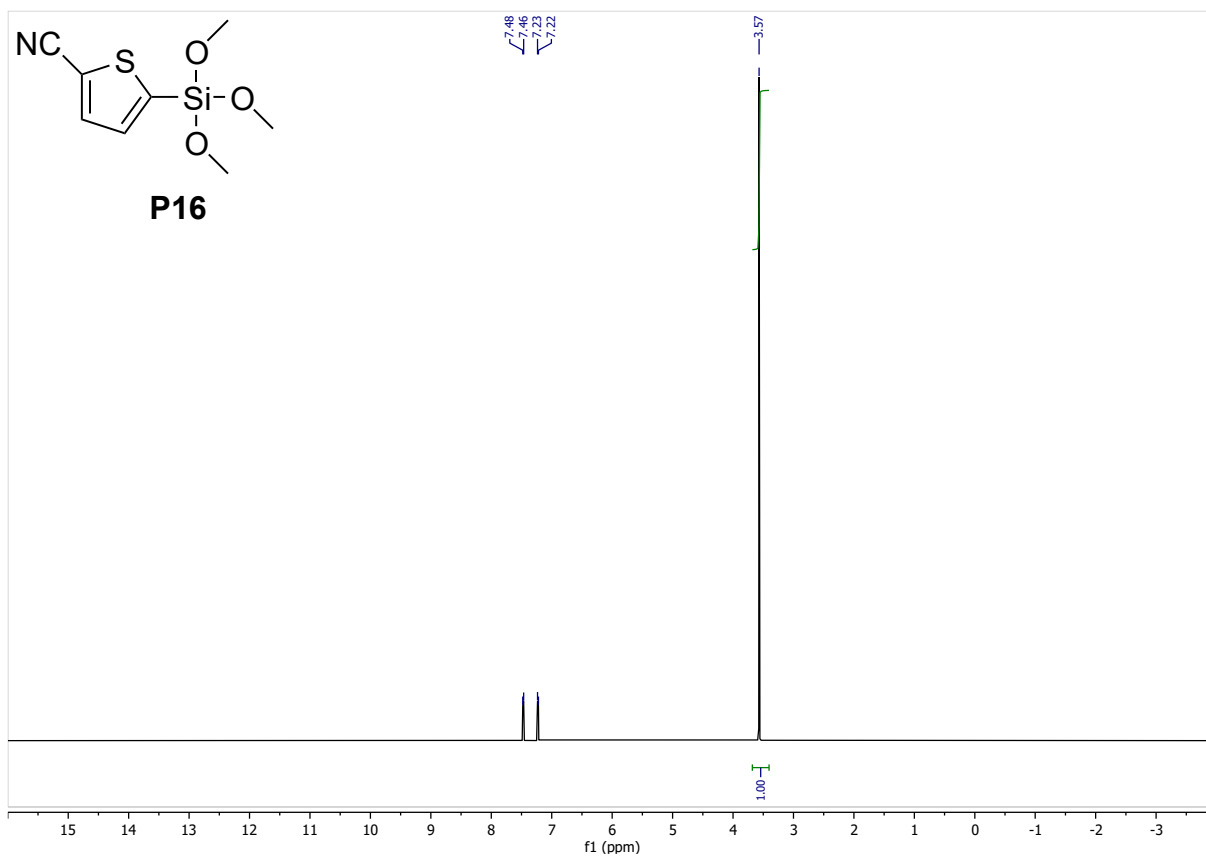


Figure 114: ^1H NMR (300 MHz, CDCl_3) spectrum of 5-(trimethoxysilyl)thiophene-2-carbonitrile (**P16**).

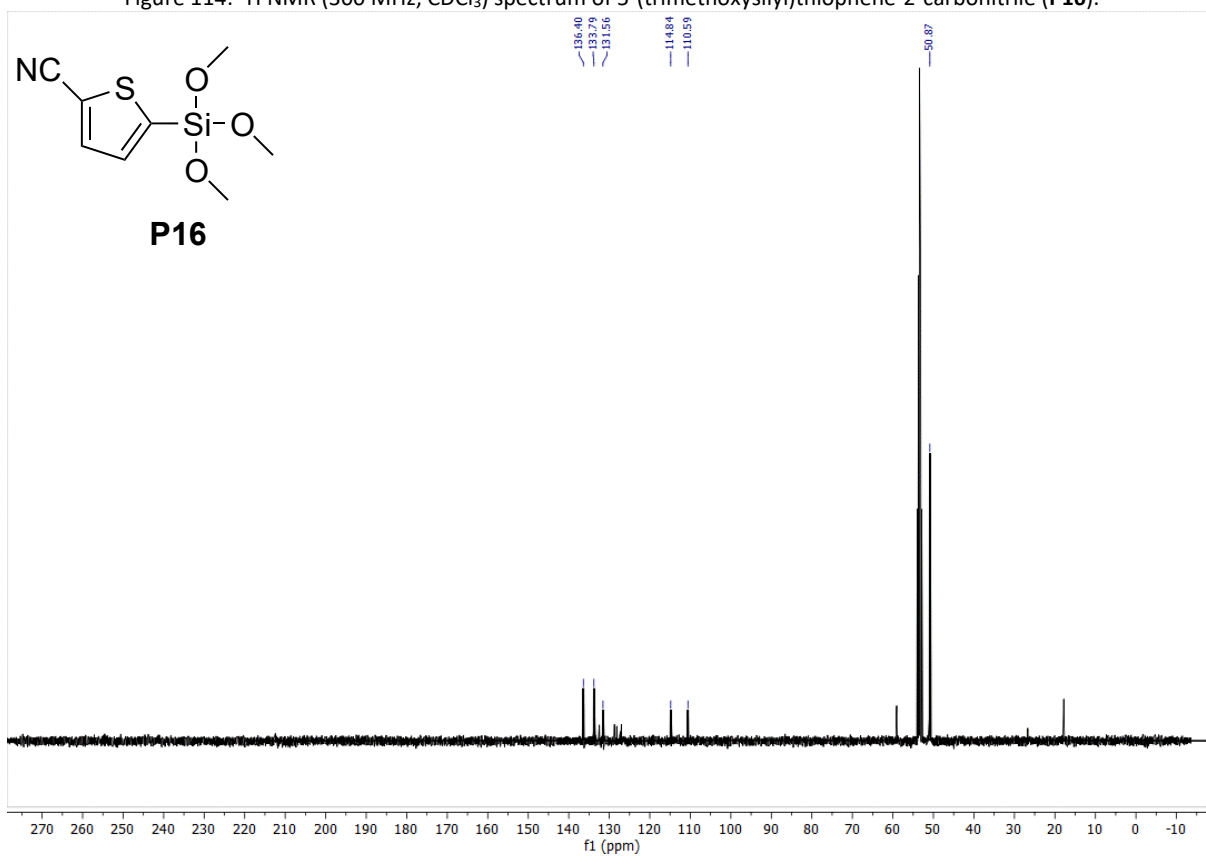


Figure 115: ^{13}C NMR (75 MHz, CDCl_3) spectrum of 5-(trimethoxysilyl)thiophene-2-carbonitrile (**P16**).

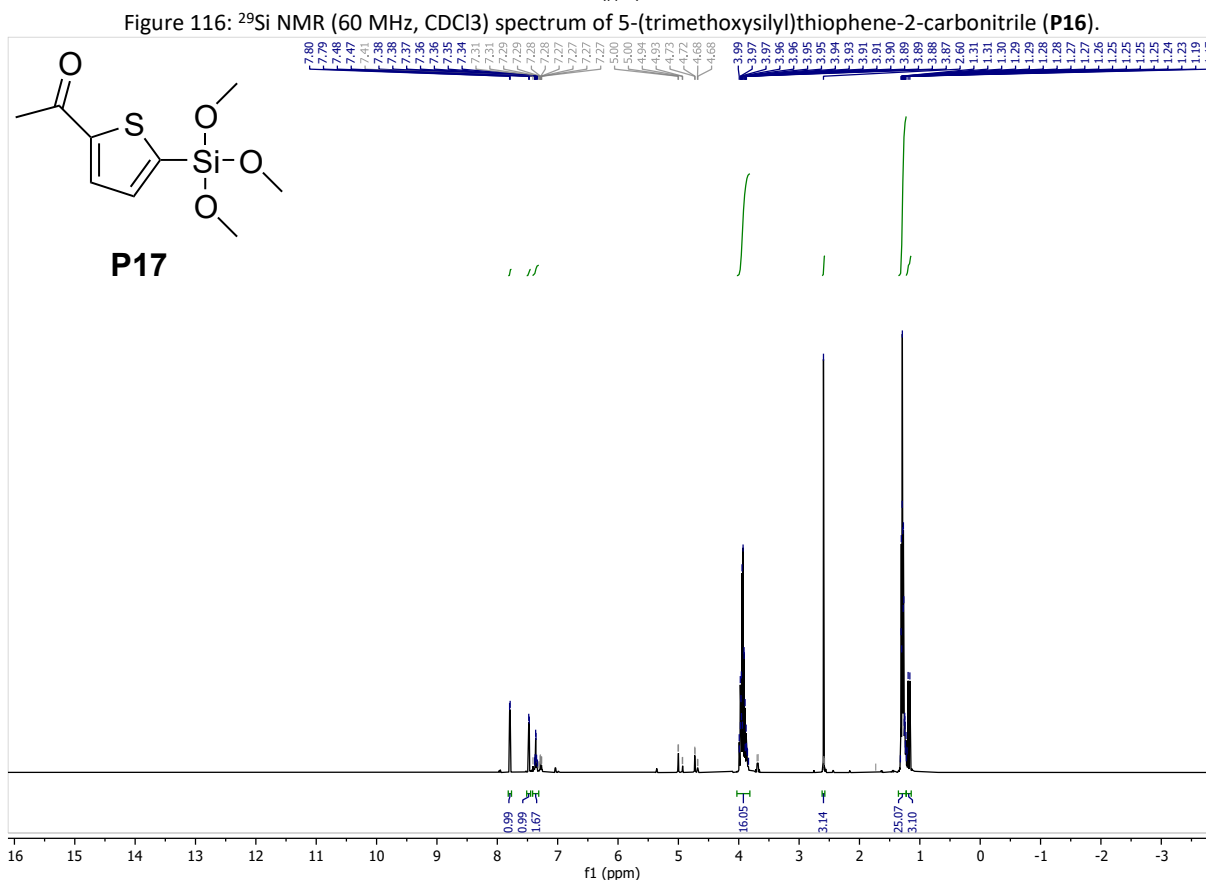
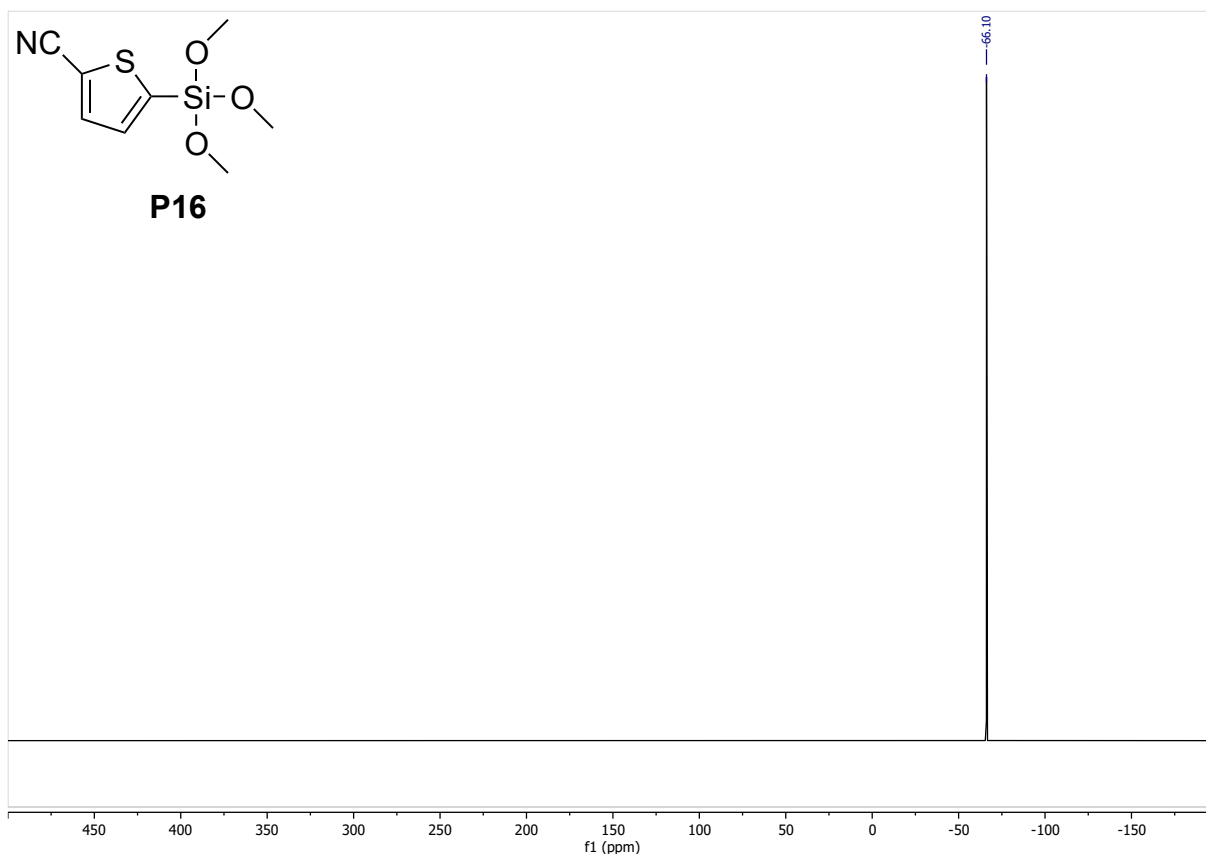


Figure 117: ^1H NMR (300 MHz, CDCl_3) spectrum of 1-(5-(trimethoxysilyl)thiophen-2-yl)ethan-1-one (**P17**).

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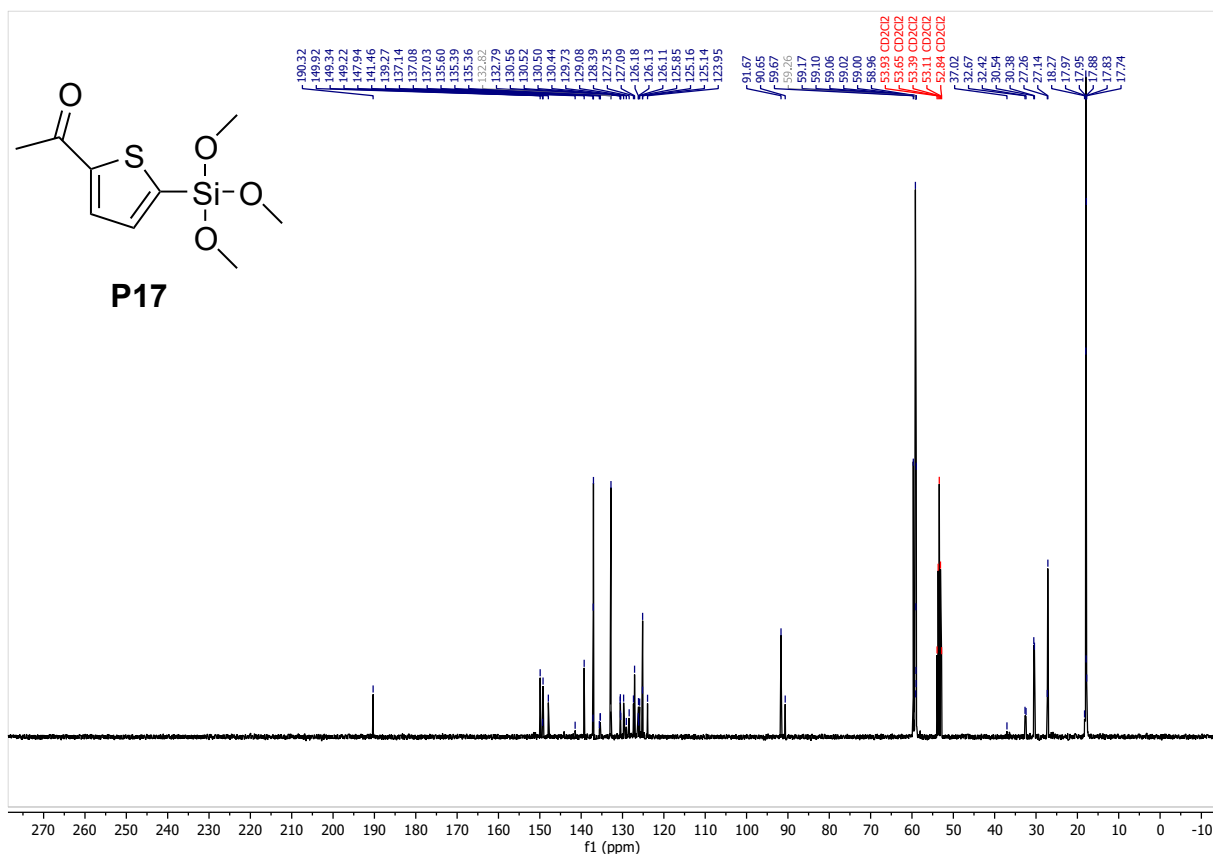


Figure 118: ¹³C NMR (75 MHz, CDCl₃) spectrum of 1-(5-(trimethoxysilyl)thiophen-2-yl)ethan-1-one (**P17**).

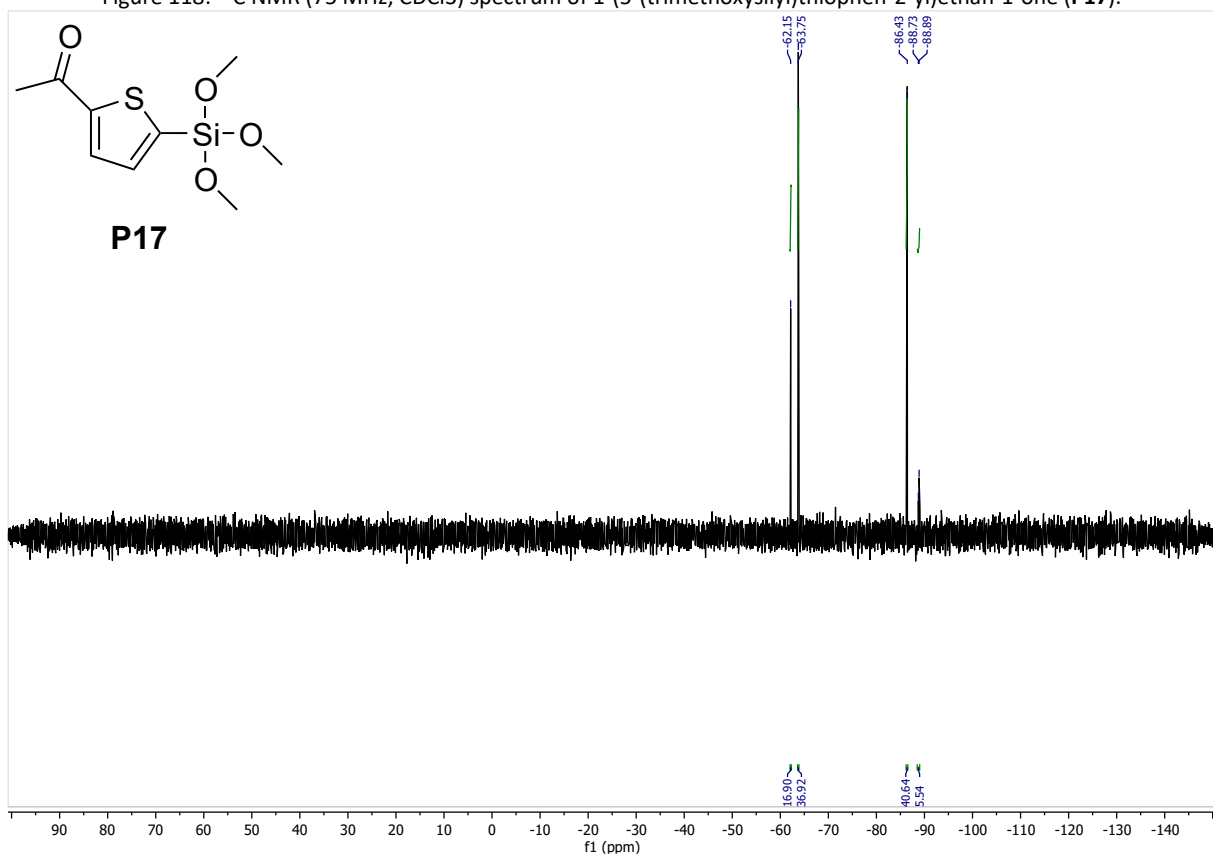


Figure 119: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of 1-(5-(trimethoxysilyl)thiophen-2-yl)ethan-1-one (**P17**).

Appendix

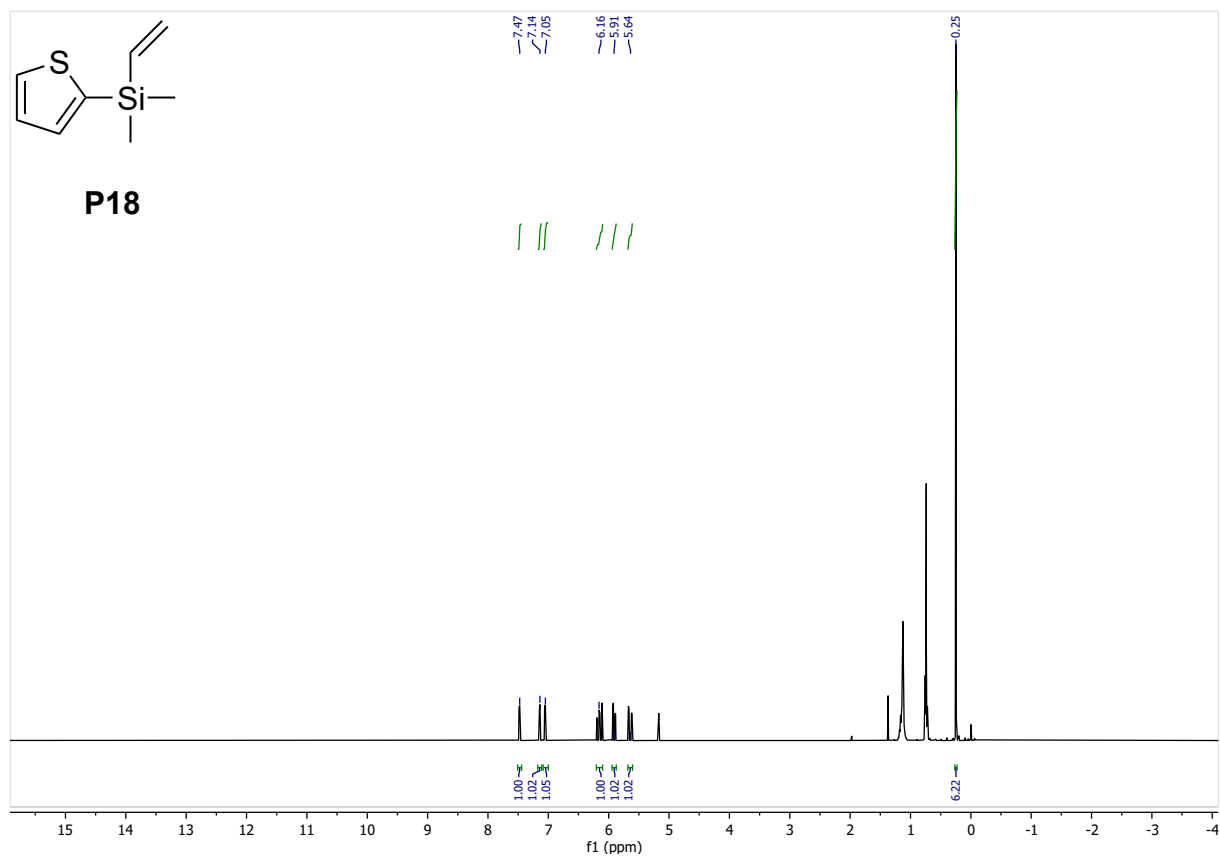


Figure 120: ¹H NMR (300 MHz, CDCl₃) spectrum of dimethyl(thiophen-2-yl)(vinyl)silane (**P18**).

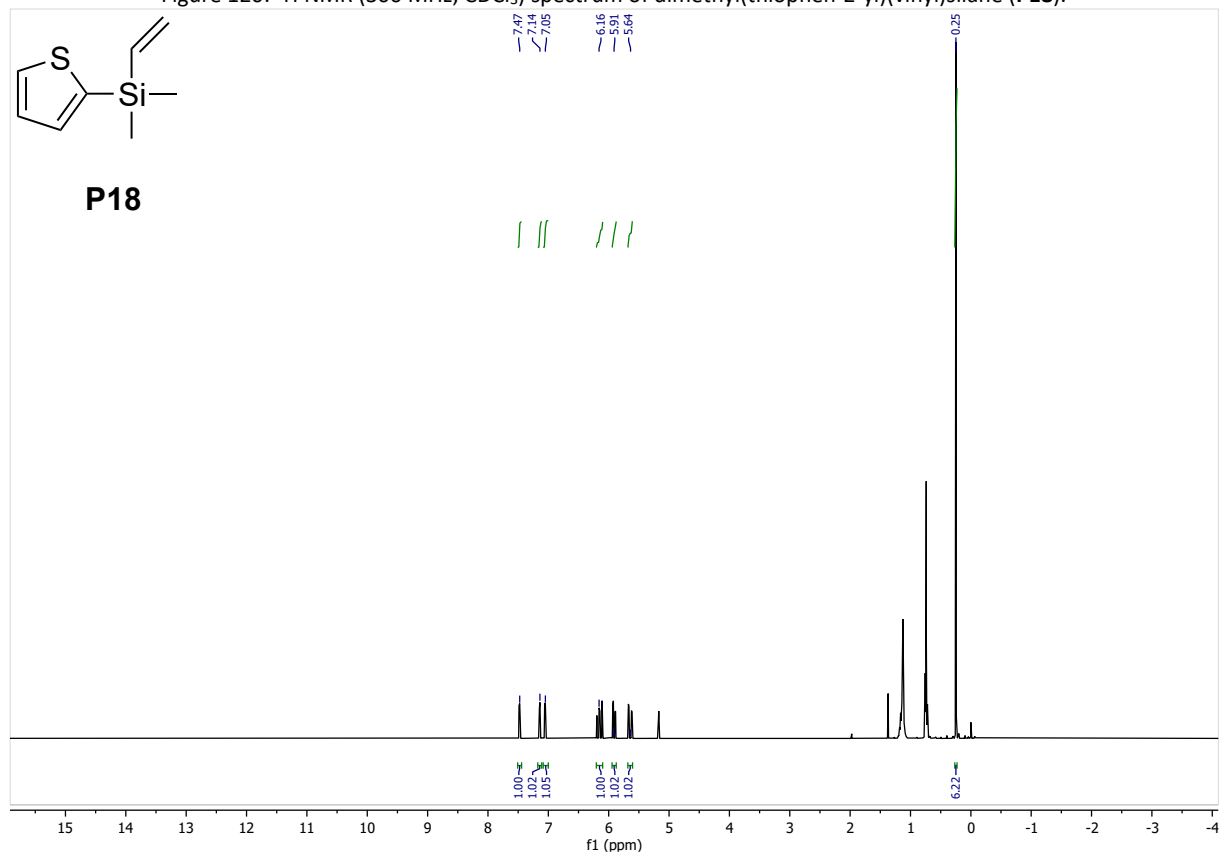


Figure 121: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of dimethyl(thiophen-2-yl)(vinyl)silane (**P18**).

Appendix

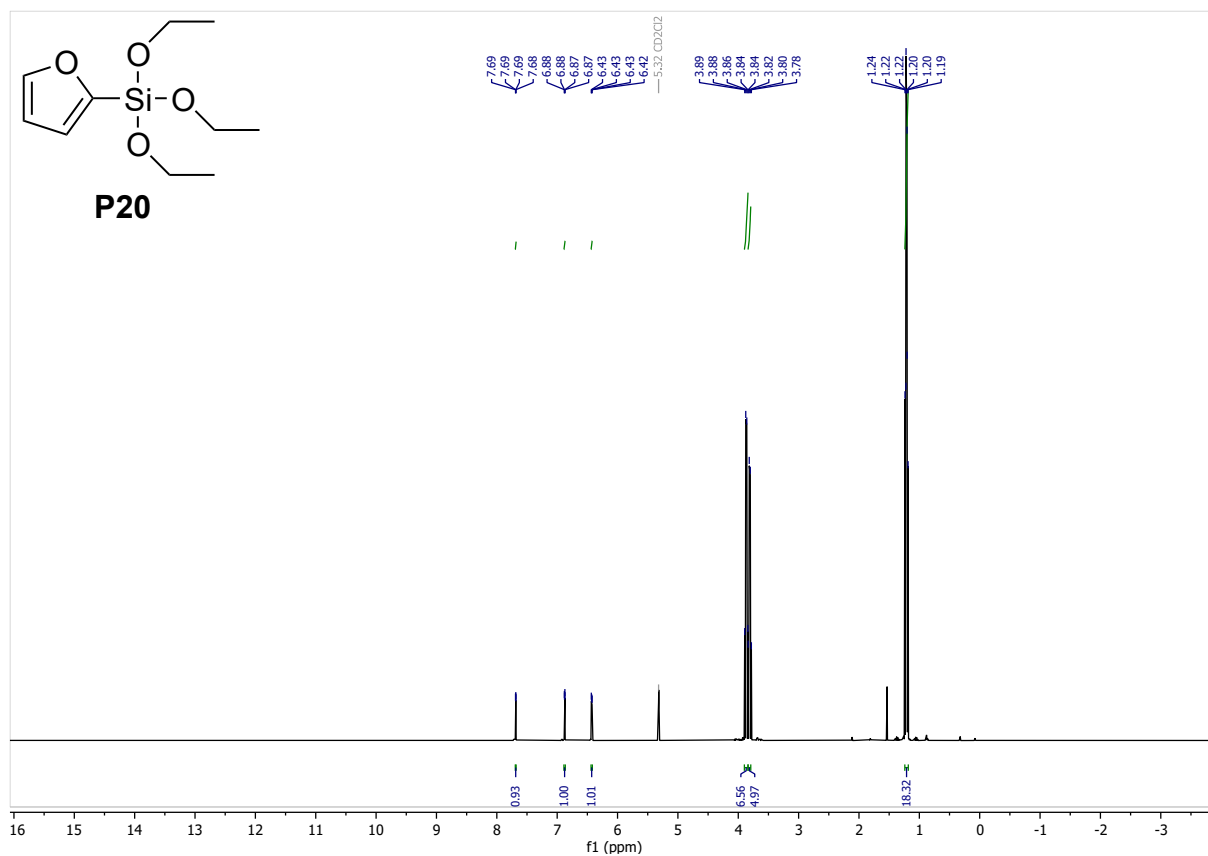


Figure 122: ^1H NMR (300 MHz, CDCl_3) spectrum of triethoxy(furan-2-yl)silane (**P20**).

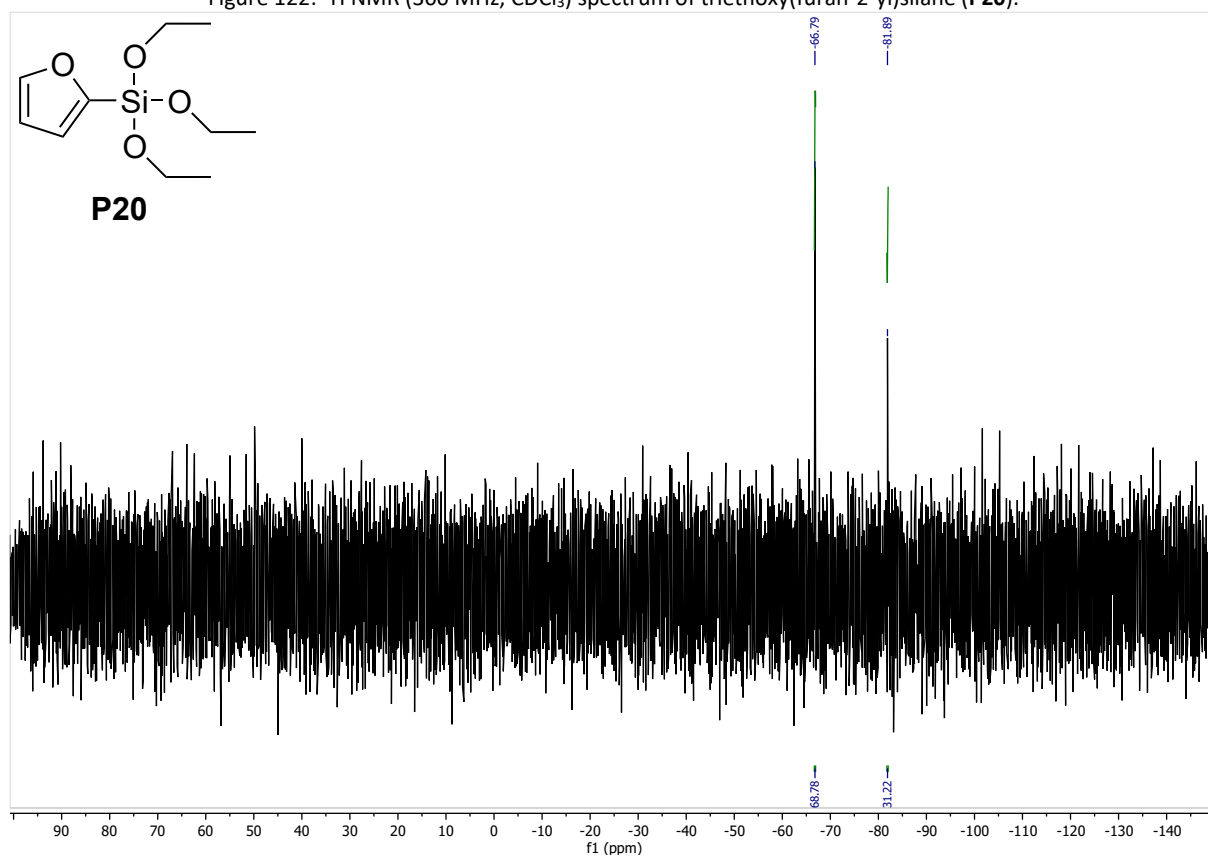


Figure 123: ^{29}Si NMR (60 MHz, CDCl_3) spectrum of triethoxy(furan-2-yl)silane (**P20**).

Appendix

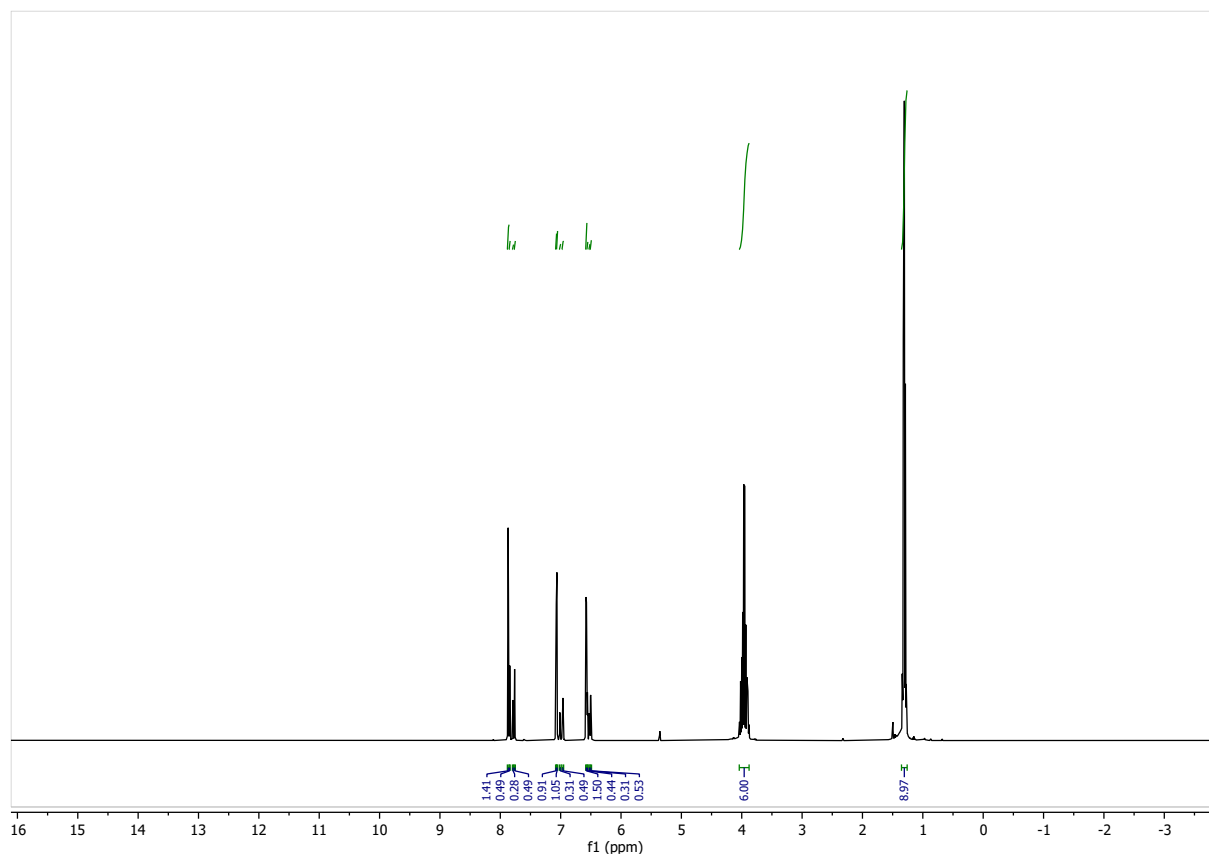


Figure 124: ¹H NMR (300 MHz, CDCl₃) spectrum of triethoxy(furan-2-yl)silane after 72 h.

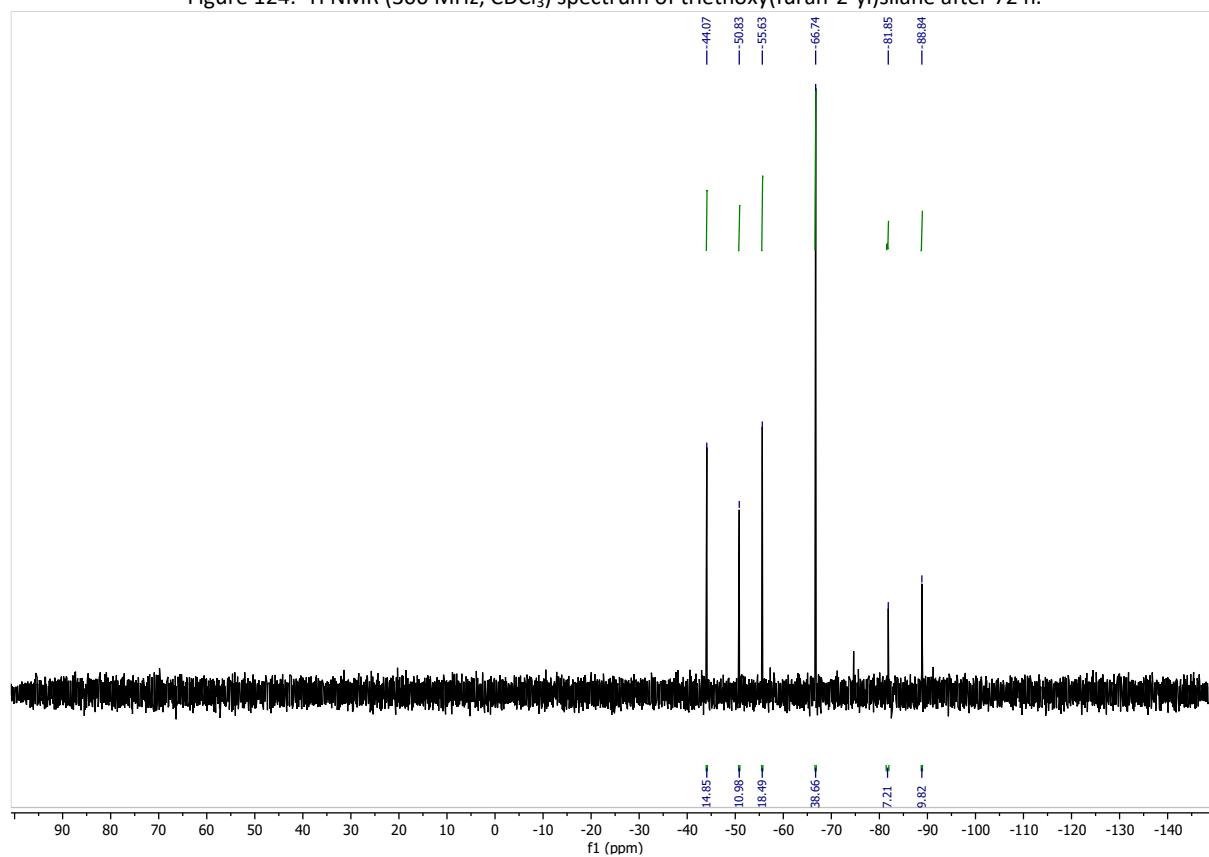


Figure 125: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of triethoxy(furan-2-yl)silane after 72 h.

Appendix

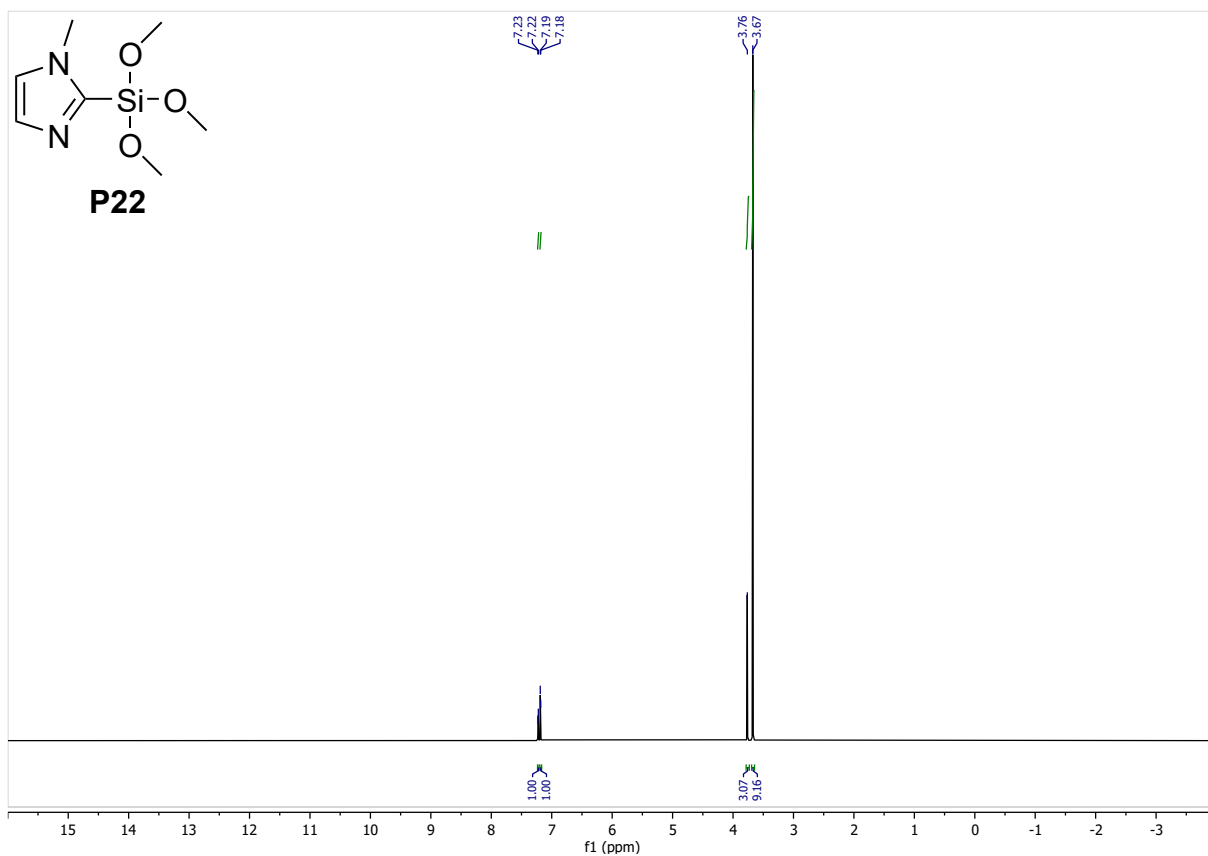


Figure 126: ¹H NMR (300 MHz, CDCl₃) spectrum of 1-methyl-2-(trimethoxysilyl)-1H-imidazole (**P22**).

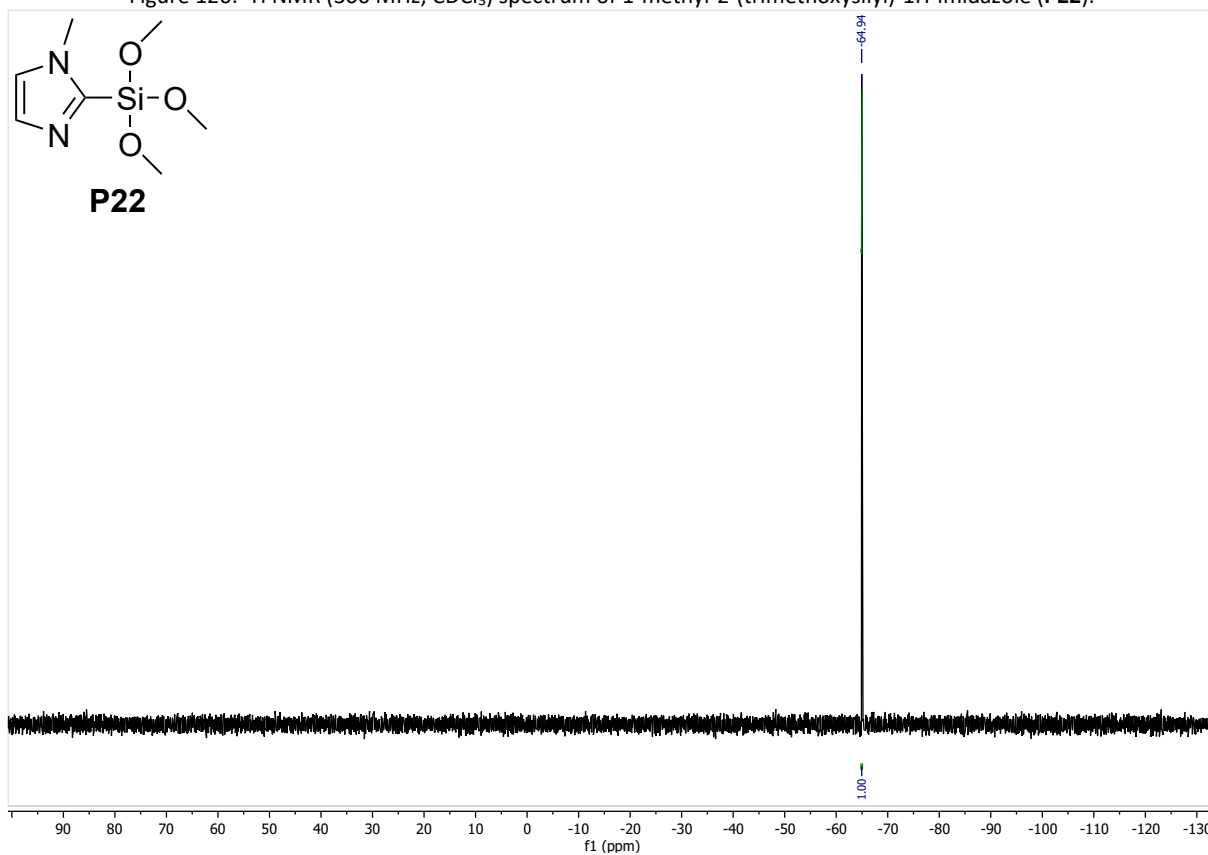


Figure 127: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of 1-methyl-2-(trimethoxysilyl)-1H-imidazole (**P22**).

Appendix

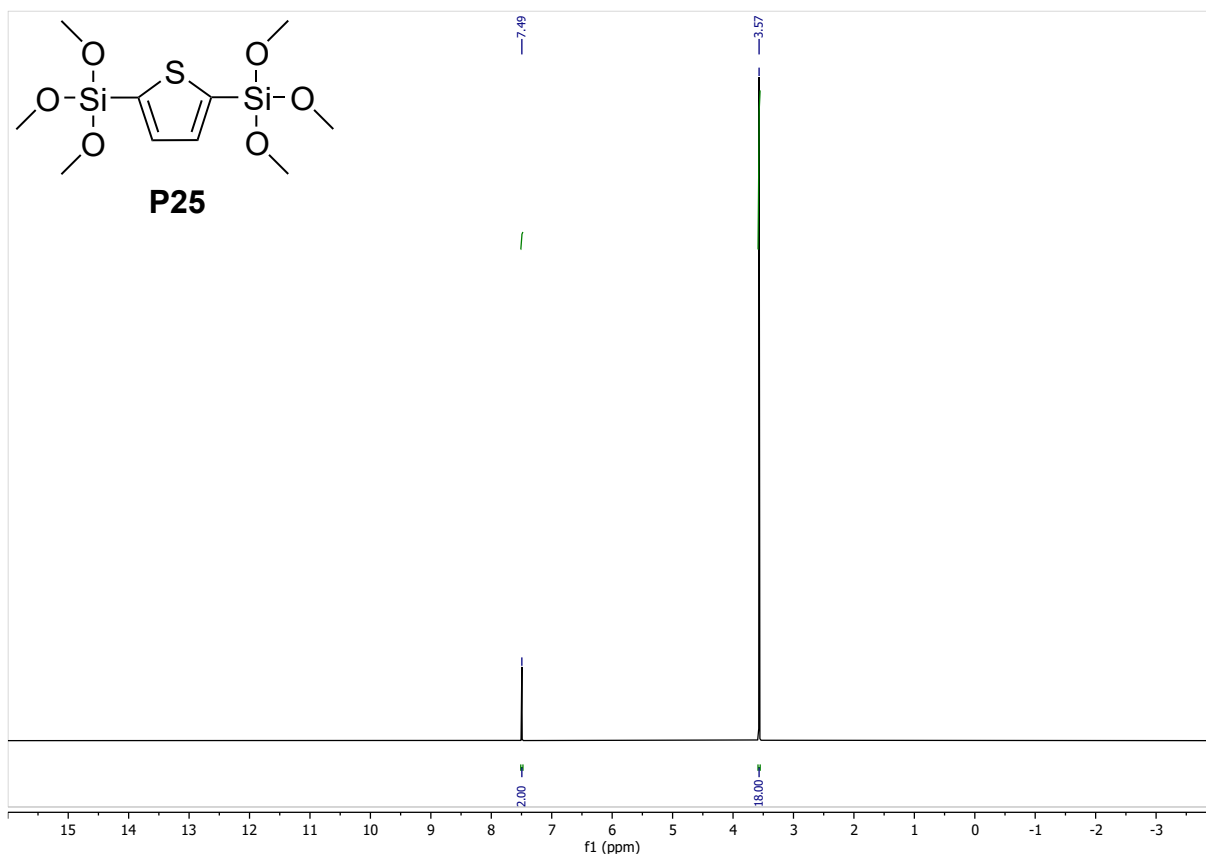


Figure 128: ¹H NMR (300 MHz, CDCl₃) spectrum of 2,5-bis(trimethoxysilyl)thiophene (**P25**).

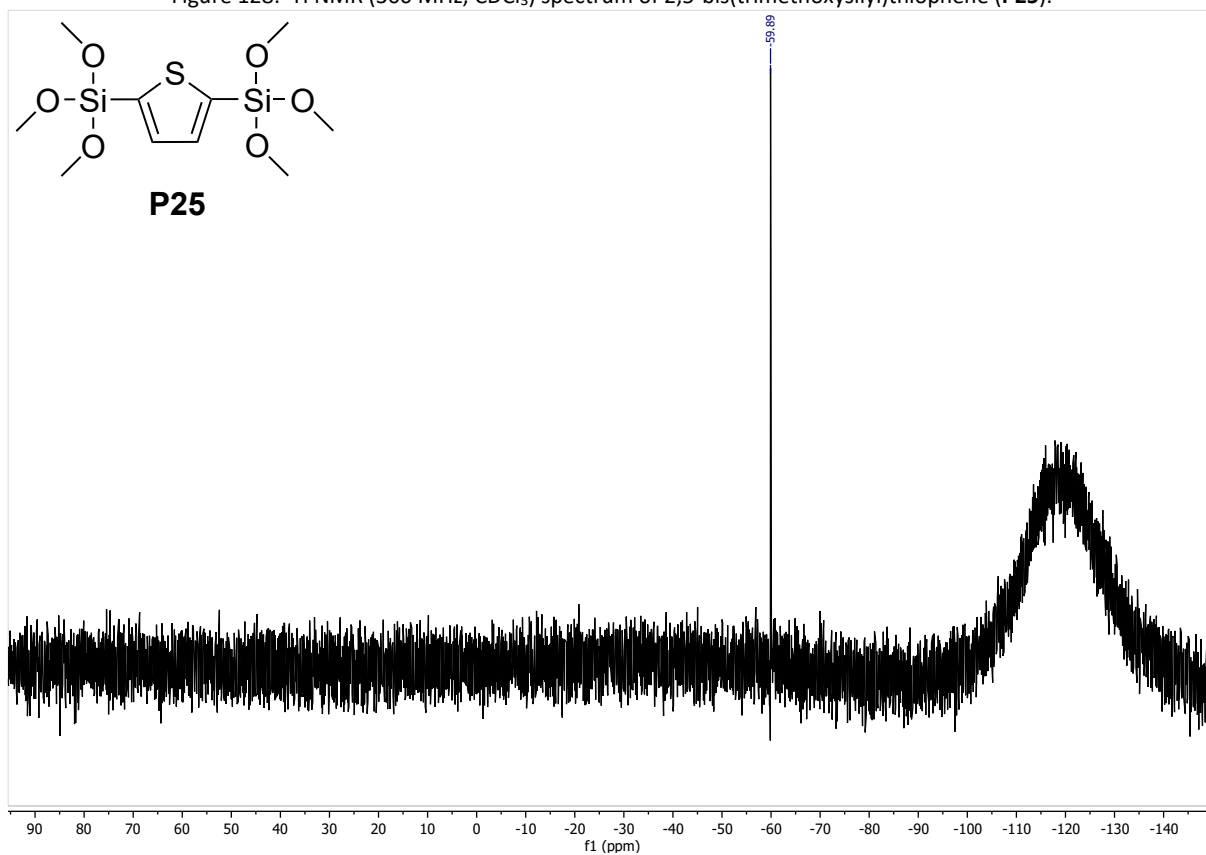


Figure 129: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of 2,5-bis(trimethoxysilyl)thiophene (**P25**).

Appendix

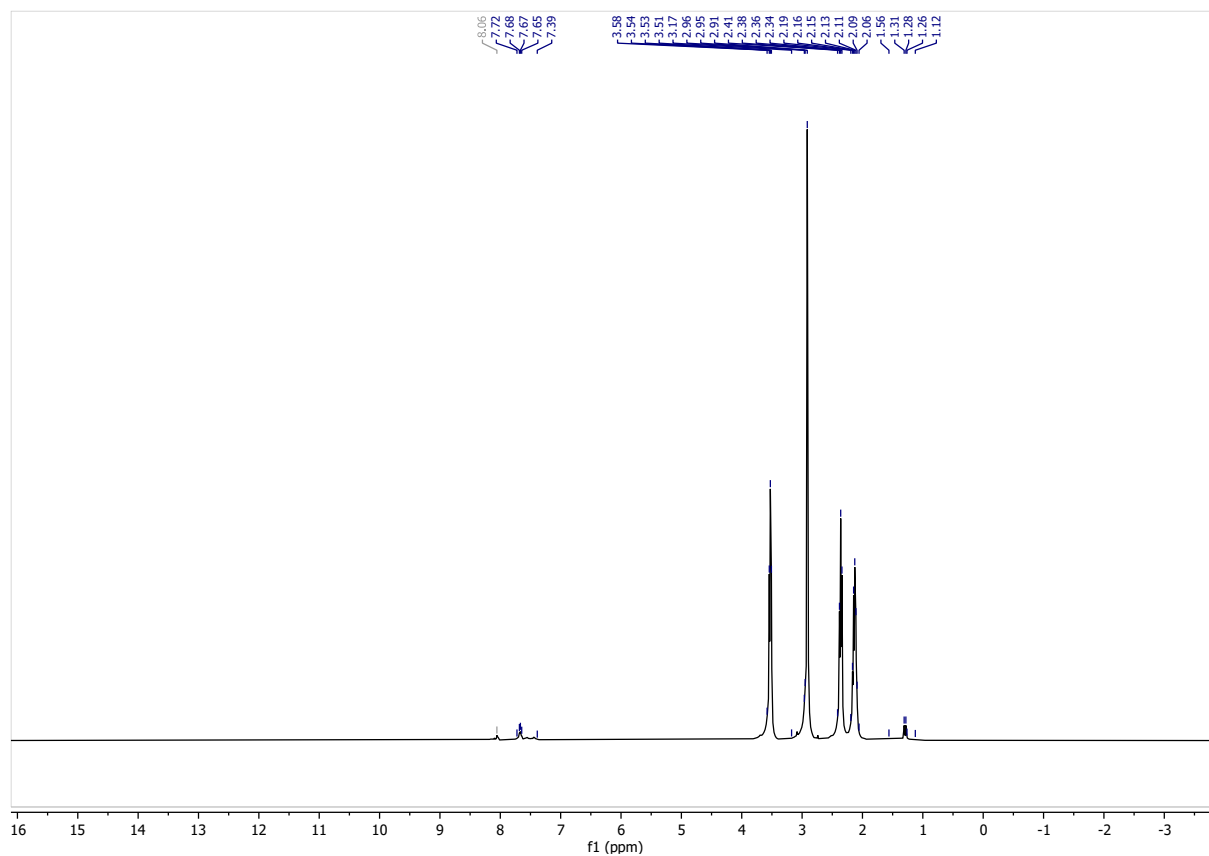


Figure 130: ^1H NMR (300 MHz, 80 $^\circ\text{C}$, CDCl_3) spectrum of complex **C1**.

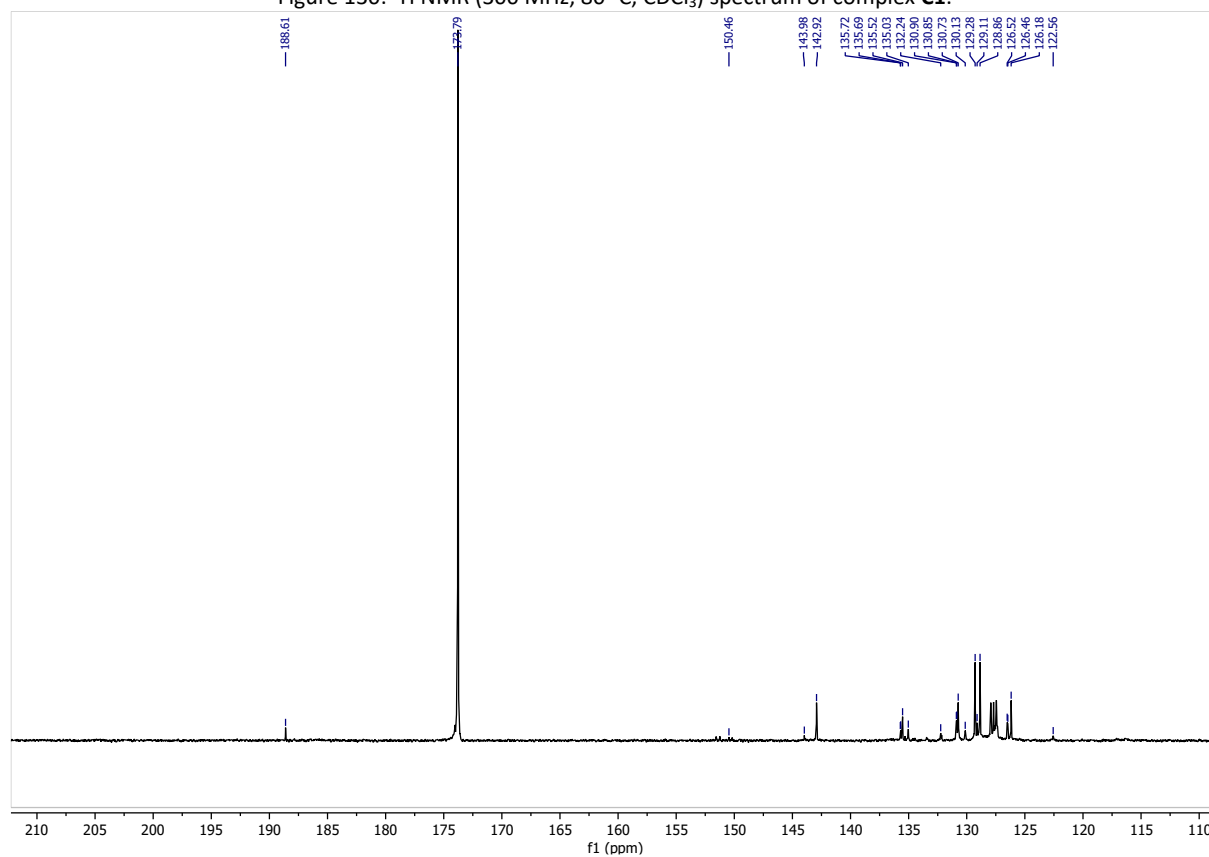


Figure 131: ^{13}C NMR (76 MHz, 80 $^\circ\text{C}$, CDCl_3) spectrum of complex **C1**.

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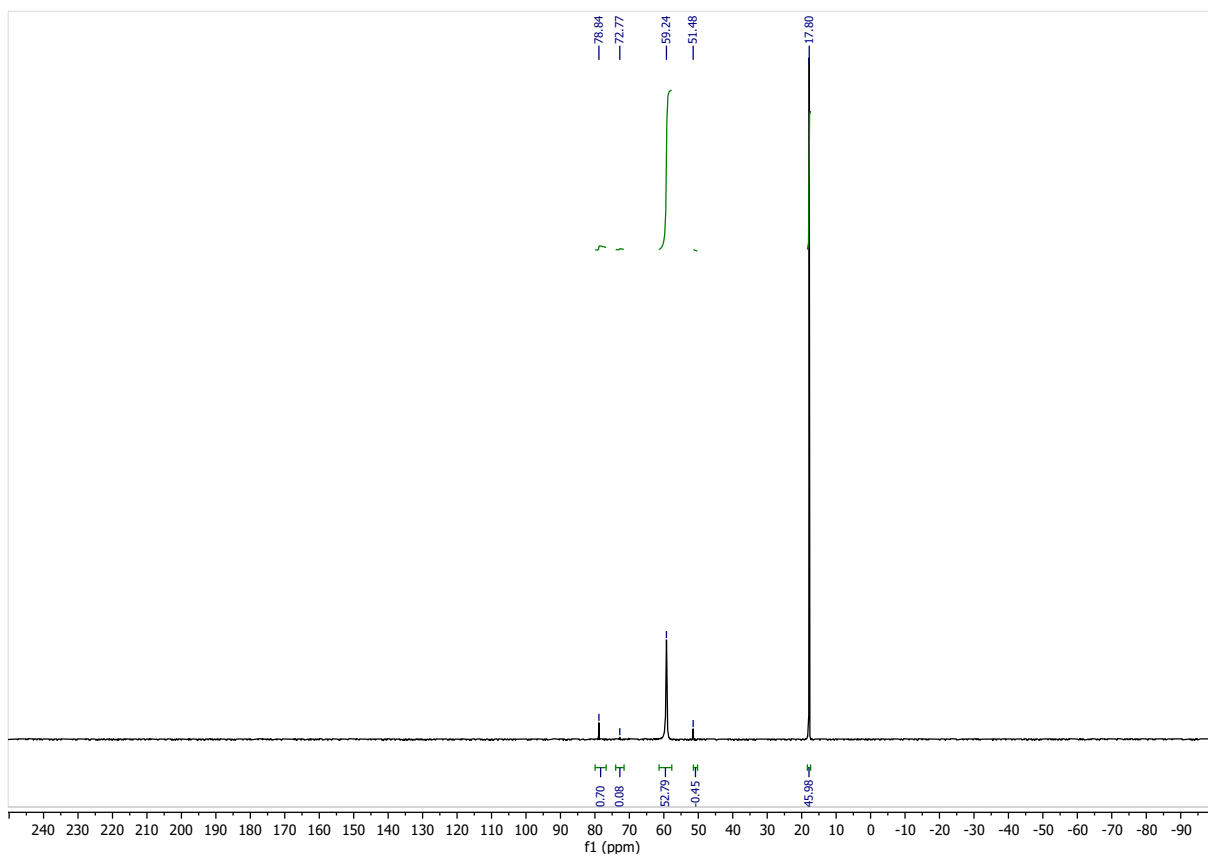


Figure 132: ^{31}P NMR (121 MHz, 80 °C, CDCl_3) spectrum of complex **C1**.

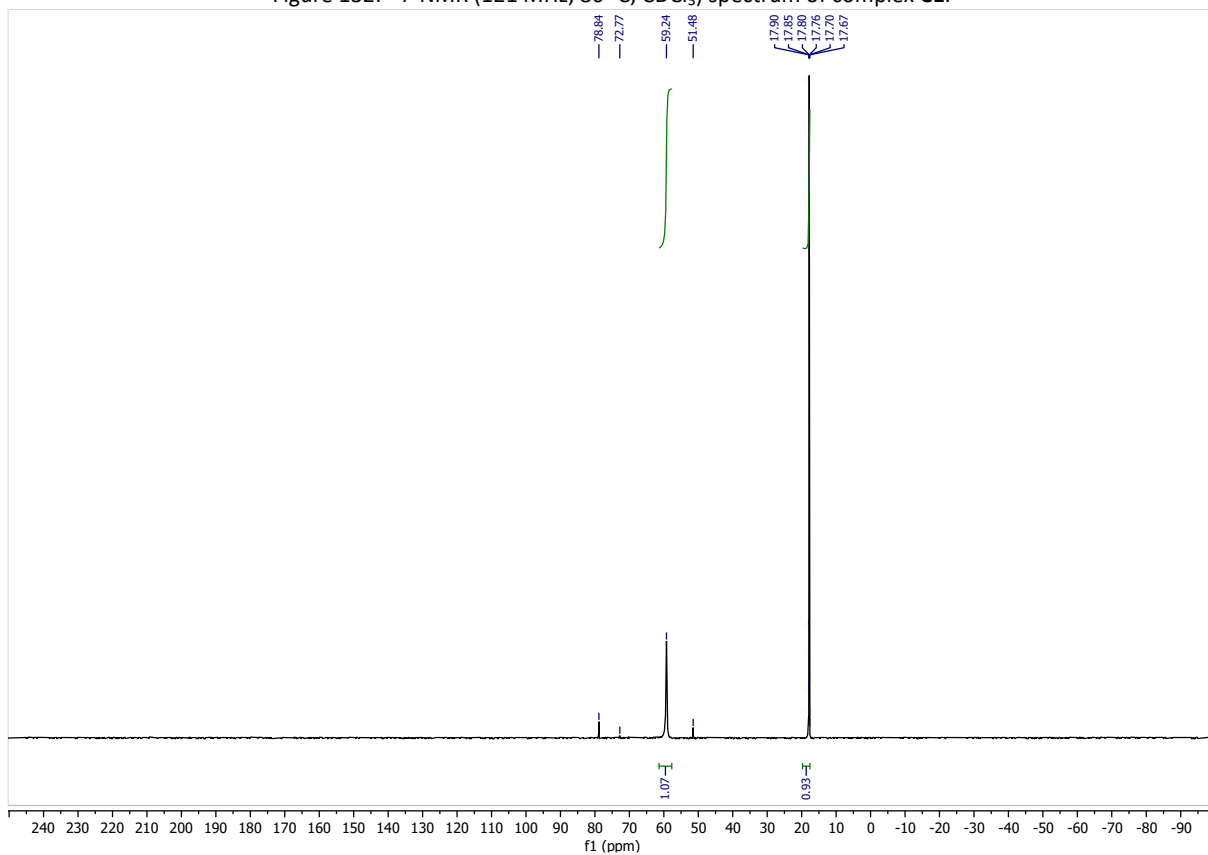


Figure 133: ^{31}P NMR (121 MHz, 80 °C, CDCl_3) spectrum of complex **C1**. Formed with one equivalent acetonitrile.

Appendix

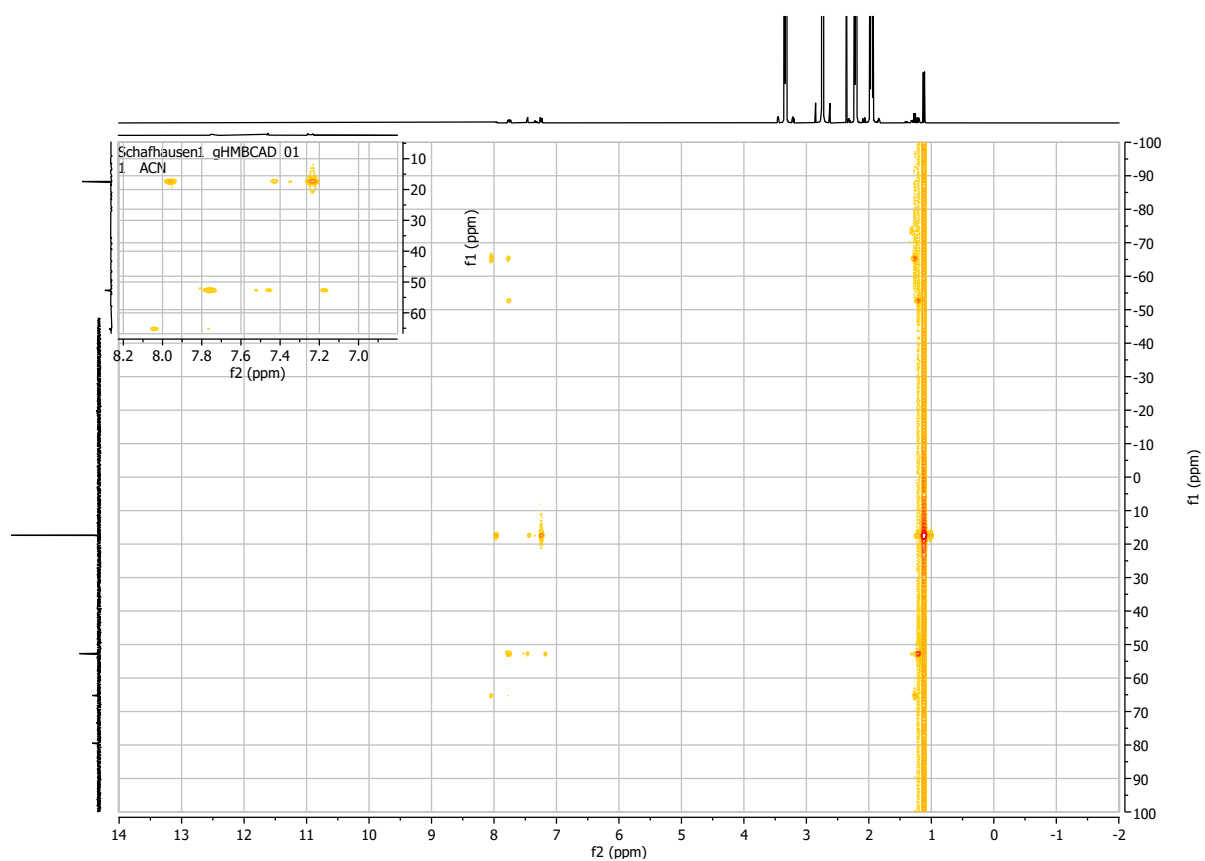


Figure 134: ^{31}P - ^1H -HMBC of **C1** in NMP.

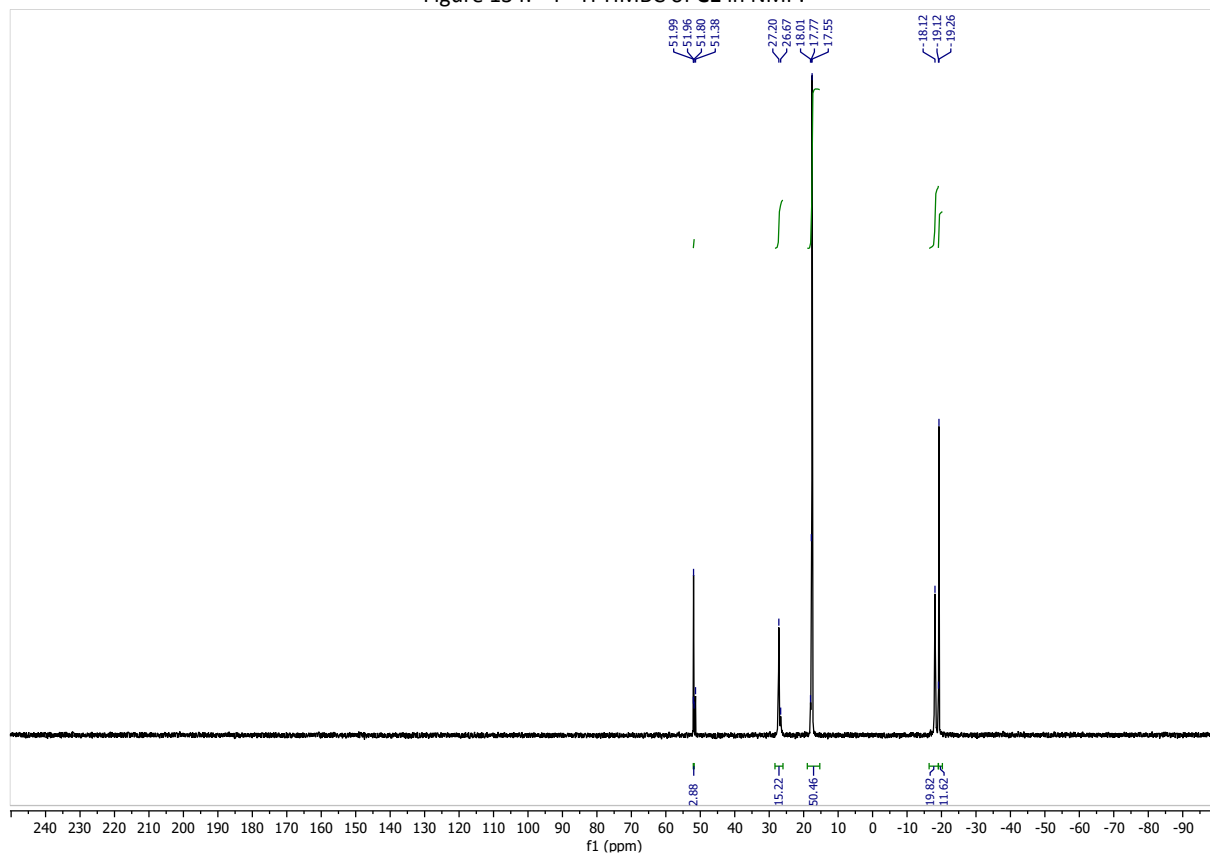
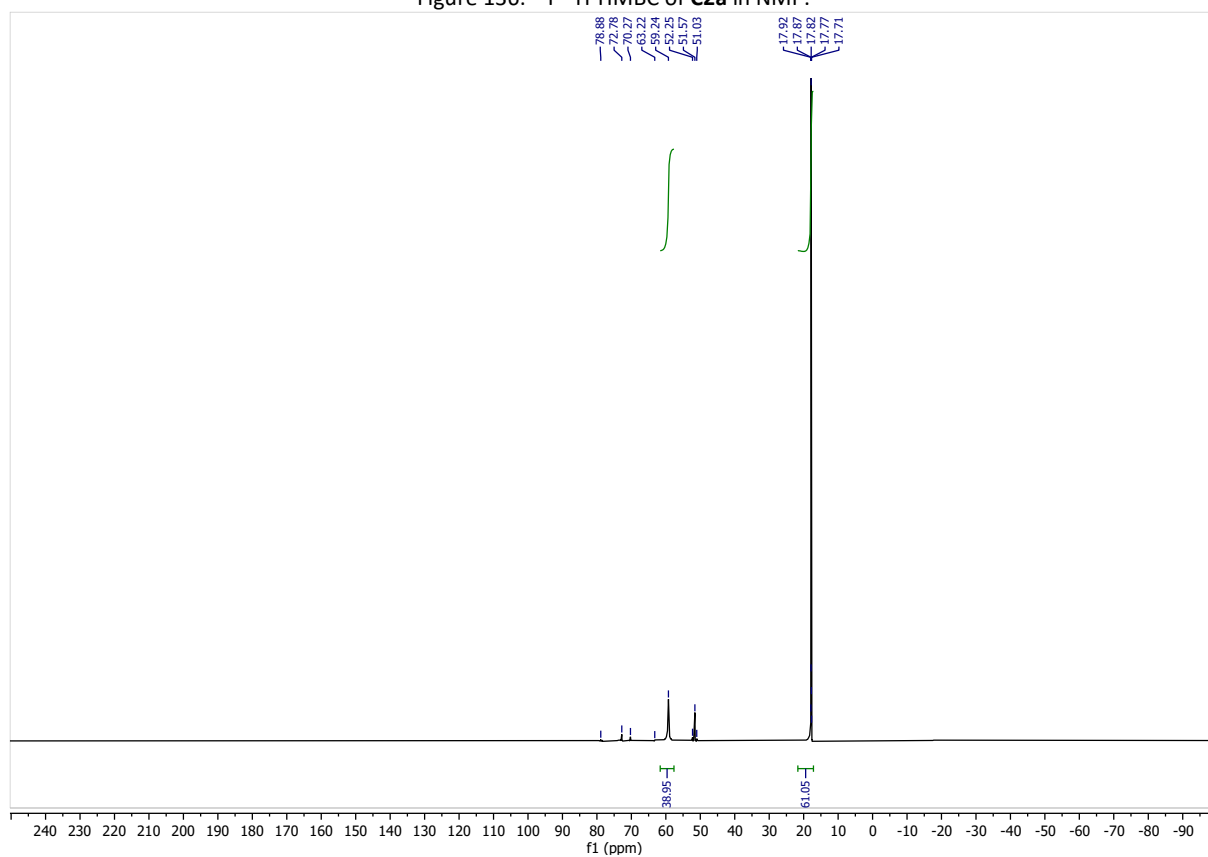
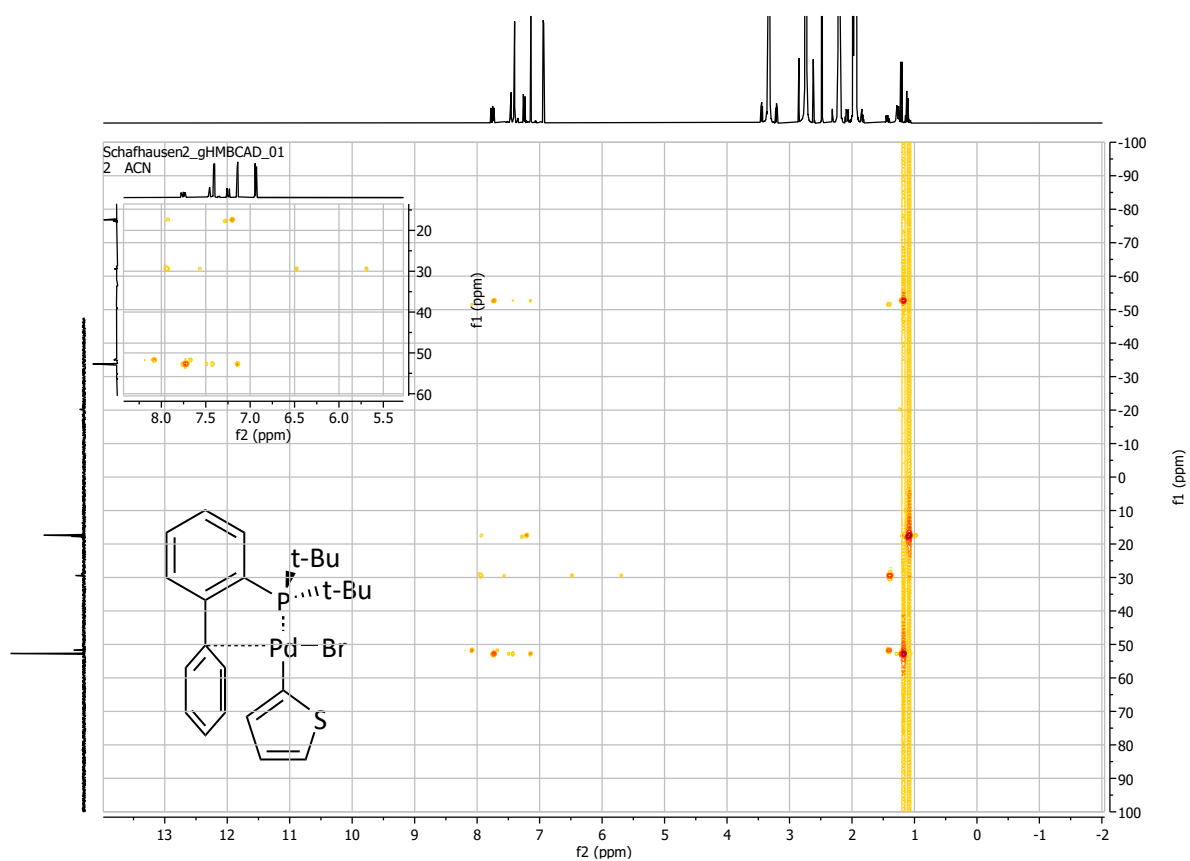


Figure 135: ^{31}P NMR (121 MHz, 80 °C, CDCl_3) spectrum of complex **C2a**.

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Appendix

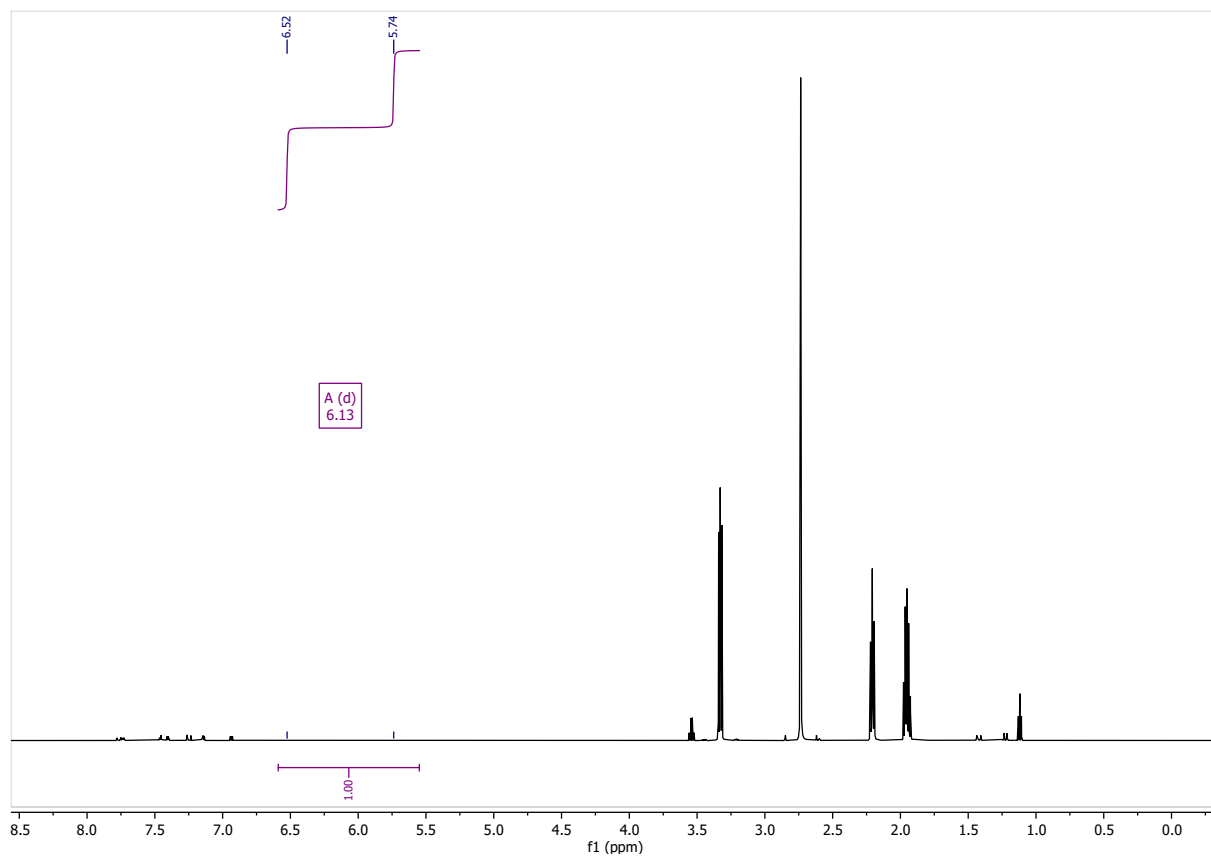


Figure 138: ¹H NMR (300 MHz, 80 °C, CDCl₃) spectrum of complex **C3**.

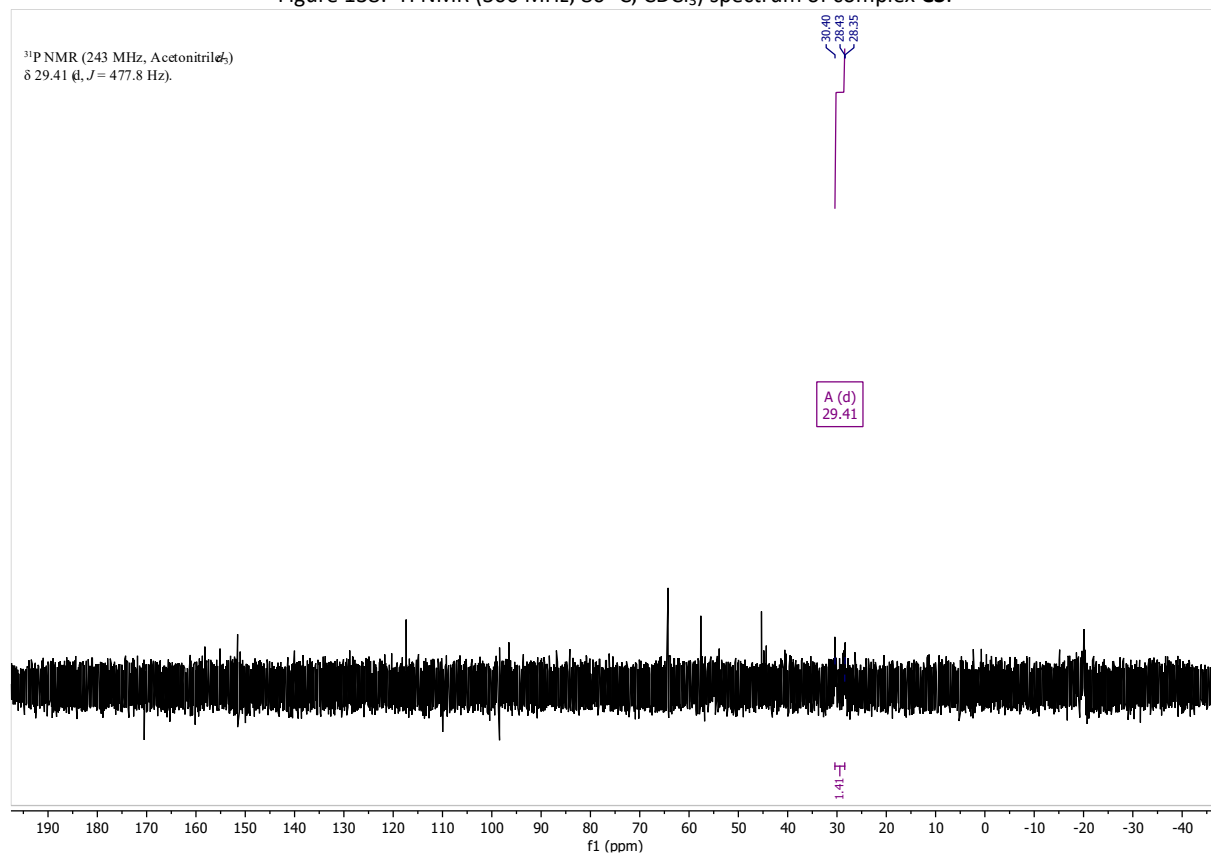


Figure 139: ³¹P NMR (121 MHz, 80 °C, CDCl₃) spectrum of complex **C3**.

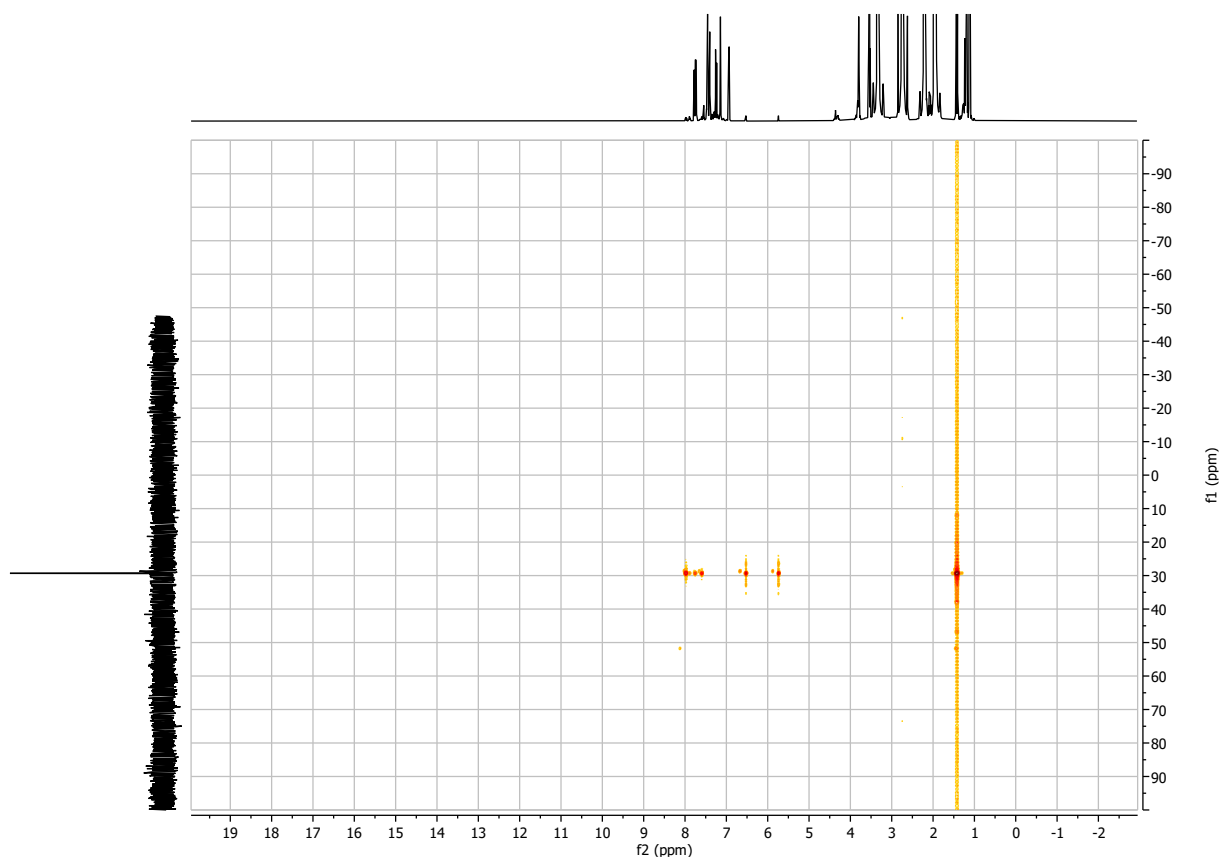


Figure 140: ^{31}P - ^1H HMBC (80 °C, CDCl_3) spectrum of complex **C3**

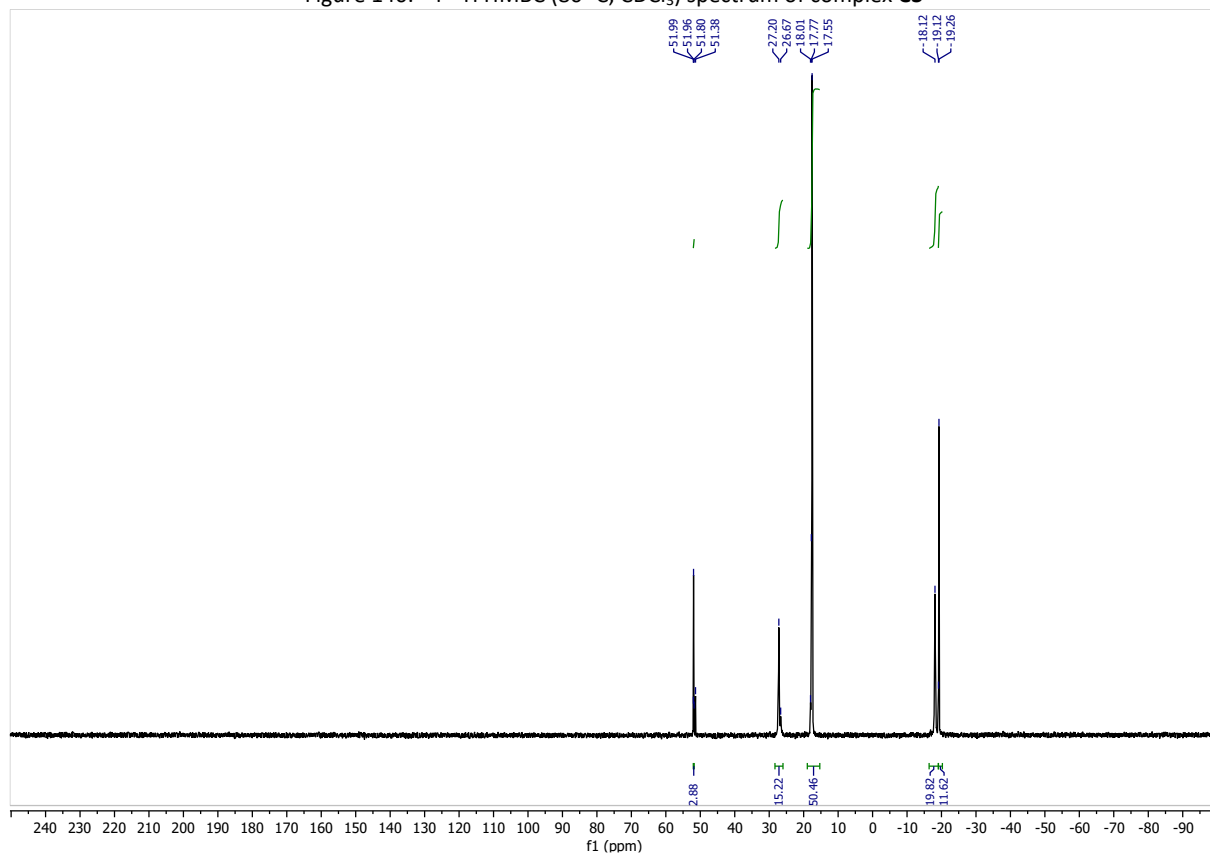


Figure 141: ^{31}P NMR (121 MHz, 80 °C, CDCl_3) spectrum of complex **C5**.

Appendix

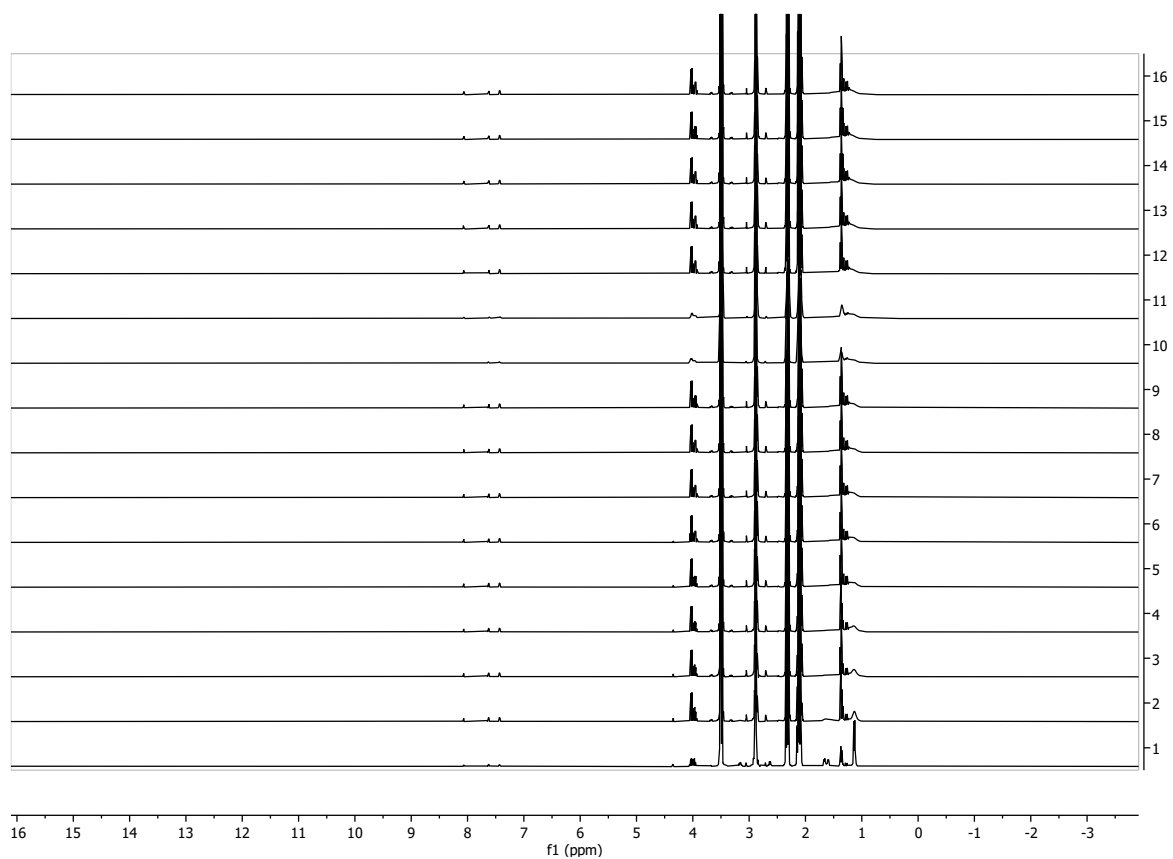


Figure 142: Time resolved ^1H -NMR of the bis(dibenzylidenacetone)palladium and JohnPhos in N-methylpyrrolidone cross-coupling of triethoxysilane and 2-bromothiophene. The reaction mixture was kept at 80 °C for 15 h, with spectrum -1 starting at 0 h and recording subsequent spectra once per hour.

Appendix

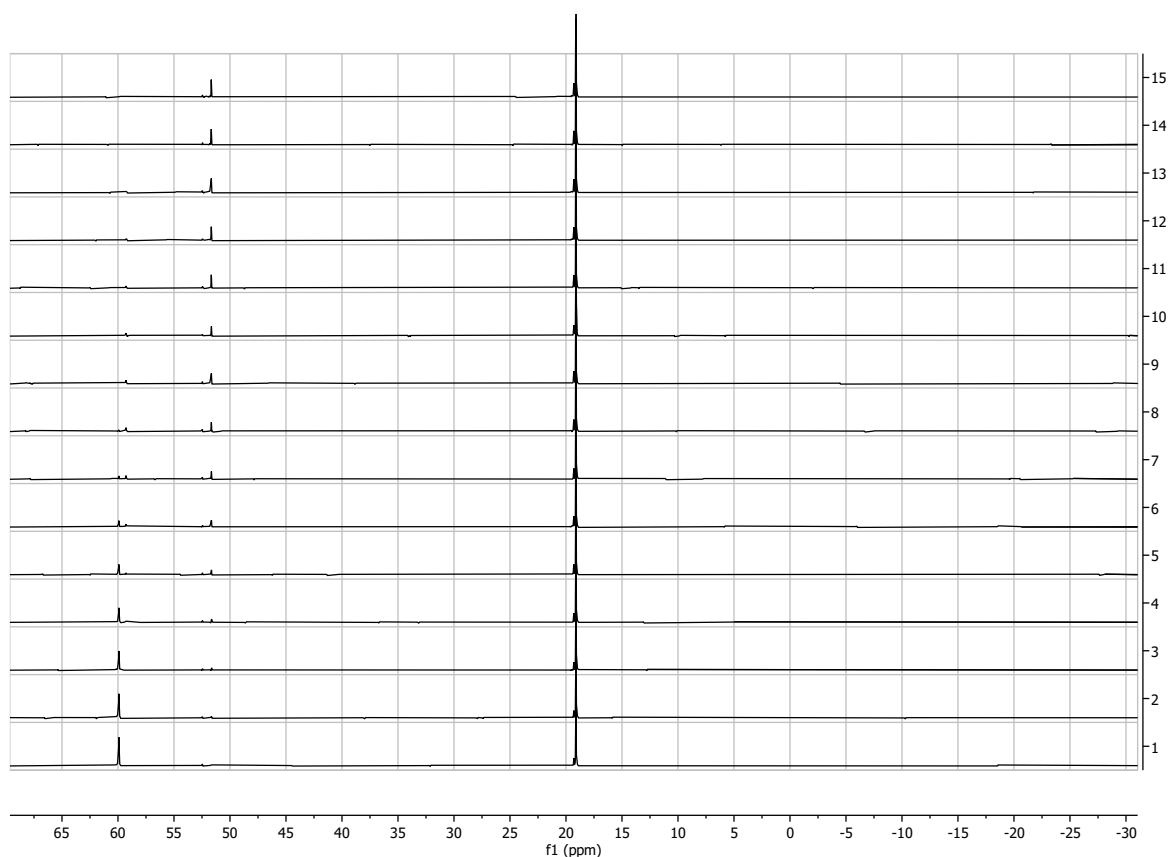


Figure 143: Time resolved ^{31}P -NMR of the bis(dibenzylidenacetone)palladium and JohnPhos in N-methylpyrrolidone cross-coupling of triethoxysilane and 2-bromothiophene. The reaction mixture was kept at 80 °C for 15 h, with spectrum -1 starting at 0 h and recording subsequent spectra once per hour.

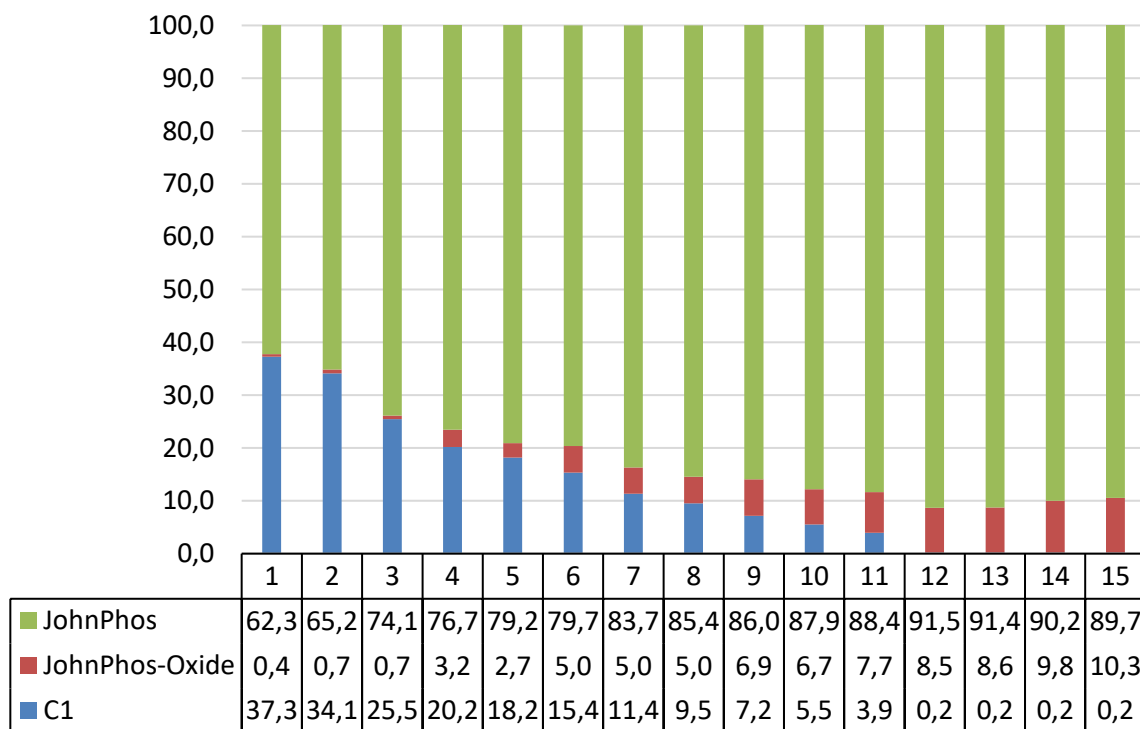


Figure 144: Visualization of time resolved ^{31}P -NMR of the bis(dibenzylidenacetone)palladium and JohnPhos in N-methylpyrrolidone cross-coupling of triethoxysilane and 2-bromothiophene. The reaction mixture was kept at 80 °C for 15 h, with spectrum -1 starting at 0 h and recording subsequent spectra once per hour.

Appendix

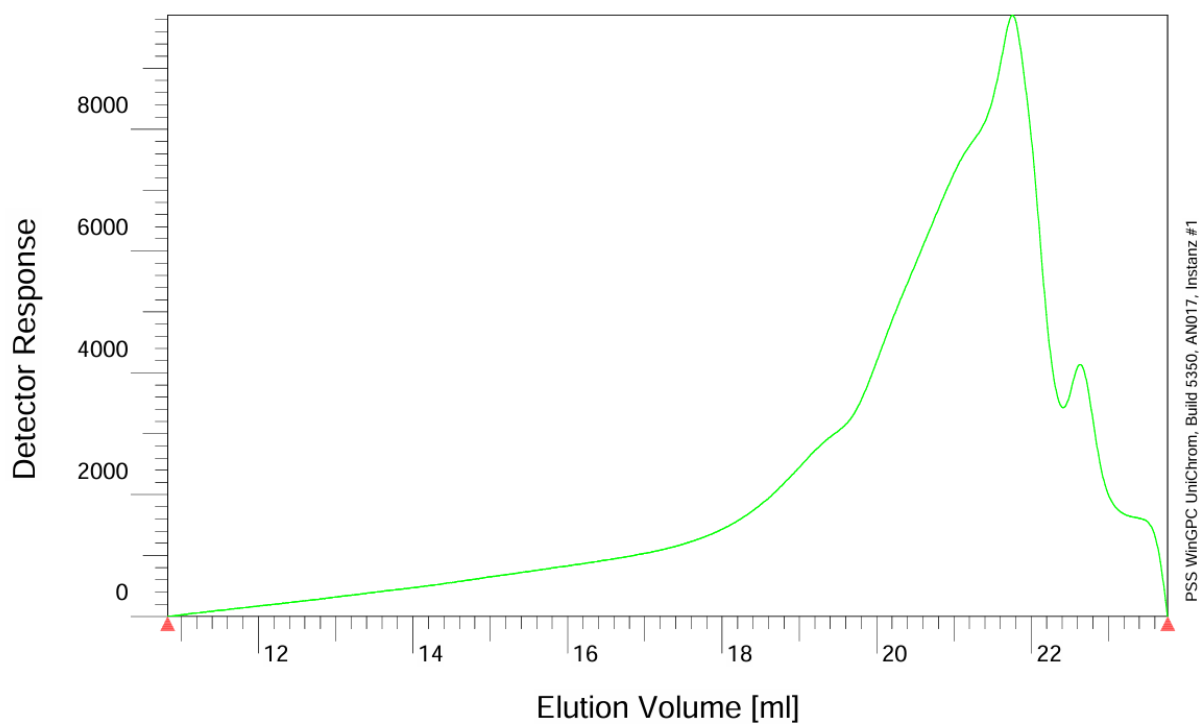


Figure 145: Raw GPC diagram for the conversion listed in Table 26, entry 1 showing the elution volume plotted against the relative refractive index detector response.

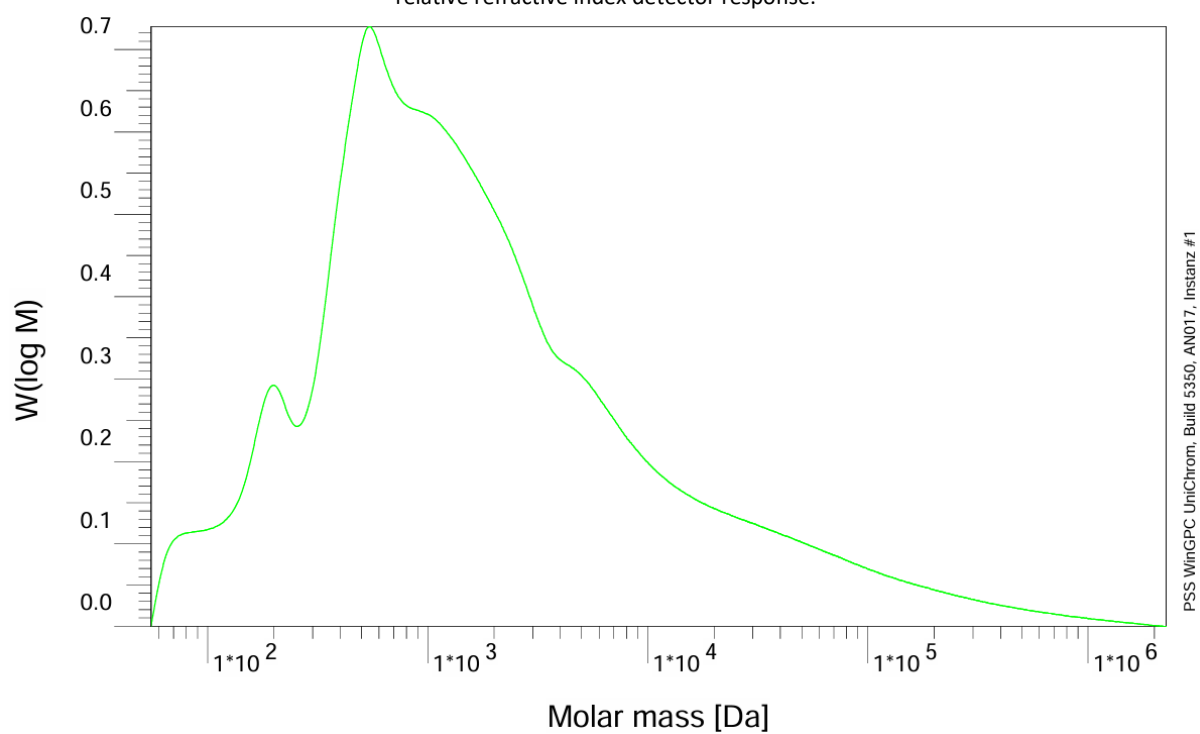


Figure 146: GPC diagram extracted from Figure 145 using a polystyrene-based calibration.

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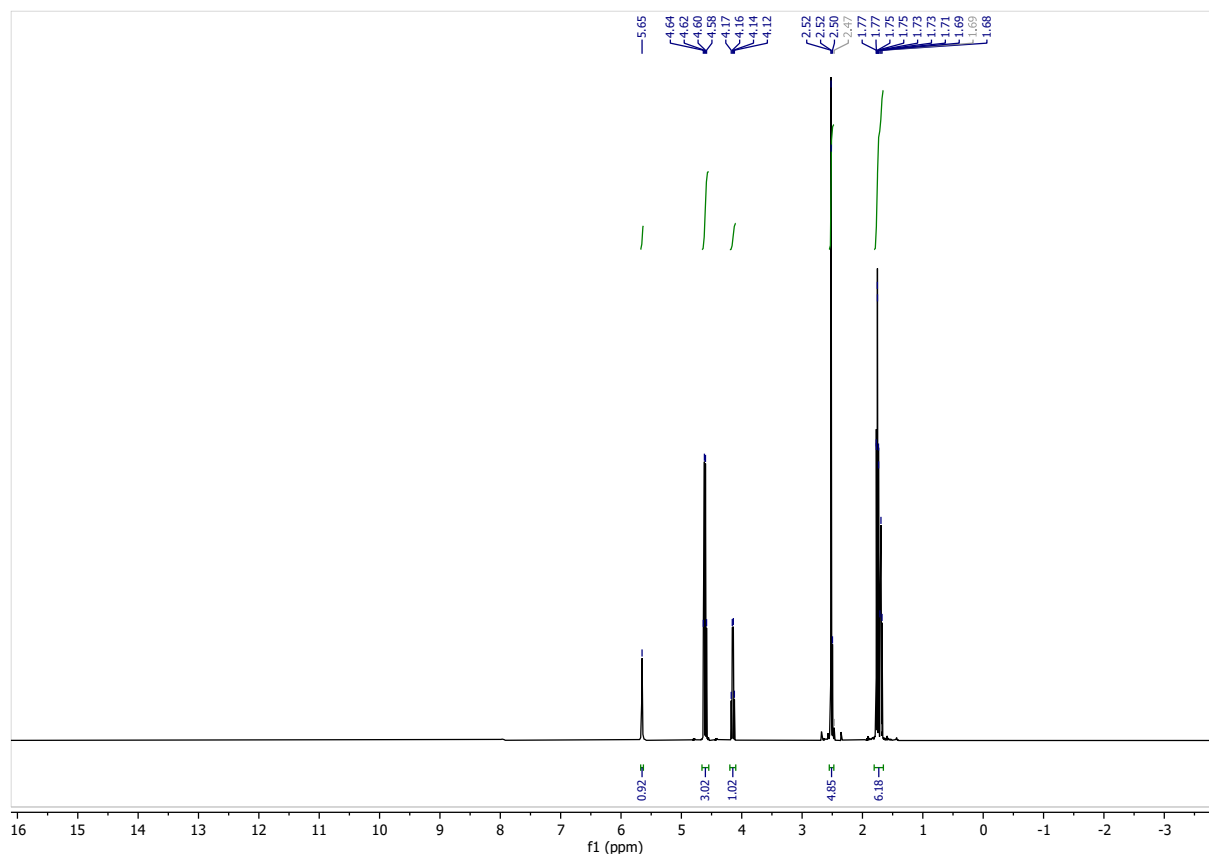


Figure 147: Exemplary ^1H NMR (300 MHz, CDCl_3) spectrum of conversion listed in Table 26, entry 1.

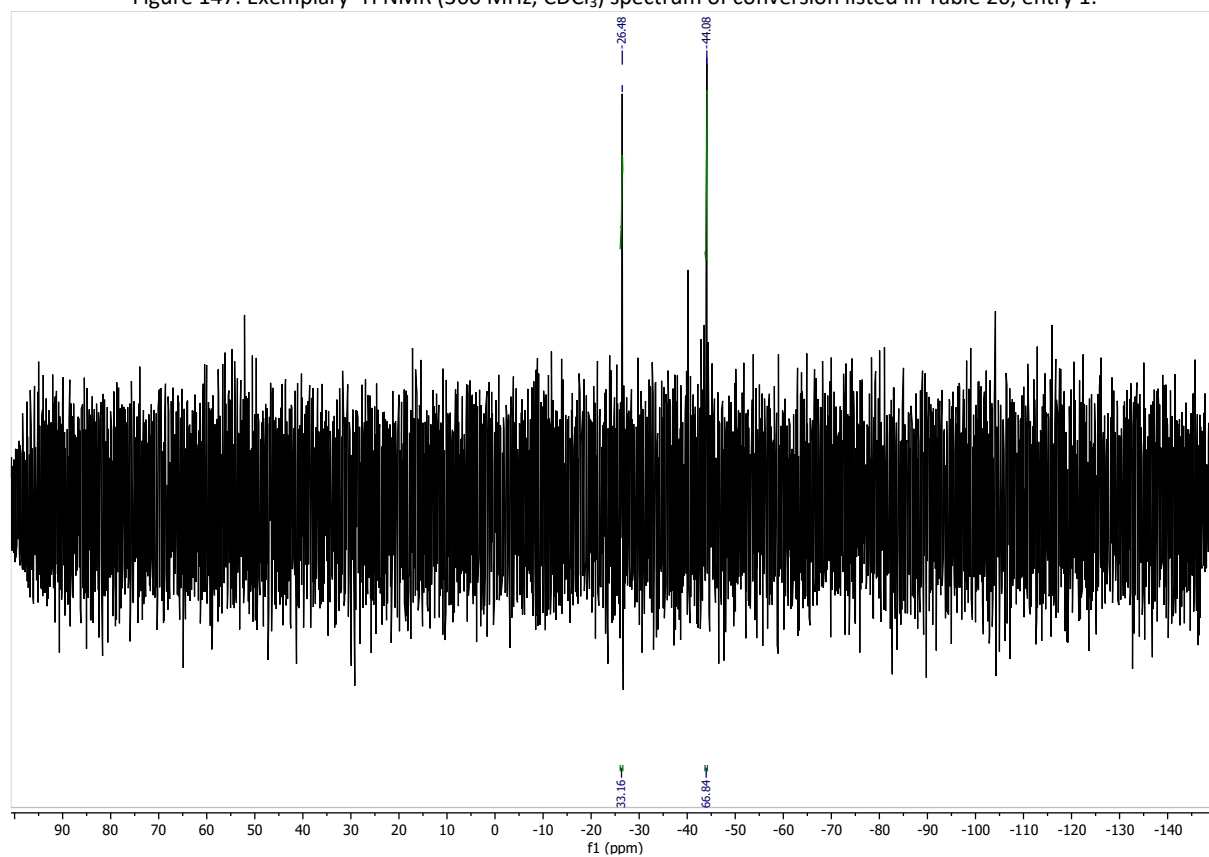


Figure 148: Exemplary ^{29}Si NMR (60 MHz, CDCl_3) spectrum of conversion listed in Table 26, entry 1.

Appendix

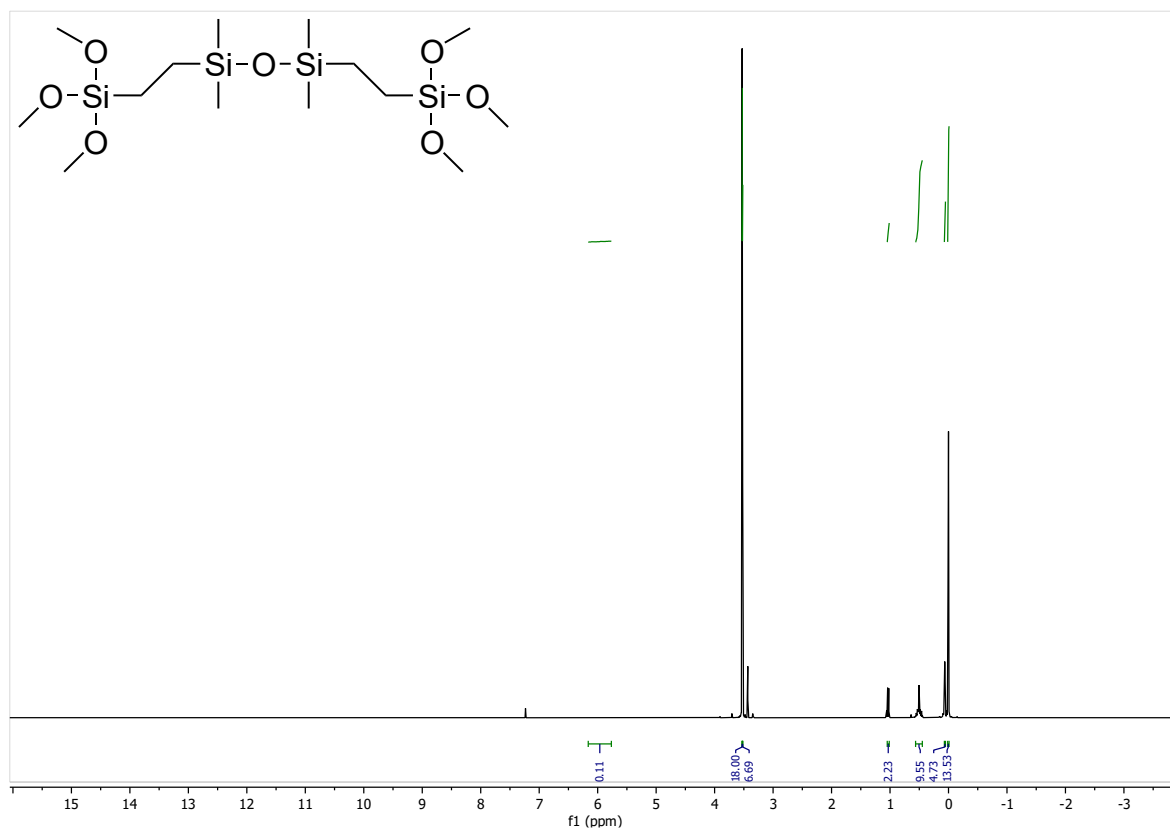


Figure 149: ¹H NMR (300 MHz, CDCl₃) spectrum of 3,3,11,11-tetramethoxy-6,6,8,8-tetramethyl-2,7,12-trioxa-3,6,8,11-tetrasilatridecane.

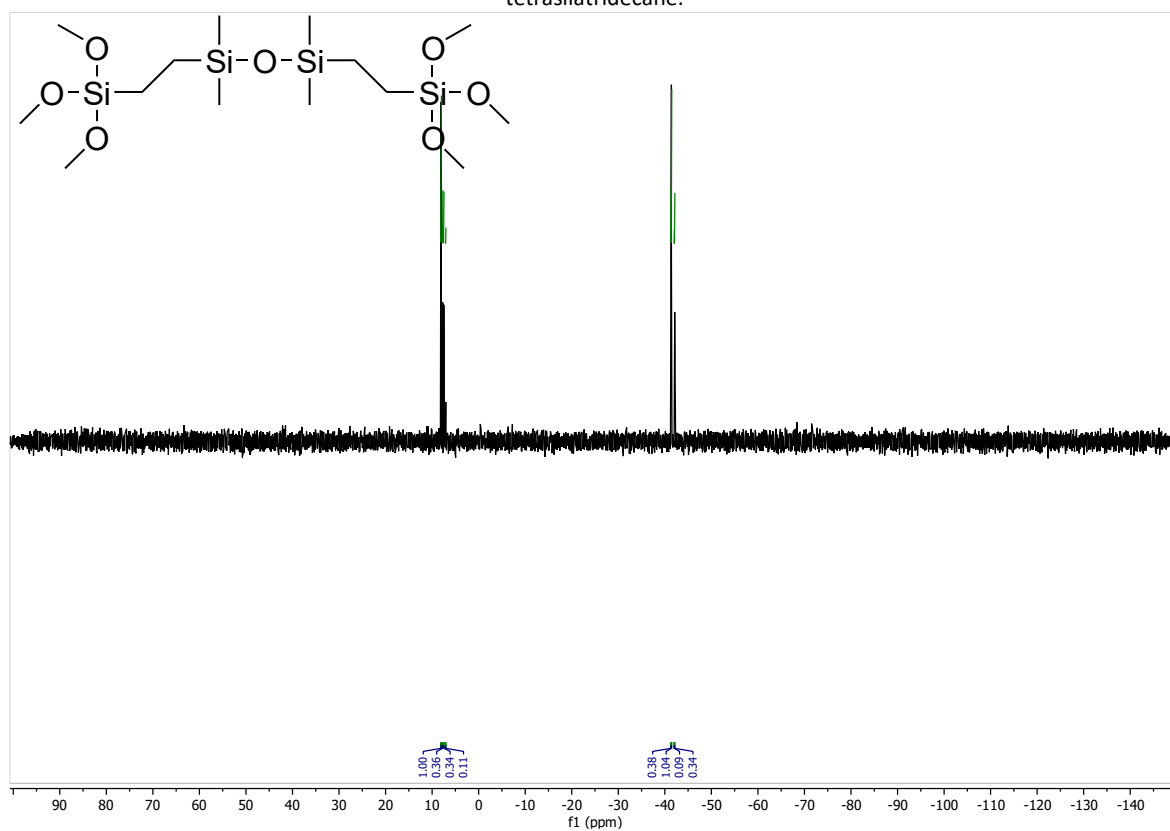


Figure 150: ²⁹Si NMR (60 MHz, CDCl₃) spectrum of 3,3,11,11-tetramethoxy-6,6,8,8-tetramethyl-2,7,12-trioxa-3,6,8,11-tetrasilatridecane.

Appendix

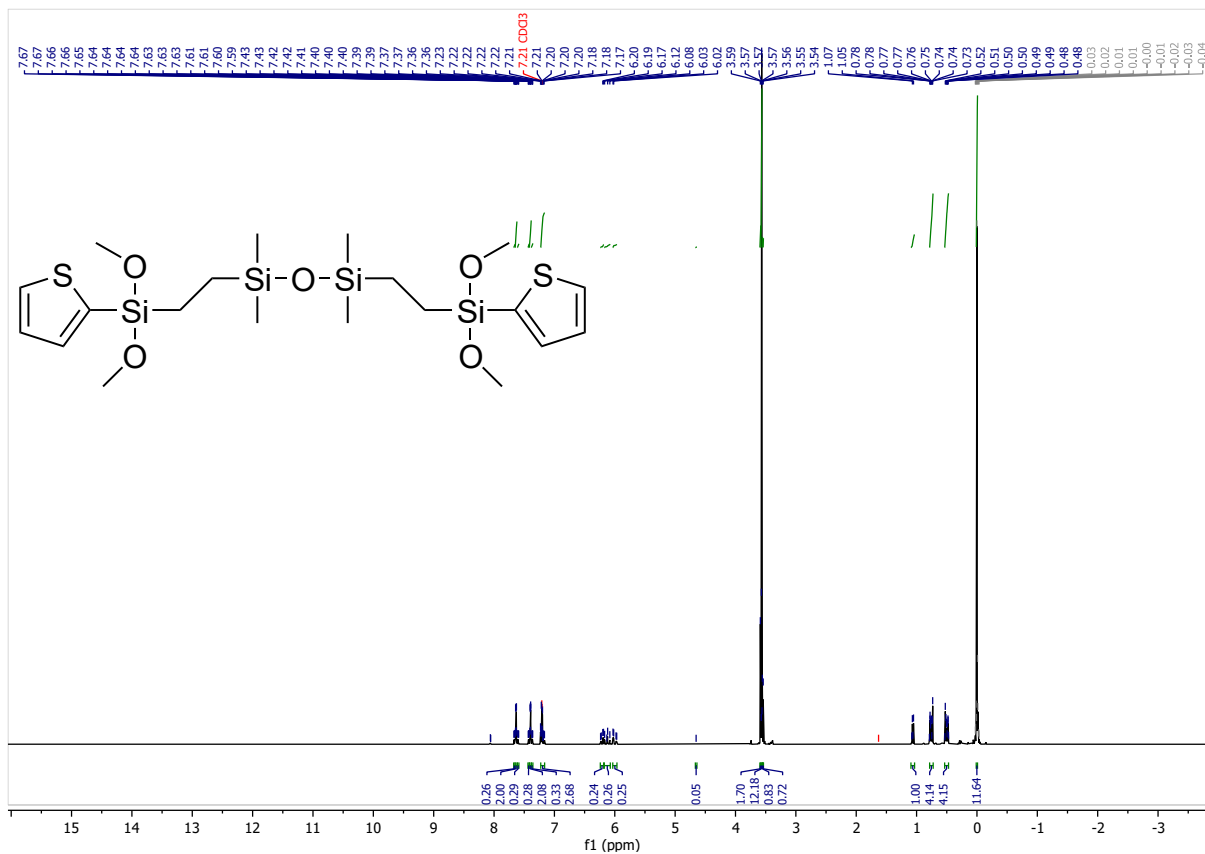


Figure 151: ^1H NMR (300 MHz, CDCl_3) spectrum of 3,11-dimethoxy-6,6,8,8-tetramethyl-3,11-di(thiophen-2-yl)-2,7,12-trioxaspiro[3,6,8,11-tetrasila]tridecane.

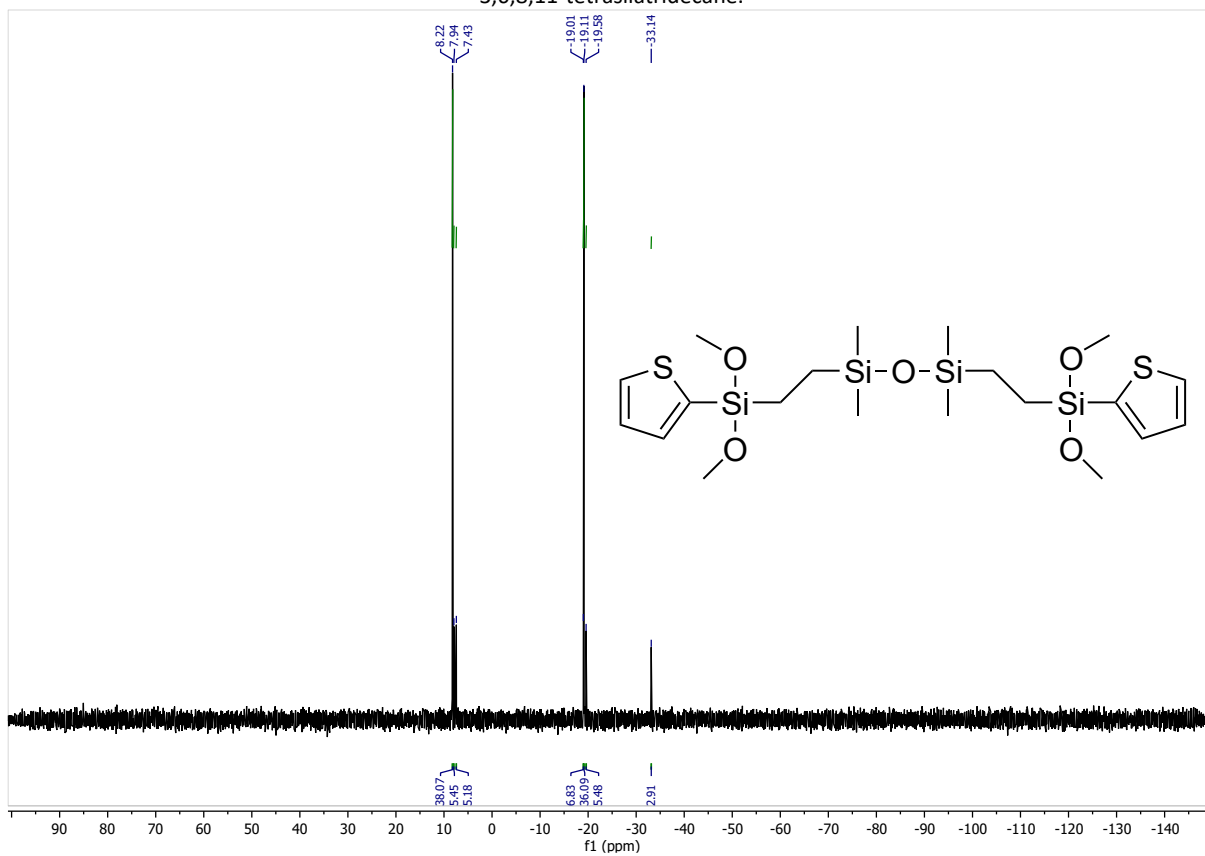


Figure 152: ^{29}Si NMR (60 MHz, CDCl_3) spectrum of 3,11-dimethoxy-6,6,8,8-tetramethyl-3,11-di(thiophen-2-yl)-2,7,12-trioxatetrasilatridecane.

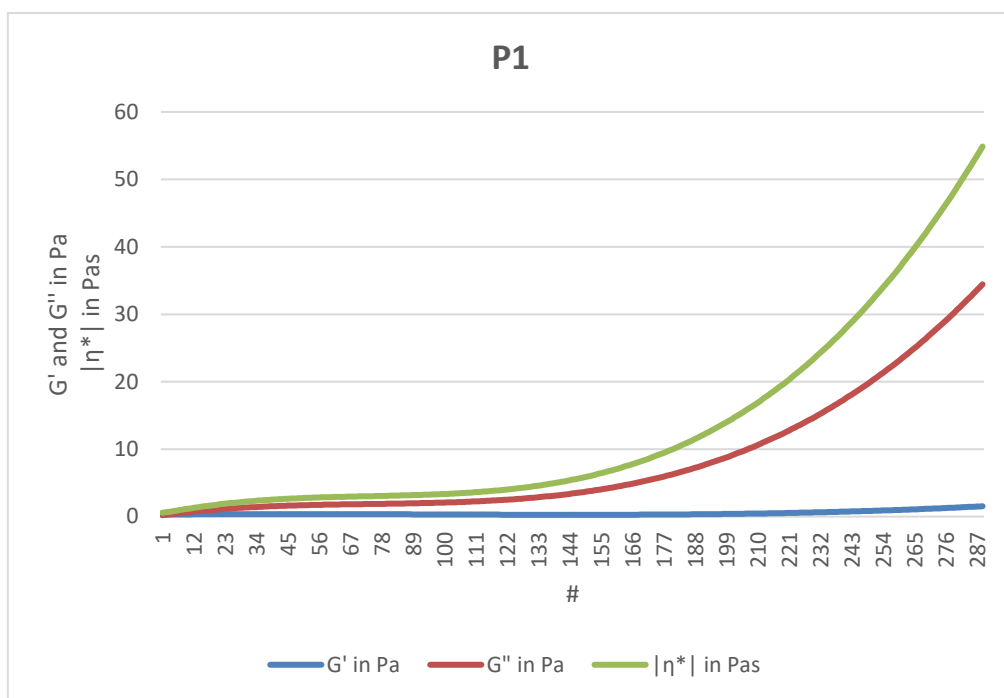


Figure 153: Time resolved rheology measurement of **P1** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions.

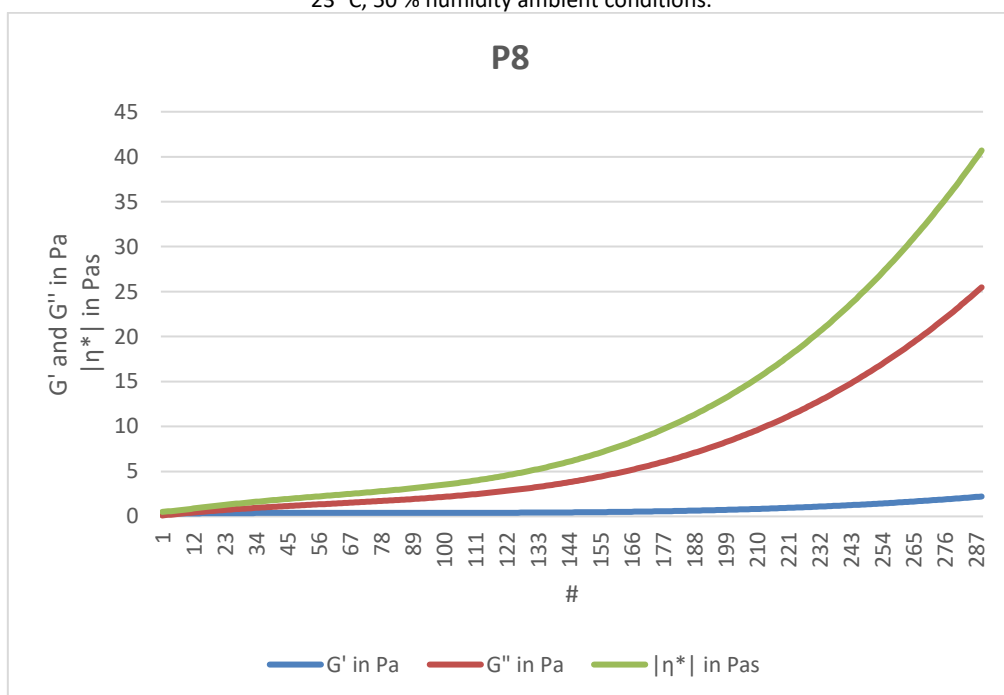


Figure 154: Time resolved rheology measurement of **P8** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions.

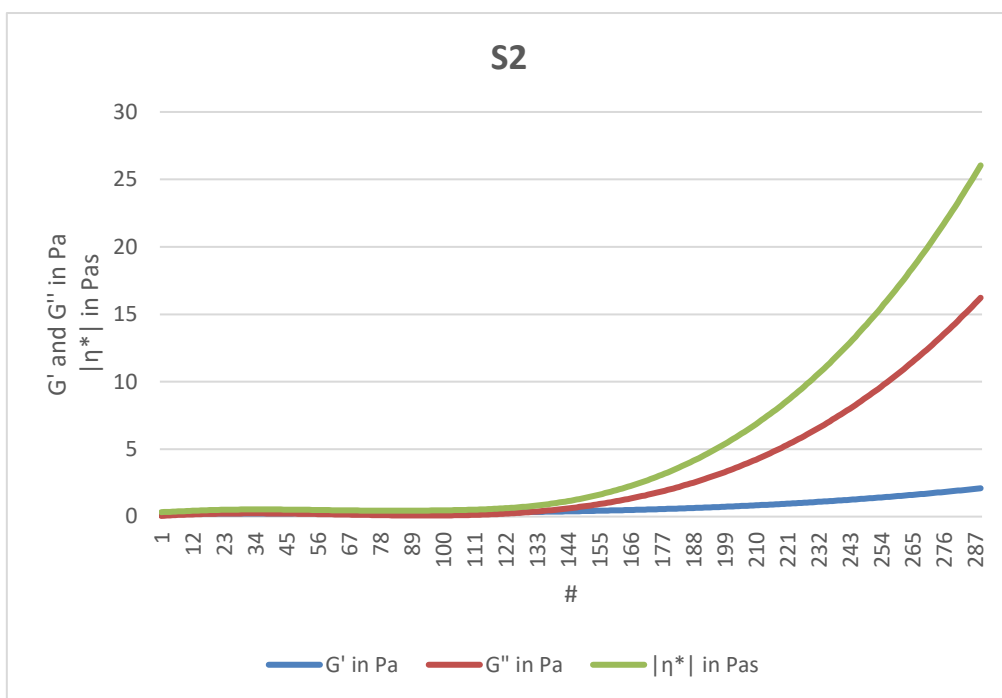


Figure 155: Time resolved rheology measurement of **S2** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions.

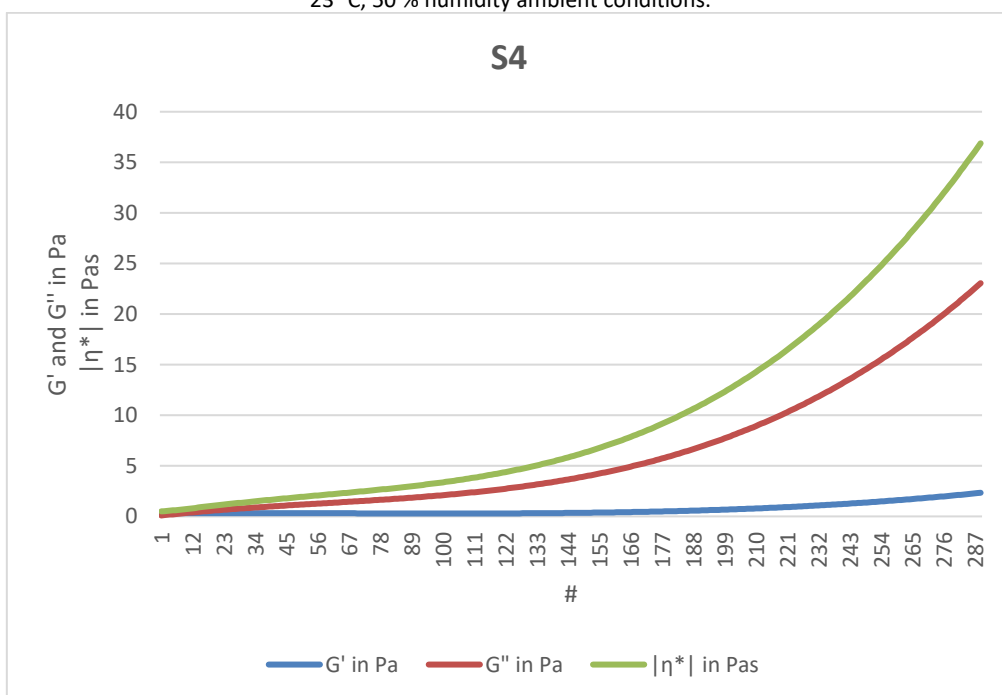


Figure 156: Time resolved rheology measurement of **S4** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions.

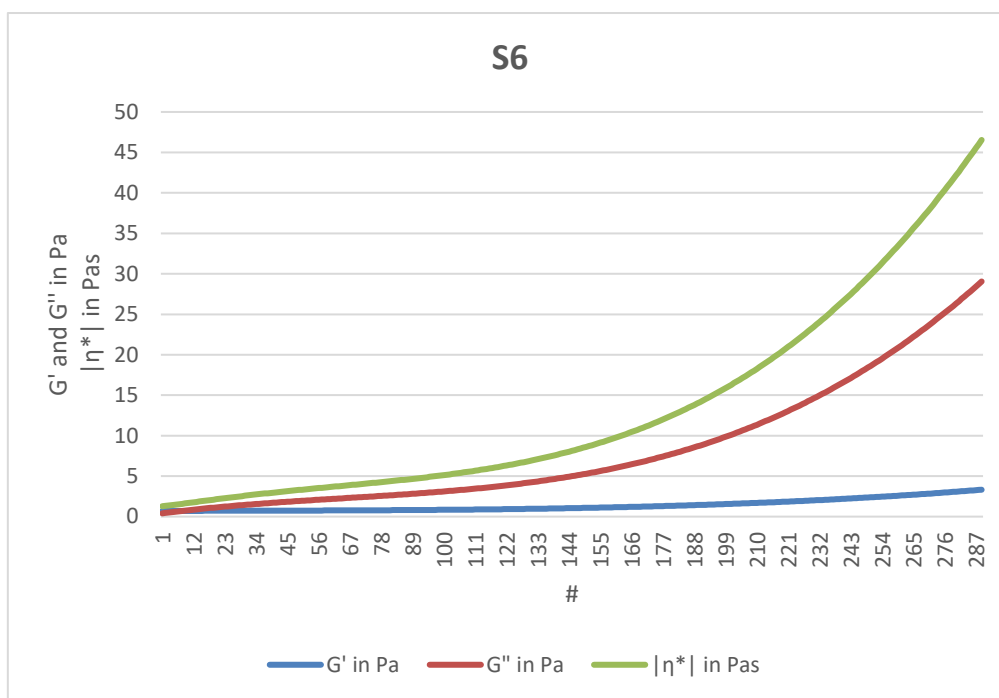


Figure 157: Time resolved rheology measurement of **S6** on a HAAKE RheoStress 1 with $\gamma = 150$, $f = 0.1$ Hz and $t = 24$ h and at 23 °C, 50 % humidity ambient conditions.

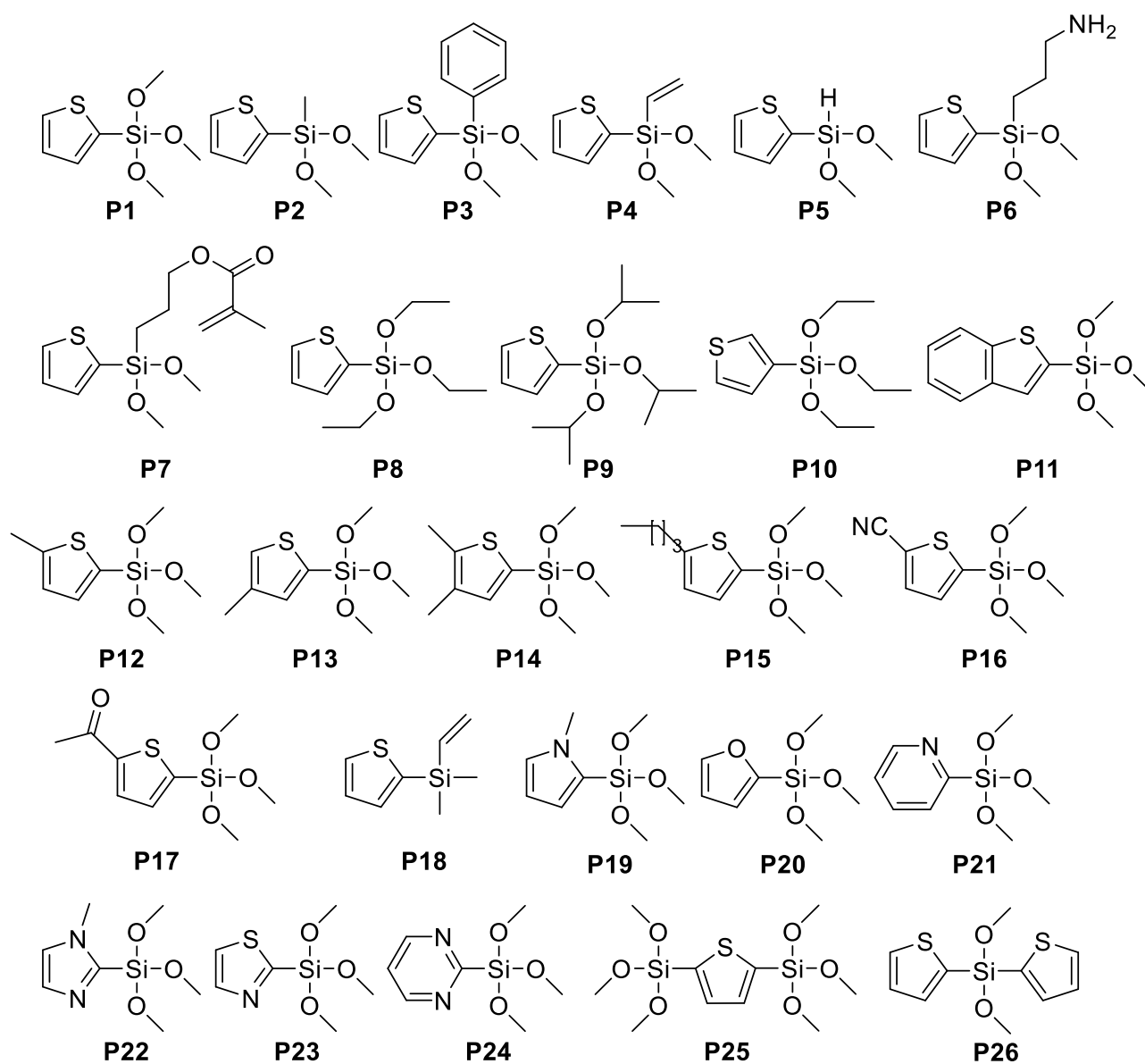


Figure 158: Overview of all abbreviated compounds in this work denoted with P.

Appendix

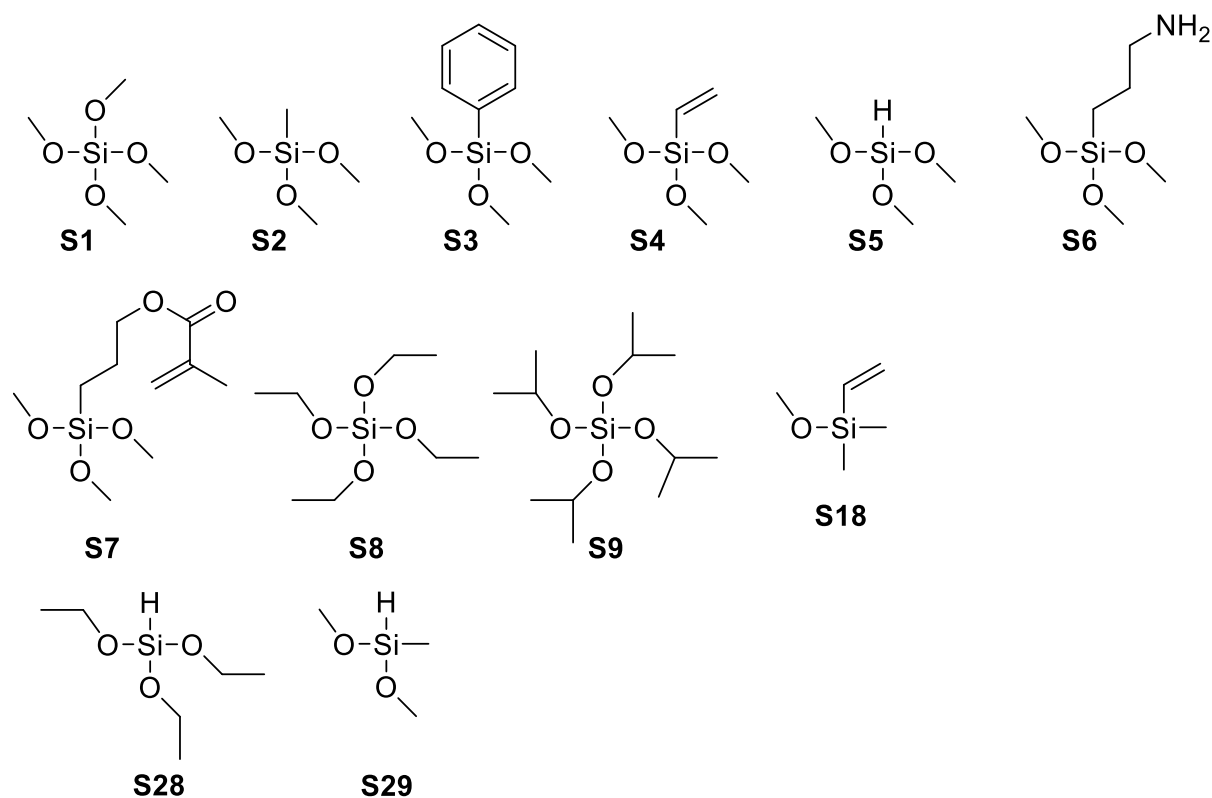


Figure 159: Overview of all abbreviated compounds in this work denoted with **S**.

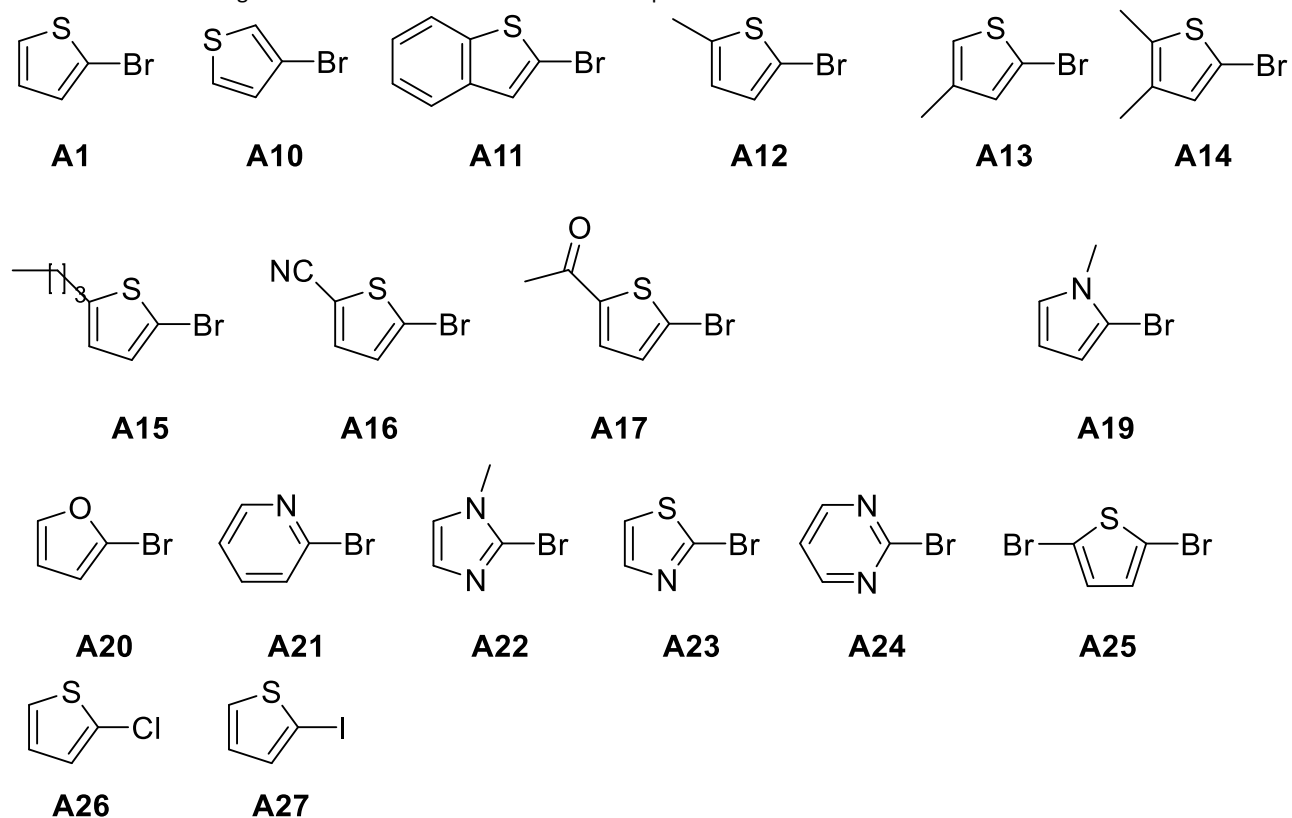
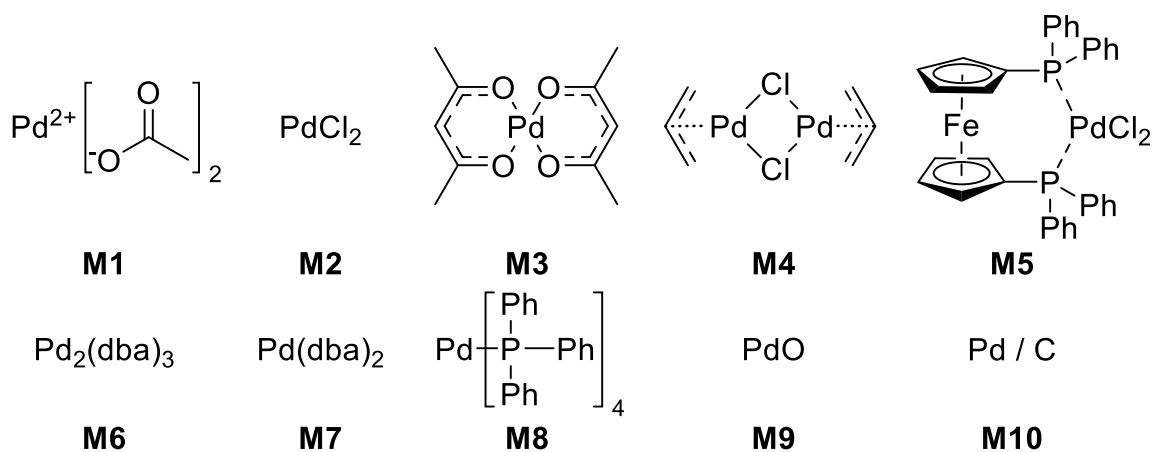
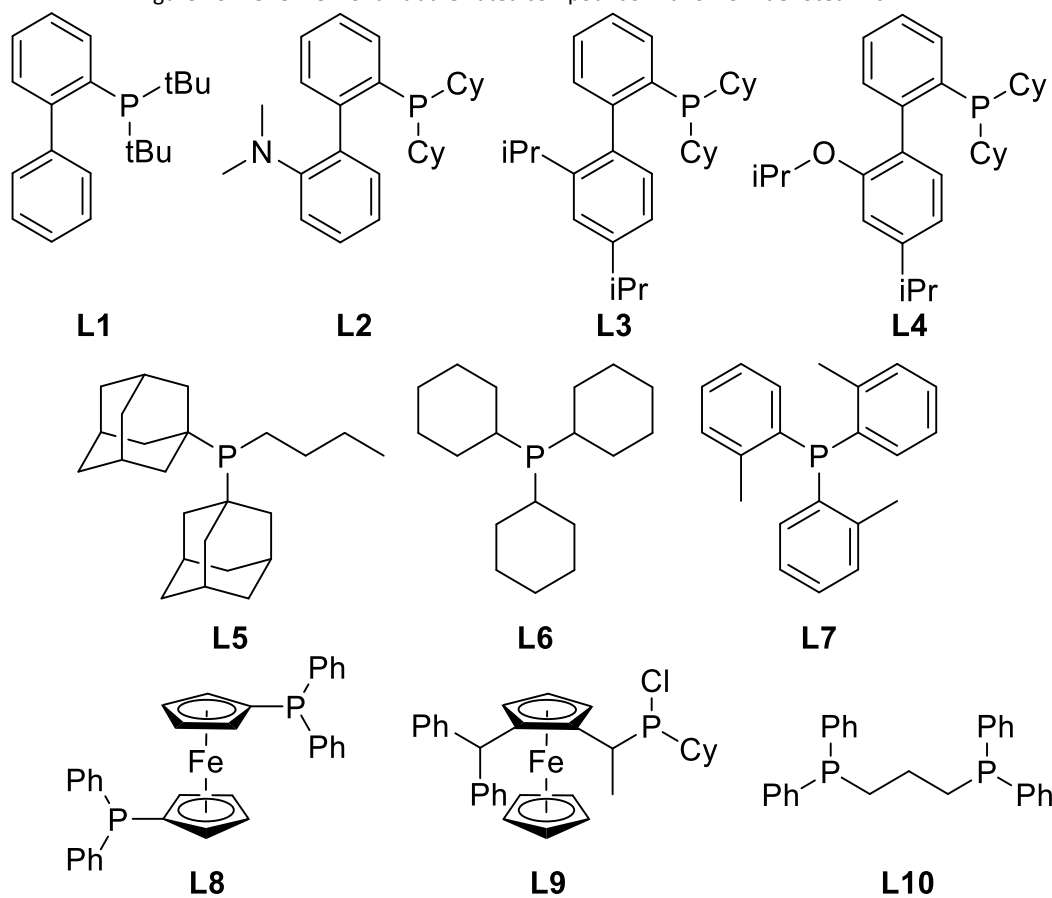


Figure 160: Overview of all abbreviated compounds in this work denoted with **A**.

Figure 161: Overview of all abbreviated compounds in this work denoted with **M**.Figure 162: Overview of all abbreviated compounds in this work denoted with **L**.

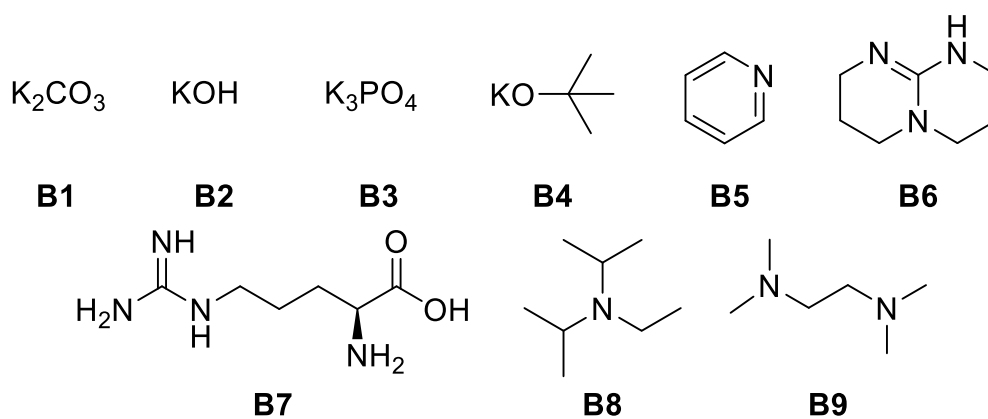


Figure 163: Overview of all abbreviated compounds in this work denoted with **B**.

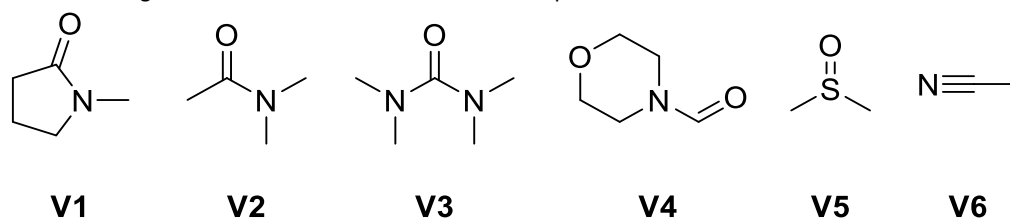


Figure 164: Overview of all abbreviated compounds in this work denoted with **V**.

A5 Curriculum Vitae

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- 02/2018 – 04/2020 **Leibniz-Institut für Katalyse e.V.**
Wissenschaftliche Hilfskraft
- Unterstützung bei wissenschaftlichen Fragestellungen
- 06/2017 – 12/2017 **Henkel AG & Co. KGaA**
Werksstudent
- Anfertigung Bachelorarbeit

Ausbildung

- 05/2020 – 07/2025 **Universität Rostock**
Promotionsstudium
- 04/2019 – 07/2019 **University College Cork**
Forschungsaufenthalt bei PD Dr. Peter Byrne
- 04/2018 – 07/2019 **Universität Rostock**

Abschluss: Master of Science Chemie

Master-Arbeit: Design and Synthesis of Novel Sulphur Based α -Silanes for Polymer End-Capping and Cross-Linking Applications

10/2014 – 12/2017

Heinrich-Heine-Universität Düsseldorf

Abschluss: Bachelor of Science Chemie

Bachelor-Arbeit: Design and Synthesis of novel functionalized silicone Polymers for elastic adhesives and sealant applications

Kenntnisse und Fähigkeiten

Sprachkenntnisse Deutsch: C2

Englisch: C1

EDV-Kenntnisse MS Office 365

Wissenschaftliche Datenbanken

Spezial-Software: MestreNova, Chemdraw, Topspin, Gaussian 16

Python

09/2021 „Project Management for Academics“ Graduiertenakademie Uni Rostock

09/2021 „Mehr als die Summe der Teile – Erfolg im Team“ Graduiertenakademie Uni Rostock

11/2021 „Führungskompetenzen“ Graduiertenakademie Uni Rostock