Chapter 2

Synthesis of para-disubstituted diphenylsilanes and fragments thereof; crystal structure of sulfonyl-acceptor compounds

2.1 Introduction

The synthesis of donor-acceptor-substituted diphenylsilanes has first been reported by Mignani et. al. [1]. They mainly focussed on silanylene-bridged diphenyl compounds with mesomeric acceptors, such as the dicyano- and tricyanovinyl-group. They have studied the effect of chain length [1a], electron-donor group [1b, c] and the number of phenyl-groups connected to the silicon-bridge [1d] on the nonlinear optical efficiency of these compounds. Our aim is to obtain materials which are transparent in the visible, while having a large nonlinearity. To improve the nonlinearity-transparency trade-off, we have synthesized disilanylene-bridged DσA-compounds with a structure similar to those of Mignani, but with strongly inductive electron-attracting groups such as the trifluoromethyl (CF₃), perfluorobutylsulfonyl (SO₂C₄F₉) and phenylsulfonyl (SO₂Ph) acceptors and with various donors. Fluorinated sulfonyl acceptors have been shown to improve the nonlinearity-transparency trade-off compared to that of a nitro acceptor when used in π-conjugated stilbenes and benzenes [2]. This is due to it’s more inductive character, which is quantitatively given by its Hammett constant [3, Chapter3]. However, the electron-attracting capacity seems to be less effective with increasing π-conjugation length when compared to the more resonance-type acceptors like the nitro and dicyanovinyl groups. In order to see whether this is also the case for the σ-bridged donor-acceptor compounds and to investigate the chain length dependency of the nonlinear optical response, a series of oligosilanes with 1, 2, 4, and 6 silicon atoms in the intermediating chain and with the dimethylamino donor (Me₂N) and perfluorobutylsulfonyl acceptor has been synthesized. The general structure of the donor-acceptor-substituted diphenylsilanes (DσA-compounds) is:

\[
\begin{align*}
D & \quad \text{Me} \quad \text{Me}_n \\
\text{Si} & \quad \text{A} \\
\end{align*}
\]

D: Donor; A: Acceptor; n = 1, 2, 4, 6

To help us understand the electronic transitions in this class of molecules, we synthesized model compounds with a structure similar to that of the donor
and acceptor parts of the DσA-compound: Me₃SiPhD(A). Compounds with this structure have extensively been studied for their optical properties by Sakurai and Shizuka and the synthesis of some of these compounds has been reported by Mignani [1,b-c] and Kira [4, 5]. The synthesis of the diphenylsilanes and their fragment compounds will be described in the first part of this chapter.

In order to incorporate a DσA-compound in a polymer backbone as a (co)monomer, it has to be functionalized with reactive groups. Polyurethanes (linear as well as crosslinked) have been shown to be a promising class of transparent materials to serve as a matrix for NLO- chromophores [6]. Because a linear polyurethane is built up from alternating diol and diisocyanate monomers, we have synthesized a diol-functionalized NLO-molecule, consisting of a di(hydroxyethyl)amino donor, SO₂C₄F₉-acceptor and a disilanyl bridge.

In the second part of this chapter, a report on the crystal structure of two disilane compounds with an acceptor substituent that contains the sulfonyl group will be given [7]. To our knowledge, no crystal structures of sulfonyl-containing donor-acceptor molecules have previously been published. Our structural study has enabled us to establish the conformation of the molecules, which provides considerable help in the understanding and analysis of experimental data on (nonlinear) optical and spectroscopic properties. It also influences the approach that must be taken in theoretical calculations of such properties.

2.2 Results and discussion

2.2.1 Synthesis of DσA-compounds and fragments thereof

Synthesis of donor-acceptor-substituted diphenylsilanes

A series of donor-acceptor-disubstituted diphenylsilanes has been obtained with various combinations of the donors: H, F, MeO, MeS and Me₂N and the acceptors: H, F, Br, CF₃, CHO, CH=CN(CN)₂, SO₂Ph and SO₂C₄F₉.

The synthetic route of the direct synthesis of donor-acceptor substituted diphenylsilanes is presented in Scheme 1. Successive coupling of the Grignard reagents of the acceptor- and donor-substituted phenylbromides to the dichlorosalane results in the asymmetrically substituted diphenylsilane.
This is due to the preference of the Grignard reagent for the non-substituted dichlorosilane. The order in which the Grignard reagents are added can also be reversed, but the reactivity of the second silicon-chlorine bond becomes less when an electron-releasing donor group is already substituted at the other silicon-chain end. Compounds obtained by this route are white, crystalline materials.

In order to obtain higher yields, the introduction of a bromophenyl group can best be performed by using a phenyllithium reagent instead of a Grignard reagent, since the reaction of 1,4-dibromobenzene with magnesium gives also partly the di-Grignard reagent. The synthesis of the bromine-acceptor compounds is presented in Scheme 2 and applies also to longer oligosilanes. However, the selectivity for the reaction of the dichlorosilane with the bromophenyllithium reagent becomes less for longer silicon chains and also the symmetric di(bromophenyl)-substituted compound can be isolated when one equivalent of lithium reagent is added. This indicates that the electron redistribution through the silicon chain as a result of introducing one aromatic group is only short range. Evidence for this is given by $^1$H and $^{29}$Si NMR spectroscopy, which will be discussed in Chapter 3. Compounds with the bromine acceptor and dimethylamino donor have a white and crystalline
appearance, the one with the methylthio donor is a white paste and those with 
the methoxy and hydrogen donors are clear viscous liquids. Scheme 3 presents 
the synthetic route of the aldehyde (CHO) and dicyanovinyl (CH=C(CN)₂) 
acceptor compounds. This route is similar to that published by Mignani et. al [1] 
who have described the synthesis of the compounds with the donors Me₂N, 
MeO and F. The aldehyde-acceptor compounds have a white crystalline 
appearance; the dicyanovinyl-acceptor compounds are crystalline and slightly 
yellow-coloured except for the dimethylamino-donor one which has an almost 
orange colour.

![Scheme 3: Synthesis of aldehyde (CHO) and dicyanovinyl (CH=C(CN)₂) acceptor DσA- compounds.](image)

The synthesis of the sulfones is outlined in Scheme 4. Aromatic 
magnesium bromides are known to react with benzenesulfonyl fluorides to 
give diphenyl sulfones [8]. The sulfonyl-phenyl (SO₂Ph)-acceptor compound 
was synthesized in this way in good yield. Since electron-withdrawing 
substituents on the benzenesulfonyl fluoride were found to increase the 
reactivity towards the Grignard reagent, we expected perfluoroalkylsulfonyl 
fluorides to react in the same manner due to the electron-withdrawing fluorine 
atoms on the alkyl chain. Using an excess of sulfonyl fluoride (100-200%), the 
perfluorobutylsulfonyl-acceptor compounds containing the dimethylamino 
donor and with various chain lengths could be obtained as slightly yellow- 
coloured crystalline materials. The methylthio-, methoxy- and hydrogen-donor- 
containing analogues look like a white paste (MeS) and clear viscous liquids 
(MeO, H).
Scheme 4: Synthesis of sulfonyl-acceptor (SO$_2$Ph and SO$_2$C$_4$F$_9$) $D\sigma A$-compounds.

A major byproduct is formed during the reaction with one equivalent of perfluorobutylsulfonyl fluoride. This side-reaction is presented in Scheme 5 and applies to the synthesis of all perfluorobutylsulfonyl-acceptor compounds in Scheme 4. Some of these dimeric byproducts have been isolated as white crystalline materials. The perfluorobutylsulfonyl-acceptor compound can react with a second Grignard reagent to form a dimeric sulfonyl compound. This is due to the leaving group character of the perfluorobutyl group, although being somewhat less than that of fluorine. By using an excess of the perfluorobutylsulfonyl fluoride the amount of dimeric byproduct can be reduced. These compounds can be classified as so called $\Lambda$-shaped molecules which are formed by one acceptor group connecting two donor groups (D-A-D), resulting in two donor-acceptor moieties within the same molecule. Throughout this thesis, this type of compounds will be called

Scheme 5: Synthesis of ‘dimeric’ sulfonyl-acceptor $D\sigma A$-compounds
Figure 2.1. \( \Lambda \)-shaped ‘dimeric’ sulfonyl-acceptor compound (D-A-D).

as the SO\(_2\)dim-acceptor compound. The dipole moment is pointing from the acceptor to the center of the \( \Lambda \)-shape (Figure 2.1). This type of molecule is non-centrosymmetric and hence will exhibit nonlinear optical behaviour. Other types of \( \Lambda \)-shaped molecules have been reported by Barzoukas et al. who have found that these molecules tend to crystallize into a non-centrosymmetric space group, thus exhibiting second-harmonic activity [9]. Moylan et al. reported about rigid triphenyl-substituted azole derivatives with two donor and one acceptor substituent, showing an exceptional thermal and polar order stability when incorporated into a polyimide polymer matrix [10].

Synthesis of compounds with the structure \( \text{Me}_3\text{(5)}\text{Si}(2)\text{PhD}(A) \)

The synthesis of fragment compounds with either a donor or acceptor group substituted at the para-position of a pentamethyldisilanylphenyl or trimethylsilylphenyl moiety is performed by the same routes as presented in Schemes 1-5. We have obtained mono- and disilanyl compounds with the substituents: Me\(_2\)N, Br, CF\(_3\), CH=C(CN)\(_2\), SO\(_2\)C\(_4\)F\(_9\) and the dimeric compounds (SO\(_2\)dim) (Figure 2.2):

\[
\text{D} = \text{Me}_2\text{N}; \ A = \text{Br, CF}_3, \text{CH=C(CN)}_2, \text{SO}_2\text{C}_4\text{F}_9, \text{SO}_2\text{dim}
\]

Figure 2.2. Synthesized compounds with the general structure \( \text{Me}_3\text{(5)}\text{Si}(2)\text{PhD}(A) \).
Two more, \( \pi \)-conjugated, model compounds with a perfluorobutylsulfonyl acceptor group and without silicon have been synthesized by the same method as presented in Scheme 4 for comparison reasons:

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{SO}_2\text{C}_4\text{F}_9 \\
\text{Me}_2\text{N} & \quad \text{SO}_2\text{C}_4\text{F}_9
\end{align*}
\]

2.2.2 Diol-functionalization of a D\( \sigma \)A-compound

Since the Me\(_2\)N-group is a strong electron donor, we have used a diol-substituted diethylaminobenzene as the donor part of the functionalized D\( \sigma \)A-compound. As an acceptor was chosen the SO\(_2\)C\(_4\)F\(_9\)-group, because of the transparency and large ground-state dipole moments (see Chapter 3) of the compounds having this acceptor. The latter property is of great importance for the electric field aligning of the NLO-chromophores in a polymer matrix. The reaction conditions under which the D\( \sigma \)A-compounds have been synthesized are not suitable for reactants containing hydroxyl (alcohol) groups, since these groups are not inert towards Grignard and alkyl(aryl)lithium reagents. Therefore, the hydroxy groups have to be protected before the reaction and deprotected afterwards to regenerate the original functional group. Furthermore, the deprotection reaction has to be selective for the protecting group. The \( t \)-butyldimethylsilyl (TBDMS) group has been shown to be a very useful hydroxy-protecting agent [11]. The silyl-ether bond of the protected alcohol group is stable towards Grignard and butyllithium reagents and the TBDMS-group can easily be removed by, for instance, 80\% acetic acid and the fluoride ion in (n-butyl)\(_4\)NF [11, 12]. A major advantage of the TBDMS-group over the frequently used tetrahydropyranyl group [13] is that its derivatives are often nicely crystalline materials and thus easily to purified. The synthetic route to the diol-functionalized D\( \sigma \)A-compound is outlined in Scheme 6. The protection of the alcohol groups of compound \( B \) is performed in the presence of imidazole in DMF giving pure \( C \) in 80\% yield. The coupling with the chlorosilane was carried out by using the BuLi/TMEDA reagent of \( C \) yielding 50\% of \( D \) (a viscous oil). For the synthesis of the sulfonyl acceptor compound \( E \) the Grignard reagent of \( D \) is reacted with the perfluorobutylsulfonyl fluoride following the same
Synthesis of \( p \)-disubstituted diphenylsilanes and fragments thereof; crystal structure.

Scheme 6: Synthesis of a \( \text{para-}(\text{HOCH}_2\text{CH}_2)_2\text{N-donor-} \) and \( \text{SO}_2\text{C}_4\text{F}_9\text{-acceptor-} \) substituted diphenylsilane.

procedure as discussed earlier for the synthesis of compounds with this acceptor. The Grignard reagent of \( D \) is made by first preparing the
BuLi/TMEDA reagent, followed by reaction with MgBr₂Et₂O [14]. This conversion is necessary, because the Grignard reagent reacts more selectively with the fluoride group (instead of the perfluorobutyl group) of the sulfonyl compound than the lithium reagent does, resulting in a smaller yield of dimeric byproduct (see previous paragraph).

The last step, the removal of the protective group, is the most crucial one. Reactions of compound E with diluted hydrogen chloride (1%), acetic acid (20%) in THF/water and with tetra-n-butylammonium fluoride resulted in cleavage of the silicon-phenyl bond. This bond is sensitive to acids, particularly when an electron-donating substituent is present at the para-position, which is the case in compound E; the para-aromatic carbon therefore has an increased susceptibility towards protonation [15]. Compound F could be obtained by a reaction with concentrated HCl (18% in EtOH/H₂O) for no longer than one minute, directly followed by neutralization with an excess of sodium bicarbonate. During the acid reaction, the amino group is protonated giving the quaternary ammonium salt; this will reduce the reactivity of the para-carbon-silicon bond towards acid cleavage (the donor has become an acceptor) and selective cleavage of the silyl ether bond takes place. Compound F can be obtained in this way in acceptable yield (50%). The dimeric byproduct, always obtained in small yields, could also be deprotected in this way, resulting in a tetrahydroxyfunctional monomer; this compound can therefore be a good candidate for use as a crosslinking NLO-chromophore.

2.2.3 Crystal structure of two sulfonyl-acceptor containing DσA-compounds

The crystal structures of two disilane compounds with an acceptor that contains the sulfonyl group have been determined, which will be referred to in this paragraph as compounds (1) and (2), respectively [7].

Single crystals suitable for x-ray diffraction could be grown from both 1 and 2, which enabled us to find the molecular conformation in the solid state. Table 2.1 lists crystal data for 1 and 2, and selected molecular data are presented in Table 2.2. Views of the molecular structures and of the unit cells of both 1 and 2 can be found in Figures 2.2 through 2.5.

For compound 1 the space group was determined to be P2₁/c, from the systematic absences of h0l: l=2n and 0k0: k=2n.
The space group of 2 was determined to be P-1, since no systematic absences have been found. The unit cell contains two crystallographically independent molecules (2A, 2B) and their inverted counterparts. Their overall geometries are similar. In our discussion below we will quote average values of bond lengths and angles except where noted.

For compounds 1 and 2 the Si-Si bond length can be given as 2.340(5) Å. This is a common value for disilanes with small substituents [16,17]. The Si-Si bond length is found to stretch considerably, however, with multiple large substituents: 2.39 Å in dodecaphenylcyclohexasilane [17]; 2.59 Å in hexa-tert-butyldisilane [18]; 2.70 Å in hexa-tert-butyl-1,3-dimethyltrisilane [19]. A value of 2.34 Å was also found for two other DA-substituted diphenyldisilanes synthesized in our laboratory [20], which contained a fluoro and a trifluoromethyl acceptor group, respectively. According to the analysis by Mignani et al. [1c], the dicyanovinyl-acceptor compound shows a Si-Si bond length of 2.325(7) Å, which is only very little below the common value of 2.34 Å. In the DA-substituted diphenyldisilane compounds, the bond characteristics thus do not seem to be affected by the σ-conjugation that is supposed to occur in these molecules.

Our results reveal that the overall conformation of the molecules 1 and 2 is very similar and characteristic for the diphenyldisilanes investigated by x-rays so far. Each shows a trans-type arrangement of the central C-Si-Si-C bonds with the phenyl rings roughly perpendicular to the plane through these bonds. Deviations from perpendicularity are largest for compound 1 and amount to 14°. The tilt between the two phenyl rings is 18° for
Table 2.1. Crystallographic and experimental data for compounds 1 and 2:

(CH$_3$)$_2$N-Ph-(SiMe$_2$)$_2$-Ph-A

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<td>SO$_2$C$_4$F$_9$</td>
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<td>Formula</td>
<td>C$<em>{24}$H$</em>{31}$NSO$_2$Si$_2$</td>
<td>C$<em>{22}$H$</em>{26}$NSO$_2$F$_9$Si$_2$</td>
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<td>Formula weight</td>
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<td>Crystal system</td>
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<tr>
<td>Space group</td>
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</tr>
<tr>
<td>c (Å)</td>
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<td>15.898(1)</td>
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</tr>
<tr>
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<td>94.31(1)</td>
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<tr>
<td>γ (°)</td>
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<td>4</td>
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<td>$D_{\text{calc}}$ (g/cm$^3$)</td>
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<td>F(000)</td>
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<td>1224</td>
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<td>+h, ±k, ±l</td>
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<td>R(F)</td>
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<td>0.083</td>
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<tr>
<td>R$_{w}$(F) ($w=1$)</td>
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<td>0.089</td>
</tr>
<tr>
<td>residual ρ (e/Å$^3$)</td>
<td>0.35</td>
<td>0.58</td>
</tr>
<tr>
<td>max shift Δ/σ (final cycle)</td>
<td>0.38</td>
<td>0.08</td>
</tr>
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</table>

compound 1 and 14° for compound 2. The C-Si-Si-C backbone is slightly twisted as shown by the torsional angles in Table 2.2; the two molecules in the cell of 2 have opposite twist. Our own quantum-chemical calculations show the trans-type configuration to be the most favourable one for high values of the first hyperpolarizability $\beta$.

The dimethylamino donor group is only slightly pyramidal in these molecules, the sum of the C-N-C bond angles summing up to 358°. This is an
indication of strong conjugation of the nitrogen lone-pair electrons with the π-system of the phenyl ring, which changes the hybridization from sp$^3$ to almost sp$^2$. Accordingly, in compound 2, the bonds between nitrogen and the ring carbon are approx. 0.1 Å shorter than the nitrogen-methyl bonds (average values: 1.37(1) Å vs. 1.46(3) Å), and the C1-N-C2 angle is only 116°. In this respect, there appear to be small distinctions between 1 and 2: In 1 the bond length difference is 0.07 Å and all three C-N-C angles are 119.5°.

In 2 the Si-C bond to the donor ring is ca 0.04 Å shorter than the Si-C bond to the acceptor ring (1.86 Å vs. 1.90 Å); in 1 this difference is only 0.01 Å but probably significant.

As regards the acceptor groups, the configuration on the sulfur atom deserves attention. In 2, the bond between sulfur and the carbon C19 in the perfluoroalkyl tail is 0.14 Å longer than the sulfur-to-ring (S-C16) bond: 1.88 Å vs. 1.74 Å. This finding is in line with the results for various compounds with (multiple) trifluoromethylsulfonyl groups attached to a phenyl ring: 1.84 vs. 1.72 Å [21a]; 1.85 vs. 1.71 Å [21b]. The perfluoroalkyl tail of 2 has a
strong electron-withdrawing character and causes C19 to bear a positive charge, which lengthens the bond to the sulfur atom which is also positively charged by the oxygen-sulfur polarization. In compound 1 sulfur is found to be symmetrically substituted: both C-S bonds are equal and relatively short, 1.77 Å. Differences in the electron density distribution around the sulfur atoms in 2 with respect to 1 are also reflected in a slight shortening of the S-O bonds (from 1.442 to 1.425 Å), an increase in the O-S-O angle from 120 to 122°, and a similar accompanying decrease in the C-S-C angle to 102° (average values for 2). This suggests that the perfluoroalkyl tail induces a somewhat larger electron density in the S-O bonds.

A further remarkable feature of the perfluoroalkyl tail is its slightly helical nature, as is apparent from Figure 2.4. A helical backbone is also found in crystalline poly(tetrafluoroethylene) [22], but the conformation of short-chain \(n\)-perfluoroalkanes is less well established. Though the geometries of the two molecules in the cell of 2 are found to be very similar, the helical twists of the tails are opposite: one is left-handed, the other right-handed. This is reflected in the values of the torsional (dihedral) angles of the S-C-C-C-C backbone (S-C19...C22 in Table 2.2), which are around 170° but have a different sign for molecules 2A and 2B. Though on the average a helical character is preserved, the temperature factors of the acceptor tail atoms are
Synthesis of p-disubstituted diphenylsilanes and fragments thereof; crystal structure.

Figure 2.4. Molecular structure of compound 2, \((\text{CH}_3)_2\text{N-Ph-} (\text{SiMe}_2)_2\text{-Ph-SO}_2\text{-C}_4\text{F}_9\).

Figure 2.5. View of the unit cell of compound 2, \((\text{CH}_3)_2\text{N-Ph-} (\text{SiMe}_2)_2\text{-Ph-SO}_2\text{-C}_4\text{F}_9\), containing two crystallographically independent molecules (2A, 2B) and their inverted counterparts.
relatively large (up to a value of 13 Å\(^2\) for the carbons and 25 Å\(^2\) for the fluorines at the tail end) and indicate some configurational freedom. There is a slight indication, just outside the error limits, of quinoid character of the phenyl rings in the donor-to-acceptor path of compound 1. The ring C-C bonds parallel to the long axis are found to be 1.387(1) Å, whereas the other ring bonds yield 1.402(7) Å (standard deviations from averaging; each individual value has a σ of 0.004 Å). Although this effect will probably be more pronounced in 2 because of the presence of a stronger acceptor, the experimental uncertainty does not allow this conclusion to be drawn.

Table 2.2. Selected bond lengths, angles and torsional angles for compounds 1 and 2

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<th>Molecule</th>
<th>1</th>
<th>2A</th>
<th>2B</th>
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<tr>
<td>(a) Bond lengths (Å)</td>
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<tr>
<td>Si1-Si2</td>
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<td>2.339(4)</td>
<td>2.336(4)</td>
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<td>Si1-C6</td>
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<td>108.3(3)</td>
<td>107.6(3)</td>
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<td>Si1-Si2-C13</td>
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<td>106.1(3)</td>
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(c) Torsional angles (°)

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\(^a^C\) corresponds to C10 in compound 1 and to C9 in 2. \(^b^C\) corresponds to C12 in compound 1 and to C11 in 2. \(^c^O\) corresponds to O1 in compound 1 and to O2 in 2. \(^d^O\) corresponds to O2 in compound 1 and to O1 in 2. \(^e^O\) Some acceptor atoms referred to have the same label but are not at comparable positions in compounds 1 and 2.
2.3 Conclusions

The synthesis of a large series of donor-acceptor compounds and fragments thereof has been performed by Grignard-type reactions. The synthesis of the perfluorobutylsulfonyl-acceptor-containing compounds gives a major byproduct, a dimeric compound, of which the amount can be reduced by using an excess of sulfonyl fluoride. A diol-functionalized D\(\sigma\)A-compound has been obtained in a fairly good yield. The last step in the reaction route, the removal of the siloxane protective groups, is the most crucial one since the reaction conditions are very strict.

It has been shown that our diphenyldisilane based donor-acceptor compounds, in the molecular crystal, show several features that reflect the functionality of donor and acceptor, and that they have the trans-type conformation, which is favourable for NLO-behaviour.

2.4 Short-hand notation of D\(\sigma\)A-compounds and fragment molecules

Table 2.3 gives an overview of the short-hand notations of all synthesized D\(\sigma\)A- and fragment compounds. The notations for the D\(\sigma\)A-compounds can be understood as follows: first, the usual notation of the acceptor group is given, except for the dicyanovinyl group which is presented as (CN)\(_2\). The acceptor notation for the dimeric compounds is SO\(_2\)dim. Secondly, the short-hand notation of the donor is given. These are N (Me\(_2\)N), S (MeS), O (MeO), F (F) and H (H). Finally, the number of intermediating silicon atoms is given. An example is (CN)\(_2\)N\(_2\): 1-(4-(2,2-dicyanovinyl)phenyl)-2-(4-(dimethylamino)phenyl)-1,1,2,2-tetramethyldisilane. The notation of the fragment compounds is somewhat different: first, the trimethylsilyl and pentamethyldisilanyl groups are abbreviated as Si and Si\(_2\), respectively. Secondly, the notation of the donor or acceptor group is given which is the same as for the D\(\sigma\)A-compounds. An example is Si(CN)\(_2\): 4-(2,2-dicyanovinyl)trimethylsilylbenzene. The notations for perfluorobutylsulfonylbenzene and 4-(perfluorobutylsulfonyl)-dimethylaminobenzene are PhSO\(_2\)C\(_4\)F\(_9\) and NPhSO\(_2\)C\(_4\)F\(_9\), respectively. These notations will be used throughout this thesis, giving a clearer illustration of the molecule being discussed than a number notation would do.
Table 2.3. Short-hand notation of silanylene-bridged DσA-compounds and fragments.

![Diagram](attachment:diagram.png)

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2.5 Experimental

2.5.1 Synthesis

General procedures

All reactions were carried out under an atmosphere of dry argon or nitrogen using standard Schlenk techniques. The reactions were performed in an environment excluded from UV-light, by using 'yellow light'. Tetrahydrofuran (THF) was allowed to stand over 3 Å molecular sieves for at least 24 hours and was then distilled from potassium (K) under a nitrogen atmosphere. Diethyl ether (Et₂O) was subsequently distilled from P₂O₅ and LiAlH₄ under a N₂ atmosphere. Et₂O used for purification purposes was distilled from P₂O₅ only. Toluene was distilled from sodium (benzophenone) under a nitrogen atmosphere. Pentane and CH₂Cl₂ were distilled from P₂O₅ and CaH₂, respectively. DMF (Merck) was stored over 3 Å molecular sieves. Acetylchloride (Merck) was distilled from CaH₂ prior to use.

Hexamethyldisilane, bromobenzene, methanol, AlCl₃, PCl₅ (Merck); 4-fluorobromobenzene, 4-bromo-N,N-dimethylaniline, 4-bromothioanisole, 1,4-dibromobenzene, n-butyllithium/hexane, malononitrile (Janssen); 4-(trifluoromethyl)bromobenzene, 4-bromoanisole, benzenesulfonyl fluoride (Aldrich); perfluorobutylsulfonyl fluoride (PCR) and magnesium (turnings, Fluka) were used as received from their commercial sources. Trimethylsilyl chloride and dichlorodimethylsilane (Janssen) were distilled under a nitrogen atmosphere prior to use.

Column chromatography was performed with silicagel (230-400 mesh ASTM, Merck). Melting points are uncorrected. UV-Visible spectra were recorded on a SLM-Aminco 3000 Array spectrometer using spectral grade solvents (Uvasol, Merck). FTIR spectra (KBr-pellets) were taken on an Mattson Galaxy FT-IR spectrometer. The absorptions are denoted as vs (very strong), s (strong), m (medium), w (weak) and sh(shoulder). ¹H NMR (200 MHz) and ¹⁹F NMR (188.15 MHz) spectra were recorded on a Varian Gemini spectrometer; ¹³C NMR (75.42 MHz, APT, proton decoupled) and ²⁹Si NMR (59.59 MHz) spectra on a Varian (VXR 300) spectrometer. Chloroform-δ (¹H and ¹³C NMR) was used as an internal standard, using δ(CDCl₃) = 7.26 ppm and 76.91 ppm, respectively, as reference values. Trifluoroacetic acid, trichlorofluoromethane (¹⁹F NMR) and TMS (²⁹Si NMR) were used as external standards. All chemical shifts reported are given in ppm and were externally referenced to TMS (0 ppm) except for the ¹⁹F NMR chemical shifts which were referenced to CFCl₃ (0 ppm) and CF₃COOH (-77 ppm). Splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were obtained with a AEI MS9 mass spectrometer at the Department of Organic Chemistry of the University of Groningen. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen.
Synthesis of chlorosilanes

1,2-dichlorotetramethyldisilane (Cl-(SiMe2)2-Cl) and chloropentamethyldisilane (Me5Si2-Cl) were prepared according to a method reported by Sakurai et al. [23]. 1-chloro-2-phenyltetramethyldisilane (Ph-(SiMe2)2-Cl) was prepared from Cl-(SiMe2)2-Cl and phenylmagnesium bromide according to a procedure reported by Kumada et al. [24]. 1,4-diphenyloctamethyltetrasilane (Ph(SiMe2)4Ph) was prepared according to Kumada et al. [24] from Ph-(SiMe2)2-Cl in refluxing toluene using an excess sodium, instead of a potassium/sodium alloy, that was divided into small particles by a vibro-mixer. 1,4-dichlorooctamethyltetrasilane (Cl-(SiMe2)4-Cl) was prepared according to Sakurai et al. [23] from Ph(SiMe2)4Ph by bubbling dry hydrogen gas (made by dropping concentrated sulfuric acid to an excess sodium chloride) through the solution at 0 °C in the presence of a catalytic amount of AlCl3. 1,6-dichlorododecamethylhexasilane (Cl-(SiMe2)6-Cl) was prepared according to a procedure reported by Gilman and Inoue [25].

Grignard reagents

A general synthetic procedure is given for the Grignard reagents of bromobenzene and p-substituted bromobenzene (substituents: Me2N, MeS, MeO, F, CF3). A 1 M solution of the bromobenzene in freshly distilled THF was added dropwise to 1.1 eq of magnetically stirred Mg activated with a crystal of iodine. After the addition was completed the reaction mixture was refluxed for 2 h. The solution was decanted from the residual magnesium and the concentration was determined by acid-base titration except for p-dimethylaminophenylmagnesium bromide which was analysed by titration with a 1 M solution of tert-butanol in p-xylene using phenanthroline as an indicator. The Grignard reaction of p-(trifluoromethyl)bromobenzene was carried out in diethyl ether because the reagent is unstable in refluxing THF.

Synthesis of compounds with the structure DPh-(SiMe2)n-PhA

1-phenyl-2-(4-dimethylaminophenyl)-1,1,2,2-tetramethyldisilane (HN2)

To a magnetically stirred solution of 5.8 g (31.2 mmol) 1,2-dichlorotetramethyldisilane in 25 ml THF, 1 eq. of dimethylaminophenylmagnesium bromide in THF was added dropwise. During the addition the reaction mixture was kept at 0 °C. After the reaction mixture was stirred for 16 hours at room temperature 1 eq. of phenylmagnesium bromide in THF was added dropwise to the cooled solution. The reaction mixture was stirred for 16 hours at room temperature, then concentrated and diethyl ether (100 ml) was added. The solution was filtered and washed three times with water (200 ml). The organic layer was dried over MgSO4 and the solvent was removed under vacuum by evaporation. The resulting white solid was purified by column chromatography with 1:1 pentane/dichloromethane (v/v) as eluent. 3.9 g (40%) of white crystals were obtained (mp 57-58 °C). 1H NMR: δ 0.28 (s, 6H, (CH3)2-N-C6H4-Si(CH3)2-), 0.33 (s, 6H, C6H5Si(CH3)2-), 2.96 (s, 6H,
UV: cyclohexane 272 nm (ε=15400), acetonitrile 273 nm (ε=19500); mass spectrum: m/e 313 (M⁺).

Exact mass determination calcld. for C₁₈H₁₉Si₂N 313.168, found 313.169.

1-(4-fluorophenyl)-2-(4′-dimethylaminophenyl)-1,1,2,2,3,3,4,4-octamethyltetrasilane (FN2)

The reaction was carried out by the same procedure as was used for HN2. First p-fluorophenylmagnesium bromide was added then p-dimethylaminophenylmagnesium bromide. The crude product was purified by crystallization from diethyl ether (-20 °C). A white crystalline solid was obtained in 30% yield (mp 56-57 °C). 1H NMR: δ 0.27 (s, 6H, (CH₃)₂N-C₆H₄-Si(CH₃)₂-), 0.31 (s, 6H, F-C₆H₄-Si(CH₃)₂-), 2.95 (s, 6H, (CH₃)₂N-C₆H₄-), 6.70-7.29 (dd, 4H, (CH₃)₂N-C₆H₄-), 6.97-7.03 (dd, 2H, 3J_H=9.0 Hz), 7.32-7.37 (dd, 2H, 3J_H=6.4 Hz) (F-C₆H₄-); 13C NMR: δ -3.63 (Si(CH₃)₂), 40.22 ((CH₃)₂N), 112.0, 134.9 (CH), 123.3, 150.7 (C) ((CH₃)₂N-C₆H₄-), 115.7 (d, 13J_C=21 Hz), 135.4 (d, 13J_C=7 Hz) (CH), 163.5 (d, 13J_C=250 Hz), 134.8 (C) (F-C₆H₄-); 29Si NMR: δ -23.02 ((CH₃)₂N-C₆H₄-Si-), -21.75 (F-C₆H₄-Si(CH₃)₂-); 19F NMR: δ 113.9 (m); FTIR: 1107 v (Si-C₆H₄), 1241 ν (Si-C₆H₄), 1598,1585 v (C-C₆H₄) cm⁻¹; UV: cyclohexane 272 nm (ε=29300), acetonitrile 273 nm (ε=28000); mass spectrum: m/e 332 (M⁺). Exact mass determination calcld. for C₁₈H₁₉Si₂FN 331.159, found 331.160.

1-(4-fluorophenyl)-4-(4′-dimethylaminophenyl)-1,1,2,2,3,3,4,4-octamethyltetrasilane (FN4)

For the synthesis of FN4 the same procedure as for FN2 was used. Instead of 1,2-dichlorotetramethyldisilane, 1,4-dichlorooctamethyldisilane was used. A white solid was obtained in 30% yield (mp 45-46 °C). 1H NMR: δ 0.02,0.03 (s, 6H, -Si-Si(CH₃)₂-Si-), 0.29 (s, 6H, (CH₃)₂N-C₆H₄-Si(CH₃)₂-), 0.33 (s, 6H, F-C₆H₄-Si(CH₃)₂-), 2.95 (s, 6H, (CH₃)₂N), 6.71-7.28 (dd, 4H, (CH₃)₂N-C₆H₄-), 7.00-7.04 (dd, 2H, 3J_H=9.3 Hz), 7.37-7.39 (dd, 2H, 3J_H=6.0 Hz) (F-C₆H₄-); 13C NMR: δ -2.68 ((CH₃)₂N-C₆H₄-Si(CH₃)₂-), -2.82 (F-C₆H₄-Si(CH₃)₂-), -5.59, -5.67 (Si-Si(CH₃)₂-Si-), -40.23 ((CH₃)₂N-), 112.0, 137.7 (CH), 124.4, 150.6 (C) ((CH₃)₂N-C₆H₄-), 114.8 (d, 13J_C=19.5 Hz), 135.4 (d, 13J_C=7.3 Hz) (CH), 163.3 (d, 13J_C=247 Hz), 135.3 (C) (F-C₆H₄-); 29Si NMR: δ -18.97 ((CH₃)₂N-C₆H₄-Si(CH₃)₂-), -17.62 (F-C₆H₄-Si(CH₃)₂-), -44.6 (Si-Si(CH₃)₂-Si-); 19F NMR: δ 113.5 (m); FTIR: 1108 v (Si-C₆H₄), 1599,1608 v (C-C₆H₄) cm⁻¹; UV: cyclohexane 274 nm (ε=24800), acetonitrile 275 nm (ε=21900); mass spectrum: m/e 447 (M⁺).

1-(4-trifluoromethyl)phenyl-2-(4′-dimethylaminophenyl)-1,1,2,2-tetramethyldisilane (CF₃N2)

The same procedure as for the synthesis of FN2 was used, with p-trifluoromethylphenylmagnesium bromide instead of p-fluorophenylmagnesium bromide. The reaction mixture was refluxed for 16 hours before adding the p-dimethylaminophenylmagnesium bromide. The mixture was refluxed for another 16 hours and worked up as FN2. The product was
purified by column chromatography with 1:1 pentane/dichloromethane (v/v) as eluent. A white solid was obtained in 35% yield (mp 88 °C). 1H NMR: δ 0.27 (s, 6H, (CH3)2N-C6H4-Si(CH3)2-), 0.31 (s, 6H, F3C-C6H4-Si(CH3)2-), 2.95 (s, 6H, (CH3)2N-), 6.70-7.24 (dd, 4H, CH(4-H), F(6-H)), 7.53-7.49 (dd, 4H, F3C-C6H4-Si(CH3)2-). 13C NMR: δ -3.75 ((CH3)2N-C6H4-Si(CH3)2-), -4.01 (F3C-C6H4-Si(CH3)2-), -40.22 ((CH3)2N-), 112.0, 134.0 (CH), 122.8, 150.8 (C) ((CH3)2N-C6H4-), 124.0 (q, ^1JC=3.7 Hz), 134.9 (CH), 130.0 (q, ^3JC=32 Hz), 145.1 (C) (F3C-C6H4-), 124.3 (q, ^1JC=272 Hz) (CF3); 29Si NMR: δ -22.84 ((CH3)2N-C6H4-Si(CH3)2-), -21.20 (F3C-C6H4-Si(CH3)2-); 19F NMR: δ -63.0; FTIR: 1108 v (Si-CH3), 1243 v (Si-CH3), 1597 v (C-C), 2934 cm^-1; UV: cyclohexane 273 nm (ε=27500), acetonitrile 274 nm (ε=23800); mass spectrum: m/e 447 (M^+). Anal. calcd for C18H26S2F3N: C, 59.89; H, 6.88; N, 3.68; F, 14.96. Found: C, 59.31; H, 6.82; N, 3.58; F, 15.36.

1-(4-trifluoromethylphenyl)-2-(4'-methylthiophenyl)-1,1,2,2-tetramethylsilasilane (CF3S2)

The same procedure was used as for the synthesis of CF3N2. The crude red-coloured reaction product was distilled under vacuum at 0.3 mbar/104 °C and a clear liquid which becomes a white solid upon cooling was obtained. After column chromatography with 4:1 pentane/dichloromethane (v/v) as eluent, a white solid was obtained in 44% yield (mp 45-46 °C). 1H NMR: δ 0.31 (s, 6H, CH3S-C6H4-Si(CH3)2-), 0.35 (s, 6H, F3C-C6H4-Si(CH3)2-), 2.48 (s, 3H, CH3S-), 7.19-7.25 (dd, 4H, CH3S-C6H4-), 7.46-7.54 (dd, 4H, F3C-C6H4-), 13C NMR: δ -4.14 (CH3S-C6H4-Si(CH3)2-), -4.23 (F3C-C6H4-Si(CH3)2-), 15.2 (CH3S-), 125.5, 134.0 (CH), 134.0, 139.3 (C) (CH3S-C6H4-), 124.1 (q, ^1JC=3.7 Hz), 133.9 (CH), 130.3 (q, ^3JC=32 Hz), 144.3 (C) (F3C-C6H4-), 125.6 (q, ^1JC=270 Hz) (CF3); 29Si NMR: δ -21.78 (CH3S-C6H4-Si(CH3)2-), -21.05 (F3C-C6H4-Si(CH3)2-); 19F NMR: δ -62.9; FTIR: 1108 v (Si-CH3), 1240 v (Si-CH3), 1599, 1608 v (C-C), 2934 cm^-1; UV: cyclohexane 270.5 nm (ε=23600), acetonitrile 269 nm (ε=22000); mass spectrum: m/e 384 (M^+). Exact mass determination calcd. for C18H26S2F3N: 384.101, found 384.101; Anal. calcd for C18H26S2F3N: C, 56.28; H, 6.04; F, 14.84. Found: C, 55.56; H, 5.99; F, 15.00.

(4-bromophenyl)-(4'-(dimethylaminophenyl)phenyl)dimethylsilane (BrN1) [1a,c]

1,4-Dibromobenzene (9.72 g, 41.2 mmol) was dissolved in freshly distilled diethyl ether and cooled to -20 °C. Then 25.7 ml of 1.6 M n-butyllithium/hexane (41.2 mmol) was added at such a rate that the temperature did not exceed -10 °C. The solution was stirred for 30 minutes at -10 °C and was then added in portions of 10 ml to a cold (-15 °C) solution of 5.3 g (41.2 mmol) dichlorodimethylsilane in 10 ml diethyl ether. A white salt precipitated while stirring for 16 hours at room temperature. To this reaction mixture was added 1 equivalent of p-dimethylaminophenylmagnesium bromide in THF and the reaction mixture was stirred for another 16 hours. The solution was concentrated and 100 ml of diethyl ether was added. The organic layer was washed three times with 200 ml of water and was then dried over MgSO4. The solvent was removed by evaporation and the white solid obtained was distilled at reduced pressure (140 °C/0.2 mbar). 9.4 g of an almost pure white solid was obtained (68%).
Recrystallization from pentane (-20 °C) gave 7 g of pure white crystals (mp 58-59 °C). \(^1\)H NMR: \(\delta 0.52\) (s, 6H, Si(CH\(\text{3}\))\(\text{2}\)), 2.99 (s, 6H, (CH\(\text{3}\))\(\text{2}\)N-), 6.76-7.40 (dd, 4H, (CH\(\text{3}\))\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-), 7.41-7.49 (dd, 4H, Br-C\(\text{6}\)H\(\text{4}\)-); \(^{13}\)C NMR: \(\delta -2.24\) ([Si(CH\(\text{3}\))\(\text{2}\)], 39.51 ([CH\(\text{3}\)]\(\text{2}\)N-), 111.3, 134.6 (CH), 121.5, 150.5 (C) ([CH\(\text{3}\)]\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-), 130.2, 135.2 (CH), 123.0, 137.7 (C) (Br-C\(\text{6}\)H\(\text{4}\)-); \(^{29}\)Si NMR: \(\delta -8.43\); UV: cyclohexane 269 nm (\(\varepsilon=21400\)), acetonitrile 272 nm (\(\varepsilon=20000\)); mass spectrum: m/e 333 (M\(^+\)). Exact mass determination calcd. for C\(\text{16}\)H\(\text{20}\)SiBrN 333.055, found 333.055.

1-(4-bromophenyl)-2-chloro-1,1,2,2-tetramethyldisilane (BrPh-(SiMe)\(\text{2}\)-Cl) [1a,b]

To a suspension of 36.45 g (1.5 mol) magnesium in 20 ml dry diethylether was added a crystal of iodine and slowly a solution of 354 g (1.35 mol) 1,2-dichlorotetramethyldisilane in 200 ml of dry ether while keeping the temperature at 10-13 °C. The resulting Grignard reagent was added to 251.1 g (1.35 mol) 1,2-dichlorotetramethyldisilane in 200 ml of dry ether while keeping the temperature at 10-13 °C. The resulting mixture was stirred for 16 hours at room temperature. The resulting Grignard reagent was added to 251.1 g (1.35 mol) 1,2-dichlorotetramethyldisilane in 200 ml of dry ether while keeping the temperature at 10-13 °C. The resulting mixture was stirred for 16 hours at room temperature. The solution was decanted and the remaining salts were washed three times with 200 ml dry ether. After removal of the solvent at reduced pressure, the residu was fractionally distilled at reduced pressure to produce 210 g (45%) of a colourless oil (bp 102-104 °C). Exact mass determination calcd. for C\(\text{16}\)H\(\text{20}\)SiBrN 391.079, found 391.079.

1-(4-bromophenyl)-2-(4'-dimethylaminophenyl)-1,1,2,2-tetramethyldisilane (BrN2) [1a,b,c]

To a solution of 50 g (163 mmol) 1-(4-bromophenyl)-2-chloro-tetramethyldisilane in 100 ml dry THF was added 1 equivalent of 1 M p-dimethylaminophenylmagnesium bromide in THF at 0 °C. The solution was stirred for 16 hours at room temperature and was then concentrated. After this, 300 ml of dry diethyl ether was added and this mixture was washed three times with 300 ml water. The organic layer was separated and dried over MgSO\(_4\). The solvent was evaporated and a white creamy solid was obtained after distilling the product twice under reduced pressure (120 °C/0.01 mm Hg). Yield: 28 g (44%), mp 70-73 °C. \(^1\)H NMR: \(\delta 0.29\) (s, 6H, (CH\(\text{3}\))\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-Si(CH\(\text{3}\))\(\text{2}\)-), 0.32 (s, 6H, Br-C\(\text{6}\)H\(\text{4}\)-Si(CH\(\text{3}\))\(\text{2}\)-), 2.97 (s, 6H, (CH\(\text{3}\))\(\text{2}\)N-), 6.72-7.25 (dd, 4H, (CH\(\text{3}\))\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-), 7.26-7.45 (dd, 4H, Br-C\(\text{6}\)H\(\text{4}\)-); \(^{13}\)C NMR: \(\delta -3.68\) ([CH\(\text{3}\)]\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-Si(CH\(\text{3}\))\(\text{2}\)-), -3.86 (Br-C\(\text{6}\)H\(\text{4}\)-Si(CH\(\text{3}\))\(\text{2}\)-), 40.17 ([CH\(\text{3}\)]\(\text{2}\)N-), 112.0, 134.9 (CH), 123.0, 151.0 (C) ([CH\(\text{3}\)]\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-), 130.7, 135.5 (CH), 123.1, 138.6 (C) (Br-C\(\text{6}\)H\(\text{4}\)-); \(^{29}\)Si NMR: \(\delta -22.99\) ([CH\(\text{3}\)]\(\text{2}\)N-C\(\text{6}\)H\(\text{4}\)-Si(CH\(\text{3}\))\(\text{2}\)-), -21.43 (Br-C\(\text{6}\)H\(\text{4}\)-Si(CH\(\text{3}\))\(\text{2}\)-); UV: cyclohexane 236 nm (\(\varepsilon=30700\)), acetonitrile 235 nm (\(\varepsilon=17000\)), 274 nm (\(\varepsilon=29500\)); mass spectrum: m/e 391 (M\(^+\)). Exact mass determination calcd. for C\(\text{18}\)H\(\text{26}\)Si\(\text{2}\)BrN 391.079, found 391.079.

1-(4-bromophenyl)-4-(4'-dimethylaminophenyl)-1,1,2,3,3,4,4-octamethylditrisilane (BrN4)

First, 1-(4-bromophenyl)-4-chlorooctamethylditrisilane was prepared by the same procedure as used for the coupling of 1,4-dibromobenzene and 1,2-dichlorodisilane, now starting with 1,4-

48
dichlorooctamethyltetrasilane (24 g, 28.4 mmol). The mixture was refluxed for 16 hours and after cooling the precipitated salts were filtered off and washed with dry ether. The monochlorotetrasilane was used without further purification. The second step was carried out in the same way as for BrN2. The blue coloured oily residu was purified by column chromatography using 3:1 pentane/dichloromethane (v/v) and then 1:1 (v/v). 12.9 g (25.4 mmol, 32%) of a white solid was obtained (mp 40-42 °C). $^1$H NMR: δ 0.31 (s, 6H, (CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-), 0.04, 0.05 (s, 6H, Br-C$_6$H$_4$-Si(CH$_3$)$_2$-), 0.10, 0.11 (s, 6H, -Ph-Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), 0.07, 0.08 (s, 6H, -Ph-Si(CH$_3$)$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), 2.95 (s, 6H, (CH$_3$)$_2$N-), 6.72-7.29 (dd, 4H, ((CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-)), 7.27-7.45 (dd, 4H, Br-C$_6$H$_4$-); $^{13}$C NMR: δ -3.05 (Br-C$_6$H$_4$-Si(CH$_3$)$_2$-), -2.69 ((CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-), -5.71, -5.58 (-Ph-Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), 40.23 ((CH$_3$)$_2$N-), 112.04, 134.73 (CH), 122.9, 150.6 (C) ((CH$_3$)$_2$N-C$_6$H$_4$-), 130.7, 135.3 (CH), 122.9, 138.9 (C) (Br-C$_6$H$_4$-); $^{29}$Si NMR: δ -18.94 (CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-), -17.26 (Br-C$_6$H$_4$-Si(CH$_3$)$_2$-), -44.53, -44.62 (-Ph-Si(CH$_3$)$_2$Si(CH$_3$)$_2$-); UV: 273 nm (ε=30350), acetonitrile 274 nm (ε=21600); mass spectrum: m/e 507 (M$^+$). Exact mass determination calc'd. for C$_{22}$H$_{38}$Si$_4$BrN 507.127, found 507.127.

1-(4-bromophenyl)-6-(4’-dimethylaminophenyl)-1,1,2,2,3,3,4,4,5,5,6,6-dodecamethylhexasilane (BrN6)

The same procedure was used as for BrN1. 1,6-dichlorododecamethylhexasilane (9.15 g, 25.8 mmol) was used as starting material. The compound was purified by column chromatography with 3:2 pentane/dichloromethane (v/v) in quantities of about 1 g. The separation should be performed quickly because the compound can degrade on the column. Yield: 4.55 g, 37%. $^1$H NMR: δ 0.34 (s, 6H, (CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-), 0.37 (s, 6H, Br-C$_6$H$_4$-Si(CH$_3$)$_2$-), 0.10, 0.11 (s, 6H, -Ph-Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), 0.07, 0.08 (s, 6H, -Ph-Si(CH$_3$)$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), 2.95 (s, 6H, (CH$_3$)$_2$N-), 6.72-7.29 (dd, 4H, ((CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-)), 7.27-7.45 (dd, 4H, Br-C$_6$H$_4$-); $^{13}$C NMR: δ -2.62 ((CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-), -3.01 (Br-C$_6$H$_4$-Si(CH$_3$)$_2$-), -4.48 (Br-C$_6$H$_4$-Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), -5.29 (Br-C$_6$H$_4$-Si(CH$_3$)$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), -5.44 ((CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), 40.23 ((CH$_3$)$_2$N-), 112.04, 134.7 (CH), 122.95, 150.5 (C) ((CH$_3$)$_2$N-C$_6$H$_4$-), 130.7, 135.2 (CH), 122.95, 138.9 (C) (Br-C$_6$H$_4$-); $^{29}$Si NMR: δ -18.89 (CH$_3$)$_2$N-C$_6$H$_4$-Si(CH$_3$)$_2$-), -17.30 (Br-C$_6$H$_4$-Si(CH$_3$)$_2$-), -39.14, -39.06 (-C$_6$H$_4$-Si(CH$_3$)$_2$Si(CH$_3$)$_2$-), -43.31, -43.38 (-C$_6$H$_4$-Si(CH$_3$)$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_2$-); UV: 274.5 nm (ε=45890), acetonitrile 276 nm (ε=47800); mass spectrum: m/e 623 (M$^+$). Exact mass determination calc'd. for C$_{28}$H$_{50}$Si$_4$BrN 623.174, found 623.174.

Chapter 2
1-(4-bromophenyl)-2-(4′-methoxyphenyl)-1,1,2,2-tetramethyldisilane (BrS2)
The same procedure was used as for the synthesis of BrN2, using the Grignard reagent of 4-
bromothioanisole in THF. A creamy white solid (73%) was obtained after distillation at reduced
pressure (150 °C/1 mm Hg) (mp 47-49 °C). 1H NMR: δ 0.32 (s, 6H, CH₃-Si(CH₃)₂), 0.33 (s, 6H, Br-C₆H₄-Si(CH₃)₂), 2.50 (s, 3H, CH₃S), 7.21-7.28 (dd, 4H, CH₃-Si(CH₃)₂), 7.23-7.45 (dd, 4H, Br-C₆H₄-);
13C NMR: δ -4.08 (CH₃-Si(CH₃)₂), Br-C₆H₄-Si(CH₃)₂), 15.6 (CH₃S); 126.1, 134.5 (CH), 139.6,
134.8 (C) (CH₃-Si(CH₃)₂), 131.1, 135.7 (CH), 123.6, 138.2 (C) (Br-C₆H₄-); 29Si NMR: δ -22.02 (CH₃-
S-C₆H₄-Si(CH₃)₂), -21.36 (Br-C₆H₄-Si(CH₃)₂); UV: cyclohexane 245 nm (ε=27100), 268.7 nm
(ε=39700), acetonitrile 245 nm (ε=19000), 267 nm (ε=30900); mass spectrum: m/e 394 (M⁺). Exact
mass determination calcd. for C₁₇H₂₅Si₂BrS 394.024, found 394.024.

1-(4-bromophenyl)-2-(4′-methoxyphenyl)-1,1,2,2-tetramethyldisilane (BrO2)
The synthesis was carried out using the same procedure as for BrN2, with the Grignard reagent of
p-bromoanisole in THF. Distillation at reduced pressure (160 °C/0.5 mbar) gave a colourless liquid
(85%). 1H NMR: δ 0.34 (s, 6H, CH₃O-C₆H₄-Si(CH₃)₂), 0.33 (s, 6H, Br-C₆H₄-Si(CH₃)₂), 3.84 (s, 3H,
CH₃O), 6.91-7.31 (dd, 4H, CH₃O-C₆H₄), 7.24-7.46 (dd, 4H, Br-C₆H₄-); 13C NMR: δ -3.84 (CH₃O-
C₆H₄-Si(CH₃)₂), -4.03 (Br-C₆H₄-Si(CH₃)₂), 54.97 (CH₃O-), 113.6, 135.1 (CH), 129.0, 160.1 (C) (CH₃O-
C₆H₄), 130.7, 135.4 (CH), 132.2, 138.1 (C) (Br-C₆H₄-); 29Si NMR: δ -22.38 (CH₃O-C₆H₄-Si(CH₃)₂), -
41.42 (Br-C₆H₄-Si(CH₃)₂); UV: cyclohexane 243 nm (ε=27300), acetonitrile 242 nm (ε=32200); mass
spectrum: m/e 378 (M⁺). Exact mass determination calcd. for C₁₇H₂₅Si₂BrO 378.047, found 378.047.

1-(4-bromophenyl)-2-(4′-fluorophenyl)-1,1,2,2-tetramethyldisilane (BrF2) [1c]
The synthesis was carried out using the same procedure as for BrN2, with the Grignard reagent of
p-fluorobromobenzene. Distillation at reduced pressure (149 °C/0.1 mm Hg) gave a colourless liquid
(53%). 1H NMR: δ 0.33 (s, 12H, -Si(CH₃)₂), 7.01-7.05 (dd, 2H, 1JHH=9 Hz), 7.31-7.35 (dd, 2H,
1JHH=6 Hz) (F-C₆H₄-), 7.21-7.46 (dd, 4H, Br-C₆H₄-); 13C NMR: δ -3.96 (F-C₆H₄-Si(CH₃)₂), -4.16 (Br-
C₆H₄-Si(CH₃)₂), 114.9 (d, 1JHH=20 Hz), 135.5 (d, 1JHH=7 Hz) (CH), 162.5 (d, 1JHH=247 Hz), 133.7 (C)
(F-C₆H₄-), 130.8, 135.3 (CH), 123.2, 137.6 (C) (Br-C₆H₄-); 29Si NMR: δ -21.69 (F-C₆H₄-Si(CH₃)₂), 21.40
(Br-C₆H₄-Si(CH₃)₂); mass spectrum: m/e 366 (M⁺). Exact mass determination calcd. for C₁₆H₂₀Si₂BrF 366.027, found 366.027.

1-(4-bromophenyl)-2-phenyl-1,1,2,2-tetramethyldisilane (BrH2)
The same procedure was used as for the synthesis of BrN2, with the Grignard reagent of bromobenzene in THF. After distillation at reduced pressure (100 °C/0.1 mbar), a colourless liquid was obtained. Subsequent purification by column chromatography with pentane gave pure BrH2 (31%). 1H NMR: δ 0.31 (s, 6H, C₆H₅-Si(CH₃)₂), 0.32 (s, 6H, Br-C₆H₄-Si(CH₃)₂), 7.32 (m, 5H, C₆H₅-),
7.21-7.43 (dd, 4H, Br-C₆H₄-); 13C NMR: δ -4.09 (C₆H₅-Si(CH₃)₂), -4.05 (Br-C₆H₄-Si(CH₃)₂), 127.7,
128.5, 133.7 (CH), 138.5 (C) (C₆H₅-), 130.7, 135.3 (CH), 123.2, 137.9 (C) (Br-C₆H₄-); 29Si NMR: δ -
21.97 (C₆H₅-Si(CH₃)₂), -21.28 (Br-C₆H₅-Si(CH₃)₂); UV: cyclohexane 243 nm (ε=20600), acetonitrile 242 nm (ε=21500); mass spectrum: m/e 348 (M⁺). Exact mass determination calcd. for C₁₆H₂₁Si₂Br 348.037, found 348.037.

1-(4-formylphenyl)-2-(4’-dimethylaminophenyl)-1,1,2,2-tetramethyldisilane (CHON2) [1a,b,c]

A solution of 12.0 g (30.6 mmol) of BrN₂ in 100 ml of freshly distilled THF was added dropwise under stirring to 2.5 g (0.103 mol) magnesium activated with a crystal of iodine. The mixture was refluxed for 16 hours. This Grignard reagent was added at room temperature to a solution of 4.6 g (63.4 mmol) DMF in 20 ml of freshly distilled THF. The reaction mixture was stirred at room temperature for 16 hours and then concentrated. Diethyl ether was added (100 ml) and the organic solution was washed twice with brine (100 ml) and water (100 ml). The organic layer was dried over MgSO₄, filtered and evaporated. The crude product (yellow creamy solid) was purified by column chromatography using 2:1 dichloromethane/pentane (v/v) as eluent. A white solid was obtained (55%) (mp 85-87 °C). ¹H NMR: δ 0.33 (s, 6H, (CH₃)₂Si(CH₃)₂), 0.40 (s, 6H, OHC-C₆H₄-Si(CH₃)₂), 2.98 (s, 6H, (CH₃)₂N), 6.73-7.26 (dd, 4H, (CH₃)₂N-C₂H₄), 7.59-7.81 (dd, 4H, OHC-C₆H₄), 10.03 (s, 1H, OHC-), ¹³C NMR: δ -3.79 ((CH₃)₂N-C₆H₄-Si(CH₃)₂), -4.16 (OHC-C₆H₄-Si(CH₃)₂), 40.08 ((CH₃)₂N), 111.9, 134.2 (CH), 123.0, 150.8 (C) ((CH₃)₂N-C₂H₄), 128.4, 134.8 (CH), 134.9, 149.2 (C) (OHC-C₆H₄), 192.6 (CHO); ²⁹Si NMR: δ -22.65 ((CH₃)₂N-C₆H₄-Si(CH₃)₂), -20.94 (OHC-C₆H₄-Si(CH₃)₂); FTIR: 1107 ν (Si-C), 1242 ν (Si-CH₃), 1594 ν (C=O) cm⁻¹; UV: cyclohexane 269 nm (ε=36300), acetonitrile 271 nm (ε=31800); mass spectrum: m/e 341 (M⁺). Anal. calcd for C₁₉H₂₇Si₂NO: C, 66.92; H, 7.98; N, 4.11; Si, 16.48. Found: C, 66.91; H, 7.98; N, 4.18; Si, 16.21.

1-(4-formylphenyl)-2-(4’-methylthiophenyl)-1,1,2,2-tetramethyldisilane (CHOS2)

This compound was synthesized in the same way as CHON2, using the Grignard reagent of BrS₂. The crude product was purified by column chromatography using 2:1 dichloromethane/pentane (v/v) as eluent. A white solid was obtained (55%), mp 50-52 °C. ¹H NMR: δ 0.33 (s, 6H, CH₃-Si(CH₃)₂), 0.38 (s, 6H, OHC-C₆H₄-Si(CH₃)₂), 2.50 (s, 3H, CH₃S-), 7.20-7.26 (dd, 4H, CH₃S-C₆H₄), 7.54-7.80 (dd, 4H, OHC-C₆H₄), 10.0 (s, 1H, CHO); ¹³C NMR: δ -4.13 (CH₃S-C₆H₄-Si(CH₃)₂), -4.31 (OHC-C₆H₄-Si(CH₃)₂), 15.2 (CH₃S-), 125.5, 134.3 (CH), 133.9, 139.3 (C) (CH₃S-C₆H₄), 128.5, 134.1 (CH), 136.1, 148.4 (C) (OHC-C₆H₄), 192.6 (CHO); ²⁹Si NMR: δ -21.66 (CH₃S-C₆H₄-Si(CH₃)₂), -20.92 (OHC-C₆H₄-Si(CH₃)₂); UV: cyclohexane 265.4 nm (ε=27300), acetonitrile 264.9 nm (ε=29200); mass spectrum: m/e 344 (M⁺). Exact mass determination calcd. for C₁₈H₂₄Si₂OS 344.109, found 344.109.
1-(4-formylphenyl)-2-(4′-methoxyphenyl)-1,1,2,2-tetramethyldisilane (CHOO2)

This compound was synthesized in the same way as CHON2, using the Grignard reagent of BrO2. The crude product was purified by column chromatography using 1:2 dichloromethane/pentane (v/v) as eluent. A colourless, viscous liquid was obtained (70%). $^1$H NMR: δ 0.33 (s, 6H, CH$_3$O-C$_6$H$_4$Si(CH$_3$)$_2$), 0.38 (s, 6H, OHCC$_6$H$_4$Si(CH$_3$)$_2$), 3.83 (s, 3H, CH$_3$O-), 6.89-7.28 (dd, 4H, CH$_3$O-C$_6$H$_4$), 7.54-7.80 (dd, 4H, OHCC$_6$H$_4$), 10.0 (s, 1H, CHO); $^{13}$C NMR: δ -3.98 (CH$_3$O-C$_6$H$_4$Si(CH$_3$)$_2$), -4.32 (OHCC$_6$H$_4$Si(CH$_3$)$_2$), 54.89 (CH$_3$O-), 113.58, 135.04 (CH), 126.82, 160.14 (C) (CH$_3$O-C$_6$H$_4$), 128.38, 134.19 (CH), 136.03, 148.62 (C) (OHCC$_6$H$_4$), 192.49 (CHO); $^{29}$Si NMR: δ -22.03 (CH$_3$O-C$_6$H$_4$Si(CH$_3$)$_2$), -20.92 (OHCC$_6$H$_4$Si(CH$_3$)$_2$); UV: cyclohexane 239.5 nm (ε=27300), 277.5 nm (ε=14250).

1-(4-formylphenyl)-2-(4′-fluorophenyl)-1,1,2,2-tetramethyldisilane (CHOF2)

This compound was synthesized in the same way as CHON2, using the Grignard reagent of BrF2. A colourless oil was obtained which was purified by column chromatography with 1:1 pentane/ether (v/v) as eluent. Recrystallization from pentane gave a white crystalline solid (25%) (mp 60-61 °C). $^1$H NMR: δ 0.34 (s, 6H, C$_6$H$_4$Si(CH$_3$)$_2$), 0.38 (s, 6H, OHCC$_6$H$_4$Si(CH$_3$)$_2$), 7.00-7.05 (dd, 2H, $^3$J$_{HF}$=9 Hz), 7.29-7.34 (dd, 2H, $^4$J$_{HF}$=5 Hz) (F-C$_6$H$_4$), 7.52-7.79 (dd, 4H, OHCC$_6$H$_4$), 10.03 (s, 1H, CHO); $^{13}$C NMR: δ -4.03 (F-C$_6$H$_4$Si(CH$_3$)$_2$), -4.39 (OHCC$_6$H$_4$Si(CH$_3$)$_2$), 115.0 (d, $^3$J$_{HF}$=20 Hz), 135.5 (d, $^3$J$_{HF}$=6.9 Hz) (CH), 162.5 (d, $^1$J$_{HF}$=249 Hz), 133.5 (C) (F-C$_6$H$_4$), 128.5, 134.2 (CH), 136.2, 148.2 (C) (OHCC$_6$H$_4$), 192.5 (CHO); $^{29}$Si NMR: δ -21.36 (F-C$_6$H$_4$Si(CH$_3$)$_2$), -20.91 (OHCC$_6$H$_4$Si(CH$_3$)$_2$); mass spectrum: m/e 316 (M$^+$). Exact mass determination calcd. for C$_{17}$H$_{31}$Si$_2$FO 316.111, found 316.111.

1-(4-(2,2-dicyanovinylphenyl)-2-(4′-dimethylaminophenyl)-1,1,2,2-tetramethyldisilane (1[1a,b,c])

To a solution of 2.6 g (7.6 mmol) of CHON2 in 30 ml methanol was added 0.5 g (7.6 mmol) of malononitrile and a drop of piperidine. The red coloured solution was stirred for 16 hours at room temperature. The yellow precipitate was filtered off and washed subsequently with methanol and pentane. After drying, a yellow crystalline solid was obtained (80%) (mp 105-106 °C). $^1$H NMR: δ 0.29 (s, 6H, (CH$_3$)$_3$N=C$_6$H$_4$Si(CH$_3$)$_2$), 0.36 (s, 6H, (NC)$_2$C=CH-C$_6$H$_4$Si(CH$_3$)$_2$), 2.96 (s, 6H, (CH$_3$)$_3$N-), 6.70-7.21 (dd, 4H, (CH$_3$)$_3$N=C$_6$H$_4$), 7.53-7.79 (dd, 4H, (NC)$_2$C=CH-C$_6$H$_4$), 7.74 (s, 1H, (NC)$_2$C=CH); $^{13}$C NMR: δ -3.86 (((CH$_3$)$_3$N=C$_6$H$_4$Si(CH$_3$)$_2$), -4.31 (((NC)$_2$C=CH-C$_6$H$_4$Si(CH$_3$)$_2$), 40.08 (((CH$_3$)$_3$N-), 112.0, 134.7 (CH), 122.2, 150.8 (C) ((CH$_3$)$_3$N=C$_6$H$_4$), 129.2, 134.7 (CH), 130.4, 150.8 (C) ((NC)$_2$C=CH-C$_6$H$_4$), 112.6, 113.8 ((NC)$_2$C=CH), 81.9 ((NC)$_2$C=CH), 160 ((NC)$_2$C=CH); $^{29}$Si NMR: δ -22.44 (((CH$_3$)$_3$N=C$_6$H$_4$Si(CH$_3$)$_2$), -20.43 (((NC)$_2$C=CH-C$_6$H$_4$Si(CH$_3$)$_2$); FTIR: 1108 ν (Si-C$_{ar}$), 1249 ν (Si-CH$_3$), 1579, 1601 ν (C-CN), 2277 ν (C=N) cm$^{-1}$; UV: cyclohexane 274 nm (ε=30700), 329 nm (ε=23800), acetonitrile 274 nm (ε=30300), 327 nm (ε=24800); mass spectrum: m/e 389 (M$^+$).
1-(4-(2,2-dicyanovinyl)phenyl)-2-(4'-methoxyphenyl)-1,1,2,2-tetramethyldisilane ((CN)2S2)
The same procedure as for the synthesis of (CN)2N2 was used with CHO2S as starting material. A slightly yellow-coloured solid was obtained in 60% yield, mp 80-81 °C. 1H NMR: δ 0.33 (s, 6H, (CH3)2Si(-)), 0.37 (s, 6H, (NC)3C=CH-C6H4-Si(CH3)2+), 2.50 (s, 3H, CH3-Si), 7.21-7.24 (dd, 4H, CH3-SiC6H4-), 7.52-7.80 (dd, 4H, (NC)3C=CH-C6H4-), 7.75 (s, 1H, (NC)2C=CH-H); 13C NMR: δ -4.06 (CH3-SiC6H4-Si(CH3)2+), -4.44 ((NC)3C=CH-C6H4-Si(CH3)2+), 15.2 (CH3-Si), 125.5, 134.6 (CH), 133.6, 139.5 (C) (CH3-SiC6H4-), 129.2, 134.6 (CH), 130.6, 149.9 (C) ((NC)3C=CH-C6H4-), 112.5, 113.5 ((NC)2C=CH-), 82.3 ((NC)2C=CH-), 159.9 ((NC)2C=CH-); 29Si NMR: δ -21.47 (CH3-SiC6H4-Si(CH3)2+), -20.36 ((NC)2C=CH-C6H4-Si(CH3)2+); UV: cyclohexane 269 nm (ε=24600), 325 nm (ε=21900), acetonitrile 267 nm (ε=25400), 331 nm (ε=22000); mass spectrum: m/e 392 (M+). Exact mass determination calc'd for C21H23Si2N2S: C, 64.34; H, 6.17; N, 7.15; Si, 14.33. Found: C, 63.85; H, 6.23; N, 7.31; Si, 13.98.

1-(4-(2,2-dicyanovinyl)phenyl)-2-(4'-methoxyphenyl)-1,1,2,2-tetramethyldisilane ((CN)2O2) [1b]
The same procedure as for the synthesis of (CN)2N2 was used with CHO02 as starting material. A red oil was obtained which was purified by column chromatography with 3:1 dichloromethane/pentane (v/v) as eluent. After recrystallization from n-hexane, a slightly yellow-coloured solid was obtained (40%) (mp 90-91 °C). 1H NMR: δ 0.32 (s, 6H, CH3-O-C6H4-Si(CH3)2+), 0.37 (s, 6H, (NC)3C=CH-C6H4-Si(CH3)2+), 3.82 (s, 3H, CH3O-), 6.89-7.27 (dd, 4H, CH3-O-C6H4-), 7.52-7.80 (dd, 4H, (NC)2C=CH-C6H4-), 7.76 (s, 1H, (NC)2C=CH-); 13C NMR: δ -3.95 (CH3-O-C6H4-Si(CH3)2+), -4.41 ((NC)3C=CH-C6H4-Si(CH3)2+), 55.02 (CH3O-), 113.7, 135.1 (CH), 128.3, 160.1 (C) (CH3O-C6H4-), 129.3, 134.8 (CH), 130.5, 150.3 (C) ((NC)2C=CH-C6H4-), 112.6, 113.8 ((NC)2C=CH-), 82.1 ((NC)2C=CH-), 160.1 ((NC)2C=CH-); 29Si NMR: δ -21.83 (CH3-O-C6H4-Si(CH3)2+), -20.42 ((NC)2C=CH-C6H4-Si(CH3)2+); UV: cyclohexane 237 nm (ε=25800), 337 nm (ε=21000), acetonitrile 237 nm (ε=23800), 333 nm (ε=20400); mass spectrum: m/e 376 (M+). Exact mass determination calc'd for C21H23Si2N2O: C, 67.06; H, 6.43; N, 7.45; Si, 14.94. Found: C, 66.65; H, 6.55; N, 7.36; Si, 14.54.

1-(4-(2,2-dicyanovinyl)phenyl)-2-(4'-fluorophenyl)-1,1,2,2-tetramethyldisilane ((CN)2F2) [1d]
The same procedure as for the synthesis of (CN)2N2 was used with CHOF2 as starting material. A yellow oil was obtained which was purified by column chromatography with 3:1 dichloromethane/pentane (v/v) as eluent. A slightly yellow-coloured solid was isolated (70%) (mp 82-83 °C). 1H NMR: δ 0.35 (s, 6H, F-C6H4-Si(CH3)2+), 0.38 (s, 6H, (NC)3C=CH-C6H4-Si(CH3)2+), 7.00-7.05 (dd, 2H, 3JHF=9 Hz), 7.29-7.33 (dd, 2H, 3JHF=6 Hz) (F-C6H4-), 7.51-7.81 (dd, 4H, (NC)3C=CH-C6H4-), 7.76 (s, 1H, (NC)2C=CH-); 13C NMR: δ -4.52 (F-C6H4-Si(CH3)2+), -4.05 ((NC)2C=CH-C6H4-).
Synthesis of p-disubstituted diphenylsilanes and fragments thereof; crystal structure.

\[ \text{Si(CH}_3\text{)}_2\text{H}_2, 115.0 \text{ (d, } ^{3}\text{J}_{\text{CF}}=19.5 \text{ Hz), 135.5 \text{ (d, } ^{3}\text{J}_{\text{CF}}=7.5 \text{ Hz) (CH), 163.5 \text{ (d, } ^{1}\text{J}_{\text{CF}}=247 \text{ Hz) 133.3 (C-}\text{F}-\text{C}_6\text{H}_4\text{-), 129.3, 134.7 (CH), 130.7, 149.6 (C) ((NC)}_2\text{C}=\text{CH-C}_6\text{H}_4\text{-), 112.7, 113.7 ((NC)}_2\text{C}=\text{CH-), 82.4 ((NC)}_2\text{C}=\text{CH-), 159.9 ((NC)}_2\text{C}=\text{CH-), 159.9 ((NC)}_2\text{C}=\text{CH-), 20}_{\text{Si}}\text{ NMR: } ^{2}\text{-21.6 (F-C}_6\text{H}_4\text{-Si(CH}_3\text{)}_2\text{-), -20.40 ((NC)}_2\text{C}=\text{CH-C}_6\text{H}_4\text{-Si(CH}_3\text{)}_2\text{-); UV: cyclohexane 229 nm (}\varepsilon=17900\text{), 335 nm (}\varepsilon=26500\text{), acetonitrile 230 nm (}\varepsilon=17500\text{), 334 nm (}\varepsilon=23700\text{); mass spectrum: m/e 364 (M\text{+}). Exact mass determination calcd. for C\text{20}\text{H}_2\text{Si}_2\text{F}_2\text{N}_2\text{=17700), 269 (}\varepsilon=17500\text{), 334 nm (}\varepsilon=23700\text{); mass spectrum: m/e 364 (M\text{+}). Exact mass determination calcd. for C\text{20}\text{H}_2\text{Si}_2\text{F}_2\text{N}_2\text{, found 364.123. Anal. calcd for C\text{20}\text{H}_2\text{Si}_2\text{F}_2\text{N}_2\text{: C, 65.64; H, 5.91; N, 7.70; Si, 15.28.}}

(4-nonafluorobutylsulfonylphenyl)(4'-dimethylaminophenyl)dimethylsilane (SO\text{2C}_4\text{F}_9\text{N1})

A solution of 5 g (15.0 mmol) of BrN1 in 25 ml THF was added slowly to magnesium (0.4 g, 16.5 mmol) activated by a crystal of iodine. This reaction mixture was refluxed for 4 hours, then cooled and added dropwise to a solution of perfluorobutylsulfonyl fluoride (14 g, 45 mmol) in 15 ml THF at 0 °C. The reaction mixture was stirred for 16 hours at room temperature, then concentrated and diethyl ether (50 ml) was added. The solution was filtered and the residual salts were washed twice with ether (40 ml). The solution was washed with brine (twice) and water after adding an equal amount of n-hexane to the ether solution. The organic layer was dried over MgSO\text{4} and then concentrated under vacuum. Crystallization from ether/hexane at -20 °C gave a white solid which was identified as the dimeric byproduct (NMR). The yellow residue was concentrated and purified by column chromatography with 2:1 pentane/dichloromethane (v/v) as eluent. Recrystallization from ether/pentane gave 2.3 g of white crystals (29%), mp 44-46 °C. \text{1H NMR: } ^{2}\text{J}_{\text{CF}}=23800); mass spectrum: m/e 537 (M\text{+}). Exact mass determination calcd. for C\text{20}\text{H}_2\text{Si}_2\text{F}_2\text{N}_2\text{, found 537.084. Anal. calcd for C\text{20}\text{H}_2\text{Si}_2\text{F}_2\text{N}_2\text{: C, 44.73; H, 3.75; N, 2.61; F, 31.84. Found: C, 44.26; H, 3.78; N, 2.66; F, 31.58.}

1-(4-nonafluorobutylsulfonylphenyl)-2-(4'-dimethylaminophenyl)-1,1,2,2-tetramethyl-disilane (SO\text{2C}_4\text{F}_9\text{N2})

The same procedure as for the synthesis of SO\text{2C}_4\text{F}_9\text{N1} was used with BrN2 as starting material. The crude reaction product was purified by column chromatography with 1:5 pentane/dichloromethane (v/v) as eluent. Recrystallization from ether/pentane gave slightly yellow-coloured crystals (26%) (mp 58-59 °C). \text{1H NMR: } ^{2}\text{J}_{\text{CF}}=17700), 269 (\varepsilon=26000), acetonitrile 239 nm (\varepsilon=16900), 270 (\varepsilon=23800); mass spectrum: m/e 537 (M\text{+}). Exact mass determination calcd. for C\text{20}\text{H}_2\text{Si}_2\text{F}_2\text{N}_2\text{SO}_2\text{C}_4\text{F}_9\text{N2}: C, 44.73; H, 3.75; N, 2.61; F, 31.84. Found: C, 44.26; H, 3.78; N, 2.66; F, 31.58.}
(F₂C₅SO₂C₄H₄Si(CH₃)₂); ¹⁹F NMR: δ -80.8 (t, -CF₂C₅F₃), -111.8, -120.9, -126.1 (-CF₂C₅F₃); FTIR: 1170vs, 1374vs v (SO₂), 1247w v (Si-CH₃), 1450w, 1105s v (Si-C)₉, 1596vs v (C-C)₉, 1140s, 1360s v (C-F) cm⁻¹. UV: cyclohexane 272 nm (ε = 32900), acetonitrile 272 nm (ε = 24900). Mass spectrum: m/e 595 (M⁺). Exact mass determination calcd for C₅H₂Si₂F₃NO₂S 595.109, measd 595.108. Anal. calcd for C₂₂H₂₆Si₂F₃NO₂S: C, 44.41; H, 4.40; N, 2.35; F, 28.74. Found: C, 44.45; H, 4.54; N, 2.33; F, 28.45.

1-(4-nonafluorobutylsulfonylphenyl)-4-(4'-dimethylaminophenyl)-1,1,2,2,3,3,4,4-octamethyltetrasilane (SO₂C₅F₃N₄)

The reaction was carried out in the same way as the synthesis of SO₂C₅F₉N₁ using BrN₄ (10.2 g, 20 mmol) as starting material. The obtained red oil was purified by column chromatography with 4:1 pentane/dichloromethane (v/v) as eluent. Recrystallization from ether/pentane gave slightly yellow-coloured crystalline material (20%), mp 65-66 °C. ¹H NMR: δ 0.31 (s, 6H, (CH₃)₂N-C₆H₄-Si(CH₃)₂), 0.41 (s, 6H, F₃C₅SO₂C₄H₄-Si(CH₃)₂), 0.04, 0.02 (s, 6H, -Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂), 2.96 (s, 6H, (CH₃)₂N-), 6.73-7.28 (dd, 4H, (CH₃)₂N-C₆H₄-H), 7.66-7.92 (dd, 4H, F₃C₅SO₂C₄H₄); ¹³C NMR: δ -2.81 ((CH₃)₂N-C₆H₄-Si(CH₃)₂), -3.52 (F₃C₅SO₂C₄H₄-Si(CH₃)₂), -5.71, -5.88 ((Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂), 40.14 (CH₃)₂N-), 112.02, 134.57 (CH), 123.82, 150.69 (C) ((CH₃)₂N-C₆H₄), 129.38, 134.69 (CH), 153.4, 131.37 (C) (F₃C₅SO₂C₄H₄), 100-120 (m, C₅F₉); ²⁹Si NMR: δ -19.09 ((CH₃)₂N-C₆H₄-Si(CH₃)₂), -15.82 (F₃C₅SO₂C₄H₄-Si(CH₃)₂), -44.28, -44.06 ((Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂); ¹⁹F NMR: δ -80.8 (t, -CF₂C₅F₃), -111.9, -120.9, -126.1 (-CF₂C₅F₃); FTIR: 1170vs, 1372v s (SO₂), 1240s v (Si-CH₃), 1100s, 1450s v (Si-C)₉, 1597 v (C-C)₉, 1140s, 1360s v (C-F) cm⁻¹; UV: cyclohexane 275 nm (ε=33650), acetonitrile 275 nm (ε=30900), 300 nm (sh) (ε=8600); mass spectrum: m/e 711 (M⁺). Exact mass determination calcd for C₂₂H₂₆Si₂F₄NO₂S 711.156, found 711.157. Anal. calcd for C₂₂H₂₆Si₂F₄NO₂S: C, 43.91; H, 5.39; N, 1.97; F, 24.05. Found: C, 43.25; H, 5.44; N, 1.86; F, 23.52.

1-(4-nonafluorobutylsulfonylphenyl)-6-(4'-dimethylaminophenyl)-1,1,2,2,3,3,4,4,5,5,6,6-dodecamethylhexasilane (SO₂C₅F₉N₆)

The same procedure was used as for the synthesis of SO₂C₅F₉N₁ using BrN₄ (4.2 g, 6.7 mmol) as starting material. The obtained yellow oil was purified by column chromatography with 3:1 pentane/dichloromethane and then 2:1 dichloromethane/pentane (v/v) as eluent. Pure SO₂C₅F₉N₆ was obtained in low yield (10%) since part of the compound decomposed on the column. Crystallization from ether/pentane gave slightly yellow-coloured crystals, mp 105-106 °C. ¹H NMR: δ 0.34 (s, 6H, (CH₃)₂N-C₆H₄-Si(CH₃)₂), 0.45 (s, 6H, F₃C₅SO₂C₄H₄-Si(CH₃)₂), 0.11 (s, 12H, Ph-Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂), 0.07, 0.05 (s, 6H, Ph-Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂), 2.97 (s, 6H, (CH₃)₂N-), 6.73-7.28 (dd, 4H, (CH₃)₂N-C₆H₄-H), 7.72-7.95 (dd, 4H, F₃C₅SO₂C₄H₄); ¹³C NMR: δ -2.66 ((CH₃)₂N-C₆H₄-Si(CH₃)₂), -3.37 (F₃C₅SO₂C₄H₄-Si(CH₃)₂), -4.49, -4.54 (Ph-Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂), -5.32, -5.51 (Ph-Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂), 40.23 ((CH₃)₂N-), 112.07, 134.66 (CH), 123.8, 150.5 (C) ((CH₃)₂N-C₆H₄), 129.45, 134.73 (CH), 131.30, 153.65 (C) (F₃C₅SO₂C₄H₄); ²⁹Si
NMR: δ -18.93 (t, (CH₃)₂N-C₆H₄-Si(CH₃)₂-), -15.75 (F₃C₄SO₂-C₆H₄-Si(CH₃)₂-), -38.79, -39.08 (Ph-Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂-), -42.86, -43.27 (Ph-Si(CH₃)₂-Si(CH₃)₂-Si(CH₃)₂-); ¹⁹F NMR: δ -80.8 (t, -CF₂C₂F₂-), -111.9, -121.0, -126.1 (-CF₂C₂F₂-); UV: cyclohexane 275 nm (ε=31200), acetonitrile 275 nm (ε=29600); mass spectrum: m/e 827 (M⁺). Exact mass determination calc. for C₃₀H₃₀Si₆F₇NO₂S 827.203, found 827.203.

1-(4-nonafluorobutylsulfonylphenyl)-2-(4'-methylthiophenyl)-1,1,2,2-tetramethyl-disilane

(SO₂C₄F₉S₂)
The same procedure was used as for the synthesis of SO₂C₄F₉N₁, using Br₂S₂ as starting material. The reddish coloured oil was purified by column chromatography with 5:1 pentane/dichloromethane (v/v) as eluent. After recrystallization from ether/pentane a white sticky solid was obtained (15%), mp 30-33 °C. ¹H NMR: δ 0.33 (s, 6H, CH₃-SiC₆H₄-Si(CH₃)₂-), 0.40 (s, 6H, F₃C₄SO₂-C₆H₄-Si(CH₃)₂-), 2.49 (s, 3H, CH₂S-), 7.19 (s, 4H, CH₃-SiC₆H₄-), 7.60-7.91 (dd, 4H, F₃C₄SO₂-C₆H₄-Si(CH₃)₂-); ¹³C NMR: δ -4.33 (CH₃-SiC₆H₄-Si(CH₃)₂-), -4.53 (F₃C₄SO₂-C₆H₄-Si(CH₃)₂-), 15.06 (CH₃S-), 125.45, 133.91 (CH), 133.13, 139.69 (C) (CH₃-C-Si(CH₃)₂-), 129.33, 134.62 (CH), 131.55, 152.16 (C) (F₃C₄SO₂-C₆H₄-); ²⁹Si NMR: δ -21.57 (CH₃-SiC₆H₄-Si(CH₃)₂-), -19.84 (F₃C₄SO₂-C₆H₄-Si(CH₃)₂-); ¹⁹F NMR: δ -80.8 (t, -BF₂C₂F₂-), -111.8, -120.9, -126.1 (-CF₂C₂F₂-); UV: cyclohexane 269 nm (ε=21800), acetonitrile 266 nm (ε=23900); mass spectrum: m/e 598 (M⁺). Exact mass determination calc. for C₂₁H₂₃Si₂F₇O₂Si₂ 598.053, found 598.053. Anal. calc. for C₂₁H₂₃Si₂F₇O₂Si₂: C, 42.18; H, 3.88; F, 28.60; S, 10.72. Found: C, 42.88; H, 3.99; F, 26.97; S, 11.39.

1-(4-nonafluorobutylsulfonylphenyl)-2-(4'-methoxyphenyl)-1,1,2,2-tetramethyl-disilane

(SO₂C₄F₉O₂)
The same procedure was used as for the synthesis of SO₂C₄F₉N₁, using BrO₂ as starting material. The obtained oil was purified by column chromatography with 3:1 pentane/dichloromethane (v/v) as eluent. A colourless, viscous liquid was obtained in 30% yield. ¹H NMR: δ 0.32 (s, 6H, CH₃O-C₆H₄-Si(CH₃)₂-), 0.39 (s, 6H, F₃C₄SO₂-C₆H₄-Si(CH₃)₂-), 3.81 (s, 3H, CH₃O-), 6.86-7.21 (dd, 4H, CH₃O-C₆H₄-), 7.59-7.90 (dd, 4H, F₃C₄SO₂-C₆H₄-Si(CH₃)₂-); ¹³C NMR: δ -4.13 (CH₃O-C₆H₄-Si(CH₃)₂-), -4.50 (F₃C₄SO₂-C₆H₄-Si(CH₃)₂-), 54.93 (CH₃S-), 113.69, 135.00 (CH), 127.89, 160.35 (C) (CH₃O-C₆H₄-), 129.35, 134.70 (CH), 131.55, 152.53 (C) (F₃C₄SO₂-C₆H₄-), 100-120 (m, -SO₂C₄F₉); ²⁹Si NMR: δ -21.91 (CH₃O-C₆H₄-Si(CH₃)₂-), -19.89 (F₃C₄SO₂-C₆H₄-Si(CH₃)₂-); ¹⁹F NMR: δ -80.8 (t, -CF₂C₂F₂-), 111.8, -120.9, -126.1 (-CF₂C₂F₂-); FTIR: 1180s, 1370vs v (SO₂), 1245vs v (Si-CH₃), 1109s v (Si-C₂), 1502s, 1594vs v (C-C)ₐr, 1137vs, 1352v v (C-F); UV: cyclohexane 237 nm (ε=25600), 277 nm (ε=9000), acetonitrile 238 nm (ε=25100), 277 nm (ε=11000); mass spectrum: m/e 582 (M⁺). Exact mass determination calc. for C₂₁H₂₃Si₂F₇O₂S 582.076, found 582.076. Anal. calc. for C₂₁H₂₃Si₂F₇O₂Si₂: C, 43.43; H, 3.98. Found: C, 44.05; H, 4.20.

1-(4-nonafluorobutylsulfonylphenyl)-2-phenyl-1,1,2,2-tetramethyldisilane (SO₂C₄F₉H₂)

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The same procedure was used as for the synthesis of SO₂F₅C₄N₁, using BrH₂ as starting material (4.65 g, 13.3 mmol). The obtained oil was purified by column chromatography with 5:1 pentane/dichloromethane (v/v) as eluent. 1.7 g of a clear liquid was obtained (23%). ¹H NMR: δ 0.35 (s, 6H, C₆H₅-Si(CH₃)₂-), 0.41 (s, 6H, F₅C₆SO₂-C₆H₄-Si(CH₃)₂-), 7.31 (m, 5H, C₆H₅-Si(CH₃)₂-), 7.59-7.89 (dd, 4H, (F₅C₆SO₂-C₆H₄-Si(CH₃)₂-), ¹³C NMR: δ -4.36 (C₆H₅-Si(CH₃)₂-), -4.51 (F₅C₆SO₂-C₆H₄-Si(CH₃)₂-), 127.83, 128.82, 133.60 (CH), 137.40 (C) (C₆H₅-Si(CH₃)₂-), 134.66, 129.34 (CH), 152.22, 131.64 (C) (F₅C₆SO₂-C₆H₄-Si(CH₃)₂-); ²⁹Si NMR: δ -21.50 (C₆H₅-Si(CH₃)₂-), -19.73 (F₅C₆SO₂-C₆H₄-Si(CH₃)₂-); ¹⁹F NMR: δ -80.8 (t, -CF₃), 111.8, -120.9, -126.1 (-CF₃); UV: cyclohexane 230 nm (ε=24400), 276 nm (ε=12700), acetonitrile 230 nm (ε=20400), 278 nm (ε=10600); mass spectrum: m/e 552 (M⁺).

Exact mass determination calcd. for C₂₀H₂₁Si₂F₉O₅S 552.066, found 552.066. Anal. calcd for C₂₀H₂₁Si₂F₉O₅S: C, 43.51; H, 3.83. Found: C, 42.21; H, 3.76.

1-(4-phenylsulfonylphenyl)-2-(4'-dimethylamino phenyl)-1,1,2,2-tetramethyldisilane (SO₂PhN2)

A solution of BrN₂ (10 g, 25.6 mmol) in THF (100 ml) was added slowly to magnesium (1.2 g, 49 mmol) activated by a crystal of iodine. The resulting mixture was refluxed for 4 hours. The Grignard reagent was added dropwise to a solution of benzenesulfonyl fluoride (4.1 g, 25.6 mmol) in THF (30 ml) at 0°C. The mixture was stirred for 16 hours at room temperature. The solution was concentrated and diethyl ether (100 ml) was added. After filtering the precipitated salts, the solution was washed three times with water (200 ml). After drying the organic layer over MgSO₄, the solvent was removed under vacuum. The white solid residue was purified by column chromatography with 1:3 pentane/dichloromethane (v/v) as eluent. Recrystallization from ether gave 6.1 g of a white crystalline material (53%) (mp 124-125°C). ¹H NMR: δ 0.26 (s, 6H, (CH₃)₂N-C₆H₅-Si(CH₃)₂-), 0.31 (s, 6H, C₆H₅-SO₂-C₆H₄-Si(CH₃)₂-), 2.95 (s, 6H, (CH₃)₂N-), 6.67-7.18 (dd, 4H, (CH₃)₂N-C₆H₅-H), 7.49-7.83 (dd, 4H, C₆H₅-SO₂-C₆H₄-H), 7.53 (m, 3H), 7.96 (d, 2H) (C₆H₅-SO₂-C₆H₄-); ¹³C NMR: δ -3.84 ((CH₃)₂N-C₆H₅-Si(CH₃)₂-), 4.13 (C₆H₅-SO₂-C₆H₄-Si(CH₃)₂-), 111.95, 134.77 (CH), 122.27, 150.73 (C) ((CH₃)₂N-C₆H₅-H), 126.18, 134.49 (CH), 140.97, 147.68 (C) (C₆H₅-SO₂-C₆H₄-), 129.15, 127.57, 132.99 (CH), 141.70 (C) (C₆H₅-SO₂-C₆H₄-). FTIR: 1150vS, 1325vS v (SO₂); 1243v w (Si-CH₃); 1447w, 1105s v (Si-C)ar; 1594vs v (C-C)ar cm⁻¹. UV: cyclohexane 269 nm (ε = 29800), acetonitrile 270 nm (ε = 25900). Mass spectrum: m/e 453 (M⁺). Exact mass determination calcd for C₂₄H₂₃Si₂NO₅S 453.161, found 453.161. Anal. calcd for C₃₂H₂₃Si₂NO₅S: C, 63.61; H, 6.90; N, 3.09; Si, 12.40. Found: C, 63.05; H, 6.98; N, 3.18; Si, 12.14.
Synthesis of p-disubstituted diphenylsilanes and fragments thereof; crystal structure.

**bis-(4'-(dimethylaminophenyl)dimethylsilanyl)phenyl)sulfone (SO_2 dimN1)**

This compound was obtained as the major byproduct of the synthesis of SO_2 C_4 F_9 N1. Crystallization of the crude reaction product from ether/hexane at -20 °C gave pure white crystals. The concentrated mother liquor can be separated by column chromatography with 2:1 pentane/dichloromethane (v/v) as eluent to obtain SO_2 C_4 F_9 N1 and then 4:1 dichloromethane/pentane (v/v) to obtain SO_2 dimN1. Total yield of SO_2 dimN1 was 4%, mp 140-143 °C. \(^1\)H NMR: δ 0.49 (s, 6H, Si(CH_3)_2), 2.95 (s, 6H, (CH_3)_2N), 6.71-7.32 (dd, 4H, (CH_3)_2N-C_6H_4), 7.61-7.84 (dd, 4H, (CH_3)_2N-SO_2); \(^13\)C NMR: δ -2.53 (Si(CH_3)_2), 39.97 ((CH_3)_2N), 111.83, 135.11 (CH), 120.99, 151.2 (C) ((CH_3)_2N-C_6H_4), 126.31, 134.72 (CH), 141.62, 146.78 (C) (-SO_2-C_6H_4); \(^29\)Si NMR: δ -8.14; UV: cyclohexane 250 nm (sh) (ε=30160), 269 nm (ε=47300), acetonitrile 269 nm (ε=42900), 250 (sh) (ε=23550); mass spectrum: m/e 572 (M^+. Exact mass determination calc. for C_{50}H_{60}N_2 Si_2 O_2 S 572.235, found 572.235.

**bis-(4'-(dimethylaminophenyl)tetramethylsilanyl)phenyl)sulfone (SO_2 dimN2)**

This compound was obtained as the major byproduct of the synthesis of SO_2 C_4 F_9 N2. It can be obtained in the same way as SO_2 dimN1 either by crystallization or by column chromatography with subsequent elution with 5:1 dichloromethane/pentane (v/v) (fraction with SO_2 C_4 F_9 N2) and 10:1 dichloromethane/ethyl acetate (v/v) (fraction with SO_2 dimN2, 5%, mp 105-107 °C). \(^1\)H NMR: δ 0.29 (s, 12H, (CH_3)_2N-C_6H_4-Si(CH_3)_2), 0.33 (s, 12H, -SO_2-C_6H_4-Si(CH_3)_2), 2.98 (s, 12H, (CH_3)_2N), 6.70-7.21 (dd, 8H, (CH_3)_2N-C_6H_4), 7.50-7.84 (dd, 8H, -SO_2-C_6H_4); \(^13\)C NMR: δ -3.84 ((CH_3)_2N-C_6H_4-Si(CH_3)_2), -4.12 (-SO_2-C_6H_4-Si(CH_3)_2), 40.17 ((CH_3)_2N), 112.02, 134.80 (CH), 122.37, 150.78 (C) ((CH_3)_2N-C_6H_4), 126.24, 134.49 (CH), 141.15, 174.56 (C) (-SO_2-C_6H_4); \(^29\)Si NMR: δ -22.74 ((CH_3)_2N-C_6H_4-Si(CH_3)_2), -20.84 (-SO_2-C_6H_4-Si(CH_3)_2); FTIR: 1163 vs, 1314 vs v (SO_2), 1245 w v (Si-C), 1445 w, 1109 vs v (Si-C=C), 1596 vs v (C=C) cm⁻¹; UV: cyclohexane 271 nm (ε=61000), acetonitrile 273 nm (ε=62400); mass spectrum: m/e 688 (M^+. Exact mass determination calc. for C_{36}H_{52} Si_2 N_2 O_2 S 688.283, found 688.284.

**bis-(4'-(methylthiophenyl)tetramethylsilanyl)phenyl)sulfone (SO_2 dimS2)**

This compound was obtained as the major byproduct of the synthesis of SO_2 C_4 F_9 S2. It can be obtained in the same way as SO_2 dimN1 either by crystallization or by column chromatography with subsequent elution with 1:1 dichloromethane/pentane (v/v) (fraction with SO_2 C_4 F_9 S2) and dichloromethane (fraction with SO_2 dimS2). A white crystalline material was obtained (8%), mp 92-93 °C. \(^1\)H NMR: δ 0.30 (s, 12H, CH_3-S-C_6H_4-Si(CH_3)_2), 0.33 (s, 12H, -SO_2-C_6H_4-Si(CH_3)_2), 2.49 (s, 6H, CH_3S), 7.18-7.20 (dd, 8H, CH_3-S-C_6H_4), 7.47-7.84 (dd, 8H, -SO_2-C_6H_4); \(^13\)C NMR: δ -4.21 (CH_3-S-C_6H_4-Si(CH_3)_2), -4.33 (-SO_2-C_6H_4-Si(CH_3)_2), 15.12 (CH_3S), 125.43, 133.93 (CH), 133.65, 139.33 (C) (CH_3-S-C_6H_4), 126.19, 134.31 (CH), 141.20, 146.73 (C) (-SO_2-C_6H_4); \(^29\)Si NMR: δ -21.72 (CH_3-S-C_6H_4-Si(CH_3)_2), -20.68 (-SO_2-C_6H_4-Si(CH_3)_2); UV: cyclohexane 270 nm (ε=41400), acetonitrile 267 nm
(\varepsilon=49500); mass spectrum: m/e 694 (M⁺). Exact mass determination calcd. for C_{34}H_{46}Si_{4}O_{2}S_{3} 694.174, found 694.175.

**bis-(4-[4′-fluorophenyl]tetramethyldisilanyl)phenyl)sulfone (SO₂dimF2)**

This compound was obtained as the major byproduct of the synthesis of SO₂C₄F₉F₂. In this synthesis the Grignard reagent of BrF₂ was added to 1 eq of nonafluorobutylsulfonyl fluoride in THF. The obtained yellow oil was purified by column chromatography with 3:1 to 1:20 pentane/dichloromethane (v/v) as eluent. A slightly yellow-coloured oil was obtained from the last fraction of the column (5%). ¹H NMR: δ 0.32 (s, 12H, F-C₆H₄-Si(CH₃)₂); 0.33 (s, 12H, -SO₂-C₆H₄-Si(CH₃)₂), 6.93-6.97 (dd, 4H, ³JHF=8.5 Hz), 7.23-7.26 (dd, 4H, ²JHF=5.5 Hz) (F-C₆H₄); 7.46-7.84 (dd, 8H, -SO₂-C₆H₄); ¹³C NMR: δ -4.08 (-SO₂-C₆H₄-Si(CH₃)₂), -4.40 (-SO₂-C₆H₄-Si(CH₃)₂), 114.9 (d, ³JCF=20 Hz), 135.4 (d, ³JCF=7 Hz) (CH), 163.1 (d, ¹JC=248 Hz) (C-F), 126.28, 134.36 (CH), 141.35, 146.65 (C) (-SO₂-C₆H₄); ²⁹Si NMR: δ -21.43 (F-C₆H₄-Si(CH₃)₂); -20.68 (-SO₂-C₆H₄-Si(CH₃)₂); ¹⁹F NMR: δ -112.39 (m, F-C₆H₄); mass spectrum: m/e 638 (M⁺). Exact mass determination calcd. for C₅₉H₆₂O₂F₂S 638.179, found 638.179.

**bis-(4-{(phenyl)tetramethyldisilanyl}phenyl)sulfone (SO₂dimH2)**

This compound was obtained as the major byproduct of the synthesis of SO₂C₄F₉H₂. Purification of the reaction product by column chromatography with 5:1 pentane/dichloromethane (v/v) as eluent gave SO₂C₄F₉H₂ in the first fraction and SO₂dimH2 (6%) in the last fraction, both as colourless liquids. ¹H NMR: δ 0.31 (s, 12H, C₆H₅-Si(CH₃)₂), 0.33 (s, 12H, -SO₂-C₆H₄-Si(CH₃)₂), 7.28 (m, 10H, C₆H₅); 7.45-7.82 (dd, 8H, -SO₂-C₆H₄); ¹³C NMR: δ -2.23 (C₆H₅-Si(CH₃)₂), -4.31 (-SO₂-C₆H₄-Si(CH₃)₂), 128.54, 133.66, 127.77 (CH), 137.9 (C) (C₆H₅); 134.41, 126.26 (CH), 146.87, 141.30 (C) (-SO₂-C₆H₄); ²⁵Si NMR: δ -21.68 (C₂H₄-Si(CH₃)₂); -20.58 (-SO₂-C₆H₄-Si(CH₃)₂); UV: cyclohexane 267 nm (\varepsilon=27480), acetonitrile 270 nm (\varepsilon=23360), 229 nm (\varepsilon=30160); mass spectrum: m/e 694 (M⁺).

**Synthesis of compounds with the structure Me₃Si(Si(2)Ph-X)**

**4-(trimethylsilyl)dimethylaminobenzene (SiN)**

To a solution of 7.6 g (70 mmol) trimethylsilyl chloride in 30 ml THF was added dropwise 70 ml of a 1 M solution of p-dimethylaminophenylmagnesium bromide in THF at 0 °C. The solution was stirred for 16 hours at room temperature and was then concentrated. Then, 200 ml of diethyl ether was added and the precipitated salts were filtered off and washed twice with diethyl ether. The combined ether solutions were washed twice with water and then dried over Na₂SO₄. The ether solution was concentrated and then distilled at reduced pressure (75 °C/0.3 mm Hg) to give 7.5 g (55%) of almost pure SiN. After column chromatography with 1:1 pentane/dichloromethane (v/v), 3.16 g (24%) of a white crystalline material was obtained, mp 24-26 °C. ¹H NMR: δ 0.25 (s, 9H,
Synthesis of p-disubstituted diphenylsilanes and fragments thereof; crystal structure.

$(CH_3)_3Si)$, 2.97 (s, 6H, $(CH_3)_2N)$, 6.76-7.41 (dd, 4H, $-C_6H_4$); $^{13}$C NMR: $\delta$ -0.9 ($((CH_3)_3Si)$, 40.21 ($((CH_3)_2N)$), 111.92, 134.29 (CH), 125.54, 150.87 (C) ($C_6H_4$); $^{29}$Si NMR: $\delta$ -5.27; UV: cyclohexane 265 nm ($\epsilon=19200$), acetonitrile 266 nm ($\epsilon=24100$); mass spectrum: m/e 193 (M$^+$). Exact mass determination calcd. for C$_{11}$H$_{19}$SiN 193.129, found 193.129. Anal. calcd for C$_{11}$H$_{19}$SiN: C, 68.40; H, 9.92; N, 7.25; Si, 14.54. Found: C, 67.83; H, 9.69; N, 7.17; Si, 14.26.

4-(pentamethyldisilanyl)dimethylaminobenzene (Si$_2$N)
The same method was used as for the synthesis of SiN, using chloropentamethyldisilane (8 g, 48 mmol) as starting material. The brown-coloured residue was distilled twice under reduced pressure (100$^\circ$C/0.5 mm Hg) to give a white crystalline solid (6.48 g, 52%), mp 47-48$^\circ$C.

$^1$H NMR: $\delta$ 0.07 (s, 9H, $(CH_3)_3Si$), 0.29 (s, 6H, -Si$(CH_3)_2$), 2.97 (s, 6H, $(CH_3)_2N$), 6.74-7.34 (dd, 4H, $-C_6H_4$); $^{13}$C NMR: $\delta$ -2.24 $(CH_3)_3Si$, -3.75 (-Si$(CH_3)_2$), 40.15 $(CH_3)_2N$), 112.0, 134.7 (CH), 124.3, 150.5 (C) ($C_6H_4$); $^{29}$Si NMR: $\delta$ -19.47 $(CH_3)_3Si$, -22.64 (-Si$(CH_3)_2$); UV: cyclohexane 270 nm ($\epsilon=27000$), acetonitrile 272 nm ($\epsilon=28100$); mass spectrum: m/e 251 (M$^+$). Exact mass determination calcd. for C$_{13}$H$_{25}$Si$_2$N 251.153, found 251.153. Anal. calcd for C$_{13}$H$_{25}$Si$_2$N: C, 62.17; H, 10.03; N, 5.58; Si, 22.37. Found: C, 61.90; H, 9.86; N, 5.76; Si, 22.17.

4-(trimethylsilyl)bromobenzene (SiBr) [26]
A solution of 35.4 g (0.15 mol) p-dibromobenzene in 50 ml of dry diethyl ether was cooled to -15$^\circ$C. Then, 0.15 mol n-butyllithium (60 ml 2.5 M in n-hexane) was added dropwise while keeping the temperature at -15 to -10$^\circ$C. After stirring for 30 min at this temperature, 16.3 g (0.15 mol) of trimethylsilyl chloride in 15 ml ether was added dropwise while keeping the temperature at -15 to -10$^\circ$C. After stirring for 16 hours at room temperature the precipitated salts were filtered off and washed with diethyl ether. The ether solutions were combined and washed with water. After drying over Na$_2$SO$_4$ and evaporating the solvent a clear liquid was obtained. Distillation at reduced pressure (48-50$^\circ$C/0.11 mbar) gave 28 g (81%) of a colourless liquid. $^1$H NMR: $\delta$ 0.07 (s, 9H, $(CH_3)_3Si$), 7.38-7.50 (dd, 4H, $-C_6H_4$); $^{13}$C NMR: $\delta$ -1.34 $(CH_3)_3Si$, 130.7, 134.8 (CH), 123.4, 139.1 (C) ($C_6H_4$); $^{29}$Si NMR: $\delta$ -3.38; UV: cyclohexane 228 nm (e=27000), acetonitrile 226 nm (e=16000); mass spectrum: m/e 228 (M$^+$). Exact mass determination calcd. for C$_9$H$_{13}$SiBr 227.997, found 227.997.

4-(pentamethyldisilanyl)bromobenzene (Si$_2$Br)
The same method was used as for the synthesis of SiBr, with chloropentamethyldisilane as reagent. A clear liquid was obtained which was distilled at reduced pressure (65-67$^\circ$C/0.2 mm Hg). The residual p-dibromobenzene can be sublimed slowly out of the distilled product at 30$^\circ$C/30.2 mm Hg). Yield: 21.1 g (45%) of Si$_2$Br. $^1$H NMR: $\delta$ 0.06 (s, 9H, $(CH_3)_3Si$), 0.33 (s, 6H, -Si$(CH_3)_2$), 7.31-7.47 (dd, 4H, $-C_6H_4$); $^{13}$C NMR: $\delta$ -2.38 $(CH_3)_3Si$, -4.15 (-Si$(CH_3)_2$), 130.8, 135.2
(CH), 123.0, 139.1 (C (-C₆H₄); ²⁹Si NMR: δ-19.33 ((CH₃)₃Si-), -20.96 (-Si(CH₃)₂); UV: cyclohexane 240 nm (ε=16600), acetonitrile 240 nm (ε=14400); mass spectrum: m/e 286 (M⁺). Exact mass determination calcd. for C₁₁H₁₉Si₂Br 286.021, found 286.021.

4-(trimethylsilyl)trifluoromethylbenzene (SiCF₃)
A solution of 11.3 g (50 mmol) p-(trifluoromethyl)bromobenzene in 50 ml of diethyl ether was added slowly to 1.34 g (55 mmol) magnesium activated with a crystal of iodine. The mixture was refluxed for 30 min and then cooled to room temperature. To this Grignard reagent was added dropwise a solution of 5.43 g (50 mmol) trimethylsilyl chloride in 10 ml of diethyl ether. The reaction mixture was refluxed for 16 hours, cooled and washed with brine and then water. The ether solution was dried over MgSO₄ and concentrated. Distillation at reduced pressure (40 °C/1 mbar) gave 4 g (37%) of a colourless liquid. ¹H NMR: δ 0.31 (s, 9H, (CH₃)₃Si-), 7.59-7.64 (dd, 4H, -C₆H₄); ¹³C NMR: δ -1.46 ((CH₃)₃Si), 124.09, (d, ³JC=3.6 Hz), 133.45 (CH), 130.64, (q, ²JC=31.7 Hz), 145.32 (C (-C₆H₄), 124.16 (q, ¹JC=262.2 Hz) (C (-CF₃), ²⁹Si NMR: δ -3.12; ¹⁹F NMR: δ -63.0; UV: cyclohexane 219 nm (ε=570), 266 nm (ε=8200), acetonitrile 219 nm (ε=595), 265 nm (ε=8800); mass spectrum: m/e 218 (M⁺). Exact mass determination calcd. for C₁₁H₁₃SiF₂ 218.074, found 218.074.

4-(pentamethyldisilanyl)trifluoromethylbenzene (Si₂CF₃) [5]
The same procedure was used as for the synthesis of SiCF₃ with chloropentamethyldisilane as reagent. After several distillations of the crude, orange-coloured product at reduced pressure (50 °C/2 mm Hg) a colourless liquid was obtained (2.4 g, 18%). ¹H NMR: δ 0.07 (s, 9H, (CH₃)₃Si-), 0.36 (s, 6H, -Si(CH₃)₂), 7.57 (bs, 4H, -C₆H₄); ¹³C NMR: δ -2.44 ((CH₃)₃Si-), -4.29 (-Si(CH₃)₂), 124.1, (q, ³JC=3.45 Hz), 133.84, (CH), 130.21, (q, ²JC=32 Hz), 145.06 (C (-C₆H₄), 124.64 (q, ¹JC=262 Hz) (-CF₃); ²⁹Si NMR: δ -19.21 ((CH₃)₃Si-), -20.78 (-Si(CH₃)₂); ¹⁹F NMR: δ -62.9; UV: cyclohexane 240 nm (ε=8900), acetonitrile 243 nm (ε=8150); mass spectrum: m/e 276 (M⁺). Exact mass determination calcd. for C₁₂H₁₉Si₂F₂ 276.098, found 276.098.

4-(2,2-dicyanovinyl)trimethylsilylbenzene (Si(CN)₂) [1c]
The synthesis of p-(trimethylsilyl)benzaldehyde (SiCHO) was with the same method as used for CHON2, starting with 10.23 g (44.6 mmol) p-trimethylsilyl)bromobenzene. The crude reaction product (4.85 g, 27.2 mmol) was used without further purification and was dissolved in 25 ml methanol. To this solution was added 1.79 g (27.2 mmol) malononitrile and 1 drop of piperidine. The solution became red and a white solid precipitated. After stirring for 3 hours at room temperature, the white solid was filtered off and was washed subsequently with cold methanol and pentane. Yield: 1.4 g (23%, mp 94-95 °C. ¹H NMR: δ 0.32 (s, 9H, (CH₃)₃Si-), 6.69-7.86 (dd, 4H, -C₆H₄), 7.78 (s, 1H, -CH=C(CN)₂); ¹³C NMR: δ -1.58 ((CH₃)₃Si-), 129.32, 134.26 (CH), 130.83 , 150.22 (C (-C₆H₄), 159.96 (-CH=C(CN)₂), 82.61 (-CH=C(CN)₂), 112.5, 113.6 (-CH=C(CN)₂); ²⁹Si NMR: δ -2.54; UV: cyclohexane 318 nm (ε=32600), acetonitrile 318 nm (ε=24700); mass spectrum: m/e 226
Synthesis of \( p \)-disubstituted diphenylsilanes and fragments thereof; crystal structure.

\( (M^+) \). Exact mass determination calcd. for \( C_{13}H_{14}SiN_2 \) 226.093, found 226.093. Anal. calcd for \( C_{13}H_{14}SiN_2 \): C, 69.08; H, 6.24; N, 12.39; Si, 12.42. Found: C, 68.76; H, 6.24; N, 12.31; Si, 12.11.

4-(2,2-dicyanovinyl)pentamethyldisilanylbenzene (\( Si_2(CN)_2 \)) \([1b]\)

The same procedure was used as for the synthesis of \( Si(CN)_2 \) starting with 9.45 g (32.9 mmol) of \( p \)-(pentamethyldisilanyl)bromobenzene. Recrystallization from pentane/ether gave 1.74 g (28%) of a yellow crystalline material, mp 88-89 °C. \(^1\)H NMR: \( \delta \) 0.07 (s, 9H, \( (CH_3)_3Si \)), 0.39 (s, 6H, -Si(\( CH_3 \))\(_2\)), 7.62-7.85 (dd, 4H, -C\(_6H_4\)); \(^13\)C NMR: \( \delta \) -2.50 ((\( CH_3 \))\(_3Si \)), -4.57 (-Si(\( CH_3 \))\(_2\)), 129.8, 134.55, 129.43 (CH), 131.6, 152.93 (C) (-C\(_6H_4\)), 159.94 (C(-CH=CH(CN))\(_2\)), 82.13 (-CH=CH(CN))\(_2\)), 112.62, 113.79 (-CH=CH(CN))\(_2\)); \(^29\)Si NMR: \( \delta \) -18.66 ((\( CH_3 \))\(_3Si \)), -19.89 (-Si(\( CH_3 \))\(_2\)); UV: cyclohexane 333 nm (\( \varepsilon=24600 \)), acetonitrile 333 nm (\( \varepsilon=20900 \)); mass spectrum: m/e 284 (M\(^+\)). Exact mass determination calcd. for \( C_{13}H_{20}Si_2N_2 \) 284.116, found 284.116. Anal. calcd for \( C_{13}H_{20}Si_2N_2 \): C, 63.41; H, 7.10; N, 9.86; Si, 19.77. Found: C, 62.52; H, 7.10; N, 9.51; Si, 19.34.

4-(nonafluorobutylsulfonyl)trimethylsilanylbenzene (\( SiSO_2C_4F_9 \))

The Grignard reagent of \( p \)-(trimethylsilyl)bromobenzene (10.0 g, 43.6 mmol) in 70 ml THF was added dropwise to a solution of 26 g (88 mmol) nonafluorobutylsulfonyl fluoride in 20 ml THF at -30 °C. The solution was stirred for 16 hours at room temperature and then concentrated. Diethyl ether was added and the precipitated salts were filtered off and washed with ether. The combined ether solutions were washed with brine and water, dried over Na\(_2\)SO\(_4\) and concentrated. The crude product was purified by column chromatography with 5:1 pentane/dichloromethane (v/v) as eluent, giving 2.6 g (13%) of a colourless liquid. \(^1\)H NMR: \( \delta \) 0.34 (s, 9H, \( (CH_3)_3Si \)), 7.80-7.97 (dd, 4H, -C\(_6H_4\)); \(^13\)C NMR: \( \delta \) -1.58 ((\( CH_3 \))\(_3Si \)), 134.35, 129.64 (CH), 132.17, 152.54 (C) (-C\(_6H_4\)), 100-120 (m, -C\(_4F_9\)); \(^29\)Si NMR: \( \delta \) -1.82; UV: cyclohexane 235 nm (\( \varepsilon=12350 \)), 274 nm (\( \varepsilon=14600 \)), acetonitrile 237 nm (\( \varepsilon=16900 \)), 275 nm (\( \varepsilon=2200 \)); mass spectrum: m/e 432 (M\(^+\)). Exact mass determination calcd. for \( C_{13}H_{13}SiF_8O_2S \) 432.026, found 432.026. Anal. calcd for \( C_{13}H_{13}SiF_8O_2S \): C, 36.14; H, 3.03. Found: C, 35.40; H, 2.99.

4-(nonafluorobutylsulfonyl)pentamethyldisilanylbenzene (\( Si_2SO_2C_4F_9 \))

The same procedure was used as for the synthesis of \( SiSO_2C_4F_9 \) with the Grignard reagent of \( p \)-pentamethyldisilanyl bromobenzene. The obtained yellow oil was purified by column chromatography with 4:1 pentane/dichloromethane (v/v) as eluent to give 4.3 g (25%) of a colourless viscous liquid. \(^1\)H NMR: \( \delta \) 0.07 (s, 9H, \( (CH_3)_3Si \)), 0.41 (s, 6H, -Si(\( CH_3 \))\(_2\)), 7.73-7.96 (dd, 4H, -C\(_6H_4\)); \(^13\)C NMR: \( \delta \) -2.59 ((\( CH_3 \))\(_3Si \)), -4.57 (-Si(\( CH_3 \))\(_2\)), 134.55, 129.43 (CH), 131.6, 152.93 (C) (-C\(_6H_4\)), 100-120 (m, -C\(_4F_9\)); \(^29\)Si NMR: \( \delta \) -18.72 ((\( CH_3 \))\(_3Si \)), -19.32 (-Si(\( CH_3 \))\(_2\)); \(^19\)F NMR: \( \delta \) -80.85 (t, -CF\(_2C_4F_9\)), -111.9, -121.0, -126.1 (-CF\(_2C_4F_9\)); UV: cyclohexane 229 nm (\( \varepsilon=10350 \)), 267 nm (\( \varepsilon=9800 \)), acetonitrile 232 nm (\( \varepsilon=9100 \)), 276 nm (\( \varepsilon=9350 \)); mass spectrum: m/e 490 (M\(^+\)). Exact mass
determination calcd. for {\text{C}}_{15}{\text{H}}_{19}{\text{Si}}_{2}{\text{F}}_{9}{\text{O}}_{2}{\text{S}} 490.050, found 490.050. Anal. calcd for {\text{C}}_{15}{\text{H}}_{19}{\text{Si}}_{2}{\text{F}}_{9}{\text{O}}_{2}{\text{S}}: {\text{C}}, 36.77; {\text{H}}, 3.91. Found: {\text{C}}, 36.37; {\text{H}}, 4.48.

bis-(4-(trimethylsilyl)phenyl)sulfone (SiSO\textsubscript{2} dim)

This compound was obtained as the major byproduct of the synthesis of SiSO\textsubscript{2}C\textsubscript{4}F\textsubscript{9}. The last fraction of the separation by column chromatography gave 0.6 g of a white solid (8%), mp 140 °C. \textsuperscript{1}H NMR: δ 0.26 (s, 18H, (CH\textsubscript{3})\textsubscript{3}Si-), 7.63-7.89 (dd, 8H, -C\textsubscript{6}H\textsubscript{4}-); \textsuperscript{13}C NMR: δ -1.54 ((CH\textsubscript{3})\textsubscript{3}Si-), 126.35, 133.9 (CH), 141.69, 147.51 (C) (-C\textsubscript{6}H\textsubscript{4}-); \textsuperscript{29}Si NMR: δ -2.70; UV: cyclohexane 247 nm (ε=22800), acetonitrile 248 nm (ε=21900); mass spectrum: m/e 362 (M\textsuperscript{+}). Exact mass determination calcd. for {\text{C}}_{18}{\text{H}}_{26}{\text{Si}}_{2}{\text{O}}_{2}{\text{S}} 362.119, found 362.119.

bis-(4-pentamethyldisilanyl)phenyl)sulfone (Si\textsubscript{2}SO\textsubscript{2} dim)

This compound was obtained as the major byproduct of the synthesis of Si\textsubscript{2}SO\textsubscript{2}C\textsubscript{4}F\textsubscript{9}. The last fraction of the separation by column chromatography with 1:3 pentane/dichloromethane (v/v) as eluent gave 1 g of a colourless, viscous liquid which solidified (9%), mp 113-115 °C. \textsuperscript{1}H NMR: δ 0.04 (s, 18H, (CH\textsubscript{3})\textsubscript{3}Si-), 0.34 (s, 12H, -Si(CH\textsubscript{3})\textsubscript{2}-), 7.57-7.88 (dd, 8H, -C\textsubscript{6}H\textsubscript{4}-); \textsuperscript{13}C NMR: δ -2.52 ((CH\textsubscript{3})\textsubscript{3}Si-), -4.41 (-Si(CH\textsubscript{3})\textsubscript{2}-), 126.29, 134.52 (CH), 141.17, 147.46 (C) (-C\textsubscript{6}H\textsubscript{4}-); \textsuperscript{29}Si NMR: δ -18.96 ((CH\textsubscript{3})\textsubscript{3}Si-), -20.26 (-Si(CH\textsubscript{3})\textsubscript{2}-); UV: cyclohexane 265 nm (ε=22850), acetonitrile 269 nm (ε=19700); mass spectrum: m/e 478 (M\textsuperscript{+}). Exact mass determination calcd. for C\textsubscript{22}H\textsubscript{38}Si\textsubscript{4}O\textsubscript{2}S 478.167, found 478.167.

nonafluorobutylsulfonylbenzene (PhSO\textsubscript{2}C\textsubscript{4}F\textsubscript{9})

A Grignard reagent of 4 g (25.5 mmol) bromobenzene in 50 ml THF was added dropwise to a solution of 15.4 g (51 mmol) nonafluorobutylsulfonyl fluoride in 20 ml THF at -30 °C. The reaction mixture was stirred for 16 hours at room temperature and was then concentrated. Diethyl ether was added and the precipitated salts were filtered off and washed with ether. The ether solutions were concentrated and the residue was distilled twice at reduced pressure (60-80 °C/0.2 mm Hg) to give 2.5 g (27%) of a colourless liquid. \textsuperscript{1}H NMR: δ 8.06 (d, 2H), 7.87 (m, 1H), 7.74 (m, 2H) (C\textsubscript{6}H\textsubscript{5}-); \textsuperscript{13}C NMR: δ 131.35, 129.69, 136.54 (CH), 132.2 (C\textsubscript{6}H\textsubscript{5}-), 100-120 (m, C\textsubscript{4}F\textsubscript{9}-); \textsuperscript{19}F NMR: δ -80.9 (t, -CF\textsubscript{2}C\textsubscript{3}F\textsubscript{7}), -111.9, -121.0, -126.1 (-CF\textsubscript{2}C\textsubscript{3}F\textsubscript{7}); UV: cyclohexane 222 nm (ε=11400), 269 nm (ε=1600), acetonitrile 225 nm (ε=18000), 270 nm (ε=1570); mass spectrum: m/e 360 (M\textsuperscript{+}). Exact mass determination calcd. for C\textsubscript{10}H\textsubscript{13}F\textsubscript{9}O\textsubscript{2}S 359.987, found 359.987. Anal. calcd for C\textsubscript{10}H\textsubscript{13}F\textsubscript{9}O\textsubscript{2}S: C, 33.36; H, 1.40. Found: C, 33.62; H, 1.79.

4-(dimethylamino)nonafluorobutylsulfonylbenzene (NPhSO\textsubscript{2}C\textsubscript{4}F\textsubscript{9})

The same procedure was used as for the synthesis of PhSO\textsubscript{2}C\textsubscript{4}F\textsubscript{9} with the Grignard reagent of 5.5 g (26.6 mmol) p-dimethylaminobromobenzene in 40 ml THF. The crude reaction product was distilled at reduced pressure (150 °C/1 mm Hg) to give a slightly yellow coloured solid.
Recrystallization from ether/pentane at -20 °C gave 3.87 g (36%) of white crystals. $^1$H NMR: $\delta$ 3.12 (s, 6H, (CH$_3$)$_2$N-), 6.72-7.76 (dd, 4H, -C$_6$H$_4$-); $^{13}$C NMR: $\delta$ 39.51 ((CH$_3$)$_2$N-), 110.65, 132.56 (CH), 114.6, 154.68 (C) (-C$_6$H$_4$-); $^{19}$F NMR: $\delta$ -80.9 (t, -C$_2$F$_3$C$_3$F$_7$), -112.7, -121.1, -126.0 (-CF$_2$CF$_2$); UV: cyclohexane 303 nm ($\varepsilon$=32900), acetonitrile 315 nm ($\varepsilon$=38200); mass spectrum: m/e 403 (M$^+$). Exact mass determination calcd. for C$_{12}$H$_{10}$F$_9$NO$_2$S 403.029, found 403.029. Anal. calcd for C$_{12}$H$_{10}$F$_9$NO$_2$S: C, 35.76; H, 2.50; N, 3.48; F, 42.43. Found: C, 35.81; H, 2.65; N, 3.41; F, 43.45.

Synthesis of a diol-functionalized D$_{\sigma}$A-compound

4-bis-(2-hydroxyethyl)amino-1-bromobenzene (B) [27]
To a cold (0 °C) solution of 50 g (0.276 mol) bis-(2-hydroxyethyl)aminobenzene (A) in 280 ml of glacial acetic acid was added slowly and with continuous shaking a solution of 46.4 g (0.29 mol) of bromine in 75 ml of glacial acetic acid. The resulting solution was stirred for half an hour at room temperature. The reaction mixture was poured into 1200 ml water and just sufficient sodium metabisulfite solution was added to remove the orange colour. This colourless solution was made alkaline by adding 500 ml of a 50% NaOH solution. The precipitate was filtered off and dried, giving 57.5 (80%) of the desired product (mp 82 °C). $^1$H NMR: $\delta$ 3.50 (t, 4H, -C$_2$H$_2$N-), 3.76 (t, 4H, -C$_2$H$_2$O-), 4.35 (s, 2H, O$_2$H), 6.52-7.30 (dd, 4H, (-C$_6$H$_4$-); $^{13}$C NMR: $\delta$ 55.3 (-C$_2$H$_2$N-), 60.3 (-C$_2$H$_2$O-), 114.1, 131.8 (CH), 108.6, 146.9 (C) (-C$_6$H$_4$-).

4-bis-(2-(t-butyldimethylsiloxy)ethyl)amino-1-bromobenzene (C)
A solution of 21.5 g (0.083 mol) of compound B, 25 g (0.165 mol) of t-butyldimethylsilyl chloride and 19.72 g (0.29 mol) of imidazole in 50 ml of dry DMF was heated at 40 °C for 20 hours. The solvent was removed at reduced pressure and the residue was dissolved in diethyl ether. This solution was washed subsequently with a saturated K$_2$CO$_3$ solution, water and dried over MgSO$_4$. The solvent was removed at reduced pressure. Distillation at 200 °C (0.1 mm Hg) gave 30.8 g (76%) of the desired product as a clear viscous liquid. $^1$H NMR: $\delta$ 0.035 (s, 12H, -Si(CH$_3$)$_2$-), 0.89 (s, 18H, -Si(CH$_3$)$_3$), 3.48 (t, 4H, -C$_2$H$_2$N-), 3.74 (t, 4H, -C$_2$H$_2$O-), 6.55-7.25 (dd, 4H, -C$_6$H$_4$-); $^{13}$C NMR: $\delta$ 55.3 (-C$_2$H$_2$N-), 60.3 (-C$_2$H$_2$O-), 114.1, 131.8 (CH), 107.4, 156.3 (C) (-C$_6$H$_4$-).

1-(4-bromophenyl)-2-(4-bis-(2-(t-butyldimethylsiloxy)ethyl)aminophenyl)-1,1,2,2-tetramethyldisilane (D)
To a solution of 20 ml of 1.6 M n-BuLi in hexane was added 3.7 g (0.032 mol) of tetramethylethylene diamine (TMEDA). This solution was cooled to -25 °C and 20 ml of diethyl ether was added. This TMEDA-BuLi complex solution was added to 13.4 g (0.028 mol) of compound C in 30 ml of diethyl ether at -20 °C. After stirring this solution for 2 hours between -20
°C and 0 °C, a solution of 10.3 g (0.030 mol) of 1-(4-bromophenyl)-2-chloro-1,1,2,2-
tetramethyldisilane in 20 ml of diethyl ether was added dropwise. This solution was allowed to
warm up slowly to room temperature and was stirred for another 16 hours. The precipitate was
filtered off and the yellow-coloured solution was washed with water and dried over MgSO4. The
solvent was removed at reduced pressure. The remaining oil was purified by column chromatography with 1:1
dichloromethane/pentane (v/v) as eluent, giving 10.9 g (50%) of a viscous oil.1H NMR: δ 0.052 (s, 12H, -O-Si(CH3)2), 0.91 (s, 18H, -Si(CH3)3), 0.27 (s, 6H, (-CH2)2N-
C6H5-Si(CH3)2), 0.31 (s, 6H, Br-C6H5-Si(CH3)2), 3.51 (t, 4H, -CH2N-), 3.76 (t, 4H, -CH2O-), 6.66-7.18
(dd, 4H, (-CH2)2N-C6H4-H), 7.24-7.43 (dd, 4H, Br-C6H4-H); 13C NMR: δ -5.33 (-O-Si(CH3)2), -3.72
((-CH2)2N-C6H4-Si(CH3)2), -3.89 (Br-C6H5-Si(CH3)2), 25.9 (-Si(CH3)3), 53.2 (-CH2N-), 60.2 (-CH2O-),
111.1, 131.8 (CH) ((-CH2)2N-C6H4-H), 137.0, 135.4 (CH) (Br-C6H4-H); 29Si NMR: δ -23.21 ((-CH2)2N-
C6H5-Si(CH3)2), -21.56 (Br-C6H5-Si(CH3)2), 20.10 (-O-Si(CH3)2).

1-(4-nonafluorobutylsulfonylphenyl)-2-(4-bis-(2-(t-butyldimethylsiloxy)ethyl)amino-phenyl)-
1,1,2,2-tetramethyldisilane (E)

To a solution of 12.1 ml of 1.6 M n-BuLi in hexane was added 2.25 g (19.4 mmol) of
tetramethylethylenediamine (TMEDA). This solution was cooled to -90 °C and 20 ml of THF was
added. To this solution was added a cold (-80 °C) solution of 13.2 g (19.4 mmol) of compound D in
20 ml of THF in small portions. The slightly red-coloured solution was stirred for 1 hour while the
temperature was kept below -50 °C. To this solution was added 19.4 mmol of MgBr2Et2O in diethyl
ether (made by adding 3.65 g (19.4 mmol) of 1,2-dibromoethane to 0.7 g (29.0 mmol) of Mg turnings
in 30 ml of diethyl ether [5]). This solution was stirred for half an hour while the temperature was
kept below -45 °C. This Grignard reagent was added in small portions to a cold (-30 °C) solution of
17.6 g (58.1 mmol) of perfluorobutylsulfonyl fluoride in 20 ml of THF. The resulting solution was
stirred for 16 hours with the temperature rising slowly to room temperature. After the solvent had
been removed at reduced pressure, the residue was dissolved in 300 ml of diethyl ether. This
solution was washed subsequently with brine and water. The solution was dried over MgSO4 and
the solvent was removed at reduced pressure, giving 13.2 g (13.7 mmol) of the crude, orange-
coloured, viscous product. This product was purified by column chromatography with 1:3
dichloromethane/pentane (v/v) as eluent, giving 3.85 g (22%) of a clear viscous oil that slowly
crystallizes at room temperature (mp 25-30 °C) (Further elution of the column with 3:1
dichloromethane/pentane (v/v) gave 500 mg (0.4 mmol) of the dimeric byproduct).1H NMR: δ
0.047 (s, 12H, -O-Si(CH3)2), 0.90 (s, 18H, -Si(CH3)3), 0.29 (s, 6H, (-CH2)2N-C6H5-Si(CH3)2), 0.39 (s,
6H, F6C5SO2-C6H5-Si(CH3)2), 3.51 (t, 4H, -CH2N-), 3.76 (t, 4H, -CH2O-), 6.65-7.13 (dd, 4H, (-CH2)2N-
C6H5-H), 7.63-7.90 (dd, 4H, F6C5SO2-C6H5-H); 13C NMR: δ -5.47 (-O-Si(CH3)2), -4.01 ((-CH2)2N-C6H5-
Si(CH3)2), -4.36 (F6C5SO2-C6H5-Si(CH3)2), 18.2 (-Si(CH3)3), 25.8 (-Si(CH3)3), 53.1 (-CH2N-), 60.2 (-
CH2O-), 111.1, 134.7 (CH), 120.9, 148.4 (C ((-CH2)2N-C6H5-), 129.3, 134.4 (CH), 131.3, 153.0 (C)
Synthesis of p-disubstituted diphenylsilanes and fragments thereof; crystal structure.

\( (\text{F}_3\text{C}_6\text{SO}_2\text{C}_4\text{H}_4\text{)}; \) \( ^{29}\text{Si} \) NMR: \( \delta \) -22.76 (\( \text{t}-\text{CH}_2\text{)}_2\text{N-C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\text{),} \) -20.07 (\( \text{F}_3\text{C}_4\text{SO}_2\text{C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\text{),} \) 20.13 (\(-\text{O-Si(}\text{CH}_3\text{)}_2\text{).} \)

1-(4-nonafluorobutylsulfonylphenyl)-2-(4-bis-(2-hydroxyethyl)aminophenyl)-1,1,2,2-tetramethyldisilane (I)

1.2 g (1.3 mmol) of compound I was dissolved in 4 ml of ethanol. To this solution was added in one portion 4 g (40 mmol) of concentrated hydrogen chloride. The reaction mixture became white turbid and warm. After vigorous stirring for only 1 minute, the reaction mixture was poured into a solution of 20 g of NaHCO\(_3\) in 500 ml of water. This solution was washed three times with diethyl ether and then dried over MgSO\(_4\). After removal of the solvent 0.9 g of a clear viscous oil was obtained. The crude product could be purified by column chromatography with diethyl ether as eluent or by crystallization from ether/pentane at -20 °C. Yield: 0.5 g (0.8 mmol) of a slightly yellow-coloured crystalline material (50%) (mp 59-61 °C). \(^1\)H NMR: \( \delta \) 0.30 (s, 6H, \(-\text{CH}_3\)) \( \text{N-C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\text{),} \) 0.40 (s, 6H, \( \text{F}_3\text{C}_6\text{SO}_2\text{C}_4\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\text{),} \) 3.61 (t, 4H, \(-\text{CH}_2\text{N}-\)), 3.89 (t, 4H, \(-\text{CH}_2\text{O}\)), 2.96 (bs, 2H, \text{OH}), 6.65-7.14 (dd, 4H, \( \text{CH}_2\text{N}-\)), 7.61-7.89 (dd, 4H, \( \text{CH}_2\text{O}\)), \( ^{13}\text{C} \) NMR: \( \delta \) -3.99 (\( \text{t}-\text{CH}_2\text{N-C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\)), -4.38 (\( \text{F}_3\text{C}_4\text{SO}_2\text{C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\)), 55.1 (\(-\text{CH}_2\text{N}\)), 60.8 (\(-\text{CH}_2\text{O}\)), 112.1, 134.7 (CH), 122.6, 148.2 (C) (\( \text{(t}-\text{CH}_2\text{)}_2\text{N-C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\)), 129.3, 134.4 (CH), 131.3, 153.0 (C) (\( \text{F}_3\text{C}_4\text{SO}_2\text{C}_6\text{H}_4\text{)}; \) \( ^{29}\text{Si} \) NMR: \( \delta \) -22.48 (\( \text{(t}-\text{CH}_2\text{)}_2\text{N-C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\)), -19.94 (\( \text{F}_3\text{C}_4\text{SO}_2\text{C}_6\text{H}_4\text{-Si(}\text{CH}_3\text{)}_2\)); \( ^{19}\text{F} \) NMR: \( \delta \) -80.8 (t, \( \text{CF}_2\text{C}_F\)), -111.8, -120.9, -126.1 (\( \text{CF}_2\text{C}_F\)); FTIR: 1174vs, 1367vs \( \text{C} = \text{Si} \) \( \nu \) cm\(^{-1}\); Mass spectrum: \( m/\text{e} \text{ 655} \) (M\(^+\)). Exact mass determination calcld for \( \text{C}_4\text{H}_3\text{SiF}_3\text{N}_2\text{O}_4\text{S} \) 655.129, measd 655.129.

2.5.2 X-Ray diffraction

Data collection was performed using graphite-monochromatized MoK\( \alpha \)-radiation (\( \lambda = 0.71073 \) Å) on a Nonius CAD4F diffractometer. Three standard reflections were measured every three hours in order to correct for scale variation (drift in the primary beam and decrease in crystal quality). Scattering factors and anomalous dispersion corrections were taken from ref. [28]. Structure solution and refinement were carried out by means of the package MolEN (Enraf Nonius, Delft). Crystal data and experimental details are collected in Table 2.1.

Compound 1 (SO\(_2\)PhN\(_2\)): Crystals were grown from a solution in ether at -20°C and were found to be colourless. Cell constants were obtained by least-squares refinement on the angular settings of 25 reflections in the range 8.1° ≤ \( \theta \) ≤ 22.1°. Data collection was performed at low temperature (140 K) using the \( \theta \)-2\( \theta \) scan technique. An intensity decrease of 1.4% was found. Lorentz and polarization corrections were applied to the data, but no absorption corrections were made. The structure was partly solved by direct methods. The remaining atoms could be revealed from Fourier difference syntheses. Anisotropic temperature factors were used for the non H-atoms
and isotropic fixed temperature factors \(B_{\text{iso}} = 4.0 \, \text{Å}^2\) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å.

Compound 2 (SO\(_2\)C\(_7\)F\(_9\)N\(_2\)): Crystals were grown from a solution in ether/pentane at -20°C and were found to have a slightly yellow appearance. Cell constants were obtained by least-squares refinement on the angular settings of 25 reflections in the range 9.9° ≤ θ ≤ 16.2°. Data collection was performed at 293 K using the θ–2θ scan technique. An intensity decrease of 4% was found and attributed to crystal decomposition. Lorentz and polarization corrections were applied to the data, but no absorption corrections were made. The structure was solved by direct methods. The H-atoms could be revealed from Fourier difference syntheses. Anisotropic temperature factors were used for the non H-atoms and isotropic fixed temperature factors \(B_{\text{iso}} = 5.0 \, \text{Å}^2\) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å.

2.6 References


Synthesis of p-disubstituted diphenylsilanes and fragments thereof; crystal structure.