CHAPTER 2

ALLYLSILANES TO QUINONOID COMPOUNDS

2.1. INTRODUCTION

Organic silicon compounds display a multitude of reactivity profiles in organic synthesis. The usefulness of organosilicon reagents in stereoselective bond forming reactions can be attributed to the large number of functional groups and reaction conditions that can be accommodated by silicon and its ability to act as electron donor and acceptor. It becomes all the more impressive that these reagents are accessible by conventional synthetic methods. The reactivity and selectivity of reactions involving organosilanes are dependent on their steric components and associated electronic effects. The range of silicon-stabilized nucleophiles containing \( \sigma \) bonded silyl group attached to participating \( \pi \) bond and their use in organic synthesis has grown considerably over the last several years. In this context, allylsilanes have emerged as remarkably useful and versatile reagents for the regio and stereoselective formation of carbon-carbon bonds and continue to manifest enormous potential in organic transformations.\(^1\) They participate in both catalyzed and uncatalyzed addition reactions with a wide range of \( \text{C}=\text{X} \ \pi \) systems (electrophiles). Evidently, the tremendous attention received by them is due to the large number of chemical transformations that can be achieved and the wide range of reaction conditions that can be tolerated by these reagents.

Allylsilanes have been used for the nucleophilic linkage of allyl group to various electrophiles.\(^2\) This has emerged as a very useful protocol since allylsilanes are relatively stable and are easily accessible by conventional synthetic methods.\(^3\) In addition to simple 1,2- and 1,4-additions, allylsilanes
having bulky substituents on silicon can be utilized to annulate olefins and carbonyls leading to a variety of four and five-membered rings ranging from carbocycles\textsuperscript{4} to tetrahydrofurans,\textsuperscript{5} oxetanes,\textsuperscript{6} azetidines\textsuperscript{7} and pyrrolidines\textsuperscript{8} in highly stereoselective manner. Another important feature of allylsilane is the ability of silicon to act as hydroxy surrogate.\textsuperscript{9} It has been demonstrated that any organo-silane containing a nucleofugal group such as a halogen, oxygen or nitrogen can be oxidized to a carbinol group with retention of configuration at the silicon bearing carbon. This, in combination with the allylsilane addition to electron deficient olefins or carbonyls has ensured the development of these reagents as valuable additions to the arsenal of synthetic organic chemists.

The emergence of allylsilane as a reagent for synthesis coincided with the advent of Hosomi-Sakurai reaction, although Sommer had studied the electrophilic cleavage of the C-Si bond of allylsilanes in the late 1940’s. The Sakurai reaction involves the nucleophilic transfer of allyl group to enones in a conjugate fashion (Scheme 1). The intramolecular version of this reaction has been subsequently used as the key step in the synthesis of several natural products like Nootkatone,\textsuperscript{10} Perforenone\textsuperscript{11} etc.

\begin{equation}
\text{EtO} 
\text{Nootkatone}
\end{equation}

\textbf{Scheme 1}

Aziridines can also be allylated using allylsilane. A recent synthesis of (-) yohimbane makes use of intramolecular allylation of an aziridine by a suitably tethered allylsilane moiety as the crucial step.\textsuperscript{12}
In another elegant application, total synthesis of Epothilones A and B, potent antitumor macrolides, was achieved by the utilization of chiral silane based bond construction methodology as the key step; the stereocenters developed during subsequent steps were dictated by the chirality induced at this stage (Scheme 3).13

**Scheme 2**

2.1.1. Allylsilanes as dipoles

In some of the reactions of enones with allyltrimethylsilane, formation of silylcyclopentanes as byproducts was observed. Subsequent optimization has shown that the yield of the silylcyclopentane ‘byproduct’ could be enhanced by
using allylsilanes with bulky silyl substituents. This marked the evolution of allylsilanes as formal dipoles. A number of electrophiles has been added to allylsilane under Lewis acid mediation furnishing heterocycles as well as carbocycles. The employment of Lewis acid is mandatory, since allylsilanes are only weakly nucleophilic.

\[ \text{Figure 1} \]

Allylsilanes bearing bulky substituents on silicon can participate as formal 1,2- or 1,3-dipoles. In this context, the most often used reagent is allyltriisopropylsilane. Some of the important examples are outlined in the following sections.

Knölker observed that a range of 1-acetyl cycloalkanes could be pentannulated using allyltriisopropylsilane in presence of TiCl₄ as the Lewis acid. This reaction was diastereoselective in the sense that anti isomer was the major or the sole product (Scheme 4).\(^{15}\)

\[ \text{Scheme 4} \]

It has been further shown that, by employing chiral allylsilanes, one can induce enatioselectivity in the cyclopentannulation reaction (Scheme 5).\(^{16}\)
The same group has reported the domino double allylsilane [3+2] addition-Wagner-Meerwein rearrangement-Friedel-Crafts alkylation-elimination reaction sequence leading to a pentacyclic ring system (Scheme 6).\(^{17}\)

\[ \text{Scheme 6} \]

Allylsilanes can act as formal 1,2-dipoles as well. For instance, a cyclobutene derivative resulted when allyltriisopropylsilane was treated with 3-butyne-1-one (Scheme 7).\(^{18}\)

\[ \text{Scheme 7} \]

The ability of allylsilane to act as formal 1,2-dipole has been elegantly employed in the synthesis of (+)-fragranol, a monoterpenoid alcohol (Scheme 8).\(^{19}\)
Scheme 8

In another study, Panek has shown that allylsilane can annulate nitrosium ion. This constitutes a simple and efficient procedure for the construction of functionalized \( \Delta^2 \)-isoxazolines, which are otherwise accessible by the dipolar cycloaddition of nitrile oxides to alkenes (Scheme 9).\(^{20}\)

\[
\text{Scheme 9}
\]

Quinonemethides also undergo addition of allylsilanes. For example, allyltrisopropylsilane added in a [3+3] fashion to the \( p \)-quinonemethide generated \textit{in situ} from \( p \)-hydroxybenzylalcohol affording tetrahydronaphthalenes in good yields (Scheme 10).\(^{21}\)

\[
\text{Scheme 10}
\]

In its reactions, allylsilane can either act as a formal 1,2-dipole or a 1,3-dipole. The control over the product distribution could in some cases be achieved by suitably selecting the Lewis acid. For example, the outcome of the
reaction between allylsilane and α-keto esters was very much dictated by the identity of the Lewis acid employed; SnCl₄ as the promoter led to in the formation of [3+2] cycloadduct while a formal [2+2] addition occurred when the promoter was TiCl₄. (Scheme 11).

Unlike most of their reactions, allylsilanes annulated chlorosulfonylisocyanate (CSI), without the use of a Lewis acid to silyl substituted pyrrolidinone derivatives (Scheme 12). This reaction makes use of the increased electrophilicity of CSI.

Allyltrisopropylsilane underwent facile addition to β-silyloxy aldehydes affording tetrahydropyran derivatives enantioselectively via a formal [4+2] cycloaddition (Scheme 13).
Boron trifluoride catalyzed [3+2] annulation of N-CBz protected-α-aminoaldehydes with allyltrimethylsilane yielded 2,3,5-trisubstituted pyrrolidines (Scheme 14).\(^{25}\)

![Scheme 14](image)

In a related reaction, trialkylsilylmethyloxazinones were obtained by the addition of allyltrimethylsilane to the iminium species generated \textit{in situ} from N-Boc protected α-methoxy piperidine (Scheme 15).\(^{26}\)

![Scheme 15](image)

In a very recent publication, West has reported the intermolecular trapping of the Nazarov intermediate by a domino electrocyclization-allylation with allylsilanes in a process that has been termed as ‘interrupted Nazarov’ reaction. Here the Nazarov oxyallyl intermediate is intercepted by the carbon nucleophile, allylsilane, to yield diastereomeric mixture of allylated cyclopentanones along with a bicyclo [2.2.1]heptanone derivative as depicted in Scheme 16.\(^{27}\)
Although oxo electrophiles have been studied extensively with regard to the formal cycloaddition of allylsilanes, their aza analogues remain largely unexplored. In the isolated example available, a mixture of two products—the formal [2+2] adduct and the allylated product—were formed when acylimines were treated with allyltriisopropylsilane in presence of various Lewis acids (Scheme 17).\(^7\)

Studies from Panek’s group have shown that chiral croylsilanes add to N-acylimines, generated \textit{in situ} under mild conditions, to afford either homoallylic carbamates or N-carbamoyl pyrrolidines depending on the reaction temperature.\(^8\)
As far as quinonoid compounds are concerned, these species have been studied very scarcely with respect to the addition of allylsilanes and that too mainly restricted to allylation reactions. A discussion of the literature available in this area is presented below.

One of the earliest reports on the addition of allylsilane to quinonoid compounds involves the allylation of 2,3-dimethyl-p-benzoquinone using allyltrimethylsilane (Scheme 19).\(^{28}\)

**Scheme 19**

Allylation of \(p\)-quinones with allyltrimethylsilane in presence of lithium perchlorate in ether (LPDE) has been reported (Scheme 20).\(^{29}\)
A mixture of formal [2+2] and [3+2] adducts resulted when 1,4-naphthoquinone was treated with allyltrimethylsilane in presence of dimethylaluminium chloride (Scheme 21).

Scheme 21

The reaction of 2-acetyl-p-naphthoquinone with allyltriphenylsilane yielded a furanonaphthoquinone derivative in good yield (Scheme 22).

Scheme 22

Photochemical addition of allyltrimethylsilane to 1,2-naphthoquinones affording a formal [2+3] adduct has also been reported. A representative example is given in Scheme 23.

Scheme 23

2.1.2. Mechanistic Aspects

A conceptual framework for the reactions involving the participation of allylsilanes may be constructed to comprise a stepwise mechanism consisting
of; a) nucleophilic addition of allylsilane forming a β-silylcation/siliranium ion b) 1,2-silyl shift (this may or may not happen) and c) quenching of the silylcation. This simple model can explain all the three possible modes of reaction of allylsilanes (Scheme 24). A similar mechanistic model is applicable to allenyl and propargylsilanes also. This model is illustrated with the prototypical allylsilane addition to methyl vinyl ketone (MVK) in the following section.

In this reaction, the initial step involves the Lewis acid assisted addition of allylsilane to MVK in a conjugate fashion affording a β-silylcation/siliranium ion. Subsequent step involves the quenching of the cation, which can take place in three different ways. The Lewis acid coordinated enolate can quench this cation intramolecularly, either through a five membered transition state (attack at the α carbon of the allylsilane, depicted as B in Scheme 24) or through a four membered transition state (attack at the β carbon, A in Scheme 24). In the former case a formal [3+2] adduct results with a concomitant 1,2-silylshift and
in the latter a \([2+2]\) adduct is formed. In both these transformations, allylsilane acts as a silyl-substituted dipole. The third pathway possible for the quenching of the cation is by the attack of a nucleophile at the silicon atom, thereby desilylating the system. Here allylsilane acts as an allylating agent.

The model proposed above offers an explanation for the role of the silyl-substituent in these transformations. If the silane bears sterically demanding substituents, the third pathway, \textit{viz.}, the attack of the nucleophile at the silicon atom is prevented and hence the possibility for allylation is eliminated (Nucleophilic displacement at silicon always follow \(S_N^2\) type mechanism).\textsuperscript{1d}

Thus, allylsilanes, having bulky silyl-substituents act as formal 1,2- or 1,3-dipoles. Conversely, when the silyl-substituents are small, the propensity for the formation of allylated products is high.

A remarkable feature of this addition is the level of stereoselectivity observed. In most of these reactions, the \textit{anti} isomer is formed in major amounts (see Scheme 3, page 3). It is because this reaction proceeds through effective \textit{suprafacial} addition of allylsilane to the double bond of the enone moiety (Scheme 24). Although these reactions do not follow concerted pathways, each step in the mechanistic cascade is sufficiently rapid that rotation about the \(C_\alpha-C_\beta\) bond is not significant. The \textit{anti} stereoselectivity observed in these reactions arises from a preference for a \textit{synclinal} transition state, in accordance with the general topological rule for Michael additions (Figure 2).\textsuperscript{34} Although four different \textit{synclinal} transition states can be written for this reaction, the annulation proceeds \textit{via} the transition state represented in Figure 2 in which the acetyl group adopts an \textit{endo} rather than \textit{exo} orientation with respect to the allylsilane moiety. This arrangement minimizes the charge separation in the dipolar transition state and may also benefit from stabilizing secondary orbital interactions.
2.1.3. The Present Work

It is worthy of note that, although Lewis acid mediated additions of allylsilanes to a host of electrophiles have been investigated, there has been only scant information available on their addition to quinonoid systems. Naphthoquinones feature prominently in these isolated reports. Quinoneimides, the aza analogs of quinones have not received any attention in this connection.

Against this literature scenario and in the context of our interest in the chemistry of quinonoid compounds in general and their cycloaddition profile in particular, it was obligatory to explore the reactivity pattern of allylsilanes to various quinonoid compounds. We have undertaken a detailed investigation of the formal cycloaddition reaction of allyltrisopropylsilane with various quinonoid compounds like substituted 1,2-benzoquinones, isatins, 1,4-benzoquinone diimides and 1,4-benzoquinone monoimides. Preliminary results on the addition of allyltrisopropylsilane to 1,2-benzoquinone diimides are also included. In certain representative cases, allyltriphenylsilane and allyltrimethylsilane have been employed in place of allyltrisopropylsilane. In the present study, a number of Lewis acids such as ZnCl₂, ZnI₂, AlCl₃, BF₃·OEt₂, SnCl₄ and TiCl₄ have been screened as promoters for these reactions.

The various quinonoid compounds selected and the different allylsilanes employed in the present study are shown in Figure 3 and Figure 4 respectively.
2.2. RESULTS AND DISCUSSION

2.2.1. Reaction of Allylsilanes with o-Quinones

Our studies were initiated with the addition of allylsilanes to o-benzoquinones mediated by Zn$^{2+}$. Thus, 4-tert-butyl-o-benzoquinone when treated with allyltriisopropylsilane in presence of stoichiometric amounts of ZnI$_2$ yielded 2-(isopropylsilyl)methyl-5-tert-butyl-7-hydroxydihydrobenzofuran 11a in high yield (Scheme 25).
The structure of the product was established by spectroscopic methods. The IR spectrum of the compound showed absorption at 3424 cm\(^{-1}\) characteristic of OH group. In the \(^1\)H NMR spectrum, C-2 proton furnished a multiplet centered at \(\delta 5.05\). The benzylic protons gave two separate doublet of doublets at \(\delta 3.32\) and 2.87. The peak at \(\delta 4.96\) was found to be exchangeable with D\(_2\)O and was assigned to the phenolic OH. The resonance signal of the \(t\)-butyl group was visible as a sharp singlet at \(\delta 1.26\). The methylene group \(\alpha\)-to the silyl substituent exhibited a multiplet centered at \(\delta 1.41\). The methyl groups of the isopropyl substituents on the silicon were discernible at \(\delta 1.09\) as a broad singlet. The aromatic protons furnished resonance signals at \(\delta 6.74\) and \(\delta 6.72\) as two separate singlets. In \(^{13}\)C NMR, the signal corresponding to C-2 was observed at \(\delta 83.45\) while that of C-3 was discernible at \(\delta 39.80\). The \(t\)-butyl group gave two signals at \(\delta 34.37\) (quaternary carbon) and \(\delta 31.77\). In the aromatic region, the signals due to oxygen substituted carbons were discernible at \(\delta 144.63\) and 143.76 while that for \(t\)-butyl substituted carbon was seen at 139.25. The signal due to methylene carbon \(\alpha\) to silicon appeared at \(\delta 18.05\) while the methyl groups collectively resonated at \(\delta 18.86\). The signal due to the three methine carbons attached to silicon was visible at \(\delta 11.38\). HRMS data for the compound was also found to be satisfactory.
3,5-Di-tert-butyl-o-benzoquinone under ZnCl$_2$ mediation yielded a product in 76% yield, which was found to be identical to 11a by IR, $^1$H NMR and $^{13}$C NMR spectra (Scheme 26).

\[ \text{Scheme 26} \]

Figure 5: $^1$H NMR spectrum of 11a
Presumably, the mechanism of the reaction involves initial 1,6-addition of the allylsilane to Lewis acid coordinated quinone to form a \( \beta \)-silylcatioid/siliranium ion. The cationic center is then quenched by the quinone carbonyl to furnish the product. This is preceded by elimination of a proton in the case of 4-\( t \)-butyl-o-benzoquinone and elimination of a \( t \)-butyl cation in the case of 3,5-di-\( t \)-butyl-o-benzoquinone to yield the product (Scheme 27).
The structure assigned for 11a was further established by methylation of the phenolic OH present in the molecule using methyl iodide in acetonitrile (Scheme 28).

![Methylation Reaction](image)

i) Mel, K₂CO₃, MeCN, 0 °C - rt, 5 h, 62%

**Scheme 28**

In the ¹H NMR spectrum of 12, the characteristic signal due to the methoxy group appeared at δ 3.86 as a singlet. The methoxy carbon resonance was discernible at δ 56.25 in ¹³C NMR spectrum.

Tritylquinone 1c on treatment with allyltriisopropylsilane in presence of stoichiometric amounts of ZnI₂ afforded the analogous adduct 11c in 56% yield (Scheme 29).

![Addition Reaction](image)

i) ZnI₂, CH₂Cl₂, -5 °C - rt, 90 min., 56%

**Scheme 29**

In the IR spectrum, the absorption corresponding to the OH group present in 11c was seen at 3340 cm⁻¹. In the ¹H NMR spectrum, the proton α to dihydrofuran oxygen was discernible as a multiplet centered at δ 5.02 while the signals due to the two protons of the benzene ring was seen as separate singlets at δ 6.55 and 6.50. ¹³C NMR spectrum further supported the structure assigned.
The carbons $\alpha$ and $\beta$ to ring oxygen gave signals at $\delta$ 83.85 and 39.74 respectively while the signal at $\delta$ 98.27 was assigned to the trityl carbon. All the other signals were in accordance with the structure assigned.

3-Methoxy-4-$t$-butyl-1,2-benzoquinone 1d under similar conditions did not show any product formation. However, when the reaction was carried out at $-78^\circ$C in presence of SnCl$_4$, the product corresponding to 11d was obtained in 48% yield (Scheme 30).

Characterization of the product was based on conventional spectroscopic data. In the IR spectrum, the peak at 3432 cm$^{-1}$ was assigned to phenolic OH. In the $^1$H NMR spectrum, the multiplet centered at $\delta$ 5.08 was typical of the methine proton $\alpha$ to ring oxygen. The methoxy protons were discernible as a singlet at $\delta$ 3.69 while the signals corresponding to $t$-butyl and isopropyl groups were seen at $\delta$ 1.19 and 1.08 respectively. All the other signals were in accordance with the structure proposed. In the $^{13}$C NMR spectrum, the characteristic signal due to the tetrahedral carbon $\alpha$ to ring oxygen was seen at $\delta$ 85.41 while the signal of the benzylic carbon was discernible at $\delta$ 42.71.

When a similar reaction was carried out with acenaphthenequinone 2, we could not obtain the cycloadduct even after repeated experimentation under a variety of conditions. However, in presence of SnCl$_4$, prolonged stirring of the reaction mixture at room temperature afforded a homoallylic alcohol, resulting from the addition of allylsilane to one of the carbonyl groups (Scheme 31).
The structure of the product was established by spectroscopic methods. In the IR spectrum, OH absorption was seen at 3380 cm\(^{-1}\) while the carbonyl absorption occurred at 1715 cm\(^{-1}\). In \(^1\)H NMR, the protons of the allyl group accorded three multiplets, at \(\delta\) 5.63, 5.03, and at 2.81. The signals due to aromatic protons were discernible at \(\delta\) 7.99 as a multiplet. The \(^{13}\)C NMR spectrum was also in agreement with the structure proposed, with terminal carbon of the allyl group displaying signal at \(\delta\) 116.80 and the signal of carbonyl carbon being present at \(\delta\) 204.35. The tetrahedral carbon in the ring gave signal at \(\delta\) 79.74. The peak at \(\delta\) 41.98 was assigned to sp\(^3\) carbon in the allyl group.

Phenanthrenequinone also did not yield the desired cycloadduct under a variety of conditions. In this case also, allylation of one of the carbonyls occurred when SnCl\(_4\) was employed as the promoter (Scheme 32).
Characterization of the product was carried out, as usual, with the aid of spectroscopic methods. Absorptions due to OH and CO groups were seen respectively at 3436 cm\(^{-1}\) and 1706 cm\(^{-1}\) in the IR spectrum. In \(^1\)H NMR, three multiplets centered at \(\delta 5.56, 4.90\) and 2.46 were characteristic of protons in allyl group. Aromatic protons gave a multiplet centered at \(\delta 7.66\). The signal at \(\delta 4.08\) was found to be exchangeable with D\(_2\)O. In \(^13\)C NMR spectrum, the signal due to carbonyl carbon was visible at \(\delta 203.81\) while carbons in the allyl group exhibited signals at \(\delta 134.62,\) 118.94 and 49.86. The peak at \(\delta 79.81\) was characteristic of tetrahedral carbon present in the ring.

Next we tried some of these reactions employing allyltrimethylsilane in place of allyltriisopropylsilane. The objective here was to gain some insight into the mechanism involved in these transformations. We reasoned that the initial site of attack of the allylsilane would be independent of the nature of the silyl substituents even though post addition sequence would largely rely on this aspect.

Allyltrimethylsilane \(9\) added to both 4-\(t\)-butyl-o-benzoquinone and 3,5-di-\(t\)-butyl-o-benzoquinone affording 3-(2-propenyl)-5-[2-(2-methyl)propyl]catechol (Scheme 33).

![Scheme 33](image)

\[\begin{align*}
1a; \ R_1 &= H, \ R_2 = \text{tBu} \\
1b; \ R_1 &= R_2 = \text{tBu}
\end{align*}\]

i) ZnCl\(_2\), CH\(_2\)Cl\(_2\), -5 °C, 30 min, Ar, 74% (from \(1a\)) 63% (from \(1b\))

The OH groups present in the product gave a broad absorption centered at 3429 cm\(^{-1}\) in the IR spectrum. In \(^1\)H NMR, signals due to the aromatic
protons were discernible as singlets at $\delta$ 6.86 and 6.65. Protons in the allyl group gave three multiplets centered at $\delta$ 5.91, 5.01 and 3.51. The $t$-butyl resonance was observed at $\delta$ 1.33 as a singlet. $^{13}$C NMR spectrum was also in agreement with the structure proposed, with the terminal olefinic carbon furnishing signal at $\delta$ 115.62. All other peaks were in agreement with the structure assigned.

Our next objective was to study the reactivity of allyltriphenylsilane in a representative case. We treated 4-$t$-butyl-$o$-benzoquinone with allyltriphenylsilane under a variety of conditions and found that only SnCl$_4$ could promote this reaction. Here again, we could not observe any cycloaddition; instead allylation of the quinone took place (Scheme 34).

![Scheme 34](image)

i) SnCl$_4$, CH$_2$Cl$_2$, -78 °C, Ar, 30 min, 65%

2.2.2. Reaction of Allylsilanes with Isatin and its Derivatives

We then turned our attention to another class of quinonoid compounds, isatin and its derivatives. N-Methylisatin was found to be unreactive towards allyltrisopropylsilane in presence of Lewis acids like ZnCl$_2$, ZnI$_2$ and AlCl$_3$. However, when boron trifluoride was used as the promoter, a product formation was observed, albeit in low yield (Scheme 35).
Subsequent optimization experiments showed that SnCl$_4$ was the Lewis acid of choice, with N-methylisatin affording the corresponding product in excellent yield (Scheme 36).

The primary structure of the product was assigned by routine spectroscopic methods. In the vibrational spectrum, the amide carbonyl of the oxindole absorbed sharply at 1725 cm$^{-1}$. The $^1$H NMR spectrum was also in agreement with the structure proposed. The methylene protons vicinal to the furan oxygen furnished separate signals; a multiplet at $\delta$ 4.39 and a doublet of a doublet centered at $\delta$ 4.29. The methine proton $\beta$ to furan oxygen afforded a multiplet centered at $\delta$ 1.98. The methylene protons adjacent to the spiro carbon were discernible at $\delta$ 2.49 and $\delta$ 2.24. The peaks at $\delta$ 7.27, $\delta$ 7.03 and $\delta$ 6.78 emanated from the resonances of aromatic protons. The isopropyl groups on silicon gave a broad singlet at $\delta$ 1.13. In the $^{13}$C spectrum, the peak at $\delta$ 81.76
was typical of the spiro carbon in structure 16a. The amide carbonyl was discernible at $\delta$ 178.43. The methylene carbon adjacent to furan oxygen yielded signal at $\delta$ 73.59 while that next to the spirocenter gave signal at $\delta$ 40.21. The signal due to the methine carbon in the furan ring was visible at $\delta$ 25.88 and the signal at $\delta$ 26.05 has been assigned to N-methyl group. Satisfactory elemental analysis was also obtained for the adduct.

Figure 7: $^1$H NMR spectrum of 16a

Figure 8: $^{13}$C NMR spectrum of 16a
It is conceivable that the mechanism of the reaction involves the initial nucleophilic addition of allylsilane to the Lewis acid coordinated keto carbonyl of isatin. The $\beta$-silylcation/siliranium ion so formed is quenched by the tin alkoxide with a concomitant sila Wagner-Meerwein rearrangement to give the product (Scheme 37).

\[ 4a + \text{Si(Pr)\textsubscript{3}} + \text{SnCl\textsubscript{4}} \rightarrow 16a \]

Scheme 37

The remaining issue to be addressed is the stereochemistry of the silyl substituent with respect to the amide group present in the product. This assumes importance since allylsilane addition is highly stereoselective. To establish the relative stereochemistry, we resorted to single crystal X-ray analysis (Figure 9). The X-ray structure established the relative stereochemistry to be syn (Scheme 38).
The observed stereochemical outcome can be rationalized along the following lines. The reaction proceeds through a synclinal transition state because in such an arrangement the separation of the charges in the transition state is minimum. Of the four synclinal transition states possible, one that is depicted below, with carbonyl of the isatin oriented \textit{endo} with respect to silane moiety, is the most favorable one.
The reaction was found to be general with various isatin derivatives affording the corresponding products in good yields. The results are summarized in Table 1.
<table>
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<th>Product</th>
<th>Yield (%)*</th>
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*isolated yield
SnCl₂, CH₂Cl₂, -5 °C – rt

Table 1

For the sake of comparison, we have carried out the above reaction employing allyltrimethylsilane instead of allyltriisopropylsilane. Due to the
presence of sterically less demanding methyl groups, we expected the allylation
of the carbonyl of the isatin. This was borne out by the actual experiment
(Scheme 40).

![Scheme 40]

Allyltributyltin was more effective for the above transformation, the
product was formed instantaneously in quantitative yield (Scheme 41).

![Scheme 41]

Although we have attempted the reaction with allyltriphenylsilane, we
could not observe any product formation. This may be attributed to the lower
nucleophilicity of allyltriphenylsilane compared to allyltrisopropylsilane.35

2.2.3. Reaction of allylsilane with quinoneimides

Investigations involving quinoneimides contribute our major endeavor
for the following reasons. First, quinoneimides have received only scant
attention and have figured only in a limited number of studies despite their long
history in chemistry. Then, allylsilanes themselves have been studied and
proved to undergo addition to a variety of electrophiles save imines. Coupled with this literature scenario, our own long-standing interest in the chemistry of quinonoid compounds provides the rational basis for our investigations.

\textbf{\textit{p-Quinone diimides}}

The reaction of \textit{p}-quinone ditoluenesulfonimide with allyltriisopropylsilane mediated by zinc chloride constituted our initial experiment. We could isolate two products from this reaction; a 2:1 adduct of allylsilane with quinoneimide, which is formed in major amounts, and a 1:1 adduct (Scheme 42).

\begin{align*}
\text{NTs} & \quad \text{Si(Pr)}_3 \\
\text{NTs} & \quad \text{Si(Pr)}_3 \\
5a & \quad 8 \\
\text{Ts} & \quad \text{Ts} \\
& \quad \text{Ts}
\end{align*}

\begin{align*}
\text{N} & \quad \text{Ts} \\
\text{N} & \quad \text{Ts} \\
18a & \quad 19a
\end{align*}

\textit{i)} \text{ZnCl}_2, \text{CH}_2\text{Cl}_2, 0 \, ^\circ \text{C} \rightarrow \text{rt}, \text{Ar}, 72 \, h, 43\% (18a), 16\% (19a)

\textbf{Scheme 42}

The structure of the adduct \textit{18a} was established by spectroscopic methods. The IR spectrum of the compound was of limited help. The characteristic peaks due to sulfonyl absorption were seen at 1330 cm\(^{-1}\) and 1110 cm\(^{-1}\). The \textit{\textsuperscript{1}H} and \textit{\textsuperscript{13}C} NMR spectra of the product suggested that it was highly symmetric. In \textit{\textsuperscript{1}H} NMR, the methine proton adjacent to nitrogen was discernible as a multiplet between \textit{\delta} 4.46-4.52. The benzylic methylene protons afforded two separate signals; a doublet of a doublet at \textit{\delta} 2.74 and a multiplet between \textit{\delta} 2.36-2.46. The signal due to methyl protons of the tosyl substituent was embedded in this multiplet. Two of the four exocyclic methylene protons furnished signal as a doublet of a doublet at \textit{\delta} 1.43 and the remaining two
Chapter 2

resonated with the isopropyl groups at δ 1.17. In $^{13}$C NMR spectrum, signal due to methine carbons $\alpha$ to the ring nitrogen was discernible at δ 62.10 while the methylene carbon $\beta$ to ring nitrogen was seen at δ 36.51. The methine carbons of the central benzene ring gave signal at δ 114.70. The resonance due to triisopropylsilylmethylene carbon was discernible at δ 19.20 while the three isopropyl groups themselves yielded two signals at δ 18.82 and δ 11.53. The compound also afforded satisfactory elemental analysis. Finally, the structure was unambiguously established by single crystal X-ray analysis.

Figure 10: $^1$H NMR spectrum of 18a
Figure 11: $^{13}$C NMR spectrum of 18a

Figure 12: Single crystal X-ray structure of 18a

The structure of the 1:1 19a adduct was also established by spectroscopic methods. This is described in a later section (see page 65).
A mechanistic rationale for the formation of the product can be given along the following lines. ZnCl₂ initially coordinates with one of the imine nitrogens. This species is comparatively stable so that another molecule of Lewis acid can coordinate with the second imine nitrogen as well. Two molecules of allylsilane then add in a conjugate fashion to this bi-coordinated species forming a bis-β-silyl cation S. Subsequent quenching of these cationic centers occurs as depicted in Scheme 43 affording the product.

Scheme 43

It was of interest to examine the influence of other Lewis acids and/or temperature on the course of this reaction. Thus, when SnCl₄ was employed as the Lewis acid, the dihydroindole derivative 19a was obtained in excellent yield (Scheme 44). It may be recalled that this was the minor product in the ZnCl₂ mediated reaction.
The structure of 19a was ascertained by analytical and spectroscopic methods. The IR spectrum showed NH absorption at 3230 cm\(^{-1}\) and the sulfonyl absorptions at 1334 and 1108 cm\(^{-1}\). The \(^1\)H NMR spectrum was in consonance with the structure proposed. The methine proton adjacent to the ring nitrogen displayed its signal as a multiplet between \(\delta 4.38-4.45\). The signal at \(\delta 6.75\) was exchangeable with D\(_2\)O and has been assigned to the NH resonance. Signals due to methylene protons in the dihydroindole core were discernible as separate doublet of doublets centered at \(\delta 2.68\) and \(\delta 1.38\). The resonance of three isopropylmethine protons displayed a multiplet centered at \(\delta 0.86\) while resonance signal of isopropyl methyl groups was seen at \(\delta 1.07\) as a broad singlet. The two methyl groups in the tosyl appendage gave separate singlets at \(\delta 2.37\) and \(\delta 2.41\). The \(^{13}\)C spectrum was also in agreement with the structure proposed. The peak at \(\delta 61.58\) was typical of the carbon \(\alpha\) to the ring nitrogen in dihydroindole derivatives. The benzylic methylene carbon displayed signal at \(\delta 36.47\) while resonance of methylene carbon attached to silicon was visible at \(\delta 19.20\). The compound also gave satisfactory microanalysis data.
A mechanistic rationale for the formation of 19a can invoke the initially formed mono-coordinated species which suffers attack by allylsilane. The β-silylcation so formed is stable enough so that another molecule of Lewis acid induces the tautomerization of the second imine nitrogen to the enamine form. The resulting species now has two metalloenamine moieties that can quench the
\( \beta \)-silyl cation offering the possibility for the formation of two products. However, the reaction proceeds by the quenching of the \( \beta \)-silyl cation by the N-terminus of the enamine moiety II affording the product (Scheme 45).

We further probed the reaction by employing boron trifluoride etherate as the Lewis acid. In this case, interestingly, allyltriisopropylsilane added to endocyclic double bond of quinoneimide in a [3+2] fashion (Scheme 46).

\[ i) \text{BF}_3\cdot\text{OEt}_2, \text{CH}_2\text{Cl}_2, \text{rt}, \text{Ar}, 90 \text{ min.}, 51\% \]

Scheme 46
As usual the assignment of the structure is based on the routine spectroscopic methods, especially, $^1$H and $^{13}$C NMR. The IR spectrum of 20a showed absorption at 3320 cm$^{-1}$ indicating the presence of NH group in the product. In proton NMR, two of the four benzylic methylene protons resonated at $\delta$ 2.62 while the signal due to the other two were discernible along with the methyl resonance as a multiplet between $\delta$ 2.34-2.37. The peak due to silyl substituted methine proton was seen at $\delta$ 1.38 while protons of the isopropyl groups in this case appeared as a multiplet between $\delta$ 0.93-1.06. The $^{13}$C spectrum was also in accordance with the structure proposed. The number of peaks in the $^{13}$C spectrum was exactly half of the total number of carbons present, thus attesting to the plane of symmetry present in the molecule.

Figure 15: $^1$H NMR spectrum of 20a
Here again, the mechanism involves the initial addition of allylsilane to the mono-coordinated imine species in a conjugate fashion forming a \( \beta \)-silylcation. A second molecule of the Lewis acid now converts the second imine nitrogen to the corresponding metallo-enamine. Unlike in the case of SnCl\(_4\) promoted reaction, here the *bis* metalloenamine formed is a strong C-terminal nucleophile\(^{36} \) which subsequently quenches the \( \beta \)-silylcation to afford the product as depicted in Scheme 47. Thus, the essential difference in SnCl\(_4\) and BF\(_3\) promoted reactions is the N-alkylation (SnCl\(_4\)) versus C-alkylation (BF\(_3\)) of the metallo-enamine intermediate formed.
The results discussed so far are summarized in Scheme 48.
No reaction was observed when 2,5-dimethyl-p-quinone dibenzenesulfonimide was treated with ZnCl₂. Similarly, BF₃.OEt₂ also failed to induce reaction. However, with SnCl₄, we were able to isolate a dihydroindole derivative 19b (Scheme 49).

![Scheme 49](image)

i) SnCl₄, CH₂Cl₂, -41 °C–rt, Ar, 5 h, 47%

The IR spectrum of the compound showed absorption at 3320 cm⁻¹ characteristic of NH stretching. In the ¹H NMR, the methine proton adjacent to the ring nitrogen of the dihydroindole showed up as a multiplet between δ 4.43-4.46. The benzylic methylene protons were discernible at δ 1.78 and δ 1.26 as separate doublet of doublets. The methyl group in the dihydroindole core gave signals at δ 2.47 and δ 1.65. The ¹³C NMR spectrum of the compound was also in agreement with the structure proposed, with the signal from the methine carbon α to ring nitrogen appearing at δ 62.26. The benzylic methylene carbon afforded signal at δ 35.95.

To gain further insight into the mechanistic aspects, we have carried out the reaction of 5a with allyltrimethylsilane under the conditions employed for reaction with allyltriisopropylsilane. In the case of promotion by ZnCl₂, we obtained a mixture of mono- and di-allylated products in the ratio 1:3. However with SnCl₄ and BF₃.OEt₂ only mono-allylated product was formed.

Our efforts to add allyltriphenylsilane to 5a under a variety of conditions were not fruitful.
Chapter 2

p-Quinone monoimides

The next phase of our study involved addition of allylsilanes to p-quinone monoimides. When p-benzoquinone monobenzenesulfonimide was treated with allyltrisopropylsilane in presence of SnCl₄, a dihydrobenzofuran derivative 21a was obtained (Scheme 50).

\[ \text{6a} \quad + \quad \text{8} \quad \rightarrow \quad \text{21a} \]

i) SnCl₄, CH₂Cl₂, -78 °C, Ar, 30 min., 91%

Scheme 50

Structure of the adduct was established by spectroscopic methods. Absorption due to NH stretching was present at 3269 cm⁻¹ in the IR spectrum. In the ¹H NMR spectrum, proton on the α carbon in the dihydrobenzofuran moiety gave signal at δ 4.95 as a multiplet while the benzylic methylene hydrogens gave separate doublet of doublets at δ 3.25 and 2.76. The singlet at δ 6.94 due to NH was found exchangeable with D₂O. In ¹³C spectrum, the signal due to α carbon was seen at δ 82.67 while benzylic carbon resonance occurred at δ 38.51. All the other signals were in agreement with the structure proposed.

The structure of the adduct was further confirmed by the methylation of the secondary amino group present in 21a.

\[ \text{21a} \quad \xrightarrow{i) \text{K₂CO₃, Mel, nBu₄NI, Ar, Acetone, reflux, 24 h, 80%}} \quad \text{22} \]

Scheme 51
In the $^1$H NMR of 22, the characteristic N-methyl protons were discernible at $\delta$ 3.11 as a sharp singlet while in $^{13}$C spectrum the N-methyl carbon resonated at $\delta$ 38.90.

When 3-methoxy-$p$-quinone monobenzenesulfonimide was treated with allyltrisopropylsilane in presence of SnCl$_4$, we observed the formation of 5-aminodihydrofuran derivative 21b (Scheme 52).

\[
\text{6b} + \text{8} \xrightarrow{i)} \text{21b}
\]

i) SnCl$_4$, CH$_2$Cl$_2$, -78 °C- r.t, Ar, 2.5 h, 72%

Scheme 52

The structure of the product was assigned on the basis of spectroscopic analysis. The NH absorption was visible at 3268 cm$^{-1}$ in the IR spectrum of the compound. In $^1$H NMR, the resonance from the proton $\alpha$ to ring oxygen was seen as a multiplet between $\delta$ 4.95-5.05. One of the benzylic protons gave signal at $\delta$ 2.81 as a doublet of a doublet while the signal from its counter part was seen along with the signal of methoxy protons as a multiplet between $\delta$ 3.25-3.33. The aromatic proton sandwiched by methoxy group and the ring oxygen was discernible at $\delta$ 6.08. The methine carbon signal was seen at $\delta$ 83.39 while the benzylic methylene carbon appeared at $\delta$ 38.61 in the $^{13}$C spectrum of the compound. The peak at $\delta$ 55.48 was assigned to the methoxy carbon resonance while the signal at $\delta$ 93.34 was attributed to the aromatic carbon C-7.

The 2-methoxy analog 6c also under the same conditions yielded the corresponding dihydrobenzofuran derivative (Scheme 53).
For 21c, the NH absorption in IR spectrum was visible at 3281 cm⁻¹. In ¹H NMR, resonance due to the proton α to the ring oxygen was observed as a multiplet between δ 4.98-5.06. The benzylic methylene protons gave two separate doublets of doublet at δ 3.20 and δ 2.79. The aromatic proton at C-6 showed signal at δ 6.39. The ¹³C NMR spectrum was also in agreement with the structure assigned. The peaks at δ 83.60 and δ 38.72 were characteristic of the α and β carbons respectively in the dihydrobenzofuran core. The signal due to C-6 of the central aromatic ring was discernible at δ 108.32.

From these experiments, it is evident that regardless of the chemical environment, SnCl₄, preferentially coordinates to imine nitrogen of the quinone monoimide. Now the allylsilane adds in a 1,4-fashion to the Lewis acid coordinated imine to form the β-silylcation/siliranium ion which is subsequently quenched by the carbonyl oxygen to afford the product (Scheme 54).
For the particular transformation under discussion, we have used other Lewis acids, viz., BF$_3$OEt$_2$, AlCl$_3$ and InCl$_3$. In all the cases the same product was formed, albeit, in lower yields.

Allyltriphenylsilane also behaved similarly affording the analogous product (Scheme 55).

The product was characterized using usual spectroscopic tools. The absorption due to the NH stretching was observed at 3269 cm$^{-1}$ in the IR spectrum. In $^1$H NMR, the characteristic signal due to $\alpha$ hydrogen atom present
in the dihydrobenzofuran ring was discernible as multiplet centered at $\delta 4.99$. The $^{13}$C NMR data also supported the proposed structure with $\alpha$ carbon in the dihydrobenzofuran ring displaying signal at $\delta 82.08$ and the benzylic methylene carbon resonating at $\delta 37.90$. The compound also afforded satisfactory HRMS data.

**o-Quinoneimides**

A preliminary investigation into the reactivity of *ortho*-quinoneimides was also carried out and for these studies, we have selected two substrates, *viz.*, 4-methyl-*o*-benzoquinone dibenzenesulfonimide and *o*-benzoquinone dibenzimide.

When 4-methyl-*o*-benzoquinone dibenzenesulfonimide was treated with allyltriisopropylsilane in presence of ZnCl$_2$ as the promoter, a formal [3+2] cycloadduct resulted (Scheme 56).

\[
\begin{align*}
\text{7a} & \quad \text{NSO}_2\text{Ph} & \quad + & \quad \text{Si(Pr)$_3$} & \quad \rightarrow & \quad \text{24} \\
\text{8} & & & & & \\
\text{i)} & \quad \text{ZnCl$_2$, CH$_2$Cl$_2$, -5 °C–rt, Ar, 3 h., 52%} & \\
\end{align*}
\]

**Scheme 56**

The structure of the [3+2] adduct was assigned on the basis of spectroscopic data. The IR spectrum of the compound showed a broad peak centered at 3378 cm$^{-1}$ indicating the presence of NH moiety. In the proton NMR spectrum, the methylene protons gave two separate multiplets; one between $\delta 3.05$-$3.41$ and the other between $\delta 2.76$-$2.95$. The signal due to the methyl group on the aromatic ring was visible at $\delta 1.96$. The solitary proton present on the central aromatic ring resonated at $\delta 6.51$ as a singlet. In the $^{13}$C NMR spectrum, the two ring methylene carbons were visible at $\delta 34.85$ and 32.57
while the methyl group on the aromatic ring gave signal at $\delta$ 21.76. The resonance signal due to ring carbon bearing the silyl group was seen at $\delta$ 17.76.

This reaction was found to be insensitive to the nature of the Lewis acid employed. Of the several Lewis acids employed, ZnCl$_2$ proved to be the catalyst of choice, with others like SnCl$_4$ and BF$_3$.OEt$_2$ turning out to be much less efficient.

With o-quinone dibenzimide the reaction took another course; allyltriisopropylsilane simply allylated the benzimide yielding the 4-allyl-o-phenylenediamine derivative 25 (Scheme 57).

\[
\begin{align*}
\text{NHCOPh} & \quad \text{NHCOPh} \\
\text{7b} & \quad \text{8} \quad \text{i)} \quad \text{ZnCl}_2, \text{CH}_2\text{Cl}_2, -5^\circ\text{C} \rightarrow \text{rt}, \text{Ar}, 3 \text{ h.}, 46\%
\end{align*}
\]

\textbf{Scheme 57}

The IR spectrum of the compound exhibited absorption at 3226 cm$^{-1}$ suggestive of the presence of the NH group. The amide carbonyl was noticeable at 1650 cm$^{-1}$. In the $^1$H NMR, the protons on the central aromatic ring gave three signals; a doublet at $\delta$ 7.24 due to C-5 proton, a singlet at $\delta$ 7.03 due to C-3 proton resonance and yet another doublet at $\delta$ 6.41 due to C-6 proton. The presence of a singlet at $\delta$ 7.03 in the aromatic region rules out the possibility of the alternate C-3 allylated structure. The peaks at $\delta$ 9.69 and $\delta$ 9.62 were exchangeable with D$_2$O thus attributable to the NH proton resonances. The protons on the allyl group manifested in the characteristic way with the internal alkenyl proton giving a signal as a multiplet between $\delta$ 5.28-5.39. Resonance signal due to terminal alkenyl protons was seen at $\delta$ 4.62-4.75 as a multiplet, while the signal due to the methylene group of the allyl moiety was discernible at $\delta$ 2.63 as a doublet. In the $^{13}$C spectrum, amide carbonyls gave signal at
δ 166.35. The carbon resonances of the allyl group were seen at δ 115.84, 132.09 and 38.87.

With o-quinoneimides also, the initial event involves the conjugate addition of allylsilane to the imide forming β-silylcation/siliranium ion (Scheme 58). The subsequent step depends on the nature of the imide substituent. If it is benzenesulfonyl group, the metalloenamine attacks the cation through its C-terminus thereby yielding the product consequent to a sila-Wagner-Meerwein rearrangement. However, with benzoyl group on the imide, this pathway is somehow prevented and the siliranium ion suffers nucleophilic attack at the silicon presumably by chloride anion to yield the allylated product. It may be mentioned that this is one of the rare instances where allyltriisopropylsilane acts as an allyl anion equivalent in its reaction with electrophiles.

\[
\begin{align*}
\text{Lewis acid} & \quad \text{Lewis acid} \\
\text{Cl} & \quad \text{Si}(\text{Pr})_3 \\
\text{NR'} & \quad \text{NR'} \\
R & \quad \text{SO}_2\text{Ph} \\
\text{Si}(\text{Pr})_3 & \quad \text{H} \\
\text{NR'} & \quad \text{COPh} \\
\text{R} & \quad \text{H} \\
\text{NR'} & \quad \text{NR'} \\
\text{R} & \quad \text{NR'} \\
\text{NHR'} & \quad \text{NHR'} \\
\text{24} & \quad \text{25}
\end{align*}
\]

Scheme 58
In conclusion, it has been shown that quinonoid compounds, viz., o-benzoquinones, isatins, p-quinoneimides and o-quinoneimides can act as efficient receptors for allylsilanes in Lewis acid promoted reactions. Both [2+3] and [3+2] addition of allylsilanes to quinonoids have been observed depending on the identity of the quinonoid compound and the conditions employed. It is worth mentioning that the structures of most of the compounds so formed closely resemble the structural framework of some naturally occurring compounds of interest. The process is remarkably facile for the synthesis of indole and benzofuran derivatives, structural motifs frequently encountered in biologically active compounds. Seratonin, psilocine, LSD etc are some of the indole derivatives, which have profound effects on brain functions. Basic structural feature identified with a variety of lignans and neolignans is a benzofuran moiety. Conceivably, this methodology of addition of allylsilanes to quinonoid compounds will find application in the synthesis of some natural products of the type mentioned and their congeners.

Figure 17
2.3. EXPERIMENTAL

**General:** All compounds were prepared as racemic mixtures. All reactions were conducted in oven-dried glasswares under an atmosphere of argon with magnetic stirring unless otherwise noted. Solvents used for experiments were distilled and dried according to literature procedures. SnCl₄ (1M solution in heptane), BF₃.OEt₂, InCl₃, allyltriisopropylsilane, allyltriphenylsilane and allyltrimethylsilane were purchased from Aldrich and used as received. TiCl₄ was of Merck make and ZnI₂ was purchased from Lancaster, both were used as supplied. All other reagents were purchased from commercial vendors and used as received. NMR spectra were recorded in Bruker 300 MHz FT-NMR spectrometer on samples dissolved in CDCl₃-CCl₄ mixtures (7/3 v/v) and chemical shifts are reported in δ (ppm) relative to Me₄Si (¹H NMR) or CDCl₃ (¹³C NMR) as internal standards. Abbreviations for NMR multiplicities are as follows: s, singlet; d, doublet; m, multiplet; dd, doublet of doublet and bs, broad singlet. Coupling constants J are reported in hertz (Hz). IR spectra were recorded in Bomem MB Series FT-IR spectrophotometer, absorbencies are reported in cm⁻¹. High resolution mass spectra were obtained using Finnigan MAT model 8430. Melting points were recorded on Mel-temp II Laboratory Devices, USA and are uncorrected. All reactions were monitored by thin layer chromatography (TLC); visualization was effected with a UV lamp and/or by staining with p-anisaldehyde/H₂SO₄ and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (100-200 mesh).

2.3.1. Preparation of quinoneimides

The quinoneimides 6a³⁵, 6b³⁶, 6c³⁷ and 7b³⁸ were prepared according to literature procedures while for the preparation of 5a, 5b, 5c and 7a, slightly modified procedures of literature reports were adopted as described below.
Preparation of 1,4-benzoquinone ditoluenesulfonimide (5a)

To a solution of 1,4-phenylenediamine (2.162 g, 20 mmol) in dry CHCl₃ was added p-toluenesulfonylchloride (7.626 g, 40 mmol) in portions over a period of 15 min. at 0 °C. After the addition is complete, the reaction mixture was brought to room temperature and stirred for 3 h. It was then poured to 2N HCl (100 mL) and filtered. The residue was washed successively with water (100 mL), 2N HCl (100 mL) and water (2 x 100 mL) and dried in vacuum oven at 70 °C. This crude sulfonamide itself was sufficient for the subsequent oxidation step.

A suspension of 1.04 g of powdered p-phenylene-di-p-toluenesulfonamide in 40 mL of glacial acetic acid was treated with 1.1 g of lead(IV) acetate (96%, Aldrich). The mixture, which became yellow within 5 min., was stirred at room temperature for 6 h. After addition of 0.15 mL of ethylene glycol, it was further stirred for 2 min. and filtered. The residue was washed with acetic acid (10 mL) and dried at room temperature. The crude diimide was then passed through a column of Celite® using CH₂Cl₂ to obtain analytically pure diimide (940 mg, 90%). mp. 210–212 °C

Preparation of 2,5-dimethyl-1,4-dibenzencesulfonimide (5b)

A solution of 2.65 mL of benzenesulfonylchloride in 5 mL of dry pyridine was added cautiously to a solution of 1.3 g of 2,5-diamino-p-xylene in 13 mL of dry pyridine. The reaction mixture was allowed to stand at room temperature overnight and then poured into mixture of ice and hydrochloric acid. The pasty mass that separated from the solution became solid
within a short time. This was powdered and washed free from acid. A solution of the wet cake in 10% aqueous sodium hydroxide was heated on a steam bath for 10 min. with charcoal. After filtration, the solution was cooled and poured into ice and hydrochloric acid. The white precipitate was collected by filtration, washed with water and dried. The yield of the product was 2.8 g (73%).

In 20 mL of pyridine, 1.43 g of 2,5-dibenzenesulfamido-\(p\)-xylene was dissolved by heating and the solution then cooled carefully to avoid the crystallization of the compound. A solution of 0.35 mL of bromine in 7 mL of pyridine was added cautiously with cooling. Within five min. after addition, the mixture was poured into ice and hydrochloric acid. The yellow compound that separated was collected by filtration, washed repeatedly with water and dried (1.16 g, 80%).

**Preparation of 1,4-benzoquinonedibenamid (5c)**

A solution of 1,4-phenylenediamine (1.94 g, 18 mmol) in 120 mL of dry tetrahydrofuran was treated with potassium carbonate (10 g, 72.5 mmol) and benzoyl chloride (5.5 g, 38 mmol) and the reaction was stirred for 12 h at 25 °C. The reaction mixture was poured into 200 mL of 10% aq. hydrochloric acid and filtered. The collected white solid was washed with water (100 mL) and hexane (100 mL) to afford \(p\)-phenylene dibenzamide (8 g).

A suspension of 1.35 g of \(p\)-phenylenedibenzamide and 1.87 g of lead(IV) acetate (99.99%, Aldrich) in 90 mL of dry, thiophene free benzene was heated under reflux for 15 h.
The reddish solution was filtered and reduced in volume to about 25 mL. Petroleum ether (bp. 80-110 °C) was added and the solution chilled in a liquid nitrogen-acetonitrile bath. The yield of quinoneimide was 1 g, 75%.

**Preparation of 4-methyl-1,2-benzoquinonedibenzenesulfonimide (7a)**

![Diagram of reaction](image)

To a solution of 3,4-diaminotoluene (6.1 g, 50 mmol) in 35 mL of pyridine, 18 g of benzenesulfonylchloride was added slowly with cooling and the mixture was allowed to stand at room temperature for 30 min. Upon pouring into 175 mL of hot 50% aq. methanol and cooling afforded 4-methyl-o-quinone dibenzenesulfonamide (12 g).

A mixture of 4-methyl-o-quinone dibenzenesulfonamide (900 mg) and lead(IV) acetate (1.4 g) was stirred in 7.5 mL of glacial acetic acid for 30 min. at room temperature. After addition of a few drops of glycerol to the thick orange slurry, it was stirred for five min. longer, cooled slightly and the orange–yellow diimide was collected on a filter. It was then washed with cold acetic acid (2 mL) and dried in a vacuum dessicator. The yield of the product was 290 mg (33%).

**Experimental Procedures and Data for the Compounds Synthesized**

2-(Triisopropylsilyl)methyl-5-tert-butyl-2,3-dihydrobenzofuran-7-ol (11a)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 4-tert-butyl-1,2-benzoquinone 1a (33 mg, 0.20 mmol) in 4 mL CH₂Cl₂ was cooled to 0 °C and ZnI₂ (76 mg, 0.24 mmol) was added. The temperature of the reaction was maintained at −5 °C-0 °C for initial 30 min. and was then allowed to attain room temperature gradually. After stirring for 1 h, the reaction was quenched with water. The mixture was extracted with CH₂Cl₂ (3 x 10 mL), and the organic layer was dried (Na₂SO₄), concentrated and the residue was subjected to
column chromatography on silica gel. Initial elution with hexane yielded unreacted 8 and subsequent elution with 1% ethylacetate in hexane afforded 11a as a pale yellow viscous liquid (61 mg, 84%).

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 3,5-di-tert-butyl-1,2-benzoquinone 1b (44 mg, 0.20 mmol) in 4 mL CH₂Cl₂ was cooled to 0 °C and ZnCl₂ (33 mg, 0.24 mmol) was added. The temperature of the reaction was maintained at -5 °C-0 °C for initial 30 min. and then allowed to attain room temperature gradually. After stirring for 4 h, the reaction was quenched with water. The mixture was extracted with CH₂Cl₂ (3 x 10 mL), and the organic layer was dried (Na₂SO₄), concentrated and the residue was subjected to column chromatography on silica gel. Initial elution with hexane yielded unreacted 8 and subsequent elution with 1% ethylacetate in hexane afforded 11a as a pale yellow viscous liquid (55 mg, 76%).

IR (cm⁻¹) : 3424, 2946, 2866, 1616, 1492, 1183, 1050, 882

¹H NMR : 6.74 (s, 1H), 6.72 (s, 1H), 5.07-4.99 (m, 1H), 4.96 (s, 1H, exchangeable with D₂O), 3.32 (dd, 1H, J = 14.9, 8.4 Hz), 2.87 (dd, 1H, J = 14.9, 8.2 Hz), 1.44–1.31 (m, 2H), 1.26 (s, 9H), 1.09 (bs, 18H), 0.87-0.83 (m, 3H)

¹³C NMR : 144.63, 143.76, 139.25, 127.46, 113.36, 112.10, 83.45, 39.80, 34.37, 31.77, 18.86, 18.05, 11.38

HRMS (EI) Calcd for C₂₂H₃₈O₂Si: 362.26410. Found: 362.26431

2-(Triisopropylsilyl)methyl-5-tert-butyl-7-methoxy-2,3-dihydrobenzofuran (12)
A solution of \textit{11a} (80 mg, 0.22 mmol) and K$_2$CO$_3$ (37 mg, 0.26 mmol) in 2 mL dry acetonitrile was cooled to 0 °C and methyl iodide (63 mg, 0.44 mmol) was added. After initial cooling, the reaction was stirred at room temperature for 5 h. Then solvent from the reaction mixture was removed and 5 mL of water was added. It was extracted with CH$_2$Cl$_2$ (3 x 10 mL) and the organic layer was washed with brine, dried (Na$_2$SO$_4$) and concentrated. The residue on silica gel column chromatography afforded \textit{12} as a pale yellow liquid (52 mg, 62%).

\textbf{IR (cm$^{-1}$)} : 2956, 2862, 1601, 1489, 1463, 1320, 1195

\textbf{\textit{1}H NMR} : 6.77 (s, 1H), 6.72 (s, 1H), 5.09–4.99 (m, 1H), 3.86 (s, 3H), 3.28 (dd, 1H, $J = 14.8, 8.2$ Hz), 2.86 (dd, 1H, $J = 14.8, 8.9$ Hz), 1.55–1.49 (m, 2H), 1.28 (s, 9H), 1.08 (s, 18H), 0.88–0.85 (m, 3H)

\textbf{\textit{13}C NMR} : 145.67, 143.96, 143.43, 128.06, 113.94, 109.52, 83.07, 56.25, 39.11, 34.51, 31.81, 18.83, 18.03, 11.33

\textbf{2-(Triisopropylsilyl)methyl-5-triphenylmethyl-2,3-dihydrobenzofuran-7-ol (11c)}

A solution of allyltriisopropylsilane \textit{8} (48 mg, 0.24 mmol) and 4-trityl-1,2-benzoquinone \textit{1c} (70 mg, 0.20 mmol) in 4 mL CH$_2$Cl$_2$ was cooled to 0 °C and ZnI$_2$ (76 mg, 0.24 mmol) was added. The temperature of the reaction was maintained at −5 °C-0 °C for initial 30 min. and then allowed to attain room temperature gradually. After stirring for 1 h. at that temperature, the reaction was quenched with water. The mixture was extracted with CH$_2$Cl$_2$ (3 x 10 mL), and the organic layer was dried (Na$_2$SO$_4$), concentrated and the residue was subjected to column chromatography on silica gel. Initial elution with hexane
yielded unreacted 8 and subsequent elution with 1% ethylacetate in hexane afforded 11c as a pale yellow viscous liquid (61 mg, 56%).

IR (cm\(^{-1}\))

<table>
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(NEAT) 1182, 1054, 697

\(^1\H NMR\)

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\(^{13}\C NMR\)

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2-(Triisopropylsilyl)methyl-5-tert-buty1-6-methoxy-2,3-dihydrobenzofuran-7-ol (11d)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 3-methoxy-4-tert-butyl-1,2-benzoquinone 1d (39 mg, 0.20 mmol) in 4 mL \(\text{CH}_2\text{Cl}_2\) was cooled to \(-78\) °C and \(\text{SnCl}_4\) (0.24 mL, 1M solution in heptane) was added. The temperature of the reaction was allowed to attain room temperature gradually. After stirring for 30 min. at room temperature, the reaction was quenched with sat. \(\text{NH}_4\text{Cl}\) and the mixture was extracted with \(\text{CH}_2\text{Cl}_2\) (3 x 10 mL). The organic layer was washed with brine (1 x 10 mL), dried with \(\text{Na}_2\text{SO}_4\) and concentrated. The resulting residue on column chromatography yielded 11d as a yellow viscous liquid (38 mg, 48%).

IR (cm\(^{-1}\))

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2-Hydroxy-2-(2-propenyl)-1(2H)-acenaphthylene (13)

A solution of allyltrisopropylsilane 8 (48 mg, 0.24 mmol) and acenaphthenequinone 2 (35 mg, 0.20 mmol) in 4 mL CH₂Cl₂ was cooled to -5 °C and SnCl₄ (0.24 mL, 1M solution in heptane) was added. The temperature of the reaction was allowed to attain room temperature gradually. After stirring for 24 h. at room temperature, the reaction was quenched with sat. NH₄Cl and the mixture was extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was washed with brine (1 x 10 mL), dried with Na₂SO₄ and concentrated. The resulting residue on column chromatography yielded 13 as a colorless solid (32 mg, 41%), mp. 149-151 °C

IR (cm⁻¹) : 3380, 1715, 1607, 1256, 1027, 791, 526 (KBr)

¹H NMR : 8.15-7.68 (m, 6H), 5.69-5.58 (m, 1H), 5.10-4.97 (m, 2H), 2.85-2.77 (m, 2H), 2.65 (s, 1H)
10-Hydroxy-10-(2-propenyl)-9-(10H)phenanthrenone (14)

A solution of allyltrihisopropylsilane 8 (48 mg, 0.24 mmol) and phenanthrenequinone 3 (42 mg, 0.20 mmol) in 4 mL CH₂Cl₂ was cooled to -5 °C and SnCl₄ (0.24 mL) was added. The temperature of the reaction was allowed to attain room temperature gradually. After stirring the reaction mixture for 24 h. at room temperature, the reaction was quenched with sat. NH₄Cl and the mixture was extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was washed with brine (1 x 10 mL), dried with Na₂SO₄ and concentrated. The resulting residue on column chromatography yielded 14 as a colorless solid (31 mg, 39%). mp. 47-48 °C

**IR (cm⁻¹)**

3436, 3073, 1706, 1603, 1458, 1292, 1208

**¹H NMR**

7.95-7.38 (m, 8H), 5.62-5.51 (m, 1H), 5.01-4.80 (m, 2H), 4.08 (s, 1H, exchangeable with D₂O), 2.54-2.38 (m, 2H)

**¹³C NMR**

203.81, 146.31, 138.51 134.62, 131.41, 129.32, 128.93, 128.41, 128.27, 128.19, 127.13, 126.25, 123.94, 123.15, 118.94, 79.81, 49.86

3-(2-Propenyl)-5-tert-butylcatechol (15)

A solution of allyltrihyphenylsilane 10 (90 mg, 0.30 mmol) and 4-tert-butyl-1,2-benzoquinone 1a (41 mg, 0.25 mmol) in 4 mL CH₂Cl₂ was cooled to
-78 °C and SnCl₄ (0.5 mL, 1M solution in heptane) was added. The reaction was maintained at that temperature throughout. After stirring for 30 min., the reaction was quenched with water. The mixture was extracted with CH₂Cl₂ (3 x 10 mL), and the organic layer was dried (Na₂SO₄), concentrated and the residue was subjected to column chromatography on silica gel. Initial elution with hexane yielded unreacted 10 and subsequent elution with 2% ethylacetate in hexane afforded 15 as a colorless viscous liquid (34 mg, 65%).

Allyltrtrimethylsilane 9 and o-quinones 1(a-b) in presence of ZnCl₂ afforded 15 (74% from 1a and 63% from 1b).

**IR (cm⁻¹):**

Neat: 3429, 2967, 2354, 1616, 1483, 1149, 1108, 876, 705

**¹H NMR:**

6.86 (s, 1H), 6.65 (s 1H), 5.97-5.84 (m, 1H), 5.39 (bs, 2H, exchangeable with D₂O), 5.04-4.96 (m, 2H), 3.53-3.50 (m, 2H), 1.33 (s, 9H)

**¹³C NMR:**

140.93, 140.85, 138.60, 127.96, 119.05, 117.63, 115.62, 113.92, 37.96, 35.08, 31.53

1-(Methyl)-3'-(triisopropylsilyl)-spiro[3H-indol-3,5'-tetrahydrofuran]-2-(1H)-one (16a)

A solution of allyltrtrimethylsilane 8 (48 mg, 0.24 mmol) and 1-methyl isatin 4a (33 mg, 0.20 mmol) in 6 mL of CH₂Cl₂ was cooled to -5 °C and SnCl₄ (0.24 mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 3 h., the reaction was quenched with NH₄Cl and extracted with CH₂Cl₂ (3 x 15 mL). The organic layer was dried (Na₂SO₄) and the residue after the removal of the solvent was
subjected to column chromatography. Elution with 10% ethylacetate in hexane afforded pure 16a as a colorless crystalline solid (65 mg, 91%). mp. 123-124 °C

IR (cm⁻¹) : 2946, 2871, 1725, 1619, 1475, 1375, 1249, 1005, 773, 673

¹H NMR : 7.27 (t, 2H, J = 7.2 Hz), 7.03 (d, 1H, J = 7.2 Hz), 6.78 (d, 1H, J = 7.2 Hz), 4.42-4.36 (m, 1H), 4.29 (dd, 1H, J = 12.4, 8.2 Hz), 3.17 (s, 3H), 2.24 (dd, 1H, J = 12.4, 7.2 Hz), 2.05-1.91 (m, 1H), 1.13 (bs, 21H)

¹³C NMR : 178.43, 143.28, 139.02, 129.17, 122.94, 122.89, 108.03, 81.76, 73.59, 40.21, 26.05, 25.88, 18.99, 11.34

Crystal data for 16a: C₂₁H₃₃N₀₂Si, FW 359.57, 0.36 x 0.33 x 0.24 mm, monoclinic, space group P2₁/c, unit cell dimensions: a = 18.3554 (6) Å, α = 90°; b = 9.5946 (3) Å, β = 110.049 (2)°; c = 12.7279 (4) Å, γ = 90°. R indices (all data) R1 = 0.0680, wR2 = 0.1452. Volume, Z = 2105.71 (12) Å³, 4. D calc = 1.134 Mg/m³. F (000) = 784. Absorption coefficient 0.125 mm⁻¹; reflections collected 35576. λ = 0.71073 Å (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995)

Analysis Calcd for C₂₁H₃₃N₀₂Si: C, 70.14; H, 9.25; N, 3.90. Found: C, 70.10; H, 9.28; N, 3.97.

3′-(Triisopropylsilyl)-spiro[3H-indol-3,5′-tetrahydrofuran]-2(1H)-one (16b)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and isatin 4b (30 mg, 0.20 mmol) in 6 mL of CH₂Cl₂ was cooled to −5 °C and SnCl₄ (0.24
mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 3 h, the reaction was quenched with sat. NH₄Cl and extracted with CH₂Cl₂ (3 x 15 mL). The organic layer was dried (Na₂SO₄) and the residue after the removal of the solvent was subjected to column chromatography. Elution with 10% ethylacetate in hexane afforded pure 16b as a colorless crystalline solid (51 mg, 74%). mp. 141-143 °C

**IR (cm⁻¹)**: 3245, 2955, 2881, 1735, 1627, 1485, 1222 (KBr)

**¹H NMR**: 9.4 (brs, 1H, exchangeable with D₂O), 7.15-7.04 (m, 2H), 6.95-6.90 (m, 1H), 6.88-6.76 (m, 1H), 4.45-4.32 (m, 1H), 4.21 (dd, 1H, J = 12.2, 6.9 Hz), 2.56-2.48 (m, 1H) 2.18 (dd, 1H, J = 12.2, 6.9 Hz), 1.99-1.89 (m, 1H), 1.05 (s, 21H)

**¹³C NMR**: 181.75, 140.64, 132.55, 129.35, 123.22, 122.91, 110.52, 82.52, 73.80, 40.56, 25.72, 19.07, 11.41

HRMS calcd for C₂₀H₃₁NO₂Si: 345.21241. Found: 345.21278

1-(Phenethyl)-3'-(triisopropylsilyl)-spiro[3H-indol-3,5'-tetrahydrofuran]-2-(1H)-one (16c)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 1-benzyl isatin 4c (48 mg, 0.20 mmol) in 6 mL of CH₂Cl₂ was cooled to -5 °C and SnCl₄ (0.24 mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 4 h, the reaction was quenched with NH₄Cl and extracted with CH₂Cl₂ (3 x 15 mL). The organic layer was dried (Na₂SO₄) and the residue after the removal of the solvent was
subjected to column chromatography. Elution with 10% ethylacetate in hexane afforded pure 16c as a colorless crystalline solid (60 mg, 68%). mp. 135-136 °C

\[
\text{IR (cm}^{-1}) : 2932, 2864, 1728, 1612, 1473, 1368, 1251, 1012, 768
\]

\[
\text{^1H NMR : 7.28-7.11 (m 7H), 6.99 (t, 1H, J = 7.2 Hz), 6.65 (d, 1H, J = 7.6 Hz), 4.86 (s, 2H), 4.55-4.39 (m, 1H), 4.33 (dd, 1H, J = 12.3, 8.2 Hz), 2.63-2.54 (m, 1H), 2.30 (dd, 1H, J = 12.2, 7.2 Hz), 2.08-1.95 (m, 1H), 1.15 (bs, 21H)}
\]

\[
\text{^13C NMR : 178.59, 142.36, 135.57, 132.02, 129.09, 128.70, 127.49, 127.16, 123.05, 122.94, 109.17, 81.80, 73.66, 43.71, 40.29, 25.96, 19.02, 17.67, 12.24, 11.36}
\]

Analysis calcd for C\textsubscript{27}H\textsubscript{37}N\textsubscript{O}\textsubscript{2}Si: C, 74.43; H, 8.56; N, 3.21. Found: C, 74.49; H, 8.65; N; 3.31.

1-(Phenyl)-3'-(triisopropylsilyl)-spiro[3H-indol-3,5'-tetrahydrofuran]-2-(1H)-one (16d)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 1-phenylisatin 4d (45 mg, 0.20 mmol) in 6 mL of CH\textsubscript{2}Cl\textsubscript{2} was cooled to -5 °C and SnCl\textsubscript{4} (0.24 mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 6 h, the reaction was quenched with NH\textsubscript{4}Cl and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 15 mL). The organic layer was dried (Na\textsubscript{2}SO\textsubscript{4}) and the residue after the removal of the solvent was subjected to column chromatography. Elution with 10% ethylacetate in hexane afforded pure 16d as a colorless crystalline solid (59 mg, 70%). mp. 128-130 °C
IR (cm⁻¹) : 3021, 1962, 1733, 1606, 1432, 1128, 1101, 876

¹H NMR : 7.92-7.81 (m, 3H), 7.31-7.16 (m, 6H), 4.36-4.31 (m, 1H), 4.27-4.24 (m, 1H), 2.45-2.40 (m, 1H), 2.29-2.21 (m, 1H), 1.94-1.92 (m, 1H), 1.14 (bs, 21H)

¹³C NMR : 179.54, 141.87, 139.46, 132.55, 131.63, 129.28, 128.67, 122.64, 121.39, 119.68, 112.42, 86.38, 74.61, 40.56, 23.87, 18.89, 11.63

HRMS Calcd for C₂₆H₃₅NO₂Si: 421.2437. Found: 421.24394

1-(p-Toluenesulfonyl)-3'-(triisopropylsilyl)-spiro[3H-indol-3,5'-tetrahydro-furan]-2-(1H)-one (16e)

A solution of allyltrisopropylsilane 8 (48 mg, 0.24 mmol) and 1-tosyl isatin 4e (60 mg, 0.20 mmol) in 6 mL of CH₂Cl₂ was cooled to −5 °C and SnCl₄ (0.24 mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 6 h., the reaction was quenched with NH₄Cl and extracted with CH₂Cl₂ (3 x 15 mL). The organic layer was dried (Na₂SO₄) and the residue after the removal of the solvent was subjected to column chromatography. Elution with 10% ethylacetate in hexane afforded pure 16e as a colorless crystalline solid (66 mg, 66%). mp. 162-164 °C

IR (cm⁻¹) : 2951, 2869, 1734, 1606, 1475, 1330, 1241, 1113, 773

¹H NMR : 7.98-7.87 (m, 3H), 7.37-7.13 (m, 5H), 4.35-4.30 (m, 1H), 4.19 (dd, 1H, J =
5-(Bromo)-3'-(triisopropylsilyl)spro[3H-indol-3,5'-tetrahydrofuran]-2-(1H)-one (16f)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 5-bromo isatin 4f (46 mg, 0.20 mmol) in 6 mL of CH₂Cl₂ was cooled to -5 °C and SnCl₄ (0.24 mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 4 h, the reaction was quenched with NH₄Cl and extracted with CH₂Cl₂ (3 x 15 mL). The organic layer was dried (Na₂SO₄) and the residue after the removal of the solvent was subjected to column chromatography. Elution with 10% ethylacetate in hexane afforded pure 16f as a colorless crystalline solid (55 mg, 65%). mp. 154-155 °C

**¹H NMR**: 9.41 (bs, 1H, exchangeable with D₂O), 7.33 (d, 1H, J = 8.1 Hz), 7.26 (s, 1H), 6.78 (d, 1H, J = 8.1 Hz), 4.50-4.39 (m, 1H), 4.30-4.23 (m, 1H), 2.55-2.47 (m, 1H), 2.30-2.24 (m, 1H), 1.96-1.92 (m, 1H), 1.14 (bs, 21H)

**¹³C NMR**: 181.33, 139.66, 134.54, 132.20, 132.08,

12.6, 8.3 Hz), 2.53-2.45 (m, 3H), 2.41 (s, 3H), 2.24 (dd, 1H, J = 12.6, 5.4 Hz), 1.95-1.86 (m, 1H), 1.10 (bs, 21H)

**¹³C NMR**: 177.36, 145.33, 138.49, 135.20, 131.09, 129.84, 129.74, 127.86, 125.21, 123.38, 113.62, 81.66, 74.19, 41.65, 25.85, 21.64, 18.96, 11.30
3-Hydroxy-3-(2-propenyl)-2-indolone (17a)

A solution of allyltrimethylsilane 9 (23 mg, 0.24 mmol) [or allyltributyltin 9' (80 mg, 0.24 mmol)] and N-methyl isatin 4a (33 mg, 0.20 mmol) in 6 mL of CH$_2$C$_2$ was cooled to -5 °C and SnCl$_4$ (0.24 mL, 1M solution in heptane) was added. The reaction was allowed to attain room temperature gradually. After stirring for 30 min., [15 min. for 9'] the reaction was quenched with NH$_4$Cl and extracted with CH$_2$C$_2$ (3 x 15 mL). The organic layer was dried (Na$_2$SO$_4$) and the residue after the removal of the solvent was subjected to column chromatography. Elution with 20% ethylacetate in hexane afforded pure 17a as a colorless crystalline solid (33 mg, 82%). [40 mg, 99%, for 9'] mp. 150–152 °C

IR (cm$^{-1}$) : 3341, 1723, 1623, 1481, 1179, 977, 672 (KBr)

$^1$H NMR : 7.35–6.84 (m, 4H), 5.72–5.79 (m, 1H), 5.11–5.04 (m, 2H), 3.48 (s, 1H, exchangeable with D$_2$O), 3.21 (s, 3H), 2.27–2.71 (m, 1H), 2.62–2.54 (m, 1H)

$^{13}$C NMR : 179.89, 140.21, 130.20, 129.21, 123.98, 122.90, 120.41, 110.08, 104.78, 77.28, 42.80, 39.20.

1,1'-bis-(p-Toluenesulfonyl)-2,2'-bis-(triisopropylsilylmethyl)-2',3'-dihydro-1'H-pyrrolo[5',4'-e]-2,3-dihydro-1H-indole (18a)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and p-quinone ditoluenesulfonimide 5a (83 mg, 0.20 mmol) in 8 mL dry CH$_2$C$_2$ was cooled to 0 °C and ZnCl$_2$ (32 mg, 0.20 mmol) was added. The temperature of the
reaction was allowed to attain room temperature gradually and the mixture was
stirred at that temperature for 72 h. It was then quenched with water and
extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layer was dried and
the residue after the evaporation of the solvent was subjected to column
chromatography on silica gel. Pure 18a was eluted out in 4% ethylacetate in
hexane as a colorless crystalline solid (70 mg, 43%). mp. 237-238 °C.
Subsequent elution with 15% ethylacetate in hexane afforded 19a (19 mg,
16%).

IR (cm⁻¹) : 2950, 2864, 1606, 1481, 1330, 1110,
(KBr) 1085, 843

¹H NMR : 7.48 (d, 4H, J = 8.0 Hz), 7.34 (s, 2H),
7.15 (d, 4H, J = 8.0 Hz), 4.52–4.46 (m, 2H),
2.74 (dd, 2H, J = 15.4, 8.9 Hz),
2.46-2.36 (m, 8H), 1.43 (dd, 2H, J =
14.4, 3 Hz), 1.24-1.10 (m, 38H), 0.85-
0.87 (m, 6H)

¹³C NMR : 143.84, 137.80, 135.38, 132.25, 129.56,
126.90, 114.70, 62.10, 36.51, 21.53,
19.20, 18.82, 11.53

Crystal data for 18a: C₄₄H₆₈N₂O₄S₂Si₂, FW 809.30 0.40 x 0.33 x 0.22 mm,
monoclinic, space group P2₁/n, unit cell dimensions: a = 7.6609 (1) Å, α = 90°;
b = 16.8556 (2) Å, β = 101.353 (1)°; c = 18.1040 (2) Å, γ = 90°. R indices (all
data) R1 = 0.0611, wR2 = 0.1025. Volume, Z = 2292.01 (5) Å³, 2. D calc =
1.173 Mg/m³. F (000) = 876. Absorption coefficient 0.210 mm⁻¹; reflections
collected-40354. λ = 0.71073 Å (Sheldrick, G. M., Siemens, Analytical X-ray
Division, Madison, WI, 1995).
Analysis Calcd for C_{44}H_{68}N_{10}O_{4}S_{2}: C, 65.30; H, 8.47; N, 3.46. Found: C, 65.18; H, 8.75; N, 3.51.

1-(p-Toluenesulfonyl)-2-(triisopropyl)-methyl-5-(p-toluenesulfonyl)-amino-2,3-dihydroindole (19a)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and p-quinone ditoluenesulfonimide 5a (83 mg, 0.20 mmol) in 8 mL dry CH_{2}Cl_{2} was cooled to -41 °C and SnCl_{4} (0.60 mL, 1M solution in heptane) was added. The reaction mixture was stirred at that temperature for 90 min. It was then quenched with sat. NH_{4}Cl and extracted with CH_{2}Cl_{2} (3 x 20 mL). The combined organic layer was dried and the residue after the evaporation of the solvent was subjected to column chromatography on silica gel. Pure 19a was eluted out in 20% ethylacetate in hexane as a pale yellow solid (92 mg, 75%). mp. 58-59 °C

\[ \text{IR (cm}^{-1} \text{): } 3230, 2950, 2873, 1603, 1490, 1334, 1108, 1093, 883, 667 \]

\[ \text{^1H NMR: } 7.59 \text{ (d, } 2\text{H, } J = 7.8 \text{ Hz), } 7.47-7.41 \text{ (m } 3\text{H), } 7.25-7.20 \text{ (m, } 3\text{H), } 7.13 \text{ (d, } 2\text{H, } J = 7.8 \text{ Hz), } 6.90 \text{ (s, } 1\text{H), } 6.75 \text{ (s, } 1\text{H, exchangeable with } D_{2}O), 4.45-4.38 \text{ (m, } 1\text{H), } 2.68 \text{ (dd, } 1\text{H, } J = 16.0, 9.0 \text{ Hz), } 2.41 \text{ (s, } 3\text{H), } 2.37 \text{ (s, } 3\text{H), } 1.38 \text{ (dd, } 1\text{H, } J = 16.0, 3.0 \text{ Hz), } 1.07 \text{ (bs, } 20\text{H), } 0.85-0.88 \text{ (m, } 3\text{H)} \]

\[ \text{^13C NMR: } 143.71, 143.62, 138.95, 136.13, 135.48, 133.60, 133.17, 129.52, 127.38, 126.95, 122.20, 120.02, 118.26, 61.58, 36.47, \]

\[ \text{TSHN} \]

\[ \text{NTs} \]

\[ \text{Si}^{(Pr)}_{3} \]
HRMS Calcd for C$_{33}$H$_{44}$N$_2$O$_4$S$_2$Si: 612.25117. Found: 612.25186

2-Triisopropylsilyl-4,7-di-p-toluenesulfonylaminoindan (20a)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and p-quinone ditoluenesulfonimide 5a (83 mg, 0.20 mmol) in 8 mL dry CH$_2$Cl$_2$ was treated with BF$_3$OEt$_2$ (0.60 mL, 1M solution in benzene) at room temperature. The reaction mixture was stirred for 90 min. It was then quenched with sat. Na$_2$CO$_3$ and extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic layer was dried and the residue after the evaporation of the solvent was subjected to column chromatography on silica gel. Pure 20a was eluted out in 20% ethylacetate in hexane as a pale yellow solid (62 mg, 51%). mp. 238-239 °C

IR (cm$^{-1}$) : 3320, 3021, 2972, 1603, 1330, 1113, 976, 748

$^1$H NMR : 7.57 (d, 4H, $J = 7.9$ Hz), 7.17 (d, 4H, $J = 7.9$ Hz), 7.09 (s, 2H), 6.62 (bs, 2H, exchangeable with D$_2$O), 2.62 (dd, 2H, $J = 15.4, 9.4$ Hz), 2.37–2.34 (m, 8H), 1.38 (m, 1H), 1.06–0.93 (m, 21H)

$^{13}$C NMR : 143.65, 139.21, 136.90, 130.01, 129.59, 127.25, 122.61, 33.54, 21.62, 19.14, 18.88, 11.50

HRMS Calcd for C$_{33}$H$_{44}$N$_2$O$_4$S$_2$Si: 612.25117. Found: 612.25198

1-(p-Toluenesulfonyl)-2-(triisopropyl)-methyl-4,7-dimethyl-5-(p-toluenesulfonyl)amino-2,3-dihydroindole (19b)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 2,4-dimethyl-1,4-quinone dibenzenesulfonimide 5b (83 mg, 0.20 mmol) in 8 mL
dry CH₂Cl₂ was cooled to -41 °C and SnCl₄ (0.60 mL, 1M solution in heptane) was added. The reaction mixture was stirred at that temperature for 60 min. and further for 4 h at room temperature. It was then quenched with sat. NH₄Cl and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layer was dried and the residue after the evaporation of the solvent was subjected to column chromatography on silica gel. Pure 19b was eluted out in 20% ethylacetate in hexane as a pale yellow solid (58 mg, 47%). mp. 86-87 °C

IR (cm⁻¹) : 3320, 2958, 2879, 1601, 1474, 1342, (KBr) 1158, 1092, 875, 664

¹H NMR : 7.77-7.75 (m, 2H), 7.61-7.44 (m, 4H), 7.39-7.26 (m, 4H), 6.97 (s, 1H), 6.75 (s, 1H, exchangeable with D₂O), 4.46-4.43 (m, 1H), 2.47 (s, 3H), 1.78 (dd, 1H, J = 15.3, 7.0 Hz), 1.65 (s, 3H), 1.26 (dd, 1H, J = 15.3, 7.0 Hz), 1.06-1.01 (m, 20H), 0.78-0.73 (m, 3H)

¹³C NMR : 143.71, 143.62, 138.95, 136.13, 135.48, 133.60, 133.17, 129.52, 127.38, 126.95, 122.20, 120.02, 118.26, 62.26, 35.95, 21.60, 19.20, 18.84, 18.81, 11.46

2-(Triisopropylsilyl)methyl-5-(p-toluenesulfonyl)amino-2,3-dihydrobenzofuran (21a)

A solution of allyltrisopropylsilane 8 (48 mg, 0.24 mmol) and p-benzoquinone monobenzenesulfonylimide 6a (50 mg, 0.20 mmol) in 4 mL dry CH₂Cl₂ was cooled to -78 °C and SnCl₄ was added. The reaction mixture was stirred at that temperature for 30 min., quenched with sat. NH₄Cl solution and extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was dried (Na₂SO₄),
concentrated and the residue on silica gel column chromatography afforded pure 21a as colorless crystalline solid (81 mg, 91%). mp. 99-101 °C

IR (cm⁻¹) : 3269, 2947, 2872, 1620, 1491, 1332, (KBr) 1218, 1165, 1095, 883, 725

¹H NMR : 7.72 (d, 2H, J = 7.0 Hz), 7.54-7.39 (m, 3H), 6.96 (s, 1H), 6.94 (s, 1H, exchangeable with D₂O), 6.63 (d, 1H, J = 8.3 Hz), 6.48 (d, 1H, J = 8.3 Hz), 4.99-4.91 (m, 1H), 3.25 (dd, 1H, J = 15.4, 8.2 Hz), 2.76 (dd, 1H, J = 15.4, 7.8 Hz), 1.35-1.25 (m, 2H), 1.06 (s, 18H), 0.87-0.85 (m, 3H)

¹³C NMR : 158.10, 139.15, 132.64, 128.63, 128.46, 128.20, 127.40, 124.46, 121.90, 109.16, 82.67, 38.51, 18.85, 18.08, 11.32

Analysis Calcd for C₂₄H₃₅NØ₃S Si: C, 64.68; H, 7.92; N, 3.14. Found: C 64.75; H, 7.95; N, 3.28.

2-(Triisopropylsilyl)methyl-5-(phenylsulfonyl)amino-6-methoxy-2,3-dihydrobenzofuran (21b)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 3-methoxy-1,4-benzoquinone monobenzenesulfonimide 6b (50 mg, 0.20 mmol) in 4 mL dry CH₂Cl₂ was cooled to -78 °C and SnCl₄ was added. The reaction mixture was stirred at that temperature for 30 min. and was allowed to attain room temperature gradually. After stirring for 2 h, it was quenched with sat. NH₄Cl solution and extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was
dried (Na₂SO₄), concentrated and the residue on silica gel column chromatography afforded pure 21b as colorless viscous liquid (68 mg, 72%).

IR (cm⁻¹) : 3268, 2941, 2890, 2865, 1621, 1498,
(Neat) 1449, 1338, 1194, 1168, 1158, 1093,
1070, 918, 725

¹H NMR : 7.64-7.30 (m, 6H), 6.48 (1H, exchangeable with D₂O), 6.08 (s, 1H), 5.05-4.95 (m, 1H), 3.33-3.25 (m, 4H), 2.81 (dd, 1H, J = 15.0, 7.9 Hz), 1.32 (t, 2H, J = 7.4 Hz), 1.08 (bs, 21H)

¹³C NMR : 158.49, 151.78, 139.50, 132.38, 128.39,
127.36, 121.74, 118.92, 117.34, 110.07,
93.34, 83.39, 55.48, 38.61, 18.89, 18.54,
18.12, 11.38, 11.17

2-(Triisopropylsilyl)methyl-5-(phenylsulfonyl)amino-7-methoxy-2,3-dihydrobenzofuran (21c)

A solution of allyltriisopropylsilane 8 (48 mg, 0.24 mmol) and 2-methoxy-1,4-benzoquinone monobenzenesulfonimide 6c (50 mg, 0.20 mmol) in 4 mL dry CH₂Cl₂ was cooled to -78 °C and SnCl₄ was added. The reaction mixture was stirred at that temperature for 30 min. and was allowed to attain room temperature gradually. After stirring for 2 h, it was quenched with sat. NH₄Cl solution and extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was dried (Na₂SO₄), concentrated and the residue on silica gel column chromatography afforded pure 21c as colorless viscous liquid (55 mg, 58%).

IR (cm⁻¹) : 3281, 3076, 2934, 1960, 1614, 1592,
2-(Triphenylsilyl)methyl-5-\(p\)-toluenesulfonyl)amino-2,3-dihydrobenzofuran (23a)

A solution of allyltriphenylsilane 10 (72 mg, 0.24 mmol) and \(p\)-benzoquinone monobenzenesulfonimide 6a (50 mg, 0.20 mmol) in 4 mL dry CH\(_2\)Cl\(_2\) was cooled to \(-78\) °C and SnCl\(_4\) was added. The reaction mixture was stirred at that temperature for 30 min. and was allowed to attain room temperature gradually. After stirring for 1 h., it was quenched with sat. NH\(_4\)Cl solution and extracted with CH\(_2\)Cl\(_2\) (3 x 10 mL). The organic layer was dried (Na\(_2\)SO\(_4\)), concentrated and the residue on silica gel column chromatography afforded pure 23a as colorless crystalline solid (89 mg, 82%). mp. 61-62 °C

**IR \((\text{cm}^{-1})\)**: 3269, 3074, 2931, 1968, 1619, 1592, 1489, 1332, 1165, 1113, 1097, 731, 703

**\(^{13}\text{C NMR}\)**: 146.38, 144.03, 139.11, 132.67, 128.84, 128.68, 127.46, 113.43, 108.32, 83.60, 55.95, 38.72, 19.23, 18.80, 17.96, 11.30

1H NMR : 7.67 (d, 2H, \(J = 7.6\) Hz), 7.54-7.47 (m, 6H), 7.37-7.34 (m, 12H), 6.83 (s, 1H), 6.73 (d, 2H, \(J = 7.2\) Hz), 7.54 (t, 1H, \(J = 7.2\) Hz), 6.63 (s, 1H, exchangeable with \(D_2O\)), 6.47 (s, 1H), 6.39 (s, 1H), 5.06-4.98 (m, 1H), 3.71 (s, 3H), 3.20 (dd, 1H, \(J = 15.3, 8.3\) Hz), 2.79 (dd, 1H, \(J = 15.3, 8.3\) Hz), 1.48 (dd, 1H, \(J = 14.3, 5.0\) Hz), 1.16 (dd, 1H, \(J = 14.3, 7.0\) Hz), 1.06 (bs, 21H)
6.67 (s, 1H, exchangeable with D₂O), 6.56 (d, 1H, J = 8.2 Hz), 6.37 (d, 1H, J = 8.2 Hz), 5.02-4.95 (m, 1H), 2.90 (dd, 1H, J = 15.6, 8.5 Hz), 2.57 (dd, 1H, J = 15.6, 7.6 Hz), 2.16 (dd, 1H, J = 14.2, 5.8 Hz), 1.73 (dd, 1H, J = 14.2, 8.5 Hz)

\[ {^{13}}C\text{ NMR} \quad : \quad 157.82, 139.18, 135.67, 134.20, 132.64, 129.72, 128.81, 128.37, 128.20, 128.02, 127.35, 124.31, 122.00, 109.27, 82.08, 37.90, 22.15 \]

Analysis Calcd for \( \text{C}_{33}\text{H}_{29}\text{N}_{3}\text{O}_{7}\text{Si} \): C, 72.36; H, 5.34; N, 2.56. Found: C, 72.41; H, 5.36; N, 2.68.

2-Triisopropylsilylmethyl-7-methyl-4,5-bis-(phenylsulfonylamino)indan (24)

A solution of allyltriisopropylsilane \( 8 \) (48 mg, 0.24 mmol) and \( 7a \) (80 mg, 0.2 mmol) in CH₂Cl₂ was cooled to -5 °C and ZnCl₂ (33 mg, 0.24 mmol) was added. The reaction mixture after stirring at that temperature for 30 min. was further stirred at room temperature for 2.5 h. It was then quenched with water (5 mL) and extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was dried (Na₂SO₄), concentrated and the residue on silica gel column chromatography afforded pure 24 as pale yellow crystalline solid (63 mg, 52%). mp. 166-167 °C

\[ \text{IR (cm}^{-1}\text{)} \quad : \quad 3378, 3029, 2972, 1605, 1333, 1110, 971, 728 \]

\[ {^{1}}\text{H NMR} \quad : \quad 7.74 (d, 4H, J = 7.5 Hz), 7.56-7.42 (m, 6H), 6.51 (s, 1H), 6.36 (s, 1H, exchangeable with D₂O), 6.21 (s, 1H,
exchangeable with D$_2$O), 3.41-3.05 (m, 1H), 2.95-2.76 (m, 3H), 1.96 (s, 3H) 1.88-1.81 (m, 1H), 1.08 (s, 18H), 0.94-0.86 (m, 3H)

$^{13}$C NMR : 145.72, 145.02, 138.12, 133.05, 128.85, 127.68, 125.25, 125.16, 119.76, 34.85, 32.57, 21.76, 19.26, 18.26, 17.76, 11.34

4-(2-propenyl)-1,2-phenylene dibenzamide (25)

A solution of 7b (63 mg, 2 mmol) and allyltriisopropylsilane 8 (48 mg, 0.24 mmol) in 4 mL dry CH$_2$Cl$_2$ was cooled to -5 °C and ZnCl$_2$ (33 mg, 0.24 mmol) was added. Reaction mixture was stirred at 0 °C for 30 min. and at room temperature for 2.5 h. It was then quenched with water (5 mL) and extracted with CH$_2$Cl$_2$ (3 x 10 mL) and the organic layer was dried (Na$_2$SO$_4$) and concentrated. The residue on silica gel column chromatography afforded (10% ethylacetate in hexane) 25 as a colorless crystalline solid (33 mg, 46%). mp. 186-188 °C

IR (cm$^{-1}$) : 3226, 1650, 1602, 1578, 1519, 1472, 910, 823, 705

$^1$H NMR : 9.69 (s, 1H, exchangeable with D$_2$O), 9.62 (s, 1H, exchangeable with D$_2$O), 8.09-8.03 (m, 4H), 7.57-7.51 (m, 6H), 7.24 (d, 1H, $J$ = 5.5 Hz), 7.03 (s, 1H), 6.41 (d, 1H, $J$ = 5.5 Hz), 5.39-5.28 (m, 1H), 4.75-4.62 (m, 2H), 2.63 (d, 2H, $J$ = 6.2 Hz)
A slurry of 21a (153 mg, 0.34 mmol) and K₂CO₃ (57 mg, 0.41 mmol) in acetone (4mL) at room temperature was treated with methyl iodide (53 mg, 0.37 mmol) and nBu₄N⁰ (7 mg, 0.017 mmol). The reaction mixture was refluxed under argon atmosphere for 24 h., cooled to room temperature and then poured into water (5 mL). CH₂Cl₂ (10 mL) was added, and the aqueous layer was separated and extracted with CH₂Cl₂ (3 x 10 mL). The combined extracts were washed with water (20 mL), brine (20 mL), dried (Na₂SO₄) and concentrated. Chromatography of the resulting residue afforded 22 (125 mg, 80%) as a pale yellow liquid.

**1R (cm⁻¹)**: 2941, 2767, 1618, 1550, 1486 1355, 1229, 1179, 1061, 1016, 931, 692, 579

**1H NMR**: 7.58-7.53 (m, 3H), 7.46-7.42 (m, 2H), 6.95 (s, 1H), 6.58-6.51 (m, 2H), 5.04-4.99 (m, 1H), 3.29 (dd, 1H, J = 15.4, 8.4 Hz), 3.11 (s, 3H), 2.80 (dd, 1H, J = 15.4, 8.1 Hz), 1.36-1.27 (m, 2H), 1.08 (bs, 18H), 0.88-0.85 (m, 3H)

**13C NMR**: 158.78, 136.88, 132.45, 128.53, 128.07, 127.98, 126.10, 124.79, 121.01, 108.81, 82.77, 38.90, 38.72, 18.82, 18.14, 11.31
2.4. REFERENCES


