Triphenylmethyl Containing Bridged Silsesquioxanes:

New Class of a Potentially New Magnetic Material

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ABSTRACT OF THE THESIS

Triphenylmethyl Containing Bridged Silsesquioxanes: New Class of a Potentially New Magnetic Material

By

Evi Evi

Several methods aimed at the design of inorganic-organic hybrid materials, alone with new organic magnetic materials, have received recent attention in many research groups worldwide. Such materials have significant applications in the emerging areas of electronics, optoelectronics, and nanotechnology.

Our research focuses on developing a synthetic route for hybrid materials with possible magnetic properties by entrapping and immobilizing an organic free radical into an inorganic-organic hybrid polymer matrix. Several hybrid material monomers, known as silsesquioxane, had been synthesized using the sol-gel process. The organic and inorganic phases are formed from two interpenetrating polymeric networks. Our organic phase is triphenylmethyl with an olefin substituent, while the inorganic phase is a silica polymer. The structures and properties of these materials have been investigated via ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy. A future application from this silsesquioxane-radical material could be as memory storage device.

ACKNOWLEDGEMENT

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I am especially indebted to my husband, Aijaz for his enormous moral encouragement, love, understanding, helpful advice, prayer, and continuous financial support. I also want to thank my daughters, Maryam and Sarah, for their understanding. Also, my great thanks to my parent's in-laws, Mr. Aziz Baig and Mrs. Saeeda Aziz, for their continuous support and prayers for my success. I owe a debt of gratitude to my sisters, Yenny, Fransiska, and Merry, for their love, encouragement, and support.

Saving the best for the last, I would like to thank my parents, Mr. Halim and Mrs. Holyta, for their endless love, patience, continuous encouragement, and support during this work and throughout my life.

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In the name of

ALLAH

The Most Compassionate, The Most Merciful

He is the One GOD:

The Creator, the Initiator,

The Designer,

To Him belong

the Most Beautiful Names:

whatever is in the heavens and on earth,

does declare His Praises and Glory:

and He is the Exalted in Might, the Wise.

Holy Quran 59:24

Chapter 1

INTRODUCTION

1. General Introduction and Historical Development

1.1. The Need for Hybrid Magnetic Material

Due to the exponential growth in the applications of computerized systems in the last two decades, there is a continuing desire for greater storage capacity in data recording systems. The most economical means of data storage is based on magnetic storage. For example, hard disk drives providing nearly half of all computer storage. At present, hard disk costs less than 10 USA cents per megabyte (MB) and represents a 50 billion dollar industry. Image data and program files as examples of large data sets take a benefit from optical and magneto-optical disk storage, but the low cost and short access times of the hard disk drive have resulted in a demand for provision of devices and storage densities with a compound growth rate approaching 60% per annum. This is greater than that of the semiconductor industry. In the year of 2005, the hard disk provision for the world wide was predicted to rise to 6000 terabytes from 1000 terabytes (in the year 2000) (1).

The evolution in magnetic data storage has changed the world started on September 13, 1956, when IBM announced the birth of the world's first disk drive 350 RAMAC random access method of accounting and control) computer system as the latest system from 305 RAMAC computer system (2). This novel way to store and retrieve data with a rotating disk enabled rapid "random" access to the data. Nowadays, it is more economical, convenient, and environmental friendly to store data on a hard disk than to store the same information on paper.

The breakthrough in magnetic materials revolutionized the design of magnetic storage disk. The low-cost and large-capacity disk drives have moved the computer users to have portable applications, such as lap-tops or iPods. Magnetic tape drives, which were developed well before the magnetic HDD, have also improved in storage density over a long period, but at a slower rate than HDDs. Now, the consumer market has been dominated by the use of optical storage (CDs and DVDs) and flash memory.

One of the most promising candidates which can have the application as the magnetic data storage is hybrid materials. Following section will give an overview of hybrid materials, their application, and current challenges for the synthesis of this novel material.

1.1.1 The Development of Hybrid Materials

Many natural or man-made hybrid materials on the (macro) molecular or nanoscale are available now, although the original birth of hybrid materials is not known exactly. Present examples of natural organic-inorganic composites are crustacean carapaces, mollusk shells, and bone, and teeth tissues in vertebrates. On the other hand, some examples of man-made hybrid materials are Egyptian ink, green bodies of china ceramics, prehistoric Maya frescos paintings, and paints in paint industries (3).

Due to several advantages possessed by hybrid materials, which will be discussed in the next section, they represent a new frontier in material chemistry, science, and engineering. They offer the potential to create and tailor materials with control at molecular level and synergic properties (4). Researches concerning hybrid materials including harnessing organic-inorganic matrixes that exhibit chemical and/or biochemical activity, electrochemical or photochemical properties, as well as magnetic or optical properties have flourished in the last decades.

1.1.2 Definition of Hybrid Materials

Hybrid material can be defined as a material having an inorganic and organic components mixed on the molecular scale (Figure 1) that can lead to improve mechanical, thermal, and chemical properties.

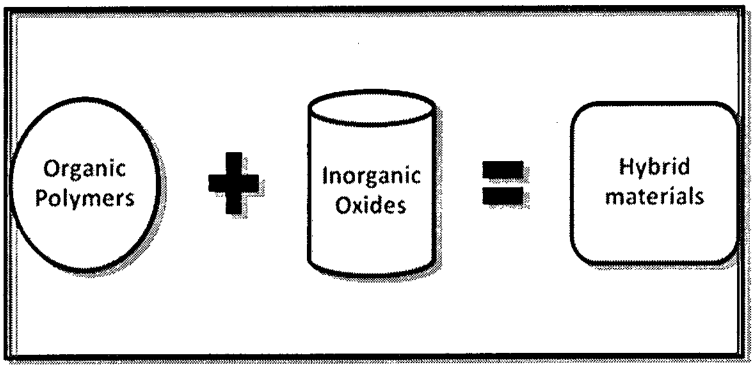


Figure 1: Illustration of the hybrid materials.

Hybrid materials can be divided into two different classes based on the interactions between the organic and inorganic components:

(i). Class I Hybrid Materials:

Organic and inorganic components are embedded by weak bonds (hydrogen, van der Waals or ionic bonds). Initial synthesis of hybrid materials (class I) involved a simple physical mixing of the organic and inorganic phases. Generally, phase separation will occur due to insolubility of the inorganic and organic phases.

Class I hybrid materials have been prepared by several methods which are as follow:

1) Organic dyes (i.e. rhodamines, pyranines, coumarins, porphyrins, and phthalocyanines) embedded in the inorganic networks (i.e. silica, aluminosilicate or transition metal oxide (ZrO_2, TiO_2). This method was developed in Reisfeld and Mackenzie research groups (5, 6). The weak interactions between the dye and the inorganic matrix account for the dispersion of the dye within the structure and the final properties of the materials (photoresponse, reversibility, stability, etc) (7).
2) Organic polymer monomers (i.e. methylmethacrylate and butadiene) embedded in the inorganic networks followed by the hydrolysis and polycondensation (8). Transparent monoliths of large size with a tunable refractive index have been obtained for optical application (9).

(ii). Class II Hybrids:

Organic and inorganic components are joined together by strong covalent bonds. The starting molecules in this class should possess two functionalities: (i) alkoxy groups (R-OM bonds) to experience hydrolysis-condensation reaction in the presence of water led to an oxo-polymer framework and (ii) stable metal (i.e. Si, Hg, Pb, P, or Zn)-to-carbon links to participate in the hydrolysis reactions.

Thus, the M-O-C bonds which are stable for hydrolysis could be the links between the organic and inorganic parts. The advantages of class II hybrid are no phase separation being observed due to the covalent bonding and the ability to control the chemical and physical properties of hybrid material, which can be achieved through the selection of organic bridging groups.

There are several methods for the synthesis of Class II hybrids, which are as follows:

(a) Hybrid obtained from organically modified silicon alkoxides.

Schmidt introduced this method by mixing a trifunctional silicon compound $RSi(OCH_3)_3$ and a tetra functional silicon $Si(OCH_3)_4$ followed by sol-gel polymerization. Schmidt later improved this process by incorporating organic monomers (i.e. vinyl, ally, or epoxy functionality) as substituents in the trifunctional silicon species followed by thermal or photochemical polymerization (10).

Table 1: Examples of class I and class II hybrid materials.

Class I	**Class II**
Maya blue is a beautiful example of man-made class I hybrid material (11).	New photopatternable ORMOCER® material for the fabrication of integrated optical and opto-electronic devices (12).
Ion conducting polymers, where the inorganic ion (often Li^+) migrates through the polymer matrix (13).	Ceramer (CERamic polyMERS) (14).
Rhodamine 610, Rhodamine 620, and Rhodamine 640 (in which organic laser dyes have been incorporated into polydimethylsiloxane and tetraethoxysilane). (15).	Ethylene and phenylene bridged polysilsesquioxane xerogels (16), sulfonated phenylene-bridged polysilsesquioxane as catalysts for acid catalyzed reactions (17).

(b) Hybrid obtained from reaction between polymer and polyfunctional alkoxy silanes introduced in Wilkes's group (18).

(c) Hybrid obtained from reaction between organic molecule (R′) with two or more trialkoxysilane [$Si(OR)_3$] groups bonded through Si-C bonds involving sol-gel polymerization developed in Shea's research group (19,20).

1.1.3 Advantages of Hybrid Materials and their Applications

One of the most obvious advantages of inorganic-organic hybrids is that they can favorably combine the different properties of organic and inorganic components in one material to create multifunctional materials. For example, inorganic particles with specific optical, electronic, or magnetic properties cooperate into organic polymer matrices.

The inorganic component provides mechanical strength and thermal stability, while the organic component participates in bonding with the inorganic building blocks (21). The organic component is also used to tailor the electronic properties of the inorganic framework by reducing the dimensionality and by mediating the electronic coupling between inorganic units. These materials can be shaped in bulk or in film, which have the application as scratch-resistant coatings for optics because of several attractive features, such as high transparency, good adhesion, corrosion protection, and easy tuning of both the refractive index and the increased in mechanical strength (22). Based on the molecular or nanoscale dimensions of the building blocks, hybrid materials are also a good candidate for many optical applications especially using silica as the inorganic components because of its low optical loss. Moreover, these materials may extend their applications to higher speed devices with either a-Si or organic semiconductors (23), nanocomposites for dental filling materials, and proton conducting membranes for the production of fuel cells (24).

1.2 Polysilsesquioxanes

One example of class II hybrid material is polysilsesquioxanes having the basic repeating units of $[RSiO_{1.5}]_n$ where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organo-functional derivatives of alkyl, alkylene, aryl, or arylene groups (25). The basic repeating unit or monomeric building block is a tetra-coordinate silicon (an organic substituent and up to three siloxane bonds). Polysilsesquioxanes are also known as t-resins which have three siloxane bonds to each silicon atom (26).

The polysilsesquioxane is divided into three types based on the architectural motifs. Type I materials are discrete polyhedral oligosilsesquioxanes (POSS) that often crystallize from solution, type II materials include amorphous oligosilsesquioxane, and the last one is type III known as bridged polysilsesquioxane in which the organic group acts as a bridge between two or more trialkoxysilyl groups (Figure 2) (25). In bridged polysilsesquioxanes, the organic group can be varied in length, rigidity, geometry of substitution and/or functionality.

Bridged polysilsesquioxane xerogels and aerogels are considered as porous materials. Generally, porosity in materials is evaluated by surface area (m^2/g), pore volume (mL/g), and average pore size (27). The research on bridged polysilsesquioxanes is introduced and has developed extensively in Shea and Loy's groups. One of their successful achievements was to develop polysilsesquioxane aerogels based on organo-bridged bis (trialkoxy) silanes that provide access to micro- and mesoporous materials with surface areas up to 1000 m^2/g, pore volumes up to 0.6 mL/g, and very well defined micro- and/or mesoporosity (28).

The preparation of bridged-polysilsesquioxanes involves sol-gel polymerization method. Once the sol-gel polymerization solution becomes a slightly viscous sol, bridged polysilsesquioxanes can be prepared as fibers, particles, thin films, or monolithic gels depending upon the processing method of the sol.

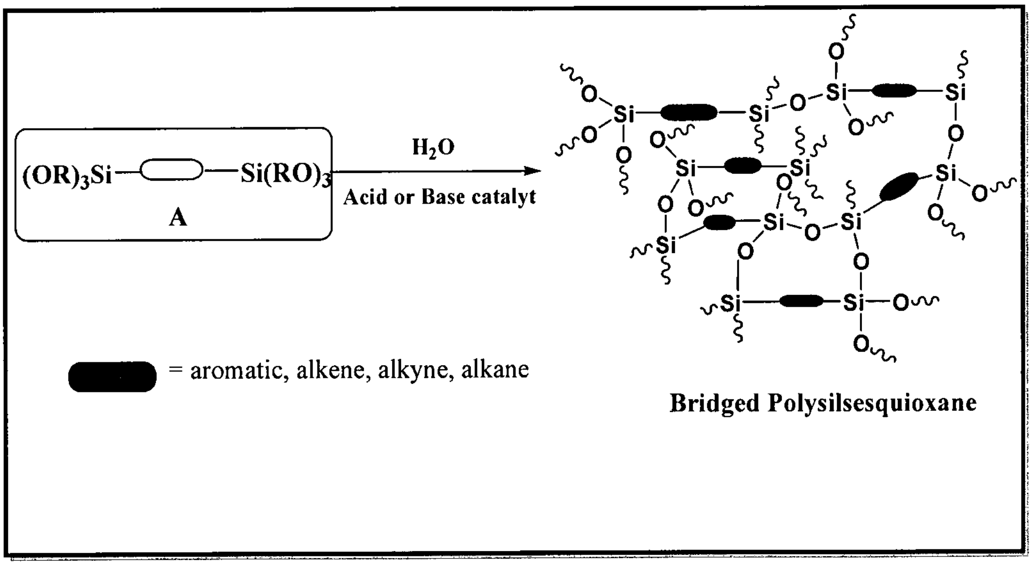


Figure 2: Bridged polysilsesquioxanes
(Redrawn and adapted from: K.J. Shea, D.A. Loy, *Chem.Rev.*, **1995,** *95,* 1431-1442)

1.2.1 Advantages of Bridged Polysilsesquioxane over Ormosil and Ormocer and their Applications.

Although ormosil and ormocer have been successfully being synthesized, however, these materials have some limitations, such as the hybrid product cannot be extended down to the molecular level and there is limitation in the mechanical and physical properties due to the selective types of organic component incorporated in the material (29). Therefore, there is still a great need for the development of better nanocomposites and hybrid materials at the nanoscale level to meet the high standards of better performance.

This thesis provides the solution to improve physical properties and mechanical strength between the organic and inorganic by using bridged polysilsesquioxane based on Shea and Loy's work. By introducing variation in the organic spacers in the bridged polysilsesquioxane, it will provide better control over homogeneity, morphology of the novel hybrid material, pore size distribution in the final products (30), and the reduction in domain sizes extended down to molecular level increased the interfacial surface areas (25). Moreover, the organic group provides an opportunity to modulate bulk properties such as porosity, thermal stability, refractive index, optical clarity, chemical function, hydrophobicity, and dielectric constant. These materials are marked by their high loading of functional groups (unattainable for surface modified silica), chemical and thermal stability with a high degree of porosity and contrary to ORMOSILs (31). One of the applications is in porous silica supports where they are modified through introduction of an organic functionality with surface change.

Thus, the fine degree of control over the bulk chemical and physical properties has made bridged polysilsesquioxanes as one of the good candidates for applications in optical devices (32), as high capacity absorbents (33), 3D information storage media (34), and proton-conducting media for fuel cells from proton-conductive polysilsesquioxane materials with covalently bound sulfonic acid functional groups (35).

1.3 Molecular Magnetism

Molecular magnetism has been developed since the discovery of diamagnetism by Faraday 1845. Most organic/molecular compounds are diamagnetic and some are paramagnetic. In 1967 Mukai and co-workers reported the first organic compound, galvinoxyl (Figure 3) having a relatively strong ferromagnetic coupling (36).

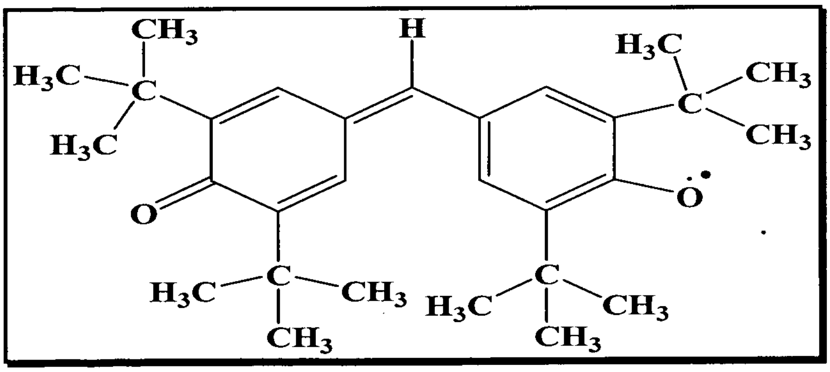


Figure 3: Galvinoxyl

(Redrawn and adapted from: J.S. Miller, *Adv. Mater.*, **2002,** *14,* 1105-1110)

The first theoretical concept of organic ferromagnets was proposed in 1963 by McConnell (37). In 1969, Mukai reported galvinoxyl crystal (Figure 3) as the first radical organic ferromagnet with positive Weiss constant (19 K) from its magnetic susceptibility measurement. Other organic ferromagnet material is para-Nitrophenyl nitronyl nitroxide ($C_{13}H_{16}$ N_3O_4) crystal discovered by Kinoshita *et.al.* (38) shown a ferromagnetic transition below 0.60 K) (Figure 4). Each molecule of *p*-NPNN has a magnetic moment because of the radical (unpaired) electron which is delocalized over the O–N–C–N–O moiety.

Recently, a series of meta-substituted polyradicals (polyarylmethyl) with star branched topologies with magnetic ordering run under high temperature containing very high spin (S=5-13) had been synthesized in Rajca's group (39). This molecule has interesting properties since it has a large number of unpaired electron spins due to its multiple radical sites; it has ferromagnetic coupling and stable at ambient temperature.

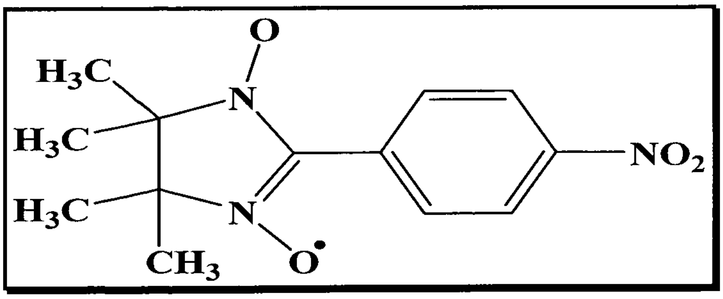


Figure 4: p-Nitrophenyl Nitronyl Nitroxide Radical

(Redrawn and adapted from: P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y.Maruyama, M. Kinoshita, *Chem.Phys.Lett.,* **1991,** *180*, 327-331).

1.3.1 Organic Porous Magnetic Material

Because of the difficulties in handling the organic magnetic carriers; i.e., the free organic radicals, there are very limited number of pure organic porous magnetic materials so far being reported. However, one research group in Spain, Veciana and colleagues (40) had synthesized several nanoporous solids having magnetic property opened a new route to the development of multifunctional molecular material, such as magnetic sensors. Their pure organic magnetic open-frameworks product was based on polychlorotriphenylmethyl (PTM) radicals, previously discovered by Ballester (41).

Veciana and co-workers combined copper atoms with a stable organic radical ligand (the polychlorinated triphenylmethyl tricarboxylic acid radical, PTMTC, $C_{22}O_6Cl_{12}$), shown in figure 5(a) to build their hybrid skeleton produced strong magnetic effects related to structural changes during solvent desorption and readsorption. Although, the idea of using radical ligands to enhance magnetic interactions is not new (42), this is the first time that they have been used in the synthesis of porous solids. The hybridized central carbon atom of the radical ligand (sp^2) stabilized by six bulky chlorine atoms, induces a planar arrangement of the PTMTC and the coordinated Cu^{2+} atoms. The resulting compound, MOROF-1 for short (for metal–organic radical open framework), $[Cu_3\ (PTMTC)_2(py)_6(EtOH)_2(H_2O)](EtOH)_{10}.(H_2O)_6$, shows a 2-D honeycomb network with very large 1-D hexagonal nanopores.

The radical ligand acts as a relay for the magnetic interactions, owing to both its spin and to conjugated double bonds favoring the magnetic interactions. It was found that the solid MOROF-1 can be considered as a ferrimagnet, in which the spins are aligned antiparallel, contributed from the Cu:PTMTC ratio (3:2). This radical also have other advantages, which are: (i) they exhibit a high thermal and chemical stability; (ii) their trigonal symmetry provides a typical template for getting channels held together by hydrogen bonds through the carboxylic groups; (iii) the molecular bulkiness and rigidity of PTM radicals is expected to prevent close packing of molecular units; and (iv) besides their structural control, hydrogen bonds have been shown to favor magnetic exchange interactions between bound organic radical molecules (43).

MOROF-1 has an application as the first example of a shape memory material to select specific solvents (solvent sensor). Other examples of magnetic nanoporous using the same paramagnetic PTMTC ligand that have been reported are two new supramolecular Co(II)-based metal–organic radical open-framework, $[Co(PTMTC)(4,4'\text{-}bpy)(H_2O)_3].6EtOH.2H_2O$ (MOROF-2) and $Co_6(PTMTC)_4(py)_{17}(H_2O)_4.(EtOH)$ (MOROF-3) (44).

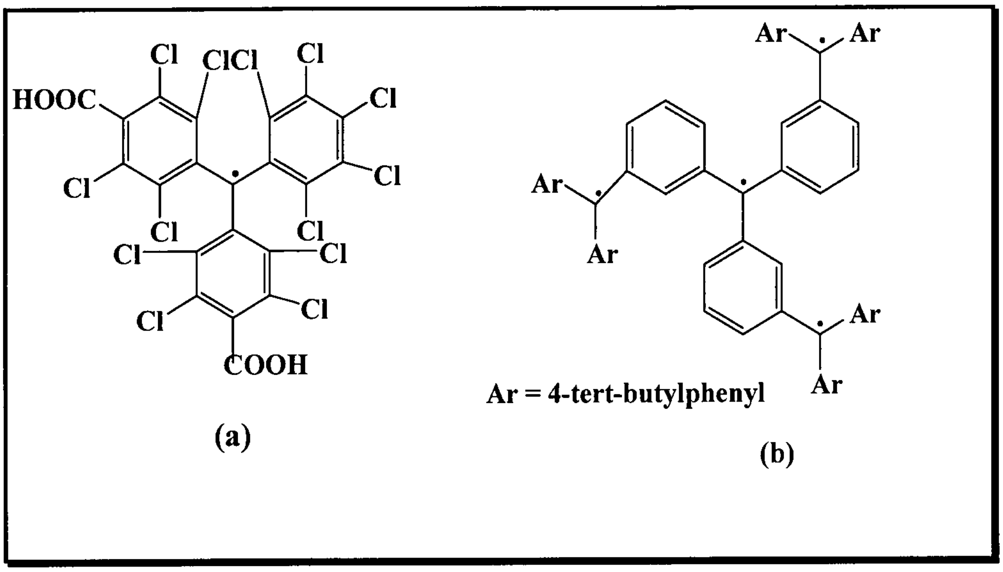


Figure 5: Structures of (a) the polychlorinated triphenylmethyl tricarboxylic acid radical (Redrawn and adapted from: D. Maspoch, D. Ruiz-Molina and J. Veciana, *Nature Mater.*, **2003**, *2*, 190–195)
(b) polyarylradical (Redrawn and adapted from: A. Rajca, J. Wongsriratanakul, S. Rajca, *J.Am.Chem.Soc.*, **2004**, *126*, 6608)

1.4 Current Challenges for the Synthesis of Hybrid Magnetic Materials

Most materials in magnetic applications are classical ferromagnets or atom-based magnetism (45) in which the magnetism is contributed by electron spins on the atomic level consist of inorganic substances (i.e. Fe, Co, Ni, Sm, Eu) with spin carriers of d and f electrons (46). Atom based magnets have some limitations: in which they require extreme conditions, such as high temperatures and pressures to form and are also insoluble. Hence, their synthesis requires a great amount of energy and it is practically impossible to fine-tune their properties according to desired specification. Thus, a new area of chemistry has recently developed molecule/organic-based magnets in order to overcome the limitation in traditional magnet and the desire to achieve something that was once thought impossible by producing magnetism in materials from spin carriers of s and p electrons (i.e C, H, N, O, S, and Se) because carbon (containing only s and p electrons) does not have a spontaneous magnetic moment in any of its allotropes.

The major advantage of molecule-based magnets is that they could potentially have much more tunable properties such as transparent, optically active, low-density, insulating or even bifunctional (ferromagnetic and conducting) and can be synthesized at ambient conditions.

Despite, the importance of pure organic porous magnetic materials, there are very limited number of papers reported because of the difficulties in handling the organic magnetic carriers; i.e., the free organic radicals. Purely organic magnetic open-framework materials are very scarce due to the complexity of their design and synthesis. The main limitation comes from the selection of a suitable organic radical, i.e., a pure organic open shell building block or constitutive unit. First, organic radicals must be both thermally and chemically stable. Second, these radicals must be substituted with suitable functional groups to provide robust linkages between themselves. And last but not least, these radicals should exhibit a large volume and rigidity to prevent interpenetration.

Organic materials can often possess interesting optical properties, as a result allowing the possibility of devices which implement new functionality. The growth, microstructural characteristics, and magnetic properties of the magnetic storage layer are the principal concerns of this review. The move to higher and higher densities requires smaller and smaller spacing losses and lower flying heights. Faster rotation rates, which are essential to lower access times and increase data rates, require stronger, harder, stiffer, and lighter substrate materials. These are usually non-metallic in order to avoid mechanically induced distortion and glass, glass ceramic, aluminium, boron and silicon carbides and silicon are being used or investigated. However, it must be remembered that the substrate material must be thermally stable and also process compatible.

Within the last decade, a great deal of research has focused on developing methods to design new hybrid organic-inorganic magnetic materials having nanoporous networks.

Therefore, the difficulty of obtaining nanoporous materials with increasing pore size dimensions and simultaneous long range magnetic properties remains a challenge.

1.5 Novelty of this Research

This research study focused on the synthesis of porous hybrid material (organic-inorganic) with possibility of having magnetic property.

Porous structures that can be of inorganic, organic and inorganic–organic composite materials are of scientific and technological importance because of the ability of the pore wall to interact with atoms, ions, molecules and supermolecules, together with the capacity of controllable pore space to load or capture liquid and gas molecules, and solid particles. The tailorable pore size and pore wall surface make porous materials highly attractive in frontier research. The pore size of porous solids can be modified through the hybrid frameworks because it seems impossible to increase the pore size dimension (47). The ability to increase the length of the carbon chains of the organic component (mainly phosphonates and carboxylates) allowed researchers to enhance the dimensions of the pores up to 30 Å, which could then be used as nanoreactors (48).

Nanoporous materials posses unique surface, structural, and bulk properties that underline their important uses in various field such as catalyst and catalyst supports (49), dielectric materials for electronic applications (50), media for optical (51) and sensor (52) applications, and selective permeability membranes (53) because of their ability to absorb and interact with atoms, ions and molecules on their large surface area and in the nanometer sized pore space (54). Currently, most of the magnetic materials have significant applications in the emerging areas of electronics, optoelectronics, magneto-mechanical (magnetic separators), and nanotechnology (sensors/high density magnetic/optical storage devices) (55).

Since not so many hybrid magnetic nanoporous materials have been reported, we would like to develop also hybrid magnetic nanoporous material using bridges silsesquioxanes. Siloxane-based organic–inorganic hybrid monoliths have been synthesized by a sol–gel process. Organic–inorganic nanocomposites materials have been regarded as new generation of high performance materials since they combine the advantages of the inorganic materials (rigidity, high stability) and the organic polymers (flexibility, dielectric, ductility and processibility)

1.6 Proposed Synthetic Strategies for this Research

Generally, there are two different approaches can be used for the formation of hybrid materials; either using building block approach or sol-gel process approach (56). However, in this research, the hybrid material was processed using sol-gel approach. The sol-gel process offers many advantages, such as high homogeneity and purity of resulting materials (57), lower processing temperature compared to the conventional process (melt processing of glass), and reacts in liquid solutions at the room temperature (58) allowing controlling and designing the materials at nanometer level.

1.6.1 Sol-Gel Process

This process has gained great importance in the last three decades following the pioneering work of Dislich (27) developed in the 1930s using silicon alkoxides as precursors from which silica was produced. One important fact which makes the silicon-based sol-gel dominated in the formation of hybrid materials is the stability of the Si-C bond toward hydrolysis resulting easier incorporation a large variety of organic groups in the network formed, which is very rare case in many metal-carbon bond (20).

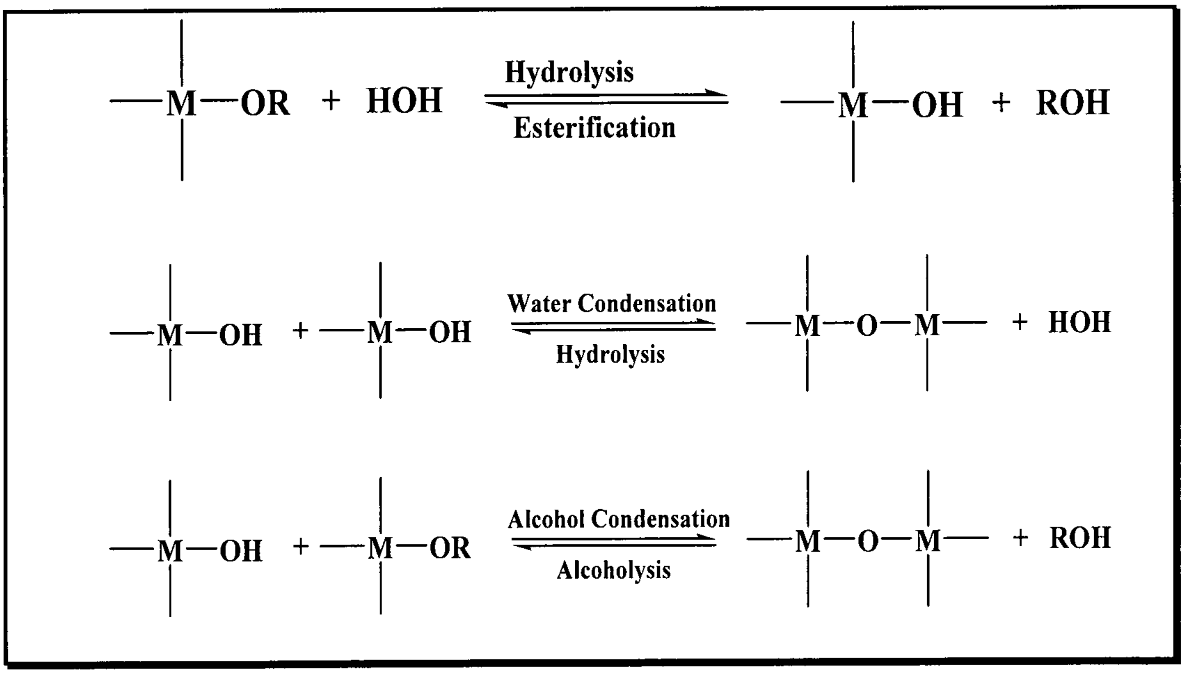
The sol-gel reaction is generally divided into two steps (20):

a. Production of an intermediate Si-OH group (silanol) by hydrolysis of silicon or metal alkoxides.
b. Formation of a new siloxane linkage (Si-O-Si), a three-dimensional network, by condensation of the silanol groups and residual alkoxyl groups.

The sol-gel polymerization can be catalyzed by either acid (i.e. aqueous HCl or 90% formic acid) or base (i.e. aqueous NH_4OH, KOH, or NaOH). Acid catalyzed hydrolysis (at low pH) is relatively slow and the resulting silica networks are mainly linear or randomly branched polymers. Also, the gel under acidic condition is generally less condensed and transparent (59).

On the other hand, based-catalyzed hydrolysis (at high pH) is more condensed, more hydrophobic (fewer SiOH groups), and opaque white with more highly branched silica networks. Therefore, base-catalyzed gels are found to be more porous xerogel and contribute to less pore collapse (25). The growth of silica polymers continues until they reach a size where a gel transformation takes place and the solutions are no longer free flowing (fluid). This point is known as the gel point. The condensation reaction will continue for a long time until the material shrinks and stiffens called ageing. This process is carried on in the drying process, where the material needs a more compact structure and an increased stiffness. In the drying process, the solvent can be removed from the porous networks by two major techniques. The first technique is air-dried resulted xerogels (25) and the second is using supercritical fluid evacuation CO_2 by directly polymerizing the monomers with formic acid resulting aerogels (60). Finally, the final structure of the material can have several forms as monoliths, films, fibers, or powders (27).

The four main steps of sol gel process are hydrolysis, condensation, drying and processing (i.e. sintering). The general sol-gel polymerization is represented in Scheme 1, where M = Si, Ti, V, Zr, etc.



Scheme 1: Summary of the key steps in sol-gel polymerization

(Redrawn and adapted from: K.J. Shea, D.A. Loy, O.Webster, *J. Am.Chem.Soc.*, **1992,** *114*, 6700-6710)

1.7 Characterization of Materials

The final product, polysilsesquioxane hybrid magnetic materials, can be characterized using ^{29}Si NMR to determine the relative proportion of different silicon species in polysilsesquioxane, electron paramagnetic resonance (EPR) or electron spin resonance (ESR) to investigate the present of radical, and Superconducting Quantum Interference Device (SQUID) for its magnetic measurement. The SQUID s a type of transistor consists of a superconducting ring that has a weak link (34). The transistor amplifies small electrical signals. The SQUID has very capability of detecting very small changes is in magnetic field.

1.8 Scope of this Dissertation

This dissertation is aimed at developing a synthetic route for hybrid materials with possible ferromagnetic properties, by incorporating an organic radical into a polysilsesquioxane matrix. The organic molecule contains free radicals, which are comprised of an odd number of electrons and exhibit magnetism caused by the spin of unpaired electron. A radical is a preferable compound compared to compound without the presence of radical due to the presence of a magnetic centre (an unpaired electron) that may be linked directly to a paramagnetic carbon atom. From a synthetic perspective, it is better to use stable radicals which have enough life time to incorporate with carbon centers.

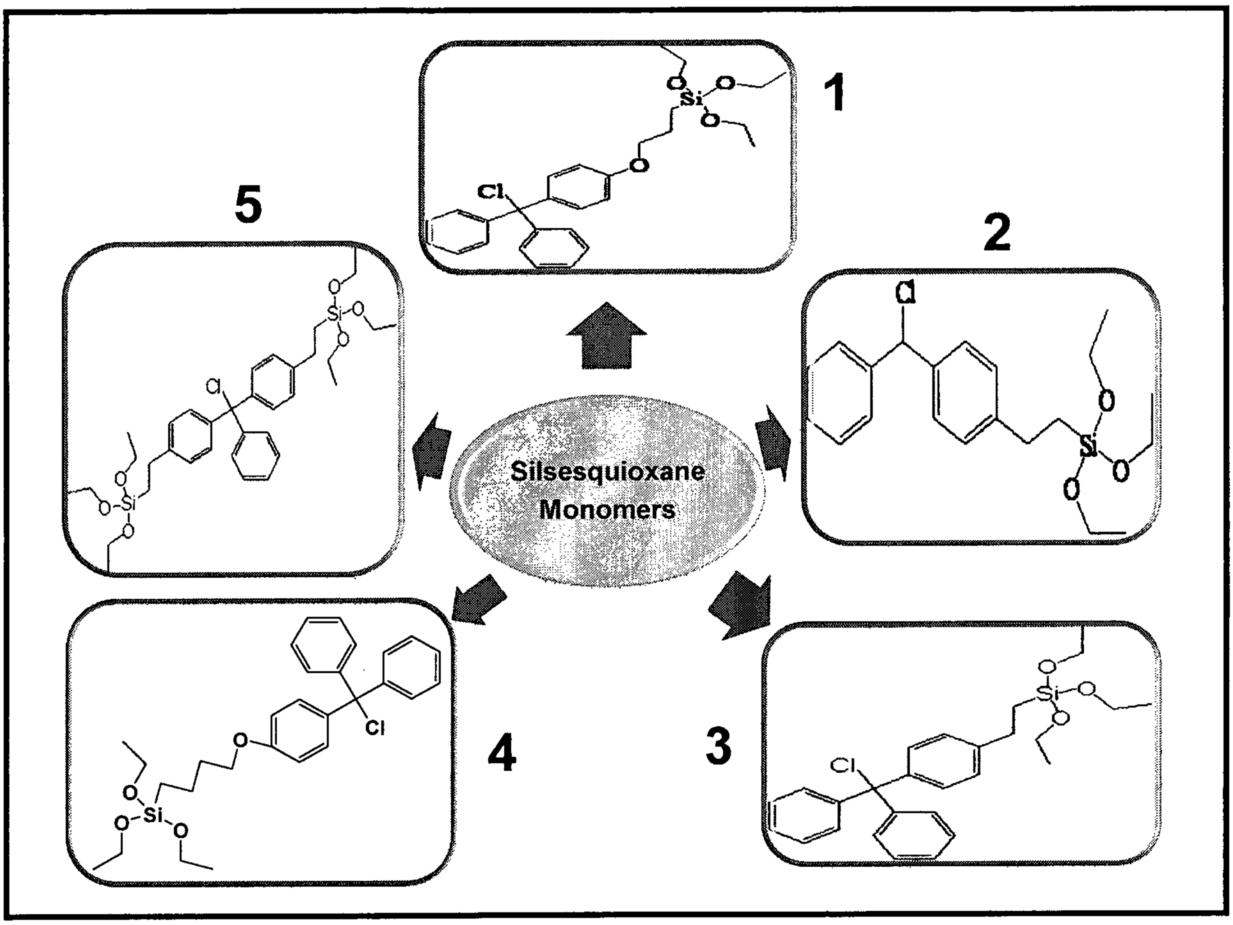
The challenges associated with the synthesizing of this hybrid material are the polysilsesquioxane precursor synthesis, and producing the radical. The major challenge is the instability of the free radical, as organic species containing unpaired electrons tend to be chemically reactive and unstable. In addition, whenever these organic molecules are bonded or come close enough to interact with each other, they naturally tend to pair their spins as antiferromagnetic interaction.

One of the most efficient methods to stabilize free radicals based on the steric shielding is by introducing bulky substituents. Even with the presence of steric bulk substituent, organic free radicals are still not stable. Thus, we propose to address this issue by entrapping and immobilizing the organic free radical component in the polymeric matrix of a bridged polysilsesquioxane. The polymeric matrix can be prepared using sol-gel method which results in the formation of siloxane (Si-O-Si) network. One of the future applications from this silsesquioxane-radical matrix material could be in memory storage device.

Neutral organic radicals possess an odd number of electrons (and hence one unpaired electron) and are often highly chemically reactive. They can be made more stable by adding aromatic rings to delocalize the unpaired electron or by introducing bulky substituents.

As shown in scheme 2 several synthesis targets could be proposed by having a longer, shorter, or more carbon chains with polysilsesquixanes. The logic behind the choice of synthesis targets is to investigate the differences in the porosity and the mechanical strength of each hybrid materials. In this research, monomor 1 and 2 of polysilsesquioxanes were synthesized successfully.

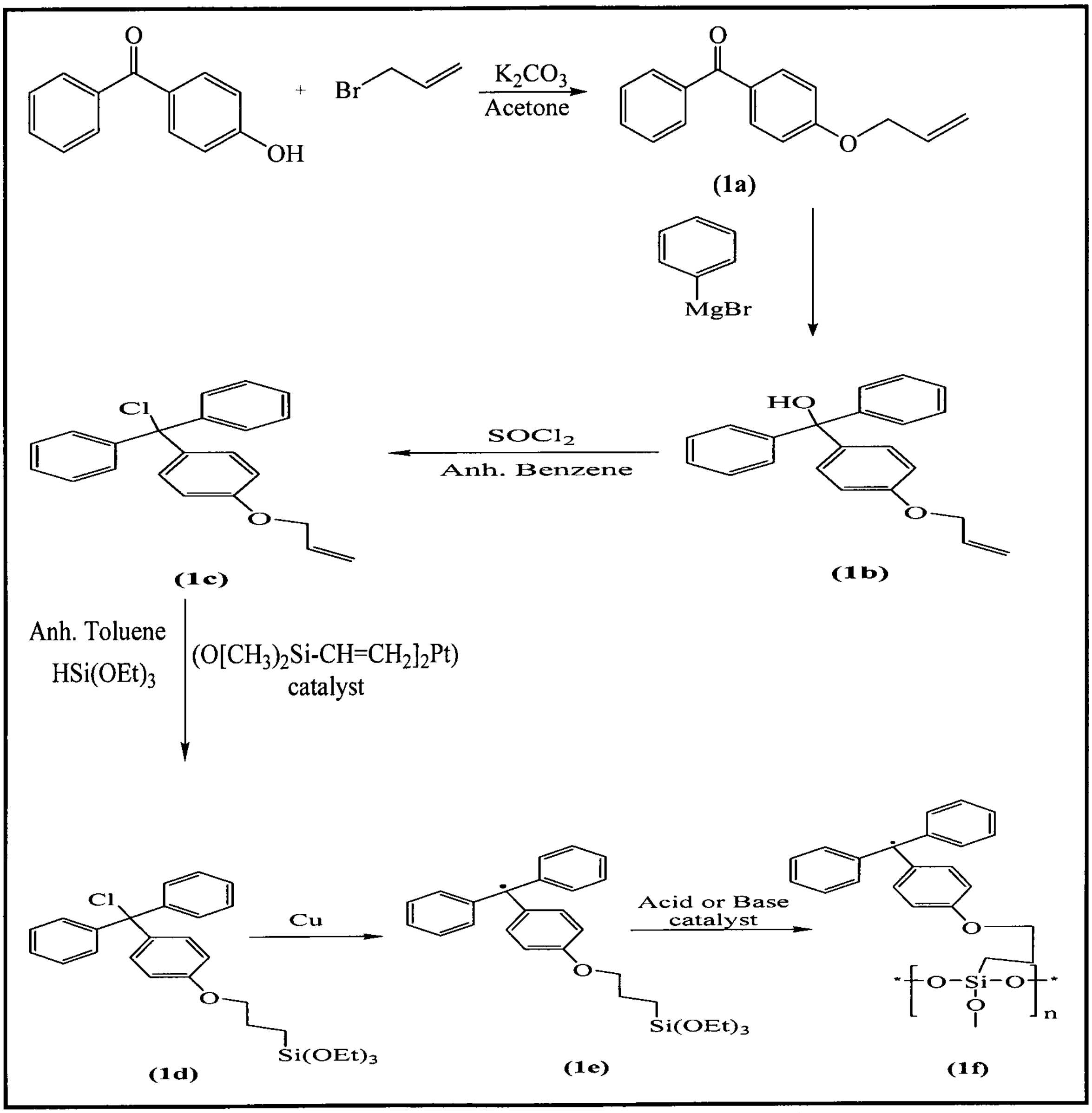
Scheme 2: Several polysilsesquixane hybrid material monomers which could be proposed.



Chapter 2

RESULTS AND DISCUSSION

A. Synthesis Route of Product 1



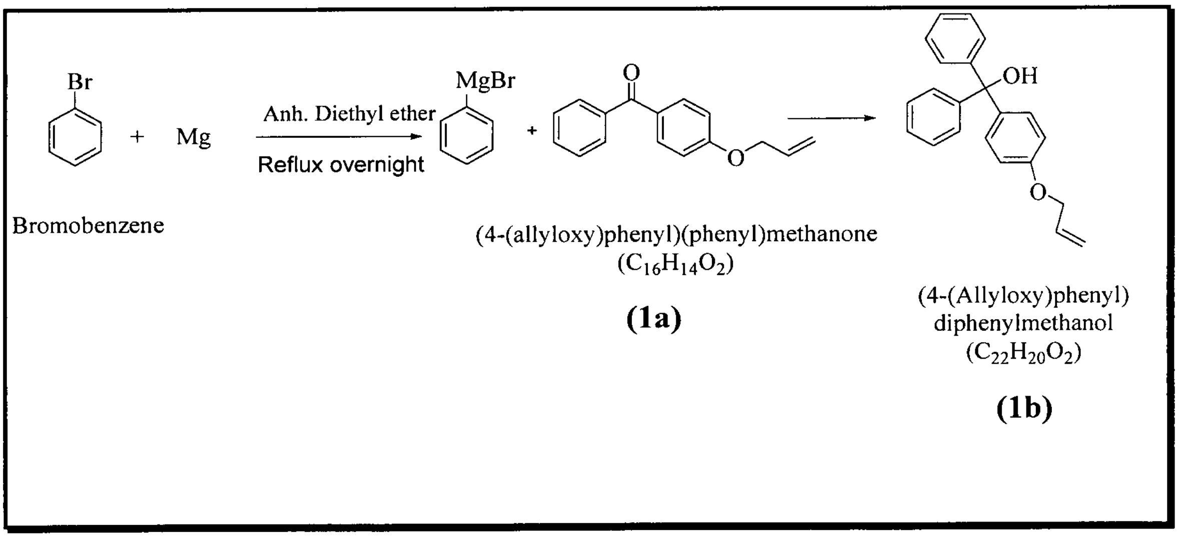
Scheme A: Synthesis Route of Product 1

*Synthesis route of monomer **(1a)** was adapted from B. Leshem, *Luminescence*, **2004,** *19*, 69-77.

2.1 Synthesis of (4-(Allyloxy) phenyl) diphenylmethanol (1b)

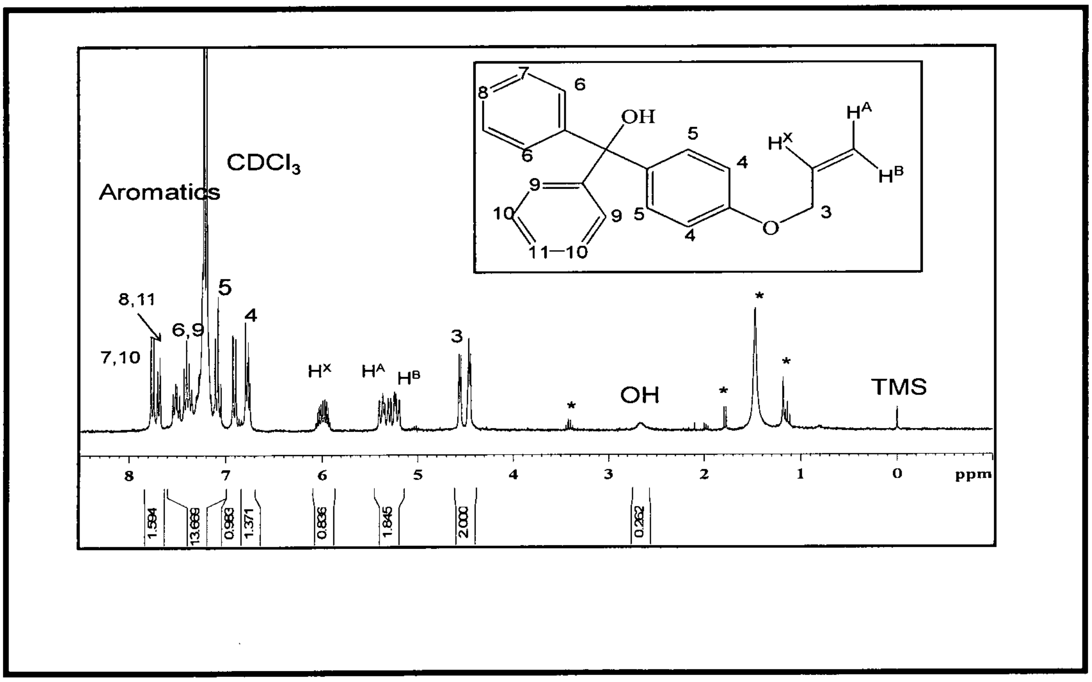
The mechanism of the formation allyoxy triphenylmethanol is via a Grignard reaction using monomer **1a** and phenyl magnesium bromide. Monomer **1a** was synthesized according to Leshem *et.al.* (61), through a Williamson ether synthesis. The qualitative result of **1b** at room temperature is viscous yellow oil and has not been reported before. The ^{1}H-NMR and ^{13}C-NMRspectra of the product **(1b)** are shown in spectra 1 and 2 respectively, below.

Scheme 3: Reaction of **1b** with **1a**; reagents and conditions.



In ^{1}H-NMR analysis, a proton directly bonded to an oxygen atom differs from a proton on a carbon atom because it is exchangeable and is subject to hydrogen bonding. The hydroxyl peak in this molecule is at δ 2.8 ppm (spectrum 1), which is exchangeable with addition of D_2O during the ^{1}H NMR measurement being taken. This proton-oxygen bonding depends also on intermolecular hydrogen bonding because hydrogen bonding decreases the electron density around the proton, thus moving the proton peak to higher frequency from TMS. In addition, the OH peak is shown as a singlet and broad. The hydroxyl group absorption of tertiary alcohol is located at the lowest field (δ 2.8 ppm) of the various alcohols, with secondary alcohol at δ 2.2 ppm and the primary at the highest field, δ 1.80 ppm. The reason for this is the inductive effect. The carbon in tertiary alcohol is more electronegative relative to hydrogen atom, which resulted in lower electron density around the tertiary alcohol, thus the proton is more exposed to the applied field and resonates at higher frequency.

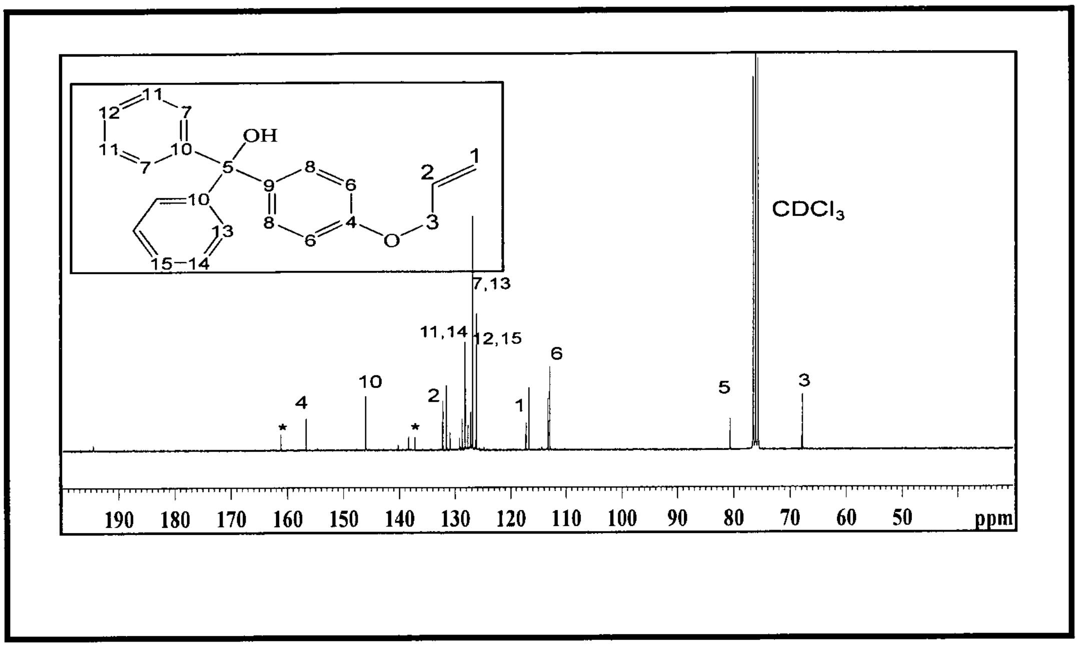
Spectrum 1: ^{1}H-NMR spectrum of **1b** in $CDCl_3$.



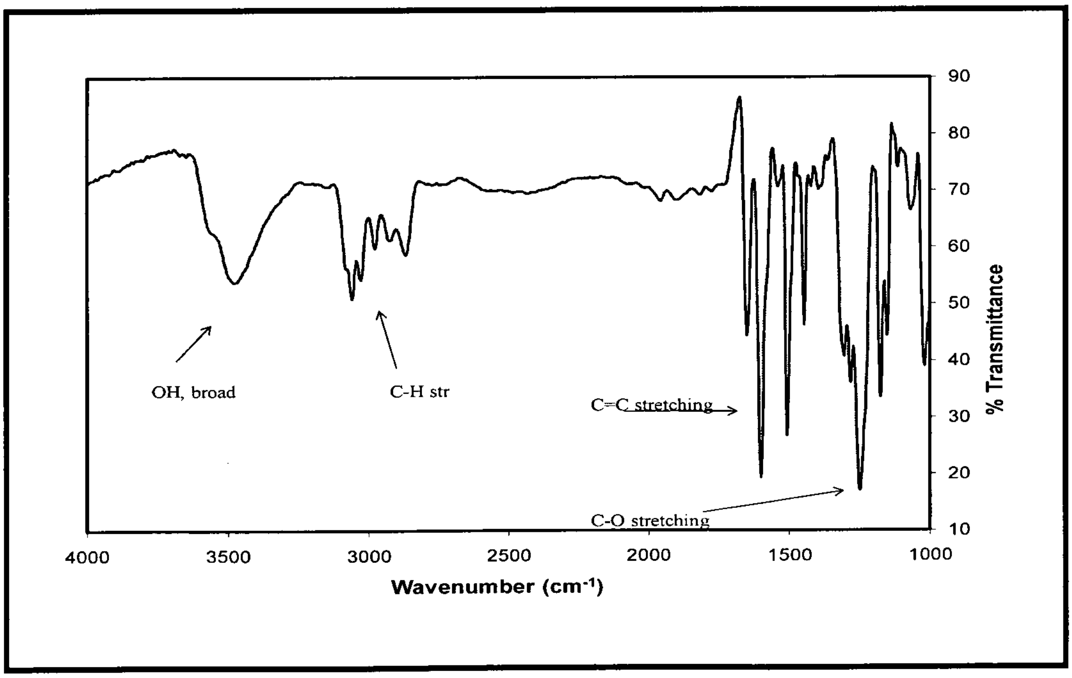
In ^{13}C-NMR (spectrum 2), the carbon center (#5) attached to hydroxyl group absorbs at higher field (δ 81.71 ppm) than carbon #4 due to the electronegative effect of oxygen atom. In contrast, the aromatic carbon (#4) bonded to an oxygen atom absorbs at the lowest field (δ 154 ppm) due to the negative inductive effect of oxygen. The other carbons of the double bonds in aromatic to the oxy group are shielded due to electron-donating ability of oxygen through resonance effect. Thus, the inductive and the resonance (mesomeric) effects play a crucial in chemical shift determination. The star symbols represent some non-reacting starting materials.

In spectrum 3, the first peak from the left shown as a broad and strong band at 3477 cm^{-1} represents the υ (O-H) of the hydroxyl group. The second peak is several strong bands around 3000 cm^{-1} representing the C-H stretching frequency. The third peak is a weak band at 1505 cm^{-1} showing an alkene (C=C) stretch, and the last peak is a sharp and strong band at 1254 cm^{-1} representing C-O stretch.

Spectrum 2: ^{13}C-NMR spectrum of **1b** in $CDCl_3$.



Spectrum 3: IR spectrum of **1b** as neat.

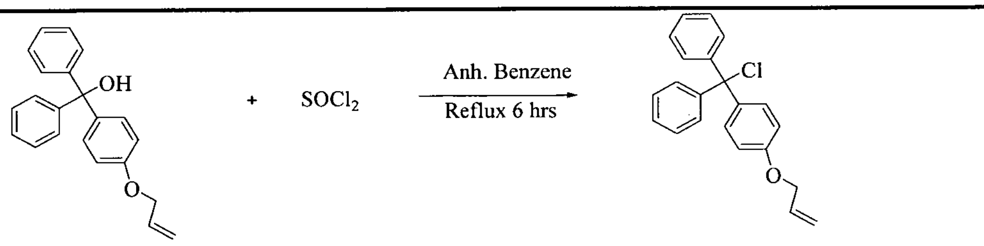


2.2 Synthesis of 1-(allyloxy)-4-(chlorodiphenylmethyl) benzene (1c).

The formation of tertiary chloride is the reaction of alcohol with thionyl chloride.

The reaction follows a S_N1 pathway formed a chlorosulfite ester as an intermediate.

Scheme 4: Reaction of **1c**, reagents and condition.



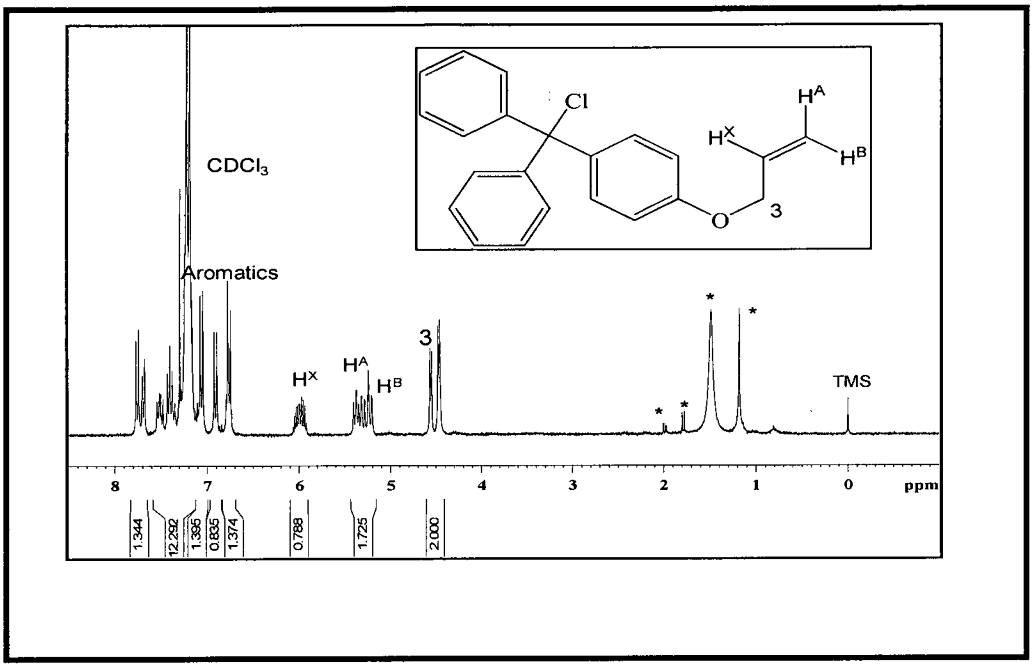
(4-(allyloxy)phenyl) diphenylmethanol
($C_{22}H_{20}O_2$)
(1b)

1-(allyloxy)-4-(chlorodiphenylmethyl)benzene
($C_{22}H_{19}ClO$)
(1c)

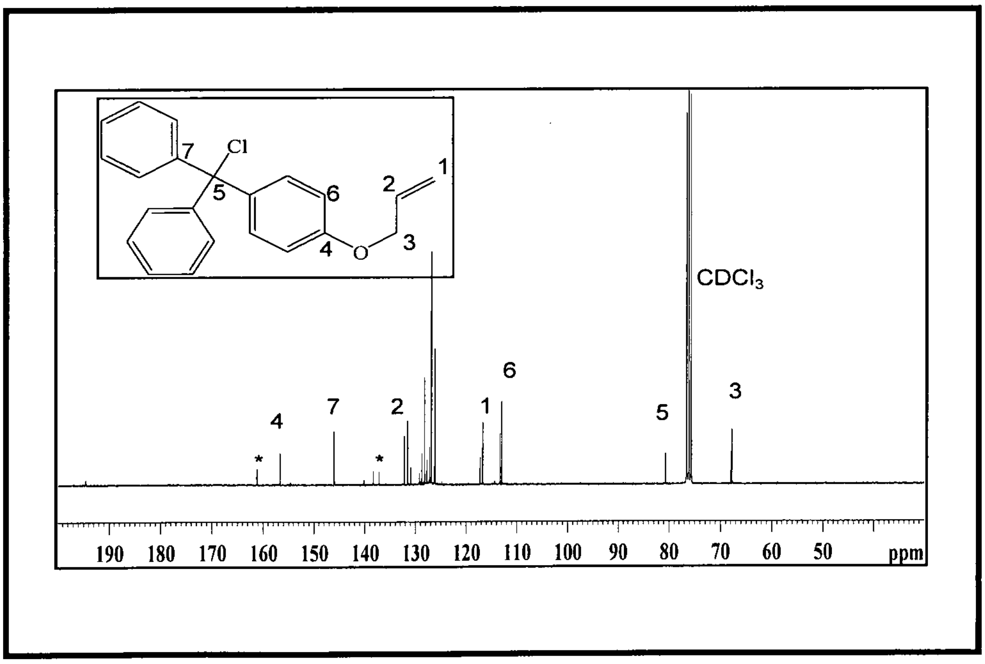
There is no absorption shown in the δ 2.0-3.0 ppm in Spectrum 4 from ^{1}H-NMR analysis, which can be assumed the OH has been substituted with chloride. However, the substitution can be seen clearly in the IR and ^{13}C-NMR spectra.

The chlorine atom absorbs at δ 81.68 ppm (spectrum 5), which is more shielded than the hydroxyl group chemical shift (δ 81.70 ppm). This is due to the effect of electronegativity. Chlorine atom is less electronegative (3.16) than oxygen atom (3.44), thus the C-Cl bond is more polarized toward the carbon atom attached to chlorine rather than the carbon attached to oxygen (62).

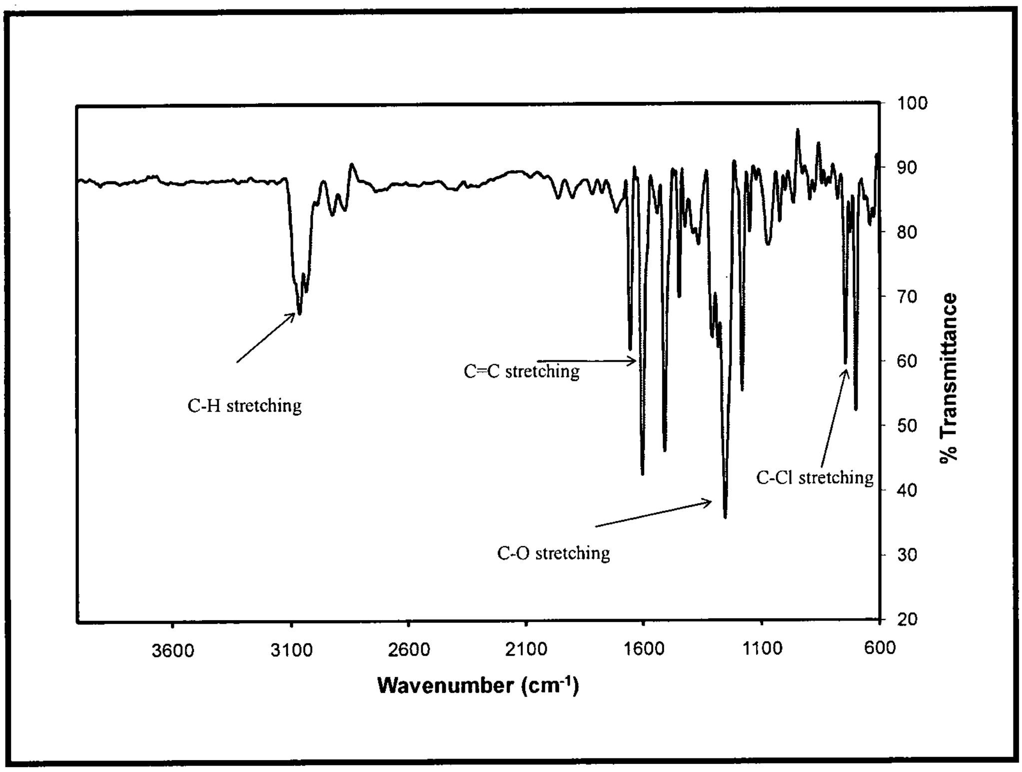
Spectrum 4: ^{1}H-NMR spectrum of **1c** in $CDCl_3$.



Spectrum 5: ^{13}C-NMR spectrum of **1c** in $CDCl_3$.



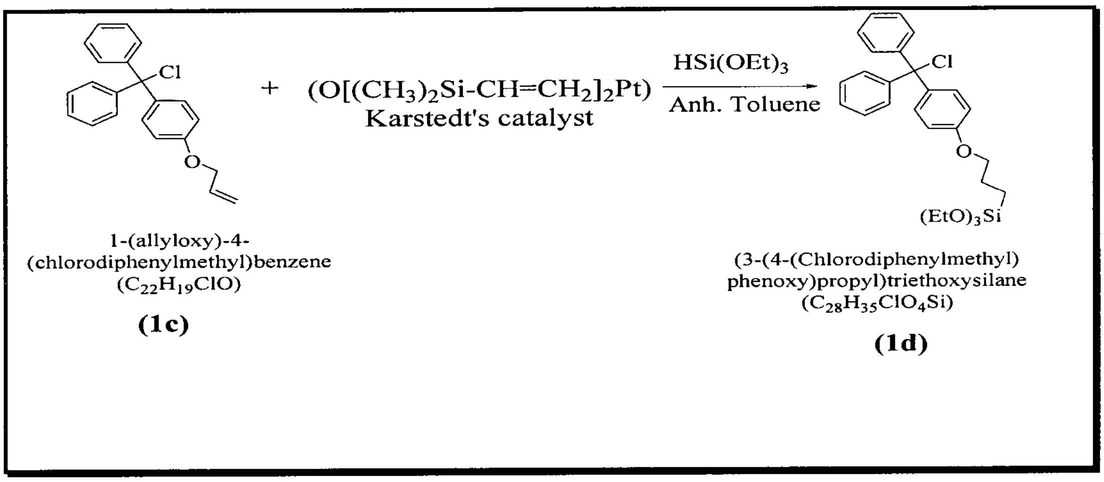
Spectrum 6: IR spectrum of **1c** as neat.



In IR spectrum (Spectrum 6), both C-Cl and C-O absorb at different frequencies. C-Cl absorbs at lower frequency (700 cm^{-1}) compared to C-O absorption (1251 cm^{-1}) due to the differences in the mass. Chlorine atom with the mass of 35.5 g/mol is heavier than oxygen atom with the mass of 16.0 g/mol. Thus a light atom will absorb at high frequency.

2.3 Synthesis of (3-(4-(Chlorodiphenylmethyl) phenoxy) propyl) triethoxysilane (1d).

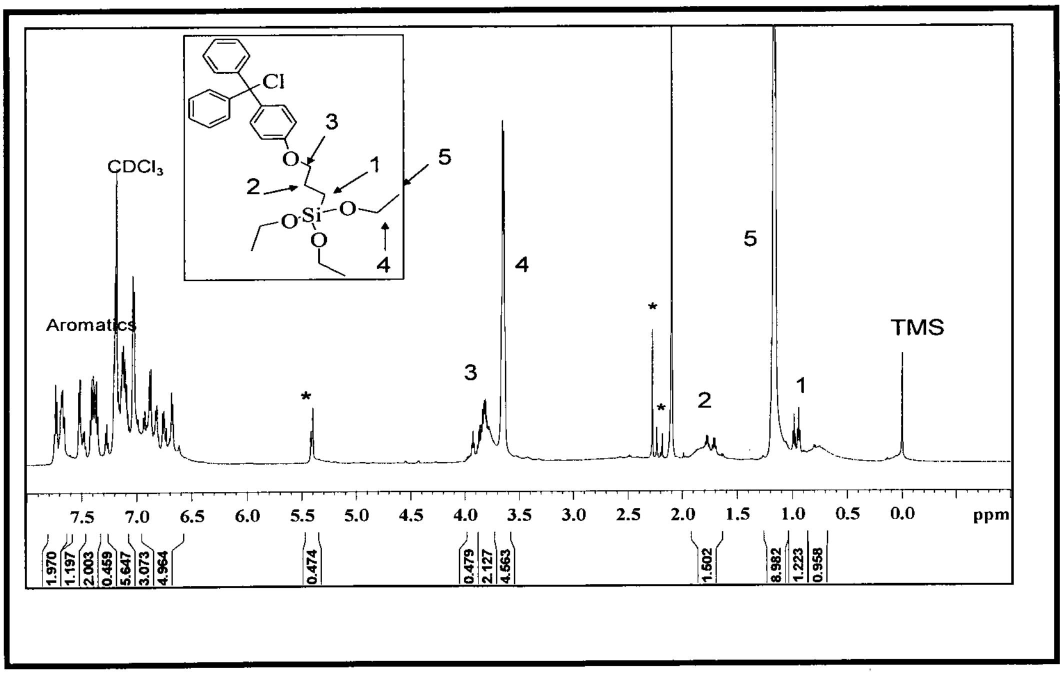
Scheme 5: Reaction of **1d.**



1-(allyloxy)-4-(chlorodiphenylmethyl)benzene
($C_{22}H_{19}ClO$)
(1c)

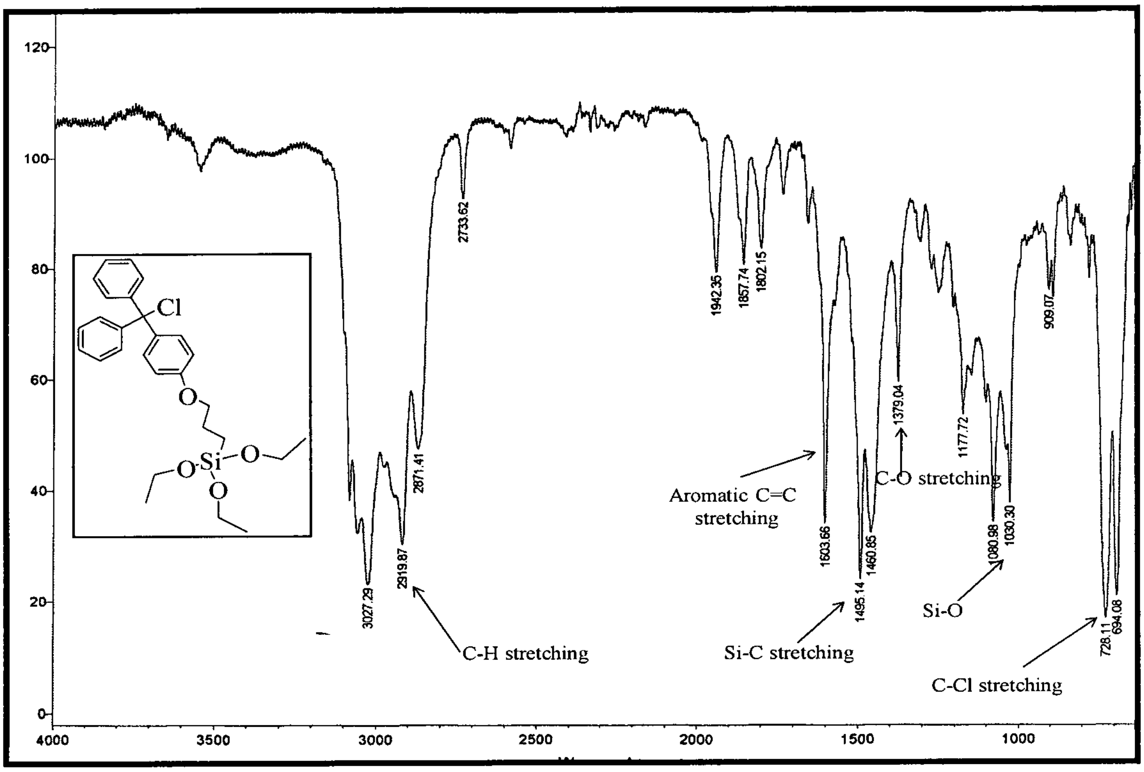
(3-(4-(Chlorodiphenylmethyl) phenoxy)propyl)triethoxysilane
($C_{28}H_{35}ClO_4Si$)
(1d)

Spectrum 7: ^{1}H-NMR spectrum of **1d** in $CDCl_3$.



Finally, the synthesis of monomer **IV** was successful using Karstedt's catalyst, (O $[(CH_3)_2Si\text{-}CH{=}CH_2]_2Pt$) and anhydrous toluene as shown in Spectrum 7. Generally, platinum is found in three different oxidation states: Pt (0), Pt (II), and Pt (IV). By looking into their structure, Karsterdt's and Speier's catalysts can be distinguished by several criteria, such as the coordination number (number of ligands around the metal centre), the metal oxidation state, and the ligands bonded to platinum center (63). Karstedt's catalyst has a ML_3 fragment with coordination number of three. Its platinum has lower oxidation state [Pt (0)], compared to the Speier's catalyst [Pt (IV)]. The chemical shift of methyl proton (#5) of triethoxysilane is located in the most shielding region (δ 0.95 ppm) among other protons because the protons are surrounded by high electron density of silicon atom (spectrum 7). The methylene protons (#3) absorb at lower field (3.82 ppm) than the methylene protons (#4) with chemical shift of 3.78 ppm. The reason is protons #3 are closed to the aromatic ring and an oxygen atom withdraw electron density (due to negative inductive effect) from the neighborhood protons, thus the protons are surrounded by less electron density. On the other hand, protons (#4) have higher shielding and higher electron density around the protons than protons (#3) because of their closeness to the electropositive silicon atom.

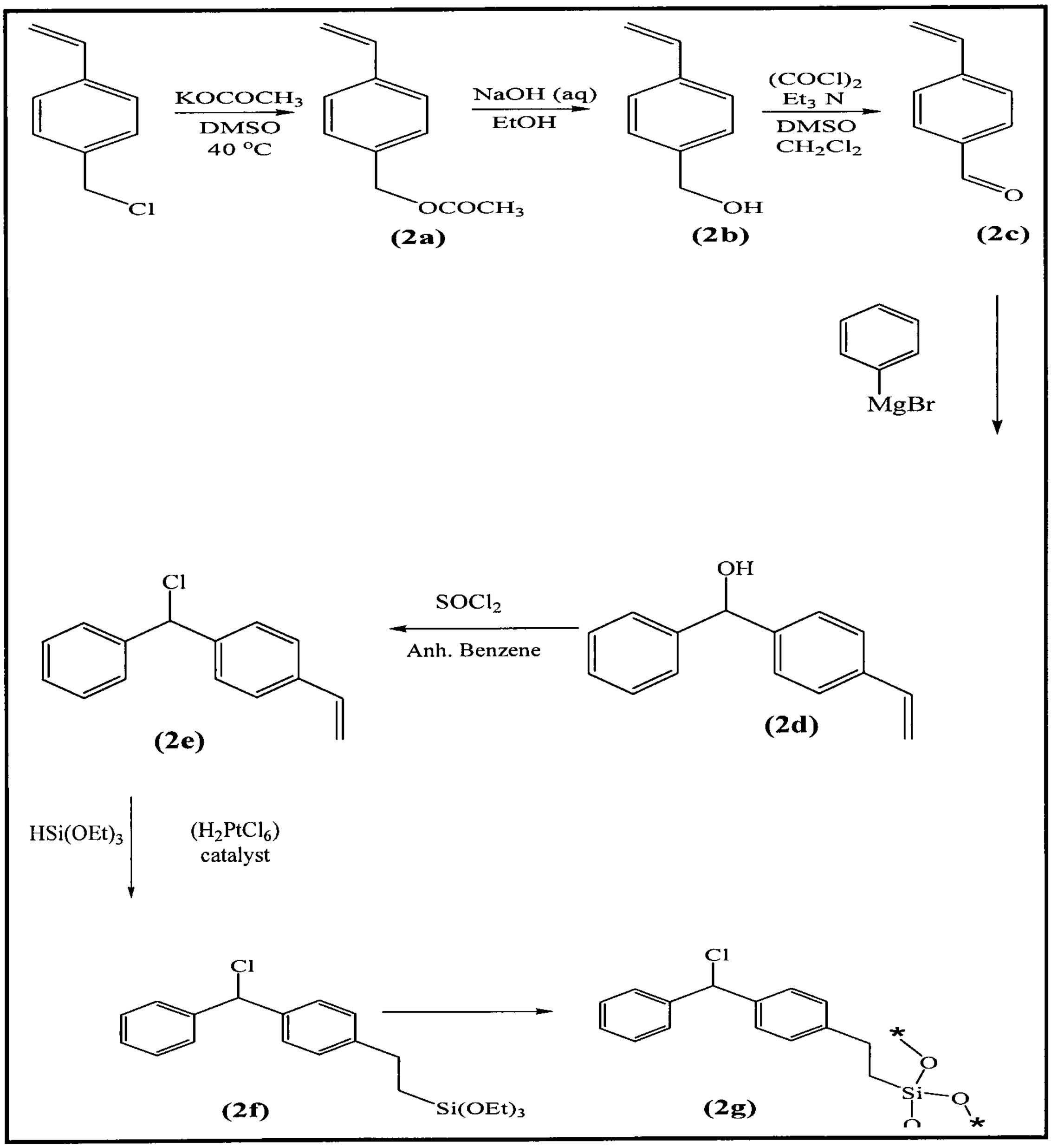
Spectrum 8: IR spectrum of **1d** as neat.



In the IR spectrum above, Si-O bond absorbs at lower wavenumber (~1100 cm^{-1}) compare to C-O bond (~1300 cm^{-1}) absorbed at higher wavenumber. This is due to the differences in atomic mass of Si and O atoms. Silicon atom is heavier (28.1 g/mol) than oxygen atom (16.0 g/mol), thus the heavier atom will absorb at lower frequency.

Therefore from the Scheme A, polysilsesquioxane monomer (1d) has been successfully synthesized.

B. Synthesis Route of Product 2



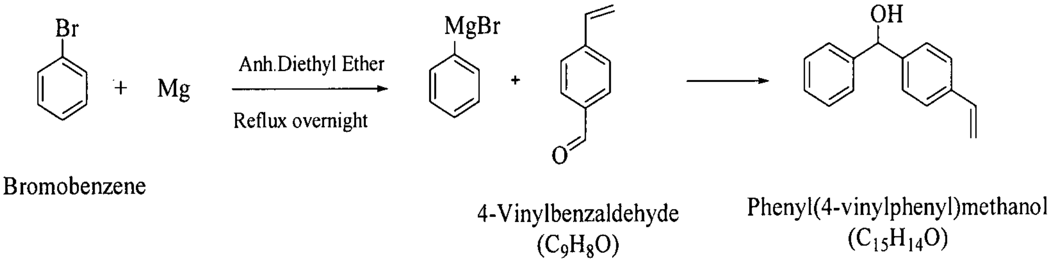
Scheme B: Synthesis Route of Product 2

*Synthesis route of monomer **(2a)** and **(2b)** were adapted from C.H. Bamford, H. Lindsay, *Polymer*, **1973,** *14*, 330. Monomer **(2c)** was adapted from M. Marx, T.T. Tidwell, *J. Org. Chem.*, **1984,** *49*, 788-793.

2.4 Synthesis of Phenyl (4-vinylphenyl) methanol (2d).

Monomer **2d** was synthesized from monomer **2c** and has never been reported before. Monomer **2a** and **2b** were reported before according to literature by Lindsay *et.al.* (64). The monomer **2c** was reported by Mark and Tidwell (65). The synthesis of secondary alcohol (Scheme 6) is similar to the tertiary alcohol of monomer **1b** (Scheme 1), except the source of its electrophile. The electrophile of monomer **1b** is a ketone functional group, while the electrophile in the secondary alcohol is an aldehyde.

Scheme 6: Reaction of **2d**, reagents and condition.

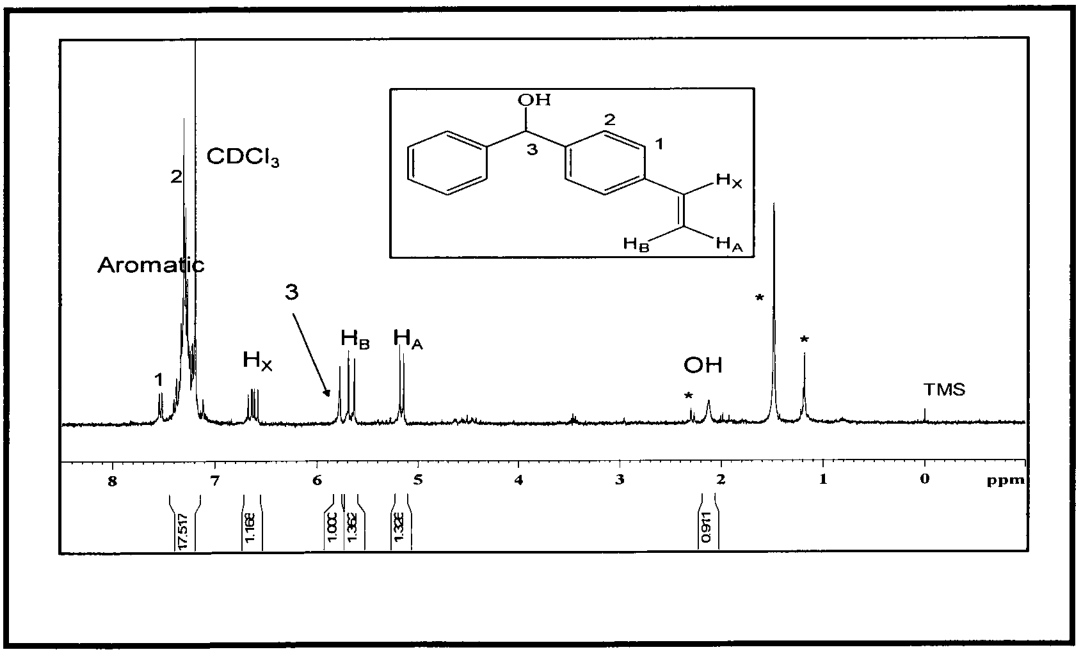


(2c) **(2d)**

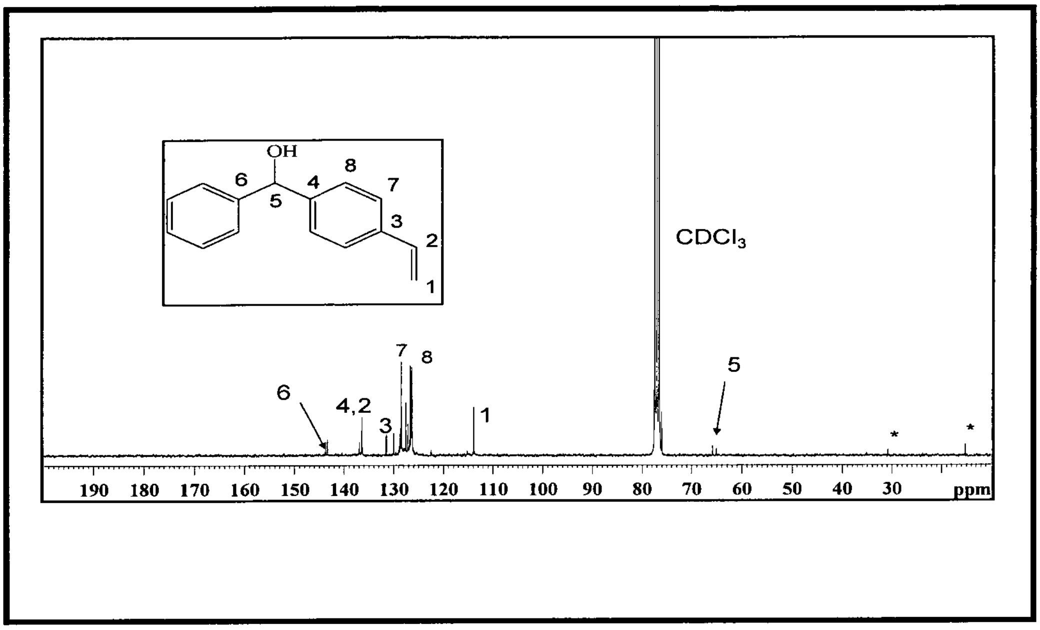
From ^{1}H-NMR spectrum, proton (#3) at carbon centre appears a singlet at 5.8 ppm because the hydroxyl proton does not couple with any protons. Proton (#3) in this monomer resonates at lower field compared to monomer **2b** of primary alcohol. The reason is van der Waals deshielding effect. Proton in monomer **2d** occupies sterically hindered position in crowded molecule resulting in van der Waals repulsion. The electron cloud of a bulky group (hindered group) will tend to repel the electron cloud surrounding the proton. Thus, proton (#3) of monomer **2d** will be deshielded and will absorb at lower field.

In ^{13}C-NMR (Spectrum 10), secondary carbon atom (#5) of monomer **2d** absorbs at higher field (δ 65.8 ppm) compared to tertiary carbon atom (#5) of monomer **1b** (Spectrum 3) having δ 81.71 ppm, also it absorbs at lower field compared to primary carbon atom (monomer B, δ 65.5 ppm). The explanation is the presence and number of substituents at α, β- or γ- position (62).

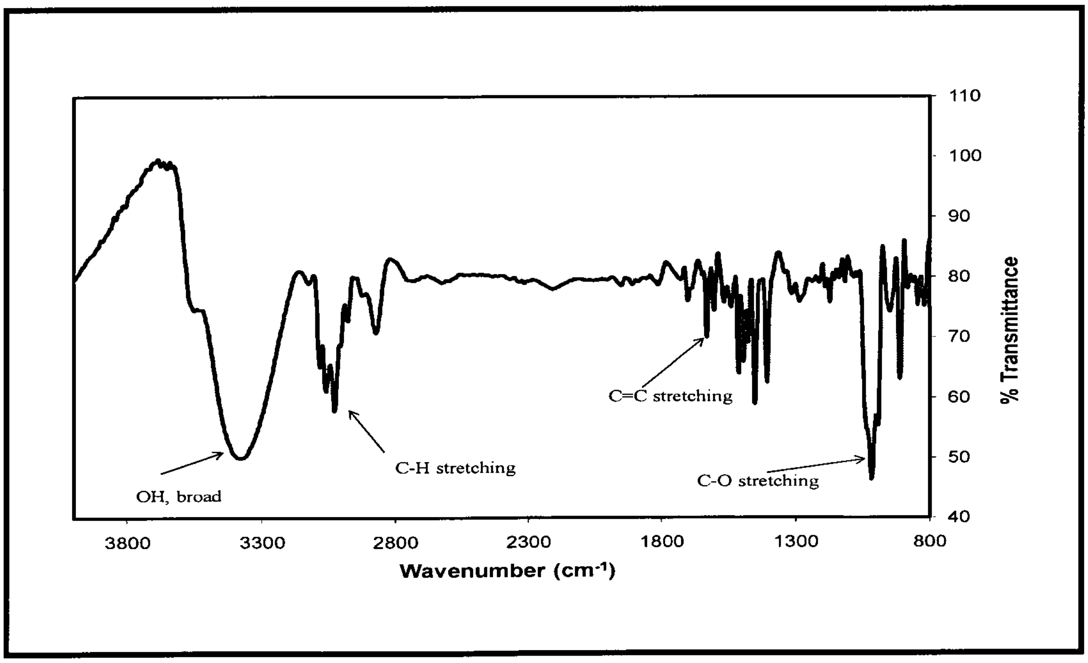
Spectrum 9: ^{1}H-NMR spectrum of **2d** in CDCl$_3$.



Spectrum 10: ^{13}C-NMR spectrum of **2d** in $CDCl_3$.



Spectrum 11: IR spectrum of **2d** as neat.

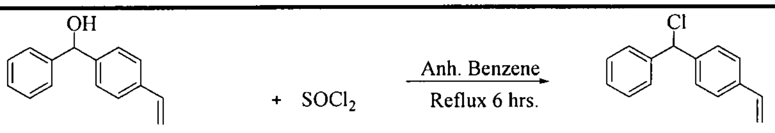


In IR spectrum (Spectrum 11), there are four absorption peaks, which can be easily identified. First peak is a broad and strong band at 3391 cm^{-1} representing a hydroxyl group, the second peak is several strong bands around 3060 cm^{-1} representing aromatic C-H stretching, the third peak is a weak band at 1629 cm^{-1} representing an alkene (C=C), and the last peak is a intense peak at 1015 cm^{-1} representing a C-O group. The stretching absorption frequency of the tertiary O-H group (3477 cm^{-1}) is higher than that of the secondary O-H (3391 cm^{-1}). This is due to the additional phenyl group in tertiary alcohol which hinders the stretching vibration of the O-H group and thus its frequency is high.

2.5 Synthesis of 1-(Chloro(phenyl)methyl)-4-vinylbenzene (2e).

The formation of secondary alkyl chloride is the reaction of secondary alcohol and thionyl chloride followed an S_N1 pathway.

Scheme 7: Reaction of **2e.**



phenyl(4-vinylphenyl)methanol
($C_{15}H_{14}O$)

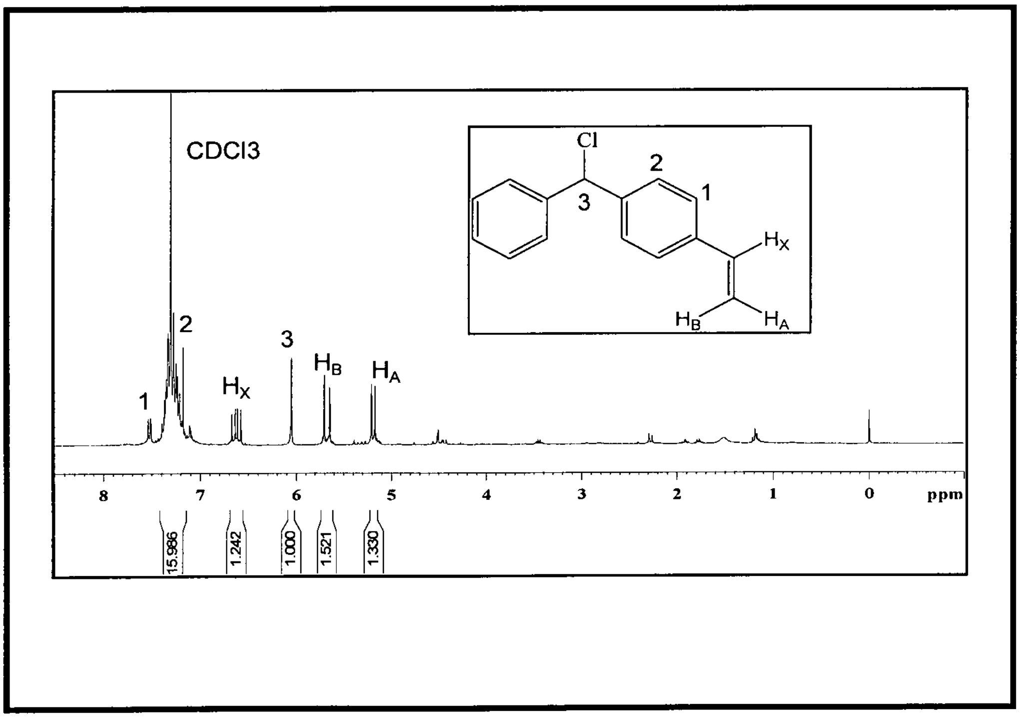
(2d)

1-(Chloro(phenyl)methyl)-4-vinylbenzene (E)
($C_{15}H_{13}Cl$)

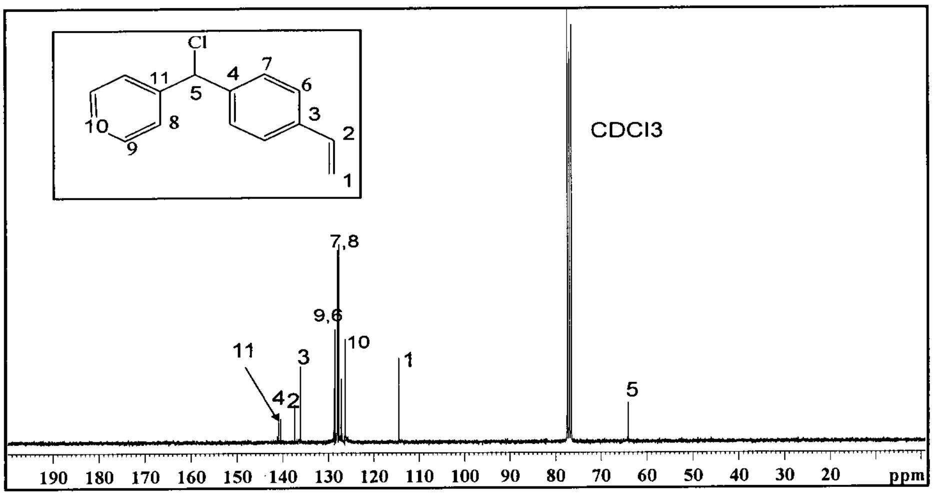
(2e)

In ^{1}H-NMR (Spectrum 12), there is no O-H peak presence showing the hydroxyl has been substituted by Cl atom. Proton (#3) bonded to C-Cl of monomer **2e** absorbs more downfield (δ 6.13 ppm) than proton bonded to C-OH (δ 5.8 ppm) in the previous monomer. This is due to the electronegativity effect. Oxygen has greater electronegativity (3.5) than chlorine atom (3.0), thus we expect the proton bonded to C-Cl will be in highly shielded area than proton bonded to C-O. However, the experimental result shows proton in monomer **2e** absorbs in deshielded area. This is because the oxygen atom bonded to hydrogen atom, which lowering its electronegativity value of monomer **2d**.

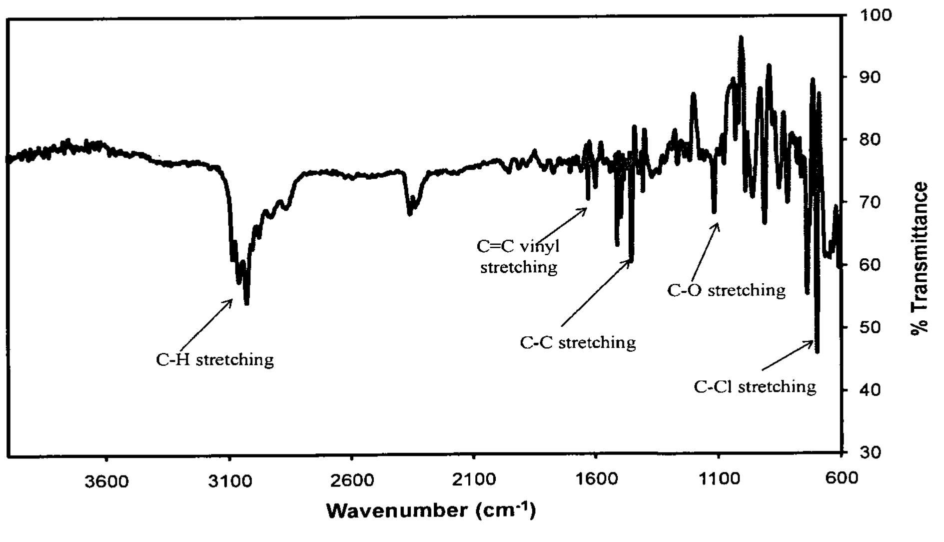
Spectrum 12: ^{1}H-NMR spectrum of **2e** in $CDCl_3$.



Spectrum 13: ^{13}C-NMR spectrum of **2e** in $CDCl_3$.



Spectrum 14: IR spectrum of **2e** as neat.



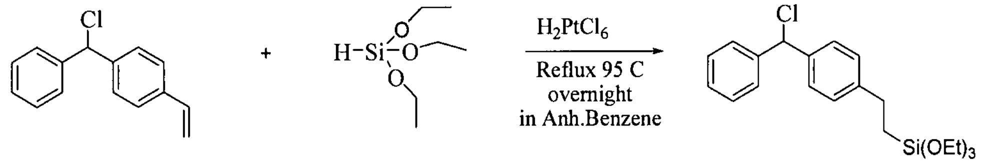
In ^{13}C-NMR (Spectrum 13), the shift of carbon atom attached to chlorine in tertiary alkyl (δ 81.68) causes a large shift to the left from the carbon position in secondary alkyl (δ 64.2) due to electronegativity consideration. The carbon in tertiary alcohol is more electronegative relative to chlorine, the electron density around the tertiary alcohol is low, and this carbon is more exposed to the applied field, thus resonate to higher frequency.

In IR spectra (Spectrum 14), the substitution of chlorine from O-H group is shown by the disappearance of broad band at higher frequency (above 3400 cm^{-1}) and the additional peak appeared at 700 cm^{-1}.

2.6 Synthesis of (4-(Chloro(phenyl)methyl) phenethyl) triethoxysilane (2f).

The synthesis involves a hydrosilylation synthesis using chloroplatinic acid catalyst as shown in Scheme 8. Chloroplatinic acid catalyst is the first “homogenous” catalyst reported for hydrosilylation by Speier, thus this catalyst is known as Speier’s catalyst (63). This catalyst has a coordination number of 6 with six ligands bonded to Pt and has octahedron structure. Its platinum has +4 oxidation state [Pt (IV)], which is higher than Karstedt’s catalyst.

Scheme 8: Reaction of **2f.**



1-(chloro(phenyl)methyl)-4-vinylbenzene
($C_{15}H_{13}Cl$)

(2e)

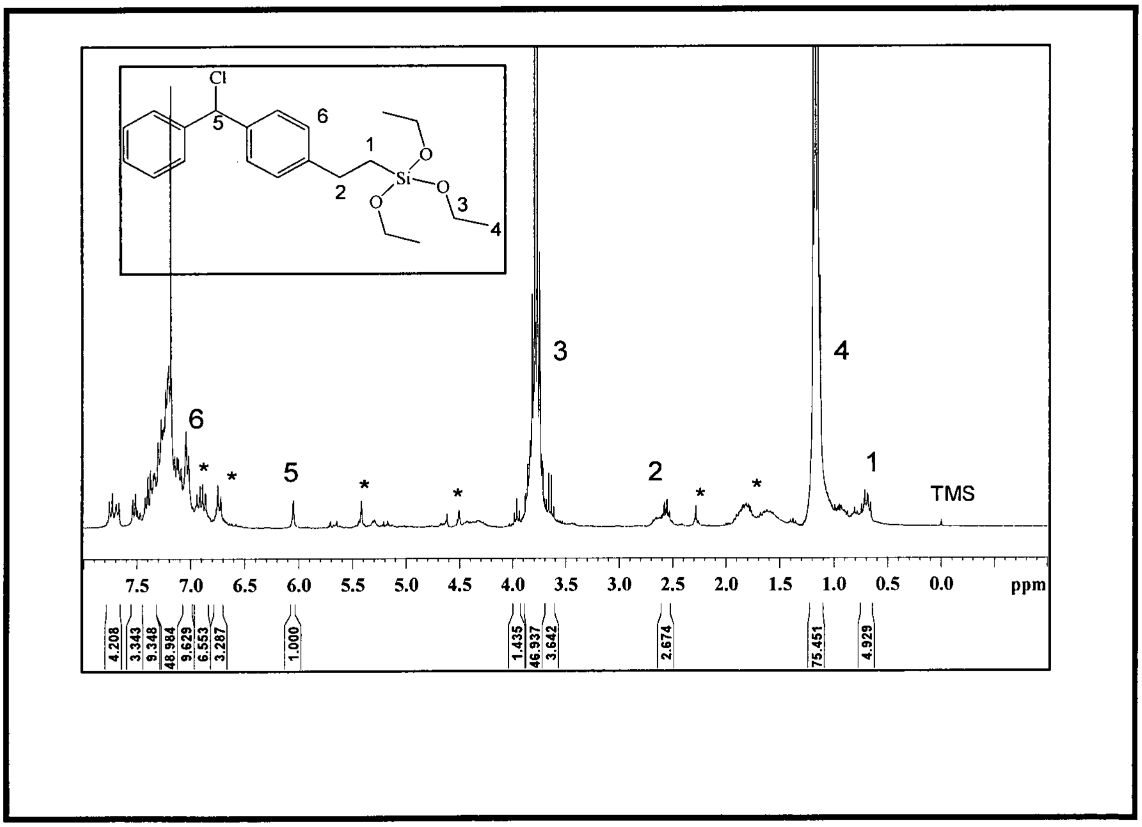
Triethoxysilane
($C_6H_{16}O_3Si$)

(4-(chloro(phenyl)methyl)phenethyl) triethoxysilane
($C_{21}H_{19}ClO_3Si$)

(2f)

The chemical shift of methyl protons (#1) of triethoxysilane absorbs at the highest field (δ 0.68 ppm) among all protons. This is because protons (#1) are bonded to the silicon atom providing high electron density source to surrounding protons. Protons (#2) absorb further left to down field area (2.62 ppm) because of their proximity to aromatic ring. The methylene protons (#3) is located in less shielded region (3.80 ppm) due to oxygen atom compared to methyl protons (#4) located in more shielded area (1.31 ppm) because they are further away from electronegative atom. Finally, proton (#5) covalently bonded to Cl atom absorbs more closely to aromatic region (6.05 ppm) because it is surrounded by two aromatic rings and electronegative atom. Thus, proton (#5) has the least electron density, the most susceptible to the applied magnetic field and at the most highly deshielded area among all protons, except protons in aromatics.

Spectrum 15: ^{1}H-NMR spectrum of **2f** in $CDCl_3$.

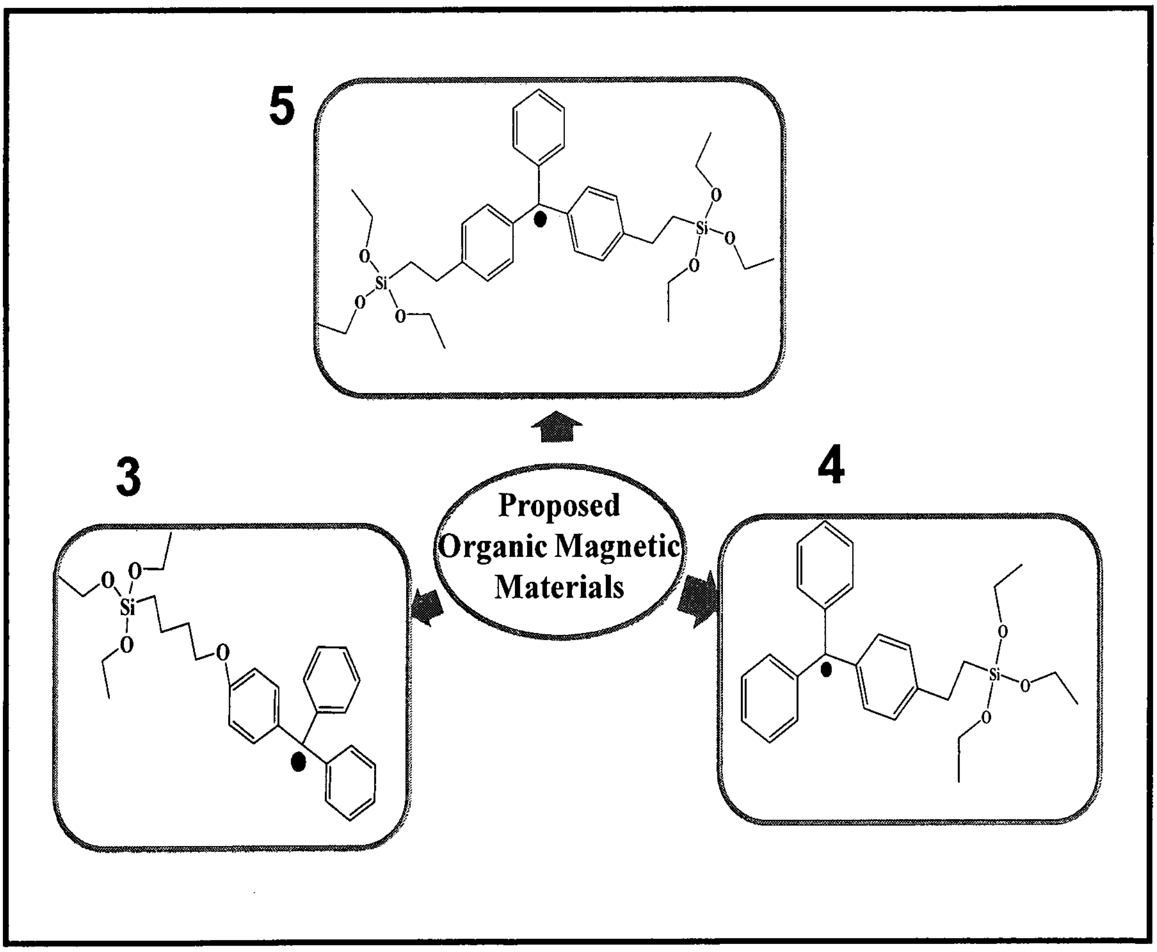


Therefore from the Scheme B, polysilsesquioxane monomer having two aromatic rings (2f) has been successfully synthesized.

In this research, several hybrid magnetic materials having shorter, longer and more carbon chains is proposed as shown in Scheme 9.

The target compounds of 3-5,potential hybrid magnetic materials, can be synthesized following the same synthetic route as product 1, shown in Scheme A.

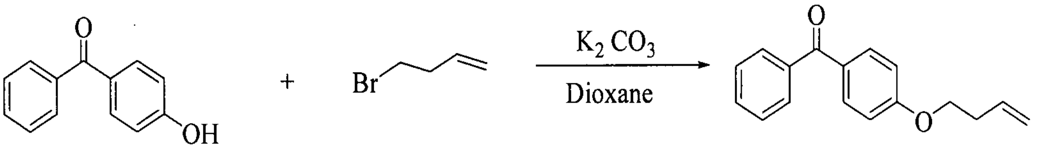
Scheme 9: Proposed hybrid magnetic materials (product 3,4, and 5).



C. Synthesis of (4-(But-3-enyloxy)phenyl) (phenyl) methanone (3a) as starting monomer for hybrid magnetic material product 3.

Monomer **(3a)** is a reaction product between 4-bromo-1-butene and 4 hydroxybenzophenone in dioxane solvent as a starting monomer to produce product 3.

Scheme 10: Reaction of **3a**; reagents and conditions



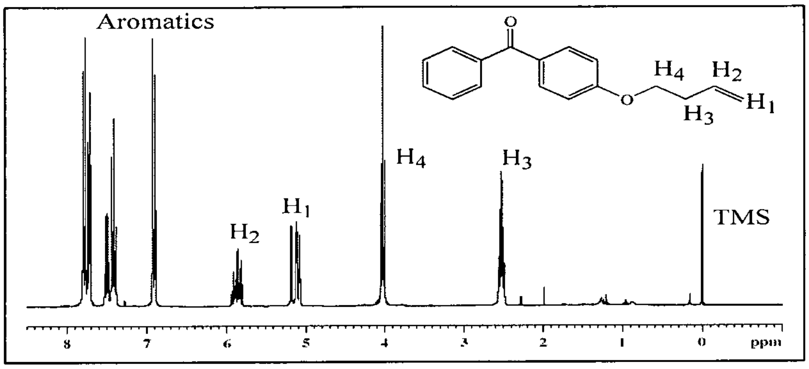
4-Hydroxybenzophenone 4-Bromo-1-Butene (4-(but-3-enyloxy)phenyl) (phenyl) methanone

(3a)

In ^{1}H-NMR analysis, monomer with long chain of hydoxyl alkenes as one of the substituent in aromatic ring, compound (3a) was also synthesized through the reaction of 4 hydroxybenzophenone and 4-bromobutene in the presence of base (K_2CO_3).

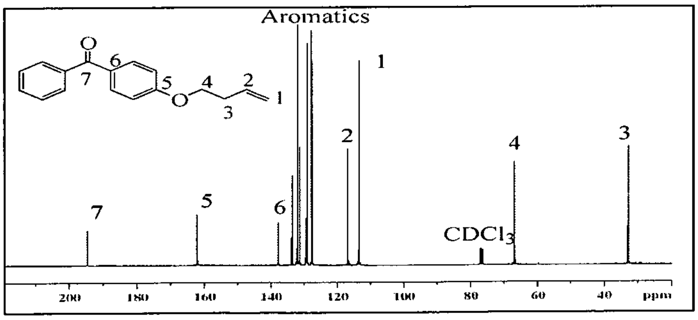
The proton nearby oxygen atom is located downfield (4.0 ppm) compared to proton closed to vinyl group (2.5 ppm) due to the electronegativity reason.

Spectrum 16: ^{1}H-NMR spectrum of **3a** in $CDCl_3$.



^{1}H-NMR (4-(But-3-enyloxy)phenyl) (phenyl) methanone

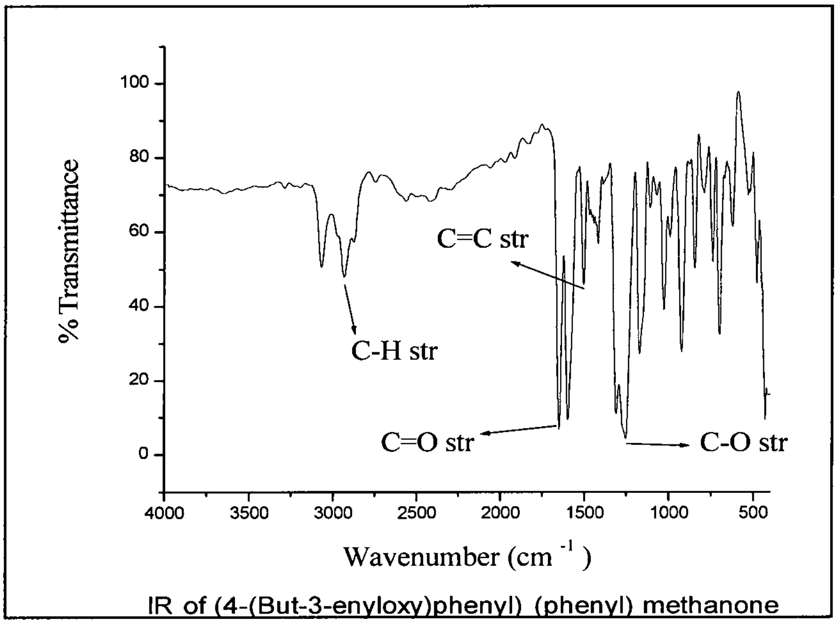
Spectrum 17: ^{13}C-NMR spectrum of **3a** in $CDCl_3$.



^{13}C-NMR (4-(But-3-enyloxy)phenyl) (phenyl) methanone

The presence of carbonyl (C=O) of benzophenone from ^{13}C NMR was the most deshielded at δ 162.2 followed by the aromatic carbon closed to oxygen atom.

Spectrum 18: IR spectrum of **3a** as neat

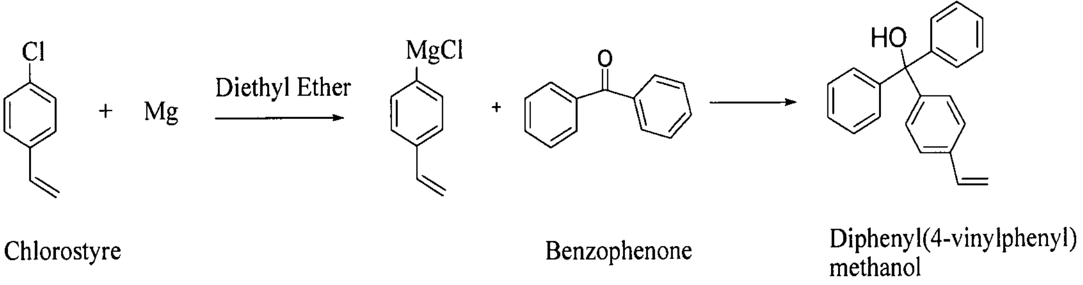


The present of C=O (ketone) and C-O are clearly shown through the IR spectra in which the C=O band absorbed at higher frequency (1650 cm^{-1}) compared to C-O band (1254 cm^{-1}).

D. Synthesis of (Diphenyl (4-vinylphenyl) methanol monomer (4a) as starting monomer for hybrid magnetic material product 4.

Monomer (**4a**) as the starting material was synthesized previously in Toy's group (66). The reaction (Scheme 11) was performed through a Grignard reaction using organometallic, magnesium, giving a product of yellow viscous oil. The characterization data matched with those of the literature.

Scheme 11: Reaction of **4a**; reagents and conditions



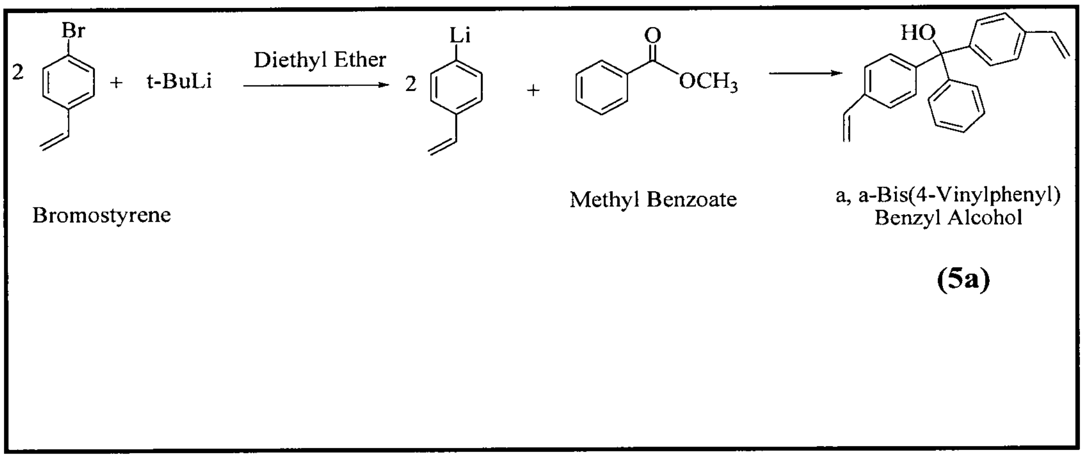
(4a)

*Synthesis route of monomer (4a) was adapted from M.K.W. Choi, P.H. Toy, *Tetrahedron*, **2004**, *60*, 2903.

E. Synthesis of α, α-Bis (4-Vinylphenyl) Benzyl Alcohol monomer (5a) as starting monomer for hybrid magnetic material product 5.

Monomer (**5a**) has been synthesized previously in Rimmer's group (67). The reaction was performed through a Grignard reaction using organometallic lithium instead of magnesium, as one of the reactant, yield yellow viscous oil, as shown in Scheme 12.

Scheme 12: Reaction of 5**a**; reagents and conditions



(5a)

*Synthesis route of monomer (5a) was adapted from A. Nzeru, J.R. Ebdon, S. Rimmer, *J.Org.Chem.*, **1997,** *62,* 8928.

In this thesis, we were succesful in synthesizing monomer 3a, 4a, and 5a as the starting materials which could lead to produce several hybrid magnetic material products 3,4,and 5.

Chapter 3

EXPERIMENTAL

General

Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy for proton and carbon were recorded on Bruker ARX 300 MHz, 400 MHz and 600 MHz. Chemical shifts are reported on the δ scale in ppm (parts per million) relative to an internal standard for proton and carbon (e.g. tetramethylsilane (TMS), $CDCl_3$, or DMSO-d_6). The splitting patterns are described as singlets (s), doublets (d), doublet of doublets (dd), triplets (t), quartet (q), and multiplets (m).

Infra-red (IR) spectra were recorded as neat or as solid sample using KBr disc using a Mattson 3000 Fourier Transform infrared (FTIR) Spectrophotometer, and absorptions are reported as wavenumbers (cm^{-1}).

Materials

4-Hydroxybenzophenone, 3-bromo-1-pentene, potassium carbonate, bromobenzene, chlorostyrene, benzophenone, 4-bromo-1-butene, t-BuLi (tert-butyl lithium), methyl benzoate, magnesium turning, triethoxysilane [$Si(OEt)_3$], platinum (0)-1, 3-divinyl-1, 1, 3, 3-tetramethyldisiloxane complex solution ($O[(CH_3)_2Si\text{-}CH{=}CH_2]_2Pt$) catalyst were obtained from Sigma-Aldrich Chemicals Canada. Thionyl Chloride ($SOCl_2$) was obtained from Alfa Aesar USA.

Sodium chloride (NaCl), sodium hydroxide (NaOH) pellets, anhydrous $MgSO_4$, anhydrous sodium sulfate (Na_2SO_4) , potassium acetate, hexane, anhydrous diethyl ether, toluene, benzene, tetrahydrofuran (THF), acetone, methanol, ethyl acetate, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), potassium carbonate, dichloromethane were obtained from Caledon Laboratories, Georgetown, Ontario, Canada. Sodium bisulfite ($NaHSO_3$) and sodium bicarbonate ($NaHCO_3$) were purchased from T.J. Baker Chemicals, USA. The DMSO-d_6 and $CDCl_3$ containing 1% v/v TMS were purchased from Cambridge Isotope Laboratories Inc., M.A., USA. Analytical thin layer chromatography (TLC) was done on commercially prepared silica gel 60F 254 coated plastic sheets (Sigma-Aldrich). For column chromatography, high purity grade (70-230 mesh, 60 A) silica gel was used.

General Preparation

Anhydrous diethyl ether, toluene, and benzene were freshly distilled under sodium benzophenone ketyl prior to use. All reactions were performed in flame-dried glassware and under nitrogen or argon. Air-sensitive solids (i.e. platinum catalyst and triethoxysilane) were handled in a glove bag under argon. After numerous attempts in purification due to the difficulty in air sensitivity of these reactions, appreciable yields and the elemental analysis are not reported.

A. Method for the Preparation of product 1

[3-(4(Chlorodiphenylmethyl)phenoxy)propyl)triethoxysilane] xerogel (1d)

Starting Material

The first compound,(4-(Allyloxy) phenyl) (phenyl) methanone **(1a)** as a starting material, was prepared according to Leshem, mp 75-77 °C (lit. mp. 77 °C) and the characterization data matched with those of the literature (61).

A.1. (4-(Allyloxy) phenyl) diphenylmethanol (1b)

In 30.0 mL of freshly dried diethyl ether was added 4-bromobenzene (1.63 g, 10.4 mmol) and magnesium (2.00×10^{-1} g, 8.37 mmol). The reaction was refluxed for 3 hours under nitrogen. During the course of reaction, reaction mixture turned a dark brown color. Then (4-(allyloxy)phenyl) (phenyl) methanone **(1a)** (7.01 mmol, 1.46 g) dissolved in 20.0 mL dry diethyl ether was added drop wise to this mixture (Grignard solution) and the reaction mixture color was changed to yellow solution. This resultant reaction mixture was left to react for six hours under inert atmosphere. After diluting the reaction mixture with 50.0 mL dry diethyl ether, it was washed subsequently with 10% HCl (100 mL), water (100 mL), saturated aqueous $NaHSO_3$ (100 mL), and NaCl (aq) (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo gave yellow oil crude product. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum indicated: δ 2.8 (s, 1H, exchangeable with D_2O), 4.6 (d, 2H), 5.3-5.5 (m, 2H), 6.4 (m, 1H), 6.9-7.9 (m, 14 H) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ 68.9, 81.70, 134.2, 118.2, 159.2, 110-140 ppm; FT-IR (neat, cm^{-1}) 3477 (O-H), 3059, 3027 (C-H aromatic ring), 2976, 2868, 1446 (C-H alkane), 1648 (C=C), 1599, 1506 (C=C aromatic ring), 1249 (C-O str).

A.2. 1-(Allyloxy)-4-(chlorodiphenylmethyl) benzene (1c)

In 20.0 mL of dry benzene, **1b** (1.62 g, 5.12 mmol) and $SOCl_2$ (1.37 g, 11.5 mmol) were refluxed for 6 hours under nitrogen. During the course of reaction, reaction mixture turned into a yellow-orange color. The yellow oil crude product was resulted after the solvent was concentrated in vacuo. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum indicated: δ 4.6 (d, 2H), 5.3-5.5 (m, 2H), 6.4 (m, 1H), 6.9-7.9 (m, 14 H) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ 68.9, 81.68, 134.7, 118.3, 158.2, 110-140 ppm; FT-IR (neat, cm^{-1}) 3061, 3032 (C-H aromatic ring), 2920, 2867, 1445 (C-H Alkane), 1653 (C=C), 1600, 1506 (C=C aromatic ring), 1251 (C-O str), 700 (C-Cl str).

A.3. (3-(4(Chlorodiphenylmethyl)phenoxy)propyl)triethoxysilane (1d)

The synthesis method was slightly similar to Zhao's experimental method (68). 1-(allyloxy)-4-(chlorodiphenylmethyl) benzene **(1c)** (1.00×10^{-1} g, 1.49 mmol) and anhydrous toluene (20.0 mL) were stirred and refluxed for 15 minutes under an argon atmosphere. Triethoxysilane (5.00×10^{-1} mL, 2.70 mmol) and a solution of catalyst (O

$[(CH_3)_2Si\text{-}CH=CH_2]_2Pt)$ in xylene solution (2.00 x 10^{-1} mL, 0.448 mmol) were transferred in a glove bag before and were subsequently added to the above solution. The resulting mixture was then heated to 80 °C for 18 hours. The crude product was filtered by gravitation filtration to remove the unreacted catalyst. The solvent was concentrated in vacuo gave red-brown oil crude product. The ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum indicated: δ 0.95 (t, 2H), 1.16 (t, 9H), 1.79 (t, 2H), 3.78 (q, 6H), 3.82 (m, 2H), 6.9-7.9 (m) ppm ; FT-IR (neat, cm^{-1}) 3027 (C-H aromatic ring), 2919, 2871 (C-H Alkane), 1603 (C=C aromatic ring stretch), 1451, 1460 (Si-C), 1080, 1030 (Si-O-C), 728 (C-Cl).

Preparation polysilsesquioxane xerogel

Bridged polysilsesquioxane xerogel was synthesized from a solution of bridged silsesquioxane monomers in THF to which was added HCl (aq). To a polyethylene (PE) vial was added monomer **1d** (1.00 x 10^{-2} g, 3.00 x 10^{-2} mmol), THF (29.7 μL, 3.70 x 10^{-1} mmol), HCl (11.8 μL, 1.00 M), H_2O (1.61 μL). The vial was capped tightly and was sonicated allowing a homogenous solution. After two days, the solution began to gel and the vial lid was taken off so that the silsesquioxane could further cross link and dry. Finally, the silsesquioxane was dried under vacuum.

B. Method for the Preparation of product 2 [(4-(Chloro (phenyl) methyl) phenethyl) triethoxysilane (2f)

Starting Materials

The starting materials for the second compound are 4-Vinylbenzyl acetate **(2a)** and (4-(vinylphenyl) methanol **(2b)** prepared according to Bamford and Lindsay (64), followed by the Swern oxidation reaction resulting 4-vinylbenzaldehyde **(2c)** prepared according to Mark and Tidwell (65). All experimental characterization data matched with those of the literature.

B.1. Phenyl (4-vinylphenyl) methanol (2d)

4-bromobenzene (3.45 g, 22.0 mmol) and magnesium (4.10×10^{-1} g, 17.0 mmol) were added and dissolved in 30.0 mL of dry diethyl ether. The reaction was refluxed for 3 hours under nitrogen. During the course of reaction, reaction mixture turned a dark brown color. Then 4-vinylbenzaldehyde **(2c)** (15.0 mmol, 2.00 g) dissolved in 20.0 mL dry diethyl ether was added drop wise to this mixture (Grignard solution) and the reaction mixture color was changed to yellow solution. This resultant reaction mixture was left to react for six hours under inert atmosphere. After diluting the reaction mixture with 50.0 mL dry diethyl ether, it was washed subsequently with 10% HCl (100 mL), water (100 mL), saturated aqueous $NaHSO_3$ (100 mL), and NaCl (aq) (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo with yellow oil crude product. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum indicated: δ 2.21 (s, 1H, exchangeable with

D_2O), 5.2-5.7 (dd, 2H), 5.8 (s, 1H), 6.7-6.9 (m), 7.2-7.4 (m, 9 H) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ 65.8, 113.2, 135.2, 126-143 ppm; FT-IR (neat, cm^{-1}) 3392 (OH, br), 3060, 3029 (C-H aromatic ring), 2870 (C-H alkane), 1629 (C=C), 1510, 1452 (C=C aromatic ring), 1015 (C-O str).

B.2. 1-(Chloro(phenyl)methyl)-4-vinylbenzene (2e)

In 20.0 mL of dried benzene, **2d** (7.00×10^{-1} g, 3.30 mmol) and $SOCl_2$ (8.80×10^{-1} g, 7.40 mmol) were refluxed for 6 hours under nitrogen. The reaction was refluxed for 6 hours under nitrogen. During the course of reaction, reaction mixture turned into a yellow-orange color. The solvent was concentrated in vacuo giving yellow oil crude product. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum indicated: δ 5.2-5.8 (dd, 2H), 6.13 (s, 1H), 6.7-6.9 (m, 1H), 7.2-7.4 (m) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ 64.2, 114.5, 135.4, 126-140.9 ppm; FT-IR (neat, cm^{-1}) 3085, 3060, 3028 (C-H aromatic ring), 2977, 2928, 2866 (C-H alkane), 1629 (C=C str), 1509, 1452 (C=C aromatic ring), 1116 (C-O str).

B.3. (4-(Chloro (phenyl) methyl) phenethyl) triethoxysilane (2f)

1-(chloro (phenyl) methyl)-4-vinylbenzene **(2e)** (4.10×10^{-1} g, 1.79 mmol) was added slowly to triethoxysilane (9.90×10^{-1} ml, 5.37 mmol) and H_2PtCl_6 catalyst (1.00×10^{-2} mg) mixture in 20.0 mL of dried benzene under argon. The solution was refluxed to

80 °C overnight. Toluene was added to the crude product and was filtered by gravitation filtration to remove unreacted catalyst. The solvent was concentrated in vacuo and red-brown oil crude product.

The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum indicated: δ 0.68 (t, 2H), 1.18 (t, 9H), 2.58 (t2H), 3.80 (q, 6H), 6.05 (s, 1H), 6.7-7.2 (m) ppm.

C. Method for the Preparation of Monomer 3a [Diphenyl (4-vinylphenyl) methanol]

Starting Materials

The starting material for monomer 3a is diphenyl (4-vinylphenyl) methanol prepared according to Toy's paper (66). All experimental characterization data matched with those of the literature.

D. Method for the Preparation of Monomer 4a [(4-(But-3-enyloxy)phenyl) (phenyl) methanone]

In a 250-ml round bottom flask, 4-hydroxybenzophenone (6.60 g, 33.0 mmol), 4-bromo-1-butene (5.32 g, 26.0 mmol), and potassium carbonate (4.56 g, 33.0 mmol) were refluxed in dioxane (150 ml) at 50 °C for 48 hours without under inert atmosphere. During the course of reaction, reaction mixture was turned into yellow cream. The solution was filtered to remove residue of potassium carbonate. The solvent from the filtrate (yellowish brown) was evaporated under vacuo and the crude product was diluted with 100 ml of CH_2Cl_2. Then, it was washed with water (3 x 100 ml) and dried with anhydrous $MgSO_4$. The crude product was then purified by column chromatography on silica by eluting with EtOAc/hexanes (1:9 v/v). The final product was yellow oil. The ^1H NMR (300 MHz, $CDCl_3$) spectrum indicated: δ 2.51 (q, 2H), 3.99 (t, 2H), 5.07 (dd, 1H), 5.83 (dd, 1H), 6.89, 7.17 – 7.76 (m, 9 H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$) δ 33.1, 67.0, 113.7, 116.9, 127.8, 129.3, 129.3, 131.5,132.2, 133.7, 137.9, 162.2, 194.8 ppm; FT-IR (neat, cm^{-1}) 3069, 2934 (C-H str), 1650 (C=O, ketone), 1505 (C=C str), 1254 (C-O str).

E. Method for the Preparation of Monomer 5a [α, α-Bis(4-Vinylphenyl) Benzyl Alcohol]

Starting Materials

The starting material for monomer 5a prepared according to the work of Rimmer, *et.al* (67). All experimental characterization data matched with those of the literature.

Chapter 4

CONCLUSION

Hybrid organic magnetic materials represent one of the most fascinating developments in materials chemistry in the last decade. The tremendous possibilities of combination of different properties in one material initiated an explosion of ideas about potential materials and applications.

In order to synthesize hybrid organic magnetic material having nanoporous morphology, such as polysilsesquioxane, a stable organic radical is required which can be incorporated in inorganic polymer network. The sol-gel process approach was used for the formation of hybrid materials due to its many advantages.

The major challenge of this research was to synthesize stable organic radical materials, as organic species containing unpaired electrons tend to be chemically reactive and unstable. This challenge was addressed by using bulky substituents having strong steric shielding. In this thesis, starting materials with varying degrees of steric shielding (as shown in scheme: **C**, **D** and **E**) have been evaluated to produce stable radicals for incorporation in a polymeric matrix. The logic behind the choice of synthesis targets is to investigate the differences in the porosity and the mechanical strength of each hybrid materials.

In first phase of this research, product 1 (**1d**), containing polysilsesquioxane, has been successfully synthesized as shown in scheme **A**. The second phase of this research was focused on the use of diphenyl organic molecules instead of triphenyl. Product 2 (**2f**) has been successfully synthesized as shown in scheme **B**. However, this does not produce a stable radical. This can be attributed to weaker steric shielding. The final phase of this research was focused to tailor the properties of organic hybrid materials by using shorter carbon chains (scheme **C**), longer carbon chains (scheme **D**), and more carbon chains (scheme **E**). Products **3a, 4a**, and **5a** were synthesized successfully. The purification of final products was extremely difficult as compounds were intractable.

Chapter 5

FUTURE WORK

Due to the importance of hybrid organic magnetic materials, it is highly recommended that the difficulties encountered here be overcome. The following suggestions were recommended:

1. The synthetic route used in this research should be continued to obtain the final organic magnetic material.
2. To investigate the presence of radical, electron paramagnetic resonance (EPR) should be used. Furthermore, Superconducting Quantum Interference Device (SQUID) should be used to measure the magnetic properties of the product.
3. Extensive investigations should be performed to work out appropriate techniques to purify the products.
4. Detailed spectroscopic analysis (including MS, 2D homo and heteronuclear NMR) as well as elemental analysis should be done to ensure full characterization of products.
5. Due to the instability of radicals, online analytical method should be developed to monitor the reaction progress.

Chapter 6

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