DEVELOPMENT AND DESIGN OF NANOMATERIAL REAGENTS IN CONJUNCTION WITH NEW METHODS FOR THEIR SYNTHETIC APPLICATIONS

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In memory of my father,
Tinashe Macmaster Kwaramba,
(Chief Executive Officer and Founder of Berida Investments Pvt. Ltd.)
-The greatest organizational genius I know.

DEDICATIONS

To my mother **Rev. Christinah Kwaramba,**
(Chief Executive Officer and Principal of ChriMac Remedial and Coaching Center)
-The greatest liberator, inspirer, righteous devotee and empowerer I know.

To my sister **Tendai Kwaramba,**
-My best friend.

To **my Creator,**
-From whom I derive my existential freedoms, life and happiness.
-Whose creative genius as well as ordination upon my life matters; and who I will only direct my worship.

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To **Dr. K. D. Berlin**,
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Title of Study: DEVELOPMENT AND DESIGN OF NANOMATERIAL REAGENTS IN CONJUNCTION WITH NEW METHODS FOR THEIR SYNTHETIC APPLICATIONS

Major Field: CHEMISTRY

Abstract: This Ph.D. deals with the integration of nanotechnology with organometallic/ organic synthetic technologies. The first part of this research sought to develop a library of novel molecular gears programmed to exploit photo-switching and electrostatic repulsion to control the molecular rotation of covalently linked triptypyrazines. Incorporation of these two modes allows for control of triptycene based gear systems using unexplored external methods. The triptypyrazine was an attractive scaffold because of its intrinsic pH and electrochemical activity, thus providing a novel construct for controlling molecular motion. This design finds relevance in the fabrication of nano-electromechanical devices and understanding controlled molecular motion.

This Ph.D. also sought to address the need to generate and recycle low cost hydrosilylation catalysts. Metal nanoparticle catalysts can potentially meet this need due to their high surface area and reactivity. Their morphology and surface texture provide avenues for selectivity in reactions. Metal-nanoparticles on a silicon matrix can be formed by reducing metal salts with silicon hydrides. Investigations towards iron-nanoparticle catalyzed hydrosilylation of unsaturated bonds were conducted. Furthermore, this research sought to develop highly functionalized silanes, as guiding scaffolds for generating chiral silicon hydrides. Fabrication of metal-nanoparticle catalysts with the same, could install surface definition on these heterogeneous green catalysts, thus allowing selectivity in their catalysis.

A bottom up approach to nanofabrication, started with the generation of a library of highly functionalized alkynyl-silane building blocks using the hydrosilylation reaction. Hydrosilylation of carbon-carbon and carbon-heteroatom unsaturated bonds has proven to be an important reaction in organic syntheses. Additionally, silicon tethers have been utilized in complex organic syntheses as a way to increase reaction rates, and selectivity. The most commonly employed silicon tethers have been disiloxanes followed by siloxanes, then silanes. Of these methods the synthesis and utilization of tethered silyl-alkynes was limited. To address this gap, this work developed methodology to prepare tethered silyl alkynes through a hydrosilylation reaction. It was established that $[IrCl(COD)]_2$ in the presence of excess COD can selectively catalyze the hydrosilylation of alkenes with alkynyl-silanes. This approach overrides traditional hydrosilylation catalysts' reactivity trends.

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Ac	Acetyl
Acac	Acetylacetonate
Add.	Additive
aq	Aqueous
APA	3-Aminopropylamnine
Br	Bromine
BF_4	Tetrafluoroborate
BnO	Benzyl ether
CH_2CI_2	Dichloromethane
CH_3CN	Acetonitrile
$CI_2Pd(PPh_3)_2$	Dichlorobis(triphenylphosphine)palladium(ll)
CCl_3CO_2H	Trichloroacetic acid
Cp*	Pentamethylcyclopentadienyl
CO	Carbon monoxide
COD	1,5-Cyclooctadiene
CsF	Cesium Fluoride
CV	Cyclic Voltammetry
CuI	Copper Iodide
$CuSO_4$	Copper Sulfate
Cyclohex.	Cyclohexane
1,2-DCE	1,2-Dichlorethane
DCM	Dichloromethane
DME	Dimethoxyethane
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
Et	Ethyl
EtMgBr	Ethylmagnesiumbromide
EtOAc	Ethylacetate
Et_2O	Diethylether
$(EtO)_3SiH$	Triethoxysilanes
$(EtO)_2MeSiH$	Diethoxymethylsilane
Et_3SiH	Triethylsilane
equiv	Equivalent
EtOH	Ethanol
hrs	Hours
GC	Gas Chromatography
H_2O	Water (distilled)
I	Iodine

*i*Pr	Isopropyl
$(i\text{Pr})_2PCH_2CH_2OMe$	Diisopropyl(2-methoxyethyl)phosphane
KF	Potassium fluoride
$KMnO_4$	Potassium permanganate
m	Minutes
M	Molar
MeCN	Acetonitrile
M-H	Metal hydride
mL	Milliliter
mmol	Millimole
MnO_2	Activated manganese dioxide
M-NPs	Metal nanoparticles
$NaBH_4$	Sodium borohydride
$NaHCO_3$	Sodium bicarbonate
NBD	Norbornadiene
N.D.	Not determined
NEMS	Nanoelectromechanical systems
NMR	Nuclear Magnetic Resonance
NMP	*N*-Methyl-2-pyrrolidone
N.R.	No reaction
PCy_3	Tricyclohexylphosphine
Pd	Palladium
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
$PdCl(PPh_3)_2$	Bis(triphenylphosphine)palladium(II) dichloride
pdi	Pyridinediimine
PEG-400	Polyethylene glycol 400
pH	Potential Hydrogens
Ph	Phenyl
PMBO	4-Methoxybenzyl ether
PMHS	Polymethylhydrosiloxane
POSS	Polyhedral- oligomeric silsesquioxane
Prod.	Product
Pt	Platinum
PVP	Polyvinylpyrrolidone
Py	Pydirine
r.b.	Round bottom
RCM	Ring closing metathesis
Red.	Reducing agent
r.t.	Room temperature
R.T.	Retention time
R_3SiH	Silicon hydride/ hydrosilane
Soln.	Solution
S.M.	Starting material
Start.	Starting material
Stab.	Stabilizing agent
Susp.	Suspension
TEA	Triethylamine

TESi-H	Triethylsilane
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsilyl
TMEDA	Tetramethylethylenediamine
Tol	Toluene
n-BuLi	n-Butyl lithium
sec-BuLi	sec-Butyl lithium
UV	Ultraviolet
Vis	Visible

CHAPTER I

NOVEL TRIPTYPYRAZINES INCORPORATING PHOTOCHEMICAL/ ELECTROCHEMICAL SWITCHABLE MOIETIES: TOWARDS MOLECULAR DEVICES

1.1 INTRODUCTION

Harnessing molecular rotatory motion at the unimolecular level is a great challenge in chemistry. Furthermore in the biochemistry field, significant evidence supports that certain enzyme complexes can exist in a variety of motion modes. [1,2,3] The interplay between mechanical and chemical processes within biochemical functions results in a complexity that is poorly understood.[4] A deeper understanding of these molecular motion processes may be needed in order to learn how natural molecular motors work together and to elucidate their principle of operation. Generating less complex organic unimolecular chemical systems that can simulate molecular motions is an avenue that provides samples that can be studied in order to better understand natural motors. In order to advance this objective, this project focused on design and synthesis of organo-chemical species that can conduct controlled molecular rotation via external control handles. Moreover, these chemical species contribute to adding a set of nanoelectromechanical systems (NEMS) in single molecular form, and thus are potential building blocks for the development of nano-machinery and electrical devices.[5,6,7]

We sought to better understand the conversion of energy into controlled rotational motion. This simple phenomenon plays important roles in both man-made devices and biological systems. Furthermore, we were inspired by the desire to better mimic and understand the molecular processes used by biological motors such as muscle fibres, flagella and cilia.[8,9,10,11,12,13,14,15,16] To address the problem of poor understanding of the conversion of chemical energy into rotational motion, developing molecules that can simulate interesting principles of rotational motion and characteristics of bio-motors were needed. To our knowledge, at the time of this research, there was no manner in which to externally control the unidirectional rotation of molecular gears that contained triptycene moieties or analogs thereof.

We sought to deliver two modes of control into these systems. The first mode of control was the incorporation of the photoswitchable moiety which can use UV/Vis irradiation as an external stimulus to control the molecular rotation. The second mode of control was the incorporation of an electrochemically/pH active moiety, which uses redox and/or pH fluctuations as external stimuli. Incorporating and combining these two modes of control within singular molecular constructions would introduce a library of novel organic molecules.

1.2 REVIEW OF LITERATURE: MOLECULAR ROTATION IN MOLECULAR MACHINES

1.2.1 Molecular Machines

The evolution of human civilization has been closely linked with the invention of novel devices and machines. The general trend in the "knowledge age" emphasizes reducing size and weight of the components employed in the machinery construction. This opens up a very diverse and dynamic field of nanotechnology research which brings together various fields of science and technology. In the

1960s Feynman proposed the idea of constructing nanoscale machines by using an atom by atom building strategy.[17] A visionary prophecy was pronounced in the mid-1980s by Drexler, where he projected the possibility of building general purpose 'nanorobots' from atomic assembly.[18] During the late 1970s within the field of supramolecular chemistry research, the idea that molecules can be convenient building blocks to construct nanoscale molecular machines or devices became complementary to the atom by atom proposal. However, a better narrative was simply using molecules which are more stable species to handle as compared to atoms.[19,20,21,22,23,24,25] Furthermore, nature uses molecules to construct biological nano-devices and nano-machines, and thus the molecular definition is a preference.[26,27] Coupled with the rapid growth of the supramolecular revolution, the design and construction of artificial molecular devices and machines opened more research opportunities due to the unlimited possibilities this approach offered.[28]

In the macroscopic world, a machine is an assembly of components made for a special purpose due to a combination of mechanisms that utilize, modify, apply, or transmit energy. The macroscopic concepts of machines can be extended to the molecular level. Thus a molecular device is an assembly of singular molecular components coherently linked together in a strategically programmed design in order to achieve a specific function. Investment of careful thought and design of each and every component of these assemblies is executed so that specific acts can be delivered, in order for the entire supramolecular assembly to provide a more complex and useful function resulting from the cooperation of the various components. A molecular machine is a particular type of molecular device in which the component parts can display changes in their relative positions as a result of some external stimulus.[29] Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices or machines; they need energy to operate and signals to communicate with the operator. The extension of these concepts to the molecular level is of interest not only for basic research, but also for the growth of nano-science and the development of nanotechnology.

1.2.2 Molecular Motion

Learning, understanding and fabricating molecular motion in molecular machines is a lucrative research area that promises to be the panacea of chemistry and scientific scholarship. There has been a considerable amount of research into controlling molecular motion, from the impressive unidirectional molecular motors designed by Feringa to the controllable shuttling motion of catenanes developed by Stoddart and others.[30,31,32] These systems, based upon the incorporation of motifs that can undergo reversible, and controlled conversions are an exciting area of research because of their potential applications as real-time molecular devices. Particular interest in these devices rests in molecular motions that are controllable via external stimuli. This includes, but is not limited to, light irradiation,[33] change in pH,[34] electrochemistry,[35] chemical reactions or addition of metal ions.[36]

1.2.3 Unidirectional Rotatory Motion of Artificial Molecular Rotator Structures

Feringa and co-workers conducted extensive research on rotation based supramolecular compounds. They made and examined systems that used exothermic chemical reactions to power unidirectional rotatory motion. These rotations were based on pre-designed chemical set-up strategies,[37,38,39,40,41,42,43,44] that, upon trigger events, they would cascade chemical processes that facilitate molecular rotation. Therefore, from their systems we could safely say, they exploited chemical energy to achieve controlled unidirectional molecular motion to produce molecular motors.

Feringa and co-workers modeled and synthesized molecules around a macroscopic rotor made up of three essential components. The rotor (rotator) is the component of the molecular system that rotated against the rest of the molecule (generally taken as that which has the smaller moment of inertia). This rotating element moves around an axis called an axle. The axle is also linked to both the rotor and stator, which is the stationary part on which the rotator turns (generally taken as that which has the larger moment of inertia)[45] (See Figure 1.1 below).

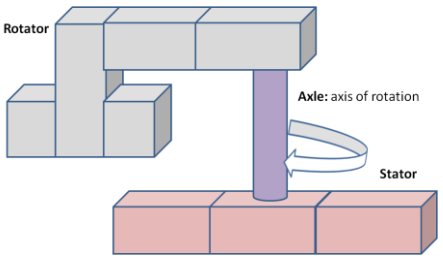


Figure 1.1 The macroscopic rotor prototype.

In their designs of molecular rotor devices/machines, the molecular rotor is rotated in a programmed fashion about an axis (axle) relative to the stator.[45] Rotation in these systems was both controlled and facilitated by a combination of chemical reactions in concert with random thermal (Brownian) motion. For example, in 2005, they developed a system which had a phenyl rotor that moved relative to a naphthyl stator about a single bond axle (See Figure 1.2 below).[46]

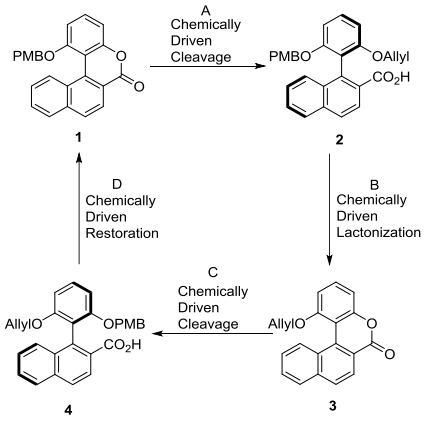


Figure 1.2. Chemical structures and reaction scheme for unidirectional chemically driven rotary motor.

To achieve rotation, it required the reduction and subsequent oxidation of **1** to give **2**. The choice of reducing agent resulted in the atropisomer shown above, and thus influenced the direction

of rotation. To continue, the deliberate rotation around the aryl naphthalene bond, lactonization of **2** to give **3**, followed by another stereoselective reductive cleavage to give **4**, delivered a clockwise rotation. Subsequent deprotection of **4**, followed by lactonization restored **1**. This four stage reaction process gave a unidirectional clockwise rotation that is controlled by chemical reactions. [46]

1.2.4 The Triptycene Containing Gear Systems

Mislow and co-workers first developed the simplest triptycene based gear system using the macroscopic bevel gear as a model.[47,48] The bevel is a gear that has the axes of the two shafts intersecting at 90 degrees and the tooth bearing faces of the gears mesh together at an angle, to transmit power between the two shafts. Molecular systems that mimic mechanical characteristics of bevel gears have been constructed using two triptycene gearing components that are linked by either an O, CH_2, S, CH or CH=CH (See Figure 1.3 below). However these gears had no external manner by which to control their rotational motion.

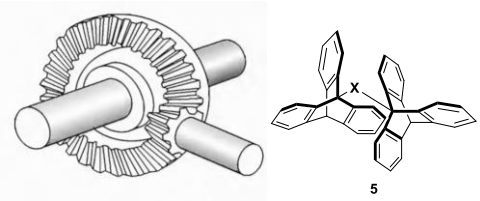


Figure 1.3 The bevel gear mechanical prototype and the bevel based molecular gear system. X = linking unit.

Kelly and co-workers designed molecular systems which focused on achieving chemically driven unidirectional rotatory motion based on the triptycene moiety. The modeling framework was by extension of the involute macroscopic gear. An involute gear is a gear that has shafts and hubs that are used as connectors or gear rotation reducers [49] (See Figures 1.4 and 1.5 below).

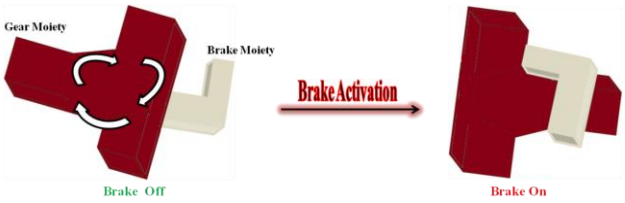


Figure 1.4. Conceptual depiction of the operation of a molecular brake.

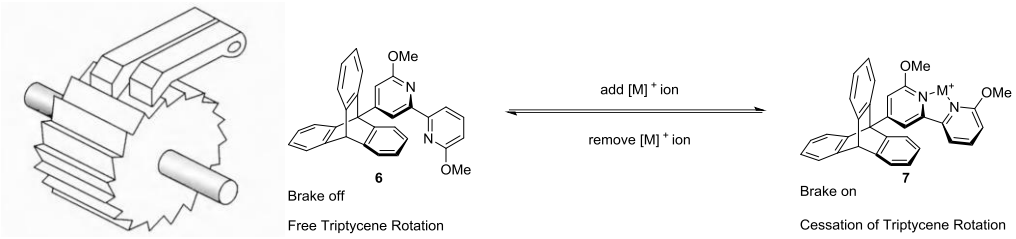


Figure 1.5 The involute gear system and involute based molecular gear system.

In this design the triptycene moiety was the rotor connected by a carbon-carbon bond axle to a bipyridyl stator moiety that was also functionalized to act as a reversible brake. The operational sequence was that, the bipyridyl brake was activated by the addition of positively charged metal ions, which could coordinate to the chelating binding site of the stator. The resulting conformational change would cause the cessation of triptycene rotation. The dissociation of the M-N dative bonds would deactivate the brake, causing triptycene rotation to resume.[49]

Later, Kelly deepened the iso-design by functionalizing both the stator and the rotator moieties of this design which gave the triptycyl[4]helicene system, which was phosgene-powered in order to attain unidirectional rotation (See Figure 1.6).[50] In this design, unidirectional rotation of triptycene moiety was programmed to depend on the friction-braking action from the helicene stator. The asymmetric skew of the helicene dictated either clockwise or anticlockwise rotation. In addition

to this unidirectional rotation dictator, the chemical energy, acquired from the rotator reacting with phosgene to lower the clockwise rotational energy barrier, promoted unidirectional rotation. The reaction of **8** with phosgene gave the strategically activated intermediate isocyanate product **9** via a phosgene. **9** then reacted with the OH group in the hydroxypropyl tether attached to the helicene. Steric bias of reacting functional groups promoted clockwise rotation of the triptycene moiety to give rotamer **11**. Urethane formation gave the chemical intermediate **12**, thus irreversibly trapping the triptycene rotamer in a relatively high-energy conformation around the triptycene/helicene axle. Thermal energy then drove the exorgenic unidirectional rotation from rotamer **12** to rotamer **13**. The rotational cycle is terminated by the reductive cleavage of the urethane to give the rotational ground state of rotamer **13**. [50]

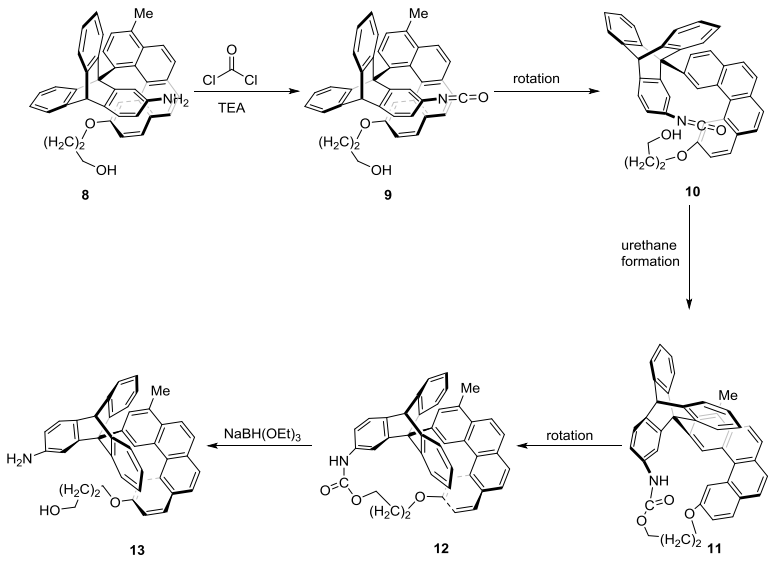


Figure 1.6 The chemical structures and reaction sequence of events in the chemically powered unidirectional rotation of the triptycyl[4]helicene system.

Bryan and co-workers designed molecular systems modeled around the spur macroscopic gear.[51] Spur gears are gears that possess teeth that are radially arrayed on the rim parallel to their axes of rotation. In their design two triptycene gears components are linked together by two polyoxycarbylene to give bistriptycene crown ether gear systems (See Figure 1.7).

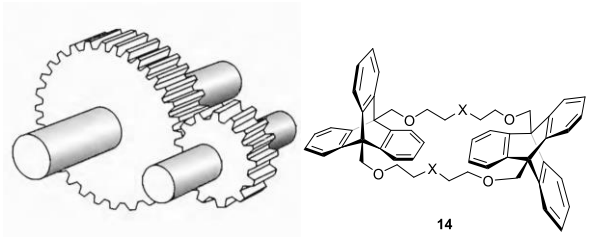


Figure 1.7 The spur gear system model and spur gear system based molecular gear system. (X = Varying chain length)

These gear designs demonstrated intramolecular gear rotation in both the solution state and solid state. Furthermore, they exhibit intermolecular gear meshing through self-assembly in the solid state. Lengthening the inter-triptycene linkers showed sterical relaxation which resulted in the distortion of the symmetry of the entire molecule in solid phase. This produced a situation where the two triptycene moieties, which are chemically equivalent in constitution, became structurally/conformationally unequal. The resulting lack of interaction between these molecular rotators resulted in less to no self-organization in a dynamic sense. Contrastingly, the short linker analogs showed internal organization of the triptycene moieties, which is necessary if these compounds were to be used in nano-construction.[48,49,50] However, the axes are not entirely parallel and remain pseudo spur gear analogs. This limits the requisite gear interaction that can give optimal interrelated or interactive rotation.[51]

Based on these systems, the triptycene moiety has proven to be a useful construct in systems attempting to harness the power of molecular rotational motion. The hydrocarbon framework of triptycene gives a very rigid gear component, hence making an excellent scaffold for further design and construction of molecular gearing systems. However, while the discovery of the systems at the time of this project's commencement gave important information to molecular rotation, these systems were impractical for nano-engineering and/or fabrication of nano-constructions.[52,53,54] In the aforementioned systems, unidirectional rotation requires chemical fueling, which involves chemical

reactions, product purifications and time in order to achieve the desired rotations. Furthermore, in Kelly's designs the helicene moiety is one dimensional, inflexible and less dynamic, thus limiting the construct to a permanent unadjustable brake function. Its rigidity also presents a consistent rate of rotation, thus limiting the rotational motion of triptycene. The information provided by the bistriptycene crown ether gear systems gives insight into the importance of self-organization, inter-gearing moiety interactions (gear meshing), and steric requirements for nano-construction using these gears. However, measurement of the systems based on the macroscopic spur gear requirements showed that their intramolecular triptycene interaction and intermolecular triptycene interaction is suboptimal.[51] Furthermore, the useful framework for triptycene rotation provided so far has not developed gear systems with additional functionalities that allow for the molecular rotation to be manipulated via user friendly external controls.

This project identified several opportunities of growth in designing triptycene based gear systems by focusing on three major architectural domains namely, the stator, the axis and lastly the rotators. The piecing together of this puzzle was also crucial. The primary objective was to construct a perfect spur molecular gear analog (See Figure 1.8 below).

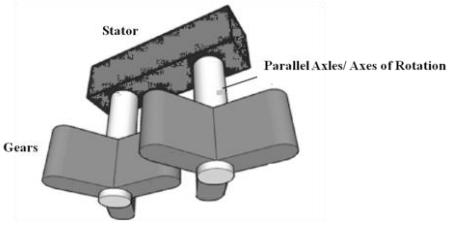


Figure 1.8 Our desired ideal spur gear system model.

To achieve this, the first structural objective was to install rigidity and atomic arrangement on the axles/axes of rotation that remained parallel to each other. Secondly, the rotator was to be programmed in such a way that we would install handles that allow unidirectional motion and transporting capability. Lastly, the stator domain would have the capacity to act as a flexible brake. This program was key for the purpose of controlling the rotation by either causing cessation of

rotation or at least stopping the unidirectional rotation. These design parameters were the guiding elements to developing this objective.

1.3 METHODOLOGY

1.3.1 Specific Aims of Study

Against this backdrop, the research conducted sought to incorporate novel components into gear systems that were covalently linked to bistriptypyrazines, thus providing a platform for four methods for controlling molecular gear systems. Furthermore, the rotatory motion of these bistriptypyrazines, whose model was bistriptycene based systems, [51] would then be controlled along five major modes: 1) photoswitchable azobenzene moieties in the stator, 2) protonatable covalent linkers in the stator, 3) protonatable gears in the rotators, 4) electrochemically active components in the rotator, and 5) a combination of the four. The hypothesis driving this research was through the azobenzene and bistriptyprazine moiety incorporations. Unidirectional gear rotation was to be achieved by way of electronic repulsion of sterically congested charged gears, whose degree of steric interaction would be changed by *cis/trans* isomerization of a photoswitchable azobenzene moiety.

Fused pyrazines were particularly attractive because their protonation at the arene nitrogens would be a source of positive charge imposition. The charged pyrazines would then repel each other in a sterically crowded dispensation, thus facilitating gear movement. Furthermore, pyrazines have been shown to undergo reversible redox reactions via cyclic voltammetry (CV).[55] These two handles were thus expected to provide a new avenue to create novel triptycene gear system analogs that were virtually unexplored. The designed incorporation of pyrazines into the triptycene scaffold was a simple permutation that sought to introduce a multi-functional component that we hoped would give two distinct modes of external control namely, change in pH and electrochemical redox chemistry. The photoactive azobenzene stator would present a photochemical control handle by irradiation

induced moiety isomerization. This would function as a controllable braking system for the envisaged unidirectional rotation.

To meet these study aims we sought to create a library of novel organic molecule(s), worthy of a wide scope of chemical interrogations that would provide a wealth of information toward NEMS development. The library of the novel target compounds would contain molecular gear systems that were made up of alkyl straight chain linkers harboring a) triptypyrazine gear moieties and b) the triptycene gear moiety. This was to be followed by azobenzene linked gear systems having a) triptypyrazine gear moieties and b) the triptycene gear moiety. Finally, the rigid xanthene linker containing gear systems with a) triptypyrazine gear moieties and b) the triptycene gear moiety (See Figure 1.9 below).

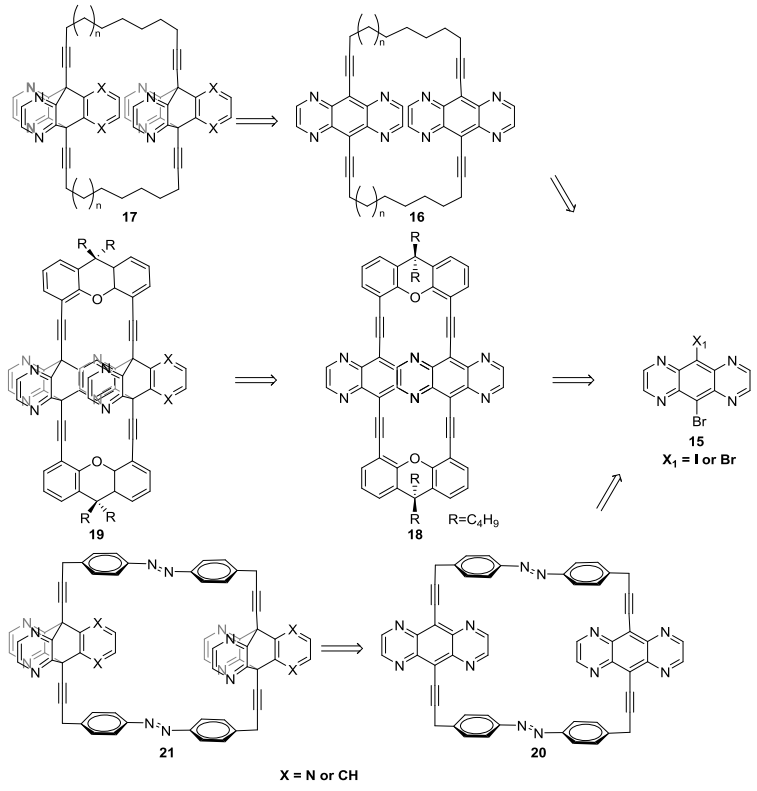


Figure 1.9 The target gear library.

1.3.2 Supramolecular Study Strategy

The target compounds would undergo complete structural characterization via the standard spectroscopic methods. Our particular interest was how the structural and relative rotational properties were going to change upon protonation of the N-atoms in the library of compounds. Cyclic-voltammetry (CV) was going to be utilized to explore the reduction potentials of the novel triptypyrazine gear systems.[55]

Based upon our computational molecular modeling during the molecular design stage of this project, the triptypyrazine gears were expected to exhibit free non-directional rotation as long as the linking unit did not bring them together. In other words, without gear meshing as a function of linking unit conformational influences, the gearing components could rotate freely with random directionality and were expected to be independent of each other.

However, for the azobenzene linked gear systems irradiation with UV light (< 300 nm) was expected to induce *trans* to *cis* isomerization. This would bring the gears into direct contact with each other. The potential twin outcomes were either cessation or slowdown of the gear rotation. Subsequent protonation or electrochemical excitation of gears in contact with each other would resume unidirectional gear rotation. Irradiation with visible light would cause *cis* to *trans* isomerization, which would free the gear from direct contact with each other. The result would release the charged gearing moieties from unidirectional rotation and return them to unhindered free rotation without the electronic influences.

1.3.3 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) studies would be used to measure expected gearing dynamics. Particularly, our probing premise of investigation would use NMR, focusing primarily on the aromatic proton nuclei of the gearing units/components in the molecular designs. The conceptual reasoning that we would use can be explained using the conceptual scheme in Figure 1.10.

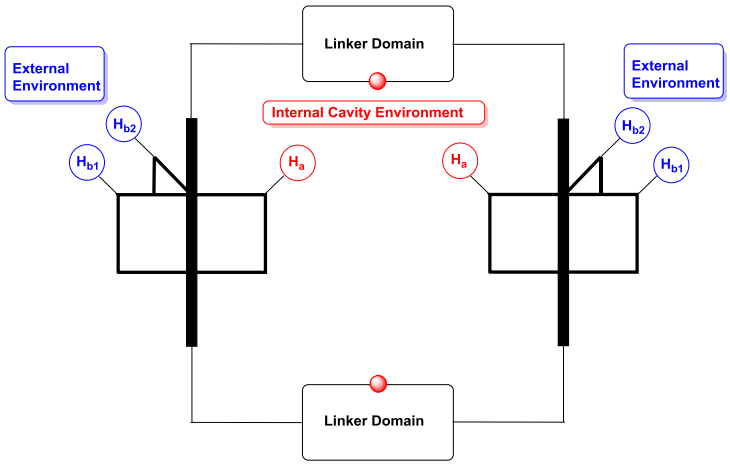


Figure 1.10 The guiding NMR gear map for investigations.

The model in Figure 1.10 shows the general molecular architecture that summarizes the whole library set we hoped to create. In this architectural map, we can safely say that there is a molecular macrocycle that has two distinct environments. One environment is internal to the macro-cycle, which is labeled the 'internal cavity environment' in the schematic map in the Figure 1.10 above. The second environment would be that outside of the macrocycle labeled as the external environment. We expected these environments to be characterized by completely different environments/domains. Therefore, by virtue of this characteristic of contrast we could measure the gearing rotation that would emanate from these designs.

Focused NMR measurements, particularly on the aromatic regions, would be aimed at exploiting the expected privilege of difference exhibited by the proton nuclei of the arene rings which would give a distinct single peak set. The fact that the aryl protons would exist in multiple environments that are a function of various stress factors and molecular conformations would provide a reliable method to measure gear rotation due to the different proton NMR peaks characterizing these protons. Hence, we expected to see a distribution of peaks labeled as H_a, H_{b1} and H_{b2} shown in the schematic representation in Figure 1.10.

1.3.3.1 The Ideal Instance of No Rotation

If we were to take proton NMR measurements in an ideal circumstance when the molecule exhibited no gear rotation, ideally one would expect to either see three distinctly different NMR peak values (H_a, H_{b1} and H_{b2}) or we would see a broad peak(s) due to the varying degrees of peaks overlapping. In any of these possible scenarios, the data collected therefrom would be enough to compare the NMR data sets. This would help in conclusively profiling and arriving at safe declarations to what was happening at the molecular level as far as gear rotation was concerned. Minimizing rotation or slowing it enough to the lowest possible levels could be achieved by low temperature NMR studies executed on the library of compounds both in liquid state studies and solid state studies. Furthermore, the compounds would have their NMR measurements conducted in a variety of chemical environments in order to test our hypothesis. The projected environments would be in the following set of chemical conditions: neutral or acidic environment. **Note:** 1) a variety pH conditions would be explored, 2) reduced pyrazine excited states, 3) oxidized pyrazine excited states, 4) sterically congested gear conformation with conditions 1 to 3, and 5) liberal gear conformations with conditions 1 to 3.

1.3.3.2 The Instances of Gear Rotation Commencement

If proton NMR measurements were taken when the molecule exhibited gearing rotations, the expectation was to witness a distinct single sharp, peak which would be a dynamic average of H_a, H_{b1} and H_{b2}. If unidirectional rotation in the same direction occurred, we expected a distinct peak set. On the contrary, if two directionalities of rotation were in attendance, we also expected a distinctly different data set of H^1 peaks, most likely two sharp peaks that might be close together. The integrations would also provide understanding as to what was happening at the molecular level with respect to the gearing units. The measurement of rotation would be conducted in different sets of environments for the envisaged library of compounds. The set of variables we intended to explore were the following: temperature variation, neutral, acidic environment or protonated forms (**Note:**

again a variety pH, reduced pyrazine excited states, oxidized pyrazine excited states, sterically congested gear conformations with conditions 1 to 3, and liberal gear conformations with conditions 1 to 3; would be examined).

We expected that the data collected from these experiments would aid in understanding the molecular dynamics with respect to gear rotation in particular. The only reason this manuscript emphasizes rotational dynamics is because our guiding hypothesis focuses on the gearing rotations of the molecule. We understood very well that the gearing would not occur in isolation because many other influences on molecular behaviors always occur in a given molecule. Molecules are not stationary, but rather dynamic. Hence, gear rotation would occur *inter alia* with other chemical occurrences.

Furthermore, we intended to attain X-ray crystallographic structures of the compounds in their ground state. This would give information that would better describe the molecular starting or original profile of the gearing components before external stressors were applied to the library of molecules.

With this data set, we hoped to introduce to the community of scholarship information that we felt would be necessary in the knowledge base as far as molecular gearing and unidirectional rotation is concerned. This could become a reference point for future work in this field and potentially provide programming handles for nano-machinery design and fabrication.

1.4 RESULTS AND DISCUSSION

1.4.1 Attempted Synthetic Strategy for the Gear Library

The retrosynthetic pathway for this project would start with the dibromopyrazino[2,3-g]quinoxaline (**15**) which would undergo a four-fold Sonogashira coupling with the terminal alkynes, followed by the Diels-Alder reaction with pyrazyne or benzynes to give the set of target compounds

(See Figure 1.11).

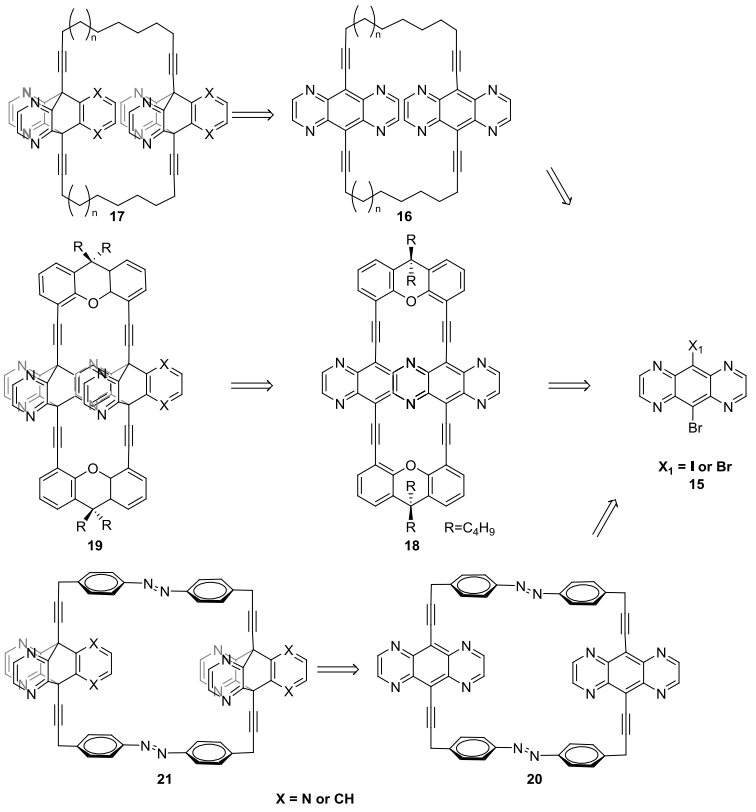


Figure 1.11 Retrosynthesis of novel triptypyrazines containing either a flexible alkyl linker, rigid linker or photo-switchable azobenzene moiety. All constructs arise from the same novel precursor.

To test our hypothesis, a decision was made to start with the synthesis of triptycene analogs of the target designs in Figure 1.11. This was to achieve two objectives, first to establish a quality synthetic route and second for economic reasons because synthesizing dibromopyrazino[2,3-g]quinoxaline (**22**) proved to be expensive. Therefore, the executed retrosynthesis, prior to the aforementioned retrosynthesis, is shown below in Figure 1.12.

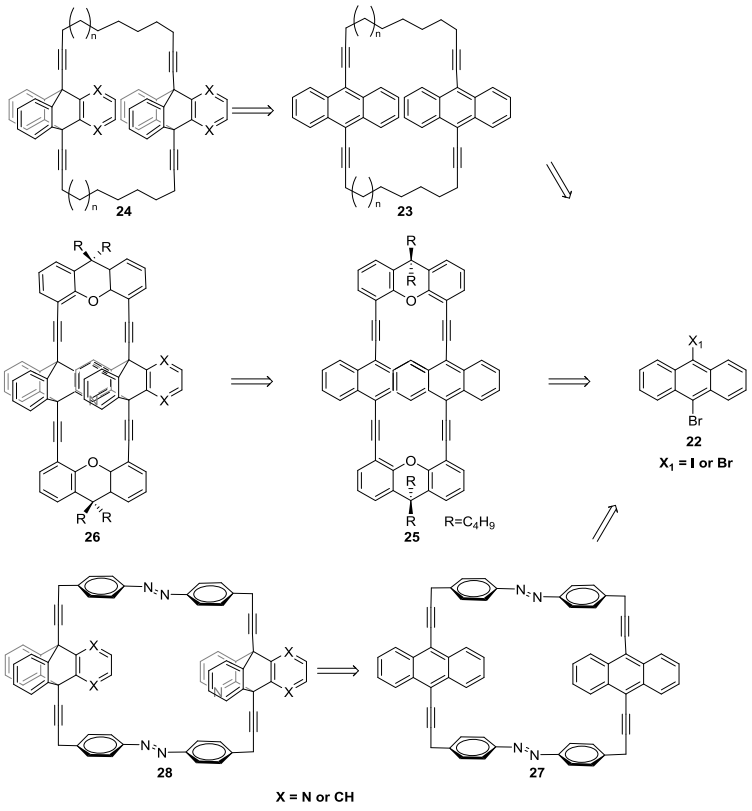


Figure 1.12 Retrosynthesis of novel triptycene containing a flexible alkyl linker, a rigid linker or photo-switchable azobenzene moiety. All constructs arise from the same novel precursor.

1.2.2 Total Synthetic Scheme

1.4.2.1 Target One: The Bistriptycene Gear Linked by Two Flexible Alkyl Chain Fragments

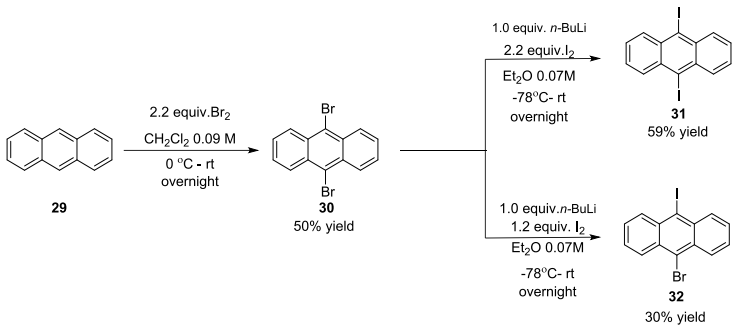


Figure 1.13 Synthesis of the halogenated **30**, **31**, and **32** precursor molecules, analogous to quinoxaline in the gear building strategy.

Bromination of anthracene to give the dibromoanthracene (**30**) at 50% yield,[56] (Figure 1.13) was followed by Sonogashira coupling with commercially available 1,9-decadiyne using $Pd(PPh_3)_4$ at 10 mol% catalytic loading (Figure 1.14).[57]

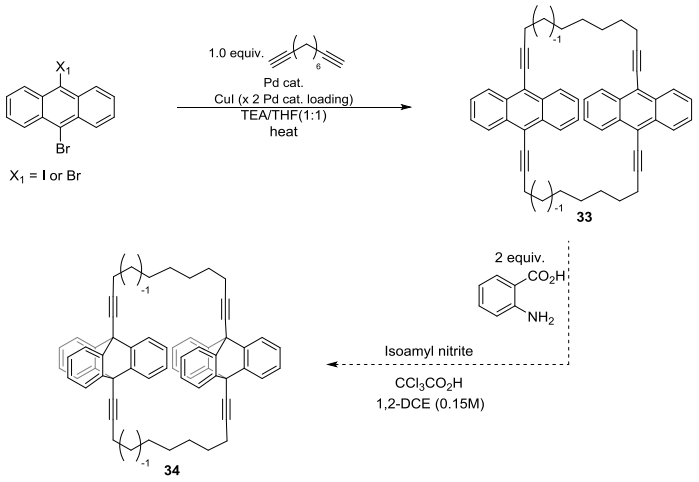


Figure 1.14 Synthesis of **33** and **34** linked by two flexible alkyl chains.

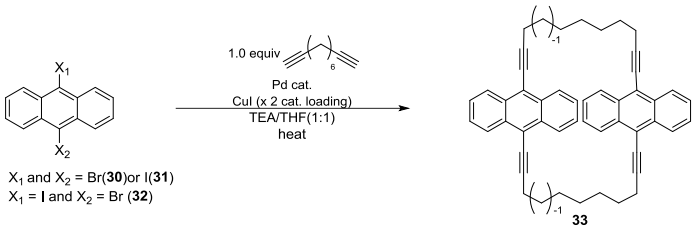
The disappearance of starting material was witnessed by TLC. However, we obtained an

unpurifiable product. The crude NMR spectrum was complex. We concluded that polymerization of the straight chain product occurred instead of the desired macrocyclization. To address this, we tried the same reaction using a more dilute solution of 0.005 M and 0.001 M from the initial 0.05 M. We obtained the same undesired result. Increasing the temperature to 120 ^{o}C from 70 ^{o}C in a high pressure vessel also gave the unintended result. Allowing the system to run from 24 to 48 to 4 days also produced the undesired result. Increasing catalytic loading from 10 mol% to 15 mol% to 20 mol% and lowering the catalytic loading to 4 % did not address our problem. Slow addition of the decadiyne using a syringe pump into a dilute system was not useful (Table 1.1).

We then decided to change the coupling substrate from 9,10-dibromoanthracene (**30**) to 9,10-diiodoanthracene (**31**).[58] Our reasoning was that perhaps the iodo-vinyl functionality would be a better oxidative addition candidate than the bromo-vinyl functionality. Transhalogenation of 9,10-dibromoanthracene (**30**) afforded a 59 % yield of diiodoanthracene(**31**).[58] Sonogashira coupling with this substrate did not give the desired product.[57] Subjecting the iodo substrate to the same series of reactions as done for the 9,10-dibromo analog (**30**) failed to yield the desired coupling product.

We decided to change the anthracene substrate to 9-bromo-10-iodoanthracene (**32**).[58] Our reasoning was that we might be able to avoid polymerization through thermally driven chemoselectivity. Sequential coupling as a function of reaction conditions would have the iodo-vinyl couple to the alkyne first under milder conditions and then later the remaining alkynes would couple to the bromo-vinyl under warmer conditions. Lithiation using 1 equivalent of the *n*-BuLi and reaction with 1 equivalent of iodine gave 9-bromo-10-iodoanthracene (**32**) (30% yield).[58] Attempted Sonogashira coupling of this substrate with 1, 9-decadiyne was also unsuccessful (Figure 1.13).

Table 1.1. Attempted Sonogashira coupling reactions for the synthesis of the precursor **33**



entry[a]	aryl-halide (1 equiv.)	catalyst	catalyst loading (mol%)	solvent 1:1 THF /TEA (M)	time (h)	t (°C)	Yield (%)
1	**30**	$Pd(PPh_3)_4$	10	0.05	24	70	0
2	**30**	$Pd(PPh_3)_4$	10	0.005	24	70	0
3	**30**	$Pd(PPh_3)_4$	10	0.001	24	70	0
4	**30**	$Pd(PPh_3)_4$	10	0.001	24	120	0
5	**30**	$Pd(PPh_3)_4$	10	0.001	24	70	0
6	**30**	$Pd(PPh_3)_4$	10	0.001	48	70	0
7	**30**	$Pd(PPh_3)_4$	10	0.001	96	70	0
8	**30**	$Pd(PPh_3)_4$	15	0.001	96	70	0
9	**30**	$Pd(PPh_3)_4$	20	0.001	96	70	0
10[b]	**30**	$Pd(PPh_3)_4$	4	0.001	96	70	0
11[b]	**32**	$Pd(PPh_3)_4$	4	0.001	96	70	0
12[b]	**31**	$Pd(PPh_3)_4$	4	0.001	96	70	0
13	**30**	$PdCl_2(PPh_3)_4$	10	0.05	24	70	0
14	**30**	$PdCl_2(PPh_3)_4$	10	0.005	24	70	0
15	**30**	$PdCl_2(PPh_3)_4$	10	0.001	24	70	0
16	**30**	$PdCl_2(PPh_3)_4$	10	0.001	24	120	0
17	**30**	$PdCl_2(PPh_3)_4$	10	0.001	24	70	0
18	**30**	$PdCl_2(PPh_3)_4$	10	0.001	48	70	0
19	**30**	$PdCl_2(PPh_3)_4$	10	0.001	96	70	0
20	**30**	$PdCl_2(PPh_3)_4$	15	0.001	96	70	0
21	**30**	$PdCl_2(PPh_3)_4$	20	0.001	96	70	0
22[b]	**30**	$PdCl_2(PPh_3)_4$	4	0.001	96	70	0
23[b]	**31**	$PdCl_2(PPh_3)_4$	4	0.001	96	70	0
24[b]	**32**	$PdCl_2(PPh_3)_4$	4	0.001	96	70	0

[a] Conditions: 1 equiv. of halogenated aryl substrates, CuI (twice Pd mol %), Pd catalyst, 1 equiv. 1,9-decadiyne, in THF/TEA, designated temperature; [b] A syringe pump was used to add the 1,9-decadiyne solution

1.4.2.2 Target Two: The Bistriptycene Gear Linked by Two Rigid Xanthene

Xanthene was initially alkylated with 1-chorobutane to generate 9,9'-dibutylxanthene (**36**) in 86% yield.[59] Iodination of 9,9-dibutylxanthene (**35**) gave a poor yield (23% yield) of 9,9-dibutyl-4,5-diiodoxanthene(**36**).[59] The poor yield prompted us to brominate the 9,9-dibutylxanthene (**35**) which gave 9,9-dibutyl-4,5-dibromoxanthene (70% yield) (Figure1.15).[56]

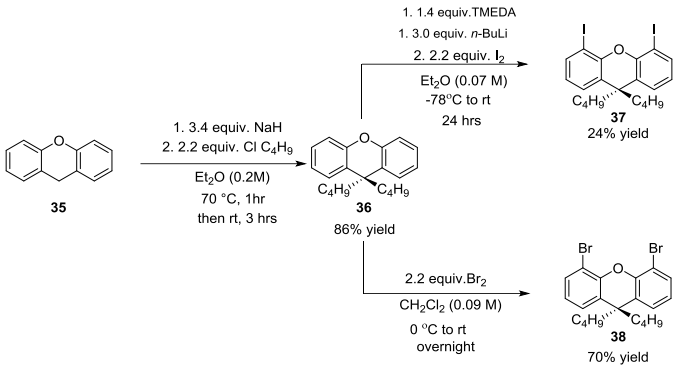
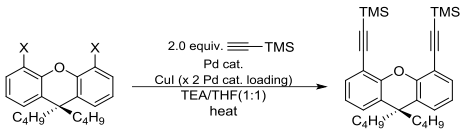


Figure 1.15 Synthesis of the **37** and **38** rigid linker precursor molecules.

Sonogashira coupling of 9,9-dibutyl-4,5-dibromoxanthene(**37**) with TMSacetylene using $Pd(PPh_3)_3$ at 10 mol% catalytic loading gave an undesired product (Table 1.2).[57] However, we witnessed the disappearance of starting material by TLC. The NMR spectrum was complex. We concluded that polymerization occurred. To address this, we tried the same reaction in a dilute solution of 0.005 M and 0.001 M from the previous 0.05 M. We obtained the same undesired result. Increasing the temperature from 70 °C to 120 °C in a high pressure vessel did not help. Allowing the system to run from 24 hr to 48 hr to 4 days was not productive. Increasing catalytic loading from 10 mol% to 15 mol% to 20 mol% did not give the desired product. Lowering the catalytic loading to 4% did not address the problem. Slow addition of the TMSacetylene using a syringe pump into a dilute system failed to give a useful product (Table 1.2). The project was terminated at this point.

Table 1.2. Attempted Sonogashira coupling reactions for the synthesis of **39**



X_1 = I(**37**) or Br(**38**) **39**

entry[a]	aryl-halide (1 equiv.)	catalyst type	catalyst loading (mol%)	solvent 1:1 THF/ TEA (M)	time (h)	t (ºC)	yield (%)
1	**38**	$Pd(PPh_3)_4$	10	0.05	24	70	0
2	**38**	$Pd(PPh_3)_4$	10	0.005	24	70	0
3	**38**	$Pd(PPh_3)_4$	10	0.001	24	70	0
4	**38**	$Pd(PPh_3)_4$	10	0.001	24	120	0
5	**38**	$Pd(PPh_3)_4$	10	0.001	24	70	0
6	**38**	$Pd(PPh_3)_4$	10	0.001	48	70	0
7	**38**	$Pd(PPh_3)_4$	10	0.001	96	70	0
8	**38**	$Pd(PPh_3)_4$	15	0.001	96	70	0
9	**38**	$Pd(PPh_3)_4$	20	0.001	96	70	0
10[b]	**38**	$Pd(PPh_3)_4$	4	0.001	96	70	0
12[b]	**37**	$Pd(PPh_3)_4$	4	0.001	96	70	0
13	**38**	$PdCl_2(PPh_3)_4$	10	0.05	24	70	0
14	**38**	$PdCl_2(PPh_3)_4$	10	0.005	24	70	0
15	**38**	$PdCl_2(PPh_3)_4$	10	0.001	24	70	0
16	**38**	$PdCl_2(PPh_3)_4$	10	0.001	24	120	0
17	**38**	$PdCl_2(PPh_3)_4$	10	0.001	24	70	0
18	**38**	$PdCl_2(PPh_3)_4$	10	0.001	48	70	0
19	**38**	$PdCl_2(PPh_3)_4$	10	0.001	96	70	0
20	**38**	$PdCl_2(PPh_3)_4$	15	0.001	96	70	0
21	**38**	$PdCl_2(PPh_3)_4$	20	0.001	96	70	0
22[b]	**38**	$PdCl_2(PPh_3)_4$	4	0.001	96	70	0
24[b]	**37**	$PdCl_2(PPh_3)_4$	4	0.001	96	70	0

[a] Conditions: 1 equiv. of halogenated xanthene substrates, CuI (twice Pd mol %), Pd catalyst, 2equiv. TMSacetylene in THF/TEA, designated temperature; [b] A syringe pump was used to add the TMSacetylene solution

The plan was to deprotect ((9,9-dibutyl-4a,9a-dihydro-9H-xanthene-4,5-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (**38**) to generate the terminal alkyne (**40**),[60] which would undergo four-fold Sonogashira coupling to give the gear precursor (**41**).[57] Diels-Alder reactions with benzyne could deliver the targeted gear (**42**) (Figure 1.16).[61]

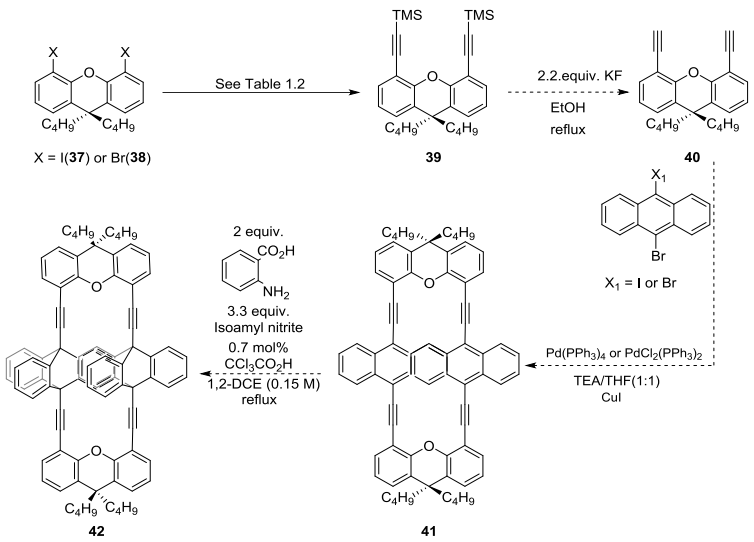


Figure 1.16 Synthesis of **42** linked by two rigid xanthene moeties.

1.4.2.3 Target Three: The Bistriptycene Gear Linked by Two Azobenzene Moieties

Iodination of aniline (**43**) gave 81% of *p*-iodoaniline (**44**) to start the azobenzene linker synthesis.[62] Oxidation of *p*-iodoaniline using MnO_2 gave a disappointing yield (16%) of 4,4-diiodoazobenzene (**45**) (Figure 1.17).[63] This prompted us to attempt oxidation using $KMnO_4$ and $CuSO_4$, but this procedure resulted in 12% yield 4,4-diiodoazobenzene (**45**) (Figure 1.17).[64] The project was terminated at this point.

The plan was to conduct Sonogashira coupling 4,4-diiodoazobenzene with 1-propyne to give the 4,4-bispropylazobenzene (**46**),[65] followed by isomerization courtesy of the 'zipper' reaction to give the terminal alkyne (**47**).[66] The latter would then undergo four-fold Sonogashira coupling to give the gear precursor (**48**).[57] Diels-Alder reaction with benzyne would deliver the desired gearing molecule (**49**) (Figure 1.17).[61] We did not do these subsequent reactions due to project termination.

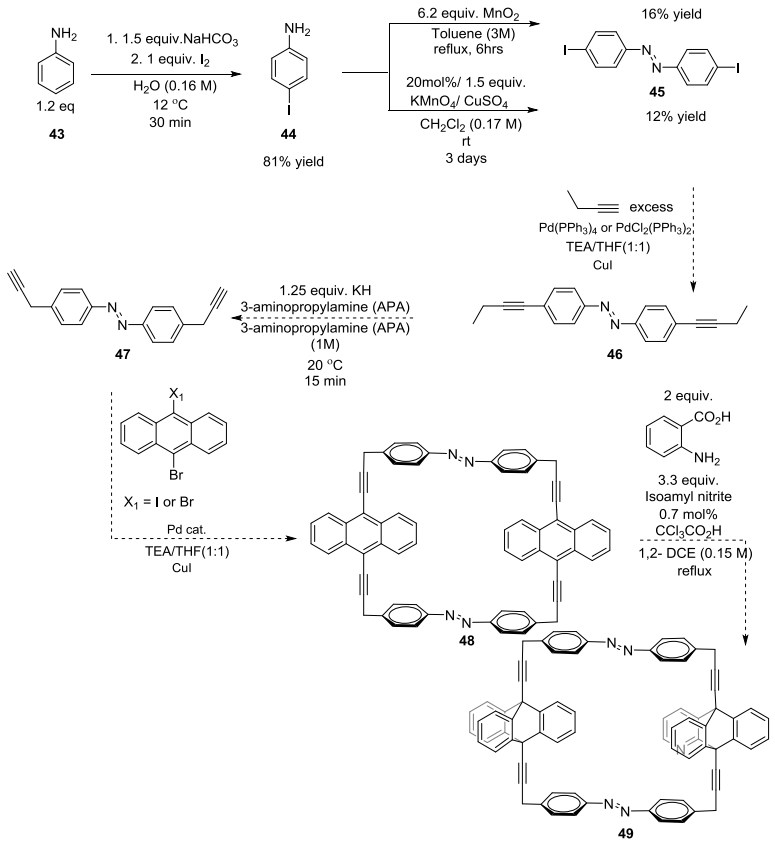


Figure 1.17 Synthesis of **49** linked by two photo-active azobenzene moieties.

The plan was that once we had established a synthetic route for anthracene based gears, we would then use it to form the pyrazino[2,3-g]quinoxaline based gears. Evidently, our synthetic execution failed because of the undesired polymerization products of the Sonogashira coupling reaction. Furthermore, low yields of critical intermediates in the synthetic pathway made the project unworkable.

1.5 CONCLUSION

The ultimate objective of this research was to be able to make a library of macromolecular gear systems that could have controlled gear rotation via external stimuli. The realization of these molecules would have allowed us to conduct extensive investigations into the properties of these novel systems, thus giving insight into the exact nature of molecular motion in these systems. Understanding these systems comprehensively and learning about their motion, and/or dynamism would have fulfilled the primary goal of this research project. The envisaged unidirectionally controlled rotation from this research via incorporation of additional functionalities would be a good addition/contribution to the knowledge base. It could allow electrochemically and photochemically active components from this research to be used as modular systems for rotationally active gears in electronic nanodevices, thus developing further the evolution of nano-machinery design.

The successes and lessons gained from this work involved the brilliant advising of Dr. L. D. Shirtcliff. I thank her for believing in me to be the custodian of this nanoengineering endeavour. We had an excellent working relationship on this particular project; and what a blessing it was to work with and have her as my adviser. However, she departed Oklahoma State University, and a new adviser was assigned to me.

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CHAPTER II

STERICALLY DIRECTED IRIDIUM-CATALYZED HYDROSILYLATION OF ALKENES IN THE PRESENCE OF ALKYNES

2.1 INTRODUCTION TO HYDROSILYLATION

Hydrosilylation, also known as hydrosilation, is the reaction that describes the addition of Si-H bonds to unsaturated bonds. The unsaturation carriers are organic compounds that may have alkene, alkyne, imine and carbonyl functionalities, to mention a few examples.[67] The chemical transformation that realizes these silane adducts can be facilitated by many catalysts. The product outcomes of this catalysis are influenced by the nature of the substrate class involved and the nature of the catalytic system employed. The catalytic system is defined by the type of metal catalyst(s) used, the solvent, temperature, concentration and the stabilizing ligand(s) employed. Hydrosilylation is a chemical transformation that offers utility in a diverse field set in chemical technology that includes nanotechnology, organic, organometalloid, inorganic, bio-organic, organometallic, polymer and materials chemistry.[67] To highlight the scope of application of this technology, we point out that hydrosilation can be used in asymmetric hydrosilylation, which is an important tool in chiral synthesis of useful organic compounds.[68] Another specific example is that a variety of materials can be synthesized by way of this hydrosilylation technology for it can allow the synthesis of new and more block copolymers, poly(silylene-divinylene), polyhedral

oligosilsesquioxane (POSS) based composites, cross linking polymers, σ-π conjugated polymers, other polymers and dendrimers.[69] Hydrosilylation has been a synthetic utility for the installation of temporary silicon tethers as a way to increase reaction rates, regio-, and stereoselectivity in facilitating rapid access to biologically active, complex molecules, and a wide scope of building blocks.[70] The most commonly employed silicon tethers have been disiloxanes followed by siloxanes and then silanes. Of these methods, the synthesis and utilization of tethered silyl alkynes has been limited.

To address this gap, this project sought to develop a method to prepare tethered silyl alkynes through an iridium-catalyzed hydrosilylation reaction. The advantage of this approach is the ability to access highly functionalized silyl-alkyne tethered building blocks that have potential applications in natural product synthesis and small molecule library development. Furthermore, the library of alkynyl-silanes presents a scaffold for developing highly functionalized silanes towards the strategic synthesis of chiral polymeric silicon hydrides for metal nanoparticle on a silicon matrix fabrication. These would be the foundation for developing novel metal nanoparticle catalysts as described in Chapter III. Highly functionalized silanes are also necessary for potential application of these tethers in dual/synergistic catalysis.

2.2 REVIEW OF LITERATURE: RELEVANT SYNOPSIS OF THE HYDROSILYLATION REACTION

Leo Sommer first introduced the chemistry of catalytic hydrosilylation to the chemical community in 1947. This was a reaction between trichlorosilane and 1-octene in the presence of acetyl peroxide. In 1957, John Speier introduced the use of chloroplatinic acid as the catalyst for the hydrosilylation of olefins. This has been followed by different catalytic offsprings that have expanded the application within silicone chemistry, organic synthesis and materials chemistry.[67] Since 1957, new catalysts and reagents have been developed that allow a vast range of organo-silane

product formation, incorporating a wide variety of functionality and selectivity with regard to their stereo-, enantio- and regiochemistry.[67,68,69] The following examples demonstrate some of the catalysts that have been developed for the purpose of hydrosilylation transformation(s). It must be noted that this selection of examples is not the complete scope of hydrosilylation technology.

In 1957, John Speier discovered that hexachloroplatinic acid H_2PtCl_6 in isopropanol was a potent catalyst for hydrosilylation. Speier was recognized for his pioneering efforts by being awarded the Kipping Award by the American Chemical Society in 1990.[67,71] This reagent proved to be an effective catalyst for hydrosilylation. This opened up platinum-based studies of the catalysis of hydrosilylation using a variety of platinum based complexes.[67-69] Other Pt catalyst systems for hydrosilylation were prepared by treating Pt complexes and salts with a host of ligands such as, but not limited to, alkadienes. A peculiar and popular platinum catalyst called the Karstedt's catalyst was also developed. The uniqueness of this catalyst is that it is silicone-soluble and is prepared by the reaction of chloroplatinic acid, H_2PtCl_6, with vinyl-silicon containing compounds, such as divinyltetramethyldisiloxane in the presence of ethanol (which aids in the dissolution of H_2PtC1_6 and the reduction of platinum). Sodium bicarbonate is added to it in order to remove the chloride and aids the reduction of platinum. The resulting catalyst from this preparation is a Pt(0) complex/colloid which contains both bridging and chelating 1,3-divinyltetramethyldisiloxane ligands. Practically, this reagent is a solution of the Pt(0) and vinyl siloxane oligomers.[71,72] The Karstedt's catalyst requires the use of inhibitors such as maleates and fumarates, during hydrosilylation reactions in order to prevent premature crosslinking of the vinylsiloxane oligomers at ambient temperature. The choice of inhibitors is influenced by the inhibitors themselves providing electron deficient double bonds, which function as ligands that prevent crosslinking reactions at ambient temperatures. They also allow long work life at ambient temperature.[71,72,73]

Beyond the use of platinum complexes for hydrosilylation, other transition metals have also been used. They include Zr, Rh, Co, Ru, Pd, Ni, Fe and some other metals. The variety of metallic catalysts allows for diversity in scientific studies around this subject by learning about the

composition of these catalysts, their catalytic mechanisms and understanding the structures together with the chemical dynamics of key intermediates during the hydrosilylation transformation.[67,74,75] Organometallic catalysts generated from zirconocene dichloride and two equivalents of butyllithium have been reported and used in the hydrosilylation of olefins such as styrene, 1-hexene and 2-pentene by the addition of a diphenylsilane.[75] This chemistry allowed for the formation of a vinylsilane by way of hydrosilylation from styrene. The important revelation that this catalyst brought was empirical evidence of an alternative mechanistic pathway for this chemical transformation. There have also been reports of the highly regioselective zirconium-catalyzed hydrosilylation of 1-alkene by the same diphenylsilane substrate.[75] These reports have revealed the occurrence of possible competing chemical transformations apart from hydrosilylation. The possibility of isomerization of internal olefins followed by the hydrosilylation of the new isomers, dihydrocoupling of the silane to form silicon oligomers and dihydrocoupling of the silane with olefin to form vinylsilanes.[75,76] This opens synthetic questions regarding selectivity but at the same time offers and opportunity for further investigations in order to create optimal conditions that favor one particular reaction transformation over the other competing side reactions.

The Wilkinson's catalyst is a common name for chlorotris(triphenylphosphine)-rhodium(I), $RhCl(PPh_3)_3$ (Ph = Phenyl). It is named after Geoffrey Wilkinson because he made the use of this catalyst popular. The compound is obtained from reacting rhodium (III) chloride with excess triphenylphosphine in refluxing ethanol (the ethanol aids in the reduction) to form a square planar, 16-electron complex.[77] This catalyst has worked as a hydrosilylation catalyst used to form *trans* products in polar solvents, with the *cis* isomers predominating in non-polar media, from π basic alkynes. This is another revelation that investigating and putting emphasis on reaction conditions can influence one product outcome over another and also furnish selectivity.[77] Other Rh-based catalysts such ($[Rh(COD)_2]BF_4$ (COD = cyclooctadiene) and $[RhCl(NBD)]_2$ (NBD = norbonadiene) have also been studied and afford the synthesis of *trans-β*-vinylsilanes.[77]

The Grubbs catalyst is a ruthenium carbene catalyst that was originally used for the olefin metathesis reaction.[78] However, expansion of its use in hydrosilylation chemistry resulted in further broadening its utility allowing for the formation of *cis*-vinylsilane products from alkynes. In this transformation the stereo- and regioselectivity of the hydrosilylation is dependent chiefly on the alkyne, silane, and solvent.[79] This further provides evidence that the nature of substrates involved is relevant in influencing selectivity and reaction outcomes.

Trost has also developed a protocol for the hydrosilylation of terminal acetylenes to give α-vinylsilanes, using the ruthenium(II) catalyst, $[Cp^*Ru(MeCN)_3]PF_6$. This catalytic hydrosilylation can also result in regioselective intra- and intermolecular hydrosilylation products from internal alkynes, to give *Z*-trisubstituted alkenes.[79,80] The Ru-based catalysts such as $[Ru(benzene)Cl_2]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$ have also demonstrated utility for accessing *cis*-β-vinylsilanes.[81]

Iron has also attaracted interest as a low cost metal for hydrosilylation.[82] The detailed presentation of the development a heterogenous iron catalyst for hydrosilylation will be described in Chapter III.

Iridium complexes with oxidation states (I), (III) and (IV) have been used for hydrosilylations of terminal alkynes and alkenes.[83,84] The cationic $[Ir(COD)(PCy_3)Py]\ [PF_6]$ and the zwitterionic Ir(I) complexes have been used to conduct the hydrosilylation of styrene to give both the β- and α-adducts.[67] The complexes of dimers $[Ir\ (\mu\text{-X})(diene)]_2$ (where X is a bridging species such as Cl, Br, OMe), have been utilized for the hydrosilylation of allyl chloride by trialkoxy- or alkoxysilanes.[67] This same class of dimeric complexes has been used for the synthesis of halopropyldimethyl-chlorosilane and silylpolyesters using dimethylchlorosilane reacting with unsaturated allyl derivatives. The $[Ir(COD)(i\text{PrPCH}_2\text{CHOMe})][BF_4]$ complex has also been used for the hydrosilylation of phenylacetylene by triethylsilane[85] Furthermore, iridium catalysts have also shown sterically influenced regio- and chemoselective hydrosilylation of terminal alkynes over internal

alkynes.[83b] Iridium-catalyzed borylation of aromatic C-H bonds has also shown to be regioselective by favoring steric over electronic control.[86]

2.2.2 Mechanisms of Hydrosilylation of Unsaturated Substrates Catalyzed by Transition-Metal Complexes

Let it be understood that literature has proposed more than one type of catalytic cycle explaining the hydrosilylation chemical transformation. The choice of a catalytic cycle is influenced by numerous factors that include the particular transition metals or groups of transition metals, the oxidation states of some transition metals, the profile of the substrates, and the reaction conditions.[68-70] The understanding of the catalytic cycle of a hydrosilylation reaction has been a difficult and slow scientific journey. This is due to the fact that characterization and isolation of the extremely reactive and fleeting catalytic intermediates, with highly efficient catalytic metals, have evaded capture and foiled experimental strategies.[67,68] However, through persistence and increased competence of scientific tools for investigation, some progress has been made on this front. The mechanisms shared *vide infra*, are examples of how diverse the mechanistic pathways for hydrosilylation are. It is this precedent that allowed this project to expand hydrosilylation chemistry further.

Transition metal complexes for hydrosilylation, ML_n (where M = metal and L= ligand), are usually but not limited to electron-rich complexes of a late transition metals such as Co(I), Rh(I), Ir(I), Fe(0), Ni(0), Pd(0), or Pt(0). They perform, among others, distinct characteristic activation functions during their catalytic process. Of special mention is the activation of the hydrosilane substrate, $HSiR_3$ and the activation of the unsaturated reaction partner. The design of a catalytic system that influences the order of preferential activation of substrates within the catalytic cycle is a worthy tool for contributing to the broadening of reaction pathways.[67-85]

2.2.2.1 Chalk-Harrod Mechanism (s)

The conventional hydrosilylation of alkenes catalyzed by the Speier catalyst is generally

assumed to proceed via the Chalk-Harrod mechanism.[67-85] In this pathway oxidative addition of the hydrosilane's Si-H group to a metal-olefin complex gives a hydrido-silyl complex. This complex is then coordinated with the unsaturated reaction partner. The resulting complex then undergoes migratory insertion of the alkene into the M-H bond (hydrometallation) to give the alkyl-silyl species. This is followed by reductive elimination of the alkyl and silyl ligands to form the hydrosilylation product. The Chalk-Harrod mechanism was proposed in the 1960s; and is the most often cited mechanism for hydrosilylation based on fundamental steps of organometallic chemistry (See Figure 2.1). [67-85]

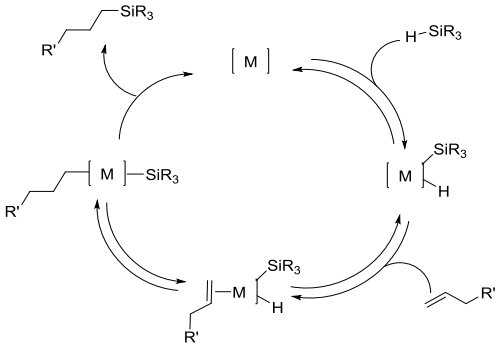


Figure 2.1 Chalk-Harrod mechanism.

It has been observed however, that some phenomena are not explained by the Chalk-Harrod mechanism. Among these is the presence of an induction period required when using some of these hydrosilylation catalysts; an explanation of colored bodies formed during the reaction process; the necessity of the co-catalysis by oxygen for some catalysts in order for the reaction to proceed; or the formation of vinylsilanes as products.[67-86] It is against this backdrop that Wrighton and coworkers proposed a modification of the Chalk-Harrod cycle to allow C-C insertion into the M-Si bond to form a M-C-C-Si complex species, followed by Si-H oxidative addition and reductive elimination of alkane from the H-M-C-C-Si complex in order to explain the formation of vinylsilanes and olefin isomerization (See Figures 2.2 and 2.3below).[87]

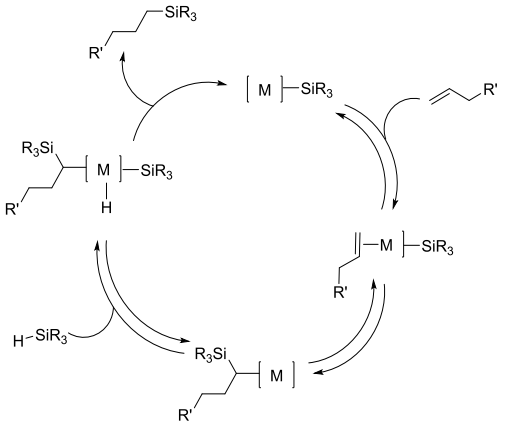


Figure 2.2 Modified Chalk and Harrod mechanism; explaining vinylsilane formation.

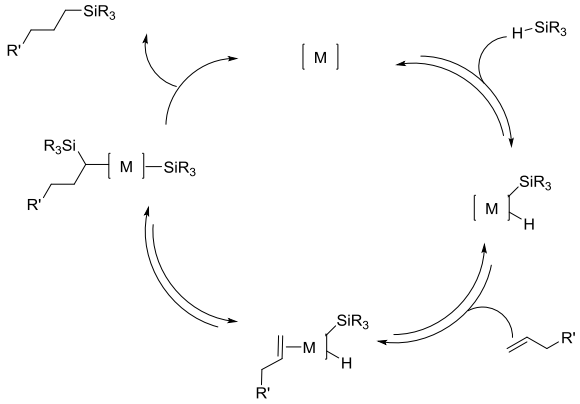


Figure 2.3 Modified Chalk and Harrod Mechanism, explaining olefin isomerization.

Another modified Chalk-Harrod mechanism proposed, by Perutz and by Brookhart, shows resting states and reactive intermediates such as Rh-Si and Co-Si/Pd-Si and bis (silyl)-metal species, respectively (See Figure 2.4). To buttress this, Roy and Taylor show the same mechanism with bis(silyl)-Pt catalyst for the Chalk-Harrod cycle (See Figure 2.4).[88,89]

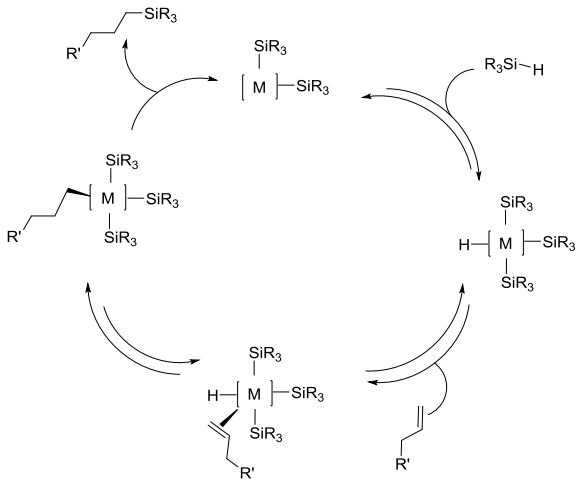


Figure 2.4 Modified Chalk and Harrod mechanism, explaining multiple silyl-metal species.

2.2.2.2 Metathetic Mechanism:

Catalysts based on metals that cannot expand or contract their coordination sphere via redox reactions in any generally useful way to catalyze, mediate hydrosilylation via σ-bond metathesis-type events within their catalytic cycle. Marks and Molander have conducted studies to this effect and various other research groups studying hydrosilylation with these types of metals have proposed the metathetic mechanism (See Figure.2.5).

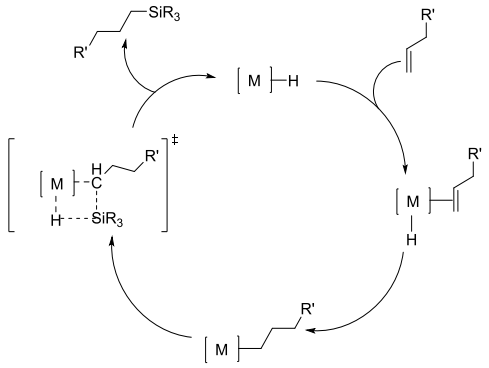


Figure 2.5 Metathetic mechanism

In this catalytic cycle the resting state is M-H complex species. Here, a π-approach of the unsaturated species occurs, and it inserts in the M-H bond to give the M-C complex intermediate.

This is followed by a M-C/H-Si metathetic reaction. It is here where regioselectivity on the unsaturated reaction partner is decided. The bond polarity on the unsaturation and steric interactions in this transition state are what govern the selectivity. This is then followed by the regeneration of the M-H catalytic intermediate complex.[90,91,92]

2.3 Temporary Tethers in Synthetic Chemistry

The application of temporary tethers[93] has been a versatile approach that has facilitated rapid access to biologically active, complex molecules and building blocks. A variety of temporary tethers[94] have been developed, ranging from silicon,[95] boron,[96] magnesium,[97] phosphorus,[98] and esters.[99] The advantages of tethered reactions are increased reaction rates between the coupling partners and high levels of regio- and stereoselectivity. Of the different approaches developed, temporary silicon tethers have been the most commonly utilized. Silicon tethers are versatile in that large assortments of silicon reagents are available, and the tether can be prepared under standard conditions in high yields. They are tolerant of a range of reaction conditions, but can be efficiently cleaved via Tamao-Fleming oxidation[100] or Hiyama cross-couplings.[101] The most common temporary silicon tethers are based on disiloxane and siloxane structural motifs.

2.4 METHODOLOGY

2.4.1 Specific Aims of Study

The focus of this project included initiating a program in the development of dual[102]/synergistic[103] catalysis utilizing temporary tethers for applications in library development. As part of this endeavor, a modular protocol to link a variety of terminal alkynes to an array of functionalized fragments was required. Silyl alkynes are ideal temporary tethers because they are easily and efficiently prepared from metal acetylides[104] and are stable under most standard reaction conditions, but can be easily cleaved under nucleophilic fluoride conditions.[105] Therefore, what was

required was an approach to link the silyl alkyne to the second coupling partner through the silicon. This has previously been accomplished with alkenyl alcohols for subsequent applications in enyne-metathesis reactions (RCM) through formation of an alkynyl siloxane (See Figure 2.6).[106]

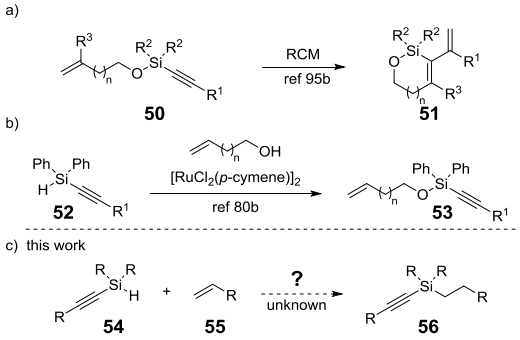


Figure 2.6 (a) The utility of an alkyne containing silicon tethered compound; (b) Ruthenium facilitated alkyne incorporation; (c) Guiding objective of this project.

A drawback of the alkynyl siloxane tether is the instability of the siloxane, which makes isolation problematic. To complement this approach and satisfy the desired requirement for a temporary silicon linker that could be carried through multiple synthetic steps, this project sought to develop a method for an alkynylsilane linker.

Hydrosilylation[107] of double and triple bonds has proven to be an important reaction/tool in organic syntheses.[108] The versatility of hydrosilylation reactions to be conducted with high levels of regio- and stereocontrol, and functional group compatibility made this a desirable approach to connect an alkynylsilane linker to an olefin or alkyne (See Figure 2.6.c.). To the best of our knowledge, at the time of this project inception, a method for the selective hydrosilylation of olefins in the presence of an alkyne had not been reported. This gap was most likely the result of the higher reactivity of the more electron rich π-basic alkyne. However, there had been a few reports demonstrating transition metal catalyzed silane alcoholysis in the presence of an alkyne (See Figure 2.6.b.).[109] Selective hydrosilylation of one alkene in the presence of another had been accomplished either using a directing group or steric bias. Based on these results, the inception of the project

speculated that it could be possible to override the inherent electronic bias for the more reactive alkyne through a sterically directed approach. Traditional transition metals that have been employed in hydrosilylation reactions are Pt, Rh, Pd, Ru, Ir, and Fe as mentioned above. These are governed by electronic control over steric control.

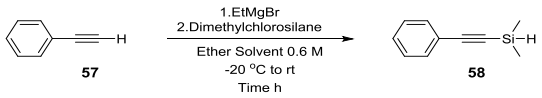
As the starting point to this investigation it was decided that iridium would be the metal of choice based on its selectivity in catalyzing hydrosilylation reactions of allyl substrates in addition to iridium catalysts demonstrating chemo- and regioselectivity by favoring steric over electronic control as mentioned earlier.

2.5 RESULTS AND DISCUSSION

2.5.1 Silicon Hydride Substrate Design and Synthesis

Investigation of the feasibility of this approach began with designing a silicon hydride partner that harbored a characteristic dimethylsilyl motif that imposed steric hindrances to the alkyne functionality on the substrate. It was decided to react phenylacetylide (**57**) with dimethylchlorosilane to generate dimethylphenylethynlysilane (**58**) (See Table 2.1.). The optimized reaction conditions for the alkynyl substrate synthesis are delineated in entry 7 in Table 2.1.

Table 2.1. Optimization of starting material, **58**[a]



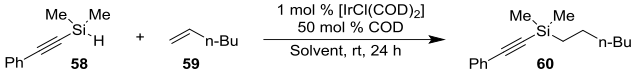
entry	solvent (0.6 M)	EtMgBr (equiv.)	dimethylchlorosilane (equiv.)	addition temperature (°C)	time (hr)	isolated yield (%)
1	THF	2	2	0	5	15[b]
2	THF	2	2	0	2.5	57[b]
3	Et_2O	1.2	1.4	0	2.5	52
4	THF	1.2	1.4	0	4	77
5	THF	1.1	1.2	-20	4	>99[b]
7	**THF**	**1.2**	**1.4**	**0**	**4**	**97**

[a] Conditions: 1) 1 equiv. alkyne (57), EtMgBr, equiv. in an ethereal solvent; 2) Dimethylchlorosilane,-20 to rt, 2-5-4hrs; [b] NMR showed evidence of grease

2.5.2 Proof of Principle Investigations and Results

Investigation of the practicality of the target hydrosilylation transformation was commenced by reacting the dimethylphenylethynylsilane (**58**) with 1-hexene (**59**), facilitated by 1 mol% of $[IrCl(COD)]_2$ catalyst, and 50 mol% COD co-ligand, a concerntration of 0.2 M in DCM. To our delight the reaction gave >99% conversion (See entry 4 Table 2.2.) and 93% isolated yield. A decision was made to investigate the solvent compatibility of this reaction together with other variables as shown in Table 2.2. COD was used for this particular screening process due to its ability to change into different co-ordination modes, provide steric hindrance, capacity for multiple bonding hepticities and had the ability to stabilize the unsaturated metal centers, depending on the electronic and steric properties of the iridium center.

Table 2.2. Solvent screening for the proof of principle reaction system

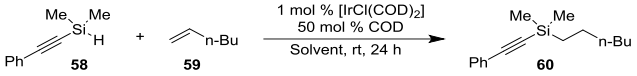


entry[a]	solvent	concentration (M)	COD (mol%)	conv.[b] (%)
1	DCM	0.2	0	76
2	DCM	0.2	10	98
3	DCM	0.2	25	89
4	DCM	0.2	50	>99
5	DCM	1	50	88[a]
6	1,2-DCE	0.2	0	77
7	1,2-DCE	0.2	10	85
8	1,2-DCE	0.2	25	80
9	1,2-DCE	0.2	50	>99
10	1,2-DCE	1	50	92[a]
11	1,2-DCE	1	0	91[a]
12	Toluene	0.2	0	83
13	Toluene	0.2	10	85
14	Toluene	0.2	25	83
15	Toluene	0.2	50	97
16	Toluene	1	50	96[a]
17	Hexane	0.2	0	37
18	Hexane	0.2	25	48
19	Hexane	0.2	50	83
20	Hexane	1	50	34
21	Et_2O	0.2	0	17
22	Et_2O	0.2	50	35
23	1,4-Dioxane	0.2	0	10
24	1,4-Dioxane	0.2	50	36
25	THF	0.2	0	7
26	THF	0.2	50	15
27	THF	1	50	18
28	DME	0.2	0	35
29	DME	0.2	0	12
30	DME	0.2	50	35
31	EtAOc	0.2	0	26
32	EtAOc	0.2	10	12
33	EtAOc	0.2	25	13
34	EtAOc	1	50	41
35	DMSO	0.2	0	0
36	DMF	0.2	0	0
37	DMF	0.2	0	0
38	MeCN	0.2	0	0
39	Isopropanol	0.2	50	1
40	Isopropanol	0.2	0	1
41	NMP	0.2	0	0
42	Neat	-	0	69
43	Neat	-	10	74
44	Neat	-	25	80
45	Neat	-	50	87
46	Neat	-	100	>99[a]

[a] Conditions: 1 mmol silane (58), 1 mmol olefin (59), 1.0 mol % $[IrCl(COD)_2]$,COD ligand, in solvent, rt, 24hrs; [b] Conversions were measured by Gas Chromatography

After completing the screen delineated in Table 2.2, the data showed nonpolar solvents were optimum ($ClCH_2CH_2Cl$, CH_2Cl_2, hexanes, or toluene) at high concentrations over 24 h. Furthermore, it was established that the reaction can be conducted neat, to give high conversions (See entry 6, Table 2.3). In addition to this it was established that catalytic loading could be lowered to 0.5 mol% $[IrCl(COD)]_2$. This demonstrated the flexibility of the reaction in question.

Table 2.3. Summary of solvent compatibility data[a]



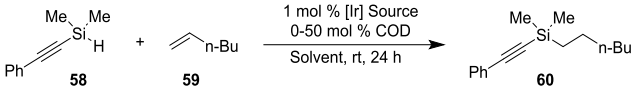
entry[a]	solvent	concentration (M)	COD (mol%)	conv.[b] (%)
1	Hexanes	0.2	50	83
2	DCM	1	50	88
3	Toluene	1	50	96
4	1,2-DCE	1	50	92
5	**1,2-DCE**	**1**	**0**	**91**
6	Neat	-	50	87

[a] Conditions: 1 mmol silane (58), 1 mmol olefin (59), 1.0 mol % $[IrCl(COD)_2]$,COD ligand, in solvent, rt, 24hrs; [b] Conversions were measured by Gas Chromatography

2.5.3 Iridium Source Investigations and Results

With the solvent compatibility in hand, different iridium sources were screened, under dichloromethane, 1,2-dichloroethane and toluene solvent systems as well as neat (See Table 2.4). The iridium sources of $IrCl_3$ and $[Ir(COD)OMe]_2$ gave poor starting material to product conversion. However, $[Ir(COD)Cl]_2$ gave the highest conversion in all compatible solvents (entries 5, 10, 15, 20, Table 2.4). Because 1,2-dichloroethane gave the best isolated yield of desired product, without the requirement of additional COD ligand for the reaction, it was employed for substrate screen using the conditions employed in entry 5, Table 2.3.

Table 2.4. Screening of iridium sources for hydrosilylation



entry[a]	solvent (0.2 M)	Catalyst	COD loading (mol%)	conv.[b] (%)
1	DCM	$[Ir(COD)OMe]_2$	0	40
2	DCM	$[Ir(COD)OMe]_2$	50	35
3	DCM	$IrCl_3$	0	0
4	DCM	$IrCl_3$	50	4
5	**DCM**	**$[Ir(COD)Cl]_2$**	**50**	**>99**
6	1,2-DCE	$[Ir(COD)OMe]_2$	0	36
7	1,2-DCE	$[Ir(COD)OMe]_2$	50	42
8	1,2-DCE	$IrCl_3$	0	0
9	1,2-DCE	$IrCl_3$	50	0
10	**1.2-DCE**	**$[Ir(COD)Cl]_2$**	**50**	**>99**
11	Toluene	$[Ir(COD)OMe]_2$	0	15
12	Toluene	[Ir(COD)OMe]2	50	14
13	Toluene	$IrCl_3$	0	2
14	Toluene	$IrCl_3$	50	1
15	**Toluene**	**$[Ir(COD)Cl]_2$**	**50**	**97**
16	Neat	$[Ir(COD)OMe]_2$	0	20
17	Neat	[Ir(COD)OMe]2	50	18
18	Neat	$IrCl_3$	0	0
19	Neat	$IrCl_3$	50	0
20	**Neat**	**$[Ir(COD)Cl]_2$**	**50**	**87**

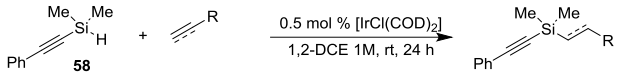
[a] Conditions: 1 mmol silane (58), 1 mmol olefin (59), 1.0 mol % [Ir] source, COD ligand, in solvent, rt, 24hrs; [b] Conversions were measured by Gas Chromatography

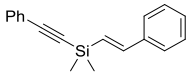
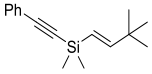
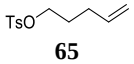
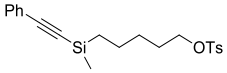
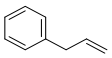
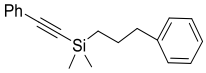
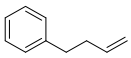
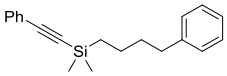
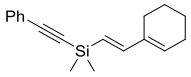
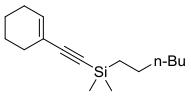
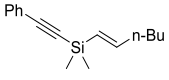
2.5.4 Initial Substrate Screening Investigations and Results

Substrate screening was conducted for a total of twenty two unsaturated substrate partners (See Tables 2.5). Of these, only eight gave us desired product, with a wide range of isolated yield data set. Hydrosilylation of sterically congested *tert*-butylacetylene (**63**) (entry 2, Table 2.5) gave the highest yield, but employing phenylacetylene (**61**) as a substrate gave, a very modest yield (entry 1, Table 2.5.). This showed troubling inconsistency. Because attempted hydrosilylation of 1-pentenol (**80**) showed effervescence that suggested alcoholysis of the silicon hydride without product formation (entry 15, Table 2.5.), the alcohol was protected (**65**) and the reaction was repeated to give a high yield (entry 3, Table 2.5.). This suggested the importance of initial protection of unsaturation partners that harbor alcohol functionality. Employing allylbenzene (**67**) gave moderate yields, (entry

4, Table 2.5). Increasing the chain length further by using (but-3-en-1-yl)benzene (**69**) gave a poor yield (entry 5, Table 2.5). This trend was unexpected because the more accessible alkene was supposed to post higher yields. To test chemoselectivity between the alkyne and alkene functionalities 1-ethynylcyclohex-1-ene (**71**) was employed and showed preferential reactivity with the alkyne, albeit at very low yield (entry 6, Table 2.5). Changing the alkynyl silane to (cyclohex-1-en-1-ylethynyl)(hexyl)dimethyl-silane(**73**), (entry 7, Table 2.5), gave modest yield. Hydrosilylation of a terminal hexyne (**74**) gave a high yield favoring the *E*-isomer (**75**) (entry 8, Table 2.5).

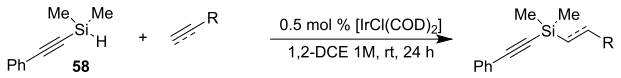
Table.2.5. Initial unsaturation partner substrate screening [a]

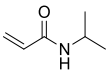
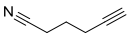
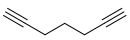
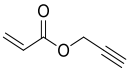
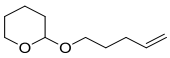


entry[a]	unsaturated substrate	product	isolated yield (%)
1	 **61**	 **62**	50
2	 **63**	 **64**	>99
3	 **65**	 **66**	86
4	 **67**	 **68**	66
5	 **69**	 **70**	38
6	 **71**	 **72**	18
7	 **59**	 **73**	42[b]
8	 **74**	 **75**	83

[a] Conditions: 1 mmol silane (58), 1 mmol unsaturated partner, 0.5 mol % $[IrCl(COD)_2]$, in 1,2-DCE (1M), rt, 24hrs; [b] (cyclohex-1-en-1-ylethynyl)dimethylsilane was used instead of (58).

Table 2.5. Initial unsaturation partner substrates screening (continued)[a]



entry	unsaturated substrate	isolated yield (%)
11	 **76**	N.R.
12	 **77**	N.R.
13	 **78**	N.R.
14	 **79**	N.R.
15	 **80**	N.R.
16	 **81**	N.R.
17	 **82**	N.R.
18	 **83**	N.R.
19	 **84**	N.R.
20	 **85**	N.R.
21	 **86**	N.R.
22	 **87**	N.R.

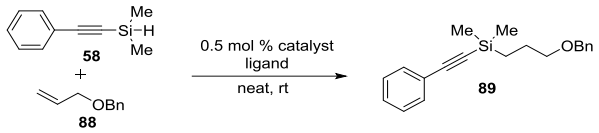
[a] Conditions: 1 mmol silane (58), 1 mmol unsaturated partner, 0.5 mol % [$IrCl(COD)_2$], in 1,2-DCE (1M), rt, 24hrs.

In summary, the reaction aforementioned gave a confusing yield trend and demonstrated a narrow substrate tolerance. Attempts to broaden the substrate scope further (entries 11-22, Table 2.5). These frustrating results prompted further consideration of the reaction system and initiated a re-optimization exercise.

2.5.5 Optimization of a More Challenging Hydrosilylation System

This time a more challenging alkene unsaturation partner, allylbenzylether (**88**), was employed. The starting reaction conditions were 0.5 mol% catalyst loading, 0.5 equivalents of COD ligand, without the use of Schlenck techniques. Microwave assistance was employed and GC was used to monitor the reaction (not TLC). While these conditions posted high conversion, the isolated yield was a disaster (see entries 1 and 2, Table 2.6). It was decided to employ conditions developed for iridium catalyzed hydrosilylation of allyl halides with chlorodimethylsilane.[110] Under these conditions the desired silylation product was formed under neat conditions with 0.5 mol % $[IrCl(COD)]_2$. However, full conversion could only be accomplished when a large excess of co-additive ligand COD was used (entry 4, Table 2.6). To obtain reproducible results and high yields of the desired product it was determined that all reagents needed to be degassed prior to use. Screening alternative diene, olefin, and amine ligands (entries 6-33, Table 2.6) resulted in varied percentage conversions and product formations. It also promoted undesired side reactions, which were not determined. Modified solvent screening, based on the solvent class initially established, showed that the amount of COD additive could be decreased, from 4.07 to 0.5 equivalents, albeit at the cost of prolonged reaction times and inconsistent conversion to products in substrate screenings (entries 34-36, Table 2.6). Attempts to shorten reactions times further under thermal microwave irradiation resulted in high conversion in 20 minutes or less (entry 37, Table 2.6). However, under thermal conditions undesirable reaction pathways became more favorable, diminishing the isolated yield of the desired product. To establish the feasibility of the original hypothesis, primarily that this reaction was reliant upon sterically controlled iridium catalysis, Speier's (H_2PtCl_6), Karstedt's ($Pt_2[(Me_2SiCH{=}CH_2)_2O]_3$), and Wilkinson's ($[(Ph)_3P]_3RhCl$) catalysts were screened (entries,40, 41, 42. Table 2.6). As expected, these classical platinum and rhodium catalysts promoted the silyl alkyne to react with itself, affording none of the desired hydrosilylation product. Conclusively, the optimized conditions became 0.5 mol% $[IrCl(COD)_2]$ and 4.07 equivalents COD at room temperature with all substrates/reagents degassed, and with gas chromatography monitoring reaction progress.

Table 2.6. Re-Optimization of hydrosilylation reaction using **88**



entry	catalyst	ligand type	ligand loading	solvent	time (h)	conv[j] (%)	yield[k] (%)
1[f]	$[IrCl(COD)]_2$	COD	0.5 equiv	-	4	87	n.d.[d]
2[f]	$[IrCl(COD)]_2$	COD	0.5 equiv	-	4	92	51
3	$[IrCl(COD)]_2$	COD	1 equiv	-	4	86	n.d.[d]
4	**$[IrCl(COD)]_2$**	**COD**	**4 equiv**	-	**4**	**98**	**88**
5	$[IrCl(COD)]_2$	None	-	-	16	72	n.d.[d]
6[b]	$[IrCl(COD)]_2$	Limonene	0.5 equiv	-	0.33	92	50
7	$[IrCl(COD)]_2$	Limonene	0.5 equiv	-	0.25	92	n.d.[d]
8	$[IrCl(COD)]_2$	Limonene	1 equiv	-	4	92	n.d.[d]
9	$[IrCl(COD)]_2$	Limonene	4 equiv	-	4	93	n.d.[d]
10	$[IrCl(COD)]_2$	Limonene	4 equiv	-	19	70	55
11	$[IrCl(COD)]_2$	2,2'-Bipyr	0.5 mol %	-	4	70	25
12[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	0.5 mol %	1,2-DCE	4	31	n.d.[d]
13[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	0.5 mol %	THF	4	31	n.d.[d]
14[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	0.5 mol %	Toluene	4	38	n.d.[d]
15[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	0.5 mol %	Neat	4	88	n.d.[d]
16[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	1 mol %	1,2-DCE	4	20	n.d.[d]
17[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	1 mol %	THF	4	29	n.d.[d]
18[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	1 mol %	Toluene	4	32	n.d.[d]
19[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	0.5 mol %	Neat	4	58	n.d.[d]
20[f]	$[IrCl(COD)]_2$	2,2'-Bipyr	2 mol %	Neat	4	48	7
21	$[IrCl(COD)]_2$	2,2'-Bipyr	1 mol %		4	70	47
22[f]	$[IrCl(COD)]_2$	1,10-phen	0.5 mol %	1,2-DCE	4	50	n.d.[d]
23[f]	$[IrCl(COD)]_2$	1,10-phen	0.5 mol %	THF	4	54	n.d.[d]
24[f]	$[IrCl(COD)]_2$	1,10-phen	0.5mol %	Toluene	4	54	n.d.[d]
25[f]	$[IrCl(COD)]_2$	1,10-phen	0.5mol %	Neat	4	90	n.d.[d]
26[f]	$[IrCl(COD)]_2$	1,10-phen	1 mol %	1,2-DCE	4	50	n.d.[d]
27[f]	$[IrCl(COD)]_2$	1,10-phen	1 mol %	THF	4	54	n.d.[d]
28[f]	$[IrCl(COD)]_2$	1,10-phen	1mol%	Toluene	4	49	n.d.[d]
29[f]	$[IrCl(COD)]_2$	1,10-phen	0.5mol %	Neat	4	91	n.d.[d]
30	$[IrCl(COD)]_2$	COD	0.5 equiv	Neat	4	92	48
31	$[IrCl(COD)]_2$	Norbornadiene	0.5 mol%	Neat	4	64	15
32[b]	$[IrCl(COD)]_2$	Carvone	0.5 mol%	Neat	0.33	91	27
33	$[IrCl(COD)]_2$	1,10-phen	2 mol %	-	4	90	47
34[a]	$[IrCl(COD)]_2$	COD	0.5 mol %	-	19	100	89
35[g]	**$[IrCl(COD)]_2$**	**COD**	**4 equiv.**	-	**24**	**100**	**93**
36[b]	$[IrCl(COD)]_2$	COD	0.5 mol %	-	19	100	89
37[b]	$[IrCl(COD)]_2$	COD	0.5 equiv	-	0.33	100	77
38	$[IrOMe(COD)]_2$	COD	4 equiv	-	24	0	n.d.
39	$IrCl_3$	none	-	-	2	100[e]	0
40	H_2PtCl_6	none	-	-	2	100[e]	0
41	Karstedt[i]	none	-	-	16	100[e]	0
42	$[(Ph)_3P]_3RhCl$	none	-	-	2	100[e]	0

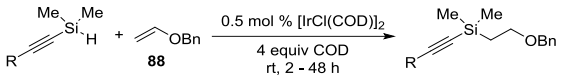
Unless otherwise mentioned conditions were: 1 mmol of dimethyl(phenylethynyl)silane, 1 mmol benzyl allyl ether , 0.5 mol % catalyst, ligand, rt; all liquid reagents were degassed; [a] 0.1 mol % $[Ir(COD)Cl]_2$, reaction 0.5 M in 1,2-dichloroethane;[b] MW, 60 °C; [c] MW, 60 °C in 1 M 1,2-dichloroethane; [d] not determined;. [e] Consumption of dimethyl(phenylethynyl)silane by GC; [f] Without degassing system; [g] in 1 M 1,2-dichloroethane; [i] $Pt_2[(Me_2SiCH{=}CH_2)_2O]_3$ [j] monitored by GC and based on consumption of benzyl allyl ether; [k] isolated by flash chromatography.

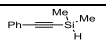
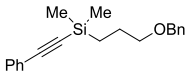
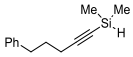
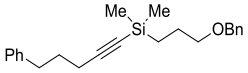
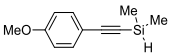
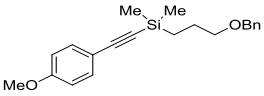
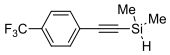
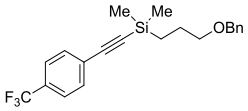
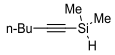
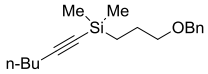
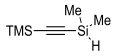
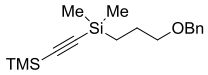
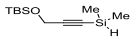
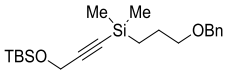
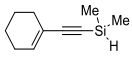
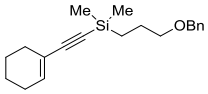
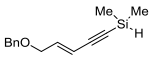
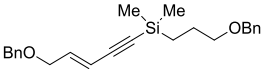
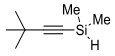
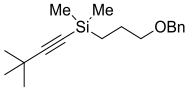
2.5.6 Final Substrate Screening Investigations of Various Silicon Hydrides

With the optimized conditions in hand, a fresh systematic substrate screening was initiated (Tables 2.7, 2.8, 2.9). The first was screening various alkynylsilanes' (entries 1-10, Table 2.7) hydrosilylation of allyl benzyl ether which summarily occurred in moderate to high yields regardless of whether the substituent on the alkyne was aliphatic or aromatic.

There was no effect on yield or reaction times when electron donating or withdrawing functional groups were incorporated into the aryl fragment of the alkynylsilanes (entries 3 and 4, Table 2.7). However, the presence of a conjugated olefin resulted in prolonged reactions of 44-48 hours (entries 8 and 9, Table 2.7). Standard alcohol protecting groups were well tolerated (entries 7 and 9, Table 2.7) and the steric hindrance of a *tert*-butyl group (entry 10, Table 2.7) did not inhibit the reaction.

Table.2.7 Substrate screening between alkynylsilanes and **88**[a]



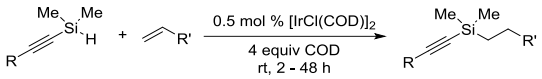
entry	starting silane substrate	product	conv[b] (%)	yield[c] (%)
1	 **58**	 **89**	98	88
2	 **90**	 **91**	91	78
3	 **92**	 **93**	96	88
4	 **94**	 **95**	97	88
5	 **96**	 **97**	99	86
6	 **98**	 **99**	93	94
7	 **100**	 **101**	89	80
8	 **102[e]**	 **103**	84	82
9	 **104[e]**	 **105**	100	64
10	 **106**	 **107**	80	75

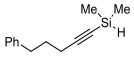
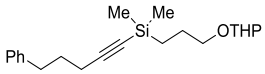
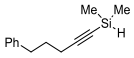
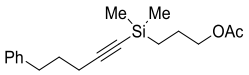
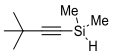
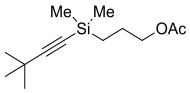
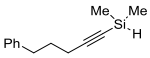
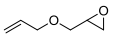
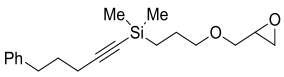
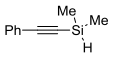
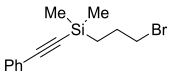
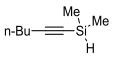
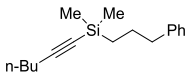
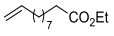
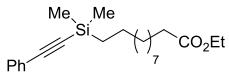
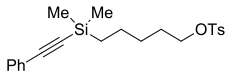
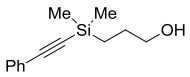
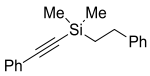
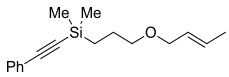
[a] Conditions: 1 equiv starting silane (1 mmol), 1 equiv **88** (1 mmol), 0.5 mol % $[IrCl(COD)]_2$, 4.07 equiv COD (0.5 mL), rt, all reagents degassed; [b] determined by GC; [c] average isolated yield of two runs; [d] a complex mixture was obtained; [e] used 2 equiv

2.5.7 Final Substrate Screening Investigations between Alkynylsilanes and Alkenes

Next was screening various alkynylsilanes with different alkene substrates (Table 2.8). The system demonstrated that it tolerates an acid labile tetrahydropyran allylether (**86**) (entry 1, Table 2.8) an epoxide (**112**) (entry 4, Table 2.8), the highly reactive allyl bromide (**114**) (entry 5, Table 2.8), an ester (**118)** (entry 7, Table 2.8), and a primary tosylate (**65**) (entry 8, Table 2.8). It must be noted that, allyl acetate (**109**) (entries 2-3, Table 2.8) only afforded moderate yields of the hydrosilylation product with the remaining mass balance being unreacted allyl acetate. The diminished yields for the allyl acetate may be due to coordination of the carbonyl to the electrophilic iridium. Furthermore, formation of an iridium π-allyl was not detected.[111] Subjection of allyl alcohol (**121**) (entry 9, Table 2.8) to the reaction conditions afforded a complex mixture.[112] Styrene and its derivatives were unreactive under these hydrosilylation conditions (entry 10, Table 2.8)[113,114] Attempts to react 1,3-dienes, isoprene and myrcene were unproductive, presumably due to chelation to the catalyst. Hydrosilylation of (*E*)-1-(allyloxy)but-2-ene (**125**) was chemoselective for the terminal olefin over the internal disubstituted alkene (entry 11, Table 2.8) with chelation to the catalyst contributing to the poor conversion and yield.

Table 2.8 Substrate screening between alkynylsilanes and alkenes[a]



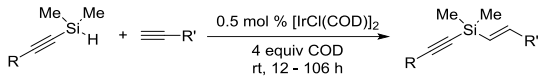
entry	starting silane substrate	starting alkene substrate	product	conv[b] (%)	yield[c] (%)
1	 **90**	 **86**	 **108**	97	81
2	 **90**	 **109**	 **110**	90	60
3	 **106**	 **109**	 **111**	94	37
4	 **90**	 **112**	 **113**	94	83
5	 **58**	 **114**	 **115**	100	92
6	 **96**	 **116**	 **117**	96	81
7	 **58**	 **118**	 **119**	84	82
8	 **58**	 **65**	 **120**	100	81
9	 **58**	 **121**	 **122**	100	C.M.[d]
10	 **58**	 **123**	 **124**	0	0
11	**58**	 **125**	 **126**	28	26

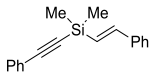
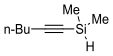
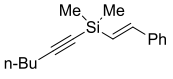
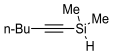
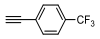
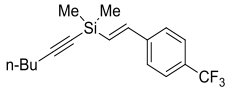
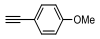
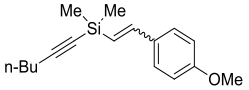
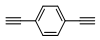
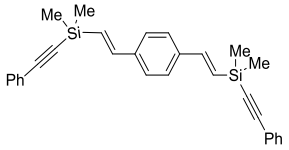
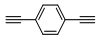
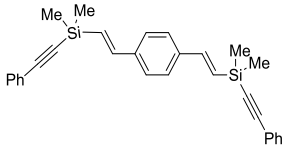
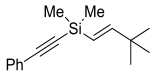
[a] Conditions: 1 equiv silane(1 mmol), 1 equiv alkene (1 mmol), 0.5 mol % $[IrCl(COD)]_2$, 4.07 equiv COD (0.5 mL), rt, all reagents degassed; [b] determined by GC; [c] average isolated yield of two runs; [d] a C.M. = complex mixture was obtained.

2.5.8 Substrate Screening Investigations between Alkynylsilanes and Alkynes

Lastly, after completing the alkene screening process, we considered the idea of examining terminal alkynes with this system[115] (Table 2.9). Phenylacetylene (**61**) was efficiently hydrosilylated with both an aromatic (**58**) and aliphatic alkynylsilane (**96**) (entries 1-2, Table 2.9). Electron donating (**130**) and withdrawing (**128**) groups on the aromaticity of phenylacetylene (entries 3-4, Table 2.9) did not affect yields, but the electron donating methoxy group (**130**) afforded a unique mixture of regioisomers. The *Z*-isomer may have resulted from *E*-*Z*-isomerization during the required prolonged reaction time.[116] Subjection of a diyne (**132**) to the reaction conditions afforded a mixture of mono- and di-hydrosilylation products with *E*-selectivity. Increasing the concentration of the silane to 4 equivalents increased the overall yield but did not affect the ratio of mono- to di-hydrosilylation (entries 5-6, Table 2.9). Hydrosilylation of sterically congested *tert*-butylacetylene (**63**) (entry 7, Table 2.9) occurred swiftly. The system was chemoselective for the terminal alkyne of an enyne (**71**) (entry 8, Table 2.9). In the presence of a nitrile (**82**), full conversion was inhibited, with a modest yield of desired product (entry 9, Table 2.9). Examination of conjugated carbonyls revealed that deactivated alkynes required extended reaction times and were low yielding (entries 10-11, Table 2.9), whereas the alkyne of propargyl acrylate (**136**) (entry 12, Table 2.9) underwent hydrosilylation in high yield but afforded a mixture of *E* and internal regioisomers. [117] As with allyl alcohol (entry 9, Table 2.8), propargyl alcohol also afforded a complex mixture, and examination of the crude reaction mixture by ^{1}H NMR analysis showed that hydrosilylation of the alkyne and silane alcoholysis did occur. However, simple protection of the alcohol with a TBS group (**139**) (entry 14, Table 2.9) afforded the desired hydrosilylation product in high yield, favoring the *E* isomer.

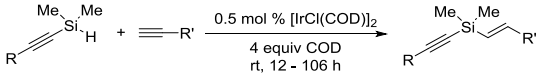
Table 2.9 Substrate screening between alkynylsilanes and alkynes[a]

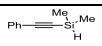
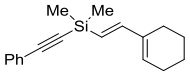
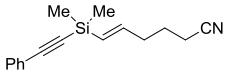
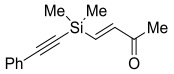
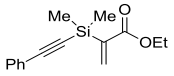
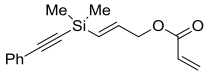
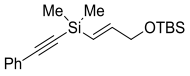


entry	starting silane substrate	starting alkyne substrate	product	conv[b] (%)	yield[c] (%)
1	 **58**	 **61**	 **62**	99	81
2	 **96**	 **61**	 **127**	88	72
3	 **96**	 **128**	 **129**	89	80
4	 **58**	 **130**	 **131**	88	73 74:19:7 E:Z:Int[d]
5	 **58**	 **132**	 **133**	77	51 62:38 Di:Mono[d]
6	 **58[e]**	 **132**	 **133**	78	80 63:37 Di:Mono[d]
7	 **58**	 **63**	 **64**	92	77

[a] Conditions: 1 equiv silane (1 mmol), 1 equiv alkyne (1 mmol), 0.5 mol % $[IrCl(COD)]_2$, 4.07 equiv COD (0.5 mL), rt, all reagents degassed; [b] determined by GC; [c] average isolated yield of two runs; [d] ratio determined by ^1H NMR of the crude reaction = internal; [e] used 2 equiv

Table 2.9 Substrate screening between alkynylsilanes and alkynes (continued)[a]



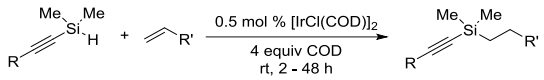
entry	starting silane substrate	starting alkyne substrate	product	conv[b] (%)	yield[c] (%)
8	 **58**	 **71**	 **72**	100	87
9	 **58**	 **82**	 **134**	68	51
10	 **58**	 **85**	 **135**	100	14
11	 **58**	**136**	 **137**	61	11 43:56 E:Int[d]
12	 **58**	 **84**	 **138**	85	74 63:37 E:Int[d]
13	 **58**	 **139**	 **140**	100	89 78:22 E:Int[d]

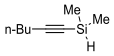
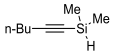
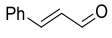
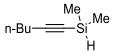
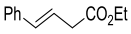
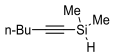
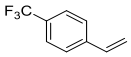
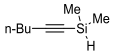
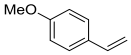
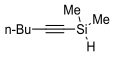
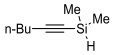
[a] Conditions: 1 equiv silane (1 mmol), 1 equiv alkyne (1 mmol), 0.5 mol % $[IrCl(COD)]_2$, 4.07 equiv COD (0.5 mL), rt, all reagents degassed; [b] determined by GC;[c] average isolated yield of two runs; [d] ratio determined by ^1H NMR of the crude reaction; [e] used 2 equiv.

2.6 CONCLUSION

By employing a steric controlled approach, hydrosilylation of alkenes with alkynylsilanes under iridium catalysis is now achievable. The system demonstrates good chemo- and regioselectivity, allowing efficient and easy access to highly functionalized alkynylsilane tethers. However, the limitations of this protocol are summarized in Table 2.10. The system is intolerant to sterically congested alkene or alkyne substrates like diphenylethene (**141**), (prop-1-yn-1-yl)-benzene (**146**), trimethyl(phenylethynyl)silane (**147**), and 1,2-diphenylethyne (**148**) (entries,1, 6, 7, and 8, Table.2.10). Chelating substrates (**76, 83, 143, 149**) also posted no reactivity to low conversion (entries 3, 9, 10, 16 and 17, Table 2.10). Styrene (**123, 144, 145**) and its derivetives with electron donating and electron withdrawing groups did not react in this system (entries 4 and 5, Table 2.10). Hydrosilylating aldehydes (**142**, **81**) did not work as shown in entries 2 and 15 of Table 2.10, nor did amide carrying substrates (**79**) (entry 13, Table 2.10). This system was not ammenable to imine or amine containing unsaturation susbstrates (**149, 79**) (entries 9, 13 and 17, Table 2.10), presumably due to coordination between the iridium and the N-lone pair, resulting in the complete shut down of the catalyst. This is not shocking, because precious metal complexes for hydrosylilation are known to be susceptible to catalyst poisoning by amine and imine functionalities.[118]

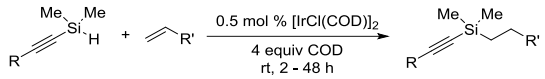
Table 2.10 Substrate screening between alkynylsilanes other unsaturation partners[a]

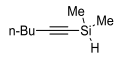
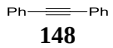
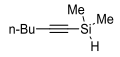
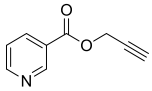
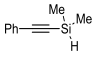
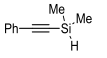
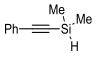
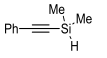
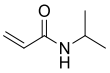
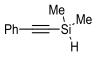
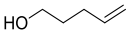
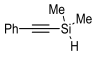
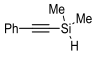
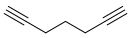
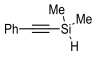
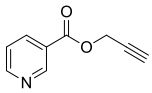


entry	starting silane substrate	starting alkyne substrate	yield[c] (%)
1	 **96**	 **141**	N.R.
2	 **96**	 **142**	N.R.
3	 **96**	 **143**	N.R.
4	 **96**	 **144**	N.R.
5	 **96**	 **145**	N.R.
6	 **96**	**146**	N.R.
7	 **96**	**147**	N.R.

[a] Conditions: 1 equiv silane (1 mmol), 1 equiv unsaturation partner (1 mmol), 0.5 mol % $[IrCl(COD)]_2$, 4.07 equiv COD (0.5 mL), rt, all reagents degassed.

Table 2.10 Substrate screening between alkynylsilanes other unsaturation partners (continued)[a]



entry	starting silane substrate	starting alkyne substrate	yield[c] (%)
8	 **96**	 **148**	N.R.
9	 **96**	 **149**	N.R.
10	 **58**	 **76**	N.R.
11	 **58**	 **150**	N.R.
12	 **58**	 **151**	N.R.
13	 **58**	 **79**	N.R.
14	 **58**	 **80**	N.R.
15	 **58**	 **81**	N.R.
16	 **58**	 **83**	N.R.
17	 **58**	 **149**	N.R.

[a] Conditions: 1 equiv silane (1 mmol), 1 equiv unsaturation partner (1 mmol), 0.5 mol % $[IrCl(COD)]_2$, 4.07 equiv COD (0.5 mL), rt, all reagents degassed; [b] determined by GC.

In summary, the scaffold class that was developed in this project provides unique alkynylsilicon tethers that have a wide scope of applications as mentioned *vide supra*. They can be used in dual and/ or synergistic catalysis which could be the next direction of this project. Furthermore, there remains more exploration in designing chiral oligomeric or polymeric silanes that

could be applied in the nanofabrication of unique metal nano-particle catalysis as will be described in Chapter III.

2.7 REFERENCES

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CHAPTER III

IRON NANOPARTICLE CATALYZED HYDROSILYLATION

3.1 INTRODUCTION

The need to generate low cost hydrosilylation catalysts, which can be reused or reclaimed, with retention of catalytic activity, and with the capacity to hydrosilylate under unconventional solvent systems is a current challenge in industrial reagent and method development. The hydrosilylation transformation reaction, as described in Chapter II, has broad industrial applications in the manufacture of silicone-based molding products, adhesives surfactants, fluids, and release coatings just to mention a few material impacts.[119] Furthermore, hydrosilylation has evolved to become one of the largest-high scale applications of industrial catalysis[120] with the predominant use of precious metals such as Pt, Rh, Pd, Ru, and/or Ir. Previously, Ashby's, Karstedt's and Speier's catalysts in particular are the most widely used platinum based compounds in industrial hydrosilylation.[121]

Holwell estimated that in 2007, the silicone industry consumed 5.6 metric tons of platinum with most of it unrecovered post catalytic processes.[122] Furthermore, the platinum market has become more volatile due to the increasing demand of the precious metal for applications in fuel cells and other competing technologies.[123] As outlined in Chapter II, most of

these traditional hydrosilylation catalysts also suffer from limitations of having multiple mechanistic pathways that promote undesired deleterious side reactions. This often necessitates excessive monitoring and multiple purification strategies coupled with the lack of catalyst recycling facility. [124] In employing some of these catalysts, high energy, low turnover frequencies, low reactivity, single runs, long reaction times, and modest selectivity characterize their catalytic profiles.[125]

High cost in concert with the aforementioned chemical, economic, and political challenges inspired this low cost catalysis replacement project. By no means does this project attempt to diminish the considerable success of precious metal hydrosilylation catalysts that are industrially used hitherto. This dissertation boasts of developing and deepening the utility of iridium based hydrosilylation catalytic technology. However, an alternative to precious metals, using low cost earth ubiquitous metals for alkyne, olefin and ketone hydrosilylations, has gained our research attention. Therefore, this endeavor sought to develop iron nanoparticle catalysts for the hydrosilylation of alkynes, alkene and carbonyl functionalities. Iron is an inexpensive and earth-abundant metal, which has recently been used in homogenous hydrosilylations.[126] Furthermore, the prospect of alternate mechanistic distinctions from iron nanoparticle heterogeneous catalysis to address the problem of deleterious side reactions coupled with all the benefits that come with metal nanoparticles described *vide infra,* was attractive.[127]

3.2 REVIEW OF LITERATURE

3.2.1 Metal Nanoparticles and Nanotechnology

Metal nanoparticles (M-NPs) have gained significant attention in science and technology finding application in several areas of science and industry.[128] Of particular importance is their application in catalysis, for they demonstrate high activity. Over the years, ease in controlled and reproducible synthesis of defined and stable metal nanoparticles has provided a wide distribution of

M-NPs, with a wide scope of applications.[128] It is important to appreciate that over the years metal nanoparticles can also be referred to as metal nanocrystals, nanopowders, nanophase metal clusters, and metal colloids. For the sake of simplicity this dissertation will use metal nanoparticles.

However, a critical question becomes, *'what does "nano" mean?'* This prefix is defined in the metric system as 10^{-9} meters. Therefore, any material that is in the size range of 1-100 nanometers, when size alone is considered, is a nanoparticle.[129] However, it must be understood that size is not the only aspect of metal nanoparticles. They also have novel properties that include optical, catalytic, electronic, and magnetic, among others.[130] Even though there has been recent increased interest in nanotechnology, it has been in existence for over two centuries. Nanomaterials were used in medieval times for coloring stained glass.[131] The physical or chemical properties of materials with nanoscale sizes can be exploited for use in various applications.[128] In fact, a signature characteristic of nanomaterial formation is that, when a material enters the nano size regime, many times its physical and chemical properties change. These include but are not limited to, particle size, color, surface area, surface texture, percentage of surface atoms, reactivity, and morphology, just to mention a few. [120-131]

3.2.2 Metal Nanoparticles *inter alia* Green Chemistry

Historically, the chemical industry neglected ecological and environmental consciousness by prioritizing profits and high production levels. However, since the 1990s, due to various scientific advocacy, a heavy emphasis on ecological and sustainable chemistry has gained significant attention. This is commonly known as green chemistry.[132] Trost, was the first champion for the concept of atom economy.[133] However, the sensationalization of the green chemistry was due to the advocacy by Warner, Anastas,[134] and Clarke.[135] Green chemistry can now be defined as the efficient use of (preferably renewable) raw materials in a manner that eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.[133-136] In pursuit of advancing the green chemistry agenda, catalysis is an area that can contribute to

achieving this goal; preferably, catalysis in unconventional solvent media, such as water or aqueous media, which is a challenge in itself.[136] The twelve principles of green chemistry are listed in Table 3.1 below.[133-136] Inspired by the green chemistry initiative, this project sought to develop metal nanoparticles from iron metal, with a vision to generate reusable catalysts, which are non-toxic and/or could be used in unconventional solvent systems, thereby meeting some of the principles in green chemistry listed in Table 3.1 below.[133-136]

Table 3.1 The 12 principles of green chemistry

1. **Synthetic methods should be designed to maximize the incorporation of all materials used in the process to create the final product.**
2. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
3. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.
4. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
5. The use of auxiliary substances (e.g., solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.
6. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
7. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
8. Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
10. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
11. Chemical products should be designed to affect their desired function while minimizing their toxicity
12. It is better to prevent waste than to treat or clean up waste after it has been created.

3.2.3 Metal Nanoparticles as **Heterogeneous Catalysts**

In the last few decades metal nanoparticles have attracted attention in catalysis applications.[137] The exploration of iron metal nanoparticles as hydrosilylation catalysts constitutes the final part of the research interests in this dissertation. The construction model for this endeavor focused on realizing one particular class of metal nanoparticles called core-shell nanoparticles. Core-shell metal nanoparticles are composed of a central core, which in this project's case is iron metal, and an outside shell of a different substance which surrounds the core (See Figure 3.1).[138]

Figure 3.1 Schematic illustration of core-shell nanoparticles with a metallic core encapsulated in a stabilizing shell surface.

A core shell metal nanoparticle is typically formed from the reduction of a transition metal salt in the presence of a stabilizing agent. The stabilizing agent's role is to cap the surface of the metallic core, thus preventing the metal from agglomeration or aggregation. The stabilizing agent achieves this by providing electrostatic and/or steric protection from agglomeration.[139] In the core shell model, stabilizing agents may be strongly coordinating ligand layers, polymers or surfactants. In some cases they can be a different metal. Another variety may be a bi-metallic core and a coordinated ligand layer. In all such cases the shell protects from agglomeration but also may give unique surface properties useful for catalysis. Therefore, this field provides avenues to control the composition of the core and shell, thus allowing for the manipulation of the metal nanoparticle properties.[140]

For many years, we have relied on using platinum or palladium heterogeneous reaction catalysts in chemical transformations. These catalysts have been used either as thin films, or as particles with a wide size distribution. However, advancement of nanotechnology has now enabled scientists and engineers to control nanoscale size, monodispersity for these metals and many other elements that become highly cost-effective and active in catalysis.[141]

When metal nanoparticles are employed in catalysis they possess a high surface area to volume ratio, providing more sites for a reaction to take place in comparison to their bulk heterogeneous counterparts. Furthermore, metal nanoparticle catalysts allow for the use of low amounts of catalytic loading in comparison to bulk (i.e. thin films or larger particle) heterogeneous catalysts in reactions, thereby saving both materials and economic cost. [142] Furthermore, the core and

shell metal nanoparticle fabrication endeavor allows for chemists to control the composition of both the core and the shell, thereby enabling the ability to manipulate the reagent materials' properties.[143]

It has been observed that catalytic reactivity is enhanced for metal nanoparticle catalysts. This is primarily because metal nanoparticles possess contracted lattice parameters because of surface unsaturation of the metal atoms that form them. This reduced interatomic distance contributes to their enhanced catalytic properties.[144]

Against this backdrop, the exploration of metal nanoparticles as potentially lucrative catalysts has grown rapidly.[145] A case in particular is that of the gold metal nanoparticles which are powerful catalysts for fuel cell reactions,[146] CO oxidation,[147] oxygen reduction reaction,[148] and methanol oxidation.[149]

3.2.4 Synthesis of Metal Nanoparticles

There are now many different techniques to produce metal nanoparticles for catalysis.[150] They can be synthesized in aqueous phase, [150,151] organic phase, [150, 152] and/or by chemical reduction of transition metal salts. [150,153] Other techniques also include the use of thermal treatment,[154] seeded growth of particles,[155] or electrochemical reduction.[156] However, this latter subset was not included in the former because the research operational framework that guided this project did not include these techniques. Furthermore, core shell nanoparticle metallic cores can be made up of a variety of compositions, such as pure metals,[157] alloyed metals,[158] metal oxides,[159] and metal sulfides.[160] This project focused on synthesizing metal nanoparticles via solution phase media because of the inherent benefits solution phase synthesis has over precipitation or deposition methods.[150,161] When metal nanoparticles are synthesized in solution phase, a wider variation of capping agents is permissible. This results in the generation of protected metal nanoparticles of uniform size due to the capping agents' regulation of the growth of the nanoparticles.[150] Furthermore, stabilizing/capping agents have the capacity to influence different rates of growth and metal nanoparticle shapes, which has an influence on whether one generates a monodisperse reaction system or not.[150,162] It also allows access

to a variety of other synthesis parameters which include different feed metal precursors, reducing agents, temperatures of reactions, and solvent systems, among other things. Solution phase methodology allows for controlled metal nanoparticle growth through parameter manipulation.[150,163]

In this synthetic framework, one of the most well developed solvent based methods for the synthesis of monodispersed metal nanoparticles is the polyol process.[164] It involves the use of a diol or polyalcohol to reduce a metal salt, resulting in a metal nanoparticle. This reaction can be much more strictly controlled by employing a selective solvent and more importantly one or more stabilizing agents may bind to the metal particle surface.[165] The twin effect of reduction and stabilization protects the metal core from undesired catalytic compromise.

The choice of stabilizing or capping agent is of great importance. Ideally the stabilizing agent must have a strong interaction with the metallic core. Therefore the goal is to generate strong bonds between metal and the capping agent, coupled with achieving these results in very fine and well dispersed metal nanoparticles.[150,166] In general, metal nanoparticles are formed by way of reacting metal ions from their salt precursor in the presence of a reducing and capping or stabilizing agent, to form a metal core that is encapsulated in a stabilizing surface matrix (See Figure 3.2). [150]

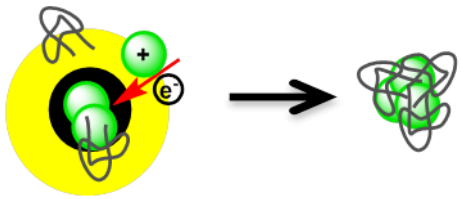


Figure 3.2 The general process for metal nanoparticle particle growth, and surface matrix formation during the synthesis of the metal nanoparticles.

3.2.5 Surface Reactivities of Metal Nanoparticles

The catalytic phenomena of metal nanoparticles depend on factors such as size, shape, morphology, and surface properties, which are derived from the stabilizing agent employed. These have impact on the regio-, chemo- or stereoselectivities of the reaction being catalyzed. Generating approaches that can control particle sizes, surface textures and morphology or the adjustment thereof is an ongoing challenge in the research and development of nanoscale catalysts.[150]

Silicon hydrides can undergo oxidative addition with every transition metal on the periodic table, thus generating metal-silyl complexes.[167] In relation to this, the active catalyst in platinum catalyzed hydrosilylations is a platinum nanoparticle capped by a silicon matrix. This is a result of platinum salt reduction by a silicon hydride.[168] Maleckza and Rahaim developed palladium nanoparticle catalysts capped by a silicon matrix from palladium salts being reduced by PMHS (polymethylhydrosiloxane). These palladium nanoparticles demonstrated functional group transformations that are highly selective and show catalytic reactivity.[169] Prior to this discovery, Crabtree and Tour had shown that silicon hydrides form palladium nanoparticles by reduction of palladium salts.[170] Against this backdrop, this project postulated that reactive low oxidation state iron catalysts can be formed via iron salt reduction with reducing agents in the presence of a stabilizer. It must be emphasized that in some cases the twin effect was anticipated for the silicon hydride being a reducing agent and also provider of the silicon based capping matrix. The envisaged impact of this approach was that, unlike existing protocols for metal nanoparticle synthesis, this route provided another avenue to adjust the nanoparticle size, surface texture, morphology and electronic properties through the variation of substituents around the silicon. In addition to the silicon matrix provision, the nature of the silicon-metal bond is such that two bonding interactions are at play, the strong σ and π bonding. This would meet the strong metal core to capping shell bonding requirement for metal nanoparticle fabrication mentioned above. Furthermore, this type of metal-silyl bonding introduces new electronic and steric surface properties that are not attainable with current ligand classes.

3.2.6 Iron Metal in Hydrosilylation Catalysis

Since the late 1960s, it has been known that iron pentacarbonyl $Fe(CO)_5$ can be used for hydrosilylation reactions.[171] However, employing this catalyst is accompanied by a dehydrogenative silylation process that produces undesired by-products, rendering it useless for industrial purposes.[172] This triggered interest in developing iron based catalysts for olefin and ketone hydrosilylation. Chirik and co-workers has reported studies of catalytic activity of an iron(0) bis(dinitrogen) complex $[(pdi)Fe(N_2)_2]$ (PDI = 2,6-$(RN = CMe)_2C_5H_3N$),which loses one equivalent of N_2 to generate the active mononitrogen four coordinate complex. This catalyst facilitates the hydrosilylation of hexene with secondary and primary silane but not the industrially relevant tertiary silane. However, it demonstrates exclusive anti-Makovnikov regioselectivity.[173] Furthermore, this system could not hydrosilylate olefins containing allyl ethers or esters.[174] In addition to the aforementioned data, other PDI/pybox iron complexes have been reported that hydrosilylate ketones with primary and secondary silane but not tertiary.[175] Later, Chirik developed PDI and terpyridine based iron complexes that facilitate tertiary silane hydrosilylation of terminal olefins with the lack of competing olefin isomerization or deleterious side reactions. They also showed compatibility with functionalized alkenes containing amines and polymeric allyl polyethers.[176] These iron based catalysts, therefore, demonstrated a large advantage over current platinum based systems. Reports of $Fe(OAc)_2$ facilitated hydrosilylation of aldehydes and ketones, using tertiary silanes as stoichiometric reductants are also known. The tertiary silanes employed were PMHS (polymethylhydrosiloxane), $(EtO)_3SiH$ or $(EtO)_2MeSiH$.[177] Interest in iron catalyzed hydrosilylation has gained significant industrial attention, resulting in numerous homogenous catalytic developments therein.[178] The iron based hydrosilylation catalysis examples aforementioned demonstrate how base-metal (iron in particular) catalyzed hydrosilylation reactions offer significant advantages such as functional-group tolerance, exclusive regioselectivity and competing activities, over traditional precious metal catalysts. Hence, to augment the progress made so far, and align the green agenda with the iron based hydrosilylation catalysis paradigm, this project postulated the use of iron(0) metal nanoparticles as contributory catalytic

reagents for hydrosilylation. At the time of this project's inception, there were no known applicable iron nanoparticle catalysts for hydrosilylation of carbon-carbon or carbon-heteroatom bonds. To close this gap, would require answering the challenge question, "How does one generate catalytically reactive low cost iron nanoparticles possessing requisite resistance to poisoning?"[179,180]

3.3 METHODOLOGY AND SPECIFIC AIMS OF STUDY:

3.3.1 Envisaged Iron Nanoparticle Hydrosilylation System Operation

The working hypothesis to answer this question through this project was by reducing iron salts with a select reducing agent in the presence of a stabilizing silicon or polymeric matrix. Iron nanoparticles of low oxidation states would form via this simple procedure, possessing highly reactive catalytic capacity for selective hydrosilylation transformations across unsaturated carbon-carbon and carbon-heteroatom linkages. The matrix environment would provide directing character to impose regioselectivity and stabilizing capacity to allow/promote reversible catalytic redox processes. The theory guiding this endeavor was that a select stabilizing/capping matrix would intertwine itself around a reduced nanoscale iron core to form small and uniform iron nanoparticles, possessing exposed active iron surfaces.[150] Uniformity on these surfaces was expected to be a function of the capping agent by way of balancing steric and electrostatic repulsions within the outer shell domain of the nanoparticles. Ideally the application of iron nanoparticle catalytic reagents would have the substrate coordinate to the catalytically active metal nanoparticle surface, allowing for the heterogeneous organometallic transformations leading to hydrosilylated product species which would subsequently dissociate from the surface and thus be released.[181] This would be accompanied by the broad metal nanoparticle catalysis benefits delineated *vide supra*.

3.3.2 Metal Nanoparticle Synthetic Approach

The first task in this project was to develop effective methods and strategies for the synthesis of an iron nanoparticle catalyzed hydrosilylation system. To meet this target, it was decided to explore the fabrication of core-shell iron nanoparticles with a variety of encapsulating matrices by systematically screening non-polymeric silicon hydride, followed by polymeric silicon hydride and finally non-silicon based polymers. Furthermore, reducing agent screening was also a variable that was explored among others. These issues will be further described in subsequent sections of this chapter.

3.4 RESULTS AND DISCUSSION

The starting point for this investigation was employing analogous reaction conditions in nanoparticle fabrication using the conditions for carbonyl hydrogenolysis facilitated by Pd nanoparticles on a silicon matrix.[182] The modifications to this series of investigations started with primarily replacing the metallic species with iron.

3.4.1 Investigations of Iron Nanoparticle Catalyzed Carbonyl Hydrosilylation

Investigation started with attempting the catalytic reduction of a carbonyl by way of hydrosylating benzophenone (**151**) with triethylsilane (**150**), using iron nanoparticles to generate (benzhydryloxy)triethylsilane (**152**). This, in itself, is an important transformation in the pharmaceutical and agrochemical industries.[183-185] The same transformation would also find use in synthesizing valuable synthetic intermediates and monomers for the production of organosilane polymers and materials.[184,185] Developing this reaction through this project's approach would offer operational simplicity coupled with meeting green chemistry principles.

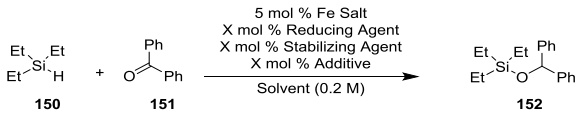
A decision was made to screen various reaction parameters, while monitoring reaction progress by gas chromatography. A calibration curve was formulated using the triethylsilane (**150**),

benzophenone (**151**) and (benzhydryloxy)triethylsilane (**152**) compounds, with mesitylene as the internal standard. Screening for a working system was initiated, using iron acetylacetonate [$Fe(acac)_3$], an air stable iron complex that dissolves in organic solvents with a track record in non-catalytic metal nanoparticle syntheses (Table 3.2).[186] Triethylsilane (**150**) was used as both the reducing agent and stabilizing agent in aqueous solvent without success (entry 1, Table 3.2). Adding a fluoride source to promote the silicon hydride reduction (entry 2, Table 3.2) resulted in the significant changes in physical properties of the systems in question, particularly visible suspension formation and the loss of the characteristic red color of iron acetylacetonate but no evidence of the intended catalytic cycle was detected. Adding excess triethylsilane (entry 3, Table 3.2) did not give a desired outcome. Employing sodium borohydride a more potent reducing agent, in entries 4 and 5, Table 3.2, did not produce the desired result. Biphasic aqueous and organic solvent regimes, of varied ratios (entries 6-10, Table 3.2) did not facilitate catalysis. A decision was made to employ toluene and subject it to all the other variations employed in the entries 1-5. Toluene, as a non-polar, high boiling and weakly coordinating solvent, was expected to assist in stabilizing the desired heterogeneous catalyst (entries 10-16, Table 3.2 and entries 17-19, Table 3.2). This gave insignificant results.

Employment of sodium borohydride produced radically different system physical properties (entries 17, 20, 21, Table 3.2) of a magnetic black suspension that was catalytically inactive. THF was employed as a solvent and subjected to the same screening process conducted for toluene (entries 22-27, Table 3.2). It was noted that $NaBH_4$ in THF systems produced an inactive brown suspension. However, agglomeration was observed in THF systems that employed CsF. Furthermore, extended reaction time coupled with reaction monitoring was tried (entry 27, Table 3.2) but did not yield the desired outcome. The dioxane solvent was screened next (entries 28-32, Table 3.2) under the same sequence of former solvents and showed no evidence of hydrosilylation. DMF based solvent systems (entries 33-37, Table 3.2) were subjected to similar screening sequences, without catalytic activity. However, the systems showed distinct physical properties, which amounted to insignificant catalysis.

This dissertation demonstrated earlier the beneficial use of 1,2-DCE as a hydrosilylation medium, however, employing it in this particular system (entries 37-43, Table 3.2) did not facilitate hydrosilylation, the same applies for dichloromethane (DCM) (entries 44-49, Table 3.2). Volatile, diethyl ether, was screened in the same sequence (entries 50-56, Table 3.2) but failed to yield the desired results. Amine and imine-containing solvents with potentially different coordinating capacities were also assessed (entries 57-67, Table 3.2) without success. DME and NMP solvents were also examined (entries 68-72, and entries 73-77, Table 3.2), and both sequences demonstrated catalytic failure. Miscellaneous follow up variations for this study, were conducted (entries 78-82, Table 3.2), but they too did not provide positive results.

Table 3.2 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **151**



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	additive (mol%)	solvent (0.2 M)	150[b] (%)	151[b] (%)	152[b] yield (%)	system's physical properties
1	TESi-H 50	-	-	H_2O	127	41	2	Red soln.
2	TESi-H 50	-	Cs F 5	H_2O	78	61	2	Brown susp.
3	TESi-H 200	-	Cs F 5	H_2O	250	63	0	Orange susp.
4	$NaBH_4$[c] 20	-	-	H_2O	135	95	0	Brown susp.
5	$NaBH_4$ 35	-	-	H_2O	72	99	0	Black susp. stuck on glass
6	TESi-H 50	-	Cs F 5	H_2O:DCE 1:4	78	61	2	Khaki susp.- stuck on glass
7	TESi-H 50	-	Cs F 5	H_2O:DCE 1:1	135	96	0	Khaki susp. .stuck on glass
8	TESi-H 50	-	Cs F 5	H_2O	31	98	0	Brown susp.
9	$NaBH_4$[c] 20	TESi-H 50	-	H_2O:THF 1:10	135	95	0	Brown susp.
10	TESi-H 50	-	Cs F 5	H_2O:Tol 1:1	139	95	0	Khaki susp.
11	TESi-H 50	-		Tol	146	96	0	Red soln.
12	TESi-H 50	-	Cs F 5	H_2O	150	99	0	Red susp.
13	TESi-H 50	-		Tol	127	41	2	Red soln.
14	TESi-H 50	-	Cs F 5	Tol	148	94	0	Khaki susp.
15	TESi-H 200	-	Cs F 15	Tol	250	63	0	Orange susp.
16	$NaBH_4$[c] 20	TESi-H 50		H_2O:Tol 1:10	136	78	0	Brown susp.

[a] Conditions were: (5 mol %) $Fe(acac)_3$, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol ketone (152), rt, 24h; [b] monitored by G.C. [c] solution phase $NaBH_4$ was injected into the reaction system.

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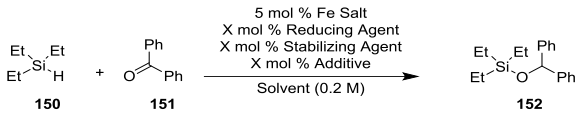
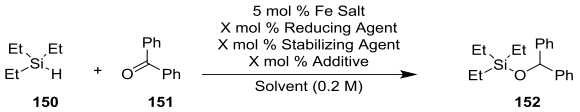
Table 3.2 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **151** (continued)



entry[a]	reducing agent (mol%)	stabilizing. agent (mol%)	additive. (mol%)	solvent (0.2 M)	time (h)	150[b] (%)	151[b] (%)	152[b] yield (%)	system's physical properties
17	$NaBH_4$ 35	TESi-H 50	-	Tol	24	148	97	0	Black susp. .stuck on glass.
18	TESi-H 50	-	Cs F 5	Tol	24	148	94	0	Khaki susp.
19	TESi-H 200	-	Cs F 15	Tol	24	250	63	0	Orange susp.
20	$NaBH_4$[c] 20	TESi-H 50	-	H_2O:Tol 1:10	24	136	78	0	Brown susp.
21	$NaBH_4$ 35	TESi-H 50	-	Tol	24	148	97	0	Black susp. stuck on magnet
22	TESi-H 50	-	-	THF	24	144	93	3	Red soln.
23	TESi-H 50	-	Cs F 5	THF	24	146	93	0	Khaki susp.
24	TESi-H 50	-	Cs F 5	THF	120	131	95	0	Black susp. stuck on glass
25	$NaBH_4$[c] 20	TESi-H 50	-	H_2O:THF 1:10	24	144	91	0	Brown susp.
26	$NaBH_4$ 35	TESi-H 50	-	THF	24	143	97	3	Brown susp.
27	TESi-H 50	-	Cs F 5	THF	120	131	95	0	Black susp. stuck on glass.
28	TESi-H 50	-	-	Dioxane	24	147	98	0	Red soln.
29	TESi-H 50	-	Cs F 15	Dioxane 0.2M	24	289	79	0	Orange soln.
30	$NaBH_4$[c] 20	TESi-H 50	-	Dioxane 1:10 0.2M	24	147	98	0	Brown susp.
31	$NaBH_4$ 35	TESi-H 50	-	Dioxane 0.2M	24	149	91	0	Brown susp.
32	TESi-H 50	TESi-H 50	Cs F 5	Dioxane 0.2M	120	127	98	0	Red soln.

[a] Conditions were: (5 mol %) $Fe(acac)_3$, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol ketone (152), rt, 24-120h; [b] monitored by G.C. [c] solution phase $NaBH_4$ was injected into the reaction system.

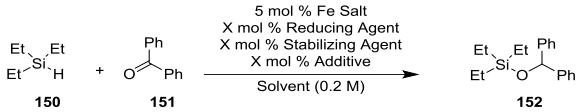
Table 3.2 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **151** (continued)



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	additve (mol%)	solvent (0.2 M)	time (h)	150[b] (%)	151[b] (%)	152[b] yield (%)	system's physical properties
33	TESi-H 50	-	-	DMF	24	134	94	0	Red soln.
34	TESi-H 50	-	Cs F 5	DMF	24	126	99	3	Orange soln.
35	TESi-H 50	-	Cs F 5	DMF	120	137	94	0	Orange soln.
36	TESi-H 200	-	Cs F 15	DMF	24	213	83	0	Black soln.
37	$NaBH_4$ 35	TESi-H 50	-	DMF 0.2M	24	31	91	0	Brown susp.
38	TESi-H 50	-	-	1,2-DCE	24	134	97	3	Red soln.
39	TESi-H 50	-	Cs F 5	1,2-DCE	24	141	99	0	Khaki susp.
40	TESi-H 50	-	Cs F 5	1,2-DCE	120	120	97	0	Khaki susp.
41	TESi-H 200	-	Cs F 15	1,2-DCE	24	223	91	0	Orange susp.
42	$NaBH_4$[c] 20	TESi-H 50	-	1,2-DCE 1:10	24	130	81	0	Brown susp.
43	$NaBH_4$ 35	TESi-H 50		1,2-DCE	24	147	96	0	Brown susp.
44	TESi-H 50	-	-	DCM	24	143	91	3	Red soln.-
45	TESi-H 50	-	Cs F 5	DCM	24	137	88	0	Khaki susp.
46	TESi-H 50	-	Cs F 5	DCM	120	128	91	0	Khaki susp.
47	TESi-H 200	-	Cs F 15	DCM	24	288	79	0	Orange susp.
48	$NaBH_4$[c] 20	TESi-H 50	-	DCM	24	127	73	0	Brown susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol ketone (152), rt, 24-120h; [b]monitored by G.C. [c]solution phase $NaBH_4$ was injected into the reaction system.

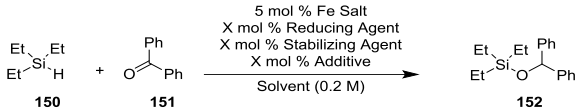
Table 3.2 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **151** (continued)



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	additive (mol%)	solvent (0.2 M)	time (h)	150[b] (%)	151[b] (%)	152[b] yield (%)	system's physical properties
49	$NaBH_4$ 35	TESi-H 50	-	DCM	24	147	96	0	Brown susp.
50	TESi-H 50	-	-	Et_2O	24	141	99	0	Red soln.
51	TESi-H 50	-	Cs F 5	Et_2O	24	149	97	0	Khaki susp.
52	TESi-H 50	-	Cs F 5	Et_2O	24	134	98	0	Khaki susp.
53	TESi-H 50	-	Cs F 5	Et_2O	120	122	95	0	Khaki susp. stuck on glass
54	TESi-H 200	-	Cs F 15	Et_2O	24	279	79	0	Khaki susp.
55	$NaBH_4$[c] 20	TESi-H 50		Et_2O	24	137	65	0	Brown susp.
56	$NaBH_4$ 35	TESi-H 50		Et_2O	24	149	91	0	Brown susp.
57	TESi-H 50	-	-	TEA	24	150	99	0	Red soln.
58	TESi-H 50	-	Cs F 5	TEA	24	145	96	4	Brown susp. stuck on glass
59	TESi-H 50	-	Cs F 5	TEA	120	143	99	0	Brown susp. stuck on glass
60	TESi-H 200	-	Cs F 15	TEA	24	291	82	0	Khaki susp.
61	$NaBH_4$[c] 20	TESi-H 50		TEA	24	134	95	0	Brown susp.
62	TESi-H 50	-	-	Py	24	150	99	0	Red soln.
63	TESi-H 50	-	Cs F 5	Py	24	145	97	0	Orange soln.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol ketone (152), rt, 24-120h; [b]monitored by G.C. [c]solution phase $NaBH_4$ was injected into the reaction system.

Table 3.2 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **151** (continued)



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	additive (mol%)	solvent (0.2 M)	time (h)	150[b] (%)	151[b] (%)	152[b] yield (%)	system's physical properties
64	-	-	Cs F 5	Py	120	141	99	0	Orange soln.
65	TESi-H 200		Cs F 15	Py	24	179	76	0	Orange soln.
66	$NaBH_4$[c] 20	TESi-H 50	-	Py	24	79	85	0	Brown susp.
67	$NaBH_4$ 35	TESi-H 50	-	Py	24	140	90	0	Brown susp.
68	TESi-H 50	-	-	DME	24	142	89	0	Red soln.
69	TESi-H 50	-	Cs F 5	DME	24	135	89	7	Brown susp.
70	TESi-H 50	-	Cs F 5	DME	120	122	92	0	Brown susp.
71	TESi-H 200	-	Cs F 15	DME	24	265	90	0	Khaki susp.
72	$NaBH_4$[c] 20-	TESi-H 50	-	DME	24	113	90	0	Brown susp.
73	TESi-H50	-	-	NMP	24	140	>99	0	Red soln. -
74	TESi-H 50	-	Cs F 5	NMP	24	128	96	3	Brown susp.
75	TESi-H 50	-	Cs F 5	NMP	120	117	92	3	Brown susp.
76	TESi-H 200	-	Cs F 15	NMP	24	221	87	7	Khaki susp.
77	$NaBH_4$[c] 20	TESi-H 50	-	NMP	24	50	96	0	Brown susp.
78	TESi-H 200	-	Cs F 15	THF	24	280	85	0	Orange susp.
79	TESi-H 50	-	Cs F 5	Dioxane	24	154	99	0	Red soln.
80	$NaBH_4$[c] 20	-	-	DMF 1:10	24	47	84	0	Brown susp.
81	TESi-H 200	-	Cs F 15	1,2-DCE	24	223	91	0	Orange susp.
82	-	-	Cs F 15	DCM	120	128	91	0	Khaki susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol ketone (152), rt, 24-120h; [b]monitored by G.C. [c]solution phase $NaBH_4$ was injected into the reaction system.

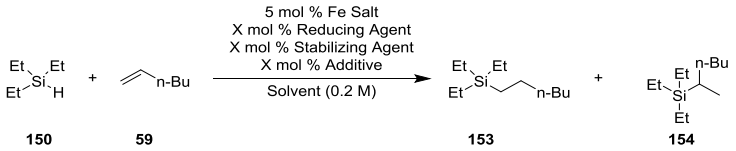
It was concluded, based on these results, that this approach was not amenable for hydrosilylation of ketones. A decision was made to examine the feasibility of this approach on carbon-carbon unsaturation substrates for they are electronically or chemically very different from carbonyls.

3.4.2 Investigation of Iron Nanoparticle Catalyzed Alkene Hydrosilylatio

To investigate the feasibility of our hypothesis, hexane (**59**) was the alkene substrate of choice for the systematic screening of iron nanoparticles as hydrosilylation catalysts. Triethylsilane (**150**) remained the silicon hydride source. Formation of silicon carbon bonds remains a lucrative process for the formation of useful organosilicons.[187] A screening exercise was initiated upon successful construction of calibration curves for triethylsilane (**150**) and triethyl(hexyl)silane (**153** and **154**) with mesitylene as the internal standard. The approach taken here was similar to that in the previous carbonyl hydrosilylation. Iron acetylacetonate and iron chloride tetrahydrate were the salts employed in this process. Triethylsilane (**150**) functioned as both the reducing agent and stabilizing/capping agent (entry 1, Table 3.3) with the reaction being conducted in aqueous media. This did not result in hydrosilylation. Extending reaction times to five days for the same system did not give the desired catalysis (entry 2, Table 3.3). However, a significant decrease in the triethylsilane was observed suggesting another reaction was taking place. Sustained effort to determine what had transpired did not provide a sound explanation to what happened. Employing CsF as a fluoride source to promote salt reduction resulted in significant change in physical properties of the system, showing a visible monodispersed suspension (entry 3, Table 3.3). However, the suspension was catalytically ineffective for hydrosilylation. $NaBH_4$ was then employed (entries 4 and 5, Table 3.3) and showed 18% yield of the desired product by GC. Repetition of this system to attain isolated yield gave a complex spectrum without the diagnostic peaks for the target compounds. The use of iron chloride tetrahydrate (entry 6, Table 3.3) did not promote a hydrosilylation process. Proceeding to employment of toluene, a non-polar solvent, following the same experimental

sequences gave encouraging results (entries 7-12, Table 3.3). It showed a distribution of yields from (2 to 10% yield). However, after redoing and attempting to isolate the compounds, it was discovered they were false positives. THF solvent systems were then subjected to sequential examinations (entries 13-17, Table 3.3) but only false positives were detected. Employment of dioxane was next on the agenda (entries 18-24, Table 3.3). This amounted to a set of unisolable positives, only detectable by GC. Aliquots of reaction systems via NMR did not show diagnostic peaks for the target compounds nor signs of product formation, but only starting materials. Hence the conclusion was a false positive accumulation. DMF was employed in subsequent screenings next (entries 25-30, Table 3.3), and very minuscule detection of product was obtained. NMR showed only starting material. For the same reason mentioned earlier in the carbonyl hydrosilylation attempts, dichloroethane was screened for alkene hydrosilylation (entries 31-37, Table 3.3). Only the $NaBH_4$ system showed signs of product formation, however, it turned out to be a false positive. DCM was screened next under the same experimental sequences (entries 38-41, Table 3.3) with no desired result. Low boiling point diethyl ether was then employed (entries 42-48, Table 3.3) without success. Amine and imine carrying solvents were tried (entries 49-50, Table 3.3 and entries 54-65, Table 3.3). They showed miniscule to no desired result. Attempts to examine entry 65, by redoing it, followed by isolation and taking NMR analyses of aliquots of the reaction system did not show product formation. DME solvent systems (entries 67-72, Table 3.3) showed insignificant product formation. Employing NMP under the same experimental protocols gave insignificant catalytic evidence (entries 73-79, Table 3.3). Acetonitrile's potential to be a stabilizing solvent was examined (entry 80-85, Table 3.3) delivered insignificant catalytic outcomes. Cyclohexane was then employed (entries 86-90, Table 3.3) without success.

Table 3.3 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **59**[a]

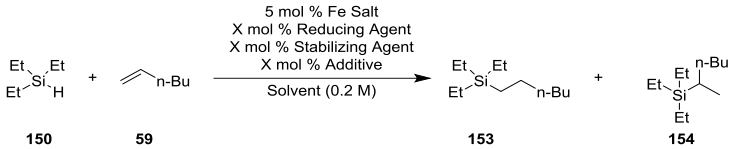


150 59 153 154

entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	time (h)	150[b] (%)	153/154[b] yield (%)	system's physical properties
1	$Fe(acac)_3$	TESi-H 50	-	-	H_2O	24	115	0	Dark red soln.
2	$Fe(acac)_3$	TESi-H50	-	-	H_2O	120	58	0	Red soln.
3	$Fe(acac)_3$	TESi-H 50		Cs F 15	H_2O	24	146	0	Khaki susp.
4	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	H_2O	24	94	18	Brown susp.
5	$Fe(acac)_3$	$NaBH_4$[c] 20	TESi-H 50	-	H_2O	24	95	0	Brown susp.
6	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	H_2O	24	126	0	Yellow soln.
7	$Fe(acac)_3$	TESi-H 50	-	-	Tol	24	135	9	Dark red soln.
8	$Fe(acac)_3$	TESi-H 50	-	-	Tol	120	129	5	Dark red soln.
9	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	Tol	24	136	2	Khaki susp.
10	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Tol	24	142	2	Brown susp.
11	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Tol	120	132	10	Brown susp.
12	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	Tol	24	136	0	White susp.
13	$Fe(acac)_3$	TESi-H 50	-	-	THF	24	135	8	Dark red soln.
14	$Fe(acac)_3$	TESi-H 50	-	-	THF	120	120	0	Dark red soln.
15	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	THF	24	117	3	Brown susp.
16	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	THF	120	111	1	Brown susp. stuck on glass
17	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	THF	24	149	0	Dark yellow soln.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkene (59), rt, 24-120h; [b]monitored by G.C. [c]solution phase $NaBH_4$ was injected into the reaction system.

Table 3.3 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **59**[a] (continued)

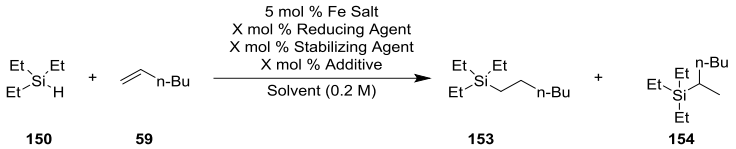


150 59 153 154

entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	time (h)	150[b] (%)	153/154[b] yield (%)	system's physical properties
18	$Fe(acac)_3$	TESi-H 50	-	-	Dioxane	24	140	12	Red soln.
19	$Fe(acac)_3$	TESi-H 50	-	-	Dioxane	120	130	2	Dark red soln.
20	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	Dioxane	24	136	2	Khaki susp.
21	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Dioxane	24	145	0.2	Brown susp.
22	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	Dioxane	24	43	3	Brown susp.
23	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Dioxane	120	135	0.4	Brown susp.
24	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	Dioxane	24	140	0	White susp.
25	$Fe(acac)_3$	TESi-H 50	-	-	DMF	24	139	1	Brown susp.
26	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	DMF	24	145	2	Brown susp.
27	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	DMF	24	18	2	Brown susp.
28	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	DMF	120	147	1	Brown susp.
29	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	DMF	24	110	0	Champaign soln.
30	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	DMF	24	130	0	Yellow/white susp.
31	$Fe(acac)_3$	TESi-H 50	-	-	1,2-DCE	24	147	0	Red soln.
32	$Fe(acac)_3$	TESi-H 50	-	-	1,2-DCE	120	132	1	Dark red soln.
33	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	1,2-DCE	24	136	2	Khaki susp.
34	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	1,2-DCE	24	127	15	Brown susp.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkene (59), rt, 24-120h;
[b]monitored by G.C.

Table 3.3 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **59**[a] (continued)

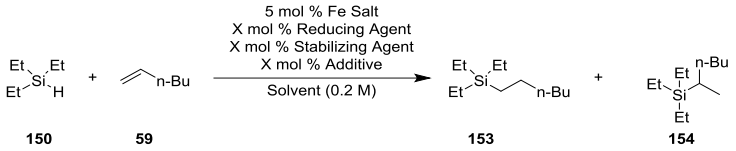


150 59 153 154

entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	time (h)	150[b] (%)	153/154[b] yield (%)	system's physical properties
35	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	1,2-DCE	24	132	2	Brown susp.
36	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	1,2-DCE	120	147	1	Brown susp.
37	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	1,2-DCE	24	132	0	White susp.
38	$Fe(acac)_3$	TESi-H 50	-	-	DCM	24	142	0	Brown susp.
39	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	DCM	24	141	2	Brown susp.
40	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	DCM	24	139	3	Brown susp.
41	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	DCM	24	139	0	White susp.
42	$Fe(acac)_3$	TESi-H 50	-	-	Et_2O	24	127	0	Red soln.
43	$Fe(acac)_3$	TESi-H 50	-	-	Et_2O	120	119	0	Red susp.
44	$Fe(acac)_3$	TESi-H 50	TESi-H 50	Cs F 15	Et_2O	24	138	1	Khaki susp.
45	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Et_2O	24	142	2	Brown susp.
46	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	Et_2O	24	136	1	Brown susp.
47	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Et_2O	120	143	1	Brown susp.
48	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	Et_2O	24	141	1	Yellow soln.
49	$Fe(acac)_3$ 5	TESi-H 50	-	-	TEA	24	144	1	Red soln.
50	$Fe(acac)_3$	TESi-H 50	-	-	TEA	120	119	0	Dark red soln.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkene (59), rt, 24-120h; [b]monitored by G.C.

Table 3.3 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **59**[a] (continued)

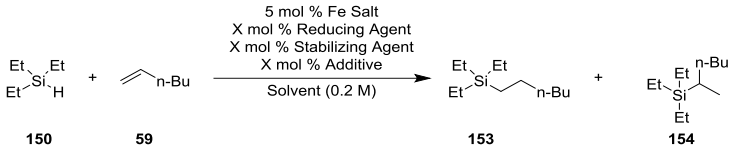


150 59 153 154

entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	time (h)	150[b] (%)	153/154[b] yield (%)	system's physical properties
51	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	Et_2O	24	136	1	Brown susp.
52	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Et_2O	120	143	1	Brown susp.
53	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	Et_2O	24	141	1	Yellow soln.
54	$Fe(acac)_3$	TESi-H 50	-	-	TEA	24	144	1	Red soln.
55	$Fe(acac)_3$	TESi-H 50	-	-	TEA	120	119	0	Dark red soln.
56	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	TEA	24	138	1	Khaki susp.
57	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	TEA	24	137	2	Brown susp.
58	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	TEA	24	135	4	Brown susp.
59	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	TEA	120	130	1	Brown susp.
60	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	TEA	24	142	2	Brown susp.
61	$Fe(acac)_3$	TESi-H 50	-	-	Py	24	147	0	Brown soln.
62	$Fe(acac)_3$	TESi-H 50	-	-	Py	120	144	0	Brown soln.
63	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	Py	24	120	0	Yellow susp.
64	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	Py 0.2M	24	142	5	Brown susp.
65	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	Py 0.2M	24	140	10	Brown susp.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkene (59), rt, 24-120h; [b]monitored by G.C.

Table 3.3 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **59**[a] (continued)

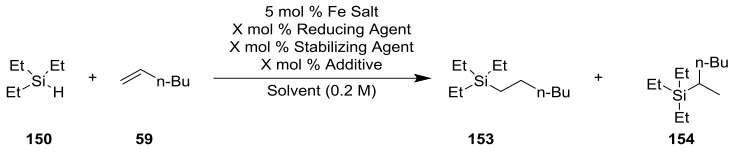


150 59 153 154

entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	time (h)	150[b] (%)	153/154[b] yield (%)	system's physical properties
66	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	Py	24	147	-	Dark yellow soln.
67	$Fe(acac)_3$	TESi-H 50	-	-	DME	24	134	1	Brown soln
68	$Fe(acac)_3$	TESi-H 50	-	-	DME	120	125	0	Dark red soln.
69	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	DME	24	130	0	Khaki susp.
70	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	DME	24	130	1	Brown susp.
71	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	DME	120	147	1	Brown susp.
72	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	DME	24	135	0	Yellow susp.
73	$Fe(acac)_3$	TESi-H 50	-	-	NMP	24	133	2	Brown soln.
74	$Fe(acac)_3$	TESi-H 50	-	-	NMP	5d	114	1	Brown solution
75	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	NMP	24	120	0	Yellow susp.
76	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	NMP	24	142	5	Brown susp.
77	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	NMP	24	10	7	Brown susp.
78	$Fe(acac)_3$	$NaBH_4$ 35	TESi-H 50	-	NMP	120	139	3	Brown susp.
79	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	NMP	24	132	3	Deep yellow soln.
80	$Fe(acac)_3$	TESi-H 50	-	-	CH_3CN	24	135	0	Red soln.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkene (59), rt, 24-120h; [b]monitored by G.C.

Table 3.3 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **59**[a] (continued)



150 59 153 154

entry[a]	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	time (h)	150[b] (%)	153/154[b] yield (%)	system's physical properties
81	TESi-H 50	-	-	CH_3CN	120	141	0	Red soln.
82	TESi-H 50	-	Cs F 15	CH_3CN	24	113	0	Champaign soln.
83	$NaBH_4$ 35	TESi-H 50	-	CH_3CN	24	97	2	Brown susp.
84	$NaBH_4$ 20	TESi-H 50	-	CH_3CN	24	78	0	Brown susp.
85	$NaBH_4$ 35	TESi-H 50	-	CH_3CN	24	95	1	Brown susp.
86	TESi-H 50	-	-	Cyclohex.	24	147	0	Red soln.
87	TESi-H 50	-	Cs F 15	Cyclohex.	24	109	6	Opaque susp.
88	$NaBH_4$ 35	TESi-H 50	-	Cyclohex.	24	134	0	Khaki susp.
89	$NaBH_4$ 20	TESi-H 50	-	Cyclohex.	24	140	1	Brown susp.
90	$NaBH_4$ 35	TESi-H 50	-	Cyclohex.	24	95	1	Brown susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkene (59), rt, 24-120h; [b]monitored by G.C.

The demonstration of what was perceived as positive results from the alkene hydrosilylation influenced the decision to try the alkyne hydrosilylation instead. Higher reactivity was expected on the alkyne substrate because of its higher π basicity.

3.4.3 Investigation of Iron Nanoparticle Catalyzed Alkyne Hydrosilylation

Investigations around this paradigm were commenced with hexyne (**74**) as the substrate. The expected product of successful hydrosilylation would be from a set of, *E*, *Z* or Int vinylsilane isomers. Vinylorganosilanes are a coveted compound class in organic synthetic chemistry.[188] The prospect of

generating an iron nanoparticle-catalyzed hydrosilation system that produces this functionality began after a calibration curve for triethylsilane (**150**) and triethyl(hex-1-en-1-yl)silane (**155, 156** and **157**) with mesitylene as internal standard was constructed. Screening experiments started with employing iron acetylacetonate [$Fe(acac)_3$] in THF with triethylsilane (**150**) being both the reductant and stabilizing/capping agent (entry 1, Table 3.4). This system did not show hydrosilylation catalytic activity. Thermally modifying the same system by heating it for 1 h (entry 2, Table 3.4) gave detection of product. Upon repeating the same conditions for isolation and NMR analysis showed only starting material. Sustained heating for 24 h, (entry 3, Table 3.4) did not give the desired product. Employing a fluoride source to promote reduction gave significant changes in the physical properties of the system by forming a suspension (entry 4, Table 3.4). However, the suspension was catalytically inactive. Sustained heating of the fluoride containing system gave the same outcome (entry 5, Table 3.4). Employing $NaBH_4$ as the reducing agent at room temperature (entry 6, Table 3.4) gave a monodisperse suspension but did not hydrosilylate. Suspecting complex formation between boron and iron, thermally driven dissociation was initiated for 1 h (entry 7, Table 3.13) but did not give the desired product. Sustained heating of the same system (entry 8, Table 3.4) did not produce hydrosilylated products. Conducting the same reaction in a mixture of THF and water (entry 9, Table 3.4) did not catalyze hydrosilylation. Changing the iron salt from an iron +3 oxidation state to a +2 oxidation state was the next strategy attempted. Iron dichloride tetrahydrate $FeCl_2{\cdot}4H_2O$, was employed and subjected to the same experimental sequences that iron acetylacetonate underwent for this hexyne substrate (entries 10-18, Table 3.4). Only entry 14 under thermal influence, showed product formation by GC. A repeat of the same conditions for NMR analysis and isolation did not show product formation. However, a side reaction occurred which gave a complex spectrum but this was not of any use for our agenda. The next iron(II) salt employed was iron dichloride hexahydrate $FeCl_2{\cdot}6H_2O$ (entries 19-27, Table 3.4). Of this series, entries 19 and 20 gave false positives; the rest did not give the desired outcomes. Iron trichloride $FeCl_3$, an alternate iron(II)) salt, was screened next, (entries 28-36, Table 3.4). This series showed miniscule to slight detection of product formation

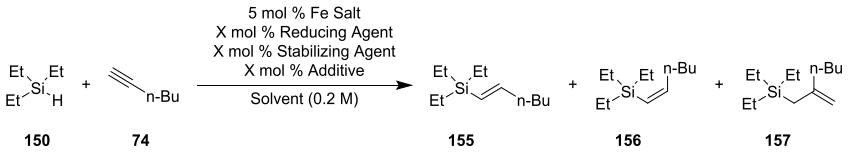
from entries 28 to 31. A repeat of these reaction conditions did not show product peaks by NMR; only starting material was present. For the rest of the following experiments, agglomeration was evident as metallic species came together and stuck on the walls of the reaction vessels (entry 35, Table 3.4). However, for the most part in this series, inactive heterogeneous suspensions were formed (entries 32-34 and 36, Table 3.4).

The glimmers of product detection in systems that had fluoride sources and/or variation of metal salts inspired a new strategy. It was decided to use stoichiometric amounts of additives. Furthermore an alternate reducing agent in EtMgBr, was also included in the screening process. Iron acetylacetonate was reacted with EtMgBr in the presence of triethylsilane, (entry 37, Table 3.4). Even though desired product formation was not evident, an interesting detection occurred. Polymerization accompanied significant consumption of triethylsilane. Attempting the same reaction in toluene (entry 38, Table 3.4) showed miniscule product formation and a decrease in triethylsilane starting material. NMR probing of this system did not show the desired product. Employing stoichiometric amounts of triethylsilane and CsF in aqueous THF solvent under sustained heating generated a significant heterogeneous system that did not show catalytic activity (entry 39, Table 3.4). Employing the same reaction conditions, except for having dry THF, did not produce a desired result (entry 40, Table 3.4). Changing the fluoride source to KF and repeating the former was also unsuccessful (entries 41 and 42, Table 3.4), but the physical properties these systems showed were consistent with the CsF systems. Iron dichloride tetrafluoride ($FeCl_2{\cdot}4H_2O$) was screened in the same way as iron acetylacetonate [$Fe(acac)_3$] in the strategic series described above (entries 43-49, Table 3.4), but that did not give the desired outcome. The next iron salt screened was iron trichloride ($FeCl_3$) under the same experimental sequences (entries 50-53, Table 3.4). Under these conditions, no product formation was detected. Given the slight indication of interesting results from employing EtMgBr as a reducing agent, stoichiometric amounts of reductant and triethylsilane as the stabilizing agent were employed (entry 54, Table 3.4) in THF. Product formation was not detected, but, interestingly, polymerization occurred with consumption of triethylsilane. Attempting the same

reaction in toluene (entry 55, Table 3.4) did not show polymerization but no product was detected. However, loss of triethylsilane was evident. Iron dichloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) with stoichiometric amounts of fluoride and triethylsilane stabilizer in aqueous THF under thermal conditions was attempted (entry 56, Table 3.4) without success. It was then decided that we should attempt to use PMHS as a reductant but also a polymeric stabilizer at 60 ^oC temperatures. This was conducted for iron acetylacetonate [$Fe(acac)_3$] in excess triethylsilane (entry 57, Table 3.4). The physical properties showed a heterogeneous suspension, however, it was catalytically inactive. Iron dichloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), iron dichloride hexahydrate ($FeCl_2 \cdot 6H_2O$), and iron trichloride ($FeCl_3$) were examined under the same conditions (entries 58-60, Table Table 3.4). They did not show desired outcome. Changing the solvent system to aqueous THF and rescreening these iron salts under the same conditions was not successful (entries 61-65, Table 3.4). Employing $NaBH_4$ as the reducing agent and using catalytic amount of PMHS (entries 66 and 67, Table 3.4), did not produce the desired result. Utilizing catalytic amounts of PMHS in the presence of catalytic amounts of fluoride source (entries 68-71, Table 3.4) showed product formation by GC, but repeating the experiments for isolation and NMR analysis did not show evidence of product formation.

Encouraged by the GC results from utilizing catalytic amounts of the reagents, we changed the solvent systems to aqueous THF and reconducted the experiments (entries 72-76, Table 3.4). Product formation was detected by GC in low amounts but isolation and NMR analysis showed starting material without product diagnostics. Thermally driving these reaction systems produced the same result (entries 77-81, Table 3.4). Employing alcoholic solvents in these systems was attempted (entries 82-87, Table 3.4) but no product was detected at all. A decision to use dichloroethane solvent for the same system was made, (entries 88 and 89, Table 3.4) and did not work.

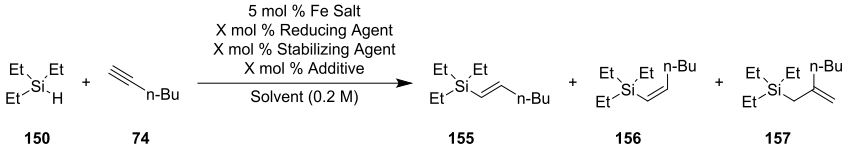
Table 3.4 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **74**[a]



entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	t (°C)	150[b] (%)	155-7[b] yield (%)	system's physical properties
1	$Fe(acac)_3$	TESi-H 50	-	-	THF	r.t.	117	0	Red soln
2[c]	$Fe(acac)_3$	TESi-H 50	-	-	THF	r.t.	131	9	Red soln.
3	$Fe(acac)_3$	TESi-H 50	-	-	THF	60	149	0	Red soln.
4	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	THF	r.t.	122	0	Yellow susp.
5[c]	$Fe(acac)_3$	TESi-H 50	-	Cs F 15	THF	r.t.	145	0	Yellow susp.
6	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	140	0	Brown susp.
7[c]	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	147	0	Brown susp.
8	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	THF	60	150	0	Brown susp.
9	$Fe(acac)_3$	$NaBH_4$ 20	TESi-H 50	-	H_2O:THF 1:4	60	131	0	Brown susp.
10	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	THF	r.t.	149	0	Brown soln.
11[c]	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	THF	r.t.	133	0	Brown soln.
12	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	-	THF	60	150	0	Brown soln.
13	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	Cs F 15	THF	r.t.	144	4	Brown susp.
14[c]	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	Cs F 15	THF	r.t.	129	24	Brown susp.
15	$FeCl_2 \cdot 4H_2O$	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	144	0	Black susp. stuck on glass
16[c]	$FeCl_2 \cdot 4H_2O$	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	144	0	Black susp. stuck on glass
17	$FeCl_2 \cdot 4H_2O$	$NaBH_4$ 20	TESi-H 50	-	THF	60	151	0	Black susp. stuck on glass
18	$FeCl_2 \cdot 4H_2O$	$NaBH_4$ 20	TESi-H 50	-	H_2O:THF 1:4	60	148	0	Black susp.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (74), designated temperature, 24 h; [b] monitored by G.C. [c]the mixture of (5 mol %) Fe-salt, (1-3 equiv) triethylsilane, stabilizer, additive, and reductant, was warmed to 60 °C for only 1hr prior to alkyne addition

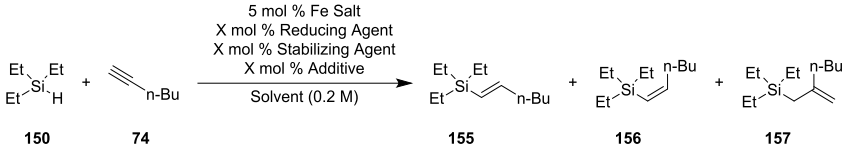
Table 3.4 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **74**[a] (continued)



entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	t (°C)	150[b] (%)	155-7[b] yield (%)	system's physical properties
19	Fe $Cl_2 \cdot 6H_2O$	TESi-H 50	-	-	THF	r.t.	141	5	Yellow soln
20[c]	Fe $Cl_2 \cdot 6H_2O$	TESi-H 50	-	-	THF	r.t.	138	9	Yellow soln
21	Fe $Cl_2 \cdot 6H_2O$	TESi-H 50	-	-	THF	60	147	0	Yellow soln.
22	Fe $Cl_2 \cdot 6H_2O$	TESi-H 50	-	Cs F 15	THF	r.t.	147	0	White susp.
23[c]	Fe $Cl_2 \cdot 6H_2O$	TESi-H 50	-	Cs F 15	THF	r.t.	148	0	White susp.
24	Fe $Cl_2 \cdot 6H_2O$	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	145	0	Black susp.
25[c]	Fe $Cl_2 \cdot 6H_2O$	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	141	0	Black susp.
26	Fe $Cl_2 \cdot 6H_2O$	$NaBH_4$ 20	TESi-H 50	-	THF	60	148	0	Black susp. stuck on glass
27	Fe $Cl_2 \cdot 6H_2O$	$NaBH_4$ 20	TESi-H 50	-	H_2O:THF 1:4	60	146	0	Black susp.
28	Fe Cl_3	TESi-H 50	-	-	THF	r.t.	129	8	Yellow soln.
29[c]	Fe Cl_3	TESi-H 50	-	-	THF	r.t.	101	12	Yellow soln.
30	Fe Cl_3	TESi-H 50	-	-	THF	60	127	15	Yellow soln.
31	Fe Cl_3	TESi-H 50	-	Cs F 15	THF	r.t.	115	4	Brown susp.
32[c]	Fe Cl_3	TESi-H 50	-	Cs F 15	THF		143	0	Brown susp.
33	Fe Cl_3	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	111	0	Black susp.
34[c]	Fe Cl_3	$NaBH_4$ 20	TESi-H 50	-	THF	r.t.	145	0	Black susp.
35	Fe Cl_3	$NaBH_4$ 20	TESi-H 50	-	THF	60	149	0	Black susp. stuck on glass
36	Fe Cl_3	$NaBH_4$ 20	TESi-H 50	-	H_2O:THF 1:4	60	139	0	Black susp.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (74), designated temperature, 24 h; [b]monitored by G.C. [c]the mixture of (5 mol %) Fe-salt, (1-3 equiv) triethylsilane, stabilizer, additive, and reductant, was warmed to 60 °C for only 1hr prior to alkyne addition

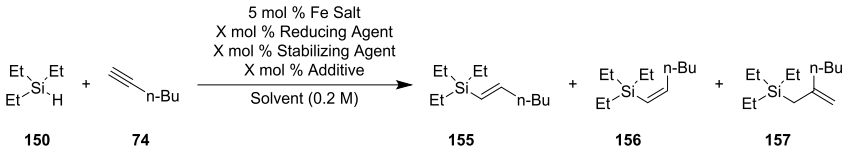
Table 3.4 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **74**[a] (continued)



entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	t (°C)	150[b] (%)	155-7[b] yield (%)	system's physical properties
37[c]	$Fe(acac)_3$	EtMgBr 18	TESi-H 50	-	THF	r.t.	30	0	Black susp.-polymerized
38[c]	$Fe(acac)_3$	EtMgBr 18	TESi-H 50	-	Toluene	r.t.	99	5	Black susp.
39	$Fe(acac)_3$	TESi-H 100	-	Cs F 100	H_2O:THF 1:4	60	152	0	Yellow susp.
40	$Fe(acac)_3$	TESi-H 100	-	Cs F 100	THF	60	168	0	Yellow susp.
41	$Fe(acac)_3$	TESi-H 100	-	KF 100	H_2O:THF 1:4	60	157	0	Yellow susp.
42	$Fe(acac)_3$	TESi-H 100	-	KF 100	THF	60	139	0	Yellow susp.
43[c]	$FeCl_2 \cdot 4H_2O$	EtMgBr 12	TESi-H 50	-	THF	r.t.	150	0	Black soln-polymerized
44[c]	$FeCl_2 \cdot 4H_2O$	EtMgBr 12	TESi-H 50	-	Toluene	r.t.	86	3	Black susp.-
45	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	Cs F 100	H_2O:THF 1:4	60	148	0	Brown susp.
46	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	Cs F 100	THF	60	149	0	Brown susp.
47	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	KF 100	H_2O:THF 1:4	60	140	0	Brown susp.
48	$FeCl_2 \cdot 4H_2O$	TESi-H 50	-	KF 100	THF	60	133	0	Brown susp. stuck on glass
49[c]	$FeCl_3$	EtMgBr 18	TESi-H 50	-	THF	r.t.	46	0	Black susp.-polymerized
50[c]	$FeCl_3$	EtMgBr 18	TESi-H 50	-	Toluene	r.t.	150	0	Black susp.
51	$FeCl_3$	TESi-H 50	-	Cs F 100	H_2O:THF 1:4	60	138	0	Brown susp.
52	$FeCl_3$	TESi-H 50	-	Cs F 100	THF	60	156	0	Brown susp.
53	$FeCl_3$	TESi-H 50	-	KF 100	H_2O:THF 1:4	60	161	0	Brown susp.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv.) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (74), designated temperature, 24 h; [b] monitored by G.C. [c]EtMgBr was added dropwise at 0 °C and the reaction was allowed to warm to rt prior to alkyne addition

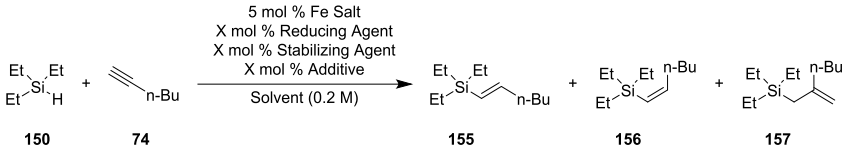
Table 3.4 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **74**[a] (continued)



entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	t (°C)	150[b] (%)	155-7[b] yield (%)	system's physical properties
54[c]	$Fe(acac)_3$	EtMgBr 100	TESi-H 100	-	THF	r.t.	99	0	Black susp.-polymerized
55[c]	$Fe(acac)_3$	EtMgBr 100.	TESi-H 100	-	Toluene	r.t.	109	0	Black susp.
56	$FeCl_2 \cdot 4H_2O$	TESi-H 100	TESi-H 100	Cs F 100.	H_2O:THF 1:4	60	118	0	Brown susp.
57	$Fe(acac)_3$	PMHS 100	-	KF 50	THF	60	129	0	Red susp.
58	$FeCl_2 \cdot 4H_2O$	PMHS 100	-	KF 50	THF	60	138	0	Brown susp.
59	$FeCl_2 \cdot 6H_2O$	PMHS 100	-	KF 50	THF	60	129	0	Blue susp.
60	$FeCl_3$	PMHS 100	-	KF 50	THF	60	142	0	Brown susp.
61	$Fe(acac)_3$	PMHS 100	-	KF 50	THF:H_2O 4:1	60	147	0	Red suspension
62	$FeCl_2 \cdot 4H_2O$	PMHS 100	-	KF 50	THF:H_2O 4:1	60	143	0	Brown susp.
63	$FeCl_2 \cdot 6H_2O$	PMHS 100	-	KF 50	THF:H_2O 4:1	60	134	0	White susp.
64	$FeCl_3$	PMHS 100	-	KF 50	THF:H_2O 4:1	60	145	0	Brown susp.
65	$Fe(acac)_3$	PMHS 100	-	KF 50	THF:H_2O 4:1	60	147	0	Red susp.
66	$Fe(acac)_3$	$NaBH_4$ 20	PMHS 15	-	THF	rt	130	0	Orange susp.
67	$FeCl_2 \cdot 4H_2O$	$NaBH_4$ 20	PMHS 10	-	THF	rt	156	0	White susp.
68	$Fe(acac)_3$	PMHS 15	-	KF 15.	THF	rt	138	7	Red susp.
69	$FeCl_2 \cdot 4H_2O$	PMHS 10	-	KF 15	THF	rt	98	28	Brown susp.
70	$FeCl_2 \cdot 6H_2O$	PMHS 10	-	KF 15	THF	rt	135	12	Brown susp.
71	$FeCl_3$	PMHS 15	-	KF 15	THF	rt	144	7	Black susp.

[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv.) triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (74), designated temperature, 24 h; [b]monitored by G.C. [c]EtMgBr was added dropwise at 0 °C and the reaction was allowed to warm to rt prior to alkyne addition

Table 3.4 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **74**[a] (continued)



entry[a]	Fe Salt (5 mol%)	red. agent (mol%)	stab. agent (mol%)	add. (mol%)	solv. (0.2 M)	t (°C)	150[b] (%)	155-7[b] yield (%)	system's physical properties
72	$Fe(acac)_3$	PMHS 15	-	KF 15.	THF:H_2O 4:1	rt	87	4	Red susp.
73	$FeCl_2 \cdot 4H_2O$	PMHS 10	-	KF 15	THF:H_2O 4:1	rt	139	9	Green soln.
74	$FeCl_2 \cdot 6H_2O$	PMHS 10	-	KF 15	THF:H_2O 4:1	rt	135	12	Brown susp.
75	$FeCl_3$	PMHS 15	-	KF 15	THF:H_2O 4:1	rt	133	19	Brown susp.
76	$Fe(acac)_3$	PMHS 15	-	KF 15.	THF:H_2O 4:1	rt	87	4	Red susp.
77	$Fe(acac)_3$	PMHS 15	-	KF 15.	THF	60	105	18	Red susp.
78	$FeCl_2 \cdot 4H_2O$	PMHS 10	-	KF 15	THF	60	145	3	Brown susp.
79	$FeCl_2 \cdot 6H_2O$	PMHS 10	-	KF 15	THF	60	141	6	Brown susp.
80	$FeCl_3$	PMHS 15	-	KF 15	THF	60	133	11	Black susp.
81	$FeCl_3$	$NaBH_4$ 20	PMHS 15	-	THF	rt	146	0	Black susp.
82	$Fe(acac)_3$	$NaBH_4$ 20	PMHS 15	-	Ethanol	rt	153	0	Brown susp.
83	$FeCl_2 \cdot 4H_2O$	$NaBH_4$ 20	PMHS 10	-	Ethanol	rt	151	0	Grey susp.
84	$FeCl_2 \cdot 6H_2O$	$NaBH_4$ 20	PMHS 10	-	Ethanol	rt	131	0	Black susp.
85	$FeCl_3$	$NaBH_4$ 20	PMHS 15	-	Ethanol	rt	156	0	Grey susp.
86	$Fe(acac)_3$	PMHS 15	-	KF 15	Ethanol	60	158	0	Red susp.
87	$Fe(acac)_3$	PMHS 100	-	KF 50	Ethanol	60	150	0	Red susp.
88	$Fe(acac)_3$	PMHS 15	-	KF 50	1,2-DCE	60	147	0	Red susp.
89	$Fe(acac)_3$	PMHS 100	-	KF 100	1,2-DCE	60	160	0	Red susp.

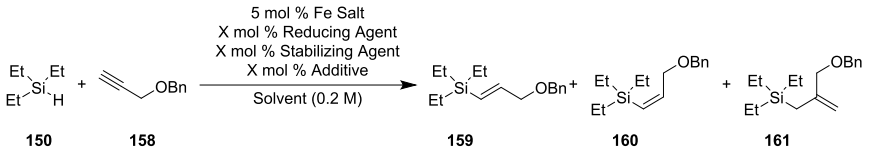
[a]Conditions were: (5 mol %) Fe-salt, (1-3 equiv.) triethylsilane(150), stabilizer, additive, reductant, and 1 mmol alkyne (74), designated temperature, 24 h; [b]monitored by G.C.

Given the promising result that the alkyne functionality had shown by GC, and realizing that we could not detect what was happening to the hexyne (**74**) quantitatively by the same method, it was decided to employ a high boiling terminal alkyne. A calibration curve was made for the ((prop-2-yn-1-yloxy) methyl)benzene substrate (**158**), triethylsilane (**150**) and (3-(benzyloxy) prop-1-en-1-yl)triethylsilane products (**159-161**). Furthermore, it was decided that broadening the scope of polymer stabilizer would also be worth exploring. Thus, a series of other polymers used in metal nanoparticle synthesis apart from PMHS were examined.[139] Screening experiments were conducted under this strategic framework.

Iron acetylacetonate [$Fe(acac)_3$] was utilized, $NaBH_4$ was the reductant and PVP was the stabilizing agent, in an alcoholic solvent (entry 1, Table 3.5). This did not produce desired results. Attempting the same reaction in aqueous ethanol of varied mixtures was unsuccessful (entries 2-3, Table 3.5). Refluxing PVP containing systems followed by addition of substrates produced minuscule product formation (entries 4-6, Table 3.5). Reaction of the iron salt with reductant in PEG-400 to make the catalyst and then transferring it into the reaction system with substrates was attempted unsuccessfully (entries 7-9, Table 3.5). Heating these systems to 60 ^{o}C did not bring desired outcomes (entries 10-12, Table 3.5). Attempting the same reaction with all ingredients in one pot from the onset, was conducted (entries 13-15, Table 3.5), but showed no catalytic activity. PMHS was employed in stoichiometric amounts, with $NaBH_4$ as the reductant (entries 16-18, Table 3.5). This did not give the desired results. Increasing the amount of PVP content to a 1:1 ratio with reductant was unsuccessful (entries 19 and 20, Table 3.5). Premaking the nanoparticles in a 1:1 mixture of PVP and PEG under reflux, then injecting the heterogeneous reaction mixture into various solvent systems with substrates was attempted (entries 21-27, Table 3.5). This strategy was unsuccessful. The same strategy was attempted using PEG only (entries 28-32, Table 3.5) without

success. Employing $NaBH_4$ in combination with PEG under the same conditions did not work (entries 33-35, Table 3.5). EtMgBr with the combination of PEG/PVP were employed (entries 36 and 43, Table 3.5), this alternative did not work. PMHS replaced PEG/PVP polymers in the following setups (entries 44-50, Table 3.5). Even though desired products were not observed, an interesting observation was that the alkyne starting material decreased in quantity. Due to the poor results from this project, it was terminated.

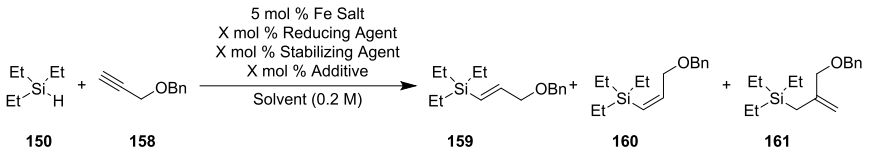
Table 3.5 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **158**[a]



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	solvent (0.2 M)	t (°C)	150[b] (%)	158[b] (%)	159-161[b] yield (%)	system's physical properties
1	$NaBH_4$ 20	PVP 5	EtOH	r.t.	97	91	0	White solid/ Green liquid
2	$NaBH_4$ 20	PVP 5	EtOH:H_2O 2:1	r.t.	94	100	0	White solid/ Green liquid
3	$NaBH_4$ 20	PVP 5	EtOH:H_2O 1:1	r.t.	97	96	0	White solid/ Green liquid
4[c]	$NaBH_4$ 20	PVP 5	EtOH	r.t.	87	85	2	Maroon susp.
5[c]	$NaBH_4$ 20	PVP 5	EtOH:H_2O 2:1	r.t.	91	91	3	Maroon susp.
6[c]	$NaBH_4$ 20	PVP 5	EtOH:H_2O 1:1	r.t.	86	97	1	Maroon susp.
7[c]	$NaBH_4$ 20	PEG 400 5	EtOH	r.t.	100	97	1	Yellow susp.
8[c]	$NaBH_4$ 20	PEG 400 5	EtOH:H_2O 2:1	r.t.	97	82	1	Yellow susp.
9[c]	$NaBH_4$ 20	PEG 400 5	EtOH:H_2O 1:1	r.t.	91	100	0	Yellow susp.
10[c]	$NaBH_4$ 20	PEG 400 5	EtOH	60	87	90	2	Brown susp.
11[c]	$NaBH_4$ 20	PEG 400 5	EtOH:H_2O 2:1	60	74	86	2	Brown susp.
12[c]	$NaBH_4$ 20	PEG 400 5	EtOH:H_2O 1:1	60	91	81	3	Brown susp.
13[c]	$NaBH_4$ 20	PEG 5	EtOH	60	81	94	0	Black susp.
14	$NaBH_4$ 20	PEG 5	EtOH:H_2O 2:1	60	86	90	0	Black susp.
15	$NaBH_4$ 20	PEG 5	EtOH:H_2O 1:1	60	88	90	0	Black susp.
16	$NaBH_4$ 20	PMHS 100	EtOH	60	91	92	1	Black susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, 1 mmol triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (158), designated temperature, 24 h; [b]monitored by G.C.; (c) (5 mol %) $Fe(acac)_3$, polymeric stabilizer, and, reductant were refluxed for six hrs and then transferred to the reaction mixture with substrates

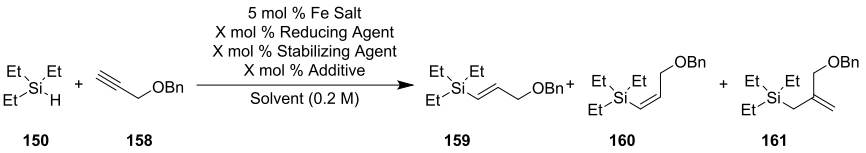
Table 3.5 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **158**[a] (continued)



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	solvent (0.2 M)	t (ºC)	150[b] (%)	158[b] (%)	159-161[b] yield (%)	system's physical properties
17	$NaBH_4$ 20	PMHS 100	EtOH: H_2O 2:1	60	92	89	0	Black susp.
18	$NaBH_4$ 20	PMHS 100	EtOH: H_2O 1:1	60	96	94	0	Black susp.
19	$NaBH_4$ 20	PVP 20	EtOH: H_2O 2:1	r.t.	94	100	0	White solid/ Green liquid
20	$NaBH_4$ 20	PVP 20	EtOH: H_2O 1:1	r.t.	97	96	0	Red/orange - white solid/ Greenish liquid
21[c]	$NaBH_4$ 20	PVP/ PEG 75	DCM	60	90	95	5	Khaki susp.
22[c]	$NaBH_4$ 20	PVP/ PEG 75	DCE	60	91	96	3	Khaki susp.
23[c]	$NaBH_4$ 20	PVP/ PEG 75	Tol	60	94	89	0	Khaki susp.
24[c]	$NaBH_4$ 20	PVP/ PEG 75	THF	60	91	90	0	Khaki susp.
25[c]	$NaBH_4$ 20	PVP/ PEG 75	Et_2O	60	94	89	0	Black susp.
26[c]	$NaBH_4$ 20	PVP/ PEG 75	$CHCl_3$	60	97	87	0	Khaki susp.
27[c]	$NaBH_4$ 20	PVP/ PEG 75	Hex	60	99	95	0	Khaki susp.
28[c]	$NaBH_4$ 20	PEG 75	DCM	60	92	94	4	Brown susp.
29[c]	$NaBH_4$ 20	PEG 75	DCE	60	92	97	0	Brown susp.
30[c]	$NaBH_4$ 20	PEG 75	Tol	60	93	89	0	Brown susp.
31[c]	$NaBH_4$ 20	PEG 75	THF	60	94	99	0	Brown susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, 1 mmol triethylsilane(150), stabilizer, additive, reductant, and 1 mmol alkyne (158), designated temperature, 24 h; [b]monitored by G.C.; [c](5 mol %) $Fe(acac)_3$, polymeric stabilizer, and, reductant were refluxed for six hrs and then transferred to the reaction mixture with substrates

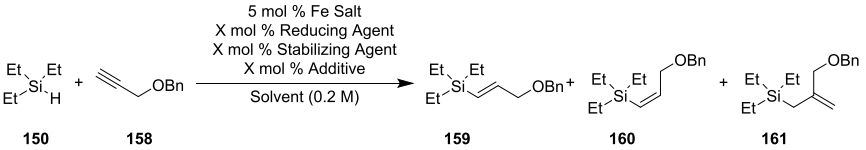
Table 3.5 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **158**[a] (continued)



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	solvent (0.2 M)	t (ºC)	150[b] (%)	158[b] (%)	159-161[b] yield (%)	system's physical properties
32[c]	$NaBH_4$ 20	PEG 75	Hex	60	92	94	4	Brown susp.
33	$NaBH_4$ 40	PEG 75	Tol	60	93	89	0	Yellow susp.
34	$NaBH_4$ 40	PEG 75	Et_2O	60	93	95	0	Brown susp.
35	$NaBH_4$ 40	PVP/PEG 75	$CHCl_3$	60	95	99	0	Brownish susp.
36[d]	EtMgBr 50	PVP/PEG 75	DCM	60	94	97	0	Brown susp.
37[d]	EtMgBr 50	PVP/PEG 75	Dioxane	60	94	99	0	Brown susp.
38[d]	EtMgBr 50	PVP/PEG 75	DCE	80	94	100	0	Brown susp.
39[d]	EtMgBr 50	PVP/PEG 75	Tol	80	93	100	0	Brown susp.
40[d]	EtMgBr 50	PVP/PEG 75	THF	80	94	99	0	Brown susp.
41[d]	EtMgBr 50	PVP/PEG 75	Et_2O	80	94	99	0	Brown susp.
42[d]	EtMgBr 50	PVP/PEG 75	$CHCl_3$	80	96	100	0	Brown susp.
43[d]	EtMgBr 50	PVP/PEG 75	Hexanes	80	94	100	0	Brown susp.
44[d]	EtMgBr 50	PMHS 50	DCM	80	95	46	0	Brown susp.
45[d]	EtMgBr 50	PMHS 50	DCE	80	96	63	0	Brown susp.
46[d]	EtMgBr 50	PMHS 50	Tol	80	96	66	0	Brown susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, 1 mmol triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (158), designated temperature, 24 h; [b]monitored by G.C.; [c](5 mol %) $Fe(acac)_3$, polymeric stabilizer, and, reductant were refluxed for six hrs and then transferred to the reaction mixture with substrates; [d]EtMgBr was added dropwise at 0 ºC to a mixture of $Fe(acac)_3$ and polymeric stabilizer; and and then transferred to the reaction mixture with substrates after warming to rt .

Table 3.5 Screening reaction conditions for iron nanoparticle catalyzed hydrosilylation of **158**[a] (continued)



entry[a]	reducing agent (mol%)	stabilizing agent (mol%)	solvent (0.2 M)	t (°C)	150[b] (%)	158[b] (%)	159-161[b] yield (%)	system's physical properties
47[c]	EtMgBr 50	PMHS 50	THF	80	99	63	2	Brown susp.
48[c]	EtMgBr 50	PMHS 50	Et_2O	80	90	78	4	Brown susp
49[c]	EtMgBr 50	PMHS 50	$CHCl_3$	80	96	63	0	Brown susp.
50[c]	EtMgBr 50	PMHS 50	Hex	80	93	92	0	Brown susp.

[a]Conditions were: (5 mol %) $Fe(acac)_3$, 1 mmol triethylsilane (150), stabilizer, additive, reductant, and 1 mmol alkyne (158), designated temperature, 24 h; [b]monitored by G.C.; [c]EtMgBr was added dropwise at 0 °C toa mixture of $Fe(acac)_3$ and polymeric stabilizer; and and then transferred to the reaction mixture with substrates after warming to rt

3.5 CONCLUSION

Iron nanoparticle catalyzed hydrosilylation under the aforementioned reaction conditions does not work. Evidence of agglomeration in many of the cases described in the data presented could be the main reason why this project was not feasible. Another potential source of inactivity might be catalytic poisoning of the nanoparticle, either by way of reacting with components of the reaction system or aggregation of the particles into forms that do not facilitate catalysis. Even though monodispersed suspensions were evident to the naked eye, they may not have been nanomaterials but rather larger inactive particles. During the course of this project, investment into measuring the particle sizes of the suspensions outlined *vide supra* was not carried out. Hence we cannot conclude with certainty that iron nanoparticles were formed. However, evidence that something transpired to the metal in the systems was determined from observing physical property changes. This chapter therefore provides an information resource for experimental strategies tried that did not facilitate iron nanoparticle hydrosilylation catalysis.

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CHAPTER IV

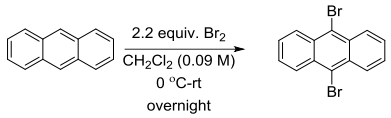
EXPERIMENTALS FOR CHAPTER I: NOVEL TRIPTYPYRAZINE GEAR SYSTEMS INCORPORATING PHOTOCHEMICAL/ELECTROCHEMICAL SWITCHABLE MOIETIES

4.1 Methods: Unless stated otherwise, all reactions were carried out in oven dried glassware under an atmosphere of argon with magnetic stirring. Reactions were monitored by thin-layer chromatography with 0.25 mm precoated silica gel plates. Visualization of all TLCs was performed by UV. Purifications were performed by silica gel flash and/or gravity chromatography with silica gel (Silicycle, 60 Å, 230-400 mesh) packed in glass columns and eluted with DCM, hexanes, or hexanes/Et_2O, unless otherwise noted.

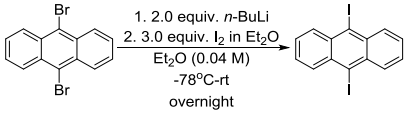
4.2 Materials: Tetrahydrofuran and TEA was freshly distilled from potassium/benzophenone under argon. All other reagents and solvents were reagent grade and used without further purification unless otherwise stated. Reagents were purchased and used directly from commercial packaging. Reaction systems requiring inert conditions were achieved by purging with argon.

4.3 Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Inova 300 MHz NMR spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) or a Bruker Avance 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) with chemical shifts reported relative to residual chloroform solvent peaks (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C). Data for ^{1}H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet, m = multiplet, or unresolved), coupling constant(s) in Hz. IR spectra were obtained as thin films on a Perkin Elmer 2000 FTIR spectrometer using NaCl plates.

4.4 Compounds synthesized and characterization data

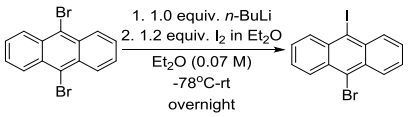


Preparation of 9,10-Dibromoanthracene: To a clean, dry, 500 mL three-necked flask equipped with a stir bar was added anthracene (10 mmol, 1.78 g) in CH_2Cl_2 (110 mL). The solution was cooled to 0 °C. The reaction vessel was connected to a HBr gas trap (bubbler containing 1 M NaOH solution). To the solution was added dropwise Br_2 (22 mmol, 3.45 g) in CH_2Cl_2 (10 mL) via an addition funnel. The mixture was stirred overnight. Upon completion, the reaction mixture was treated with saturated Na_2SO_3. The product was filtered out and recrystallized (hot $CHCl_3$) to afford the pure product as yellow needles, 1.25g (50% yield); mp 218-220 °C;[189] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61-8.52 (m, 4H) , 7.66-7.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.03, 128.26, 127.44, 123.52. Physical and spectral data were consistent with those reported in the literature.[189]

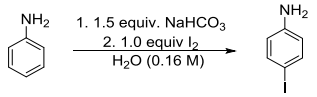


Preparation of 9, 10-Diiodoanthracene: To a clean, dry, 500 mL three-necked flask, equipped with a stir bar was added 9,10-dibromoanthracene (4.4 mmol 1.48 g) in 100 mL Et_2O. The solution was purged with argon and cooled to -78 °C. *n*-Butyllithium (8.8 mmol, 7.48 mL in 1.3 M hexanes) was added dropwise over the course of 30 min to the reaction mixture. The mixture was stirred for 45 min after which dissolved iodine (13.2 mmol, 3.35 g in 15 mL of Et_2O) was added dropwise to the reaction mixture at -78°C. The reaction mixture was stirred for 24 h and also allowed to warm to room temperature. The etheral solution was washed several times with saturated Na_2SO_3 (aq) and dried ($MgSO_4$). The solvent was removed by evaporation to reveal a pale yellow solid. The crude product was purified by recrystallization ($CHCl_3$) to give 1.10 g (58% yield) yellow needles of the 9,10-diiodoanthracene; mp 218-220 °C; [190,191] ^{1}H NMR (300 MHz $CDCl_3$) δ 8.58-8.52 (m, 4H), 7.65-

7.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.03, 128.26,127.44,123.52. Physical and spectral data were consistent with those reported in the literature.[190,191]

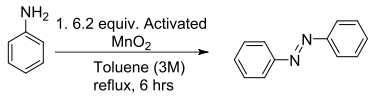


Preparation of 9-Bromo-10-iodoanthracene: To a clean, dry, 250 mL three-necked flask, equipped with a stir bar was added 9,10-dibromoanthracene (7.4 mmol, 2.5 g) in 50 mL THF. The solution was purged with argon and then cooled to -78 °C. *n*-Butyllithium (4.4 mmol, 3.74 mL in 1.3 M hexane) was added dropwise over the course of 30 min. The resulting mixture was stirred for 3 h at this temperature. To the resulting clear red solution, was added dropwise a solution of iodine (9.56 mmol, 2.43 g in 7.5 mL of Et_2O). After the addition was complete, the reaction mixture was stirred for 1 h at -78 °C, and was then allowed to warm to room temperature overnight. The etheral solution was washed several times with saturated Na_2SO_3 (aq) and dried ($MgSO_4$). The solvent was removed under vacuum to reveal a pale yellow solid. The crude product was purified by an ether silica-gel column, followed by recrystallization ($CHCl_3$) to afford 0.85 g (30% yield) of the bromoiodo compound as yellow fiber-like crystals; mp 219-220 °C;[191] ^{1}H NMR (300 MHz $CDCl_3$) δ 8.36-8.30 (m, 4H), 7.86-7.79 (m,4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.06, 128.54, 127.95, 127.46. Physical and spectral data were consistent with those reported in the literature.[191]

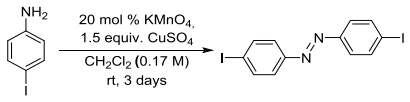


Preparation of *p*-iodoaniline: To a clean, dry, 1 L round-bottomed flask equipped with a stir bar was added aniline (0.215 mol, 19.6 mL), sodium bicarbonate (0.32 mol, 27.0 g), and 200 mL of distilled H_2O. The mixture was cooled to 12-15 °C by the addition of small amounts of ice. The system was vigorously stirred, and powdered iodine (0.18 mol, 45.47 g) was added in portions at intervals of two to three minutes. Stirring was continued for 30 min until the color of free iodine in

the solution disappeared. The crude *p*-iodoaniline, separated as a dark crystalline mass, was collected on a Büchner funnel, pressed as free from water as possible, and dried in the air. The dry crude *p*-iodoaniline was placed in a 1 L round-bottomed flask and 500 mL of hexane was added. The flask was fitted with an air-cooled, reflux condenser and heated to a temperature of 75-80 °C. The flask was shaken frequently until saturation was complete. The hot solution was slowly decanted into a beaker set in an ice-salt mixture. The *p*-iodoaniline crystallized immediately into colorless needles which were filtered and dried in air 38.3 g (81% yield); mp 62-63 °C.[192] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.39 (d, *J* = 9.0 Hz, 2H), 6.49-6.46 (d, *J* = 9.0 Hz, 2H), 3.67 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.00, 137.85, 117.24, 79.33. Physical and spectral data were consistent with those reported in the literature.[192193]

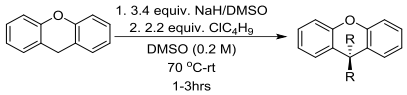


Preparation of Azobenzene: To a clean, dry, 50 mL, two-necked round bottomed flask equipped with a stir bar was added 1.0 mL of aniline (32.0 mmol, 3.0 g,), activated MnO_2 (197 mmol, 5.7 g), and toluene (10.0 mL). The reaction mixture was refluxed for 6 h while connected to a Dean-Stark apparatus. The precipitate was filtered off, and the solvent was evaporated invacuo. The residue was subjected to column chromatography with hexanes, followed by recrystallization (heptane) to give orange crystals, 160 mg (16% yield), mp 69-70 °C;[194] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 4H), 7.51 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.63, 130.97, 129.07, 122.82. Physical and spectral data were consistent with those reported in the literature.[192,195]

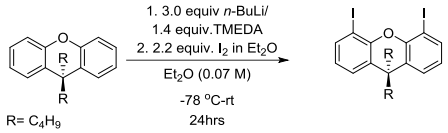


Preparation of 4,4'-Diiodoazobenzene: To a clean, dry, 200-mL round-bottomed flask equipped

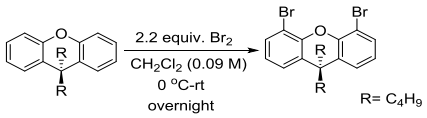
with a stir bar was added 4-iodoaniline (13.7 mmol, 3 g) dissolved in 80 mL of degassed dichloromethane under an argon atmosphere. To this was added a finely ground mixture of $KMnO_4$ (3.13 mmol, 5.1 g) and $CuSO_4 \cdot 5H_2O$ (20.26 mmol, 5.1 g). The reaction mixture was stirred at room temperature for 3 days, and, then was filtered through Celite and subjected to column chromatography with hexanes to afford an orange solid 0.4 g, (12% yield), mp: 242-244 °C; [196] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.0 Hz, 4H), 7.66 (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.42, 138.41, 124.51, 110.00. Physical and spectral data were consistent with those reported in the literature.[195, 196]



Preparation of 9,9-dibutylxanthene: Dry DMSO (30 mL) was added to NaH (38.1 mmol 1.96 g 30 wt% in mineral oil) in a two-necked, 100-mL round-bottomed flask. The suspension was heated to 70 °C under an argon atmosphere. After stirring for 2 h, the reaction mixture was cooled to room temperature, and a solution of xanthene (11.1 mmol, 2.0 g) in DMSO (30 mL) was added dropwise. The solution turned deep red. 1-Chlorobutane (24.9 mmol, 2.6 mL) was added dropwise at room temperature. After stirring for 1 h, the reaction mixture was poured into water (200 mL). The aqueous layer was extracted with Et_2O (100 mL x 5). The combined organic extracts were dried ($MgSO_4$). After removal of $MgSO_4$, the solvent was evaporated. The residue passed over a silica gel column of 9:1 hexane/DCM, to afford a colorless solid of 9,9-dibutylxanthene 4.06 g (86 % yield);[197] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30 (d, *J* = 9.0 Hz, 2H), 7.18 (t, *J* = 6.0 Hz, 2H), 7.06 (m, 8H), 1.92 (t, *J* = 9.0 Hz, 4H), 1.12 (m, 4H), 0.87 (m, 4H), 0.71 (t, *J* = 6.0Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.39, 130.47, 128.91, 127.33, 117.19, 115.62, 45.20, 42.71, 29.70, 26.92, 22.82, 13.84. Physical and spectral data were consistent with those reported in the literature.[197]



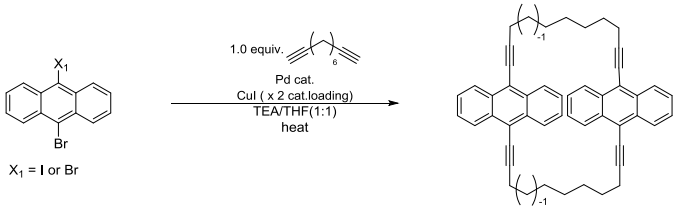
Preparation of 9,9-dibutyl-4,5-diiodoxanthene: TMEDA (3.58 mmol, 0.59 mL) was added to a solution of 9,9-dibutylxanthene (2.7 mmol, 0.8 g) in 25 mL of Et_2O under argon atmosphere in a two-necked, 100 mL round-bottomed flask. The solution was cooled to -78 °C, and *n*-BuLi (7.7 mmol, 5.53 mL in 1.4 M hexane/cyclohexane) was added. The reaction mixture was allowed to warm to room temperature with continued stirring. After stirring for 12 h, the reaction mixture was cooled to -78 °C. A solution of iodine (6.00 mmol, 1.52 g) in 15 mL of Et_2O was added dropwise. After stirring the reaction mixture for 12 h, saturated $Na_2S_2O_3$ aq (150 mL) was added to quench the reaction. The aqueous layer was extracted with Et_2O (100 mL x 5), and the organic layer was dried ($MgSO_4$). After removal of $MgSO_4$, the solvent was evaporated. The residue was subjected to column chromatography with hexane:CH_2Cl_2 (9:1) as the eluent. Recrystallization (hot ethanol) gave a colorless solid of 9,9-dibutyl-4,5-diiodoxanthene 0.37 g (23 % yield);[197, 198] ^{1}H NMR (300 MHz $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 6.0 Hz, 2H), 7.43 (m, 2H), 2.31 (t, *J* = 9.0 Hz, 4H), 1.50 (m, 4H), 1.25 (m, 4H), 1.09 (t, *J* = 6.0 Hz, 6H); ^{13}C ($CDCl_3$, 75 MHz) δ 150.38, 130.47, 128.91, 128.90, 127.32, 117.93, 115.30, 45.20, 42.71, 29.71, 26.91, 22.86, 13.84. Physical and spectral data were consistent with those reported in the literature.[197, 198]



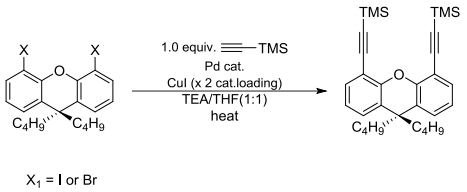
Preparation of 9,9-dibutyl-4,5-dibromoxanthene: To a clean, dry, 25-mL three-necked flask equipped with a stir bar was added 9,9-dibutylxanthene (0.34 mmol, 100 mg) in CH_2Cl_2 (3.8 mL). The solution was cooled to 0 °C. The reaction evolved HBr and was best connected to a HBr gas trap (bubbler containing 1 M NaOH solution). To the solution was added dropwise Br_2 (0.74 mmol, 0.04

mL) in 0.3 mL of CH_2Cl_2 using an addition funnel. The reaction mixture was allowed to warm to room temperature with stirring overnight. The reaction mixture was then quenched with saturated Na_2SO_3. The reaction mixtures was concentrated and then subjected to column chromatography hexane:DCM (9:1) to afford a yellow solid 0.11 g (70% yield).[189, 199] ^{1}H NMR (300 MHz $CDCl_3$) δ 7.77 (d, *J* = 9.0 Hz, 2H), 7.66 (d, *J* = 6.0 Hz, 2H), 7.51 (m, 2H), 2.41 (t, *J* = 9.0 Hz, 4H), 1.61 (m, 4H), 1.35 (m, 4H), 1.29 (t, *J* = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.38, 130.47, 128.90, 127.32, 117.93, 116.02, 45.20, 42.71, 29.70, 26.91, 22.82, 13.84. Physical and spectral data were consistent with those reported in the literature.[198, 199]

General Sonogashira Coupling Procedure: THF and TEA were distilled from potassium/benzophenone prior to use. All other chemicals were of either reagent grade and were used upon establishing purity by NMR, or substrates were synthesized and purified prior to use. To a stirred mixture of halogenated aryl substrates (2.0 equiv.), CuI (twice cat mol %), either $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ (4-20 mol%) in a 1:1 ratio of THF/TEA (0.01-0.5 M) at 70-120 ^{o}C, was added a solution of (1-2 equiv.) of terminal diyne (either dropwise or by syringe pump). The reaction was monitored by TLC. Upon reaction completion, the solvent was evaporated in vacuo, and the residue was treated with dichloromethane (100mL). Filtration through Celite followed by evaporation of the solvent gave crude residue and was subjected to column chromatography.[200]



Preparation of hexyl-linked gear precursor: Following the general Sonogashira coupling procedure, 9,10-dihaloanthracene (2.0 equiv.) and (1-2 equiv.) of 1,9-decadiyne were reacted under various reaction conditions without success.



Preparation of xanthene-linked diyne: Following the general Sonogashira coupling procedure, 9,10-dihaloxanthene (1.0 equiv.) and TMSacetylene (2.0 equiv.) were reacted under various reaction conditions without success.

4.5 REFERENCES

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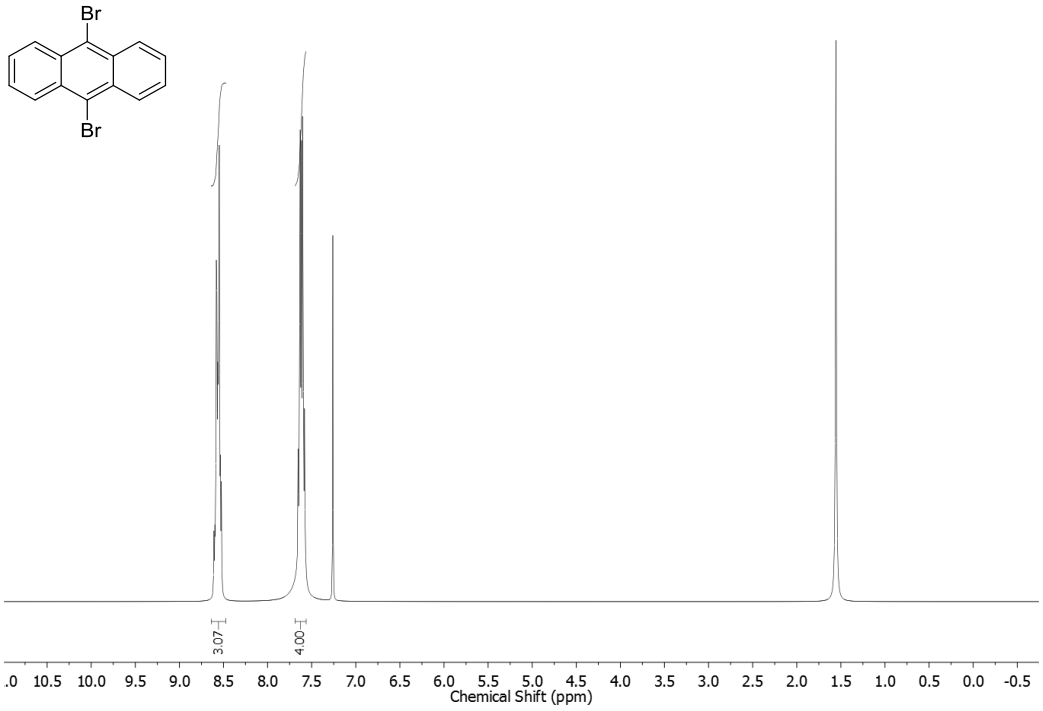
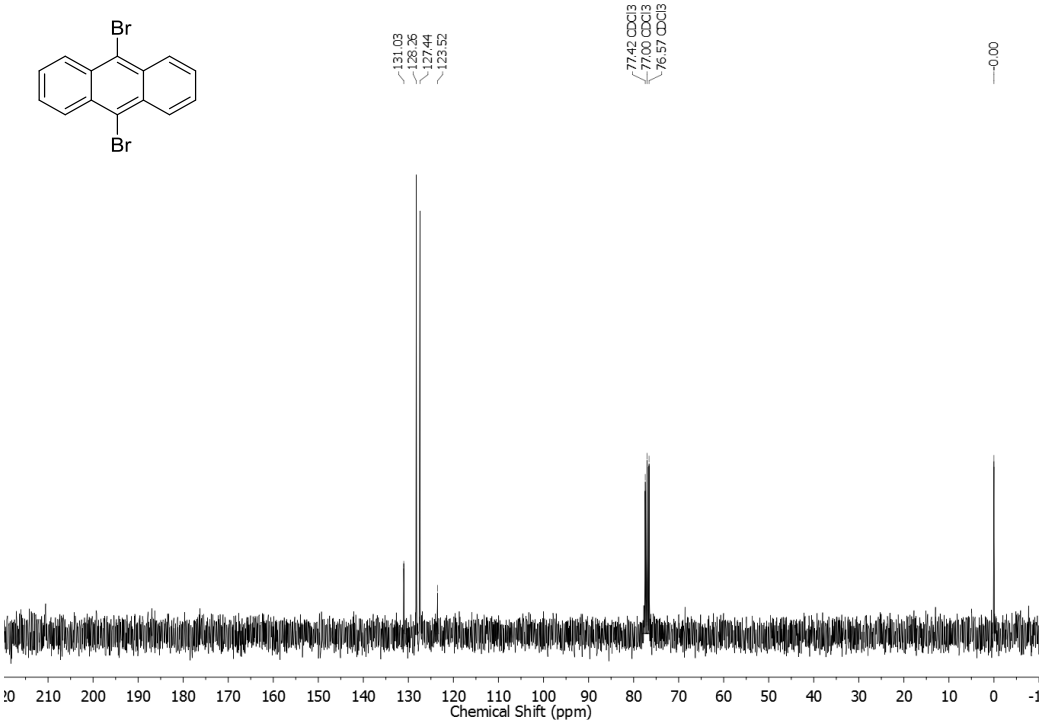
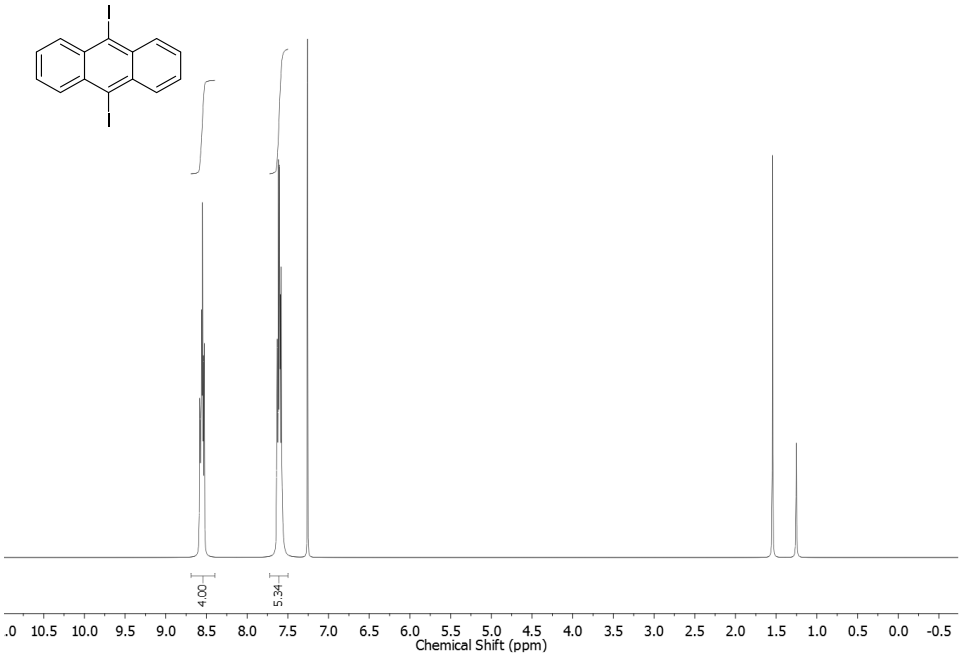
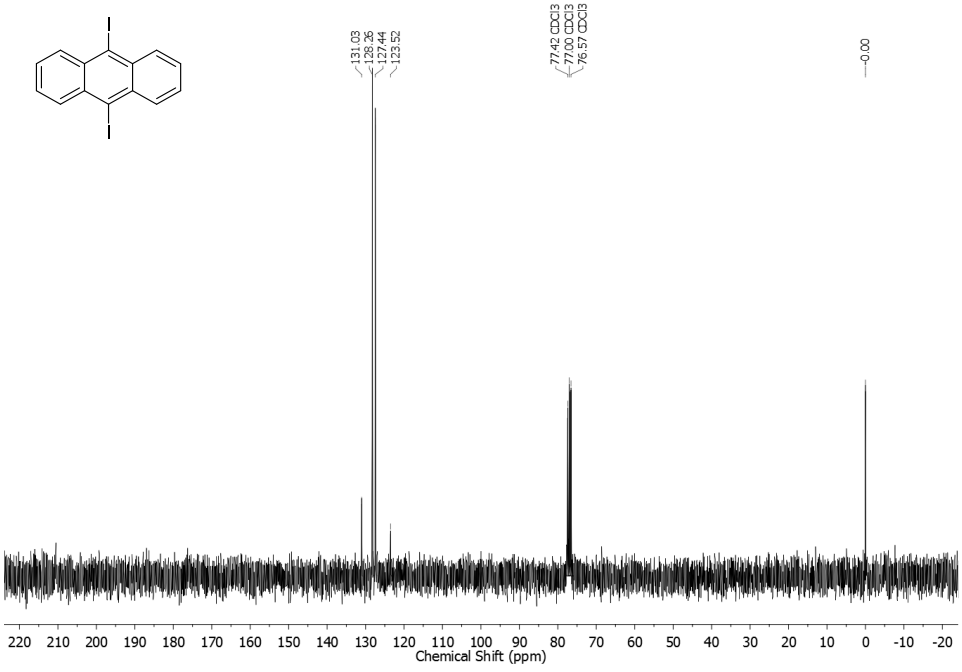
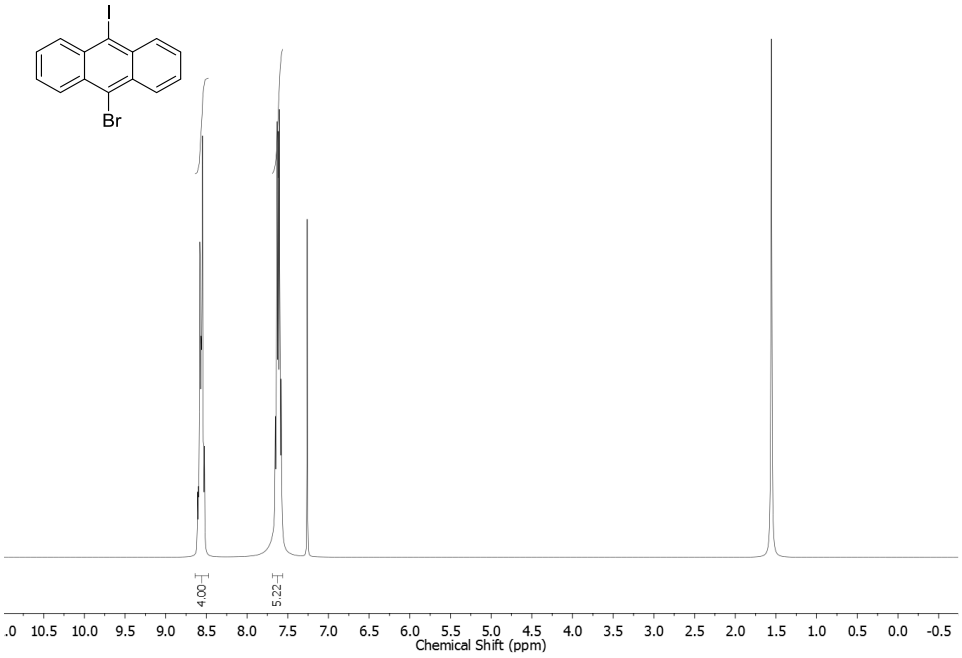
4.6 ^{13}C and ^{1}H NMR SPECTRA

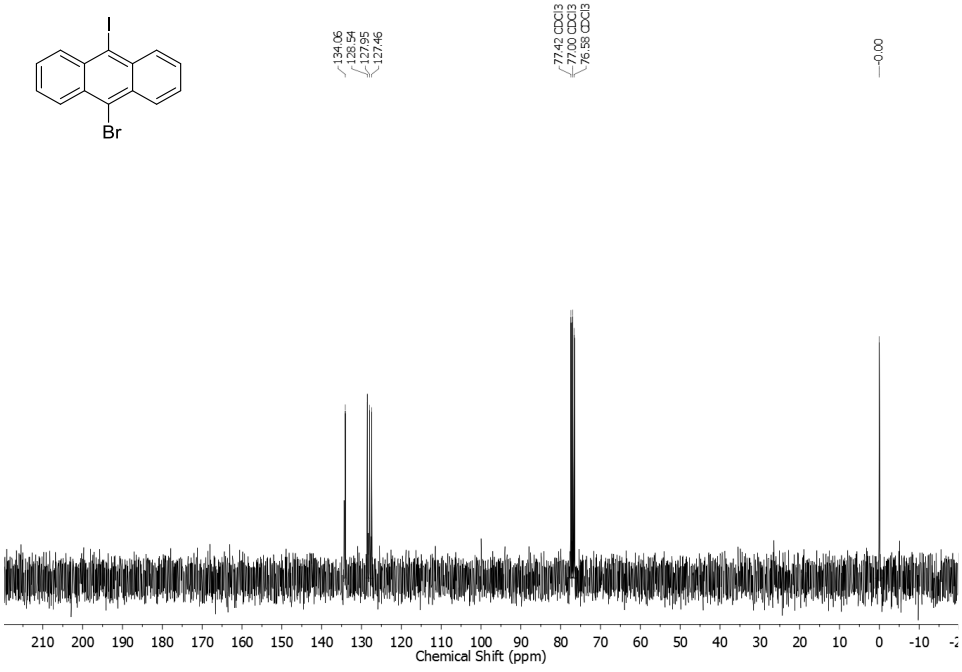





4.00
5.34
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
Chemical Shift (ppm)


131.03
128.35
127.44
123.52
77.42 CDCl3
77.00 CDCl3
76.57 CDCl3
0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift (ppm)


I
Br
4.00
5.22
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
Chemical Shift (ppm)


I
Br
134.06
128.54
127.95
127.46
77.42 CDCl3
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76.58 CDCl3
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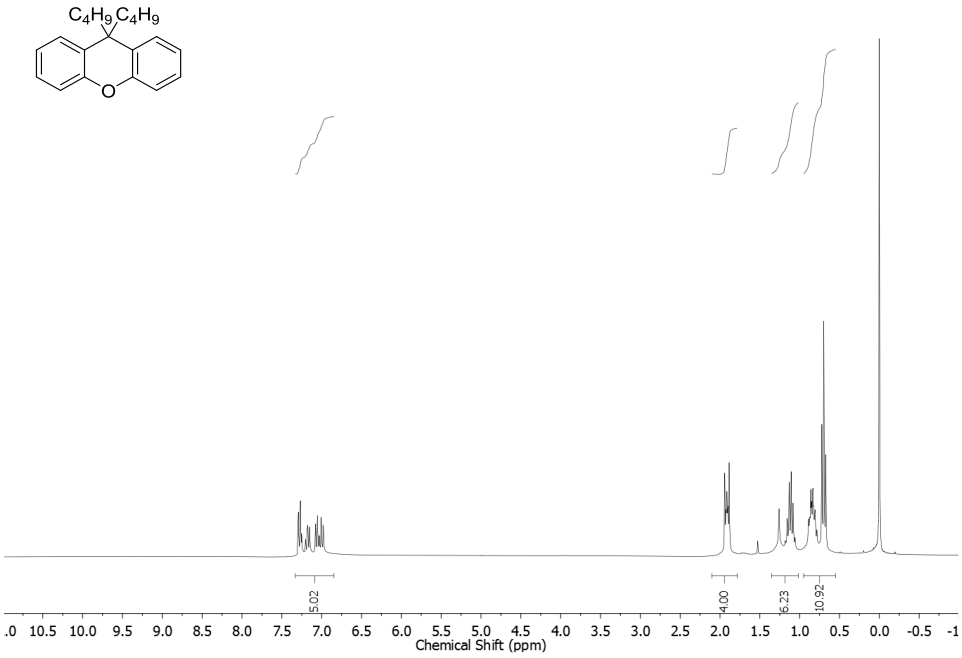
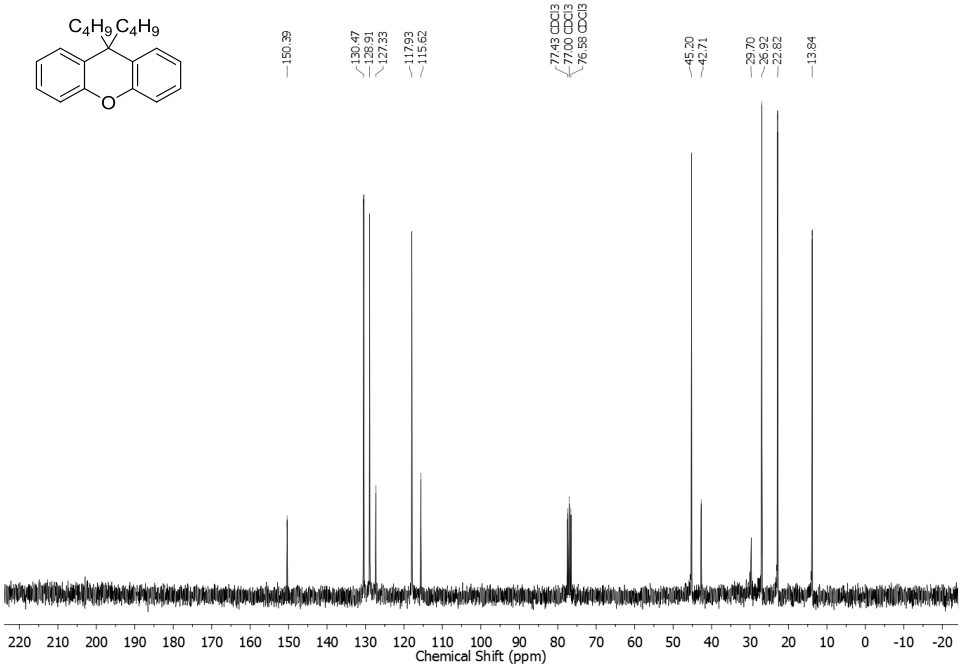
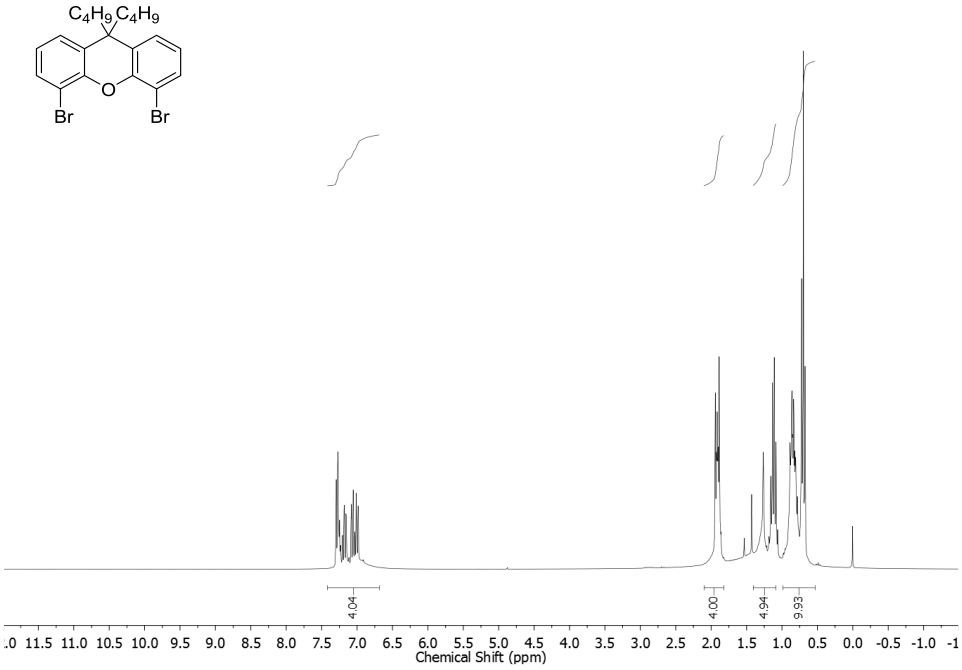
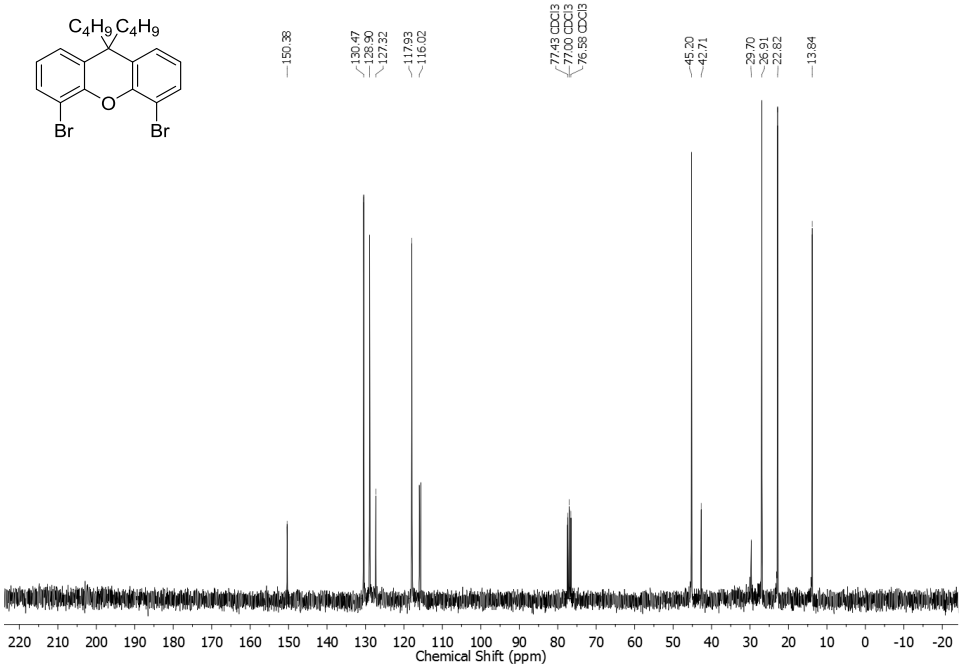
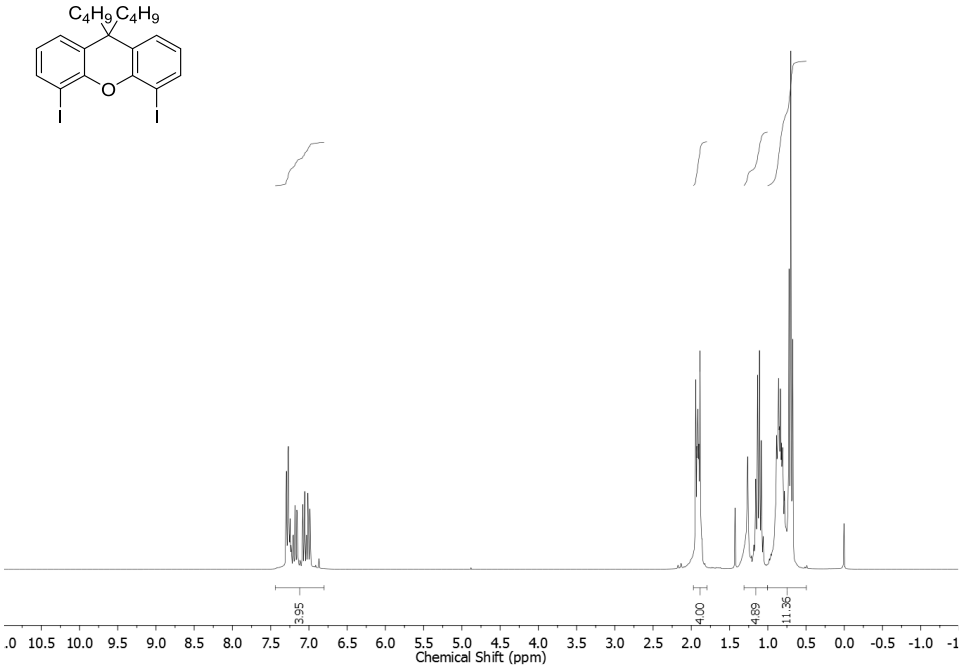
Chemical Shift (ppm)


C_4H_9 C_4H_9
O
5.02
4.00
6.23
10.92
Chemical Shift (ppm)


C_4H_9 C_4H_9
O
150.39
130.47
128.91
127.33
117.93
115.62
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
45.20
42.71
29.70
26.92
22.82
13.84
Chemical Shift (ppm)


C4H9 C4H9
Br
Br
O
4.04
4.00
4.94
9.93
Chemical Shift (ppm)


C4H9 C4H9
Br
Br
O
150.38
130.47
128.90
127.32
117.93
116.02
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
45.20
42.71
29.70
26.91
22.82
13.84
Chemical Shift (ppm)


C4H9 C4H9
O
I
I
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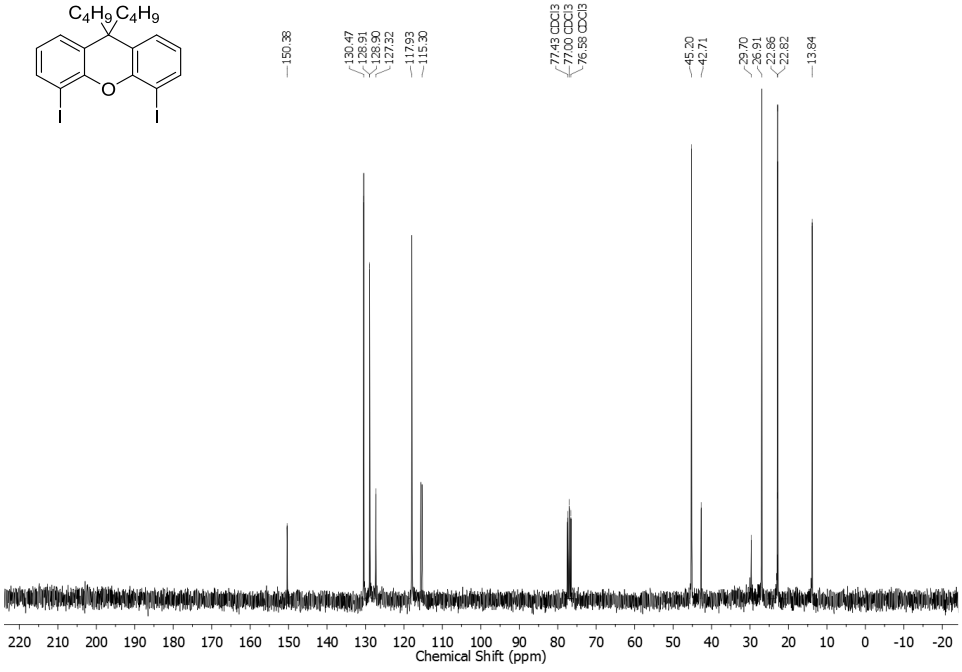
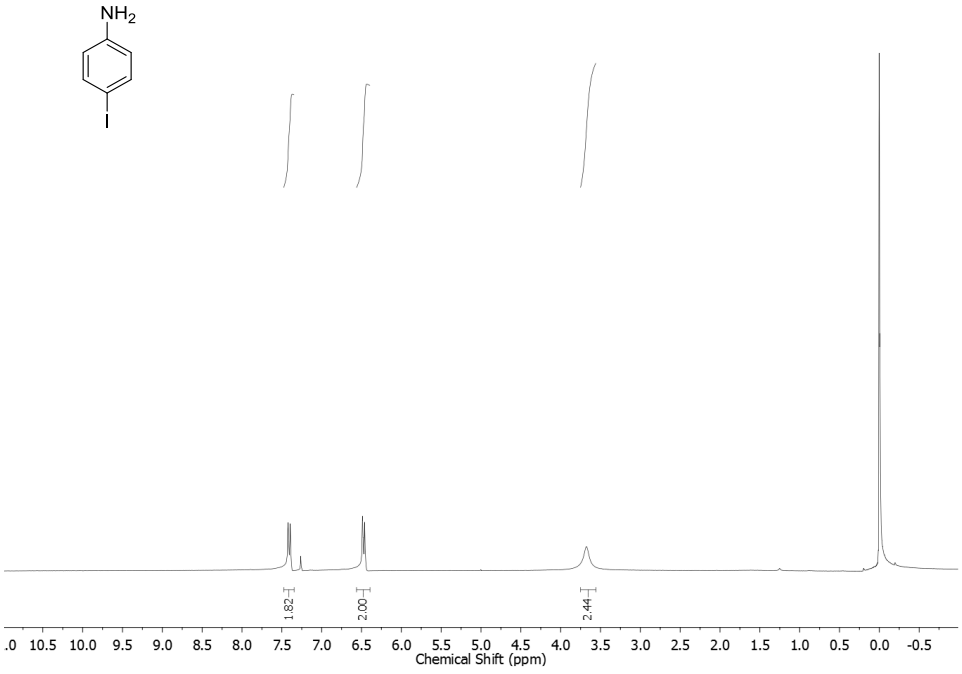
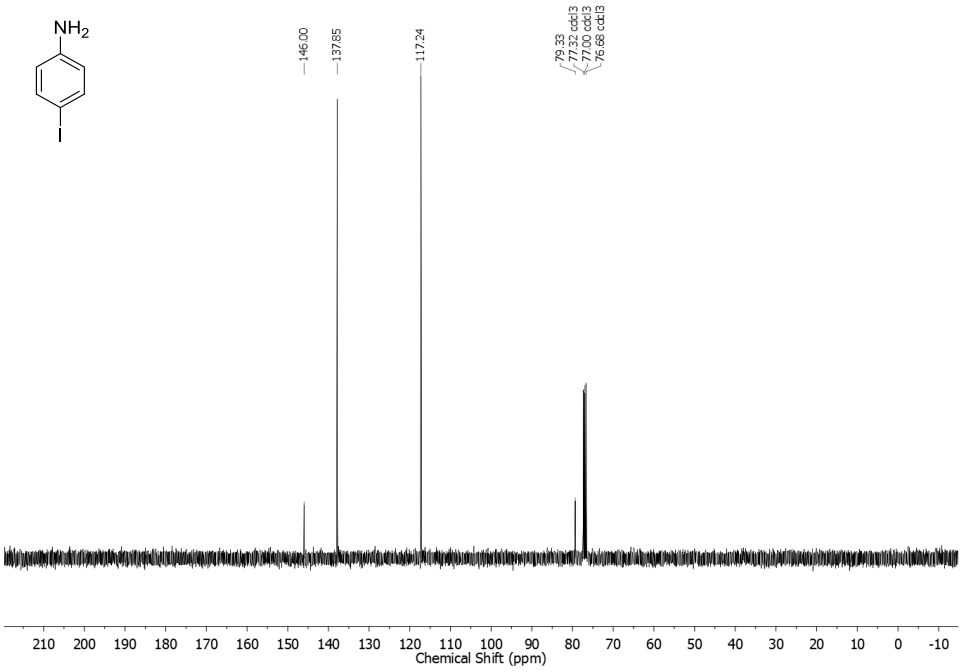
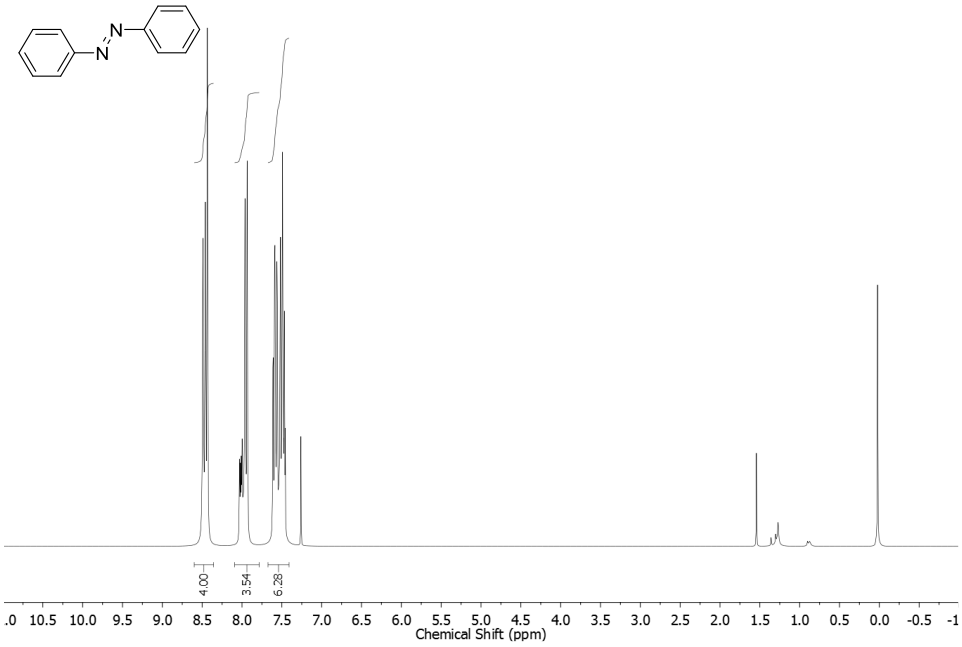
4.00
4.89
11.36
Chemical Shift (ppm)


C4H9 C4H9
O
I
I
150.38
130.47
128.91
128.90
127.32
117.93
115.30
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
45.20
42.71
29.70
26.91
22.86
22.82
13.84
Chemical Shift (ppm)


NH2
I
1.82
2.00
2.44
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
Chemical Shift (ppm)


NH2
I
146.00
137.85
117.24
79.33
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


4.00
3.54
6.28
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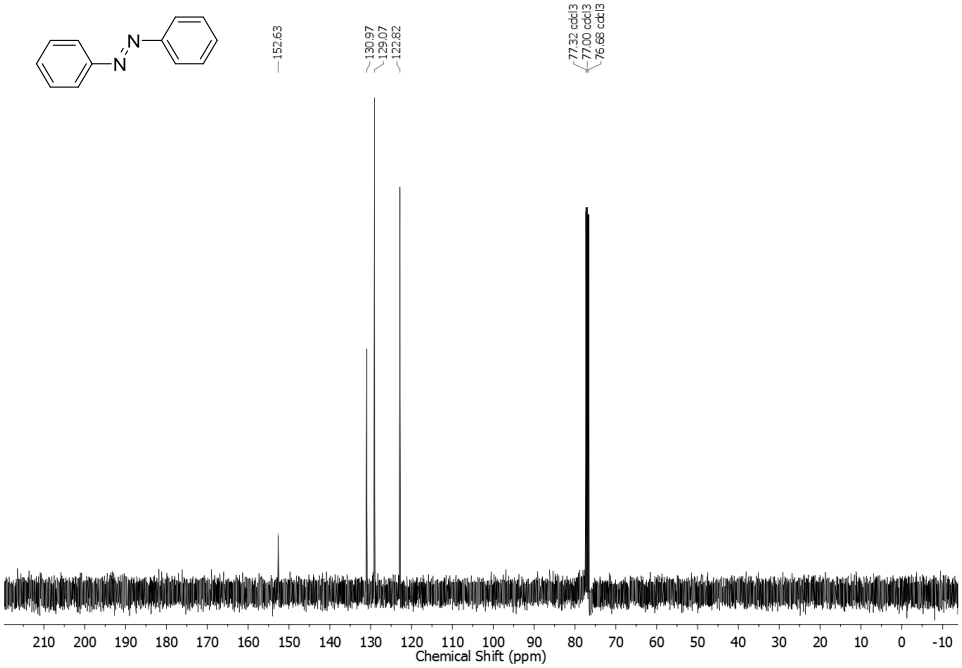
Chemical Shift (ppm)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130.97
129.07
122.82
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
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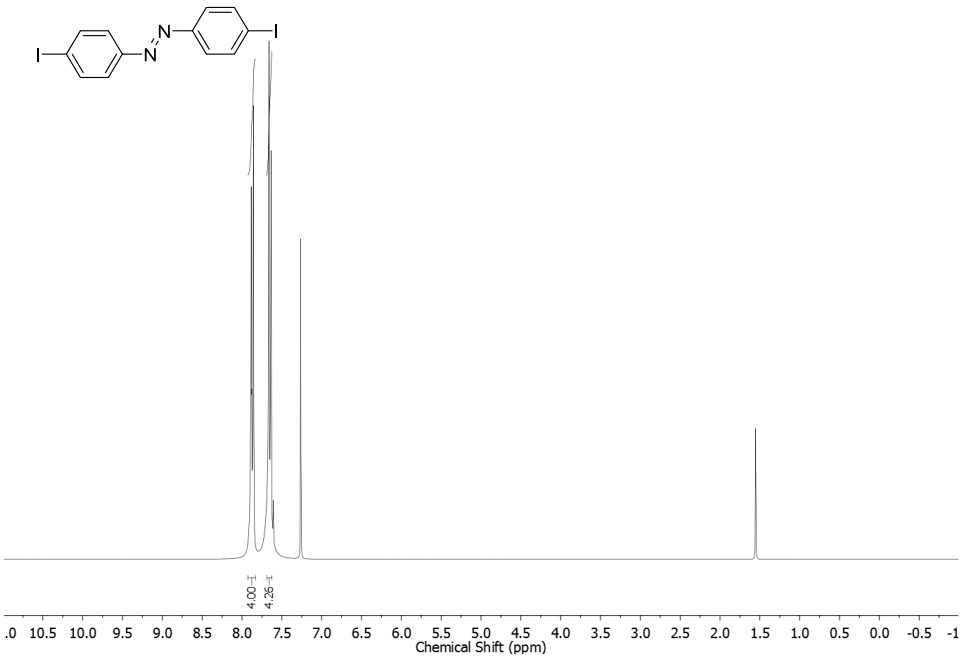
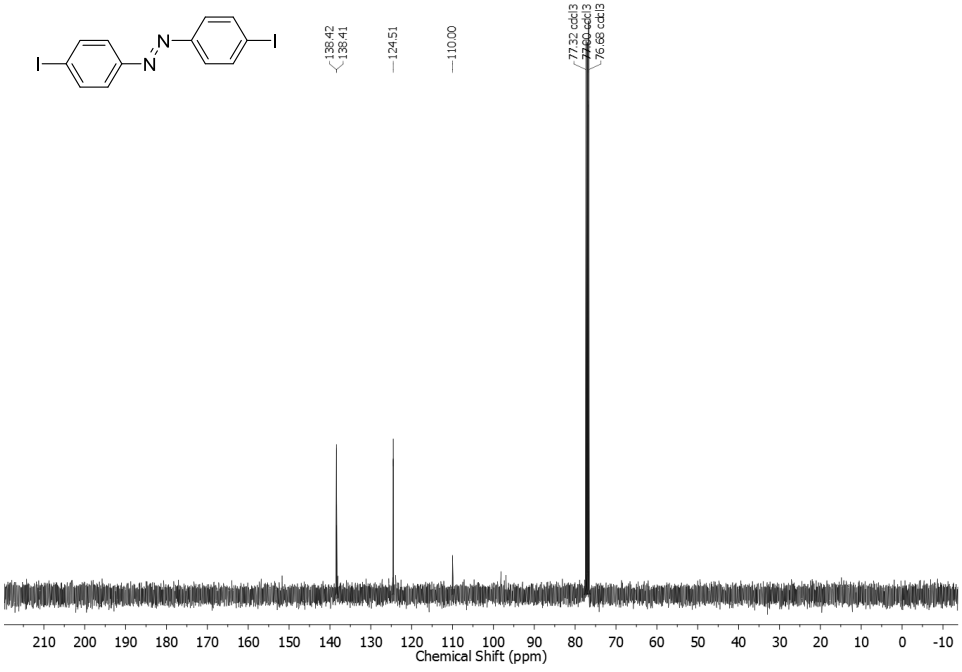
Chemical Shift (ppm)


I
N
N
I
4.00
4.26
Chemical Shift (ppm)


I
N
N
I
138.42
138.41
124.51
110.00
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
Chemical Shift (ppm)

CHAPTER V

EXPERIMENTALS FOR CHAPTER II: STERICALLY DIRECTED IRIDIUM-CATALYZED HYDROSILYLATION OF ALKENES IN THE PRESENCE OF ALKYNES

5.1 Methods: Unless stated otherwise, all reactions were carried out in oven dried or flame dried glassware under an atmosphere of argon with magnetic stirring. Reactions were monitored by thin-layer chromatography with 0.25 mm precoated silica gel plates or by gas chromatography. Visualization of all TLCs was performed by UV and/or staining with phosphomolybdic acid, $KMnO_4$, or Seebach's stain. Purifications were performed by silica gel flash chromatography with silica gel (Silicycle, 60 Å, 230-400 mesh) packed in glass columns and eluting with hexanes:Et_2O unless otherwise noted.

5.2 Materials: Tetrahydrofuran was freshly distilled from sodium/benzophenone under argon. Dichloromethane and 1,2-dichloroethane were freshly distilled from calcium hydride under argon. All other reagents and solvents were reagent grade and used without further purification unless otherwise stated. Benzyl allyl ether,[201] allyl tetrahydropyranyl ether,[202] *t*-butyldimethylsilyl propargyl ether,[203] pent-4-en-1-yl 4-methylbenzenesulfonate,[204] and (E)-1-(allyloxy)but-2-ene[205] were prepared using standard literature procedures. The remaining substrates were purchased and thoroughly degassed before use in the hydrosilylation reactions. **All solvents and reagents were degassed by either purging with argon or by standard freeze-thaw methods**

5.3 Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Inova 400 MHz NMR spectrometer or a Bruker Avance 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) with chemical shifts reported relative to residual chloroform solvent peaks (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C). Data for ^{1}H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet, m = multiplet, or unresolved), coupling constant(s) in Hz. IR spectra were obtained as thin films on a Perkin Elmer 2000 FTIR spectrometer using NaCl plates. High Resolution Mass Spectra (HRMS) were determined using a Thermo LTQ-OrbitrapXL mass spectrometer operated in FT mode to provide a nominal resolution of 100,000.

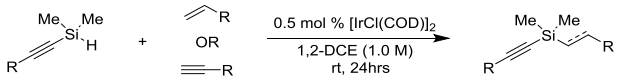
5.4 General Procedure A for Preparation of Alkynyl-Silanes

A flame-dried, 50-mL, round-bottomed flask was charged with 1 equivalent of terminal alkyne (10 mmol) in dry THF (20 mL), followed by attaching a balloon of argon. The flask was placed in an ice bath and the mixture was cooled to 0 °C. Once equilibrated, EtMgBr (12 mmol, 3 M solution in Et_2O) was added dropwise. After complete addition, the mixture was stirred for 5 min and then warmed to room temperature. After cooling to 0 °C, dimethylchlorosilane (14 mmol) was added dropwise to the reaction mixture. After stirring for 15 min at 0 °C the mixture was warmed to room temperature and stirred for 4 h. The reaction was quenched with saturated NH_4Cl (aq). The solution was extracted 3 times (Et_2O) and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The crude material was purified by flash chromatography using DCM as the eluting solvent.

5.5 Representative Solvent Screening Procedure:

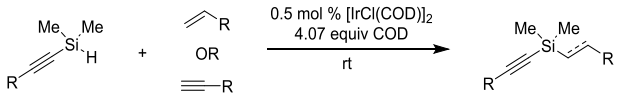
To a dry, 10-mL, round-bottomed flask under argon were sequentially added $[Ir(COD)Cl]_2$ (0.005 mmol, 0.0034 g), COD (0-0.5 mmol, 0-0.25 mL), 1-hexene (1.0 mmol, 0.124 mL), DCE (0.2-1 M, 1-5 mL), and dimethyl(phenylethynyl)silane (1.0 mmol, 0.172 mL). The reaction was stirred for 24 hrs and then an aliquot was analyzed by GC after the reaction was done. The reaction was concentrated *in vacuo* and the crude product was purified by flash chromatography (hexanes:Et_2O; 95:1) to afford 0.227 g (93%) of hexyldimethyl(phenylethynyl)silane as a light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.30- 7.28 (m, 3H), 1.41-1.29 (m, 8H), 0.89 (t, J = 9.5 Hz, 3H), 0.74-0.64 (m, 2H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 128.4, 128.2, 123.2, 105.4, 93.6, 32.9, 31.6, 23.8, 22.6, 16.2, 14.1, -1.7; IR (neat) 3080, 3057, 3033, 2957, 2922, 2855, 2158, 1956, 1877, 1802, 1670, 1598, 1573, 1555, 1488, 1466, 1443, 1409, 1249, 1219, 840 cm^{-1}. HRMS (ESI) Calcd for $C_{16}H_{25}Si$ $[M+H]^+$: 245.1720, Found: 245.1739.

5.6 General Procedure B for Initial Screening Process for Hydrosilylation of Alkenes or Alkynes:



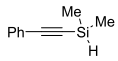
A dry, 10-mL, round-bottomed flask was charged with $[IrCl(COD)]_2$ (0.005 mmol, 0.0034 g), sealed with a septum, and evacuated and refilled with argon three times. A balloon of argon was attached to the flask followed by the sequential addition of 1,2-DCE 1mL, alkene/alkyne (1.0 mmol), and then silane (1.0 mmol) (if any reagent was a solid, it was added to the flask with the iridium catalyst). The reaction was stirred at room temperature for 24 h and monitored by TLC analysis. The reaction was concentrated, and the crude material was purified by flash chromatography.

5.7 General Procedure C for the Hydrosilylation of Alkenes or Alkynes after System Re-Optimization

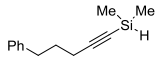


A dry, 10-mL, round-bottomed flask was charged with $[IrCl(COD)]_2$ (0.005 mmol, 0.0034 g), sealed with a septum, and evacuated and refilled with argon three times. A balloon of argon was attached to the flask followed by the sequential addition of 1,5-cyclooctadiene (4.07 mmol, 0.5 mL), alkene/alkyne (1.0 mmol), and then silane (1.0 mmol) (if any reagent was a solid it was added to the flask with the iridium catalyst). The reaction was stirred at room temperature until complete as monitored by GC analysis. The reaction was concentrated, and the crude material was purified by flash chromatography.

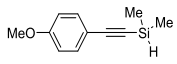
5.9 Compounds Synthesized and Characterization Data



Preparation of Dimethyl(phenylethynyl)silane: Following general procedure A, phenyl acetylene (70.0 mmol, 7.74 mL) was reacted to afford 11.22 g (98%) of dimethyl(phenylethynyl)silane as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.33-7.28 (m, 3H), 4.28 (sept, *J* = 4.0 Hz, 1H), 0.33 (d, *J* = 4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 128.7, 128.2, 122.8, 106.4, 91.1, -3.0. Physical and spectral data were consistent with those reported in the literature.[206]

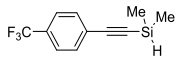


Preparation of Dimethyl(5-phenylpent-1-yn-1-yl)silane: Following general procedure A, 5-phenyl-1-pentyne (50.0 mmol, 7.59 mL) was reacted to afford 10.03 g (99%) of dimethyl(5-phenylpent-1-yn-1-yl)silane as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 2H), 7.26-7.16 (m, 3H), 4.16 (m, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.27 (td, *J* = 7.1, 1.2 Hz, 2H), 1.87 (p, *J* = 7.1 Hz, 2H), 0.26 (d, *J* = 3.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 128.5, 128.4, 125.9, 108.6, 82.0, 34.7, 30.0, 19.3, -2.7. Physical and spectral data were consistent with those reported in the literature.[207]

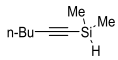


Preparation of ((4-Methoxyphenyl)ethynyl)dimethylsilane: Following general procedure A, ethynylanisole (10.0 mmol, 1.30 mL) was reacted to afford 1.89 g (99%) of ((4-methoxyphenyl)ethynyl)dimethylsilane as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (d, J = 8.6 Hz, 2H), 6.86-6.78 (d, *J* = 9.4 Hz, 2H), 4.26 (s, *J* = 3.8 Hz, 1H), 0.31 (d, *J* = 3.8 Hz, 6H);

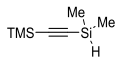
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 133.5, 114.9, 113.8, 106.5, 89.4, 55.2, -2.9. Physical and spectral data were consistent with those reported in the literature.[208]



Preparation of Dimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane: Following general procedure A, (4-(trifluoromethyl)phenylethyne (5.0 mmol, 0.82 mL) was reacted to afford 1.11 g (97%) of dimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane as a bright yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 4.29 (sept, *J* = 3.5 Hz, 1H), 0.34 (d, *J* = 3.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 130.2, 126.6, 125.2, 122.5, 104.6, 94.1, -3.2; IR (neat) 3054, 2967, 2641, 2165, 1923, 1678, 1614, 1573, 1513, 1405, 1323, 1296, 1253, 1016, 884, 842 cm^{-1}. HRMS (ESI) Calcd for $C_{11}H_{12}F_3Si$ $[M+H]^+$: 229.0655, Found: 229.0671.

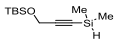


Preparation of Hex-1-yn-1-yldimethylsilane: Following general procedure A, 1-hexyne (20.0 mmol, 2.31 mL) was reacted to afford 2.05 g (98%) of hex-1-yn-1-yldimethylsilane as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (sept, *J* = 3.9 Hz, 1H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.51 (sex, *J* = 7.0, 7.8, 2.3 Hz, 2H), 1.4 (quin, *J* = 7.8, Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.22 (d, *J* = 3.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.2, 81.2, 30.6, 21.9, 19.6, 13.6, -2.7. Physical and spectral data were consistent with those reported in literature.[209]

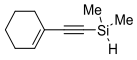


Preparation of ((Dimethylsilyl)ethynyl)trimethylsilane: Following general procedure A, trimethylsilyl acetylene (10.0 mmol, 1.41 mL) was reacted to afford 1.53 g (98%) of ((dimethylsilyl)ethynyl)trimethylsilane as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (sept, *J* =

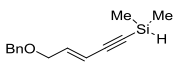
3.9 Hz, 1H), 0.24 (d, *J* = 3.9 Hz, 6H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.7, 110.5, -0.2, -3.0. Physical and spectral data were consistent with those reported in literature.[210]



Preparation of *tert*-Butyl((3-(dimethylsilyl)prop-2-yn-1-yl)oxy)dimethylsilane: Following general procedure A, *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (10.0 mmol, 1.75 mL) was reacted to afford 1.87 g (82%) of *tert*-butyl ((3-(dimethylsilyl) prop-2-yn-1-yl)oxy)dimethylsilane as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (s, 2H), 4.12 (sept, *J* =3.9 Hz,1H), 0.91 (s, 9H), 0.24 (d, *J* =3.9 Hz, 6H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.9, 86.7, 52.2, 25.8, 18.3, -3.2, -5.1; IR (neat) 2929, 2898, 2858, 2711, 2180, 2141, 1472, 1463, 1408, 1390, 1361, 1255, 1099, 1004, 938, 883 cm^{-1}. HRMS (ESI) Calcd for $C_{11}H_{25}OSi_2$ $[M+H]^+$: 229.1438, Found: 229.1430.

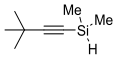


Preparation of (Cyclohex-1-en-1-ylethynyl)dimethylsilane: Following general procedure A, cyclohex-1-en-1-ylethyne (3.0 mmol, 0.35 mL) was reacted to afford 0.37 g (93%) of (cyclohex-1-en-1-ylethynyl)dimethylsilane as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (m, 1H), 4.18 (sept, *J* = 3.9 Hz, 1H), 2.14-2.06 (m, 4H), 1.64-1.55 (m, 4H), 0.24 (d, *J* = 3.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 120.6, 108.6, 87.8, 28.9, 25.7, 22.2, 21.4, -2.8. Physical and spectral data were consistent with those reported in literature.[211]

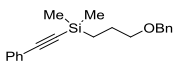


Preparation of (*E*)-(5-(Benzyloxy)pent-3-en-1-yn-1-yl)dimethylsilane: A flame-dried, round-bottomed flask was charged with THF and cooled to 0 °C. Sodium hydride (11.0 mmol, 0.44 g, 80%

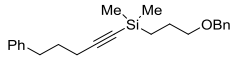
dispersion) was added quickly, and trans-2-penten-4-yn-1-ol (10.0 mmol, 0.93 mL) was added dropwise over 3-5 min. The resulting solution was stirred for 30 min, and benzyl bromide (11.0 mmol, 1.14 mL) was added dropwise. After stirring for 15 min, the reaction was allowed to warm to room temperature and stirred an additional 24h. The reaction was diluted with Et_2O and quenched with saturated NH_4Cl. The layers were separated, and the organic layer was washed with brine, dried ($MgSO_4$), filtered, and concentrated. The crude product was passed through a silica gel plug with hexanes:EtOAc; (9:/5) as eluent and concentrated. The crude (*E*)-((pent-2-en-4-yn-1-yloxy)-methyl)benzene (10.0 mmol, 1.72 g) was subjected to general procedure A without further purification to afford 2.27 g (98%) of (*E*)-(5-(benzyloxy)pent-3-en-1-yn-1-yl)dimethylsilane as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.23 (m, 5H), 6.37-6.25 (ddt, *J* = 15.6, 5.5, 2.3 Hz, 1H), 5.82 (dm, *J* = 18.0 Hz, 1H), 4.53 (s, 2H), 4.21 (m, 1H), 4.08 (dt, *J* = 5.5, 1.9 Hz, 2H), 0.32-0.23 (dd, *J* = 3.8, 1.9 Hz , 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.9, 128.4, 127.7, 127.6, 111.2, 104.4, 92.0, 72.3, 69.5, -3.1; IR (neat) 3031, 2133, 1632, 1454, 1251, 953, 882, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{19}OSi$ $[M+H]^+$: 231.1200, Found: 231.1192.



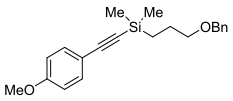
Preparation of (3,3-Dimethylbut-1-yn-1-yl)dimethylsilane: Following general procedure A, 3,3-dimethylbut-1-yne (10.0 mmol, 1.23 mL) was reacted to afford 1.09 g (78%) of (3,3-dimethylbut-1-yn-1-yl)dimethylsilane as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (sept, *J* =5.1 Hz, 1H), 1.22 (s, 9H), 0.20 (d, *J* = 5.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.4, 78.9, 30.9, 28.2, -2.6. Physical and spectral data were consistent with those reported in literature.[212]



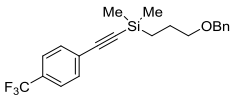
Preparation of (3-(Benzyloxy)propyl)dimethyl(phenylethynyl)silane: Allyl benzyl ether (1.0 mmol, 0.147 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.172 mL) were subjected to general hydrosilylation procedure to afford 0.271 g (88%) of (3-(Benzyloxy)propyl)dimethyl(phenylethynyl)-silane as a light brown oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.38-7.28 (m, 8H), 4.55 (s, 2H), 3.54 (t, *J* = 7.0 Hz, 2H), 1.82 (q, *J* = 6.6 Hz, 2H), 0.82 – 0.72 (m, 2H), 0.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 131.9, 128.5, 128.3, 128.1, 127.6, 127.4, 123.0, 105.7, 93.0, 72.9, 72.8, 24.1, 12.3, -1.8; IR (neat) 3081, 3063, 3032, 2956, 2931, 2850, 2790, 2246, 2147, 1949, 1880, 1805, 1771, 1671, 1652, 1647, 1598, 1574, 1553, 1540, 1522, 1506, 1494, 1488, 1454, 1443, 1412, 1250, 1099, 910, 847 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{25}OSi$ $[M+H]^+$: 309.1669, Found: 309.1662.



Preparation of (3-(Benzyloxy)propyl)dimethyl(5-phenylpent-1-yn-1-yl)silane: Allyl benzyl ether (1.0 mmol, 0.154 mL) and dimethyl(5-phenylpent-1-yn-1-yl)silane (1.0 mmol, 0.321 mL) were subjected to general hydrosilylation procedure Cto afford 0.273 g (78%) of (3-(Benzyloxy)propyl)-dimethyl(5-phenylpent-1-yn-1-yl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.22 (m, 7H), 7.24-7.13 (m, 3H), 4.52 (m, 2H), 3.49 (td, *J* = 6.9, 0.9 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.24 (td, *J* = 7.1, 0.8 Hz, 2H), 1.84 (q, *J* = 7.1 Hz, 2H), 1.78 – 1.70 (m, 2H), 0.70 – 0.60 (m, 2H), 0.16 (d, *J* = 1.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.7, 128.5, 128.32, 128.31, 127.6, 127.4, 125.9, 107.7, 83.9, 73.0, 72.8, 34.7, 30.2, 24.2, 19.3, 12.5, -1.6; IR (neat) 3085, 3063, 3027, 2172, 1949, 1875, 1807, 1602, 1584, 1274, 1250, 839, 699 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{31}OSi$ $[M+H]^+$: 351.2139, Found: 351.2131.

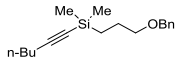


Preparation of (3-(Benzyloxy)propyl)((4-methoxyphenyl)ethynyl)dimethylsilane: Allyl benzyl ether (1.0 mmol, 0.154 mL) and ((4-methoxyphenyl)ethynyl)dimethylsilane (1.0 mmol, 0.231 mL) were subjected to general hydrosilylation procedure C to afford 0.299 g (88%) of (3-(Benzyloxy)-propyl)((4-methoxyphenyl)ethynyl)dimethylsilane as a yellow-green oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.23 (m, 7H), 6.88-6.77 (m, 2H), 4.53 (s, 2H), 3.81 (s, 3H), 3.51 (t, *J* = 6.8 Hz, 2H), 1.84-1.71 (m, 2H), 0.77-0.67 (m, 2H), 0.22 (d, *J* = 1.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 138.6, 133.4, 128.3, 127.6, 127.4, 115.2, 113.8, 105.8, 91.3, 73.0, 72.8, 55.2, 24.1, 12.4, -1.7; IR (neat) 3031, 3003, 2956, 2932, 2854, 2154, 1605, 1508, 1249, 1171, 1032, 832, 773, 736, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{27}O_2Si$ $[M+H]^+$: 339.1775, Found: 339.1747.

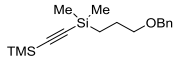


Preparation of (3-(Benzyloxy)propyl)dimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane: Allyl benzyl ether (1.0 mmol, 0.147 mL) and ((4-(trifluoromethyl)phenyl)ethynyl)silane (1.0 mmol, 0.195 mL) were subjected to general hydrosilylation procedure C to afford 0.331 g (88%) of (3-(Benzy-loxy)propyl)dimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane as an orange-brown oil after flash chromatography (hexanes:Et_2O; 95:5);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 4H), 7.47-7.28 (m, 5H), 4.55 (s, 2H), 3.51 (t, *J* = 7.0 Hz, 2H), 1.82-1.74 (m, 2H), 0.81-0.69 (m, 2H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 132.2, 128.3, 127.6, 127.5, 125.2, 125.12, 125.08, 125.05, 104.0, 96.2, 72.87, 72.85, 24.1, 12.2, -1.9; IR (neat) 3088, 3065, 3031, 2958, 2932, 2856, 2791, 2245, 1947, 1922,

1747, 1678, 1614, 1570, 1538, 1512, 1496, 1478, 1455, 1405, 1362, 1251, 1235, 994, 955, 909, 846 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{24}F_3OSi$ $[M+H]^+$: 377.1543, Found: 377.1528.

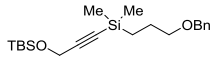


Preparation of (3-(Benzyloxy)propyl)(hex-1-yn-1-yl)dimethylsilane: Allyl benzyl ether (1.0 mmol, 0.136 mL) and hex-1-yn-1-yldimethylsilane (1.0 mmol, 0.157 mL) were subjected to general hydrosilylation procedure C to afford 0.248 g (86%) of (3-(Benzyloxy)propyl)(hex-1-yn-1-yl)-dimethylsilane as a khaki-yellowish oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 4.53 (s, 2H), 3.49 (t, *J* = 7.0 Hz, 2H), 2.23 (t, *J* = 6.6 Hz, 2H), 1.77-1.69 (m, 2H), 1.53-1.37 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.69-0.59 (m, 2H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.3, 127.6, 127.4, 108.3, 83.1, 73.0, 72.8, 30.7, 24.1, 21.9, 19.5, 13.6, 12.5, -1.6; IR (neat) 3088, 3065, 3031, 2958, 2932, 2861, 2790, 2244, 2173, 1947, 1870, 1807, 1603, 1585, 1559, 1496, 1466, 1453, 1412, 1362, 1249, 980, 951, 910, 861, 839 cm^{-1}. HRMS (ESI) Calcd for $C_{18}H_{29}OSi$ $[M+H]^+$: 289.1982, Found: 289.1975.

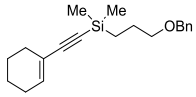


Preparation of (3-(Benzyloxy)propyl)dimethyl((trimethylsilyl)ethynyl)silane: Allyl benzyl ether (1.0 mmol, 0.147 mL) and ((dimethylsilyl)ethynyl)trimethylsilane (1.0 mmol, 0.136 mL) were subjected to general hydrosilylation procedure C to afford 0.271 g (94%) of (3-(Benzyloxy)-propyl)dimethyl((trimethylsilyl)ethynyl)silane as a khaki oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 4.51 (s, 2H), 3.48 (t, *J* = 7.0 Hz, 2H), 1.70 (m, 2H), 0.71-0.57 (m, 2H), 0.16 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.3, 127.6, 127.5, 114.6, 112.7, 72.9, 72.8, 24.0, 12.2, -0.1, -1.8; IR (neat) 3088, 3065, 3031, 2959, 2932, 2855, 2790, 2244, 2104, 1947, 1869, 1807, 1669, 1603, 1587, 1558, 1539, 1477, 1455,

1409, 1361, 1250, 1100, 992, 909, 840 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{29}OSi_2$ $[M+H]^+$: 305.1751, Found: 305.1742.

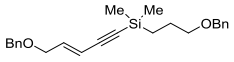


Preparation of 6,6,11,11,12,12-Hexamethyl-1-phenyl-2,10-dioxa-6,11-disilatridec-7-yne: Allyl benzyl ether (1.0 mmol, 0.147 mL) and tert-butyl((3-(dimethylsilyl)prop-2-yn-1-yl)oxy)-dimethylsilane (1.0 mmol, 0.147 mL) were subjected to general hydrosilylation procedure C to afford 0.301 g (80%) of 6,6,11,11,12,12-hexamethyl-1-phenyl-2,10-dioxa-6,11-disilatridec-7-yne as a light brown oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 4.51 (s, 2H), 4.30 (s, 2H), 3.46 (t, *J* = 7.0 Hz, 2H), 1.74-1.66 (m, 2H), 0.90 (s, 9H), 0.69-0.59 (m, 2H), 0.15 (s, 6H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.3, 127.6, 127.5, 105.1, 88.6, 72.9, 72.8, 52.3, 25.8, 24.0, 18.3, 12.2, -2.0, -5.1; IR (neat) 3088, 3065, 3030, 2929, 2857, 2710, 2246, 2176, 1946, 1809, 1647, 1587, 1558, 1471, 1463, 1455, 1411, 1251, 1203, 1095, 910, 838 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{37}O_2Si_2$ $[M+H]^+$: 377.2327, Found: 377.2317.

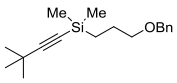


Preparation of (3-(Benzyloxy)propyl)(cyclohex-1-en-1-ylethynyl)dimethylsilane: Allyl benzyl ether (1.0 mmol, 0.136 mL) and cyclohex-1-en-1-ylethynyl)dimethylsilane (2.0 mmol, 0.230 mL) were subjected to general hydrosilylation procedure C to afford 0.228 g (82%) of (3-(benzyloxy)-propyl)(cyclohex-1-en-1-ylethynyl)dimethylsilane as a light yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.20 (m, 5H), 6.11 (m, 1H), 4.54 (s, 2H), 3.41 (t, *J* =7.0 Hz, 2H), 2.04 (m, 4H), 1.66 (m, 2H), 1.52 (m, 4H), 0.65-0.54 (m, 2H), 0.09 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.3, 128.3, 127.6, 127.4, 120.7, 108.0, 89.7, 73.0, 72.8, 29.1, 25.6, 24.1, 22.2, 21.4, 12.4, -1.6; IR (neat) 3087, 3064, 3029, 2930, 2858, 2790, 2245, 1946, 1874, 1807, 1722, 1684, 1626, 1903, 1586, 1558, 1539, 1495, 1476, 1454, 1412, 1348, 1249, 1165, 1100, 1044, 1028, 992, 967, 910, 864, 839 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{29}OSi$ $[M+H]^+$: 313.1982, Found: 313.1975.

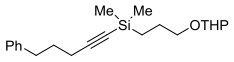


Preparation of (*E*)-(5-(benzyloxy)pent-3-en-1-yn-1-yl)(3-(benzyloxy)propyl)dimethylsilane: Allyl benzyl ether (1.0 mmol, 0.154 mL) and (*E*)-(5-(benzyloxy)pent-3-en-1-yn-1-yl)dimethylsilane (1.0 mmol, 0.210 mL) were subjected to general hydrosilylation procedure C to afford 0.243 g (64%) of (*E*)-(5-(benzyloxy)pent-3-en-1-yn-1-yl)(3-(benzyloxy)propyl)dimethylsilane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.23 (m, 10H), 6.26 (dt, *J* = 16.0, 5.4 Hz, 1H), 5.80 (dt, *J* = 16.0, 1.8 Hz, 1H), 4.52 (s, 4H), 4.07 (dd, *J* = 5.4, 1.8 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 1.73 (m, 2H), 0.75-0.63 (m, 2H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.6, 137.9, 128.4, 128.3, 127.7, 127.63, 127.62, 127.5, 111.5, 103.7, 94.1, 72.9, 72.8, 72.2, 69.6, 24.1, 12.3, -1.8; IR (neat) 3030, 2855, 2173, 2131, 1720, 1714, 1600, 1454, 1250, 954, 840, 774 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{31}O_2Si$ $[M+H]^+$: 379.2088, Found: 379.2075.

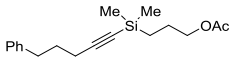


Preparation of (3-(Benzyloxy)propyl)(3,3-dimethylbut-1-yn-1-yl)dimethylsilane: Allyl benzyl ether (1.0 mmol, 0.154 mL) and (3,3-dimethylbut-1-yn-1-yl)dimethylsilane (1.0 mmol, 0.097 mL) were subjected to general hydrosilylation procedure C to afford 0.109 g (75%) of (3-(benzyloxy)propyl)(3,3-dimethylbut-1-yn-1-yl)dimethylsilane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 4.52 (s,

2H), 3.48 (t, *J* = 6.9 Hz, 2H), 1.80-1.62 (m, 2H), 1.21 (s, 9H), 0.63-0.57 (m, 2H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.3, 127.6, 127.4, 116.7, 80.6, 73.1, 72.8, 31.0, 28.1, 24.1, 12.6, -1.4; IR (neat) 3340, 3065, 3033, 2869, 2193, 2153, 1721, 1705, 1362, 1274, 1251, 1100, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{27}O_2Si$ [M+H]$^+$: 289.1982, Found: 289.1986.

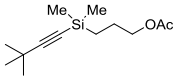


Preparation of Dimethyl(5-phenylpent-1-yn-1-yl)(3-((tetrahydro-2H-pyran-2-yl)oxy)propyl)silane: 2-Allyloxytetrahydropyran (1.0 mmol, 0.147 mL) and dimethyl(5-phenylpent-1-yn-1-yl)silane (1.0 mmol, 0.321 mL) were subjected to general hydrosilylation procedure C to afford 0.278 g (81%) of dimethyl(5-phenylpent-1-yn-1-yl)(3-((tetrahydro-2H-pyran-2-yl)oxy)propyl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.23-7.14 (m, 3H), 4.59 (dd, *J* = 4.5, 2.8 Hz, 1H), 3.88 (m, 1H), 3.73 (dt, *J* = 9.5, 7.1 Hz, 1H), 3.54-3.45 (m, 1H), 3.40 (dt, *J* = 9.5, 7.0 Hz, 1H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 1.83 (p, *J* = 7.5 Hz, 2H), 1.75-1.66 (m, 4H), 1.62-1.44 (m, 4H), 0.71-0.54 (m, 2H), 0.15 (d, *J* = 0.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 128.5, 128.3, 125.8, 107.7, 98.8, 83.9, 70.2, 62.4, 34.7, 30.8, 30.2, 25.5, 24.2, 19.7, 19.3, 12.5, -1.6; IR (neat) 3026, 2941, 2869, 2172, 1603, 1454, 1249, 1201, 1182, 1078, 869, 839, 815, 773 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{33}O_2Si$ [M+H]$^+$: 345.2244, Found: 345.2252.

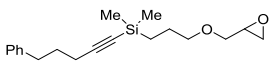


Preparation of 3-(Dimethyl(5-phenylpent-1-yn-1-yl)silyl)propyl acetate: Allyl acetate (1.0 mmol, 0.108 mL) and dimethyl(5-phenylpent-1-yn-1-yl)silane (1.0 mmol, 0.321 mL) were subjected to general hydrosilylation procedure C to afford 0.181 g (60%) of 3-(dimethyl(5-phenylpent-1-yn-1-

yl)silyl)propyl acetate as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 2H), 7.23-7.14 (m, 3H), 4.06 (t, *J* = 7.0 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.04 (d, *J* = 0.5 Hz, 3H), 1.84 (p, *J* = 7.7 Hz, 2H), 1.77-1.68 (m, 2H), 0.67-0.56 (m, 2H), 0.16 (d, *J* = 0.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 141.5, 128.5, 128.3, 125.9, 108.0, 83.5, 66.8, 34.7, 30.2, 23.2, 21.0, 19.3, 12.3, -1.6; IR (neat) 3027, 2952, 2172, 1741, 1603, 1454, 1237, 840, 772 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{27}O_2Si$ $[M+H]^+$: 303.1775, Found: 303.1782.

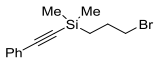


Preparation of 3-((3,3-Dimethylbut-1-yn-1-yl)dimethylsilyl)propylacetate: Allyl acetate (1.0 mmol, 0.108 mL) and (3,3-dimethylbut-1-yn-1-yl)dimethylsilane (1.0 mmol, 0.097 mL) were subjected to general hydrosilylation procedure C to afford 0.045 g (37%) of 3-((3,3-dimethylbut-1-yn-1-yl)dimethylsilyl)propyl acetate as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 4.05 (t, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.75-1.63 (m, 2H), 1.20 (s, 9H), 0.62-0.52 (m, 2H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 117.0, 80.2, 66.9, 31.0, 28.1, 23.2, 21.0, 12.4, -1.5; IR (neat) 2969, 2153, 1744, 1457, 1385, 1363, 1250, 1236, 840, 772 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{25}O_2Si$ $[M+H]^+$: 241.1618, Found: 241.1634.

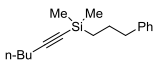


Preparation of Dimethyl(3-(oxiran-2-ylmethoxy)propyl)(5-phenylpent-1-yn-1-yl)silane: Allyl glycidyl ether (1.0 mmol, 0.118 mL) and dimethyl(5-phenylpent-1-yn-1-yl)silane (1.0 mmol, 0.321 mL) were subjected to general hydrosilylation procedure C to afford 0.264 g (83%) of dimethyl(3-

(oxiran-2-ylmethoxy)propyl)(5-phenylpent-1-yn-1-yl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.23-7.14 (m, 3H), 3.71 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.49 (qt, *J* = 9.2, 6.9 Hz, 2H), 3.39 (dd, *J* = 11.5, 5.8 Hz, 1H), 3.19-3.10 (m, 1H), 2.79 (dd, *J* = 5.0, 4.1 Hz, 1H), 2.72 (dd, *J* = 7.9, 7.3 Hz, 2H), 2.60 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.83 (d, *J* = 7.2 Hz, 2H), 1.78-1.62 (m, 2H), 0.69 - 0.56 (m, 2H), 0.15 (d, *J* = 0.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 128.5, 128.3, 125.8, 107.7, 83.8, 74.1, 71.4, 50.8, 44.3, 34.7, 30.2, 24.1, 19.3, 12.4, -1.6; IR (neat) 3085, 2999, 2932, 2172, 1603, 1250, 1108, 840, 772, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{29}O_2Si$ $[M+H]^+$: 317.1931, Found: 317.1927.

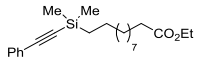


Preparation of (3-Bromopropyl)dimethyl(phenylethynyl)silane: Allyl bromide (1.0 mmol, 0.087 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.259 g (92%) of (3-bromopropyl)dimethyl(phenylethynyl)-silane as a yellow oil after flash chromatography (hexanes/Et_2O: 95/5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.41 (m, 2H), 7.37-7.24 (m, 3H), 3.46 (t, *J* = 7.0 Hz, 2H), 2.07-1.95 (m, 2H), 0.91-0.76 (m, 2H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 128.6, 128.2, 122.8, 106.1, 92.4, 36.8, 27.8, 15.4, -1.8; IR (neat) 3008, 3056, 3032, 2958, 2930, 2158, 1488, 1250, 845, 782, 757, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{18}BrSi$ $[M+H]^+$: 281.0356, Found: 281.0381.

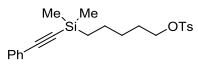


Preparation of Hex-1-yn-1-yldimethyl(3-phenylpropyl)silane: Allyl benzene (1.0 mmol, 0.132 mL) and hex-1-yn-1-yldimethylsilane (1.0 mmol, 0.157 mL) were subjected to general

hydrosilylation procedure C to afford 0.209 g (81%) of hex-1-yn-1-yldimethyl(3-phenylpropyl)silane as a light brown oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 7.26-7.22 (m, 3H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.28 (t, *J* = 6.6 Hz, 2H), 1.81-1.74 (m, 2H), 1.59-1.44 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.76-0.62 (m, 2H), 0.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.5, 128.2, 125.6, 108.3, 83.3, 39.5, 30.7, 25.9, 21.9, 19.6, 16.2, 13.6, -1.5; IR(neat) 3085, 3063, 3027, 2958, 2929, 2173, 1940, 1866, 1802, 1604, 1584, 1559, 1453, 1428, 1410, 1379, 1298, 1249, 860, 837, 788, 763, 745, 698 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{27}Si$ $[M+H]^+$: 259.1877, Found: 259.1877.

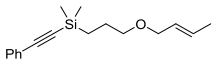


Preparation of Ethyl 11-(dimethyl(phenylethynyl)silyl)undecanoate: Ethyl undecylenoate (1.0 mmol, 0.242 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.304 g (82%) of ethyl 11-(dimethyl(phenylethynyl)silyl)-undecanoate as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.40 (m, 2H), 7.34-7.22 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.67-1.58 (m, 2H), 1.49-1.20 (m, 17H), 0.72-0.63 (m, 2H), 0.21 (d, *J* = 0.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 131.9, 128.4, 128.2, 123.2, 105.4, 93.5, 60.1, 34.4, 33.2, 29.50, 29.48, 29.3, 29.26, 29.1, 25.0, 23.8, 16.2, 14.3, -1.7; IR (neat) 2924, 2854, 2158, 1737, 1488, 1248, 844, 806, 757 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{37}O_2Si$ $[M+H]^+$: 373.2557, Found: 373.2545.

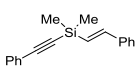


Preparation of 5-(Dimethyl(phenylethynyl)silyl)pentyl 4-methylbenzenesulfonate: Pent-4-en-1-yl 4-methylbenzenesulfonate (1.0 mmol, 0.182 mL) and dimethyl(phenylethynyl)silane (1.0 mmol,

0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.326 g (81%) of 5-(dimethyl(phenylethynyl)silyl)pentyl 4-methylbenzenesulfonate as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.50-7.41 (m, 2H), 7.38-7.18 (m, 5H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 1.71-1.58 (m, 2H), 1.47-1.32 (m, 4H), 0.68-0.58 (m, 2H), 0.20 (d, *J* = 0.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 133.2, 131.9, 129.8, 128.5, 128.2, 127.8, 123.0, 105.7, 93.1, 70.6, 28.8, 28.5, 23.2, 21.6, 15.9, -1.8; IR (neat) 3056, 2925, 2157, 1598, 1443, 1360, 1249, 1177, 843, 813, 733 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{29}O_3SSi$ $[M+H]^+$: 401.1601, Found: 401.1919.

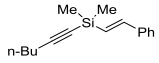


Preparation of (*E*)-(3-(but-2-en-1-yloxy)propyl)dimethyl(phenylethynyl)silane : (*E*)-1-(Allyloxy)but-2-ene (1.0 mmol, 0.10 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.071 g (26%) of (*E*)-(3-(but-2-en-1-yloxy)propyl)dimethyl(phenylethynyl)silane of (*E*)-(3-(but-2-en-1-yloxy)propyl)dimethyl-(phenylethynyl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 98:2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.39 (m, 2H), 7.39-7.24 (m, 3H), 5.83-5.52 (m, 2H), 3.91 (dt, *J* = 6.1, 1.2 Hz, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 1.88-1.61 (m, 5H), 0.79-0.59 (m, 2H), 0.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 129.2, 128.5, 128.2, 127.8, 123.1, 105.7, 93.1, 72.7, 71.5, 24.1, 17.8, 12.4, -1.8; IR (neat) 3079, 3056, 3017, 2930, 2854, 2158, 1671, 1488, 1443, 1249, 1104, 966, 847, 804 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{25}OSi$ $[M+H]^+$: 273.1669, Found: 273.1667.

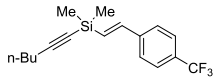


Preparation of (*E*)-dimethyl(phenylethynyl)(styryl)silane: Phenylacetylene (1.0 mmol, 0.110 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to the hydrosilylation

procedure C to afford 0.213 g (81%) of (*E*)-dimethyl(phenylethynyl)(styryl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56- 7.42 (m, 4H), 7.43-7.23 (m, 6H), 7.12 (dd, *J* = 19.0, 1.5 Hz, 1H), 6.49 (dt, *J* = 19.1, 1.9 Hz, 1H), 0.41 (d, *J* = 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 138.0, 132.0, 128.6, 128.5, 128.3, 128.2, 126.6, 125.5, 123.0, 106.3, 92.2, -1.0; IR (neat) 3079, 2158, 1604, 1249, 989, 845, 806 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{19}Si$ $[M+H]^+$: 263.1251, Found: 263.1243.

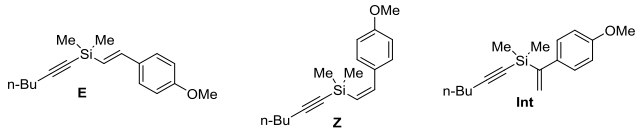


Preparation of (*E*)-hex-1-yn-1-yldimethyl(styryl)silane: Phenyl acetylene (1.0 mmol, 0.110 mL) and hex-1-yn-1-yldimethylsilane (1.0 mmol, 0.157 mL) were subjected to general hydrosilylation procedure C to afford 0.184 g (76%) of (*E*)-hex-1-yn-1-yldimethyl(styryl)silane as an orange oil after flash chromatography (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 9.0, 1.6 Hz, 2H), 7.35 (dd, *J* = 7.0, 1.6 Hz, 2H), 7.28 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.08 (d, *J* = 19.1 Hz, 1H), 6.46 (d, *J* = 18.8 Hz, 1H), 2.29 (t, *J* = 7.0 Hz, 2H), 1.50 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.1, 128.5, 128.2, 126.6, 126.2, 109.1, 82.3, 30.7, 21.9, 19.7, 13.6, -0.8; IR (neat) 3103, 3079, 3059, 3024, 2938, 2930, 2873, 2174, 2026, 1942, 1876, 1802, 1747, 1683, 1655, 1606, 1574, 1539, 1511 1505, 1494, 1466, 1446, 1428, 1248, 989, 850 cm^{-1}. HRMS (ESI) Calcd for $C_{16}H_{23}Si$ $[M+H]^+$: 243.1564, Found: 243.1556.



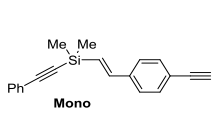
Preparation of (E)-hex-1-yn-1-yldimethyl(4-(trifluoromethyl)styryl)silane:
(Trifluoromethyl)phenyl-ethyne (1.0 mmol, 0.163 mL) and hex-1-yn-1-yldimethylsilane (1.0 mmol, 0.157 mL) were subjected to general hydrosilylation procedure C to afford 0.248 g (80%) of (*E*)-hex-1-yn-1-yldimethyl(4-(trifluoromethyl)styryl)silane as a yellow oil after flash chromatography (hexanes:EtO_2; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz,

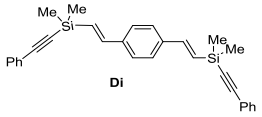
2H), 7.07 (d, *J* = 18.8 Hz, 1H), 6.55 (t, *J* = 19.1 Hz, 1H), 2.27 (t, *J* = 6.6 Hz, 2H), 1.58-1.39 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.4, 129.8, 126.7, 125.5, 125.43, 125.39, 109.6, 81.8, 30.7, 22.0, 19.6, 13.6, -1.0; IR (neat) 3010, 2960, 2932, 2874, 2175, 1917, 1614, 1574, 1558, 1555, 1467, 1429, 1250, 850, 822, 807 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{22}F_3Si$ $[M+H]^+$: 311.1437, Found: 311.1447.



Preparation of (*E*)-hex-1-yn-1-yl(4-methoxystyryl)dimethylsilane; (*Z*)-hex-1-yn-1-yl(4-methoxystyryl)dimethylsilane; hex-1-yn-1-yl(1-(4-methoxyphenyl)vinyl)dimethylsilane: (4-(methoxy)phenyl-ethyne (1.0 mmol, 0.130 mL) and hex-1-yn-1-yldimethylsilane (1.0 mmol, 0.157 mL) were subjected to general hydrosilylation procedure C to afford 0.199 g (73%, 74:19:7; *E*:*Z*:Int) of (*E*)-hex-1-yn-1-yl(4-methoxystyryl)dimethylsilane; (*Z*)-hex-1-yn-1-yl(4-methoxystyryl)dimethylsilane; hex-1-yn-1-yl(1-(4-methoxyphenyl)vinyl)dimethylsilane as an inseparable mixture of a yellow oil after flash chromatography (hexanes).[213,214,215] ***E*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 19.2 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.26 (d, *J* = 19.1 Hz, 1H), 3.82 (s, 3H), 2.26 (t, *J* = 7.04 Hz, 2H), 1.55-1.38 (m, 4H), 0.92 (t, *J* = 6.6Hz, 3H), 0.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.61, 131.1, 127.8, 113.82, 113.2, 108.93, 82.49, 55.25, 30.69, 21.93, 19.64, 13.61, -0.76; ***Z*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.69 (d, *J* = 16.2 Hz, 1H), 3.82 (s, 3H), 2.26 (t, *J* = 7.04 Hz, 2H), 1.55-1.38 (m, 4H), 0.92 (t, *J* = 6.6Hz, 3H), 0.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.59, 130.0, 123.3, 113.80, 113.18, 108.93, 82.47, 55.24, 30.67, 21.91, 19.64, 13.61, -0.77; **Int:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.91 (d, *J* = 4.0 Hz, 1H), 5.72 (d, *J* = 4.0 Hz, 1H), 3.81 (s, 3H), 2.22 (t, *J* = 6.6 Hz, 2H), 1.55-1.38 (m,

4H), 0.90 (t, *J* = 9.0 Hz, 3H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.2, 132.0, 126.8, 113.7, 113.5, 108.91, 83.6, 55.19, 30.58, 21.88, 19.62, 13.59, 0.05; IR (neat) 3061, 3031, 2958, 2872, 2835, 2173, 1990, 1885, 1770, 1683, 1606, 1571, 1558, 1554, 1538, 1508, 1504, 1464, 1441, 1428, 909, 842 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{25}OSi$ $[M+H]^+$: 273.1669, Found: 273.1661.

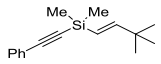




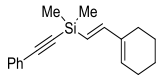
Preparation of (*E*)-(4-ethynylstyryl)dimethyl(phenylethynyl)silane and 1,4-bis((*E*)-2-(dimethyl(phenylethynyl)silyl)vinyl)benzene: 1,4-Diethynylbenzene (1.0 mmol, 0.1262 g) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.195 g (51%, 62:38, Di:Mono) of (*E*)-(4-ethynylstyryl)dimethyl-(phenylethynyl)silane and 1,4-bis((*E*)-2-(dimethyl(phenylethynyl)silyl)vinyl)benzene as an inseparable mixture of a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); **Di:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.39 (m, 8H), 7.38-7.22 (m, 6H), 7.08 (dd, *J* = 19.0, 1.2 Hz, 2H), 6.53 (dd, *J* = 19.0, 1.2 Hz, 2H), 0.41 (d, *J* = 1.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 138.3, 132.3, 132.0, 128.7, 128.2, 127.2, 126.9, 126.5, 125.7, 122.86, 121.8, 106.5, 91.8, -1.1; **Mono:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.39 (m, 6H), 7.38-7.22 (m, 3H), 7.11 (dd, *J* = 19.0, 1.4 Hz, 2H), 6.51 (dd, *J* = 19.0, 1.3 Hz, 2H), 3.14 (d, *J* = 1.1 Hz, 1H), 0.41 (d, *J* = 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 137.9, 132.1, 131.9, 128.6, 122.94, 106.4, 92.1, 83.6, 78.0, -1.0; IR (neat) 3079, 2960, 2159, 1602, 1488, 1251, 847, 798, 757 cm^{-1}; **Di:** HRMS (ESI) Calcd for $C_{30}H_{31}Si_2$ $[M+H]^+$: 447.1959, Found: 447.1942; **Mono:** HRMS (ESI) Calcd for $C_{20}H_{19}Si$ $[M+H]^+$: 287.1251, Found: 287.1241.

Preparation of (*E*)-(4-Ethynylstyryl)dimethyl(phenylethynyl)silane and 1,4-bis((*E*)-2-(dimethyl(phenylethynyl)silyl)vinyl)benzene: 1,4-Diethynylbenzene (1.0 mmol, 0.1262 g) and dimethyl(phenylethynyl)silane (2.0 mmol, 0.526 mL) to the general hydrosilylation procedure C afforded 0.3102 g (80%, 63:37, Di:Mono) of (*E*)-(4-ethynylstyryl)dimethyl-(phenylethynyl)silane and

1,4-bis((*E*)-2-(dimethyl(phenylethynyl)silyl)vinyl)benzene as an inseparable mixture of a yellow oil after flash chromatography (hexanes:Et_2O; 95:5). See above for spectral data.

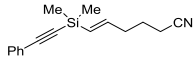


Preparation of (*E*)-(3,3-dimethylbut-1-en-1-yl)dimethyl(phenylethynyl)silane: 3,3-Dimethyl-1-butyne (1.0 mmol, 0.123 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.187 g (77%) of (*E*)-(3,3-dimethylbut-1-en-1-yl)dimethyl(phenylethynyl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.44 (m, 2H), 7.36-7.22 (m, 3H), 6.26 (dd, *J* = 18.9, 0.8 Hz, 1H), 5.65-5.51 (m, 1H), 1.03 (d, *J* = 0.7 Hz, 9H), 0.30 (d, *J* = 0.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 132.0, 128.5, 128.2, 123.2, 119.3, 105.7, 93.1, 35.2, 29.0, -0.9; IR (neat) 3081, 3057, 3033, 2960, 2159, 1613, 1488, 1362, 1248, 1235, 993, 842, 798, 750, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{23}Si$ $[M+H]^+$: 243.1564, Found: 243.1555.

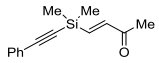


Preparation of (*E*)-(2-(cyclohex-1-en-1-yl)vinyl)dimethyl(phenylethynyl)silane: 1-Ethynyl-cyclohexene (1.0 mmol, 0.118 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) was subjected to general hydrosilylation procedure C to afford 0.237 g (87%) of (*E*)-(2-(cyclohex-1-en-1-yl)vinyl)dimethyl(phenylethynyl)silane as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.40 (m, 2H), 7.40-7.17 (m, 3H), 6.74 (d, *J* = 18.9 Hz, 1H), 5.90 (tt, *J* = 2.6, 1.4 Hz, 1H), 5.72 (d, *J* = 18.9 Hz, 1H), 2.18 (tq, *J* = 5.6, 2.4 Hz, 2H), 1.79-1.45 (m, 6H), 0.38 - 0.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 137.2, 132.2, 132.0, 128.5, 128.1,

123.1, 120.3, 105.9, 92.8, 26.0, 24.0, 22.5, 22.4, -0.9; IR (neat) 3076, 3057, 3019, 2929, 2158, 1633, 1249, 985, 847, 757, 734, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{23}Si$ $[M+H]^+$: 267.1564, Found: 267.1558.

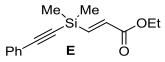


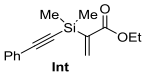
Preparation of (*E*)-6-(dimethyl(phenylethynyl)silyl)hex-5-enenitrile: 5-Cyano-1-pentyne (1.0 mmol, 0.105 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.129 g (51%) of (*E*)-6-(dimethyl(phenylethynyl)silyl)hex-5-enenitrile as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.42 (m, 2H), 7.38-7.27 (m, 3H), 6.20 (dt, *J* = 18.5, 6.3 Hz, 1H), 5.77 (dt, *J* = 18.5, 1.5 Hz, 1H), 2.56-2.25 (m, 4H), 1.82 (p, *J* = 7.3 Hz, 2H), 0.32-0.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 132.0, 129.0, 128.6, 128.2, 122.9, 119.5, 106.1, 92.2, 35.0, 24.1, 16.5, -1.1; IR (neat) 2958, 2247, 2158, 1618, 1488, 1249, 1220, 989, 841, 758, 691 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{20}NSi$ $[M+H]^+$: 254.1360, Found: 254.1351.



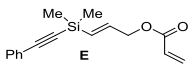
Preparation of (*E*)-4-(Dimethyl(phenylethynyl)silyl)but-3-en-2-one: Subjection of 3-butyn-2-one (1.0 mmol, 0.078 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.040 g (14%) of (*E*)-4-(dimethyl(phenylethynyl)-silyl)but-3-en-2-one as a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.40 (m, 2H), 7.39-7.27 (m, 3H), 7.01 (d, *J* = 19.1 Hz, 1H), 6.65 (d, *J* = 19.1 Hz, 1H), 2.32 (s, 3H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 144.3, 143.4, 132.0, 129.0,

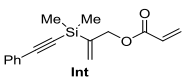
128.3, 122.4, 107.3, 90.1, 26.5, -1.7; IR (neat) 3058, 2159, 1697, 1679, 1594, 1443, 1252, 846, 811 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{17}OSi$ $[M+H]^+$: 229.1043, Found: 229.1037.





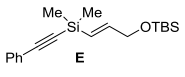
Preparation of Ethyl (*E*)-3-(dimethyl(phenylethynyl)silyl)acrylate and ethyl 2-(dimethyl(phenylethynyl)silyl)acrylate: Ethyl propiolate (1.0 mmol, 0.101 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford 0.028 g (11%, 43:56 *E*:Int) of ethyl (*E*)-3-(dimethyl(phenylethynyl)-silyl)acrylate and ethyl 2-(dimethyl(phenylethynyl)silyl)acrylate as an inseparable mixture of a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ***E*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.41 (m, 2H), 7.35-7.25 (m, 3H), 7.21 (d, *J* = 18.7 Hz, 1H), 6.44 (d *J* = 18.7 Hz, 1H), 4.20 (q *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 145.3, 142.0, 135.7, 132.0, 128.9, 128.24, 107.2, 90.2, 60.6, 14.2, -1.7; **Int:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.41 (m, 2H), 7.35-7.25 (m, 3H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.44 (d, *J* = 3.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 3H), 0.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.0, 132.0, 128.8, 128.24, 128.20, 122.5, 107.0, 91.2, 60.6, 14.2, -1.0; IR (neat) 3081, 3058, 3033, 2963, 2160, 1724, 1488, 1251, 1226, 849, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{19}O_2Si$ $[M+H]^+$: 259.1149, Found: 259.1141.



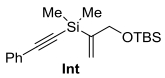


Preparation of (*E*)-3-(dimethyl(phenylethynyl)silyl)allyl acrylate and 2-(dimethyl(phenylethynyl)silyl)allyl acrylate: Propargyl acrylate (1.0 mmol, 0.110 mL) and

dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C to afford an inseparable mixture of 0.200 g (74%, 63:37 *E*:Int) of (*E*)-3-(dimethyl-(phenylethynyl)silyl)allyl acrylate and 2-(dimethyl(phenylethynyl)silyl)allyl acrylate as an inseparable mixture of a yellow oil after flash chromatography (hexanes:Et_2O; 95:5); ***E*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.40 (m, 2H), 7.38-7.20 (m, 3H), 6.46 (ddd, *J* = 17.3, 4.7, 1.5 Hz, 1H), 6.18 (ddd, *J* = 17.4, 10.4, 5.6 Hz, 2H), 6.01 (dtd, *J* = 18.6, 1.7, 0.7 Hz, 1H), 5.87 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.74 (ddd, *J* = 4.9, 1.7, 0.6 Hz, 2H), 0.33 (d, *J* = 0.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 141.4, 132.0, 131.1, 129.2, 128.7, 128.22, 128.19, 122.8, 106.4, 91.6, 66.4, -1.3; **Int:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.40 (m, 2H), 7.38-7.20 (m, 3H), 6.46 (ddd, *J* = 17.3, 4.7, 1.5 Hz, 1H), 6.35 (dtd, *J* = 18.6, 4.9, 0.7 Hz, 1H), 5.96-5.88 (m, 1H), 5.84 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.72 (dtd, *J* = 2.2, 1.4, 0.6 Hz, 1H), 4.92 (td, *J* = 1.6, 0.7 Hz, 2H), 0.38 (d, *J* = 0.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.75, 143.4, 132.0, 130.9, 128.7, 128.4, 128.15, 127.6, 122.7, 106.7, 91.0, 67.8, -1.5; IR (neat) 2961, 2159, 1727, 1624, 1251, 1184, 1050, 984, 848, 809, 758, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{19}O_2Si$ $[M+H]^+$: 271.1149, Found: 271.1140.



E

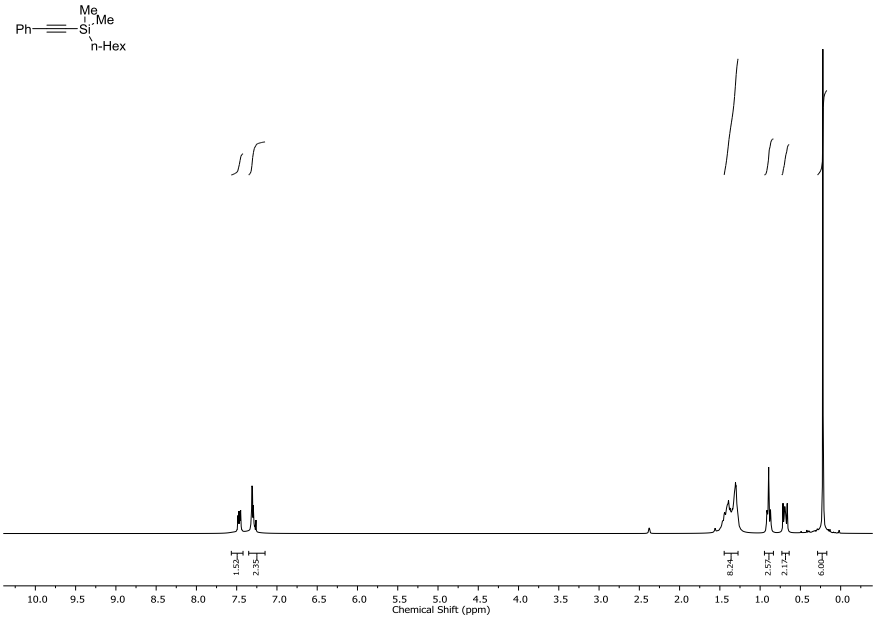


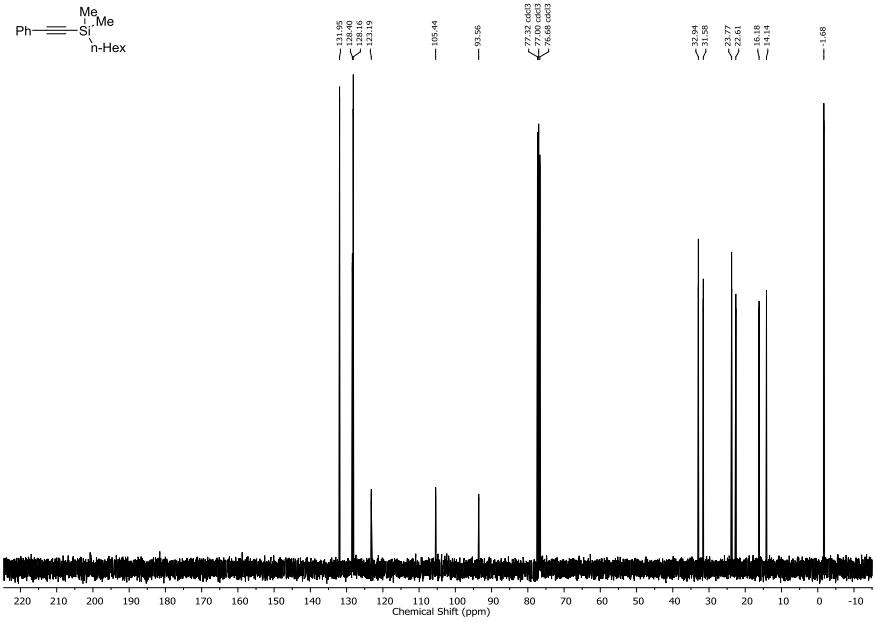
Int

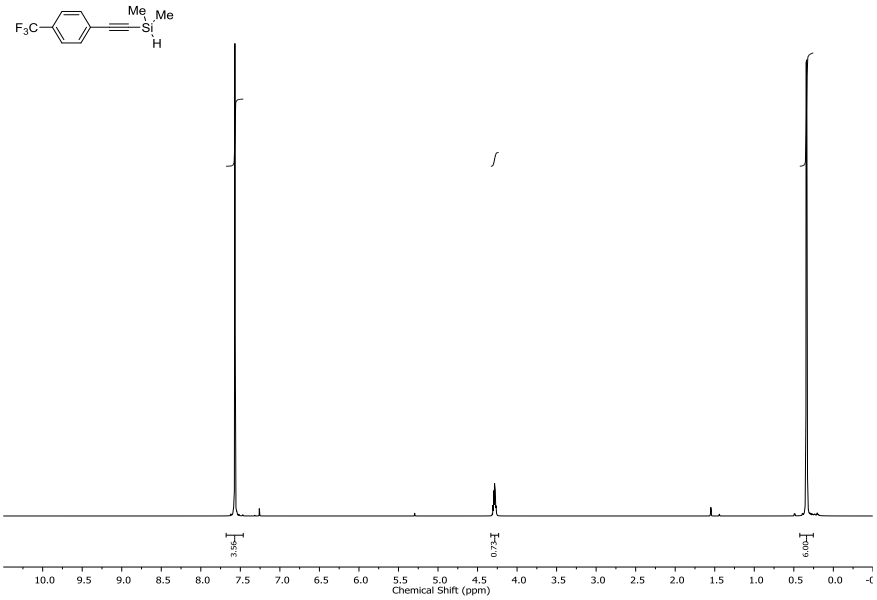
Preparation of (*E*)-tert-butyl((3-(dimethyl(phenylethynyl)silyl)allyl)oxy)dimethylsilane and tert-butyl((2-(dimethyl(phenylethynyl)silyl)allyl)oxy)dimethylsilane: *tert*-Butyldimethyl(prop-2-yn-1-yloxy)silane (1.0 mmol, 0.208 mL) and dimethyl(phenylethynyl)silane (1.0 mmol, 0.263 mL) were subjected to general hydrosilylation procedure C afforded 0.293 g (89%, 78:22 *E*:Int) of (*E*)-*tert*-butyl((3-(dimethyl(phenylethynyl)silyl)allyl)oxy)dimethylsilane and *tert*-butyl((2-(dimethyl(phenylethynyl)silyl)allyl)oxy)dimethylsilane as an inseparable mixture of a yellow oil after

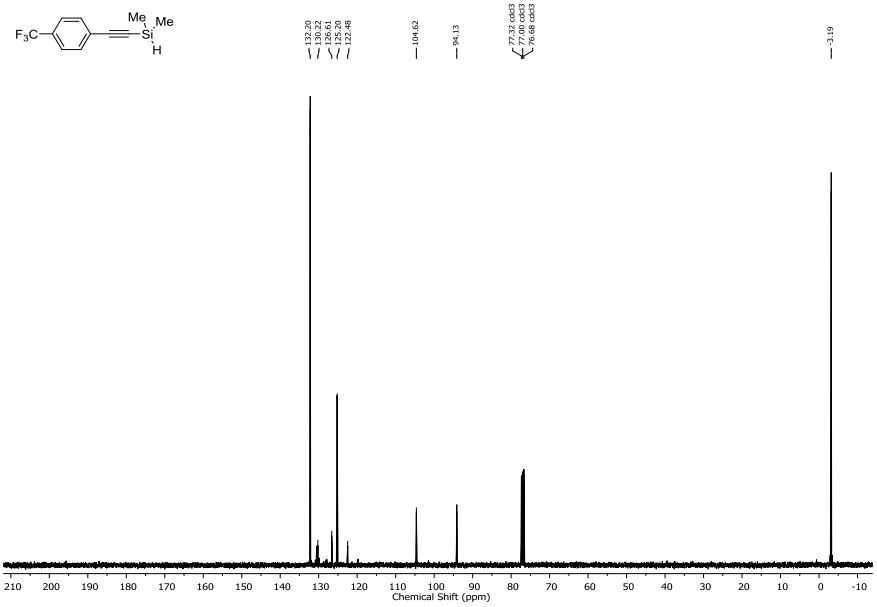
flash chromatography (hexanes:Et_2O; 95:5); ***E*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.41 (m, 2H), 7.37-7.27 (m, 3H), 6.35 (dt, *J* = 18.5, 3.9 Hz, 1H), 5.96 (ddd, *J* = 18.5, 2.2, 1.6 Hz, 1H), 4.26 (dd, *J* = 3.8, 1.9 Hz, 2H), 0.93 (d, *J* = 1.0 Hz, 9H), 0.31 (s, 6H), 0.09 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 132.0, 128.5, 128.2, 124.4, 123.0, 106.0, 92.4, 65.5, 26.0, 18.5, -1.1, -5.2; **Int:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.40 (m, 2H), 7.37-7.27 (m, 3H), 5.93 (dt, *J* = 3.1, 2.0 Hz, 1H), 5.60 (dt, *J* = 3.2, 1.8 Hz, 1H), 4.40 (t, *J* = 2.0 Hz, 2H), 0.93 (s, 9H), 0.35 (d, *J* = 0.6 Hz, 6H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 132.0, 128.6, 128.2, 123.9, 123.0, 106.2, 92.0, 66.2, 26.0, 18.5 ,-1.4, -5.4; IR (neat) 3058, 2956, 2929, 2857, 2160, 1697, 1488, 1389, 1361, 1253, 1220, 1070, 842 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{31}OSi_2$ $[M+H]^+$: 331.1908, Found: 331.1899.

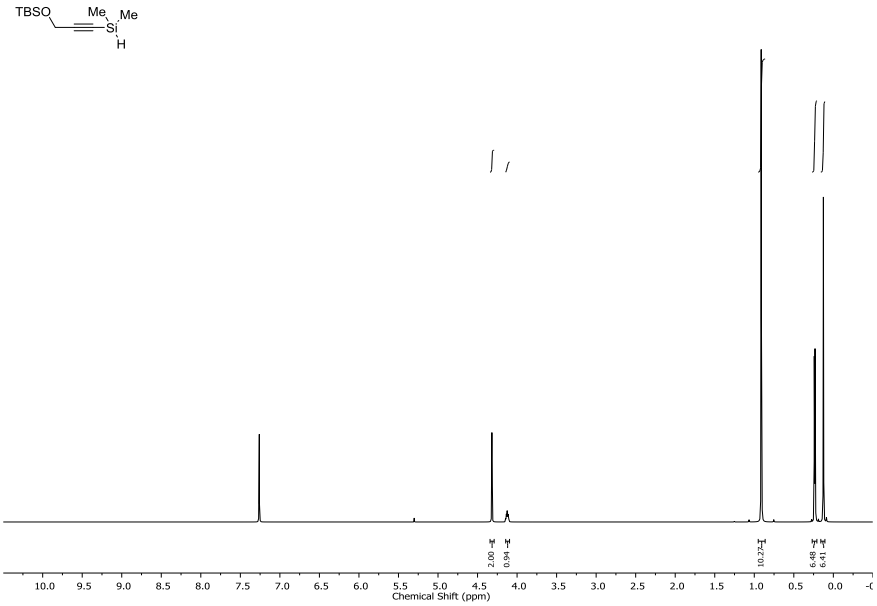
5.10 ^{13}C and ^{1}H NMR SPECTRA

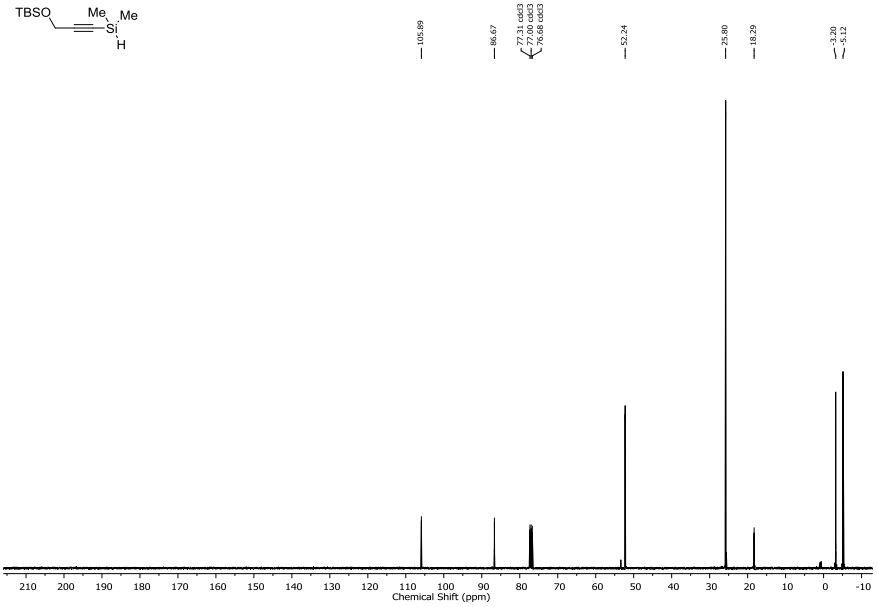


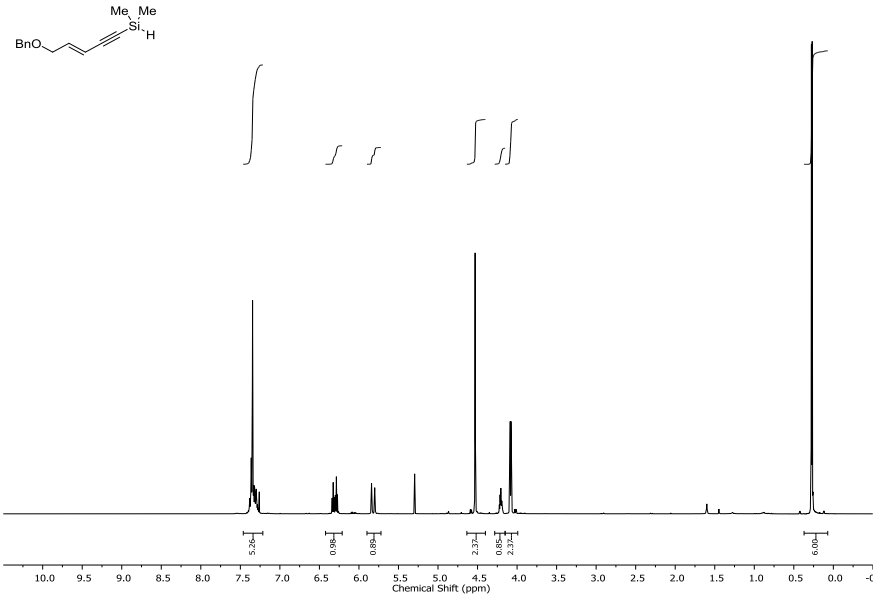


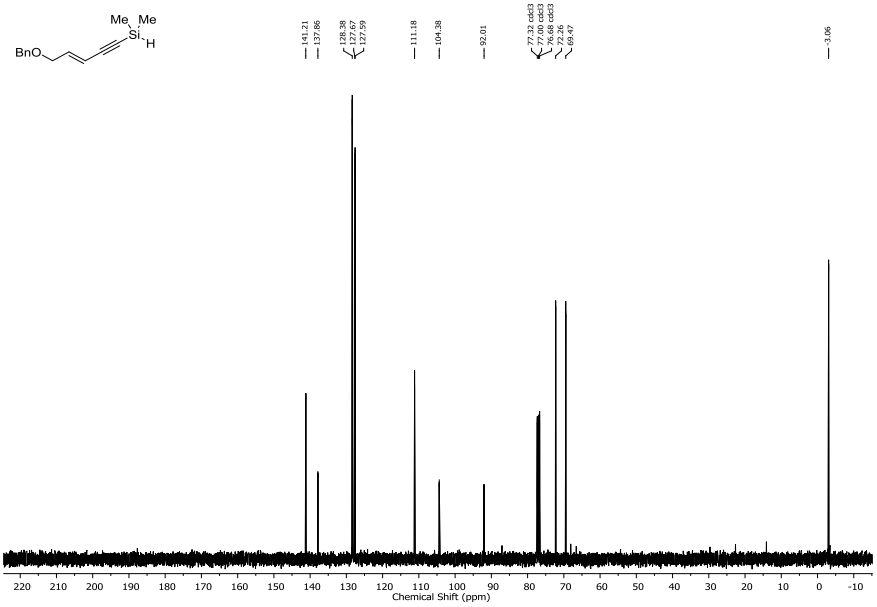

Me
Me
Si
H
F3C
3.56
0.73
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

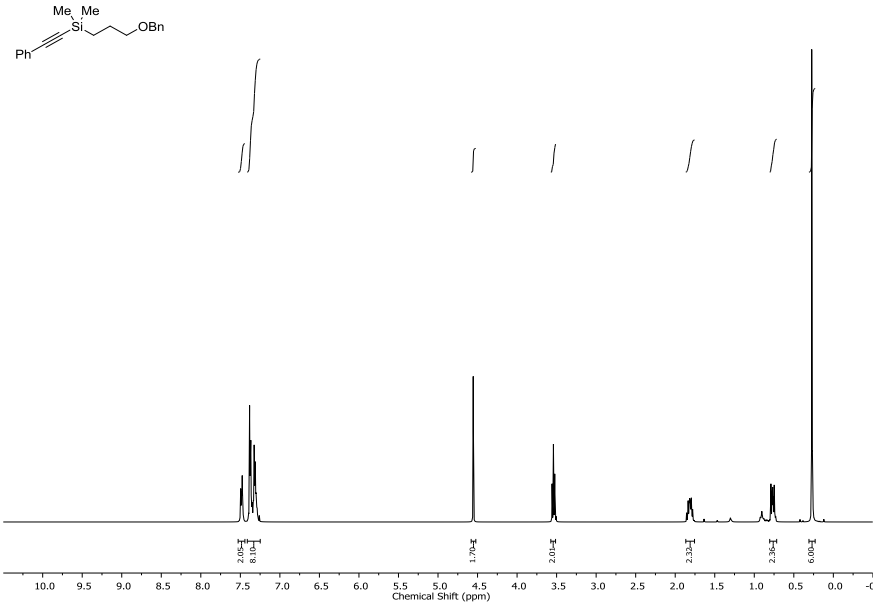

Me
Me
Si
H
F3C
132.20
130.21
126.61
125.20
122.48
104.62
94.13
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
-3.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

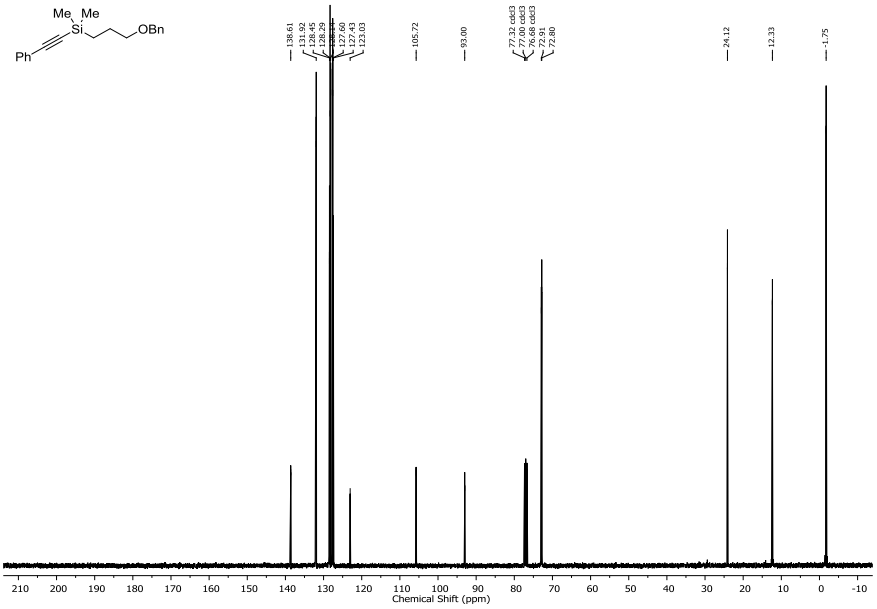

TBSO
Me
Me
Si
H
2.00
0.94
10.27
6.48
6.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

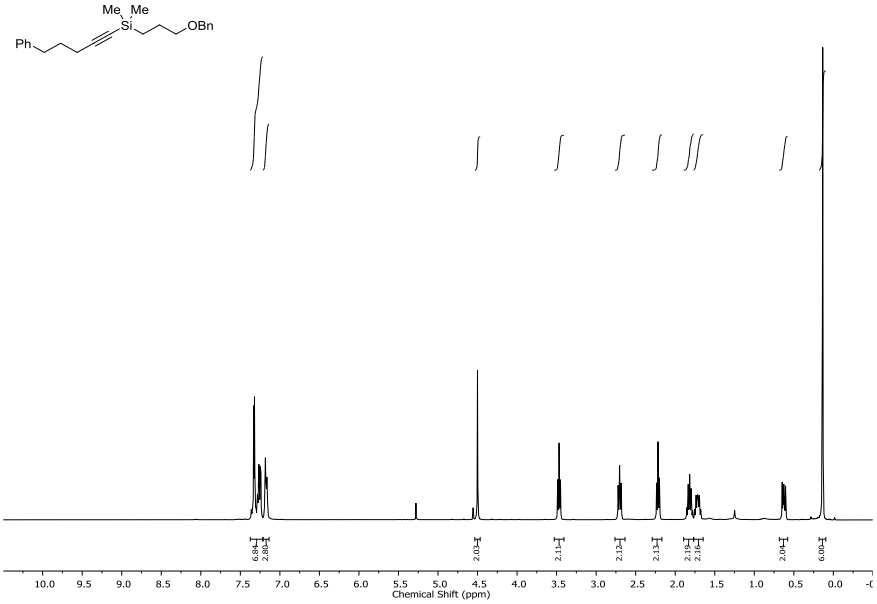

TBSO
Me
Me
Si
H
105.89
86.67
77.31 cdcl3
77.00 cdcl3
76.68 cdcl3
52.24
25.80
18.29
-3.70
-5.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

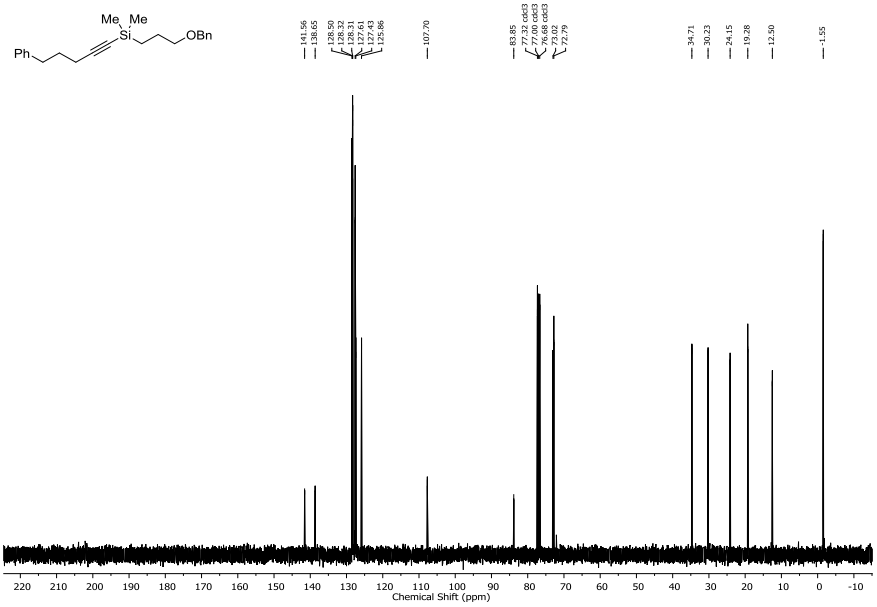

Me
Me
Si
H
BnO
5.26
0.98
0.89
2.37
0.85
2.37
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

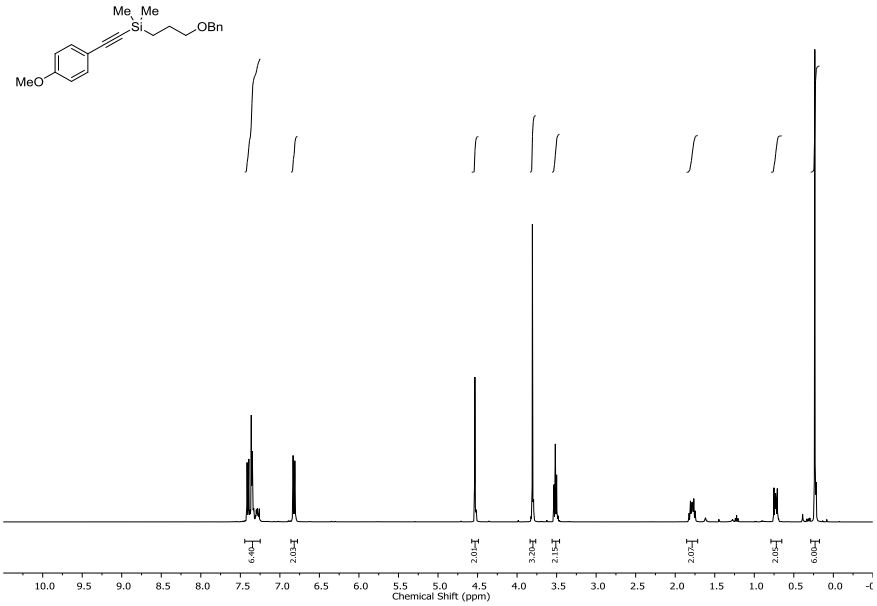

Me
Me
Si
H
BnO
141.21
137.86
128.38
127.67
127.59
111.18
104.38
92.01
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
72.26
69.47
-3.06
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

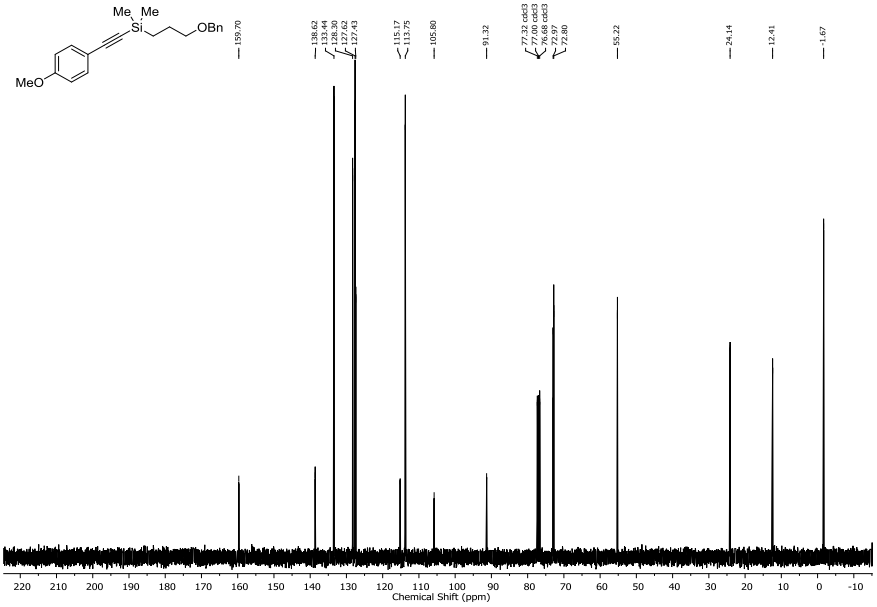

Me Me
Si
OBn
Ph
2.05
8.10
1.70
2.01
2.33
2.36
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

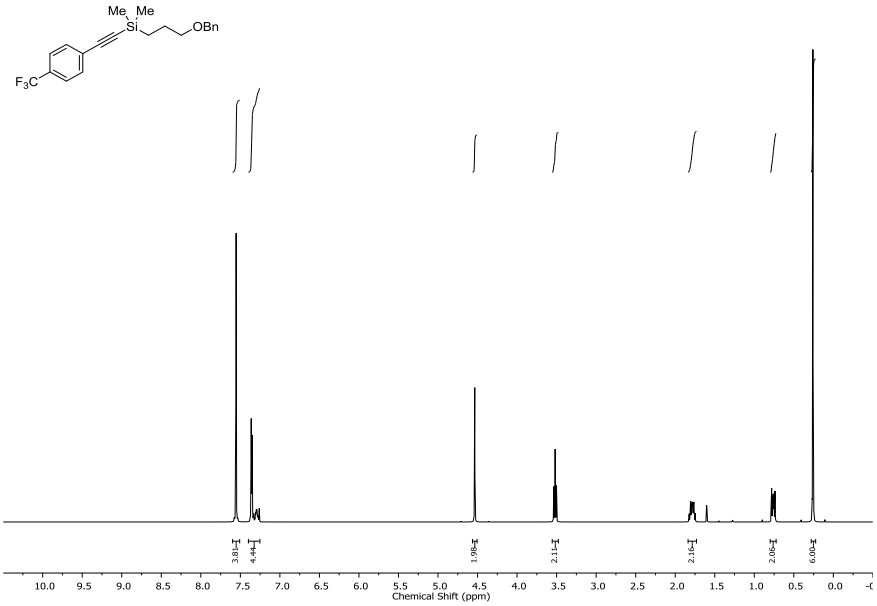

Me Me
Si
OBn
Ph
138.61
131.92
128.45
128.29
127.60
127.43
123.03
105.72
93.00
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
72.91
72.80
24.12
12.33
-1.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

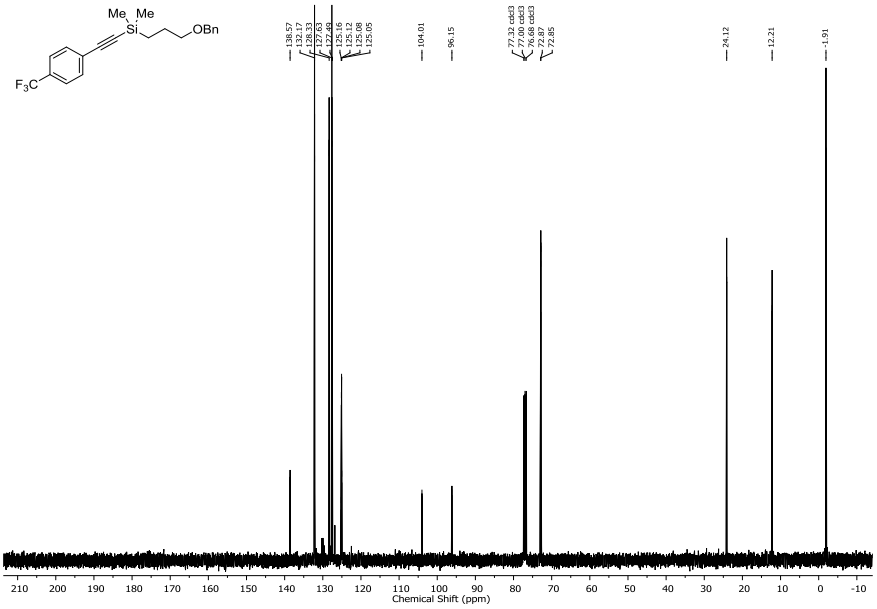

Me Me
Si
OBn
Ph
6.84
2.86
2.03
2.11
2.13
2.15
2.19
2.16
2.04
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

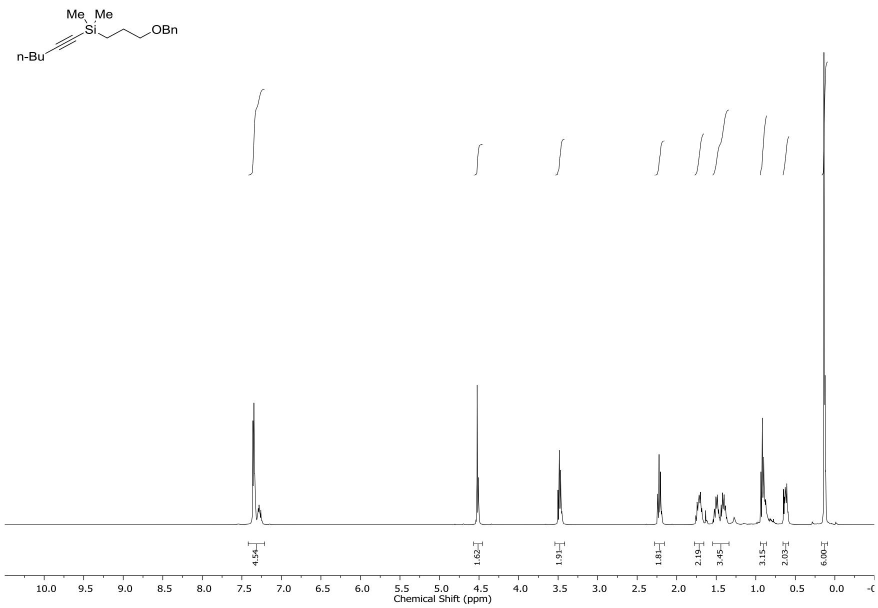

Me Me
Si
OBn
Ph
141.56
138.65
128.59
128.32
128.31
127.61
127.43
125.86
107.70
83.85
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
72.61
72.29
34.71
30.23
24.15
19.28
12.50
-1.55
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


Me
Me
Si
OBn
MeO
6.40
2.03
2.01
3.20
2.15
2.07
2.05
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

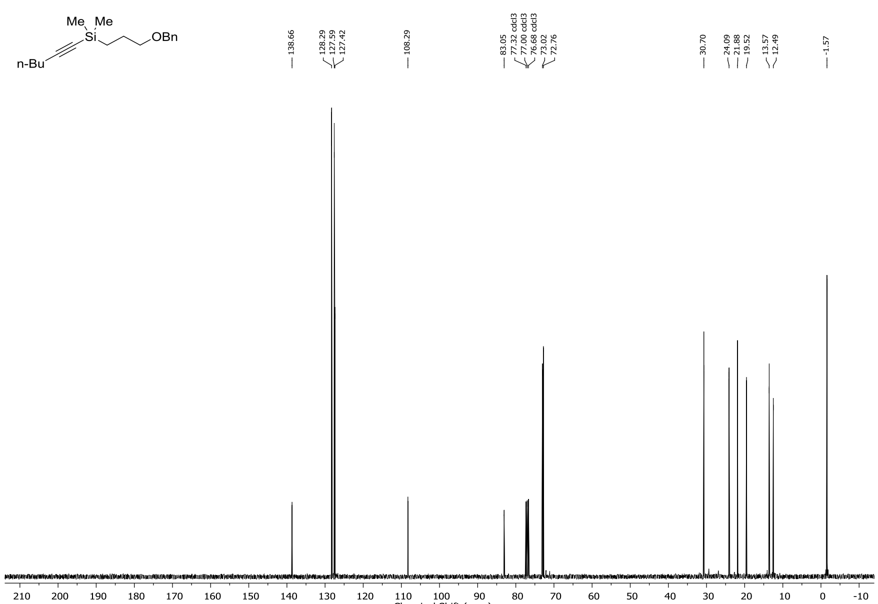

Me
Me
Si
OBn
MeO
159.70
138.62
133.44
128.30
127.63
127.43
115.17
113.75
105.80
91.32
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
73.07
72.80
55.22
24.14
12.41
-1.67
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


Me
Me
Si
OBn
F3C
3.81
4.44
1.98
2.11
2.16
2.06
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

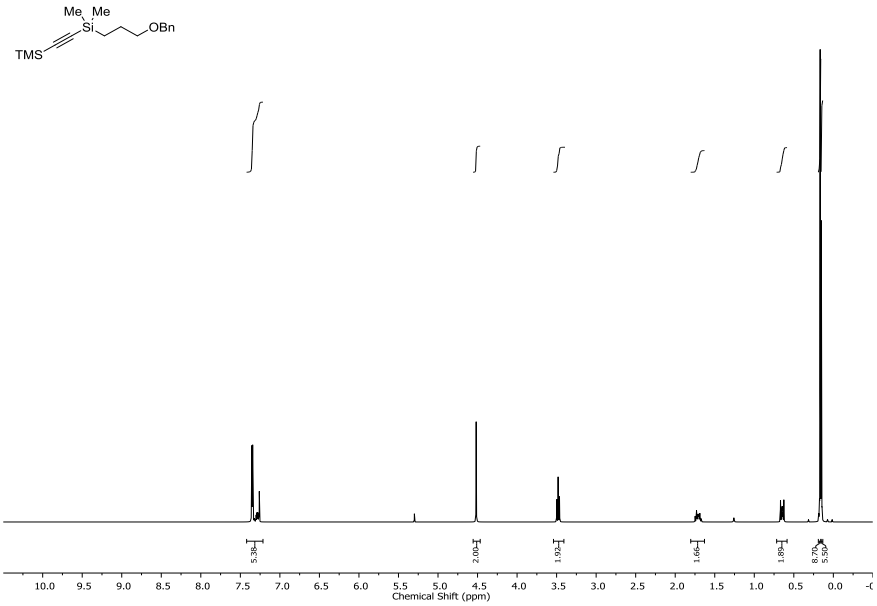

Me
Me
Si
OBn
F3C
138.57
132.17
128.33
127.63
127.48
125.16
125.12
125.08
125.05
104.01
96.15
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
73.07
72.85
24.12
12.21
-1.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

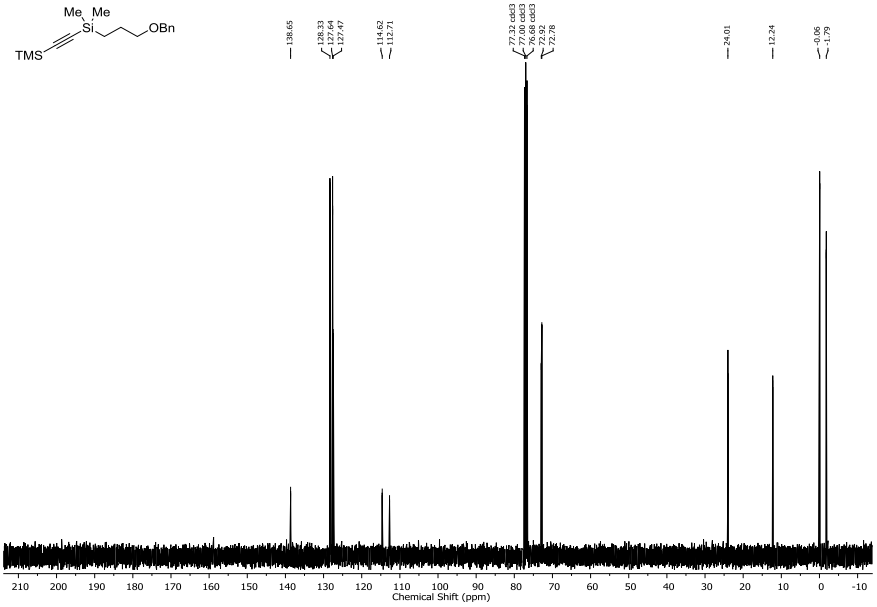


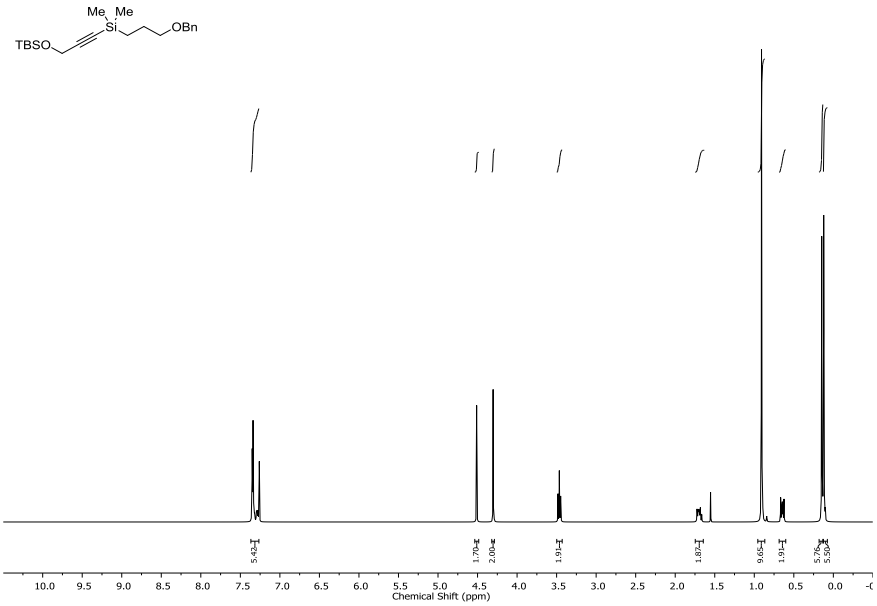
Me Me
Si
OBn
n-Bu
4.54
1.62
1.91
1.81
2.19
3.45
3.15
2.03
6.00
Chemical Shift (ppm)

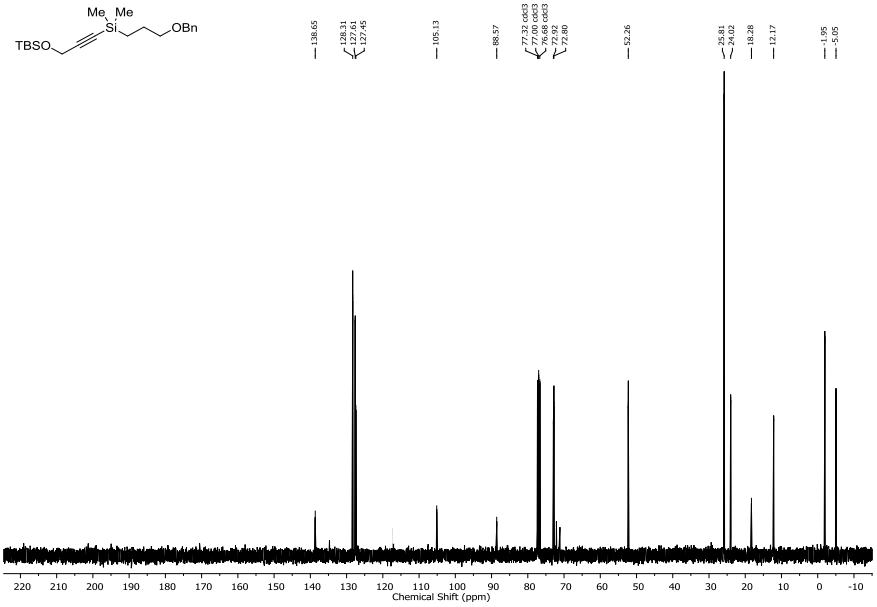


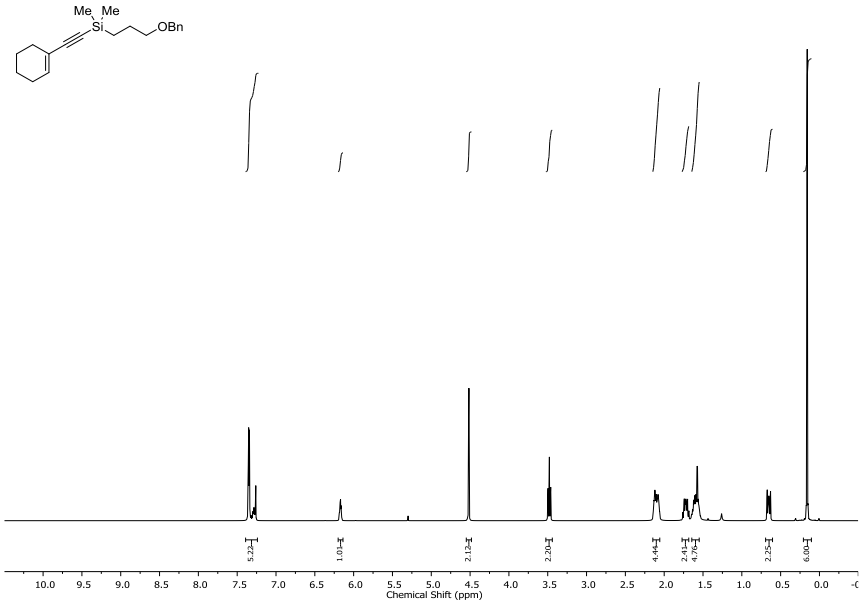
Me Me
Si
OBn
n-Bu
138.66
128.29
127.59
127.42
108.29
83.05
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
73.02
72.76
30.70
24.09
21.88
19.52
13.57
12.49
-1.57
Chemical Shift (ppm)

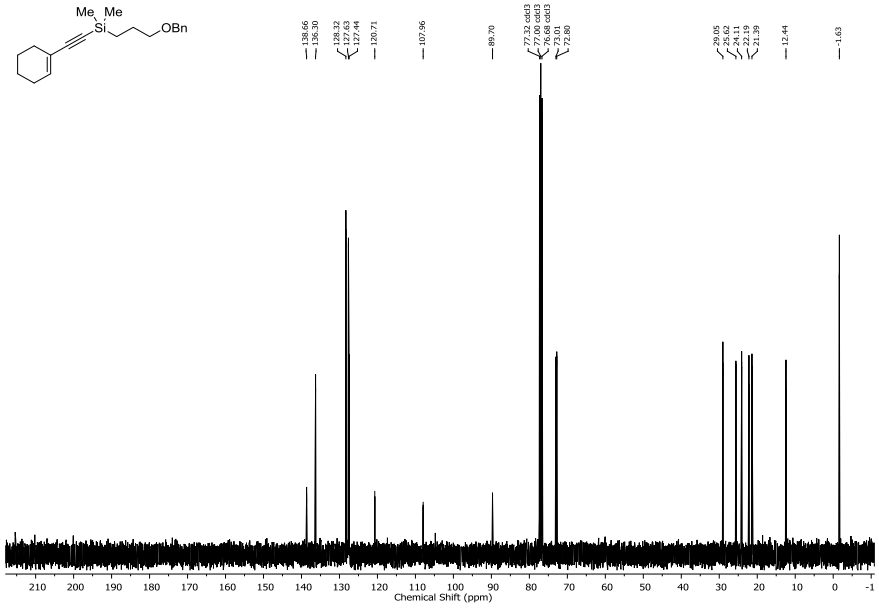

Me
Me
Si
OBn
TMS
5.38
2.00
1.99
1.66
1.89
8.74
5.50
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

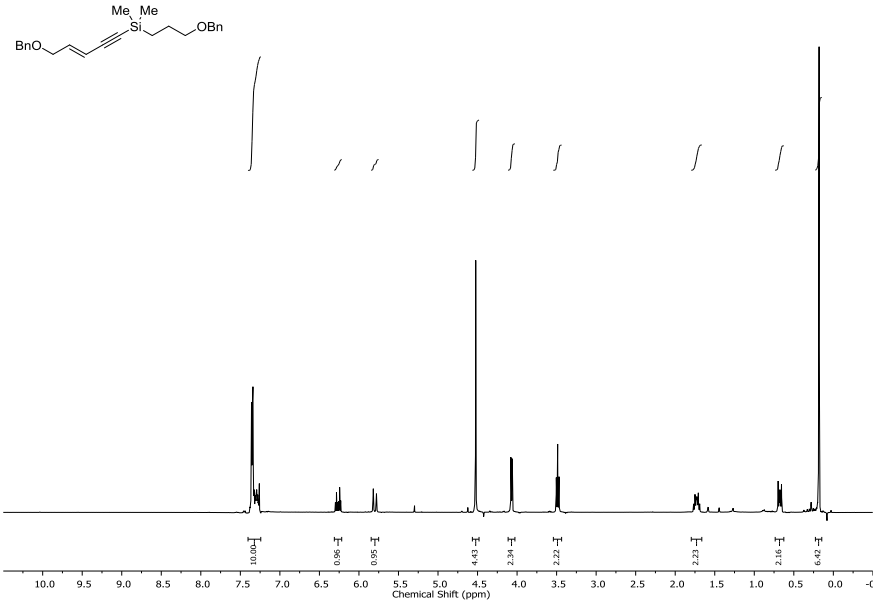

Me
Me
Si
OBn
TMS
138.65
128.33
127.64
127.47
114.62
112.71
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
72.32
72.28
24.01
12.24
-0.06
-1.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

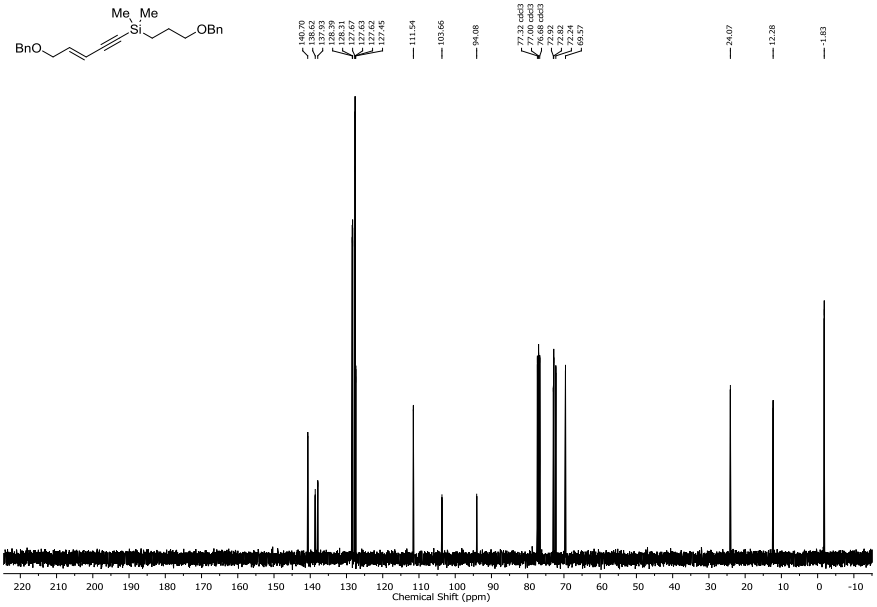

Me Me
Si
TBSO
OBn
5.43
1.70
2.00
1.91
1.87
9.65
1.91
5.76
5.50
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

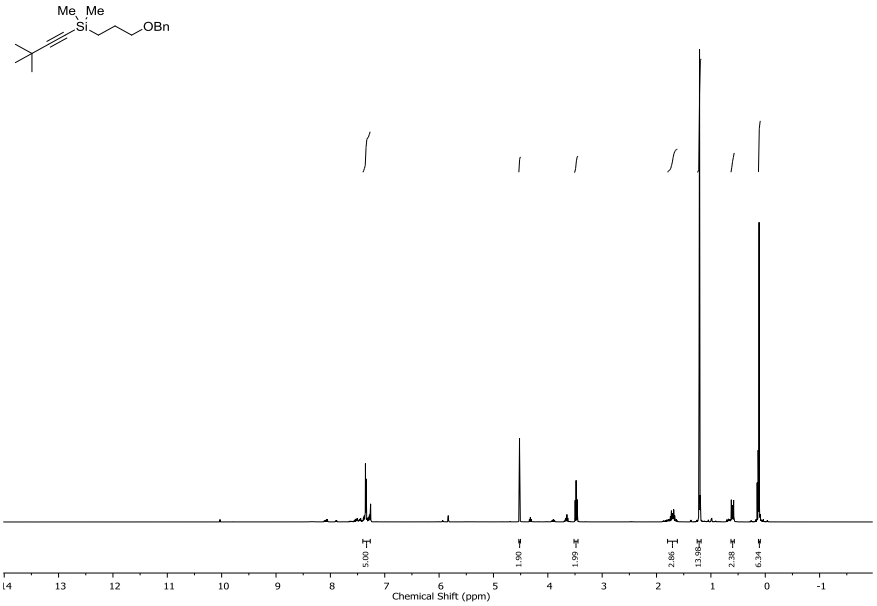

Me Me
Si
TBSO
OBn
138.65
128.31
127.61
127.45
105.13
88.57
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
73.10
72.80
52.26
25.81
24.02
18.28
12.17
-1.95
-5.05
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

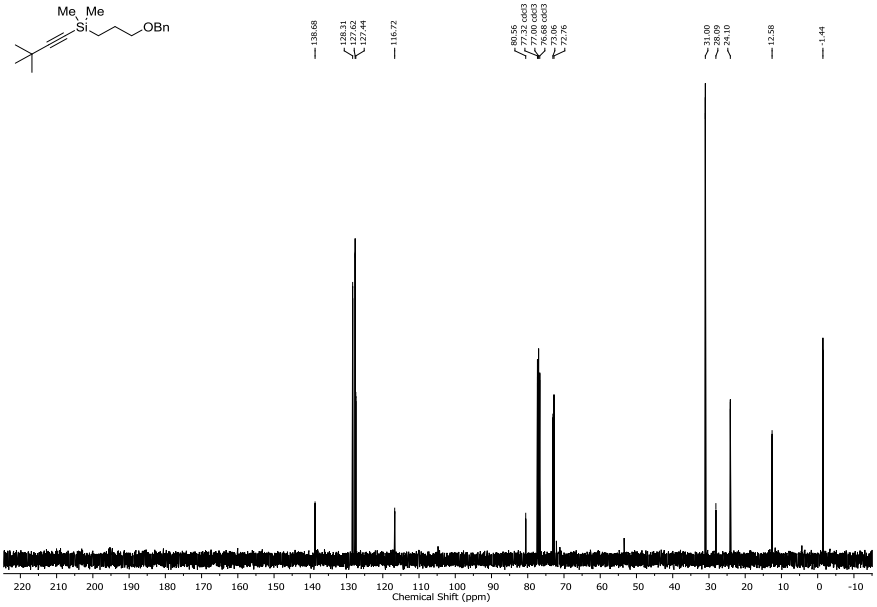

Me
Me
Si
OBn
5.25
1.01
2.13
2.20
4.44
2.41
4.00
2.25
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

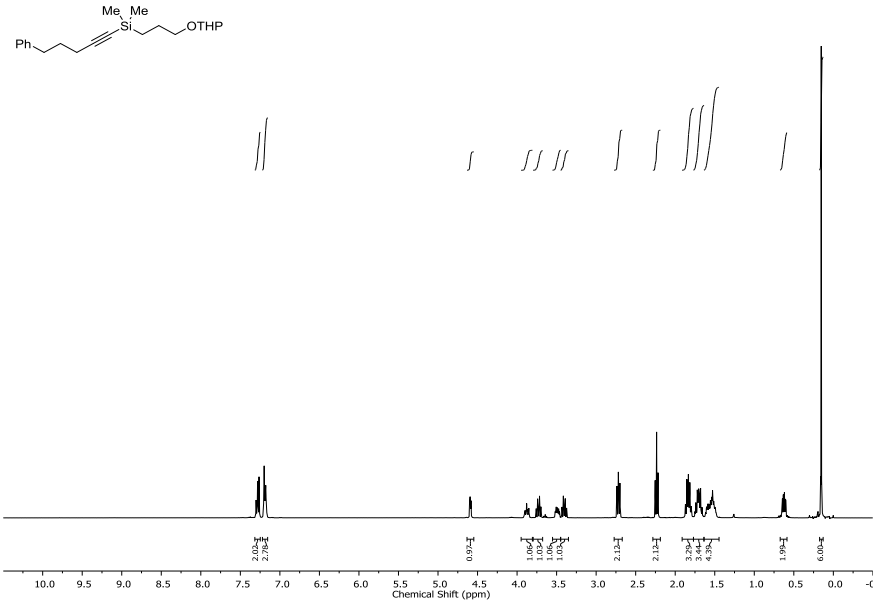

Me
Me
Si
OBn
138.66
136.30
128.32
127.68
127.44
120.71
107.96
89.70
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
73.01
72.80
29.05
25.62
24.11
22.19
21.39
12.44
-1.63
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
Chemical Shift (ppm)

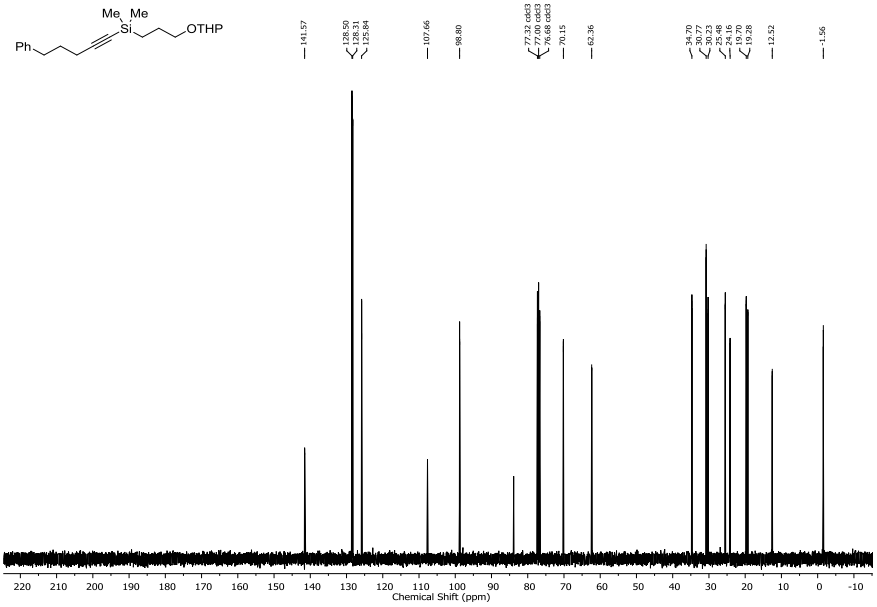

Me
Me
Si
BnO
OBn
10.00
0.96
0.95
4.43
2.34
2.22
2.23
2.16
6.42
Chemical Shift (ppm)

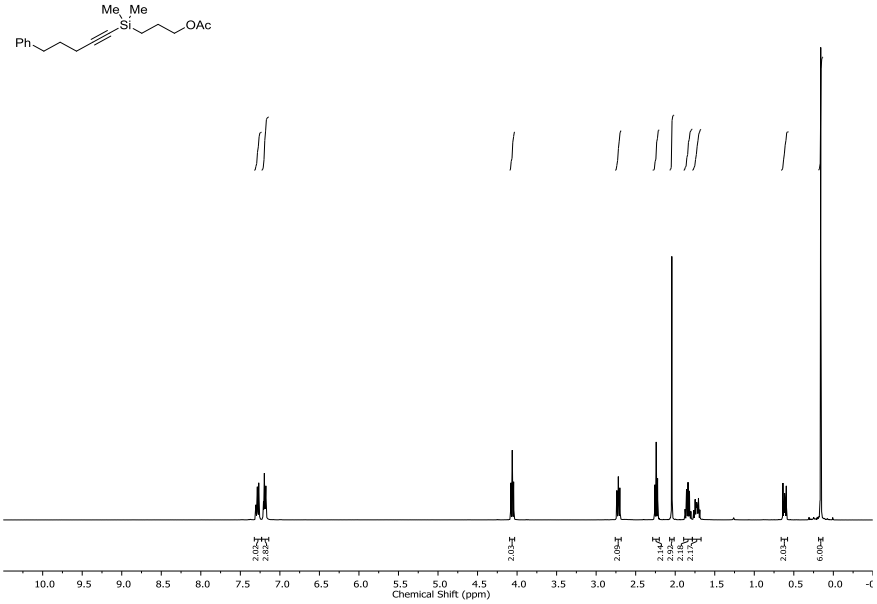

Me
Me
Si
BnO
OBn
140.70
138.62
137.93
128.39
128.31
127.67
127.63
127.62
127.45
111.54
103.66
94.08
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
72.92
72.82
72.24
69.07
24.07
12.28
-1.83
Chemical Shift (ppm)

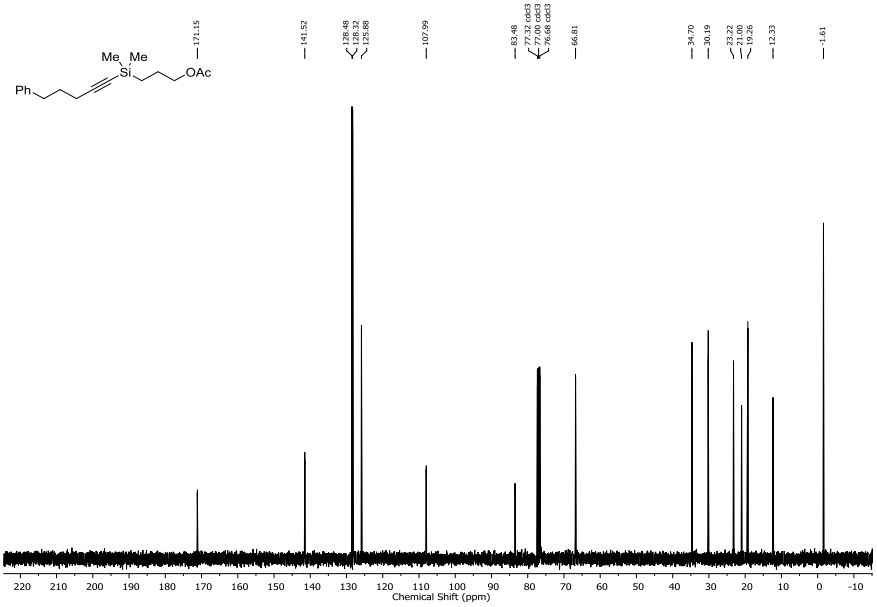

Me
Me
Si
OBn
5.00
1.90
1.99
2.86
13.98
2.38
6.34
Chemical Shift (ppm)

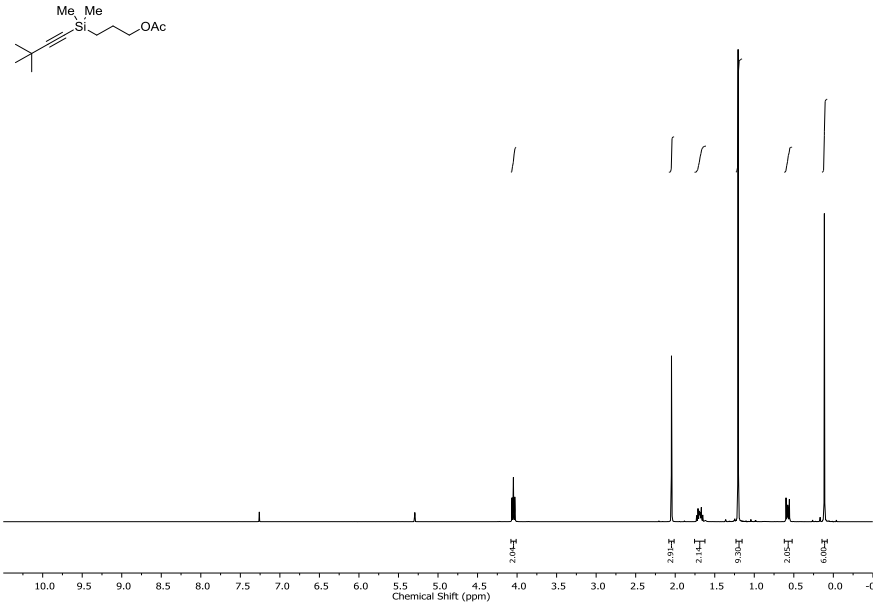

Me
Me
Si
OBn
138.68
128.31
127.62
127.44
116.72
89.56
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
70.66
72.76
31.00
28.09
24.10
12.58
-1.44
Chemical Shift (ppm)

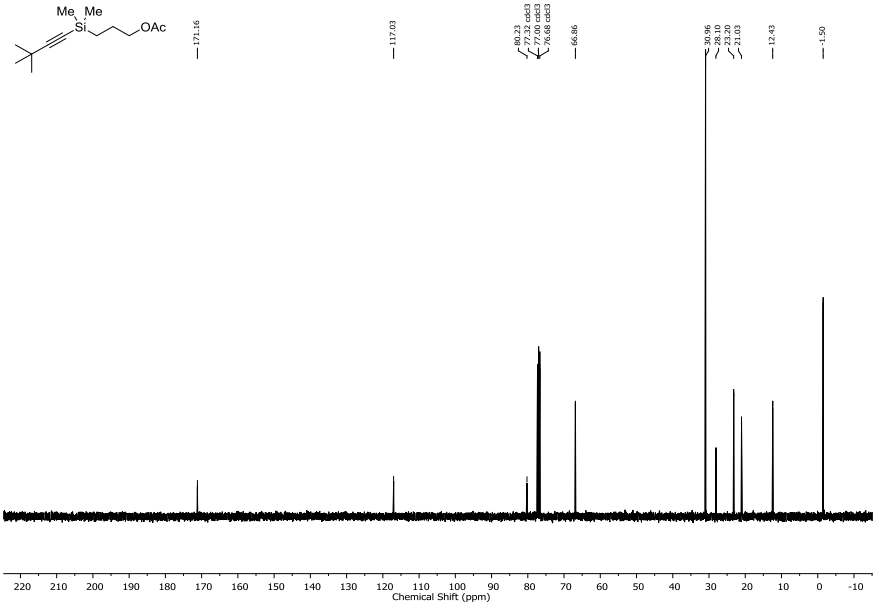

Me Me
Si
OTHP
Ph
2.03
2.76
0.97
1.00
1.02
1.06
1.03
2.15
2.11
3.29
3.44
4.35
1.99
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

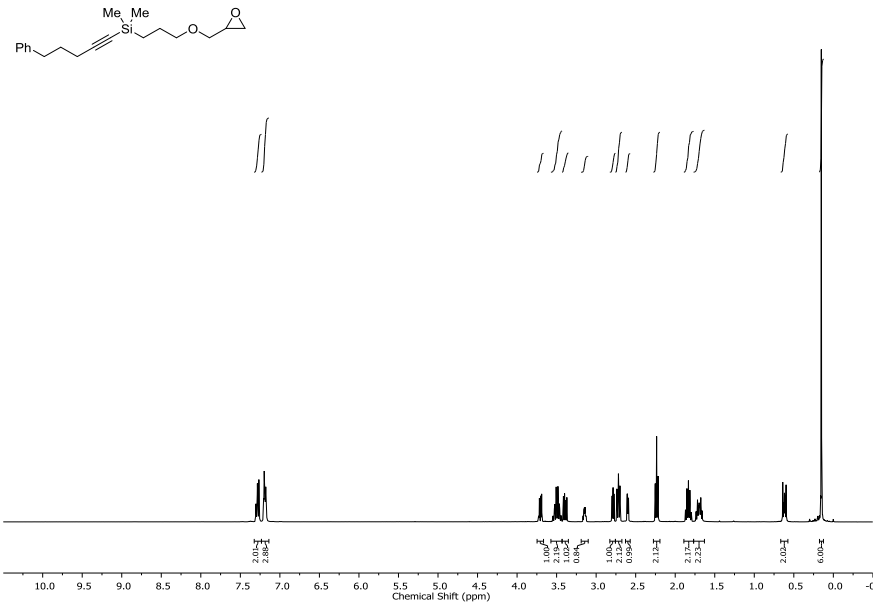

Me Me
Si
OTHP
Ph
141.57
128.59
128.31
125.84
107.66
88.80
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
70.15
62.36
34.70
30.77
30.33
25.48
24.16
19.70
19.08
12.52
-1.56
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

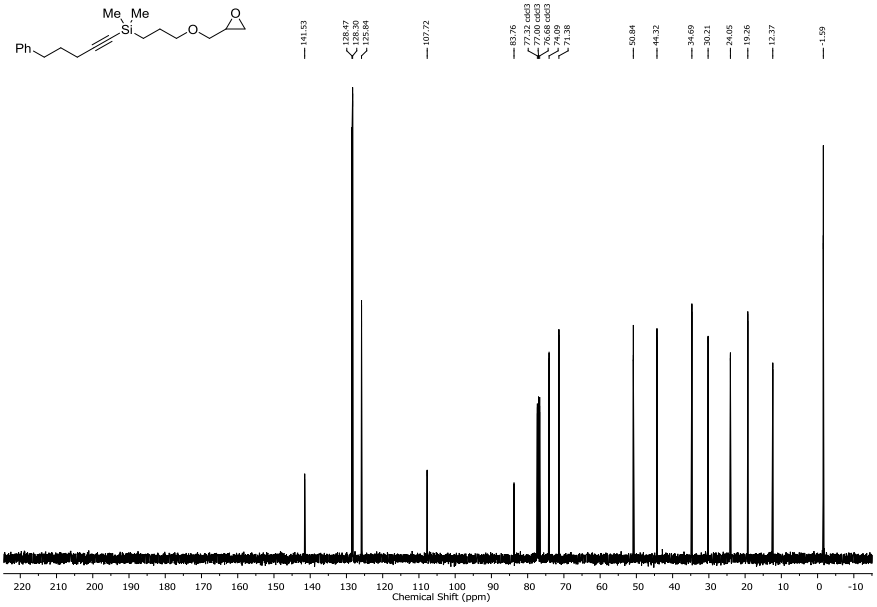

Me Me
Si
OAc
Ph
2.03
2.85
2.03
2.09
2.14
2.06
2.10
2.11
2.03
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

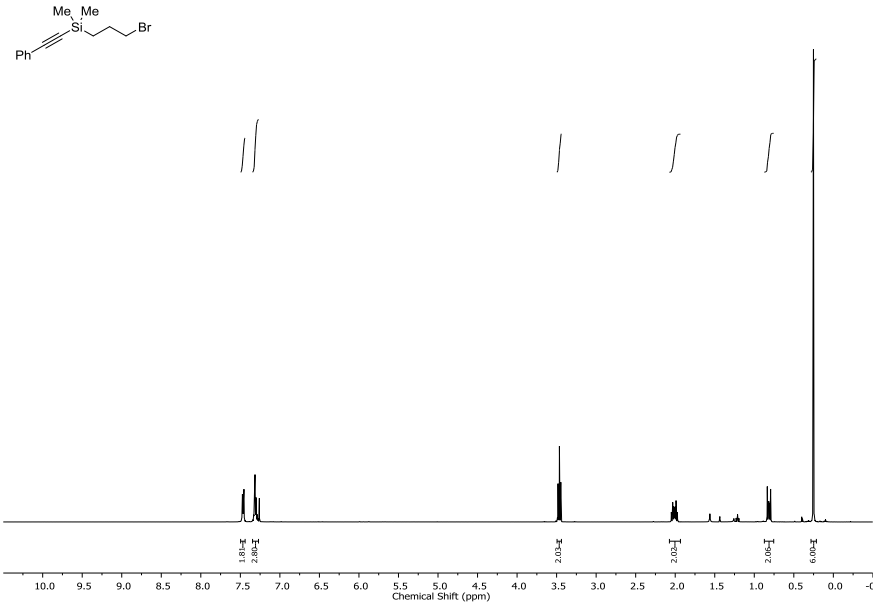

Me Me
Si
OAc
Ph
171.15
141.52
128.48
128.32
125.88
107.99
83.46
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
66.81
34.70
30.19
23.22
21.00
19.06
12.33
-1.61
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

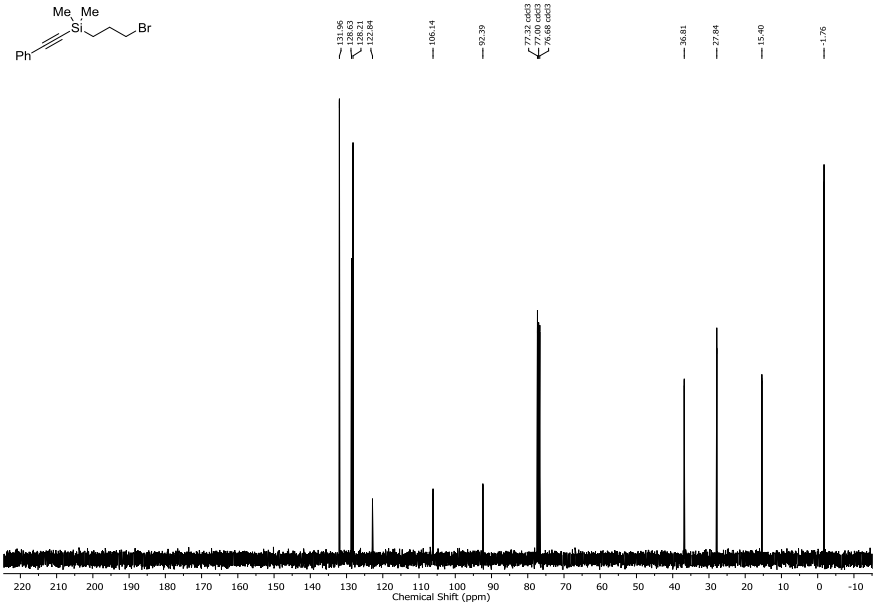

Me
Me
Si
OAc
2.04
2.91
2.14
9.30
2.05
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

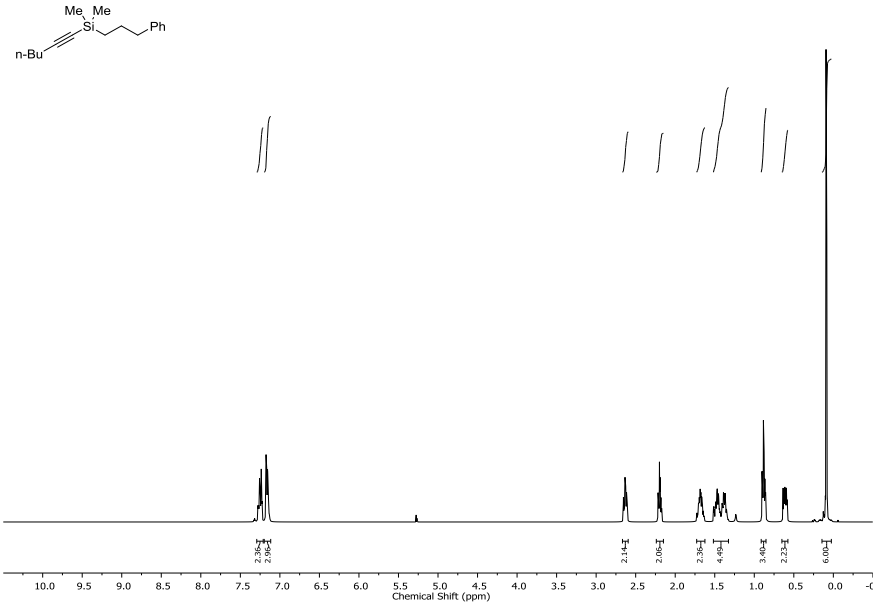

Me
Me
Si
OAc
171.16
117.03
80.23
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
66.86
30.96
28.10
23.20
21.03
12.43
-1.50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

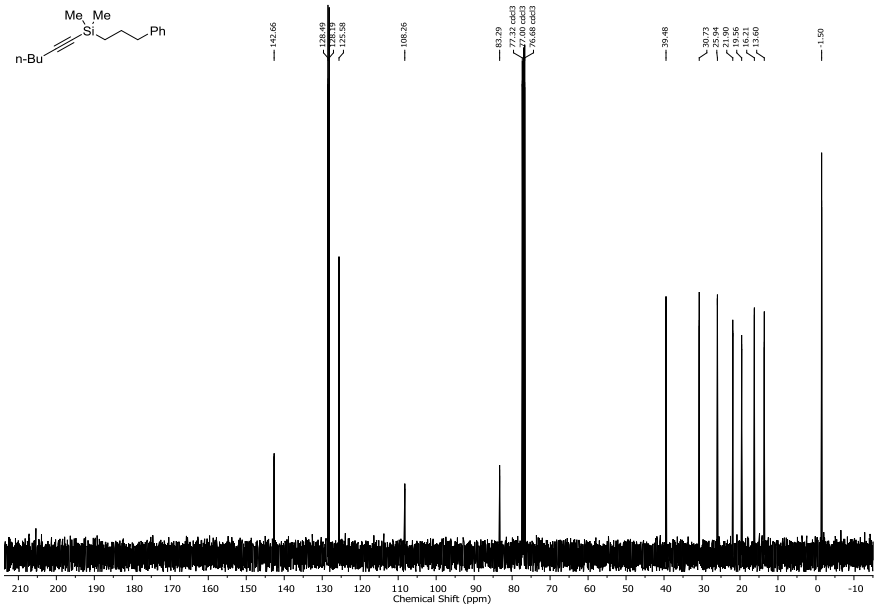

Me
Me
Si
O
Ph
O
2.01
2.88
1.07
2.13
2.04
0.84
1.00
2.15
0.99
2.19
2.17
2.25
2.09
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

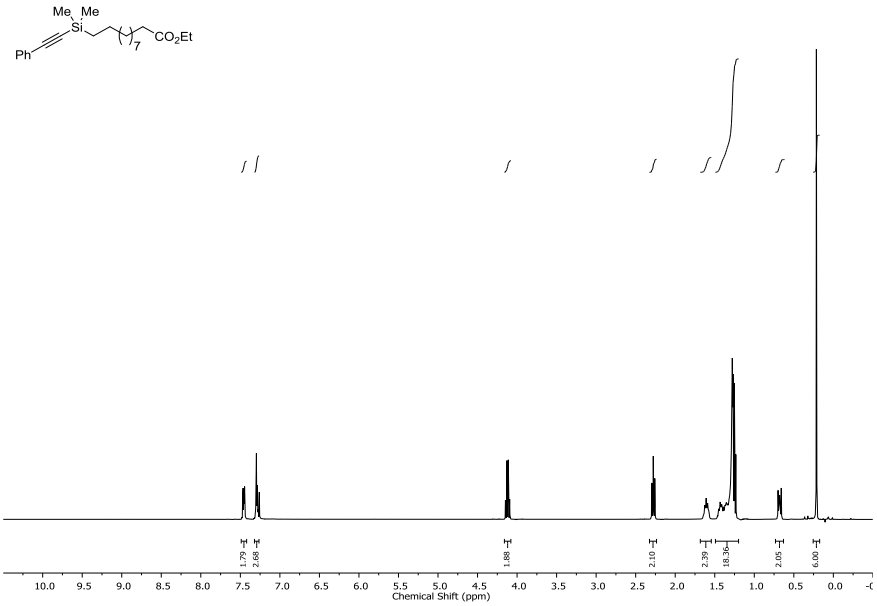

Me
Me
Si
O
Ph
O
141.53
128.47
128.39
125.84
107.72
83.76
77.23 cdcl3
77.00 cdcl3
76.68 cdcl3
74.09
71.38
50.84
44.32
34.69
30.21
24.05
19.26
12.37
-1.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

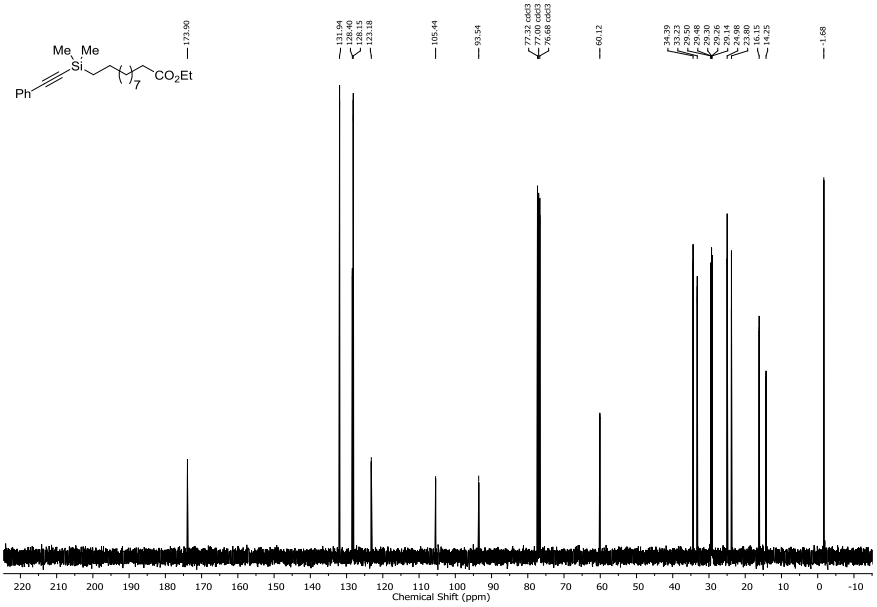

Me
Me
Si
Br
Ph
1.81
2.80
2.03
2.03
2.06
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

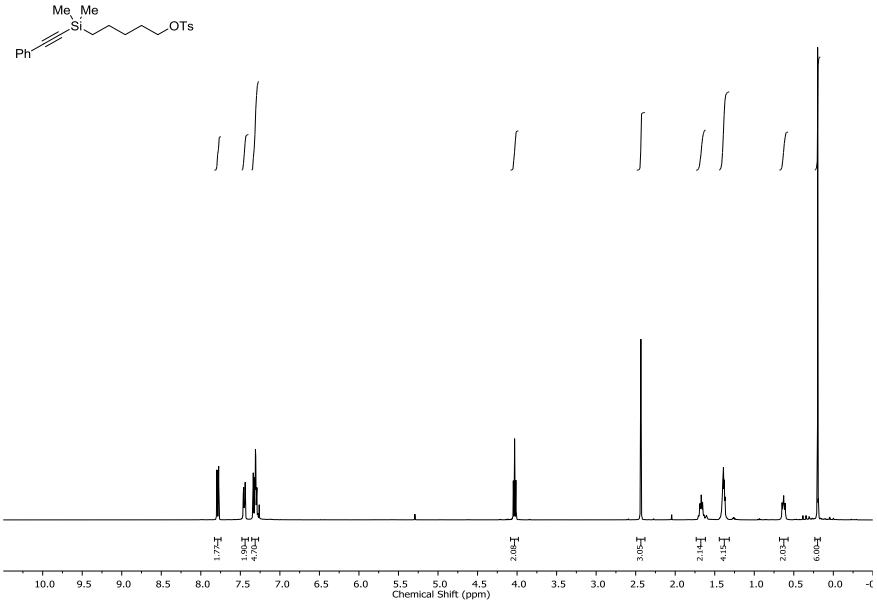

Me
Me
Si
Br
Ph
131.96
128.63
128.31
122.84
106.14
92.39
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
36.81
27.84
15.40
-1.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

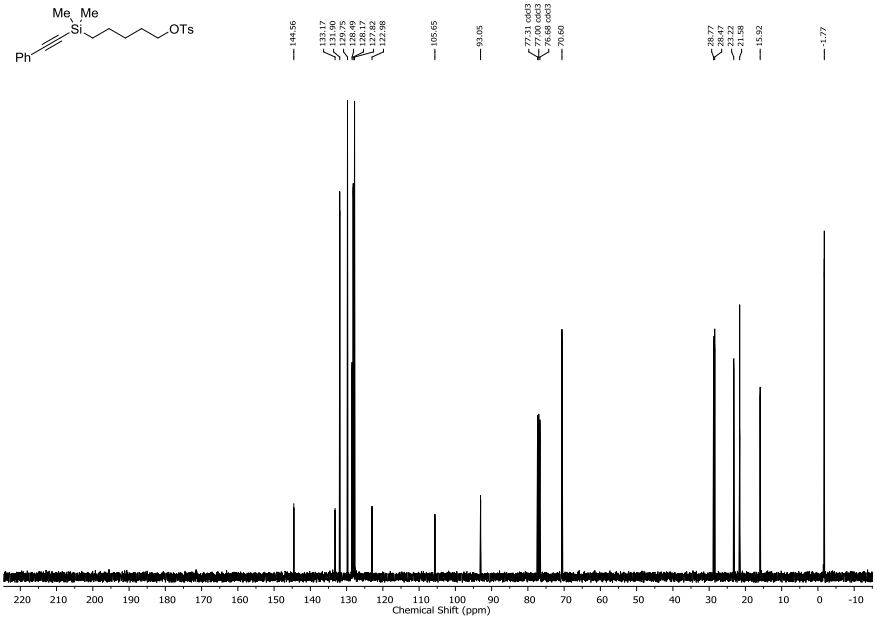

Me
Me
Si
Ph
n-Bu
2.36
2.96
2.14
2.06
2.36
4.49
3.40
2.25
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

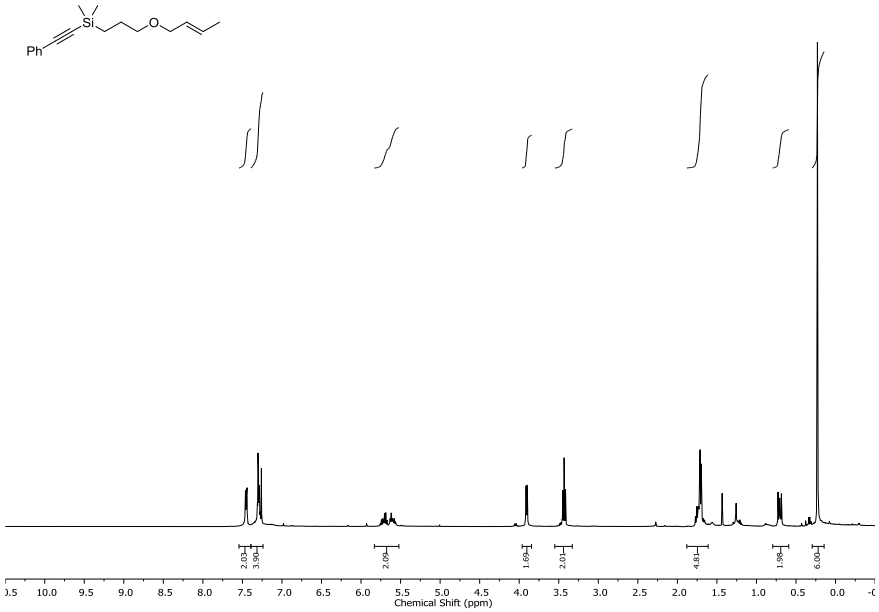

Me
Me
Si
Ph
n-Bu
142.66
128.49
128.19
126.98
108.26
83.39
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
39.48
30.73
25.94
21.90
18.36
16.21
13.60
1.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

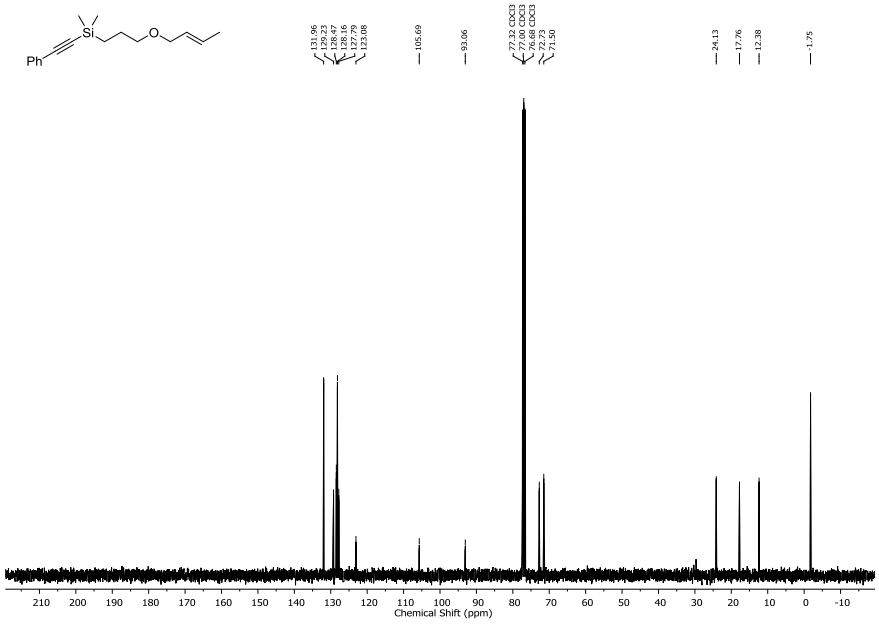

Me Me
Si
Ph
CO2Et
7
1.79
2.68
1.88
2.10
2.39
18.36
2.05
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

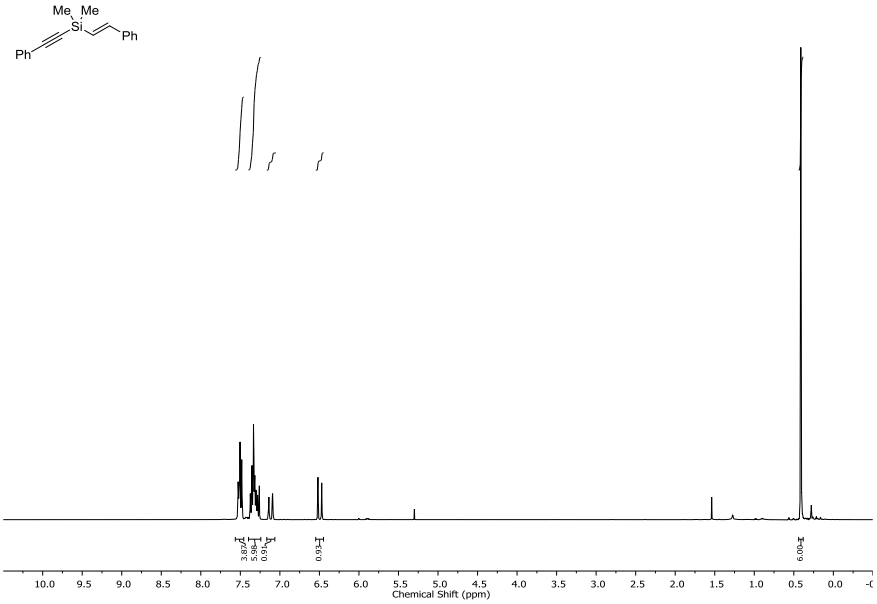

Me Me
Si
Ph
CO2Et
7
173.90
131.94
128.40
128.15
123.18
105.44
93.54
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
60.12
34.39
33.23
29.50
29.48
29.30
29.26
29.14
24.96
22.80
16.15
14.25
-1.68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

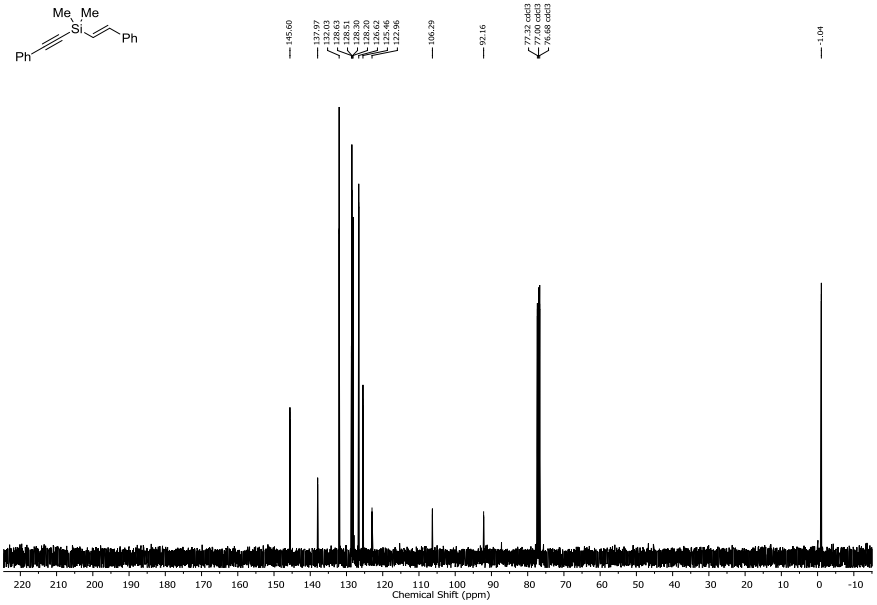

Me
Me
Si
OTs
Ph
1.77
1.90
4.76
2.08
3.05
2.14
4.15
2.05
6.00
Chemical Shift (ppm)

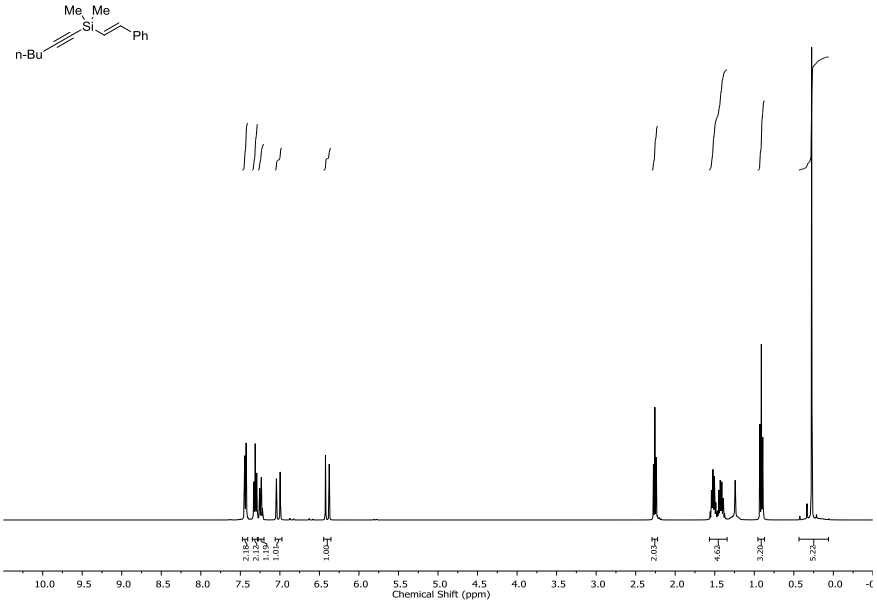

Me
Me
Si
OTs
Ph
144.56
133.17
131.90
130.25
128.49
128.17
127.98
122.98
105.65
93.05
77.31 cdcl3
77.00 cdcl3
76.68 cdcl3
70.60
28.77
28.47
23.22
21.58
15.92
-1.77
Chemical Shift (ppm)

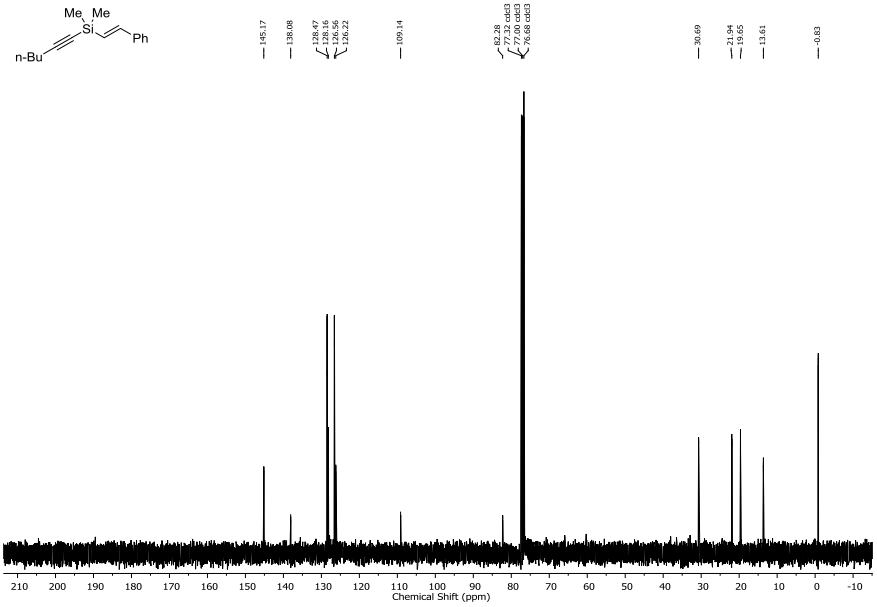

Si
O
Ph
2.03
3.90
2.09
1.69
2.01
4.81
1.98
6.00
Chemical Shift (ppm)

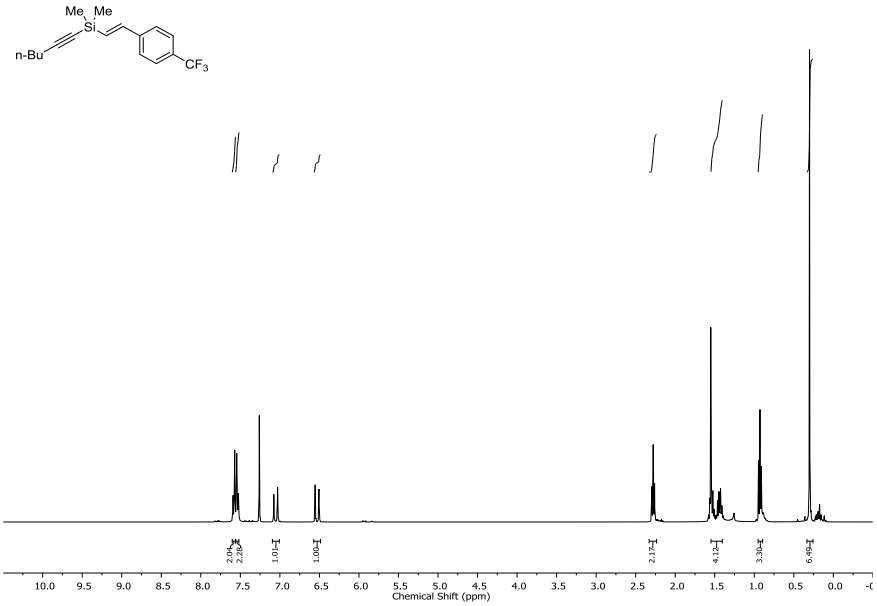

Si
O
Ph
131.96
129.23
128.47
128.16
127.79
123.08
105.69
93.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
72.73
71.50
24.13
17.76
12.38
-1.75
Chemical Shift (ppm)

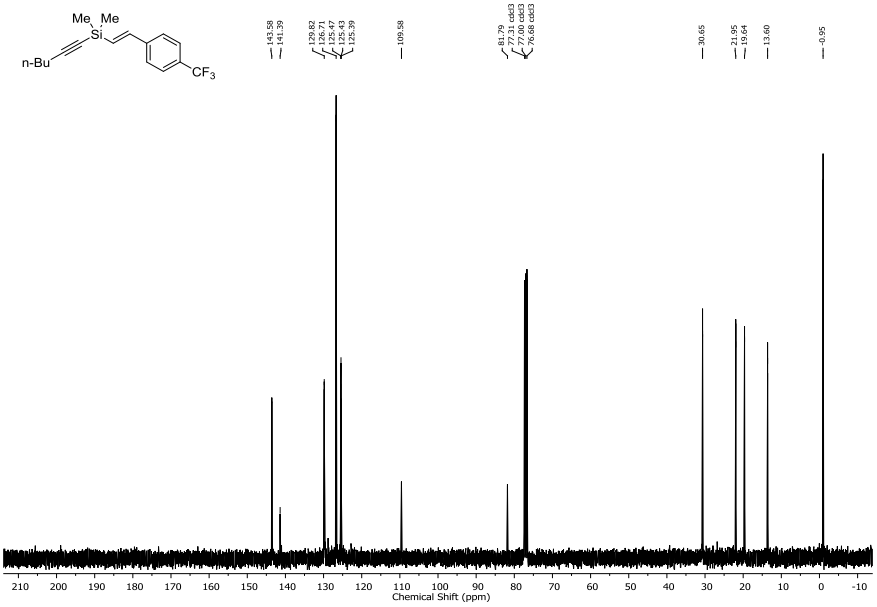

Me
Me
Si
Ph
Ph
3.87
5.98
0.91
0.91
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

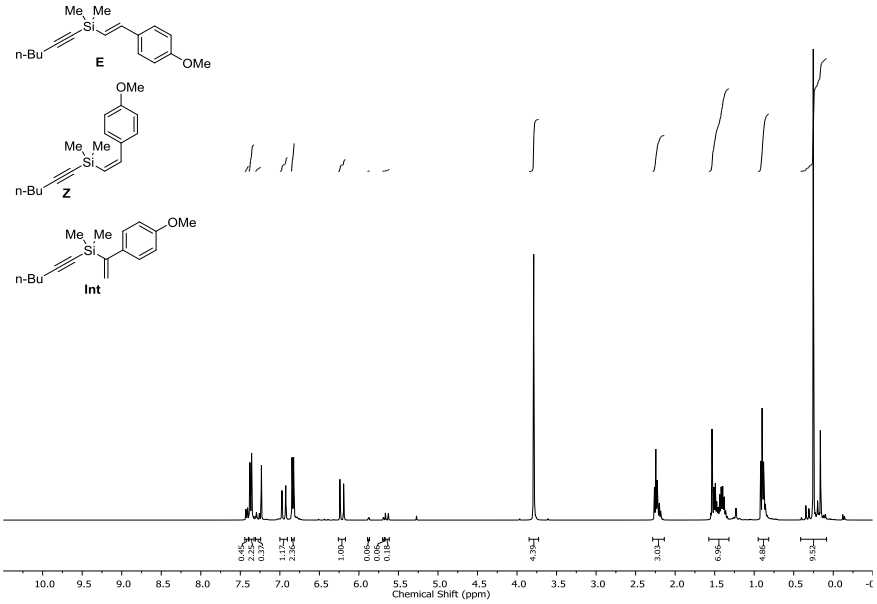

Me
Me
Si
Ph
Ph
145.60
137.97
132.03
128.63
128.51
128.39
128.20
126.62
125.46
122.96
106.29
92.16
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
1.04
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


Me
Me
Si
Ph
n-Bu
2.18
2.13
1.19
1.01
1.00
2.03
4.63
3.20
5.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)


Me
Me
Si
Ph
n-Bu
145.17
138.08
128.47
128.16
126.56
126.22
109.14
82.28
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
30.69
21.94
19.65
13.61
-0.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


Me
Me
Si
n-Bu
CF3
2.04
2.29
1.01
1.00
2.17
4.15
3.30
6.49
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)


Me
Me
Si
n-Bu
CF3
143.58
141.39
129.82
126.71
125.47
125.43
125.39
109.58
81.73
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
30.65
21.95
19.64
13.60
-0.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)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E
OMe
OMe
Me Me
Si
n-Bu
Z
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Me Me
Si
n-Bu
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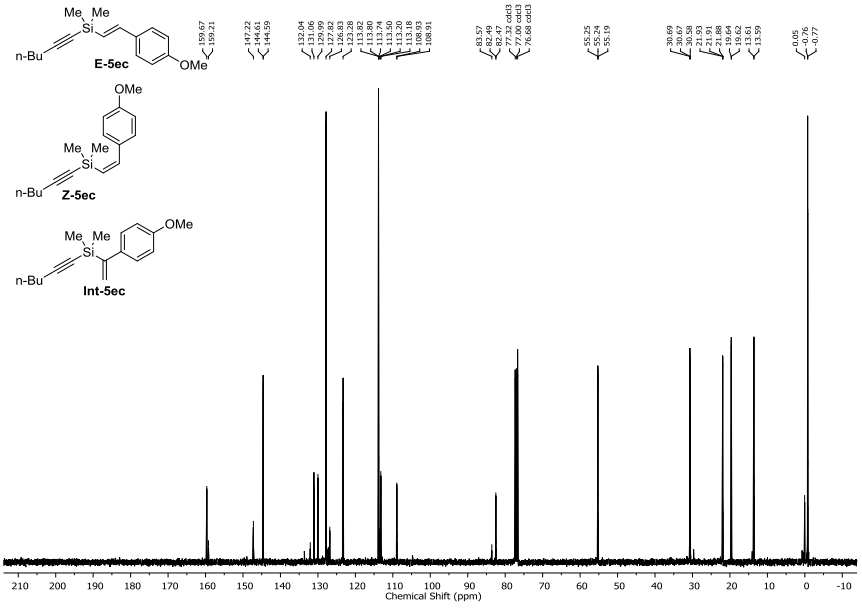
2.25
0.35
1.17
2.36
1.00
0.06
0.05
0.18
4.39
3.03
6.96
4.86
9.52
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)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E-5ec
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113.74
113.50
113.30
113.18
108.93
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83.57
82.49
82.47
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77.00 cdcl3
76.68 cdcl3
55.25
55.24
55.19
30.69
30.67
30.58
21.93
21.91
21.88
19.64
19.60
13.61
13.59
0.05
-0.76
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OMe
Me Me
Si
n-Bu
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OMe
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Si
n-Bu
Int-5ec
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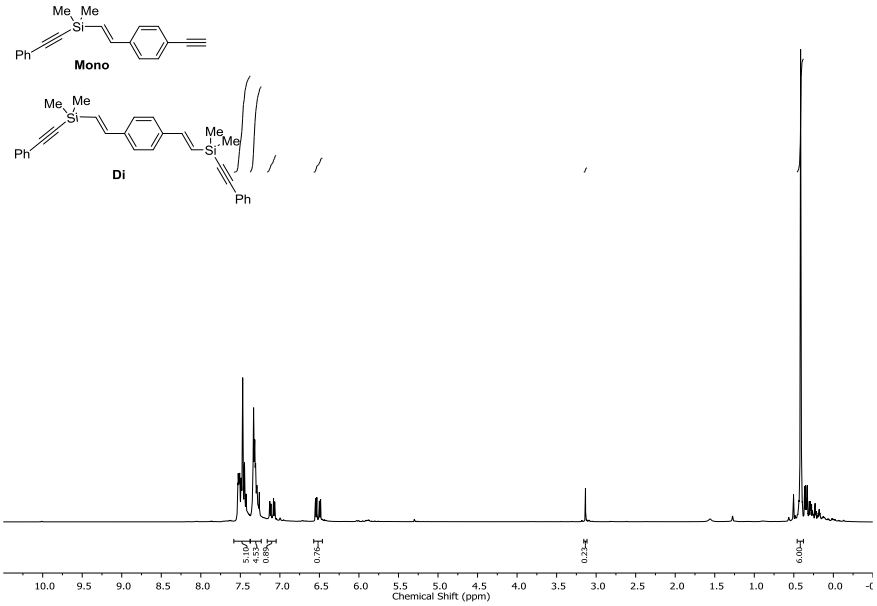
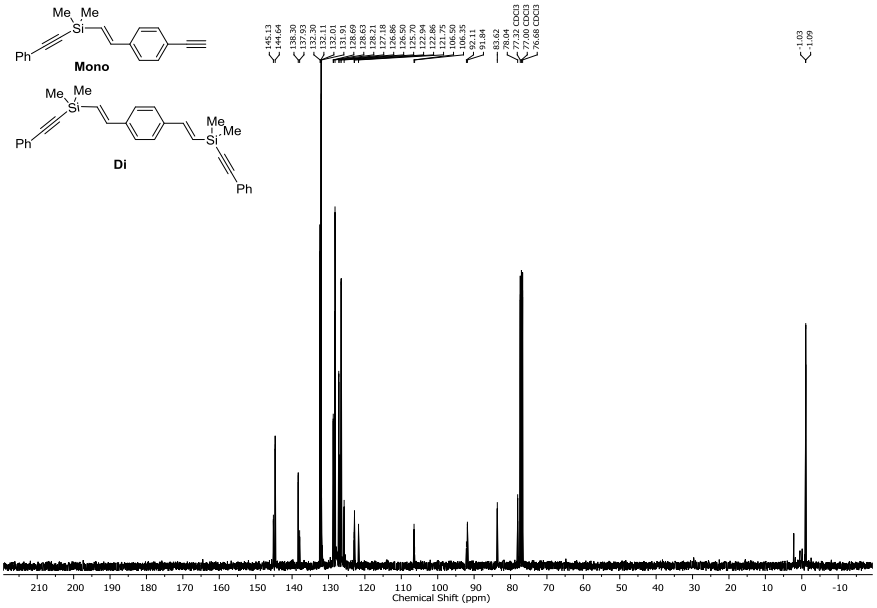
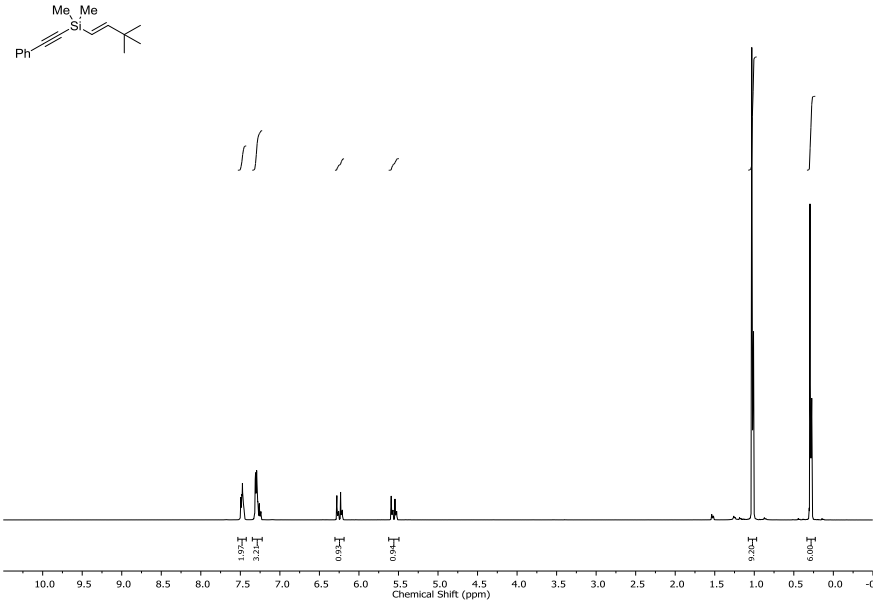
Chemical Shift (ppm)


Mono
Di
Chemical Shift (ppm)


Mono
Di
Chemical Shift (ppm)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0.94
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6.00
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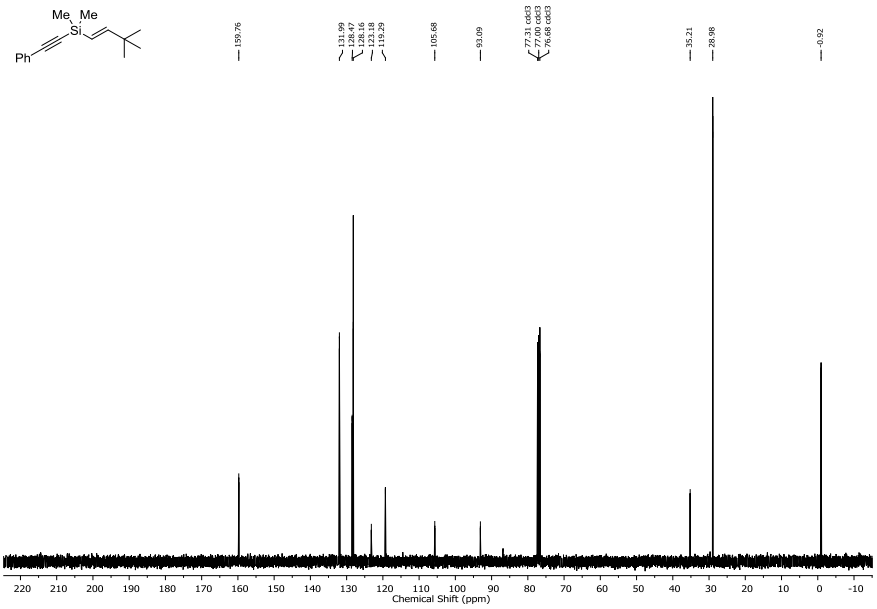
Chemical Shift (ppm)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Si
Ph
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119.29
105.68
93.09
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77.00 cdcl3
76.68 cdcl3
35.21
28.98
-0.92
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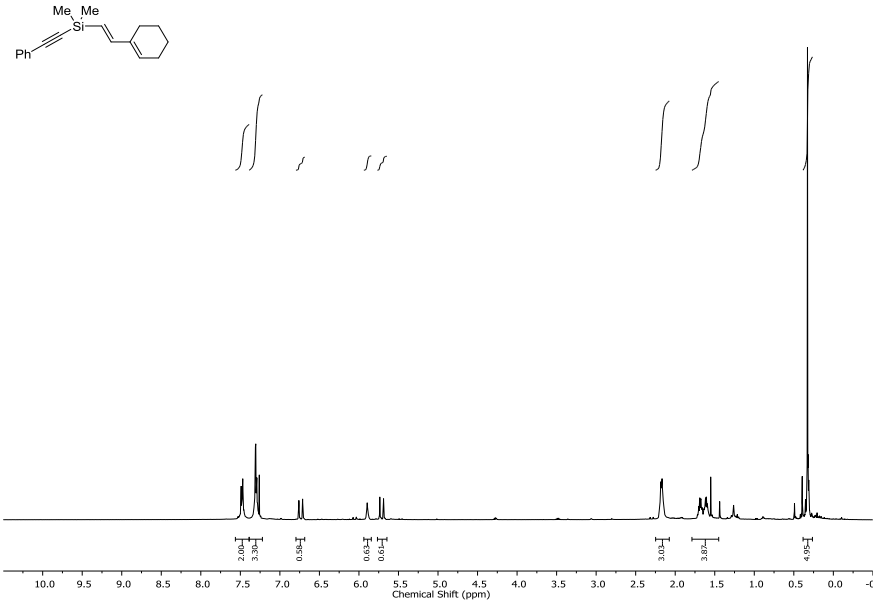
Chemical Shift (ppm)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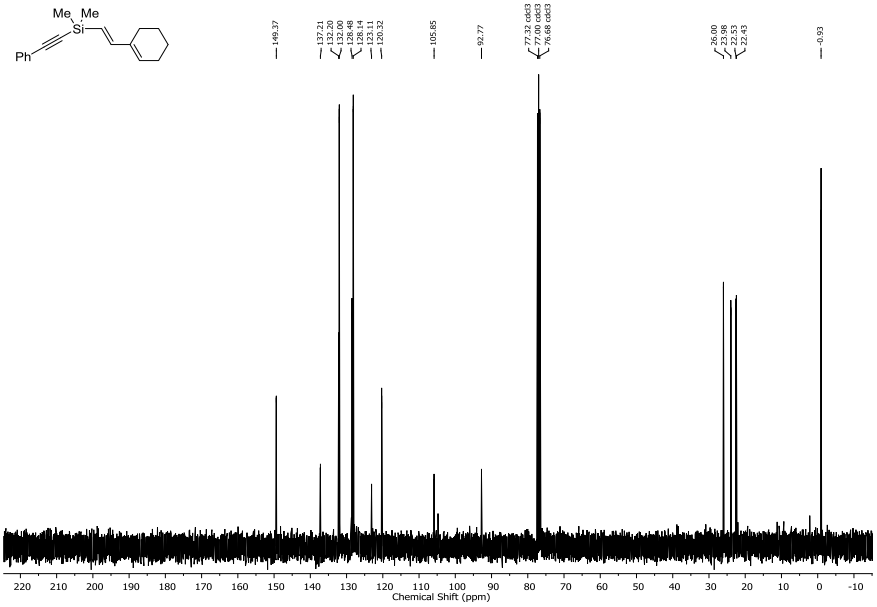
Chemical Shift (ppm)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22.53
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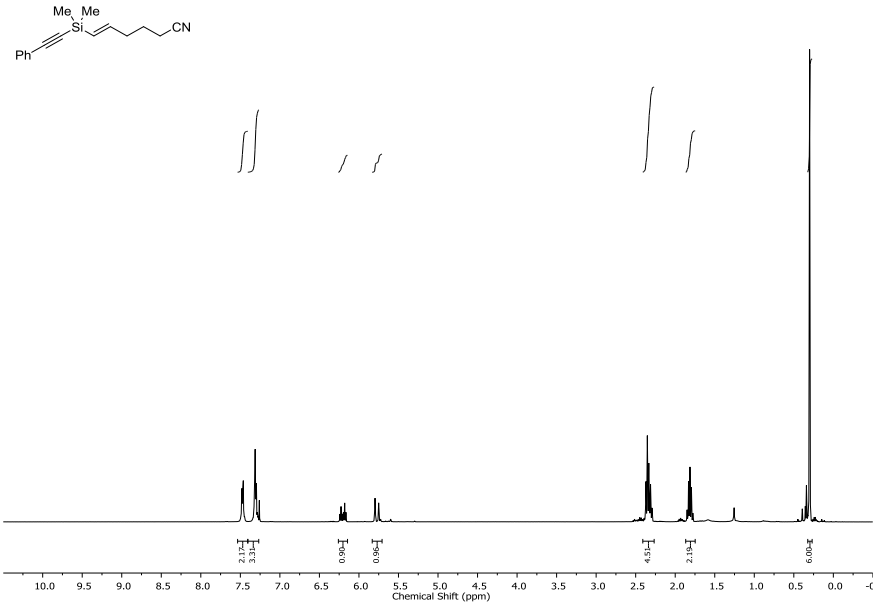
Chemical Shift (ppm)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Ph
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0.98
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6.00
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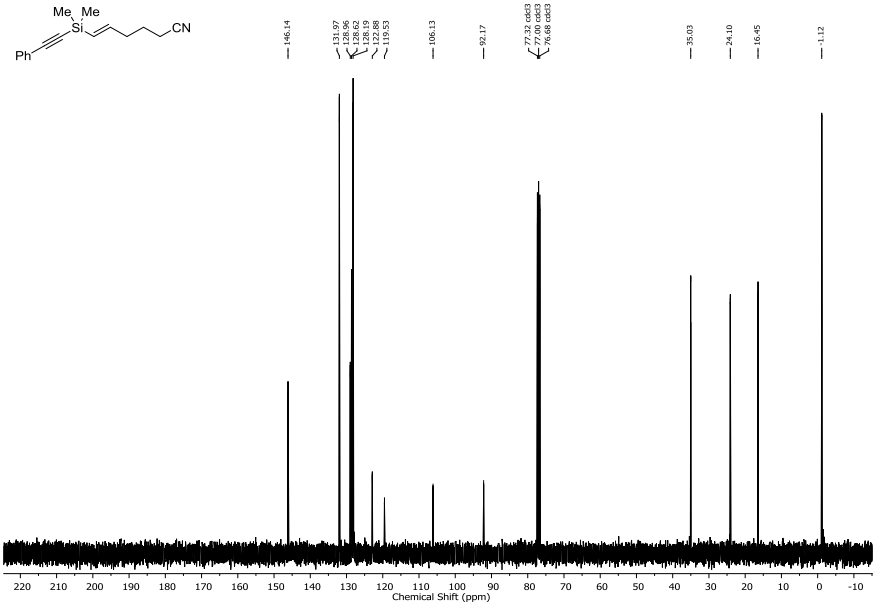
Chemical Shift (ppm)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CN
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106.13
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77.00 cdcl3
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24.10
16.45
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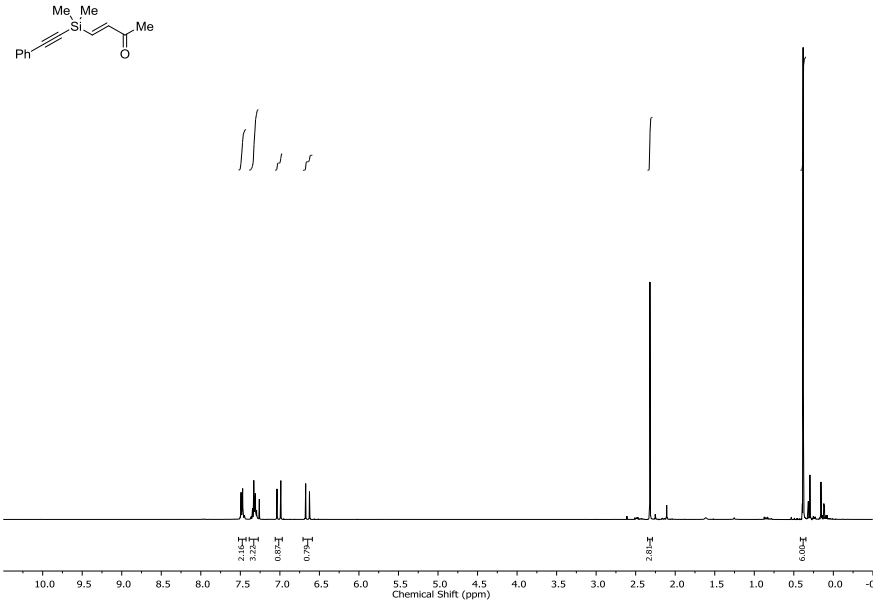
Chemical Shift (ppm)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Si
Me
Ph
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6.00
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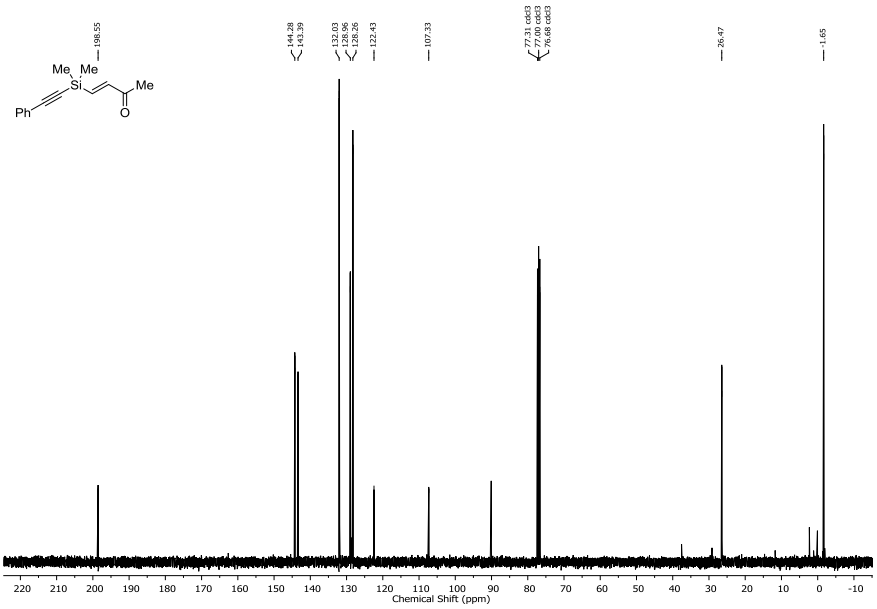
Chemical Shift (ppm)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128.26
122.43
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77.00 cdcl3
76.68 cdcl3
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1.65
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Si
Me
Ph
O
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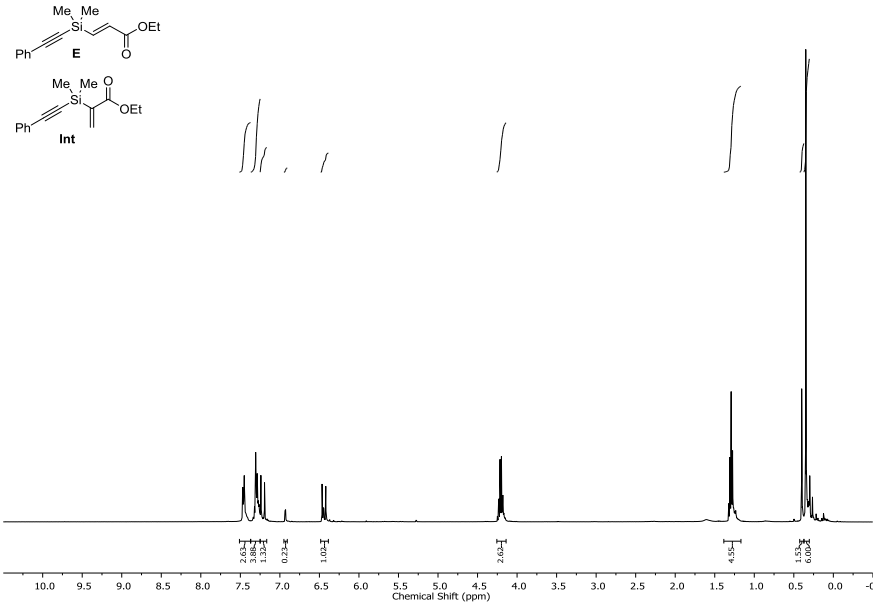
Chemical Shift (ppm)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Si
OEt
Ph
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Int
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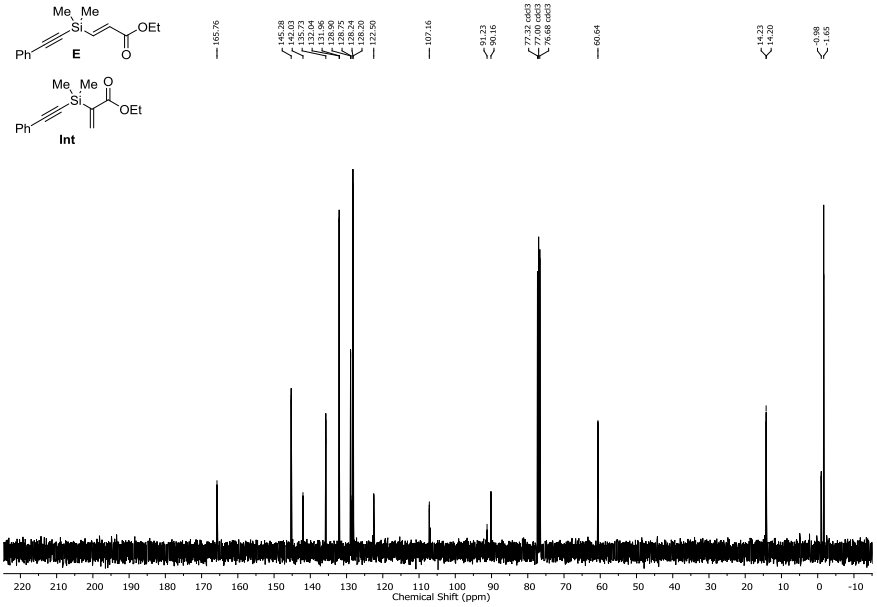
2.68
4.50
1.55
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)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Si
OEt
Ph
E
Int
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131.96
128.99
128.75
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122.50
107.16
91.23
90.16
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
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14.23
14.20
0.98
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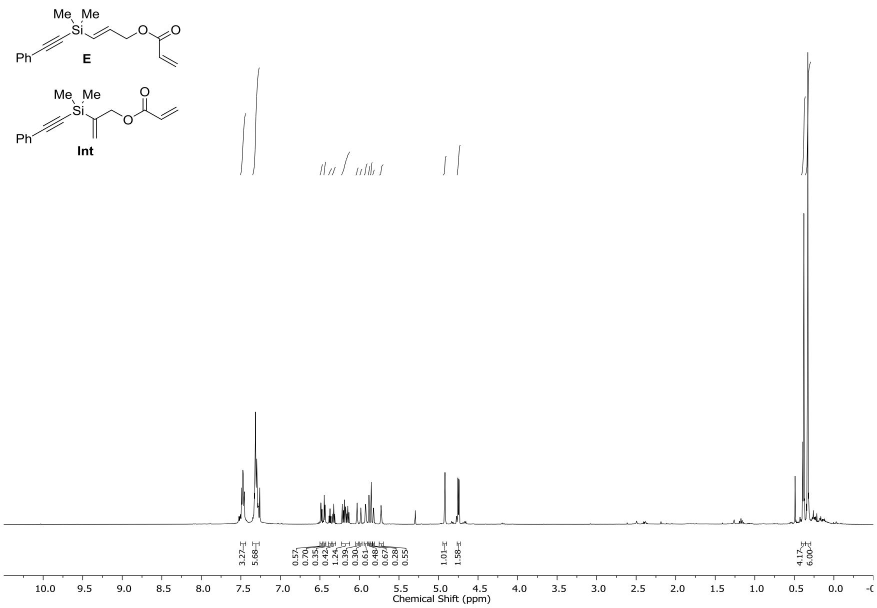
Chemical Shift (ppm)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E
Me Me
Si
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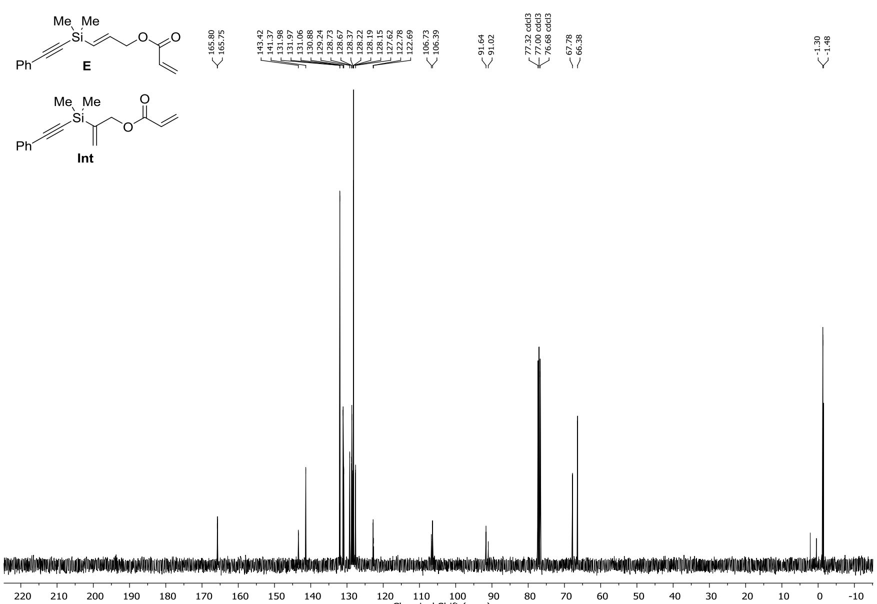
Ph
Int
Chemical Shift (ppm)


Me Me
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Ph
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Ph
Int
165.80
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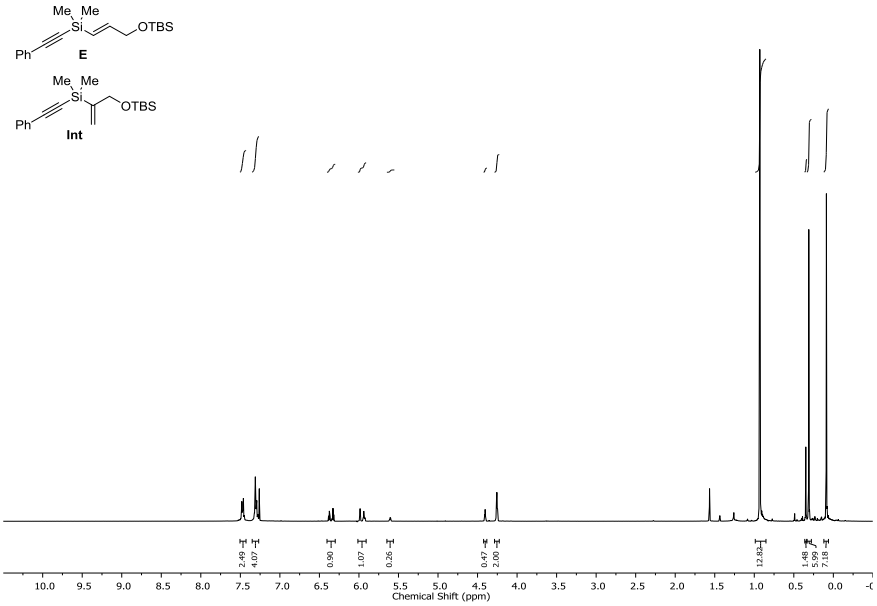
Chemical Shift (ppm)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Ph
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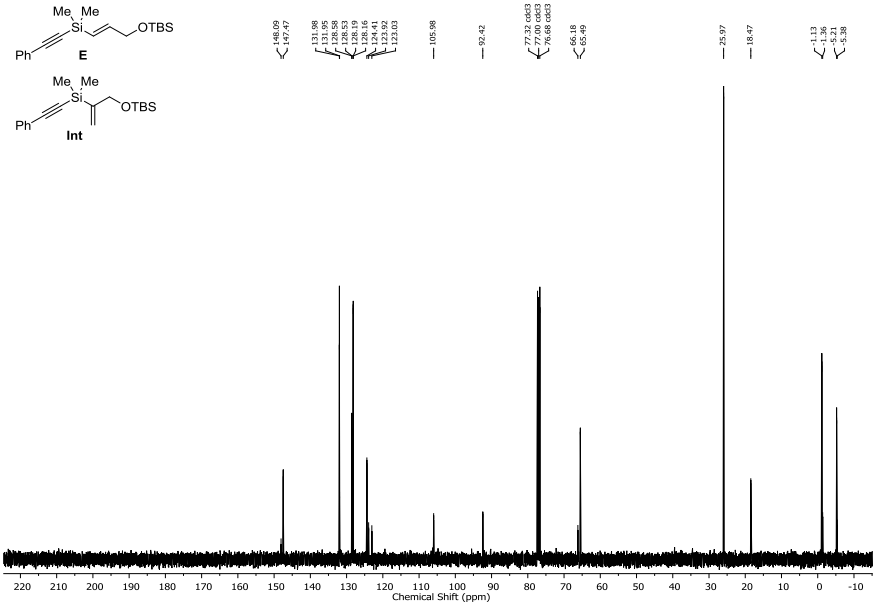
Chemical Shift (ppm)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124.40
123.03
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66.18
65.99
25.97
18.47
1.13
1.36
-5.21
-5.38
Chemical Shift (ppm)

5.11 REFERENCES

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CHAPTER VI

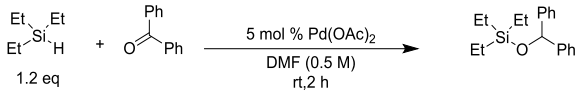
EXPERIMENTALS FOR CHAPTER III: IRON NANOPARTICLE CATALYZED HYDROSILYLATION

6.1 Methods: Unless stated otherwise, all reactions were carried out in oven dried or flame dried glassware under an atmosphere of argon, with magnetic stirring. Reactions were monitored by thin-layer chromatography with 0.25 mm precoated silica gel plates or by Gas Chromatography. Visualization of all TLCs was performed by UV and/or staining with phosphomolybdic acid, $KMnO_4$, or Seebach's stain. Purifications were performed by silica gel flash chromatography with silica gel (Silicycle, 60 Å, 230-400 mesh) packed in glass columns and eluting with hexanes/Et_2O unless otherwise noted.

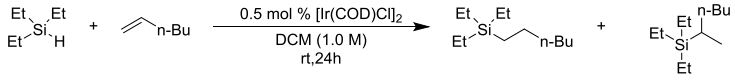
6.2 Materials: All solvents were freshly distilled or purified under vacuum using standard procedures to ensure dry and inert conditions. All other reagents were purified and degassed to an inert medium. All reaction systems were conducted under argon. To maximize inert conditions reagents were also subjected to standard freeze-thaw methods.

6.3 Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Inova 400 MHz NMR spectrometer or a Bruker Avance 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) with chemical shifts reported relative to residual chloroform solvent peaks (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C). Data for ^{1}H NMR was recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet, m = multiplet, or unresolved), coupling constant(s) in Hz. IR spectra were obtained as thin films on a Perkin Elmer 2000 FTIR spectrometer using NaCl plates.

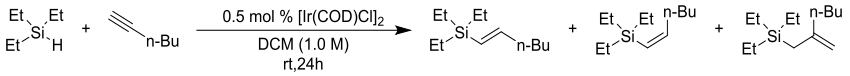
6.4 Target Compounds Synthesized and Characterization Data



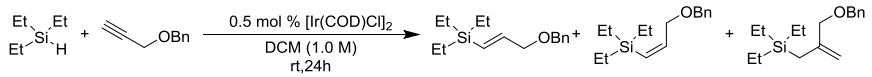
Preparation of (benzhydryloxy)triethylsilane: To a dry, 10-mL, round-bottomed flask under argon were sequentially added $Pd(OAc)_2$ (0.005 mmol, 0.0034 g), benzophenone (1.0 mmol, 0.182 g), DMF (0.5 M, 2 mL), and triethylsilane (1.2 mmol, 0.174 mL). The reaction was stirred for 2 hrs after which the solution was directly loaded on a silica gel column. The reaction mixture was purified by flash chromatography (pet ether) to afford 0.259 g (87%) of (benzhydryloxy)triethylsilane a clear oil;[216] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.0Hz 4H), 7.29 (t, J = 6.0 Hz, 4H), 7.23 (d, J = 6.0 Hz, 2H), 5.77 (s, 1H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.59 (q, *J* = 8.0) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.22, 128.11, 126.92, 126.31, 76.35, 6.76, 4.85. Physical and spectral data were consistent with those reported in the literature.[217],



Preparation of triethyl(hexyl)silane: To a dry, 10-mL, round-bottomed flask under argon was sequentially added $[Ir(COD)Cl]_2$ (0.005 mmol, 0.0034 g),1-hexene (1.0 mmol, 0.124 mL), DCE (1 M, 1 mL), and triethylsilane (1.0 mmol, 0.160 mL). The reaction was stirred for 24 hrs and then an aliquot was analyzed by GC. The reaction was concentrated in vacuo, and the crude product was purified by flash chromatography (hexanes:Et_2O; 95:1) to afford 0.15 g (73%) of triethyl(hexyl)silane a light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51-1.20 (m, 16H), 0.96-0.82 (m, 27H), 0.54-0.43 (m, 12H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.11, 22.96, 17.51, 17.31, 17.28, 17.09, 13.73, 13.59, 7.42, 7.40, 7.30, 7.27, 3.55, 3.32, 3.13, 3.06. Physical and spectral data were consistent with those reported in the literature.[218, 219]



Preparation of triethyl(hex-1-en-1-yl) silane: To a dry, 10-mL round-bottomed flask under argon $[Ir(COD)Cl]_2$ (0.005 mmol, 0.0034 g), 1-hexene (2.0 mmol, 0.232 mL), DCE (1 M, 1 mL), and triethylsilane (2.0 mmol, 0.320 mL) were sequentially added. The reaction was stirred for 24 hrs and then an aliquot was analyzed by GC. The reaction was concentrated in vacuo, and the crude product was purified by flash chromatography (hexanes) to afford 0.3529 g (89%) of triethyl(hex-1-en-1-yl) silane as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41-6.34 (m, 1H), 6.04 (m, 1H), 5.89 (s, 2H), 5.55 (d, *J* = 16Hz, 1H), 5.40 (d, J = 12 Hz), 2.21(t, *J* = 8 Hz, 4H), 2.11(q, *J* = 8 Hz, 2H), 1.95 (m, 4H), 1.50 -1.24(m, 4H), 1.08-0.76 (m, 36H), 0.64-0.43 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.77, 128.62, 127.38, 126.21, 125.47, 36.77, 34.98, 33.65, 31.62, 31.04, 29.18, 23.11, 22.21, 17.31, 14.15, 13.93, 13.65, 7.47, 7.37, 7.35, 3.55, 3.26, 3.13. Physical and spectral data were consistent with those reported in the literature.[220]



Preparation of (3-(benzyloxy) prop-1-en-1-yl)triethyl silane: To a dry, 10-mL round-bottomed flask under argon was sequentially added $[Ir(COD)Cl]_2$ (0.005 mmol, 0.01 g), ((prop-2-yn-1-yloxy) methyl)benzene (3.0 mmol, 0.4338 mL), DCE (1 M, 1 mL), and dimethyl(phenylethynyl)silane (3.0 mmol, 0.4792 mL). The reaction was stirred for 24 hrs and then an aliquot was analyzed by GC. The reaction was concentrated in vacuo, and the crude product was purified by flash chromatography (DCM) to afford 0.227 g (51%) of (3-(benzyloxy) prop-1-en-1-yl)triethyl silane as a light brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.00 (m, 15H), 6.37 (s, 2H), 6.18(d, *J* = 20 Hz), 5.98 (d, *J* = 8 Hz), 5.90 (d, *J* = 12 Hz, 1H), 4.76 (s, 2H), 4.70 (s, 2H), 4.52 (s, 2H), 4.29 (s, 2H), 4.07 (s, 2H), 4.02 (s, 2H), 0.97-0.86 (m, 9H), 0.63-0.48(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.55, 142.85, 136.88,

128.56, 128,36, 128,34, 128.18, 127.79, 127.65, 127.58, 127.47, 127.33, 110.00, 73.35, 73.29, 72.10, 72.07, 7.41, 7.35, 3.35, 3.25, 3.09. Physical and spectral data were consistent with those reported in the literature.[221, 222, 223]

6.5 General Screening Procedures for Reaction Conditions:

Procedure A: To a dry, 10-mL, microwave-tube was added (0.05 mmol) iron salt, solvent (5ml, 0.2M), stabilizing/capping agent (0-100mol %), reducing agent (0-100 mol %), additive (0-100 mol %), triethylsilane (1-3.0 mmol) and unsaturated substrate (1.0 mmol) were sequentially added. The reaction was vigorously stirred for 24-120 hrs, and then an aliquot was analyzed by GC as the reaction progressed.

Procedure B: To a dry , 10-mL, microwave-tube was added (0.05 mmol) iron salt, solvent (5ml, 0.2M), stabilizing/capping agent (0-100mol %), reducing agent (0-100 mol %), additive (0-100 mol %), triethylsilane (1-3.0 mmol) and unsaturated substrate (1.0 mmol) were sequentially added. The reaction was vigorously stirred for 24 hrs and warmed up from (0-80 ^{o}C), and then an aliquot was analyzed by GC as the reaction progressed.

Procedure C: To a dry, 50-mL, round-bottomed flask was added (1 mmol), iron salt, solvent (20 ml, 0.05 M), stabilizing/capping agent (1-7.5 mmol), additive (0-7.5 mmol) and reducing agent (1-7.5 mmol). The reaction was warmed from room temperature to reflux for 1-6 h, then 1 ml aliquots of this mixture were transferred to a 4 ml solution of triethylsilane (1-3.0 mmol), and unsaturated substrate (1.0 mmol) was added. The reaction was vigorously stirred for 24 hrs and, then was warmed up from (22-80 ^{o}C), and then an aliquot was analyzed by GC as the reaction progressed.

6.6 REFERENCES

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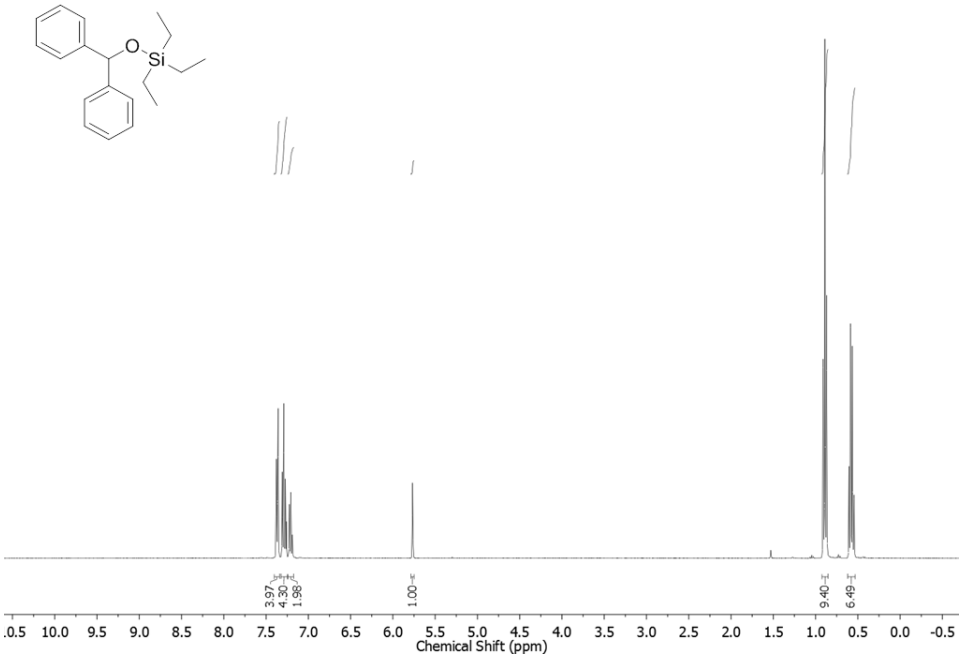
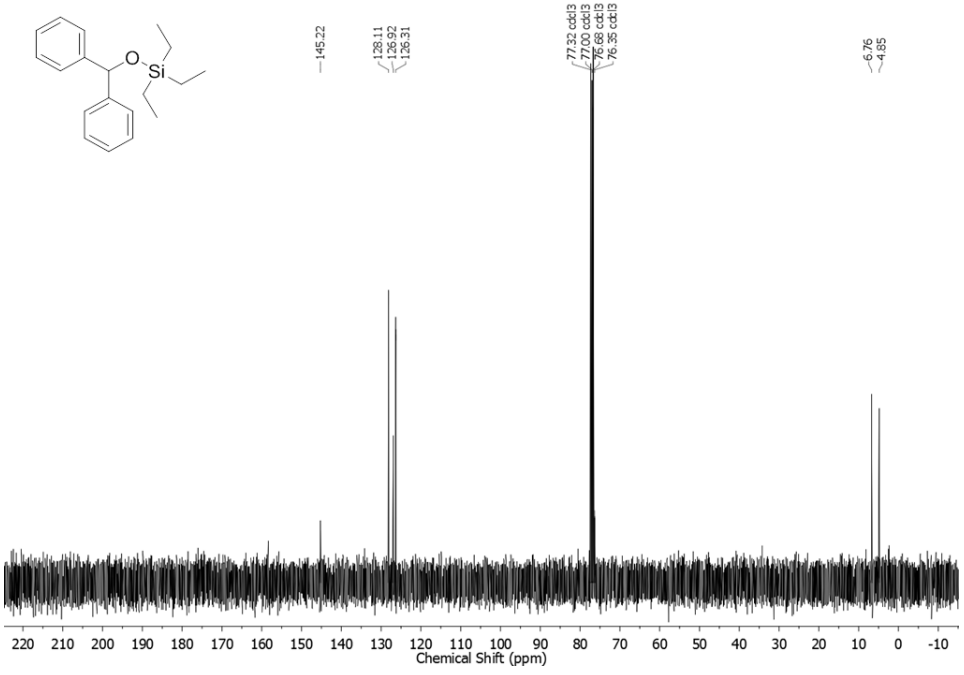
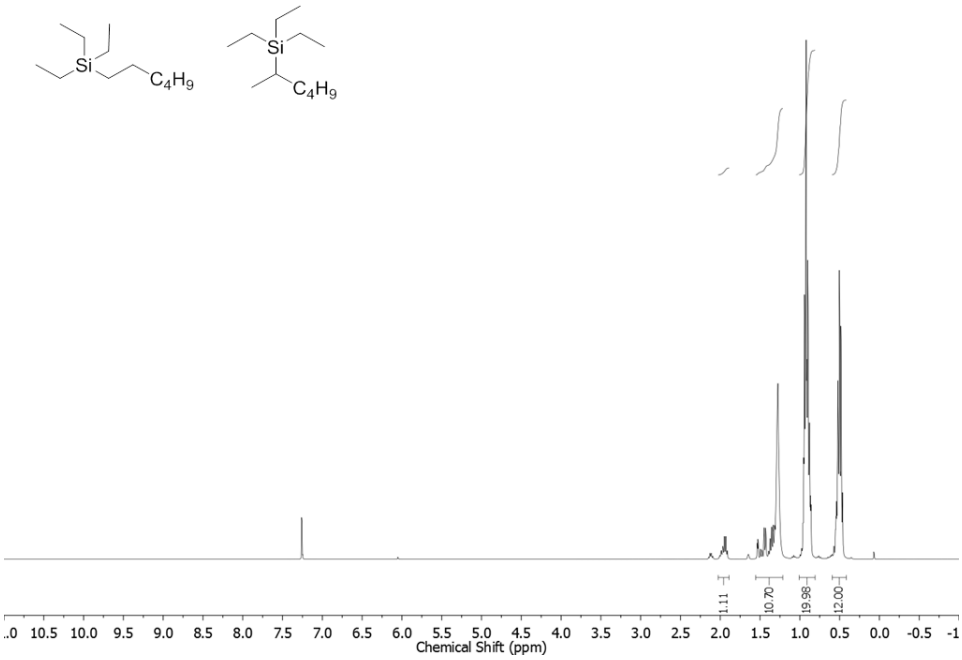
6.7 ^{13}C and ^{1} H NMR SPECTRA



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Si
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19.98
12.00
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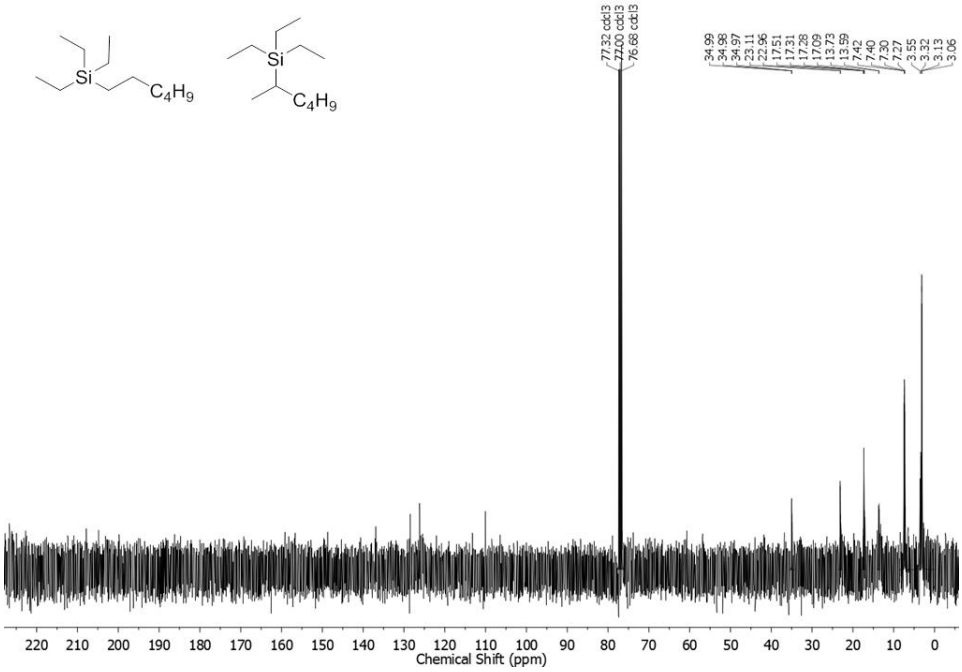
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C4H9
Si
C4H9
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77.00 cdcl3
76.68 cdcl3
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34.98
34.97
23.11
22.96
17.51
17.31
17.28
17.09
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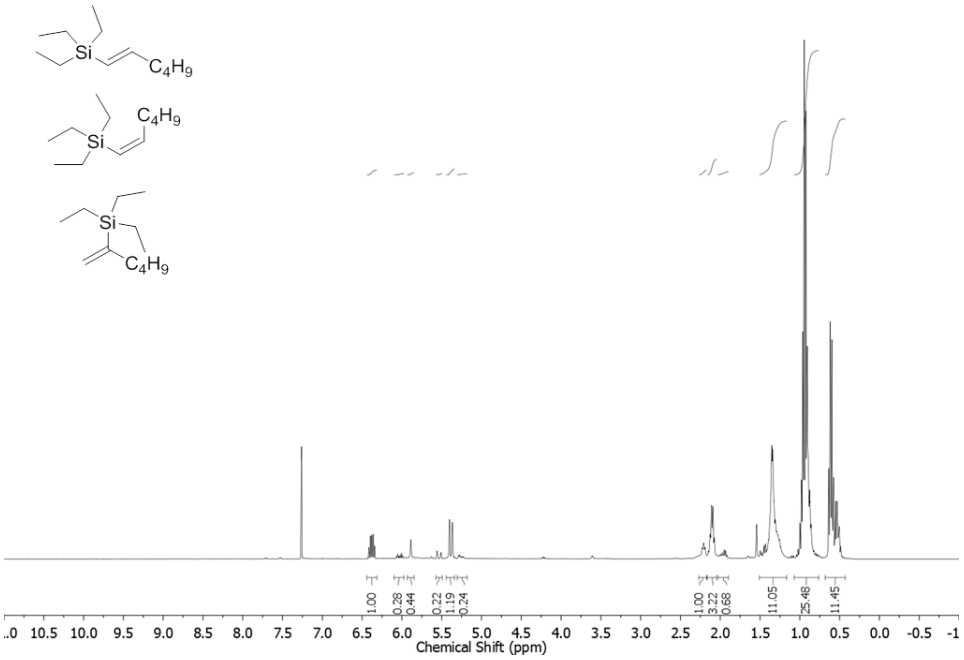
3.32
3.13
3.06
Chemical Shift (ppm)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C4H9
Si
C4H9
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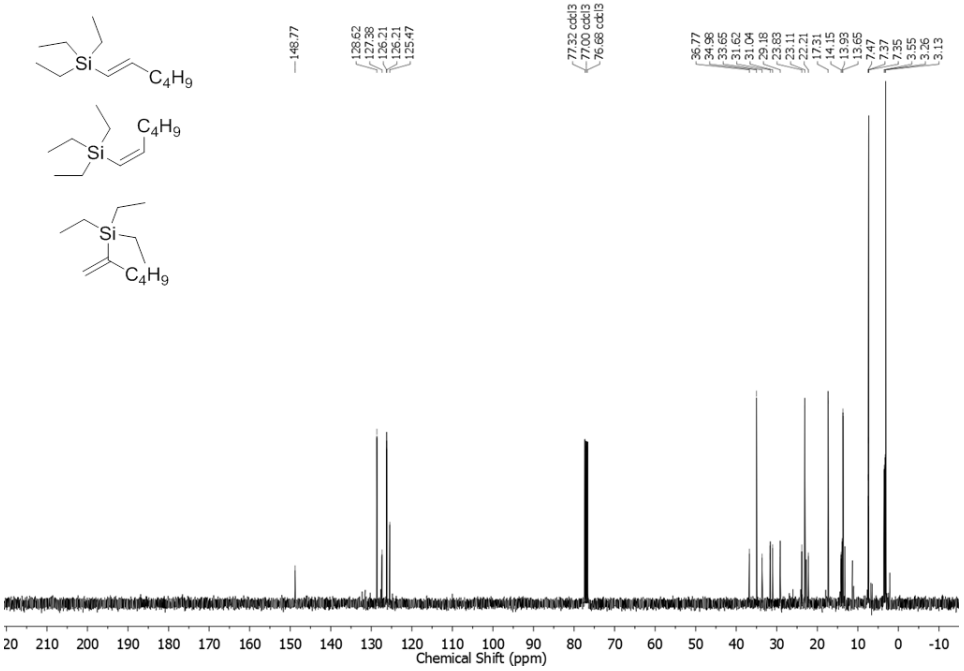
Chemical Shift (ppm)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C4H9
Si
C4H9
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126.21
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77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
36.77
34.98
33.65
31.62
31.04
29.18
23.83
23.11
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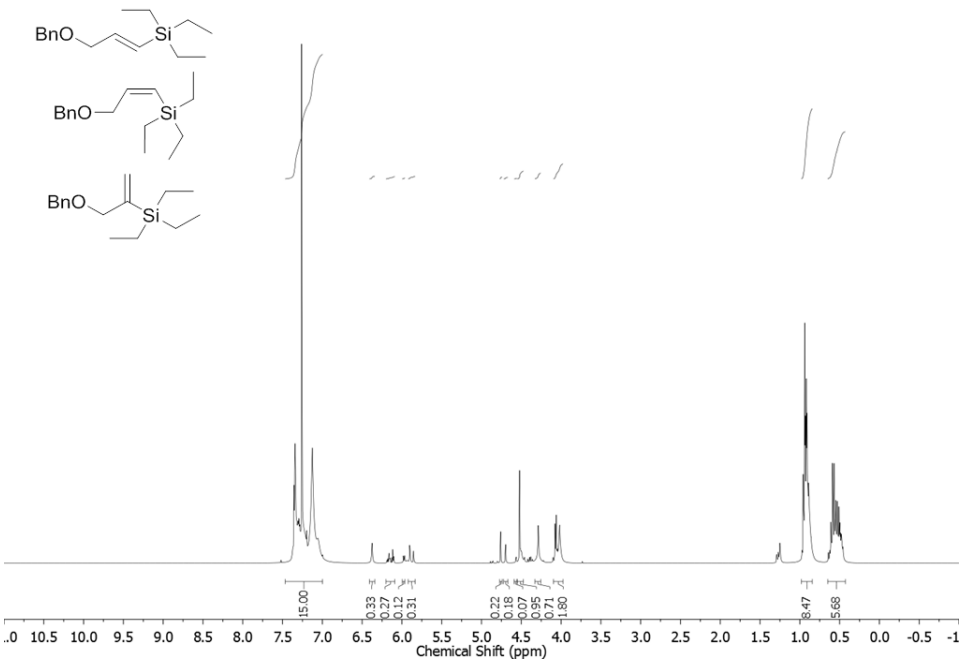
3.26
3.13
Chemical Shift (ppm)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BnO
Si
BnO
Si
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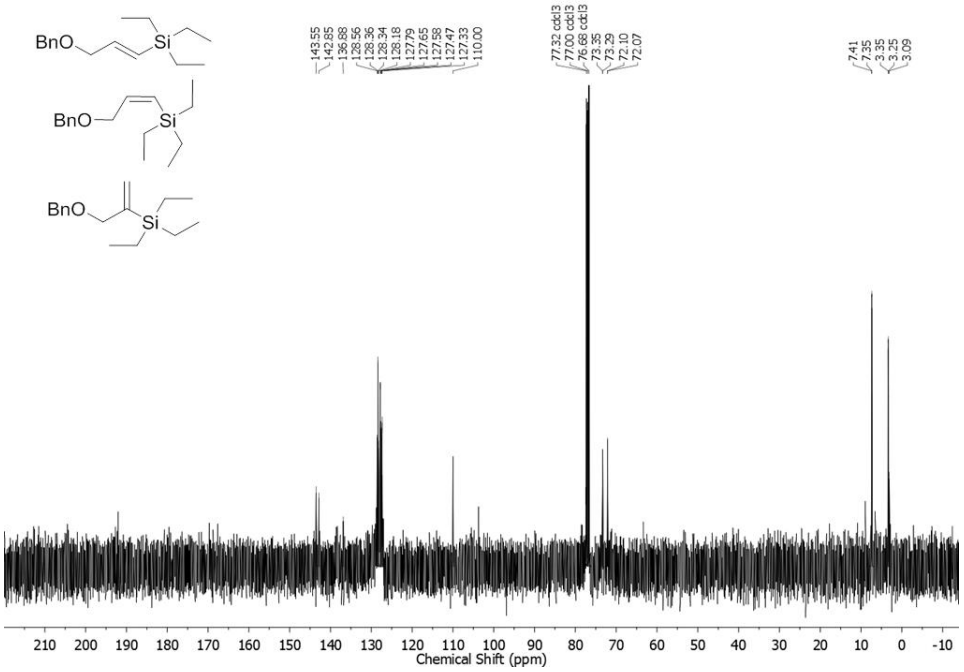
Chemical Shift (ppm)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BnO
Si
BnO
Si
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127.79
127.65
127.58
127.47
127.33
110.00
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
73.35
73.29
72.10
72.07
7.41
7.35
3.35
3.25
3.09
Chemical Shift (ppm)

VITA

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