Universität Bremen

Inaugural-Dissertation

towards the academic degree

Doctor rerum naturalium (Dr. rer. nat.)

Functionalized Silyl-BINOLs and their Use as Building Blocks for the Synthesis of Chiral Sila-Macrocycles.

Submitted to the Institute of Chemistry and Biology,

University of Bremen

by

Nelly Rivas King

from Panama City

Bremen, April 2012

This work was carried out under the supervision of Prof. Dr. Jens Beckmann from November 2008 to May 2010 at the Institute of Chemistry and Biochemistry, at the Free University of Berlin and from June 2010 to December 2011 at the Institute of Chemistry and Biology, at the University of Bremen.

1st Referee: Prof. Dr. Jens Beckmann

2nd Referee: Dr. Vladimir A. Azov

Date of Disputation: 01.06.2012

Este trabajo es dedicado primero que todo a Dios por haberme permitido vivir cada una de las experiencias que conllevaron a su culminación,

a mis padres Thelma y Gilberto, quienes me inculcaron el deseo de superación y con tanto amor se esforzaron para que yo pudiese tener una profesión,

y a mi querida hermana Elizabeth, quien sin dudar ha apoyado siempre cada uno de mis sueños.

Acknowledgments

Writing this thesis would not have been achievable without the guidance, contributions, and help of remarkable people, who supported me in all possible ways during the last three years.

I would like to start by expressing my sincerest gratitude to my advisor Prof. Dr. Jens Beckmann, whose valuable ideas and knowledge are responsible for the success of this study. I appreciate very much his friendly supervision and encouragement during the time it took me to complete the research and write this dissertation.

I am grateful to the members of the defense committee, Dr. Vladimir A. Azov, Dr. Andreas Hartwig, Dr. Malte Hesse, Dipl. Chem. Alexandra Schütrumpf and Artem Schröder for giving their time and expertise to read and evaluate this work.

I owe my gratitude to the Panama government which, throughout its National Secretary of Science and Technology (SENACYT), provided me with the necessary financial support to complete the doctorate degree in Germany.

I also would like to thank Pamela Finke and Emanuel Hupf who closely looked at the final version of the thesis for English style and grammar, correcting both and offering suggestions for improvement.

I wish to thank the coworkers of the service departments and workshops of the Free University of Berlin and the University of Bremen for their support and timely fulfillment of all the required tasks. Particularly, I would like to acknowledge the cooperation of Dr. Andreas Springer and Dr. Thomas Dülcks from the mass spectrometry departments for their incessant effort to provide accurate results. Also, I am indebted to Dr. Malte Hesse, Dr. Enno Lork and Peter Brackmann, who executed the measurement and resolution of the presented crystal structures. Besides, I convey special thanks to Dr. Mirko Weinhold, who gently invested his time to carry out the GPC analysis of the polymeric products. I was as well benefited by the skills and knowledge in NMR techniques of Dipl. Chem. Johannes Stelten who was always willing to help and patiently assisted me to measure and resolve complicated structures.

I want to warmly thank the members of the Beckmann research group for promoting and stimulating not only a pleasant work atmosphere, but also a welcoming social environment. I definitely have to mention the former fellows of the group, Usman Ahmad, Marian Graßmann, and Jens Bolsinger, who shared their experience and provided fruitful suggestions to improve my research. To my actual colleagues, Ole Mallow, Maxie Hesse, Alexandra Schütrumpf, Pamela Finke and Emanuel Hupf, with whom I have made all the way from Berlin to Bremen, I am deeply grateful for their friendship and constant support in all imaginable aspects. Besides, I wish to offer my earnest thanks to the new group members, Andreas Denhof, Sarah Janoschek and Nadine Danz for their great amity which has granted an enjoyable time in Bremen.

It is my fortune to gratefully acknowledge the members of my family because without their encouragement and understanding it would have been impossible to finish this work. Especially, I need to praise my parents, Thelma and Gilberto, who have sacrificed so much to see their children succeed. Words fail me to express my appreciation to my sister Elizabeth and my brother-in-law Ricardo for their endless love and unconditional support. Foremost, I thank my fiancé Andrè who has always been beside me during the happy and hard moments to push me and motivate me. Also, I extend my loving thanks to Margret and Heinrich Niermann who let me own a beautiful family in Germany.

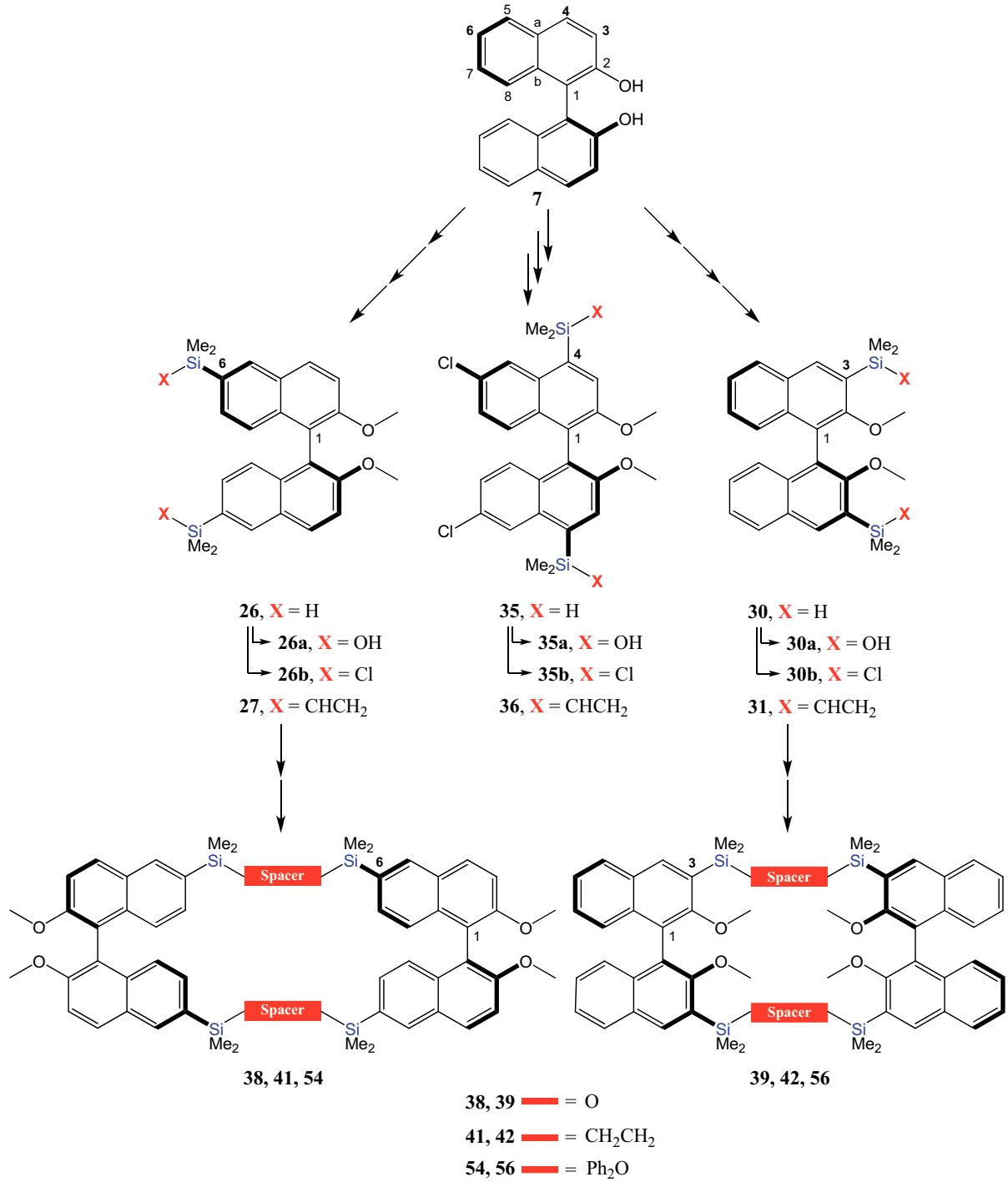
Last but by any mean not least, I would like to pay high regards to my good friends Sofia, Jeremì, Magda, Paolo, Giulio, Melissa, Jhonny, Maribel, and Heinrich for their sincere love, care, moral support and about all for the beautiful memories of these years abroad.

Abstract

In this work, the axially chiral 1,1'-bi-2-naphthol (BINOL) have been used as starting material to produce chiral organosilanes in moderate to excellent yields. Among them, hydrosilanes (*S*)-6,6'-bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthyl (**26**), (*S*)-3,3'-bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthyl (**30**), and (*S*)-4,4'-bis(dimethylsilyl)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthyl (**35**) are reported. These compounds were further converted into their respective silanols, (*S*)-6,6'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**26a**), (*S*)-3,3'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene **(30a**), and (*S*)-6,6'-dichloro-4,4'-bis(dimethylhydroxysilyl)2,2'-dimethoxy-1,1'-binaphthalene (**35a**) by oxidation in the presence of Pearlmans catalyst in H_2O. Also, chlorination of hydrosilanes **26**, **30**, and **35** with CCl_4 and $PdCl_2$ afforded chlorosilanes (*S*)-6,6'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**26b**), (*S*)-3,3'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**30b**), and (*S*)-6,6'-dichloro-4,4'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**35b**) in quantitative yields. Additionally, the synthesis and characterization of novel vinylsilanes (*S*)-6,6'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**27**), (*S*)-3,3'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**31),** and (*S*)-6,6'-dichloro-4,4'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**36**) is described. Other chiral organosilanes containing chloromethylsilane groups were synthesized, from which novel compounds bearing organotin moieties were afforded. Besides, chiral sila-macrocycles were prepared using the above mentioned chiral organosilane building blocks. Thus, cyclic siloxanes (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyltetrasiloxane (**38**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyltetrasiloxane (**39**) were obtained from hydrosilanes (**26** and **30**) or silanols (**26a** and **30a**). Novel macrocycles (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyldiethylsilane (**41**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyldiethylsilane (**42**) possessing an aliphatic bridge were conveniently prepared via hydrosilylation reaction of vinylsilanes (**27** and **31**) with hydrosilanes (**26** and **30**) using Karstedt catalyst, respectively. In addition, chlorosilanes (**26b** and **30b**) were used to prepare macrocycles connected by an aromatic ligand. Besides, functionalization of macrocycles **38** – **42** by demethylation, bromination, and silylation was attempted.

Graphical Abstract

Functionalization of the 6,6'-, 4,4'-, and 3,3'-positions of BINOL affording silicon-containing chiral compounds and their subsequently use to prepare chiral sila-macrocycles is presented.



Zusammenfassung

In der vorliegenden Arbeit wurde das axial chirale 1,1'-Bi-2-naphthol (BINOL) als Startmaterial eingesetzt, um chirale Organosilane in moderaten bis exzellenten Ausbeuten darzustellen. So wurden unter anderem die Hydrosilane (*S*)-6,6'-Bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthyl (**26**), (*S*)-3,3'-Bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthyl (**30**), und (*S*)-4,4'-Bis(dimethylsilyl)-6,6'-dichlor-2,2'-dimethoxy-1,1'-binaphthyl (**35**) synthetisiert. Diese Verbindungen wurden im Weiteren durch Oxidation unter Verwendung des Pearlman Katalysators in Wasser zu den jeweiligen Silanolen (*S*)-6,6'-Bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthol (**26a**), (*S*)-3,3'-Bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthol **(30a**) und (*S*)-6,6'-Dichlor-4,4'-bis(dimethylhydroxysilyl)2,2'-dimethoxy-1,1'-binaphthol (**35a**) umgesetzt. Chlorierung der Hydrosilane **26**, **30** und **35** mit CCl_4 und $PdCl_2$ ergab in jeweils quantitativer Ausbeute die Chlorsilane (*S*)-6,6'-Bis(dimethylchlorsilyl)-2,2'-dimethoxy-1,1'-binaphthol (**26b**), (*S*)-3,3'-Bis(dimethylchlorsilyl)-2,2'-dimethoxy-1,1'-binaphthol (**30b**) und (*S*)-6,6'-Dichlor-4,4'-bis(dimethylchlorsilyl)-2,2'-dimethoxy-1,1'-binaphthol (**35b**). Zudem wird die Darstellung und Charakterisierung der neuartigen Vinylsilane (*S*)-6,6'-Bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthol (**27**), (*S*)-3,3'-Bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthol (**31**) und (*S*)-6,6'-Dichlor-4,4'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthol (**36**) beschrieben. Weitere chirale Organosilane mit Chlormethylsilangruppen wurden synthetisiert, welche einen Zugang zu neuartigen Verbindungen mit Organozinngruppen ermöglichten. Unter Verwendung der o.g. chiralen Organosilane als Startkomponente konnten chirale Sila-Makrozyklen dargestellt werden. So wurden die zyklischen Siloxane (*S,S*)-2,2',10,10'-Tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyltetrasiloxan (**38**) und (*S,S*)-2,2',10,10'-Tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyltetrasiloxan (**39**) ausgehend von Hydrosilanen (**26** und **30)** oder Silanolen (**26a** und **30a**) erhalten. Die neuartigen Makrozyklen (*S,S*)-2,2',10,10'-Tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyldiethylsilan (**41**) und (*S,S*)-2,2',-10,10'-Tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyldiethylsilan (**42**) mit aliphatischer Linkereinheit wurden jeweils durch Hydrosilylierung von Vinylsilanen (**27** und **31**) mit Hydrosilanen (**26** und **30**) unter Verwendung des Karstedt Katalysators dargestellt. Zudem wurden Chlorsilane (**26b** und **30b**) verwendet, um Makrozyklen zu synthetisieren, welche über einen aromatischen Linker verbunden sind. Ausserdem wurde die Funktionalisierung der Makrozyklen **38** – **42** durch Demethylierung, Bromierung und Silylierung versucht.

Table of Contents

List of Figures

List of Tables

List of Schemes

List of Abbreviations and Symbols

Å	Angstrøm
AIBN	Azobisisobutyronitrile
BINOL	1,1'-bi-2-naphthol
DCM	Dichloromethane
DMF	Dimethyl formamide
DVB	Divinylbenzene
ee	enantiomeric excess
EI-MS	Electronic impact mass spectrometry
ESI-TOF	Electrospray ionization-time of flight mass spectrometry
EtOAc	Ethyl acetate
Et_3N	Triethylamine
Et_2O	Diethyl ether
FT IR	Fourier Transform Infra Red Spectroscopy
s	strong
m	medium
w	weak
v	very
spr	sharp
b	broad
GPC	Gel Permeation Chromatography
Mw	Weight Average Molecular Weight
Mn	Number Average Molecular Weight
Mw/Mn	Polydispersity
Hx	Hexane
HPLC	High Performance Liquid Chromatography
MeOH	Methanol
n-BuLi	*n*-Butyl lithium
NMR	Nuclear MagneticResonance
^{n}J	Coupling constant
δ	Chemical shift
s	singulet
d	doublet
t	triplet
m	multiplet
ppm	parts per million
RSD	Relative Standard Deviation
rt	room temperature
TfOH	Trifluoromethanesulfonic acid
TMEDA	Tetramethylethylene diamine
THF	Tetrahydrofuran

1 Introduction

1.1 General Aspects

For decades scientists have been trying to imitate natural systems to produce functional compounds and materials. The best examples are the work of Pedersens,[1] Lehn,[2] and Cram[3] who, inspired by the behaviour of enzymes, individually prepared and studied high selective molecules capable of interacting with specific structures. Their outstanding results, awarded with the 1987 Nobel Prize in Chemistry, gave rise to the field of host-guest chemistry and have served as base for the development and synthesis of new chemical architectures with exceptional characteristics.

Because of its ability of enantioselective complexation, crown ether type macrocycles were the first structures employed for molecular recognition studies. Since then, many different chiral macrocycle systems have been designed and synthesized as chiral host molecules to help chemists explaining the mechanism of host-guest interaction and chiral recognition. The achievements obtained in these fields have been not only limited to the understanding of complex mechanisms in living organisms, but have also been an important tool for the improvement of synthetical and analytical methods.

Nowadays, it is possible to synthesize tailor-made molecular catalysts able to recognize a substrate according to its chirality (enantiodiscrimination) and, after liberating the reaction product, regenerate to its active form.[4] In the same way, chiral porous membranes are prepared in a mode that a specific enantiomer of an enantiomeric mixture could be rapidly and efficiently isolated.[5] HPLC methods with a chiral stationary phase for determination of enantiomeric purity have gained a dominant position owned to its high reliability and sensitivity.[6] Like these, there are many other examples, later discussed, which demonstrate that the study, construction and functionalization of chiral systems is of paramount scientific importance and plays a fundamental role in socio-economic areas where chiral products are the merchandise.[7]

The opportunities of research in this area are widespread. Every year pharmaceutical companies and investigation programs direct much effort to continue with the development of this on growing field. In this sense, we have focused our attention on the synthesis of chiral macrocycles and their careful characterization, hoping to contribute with the challenging processes of creating practical materials.

1.2 Approaches to Chiral Technology

In general, chirality is recognized as an area of great scientific and commercial significance. Over the past two decades, preparation of chiral systems in the nanoscale and supramolecular levels has attracted considerable attention. Particularly, most interest has been focused in chiral systems with the ability to imitate complex biochemical processes. This has led to the development of chiral systems, which find applications in enantioselective events such as asymmetric synthesis, enantioseparations, analytical technologies for assay of enantiopure substances, and methods for assignment of absolute configuration.[7]

Efficient strategies in asymmetric catalysis using chiral systems have allowed the optimization of mechanisms for the obtention of enanatiomerically pure agrochemicals, pharmaceuticals, and flavors.[8] Turro and co-workers, for instance, reported the synthesis of asymmetrically modified zeolites with high stereo-selectivity.[9] As exemplified in Figure 1, this material was successfully employed for the photo-oxygenation of chiral enecarbamates producing enantiopure compounds with an enantiomeric excess (ee) of about 50%.

Catalysts with high stereo-selectivity have been also described by Lin *et al*.[10] They prepared nanoporous zirconium phosphonates (Figure 2) containing chiral dihydroxy functionalities which have shown to catalyze heterogeneously the addition of diethylzinc to a wide range of aromatic alehydes. The chiral secondary alcohols obtained, presented an enantiopurity of up to 72% ee.

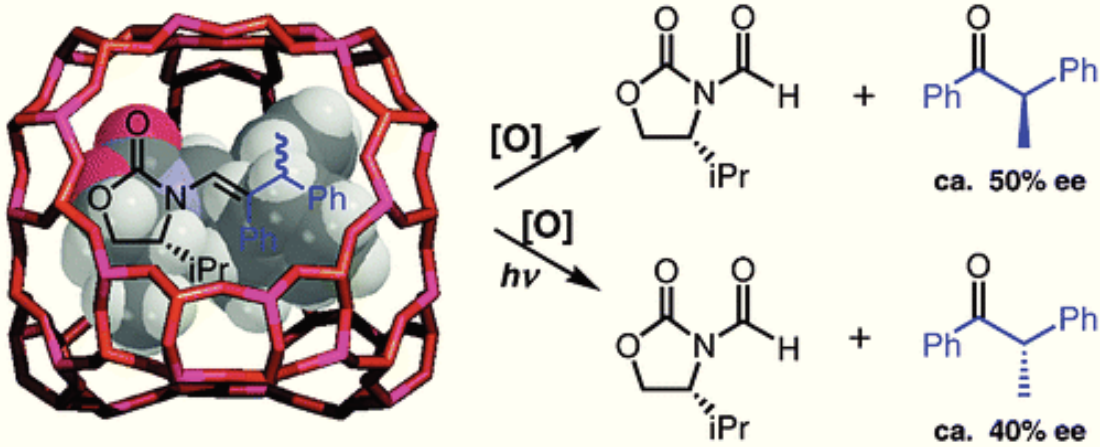


Figure 1. Zeolite supercages modified with chiral inductors for enantioselective photo-oxidation of enecarbamates. (Reprinted from *Org. Lett*. **2003**, *5*, 2025).[9]

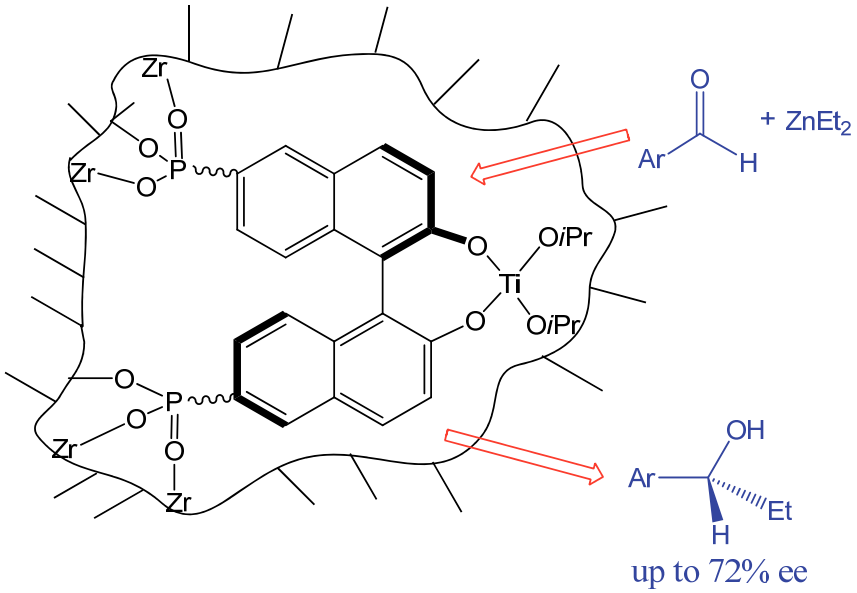


Figure 2. Chiral nanoporous solids based on 1,1'-bi-2-naphthyl-derived Zr phosphonates for catalysis of diethylzinc addition to aromatic aldehydes. (Reprinted from *J. Mol. Catal. A: Chem.* **2004**, *215*, 177).[10]

The enantiomeric recognition properties of chiral systems can be also extended to the preparation of useful molecular devices for biochemical and pharmaceutical studies,[11] as well as for the development of novel sensors.[12] In this context, the group of Prince demonstrated that conformationally ordered oligomers can serve as a platform for the construction of synthetic receptors.[13] They synthesized an *m*-phenylene ethynylene oligomer which tends to fold into two helical conformations, labeled as **M** and **P** in Figure 3. The cavity created in enantiomers **M** and **P** showed high-affinity binding site for small molecules. The different binding ability of the two enantiomers with respect to a chiral guest was then used for enantiomeric recognition. As follows, the absolute configuration of several small chiral guests was differentiated.

Another significant use given to systems with chiral specificity has been the preparation of chiral porous membranes for enantiomeric separations. Ultrafiltration using such materials has become popular, especially in the production of pharmaceuticals and food products, where the chiral separation of one specific enantiomer from others is required. For example, bio-nanotube membranes based on alumina films with cylindrical pores have been successfully employed to separate two enatiomers of the chiral drug shown in Figure 4.[14] Within the pores of the films, silica nanotubes were chemically synthesized and an antibody that selectively binds to one of the enantiomers was attached to the inner walls of the silica nanotubes. Then, the enantiomer that specifically binds to the antibody is selectively transported by the membrane.

Other membrane systems, like immobilized DNA[5] and chiral imprinted sol-gel thin films[15] have also shown enantioselective properties for chiral separations.

The examples above described represent some of the most prominent applications of chiral systems reported in the literature. They were selected from outstanding scientific journals and are supposed to give an overview of the great positive impact of studies involving chiral systems.

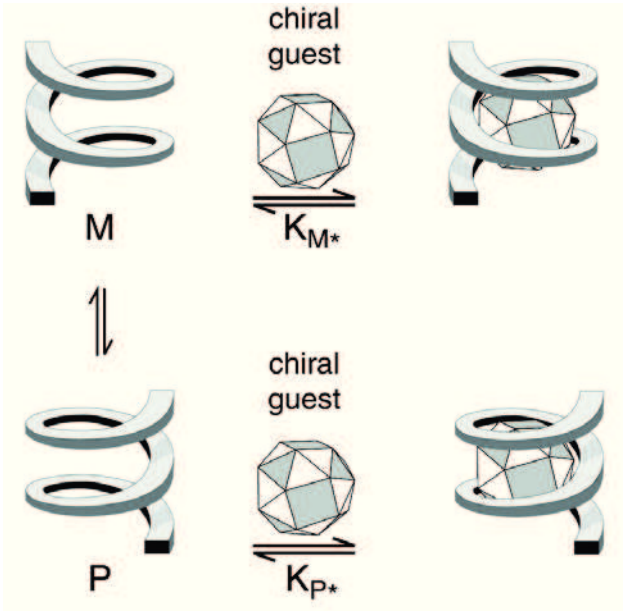


Figure 3. Association models of helical conformations of *m*-phenylene ethynylene oligomer and a chiral guest. (Reprinted from *J. Am: Chem. Soc*. **2000**, *122*, 2758).[13]

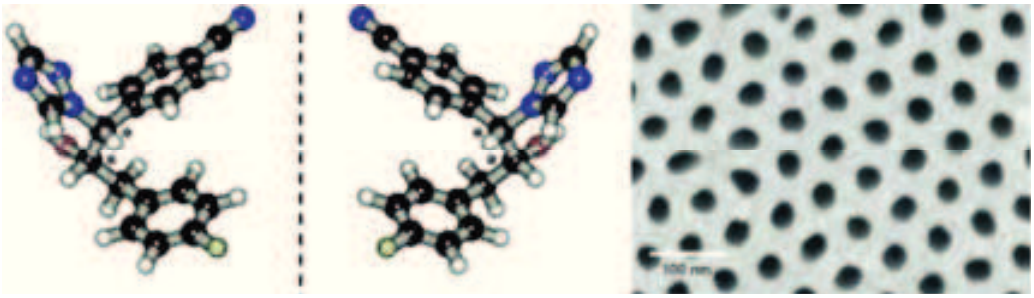
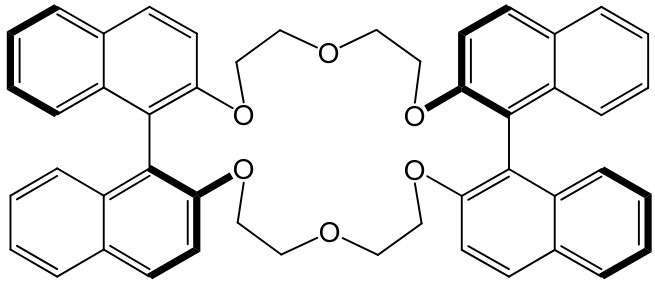


Figure 4. (**A**) Three dimensional structures of drug enantiomers. (**B**) Scanning electron micrograph of alumina membrane surface used for enantiomeric separations. (Reprinted from *Science* **2002**, *296*, 2198).[14]

1.3 Chiral Macrocycles

The design and synthesis of macrocyclic compounds provided with a chiral cavity has emerged as an important topic of research in a variety of fields. These chemical structures are among the simplest form of chiral systems and their interesting architectures have allowed their use in numerous applications, including host-guest chemistry,[16] catalysis,[4, 17] chemical sensing, and material science.[18]

The earliest chiral optically active macrocycles were reported back in 1973 by Cram *et al.*[19] They consisted of crown ethers containing a binaphthyl moiety as chiral unit, like macrocycle **1**, illustrated in Figure 5. The systematic scrutiny of these molecules provided chiral hosts that complex differentially enantiomers, demonstrating the high selective recognition properties of crown ethers.[20] Until that moment, it was believed that molecular recognition was the result of unique properties of complex biomolecules. Nevertheless, the success of Cram in imitating such phenomena using relatively simple synthetic compounds has proven that biological behaviour can be engineered into small molecules.



1

Figure 5. Crown ether-type binaphthyl macrocycle **1**, reported in 1973 by Cram *et al*.[19]

The principles established for the synthesis of chiral crown ethers could be applied to produce different types of host macrocyclic molecules. As a result, a variety of natural and synthetic chiral compounds have been used as chiral subunits for constructing structures capable of enantiomeric recognition of chiral guests. The ongoing development of chiral building blocks has resulted in the production of an ample diversity of macrocycles exhibiting chiral recognition behavior. The efficacy of these compounds are extremely valuable in areas involving metal chelation or extraction, enzyme mimics, antibiotics, and natural products.[21]

For example, the synthesis of chiral macrocycles based on a pyridine-18-crown-6 system, like compounds **2** and **3** (Figure 6), were recently reported.[21] D-amino acid derivatives were used as chirality source, providing the resulting products with a C_2-symmetry axis. Enantiomeric recognition studies displayed the strong complexation properties of these macrocycles towards D- and L-amino acid methyl ester hydrochloride salts.

Similar observations were also described for chiral aza-crown macrocycles containing a *trans*-1,2-diaminocyclohexane subunit, like macrocycle **4** (Figure 7).[22] This sort of compounds exhibited evidence of enantiomeric discrimation of mandelic acid. As shown in Figure 7, they tend to undergo complex formation with the enantiomers of the acid allowing the accurate determination of ee by ^{1}H NMR spectroscopy.

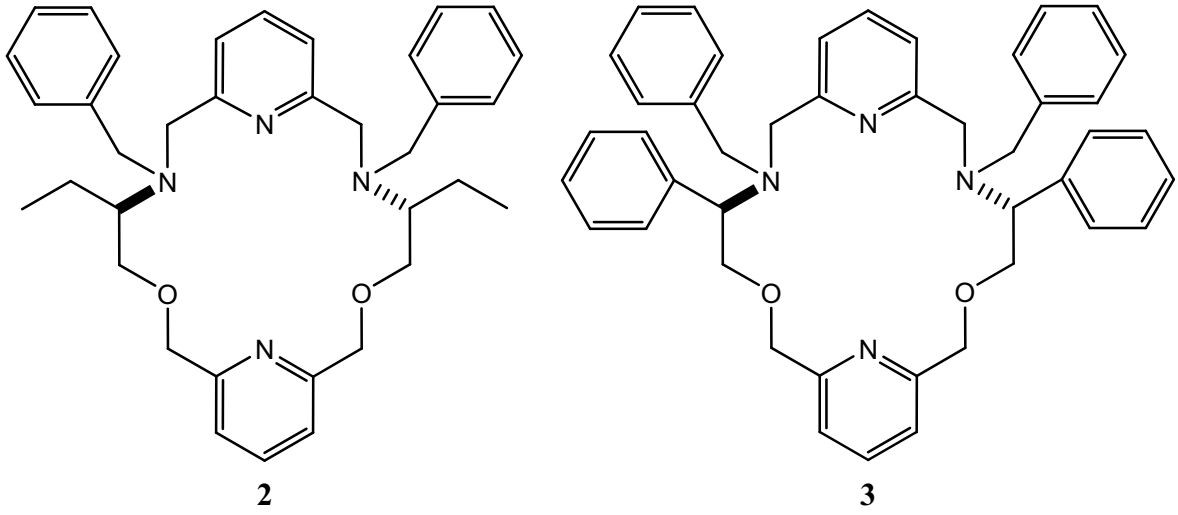


Figure 6. C_2-symmetric chyral pyridine-18-crown-6 type macrocycles **2** and **3**.[21]

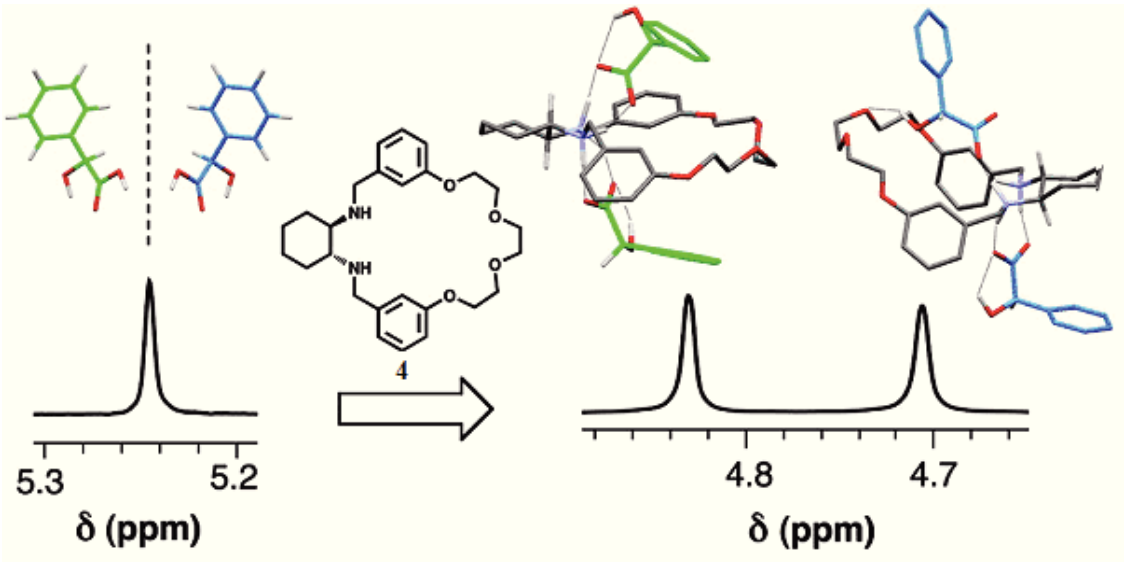
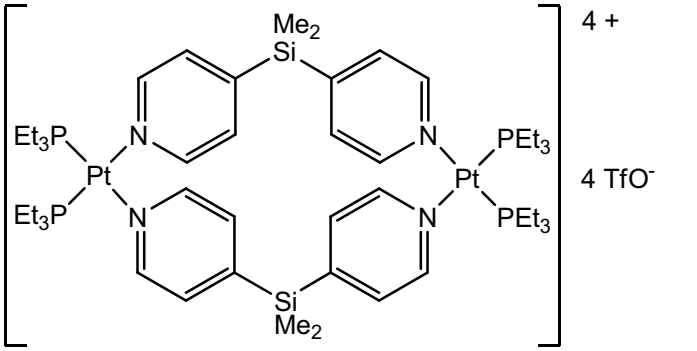
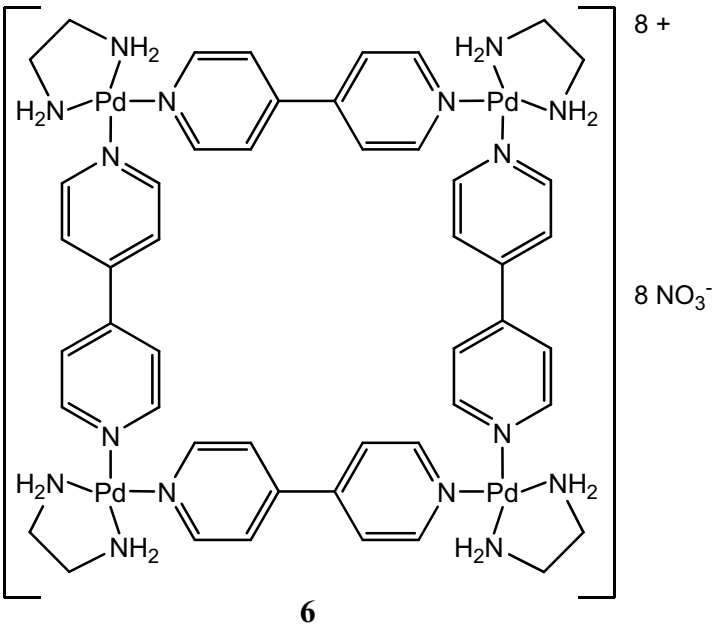


Figure 7. Aza-crown chiral macrocycle **4** used as solvating agent for mandelic acid derivates. (Reprinted from *J. Org. Chem.* **2011**, *76*, 10020).[22]

Even though the chemistry of chiral macrocycles has evolved tremendously, a major obstacle has been the limited number of convenient, versatile, and high yielding synthetic routes to functionalized macrocycles. Among the different approaches reported, the combination of metal and organic fragments has been particularly fruitful.[23] This procedure, based on "self-assembly" processes utilizing reversible bond forming reactions, has resulted in the preparation of new metal-containing macrocycles with interesting properties.[24] The metallomacrocycles afforded by this manner, like compounds **5** and **6** shown in Figure 8, have a shape and size that is confided by the geometry and length of the building blocks.



5



6

Figure 8. Metallomacrocycles **5** and **6**.[24]

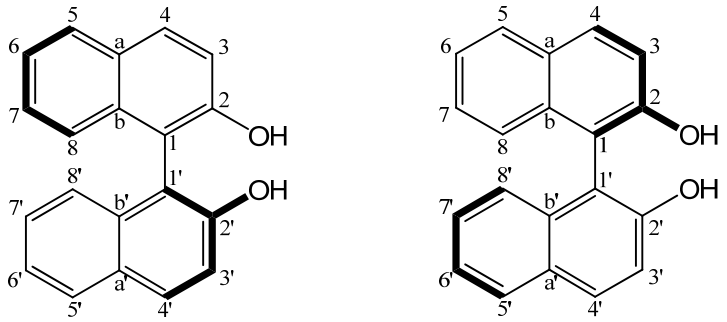
However, for many applications it is essential that the resulting macrocycle be build with a strong covalent network. The rigidity derived from the conformational stability of a covalent cyclic structure is related to the possibility of enhancing the recognition or complexation properties towards suitable inclusion guests. Therefore, much effort has been directed to the developing of alternative synthetic strategies which could supply this requirement. In this context, Coluccini *et al.* reported the direct formation of several rigid, homochiral macrocycles by esterification reactions of aromatic carboxylic acids in combination with an axially-chiral, suitable dibenzylic alcohol, derived from 1,1'-bi-2-naphthol (BINOL).[25] The resulted cyclic adducts were able to afford stable complexes with C_{60}.

As it could be deduced, the key step for the successful preparation of a desired functional cyclic structure is to identify the right combination of building blocks and connecting units which can provide a product with specified characteristics.

Considering that simple modifications of the building blocks would afford different functionalities, chiral architectures with derivatization potential continue to emerge as valuable subunits for the design of various assemblies. Given their robustness and their relatively easy functionalization, BINOL based synthons have been suggested as excellent precursors for the preparation of functional macrocyclic structures.[26]

1.3.1 BINOL as Chiral Building Block

The (*S*)- and (*R)*-enantiomers of 1,1'-bi-2-naphthol (BINOL), labeled as **7** and **8** in Figure 9, have become some of the best known atropisomers possessing axial chirality utilized as beneficial auxiliary providing a chiral environment.[27] The chiral chemistry based on the C_2-symmetric BINOL results quite attractive due to the commercial availability of both of its enantiomers and the wide amount of existing protocols for the versatile chemical modifications on its aromatic core.[28] This versatility can be further expanded by derivatization of the phenolic OH groups or their replacement with *C*, *S*, *N* and *P* functionalities.[24a, 26]



7
(*S*)-enantiomer

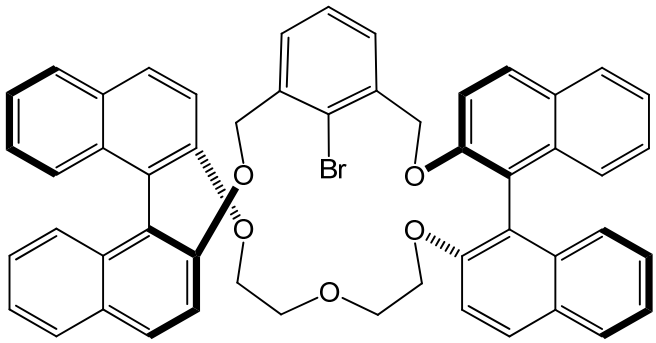
8
(*R*)-enantiomer

Figure 9. (*S*)- and (*R*)-enantiomers of 1,1'-bi-2-naphthol (BINOL).

One of the first examples of chiral macrocycles derived from BINOL was the (*S*,*S*)-bis(1,1'-bi-2-naphtho)-22-crown-6 (**1**), described by Cram *et al.* (Figure 5).[19] This macrocycle showed high enantioselective binding properties. According to the conclusions of Cram, the cooperation of the two binaphthyl units in this molecular host allows more efficient enantioselective discrimination.

To date, many other examples of binaphthocrown macrocycles with outstanding properties have been published.[29] For instance, to incorporate other functional groups into the frame of the binaphthyl macrocycle, Kiyooka and coworkers synthesized the optical active crown ether-type macrocycle **9** (Figure 10) containing bromine atoms.[29] Additional binaphthocrown macrocycles bearing amine groups have been described.[6, 12, 30] The use of these compounds in host-guest processes and sensing fields has been successfully demonstrated.

Since many of the exceptional characteristics depicted by binaphthocrowns are owned to the presence of the 1,1'-binapthyl moiety, attention has gradually shifted to the preparation of cyclic structures containing the BINOL unit. As Mazaleyrat *et al.* nicely described, some further remarkable advantages that working with BINOL provides are: *the transformation of achiral architectures to chiral, the possibility of resolution of otherwise scarcely accessible structures, the presence of supplementary steric and chiral barriers,* and taking into account that the 1,1'-binaphthyl chromophore is photoactive, *the opportunity for photophysical studies*.[31]



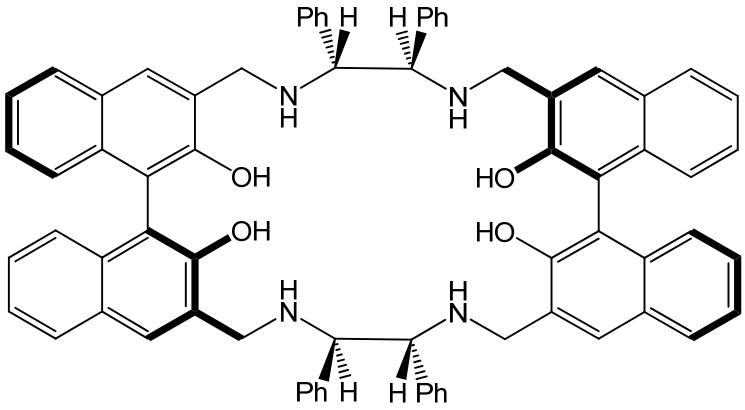
9

Figure 10. Crown ether-type binaphthyl macrocycle **9**.[19, 29]

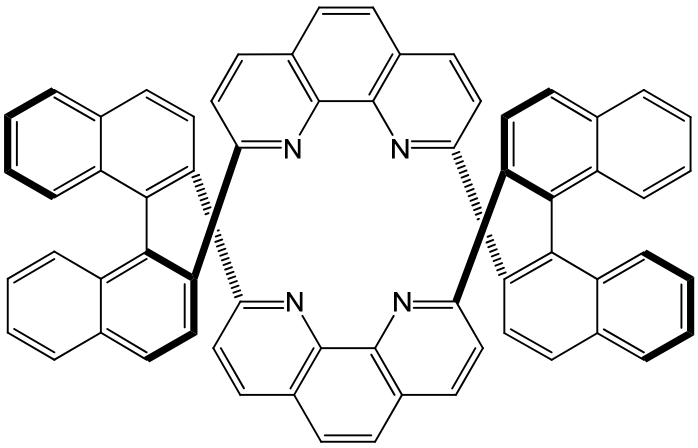
Among the uses of chiral ligands derived from BINOL, perhaps the most discussed are in the field of asymmetric catalysis. Several reports have been published describing the efficacy of highly enantioselective bis(binaphthyl) macrocycle catalysts for a number of organic reactions.[27a] Brunner and coworkers reported macrocycle **10** (Figure 11) as ligand in a Cu-(II)-catalyzed cyclopropanation of styrene with ethyl diazoacetate.[32] Also, the group of Cram reported the rigid bis(binaphthyl) macrocycle **11**, containing phenanthroline units which could be used as chiral ligands for applications in asymmetric catalysis.[33]

Other interesting macrocyclic binaphthol dimers were reported by Harada *et. al.,* who described the asymmetric synthesis of compound **12** (Figure 12A), through assembling of 3,3'-diethynyl-BINOL and 1,3-phenylene units via a Sonogashira coupling reaction.[34] In a similar way, Diederich and coworkers reported the preparation and characterization of further macrocyclic structures incorporating three or four binaphthyl units by coupling of terminal acetylenic units introduced in the 3,3'-positions of BINOL.[26a]

Furthermore, the group of Srinivas described the preparation of BINOL-*m*-phenylenediamine-derived macrocycle **13** (Figure 12B) by direct condensation of (*R*)-BINOL bis-acid with suitably substituted *m*-phenylenediamine analog.[35] The remarkable feature of this macrocycle is the ready accessibility to its optically pure form.



10



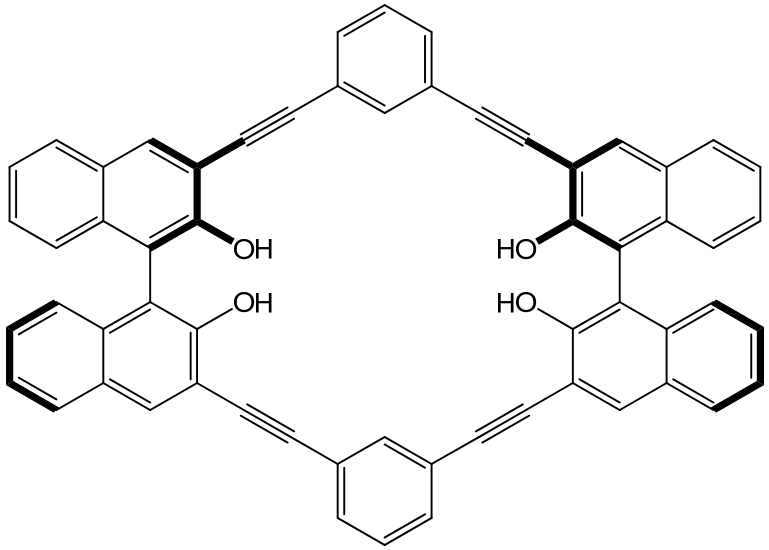
11

Figure 11. Bis(binaphthyl) macrocycles **10** and **11** used as ligands for asymmetric catalysis.[32b]

As the above mentioned examples demonstrate, the exceptional C_2 symmetric binaphthyl structure and its stable chiral configuration have allowed the preparation of fascinating macrocyclic structures with remarkable properties. Due to the varied functionalities of the binaphthyl core, the interest in the design of binaphthyl-based chiral hosts for chiral recognition and catalysts for asymmetric synthesis keeps on being a main topic of research.

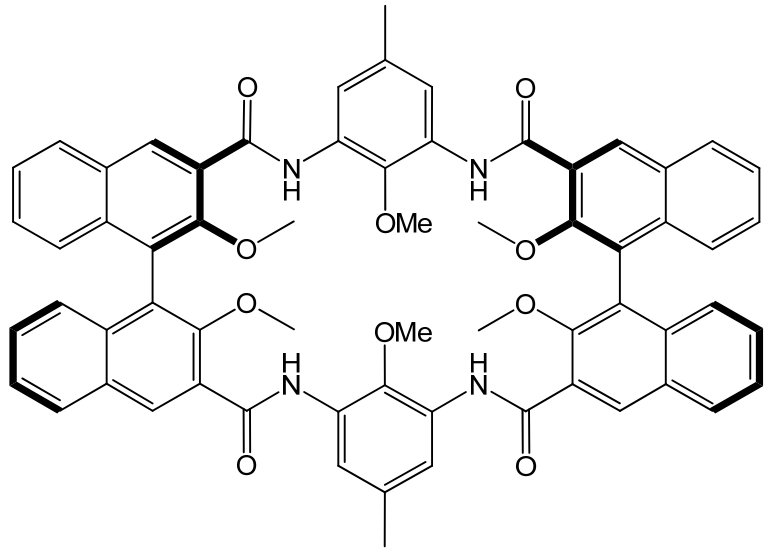
In addition to all the advantages already mentioned, the rigidity and chirality of ligands based on the binaphthyl framework offers an enormous opportunity in the design of new materials with potentially exciting applications. Thus, the use of binaphthyls for material science is emerging as a promising field.

A



12

B



13

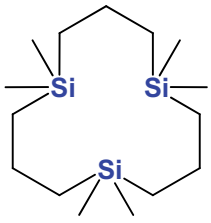
Figure 12. (**A**) 1,3-Phenylene bridged macrocyclic binaphthol dimer **12**, prepared by Sonogashira coupling reaction.[34] (**B**) BINOL-*m*-phenylenediamine-derived macrocycle **13**, synthetized by condensation of binaphthol bis-acid and suitable *m*-phenylenediamine analog.[35]

1.3.2 Silicon Derivates as Linking Units

Because of the additional chemical and physical properties that elements like silicon, nitrogen, oxygen and sulfur could grant to a macrocyclic assembly, these elements have been suggested as beneficial endocyclic constituents.[36] Among them, silicon results very attractive due to the fact that it forms bonds with most of the other elements in the periodic table, offering a wide range of possibilities for creating novel compounds. More importantly, the low toxicity of silicon species and their by-products could allow their use in pharmaceutical processes.

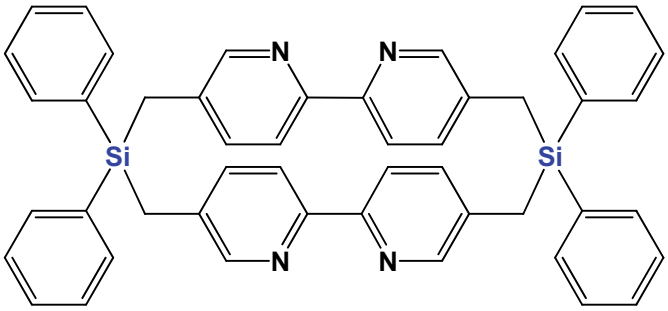
Other interesting characteristic of silicon-containing compounds, perhaps one of the most striking, is the ability of silicon to expand its valence shell providing additional coordination sites to the structure. Jung and Xia, for example, suggested that a cyclic polysilane with the right ring size and the correct substituent on silicon, like compound **14** (Figure 13), might be able to bind halide ions via partial bonding of the halide to each silicon atom, thereby effecting partial pentacovalency at each silicon.[37] These observations considerably increment the interest in silicon derivates to be used as suitable precursors in the preparation of macrocyclic compounds for applications that include host-guest chemistry.

The ready availability of silicon derivates and their special properties, as well as their exceptional chemistry, have led to the production of novel stable cyclic compounds. For instance, the group of Kaes reported the synthesis of disilamacrocycle **15**, shown in Figure 14, composed of two 2,2'-bipyridines interconnected at the 4-positions by two -CH_2SiCH_2- fragments. The strategy employed to obtain this product was based on the "one pot" reaction of the dilithium salt of 4,4'-dimethyl-2,2'-bipyridine with diphenyldichlorosilane (Ph_2SiCl_2).[38]



14

Figure 13. 12-Silacrown-3 (**14**), proposed as complexing agent for halide ions.[37]



15

Figure 14. Disilamacrocycle **15** obtained by reaction of the dilithium salt of dimethylbipyridine with Ph_2SiCl_2.[38]

When compared to their carbon analogues, macrocyclic compounds bearing silicon atoms show increased bond angle flexibility, decreased conformational rigidity, and longer bond lengths to silicon.[39] These features contribute to the formation of novel optical and electronic properties, which make them suitable for a great amount of applications. Moreover, their good chemophysical characteristics including solubility, high thermal and electrical stability, as well as very low surface energy, make these assemblies attractive for uses in the material field.

Even though, the synthesis of silicon-containing macrocycles should result in advantageous architectures, there has been little emphasis on the potential use of such compounds and their derivatives. Only few examples of macrocyclic compounds bearing silicon in an endocyclic mode have been described. Up to now synthetic efforts toward silacalixarenes,[40] silacrowns,[37] and silacyclophanes,[38] have been reported.

Some interesting silacyclophanes described in the literature are illustrated in Figure 15. Novel silicon-bridged macrocycle **16** was prepared in the group of Lee by quadruple cycloadditive macrocyclization and intramolecular nitrile oxide dimerization.[41] Sudjakar *et al.* synthesized siloxane-tethered cyclophane **17** making use of hydrolytic condensation of the corresponding bis[(dimethylvinylsilyl)*i*-propoxy]arenes.[42]

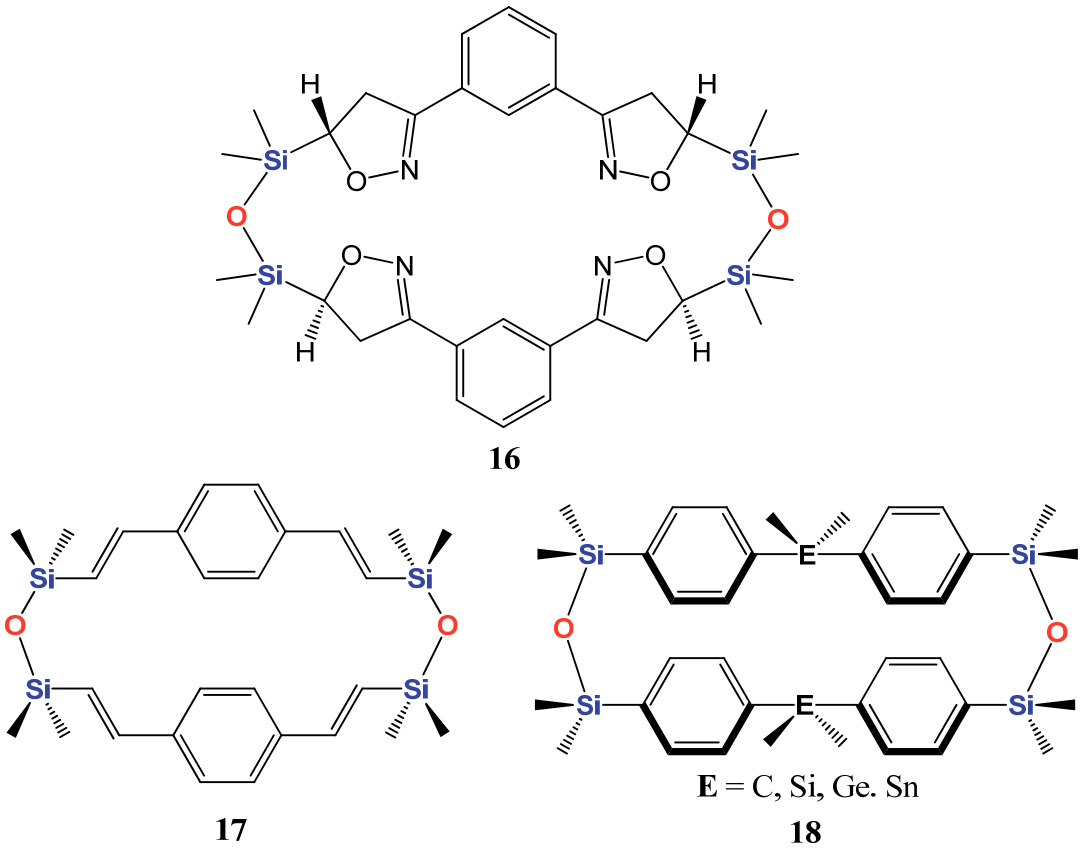


Figure 15. Novel silacyclophanes **16**-**18**.

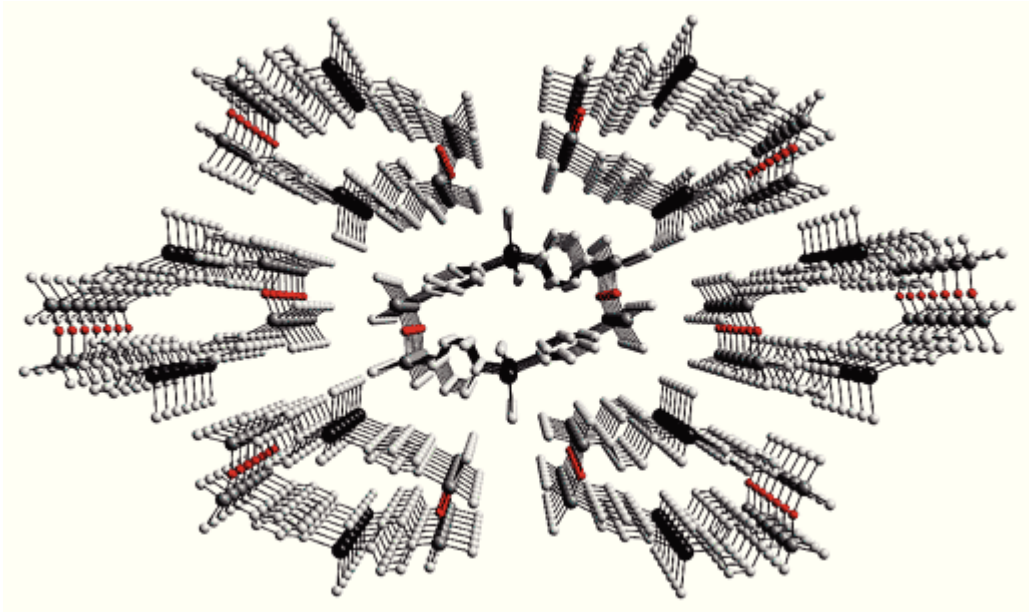


Figure 16. Perspective view of silacyclophane **18**, where **E** = Sn, along the crystallographic a-axis. (Reprinted from *Organometallics* **2005**, *24*, 3629).[43]

Likewise, Beckmann and coworkers reported the incorporation of the group 14 elements into the siloxane-bridged paracyclophanes depicted as **18** in Figure 15.[43] The methodology employed to obtain these novel compounds presented the advantage that no harsh reagents were required. Also, the shape and lengths of the organometallic spacers used made possible the preparation for the first time of silacyclophanes with nanoscale cavities and channels, as Figure 16 illustrates.

The chemistry and properties of silicon containing compounds are, without a doubt, exceptionally valuable in numerous areas of research. In our group, we have been interested in the developing of this chemistry in order to exploit silicon derivates for the design and synthesis of innovative structures.

2 Scope and Objectives

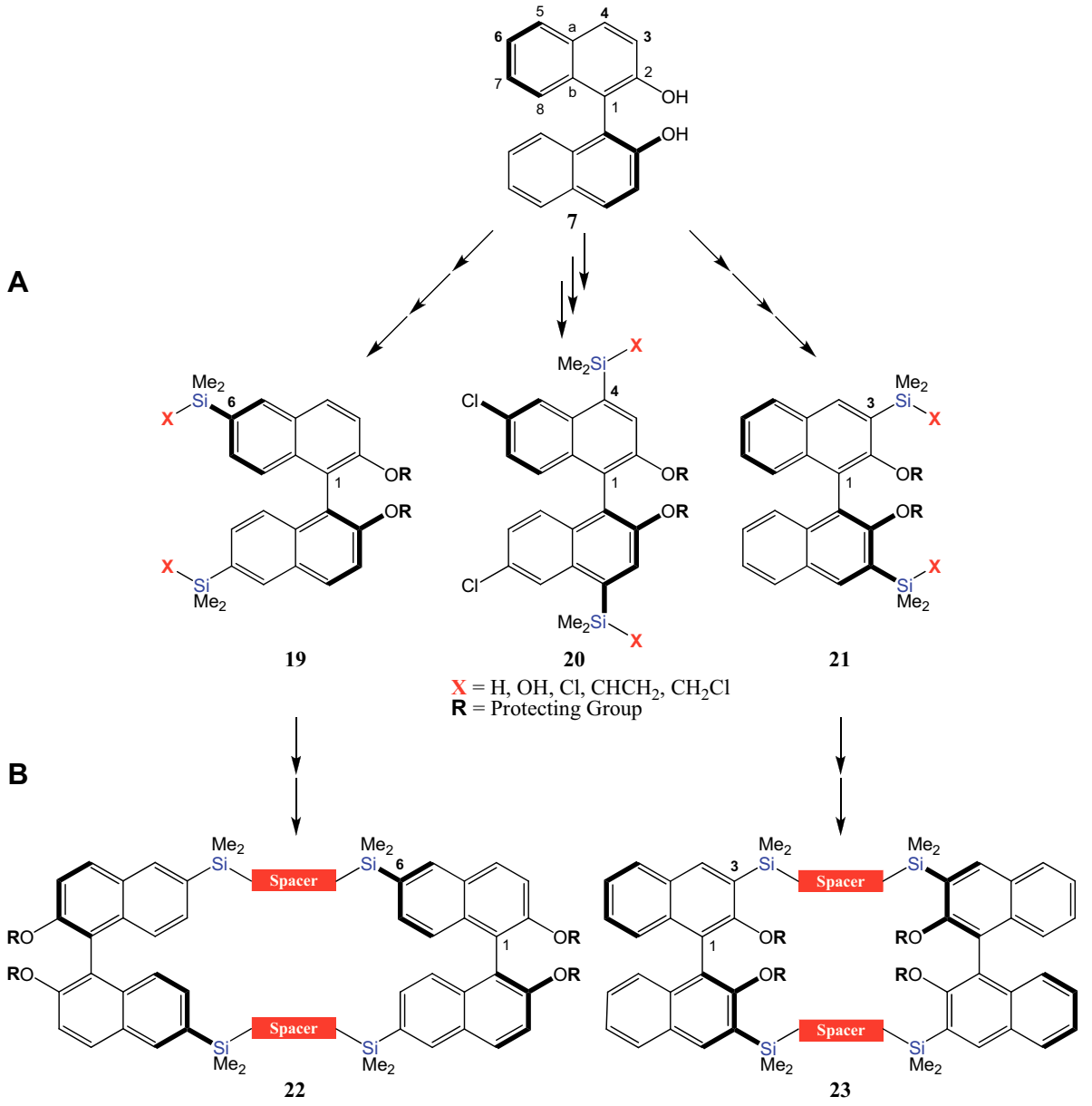
The main goal of this project was the design and preparation of novel chiral silicon-containing macrocycles with potential application as host molecules.

In view of the possibility to predict and control the chirality of the aimed products, we planned to employ binaphthyl frameworks as source of chirality. Then, taking advantage of the ready availability in enantiopure form of its enantiomers, functionalization of the 3-, 4-, and 6-positions of the BINOL core was devised as exemplified in Scheme 1A.

Linking units derived from Lewis acidic main group elements could offer a mechanism for fine-tuning the adsorption characteristics of chiral cavities through moderating the element hypervalency. Accordingly, we were interested in the endocyclic incorporation of silicon into the macrocycle cavity. For that reason, use of organosilicon fragments with easily modifiable structural and chemical properties such as: -SiH, -SiOH, -SiCl, -$SiCHCH_2$, or -$SiCH_2Cl$, was proposed for the derivatization of the binaphthyl units to obtain chiral precursor like **19**-**21** (Scheme 1) possessing reactive silicon nodes.

Even though the literature is rich in descriptions of macrocyclic systems, the synthesis of chemically and thermally stable architectures that contain specific cavity sizes, functionality and chiral channels still represents a considerable challenge. Therefore, use of efficient methods which could provide the target cyclic compounds in significant yields was approached. The central idea of the intended synthetical strategies was based on the linkage of the silicon-containg chiral ligands derived from BINOL using either flexible spacers or more rigid aromatic-based joints to obtain macrocycles from the type **22** and **23**, shown in Scheme 1B. In this way, the cavity size of the cyclic assemblies could be modified depending on the nature of the connectors.

Moreover, if possible, functionalization of the produced macrocycles would be attempted.



Scheme 1. Reaction pathways to the formation of chiral silicon-containing macrocycles. (**A**) Functionalization of the 6,6'-, 4,4'-, and 3,3'-positions of the BINOL core. (**B**) Linkage of the silicon-containing chiral ligands using either flexible spacers or more rigid aromatic-based joints.

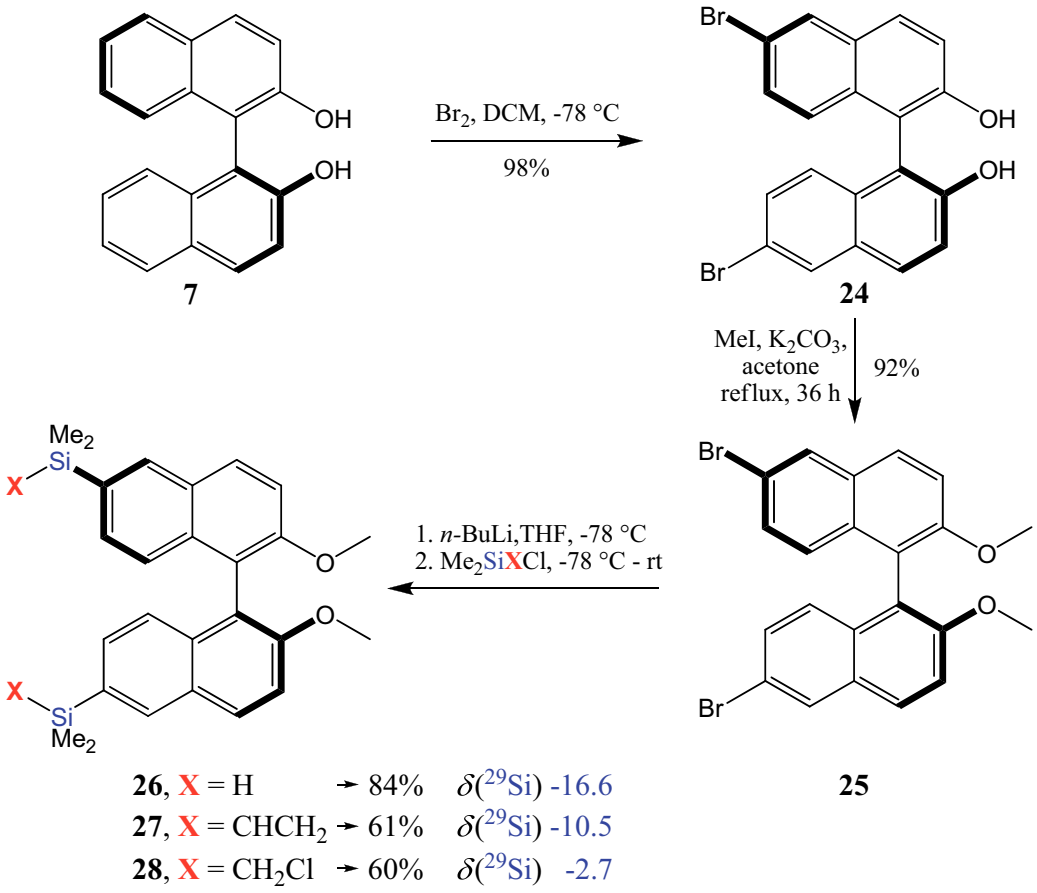
3 Results and Discussion

3.1 Silyl Functionalization of BINOL

Selective functionalization of the 3,3'-, 4,4'-, and 6,6'- positions of BINOL has shown to provide chiral ligands useful as building blocks for the construction of supramolecular structures, compounds with interesting optical and electronic properties in material science, as well as chiral inductors in asymmetric catalysis.[27a] For that reason, many synthetic protocols for derivatization of the BINOL framework have been devised and are currently available.[44] Among them, bromination at the aimed position, followed by introduction of the desired substituent has resulted very efficient for the functionalization of BINOL. Hence, taking into account that organosilanes are normally afforded through transmetallation of lithium organyles or Grignard reagents,[45] brominated BINOL derivates were prepared to be used as starting materials for the synthesis of silyl-BINOL building blocks (Schemes 2 and 4). Also, it is well known that alkyl protection of the BINOL hydroxyl functions offers direct access to the 3,3'- positions of the BINOL core. This synthetic route was explored, as exemplified in Scheme 3, to afford further silyl-BINOL derivates.

3.1.1 Functionalization of 6,6'-Positions

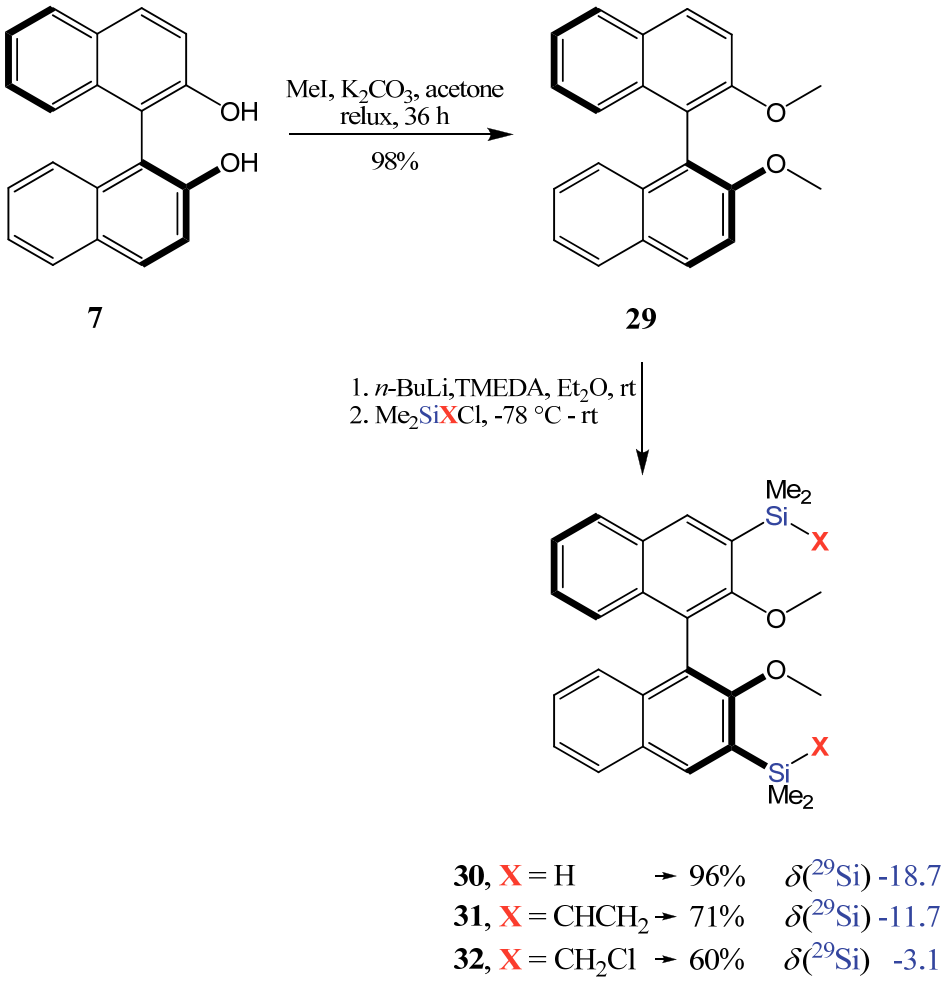
Silyl functionalization 6,6'-positions of BINOL was carried out in a three step synthesis, as shown in Scheme 2. First, bromination of (*S*)-BINOL (**7**) in dichloromethane at -78 °C selectively afforded (*S*)-6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene (**24**) as a yellow solid in almost quantitative yield. Compound **24** was subsequently used without further purification for the preparation of the required organolithium precursors. For that, protection of BINOL hydroxyl groups was necessary. Thus, brominated precursor **24** was reacted with iodomethane (MeI) in acetone to obtain (*S*)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**25**) as a colourless solid in 92% yield. Treatment of **25** with three equivalents of *n*-buthyllithium (*n*-BuLi) allowed metallation by lithium-bromine exchange at the 6,6'-positions. Then, silylation of the lithiated intermediates by addition of suitable chlorodimethylsilane derivatives to -78 °C cooled solution of the precursors in THF provided the expected 6,6'-silyl-BINOL compounds **26**, **27**, and **28** (Scheme 2).



Scheme 2. General procedure for the preparation of 6,6'-silyl-BINOL building blocks.

3.1.2 Functionalization of 3,3'-Positions

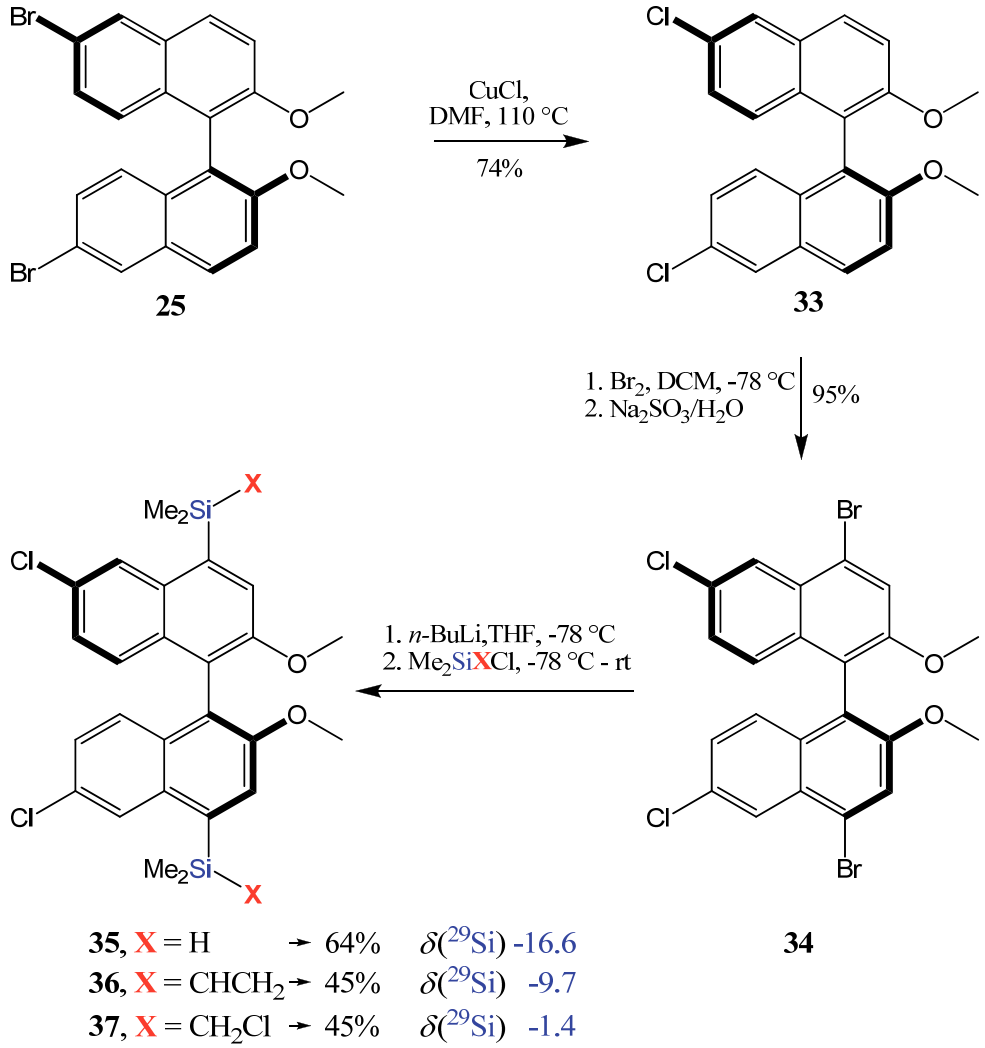
In general, introduction of substituents at the 3,3'-positions of BINOL is accomplished via a two step protocol that involves treatment of a suitable protected BINOL with an organolithium reagent, followed by reaction with an electrophile.[46] This approach, illustrated in Scheme 3, was used to prepare the 3,3'-organosilane-BINOL derivates **30**, **31**, and **32**. Because the ortho-directed lithiation of arene compounds is mainly governed by the formation of a *n*-BuLi/TMEDA dimer and its complexation with a methoxy protecting group,[47] the hydroxyl functions of (*S*)-BINOL (**7**) were first protected using MeI to afford (*S*)-2,2'-dimethoxy-1,1'-binaphthalene (**29**) as a colorless solid in almost quantitative yield. Then, compound **29** was subjected to ortho-directed lithiation and the obtained organolithium reagent was reacted with an appropriate silane derivative to provide 3,3'-silyl-BINOL building blocks.



Scheme 3. General procedure for the preparation of 3,3'-silyl-BINOL building blocks.

3.1.3 Functionalization of 4,4'-Positions

It has been demonstrated that when the 6,6'- positions of BINOL are occupied, additional bromination eventually occurrs at the 4,4'- positions.[48] Thus, as shown in scheme 4, to selectively functionalize BINOL positions 4,4'-, preparation of chlorinated precursor (*S*)-6,6-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (**33**) was necessary. Compound **33** was afforded as a brown solid in 74% yield using copper chloride (CuCl) in DMF at reflux temperature, as described by Lin *et al.*[49] This procedure requires the use of a high boiling solvent to increase the solubility of brominated precursor **25**. After two days of reaction, product **33** was isolated by extraction with ethyl acetate. Further bromination of precursor **33** afforded tetrahalogenated (*S*)-6,6'-dichloro-4,4'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene (**34**). Finally, treatment of **34** with *n*-BuLi provided the lithiated intermediate which, reacted with proper silane derivates, afforded 4,4'-silyl-BINOL precursors **35**, **36**, and **37**.



Scheme 4. General procedure for the preparation of 4,4'-silyl-BINOL building blocks.

3.2 Silyl-BINOL Building Blocks

When compared to other organometallic precursors, silicon containing compounds are readily available and fairly stable. As it is described below, use of inexpensive reactants and efficient procedures have provided a series of interesting functionalized silyl-BINOL building blocks with potential applications in the development of new type of materials.

3.2.1 Hydrosilanes

Due to the high and specific reactivity of the Si-H bond, hydrosilanes hold considerable practical importance. Their use as synthetic precursors for the preparation of a number of silicon containing compounds, including silyl-metal complexes, is well established.[50] Thus, preparation of hydrosilanes **26**, **30**, and **35** was aimed taking into account that hydrosilanes are good candidates as hydrogen source for various applications[51] and that the Si-H bonds could serve as chemical hooks for attaching desired functionalities, leading to other versatile precursors.

Silylation of BINOL 6-positions was accomplished, as exemplified in Scheme 2, by reaction of dimethylchlorosilane (Me_2SiHCl) with the lithiated reagent derived from precursor **25**. As a result, (*S*)-6,6'-bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**26**) was successfully generated.

Introduction of hydrosilane functionality Me_2SiH- in the 3,3'- positions of BINOL was examined by ortho-lithiation of methoxy-protected BINOL **29** followed by addition of Me_2SiHCl at -78 °C. The reaction effectively afforded novel derivate (*S*)-3,3'-bis(dimethylsilyl)-2,2'dimethoxy-1,1'-binaphthalene (**30**) displayed in Scheme 3.

To prepare 4,4'-hydrosilane-BINOL derivate (*S*)-6,6'-dichloro-4,4'-bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**35**), lithiated intermediate resulting from the Br-Li exchange in the 4,4'-positions of tretrahalogenated precursor **34** was treated with Me_2SiHCl using the conditions described in Scheme 4.

Purification of crude products by column chromatography afforded compound **26** as yellow solid in 84% yield. Compounds **30** and **35** were isolated as colourless solids in 96% and 60% yield, respectively.

Crystallization of the achieved precursors was only successful for 3,3'-hydrosilane derivate **30** in toluene, which crystallizes in the orthorhombic system, space group $P2_12_12_1$. X-ray analysis of the obtained crystals provided the molecular structure shown in Figure 17, selected bond parameters are collected in Table 1.

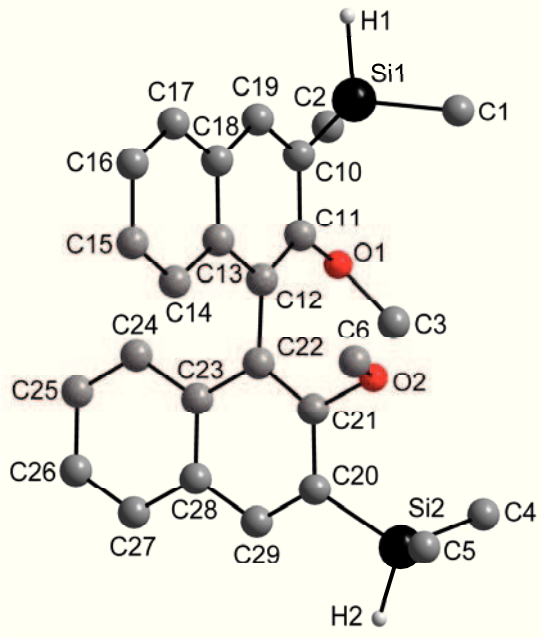


Figure 17. Molecular structure of hydrosilane precursor **30**.

Table 1. Selected bond parameters for **30**, bond distances [Å] and angles [°].

Si1-C1	1.839(4)	C11-C12-C22	122.6(2)
Si1-C2	1.859(4)	C13-C12-C22	119.9(2)
Si1-C10	1.880(3)	C12-C22-C23	119.5(2)
Si1-H1	1.536(3)	C12-C22-C21	121.9(2)
Si2-C5	1.852(5)		
Si2-C4	1.856(5)		
Si2-C20	1.881(3)		
Si2-H2	1.396(3)		

Because it plays a significant role in the discriminating ability of BINOL and its derivates, the dihedral angle θ between the two naphthalene rings is an important quantity for describing the chiral properties of these types of compounds. X-ray diffraction studies of nonsubstituted 1,1'-binaphthyl in crystalline form have revealed the presence of two conformers of each enantiomer.[52] When the value of θ is less than 90°, BINOL is referred as a (*S*)- or (*R*)-*cisoid* conformer, whereas, when the dihedral angle is greater than 90° it is known as a (*S*)- or (*R*)-*transoid* conformer.[27a] The dihedral angle between the two naphthalene rings in compound **30** was found 119.9(2)° indicating that it displays a (*S*)-*transoid* conformation.

Complete characterization of hydrosilane precursors was carried out by NMR, IR and EI MS techniques. A typical septet corresponding to the coupling of the hydrosilane proton with the methyl groups of Me_2SiH- was observed in the ^1H NMR spectrum of 6,6'-functionalyzed compound **26** at δ 4.55 ppm, for 3,3'-functionalized compound **30** at δ 4.63 ppm, and at δ 4.94 ppm for 4,4'-functionalized compound **35**.

The chemical shift of the methyl groups in the ^{13}C NMR spectra, another relevant characteristic of this type of compounds, was detected as a singlet at δ -3.70 ppm for precursor **26**, as two singlets at δ -3.33 and δ -3.44 ppm for **30**, and also as two singlets at δ -2.90 and δ -2.94 ppm for **35**. In addition, ^{29}Si NMR spectra of **26**, **30** and **35** displayed resonances at δ -16.6, δ -18.7, and δ -17.8 ppm, respectively.

The distinctive Si-H stretching vibrations were detected by IR examination of **26** at 2121 cm^{-1}, at 2118 cm^{-1} for **30**, and at 2119 cm^{-1} for **35**.

Optical rotation data for the isolated hydrosilanes and their respective precursors were taken in THF and are displayed in Table 2. The sing of the specific rotation $[\alpha]_\lambda^{20}$ of functionalized (*S*)-6,6'-silyl-BINOL **26** and (*S*)-3,3'-silyl-BINOL **30** reverts from the observed for (-)-(*S*)-BINOL **7** and precursors **24**, **25**, and **29**. Also, an increment in the value of $[\alpha]_\lambda^{20}$ was observed for 3,3'-functionalized product **30** when compared to the observed for starting materials **7** and **29**. On the other hand, the sign of the $[\alpha]_\lambda^{20}$ detected for (*S*)-4,4'-silyl-BINOL **35** did not vary from the displayed for its precursors **7**, **24** and **34**. However, the value decreases to that of compound **34**.

Table 2. Optical rotation data of chiral hydrosilanes in THF.

Compound	*c* (g/100 ml)	$[\alpha]$ (deg)	$[\alpha]_{\lambda}^{20}$ (deg)
(*S*)-BINOL **7**	0.40	-144	-35.6
(*S*)-Br-BINOL **24**	0.34	+90	+26.1
(*S*)-Br-BINOL-OMe **25**	0.14	-3	-2.2
(*S*)-BINOL-OMe **29**	0.26	-179	-68.7
(*S*)-Cl-Br-BINOL-OMe **34**	0.38	-254	-67.6
6,6'-hydrosilane **26**	0.28	+92	+32.6
3,3'-hydrosilane **30**	0.27	+255	+94.2
4,4'-hydrosilane **35**	0.18	-100	-54.3

Isolation of the desired products was verified by EI MS. Molecular ion *m/z* = 430 $[M]^+$ measured from products **26** and **30** were consistent with the exact mass calculated for the proposed structures ($C_{26}H_{30}O_2Si_2$ = 430.2 g/mol). Molecular ion *m/z* = 498.0 $[M]^+$, obtained from analysis of **35**, coincided with the exact mass of the presented structure ($C_{26}H_{28}Cl_2O_2Si_2$ = 498.1 g/mol).

Examination of the reaction yields obtained for the preparation of hydrosilane precursors **26**, **30**, and **35** suggests that silylation of the 4-positions occurred relatively slower than the silylation of 3- and 6-positions. It was noticed from the ^{13}C NMR data that when the Me_2SiH-group is in the 3-positions of BINOL, the methyl groups show a significant difference in the chemical shift due to their diastereotopicity. However, this effect is less noticeable in the case of the 4,4'-functionalized precursor and not at all detected for the 6,6'-derivatized compound.

3.2.2 Silanols

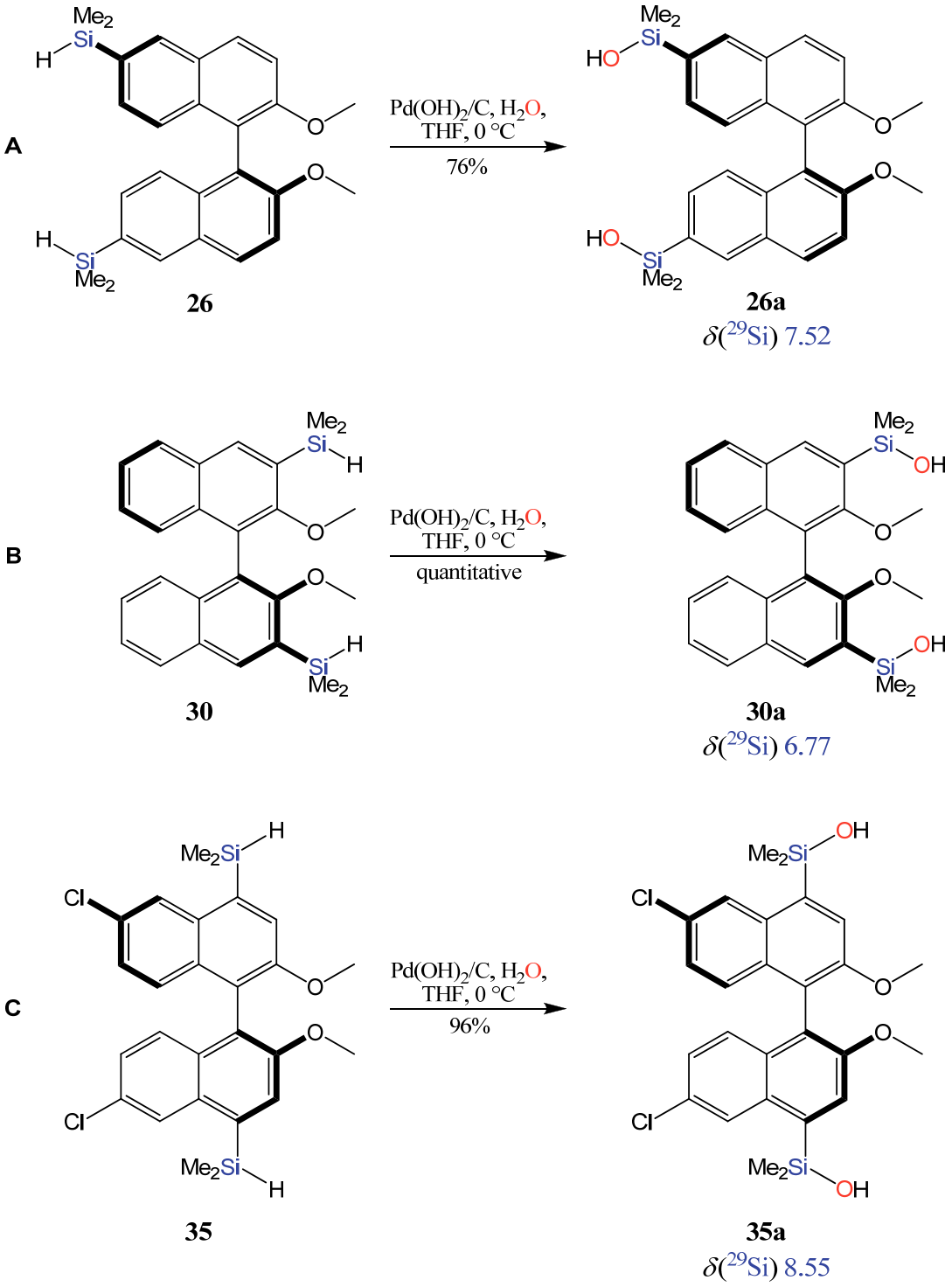
Application of organosilanols in polymer and material sciences, along with their use in organic, inorganic, and organometallic chemistry is well established.[53] Hence, considering the widespread utility of such versatile compounds, preparation of building blocks containing Si-OH moieties is a very attractive and promising goal.

Usually, hydrosilanes (Si-H) could be converted into the respective silanols (Si-OH) by hydrolysis reaction under acidic or basic conditions or by oxidation with stoichiometric amounts of strong oxidants such as O_2, O_3, H_2O_2, $PhCO_3H$, $AgNO_3$, $AgNO_2$, dioxiranes or $KMnO_4$.[53d] However, the harsh conditions that these methods require frequently promote condensation of the formed silanols to the siloxanes.

An interesting possibility for conversion of Si-H into Si-OH is the use of metal catalysts based on Cu,[54] Rh,[55] or Ru[56] using H_2O and/or O_2 as oxygen source. Nevertheless, in some cases, removal of these homogeneous catalysts makes the isolation of the desired products difficult. To facilitate the separation of the catalyst and purification of the silanols, use of immobilized transition metals on solid supports as catalyst has shown to have great advantages.[57] In this context, it has been demonstrated that the use of Pearlman's catalyst [$Pd(OH)_2$/C] for the oxidation of hydrosilanes affords the corresponding silanols in good yields.[58]

This method, described by Beckmann *et al.*,[58] was applied to oxidize hydrosilanes **26**, **30**, and **35** into the corresponding silanols (*S*)-6,6'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**26a**), (*S*)-3,3'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene **(30a**), and (*S*)-6,6'-dichloro-4,4'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**35a**) shown in Scheme 5.

With the addition of the first drops of a THF solution of the hydrosilanes to a cooled THF suspension of the catalyst and H_2O, immediately evolution of H_2 was observed. Few minutes after entire addition of the precursors, evolution of H_2 ceased indicating that the reaction was completed. The mixtures were allowed to stir in solution for an additional hour. Isolation of the products was effectuated removing the catalyst by filtration and the solvent under reduced pressure.



Scheme 5. Preparation of silanol building blocks.

Whereas silanol **35a** was obtained as a pale yellow solid in 96% yield, silanols **26a** and **30a** were afforded as colourless glass-like solids in 76% and quantitative yields, respectively.

Entire oxidation of the precursors was confirmed by ^{1}H NMR analysis, from which no chemical shifts for hydrosilane protons were detected. Also, shifting observed by ^{29}Si NMR of the Si resonance to lower field indicated that functionalization on the Si atoms occurred.

^{29}Si NMR spectrum of the product obtained from 6,6'-hydrosilane precursor **26** showed signals at δ 7.52 ppm, assigned to silanol **26a**, and at δ -3.02 ppm, a typical resonance of disiloxanes. The spectrum of the product derived from 3,3'-functionalized compound **8** displayed only one chemical shift at δ 6.77 ppm implying that just silanol **30a** was generated. The product accomplished from precursor **35** displayed a main signal at δ 8.55 ppm and dispensable traces of a condensation product, evidenced by a chemical shift at δ 0.88 ppm.

To minimize the generation of condensation by-products, repetition of the procedure was examined strictly controlling the temperature and reducing the reaction time after gas evolution. No considerable changes in the results were observed from these variations. Based on this, it is assumed that self condensation may occur after isolation of the products as a consequence of sterical exposure of the hydroxyl group in Me_2Si-OH.

The optical activity of the isolated products was evaluated in THF. As Table 3 illustrates, the value of the specific rotation $[\alpha]_{\lambda}^{20}$ of silanols **26a**, **30a**, and **35a**, were relatively lower than the calculated for their hydrosilane precursors. In all three cases, the sign of the molecular optical rotation of the products resulted equal to that of the starting materials. When compared to each other, the 3,3'-functionalized compound **30a** showed the highest optical activity ($[\alpha]_{\lambda}^{20} = +75.2°$).

Table 3. Optical rotation data of chiral silanols in THF.

Compound	*c* (g/100 ml)	[α] (deg)	$[\alpha]_{\lambda}^{20}$ (deg)
6,6'-silanol **26a**	0.13	+40	+31.3
3,3'-silanol **30a**	0.19	+145	+75.2
4,4'-silanol **35a**	0.12	-31	-25.8

As demonstrated from the obtained yields, palladium catalyzed oxidation of hydrosilanes resulted an efficient and fast method for the preparation of silanol precursors **26a**, **30a**, and **35a**.

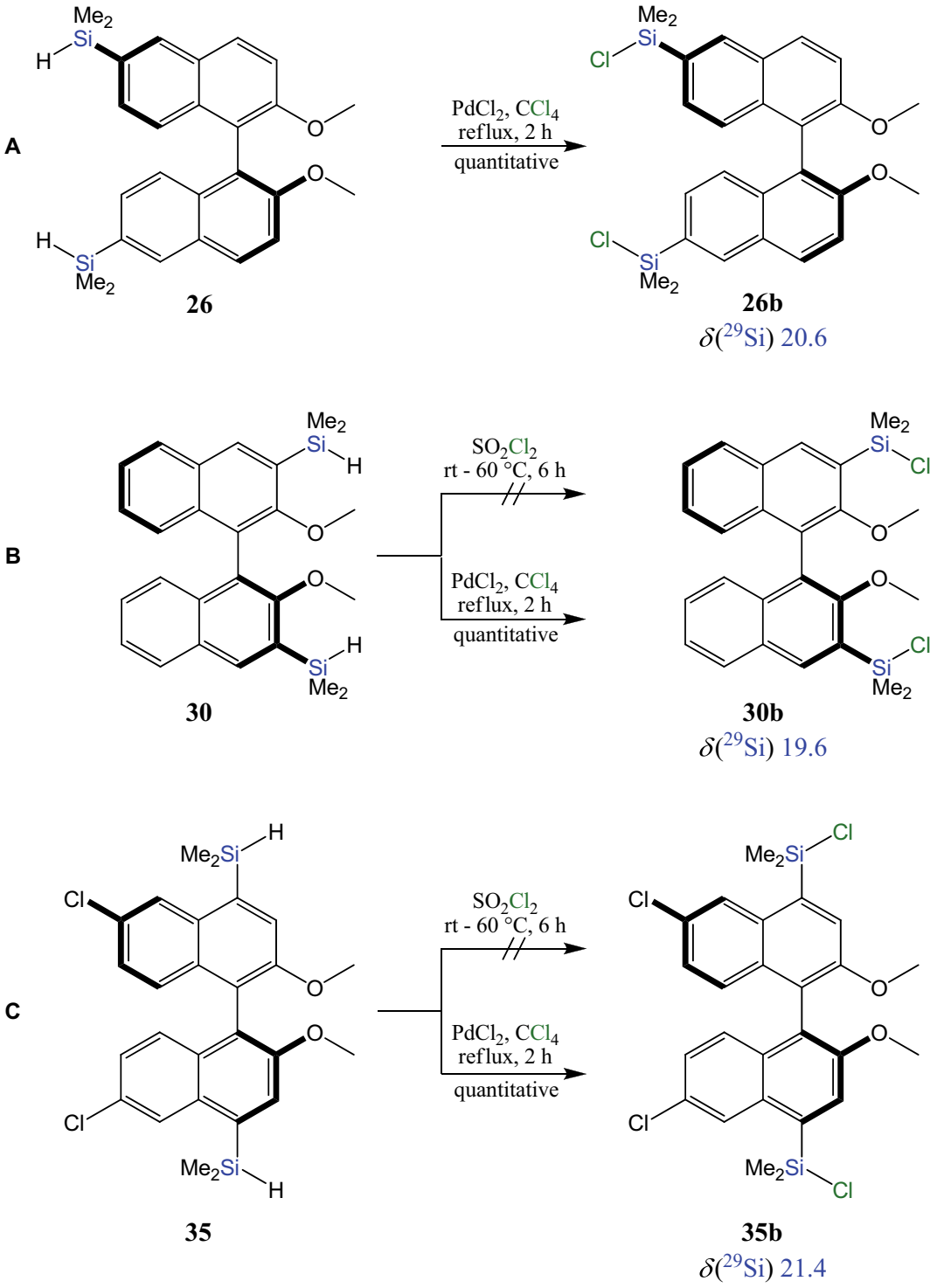
3.2.3 Chlorosilanes

Besides silanols, chlorosilanes are among the most valuable silicon containing compounds. They have been broadly used as starting material or reagent in synthetic organosilicon chemistry.[39] A considerable amount of methods for their preparation from hydrosilanes are available to date. These procedures include the use of chlorinating agents such as SO_2Cl_2[59] or CCl_4 in the presence of catalysts like $CuCl_2$,[60] $NiCl_2$,[61] Pd/C[62] or $PdCl_2$[63].

For the derivatization of hydrosilane-BINOL precursors **30** and **35** to produce building blocks bearing the reactive Me_2Si-Cl group, use of SO_2Cl_2 was examined (Scheme 6). Both precursors were treated with an excess of the reactant, first at room temperature and subsequently increasing the temperature to 60 °C. After 6 hours of reaction the excess of SO_2Cl_2 was removed under reduced pressure and the remaining product subjected to spectroscopic analysis. The collected NMR data indicated that the hydrosilane precursors remained unreacted. The reaction was repeated several times varying the reaction conditions without success.

Preparation of (*S*)-6,6'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**26b**), (*S*)-3,3'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**30b**), and (*S*)-6,6'-dichloro-4,4'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**35b**) illustrated in Scheme 6, was then afforded by addition of catalytic amounts of $PdCl_2$ to stirring solutions of **26**, **30**, and **35** in CCl_4. Each mixture was allowed to react for 2 hours at reflux temperature. Removal of the catalyst by filtration and volatiles under reduced pressure furnished the desired compounds as moisture sensitive yellow solids.

No remaining traces of starting materials were detected either by ^{1}H NMR or ^{13}C NMR, indicating that the reactions proceeded quantitatively. Analysis of the products by ^{29}Si NMR demonstrated the unique formation of the chlorosilane derivates. Considerably downfield shifted resonance at δ 20.6, δ 19.6, and δ 21.4 ppm were observed in the spectra of **26b**, **30b**, and **35b**, respectively.



Scheme 6. Preparation of chlorosilane building blocks.

The results compiled in Scheme 6, indicate that all the hydrosilanes evaluated were successfully transformed into the corresponding chlorosilanes. Quantitative achievement of all of the products proved that CCl_4 worked very well as chlorinating agent in the presence of $PdCl_2$ as catalyst.

3.2.4 Vinylsilanes

Functionalization of organosilane compounds with a vinyl substituent make them useful as starting material for a wide variety of synthetic processes.[64] There are many feasible applications described for vinylsilanes,[65] being their use as source of hydrogen acceptor among the most exploited.[66] Considering this, derivates **27**, **31** and **36** were synthesized.

As shown in Scheme 2, reaction between silane precursor dimethylchlorovinylsilane [$Me_2Si(CH=CH_2)Cl$] and the organolithium compound derived from **25** gave (*S*)-6,6'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**27**). Likewise, following the procedure described in Scheme 3, reaction of $Me_2Si(CH=CH_2)Cl$ with Li-intermediate produced from ortho-lithiation of compound **29** achieved (*S*)-3,3'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**31**). Also, (*S*)-6,6'-dichloro-4,4'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**36**) was afforded after reaction of tetrahalogenated-BINOL derivate **34** with *n*-BuLi and the silane precursor (Scheme 4).

Pure products were isolated from column chromatographic separations, after which compounds **27**, **31**, and **36** were obtained as colourless solids in 61%, 71% and 45% yields, respectively.

NMR data of the pure products, as well as ESI MS analysis confirmed the proposed structures. Characterization by ^1H NMR showed typical chemical shifts of vinyl protons at δ 6.38, 6.11, and 5.84 ppm for 6,6'-functionalyzed compound **27**, δ 6.52, 6.13 and 5.87 ppm for 3,3'-functionalyzed compound **31**, and at δ 6.59, 6.24 and 6.00 ppm for 4,4'-functionalyzed compound **36**. Also, the corresponding vinyl carbons were identified at δ 138.1 and 132.7 ppm in the ^{13}C NMR spectrum of **27**. Consistently, the spectrum of **31** exhibited chemical shifts of vinyl carbons at δ 138.9 and 132.1 ppm, and the spectrum of **37** at δ 138.1 and 133.6 ppm. Besides, ^{29}Si NMR analysis of **27**, **31**, and **36** detected unique singlets at δ -10.5, δ -11.7, and δ -9.7 ppm, respectively.

Analysis of the optical rotation of **27** and **31** (Table 4) indicated a reversion of the sign and an increment in the value of the specific rotation $[\alpha]_{\lambda}^{20}$ of their precursors **25** ($[\alpha]_{\lambda}^{20}$ = -2,2°) and **29** ($[\alpha]_{\lambda}^{20}$ = -68.7°), respectively. Moreover, 4,4'-derived-vinylsilane **36** showed a lower specific rotation than its precursor **34** ($[\alpha]_{\lambda}^{20}$ = -67.6°), as well as the measured from the rest of the chiral vinylsilane builing blocks.

Table 4. Optical rotation data of chiral vinylsilanes in THF.

Compound	*c* (g/100 ml)	[α] (deg)	$[\alpha]_{\lambda}^{20}$ (deg)
6,6'-vinylsilane **27**	0.12	+53	+43.4
3,3'-vinylsilane **31**	0.14	+107	+75.4
4,4'-vinylsilane **36**	0.23	-81	-37.0

The described synthetic routes provided novel vinylsilane-BINOL building blocks in good yields. The vinyl group of these compounds provides an important tool for further derivatization.

3.2.5 Chloromethylsilanes

Attracted by all the possible reactions to which a chloromethylsilane functionality could be subjected,[68] builing blocks containing this group were prepared. For instance, Kim *et al* reported the synthesis of 1,2-amino alcohols by using the Grignard reagent derived from phenylchlorodimethylsilane.[67] Also, use of the last was described by the group of Hammerschmidt for the preparation of chiral methanols.[68] More interestingly, Hudrlik and co-workers were able to convert phenyl- and alkenyl(chloromethyl)silanes to benzyl- and allylsilanes.[69]

For the preparation of (*S*)-6,6'-bis(dimethylchloromethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**28**) presented in Scheme 2, lithiated precursor derived from compound **25** was treated with dimethyl(chloromethyl)chlorosilane [$Me_2(ClCH_2)SiCl$]. Also, ortho-lithiation of compound **29** followed by reaction with the silane derivate afforded (*S*)-3,3'-bis(dimethylchloromethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**32**). In addition, use of the silane precursor in the procedure described for the functionalization of BINOL positions 4,4'- (Scheme 4) gave (*S*)-6,6'-dichloro-4,4'-bis(dimethylchloromethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (**37**).

Crude materials were subjected to column chromatography to furnish pure products **28** and **32** as colourless oils in 45% and 60% yields, and compound **37** as colorless solid in 45% yield. Complete characterization of the products by NMR, IR and MS techniques supported the proposed structures.

^{1}H NMR spectra of compounds **28**, **32,** and **37** displayed well-defined singlets assigned to the methylene protons at δ 3.02, δ 3.14, and δ 3.30 ppm, respectively. Also, the equivalent chemical shift of the methylene carbons were detected for each product by ^{13}C NMR analysis at δ 30.5, δ 31.0, and δ 30.5 ppm. In the same order, ^{29}Si NMR study of the samples showed resonances at δ -2.70, δ -3.08 and δ -1.44 ppm in the corresponding spectra.

Optical rotation data in THF of chiral chloromethylsilanes **28**, **32** and **37**, are collected in Table 5. It was found that the magnitude of the specific rotation of 6,6'-, and 3,3'-functionalyzed compounds was much higher than their respective binaphthol precursors **25** ($[\alpha]_{\lambda}^{20}$ = -2,2°) and **29** ($[\alpha]_{\lambda}^{20}$ = -68.7°), respectively. Conversely, the specific rotation of 4,4'-functionalized chloromethylsilane **37** resulted lower than that from its precursor, compound **34** ($[\alpha]_{\lambda}^{20}$ = -67.6°).

Incorporation of a -$Me_2(ClCH_2)Si$- function into the BINOL framework to generate novel and interesting compounds, could be achieved in good yields without inconveniences.

Table 5. Optical rotation data of chiral chloromethylsilanes in THF.

Compound	*c* (g/100 ml)	$[\alpha]$ (deg)	$[\alpha]_{\lambda}^{20}$ (deg)
6,6'-chloromethylsilane **28**	0.11	+110	+100.0
3,3'-chloromethylsilane **32**	0.17	+190	+113.1
4,4'-chloromethylsilane **37**	0.17	-79	-46.2

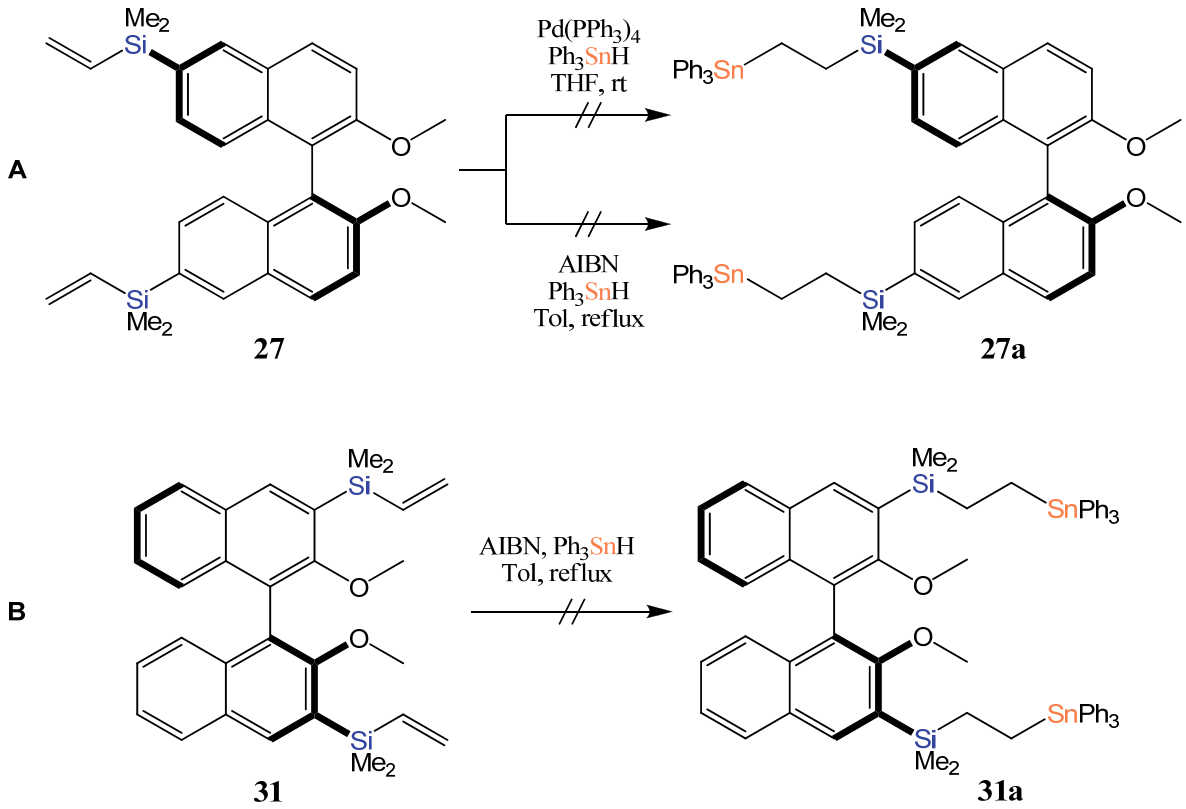
3.2.6 Tin Derivates

It has been demonstrated that organotin compounds tend to form ladder arrangements with organic spacers to produce cage-like structures with potential applications in host-guest chemistry.[70] With that in mind, preparation of tin-containing precursors with functionality so that cyclization could be effectuated in subsequent steps was effort.

3.2.6.1 Hydrostannylation of Vinylsilane Building Blocks

Oshima *et al*., reported the hydrostannylation of a series of allenes, including $PhMe_2SiCH=C=CH_2$, with triphenyltin hydride (Ph_3SnH) in the presence of catalytic amount of $Pd(PPh_3)_4$ in tetrahydrofuran at room temperature.[71] Considering their successful results, this method was first explored for the preparation of (*S*)-6,6'-bis[dimethyl(triphenylstannyl)ethylsilyl]-2,2'-dimethoxy-1,1'-binaphthalene (**27a**), as shown in Scheme 7A. The reaction progression was constantly monitored by tin layer chromatography (TLC). After 24 h of stirring at room temperature, only starting materials were detected. Therefore, the mixture was slowly heated until reflux temperature and allowed to react for another 24 h. Further workup and removal of volatiles resulted in formation of hexaphenylditin ($Ph_3Sn\text{-}SnPh_3$) and starting material **27**.

Because of the failed attempts in the preparation of **27a** by Pd-catalyzed hydrostannylation, the reaction was further explored by radical activation. Thus, simultaneous hydrostannylation of 6,6'-functionalized precursor **27** and 3,3'-functionalized precursor **31** (Scheme 7B) was essayed using azobisisobutyronitrile (AIBN) as initiator.



Scheme 7. Attempted hydrostannylation of vinylsilanes.

Hydrostannylation of **27** and **31** under radical conditions was carried out in toluene at reflux temperature during 72 h. After this time, the solvent was removed under reduced pressure and the remained crude products were analyzed by ^{1}H NMR. The obtained spectra showed characteristic resonances for vinyl functions in the same proportion than the observed for the precursors. Hence, the reactions were essayed using more AIBN and Ph_3SnH, also allowing the precursors to react for longer time. Again, analysis of the resulted mixtures showed no evidence of formation of desired products **27a** or **31a**.

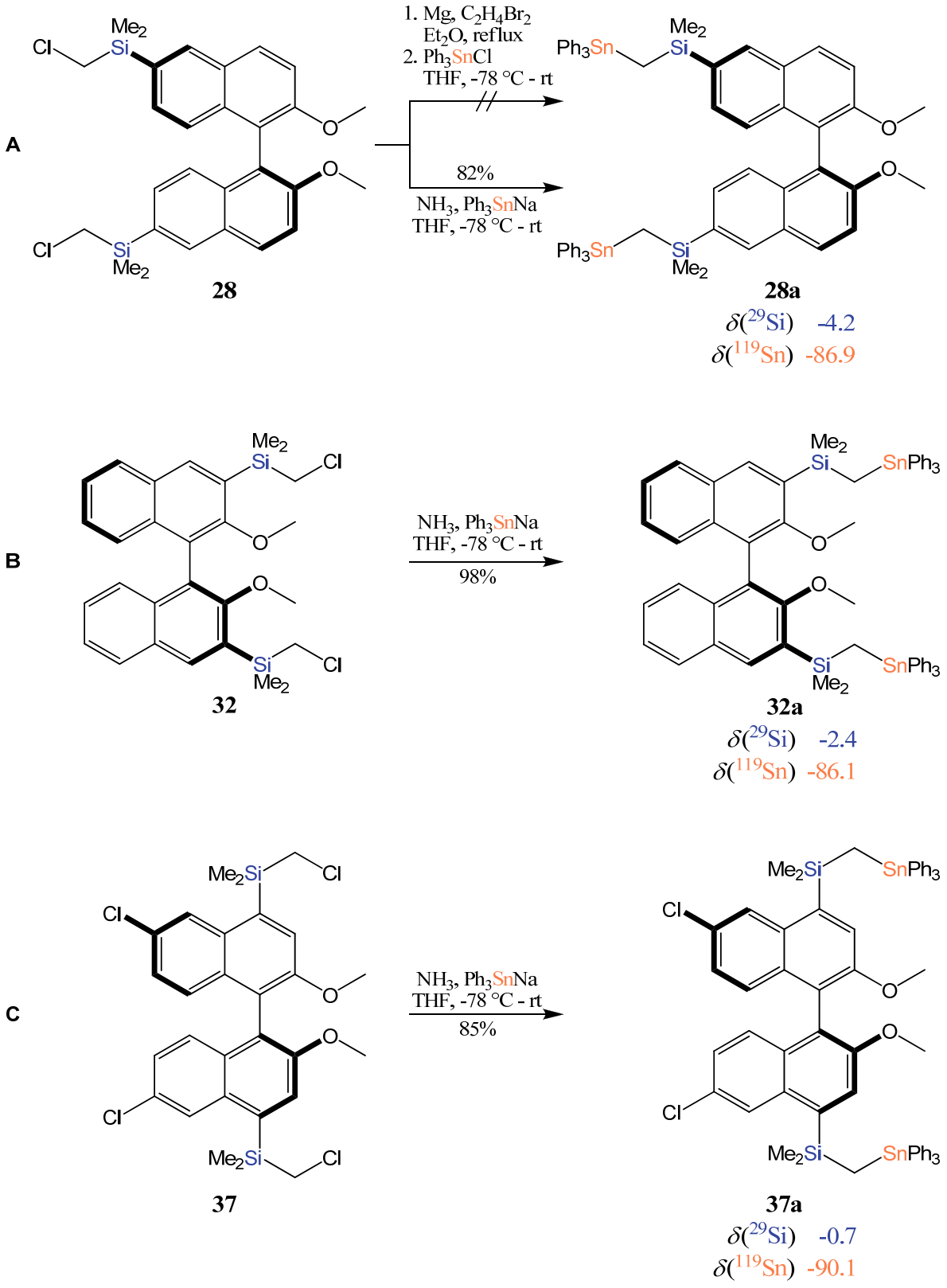
Similar observations were described by Kavanagh *et al.*,[72] who recently reported the results of a series of free radical hydrostannylation of alkenes of differing steric and electronic demand using several stannane precursors. They noticed that alkenes bearing electron donating groups failed to react with bulky stannanes under free radical standard conditions (AIBN as initiator). This behaviour was attributed to the fact that substrates containing electron-donating groups do not match well with the nucleophilic properties of the incipient stannyl radical.[73] It was particularly noteworthy that the more sterically encumbered stannanes were, the more sensitive they were to electronic demand of the alkene.

Because the attempts of hydrostannylation of compounds **27** and **31** failed, the reaction was not tried for 4,4'- derivate precursor **36.**

3.2.6.2 Stannylation of Chloromethylsilane Building Blocks

Derivatization of Me_2SiCH_2Cl-containing silyl-BINOL builing blocks **28**, **32**, and **37** was carried out in pursuit of preparing chiral organotin derivates. Accordingly, to prepare (*S*)-6,6'-bis[dimethyl(triphenylstannylmethyl)silyl]-2,2'-dimethoxy-1,1'-binaphthalene (**28a**), precursor **28** was first subjected to standard Grignard reaction with Mg in Et_2O at reflux temperature, followed by addition of the obtained mixture to a cooled solution of triphenyltin chloride (Ph_3SnCl) in THF. To our disappointment, this intent resulted in returned starting material, indicating that the Grignard reagent derived from **28** did not form. Although the preparation of Grignard reagents from the type R_3SiCH_2MgCl (where R is either aromatic, aliphatic or both) is well established,[70b, 74] any attempt of obtaining **28a** by this manner failed.

Then, as shown in Scheme 8, desired compound **28a** was obtained in 82% yield by reaction of precursor **28** with *in situ* prepared triphenylstannyl sodium (Ph_3SnNa) in liquid ammonia. The same reaction procedure was effectively employed for derivatization of 3,3'- and 4,4'-functionalized precursors **32** and **37**. The selected synthetic route afforded (*S*)-3,3'-bis[dimethyl(triphenylstannylmethyl)silyl]-2,2'-dimethoxy-1,1'-binaphthalene (**32a**) in 98% yield and (*S*)-6,6'-dichloro-4,4'-bis[dimethyl(triphenylstannylmethyl)silyl]-2,2'-dimethoxy-1,1'-binaphthalene (**37a**) in 85% yield. All products were isolated as colourless solids after removal of volatiles.



Scheme 8. Preparation of tin-containing silane building blocks.

Achievement of the desired products was confirmed by NMR and ESI MS analysis. It was noticed in the ^{1}H NMR spectrum of product **28a** that the resonance of the methylene protons was shifted to higher field from δ 3.02 ppm, observed for the starting material, to δ 0.89 ppm. Also, spectra of **32a** and **37a** showed resonances of methylene protons at δ 1.02 and δ 1.13 ppm, respectively.

The shielding effect upon the methylene atoms was even more evident in the ^{13}C NMR where the chemical shift changed from δ 30.5 ppm for precursor **28** to δ -5.53 ppm for product **28a**. Similarly, shifting of resonances δ 31.0 to δ -5.61 ppm and δ 30.5 to δ -4.54 ppm was detected for **32a** and **37a**.

Analysis by ^{29}Si NMR showed the chemical shift of the silicon atoms in product **28a** at δ -4.16 ppm and one singlet at δ -86.9 ppm was observed in its ^{119}Sn NMR spectrum. Compound **32a** displayed a resonance at δ -2.37 ppm in the ^{29}Si NMR spectrum and at δ -86.1 ppm by ^{119}Sn NMR. Likewise, analysis by ^{29}Si NMR of derivate **37a** showed a resonance at δ -0.72 ppm and at δ -90.1 ppm by ^{119}Sn NMR.

Identity of desired products **28a** and **32a** was verified by a molecular ion *m/z* = 1195 $[M+K]^{+}$ measured by ESI MS consistent with the exact mass ($C_{64}H_{62}O_2Si_2Sn_2$+K) = 1195 g/mol calculated for the proposed structures. Also, molecular ion *m/z* = 1249 $[M+Na]^{+}$ detected from **37a** confirmed the obtention of the desired product ($C_{64}H_{60}Cl_2O_2Si_2Sn_2$+Na) = 1249 g/mol.

The values of the specific rotation $[\alpha]_{\lambda}^{20}$ of the afforded tin-containing building blocks were notably lower than the observed from their corresponding chloromethylsilane-derived precursors **28**, **32** and **37** (Table 6). Still, the sign of the $[\alpha]_{\lambda}^{20}$ was in agreement with that of the initial materials.

Table 6. Optical rotation data of chiral tin-containing silanes building blocks in THF.

Compound	*c* (g/100 ml)	$[\alpha]$ (deg)	$[\alpha]_{\lambda}^{20}$ (deg)
6,6'-tin-containing silane **28a**	0.12	+66	+55.9
3,3'-tin-containing silane **32a**	0.31	+115	+37.0
4,4'-tin-containing silane **37a**	0.19	-40	-21.4

The presented results exemplified an efficient and inexpensive way for the functionalization of chloromethylsilane precursors to obtain novel tin derivatives.

3.3 Chiral Sila-Macrocycles

Macrocycles bearing a chiral cavity have attracted considerable attention due to their many applications in important processes such as molecular or chiral recognition, catalysis, drug delivery, and enantioselective separations. The group of Lin has made large contributions in this area, reporting interesting molecular geometries in which transition metals have been combined with organic ligands to produce chiral macrocycles with outstanding properties.[7a]

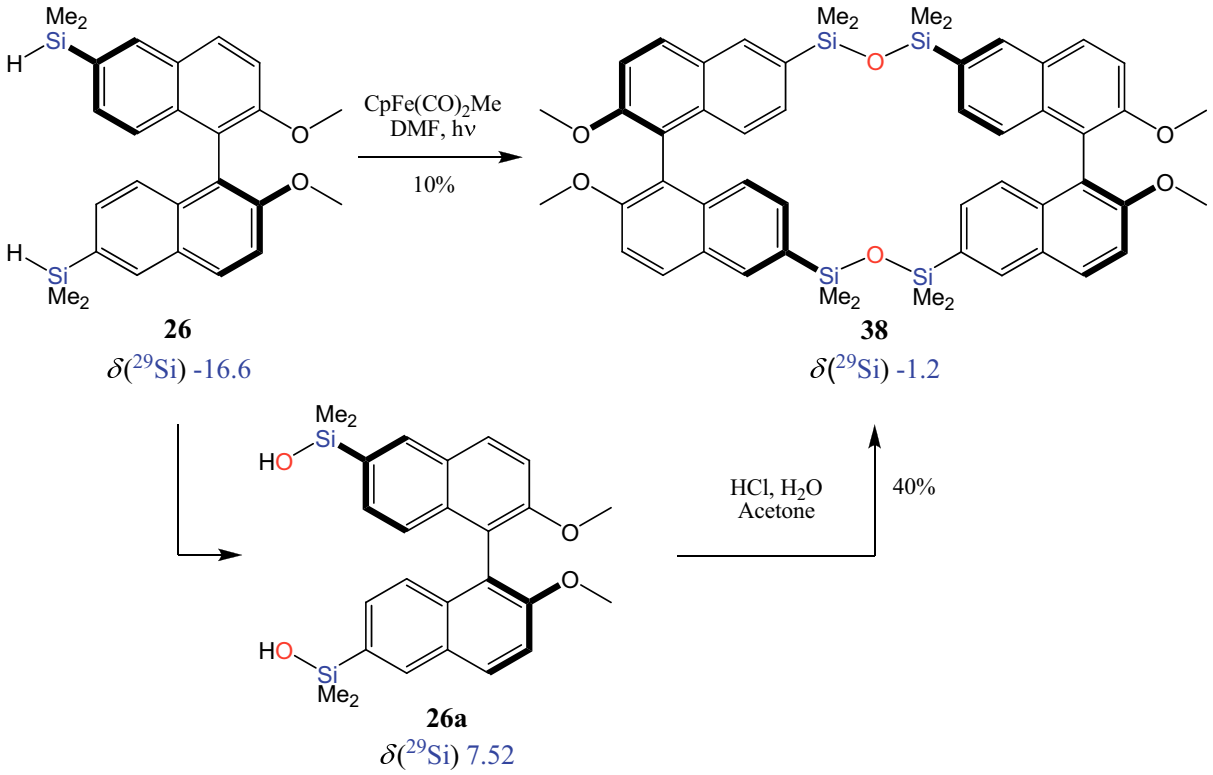
As Shea,[75] Lambert,[76] and Beckmann[43] *et al.* demonstrated, the use of main group elements, especially silicon, also affords macrocyclic molecules with structural integrity, uniform pores, and adjustable cavities. Working with silicon as linking unit for the preparation of cyclic structures has shown to offer the advantages of producing compounds with low toxicity, which represents the assembly of cavities with safer environment. Besides, cheaper starting materials could be employed. Thus, the efficiency of the previously described silyl-BINOL precursors as building blocks for the preparation of chiral sila-macrocycles was studied.

3.3.1 Chiral Sila-Macrocycles from Silanol Precursors

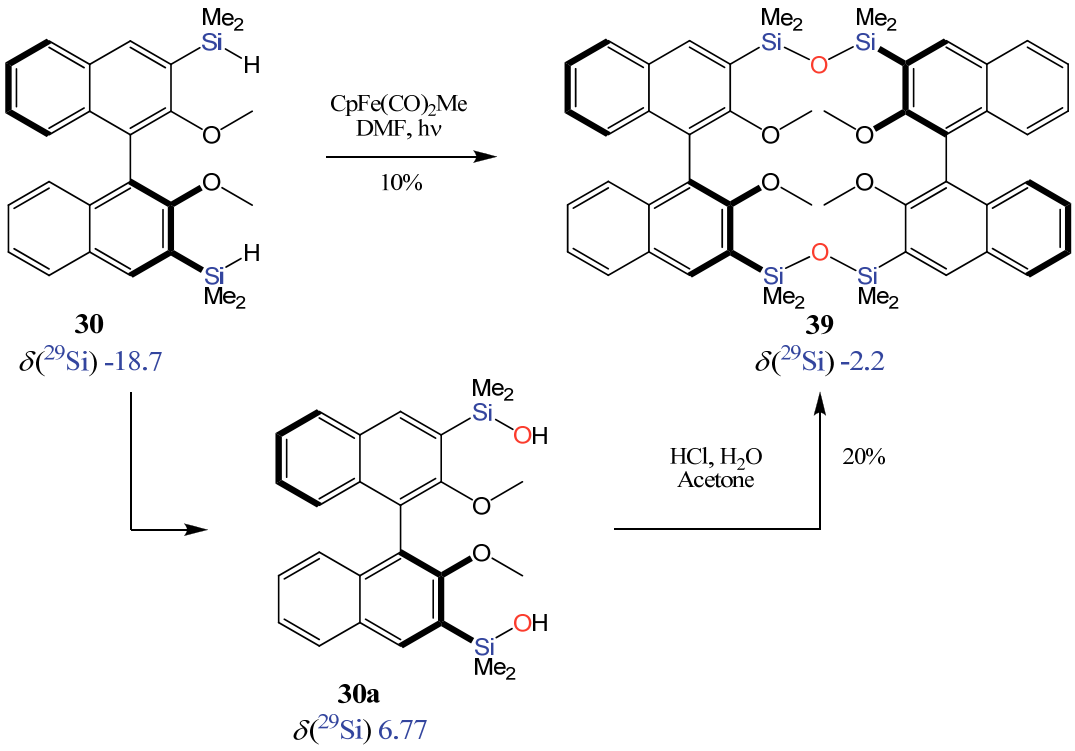
Cyclic siloxanes with well defined architectures and interesting properties are challenging synthetic targets. These compounds have attracted considerable attention because their novel electronic and optical attributes allow their use in industrial processes.[77] Also, exceptional examples of siloxane-derived compounds like siloxanes analogues of crown ethers[78] and siloxane-bridged cyclophanes[42-43, 79] have shown potential applications in host-guest chemistry.

There are excellent protocols for the preparation of siloxanes, being among the most popular the dehydrogenative coupling of hydrosilanes, catalytic condensation of silanols and controlled hydrolysis of chlorosilanes. However, there is not a standard procedure which works well with all precursors. Hence, several methods and precursors were tested in order to produce siloxanes **38**, **39** and **40**, shown in Schemes 9, 10 and 11, respectively.

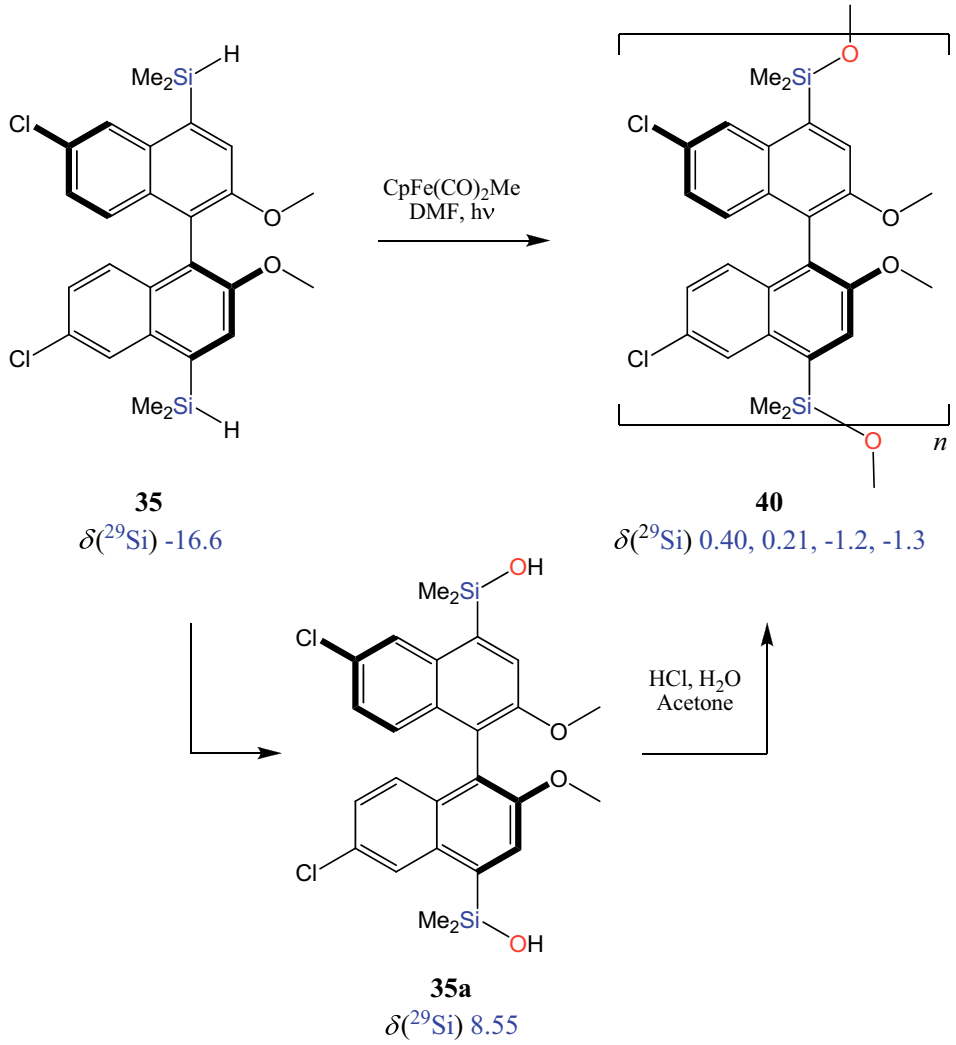
First, hetereo-dehydrocoupling of 6,6'-, 3,3'-, and 4,4'-functionalyzed hydrosilanes **26**, **30**, and **35** in the presence of cyclopentadienyl-dicarbonyl(methyl)iron [$CpFe(CO)_2Me$] as catalyst was essayed. For that, a solution of the precursors in DMF, used as oxygen source, was heated at 80 °C during 10 h. The reaction progression was constantly monitored by TLC. Because no product was formed after this time, the mixture was then irradiated with UV light at 400 W for 3 h. At this point, no more evidence of the hydrosilane precursors was observed. Then, removal of solvent under reduced pressure and purification by column chromatography afforded desired macrocycles (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyltetrasiloxane (**38**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyltetrasiloxane (**39**), as microcrystaline colourless solid in 10% yield each. Product **40** was obtained as a complex polymeric mixture.



Scheme 9. Reaction pathways to cyclic siloxane **38**.



Scheme 10. Reaction pathways to cyclic siloxane **39**.



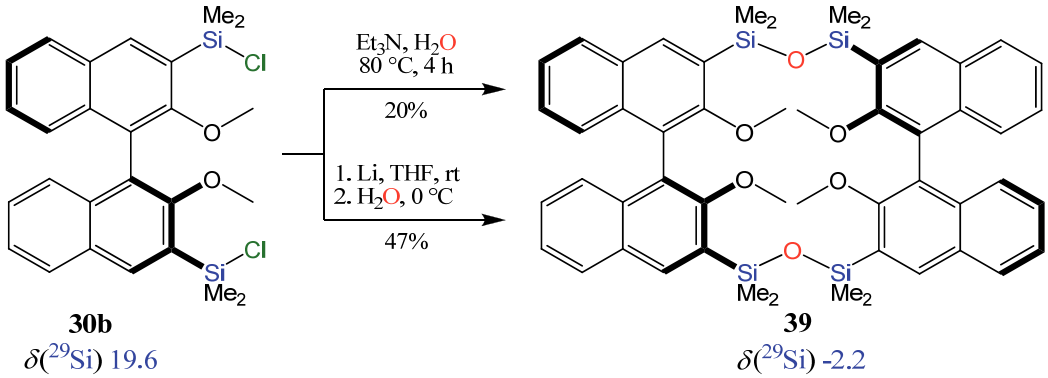
Scheme 11. Reaction pathways to product **40**.

The direct synthesis of siloxanes **38**, **39** and **40** from the hydrosilane precursors was not a trivial task and the resulting yields were very low. Variation in the concentration of precursors, increment of the catalyst amount and following strict reaction conditions made no significant changes in the results.

Thus, preparation of the discussed cyclic siloxanes was also examined by acid catalyzed condensation of silanols derivates **26a**, **30a** and **35a**. A mixture of the respective precursor in acetone, H_2O and hydrochloric acid was allowed to react at room temperature for several days until no more evidence of the silanol precursor was observed by TLC. Subsequently, the volatiles were distilled off and the afforded solids were subjected to column chromatography. In this case, pure products **38** and **39** were achieved in 40% and 20% yield, respectively. Product **40** was obtained as a polymeric mixture.

Since the yield of formation of disiloxane **39** was still poor, triethylamine (Et_3N) mediated hydrolysis of chlorosilane-BINOL precursor **30b** was explored as illustrated in Scheme 12. Slow addition of H_2O to a 80 °C heated solution of the chlorosilane in Et_3N, followed by reflux during 4 h gave a mixture of disiloxane **39** (20%) and silanol **30a** (80%).

Further attempt to achieve **39** in a higher quantity was effectuated by reaction of **30b** with lithium-granulates. The respective lithium derivate produced was then carefully treated with H_2O at 0 °C. After workup, **39** was isolated in 47% yield.



30b
$\delta(^{29}Si)$ 19.6

39
$\delta(^{29}Si)$ -2.2

Scheme 12. Preparation of disiloxane macrocycle **39** from chlorosilane **30b**.

Any attempt to grow crystals from **38** suitable for crystallographic analysis failed. However, recrystallization of **39** in toluene gave crystals which could be successfully studied.

Macrocycle **39** crystallizes in the orthorhombic system, space group $P2_12_12_1$. The molecular structure aided is shown in Figure 18 and the respective selected bond parameters are collected in Table 7.

The intramolecular distances of siloxane oxygen atoms O5···O6 (8.0 Å) and silicon atoms Si2···Si3 (9.6 Å) indicate the formation of a nanosized cavity. The dihedral angle between the two naphthyl moieties in macrocycle **39** was found 120.2(7)°, that is, it preserves the *transoid* conformation.

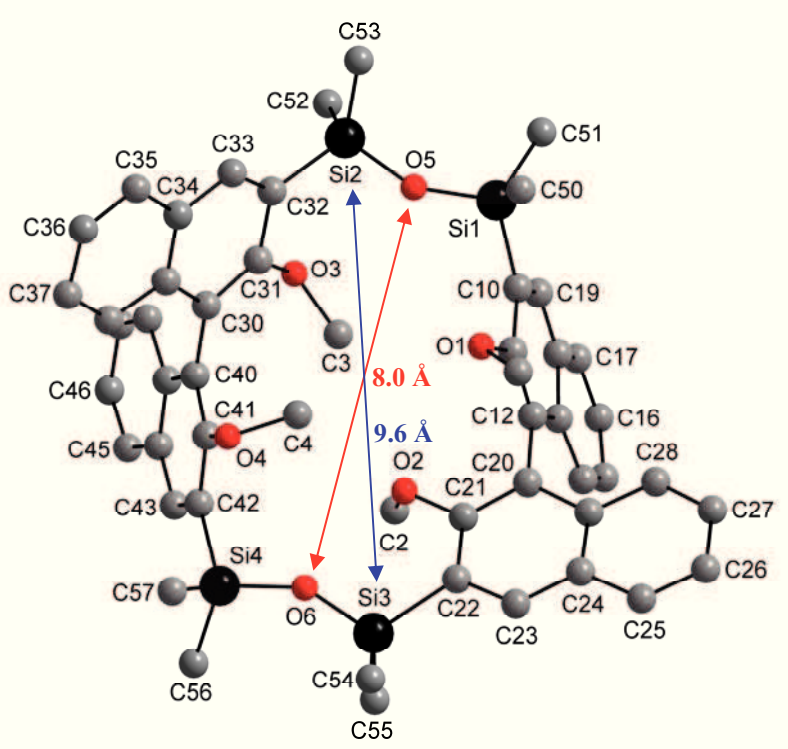


Figure 18. Molecular structure of macrocyclic siloxane **39**.

Table 7. Selected bond parameters for **39**, bond distances [Å] and angles [°].

Si1-C10	1.887(9)	Si1-O5-Si2	152.3(5)
Si1-C50	1.850(1)	Si3-O6-Si4	147.8(5)
Si1-C51	1.838(1)	C10-Si1-O5	107.6(4)
Si1-O5	1.608(7)	C32-Si2-O5	107.2(4)
Si2-C32	1.851(9)	C22-Si3-O6	113.3(4)
Si2-C52	1.83(1)	C42-Si4-O6	108.0(4)
Si2-C53	1.875(9)	C10-C11-Si1	122.3(7)
Si2-O5	1.615(8)	C31-C32-Si2	119.5(6)
Si3-C22	1.895(8)	C21-C22-Si3	123.8(6)
Si3-C54	1.83(1)	C42-C41-Si4	120.5(7)
Si3-C55	1.80(2)	C12-C20-C21	118.5(7)
Si3-O6	1.572(8)	C12-C20-C29	120.6(7)
S4-C42	1.89(1)	C20-C12-C13	119.9(8)
S4-C56	1.88(1)	C20-C12-C11	120.2(8)
S4-C57	1.83(1)	C39-C30-C40	123.0(8)
S4-O6	1.644(7)	C31-C30-C40	119.6(8)
		C30-C40-C41	122.4(8)
		C30-C40-C49	120.2(7)

Complete characterization of the obtained solids **38** and **39** by spectroscopic and spectrometric techniques supported the proposed structures. The ^{29}Si NMR spectrum of **38** showed only one resonance at δ -1.2 ppm, different than that of hydrosilane precursor **26** (δ -16.6 ppm) or silanol **26a** (δ 7.52 ppm). Similarly, the ^{29}Si NMR spectrum of **39** consisted of one displacement at δ -2.2 ppm. By contrast, ^{29}Si NMR analysis of **40** displayed a main peak at δ 0.4 ppm and some other small peaks at δ -0.2, -1.2, and -1.3 ppm.

Measurement of the optical activity in THF of cyclic siloxanes **38** and **39**, provided specific rotations of $[\alpha]_{\lambda}^{20}$ = +23.8 (c = 0.21) and $[\alpha]_{\lambda}^{20}$ = +66.0 (c = 0.20), respectively. Both values were lower than the displayed values for hydrosilane or silanol precursors (Tables **2** and **3**). It was also noticed that the sign of the specific rotation $[\alpha]_{\lambda}^{20}$ of the products was in agreement with that of the initial compounds.

In general, it was noticed that catalyzed dehydrocoupling of hydrosilanes **26**, **30** and **35** resulted in very poor formation of the attempted cyclic siloxanes. Better results were obtained when silanols **26a**, **30a** and **35a**, or chlorosilane **30b** were used as starting materials.

3.3.2 Chiral Sila-Macrocycles from Hydrosilane and Vinylsilane Precursors

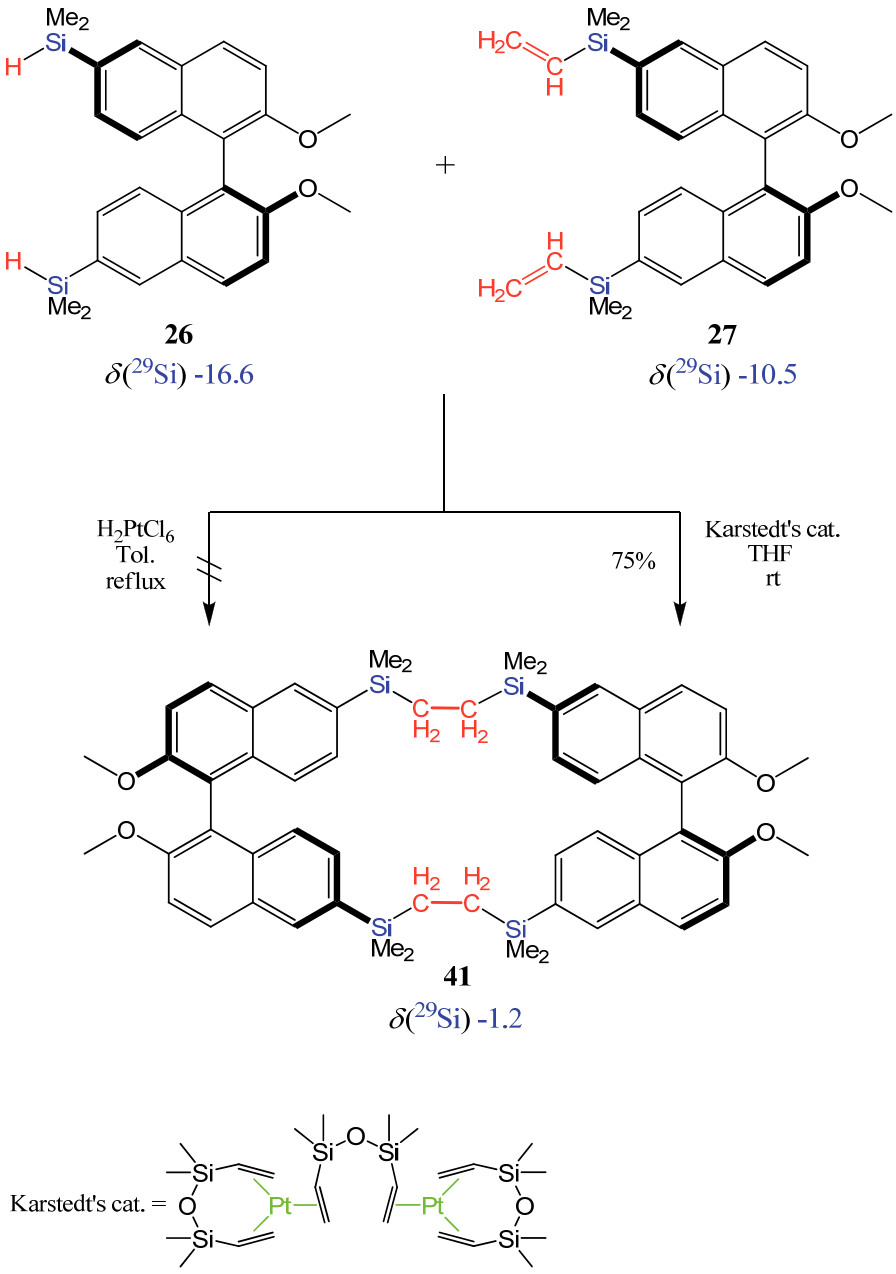
It has been demonstrated that Hydrosilylation could be successfully employed for the synthesis of macrocyclic compounds by ring-closing processes.[80] One of the most relevant examples of this type of mechanism was presented by Setaka *et al*.[81] They reported the first silicon-based macrocycle bridged by a 1,4-phenylene group afforded by ring-closing hydrosilylation between the adequate vinylsilane and hydrosilane. Taking into account their outcomes, behaviour of appropriated precursors toward hydrosilylation was evaluated.

Following the reaction conditions illustrated in Scheme 13, hydrosilylation between 6,6'-hydrosilane **26** and 6,6'-vinylsilane **27** in the presence of catalytic amounts of H_2PtCl_6 (Speier catalyst) was tried. After keeping the mixture several days under reflux temperature in toluene, only unreacted staring materials were recovered. Then, the reaction was examined using Karstedt's catalyst, a modified version of the Speier catalyst which has shown to have higher activity in hydrosilylation processes.[82] Treatment of precursors **26** and **27** at room temperature with Karstedt's catalyst in THF afforded (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyltetraethylsilane (**41**).

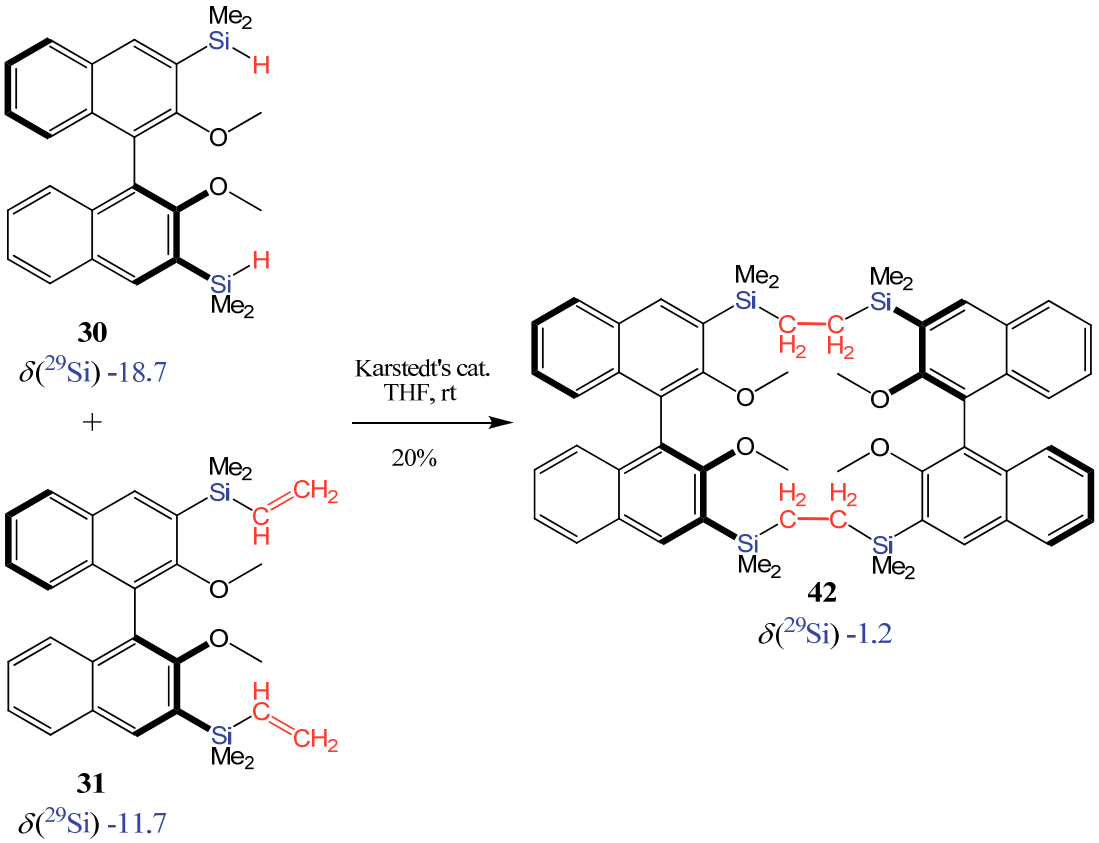
In the same way, use of 3,3'-hydrosilane **30** and 3,3'-vinylsilane **31** gave (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyltetraethylsilane (**42**) shown in Scheme 14.

A polymeric mixture, referred as product **43** (Scheme 15), was obtained when 4,4'-derived precursors **35** and **36** were subjected to hydrosilylation.

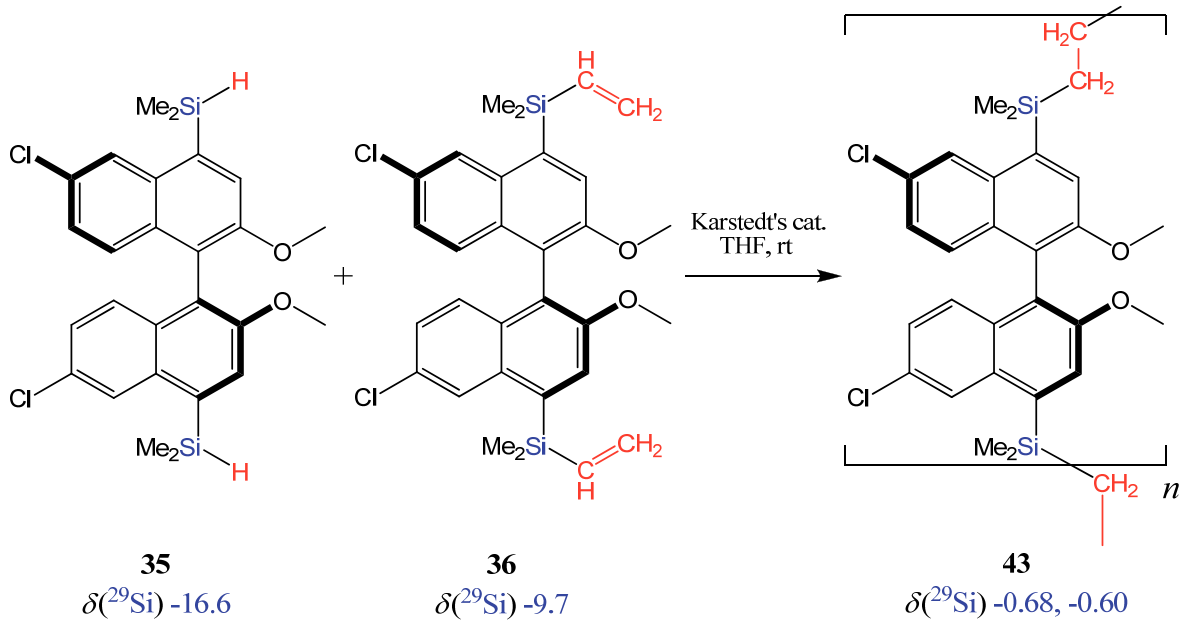
All raw products were subjected to column chromatography to isolate the desired compounds. This provided macrocycles **41** and **42** as glass-like colourless solids in 75% and 20% yields, respectively. Any attempt of purification of **43** failed.



Scheme 13. Preparation of macrocycle **41** by hydrosilylation.



Scheme 14. Preparation of macrocycle **42** by hydrosilylation.



Scheme 15. Hydrosilylation of 4,4'-vinylsilane **36**.

Crystallization of pure products **41** and **42** were tested in several solvents. While no success was achieved with **41**, crystals suitable for X-ray crystallography were obtained from **42** in toluene. Analysis of the afforded crystals provided the molecular structure showed in Figure 19. The respective selected bond parameters are collected in Table 8.

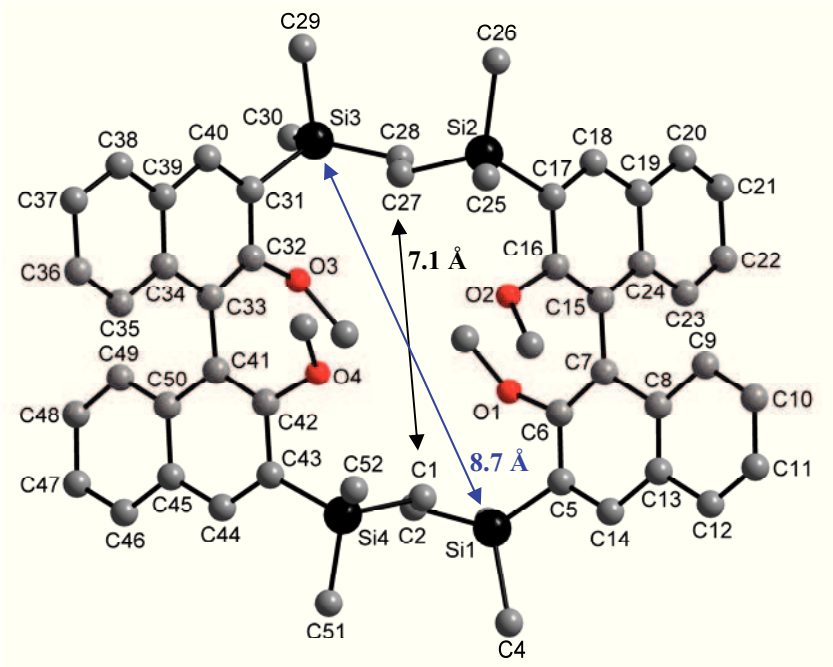


Figure 19. Molecular structure of macrocycle **42**.

Table 8. Selected bond parameters for **42**, bond distances [Å] and angles [°].

Si1-C2	1.91(2)	Si1-C2-C5	104.91(1)
Si1-C3	1.753(1)	Si1-C5-C6	118.34(1)
Si1-C4	2.000(9)	Si2-C17-C16	118.72(1)
Si1-C5	1.893(2)	Si2-C17-C27	108.85(1)
Si2-C17	1.91(1)	Si3-C31-C28	109.50(1)
Si2-C25	1.918(1)	Si3-C31-C32	119.38(1)
Si2-C26	1.915(6)	Si4-C1-C43	109.90(1)
Si2-C27	1.893(4)	Si4-C42-C43	117.94(1)
Si3-C28	1.883(2)	C16-C15-C7	120.47(1)
Si3-C29	1.942(4)	C24-C15-C7	119.92(2)
Si3-C30	1.618(3)	C15-C7-C6	124.51(1)
Si3-C31	1.900(8)	C15-C7-C8	120.07(2)
S4-C43	1.869(4)	C33-C41-C50	116.87(1)
S4-C51	1.839(4)	C33-C41-C42	121.65(2)
S4-C52	1.915(1)	C32-C33-C41	120.91(1)
S4-C1	1.92(2)	C34-C33-C41	119.95(1)
C1-C2	1.507(0)		
C27-C28	1.495(1)		

Macrocycle **42** crystallizes in the monoclinic system, space group $P12_11$. Same as cyclic siloxane **39**, it adopts the *transoid* conformation with a dihedral angle of 119.95(1)°. Besides, the intermolecular distances of carbon atoms C1⋯C27 (7.1 Å) and silicon atoms Si1⋯Si3 (8.7 Å) reveal the nanosize of the cavity.

Examination of **41** and **42** by NMR spectroscopy confirmed the suggested structures. A singlet at δ -1.2 ppm, characteristic of silicon atoms bonded to aliphatic groups,[83] was detected by ^{29}Si NMR analysis, in both cases. Ethyl connecting units were identified by ^{1}H NMR as singlets at δ 0.84 ppm for **41** and δ 0.86 ppm for **42**. This group displayed in the ^{13}C NMR spectrum of **41** a resonance at δ 8.0 ppm and at δ 9.0 ppm in the spectrum of **42**.

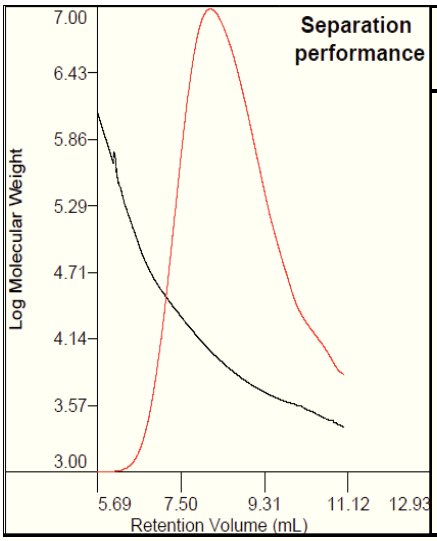
NMR study of product **43** was difficult due to the complexity of the mixture. Resonances at δ -0.68 and -0.60 ppm were detected by ^{29}Si NMR. The ^{1}H NMR and ^{13}C NMR spectra of the studied sample consisted of complicated set of signals which could not be properly assigned.

The magnitude of the specific rotation $[\alpha]_{\lambda}^{20}$ of optical active macrocycles **41** and **42** was determined in THF. The obtained value for 6,6'-functionalyzed compound **41** ($[\alpha]_{\lambda}^{20}$ = +110.0; c = 0.06) was much higher than the measured from hydrosilane and vinylsilane precursors **26** and **27**. By contrary, specific rotation of 3,3'-funcitionalyzed compound **42** ($[\alpha]_{\lambda}^{20}$ = +21.9; c = 0.13) resulted lower than the observed from corresponding precursors **30** and **31**.

Macrocyclization is normally a low yield process accompanied by a considerable amount of oligo- and polymeric by-products. Therefore, gel permeation chromatography (GPC) of raw products was used to determine the molecular weight of the formed polymers.

GPC study results of the obtained crude product from 6,6'-functionalyzed precursors **26** and **27** are presented in Table 9. As indicated in the table, polymers with an average molecular weight (Mw) of $11.4 \cdot 10^3$ g/mol were detected, which suggested a degree of polymerization of 25. Similar results were observed from GPC of hydrosilylation product of 3,3'-functionalyzed precursors **30** and **31**. The outcomes, reported in Table 10, revealed the formation of polymers with Mw = $7.4 \cdot 10^3$ g/mol and a degree of polymerization of 16. No GPC analysis of hydrosilylation product of 4,4'-functionalyzed precursors **35** and **36** was performed.

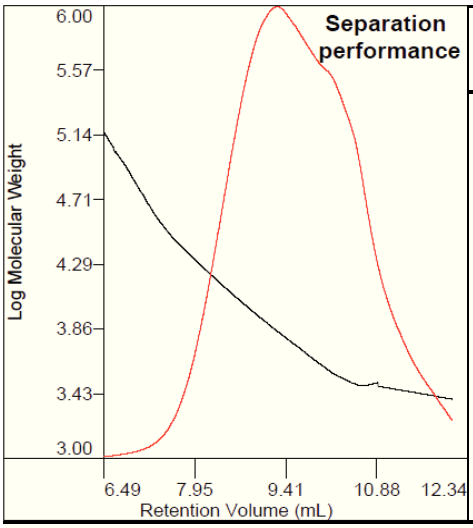
Table 9. GPC analysis of the resulting product from hydrosilylation of 6,6'-precursors **26** and **27**.



	Mw [g/mol]	Mn [g/mol]	Mw/Mn	Recovery [%]
	11419	6803	1.70	94.1
	11449	6877	1.70	94.0
	11327	6720	1.70	93.3
Average	**11398**	**6800**	**1.70**	**93.9**
RSD	51.9	64.1	0.01	0.36
RSD %	0.45	0.94	0.58	0.38

Monomer [g/mol]	457
Degree of Polymerization	***25***

Table 10. GPC analysis of the resulting product from hydrosilylation of 3,3'-precursors **30** and **31**.



	Mw [g/mol]	Mn [g/mol]	Mw/Mn	Recovery [%]
	7431	5092	1.50	175.6
	7389	5128	1.40	174.5
	7356	5124	1.40	173.5
Average	**7392**	**5115**	**1.43**	**174.5**
RSD	30.7	16.1	0.05	0.86
RSD %	0.42	0.31	0.70	0.49

Monomer [g/mol]	457
Degree of Polymerization	***16***

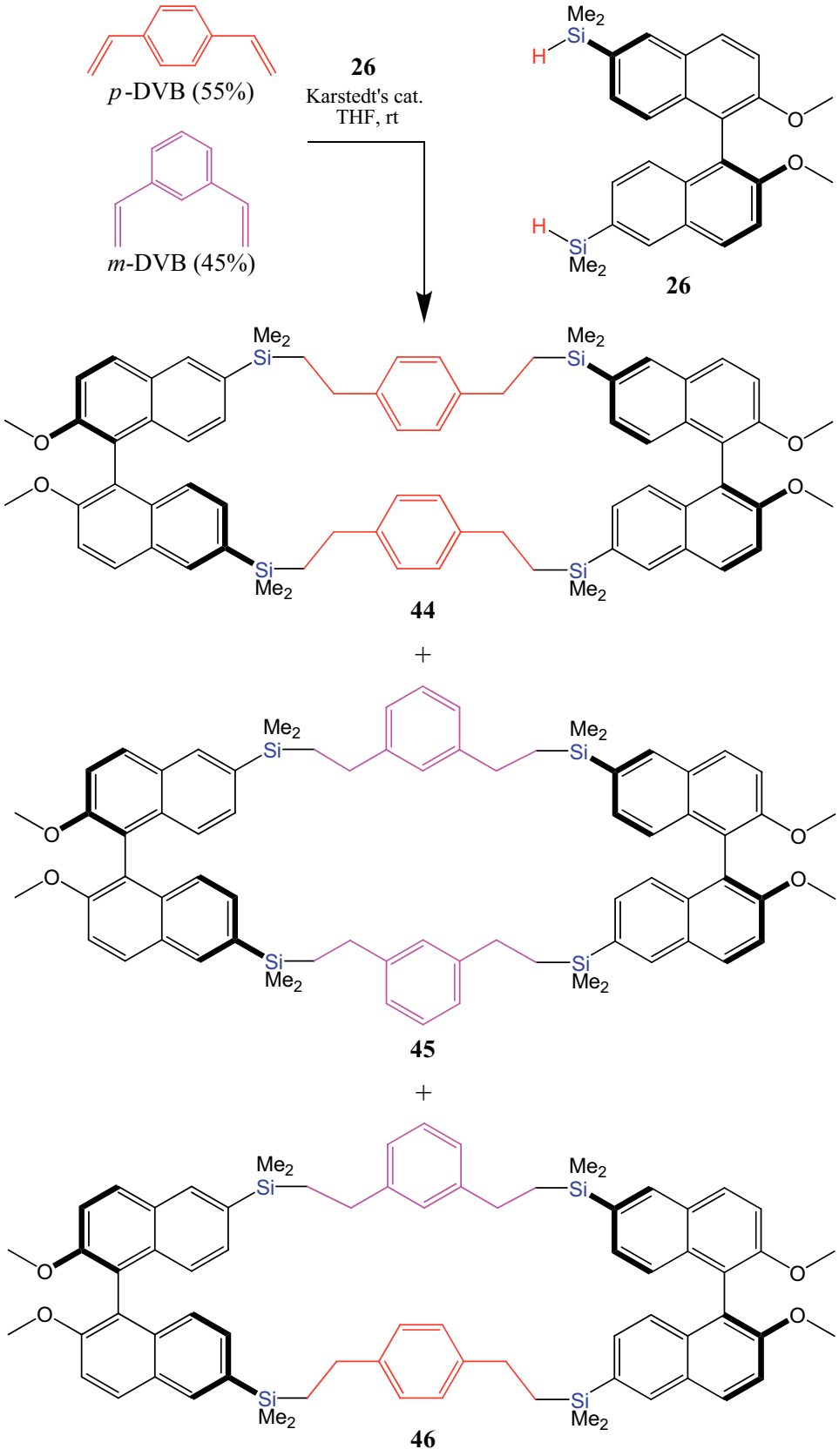
Hydrosilylation of the studied precursors provided satisfactory results. Therefore, preparation of macrocycles with a bigger cavity following this procedure was evaluated. In this context, hydrosilylation of divinylbenzene (DVB) using hydrosilanes **26** and **30** was explored to produce (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-bis(4-ethylphenyl)octamethylsilane (**44**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',-11,11'-bis(4-ethylphenyl)octamethylsilane (**47**) (Schemes 16 and 17), respectively.

For the preparation of macrocycles **44** and **47** we struggle with the problem that DVB is, in general, commercially available as a 2:1 mixture of 1,4-DVB (*p*-DVB) and 1,3-DVB (*m*-DVB) isomers. Besides, its synthesis requires expensive catalyst and ligands,[84] long multiple-steps reaction protocols,[84a] low yielding procedures,[85] or harsh conditions,[88] difficult to handle at laboratory scale. Accordingly, a 55% mixture of *p*-DVB/*m*-DVB was acquired from a commercial source and employed in order to investigate the efficiency of the proposed reaction.

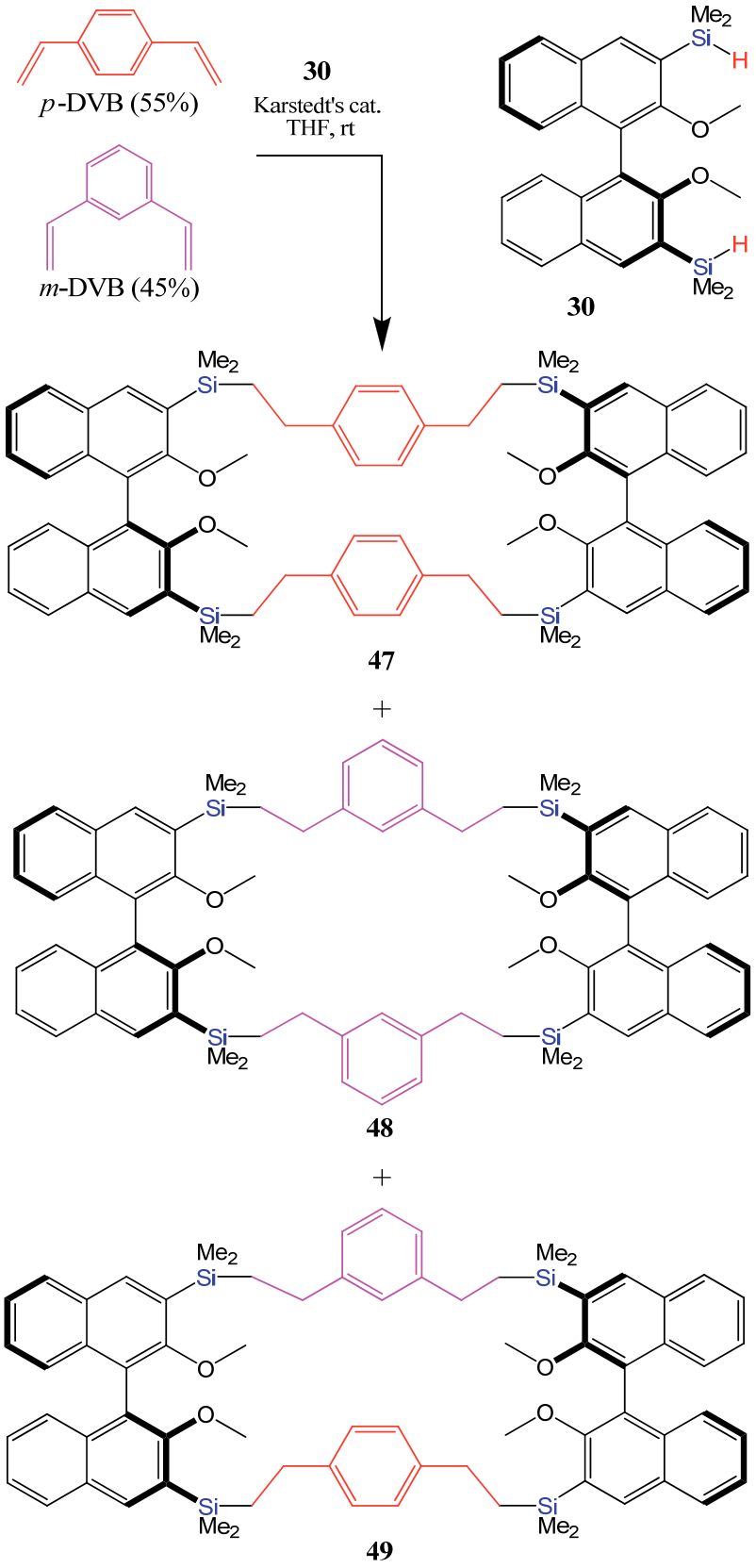
The obtained crude products were subjected to several separation procedures for purification, including column chromatography and HPLC techniques by normal- and reverse-phase. Although continuous attempts for isolation of the desired macrocycles were effectuated, only mixtures were attained. Accordingly, the cleanest mixture of macrocycle isomers elucidated from the reaction of 6,6'-functionalyzed precursor **26** (Scheme 16) was afforded in 53% yield. In the same way, the yield of macrocycle formation from hydrosilylation with 3,3'-hydrosilane **30** was calculated as 33%.

Generation of the proposed macrocycle isomers were mostly evidenced by ^{1}H and ^{13}C NMR analysis of the products. All recorded spectra showed a main set of signals (described in the experimental part), assigned to macrocycles **44** and **47**, together with similar less intense shifts. By ^{29}Si NMR analysis, a resonance at δ -2.9 ppm was detected for **44** and at δ -3.2 ppm for **47**, which is consistent with the expected results.

As expected, hydrosilylation of the used mixture of *p*-DVB afforded not only the desired macrocycles **44** and **47**, but also macrocycle isomers **45** and **48,** corresponding to the hydrosilylation of the *m*-DVB precursor; and probably macrocycles **46** and **49** which would be the predictable products resulting when the *p*- and *m*-isomers form a cycle.



Scheme 16. Hydrosilylation with 6,6'-hydrosilane **26** of a 55% *p*-DVB mixture.



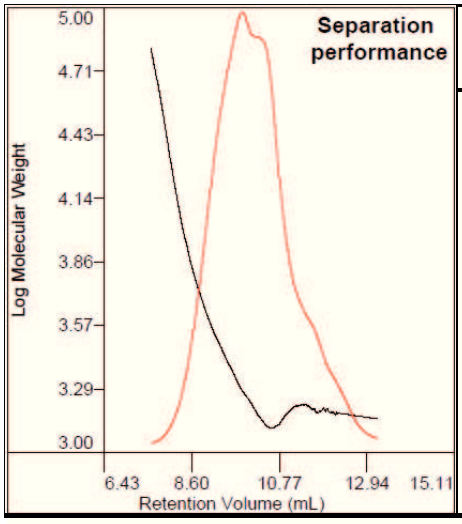
Scheme 17. Hydrosilylation with 3,3'-hydrosilane **30** of a 55% *p*-DVB mixture.

Crude products were also subjected to GPC analysis, obtaining the results summarized in Tables 11 and 12. When hydrosilylation was performed using 6,6'-derivate **26**, polymers with an average molecular weight $Mw = 2.6 \cdot 10^3$ g/mol were detected. The degree of polymerization of the analyzed sample was then calculated to be 5.

On the other hand, GPC analysis of the product derived from 3,3'-functionalyzed BINOL hydrosilane **30** indicated the presence of a mixture with an average molecular weight $Mw = 1.4 \cdot 10^3$ g/mol. Considering that the monomer would have a molecular weight of 560 g/mol, the degree of polymerization would be 2, indicating the main formation of dimeric species.

As previously mentioned, affording an isomeric mixtures of **44** and **47** was essentially due to the use of *p*-DVB/*m*-DVB, which subsequently prevented the isolation of the aimed products. Hence, it could be assumed that catalytic hydrosilylation of pure allylic derivates by hydrosilane precursors **26** and **30** would produce macrocycles which cavity sizes could be varied by adequate selection of the precursors.

Table 11. GPC analysis of the resulting product from hydrosilylation of *p*-DVB with 6,6'-precursor **26**.

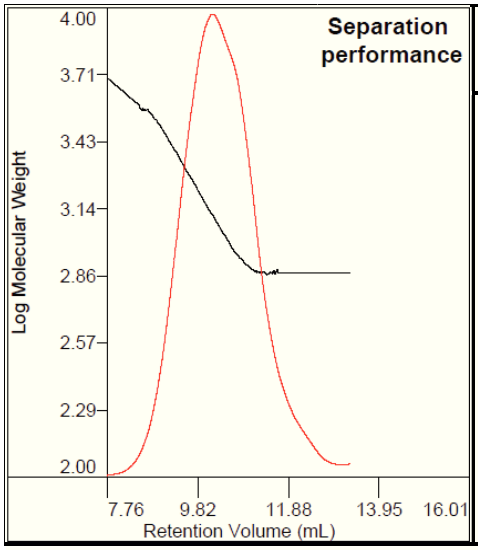


	Mw [g/mol]	Mn [g/mol]	Mw/Mn	Recovery [%]
	2620	1883	1.40	99.3
	2681	1991	1.30	99.8
	2569	1765	1.50	96.3
Average	**2623**	**1880**	**1.40**	**98.5**
RSD	45.8	92.3	0.04	1.54
RSD %	1.74	4.91	2.85	1.57

Monomer [g/mol] 560

Degree of Polymerization ***5***

Table 12. GPC analysis of the resulting product from hydrosilylation of *p*-DVB with 3,3'-precursor **30**.

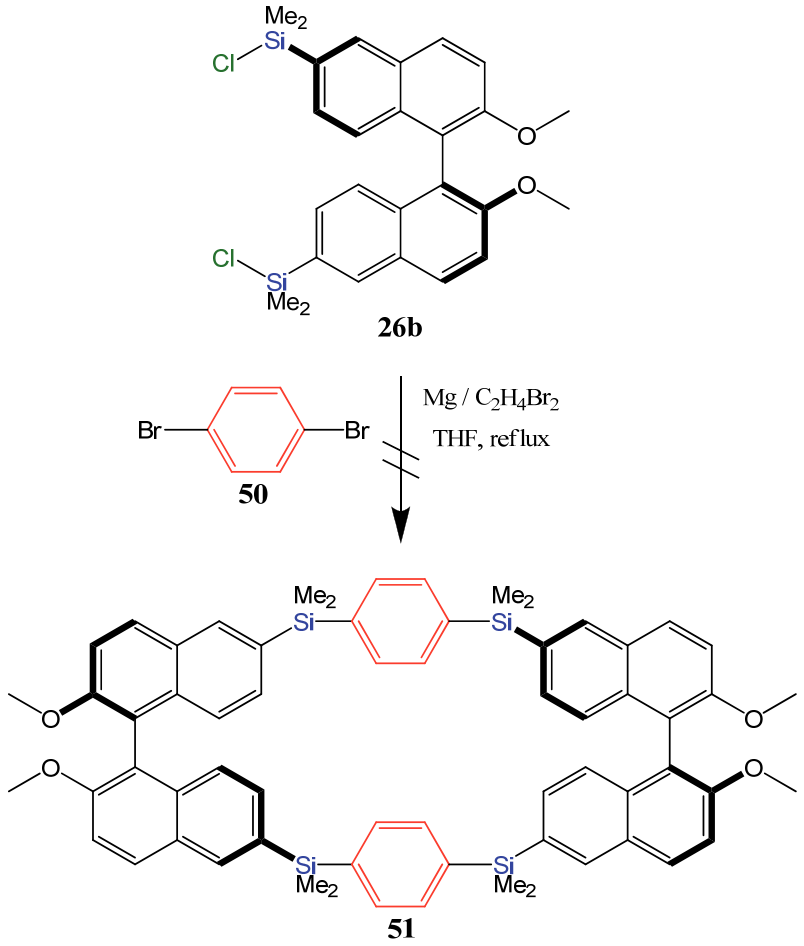


	Mw [g/mol]	Mn [g/mol]	Mw/Mn	Recovery [%]
	1392	1143	1.20	100.6
	1385	1134	1.20	100.2
	1377	1109	1.20	100.5
Average	**1385**	**1129**	**1.20**	**100.4**
RSD	6.13	14.4	0.00	0.17
RSD %	0.44	1.27	0.00	0.17
Monomer [g/mol]	560			
Degree of Polymerization	***2***			

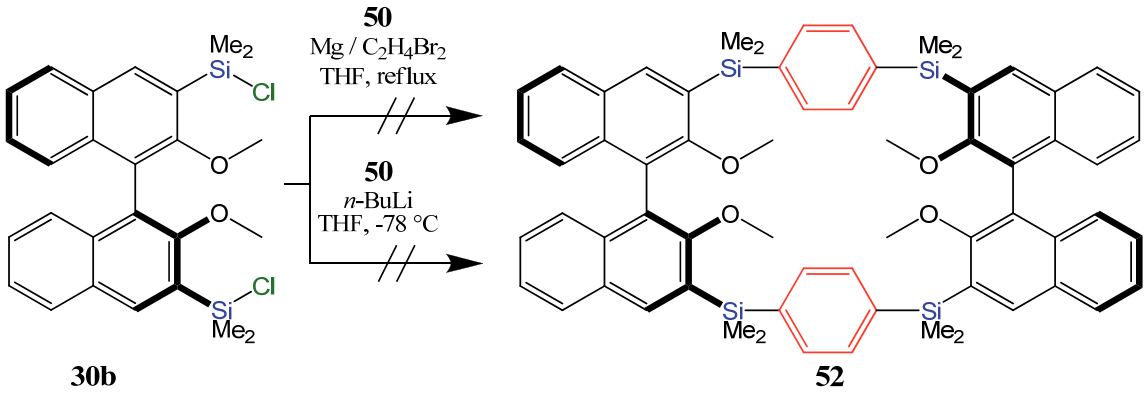
3.3.3 Chiral Sila-Macrocycles from Halogenated Precursors

Macrocycles containing π-electronic environment result attractive because they are expected to have exceptional electric, magnetic, optical, and thermal properties.[83, 89] Interested in the preparation of such systems, reaction of halogenated silyl-BINOL precursors **26b** and **30b** with aromatic Grignard reagents was evaluated.

In a first attempt to obtain macrocycles **51** and **52** (Schemes 18 and 19, respectively) a Grignard reagent was prepared during 8 h from *p*-dibromobenzene (**50**). The afforded solution was added to **26b** or **30b** dissolved in THF. The resulting mixtures containing 1:1 equivalents of chlorinated precursors and Grignard compound were individually reacted at reflux temperature. After 48 h, the reaction was stopped by addition of water. Extraction with EtOAc followed by removal of volatiles afforded yellow oils for both precursors.



Scheme 18. Treatment of compound **26b** with an aromatic Grignard reagent.



Scheme 19. Treatment of compound **30b** with an aromatic Grignard reagent and a lithiated aromatic precursor.

^{29}Si NMR analysis of the crude product derived from 6,6'-chlorosilyl-BINOL **26b** displayed typical displacements for silanol at δ 7.82 ppm, polysiloxane at δ -0.92 ppm, and disiloxane at δ -3.03 ppm. Two other resonances were detected at δ -7.98 and -8.10 ppm. It was assumed that the last corresponds to product **51**, because it is known that silicon atoms bonded to an aromatic functional group would produce a resonance between δ -7.00 and -10.0 ppm.[83] The mixture was subjected several times to column chromatography, but mass spectrometry analysis of the isolated fractions showed no molecular ion coinciding with the calculated for the desired product (*m/z* = 1008). Also, ^{1}H and ^{13}C NMR data were not consistent with the expected signals.

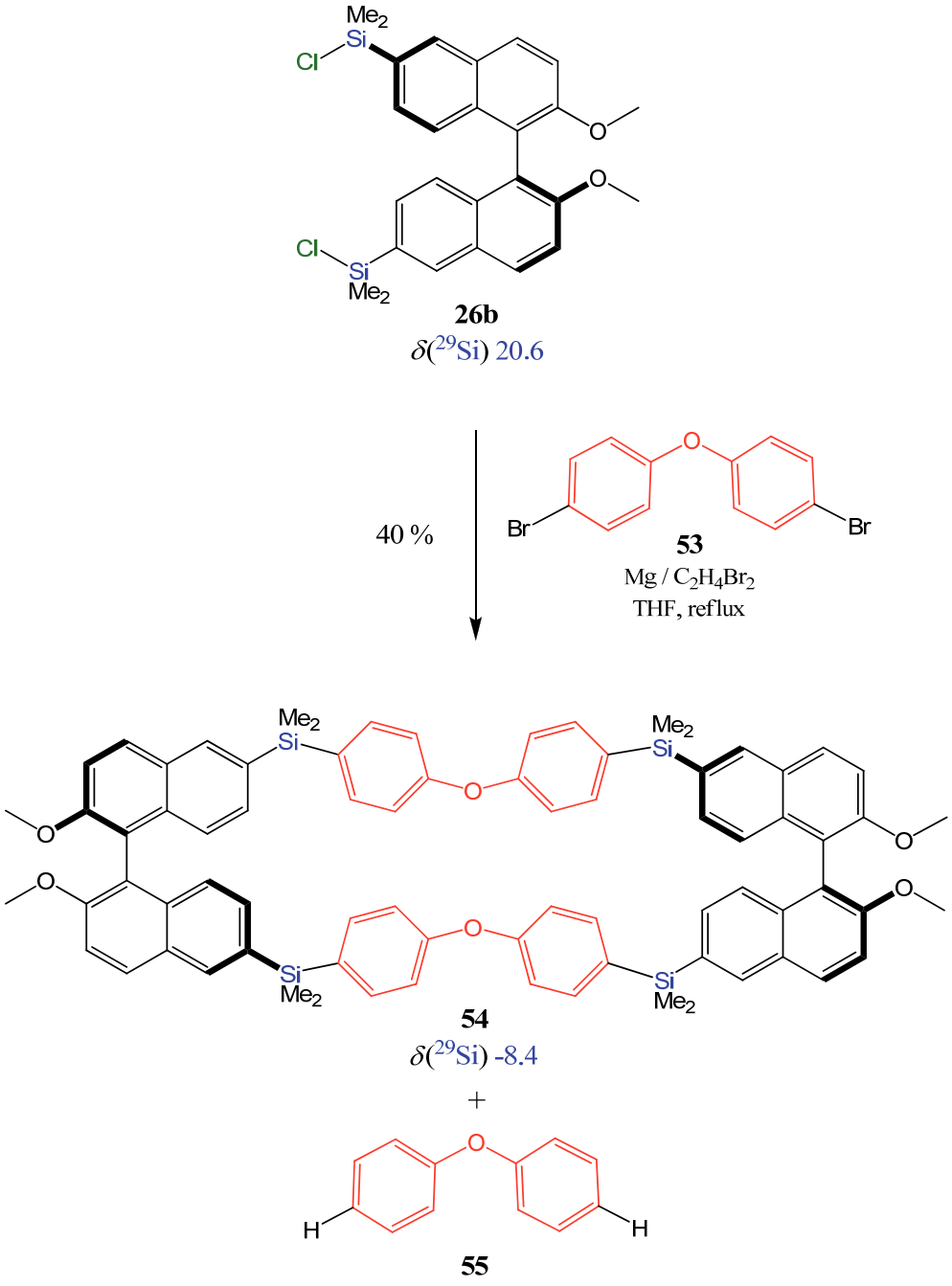
The obtained product from 3,3'-BINOL-chlorosilane **30b** consisted of a mixture of silanol [δ(^{29}Si) 6.4 ppm] and disiloxane [δ(^{29}Si) -2.5 ppm]. Given that these compounds are normally afforded from the hydrolysis of chlorosilanes, it could be assumed that no reaction between **30b** and the Grignard reagent occurred under the described conditions. Consequently, the byproducts were formed by quenching of the reaction with water.

In view of the failed results, repetition of the reaction was performed varying the temperature, reaction time, and the amount of reactants. Unluckily, none of these changes provided the attempted compounds.

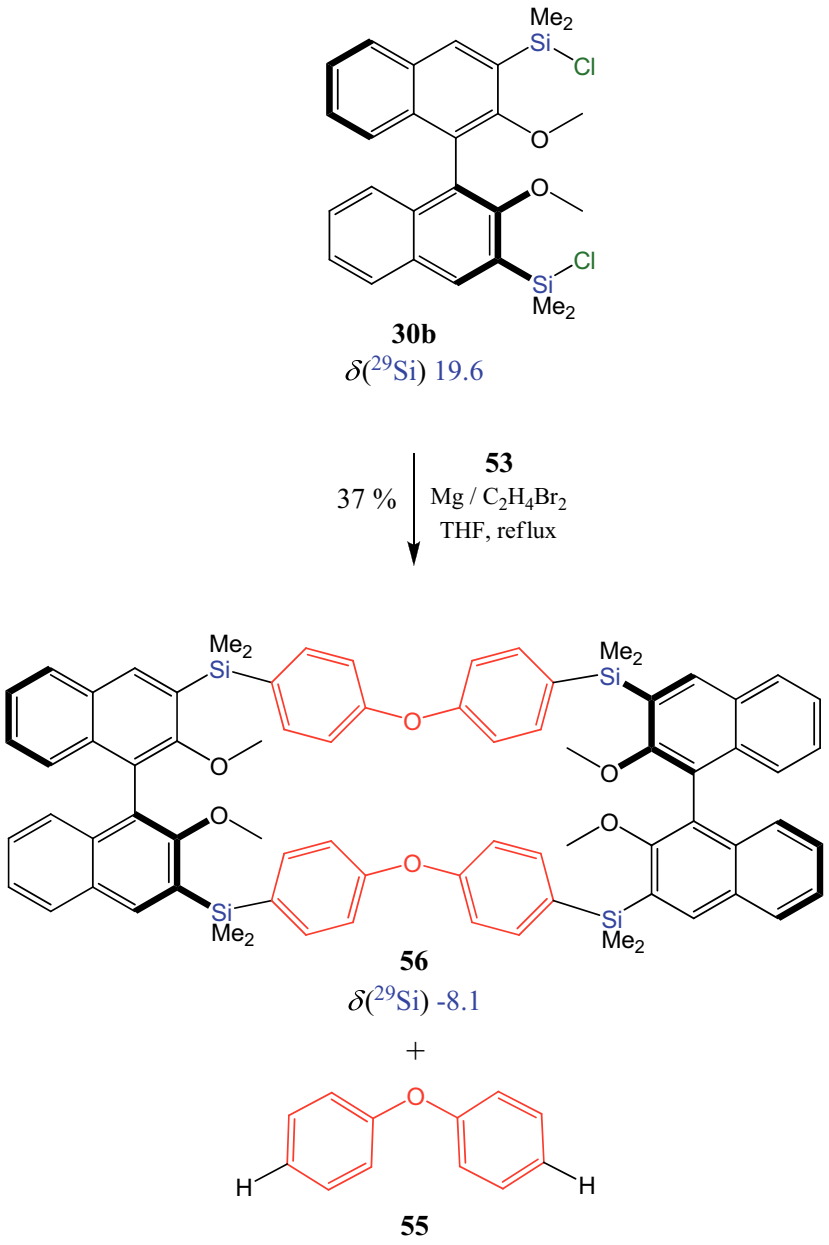
Considering that no macrocycles were afforded by the above discussed method, the reaction was explored using the lithiated derivative of **50** instead of the Grignard precursor. The procedure was essayed only with 3,3'-chlorosilane **30b**, as exemplified in Scheme 19. Unfortunately, following this route, only a disiloxane [δ(^{29}Si) -3.5 ppm] was achieved. Thus, no further assays were experimented with *p*-dibromobenzene.

As an alternative to brominated precursor **50**, *p*-dibromophenylether (**53**) was evaluated for the preparation of rigid macrocycles with an aromatic bridge. The Grignard reagent of **53** was generated as usual in a ratio of 2.6 equivalents. Then, the last was allowed to react during 72 h with compounds **26b** or **30b**, as Schemes 20 and 21 illustrate, in an effort to produce macrocycles **54** and **56**. After work up, yellow solids were obtained in both cases.

Evaluation by ^{29}Si-NMR of the crude products derived from 6,6'-BINOL precursor **26b** indicated the main formation of a Si-Ar bond suggested by a singlet at δ -8.4 ppm. Also, minimum amounts of silanol δ 7.8 ppm, and disiloxane δ -3.0 ppm were detected. Similarly, ^{29}Si NMR spectrum of the product obtained from precursor **30b** displayed a main resonance at δ -8.9 ppm and characteristic displacement for disiloxane at δ -2.3 ppm.



Scheme 20. Treatment of an aromatic Grignard reagent with chlorinated precursor **26b**.



Scheme 21. Treatment of an aromatic Grignard reagent with chlorinated precursor **30b**.

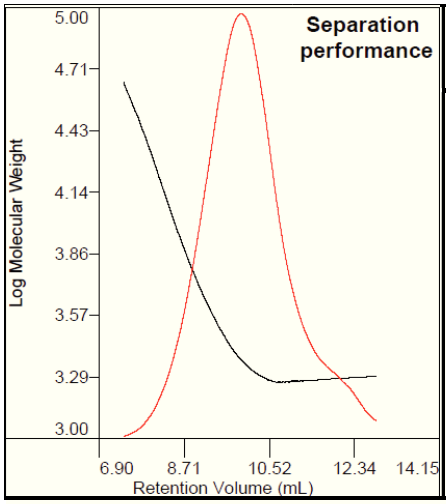
Column chromatography was employed to isolate desired macrocycles **54** and **56**. However, due to the high formation of diphenyl ether (**55**), by-product obtained from the hydrolysis of unreacted Grignard reagent, these compounds could not be elucidated in pure form. Even so, formation of **54** and **56** was verified by NMR analysis of the separated fractions. Additionally, mass spectra of the studied fractions displayed a molecular ion (*m/z* = 1193) coinciding with the proposed structures for **54** and **56**.

Moreover, formation of polymeric mixtures was demonstrated by GPC analysis of the resulting crude products. As shown in Table 13, polymers with a degree of polymerization of 6 and an average molecular weight $Mw = 3.3 \cdot 10^3$ g/mol were detected in the mixture derived from 6,6'-functionalyzed precursor **26b**. Likewise, polymers with average molecular weight $Mw = 3.1 \cdot 10^3$ g/mol and degree of polymerization of 5 were obtained from 3,3'-functionalyzed precursor **30b** (Table 14).

Modification of the reaction conditions were studied in order to improve the generation of the desired macrocycles. From the noted observations it is important to mention that when a solution of the precursor was added to the Grignard reagent, instead of the opposite, no reaction occurred. Also, when a Grignard reagent prepared in less than 8 h was used, major formation of silanol and disiloxane was afforded, indicating low concentration of Grignard compound. The concentration of the last was varied from 1.0 to 2.6 and 3.5 equivalents, obtaining the best results when 2.6 equivalents were used. Independently of the reaction time (8 h, 24 h, or 72 h), silanol, disiloxane, and diphenylether (product of hydrolysis of the Grignard reagent) were always obtained as by-products.

Despite the fact that it was not possible to isolate the target compounds and that the best conditions for major formation **54** and **56** were not established, it was proven that reaction of halogenated precursors **26b** and **30b** with an aromatic Grignard reagent did work. Hence, it could be suggested that by appropriate selection of reactants, **26b** and **30b** could afford interesting macrocycles.

Table 13. GPC analysis of the resulting product from Grignard reaction of 6,6'-precursor **26b**.

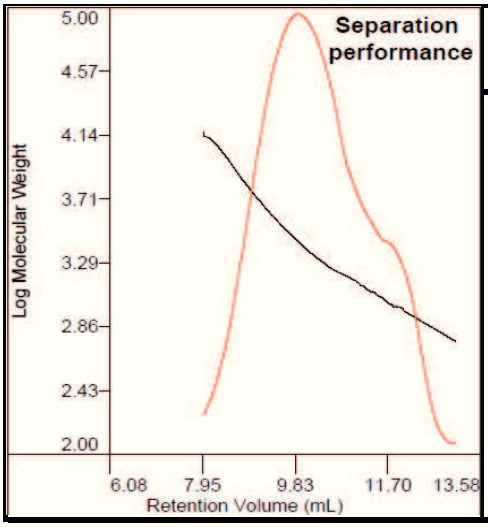


	Mw [g/mol]	Mn [g/mol]	Mw/Mn	Recovery [%]
	3336	2496	1.30	100.9
	3358	2484	1.40	101.8
	3347	2486	1.30	101.6
Average	**3347**	**2489**	**1.33**	**101.4**
RSD	8.98	5.25	0.05	0.39
RSD %	0.27	0.21	3.54	0.38

Monomer [g/mol] 597

Degree of Polymerization ***6***

Table 14. GPC analysis of the resulting product from Grignard reaction of 3,3'-precursor **30b**.



	Mw [g/mol]	Mn [g/mol]	Mw/Mn	Recovery [%]
	2981	1933	1.50	117.8
	3061	2028	1.50	104.7
	3132	2030	1.50	108.8
Average	**3058**	**1997**	**1.50**	**110.4**
RSD	61.7	45.3	0.00	6.00
RSD %	2.02	2.27	0.00	5.43

Monomer [g/mol] 597

Degree of Polymerization ***5***

3.3.4 Chiral Sila-Macrocycles from Tin Derivates

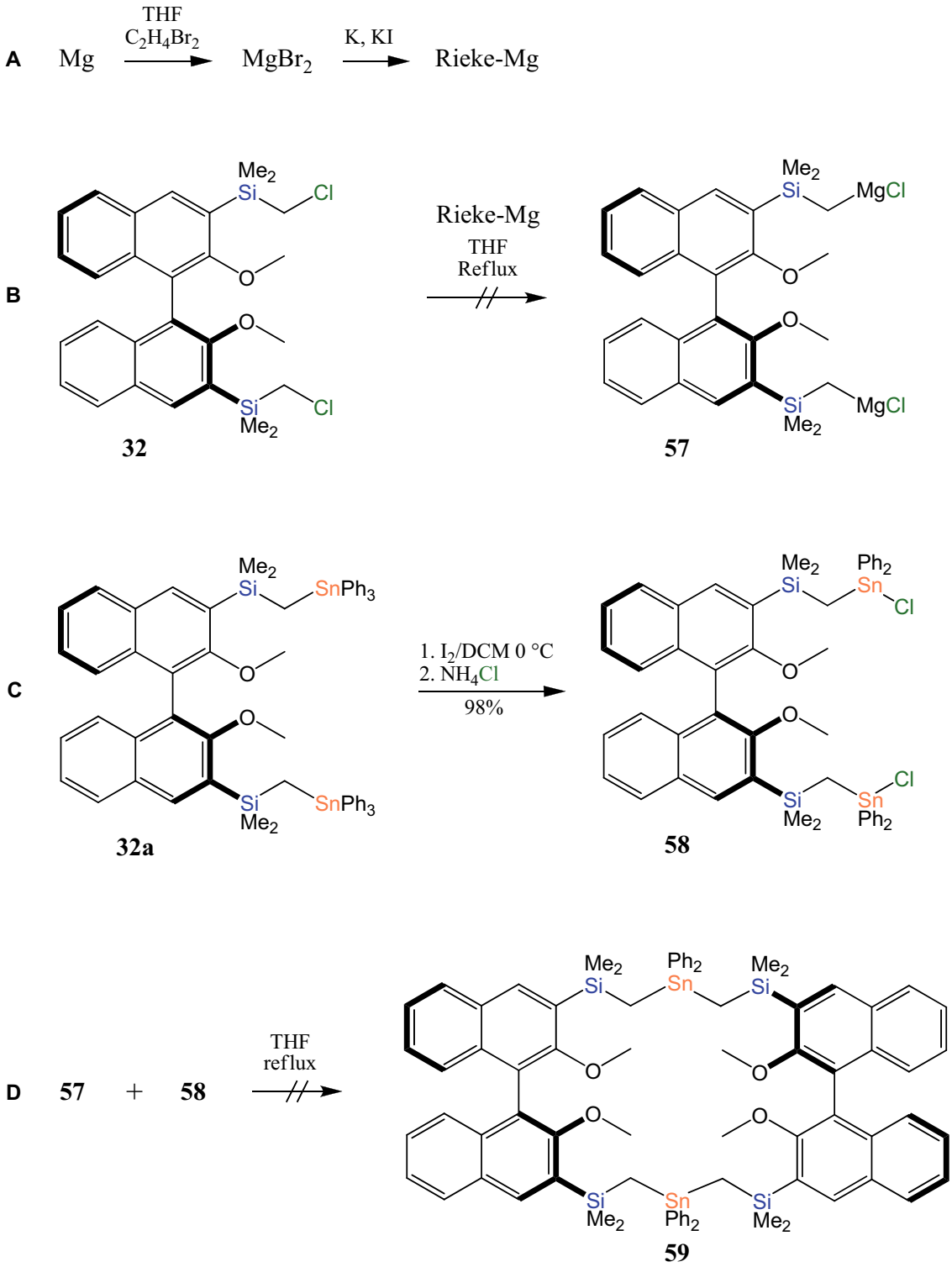
As a result of their widespread utility in industrial, agricultural and biological processes, organotin(IV) compounds have received much interest.[86] Especially organotin macrocycles are attractive for their potential applications in molecular recognition, storage, absorption, separation and catalysis.[87] The properties of these compounds will mostly depend on the nature of the organic substituents on the tin(IV) atom and their coordination modes.[86, 88] Therefore, it was planned to use chiral tin derivatives **28a** and **32a** (Scheme 8) for the synthesis of macrocycles**,** which given the background, could provide compounds with exceptional characteristics.

Incorporation of tin into a macrocyclic structure was essayed following the synthetic route depicted in Scheme 22. The basic idea was to prepare Grignard reagent **57** from precursor **32**, and halogenated Sn-precursor **58** from compound **32a**. Then, in order to produce tin-containing macrocycle **59**, compounds **57** and **58** would be reacted.

Previous attempts for generation of a Grignard reagent derived from chloromethyldimethyl-silane precursor **28** by standard procedures failed (Scheme 8). Thus, synthesis of **57** was explored following the method described by Rieke *et al.* for preparation of Grignard reagents from relatively unreactive halides.[89] Accordingly, compound **32** was reacted with highly reactive Mg, afforded as the reaction in Scheme 22A indicates. Compound **58** was achieved in almost quantitative yield as a colorless solid by treatment of **32a** with diiodine and ammonium chloride (Scheme 22C).

Subsequently, the resulted product of reaction shown in Scheme 22B diluted in THF was slowly added to a stirring solution of **58** in the same solvent. The mixture was allowed to react for 12 h at reflux temperature. After workup and solvent removal, a colorless solid was obtained.

NMR analysis of the afforded product showed no characteristic signals coinciding with the proposed structure. Since mostly starting material **58** was recovered, it was assumed that product **57** was not formed and consequently the reaction did not work. No additional tests for the synthesis of **59** following this procedure were effectuated.



Scheme 22. Attempt of preparation of a Sn-containing macrocycle.

3.4 Macrocycle Functionalization

Some of the above described macrocycles were subjected to different reactions for their functionalization in order to analyze their efficiency as building blocks for the construction of supramolecular structures.

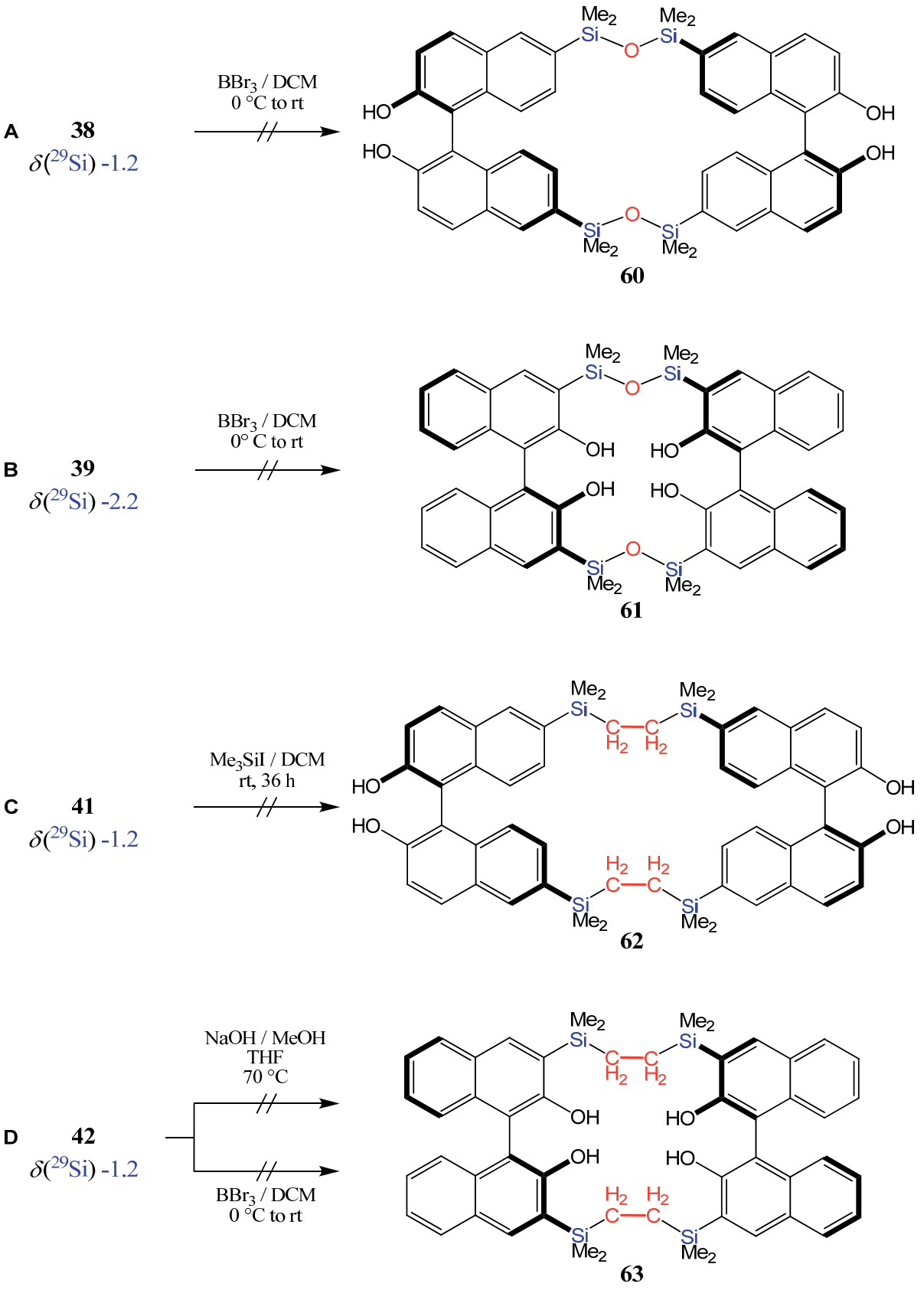
3.4.1 Demethylation

Considering that providing the prepared macrocycles with free hydroxyl groups could allow their use in further coordination reactions, deprotection of the hydroxyl functions of the BINOL moieties was aimed.

Some of the methods described in the literature for demethylation include the use of a strong Lewis acid like boron tribromide (BBr_3).[20] Cyclic siloxane **38** was subjected to reaction with this reagent for the preparation of **60** (Scheme 23A). NMR analysis of the obtained product indicated that not only reaction in the metoxy group occurred, but also in the siloxane function. ^{29}Si NMR spectrum of the sample consisted of a series of resonances characteristic for hydrosilane (δ -18.9 ppm), silanol (δ 7.7 ppm), polysiloxane (δ -0.8 ppm), and disiloxane (δ -2.3 ppm). The presence of these NMR shifts evidenced that BBr_3 also attacks the Si-O bond.

The same reaction procedure was applied to the 3,3'-derived cyclic siloxane **39** (Scheme 23B). Again, the presence of a minimum amount of desired product **61** together with a mixture of some other silane derivatives was observed in the ^{29}Si NMR spectrum of the crude product. Similar to the previous reaction, characteristic signals for hydrosilane (δ -18.9 ppm), polysiloxane (δ -0.8 ppm), and disiloxane precursor (δ -2.3 ppm) were detected. Variation of the reaction conditions and concentration of reactants made no difference in the obtained results.

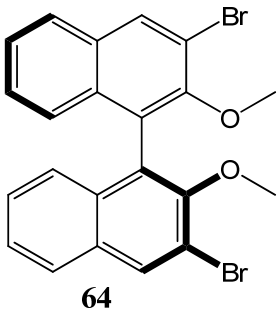
Deprotection of the hydroxyl functions of macrocycles **41** and **42**, connected by an aliphatic bridge, was also attempted. First, the reaction was explored using trimethyliodosilane (Me_3SiI) and macrocycle **41** in the conditions described in Scheme 23C. Unfortunately, NMR analysis of the obtained material showed no evidence for demethylation and only starting material was detected.



Scheme 23. Attempts of hydroxyl deprotection.

Then, macrocycle **42** was treated with NaOH solution in methanol at reflux temperature using THF as solvent to prepare compound **63** (Scheme 23D). Unluckily, only starting material was recovered after several hours of stirring. The reaction time was varied from 24 to 36 and 72 hours, observing no improvement in the results.

In another effort to synthesize **63**, compound **42** was subjected to reaction with BBr_3. As a result, the aryl-silicon bond was cleaved by the Lewis acid affording dibrominated compound **64** instead (Figure 20).



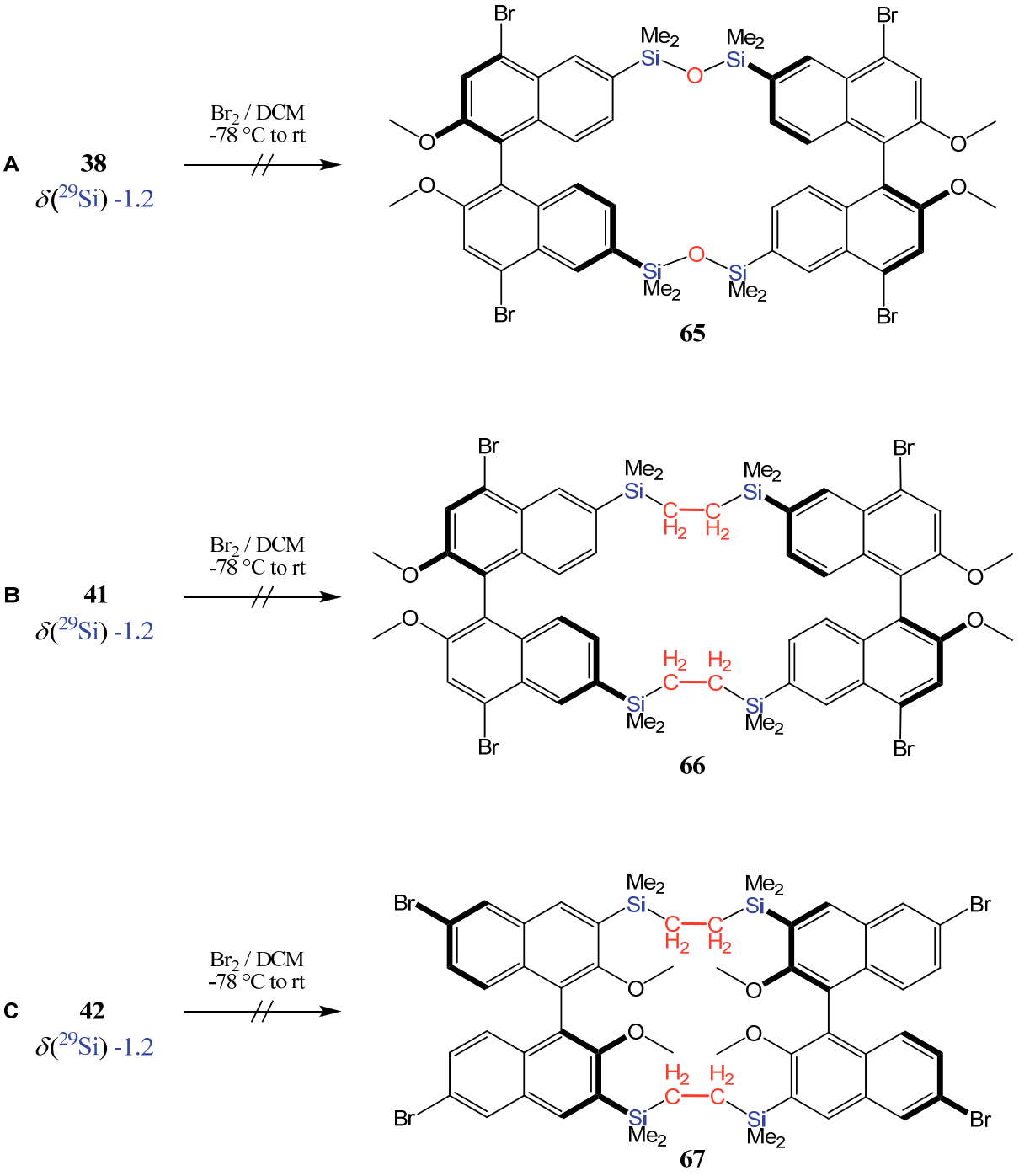
64

Figure 20. Undesired product obtained from treatment of macrocycle **42** with BBr_3.

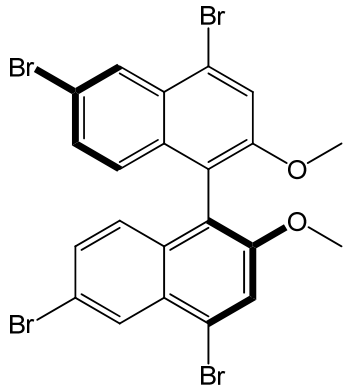
3.4.2 Bromination

Since a brominated macrocycle will offer the possibility of preparing supramolecular structures of higher order, functionalization of the available position in the BINOL framework of macrocycles **38**, **41**, and **42** was attempted.

It is described that when the positions 6 of BINOL are occupied, the next to be substituted are the positions 4. Thus, direct bromination of 6,6'-derived siloxane **38** and macrocycle **41** was explored (Scheme 24A and B). It was expected that bromination of these compounds would provide products **65** and **66**, as Scheme 24 illustrates. Unsuccessfully, besides bromination of the 4-positions, cleavage of the aryl-silicon bond also occurred forming tetrabrominated compound **68** shown in Figure 21.



Scheme 24. Attempts to brominate macrocycles **38**, **41**, and **42**.



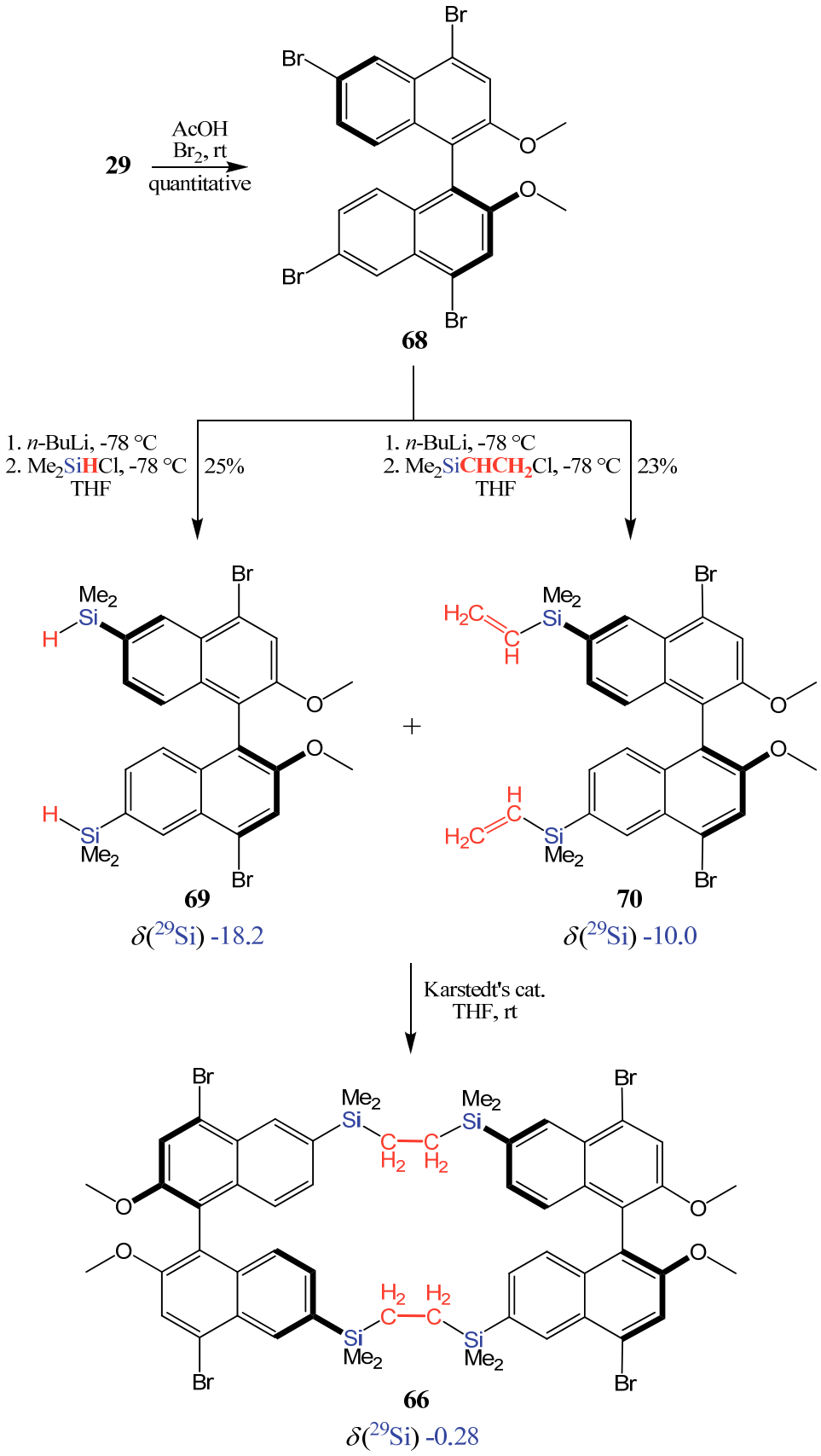
68

Figure 21. Undesired product obtained from the treatment of macrocycles **38** and **41** with Br_2.

Even though activation of the 6-positions of BINOL is afforded when the hydroxyl functions are unprotected, preparation of compound **67** was attempted by direct bromination of methoxy protected macrocycle **42** (Scheme 24C). As suspected, bromination of the 4-positions did not take place. Instead, aromatic electrophilic ipso substitution of the silane group occurred resulting in the formation of dihalogenated compound **64** (Figure 20).

In order to provide a brominated macrocycle, synthesis of 4,4',13,13'-tetrabrominated macrocycle **66** was explored following the route described in Scheme 25. For that, methoxy protected BINOL derivative **29** was brominated in acetic acid (AcOH) to obtain quantitatively tetrabrominated compound **68**. Lithiation of **68** using 2.5 equivalents of *n*-BuLi, followed by addition of 3.0 equivalents of the respective silane derivates afforded (*S*)-6,6'-bis(dimethylsilyl)-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**69**) and (*S*)-6,6'-bis(dimethylvinylsilyl)-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**70**) in 25% and 23% yield, respectively, after purification by column chromatography. These compounds were subjected to hydrosilylation reaction during 24 h using Karstedt's catalyst.

NMR analysis of the obtained product verified the formation of compound **66**, but remaining starting materials **69** and **70** were still detected, indicating that the reaction was not complete. No additional reactions were essayed varying the reaction conditions because the main interest of the trial was to observe if formation of a brominated macrocycle could be afforded in this way.

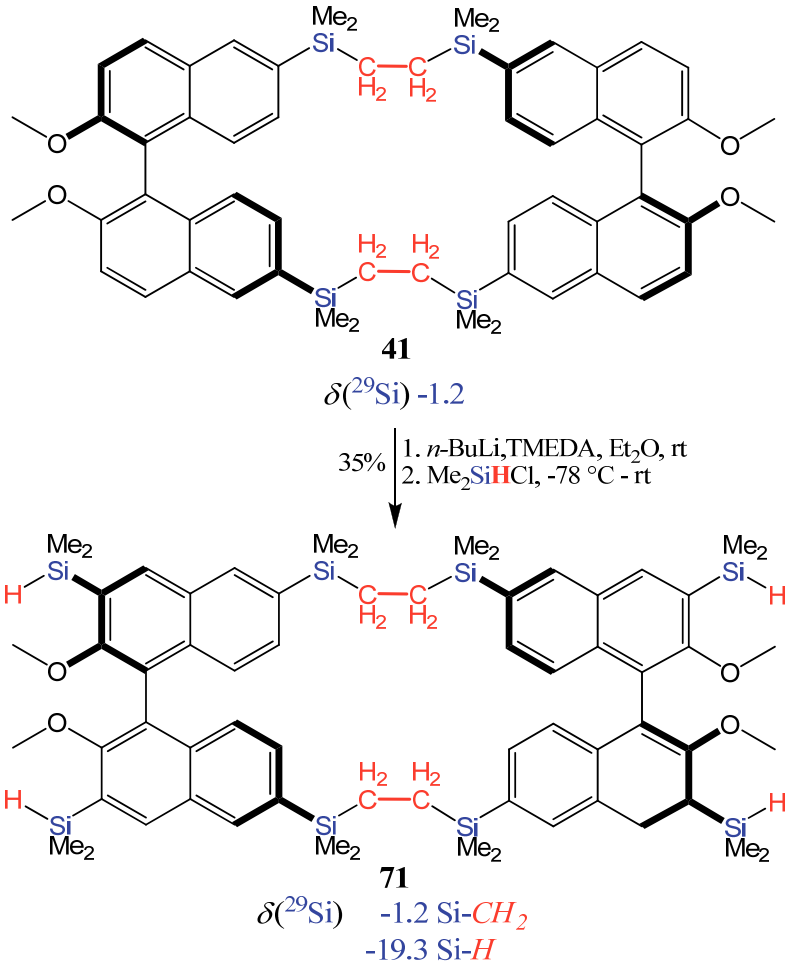


Scheme 25. Preparation of brominated macrocycle **66** by hydrosilylation.

Considering the results obtained for the preparation of macrocycles **41** and **42** by hydrosilylation, it is assumed that the use of equimolar amount of **69** and **70**, and a longer reaction time would lead to the complete conversion of the precursors into the desired functionalized macrocycle **66**. It could also be assumed that preparation of brominated cyclic siloxane **65** would be feasible by Pd catalyzed oxidation of brominated hydrosilane precursor **69** followed by condensation reaction.

3.4.3 Silylation

An advantageous characteristic of the methoxy-protected 6,6'-derived macrocycles here presented is the possibility of making use of ortho-lithiation for the incorporation of new substituents in the 3-positions. For instance, macrocycle **41** was subjected to this procedure in pursuit of preparing functionalized compound **71**, shown in Scheme 26.



Scheme 26. Silylation of macrocycle **41** to prepare functionalized macrocycle **71**.

Complexation of the methoxy protecting group of the precursor with a *n*-BuLi/TMEDA dimer activates the ortho positions of the BINOL framework allowing selective functionalization in these sites. Addition of Me_2SiHCl to the activated intermediate afforded product **71** in 35% yield, after purification by column chromatography. Complete characterization of the obtained yellow solid confirmed the proposed structure.

Further reactions of the hydrosilane group would produce some other functional compounds.

4 Conclusions

Functionalization of the 3-, 4-, and 6-positions of BINOL with convenient silane derivates affording chiral organosilanes has been described. Also, the use of these chiral organosilanes as building blocks for the preparation of chiral sila-macrocycles was successfully established.

Transmetallation of lithium organyls in the BINOL target positions provided hydrosilane, vinylsilane, and chloromethylsilane derivates in very good yields. These compounds were further converted into valuable functional precursors, such as chiral silanols and chlorosilanes achieved from the hydrosilanes. Even though, attempts to derivatize the vinylsilanes to produce tin-containing compounds by hydrostannylation failed, these compounds were successfully obtained from the chloromethylsilane precursors in good yields.

The synthesized organosilanes were effectively employed for the preparation of chiral macrocycles. Thus, cyclic siloxanes (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyltetrasiloxane (**38**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyltetrasiloxane (**39**) were obtained from hydrosilane, silanol, and chlorosilane derivates, affording the best yields when silanols were used as starting materials.

In addition, it was proven that hydrosilylation of chiral vinylsilanes by hydrosilanes in the presence of Karstedt's catalyst provides macrocycles (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyldiethylsilane (**41**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyldiethylsilane (**42**). Besides, it was determined that hydrosilylation with the hydrosilane building blocks could be extended to other precursors. For instance, a mixture of *p*- and *m*-divinylbenzene was hydrosilylated following the described conditions affording the respective macrocycle isomers.

Evaluation of chlorosilane derivates as starting materials showed that, with appropriate Grignard reagents, these compounds would produce attractive macrocycles with an aromatic bridge. That was evidenced by the obtention of macrocycles (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-bis(4-phenoxyphenyl)-octamethylsilane (**54**) and (*S,S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-bis(4-phenoxyphenyl)-octamethylsilane (**56**) using dibromophenyl ether as Grignard precursor. Unfortunately, these compounds could not be isolated purely.

To gain information about the reactivity of prepared macrocycles **38**, **39**, **41**, and **42**, these compounds were subjected to several functionalization procedures. Thus, different protocols for demethylation of the hydroxyl functions were tested. The methods essayed provided either undesired products or recovered starting materials. Therefore, it is strongly recommended to use alkyl protecting groups other than methyl to facilitate their subsequent removal.

Similarly, direct bromination of these macrocycles resulted in cleavage of the BINOL-Si bond. However, it was confirmed that functionalyzed brominated macrocycles could be afforded from brominated precursors (*S*)-6,6'-bis(dimethylsilyl-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**69**) and (*S*)-6,6'-bis(dimethylvinylsilyl-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**70**).

More importantly, it was verified that ortho-directed lithiation of 6,6'-functionalized macrocycle **41** facilitates the introduction of further useful groups in the 3,3'-positions of the BINOL framework. That indicates that the sila-BINOL macrocycles having unsubstituted 3-positions could be subsequently derivatized.

5 Experimental Section

5.1 Materials and General Procedures

Oxygen and water sensitive reactions were carried out in oven-dried glass material under inert-atmosphere (Argon grade 4.6) and Schlenk techniques with the use of high vacuum (until $1 \cdot 10^{-3}$ mbar).

5.1.1 Solvents

When indicated, solvents were dried by standard procedures.[90]

- Diethylether and tetrahydrofurane were left over potassium hydroxide and distilled from sodium and benzophenone before used.
- Tetrachloromethane and chloroform were left over calcium chloride and distilled from phosphorus pentaoxide before used.
- *N,N*-dimethylformamide was distilled from phosphorus pentaoxide before used.
- Tetramethylethylendiamine was left over potassium hydroxide and distilled from sodium before used.
- Dichloromethane, toluene, and *n*-hexane were directly collected from a Solvent Purification System SPS-800 from *M. Braun*.

5.1.2 Starting Materials

All chemicals were obtained from commercial sources and used without further purification. The listed reagents were prepared from commercially acquired (*S*)-2,2'-dihydroxy-1,1'-binaphthalene (**7**) following the methods described in the literature.

- (*S*)-6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene (**24**), (*S*)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (**33**), and (*S*)-4,4'-dibromo-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (**34**).[91]
- (*S*)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**25**), and (*S*)-2,2'-dimethoxy-1,1'-binaphthalene (**29**).[92]
- (*S*)-6,6',4,4'-tetrabromo-2,2'-dimethoxy-1,1'-binaphthalene (**69**).[93]

5.2 Analytical Methods

5.2.1 NMR Spectroscopy

NMR spectra (^{1}H-NMR, ^{13}C{^{1}H}-NMR, ^{29}Si{^{1}H}-NMR, ^{119}Sn{^{1}H}-NMR) were recorded on the spectrometers AVANCE DPX-200, AVANCE NB-360 from *Bruker*, or JNM-LA 400 FT from *Jeol*. All chemical shifts δ are reported in ppm, relative to the carbon (δ = 77.00 ppm) or proton (δ = 7.26 ppm) resonances of deuterated chloroform, and coupling constants ^{n}J are given in Hz. The multiplicities are designated with *s* (singulet), *d* (doublet), *t* (triplet), *q* (quartet) and *m* (multiplet). All measurements were carried out at room temperature.

5.2.2 IR Spectroscopy

Fourier Transform Infrared (FT IR) spectra were recorded on a Nexus 670 FT-IR spectrometer from *Nicolet*. The stretching bands are given in wave number (cm^{-1}) and designated with *s* (strong), *m* (medium) and *w* (weak).

5.2.3 Mass Spectrometry

Electronic Impact Mass (EI MS) spectra were measured on a MAT 711 spectrometer, Varian MAT. Electron Energy for EI was set to 70 eV or 80 eV. Electrospray Ionization-Time of Flight Mass (ESI-TOF MS) spectra were measured on an Agilent 6210 ESI-TOF, Agilent Technologies. Solvent flow rate was adjusted to 4 µL/min, Spray voltage set to 4 kV. Drying gas flow rate was set to 15 psi (1 bar). All other parameters were adjusted for maximum abundance of the relative $[M+H]^+$.

5.2.4 X-Ray Crystallography

Crystallographic data were recorded on a *STOE* IPDS 2T diffractometer at 150 K or on a Siemens P4-diffractometer at 173 K with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97[94] implemented in the program WinGX 2002.[95] Figures were created using the program DIAMOND.[96]

5.2.5 Polarimetry

All specific rotations were measured in THF with a Perkin-Elmer polarimeter model *243* at a wavelength λ = 589 nm and a temperature T = 20 °C. Specific rotations $[\alpha]_\lambda^T$ were calculated using the following equation:

$$[\alpha]_\lambda^T = \frac{\alpha}{c \cdot l}$$

Where,

- $[\alpha]_\lambda^T$ = specific rotation in $\left[\frac{deg \cdot cm^2}{g}\right]$ at a temperature T and at a wavelength λ.
- α = observed rotation in degrees.
- c = concentration in g / 100 ml
- l = cell path length in dm.

5.2.6 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was effectuated in a triple detection Size-exclusion chromatography system (SEC^3,Viscotek, USA) consisting of a online two channel degasser, a high pressure pump, an autosampler (all parts integrated in the GPCmax, Viscoteck, USA), a 0.5 µm stainless steel in-line filter with a nylon membrane, one connected precolumn (Phenogel 7.8x50 mm), a temperature controlled triple detector array (TDAmax 305, Viscotek, USA) with a differential refractometer at λ = 660 nm (RID 3580), a right angle (90°) light scattering detector (RALS) and a low angle (7°) light scattering detector (LALS 270-03) with a semiconductor laser diode at λ = 670 nm and a four capillary, differential Wheatstone bridge viscometer. The SEC conditions were as follows: a degassed THF solution was used as eluent, the sample concentration was 10-15 mg/ml and samples were dissolved for 24 h under shaking, injection volumina varied from 10 to 100 µL, flow rate was maintained at 0.7 ml/min, and the column and detector temperature were kept at 30 °C. A polystyrene standard (MW = 19,900, [h] = 0.1386 dL/g, MW/MN = 1.02) was used to normalize the viscometer and the light scattering detectors (Agilent, England). Data acquisition and processing were carried out by use of OmniSEC 4.1 software (Viscotek Corporation,USA). During molecular weight calculation a dn/dc of 0.184 was used for the samples.

5.2.7 Column Chromatography

For column chromatographic separations, silica gel 60 (230–400 mesh, 40-63 μm) was purchased from Merck.

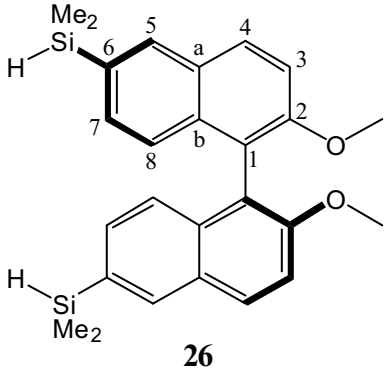
5.3 Synthesis of Silyl-Functionalized BINOLs

5.3.1 General Procedure for the Silylation of 6,6'-Positions of BINOL

A solution of (*S*)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**25**)[92] (2.00 g, 4.24 mmol) in dried THF (100 ml) was cooled to -78 ºC. At this temperature, *n*-BuLi in Hx 2.5 M (5.00 ml, 12.6 mmol) was slowly added. The reaction mixture was stirred maintaining the temperature at -78 ºC for 1 h. After this time, a suitable chlorodimethylsilane derivative (25.2 mmol) was added dropwise in a period of 15 min. The mixture was allowed to slowly warm to rt overnight. The reaction was stopped by addition of water and stirred for additional 4 h. The organic layer was separated, washed with water, and dried over Na_2SO_4. Complete removal of volatiles and purification by flash chromatography (Hx-EtOAc 98:2) afforded the desired products.

(*S*)-6,6'-bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (26).

Use of $ClMe_2SiH$ (2.80 ml, 25.2 mmol) in the general procedure gave 1.53 g (3.55 mmol) of compound **26** as a colorless oil (Yield: 84 %).



26

$C_{26}H_{30}O_2Si_2$

$[\alpha]_{\lambda}^{T}$ = +32.6 (c = 0.28, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.11 (s, 2H; H$_5$), 8.02 (d, ^{3}J(H,H)=9 Hz, 2H; H$_3$), 7.48 (d, ^{3}J(H,H)=9 Hz, 2H; H$_4$), 7.37 (d, ^{3}J(H,H)=8 Hz, 2H; H$_7$), 7.14 (d, ^{3}J(H,H)=8 Hz, 2H; H$_8$), 4.55 (m, 2H; Si*H*(CH$_3$)$_2$), 3.76 (s, 6H; O*CH$_3$*), 0.37 ppm (d, ^{3}J(H,H)=4 Hz, 12H; SiH(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.4 (s, C$_2$), 134.9 (s, C$_5$), 134.4 (s, C$_6$), 131.6 (s, C$_a$), 130.7 (s, C$_7$), 129.6 (s, C$_4$), 128.7 (s, C$_b$), 124.4 (s, C$_8$), 119.2 (s, C$_1$), 114.0 (s, C$_3$), 56.7 (s, O*CH$_3$*), -3.70 ppm (s, SiH(*CH$_3$*)$_2$).

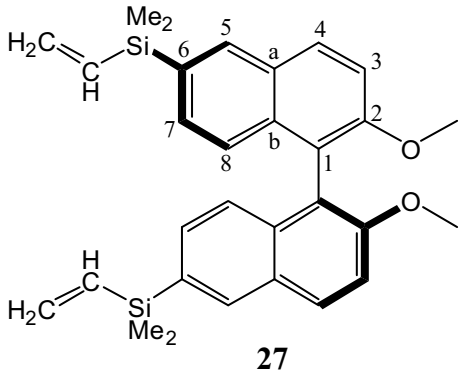
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -16.6 ppm (s).

FT IR: $\tilde{\nu}$ = 1061 (m$_{srp}$, (Si-BINOL)), 1258 (s$_{srp}$, (Si-CH$_3$)), 2121 cm^{-1} (m$_b$, (Si-H)).

EI MS (80 eV, 80 ºC): *m/z* = 430.2 [M]$^+$, calculated for **26** (C$_{26}$H$_{30}$O$_2$Si$_2$) = 430.2 g/mol.

(*S*)-6,6'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (27).

Use of ClMe$_2$SiCHCH$_2$ (3.50 ml, 25.2 mmol) in the general procedure gave 1.25 g (2.59 mmol) of compound **27** as colorless solid (Yield: 61 %).



27

C$_{30}$H$_{34}$O$_2$Si$_2$

$[\alpha]_{\lambda}^{T}$ = +43.4 (c = 0.13, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.10 (s, 2H; H$_5$), 8.02 (d, ^{3}J(H,H)=9 Hz, 2H; H$_3$), 7.48 (d, ^{3}J(H,H)=9 Hz, 2H; H$_4$), 7.38 (dd, ^{4}J (H,H)=1 Hz, ^{3}J(H,H)=8 Hz, 2H; H$_7$), 7.15 (d, ^{3}J(H,H)=8 Hz, 2H; H$_8$), 6.38 (dd, ^{3}J(H,H)=20 Hz, ^{3}J(H,H)=15 Hz, 2H; Si*CH*CH$_2$), 6.11 (dd, ^{3}J(H,H)=15 Hz, ^{2}J(H,H)=4 Hz, 2H; SiCH*CH$_2$*), 5.84 (dd, ^{3}J(H,H)=20 Hz, ^{2}J(H,H)=4 Hz, 2H; SiCH*CH$_2$*), 3.79 (s, 6H; O*CH$_3$*), 0.40 ppm (s, ^{3}J(H,H)=4 Hz, 12H; Si(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.4 (s, C$_2$), 138.1 (s, *CH*CH$_2$), 134.6 (s, C$_5$), 134.3 (s, C$_6$), 132.7 (s, CH*CH$_2$*), 132.6 (s, C$_a$), 130.6 (s, C$_7$), 129.6 (s, C$_b$), 128.7 (s, C$_4$), 124.3 (s, C$_8$), 119.3 (s, C$_1$), 114.0 (s, C$_3$), 56.8 (s, O*CH$_3$*), -2.83 ppm (s, Si(*CH$_3$*)$_2$).

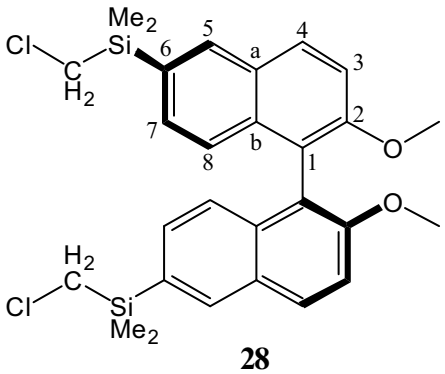
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -10.5 ppm (s).

FT IR: $\tilde{\nu}$ = 1057 (m$_{srp}$, (Si-BINOL)), 1247 (s$_{srp}$, (Si-CH$_3$)), 1613 cm^{-1} (m$_{srp}$, (Si-CHCH$_2$)).

ESI MS (250 eV): *m/z* = 505.2 [M+Na]$^{+}$, calculated for **27** (C$_{30}$H$_{34}$O$_2$Si$_2$+Na) = 505.7 g/mol.

(*S*)-6,6'-bis(dimethylchloromethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (28).

Use of ClMe$_2$SiCH$_2$Cl (3.40 ml, 25.2 mmol) in the general procedure gave 1.00 g (1.90 mmol) of compound **28** as colorless oil (Yield: 45 %).



28

C$_{28}$H$_{32}$Cl$_2$O$_2$Si$_2$

$[\alpha]_{\lambda}^{T}$ = +100.0 (c = 0.11, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.11 (s, 2H; H$_5$), 8.02 (d, ^{3}J(H,H)=9 Hz, 2H; H$_3$), 7.49 (d, ^{3}J(H,H)=9 Hz, 2H; H$_4$), 7.35 (dd, ^{4}J (H,H)=1 Hz, ^{3}J(H,H)=8 Hz, 2H; H$_7$), 7.14 (d, ^{3}J(H,H)=8 Hz, 2H; H$_8$), 3.78 (s, 6H; O$\underline{CH_3}$), 3.02 (s, 4H; Si$\underline{CH_2}$Cl), 0.50 (s, 6H; Si($\underline{CH_3}$)$_2$), 0.49 ppm (s, 6H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.6 (s, C$_2$), 134.8 (s, C$_5$), 134.6 (s, C$_6$), 130.3 (s, C$_7$), 130.1 (s, C$_4$), 129.8 (s, C$_a$), 128.6 (s, C$_b$), 124.5 (s, C$_8$), 119.1 (s, C$_1$), 114.1 (s, C$_3$), 56.7 (s, O$\underline{CH_3}$), 30.5 (s, $\underline{CH_2}$Cl), -4.48 ppm (s, Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -2.74 ppm (s).

FT IR: $\tilde{\nu}$ = 1061 (m$_{srp}$, (Si-BINOL)), 1249 (s$_{srp}$, (Si-CH$_3$)).

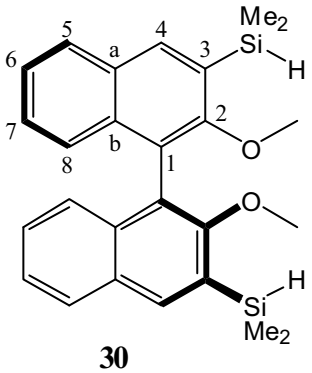
EI MS (80 eV, 140 ºC): *m/z* = 525.9 [M]$^{+}$, calculated for **28** (C$_{28}$H$_{32}$Cl$_2$O$_2$Si$_2$) = 526.1 g/mol.

5.3.2 General Procedure for the Silylation of 3,3'-Positions of BINOL

To a solution of TMEDA (2.90 ml, 19.2 mmol) in Et$_2$O (250 ml) was added at rt under argon pressure 2.5 M *n*-BuLi in Hx (7.70 ml, 19.2 mmol). The solution was stirred for 15 min and (*S*)-2,2'-dimethoxy-1,1'-binaphthalene (**29**)[92] (2.00 g, 6.36 mmol) was added in one portion. The reaction mixture was stirred at rt for 3 h. The resulting light brown suspension was cooled to -78 ºC and a suitable chlorodimethylsilane derivative (38.4 mmol) was added over a period of 15 min. The mixture was allowed to warm to rt overnight. The reaction was quenched with water and stirred for additional 4 h. The resulting solution was diluted with Et$_2$O and water. The organic layer was washed several times with water and dried over Na$_2$SO$_4$. Complete removal of volatiles and purification by flash chromatography (Hx-EtOAc 98:2) afforded the desired products.

(*S*)-3,3'-bis(dimethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (30).

Use of $ClMe_2SiH$ (4.26 ml, 38.4 mmol) as silane derivative in the general procedure gave 2.63 g (6.12 mmol) of compound **30** as colorless oil (Yield: 96 %).



30

$C_{26}H_{30}O_2Si_2$

$[\alpha]_{\lambda}^{20}$ = +94.2 (c = 0.27, THF)

^{1}H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.01 (s, 2H; H_4), 7.77 (d, ^3J(H,H)=8 Hz, 2H; H_5), 7.25 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H_6), 7.14 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H_7), 7.07 (d, ^3J(H,H)=8 Hz, 2H; H_8), 4.52 (m, 2H; Si*H*$(CH_3)_2$), 3.21 (s, 6H; O*CH*$_3$), 0.35 ppm (d, ^3J(H,H)=7 Hz, 12H; SiH(*CH*$_3$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 160.6 (s, C_2), 137.3 (s, C_4), 135.8 (s, C_b), 131.8 (s, C_3), 130.2 (s, C_a), 128.0 (s, C_5), 126.8 (s, C_7), 125.7 (s, C_8), 124.4 (s, C_6), 122.0 (s, C_1), 60.3 (s, O*CH*$_3$), -3.35 (s, SiH(*CH*$_3$)$_2$), -3.44 ppm (s, SiH(*CH*$_3$)$_2$).

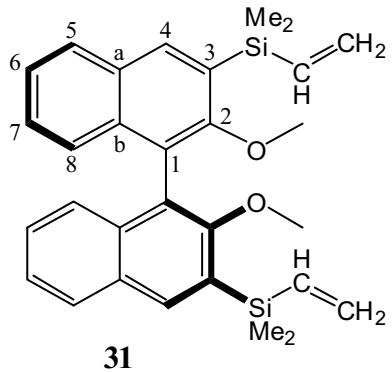
^{29}Si{^{1}H}-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -18.8 ppm (s).

FT IR: $\tilde{\nu}$ =1060 (m_{srp}, (Si-BINOL)), 1223 and 1247 (m_{srp}, (Si-CH_3)), 2118 cm^{-1} (m_b, (Si-H)).

EI MS (80 eV, 50 ºC): *m/z* = 430.0 $[M]^+$, calculated for **30** ($C_{26}H_{30}O_2Si_2$) = 430.2 g/mol.

(*S*)-3,3'-bis(dimethylvinylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (31).

Use of $ClMe_2SiCHCH_2$ (5.80 ml, 38.4 mmol) as silane derivative in the general procedure gave 2.17 g (4.51 mmol) of compound **31** as colorless oil (Yield: 71 %).



31

$C_{30}H_{34}O_2Si_2$

$[\alpha]_{\lambda}^{20}$ = +75.4 (c = 0.14, THF)

^{1}H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.10 (s, 2H; H_4), 7.90 (d, ^3J(H,H)=8 Hz, 2H; H_5), 7.38 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H_6), 7.26 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H_7), 7.24 (d, ^3J(H,H)=8 Hz, 2H; H_8), 6.52 (dd, ^3J(H,H)=20 Hz, ^3J(H,H)=15 Hz, 2H; Si*CH*CH_2), 6.13 (dd, 2H; SiCH*CH$_2$*), 5.87 (dd, 2H; SiCH*CH$_2$*), 3.23 (s, 6H; O*CH$_3$*), 0.51 (s, 6H; Si(*CH$_3$*)$_2$), 0.52 ppm (s, 6H; Si(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 161.0 (s, C_2), 138.9 (s, *CH*CH_2), 137.4 (s, C_4), 135.9 (s, C_b), 132.6 (s, C_3), 132.1 (s, CH*CH$_2$*), 130.1 (s, C_a), 128.1 (s, C_5), 126.7 (s, C_7), 125.7 (s, C_8), 124.2 (s, C_6), 121.2 (s, C_1), 60.0 (s, O*CH$_3$*), -2.24 (s, Si(*CH$_3$*)$_2$), -2.28 ppm (s, Si(*CH$_3$*)$_2$).

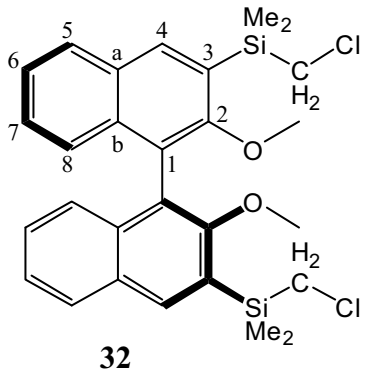
^{29}Si{^{1}H}-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -11.7 ppm (s).

FT IR: $\tilde{\nu}$ = 1060 (m_{srp}, (Si-BINOL)), 1223 and 1245 (m_{srp}, (Si-CH_3)), 1574 cm^{-1} (m_{srp}, (Si-$CHCH_2$)).

ESI MS (250 eV): *m/z* = 505.2 $[M+Na]^+$, calculated for **31** ($C_{30}H_{34}O_2Si_2$+Na) = 505.2 g/mol.

(*S*)-3,3'-bis(dimethylchloromethylsilyl)-2,2'-dimethoxy-1,1'-binaphthalene (32).

Use of $ClMe_2SiCH_2Cl$ (5.10 ml, 38.4 mmol) as silane derivative in the general procedure gave 2.03 g (3.81 mmol) of compound **32** as colorless oil (Yield: 60 %).



32

$C_{28}H_{32}Cl_2O_2Si_2$

$[\alpha]_{\lambda}^{20}$ = +113.1 (c = 0.17, THF)

^{1}H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.05 (s, 2H; H_4), 7.87 (d, ^3J(H,H)=8 Hz, 2H; H_5), 7.37 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H_6), 7.26 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H_7), 7.20 (d, ^3J(H,H)=8 Hz, 2H; H_8), 3.14 (d, ^2J(H,H)=1 Hz, 4H; $\underline{CH_2}$Cl), 3.13 (s, 6H; O$\underline{CH_3}$), 0.52 (s, 6H; Si($\underline{CH_3}$)$_2$), 0.49 ppm (s, 6H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 160.9 (s, C_2), 137.7 (s, C_4), 136.2 (s, C_b), 130.3 (s, C_3), 130.1 (s, C_a), 128.4 (s, C_5), 127.4 (s, C_7), 125.8 (s, C_8), 124.6 (s, C_6), 120.8 (s, C_1), 59.9 (s, O$\underline{CH_3}$), 31.0 (s, $\underline{CH_2}$Cl), -3.32 (s, Si($\underline{CH_3}$)$_2$), -3.61 ppm (s, Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -3.08 ppm (s).

FT IR: $\tilde{\nu}$ = 1060 (m_{srp}, (Si-BINOL)), 1224 and 1253 (m_{srp}, (Si-CH_3)), 1574 cm^{-1} (m_{srp}, (Si-CH_2Cl)).

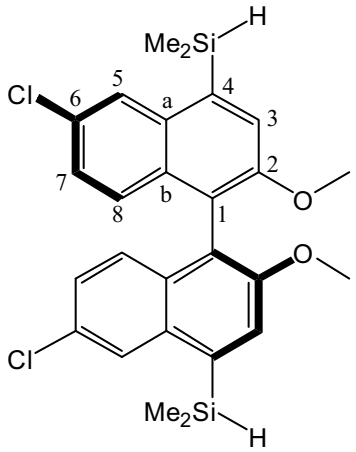
ESI MS (220 eV): *m/z* = 549.1 $[M+Na]^+$, calculated for **32** ($C_{28}H_{32}Cl_2O_2Si_2$+Na) = 550.6 g/mol.

5.3.3 General Procedure for the Silylation of the 4,4'-Positions of BINOL

To a solution of (*S*)-4,4'-dibromo-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (**34**)[91] (2.00 g, 3.70 mmol) in 100 ml of dried THF at -78 ºC was added 2.5 M *n*-BuLi in Hx (4.43 ml, 11.1 mmol) dropwise. After the addition, the reaction mixture was allowed to stir at -78 ºC for additional 4 h. Then, a suitable chlorodimethylsilane derivative (14.8 mmol) was added dropwise over a period of 15 min. The reaction mixture was allowed to slowly warm to rt and stirred for 12 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with water and dried over Na_2SO_4. The organic volatiles were removed under reduced pressure to give a residue which was further purified by flash chromatography (Hx-EtOAc 98:2).

(*S*)-4,4'-bis(dimethylsilyl)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (35)

Use of $ClMe_2SiH$ (1.64 ml, 14.8 mmol) in the general procedure gave 1.10 g (2.21 mmol) of product **35** as colorless oil (Yield: 60%).



35

$C_{26}H_{28}Cl_2O_2Si_2$

$[\alpha]_{\lambda}^{20}$ = -54.3 (c = 0.18, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.09 (d, ^{4}J(H,H)=2 Hz, 2H; H$_5$), 7.69 (s, 2H, H$_3$), 7.17 (dd, ^{4}J(H,H)=2 Hz, ^{3}J(H,H)=9 Hz, 2H; H$_7$), 7.05 (d, ^{3}J(H,H)=9 Hz, 2H; H$_8$), 4.94 (m, 2H; Si*H*(CH$_3$)$_2$), 3.79 (s, 6H; O*CH$_3$*), 0.61 ppm (d, ^{3}J(H,H)=4 Hz, 12H; SiH(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 154.3 (s, C$_2$), 137.5 (s, C$_a$), 133.6 (s, C$_4$), 132.5 (s, C$_6$), 129.7 (s, C$_b$), 127.8 (s, C$_7$), 127.1 (s, C$_8$), 126.7 (s, C$_5$), 122.8 (s, C$_3$), 121.2 (s, C$_1$), 57.0 (s, O*CH$_3$*), -2.90 (s, SiH(*CH$_3$*)$_2$), -2.94 ppm (s, SiH(*CH$_3$*)$_2$).

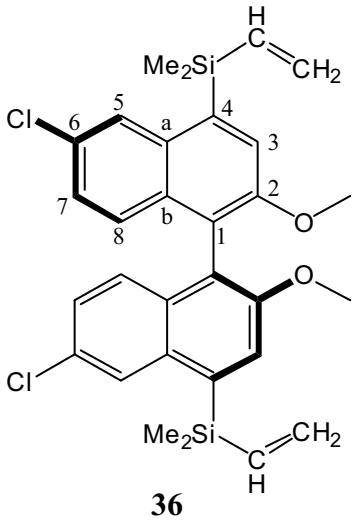
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -17.9 (s).

FT IR: $\tilde{\nu}$ = 1067 (m$_{srp}$, (Si-BINOL)), 1257 (s$_{srp}$, (Si-CH$_3$)), 2119 cm^{-1} (m$_b$, (Si-H)).

EI MS (80 eV, 140 ºC): *m/z* = 498.0 [M]$^+$, calculated for **35** (C$_{26}$H$_{28}$Cl$_2$O$_2$Si$_2$) = 498.1 g/mol.

(*S*)-4,4'-bis(dimethylvinylsilyl)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (36).

Use of ClMe$_2$SiCHCH$_2$ (2.04 ml, 14.8 mmol) in the general procedure gave 0.918 g (1.66 mmol) of product **36** as colorless solid (Yield: 45%).



36

C$_{30}$H$_{32}$Cl$_2$O$_2$Si$_2$

$[\alpha]_{\lambda}^{20}$ = -37.0 (c = 0.22, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.15 (s, 2H, H$_5$), 7.72 (s, 2H, H$_3$), 7.18 (d, ^{3}J(H,H)=2 Hz, 2H; H$_8$), 7.08 (d, ^{3}J(H,H)=9 Hz, 2H; H$_7$), 6.59 (dd, ^{3}J(H,H)=20 Hz, ^{3}J(H,H)=15 Hz, 2H; Si*CH*CH$_2$), 6.24 (dd, ^{3}J(H,H)=15 Hz, ^{2}J(H,H)=4 Hz, 2H; SiCH*CH$_2$*), 6.00 (dd, ^{3}J(H,H)=20 Hz, ^{2}J(H,H)=4 Hz, 2H; SiCH*CH$_2$*), 3.79 (s, 6H; O*CH$_3$*), 0.67 ppm (s, 12H; SiH(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 154.0 (s, C$_2$), 138.1 (s, *CH*CH$_2$), 137.9 (s, C$_a$), 133.6 (s, CH*CH$_2$*), 133.4 (s, C$_4$), 132.4 (s, C$_6$), 129.1 (s, C$_b$), 127.6 (s, C$_7$), 127.1 (s, C$_8$), 126.6 (s, C$_5$), 122.9 (s, C$_3$), 121.0 (s, C$_1$), 56.7 (s, O*CH$_3$*), -1.57 ppm (s, Si(*CH$_3$*)$_2$).

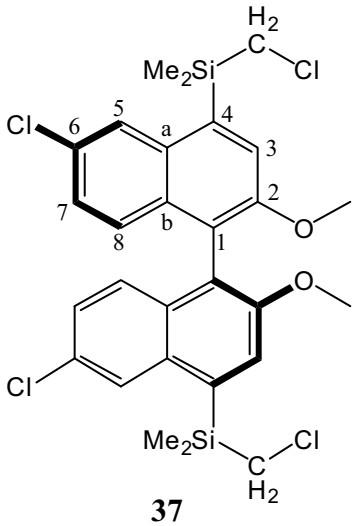
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -9.73 (s).

FT IR: $\tilde{\nu}$ = 1069 (m$_{srp}$, (Si-BINOL)), 1226 and 1258 (s$_{srp}$, (Si-CH$_3$)), 1564 cm^{-1} (m$_{srp}$, (Si-CHCH$_2$)).

ESI MS (200 eV): *m/z* = 573.1 [M+Na]$^{+}$, calculated for **36** (C$_{30}$H$_{32}$Cl$_2$O$_2$Si$_2$+Na) = 573.1 g/mol.

(*S*)-4,4'-bis(dimethylchloromethylsilyl)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (37).

Use of ClMe$_2$SiCH$_2$Cl (1.95 ml, 14.8 mmol) in the general procedure gave 1.00 g (1.68 mmol) of product **37** as colorless solid (Yield: 45%).



37

C$_{28}$H$_{30}$Cl$_4$O$_2$Si$_2$

$[\alpha]_{\lambda}^{20}$ = -46.2 (c = 0.17, THF)

^{1}H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.02 (d, ^{4}J(H,H)=2 Hz, 2H; H_5), 7.73 (s, 2H, H_3), 7.19 (dd, ^{4}J(H,H)=2 Hz, ^{3}J(H,H)=9 Hz, 2H; H_7), 7.08 (d, ^{3}J(H,H)=9 Hz, 2H; H_8), 3.78 (s, 6H; O$\underline{CH_3}$), 3.30 (s, 4H; Si$\underline{CH_2}$Cl), 0.74 ppm (s, 12H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 153.9 (s, C_2), 135.7 (s, C_a), 133.3 (s, C_4), 132.3 (s, C_6), 129.6 (s, C_b), 127.8 (s, C_7), 126.9 (s, C_8), 126.4 (s, C_5), 122.9 (s, C_3), 121.3 (s, C_1), 56.7 (s, OCH_3), 30.5 (s, Si$\underline{CH_2}$Cl), -2.68 ppm (s, Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -1.44 (s).

FT IR: $\tilde{\nu}$ = 1067 (m_{srp}, (Si-BINOL)), 1226 and 1251 (s_{srp}, (Si-CH_3)).

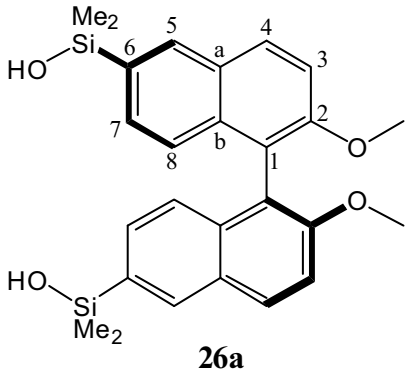
EI MS (80 eV, 80 ºC): *m/z* = 595.7 $[M]^+$, calculated for **37** ($C_{28}H_{30}Cl_4O_2Si_2$) = 594.0 g/mol.

5.3.4 General Procedure for the Synthesis of Silanols

To an ice-cooled suspension of Pearlman's catalyst [$Pd(OH)_2$/C] (12.0 mg) in THF (29.0 ml) and water (3.00 ml) was slowly added a solution of the corresponding hydrosilane precursor (5.80 mmol) in THF (9 ml). After the evolution of hydrogen ceased, the reaction mixture was stirred at rt for 1 h. The catalyst was filtered off and the solvent removed at 30 °C under reduced pressure. Diethylether (29.0 ml) was added to the remaining residue. Most of the aqueous layer was removed with a pipet and the organic layer was dried over Na_2SO_4. Removal of volatiles under reduced pressure afforded the desired products.

(*S*)-6,6'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene (26a).

Use of 2.50 g (5.80 mmol) of **26** in the general procedure afforded 2.04 g (4.41 mmol) of compound **26a** as colourless solid (Yield: 76%).



26a

$C_{26}H_{30}O_4Si_2$

$[\alpha]_{\lambda}^{20}$ = +31.3 (c = 0.13, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.11 (s, 2H; H$_5$), 7.99 (d, ^3J(H,H)=9 Hz, 2H; H$_3$), 7.45 (d, ^3J(H,H)=9 Hz, 2H; H$_4$), 7.36 (dd, ^4J (H,H)=1 Hz, ^3J(H,H)=8 Hz, 2H; H$_7$), 7.07 (d, ^3J(H,H)=8 Hz, 2H; H$_8$), 3.75 (s, 6H; O$\underline{CH_3}$), 0.43 ppm (d, ^3J(H,H)=4 Hz, 12H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.5 (s, C$_2$), 134.6 (s, C$_6$), 134.1 (s, C$_5$), 133.4 (s, C$_a$), 129.9 (s, C$_7$), 129.7 (s, C$_4$), 128.6 (s, C$_b$), 124.5 (s, C$_8$), 119.2 (s, C$_1$), 114.1 (s, C$_3$), 56.8 (s, O$\underline{CH_3}$), 0.04 ppm (s, Si($\underline{CH_3}$)$_2$), 0.02 ppm (s, Si($\underline{CH_3}$)$_2$).

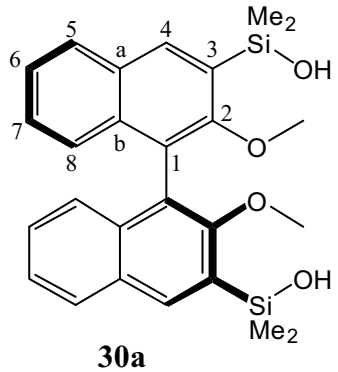
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = 8.55 ppm (s).

FT IR: $\tilde{\nu}$ = 1016 (m$_{srp}$, (Si-BINOL)), 1257 (s$_{srp}$, (Si-CH$_3$)).

EI MS (80 eV, 80 ºC): *m/z* = 462.1 [M]$^+$, calculated for **26a** ($C_{26}H_{30}O_4Si_2$) = 462.2 g/mol.

(*S*)-3,3'-bis(dimethylhydroxysilyl)-2,2'-dimethoxy-1,1'-binaphthalene (30a)

Use of 2.50 g (5.80 mmol) of **30** in the general procedure afforded 2.68 g (5.80 mmol) of compound **30a** as colourless solid (Yield: quantitative).



30a

$C_{26}H_{30}O_4Si_2$

$[\alpha]_{\lambda}^{20}$ = +75.2 (c = 0.19, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.16 (s, 2H; H$_4$), 7.91 (d, ^3J(H,H)=8 Hz, 2H; H$_5$), 7.45 - 7.31 (m, 4H; H$_6$, H$_7$), 7.25 (d, 2H; H$_8$), 3.22 (s, 6H; O$\underline{CH_3}$), 0.56 (s, 6H; Si($\underline{CH_3}$)$_2$), 0.52 ppm (s, 6H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 160.6 (s, C$_2$), 136.7 (s, C$_4$), 135.9 (s, C$_b$), 133.0 (s, C$_3$), 130.3 (s, C$_a$), 128.4 (s, C$_5$), 127.2 (s, C$_7$), 125.8 (s, C$_8$), 124.6 (s, C$_6$), 121.5 (s, C$_1$), 60.4 (s, O$\underline{CH_3}$), 1.30 (s, Si($\underline{CH_3}$)$_2$), 0.53 ppm (s, Si($\underline{CH_3}$)$_2$).

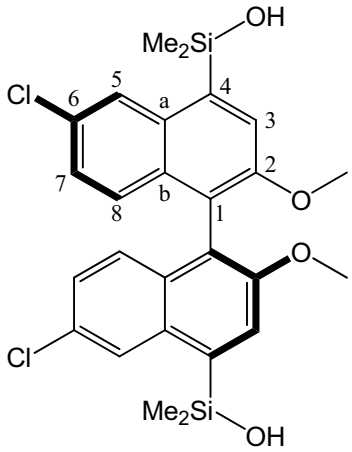
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = 6.77 ppm (s).

FT IR: $\tilde{\nu}$ =1060 (m$_{srp}$, (Si-BINOL)), 1222 and 1249 (m$_{srp}$, (Si-CH$_3$)).

EI MS (70 eV): *m/z* = 462.0 [M]$^+$, calculated for **30a** ($C_{26}H_{30}O_4Si_2$) = 462.2 g/mol.

(*S*)-4,4'-bis(dimethylhydroxysilyl)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (35a)

Use of 2.90 g (5.80 mmol) of **35** in the general procedure gave 2.96 g (5.57 mmol) of product **35a** as colorless solid (Yield: 96%).



35a

$C_{26}H_{28}Cl_2O_4Si_2$

$[\alpha]_{\lambda}^{20}$ = -25.8 (c = 0.12, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.27 (d, ^4J(H,H)=2 Hz, 2H; H$_5$), 7.79 (s, 2H, H$_3$), 7.16 (dd, ^4J(H,H)=2 Hz, ^3J(H,H)=9 Hz, 2H; H$_7$), 7.08 (d, ^3J(H,H)=9 Hz, 2H; H$_8$), 3.75 (s, 6H; O*CH$_3$*), 0.67 ppm (d, ^3J(H,H)=4 Hz, 12H; Si(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 154.2 (s, C$_2$), 138.9 (s, C$_a$), 133.2 (s, C$_4$), 132.6 (s, C$_6$), 129.6 (s, C$_7$), 127.7 (s, C$_5$), 127.1 (s, C$_8$), 127.0 (s, C$_b$), 122.4 (s, C$_3$), 121.5 (s, C$_1$), 57.0 (s, O*CH$_3$*), 1.73 (s, Si(*CH$_3$*)$_2$), 1.22 ppm (s, SiH(*CH$_3$*)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = 8.56 (s).

FT IR: $\tilde{\nu}$ = 1017 (m$_{srp}$, (Si-BINOL)), 1258 (s$_{srp}$, (Si-CH$_3$)).

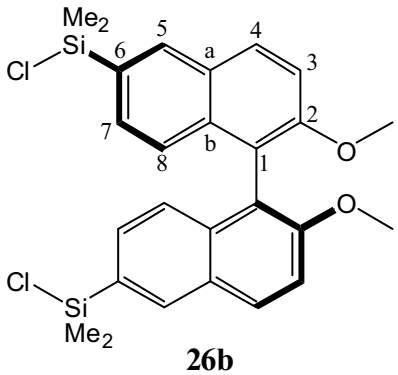
ESI MS (200 eV): *m/z* = 553.2 [M+Na]$^+$, calculated for **35a** ($C_{26}H_{28}Cl_2O_4Si_2$+Na) = 553.1 g/mol.

5.3.5 General Procedure for the Synthesis of Chlorosilanes

To a Schlenk flask containing the corresponding hydrosilane precursor (5.80 mmol) and a catalytic amount of $PdCl_2$ (51.8 mg, 0.292 mmol) was added dried CCl_4 (100 ml). The mixture was refluxed for 2 h under argon atmosphere. After this time, the solvent was removed under reduced pressure and toluene (50.0 ml) was added. A suspension was formed and the solution was filtered off. Removal of the solvent under reduced pressure afforded the desired products.

(*S*)-6,6'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (26b).

Use of 2.50 g (5.80 mmol) of **26** in the general procedure gave 2.90 g (5.80 mmol) of product **26b** as colorless solid (Yield: quantitative).



26b

$C_{26}H_{28}Cl_2O_2Si_2$

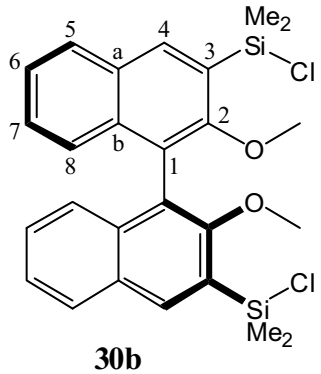
^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.16 (s, 2H; H$_5$), 8.03 (d, ^3J(H,H)=9 Hz, 2H; H$_3$), 7.49 (d, ^3J(H,H)=9 Hz, 2H; H$_4$), 7.40 (d, ^3J(H,H)=8 Hz, 2H; H$_7$), 7.12 (d, ^3J(H,H)=8 Hz, 2H; H$_8$), 3.79 (s, 6H; O$\underline{CH_3}$), 0.73 ppm (d, ^3J(H,H)=4 Hz, 12H; SiCl($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 156.1 (s, C$_2$), 135.0 (s, C$_6$), 134.7 (s, C$_5$), 130.6 (s, C$_a$), 130.3 (s, C$_4$), 129.5 (s, C$_7$), 128.6 (s, C$_b$), 124.9 (s, C$_8$), 119.2 (s, C$_1$), 114.4 (s, C$_3$), 56.9 (s, O$\underline{CH_3}$), 2.31 (s, SiCl($\underline{CH_3}$)$_2$), 2.28 ppm (s, SiCl($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = 20.6 ppm (s).

(*S*)-3,3'-bis(dimethylchlorosilyl)-2,2'-dimethoxy-1,1'-binaphthalene (30b).

Use of 2.50 g (5.80 mmol) of **30** in the general procedure gave 2.90 g (5.80 mmol) of product **30b** as colorless solid (Yield: quantitative).



30b

$C_{26}H_{28}Cl_2O_2Si_2$

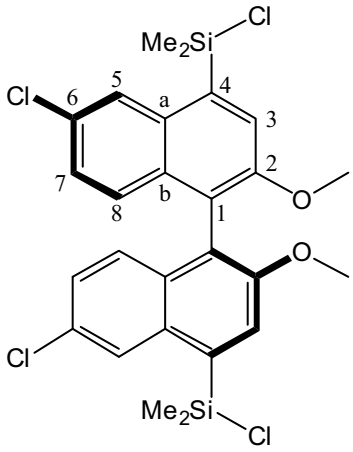
^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.24 (s, 2H; H$_4$), 7.82 (d, ^3J(H,H)=8 Hz, 2H; H$_5$), 7.28 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H$_6$), 7.18 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H$_7$), 7.11 (d, ^3J(H,H)=8 Hz, 2H; H$_8$), 3.07 (s, 6H; O*CH$_3$*), 0.66 (s, 6H, SiCl(*CH$_3$*)$_2$), 0.64 (s, 6H, SiCl(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 160.1 (s, C$_2$), 137.9 (s, C$_4$), 136.3 (s, C$_b$), 130.0 (s, C$_3$), 129.8 (s, C$_a$), 128.7 (s, C$_5$), 127.6 (s, C$_7$), 125.6 (s, C$_8$), 124.6 (s, C$_6$), 120.4 (s, C$_1$), 59.8 (s, O*CH$_3$*), 3.23 (s, SiCl(*CH$_3$*)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ= 19.6 ppm (s).

(*S*)-4,4'-bis(dimethylchlorosilyl)-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (35b).

Use of 2.90 g (5.80 mmol) of **35** in the general procedure gave 3.30 g (5.80 mmol) of product **35b** as colorless solid (Yield: quantitative).



35b

$C_{26}H_{26}Cl_4O_2Si_2$

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.08 (d, ^4J(H,H)=2 Hz, 2H; H$_5$), 7.74 (s, 2H, H$_3$), 7.10 (dd, ^4J(H,H)=2 Hz, ^3J(H,H)=9 Hz, 2H; H$_7$), 6.96 (d, ^3J(H,H)=9 Hz, 2H; H$_8$), 3.81 (s, 6H; O*CH$_3$*), 0.87 ppm (s, 12H; SiCl(*CH$_3$*)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 153.8 (s, C$_2$), 135.0 (s, C$_a$), 132.5 (s, C$_4$), 132.4 (s, C$_6$), 130.0 (s, C$_b$), 128.2 (s, C$_7$), 127.2 (s, C$_8$), 126.5 (s, C$_5$), 122.6 (s, C$_3$), 122.1 (s, C$_1$), 56.7 (s, O*CH$_3$*), 3.72 (s, SiCl(*CH$_3$*)$_2$), 3.66 ppm (s, SiCl(*CH$_3$*)$_2$).

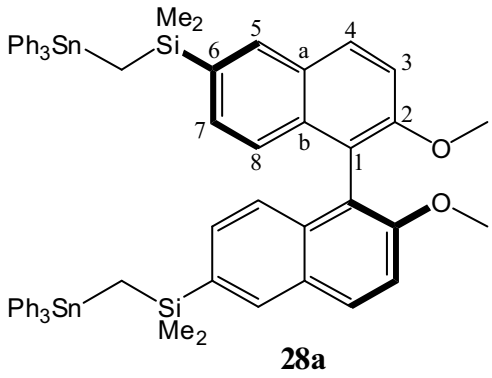
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = 21.4 (s).

5.3.6 General Procedure for the Synthesis of Tin Derivates

To a magnetically stirred suspention of Ph_3SnNa (283 mg, 0.760 mmol) in THF at -78 °C, prepare from Ph_3SnCl (0.293 mg, 0.760 mmol), sodium (34.0 mg, 1.48 mmol) and NH_3 (5.00 ml), was added dropwise a solution of the corresponding chloromethylsilane precursor (0.379 mmol) in THF (5.00 ml) over 10 min. The reaction mixture was stirred at -78 °C for 3 h and allowed to warm to rt overnight. After removing the solvent in vacuum, Et_2O was added and the precipitate (NaCl) was filtered off. The filtrate was washed several times with a saturated solution of KF and water. After that, the organic layer was dried over Na_2SO_4. Removal of volatiles furnished the desired products.

(*S*)-6,6'-bis(triphenylstannylmethyl)dimethylsilyl-2,2'-dimethoxy-1,1'-binaphthalene (28a).

Use of **28** (200 mg, 0.379 mmol) in the general procedure afforded 360 mg (0.311 mmol) of **28a** as colorless solid (Yield: 82 %).



28a

$C_{64}H_{62}O_2Si_2Sn_2$

$[\alpha]_{\lambda}^{20}$ = +55.9 (c = 0.12, THF)

^{1}H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.01 (s, 2H; H_5), 7.92 (d, ^3J(H,H)=9 Hz, 2H; H_3), 7.72 (m, 2H; H_7), 7.58 – 7.34 (m, 32H; H_4, $SnPh_3$), 7.17 (d, ^3J(H,H)=8 Hz, 2H; H_8), 3.85 (s, 6H; O$\underline{CH_3}$), 0.89 (s, 4H; Si$\underline{CH_2}$Sn), 0.35 ppm (s, 12H; Si($\underline{CH_3}$)$_2$).

$^{13}C\{^1H\}$-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 155.3 (s, C_2), 139.3 [$^1J(^{117/119}Sn,^{13}C)$ = 241/253 Hz; C_I)], 137.0 (s, C_5), 136.7 [$^2J(^{117/119}Sn,^{13}C)$ = 19 Hz; C_o)], 134.9 (s, C_6), 134.3 (s, C_a), 134.2 (s, C_7), 130.2 (s, C_4), 129.6 (s, C_b), 128.5 (C_p), 128.1 [$^3J(^{117/119}Sn,^{13}C)$ = 25 Hz; C_m)], 124.4 (s, C_8), 119.3 (s, C_1), 113.9 (s, C_3), 56.7 (s, O$\underline{CH_3}$), 0.17 (s, Si($\underline{CH_3}$)$_2$), 0.03 (s, Si($\underline{CH_3}$)$_2$), -5.53 ppm (s, Si$\underline{CH_2}$Sn).

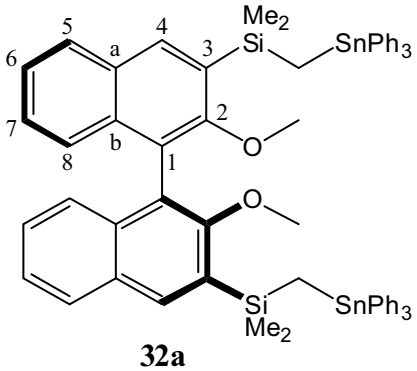
$^{29}Si\{^1H\}$-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -4.16 ppm (s).

$^{119}Sn\{^1H\}$-NMR (148.9 MHz, $[D_1]CHCl_3$): δ = -86.9 ppm (s).

ESI MS (220 eV): *m/z* = 1179.4 $[M+Na]^+$, calculated for **28a** ($C_{64}H_{62}O_2Si_2Sn_2$+Na) = 1179.2 g/mol.

(*S*)-3,3'-bis(triphenylstannylmethyl)dimethylsilyl-2,2'-dimethoxy-1,1'-binaphthalene (32a).

Use of **32** (200 mg, 0.379 mmol) in the general procedure afforded 430 mg (0.371 mmol) of **32a** as colorless solid (Yield: 98%).



32a

$C_{64}H_{62}O_2Si_2Sn_2$

$[\alpha]_\lambda^{20}$ = +37.0 (c = 0.31, THF)

^1H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.00 (s, 2H; H_4), 7.76 (d, ^3J(H,H)=8 Hz, 2H; H_5), 7.56 – 7.52 (m, 14H; H_6, $SnPh_3$), 7.37 – 7.33 (m, 22H; H_7, H_8, $SnPh_3$), 3.16 (s, 6H; O$\underline{CH_3}$), 1.02 (s, 4H; Si$\underline{CH_2}$Sn), 0.43 ppm (d, ^3J(H,H)=1 Hz, 12H; Si($\underline{CH_3}$)$_2$).

$^{13}C\{^1H\}$-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 161.1 (s, C_2), 139.7 [$^1J(^{117/119}Sn,^{13}C)$ = 251/240 Hz; C_I)], 137.4 (s, C_4), 137.1 [$^2J(^{117/119}Sn,^{13}C)$ = 18 Hz; C_o)], 135.9 (s, C_b), 130.0 (s, C_3), 129.0 (s, C_a), 128.9 (C_p), 128.5 [$^3J(^{117/119}Sn,^{13}C)$ = 25 Hz; C_m)], 128.0 (s, C_5), 126.8 (s, C_7), 125.8 (s, C_8), 124.2 (s, C_6), 121.0 (s, C_1), 59.9 (s, O$\underline{CH_3}$), 1.00 (s, Si($\underline{CH_3}$)$_2$), 0.98 (s, Si($\underline{CH_3}$)$_2$), -5.61 ppm (s, Si$\underline{CH_2}$Sn).

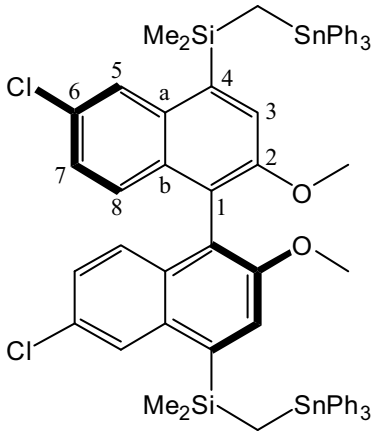
$^{29}Si\{^1H\}$-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -2.47 ppm (s).

$^{119}Sn\{^1H\}$-NMR (148.9 MHz, $[D_1]CHCl_3$): δ = -86.22 ppm (s).

ESI MS (300 eV): *m/z* = 1195.2 $[M+K]^+$, calculated for **32a** ($C_{64}H_{62}O_2Si_2Sn_2$+K) = 1195.2 g/mol.

(*S*)-4,4'-bis(triphenylstannylmethyl)dimethylsilyl-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene (37a).

Use of **37** (225 mg, 0.379 mmol) in the general procedure afforded 395 mg (0.322 mmol) of **37a** as colorless solid (Yield: 85%).



37a

$C_{64}H_{60}Cl_2O_2Si_2Sn_2$

$[\alpha]_\lambda^{20}$ = -21.4 (c = 0.19, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.16 (d, ^{4}J(H,H)=2 Hz, 2H; H$_5$), 7.59 – 7.44 (m, 14H; H$_3$, SnPh$_3$), 7.38 – 7.35 (m, 18H; SnPh$_3$), 7.14 (dd, ^{4}J(H,H)=2 Hz, ^{3}J(H,H)=9 Hz, 2H; H$_7$), 7.02 (d, ^{3}J(H,H)=9 Hz, 2H; H$_8$), 3.64 (s, 6H; O$\underline{CH_3}$), 1.13 (s, 4H; Si$\underline{CH_2}$Sn), 0.61 ppm (s, 12H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 153.9 (s, C$_2$), 139.7 [^{1}J($^{117/119}$Sn,^{13}C) = 251/240 Hz; C$_I$)], 137.6 (s, C$_a$), 137.0 [^{2}J($^{117/119}$Sn,^{13}C) = 18 Hz; C$_o$)], 133.3 (s, C$_4$), 132.7 (s, C$_6$),), 129.2 (s, C$_b$), 129.0 (s, C$_p$), 128.5 [^{3}J($^{117/119}$Sn,^{13}C) = 25 Hz; C$_m$)], 127.2 (s, C$_7$), 126.7 (s, C$_8$), 126.7 (s, C$_5$), 122.3 (s, C$_3$), 120.7 (s, C$_1$), 56.2 (s, O$\underline{CH_3}$), 3.29 s, Si($\underline{CH_3}$)$_2$), 1.73 (s, Si($\underline{CH_3}$)$_2$), -4.54 ppm (s, Si$\underline{CH_2}$Sn).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -0.63 (s).

^{119}Sn{^{1}H}-NMR (148.9 MHz, [D$_1$]CHCl$_3$): δ = -90.0 ppm (s).

ESI MS (220 eV): *m/z* = 1249 [M+Na]$^{+}$, calculated for **37a** ($C_{64}H_{60}Cl_2O_2Si_2Sn_2$+Na) = 1249 g/mol.

5.4 Synthesis of Chiral Sila-Macrocycles

5.4.1 General Procedure for the Synthesis of Cyclic Siloxanes

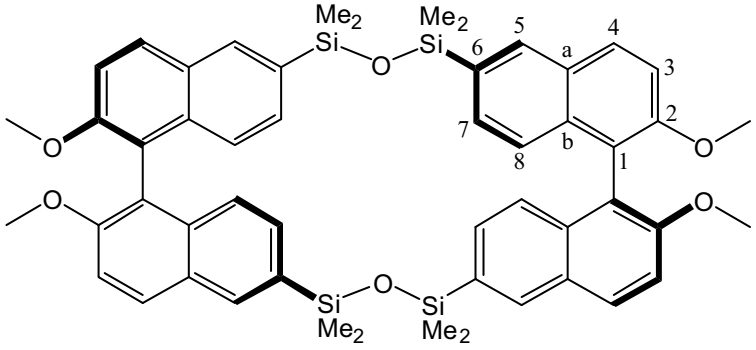
Method 1: A solution of a suitable hydrosilane (0.580 mmol) and [CpFe(CO)$_2$Me] (4 mol %, 0.023 mmol, 5.00 mg) in DMF (2.5 ml) was irradiated with 125 W medium-pressure mercury arc lamp at 25 °C for 3 h under argon atmosphere. Removal of volatile materials under reduced pressure afforded a brown solid which was directly purified by flash chromatography.

Method 2: A solution of a suitable silanol (1.00 mmol) in acetone (70.0 ml) was diluted with water (10.0 ml) and concentrated HCl (2.00 µL) was added. The solution was capped and left standing for 15 days.

(*S*,*S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-6,6',14,14'-octamethyltetrasiloxane (38).

Use of 250 mg (0.580 mmol) of hydrosilane **26** in *method 1* afforded 53.4 mg (0.060 mmol) of compound **38** as colourless solid (Yield: 10%).

When 500 mg (1.00 mmol) of silanol **26a** in *method 2* was used, 356 mg (0.40 mmol) of desired product **38** was afforded (Yield: 40%).



38

$C_{52}H_{56}O_6Si_4$

$[\alpha]_{\lambda}^{20}$ = +23.8 (c = 0.21, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 7.90 (s, 4H; H$_5$), 7.87 (s, 4H; H$_3$), 7.39 (d, ^3J(H,H)=9 Hz, 4H; H$_4$), 7.00 (d, ^3J(H,H)=9 Hz, 4H; H$_7$), 6.73 (d, ^3J(H,H)=8 Hz, 4H; H$_8$), 3.76 (s, 12H; O$\underline{CH_3}$), 0.39 ppm (d, ^3J(H,H)=4 Hz, 24H; SiO($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.5 (s, C$_2$), 134.5 (s, C$_6$), 134.2 (s, C$_a$), 133.8 (s, C$_5$), 130.3 (s, C$_7$), 129.8 (s, C$_4$), 128.6 (s, C$_b$), 124.2 (s, C$_8$), 119.4 (s, C$_1$), 114.0 (s, C$_3$), 57.0 (s, O$\underline{CH_3}$), 1.33 ppm (s, SiO($\underline{CH_3}$)$_2$), 0.84 ppm (s, SiO($\underline{CH_3}$)$_2$).

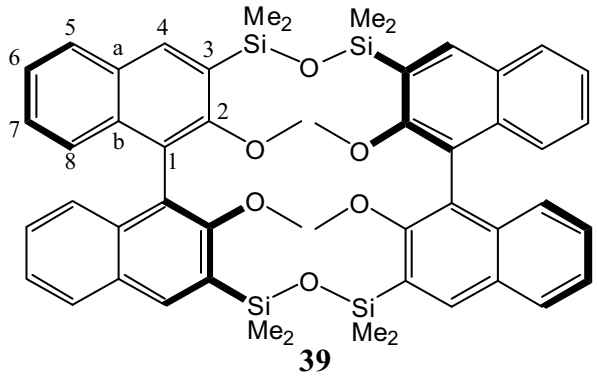
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -1.15 ppm (s).

EI MS (70 eV): *m/z* = 888 [M]$^+$, calculated for **38** ($C_{52}H_{56}O_6Si_4$) = 888 g/mol.

(*S*,*S*)-2,2',10,10'-tetramethoxy-1,1',9,9'-bis(binaphthyl)-3,3',11,11'-octamethyltetrasiloxane (39).

Use of 250 mg (0.580 mmol) of hydrosilane **30** in *method 1* afforded 54.1 mg (0.061 mmol) of compound **39** as colourless solid (Yield: 10%).

When 500 mg (1.00 mmol) of silanol **30a** in *method 2* was used, 178 mg (0.20 mmol) of desired product **39** was afforded (Yield: 20%).



39

$C_{52}H_{56}O_6Si_4$

$[\alpha]_{\lambda}^{20}$ = +66.0 (c = 0.20, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.08 (s, 4H; H$_4$), 7.85 (d, ^3J(H,H)=8 Hz, 4H; H$_5$), 7.31 (dd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 4H; H$_6$), 7.28 (dd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 4H; H$_7$), 7.19 (d, ^3J(H,H)=8 Hz, 4H; H$_8$), 2.30 (s, 12H; O$\underline{CH_3}$), 0.58 (s, 12H; SiO($\underline{CH_3}$)$_2$), 0.44 ppm (s, 12H; SiO($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 160.8 (s, C$_2$), 136.4 (s, C$_a$), 135.7 (s, C$_5$), 134.1 (s, C$_b$), 129.9 (s, C$_4$), 128.1 (s, C$_1$), 126.5 (s, C$_6$), 125.7 (s, C$_7$), 124.0 (s, C$_8$), 122.3 (s, C$_3$), 60.0 (s, O$\underline{CH_3}$), 1.98 (s, SiO($\underline{CH_3}$)$_2$), 1.83 ppm (s, SiO($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -2.30 ppm (s).

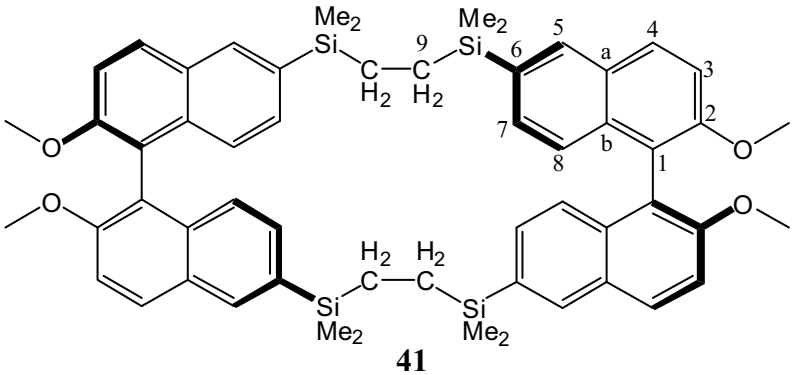
ESI MS (400 eV): *m/z* = 911.3 [M+Na]$^+$, calculated for **39** ($C_{52}H_{56}O_6Si_4$+Na) = 911.3 g/mol.

5.4.2 General Procedure for Hydrosilylation.

In a Schlenk flask under argon atmosphere, a suitable hydrosilane derivative (2.32 mmol), a vinyl derivative (2.32 mmol), one drop of Karstedt catalyst, and 5.00 ml of THF were mixed and stirred overnight at rt. Solvent removal followed by flash chromatography (Tol 100%) afforded the desired products.

(*S,S*)-2,2',11,11'-tetramethoxy-1,1',10,10'-bis(binaphthyl)-6,6',15,15'-octamethyldiethyl-silane (41).

Use of 1.00 g of compound **26** and of 1.12 g of **27** in the general procedure afforded 1.59 g (1.74 mmol) of pure product **41** as yellow solid (Yield: 75%).



41

$C_{56}H_{64}O_4Si_4$

$[\alpha]_{\lambda}^{20}$ = +110.0 (c = 0.06, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.09 (s, 4H; H$_5$), 8.01 (d, ^3J(H,H)=9 Hz, 4H; H$_3$), 7.48 (d, ^3J (H,H)=9 Hz, 4H; H$_4$), 7.40 (d, ^3J(H,H)=8 Hz, 4H; H$_7$), 7.21 (d, ^3J(H,H)=8 Hz, 4H; H$_8$), 3.81 (s, 12H; O$\underline{CH_3}$), 0.84 (s, 8H; CH_2CH_2), 0.38 ppm (d, ^3J(H,H)=2 Hz, 24H; R$_2$Si($\underline{CH_3}$)$_2$).

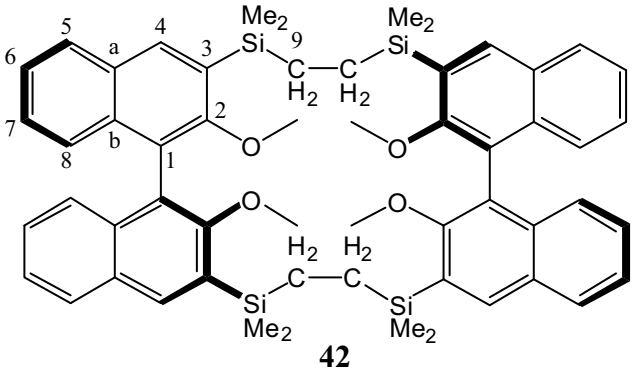
^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.4 (s, C$_2$), 134.4 (s, C$_4$), 134.4 (s, C$_6$), 133.8 (s, C$_a$), 130.7 (s, C$_5$), 129.7 (s, C$_7$), 128.9 (s, C$_b$), 124.4 (s, C$_8$), 119.5 (s, C$_1$), 114.1 (s, C$_3$), 56.9 (s, O$\underline{CH_3}$), 8.02 (s, C$_9$), -3.32 ppm (s, R$_2$Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -1.24 ppm (s).

EI MS (70 eV, 200 ºC): *m/z* = 912 $[M]^+$, calculated for **41** ($C_{56}H_{64}O_4Si_4$) = 912 g/mol.

(*S*,*S*)-2,2',11,11'-tetramethoxy-1,1',10,10'-bis(binaphthyl)-3,3',12,12'-octamethyldiethyl-silane (42).

Use of 1.00 g of compound **30** and of 1.12 g of **31** in the general procedure afforded 0.424 g (0.464 mmol) of pure product **42** as colorless solid (Yield: 20%).



42

$C_{56}H_{64}O_4Si_4$

$[\alpha]_\lambda^{20}$ = +21.9 (c = 0.13, THF)

^{1}H-NMR (399.6 MHz, $[D_1]CHCl_3$): δ = 8.14 (s, 4H; H_4), 7.93 (d, ^3J(H,H)=8 Hz, 4H; H_5), 7.41 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 4H; H_6), 7.26 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 4H; H_7), 7.18 (d, ^3J(H,H)=8 Hz, 4H; H_8), 3.32 (s, 12H, O$\underline{CH_3}$), 0.86 (s, 8H, Si$\underline{CH_2}(CH_3)_2$), 0.57 (s, 12H, $SiCH_2(\underline{CH_3})_2$), 0.33 ppm (s, 12H, $SiCH_2(\underline{CH_3})_2$).

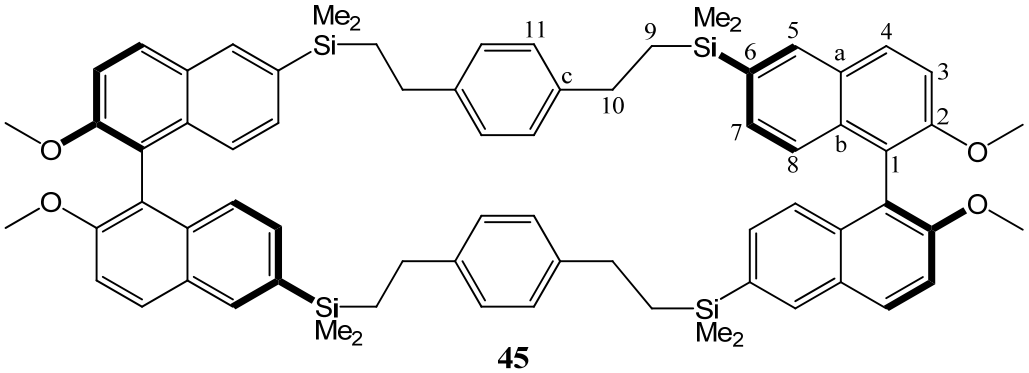
^{13}C{^{1}H}-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 161.1 (s, C_2), 137.8 (s, C_4), 136.2 (s, C_b), 132.7 (s, C_a), 130.0 (s, C_3), 128.1 (s, C_5), 126.7 (s, C_7), 125.9 (s, C_8), 124.2 (s, C_6), 121.0 (s, C_1), 59.7 (s, O$\underline{CH_3}$), 8.97 (s, Si$\underline{CH_2}(CH_3)_2$), -1.36 (s, $SiCH_2(\underline{CH_3})_2$),-3.25 ppm (s, $SiCH_2(\underline{CH_3})_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -1.16 ppm (s).

ESI MS (400 eV): *m/z* = 935.4 $[M+Na]^+$, calculated for **42** ($C_{56}H_{64}O_4Si_4$+Na) = 935.4 g/mol.

(*S,S*)-2,2',13,13'-tetramethoxy-1,1',12,12'-bis(binaphthyl)-6,6',17,17'-bis(4ethylphenyl)octamethylsilane (45).

Use of 1.00 g of compound **26** and of 0.302 g of 1,4-divinylbenzene (55%, 0,914 g/ml) in the general procedure afforded 1.38 g (1.23 mmol) of product **45** as a colorless isomeric mixture (Mixture yield: 53%).



45

$C_{72}H_{80}O_4Si_4$

$[\alpha]_{\lambda}^{20}$ = +62.1 (c = 0.14, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.03 (s, 4H; H$_5$), 7.98 (d, ^3J(H,H)=9 Hz, 4H; H$_3$), 7.45 (d, ^3J (H,H)=9 Hz, 4H; H$_4$), 7.34 (d, ^3J(H,H)=9 Hz, 4H; H$_7$), 7.15 (dd, ^3J(H,H)=8 Hz, 8H; H$_{11}$), 6.99 (d, ^3J(H,H)=7 Hz, 4H; H$_8$), 3.77 (s, 12H; O$\underline{CH_3}$), 2.62 (m, 8H; H$_{10}$), 1.14 (m, 8H; H$_9$), 0.32 ppm (d, ^3J(H,H)=2 Hz, 24H; R$_2$Si($\underline{CH_3}$)$_2$).

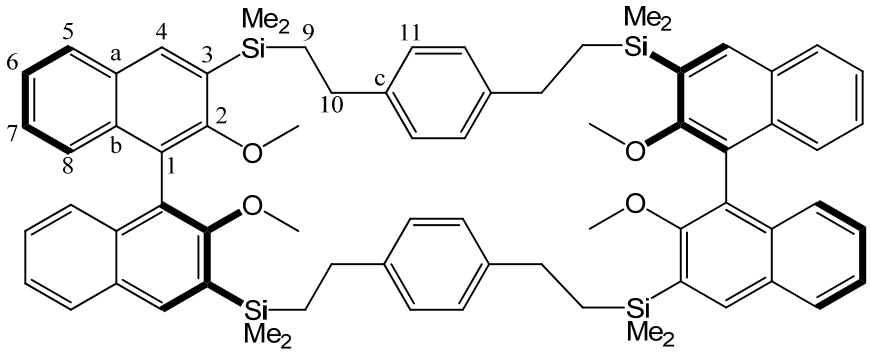
^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 155.5 (s, C$_2$), 145.2 (s, C$_c$), 134.5 (s, C$_5$), 133.5 (s, C$_6$), 130.7 (s, C$_7$), 129.7 (s, C$_4$), 128.9 (s, Ca), 128.4 (s, C$_b$), 127.8 (s, C$_{11}$), 124.5 (s, C$_8$), 125.1 (s, C$_{12}$), 119.4 (s, C$_1$), 114.2 (s, C$_3$), 57.0 (s, O$\underline{CH_3}$), 30.1 (s, C$_{10}$), 17.9 (s, C$_9$), -2.90 ppm (s, R$_2$Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -2.94 ppm (s).

EI MS (70 eV, 200 ºC): *m/z* = 1120 [M]$^+$, calculated for **45** ($C_{72}H_{80}O_4Si_4$) = 1120 g/mol.

(*S,S*)-2,2',13,13'-tetramethoxy-1,1',12,12'-bis(binaphthyl)-3,3',14,14'-bis(4-ethylphenyl)octamethylsilane (48).

Use of 1.00 g of compound **30** and 0.302 g of 1,4-divinylbenzene (55%, 0.914 g/ml) in the general procedure afforded 0.858 g (0.766 mmol) of product **48** as a colorless isomeric mixture (Mixture yield: 33%).



48

$C_{72}H_{80}O_4Si_4$

$[\alpha]_{\lambda}^{20}$ = +40.0 (c = 0.07, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.09 (s, 4H; H$_4$), 7.92 (d, ^3J(H,H)=8 Hz, 4H; H$_5$), 7.41 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=4 Hz, 4H; H$_6$), 7.30 (d, ^3J(H,H)=4 Hz, 8H; H$_{11}$), 7.21 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=4 Hz, 4H, H$_7$), 7.06 (d, ^3J(H,H)=6 Hz, 4H; H$_8$), 3.20 (s, 12H, O$\underline{CH_3}$), 2.66-2.55 (m, 8H, H$_{10}$), 1.42-1.30 (m, 8H, H$_9$), 0.48 (s, 12H, R$_2$Si($\underline{CH_3}$)$_2$), 0.45 ppm (s, 12H, R$_2$Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 161.4 (s, C$_2$), 145.6 (s, C$_c$), 137.2 (s, C$_4$), 136.0 (s, C$_b$), 132.9 (s, C$_3$), 130.2 (s, C$_a$), 128.2 (s, C$_5$), 127.9 (s, C$_{11}$), 126.9 (s, C$_7$), 125.9 (s, C$_8$), 125.3 (s, C$_{12}$), 124.4 (s, C$_6$), 121.2 (s, C$_1$), 60.0 (s, O$\underline{CH_3}$), 30.5 (s, C$_{10}$), 18.4 (s, C$_9$), -1.99 (s, Si($\underline{CH_3}$)$_2$), -2.14 ppm (s, Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -3.33 ppm (s).

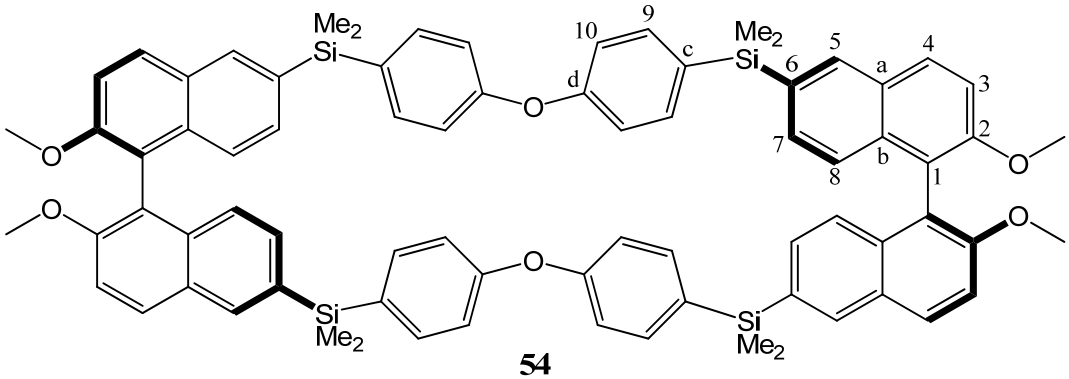
EI MS (70 eV): *m/z* = 1120 [M]$^+$, calculated for **48** ($C_{56}H_{64}O_4Si_4$) = 1120 g/mol.

5.4.3 General Procedure for Grignard Reactions

Magnesium turnings (500 mg, 20.6 mmol) were placed in an oven-dried three necked flask equipped with a dropping funnel, argon inlet, reflux condenser and a magnet. After activation of magnesium with 1,2-dibromoethane (0.050 ml, 0.577 mmol), 4,4'-dibromodiphenylether (1.00 g, 2.12 mmol) dissolved in dry THF was slowly added. When the addition was completed, the reaction mixture was heated at reflux temperature for 8 h. Then, using a canula the resulting solution was transferred to a three necked flask also equipped with a dropping funnel, argon inlet, and reflux condenser. Next, a suitable halogenated silane building block (0.801 mmol) in THF was slowly dropped to the Grignard solution. After complete addition, the mixture was allowed to react at reflux temperature for 72 h. Subsequently, the mixture was allowed to cool to rt and quenched with water. The organic layer was separated, washed several times with water, and dried over Na_2SO_4. Removal of volatiles afforded a solid which was subjected to column chromatography (Hx-EtOAc 95:5).

(*S*,*S*)-2,2',12,12'-tetramethoxy-1,1',11,11'-bis(binaphthyl)-6,6',16,16'-octamethyl-di(4-phenoxyphenyl)tetrasilane (54).

Use of 400 mg (0.801 mmol) of halogenated compound **26b** as silane building block in the general procedure gave 300 mg of a yellow solid, characterized as a mixture of product **54** and diphenyl ether. Using ^{1}H-NMR integrals, the amount of **54** in the mixture was determined as 235 mg (0.197 mmol). (Yield: 22 %, according to the calculated amount of **54** in the mixture).



54

$C_{76}H_{72}O_6Si_4$

$[\alpha]_{\lambda}^{20}$ = +10.9 (c = 0.12, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.05 (s, 4H; H$_5$), 7.98 (d, ^{3}J(H,H)=9 Hz, 4H; H$_3$), 7.52 (d, ^{3}J(H,H)=8 Hz, 8H; H$_{10}$), 7.46 (d, ^{3}J (H,H)=9 Hz, 4H; H$_4$), 7.27 (d, ^{3}J(H,H)=8 Hz, 4H; H$_7$), 7.10 (d, ^{3}J(H,H)=8 Hz, 4H; H$_8$), 6.98 (d, ^{3}J(H,H)=8 Hz, 8H; H$_9$), 3.78 (s, 12H; O$\underline{CH_3}$), 0.60 ppm (d, ^{3}J(H,H)=2 Hz, 24H; R$_2$Si($\underline{CH_3}$)$_2$).

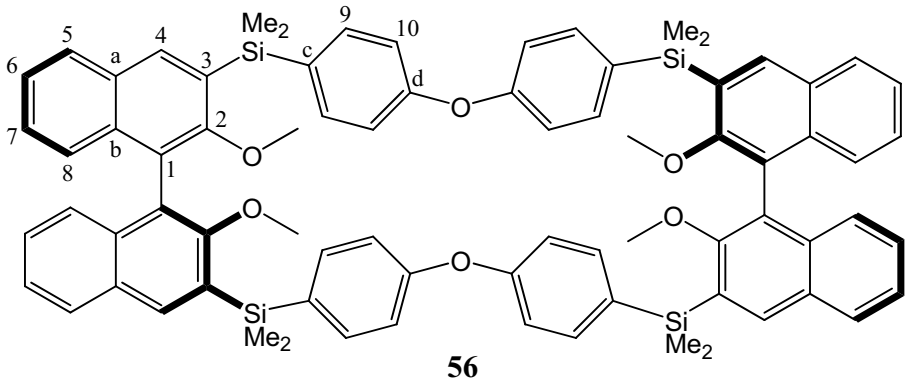
^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 158.2 (s, C$_d$), 155.6 (s, C$_2$,), 136.0 (s, C$_{10}$), 135.1 (s, C$_5$), 134.5 (s, C$_6$), 132.7 (s, C$_a$), 131.0 (s, C$_7$), 129.2 (s, C$_b$), 124.5 (s, C$_4$), 123.6 (s, C$_8$), 121.1 (s, C$_c$), 118.1 (s, C$_9$), 117.7 (s, C$_1$), 114.7 (s, C$_3$), 57.0 (s, O$\underline{CH_3}$), -2.0 ppm (s, R$_2$Si($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -8.14 ppm (s).

EI MS (70 eV, 200 ºC): *m/z* = 1193 [M]$^{+}$**,** calculated for **54** (C$_{56}$H$_{64}$O$_4$Si$_4$) = 1193 g/mol.

(*S,S*)-2,2',12,12'-tetramethoxy-1,1',11,11'-bis(binaphthyl)-3,3',13,13'-octamethyl-di(4-phenoxyphenyl)tetrasilane (56).

Use of 400 mg (0.801 mmol) of halogenated compound **8b** as silane building block in the general procedure gave 145 mg of a yellow solid, characterized as a mixture of product **56** and diphenyl ether. Using ^{1}H-NMR integrals, the amount of **56** in the mixture was determined as 120 mg (0.100 mmol). (Yield: 12 %, according to the calculated amount of **56** in the mixture).



56

C$_{76}$H$_{72}$O$_6$Si$_4$

$[\alpha]_{\lambda}^{20}$ = +26.2 (c = 0.06, THF)

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 7.99 (s, 4H; H$_4$), 7.83 (d, ^{3}J(H,H)=8 Hz, 4H; H$_5$), 7.57 (d, ^{3}J(H,H)=8 Hz, 8H; H$_9$), 7.35 (dd, ^{3}J(H,H)=8 Hz, ^{4}J(H,H)=2 Hz, 4H; H$_6$), 7.10 (ddd, ^{3}J(H,H)=7 Hz, ^{4}J(H,H)=1 Hz, 4H; H$_7$), 7.01 (d, ^{3}J(H,H)=8 Hz, 4H; H$_8$), 6.98 (d, ^{3}J(H,H)=8 Hz, 8H; H$_{10}$), 2.90 (s, 12H, O$\underline{CH_3}$), 0.66 (s, 12H, Si($\underline{CH_3}$)$_2$), 0.65 ppm (s, 12H, Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 161.2 (s, C$_2$), 158.2 (s, C$_d$), 137.7 (s, C$_4$), 135.8 (s, C$_b$), 135.7 (s, C$_9$), 133.3 (s, C$_c$), 132.6 (s, C$_3$), 130.2 (s, C$_a$), 128.3 (s, C$_5$), 127.0 (s, C$_7$), 125.8 (s, C$_8$), 124.4 (s, C$_6$), 121.4 (s, C$_1$), 118.0 (s, C$_{10}$) 59.9 (s, O$\underline{CH_3}$), -1.37 (s, Si ($\underline{CH_3}$)$_2$), -1.67 ppm (s, Si ($\underline{CH_3}$)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -8.96 ppm (s).

EI MS (70 eV): *m/z* = 1192 [M]$^{+}$, calculated for **56** ($C_{76}H_{72}O_6Si_4$) = 1192 g/mol.

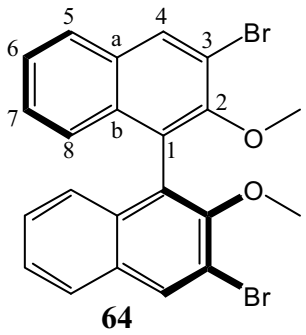
5.5 Functionalization of Chiral Sila-Macrocycles

5.5.1 General Procedure for Demethylation with BBr_3

To an ice-cooled solution of the target compound (0.500 mmol) in DCM (50.0 ml), BBr_3 in DCM 1.0 M (2.50 ml, 2.50 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The excess of BBr_3 was decomposed by slowly addition of water. The organic layer was washed several times with water and dried over Na_2SO_4. The products obtained after removal of volatiles were characterized by NMR spectroscopy.

(*S*,*S*)-3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (64).

Treatment of macrocycle **42** (456 mg, 0.500 mmol) with BBr_3 as described in the general procedure resulted in the formation of compound **64** (220 mg, 0.465 mmol).



64

$C_{22}H_{16}Br_2O_2$

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.29 (s, 2H; H$_4$), 7.84 (d, ^3J(H,H)=8 Hz, 2H; H$_5$), 7.45 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H$_6$), 7.29 (ddd, ^3J(H,H)=8 Hz, ^4J(H,H)=1 Hz, 2H; H$_7$), 7.10 (d, ^3J(H,H)=8 Hz, 2H; H$_8$), 3.53 (s, 6H, O$\underline{CH_3}$).

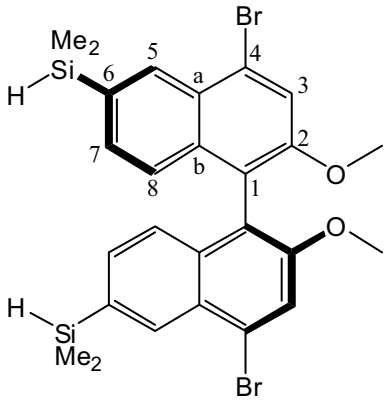
^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 152.6 (s, C$_2$), 133.1 (s, C$_4$), 131.6 (s, C$_b$), 127.3 (s, C$_5$), 127.0 (s, C$_7$), 126.7 (s, C$_a$), 126.0 (s, C$_8$), 125.9 (s, C$_6$), 117.6 (s, C$_1$), 114.4 (s, C$_3$), 61.2 (s, O$\underline{CH_3}$).

5.5.2 Bromination

For the preparation of a macrocycle containing Br-functionalities, brominated precursors (*S*)-6,6'-bis(dimethylsilyl)-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**69**) and (*S*)-6,6'-bis(dimethylvinylsilyl)-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**70**) were synthesized as indicated in the following procedures.

(*S*)-6,6'-bis(dimethylsilyl)-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (69).

A solution of (*S*)-6,6',4,4'-tetrabromo-2,2'-dimethoxy-1,1'-binaphthalene (**68**) (2.00 g, 3.17 mmol) in dried THF (100 ml) was cooled to -78 ºC. At this temperature, *n*-BuLi in Hx 2.5 M (3.50 ml, 8.75 mmol) was slowly added. The reaction mixture was stirred at -78 ºC for 1 h. After this time, $ClMe_2SiH$ (1.20 ml, 10.8 mmol) was added dropwise in a period of 10 min. The mixture was allowed warm up to rt overnight. The reaction was quenched with water and stirred for additional 4 h. The organic layer was separated, washed with water and dried over Na_2SO_4. Complete removal of volatiles and purification by flash chromatography (Hx-EtOAc 98:2) afforded 0.466 g (0.792 mmol) of compound **69** as yellow solid (Yield: 25 %).



69

$C_{26}H_{28}Br_2O_2Si_2$

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.44 (s, 2H; H$_5$), 7.83 (s, 2H; H$_3$), 7.41 (d, ^3J(H,H)=9 Hz, 2H; H$_7$), 7.15 (d, ^3J(H,H)=9 Hz, 2H; H$_8$), 5.11 (m, 2H; Si*H*(CH$_3$)$_2$), 3.87 (s, 6H; O*CH$_3$*), 0.75 ppm (d, ^3J(H,H)=4 Hz, 12H; SiH(*CH$_3$*)$_2$).

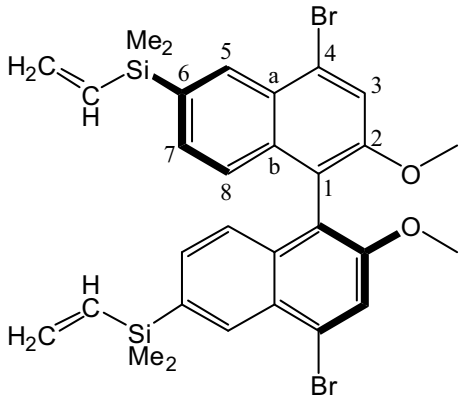
^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 154.2 (s, C$_2$), 137.3 (s, C$_a$), 134.0 (s, C$_4$), 132.6 (s, C$_6$), 129.8 (s, C$_b$), 129.4 (s, C$_7$), 127.8 (s, C$_8$), 122.4 (s, C$_5$), 121.0 (s, C$_3$), 117.8 (s, C$_1$), 56.7 (s, O*CH$_3$*), -3.02 ppm (s, SiH(*CH$_3$*)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -18.2 ppm (s).

EI MS (70 eV, 200 ºC): *m/z* = 586 [M]$^+$, calculated for **69** ($C_{26}H_{28}Br_2O_2Si_2$) = 586 g/mol.

(*S*)-6,6'-bis(dimethylvinylsilyl)-4,4'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (70).

Use of $ClMe_2SiCHCH_2$ (1.50 ml, 10.8 mmol) as silane derivate in the procedure described for **69** gave 0.467 g (0.729 mmol) of compound **70** as colorless solid (Yield: 23 %).



70

$C_{30}H_{32}Br_2O_2Si_2$

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.37 (s, 2H; H$_5$), 7.75 (s, 2H; H$_3$), 7.32 (d, ^3J(H,H)=8 Hz, 2H; H$_7$), 7.06 (d, ^3J(H,H)=8 Hz, 2H; H$_8$), 6.63 (dd, ^3J(H,H)=20 Hz, ^3J(H,H)=15 Hz, 2H; Si<u>*CH*</u>CH$_2$), 6.27 (dd, ^3J(H,H)=15 Hz, ^2J(H,H)=4 Hz, 2H; SiCH<u>*CH$_2$*</u>), 6.04 (dd, ^3J(H,H)=20 Hz, ^2J(H,H)=4 Hz, 2H; SiCH<u>*CH$_2$*</u>), 3.81 (s, 6H; O<u>*CH$_3$*</u>), 0.71 ppm (s, 12H; Si(<u>*CH$_3$*</u>)$_2$).

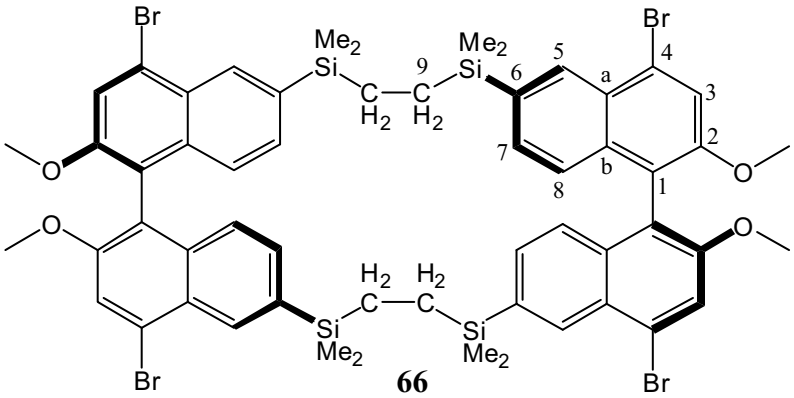
^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 154.2 (s, C$_2$), 138.2 (s, <u>*CH*</u>CH$_2$), 138.0 (s, C$_5$), 134.1 (s, C$_6$), 133.8 (s, CH<u>*CH$_2$*</u>), 132.8 (s, C$_a$), 130.6 (s, C$_7$), 129.2 (s, C$_b$), 127.9 (s, C$_4$), 122.9 (s, C$_8$), 121.0 (s, C$_1$), 117.5 (s, C$_3$), 56.8 (s, O<u>*CH$_3$*</u>), -1.42 ppm (s, Si(<u>*CH$_3$*</u>)$_2$).

^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -10.1 ppm (s).

EI MS (70 eV, 200 ºC): *m/z* = 638 $[M]^+$, calculated for **70** ($C_{26}H_{28}Br_2O_2Si_2$) = 638 g/mol.

(*S,S*)-2,2',11,11'-tetramethoxy-1,1',10,10'-bis(binaphthyl)-4,4',13,13'-tetrabromo-6,6',15,15'-octamethyldiethylsilane (66).

In a Schlenk flask under argon atmosphere, hydrosilane **69** (276 mg, 0.468 mmol), vinyl derivative **70** (300 mg, 0.468 mmol), one drop of Karstedt catalyst, and 3.00 ml of THF were mixed and stirred overnight at rt. Solvent removal followed by flash chromatography (Hx-EtOAc 98:2) afforded 134 mg of a mixture of product **66** and precursor **70**. Using ^{1}H-NMR integrals, the amount of **66** in the mixture was determined as 58.0 mg (0.047 mmol). (Yield: 10 %, according to the calculated amount of **66** in the mixture).



66

$C_{56}H_{60}Br_4O_4Si_4$

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.34 (s, 4H; H$_5$), 7.72 (s, 4H; H$_3$), 7.30 (d, ^{3}J(H,H)=9 Hz, 4H; H$_4$), 7.03 (d, ^{3}J(H,H)=8 Hz, 4H; H$_7$), 3.80 (s, 12H; O$\underline{CH_3}$), 1.67 (s, 8H, Si$\underline{CH_2}$(CH$_3$)$_2$), 0.68 ppm (s, 24H; Si($\underline{CH_3}$)$_2$).

^{13}C{^{1}H}-NMR (100.4 MHz, [D$_1$]CHCl$_3$): δ = 154.2 (s, C$_2$), 138.1 (s, C$_5$), 134.1 (s, C$_6$), 132.8 (s, C$_a$), 130.4 (s, C$_7$), 129.2 (s, C$_b$), 128.0 (s, C$_4$), 122.6 (s, C$_8$), 121.1 (s, C$_1$), 117.5 (s, C$_3$), 56.8 (s, O$\underline{CH_3}$), 8.43 (s, Si$\underline{CH_2}$(CH$_3$)$_2$), 1.19 ppm (s, Si($\underline{CH_3}$)$_2$).

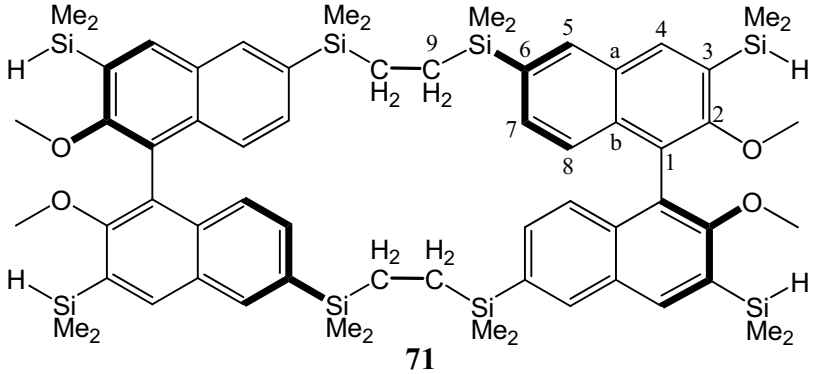
^{29}Si{^{1}H}-NMR (79.3 MHz, [D$_1$]CHCl$_3$): δ = -0.28 ppm (s).

ESI MS (250 eV): *m/z* = 1251.1 [M+Na]$^{+}$, calculated for **66** ($C_{30}H_{34}O_2Si_2$+Na) = 1251.0 g/mol.

5.5.3 Silylation

(*S,S*)-2,2',11,11'-tetramethoxy-1,1',10,10'-bis(binaphthyl)-3,3',12,12'-bis(dimethylsilyl-6,6',15,15'-octamethyldiethylsilane (71).

To a solution of TMEDA (0.35 ml, 2.32 mmol) in diethyl ether (30,0 ml), 2.5 M *n*-BuLi in Hx (1.00 ml, 2.50 mmol) was added at rt under argon pressure. The solution was stirred for 15 min and compound **41** (400 mg, 0.440 mmol) was added in one portion. The reaction mixture was stirred at rt for 3 h. The resulting suspension was cooled to -78 ºC and $ClMe_2SiH$ (0.500 ml, 4.40 mmol) was added over a period of 5 min. The mixture was allowed to warm to rt overnight. The reaction was stopped by addition of water and stirred for additional 4 h. The resulting solution was diluted with diethyl ether and water. The organic layer was washed with water and dried over Na_2SO_4. Complete removal of volatiles and purification by flash chromatography (Hx-EtOAc 98:2) furnished 176 mg (0.154 mmol) of product **71** as an orange amorphous solid. (Yield = 35 %)



71

$C_{64}H_{88}O_4Si_8$

^{1}H-NMR (399.6 MHz, [D$_1$]CHCl$_3$): δ = 8.15 (s, 4H; H$_5$), 8.06 (s, 4H; H$_7$), 7.44 (dd, ^3J (H,H)=9 Hz, 4H; H$_4$),), 7.19 (d, ^3J(H,H)=8 Hz, 4H; H$_8$), 4.67 (m, 4H; Si$\underline{H}$(CH$_3$)$_2$), 3.36 (s, 12H; O$\underline{CH_3}$), 0.79 (s, 8H; CH_2CH_2), 0.50 (s, 24H, Si($\underline{CH_3}$)$_2$), 0.33 ppm (s, 24H; SiH($\underline{CH_3}$)$_2$).

$^{13}C\{^1H\}$-NMR (100.4 MHz, $[D_1]CHCl_3$): δ = 161.0 (s, C_2), 137.6 (s, C_4), 136.2 (s, C_6), 135.2 (s, C_a), 134.5 (s, C_5), 131.3 (s, C_7), 129.9 (s, C_b), 124.9 (s, C_8), 122.1 (s, C_1), 114.2 (s, C_3), 60.6 (s, O$\underline{CH_3}$), 8.04 (s, C_9), -1.19 (s, $R_2Si(\underline{CH_3})_2$), -3.25 ppm (s, $R_2Si(\underline{CH_3})_2$).

$^{29}Si\{^1H\}$-NMR (79.3 MHz, $[D_1]CHCl_3$): δ = -1.20 ppm (s); -19.3 ppm (s).

EI MS (70 eV, 200 ºC): *m/z* = 1144 $[M]^+$**,** calculated for **70** ($C_{64}H_{88}O_4Si_8$) = 1144 g/mol.

6 Bibliography

[1] C. J. Pedersen, *Angew. Chem.* **1988**, *100*, 1053.

[2] J.-M. Lehn, *Angew. Chem.* **1988**, *100*, 91.

[3] D. J. Cram, *Angew. Chem.* **1988**, *100*, 1041.

[4] R. M. Kellogg, *Angew. Chem.* **1984**, *96*, 769.

[5] A. Higuchi, Y. Higuchi, K. Furuta, B. O. Yoon, M. Hara, S. Maniwa, M. Saitoh, K. Sanui, *J. Membr. Sci.* **2003**, *221*, 207.

[6] T. Ema, K. Hamada, K. Sugita, Y. Nagata, T. Sakai, A. Ohnishi, *J. Org. Chem.* **2010**, *75*, 4492.

[7] a) S. J. Lee, W. Lin, *Acc. Chem. Res.* **2008**, *41*, 521; b) D. B. Amabilino, *Chem. Soc. Rev.* **2009**, *38*, 669.

[8] M. Diéguez, O. Pàmies, C. Claver, *Chem. Rev.* **2004**, *104*, 3189.

[9] T. Poon, N. J. Turro, J. Chapman, P. Lakshminarasimhan, X. Lei, W. Adam, S. G. Bosio, *Org. Lett.* **2003**, *5*, 2025.

[10] H. L. Ngo, A. Hu, W. Lin, *J. Mol. Catal. A: Chem.* **2004**, *215*, 177.

[11] W.-L. Wong, K.-H. Huang, P.-F. Teng, C.-S. Lee, H.-L. Kwong, *Chem. Commun.* **2004**, 384.

[12] Q. Miao, H. Huang, X. Huang, Y. Xu, L. Zong, Y. Cheng, *Polym. Int.* **2010**, *59*, 712.

[13] R. B. Prince, S. A. Barnes, J. S. Moore, *J. Am. Chem. Soc.* **2000**, *122*, 2758.

[14] S. B. Lee, D. T. Mitchell, L. Trofin, T. K. Nevanen, H. Söderlund, C. R. Martin, *Science* **2002**, *296*, 2198.

[15] S. Fireman-Shoresh, D. Avnir, S. Marx, *Chem. Mater.* **2003**, *15*, 3607.

[16] a) C. Seel, F. Vögtle, *Angew. Chem., Int. Ed.* **1992**, *31*, 528; b) F. P. Schmidtchen, M. Berger, *Chem. Rev.* **1997**, *97*, 1609; c) T. Govender, H. K. Hariprakasha, H. G. Kruger, A. P. Marchand, *Tetrahedron: Asymmetry* **2003**, *14*, 1553.

[17] M. Widhalm, G. Klintschar, *Chem. Ber.* **1994**, *127*, 1411.

[18] V. H. Gessner, J. F. Tannaci, A. D. Miller, T. D. Tilley, *Acc. Chem. Res.* **2011**, *44*, 435.

[19] E. P. Kyba, M. G. Siegel, L. R. Sousa, G. D. Y. Sogah, D. J. Cram, *J. Am. Chem. Soc.* **1973**, *95*, 2691.

[20] D. S. Lingenfelter, R. C. Helgeson, D. J. Cram, *J. Org. Chem.* **1981**, *46*, 393.

[21] P. Deniz, Y. Turgut, M. Togrul, H. Hosgoren, *Tetrahedron* **2011**, *67*, 6227.

[22] T. P. Quinn, P. D. Atwood, J. M. Tanski, T. F. Moore, J. F. Folmer-Andersen, *J. Org. Chem.* **2011**, *76*, 10020.

[23] a) B. J. Holliday, C. A. Mirkin, *Angew. Chem., Int. Ed.* **2001**, *40*, 2022; b) E. Zangrando, M. Casanova, E. Alessio, *Chem. Rev.* **2008**, *108*, 4979; c) B. H. Northrop, H.-B. Yang, P. J. Stang, *Chem. Commun.* **2008**, 5896.

[24] M. P. López-Alberca, M. J. Mancheño, I. Fernández, M. Gómez-Gallego, M. A. Sierra, C. Hemmert, H. Gornitzka, *Eur. J. Inorg. Chem.* **2011**, *2011*, 842.

[25] C. Coluccini, D. Dondi, M. Caricato, A. Taglietti, M. Boiocchi, D. Pasini, *Org. Biomol. Chem.* **2010**, *8*, 1640.

[26] a) S. Anderson, U. Neidlein, V. Gramlich, F. Diederich, *Angew. Chem., Int. Ed.* **1995**, *34*, 1596; b) U. Neidlein, F. Diederich, *Chem. Commun.* **1996**, 1493; c) A. Bähr, A. S. Droz, M. Püntener, U. Neidlein, S. Anderson, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1998**, *81*, 1931.

[27] a) L. Pu, *Chem. Rev.* **1998**, *98*, 2405; b) Y. Chen, S. Yekta, A. K. Yudin, *Chem. Rev.* **2003**, *103*, 3155.

[28] É. Kőszegi, A. Grün, I. Bitter, *Supramol. Chem.* **2008**, *20*, 565.

[29] S.-i. Kiyooka, M. Tada, S. Kan, M. Fujio, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2595.

[30] a) R. Sakai, T. Yonekawa, I. Otsuka, R. Kakuchi, T. Satoh, T. Kakuchi, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1197; b) G. Fukuhara, Y. Inoue, *Chem.-Eur. J.* **2010**, *16*, 7859; c) G. Fukuhara, Y. Inoue, *Chem. Commun.* **2012**, *48*, 1641.

[31] J.-P. Mazaleyrat, K. Wright, M.-V. Azzini, A. Gaucher, M. Wakselman, *Tetrahedron Lett.* **2003**, *44*, 1741.

[32] a) H. Brunner, H. Schiessling, *Angew. Chem., Int. Ed.* **1994**, *33*, 125; b) H. Brunner, H. Schießling, *Bull. Soc. Chim. Belg.* **1994**, *103*, 119.

[33] J. K. Judice, S. J. Keipert, D. J. Cram, *J. Chem. Soc., Chem. Commun.* **1993**, 1323.

[34] T. Harada, S.-i. Matsui, T. M. T. Tuyet, M. Hatsuda, S. Ueda, A. Oku, M. Shiro, *Tetrahedron: Asymmetry* **2003**, *14*, 3879.

[35] D. Srinivas, R. Gonnade, P. R. Rajamohanan, G. J. Sanjayan, *Tetrahedron Lett.* **2008**, *49*, 2139.

[36] S. Sudhakar, G.-H. Lee, Y. Wang, J.-H. Hsu, T.-Y. Luh, *J. Organomet. Chem.* **2002**, *646*, 167.

[37] M. E. Jung, H. Xia, *Tetrahedron Lett.* **1988**, *29*, 297.

[38] C. Kaes, M. Wais Hosseini, R. Ruppert, A. De Cian, J. Fischer, *Tetrahedron Lett.* **1994**, *35*, 7233.

[39] M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry.*, John Wiley & Sons, New York **1999**.

[40] B. König, M. Rödel, P. Bubenitschek, P. G. Jones, *Angew. Chem., Int. Ed.* **1995**, *34*, 661.

[41] C. W. Lee, G. Tae Hwang, B. H. Kim, *Tetrahedron Lett.* **2000**, *41*, 4177.

[42] S. Sudhakar, J.-H. Hsu, Y.-H. Liu, Y. Wang, D.-S. Yang, B.-Y. Jin, T.-Y. Luh, *Silicon Chem.* **2002**, *1*, 403.

[43] J. Beckmann, A. Duthie, G. Reeske, M. Schürmann, *Organometallics* **2005**, *24*, 3629.

[44] S. G. Telfer, R. Kuroda, *Coord. Chem. Rev.* **2003**, *242*, 33.

[45] N. Krause, *Metallorganische Chemie: selektive Synthesen mit metallorganische Verbindungen*, Spektrum Akademischer Verlag GmbH, Heidelberg Berlin Oxford, **1996**.

[46] Q.-S. Guo, B. Liu, Y.-N. Lu, F.-Y. Jiang, H.-B. Song, J.-S. Li, *Tetrahedron: Asymmetry* **2005**, *16*, 3667.

[47] S. T. Chadwick, R. A. Rennels, J. L. Rutherford, D. B. Collum, *J. Am. Chem. Soc.* **2000**, *122*, 8640.

[48] Q.-S. Hu, V. Pugh, M. Sabat, L. Pu, *J. Org. Chem.* **1999**, *64*, 7528.

[49] S. J. Lee, W. Lin, *J. Am. Chem. Soc.* **2002**, *124*, 4554.

[50] J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1998**, *99*, 175.

[51] S. T. Tan, J. W. Kee, W. Y. Fan, *Organometallics* **2011**, *30*, 4008.

[52] C. I. Sainz-Díaz, A. P. Martín-Islán, J. H. E. Cartwright, *J. Phys. Chem. B* **2005**, *109*, 18758.

[53] a) S. E. Denmark, N. S. Werner, *J. Am. Chem. Soc.* **2008**, *130*, 16382; b) K. Hirabayashi, A. Mori, J. Kawashima, M. Suguro, Y. Nishihara, T. Hiyama, *J. Org. Chem.* **2000**, *65*, 5342; c) K. Hirabayashi, J. Kawashima, Y. Nishihara, A. Mori, T. Hiyama, *Org. Lett.* **1999**, *1*, 299; d) P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147; e) D. Steinhuebel, J. M. Baxter, M. Palucki, I. W. Davies, *J. Org. Chem.* **2005**, *70*, 10124.

[54] U. Schubet, C. Lorenz, *Inorg. Chem.* **1997**, *36*, 1258.

[55] M. Shi, K. M. Nicholas, *J. Chem. Res. Syn.* **1997**, 400.

[56] M. Lee, S. Ko, *J. Am. Chem. Soc.* **2000**, *122*, 12011.

[57] G. H. Barnes, N. E. Daughenbaugh, *J. Org. Chem.* **1966**, *31*, 885.

[58] J. Beckmann, D. Dakternieks, A. Duthie, R. C. Foitzik, *Silicon Chem.* **2003**, *2*, 27.

[59] a) K. M. Welsh, J. Y. Corey, *Organometallics* **1987**, *6*, 1393; b) J. Beckmann, S. L. Jänicke, *Eur. J. Inorg. Chem.* **2006**, *2006*, 3351; c) W. P. Neumann, K.-D. Schultz, R. Vieler, *J. Organomet. Chem.* **1984**, *264*, 179.

[60] A. Kunai, T. Sakurai, E. Toyoda, M. Ishikawa, *Organometallics* **1996**, *15*, 2478.

[61] A. Kunai, J. Ohshita, *J. Organomet. Chem.* **2003**, *686*, 3.

[62] L. H. Sommer, J. D. Citron, *J. Org. Chem.* **1967**, *32*, 2470.

[63] a) C. Ferreri, C. Costantino, C. Chatgilialoglu, R. Boukherroub, G. Manuel, *J. Organomet. Chem.* **1998**, *554*, 135; b) Y. Nagai, K. Yamazaki, I. Shiojima, *J. Organomet. Chem.* **1967**, *9*, P25.

[64] E. Langkopf, D. Schinzer, *Chem. Rev.* **1995**, *95*, 1375.

[65] M. J. Curtis-Long, Y. Aye, *Chem.-Eur. J.* **2009**, *15*, 5402.

[66] B. Marciniec, H. Lawicka, B. Dudziec, *J. Organomet. Chem.* **2008**, *693*, 235.

[67] C. H. Ko, D. Y. Jung, M. K. Kim, Y. H. Kim, *Synlett* **2005**, *2005*, 304.

[68] B. Peric Simov, F. Wuggenig, K. Mereiter, H. Andres, J. France, P. Schnelli, F. Hammerschmidt, *J. Am. Chem. Soc.* **2005**, *127*, 13934.

[69] P. F. Hudrlik, Y. M. Abdallah, A. K. Kulkarni, A. M. Hudrlik, *J. Org. Chem.* **1992**, *57*, 6552.

[70] a) J. Beckmann, D. Dakternieks, A. Duthie, F. Sheen Kuan, K. Jurkschat, M. Schurmann, E. R. T. Tiekink, *New J. Chem.* **2004**, *28*, 1268; b) J. Beckmann, D. Dakternieks, A. Duthie, F. S. Kuan, E. R. T. Tiekink, *J. Organomet. Chem.* **2003**, *688*, 56.

[71] Y. Ichinose, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2693.

[72] Y. Kavanagh, L. Ford, C. H. Schiesser, *Organometallics* **2011**, *30*, 4387.

[73] L. Ford, U. Wille, C. H. Schiesser, *Helv. Chim. Acta* **2006**, *89*, 2306.

[74] a) A. E. A. Hassan, A. F. El-Farargy, T. N. Mitchell, *J. Organomet. Chem.* **2011**, *696*, 2971; b) M. B. Faraoni, V. I. Dodero, J. C. Podestá, *ARKIVOC* **2005**, *12*, 88.

[75] J. H. Small, D. J. McCord, J. Greaves, K. J. Shea, *J. Am. Chem. Soc.* **1995**, *117*, 11588.

[76] J. B. Lambert, S. R. Singer, *J. Organomet. Chem.* **2004**, *689*, 2293.

[77] a) S. Napier, S. M. Marcuccio, H. Tye, M. Whittaker, *Tetrahedron Lett.* **2008**, *49*, 3939; b) N. Naga, Y. Kihara, T. Miyanaga, H. Furukawa, *Macromolecules* **2009**, *42*, 3454.

[78] J. S. Ritch, T. Chivers, *Angew. Chem., Int. Ed.* **2007**, *46*, 4610.

[79] a) M. Oba, Y. Watanabe, K. Iwai, H. Ohtaki, K. Nishiyama, *J. Organomet. Chem.* **2001**, *629*, 44; b) A. Sekiguchi, T. Yatabe, C. Kabuto, H. Sakurai, *Angew. Chem., Int. Ed.* **1989**, *28*, 757.

[80] a) K. J. Kulicke, B. Giese, *Synlett* **1990**, *1990*, 91; b) R. J. Fessenden, W. D. Kray, *J. Org. Chem.* **1973**, *38*, 87; c) H. Sakurai, T. Hirose, A. Hosomi, *J. Organomet. Chem.* **1975**, *86*, 197.

[81] W. Setaka, K. Sato, A. Ohkubo, C. Kabuto, M. Kira, *Chem. Lett.* **2006**, *35*, 596.

[82] A. González-Campo, C. Viñas, F. Teixidor, R. Núñez, R. Sillanpää, R. Kivekäs, *Macromolecules* **2007**, *40*, 5644.

[83] Y. Apeloig, in *The Chemistry of Organic Silicon Compounds., Vol. 1* (Eds.: S. Patai, Z. Rappoport), Wiley, **1989**, pp. 512.

[84] a) M. Ludwiczak, M. Majchrzak, B. Marciniec, M. Kubicki, *J. Organomet. Chem.* **2011**, *696*, 1456; b) P. H. Lee, S. W. Lee, D. Seomoon, *Org. Lett.* **2003**, *5*, 4963.

[85] P. A. Kraakman, E. T. J. Nibbering, W. H. De Wolf, F. Bickelhaupt, *Tetrahedron* **1987**, *43*, 5109.

[86] L. Pellerito, L. Nagy, *Coord. Chem. Rev.* **2002**, *224*, 111.

[87] a) F. Wurthner, C.-C. You, C. R. Saha-Moller, *Chem. Soc. Rev.* **2004**, *33*, 133; b) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem., Int. Ed.* **2004**, *43*, 1466; c) M. W. Hosseini, *Acc. Chem. Res.* **2005**, *38*, 313.

[88] a) D. Moon, M. S. Lah, *Inorg. Chem.* **2005**, *44*, 1934; b) D. Moon, J. Song, B. J. Kim, B. J. Suh, M. S. Lah, *Inorg. Chem.* **2004**, *43*, 8230; c) V. Sharma, R. K. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. B. Hursthouse, M. E. Light, *J. Organomet. Chem.* **2002**, *651*, 98.

[89] R. D. Rieke, S. E. Bales, P. M. Hudnall, G. S. Poindexter, *Org. Synth.* **1980**, *59*, 85.

[90] W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, **1996**.

[91] Y. Cui, O. R. Evans, H. L. Ngo, P. S. White, W. Lin, *Angew. Chem., Int. Ed.* **2002**, *41*, 1159.

[92] P. Wipf, J.-K. Jung, *J. Org. Chem.* **2000**, *65*, 6319.

[93] L.-Z. Gong, Q.-S. Hu, L. Pu, *J. Org. Chem.* **2001**, *66*, 2358.

[94] G. M. Sheldrick, *SHELXS-97, Programm for Crystal Structure Solution*, Universität Göttingen, **1997**.

[95] L. Farrugia, WinGX, V. 1.70.01, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[96] DIAMOND, *K. Brandenburg, C. I. G. Berndt* **2002**, *V2.1d.*

Appendix

Table 15. Crystal data and structure refinement for **30**, **39**, and **42**.

	30	**39**	**42**
Formula Sum	$C_{26}H_{30}O_2Si_2$	$C_{52}H_{56}O_6Si_4$	$C_{56}H_{64}O_4Si_4$
Formula weight , g · mol^{-1}	430.68	888.32	913.43
Crystal system	*orthorhombic*	*orthorhombic*	*tetragonal*
Crystal size, mm	0.30x0.30x0.30	0.29x0.08x0.05	0.20x0.10x0.04
Space group	$P2_12_12_1$	$P2_12_12_1$	$P4_12_12$
a, Å	9.056(2)	13.8171(18)	10.0012(2)
b, Å	14.051(2)	18.5214(18)	10.0012(2)
c, Å	19.401(3)	18.964(2)	51.325(3)
α, °	90	90	90
β, °	90	90	90
γ, °	90	90	90
V, Å^3	2468.7(8)	4853.12(10)	5133.8(3)
Z	4	1	4
ρ_{calcd}, g cm^{-3}	1.159	1.217	1.182
T, K	173	150	100
μ(Mo Kα), mm^{-1}	0.162	0.170	0.160
F(000)	920	1888	1952
2θ range, °	5.1 to 55.0°	2.4 to 25.2°	2.1 to 27.5°
index ranges	$-11 \le h \le 11$	$-16 \le h \le 16$	$-12 \le h \le 12$
	$-18 \le k \le 18$	$-19 \le k \le 22$	$-12 \le k \le 12$
	$-25 \le l \le 25$	$-22 \le l \le 22$	$-66 \le l \le 66$
Collcd Reflections	13650	36315	69524
Completeness to θ_{max},%	99.9	98.8	99.9
Reflections with $I > 2\delta(I)$	5672	8578	3518
Refined Parameters	283	559	305
GooF (F^2)	1.039	0.530	1.169
R_1(F) $I > 2\delta(I)$	5.22 %	5.26 %	7.38%
$wR_2(F^2)$ (all data)	13.75 %	12.50 %	14.14%
Flack Parameter	0.06(1)	0.00(2)	0(10)
Largest diff peak/hole, e Å^{-3}	0.26 / -0.20	0.17 / -0.20	0.63 / -0.80

List of Publications

Beckmann, J.; Rivas King, N. **Functionalized Silyl-BINOLs. Building Blocks for Chiral Sila-Macrocycles.** *GDCh-Wissenschaftsforum Chemie 2011*. Bremen, Germany. September 2011. Poster WÖ029 (Abstract 5076_0580).

Beckmann, J.; Rivas King, N. **Functionalized Silyl-BINOLs. Building Blocks for Chiral Sila-Macrocycles.** *XIV Norddeutsches Doktorandenkolloquium*. Hannover, Germany. September 2011. Oral Presentation V02 (Abstract book p. 10).

Beckmann, J.; Rivas King, N. **Functionalized Silyl-BINOLs. Building Blocks for Chiral Sila-Macrocycles.** *XVI International Symposium on Silicon Chemistry*. Hamilton, Ontario, Canada. August 2011. Poster 221 and Short Oral Presentation. (Abstract 221).