

Professor Tien-Yau Luh

A Tribute



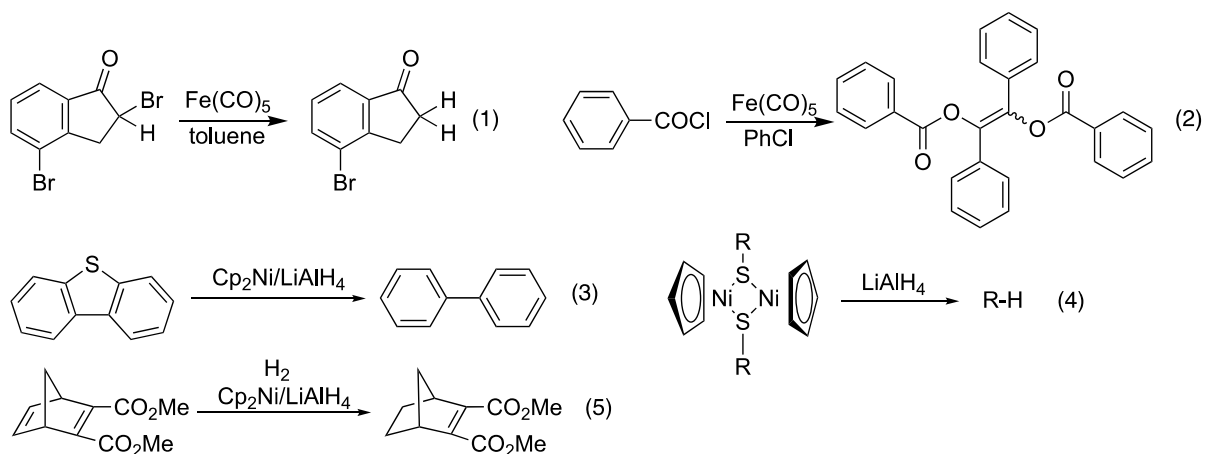
This special issue of Arkivoc (Archive for Organic Chemistry) is dedicated to Professor Tien-Yau Luh on the occasion of his 76th anniversary

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Tien-Yau Luh was born in Wuhan on Mainland China in 1946 immediately after the end of World War II. The civil war in China had just started and the country was in chaos. In January of 1948, his father, a civil engineer, moved the family from Shanghai to Taipei where Dr. Luh grew up in a peaceful atmosphere. He had wanted to study chemistry since the age of sixteen, and was admitted to the National Taiwan University (NTU) in 1963. Inspired by Professor Yau-Tang Lin, his organic chemistry teacher, he was determined to pursue an academic career in this area. After graduation, he spent a year in Professor Lin's laboratory at NTU working on natural product isolation before undertaking the one-year mandatory military service in Taiwan. In 1969, he joined the University of Chicago and in 1974 was awarded his Ph.D. working on physical organic chemistry (with Leon M. Stock). He spent two years at the University of Minnesota as a postdoc studying synthetic methodology and heterocyclic chemistry (with Paul G. Gassman) and in 1976 at the Chinese University of Hong Kong as a lecturer in chemistry. He was promoted to Senior Lecturer in the mid-eighties and returned to his Alma Mater in 1988 as Professor of Chemistry. Throughout the years at NTU, he has held several prestigious professorships such as National Chair and NTU Chair and won numerous awards in Taiwan. From the fall of 2001 to 2004, he was on secondment from the NTU to serve as Director and Distinguished Research Fellow of the Institute of Chemistry, Academia Sinica. He has published over 305 papers and two books, delivered more than 300 research seminars all over the world including the prestigious Schulich Lecture in Technion, Israel, the Yoshida Lecture at Kyoto and Osaka, Japan and JSPS Visiting Professorship. He has served as a member of advisory boards for *ChemComm*, *Chem. Eur. J.*, *Chem. Asian J.*, *Bull. Chem. Soc. Jpn.*, *Chem. Rec.*, *Tetrahedron*, *Tetrahedron Lett.*, and *J. Organomet. Chem. etc.* and organized the 11th OMCOS meeting in Taipei in 2001. He has been a member of the Chemical Society Located in Taipei, the American Chemical Society and is a fellow of the Royal Society of Chemistry.

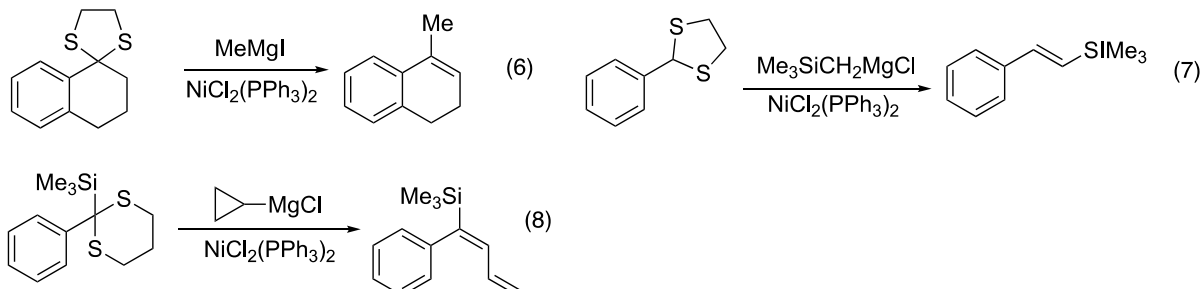
Beginning of Independent Research

Dr. Luh started his independent research in organometallic chemistry directed towards organic synthesis. In the beginning, he focused on metal carbonyl-mediated homolytic carbon-halogen cleavage reactions (Eqs 1 and 2).^{1,2} After a brief exploration of homogeneous organonickel reagents mimicking Raney nickel-promoted desulfurization (Eqs 3 and 4)^{3,4} and catalytic hydrogenation (eq 5),⁵ his group discovered four new kinds of transformation involving the dithioacetal functionality by the direct conversion of two carbon-sulfur bonds into two carbon-carbon bonds or a double bond.^{6,7}

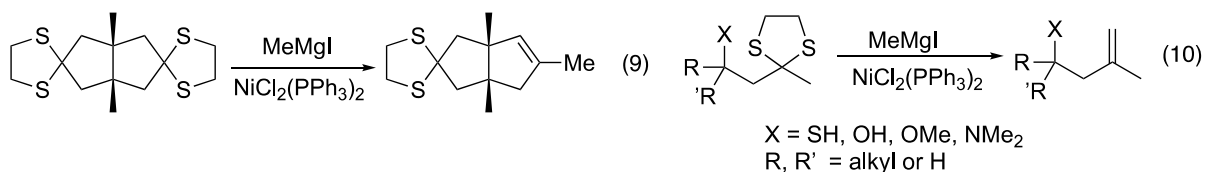


Dithioacetals in synthesis

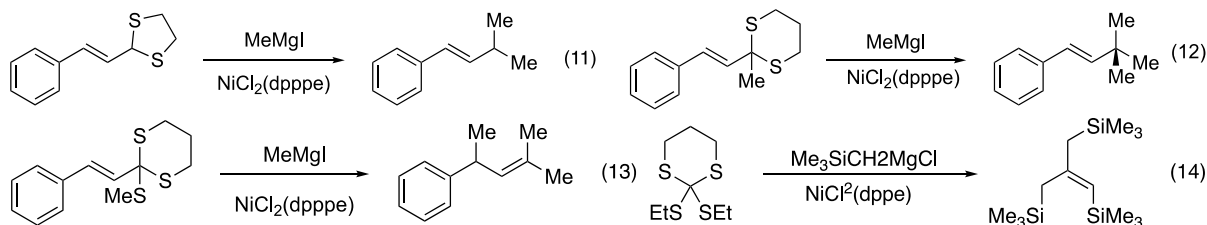
The $\text{NiCl}_2(\text{PPh}_3)_2$ -catalyzed reaction of benzylic dithioacetal with MeMgI affords the corresponding styrenes in good to excellent yields (Eqs 6 and 7).⁸ When a cyclopropyl Grignard reagent is used, aryl-substituted butadienes are obtained (Eq 8).^{9,10} The reaction is particularly useful for the synthesis of vinylsilanes or silyl-substituted butadienes (eqs 7 and 8).^{11,12}



Simple aliphatic dithioacetals do not undergo nickel-catalyzed olefination under these conditions. However, in the presence of a proximal heteroatom substituent (such as OR , NR_2 , SR , or a dithioacetal group), olefination of the aliphatic dithioacetal moiety takes place. Chelation with the nickel catalyst may proceed so that the two C-S bonds in the dithioacetal moiety can be activated sequentially to give the corresponding olefinic products (eqs 9 and 10).¹³⁻¹⁶

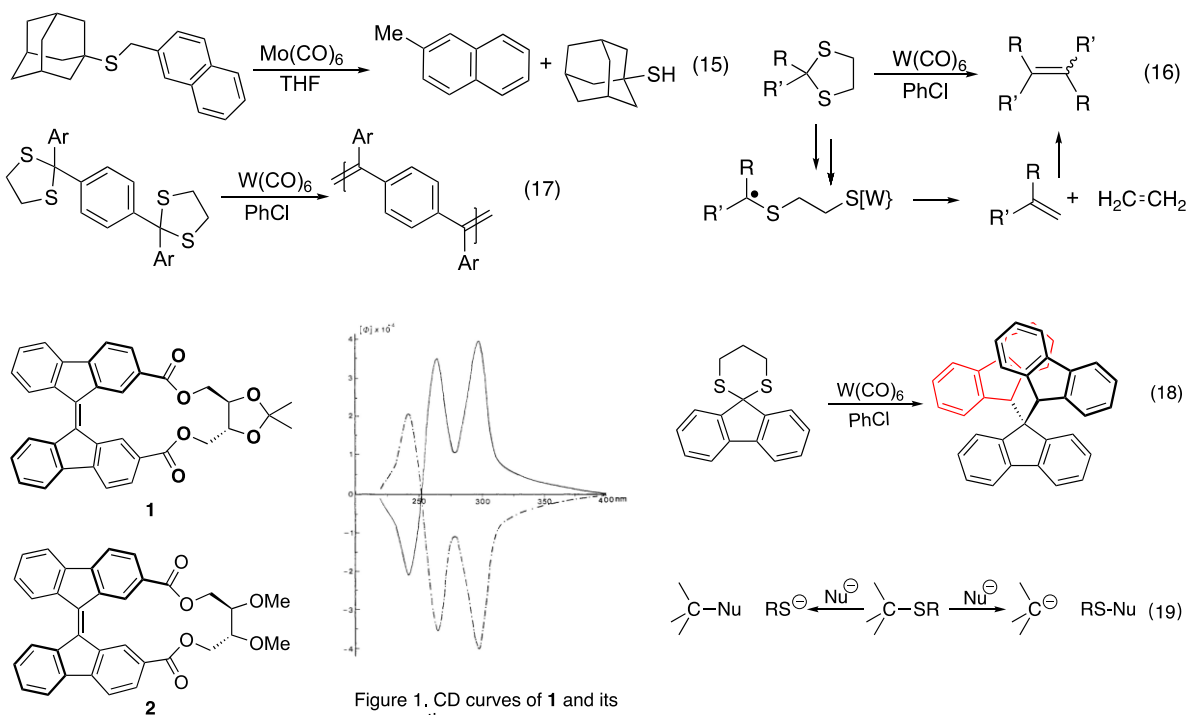


When the two Ph_3P ligands in the nickel catalyst are replaced by a bidentate ligand such as $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), the two carbon-sulfur bonds in allylic dithioacetals are converted into a geminal dimethyl group in excellent yield (eqs 11 and 12).^{17,18} Under similar conditions, allylic orthoesteres give the corresponding trimethylation products (eq 13).¹⁹ Nickel-catalyzed alkylative alkenation of tetrathioorthocarbonate with a Grignard reagent was also explored (eq 14).²⁰



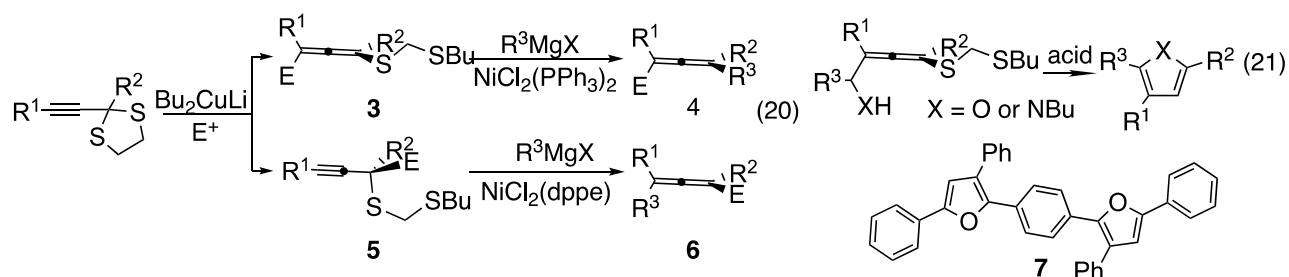
Group 6 metal carbonyls are known to promote homolytic cleavage of the C-S bond (eq 15).²¹ Thermolysis of dithiolanes in the presence $\text{W}(\text{CO})_6$ in chlorobenzene gives the dimeric alkenes in excellent yields (eq 16).²² The benzylic radical thus generated may undergo fragmentation to yield the thioketone intermediate and ethylene gas which is trapped as dibromoethane.²³ The reaction can occur both inter- or intramolecularly for the synthesis of polysubstituted phenylene-vinylenes (eq 17)²⁴ or optically active bifluorenylindenes **1**.²⁵ The CD curves for **1** and its enantiomer is shown in Figure 1. The racemization barrier for less strained **2** is 12 kcal/mol.

The six-membered dithiane does not lead to a similar fragmentation. The dimeric alkene is obtained in low yield and the trimer is isolated as the major product (eq 18).²⁶



Annulation of propargylic dithioacetals leading to furans or pyrroles

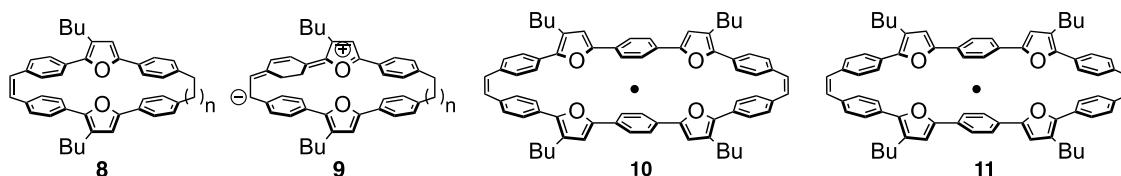
Carbon and sulfur have similar electronegativity. Hence, a nucleophile can either attack at carbon, generating a sulfide leaving group or at sulfur producing a carbanion leaving group (eq 19). Thus, propargylic dithioacetal is treated with Bu_2CuLi or BuLi followed by reaction with a hard electrophile to afford the corresponding allenyl thioether **3**, selectively. When a soft electrophile is used, the reaction gives the corresponding substituted alkyne **4**. Reaction of **3** or **4** with a Grignard reagent in the presence of a nickel catalyst gives the corresponding coupling products **5** or **6**, respectively (eq 20).^{27,28} Treatment of an allenyl carbinol with trifluoroacetic acid yields the corresponding substituted furan selectively. In a similar manner, annulation of an imine analog with $\text{BF}_3 \cdot \text{OEt}_2$ gives the corresponding pyrrole (eq 21).²⁹



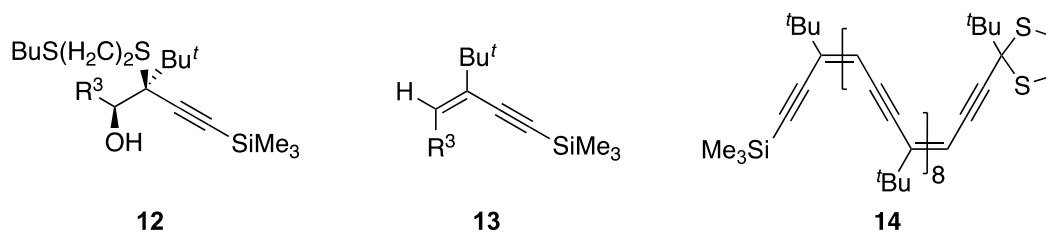
Furan-containing pentaaryl **7**, synthesized by annulation of terephthalaldehyde (*cf.* eq 21),³⁰ has been shown to be a very good hole-transporting material in electro-luminescent devices.^{31,32} The efficiency appears to be better than the widely used α -NPD(*N,N'*-bis-1-naphthyl-*N,N'*-bisphenyl-2,2'-dimethylbenzidine). Alternating benzene-furan oligomers up to the 37-mer are obtained by a bi-directional iterative annulation

reaction.³³ Combining annulation with various coupling reactions can furnish a sequence-controlled synthesis³⁴ of oligomers.^{33,35}

When the furan is incorporated into the strained cyclophanene system **8**, second-order optical nonlinearity is observed. Furan is an electron-rich heteroaromatic moiety. The bridging pyramidalized double bond can be considered as an electron withdrawing group. The $\mu\beta_{1.91}$ values measured by the EFISH method are $110\text{--}530 \times 10^{-48}$ esu for **8** ($n = 1\text{--}5$) in the same order (450×10^{-48} esu) as for DANS (4-dimethylamino-4'-nitrostilbene).³⁶ The dipolar character for **8** may arise from the contribution of the resonance structure **9**. It is striking to note that the $\beta_{1.32}$ value obtained by hyper-Rayleigh scattering for centro-symmetric **10** is 530×10^{-30} esu, which is comparable to that for **11** (506×10^{-30} esu). Presumably, the resonance contribution in **9** may desymmetrize the structure for **10**, resulting in optical nonlinearity.³⁷

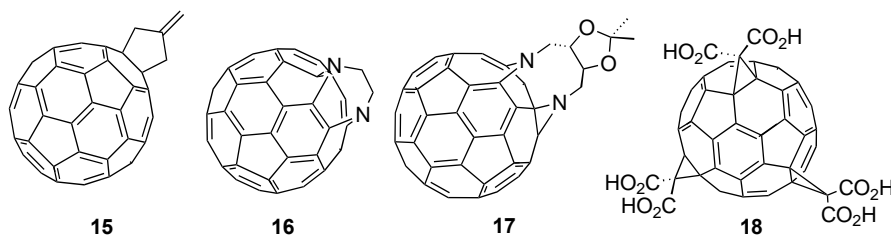


When R^1 is a sterically hindered *tert*-butyl group and R^2 is Me_3Si in eq 20, reaction of the propargylic dithioacetal with BuLi followed by an aldehyde gives the carbinol **12**, which is converted stereoselectively under Mitsunobu conditions into the corresponding enyne **13**.³⁸ This transformation has been used for the iterative synthesis of *Z*-oligodiacylenes **14**.³⁹



Derivatization of C_{60} and biomedical applications of water soluble C_{60} derivatives

After a brief exploration on the derivatization of C_{60} (e.g. **15**–**17**),^{40–42} Dr. Luh collaborated with biomedical specialists in the US and in Taiwan to examine the quenching of reactive oxygen species by water soluble C_{60} derivative **18**.⁴³ Compound **18** is capable of inactivating Dengue-2 virus⁴⁴ and inhibits *E. coli*-induced meningitis⁴⁵ and Group Streptococcus infection.⁴⁶ Notably, the presence of both hydrophilic and hydrophobic sites on the C_{60} scaffold in **18** appears to be critical for the biomedical reactivity both in vitro and in vivo.



At-Silylene-Divinylarene Copolymers

During the nineteen nineties, Dr. Luh shifted his research interests to materials chemistry and polymer science. He used his expertise in organic synthesis to design and synthesize various kinds of unusual polymers and study

their conformations and photophysical properties. As shown in eq. 22, vinyl silanes can readily be synthesized by the silylolefination reaction of benzylic dithioacetals.¹¹ This reaction can be used for the synthesis of bis-silyl hydrides **19**,⁴⁷ which undergo hydrosilylation^{48,49} with an alkyne in the presence of Wilkinson catalyst to form divinylsilane **20**, or with a bis-alkyne **21** to yield *alt*-silylene-divinylarene copolymers **24** or **25** (eq 22). Notably, either homopolymer **22** ($Ar^1 = Ar^2$) or regioregular alternating copolymers **26** or **27** ($Ar^1 \neq Ar^2$) can be obtained.

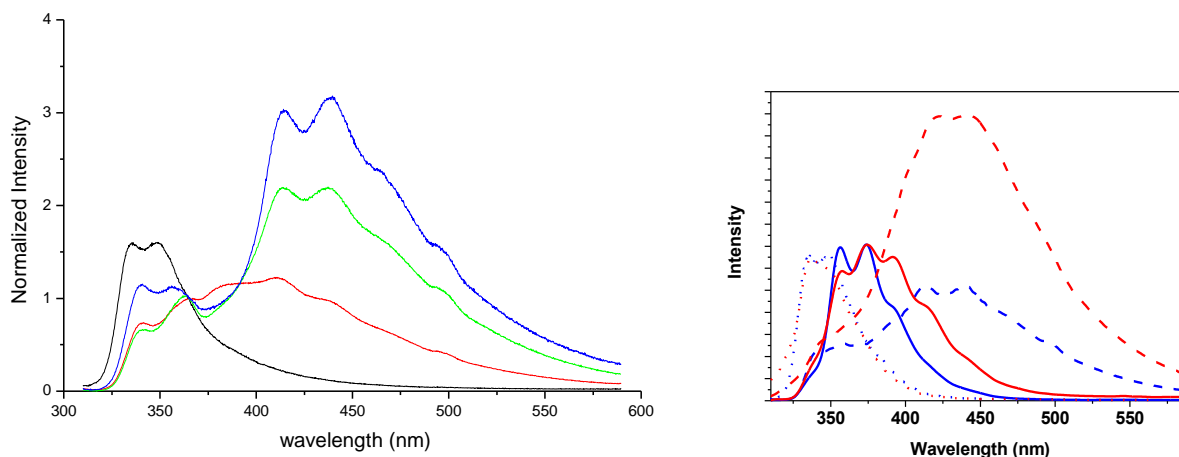
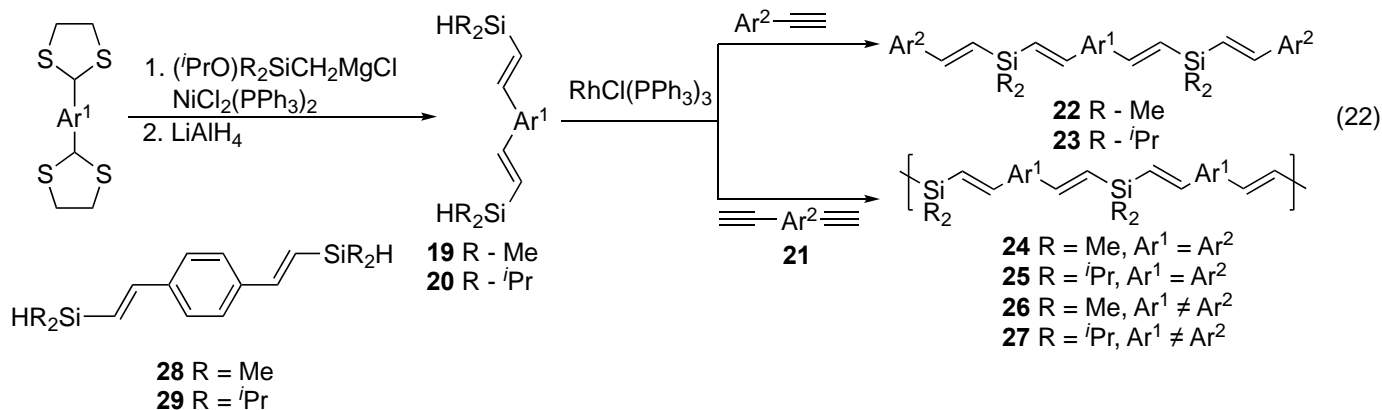
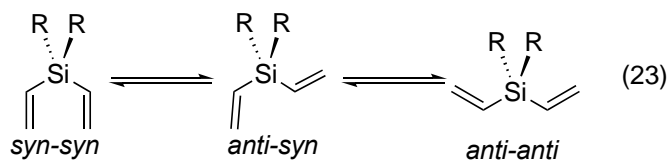
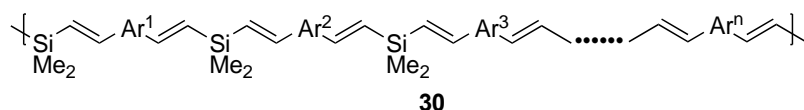


Figure 2. (a) Emission spectra of **24** of different molecular weights (M_n 2,200-red, 7,500-green, and 11,000-blue) in DCM ($\lambda_{ex} = 330$ nm). (b) Comparison of the emission spectra (R = Me-blue vs R = *i*Pr-red) of monomers **28** and **29** (dotted), dimers **22** and **23**, and polymers **24** and **25**.

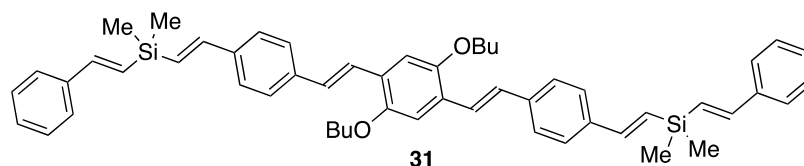
Due to the presence of an insulating tetrahedral silylene moiety to link the adjacent divinylarene chromophores, the polymers are highly folded. There is a possibility that two divinylarene chromophores may contact each other through space resulting in unusual photophysical properties. Figure 2a shows the molecular weight-dependent emission profiles of **24**. Interestingly, vibronic structure is observed in the emission in the blue light region and its intensity increases with increasing degree of polymerization. Replacement of two methyl substituents on silicon in **24** by isopropyl groups giving **25** was shown to enhance the intensity of emission around 420 nm, while the degree of polymerization for these two polymers is similar (Figure 2b).⁵⁰ The emission spectra of the corresponding monomers **28** and **29** and dimers **22** and **23** are also shown in Figure 2b. Presumably, the bulky isopropyl group exerts the Thorpe-Ingold effect to change the local conformation that would affect the folding behavior of the polymer (Eq 23).^{51,52} Accordingly, the chances for through-space interactions between two chromophores would be higher and the intensity of the emission profiles in the blue light region would be enhanced due to ground state interactions between chromophores.⁴⁷



Polymers **26** and **27** are binary systems, where Ar¹ can be a donor chromophore and Ar² is an acceptor chromophore. Fluorescence resonance energy transfer (FRET)⁵³ photoinduced electron transfer (PET)⁵⁴⁻⁵⁶ can occur readily. If the two acetylene moieties in **21** can be differentiated, this strategy could be extended towards oligomers having regioregular arrangements of multiple chromophores⁵⁷⁻⁶¹ and/or the sequence-controlled synthesis of polymers³⁴ without repeating units **30**.⁶²



A silyl-substituted terphenylene-tetravinylene **31** has been shown to have the brightest blue emission in an electroluminescent device.⁶³



Alt-Isopropylidene-4,β-styrylene copolymers

In the previous section, the silylene moiety in *alt*-silylene-divinylarene copolymers is considered an insulating spacer. The silicon atom has empty 3d orbitals which may form ππ-dπ interactions with the lone pair electron at the position α to silicon. Conjugation between the silylene motif with the heteroaromatic ring through the Si-heteroatom bond has been described.⁶⁴ By adopting the recently discovered tandem olefination dimerization of benzylic dithioacetals (eq 24),⁶⁵ polymer containing styrene motifs separated by isopropylidene spacers **33** were obtained from the nickel-catalyzed olefination of bis-dithioacetal **32** with MeZnI (eq 25).⁶⁶ The emission profiles of **33** of different m/n ratios are shown in Figure 3.

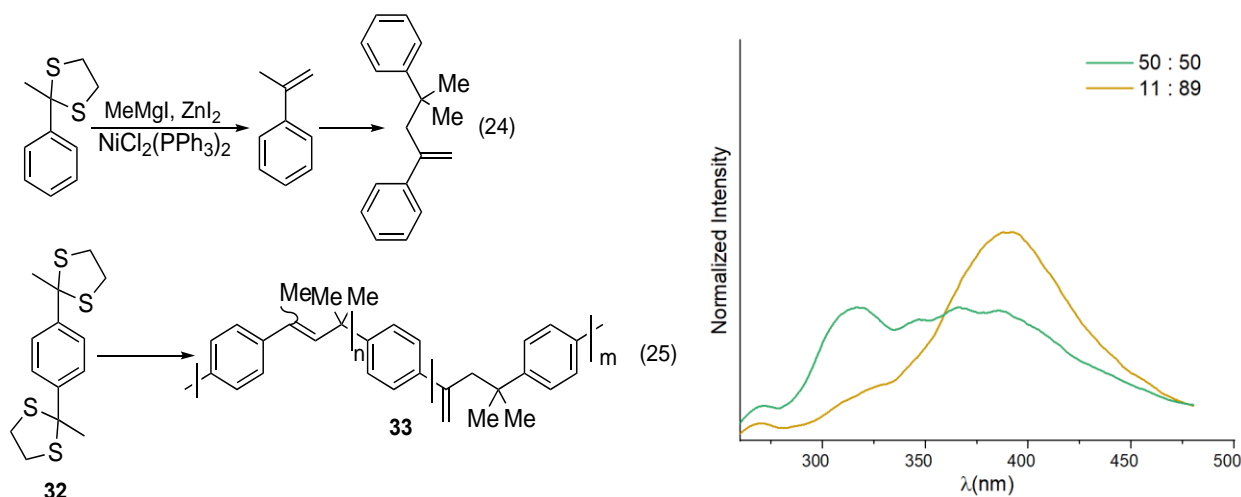
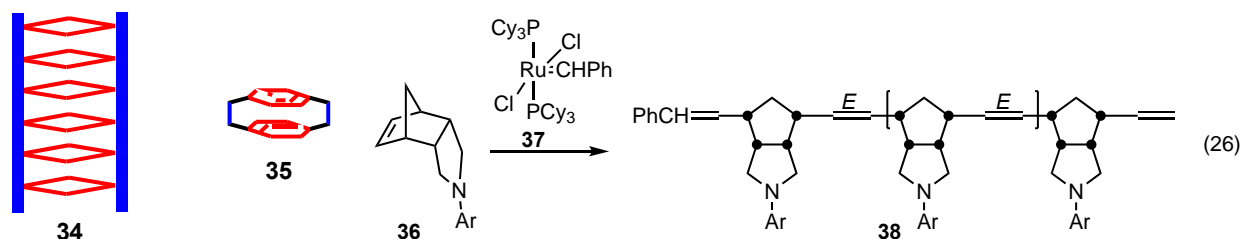


Figure 3. Emission profiles for **33** (m/n = 50/50 green; m/n = 11/89 earth) with λ_{ex} - 259 nm.

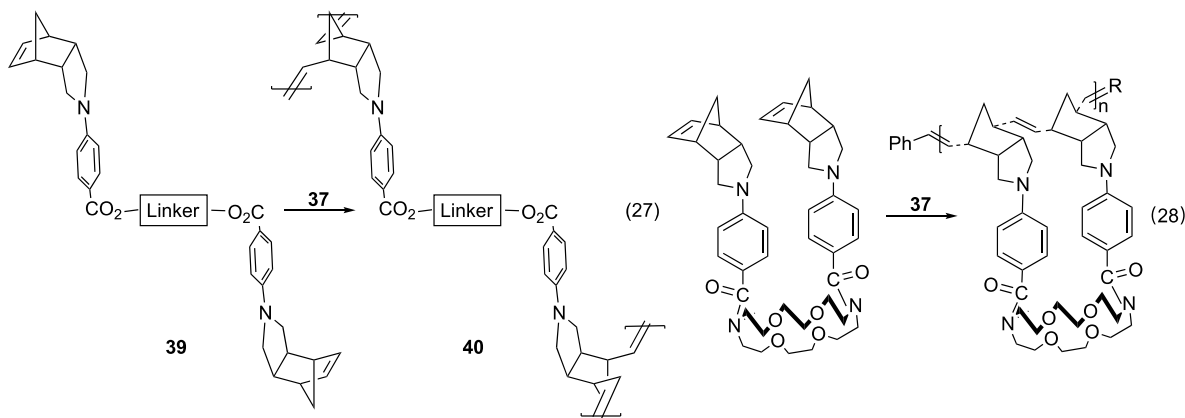
By comparing the pattern of emissions for **24** and **33**, both of which exhibit intrinsic emission from the monomeric chromophores, emissions due to interaction between adjacent chromophores and through space interactions between nonadjacent chromophores are observed. The role of the dimethylsilylene linker was similar to that of the isopropylidene motif as an insulating spacer. In other words, it seems less likely that there would be any conjugation between the silylene moiety and the π -system in these copolymers.

Ladderphanes

Ladderphane **34** is defined as multiple layers of cyclophanes **35** where the tethers are part of the polymeric backbones.⁶⁷⁻⁷⁰ It can be symmetric or unsymmetric depending on whether two polymeric strands are or are not, the same. A DNA molecule belongs to a special kind of unsymmetric isotactic ladderphane. Accordingly, stereochemical control, if any, might be essential to construct the polymeric strands in a ladderphane.



Ring opening metathesis polymerization (ROMP) of norbornene appended with N-arylpyrrolidene pendant **36** using the Grubbs first generation catalyst **37** gives the corresponding isotactic polynorbornene **38** with all double bonds in E-configuration and all pendants aligned in a similar direction (Eq 26). The conformation of the pendants was determined by ¹³C NMR and by nonlinear optical techniques (hyper Rayleigh scattering and EFISH).⁷¹⁻⁷³ Double stranded ladderphanes **40** are conveniently synthesized by **37**-catalyzed ROMP of bisnorbornenes **39** (Eq 27). The linkers have to be rigid and connected to the polymeric backbones *via* ester linkages. They can be oligoaryls,^{68,74} metallocycles,⁷⁵ three-dimensional organic⁷⁶ or organometallic^{67,77,78} species as long as the span is smaller than that of the monomeric unit. When a flexible linker like a crown ether is used, cyclopolymerization may take place to form a single stranded polymer having hammock-like pendant (Eq 28).⁷⁹



Ladderphanes can assemble on the highly ordered pyrolytic graphite (HOPG) surface to form a regular pattern of arrays. The scanning tunneling microscopic (STM) images of representative examples are shown in Figure 4. Dihydroxylation of **40** with OsO₄ in the presence of NMO gives the corresponding poly-alcohols **41** (eq

29). The STM image of **41** and the possible structure are shown in Figure 5 It is interesting to note that equal lengths of the polymer tend to aggregate together.

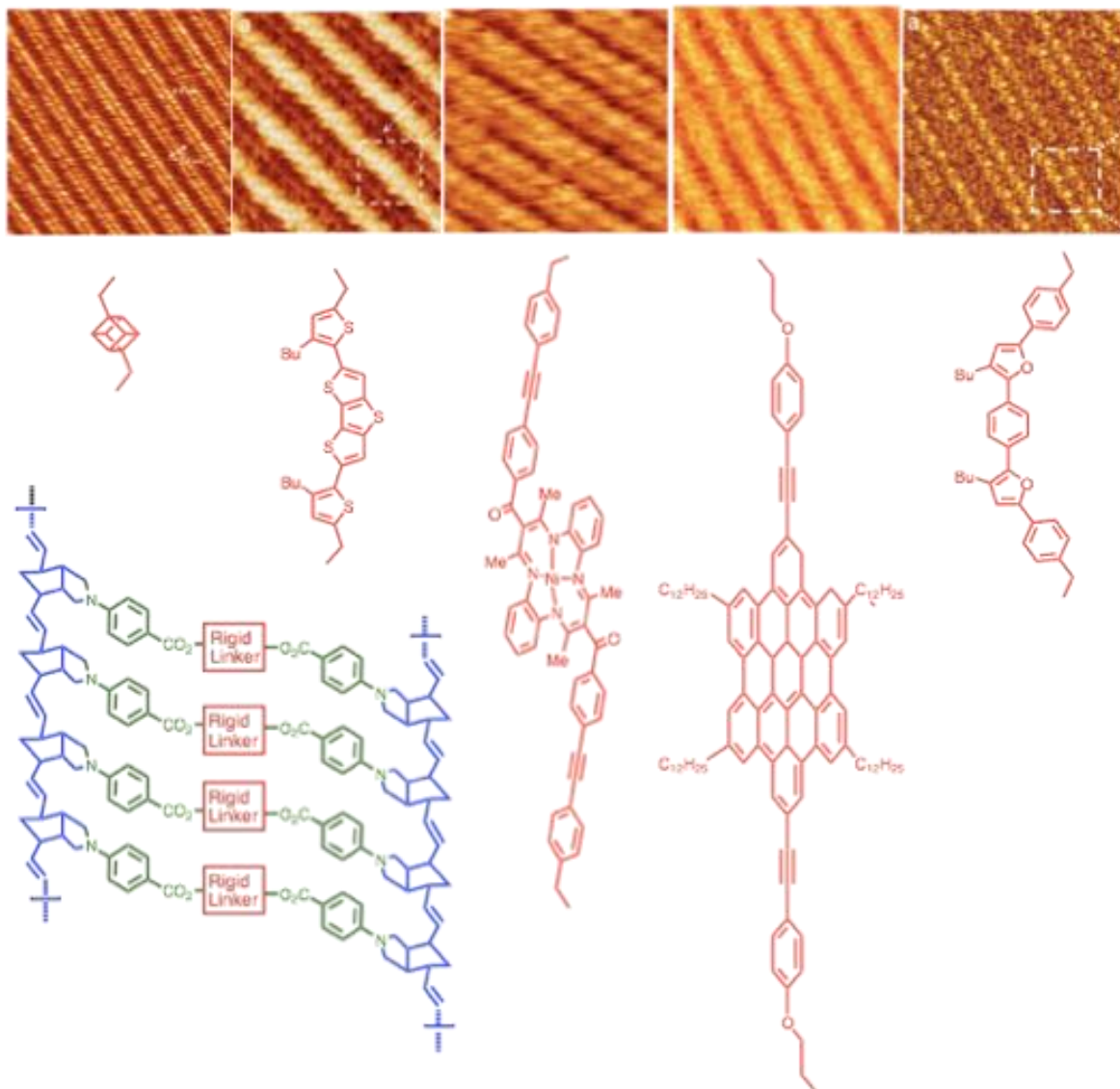
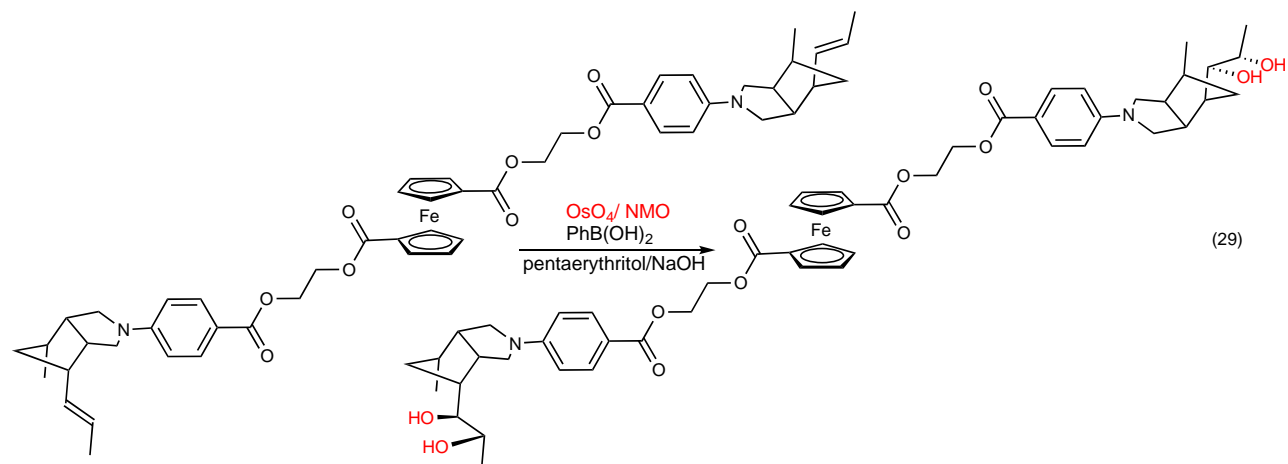


Figure 4. STM images of selected ladderphanes on HOPG.



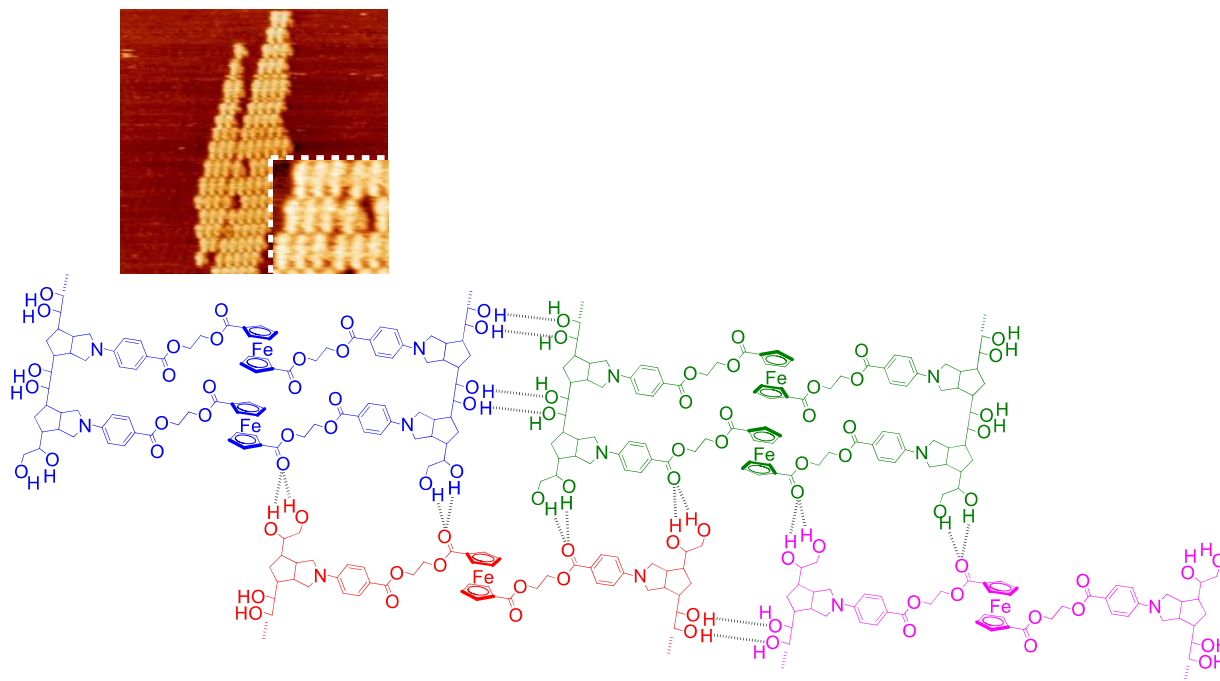


Figure 5. STM images of **41** and its possible structure around the terminals of four polymeric strip showing hydrogen bonding interactions.

Replication and sequential polymerization

The above-mentioned ladderphanes are symmetric. Two routes have been developed for the synthesis of unsymmetric ladderphanes **42** (Figure 6). The replication route uses a parent single stranded polymer **43** having pendants that are employed to react with small molecules **44** to form **45** that have another polymerizable group on each pendant for the second polymerization giving **42**.⁸⁰ Polymer **45** can also be obtained from the polymerization of **46** containing two orthogonal polymerizable groups.

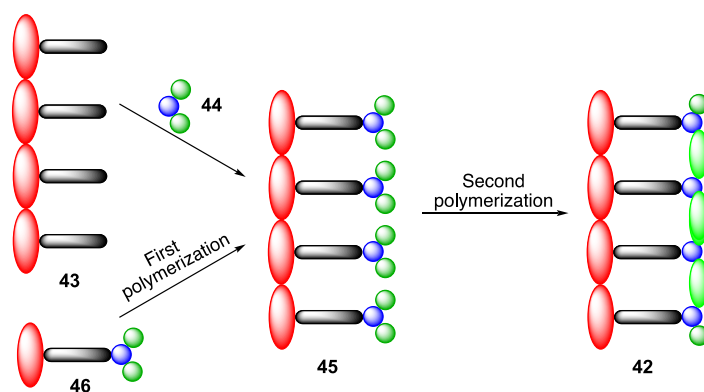
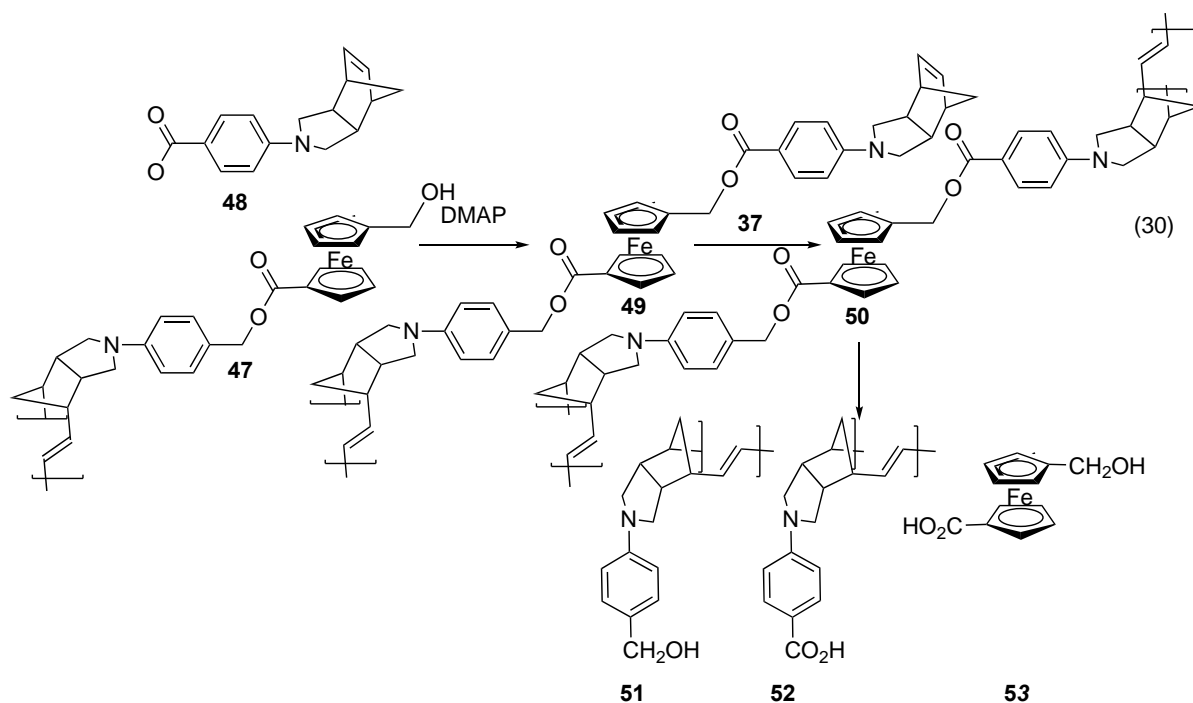


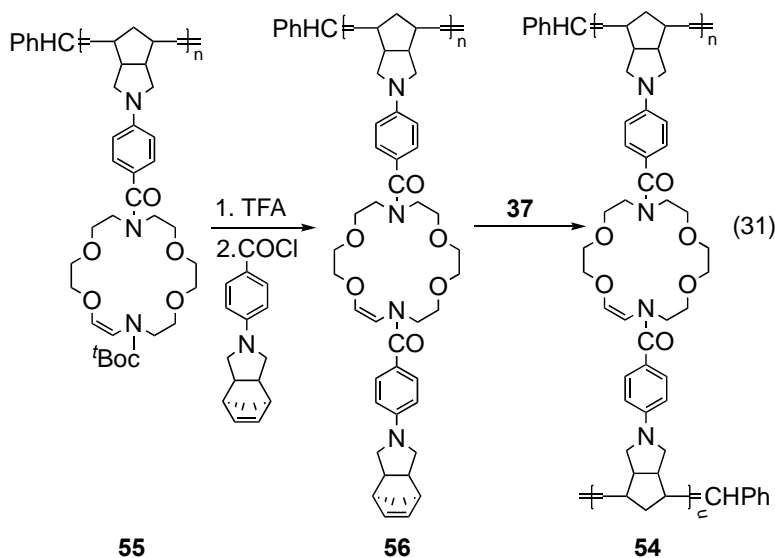
Figure 6. Replication and sequential polymerization for the synthesis of unsymmetric ladderphanes.

By using replication protocol, polynorbornene derivative **47** is esterified with **48** to afford **49** that is subject to **37**-catalyzed ROMP to give unsymmetric double stranded ladderphane **50**. Base mediated hydrolysis of **50** yields parent polynorbornene alcohol **51**, polynorbornene carboxylic acid **52** and ferrocene linker **53**.

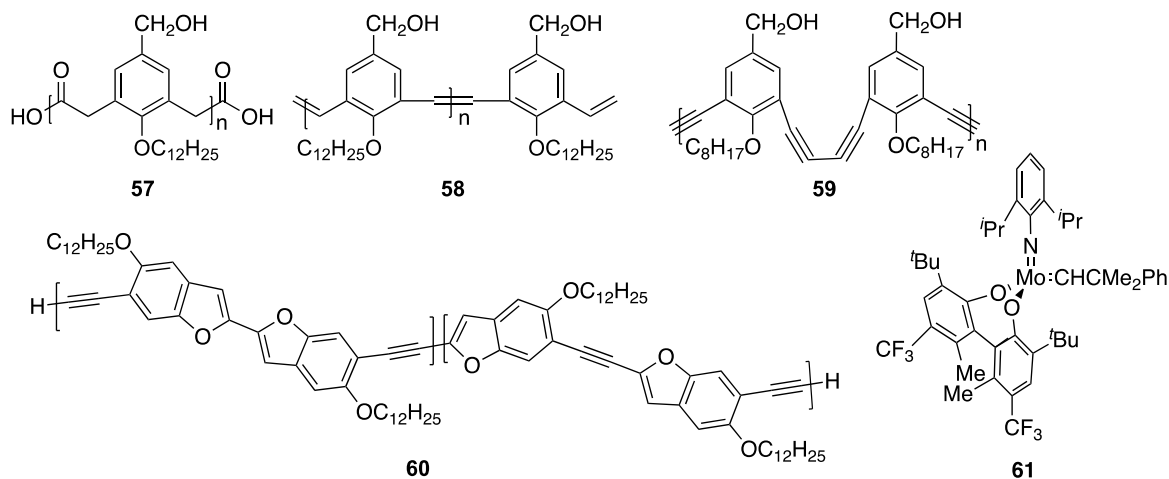
Notably, PDI for the methyl ester of **52** (1.3) is similar to that of **50** (1.2), and both polymers have the same isotactic stereochemistry (eq 30).⁸¹



As shown in eq 28, crown ether containing double stranded polymer **54** cannot be obtained directly from the bisnorbornene derivative. A replication protocol offers a possible route for the synthesis of **54**. Protected crown ether appended single stranded polynorbornene **55** is treated with trifluoroacetic acid to give the unprotected crown ether which is converted into the norbornene-substituted amide **56**. Double stranded polymer is obtained by **37**-catalyzed ROMP of **56** (Eq 31).⁸²

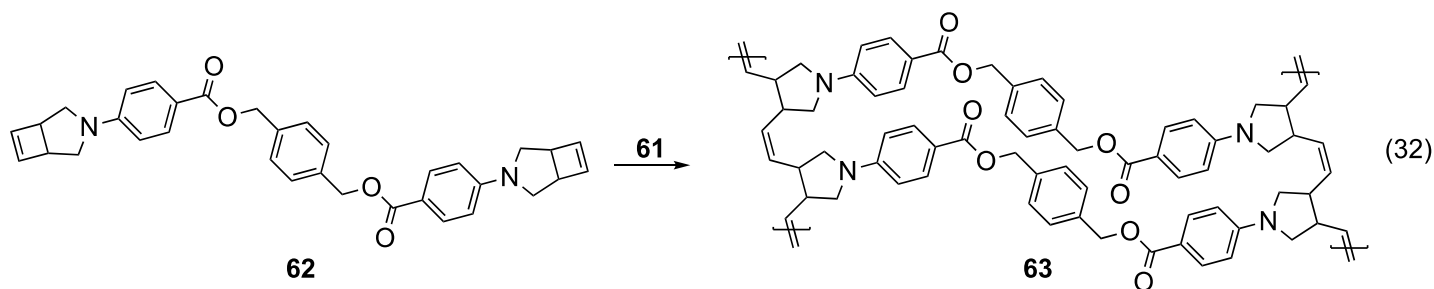


In line with sequential polymerization, several polymers **57-60** are obtained with retroactively narrow polydispersity (1.17-1.42). Notably, the second polymerization reactions use typical condensation polymerization (cross metathesis, Claisen condensation or Glaser oxidation and annulation etc.)^{83,84}



Miscellaneous metathesis reactions

The metathesis reaction mentioned in the previous section concerns mainly a norbornene-based reaction. Cyclobutene analogues, however, give a mixture of *E* and *Z*-double bonds in polycyclobutenes, but when the Grubbs catalyst **37** is used. In the presence of the Schrock-Hoveyda catalyst **61**, the double bonds in the formed polycyclobutenes are exclusively *cis*.⁸⁵ In a similar manner, polynorbornene with all double bonds in *Z*-configuration is obtained.⁸⁶ Ladderphane **63** is synthesized from **61**-catalyzed ROMP of **62** and all the double bonds are *cis* (Eq 32).⁸⁶



ROMP of a cyclopropane derivative has been shown to give the corresponding ring opening polymer stereoselectively.⁸⁷⁻⁸⁹ In line with the interests of TY's group in ladderphane chemistry, incorporation of a four-membered nitrogen heterocycle, namely the azetidine ring, spirally connected to the cyclopropane moiety forming **64**, is a unique design for the stereospecific ROMP of a cyclopropane. Treatment of **64** with a catalytic amount of **37** gives substituted poly(methylene-*E*-vinylene) **65** in addition to cyclohexadiene derivative **66**. The yields of **65** and **66** are over 95%. Notably, all double bonds in **65** are *trans* and **66** would be responsible for all *cis* double bonds formed during the reaction. A plausible mechanism to rationalize the formation of these products is outlined in Figure 7.

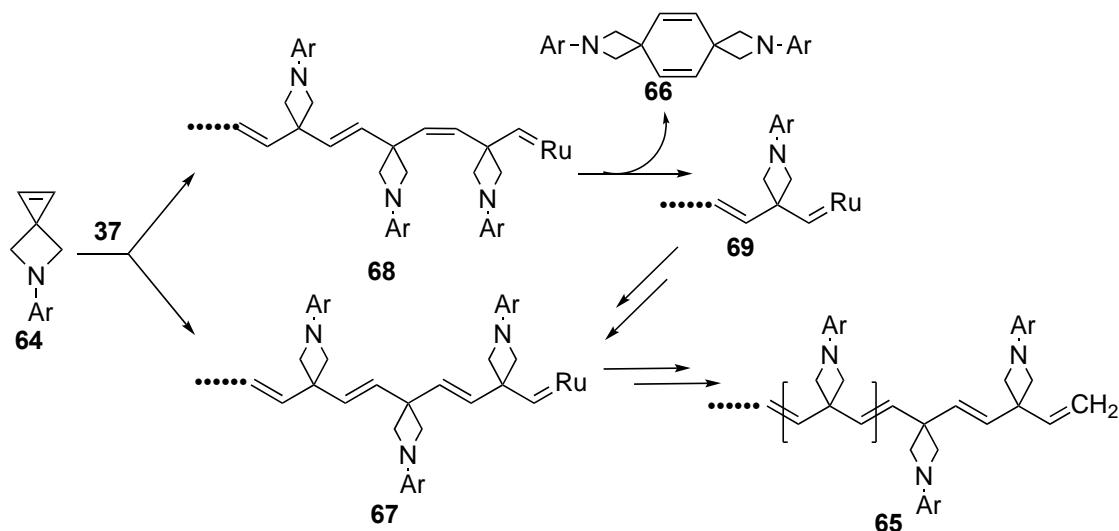


Figure 7. Self-repairing mechanism to the stereospecific formation of **65** from **37**-catalyzed ROMP of **64**.

When the metathesis reaction proceeds smoothly giving intermediate **67** having all double bonds in *E*-configuration, continuous elongation of the polymeric chain length leads to **65**. On the other hand, if the intermediate **68** is generated, the catalyst senses the conformational change around the reaction center. Ring closure metathesis immediately takes place to chop off cyclohexadiene **66** and regenerate intermediate **69** which contains all double bonds in *trans* configuration. Continuing metathesis polymerization would eventually lead to **65**. Such a self-repairing tactic has demonstrated the stereospecificity of the overall transformation shown in Figure 6.⁹⁰

In general, the ruthenium-catalyzed ROMP reaction is quenched by ethyl vinyl ether (EVE) to generate a Fischer-type carbene **70** which is much less reactive than ordinary alkyl or aryl-substituted ruthenium-carbene.⁹¹ They have been used sporadically in small molecules^{92,93} and in polymer synthesis^{94,95}. A systematic study on the relative reactivity for the ring opening cross metathesis of different strained cycloalkenes with a large excess of EVE for the synthesis of electron rich alkenes is shown in Figure 8.⁹⁶ The t_{50} is defined as the time required for the consumption of 50% of the starting material.

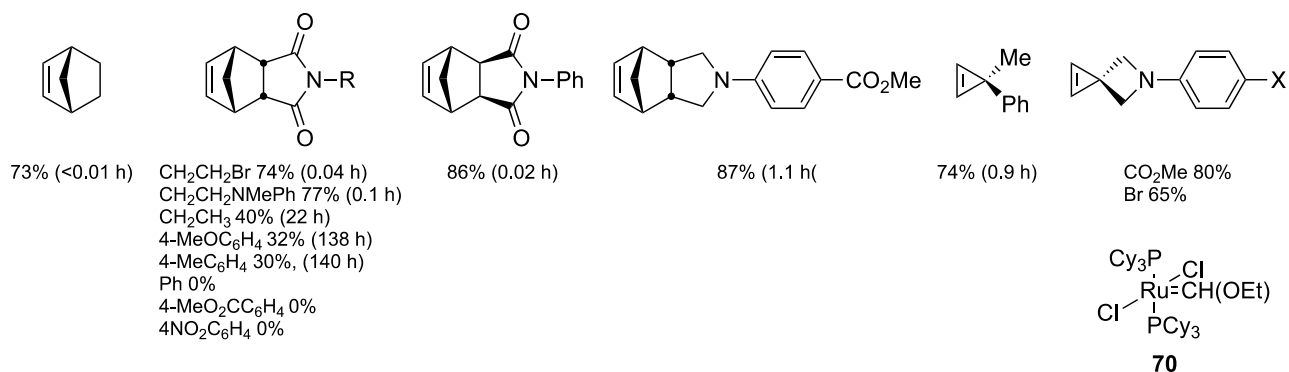


Figure 8. Yield (t_{50}) of the **70**-catalyzed ROCM of strained cycloalkene with excess EVE.

Education and Teaching

Since 1976, over 165 young talents have worked in Dr. Luh's laboratories as post-docs, Ph.D., M.S., undergraduate students, research or teaching assistants. Now, 62 of them hold faculty positions all over the world and some have been highly visible in the chemical community. Many of those working in the industrial sector have also obtained influential positions.

Being a professor at a university, teaching is an integral part of an academic career. In the past forty some years, he has spent many of his teaching hours to design a syllabus in organic chemistry for bio-orientated students. Many of his ideas have been included in an article recently published in *Trends in Chemistry*.⁹⁷

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