METHODS FOR THE SYNTHESIS OF OLIGOTHIOPHENES

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Abstract – Methods of synthesis of oligothiophenes using thiophene
lithium, copper, magnesium, zinc, boron, silicon and tin derivatives
and also cyclization reactions have been reviewed.

1. INTRODUCTION

Among the various π-conjugated organic materials[1-5] for which the control of the solid-state characteristic is of utmost importance for the industrial applications are α-conjugated oligothiophenes and polythiophenes.[6-13] Owing to their electrical conductivity and field effect mobility, photochromic properties and high photoluminescence efficiencies oligothiophenes are emerging as promising organic materials for application in field effect transistors, diodes and electroluminescent devices. Thiophene-based materials are particularly attractive, as these compounds are characterized by an excellent environmental and thermal stability. The many interesting and novel functionalized oligothiophenes that have been reported commonly require separate synthetic strategies. Metal-mediated coupling reactions (such as Kumada, Suzuki – Miyaura and Stille) leading to the formation of carbon-carbon bond have become useful and convenient methods for the synthesis of oligothiophenes. In present review we summarized recent synthetic investigations for the synthesis of oligothiophenes.

2. OXYDATIVE COUPLING

One of the most useful synthetic pathways for the preparation of oligothiophenes is the oxidative coupling of thienyllithium derivatives in the presence of $CuCl_2$ or $Fe(acac)_3$ (Scheme 1).[14-18] As a rule these reactions proceed in high yields. It is worth noting that in some cases this procedure is much simpler than those (cross-coupling of Grignard, zinc, or trialkyltin derivatives with bromothiophenes) developed so far.[19] One of the longest oligothiophenes – octadodecylhexadecithiophene – was obtained in 19 % yield after coupling of the corresponding lithiooctithiophene with $CuCl_2$.[20] However, in spite of the great advantage, this process has some restrictions. Thus, oxidative coupling of thienyllithium compounds can be only used for the synthesis of symmetrical oligothiophenes with even amount of the thiophene

rings (bithiophenes, quaterthiophenes, and sexithiophenes).[14-18] This method excludes the synthesis of thiophene-based materials with various functional groups reacting with lithiation agents and has been used for preparation of oligothiophenes with alkyl, trialkylsilyl, aryl, and alkylsulfanyl substituents.[14-18]
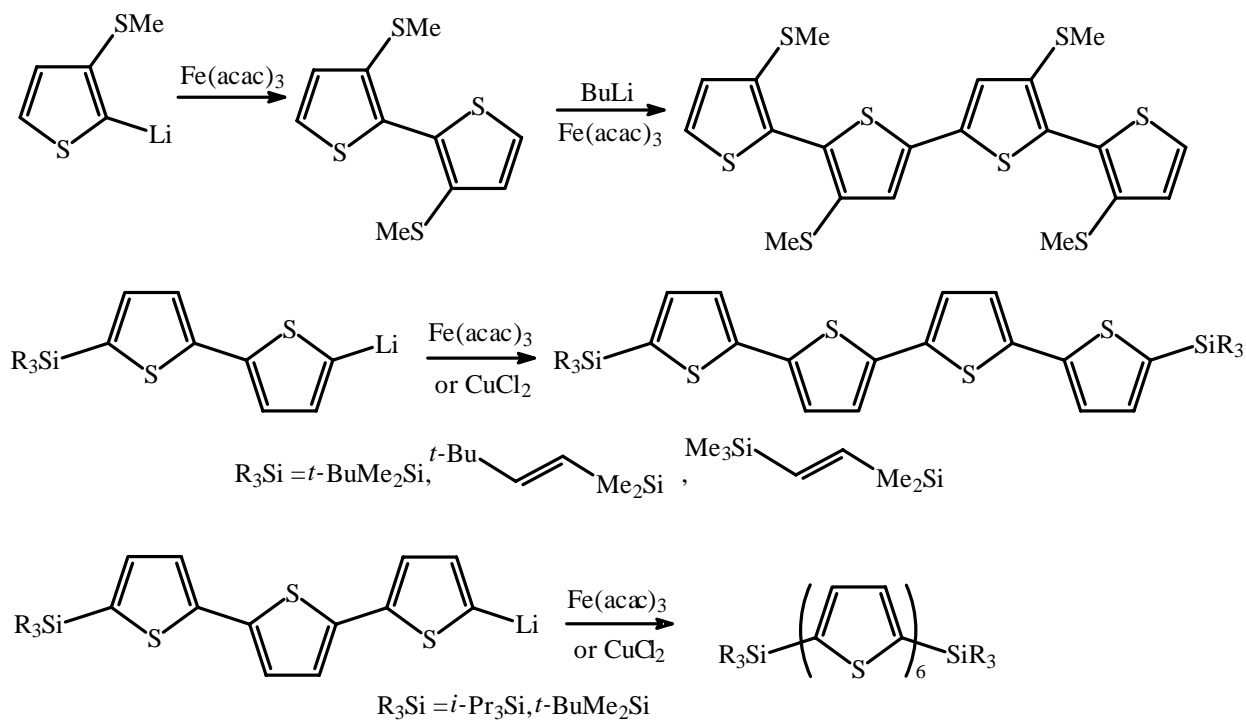
Scheme 1

Ferric chloride ($FeCl_3$) was successfully used for synthesis of polythiophenes from α−unsubstituted thiophenes. It was found that 3-butylsulfanyl-2,2'-bithiophene converts into tris(butylsulfanyl)sexithiophene in 70% yield by oxidative coupling with $FeCl_3$ in $CHCl_3$–$MeNO_2$ (Scheme 2).[21]
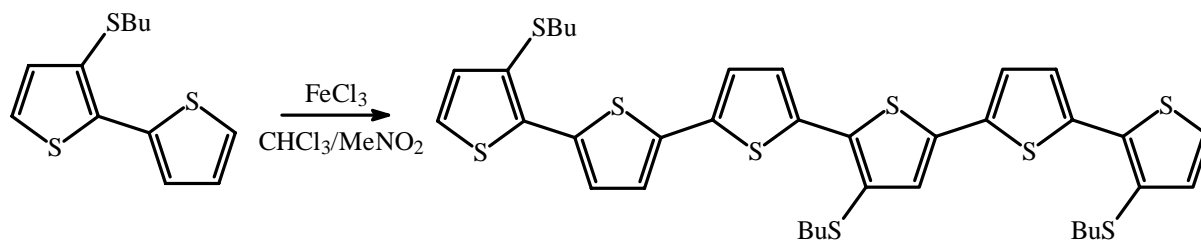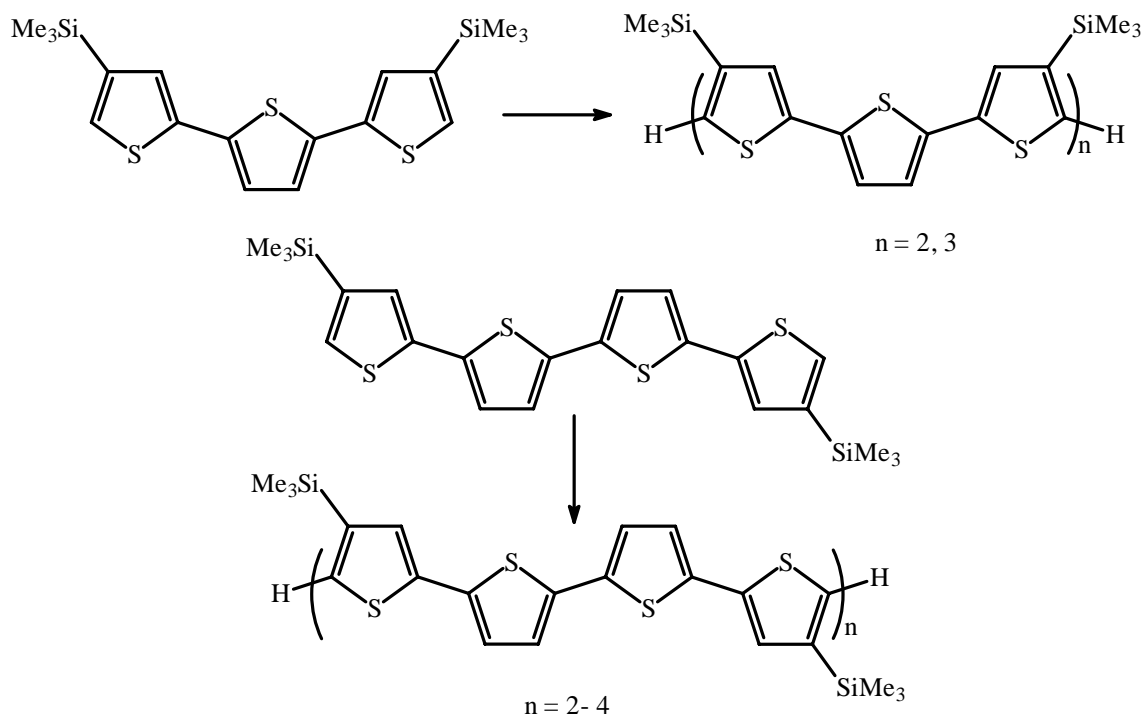

Scheme 2

The formation of one isomer from possible four that could in principle derive from starting bithiophene can be explained by considering the deactivation effect of the 3-butylsulfanyl group on the 5-position of thiophenes and bithiophenes.[21]

Cerium(IV) oxidative dimerization of 4,4"-bis(trimethylsilyl)-2,2':5',2"-terthiophene and the quaterthiophene analog has been studied (Scheme 3).[22] Coupling of terthiophene with ceric ammonium sulfate as oxidizing agent gives the mixture of sexithiophene (48 %) and nonithiophene (11 %) along with higher oligothiophenes. Under the same conditions quaterthiophene yields octithiophene (66 %),

dodecithiophene (4-7 %) and hexadecithiophene (0.5-2 %). Octithiophene was oligomerized on reaction of cerium sulfate in dichloroethane at room temperature to correspondent sexadecithiophene (35 %) tetracosithiophene (11 %) and a mixture of higher isomers.
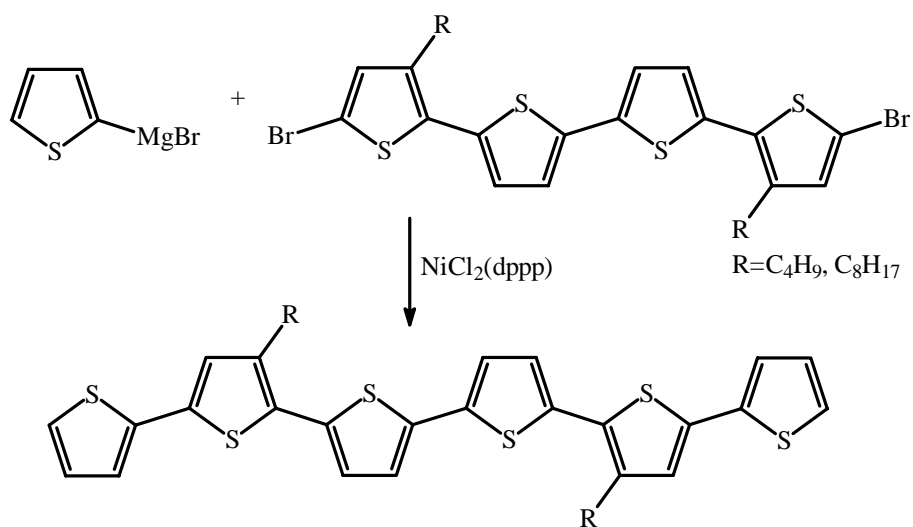

Scheme 3

3. CROSS-COUPLING OF THIENYLMAGNESIUM BROMIDES WITH BROMOTHIOPHENES

Transition metal-catalyzed methods for the synthesis of oligothiophenes have been developed within last years; among these the nickel-catalyzed coupling of Grignard compounds with bromothiophenes represents the most direct procedure. This, so-called Kumada coupling generally affords good yields and high purity of products.[23-27]

Bi-, ter-, and quaterthiophenes with a range of alkyl substituents at specific sites can be prepared by this method (Scheme 4).[23-27] For dimeric and trimeric products the yield is almost quantitative, it decreases for quaterthiophenes to 30-40%.

The same method was used for synthesis of silyl-capped oligothiophenes[28, 29] and phenyl-capped bi-, ter-, quarter-, and quinquethiophenes (Scheme 5).[30]

Bi- and terthiophenes bearing terminal phenyl groups were prepared in diethyl ether, while for synthesis of tetra- and pentamers anisole was used as solvent. This is due to the starting materials 5,5'-dihalo-2,2'-bithiophene and 5,5''-dihalo-2,2':5',2''-terthiophene are both barely soluble in diethyl ether, but can readily be dissolved in anisole. On the contrary to bi- and terthiophene, the quantitative formation of quaterthiophene (40 %) and quinquethiophene (30 %) was not achieved. The reason for this would be that

a monohalide generated from the equimolar coupling reaction precipitates and does not react with the second molecule of Grignard reagent.

In spite of the fact that Kumada method is impractical for the preparation of oligomers containing more than five rings, some sexithiophenes were obtained by this route in 59 (R=Bu) and 25% (R= C_8H_{17}) yields (Scheme 6).[31]

Scheme 4

n = 1 - 3

Scheme 5

Scheme 6

Oligothiophenes with functional aldehyde group can be synthesized after transformation of aldehyde substituents to acetal and subsequent condensation with thienylmagnesium bromide in the presence of $NiCl_2(dppp)$.[32]
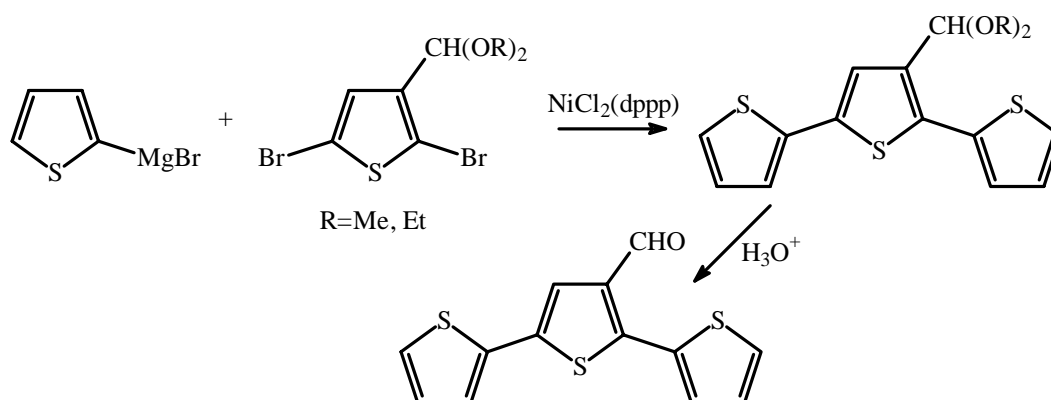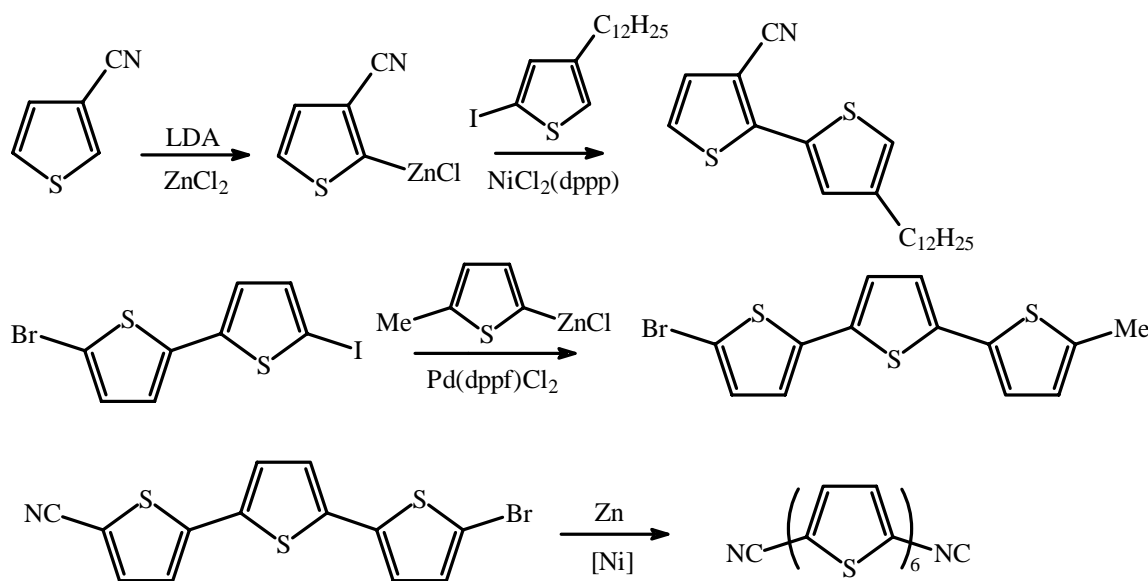

Scheme 7

The acetal group is easily hydrolyzed to give aldehyde-containing oligothiophene. However, attempts to perform the Kumada reaction on a larger scale resulted in poor yields and complications in isolating of pure product because of incomplete reaction of dibromide. Application of Suzuki – Miyaura method avoids these complications and gives the target terthiophene aldehyde in multigram quantities in high yield (Scheme 7).[32]

4. CROSS-COUPLING OF THIENYLZINC CHLORIDES AND BROMIDES WITH BROMOTHIOPHENES

In some cases cross-coupling of thienylzinc chlorides with bromothiophenes (Negishi coupling) was chosen for synthesis of oligothiophenes instead of Kumada method,[16,33,34] for example due to

incompatibility of cyano group with Grignard reagents. Selective lithiation of 3-cyanothiophene with LDA is followed by transmetallation with $ZnCl_2$ to give 3-cyanothienyl-2-zinc chloride, which is then coupled with 2-iodo-4-dodecylthiophene using $NiCl_2(dppp)$ as catalyst to give bithiophene in 33% yield (Scheme 8).[33] The same procedure was applied for preparation of 3-phenylsubstituted bithiophenes.[32] α,ω−Dicyanosexithiophene was obtained in 46 % yield by the addition of 5-bromo-5´´-cyanoterthiophene to the homocoupling catalyst $(Ph_3P)_3Ni$, generated *in situ* from nickel dichloride and triphenylphosphine, and zinc (Scheme 8).[34]
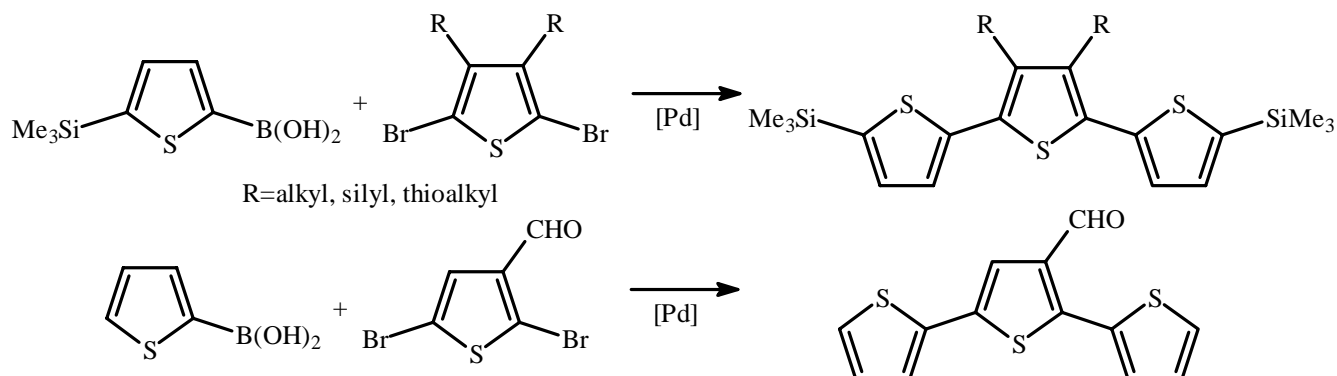

Scheme 8

Different reactivity of thienylzinc derivatives relative to iodo- and bromothiophenes was used for the synthesis of monobromooligothiophenes (Scheme 8) and oligothiophenes-functionalized 9,9'-spirobifluorene.[35]

5. SUZUKI – MIYAURA COUPLING

The synthesis of thiophene oligomers is generally carried out by reacting thienyl bromides or iodides with organoboron derivatives in the presence of palladium catalysts.[32,36-40] This method was successfully used for synthesis of oligothiophenes with alkyl, silyl, thioalkyl, and formyl substituents (Scheme 9).

Recently it has been shown that the application of microwaves is very efficient for the preparation of oligothiophenes *via* Suzuki-Miyaura coupling under mild conditions. 2,5´-Dibromo-3,3´-dimethyl-2,2´-bithiophene was coupled with 2-thiophene boronic acid under the action of microwaves using water/toluene as a solvent, a quaternary salt (Bu_4NBr), K_2CO_3 and $Pd(OAc)_2$ as the catalyst. The reaction afforded quaterthiophene in 70% yield within a reaction time not exceeding 5 min. In the same conditions sexithiophene was obtained in 66% yield. In this case, besides the starting material, the reaction mixture

also contained some monobromoquinquethiophene that did not react further with 2-thiopheneboronic acid even on changing reaction conditions and time (Scheme 10).[41]
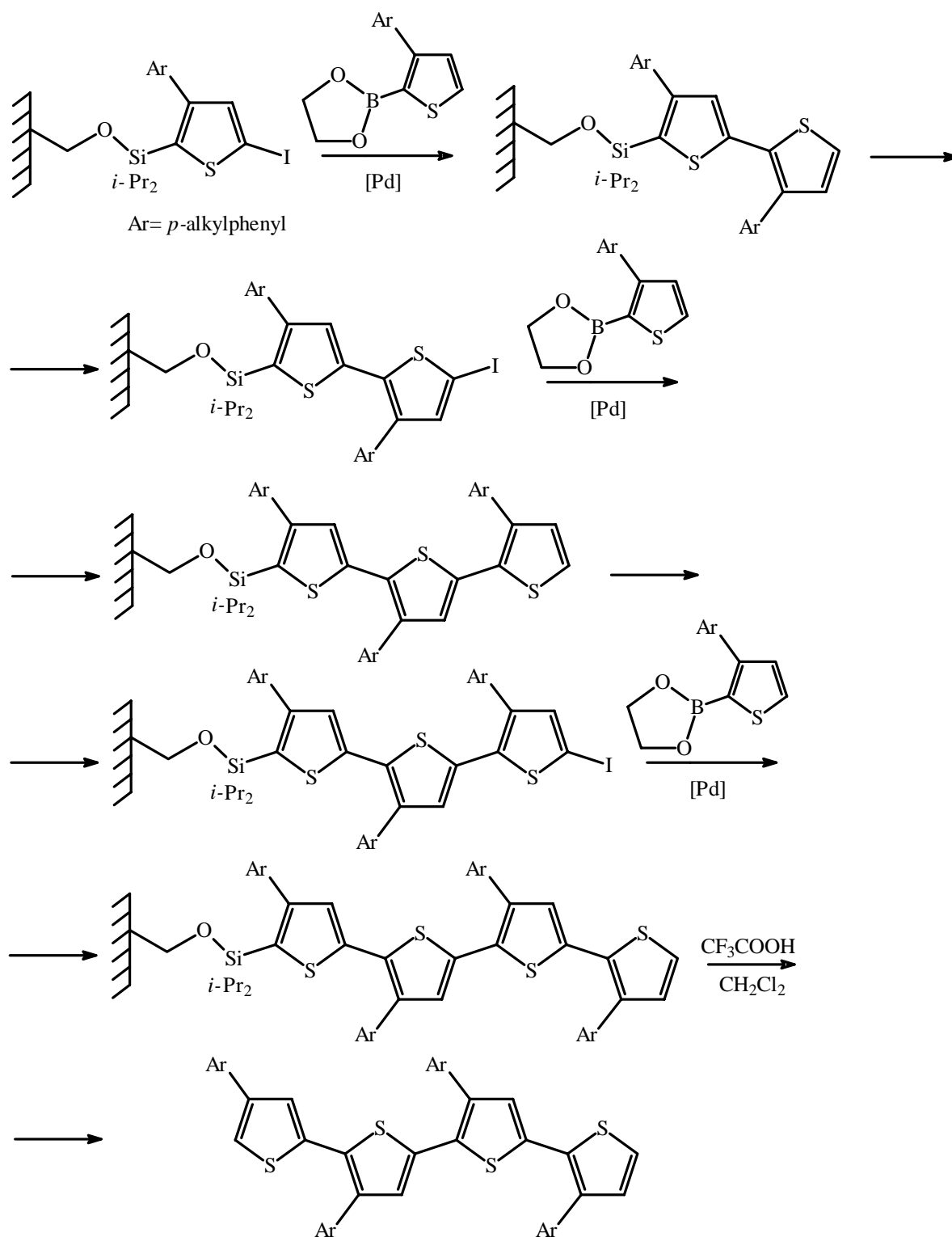

Scheme 9
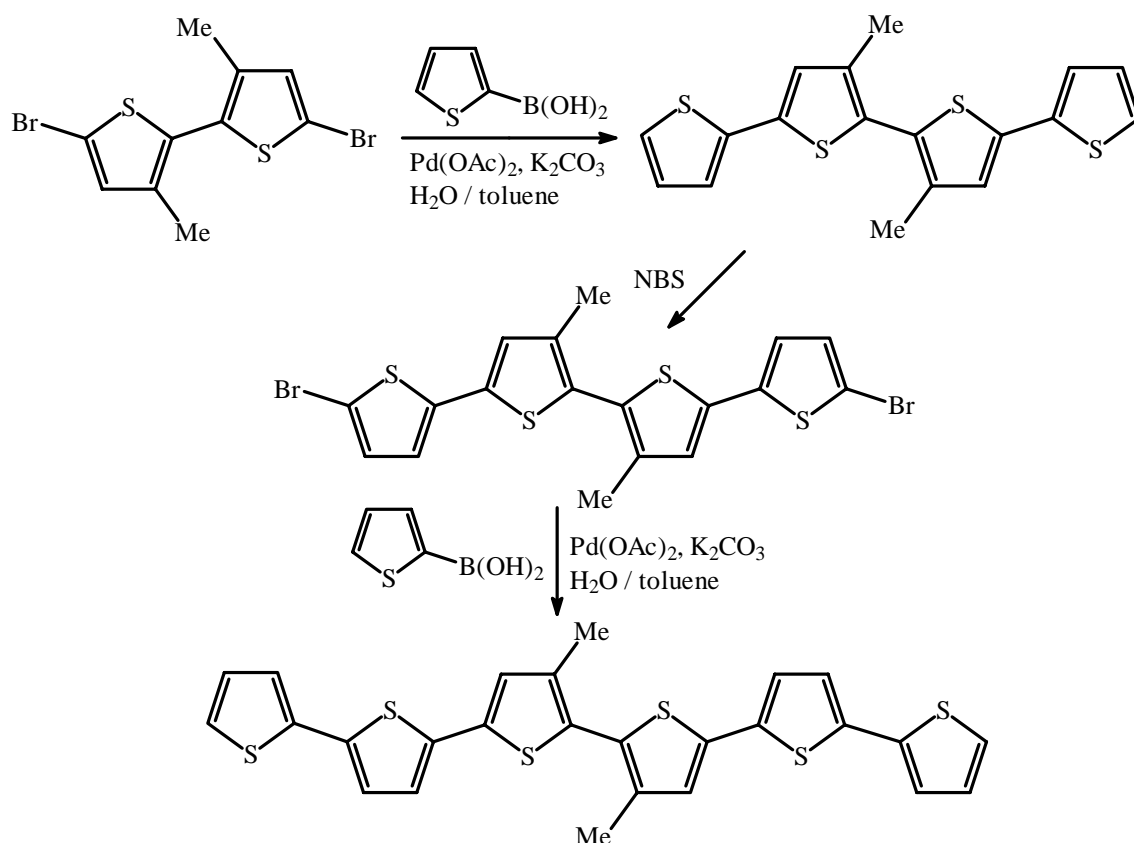
Scheme 10

The regioregular solid-phase synthesis of head-to-tail oligo(3-p-alkylphenylthiophenes) anchored to the hydroxymethylated polystyrene is based on the stepwise addition approach.[42-44] Oligomer growth is achieved by an iterative sequence of iodination and Suzuki-Miyaura cross-coupling with thiophene boronic esters. The coupling for the preparation of dimeric, trimeric and tetrameric products required a (Ph$_3$P)$_4$Pd catalyst. The first thiophene group was loaded into hydroxymethylated polystyrene by reaction of 2-chlorodiisopropylsilyl-3-(p-alkylphenyl)thiophene in the presence of imidazole. Finally, ter- and quaterthiophenes were liberated from the resin by treating the derivatized polymer support with 10 % trifluoroacetic acid in methylene chloride (Scheme 11).
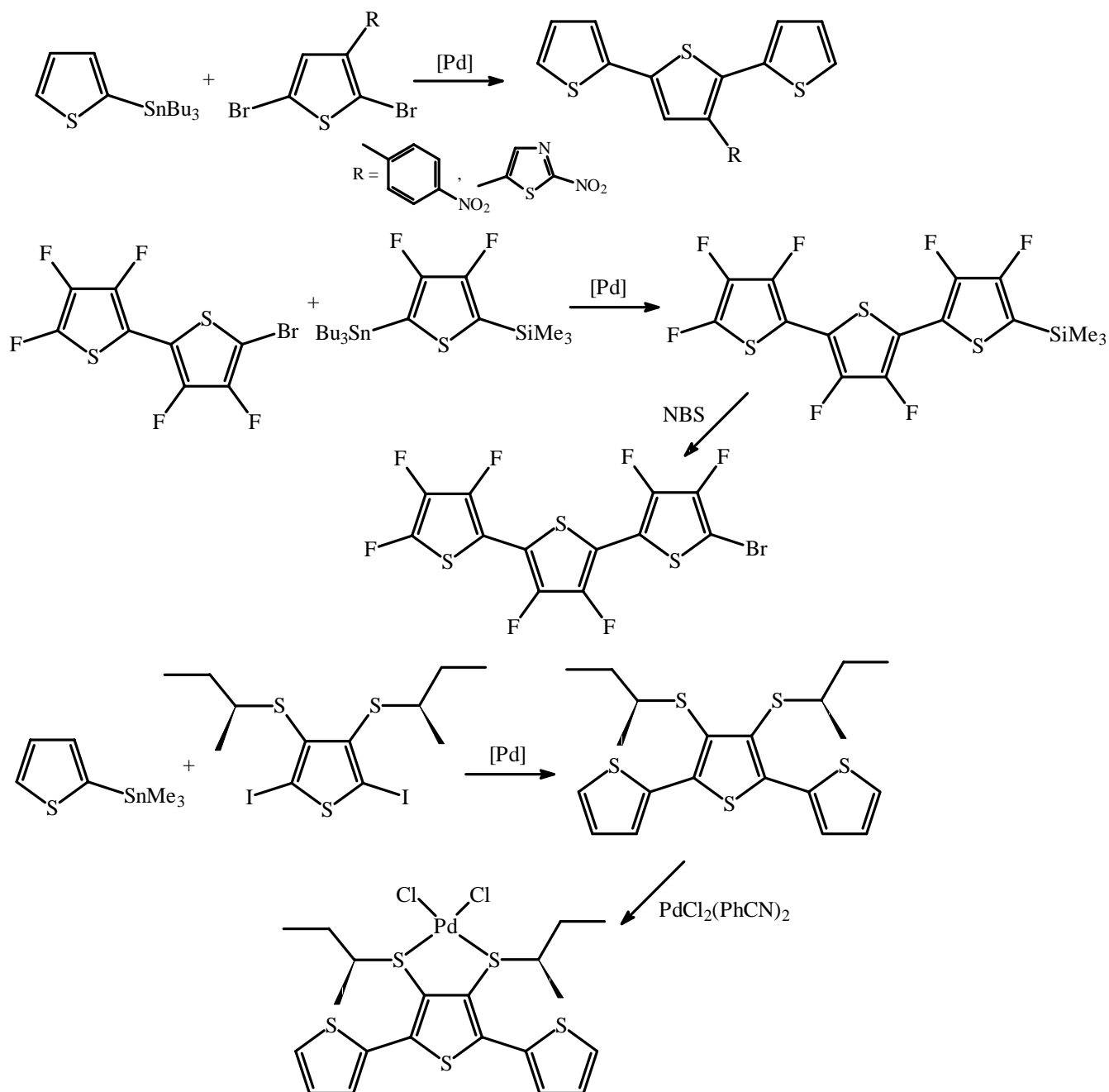
Scheme 11

6. CROSS-COUPLING OF THIENYLSTANNANES WITH BROMO- AND IODOTHIOPHENES

The formation of C-C bonds using the Stille cross-coupling reaction is a very powerful method for the synthesis of polyconjugated systems. The reaction usually involves the cross coupling of an organic halide and an organotin compound. As a rule commercially available $(Ph_3P)_4Pd$ has been used to prepare

oligothiophenes through the Stille coupling. The palladium catalyzed reaction of 2,5´´´-dibromo-3,4´,3´´, 3´´´-tetra(methylthio)quaterthiophene with 2-trialkylstannylthiophenes was studied in the presence of triphenylphosphine, triphenylarsine and tri(2-furyl)phosphine as the palladium ligands and with THF or toluene as solvents at the refluxing temperatures.[44]

Scheme 12

It has been shown that the yields with $(Ph_3As)_4Pd$ generated in situ are from 5 to 15% greater than those obtained with the commercial catalyst. The Stille reaction was used for synthesis of oligothiophenes with even and odd amounts of thiophene heterocycles[16,40,44-58] as well as for polythiophenes.[59-62] This method is convenient for preparation of oligothiophenes containing various functional groups. 3´-(4-Nitrophenyl)-

and 3´-(5-nitro-2-thiazolyl)-2,2´:5´,2´-terthiophenes were obtained by coupling of 2-trimethylstannylthiophene with corresponding 3-substituted 2,5-dibromothiophene in the presence of $(Ph_3P)_2PdCl_2$. The yield of products is more than 60%.[45] The Stille coupling of 3,4-difluoro-2-trimethylsilyl-5-tributylstannylthiophene with perfluoro-5-bromobithiophene $[(Ph_3P)_2PdCl_2]$ afforded perfluoro-5-trimethylsilylterthiophene, which after bromination gave perfluoro-5-bromothiophene in 50% yield.[46] The 2,5-diiodo derivative of 3,4-bis[3-*(S)*-methylbutylthio]thiophene reacts with 2-trimethylstannylthiophene to form corresponding terthiophene. The reaction of this terthiophene with $PdCl_2(PhCN)_2$ in dichloromethane proceeded as exchange of benzonitrile ligands by the thioether side chains of thiophene derivative (Scheme 12).[47]

In the series of quaterthiophenes compounds based on various combinations of thiophene and 3,4-ethylenedioxythiophene (EDOT) moieties have been synthesized by catalytic $[(Ph_3P)_4Pd]$ coupling of 5,5´-bis(tributylstannyl)bis(ethylenedioxy)bithiophene with 2-bromothiophene or 5,5´-dibromobithiophene with 2-tributylstannyl-3,4-ethylenedioxythiophene in 47% yield.[48,49] α,ω–Methyl carboxylate capped tetramer was prepared by reaction between methyl 2-bromothiophene-5-carboxylate and 5,5´-bis(trimethylstannyl)-2,2´-bithiophene (Scheme 13).[50]
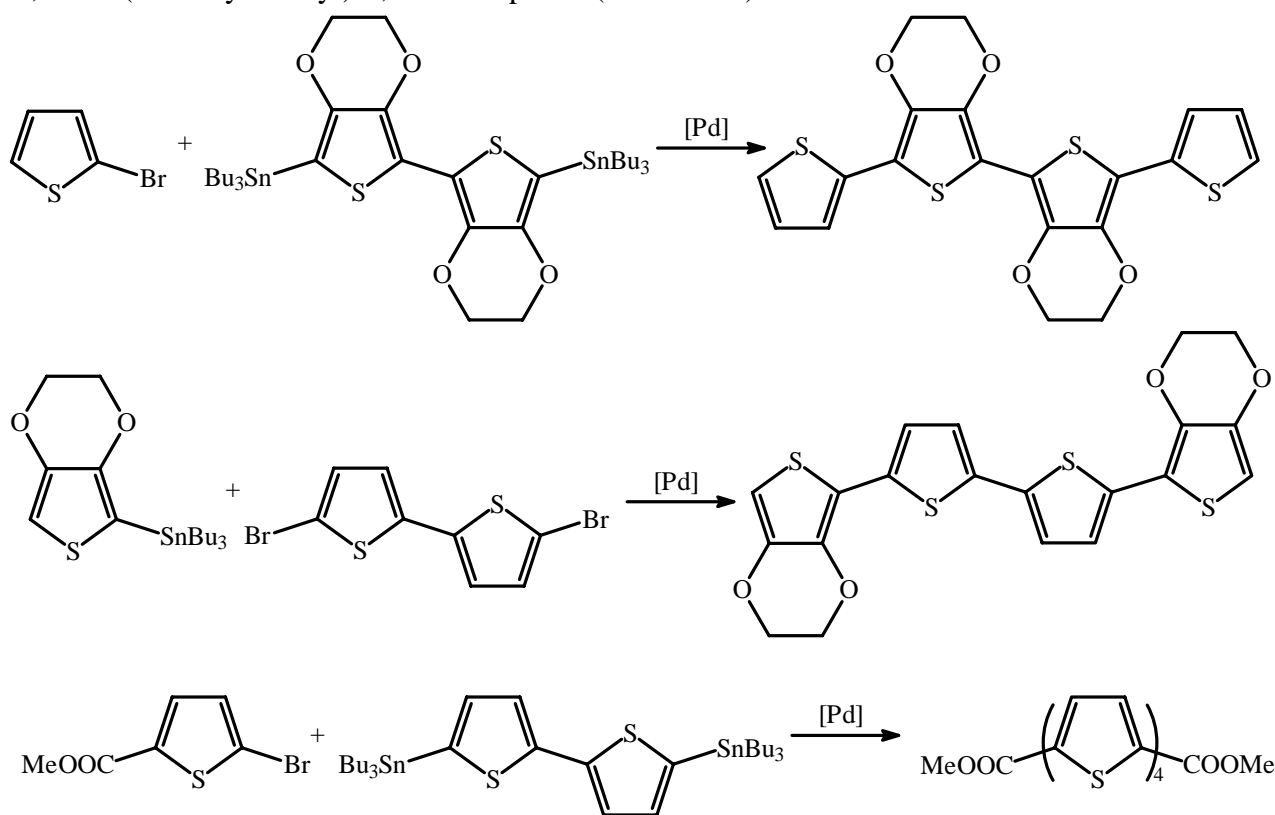
Scheme 13

3´,4´,3´´,4´´-Tetranitroquaterthiophene was obtained by cross-coupling of 5,5´-dibromo-3,4,3´,4´-tetranitro-2,2´-bithiophene with 2-tributylstannylthiophene $[(Ph_3P)_2PdCl_2]$ in 84% yield. Subsequent

reduction of tetranitro derivative (SnCl$_2$, HCl, EtOH) led to formation of correspondent 3´,4´,3´´,4´´-tetraaminoquaterthiophene (yield 90%). N-Silylation of the diaminothiophene units by 1,2-bis(chlorodimethylsilyl)ethane improved the solubility in organic solvents and made the amino moieties inert during a series of reactions (bromination, lithiation, stannylation) giving higher oligomers (Scheme 14).[51]
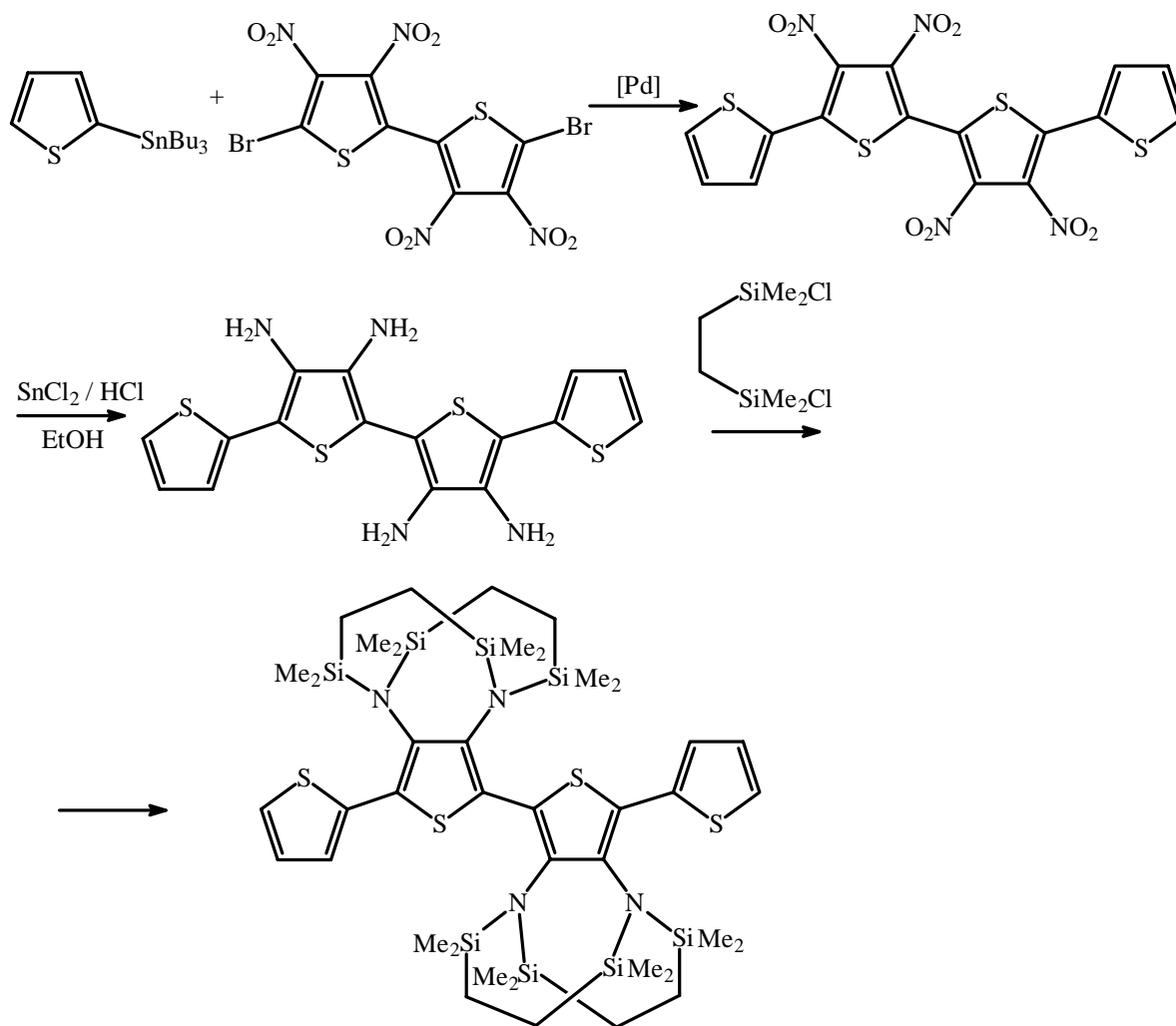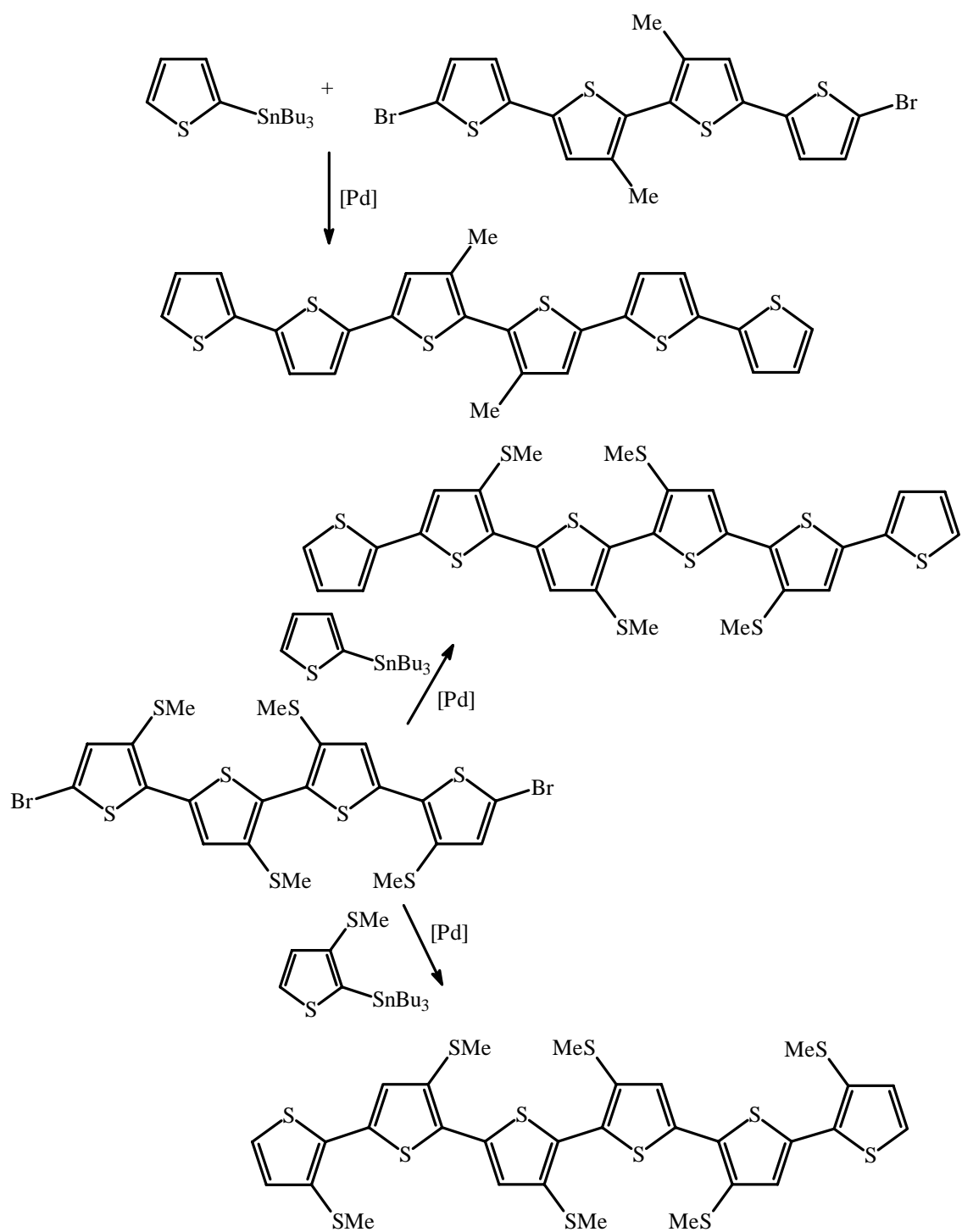

Scheme 14

For the synthesis of quaterthiophenes containing β-hydroxyethyl substituents protected by tetrahydropyranyl group or α-dimethylchloromethylsilyl substituent the Stille coupling of monobromobithiophenes with monostannylbithiophenes has been used (Scheme 15). [52, 53]

2-Tributylstannyl-5-dimethyl(*tert*-butyl)silylthiophene reacted under reflux in toluene with 5,5´´-dibromoterthiophene in the presence of (Ph$_3$As)$_4$Pd to form silyl-capped quinquethiophene in 57 % yield (Scheme 16). This product was applied for the fabrication of thin film field effect transistor.[16]

Various β-alkyl[40,54] and thioalkyl substituted sexithiophenes[55] were synthesized by catalytic condensation of α,ω-dibromoquaterthiophenes with 2-tributylstannyl thiophene derivatives (Scheme 17).

Scheme 15

Scheme 16

Scheme 17

Conjugated sexithiophenes carrying diperfluorohexyl groups[56] and chiral (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecyl esters[57] at both the α- and ω-positions were prepared by the Stille cross-coupling of bisstannylbithiophene and correspondent 5-substituted 5´-bromobithiophenes in the presence of (Ph$_3$P)$_4$Pd (Scheme 18).
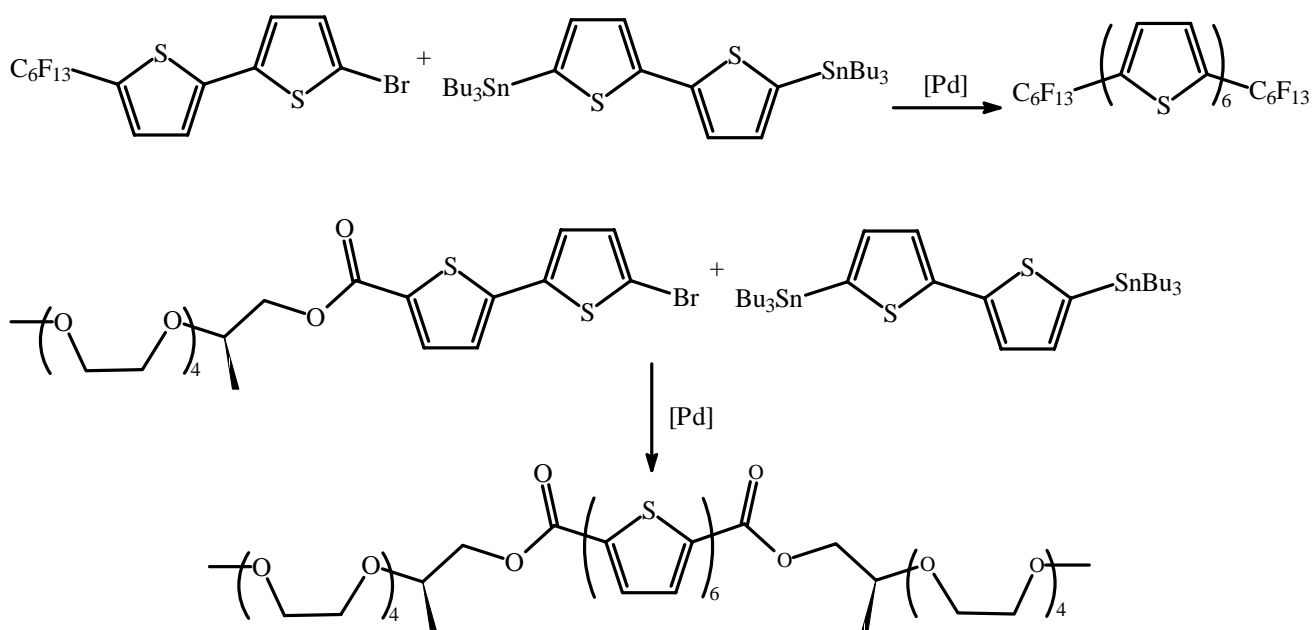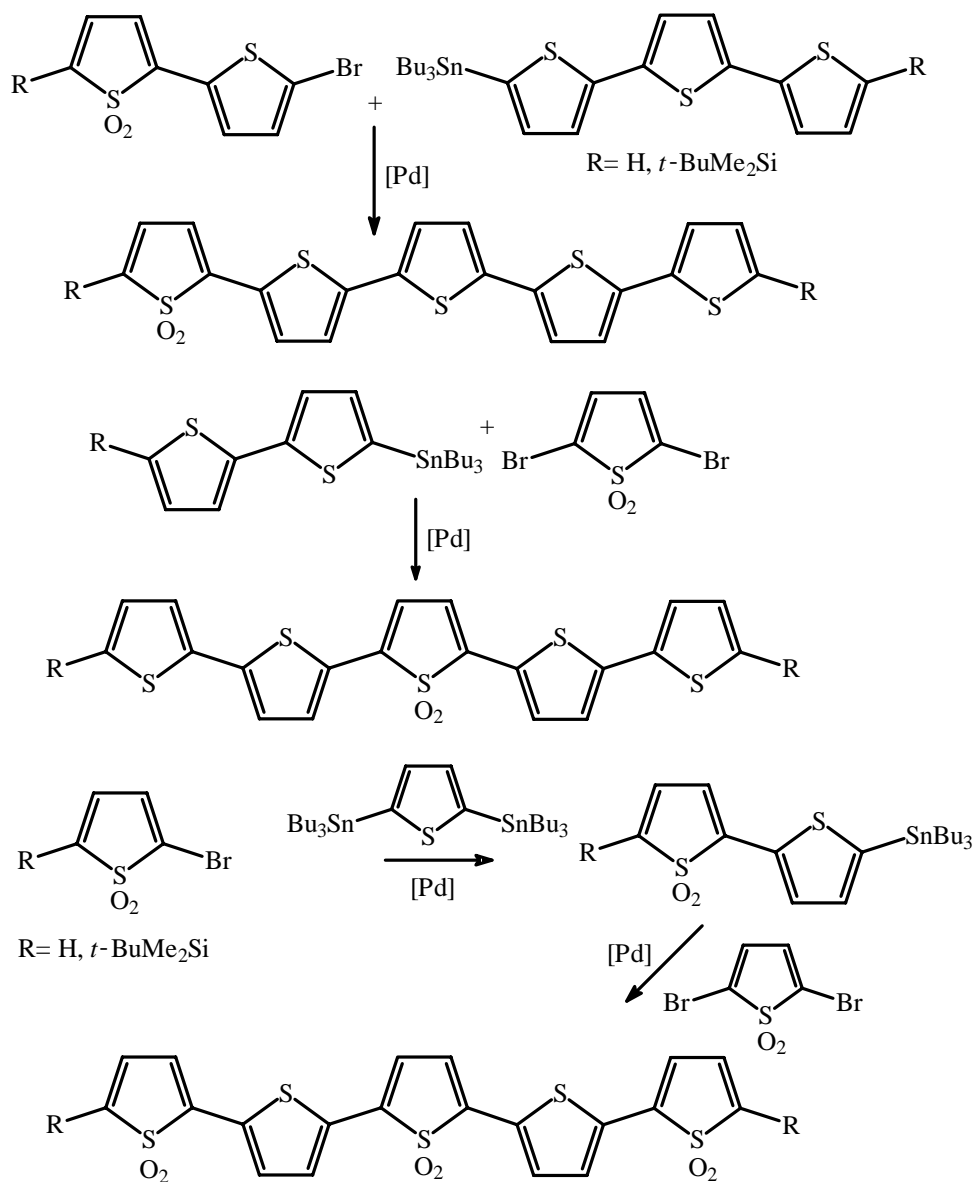
Scheme 18

Using stannyl and bromo oligothiophene derivatives containing 3,4-diaminothiophene fragment protected by 1,2- bis(dimethylsilyl)ethane unit as a building blocks for the Stille coupling the extended oligomers with 11, 14 and 28 thiophene groups were obtained.[58] The chemical modification of the amino groups to thiadiazole ring induces an appreciable red shift of the absorption band.

The coupling of brominated thiophene-1,1-dioxides with thienylstannanes in the presence of a palladium catalyst allows for the easy and selective insertion of thiophene-1,1-dioxide moieties into the skeleton of bi-, ter-, quater- and quinquethiophenes.[63-67] The reaction of monobrominated thiophene-1,1-dioxides with thienylstannanes in the presence of $(Ph_3P)_4Pd$ leads to formation of oligothiophenes containing thiophene-1,1-dioxide units at the terminal positions, whereas the coupling of 2,5-dibrominated thiophene-1,1-dioxides with thienylmonostannanes allows the insertion of a thiophene-1,1-dioxide unit in the central position of molecular skeleton. Compounds characterized by alternating aromatic and nonaromatic units were prepared by Stille coupling using various building blocks (Scheme 19). The reaction time required for the formation of C - C bond in the case of thiophene-1,1-dioxide derivatives decreases from the hours to minutes as compared with parent oligothiophenes. A new approach to the synthesis of substituted bithiophene and polymers containing thiophene was published recently.[68] It was found that $(Ph_3P)_2PdCl_2$-catalyzed reaction of hexabutyldistannane with bromo substituted thiophene generated bithiophene in good yields (Scheme 20).

It has been shown that in some cases the Stille cross-coupling proceeds with low selectivity.[18,40,69,70] For example when Stille type reaction was applied to 5, 5´-dibromobithiophene and 2-trimethylstannyl-3-butylthiothiophene in a 1:2 molar ratio in the presence of $(Ph_3P)_2PdCl_2$ as a catalyst, the 3,3´´´´´-bis(butylthio)sexithiophene was obtained as a main product (45%) together with 3-butylthio-5´´-
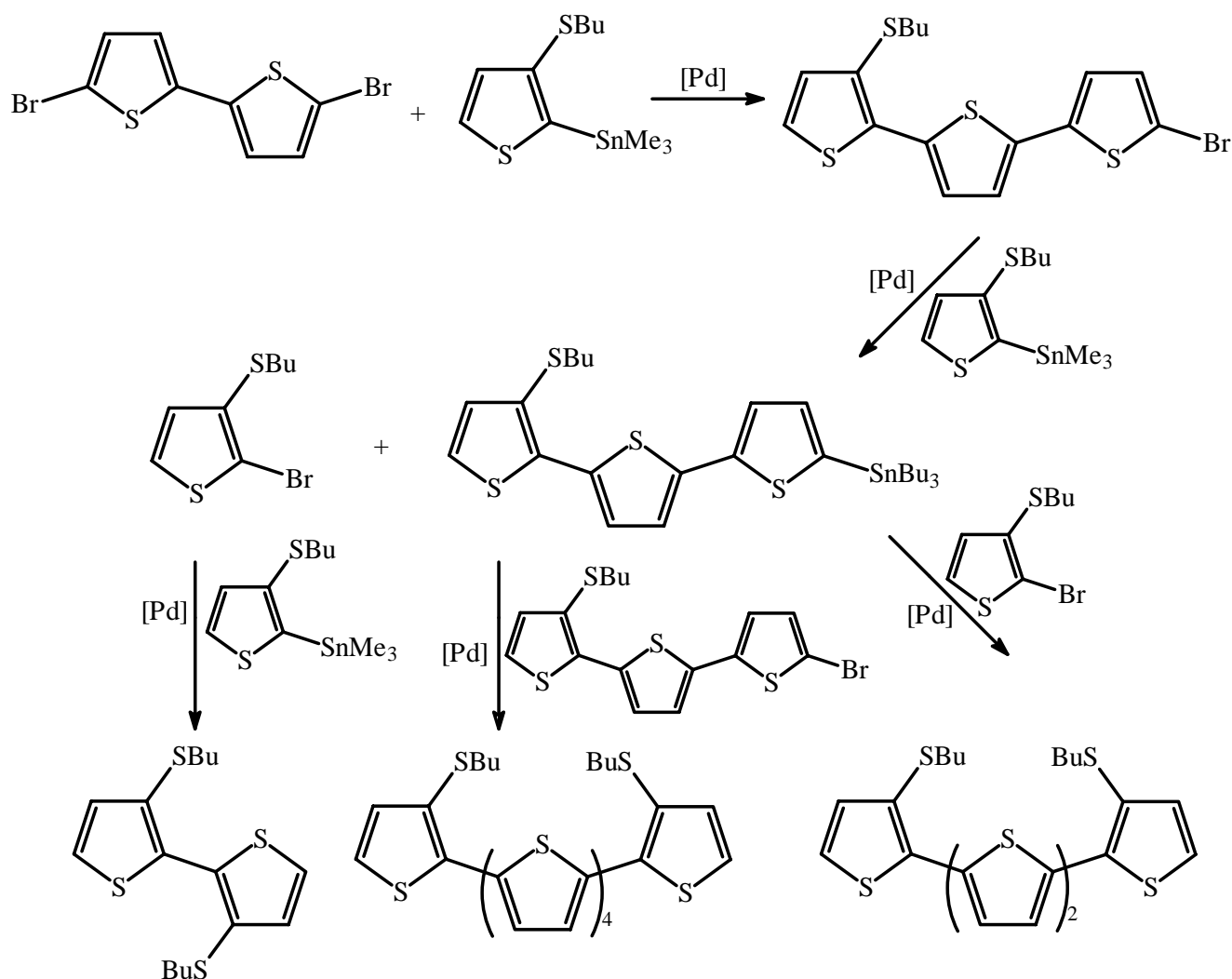
bromoterthiophene (17%), the expected 3,3´´´-bis(butylthio)quaterthiophene (21%) and 3,3´-bis(butylthio)butylthiohene (17%).[70] The formation of these products could be explained by the process which exchange the functional groups of reagents. The proposed mechanism of the reaction is depicted in Scheme 21.

Scheme 19
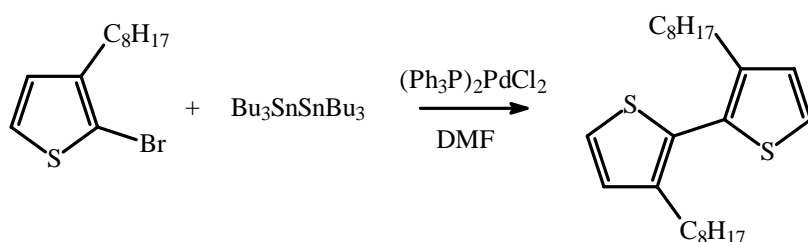
Scheme 20

Scheme 21

7. CYCLIZATION

Besides transition metal-catalyzed aryl-aryl cross-coupling reactions, for the synthesis of oligothiophenes various methods starting from acyclic precursors have been studied. A complete series of structurally well-defined 3,4-dibutyl-substituted oligothiophenes was synthesized by cyclization of oligothiophenebutadiyne precursors with sodium sulfide nonahydrate in boiling 2-methoxyethanol (Scheme 22). The reaction cleanly gave trimer (m=1) in 61%, heptamer (m=3) in 80%, and undecamer in 73% yield respectively. The initial symmetric 1,3-butadiynes are accessible in good yields through oxidative coupling of acetylenes with the aid of copper salts.[71] The same synthetic route was applied for the preparation of very long oligothiophenes, such as tridecamer, icosamer, and heptacosamer, containing β-octyl substituents.[72] For the synthesis of such long oligomers, hard work on purification is inevitable. The reaction of cyclization has the advantage of less contamination with analogous oligothiophene byproducts.

Scheme 22

Synthetic strategy for the preparation of the first fully α-conjugated macrocyclic oligothiophenes involves oxidative coupling of α,ω-diethynylter- and quinquethiophenes performed under pseudo-high-dilution conditions and subsequent cyclization by sulfur nucleophiles.[73] At the first step pyridine solution of oligothiophenes were added by means of syringe-pump over 3 days to a slurry of anhydrous CuCl and CuCl$_2$ in pyridine at room temperature. In both cases the cyclotrimeric and cyclotetrameric products were isolated in 2–12% yields. Transformation of three diyne units in trimeric compounds resulted in cyclo[12]thiophene and cyclo[18]thiophene in 23 and 27% yield, respectively. Cyclo[16]thiophene was isolated in 7% yield after the reaction of the four diyne units in macrocycle obtained by tetramerization of α,ω-diethynylterthiophene (Scheme 23).

The efficient incorporation of thiophene-1-oxide unit into the backbone of terthiophene and quinquethiophene chains was based on the zirconocene cyclization of diynes and following reaction of zirconacyclopentadiene derivatives with SO$_2$ (Scheme 24).[74,75] The yields for these one-pot reactions are generally quite high (50 - 75%).
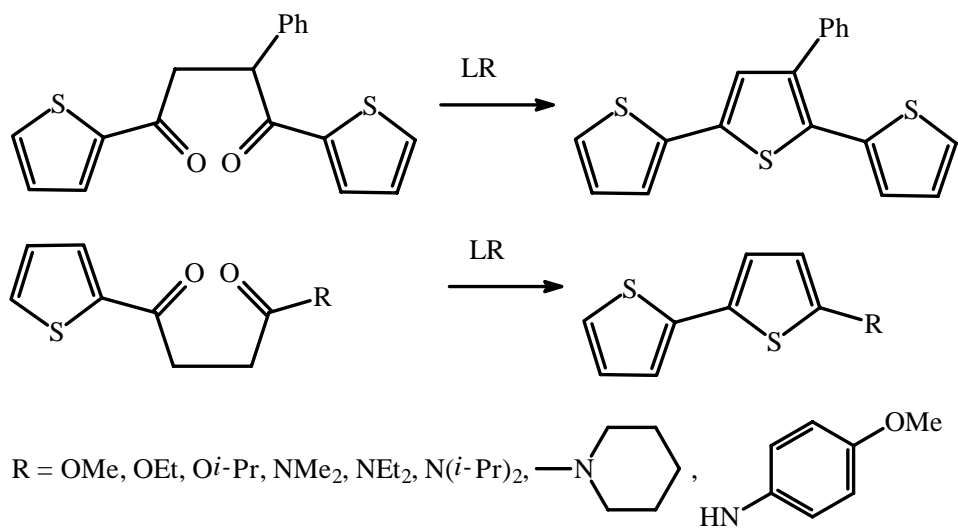
Scheme 23

1,4-Diketones can be cyclized by means of sulfur donors such as phosphorous pentasulfide or Lawesson's reagent (LR) to the correspondent thiophenes in good yields.[76-77] However, the side reaction leads to furans which are difficult to separate.[78] 5-Substituted bithiophenes were obtained from thienyl-containing γ-keto esters and γ-keto amides by LR treatment.[79] The yields of 5-alkoxybithiophenes were improved on addition of a 20% excess of Lawesson's reagent (Scheme 25).
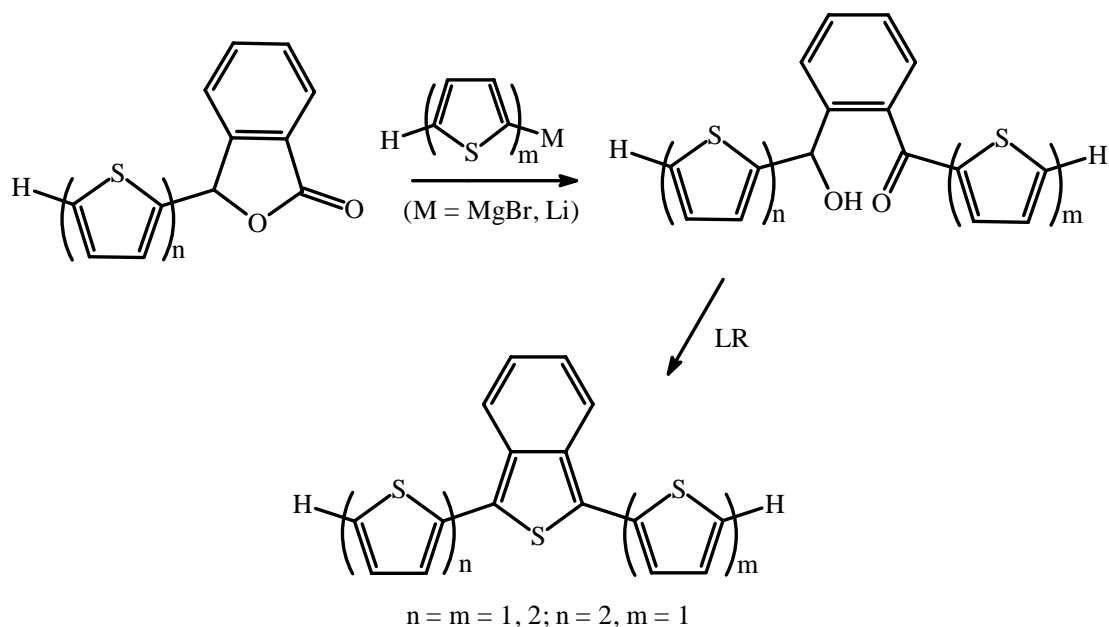
n = 1, 2

Scheme 24

R = OMe, OEt, O*i*-Pr, NMe$_2$, NEt$_2$, N(*i*-Pr)$_2$, —N(piperidine), (4-MeO-C$_6$H$_4$)NH—
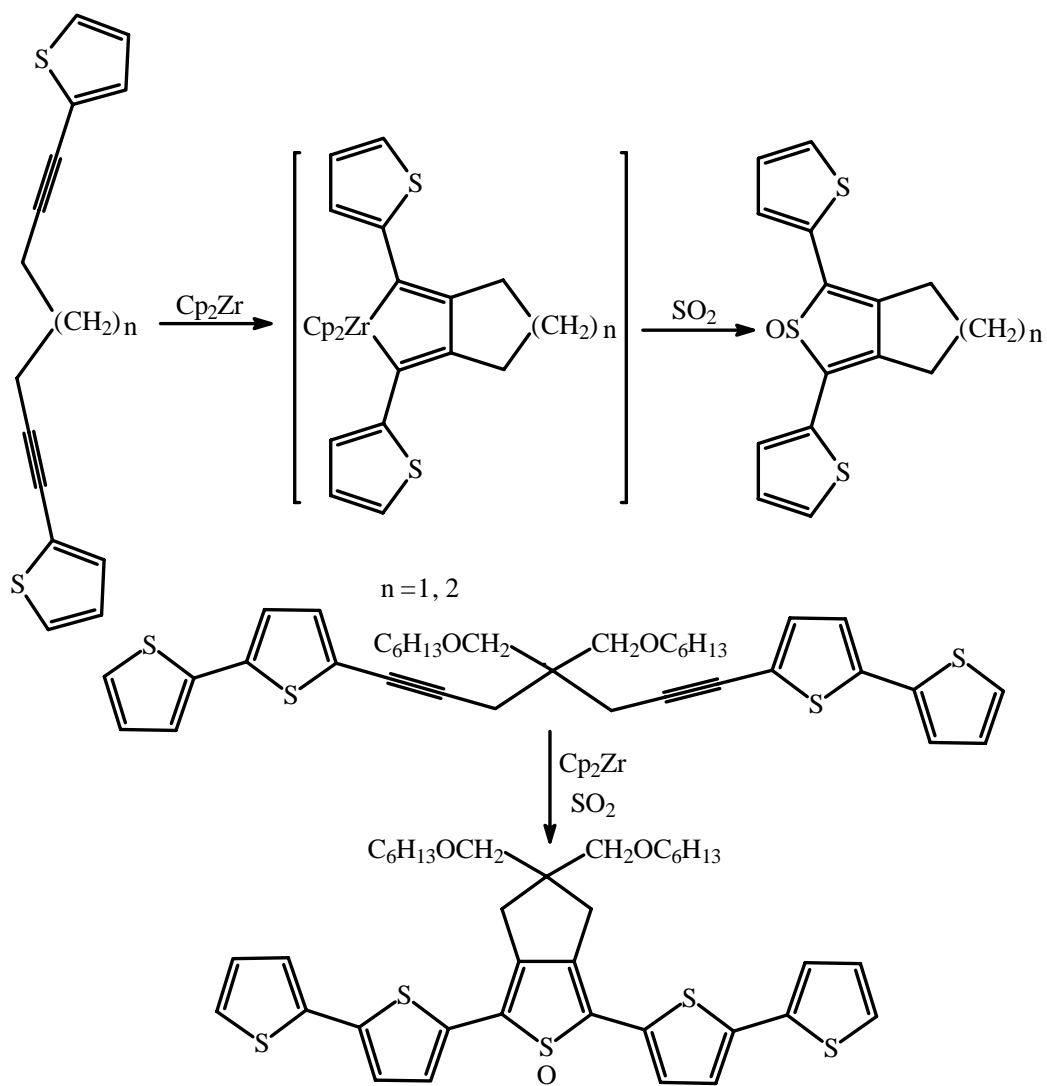
Scheme 25

A number of benzo[c]oligothiophenes have been synthesized by cyclization of o-thenoyl substituted benzylic alcohols obtained by the action of thienylmagnesium bromide or bithienyllithium on 2-thienyl substituted isobenzofuranones (Scheme 26).[80]
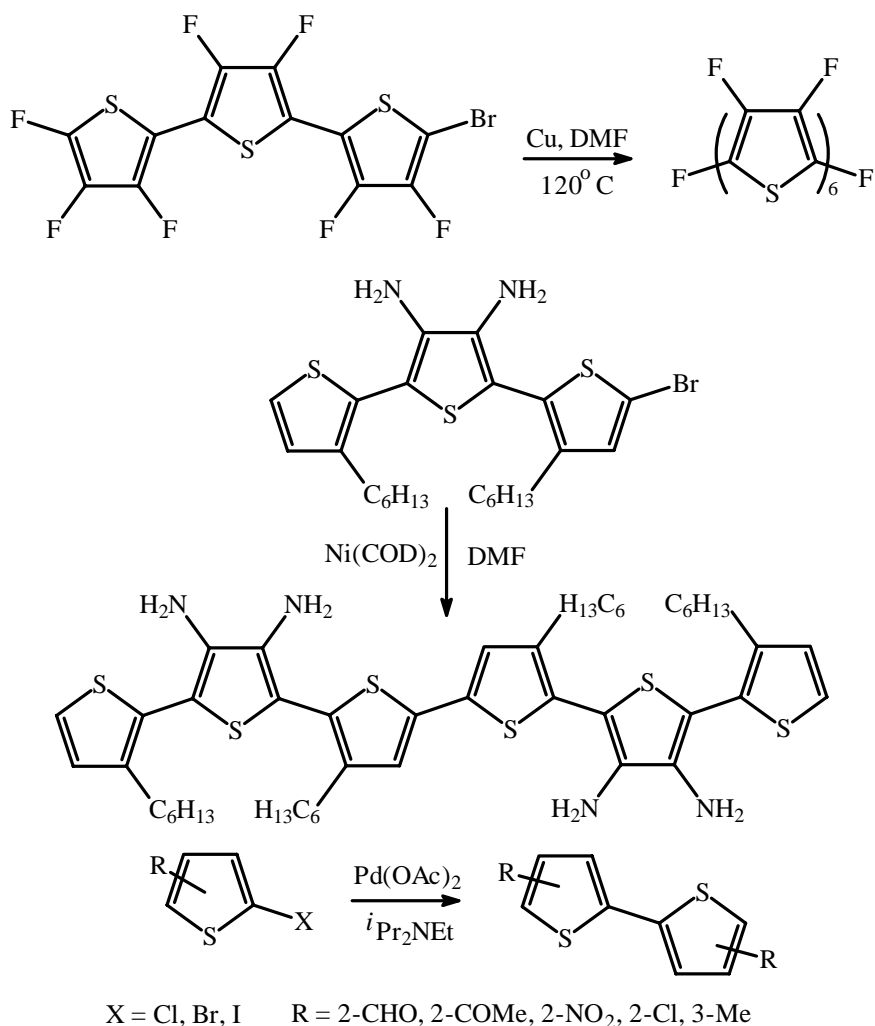

Scheme 26

8. OTHER METHODS

Copper(I) iodide-catalyzed homocoupling of chlorodimethyl(2-thienyl)silane and fluorodimethyl(2-thienyl)silane in the presence of tetrabutylammonium fluoride at room temperature during 5 min affords 2,2´-bithiophene in 71 and 75% yields respectively (Scheme 27).[81]

X = F, Cl
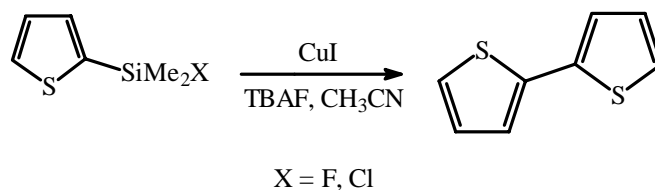
Scheme 27

The literature offers several methods for the synthesis of symmetrical oligothiophenes by homocoupling of halo derivatives. Ullmann reaction is one of the routs to prepare these compounds, but this method requires a stoichiometric amount of copper and high temperature. The Ullmann coupling of perfluoro-5-bromoterthiophene in DMF provided perfluorosexithiophene in 57% yield (Scheme 28).[46] Recently, other chemical methods have been developed and the chelated nickel(0) complexes (with Ph$_3$P, 2,2´-bipyridine, COD) were used for homocoupling of functional compounds. Thus, sexithiophene with 3,4-diamino

fragment was obtained by the reaction of corresponding monobromo terthiophene with Ni(COD)$_2$ in 61% yield (Scheme 28).[58]

X = Cl, Br, I   R = 2-CHO, 2-COMe, 2-NO$_2$, 2-Cl, 3-Me

Scheme 28

Thiophene halides bearing various activating groups were successfully coupled in good to excellent yields by using Pd(OAc)$_2$ as catalyst (Scheme 28). In all cases diisopropylethylamine appears to be the most efficient and selective base. Toluene was used as a solvent in order to avoid the carbon-halogen bond reduction.[82]

ACKNOWLEGMENT

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