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REVIEW

Sonogashira Coupling Reaction and its Application in Dendrimer Synthesis

PRITAM ROY CHOWDHURY[1], DEBABRATA SINGHA[2], SUDESHNA SAWOO[1], MANAS GHOSH[2,*] and NILASISH PAL[1,*]

[1]Department of Chemistry, Seth Anandram Jaipuria College, Kolkata-700005, India
[2]Department of Chemistry, Physical Chemistry Section, Visva-Bharati University, Santiniketan, Birbhum-731235, India

*Corresponding authors: E-mail: np.chemistry@sajaipuriacollege.ac.in; pcmg77@rediffmail.com

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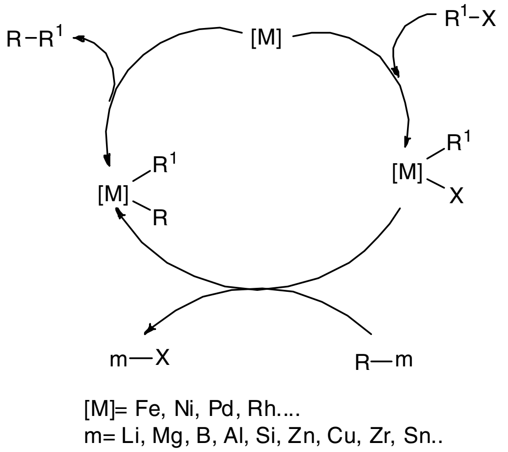
Sonogashira cross-coupling process is a synthetic method for producing aryl-alkyne conjugates. In last few years, several researchers have been able to explore the divergent and convergent approaches of dendrimer synthesis. Dendrimers are radially symmetrical molecules which are nanoscale in size and have a well-defined homogeneous and monodisperse structure with symmetric or asymmetric core, inner shell and outer shell. Several dendrimers have been produced *via* various C-C coupling processes. In present review, we focused on the synthesis of few dendrimers using the Sonogashira Coupling reaction as a vital steps.

Keywords: Cross-coupling, Divergent synthesis, Convergent synthesis, Dendrimers, Sonogashira reaction, Tetraphenyl methane.

INTRODUCTION

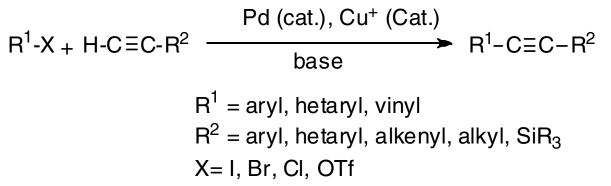
The C-C coupling reaction refers to the class of organic synthesis, which involves joining two carbons with the help of a metal catalyst [1-3]. The most important kind of such reaction is the cross-coupling reaction type [4-7]. This sort of reaction usually requires an organometallic reagents as a counter part such as organosilicon, organotin and organoboron which have been described since the early 1970s. There have been several successful applications of electrophiles and metal complexes in these coupling processes, resulting in the development of numerous molecular assembly synthesis techniques. As a result, cross-coupling processes are often utilized in a broad range of organic synthetic applications [8-12], including liquid crystals, natural products, pharmaceuticals and polymers. A basic catalytic cycle for the cross-coupling reaction [13,14] involves in a sequence of transmetallation, oxidative addition and reductive elimination steps to carry out the process (**Scheme-I**). The oxidative addition step is the slowest or rate-determining step [15] and the strength of the C-X bond (X= halides or pseudohalides) is a key factor for the successful reaction condition.

There are two major factors which affects the cross-coupling reactions are (i) the increased activity and stability of the catalytic systems and (ii) the reagents like halides, pseudohalides, and organometallic nucleophiles, which are being used.



Scheme-I: Catalytic cycle for the cross-coupling reaction with the metal catalyst and organometallic reagent

Different types of cross-coupling reactions catalyzed by palladium [16,17] are deemed as a fundamental step in the chemical synthesis. Preparation of aryl-alkynes or conjugated enynes *via* the C_{sp2}-C_{sp} coupling reaction [18-20] between an aryl or alkenyl halides or triflates and a terminal alkyne employing palladium as catalyst is well known as Sonogashira coupling (also called as Sonogashira-Hagihara coupling) reaction (**Scheme-II**).

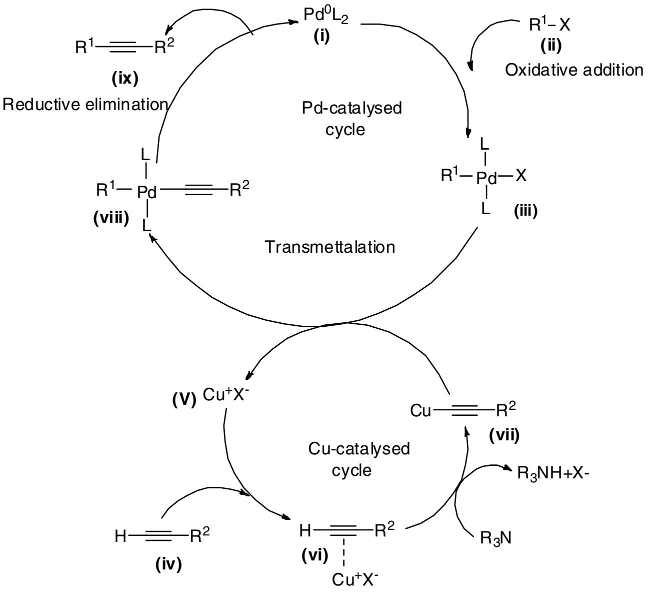


Scheme-II: Mechanism of Sonogashira cross-coupling reaction using palladium catalyst

Heck & Dieck [21] and Cassar [22] individually reported the palladium catalyzed coupling reactions using phosphine-palladium catalysts at 100 °C, which was improved by Sonogashira *et al.* [23], who reported that the reaction rates were greatly increased due to the addition of copper (I) iodide, allowing the alkynylation to be performed at room temperature. Consequently, Sonogashira-Hagihara coupling [24-26] became the most widely used technique for alkynylation of aryl or vinyl halides. Some recent advances in the progression of 'copper-free' catalytic systems [27] capable of carrying out this reaction are meant to prevent homo-coupling products of the terminal alkyne (known as Glaser-Hay coupling) [28], the major reaction product is formed in addition to the desired reaction product. The Sonogashira cross-coupling reaction has been extensively utilized to construct dendrimers [29], conjugated oligomers and polymers, substituted alkynes, natural product intermediates, medicines and optical materials, among other things.

This article focused primarily on the Sonogashira coupling reaction mediated development in C-C bond formation for dendritic molecule synthesis.

Mechanistic discussion: Although it is commonly assumed [30] that the homogeneous copper co-catalyzed Sonogashira reaction occurs *via* two distinct cycles, the palladium cycle and the copper cycle, the true mechanism of the homogeneous copper co-catalyzed reaction is yet unknown (**Scheme-III**). The palladium catalytic cycle is a classic one, which involves the catalytically active species $Pd(0)L_2$ complex to create a C-C bond after generated *in situ* and stabilized by a ligand like a phosphane. The Pd(0) complexes, such as $Pd(PPh_3)_4$ or Pd(II) complexes, such as $PdCl_2(PPh_3)_2$, may be used in such catalytic cycle. Amines or inorganic bases used to reduce Pd(II) to Pd(0). The rate-determining phase of the coupling reaction occurs when complex $[Pd(0)L_2]$ interacts with an aryl or vinyl halide (ii) to create $[Pd(II)L_2R_1X]$ complex (iii) by oxidative addition. The rate of addition of ArX (where X = Cl, Br, I) is ArI > ArBr > ArCl. As mentioned above, this phase is preceded by the formation of a bond between the halogen atom and palladium metal, making it an electron-donating step. This results in a more stable complex being formed on the substrates that include strong electron-donating groups (**Scheme-II**). This increases the overall rate of the subsequent step, while the presence of an electron withdrawing group retarded the addition reaction to occur. The terminal alkyne (iv) interacted with Cu(I) in the addition of a base to form the copper acetylide $[R^2\text{-}C{\equiv}C\text{-}Cu]$ complex in the copper catalytic cycle (vii). The $[Pd(II)L_2R^1X]$ and $[R_2\text{-}C{\equiv}C\text{-}Cu]$ complexes are then transmetallated (iii and vii) to generate the $[R^1Pd(II)L_2C{\equiv}CR^2]$ complex (viii), which then participates in reductive elimination to yield the desired cross-coupled product (ix) $[R^1\text{-}C{\equiv}C\text{-}R^2]$ and the catalyst $[Pd(0)L_2]$ is regenerated [19,31].

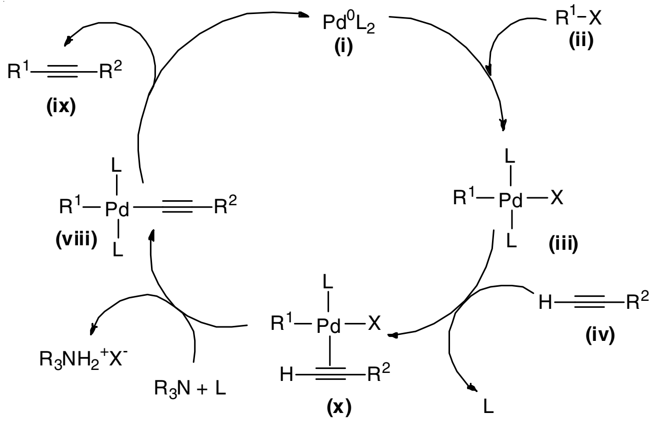


Scheme-III: Cross-coupling reaction mechanism of copper catalyzed Sonogashira reaction

Limitations of Sonogashira coupling: In the methodologies for alkyne synthesis, the Sonogashira coupling reaction is one of the most significant and widely used reactions due to the flexibility of designing its products. The most widely employed Pd-catalysts for this process are $PdCl_2(PPh_3)_2$, $PdCl_2/PPh_3$ or $Pd(PPh_3)_4$ in conjunction with the co-catalyst, CuI and excess of organic amines such as di-isopropylamine, *n*-butylamine, triethylamine, morpholine, piperdine, *etc.* as bases as well as solvents [28]. Despite its stability, simplicity and broad application, this coupling has several drawbacks. In the presence of CuI, an unwanted alkyne homo-coupled (Glasser coupling) side product was produced. Conventional Sonogashira process is limited to aryl iodide/bromide or stimulated chlorides, *i.e.* a particular substrate and careful tailoring of reaction conditions in an inert environment are required. Under mild reaction conditions, it also displays weak coupling with unactivated halides as well as negligible catalyst turnover.

Cu-free Sonogashira coupling: According to the literature [32-36], the principle of the copper-free Sonogashira coupling reaction is not broadly used. A four-coordinated palladium complex is produced by oxidative addition in the first step. Because the basicity of the amine is insufficient to deprotonate the alkyne, a neutral ligand dissociates and a π-alkyne-palladium complex forms. The final product and $[Pd(0)L_2]$ catalyst is produced by a series of *cis*/*trans*-isomerization and reductive elimination steps. **Scheme-IV** depicts the suggested mechanism of the Cu-free Soogashira reaction [37,38].

Applications of Sonogashira coupling: Despite of several limitations, the Sonogashira cross coupling process has been used in various fields because of its utility in formation of C-C bonds. This reaction is also performed in an aqueous solution and with a mild base at an ambient temperature to produce

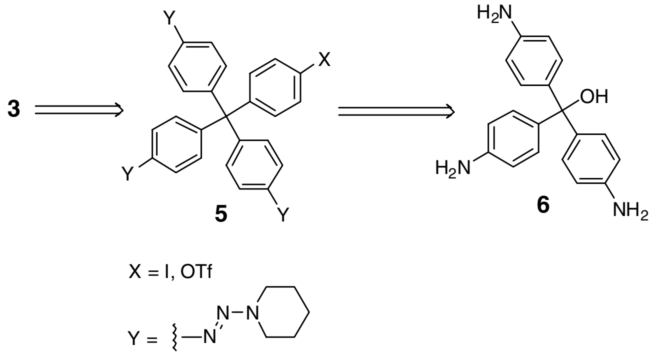


L = Phosphane, base, solvent or alkyne

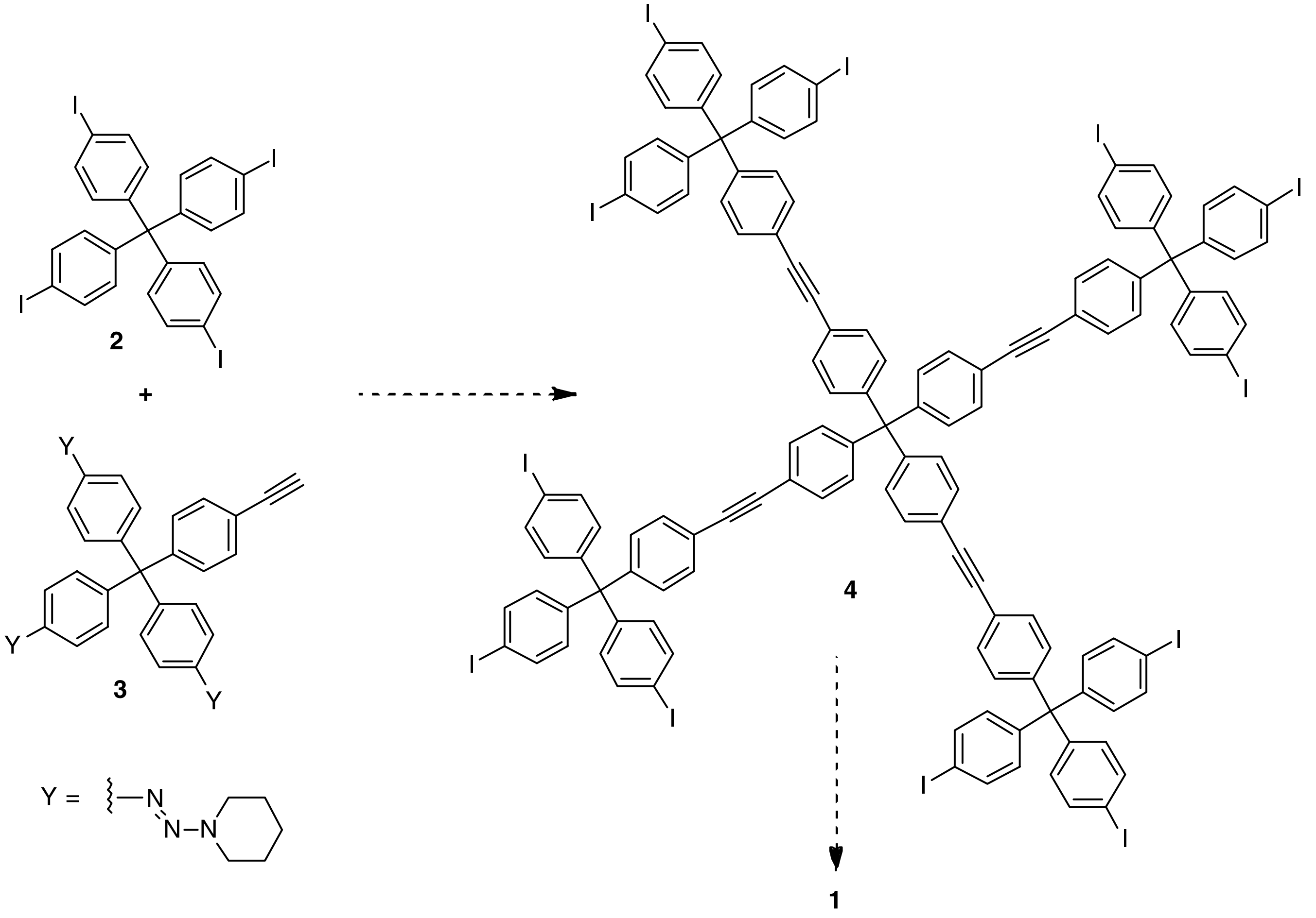
Scheme-IV: Cu-free Sonogashira reaction and its mechanism

complicated molecules. The most recent applications of the Sonogashira coupling [30,39-43] are (i) organic synthesis; (ii) synthesis of molecular material; (iii) natural products synthesis; (iv) synthesis of pharmaceuticals and agrochemicals, and (v) nucleoside and oligonucleotide chemistry.

Divergent synthesis of tetraphenylmethane dendrimers: Shape-persistent dendrimers are a unique class of nano-objects with an unusual 3D architecture. Synthesis of tetraphenylmethane ethynylene based dendrimers using Sonogashira cross coupling is described by Torneiro & Urzua [44]. They chose tetra-iodide **2** as their starting material (**Scheme-V**) since it is widely available [45-47]. In synthesizing numerous arylacetylene systems [48], they linked the alkyne fuctional group to the central branching unit **3**, which comprises three triazene, functional groups, to the rest of chain. After triazene replacement, the coupling of **3** (4 equivalent) with the core **2** resulted in the iodo-terminated first generation (1G) dendrimer **4** (**Scheme-V**). This chemical might be used as a substrate for a second coupling reaction using **3** or other tetraphenyl-methane ethynylene derivatives to produce second generation (2G) dendrimers (**Scheme-VI**).

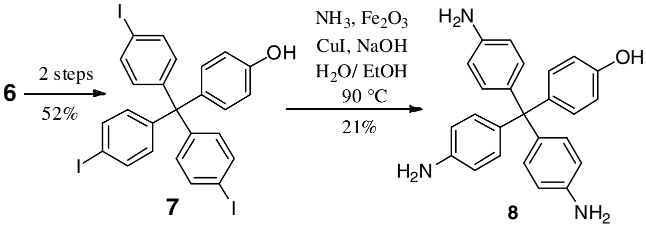


Scheme-VI: Retrosynthesis of building block **3**



Scheme-V: Dendrimer 1 is reached through a detour

Intermediate **8** is produced from **6** (**Scheme-VII**) [49] by amination of triiodide **7**. Dracel & Wu [50] conducted NH_3 amination of **7** in Fe_2O_3, CuI and NaOH, yielding the desired product **8** in 21% yield.



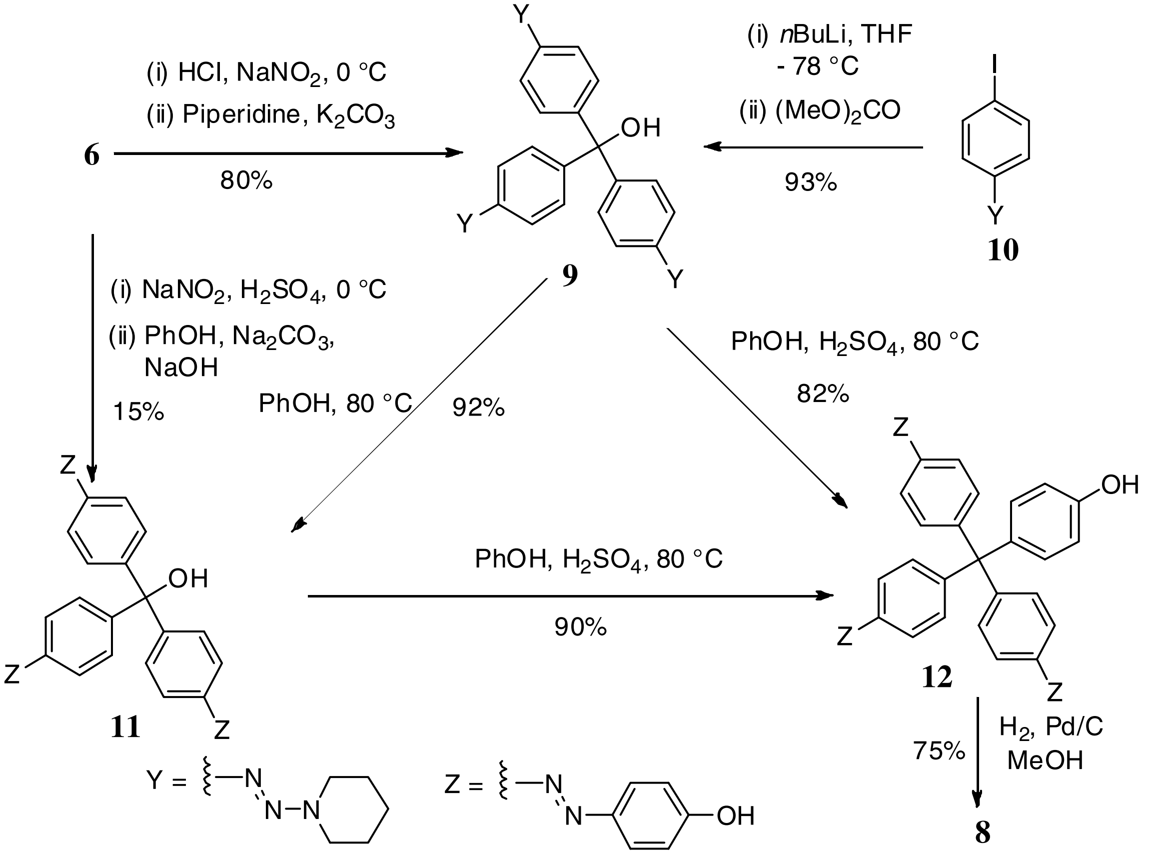
Scheme-VII: Synthesis of intermediate **8**

Because of the low yield in the previous transformation, they decided to test an alternate synthetic method, in which they thought of inserting triazene groups in **6** and then using the acid-catalyzed Fridel-Craft's reaction with phenol to construct the triphenyl-methane skeleton. The *tris*(triazene) **9** was made in high yield from the diazonium salt trapped with piperdine (**Scheme-VIII**) and in an other way, from the triazene **10** by treating it with *n*-BuLi and then reacting the organolithium compound with dimethyl carbonate to generate the final product with 93% yield (**Scheme-IX**).

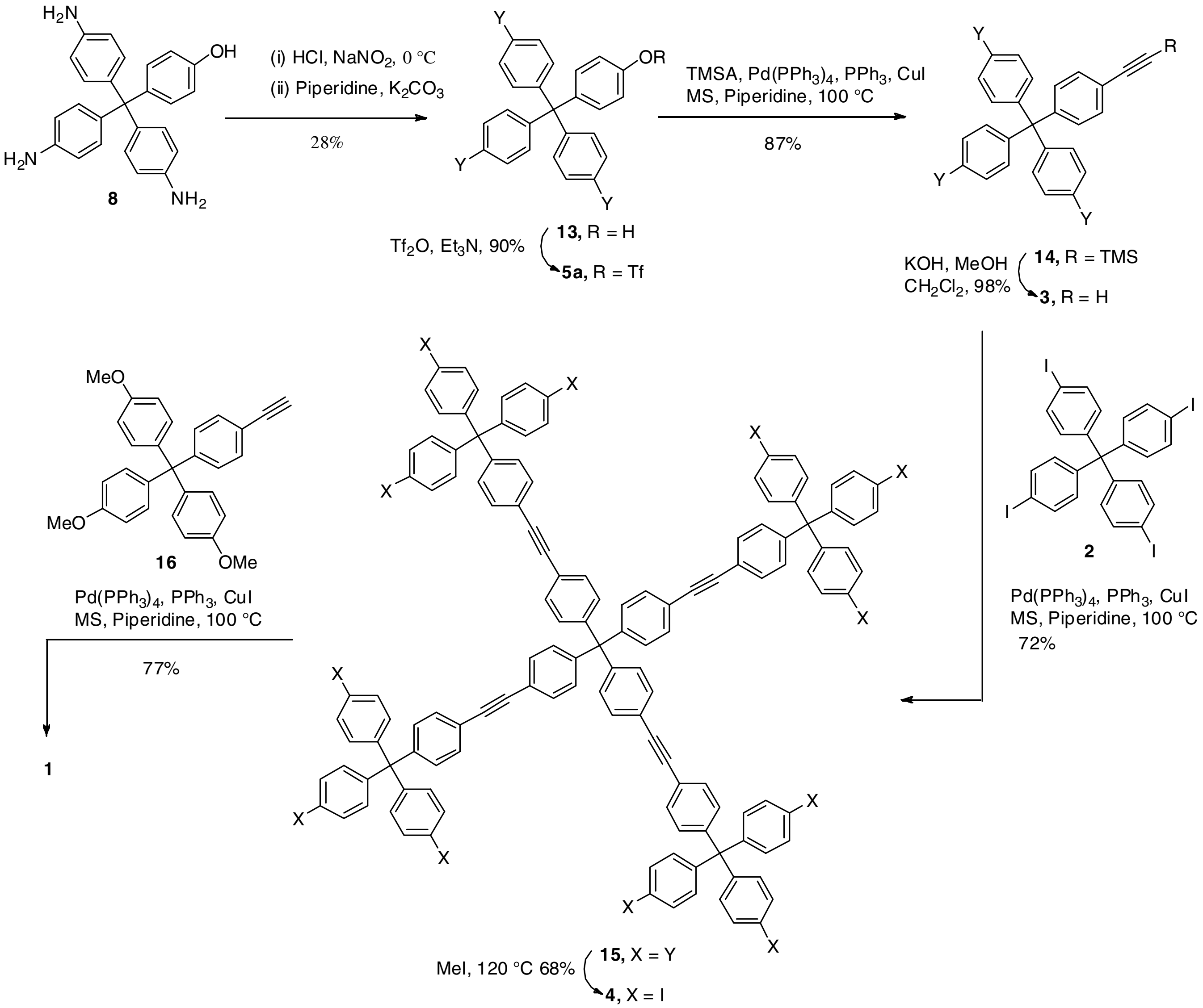
Synthesis of tetraphenylethylene-based conjugated dendrimers: A simple convergent approach for making conjugated dendrimers [51-56] with a tetraphenyl ethylene (TPE) moiety as dendrons, triphenylamine as a core were created using a convergent synthetic approach using the three-fold Sonogashira coupling process. These dendrimers are soluble in organic solvents and produce blue and violet colour.

In **Scheme-X**, 4-bromo benzophenone was treated with diphenylmethyl lithium at a lower temperature, followed by acid-catalyzed dehydration of the resulting alcohol, yielding 1-(4-bromo phenyl)-1,2,2-triphenylethylene (**17**) in a good yield. At temperatures between 60 °C and room temperature, **17** reacts with *n*-BuLi in Et_2O or THF, followed by the addition of DMF, to create the anticipated aldehyde **18** in a 50% yield. The yield of **18** was enhanced to 70% when the reaction was carried out using the identical halogen-metal exchange process in benzene at 60 °C for 2 h, after that, the precipitated lithio intermediate is quenched with DMF to complete the reaction. In addition, at 20 °C, the Witting reaction of aldehyde **18** with methylphosphonium bromide ions with the presence of *n*-BuLi yields 70% vinyl tetraphenylethylene (**19**). They employed the Sonogashira-Hagihara coupling procedure to attach alkynyl conjugation to the TPE peripheral unit at first.

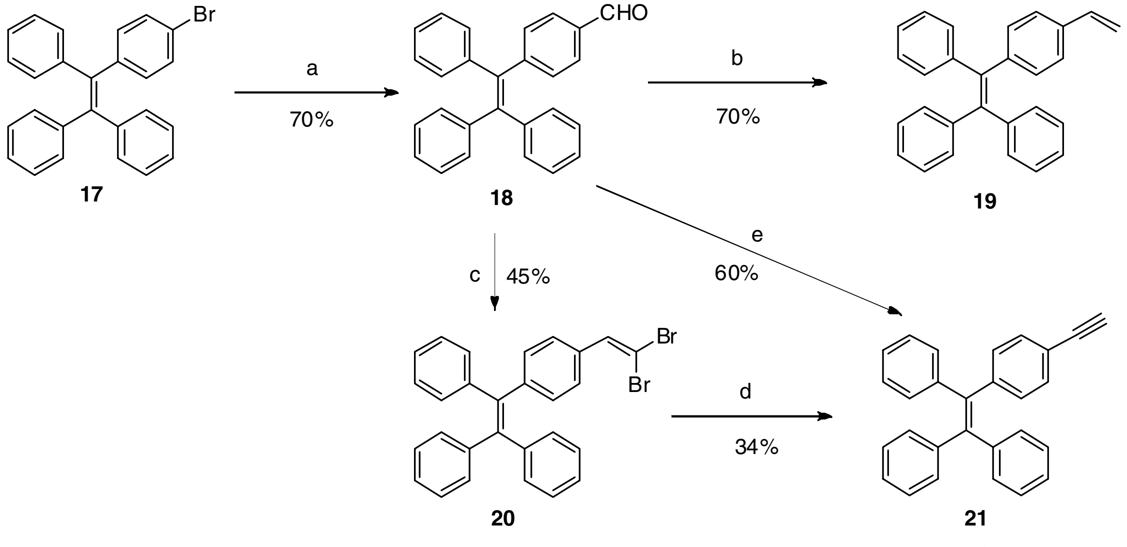
A number of different procedures employing the triple Sonogashira reaction have been investigated. The central molecule, *tris*(4-iodophenyl)amine (**22**), was synthesized from triphenylamine using iodine and mercury oxide, according to the published procedure [57]. The TPA-TPE dendrimer (**23**) was synthesized with a high yield of 75% *via* a three-step Sonogashira coupling between **22** and alkyne **21** (**Scheme-XI**).



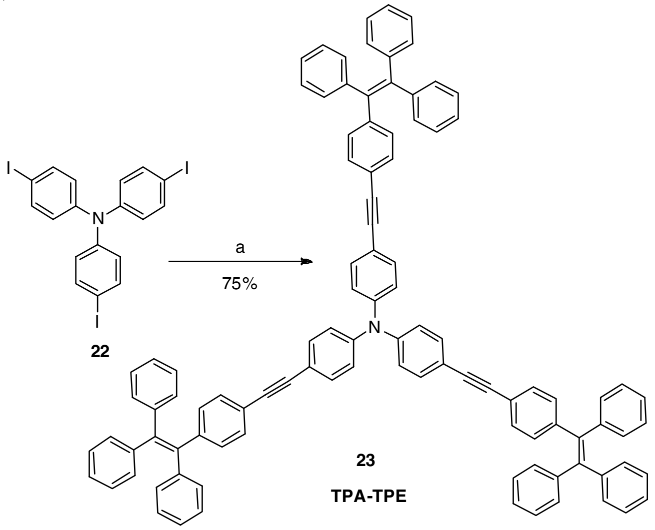
Scheme-VIII: Alternate synthesis of **8**



Scheme-IX: Dendrimer **1** has been synthesized to its final state

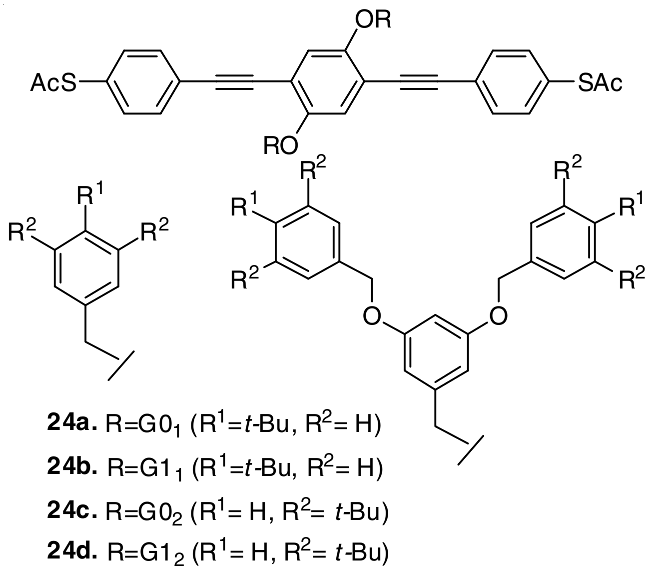


Scheme-X: Reagents and physical conditions: (a) *n*-BuLi (2 equiv), benzene, 60 ºC, 2 h, then DMF, rt, 6h; (b) $Ph_3P^+CH_3Br^-$, *n*-BuLi, THF, -20 ºC to rt, 6 h; (c) CBr_4, PPh_3, CH_2Cl_2, -10 ºC to rt, 4 h; (d) *n*-BuLi, THF, -78 ºC, 1 h; (e) $[Ph_3PCH_2Br]^+ Br^-$, *t*-BuOK, THF, -78 ºC, 1 h, then r t, 24 h



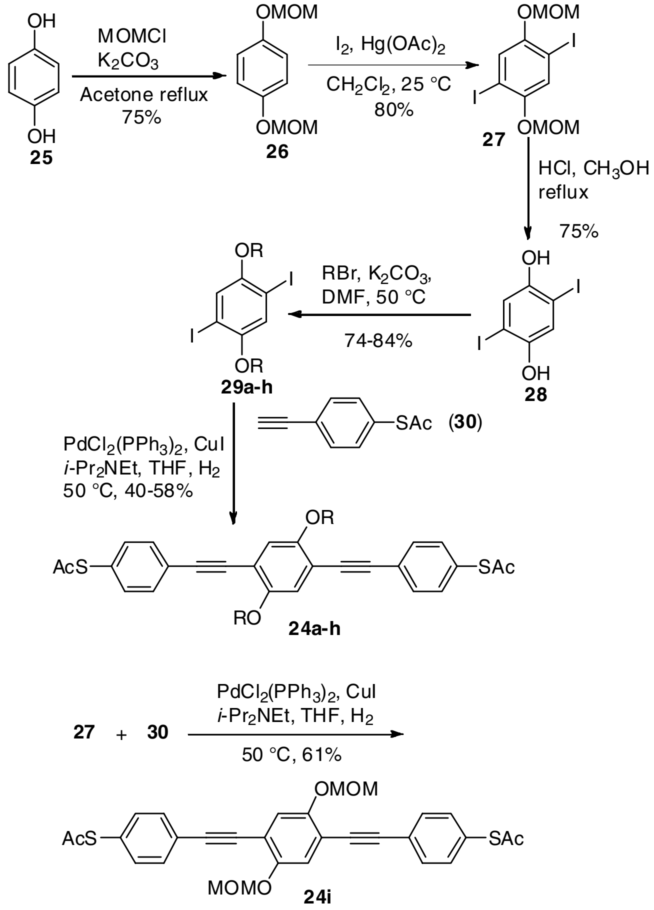
Scheme-XI: Reagents and physical conditions: (a) **21** (4 equiv), $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 24 h

Production of oligo(phenylene ethynylene)s and dendrimer "shells": Thiol groups at the terminal ends of oligophenylene ethyelenes (OPEs) [58] connect nanoscale grooved metallic electrodes. Dendrimer groups act as "shells," enabling the nanoscopic environment around the OPE "core" to be customized (**Scheme-XII**).

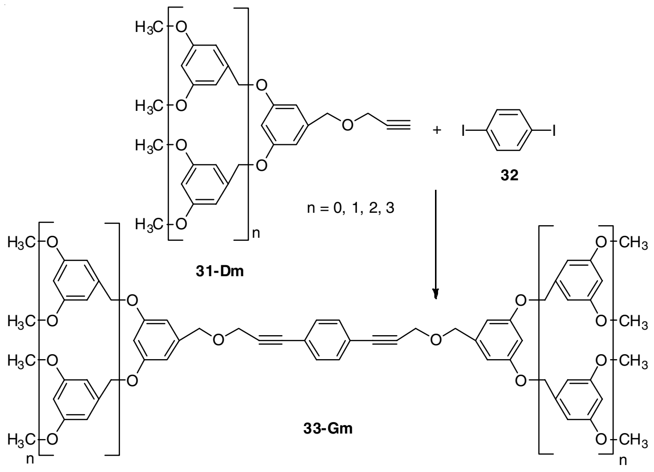


Scheme-XII: OPEs have a dendrimer "shell" as part of their structure

After that, the synthesis of oligophenylene ethyelenes (OPEs) was carried out (**Scheme-XIII**). First, 4-ethynyl-1-thioacetyl-benzene (**30**) was synthesized from 4-iodo benzene sulfonyl chloride according to the methods described in the literature [59,60]. After that, the synthesis of OPEs was carried out (**Scheme-XIV**). Compound **26** was next synthesized by protecting the phenolic hydroxy group of hydroquinone (**25**) with the MOM group, resulting in a 75% yield [61]. Compound **27** was then synthesized using I_2 and $Hg(OAc)_2$ to generate an 80% yield [62]. Following that, deprotection of **27** with HCl resulted in a 95% yield of the key intermediate diphenol **28**.



Scheme-XIII: Synthesis of OPEs



Scheme-XIV: Sonogashira coupling reaction of alkyne-functionalized dendrons used to create dendrimers. Chemicals and conditions: $Pd(PPh_3)_4$, CuI, DBU, DMF, rt, $Pd(PPh_3)_4$

Following that, intermediate diphenol **28** was treated with a variety RBr in the presence of K_2CO_3 to obtain high yields of compounds **29a-h**. Then, at 50 ºC under hydrogen atmosphere, compounds **29a-h** or **27** were exposed to palladium-catalyzed Sonogashira reaction with **30** to generate the final compounds **24a-i**. It was also discovered that when the reaction was carried out in an inert environment, the yield was very poor due to creating a homo-coupling product of **30**.

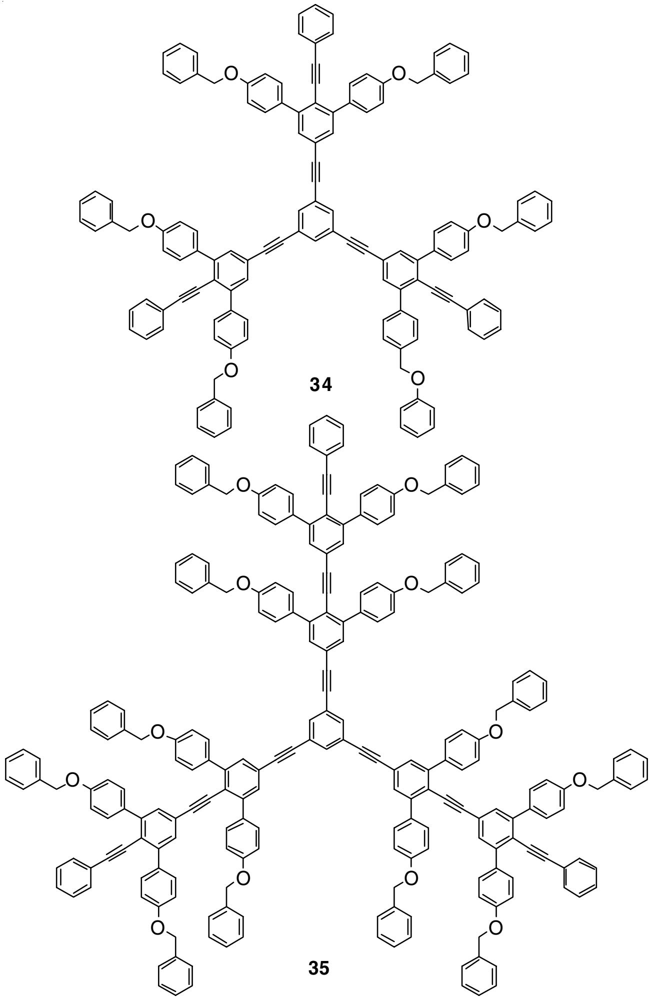
Sonogashira coupling of alkyne-focal Frechet type dendrons yields dendrimers: Branched and regular macromolecules, dendrimers [62-65] have been used as functional items in the fields of nanotechnology and nanoscience [66-69]. The Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction between alkynes and azides is a prototypical reaction of click chemistry [70-73].

The Frechet-type dendrimers, connected by 1,4-diethynylbenzene, were synthesized utilizing a convergent technique including alkyne functionalized Frechet-type dendrons **31-Dm** (**Scheme-XIV**). Alkyne-functionalized Frechet-type dendrons **31-Dm** were obtained by propargylation of the appropriate dendritic benzyl alcohol with propargyl bromide. To find the most suitable conditions for the reaction of dendrons **31-D1** and 1,4-diiodobenzene (**32**) *via* Sonogashira reaction with alkyne dendrons with various conditions in different solvents, different amine bases such as piperidine, diisopropylamine, triethylamine, piperazine and 1,8-diazabicycloundec-7-ene (DBU) and palladium as catalysts. As reported that using DMF as a solvent, DBU as base and $Pd(PPh_3)_4$ as a catalyst in the presence of CuI resulted in a high yield of the desired product.

Synthesis of snowflake like dendrimers: Kozaki & Okada [74] reported synthesis of snowflake-like dendrimers with a brancehed π-conjugated system by site selective approach. They adopted a strategy in which they use a dialkyltriazeno unit as key protecting group [75-80] (**Scheme-XV**).

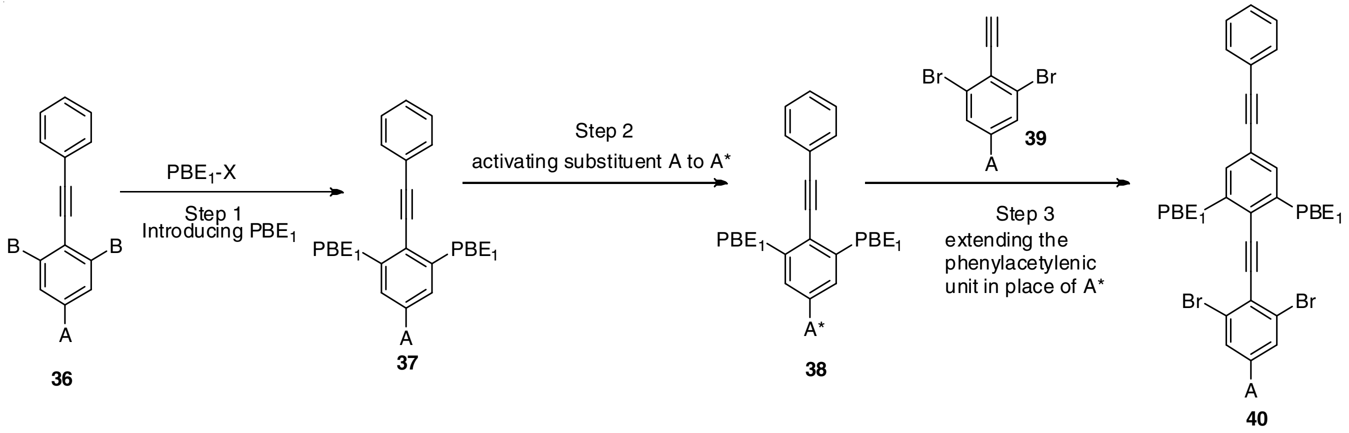
Scheme-XVI depicts the technique for the site-specific synthesis of branched dendrons. Three stages are repeated to complete the synthesis: (i) replacing B on the AB_2-diphenyl acetylene with branching poly(benzyl ether) branches (PBEn, where n is the number of generations); (ii) activating A to A*, resulting in **38**; and (iii) extending the phenyl acetylenic unit in lieu of A*, resulting in **40**. The generation number (n) of the integrating PBEn grows as the number of cycles increases.

Scheme-XVII was used to prepare key intermediates. Iron powder was used to reduce the nitro group [74,81] in **41**, yielding **42** modest yields. The amino group of **42** was changed to a diethyl triazeno group [74,82] by treating it with *tert*-butyl nitrate, trifluroborane etherate and then diethylamine to generate key compound **43**, which was employed as a key in the protection-activation of group A.

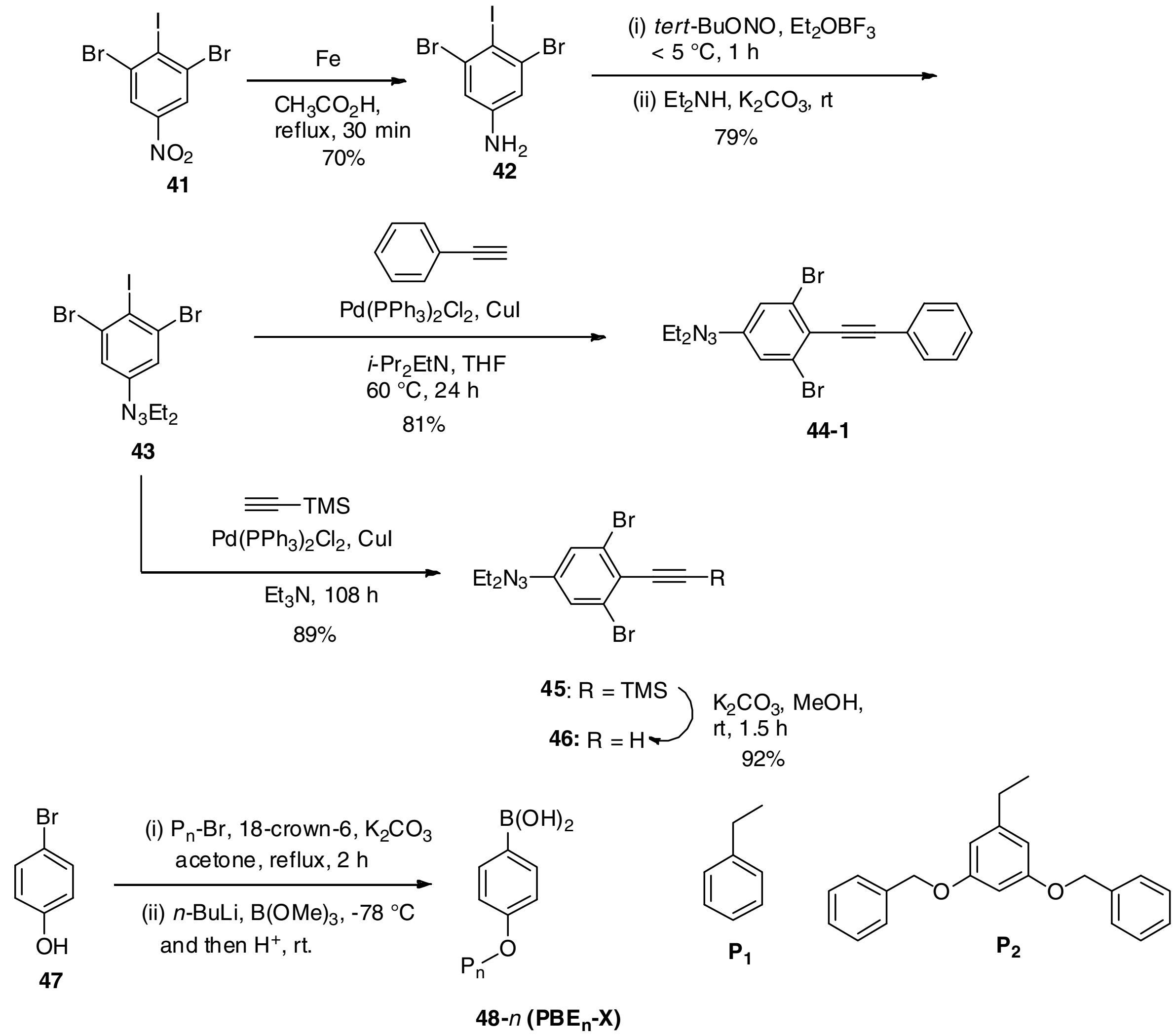


Scheme-XV: Dendrimers in the form of snowflakes

Snowflake shaped dendrimers **34** and **35** were synthesized *via* a convergent approach using these essential compounds (**Scheme-XVIII**). Suzuki coupling of diphenyl acetylene **44** with **48** (2 equiv) yielded dendritic branches **49** (**37** in **Scheme-XVI**) in 88% yield and dendritic branch **49** was heated to 120 ºC in a sealed tube with iodomethane to yield first-generation dendritic branch **50** (**38**, A*=I) in 87%yield. In 57% of cases, the second cycle of a series of reactions yielded second



Scheme-XVI: A description of the steps involved in the site-selective formation of branching dendrons



Scheme-XVII: Preparation of key intermediates

generation dendritic branch of **50**. A Sonogashira coupling of dendritic branches **50-n** (n = 1 or 2) with 1,3,5-triethynylbenzene **51** yielded target dendrimers **34** and **35** as white and yellow powders in 70% and 48%, respectively. Dendrimers **34** and **35** were described using conventional spectroscopic methods and were soluble in organic solvents such as THF, chloroform and toluene.

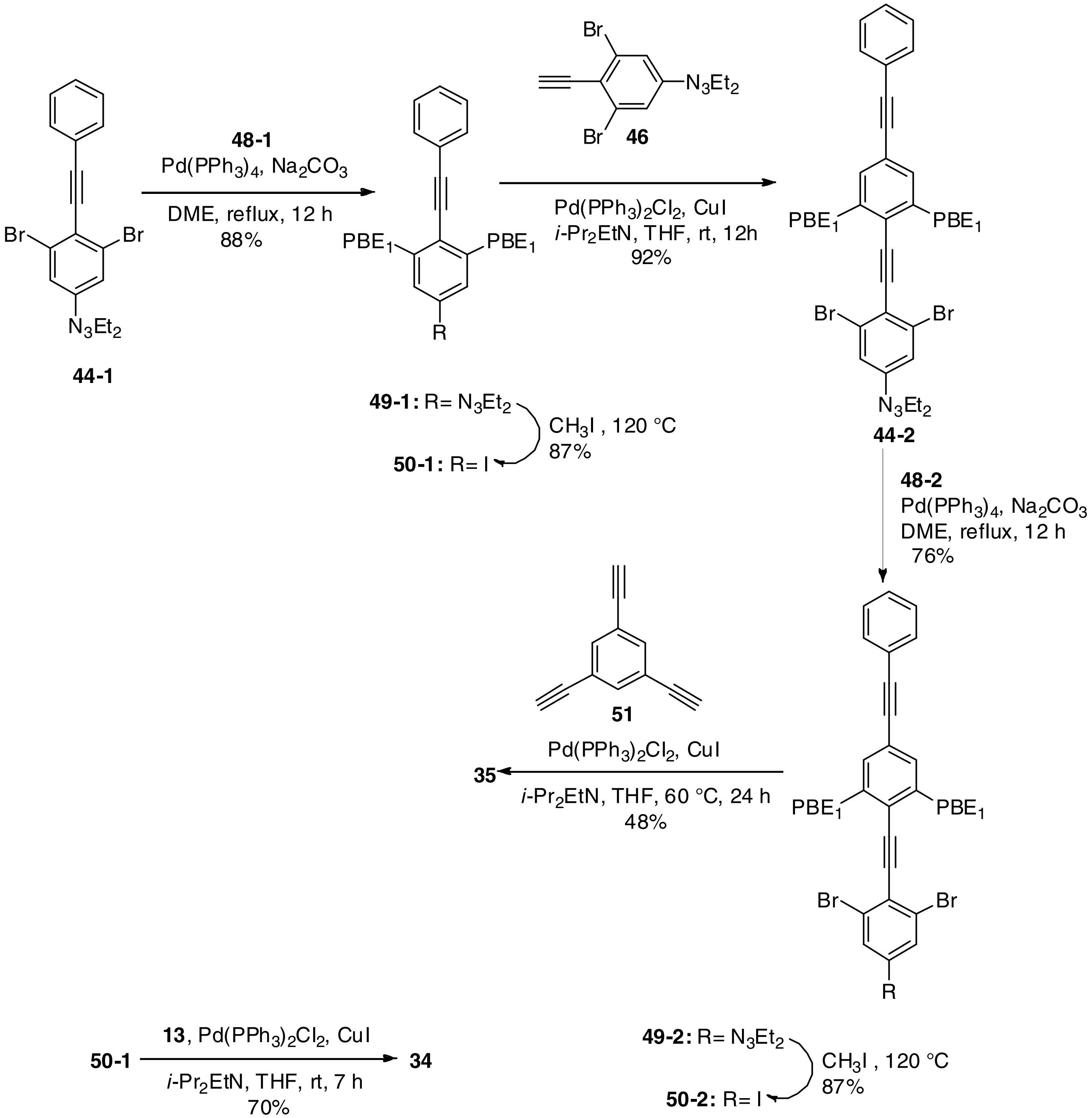
Janus dendrimer type multivalent donor-acceptor synthesis: A convergent multistep process for constructing a Janus-type multivalent donar-acceptor [84-87] system has been reported by Diederich *et al.* [83]. The coupling between two differently ferrocene (Fc) substituted dendrons and a final cycloaddition-retroelctrocyclization (CARE) reaction with tetracyanoethene that occurs regioselectively at only one of the rigidly linked dendrons form the basis of the synthetic procedure. A convergent synthetic approach utilizing dendrons of various polarity yielded the first Janus dendrimer.

To synthesize the Janus dendrimer type system **53** (**Scheme-XXV**), two dendrimers were needed, Dendron **69** and the new dendron **86**, with one hemisphere containing ferrocene donar terminii and the other hemisphere containing distinct donor substituent TCBDs, arising from the CARE reaction. They produced dendron **69** precursor **59** from 2,6-diiodo-4-nitroaniline (**54**) through **55**, **56** and **57**. The Suzuki coupling of **57** with 4-bromo phenyl boronic acid produces bromo compound **58**, which is subsequently reacted with I_2/*n*-BuLi in THF to produce highly reactive iodo compound **59** (**Scheme-XIX**).

Another precursor, **65** was synthesized from 4-iodoaniline, (**60**) *via* the formation of **61**, **62** and **63** following the literature procedure [88,89]. Then **63** undergoes Suzuki coupling with ferrocene boronic acid to give the compound **64**, which reacts with *n*-Bu_4NF (TBAF) in THF and gives the Dendron precursor **65** (**Scheme-XX**).

Sonogashira coupling of both precursors **59** and **65** give the triazene **66**, which was further reacted with methyl iodide to give iodo compound **67.** Sonogashira coupling of **67** with TMS-acetylene gives the compound **68**. Removal of TMS group from **68** upon treatment with K_2CO_3 gives the target dendron **69** (**Scheme-XXI**).

They have synthesized another precursor **77** to dendron **79** from the same starting material **54**. Diazotization of **54** followed by reduction and diazotization give **70**, **71** and **72**, respectively. Cross coupling of **72** with an excess of 4-ethynyl-*N*,*N*-dihexylaniline, **73** gives **74**, which reacts with Me_3SiCl/



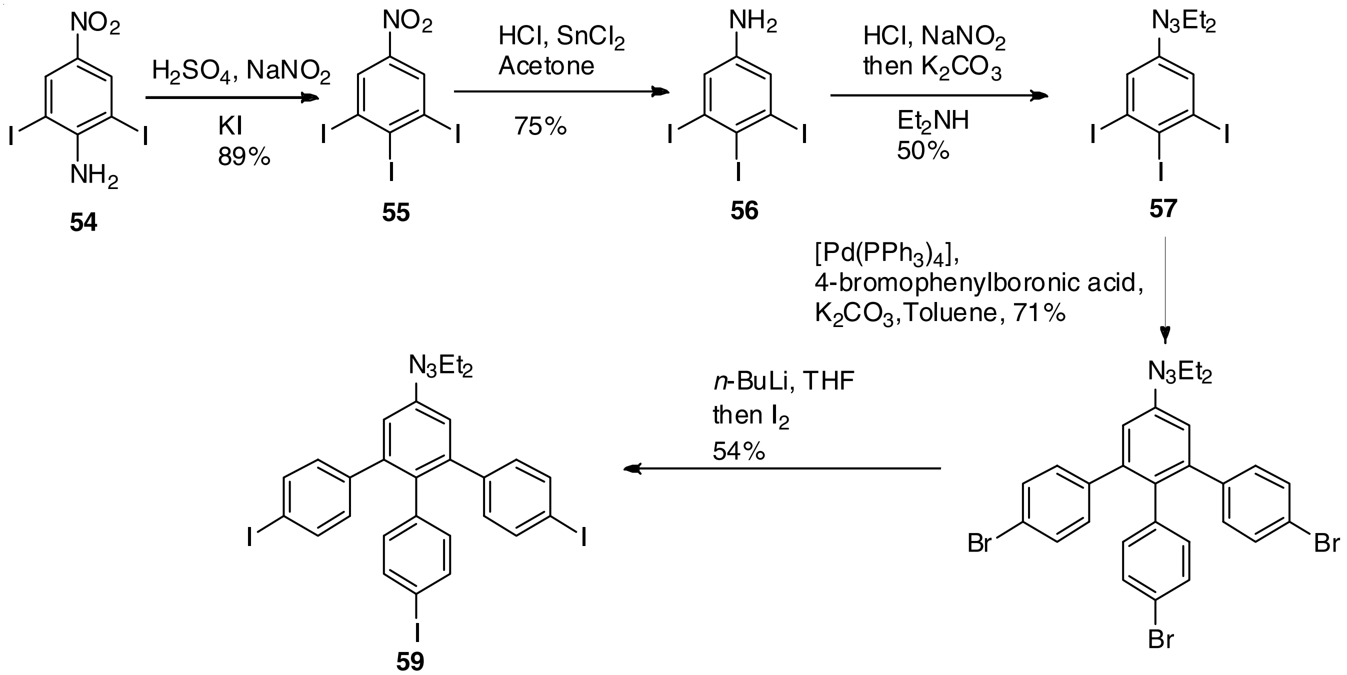
Scheme-XVIII: Synthesis of dendrimer **34** and **35**

NaI under mild reaction condition (CCl_4/MeCN, 60 ºC, 20 min) to give iodo compound **75**. Then another coupling of **75** with TMS-acetylene gives **76**. Removal of TMS group from **76** upon treatment with K_2CO_3 gives the precursor **77** (**Scheme-XXII**).

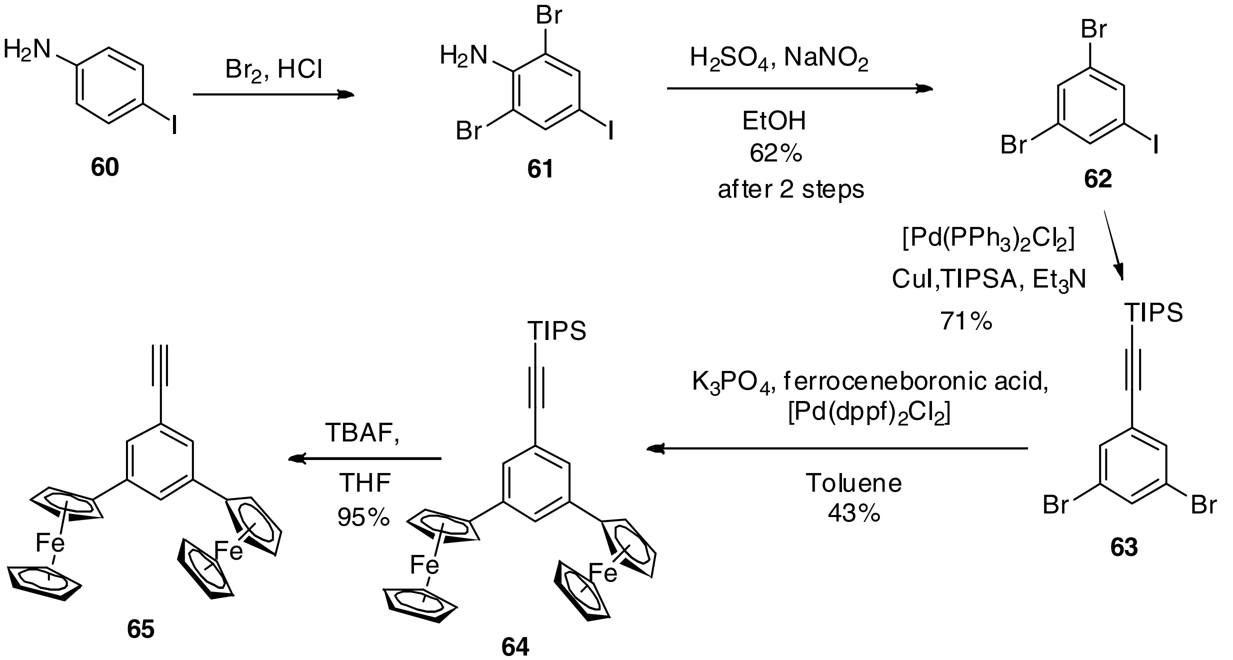
The precursor **59** and **77** produces triazene **78** (**Scheme-XXIII**). But they failed to synthesize the dendron **79** due to problems with the quaternization of aniline moieties.

The synthesis of **86** began with commercially available 1,3,5 tribromo benzene (**80**) coupled with TMS acetylene in a single Sonogashira to yield alkyne **81**. The coupling of dendrons **69** and **86** yielded the multivalent precursor **87** to target **53** in 57% yield (**Scheme-XXIV**), but it was accompanied by homo-coupling of terminal alkyne **69**, which yielded **88** as a side product in 20%.

Synthesis of alkynyl *bis*(bidentate phosphine) organometallic dendrimers through convergent methods: According to Humphrey *et al.* [90], dendrimers are a class of monodisperse hyper-branched molecules that have uses in medical diagnostics and potential applications in domains such as photoactive device, molecular recognition, catalysis, *etc*. [91-93]. Rigid aryl-alkynyl branched organometallic dendrimers



Scheme-XIX: Synthesis of precursor **59** to dendron **69**

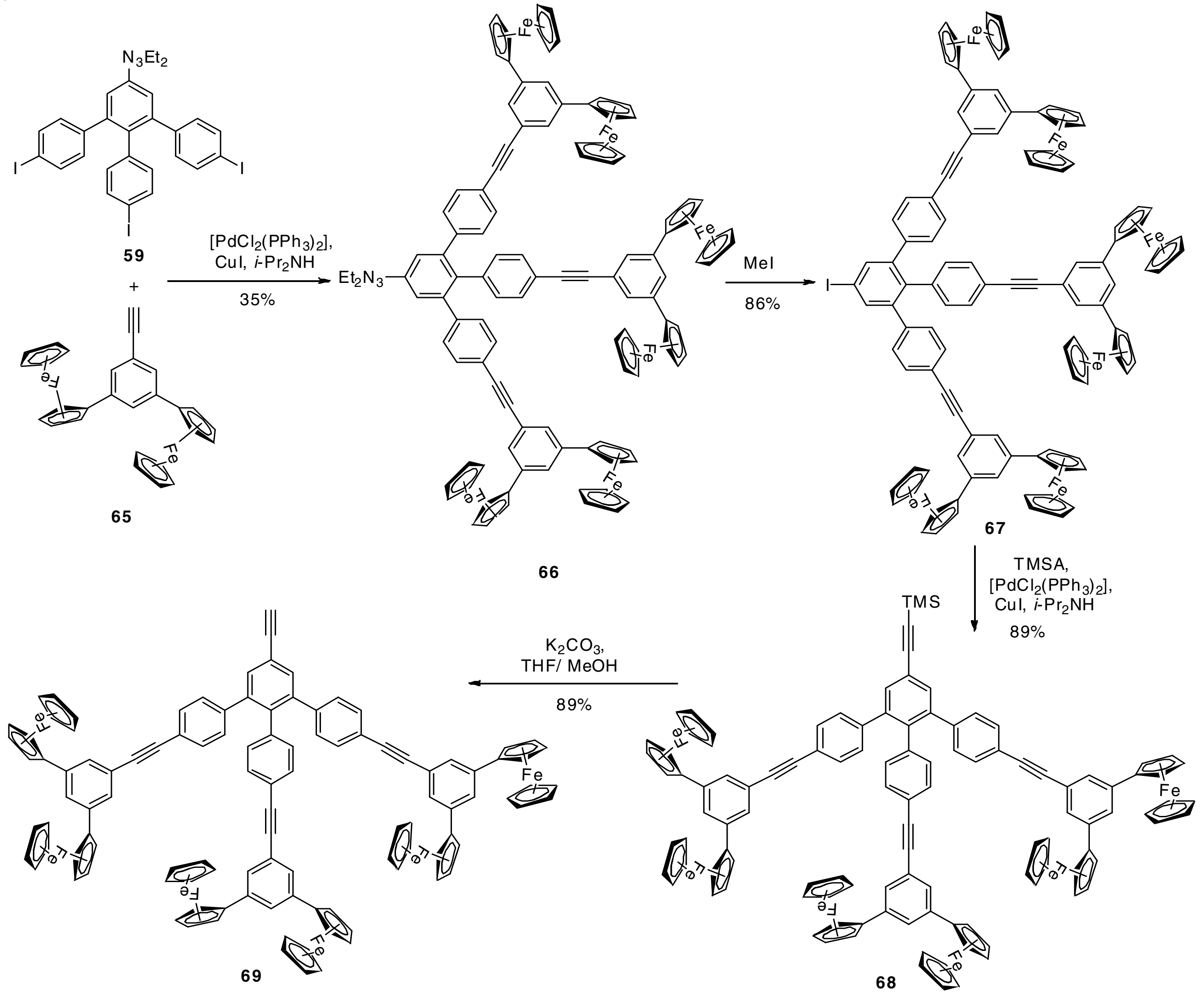


Scheme-XX: A Precursor **65** to dendron **69** synthesis was carried out

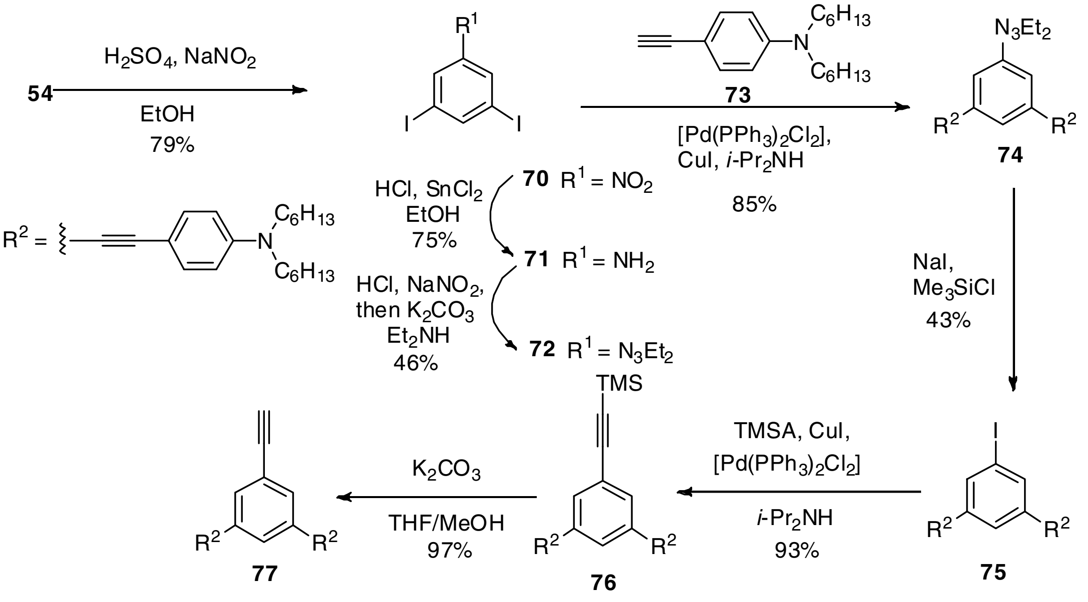
[94,95] incorporating ruthenium metal within the branched structure has been constructed using the procedure described by Takahashi *et al*. [96-99] and Leininger *et al*. [100].

Synthesis of zero-generation dendrimers: The aryl-alkynyl dendrimers containing platinum have square planar geometry, therefore no steric hindrance to tri-platinating triethynyl benzene and mesitylene [99,100]. Integrating a "spacer" unit into the core is the initial stage in alkynyl ruthenium dendrimer formation (**Scheme-XXV**).

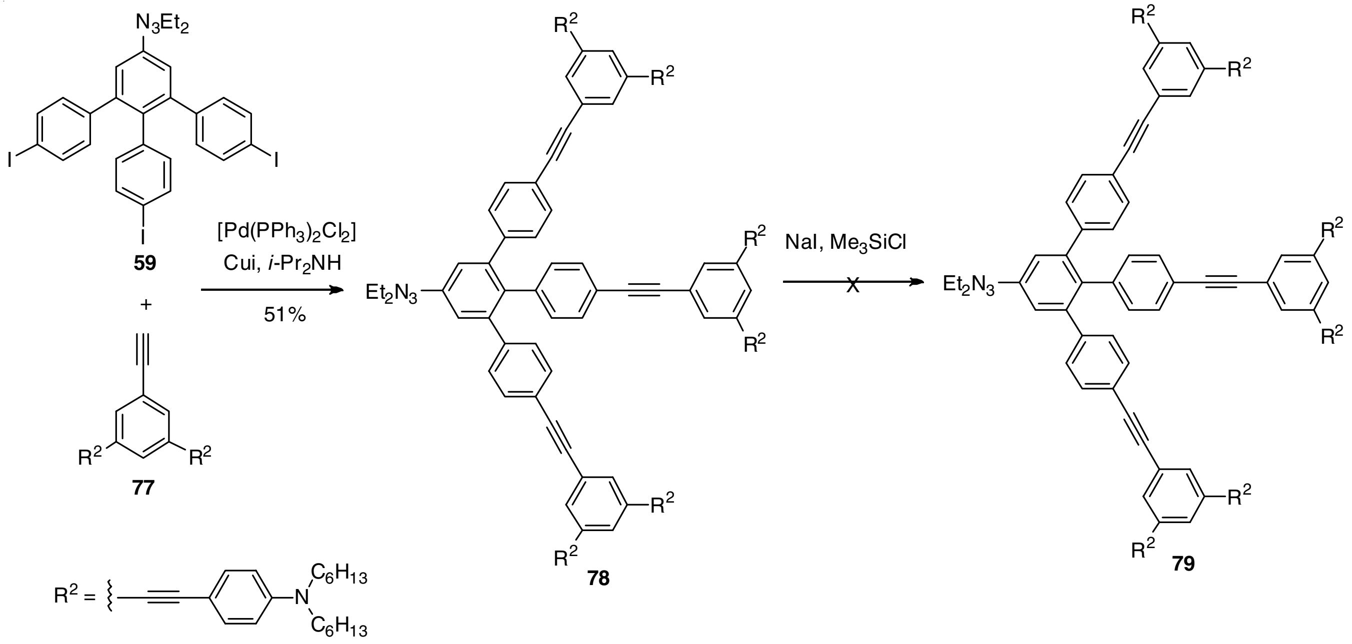
The coupling reaction of 1,3,5-trithynyl benzene with three equivalent of 1-iodo-4-trimethyl silylethynyl benzene in the presence of a $[PdCl_2(PPh_3)_2]$/CuI catalyst in triethylamine afforded *tris*(4-trimethyl silylethnylphenyl) derivative **89**, subsequent desilylation with fluoride giving the compound **90**, the reaction of compound **90** with *cis*-$[RuCl_2(L_2)_2]$ (L_2= dppe, dppm) in dichloromethane in the presence of PF_6^- give the trivinylidene complexes **91** and **92**, deprotonation of **91** and **92** complexes with NEt_3 give trialkynyl complexes **93** and **94**.



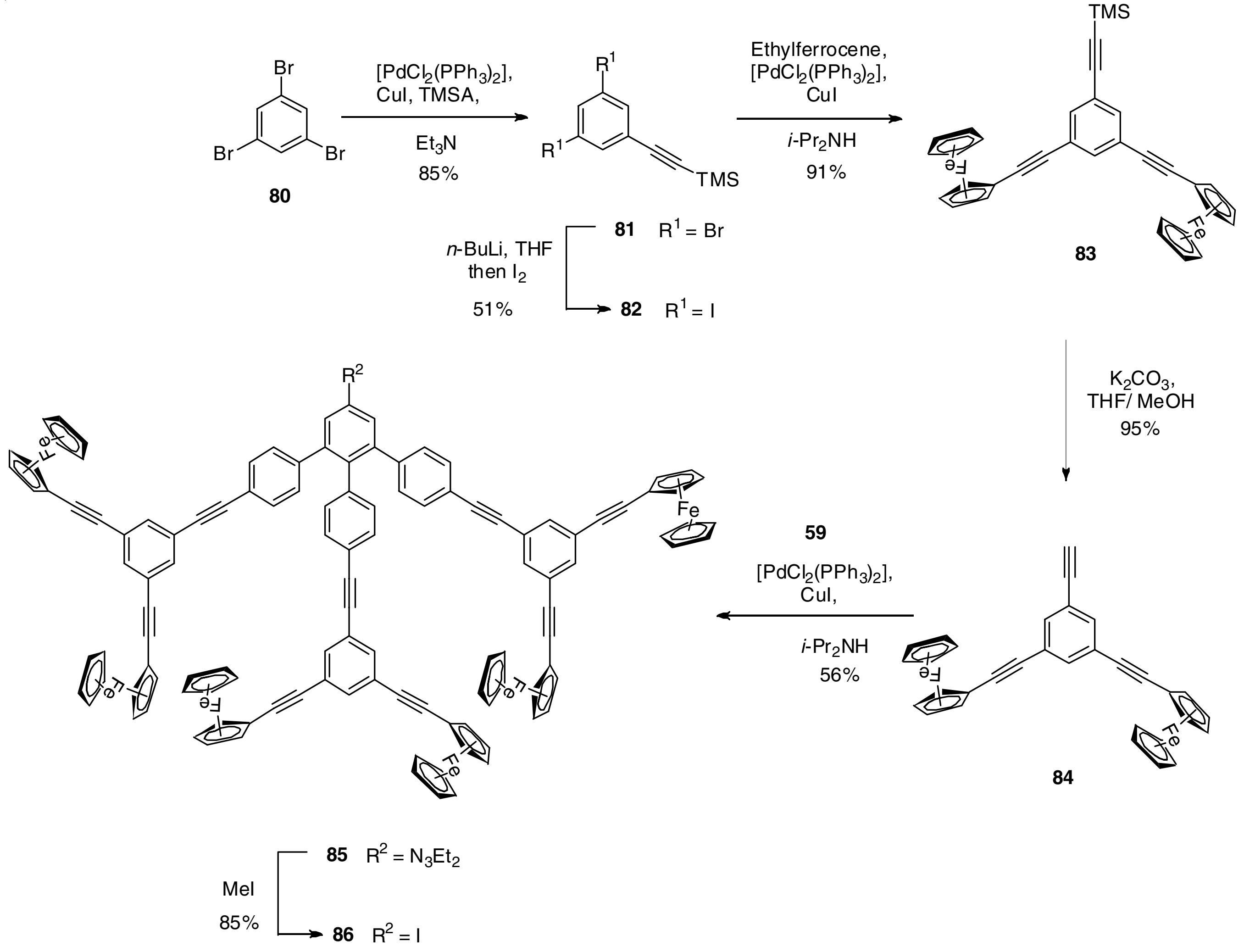
Scheme-XXI: Synthesis of dendron **69**



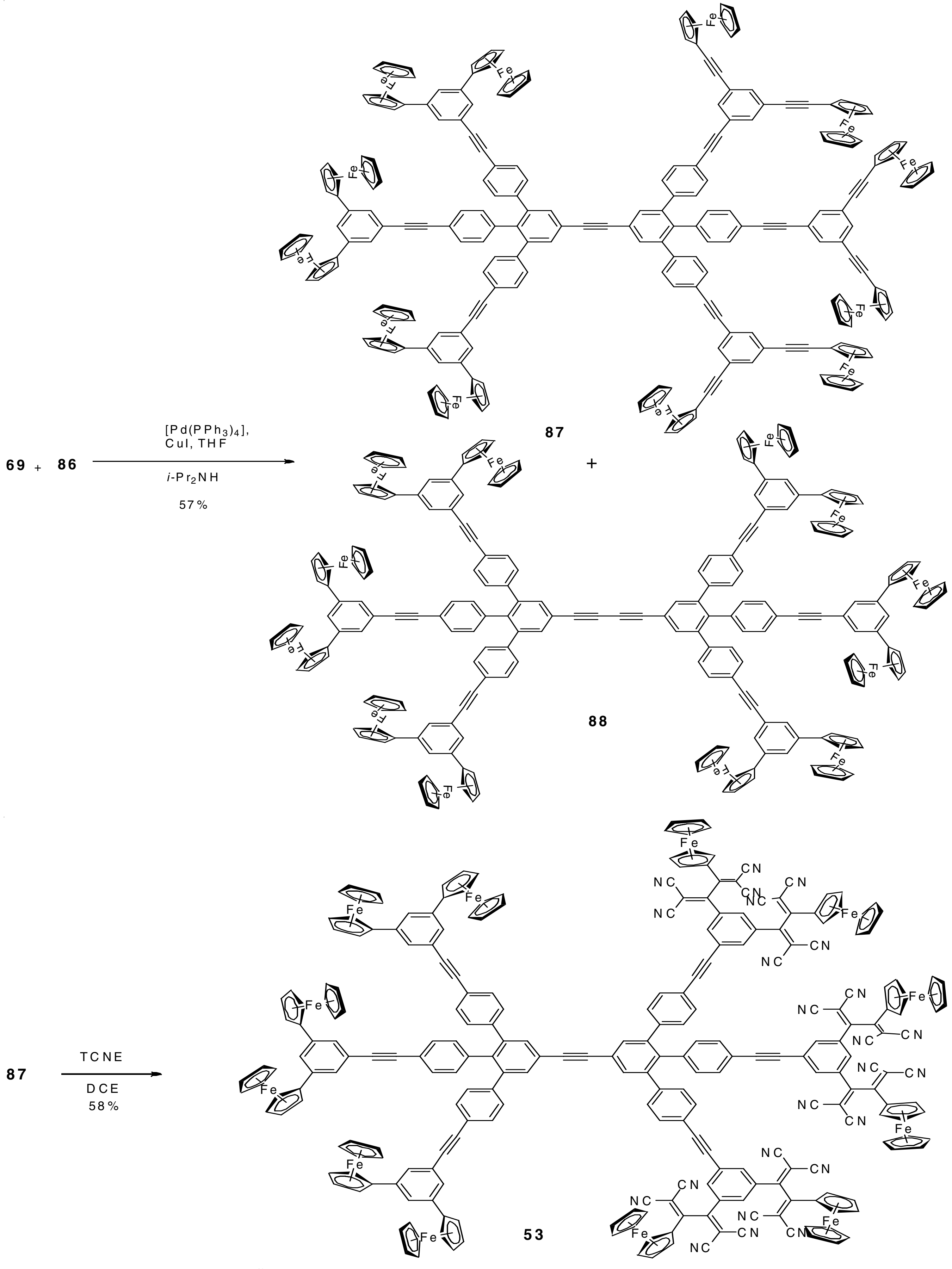
Scheme-XXII: Precursor **77** to Dendron **79** synthesized in the study



Scheme-XXIII: Attempted synthesis of dendron **79**



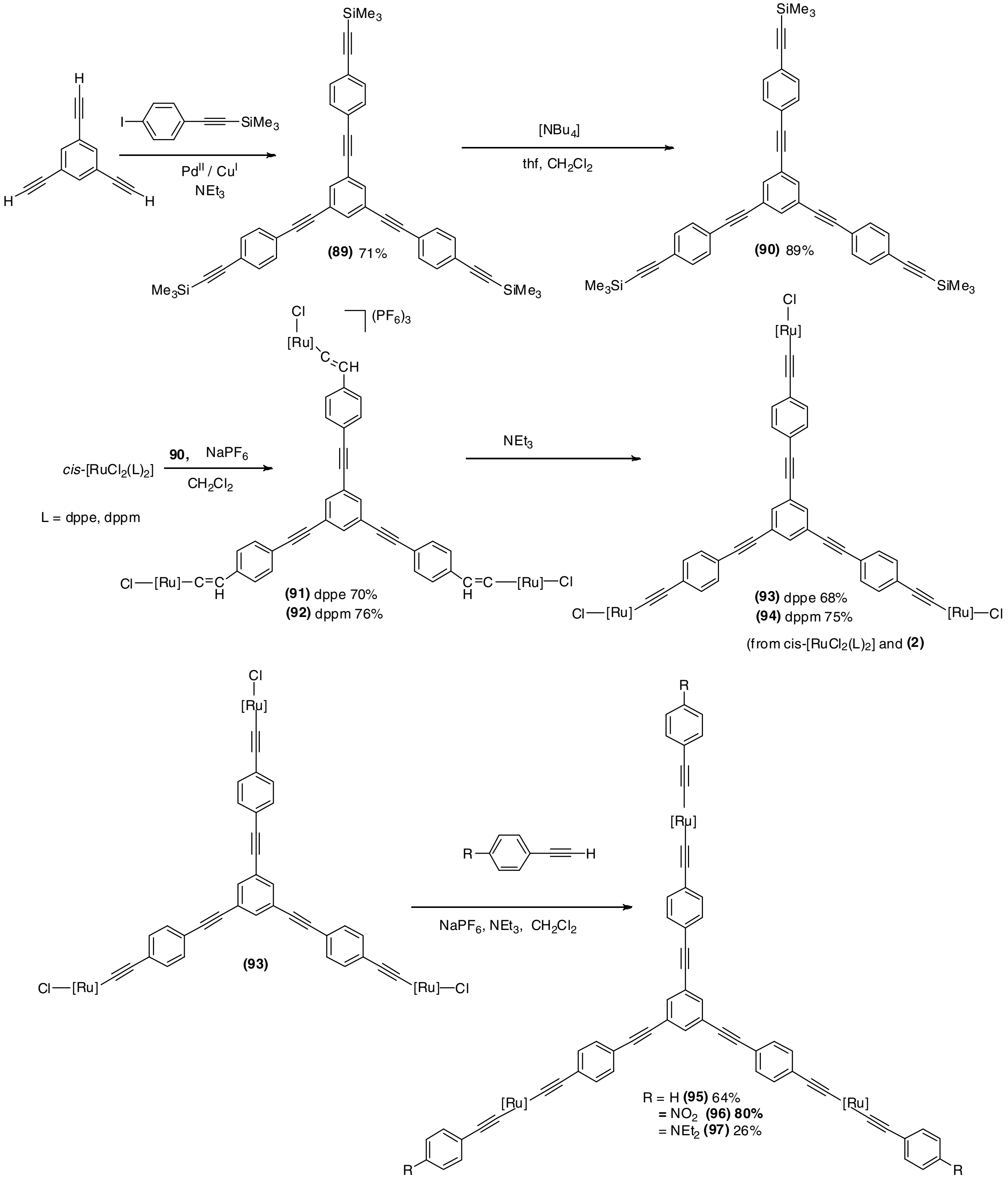
Scheme-XXIV: Synthesis of dendron **86**



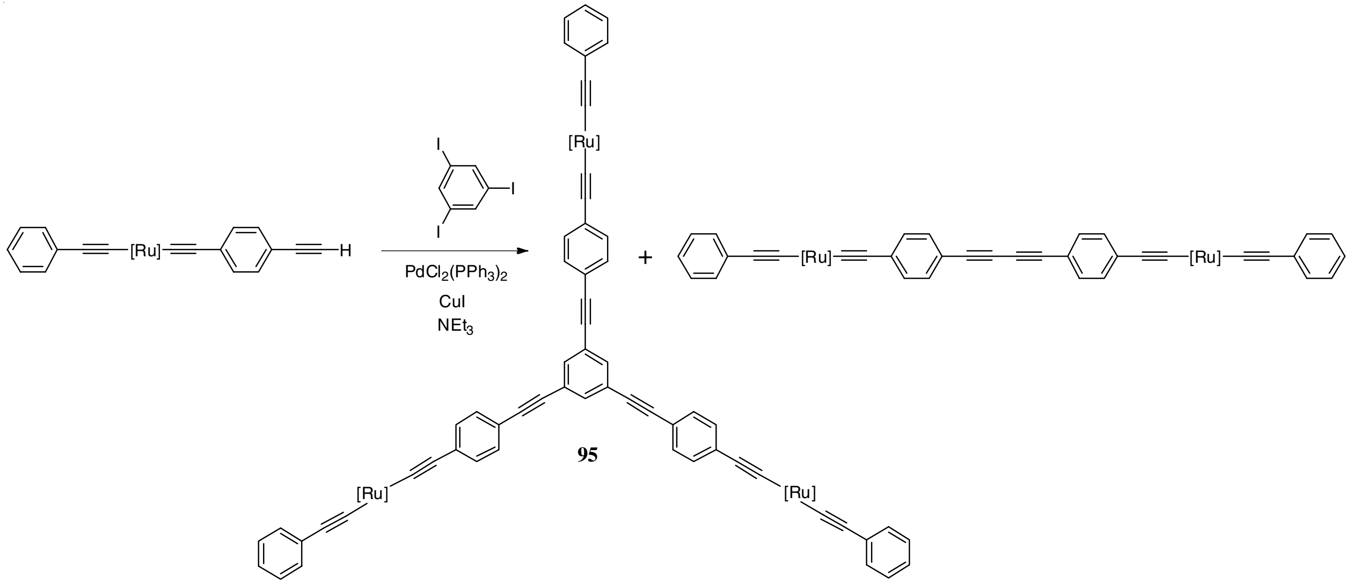
Scheme-XXV: Synthesis of Janus-type donor-acceptor system **53**

The reaction of compound **93** with phenyl acetylene or its 4-nitro or 4-diethylamino functionalized counterparts leads to *tris*-di(alkynyl) complexes **95-97** through the intermediacy trivinylidene complexes (**Schemes XXVI** and **XXVII**).

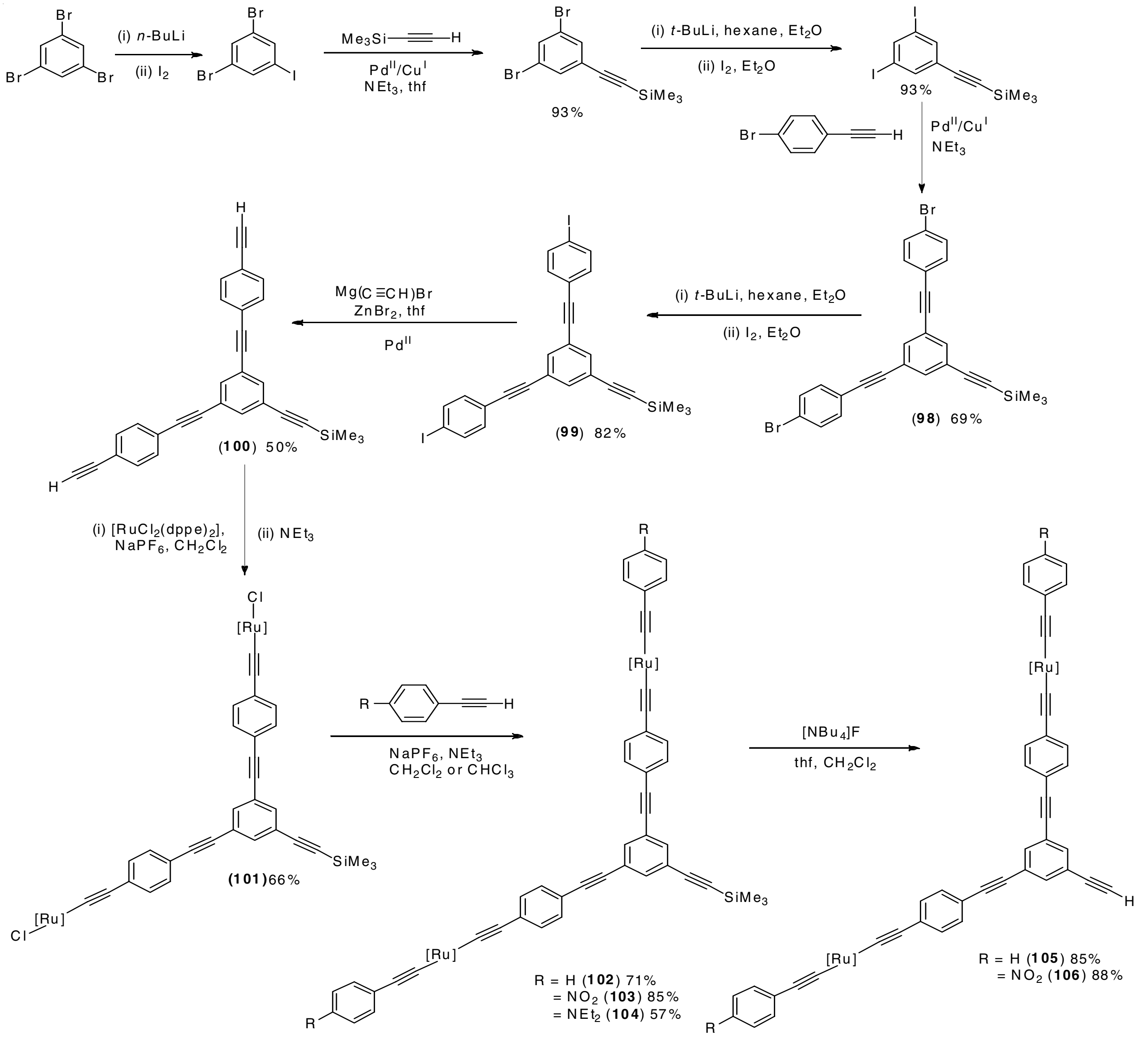
First generation dendrimer synthesis: In **Scheme-XXVIII**, a convergent method for dendrimer synthesis by Sonogashira-coupling is described. Coupling between 1,3-diiodo-5-trimethyl silylethnyl benzene with 1-bromo-4-ethynyl benzene in the presence of [$PdCl_2(PPh_3)_2$] and copper(I) iodide yields **98**, which may then be *trans*-halogenated to generate the diiodo analogue **99**. The organic dendron **100** was created with the combination of diiodide **99** and palladium(II)/



Scheme-XXVI: Preparation of compounds **89-97** ([Ru] = *trans*-[Ru](dppe)$_2$ or *trans*-[Ru](dppm)$_2$)

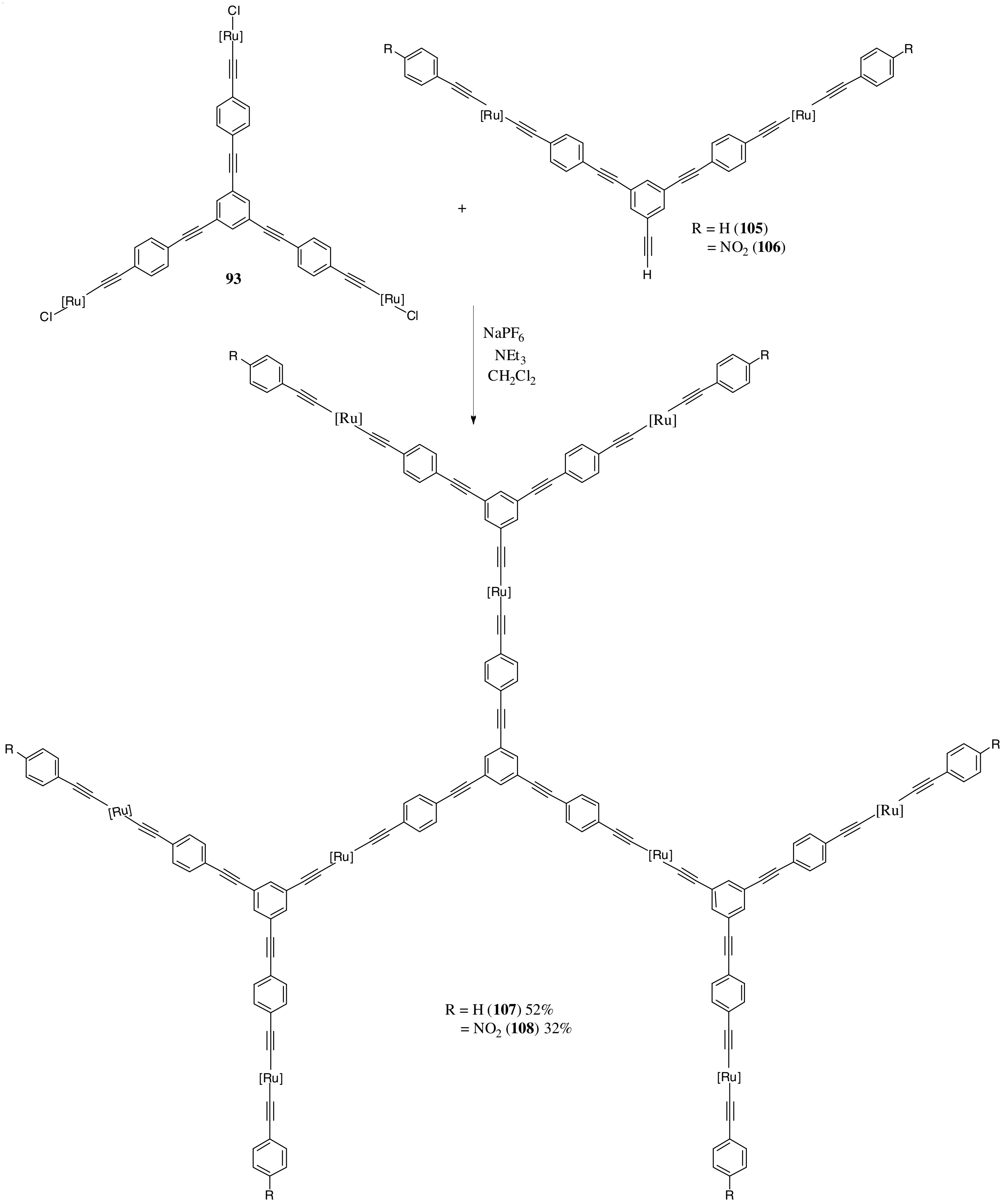


Scheme-XXVII: Preparation of **95** from *trans*-[Ru(C≡CPh)(4-C≡CC$_6$H$_4$C≡CH)(dppe)$_2$] ([Ru] = *trans*-Ru(dppe)$_2$)



Scheme-XXVIII: Wedges preparation **98-106** ([Ru] = *trans*-Ru(dppe)$_2$)

copper(II) catalysts. Compound **100** reacts with *cis*-[RuCl$_2$(dppe)$_2$] in the presence of NaPF$_6$ to form a divinylidene complex [101], which is deprotonated *in situ* by triethylamine to form dialkynyl complex **101**. The *bis*-di(alkynyl) complexes **102-104** are formed when compound **101** reacts with phenyl acetylene or its 4-niro or 4-diethylamino functionalized counterparts in the presence of NaPF$_6$ and base. Trimethylsilyl protecting group is removed by fluoride treatment, followed by a smooth reaction with **102** and **103** to provide *bis*-dialkynyl complexes **105** and **106**.



Scheme-XXIX: 107 and **108** preparation ([Ru] = *trans*-Ru(dppe)$_2$)

In the final step of such dendrimer synthesis is to couple the organometallic core (**Scheme-XXVIII**), with 3 equivalents of **105** or **106** in the presence of $NaPF_6$ and triethylamine generate the first generation dendrimer complex **107** or **108** accordingly (**Scheme-XXIX**).

Conclusion

The Sonogashira coupling has been shown in this study as a significant process of formation of C-C bond with rising applications in various domains of modern science including synthetic chemistry and material science domains. Identifying novel compounds of interest accessible *via* this process has expanded considerably in recent years, prompting search for more convenient reaction conditions and efficient catalyst. The Sonogashira coupling process is used to synthesize dendrimers successfully. A dendrimer is a molecule that lies between the interface of molecular and polymer chemistry. Although the Sonogashira coupling reaction has progressed significantly in recent years for different dendrimer construction, rooms are still open for many improvements to be made with the dendrimer preparation. The Sonogashira cross coupling is poised to be one of the the most interesting aryl-alkynyl coupling for the next several years, with all of these hurdles in place and rising interest in the various products produced.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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