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Synthesis of phosphonium cascade molecules

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SYNTHESIS OF PHOSPHONIUM CASCADE MOLECULES

BY

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A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

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ABSTRACT

Synthesis of Phosphonium Cascade Molecules

By

Kasthuri Rengan

Advisor: **Professor Robert Engel**

The synthesis of a series of cascade molecules (dendrimers) in which the core and branch points are phosphonium sites has been accomplished. The primary cores of these cascade molecules are either tridirectional, tetradirectional, or pentadirectional for the development of the generations of the cascade structure. Secondary branch points, also phosphonium ion sites, are all tridirectional for the development of further generations of the cascade structure. The phosphonium cascades represent a novel addition to the general class of dendrimeric molecules. Numerous possibilities exist for the use of such structures in ion exchange and other supramolecular processes.

Dedicated to my parents, brothers, and sisters

Acknowledgements

I would like to express my deep sincerity and appreciation to my mentor Dr. Robert Engel, whose patience, understanding, guidance, and continued faith in me, made my successful completion of the program of study possible.

I extend my thanks to all my colleagues, especially Dr. John Boulos, who not only helped in the research but provided an amicable atmosphere in the laboratory.

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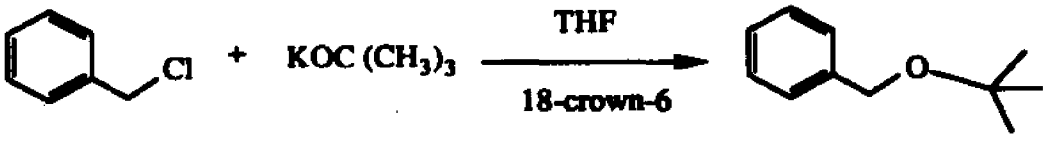
INTRODUCTION

General

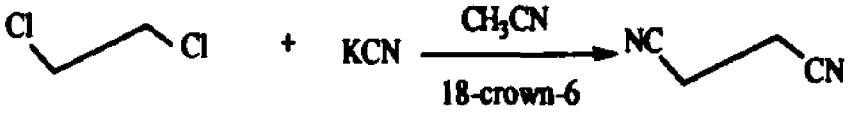
Although it has long been recognized in the functioning of biochemical systems, it is only in relatively recent years that there has been developed a significant interest in the concept of "supramolecular chemistry" involving non-biological molecules.[1] Recently, Lehn, *et al.* have reported[2] the synthesis of a variety of supramolecules and also explored the use of such supramolecules in organic syntheses as well as in biological studies. Supramolecular chemistry, that is the transient interactions of two or more molecules allowing further covalent changes (such as are present in biological systems with enzyme-substrate binding or lipid packing into membrane components), has been recognized of late to be of use in laboratory synthetic procedures. The most prominent examples of this utility are given by the cryptates.

The development of cryptates of alkali metal ions has facilitated the performance of a variety of organic syntheses.[3] Association of the alkali metal cation of an inorganic reagent with a cryptate, such as potassium ion with 18-crown-6, allows the chemically active anion to exist in a non-associated form in a relatively apolar organic solvent. This type of association may readily be applied to organic syntheses. For example, as illustrated below, use of 18-crown-6 eliminates the normal association of the *t*-butoxide anion with the potassium ion and thereby renders the anion more nucleophilic. This approach allows

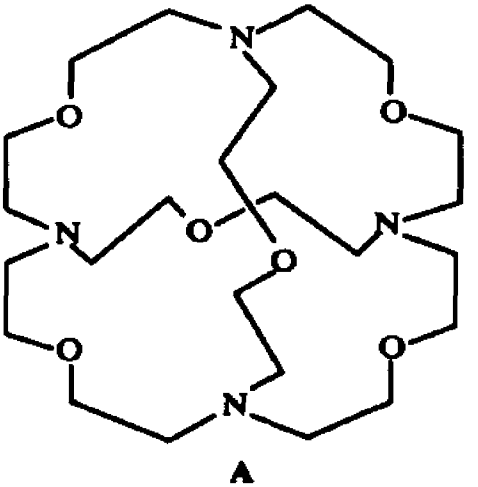
high yields of *t*-butyl ethers to be obtained in a modified Williamson synthesis.[4]



In another nucleophilic substitution reaction involving such "naked anions", potassium cyanide in acetonitrile reacts with alkyl halides in the presence of 18-crown-6 to give nitriles more rapidly and in higher yields than can be attained by "conventional" methods.[5]

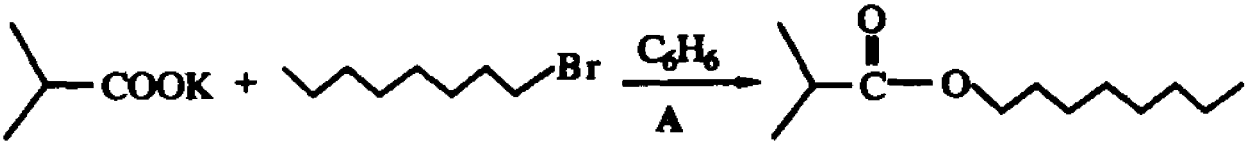


Ester formation *via* the displacement of a halide by a carboxylate salt is facilitated through the addition to the reaction mixture of the spheroidal macrotricyclic cryptate **A** [6-8] (Fig. 1).

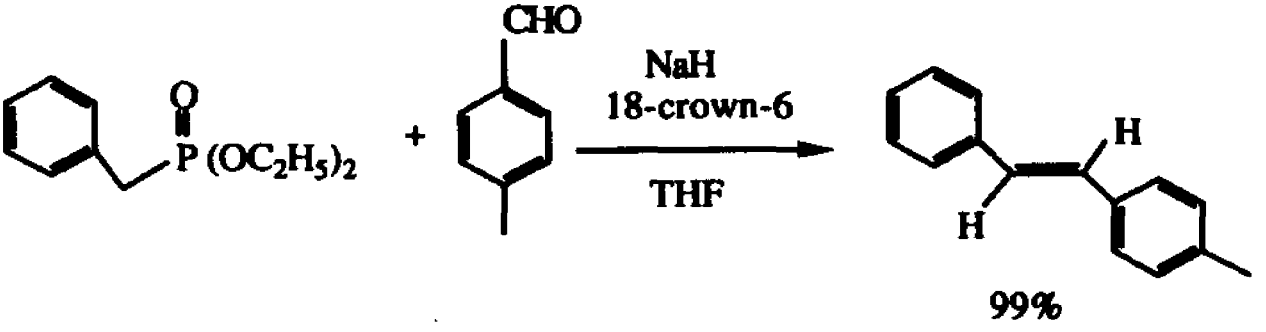


A

Fig. 1



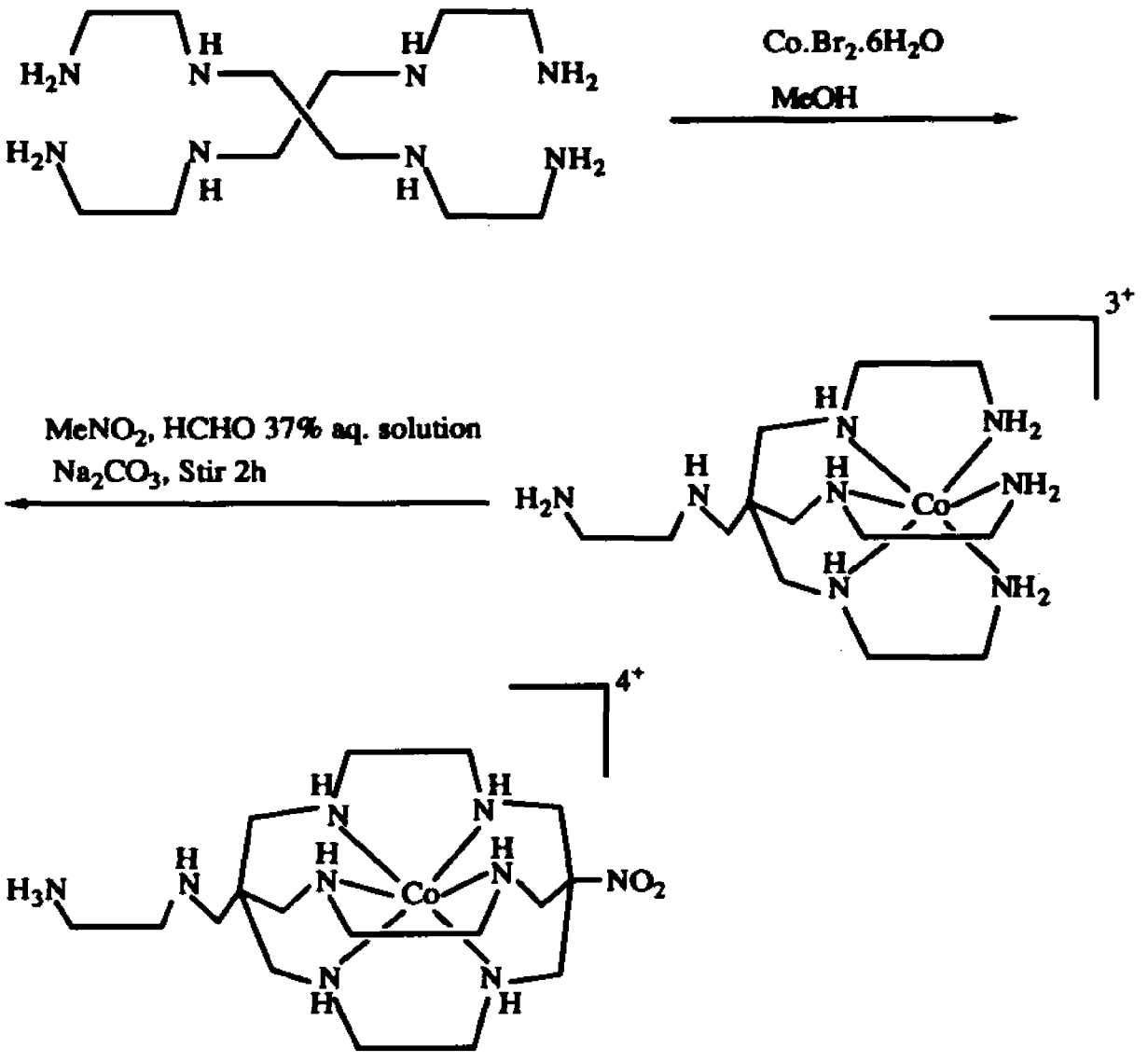
In a reaction other than a nucleophilic substitution process, 18-crown-6 facilitates the Horner reaction of benzyl phosphonates with carbonyl compounds. The phosphonate anion is formed by reaction of the benzylphosphonate with sodium hydride in tetrahydrofuran.[9]



99%

Functionalized crown ethers have also been used to accomplish enhanced organic syntheses through specific associations. For example, facilitated peptide syntheses have been performed using thiol-substituted crown ethers to bind the "growing" peptide chain and the incoming amino acid.[10] This type of facilitated reaction closely mimics the simple model[11] of enzyme catalysis.

Recently, a multi-dendate cation-encapsulating agent bearing a reactive pendant arm has been studied.[12] Such an appendage to the complexing center should allow a further reactivity to be associated with it (Scheme 1).



Scheme 1

The examples noted above of supramolecular chemistry have all involved "internal interactions". Another category of supramolecular chemistry involves binding at the surface of a host molecule. In such instances distinction between the "host" and "guest" species becomes less clear. Assignment of the terms is a matter of perspective.

Cascade Molecules

The cascade molecules (or dendrimers) are an interesting class of structures which have been developed in recent years. Recently, Tomalia, *et al.* have prepared a series of cascade molecules which are collectively known as starburst dendrimers,[13] and this branch of "supramolecular chemistry" should spark new developments in both organic and macromolecular chemistry. These molecules incorporate structural repetition in an ordered manner, starting with an initiation core from which emanate two or more identical branches, each branch containing further branch sites. With successive generations of branch sites, a cascade structure develops a geometry akin to that of a fractal set. These molecules have significant potential to serve as models for biological supramolecular interactions as well as for ionic interactions of the type found with cryptates and classical ion exchange polymers.

"Cascade" molecules, originally designed to provide molecular cavity topology without the size restrictions of the cyclic cryptates,[14] may be described in structural terms as those which incorporate three components. These include: (1) a core or foundation site for the diverging branches of the cascade; (2) one or more branching chains emanating from the core site, each chain leading to a further branch point (a secondary core); (3) a terminal functionality for each of the branches. The cascade molecules differ from ordinary polymeric species in that each unit added (branch with secondary core)

permits more than one further monomeric species to link to it. This is shown graphically below for a "unidirectional" cascade system with dual branching characteristics. Each "dot" represents a branch point with the lines being the branching chains emanating from each core. The geometric characteristics of such a species have led to its description as a chemical " tree" [15] (Fig. 2).

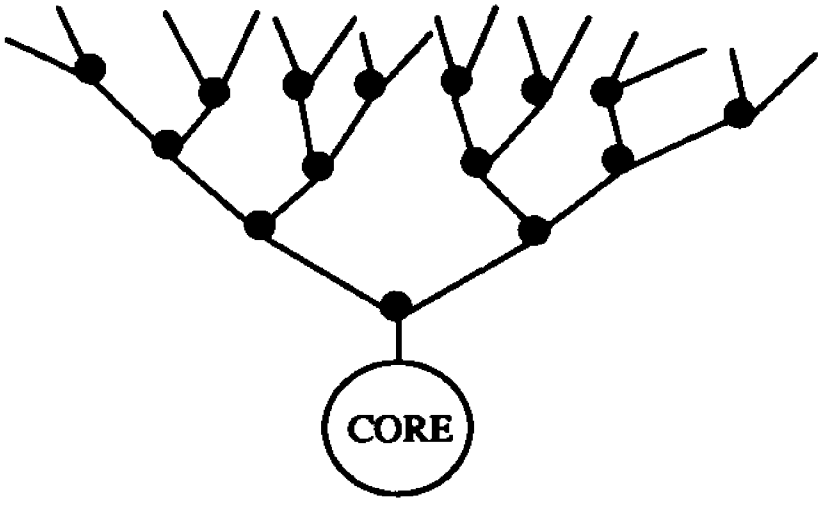


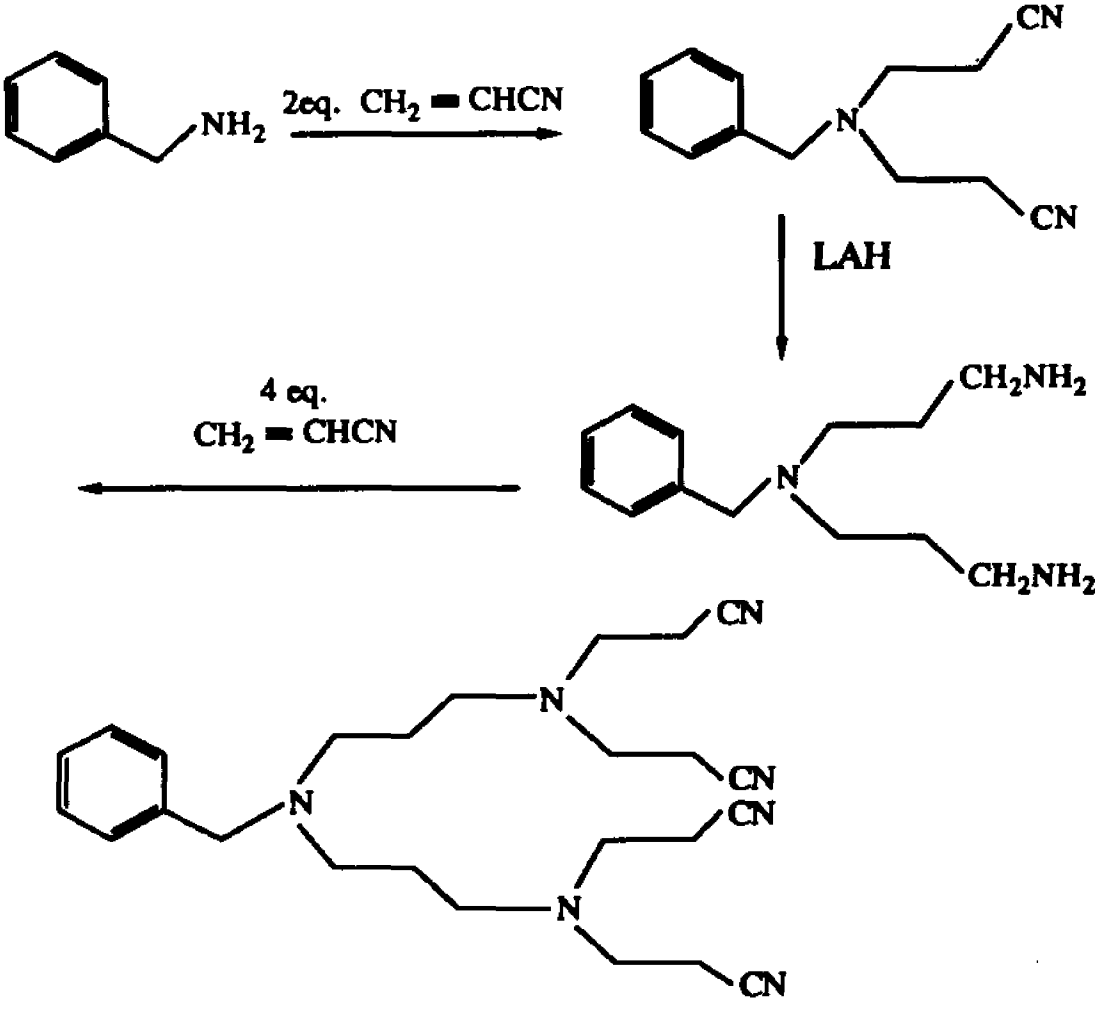
Fig. 2

An architectural analysis of trees is applicable to the design of cascade molecules.[16] The design of cascade molecule construction must incorporate proper functionality at the growing termini such that further increases in size may be carefully controlled.[17,18] The choice of the principal and secondary cores determines the directional characteristics of the branches and the overall shape of the molecule.

To date, a small variety of cascade molecules has been synthesized. The prototype cascade molecules synthesized involved primary alkyl amino groups attached at the core and branch points.[14] Michael addition of each of the primary amino functions with

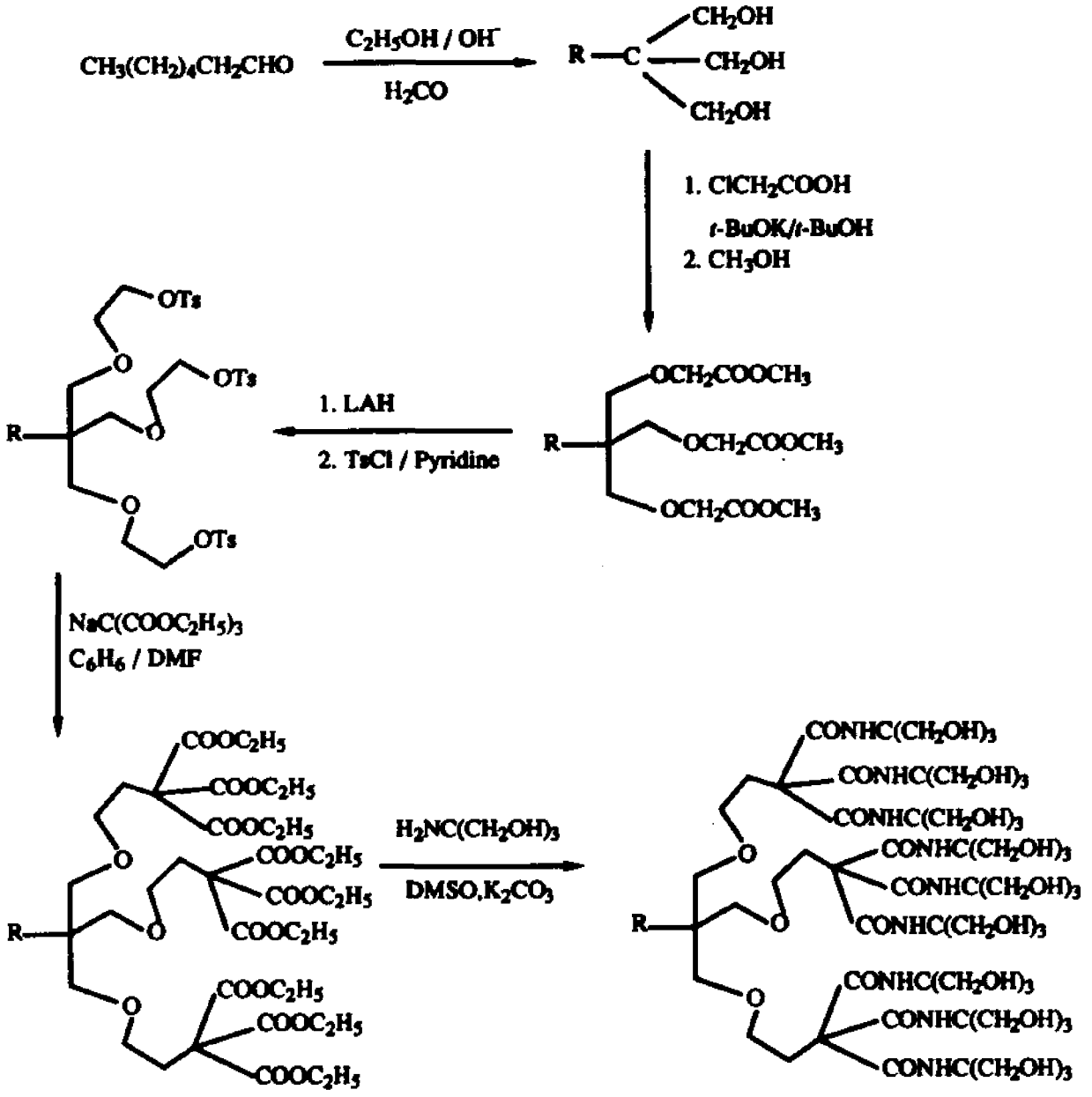
two units of acrylonitrile provided dual branching with a cyano function at the termini of the branches (Scheme 2). (A similar approach has been used starting[19] with nitromethane and acrylonitrile.)

Both nitrile functions were reduced to primary amino functions for further development of the cascade. Both unidirectional (benzylamine and cyclohexylamine cores) and bidirectional (ethylenediamine and 2,6-diaminomethylpyridine cores) were used in this work.



Scheme 2

A unidirectional "tree" structure bearing hydroxyl groups was generated starting with an alkyl halide at the core with triple branching provided by displacement of the halide using triethyl sodiomethane tricarboxylate.[15,20] Reduction of the pendant carboxylate esters provided primary alcohol termini which were further modified for subsequent extension of the branching system, again using sodiomethanetricarboxylate. Upon reduction of the ester linkages a cascade molecule bearing multiple hydroxyl groups at its surface was obtained (Scheme 3). These molecules, referred to as "arborols', bear characteristics of "unimolecular micelles" derived from an architectural model of trees, specifically the Leeuwenberg model. This cascade design generates a molecular structure, having an outer surface covered with polar functional groups. Since this model is based on a simple mathematical progression [$X_n = E^{n-1}$], it denotes a new class of cascade structures. Since these cascades are based on arboreal design, they are logically called *arborols*. Sylvanols are thus the polyspherical cascade analogues.



Scheme 3

In a similar manner was generated a series of bidirectional cascade molecules.[21] A series of linear α,ϖ-aliphatic dihalides was functionalized with triethyl sodiomethanetricarboxylate. "Dumbbell" shaped bidirectional arborols bearing nine free hydroxyl groups at each end were then formed by amidation of the hexaester with tris(hydroxymethyl)aminomethane.

All of the bidirectional triply branched arborols thus formed were found to be water soluble. That which is illustrated below (described as a [9]-10-[9] arborol) also exhibited reversible formation of a gel with rod shaped components (Fig. 3).

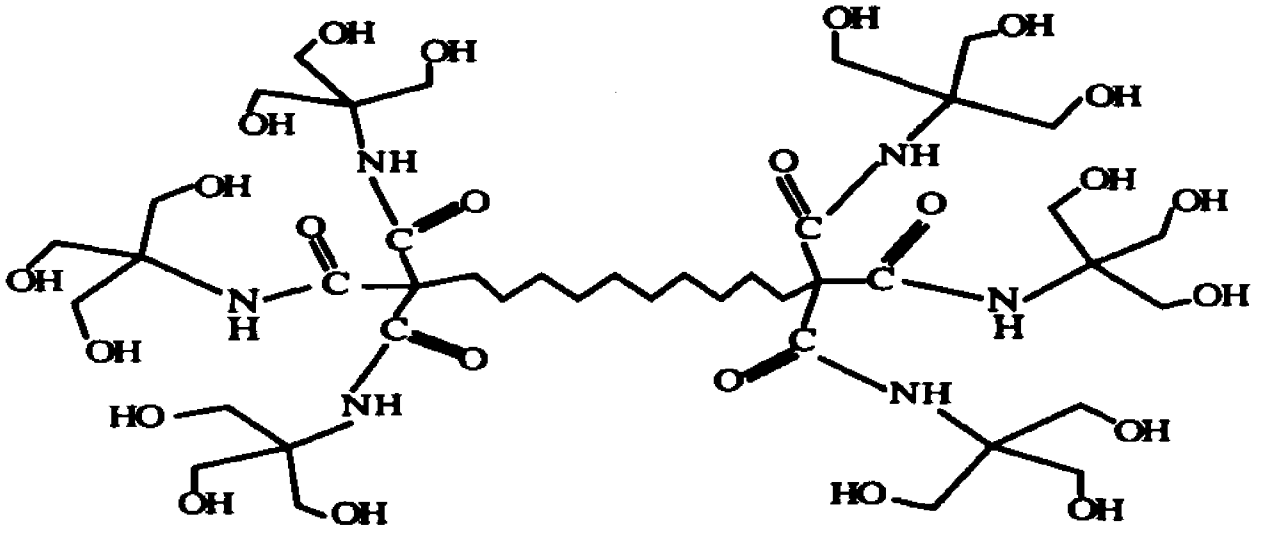
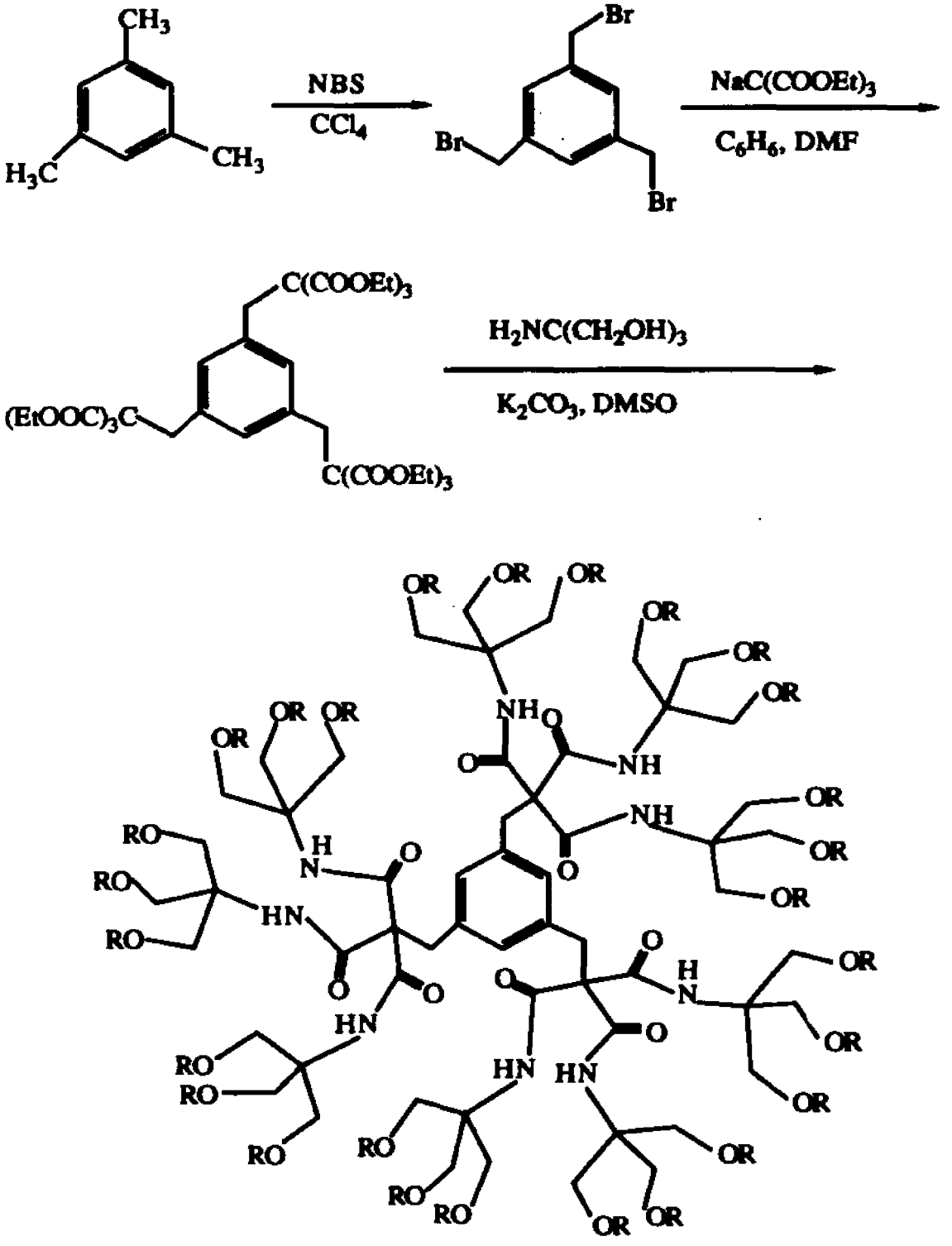


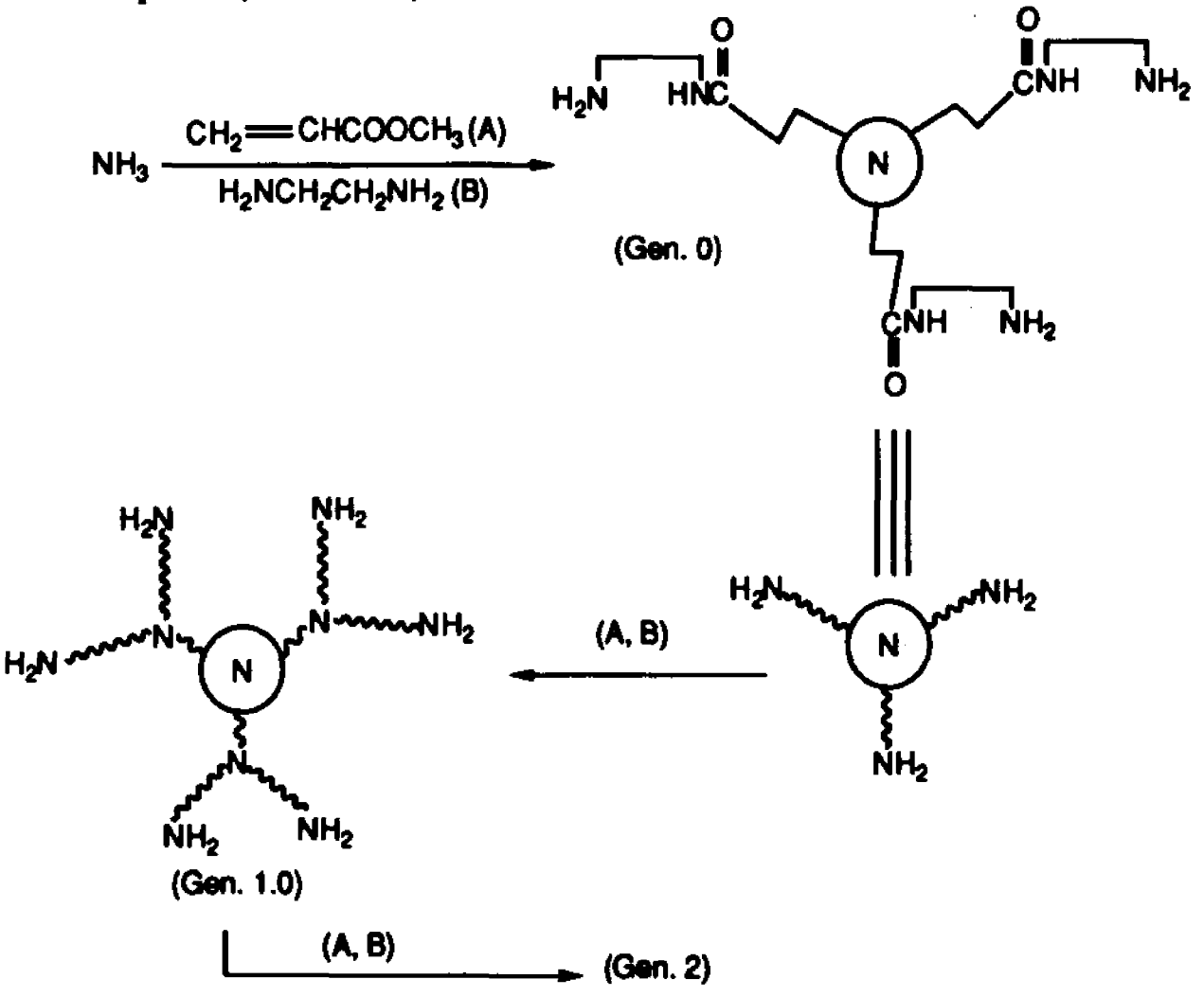
Fig. 3 Bidirectional arborol bearing a decamethylene core

Tridirectional cascade molecules have been prepared starting from both mesitylene[22] and ammonia cores.[23,24] That generated using a mesitylene core incorporated triple branching using the triethyl sodiomethane tricarboxylate-tris(hydroxymethyl) aminomethane route as noted above for arborol synthesis (Scheme 4). In this instance, however, the hydroxyl groups were converted to benzoate esters generating a surface on the spherical cascades less hydrophilic than for the simple arborols. This material was found to be quite soluble in typical organic solvents and insoluble in water, but still hygroscopic.



Scheme 4 R= H, COC_6H_5

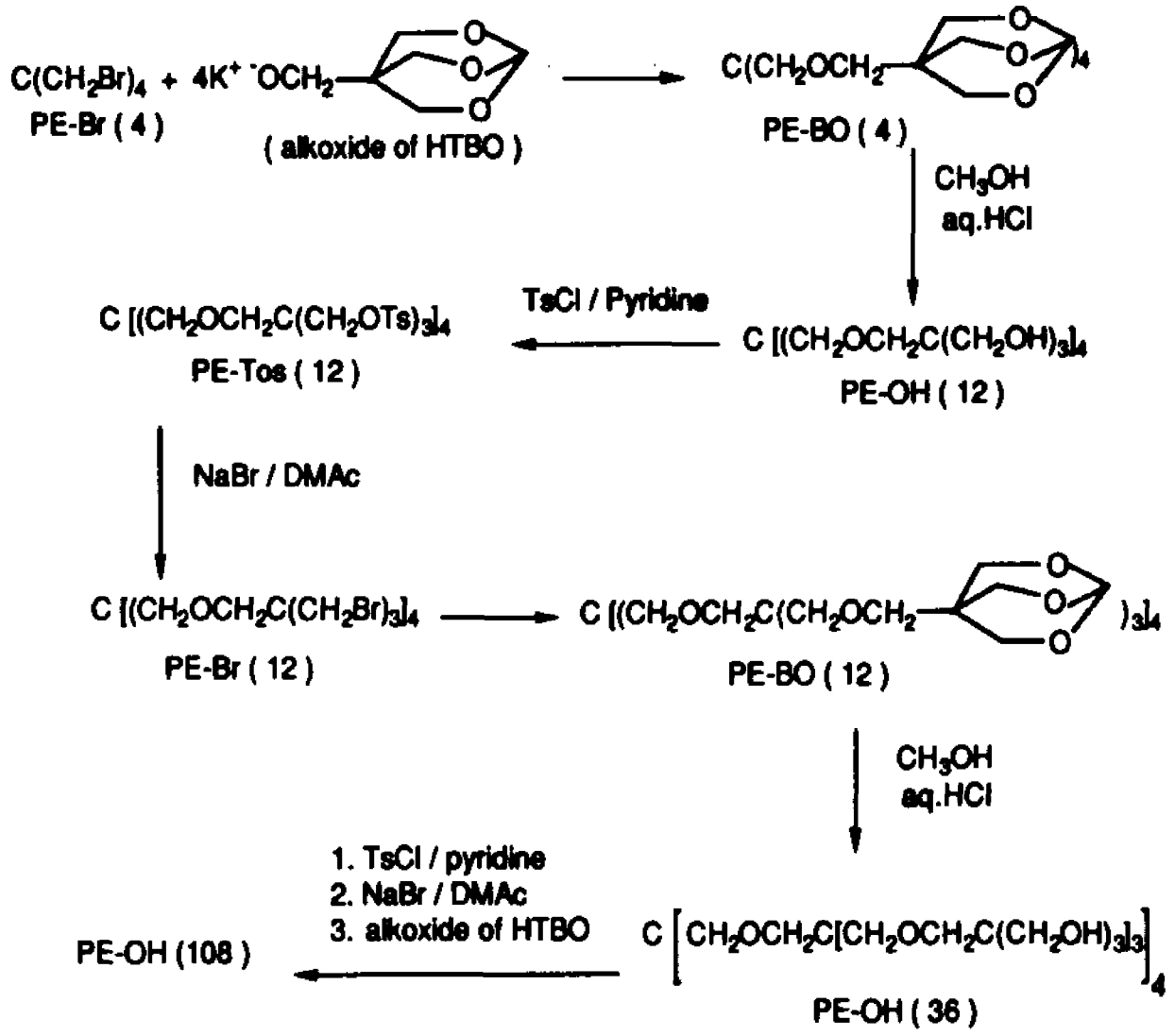
In the instance of the tridirectional cascade generated with an ammonia core, branches were attached using Michael addition with methyl acrylate. The resultant species, with ester termini, was subjected to ethylenediamine amidation followed by further Michael addition at each end of the new primary amino termini with methyl acrylate to give polyamidoamine (PAMAM) dendrimers. In this manner a cascade was generated with tridirectional characteristics at the primary core, but bidirectional characteristics at each further branch point (Scheme 5).



Scheme 5

Two reports of the preparation of tetradirectional cascade molecules have been made. The first of these involved a route completely analogous to that described above for the arborols.[25, 26] A hydrocarbon core derived from 1,5-dibromo-3,3-bis(2-bromoethyl)pentane was used with triethyl sodiomethane tricarboxylate followed by amidation with tris(hydroxymethyl)aminomethane. The resultant spherical cascade molecule is reported to be water soluble and capable of providing aqueous solubilization of a variety of organic materials by their inclusion within the folds of the hydrophobic branches.

A polyether cascade molecule derived from a pentaerythritol core (using pentaerythritol tetrabromide) has been reported.[27] This is an interesting anomaly to anticipated organic chemistry as the neopentyl halide system is generally quite sluggish in such displacement reactions. Displacement of the bromides using 4-(hydroxymethyl)-2,6,7-trioxabicyclo[2,2,2]octane (as its sodium salt) provides the triply branched-tetradirectional structure. Conversion of the surface hydroxyl groups to halides allows further branching using the same type of displacement reaction. Continued reaction through three levels of secondary branch points has been accomplished. With attempted further development of the cascade, the packing of the functional groups became too congested for complete reaction to occur (Scheme 6).



Scheme 6

A "tentacled iron sandwich" has been decribed[28] which holds the potential for use as a planar hexadirectional cascade core. Also, a series of "star-comb" polymers based on polybutadiene have been prepared and the viscoelastic properties of their melts have been studied.[29] Finally, a series of "starburst" dendrimers has been prepared using 2,4-dinitrofluorobenzene (as the core) in reaction with substituted anilines.[30]

Highly branched polymers have received considerable synthetic[31-34] and theoretical[35-38] attention recently. Perhaps the earliest relevant examples of such highly branched structures are the cascade molecules of Vogtle[35] which had relatively low molecular weights. Later, and almost simultaneous work by Tomalia[32] and Newkome[33] produced truly macromolecular hyperbranched polymers, such as the the starburst polymers. The interest in these macromolecules is due to their novel, highly branched, globular structure that is reminiscent of many important biological molecules. The discovery of new phenomena or new properties may be expected from the study of these uniquely shaped and non-entangled macromolecules.

Starburst dendrimers are three-dimensional, highly ordered oligomeric and polymeric compounds formed by reiterative sequences starting from smaller molecules,"initiator cores" such as ammonia or pentaerythritol. Protecting group strategies are crucial in these syntheses, which proceed *via* discrete "Aufbau" stages referred to as generations. Critical molecular design parameters such as size, shape, and surface chemistry may be controlled by the reactions and synthetic building blocks used. Starburst dendrimers can mimic certain properties of micelles and liposomes and even those of biomolecules and the still more complicated, but highly organized, building blocks of biological systems. Numerous applications of these compounds are conceivable , particularly in

mimicking the functions of large biomolecules as drug carriers and immunogens. This new branch of "supramolecular" chemistry should spark additional developments in organic and macromolecular chemistry.

The resulting covalent architecture can be systematically controlled by stepwise reiterative reaction sequences (generations). This process involves the following steps.

1. Start with an initiator core I possessing N_c reactive sites (*e.g.*, N_c =3 for ammonia).

2. Choose a reaction sequence so that each of the Nc reactive sites adds a reactant B_1 possessing N_b (N_b>1) new reactive sites, which introduce multiplicity, to obtain dendrimer[39] D_0 of generation 0. With ammonia as initiator core , α β-alanine derivative (N_b = 2) might be chosen as reactant.

3. Use protection/deprotection strategies to ensure that B_1 reacts with all reactive sites of I, but that no reactions occur at the new reactive sites on B_1 of dendrimer D_0.

4. Define an iterative sequence involving addition of new reactants B_{i+2} to the molecule D_i of generation i to form a new dendrimer D_{i+1} of generation i+1.

In this fashion, it is possible to control size, shape, topology, flexibility, and surface chemistry at the molecular levels.

Such space-filling, terminally functionalized molecular organizations have been coined "starburst dendrimers".[39] One can grow predictable, stoichiometric structures up to a self-limited dimension (generation), which is determined by N_c and N_b as well as by the dimensions of the structural components. The branching implicit in Nb>1 leads to geometric increase in the number of atoms for each generation. For example, the number of β-alanine monomers for starburst polyamidoamines (PAMAMs) with ammonia as initiator core is 3, 9, 21, 45, 93, 189, 381, 765, and 1533 for generations 0-8, respectively. Since the overall size can only grow linearly because of the constraints of the covalent bonds, these systems eventually become congested and change from an open, starfish-shaped molecule to a ball-shaped structure. All of these cascade molecules undergo a variety of surface reactions through the terminal functional groups present at the exterior surface.

Thus, all of the above synthetic work [32-34] had primarily been directed towards the synthesis of dendritic macromolecules by a divergent methodology. In these cases, growth occurs from a central core by successive stepwise addition and activation steps which multiply the number of branches. A significant feature of this methodology is the rapid increase in the number of reactive groups at the periphery of the growing macromolecule. Potential problems which may arise as growth is pursued include incomplete reaction of these terminal groups, which would lead to imperfections in the next

generation, or the large excesses of reagents that are required to force reactions to occur. This, in turn, presents difficulties in purification. Very recently, Hawker[40] has reported a new approach and methodology for the synthesis of dendritic molecules which overcomes these problems and may be used for different families of structures.

To date the cascade molecules which have been synthesized have involved doubly, triply, and quadruply directed branch points and cores, all being electrically neutral sites. Although there has been a significant synthetic effort for the generation of new cascade molecules in recent years, no compounds have been prepared in which the primary and/or secondary cores are ionic sites. The construction of dendrimers in which are incorporated large numbers of symmetrically distributed charged sites is a serious problem of organic synthesis which in itself is challenging and generates materials of interesting and potentially useful characteristics.

Phosphonium cascade molecules

Efforts of this laboratory have resulted[41-43] in the synthesis of a series of cascade molecules in which the primary core and secondary branch points are positively charged, phosphonium ion sites. Thus, the cascade incorporates a geometrically increasing number of positively charged sites. Starting from a properly functionalized alkyltriaryl- or tetraarylphosphonium salt, cascade molecules have been constructed in the covalent structure in which are present up to forty cationic sites. These molecules thus incorporate a large (defined) number

of cationic sites within the cascade structure, having an equal number of associated anions.

The building unit for the phosphonium cascade molecules which have been synthesized is tri(*p*-methoxymethylphenyl) phosphine (TMMPP), synthesized by the reaction of the Grignard derived from *p*-(methoxymethyl) bromobenzene with phosphorus trichloride.[44] Five individual cascade series have been prepared from this fundamental unit (initiation core). Three of these involve the initial reaction of the TMMPP with methyl iodide, benzyl bromide or octadecyl bromide to generate the simple quaternary phosphonium salt. From each of these primary cores there emanate three branches of the developing cascade, and this leads to the formation of tridirectional cascade molecules. In the fourth series, the TMMPP has been quaternized with another unit for a developing branch, using *p*-(methoxymethyl) bromobenzene in the presence of nickel(II) bromide[45-47] at elevated temperature and pressure. From this primary core (initiation core) there emanate four branches of the developing cascade leading to the formation of tetradirectional cascade molecules.

In the fifth series the TMMPP has been oxidized to the corresponding oxide[48] and from this neutral initiation core there emanate three branches of the developing cascade leading to the formation of tridirectional cascade molecules. The five fundamental cores for the cascade structures are shown below (Fig. 4).

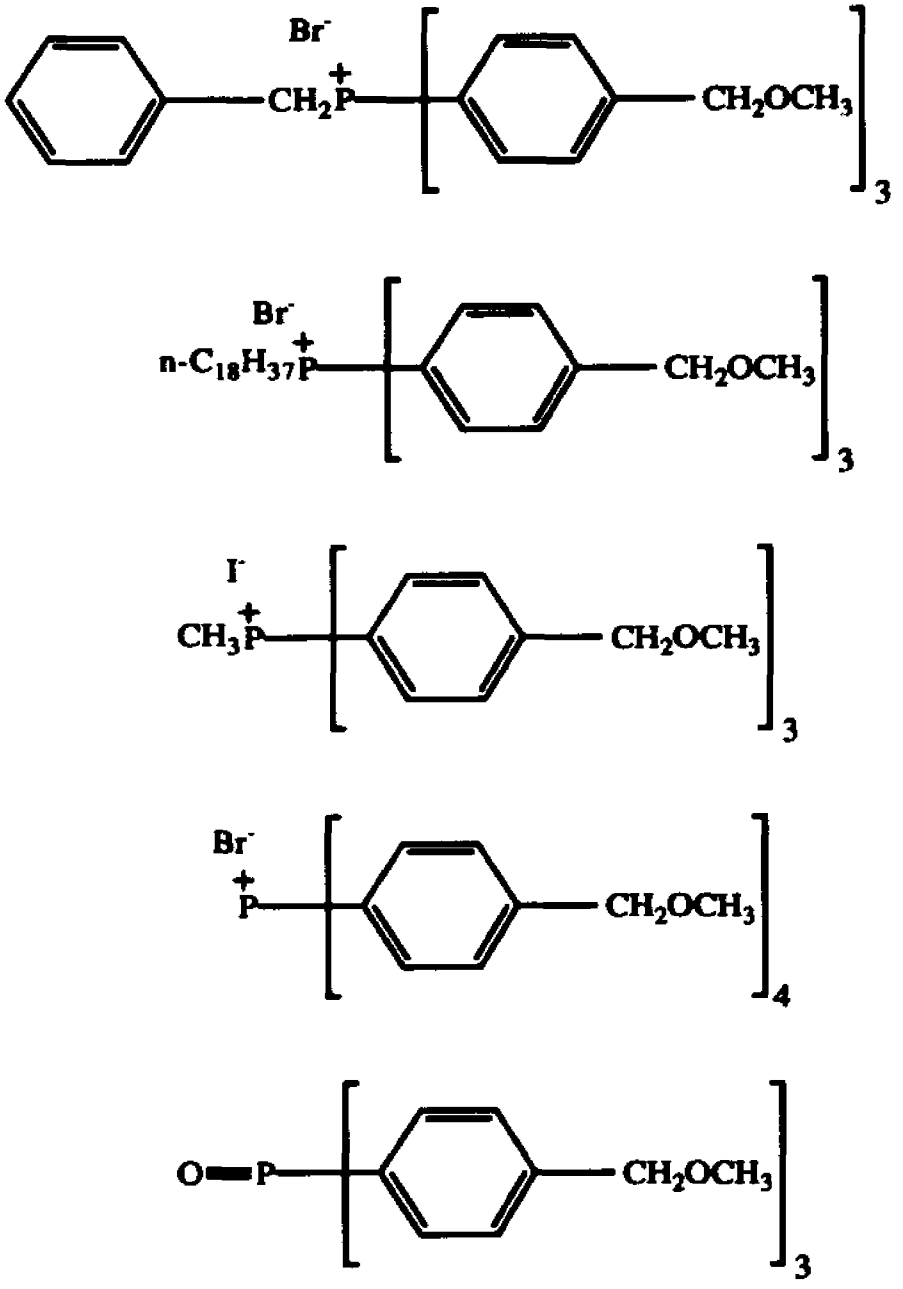
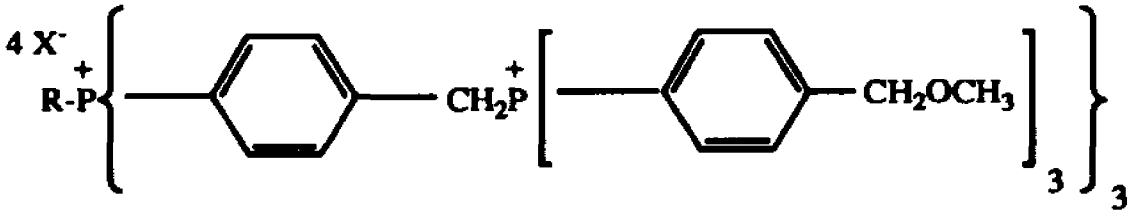


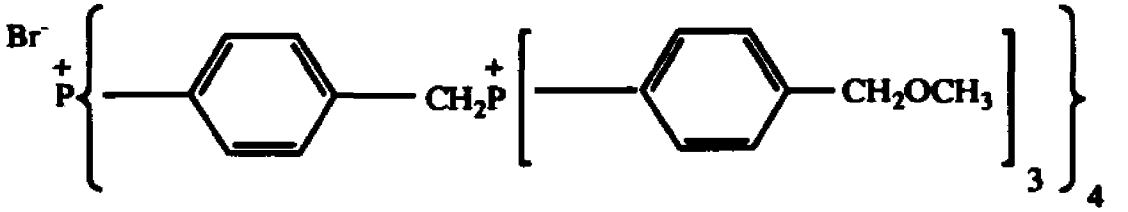
Fig. 4

The approach to the development of the cascade structure for each of these primary core units has been to deprotect the benzylic ether linkage, generating a benzylic halide site, followed by phosphonium ion formation using an excess of TMMPP. The methyl ether linkage was determined to be of the anticipated high

stability during Grignard reaction and phosphonium ion formation, but immediately susceptible to cleavage with trimethylsilyl iodide.[49,50] Thus the cleavage of the benzylic ether linkage is accomplished by treatment of the core material with excess trimethylsilyl iodide in acetonitrile. The reaction leading to cleavage of a benzylic ether linkage goes to completion within 4 hours, yielding the benzylic iodide and the trimethylsilyl ether of methanol. The latter by-product is easily removed along with the solvent by evaporation at reduced pressure. The residual trisbenzylic iodide (or tetrakisbenzylic iodide) is reactive with moisture and is used immediately in a continuing reaction with excess TMMPP. In this manner structures containing three, four and five positive charges (as shown below) in the cascade structure have been prepared (Fig. 5).



R = CH_3, $C_6H_5CH_2$, n-$C_{18}H_{37}$



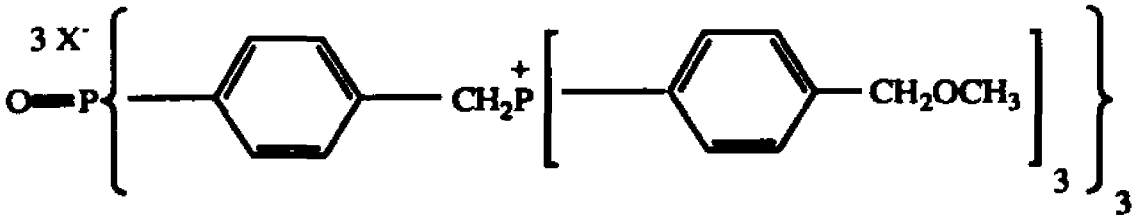


Fig. 5

Cascade structures developed with the first and third of these species have the fundamental shape of a "bulb" growing out from a "stem". The second of the structures noted above has a spherical array of branches about the primary core. Continued efforts will elaborate on the nature of the "stem", enlarging it and providing functionalization for further chemical reactions.

The third of the structures noted above has a reactive phosphoryl group at the initiation core site. In general, cascade molecules undergo a variety of reactions[51] through the terminal functional groups present at the outer surface.

The third of the above cascade molecules synthesized can undergo reaction at the initiation site. Thus the third cascade molecule has been converted to the corresponding phosphine[52] derivative by means of reduction of the phosphoryl group present at the initiation site and then complexed with gold (I) chloride[53] to give the following complex (Fig. 6).

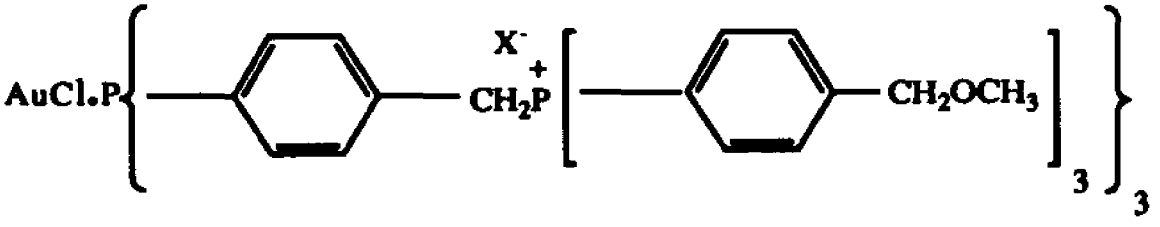


Fig. 6

For the species with tridirectional primary cores (the first series of the above three structures of Fig. 5), the cascade structure has been elaborated to two further layers of phosphonium sites. Similarly, for the species with tetradirectional primary core (the second of the three structures), the cascade structure has been elaborated to one more layer of phosphonium site. The procedure used for this has been fundamentally same as that used for the first cascade layer as noted previously. These molecules thus incorporate a large (defined) number of cationic sites within the cascade structures, having an equal number of associated anions and bear multiple methoxy groups at its surface. The complete reaction sequences involved in the synthesis of cascade molecules as well as the analytical/spectroscopic details are fully discussed in the **Results and Discussion section.**

The final task is to synthesize cascade molecules with a pentadirectional core structure. Due to its ability to form covalent bonds to five atoms at a time, the phosphorus is a particularly good candidate for the generation of cascade molecules to be synthesized in more than four directions. The fundamental core structure for the pentadirectional cascade molecules to be synthesized in this effort is to be synthesized using materials discussed in the previous section. The standard approach involving reaction of a quaternary phosphonium salt with an aryl lithium reagent or Grignard is to be used.[54-65] The fundamental core for this cascade structure is shown below (Fig. 7).

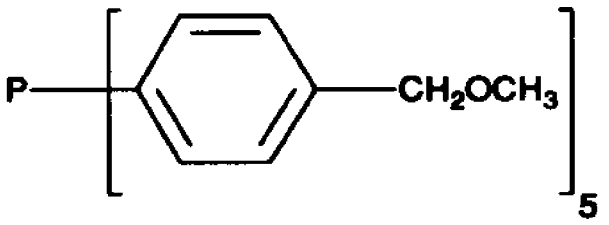


Fig. 7

The deprotection of the benzylic ether linkage has been done using iodotrimethylsilane to generate a benzylic halide site. Displacement of the leaving group using the previously described triarylphosphine (TMMPP) will begin a pentadirectional cascade with phosphonium ion secondary cores (Fig.8).

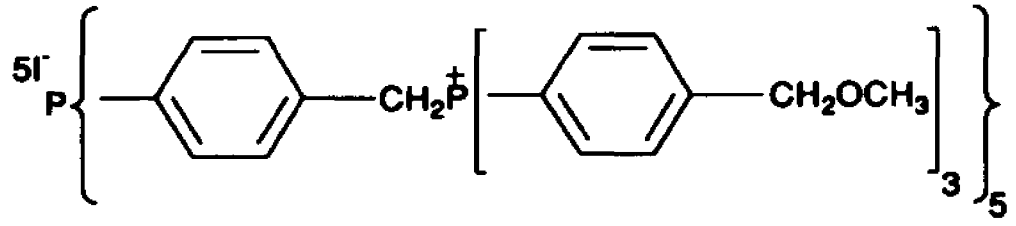


Fig.8

The Significance of the cascade molecules for further study

The intriguing structural aspects of cascade molecules make them particularly worthy of further intensive investigation. Several points may be noted in support of this statement.

First, while bearing some similarities to ordinary polymers, cascade molecules have a higher degree of structural definition. Cascade molecules can be designed and synthesized to be of a particular size and molecular weight. As an analogy, they would have a similar relationship to ordinary polymers as does the molecule decaphenylalanine to a preparation of "polyphenylalanine of molecular

weight approximately 1500".

Second, cascade molecules can be designed and synthesized with a high degree of control of the surface and internal functionality relative to the surrounding media than can be easily accomplished with ordinary polymeric species. The degree of solvent penetrability to the interior of the species could presumably be regulated by variation of the length and functionality of the branches. Concerns regarding the variations of conformation with solvent change which occur when using ordinary functionalized polymers can be minimized.

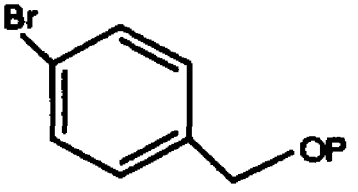
Third, the cascade structure is expected to allow the existence of discrete molecules bearing large numbers of separated electrical charge while maintaining solubility in apolar media. Through proper choice of the functionality of the branch points (secondary cores) and the intervening branch units, high electrical charge can be "buried" within a hydrophobic surface. Such materials are of practical interest for purposes of phase transfer catalysis and ion exchange. While of interest for their solvation characteristics, the cascade molecules prepared to date have been limited to neutral species bearing relatively polar surfaces. The tridirectional "benzoylated arborol" noted above exhibited a somewhat less hydrophilic surface than the others, but still bore a moderately polar functionality available to surrounding molecules.

Finally, the existence of a "core" of modifiable functionality and directional aspects for the attached cascade holds promise for the

ready preparation and investigation of species which can mimic surface interactions of enzymatic structures. Structures can be designed and synthesized in which two sites of coordinated interaction can be placed in close spatial proximity while being connectively distant. With a cascade molecule this can be accomplished with a soluble or insoluble macromolecular surface without significant concern for conformational variation as would be the situation with ordinary linear macromolecules. A difficulty in the creation of such materials to serve as enzyme models lies in the design of cascade systems which will "fold back" upon the core with predictable and reasonable levels of cascade generation. Although sufficient crowding of surface functionalities has been created in a tetradirectional cascade to hinder further reaction,[66,67] no cascade molecule has thus far been prepared which would incorporate proximate relationship of the core with the developing cascade volume surface. A system of more highly coordinated primary and secondary cores is likely required for this to be obtained.

RESULTS AND DISCUSSION

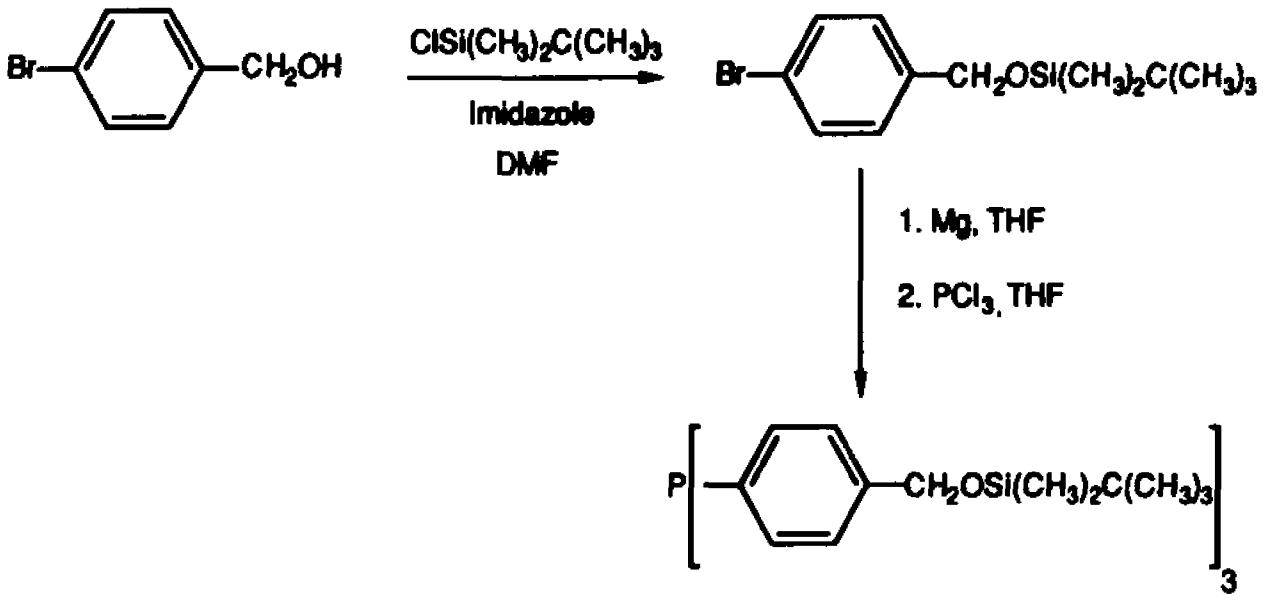
The approach toward the synthesis of dendrimers bearing numerous phosphonium sites within the covalent structures involves the design and preparation of a suitable reagent to serve as the reiterative structural component. This component must be capable of forming a phosphonium ion species in a facile manner, and contain, in addition, several symmetrically distributed masked sites, each of which upon activation is capable of reaction with additional units of the original reagent. The fundamental building block in the present proposal for the synthesis of cascade molecules using phosphonium sites as the primary and secondary cores is a protected *p*-bromobenzyl alcohol may be protected[68] either as the *t*-butyldimethylsilyl ether or as the *t*-butyl ether (Fig. 9).



P = —C $(CH_3)_3$, —Si $(CH_3)_2$C $(CH_3)_3$

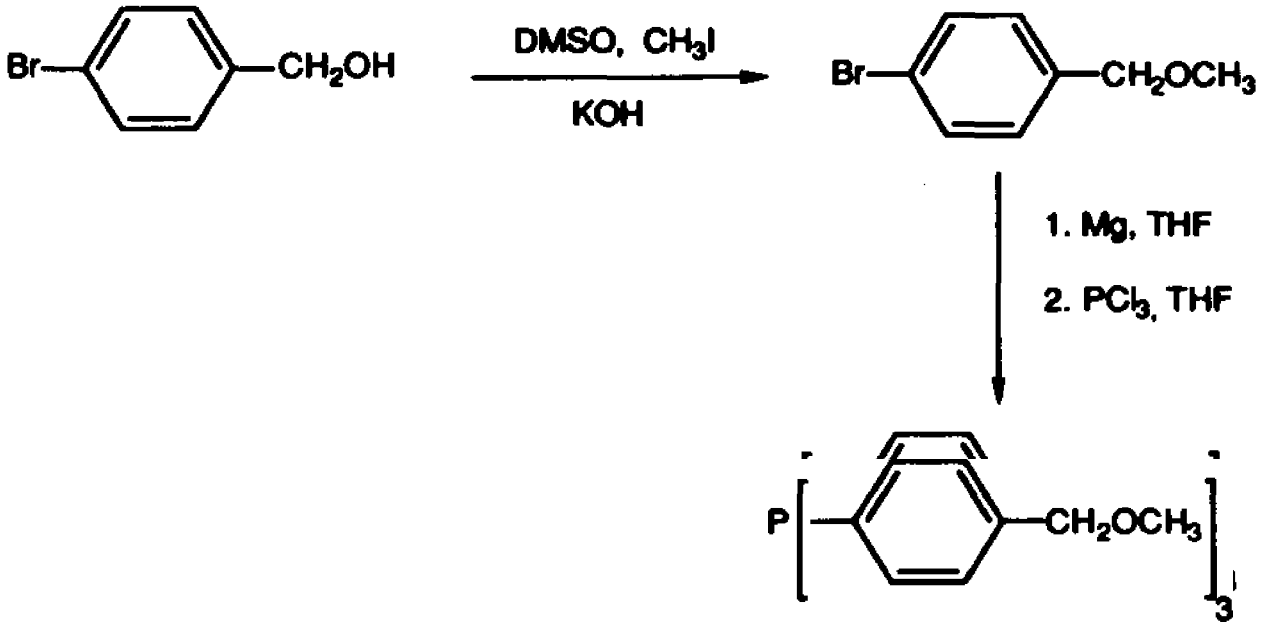
Fig. 9

The initial attempt which has been made for the construction of the cascade species involved the preparation of the *t*-butyldimethylsilyl ether of *p*-bromobenzyl alcohol **1**, and this was achieved easily in excellent yield according to the known procedure and its use attempted in the Grignard reaction with phosphorus trichloride (Scheme 7).



Scheme 7 **1**

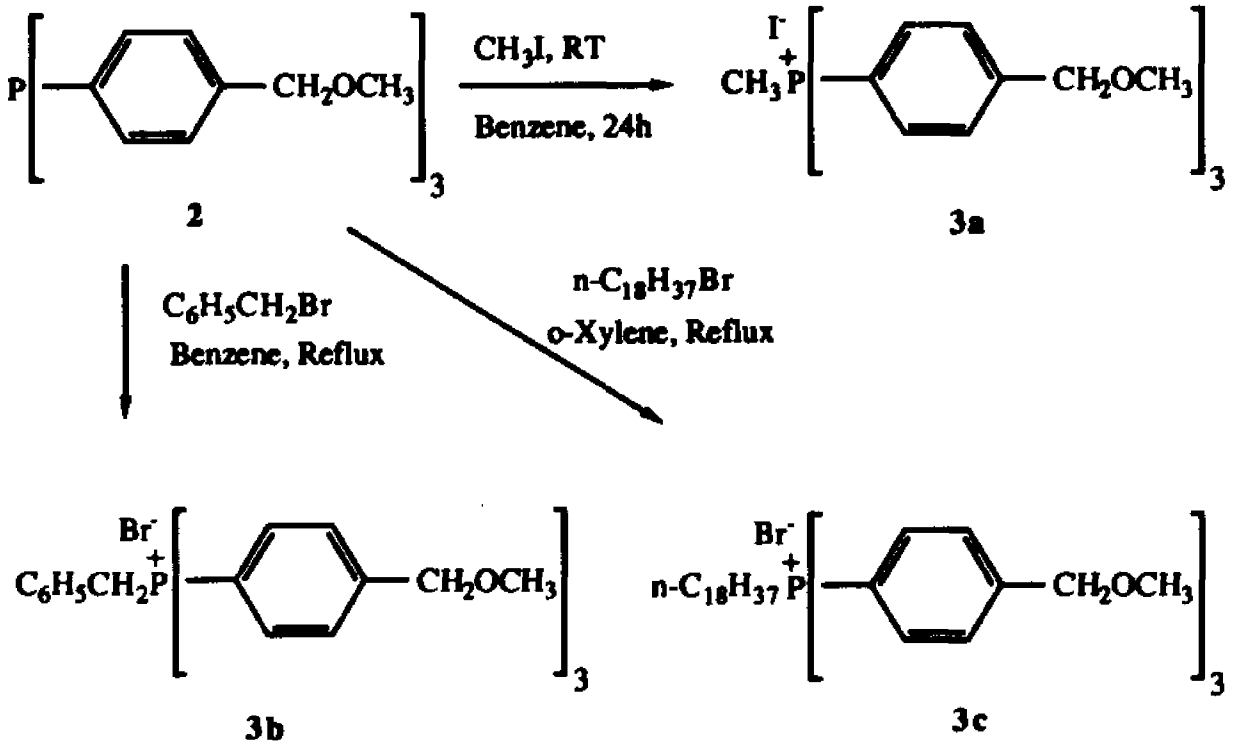
While small quantities of the target material could be isolated, most of the starting material had undergone cleavage of the silyl ether linkage leading to unusable side-products as confirmed by ^{1}H nmr spectroscopy. Further, attempts to use tertiary ether linkages initially as protection for the incipient branch points in the first reaction proved fruitless. On the otherhand, the methyl ether of *p*-bromobenzyl alcohol was prepared in quantitative yield by the method reported[69] by Johnstone for alkylation of alcohols to give ethers. To serve as the fundamental reiterative component of the phosphonium cascade species, the triaryl phosphine **2** (tri(*p*-methoxymethyl)phenylphosphine = **TMMPP**) has been prepared (Scheme 8) and stored under argon gas due to its high reactivity with moisture.



Scheme 8. **2**

Tridirectional cascade molecules

The completion of the primary phosphonium ion core is accomplished as illustrated in Scheme 9. The phosphine center of **2** is quaternized by reaction with an alkyl halide to generate the primary core for a tridirectional development of the cascade. Methyl, benzyl, octadecyl halides have been used to generate the simple quaternary phosphonium salts and from each of these primary cores there emanate three branches of the developing cascade for the generation of the tridirectional cascade molecules.

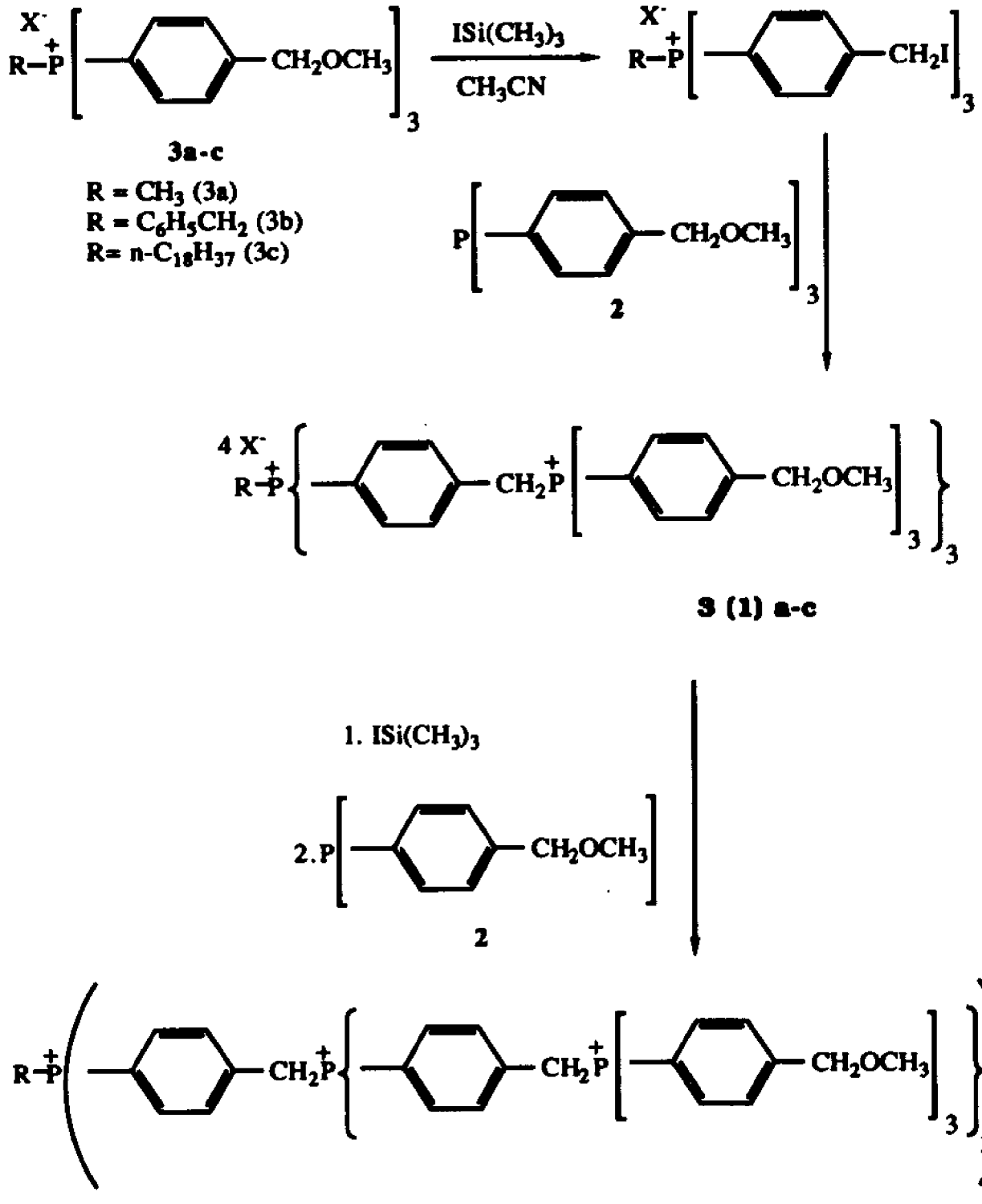


Scheme 9

All of the above primary phosphonium ion cores were confirmed by ^{31}P and ^{1}H NMR spectroscopy (see Table 1).

The approach to the development of the cascade structure for each of these primary core units has been to deprotect the benzylic ether linkage, generating a benzylic halide site, followed by phosphonium ion formation using an excess of TMMPP. Cleavage of the benzylic ether linkage is accomplished by treatment of the core material with excess trimethylsilyl iodide in acetonitrile. This reaction of benzylic ethers is known to proceed readily and selectively at room temperature to yield benzylic iodide in excellent yield. The reaction leading to cleavage of a benzylic ether linkage of the above primary cores goes to completion in 3-4 hours, yielding the

benzylic iodide and the trimethylsilyl ether of methanol. The latter by-product is easily removed along with the solvent by evaporation at reduced pressure. The trisbenzylic iodide is confirmed by ^1H NMR in which the peak for O-CH_3 moeity has completely disappeared. Hence it is an ideal route for simultaneous deprotection and activation for the present synthetic aim. Thus the benzylic ether function in **3a-c** is efficiently cleaved using trimethylsilyl iodide. The residual trisbenzylic iodide is reactive with moisture and is used immediately in a continuous reaction with excess TMMPP. The approach for incorporation of successive generations of the cascade structure is illustrated in Scheme 10 for the system beginning with **3a-c**. (Structures for generations beyond the primary core are indicated using the generation number in parentheses along with the number of the primary core structure.)


ISi(CH3)3
CH3CN
CH2OCH3
CH2I
3a-c
R = CH3 (3a)
R = C6H5CH2 (3b)
R= n-C18H37 (3c)
2
4 X-
3 (1) a-c
1. ISi(CH3)3
2.P
2
3(2) a-c

Scheme10

The reaction of trimethylsilyl iodide with the core material leads to the formation of a significant amount of iodine as a side-product which contaminates the target material. However, no attempts at purification are made at this stage owing to the high reactivity of the target material. Rather, purification is performed after further reaction with TMMPP in refluxing acetonitrile solution. The successive generations of cascade species were isolated as dark semi-solid materials which were readily soluble in most solvents. In each instance purification at this stage is accomplished by initial removal of solvent under reduced pressure followed by flash chromatography on silica gel. Finally, after removal of solvent and excess TMMPP, the material is passed through a column of Dowex 2-X8 in the iodide form using a mixed solvent of ethanol and water. On evaporation of the solvent the growing cascade structure is isolated as hydroscopic solid which is air stable. The purified materials exhibited spectra (^{1}H NMR, ^{31}P NMR, IR) and elemental analysis in accord with the proposed structures (Table 1). Interestingly, the solubility characteristics of the purified materials were significantly different from that in the crude state. While still exhibiting significant solubility in a variety of solvents, the solubility of the purified materials were notably lower than that of the crude materials. The higher generation cascade molecules maintained solubility in low molecular weight alcohols and acetonitrile, although the ready solubility in acetone, chloroform, and dimethyl sulfoxide had decreased with **3(3)b**. Although all species were significantly hydroscopic, water solubility decreased with the higher generation

cascade species. Adsorbed water is easily removed in *vacuo* without damage to the fundamental structure.

Analysis of the cascade species elaborated a single layer beyond the core using thin layer chromatography exhibits a single spot, distinct from the starting material and TMMPP.

For each of the examples (**3(2)a** and **3(2)b**), reactions 1 and 2 of scheme 10 were repeated for one further generation of the cascade structure. This results in each instance in the formation of species containing forty cationic (phosphonium) sites embedded within their structures. The resulting third generation cascade species (**3(3) a** & **3(3)b**) were purified by the addition of diethyl ether to the solution of cascade species in acetonitrile solution and the precipitated pure cascade species were filtered.

Each of the first two reaction sequences (1 and 2 of Scheme 10) for the introduction of further generations of the cascade (**3(1) a-c** and **3(2) a-c**) provided a moderate yield (22-92%) of purified product. The reaction sequence to form the third generation cascade materials (**3(3)a** and **3(3)b**) , however gave pure products in only poor yield (15-20%), and the pure materials exhibited no significant solubility in most of the solvents, except for acetonitrile. Suitable solubility was found in acetonitrile-d_3 to allow the measurement of NMR spectra.

The solubility characteristics and analytical data for the tridirectional cascade materials synthesized are summarised in Table 1.

Table 1 - Analytical and Solubility Data for Tridirectional Cascade Molecules

Compound	R	^{1}H NMR (δ 60 MHz)*	^{31}P NMR (δ)#	Formula	C/H Anal. Calcd.(Found)	Solubility§
3a	CH_3	3.2 [3H, d, J=24] 3.4 [9H, s] 4.6[6H, s] 7.6-8.0 [12H, m]	21.4	$C_{25}H_{30}O_3PI$	C: 55.98(55.90) H: 5.64(5.59)	sol. (a-g)
3b	$C_6H_5CH_2$	3.4[9H, s] 4.5[8H, br] 7.2-7.7[17H, m]	22.7	$C_{31}H_{34}O_3PBr$	C: 63.81(64.03) H: 6.21(6.30)	sol. (a-g)
3c	$C_{18}H_{37}$	0.9 [3H, t, J=6] 1.3 [30H, br] 2.3 [2H, m] 3.4 [9H, s] 3.6-4.2 [2H, m] 4.6 [6H, br] 7.6-8.0 [12H, m]	41.00	$C_{42}H_{64}O_3PBr$	C: 69.30(69.12) H:8.79(8.49)	sol. (a-g)
3(1)a	CH_3	3.2 [3H, d, J=22] 3.4 [27H, br] 4.5 [24H, br] 7.3-7.9 [48H, m]	21.8 , 29.3	$C_{94}H_{102}O_9P_4I_4$	C: 56.24(56.01) H: 5.12(5.27)	sol. (b-g) sl. sol. (a)

Table 1 - Analytical and Solubility Data for Tridirectional Cascade Molecules (contd.)

Compound	R	^{1}H NMR (δ 60 MHz)*	^{31}P NMR (δ)#	Formula	C/H Anal. Calcd.(Found)	Solubility§
3(1)b	$C_6H_5CH_2$	3.3 [27H, s] 4.5 [26H, br] 7.1-7.9 [53H, m]	22.0, 28.0	$C_{100}H_{106}O_9P_4BrI_3$	C: 58.98(59.00) H: 5.25(5.29)	sol. (b-g) sl.sol. (a)
3(1)c	$C_{18}H_{37}$	0.9 [3H, t, J=6] 1.3 [30H, br] 2.3 [2H, m] 3.4 [27H, s] 3.6-4.2 [2H, m] 4.6 [24H, br] 7.6-8.0 [48H, m]	41.0, 29.0	$C_{111}H_{136}O_9P_4I_4$	C: 59.36(59.06) H:6.10(6.01)	sol. (b-g) sl.sol. (a)
3(2)a	CH_3	3.2 [3H, d, J=21] 3.4 [81H, s] 4.5 [78H, br] 7.1-7.8 [156H, m]	21.9, 29.6	$C_{301}H_{318}O_{27}P_{13}I_{13}$	C: 56.31(56.19) H: 4.99(5.28)	sol. (b-g) sl. sol. (a)
3(2)b	$C_6H_5CH_2$	3.5 [81H, s] 4.6 [80H, br] 7.1-7.9 [161H, m]	23.0, 30.1	$C_{307}H_{322}O_{27}P_{13}I_{13}$	C: 56.60(56.21) H: 4.94(5.30)	sol. (b-g) sl. sol. (a)

Table 1 - Analytical and Solubility Data for Tridirectional Cascade Molecules (contd.)

Compound	R	^{1}H NMR (δ 60 MHz)*	^{31}P NMR (δ)#	Formula	C/H Anal. Calcd.(Found)	Solubility§
3(2)c	$C_{18}H_{37}$	0.9 [3H, t, J=6] 1.3 [32H, s] 2.3 [2H, m] 3.4 [81H, s] 4.6 [78H, br] 7.1-7.8 [156H, m]	40.0, 28.5	$C_{318}H_{352}O_{27}P_{13}I_{13}$	C: 57.21(56.97) H: 5.27(5.39)	sol. (b-g) sl. sol. (a)
3(3)a	CH_3	3.2-3.5 [247H, br] 4.5 [240H, br] 7.1-7.9 [480H, m]	29.0	$C_{922}H_{966}O_{81}P_{40}I_{40}$	C: 56.33(56.30) H: 4.95(4.70)	sol. (b-g) sl. sol. (a)
3(3)b	$C_6H_5CH_2$	3.5 [243H, s] 4.5 [242H, br] 7.2-7.8 [485H, m]	30.0	$C_{928}H_{970}O_{81}P_{40}I_{40}$	C: 58.98(58.58) H: 4.91(5.11)	sol. (b,f,g) sl. sol. (c-e) insol. (a)

* Deuteriochloroform or deuterioacetonitrile solution, relative to TMS

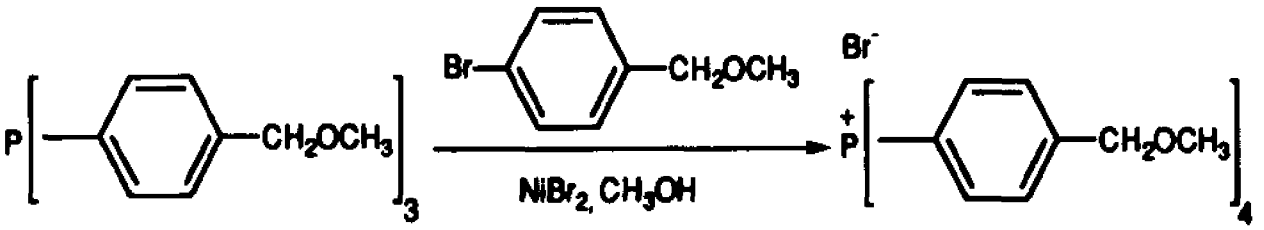
Deuteriochloroform or deuterioacetonitrile solution, relative to 85% H_3PO_4, 81MHz

§ a-water; b-acetonitrile; c-chloroform; d-acetone; e-DMSO; f-ethanol; g-methanol

As can be seen from Table 1, in each instance the ^{31}P NMR signal for the phosphonium branch occured ~8 ppm downfield (28 ppm downfield relative to external 85% phosphoric acid) from that for the initiation core phosphonium sites (21 ppm for **3(1)a-b** &**3(2)a-b** and 41 ppm for **3(1)c** & **3(2)c** downfield relative to external 85% phosphoric acid). First, second, and third generation phosphonium sites were indistinguishable from each other by their ^{31}P NMR chemical shifts. With the third generation species **3(3)a** and **3(3)b** only one signal for phosphorus could be observed in the ^{31}P NMR spectrum. While in the ^{31}P spectra of prior generation species separate signals could be observed for the core and peripheral phosphonium ion sites, the separation of the two signals was insufficient in these two instances for the smaller core signal to be observed. The large signal for the peripheral phosphonium ion sites overlapped the region of the core signal.

Tetradirectional cascade molecules

For the generation of the primary core for a tetradirectional development of the cascade, the phosphine center of **2** is quaternized by reaction with *p*-methoxymethylbromobenzene at elevated temperature and pressure in the presence of nickel bromide as catalyst (Scheme 11).

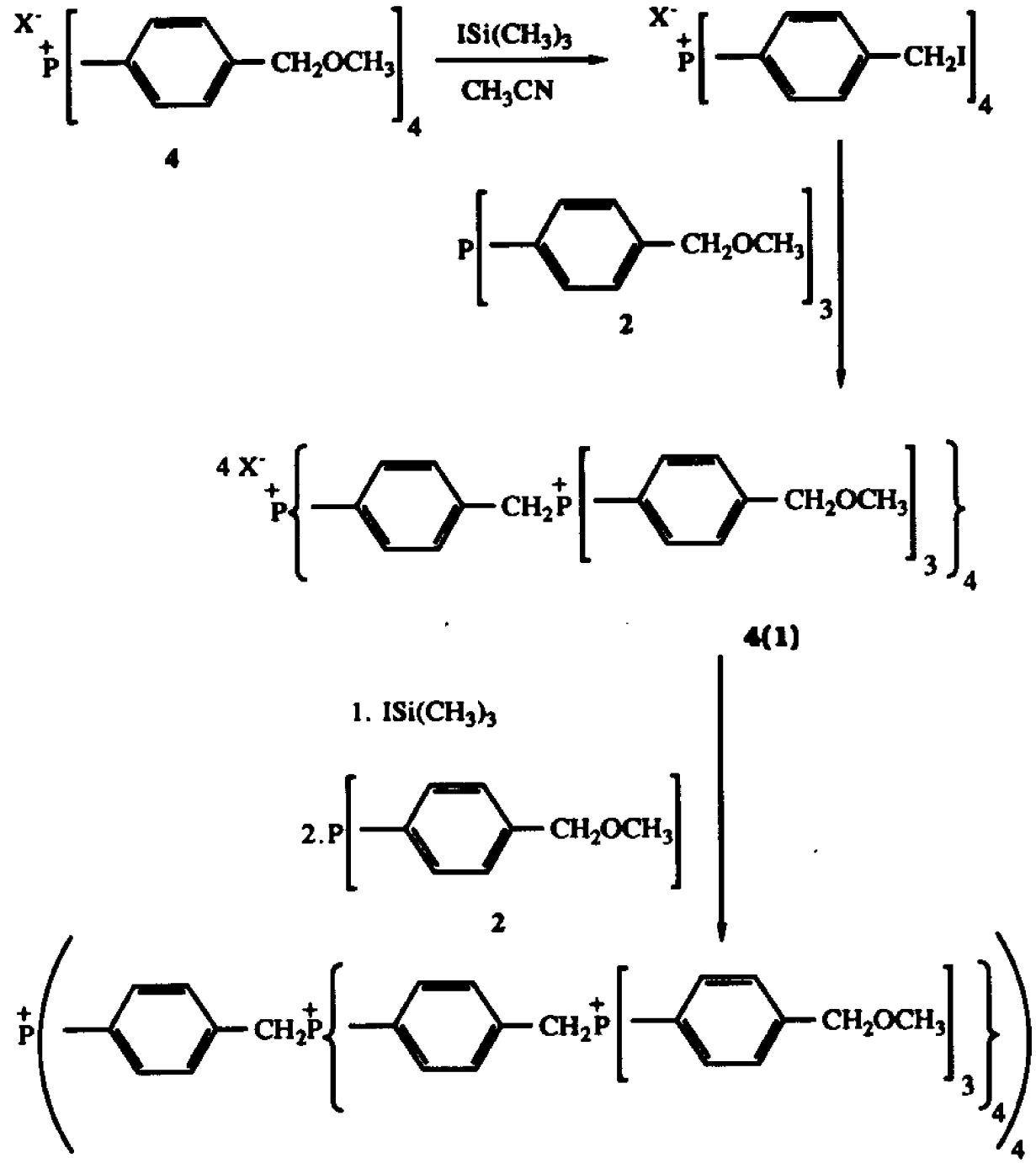


2 **Scheme 11** **4**

The above reaction leading to the formation of the primary core for tetradirectional cascade molecule provided pure product in only poor yield (7%). Successive generations of the cascade structure are introduced as *per* Scheme 12 *via* treatment with iodotrimethylsilane followed by an excess of tri(*p*-methoxymethylphenyl)phosphine (in a similar way to the generation of tridirectional cascade molecules). Each of the first two reaction sequences (1 and 2 of Scheme 12) provided a moderate yield (23% for 4(1) and 93% for 4(2)) of purified product.

Each of these generations was purified by flash chromatography on silica gel using a mixed solvent of ethanol and acetonitrile. These purified cascade molecules showed a single spot at the origin in TLC experiment (with silica gel coating and acetonitrile as solvent), distinct from the starting material and TMMPP. The solubility of these purified cascade molecules was found to be very similar to that found for the tridirectional cascade molecules.

The solubility characteristics and analytical data for the tetradirectional cascade materials synthesized are summarised in Table 2.



Scheme 12

Table 2 - Analytical and Solubility Data for Tetradirectional Cascade Molecules

Compound	^{1}H NMR (δ 60 MHz)*	^{31}P NMR (δ)#	Formula	C/H Anal. Calcd.(Found)	Solubility§
4	3.5 [12H, s] 4.6 [8H, s] 7.6-7.9 [16H, AA'BB']	20.9	$C_{32}H_{36}O_4PBr$	C: 64.54(64.18) H: 6.09(6.29)	sol. (a-g)
4(1)	3.4 [36H, s] 4.6 [32H, br] 6.8-7.8 [64H, m]	21.5, 28.0	$C_{124}H_{132}O_{12}P_5I_5$	C: 57.20(56.95) H: 5.11(5.32)	sol. (b-g) sl.sol. (a)
4(2)	3.4 [108H, s] 4.5 [104H, br] 6.8-7.8 [208H, m]	21.0, 28.0	$C_{400}H_{420}O_{36}P_{17}I_{17}$	C: 56.59(56.37) H: 4.98(5.11)	sol. (b-g) sl. sol. (a)

* Deuteriochloroform or deuterioacetonitrile solution, relative to TMS

Deuteriochloroform or deuterioacetonitrile solution, relative to 85% H_3PO_4, 81MHz

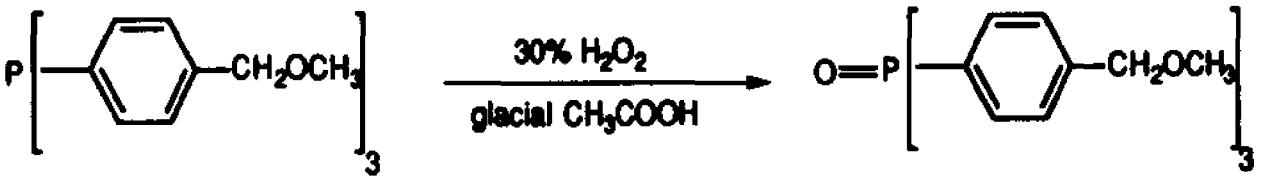
§ a-water; b-acetonitrile; c-chloroform; d-acetone; e-DMSO; f-ethanol; g-methanol

As can be seen from Table 2, in each instance the ^{31}P NMR signal for the phosphonium branch (for tetradirectional cascade molecules) occurred at ~8 ppm downfield (28 ppm downfield relative to external 85% phosphoric acid) from that for the initiation core phosphonium sites (21 ppm downfield relative to 85% phosphoric acid). Again, similar to tridirectional cascade molecules, first and second generation phosphonium sites were indistinguishable from each other by their ^{31}P NMR chemical shifts. All of these compounds are found to be hydroscopic as can be seen from their elemental analysis values.

Tridirectional cascade molecules containing neutral phosphoryl group at the primary core site

So far, cascade molecules (tridirectional and tetradirectional) have been prepared containing cationic (phosphonium) initiation site at the primary core and secondary core as well. All of these molecules could undergo a variety of reactions through the terminal functional groups ($O\text{-}CH_3$) present at the outer surface. A new tridirectional cascade molecule has been prepared containing a reactive phosphoryl group at the initiation site and phosphonium ion at the developing secondary branch. This kind of cascade molecule can undergo reaction at the initiation site and indeed, the phosphoryl group of these molecule has been reduced to the phosphine successfully and then complexed with gold (1) chloride.

The primary core for the above tridirectional cascade molecule has been prepared successfully by oxidation of the phosphine **2** using Hydrogen Peroxide in glacial acetic acid as per the Scheme 13.

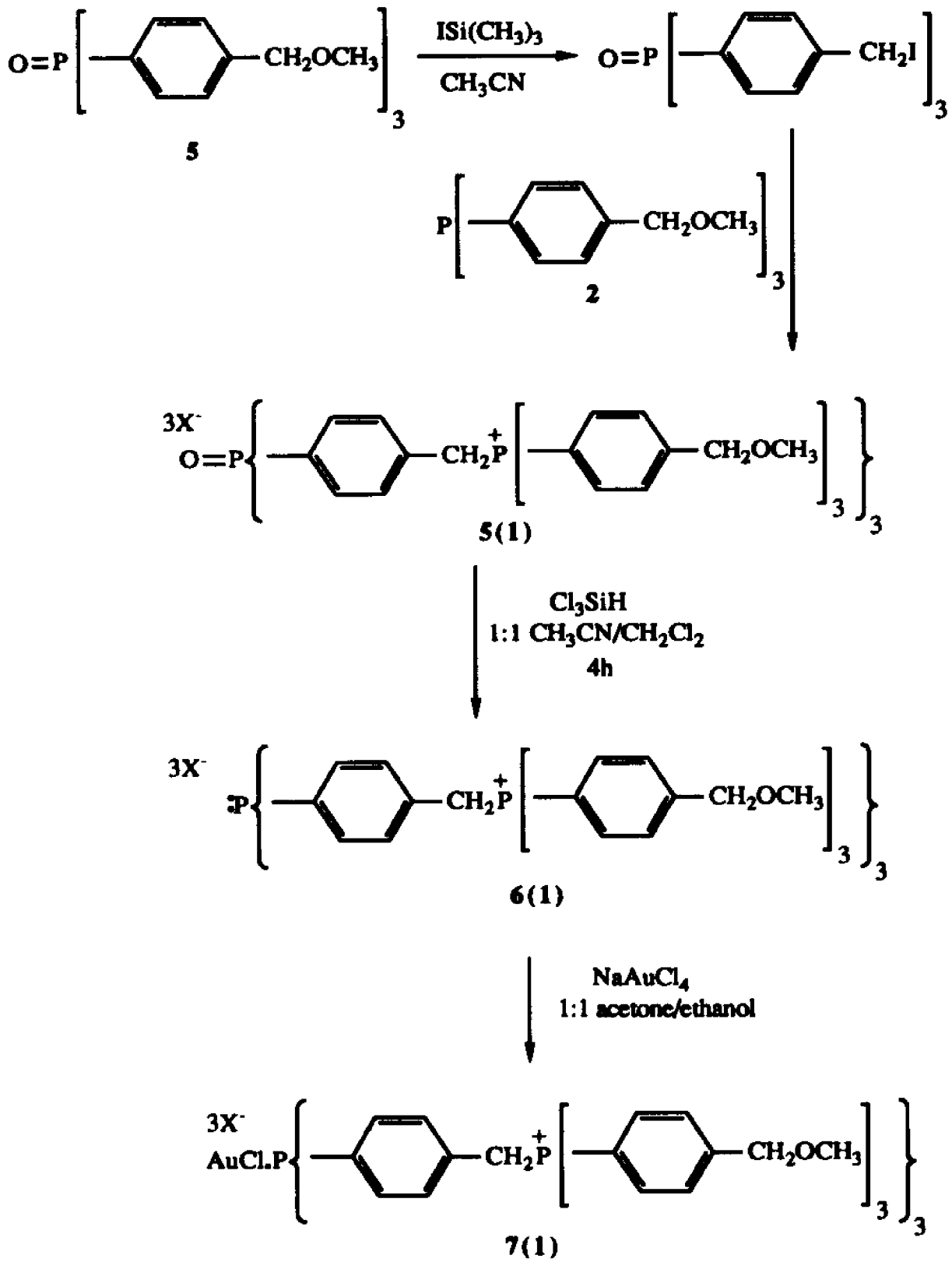


2 **5**

Scheme 13

The compound **5** was obtained in 90% yield and was further purified by flash chromatography on silica gel using a mixed solvent of ethanol and acetonitrile. Pure compound **5** showed a single spot in TLC experiment using acetonitrile as eluent with R_f value of 0.62. The compound **5** was found to be soluble in a variety of solvents including ethanol,chloroform,methanol and DMSO. The ^{31}P NMR showed a single peak at ~30 ppm.

The tridirectional development of the cascade structure for the above primary core containing phosphoryl group was achieved easily as per Scheme14 *via* treatment with iodotrimethylsilane followed by an excess of tri(*p*-methoxymethylphenyl)phosphine (in a similar way to the generation of tri and tetradirectional cascade molecules). The ^{31}P NMR of **5(1)** showed two peaks, one at ~30 ppm (due to Phosphoryl group) and the other at ~28 ppm (due to secondary phosphonium branch). Elemental analysis indicated the compound to be hydroscopic.


O=P
CH2OCH3
3
5
ISi(CH3)3
CH3CN
CH2I
P
2
3X-
CH2P+
5(1)
Cl3SiH
1:1 CH3CN/CH2Cl2
4h
6(1)
NaAuCl4
1:1 acetone/ethanol
AuCl.P
7(1)

Scheme 14

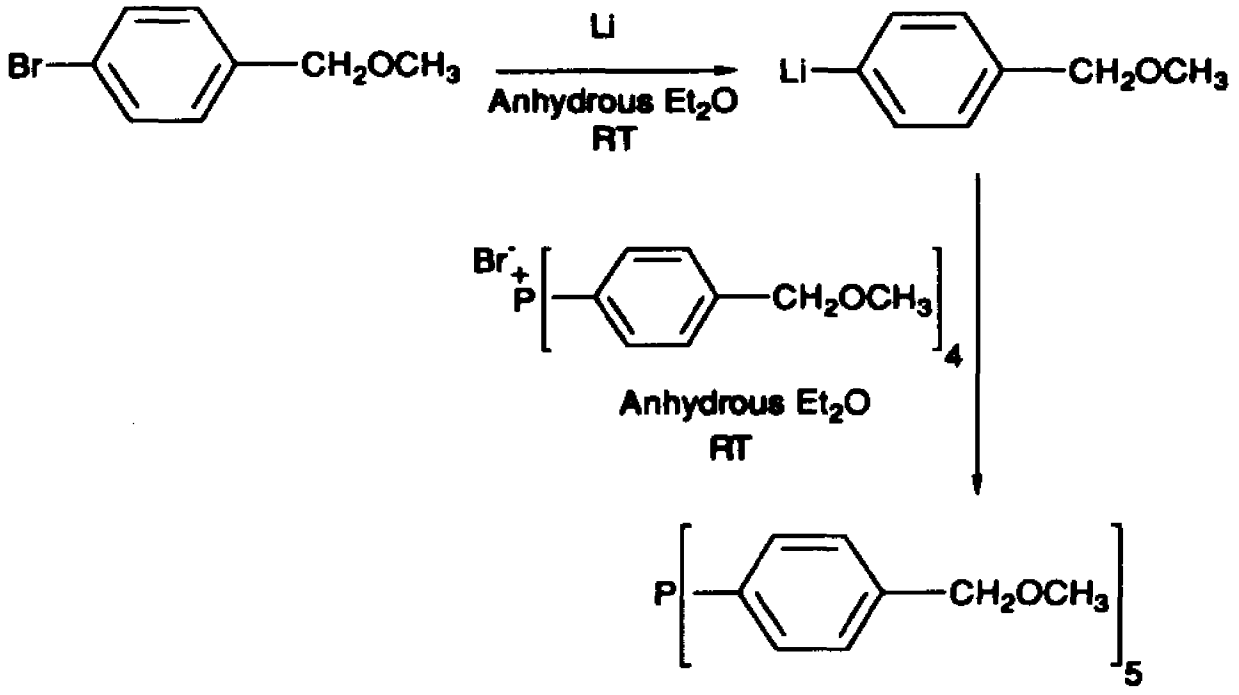
The compound **5(1)** containing a phosphoryl group at the initiation site was reduced successfully using trichlorosilane in 1:1 acetonitrile/methylene chloride to give **6(1)** (Scheme 14) containing phosphine center at the initiation site. The ^{31}P NMR spectrum of **6(1)** showed two peaks, one at ~ -16 ppm due to phosphine center at the initiation site and the other at ~28 ppm due to secondary phosphonium site. The compound 6(1) was stored under argon gas due to its extreme air sensitivity and used immediately in further reaction.

The compound **6(1)** was converted without any difficulty to the corresponding gold (I) complex **7(1)** by treating with sodium tetrachloroaurate (III) in 1:1 acetone/ethanol (Scheme 14). The electronic spectra of **7(1)** showed, in addition to bands due to the aromatic ligands, a single band at 275 nm presumably of the gold-to-ligand charge-transfer.

Pentadirectional cascade molecules

In addition to dendrimers bearing a phosphonium ion core surrounded by repeating branch phosphonium ion sites, a quinquedirectional core [P(V)] has been synthesized[70] with associated phosphonium ion branch points. In this instance the core is neutral while the branch points are positively charged.

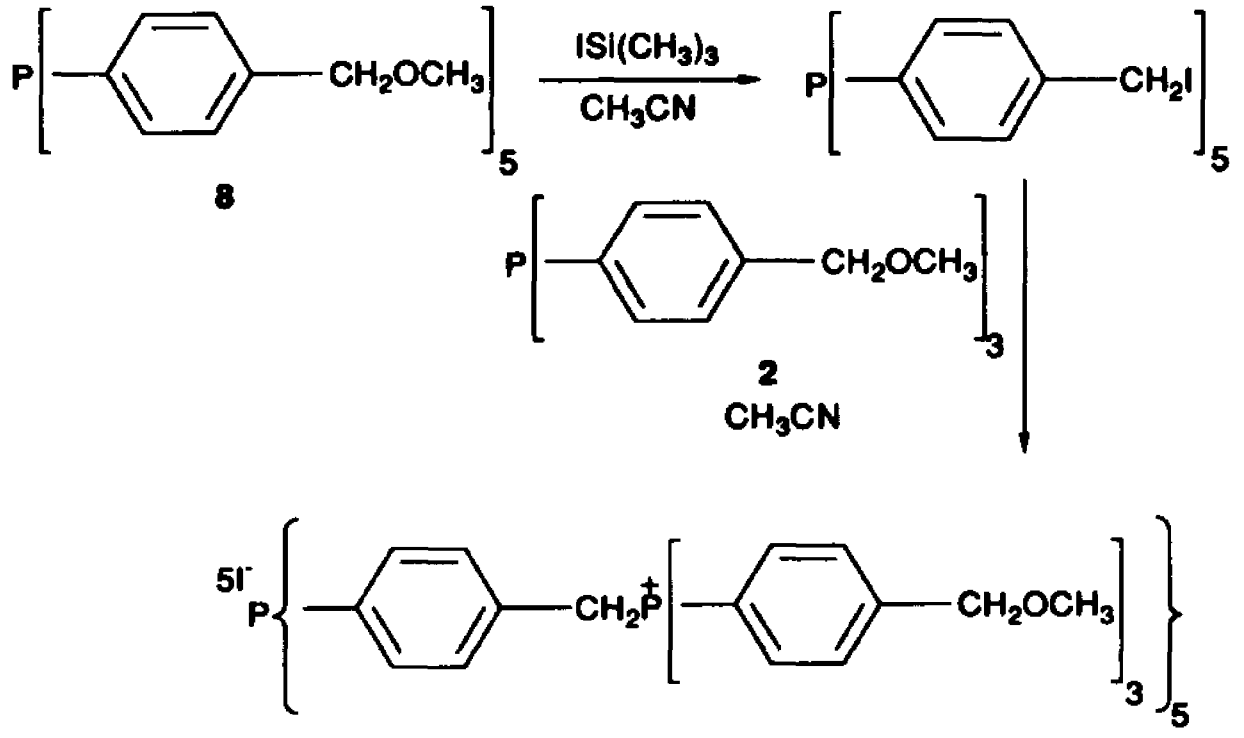
The primary quinquedirectional core [P(V)] has been prepared successfully by the reaction of a quaternary phosphonium salt **4** with an aryl lithium reagent as per the Scheme 15.



Scheme 15 8

The above reaction leading to the formation of phosphorane **8** was accompanied by the formation of Lithium bromide as side product which was filtered from the reaction mixture. This quinquedirectional core **8** was obtained in 83% yield and was found to be soluble in a variety of solvents including chloroform,ethanol and acetonitrile but insoluble in water. The ^{31}P NMR spectrum of **8** showed a single peak at -94 ppm.

The pentadirectional development of the cascade structure for the above quinquevalent phosphorus was achieved easily as per the Scheme 16 *via* treatment with iodotrimethylsilane followed by an excess of TMMPP (in a similar way to the generation of tri and tetradirectional cascade molecules as discussed in the previous section).



Scheme 16 **8(1)**

The ^{31}P NMR of compound **8(1)** showed two peaks, one at -95 ppm (due to primary quinquevalent core) and the other at 29 ppm (due to secondary phosphonium branch).

EXPERIMENTAL SECTION

General

All chemicals were of commercial reagent quality and were used without further purification with the following exceptions: benzene and tetrahydrofuran were distilled over sodium hydride and stored over molecular sieves; chloroform was distilled over phosphorus pentoxide; acetonitrile was distilled and stored over molecular sieves; phosphorus trichloride was freshly distilled prior to use. Silica gel for preparative chromatography was from Baker (230-400 mesh). Infrared spectra were measured using a Perkin-Elmer 1600 FTIR. UV spectra were measured using CARY 14DS with AVIV associates upgrade. The ^{1}H NMR spectra were measured using either a Varian EM360 (60MHz) or IBM-Bruker WP200SY (200MHz) instrument. The ^{31}P NMR spectra were measured using the IBM-Bruker instrument operating at 81 MHz. Ion exchange was performed using DOWEX 2-X8 (20-50 mesh) in the iodide form. Elemental analyses were performed by Desert Analytics, Tucson, Arizona, or Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of p-(methoxymethyl)bromobenzene

To dimethyl sulfoxide (175 mL) was added powdered KOH (18.0 g, 321 mmol). After stirring for 5 min, *p*-bromobenzyl alcohol (15.0 g, 80.2 mmol) was added, followed immediately by iodomethane (2.8 g, 160 mmol). The resulting solution was stirred at room temperature for 30 min after which the mixture was poured into water (350 mL)

and extracted with methylene chloride (4 X 200 mL). The combined organic extracts were washed with water (5 X 100 mL), dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give the pure *p*-(methoxymethyl)bromobenzene (15.5 g, 96%) which exhibited NMR and IR spectra, and elemental analysis in accord with the proposed structure. ^1H NMR (200 MHz; $CDCl_3$; δ) 3.4 [3H, s], 4.4 [2H, s], 7.1-7.5 [4H, AA'BB']. Calcd. for C_8H_9OBr: C, 47.79; H, 4.51. Found: C, 47.82; H, 4.47.

Preparation of p-(t-butyldimethylsilyloxymethyl)bromobenzene

To dimethyl formamide (200 mL) was added *p*-bromobenzyl alcohol (15.0 g, 80.2 mmol). After stirring for10 min, imidazole (5.5 g, 80.7 mmol) was added, followed by *t*-butyldimethylsilylchloride (12.1 g, 80.2 mmol). The resulting solution was stirred at room temperature for 24 h and the solvent was removed at reduced pressure and the residue was filtered. The filtrate was dissolved in 150 mL of ethyl acetate and washed with water (3 X 100 mL), dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give the pure *p*-(*t*-butyldimethylsilyloxymethyl)bromobenzene (15.1 g, 62%) which exhibited NMR and IR spectra, and elemental analysis in accord with the proposed structure. ^1H NMR (60MHz; $CDCl_3$; δ) 0.0 [6H, s], 0.8 [9H, s], 4.4 [2H, s], 7.1-7.5 [4H, AA'BB']. Calcd. for $C_{13}H_{21}OSiBr$: C, 51.77; H, 6.97. Found: C, 51.98; H, 7.02.

Attempted synthesis of tri(p-t-butyldimethylsilyloxymethyl) phenyl phosphine **(1)**

In a 1 L 3-neck flask fitted with a paddle stirrer, dropping funnel, and reflux condenser were placed magnesium turnings (1.18 g, 48.5 mmol) and dry THF (15 mL). The flask was flushed continuously with nitrogen. A solution of *p*-(*t*-butyldimethylsilyloxymethyl) bromobenzene (14.48 g, 48.1 mmol) in dry THF (125 mL) was added dropwise to the mixture. After completion of addition, the reaction mixture was heated at reflux for 45 min using steam heat. At this time the reaction mixture was cooled with ice and further THF (40 mL) was added. A solution of phosphorus trichloride (2.19 g, 15.9 mmol) in THF (20 mL) was then added dropwise over a period of 45 min with continuous stirring. After the addition, the reaction mixture was stirred at room temperature for 30 min, and allowed to stand overnight. Hydrochloric acid (40 mL concentrated in 130 mL of water) was added slowly with cooling in an ice bath and continuous stirring. The reaction mixture was concentrated under reduced pressure and the residual aqueous solution was extracted with ether (3 X 50 mL). The organic portions were combined, dried ($MgSO_4$), filtered, evaporated under reduced pressure to give semi-solid. ^1H NMR of this semi-solid showed that most of the starting material had undergone cleavage of the silyl ether linkage leading to unusable side-products. Further, attempts to use tertiary ether linkages initially as protection for the incipient branch points in the first reaction proved fruitless. On the otherhand, the methyl ether of *p*-bromobenzyl alcohol was

prepared in quantitative yield by the method reported by Johnstone and tri(*p*-methoxymethyl)phenyl phosphine was prepared as shown below.

Preparation of tri(p-methoxymethyl)phenylphosphine **(2)**

In a 1 L 3-neck flask fitted with a paddle stirrer, dropping funnel, and reflux condenser were placed magnesium turnings (3.02 g, 124 mmol) and dry THF (25 mL). The flask was flushed continuously with nitrogen. A solution of *p*-(methoxymethyl) bromobenzene (25.0 g, 124 mmol) in dry THF (175 mL) was added dropwise to the mixture. After completion of addition, the reaction mixture was heated at reflux for 45 min using steam heat. At this time the reaction mixture was cooled with ice and further THF (60 mL) was added. A solution of phosphorus trichloride (5.70 g, 41.6 mmol) in THF (25 mL) was then added dropwise over a period of 45 min with continuous stirring. After the addition, the reaction mixture was stirred at room temperature for 30 min, and allowed to stand overnight. Hydrochloric acid (50 mL concentrated in 150 mL water) was added slowly with cooling in an ice bath and continuous stirring. The reaction mixture was concentrated under reduced pressure and the residual aqueous solution was extracted with ether (3 X 50 mL). The organic portions were combined, dried ($MgSO_4$), filtered, evaporated under reduced pressure to give the pure tri(*p*-methoxymethyl)phenylphosphine **(2)** (10.1 g, 62% yield) as semi-solid which exhibited ^{1}H and ^{31}P NMR, and IR spectra, and elemental analysis in accord with the proposed structure. ^{1}H NMR (60 MHz, $CDCl_3$, δ) 3.4 [9H, s], 4.5 [6H, s],

7.1-7.9 [12H, AA'BB']. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) -16. Calcd. for $C_{24}H_{27}O_3P$: C, 73.08; H, 6.90. Found: C, 72.94; H, 6.81.

Preparation of methyl tri(p-methoxymethyl)phenylphosphonium iodide (**3a**)

A solution of **2** (1.0 g, 2.5 mmol) in dry benzene (15 mL) was placed in a 100 mL flask fitted with a reflux condenser and which was flushed continuously with dry nitrogen. A solution of methyl iodide (0.73 g, 5.0 mmol) in benzene (10 mL) was added to the reaction solution which was stirred at room temperature for 24 hr. The solvent was removed from the reaction mixture under reduced pressure and the residue was subjected to flash chromatography on silica gel with acetonitrile to give the pure methyl tri(*p*-methoxymethyl)phenyl phosphonium iodide **3a** (1.31 g, 96% yield) which exhibited spectra and elemental analysis in accord with the proposed structure (Table 1).

Preparation of First-generation Tridirectional Phosphonium Cascade Molecule (**3(1)a**)

A solution of **3a** (0.5 g, 0.93 mmol) in dry acetonitrile (25 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (1.12 g, 5.59 mmol) in dry acetonitrile (15 mL) was added slowly with continuous stirring. The reaction mixture was

refluxed for 16 hr, and then cooled. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in dry acetonitrile (40 mL) and placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (1.1 g, 2.80 mmol) in dry acetonitrile (35 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **3(1)a** (1.01 g) was isolated in 54% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of Second-generation Tridirectional Phosphonium Cascade Molecule (**3(2)a**)

A solution of **3(1)a** (0.29 g, 0.15 mmol) in dry acetonitrile (25 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (0.52 g, 2.60 mmol) in dry acetonitrile (25 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 16 hr, and then cooled. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved

in acetonitrile (35 mL) and the solution was placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (0.52 g, 1.31 mmol) in dry acetonitrile (40 mL) was added slowly with continuous stirring. The solution was refluxed for 30 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **3(2)a** (0.51 g) was isolated in 55% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of Third-generation Tridirectional Phosphonium Cascade Molecule (**3(3)a**)

A solution of **3(2)a** (0.20 g, 0.032 mmol) in dry acetonitrile (20 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. There was then added slowly with continuous stirring a solution of iodotrimethylsilane (0.34 g, 1.68 mmol) in dry acetonitrile (25 mL), and the mixture was heated at reflux for 24 hr. After this time the solution was cooled to room temperature and the solvent was removed at reduced pressure to give the crude benzylic iodide. The crude benzylic iodide was dissolved in dry acetonitrile (20 mL) and placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. There was added a solution of **2** (0.34 g, 0.86 mmol) in dry

acetonitrile (30 mL) and the reaction mixture was heated at reflux for 4 days. After this time the solution was cooled and the solvent was evaporated under reduced pressure to give the crude product. The crude material was purified by passage through a DOWEX 2-X8 in the iodide form, eluting with 30% aqueous ethanol. The eluents were evaporated under reduced pressure to give the pure **3(3)a**. This compound **3(3)a** was further purified by the addition of diethylether to a solution of **3(3)a** in acetonitrile and the target material precipitated from solution and was collected by filtration and dried. In this manner pure **3(3)a** (0.08 g) was isolated in 15% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of benzyl tri(p-methoxymethyl)phenylphosphonium bromide (**3b**)

A solution of **2** (0.54 g, mmol) in dry benzene (15 mL) was placed in a 100 mL round-bottomed flask fitted with reflux condenser and which was flushed continuously with dry nitrogen. A solution of bromobenzene (0.235 g, 1.37 mmol) in benzene (10 mL) was added to the reaction solution which was refluxed for 24 hr. After cooling, the solvent was removed at reduced pressure and the residue was subjected to flash chromatography on silica gel eluting with acetonitrile to yield **3b** (0.73 g, 94% yield) which exhibited spectra and elemental analysis in accord with the proposed structure.

Preparation of First-generation Tridirectional Phosphonium Cascade Molecule **(3(1)b)**

A solution of **3b**(0.73 g, 1.29 mmol) in dry acetonitrile (30 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (1.55 g, 7.75 mmol) in dry acetonitrile (30 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 16 hr, and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in dry acetonitrile (55 mL) and placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (1.53 g, 3.87 mmol) in dry acetonitrile (35 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **3(1)b** (0.5 g) was isolated in 22% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of Second-generation Tridirectional Phosphonium Cascade Molecule **(3(2)b)**

A solution of **3(1)b** (0.19 g, 0.093 mmol) in dry acetonitrile (25 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (0.337 g, 1.68 mmol) in dry acetonitrile (20 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 20 hr, and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in acetonitrile (30 mL) and the solution was placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (0.34 g, 0.84 mmol) in dry acetonitrile (30 mL) was added slowly with continuous stirring. The solution was refluxed for 30 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **3(2)b** (0.38 g) was isolated in 64% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of Third-generation Tridirectional Phosphonium Cascade Molecule **(3(3)b)**

A solution of **3(2)b** (0.11 g, 0.017 mmol) in dry acetonitrile (10 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. There was then added slowly with continuous stirring a solution of iodotrimethylsilane (0.18 g, 0.92 mmol) in dry acetonitrile (10 mL), and the mixture was heated at reflux for 24 hr. After this time the solution was cooled to room temperature and the solvent was removed at reduced pressure to give the crude benzylic iodide. The crude benzylic iodide was dissolved in dry acetonitrile (25 mL) and placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. There was added a solution of **2** (0.180 g, 0.45 mmol) in dry acetonitrile (20 mL) and the reaction mixture was heated at reflux for 3 days. After this time the solution was cooled and the solvent was evaporated under reduced pressure to give the crude product. The crude material was purified by passage through a DOWEX 2-X8 in the iodide form, eluting with 30% aqueous ethanol. The eluents were evaporated under reduced pressure to give the pure **3(3)b**. This compound **3(3)b** was further purified by the addition of diethylether to a solution of **3(3)b** in acetonitrile and the target material precipitated from solution and was collected by filtration and dried. In this manner pure **3(3)b** (0.07 g) was isolated in 21% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of octadecyl tri(p-methoxymethyl)phenyl Phosphonium bromide (3c)

A solution of **2** (0.82 g, 2.08 mmol) in dry *o*-xylene (25 mL) was placed in a 100 mL round-bottomed flask fitted with reflux condenser and which was flushed continuously with dry nitrogen. A solution of octadecylbromide (0.70 g, 2.08 mmol) in *o*-xylene (15 mL) was added to the reaction solution which was refuxed at 145° C for 48 hr and then cooled to room temperature. The solvent was removed from the reaction mixture under reduced pressure and the residue was washed with n-hexane (30 mL) to remove any unreacted octadecyl bromide and then finally subjected to flash chromatography on silica gel with acetonitrile to give the pure phosphonium salt **3c** (0.25 g, 17% yield) which exhibited spectra and elemental analysis in accord with the proposed structure (Table 1).

Preparation of First-generation Tridirectional Phosphonium Cascade Molecule **(3(1)c)**

A solution of **3c** (0.13 g, 0.18 mmol) in dry acetonitrile (15 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (0.22 g, 1.08 mmol) in dry acetonitrile (10 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 24 hr, and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude

benzylic iodide was dissolved in dry acetonitrile (25 mL) and placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (0.21 g, 0.54 mmol) in dry acetonitrile (10 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 80% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **3(1)c** (0.37 g) was isolated in 92% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of Second-generation Tridirectional Phosphonium Cascade Molecule **(3(2)c)**

A solution of **3(1)c** (0.43 g, 0.19 mmol) in dry acetonitrile (20 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (0.68 g, 3.42 mmol) in dry acetonitrile (10 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 20 hr and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in acetonitrile (20 mL) and the solution was placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2**

(0.68 g, 1.71 mmol) in dry acetonitrile (10 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 80% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **3(2)c** (1.55 g) was isolated in 68% yield which exhibited spectra and analysis in accord with the proposed structure (Table 1).

Preparation of tetra(p-methoxymethyl)phenylphosphonium bromide (**4**)

A solution of **2** (0.500 g, 1.26 mmol) in dry methanol (5mL) was placed in a pressure tube with a teflon needle valve along with *p*-(methoxymethyl)bromobenzene (0.225 g, 1.26 mmol) and anhydrous nickel(II) bromide (0.007 g, 0.032 mmol). The tube was flushed continuously with dry nitrogen and closed. The closed tube was kept in an oil bath maintained at 180° for 48 hr. After cooling to room temperature, the solvent was evaporated at reduced pressure to give the crude product, which was purified by flash chromatography on silica gel (50 g) using 1:1 acetonitrile/ethanol mixture as eluent. In this manner was isolated pure **4** (0.050 g, 7%) which exhibited spectra and analysis in accord with the proposed structure (Table 2).

Preparation of the First-generation Tetradirectional Cascade Molecule (4(1))

A solution of **4** (0.040 g, 0.067 mmol) in dry acetonitrile (15 mL) was placed in a 100 mL round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. To it was added slowly with continuous stirring a solution of iodotrimethylsilane (0.110 g, 0.538 mmol) in dry acetonitrile (5 mL). The reaction mixture was refluxed for 16 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude benzylic iodide. The crude iodide so obtained was dissolved in dry acetonitrile (25 mL) and placed in a 100 mL round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. To it was added slowly with continuous stirring a solution of **2** (0.15 g, 0.38 mmol) in dry acetonitrile (10 mL). The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product which was passed through a DOWEX 2-X8 column in the iodide form using 30% aqueous ethanol as eluent. The material isolated from this treatment was further purified by flash chromatography on silica gel (40 g) eluting with a 1:1 mixture of acetonitrile/ethanol. Evaporation of the eluents gave the pure **4(1)** (0.040 g, 23%) which exhibited spectra and analysis in accord with the proposed structure (Table 2).

Preparation of the Second-generation Tetradirectional Cascade Molecule (**4(2)**)

A solution of **4(1)** (0.030 g, 0.012 mmol) in dry acetonitrile (15 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. To it was added slowly with continuous stirring a solution of iodotrimethylsilane (0.056 g, 0.27 mmol) in dry acetonitrile (5 mL). The mixture was refluxed for 16 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude iodide. The crude iodide thus obtained was dissolved in dry acetonitrile (25 mL) and placed in a 100 mL round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. There was added to it a solution of **2** (0.110 g, 0.290 mmol) in dry acetonitrile (10 mL) and the reaction mixture was heated at reflux for 24 hr. After this time the solvent was evaporated under reduced pressure to give the crude product, which was purified by passing through a DOWEX 2-X8 column in the iodide form and then subjected to flash chromatography on silica gel (40 g) eluting with a 1:1 mixture of acetonitrile/ethanol. Upon evaporation of the eluent there could be isolated pure **4(2)** (0.078 g, 93%) which exhibited spectra and analysis in accord with the proposed structure (Table 2).

Preparation of tri(p-methoxymethyl)phenyl phosphine oxide (**5**)

To an ice-cold solution of **2** (1.00 g, 2.53 mmol) in glacial acetic acid (8 mL) was added dropwise during stirring 30% aqueous hydrogen peroxide (1 mL). After this the reaction mixture was poured into 100 mL of water. The oxide was precipitated as white solid and was collected by filtration to give the crude **5** (0.80 g) in 77% yield. The compound **5** was further purified by flash chromatography on silica gel (50 g) using acetonitrile as eluent to yield pure **5** (0.500 g, 48% yield). ^{1}H NMR (60 MHz, $CDCl_3$ δ) 3.4 [9H, s], 4.5 [6H, s], 7.2-7.9 [12H, AA 'BB']. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) +30. Calcd. for $C_{24}H_{27}O_4P$: C, 70.16; H, 6.57. Found: C, 69.85; H, 6.66.

Preparation of tri(p-methoxymethyl)phenyl phosphine sulfide

A solution of **2** (1.00 g, 2.53 mmol) in dry toluene (30 mL) was taken in a 100 mL round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of sulfur (0.16 g, 5.06 mmol) in dry toluene (10 mL) was added to the reaction solution which was refluxed for 48 hr and then cooled to room temperature. Excess sulfur was removed by filtration and the solvent was removed at reduced pressure to yield the required product (0.98 g, 91% yield). ^{1}H NMR (60 MHz, $CDCl_3$ δ) 3.4 [9H, s], 4.5 [6H, s], 7.2-7.9 [12H, AA 'BB']. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4)

+43. Calcd. for $C_{24}H_{27}O_3PS$: C, 67.53; H, 6.33. Found: C, 67.05; H, 6.38.

Preparation of First-generation Tridirectional Phosphonium Cascade Molecule (**5(1)**)

A solution of **5** (0.49 g, 1.2 mmol) in dry acetonitrile (20 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (1.43 g, 7.2 mmol) in dry acetonitrile (35 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 16 hr and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in dry acetonitrile (45 mL) and placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (1.41 g, 3.60 mmol) in dry acetonitrile (35 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **5(1)** (1.43 g) was isolated in 63% yield which exhibited spectra and analysis in accord with the proposed structure. ^1H NMR (60 MHz, $CDCl_3$ δ) 3.4 [27H, br], 4.5 [24H, br], 7.3-7.9 [48H, m].

^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) +28.0, +30.0. Calcd. for $C_{93}H_{99}O_{10}P_4I_3$: C, 59.37; H, 5.30. Found: C, 59.00; H, 5.38.

Preparation of Second-generation Tridirectional Phosphonium Cascade Molecule **(5(2))**

A solution of **5 (1)** (0.58 g, 0.31 mmol) in dry acetonitrile (25 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (0.56 g, 2.8 mmol) in dry acetonitrile (30 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 16 hr and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in dry acetonitrile (45 mL) and placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (1.1 g, 2.78 mmol) in dry acetonitrile (30 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure product **5(2)** (1.49 g) was isolated in 77% yield which exhibited spectra and analysis in accord with the proposed structure. ^1H NMR

(60 MHz, $CDCl_3$ δ) 3.4 [81H, br], 4.5 [78H, br], 7.2-7.9 [156H, m]. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) +28.0, +30.0. Calcd. for $C_{300}H_{315}O_{28}P_{13}I_{12}$: C, 57.24; H, 5.00. Found: C, 57.01; H, 5.14.

Preparation of the phosphine derivative (**6(1)**) *from the first generation tridirectional cascade molecule* (**5(1)**)

A solution of **5(1)** (0.770 g, 0.41 mmol) in 1:1 mixture of dichloromethane/acetonitrile (40 mL) was placed in a round-bottomed flask fitted with a reflux condenser and the solution was stirred at room temperature. To this solution was added trichlorosilane (0.61 g, 4.51 mmol) and the resulting solution was stirred for 4 hr. The solution was evaporated and the residue was dissolved in dichloromethane (90 mL) and then neutralized with 1 mL of 30% KOH. The organic layer was dried over molecular sieves and the solvent was removed at reduced pressure to give the required phosphine **6(1)** (0.76 g, 99.6% yield). ^1H NMR (60 MHz, $CDCl_3$ δ) 3.4 [27H, br], 4.5 [24H, br], 7.3-7.9 [48H, m]. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) +28.0, -16.0. Calcd. for $C_{93}H_{99}O_9P_4I_3$: C, 59.89; H, 5.31. Found: C, 59.20; H, 5.58.

Preparation of the gold (I) complex (**7(1)**) *from the phosphine derivative* (**6(1)**)

Sodium teterachloroaurate (III) (0.05 g, 0.12 mmol) was dissolved in a 1:1 mixture of acetone and ethanol (10 mL) and the phosphine derivative **6(1)** (0.45 g, 0.24 mmol) in chloroform (15 mL) was added with stirring. The solution became warm, the yellow colour disappeared, and a white precipitate formed. After filtration, the solvent was removed at reduced pressure to give the required gold (I) complex **7(1)** (0.49 g, 97% yield). ^{1}H NMR (60 MHz, $CDCl_3$ δ) 3.4 [27H, br], 4.5 [24H, br], 7.3-7.9 [48H, m]. UV spectra (1 X 10^{-5} mol dm^{-3} solution in $CHCl_3$) 275 nm. Calcd. for $C_{93}H_{99}O_9P_4I_3AuCl$: C, 53.30; H, 4.72. Found: C, 52.81; H, 4.58.

Preparation of pental(p-methoxymethyl)phosphorane (**8**)

Dry diethylether (10 mL) was taken in a 100 mL round-bottomed flask fitted with a reflux condenser and was flushed continuously with argon gas. Lithium (0.05 g, 7.2 mmol) was added to the flask and a solution of *p*-(methoxymethyl)bromobenzene (0.031 g, 0.16 mmol) in diethyl ether (10 mL) was added to the flask. The solution was stirred at room temperature for 12 hr and allowed to stand overnight. Tetra(*p*-methoxymethyl)phosphonium bromide (0.09 g, 0.15 mmol) was added to the reaction flask and the solution was stirred at room temperature for 3 days. Lithium bromide was precipitated from the solution as a white powder and was filtered. The

solvent was removed at reduced pressure to give the required phosphorane **8** (0.08 g, 83%). ^{1}H NMR (60 MHz, $CDCl_3$ δ) 3.4 [15H, s], 4.5 [10H, s], 7.3-7.9 [20H, m]. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) -94 ppm. Calcd. for $C_{40}H_{45}O_5P$: C, 75.45; H, 7.12. Found: C, 75.43; H, 7.12.

Preparation of First-generation Pentadirectional Phosphonium Cascade Molecule (**8(1)**)

A solution of **8** (0.08 g, 0.13 mmol) in dry acetonitrile (25 mL) was placed in a round-bottomed flask fitted with a reflux condenser and flushed continuously with dry nitrogen. A solution of iodotrimethylsilane (0.25 g, 1.30 mmol) in dry acetonitrile (10 mL) was added slowly with continuous stirring. The reaction mixture was refluxed for 16 hr and then cooled to room temperature. The solvent was evaporated under reduced pressure to give the crude benzylic iodide, which was used without further purification. The crude benzylic iodide was dissolved in dry acetonitrile (40 mL) and placed in a round-bottomed flask fitted with reflux condenser and flushed continuously with dry nitrogen. A solution of **2** (0.300 g, 0.76 mmol) in dry acetonitrile (35 mL) was added slowly with continuous stirring. The solution was refluxed for 24 hr and then cooled to room temperature. The solvent was removed at reduced pressure to give the crude product. The pure product was isolated by passage through a DOWEX 2-X8 column in the iodide form, eluting with 30% aqueous ethanol, and evaporation of the solvent. In this manner the pure

product **8(1)** (0.370 g) was isolated in 95% yield. ^{1}H NMR (60 MHz, $CDCl_3$ δ) 3.4 [45H,s], 4.5 [40H, br], 7.3-7.9 [80H, m]. ^{31}P NMR (81 MHz, $CDCl_3$, ppm relative to external H_3PO_4) -95.0, 29.0. Calcd. for $C_{155}H_{165}O_{15}P_6I_5$: C, 60.28; H, 5.38. Found: C, 60.32; H, 5.40.

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