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# Solution phase studies towards the synthesis of triarylamine oligomers using a germanium linker on a solid support

R. Anémian,[a,*] D. C. Cupertino,[a] P. R. Mackie[a] and S. G. Yeates[b]

[a]*Merck Chemicals Ltd, LC-Manchester Technical Centre, Hexagon Tower, Blackley, Manchester M9 8ZS, UK*
[b]*School of Chemistry, The University of Manchester, Manchester M13 9PL, UK*

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**Abstract**—In this letter, we describe the iterative solution phase synthesis of a triarylamine trimer as proof of concept towards the synthesis of oligomeric materials by solid-phase synthesis. Our model system utilises the stability of germanium linkers to nucleophilic conditions to develop efficient steps towards oligomer synthesis via (i) selective deprotection of *tert*-butyl-dimethyl-silyl ether (OTBDMS) functionality, (ii) conversion to reactive trifluoromethanesulfonate (triflate) functionality and (iii) Suzuki cross-coupling reactions.


## 1. Introduction

Conjugated oligomers are at the core of several emerging technologies as active materials for electronic and photonic applications such as organic light-emitting diodes,[1] organic field-effect transistors[2] and photovoltaic devices.[3] Key properties in such materials include stability and processability during fabrication, high charge mobility in a device and perhaps most critically, high purity.[4] A number of oligomeric materials have been reported in the literature, including alkylthiophenes,[5] fused thiophenes,[6] dialkylfluorenes[7] and triarylamines.[8] Of these materials, triarylamine oligomers have been shown to offer an excellent compromise between performance and stability.[9] Solution phase chemistry has been used successfully to synthesise a variety of oligomers using repetitive transition metal catalysed cross-coupling, however, control over the structure of such materials can be exceedingly difficult. The result of this lack of control is that some materials have been difficult to synthesise using traditional techniques, or require arduous purification to achieve the required purity for electronics applications. Indeed, the purification process based on column chromatography of intermediates is time consuming and sometimes quite inefficient, resulting in very low yields. Recent publications[10–12] have clearly demonstrated both the advantages and the versatility of solid-phase organic synthesis (SPOS) in the iterative preparation of π-conjugated oligomers. The major benefits over traditional solution phase techniques include (i) ease of purification of the target oligomer, (ii) ability to use excess reagents (which can be easily removed by filtration) to drive reactions to completion, (iii) prevention of homocoupling reactions by virtue of site isolation of growing oligomer chains and (iv) the amenability of the process to automation. However, a potential drawback of the SPOS technique is that cleavage of the product from the resin can leave a functional group on the oligomer, which can have a dramatic outcome on its properties. To circumvent this problem, some workers have developed traceless linker systems, which provide an elegant means to cleave oligomers from solid supports, whilst leaving no undesirable functionality on the target material.[13]

In this communication, we describe solution phase studies directed towards the development of the solid-phase synthesis of high purity triarylamine oligomers using a germanium linker on a solid support. This new class of linker, which can be readily cleaved by protodegermylation of the Ge–Ar bond, fulfils the criteria required of a traceless linker.[14] In addition, germanium linkers display an enhanced stability towards both bases and nucleophiles and a greater susceptibility to electrophilic *ipso*-demetallation than their silicon counterparts.[15]

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* Corresponding author. Tel.: +44 (0)161 721 1028; fax: +44 (0)161 720 9138; e-mail: remi.anemian@merckchem.com

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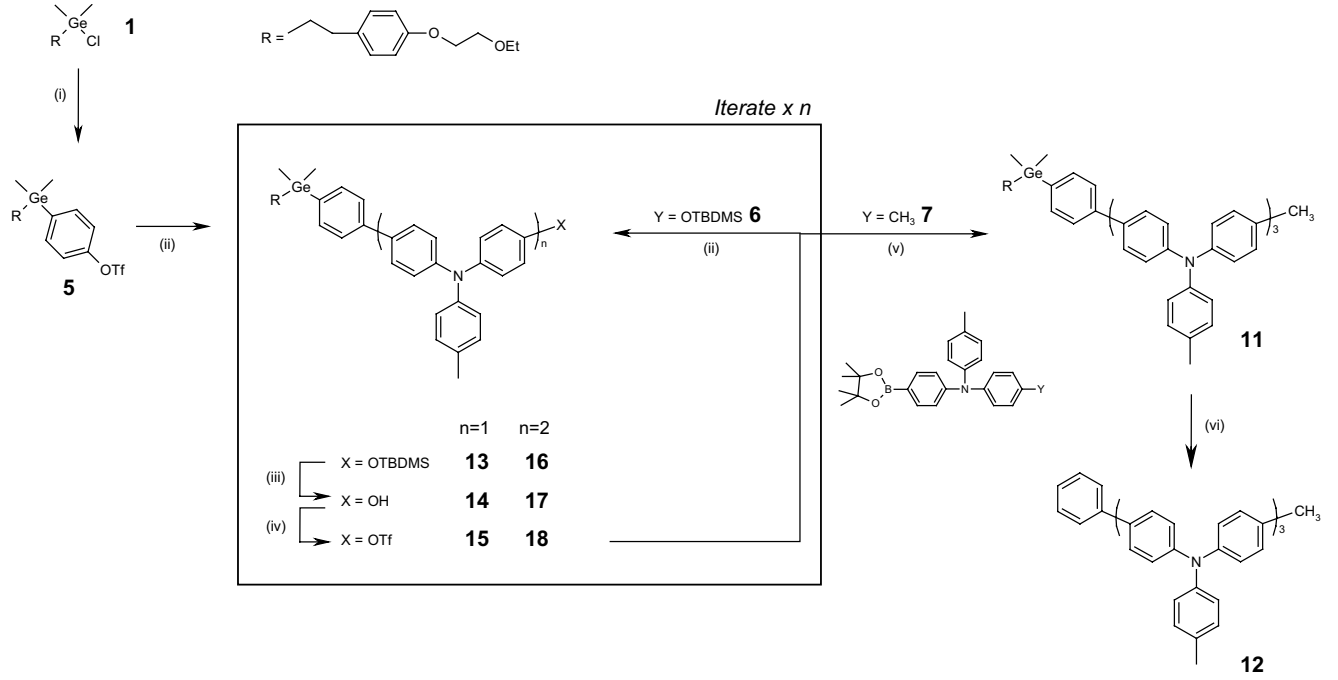
These properties arise due to the greater β-effect of germanium[16] when compared with silicon based systems. By way of a contrast, arylsilane based linkers require harsh conditions to effect cleavage of electron-deficient aromatic systems.[17] Recent developments on the synthesis of germanium-based linkers have allowed the 'fine-tuning' of such linkers for specific applications thus allowing them to show a wider potential in solid-phase synthesis.[18]

## 2. Results and discussion

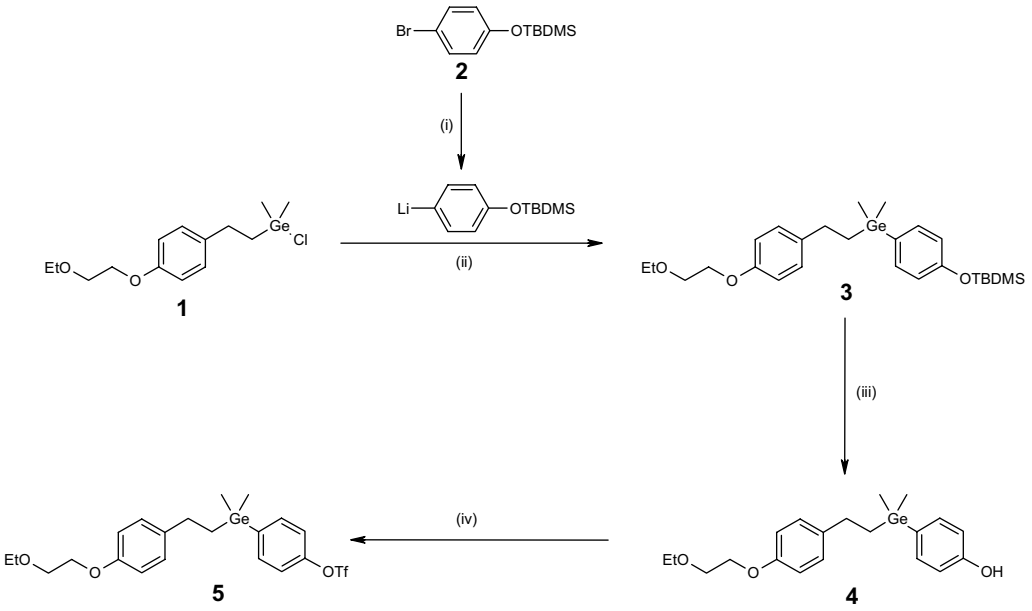
The synthetic approach we used in the iterative solution phase synthesis of a model triarylamine oligomer is outlined in Scheme 1 and may be summarised by the following steps: (i) synthesis and activation of the germanium linker system, (ii) coupling of the first protected monomer to the linker, (iii) deprotection of the *tert*-butyldimethyl-silyl ether (OTBDMS) group, (iv) conversion to an activated trifluoromethanesulfonate (triflate) coupling precursor followed by a repeat of (ii) with cross-coupling of a second, third, *n*th protected (or (v) an end-capping) monomer and lastly (vi) cleavage of the oligomer from the germanium-based linker. In this scheme, steps (ii), (iii) and (iv) may be repeated as often as required to build-up the target oligomer.

Assembly of the oligomer is a step-wise process in which each monomer unit is added sequentially through a transition metal mediated coupling. Such an approach is directly transferable to the solid phase, where high purity oligomers with well-defined structures (i.e., no deletions) may be produced by simply using an excess of the chosen monomer at stage (ii). Our approach uses conditions which are compatible with the germyl linker, in that electrophilic reagents are avoided due to the sensitivity of the linker to *ipso*-degermylation. Typically, transition metal mediated couplings require the presence of a halogen substituent on one or both of the coupling partners. Such halogen substituents are usually introduced by way of an electrophilic halogenation of the monomer, which would result in cleavage of the germanium linker.[14] Suzuki cross-coupling reactions using pseudohalogens such as a triflate group represent a useful alternative as they may be introduced into the growing oligomer by a means that is compatible both with the requirements of the germanium linker, and with the protection strategy employed in this synthetic scheme. Specifically, aryl-triflate reagents are accessible from phenols and can be readily incorporated into both the linker and monomer units. Prior to coupling, the phenol functionality is protected as an OTBDMS group in order to avoid any interference which may occur with the Suzuki cross-coupling conditions. The choice of the protecting group was based on the fact that protection and deprotection should not affect the germyl linkage to the solid support. It has been noted in the literature that there is an orthogonal susceptibility of α-silyl and α-germyl substituted thiophene derivatives towards nucleophilic *ipso*-protodemetallation.[19] In this work, we demonstrate the selectivity between α-silyloxy and α-germyl substituted triarylamines towards cleavage by nucleophiles.

The synthesis and activation of the germanium linker system is described in Scheme 2. The synthesis of the linker began from {2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-




**Scheme 1.** Key steps in the iterative solution phase synthesis of triarylamine oligomer **12** as a model system for the solid phase. (i) See Scheme 2 for synthesis and activation of linker system, (ii) $Pd(Ph_3)_4$, $Na_2CO_3$(aq) (2 M), 1,2-dimethoxyethane, 80 °C, (iii) $NBu_4F$, THF, ambient temperature (iv) trifluoromethane sulfonic anhydride, pyridine, 0 °C, (v) $Pd(Ph_3)_4$, $Na_2CO_3$(aq) (2 M), 1,2-dimethoxyethane, 80 °C, (vi) trifluoroacetic acid (1% in dichloromethane).



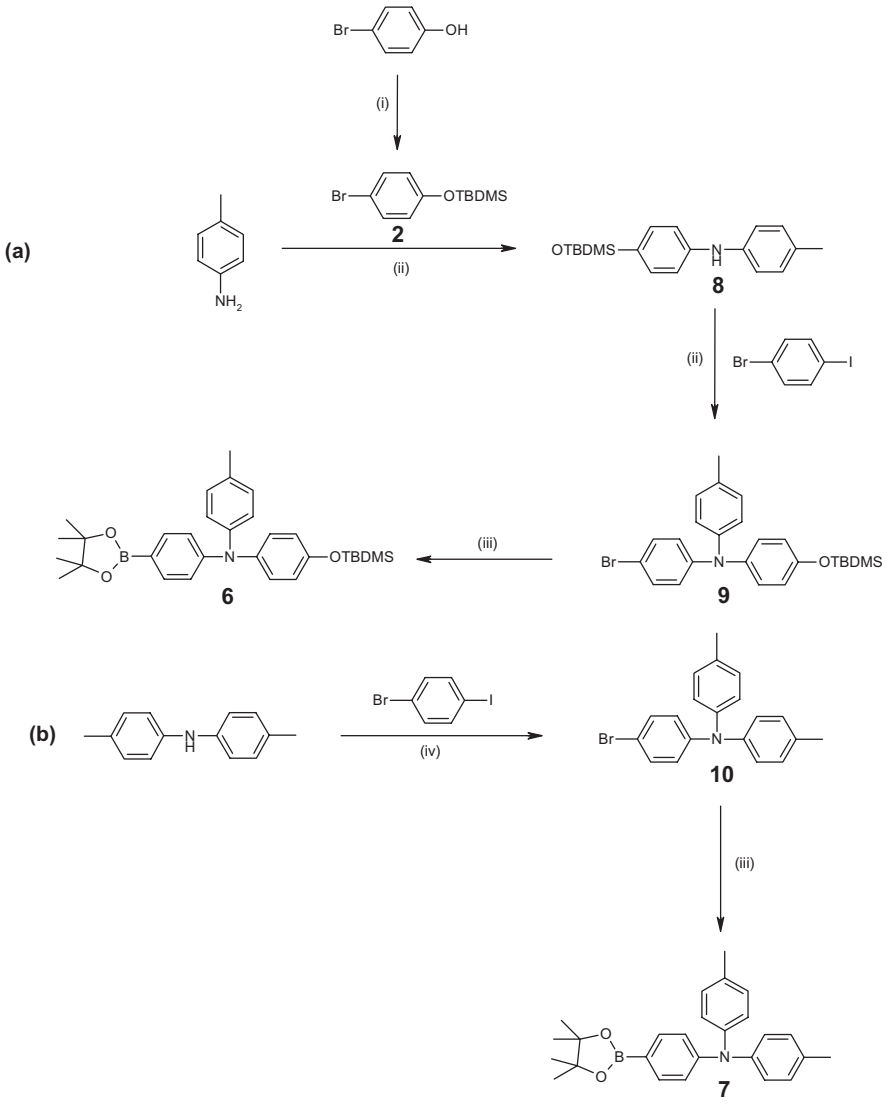

**Scheme 2.** Synthesis and activation of the model linker system: (i) *n*-BuLi (2.5 M in hexanes), THF, −78 °C, (ii) toluene, ambient temperature, (iii) $NBu_4F$, THF, ambient temperature, (iv) trifluoromethane sulfonic anhydride, pyridine, 0 °C.

dimethyl-germyl-chloride,[18] **1**. This was chosen for the solution phase model because it is possible to develop a synthetic methodology using this linker, which may be transferred directly to the solid phase. In the model linker (Scheme 2), the ethoxyether substituent provides a solution phase surrogate, which mimics polyethylene glycol (PEG) based resins such as Quadragel™[20] or Hypogel™. By transmetallation of {2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germyl-chloride **1** with lithiated (4-bromo-phenoxy)-*tert*-butyl-dimethyl-silane[21] **2**, it is possible to synthesise the OTBDMS functionalised linker **3** in 77% yield. It was then possible to establish the optimum conditions to (i) deprotect the OTBDMS group and (ii) convert the resultant phenol into the corresponding triflate without affecting the α-germyl linkage. The selectivity of cleavage of the OTBDMS group over the α-germyl linker was achieved using tetrabutylammonium fluoride (TBAF), confirming the relative stability of aryl-germanes towards nucleophiles when compared to aryl-siloxanes. Deprotection of the OTBDMS group was achieved in 76% yield to give the corresponding phenol **4** with no detectable cleavage of the germyl linker. Finally, conversion of the phenol **4** into the triflate derivative **5** was achieved using trifluoromethanesulfonic anhydride in anhydrous pyridine.

To apply our step-wise growth strategy based on Suzuki cross-coupling, we developed two triarylamine monomers, the first, **6**, was functionalised with (i) a boronic acid ester and (ii) a protected phenol group, which was subsequently deprotected and activated as a triflate precursor for the next coupling. The second monomer, **7**, features only the boronic acid ester reactive group. Monomer **6** was designed to grow the oligomer in a controlled step-wise manner whereas monomer **7** was designed to 'end-cap' the oligomer after the growth process. Monomer **6** was prepared (Scheme 3a) in three steps using Buchwald[22] reaction conditions from 2,4-dimethylaniline, 1-iodo-4-bromobenzene and 4-bromophenoxy-*tert*-butyldimethylsilane[21] **2**. The resultant intermediate **9** was then converted to the corresponding boronic acid ester **6** using standard conditions. The second monomer, [4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-di-*p*-tolylamine, **7**, was prepared (Scheme 3(b)) in two steps from di-*p*-tolylamine and 1-iodo-4-bromobenzene by a standard Ullmann procedure.[23] Again, the (4-bromo-phenyl)-di-*p*-tolyl-amine intermediate, **10**, was converted to the corresponding boronic acid ester **7** in good yield.

Aryl-triflate functionalised compounds are known to undergo very clean and efficient Suzuki cross-coupling reactions catalysed by palladium.[24] However, literature procedures for this cross-coupling reaction were found to be incompatible with the germanium linker. This was attributed to the presence of halogenated alkali metal salts in such procedures. We subsequently developed a procedure which omitted the use of such salts and allowed us to couple the first protected triarylamine monomer **6** to the activated linker **5** in 84% yield. No detectable cleavage of the germyl linker was observed under these conditions. A minor impurity was observed, namely, 4-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenol, **4**, which was formed by the competitive hydrolysis of the triflate functionality in **5**. To drive the cross-coupling reaction to completion, it would be possible to re-activate the phenol to the corresponding triflate derivative **5** (Scheme 2) and react this further with a monomer. Such a procedure would be particularly useful when carrying out this reaction on a polymer support and is directly analogous to double coupling strategies described in the literature.[25]

As proof of concept of the step-wise construction of an oligomer, we determined to synthesise a triarylamine trimer **11** (Scheme 1). Typical yields for each iterative step:




**Scheme 3.** Synthesis of triarylamine monomers: (a) [4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-*p*-tolyl-amine **16** and (b) [4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-di-*p*-tolyl-amine **18**; (i) *tert*-butyldimethylsilylchloride, imidazole, DMF, ambient temperature, (ii) $NaOBu^t$, $Pd_2dba_3$, *rac*-binap, toluene, 100 °C, (iii) *n*-BuLi (2.5 M in hexanes), THF, −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, (iv) KOH, *o*-xylene, CuCl, 1,10-phenanthroline, 100 °C.

**Table 1.** Typical yields (%) of iterative steps for step-wise growth of triarylamine oligomer **11**

| | Number iterative steps | | |
|---|---|---|---|
| | **0** | **1** | **2** |
| (i) Yield of cleavage of TBDMS protecting group (%) | 76 | 90 | 75 |
| (ii) Yield of conversion to triflate precursor (%) | 87 | 86 | 92 |
| (iii) Yield of cross-coupling reaction (%) | 84 | 71 | 75 |

(i) cleavage of the OTBDMS group, (ii) conversion of the resultant phenol to a triflate precursor and (iii) cross-coupling with another monomer are summarised in Table 1.

The final step of the synthesis is the release of the oligomer from the germanium-based linker by electrophilic *ipso*-degermylation. By treatment with trifluoroacetic acid (TFA), quantitative cleavage of the aryl-germanium bond is achieved, yielding the H-capped triarylamine trimer **12**.

## 3. Conclusion

In summary, we have described the step-wise preparation of triarylamine oligomers in solution as proof of concept towards the synthesis of such oligomers on a solid support. Our model system utilises a germanium linker, which demonstrates a greater stability to nucleophilic conditions relative to arylsiloxane functionality. We have established the efficiency and the compatibility of the key steps in the oligomer build-up with the germanium linker, namely (i) selective deprotection of the

OTBDMS group, (ii) conversion of the resultant phenol to a triflate coupling precursor and (iii) cross-coupling. We are currently transferring this model to a solid support and adapting the synthetic strategy to accommodate other monomers.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.07.150.

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