Palladium Catalysis in the Synthesis of Polyaniline-Related Materials

By Joseph P. Sadighi

B. A. Chemistry, Williams College, 1994

Submitted to the Department of
Chemistry in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY IN
INORGANIC CHEMISTRY

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Massachusetts Institute of Technology

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Abstract

The palladium-catalyzed aryl amination reaction, in conjunction with an orthogonal protective group scheme, forms the basis of two routes to oligoaniline precursors. One method consists of a bidirectional chain growth from a symmetric core piece, whereas the other involves a divergent-convergent synthesis of nonsymmetric fragments, followed by coupling to a symmetric core fragment. The oligoaniline precursors are soluble in a variety of common organic solvents, and are easily converted to the deprotected oligoanilines. The method allows the preparation of odd or even chain lengths, as long as a 24-mer, and the incorporation of a variety of functional groups. The effects of chain length and substitution upon oligomer behavior have been investigated by electronic absorption spectroscopy and cyclic voltammetry.

Certain aspects of aryl amination methodology, arising from or applicable to the synthesis of polyaniline derivatives, are described. Commercially available benzophenone imine serves as a convenient ammonia equivalent in the palladium-catalyzed amination of aryl halides and triflates. The chelating ligand bis[2-(diphenylphosphino)phenyl] ether (DPEphos), in combination with palladium acetate, forms a

highly active catalyst system for the coupling of anilines with aryl bromides. A modification in the experimental procedure for aryl amination allows the use of palladium chloride, the least expensive compound of palladium, as the palladium source. A new copper-mediated method has been developed for the synthesis of 2-(di-*tert*-butylphosphino)biphenyl, a versatile ligand developed by Wolfe and Buchwald for palladium-catalyzed cross-coupling reactions, on multigram scale. The use of this ligand in aryl amination reactions is described.

The synthetic methods for the synthesis of oligoanilines have been modified to afford a wider variety of polyaniline-related materials. The preparation of ring-substituted monomers for incorporation into internally functionalized oligoanilines is described. The synthesis of protected polyaniline derivatives by step-growth polymerization or copolymerization of suitable monomers has been achieved. A new analogue of polyaniline, a poly(aminophenothiazine), has also been synthesized by palladium catalysis.

Thesis Supervisor: Stephen L. Buchwald

Title: Camille Dreyfus Professor of Chemistry

Acknowledgments

First, I would like to thank my research supervisor, Professor Stephen Buchwald, for all of his guidance and support since I joined his group. He has taught me a great deal, not only about chemistry but about developing a sense of strategy to be successful in research. He allowed me to work on a project that fascinated me, and I am grateful for all his encouragement and enthusiasm. He has given me a generous degree of latitude in pursuing my research, and at the same time provided direction when I was unsure which way to turn next. And I must add, I have enjoyed my dealings with him on a personal level, from his instructions on drinking Coke to his restrained and fair characterizations of my political views.

In the course of our foray into materials chemistry, Steve has made one suggestion with particular frequency: "Talk to Tim." Professor Timothy Swager has been extremely generous in so many ways, including helpful discussions, incisive suggestions, patient proofreading, and access to the instrumentation in his labs. His guidance has been invaluable, his good humor unflagging. I am greatly in his debt.

I have also benefited from my interactions with Professor Gregory Fu, and I am grateful for the close relationship between the Buchwald and Fu groups. I greatly enjoyed my stint as a teaching assistant for Professor Daniel Kemp, and I would like to thank him for an early chat about protective group chemistry, which helped me to find the approach that ultimately worked. And I wish to thank all the other chemistry faculty I've been privileged to learn from in the course of my graduate studies.

Before I came to MIT, a number of chemistry professors took me under their wing, and I am deeply grateful to all of them. At Williams College, Professor J. Hodge Markgraf was my senior thesis advisor; Professor Lawrence Kaplan and Professor Cassandra Eagle (now at Appalachian State University) were my mentors and friends. Professor David Bickar of Smith College spent an enormous amount of time with me,

teaching me lab chemistry and (especially) discussing ideas, since I first became interested in chemistry. Each of them contributed to my decision to pursue a career in chemistry—or, rather, to my realization that chemistry was what I had to do.

I am grateful to all of my colleagues, past and present, in the Buchwald group, for the experience of working with them, whether indirectly or as collaborators. I'm going to omit specific mention of a lot of people I like and admire very much, and single out just three of them. I would like to thank Andy Peat, my baymate during a very stressful year and a half, for his advice and constant good cheer, which helped me immensely. Rob Singer arrived as a postdoc just as the oligoaniline project began to work out; his enthusiasm, synthetic expertise and intellectual contributions were indispensable in bringing the project to fruition. Mike Frid has been a frequent late-night lab partner and a good friend.

I would like to thank several current and former members of the Swager group. Richard Kingsborough, Sherry Zhu, and Debra Lightly were most generous with their time in teaching me the use of the potentiostat. Raquel Gimenez and Vance Williams were very helpful in showing me how to run gel permeation chromatography.

I thank my friends outside of lab for keeping up my morale, for their understanding of all declined invitations and all lapses in contact, for their patience on all occasions when I kept them waiting because I just had to do one more thing before leaving lab. Thanks in particular to Jim Bruneau, George Mautner, and Kim Cobb.

Finally, I thank my family for all their love and support. My sister Sheila has lived in Boston for the last three years, and although I've seen her absurdly seldom, I've been very glad she was close by. My parents have provided me with a great many opportunities, and have always encouraged me without ever pressuring me. They have always believed in me, even when I didn't; they have been reassuring when things went badly, and thrilled for me when things went well. I hope someday to earn all they've given me already.

Preface

Parts of this thesis have been adapted from articles co-written by the author. The following articles were reproduced in part with permission from the American Chemical Society:

"A General Synthesis of End-Functionalized Oligoanilines via Palladium-Catalyzed Amination" Robert A. Singer, Joseph P. Sadighi, and Stephen L. Buchwald *J. Am. Chem. Soc.* **1998**, *120*, 213–214.

"Palladium-Catalyzed Synthesis of Monodisperse, Controlled-Length and Functionalized Oligoanilines" Joseph P. Sadighi, Robert A. Singer, and Stephen L. Buchwald *J. Am. Chem. Soc.* **1998**, *120*, 4960–4976.

"Novel Electron-Rich Bulky Phosphine Ligands Facilitate the Palladium-Catalyzed Preparation of Diaryl Ethers" Attila Aranyos, David W. Old, Ayumu Kiyomori, John P. Wolfe, Joseph P. Sadighi, and Stephen L. Buchwald. *J. Am. Chem. Soc.* **1999**, *121*, 4369–4378.

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"An Ammonia Equivalent for the Palladium-Catalyzed Amination of Aryl Halides and Triflates" John P.Wolfe, Jens Åhman, Joseph P. Sadighi, Robert A. Singer, and Stephen L. Buchwald *Tetrahedron Lett.* **1997**, *38*, 6367–6370.

"A Highly Active Palladium Catalyst System for the Arylation of Anilines" Joseph P. Sadighi, Michele C. Harris, and Stephen L. Buchwald *Tetrahedron Lett.* **1998**, *39*, 5327–5330.

Respective Contributions

Much of the work described in this thesis is the result of collaborative efforts. Specific notes are included for compounds not synthesized by the author; some general comments are given here.

The study on oligoanilines was carried out in close collaboration with Dr. Robert Singer. The protective group strategy and this application of the divergent-convergent approach were developed by the author; the bidirectional growth strategy for the rapid synthesis of substituted octamers was developed by Dr. Singer. The procedure for BOC-protection was developed by Dr. Singer, as was the use of sodium acetate as an additive in the bromodesilylation reaction. Both procedures represent significant improvements over the author's original methods. The methods for deprotection were developed by the author; preparative thermolysis of the octamers was carried out by Dr. Singer. Initial experiments involving electronic absorption spectroscopy and cyclic voltammetry were carried out collaboratively; the data presented herein were obtained by the author. Experimental procedures are provided for all compounds described in this chapter.

In the chapter on methodology, substrate tables include the collected results; experimental procedures are provided for those compounds prepared by the author. The benzophenone imine methodology was carried out in collaboration with Dr. John Wolfe, Dr. Jens Åhman and Dr. Robert Singer. Aryl amination reactions using the ligand DPEphos were carried out in collaboration with Ms. Michele Harris. The copper-mediated synthesis of 2-(di-*tert*-butylphosphino)biphenyl appears in the article "Novel Electron-Rich Bulky Phosphine Ligands Facilitate the Palladium-Catalyzed Preparation of Diaryl Ethers," by Attila Aranyos, David W. Old, Ayumu Kiyomori, John P. Wolfe, Joseph P. Sadighi, and Stephen L. Buchwald (*J. Am. Chem. Soc.* **1999**, *121*, 4369–4378), and is the author's sole contribution to that work; the preparation of diaryl ethers is therefore outside the scope of this chapter. The study of this ligand and its analogues in aryl amination reactions was carried out in collaboration with Dr. Wolfe and Dr. Hiroshi Tomori.

The synthesis of protected polyanilines by palladium-catalyzed step-growth polymerization, described in Chapter Three, was suggested independently by Dr. Singer and by the author. Dr. Thomas Mackewitz first prepared the monomers **52a** and **53**, and carried out the first polymerization reactions. The polymerization results described in this chapter are those obtained by the author.

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Introduction

Electrically conducting polymers are the focus of intensive current research, from the perspective of both basic science and practical applications. The driving force behind this interest is the promise, increasingly realized, of materials combining the electrical conductivity of a metal with the processability of plastics. Of particular interest for device applications is the control of the physical, electrical and chemical properties of a π-conjugated system by the incorporation of functional groups in the polymer backbone.[1] The recent burst of activity in conducting polymer research dates back to the discovery in 1977 that polyacetylene undergoes a dramatic increase in electrical conductivity upon exposure to iodine vapor;[2] since then, a variety of polymers with extended π-systems have been shown to display high electrical conductivities. Semiconductivity in conjugated polymers, however, had been demonstrated years earlier, and one of the first examples studied was polyaniline.[3]

Polyaniline was produced as early as 1840 by the chemical oxidation of aniline in acidic solution;[4] in 1862, the electrochemical oxidation of aniline sulfate in aqueous solution, giving rise to an insoluble blue pigment, was described.[5] Several studies of the chemical nature of "aniline black" were carried out around the beginning of this century. The chemical oxidation product of aniline was described as an octamer, and four oxidation states were described.[6] In 1961, a partially oxidized polyaniline, in the form of its hydrochloride salt, was shown to be a semiconductor, and a large difference in conductivity between this material and its neutral form was observed.[3a]

The preparation and principal forms of polyaniline are illustrated in Figure 1. Emeraldine, the intense green conductive form, is obtained directly from the polymerization reaction, as both chemical and electrochemical polymerization are carried out in acidic solution. Deprotonation of this form affords the emeraldine base, a deep blue-purple insulator. Reduction of emeraldine affords the leucoemeraldine form, a nearly colorless insulator; oxidation, with concomitant deprotonation, gives rise to the violet pernigraniline form, also an insulator.

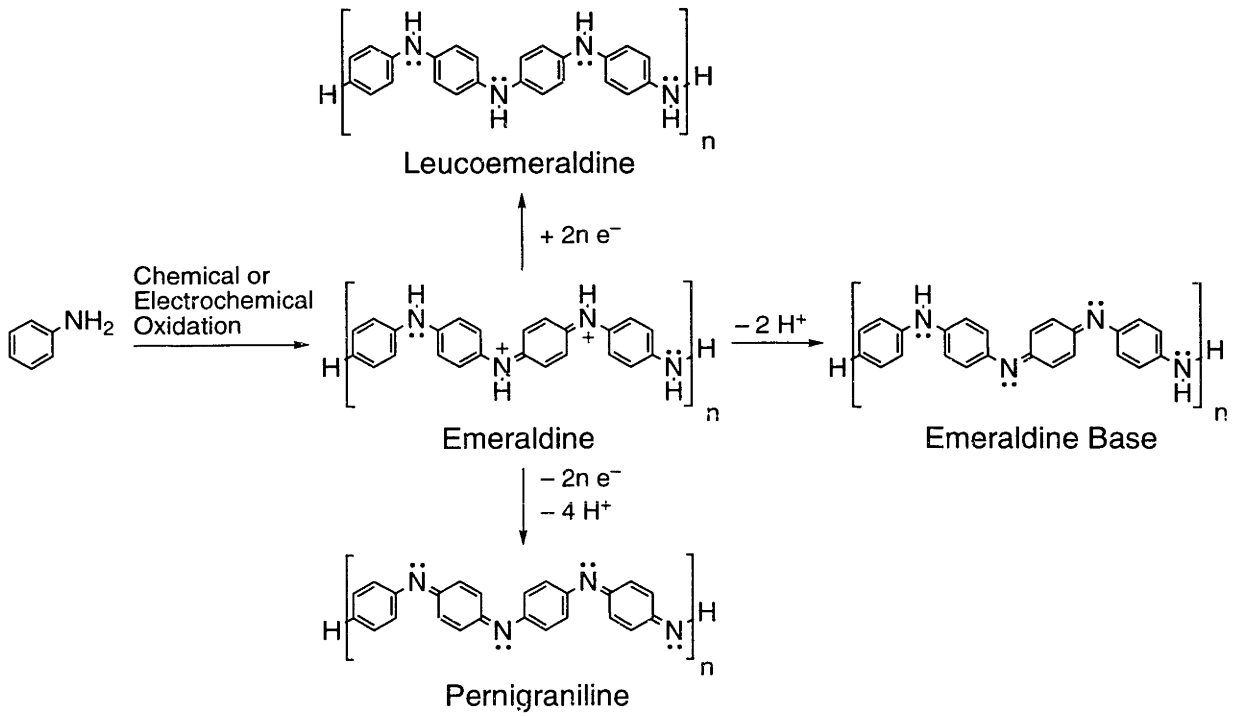


Figure 1. Preparation and principal forms of polyaniline.

The intractability of polyaniline, as it was originally prepared, hindered the investigation of its electrical properties. In light of the then-recent discovery of high conductivity in doped polyacetylene, the discovery in 1980 that aniline could be electropolymerized to form thin, conductive films[7] did much to reignite interest in this polymer. Many advances in polyaniline chemistry in the 1980s, such as the fabrication of polyaniline-based microelectronic devices,[8] were made using the electropolymerized form of polyaniline. More recently, advances in solution-processing of polyaniline have greatly improved its practical utility. The emeraldine base form may be processed as a solution in dipolar aprotic solvents such as *N*-methylpyrrolidinone (NMP), then protonated to afford the conductive form. When certain strong organic acids are used, the emeraldine salt form is itself a soluble and processable material.[9] Films of emeraldine camphorsulfonate, formed by evaporation of its solutions in *m*-cresol, display far higher conductivities than had previously been observed for polyaniline (as high as 583 S/cm, compared to *ca.* 1–10 S/cm).[10]

Among conductive polymers, polyaniline is remarkable for the stability of its conductive form to air and moisture.[11] Its electrical and optical properties may be tuned easily and reversibly by changes in oxidation state[12a] or in degree of protonation.[12b] Polyaniline has been studied for use in numerous practical applications, including rechargeable organic batteries,[13] electrochromic displays,[14] electromechanical actuators,[15] anticorrosion coatings for steel,[16] antistatic materials,[17] and electromagnetic interference shielding.[18]

Although the conductivity of polyaniline is high enough to make it attractive in such applications, further improvements remain desirable. It has been predicted that the conductivity of polyaniline would be 1000-fold higher, comparable to that of copper or silver, if all available charge carriers actually contributed to its conductivity.[19] The comparatively low conductivity of polyaniline has been ascribed to various causes, including tautomeric and conformational isomerism[20] and the presence of defects in the polymer chain. The radical nature of the oxidative polymerization reactions can result in regiochemical errors, with occasional ortho-linking of the monomers, or tail-to-tail coupling of radicals to form benzidine moieties.[21]

To investigate the importance of such defects, efforts have been made to prepare regiopure polyaniline. Wudl *et al.* modified their synthesis of phenyl-capped octaaniline (*vide infra*) to prepare polyaniline with exclusively para regiochemistry, by the polycondensation of 1,4-phenylenediamine with dihydroxyterephthalic acid. The authors note that stringent technique is crucial to the success of the reaction.[22] The material prepared by this method appears to behave similarly to conventionally prepared polyaniline. The polymerization of 4-bromoaniline using an Ullmann coupling reaction,[23a] and more recently using palladium catalysis,[23b] have recently been reported; however, the reaction conditions are harsh, and the characterization of the products was ambiguous.

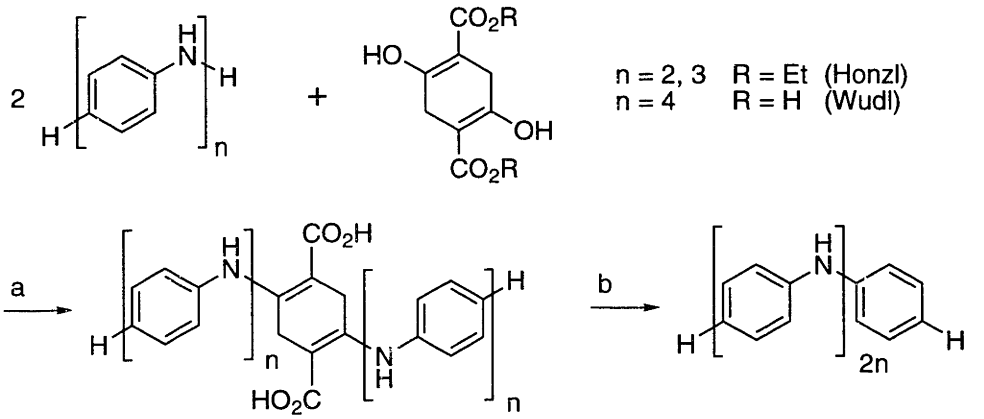
The non-oxidative polymerization methods do not appear to be readily adaptable to the synthesis of substituted polyanilines, or of polyaniline analogues. For example, the use of benzidine in the Wudl polycondensation reaction, in place of 1,4-phenylenediamine, results in a very sluggish reaction and hence a much less efficient polymerization. Substituted polyanilines may be prepared by the oxidative polymerization of ring-substituted[24] or *N*-substituted[25] aniline monomers. However, a limited range of polymer architectures is accessible by these methods: the substituent is usually present on every aniline unit. Moreover, the resulting polymers are less efficient conductors of electricity than the parent polyaniline; increased steric interactions disrupt the coplanarity between aryl rings, decreasing the conjugation of the polymer chain.

Soon after polyaniline was identified as an electrical conductor, Honzl *et al.* prepared and investigated the first phenyl-capped oligoanilines of controlled chain length as models for the poorly defined polymer, and demonstrated substantial electrical conductivity in the longer oligomers on doping with iodine.[26] The synthetic method involved the condensation of small oligoanilines (dimer, trimer and tetramer)[27] with diethyl dihydroxyterephthalate, followed by hydrolysis, decarboxylation, and aromatization. This sequence afforded phenyl-capped tetraaniline and hexaaniline; diazotization and reduction of tetraaniline gave rise to phenyl-capped trianiline. The authors apparently did not isolate phenyl-capped octaaniline from the condensation reaction when tetraaniline was used.

In 1986, Wudl and coworkers modified and simplified the Honzl condensation approach (Scheme 1) and succeeded in obtaining phenyl-capped octaaniline.[28] This compound proved identical to bulk polyaniline by ESR, UV–vis, and IR spectroscopy, and displayed conductivity on the same order of magnitude as that of the bulk polymer, demonstrating that useful electrical properties may be realized even in relatively short

oligoaniline systems. The oligomers may therefore be of interest in themselves, and not merely as models for the bulk polymer.

Scheme 1[a]



[a] Oligoaniline Synthesis of Honzl[26] and Wudl.[28] Key: (a) Δ, then (for R = Et) NaOH, EtOH, dioxane, Δ; (b) Δ, O_2.

Wudl's findings have generated considerable interest in oligoanilines, and a number of synthetic routes have been reported in recent years. These include oxidative oligomerization methods, and metal-mediated or metal-catalyzed methods. MacDiarmid, Epstein *et al.*, in a modern variation of the Wilstätter-Moore approach, have described the oxidative dimerization of *N*-phenyl-1,4-phenylenediamine to tetraaniline. They report that oxidation of tetraaniline with ammonium peroxydisulfate may be used to obtain octaaniline or a 16-mer; the selectivity in each case has not been explained.[29] Wei and coworkers have developed an oligomer synthesis based on the electrophilic addition of lower oligomers, in their oxidized forms, to diphenylamine or analogous compounds.[30] This method has been used to prepare oligoanilines as large as heptaaniline, and phenyl-capped oligoanilines as large as the octamer. Examples of these oxidative coupling methods are illustrated in Figure 2. The potential regiochemical ambiguities of these methods were not discussed.

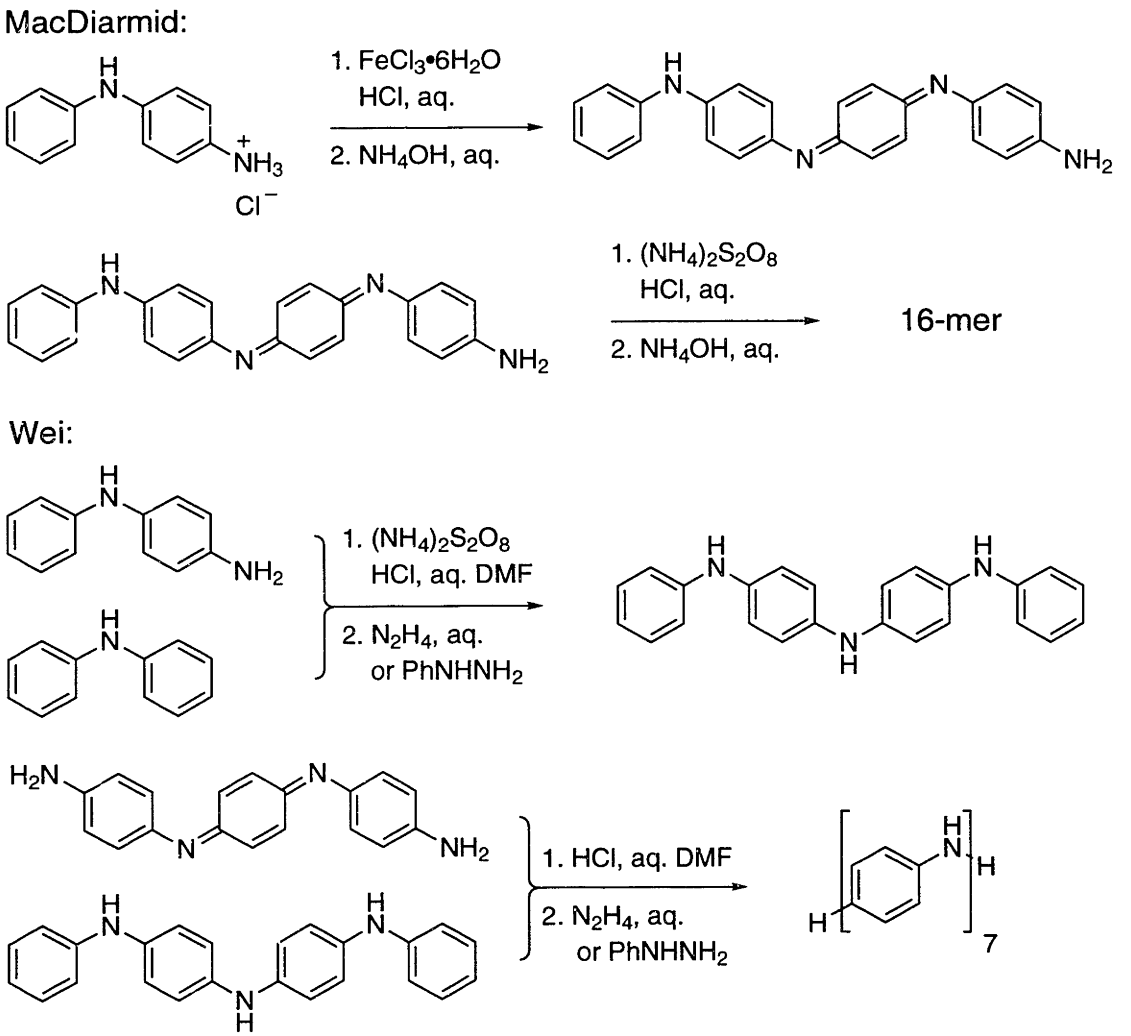


Figure 2. Oxidative coupling methods for the synthesis of oligoanilines.[29, 30]

A titanium alkoxide-mediated coupling of anilines with phenols has been used to prepare phenyl-capped tetraaniline and pentaaniline.[31] An Ullmann coupling reaction between acetanilides and 4-iodonitrobenzene was used in an iterative coupling/reduction sequence;[32] deacetylation of the protected products afforded aniline dimer, trimer and tetramer, the starting anilines for the Wudl-Honzl oligoaniline synthesis.[26, 28] These methods are outlined in Figure 3.

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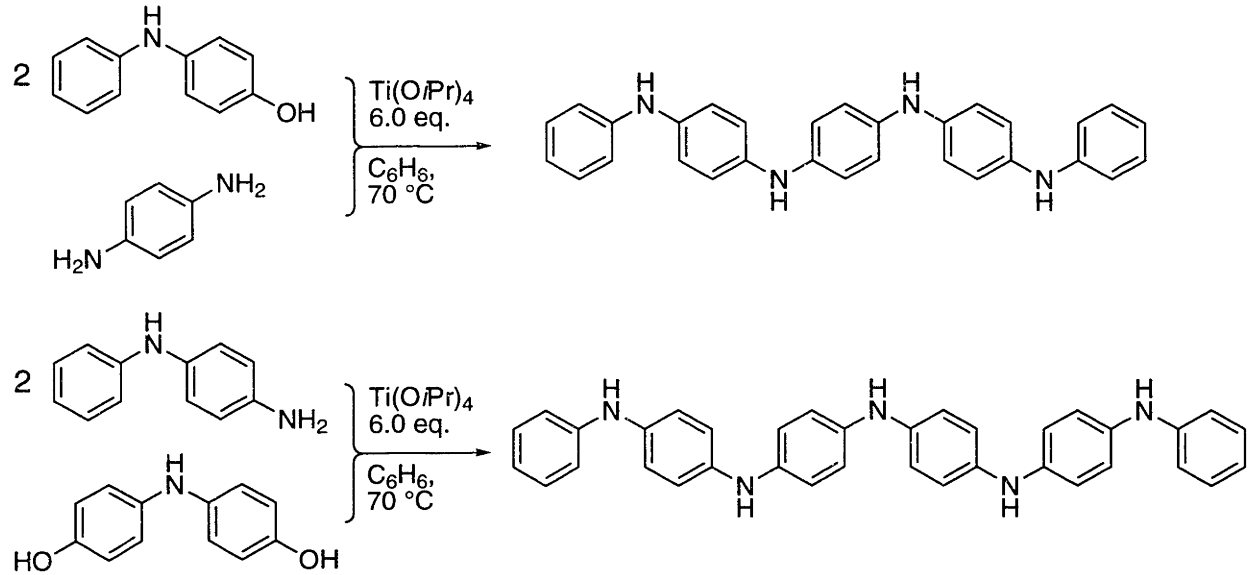
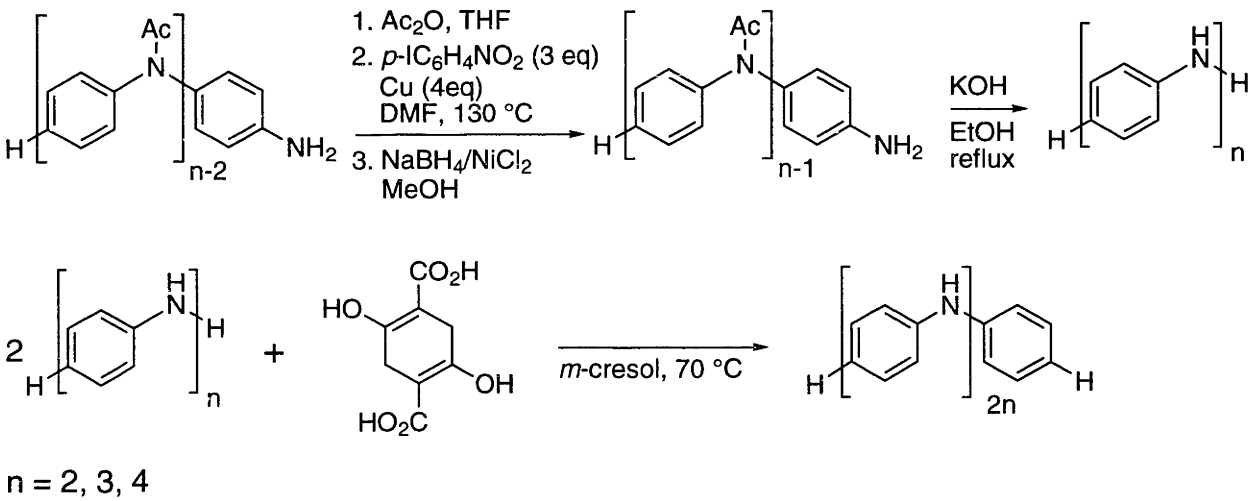


Rebourt:



n = 2, 3, 4

Figure 3. Metal-mediated oligoaniline syntheses.[31, 32]

The methods described above provide access to a number of phenyl-capped oligoanilines, up to chain lengths which display substantial electrical conductivity. They do not, however, appear to be easily applied to the preparation of functionalized oligomers. We wished to explore whether palladium catalysis could be used to construct the carbon-nitrogen bond framework of oligoanilines, in a potentially versatile synthetic route to these materials. Such a method might also be adapted to

the preparation of polyanilines with previously inaccessible substituent patterns, and of new polymers analogous to polyaniline.

The palladium-catalyzed amination of aryl halides and triflates[33] constitutes a powerful method for the synthesis of a wide variety of arylamines. Previously existing methods for the preparation of arylamines suffered from various limitations. The most prevalent electrophilic method is the nitration of an arene, followed by reduction to give a primary aniline.[34a] The nitroarenes may also be converted to *N*-alkylanilines by reductive alkylation,[34b] or to *N,N*-dimethylanilines by reductive dimethylation.[34c] The nitration reaction, however, usually involves strongly acidic and/or electrophilic conditions which are incompatible with certain functional groups. Moreover, the reaction often gives rise to product mixtures. A lesser-known electrophilic method, used for the synthesis of diarylamines, is the addition of arylnitrenium ions, generated from aryl azides in acidic solution, to arenes.[35] This method was used to synthesize a number of previously unknown products; however, the same drawbacks which apply to the nitration reaction, and the need to prepare and isolate the aryl azide starting materials, limit its practical utility.

Certain simple diarylamines, such as diphenylamine, *N*-phenyl-1,4-phenylenediamine, and *N,N*-diphenyl-1,4-phenylenediamine, are available from condensation reactions, involving an aniline and a phenol or an aniline and an aniline salt.[36] The reaction temperatures are generally quite high, and the scope of the reactions is limited. The titanium-mediated condensation shown in Figure 3 occurs under remarkably mild conditions, but the use of several equivalents of titanium reagent is required. The generality of the reaction with respect to other functional groups or substitution patterns was not discussed.[31]

The preparation of diarylamines by nucleophilic aromatic substitution requires the presence of strongly electron-withdrawing groups on the aryl halide or pseudohalide, and often requires harsh reaction conditions. For example, the reaction

between aniline and 1-fluoro-4-nitrobenzene requires high temperatures[37a] or pressures[37b] to proceed efficiently. Anilines can react with unactivated aryl halides when a base such as sodium amide is employed; these reactions proceed through benzyne intermediates, and thus afford mixtures of the product regioisomers.[38] The strongly basic conditions are incompatible with numerous functional groups.

The copper-mediated coupling of anilines with aryl halides,[39a] in an Ullmann-type reaction, is applicable primarily when the aryl halide contains an electron-withdrawing group such as a nitro group or ester function. In the similar Goldberg reaction, acetanilides are coupled with aryl halides in the presence of potassium carbonate and copper iodide; electron-withdrawing groups must be present in the amide starting material.[39b] High temperatures are frequently necessary for these reactions. The use of phenylbismuth reagents[40a] and aryllead reagents[40b] as arylating agents, in the presence of a copper catalyst, broadens the scope of the reaction considerably, and allows milder reaction conditions to be used; however, the heavy metal organyls must be prepared and isolated, and used in stoichiometric quantities.

Early examples of palladium-catalyzed and palladium-mediated arylamine formation are illustrated in Figure 4. The use of palladium catalysis in aryl amination

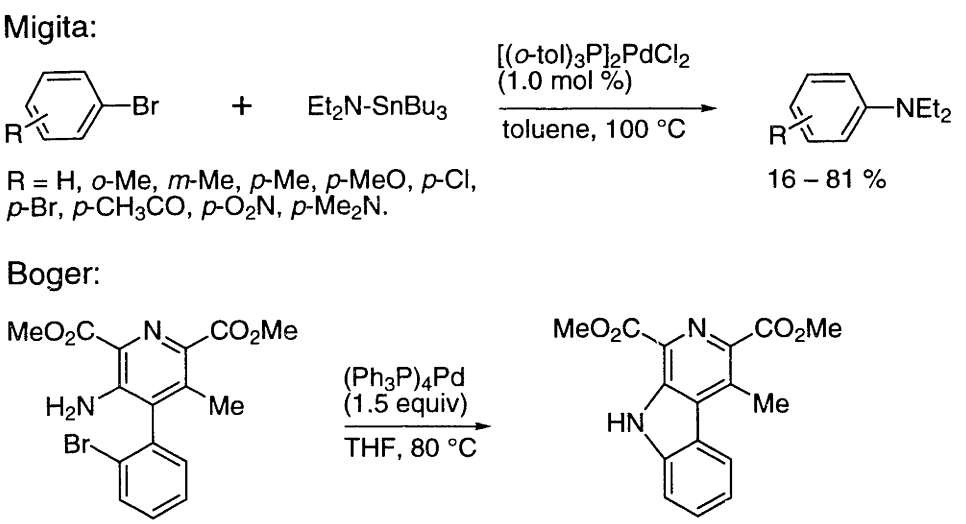
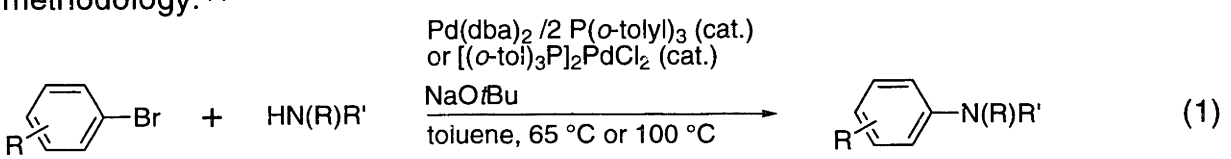


Figure 4. Early examples of palladium-catalyzed arylamine formation.[41, 42]

was initially reported in 1983 by Migita *et al.*, who demonstrated the cross-coupling of (*N,N*-diethylamino)tri-*n*-butylstannane with aryl bromides, using a palladium catalyst with tri-*o*-tolylphosphine as the supporting ligand.[41] The following year, Boger and coworkers used stoichiometric tetrakis(triphenylphosphine)palladium (0) to effect an intramolecular aryl amination, in their total synthesis of lavendamycin methyl ester.[42]

In 1994, Guram and Buchwald developed a procedure for the preparation of aminostannanes from (*N,N*-diethylamino)tri-*n*-butylstannane *in situ*. This advance expanded the scope of the Migita aryl amination protocol, allowing a wider variety of arylamines to be produced.[43] Arylamines derived from a primary alkylamine, however, remained inaccessible, and the removal of the stoichiometric organotin byproduct required non-trivial workup procedures. The development of tin-free reaction conditions, in which an amine was coupled directly with an aryl bromide in the presence of sodium *tert*-butoxide (eq 1), represented a significant improvement in this methodology.[44]



(1)

The new reaction conditions allowed the efficient preparation of a number or arylamines; however, the scope remained limited, particularly in the case of primary amines, including aniline. Modifications of the procedure permitted the catalytic amination of aryl iodides,[45] and the formation of nitrogen heterocycles by cyclization of amines, amides, and sulfonamides.[44a, 46] Some of the heterocycles were prepared using other monodentate phosphine ligands, such as triphenylphosphine[44a, 46a, 46b] or tri-2-furylphosphine.[46a]

The discovery that chelating bisphosphines could serve as useful ligands for palladium-catalyzed aryl amination[47] came as a surprise, in light of earlier mechanistic studies[48] and preliminary experiments.[43] In the course of a study on the arylation of optically active amines, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) was

found to suppress a side reaction, involving β-hydride elimination from (amido)palladium (II) intermediates, which led to loss of enantiomeric excess.[49] The efficiency of the BINAP-based catalyst system led to its investigation in the arylation of other types of amine. This catalyst system proved effective at far lower catalyst loadings than the tri-*o*-tolylphosphine-based system, and displayed far wider scope.[50]

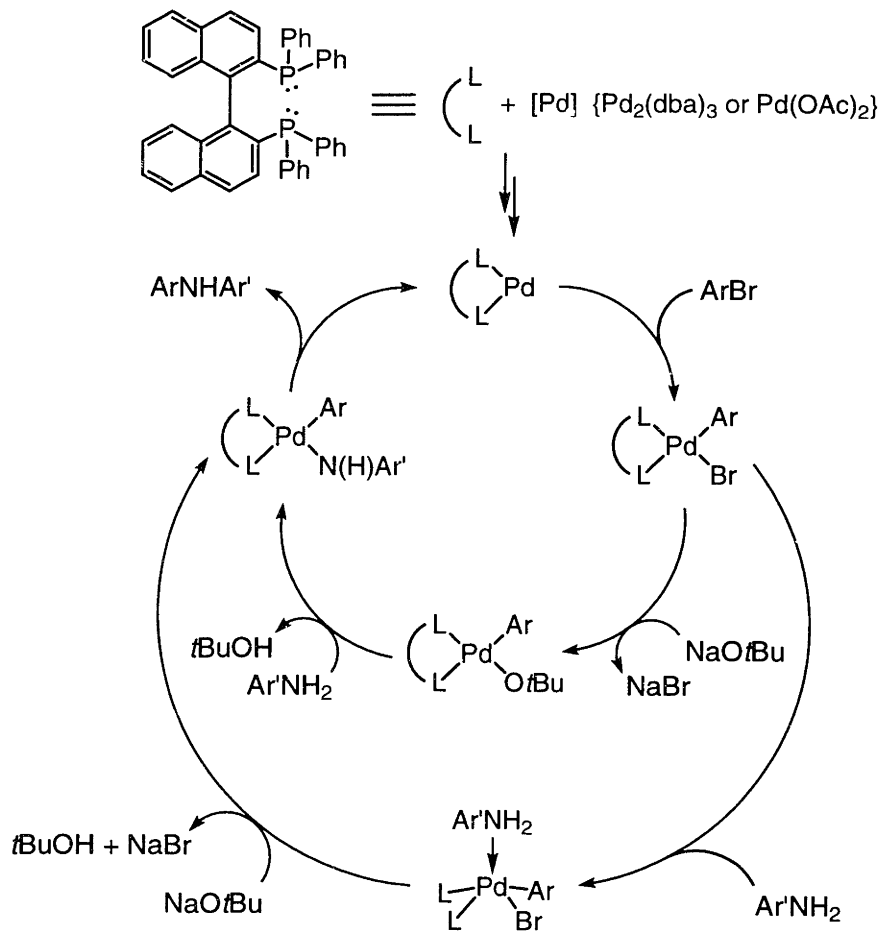


Figure 5. Proposed catalytic cycle for the arylation of anilines.[51]

One aspect of this wider scope is particularly relevant to the synthesis of polyaniline-related materials. Two problems are believed to affect the arylation of primary amines using the tri-*o*-tolylphosphine-based system. The (amido)palladium (II) intermediate may undergo β-hydride elimination, giving rise to the reduced arene byproduct derived from the aryl bromide. Moreover, primary amines have been found

to displace the phosphine ligand from the monophosphine)palladium (II) (aryl) halide, forming catalytically inactive palladium (II) bis-amine complexes.[52] The chelating ligand BINAP appparently resists displacement, and the palladium/BINAP system in most cases allows the efficient transformation of primary anilines into diarylamines.

A possible catalytic cycle for this process is shown above, in Figure 5. The active catalyst species is generated *in situ* from either a palladium (0) precursor, tris(dibenzylideneacetone) dipalladium, or from palladium (II) acetate. Oxidative addition of the aryl bromide affords a (BINAP)palladium (aryl) bromide complex.[53] Conversion of this intermediate to the corresponding (BINAP)palladium (aryl) amido complex might occur through coordination of amine followed by deprotonation, or through a palladium alkoxide intermediate.[51] Reductive elimination forms the C–N bond and regenerates the active catalyst species.

The high efficiency and broad substrate scope of the reaction make it an ideal method for the preparation of novel oligoaniline derivatives. Chapter 1 describes the development of a general route to oligoanilines, using palladium catalysis to assemble the aryl-nitrogen framework and an orthogonal protective group scheme to control the course of the reactions. The protective groups confer excellent solubility upon the products, and are easily removed to form the electroactive oligomers. This method offers great synthetic flexibility: even- or odd-numbered oligomers may be prepared, and functional groups may be introduced at the ends of the chains to modify the properties of the materials without disrupting the coplanarity between rings. Nonsymmetric oligoaniline derivatives from dimer through decamer, and a 16-mer, have been prepared; these are useful chiefly as building blocks for other materials. We have prepared and investigated phenyl-capped heptaaniline through decaaniline, a series of end-functionalized octaanilines, and the phenyl-capped 16-mer and 24-mer.

Certain recent advances in the methodology of palladium-catalyzed aryl amination have been enmeshed with the synthesis of polyaniline-related materials. Some, such as the development of an ammonia surrogate for catalytic amination reactions, or the use of a simpler chelating phosphine as a supporting ligand, have arisen from the materials research; others, particularly the development of monodentate supporting ligands for highly active catalysts, were discovered in another context but found important application in the synthesis of oligoaniline derivatives. Their applications in oligoaniline synthesis are included in Chapter 1; methodological investigations are detailed in Chapter 2.

Finally, the methods for oligoaniline synthesis have been adapted to the preparation of novel oligoaniline and polyaniline analogues, as described in Chapter 3. For the synthesis of internally substituted oligoanilines, and eventually of substituted polyanilines with precisely controlled substituent patterns, a number of substituted monomer equivalents have been prepared. The palladium-catalyzed coupling of oligomer fragments has been modified to produce protected polyanilines, with average chain lengths well above those required for electrical conductivity. A palladium-catalyzed polymerization reaction has also been used in the preparation of a previously inaccessible heterocycle-derived polymer, poly-(3-amino-10-decylphenothiazin-7-yl).

Chapter One:

Synthesis of Monodisperse, Functionalized Oligoanilines

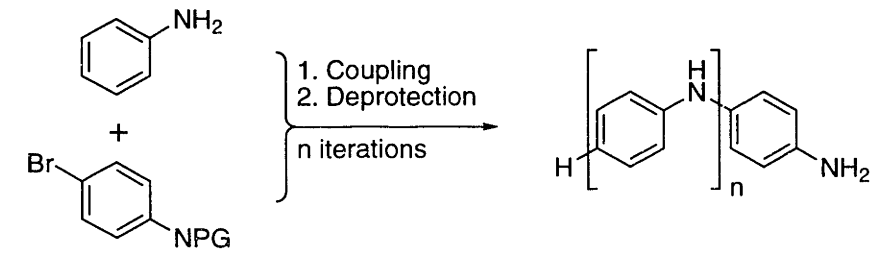
1.1—Synthesis of Protected Oligoanilines

Several strategies,[54] illustrated in Figure 6, may be envisioned for the synthesis of discrete oligoanilines by sequences of aryl amination and deprotection. The reaction of an arylamine with a protected 4-bromoaniline, followed by deprotection, would result in an increase in chain length of one unit for each iteration. The disadvantages of such a method are the relatively slow increase in chain length for a given number of steps, and the increasing difficulty of separating the products from any unreacted starting material or byproducts as the chain length increases. An outward growth of the oligoaniline from a symmetric core would permit the chain to grow by two units in one iteration, resulting in a larger difference in size between starting material and desired product. As in the monodirectional strategy, the chain length increases by the same increment with each iteration of the sequence.

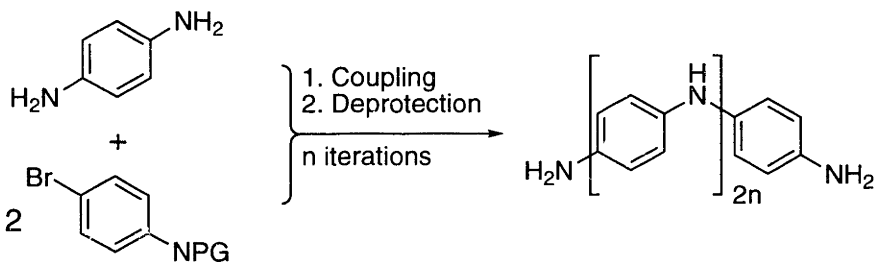
A geometric growth in chain length is possible using a divergent-convergent approach.[55] The first example of a divergent-convergent approach was the preparation of monodisperse oligoethylenes as large as the 96-mer.[56] The first application of this strategy to π-conjugated oligomers was the synthesis of linear α-thiophene-alkynylene oligomers as long as 120 Å by Tour and coworkers.[57] In this strategy, a suitably protected oligomer is divided into two portions; one is converted to an arylamine, and the other to an aryl bromide. The coupling of the two produces a homologous oligomer, with a doubling in chain length.

For electrochemical studies and applications of oligoanilines, symmetric products are desirable, to avoid complications arising from parallel and antiparallel orientations between chains, and to avoid the possibility of oxidative polymerization of the oligomers. Our synthetic methods combine the divergent-convergent approach with a modified bidirectional approach, which links the chain fragments to form a symmetric oligomer.

Monodirectional Growth:



Bidirectional Growth:



Divergent-Convergent Growth:

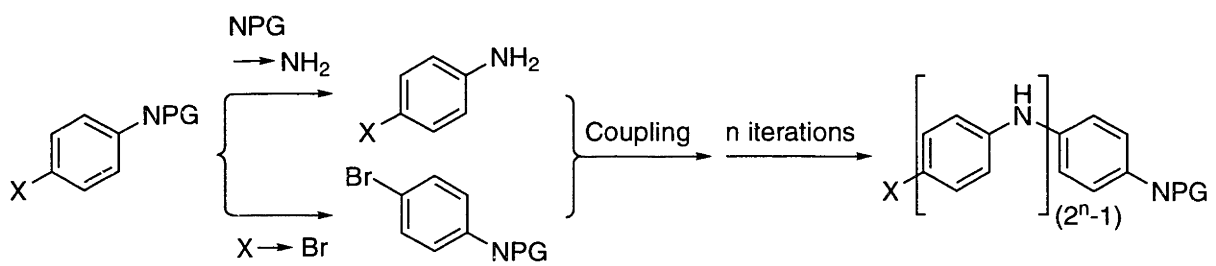
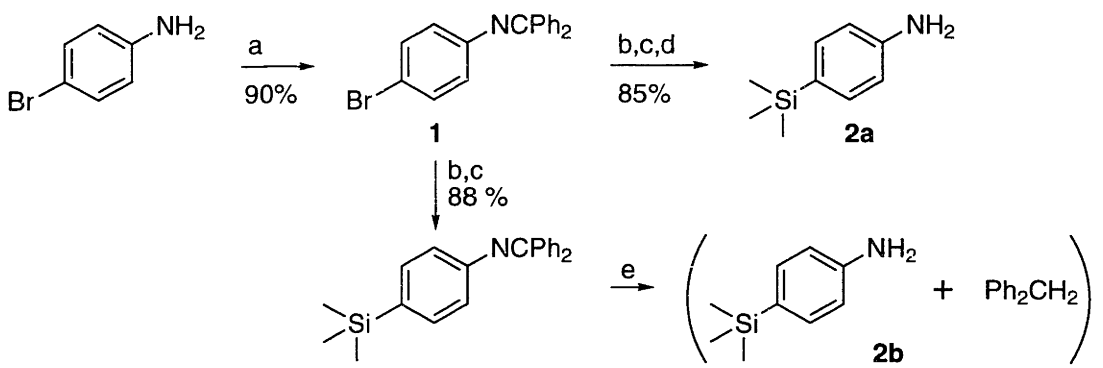


Figure 6. Possible strategies for the synthesis of oligoanilines by aryl amination.

The application of the divergent-convergent strategy to oligoaniline synthesis requires the use of suitable equivalents for the aryl bromide and arylamine functional groups, so that each may be unmasked without affecting the other. The facile electrophilic substitution of the trimethylsilyl group[58] allows it to function as a masked aryl bromide. The nitrogen protecting group was therefore required to be stable to the reaction conditions of bromodesilylation, as well as to those of the aryl amination reaction, and to be removable without the use of strong acid, which would cleave the aryl-silicon bond.

After investigating a number of possibilities, we found the diphenylmethylene group to be extremely useful for several reasons. Condensation of 4-bromoaniline with benzophenone is easily carried out on large scale and in high yield. The resulting *N*-(diphenylmethylene)-4-bromoaniline (**1**) is a convenient substrate for palladium-catalyzed aryl amination; the reactions proceed rapidly and cleanly, with no detectable transamination, and the diphenylmethylene group imparts excellent crystallinity to the products. This protective group is stable to bromine under the conditions used in bromodesilylation. The free primary amine may be liberated by hydrogenolysis,[59] or by treatment with hydroxylamine under weakly acidic conditions.[60] Finally, the stability of the imine to alkyllithium reagents at low temperature allows halogen-metal exchange to be carried out on **1**, leading to a convenient preparation of 4-(trimethylsilyl)aniline (**2**),[61] as shown in Scheme 2.

Scheme 2[a]

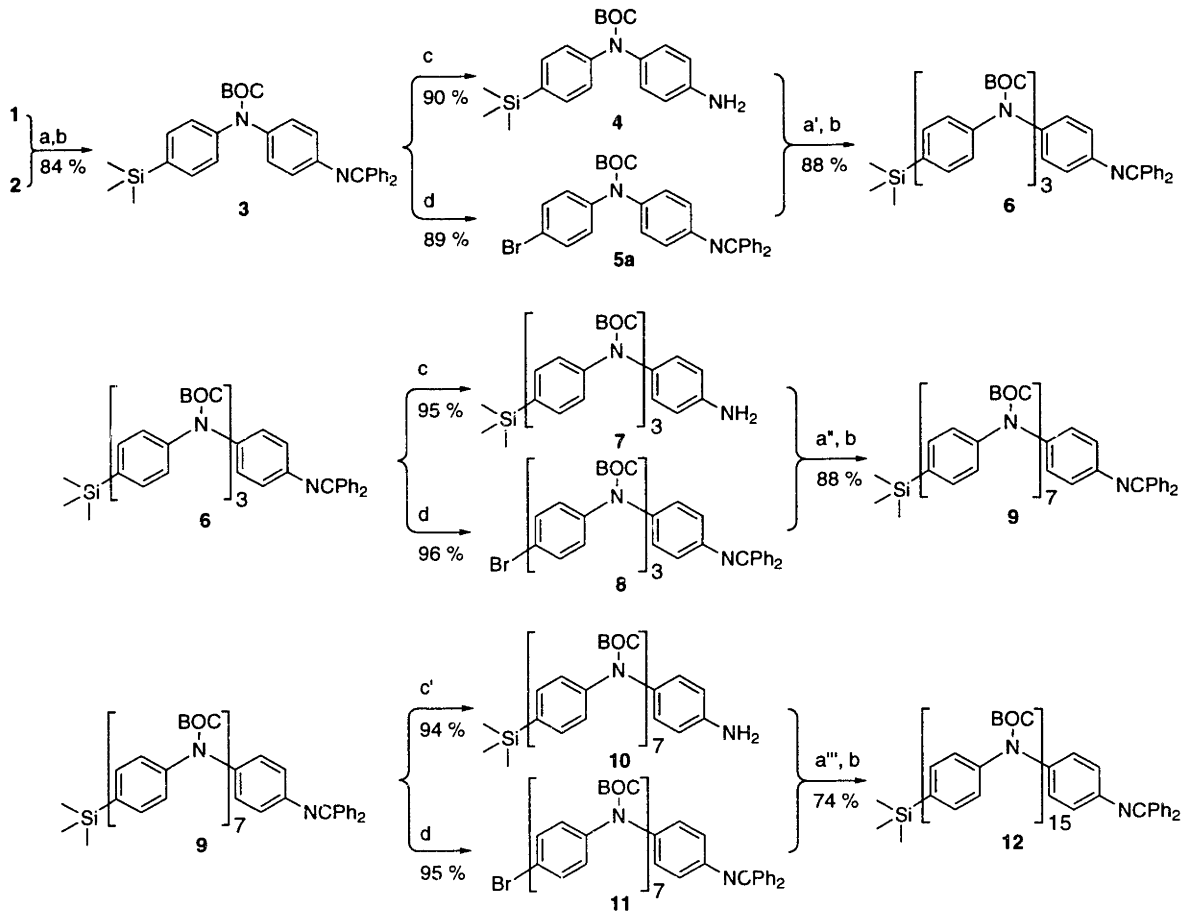


[a] Key: (a) Ph_2CO, 5Å mol. sieves, $PhCH_3$, 110 °C; (b) *n*-C_4H_9Li, THF, –78 °C; (c) $(CH_3)_3SiCl$, THF, –78 °C; (d) $H_2NOH{\cdot}HCl$ (1.5 eq), NaOAc (2 eq), CH_3OH. (e) NH_4^+ HCO_2^- (12 eq), 10 % Pd/C (0.1 eq Pd), CH_3OH, 60 °C.

This aniline may be isolated in pure form (**2a**) by treatment of *N*-(diphenylmethylene)-4-(trimethylsilyl)aniline with hydroxylamine, followed by precipitation of benzophenone oxime and distillation. In an experimentally simpler variation, the precursor imine may be isolated and purified, then subjected to hydrogenolysis. The crude 4-(trimethylsilyl)aniline is obtained after a simple workup as an equimolar

mixture with diphenylmethane (**2b**), and may be used directly in palladium-catalyzed cross-coupling.

Scheme 3[a]



[a] Key (sums indicate separate portions): (a) $Pd_2(dba)_3$ (0.25 mol %), *S*-BINAP[62] (0.75 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (a') $Pd_2(dba)_3$ (0.5 mol %), DPEphos[63] (1.1 mol %), NaO*t*Bu (1.4 eq), $PhCH_3$, 80 °C; (a") $Pd(OAc)_2$ (0.5 mol %), then $Pd_2(dba)_3$ (1 mol %), DPEphos (1.1 + 2.4 mol %), NaO*t*Bu (1.4 eq), $PhCH_3$, 80 °C; (a"') $Pd_2(dba)_3$ (2.0 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (b) $(BOC)_2O$ (1.3 eq), 4-DMAP (0.2 eq), THF, reflux; (c) NH_4^+ HCO_2^- (12 eq), 10 % Pd/C (0.1 eq Pd), THF/CH_3OH, 60 °C; (c') NH_4^+ HCO_2^- (2 x 12 eq), 10 % Pd/C (0.1 + 0.05 eq Pd), $PhCH_3/C_2H_5OH$, 80 °C; (d) NaOAc (1 eq), Br_2 (2 eq), THF, –78 to 0 °C.

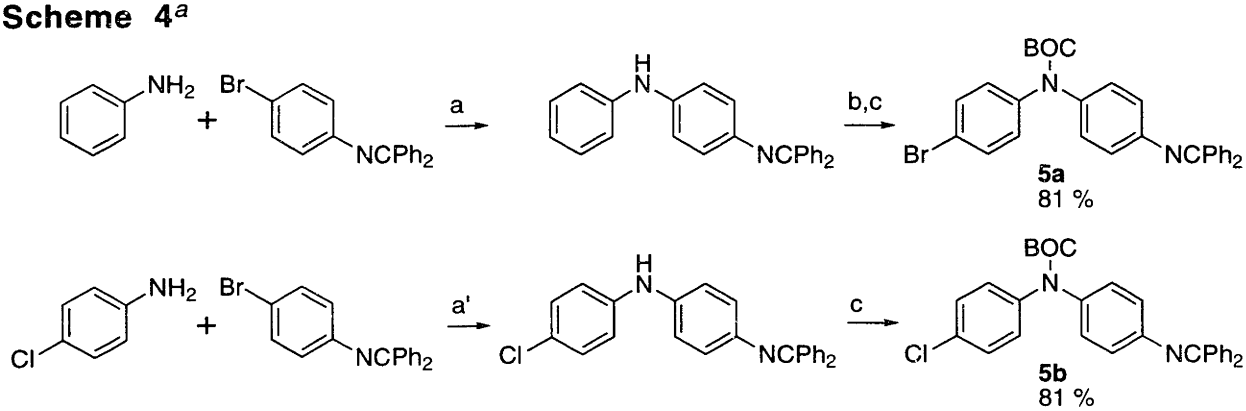
A series of oligoaniline derivatives was prepared, originally using BINAP as the supporting ligand for palladium-catalyzed cross-coupling reactions.[62] A number of the intermediates were later prepared by simplified methods, involving more direct synthetic routes or more recently developed catalyst systems. These intermediates

are presented in the order of the original series; the newer methods therefore appear out of chronological order.

Palladium-catalyzed coupling of **1** and **2** affords an aniline dimer with a masked bromide at one end and a protected amine at the other. Protection of the internal NH group as its *tert*-butyl carbamate (BOC) derivative forms a dimer derivative (**3**) which may be homologated by the divergent-convergent approach as shown in Scheme 3. The chain-length doubling has been repeated up to the 16-mer stage (**12**). The *tert*-butyl carbamate prevents the oxidation of the phenylenediamine moieties to quinonediimines, allows bromodesilylation to occur without detectable over-bromination, and confers excellent solubility upon the oligomer derivatives. Several chain fragments (**5**, **7**, **10**) used in the synthesis of symmetric oligomers were prepared in this manner. The reactions are easily carried out on multigram scale; the yield for each step is high, and the intermediates are easily purified by crystallization.

More direct routes to the dimer halides **5**, not requiring the preparation of 4-(trimethylsilyl)aniline (**2**), are illustrated below, in Scheme 4. The coupling of **1** with aniline, followed by regioselective para-bromination[64] and BOC-protection of the diarylamine coupling product, affords dimer bromide **5a**.

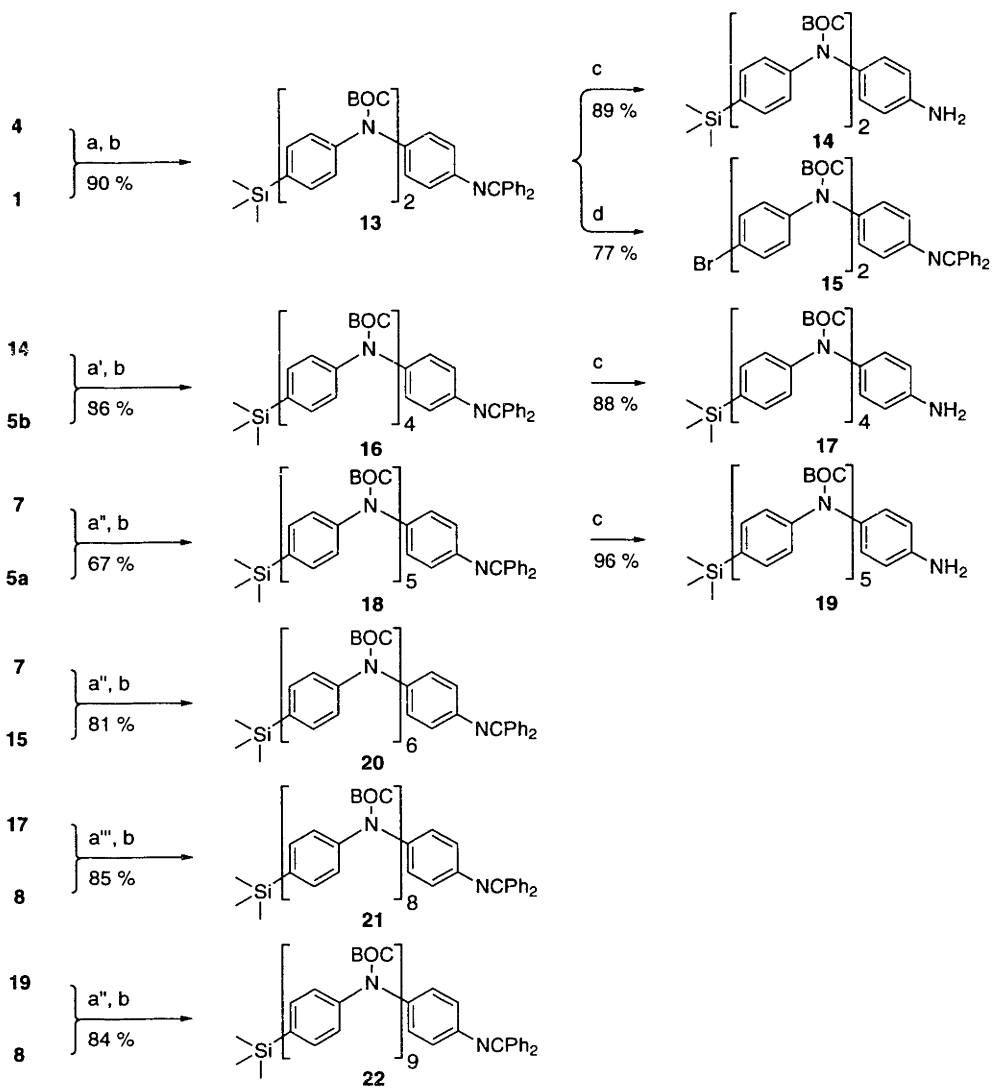
Scheme 4[a]



[a] Key: (a) $Pd_2(dba)_3$ (0.25 mol %), *S*-BINAP (0.75 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (a') $Pd_2(dba)_3$ (0.25 mol %), DPEphos (0.75 mol %), NaO*t*Bu (1.4 eq), $PhCH_3$, 80 °C; (b) $(n\text{-}C_4H_9)_4N^+ Br_3^-$ (1.1 eq), CH_2Cl_2, rt, 30 min; (c) $(BOC)_2O$ (1.1 eq), 4-DMAP (0.1 eq), THF, reflux; (c') $(BOC)_2O$ (1.3 eq), 4-DMAP (0.2 eq), THF, 65 °C.

Dimer chloride **5b** is available, still more directly, by the coupling of **1** with 4-chloroaniline, followed by BOC-protection. The palladium/DPEphos catalyst system is inert to aryl chlorides under the reaction conditions employed, and the reaction is quite clean. Palladium-catalyzed amination of **5b** is accomplished using 2-(di-*tert*-butylphosphino)biphenyl (Section 2.4) as the supporting ligand.

Scheme 5.[a]

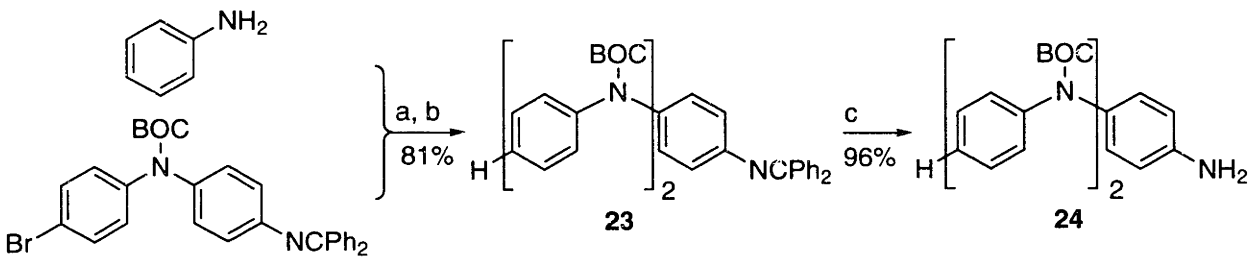


[a] Key: (a) $Pd_2(dba)_3$ (0.50 mol %), DP[illegible]s (1.2 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (a') $Pd_2(dba)_3$ (0.25 mol %), (*o*-biphenyl)P(*t*-E[illegible].0 mol %), NaO*t*Bu (1.4 eq), $PhCH_3$, 80 °C; (a") $Pd_2(dba)_3$ (2.0 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (a"') $Pd_2(dba)_3$ (0.50 mol %), (*o*-biphenyl)P(*t*-Bu)$_2$ (2.0 mol %), NaO*t*Bu (1.4 eq), $PhCH_3$, 80 °C; (b) $(BOC)_2O$ (1.2–1.3 eq), 4-DMAP (0.2–0.5 eq), THF, 60 °C–reflux; (c) $NH_4^+ HCO_2^-$ (12–15 eq), 10 % Pd/C (0.1 eq Pd), THF/CH_3OH, 60–65 °C; (d) NaOAc (1 eq), Br_2 (2 eq), THF, –78 to 0 °C.

The coupling of chain fragments of unequal lengths has been used to prepare protected oligomers with odd or even numbers of aniline units, as long as the decamer (**22**). Most of these products were not elaborated further; they are included to illustrate the generality of the synthetic method. The synthesis of these compounds is outlined above, in Scheme 5.

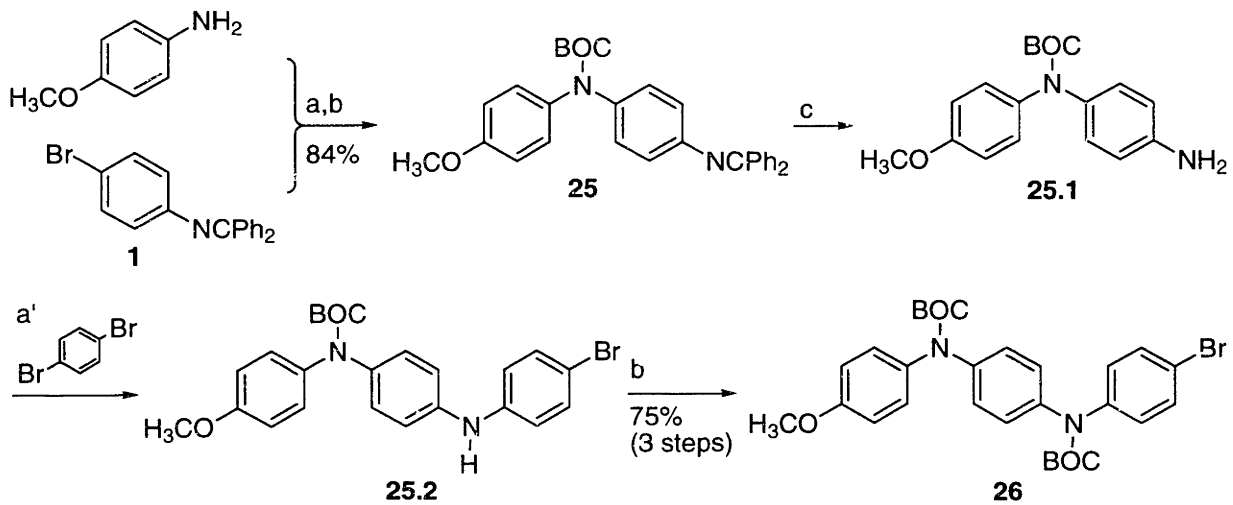
Other nonsymmetric chain fragments, used in the synthesis of symmetrical oligomer derivatives, are readily prepared using this synthetic methodology; the synthesis of a trimer derivative (**24**) is shown in Scheme 6.

Scheme 6[a]



[a] Key: (a) $Pd_2(dba)_3$ (1 mol %), *S*-BINAP (2.5 mol %), NaO*t*Bu (1.4 eq), toluene, 80 °C; (b) $(BOC)_2O$ (1.5 eq), 4-DMAP (0.2 eq), THF, 60 °C; (c) 5 % Pd/C (0.1 eq Pd), NH_4^+ HCO_2^- (15 eq), THF/CH_3OH, 60 °C.

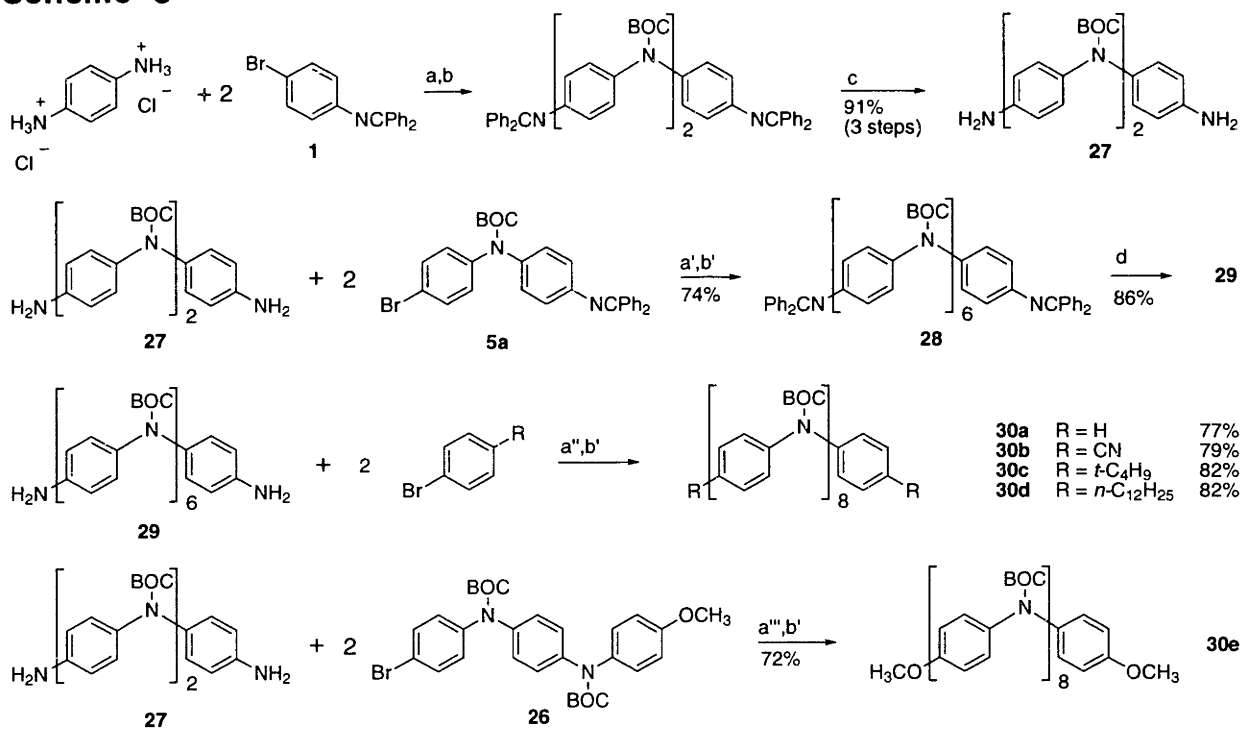
Scheme 7[a]



[a] Key: (a) $Pd_2(dba)_3$ (0.5 mol %), *S*-BINAP (1.5 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (a') $Pd_2(dba)_3$ (1 mol %), *S*-BINAP (3 mol %), NaO*t*Bu (1.4 eq), THF, reflux; (b) $(BOC)_2O$ (1.5 eq), 4-DMAP (0.1 eq), THF, reflux; (c) 20% $Pd(OH)_2/C$ (0.1 eq Pd), NH_4^+ HCO_2^- (20 eq), EtOH, 60 °C. Sequence carried out by Dr. Robert Singer.

The synthesis of aryl bromide **26** (Scheme 7) is noteworthy for the selective monoamination of 1,4-dibromobenzene; the highly electron-rich coupling product **25.2** reacts so slowly with the palladium catalyst that, under these conditions, the amination stops cleanly at this stage. Protection of the secondary amine as its BOC derivative results in an aryl bromide substrate (**26**) which is activated toward oxidative addition.

Scheme 8[a]



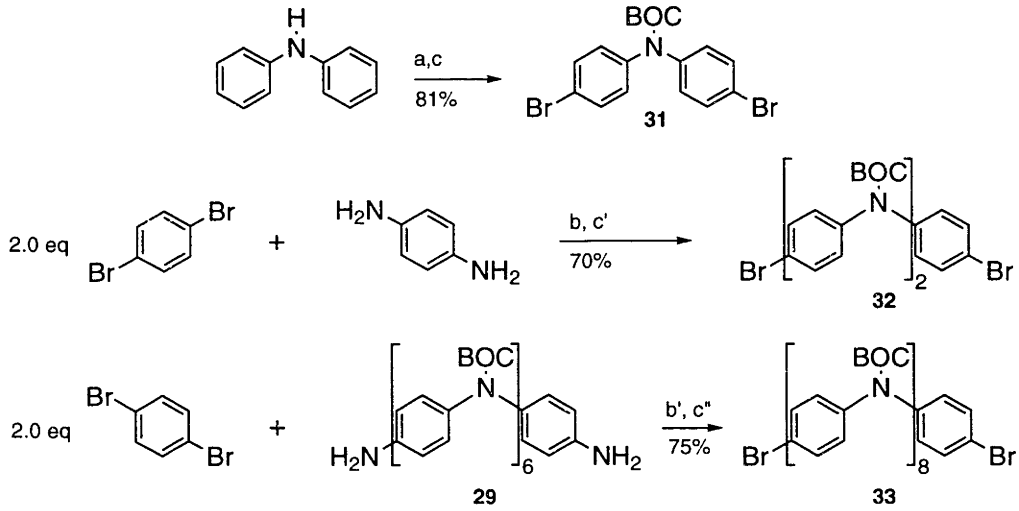
[a] Key: (a) $Pd(OAc)_2$ (1 mol %), *S*-BINAP (1.5 mol %), NaO*t*Bu (4.5 eq), toluene, 80 °C; (a') $Pd_2(dba)_3$ (3 mol %), *S*-BINAP (7 mol %), NaO*t*Bu (2.8 eq), toluene/Et_3N, 90 °C; (a'') $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (6 mol %), NaO*t*Bu (2.5 eq), THF, reflux; (a''') $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (5 mol %), NaO*t*Bu (2.5 eq), toluene, 80 °C; (b) $(BOC)_2O$ (3 eq), 4-DMAP (0.1 eq), THF/toluene, reflux; (b') $(BOC)_2O$ (3 eq), 4-DMAP (0.1 eq), THF, reflux; (c) $H_2NOH{\cdot}HCl$ (2.5 eq), pyridine (4 eq), $CHCl_3$/THF/EtOH, rt; (d) 20% $Pd(OH)_2/C$ (0.4 eq Pd), NH_4^+ HCO_2^- (20 eq), THF/EtOH, 70 °C. Sequence carried out by Dr. Robert Singer.

The synthesis of substituted octamers **30** was carried out by the bidirectional approach illustrated in Scheme 8. The symmetric N_4-diamine **27** is obtained by the reaction of 1,4-phenylenediamine with two equivalents of monomer **1**, followed by

BOC-protection and imine cleavage.[65] Iteration of the sequence using aryl bromide **5a** allows more rapid growth, giving the N_8-diamine **29**. This diamine reacts with simple aryl bromides to give a variety of α,ω-disubstituted phenyl-capped octamers (**30a–d**) from a common precursor. Alternatively, the N_4-diamine **27** may be converted directly to a capped octamer by reaction with the appropriate N_2-aryl bromide, as in the synthesis of the bis(methoxy)-substituted octamer (**30e**).

Symmetric oligomers also result from the reaction of arylamines with symmetric dibromides, prepared as shown in Scheme 9; odd- or even-numbered oligomers may be obtained, depending on the core piece used. Regioselective *para*-bromination of diphenylamine[64] affords 4,4'-dibromodiphenylamine, which is activated toward aryl amination by conversion to its BOC derivative (**31**).

Scheme 9[a]

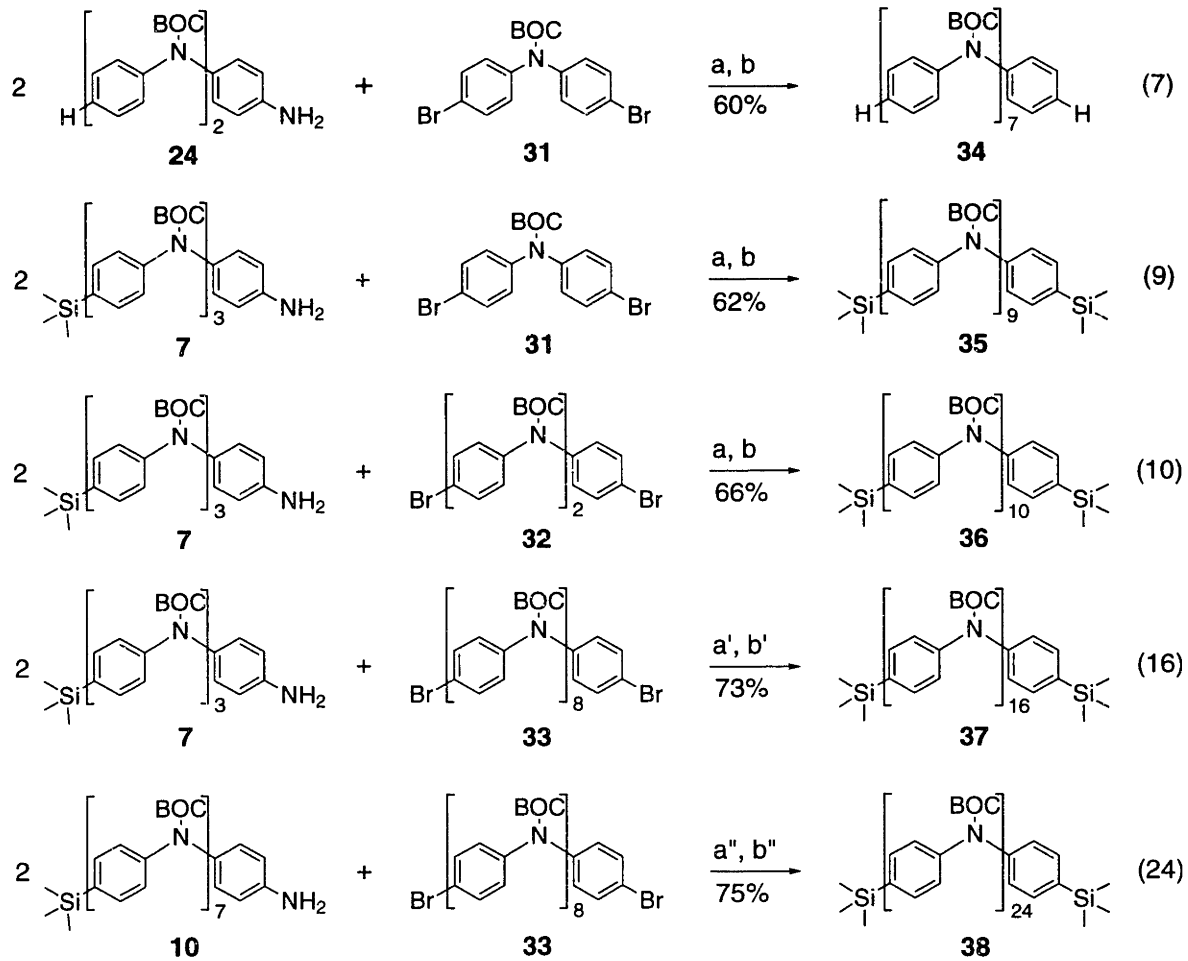


[a] Key: $(n\text{-}C_4H_9)_4N^+Br_3^-$ (2 eq), CH_2Cl_2, rt, 5 min; (b) $Pd_2(dba)_3$ (1.2 mol %), *S*-BINAP (3.7 mol %), NaO*t*Bu (2.6 eq), THF, reflux; (b') $Pd(OAc)_2$ (4 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (2.6 eq), toluene/Et_3N, 90 °C; (c) $(BOC)_2O$ (1.1 eq), 4-DMAP (0.2 eq), THF, reflux; (c') $(BOC)_2O$ (3.5 eq), 4-DMAP (0.2 eq), THF, reflux; (c") $(BOC)_2O$ (3.5 eq), 4-DMAP (0.1 eq), THF/toluene/Et_3N, 67 °C. Compound **33** was synthesized by Dr. Robert Singer.

Even-numbered dibromides (**32**, **33**) are prepared by the coupling of diamines with two equivalents of 1,4-dibromobenzene (see the preparation of **26**, above), followed by BOC-protection. Scheme 10 illustrates the synthesis of phenyl-capped heptamer

34, and a series of α,ω-bis-(trimethylsilyl) phenyl-capped oligomers: nonamer **35**, decamer **36**, 16-mer **37**, and 24-mer **38**.

Scheme 10[a]



[a] Key: (a) $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (2.9 eq), toluene, 80 °C; (a') $Pd(OAc)_2$ (4 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (2.8 eq), toluene/Et_3N, 90 °C; (a") $Pd(OAc)_2$ (6 mol %), *S*-BINAP (7.2 mol %), NaO*t*Bu (3 eq), toluene/Et_3N, 90 °C; (b) $(BOC)_2O$ (2.5 eq), 4-DMAP (0.5 eq), THF, 60 °C; (b') $(BOC)_2O$ (3.5 eq), 4-DMAP (0.1 eq), THF/toluene/Et_3N, 67°C; (b") $(BOC)_2O$ (4 eq), 4-DMAP (0.2 eq), THF/toluene/Et_3N, 67°C. Compounds **37** and **38** were prepared by Dr. Robert Singer.

The protected oligomers exhibit good solubility in numerous common solvents; they are moderately soluble in tetrahydrofuran and hot alcohols, highly soluble in toluene, and extremely soluble in dichloromethane and chloroform. Characterization of the oligomers by NMR spectroscopy is thus quite facile. The proton NMR spectra may be used not only to ascertain the purity of the materials, but to confirm their chain

lengths. This may be accomplished in **34–38** by integration of the trimethylsilyl resonances relative to the BOC resonances; moreover, the endgroup protons meta to the nitrogen display a distinctive doublet, downfield from the other aryl resonances. The spectra of decamer **36** and of 24-mer **38** are shown in Figure 7.

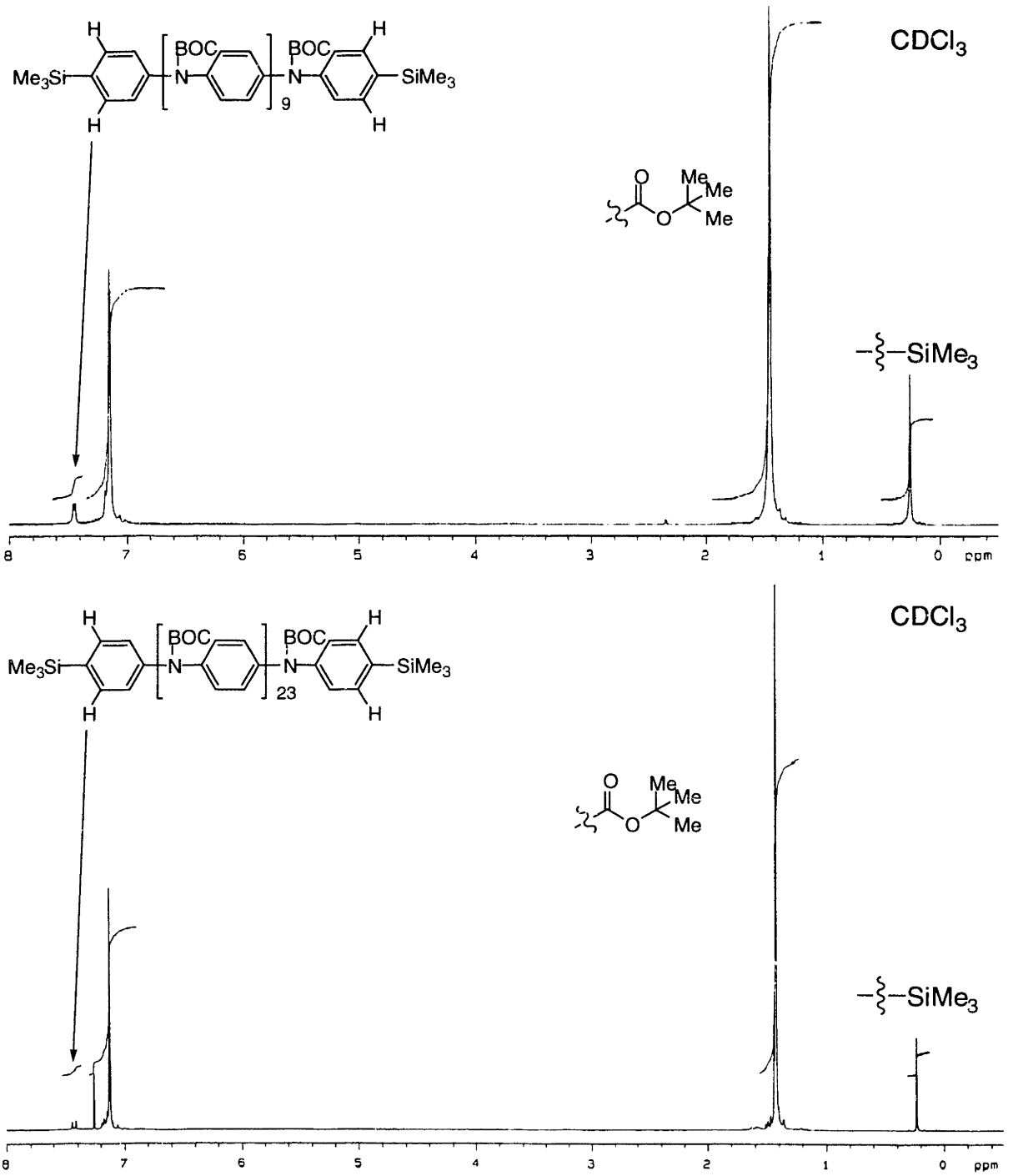


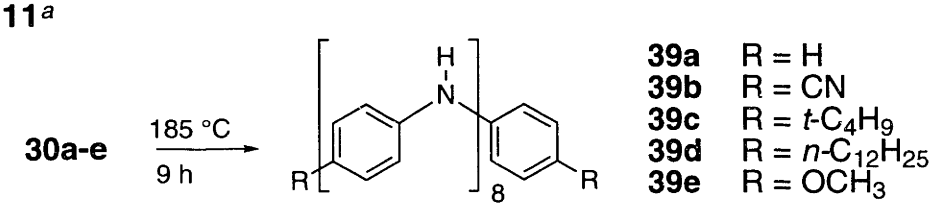
Figure 7. ^{1}H NMR spectra of protected decamer **36** and 24-mer **38**.

Removal of the *tert*-butyl carbamate groups decreases the solubility of the materials considerably; however, the deprotected oligoanilines are sufficiently soluble in polar aprotic solvents such as *N,N*-dimethylformamide and *N*-methylpyrrolidinone to permit their characterization by UV–vis spectroscopy, and the preparation of films for electrochemical studies. Deprotected oligoanilines as long as the decamer could be characterized by ^{1}H NMR. To examine the solubilizing influence of alkyl groups at the termini of oligoanilines, we prepared the bis(*tert*-butyl)- and bis(*n*-dodecyl)-substituted octaanilines **39c** and **39d**, but these exhibited the same solubility as the other oligoanilines. In any case, the facile cleavage of the BOC groups allows them to function as removable solubilizing groups.

1.2—Deprotection of Oligoaniline Precursors

Thermolysis of the protected oligomers under an inert atmosphere results in clean and quantitative removal of the BOC group,[66] affording the oligoaniline in its lowest oxidation state as shown in Scheme 11. Infrared spectroscopy of a thin film of **30a** on a NaCl plate, heated under argon at 185 °C, showed that the complete disappearance of the carbonyl absorption required a reaction time of approximately 7 hours. Likewise, ^{1}H NMR spectroscopy of **30a**, heated at 185 °C in DMSO-d_6 solution, indicated a reaction time of nearly 7 hours for the complete loss of the *tert*-butyl resonance. The preparation of octaanilines **39a-e** was accomplished by heating the powders in Schlenk tubes under argon for 9 hours.

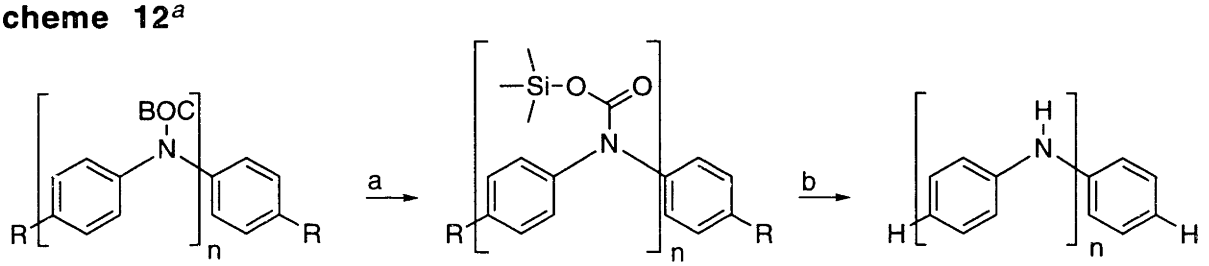
Scheme 11[a]



[a] : Carried out by Dr. Robert Singer.

Alternatively, the BOC group may be cleaved using iodotrimethylsilane. The protected oligomers react rapidly with iodotrimethylsilane to form the corresponding trimethylsilyl carbamates.[67] The trimethylsilyl carbamate group confers the same solubility as the *tert*-butyl carbamate, but is extremely labile in the presence of moisture or protic solvents. For preparative purposes, a solution of the trimethylsilyl carbamate is prepared in dichloromethane; subsequent addition of excess methanol causes the deprotected oligoaniline to precipitate immediately. Phenyl-capped heptaaniline (**40**), nonaaniline (**41**), decaaniline (**42**), 16-mer (**43**), and 24-mer (**44**) were prepared by this method, as shown in Scheme 12. Note that the acid generated upon reaction of the remaining iodotrimethylsilane with methanol effects the protodesilylation of arylsilanes **35–38** in the same operation. Octaanilines prepared by this method were analytically and spectroscopically identical to those prepared by thermolysis. Solutions of the trimethylsilyl carbamates in dichloromethane may be evaporated to form films, which are converted to their redox-active, deprotected forms by immersion in alcohols or in aqueous solutions. All samples used in electrochemical studies were prepared in this manner.

Scheme 12[a]



n = 7, R = H: **34**
n = 9, R = $Si(CH_3)_3$: **35**
n = 10, R = $Si(CH_3)_3$: **36**
n = 16, R = $Si(CH_3)_3$: **37**
n = 24, R = $Si(CH_3)_3$: **38**

n = 7: **40**
n = 9: **41**
n = 10: **42**
n = 16: **43**
n = 24: **44**

[a] Key: (a) $(CH_3)_3SiI$ (1.2n eq), CH_2Cl_2, rt; (b) CH_3OH (excess), Et_3N, CH_2Cl_2, rt.

The proton NMR spectra of the protected decamer **36** and the deprotection product **42** are shown in Figure 8. Because the deprotection product is essentially

insoluble in chloroform, and only very sparingly soluble even in dimethyl sulfoxide, its spectrum was obtained in *N,N*-dimethylformamide-d_7 solution. The complete disappearance of the BOC and trimethylsilyl resonances is apparent, and the N–H resonances are visible as five distinct signals.

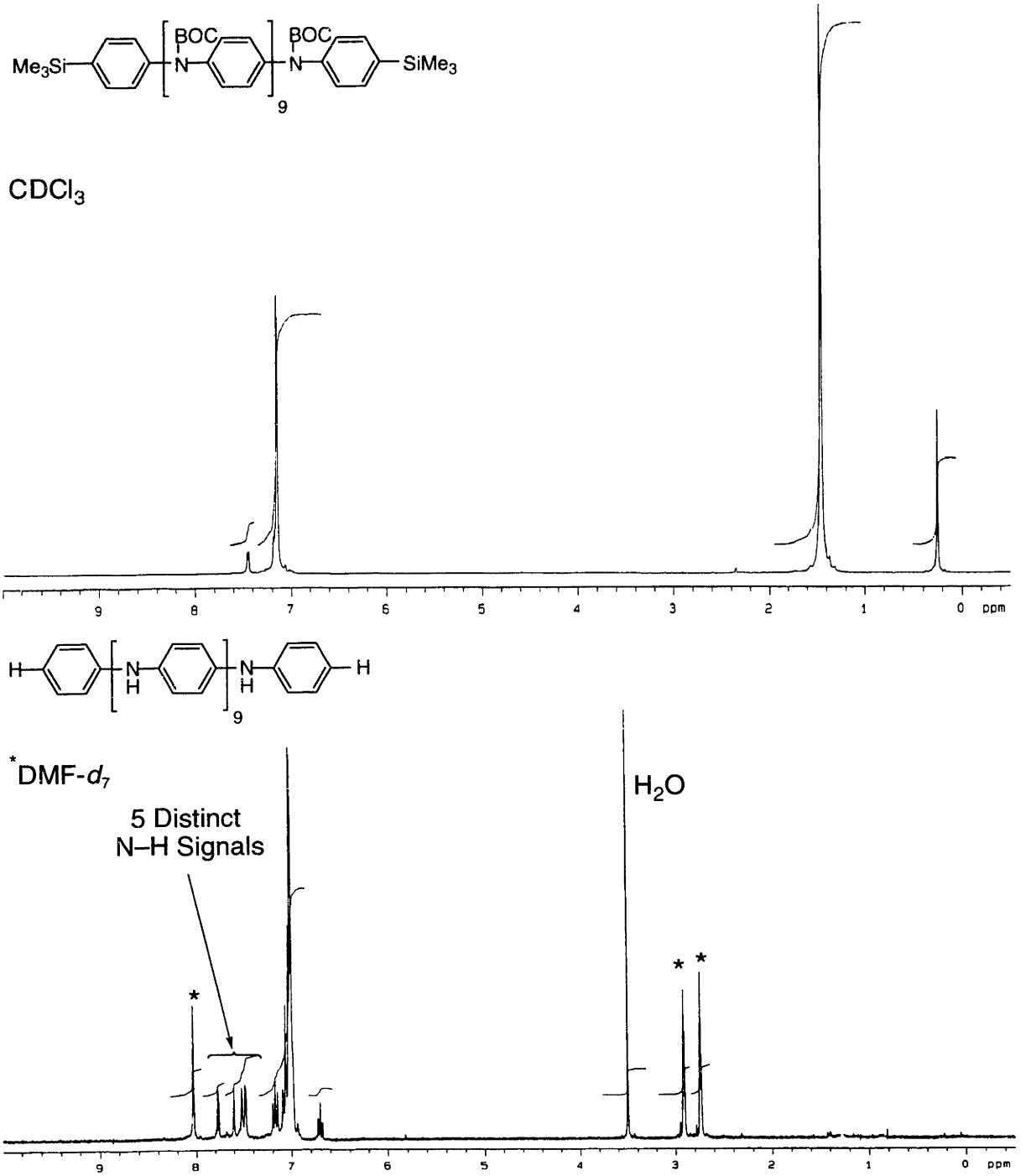


Figure 8. ^{1}H NMR spectra of protected decamer **36** and deprotected decamer **42**.

The efficiency of the deprotection may also be verified by infrared spectroscopy, as shown in Figure 9. The spectrum of a thin film of protected decamer **36** on a NaCl plate is given for comparison (top). A solution of **36** in dichloromethane was treated with iodotrimethylsilane, and the resulting trimethylsilyl carbamate solution was evaporated onto a NaCl plate to form a thin film. The plate was immersed briefly in methanol and dried; the infrared spectrum of the film (bottom) shows the complete disappearance of the carbonyl stretch, and the appearance of the N–H stretch.

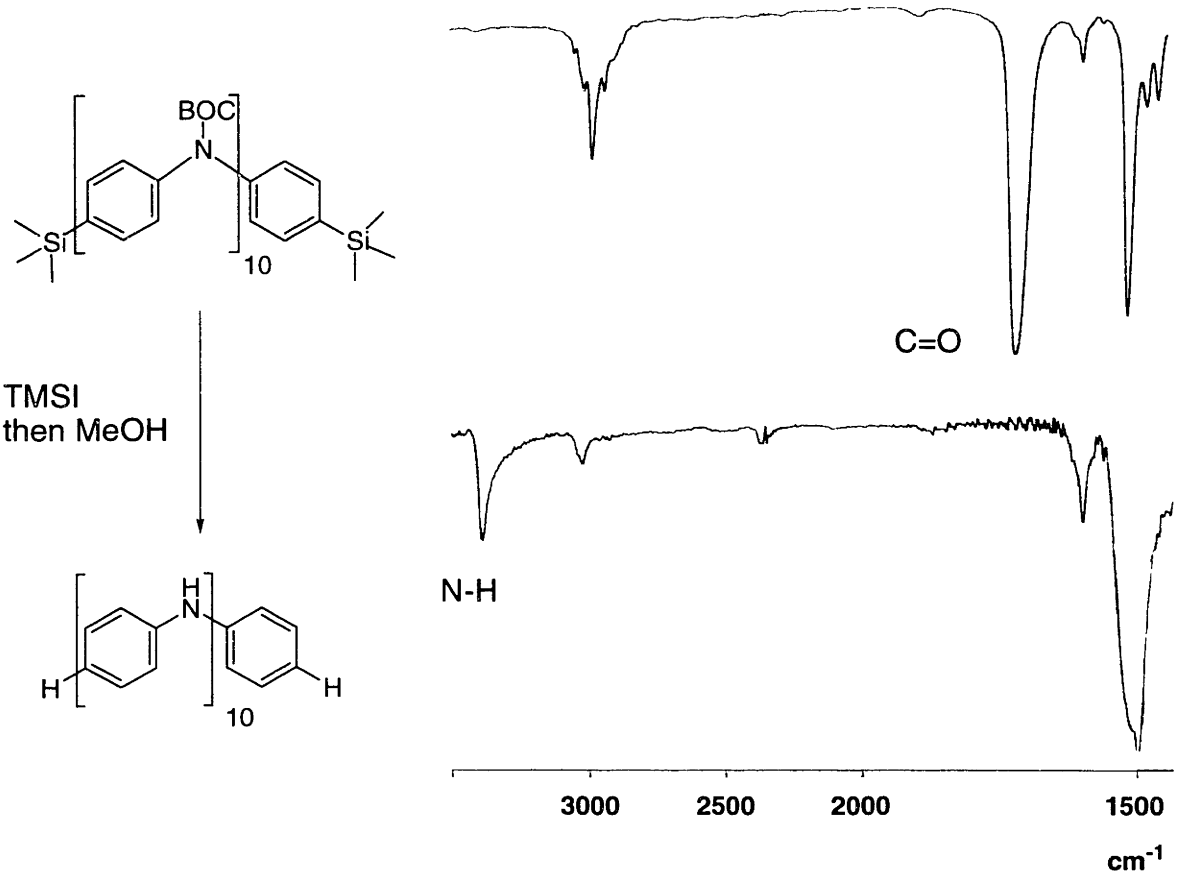


Figure 9. IR spectroscopy of decamer **36**, and of deprotected decamer **42**.

The lowest oxidation state of polyaniline is the insulating leucoemeraldine form, in which all nitrogen atoms are neutral and sp^3-hybridized, and all aromatic rings are in the benzenoid form. Oxidation of half of the phenylenediamine moieties to their quinonediimine forms results in the emeraldine form, which is conductive when the

imine nitrogen atoms are protonated. This form has been described as a repeating semiquinoid cation to explain its paramagnetism and electrical conductivity.[68] Oxidation of all phenylenediamine moieties to their quinoid forms gives rise to the pernigraniline form, with significant (though not necessarily complete) deprotonation under most conditions. Even when generated by oxidation under extremely nonbasic conditions, and thus probably in its fully protonated form, pernigraniline is an insulator.[69] These oxidation states are illustrated in Figure 10.

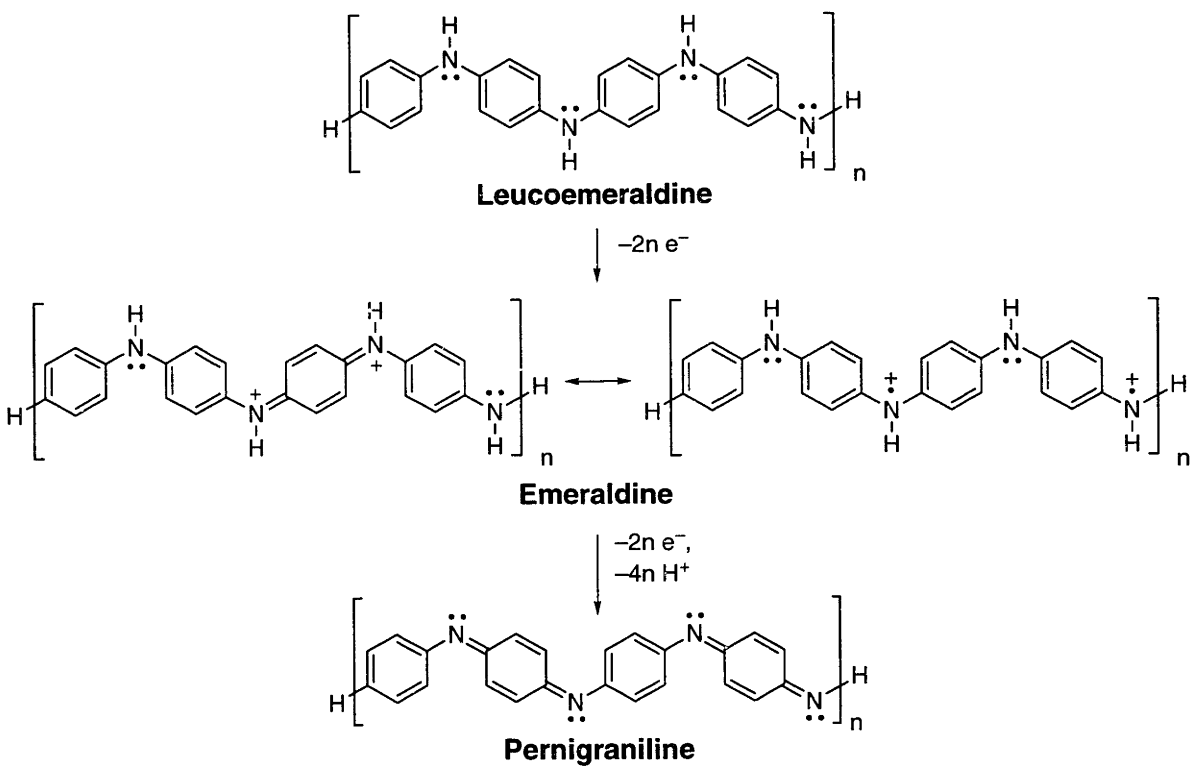


Figure 10. Oxidation states of polyaniline.

Electrochemical studies of polyaniline show two oxidation waves of equal intensity, consistent with the transitions shown in Figure 10. In contrast, the cyclic voltammogram of phenyl-capped octaaniline, published by Wudl,[22] displays a distinct split in the second oxidation wave, suggesting an intermediate "nigraniline" form[6] in the oxidation from the emeraldine to the pernigraniline form.

We wished to investigate effects of susbtitution in octaanilines, and the effects of chain length on oligoaniline redox behavior. We have examined the oligoanilines in varying degrees of oxidation and protonation by UV–vis spectroscopy, and have studied their electrochemical behavior by cyclic voltammetry.

1.3—Electronic Absorption Spectroscopy of Oligoanilines

Under neutral conditions, the UV–vis spectra of the oligoanilines (**39–44**) in a given oxidation state are essentially identical; no significant changes result from substitution or from variations in chain length. The leucoemeraldine forms exhibit a single strong absorption at 334–338 nm; lower-energy transitions are observed for the partially and fully oxidized states. Oxidation of a colorless leucoemeraldine solution in dilute DMF by silver (I) oxide results in an intense blue-purple solution of the emeraldine base, with a sharp peak at 320 nm and a broad band at 620 nm. Silver (II) oxide in DMF converts the leucoemeraldine to a red-pink pernigraniline solution, with a sharp peak at 320 nm and a broad band at 520 nm. The strong blue shift of this band, compared to that of emeraldine, reflects the more difficult charge-transfer transition in the pernigraniline state.

The addition of a drop of sulfuric acid (a large excess) to the UV–vis samples of the emeraldine and pernigraniline forms produces a green color. Protonation of the emeraldine form of phenyl-capped octaaniline (**39a**) causes the higher-energy absorption to broaden and split, with a new absorption visible near 400 nm. A similar peak has been observed in polyaniline, and has been attributed to transitions from the half-filled polaron band to the π^* band.[70] A lower-energy absorption begins at *ca.* 540 nm and increases in intensity up to the spectrometer's limit at 1050 nm. In polyaniline, this absorption is ascribed to transitions within the half-filled band.[71] In the case of the pernigraniline, the lower-energy absorption is broadened, and its maximum is red-shifted from 520 nm to 830 nm. The UV–vis spectra of phenyl-capped octaaniline (**39a**) are shown in Figure 11.

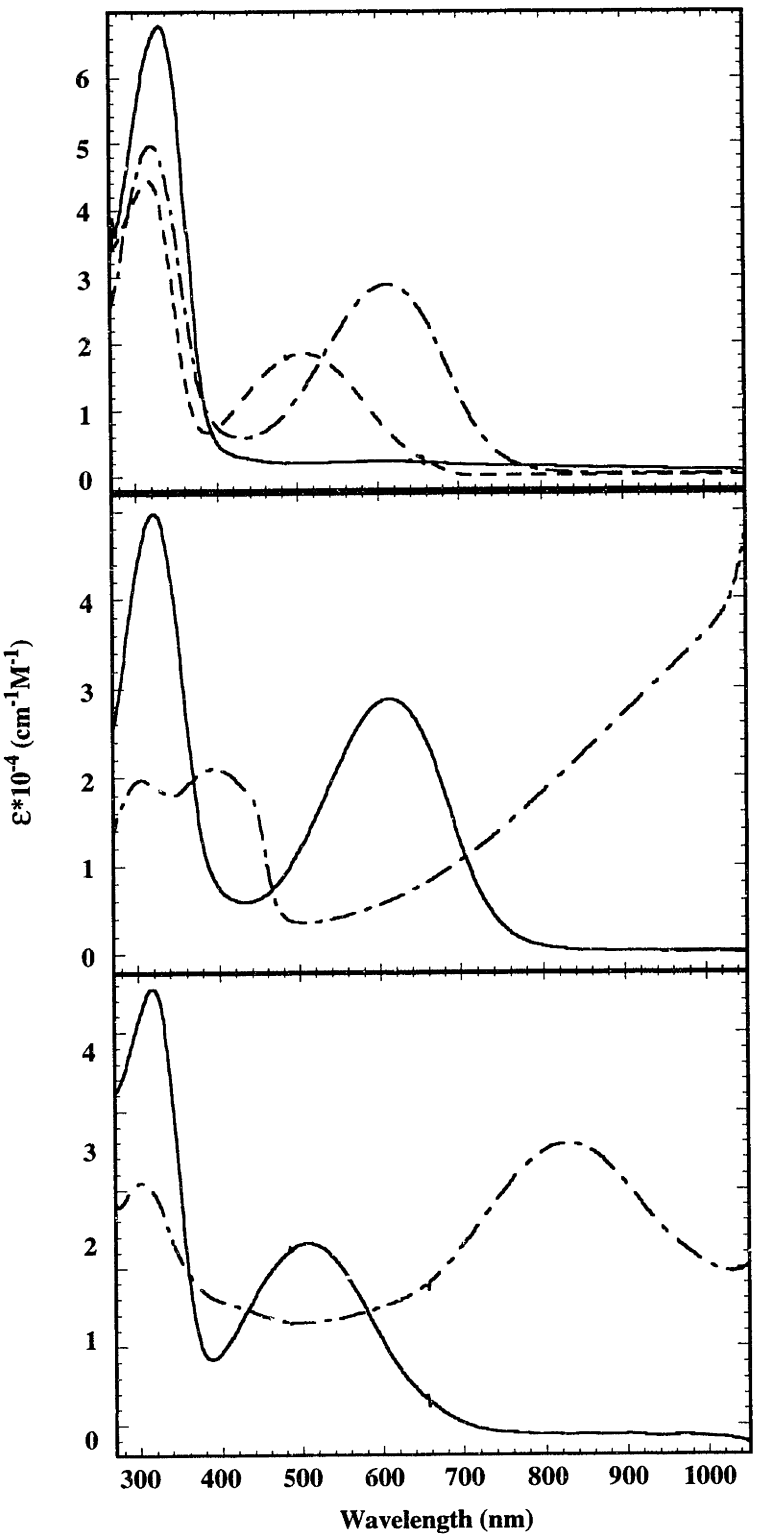


Figure 11. UV–vis spectra of phenyl-capped octaaniline (**39a**) in DMF. (top) Leucoemeraldine, ——— ; emeraldine, — - ; pernigraniline, – – – . Emeraldine (middle) and pernigraniline (bottom): in neutral solution, ——— ; acidified, — - .

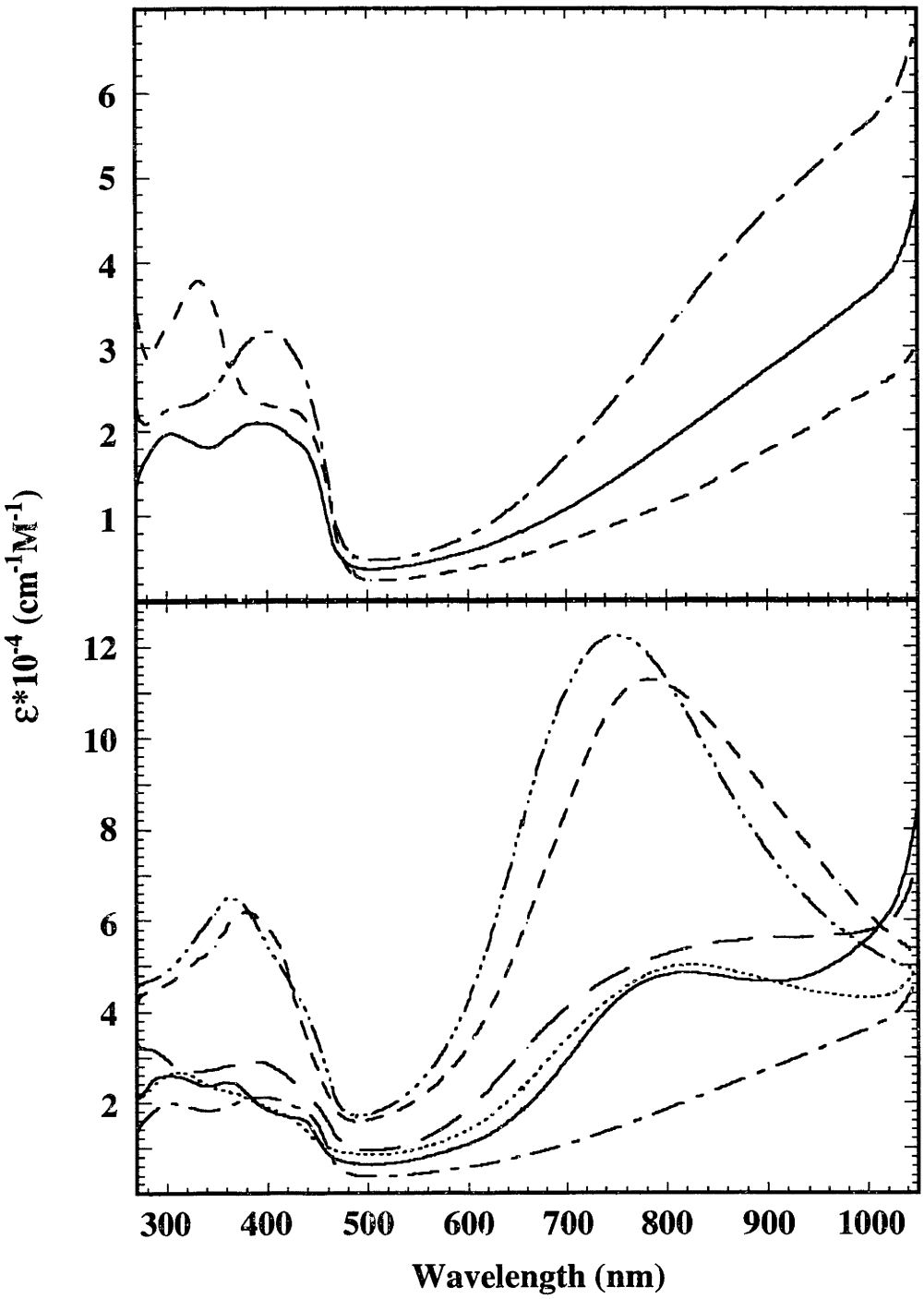


Figure 12. (top) α,ω-Substituent effects upon the protonated emeraldine form of phenyl-capped octaanilines in DMF: H (**39a**), ——— ; CN (**39b**), – – – ; OCH_3 (**39e**), — - . (bottom) Protonated emeraldines of phenyl-capped oligoanilines in DMF: 7-mer (**40**), ——— ; 8-mer (**39a**), — - ; 9-mer (**41**), ····· ; 10-mer (**42**), — — — ; 16-mer (**43**), – – –; 24-mer (**44**), — - - - .

The spectra of the protonated emeraldine forms vary considerably with changes in electron density or in chain length, as shown in Figure 12. The absorbance in the near-IR region of **39** becomes more intense with the increase in electron density from the cyano-substituted to the methoxy-substituted octamer. The twin peaks at 310 and 400 nm, of nearly equal intensity for phenyl-capped octaaniline, show complementary patterns for the cyano- and methoxy-substituted analogues. A comparison of the spectra for different chain lengths shows subtle differences between heptamer, nonamer, and decamer; the distinct curvature in the shape of the near-IR absorption contrasts with the near-linear slope observed for the octamer. In the longer oligomers (16-mer and 24-mer), this absorption shows a much more definite maximum, occurring at somewhat shorter wavelengths. The reason for this is unclear. Some UV–vis spectra of polyaniline display a continuous increase in absorbance from *ca.* 500 nm into the near-IR region;[71] others show a maximum at *ca.* 800 nm, with a steep drop in absorbance at higher wavelengths.[70] The difference may stem from physical differences arising from different sample preparation. In the case of **43** and **44**, the emeraldine salts (like those of polyaniline[22]) exist as colloidal suspensions in DMF (which settle after standing for several hours). Perhaps these longer chains fold onto themselves, shortening their effective conjugation length and causing a blue-shift in the low-bandgap absorption.

1.4—Electrochemical Studies of Oligoanilines

Cyclic voltammetry of the oligoanilines affords valuable insight into the electronic structures of the oxidized forms. We wished to examine, for instance, whether the presence of electron-donating or electron-withdrawing groups at the chain ends would affect the redox behavior of phenyl-capped octaaniline, or whether the electronic effects would be insignificant for the chain as a whole. The salient question with regard to chain length is the behavior of those oligoanilines that do not correspond to the tetraaniline-based model depicted in Figure 10. Phenyl-capped

heptaaniline, nonaaniline, and decaaniline behave quite similarly to the octaaniline upon chemical oxidation, but the nature of the "emeraldine" and "pernigraniline" forms obtained for these chain lengths is not obvious *a priori*. If the oligoaniline framework were able to stabilize radical cations effectively, either by resonance or by π-stacking between chains,[72] several odd-electron states would be accessible for the heptamer and nonamer, and the decamer emeraldine might be the five-electron oxidation product, containing five equivalent semiquinoid moieties.

The electrochemical studies discussed below employed thin films of the oligoanilines on ITO (indium-tin oxide) coated glass electrodes. The films were prepared by evaporation of a dilute solution of the trimethylsilyl carbamate in dichloromethane, followed by immersion in the electrolyte, dilute aqueous sulfuric acid.[73] The first cycle of each film indicated significant loss of material (approximately 20–30%) during the reduction,[74] but the films exhibited good stability after this break-in scan.

In dilute hydrochloric acid, the major peaks diminish in intensity with each scan, while a broad peak grows in at *ca.* 0.55 V in the oxidation wave and 0.40 V in the reduction wave. This degradation had been observed previously for both phenyl-capped octaaniline and bulk polyaniline.[22] In dilute sulfuric acid, however, this degradation occurs more slowly.

Integration of the oxidation peaks of phenyl-capped octaaniline (5.0 nanomoles) in the first scan corresponded reproducibly, within two percent, to the removal of eight electrons per molecule, but the oxidations occurred at markedly higher potentials than in subsequent scans. The reduction peaks in the first scan represent a significantly smaller area than the oxidation peaks, but subsequent scans showed good reversibility. In the discussion of oxidation states below, the total number of electrons removed from each molecule is determined by integration of the oxidation peaks in the first scan; the oxidation states of each compound are

determined by comparison of the relative peak areas in the second (*i.e.*, first stable) scan.

Phenyl-capped octaaniline (**39a**) oxidizes from the leucoemeraldine to the emeraldine form in one four-electron step. In contrast, the oxidation from emeraldine to pernigraniline shows a split, with peaks at 0.79 V and at 0.90 V. This split is highly sensitive to changes in electron density at the chain termini. The methoxy groups of **39e** cause a larger split in the emeraldine-pernigraniline oxidation wave, with peaks at 0.66 V and at 0.87 V, whereas the cyano groups of **39b** cause the split to disappear entirely, with a smooth four-electron oxidation centered at 0.84 V. This disparity is consistent with formation of the nigraniline form, with three quinoid moieties, by a two-electron oxidation of emeraldine. The greater partial positive charge adjacent to the chain ends, compared to the emeraldine state, would be stabilized by resonance with the methoxy group, as shown in Figure 13, and destabilized by conjugation with the cyano group.

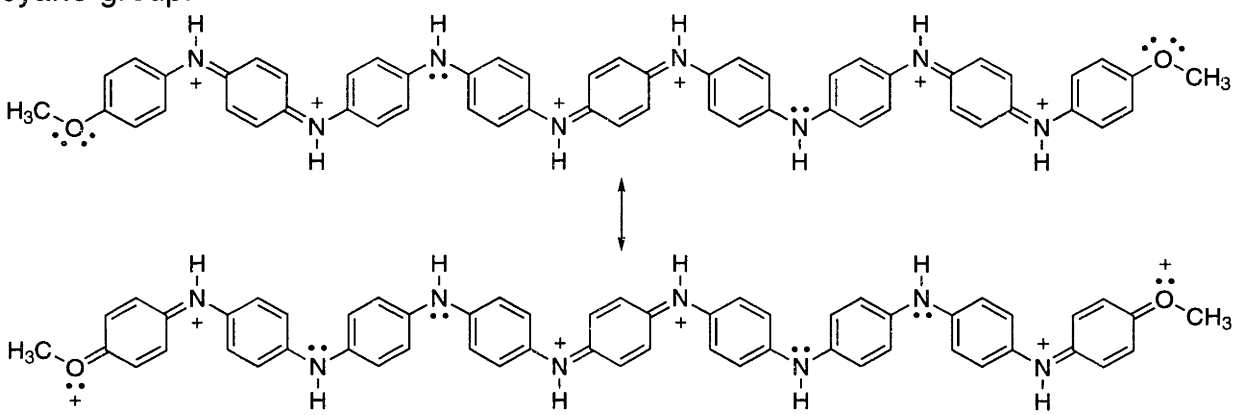


Figure 13. Stabilization of a nigraniline oxidation state by π-donating substituents.

Figure 14 shows the cyclic voltammograms obtained for **39–42**, with proposed oxidation mechanisms for some of the oxidation steps. The intermediates are depicted in their expected major resonance forms. For many of the intermediates the degree of protonation may vary, and several tautomers may exist in addition to those shown.

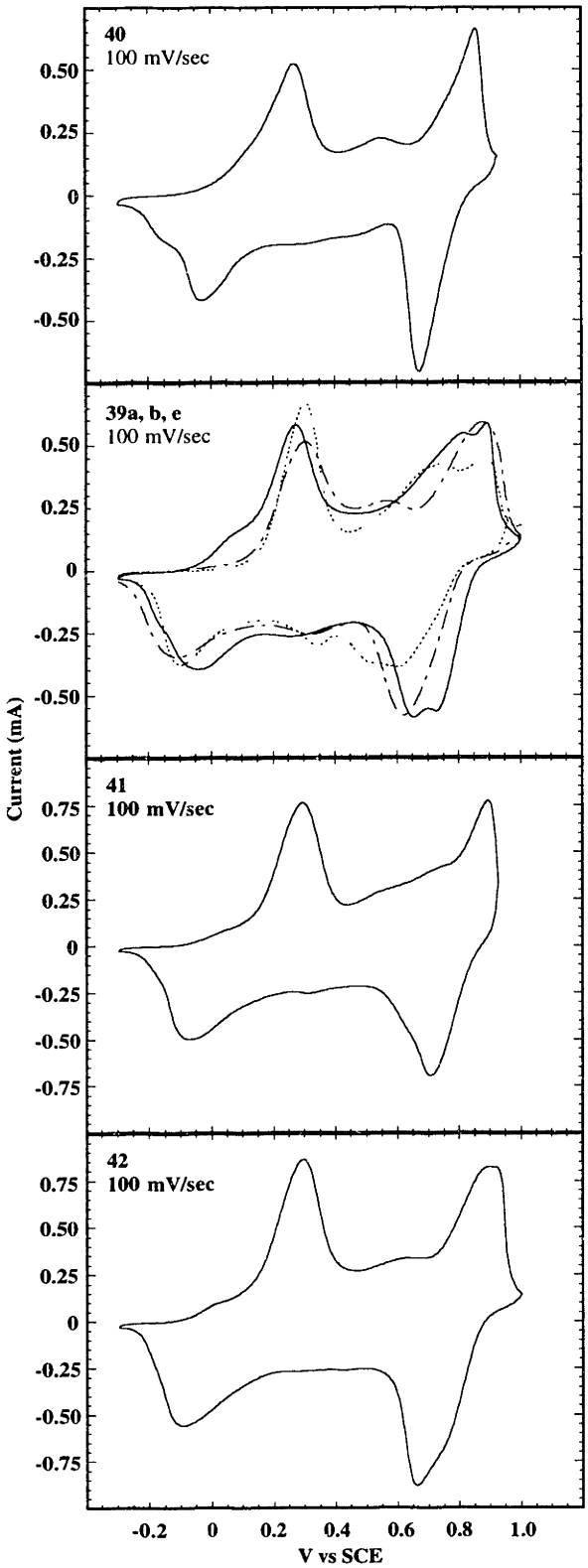
In the cyclic voltammogram of phenyl-capped heptaaniline, two reversible oxidations occur as the potential is increased from –0.3 V to 0.95 V. Integration of the

first scan for a known film quantity showed that only six electrons were removed per molecule of heptaaniline, reproducibly within three percent. Comparison of the areas of the two oxidation peaks showed the first to be approximately twice as large as the second,[75] suggesting that the heptaaniline undergoes a four-electron oxidation followed by a two-electron oxidation.

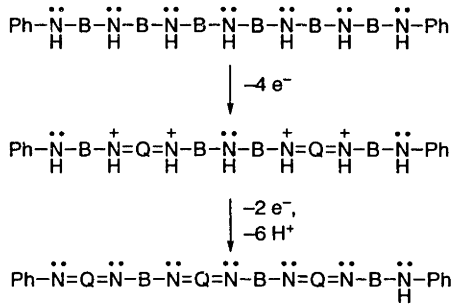
Similarly, oxidation of phenyl-capped nonaaniline within the same potential range results in the removal of only eight electrons per molecule. The cyclic voltammogram displays two oxidation waves, corresponding in area to two four-electron oxidations. The second of these displays a prominent shoulder at the left side. We believe that the extra nitrogen lone pair, relative to phenyl-capped octaaniline, allows oxidation to a mixture of several nonequivalent but energetically similar nigraniline-like states, beginning at relatively low potentials, en route to the formation of the eight-electron oxidation product.

Oxidation of phenyl-capped decaaniline from –0.3 V to 1.0 V results in the removal of ten electrons, consistent with the conversion of all five phenylenediamine moieties to their quinoid forms. The cyclic voltammogram displays two oxidation waves, the first of which encompasses approximately 50 % more area than the second.[75] The oxidation of phenyl-capped decaaniline thus appears to proceed *via* a six-electron oxidation, followed by a four-electron oxidation.

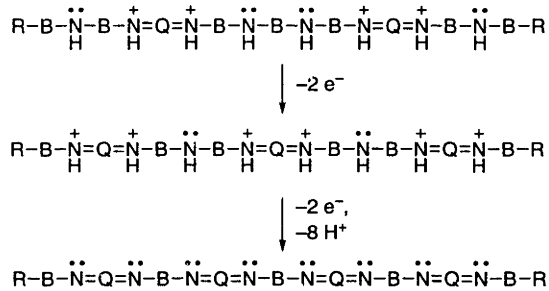
The simplest electrochemical behavior is that of the 16-mer (**43**) and the 24-mer (**44**). Cyclic voltammograms of these oligomers are shown in Figure 15; due to the high molecular weight of **44**, a smaller molar quantity (2.5 nmol) was used to obtain a thin film. In contrast to phenyl-capped octaaniline, these longer tetraaniline multiples display no distinct intermediate in the oxidation of their emeraldine forms. The oxidation from the leucoemeraldine to the pernigraniline state, like that of the bulk polymer, results in two peaks of equal area.



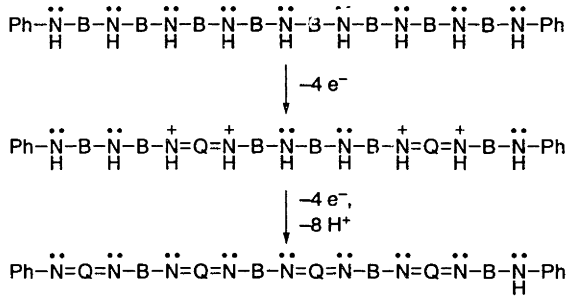
Phenyl-Capped Heptaaniline:



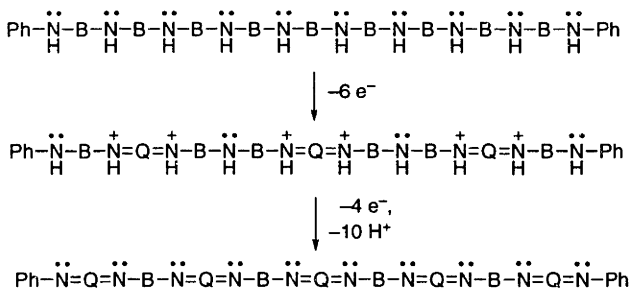
Phenyl-Capped Octaanilines:



Phenyl-Capped Nonaaniline:



Phenyl-Capped Decaaniline:



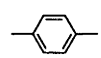
B =  , Q = 

Figure 14. CV of phenyl-capped 7-mer **40**, 8-mers **39** (H, **39a**, ——; CN, **39b**, — - ; OCH_3, **39e**, ·····), 9-mer **41**, and 10-mer **42**. Proposed oxidation mechanisms at right.

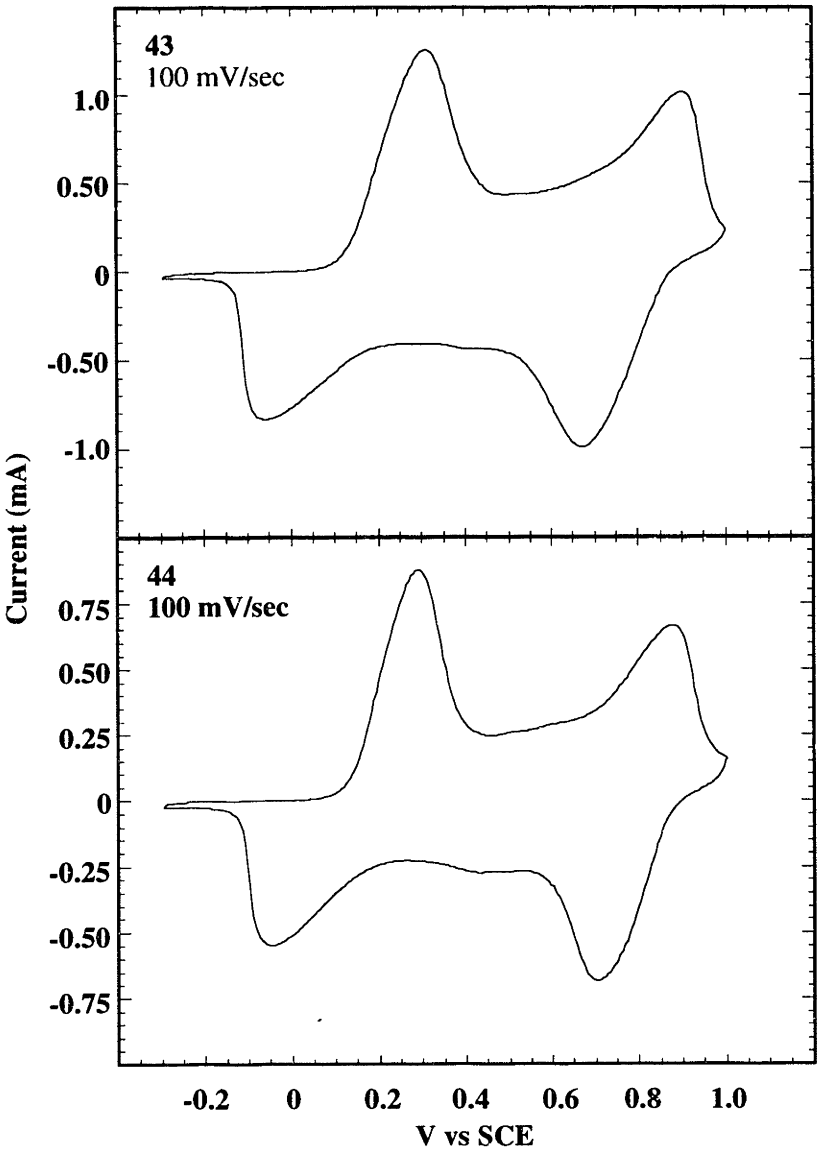


Figure 15. Cyclic voltammetry of phenyl-capped 16-mer (**43**) and phenyl-capped 24-mer (**44**), same conditions as above.

The even-numbered oligomers investigated here are stable at potentials up to and beyond +1.0 V vs. SCE, and polyaniline in nonnucleophilic solvents has been found to be stable at very high potentials.[69] In marked contrast, the odd-numbered oligomers are unstable at potentials above 0.95 V (Figure 16). At higher potentials a third oxidation peak is observed, at 1.07 V for the heptaaniline and 1.08 V for the nonaaniline, with no corresponding reduction peak. This two-electron oxidation

occurs only once for each film: a second scan to 1.25 V fails to reproduce this peak, and the voltammogram resembles that of an even-numbered oligomer.

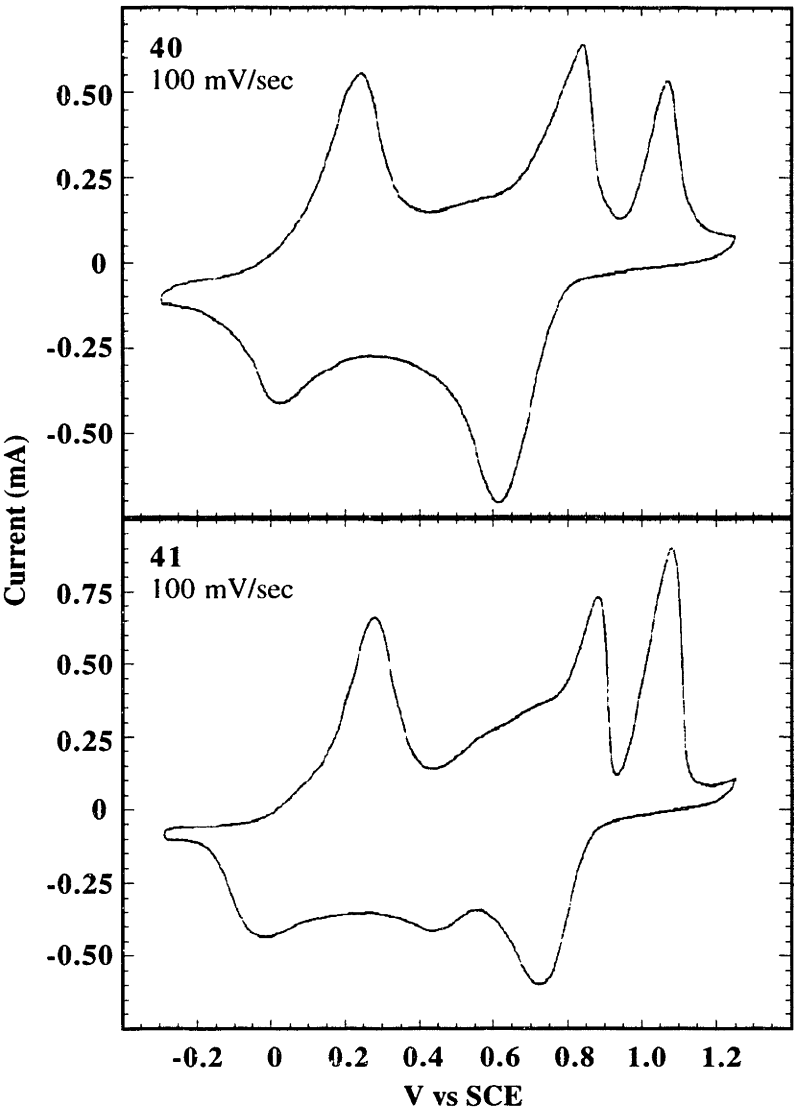


Figure 16. Irreversible oxidation of phenyl-capped heptaaniline (**40**) and nonaaniline (**41**) at high potential, same conditions as above.

The irreversibility of the oxidation, and the fact that no corresponding peak is observed for even-numbered oligomers, is consistent with the formation of a highly unstable odd-electron species, followed by decomposition to a species which undergoes facile one-electron oxidation. Two plausible mechanisms for the further oxidation are illustrated in Figure 17.

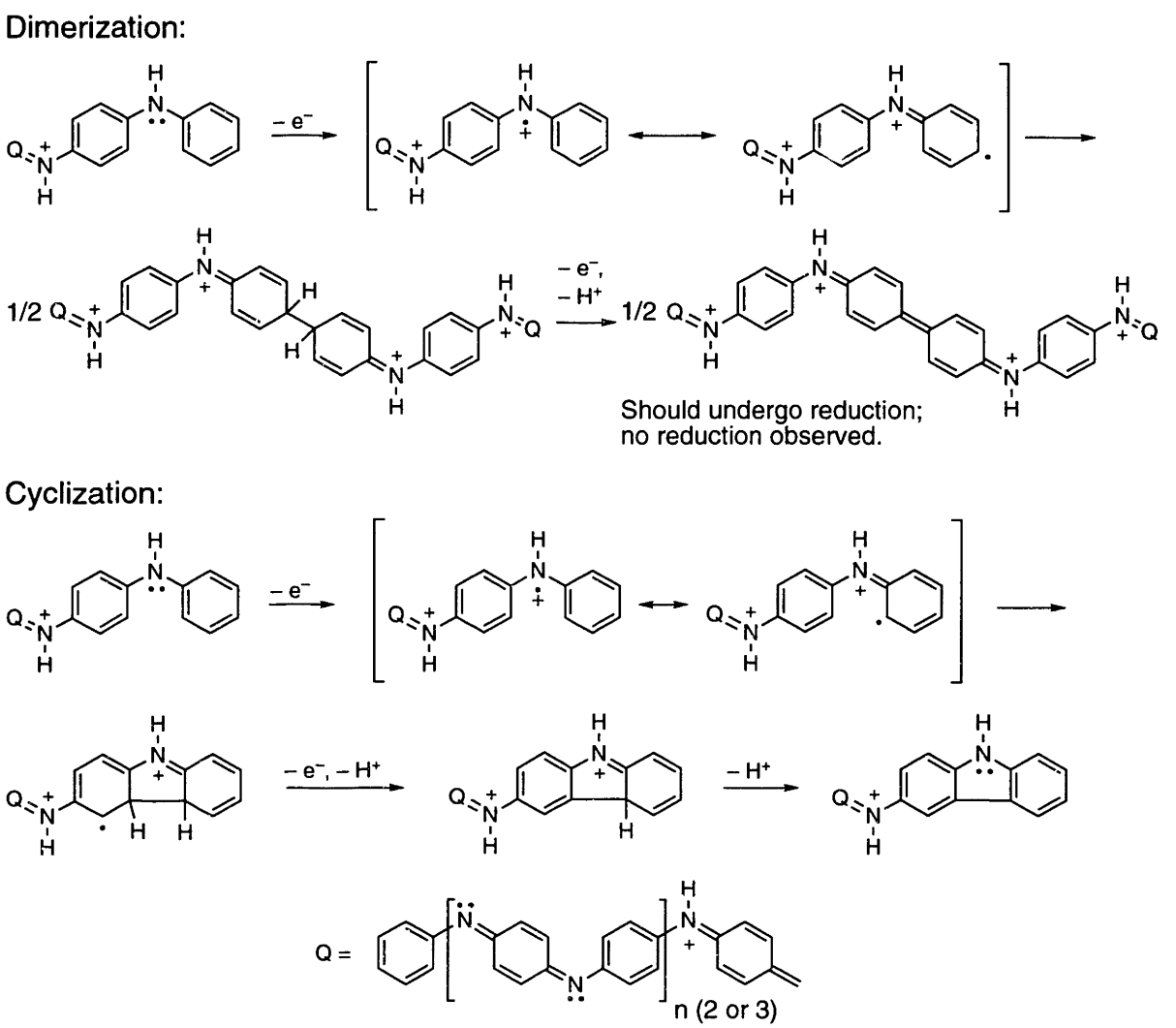


Figure 17. Proposed carbazole formation in odd-numbered oligoanilines at high potential.

Of the two mechanisms shown, the cyclization mechanism is more consistent with the observed behavior. The oxidation pattern does not rule out the tail-to-tail dimerization of the radical cation, followed by dehydrogenation, but the product of this reaction should be reduced easily to a benzidine derivative during the reduction wave. Intramolecular C–C bond formation by the odd-electron cation, followed by deprotonation and one-electron oxidation to the carbazole, represents one possible explanation for the observed behavior. Since the carbazole moiety is quite difficult to oxidize,[76] the product would contain an even number of oxidizable nitrogen atoms, and the formation of additional carbazole units during a subsequent scan would not be

expected. For simplicity, only one product is shown, although the cyclization could also occur in the middle of the chain.

Concluding Remarks

Using palladium catalysis and an orthogonal protective group strategy, we have developed divergent-convergent and convergent methods in the synthesis of well-defined, air-stable oligoaniline precursors, soluble in a variety of common organic solvents. These precursors are easily deprotected to form the leucoemeraldine forms of the corresponding oligoanilines. The synthetic methods are highly versatile, allowing the synthesis of end-functionalized oligoanilines, and the preparation of even or odd chain lengths.

The presence of electron-donating or electron-withdrawing groups at the chain ends results in significant modifications of the UV–vis spectra and electrochemical behavior of phenyl-capped octaaniline. An increase in electron density results in more intense electronic absorption by the emeraldine in the low bandgap region, and stabilizes the electrochemically observed nigraniline state. The electrochemistry of the heptamer, nonamer, and decamer illustrates the importance of electron-pairing in the redox behavior of these compounds. Oxidation of oligoanilines occurs through even-electron transitions when possible; thus, the decamer oxidizes in unequal steps, and the odd-numbered oligomers generate radical cations only transiently and at high potential. Our observations suggest that the ability of polyaniline to stabilize an unpaired electron through resonance or π-stacking is limited.

Chapter Two:
Aryl Amination Methodology Relevant to Materials Synthesis

2.1—Benzophenone Imine as a Surrogate for Ammonia

In developing synthetic methods for the preparation of controlled-length oligoanilines, we found the benzophenone imine moiety to be a very useful protected form of a primary aniline. As described in the previous chapter, this protective group is stable to strong nucleophiles such as sodium *tert*-butoxide and *n*-butyllithium, and to electrophiles such as bromine, yet is easily removed under mild conditions. Oligoanilines containing the benzophenone imine group are soluble in a variety of common solvents, and are easily crystallized. In light of the advantages of this protective group, we wondered whether the commercially available parent compound, benzophenone imine, might serve as a nucleophile in palladium-catalyzed or related cross-coupling reactions.

At that time, no method existed for the palladium-catalyzed conversion of aryl halides to primary anilines.[77] The palladium-catalyzed arylation of ammonia itself has not been reported to date. The transformation may at first glance seem a nonproductive one, since aryl halides are often prepared from the corresponding anilines via the Sandmeyer route;[78] the primary anilines are generally prepared via nitration followed by reduction.[34a] However, for certain substrates, the desired regioselectivity may not be achieved by this sequence, or functional groups already present may be incompatible with electrophilic or reducing conditions. As a result, a number of methods have been explored for the conversion of aryl halides to primary anilines, as shown in Figure 18.

A copper-catalyzed variation of the Gabriel phthalimide synthesis, allowing the transformation of aryl halides, has been demonstrated;[79] however, the scope of the method is limited. Only aryl bromides and aryl iodides undergo the reaction, and low yields are obtained when electron-donating substituents are present. The reaction is reported to be sensitive to steric factors, and polycyclic aromatic halides with the halogen in the 1-position are not observed to react. In addition, the conditions for

hydrazinolysis of the phthalimide product are incompatible with functional groups such as ketones or esters. Another method for the conversion of aryl halides to primary anilines is the reaction of Grignard or aryllithium reagents with various azide reagents, followed by hydrolysis of the triazene intermediate.[80] These methods are useful in a number of cases, and allow the amination of arenes via directed lithiation of suitable substrates; however, their functional group compatibility is necessarily limited.

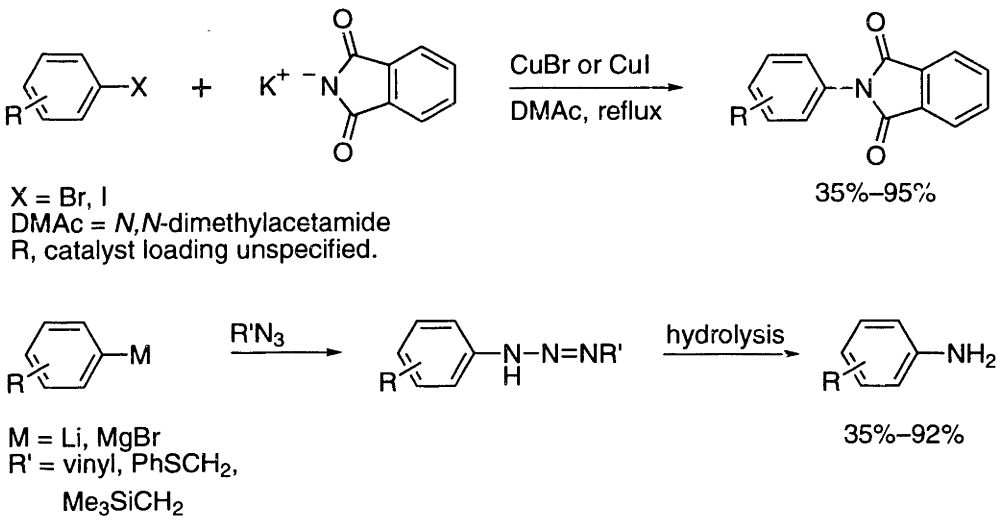
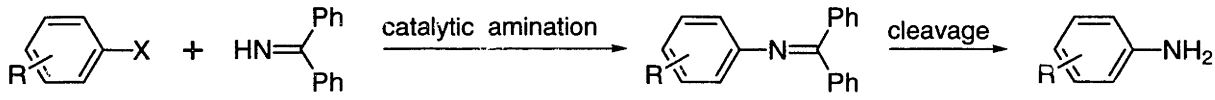
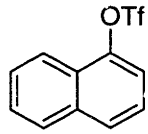
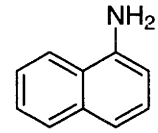
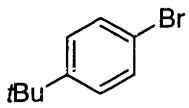
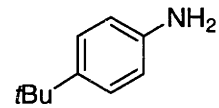
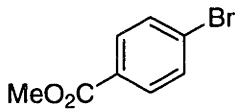
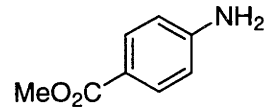
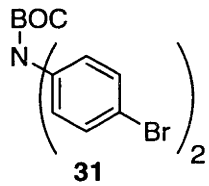
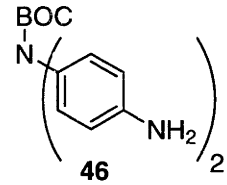


Figure 18. Previous methods for conversion of aryl halides to primary anilines.[79,80]

We found that the palladium- and nickel-catalyzed aminations of aryl bromides,[47a; 50a, e] chlorides,[81] iodides[50h] and triflates[50d] proceed efficiently when benzophenone imine is used as the coupling partner. Benzophenone imine is an excellent coupling partner for several reasons, including the sp^2-hybridization of the nitrogen atom,[82] and the absence of hydrogen atoms vicinal to the nitrogen.[83] In many cases it may be advantageous to retain the imine moiety; Table 1 shows four examples in which the *N*-arylated imines were isolated prior to deprotection. In all of these cases, the imine products were highly crystalline, and were easily isolated by crystallization from methanol. Subsequent cleavage of the imines, affording the primary anilines, was effected by acidic hydrolysis, hydrogenolysis, or transamination with hydroxylamine. Note that Entry 4, an odd-numbered diamine potentially useful in oligoaniline synthesis, was not readily available by other methods.

Table 1: Palladium-catalyzed amination of aryl bromides and triflates.

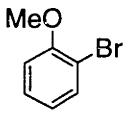
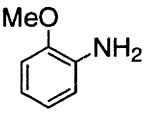
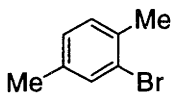
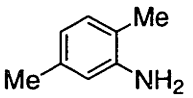
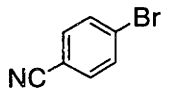
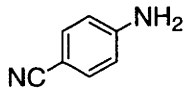
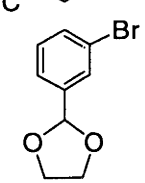
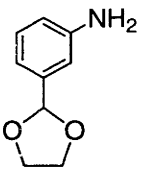
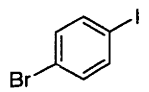
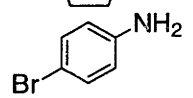
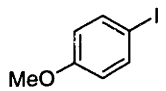
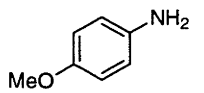
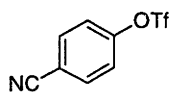
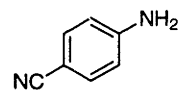
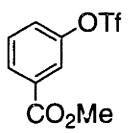
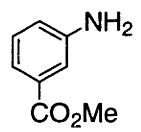
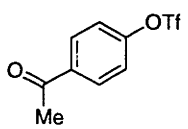
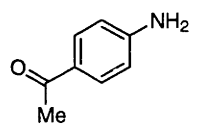
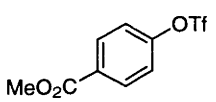
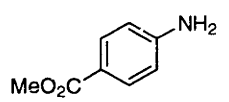
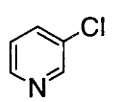
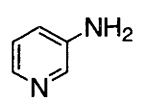


Entry	Substrate	Yield **x** (%)[e]	Cleavage Conditions	Product	Yield (%)[e,f]
1		85%[a]	cat. HCl wet THF rt		98%
2		90%[b]	$NH_4^+ HCO_2^-$ cat Pd/C MeOH/60° C		84%
3		75%[c]	$NH_2OH•HCl$ NaOAc MeOH/rt		88%
4	 **31**	91%[d]	$NH_4^+ HCO_2^-$ cat Pd/C MeOH/60° C	 **46**	95%

(a) 1 mol % $Pd(OAc)_2$, 1.5 mol % BINAP, 1.4 eq Cs_2CO_3, THF, 65 °C, 16 h. Carried out by Dr. Robert Singer. (b) 0.25 mol% $Pd_2(dba)_3$, 0.75 mol% BINAP, 1.4 eq NaO*t*Bu, toluene, 80 °C, 13 h. Carried out by Dr. John Wolfe. (c) 2 mol% $Pd(OAc)_2$, 3 mol% BINAP, 1.4 eq Cs_2CO_3, toluene, 100 °C, 5 h. Carried out by Dr. John Wolfe. (d) 0.25 mol% $Pd_2(dba)_3$, 0.75 mol% BINAP, 1.4 eq NaO*t*Bu, toluene, 80 °C, 6 h. (e) Isolated yields reported are an average of two runs. (f) Yields based on imine.

Alternatively, the aryl halides may be converted to the corresponding anilines without isolation of the intermediate imine; the results for this sequence are given in Table 2. Reactions involving aryl triflates were carried out using cesium carbonate as base, instead of sodium *tert*-butoxide, to avoid hydrolysis of the triflate;[81e] the use of this weaker base also permits the presence of a methyl ester (Entries 8 and 10) or an enolizable ketone (Entry 9) in the substrate.[81f] The variety of conditions available for the imine cleavage allows the deprotection to be carried out without affecting these functional groups or a benzylic acetal (Entry 4).

Table 2: Palladium-catalyzed imine arylation and subsequent cleavage.

Entry	Substrate	Product	Time	Cleavage[h]	Yield (%)[i]
1			5 h[d]	B	87
2[a]			19 h[d]	B	77
3			1.5 h[d]	A	97
4			1.5 h[d]	A	89
5[a]			48 h[e]	C	91
6[b]			14 h[e]	A	88
7[c]			4.5 h[f]	A	84
8[c]			20 h[f]	A	80
9[c]			4 h[f]	C	83
10[c]			5 h[f]	A	89
11[a]			16 h[g]	A	81

(a) Carried out by Dr. John Wolfe. (b) Carried out by Dr. Robert Singer. (c) Carried out by Dr. Jens Åhman. (d) 0.25 mol % $Pd_2(dba)_3$ (except entry 1, 0.50 mol % $Pd_2(dba)_3$), 0.75 mol % BINAP, 1.4 eq NaO*t*Bu, toluene, 80 °C. (e) 1.0 mol % $Pd_2(dba)_3$, 3.0 mol% BINAP, 1.4 eq NaO*t*Bu, 1.4 eq 18-Crown-6, THF, rt. (f) 3 mol % $Pd(OAc)_2$, 4.5 mol % BINAP, 1.4 eq Cs_2CO_3, THF, 65 °C. (g) 5 mol % $Ni(COD)_2$, 10 mol % DPPF, 1.4 eq NaO*t*Bu, toluene, 100 °C. (h) Method A: $H_2NOH{\bullet}HCl$/NaOAc, MeOH, rt; Method B: NH_4^+ HCO_2^-, Pd/C (cat.), MeOH, 60 °C; Method C: cat. HCl, wet THF, rt. (i) Isolated yields reported are an average of two runs.

In summary, we have demonstrated the utility of benzophenone imine as a substitute for ammonia in the palladium- and nickel-catalyzed amination of aryl halides and triflates. The preceding section describes the initial investigation of this process; examples of benzophenone imine arylation have subsequently been demonstrated using the ligands DPEphos and 2-(di-*tert*-butylphosphino)biphenyl, and are included in the discussions of those ligands (Section 2.2 and 2.4, respectively). When the protected anilines are the desired products, the *N*-aryl imines are in most cases easily isolated by crystallization, and are stable to column chromatography; the crude products may also be deprotected directly. The couplings and subsequent deprotections proceed in uniformly high yields.

2.2—Aryl Amination Reactions Employing DPEphos

Our original method for the synthesis of linear oligoaniline derivatives relied on the $Pd_2(dba)_3$/BINAP or $Pd(OAc)_2$/BINAP catalyst system for the coupling of primary anilines with aryl bromides; we found that relatively high catalyst loadings were necessary, except for couplings involving *N*-(diphenylmethylene)-4-bromoaniline. Although the reactions proceeded cleanly, the need to use several mole percent of the BINAP ligand (moderately expensive even in its racemic form) in large-scale reactions prompted us to search for a more efficient catalyst system, or for potentially inexpensive alternatives to BINAP. At the same time, in our ongoing examination of the efficiency of various phosphine ligands in other C–N bond formation reactions, we sought a convenient route to a family of chelating bisphosphine derivatives, in which steric and electronic properties could be easily modified.

A number of new chelating bisphosphines had been prepared by van Leeuwen *et al.*[84] The general method consists of the directed double lithiation of diphenyl ether, or of heterocycles containing this structural motif, followed by reaction of the *in situ*-

generated aryllithium with chlorodiphenylphosphine. The preparation of the parent ligand, bis[2-(diphenylphosphino)phenyl] ether (DPEphos), is shown in Figure 19. These ligands were first examined in the rhodium-catalyzed hydroformylation of olefins;[84] the bite angles of several complexes of the phosphines with formally zerovalent palladium, as the (bisphosphine)palladium(tetracyanoethylene) complexes, have been measured by X-ray crystallography.[85]

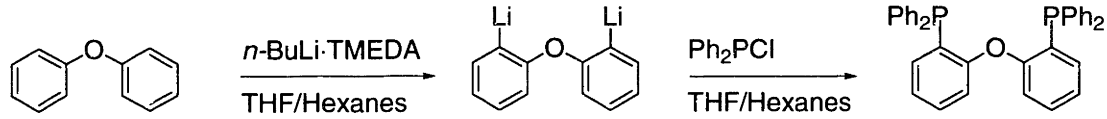
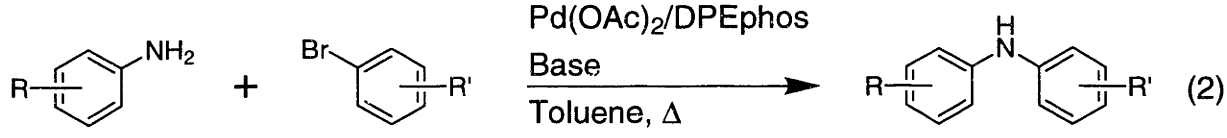


Figure 19: Synthesis of DPEphos.[84]

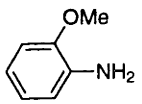
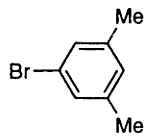
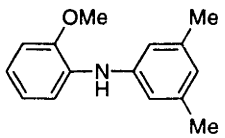
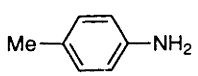
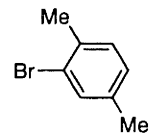
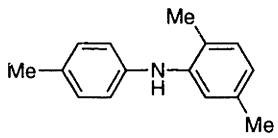
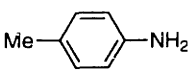
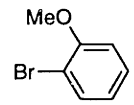
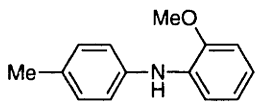
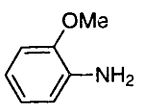
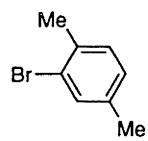
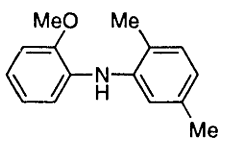
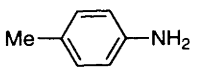
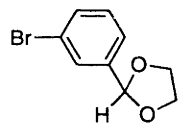
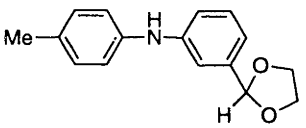
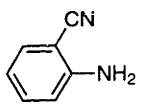
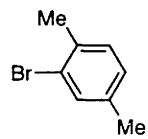
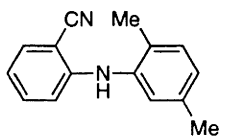
In view of its efficient, one-pot synthesis on multigram scale, from inexpensive starting materials, DPEphos is potentially attractive as a ligand in palladium-catalyzed aryl amination reactions. We have found that the $Pd(OAc)_2$/DPEphos system is an efficient catalyst for the arylation of primary anilines by aryl bromides (Eq 2); the results are summarized in Table 3. For comparison, coupling reactions using the ligands *rac*-BINAP and DPPF under the same conditions are shown.



(2)

The coupling of relatively unhindered anilines and aryl bromides proceeds fairly rapidly in toluene at 80 °C, using 0.5 mol % $Pd(OAc)_2$/DPEphos (L/Pd = 1.5) in the presence of sodium *tert*-butoxide as base. Even an electron-rich aryl bromide such as 2-bromoanisole, expected to be a less active substrate than the electronically neutral aryl bromides,[86] reacts rapidly and completely under these conditions. In this reaction, DPEphos is as effective a ligand as *rac*-BINAP, and considerably more effective than DPPF. The efficiency of the new catalyst is particularly evident in the coupling of *o*-anisidine with 2-bromo-*p*-xylene, under solvent-free conditions, at a catalyst loading of 0.05 mol %.

Table 3. Catalytic arylation of anilines using $Pd(OAc)_2$/DPEphos.[a]

Entry	Aniline	Bromide	Product	mol % Pd	Rxn Time (h)	Yield (%)[b]
1				0.5	2.5	96
2				0.5	3	95
3				0.5 DPEphos *rac*-BINAP DPPF	3	 94 (94) (44)
4				0.05	21	90
5[c]				0.5	7	80
6[d]				2 DPEphos *rac*-BINAP DPPF	16	 87 82 20

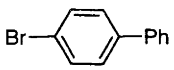
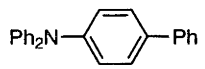
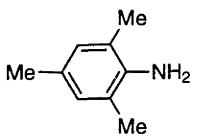
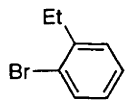
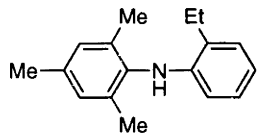
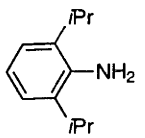
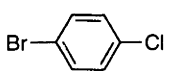
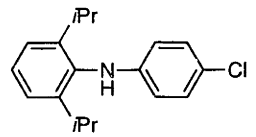
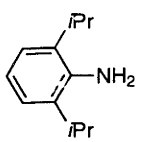
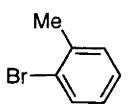
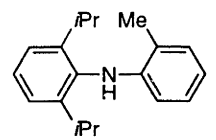
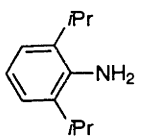
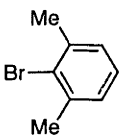
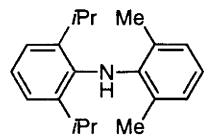
(a) Unless otherwise specified, reactions were run at 80 °C with 1.0 mmol ArBr, 1.2 mmol $Ar'NH_2$, 1.4 mmol NaO*t*Bu, cat. $Pd(OAc)_2$, and cat. ligand (1.5 equiv./Pd). Concentration: 2 mL toluene/mmol ArBr, except entry 4 (neat, 10 mmol scale) and entry 5 (3 mL toluene/mmol ArBr). (b) Products isolated by flash chromatography on silica gel, except entries 4 and 5 (recryst. from MeOH). All yields are an average of two runs. Yields in parentheses obtained by GC using an internal standard; all other yields represent isolated compounds estimated to be >95% pure by ^1H NMR, GC analysis and combustion analysis. All compounds were characterized by NMR (^1H, ^{13}C) and IR. (c) Reaction carried out by Ms. Michele Harris. (d) Run at 100 °C using Cs_2CO_3 as base.

Arylation of 2-aminobenzonitrile, a relatively poor nucleophile, proceeds smoothly in the presence of 2 mol % catalyst, with cesium carbonate as the base. Unlike sodium *tert*-butoxide, cesium carbonate is compatible with substrates containing functional groups such as methyl esters or enolizable ketones, or nitro groups. In this case, control reactions show that nitriles are attacked to a small but significant extent by primary anilines in the presence of sodium *tert*-butoxide; the

resulting amidines apparently poison the catalyst and prevent the reaction from proceeding.[87] As in the coupling of the electron-rich aryl bromide 2-bromoanisole, DPEphos performs comparably to *rac*-BINAP, and more effectively than DPPF.

The $Pd(OAc)_2$/DPEphos catalyst system allows the preparation of diarylamines with a high degree of steric crowding, as illustrated in Table 4. Although good selectivities are observed for the monoarylation of anilines under the conditions of this study—the product diarylamines are less nucleophilic and more sterically hindered

Table 4. Arylation of diphenylamine and hindered anilines[a]

Entry	Aniline	Bromide	Product	mol % Pd	Rxn Time (h)	Yield (%)
1	Ph_2NH			1	14	84
2[b]				0.5	12	99
3[b]				0.5	18	95
4[b]				0.5	18	94
5				5 DPEphos *rac*-BINAP DPPF	18	 90 87 88

(a) Reactions were run at100 °C with 1.0 mmol ArBr, 1.2 mmol amine, 1.4 mmol NaO*t*Bu, cat. $Pd(OAc)_2$, cat. ligand (1.5 equiv./Pd) and 2 mL toluene/mmol ArBr. Products isolated by flash chromatography on silica gel, except entry 1 (recryst. from EtOH). All yields are an average of two runs, and represent isolated yields of compounds estimated to be >95 % pure by ^1H NMR, GC analysis and combustion analysis. All compounds were characterized by NMR (^1H, ^{13}C) and IR. (b) Reaction conducted by Ms. Michele Harris.

than primary anilines—diphenylamine has been arylated in good yield, using a catalyst loading of 1 mol % and a reaction temperature of 100 °C. A catalyst loading of 0.5 mol % is sufficient to effect the coupling of 2,4,6-trimethylaniline with 2-ethylbromo-

benzene, or of 2,6-diisopropylaniline with a para-substituted or even an ortho-monosubstituted aryl bromide. A catalyst loading of 5 mol % allows the coupling of 2,6-diisopropylaniline with the more hindered substrate 2-bromo-*m*-xylene; the DPEphos ligand is as effective as *rac*-BINAP or DPPF for this reaction. This catalyst system was subsequently shown by Singer and Buchwald to be effective in the arylation of anilines and of benzophenone imine with a highly hindered binaphthyl monotriflate, using cesium carbonate as base.[88]

In preliminary studies, DPEphos has not been found to be an effective supporting ligand in the arylation of *N*-alkylanilines or (in contrast to the BINAP-based system) of alkylamines. In the coupling of *n*-hexylamine, pyrrolidine, *N*-methylaniline or *N*-ethylaniline with 1-bromo-4-*tert*-butylbenzene, slow consumption of aryl halide, and/or formation of large quantities of arene side product, was observed by GC analysis The reaction between *n*-hexylamine and 4-bromobenzonitrile or 4-bromobenzophenone proceeds rapidly, and with very little formation of the arene side product, but considerable quantities of diarylated product were formed.

To explore whether the efficiency of DPEphos as a ligand in the arylation of anilines arises from the flexibility of the diphenyl ether backbone, we examined a related ligand with a more constrained framework, 2,7-di-*tert*-butyl-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (hereafter DBXP, for di-*tert*-butyl-Xantphos, shown in Figure 20).[89] The increased rigidity of the Xantphos derivative, relative to DPEphos, does not diminish its efficiency as a ligand for aniline arylation. A comparison of reaction rates, monitored by GC analysis, for the coupling of *p*-toluidine with 1-bromo-4-*tert*-butylbenzene showed no significant difference between catalyst systems based on these two ligands. Like the $Pd(OAc)_2$/DPEphos catalyst system, the $Pd(OAc)_2$/DBXP system was relatively inefficient for the coupling of *n*-hexylamine or pyrrolidine with 1-bromo-4-*tert*-butylbenzene, with slow consumption of aryl bromide and considerable formation of arene byproduct.[90] Two significant differences between

these ligands were observed. The $Pd(OAc)_2$/DBXP system effected a rapid and clean coupling of *N*-methylaniline with 1-bromo-4-*tert*-butylbenzene, with only trace arene formation. This catalyst system is also considerably more active than the $Pd(OAc)_2$/DPEphos system for the formation of triarylamines. The source of this difference in reactivity is unclear, and may stem from the greater bite angle of the Xantphos ligand rather than the more rigid framework.[84]

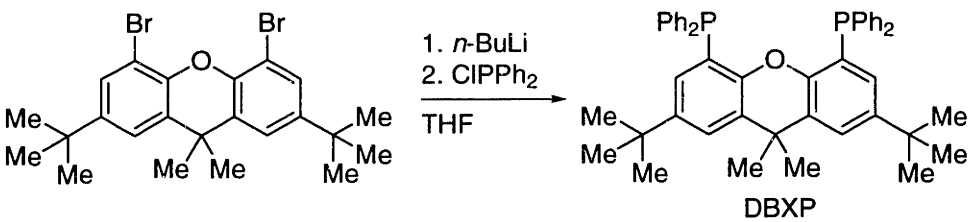


Figure 20. Preparation of a Xantphos derivative.

The ligand DBXP, and subsequently the parent Xantphos (preferred, due to its preparation from a less expensive precursor), have been applied to other types of carbon–nitrogen bond formation. Harris and Buchwald have examined Xantphos in the synthesis of alkyldiarylamines, and found it to be useful for the coupling of electronically neutral or electron-deficient *N*-alkylanilines with electron-poor aryl halides.[91a] Wagaw, Yang and Buchwald have found the $Pd(OAc)_2$/Xantphos system to be uniquely effective in promoting the arylation of benzophenone *N*-arylhydrazones.[91b] Yang and Buchwald have used Xantphos as a ligand in the intramolecular arylation of an acetamide to form a seven-membered ring; they have also demonstrated the formation of five-membered rings by intramolecular arylation of acetamides and carbamates using the $Pd(OAc)_2$/DPEphos system.[91c]

In conclusion, the chelating ligand DPEphos, in combination with $Pd(OAc)_2$, forms a highly active catalyst system for the coupling of primary anilines with aryl bromides. This ligand and its xanthene analogues have since been applied to other types of carbon–nitrogen bond formation. The efficiency of this catalyst system equals

that of $Pd(OAc)_2$/*rac*-BINAP, and equals or exceeds that of $Pd(OAc)_2$/DPPF, in all examples compared. The ready accessibility of DPEphos, a known compound amenable to large-scale synthesis,[92] further increases its utility in these reactions.

2.3—Palladium Chloride in Aryl Amination Reactions

In light of the low cost of DPEphos, and its potential attractiveness in industrial applications of aniline arylation, we wondered whether a relatively inexpensive source of palladium could be used as well. Palladium chloride is available at approximately half the cost of palladium acetate.[93] Apart from the issue of cost, we were perplexed that this very common palladium source did not appear to be useful for palladium-catalyzed aryl amination reactions.

In the course of mechanistic experiments involving the $Pd(OAc)_2$/BINAP system, Wolfe and Buchwald found that the order in which the reactants are combined can greatly affect the generation of the active catalyst. The premixing of catalyst precursors prior to the addition of other reactants apparently results in a more complete generation of the active catalyst from palladium acetate; much faster reaction rates were observed when this modification was used, particularly in the coupling of aniline with 1-bromo-4-*tert*-butylbenzene. The difference is ascribed to the formation of palladium (II) *tert*-butoxide complexes which resist phosphine complexation. When $Pd_2(dba)_3$ is used as the palladium source, the reaction rate is found to be independent of the order of addition.[94] In the study of DPEphos described above, the same effect on reaction rate was observed; thus, for all examples given, the substrates and catalyst precursors were dissolved prior to the addition of base.

It is unsurprising, then, that previous attempts to use palladium chloride as the palladium source had been unsuccessful: palladium chloride is very sparingly soluble in these reaction mixtures, inhibiting the precomplexation of palladium and ligand. We found, on the other hand, that when the palladium chloride and ligand were in

homogeneous solution prior to the addition of base, the reactions proceeded smoothly. Because palladium chloride is quite poorly soluble in toluene and tetrahydrofuran, the palladium chloride is heated in the neat amine in the presence of ligand until a clear solution is obtained, then the other components are added. This technique has been demonstrated for several catalyst systems, as shown in Figure 21.

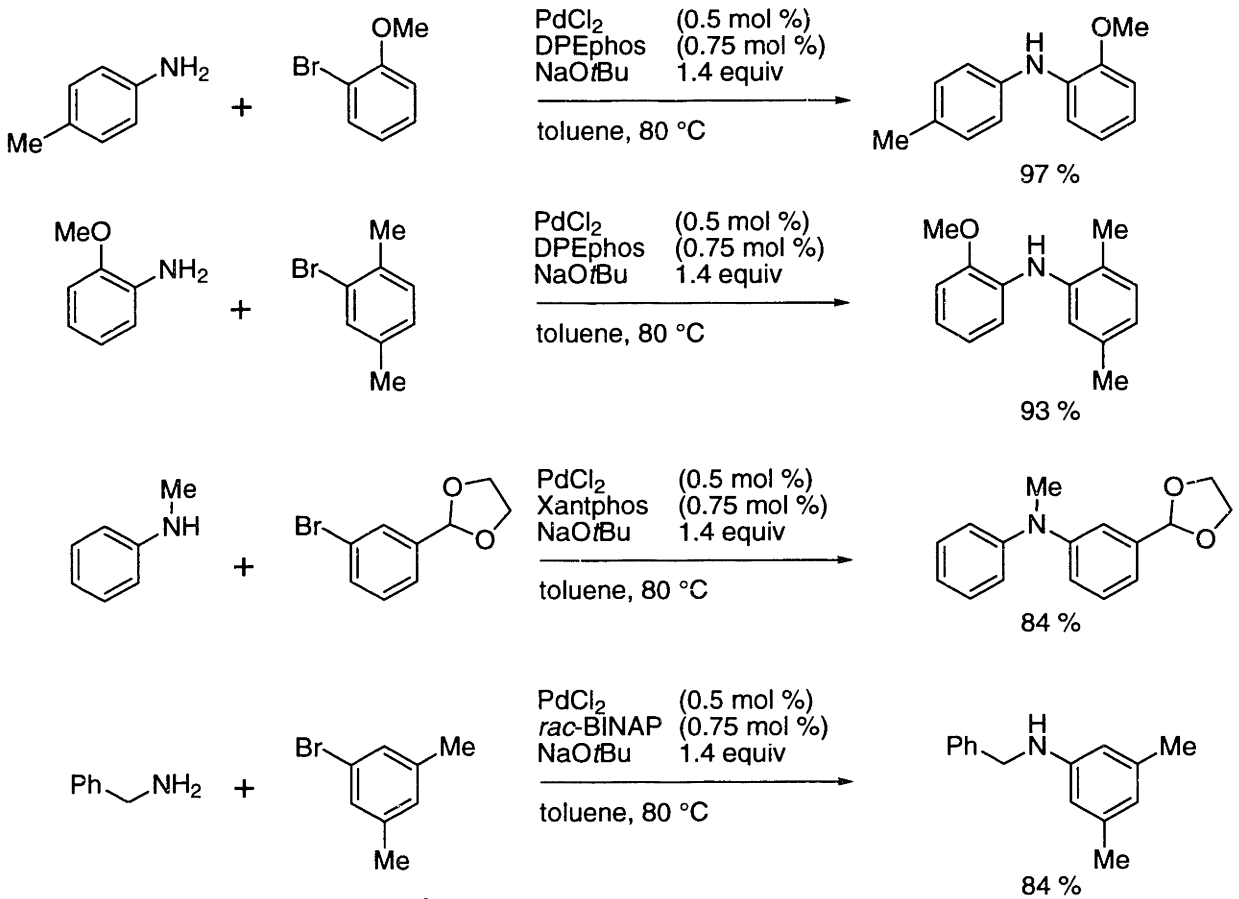


Figure 21. Aryl amination reactions using $PdCl_2$-based catalysts. Yields are averaged for two runs and represent material estimated to be ≥95 % pure.

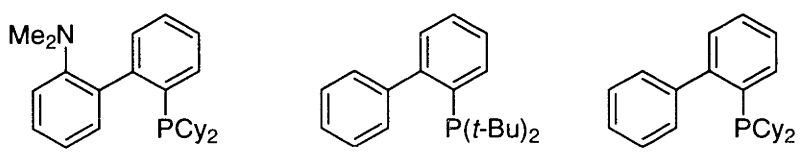
2.4—2-(Di-*tert*-butylphosphino)biphenyl:

Synthesis, and Use in Aryl Amination Reactions

A continuing goal of the palladium-catalyzed aryl amination methodology has been the development of highly active catalyst systems. In the amination of aryl bromides using the palladium acetate/BINAP catalyst system, ^1H NMR studies by Wolfe suggested that the rate-limiting step was oxidative addition.[94] The oxidative

addition of aryl chlorides to palladium is considerably more difficult. Until recently, very few systems existed for catalytic aminations of aryl chlorides.[95] Several new catalyst systems, however, use highly electron-rich phosphine ligands to facilitate oxidative addition, and a high degree of steric hindrance to prevent the reductive elimination step from being slowed prohibitively.[96] One of these, employing palladium acetate and the ligand 2-dimethylamino-2'-dicyclohexylphosphinobiphenyl (**47**),[96d] was shown to effect the catalytic amination of aryl bromides at room temperature,[97] and of aryl chlorides at 80 °C; the activated aryl chloride 4-chlorobenzonitrile were transformed even at room temperature. Substrates containing functional groups sensitive to sodium *tert*-butoxide were successfully converted to arylamines using tribasic potassium phosphate as the base, a practical improvement over the more expensive cesium carbonate.

The more sterically encumbered *tert*-butyl analogue of **47** was prepared for use in the palladium-catalyzed arylation of phenols; subsequently, the desamino analogue, 2-(di-*tert*-butylphosphino)biphenyl (**48**) was prepared for comparison, to examine the importance of the dimethylamino group.[98] This phosphine was found by Wolfe to be a highly effective ligand for palladium-catalyzed aryl amination reactions: catalyst systems based on this ligand displayed high activity and wide substrate scope. For some substrate combinations, the related 2-dicyclohexylphosphino-biphenyl (**49**) was a somewhat more effective ligand. These ligands, shown in Figure 22, are air-stable, crystalline solids.[99]



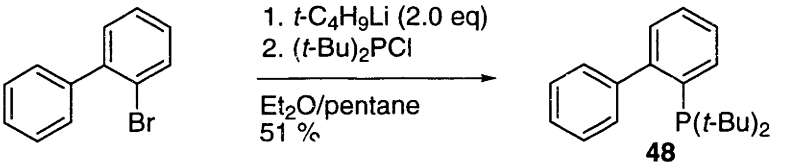
47 **48** **49**

Figure 22. Electron-rich, sterically hindered phosphine ligands for aryl amination.

In the initial method for the preparation of 2-(di-*tert*-butylphosphino)biphenyl (Scheme 13),[100] 2-bromobiphenyl in diethyl ether solution was subjected to halogen-

metal exchange with 2.0 equivalents of *tert*-butyllithium. The resulting 2-biphenyllithium was converted to **48** in yields of up to 51 % by refluxing with di-*tert*-butylchlorophosphine for at least 27 hours. If *n*-butyllithium is used instead of *tert*-butyllithium in the halogen-metal exchange, the byproduct 1-bromobutane competes with the very hindered chlorophosphine in the reaction with the aryllithium. The reaction times could not be shortened by running the reaction in tetrahydrofuran at higher temperatures, as metallation of the solvent predominated.

Scheme 13.



48

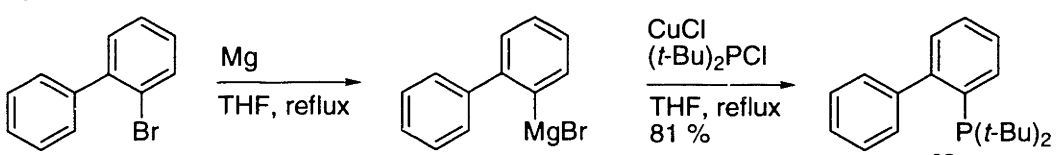
In view of the promising preliminary results obtained using **48** in palladium-catalyzed cross-coupling reactions, we desired a more convenient synthetic route to this phosphine. In particular, we wished to avoid the use of the pyrophoric *tert*-butyllithium in larger-scale preparations. The reaction between 2-biphenylmagnesium bromide and di-*tert*-butylchlorophosphine was therefore examined. The reactants appeared to be entirely inert to each other in refluxing tetrahydrofuran: no formation of product was observed after 10 hours. In an attempt to increase the nucleophilicity of the Grignard reagent, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was added to the reaction mixture. A slow reaction to form the desired product (15 % conversion after 20 hours; 20 % conversion after 30 hours, as judged by GC analysis) was observed.

At this point, a stoichiometric quantity of copper (I) bromide (dimethyl sulfide) complex was added to the reaction mixture. It was hoped that the resulting arylcopper (I) species,[101] although less nucleophilic than an aryllithium or aryl Grignard reagent, would be more reactive toward the chlorophosphine, as a result of the affinity of the

copper for phosphorus. Moreover, the copper (I) center might plausibly participate in the cleavage of the P–Cl bond through an electron-transfer process.[102]

Indeed, the addition of the copper (I) complex caused a substantial increase in product formation; minor byproducts of the reaction included biphenyl, and the quaterphenyl derived from dimerization of the Grignard reagent. Subsequent experiments showed that the presence of TMEDA is unnecessary, and that the inexpensive copper (I) chloride may be substituted for copper (I) bromide (dimethyl sulfide). The phosphine product was found to precipitate from the reaction mixture in the form of an insoluble complex, believed to be the copper (I) chloride adduct. This complex may be isolated, washed free of organic impurities, and decomposed by treatment with aqueous ammonium hydroxide. An ethereal extract of the resulting mixture contains the phosphine product in greater than 98 % purity. Although the crude product has been used as a ligand in aryl amination reactions, we find the recrystallized ligand to be more conveniently handled. This method, outlined in Scheme 14, has been used by Aranyos to prepare the extremely hindered 2-[di-(1-adamantyl)phosphino]biphenyl, and by Wolfe to prepare 1-(di-*tert*-butylphosphino)-*o*-terphenyl.[98]

Scheme 14.

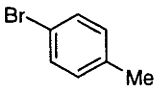
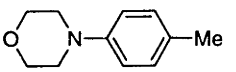
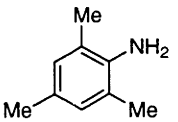
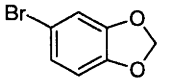
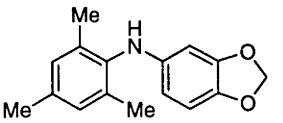
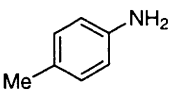
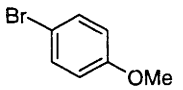
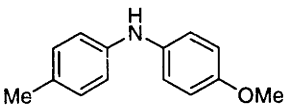
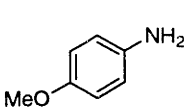
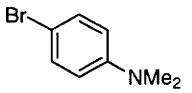
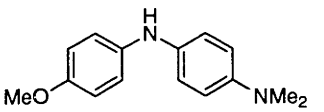
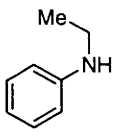
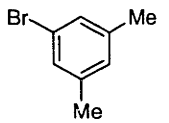
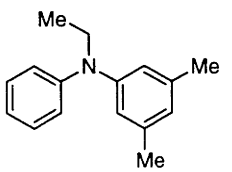


48

Palladium catalyst systems based on ligand **48** display a broad substrate scope for the arylation of amines; aryl bromides, chlorides and triflates undergo efficient cross-coupling. For many types of amine, catalysts derived from palladium acetate give good results; however, for most reactions involving primary anilines, and in attempted arylations of benzophenone imine, incomplete conversions are observed, and $Pd_2(dba)_3$ must be used instead.[103] The arylation of alkylamines and *N*-

alkylanilines proceeds in high yield, generally with little or no formation of arene byproduct.[83] The results for the cross-coupling of amines with aryl bromides are summarized below, in Table 5. This catalyst system represents a major improvement over previous systems for the amination of highly electron-rich aryl bromides. Reactions such as Entries 3 and 4 have been observed to proceed only slowly and incompletely when catalyst systems based on BINAP or DPEphos are employed instead. In light of its efficiency in the coupling of primary anilines with electron-rich aryl bromides, the $Pd_2(dba)_3$/**48** catalyst system has been applied to the synthesis of oligoaniline and polyaniline derivatives, as described in Chapters 1 and 3.

Table 5: Palladium-catalyzed amination of aryl bromides using ligand **48**.

Entry	Amine	Bromide	Product	Rxn Time (h)	Yield (%)
1[b]				20	92
2				2	97
3[c]				2.5	90
4[c]				2	93
5				3	82

(a) Reactions were run at 80 °C with 1.0 mmol ArBr, 1.2 mmol amine, 1.4 mmol NaO*t*Bu, 0.5 mol % $Pd(OAc)_2$, ligand **46** (1 mol %) and 2 mL toluene/mmol ArBr. Products isolated by flash chromatography on silica gel. All yields are an average of two runs, and represent isolated yields of compounds estimated to be >95 % pure by ^1H NMR, GC analysis and combustion analysis. (b) Reaction conducted by Mr. John Wolfe. (c) $Pd_2(dba)_3$ used in place of $Pd(OAc)_2$.

A wide variety of aryl chlorides may be converted efficiently to the corresponding arylamine derivatives using palladium catalyst systems derived from **48** or **49**. Cross-coupling reactions of unactivated aryl chlorides, using sodium *tert*-butoxide as base, are summarized in Table 6. In most cases, the catalyst system derived from **48** gives good results. A catalyst loading of 0.5 mol % palladium is usually sufficient; in some cases, such as Entry 17, as little as 0.05 mol % palladium was sufficient (97 % recrystallized yield on 10 mmol scale). For some substrate combinations, such as Entry 13, **49** is a more effective supporting ligand than **48**. The reasons for this difference in efficiency are unclear at this time. Aliphatic amines, primary anilines, and *N*-alkylanilines undergo arylation readily. Although good selectivity is observed for diarylamine formation from primary anilines, with generally less than one percent of the overarylation product observed, the $Pd(OAc)_2$/**48** catalyst transforms diphenylamine to a triarylamine under rather mild conditions (Entry 2). The palladium-catalyzed arylation of benzophenone hydrazone is a versatile method for the synthesis of substrates for the Fischer indole synthesis.[91b] As shown in Entry 8, the use of the $Pd_2(dba)_3$/**48** catalyst system allows an aryl chloride to be used in this process. The conversion of aryl chlorides to protected primary anilines by cross-coupling with benzophenone imine had been demonstrated using a nickel-based catalyst system, as shown in Section 2.1. The use of $Pd_2(dba)_3$/**48** to catalyze this transformation (Entry 16) represents an experimental simplification of this process.

The Pd/**48** catalyst systems show a high activity even toward electron-rich aryl chlorides such as 2-chloroanisole and 4-chloroanisole, and tolerate considerable steric hindrance on the aryl chloride substrate. Thus 2-chloro-*p*-xylene reacts readily with benzylamine at slightly higher temperatures and catalyst loading than the usual conditions (Entry 24), and a catalyst loading of 4 mole percent palladium allows the coupling with even the highly hindered 2,6-diisopropylaniline (Entry 23) to proceed with reasonable efficiency.

Table 6: Palladium-catalyzed amination of unactivated aryl chlorides.[a]

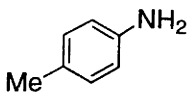
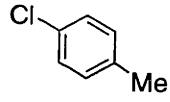
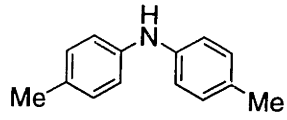
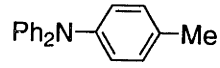
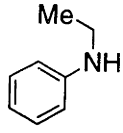
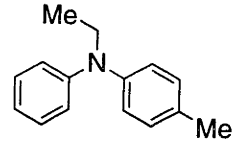
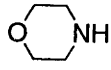
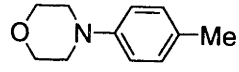
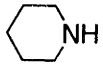
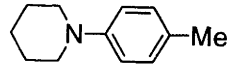
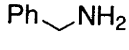
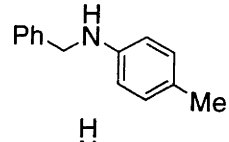
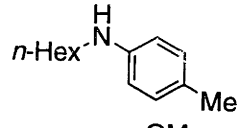
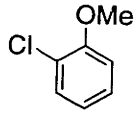
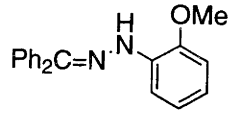
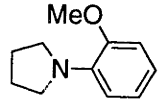
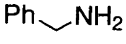
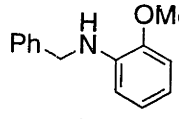
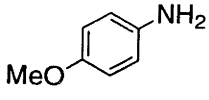
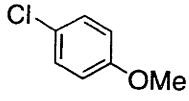
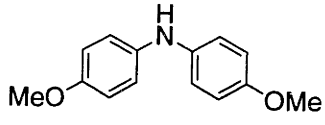
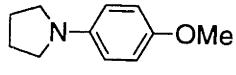
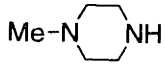
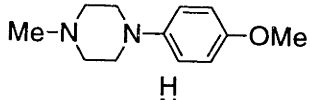
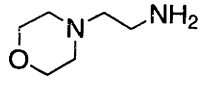
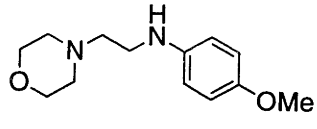
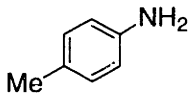
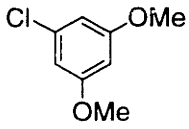
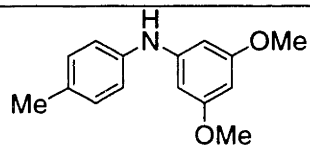
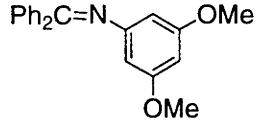
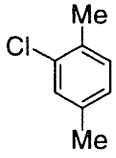
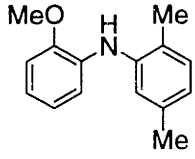
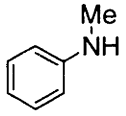
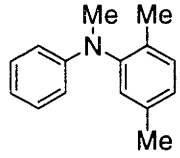
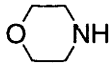
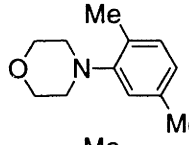
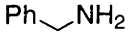
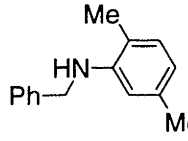
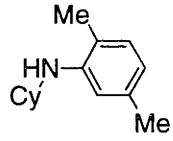
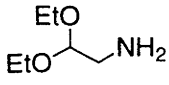
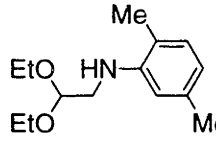
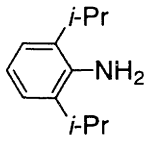
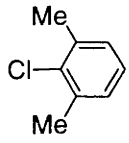
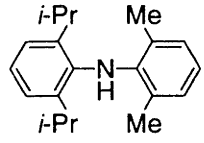
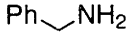
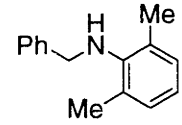
Entry	Amine	Chloride	Product	Rxn Time (h)	Yield (%)
1[b]				2.5	90
2	Ph_2NH			12	90
3[h]				18	93
4[h]				4	93
5[h]				23	86
6[h]				5	89
7[h]	*n*-$HexNH_2$			19	85
8[b]	$Ph_2C{=}N{-}NH_2$			2.5	91
9[h]				16	88
10[h]				18	96
11[b]				8	94
12[d, h]				23	92
13[c, f, i]				21	82
14[g, i]				24	86

Table 6: Palladium-catalyzed amination of unactivated aryl chlorides (cont.).[a]

Entry	Amine	Chloride	Product	Rxn Time (h)	Yield (%)
15[b]				2.5	95
16[b, c, d, i]	$Ph_2C{=}NH$			18	99
17[b]				2.5 14	97 97[b']
18[h]				3	90
19[i]				24	89
20[h]				24	96
21[d, h]	$CyNH_2$			19	98
22[i]				15	99
23[b, e]				20	73
24[g, i]				24	86

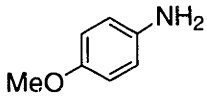
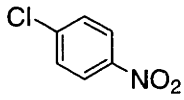
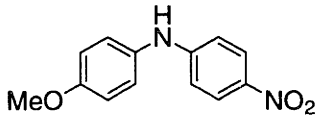
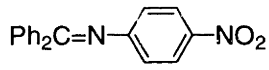
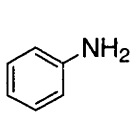
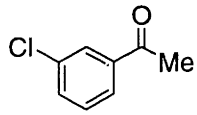
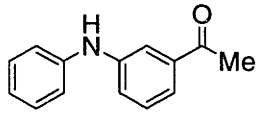
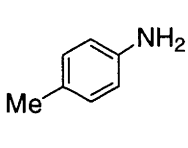
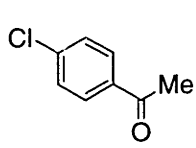
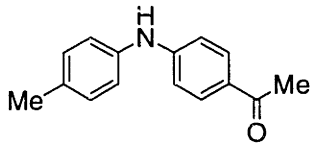
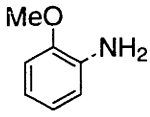
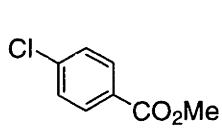
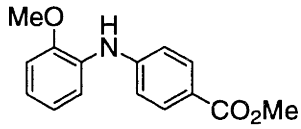
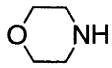
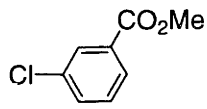
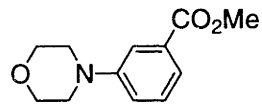
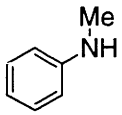
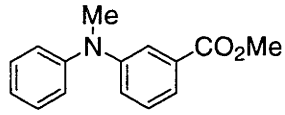
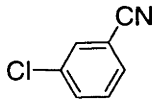
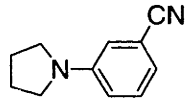
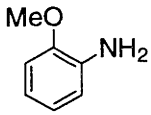
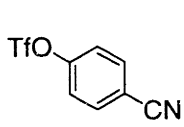
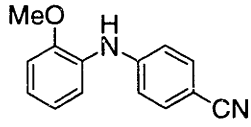
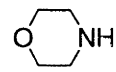
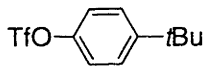
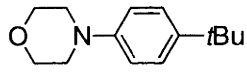
(a) Reaction conditions: 1.0 mmol aryl chloride, 1.2 mmol amine, 1.4 mmol NaO*t*Bu, 0.5 mol % $Pd(OAc)_2$, **48** (L:Pd = 2:1), toluene (2 mL/mmol ArCl), 80 °C. Reaction times have not been minimized. (b) $Pd_2(dba)_3$ (0.25 mol %) used in place of $Pd(OAc)_2$. (b') 0.025 mol % $Pd_2(dba)_3$. (c) Ligand **49** used in place of **48**. (d) 1.0 mol % $Pd(OAc)_2$. (e) 2.0 mol % $Pd_2(dba)_3$. (f) Run at 100 °C. (g) Run at 110 °C. (h) Carried out by Dr. John Wolfe. (i) Carried out by Dr. Hiroshi Tomori

A number of substrates containing base-sensitive functional groups undergo efficient cross-coupling, catalyzed by the new catalyst systems, when tribasic potassium phosphate is used as base instead of sodium *tert*-butoxide. Reactions carried out using this milder base are summarized in Table 7. Even relatively difficult aryl chloride substrates, in which the base-sensitive group is not in the activating ortho or para position, undergo amination under reasonably mild conditions. It is noteworthy that the aryl chloride couplings in Table 7 would not be feasible using the previously developed nickel-catalyzed method,[81] since the use of bases weaker than sodium *tert*-butoxide with the nickel catalyst systems has not been achieved.

In many cases, ligand **49** gave substantially better results than ligand **48** when the weaker base was used. However, for the coupling of 1-chloro-4-nitrobenzene with *p*-anisidine (Entry 1), or the triflate aminations examined so far (Entries 9 and 10), the $Pd_2(dba)_3$/**48** catalyst system functions effectively. The factors governing the relative efficiencies of these ligands are unclear, although it might be relevant that the oxidative additions in these three cases give rise to particularly electron-deficient metal centers,[104] which should facilitate the coordination and deprotonation of amine. The question remains, however, why this process should be more difficult when the ligand on palladium is **48** rather than **49**.

In summary, the sterically demanding, electron-rich ligand **48**, and the closely related **49**, are extremely useful ligands for palladium aryl amination catalysts, giving rise to highly active and general catalyst systems.[92] A new copper-mediated method for the coupling of Grignard reagents with chlorophosphines allows the facile preparation of **48** on multigram scale, and affords access to even bulkier analogues of this phosphine. The high activity of the $Pd_2(dba)_3$/**48** catalyst system toward highly electron-rich aryl bromides renders it useful in the synthesis of oligoaniline and polyaniline derivatives.

Table 7: Palladium-catalyzed aryl aminations using K_3PO_4 as base.[a]

Entry	Amine	Halide	Product	Rxn Time (h)	Yield (%)
1[c, d]				17	91
2	$Ph_2C{=}NH$			16	82
3[h]				22	81
4[e, h]				18	95
5[e]				14	95
6[h]				20	93
7[h, i]				20	88
8[h]				40	81
9[c, d, e]				1.5	85
10[c, d, f, g]				26	92

(a) Reaction conditions: 1.0 mmol ArX, 1.2 mmol amine, 1.4 mmol K_3PO_4, 0.5 mol % $Pd_2(dba)_3$, 2.0 mol % **49**, DME (2 mL/mmol ArX), 100 °C. Reaction times have not been minimized. (b) $Pd(OAc)_2$ (1.0 mol %) used in place of $Pd_2(dba)_3$. (c) Ligand **48** used in place of **49**. (d) Reaction run in THF solvent. (e) Reaction run at 80 °C. (f) Reaction run at 65°C. (g) Reaction carried out by Mr. John Wolfe. (h) Reaction carried out by Dr. Hiroshi Tomori. (i) Reaction proceeded to 99 % conversion.

Chapter Three:

New Directions in the Synthesis of Oligoaniline and Polyaniline Derivaties

As described in Chapter 1, the palladium-catalyzed coupling of anilines with aryl bromides, using a suitable combination of protective groups, can be used to obtain oligoaniline derivatives with a variety of chain lengths. These derivatives have been prepared in nonsymmetric or symmetric (end-capped) forms, the latter bearing electron-donating, electron-withdrawing, hydrocarbon, or trimethylsilyl substituents on the terminal aryl rings. In light of the facile handling of the intermediates, and the wide scope of the aryl amination reaction, the general method appears promising for the preparation of other types of polyaniline-related materials. The following chapter details recent efforts toward the preparation of ring-substituted 4-bromoaniline equivalents, protected polyaniline derivatives, and a new aminophenothiazine-derived polymer. It should be emphasized that these results are preliminary in nature, representing the first successful steps toward these products rather than definitive studies. They are included here in the hope that they will serve as a useful starting point for future efforts.

3.1—Synthesis of Ring-Substituted Monomers for Oligoanilines

The synthesis of ring-substituted polyanilines, with modified physical, chemical or electrical properties, has attracted considerable attention. Polyaniline bearing sulfonate groups, a water-soluble, self-doping polymer, has been prepared by the sulfonation of polyaniline,[105] or more recently by the polymerization of anilinesulfonic acids.[106] Polyaniline has also been synthesized with alkyl and alkoxy[107] substituents, to increase the solubility of the conductive form in solvents such as dichloromethane or chloroform. Other ring-substituents have been incorporated, including cyano,[108] nitro,[109] fluoro,[110] and heavier halogen substituents.[111]

The drawback of the substituents is that they tend to force the aryl rings out of coplanarity, decreasing the conjugation of the π-system[112] and reducing conductivity.[113] Moreover, existing methods for the synthesis of substituted

polyanilines are relatively inflexible with respect to the polymer architecture. The polymerization of substituted anilines affords polymers substituted at every ring; the polymerization of aniline followed by functionalization, as in the sulfonation, may give random and variable distributions of substituents. Oxidative copolymerization of aniline with substituted anilines gives rise to random copolymers,[114] although in one case the addition of toluidine after the oxidative polymerization of aniline gave rise to a diblock copolymer.[115]

The method described in Chapter 1 for the synthesis of oligoaniline derivatives should, in principle, be readily adaptable to the synthesis of oligoanilines bearing substituents along the chain rather than at the ends. The development of a flexible route to such materials would allow the steric and electronic effects of a given substituent at a specific site to be investigated. It is plausible that one or two substituents in an octaaniline chain could significantly affect the electronic properties of the molecule as a whole, with a much smaller geometric disruption than would be produced by substitution at every ring. Such investigations would facilitate the design of sensory materials based on substituted polyanilines, and a general synthetic route would aid in their preparation.

For the synthesis of internally substituted oligomers by the strategy detailed in Chapter 1, ring-substituted analogues of **1** are necessary. Relatively few substituted analogues of 4-bromoaniline are commercially available; exceptions include the 4-bromotoluidines, and 5-amino-2-bromobenzotrifluoride. The monomers are therefore synthesized by para-bromination of substituted anilines, followed by protection of the amine group as its benzophenone imine derivative.

The bromination of aniline, *N*-alkylanilines, diphenylamine, and aminopyridines by tetra-*n*-butylammonium tribromide is known to proceed with excellent selectivity for the para position, with very little if any overbromination under most circumstances.[64] This procedure was readily applied to the bromination of ring-substituted anilines. A

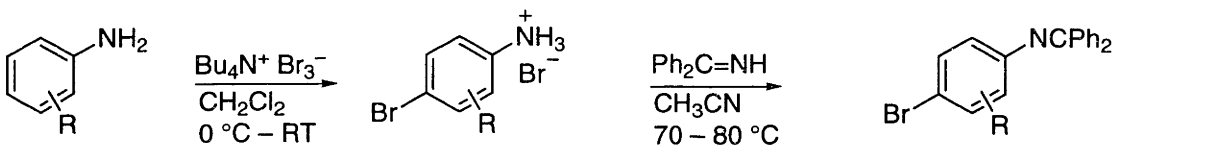
number of anilines have previously been para-brominated using the mild brominating agent 2,4,4,6-tetrabromo-2,5-cyclohexadienone, and yields are generally high.[116] The use of tetra-*n*-butylammonium tribromide was preferred here because the bromination products may be isolated without the necessity of distillation or chromatography. The bromoanilines are obtained in the form of their hydrobromide salts (**50**), which precipitate as solids from dichloromethane solution. Small portions of the salts were neutralized and analyzed by GC. In the case of *o*-anisidine, 2-aminobenzyl alcohol, and 2-aminophenethyl alcohol, the precipitated products are formed in sufficient (> 95 %) purity to be used without further purification. The bromination products of 3-aminobenzonitrile (**50b**) and of 3-aminobenzyl alcohol (**50d**) were formed in somewhat lower purity, and were recrystallized from ethanol. For the cyano compound **50b**, the purity increased only slightly with each recrystallization, and three recrystallizations were carried out. In the case of **50d**, a single recrystallization gave highly pure material.

Except in the preparation of **50d**, in which heavier byproducts were observed by GC analysis (and were completely removed in the recrystallization), the minor impurity in each crude precipitated product was the non-brominated aniline. Longer reaction times or the use of excess brominating agent give the same result. It is possible that the product hydrobromide, before precipitation begins, can transfer a proton to the starting material, which precipitates as its insoluble hydrobromide and fails to react thereafter. Most of this coprecipitate, as stated, may be removed by recrystallization. After purification, portions of the hydrobromide salts were neutralized and analyzed by ^{1}H NMR to confirm the regioselectivity of the bromination. The splitting patterns for the aryl protons in each case clearly showed that bromination had occurred para to the amine group; other regioisomers are not visible.

Protection of the aniline group as its benzophenone imine derivative is accomplished by transamination with benzophenone imine in acetonitrile suspension.

In the case of the commercially available 5-amino-2-bromobenzotrifluoride, methanesulfonic acid was added to the mixture of the neutral aniline and benzophenone imine. The resulting *N*-aryl imines may be purified in most cases by crystallization. In the case of the methoxy-substituted imine **51a**, the crude product resisted crystallization, and seed crystals had to be prepared by filtration of a few millgrams of crude material through silica gel. The addition of these crystals to the remainder of the material initiated crystallization. Attempts to crystallize the imine derived from **50e** were unsuccessful, and the product was purified by column chromatography instead. The trifluoromethyl-substituted imine **51f**, in crude form, had a tendency to oil out of solution, and crystallization occurred only after several attempts.

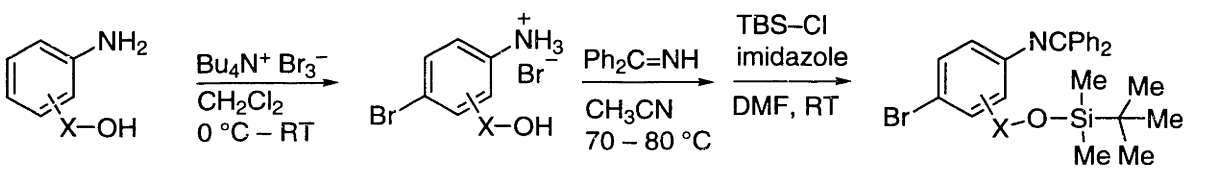
Scheme 15



R = 2-OCH_3
3-CN

50a 92 %
50b 53 %

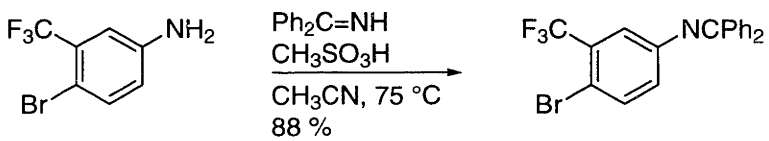
51a 77 % (71 % overall)
51b 87 % (46 % overall)



X = 2-CH_2–
3-CH_2–
2-CH_2CH_2–

50c 63 %
50d 56 %
50e 78 %

51c 90 % (42 % overall)
51d 90 % (43 % overall)
51e 97 % (70 % overall)



51f 88 %

The hydroxyalkyl-substituted imines derived from **50c–e** were then protected as their *tert*-butyldimethylsilyl (TBS) derivatives, according to the procedure of Corey.[117] These products (**51c–e**) resisted attempts at crystallization but were readily purified by column chromatography. The bright yellow color of the imines was particularly useful in locating the product during chromatography. The products contain a small proportion of their non-bromo analogues, as much as 5 % in **51e**; however, the non-bromo compound should not interfere with the coupling reaction, and coupling products of the sort prepared in Chapter 1 may be separated quite easily from monomer starting materials. The preparation of ring-substituted monomers (**51a–f**) from commercially available anilines is illustrated in Scheme 15.

3.2—Protected Polyanilines via Step-Growth Polymerization

The synthesis of polyanilines by the coupling of amines with aryl halides is of interest due to the regioselectivity attainable in this strategy; also, a mild and versatile coupling reaction could allow the presence of functional groups which would be incompatible with the chemical or electrochemical polymerization methods. The simplest metal-catalyzed synthesis of polyaniline would consist of the polymerization of 4-chloroaniline or 4-bromoaniline, or the copolymerization of 1,4-phenylenediamine with 1,4-dichlorobenzene or 1,4-dibromobenzene. The polymerization of haloanilines using copper catalysis has been reported;[23a] both *meta*- and *para*-haloanilines were polymerized. The reaction temperatures are quite high (250 °C), and the workup procedures are complicated. In the case of the *para*-haloanilines, the leucoemeraldine product initially formed is catalytically dehydrogenated to give an oxidized form of the polymer. Molecular weights as high as 3,900 (*ca.* 40 aniline units) were calculated from the elemental analysis for the residual halogen; however, the possibility of copper-catalyzed dehalogenation of the endgroup (using the leucoemeraldine as a transfer hydrogenation agent), which would inflate the numbers

calculated by this method, was not discussed. Recently, the palladium-catalyzed self-coupling of 4-bromoaniline, using the BINAP-derived catalyst system, was reported to afford a polymer;[23b] however, the characterization of this product was ambiguous in that the observations would also be consistent with low oligomers. Moreover, the reaction conditions (one week at 120 °C, using 5 mol % palladium) and the nontrivial workup are drawbacks to this method.

Generally, the palladium-catalyzed amination of aryl bromides appears to be particularly difficult when an N–H substituent is present in the para position.[118] (This observation was used to advantage in the preparation of **26** and **32**, in which the coupling of an aniline with 1,4-dibromobenzene resulted in the selective substitution of only one bromo group.) Perhaps for this reason, most reports of polymerization using palladium-catalyzed aryl amination describe the preparation of meta-linked polyanilines, or of *N*-substituted para-linked polyanilines.

The first polymerization by palladium-catalyzed amination involved the coupling of aliphatic cyclic secondary amines such as piperazine or an alkylene(bis-4,4'-piperidine) with 1,3- and 1,4-dibromobenzene, using a palladium catalyst with tri-*o*-tolylphosphine as the supporting ligand.[119] Subsequently, several reports described the use of the palladium/BINAP catalyst system to prepare meta-linked polyaniline[120] and its analogues, including copolymers prepared from 1,3-phenylenediamine and dibromides such as 2,6-dibromopyridine[120a,b] or 4,4'-dibromodiphenyl ether,[120b] and branched polymers from the polymerization of 3,5-dibromoaniline.[120c] The tri-*o*-tolylphosphine-derived catalyst system has been used to synthesize *N*-arylpolyanilines with both meta- and para-linkages, including donor-acceptor copolymers.[121] The *meta*-polyanilines are of interest as magnetic materials.

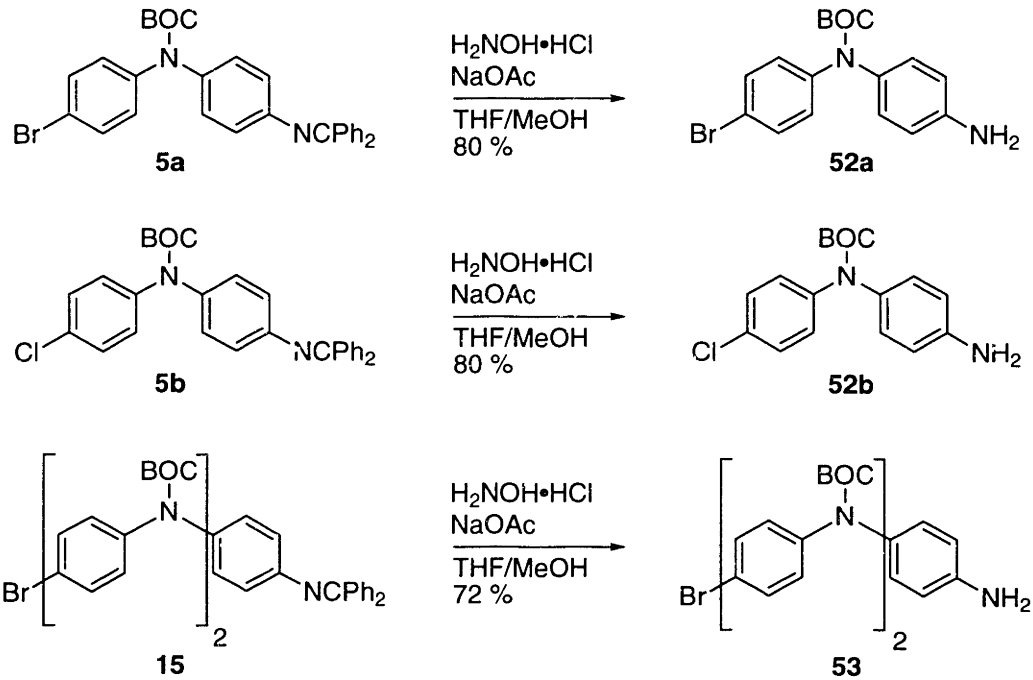
In the synthesis of controlled-length oligoanilines, described in Chapter 1, BOC-protected 4-bromodiarylamines were found to undergo efficient cross-coupling with anilines. Moreover, the solubility of the oligoaniline derivatives in common low-

boiling solvents, such as dichloromethane and tetrahydrofuran, was greatly improved relative to the parent compounds. This methodology appeared promising for the synthesis of highly soluble, BOC-protected polyaniline precursors, which like the oligomers would be easily converted the electroactive material. An oligomer with an aryl bromide at one end, a primary amine at the other, and BOC-protected secondary amine groups along the chain would be expected to undergo polymerization under cross-coupling conditions similar to those developed for oligoaniline synthesis. Similarly, a suitable dibromide such as **31** could undergo palladium-catalyzed copolymerization with diamines.

The first experiments of this kind were carried out by Dr. Thomas Mackewitz,[122] who prepared the bifunctional monomers **54a** and **55** by deprotection of the corresponding imines. The imine cleavage was carried out using hydroxylamine, as hydrogenolysis would be expected to cleave the aryl-bromine bond as well.[123] These monomers, when subjected to palladium-catalyzed aryl amination using BINAP as the supporting ligand, formed mostly insoluble masses of product. The reaction of dibromide **31** with diamine **46** gave similar results. Before conversion to their fully BOC-protected derivatives, the crude products had to be dried, dislodged from the reaction vessel, pulverized, and triturated with water (to remove excess base), methanol or isopropanol (to remove water and low oligomers), and ether (to remove alcohol). Subsequent BOC-protection afforded materials soluble in chloroform, and the polymeric structure was confirmed by ^{1}H NMR spectroscopy. The products were obtained as crude amorphous solids, containing residual di-*tert*-butyl dicarbonate. Analysis of the materials by ^{31}P spectroscopy showed a signal for a triarylphosphine, indicating either that the catalyst was mixed with the products, or that aryl exchange had occurred, resulting in the incorporation of phosphines into the polymer backbone.[124] Subsequent work was undertaken to simplify and improve the process, and to obtain purer polymers.

The preparation of monomers suitable for the polymerization process is illustrated in Scheme 16. Because newer aryl amination conditions allow the cross-coupling of aryl chlorides, monomer **52b** was prepared. The precursor **5b** is synthesized more directly than its bromo analogue, **5a**, by the coupling of 4-chloroaniline with **1** followed by BOC-protection, as shown in Scheme 4 (Chapter 1). The monomers are easily purified by recrystallization from isopropanol; the deprotection byproduct, benzophenone oxime, remains in solution.

Scheme 16.[a]



[a] : **52a** and **53** were first prepared by Dr. Thomas Mackewitz.

Polymerization of **52a**, using the initially developed procedure (trituration of the polymerization product followed by BOC-protection) afforded a red-brown solid, soluble in chloroform and dichloromethane. A considerable quantity of a rubbery red solid, insoluble in dichloromethane, *N,N*-dimethylacetamide and pyridine, was also formed. On prolonged drying, this material formed opaque, elastic leaves, which could not be pulverized. The material was analyzed by infrared spectroscopy of a neat sample; the salient features of the spectrum were sharp peaks assigned to the

carbonyl and N–H stretches. The byproduct is thus believed to be a fraction of the crude coupling product which did not undergo the BOC-protection reaction. A similar byproduct formed to varying extents in all polymerizations, except run 4 in Table 8.

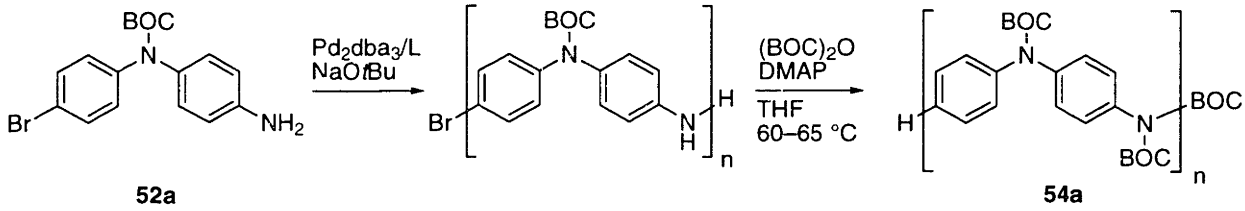
Reprecipitation of the soluble fraction from a mixture of dichloromethane and ethanol was found to afford **54a** as a tan powder, with a very clean ^{1}H NMR spectrum showing a single resonance at 7.14 ppm for the aryl protons, and a singlet at 1.44 ppm for the BOC protons. Analysis by ^{31}P showed no detectable peaks after several thousand scans, indicating that BINAP was successfully removed in the reprecipitation, and that incorporation of phosphine into the polymer itself is minimal. The solubility of the product in tetrahydrofuran was slight, but sufficient to permit analysis by gel permeation chromatography.

Selected results[125] for the polymerization of **52a**, by the original procedure and by certain variations on it, are presented in Table 8. It should be noted that the BOC groups account for slightly over half the molecular weight of the polymers. For comparison, polyaniline prepared by room-temperature persulfate oxidation of aniline has M_w = 52,700, M_n = 21,000; PDI = 2.5.[126] Other studies have reported much lower and broader molecular weight distributions: M_w = 69,000, M_n = 7,700; PDI = 9.0.[127] Oxidation at low temperatures in the presence of lithium chloride gives polymers with much higher molecular weights (M_w = 153,000; M_n and PDI not reported).[128] Electrochemical polymerization has been shown to give a polymer with M_w = 22,000–40,000, M_n = 14,000–21,000. Again, the addition of lithium chloride has been used to obtain very large molecular weights, as high as M_w = 160,000.[129]

The molecular weights reported here for BOC-protected polyanilines, measured with respect to polystyrene standards, are relative; however, they are believed to be reasonably accurate. For example, nonamer **21**, with a molecular weight of 1,859, was measured by GPC to have M_n = 1,957, an error of 5 %. Endgroup analysis of a short polymer (**54a**, run 2) may be carried out by integration of its ^{1}H NMR spectrum.

A singlet at 7.14 ppm predominates in the aryl region, but a faint doublet at 7.40 ppm, similar to that seen in the spectrum of 24-mer **38** (Figure 7, Chapter 1) is visible. The relative intensities of these resonances indicated a DP of approximately 12 (corresponding to M_n = 4,800), in very close agreement with the M_n of 4,820 measured by GPC. Attempts to measure the molecular weights of polymers **54a** by GPC using light-scattering detection[130] gave highly misleading results, probably because of the pale red-brown color of the solutions.

Table 8.[a]



52a **54a**

Run	Ligand	Solvent	Rxn Temp (°C)	Time (h)	Yield **54a** (%)[b]	M_w[c]	M_n[c]	DP[d]
1[e,g]	*rac*-BINAP	$PhCH_3$	80	24	44	45,300	11,400	29
2[e]	*rac*-BINAP	$PhCH_3$	80	24	44	16,900	4,820	12
3[e,h]	DPEphos	THF	65	18	69	23,200	10,900	28
						1,790	1,440	3
4[e]	DPEphos	CH_2Cl_2	65	18	69	9,640	4,170	10
5[f]	**48**	THF	60	1	65	42,900	12,500	32
6[f]	**48**	THF	60	8	63	34,500	12,100	31

(a) Conditions listed in table refer to the polymerization reaction. Substrate concentration: runs 1–2, 0.33 M; runs 3–6, 0.25 M. Except for run 1, only the CH_2Cl_2-soluble fraction was subjected to BOC-protection. BOC-protection was carried out using 0.2–0.5 eq. DMAP, 1.4–1.5 eq. $(BOC)_2O$, 6–16 h. (b) Yields calculated based on M_n. (c) Relative values, measured by GPC and calibrated against polystyrene standards. (d) Number-averaged degree of polymerization, reflecting number of couplings per chain. Each monomer contains two aniline units. (e) 1 mol % $Pd_2(dba)_3$; 3 mol % L. (f) 0.5 mol % $Pd_2(dba)_3$; 2 mol % L. (g) Coupling product was triturated with H_2O, *i*-PrOH and Et_2O prior to BOC-protection. (h) Bimodal distribution; M_w/M_n ratio (PDI) artificially low due to overlap between peaks.

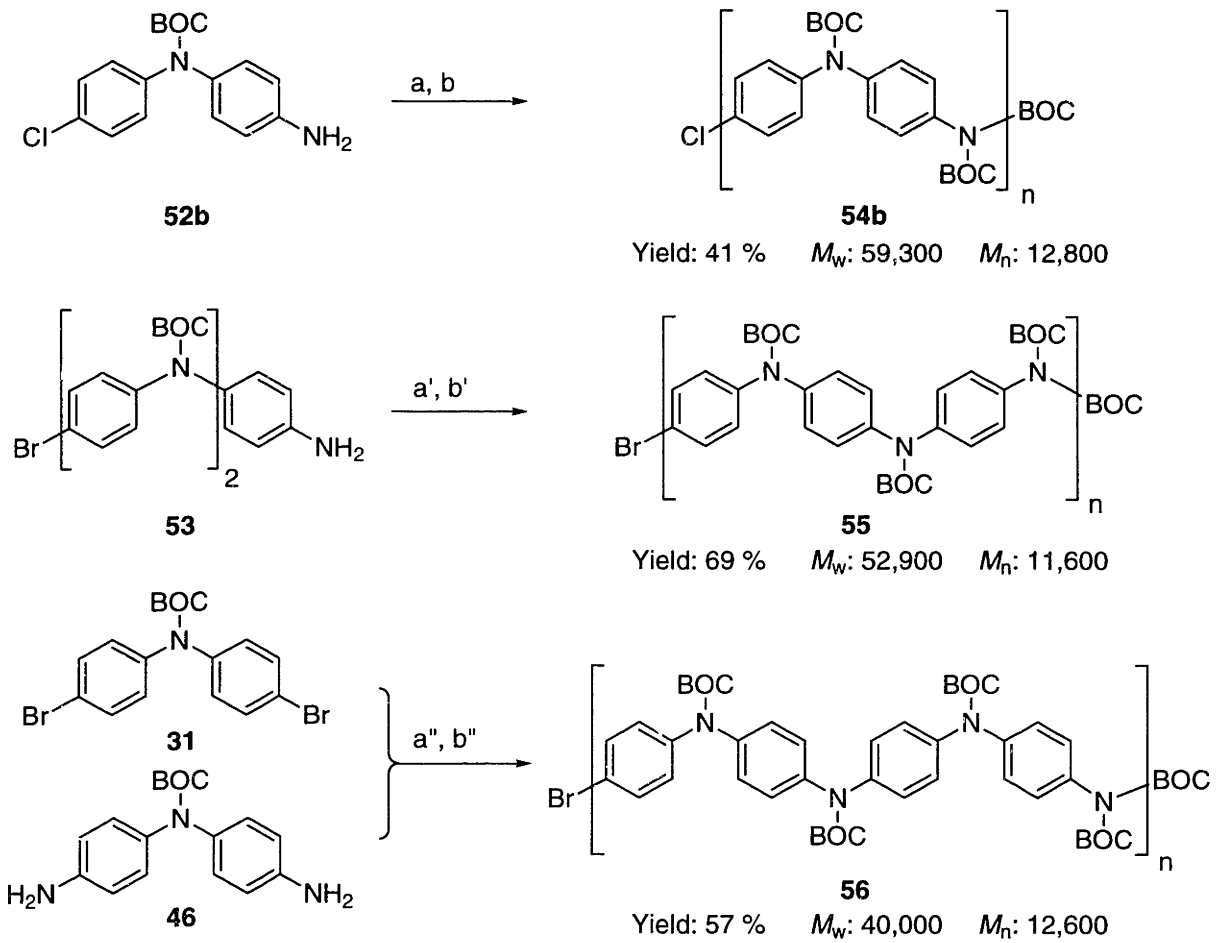
The polymer obtained after trituration of the coupling product, BOC-protection and reprecipitation was found to have a weight-averaged molecular weight (M_w) of 45,300 and a number-averaged molecular weight (M_n) of 11,400. These weights correspond to a polydispersity index (PDI) of 4.0, and a number-averaged degree of polymerization (DP, the average number of couplings per chain) of over 29. Since the monomer is derived from an aniline dimer, the average chain length is greater than 58 aniline units. When the crude polymerization product of **52a** was dissolved in dichloromethane (to the extent possible), subjected to an aqueous workup and filtered prior to BOC-protection, the molecular weight was lower (run 2: M_w = 16,900, M_n = 4,820; PDI = 3.5). It appears, then, that part of the insoluble portion of the coupling product is solubilized on conversion to the fully BOC-protected material.

The palladium-catalyzed polymerization of **52a** was also carried out using DPEphos as the supporting ligand. The polymerization in toluene gave a product similar to that obtained using BINAP as a ligand; the trituration procedure was necessary to prepare the insoluble coupling product for BOC-protection. When the polymerization was carried out in tetrahydrofuran (run 3), the crude polymerization product dissolved readily in dichloromethane, and an aqueous workup could be carried out. The BOC-protected product showed a bimodal distribution, with a low-molecular-weight shoulder indicating the presence of oligomeric materials. A soluble initial product was also obtained when the polymerization was carried out in dichloromethane (run 4); the molecular weight for the isolated product was rather low.

The use of 2-(di-*tert*-butylphosphino)biphenyl (**48**) as the supporting ligand (run 5, 6) resulted in a more rapid and efficient polymerization than was achieved using DPEphos. The higher M_w obtained in run 5, compared to run 6, is puzzling and may be anomalous; the noteworthy point is that the polymerization is apparently complete after the shorter period of time. The ^1H and ^{13}C NMR spectra for the product of run 6 are shown in Figure 23; note that the polymer endgroups are not discernible.

Figure 23. ^{1}H and ^{13}C NMR spectra of **54a** in $CDCl_3$.

Scheme 17.



Key: Products isolated by reprecipitation from CH_2Cl_2/EtOH. Molecular weights measured by GPC (polystyrene standards). (a) $Pd_2(dba)_3$, 1.0 mol %; **48**, 4.0 mol %; NaO*t*Bu, 1.4 eq; THF, 2 mL per mmol **52b**; 80 °C, 8 h. (b) $(BOC)_2O$, 2.0 eq; DMAP, 0.5 eq.; THF, 10 mL per mmol **52b**; 65 °C, 6 h. (a') $Pd_2(dba)_3$, 0.5 mol %; **48**, 2.0 mol %; NaO*t*Bu, 1.4 eq.; $PhCH_3$, 2 mL per mmol **53**; 80 °C, 6 h. (b') $(BOC)_2O$, 3.0 eq; DMAP, 0.5 eq.; THF, 5 mL per mmol **53**; pyridine, 1 mL per mmol **53**; 65 °C, 4 h. (a") $Pd_2(dba)_3$, 0.5 mol % per bromide; **48**, 2.0 mol % per bromide; NaO*t*Bu, 1.4 eq per bromide.; THF, 4 mL per mmol **31**; 80 °C, 6 h. (b") $(BOC)_2O$, 2.0 eq per amine; DMAP, 0.5 eq. per amine; THF, 10 mL per mmol **46**; 65 °C, 6 h.

Other polymerization reactions carried out using the 2-(di-*tert*-butylphosphino)-biphenyl-based catalyst system are shown in Scheme 17.[125] Polymer **54b**, derived from aryl chloride monomer **52b,** was spectroscopically identical to polymers prepared from the corresponding aryl bromide, with a similar molecular weight. Monomer **53**, prepared from a trimer bromide, was also converted easily to a polymer

(**55**). It was hoped that the higher proportion of protected nitrogen atoms in the coupling product (two-thirds, rather than one-half) would increase its solubility, and that higher molecular weights would be attained before the coupling product precipitated from solution. The molecular weight of the protected polymer, however, was similar to those observed in the polymerization of dimer derivatives **52a** and **52b**. Finally, the copolymerization of dibromide **31** with diamine **46**, followed by BOC-protection, afforded a soluble polymer (**56**) with molecular weight comparable to those of the other polymers. For simplicity, polymer **56** is shown with bromo and amino endgroups, although the α,ω-dibromo- and α,ω-diamino-teminated polymers are expected to be present as well. The ^{1}H and ^{13}C NMR spectra of this copolymer were identical to those observed for the other polymers (except the short polymers in Table 8, run 2 and run 4). The chain length is thus too large for the difference in end groups to be discernible.

The polydispersities of polymers **54–56** are high, ranging from 2.3 for the low-molecular-weight **54a** prepared in dichloromethane, to 4.6 for **54b**. The reason for this is unclear at this time; the effect of various reaction parameters on the molecular weight distribution needs further investigation, and the optimum reaction conditions remain to be determined. The degrees of polymerization, although low compared to those of conventional polyaniline, are well above those required for substantial conductivity,[28] and compare favorably with those obtained in other polymerization reactions based on palladium-catalyzed aryl amination.[120, 121]

In summary, the methods developed for the synthesis of controlled-length oligoaniline derivatives have been adapted to the preparation of polyaniline derivatives. The polymerization has been demonstrated using aniline dimer derivatives, including an aryl chloride, and an aniline trimer derivative. The copolymerization of a diamine with a dibromide has also been achieved. A two-step sequence of coupling and acylation affords the fully BOC-protected leucoemeraldine

form, which is highly soluble in chlorinated solvents, and sufficiently soluble in tetrahydrofuran to permit molecular weight determination by gel permeation chromatography. This methodology is potentially adaptable to the synthesis of polymers bearing substituents on every two, three or more rings, depending on the choice of monomer; an alternating sequence of substituents should be accessible through the copolymerization of diamines with dibromides.

3.3—Synthesis of a Soluble Aminophenothiazine Polymer

A variety of oligoaniline and polyaniline derivatives are accessible using palladium-catalyzed cross-coupling to construct the carbon-nitrogen bond framework. As new, more active catalyst systems have been developed, a wider range of substrates may be employed. The palladium catalyst system using 2-(di-*tert*-butylphosphino)biphenyl (**48**) as supporting ligand, for example, is capable of coupling anilines with highly electron-rich aryl bromides. This catalyst system appeared promising for the construction of novel polyaniline analogues containing electron-rich heterocycles.

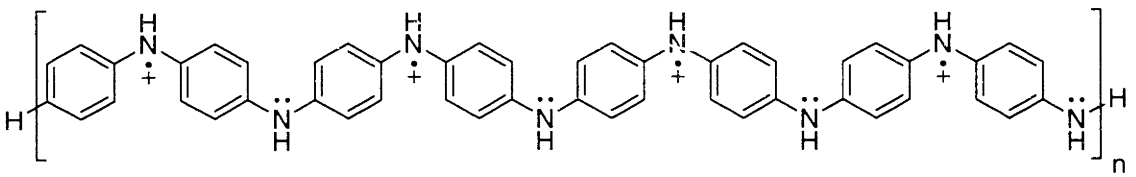
Previous examples of polymers of this type include copolymers of aniline with five-membered heterocycles. Aniline-thiophene copolymers may be prepared with a random sequence, by the oxidative copolymerization of aniline in the presence of thiophene,[131] or in controlled sequence by the oxidative polymerization of 4-thienylanilines.[132] The latter polymers were doped to give semiconducting materials, with conductivities of up to 10^{-3} S/cm. A related polymer was obtained by the copolymerization of dibromothiophenes with *p*-phenylenediamines under Ullmann conditions.[133] Aniline has also been copolymerized with bithiophene[134] and pyrrole.[135]

The chemistry of the electron-rich heterocycle phenothiazine, which is commercially available and inexpensive, has been studied extensively. Its derivatives

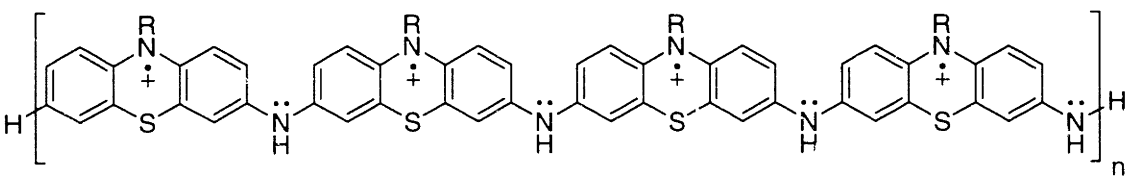
have found widespread use as dyes; methylene blue is an oxidized diaminophenothiazine. A number of phenothiazines are pharmacologically active, displaying anthelmintic, antitrypanosomal, and antileishmanial activity.[136] Several *N*-alkylphenothiazine derivatives such as chlorpromazine show sedative or antipsychotic activity and are used in the treatment of mental disorders.[137]

Phenothiazine adopts a nonplanar conformation to minimize the antiaromatic character of its 16-electron π-system. The loss of an electron from this system is quite facile, and phenothiazines readily form stable radical cations.[138] Even these monomeric species have been shown to be semiconductors, with conductivities as high as 10^{-4} S/cm.[139] Analogues of polyaniline incorporating phenothiazine moieties might display a greater polyradical character than the parent polyaniline. The structures are compared in Figure 24. In the phenothiazine-derived polymer, the radical cations would presumably be delocalized in the phenothiazine ring system; to emphasize the analogy, the polymer is depicted with nitrogen-centered radicals.

Polyaniline, emeraldine form:



Poly(3-amino-10-alkylphenothiazine), "emeraldine form":



R = alkyl

Figure 24. Conductive forms of polyaniline and proposed phenothiazine polymer.

The conductive form of polyaniline, as stated previously, is typically depicted as a repeating semiquinoid cation in discussions of its conductivity. This representation is exaggerated, however. ESR studies of the protonated emeraldine form have shown

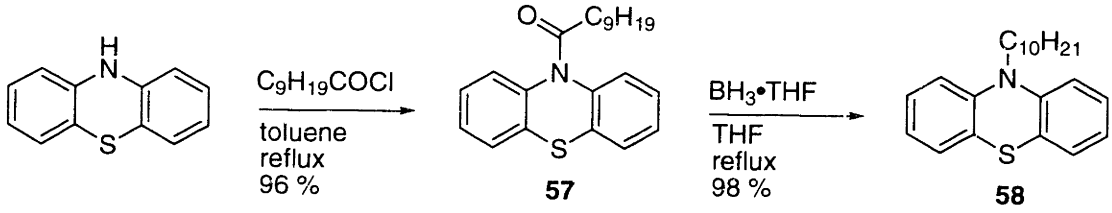
spin densities of approximately 0.1 spins per octamer unit,[140] and our own studies (Chapter 1, section 1.4) indicate that the formation of odd-electron oligoanilines is unfavorable. The discrepency between the predicted and actual conductivity of polyaniline,[19] discussed in the Introduction, might be related in part to the predominance of electron-pairing in the conduction band. A polymer based on a 3-aminophenothiazine repeat unit would be of interest as an emeraldine analogue with more accessible polyradical forms. The conductivity of this polymer, relative to that of polyaniline, might be higher, due to the increase in unpaired electron character, or lower, due to the non-degeneracy of the nitrogen atoms and the resulting greater localization of the cation radicals.

The tricyclic molecule phenothiazine is substantially less soluble in most solvents than diphenylamine, due to its greater rigidity. Aminophenothiazine polymers might therefore be expected to be quite intractable relative to polyaniline; however, the expected decrease in solubility may be offset by the incorporation of *N*-alkyl groups. The solubility of *N*-alkylpolyanilines in solvents such as tetrahydrofuran is improved greatly relative to polyaniline. The electrical conductivity, however, is decreased considerably, because steric interactions between the substituent and the ortho-hydrogen atoms of the aryl rings diminish the conjugation between rings.[25] In phenothiazine, the constrainment of the aryl rings by the sulfur atom would prevent this disruption.

The phenothiazine-derived polymer was synthesized with *n*-decyl groups at the 10-position, the ring nitrogen atom, of each phenothiazine group. The synthetic strategy consisted of the palladium-catalyzed copolymerization of a diamine and a dibromide, both prepared from a common precursor. The goal of this strategy was to obtain the electroactive polymer in a soluble form, directly from the coupling of relatively simple monomers, without resorting to the use of protective groups.

The preparation of 10-decylphenothiazine (**58**) has been acomplished previously, in less than 10 % yield, by the alkylation of phenothiazine with *n*-decyl bromide, using copper metal as a catalyst.[141] We found it more convenient to prepare this compound in two nearly quantitative steps, as shown in Scheme 18. Phenothiazine was converted to its 10-decanoyl derivative by heating with decanoyl chloride in toluene according to a standard acylation procedure; no added base is necessary.[142] The reaction is conveniently carried out on large scale, and the product **57** is easily purified by recrystallization. The reduction of **57** to **58** is accomplished cleanly by heating with borane in tetrahydrofuran solution.[143]

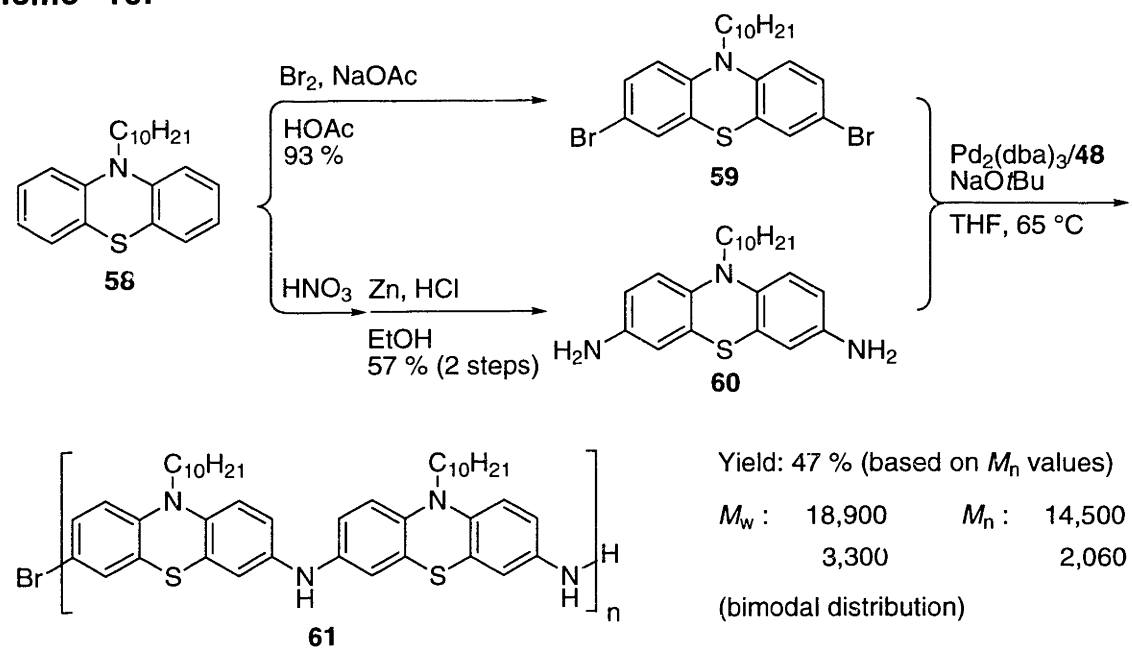
Scheme 18.



The electrophilic substitution of 10-alkylphenothiazines generally occurs under mild conditions, with the 3- and 7-positions the preferred sites for electrophilic attack. Bromination of 10-decylphenothiazine, using bromine in acetic acid buffered with sodium acetate, affords 3,7-dibromo-10-decylphenothiazine **59** in high yield. The analogous bromination of 10-methylphenothiazine had been reported previously.[144] Similarly, treatment of 10-ethylphenothiazine with nitric acid is known to form 3,7-dinitro-10-ethylphenothiazine-5-oxide.[145] Nitration of 10-decylphenothiazine in this fashion, followed by reduction with zinc in acetic acid, afforded 3,7-diamino-10-decylphenothiazine (**60**) in 57 % yield. Both **59** and **60** were obtained in regiopure form; their ^1H NMR spectra were consistent with the 3,7-disubstitution pattern, and no resonances due to other regioisomers were apparent. The preparation of NMR samples from **60** requires the use of degassed solvents under inert atmosphere, to avoid excessive paramagnetic line-broadening.

The palladium-catalyzed copolymerization of **59** with **60** may be achieved in tetrahydrofuran solution, using di-(*tert*-butylphosphino)biphenyl (**48**) as the supporting ligand and sodium *tert*-butoxide as base. The resulting polymer, poly(3-amino-10-decylphenothiazin-7-yl) (**61**, Scheme 19), is apparently somewhat air-sensitive in solution, although an aqueous workup of the reaction mixture is possible if sodium dithionite is present as a reducing agent. The polymer could also be reprecipitated from a mixture of dichloromethane and ethanol, containing a trace of hydrazine hydrate, under a slow stream of nitrogen. The product is obtained in moderate yield as an amorphous solid.

Scheme 19.



Yield: 47 % (based on M_n values)

M_w : 18,900 M_n : 14,500

3,300 2,060

(bimodal distribution)

In contrast to the polyaniline derivatives described in Section 3.2, polymer **61** is considerably more soluble in tetrahydrofuran than in chlorinated solvents, and appears to be sparingly soluble in benzene or toluene. Characterization by NMR was therefore carried out in tetrahydrofuran-d_8 solution. As in the case of **60**, some care must be taken to exclude air from the solution. The ^{1}H NMR spectrum shows a pattern of broadened singlets consistent with the desired structure; the ^{13}C NMR spectrum

displays a similar pattern to that of **60**, indicative of comparably electron-rich phenothiazines arranged in a pseudo-symmetric structure.

Analysis of a tetrahydrofuran solution of **61** by gel permeation chromatography, calibrated relative to polystyrene standards, showed two overlapping peaks of equal intensity. The peak at lower molecular weight indicated the presence of oligomers, with M_w = 3,300, and M_n = 2,060, corresponding to *ca* 6 phenothiazine units. The peak at higher molecular weight shows the presence of longer polymers, with M_w = 18,900, and M_n = 14,500, corresponding to *ca* 40 phenothiazine units. Note that the M_w/M_n ratios are artificially low, due to the overlap between peaks.

Further studies will be necessary to improve the polymerization reaction, to obtain longer polymers with monomodal molecular weight distributions. Electrochemical studies of the aminophenothiazine polymer remain to be carried out, for comparison to polyaniline. At present, a relatively simple route to a new π-conjugated polymer has been demonstrated, using palladium-catalyzed aryl amination to copolymerize simple monomers. This polymer represents one of the numerous novel architectures which are potentially accessible using palladium-catalyzed carbon-nitrogen bond formation.

Experimental Procedures

General Information. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Varian XL-300, UN-300, Mercury 300 or VXR-500 spectrometers and referenced with respect to residual solvent. Phosphorus nuclear magnetic resonance spectra were recorded on Varian UN-300, Mercury 300 or VXR-500 spectrometers and referenced with respect to an external 85 % phosphoric acid standard. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR spectrometer, or by placing a few milligrams of the neat compound on the DiComp probe tip of an ASi ReactIR 1000 *in situ* infrared spectrometer. UV–Vis spectra were obtained using a Hewlett-Packard 8453A spectrophotometer. FAB mass spectra were recorded on a Finnigan MAT System 8200 using a 3-nitrobenzyl alcohol matrix. Elemental analyses were carried out by E & R Microanalytical Laboratory Inc., Parsippany, NJ, or by Atlantic Microlab Inc., Norcross, GA. Gas chromatographic analyses were carried out on a Hewlett-Packard HP-5890 Series II gas chromatograph, fitted with an HP-1 capillary column (25 m, 0.20 mm, 0.11 μm). Thin layer chromatography was carried out on E. Merck SIlica Gel 60 F-254 TLC plates. Preparative flash column chromatography was performed on ICN flash silica gel, 32–63 μ, 230–400 mesh. Melting points were obtained using a Haake Buchler or MelTemp melting point apparatus and are uncorrected.

Reactions under an argon atmosphere were carried out in oven-dried glassware using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Toluene was distilled under nitrogen from molten sodium. Dichloromethane used in oligomer deprotections was purchased in anhydrous form from Aldrich Chemical Company and stored under nitrogen over activated 3Å molecular sieves. Absolute ethanol was purchased from Pharmco and used as supplied. Diethyl ether, analytical reagent grade, was purchased from Mallinckrodt and used as supplied. *N*-Methylpyrrolidinone, anhydrous, and *N,N*-dimethylformamide, reagent grade, were purchased from Aldrich Chemical Company

and used as supplied. Tetrahydrofuran-d_8 and C_6D_6 used for ^1H NMR spectroscopy of air-sensitive compounds were vacuum-transferred from sodium benzophenone ketyl and stored in a Vacuum Atmospheres glovebox under nitrogen. Other deuterated solvents were purchased from Cambridge Isotope Laboratories and used as supplied. All other solvents were of liquid chromatography grade quality, purchased from EM Science and used as supplied.

Molecular sieves were purchased from Aldrich Chemical Company and activated at 180 °C and 10^{-3} mm Hg for 12 hours prior to use. Sodium *tert*-butoxide was purchased from Aldrich Chemical Company and stored in a Vacuum Atmospheres glovebox under nitrogen. Small amounts were removed from the glovebox as needed, stored in a dessicator for up to one week, and weighed in the air. 4-Bromoaniline, 4-chloroaniline, benzophenone, chlorotrimethylsilane, *p*-anisidine, di-*tert*-butyl dicarbonate solution (1.0 M in tetrahydrofuran), tetra-*n*-butylammonium tribromide, palladium hydroxide (moist, 20 % on carbon), 1,4-phenylenediamine dihydrochloride, aniline, diphenylamine, 4-bromo-*tert*-butylbenzene, 4-bromobenzonitrile, ammonium formate, hydroxylamine hydrochloride, hexamethyldisilane, benzophenone imine, methanesulfonic acid, imidazole, phenothiazine, decanoyl chloride, and borane (1.0 M in tetrahydrofuran) were purchased from Aldrich Chemical Company and used as supplied. Di-*tert*-butyl dicarbonate, 4-dimethylaminopyridine, 2-bromobiphenyl, 3-aminobenzonitrile, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, and 5-amino-2-bromobenzotrifluoride were purchased from Lancaster Synthesis Inc. and used as supplied. 4-Bromo-*n*-dodecylbenzene was purchased from TCI America and used as supplied. *tert*-Butyldimethylsilyl chloride was purchased from FMC Chemical and used as supplied. Tribasic potassium phosphate, anhydrous, was purchased from Fluka and used as supplied. Cesium carbonate, a gift from Chemetall, was used as supplied. *S*-BINAP, a gift from Pfizer, was used as supplied. *rac*-BINAP, tris(dibenzylidene-acetone)

dipalladium, palladium acetate, palladium chloride, palladium on carbon, *n*-butyllithium (1.60 M in hexanes), bromine, copper (I) chloride, diphenylchlorophosphine and di-*tert*-butylchlorophosphine were purchased from Strem Chemical Company and used as supplied. All other inorganic reagents were analytical reagent grades, purchased from Mallinckrodt and used as supplied. Substrates for methodological investigations, unless otherwise indicated in the experimental section, were purchased from commercial sources and used as supplied, except that liquid amines and 4-bromo-1,2-(methylenedioxy)benzene were filtered, neat, through a small column of activated alumina prior to use. The ligand Xantphos[84] was prepared by Ms. Michele C. Harris. The ligand 2-(dicyclohexylphosphino)-biphenyl (**49**) was prepared by Dr. John P. Wolfe.[92]

Synthesis—Chapter 1

***N*-(Diphenylmethylene)-4-bromoaniline (1).** The method of Taguchi and Westheimer[145] was modified as follows: Benzophenone (455 g, 2.50 moles), 4-bromoaniline (473 g, 2.75 moles), and molecular sieves (5Å, 1.25 kg), were placed in an oven-dried 5-L flask, which was fitted with a reflux condenser and a vacuum adapter. The flask was evacuated and backfilled with argon. The vacuum adapter was replaced with a rubber septum, and a needle attached through Tygon tubing to an oil bubbler was inserted through the septum. Toluene (1.2 L) was added via syringe, and the resulting mixture was heated to gentle reflux and shaken occasionally; an intense yellow color soon developed. Analysis by GC after 18 hours showed that product formation was nearly complete. The mixture was allowed to cool to room temperature, and the yellow solution was decanted from the molecular sieves, which were washed with diethyl ether until the filtrate was colorless. The organic solutions were combined and concentrated *in vacuo* to give an orange oil, 900 mL. Methanol (*ca.* 80 mL) and a seed crystal of authentic product were added. The product was allowed to crystallize at 0 °C and collected by filtration. The mother liquor was further

concentrated. A second crop of crystals formed and was isolated by filtration. Recrystallization of the combined product from methanol afforded the title compound as yellow crystals (760 g, 90 %): mp 82–83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, J = 6.9, 1.6 Hz, 2H), 7.52–7.39 (m, 3H), 7.32–7.23 (m, 5H), 7.11 (dd, J = 8.4, 1.9 Hz, 2H), 6.61 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 150.4, 139.5, 136.1, 131.6, 131.0, 129.5, 128.8, 128.3, 128.2, 122.8, 116.3, 103.6; IR (neat, cm^{-1}) 3058, 3024, 1615, 1478. Anal. Calcd for $C_{19}H_{14}BrN$: C, 67.87; H, 4.20. Found: C, 68.08; H, 4.28 .

4-(Trimethylsilyl)aniline (2a).[61] Aryl bromide **1** (16.8 g, 50.0 mmol) was dissolved in tetrahydrofuran (250 mL) in a dry Schlenk flask under argon. The resulting solution was cooled with stirring to –78 °C. A solution of *n*-butyllithium in hexanes (1.60 M, 31.5 mL, 50.4 mmol) was added dropwise via syringe, causing the yellow solution to turn a deep red color. The reaction mixture was stirred for 30 minutes at –78 °C. Chlorotrimethylsilane (6.5 mL, 51 mmol) was added dropwise *via* syringe over 5 min, causing the red solution to turn a light orange color. The reaction mixture was warmed to room temperature and stirred for 45 min. Triethylamine (10 mL) and methanol (20 mL) were added, resulting in a cloudy, pale yellow suspension. The suspensions obtained from two reactions carried out in this manner were combined and concentrated; the solid residue was taken up in diethyl ether (250 mL) and washed with brine (100 mL). The aqueous phase was extracted with two 75-mL portions of diethyl ether. The organic solutions were combined, dried over potassium carbonate, filtered, and concentrated.

The crude imine, a yellow solid, was dissolved in methanol (200 mL) in an Erlenmeyer flask. Sodium acetate (16.4 g, 200 mmol) and hydroxylamine hydrochloride (10.4 g, 150 mmol) were added with rapid stirring. After 5 min, solid potassium bicarbonate (15 g, 150 mmol) was added, and the mixture was stirred for 30 min. Diethyl ether (100 mL) was added, and the mixture was filtered to remove

precipitated salts. The collected solid was dissolved in water (200 mL), and the resulting solution was extracted with two 50-mL portions of diethyl ether. The combined organic solutions were dried over potassium carbonate, filtered, and concentrated. The residue was taken up in dichloromethane (20 mL), cooled to –78 °C, and filtered to remove the precipitated benzophenone oxime. The collected solid was suspended in dichloromethane to dissolve adsorbed **2**, and the mixture was cooled to –78 °C and filtered. The filtrates were combined and concentrated *in vacuo*, and the precipitation of benzophenone oxime was repeated as described above. The crude aniline was distilled from calcium hydride under high vacuum, affording the title compound as a colorless oil (14.1 g, 85 %): bp 44 °C/0.01 mm Hg (lit.[61] 102 °C/6 mm Hg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 8.1 Hz, 2H), 3.75 (s, 2H), 0.29 (s, 9H).

4-(Trimethylsilyl)aniline/Diphenylmethane (2b). The halogen-metal exchange/trimethylsilylation sequence and workup described above were used to convert *N*-(diphenylmethylene)-4-bromoaniline (13.31 g, 39.6 mmol) to *N*-(diphenylmethylene)-4-(trimethylsilyl)aniline. Recrystallization from methanol afforded the imine as yellow crystals, 11.49 g (88 %): mp 92–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.47–7.40 (m, 3H), 7.31–7.25 (m, 5H), 7.16–7.12 (m, 2H), 6.73 (d, J = 8.2 Hz, 2H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 151.8, 140.0, 136.4, 134.5, 133.8, 130.9, 129.8, 129.5, 128.8, 128.4, 128.1, 120.5, –0.8; IR (neat, cm^{-1}) 3066, 3051, 3037, 3024, 2956, 2894, 1972, 1615, 1590, 1548, 1492, 1445, 1389, 1318, 1293, 1277, 1245, 1225, 1185, 1110, 1073, 959, 913, 837, 824, 782, 758, 724, 693. Anal. Calcd for $C_{22}H_{23}NSi$: C, 80.19; H, 7.04. Found: 80.09, 6.98.

The recrystallized imine may be cleaved by hydrogenolysis; the resulting mixture consists of equimolar 4-trimethylsilylaniline and diphenylmethane, and is sufficiently pure to be used in aryl amination reactions. The imine (1.65 g, 5.00 mmol), ammonium formate (3.78 g, 60.0 mmol), and palladium on carbon (10 wt. %, 0.532 g,

0.50 mmol Pd) were placed in a dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and methanol (30 mL) was added via syringe.[146] The septum was replaced with a loose-fitting plastic cap, and the reaction mixture was heated to 60 °C with stirring. A steady effervescence began within a few seconds. Analysis of the reaction mixture by TLC after 3 h indicated complete consumption of the starting imine. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in diethyl ether (50 mL), filtered through Celite, and concentrated *in vacuo*. The product was obtained as a colorless oil, 1.60 g (mass balance, 96 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.35 (m, 6H), 7.29–7.26 (m, 6H), 6.75 (d, J = 8.3 Hz, 2H), 4.07 (s, 2H), 3.72 (broad s, 2H), 0.320 (s, 9H). Residual diethyl ether is also present to the extent of 3 mol % (*ca.* 1 wt. %) as judged by integration. This crude product may be used without further purification.

Dimer 3. Aryl bromide **1** (25.15 g, 74.8 mmol), arylamine **2a** (13.0 g, 78.6 mmol), sodium *tert*-butoxide (10.06 g, 105 mmol), tris(dibenzylideneacetone) dipalladium (0.171 g, 0.187 mmol, 0.25 mol %), and *S*-BINAP (0.349 g, 0.560 mmol, 0.75 mol %) were placed in a dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (75 mL) was added via syringe. The reaction mixture was heated to a gentle reflux. Analysis by TLC after 17 h showed complete consumption of aryl bromide **1**. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (200 mL), washed with brine, dried over potassium carbonate, and concentrated. The crude product, 4-dimethyl-aminopyridine (1.64 g, 13.4 mmol, 20 mol %), and di-*tert*-butyl dicarbonate (21.90 g, 100 mmol) were dissolved in tetrahydrofuran (67 mL) in a Schlenk flask under argon. The resulting solution was heated to 60 °C with stirring. After 2 h the solution was cooled to room temperature and concentrated *in vacuo*. Crystallization of the product

from methanol afforded dimer **3** as pale yellow crystals (32.89 g, 84 %): mp 123–124 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.0 Hz, 2H), 7.49–7.40 (m, 5H), 7.28 (d, J = 6.2 Hz, 3H), 7.19 (d, J = 8.2 Hz, 4H), 6.98 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.7 Hz, 2H), 1.41 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 154.0, 149.5, 143.9, 139.8, 138.4, 137.0, 136.4, 133.8, 131.0, 129.7, 129.5, 128.8, 128.4, 128.1, 127.9, 125.3, 121.6, 81.1, 28.4, –0.9; IR (neat, cm^{-1}) 3059, 3022, 2954, 1711, 1500, 1327, 1162, 852. Anal. Calcd for $C_{33}H_{36}N_2O_2Si$: C, 76.11; H, 6.97. Found: C, 76.06; H, 7.18.

Dimer amine 4. A Schlenk flask was charged with dimer **3** (3.64 g, 7.00 mmol), ammonium formate (5.30 g, 84.0 mmol), and palladium on carbon (10 wt. %, 0.740 g, 0.70 mmol Pd) and purged with argon. Methanol (100 mL) was added, and the resulting mixture was heated with stirring to 60 °C. Analysis by TLC after 45 min showed complete consumption of imine **3**. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane, and the resulting solution was filtered through Celite and concentrated *in vacuo*. The white solid residue was triturated with hexanes (20 mL), cooled to 0 °C, and filtered to afford arylamine **4** as a white solid (2.25 g, 90 %): mp 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 8.5 Hz, 2H), 3.66 (s, 2H), 1.45 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 144.7, 144.1, 136.7, 134.1, 133.7, 128.8, 125.2, 115.4, 80.9, 28.4, –0.9; IR (neat, cm^{-1}) 3465, 3367, 3227, 2955, 1696, 1515, 1162, 852. Anal. Calcd for $C_{20}H_{28}N_2O_2Si$: C, 67.38; H, 7.92. Found: C, 67.54; H, 7.99.

Dimer bromide 5a. Procedure A: A Schlenk flask was charged with dimer **3** (7.29 g, 14.0 mmol) and sodium acetate (1.15 g, 14.0 mmol) and purged with argon. Tetrahydrofuran (100 mL) was added, and the resulting mixture was cooled to –78 °C with stirring. Bromine (1.50 mL, 29.1 mmol) was added dropwise, causing the mixture to turn a deep green-brown color. The mixture was stirred for 10 min at –78 °C, then warmed to 0 °C. Analysis by TLC after 20 min indicated complete consumption of

arylsilane **3**. A solution of sodium bicarbonate (0.5 M) and sodium sulfite (0.5 M) in water was added to the reaction mixture with vigorous stirring, dispelling the brown color. The mixture was transferred to a separatory funnel containing diethyl ether (50 mL). The phases were separated, and the aqueous phase was extracted with two 50-mL portions of diethyl ether. The ether portions were combined, dried over potassium carbonate, filtered, and concentrated *in vacuo*, giving a yellow oil which crystallized on standing. Recrystallization of the product from a 4:1 mixture of hexanes and ethyl acetate afforded aryl bromide **5** as pale yellow crystals (6.55 g, 89 %): mp 161–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.7 Hz, 2H), 7.49–7.36 (m, 5H), 7.28 (d, J = 8.8 Hz, 3H), 7.13 (dd, J = 7.8, 2.0 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 153.6, 149.6, 142.4, 139.5, 137.8, 136.2, 131.6, 131.0, 129.6, 129.5, 128.8, 128.4, 128.0, 127.7, 127.5, 121.6, 118.3, 81.3, 28.3; IR (neat, cm^{-1}) 3058, 2977, 1711, 1489, 1325, 1161, 697. Anal. Calcd for $C_{30}H_{27}BrN_2O_2$: C, 68.31; H, 5.16. Found: C, 68.53; H, 5.35.

Procedure B: Aryl bromide **1** (14.1 g, 41.8 mmol), aniline (4.00 mL, 43.9 mmol), sodium *tert*-butoxide (5.63 g, 58.5 mmol), $Pd_2(dba)_3$ (95.7 mg, 0.105 mmol, 0.50 mol % Pd), and *S*-BINAP (0.195 g, 0.314 mmol, 0.75 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (80 mL) was added via syringe. The reaction mixture was heated to a gentle reflux. Analysis by TLC after 24 hours showed complete consumption of the starting bromide. The mixture was cooled to room temperature, taken up in ethyl acetate (80 mL), and washed with a 2.0 M aqueous sodium hydroxide solution (80 mL), followed by brine (80 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated *in vacuo*. The residue was taken up in dichloromethane (88 mL), and tetra-*n*-butylammonium tribromide (23.3 g, 48.3 mmol) was added in one portion with stirring. After 30 min, a saturated aqueous solution of sodium sulfite (80 mL) was added. The mixture was

stirred for 10 min, then 2.0 M aqueous sodium hydroxide solution (40 mL) was added. The layers were separated and the organic phase was washed with brine (80 mL), dried over sodium sulfate, filtered. and concentrated *in vacuo*. The residual solid, 4-dimethylaminopyridine (0.536 g, 4.39 mmol, 11 mol %) and di-*tert*-butyl dicarbonate (1.054 g, 4.82 mmol) were dissolved in tetrahydrofuran (50 mL). The resulting solution was heated to reflux. After 3 h at reflux the solution was cooled to room temperature and concentrated *in vacuo*. Crystallization of the residue from methanol afforded aryl bromide **5a** as pale yellow crystals (18.7 g, 81 %). Spectroscopic data were identical to those reported above; mp 159–160 °C. Anal. Calcd for $C_{30}H_{27}BrN_2O_2$: C, 68.31; H, 5.16. Found: C, 68.52; H, 5.33.

Dimer chloride 5b. Aryl bromide **1** (5.04 g, 15.0 mmol), 4-chloroaniline (2.10 g, 16.5 mmol), sodium *tert*-butoxide (2.02 g, 21.0 mmol), tris(dibenzylidene)acetone dipalladium (34.3 mg, 0.0375 mmol, 0.5 mol % Pd), and DPEphos (48.5 mg, 0.090 mmol, 0.6 mol %) were placed in a dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (30 mL) was added via syringe. The reaction mixture was heated to 80 °C with stirring. Analysis by TLC after 6 h indicated the complete consumption of starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in diethyl ether (75 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and transferred to a dried Schlenk flask. The flask was stoppered, and the solution was concentrated *in vacuo*; the flask was then backfilled with argon and the stopper was replaced with a rubber septum.

Tetrahydrofuran (40 mL) was added to the crude coupling product via syringe. The flask was opened, and 4-dimethylaminopyridine (0.367 g, 3.00 mmol) was added in one portion. The septum was replaced, and the flask was purged with argon for 5 min. Di-*tert*-butyl dicarbonate (4.6 mL, 20 mmol) was added via syringe, and the resulting solution was heated to 65 °C with stirring. Effervescence began shortly

thereafter. Analysis by TLC after 3 h indicated the complete consumption of the starting amine and excess 4-chloroaniline. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in methanol (50 mL); the resulting solution soon deposited a yellow-orange precipitate. The mixture was cooled to 0 °C and the product was collected by filtration. Recrystallization from toluene/isopropanol gave a product which was pure as judged by TLC analysis; however, analysis by ^{1}H NMR even after prolonged drying under vacuum showed the presence of some residual isopropanol. Recrystallization from toluene/*n*-heptane afforded the title compound as yellow crystals, 5.89 g (81 %): mp 166–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.49–7.42 (m, 3H), 7.29–7.22 (m, 5H), 7.15–7.08 (m, 4H), 6.96 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 153.7, 149.6, 141.9, 139.6, 138.0, 136.2, 131.1, 130.5, 129.7, 129.5, 128.9, 128.7, 128.4, 128.1, 127.7, 127.3, 121.6, 81.4, 28.3; IR (neat, cm^{-1}) 3056, 3033, 3024, 3002, 2973, 1698, 1613, 1594, 1573, 1494, 1337, 1293, 1223, 1158, 1142, 1088, 1056, 1015, 959, 853, 836, 787, 768, 697, 677, 666. Anal. Calcd for $C_{30}H_{27}ClN_2O_2$: C, 74.60; H, 5.63. Found: C, 74.70; H, 5.62.

Tetramer 6. Dimer amine **4** (1.569 g, 4.40 mmol), dimer bromide **5** (2.11 g, 4.00 mmol), sodium *tert*-butoxide (0.538 g, 5.60 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.0.020 mmol, 1 mol % Pd), and DPEphos (23.7 mg, 0.044 mmol, 1.1 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (8 mL) was added via syringe. The reaction mixture was heated with stirring to 80 °C. Analysis by TLC after 24 h indicated complete consumption of the starting bromide. The mixture was cooled to room temperature, taken up in diethyl ether (100 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual solid and 4-dimethylaminopyridine (0.0977 g, 0.80 mmol, 20 mol %) were placed in an oven-dried Schlenk tube under

argon. Di-*tert*-butyl dicarbonate (1.25 mL, 5.44 mmol) was added via syringe, followed by tetrahydrofuran (16 mL). The resulting solution was heated with stirring to 60 °C. Analysis by TLC after 6 h indicated the complete consumption of the starting material. The solution was cooled to room temperature and concentrated *in vacuo*. Crystallization of the residual solid from ethanol afforded tetramer **6** as pale yellow microcrystals (3.21 g, 88 %): mp 131–133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.50–7.42 (m, 5H), 7.28 (m, 3H), 7.19–7.10 (m, 12H), 6.98 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 1.47 (s, 9H), 1.45 (s, 9H), 1.41 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 154.1, 154.0, 149.5, 143.5, 140.8, 140.6, 140.5, 139.8, 138.3, 137.8, 136.4, 134.0, 131.1, 129.8, 129.6, 129.0, 128.5, 128.2, 127.8, 127.5, 127.3, 127.2, 126.4, 126.2, 121.7, 81.6, 81.3, 28.4, –0.9; IR (neat, cm^{-1}) 3008, 2977, 1711, 1509, 1327, 1161, 851, 756. Anal. calcd for $C_{55}H_{62}N_4O_6Si$: C, 73.14; H, 6.92. Found: C, 72.79; H, 6.86.

Tetramer amine 7. Tetramer **6** (4.155 g, 4.6 mmol), ammonium formate (4.061 g, 64.4 mmol), and palladium on carbon (5 wt. %, 0.979 g, 0.460 mmol Pd) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and methanol (25 mL) and tetrahydrofuran (15 mL) were added via syringe. The resulting mixture was heated to 50 °C with stirring. Analysis by TLC after 11 h indicated complete consumption of the starting imine. The mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (75 mL), and the resulting mixture was filtered through Celite and concentrated. The white solid residue was triturated with hexanes (30 mL), cooled to 0 °C, and collected by filtration to afford amine **7** as a white solid (3.24 g, 95 %): mp 190–192 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 5.0 Hz, 2H), 7.18–7.09 (m, 10H), 6.97 (d, J = 5.0 Hz), 6.62 (d, J = 5.0 Hz, 2H), 3.67 (s, 2H), 1.46 (s, 9H), 1.44 (s, 18H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 153.91, 153.88, 144.8, 143.4, 141.2, 140.4, 140.4, 139.6, 137.7,

133.9, 133.9, 129.01, 128.6, 127.4, 127.2, 127.1, 126.4, 126.2, 126.0, 115.4, 81.4, 81.4, 81.0, 28.4, 28.4, 28.4, –0.9; IR (neat, cm^{-1}) 3472, 3366, 2978, 1708, 1508, 1331, 1161, 1055, 844. Anal. Calcd for $C_{42}H_{54}N_4O_6Si$: C, 68.26; H, 7.36. Found: C, 68.38; H, 7.52.

Tetramer bromide 8. Tetramer (5.09 g, 5.64 mmol) and sodium acetate (0.463 g, 5.64 mmol) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (30 mL) was added via syringe. The reaction mixture was cooled to –78 °C with stirring, and bromine (0.58 mL, 11.2 mmol) was added dropwise via syringe; the reaction mixture turned a deep green-brown color. The mixture was stirred for 10 min at –78 °C, then warmed to 0 °C. Analysis by TLC after 20 min indicated the complete consumption of the arylsilane starting material. The flask was opened, and the mixture was added via pipette to a rapidly stirred aqueous solution of sodium sulfite (saturated, 200 mL) containing potassium carbonate (*ca.* 20 g). The resulting two-phase mixture was stirred for 5 min, then poured into a separatory funnel. Dichloromethane (100 mL) was added; the organic layer was separated, and the aqueous phase was extracted with two 50-mL portions of dichloromethane. The organic phases were combined, dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual solid was recrystallized from ethanol, affording the title compound as pale yellow microcrystals, 4.91 g (96 %): mp 174–176 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.5, 1.6 Hz, 2H), 7.50–7.35 (m, 6H), 7.27 (d, J = 8.5 Hz, 2H), 7.12 (dd, J = 7.7, 1.5 Hz, 2H), 7.02 (dd, J = 9.0, 2.1 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 153.5, 149.4, 142.3, 139.4, 137.8, 136.1, 131.5, 130.9, 129.5, 129.3, 128.7, 128.2, 127.9, 127.5, 127.4, 121.5, 118.1, 81.2, 28.2; IR (neat, cm^{-1}) 1710. Anal. Calcd for $C_{52}H_{53}BrN_4O_6$: C, 68.64; H, 5.87. Found: C, 68.38; H, 5.85

Octamer 9. Tetramer amine **7** (7.58 g, 10.3 mmol), tetramer bromide **8** (8.49 g, 9.33 mmol), palladium acetate (20.9 mg, 0.0933 mmol, 1 mol %), and DPEphos (60.3 mg, 0.112 mmol, 1.2 mol %) were dissolved in toluene (50 mL) in a Schlenk tube under argon. The reaction mixture was stirred for 5 min, then the flask was opened and sodium *tert*-butoxide (1.26 g, 13.1 mmol) was added. The septum was replaced and the flask was purged with argon for 5 min, then the reaction mixture was heated to 80 °C with stirring. Analysis by TLC after 18 h indicated incomplete consumption of the starting bromide. The reaction mixture was cooled to room temperature, the flask was opened, and tris(dibenzylideneacetone) dipalladium (0.0854 g, 0.0933 mmol, 2 mol % Pd) and DPEphos (0.121 g, 0.224 mmol, 2.4 mol %) were added. The septum was replaced, the flask was purged with argon for 5 min, and the reaction mixture was heated to 80 °C with stirring. Analysis by TLC after 18 h indicated the complete consumption of the starting bromide. The reaction mixture was cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated. The residue, 4-dimethylaminopyridine (0.228 g, 1.87 mmol, 20 mol %), and di-*tert*-butyl dicarbonate (3.05 mL, 13.3 mmol) were dissolved in tetrahydrofuran (40 mL) in a Schlenk tube under argon. The resulting solution was heated to 60 °C. Analysis by TLC after 4 h indicated the complete consumption of the starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residual solid was crystallized, then recrystallized, from toluene/ethanol, affording octamer **9** as pale yellow microcrystals (13.4 g, 88 %): mp 169–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.50–7.39 (m, 8H), 7.28–7.26 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.16–7.13 (m, 24H), 6.97 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 1.45 (s, 9H), 1.43 (s, 45H), 1.39 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 153.7, 153.7, 153.6, 149.2, 143.2, 140.5, 140.2, 140.1, 139.5, 138.0, 137.5, 136.1, 133.7, 130.8, 129.5,129.3, 128.6, 128.2, 127.9, 127.4, 127.2, 127.0, 126.8,

126.1, 125.8, 121.3, 81.3, 81.2, 80.9, 28.2, –1.1; IR (neat, cm^{-1}) 1712. Anal. Calcd for $C_{99}H_{114}N_8O_{14}Si$: C, 71.28; H, 6.88. Found: C, 71.07; H, 7.00.

Octamer amine 10. Octamer (5.84 g, 3.50 mmol) was placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (30 mL) was added via syringe, followed by ethanol (50 mL). The resulting mixture was stirred for 5 min at 70 °C, then cooled to room temperature. The flask was opened, and ammonium formate (2.65 g, 42.0 mmol) was added. The flask was purged with argon for 3 min, then palladium on carbon (10 wt. %, 0.372 g, 0.350 mmol Pd) was added. The septum was replaced, a vent needle connected to an oil bubbler was inserted through the septum, and the reaction mixture was heated to 70 °C with stirring. Analysis by TLC after 2 h indicated an incomplete consumption of starting material. The reaction mixture was cooled to room temperature, the flask was opened, and an additional portion of catalyst (0.186 g, 0.175 mmol Pd) was added, followed by ammonium formate (2.65 g, 42.0 mmol). The septum was replaced, the flask was purged with argon for 5 min, and the reaction mixture was heated to 70 °C with stirring. Analysis by TLC after 2 h indicated the complete consumption of starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (100 mL) and filtered through Celite, then concentrated *in vacuo* until a thick oil was obtained. The product was crystallized by addition of hexanes, then recrystallized from ethanol containing a small proportion of dichloromethane, affording the title compound as white microcrystals, 4.98 g (95 %): mp 168–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.14–7.12 (m, 24H), 7.02 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 3.65 (broad s, 2H), 1.44 (s, 9H), 1.43 (s, 54 H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 153.6, 153.6, 144.6, 143.2, 141.0, 140.3, 140.3, 140.1, 140.1, 140.0, 139.3, 137.5, 133.7, 128.8, 128.4, 127.2, 127.0, 126.8, 126.2, 125.8, 115.1, 81.3, 81.2, 80.8, 28.1, –1.2; IR (neat, cm^{-1})

3468, 3368, 1710. Anal. Calcd for $C_{86}N_{106}N_8O_{14}$: C, 68.68; H, 7.10. Found: C, 68.43; H, 6.86.

Octamer bromide 11. Octamer **9** (3.45 g, 2.07 mmol) and sodium acetate (0.172 g, 2.10 mmol) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (13 mL) was added via syringe. The resulting suspension was cooled to –78 °C with stirring. Bromine (0.22 mL, 4.2 mmol) was added dropwise via syringe, causing the mixture to turn a deep blue-green color. The reaction mixture was stirred for 10 min at –78 °C, then warmed to 0 °C; the color changed to yellow-brown. Analysis by TLC after 1 h indicated the complete consumption of the starting arylsilane. Triethylamine (5 mL, 36 mmol) was added via syringe; the solution lightened in color and a precipitate formed. The flask was opened, and the mixture was added via pipette to a rapidly stirred aqueous solution of sodium sulfite (saturated, 200 mL) containing potassium carbonate (*ca.* 50 g). The resulting two-phase mixture was stirred for 10 min, then poured into a separatory funnel. Dichloromethane (100 mL) was added; the organic layer was separated, and the aqueous phase was washed with two 50-mL portions of dichloromethane. The organic phases were combined, dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual solid was recrystallized from ethanol containing a small proportion of dichloromethane, affording the title compound as pale yellow microcrystals, 3.31 g (95 %): mp 170–172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 7.2 Hz, 2H), 7.43–7.40 (m, 5H), 7.30–7.24 (m, 3H), 7.13–7.07 (m, 28H), 6.96 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 1.44 (s, 54H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 153.9, 153.9, 153.8, 153.8, 153.5, 149.3, 142.1, 140.7, 140.6, 140.4, 140.4, 140.2, 140.2, 140.0, 140.0, 138.1, 136.2, 131.9, 131.0, 130.0, 129.4, 128.8, 128.5, 128.4, 128.1, 127.6, 127.3, 127.2, 127.0, 126.3, 121.5, 119.1, 82.5, 81.8, 81.6, 81.5, 81.5, 81.5, 81.1, 28.3; IR (neat, cm^{-1}) 2975, 1708, 1509, 1368, 1328, 1310,

1289, 1254, 1227, 1156, 1056, 1017, 843, 766, 699. Anal. Calcd for $C_{96}H_{105}BrN_8O_{14}$: C, 68.85; H, 6.32. Found: C, 68.59; H, 6.31.

16-mer (12). Octamer amine **10** (1.02 g, 0.676 mmol), octamer bromide **11** (1.07 g, 0.638 mmol), sodium *tert*-butoxide (0.0865 g, 0.900 mmol), tris(dibenzylideneacetone) dipalladium (11.7 mg, 0.0128 mmol, 4 mol % Pd), and *S*-BINAP (19.1 mg, 0.0307 mmol, 4.8 mol %) were placed in an oven-dried Schlenk tube, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (6 mL) was added via syringe. The mixture was heated to a gentle reflux with stirring. Analysis by TLC after 12 h indicated incomplete consumption of the starting materials; analysis by TLC after 36 h indicated the complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in dichloromethane (75 mL), and washed with water (25 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*.

The tube was opened, and 4-dimethylaminopyridine (0.031 g, 0.25 mmol), and solid di-*tert*-butyl dicarbonate (0.419 g, 1.92 mmol) were added. The tube was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe. The resulting clear solution was heated to 60 °C with stirring; a slow effervescence began within a few seconds. After 14 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residual solid was recrystallized from ethanol containing a small proportion of dichloromethane, affording the title compound as pale yellow microcrystals, 1.50 g (74 %): mp 182.5–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 4.4 Hz, 2H), 7.48–7.38 (m, 5H), 7.27–7.24 (m, 3H), 7.18–7.10 (m, 60H), 6.96 (d, J = 5.2 Hz, 2H), 6.68 (d, J = 5.0 Hz, 2H), 1.44 (s, 135H), 1.40 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 153.9, 153.9, 153.8, 149.4, 143.4, 140.7, 140.5, 140.3, 139.7, 138.2, 137.7, 136.3, 133.9, 131.0, 129.7, 129.5, 129.2, 128.8, 128.4, 128.1,

127.6, 127.5, 127.2, 127.1, 126.3, 126.1, 125.5, 121.6, 81.5, 81.5, 81.5, 81.2, 28.4, –0.9; IR (neat, cm^{-1}) 2978, 2931, 1708, 1502, 1361, 1320, 1249, 1155, 1049, 844, 750. Anal. Calcd for $C_{187}H_{218}N_{16}O_{30}Si$: C, 70.23; H, 6.87. Found: C, 70.35; H, 7.11.

Trimer 13. Dimer amine **4** (4.12 g, 11.6 mmol), aryl bromide **1** (3.70 g, 11.0 mmol), sodium *tert*-butoxide (1.480 g, 15.4 mmol), tris(dibenzylideneacetone) dipalladium (0.0504 g, 0.055 mmol, 1 mol % Pd), and DPEphos (0.0711 g, 0.132 mmol, 1.2 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (22 mL) was added via syringe. The reaction mixture was heated to a gentle reflux with stirring. Analysis by TLC after 10 h indicated the complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in dichloromethane (100 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and transferred to an oven-dried Schlenk flask. The flask was stoppered, and the solution was concentrated *in vacuo*; the flask was then backfilled with argon.

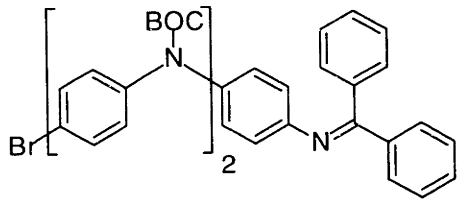
The flask was opened, and 4-dimethylaminopyridine (0.267 g, 2.20 mmol) was added. The flask was capped with a rubber septum, and di-*tert*-butyl dicarbonate (3.05 mL, 13.3 mmol) was added via syringe, followed by tetrahydrofuran (25 mL). The reaction mixture was heated to 60 °C with stirring; a steady effervescence soon commenced. Analysis by TLC after 6 h indicated the complete consumption of the coupling product. The mixture was cooled to room temperature and concentrated *in vacuo*. The resulting red oil was crystallized from ethanol, affording the product as yellow crystals, 7.03 g (90 %): mp 178.5–181 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 4.8 Hz, 2H), 7.47–7.39 (m, 6H), 7.26 (d, J = 2.2 Hz, 2H), 7.17 (d, J = 4.9 Hz, 2H), 7.13–7.10 (m, 6H), 6.97 (d, J = 5.1 Hz, 2H), 6.68 (d, J = 5.1 Hz, 2H), 1.46 (s, 9H), 1.40 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 154.0, 154.0, 149.4, 143.5, 140.7, 139.9, 139.7, 136.3, 133.9, 131.0, 129.7, 129.5, 128.9, 128.4, 128.1, 127.7,

127.3, 126.3, 126.1, 121.6, 82.5, 81.4, 81.2, 28.4, 28.4, –0.9; IR (neat, cm^{-1}) 2975, 1708, 1625, 1511, 1501, 1368, 1345, 1328, 1279, 1248, 1164, 1059, 857, 845, 835, 822, 766, 751, 699. Anal. Calcd for $C_{44}H_{49}N_3O_4Si$: C, 74.23; H, 6.94. Found: C, 74.35; H, 7.00.

Trimer Amine 14. Trimer **13** (3.56 g, 5.00 mmol), ammonium formate (4.73 g, 75.0 mmol), and palladium on carbon (10 wt. %, 0.532 g, 0.500 mmol Pd) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe, followed by methanol (20 mL). The septum was replaced with a loose-fitting plastic cap, and the reaction mixture was heated to 60 °C. Analysis by TLC after 90 min indicated the complete consumption of starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (50 mL) and filtered through Celite, then concentrated *in vacuo*. The residual oil was crystallized from hexanes, affording the product as a white solid, 2.44 g (89 %): mp 161.5–163 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.18–7.11 (m, 6H), 6.98 (d, J = 8.7 Hz 2H), 6.62 (d, J = 8.7 Hz, 2H), 3.66 (s, 2H), 1.46 (s, 9H), 1.44 (s, 9H), 0.249 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 154.0, 144.8, 143.5, 141.1, 139.8, 137.6, 134.0, 133.9, 128.7, 127.3, 126.4, 126.1, 115.4, 81.4, 81.1, 28.5, 28.4, –0.9; IR (neat, cm^{-1}) 3456, 3367, 2979, 1704, 1688, 1521, 1511, 1370, 1335, 1285, 1248, 1164, 1057, 857, 839, 820, 766, 754. Anal. Calcd for $C_{31}H_{41}N_3O_4Si$: C, 67.97; H, 7.54. Found: C, 68.10; H, 7.54.

Trimer Bromide 15. Trimer **13** (2.00 g, 2.81 mmol) and sodium acetate (0.231 g, 2.81 mmol) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (14 mL) was added via syringe. The reaction mixture was cooled to –78 °C with stirring, and bromine (0.29 mL, 5.6 mmol) was added dropwise via syringe; the reaction mixture turned a deep green-brown color.

The mixture was stirred for 10 min at –78 °C, then warmed to 0 °C. Analysis by TLC after 20 min indicated the complete consumption of the arylsilane starting material. The flask was opened, and the mixture was added via pipette to a rapidly stirred aqueous solution of sodium sulfite (saturated, 200 mL) containing potassium carbonate (*ca.* 50 g). The resulting two-phase mixture was stirred for 10 min, then poured into a separatory funnel. Dichloromethane (100 mL) was added; the organic layer was separated, and the aqueous phase was washed with two 50-mL portions of dichloromethane. The organic phases were combined, dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual solid was crystallized, then recrystallized, from ethanol, affording the title compound as pale yellow microcrystals, 1.56 g (77 %): mp 182–183 °C;



^{1}H NMR ($CDCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.7 Hz, 2H), 7.49–7.40 (m, 5H), 7.28–7.24 (m, 3H), 7.14–7.06 (m, 8H), 6.97 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.5 Hz, 2H), 1.48 (s, 9H),

1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 153.9, 153.6, 149.5, 142.2, 141.0, 139.6, 139.4, 138.1, 136.3, 131.9, 131.0, 129.7, 129.5, 128.9, 128.5, 128.4, 128.1, 127.8, 127.2, 126.3, 121.6, 119.0, 81.8, 81.2, 28.4; IR (neat, cm^{-1}) 3058, 3002, 2983, 2968, 2931, 1712, 1513, 1501, 1366, 1316, 1291, 1277, 1254, 1158, 1056, 1013, 847, 826, 762, 697, 670.

Pentamer 16. Trimer amine **14** (0.845 g, 1.54 mmol), dimer chloride **5a** (0.676 g, 1.40 mmol), sodium *tert*-butoxide (0.188 g, 1.96 mmol), tris(dibenzylidene-acetone) dipalladium (3.2 mg, 0.0035 mmol, 0.5 mol % Pd), and 2-(di-*tert*-butyl-phosphino)biphenyl (4.2 mg, 0.014 mmol, 1.0 mol %) were placed in an oven-dried, resealable Schlenk tube. The tube was fitted with a Teflon screwcap, evacuated, and backfilled with argon. The screwcap was replaced with a rubber septum, and toluene (4 mL) was added via syringe. The septum was replaced with the Teflon screwcap; the tube was sealed, and the reaction mixture was heated to 80 °C with stirring. Analysis by TLC after 12 h indicated the complete consumption of the aryl chloride starting material. The reaction mixture was cooled to room temperature, taken up in dichloromethane (50 mL), washed with water (50 mL), dried over anhydrous potassium carbonate, and filtered. The resulting solution was transferred to an oven-dried Schlenk flask. The flask was stoppered; the solution was concentrated *in vacuo*, and the flask was backfilled with argon.

The septum was removed, and 4-dimethylaminopyridine (0.034 g, 0.28 mmol) was added. The septum was replaced, and the flask was purged with argon for 5 min. Di-*tert*-butyl dicarbonate (0.43 mL, 1.9 mmol) was added via syringe, followed by tetrahydrofuran (5 mL). The reaction mixture was heated to 60 °C with stirring; a steady effervescence began within a few seconds. Analysis by TLC after 3 h indicated the complete consumption of the starting amine. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting orange solid was crystallized from ethanol, and the product was recrystallized from toluene/ethanol,

affording the title compound as pale yellow microcrystals, 1.32 g (86 %): mp 191–193 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.46–7.41 (m, 5H), 7.29–7.26 (m, 3H), 7.19–7.09 (m, 16H), 6.97 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 1.46 (s, 9H), 1.45 (s, 18H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 153.9, 153.8, 153.8, 149.2, 143.3, 140.6, 140.4, 140.3, 140.2, 140.2, 139.6, 138.1, 137.6, 136.1, 133.9, 131.0, 129.6, 129.4, 128.8, 128.3, 128.0, 127.6, 127.4, 127.1, 127.0, 126.2, 126.0, 121.5, 81.5, 81.5, 81.2, 28.4, –0.9; IR (neat, cm^{-1}) 3002, 2975, 2935, 1706, 1511, 1368, 1328, 1293, 1252, 1160, 1059, 861, 839, 824, 766, 699. Anal. Calcd for $C_{66}H_{75}N_5O_8Si$: C, 72.43; H, 6.91. Found: C, 72.25; H, 6.94.

Pentamer Amine 17. Pentamer **16** (1.20 g, 1.10 mmol), ammonium formate (0.832 g, 13.2 mmol), and palladium on carbon (10 wt. %, 0.117 g, 0.110 mmol Pd) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (5 mL) was added via syringe, followed by methanol (10 mL). The septum was replaced with a loose-fitting plastic cap, and the reaction mixture was heated to 65 °C with stirring. Analysis by TLC after 1 h indicated the complete consumption of starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (50 mL) and filtered through Celite, then concentrated *in vacuo*. The residual solid was triturated with cold hexanes, then recrystallized from ethanol, affording the title compound as white microcrystals, 0.896 g (88 %): mp 145–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.19–7.07 (m, 14H), 6.97 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.4 Hz), 3.67 (broad s, 2H), 1.46 (s, 9H), 1.44 (s, 27H), 0.254 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 153.8, 144.7, 143.3, 141.1, 140.3, 140.2, 140.1, 139.4, 137.6, 133.8, 133.7, 128.5, 127.4, 127.1, 127.0, 126.3, 126.0, 115.3, 81.5, 81.4, 81.0, 28.4, –0.9; IR (neat, cm^{-1}) 3444, 3371, 2977, 1710, 1513, 1368, 1322,

1287, 1252, 1162, 1059, 841, 830, 764. Anal. Calcd for $C_{53}H_{67}N_5O_8Si$: C, 68.43; H, 7.26. Found: C, 68.38; H, 7.26.

Hexamer 18. Tetramer amine **7** (2.14 g, 2.90 mmol), dimer bromide **5a** (1.39 g, 2.63 mmol), sodium *tert*-butoxide (0.354 g, 3.69 mmol), tris(dibenzylideneacetone) dipalladium (24.1 mg, 0.026 mmol, 2 mol % Pd), and *S*-BINAP (49.1 mg, 0.079 mmol, 3 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe. The mixture was heated to a gentle reflux with stirring. Analysis by TLC after 12 h indicated incomplete consumption of the starting materials. The reaction mixture was cooled to room temperature, the flask was opened, and additional portions of base (0.354 g, 3.69 mmol), tris(dibenzylideneacetone) dipalladium (24.1 mg, 0.026 mmol, 2 mol % Pd), and *S*-BINAP (49.1 mg, 0.079 mmol, 3 mol %) were added. The septum was replaced, and the flask was purged with argon for 5 min. The reaction mixture was heated to a gentle reflux. Analysis by TLC after a total of 30 h indicated the complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in dichloromethane (75 mL), and washed with water (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, using 2:1 hexanes: ethyl acetate as the eluant, then used in the next step.

The hexamer coupling product, 4-dimethylaminopyridine (0.0605 g, 0.539 mmol), and solid di-*tert*-butyl dicarbonate (0.706 g, 3.23 mmol) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe. The resulting clear solution was heated to a gentle reflux; a slow effervescence began within a few seconds. Analysis by TLC after 24 h indicated the complete consumption of the starting amine. The solution was cooled to room

temperature and concentrated *in vacuo*. The residual solid was recrystallized from methanol, affording the title compound as pale yellow microcrystals, 2.27 g (67 %): mp 136.5–139.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.46–7.41 (m, 5H), 7.28–7.25 (m, 3H), 7.19–7.10 (m, 20H), 6.97 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.6 Hz, 2H), 1.46 (s, 9H), 1.44 (s, 27H), 1.40 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 154.0, 153.9, 153.8, 149.4, 143.4, 140.7, 140.5, 140.4, 140.3, 140.2, 139.7, 138.1, 137.7, 136.2, 133.9, 131.0, 129.7, 129.5, 128.9, 128.4, 128.1, 127.7, 127.5, 127.2, 127.1, 126.3, 126.1, 121.6, 81.6, 81.5, 81.5, 81.5, 81.2, 28.4, –0.9; IR (neat, cm^{-1}) 2975, 2933, 1710, 1509, 1368, 1322, 1291, 1252, 1158, 1056, 839, 764, 697. Anal. Calcd for $C_{77}H_{88}N_6O_{10}Si$: C, 71.93; H, 6.90. Found: C, 71.68; H, 7.17.

Heptamer 20. Tetramer amine **7** (1.55 g, 2.10 mmol), trimer bromide **15** (1.44 g, 2.00 mmol), sodium *tert*-butoxide (0.269 g, 2.80 mmol), tris(dibenzylideneacetone) dipalladium (36.6 mg, 0.040 mmol, 4 mol % Pd), and *S*-BINAP (59.8 mg, 0.096 mmol, 4.8 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (8 mL) was added via syringe. The mixture was heated to a gentle reflux with stirring. Analysis by TLC after 11 h indicated incomplete consumption of the starting materials; analysis after 28 h indicated the complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in dichloromethane (75 mL), and washed with water (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered through a plug of silica gel, and concentrated *in vacuo*, affording a red solid.

The heptamer coupling product, 4-dimethylaminopyridine (0.0449 g, 0.400 mmol), and solid di-*tert*-butyl dicarbonate (0.572 g, 2.62 mmol) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe. The resulting clear solution was heated to a gentle reflux; a slow

effervescence began within a few seconds. Analysis by TLC after 12 h indicated the complete consumption of the starting amine. The solution was cooled to room temperature and concentrated *in vacuo*. The residual solid was recrystallized from ethanol, affording the title compound as pale yellow microcrystals, 2.39 g (81 %): mp 181–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.46–7.41 (m, 5H), 7.28–7.25 (m, 3H), 7.19–7.10 (m, 24H), 6.97 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 1.46 (s, 9H), 1.44 (s, 36H), 1.40 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 153.9, 153.8, 153.8, 149.3, 143.3, 140.7, 140.5, 140.4, 140.2, 139.6, 138.1, 137.6, 136.2, 133.9, 131.0, 129.6, 129.4, 128.8, 128.3, 128.0, 127.6, 127.4, 127.2, 127.0, 126.3, 126.0, 121.5, 81.5, 81.5, 81.4, 81.4, 81.1, 28.3, –1.0; IR (neat, cm^{-1}) 2975, 2935, 1710, 1511, 1368, 1328, 1287, 1254, 1225, 1160, 1057, 1017, 855, 836, 764, 699. Anal. Calcd for $C_{88}H_{101}N_7O_{12}Si$: C, 71.57; H, 6.64. Found: C, 71.42; H, 6.98.

Nonamer 21. Pentamer amine **17** (0.424 g, 0.456 mmol), tetramer bromide **8** (0.395 g, 0.434 mmol), sodium *tert*-butoxide (0.0584 g, 0.608 mmol), tris(dibenzylideneacetone) dipalladium (2.0 mg, 0.0022 mmol, 1.0 mol % Pd), and 2-(di-*tert*-butylphosphino)biphenyl (**48**, 2.6 mg, 0.0088 mg, 2.0 mol %) were placed in an oven-dried, resealable Schlenk tube. The tube was fitted with a Teflon screwcap, evacuated, and backfilled with argon. The screwcap was replaced with a rubber septum, and toluene (1.6 mL) was added via syringe. The septum was replaced with the Teflon screwcap; the tube was sealed, and the reaction mixture was heated to 60 °C with stirring. Analysis by TLC after 8 h indicated the complete consumption of the aryl bromide starting material. The reaction mixture was cooled to room temperature, taken up in dichloromethane (50 mL), washed with water (50 mL). The aqueous phase was extracted with dichloromethane (15 mL). The combined organic portions were dried over anhydrous potassium carbonate and filtered; the resulting solution was transferred to an oven-dried Schlenk flask. The flask was stoppered; the solution was concentrated *in vacuo*, and the flask was backfilled with argon.

The septum was removed, and 4-dimethylaminopyridine (0.0212 g, 0.174 mmol) was added. The septum was replaced, and the flask was purged with argon for 5 min. Di-*tert*-butyl dicarbonate (0.12 mL, 0.52 mmol) was added via syringe, followed by tetrahydrofuran (2 mL). The reaction mixture was heated to 60 °C with stirring; a steady effervescence began within a few seconds. Analysis by TLC after 4 h indicated the complete consumption of the starting amine. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting orange solid was crystallized from toluene/ethanol, affording the title compound as pale yellow microcrystals, 0.687 g (85 %): mp 183–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.3 Hz, 2H), 7.46–7.40 (m, 5H), 7.28–7.27 (m, 3H), 7.19–7.10 (m, 32H), 6.97 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 8.3 Hz, 2H), 1.45 (s, 63H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 153.8, 153.7, 153.7, 149.2, 143.2, 140.6, 140.4, 140.3, 140.2, 140.2, 140.1, 139.5, 138.0, 137.6, 136.1, 133.8, 130.9, 129.6, 129.4, 128.8, 128.3, 128.0, 127.5, 127.3, 127.1, 127.0, 126.2, 125.9, 121.5, 81.5, 81.4, 81.4, 81.1, 28.4, –0.9; IR (neat, cm^{-1}) 2975, 2933, 1708, 1509, 1368, 1328, 1310, 1289, 1252, 1156, 1054, 1017, 837, 766, 697. Anal. Calcd for $C_{110}H_{127}N_9O_{16}Si$: C, 71.06; H, 6.88. Found: C, 70.95; H, 6.81.

Decamer 22. Hexamer **18** (1.16 g, 0.900 mmol), ammonium formate (0.851 g, 13.5 mmol), and palladium on carbon (5 wt. %, 0.192 g, 0.090 mmol Pd) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe, followed by methanol (10 mL). The septum was replaced with a loose-fitting plastic cap, and the reaction mixture was heated to 65 °C with stirring. Analysis by TLC after 2 d indicated the complete consumption of starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (50 mL) and filtered through Celite, then concentrated *in vacuo* until

a thick oil was obtained. The addition of hexanes (50 mL) caused the hexamer amine (**19**) to precipitate as white microcrystals, 0.965 g (96 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.19–7.11 (m, 18H), 6.98 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H), 3.70 (broad s, 2H), 1.45 (s, 9H), 1.44 (s, 36H), 0.25 (s, 9H).

Hexamer amine **19** (0.906 g, 0.808 mmol), tetramer bromide **8** (0.728 g, 0.800 mmol), sodium *tert*-butoxide (0.108 g, 1.12 mmol), tris(dibenzylideneacetone) dipalladium (14.7 mg, 0.016 mmol, 4 mol % Pd), and *S*-BINAP (23.9 mg, 0.038 mmol, 4.8 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (12 mL) was added via syringe. The mixture was heated to 65 °C with stirring. Analysis by TLC after 17 h indicated the complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in dichloromethane (75 mL), and washed with water (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered through a plug of silica gel, and transferred to an oven-dried Schlenk flask. The flask was stoppered, the solution was concentrated *in vacuo*, and the flask was backfilled with argon.

The flask was opened, and 4-dimethylaminopyridine (0.0489 g, 0.400 mmol) and solid di-*tert*-butyl dicarbonate (0.231 g, 1.06 mmol) were added. The septum was replaced, the flask was purged with argon for 5 min, and tetrahydrofuran (10 mL) was added via syringe. The reaction mixture was heated to 65 °C with stirring; a slow effervescence began within a few seconds. Analysis by TLC after 12 h indicated the complete consumption of the starting amine. The solution was cooled to room temperature and concentrated *in vacuo*. The residual solid was recrystallized from chloroform/ethanol, affording the title compound as pale yellow microcrystals, 1.38 g (84 %): mp 185.5–188.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.46–7.41 (m, 5H), 7.28–7.25 (m, 3H), 7.19–7.10 (m, 36H), 6.97 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 1.44 (s, 72H), 1.40 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 168.8, 153.8, 153.8, 149.3, 143.3, 140.7, 140.4, 140.2, 139.6, 138.1, 137.6, 136.2, 133.9, 130.9, 129.6, 129.4, 128.8, 128.3, 128.0, 127.6, 127.4, 127.2, 126.3, 126.0, 121.5, 81.5, 81.4, 81.4, 81.1, 28.3, –1.0; IR (neat, cm^{-1}) 2973, 2935, 1708, 1509, 1368, 1329, 1310, 1289, 1254, 1229, 1156, 1056, 1017, 839, 764, 697. Anal. Calcd for $C_{121}H_{140}N_{10}O_{18}Si$: C, 70.87; H, 6.88. Found: C, 70.77; H, 7.00.

***N*-(Diphenylmethylene)-*N'*,*N''*-bis(*tert*-butoxycarbonyl)-teraniline (23).** Dimer bromide **5a** (3.06 g, 5.80 mmol), aniline (0.56 mL, 6.1 mmol), sodium *tert*-butoxide (0.8072 g, 8.40 mmol), $Pd_2(dba)_3$ (54.9 mg, 0.060 mmol, 1.0 mol %), and *S*-BINAP (89.7 mg, 2.5 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated,.and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (20 mL) was added via syringe. The reaction mixture was heated to 80 °C with stirring. Analysis by TLC after 14 h indicated complete consumption of the starting bromide. The mixture was cooled to room temperature and taken up in diethyl ether (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated*in vacuo.* The residue, di-*tert*-butyl dicarbonate (1.53 g, 7.0 mmol), and 4-dimethylaminopyridine (0.131 g, 1.16 mmol, 20 mol %) were dissolved in tetrahydrofuran (15 mL) in a Schlenk flask under argon. The reaction mixture was heated with stirring to 60 °C. After 3 h the solution was cooled to room temperature and concentrated *in vacuo.* The solid residue was crystallized from ethanol. Recrystallization of the product from ethanol afforded the title compound as pale yellow microcrystals (3.00 g, 81 %): mp 149–151 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2H), 7.48–7.38 (m, 3H), 7.33–7.24 (m, 5H), 7.21–7.16 (m, 3H), 7.14–7.07 (m, 6H), 6.97 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 1.45 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 154.0, 149.4, 143.0, 140.6, 140.0, 139.7, 138.2, 136.3, 131.0, 129.7, 129.5, 128.9, 128.4, 128.1, 127.7, 127.2, 127.0, 126.3, 125.9, 121.6, 81.4, 81.2, 28.4, 28.4; IR (neat, cm^{-1})

2977, 2930, 1710, 1509, 1324, 1161, 758, 696. Anal. Calcd for $C_{41}H_{41}N_3O_4$: C, 76.97; H, 6.46. Found: C, 77.16; H, 6.70.

***N*-Phenyl-*N'*-(4-aminophenyl)-*N,N'*-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (24).** Imine **23** (1.245 g, 1.95 mmol), ammonium formate (1.840 g, 29.2 mmol), and palladium on carbon (5 %, 0.414 g, 1.95 mmol Pd) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and methanol (8 mL) was added *via* syringe, followed by tetrahydrofuran (4 mL). The reaction mixture was heated to 60 °C with stirring. Analysis by TLC after 90 min showed incomplete consumption of the starting imine. An additional portion of palladium on carbon (5 %, 0.414 g, 1.95 mmol Pd) was added, and the solid ammonium formate which collected above the mixture was periodically redissolved. Analysis by TLC after 2 h showed complete consumption of the starting imine. The mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane, and the resulting mixture was filtered through Celite and concentrated *in vacuo*. The residual white solid was triturated in hexanes (30 mL), cooled to 0 °C, and collected by filtration, affording the title compound as a white solid (0.884 g, 96 %): mp 180–182 °C with slow decomposition; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.2, 3.9 Hz, 2H), 7.21–7.10 (m, 7H), 6.98 (dd, J = 5.3, 1.2 Hz, 2H), 6.62 (dd, J = 5.3, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 154.0, 144.8, 143.0, 141.0, 139.8, 134.0, 129.1, 128.8, 128.7, 128.6, 127.2, 127.0, 126.4, 126.2, 125.8, 115.4, 81.3, 81.0, 28.4, 28.4; IR (neat, cm^{-1}) 3460, 3366, 3037, 2978, 2919, 1702, 1508, 1337, 1161, 1055. Anal. Calcd for $C_{28}H_{33}N_3O_4$: C, 70.71; H, 6.99. Found: C, 70.84; H, 6.78.

***N*-(Diphenylmethylene)-4-[4-methoxy-*N*-(*tert*-butoxycarbonyl)-anilino]aniline (25).** Aryl bromide **1** (2.60 g, 7.74 mmol), *p*-anisidine (1.00 g, 8.13 mmol), sodium *tert*-butoxide (1.04 g, 10.8 mmol), $Pd_2(dba)_3$ (35.0 mg, 0.0387 mmol,

1.0 mol %), and *S*-BINAP (72.0 mg, 0.116 mmol, 1.5 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and methanol (8 mL) was added via syringe, followed by tetrahydrofuran (25 mL). The reaction mixture was heated to reflux. After 18 h, the mixture was cooled to room temperature. 4-Dimethylamino-pyridine (47.0 mg, 0.774 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 11.6 mL, 11.6 mmol) were added, and the resulting mixture was heated to reflux. After 3 h the reaction mixture was cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (25 mL), filtered through Celite, and concentrated *in vacuo*. Crystallization of the residual solid from methanol afforded the title compound as yellow microcrystals (3.11 g, 84 %): mp 148–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 7.1 Hz, 2H), 7.50–7.36 (m, 4H), 7.25 (d, J = 6.0 Hz, 2H), 7.11 (d, J = 7.1 Hz, 2H), 7.07 (d, J = 9.1 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 9.1 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 157.0, 153.9, 148.4, 139.4, 138.5, 130.7, 129.4, 129.2, 128.5, 128.1, 127.8, 127.6, 126.8, 121.2, 113.7, 80.6, 55.4, 28.3; IR (neat, cm^{-1}) 1705, 1612. Anal. Calcd for $C_{31}H_{30}N_2O_3$: C, 77.80; H, 6.32. Found: C, 77.77; H, 6.38.

***N*-(4-Methoxyphenyl)-*N"*-(4-bromophenyl)-*N,N'*-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (26).** Imine **25** (1.00 g, 2.09 mmol), ammonium formate (2.64 g, 41.8 mmol), and palladium hydroxide on carbon (20 %, 0.291 g, 0.209 mmol Pd), were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and ethanol (20 mL) was added. The reaction mixture was heated at 60 °C for 30 min, then cooled to room temperature, taken up in ethyl acetate (40 mL), and filtered through Celite. The filtrate was diluted with ethyl acetate (60 mL), washed with a 2.0 M aqueous solution of sodium hydroxide (100 mL) and with brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*.

The residual white solid, 1,4-dibromobenzene (0.470 g, 1.99 mmol), sodium *tert*-butoxide (0.268 g, 2.79 mmol), $Pd_2(dba)_3$ (18.2 mg, 0.0199 mmol, 1.0 mol %), and *S*-BINAP (37.2 mg, 0.0598 mmol, 3.0 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe. The resulting mixture was heated at reflux for 24 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (24.0 mg, 0.199 mmol, 10 mol %) was added. The septum was replaced, a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 3.0 mL, 3.0 mmol) was added via syringe, and the resulting mixture was heated to reflux. After 3 h, the reaction mixture was cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (10 mL), filtered through Celite, and concentrated *in vacuo*. Crystallization of the residual solid from methanol containing a small proportion of dichloromethane afforded the title compound as white microcrystals (0.847 g, 75 %): mp 169–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 2H), 7.17–7.06 (m, 8H), 6.84 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 153.9, 153.4, 142.0, 141.0, 139.3, 135.6, 131.7, 128.5, 128.3, 127.0, 126.4, 118.9, 114.1, 81.6, 81.1, 55.4, 28.2, 28.2; IR (neat, cm^{-1}) 1709. Anal. Calcd for $C_{29}H_{33}BrN_2O_5$: C, 61.16; H, 5.84. Found: C, 61.15; H, 5.81.

Tetramer diamine 27. 1,4-Phenylenediamine dihydrochloride (4.53 g, 25.0 mmol), aryl bromide **1** (17.0 g, 50.5 mmol), sodium *tert*-butoxide (10.8 g, 113 mmol), $Pd(OAc)_2$ (0.0561 g, 0.250 mmol, 1.0 mol %), and *S*-BINAP (0.234 g, 0.375 mmol, 1.5 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (200 mL) was added via syringe. The reaction mixture was heated at 80 °C for 24 h, then cooled to room temperature. The flask was opened, and 4-dimethylamino-pyridine (305 mg, 2.50 mmol, 10 mol %) was added. The septum was replaced, and a

solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 87.5 mL, 87.5 mmol) was added via syringe, followed by tetrahydrofuran (50 mL). The resulting mixture was heated to 80 °C with stirring. After 24 h the hot reaction mixture was poured into hot ethanol (400 mL). Heating was discontinued and the mixture was allowed to stand for 6 h. The yellow powder which formed was collected by filtration. The crude product and hydroxylamine hydrochloride (4.34 g, 62.5 mmol) were suspended in pyridine (8.1 mL, 100 mmol), chloroform (400 mL), tetrahydrofuran (100 mL), and ethanol (50 mL). The suspension was stirred for 3 h, then treated with triethylamine (34.8 mL, 250 mmol). After an additional 3 h the reaction mixture was concentrated *in vacuo*. The residual solid was heated in isopropanol (600 mL), chloroform (120 mL) and water (60 mL) for 10 min, then allowed to cool to room temperature and to stand for 12 h. The precipitated product was collected by filtration, washed with water followed by isopropanol, and dried *in vacuo* to afford diamine **15** as a white powder (11.1 g, 91 %): mp 208–211 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.06 (s, 4H), 6.81 (d, J = 8.4 Hz, 4H), 6.49 (d, J = 8.4 Hz, 4H), 5.11 (s, 4H), 1.33 (s, 18 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.4, 146.9, 140.2, 131.1, 128.0, 125.9, 113.8, 79.6, 27.8; IR (neat, cm^{-1}) 3460, 3364, 1707. Anal. Calcd for $C_{28}H_{34}N_4O_4$: C, 68.55; H, 6.99. Found: C, 68.57; H, 7.05.

Octamer bis-imine 28. Diamine **27** (4.23 g, 8.63 mmol), dimer bromide **5a** (9.56 g, 18.1 mmol), sodium *tert*-butoxide (2.32 g, 24.2 mmol), $Pd(OAc)_2$ (0.116 g, 0.518 mmol, 6.0 mol %), and *S*-BINAP (0.376 g, 0.604 mmol, 7.0 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (43 mL) was added via syringe, followed by triethylamine (11 mL). The reaction mixture was heated at 90 °C for 48 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (105 mg, 0.863 mmol, 10 mol %) was added. The septum was replaced, and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 34.5 mL, 34.5 mmol) was added via syringe, followed by tetrahydrofuran (20 mL). The

resulting mixture was heated at 67 °C for 24 h, then cooled to room temperature. Ethyl acetate (100 mL) and a 2.0 M aqueous solution of sodium hydroxide (60 mL) were added. The mixture was stirred for 15 minutes, then partitioned between ethyl acetate (100 mL) and water (250 mL). The organic layer was washed with brine (200 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The residual solid was crystallized from a mixture of chloroform and isopropanol, affording bis-imine **16** as yellow microcrystals (10.1 g, 74 %): mp 154–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 7.0 Hz, 4H), 7.48–7.381 (m, 8H), 7.27–7.23 (m, 8H), 7.11 (s, 16H), 7.08 (s, 4H), 6.95 (d, J = 8.4 Hz, 4H), 6.67 (d, J = 8.4 Hz, 4H), 1.42 (s, 36 H), 1.38 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 153.6, 153.5, 149.0, 140.5, 140.1, 140.0, 140.0, 139.4, 139.4, 137.9, 136.0, 130.7, 130.7, 129.4, 129.2, 128.6, 128.1, 127.8, 127.4, 126.9, 126.8, 126.0, 121.3, 81.3, 81.3, 81.0, 28.3; IR (neat, cm^{-1}) 1711. Anal. Calcd for $C_{98}H_{102}N_8O_{12}$: C, 74.31; H, 6.49. Found: C, 74.36; H, 6.54.

Octamer diamine 29. Bis-imine **28** (3.00 g, 1.89 mmol), ammonium formate (2.39 g, 37.9 mmol), and 20 % palladium hydroxide on carbon (0.758 mmol) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (50 mL) was added via syringe, followed by ethanol (25 mL). The resulting mixture was heated to 70 °C, causing an effervescence which slowed after *ca.* 30 min An additional portion of ammonium formate (2.39 g, 37.9 mmol) was added. Ammonium formate was added in small portions every 60 min until conversion to the diamine was complete as judged by TLC analysis. The mixture was cooled to room temperature, taken up in ethyl acetate (40 mL), and filtered through Celite. The filtrate was diluted with a 2:1 mixture of hexanes and ethyl acetate (40 mL). The resulting solution was washed with a 2.0 M aqueous solution of sodium hydroxide (40 mL) and with brine (40 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Crystallization of the residual solid from a mixture of hexanes

and isopropanol afforded diamine **17** as white microcrystals (2.03 g, 86 %): mp 169–172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–7.07 (m, 20H), 6.96 (d, J = 8.4 Hz, 4H), 6.60 (d, J = 8.4 Hz, 4H), 3.65 (bs, 4H), 1.43 (s, 54 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 153.6, 153.6, 144.6, 141.0, 140.3, 140.1, 140.0, 139.4, 137.8, 133.7, 128.4, 126.9, 126.9, 126.8, 126.2, 115.1, 81.2, 81.2, 80.7, 28.2, 28.1; IR (neat, cm^{-1}) 3460, 3369, 1702. Anal. Calcd for $C_{72}H_{86}N_8O_{12}$: C, 68.88; H, 6.90. Found: C, 68.68; H, 6.84.

General Procedure for the Conversion of Octamer Diamine 29 to Octamers 30a–d. Diamine **29** (1.26 g, 1.00 mmol), aryl bromide (2.30 mmol), sodium *tert*-butoxide (0.240 g, 2.50 mmol), $Pd_2(dba)_3$ (18.7 mg, 0.0204 mmol, 2.0 mol %), and *S*-BINAP (38.1 mg, 0.0613 mmol, 6 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe. The reaction mixture was heated at reflux for 48 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (12.0 mg, 0.100 mmol, 10 mol %) was added. The septum was replaced, and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 3.5 mL, 3.5 mmol) was added via syringe. The resulting mixture was heated at reflux for 3 h, then cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (10 mL), filtered through Celite, and concentrated *in vacuo*. The residue was purified by crystallization.

Phenyl-capped octamer 30a. Obtained as pale yellow microcrystals from a 6:1 mixture of methanol and chloroform in 77 % yield: mp 171–173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (t, J = 8.7 Hz, 2H), 7.20–7.15 (m, 4H), 7.13 (s, 32H), 1.44 (s, 18H), 1.43 (s, 54H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 153.6, 153.6, 142.8, 140.5, 140.2, 140.0, 128.7, 127.0, 125.7, 81.3, 81.3, 81.2, 28.2; IR (neat, cm^{-1}) 1711; HRMS (FAB) *m/z* 1606.8043 (1606.8037 calcd for $C_{94}H_{110}N_8O_{16}$, M^+). Anal. Calcd for $C_{94}H_{110}N_8O_{16}$: C, 70.22; H, 6.90. Found: C, 70.25; H, 6.91.

α,ω-Bis(cyano)-phenyl-capped octamer 30b. Obtained as pale yellow microcrystals from methanol in 79 % yield: mp 163–166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.0 Hz, 4H), 7.31 (d, *J* = 9.0 Hz, 4H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.16–7.13 (m, 24H), 7.08 (d, *J* = 8.7 Hz, 2H), 1.44 (s, 36H), 1.43 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 153.5, 151.6, 147.0, 140.2, 140.1, 140.1, 140.1, 136.9, 132.5, 128.2, 128.0, 127.3, 127.0, 126.7, 125.6, 82.6, 82.2, 81.3, 28.2, 27.9; IR (neat, cm^{-1}) 1713; HRMS (FAB) *m/z* 1656.7952 (1656.7945 calcd for $C_{96}H_{114}N_8O_{16}$, M^+). Anal. Calcd for $C_{96}H_{114}N_8O_{16}$: C, 69.55; H, 6.57. Found: C, 69.24; H, 6.68.

α,ω-Bis(*tert*-butyl)-phenyl-capped octamer 30c. Obtained as pale yellow microcrystals from a 10:1 mixture of ethanol and chloroform in 82 % yield: mp 172–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 9.0 Hz, 4H), 7.12 (s, 28H), 7.10 (d, *J* = 9.0 Hz, 4H), 1.44 (s, 18H), 1.43 (s, 54H), 1.29 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 153.6, 153.6, 148.6, 140.6, 140.2, 140.1, 139.9, 127.0, 126.3, 125.6, 81.3, 81.3, 81.0, 24.4, 31.3, 28.2; IR (neat, cm^{-1}) 1713; HRMS (FAB) *m/z* 1718.9275 (1718.9292 calcd for $C_{102}H_{126}N_8O_{16}$, M^+). Anal. Calcd for $C_{102}H_{126}N_8O_{16}$: C, 71.22; H, 7.38. Found: C, 71.02; H, 7.27.

α,ω-Bis(*n*-dodecyl)-phenyl-capped octamer 30d. Obtained as pale yellow microcrystals from a 10:1 mixture of ethanol and chloroform in 82 % yield: mp 172–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–7.08 (m, 36H), 2.57 (t, *J* = 8.0 Hz, 4H), 1.65–1.53 (m, 4H), 1.43 (s, 72H), 1.32–1.20 (m, 36H), 0.88 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 153.7, 153.6, 140.6, 140.3, 140.2, 139.8, 128.7, 127.0, 126.9, 126.8, 81.3, 81.3, 81.0, 35.4, 31.9, 31.3, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.2, 27.9, 22.6, 14.1; IR (neat, cm^{-1}) 1712. Anal. Calcd for $C_{118}H_{158}N_8O_{16}$: C, 72.88; H, 8.19. Found: C, 72.71; H, 8.24.

α,ω-Bis(methoxy)-phenyl-capped octamer 30e. Aryl bromide **26** (0.300 g, 0.527 mmol), diamine **27** (0.123 mg, 0.251 mmol), sodium *tert*-butoxide (60 mg, 0.627 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.00502 mmol), and *S*-BINAP (9.4 mg, 0.0151 mmol)

were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (3 mL) was added via syringe. The reaction mixture was heated at 80 °C for 48 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (3.1 mg, 0.0251 mmol, 10 mol %) was added. The septum was replaced, and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 0.88 mL, 0.88 mmol) was added via syringe. The resulting mixture was heated at reflux for 3 h, then cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (6 mL), filtered through Celite, and concentrated *in vacuo*. Crystallization of the residual solid from a mixture of isopropanol and water afforded **30e** as white microcrystals (0.301 g, 72 %): mp 173–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 28H), 7.11 (d, J = 9.0 Hz, 4H), 6.84 (d, J = 9.0 Hz, 4H), 3.79 (s, 6H), 1.43 (s, 72H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 153.9, 153.6, 140.8, 140.2, 139.7, 135.8, 128.4, 127.0, 126.9, 114.1, 81.3, 81.2, 81.0, 55.4, 28.2; IR (neat, cm^{-1}) 1711; HRMS (FAB) *m/z* 1666.8244 (1666.8251 calcd for $C_{96}H_{114}N_8O_{18}$, M^+). Anal. Calcd for $C_{96}H_{114}N_8O_{18}$: C, 69.13; H, 6.89. Found: C, 69.28; H, 7.11.

***N*-(*tert*-Butoxycarbonyl)-4,4'-dibromodiphenylamine (31).** Diphenylamine (4.231 g, 25.0 mmol) was converted to 4,4'-dibromodiphenylamine by the method of Berthelot *et al.*[64] The crude product and 4-dimethylaminopyridine (0.611 g, 5.00 mmol, 20 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (20 mL) was added via syringe, followed by di-*tert*-butyl dicarbonate (6.30 mL, 27.5 mmol). The resulting solution was heated at reflux for 1 h, then cooled to room temperature and concentrated *in vacuo*. Crystallization of the residual solid from methanol afforded the title compound as white crystals with a faint pink cast (8.65 g, 81 % based on diphenylamine): mp 113–115 °C; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.7 Hz, 4H), 7.08 (d, J = 8.7 Hz, 4H), 1.46 (s,

9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 141.9, 132.1, 128.7, 119.5, 82.2, 28.4; IR (neat, cm^{-1}) 2977, 1712, 1488, 1322, 1160, 1072, 1011, 824. Anal. Calcd for $C_{17}H_{17}Br_2NO_2$: C, 47.80; H, 4.01. Found: C, 48.02; H, 3.87.

***N,N'*-Bis(4-bromophenyl)-*N,N'*-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (32).** 1,4-Phenylenediamine (1.00 g, 9.25 mmol) 1,4-dibromobenzene (4.58 g, 19.4 mmol), sodium *tert*-butoxide (2.31 g, 24.0 mmol), $Pd_2(dba)_3$ (0.085 g, 0.093 mmol, 1.0 mol %), and *S*-BINAP (0.173 g, 0.278 mmol, 3.0 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (20 mL) was added via syringe. The reaction mixture was heated to a gentle reflux. Analysis by TLC after 15 h indicated an incomplete reaction. Additional portions of $Pd_2(dba)_3$ (0.020 g, 0.022 mmol, 0.24 mol %) and *S*-BINAP (0.040 g, 0.064 mmol, 0.69 mol %) were added. Analysis by TLC after a further 15 h at reflux indicated a complete reaction. The mixture was cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (0.226 g, 1.85 mmol, 20 mol %) was added. The septum was replaced, and di-*tert*-butyl dicarbonate (7.07 g, 32.4 mmol) was added via syringe. The resulting solution was heated at a gentle reflux for 3h, then cooled to room temperature and filtered through a plug of silica gel and Celite, which was then washed with a 1:1 mixture of hexanes and ethyl acetate. The filtrate was concentrated *in vacuo*. Crystallization of the residual solid from methanol containing a small proportion of chloroform afforded the title compound as white crystals (3.98 g, 70 %): mp 174–176 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 8.6 Hz, 4H), 7.12 (s, 4H), 7.07 (d, J = 8.6 Hz, 4H), 1.43 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 141.9, 140.1, 131.8, 128.4, 127.1, 119.1, 81.7, 28.2; IR (neat, cm^{-1}) 2976, 1711, 1510, 1488, 1322, 1159. Anal. Calcd for $C_{28}H_{30}Br_2N_2O_4$: C, 54.39; H, 4.89. Found: C, 54.15; H, 4.79.

Octamer dibromide 33. Diamine **17** (2.03 g, 1.62 mmol), 1,4-dibromobenzene (0.955 g, 4.05 mmol), sodium *tert*-butoxide (0.404g, 4.20 mmol), $Pd(OAc)_2$ (14.5 mg, 0.0648 mmol, 4.0 mol %), and BINAP (48.4 mg, 0.0778 mmol, 5 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (15 mL) was added via syringe, followed by triethylamine (3 mL). The reaction mixture was heated at 90 °C for 48 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (20.0 mg, 0.162 mmol, 10 mol %) was added. The septum was replaced, and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 5.7 mL, 5.7 mmol) was added via syringe. The resulting mixture was heated at 67 °C for 3 h, then cooled to room temperature, and partitioned between ethyl acetate (50 mL) and a 2.0 M aqueous solution of sodium hydroxide (25 mL). The organic layer was washed with brine (30 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. Crystallization of the residual solid from isopropanol afforded dibromide **21** as white microcrystals (2.15 g, 75 %): mp 145–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 4H), 7.12 (s, 28H), 7.07 (d, J = 7.8 Hz, 4H), 1.43 (s, 72 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 153.8, 153.6, 153.4, 145.1, 142.0, 140.6, 140.4, 140.2, 139.9, 139.7, 137.6, 133.1, 131.8, 128.4, 128.3, 127.9, 127.0, 124.1, 119.0, 81.6, 81.4, 81.2, 81.1, 28.2; IR (neat, cm^{-1}) 1712. Anal. Calcd for $C_{94}H_{108}Br_2N_8O_{16}$: C, 63.94; H, 6.16. Found: C, 63.76; H, 5.93.

Phenyl-capped heptamer 34. Arylamine **24** (0.799 g, 1.68 mmol), dibromide **31** (0.326 g, 0.764 mmol), sodium *tert*-butoxide (0.215 g, 2.24 mmol), $Pd_2(dba)_3$ (14.0 mg, 0.0153 mmol, 2 mol %), and *S*-BINAP (22.8 mg, 0.0366 mmol, 4.8 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (6 mL) was added via syringe. The reaction mixture was heated at 80 °C with stirring for 27 h, then cooled to room temperature and taken up in dichloromethane (75

mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated *in vacuo*. The residue and 4-dimethylamino-pyridine (46.4 mg, 0.38 mmol, 25 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe, followed by a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 2.0 mL, 2.0 mmol). The resulting solution was heated at 60 °C with stirring for 6 h, then cooled to room temperature and concentrated *in vacuo*. The residual solid was crystallized from ethanol containing a small proportion of chloroform, and recrystallized from a mixture of ethanol and toluene, to afford heptamer **22** as white crystals (0.647 g, 60 %): mp 168–170 °C with slow decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (at, 4H), 7.21–7.16 (m, 4H), 7.14 (ad, 26H), 1.45 (s, 27H), 1.44 (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 153.9, 153.9, 143.0, 140.6, 140.4, 140.2, 128.9, 127.2, 127.2, 125.9, 81.6, 81.5, 81.4, 28.4; IR (neat, cm^{-1}) 2977, 2931, 1711, 1509, 1327, 1161, 1057, 757. Anal. Calcd for $C_{83}H_{97}N_7O_{14}$: C, 70.37; H, 6.90. Found: C, 70.15; H, 6.98.

α,ω-Bis(trimethylsilyl)-phenyl-capped nonamer 35. Arylamine **7** (1.301 g, 1.76 mmol), dibromide **31** (0.342 g, 0.800 mmol), sodium *tert*-butoxide (0.215 g, 2.24 mmol), $Pd_2(dba)_3$ (14.7 mg, 0.016 mmol, 2 mol %), and *S*-BINAP (23.9 mg, 0.0384 mol, 4.8 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (7 mL) was added via syringe. The reaction mixture was heated at 80 °C with stirring for 27 h, then cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated *in vacuo*. The residue and 4-dimethylaminopyridine (48.9 mg, 0.400 mmol, 50 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added

via syringe, followed by a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 2.0 mL, 2.0 mmol). The resulting solution was heated at 60 °C with stirring for 6 h, then cooled to room temperature and concentrated *in vacuo.* The residual solid was crystallized from ethanol containing a small proportion of chloroform, and recrystallized from a mixture of ethanol and toluene, to afford nonamer **23** as white crystals (0.970 g, 62 %): mp 183–185 °C with slow decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 4H), 7.18 (d, J = 8.3 Hz, 4H), 7.14 (s, 32H), 1.46 (s, 18H), 1.44 (s, 63H), 0.25 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 153.9, 143.4, 140.5, 140.3, 140.3, 137.7, 133.9, 127.5, 127.2, 126.1, 81.6, 81.5, 81.5, 81.4, 28.4, 28.4, –0.9; IR (neat, cm^{-1}) 2976, 2932, 1713, 1509, 1327, 1161, 1057, 851, 756. Anal. Calcd for $C_{111}H_{139}N_9O_{18}Si_2$: C, 68.60; H, 7.21. Found: C, 68.57; H, 7.13.

α,ω-Bis(trimethylsilyl)-phenyl-capped decamer 36. Arylamine **7** (1.301 g, 1.76 mmol), dibromide **32** (0.495 g, 0.800 mmol), sodium *tert*-butoxide (0.215 g, 2.24 mmol), $Pd_2(dba)_3$ (14.7 mg, 0.016 mmol, 2 mol %), and *S*-BINAP (23.9 mg, 0.0384 mol, 4.8 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (7 mL) was added via syringe. The reaction mixture was heated at 80 °C with stirring for 27 h, then cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated *in vacuo.* The residue and 4-dimethylaminopyridine (48.9 mg, 0.400 mmol, 50 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (10 mL) was added via syringe, followed by a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 2.0 mL, 2.0 mmol). The resulting solution was heated at 60 °C with stirring for 6 h, then cooled to room temperature and concentrated *in vacuo.* The residual solid was crystallized from ethanol containing a small proportion of chloroform, and

recrystallized from a mixture of ethanol and toluene, to afford decamer **36** as white crystals (1.128 g, 66 %): mp 188–189 °C with slow decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 4H), 7.19–7.14 (m, 40H), 1.46 (s, 36H), 1.44 (s, 54H), 0.25 (s, 18H); IR (neat, cm^{-1}) 2977, 2931, 1713, 1509, 1328, 1161, 1057, 851, 756. Anal. Calcd for $C_{122}H_{152}N_{10}O_{20}Si_2$: C, 68.64; H, 7.18. Found: C, 68.84; H, 7.31.

α,ω-Bis(trimethylsilyl)-phenyl-capped 16-mer 37. Dibromide **33** (0.750 g, 0.425 mmol), arylamine **7** (0.659 g, 0.892 mmol), sodium *tert*-butoxide (0.114 g, 1.19 mmol), $Pd(OAc)_2$ (3.8 mg, 0.0170 mmol, 4.0 mol %), and BINAP (12.7 mg, 0.0204 mmol, 4.8 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (3 mL) was added via syringe, followed by triethylamine (1 mL). The reaction mixture was heated at 90 °C with stirring for 18 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (5.00 mg, 0.0425 mmol, 10 mol %) was added. The septum was replaced, and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 1.49 mL, 1.49 mmol) was added via syringe. The resulting mixture was heated at 67 °C for 3 h, then cooled to room temperature and partitioned between ethyl acetate (30 mL) and a 2.0 M aqueous solution of sodium hydroxide (20 mL). The organic layer was washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. Crystallization of the residual solid from a 10:1 mixture of methanol and chloroform afforded 16-mer **25** as white crystals (1.01 g, 73 %): mp 182–185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4, 4H), 7.13 (s, 60H), 1.43 (s, 144H), 0.24 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 143.2, 140.4, 140.2, 137.5, 128.2, 127.0, 126.6, 125.9, 81.3, 28.2, –1.1; IR (neat, cm^{-1}) 1713. Anal. Calcd for $C_{188}H_{233}N_{16}O_{32}Si$: C, 68.80; H, 7.06. Found: C, 68.53; H, 6.85.

α,ω-Bis(trimethylsilyl)-phenyl-capped 24-mer (38). Dibromide **33** (0.177 g, 0.100 mmol), arylamine **10** (0.316 g, 0.210 mmol), sodium *tert*-butoxide

(0.0288 mg, 0.300 mmol), $Pd(OAc)_2$ (1.3 mg, 6.0 μmol, 6.0 mol %), and BINAP (4.5 mg, 7.2 μmol, 7.2 mol %) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and toluene (2 mL) was added via syringe, followed by triethylamine (0.5 mL). The reaction mixture was heated at 90 °C with stirring for 18 h, then cooled to room temperature. The flask was opened, and 4-dimethylaminopyridine (2.40 mg, 0.0200 mmol, 20 mol %) was added. The septum was replaced, and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 0.40 mL, 0.40 mmol) was added via syringe. The resulting mixture was heated at 67 °C for 4 h, then cooled to room temperature, and partitioned between ethyl acetate (30 mL) and a 2.0 M aqueous solution of sodium hydroxide (20 mL). The organic layer was washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. Crystallization of the residual solid from isopropanol afforded 24-mer **38** as white crystals (362 mg, 75 %): mp 185–188 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4, 4H), 7.13 (s, 92H), 1.44 (s, 18H), 1.43 (s, 198H), 0.24 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 143.0, 140.2, 140.0, 137.3, 133.6, 128.0, 127.2, 126.9, 125.8, 81.3, 28.3, –1.1; IR (neat, cm^{-1}) 1714. Anal. Calcd for $C_{272}H_{334}N_{24}O_{48}Si_2$: C, 68.89; H, 7.00. Found: C, 69.06; H, 6.93.

Chain-Length Confirmation for 16-mer and 24-mer by ^{1}H NMR. The oligomer and hexamethylbenzene were weighed into a vial, dissolved in CD_2Cl_2 (0.75 mL), and transferred to an NMR tube. Three samples were prepared for each oligomer. Each spectrum was recorded with 16 scans and a relaxation delay of 20 seconds. Relative integration of the resonances for the internal standard, the BOC groups and the trimethylsilyl endgroups yielded the ratios of repeat units to end groups; for each oligomer, the average ratio of the three runs was taken.

BOC/TMS ratio calcd for 16-mer **37**: 8/1. Found: (8.6±0.3)/1.

BOC/TMS ratio calcd for 24-mer **38**: 12/1. Found: (12.5±0.1)/1.

Iodotrimethylsilane. Iodotrimethylsilane was prepared from iodine and hexamethyldisilane according to the procedure of Seitz and Ferreira,[147] except for the use of 1.05 equiv hexamethyldisilane to ensure complete consumption of iodine. The product was vacuum-transferred from a trace of zinc dust and stored in a resealable Schlenk tube under argon, over copper wire. The colorless liquid was approximately 95 % pure as judged by ^{1}H NMR, the remainder consisting principally of hexamethyldisilane.

General Procedure for Deprotection of Oligomers by Thermolysis. The protected oligomer was placed in an oven-dried Schlenk tube, which was stoppered, evacuated, and backfilled with argon. The material was heated for 9 h at 185 °C, then cooled to room temperature. The deprotected oligomers were obtained as powders in quantitative yield.

Phenyl-capped octaaniline (39a): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.76 (s, 2H), 7.59 (s, 2H), 7.51 (s, 2H), 7.49 (s, 2H), 7.18 (t, J = 7.4 Hz, 4H), 7.10–6.96 (m, 32H), 6.71 (t, J = 7.4 Hz, 2H); IR (neat, cm^{-1}) 3388, 1598, 1514, 1495, 1292, 1214, 814, 744, 697. 509; UV–vis (NMP) λ_{max} 337 nm (ε = 6.6 x 10^4). Anal. Calcd for $C_{54}H_{46}N_8$: C, 80.37; H, 5.75. Found: C, 80.24; H, 5.62.

α,ω-Bis(cyano)-phenyl-capped octaaniline (39b): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 8.60 (s, 2H), 7.79 (s, 2H), 7.58 (d, J = 8.4 Hz, 4H), 7.53 (s, 2H), 7.52 (s, 2H), 7.14–6.98 (m, 28H); IR (neat, cm^{-1}) 3385, 2213, 1602, 1498, 1293, 1237, 1172, 815, 515; UV–vis (NMP) λ_{max} 336 nm (ε = 7.3 x 10^4). Anal. Calcd for $C_{56}H_{44}N_{10}$: C, 78.48; H, 5.17. Found: C, 78.53; H, 4.95.

α,ω-Bis(*tert*-butyl)-phenyl-capped octaaniline (39c): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.60 (s, 2H), 7.48 (s, 2H), 7.43 (s, 2H), 7.41 (s, 2H), 7.16 (d, J = 8.7 Hz, 4H), 6.93 (d, J = 8.7 Hz, 4H), 6.88–6.82 (m, 28H), 1.22 (s, 18H); IR (neat, cm^{-1}) 3389, 2957, 1610, 1499, 1291, 815; UV–vis (NMP)

λ_{max} 336 nm ($\varepsilon = 7.8 \times 10^4$); HRMS (FAB) *m/z* 918.5090 (918.5097 calcd for $C_{62}H_{62}N_8$, M^+).

α,ω-Bis(*n*-dodecyl)-phenyl-capped octaaniline (39d): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.64 (s, 2H), 7.54 (s, 2H), 7.49 (s, 2H), 7.48 (s, 2H), 7.06–6.94 (m, 36H), 2.51 (t, J = 7.5 Hz, 4H), 1.61–1.50 (m, 4H), 1.36–1.24 (m, 36H), 0.88 (t, J = 6.2, 6H); IR (neat, cm^{-1}) 3390, 2922, 2852, 1610, 1515, 1498,1293, 1215, 815; UV–vis (NMP) λ_{max} 336 nm ($\varepsilon = 7.3 \times 10^4$). Anal. Calcd for $C_{78}H_{94}N_8$: C, 81.92; H, 8.28. Found: C, 81.74; H, 8.09.

α,ω-Bis(methoxy)-phenyl-capped octaaniline (39e): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.48 (s, 4H), 7.47 (s, 4H), 7.01 (d, J = 8.7 Hz, 4H), 6.99 (s, 28H), 6.84 (d, J = 8.7 Hz, 4H), 3.74 (s, 6H); IR (neat, cm^{-1}) 3389, 1514, 1498, 1292, 1237, 815, 515; UV–vis (NMP) λ_{max} 335 nm ($\varepsilon = 5.38 \times 10^4$). Anal. Calcd for $C_{56}H_{50}N_8O_2$: C, 77.57; H, 5.81. Found: C, 77.37; H, 5.75.

General Procedure for Preparative Deprotection of Oligomers by Iodotrimethylsilane. The protected oligomer (0.020 mmol) was placed in an oven-dried Schlenk tube, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and anhydrous dichloromethane (5.0 mL) was added via syringe. Iodotrimethylsilane (20 % excess) was added dropwise, with stirring, causing the solution to turn a pale yellow color. The solution was stirred for 15-30 min, then degassed methanol (200 μL) was added dropwise. Within seconds, the clear solution became cloudy and deposited a pale yellow precipitate. Degassed triethylamine (200 μL) was added, and the suspension was vacuum-filtered rapidly under air. The collected product was washed with degassed methanol (5 mL) and dried *in vacuo*, affording a white powder.

Phenyl-capped heptaaniline (40). No melting observed below 360 °C. ^{1}H NMR (500 MHz, DMF-d_7) δ 7.79 (s, 2H), 7.62 (s, 2H), 7.54 (s, 2H), 7.52 (s, 1H), 7.18 (t, J = 7.8 Hz, 4H), 7.09–6.99 (m, 28H), 6.71 (t, J = 7.1 Hz, 2H); ^{13}C (125 MHz, DMF-d_7)

δ 147.3, 141.0, 139.7, 139.2, 138.8, 138.1, 136.2, 131.5, 130.1, 122.2, 120.3, 119.6, 119.3, 119.0, 119.0, 118.2, 115.8; IR (neat, cm^{-1}) 3387, 3025, 1598, 1512, 1302, 814; UV–vis (DMF) λ_{max} 334 nm ($\varepsilon = 7.9 \times 10^4$). Anal. Calcd for $C_{48}H_{41}N_7$: C, 80.53; H, 5.77. Found: C, 80.52; H, 5.54.

Phenyl-capped nonaaniline (41). No melting observed below 360 °C. ^1H NMR (500 MHz, DMF-d_7) δ 7.77 (s, 2H), 7.60 (s, 2H), 7.52 (s, 2H), 7.49 (s, 3H), 7.18 (t, J = 12.0 Hz, 4H), 7.09–7.00 (m, 36H), 6.70 (t, J = 12.5 Hz, 2H); ^{13}C NMR (125 MHz, DMF-d_7) δ 146.5, 140.3, 139.0, 138.6, 138.3, 138.2, 137.9, 137.3, 135.5, 129.4, 121.4, 119.5, 118.9, 118.7, 118.6, 118.4, 118.2, 118.2, 117.4, 115.0; IR (KBr, cm^{-1}) 3386, 3021, 1598, 1496, 1290, 814; UV–vis (DMF) λ_{max} 336 nm ($\varepsilon = 8.4 \times 10^4$). Anal. Calcd for $C_{60}H_{51}N_9$: C, 80.24; H, 5.72. Found: C, 79.99; H, 5.61.

Phenyl-capped decaaniline (42). No melting observed below 360 °C. ^1H NMR (500 MHz, DMF-d_7) δ 7.77 (s, 2H), 7.60 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.48 (s, 2H), 7.18 (t, J = 13.0 Hz, 4H), 7.09–6.98 (m, 40H), 6.71 (t, J = 12.0 Hz, 2H); ^{13}C NMR (125 MHz, DMF-d_7) δ 147.3, 141.1, 139.8, 139.3, 139.2, 139.1, 138.9, 138.7, 138.1, 136.2, 134.9, 130.1, 122.2, 120.3, 119.7, 119.5, 119.4, 119.3, 119.2, 119.0, 118.9, 118.2, 115.7; IR (KBr, cm^{-1}) 3386, 3021, 1598, 1496, 1289, 815; UV–vis (DMF) λ_{max} 336 nm ($\varepsilon = 1.1 \times 10^5$). Anal. Calcd for $C_{66}H_{56}N_{10}$: C, 80.13; H, 5.71. Found: C, 79.93; H, 5.64.

Phenyl-capped 16-mer (43). No melting observed below 360 °C. IR (KBr, cm^{-1}) 3378, 3021, 1596, 1496, 1284, 814; UV–vis (DMF) λ_{max} 338 nm ($\varepsilon = 1.8 \times 10^5$). Anal. Calcd for $C_{102}H_{86}N_{16}$: C, 79.77; H, 5.64; N, 14.59. Found: C, 79.59; H, 5.46; N, 14.38.

Phenyl-capped 24-mer (44). No melting observed below 360 °C. IR (KBr, cm^{-1}) 3378, 3025, 1596, 1496, 1284, 814; UV–vis (DMF) λ_{max} 338 nm ($\varepsilon = 2.2 \times 10^5$). Anal. Calcd for $C_{150}H_{126}N_{24}$: C, 79.55; H, 5.61; N, 14.84. Found: C, 79.52; H, 5.54; N, 14.66.

Preparation of films for electrochemistry. The protected oligomer (10.0 μmol, except 5.00 μmol in the case of **44**) was placed in an oven-dried Schlenk tube, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and anhydrous dichloromethane (5.0 mL) was added via syringe. Iodotrimethylsilane (20 % excess) was added dropwise, with stirring, causing the solution to turn a pale yellow color. The solution was stirred for 15 min, then concentrated and dried *in vacuo* to remove excess iodotrimethylsilane. The residual solid was dissolved in anhydrous dichloromethane (20.0 mL), forming a clear solution. An aliquot of 10.0 μL was withdrawn *via syringe* and allowed to evaporate on an ITO-coated glass slide.

Electrochemistry. Electrochemical studies were carried out using an EcoChemie Autolab potentiostat. Cyclic voltammograms were recorded at a scan rate of 100 mV/s in a three-electrode cell with a platinum foil counter electrode and a SCE reference electrode. Working electrodes were prepared by evaporation of an oligomer trimethylsilylcarbamate solution, prepared as described above, onto ITO-coated spectroelectrochemistry slides (40 Ω, coated both sides) purchased from Delta Technologies, Limited. Experiments were run under noncontrolled atmosphere using 1.0 M aqueous sulfuric acid as the electrolyte.

Chapter 2:

***N*-(*tert*-Butoxycarbonyl)-4,4'-bis(*N*-diphenylmethylene-amino)diphenylamine (45).** Aryl bromide **31** (0.427 g, 1.00 mmol), sodium *tert*-butoxide (0.269 g, 2.80 mmol), tris(dibenzylideneacetone) dipalladium (4.6 mg, 0.005 mmol, 0.5 mol % Pd per bromide), and *S*-BINAP (9.4 mg, 0.015 mmol, 0.75 mol % per bromide) were placed in an oven-dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and benzophenone imine (0.37 mmol, 2.2 mmol) was added via syringe, followed by toluene (4 mL). The mixture was heated to 80 °C with stirring. Analysis by TLC after 6

h indicated complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in dichloromethane (75 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The yellow solid residue was recrystallized from methanol, affording the title compound as yellow crystals, 0.574 g (91 %): mp 156–157.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 7.2 Hz, 4H), 7.47–7.38 (m, 6H), 7.27–7.20 (m, 6H), 7.14–7.11 (m, 4H), 6.93 (d, J = 8.7 Hz), 6.65 (d, J = 8.7 Hz), 1.37 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 153.9, 148.6, 139.7, 138.6, 136.2, 130.9, 129.7, 129.4, 128.8, 128.3, 128.1, 126.9, 121.4, 80.8, 28.4; IR (neat, cm^{-1}) 2975, 1708, 1613, 1499, 1446, 1326, 1162, 695. Anal. Calcd for $C_{43}H_{37}N_3O_2$: C, 82.27; H, 5.94. Found: C, 82.33; H, 5.85.

***N*-(*tert*-Butoxycarbonyl)-4,4'-diaminodiphenylamine (46).** Palladium on carbon (5 wt. %, 0.341 g, 0.16 mmol Pd), ammonium formate (1.01 g, 16.0 mmol), and **45** (0.502 g, 0.800 mmol) were placed in a dried Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (4 mL) and methanol (8 mL) were added via syringe. A needle connected to an oil bubbler was inserted through the septum, and the reaction mixture was heated to 60 °C with stirring. A steady effervescence soon ensued. Analysis by TLC after 2 h indicated complete consumption of the starting imine. The mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (50 mL), filtered through Celite, and concentrated *in vacuo*. The resulting white solid was triturated with hexanes (20 mL), cooled to 0 °C, and collected by filtration. The title compound was obtained as white crystals, 0.233 g (97 %): mp 202–205 °C with decomposition; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, J = 8.7 Hz, 4H), 6.61 (d, J = 8.7 Hz, 4H), 3.60 (s, 4H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 144.1, 134.7, 127.9, 115.2, 80.5, 28.5; IR (neat, cm^{-1})

3468, 3435, 3368, 2976, 1673, 1615, 1514, 1359, 1279, 1228, 1161, 1058, 851, 767. Anal. Calcd for $C_{17}H_{21}N_3O_2$: C, 68.20; H, 7.07. Found: C, 68.38; H, 7.25.

o-Anisidine.[148a] Sodium *tert*-butoxide (0.135 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (4.6 mg, 0.005 mmol, 1 mol % Pd), and *S*-BINAP (9.4 mg, 0.015 mmol, 1.5 mol %) were placed in an oven-dried Schlenk tube, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and 2-bromoanisole (0.125 mL, 1.00 mmol) was added via syringe, followed by benzophenone imine (0.20 mL, 1.2 mmol) and toluene (2 mL). The reaction mixture was heated to 80 °C with stirring. Analysis by GC after 7.5 h indicated the complete consumption of starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in diethyl ether (50 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, transferred to a Schlenk flask, and concentrated *in vacuo*, affording the crude imine as a thick yellow oil.

Palladium on carbon (5 wt. %, 0.213 g, 0.10 mmol Pd) and ammonium formate (0.946 g, 15.0 mmol) were added to the flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and methanol (10 mL) was added via syringe. A needle connected to an oil bubbler was inserted through the septum, and the reaction mixture was heated to 60 °C with stirring. A steady effervescence began after a few seconds. Analysis by GC after 5 h indicated the complete consumption of the starting imine, and of the excess benzophenone imine. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in dichloromethane (50 mL), filtered through Celite, and concentrated *in vacuo*. The product was isolated by flash column chromatography on silica gel, using hexanes: ethyl acetate (4:1) as the eluant. The title compound was obtained as a pale yellow oil, 0.110 g (89 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82–6.64 (m, 4H), 3.87 (s, 3H), 3.80 (broad s, 2H).

4-Aminobenzonitrile.[148b] 4-Bromobenzonitrile (0.182 g, 1.00 mmol), sodium *tert*-butoxide (0.135 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (2.3 mg, 0.0025 mmol, 0.5 mol % Pd), and *S*-BINAP (4.7 mg, 0.0075 mmol, 0.75 mol %) were placed in an oven-dried Schlenk tube, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and benzophenone imine (0.20 mL, 1.2 mmol) was added via syringe, followed by toluene (2 mL). The reaction mixture was heated to 80 °C with stirring. Analysis by GC after 90 min showed complete consumption of the starting aryl bromide. The reaction mixture was cooled to room temperature, taken up in diethyl ether (75 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*.

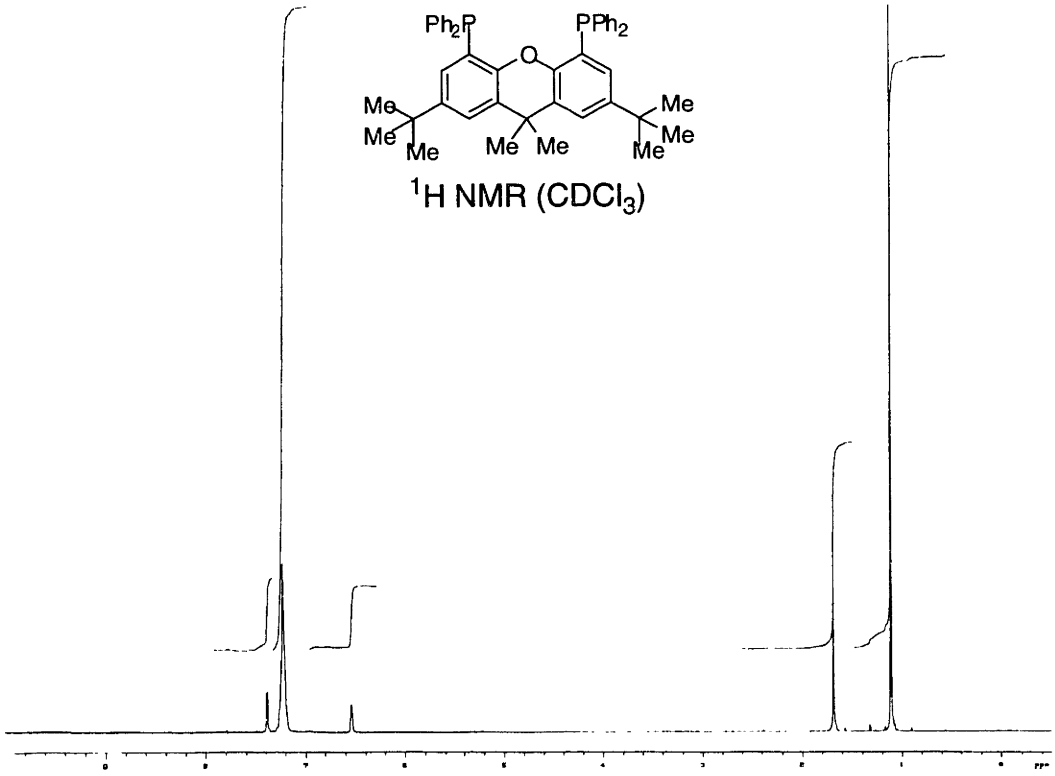
The resulting yellow solid was transferred to an Erlenmeyer flask. Methanol (10 mL) was added with stirring, giving a yellow suspension. Sodium acetate (0.246 g, 3.00 mmol)), was added as a solid, in one portion, followed by hydroxylamine hydrochloride (0.104 g, 1.50 mmol). Analysis of the reaction mixture after 15 min indicated complete consumption of the starting imine. Solid potassium carbonate (*ca.* 1 g) was added, and the mixture was concentrated *in vacuo*. The residue was taken up in diethyl ether (75 mL), washed with brine (50 mL), filtered, and concentrated *in vacuo*. Flash column chromatography on silica gel, using hexanes: ethyl acetate (3:2) as the eluant, afforded the title compound as a white solid, 0.116 g (98 %): mp 83–84.5 °C (authentic sample: 83–85 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 8.1 Hz, 2H), 4.18 (s, 2H).

2-(3-Aminophenyl)-1,3-dioxolane.[149] The procedure followed was identical to that described above, except for the use of 2-(3-bromophenyl)-1,3-dioxolane as the aryl bromide. Flash column chromatography on silica gel, using hexanes:ethyl acetate (2:3) as the eluant, afforded the title compound as a pale yellow oil, 0.148 g (90 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (dd, J = 7.8, 7.8 Hz, 1H), 6.88 (d,

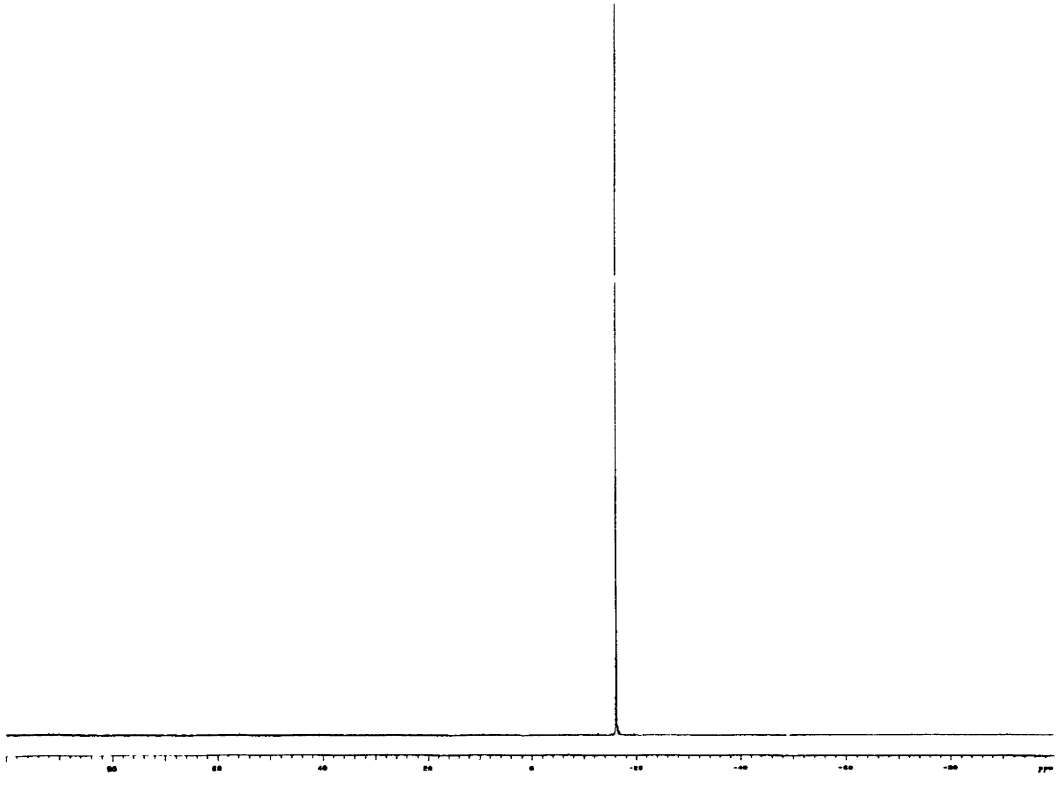
J = 7.5 Hz, 1H), 6.82 (s, 1H), 6.69 (dd, J = 7.8, 2.1 Hz, 1H), 5.75 (s, 1H), 4.15–4.08 (m, 2H), 4.07–4.00 (m, 2H), 3.70 (broad s, 2H); IR (neat, cm^{-1}) 3454, 3360, 3321, 2962, 2880, 1624, 1593, 1529, 1491, 1466, 1395, 1316, 1211, 1184, 1091, 1023, 997, 947, 872, 783, 720, 696, 668. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71. Found: C, 65.67; H, 6.96.

Bis[2-(diphenylphosphino)phenyl] ether (DPEphos). This compound was prepared according to the procedure of van Leeuwen *et al.*[84] Recrystallization of the precipitated material from isopropanol containing a small quantity of dichloromethane afforded the title compound as white crystals, 29.95 g (49 %): mp 185–185.5 °C (lit.[84] 175–176 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.31–7.22 (m, 20H), 7.04–6.99 (m, 2H), 6.91–6.87 (m, 2H), 6.78–6.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 159.3, 136.8, 136.7, 134.1, 134.0, 134.0, 130.3, 129.2, 129.1, 128.6, 128.4, 128.4, 128.4, 123.7, 118.2 (observed complexity due to P–C splitting; definitive assignments have not been made); ^{31}P NMR (125 MHz, $CDCl_3$) δ –16.4; IR (neat, cm^{-1}) 3064, 3051, 3014, 3000, 1582, 1563, 1476, 1459, 1432, 1395, 1308, 1270, 1258, 1245, 1221, 1179, 1156, 1125, 1092, 1069, 1036, 1027, 1000, 878, 797, 745, 733, 693. Anal. Calcd for $C_{36}H_{28}OP_2$: C, 80.29; H, 5.24. Found: C, 80.55; H, 5.23.

2,7-Di-*tert*-butyl-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene. A dry Schlenk flask was charged with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (2.40 g, 5.00 mmol), stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (90 mL) was added via syringe. The resulting solution was cooled to –78 °C with stirring, and a solution of *n*-butyllithium in hexanes (1.6 M, 6.9 mL, 11 mmol) was added via syringe. The mixture was stirred at –78 °C; within 20 min, a white suspension had formed. After 3 h, a solution of diphenylchlorophosphine (2.43 g, 11 mmol) in tetrahydrofuran (10 mL) was added via cannula, over a period of 10 min. The resulting mixture was stirred 3 h at –78 °C, then warmed to room temperature and concentrated



^{1}H NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

in vacuo. The residue was taken up in dichloromethane (100 mL) and washed with a 2 M aqueous solution of sodium hydroxide (100 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The resulting pale yellow oil resisted attempts at crystallization. Flash column chromatography on silica gel, using dichloromethane: ethanol (99:1) as the eluant, followed by recrystallization from toluene/ethanol, afforded the title compound as white crystals, 1.76 g (51 %): mp 194–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 2.3 Hz, 2H), 7.25–7.21 (m, 20H), 6.54 (d, J = 2.3 Hz, 2H), 1.69 (s, 6H), 1.12 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 150.7, 150.6, 145.4, 137.9, 137.9, 137.8, 134.3, 134.2, 134.1, 134.0, 133.9, 129.6, 129.0, 128.3, 128.2, 128.2, 128.2, 124.9, 124.8, 124.8, 123.1, 35.0, 34.7, 32.4, 31.5 (observed complexity in aryl region due to P–C splitting; definitive assignments havenot been made); ^{31}P NMR (125 MHz, $CDCl_3$) δ −16.2; IR (neat, cm^{-1}) 3070, 3053, 2962, 2904, 2867, 2802, 1584, 1476, 1432, 1422, 1393, 1362, 1324, 1308, 1264, 1247, 1210, 1189, 1111, 1098, 1028, 880, 863, 745, 695.

General procedure for the coupling of amines with aryl halides, using DPEphos as the supporting ligand:

Palladium acetate (1.1 mg, 0.005 mmol, 0.5 mol %) and DPEphos (4.0 mg, 0.0075 mmol, 0.75 mol %), were placed in an oven-dried Schlenk tube, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a septum; arylamine (1.20 mmol) and aryl bromide (1.00 mmol) were added to the tube via syringe, followed by toluene (2 mL). The resulting mixture was stirred for 5 min at room temperature, affording a clear yellow solution. The tube was opened, and solid sodium *tert*-butoxide (0.135 g, 1.40 mmol) was added in one portion, causing the solution to turn a deep red color. The septum was replaced, the tube was purged for 3 min with argon, and the reaction mixture was heated with stirring at 80 °C until the aryl bromide had been consumed as judged by GC analysis. The mixture was then cooled

to room temperature, taken up in diethyl ether (40 mL), and washed with brine. The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel.

Note: In cases where the arylamine or aryl halide was a solid, the reactant was added with the base and catalyst precursors.

***N*-(2-Methoxyphenyl)-3,5-dimethylaniline.** The general procedure was followed, with a reaction time of 2.5 h, for the coupling of *o*-anisidine with 5-bromo-*m*-xylene, at a scale of 2.0 mmol. The title compound was obtained as a pale yellow oil, 0.440 g (97 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, 1H), 6.99–6.91 (m, 3H), 6.86 (d, J = 0.7 Hz, 2H), 6.78 (d, J = 0.7 Hz, 1H), 6.16 (s, 1H), 3.94 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 142.9, 139.1, 133.4, 123.2, 121.0, 119.8, 116.6, 115.1, 110.7, 55.8, 21.7; IR (neat, cm^{-1}): 3411, 3001, 2939, 2917, 2854, 2833, 1590, 1526, 1491, 1463, 1407, 1377, 1345, 1295, 1262, 1243, 1216, 1177, 1116, 1048, 1029, 829, 742. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 79.42; H, 7.72.

***N*-(*p*-Tolyl)-2,5-dimethylaniline.**[35] The general procedure was followed, with a reaction time of 3 h, for the coupling of *p*-toluidine with 2-bromo-*p*-xylene. The title compound was obtained as a red-orange solid, 0.202 g (95 %): mp 48–49 °C (lit.[35] 49.5–50.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.09 (m, 3H), 7.04 (s, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 7.8 Hz, 1H), 5.29 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 141.3, 136.6, 130.9, 130.5, 130.0, 124.1, 122.0, 118.8, 118.1, 21.4, 20.9, 17.6; IR (neat, cm^{-1}): 3394, 3018, 2919, 2861, 1612, 1586, 1516, 1460, 1394, 1310, 1239, 1117, 805. Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11. Found: C, 85.36; H, 8.10.

***N*-(*p*-Tolyl)-*o*-anisidine.**[35] The general procedure was followed, with a reaction time of 3 h, for the coupling of *p*-toluidine with 2-bromoanisole. The title

compound was obtained as a pale yellow oil, 0.203 g (95 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 7.8 Hz, 1H), 7.19–7.12 (m, 4H), 6.96–6.88 (m, 3H), 6.15 (s, 1H), 3.95 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 140.1, 134.0, 131.1, 130.0, 121.0, 119.8, 119.3, 113.8, 110.6, 55.7, 20.9; IR (neat, cm^{-1}): 3411, 3022, 2937, 2835, 1600, 1518, 1460, 1243, 1115, 1029, 809, 741. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 78.72; H, 7.26.

***N*-(2-Methoxyphenyl)-2,5-dimethylaniline.** The general procedure was modified as follows: The reaction was run without solvent, with a reaction time of 14 h, using 12 mmol *o*-anisidine, 10 mmol 2-bromo-*p*-xylene, 14 mmol sodium *tert*-butoxide, 0.005 mmol palladium acetate (0.05 mol %), and 0.0075 mmol ligand (0.075 mol %). After the usual workup, the product was purified by recrystallization from ethanol, affording the title compound as white crystals with a faint pink cast, 2.12 g (93 %): mp 89–90.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.06 (dd, J = 7.5, 2.0 Hz, 1H), 6.94–6.84 (m, 3H), 6.80 (d, J = 7.5 Hz, 1H), 5.86 (s, 1H), 3.93 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 140.8, 136.5, 134.2, 130.9, 126.5, 123.2, 121.1, 120.5, 119.3, 114.6, 110.6, 55.8, 21.4, 17.7; IR (neat, cm^{-1}): 3425, 3002, 2919, 2849, 1598, 1523, 1501, 1452, 1415, 1243, 1118, 1030, 741. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 79.48; H, 7.66.

***N*-(2-Cyanophenyl)-2,5-dimethylaniline.** The general procedure was followed, using cesium carbonate in place of sodium *tert*-butoxide as the base and a reaction time of 14 h, for the coupling of 2-aminobenzonitrile with 2-bromo-*p*-xylene. The title compound was obtained as a pale yellow solid, 0.196 g (88 %): mp 102–103.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.6, 1.5 Hz, 1H), 7.33 (ddd, J = 8.6, 8.2, 1.5 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.08 (s, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.81–6.75 (m, 2H), 6.09 (s, 1H), 2.34 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 137.7, 137.0, 134.1, 133.0, 131.3, 130.1, 126.7, 125.3, 118.4, 117.9, 113.7, 97.3, 21.1, 17.6; IR (neat, cm^{-1}): 3332, 3020, 2921, 2861, 2214, 1603, 1577, 1499,

1457, 1319, 1296, 1163, 752. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35. Found: C, 81.13; H, 6.24.

4-(Diphenylamino)biphenyl.[150] The general procedure was followed for the coupling of diphenylamine with 4-bromobiphenyl, with the following modifications: Diphenylamine was present in 5 % excess relative to the aryl bromide, and 1.0 mol % palladium acetate and 1.5 mol % DPEphos were used. After 14 h at 100 °C, the aryl bromide was completely consumed as judged by GC analysis. The workup was carried out as described in the general procedure, and the product was purified by recrystallization from ethanol, affording the title compound as white crystals, 0.277 g (86 %): mp 110–111.5 °C (lit.[150] 114 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.52–7.42 (m, 4H), 7.35–7.29 (m, 5H), 7.17 (d, J = 8.5 Hz, 6H), 7.06 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 147.4, 140.9, 135.3, 129.5, 128.9, 128.0, 127.0, 126.9, 124.6, 124.1, 123.1; IR (neat, cm^{-1}): 3059, 3031, 1591, 1518, 1485, 1326, 1278, 909, 838, 754, 696. Anal. Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96. Found: C, 89.88; H, 5.73.

2,6-Diisopropyl-2',6'-dimethyldiphenylamine. The general procedure was used for the coupling of 2,6-diisopropylaniline with 2-bromo-*m*-xylene, except that the reaction was carried out at 100 °C, using 5 mol % palladium acetate and 6 mol % DPEphos. The title compound was isolated as a pink solid, 0.257 g (91 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–7.12 (m, 3H), 6.97 (d, J = 7.5 Hz, 2H), 6.76 (t, J = 7.5 Hz, 1H), 4.82 (s, 1H), 3.18 (sept, J = 6.8 Hz, 2H), 2.01 (s, 6H), 1.16 (s, 6H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 143.3, 139.0, 129.7, 125.8, 125.0, 123.4, 119.8, 28.3, 23.7, 19.6; IR (neat, cm^{-1}): 3434, 3061, 2961, 2926, 2867, 2729, 1596, 1473, 1446, 1382, 1362, 1333, 1300, 1274, 1225, 1102, 794, 759, 733. Anal. Calcd for $C_{20}H_{27}N$: C, 85.35; H, 9.67. Found: C, 85.40; H, 9.89.

General procedure for the coupling of amines with aryl halides, using palladium chloride as the catalyst precursor:

Arylamine (2.40 mmol), palladium chloride (1.8 mg, 0.010 mmol, 0.5 mol %), and bisphosphine (0.015 mmol, 0.75 mol %) were placed in a dried, resealable Schlenk tube, which was fitted with a Teflon screwcap, evacuated, and backfilled with argon. The tube was sealed, and its contents were heated at 80 °C until a clear solution formed (*ca.* 10–20 min). The tube was then cooled to room temperature, and the Teflon screwcap was replaced with a rubber septum. Toluene (2 mL) was added via syringe, followed by aryl bromide. The resulting solution was stirred for a few seconds, then the septum was removed. Sodium *tert*-butoxide was added, then the septum was replaced. An additional portion of toluene (2 mL) was added, to wash into the reaction any base adhering to the side of the tube. The tube was purged with argon for 3 min, then the septum was replaced with the Teflon screwcap. The tube was sealed, and its contents were heated at 80 °C with stirring until the starting aryl bromide was completely consumed as judged by GC analysis. The reaction mixture was then cooled to room temperature, taken up in diethyl ether (50 mL), and washed with brine (30 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel.

***N*-(*p*-Tolyl)-*o*-anisidine.**[35] The general procedure was used to couple *p*-toluidine with 2-bromoanisole, using DPEphos as the supporting ligand and a reaction time of 2.5 h. The product was isolated as a colorless oil, 0.413 g (97 %). The identity and purity of the sample were verified by comparison of its ^{1}H NMR spectrum and gas chromatogram to those obtained for the sample prepared as described in Section 2.2.

***N*-(2-Methoxyphenyl)-2,5-dimethylaniline.** The general procedure was used to couple *o*-anisidine with 2-bromo-*p*-xylene, using DPEphos as the supporting ligand and a reaction time of 4 h. The product was isolated as a white solid, 0.424 g

(93 %). The identity and purity of the sample were verified by comparison of its melting point (88.5–90.5 °C), ^{1}H NMR spectrum and gas chromatogram to those obtained for the sample prepared as described in Section 2.2.

2-[3-(*N*-Methylanilino)phenyl]-1,3-dioxolane. The general procedure was used to couple *N*-methylaniline with 2-(3-bromophenyl)-1,3-dioxolane, using Xantphos as the supporting ligand and a reaction time of 1 h, 45 min. The product was isolated as a colorless oil, 0.470 g (92 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.31 (m, 3H), 7.23 (m, 1H), 7.16–7.02 (m, 5H), 5.82 (s, 1H), 4.17–4.12 (m, 2H), 4.11–4.03 (m, 2H), 3.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 148.8, 139.0, 129.3, 129.2, 121.7, 121.0, 120.8, 119.0, 117.7, 103.8, 65.3, 40.4; IR (neat, cm^{-1}): 3060, 3037, 2950, 2885, 2815, 1609, 1586, 1494, 1457, 1447, 1391, 1345, 1258, 1198, 1131, 1090, 1073, 1027, 994, 963, 946, 917, 878, 836, 783, 753, 695, 652. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71. Found: C, 75.36; H, 6.75.

***N*-(3,5-Dimethylphenyl)-benzylamine.** The general procedure was used to couple benzylamine with 5-bromo-*m*-xylene, using *rac*-BINAP as the supporting ligand and a reaction time of 4 h. The product was isolated as a colorless oil, 0.368 g (87 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.31 (m, 5H), 6.44 (s, 1H), 6.33 (s, 2H), 4.35 (s, 2H), 3.94 (broad s, 1H), 2.28 (s, 6H). The identity and purity of the sample were verified by comparison of its ^{1}H NMR spectrum and gas chromatogram to those obtained for an authentic sample.[47a]

2-(Di-*tert*-butylphosphino)biphenyl (48). Magnesium turnings (1.386 g, 57 mmol) were placed in a dried 500 mL Schlenk flask, which was stoppered, evacuated and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (50 mL) was added via syringe, followed by 2-bromobiphenyl (9.5 mL, 55 mmol). The resulting mixture was stirred at room temperature for 5 min, then heated to 65 °C. After 5 min, Grignard formation had visibly commenced, and additional tetrahydrofuran (150 mL) was added via syringe. The reaction mixture was

stirred for 90 min at 65 °C, then cooled to room temperature. The septum was removed, and cuprous chloride (5.84 g, 59 mmol) was added in one portion. The septum was replaced, and the reaction vessel was purged with argon for 5 min. Di-*tert*-butylchlorophosphine (10 g, 55 mmol) was added via syringe, and the resulting brown-green suspension was heated to 65 °C.

After 4.5 h, the mixture was cooled to room temperature and concentrated in vacuo. The residual gray solid was suspended in diethyl ether (200 mL), then collected by suction filtration. The filter cake was washed with six 25-mL portions of diethyl ether, then placed in a 1-L Erlenmeyer flask and resuspended in diethyl ether (250 mL). Ammonium hyrdoxide (concentrated aqueous, 600 mL) was added, and the mixture was stirred for 1 h, giving rise to a colorless ether phase and a deep blue-purple aqueous phase with a white precipitate. The mixture was poured into a 1-L separatory funnel, the layers were separated, and the aqueous phase was extracted with two 50-mL portions of diethyl ether. The combined ether extracts were dried over solid potassium carbonate, filtered through Celite, and concentrated *in vacuo* to give a nearly colorless oil which crystallized on standing. The product was recrystallized in two crops from methanol, affording the title compound as colorless needles (13.46 g, 82%): mp 85.5–86.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d of t, J = 6.9, 1.9 Hz, 1H), 7.41–7.30 (m, 5H), 7.30–7.21 (m, 3H), 1.16 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 151.3, 144.0, 144.0, 135.9, 135.7, 135.5, 135.5, 130.8, 130.8, 128.5, 127.3, 126.6, 125.9, 33.0, 32.8, 31.0, 30.9 (observed complexity due to P–C splitting; definitive assignments have not been made); ^{31}P NMR (125 MHz, $CDCl_3$) δ +18.7; IR (neat, cm^{-1}): 3060, 2981, 2956, 2941, 2894, 2861, 1598, 1584, 1472, 1459, 1362, 1173, 810, 778, 758, 700. Anal. Calcd for $C_{20}H_{27}P$: C, 80.50; H, 9.12. Found: C, 80.51; H, 9.29.

General procedure for the coupling of amines with aryl halides, using 2-(di-*tert*-butylphosphino)biphenyl as the supporting ligand:

An oven-dried, resealable Schlenk tube was charged with sodium *tert*-butoxide (0.135 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (2.3 mg, 0.0025 mmol, 0.5 mol % Pd), and 2-(di-*tert*-butylphosphino)biphenyl (3.0 mg, 0.010 mmol). The tube was capped with a Teflon screwcap, evacuated and backfilled with argon. The screwcap was replaced with a rubber septum, and arylamine (1.2 mmol) was added via syringe, followed by aryl halide (1.0 mmol) and toluene (2 mL). The septum was replaced with the Teflon screwcap, and the tube was sealed. The contents were heated at 80 °C, with stirring, until analysis by gas chromatography indicated complete consumption of the starting aryl bromide. The reaction mixture was then cooled to room temperature, taken up in diethyl ether (50 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel, using hexanes/ethyl acetate as the eluant.

Note: In cases where the arylamine or aryl halide was a solid, the reactant was added with the base and catalyst precursors.

***N*-Mesityl-3,4-(methylenedioxy)aniline.**[40b] The general procedure, using palladium acetate (0.5 mol %) as the palladium source and a reaction time of 4 h, was used to couple 2,4,6-trimethylaniline with 4-bromo-1,2-(methylenedioxy)benzene. The title compound was obtained as a pale yellow solid, 0.245 g (96 %): mp 104.5–106.5 °C (lit.[40b] 77–79 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.65 (d, J = 8.3 Hz, 1H), 6.14 (d, J = 2.1 Hz, 1H), 5.97 (dd, J = 8.3, 2.3 Hz, 1H), 5.87 (s, 2H), 4.98 (s, 1H), 2.33 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 142.5, 140.1, 136.4, 135.7, 135.3, 129.4, 108.7, 105.4, 100.8, 96.5, 21.1, 18.4; IR (neat, cm^{-1}) 3369, 2953, 2917, 2885, 2856, 1632, 1615, 1497, 1482, 1245, 1227, 1194, 1038, 944, 932, 859, 822, 795. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71. Found: C, 75.20; H, 6.76.

***N*-(*p*-Tolyl)-*p*-anisidine.**[40b] The general procedure was followed, with a reaction time of 2.5 h, for the coupling of *p*-toluidine with 4-bromoanisole. Excess *p*-toluidine was removed in the workup by extraction with 1 M aqueous phosphoric acid. The title compound was obtained as a pale yellow solid, 0.194 g (91 %): mp 81–83 °C (lit.[40b] 82–83 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H) 5.42 (s, 1H), 3.81 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 142.5, 136.8, 130.0, 129.5, 121.3, 116.7, 114.8, 55.8, 20.8; IR (neat, cm^{-1}) 3415, 3026, 3014, 2952, 2911, 2858, 2836, 1613, 1582, 1515, 1466, 1316, 1295, 1241, 1225, 1179, 1125, 1105, 1032, 812, 768, 704. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 78.78; H, 7.02.

4-Methoxy-4'-(dimethylamino)diphenylamine.[151] The general procedure was followed, with a reaction time of 2 h, for the coupling of *p*-anisidine with 4-bromo-*N,N*-dimethylaniline. The title compound was obtained as a pale yellow solid, 0.229 g (95 %): mp 77–78 °C (lit.[151] 78 °C); ^{1}H NMR (300 MHz, C_6D_6) δ 6.97 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 4.78 (s, 1H), 3.37 (s, 3H), 2.57 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 154.6, 147.2, 140.1, 135.6, 121.8, 118.9, 115.4, 115.1, 55.6, 41.6; IR (neat, cm^{-1}) 3273, 3039, 3013, 2966, 2954, 2879, 2832, 2792, 1507, 1476, 1457, 1437, 1304, 1295, 1252, 1237, 1208, 1169, 1129, 1034, 938, 818, 797, 762, 731. Anal. Calcd for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49. Found: C, 74.23; H, 7.47.

***N*-Ethyl-*N*-(3,5-dimethylphenyl)aniline.**[50c] The general procedure, using palladium acetate (0.5 mol %) as the palladium source and a reaction time of 3 h, was followed for the coupling of *N*-ethylaniline with 5-bromo-*m*-xylene. The title compound was obtained as a pale yellow oil, 0.188 g (84 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.8, 8.5 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.92 (t, J = 8.5 Hz, 1H), 6.67 (s, 2H), 6.65 (s, 1H), 3.77 (q, J = 6.8 Hz, 2H), 2.28 (s, 6H), 1.23 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 147.8, 139.0, 129.3, 123.6, 120.6, 120.3, 119.6, 46.6, 21.7, 13.0;

IR (neat, cm^{-1}) 3035, 2972, 2917, 2869, 1590, 1495, 1470, 1370, 1351, 1289, 1268, 1250, 1191, 1129, 1106, 1071, 1032, 992, 847, 824, 809, 749, 693. Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50. Found: C, 84.99; H, 8.69.

***N*-(*p*-Tolyl)diphenylamine.**[152] The general procedure, using palladium acetate (0.5 mol %) as the palladium source and a reaction time of 3 h, was followed for the coupling of diphenylamine with 4-chlorotoluene. The title compound was obtained as a white solid, 0.242 g (93 %): mp 66–67.5 °C (lit.[152] 68.8 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, 7.3 Hz, 4H), 7.11–6.96 (m, 10H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 145.4, 132.9, 130.1, 129.3, 125.1, 123.8, 122.4, 21.0; IR (neat, cm^{-1}) 3085, 3058, 3033, 3004, 2975, 2919, 2860, 1594, 1582, 1509, 1490, 1449, 1323, 1293, 1274, 1171, 1150, 1111, 1075, 1028, 917, 899, 888, 814, 749, 712, 695. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61. Found: C, 88.01; H, 6.84.

Benzophenone *N*-(2-methoxyphenyl)hydrazone.[153] The general procedure was followed, with a reaction time of 2.5 h, for the reaction of benzophenone hydrazone with 2-chloroanisole. The product was purified by recryastallization from ethanol, affording the title compound as pale yellow crystals, 0.278 g (92 %): mp 101.5–102.5 °C (lit.[153] 101 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.66–7.50 (m, 5H), 7.40–7.30 (m, 5H), 7.01 (td, J = 7.7, 1.7 Hz, 1H), 6.85–6.77 (m, 2H), 3.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 145.0, 138.8, 134.4, 133.2, 129.7, 129.3, 129.2, 128.3, 128.1, 126.7, 121.7, 119.3, 112.5, 110.2, 55.7; IR (neat, cm^{-1}) 3342, 3060, 3010, 2970, 2945, 2840, 1602, 1561, 1511, 1494, 1457, 1441, 1432, 1322, 1256, 1218, 1181, 1127, 1025, 917, 766, 743, 702. Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00. Found: C, 79.48; H, 6.09.

Di-*p*-tolylamine.[35] The general procedure was followed, with a reaction time of 2.5 h, for the coupling of *p*-toluidine with 4-chlorotoluene. Excess *p*-toluidine was removed in the workup by extraction with 1 M aqueous phosphoric acid. The title compound was obtained as a white solid, 0.185 g (93 %): mp 78–79 °C (lit.[35] 79 °C);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, J = 8.2 Hz, 4H), 6.98 (d, J = 8.4 Hz, 4H), 5.53 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 130.3, 130.0, 118.1, 20.8; IR (neat, cm^{-1}) 3419, 3026, 2914, 2860, 1609, 1589, 1515, 1320, 1239, 1227, 1177, 1123, 1108, 1381, 1040, 880, 805, 772, 704. Anal. Calcd for $C_{14}H_{11}N$: C, 85.24; H, 7.66. Found: C, 85.29; H, 8.02.

4,4'-Dimethoxydiphenylamine.[40b] The general procedure was followed, with a reaction time of 8 h, for the coupling of *p*-anisidine with 4-chloroanisole. The title compound was obtained as a pale yellow solid, 0.217 g (95 %): mp 99.5–101.5 °C (lit.[40b] 101–103 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (d, J = 8.9 Hz, 4H), 6.84 (d, J = 9.0 Hz, 4H), 5.32 (s, 1H), 3.80 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 138.1, 119.7, 114.9, 55.8; IR (neat, cm^{-1}) 3421, 3031, 3014, 2958, 2939, 2916, 2840, 1513, 1466, 1441, 1299, 1248, 1218, 1179, 1115, 1030, 830, 818, 762, 708. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59. Found: C, 73.51; H, 6.74.

***N*-(*p*-Tolyl)-3,5-dimethoxyaniline.** The general procedure was followed, with a reaction time of 2.5 h, for the coupling of *p*-toluidine with 5-chloro-*m*-xylene. Excess *p*-toluidine was removed in the workup by extraction with 1 M aqueous phosphoric acid. The title compound was obtained as a white solid, 0.228 g (94 %): mp 66.5–67.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.20 (d, J = 2.1 Hz, 2H), 6.05 (t, J = 2.2 Hz, 1H), 5.64 (s, 1H), 3.77 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 146.3, 139.9, 131.6, 130.0, 120.0, 95.1, 92.5, 55.4, 20.9; IR (neat, cm^{-1}) 3367, 3012, 2966, 2937, 2840, 1594, 1513, 1478, 1459, 1254, 1200, 1189, 1165, 1144, 1057, 924, 822, 810, 770, 720, 683. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04. Found: C, 74.06; H, 7.23.

***N*-(2-Methoxyphenyl)-2,5-dimethylaniline.** The general procedure was followed, with a reaction time of 2.5 h, for the coupling of *o*-anisidine with 2-chloro-*p*-xylene. Excess *o*-anisidine was removed in the workup by extraction with 1 M

aqueous phosphoric acid. The title compound was obtained as a white solid, 0.228 g (94 %): mp = 89–90.5 °C. Spectroscopic data were identical to those reported below.

***N*-(2-Methoxyphenyl)-2,5-dimethylaniline (Low catalyst loading).** The general procedure was modified as follows: The reaction was run in 5 mL toluene, with a reaction time of 14 h, using 12 mmol *o*-anisidine, 10 mmol 2-chloro-*p*-xylene, 14 mmol sodium *tert*-butoxide, 0.0025 mmol tris(dibenzylideneacetone) dipalladium (0.05 mol % Pd), and 0.01 mmol ligand (0.1 mol %). Excess *o*-anisidine was removed in the workup by extraction with 1 M aqueous phosphoric acid. The product was purified by recrystallization from methanol, affording the title compound as white crystals, 2.20 g (97 %): mp = 90–91.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.05 (dd, J = 7.66, 2.2 Hz, 1H), 6.93–6.84 (m, 3H), 6.79 (d, J = 7.6 Hz, 1H), 5.86 (s, 1H), 3.93 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 140.8, 136.5, 134.2, 130.9, 126.4, 123.1, 121.0, 120.4, 119.3, 114.6, 110.5, 55.8, 21.4, 17.7; IR (neat, cm^{-1}) 3411, 3062, 3045, 3006, 2964, 2933, 2919, 2856, 2836, 1598, 1576, 1521, 1501, 1449, 1412, 1341, 1293, 1243, 1220, 1179, 1115, 1048, 1030, 1000, 886, 809, 772, 741, 708. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 79.18; H, 7.56.

2,6-Diisopropyl-2',6'-dimethyldiphenylamine. The general procedure was followed, using 0.02 mmol tris(dibenzylideneacetone) dipalladium (4 mol % Pd), and 0.08 mmol ligand (8 mol %), and a reaction time of 20 h. The title compound was isolated as a white solid, 0.212 g (75 %): mp 40.5–44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–7.11 (m, 3H), 6.96 (d, J = 7.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 4.81 (s, 1H), 3.17 (sept, 6.8 Hz, 1H), 2.00 (s, 6H), 1.15 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 143.3, 139.0, 129.7, 125.8, 125.0, 123.4, 119.8, 28.3, 23.7, 19.6; IR (neat, cm^{-1}) 3421, 3064, 3041, 3027, 2958, 2925, 2867, 1590, 1470, 1447, 1378, 1362, 1333, 1275, 1225, 1098, 1179, 1162, 1057, 1034, 990, 938, 920, 888, 793, 768, 737, 695, 683. Anal. Calcd for $C_{20}H_{27}N$: C, 85.35; H, 9.67. Found: C, 85.11; H, 9.56.

4-Methoxy-4'-nitrodiphenylamine.[154] An oven-dried, resealable Schlenk tube was charged with *p*-anisidine (0.148 g, 1.20 mmol), 1-chloro-4-nitrobenzene (0.158 g, 1.00 mmol), tripotassium phosphate (0.297 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (4.6 mg, 0.005 mmol, 1.0 mol % Pd), and 2-(di-*tert*-butylphosphino)biphenyl (6.0 mg, 0.020 mmol, 2.0 mol %). The tube was capped with a Teflon screwcap, evacuated and backfilled with argon. The screwcap was replaced with a rubber septum, and tetrahydrofuran (2 mL) was added via syringe. The septum was replaced with the Teflon screwcap; the tube was sealed, and the contents were heated to 100 °C with stirring. Analysis by gas chromatography after 14 h indicated complete consumption of the starting aryl chloride. The reaction mixture was then cooled to room temperature, taken up in diethyl ether (75 mL), and washed with a 1 M aqueous solution of phosphoric acid (50 mL), followed by water (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The crude product was purified by recrystallization from ethanol, affording the title compound as orange crystals, 0.222 g (91 %): mp 152–152.5 °C (lit.[154] 151 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 9.2 Hz, 2H), 7.17 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.77 (d, J = 9.2 Hz, 2H), 6.15 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 151.9, 139.2, 132.2, 126.5, 125.7, 115.1, 112.8, 55.7; IR (neat, cm^{-1}) 3325, 3191, 3124, 3110, 3082, 3066, 3041, 3022, 2954, 2931, 2906, 2835, 1592, 1544, 1526, 1511, 1480, 1461, 1445, 1320, 1293, 1231, 1181, 1167, 1111, 1028, 1000, 830, 812, 801, 762, 749, 697, 675. Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95. Found: C, 63.73, H, 4.86.

***N*-(Diphenylmethylene)-4-nitroaniline.**[155] An oven-dried, resealable Schlenk tube was charged with 1-chloro-4-nitrobenzene (0.158 g, 1.00 mmol), tripotassium phosphate (0.297 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (4.6 mg, 0.005 mmol, 1.0 mol % Pd), and 2-(dicyclohexylphosphino)biphenyl (7.0 mg, 0.020 mmol, 2.0 mol %). The tube was capped with a Teflon screwcap, evacuated and

backfilled with argon. The screwcap was replaced with a rubber septum, and benzophenone imine (0.19 mL, 1.1 mmol) was added via syringe, followed by 1,2-dimethoxyethane (2 mL). The septum was replaced with the Teflon screwcap; the tube was sealed, and the contents were heated to 100 °C with stirring. Analysis by gas chromatography after 14 h indicated complete consumption of the starting aryl chloride. The reaction mixture was then cooled to room temperature, taken up in diethyl ether (50 mL), and washed with brine (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The crude product was purified by recrystallization from toluene/ethanol, affording the title compound as yellow crystals, 0.249 g (82 %): mp 157–159 °C (lit.[155] 156 °C); ^{1}H NMR (75 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 2H), 7.77 (broad s, 2H), 7.44 (broad s, 2H), 7.32 (broad s, 4H), 7.12 (broad s, 2H), 6.81 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 157.7, 143.5, 138.6, 135.4, 131.7, 129.8, 129.4, 128.5, 124.8, 121.1; IR (neat, cm^{-1}) 3064, 2927, 2844, 1586, 1511, 1441, 1339, 1318, 1293, 1231, 1110, 959, 849, 785, 756, 706, 693, 666. Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67. Found: C, 75.33; H, 4.65.

Methyl 4-(2-methoxyphenyl)aminobenzoate. An oven-dried, resealable Schlenk tube was charged with methyl 4-chlorobenzoate (0.171 g, 1.00 mmol), tripotassium phosphate (0.297 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (4.6 mg, 0.005 mmol, 1.0 mol % Pd), and 2-(dicyclohexylphosphino)biphenyl (7.0 mg, 0.020 mmol, 2.0 mol %). The tube was capped with a Teflon screwcap, evacuated and backfilled with argon. The screwcap was replaced with a rubber septum, and *o*-anisidine (0.14 mL, 1.2 mmol) was added via syringe, followed by 1,2-dimethoxyethane (2 mL). The septum was replaced with the Teflon screwcap; the tube was sealed, and the contents were heated to 80 °C with stirring. Analysis by gas chromatography after 14 h indicated complete consumption of the starting aryl chloride. The reaction mixture was then cooled to room temperature, taken up in

diethyl ether (50 mL), and washed with a 1 M aqueous solution of phosphoric acid (2 x 50 mL), followed by water (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel, using 2:1 hexanes: ethyl acetate as the eluant, to afford the title compound as a red oil, 0.244 g (95 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 8.9 Hz, 2H), 7.01–6.91 (m, 3H), 6.41 (s, 1H), 3.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 149.7, 147.7, 131.5, 130.6, 122.4, 121.3, 120.9, 117.9, 115.3, 111.0, 55.8, 51.9; IR (neat, cm^{-1}) 3402, 3354, 2998, 2948, 2838, 1704, 1609, 1590, 1522, 1505, 1486, 1461, 1434, 1337, 1312, 1275, 1243, 1212, 1173, 1106, 1048, 1027, 967, 855, 841, 783, 768, 743, 699, 670. Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88. Found: C, 69.86; H, 5.83.

2-Methoxy-4-cyanodiphenylamine. An oven-dried, resealable Schlenk tube was charged with tripotassium phosphate (0.297 g, 1.40 mmol), tris(dibenzylideneacetone) dipalladium (2.3 mg, 0.0025 mmol, 0.5 mol % Pd), and 2-(di-*tert*-butylphosphino)biphenyl (3.0 mg, 0.010 mmol, 1.0 mol %). The tube was capped with a Teflon screwcap, evacuated and backfilled with argon. The screwcap was replaced with a rubber septum, and *o*-anisidine (0.14 mL, 1.2 mmol) was added via syringe, followed by 4-cyanophenyl triflate (0.18 mL, 1.0 mmol) and tetrahydrofuran (2 mL). The septum was replaced with the Teflon screwcap; the tube was sealed, and the contents were heated to 80 °C with stirring. Analysis by gas chromatography after 2.5 h indicated complete consumption of the starting aryl triflate. The reaction mixture was then cooled to room temperature, taken up in diethyl ether (50 mL), and washed with a 1 M aqueous solution of phosphoric acid (2 x 30 mL), followed by water (30 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The crude product was purified by recrystallization from ethanol/hexanes, affording the title compound as pale yellow needles, 0.194 g (87 %):

mp 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 7.5 Hz, 1H), 7.08–6.94 (m, 5H), 6.38 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 147.6, 133.8, 129.7, 123.4, 120.9, 120.1, 118.9, 115.6, 111.2, 101.8, 55.8; IR (neat, cm^{-1}) 3321, 3045, 3002, 2968, 2929, 2831, 2217, 1611, 1598, 1586, 1522, 1507, 1488, 1459, 1341, 1328, 1295, 1248, 1175, 1111, 1028, 830, 820, 741. Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39. Found: C, 74.95; H, 5.32.

Chapter 3

***N*-(Diphenylmethylene)-4-bromo-2-methoxyaniline (51a).** Tetra-*n*-butylammonium tribromide (9.74 g, 20.2 mmol) was placed in an Erlenmeyer flask, dissolved with stirring in dichloromethane (100 mL), and cooled to 0 °C. A solution of *o*-anisidine (2.25 mL, 20.0 mmol) in dichloromethane (50 mL) was added via pipette, over a period of *ca.* 5 min. The yellow color of the solution faded during the addition of *o*-anisidine, and a white precipitate formed. The solution was stirred 1 h at 0 °C, then the precipitate was collected by filtration and washed with cold dichloromethane (2 x 20 mL), affording 4-bromo-2-methoxyaniline hydrobromide (**50a**) as white crystals, 5.22 g (92 %); analysis of a neutralized sample by GC showed the presence of 1 % *o*-anisidine. ^{1}H NMR (300 MHz, $CDCl_3$, neutralized sample) δ 6.91 (dd, J = 7.9, 2.1 Hz, 1H), 6.89 (d, J = 1.8 Hz, 1H), 6.58 (d, J = 7.9 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 2H).

The hydrobromide salt (5.00 g, 17.7 mmol) was placed in an oven-dried Schlenk flask, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and dry acetonitrile (40 mL) was added via syringe, followed by benzophenone imine (2.85 mL, 17.0 mmol). The resulting suspension was heated to 80 °C with stirring. Analysis by GC after 2.5 h indicated the complete consumption of benzophenone imine. The mixture was cooled to room temperature and concentrated *in vacuo*. The residual solid was taken up in diethyl ether (75 mL) and washed with an aqueous solution of sodium hydroxide (1 M, 50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered,

and concentrated *in vacuo*, affording a thick yellow oil which resisted attempts at crystallization. An aliquot (*ca.* 50 mg) was removed and filtered through a glass pipette containing a 5-cm column of silica gel, using 9:1 hexanes: ethyl acetate as the eluant. Only the intense yellow band was collected; this solution was concentrated *in vacuo*, affording a yellow oil which crystallized from isopropanol. The crude product was taken up in isopropanol (30 mL), and the seed crystals were added, causing rapid crystallization. The mixture was cooled to 0 °C; the precipitate was collected by filtration and washed with cold isopropanol (5 mL), affording the title compound as yellow crystals, 4.80 g (77 %): mp 99.5–101 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2H), 7.49–7.39 (m, 3H), 7.29–7.25 (m, 3H), 7.15–7.12 (m, 2H), 6.88–6.85 (m, 2H), 6.48 (dd, J = 8.6, 1.3 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 150.3, 140.3, 139.2, 136.6, 131.0, 129.6, 128.9, 128.7, 128.3, 127.9, 123.5, 122.2, 116.3, 114.5, 55.8; IR (neat, cm^{-1}) 3082, 3062, 3027, 3002, 2962, 2939, 2902, 2846, 2829, 1615, 1596, 1580, 1482, 1459, 1443, 1391, 1318, 1295, 1283, 1243, 1210, 1183, 1144, 1119, 1075, 1030, 1003, 959, 917, 859, 841, 824, 795, 785, 764, 743, 695, 679, 662. Anal. Calcd for $C_{20}H_{16}BrNO$: C, 65.59; H, 4.40. Found: C, 65.62; H, 4.41.

5-[*N*-(Diphenylmethylene)amino]-2-bromobenzonitrile (51b). 3-Aminobenzonitrile (2.36 g, 20.0 mmol) was placed in an Erlenmeyer flask and dissolved in dichloromethane (100 mL). The resulting solution was added via pipette, over *ca.* 10 min., to a solution of tetra-*n*-butylammonium tribromide (9.74 g, 20.2 mmol) in dichloromethane (100 mL). A white precipitate slowly formed, and the yellow color of the mixture gradually faded. After 16 h, the precipitate was collected by filtration. Analysis of a neutralized aliquot by GC showed a 9:1 ratio of the presumed product to the starting material. The product was recrystallized three times from ethanol, affording 5-amino-2-bromobenzonitrile hydrobromide (**50b**) as white crystals, 2.94 g (53 %): analysis of a neutralized sample by GC showed greater than 98 % purity; ^{1}H

NMR (300 MHz, $CDCl_3$, neutralized sample) δ 7.39 (d, J = 8.7 Hz, 1H), 6.93 (d, J = 2.8 Hz, 1H), 6.75 (dd, J = 8.7, 2.8 Hz, 1H), 3.93 (s, 2H).

Transamination with benzophenone imine was carried out according to the procedure described above, using the hydrobromide salt (2.78 g, 10.0 mmol) and benzophenone imine (1.71 mL, 10.2 mmol) in dry acetonitrile (30 mL), with a reaction time of 12 h. The crude product was purified by recrystallization from ethanol, affording the title compound as pale yellow needles, 3.15 g (87 %; 46 % based on 3-aminobenzonitrile): mp 125–127.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.0, 1.5 Hz, 2H), 7.55–7.30 (m, 7H), 7.11–7.08 (m, 2H), 7.00 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.6, 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 151.0, 138.6, 135.0, 133.3, 131.7, 129.6, 129.5, 129.3, 128.5, 128.5, 127.0, 126.5, 118.7, 117.2, 115.7; IR (neat, cm^{-1}) 3059, 2233, 1619, 1596, 1581, 1464, 1446, 1318, 1295, 1272, 786, 696, 670. Anal. Calcd for $C_{20}H_{13}BrN_2$: C, 66.50; H, 3.63. Found: C, 66.48; H, 3.60.

***N*-(Diphenylmethylene)-4-bromo-2-(*tert*-butyldimethylsiloxymethyl)aniline (51c).** Bromination of 2-aminobenzyl alcohol was carried out according to the procedure described above, using aminobenzyl alcohol (2.00 g, 16.2 mmol) and tetra-*n*-butylammonium tribromide (7.91 g, 16.4 mmol). After a reaction time of 5 min, the reaction mixture was cooled to 0 °C and filtered. The collected product was washed with cold dichloromethane (2 x 10 mL), and dried *in vacuo*, affording the crude 2-amino-5-bromobenzyl alcohol hydrobromide (**50c**) as white crystals, 3.54 g (63 %): analysis of a neutralized sample by GC indicated 95 % purity, the remainder consisting of 2-aminobenzyl alcohol; ^{1}H NMR (300 MHz, $CDCl_3$, neutralized sample) δ 7.26–7.18 (m, 2H), 6.58 (d, J = 8.3 Hz, 1H), 4.62 (d, J = 4.3 Hz, 2H), 4.19 (s, 2H), 1.72 (indistinct triplet, coupling constant not found; 1H).

Transamination with benzophenone imine was carried out according to the procedure described above, using the hydrobromide salt (3.40 g, 12.0 mmol) and benzophenone imine (2.05 mL, 12.2 mmol) in dry acetonitrile (30 mL), with a reaction

time of 2 h. The crude product was isolated as an oil, which crystallized from 9:1 hexanes: ethyl acetate. Recrystallization from a mixture of toluene and ethanol afforded pale yellow crystals, 3.31 g (75 %): mp 146–148.5 °C; ^{1}H NMR is consistent with the desired imine, but indicates the presence of *ca.* 2 mol % (0.5 wt. %) toluene, and 2 mol % of the non-bromo analogue.

Conversion of the benzylic alcohol to its *tert*-butyldimethylsilyl ether was carried out according to the procedure of Corey:[117] The alcohol (1.10 g, 3.00 mmol), *tert*-butyldimethylsilyl chloride (0.543 g, 3.60 mmol), and imidazole (0.511 g, 7.51 mmol) were placed in an oven-dried Schlenk tube, which was stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and *N,N*-dimethylformamide (3 mL) was added via syringe. The reaction mixture was stirred at room temperature. Analysis by GC after 13 h indicated the complete consumption of the starting alcohol. The mixture was taken up in diethyl ether (50 mL), and washed with a saturated aqueous solution of sodium bicarbonate (25 mL), followed by water (2 x 25 mL). The ethereal solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual oil was purified by flash column chromatography on silica gel, using 4:1 hexanes: ethyl acetate as the eluant. This procedure gave an incomplete separation between the desired product and a faint contaminant at slightly lower R_f. The pure fractions were set aside, and the rest were concentrated *in vacuo* and purified again by flash column chromatography on silica gel, using 19:1 hexanes: ethyl acetate as the eluant. The product fractions were combined and concentrated *in vacuo*, affording the title compound as a thick yellow oil, 1.29 g (90 %; 42 % overall from 2-aminobenzyl alcohol): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 6.8 Hz, 2H), 7.55–7.40 (m, 4H), 7.32–7.25 (m, 3H), 7.12 (dd, J = 7.7, 1.8 Hz, 2H), 7.05 (dd, J = 8.5, 2.3 Hz, 1H), 6.18 (d, J = 8.5 Hz, 1H), 4.67 (s, 2H), 0.93 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 147.3, 139.4, 135.9, 134.8, 131.1, 129.9, 129.8, 129.6, 129.3, 129.2, 128.4, 128.3, 120.9, 116.6, 61.7, 26.2,

18.6, –5.1; IR (neat, cm^{-1}) 3083, 3062, 3026, 2954, 2929, 2884, 2856, 1623, 1598, 1578, 1490, 1470, 1447, 1405, 1389, 1362, 1316, 1291, 1252, 1223, 1183, 1148, 1121, 1088, 1069, 1030, 1003, 957, 940, 915, 884, 872, 836, 816, 776, 735, 693, 662. Anal. Calcd for $C_{26}H_{30}BrNOSi$: C, 64.99; H, 6.29. Found: C, 64.77; H, 5.90.

***N*-(Diphenylmethylene)-4-bromo-3-(*tert*-butyldimethylsiloxymethyl)aniline (51d).** Bromination of 2-aminobenzyl alcohol was carried out according to the procedure described above, using aminobenzyl alcohol (2.46 g, 20.0 mmol) and tetra-*n*-butylammonium tribromide (9.74 g, 20.2 mmol). After a reaction time of 10 min, the reaction mixture was filtered. The collected solid was washed with dichloromethane (2 x 10 mL), then recrystallized from ethanol, affording 5-amino-2-bromobenzyl alcohol hydrobromide (**50d**) as white crystals, 3.18 g (56 %): analysis of a neutralized sample by GC indicated >99 % purity; ^{1}H NMR (300 MHz, $CDCl_3$, neutralized sample) δ 7.28 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 2.8 Hz, 1H), 6.50 (dd, J = 8.4, 2.8 Hz, 1H), 4.66 (d, J = 5.8 Hz, 2H), 3.72 (s, 2H), 2.01 (t, J = 6.0 Hz, 1H).

Transamination with benzophenone imine was carried out according to the procedure described above, using the hydrobromide salt (2.83 g, 10.0 mmol) and benzophenone imine (1.71 mL, 10.2 mmol) in dry acetonitrile (40 mL), with a reaction time of 3 h. The crude product was recrystallized twice from ethanol, affording the imine as pale yellow crystals, 3.11 g (85 %): mp 162–165 °C; ^{1}H NMR is consistent with the desired imine.

Conversion of the benzylic alcohol to its *tert*-butyldimethylsilyl ether was carried out according to the procedure described above, using the alcohol (1.10 g, 3.00 mmol), *tert*-butyldimethylsilyl chloride (0.543 g, 3.60 mmol), and imidazole (0.511 g, 7.51 mmol), and a reaction time of 13 h. The product was isolated after flash column chromatography, using 19:1 hexanes: ethyl acetate, as a yellow solid, 1.30 g (90 %; 43 % overall based on 3-aminobenzyl alcohol): mp 80.5–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 6.8 Hz, 2H), 7.49–7.38 (m, 3H), 7.30–7.24 (m, 4H), 7.12–7.09 (m,

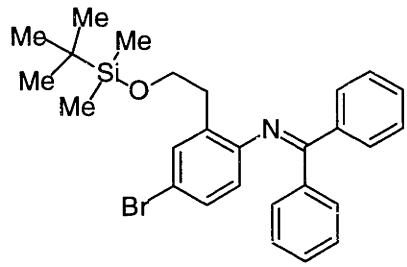
2H), 6.92 (d, J = 2.6 Hz, 1H), 6.51 (dd, J = 7.8, 2.6 Hz, 1H), 4.59 (s, 2H), 0.92 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 150.9, 140.6, 139.7, 136.1, 132.1, 131.1, 129.7, 129.6, 128.9, 128.4, 128.3, 121.0, 120.4, 114.8, 64.7, 26.2, 18.6, –5.2; IR (neat, cm^{-1}) 3083, 3060, 3031, 2958, 2927, 2883, 2856, 1611, 1600, 1576, 1470, 1461, 1445, 1368, 1318, 1297, 1254, 1225, 1171, 1129, 1092, 1019, 1007, 973, 940, 880, 855, 839, 822, 774, 747, 729, 699, 672. Anal. Calcd for $C_{26}H_{30}BrNOSi$: C, 64.99; H, 6.29. Found: C, 65.35; H, 6.13.

***N*-(Diphenylmethylene)-4-bromo-2-[2-(*tert*-butyldimethylsiloxy)ethyl]aniline (51e).** Bromination of 2-aminophenethyl alcohol was carried out according to the procedure described above, using the aniline (1.39 g, 10.1 mmol), and tetra-*n*-butylammonium tribromide (9.74 g, 20.2 mmol). After a reaction time of 10 min, the reaction mixture cooled to 0 °C and filtered. The collected solid was washed with dichloromethane (2 x 10 mL) and dried *in vacuo*, affording 2-amino-5-bromophenethyl alcohol hydrobromide (**50e**) as white crystals, 2.32 g (78 %): analysis of a neutralized sample by GC indicated >98 % purity; ^{1}H NMR (300 MHz, $CDCl_3$, neutralized sample) δ 7.15–7.12 (m, 2H), 6.56 (d, J = 8.8 Hz, 1H), 3.88 (broad s, 2H), 3.85 (t, J = 6.1 Hz, 2H), 2.71 (t, J = 6.1 Hz, 2H), 2.32 (broad s, 1H).

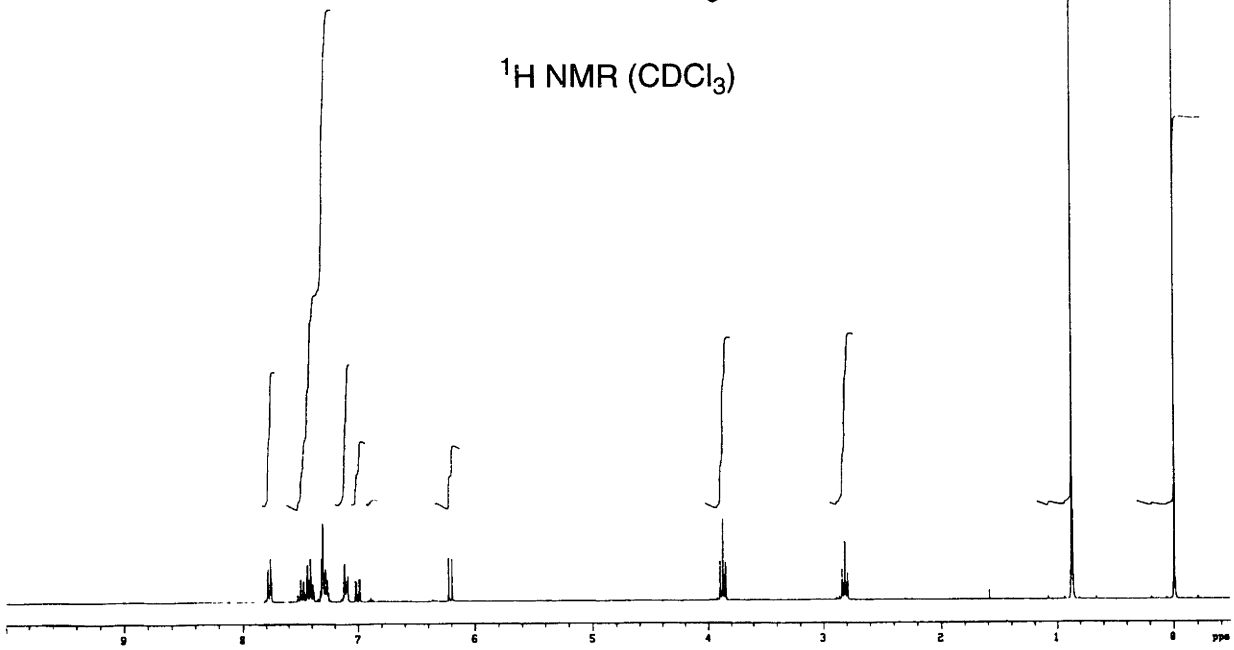
Transamination with benzophenone imine was carried out according to the procedure described above, using the hydrobromide salt (2.08 g, 7.00 mmol) and benzophenone imine (1.20 mL, 7.15 mmol) in dry acetonitrile (40 mL), with a reaction time of 3 h. The crude product waspurified by flash column chromatography on silica gel, using 4:1 hexanes: ethyl acetate as the eluant, affording a yellow solid, 2.47 g (93 %): mp 83–87 °C; ^{1}H NMR is consistent with the desired imine, but indicates the presence of the nonbromo analogue, *ca.* 5 %.

The hydroxyl group was converted to its *tert*-butyldimethylsilyl ether according to the procedure described above, using the alcohol (2.32 g, 6.10 mmol), *tert*-butyldimethylsilyl chloride (1.10 g, 7.32 mmol), and imidazole (1.04 g, 15.3 mmol), and

a reaction time of 14 h. The product was isolated after flash column chromatography, using 19:1 hexanes: ethyl acetate as the eluant, as a thick yellow oil, 2.94 g (97 %; 70 % overall based on 3-aminobenzyl alcohol): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 6.8 Hz, 2H), 7.49–7.41 (m, 3H), 7.31–7.27 (m, 4H), 7.10 (dd, J = 7.7 Hz, 1.8 Hz, 2H), 7.00 (dd, J = 8.5, 2.3 Hz, 1H), 6.21 (d, J = 8.2 Hz, 1H), 3.87 (t, J = 7.0 Hz, 2H), 2.82 (t, J = 7.0 Hz, 2H), 0.87 (s, 9H), –0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 148.9, 139.5, 136.0, 133.2, 132.7, 131.0, 129.6, 129.4, 129.2, 129.0, 128.3, 128.3, 121.4, 116.3, 62.4, 35.6, 26.2, 18.5, –5.1. (Faint resonances are also visible in the ^{1}H and ^{13}C NMR spectra which arise from the presence of the non-bromo analogue, *ca.* 5 %.) IR (neat, cm^{-1}) 3083, 3062, 3026, 2954, 2929, 2894, 2885, 2856, 1615, 1598, 1578, 1472, 1445, 1316, 1293, 1254, 1227, 1181, 1148, 1115, 1092, 1032, 1005, 957, 938, 922, 891, 872, 834, 776, 747, 695, 679, 664.



^{1}H NMR ($CDCl_3$)



5-[*N*-(Diphenylmethylene)amino]-2-bromobenzotrifluoride (51f). An oven-dried Schlenk flask was charged with 5-amino-2-bromobenzotrifluoride (3.60 g, 15.0 mmol), stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and benzophenone imine (2.65 mL, 15.8 mmol) was added via syringe, followed by dry acetonitrile (25 mL). The resulting mixture was stirred until a homogeneous solution was obtained, then methanesulfonic acid (1.00 mL, 15.4 mmol) was added via syringe. A clear, red-brown solution resulted; after a few minutes, a white precipitate formed. The resulting mixture was heated with stirring to 75 °C. After 2 h, the reaction was judged to be complete according to GC analysis. The reaction mixture was cooled to room temperature, taken up in diethyl ether (100 mL), and washed with an aqueous solution of sodium hydroxide (1 M, 50 mL). The aqueous phase was separated and extracted with diethyl ether (2 x 25 mL). The organic portions were combined, dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The product was obtained as a yellow oil which crystallized on standing. Recrystallization from methanol containing a small proportion of water afforded the title compound as yellow crystals, 5.34 g (88 %): mp 87–87.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.55–7.29 (m, 7H), 7.13–7.09 (m, 3H), 6.68 (dd, J = 8.4, 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 150.5, 138.9, 135.4, 135.1, 131.5, 129.6, 129.4, 129.3, 128.5, 128.5, 125.4, 122.8 (q, J = 272 Hz), 121.3 (q, J = 5.5 Hz), 113.4; IR (neat, cm^{-1}) 3085, 3068, 3054, 3037, 3024, 1613, 1600, 1567, 1470, 1445, 1403, 1316, 1297, 1270, 1252, 1218, 1187, 1173, 1158, 1131, 1119, 1098, 1075, 1019, 1001, 957, 932, 922, 884, 841, 785, 772, 753, 726, 695, 677, 662. Anal. Calcd for $C_{20}H_{13}BrF_3N$: C, 59.43; H, 3.24. Found: C, 59.50; H, 3.14.

***N*-(*tert*-Butoxycarbonyl)-*N*-(4-bromophenyl)-1,4-phenylenediamine (52a).** Dimer bromide **5a** (4.63 g, 8.77 mmol) was placed in an Erlenmeyer flask and dissolved in methanol (20 mL) with stirring. Sodium acetate (1.31 g, 16.0 mmol) was added, followed by hydroxylamine hydrochloride (0.834 g, 12.0 mmol). The resulting

suspension was stirred at room temperature. After 2 h, triethylamine (2 mL, 15 mmol) was added. The reaction mixture was concentrated *in vacuo*, taken up in dichloromethane (75 mL), and washed with water (25 mL). The resulting solution was ried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residue was crystallized, then recrystallized, from isopropanol, affording the product as white crystals, 2.55 g (80 %): mp 170–172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 3.68 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 144.9, 142.7, 133.6, 131.6, 128.6, 127.7, 118.2, 115.4, 81.3, 28.5; IR (neat, cm^{-1}) 3467, 3363, 2993, 2973, 1688, 1627, 1519, 1490, 1474, 1370, 1341, 1281, 1256, 1225, 1158, 1131, 1100, 1069, 1057, 1034, 1013, 959, 853, 837, 824, 795, 764, 710, 699. Anal. Calcd for $C_{17}H_{19}BrN_2O_2$: C, 56.21; H, 5.27. Found: C, 56.43: H, 5.18.

***N*-(*tert*-Butoxycarbonyl)-*N*-(4-chlorophenyl)-1,4-phenylenediamine (52b).** Dimer chloride **5b** (2.03 g, 4.19 mmol) and sodium acetate (0.689 g, 8.40 mmol) were placed in an Erlenmeyer flask. Methanol (20 mL) was added, followed by tetrahydrofuran (8 mL). Hydroxylamine hydrochloride (0.438 g, 6.30 mmol) was added in one portion to the stirred suspension. The reaction mixture gradually faded in color from yellow to white. Analysis by TLC after 15 minutes indicated the complete consumption of the starting imine. The mixture was concentrated *in vacuo*, taken up in diethyl ether (75 mL) and washed with a saturated aqueous solution of sodium bicarbonate. The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residue was recrystallized from isopropanol, affording the title compound as white crystals, 1.06 g (80 %): mp 166.5–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 9.0 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 3.69 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 144.9, 142.2, 133.6, 130.3, 128.6, 128.6, 127.4, 115.4, 81.3, 28.5; IR (neat, cm^{-1}) 3465, 3363, 2995, 2979, 1688, 1626, 1519, 1492, 1476, 1370, 1343,

1281, 1256, 1227, 1158, 1092, 1057, 1017, 959, 852, 839, 826, 797, 766, 712. Anal. Calcd for $C_{17}H_{19}ClN_2O_2$: C, 64.05; H, 6.01. Found: C, 64.02; H, 6.00.

***N*-(4-Bromophenyl)-*N'*-(4-aminophenyl)-*N,N'*-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (53).** Trimer bromide **15** (3.25 g, 4.52 mmol) was placed in an Erlenmeyer flask, and dissolved with stirring in tetrahydrofuran (70 mL). Methanol (10 mL) was added, followed by pyridine (1.0 mL, 12 mmol). Hydroxylamine hydrochloride (0.439 g, 6.35 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 3 h, then triethylamine (2.5 mL, 18 mmol) was added. The resulting mixture was poured into an aqueous solution of sodium hydroxide (1.0 M, 300 mL) and extracted with ethyl acetate (100 mL). The organic layer was removed, and the aqueous phase was extracted with ethyl acetate (2 x 100 mL). The organic portions were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was recrystallized from a mixture of dichloromethane and isopropanol, affording the title compound as white microcrystals, 1.81 g (72 %): mp 179–181.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.5 Hz, 4H), 6.97 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 3.68 (s, 2H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 153.6, 144.8, 142.1, 141.3, 139.1, 133.8, 131.8, 128.6, 128.5, 127.1, 126.4, 118.9, 115.4, 81.7, 81.1, 28.5, 28.4. IR (neat, cm^{-1}) 3454, 3369, 3006, 2977, 2931, 1710, 1692, 1627, 1511, 1490. 1455, 1424, 1391, 1368, 1335, 1287, 1260, 1223, 1162, 1113, 1069, 1057, 1032, 1023, 1013, 959, 857, 837, 826, 795, 764, 749, 729, 712. Anal. Calcd for $C_{28}H_{32}BrN_3O_4$: C, 60.65; H, 5.82. Found: C, 60.64; H, 5.89.

Representative procedure for the preparation of poly[*N*-(*tert*-butoxycarbonyl)aniline] (54–56): Monomer **52a** (0.182 g, 0.500 mmol), sodium *tert*-butoxide (0.0673 g, 0.700 mmol), tris(dibenzylideneacetone) dipalladium (2.3 mg, 0.0025 mmol, 1 mol % Pd), and 2-di(*tert*-butylphosphino)biphenyl (3.0 mg, 0.010

mmol, 2 mol %) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with argon. The screwcap was replaced with a rubber septum, and tetrahydrofuran (2 mL) was added via syringe. The septum was replaced with the screwcap; the tube was sealed, and its contents were heated to 60 °C with stirring, forming a clear yellow-orange solution. A fine white precipitate was visible within seconds. After 1 h, the mixture was cooled to room temperature, taken up in dichloromethane (75 mL), and washed with water (50 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered, and transferred to an oven-dried Schlenk tube. The tube was stoppered, the solution was concentrated *in vacuo*, and the tube was backfilled with argon. The stopper was removed, and 4-dimethylaminopyridine (0.031 g, 0.25 mmol) was added. The tube was capped with a rubber septum and purged with argon for 3 min. Di-*tert*-butyl dicarbonate (0.23 mL, 1.0 mmol) was added via syringe, followed by tetrahydrofuran (5 mL). The resulting mixture was heated to 65 °C with stirring. A slow effervescence began within seconds. After 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residual solid was taken up in dichloromethane (50 mL); the resulting mixture was filtered through Celite, removing a small quantity of insoluble, gelatinous material, then concentrated *in vacuo*, yielding an amorphous red-orange solid. This crude product was dissolved in dichloromethane (*ca.* 2 mL) and the resulting solution was brought to a boil. Ethanol (*ca.* 15 mL) was added slowly, and the solution was boiled until cloudiness was evident. On cooling, the mixture deposited a tan-yellow powder, 0.127 g (65 % based on M_n): No definite melting point (solid slowly turns purple above 180 °C, and blackens above 200 °C, with decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (s, 4H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 140.2, 127.2, 81.5, 28.4; IR (neat, cm^{-1}) 2975, 2933, 1710, 1509, 1368, 1326, 1304, 1289, 1254, 1156, 1056, 1017, 851, 834, 766. Anal. Calcd for $(C_{22}H_{26}N_2O_4)_n$: C, 69.09; H, 6.85. Found: C, 68.98; H, 6.97.

Note: This general procedure was followed for most polymerizations. Coupling reactions carried out using *rac*-BINAP or DPEphos as supporting ligand employed tris(dibenzylideneacetone) dipalladium as the palladium source, with 1.5 equiv. of bisphosphine per palladium. In Table 8, run 1, the crude polymerization mixture was concentrated *in vacuo*; the residue was scraped from the flask, pulverized in a mortar and pestle, and triturated with diethyl ether, water, isopropanol, and again with diethyl ether according to the procedure of Mackewitz.[122] Differences in temperature, time, concentration and catalyst loading are noted in the text. For copolymerization reactions, equimolar amounts (0.25 mmol) of diamine **46** and dibromide **31** were employed. Spectroscopic data (^{1}H and ^{13}C NMR) and behavior during attempted melting point measurement were identical for all polymer preparations, except for Table 8, runs 2 and 4, which display small doublets at 7.40 ppm, attributed to endgroups, in their ^{1}H NMR spectra. The product of Table 8, run 2 partially liquefies with decomposition above 185 °C.

10-Decanoylphenothiazine (57). The general procedure[142] for the acylation of phenothiazine was followed. A round-bottom flask fitted with a reflux condenser was capped with a rubber septum and purged with argon. The flask was opened, and phenothiazine (42.0 g, 0.211 mol) was added. The septum was replaced, and toluene (100 mL) was added via syringe, followed by decanoyl chloride (50 mL, 0.24 mol). The resulting mixture was stirred at room temperature for 5 min, then heated to 60 °C with stirring. After a few minutes, the suspension thickened, forming a crystalline mass which redissolved with effervescence on continued stirring. The reaction mixture was then heated at reflux, giving a clear orange solution, which faded in color to pale yellow after *ca.* 20 min. After 2 h, the reaction mixture was cooled to room temperature and taken up in diethyl ether (100 mL), and washed with a saturated aqueous solution of sodium bicarbonate (50 mL), an aqueous solution of ammonia (1 M, 50 mL), and an aqueous solution of dibasic sodium phosphate (1 M,

50 mL). An emulsion formed, and the mixture was diluted with diethyl ether (300 mL) and water (300 mL). The phases were separated, and the aqueous phase was extracted with diethyl ether (2 x 75 mL). The combined ether portions were dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The product was recrystallized from methanol, affording the title compound as white crystals, 71.5 g (96 %): mp 70–71.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 2H), 7.45 (dd, J = 7.6, 1.5 Hz, 2H), 7.33 (ddd, J = 7.6, 7.6, 1.5 Hz, 2H), 7.23 (ddd, J = 7.6, 7.5, 1.5 Hz, 2H), 2.47 (t, J = 7.5 Hz, 2H), 1.60 (m, 2H), 1.20 (s, 12H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 139.0, 133.4, 128.0, 127.4, 127.0, 126.8, 34.3, 31.9, 29.4, 29.4, 29.3, 29.1, 25.4, 22.7, 14.2; IR (neat, cm^{-1}) 2921, 2854, 1667, 1478, 1461, 1447, 1364, 1310, 1299, 1281, 1252, 1237, 1173, 1100, 1030, 768, 729, 697, 662. Anal. Calcd for $C_{22}H_{27}NOS$: C, 74.74; H, 7.70. Found: C, 74.67; H, 7.71.

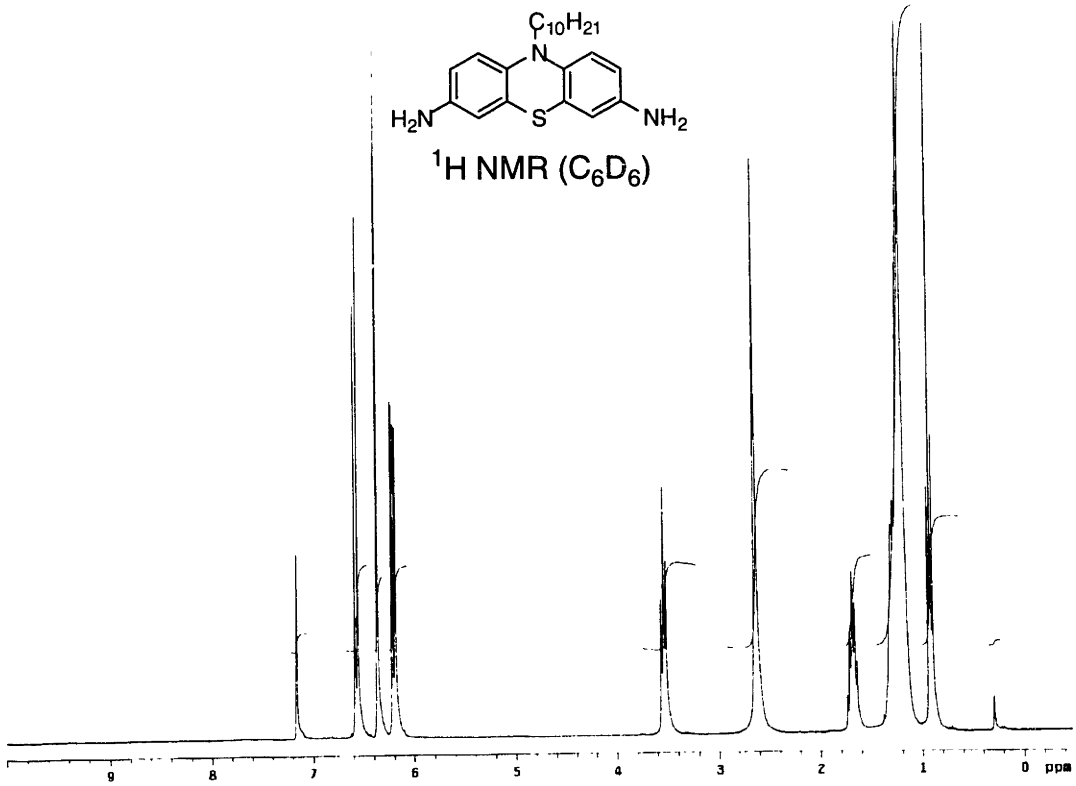
10-Decylphenothiazine (58).[141] An oven-dried Schlenk flask was charged with 10-decanoylphenothiazine (7.07 g, 20.0 mmol), stoppered, evacuated, and backfilled with argon. The stopper was replaced with a rubber septum, and tetrahydrofuran (20 mL) was added via syringe, causing a clear, colorless solution to form. A solution of borane in tetrahydrofuran (1.0 M, 40 mL, 40 mmol) was added via syringe over *ca.* 5 min. A slight effervescence and warming of the flask were apparent after a few minutes. The solution was heated to 65 °C. Analysis by GC after 30 min indicated the complete disappearance of the starting material. The solution was cooled to 0 °C with stirring. Hydrochloric acid (2 M, 40 mL, 80 mmol) was added cautiously via syringe, dropwise at first, then more rapidly as the vigorous effervescence slowed. The mixture was allowed to warm to room temperature, with stirring. After 15 min, the flask was opened and brine (50 mL) was added, followed by an aqueous solution of sodium hydroxide (6 M, 30 mL, 180 mmol), and diethyl ether (50 mL). The organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 x 25 mL). The organic portions were combined, dried over anhydrous

potassium carbonate, filtered through a plug of silica gel, and concentrated *in vacuo*. The title compound was obtained as a pale yellow oil, 6.66 g (98 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.15 (m, 4H), 6.96–6.87 (m, 4H), 3.86 (t, J = 7.2 Hz, 2H), 1.86–1.78 (m, 2H), 1.48–1.43 (m, 2H), 1.29 (s, 14H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 127.6, 127.3, 125.0, 122.5, 115.5, 47.6, 32.1, 29.7, 29.7, 29.5, 29.5, 27.2, 27.1, 22.9, 14.4.

3,7-Dibromo-10-decylphenothiazine (59). In an Erlenmeyer flask, 10-decylphenothiazine (1.63 g, 4.80 mmol) was dissolved in glacial acetic acid (25 mL) with stirring. Sodium acetate (0.804 g, 9.80 mmol) was added in one portion. A solution of bromine (0.50 mL, 9.7 mmol) in glacial acetic acid (5 mL) was added dropwise, resulting in the formation of a deep purple suspension. Analysis by TLC after 4 h indicated the complete consumption of the starting material. The mixture was concentrated *in vacuo*, then taken up in diethyl ether (75 mL) and washed with an aqueous solution of sodium hydroxide (2 M, 75 mL, 150 mmol), in which *ca.* 2 g sodium dithionite had been dissolved. The resulting solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual oil was purified by flash column chromatography on silica gel, using 19:1 hexanes: ethyl acetate as the eluant, affording the title compound as a pale yellow oil, 2.21 g (93 %): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.21 (m, 4H), 6.68 (d, J = 8.3 Hz, 2H), 3.75 (t, J = 7.1 Hz, 2H), 1.77–1.72 (m, 2H), 1.39–1.34 (m, 2H), 1.25 (m, 14H), 0.90 (t, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 130.2, 129.8, 126.5, 116.8, 114.9, 47.8, 32.1, 29.7, 29.7, 29.5, 29.4, 27.0, 26.8, 22.9, 14.4; IR (neat, cm^{-1}) 3062, 2952, 2923, 2852, 1586, 1482, 1453, 1412, 1387, 1378, 1329, 1301, 1270, 1250, 1233, 1110, 1083, 868, 803, 751, 722. Anal. Calcd for $C_{22}H_{25}Br_2NS$: C, 53.13; H, 5.47. Found: C, 53.43; H, 5.58.

3,7-Diamino-10-decylphenothiazine (60). In an Erlenmeyer flask, 10-decylphenothiazine (0.850 g, 2.50 mmol) was dispersed with stirring in nitric acid (70

% aqueous, 15 mL, 240 mmol) at 0 °C. Some nitrogen dioxide was evolved, and a solid mass formed. Cooling was discontinued; the reaction mixture was stirred at room temperature for 10 min, then heated to 80 °C. The resulting two-phase mixture was stirred vigorously for *ca.* 30 min until the slow evolution of nitrogen dioxide ceased. Analysis by TLC indicated that the starting material had been completely consumed. The mixture was cooled to room temperature, poured into water (100 mL), and extracted with ethyl acetate (100 mL). The organic phase was separated and washed with a saturated aqueous solution of sodium bicarbonate (75 mL). The resulting solution was dried over anhydrous potassium carbonate, filtered through a plug of silica gel over Celite, and concentrated *in vacuo*. The resulting amorphous solid was crystallized from ethanol, affording the presumed 3,7-dinitro-10-decylphenothiazine-5-oxide (0.962 g, 86 %). A portion of this material (0.757 g, 1.70 mmol) was placed in an Erlenmeyer flask and dissolved in ethanol (85 mL) with heating and stirring. Hydrochloric acid (concentrated, 5.0 mL, 60 mmol) was added. Zinc dust (1.63 g, 25 mmol) was added in small portions, causing the solution to boil and a deep purple color to form. As the addition of zinc dust was completed, after *ca.* 15 min, this color faded. Analysis by TLC indicated the complete consumption of starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was taken up in diethyl ether (75 mL), and washed with an aqueous solution of sodium hydroxide (2 M, 100 mL, 200 mmol). The resulting red-orange solution was washed with water (3 x 50 mL), giving rise to deep purple aqueous extracts. The ethereal solution was dried over anhydrous potassium carbonate, filtered, and concentrated *in vacuo*. The residual oil was purified by column chromatography, using 1:1 hexanes: ethyl acetate as the eluant, affording the title compound as a light green solid, 0.415 g (66 %; 57 % based on 10-decylphenothiazine): mp 76–78 °C;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H_2N
S
NH_2
^1H NMR (C_6D_6)
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8
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2
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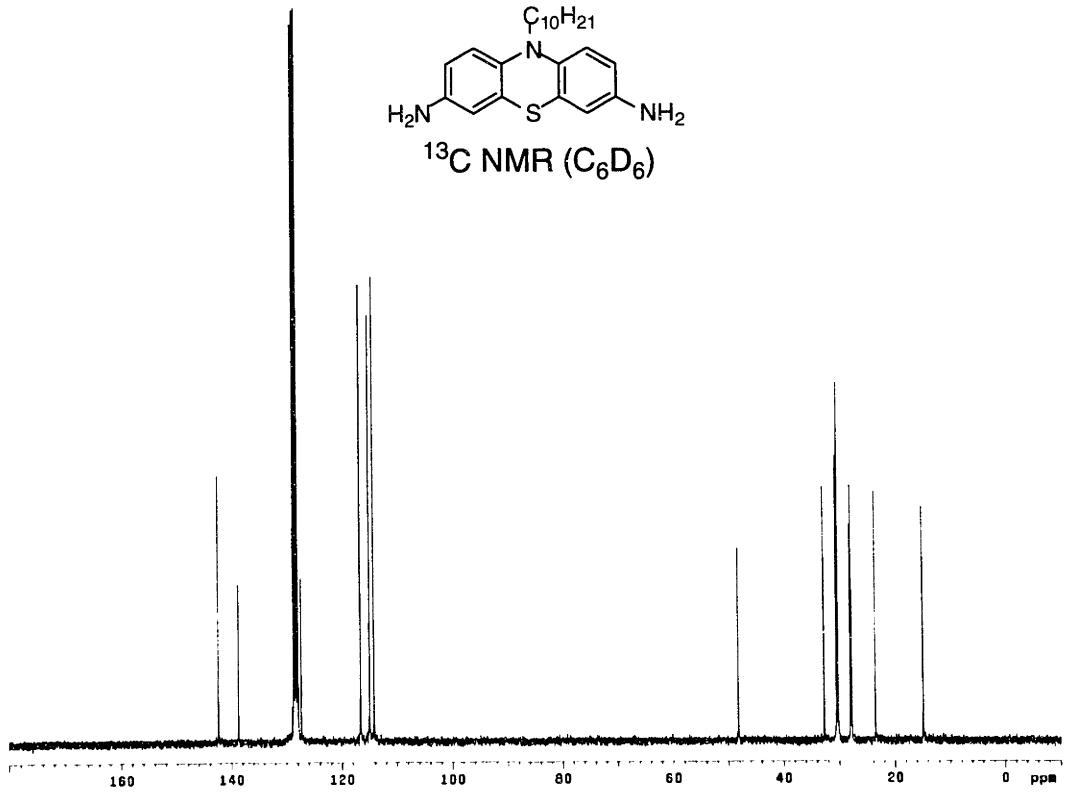
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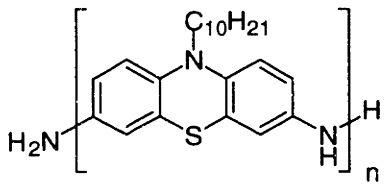
N
H_2N
S
NH_2
^{13}C NMR (C_6D_6)
160
140
120
100
80
60
40
20
0 ppm

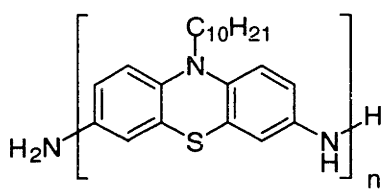
^{1}H NMR (300 MHz, C_6D_6; sample was prepared in the glovebox; dissolution in $CDCl_3$ under air gave a paramagnetic solution) δ 6.57 (d, J = 8.5 Hz, 2H), 6.37 (d, J = 2.6 Hz, 2H), 6.20 (dd, J = 8.5, 2.6 Hz, 2H), 3.54 (t, J = 7.0 Hz, 2H), 2.64 (s, 4H), 1.71–1.64 (m, 2H), 1.31–1.20 (m, 14H), 0.92 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.4, 138.7, 127.4, 116.7, 115.0, 114.2, 48.3, 32.8, 30.5, 30.4, 30.2, 30.2, 28.0, 27.8, 23.6, 14.9; IR (neat, cm^{-1}) 3377, 3267, 2917, 2848, 1596, 1505, 1472, 1432, 1331, 1301, 1256, 1221, 1152, 907, 876, 803, 793, 729, 691. Anal. Calcd for $C_{22}H_{29}N_3S$: C, 71.50; H, 8.45. Found: C, 71.45; H, 8.59.

Poly(3-amino-10-decylphenothiazin-7-yl) (61). An oven-dried, resealable Schlenk tube was charged with 3,7-diamino-10-decylphenothiazine (0.150 g, 0.406 mmol), sodium *tert*-butoxide (0.109 g, 1.13 mmol), tris(dibenzylideneacetone) dipalladium (3.7 mg, 0.004 mmol, 1 mol % Pd per amine), and 2-(di-*tert*-butylphosphino)biphenyl (4.8 mg, 0.016 mmol, 2 mol % per amine). The tube was capped with a Teflon screwcap, evacuated, and backfilled with argon. The screwcap was removed, and 3,7-dibromo-10-decylphenothiazine (0.201 g, 0.404 mmol) was added via pipette. The tube was again capped, evacuated, and backfilled with argon. The screwcap was replaced with a rubber septum, and tetrahydrofuran (1.6 mL) was added via syringe. The tube was purged with argon for 3 min, then the screwcap was replaced. The tube was sealed and its contents were heated to 65 °C with stirring. A deep red solution formed, and precipitation was visible within seconds. Analysis by TLC after 6 h indicated the near-complete consumption of the starting materials; however, a substantial spot at high R_f indicated the presence of low oligomers. The mixture was cooled to room temperature; the tube was opened, and an additional portion of tris(dibenzylideneacetone) dipalladium (3.7 mg, 0.004 mmol, 1 mol % Pd per amine) was added, followed by 2-(di-*tert*-butylphosphino)biphenyl (4.8 mg, 0.016 mmol, 2 mol % per amine). The tube was purgen with argon for 3 minutes; the screwcap was then replaced, the tube was sealed, and its contents were heated to 65

°C with stirring. Analysis by TLC after 12 h indicated the complete consumption of the starting materials, with essentially no product spots above the baseline. The mixture was cooled to room temperature, and taken up in dichloromethane. Some precipitation was visible. The resulting mixture was washed with a saturated aqueous solution of sodium bicarbonate (50 mL), in which a small quantity of sodium dithionite (*ca.* 1 g) had been dissolved. The organic phase was dried over anhydrous potassium carbonate, filtered (some insoluble material was removed), and concentrated *in vacuo*. The resulting yellow-brown, amorphous solid was reprecipitated from a mixture of dichloromethane and ethanol, containing a trace of hydrazine hydrate, under a slow stream of nitrogen. The product was obtained as a light brown solid, 0.136 g (47 %, based on the measured M_n values): No definite melting point; sinters above *ca.* 120 °C; ^{1}H NMR (300 MHz, THF-d_8; sample was prepared in the glovebox) δ 6.85 (s, 1H), 6.81–6.75 (m, 6H), 3.76 (broad s, 2H), 1.73 (broad s, 2H), 1.43 (broad s, 2H), 1.27 (s, 12H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, THF-d_8; sample was prepared in the glovebox) δ 140.3, 140.0, 126.8, 117.4, 117.1, 116.5, 48.2, 33.1, 30.8, 30.7, 30.5, 28.2, 28.1, 23.8, 14.7; IR (neat, cm^{-1}) 3328, 2921, 2852, 1590, 1501, 1459, 1295, 1239, 1214, 1370, 1142, 1106, 1050, 946, 855, 799, 720.



^{1}H, THF-d_8



^{13}C, THF-d_8

References and Notes

(1) For reviews of conducting polymers, including applications and novel properties obtained through functionalization, see: (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205. (b) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27–34. (c) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201–207. (d) Fabre, B.; Simonet, J. *Coord. Chem. Rev.* **1998**, *178–180*, 1211–1250. (e) Stenger-Smith, J. D. *Prog. Polym. Sci.* **1998**, *23*, 57–79.

(2) (a) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578–580. (b) Chiang, C. K.; Fincher, C. R. Jr.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098–1101.

(3) (a) Parini, V. P.; Kazakova, Z. S.; Berlin, A. A. *Vysokomolekul Soedin.* **1961**, *3*, 1870–1873. (b) Pohl, H. A.; Engelhardt, E. H. *J. Phys. Chem.* **1962**, *66*, 2085–2095.

(4) Fritsche, J. *J. Prakt. Chem.* **1840**, *20*, 453–459.

(5) Letheby, H. *J. Chem. Soc. 15*, 161–163.

(6) Early studies described a "nigraniline" oxidation state in polyaniline. Described as an intermediate between emeraldine and pernigraniline, it may well have been a mixture of the two. This possibility was not discussed, and the evidence was inconclusive: (a) Willstätter, R.; Dorogi, S. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 2147–2168. (b) Willstätter, R.; Dorogi, S. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 4118–4135. (c) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1910**, *97*, 2388–2403. (d) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1912**, *101*, 1117–1123.

(7) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *111*, 111–114.

(8) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 6627–6631. See also ref. 12a.

(9) (a) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91–97. (b) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *57*, 3514–3519. (c) Pron, A.; Osterholm,

J. E.; Smith, P.; Heeger, A. J.; Laska, J.; Zagorska, M. *Synth. Met.* **1993**, *57*, 3520–3525.

(10) Holland, E. R.; Pomfret, S. J.; Adams, P. N.; Abell, L.; Monkman, A. P. *Synth. Met.* **1997**, *84*, 777–778.

(11) (a) Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2385-2400. (b) Chen, S.-A.; Fang, W.-G. *Macromolecules* **1991**, *24*, 1242–1248.

(12) (a) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441–1447. (b) Chiang, J.-C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193–205.

(13) MacDiarmid, A. G.; Mu, S.-L.; Somasiri, N. L. D.; Wu, G. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 187–190.

(14) Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *161*, 419–423.

(15) (a) Kaneto, K.; Kaneko, M.; Min, Y.; MacDiarmid, A. G. *Synth. Met* **1995**, *71*, 2211–2213. (b) Takashima, W.; Kaneko, M.; Kaneto, K.; MacDiarmid, A. G. *Synth. Met.* **1995**, *71*, 2265–2266.

(16) (a) DeBerry, D. W. *J. Electrochem. Soc.* **1985**, *132*, 1022–1026. (b) Ahmad, N.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 103–110. (c) Lu, W.–K.; Elsenbaumer, R. L.; Wessling, B. *Synth. Met.* **1995**, *71*, 2163–2166.

(17) (a) Park, Y. H.; Kim, Y. K.; Nam, S. W. *J. Appl. Polym. Sci.* **1991**, *43*, 1307-1313. (b) Ohtani, A.; Abe, M.; Ezoe, M.; Doi, T.; Miyata, T.; Miyake, A. *Synth. Met.* **1993**, *57*, 3696–3701.

(18) (a) Taka, T. *Synth. Met.* **1991**, *41*, 1177–1180. (b) Colaneri, N. F.; Shacklette, L. W. *IEEE Trans. Instrum. Meas.* **1992**, *41*, 291. (c) Joo, J.; Epstein, A. J. *Appl. Phys. Lett.* **1994**, *65*, 2278–2280.

(19) Kohlman, R. S.; Zibold, A.; Tanner, D. B.; Ihas, G. G.; Ishiguro, T.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. Lett.* **1997**, *78*, 3915–3918.

(20) MacDiarmid, A. G.; Zhou, Y.; Feng, J. *Synth. Met.* **1999**, *100*, 131–140.

(21) For example, the initial oxidation of aniline gives rise to a benzidine: Johnson, B. J.; Park, S.-M. *J. Electrochem. Soc.* **1996**, *143*, 1277–1282.

(22) Wudl, F.; Angus, R. O.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677–3684.

(23) (a) Baikina, N. D.; Kopylov, V. V.; Pravednikov, A. N. *Polym. Sci. U.S.S.R. (Engl. Trans.)* **1973**, *15*, 1968. (b) Pomerantz, M.; Mire, D. E. *Polym. Prepr.–Am. Chem. Soc., Div. Polym. Chem.* **1998**, *39*, 128–129.

(24) (a) D'Aprano, G.; Leclerc, M.; Zotti, G. *J. Electroanal. Chem.* **1993**, *351*, 145–158. (b) Kilmartin, P. A.; Wright, G. A. *Synth. Met.* **1997**, *88*, 153–162. See also Refs. 106–111.

(25) (a) Watanabe, A.; Mori, K.; Iwabuchi, A.; Iwasaki, Y.; Nakamura, Y.; Ito, O. *Macromolecules* **1989**, *22*, 3521–3525. (b) Chevalier, J.-W.; Bergeron, J.-Y.; Dao, L. H. *Macromolecules* **1992**, *25*, 3325–3331. (c) Lian, A.; Besner, S.; Dao, L. H. *Synth. Met.* **1995**, *74*, 21–27. (d) Hwang, G.-W.; Wu, K.-Y.; Hua, M.-Y.; Lee, H.-T.; Chen, S.-A. *Synth. Met.* **1998**, *92*, 39–46. The alkylation or acylation of emeraldine and its anions has also been reported: Mikhael, M. G.; Padias, A. B.; Hall, H. K. Jr. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 1673–1679.

(26) Honzl, J.; Tlustáková, M. *J. Polym. Sci. C* **1968**, *21*, 451–462.

(27) Willstätter, R.; Moore, C. W. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2665–2689.

(28) Lu, F.-L.; Wudl, F.; Nowak, M.; Heeger, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 8311–8313.

(29) Zhang, W. J.; Feng, J.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *84*, 119–120.

(30) Wei, Y.; Yang, C.; Wei, G.; Feng, G. *Synth. Met.* **1997**, *84*, 289–291.

(31) Ochi, M.; Furusho, H.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1749–1752.

(32) Rebourt, E.; Joule, J. A.; Monkman, A. P. *Synth. Met.* **1997**, *84*, 65–66.

(33) For recent reviews of palladium-catalyzed carbon-nitrogen bond formation and related processes, see: (a) Hartwig, J. F. *Synlett* **1997**, 329–340. (b) Barañano, D.; Mann, G.; Hartwig, J. F. *Curr. Org. Chem.* **1997**, *1*, 287–305. (c) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805–818. (d) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860. (e) Hartwig, J. F. *Angew. Chem. Int. Ed.* **1998**, *37*, 2046–2067. (f) Yang, B. Y.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125–146.

(34) (a) March, J. *Advanced Organic Chemistry*; 4th ed., John Wiley & Sons: New York, 1992. (b) Emerson, W. E. *Org. Reactions* **1948**, *4*, 174–255. (c) Romanelli, M. G.; Becker, E. I. *Org. Synth. Coll. 5*, **1973**, 552–554.

(35) Sundberg, R. J.; Sloan, K. B. *J. Org. Chem.* **1973**, *38*, 2052–2057.

(36) Diphenylamine is made in this way: The Merck Index, Twelfth Edition; Budavari, S. (ed.); Merck & Co., Inc., Whitehouse Station, 1996.

(37) (a) Lantz, P.; Obellianne, P. *Bull. Soc. Chim. Fr.* **1956**, 311–317. (b) Kotsuki, H.; Kobayaski, S.; Matsumoto, K.; Suenaga, H.; Nishizawa, H. *Synthesis* **1990**, *12*, 1147–1148.

(38) Heaney, H. *Chem. Rev.* **1962**, *62*, 81–97.

(39) (a) Ullmann, F.; Kipper, H. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2120–2126. (b) Goldberg, I. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 4541–4546.

(40) (a) Barton, D. H. R.; Finet, J.-P.; Khamsi, J. *Tetrahedron Lett.* **1986**, *27*, 3615–3618. (b) Barton, D. H. R.; Donnelly, D. M. X.; Finet, J.-P.; Guiry, P. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2095–2102.

(41) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927–928.

(42) Boger, D. L.; Panek, J. S. *Tetrahedron Lett.* **1984**, *25*, 3175–3178.

(43) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901–7902.

(44) (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1348–1350. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609–3612.

(45) Wolfe, J.P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133–1135.

(46) (a) Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525–7546. (b) Peat, A. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 1028–1030. (c) Peat, A. J.; Aoki, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 3068–3073.

(47) (a) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215–7216. (b) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217–7218.

(48) (a) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969–5970. (b) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030–3039. (c) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708–4709. (d) Hartwig, J. F.; Paul, F. *J. Am. Chem. Soc.* **1995**, *117*, 5373–5374.

(49) Wagaw, S.; Rennels, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 8451–8458.

(50) (a) Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 72407241. (b) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 6066–6068. (c) Marcoux, J.–F.; Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1568–1569. (d) Åhman, J.; Buchwald, S. L. *Tetrahedron Lett.* **1997**, *38*, 6366–6366. (e) Wolfe, J. P.; Buchwald, S. L. *Tetrahedron Lett.* **1997**, *38*, 6359–6362.

(51) The stoichiometric reaction of amines with arylpalladium *tert*-butoxide complexes has been demonstrated: Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109–13110. The evidence for the importance of this intermediate in the catalytic cycle, however, remains inconclusive.

(52) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 3534–3542.

(53) The mechanism is apparently more complicated when the catalyst is generated from $Pd_2(dba)_3$ and BINAP. The complex [BINAP]Pd(dba), which forms when the catalyst precursors are mixed, has been isolated, and is a kinetically competent catalyst source. However, it does not appear to react with aryl bromides in the absence of the other reactants. Wolfe, J. P.; Palucki, M.; Buchwald, S. L., unpublished results.

(54) For a review of synthetic approaches to conjugated macromolecules with precise length, see: (a) Tour, J. M. *Trends Polym. Sci.* **1994**, *2*, 332–342. (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–553.

(55) The divergent-convergent approach was subsequently used in the synthesis of *N*-aryl-*m*-oligoanilines as large as the 16-mer: Louie, J.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 6737–6739. Prior to our work, these authors reported a stepwise synthesis of triarylamine dendrimers: Louie, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 11695–11696.

(56) For the first example of a divergent-convergent synthesis, used to prepare monodisperse polyethylenes, see: Igner, E.; Paynter, O. I.; Simmonds, D. J.; Whiting, M. C. *J. Chem. Soc. Perkin Trans. 1* **1987**, 2447–2454.

(57) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348–2350.

(58) For a review of electrophilic substitutions of arylsilanes, see: Bennetau, B.; Dunogues, J. *Synlett* **1993**, 171–176.

(59) Wessjohann, L.; McGaffin, G.; de Meijere, A. *Synthesis* **1989**, 359–363.

(60) Fasth, K.-J.; Antoni, G.; Langström, B. *J. Chem. Soc. Perkin Trans. 1* **1988**, 3081–3084.

(61) This compound had been obtained previously by an analogous sequence using 4-bromo-*N,N*-bis(trimethylsilyl)aniline: Walton, D. R. M. *J. Chem. Soc. C* **1966,**

1706–1707. We found it more convenient to use the crystalline and moisture-stable *N*-(diphenylmethylene)-4-bromoaniline.

(62) For reasons of availability at the time that this work was carried out, we employed *S*-BINAP. The significantly less expensive racemic form, now available commercially from Strem Chemical Company, is an equally effective ligand in these coupling reactions, with no observable differences in yields.

(63) DPEphos = bis[2-(diphenylphosphino)phenyl] ether; see ref. 84, 92. For other reaction examples see Section 2.2.

(64) Berthelot, J.; Guette, C.; Essayegh, M.; Desbene, P. L.; Basselier, J. J. *Synth. Commun.* **1986**, *16*, 1641–1645.

(65) The corresponding N_3-diamine, a core piece for odd-numbered oligomers, has been prepared; see Chapter 2, Section 1.

(66) Thermal deprotection of BOC-protected pyrroles and indoles has been reported to proceed more rapidly: Rawal, V. H.; Jones, R. J.; Cava, M. P. *J. Org. Chem.* **1987**, *52*, 19–28.

(67) Removal of benzyl and *tert*-butyl carbamate groups from peptides using TMSI is well known: Lott, R. S.; Chauhan, V. S.; Stammer, C. H. *J. Chem. Soc. Chem. Commun.* **1979**, 495–496.

(68) Stafström, S.; Brédas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B. *Phys. Rev. Lett.* **1987**, *59*, 1464–1467.

(69) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869–7879. For other discussions of polyaniline oxidation states, see Refs. 3–5.

(70) Huang, W. S.; MacDiarmid, A. G. *Polymer* **1993**, *34*, 1833–1845.

(71) Nicolau, Y. F.; Beadle, P. M.; Banka, E. *Synth. Met.* **1997**, *84*, 585–586.

(72) For a review of π-dimers and π-stacks in conducting polymers, see: Miller, L. L.; Mann, K. R. *Acc. Chem. Res. 1996*, **29**, 417–423.

(73) The indium-tin oxide coating is known to be unstable to strong acids; however, immersion of the slides in 1.0 M sulfuric acid, for the short time periods involved in these CV studies, caused no discernible degradation.

(74) The cause of this material loss is unclear. It is possible that the evolution of carbon dioxide during hydrolysis causes blistering of the films, with some initial physical instability.

(75) Some ambiguity is involved in assigning the peak areas, but the first peak is clearly larger, in the CVs of both the heptaaniline and the decaaniline, for any reasonable choice of demarcation. The narrow peak at high potential is smaller than it appears.

(76) Carbazole itself undergoes anodic oxidation at + 1.16 V relative to SCE: Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 1159. Conjugation of the carbazole moiety with a protonated iminoquinone might well raise the oxidation potential beyond the range investigated here.

(77) Subsequently, several reports of this reaction have appeared. (a) Hartwig and coworkers studied the arylation of benzophenone imine and of certain azoles: (a) Mann, G.; Hartwig, J. F.; Driver, M. S.; Fernández-Rivas, C. *J. Am. Chem. Soc.* **1998**, *120*, 827–828. (b) Allylamine and diallylamine have been examined as alternative ammonia surrogates: Jaime-Figueroa, S.; Liu, Y.; Muchowski, J. M.; Putman, D. G. *Tetrahedron Lett.* **1998**, *39*, 1313–1316. (c) An elegant variation uses molecular nitrogen, stoichiometric titanium complexes, and a palladium catalyst to convert aryl halides to the corresponding *N,N*-bis(trimethylsilyl)-anilines, which may be hydrolyzed to give primary anilines: Hori, K.; Mori, M. *J. Am. Chem. Soc.* **1998**, *120*, 7651–7652.

(78) Hodgson, H. H. *Chem. Rev.* **1947**, *40*, 251–277.

(79) Bacon, R. G. R.; Karim, A. *Chem. Commun.* **1969**, 578.

(80) (a) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 2483–2485. (b) Hassner, A.; Munger, P.; Belinka, B. A. Jr. *Tetrahedron Lett.* **1982**, *23*, 699–702. (c) Nishiyama, K.; Tanaka, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1322–1323.

(81) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054–6058.

(82) The sp^2-hybridized nitrogen should be more electronegative than the sp^3-hybridized nitrogen in amines. Hartwig has examined reductive elimination reactions of (imido)palladium (II) aryl complexes and found them to be quite fast (see Ref. 77a).

(83) β-Hydride elimination is well known in late transition metal amido complexes; see: (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188. (b) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55C57. (c) Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626–3633. In the amination reactions, the product of this side-reaction is a palladium (aryl) hydride complex, which forms the arene by reductive elimination. This reaction can often be suppressed to varying degrees by a judicious choice of ligand, but remains problematic in some cases.

(84) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081–3089.

(85) Kranenburg, M.; Delis, J. G. P.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Veldman, N.; Spek, A. L.; Goubitz, K.; Fraanje, J. *J. Chem. Soc., Dalton Trans.* **1997**, 1839–1849.

(86) Oxidative addition, believed to be the rate-limiting step in the catalytic cycle (see Ref. 94), is slowed by electron-donating substituents on the aryl halide; see, for example: Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810–1817, and references cited therein.

(87) Aniline has been shown to be slightly more acidic than *tert*-butanol in dimethyl sulfoxide solution: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

Presumably the anilide anion attacks the nitrile. Aliphatic amines, which are less acidic, apparently do not attack aromatic nitriles when sodium *tert*-butoxide is used as the base (ref. 47a).

(88) Singer, R. A.; Buchwald, S. L. *Tetrahedron Lett.* **1999**, *40*, 1095–1098.

(89) Note that Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, had been reported by van Leeuwen and coworkers (ref. 84); we prepared this variant simply because the dibromide precursor was on hand at the time this work was carried out, whereas 9,9-dimethylxanthene was back-ordered.

(90) van Leeuwen and coworkers have reported that Xantphos is an effective ligand in the coupling of aliphatic amines with 4-bromobenzonitrile: Guari, Y.; van Es, D. S.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron Lett.* **1999**, *40*, 3789–3790.

(91) (a) Harris, M. C.; Buchwald, S. L. *Tetrahedron Lett.* **1999**, in press. (b) Wagaw, S.; Yang, B. H.; Buchwald, S. L. Submitted for publication. For related prior work see: Wagaw, S.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6621–6622. (c) Yang, B. H.; Buchwald, S. L. *Org. Lett.* **1999**, *1*, 35–38.

(92) This ligand is now commercially available from Strem Chemical.

(93) This comparison was calculated per mole of palladium, using Johnson-Matthey Alfa ÆSAR 1999 list prices, based on the largest available quantities of each.

(94) Wolfe, J. P. Late Transition Metal Catalyzed C–N and C–C Bond Forming Reactions, pp. 70–73. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, May 1999.

(95) The first palladium-catalyzed aminations of aryl chlorides to be reported in the open literature required activated substrates, and employed rather harsh conditions. Moreover, mixtures of regioisomers were formed, casting doubt on the true mechanism of the process: (a) Beller, M.; Riermeier, T. H.; Reisinger, C.-P.; Herrmann, W. A. *Tetrahedron Lett.* **1997**, *38*, 2073–2074. (b) Reddy, N. P.; Tanaka, M.

Tetrahedron Lett. **1997**, *38*, 4807–4810. A nickel-catalyzed system has also been reported; see Ref. 81.

(96) (a) Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617–620. (b) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367–2370. (c) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369–7370. (d) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722–9723.

(97) Previously, the only amination reactions reported to proceed at room temperature were those of aryl iodides, using sodium *tert*-butoxide as the base and stoichiometric 18-crown-6 as an additive; see Ref. 50b.

(98) Aranyos, A.; Old, D. W.; Kiyomori, A.; Wolfe, J. P.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4369–4378.

(99) In contrast, tri-*tert*-butylphosphine (Ref. 96a, b) exhibits some inconvenient handling characteristics. Its melting point is very near room temperature, complicating its handling as a liquid or as a solid, and it is quite air-sensitive.

(100) Wolfe, J. P.; Aranyos, A.; Fox, J. M.; Buchwald, S. L. Unpublished results.

(101) For recent examples of the use of organocopper complexes generated from Grignard reagents and copper (I) salts, see: (a) Burns, D. H.; Miller, J. D.; Chan, H.-K.; Delaney, M. D. *J. Am. Chem. Soc.* **1997**, *119*, 2125–2133. (b) Kanai, M.; Nakagawa, Y.; Tomioka, K. *Tetrahedron* **1999**, *55*, 3843–3854.

(102) To examine this possibility, we have attempted to use zinc chloride in place of cuprous chloride, and observed no phosphine formation. However, more reactive chlorophosphines react well with organozinc reagents: Langer, F.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 4591–4594.

(103) The reason for the difference in efficiency between $Pd_2(dba)_3$ and $Pd(OAc)_2$, for most aniline couplings, is unclear. Since a sterically hindered aniline, 2,4,6-trimethylaniline, works well with $Pd(OAc)_2$, we speculate that with smaller

anilines, catalytically inactive anilide-bridged palladium complexes might form; analogous complexes have been formed from aliphatic amines in the $(o\text{-tol})_3P$/Pd system (Widenhoefer, R. A.; Buchwald, S. L., unpublished results). Dibenzylideneacetone, acting as a weak auxiliary ligand, might prevent this side reaction.

(104) The *p*-nitro group enhances the π-acceptor characteristics of the aryl group, rendering the metal more Lewis-acidic. Arylpalladium triflates have been shown to be cationic; see: Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810–1817.

(105) (a) Wei, X.-L.; Epstein, A. J. *Synth. Met.* **1995**, *74*, 123–125. (b) Wei, X.-L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 2545–2555. (c) Lee, W.; Du, G.; Long, S. M.; Epstein, A. J.; Shimizu, S.; Saitoh, T.; Uzawa, M. *Synth. Met.* **1997**, *84*, 807–808. (d) Shimizu, S.; Saitoh, T.; Uzawa, M.; Yuasa, M.; Yano, K.; Maruyama, T.; Watanabe, K. *Synth. Met.* **1997**, *85*, 1337–1338.

(106) Chan, H. S. O.; Neuendorf, A. J.; Ng, S.-C.; Wong, P. M. L.; Young, D. J. *Chem. Commun.* **1998**, 1327–1328.

(107) (a) D'Aprano, G.; Leclerc, M.; Zotti, G.; Schiavon, G. *Chem. Mater.* **1995**, *7*, 33–42. (b) Gazotti, W. A.; De Paoli, M.-A. *Synth. Met.* **1996**, *80*, 263–269. (c) Raghunathan, A.; Kahol, P. K.; McCormick, B. J. *Synth. Met.* **1999**, *100*, 205–216.

(108) Ranger, M.; Leclerc, M. *Synth. Met.* **1997**, *84*, 85–86.

(109) Nitro-substituted polyanilines have been predicted to possess a particularly low bandgap: Vaschetto, M. E.; Retamal, B. A. *J. Phys. Chem. A* **1997**, *101*, 6945–6950. In fact, the polymers are essentially insulators. This has been attributed to highly incomplete doping (ref. 108). It is conceivable that a lower level of substitution would allow bandgap modification, without rendering the polymer too nonbasic for sufficient doping.

(110) Kwon, A. H.; Conklin, J. A.; Makhinson, M.; Kaner, R. B. *Synth. Met.* **1997**, *84*, 95–96.

(111) Díaz, F. R.; Sánchez, C. O.; del Valle, M. A.; Tagle, L. H.; Bernede, J. C.; Tregouet, Y. *Synth. Met.* **1998**, *92*, 99–106.

(112) Epstein, A. J.; MacDiarmid, A. G. *Synth. Met.* **1991**, *41–43*, 601–606.

(113) Sulfonated polyanilines can display rather good electrical conductivity (ref 105b), as can polyanilines bearing small alkoxy groups such as methoxy and ethoxy (ref. 108a). Most ring-substituted polyanilines, however, exhibit dramatic decreases in conductivity, usually of several orders of magnitude.

(114) Conklin, J. A.; Huang, S.-C.; Huang, S.-M.; Wen, T.; Kaner, R. B. *Macromolecules* **1995**, *28*, 6522–6527, and references cited therein.

(115) Mattoso, L. H. C.; Oliveira, O. N. Jr; Faria, R. M.; Manohar, S. K. Epstein, A. J.; MacDiarmid, A. G. *Polymer Int.* **1994**, *35*, 89–93.

(116) Fox, G. J.; Hallas, G.; Hepworth, J. D.; Paskins, K. N. *Org. Synth. Coll.*, **1988**, *6*, 181–183.

(117) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190–6191.

(118) Very recently, the palladium-catalyzed polymerization of 4-bromoaniline using 2-(di-*tert*-butylphosphino)biphenyl (**48**) was found to result in the complete consumption of starting material under mild conditions (80 °C) and at rather low catalyst loading (1 mol % Pd). The coupling product was rather insoluble, and the ^{1}H NMR spectrum of the chloroform-soluble fraction indicated the presence of multiple species. This procedure has not been investigated further as of this writing.

(119) Kanbara, T.; Honma, A.; Hasegawa, K. *Chem. Lett.* **1996**, 1135–1136. See also: Kanbara, T.; Izumi, K.; Narise, T.; Hasegawa, K. *Polym. J.* **1998**, *1*, 66–68.

(120) (a) Kanbara, T.; Izumi, K.; Nakadani, Y.; Narise, T.; Hasegawa, K. *Chem. Lett.* **1997**, 1185–1186. (b) Kanbara, T.; Nakadani, Y.; Hasegawa, K. *Polym. J.* **1999**, *2*, 206–209. (c) Spetseris, N.; Ward, R. E.; Meyer, T. Y. *Macromolecules* **1998**, *31*, 3158–3161.

(121) Goodson, F. E.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 1700–1703.

(122) Mackewitz, T. W.; Buchwald, S. L. Unpublished results.

(123) Even the less reactive aryl chlorides are labile to transfer hydrogenolysis; see for example: Entwistle, I. D.; Johnstone, R. A. W.; Povall, T. J. *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1300–1301.

(124) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441–12453.

(125) The selected results are those of the successful experiments in a preliminary survey of reaction conditions. Because a systematic study has not yet been carried out, a discussion of the effects of variations in conditions would be premature and likely misleading.

(126) Hsu, C.-H.; Peacock, P. M.; Flippen, R. B.; Manohar, S. K.; MacDiarmid, A. G. *Synth. Met.* **1993**, *60*, 233–237.

(127) Wu, G. C.; DeGroot, D. C.; Marcy, H. O.; Schindler, J. L.; Kannewurf, C. R.; Bakas, T.; Papaefthymiou, V.; Hirpo, W.; Yesinowski, J. P.; Liu, Y. J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 9229–9242.

(128) Adams, P. N.; Laughlin, P. J.; Monkman, A. P. *Synth. Met.* **1996**, *76*, 157–160.

(129) Mattoso, L. H. C.; Faria, R. M.; Bulhões, L. O. S.; MacDiarmid, A. G. *Polymer* **1994**, *35*, 5104–5108.

(130) Wyatt, P. J. *Anal. Chim. Acta* **1993**, *272*, 1–40.

(131) (a) Talu, M.; Kabasakaloglu, M.; Oskoui, H. R. *J. Polym. Sci. A: Polymer Chem.* **1996**, *34*, 2981–2989. (b) Can, M.; Pekmez, K.; Pekmez, N.; Yildiz, A. *Synth. Met.* **1999**, *104*, 9–17.

(132) Ng, S. C.; Xu, L. G.; Chan, H. S. O. *Synth. Met.* **1998**, *94*, 185–191.

(133) (a) Polis, D. W.; Young, C. L.; MacLean, M. R.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3231–3236. (b) Young, C. L.; Polis, D. W.; Bain, A. N.; Sapochak, L. S.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3236–3242.

(134) Liang, Q. Y.; Neoh, K. G.; Kang, E. T.; Tan, K. L.; Wong, H. K. *Eur. Polym. J.* **1992**, *28*, 755–763.

(135) (a) Wei, Y.; Tian, J.; Hsueh, K. F. *Polym. Mater. Sci. Eng.* **1994**, *71*, 586–587. (b) Sari, B.; Talu, M. *Synth. Met.* **1998**, *94*, 221–227.

(136) See, for example: Pearson, R. D.; Manian, A. A.; Harcus, J. L.; Hall, D.; Hewlett, E. L. *Science* **1982**, *217*, 369–371.

(137) The Merck Index, Twelfth Edition; Budavari, S. (ed.); Merck & Co., Inc., Whitehouse Station, 1996.

(138) Biehl, E. R.; Chiou, H.-s.; Keepers, J.; Kennard, S.; Reeves, P. C. *J. Heterocycl. Chem.* **1975**, *12*, 397–399.

(139) Ortiz Arrufat, A.; Fernandez-Alonso, J. I.; Pardo, A.; Llabres, J. *Mol. Pharmacol.* **1979**, *16*, 1040–1045.

(140) Wudl *et al.* have compared the conductive forms of oxidatively polymerized polyaniline, polyaniline prepared by regiospecific polycondensation, and phenyl-capped octaaniline, and found similar values for all three (Ref. 22). Interestingly, the thorough removal of low-molecular-weight components from the oxidative polymerization product is reported to decrease the number of spins per octaaniline by half.

(141) Gilman, H.; Shirley, D. A. *J. Am. Chem. Soc.* **1944**, *66*, 888–893.

(142) Chan, C.; Yin, H.; Garforth, J.; McKie, J. H.; Jaouhari, R.; Speers, P.; Douglas, K. T.; Rock, P. J.; Yardley, V.; Croft, S.; Fairlamb, A. H. *J. Med. Chem.* **1998**, *41*, 148–156.

(143) Brown, H. C.; Heim, P. *J. Org. Chem.* **1973**, *38*, 912–916.

(144) Ebdrup, S. *Synthesis* **1998**, 1107–1109.

(145) Taguchi, K.; Westheimer, F. H. *J. Org. Chem.* **1971**, *36*, 1570–1572.

(146) This reaction is carried out under argon; we have observed that, under air, palladium on carbon may ignite upon contact with methanol. Once started, the imine hydrogenolysis reaction does not require rigorously air-free conditions.

(147) Seitz, D. E.; Ferreira, L. *Synth. Commun.* **1979**, 931–939.

(148) Purity was verified by comparison with commercial samples: (a) *o*-Anisidine, 99+ %, Aldrich Chemical Company. (b) *p*-Aminobenzonitrile, Eastman Kodak Chemical Company.

(149) (a) Manecke, G.; Middeke, H.-J. *Angew. Makromol. Chem.* **1980**, *91*, 179–201. (b) Manecke, G.; Vogt, H.-G. *J. Solid-Phase Biochem.* **1979**, *4*, 233243.

(150) Piccard, J.; de Montmollin, F. *Helv. Chim. Acta* **1923**, *6*, 1011–1019.

(151) Wieland, H. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1313–1328.

(152) Marsden, R. J. B. *J. Chem. Soc.* **1937**, 627.

(153) Busch, M.; Kunder, H. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 317–334.

(154) Ullmann, F.; Jüngel, K. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 1077–1083.

(155) Reddelien, G. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 1355–1364.

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