The Synthesis of Bromoethoxy and Vinylbenzyloxy Substituted NLO Chromophores

Michael Joseph Matuszewski

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THE SYNTHESIS OF BROMOETHOXY AND VINYL BENZYLOXY SUBSTITUTED NLO CHROMOPHORES

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science

By

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B.S., St. Norbert College, 2000

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Matuszewski, Michael J. M.S., Department of Chemistry, Wright State University, 2002. The Synthesis of Bromoethoxy and Vinylbenzyloxy Substituted NLO Chromophores.

Multiphoton-absorption processes have recently attracted growing interest because of the potential impact on a wide spectrum of applications, ranging from data storage to photodynamic therapy. From the materials standpoint, particular interest is centered in designing chromophores that exhibit a large two-photon cross-section. The current research is focused on establishing synthetic routes that lead to the formation of derivatives of N,N-diphenyl-(7-benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine which contain meta functionalization. A bromoethoxy functionalized chromophore, N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine, was synthesized and used as a polymer pendent while a vinylbenzyloxy chromophore, N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine, was synthesized as a hydrosilation substrate. A compound containing three chromophores, 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylanilino)phenoxy)methyl)benzene, has been synthesized to determine if a larger two-photon cross-section ($\sigma_2$) could be obtained by increasing the number of chromophore units in a single molecule.
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DEDICATION

To my family especially my parents, Michael and Jackie Matuszewski, and my great-grandmother, Clara Fleischman, thank you for all of the love and support you have given me throughout my life. To my fiancé and soon to be wife, Donna, who was there to support me through these last few stressful months, you helped me to stay sane. I love you all.
ACKNOWLEDGMENTS

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INTRODUCTION

Organic materials that exhibit significant nonlinear optical (NLO) absorptivities have become very important compounds and the search for these materials has increased dramatically over the past few years.\textsuperscript{1} One of the more interesting nonlinear optical absorption processes being studied is two-photon absorption. This process has been the subject of interest in many different scientific groups including chemistry, photonics, and biology. Two-photon absorption is an important process in the area of photonics because, as an analog of electronics, photons rather than electrons can be used to acquire, store, process and transmit information.\textsuperscript{2} The use of photons offers numerous advantages over electrons. The main advantage is an increase in speed of several orders of magnitude as compared to those obtained by the use of electrons. Some of the other advantages include the absence of interference from magnetic and electrical sources, the complete compatibility with existing fiber-optic networks, and the ability to use three-dimensional connectivity in photonic circuits to produce smaller optical chips.\textsuperscript{3} As a result, there have been several technological applications that utilize the two-photon absorption process. Some of the more interesting applications include three-dimensional optical data storage\textsuperscript{4,5}, two-photon photodynamic noninvasive cancer therapy\textsuperscript{1}, optical power limiting\textsuperscript{1,5}, two-photon induced biological caging studies\textsuperscript{5}, and two-photon confocal microscopy for the nondestructive evaluation of paint.\textsuperscript{4}
With these results as a basis, the objectives of this research were 1) to synthesize functionalized advanced optical chromophores for studies to investigate their two-photon cross-sections and 2) to characterize these new chromophores.
HISTORICAL

Nonlinear Optical Materials

There are two main classes of nonlinear optical (NLO) materials. The first class is bulk material and it is believed that nonlinearity in this type of material arises from electrons not associated with individual nuclei, such as those found in semiconductors or metals. The optical nonlinearity of this material is determined by the electronic state of the bulk medium. A few examples of this type of material are quantum-well structures and inorganic crystals, such as potassium dihydrogen phosphate.2,3

The second major class is molecular materials. This class represents an ensemble of molecular units that are chemically bonded by weak interactions with each other in bulk via dipole forces and/or van der Waals interactions. The optical nonlinearity in this class is determined by the electronic state of the bulk medium. The nonlinearity can also be described as the deformation of the electronic clouds within each molecule that arise in the presence of an intense electric field of an applied pulse. A few examples of molecular materials include polymers and organic crystals.2,6

Recently, molecular materials, mainly organic systems, have become increasingly recognized as the materials of the future. This is due to the fact that with the help of synthetic chemistry, their molecular nature can be altered to give rise to optimized structures that maximize nonlinear responses and other significant properties.2 Some of the other advantages offered by organic molecular materials include improved thermal stability, the potential for significant cost saving, and superior processibility when
compared to inorganic systems.\(^3\) It has been shown that molecular engineering can be used to maximize the optical nonlinearity of these compounds.\(^2\)

**Nonlinear Optical Effects in Organic Systems**

As a result of the \( \sigma \) bonding that exists in organic materials, organic molecular materials have been shown to exhibit the largest nonresonant optical nonlinearities. By its nature, a nonresonant optical nonlinearity would have the fastest response time. The only factor limiting the response time is the width of the driving pulse laser. Due to advances in laser technology, current lasers can achieve femtosecond pulses. Femtosecond responses have been shown to occur in organic systems.\(^2\)

Organic molecular mediums, such as a polymeric solid, have been viewed as being nonconductive, nonmagnetic, and having their electrons tightly bound to the nuclei. As a result, their interaction with light can be regarded in the framework of a dielectric subjected to an electric field. Since the charge distribution induced in the molecule by the field can be readily approximated by an induced dipole, this approach has come to be known as the dipole approximation.\(^2\) The induced dipole moment (\( \mathbf{\mu}_{\text{ind}} \)) can be found by utilizing the following equation:

\[
\mathbf{\mu}_{\text{ind}} = -e \mathbf{r}
\]

where \( e \) is the electronic charge and \( \mathbf{r} \) is the field induced displacement. The bulk polariztion (\( P \)) that arises as a result of the induced dipole is found by:

\[
P = -Ne \mathbf{r}
\]

where \( N \) is the electron density of the medium. When a medium is subjected to an electric field of relatively low strength, the optical response is linear and the polarization can be determined from the following equation:
\[ P = \chi^{(1)} E \]

where \( \chi^{(1)} \) is the linear susceptibility and \( E \) is the applied electric field. However, when the medium is subjected to an intense electric field, such as that due to an intense laser pulse, the optical response becomes nonlinear and the polarization can be described in terms of a power series expansion of the applied field \( E \):

\[ P = \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \ldots \]

where \( \chi^{(1)} \) is the aforementioned linear susceptibility, \( \chi^{(2)} \) is the second-order nonlinear susceptibility and \( \chi^{(3)} \) is the third-order nonlinear susceptibility. Higher-order terms that describe higher-order processes are possible, but for most materials they are usually difficult to observe.

Third-order optical processes arise from the combination of the resonant effects that are seen as the imaginary portion of \( \chi^{(3)} \) and the nonresonant effects which are regarded as the real portion of \( \chi^{(3)} \). The imaginary portion describes a decrease in intensity of the incident beam in the medium resulting from an exchange of energy between the medium and the optical field. This research focuses on the third-order process of two-photon absorption for eye and sensor protection, therefore, the current discussion will be limited to this area.

**Two-Photon Absorption**

The two-photon absorption process was first theoretically predicted in 1931 by Göppert-Mayer and was confirmed experimentally in the 1960s by Peticolas. Two-photon absorption is a third-order nonlinear optical process and is described by the imaginary part of the third-order nonlinear susceptibility \( \chi^{(3)} \). There are two key features of the two-photon absorption process. The first is the ability to create excitation states by
utilizing photons of half the nominal excitation energy providing better penetration in an absorbing or scattering media.\textsuperscript{5} This feature can be understood by utilizing the general mechanism for two-photon absorption illustrated in Figure 1.\textsuperscript{10}

![Figure 1: General mechanism for two-photon absorption](image)

Initially, an intense laser is applied and allows for the simultaneous absorption of two photons by a molecule. The combined energy of the two photons accesses a stable excited state of the molecule. The molecule then undergoes nonradiative decay to an excited singlet state followed by a one photon emission to the ground state. This emission occurs at a higher frequency, $w_1$, than either of the previous single photonic absorptions. In general, two-photon absorption involves the concerted interaction of both photons that combine their energies to produce an electronic excitation similar to one that would be created by a single photon of a shorter wavelength.\textsuperscript{11} This process allows for two-photon absorbing organic materials to absorb infrared (IR) radiation and emit in the visible (vis) region of the spectrum.
The second key feature is the incident intensity dependence of the process. In the two-photon absorption process, the rate of energy absorption is proportional to the square of the incident intensity.\(^1\) This dependence allows for the excitation of chromophores with a high degree of spatial selectivity in three dimensions by utilizing a laser beam that is tightly focused.\(^5\) As previously mentioned, the imaginary portion of the third-order process describes a decrease in the intensity of the incident beam as it propagates through a medium. The intensity of the incident beam can be found by:

$$\frac{dI}{dz} = -(aI + bI^2)$$

where \(z\) is the direction of propagation, \(a\) is the linear absorption coefficient, and \(b\) is the two-photon absorption coefficient.\(^7\) The two-photon absorption coefficient (\(b\)) is related to the absorption cross-section (\(\sigma_2\)) by the following equation:

$$\sigma_2 = \frac{b}{N_A d_0 \times 10^{-3}}$$

where \(N_A\) is Avagadro’s number and \(d_0\) is the concentration. The two-photon cross section is related to the imaginary part of \(\sigma^{(3)}\) by the following equation:

$$\sigma_2 = \frac{8\pi^2 h^2 n_0^2 c^2 N}{N} \Im(\sigma^{(3)})$$

where \(N\) is the number of absorbing molecules per unit volume, \(c\) is the speed of light in a vacuum, and \(n_0\) is the index of refraction.

Two-photon absorption can be described at the molecular level as \(\sigma_2'\), which is related to \(\sigma_2\) by the following formula:

$$\sigma_2' = h\sigma_2$$

where \(h\) is Planck’s constant and \(\sigma\) is the frequency of the laser used in the experiment.\(^{13}\)
Third-Order Nonlinear Optical Chromophore Design

There are two different classes of two-photon absorbing chromophores, which are illustrated in Figure 2. The first class (Type I) is the symmetrical chromophore, which consists of a polarizable bridge flanked by either a pair of heterocyclic -electron donors or -electron acceptors. A basic example of a Type I chromophore consists of an electron rich thiophene bridge flanked by either diphenylamino or benzothiazole functionality.

The second class (Type II) is the asymmetrical chromophore, which consists of a polarizable bridge flanked on one side by a heterocyclic -electron donor and on the other by a -electron acceptor. A basic Type II chromophore that shows a decent two-photon cross-section consists of a fluorene bridge flanked by a diphenylamino and a benzothiazole functionality. This compound also utilizes alkyl chains, such as ethyl chains, on the fluorene to increase solubility.

![Figure 2: Types of two-photon chromophores](image)

Experimental measurement of two-photon activity have shown that Type II chromophores provide a superior cross-sectional measurement as compared to Type I compounds. Since a large amount of current research has been focused solely on the
Type II chromophores, the remaining discussion will be limited to these asymmetric compounds.

**Recent Type II Chromophore Synthesis**

Some of the most recent synthetic approaches to obtaining two-photon chromophores have been reported by Belfield, et. al.\(^\text{11}\) These chromophores include nitro 3 and phosphonate 5 derivatives of 2-bromo-(N,N-diphenylamino)-9,9-diethyl-9H-fluorene 1. Other chromophores include 2-(9,9-didecyl-7-nitro-9H-fluoren-2-yl)benzothiazole 8, N,N-diphenyl-9,9-didecyl-7-nitro-9H-fluoren-2-ylamine 10, N,N-diphenyl-(7-benzothiazol-2-yl)-9,9-didecyl-9H-fluoren-2-ylamine 13, and (N,N-bis(4-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-didecyl-9H-fluoren-2-ylamine 15.

Compounds 3 and 5 were synthesized via palladium-catalyzed Heck coupling reactions between compound 1 and either 4-nitrostyrene 2 or diethyl 4-vinylphenylphosphonate 4.\(^\text{1}\) Compound 8 was obtained via a palladium-catalyzed Stille coupling between 7-iodo-9,9-didecyl-2-nitro-9H-fluorene 6 and 2-(tri-n-butylstannyl)benzothiazole 7. Compound 10 was synthesized utilizing a copper catalyzed Ullmann condensation reaction between 1 and diphenylamine 9. Compounds 13 and 15 were synthesized via the copper mediated Ullmann reaction between 7-(benzothiazol-2-yl)-9,9-didecyl-9H-fluoren-2-ylamine 11 and iodobenzene 12 or 4-methoxyiodobenzene 14, respectively.\(^\text{11}\)
Chemical reactions involving copper-bronze, 18-crown-6, K$_2$CO$_3$, and 1,2-dichlorobenzene at 180°C.
**Current Research**

Highly aromatic third-order chromophores can be synthesized using several different reactions. The following discussion is focused mainly on the palladium catalyzed amination reaction that is shown in Figure 3.12

![Figure 3](image)

**Figure 3.** General catalytic cycle for palladium catalyzed amination reaction.

The Air Force Research Laboratory has committed considerable funding to researching two-photon absorbing chromophores because of the promise of two-photon technology as a material for sensor protection and as an imaging tool for the nondestructive evaluation of aircraft coatings. Some of the early successes include a series of chromophores synthesized by a palladium-catalyzed coupling reaction. Some of the chromophores include 4-(9,9-didecyl-7-(2-thienyl)-9H-fluoren-2-yl)pyridine 18, 7-(2-thienyl)-7’-(4-pyridyl)-9,9,9’,9’-tetradeccyl-2,2’-bi-9H-fluorene 20, N,N-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-didecyl-9H-fluoren-2-ylamine 23, N,N-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-diethyl-9H-fluorene-2-amine 25, N,N-bis((3-methoxyphenyl)-7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-9H-fluoreny-2-yl)amine 27, and N,N-bis(3-hydroxyphenyl)-7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-9H-fluoren-2-ylamine 29.
Compounds 18 and 20 were synthesized via coupling reactions between 4-(7-bromo-9,9-didecyl-9H-fluoren-2-yl)pyridine 16 and 2-(tributylstannyl)thiopene 17 or 2-(7-tributylstannyl-9,9-didecyl-9H-fluoren-2-yl)thiopene 19, respectively. Compound 23 was obtained by the coupling of 4-vinylpyridine 22 with N,N-diphenyl-7-bromo-9,9-didecyl-9H-fluoren-2-ylamine 21. The synthesis of compound 25 was accomplished in two steps by first reacting diphenylamine 9 with n-butyllithium. The resulting organolithium compound then undergoes a palladium-catalyzed coupling with 4-[2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)ethenyl]pyridine 24. Compound 27 is obtained in a similar fashion as compound 25. N,N-di(3-methoxydiphenyl)amine 26 undergoes a reaction with n-butyllithium and the resulting organolithium is catalytically coupled to compound 24. Compound 29 is obtained by the coupling of 4-vinylpyridine 22 and N,N-bis(3-hydroxyphenyl)-7-bromo-9,9-diethyl-9H-fluoren-2-ylamine 28. Results of two-photon measurements on these compounds are listed in Table 1.\textsuperscript{13}
Table 1. Two-Photon Absorption Characteristics of Compounds 18, 20, 23, 25, 27, and 29 in THF at a wavelength of 800 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>Linear Abs. (Upconv. Em.)</th>
<th>(\beta') (x 10(^{-48}) cm(^4) sec ph molecule)</th>
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<tr>
<td>18</td>
<td>345 (410)</td>
<td></td>
<td>1.31</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td></td>
<td>1.57</td>
</tr>
<tr>
<td>23</td>
<td>390 (492)</td>
<td></td>
<td>115.6</td>
</tr>
<tr>
<td>25</td>
<td>388 (488)</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>27</td>
<td>386 (488)</td>
<td></td>
<td>114.8</td>
</tr>
<tr>
<td>29</td>
<td>392 (500)</td>
<td></td>
<td>103</td>
</tr>
</tbody>
</table>

Recently, Air Force research groups have reported a number of two-photon absorbing chromophores including N,N-diphenyl-(7-benzothiazol-2-yl)-9,9-diethyl-9H-fluorene-2-ylamine 31, N,N-diphenyl-(7-benzoxazol-2-yl)-9,9-diethyl-9H-fluorene-2-ylamine 34, N,N-diphenyl-7-benzoyle-9,9-diethyl-9H-fluoren-2-ylamine 35, N,N-diphenyl-(7-quinoxaline-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 38, N,N-diphenyl-(9,9-didecyl-7-(1-phenylbenzimidazol-2-yl)-9H-fluoren-2-ylamine 41, and N,N-diphenyl-(7-(4,5-diphenylimidazol-2-yl)-9,9-didecyl-9H-fluoren-2-ylamine 43.

The synthesis of compound 31 was accomplished via a copper-catalyzed amination of 2-(7-bromo-9,9-diethylfluoren-2-yl)benzothiazole 30 with diphenylamine 9. Direct arylation of benzoxazole 33 with N,N-diphenyl-(7-bromo-9,9-diethyl-9H-fluoren-2-ylamine 32 utilizing a palladium (0)/copper (I) catalyst system produced compound 34. Compound 35 was synthesized in a two-step reaction involving a metal-halogen exchange reaction of 32 with n-butyllithium, followed by reaction of the resulting organolithium with benzonitrile. The synthesis of compound 38 was accomplished via a Stille coupling reaction between the tri-n-butyltin derivative 36 of compound 32 and 2-iodoquinoxaline 37. The synthesis of compound 41 was carried out by reacting N-phenyl-
1,2-phenylenediamine 40 with 7-(diphenylamino)-9,9-diethylfluorene-2-carboxyaldehyde 39. This was followed by the oxidation of the “Schiff’s Base” intermediate with copper acetate. Compound 43 was obtained by reacting benzil and ammonium acetate with compound 39. Results of two-photon measurements for these compounds are listed in Table 2.

Table 2. Two-Photon Absorption Characteristics of Compounds 31, 34, 35, 38, 41, and 43 in THF at a wavelength of 800 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Linear Abs. (Upconv. Em.)</th>
<th>$\Delta_{2}'$ ($\times 10^{-48}$ cm$^4$ sec ph molecule)</th>
<th>$\Delta_{2}'$/MW ($\times 10^{-50}$ cm$^4$ sec mole ph molecule g)</th>
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<tr>
<td>31</td>
<td>391.5 (479)</td>
<td>4.7</td>
<td>97.7</td>
<td>17.6</td>
</tr>
<tr>
<td>34</td>
<td>389 (468)</td>
<td>1.1</td>
<td>22.7</td>
<td>4.5</td>
</tr>
<tr>
<td>35</td>
<td>386 (490)</td>
<td>4.1</td>
<td>84.5</td>
<td>17.1</td>
</tr>
<tr>
<td>38</td>
<td>402.5 (552)</td>
<td>1.9</td>
<td>39.2</td>
<td>7.6</td>
</tr>
<tr>
<td>41</td>
<td>370 (439)</td>
<td>3.3</td>
<td>67.1</td>
<td>8.3</td>
</tr>
<tr>
<td>43</td>
<td>384 (449)</td>
<td>0.2</td>
<td>3.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>

14
Pd(OAc)$_2$/CuI/PPh$_3$
Cs$_2$CO$_3$/DMF

I)n-BuLi
II)PhCN
III)H$_3$O$^+$

Pd. Cat

I)n-BuLi
II)Bu$_3$SnCl

Pd. Cat
It has been shown that (7-benzothiazol-2-yl-9,9-diethylfluoren-2-yl)diphenylamine 31 has one of the best two-photon cross-sectional measurements for a Type II chormophore with no further functionalization on either the $\pi$-electron donor or the $\pi$-electron acceptor. As a result, most of the current Air Force research has been focused on functionalizing this chromophore at the meta and para positions of the diphenylamine in the hopes that the resulting chromophore can be incorporated into a
coating matrix amenable to device fabrication and that the two-photon cross-section will be increased.

Air Force research into chromophores with functionalization at the para position has, thus far, produced four compounds. These compounds include N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazoyl)-9,9-diethyl-2-fluorenyl]amine 46, N-phenyl-N-[4-(4-ethenylphenyl)phenyl]-N-[7-(2-benzothiazoyl)-9,9-diethyl-2-fluorenyl]amine 47, N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benzothiazoyl)-9,9-diethyl-2-fluorenyl]amine 48, and N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benzothiazoyl)-9,9-diethyl-2-fluorenyl]amine 49.
Bu$_3$Sn \[\rightarrow\] Pd(PPh$_3$)$_4$, Toluene

I) n-BuLi
II) DMF/THF

47

46

48
Compound 46 was synthesized in a one-step reaction using a palladium catalyzed monoamination of 4,4’-dibromophenyl 45 using N-phenyl-N-[7-(2-benzothiazoyl)-9,9-diethyl-2-fluorenyl]amine 44. Compound 47 was synthesized via a Stille coupling reaction of 46 with vinyl tributyltin. Synthesis of compound 48 was accomplished in a two-step synthesis involving a halogen-metal exchange reaction of 46 with n-butyllithium followed by reaction of the resulting the organolithium with dimethylformamide. Compound 49 was synthesized via a reduction of 48 using sodium borohydride.³

There have been two reported Air Force research chromophores with functionalization at the meta position: N-phenyl-N-(3-benzyloxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51 and N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.
The synthesis of compound 51 was accomplished using a palladium-catalyzed coupling reaction between compound 30 and 3-benzyloxydiphenylamine 50. Compound 52 was obtained by an ether cleavage of compound 51 using pyridine hydrochloride.\(^7\)

With these results as a basis, the objectives of this research were 1) to synthesize functionalized advanced optical chromophores for studies to investigate their two-photon cross-sections and 2) to characterize these new chromophores.
EXPERIMENTAL

Instrumentation and Chemicals

An Electrothermal capillary melting point apparatus equipped with a thermocouple was used to obtain melting points. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC-200 spectrometer ($^1$H and $^{13}$C), with tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded with a Perkin Elmer 1600 Series FTIR spectrometer using KBr pellets. Elemental analysis and mass spectrometry were done by Materials Laboratory Sample Analysis (MLSA). All reagents were purchased from Aldrich Chemical Company and used without further purification.

2,7-Dibromofluorene (54)

A mixture of fluorene 53 (153.02g, 0.92 mol) and iodine (2.88 g, 0.012 mol) in methylene chloride (1100 mL) was mechanically stirred at room temperature. A solution of bromine (100 mL, 1.941 mol) and methylene chloride (150 mL) was added dropwise over a period of 3 h. The addition of the bromine/methylene chloride solution caused the mixture to change from yellow in color to a deep red. The solution was allowed to stir for 15 min. A sodium bisulfite solution (15 g NaSO$_3$, 950 mL H$_2$O) was added until the mixture became colorless and the two-phase mixture was then allowed to stir overnight. Methylene chloride was removed, water was added (800 mL) and a white precipitate
formed. The mixture was cooled to 50°C in a water bath and the precipitate was filtered and washed with water (5 L). The solid was refluxed in ethanol (1000 mL) for 2.5 h, filtered, and washed with ethanal (500 mL) to afford 54 (270.82 g, 91%) as white crystals: m.p. 166-169°C; IR (KBr) cm⁻¹ 2897 (C-H), 1598 and 1453 (Ar-C=C), 814 (C-H out-of-plane); ¹H NMR (CDCl₃) δ 3.82 (s, 2H, CH₂), 7.48-7.75 (m, 6H, Ar-H); ¹³C NMR (CDCl₃) ppm 36.97, 121.36, 121.59, 128.70, 130.55, 140.08, 145.20; mass spectrum, m/z (relative intensity) 326, 324, 322 (M⁺, 21.27, 41.29, 21.86), 163 (100). Anal. Calcd for C₁₃H₈Br₂: C, 48.19; H, 2.49; Br, 49.34. Found: C, 48.20; H, 2.64.

2,7-Dibromo-9,9-diethyl-9H-fluorene (55)

A mixture of 2,7-dibromofluorene (252.50 g, 0.78 mol) and potassium hydroxide (222.15 g, 3.96 mol) in dimethyl sulfoxide (455 mL) was cooled to 10°C using an ice bath. Bromoethane (208 mL, 2.78 mol) was added dropwise over 2 h to maintain an internal temperature of 10-15°C. The addition of the bromoethane caused the solution to change from dark red in color to a deep purple. The solution was mechanically stirred overnight. The reaction mixture was poured into water (2 L) and stirred for 1.5 h, filtered and washed with water (5 L). The dried solid was refluxed in ethanol (1000 mL) for 2.5 h, filtered, and washed with ethanol (500 mL) to afford 55 (305.83 g, 96%) as a cream colored powder: m.p. 156-159°C; IR (KBr) cm⁻¹ 1572 and 1449 (Ar-C=C), 2959, 2916 and 2872 (C-H), 814 (C-H out-of-plane); ¹H NMR (CDCl₃) δ 0.36 (t, 6H, CH₃), 2.05 (q, 4H, CH₂), 7.45-7.60 (m, 6H, Ar-H); ¹³C NMR (CDCl₃) ppm 8.88, 33.08, 57.18, 121.56, 121.96, 126.71, 130.67, 139.91, 152.18; mass spectrum, m/z (relative intensity) 382, 381,
380 (M⁺, 25.22, 8.66, 53.85), 270 (100). Anal. Calcd for C₁₇H₁₆Br₂: C, 53.72; H, 4.24; Br, 42.06. Found: C, 53.60; H, 4.20.

2-Bromo-7-formyl-9,9-diethyl-9H-fluorene (56)

A solution of 2,7-dibromo-9,9-diethyl-9H-fluorene (150.05 g, 0.39 mol) in THF (938 mL) was cooled to –78°C using a dry-ice/ acetone bath. A solution of n-butyllithium in hexanes (1.6 M, 250 ml) was added dropwise over 30 min in order to maintain an internal temperature of –70°C. The clear yellow solution was stirred to 25 min and dimethylformamide (58 mL) in THF (63 mL) was added dropwise over 15 min. The addition of the dimethylformamide caused the solution to change from yellow in color to light red. The solution was stirred for 1 h and warmed to 0°C. A solution of hydrochloric acid (38 mL) in water (63 mL) was added slowly over 10 min and the solution was stirred overnight while warming at room temperature. The addition of the hydrochloric acid caused the solution to change from light red in color to light green. The solution was diluted with toluene (500 mL) and the organic layer was separated, washed twice with a saturated solution of sodium bicarbonate solution and dried with magnesium sulfate. The toluene was distilled off under reduced pressure. Ethanol (200 mL) was added, distilled off and the solid was slurried in ethanol (400 mL). The slurry was filtered to afford 56 (121.59 g, 94%) as a white powder: m.p. 126-128°C; IR (KBr) cm⁻¹ 2961 and 2925 (C-H), 2857 and 2812 (aldehydic C-H), 1688 (C=O); ¹H NMR (CDCl₃) 0.36 (t, 6H, CH₃), 2.10 (q, 4H, CH₂), 7.48-7.85 (m, 6H, Ar-H), 10.05 (s, 1H, CHO); ¹³C NMR (CDCl₃) ppm 8.86, 32.96, 57.07, 120.52, 122.67, 123.55, 123.62, 126.98, 130.94, 131.06, 136.07, 139.36, 147.14, 150.75, 153.88, 192.57; mass spectrum, m/z (relative intensity) 330, 328
2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole (30)

A mixture of 2-bromo-7-formyl-9,9-diethyl-9H-fluorene (203.03 g, 0.62 mol) and 2-aminothiophenol 57 (68 mL) in dimethyl sulfoxide (270 mL) was heated to 150°C for 1 h. The reaction mixture was poured into a solution containing sodium chloride (164.5 g), water (940 mL) and crushed ice (1175 g) resulting in a light green precipitate. The solution was stirred overnight, filtered, and washed with water (10 L). The crude product was slurried in a solution of water (1960 mL) and acetic acid (60 mL) for 4 h, filtered, and washed with water (3 L). The solids were refluxed in ethanol (1 L) for 4 h, filtered, and washed with cold ethanol (500 mL) to afford 30 (205.24 g, 76%) as a light gray powder: m.p. 132-134°C; IR (KBr) cm⁻¹ 2962, 2921 and 2874 (C-H), 1508 and 1454 (Ar-C=C), 1238 (C-N); ¹H NMR (CDCl₃) δ 0.40 (t, 6H, CH₃), 2.10 (m, 4H, CH₂), 7.35-8.15 (m, 10H, Ar-H); ¹³C NMR (CDCl₃) ppm 9.01, 33.13, 57.27, 120.65, 122.02, 122.05, 122.621, 123.54, 125.62, 126.84, 127.80, 130.76, 133.20, 135.44. 139.98, 143.86, 150.88, 153.28, 154.65, 168.85; mass spectrum, m/z (relative intensity) 435, 433 (M⁺, 20.67, 16.69), 406, 404 (28.58, 24.78), 325 (100). Anal. Calcd for C₂₄H₂₀BrNS: C, 66.37; H, 4.64;N, 3.23; S, 7.38. Found: C, 66.15; H, 4.77; N, 3.11; S, 7.39.

Palladium Catalyst (Pd(dba)₂) (58)

A mixture of dibenzilidene acetone (13.80 g, 0.059 mol), sodium acetate (11.70 g, 0.143 mol), and methanol (450 mL) was heated at 40°C. Palladium chloride (3.15 g,
0.018 mol) was added and the hot mixture was stirred for 4 h. The addition of the palladium chloride caused the reaction to change from yellow in color to dark red. The mixture was allowed to stir overnight resulting in a dark purple precipitate. The mixture was cooled to room temperature, filtered, washed with acetone (50 mL) and water (300 mL) and dried under vacuum (48 h) to afford 7 as a dark purple powder.

N-phenyl-N-(3-benzyloxyphenyl) -7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (51)  

A mixture of 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30 (16.5 g, 0.038 mol), 3-benzyloxydiphenylamine 50 (12.5 g, 0.045 mol) and toluene 300 mL was refluxed for 45 min. The reaction was cooled to room temperature and Pd(dba)$_2$ (0.4329 g), dppf (diphenylphosphinoferrorocene) (0.4072 g, 7.35 x10$^{-4}$ mol) and sodium t-butoxide (5.37 g, 0.56 mol) were added to the solution. The reaction was heated at 85°C overnight. A saturated solution of HCl/H$_2$O (100 mL) was added and the solution was extracted out of toluene (200 mL). The toluene layer was dried with magnesium sulfate and rotary-evaporated to dryness. The crude product was chromatographed on silica using 1:1 toluene/hexanes followed by toluene as eluent and recrystallized from toluene/heptane (100 mL) to afford 51 (92%, 21.81 g) as yellow crystals: m.p. 181-183°C (lit. 181-183°C); IR (KBr) cm$^{-1}$ 3060 and 3051 (Ar-C-H), 2962 and 2918 (C-H), 1592 and 1488 (Ar-C=C); $^1$H NMR $^{[d]}$(CDCl$_3$) 0.43 (t, 6H, CH$_3$), 1.96-2.15 (m, 4H, CH$_2$), 4.99 (s, 2H, CH$_2$), 6.68-8.13 (m, 24H, Ar-C-H); $^{13}$C NMR ppm (CDCl$_3$) 9.08, 33.09, 56.88, 70.37, 109.57, 110.82, 116.92, 119.54, 119.84, 121.48, 121.88, 121.99, 123.38, 123.47, 124.05, 124.91, 125.41, 126.72, 127.73, 127.97, 128.38, 129.00, 129.72, 130.30, 131.96, 135.37, 135.95, 137.26, 144.92, 148.08, 149.39, 149.54, 151.15, 152.50, 154.69, 160.10, 169.28; mass
N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (52)

A mixture of N-phenyl-N-(3-benzyloxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51 (19.70 g, 0.03 mol) and pyridine hydrochloride (170.00 g, 1.47 mol) was heated to 200 °C for 1.5 h in an oil bath. The solution was poured into warm water (1400 mL), stirred for 20 min, filtered, and the precipitate was washed with warm water. The red precipitate was slurried in ammonium hydroxide (10%) and allowed to stir overnight, filtered, and the yellow residue was recrystallized from ethyl acetate (2550 mL, charcoal) to afford 52 (14.01 g, 83%) as bright yellow crystals: m.p. 246-248 °C; IR (KBr) cm⁻¹ 3500-3350 (OH), 3060 (Ar-C-H), 2962 and 2945 (C-H), 1596 and 1488 (Ar-C=C); ¹H NMR [DCON(CD₃)₂] 0.31 (t, 6H, CH₃), 1.85-2.14 (m, 4H, CH₂), 6.41-8.22 (m, 19H, Ar-C-H); ¹³C NMR ppm [DCON(CD₃)₂] 8.83, 32.81, 56.94, 111.03, 111.62, 115.33, 119.62, 120.63, 122.09, 122.26, 122.88, 123.46, 124.12, 126.05, 127.32, 127.84, 130.12, 132.15, 135.55, 135.94, 145.31, 148.47, 149.00, 149.61, 151.39, 152.65, 154.90, 159.62, 162.91, 168.77; mass spectrum, m/z (relative intensity) 538 (M⁺, 100), 509 (33.32), 494 (8.98), 269(38.05). Anal. Calcd for C₃₆H₃₀N₂O₅: C, 80.26; H, 5.61; N, 5.20; O, 2.97; S, 5.95. Found: C, 80.24; H, 5.69; N, 5.01; O, 3.37; S, 6.03.
N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (60)

A mixture of 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30 (21.78 g, 0.05 mol), 3-methoxydiphenylamine 59 (7.25 g, 0.06 mol), and toluene (300 mL) was heated to reflux for 45 min. The reaction was cooled to room temperature and Pd(dbq)_{2} (0.4880 g), dppf (diphenylphosphinoferrocene) (0.4430 g, 8.49x10^{-4} mol), and sodium t-butoxide (6.54 g, 0.068 mol) were added and the mixture heated at 80°C overnight. The reaction mixture was cooled and a saturated solution of water and sodium chloride (100 mL) was added. The reaction was extracted with toluene (200 mL), the toluene layer was dried with magnesium sulfate and rotary-evaporated to dryness. The crude product was refluxed in ethanol (200 mL) for six h and allowed to stir at room temperature overnight. The product was filtered, washed with ethanol (500 mL), and dried under vacuum to afford 60 (19.89 g, 72%) as a yellow powder: m.p. 169-170°C; IR (KBr) cm^{-1} 3059 (Ar-C-H), 2962 and 2926 (C-H), 1595 and 1487 (Ar-C=C), 1200 (C-O); ^{1}H NMR [ (CDCl_{3}) 0.46 (t, 3H, CH_{3}), 1.89-2.28 (m, 4H, CH_{2}), 3.90 (s, 3H, CH_{3}), 6.60-8.10 (m, 19H, Ar-C-H); ^{13}C NMR ppm (CDCl_{3}) 9.05, 33.08, 55.63, 56.79, 108.86, 109.86, 116.79, 119.44, 121.46, 121.88, 121.98, 123.38, 123.46, 124.01, 124.89, 125.40, 126.71, 127.73, 129.70, 130.29, 131.95, 135.37, 144.93, 148.14, 148.42, 149.55, 151.14, 152.50, 154.69, 160.90, 169.27; mass spectrum, m/z (relative intensity) 552 (M^{+}, 100), 523 (11.90), 276 (20.22). Anal. Calcd for C_{37}H_{32}N_{2}OS: C, 80.40; H, 5.84; O, 2.89; N, 5.07; S, 5.80. Found: C, 80.14; H, 5.94; O, 3.19; N, 4.86; S,
N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (52)

A mixture of N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60 (9.76g, 0.018 mol) and pyridine hydrochloride (100g, 0.866mol) was heated to 200°C for 18 h in an oil bath. The solution was poured into warm water (1400 mL), stirred for 20 min, filtered, and the precipitate was washed with warm water. The red precipitate was slurried in 500 mL ammonium hydroxide (10%) and allowed to stir overnight, filtered, and the yellow residue was recrystallized from ethyl acetate (2550 mL, charcoal) to afford 52 (6.51g, 68%) as bright yellow crystals: m.p. 245-248°C; IR (KBr) cm⁻¹ 3500-3350 (OH), 3060 (Ar-C-H), 2962 and 2923 (C-H), 1595 and 1489 (Ar-C=C);¹H NMR [(CD₃)₂SO] 0.31 (t, 6H, CH₃), 1.87-2.14 (m, 4H, CH₂), 6.41-8.22 (m, 19H, Ar-C-H), 9.38 (s, 1H, O-H); ¹³C NMR ppm 8.80, 32.77, 56.92, 111.00, 111.58, 115.30, 119.59, 120.59, 122.06, 122.23, 122.86, 123.43, 123.72, 124.90, 126.02, 127.30, 127.81, 130.10, 130.73, 132.13, 135.52, 135.90, 145.29, 148.44, 148.97, 149.59, 151.37, 152.62, 154.87, 159.60, 162.89, 168.74; mass spectrum, m/z (relative intensity) 538 (M⁺, 100), 509 (18.48), 494 (9.41), 269(31.46). Anal. Calcd for C₃₆H₃₀N₂OS: C, 80.26; H, 5.61; N, 5.20; O, 2.97; S, 5.95. Found: C, 80.32; H, 5.81; N, 5.49; O, 3.31; S, 5.85.

N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (61)

A solution of N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52 (5.00 g, 0.0093 mol), potassium hydroxide (2.68 g, 0.048 mol), and toluene (250 mL) was refluxed, distilled (to remove water/toluene) under a nitrogen atmosphere and cooled to room temperature using a water bath. After the addition of 1, 2-
dibromoethane (8.48 mL, 0.098 mol) and 18-crown-6 (0.11 g, 4.22x10^{-4} mol), the mixture was refluxed for 3 h. The mixture was poured into water (400 mL) and the resulting oil was extracted with toluene (300 mL). The toluene was washed with 5% NaOH (300 mL), H₂O (1000 mL), dried with magnesium sulfate and rotary-evaporated to dryness to afford a yellow oil. The crude product was chromatographed on silica using 90% toluene/10% heptane as the eluent and recrystallized from hexanes (250 mL) to afford 61 (3.95 g, 66%) as a yellow powder: m.p. 136-139°C; IR (KBr) cm⁻¹ 3028 (Ar-C-H), 2959 and 2924 (C-H), 1588 and 1487 (Ar-C=C), 1276 (C-N), 1196 (C-O); ¹H NMR (CDCl₃) δ 0.40 (t, 6H, CH₃), 1.80-2.18 (m, 4H, CH₂), 3.80 (t, 2H, CH₂), 4.20 (t, 2H, CH₂), 6.65-8.15 (m, 19H, Ar-H); ¹³C NMR (CDCl₃) ppm 113.0, 125.7, 125.9, 127.3, 129.7, 130.4, 135.6, 144.8, 148.3, 149.6, 150.1, 152.5, 154.6, 159.3, 169.2; mass spectrum, m/z 646, 644 (M⁺, 100, 92.45). Anal. Calcd for C₃₈H₇₅BrN₂OS: C, 70.69; H, 5.15; N, 4.34; O, 2.48; S, 4.97; Br, 12.37. Found: C, 70.74; H, 5.38; N, 4.19; O, 2.87; S, 5.01; Br, 12.49.

N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (63)

A mixture of N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52 (5.00 g, 0.0093 mol) and N,N-dimethylformamide (125 mL) was cooled to 0°C using an ice bath. Potassium hydroxide (0.99 g, 0.0176 mol) was added followed by the dropwise addition of vinylbenzyl chloride 62 (2 mL, 0.014 mol). Addition of the vinylbenzyl chloride caused the mixture to change from yellow in color to light brown. The reaction was stirred overnight. Potassium carbonate (2.07 g, 0.015
mol) and 3-sulfobenzoic acid (3.36 g, 0.015 mol) were added and the mixture was stirred overnight to remove any excess vinylbenzyl chloride. The mixture was poured into water (500 mL) and the product was collected by vacuum filtration. The solid was refluxed in ethanol (200 mL) for 1 h, filtered and washed with water (200 mL). The crude product was chromatographed on silica using 1:1 toluene/heptane as the eluent and recrystallized from hexanes (300 mL) to afford 63 (3.39 g, 56%) as yellow crystals: m.p. 173-174°C; IR (KBr) cm⁻¹ 3430 (Ar-C-H), 2960 and 2922 (C-H), 1593 and 1487 (Ar-C=C), 1275 (C-N), 1219 (C-O); ¹H NMR (CDCl₃) δ 0.39 (t, 6H, CH₃), 1.94-2.13 (m, 4H, CH₂), 4.95 (s, 2H, CH₂), 5.26 (d, 1H, CH), 5.76 (d, 1H, CH), 6.65-6.77 (m, 1H, CH), 7.02-8.14 (m, 23H, Ar-H); ¹³C NMR (CDCl₃) ppm 9.03, 33.08, 56.88, 70.12, 109.69, 110.85, 114.54, 116.93, 119.52, 119.58, 119.86, 121.53, 121.86, 121.98, 123.48, 124.04, 124.91, 126.76, 126.83, 126.87, 127.76, 128.11, 129.74, 130.33, 131.99, 135.39, 135.96, 136.85, 136.95, 137.72, 144.93, 148.08, 148.39, 149.55, 151.17, 152.51, 160.04, 169.28; mass spectrum, m/z (relative intensity) 654 (M⁺, 60.97), 537 (11.44), 493 (19.33). Anal. Calcd for C₄₅H₃₈N₂O₅S: C, 82.53; H, 5.85; O, 2.44; N, 4.28; S, 4.90. Found: C, 82.48; H, 5.99; O, 2.37; N, 4.12; S, 4.93.

3-(4-Vinylbenzyloxy)diphenylamine (65)

A mixture of 3-hydroxydiphenylamine 64 (7.89 g, 0.043 mol) and N,N-dimethylformamide (50 mL) was cooled to 0°C using an ice bath. Potassium carbonate (11.89 g, 0.086 mol) was added followed by the dropwise addition of vinylbenzyl chloride 62 (6.00 mL, 0.043 mol) under a nitrogen atmosphere. The reaction mixture was stirred overnight. The mixture was poured into water (600 mL) and mechanically stirred for 30 min. The solution was extracted with toluene. The toluene was dried with
magnesium sulfate, filtered, and rotary-evaporated to afford a brown oil. The crude product was chromatographed on silica using toluene as an eluent and recrystallized in hexanes (100 mL) to afford 65 (9.22 g, 72%) as a brown crystal: m.p. 68-70°C; IR (KBr) cm⁻¹ 3389 (N-H); 3032 (Ar-C-H); 2858 (C-H), 1593 and 1490 (Ar-C=C), 1274 (C-N), 1156 (C-O); ¹H NMR (CDCl₃) δ 5.08 (s, 2H, CH₂), 5.32 (d, 1H, CH), 5.73 (s, 1H, N-H), 5.83 (d, 2H, CH₂); 6.65-6.70(m, 1H, CH), 6.69-7.51(m, 13H, Ar-H); ¹³C NMR (CDCl₃) ppm 70.12, 104.51, 107.60, 110.88, 114.54, 118.80, 121.72, 126.88, 128.12, 129.81, 130.58, 136.92, 137.07, 137.73, 143.14, 145.03, 160.24; mass spectrum, m/z (relative intensity) 301 (M⁺, 19.53), 117 (100), 91 (8.30). Anal. Calcd for C₂₁H₁₉NO: C, 83.68; H, 6.35; N, 4.65; O, 5.30. Found: C, 83.69; H, 6.43; N, 4.52; O, 5.37.

**N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (63)**

A mixture of 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30 (2.18 g, 0.005 mol) and toluene (50 mL) was heated to reflux for 45 min. The reaction was cooled to room temperature and 65 (1.81 g, 0.006 mol), Pd(dba)₂ (0.0572 g, 9.95x10⁻⁵ mol), dppf (diphenylphosphinoferrocene) (0.0536 g, 9.67x10⁻⁵ mol), and sodium t-butoxide (0.721 g, 0.0075 mol) were added to the solution and the reaction was heated at 70°C overnight. The reaction was poured into water (250 mL) and extracted with toluene (200 mL). The toluene layer was dried with magnesium sulfate and rotary-evaporated to dryness. The crude product was chromatographed on silica using 1:1 toluene/hexanes followed by toluene as eluent and recrystallized from hexanes (300 mL) to afford 63 (1.82 g, 55%) as yellow crystals: m.p. 173-174°C; IR (KBr) cm⁻¹ 3432 (Ar-C-H), 2959 and 2922 (C-H), 1595 and 1459 (Ar-C=C), 1276 (C-N), 1193 (C-O); ¹H NMR (CDCl₃) 0.41 (t, 6H,
Trimethyl 1,3,5-benzenetricarboxylate (67)

Trimesic acid 66 (20 g, 0.095mol), methanol (200 mL), and concentrated sulfuric acid (10 mL) were refluxed for 1 h. The solution was colorless throughout the reflux. The solution was allowed to stir overnight at room temperature. The white precipitate that formed was filtered and washed with methanol (200 mL). The solids were slurried in water and sodium hydride carbonate to neutralize the acid, filtered and washed with water (500 mL). The solid was recrystallized using methanol to afford 67 (21.17 g, 88%) as a white powder: m.p. 145-147°C; IR (KBr) cm⁻¹ 3091 and 3012 (Ar-C-H), 2958 and 2845 (C-H), 1731 (C=O); ¹H NMR(CDCl₃) δ 3.99 (s, 9H, CH₃), 8.83 (s, 3H, Ar-H); ¹³C NMR (CDCl₃) ppm 53.01, 131.57, 134.94, 165.75; mass spectrum, m/z (relative intensity) 252 (M⁺, 26.73), 221 (100), 193 (22.85); Anal. Calcd for C₁₂H₁₂O₆: C, 57.14; H, 4.80; O, 38.06. Found: C, 57.14; H, 4.74.
1,3,5-Tris(hydroxymethyl)benzene (68) 15

A boiling mixture of lithium aluminum hydride (7.54 g, 0.20 mol) and toluene (155 mL), a mixture of warm trimethyl 1,3,5-benzenetricarboxylate (12.60 g, 0.050 mol) in toluene (85 mL) was added drop-wise over a period of 1 h. The reaction boiled for 1 hr and was then cooled to room temperature. Ethyl acetate (25 mL) was slowly added followed by the drop-wise additions of 3.5 M sulfuric acid (55 mL), methanol (145 mL), and ammonium hydroxide to neutralize the reaction. The resulting solids were boiled in ethyl acetate (350 mL) for 2 h., filtered, and washed with ethyl acetate (200 mL). The solids were again boiled in ethyl acetate (350 mL) for 2 h., filtered, and washed with ethyl acetate (200 mL). The filtrates were rotary-evaporated and the resulting solids were recrystallized in ethylacetate (250 mL) to afford 68 (70%, 5.86 g) as white crystals: m.p. 76-78ºC (lit. 75-77ºC); IR (KBr) cm⁻¹ 3550-3250 (O-H), 3003 (Ar-C-H), 2888 and 2850 (C-H); ¹H NMR [(CD₃COCD₃) 4.50 (t, 3H, O-H), 4.62 (d, 6H, CH₂), 7.25 (s, 3H, Ar-C-H); ¹³C NMR (CD₃COCD₃) ppm 64.31, 123.81, 142.63; mass spectrum, m/z (relative intensity) 168 (M⁺, 31.49), 104 (29.54), 79 (100). Anal. Calcd for C₉H₁₂O₃: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.25; H, 7.15.

1,3,5-Tris(bromomethyl)benzene (69) 16

Hydrobromic acid (57 mL) and 1,3,5-tris(hydroxymethyl)benzene (2.00 g, 0.018 mol) was refluxed for 30 min. The reaction was cooled in an ice-bath and the resulting oil crystallized. The solids were filtered, washed with water (150 mL) and dried in a vacuum desiccator overnight. The solids were dissolved in methylene chloride, dried with magnesium sulfate, and rotary-evaporated with no heat. The solids were recrystallized in
cyclohexanes (100 mL) to afford 69 (86%, 3.64 g) as a white solid: m.p. 98-100°C (lit. 94-99°C); IR (KBr) cm\(^{-1}\) 3025 (Ar-C-H), 2971 (C-H); \(^1\)H NMR \((\text{CDCl}_3)\) 4.44 (s, 6H, CH\(_2\)), 7.35 (s, 3H, Ar-H); \(^{13}\)C NMR ppm (CDCl\(_3\)) 32.63, 130.00, 139.48; mass spectrum, m/z (relative intensity)360, 358, 356 (M\(^+\), 6.41, 20.95, 22.07), 276(100). Anal. Calcd for C\(_9\)H\(_9\)Br\(_3\): C, 30.44; H, 2.54; Br, 67.17. Found: C, 30.44; H, 2.56.

1,3,5-Tris(anilinophenoxy)methyl)benzene (70)

Potassium carbonate (8.85 g, 0.064 mol) was added to a solution 3-hydroxydiphenylamine 64 (5.93 g, 0.032 mol) and N,N-dimethylformamide (85 mL) while the reaction was being cooled in an ice bath. This was followed by the addition of 1,3,5-tris(bromomethyl)benzene (3.00 g, 0.008 mol) and the reaction stirred overnight. The solution was poured into water (300 mL) and stirred for 1 h. The mixture was extracted with toluene (250 mL), washed with 5% NaOH (300 mL) and water (1200 mL). The toluene solution was dried with magnesium sulfate and rotary-evaporated. The crude product was chromatographed on silica using toluene as an eluent and dried under vacuum to afford 70 (4.22 g, 75%) as brown crystals: m.p. 57-59°C; IR (KBr) cm\(^{-1}\) 3388 (N-H), 3035 (Ar-C-H), 2920 and 2869 (C-H), 1593 and 1493 (Ar-C=C), 1239 (C-N), 1156 (C-O); \(^1\)H NMR (CDCl\(_3\)) \([\delta\) 5.00 (s, 6H, CH\(_2\)), 5.70 (s, 3H, NH), 6.50-7.50 (m, 30H, Ar-C-H)]; \(^{13}\)C NMR (CDCl\(_3\)) ppm 69.69, 104.13, 107.14, 110.51, 118.49, 121.38, 125.94, 129.43, 130.19, 138.00, 142.76, 144.71, 159.83; mass spectrum, m/z (relative intensity) 669 (M\(^+\), 24.12), 486 (5.28), 300 (32.55), 185 (100). Anal. Calcd for C\(_{45}\)H\(_{39}\)N\(_3\)O\(_3\): C, 80.69; H, 5.87; N, 6.27; O, 7.17. Found: C, 80.40; H, 6.18; N, 5.90; O, 7.13.
1,3,5-Tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)lanilino)phenoxy)methyl)benzene (71)

Compound 70 (0.5 g, 7.46x10^{-4} mol), 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30 (1.30 g, 0.003 mol) and toluene (50 mL) were refluxed for 45 min. The solution was cooled to room temperature and dppf (0.0194 g, 3.51x10^{-5} mol), Pd(dba)$_2$ (0.0213 g, 3.70x10^{-5} mol), and sodium t-butoxide (0.31 g, 3.23x10^{-3} mol) were added. The reaction was heated at 80°C overnight. The mixture was poured into water (50 mL) and extracted with toluene (50 mL). The toluene layer was dried with magnesium sulfate and rotary-evaporated. The resulting oil was chromatographed on a silica column using 1:1 toluene/heptane as eluent to afford 71 (33%, 0.44 g) as yellow crystals: m.p. 332-333°C; IR (KBr) cm$^{-1}$ 3059 (Ar-C-H), 2962, 2922 and 2873 (C-H), 1593 and 1488 (Ar-C=C); $^1$H NMR (CDCl$_3$) 0.46 (t, 18H, CH$_3$), 1.89-2.20 (m, 12H, CH$_2$), 4.96 (s, 6H, CH$_2$), 6.60-8.18 (m, 60H, Ar-H); $^{13}$C NMR ppm (CDCl$_3$) 9.13, 33.09, 56.87, 70.01, 109.49, 110.75, 117.02, 118.82, 119.57, 119.89, 121.51, 121.89, 122.02, 123.41, 123.53, 124.06, 125.43, 126.45, 126.75, 127.77, 129.74, 130.38, 131.99, 135.39, 135.97, 138.12, 144.90, 148.06, 148.36, 149.57, 151.16, 152.51, 154.71, 159.96, 169.26; MALDI mass spectrum 1731 (M$^+$. Anal. Calcd for C$_{117}$H$_{96}$N$_6$O$_3$S$_3$: C, 81.22; H, 5.59; N, 4.86; O, 2.77; S, 5.56. Found: C, 81.20; H, 5.85; N, 4.64; O, 3.23; S, 5.44.
RESULTS AND DISCUSSION

2,7-Dibromofluorene (54)

Electrophilic bromination of fluorene 53 involved the use of iodine as a catalyst to yield 2,7-dibromofluorene. The IR spectrum (Figure 38) of 54 contains absorptions attributable to aliphatic C-H stretching at 2897 cm\(^{-1}\) and aromatic C=C stretching at 1598 and 1453 cm\(^{-1}\). The mass spectrum of 54 displays a characteristic peak pattern for a dibrominated compound with the peaks at 322, 324 and 326 (M, M+2, M+4). The \(^1\)H NMR spectrum (Figure 39) of compound 54 exhibits 1) a singlet at 3.82 \(\delta\) representing two aliphatic hydrogens labeled a in Figure 4, and 2) a multiplet at 7.48-7.75 \(\delta\) representing six aromatic hydrogens labeled b in Figure 4.

![Figure 4. \(^1\)H NMR assignments for 2,7-dibromofluorene 54.](image)

The \(^{13}\)C NMR spectrum (Figure 40) of 54 exhibits seven unique carbon absorptions. A comparison of the predicted \(^{13}\)C and the actual \(^{13}\)C absorptions of 2,7-dibromofluorene 54 is shown in Figure 5.
Figure 5. Predicted (left) and actual (right) $^{13}$C NMR absorptions for 2,7-dibromofluorene 54.

2,7-Dibromo-9,9-diethyl-9H-flourene (55)

Alkylation of 54 was carried out using potassium hydroxide and ethyl bromide in DMSO. The IR spectrum (Figure 41) of compound 55 contains absorptions attributable to aliphatic C-H stretching at 2959, 2916, and 2872 cm$^{-1}$, and aromatic C=C stretching at 1572 and 1449 cm$^{-1}$. The mass spectrum showed the characteristic peak pattern for a dibrominated compound with the peaks at 378, 380, and 382 (M, M+2, M+4). The $^1$H NMR spectrum (Figure 42) of compound 55 exhibits 1) a triplet at 0.36 $\delta$ representing six aliphatic hydrogens labeled a in Figure 6, 2) a quartet at 2.05 $\delta$ representing four aliphatic hydrogens labeled b in Figure 6, and 3) a multiplet at 7.45-7.60 $\delta$ representing six aromatic hydrogens labeled c in Figure 6. The $^{13}$C NMR spectrum (Figure 43) of compound 55 exhibits nine unique carbon absorptions. A comparison of the predicted $^{13}$C and the actual $^{13}$C NMR absorptions is shown in Figure 7.
2-Bromo-7-formyl-9,9-diethyl-9H-fluorene (56)

The synthesis of 2-bromo-7-formyl-9,9-diethyl-9H-fluorene 56 involved a reaction of 55 with butyllithium in THF followed by the reaction of the organolithium with dimethylformamide (DMF). The IR spectrum (Figure 44) of compound 56 contains absorptions attributable to aliphatic C-H stretching at 2961 and 2925 cm\(^{-1}\), aldehydic C-H stretching at 2857 and 2812 cm\(^{-1}\), as well as an aldehyde carbonyl absorption at 1688 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 45) of 56 exhibits 1) a triplet at 0.36 \(\delta\) representing six aliphatic hydrogens labeled a in Figure 8, 2) a quartet at 2.10 \(\delta\) representing four
aliphatic hydrogens labeled b in Figure 8, 3) a multiplet at 7.48-7.85 ppm representing six aromatic hydrogens labeled c in Figure 8, and 4) a singlet at 10.05 ppm representing one aldehydic hydrogen labeled d in Figure 8. The $^{13}$C NMR spectrum (Figure 46) of 56 exhibits sixteen unique carbon absorptions. A comparison of the predicted $^{13}$C and the actual $^{13}$C NMR absorptions is shown in Figure 9.

Figure 8. $^1$H NMR assignments for 2-bromo-7-formyl-9,9-diethyl-9H-fluorene 56.

Figure 9. Predicted (left) and actual (right) $^{13}$C NMR absorptions for 2-bromo-7-formyl-9,9-diethyl-9H-fluorene 56.

2-(7-Bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole (30)

The conversion of 56 into 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30 involved the use of 2-aminothiophenol 57 in DMSO. The IR spectrum (Figure 47) of compound 30 contains absorptions attributable to aliphatic C-H stretching at 2962, 2921, and 2874 cm$^{-1}$, aromatic C=C stretching at 1508 and 1454 cm$^{-1}$, as well as a C-N stretch
at 1238 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 48) of compound 30 exhibits 1) a triplet at 0.40 ppm representing six aliphatic hydrogens labeled \(a\) in Figure 10, 2) a multiplet at 2.10 ppm representing four aliphatic hydrogens labeled \(b\) in Figure 10, and 3) a multiplet at 7.35-8.15 ppm representing ten aromatic hydrogens labeled \(c\) in Figure 10.

Figure 10. \(^1\)H NMR assignments for 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30.

The \(^13\)C spectrum (Figure 49) of compound 30 exhibits twenty-two unique carbon absorptions. A comparison of the predicted \(^13\)C and the actual \(^13\)C NMR absorptions is shown in Figure 11.
Figure 11. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for 2-(7-bromo-9,9-diethyl-9H-flouren-2-yl)benzothiazole 30.

N-phenyl-N-(-3-benzyloxyphenyl) -7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (51)

The coupling of 2-(7-bromo-9,9-diethyl-9H-flouren-2-yl)benzothiazole 30 with 3-benzyloxydiphenylamine 50 was accomplished using dpf (diphenylphosphinoferrocene), Pd(dba)$_2$, and sodium t-butoxide resulting in the formation of 2(7-(3-benzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole.

The IR spectrum (Figure 50) of compound 51 shows absorptions attributable to aromatic C-H stretching at 3060 and 3051 cm$^{-1}$, aliphatic C-H stretching at 2962 and 2918 cm$^{-1}$, and aromatic C=C stretching at 1596 and 1488 cm$^{-1}$. 
Figure 12. $^1$H NMR assignments for N-phenyl-N-(3-benzyloxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51.

The $^1$H NMR spectrum (Figure 51) of compound 30 exhibits 1) a triplet at 0.43 representing six aliphatic hydrogens labeled a in Figure 12, 2) a multiplet at 1.96-2.15 representing four aliphatic hydrogens labeled b in Figure 12, 3) a singlet at 4.99.
representing two benzylic hydrogens labeled \( \mathbf{c} \) in Figure 12, and 4) a multiplet at 6.68-8.13 \( \mathbf{d} \) representing twenty-four aromatic hydrogens labeled \( \mathbf{d} \) in Figure 12. The \(^{13}\text{C} \) NMR spectrum (Figure 52) of compound 51 exhibits thirty-seven unique carbon absorptions. A comparison of the predicted \(^{13}\text{C} \) and actual \(^{13}\text{C} \) absorptions is shown in Figure 13.

**Figure 13.** Predicted (top) and actual (bottom) \(^{13}\text{C} \) NMR absorptions for N-phenyl-N-(3-benzyloxyphenyl) -7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51.
N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (52)

The cleavage of the benzyl protecting group of N-phenyl-N-(3-benzyloxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51 using pyridine hydrochloride yielded N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52. The IR spectrum (Figure 53) of compound 52 shows absorptions attributable to the phenolic O-H at 3500 to 3350 cm\(^{-1}\), aromatic C-H at 3060 cm\(^{-1}\), and aliphatic C-H at 2962 and 2945 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 54) of compound 52 exhibits 1) a triplet at 0.31 \(\delta\) representing six aliphatic hydrogens labeled \(a\) in Figure 14, 2) a multiplet at 1.85-2.14 \(\delta\) representing four aliphatic hydrogens labeled \(b\) in Figure 14, and 3) a multiplet at 6.41-8.22 \(\delta\) representing nineteen aromatic hydrogens labeled \(c\) in Figure 14. The \(^{13}\)C NMR spectrum (Figure 55) of compound 52 exhibits thirty-two unique carbon absorptions. A comparison of the predicted \(^{13}\)C and actual \(^{13}\)C absorptions of 52 is shown in Figure 15.
Figure 14. $^1$H NMR assignments for N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.

Figure 15. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.

N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (60)

The coupling of 2-(7-bromo-9,9-diethyl-9H-flouren-2-yl)bentothiazole 30 and 3-methoxydiphenylamine 59 was accomplished using dppf (diphenylphoshinoferrocene),
Pd(dba)$_2$, and sodium t-butoxide resulting in the formation of N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60. The IR spectrum (Figure 56) of compound 60 shows absorptions attributable to aromatic C-H stretching at 3059 cm$^{-1}$, aliphatic C-H stretching at 2962 and 2926 cm$^{-1}$, and aromatic C=C stretching at 1595 and 1487 cm$^{-1}$. The $^1$H NMR spectrum (Figure 57) of compound 60 exhibits 1) a triplet at 0.46 representing six aliphatic hydrogens labeled a in Figure 16, 2) a multiplet at 1.86-2.28 representing four aliphatic hydrogens labeled b in Figure 16, 3) a singlet at 3.90 representing two aliphatic hydrogens labeled c in Figure 16, and 4) a multiplet at 6.60-8.10 representing nineteen aromatic hydrogens labeled d in Figure 16. The $^{13}$C NMR spectrum (Figure 58) of compound 60 exhibits thirty-one unique carbon absorptions. A comparison of the predicted $^{13}$C and actual $^{13}$C absorptions of compound 60 is shown in Figure 17.
Figure 16. $^1$H NMR assignments for N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60.

Figure 17. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60.
N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (52)

The cleavage of the methyl protecting group of N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60 using pyridine hydrochloride yielded N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52. The IR spectrum (Figure 53) of compound 52 shows absorptions attributable to the phenolic O-H at 3500 to 3350 cm\(^{-1}\), aromatic C-H at 3060 cm\(^{-1}\), and aliphatic C-H at 2962 and 2923 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 54) of compound 52 exhibits 1) a triplet at 0.31 \(d\) representing six aliphatic hydrogens labeled \textit{a} in Figure 18, 2) a multiplet at 1.87-2.14 \(d\) representing four aliphatic hydrogens labeled \textit{b} in Figure 18, and 3) a multiplet at 6.41-8.22 \(d\) representing nineteen aromatic hydrogens labeled \textit{c} in Figure 18.

The \(^{13}\)C NMR spectrum (Figure 55) of compound 52 exhibits thirty-two unique carbon absorptions. A comparison of the predicted \(^{13}\)C and actual \(^{13}\)C absorptions of 52 is shown in Figure 19.
Figure 18. $^1$H NMR assignments for N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.

Figure 19. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.

N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (61)

Alkylation of N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52 involved a reaction with potassium hydroxide, 18-crown-6, and
1,2-dibromoethane in toluene yielding 2-(7-(3-(2-bromoethoxy)diphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole 61. The IR spectrum (Figure 59) of compound 61 contains absorptions attributable to aromatic C-H stretching at 3028 cm⁻¹, aliphatic C-H stretching at 2959 and 2924 cm⁻¹, and aromatic C=C stretching at 1588 and 1487 cm⁻¹.

Figure 20. ¹H NMR assignments for N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 61.
The $^{1}H$ NMR spectrum (Figure 60) of compound 61 exhibits 1) a triplet at 0.40 d representing six aliphatic hydrogens labeled a in Figure 20, 2) a multiplet at 1.80-2.18 d representing four aliphatic hydrogens labeled b in Figure 20, 3) a triplet at 3.80 d representing two aliphatic hydrogens bound to the carbon connected to an oxygen labeled c in Figure 20, 4) a triplet at 4.20 d representing two aliphatic hydrogens bound to a carbon connected to a halogen labeled d in Figure 20, and 5) a multiplet at 6.65-8.15 d representing nineteen aromatic hydrogens labeled e in Figure 20. The $^{13}C$ NMR spectrum (Figure 61) of compound 61 exhibits thirty-four unique carbon absorptions. A comparison of the predicted $^{13}C$ and actual $^{13}C$ absorptions of 61 is shown in Figure 21.
Figure 21. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 61.

N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (63)

Alkylation of 52 was carried out using potassium hydroxide and vinylbenzyl chloride 62 in DMF. The IR spectrum (Figure 62) of compound 63 contains absorptions
attributable to aromatic C-H stretching at 3430 cm$^{-1}$, aliphatic C-H stretching at 2960 and 2922 cm$^{-1}$, aromatic C=C stretching at 1593 and 1487 cm$^{-1}$, as well as a C-N stretch 1275 cm$^{-1}$. The $^1$H NMR spectrum (Figure 63) of compound 63 exhibits 1) a triplet at 0.39

![Figure 22. $^1$H NMR assignments for N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.]

representing six aliphatic hydrogens labeled a in Figure 22, 2) a multiplet at 1.94-2.13 representing four aliphatic hydrogens labeled b in Figure 22, 3) a singlet at 4.95 representing two benzylic hydrogens labeled c in Figure 22, 4) a doublet at 5.26 representing one vinylic hydrogen labeled d in Figure 22, 5) a doublet at 5.76 representing one vinylic hydrogen labeled e in Figure 22, 6) a multiplet at 6.65-6.77 representing one vinylic hydrogen labeled f in Figure 22, and 7) a multiplet at 7.02-8.14 representing twenty-three aromatic hydrogens labeled g in Figure 22. The $^{13}$C NMR spectrum (Figure 64) of compound 63 exhibits thirty-eight unique carbon absorptions. A comparison of predicted $^{13}$C and actual $^{13}$C absorptions of 63 is shown in Figure 23.
Figure 23. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.

3-(4-Vinylbenzyloxy)diphenylamine (65)

The alkylation of 3-hydroxydiphenylamine 64 involved a reaction with vinylbenzyl chloride 62 and potassium carbonate in DMSO. The IR spectrum (Figure 65) of compound 65 contains absorptions attributable to a secondary amine N-H stretch
at 3389 cm\(^{-1}\), aliphatic C-H stretching at 2858 cm\(^{-1}\), and aromatic C=C stretching at 1593 and 1490 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 66) of compound 65 exhibits 1) a singlet at 5.08 \(\delta\) representing two benzylic hydrogens labeled \(a\) in Figure 24, 2) a doublet at 5.32 \(\delta\) representing one vinylic hydrogen labeled \(b\) in Figure 24, 3) a broad singlet at 5.73 \(\delta\) representing the hydrogen bound to the nitrogen labeled \(c\) in Figure 24, 4) a doublet at 5.83 \(\delta\) representing one vinylic hydrogen labeled \(d\) in Figure 24, 5) a multiplet at 6.60-6.70 \(\delta\) representing one vinylic hydrogen labeled \(e\) in Figure 24, and 6) a multiplet at 6.69-7.51 \(\delta\) representing thirteen aromatic hydrogens labeled \(f\) in Figure 24. The \(^{13}\)C NMR spectrum (Figure 67) of compound 65 exhibits seventeen unique carbon absorptions. A comparison of the predicted \(^{13}\)C and the actual \(^{13}\)C NMR absorptions of 65 is shown in Figure 25.

**Figure 24.** \(^1\)H NMR assignments for 3-(4-vinylbenzyloxy)diphenylamine 65.
Figure 25. Predicted (right) and actual (left) $^{13}$C NMR absorptions 3-(4-vinylbenzyloxy)diphenylamine.

N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (63)

The coupling reaction between 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole and 3-(4-vinylbenzyloxy)diphenylamine was accomplished using Pd(dba)$_2$, dpf, and sodium t-butoxide resulting in the formation of 2-(7-(3-vinylbenzyloxydiphenylamino)-9,9-diethyl-2-fluorenyl)benzothiazole. The IR spectrum (Figure 62) of compound 63 shows absorptions attributable to aromatic C-H stretching at 3432 cm$^{-1}$, aliphatic C-H stretching at 2959 and 2922 cm$^{-1}$ and aromatic C=C stretching at 1595 and 1459 cm$^{-1}$. The $^1$H NMR spectrum (Figure 63) of compound 63 exhibits 1) a triplet at 0.41 $^3$ representing six aliphatic hydrogens labeled $a$ in Figure 26, 2) a multiplet at 6.64-6.81 $^4$ representing four aliphatic hydrogens labeled $b$ in Figure 26, 3) a singlet at 4.96 $^5$ representing two benzylic hydrogens labeled $c$ in Figure 26, 4) a doublet at 5.26
representing one vinylic hydrogen labeled \( d \) in Figure 26, 5) a doublet at 5.76 
representing one vinylic hydrogen labeled \( e \) in Figure 26, 6) a multiplet at 6.64-6.81 

**Figure 26.** \(^1\)H NMR assignments for N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.

representing one vinylic hydrogen labeled \( f \) in Figure 26, and 7) a multiplet at 7.02-8.13

representing twenty-three aromatic hydrogens labeled \( g \) in Figure 26. The \(^{13}\)C NMR
spectrum (Figure 64) of compound 63 exhibits thirty-nine unique carbon absorptions. A comparison of predicted $^{13}$C and actual $^{13}$C absorptions is shown in Figure 27.

Figure 27. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions N-phenyl-N-(3-(4-vinylbenzylxyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.

Trimethyl 1,3,5-benzenetricarboxylate (67)

The esterification of trimesic acid 66 was accomplished using methanol and concentrated sulfuric acid. The IR spectrum (Figure 68) of compound 67 shows absorptions attributable to aromatic C-H stretching at 3091 and 3012 cm$^{-1}$, aliphatic C-H
Figure 28. $^1$H NMR assignments for trimethyl 1,3,5-benzenetricarboxylate 67. Stretching at 2958 and 2845 cm$^{-1}$, and an ester C=O stretch at 1731 cm$^{-1}$. The $^1$H NMR spectrum (Figure 69) of compound 67 exhibits 1) a singlet at 3.99 $d$ representing nine aliphatic hydrogens labeled $a$ in Figure 28, and 2) a singlet at 8.83 $d$ representing three aromatic hydrogens labeled $b$ in Figure 28. The $^{13}$C NMR spectrum (Figure 70) of compound 67 exhibits four unique carbon absorptions. A comparison of the predicted $^{13}$C and actual $^{13}$C absorptions is shown in Figure 29.

Figure 29. Predicted (left) and actual (right) $^{13}$C NMR absorptions for trimethyl 1,3,5-benzenetricarboxylate 67.
1,3,5-Tris(hydroxymethyl)benzene (68)

The reduction of trimethyl 1,3,5-benzenetricarboxylate 67 was accomplished using lithium aluminum hydride followed by washing with ethyl acetate, 3.5 M sulfuric acid, methanol and ammonium hydroxide to remove excess lithium salts resulting in the formation of 1,3,5-tris(hydroxymethyl)benzene 68. The IR spectrum (Figure 71) of compound 68 shows absorptions attributable to O-H stretching at 3550-3250 cm\(^{-1}\), aromatic C-H stretching at 3003 cm\(^{-1}\), aliphatic C-H stretching at 2888 and 2850 cm\(^{-1}\).

Figure 30. \(^1\)H NMR assignments for 1,3,5-tris(hydroxymethyl)benzene 68.

The \(^1\)H NMR spectrum (Figure 72) of compound 68 exhibits 1) a triplet at 4.50 representing three alcohol hydrogens labeled \(a\) in Figure 30, 2) a doublet at 4.62 representing six benzylic hydrogens labeled \(b\) in Figure 30, and 3) a singlet at 7.25 representing three aromatic hydrogens labeled \(c\) in Figure 30. The \(^{13}\)C NMR spectrum (Figure 73) of compound 68 exhibits three unique carbon absorptions. A comparison of the predicted \(^{13}\)C and the actual \(^{13}\)C is shown in Figure 31.
1,3,5-Tris(bromomethyl)benzene (69)

The conversion of 1,3,5-tris(hydroxymethyl)benzene 68 to 1,3,5-tris(bromomethyl)benzene 69 was accomplished by boiling the former in HBr. The IR spectrum (Figure 74) of compound 69 shows absorptions attributable to aromatic C-H stretching at 3025 cm⁻¹ and aliphatic C-H stretching at 2971 cm⁻¹. The ¹H NMR spectrum (Figure 75) of compound 69 exhibits 1) a singlet at 4.44 ppm representing six benzylic hydrogens labeled a in Figure 32 and 2) a singlet at 7.35 ppm representing three aromatic
Figure 32. $^1$H NMR assignments for 1,3,5-tris(bromomethyl)benzene 69.

hydrogens labeled $b$ in Figure 32. The $^{13}$C NMR spectrum (Figure 76) of compound 69 exhibits three unique carbon absorptions. A comparison of the predicted $^{13}$C and actual $^{13}$C absorptions of compound 69 is shown in Figure 33.

Figure 33. Predicted (left) and actual (right) $^{13}$C NMR absorptions for 1,3,5-tris(bromomethyl)benzene 69.

1,3,5-Tris(anilinophenoxymethyl)benzene (70)

Alkylation of 3-hydroxydiphenylamine 64 was carried out using potassium carbonate and 1,3,5-tris(bromomethyl)benzene 69 in DMF. The IR spectrum (Figure 77) of compound 70 shows absorptions attributable to N-H stretching at 3388 cm$^{-1}$, aromatic C-H stretching at 3035 cm$^{-1}$, aliphatic C-H stretching at 2920 and 2869 cm$^{-1}$, and aromatic C=C stretching at 1593 and 1493 cm$^{-1}$. The $^1$H NMR spectrum (Figure 78) of compound 70 exhibits 1) a singlet at 5.00 $d$ representing six benzylic hydrogens labeled $a$ in Figure 34, 2) a singlet at 5.70 $d$ representing three nitrogen bound hydrogens labeled $b$ in Figure 34, and 3) a multiplet at 6.50-7.50 $d$ representing thirty aromatic hydrogens labeled $c$ in Figure 34. The $^{13}$C NMR spectrum (Figure 79) of compound 70 exhibits
thirteen unique carbon absorptions. A comparison of the predicted $^{13}$C and actual $^{13}$C absorptions is shown in Figure 35.
Figure 34. $^1$H NMR assignments for 1,3,5-tris(anilinophenoxyethyl)benzene 70.
Figure 35. Predicted (top) and actual (bottom) $^{13}$C NMR for absorptions 1,3,5-tris(anilinophenoxy)methyl)benzene 70.

1,3,5-Tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)anilino)phenoxy)methyl)benzene (71)

A metal-halogen exchange reaction between butyl lithium and 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30 followed by the reaction of the resulting organolithium compound with 70 yielded 71. The IR spectrum (Figure 80) of compound 71 shows absorptions attributable to aromatic C-H stretching at 3059 cm$^{-1}$, aliphatic C-H stretching at 2962, 2922, and 2873 cm$^{-1}$, and aromatic C=C stretching at 1593 and 1488 cm$^{-1}$. The $^1$H NMR spectrum (Figure 81) of compound 71 exhibits 1) a triplet at 0.46 representing eighteen aliphatic hydrogens labeled a in Figure 36, 2) a multiplet at 1.89-2.20 representing twelve aliphatic hydrogens labeled b in Figure 36, 3) a singlet at 4.96 representing six benzylic hydrogens labeled c in Figure 36, and 4) a multiplet at 6.60-8.18 representing sixty aromatic hydrogens labeled d in Figure 36. The $^{13}$C NMR
spectrum (Figure 82) of compound 71 exhibits thirty-five unique carbon absorptions. A comparison of the predicted $^{13}$C and the actual $^{13}$C absorptions is shown in Figure 37.
Figure 36. $^1$H NMR assignments for 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylanilino)phenoxy)methyl)benzene 71.
Figure 37. Predicted (top) and actual (bottom) $^{13}$C NMR absorptions for 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylanilino)phenoxymethyl)benzene 71.
Conclusions and Future Work

• Three new functionalized chromophores, N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (61), N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (63), and 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylanilino)phenoxy)methyl)benzene (71) were successfully synthesized and characterized.

• Measurements of the two-photon absorption, $\mathcal{D}_2$ and $\mathcal{D}_2'$, were carried out at SUNY Buffalo. The following chart shows the information for the three aforementioned chromophores compared to N,N-diphenyl-(7-benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine (31).

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\mathcal{D}_2$ (x $10^{-48}$ cm$^4$ sec ph molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>391.5 (479)</td>
<td>97.7</td>
</tr>
<tr>
<td>61</td>
<td>390.5 (471.6)</td>
<td>81</td>
</tr>
<tr>
<td>63</td>
<td>391.5 (472)</td>
<td>70</td>
</tr>
<tr>
<td>71</td>
<td>391.5 (473)</td>
<td>186</td>
</tr>
</tbody>
</table>

• The functionalization of the diphenylamino portion of the two-photon chromophore does not enhance and slightly degrades the two-photon cross-section for the compound. The attachment of three two-photon chromophores to a central core does not result in a linear enhancement of the two-photon cross-section for the molecule.
Figure 38. IR spectrum of 2,7-dibromofluorene 54.

Figure 39. $^1$H NMR spectrum of 2,7-dibromofluorene 54.
Figure 40. $^{13}$C NMR spectrum of 2,7-dibromofluorene 54.

Figure 41. IR spectrum of 2,7-dibromo-9,9-diethyl-9H-fluorene 55.
Figure 42. $^1$H NMR spectrum of 2,7-dibromo-9,9-diethyl-9H-fluorene 55.

Figure 43. $^{13}$C NMR spectrum of 2,7-dibromo-9,9-diethyl-9H-fluorene 55.
Figure 44. IR spectrum of 2-bromo-7-formyl-9,9-diethyl-9H-fluorene 56.

Figure 45. $^1$H NMR spectrum of 2-bromo-7-formyl-9,9-diethyl-9H-fluorene 56.
Figure 46. $^{13}$C NMR spectrum of 2-bromo-7-formyl-9,9-diethylfluorene 56.

Figure 47. IR spectrum of 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30.
Figure 48. $^1$H NMR spectrum of 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30.

Figure 49. $^{13}$C NMR spectrum of 2-(7-bromo-9,9-diethyl-9H-fluoren-2-yl)benzothiazole 30.
Figure 50. IR spectrum of N-phenyl-N-((-3-benzyloxyphenyl))-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51.

Figure 51. $^1$H NMR spectrum of N-phenyl-N-((-3-benzyloxyphenyl))-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51.
Figure 52. $^{13}$C NMR spectrum of N-phenyl-N-(3-benzyloxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 51.

Figure 53. IR Spectrum of N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.
Figure 54. $^1$H NMR spectrum of N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.

Figure 55. $^{13}$C NMR spectrum of N-phenyl-N-(3-hydroxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 52.
Figure 56. IR spectrum of N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60.

Figure 57. $^1$H NMR spectrum of N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60.
Figure 58. $^{13}$C NMR spectrum of N-phenyl-N-(3-methoxyphenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 60.

Figure 59. IR spectrum of N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 61.
Figure 60. $^1$H NMR spectrum of N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 61.

Figure 61. $^{13}$C NMR spectrum of N-phenyl-N-(3-(2-bromoethoxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 61.
Figure 62. IR spectrum of N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.

Figure 63. $^1$H NMR spectrum of N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.
Figure 64. $^{13}$C NMR spectrum of N-phenyl-N-(3-(4-vinylbenzyloxy)phenyl)-7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylamine 63.

Figure 65. IR spectrum of 3-(4-vinylbenzyloxy)diphenylamine 65.
Figure 66. $^1$H NMR spectrum of 3-(4-vinylbenzyloxy)diphenylamine 65.

Figure 67. $^{13}$C NMR spectrum of 3-(4-vinylbenzyloxy)diphenylamine 65.
Figure 68. IR spectrum of trimethyl 1,3,5-benzenetricarboxylate 67.

Figure 69. $^1$H NMR spectrum of trimethyl 1,3,5-benzenetricarboxylate 67.
Figure 70. $^{13}$C NMR spectrum of trimethyl 1,3,5-benzenetricarboxylate 67.

Figure 71. IR spectrum of 1,3,5-tris(hydroxymethyl)benzene 68.
Figure 72. $^1$H NMR spectrum of 1,3,5,-tris(hydroxymethyl)benzene 68.

Figure 73. $^{13}$C NMR spectrum of 1,3,5,-tris(hydroxymethyl)benzene 68.
Figure 74. IR spectrum of 1,3,5-tris(bromomethyl)benzene 69.

Figure 75. $^1$H NMR spectrum of 1,3,5-tris(bromomethyl)benzene 69.
Figure 76. $^{13}$C NMR spectrum of 1,3,5-tris(bromomethyl)benzene 71.

Figure 77. IR spectrum of 1,3,5-tris(anilinophenoxymethyl)benzene 70.
Figure 78. $^1$H NMR spectrum of 1,3,5-tris(anilinophenoxyethyl)benzene 70.

Figure 79. $^{13}$C NMR spectrum of 1,3,5-tris(anilinophenoxyethyl)benzene 70.
Figure 80. IR spectrum of 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)anilino)phenoxymethyl)benzene 71.

Figure 81. $^1$H NMR spectrum of 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)anilino)phenoxymethyl)benzene 71.
Figure 82. $^{13}$C NMR spectrum of 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylanilino)phenoxymethyl)benzene 71.

Figure 83. $^{13}$C NMR spectrum of 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-ylanilino)phenoxymethyl)benzene 71 from 140-100 ppm.
Figure 84. $^{13}$C NMR spectrum of 1,3,5-tris(3-(N-phenyl-4-(7-(benzothiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)anilino)phenoxymethyl)benzene 71 from 180-140 ppm.
APPENDIX I

The following pages contain images of a poster entitled “Functionalization of Thermally Stable NLO Chromophores” presented at the American Chemical Society Meeting (Organic Division and Sci-Mix Poster session) held in San Diego, CA in April, 2001. The following pages contain images of a poster entitled “Synthesis of Functionalized NLO Chromophores” presented at the American Chemical Society Dayton Section Poster Session held in Dayton, OH in March, 2002.
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---

**Two-Photon Absorption (TPA)**

- Third-order nonlinear response coupled with the electronic and vibrational resonances yields phenomena such as two-photon absorption. (First predicted in 1931 - Goppert-Mayer)

- Two-photon absorption is described at the molecular level as an absorption cross section $\sigma_2$.

\[
\sigma_2 = \text{rate of energy absorption in ground state} / \text{incident energy flux}
\]

---

[Diagram of two-photon absorption process]

- $\omega$: Invisible-IR  
- $\Omega$: TPA Material  
- $\omega$: Visible
**Landmarks of Two-Photon Technology**

- **1931**: Theoretical Prediction of 2-Photon Abs.
- **1936**: 2 PA Observed Experimentally in CaF$_2$:Eu$^{3+}$
- **1967**: Multi-photon Spectroscopy
- **1972**: 2 PA Organic Dyes Rodamine 6G & B cross-section measured 15 G-M (532)
- **1990**: 2 Photon LSCM Invented
- **1995**: 2-Photon Pumped Cavity Lasing Hollow fiber & Doped Polymer Rod APSS Synthesized 3800 G-M (800 nm)
- **1996**: Synthesis & Characterization AF-50 19,350 G-M (800 nm)
- **1997**: BDBAS Synthesized 17,700 G-M (600 nm)
- **1999**: 2-Photon NDE of Paints & Coatings using APSS & AF-15

1 Gippert-Mayer (G-M) = 1 x 10$^{-50}$ cm$^2$ sec/ photon molecule

---

**Upconverted Fluorescence Emission for Selected Chromophores**

- 1 (453)
- 2 (465)
- 3 (475)
- 4 (488)
--Benzene (476)
- THF (492)
- 5a (521)
- 7 (500)
- Benzene (463)
- THF (491)
Synthetic Objectives

- Develop derivatization chemistry to enable the incorporation of highly active two-photon AFX chromophores into suitable matrix materials via
  - Catalytic hydrosilylation (advanced optical composites)
  - Sol-gel process (two-photon responsive aircraft coating)

DAGSI* Project Objectives

The objective of this program is the design and implementation of advanced optical composites for Air Force and Ohio Industry applications. An optical composite is defined as any system where solid materials are incorporated into polymer hosts to integrate the optical performance characteristic of both materials. Advanced optical composites for protecting eyes and sensors from laser radiation are of particular interest to the Hardened Materials Branch in the Materials Directorate/AFRL. In industry, there are a wide variety of applications for advanced optical composites including imaging, printing, fiber optics and solid state lasers. The research of the DAGSI project is intended to overcome current shortfalls in materials performance by the synergistic design of compatible chromophore/matrix combinations.

* Dayton Area Graduate Studies Institute
Basic Chromophore Component Synthesis

Yield: 99% m.p. 159-166°

\[
\text{C}_2\text{H}_5\text{Br, KOH} \quad \text{KI, DMSO}
\]

Yield: 85% m.p. 156-158°

\[
\text{CH}_2\text{Cl}_2/I_2
\]

Yield: 78% m.p. 128-130°

Yield: 74% m.p. 133-136°

Yield: 74% m.p. 133-136°

Phenol Substituted Chromophore

\[
\text{Phenol Substituted Chromophore}
\]

Yield: 87% m.p. 181-183°

\[
\text{K}_2\text{CO}_3 \quad \text{DMF}
\]

Yield: 83% m.p. 246-247°

\[
\text{Pyridine-HCl} \quad 200°
\]

Yield: 87% m.p. 181-183°
**Phenol Facilitated Pendent Attachment**

\[
\text{Phenol} + \text{CH}_2\text{Cl}_2 \xrightarrow{\text{DMF, KOH}} \text{Product}
\]

- 71% yield, m.p. 150-152°C
- 66% yield, m.p. 136-139°C

**Hydrosilation Substrate**

**Nucleophilic Substitution Substrate**

**Bromo Substituted Chromophore Synthesis**

\[
\text{Bromo Substituted Chromophore} + \text{NH}_2 \xrightarrow{\text{Pd(dba)}_2\text{dppf}} \text{Product}
\]

- Yield: 88%, m.p. 174-175°C
- Yield: 82%, m.p. 216-217°C
- Yield: 45%, m.p. 174-175°C
APPENDIX II

The following pages contain images of a poster entitled “Synthesis of Functionalized NLO Chromophores” presented at the American Chemical Society Dayton Section Poster Session held in Dayton, OH in March, 2002.
Objective

- The objective of my work is the design and implementation of advanced optical composites for Air Force applications.
- Mainly the design of optical chromophores that exhibit large two-photon cross-sections.

General Mechanism for TPA

Examples of cross sections for some similar chromophores

Increase of cross section believed to be due to steric hinderance of the longer alkyl chains inhibiting aggregate formation.

<table>
<thead>
<tr>
<th>Figure</th>
<th>$\sigma^2$ ($\times 10^{-48}$ cm$^4$ sec ph molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>106.1</td>
</tr>
<tr>
<td>3</td>
<td>115.6</td>
</tr>
<tr>
<td>4</td>
<td>97.7</td>
</tr>
</tbody>
</table>

Applications

New Molecular Structures

2-Photon Photocuring
Low Energy Cure

Microfabrication

Optical Power Limiting
Eye and Sensor Protection

Photodynamic Therapy
Noninvasive Cancer Treatment

2-Photon Confocal Microscopy
NDE of Paint

2-Photon Pumped Upconverted Lasing
Blue Light From a Plastic Laser

3 D Optical Data Storage
1000 CDs in 1 cm$^3$
Fluorene Reactions

Polymer Branch AFRL / MLBP

Department of Chemistry

WSU

Fluorene Reactions

\[
\text{Br}_2 \rightarrow \text{Br} - \text{Br} \rightarrow \text{CHO} + \text{NH}_2 \rightarrow \text{CHO} + \text{NH}_2 \rightarrow \text{Br} - \text{Br} \rightarrow \text{KOH/ DMSO} \rightarrow \text{I. BuLi/THF} \rightarrow \text{II. DMF (-78°C)}
\]

270.82 g (91%) m.p.=166-169°C

281.37 g (95 %) m.p.=156-159°C

119.62 g (92%) m.p.=126-128°C

205.24 g (76%) m.p.=132-134°C Overall yield=60%

Phenol Formation

Polymer Branch AFRL / MLBP

Department of Chemistry

WSU

Phenol Formation

\[
\text{Br} - \text{S} + \text{N} + \text{H} \rightarrow \text{OCH}_3 \rightarrow \text{N} \rightarrow \text{S} \rightarrow \text{I. Toluene} \rightarrow \text{II. dppf Pd(dba)_2 NaO+But}
\]

72 % yield m.p.=169-170°C

68 % yield m.p.=245-248°C Overall yield=49%
Vinylbenzyloxy Chromophore

Polymer Branch AFRL / MLBP

Department of Chemistry

Vinylbenzyloxy Chromophore

Polymer Branch AFRL / MLBP

Department of Chemistry

AF-344 Hydrosilation Substrate
71% yield m.p.=173-174°C
\( \delta \approx 70 \)

72% yield m.p.=68-70°C

79% yield m.p.=173-175°C
Overall yield=57%
**Bromoethoxy Chromophore**

AF-343

Nucleophilic Substitution Substrate

79% yield

m.p. = 173-175°C

$\eta$ = 81

**Polymer Formation**

m = 100, n = 0

m = 50, n = 50
1,3,5-Tris(bromomethyl) benzene

Polymer Branch AFRL / MLBP
Department of Chemistry

CH₂OH

H₂SO₄

I) H₂SO₄/ THF

II) MeOH/ NH₄OH

III) EIOAc

63% yield
m.p.=144-146°C

70% yield
m.p.=76-78°C

93.9% yield
m.p.=98-100°C


Present Reaction

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Department of Chemistry

CH₂Br

HBr

BrH₂

H₂SO₄

I.Toluene

II.dppf   Pd(dba)₂   NaO+But

700°C

75% yield
m.p.=57-59°C

AF-515

33% yield
m.p.=332-333°C

Overall yield=25%

[2',2'=186]
Conclusions

- Able to successfully synthesis and characterize three new NLO chromophores and the necessary intermediates
- Shown that the bromoethoxy chromophore can be successfully incorporated into a polymer

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REFERENCES


VITA

Michael J. Matuszewski was born on June 26, 1978 in Antigo, WI. He graduated with a Bachelor of Science Degree in Chemistry at St. Norbert College in 2000. He expects to receive a Master of Science Degree in June of 2002.