SYNTHESES AND CHARACTERIZATIONS OF LINEARLY EXTENDED THIAZINIUM SALTS AS ORGANIC SEMICONDUCTORS

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SYNTHESES AND CHARACTERIZATIONS
OF LINEARLY EXTENDED
THIAZINIUM SALTS AS ORGANIC SEMICONDUCTORS

BY

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B.S., Hebei University of Technology, China, 2006

THESIS

Submitted to the University of New Hampshire
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the Requirements for the Degree of

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in
Chemistry

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This thesis has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemistry by:

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40a, 41a: R₁, R₂ = (CH₂)₄;
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40d, 41d: R₁=CH₃, R₂ = C₆H₅;
40e, 41e: R₁=CH₃, R₂ = CH₂C₆H₅;

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ABSTRACT
SYNTHESES OF LINEARLY EXTENDED THIAZINIUM SALTS AS ORGANIC SEMICONDUCTORS

by

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University of New Hampshire, December, 2014

Organic semiconductors have been the subject of both academic and industrial interest due to their potential advantages over inorganic semiconductors. Based on the type of charge transporting (hole or electron), organic semiconductors can be categorized as n-type (electron transporting) or p-type (hole transporting). Most attention has been concentrated on the development of p-type organic semiconductors and their development has led to dramatic enhancements in the performance of hole transporting material. However, the investigation and application of electron transporting organic semiconductors has not drawn as much attention. In this project, we focus on the exploration, design, synthesis and characterization of novel n-type organic semiconductors.

A series of novel compounds, linearly extended thiazinium salts (LETS) with structures similar to methylene blue were designed. Methylene blue itself has several characteristics that are associated with potential n-type semiconductors, such as a positively charged backbone, water-solubility, stability, intense absorption in the visible region, a relatively small HOMO-LUMO gap, potential high charge carrier mobility and strong π-π stacking in its solid state crystal structure. A new molecule, 3,9-
bis(dimethylamino)dibenzo[b,i]phenothiazin-6-ium chloride, was selected as one of several compounds for a computational (DFT) investigation for comparison to methylene blue. The calculated results showed that the new molecule has an even smaller HOMO-LUMO gap than 0.76 eV and a maximum absorption of light at approximately 790 nm. The computational study provided impetus to synthesize and characterize LETS compounds.

Three synthetic schemes have been explored for the synthesis of LETS compounds. A thionation reaction involving elemental sulfur, a coupling reaction and a Friedel-Crafts acylation have all been utilized to synthesize a precursor of LETSs, 13H-dibenzo[b,i]phenothiazine.
CHAPTER 1

INTRODUCTION

1.1 Brief Introduction to Organic Semiconductors

Organic semiconductors have been of great interest in both academic and industrial fields over the past two decades due to their optoelectronic properties which are suited for manufacturing electronic devices. Additionally, properties such as higher charge carrier mobility or HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gap can be tuned by introducing new substituents or by extending the conjugation of the compound. Organic electronic devices can be fabricated using inexpensive solution-processing technique. Organic films can be easily deposited on flexible, large-area and low-cost substrates such as plastic, glass and metal foil. Another advantage of organic materials is that they can be functionalized to enhance certain properties such as conductivity, solubility, or stability in order to meet a variety of demands in material processing, device fabrication or applications. Organic semiconductors open up new opportunities to many exciting and advanced applications which cannot be achieved by conventional inorganic semiconductors.

Organic semiconductors can be divided into two groups based on molecular weight: small molecules (including monomers and oligomers) and organic polymers.
Some examples of these two types of semiconductor materials are listed in **Figure 1** and **Figure 2**.

**Figure 1**: Examples of small molecule organic semiconductors

**Figure 2**: Examples of polymer organic semiconductors
Organic semiconductors can also be categorized as p-type (hole-transporting) or n-type (electron-transporting) based on the charge carrier (holes or electrons) in the materials. Generally speaking, the development of p-type organic semiconductors is more advanced than the development of n-type organic semiconductors. Much attention has been focused on hole transporting semiconductors and a dramatic increase in performance has been achieved over the past few years. The performance of some organic donors in OFETs is comparable to that of traditional inorganic semiconductor silicon. However, much less effort has been devoted to the development of n-type organic semiconductor, which is slowing the advancing of organic electronics.

1.2 n-Type Organic Semiconductors

1.2.1 Classification of Commonly Used n-type Organic Semiconductors

N-type organic semiconductors are either electron-deficient small molecules or polymeric π-conjugated systems. Although the development of n-type semiconductors has lagged behind p-type materials, much effort has been devoted to the design and exploration of novel electron transporting materials due to the advantages of organic semiconductors over conventional silicon. Several classes of n-type materials are discussed below.

(1) Siloles (silacyclopentadienes)

Siloles (silacyclopentadienes) are a group of conjugated five-membered silacyclics (Figure 3). They have drawn attention as organic semiconducting materials because they can display high electron mobility in organic electronics. The silole core can exhibit σ*-π* conjugation by mixing of the σ* orbital on silicon atom and the π* orbitals
provided by the diene.\textsuperscript{7} Through this $\sigma^*-\pi^*$ conjugation, the LUMO can be lowered in energy to accept electrons. In addition to the $\sigma^*-\pi^*$ conjugation, various substituents on the silole backbone play an important role in determining the electronic structures, energy levels, absorption, emission, and charge transporting properties of these materials.\textsuperscript{8} Therefore, it is possible to enhance the electronic properties of siloles by modifying their molecular structures, and find better applications in organic electronics.\textsuperscript{9} For instance, molecules 13,\textsuperscript{10} 14,\textsuperscript{11} 15,\textsuperscript{12} and 16\textsuperscript{13,12} have been studied by several research groups as OLED materials.

![Chemical structures of several silole molecules](image)

Figure 3: Chemical structures of several silole molecules

(2) Rylene Diimides

Rylene diimides are a class of electron-deficient molecules which exhibit relatively high electron affinities, high electron mobilities, and excellent chemical, thermal, and photochemical stabilities due to the conjugation of two sets of $\pi$-accepting imide substituents with a naphthyl aromatic system.\textsuperscript{14} The rylene diimides include small molecules such as naphthalene diimides (NDIs) and perylene diimides (PDIs) (17-20), and NDI and PDI-incorporated polymers (21, 22) (Figure 4). In NDIs and PDIs, the
aromatic π-conjugated system plays a significant part in determining the charge transport properties. The electron transport properties, together with the crystal packing can be manipulated by adding substituents to either the N sites or the aromatic systems. Introducing electron-withdrawing groups such as CN or F to the N atom or the aromatic core can stabilize the rylene diimide-based devices under ambient conditions (19, and 20). Compared with small molecules, the NDI and PDI-incorporated polymers or oligomers can improve the solution process in device fabrication and power conversion efficiency. Overall, rylene diimides can be used in a variety of electronic and optoelectronic organic devices, such as OLEDs, OPVs, OFETs, dye lasers, optical switches and photoconductors.


(3) n-Type Acene Derivatives

Linearly fused aromatic systems, such as pentacene (1) and rubrene (23) are widely known p-type organic materials with excellent performance when used as semiconductors. However, they can also be treated as n-type materials in organic devices by carefully selecting the proper metal electrode and dielectric material. The problems with charge injection into the LUMO and charge trapping at the dielectric interface can be addressed, and electron transport properties can be detected in these classic p-type semiconductors. Pentacene has been shown both electron and hole
transport properties in films using an inert hydroxyl-free parylene C dielectric and calcium source/drain electrodes.\textsuperscript{25}

n-Type performance of acenes in organic electronic devices can also be achieved by introducing strong electron-withdrawing groups (\textsuperscript{24-26}) or by incorporating a PDI moiety (\textsuperscript{27}) into the conjugated system, which can stabilize the reduced state of the molecules. Perfluorination is particularly attractive because it can lower the LUMO energy of the compound, while preserving the solid-state packing to a large extent. Among all the substituted molecules, perfluoropentacene (\textsuperscript{24}) is an excellent example of this strategy.\textsuperscript{26} Thus, acene materials (\textbf{Figure 5}), with the appropriate structural modifications, can also be used as n-type semiconductors.

\textbf{Figure 5}: Chemical structures of several acene derivatives
(4) Fullerene-based n-type materials

[60] Fullerene (6) was first observed in 1985 by Smalley and coworkers.\textsuperscript{27} In the following years, much attention has been focused on readily available C\textsubscript{60} and fullerene-based compounds due to their relatively low LUMO energy level. [60] Fullerene is an excellent electron acceptor and is able to accept up to six electrons in solution because its LUMO is triply degenerate. As an electron transport compound, C\textsubscript{60} has been broadly studied and utilized in organic electronics, particularly in OFETs and OPVs.\textsuperscript{28}

However, [60] Fullerene shows poor solubility in common organic solvents thereby constraining film deposition to thermal evaporation. In order to improve the solubility to facilitate device fabrication in solution as well as to tune the electronic properties of [60] fullerene and its derivatives, great effort has been made to functionalize C\textsubscript{60} with a variety of functional groups. Some of the examples are showed in Figure 6.
1.2.2 General Characteristics for Design of n-Type Organic Semiconductor

In general, there are no standard rules to design or describe an electron-transporting material due to the diversity of device requirements. Different organic electronics require materials with different properties. A given organic semiconductor material may have different efficiencies in different organic devices. Also, application of different fabrication techniques may affect the performance of optoelectronic devices to some extent.

Nonetheless, there are indeed several desirable characteristics for practical electron transporting organic semiconductors. First, the molecule should be readily synthesized from commercially available starting materials. Second, it should be strongly electron-withdrawing which is essential for electron attraction. Third, the compound
must be physically and thermally stable for both material processing and device fabrication. Finally, the highly conjugated molecule should have a small HOMO-LUMO gap and intense absorption of long wavelength light which can trigger and enable effective electron injection and charge collection at interfaces. In other words, the charge carrier (electrons) can smoothly move within the π-conjugated molecular system.\(^{30}\)

These characteristics are significant but not sufficient for n-type organic semiconductors. Some of the characteristics can be optimized by modifying the structure of the material. Moreover, it is important to realize that some of these characteristics are only meaningful when implemented into organic devices; they are not intrinsic properties of the material itself. Therefore, a material can be called an n-type organic semiconductor only when it can be utilized in an electronic device.

### 1.2.3 Applications and Challenges of Organic Semiconductors

N-type organic semiconductors have potential applications in optoelectronics including organic photovoltaic devices (OPV), organic light-emitting diodes (OLED) and organic field effect transistors (OFETs).\(^{31}\)

Although a variety of n-type materials have been synthesized and incorporated into different kinds of organic electronic devices, further improvement regarding the syntheses, material stability and processibility, device fabrication and performance are necessary. Organic chemistry has become a useful tool to control and address several issues at the molecular level. However, the complexity of fabricating a high performance device is still a challenge when taking all potential properties of the material into consideration.
1.3 Methylene Blue (MB)

1.3.1 Properties of Methylene Blue and Derivatives

Methylene blue, 3,7-bis(dimethylamino)phenazothiazin-5-ium chloride, is a heteroaromatic phenothiazine derivative with a positive charge delocalized throughout the extended π-system bearing two electron-donating amino substituents at the 3 and 7 positions (Figure 7), which makes methylene blue a stabilized salt. Methylene blue displays a strong absorption in the red region of the visible light with a maximum molar absorptivity of 85,000 M$^{-1}$cm$^{-1}$ at 664 nm in aqueous solution, which gives it a characteristic blue color.\(^{32}\) By contrast, anthracene, the 3-ring neutral acene, only shows a maximum absorption at 357 nm\(^{33}\) in THF under UV-Vis. (Figure 8).

![Figure 7: Methylene blue](image)

![Figure 8: Chemical structures of methylene blue (34) and anthracene (36)](image)

The crystal structures of unsubstituted acenes often display herringbone packing arrangements (edge to face arrangement) (Figure 9).\(^{34}\) This solid state structure reduces
their potential as organic semiconductors in thin-film electronic devices where the transmission of electrons and holes is required. **Figure 9** shows that CH…π interactions are playing the dominant intermolecular interactions in the herringbone motif.

**Figure 9**: Crystal structures for anthracene\(^{35}\) (left) and pentacene\(^{36}\) (right)

An X-ray crystal structure for MB has been reported (**Figure 10**). The crystal structure reveals planar methylene blue molecules surrounded by water molecules, twenty per unit cell, that form an important H-bonding network throughout the lattice.\(^{37}\) The methylene blue molecules in the lattice enjoy face-to-face π-π stacking interactions with one another. The distance between nearest neighbor methylene blue molecules is 3.496 Å, nearly the same distance as observed between the graphene planes in graphite (3.354 Å)\(^{38}\). This packing motif is preferred to a herringbone architecture because it allows for stronger π-π interactions and higher charge carrier mobility.\(^{39}\)
1.3.2 Applications of Methylene Blue and Derivatives

Methylene blue is a commonly used dye for textiles because of its characteristic color.\textsuperscript{40} And it has been extensively used as a redox indicator in both chemical and biological fields due to the color change in oxidation and reduction phases. It shows a deep blue color in its oxidized state, and it turns to colorless when reduced (Scheme 1).\textsuperscript{41} More recently, methylene blue has been used as a histochemical stain,\textsuperscript{42} photosensitizer\textsuperscript{43} and drug to treat a variety of modern diseases.\textsuperscript{44}

\begin{center}
\textbf{Scheme 1}: The redox-cycling of methylene blue
\end{center}

1.3.3 Synthetic Routes to Methylene Blue
1.3.3.1 Synthetic Routes to Methylene Blue and its derivatives

Ihara and coworkers have reported a convenient method to synthesize a series of novel phenothiazinium salts (Scheme 2).\textsuperscript{45} Commercially available phenothiazine is treated with iodine in chloroform to generate the corresponding aromatized iodide salt. Subsequent nucleophilic substitution with a secondary amine affords the amino-substituted phenothiazinium iodide. Finally, replacing the iodide with chloride using an ion exchange resin generates the methylene blue derivatives.

**Scheme 2:** The synthetic scheme to MB derivatives

1.3.3.2 Phenothiazine: A Methylene Blue Precursor

1.3.3.2.1 First Synthetic Route to Phenothiazine

Traditionally, phenothiazine is synthesized using diphenylamine and sulfur in the presence of catalytic iodine at high temperature (Scheme 3).\textsuperscript{46,47} When di-substituted diphenylamines are employed, the reaction will lead to a mixture of regioisomers with varying yield depending on the type and position of substituents.\textsuperscript{48,49,50} Thus, this is an efficient and straightforward approach to make a methylene blue precursor in high yield, but it is not well suited for substituted phenothiazines.
1.2.3.2 Second Synthetic Route to Phenothiazine and derivatives

The second method widely used to synthesize phenothiazine and its derivatives is a coupling reaction. A Smiles Rearrangement based on a four-step protocol (Scheme 4) was developed by Harry Yale.\textsuperscript{51} A mixture of 2-aminobenzenethiol 43 and 2,5-dichloronitrobenzene 44 in isopropanol was added dropwise to a solution of potassium hydroxide in ethanol. The mixture was stirred and refluxed for 3 h to generate sulfide 45. The compound 45, acetic anhydride, pyridine and Darco were heated under steam-bath for 2 h to give acetamido derivative 46. Compound 46 was then added to a solution of acetone and potassium hydroxide in ethanol. The mixture was distilled via steam-bath under nitrogen. As the concentration of the mixture increased, 47 was first formed, then final product 48 was synthesized. Although 3-chlorophenothiazine 48 was synthesized through this route, the method has limitations including multiple steps and the difficulty associated with the synthesis of suitable derivatives.\textsuperscript{52,53}
Scheme 4: Smiles rearrangement method to synthesize phenothiazine derivative

To overcome this problem, a sequential controlled CuI-ligand-catalyzed coupling reaction was developed to form new C-S and C-N bonds in high yield by Ma and coworkers (Scheme 5). It started with 2-iodoaniline 49 and 2-bromobenzenethiol 50. The formation of the C-S bond is preferred over the formation of a C-N bond. Compound 51 is formed as an intermediate before phenothiazine 38. Although this reaction offers a more general and efficient procedure to achieve heterocyclic compounds, it still has the drawbacks of forming several by-products. In Ma’s synthetic route, each of the reactants, 2-iodoanilines and 2-bromobenzenethiols, have two reactive centers. Therefore, the reaction yields three possible products, including two by-products from self-coupling.
Noticing the shortcomings in reported syntheses (such as long reaction time, possibility of self-coupling, expensive palladium catalyst and ligand, narrow range of reaction substrates, strictly sequential controlled reaction condition and multiple reaction steps) and the advantages of Cu catalysts in syntheses of heterocyclic compounds using ortho-dihalides, Zeng and coworkers reported a modified scheme with aryl ortho-dihalides and ortho-aminobenzenethiols as starting materials (Scheme 6). This method does not suffer from the drawbacks mentioned above. The reaction conditions have been optimized to find the most efficient catalysts, bases, solvents, and halogen substituents. Zeng and coworkers also proposed a possible mechanism for this ligand-free coupling reaction. In this mechanism, the ortho-aminobenzenethiol (52) acts as a ligand in an Ullmann coupling reaction (Scheme 7).
1.4 Synthesis and Characterization of Methylene Blue Derivative for Potential Use as n-Type Organic Semiconductor Material

The optoelectric and structural properties of methylene blue, such as small HOMO-LUMO gap, positively charged backbone, intense absorption in visible light, face-to-face arrangement in the solid state, and so on, are characteristics that are associated with n-type organic semiconductor materials. Thus, methylene blue derivatives can be viewed as a potential new class of n-type organic semiconductors. Their syntheses and characterizations will be discussed in the following chapters.
CHAPTER 2

COMPUTATIONAL MODELING

2.1 Linearly Extended Thiazinium Salts (LETS)

Methylene blue (34) is a cationic heterocyclic compound with maximum absorption of light around 650 nm and a relatively small HOMO-LUMO gap of approximately 2 eV (Table 1). The phenothiazinium backbone shows a strong electron-accepting tendency because it is cationic and has a substantially lower LUMO energy (-3.25 eV) than anthracene (-2.04 eV). Moreover, methylene blue is a stable salt and has relatively good solubility in water. These properties are required, but are not sufficient for use as an n-type organic semiconductor.

Building upon the promising characteristics of methylene blue, we propose a series of new compounds: linearly extended thiazinium salts (LETS) (Figure 11). Our expectation is that LETS compounds will possess even smaller HOMO-LUMO gaps while maintaining excellent stability. Unlike the acenes with an isoelectronic \(\pi\)-system, LETS compounds should resist oxidation. Since there is little physical or chemical information about the proposed new LETS compounds, computational modeling was utilized to explore and investigate their properties.
2.2 Computational Modeling

The frontier orbital energies, HOMO-LUMO gaps and UV-Vis $\lambda_{\text{max}}$ values were calculated for select molecules. Geometries were optimized using density functional theory (DFT) at the B3LYP/6-31+G* level of theory and single point energies were calculated at the B3LYP/6-311+G** level of theory. The results are shown in Table 1.

The molecules of Table 1 are grouped in threes according to structure: 36, 55, 1; 38, 56, 57; 58, 59, 60; and 34, 61, 54.

<table>
<thead>
<tr>
<th>Structures</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Gap (eV)</th>
<th>UV-Vis $\lambda_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-5.57</td>
<td>-2.04</td>
<td>3.53</td>
<td>363</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 55" /></td>
<td>-5.20</td>
<td>-2.46</td>
<td>2.74</td>
<td>463</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 1" /></td>
<td>-4.94</td>
<td>-2.76</td>
<td>2.18</td>
<td>580</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 38" /></td>
<td>-5.35</td>
<td>-0.87</td>
<td>4.48</td>
<td>301</td>
</tr>
<tr>
<td>Structure</td>
<td>HOMO</td>
<td>LUMO</td>
<td>Gap</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
<td>------</td>
<td>-----</td>
<td>---------------</td>
</tr>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>-5.41</td>
<td>-1.44</td>
<td>3.97</td>
<td>358</td>
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<tr>
<td><img src="image2" alt="Structure" /></td>
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<td>-1.51</td>
<td>3.96</td>
<td>395</td>
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<tr>
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<td>-4.94</td>
<td>0.63</td>
<td>642</td>
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<tr>
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<td>0.58</td>
<td>672</td>
</tr>
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<td><img src="image5" alt="Structure" /></td>
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<td>-5.00</td>
<td>0.51</td>
<td>899</td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
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<td>-3.25</td>
<td>1.98</td>
<td>541</td>
</tr>
<tr>
<td><img src="image7" alt="Structure" /></td>
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<td>-3.31</td>
<td>2.05</td>
<td>557</td>
</tr>
<tr>
<td><img src="image8" alt="Structure" /></td>
<td>-4.98</td>
<td>-4.05</td>
<td>0.93</td>
<td>744</td>
</tr>
</tbody>
</table>

For the fully conjugated neutral series (i.e., the acenes 36, 55 and 1), we see that HOMO energies undergo a sharp rise while LUMO energies undergo a sharp decline as the number of rings increases from three to five. The resulting HOMO-LUMO gaps shrink by 1.35 eV over this series with a simultaneous red shift in λ<sub>max</sub> values by 217 nm.

Conversely, the fully conjugated cation series (LETS compounds 58, 59 and 60) show only modest increases in HOMO energies and modest declines in LUNO energies.
as the number of rings increase from three to five. Likewise, the HOMO-LUMO gaps decrease over this series, but only by 0.12 eV.

The introduction of dimethylamine substituents in the series 34, 61 and 54 seems to partially restore the “acene-like” response of increased conjugation. Thus, the HOMO-LUMO gaps decrease by 1.05 eV upon moving from the three-ring compound 34 to the five-ring compound 54. This result may indicate an acene-like π-system in which charge is largely located on exocyclic N, as in the resonance form below (Figure 12):

![Resonance structure of compound 54](image)

**Figure 12**: Resonance structure of compound 54

For the phenothiazine series that lacks full conjugation (i.e., 38, 56 and 57), relatively low HOMO energies are accompanied by relatively high LUMO energies resulting in HOMO-LUMO gaps at or above approximately 4 eV. This was expected for compounds of this type that lack full conjugation across the multi-ring scaffold.

In order to judge the validity of the calculations, the calculated HOMO-LUMO values were compared to experimental HOMO-LUMO values in few cases (Table 2).

<table>
<thead>
<tr>
<th>Structures</th>
<th>HOMO-LUMO Gap (eV) (Calc.)</th>
<th>HOMO-LUMO Gap (eV) (Expt.)</th>
<th>UV-Vis (λ&lt;sub&gt;max&lt;/sub&gt;) (Calc.)</th>
<th>UV-Vis (λ&lt;sub&gt;max&lt;/sub&gt;) (Expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 38" /></td>
<td>4.48</td>
<td>3.38&lt;sup&gt;a&lt;/sup&gt;</td>
<td>301</td>
<td>315</td>
</tr>
</tbody>
</table>

<sup>a</sup> Estimated value.
<table>
<thead>
<tr>
<th>Structure</th>
<th>HOMO-LUMO Gap</th>
<th>Max Visible Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 36" /></td>
<td>3.53</td>
<td>3.20&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><img src="image" alt="Structure 34" /></td>
<td>1.98</td>
<td>1.81&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><img src="image" alt="Structure 55" /></td>
<td>2.74</td>
<td>2.54&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><img src="image" alt="Structure 1" /></td>
<td>2.18</td>
<td>2.08&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

(a: The HOMO-LUMO gaps are determined from the onset of maximum visible absorption band in UV-Vis spectra. The onset is defined as the intersection between the baseline and a tangent line that touches the point of inflection.

b: The HOMO-LUMO gaps and maximum visible absorption is obtained directly from the published paper.<sup>60</sup>

c: The HOMO-LUMO gaps is obtained directly from the paper published by Miller group.<sup>61</sup> )

Overall, the calculations provide strong impetus to synthesize and characterize LETS compounds like 54.
3.1 Synthesis of Methylene Blue

Based on the synthetic strategy discussed in Schemes 2 and 3, a synthesis of methylene blue iodide 40 was reproduced following a modified procedure (Scheme 8). First, the phenothiazine 38 was generated by thionation of diphenylamine 42 with elemental sulfur in the presence of catalytic amount of iodine without solvent. Subsequent aromatization using iodine in chloroform afforded multiiodide salt 39. Compound 39 shows poor solubility and could not be fully characterized by NMR spectroscopy. Despite this disadvantage, treating the multiiodide salt 39 with dimethylamine in methanol for 4 h at room temperature gave 3,7-bis(dimethylamino)phenothiazin-5-ium iodide 40, which was characterized by $^1$H-NMR, UV-Vis and MALDI-TOF-MS.

Scheme 8: The synthetic scheme to 3,7-bis(dimethylamino)phenothiazin-5-ium iodide, methylene blue iodide
Iodide 40 exhibits a similar absorption as methylene blue chloride in the visible region of the UV-Vis spectrum due to their similar structure (Figure 13). Both of them have $\lambda_{\text{max}}$ at 652 nm (in MeOH).

Figure 13: UV-Vis spectra of methylene blue iodide (top) and chloride (bottom)

However, methylene blue 34 shows greater solubility than methylene blue iodide 40 in a variety of solvents. The poor solubility of compound 40 could limit its
applications in several ways. Methylene blue 34, on the other hand, is widely used in dyes, pigments, photosensitizers and indicators.

The successful preparation of iodide 40 following the strategy of Wainwrigh, Ihara and Dolphin 45,63,64 allows for the application of a modified synthetic route to LETS compounds, as described below.

3.2 Syntheses of Linear Extended Thiazinium Salts (LETS)

3.2.1 Proposed Synthetic Scheme to LETS Compounds

Based on the synthetic scheme (Scheme 2 and 3) of methylene blue, 45,63,64, a modified method was proposed (Scheme 9) to synthesize 3,9-bis(dimethylamino)dibenzo[b,i]phenothiazin-6-ium iodide 63, a linearly extended thiazinium salt with five fused aromatic rings in the backbone containing nitrogen and sulfur at the 6 and 13 positions, respectively. Similar to methylene blue, compound 63 should be stabilized by resonance delocalization of the positive charge on sulfur to the amino groups at the 3 and 9 positions (Figure 14).

First, 13H-dibenzo[b,i]phenothiazine 57 could be aromatized to give the corresponding iodide salt 62. Compound 62 could then be obtained via amination with dimethylamine. Given that methylene blue iodide was synthesized in a similar fashion and the synthetic route has been successfully reproduced following the same procedure without difficulty, the synthesis outlined in Scheme 9 seems promising.
The proposed synthetic scheme to synthesize 3,9-
bis(dimethylamino)dibenzo[b,i]phenothiazin-6-iium iodide

Scheme 9: The proposed synthetic scheme to synthesize 3,9-
bis(dimethylamino)dibenzo[b,i]phenothiazin-6-iium iodide

Figure 14: The resonance structure of LETS compounds

3.2.2 Precursor of LETSs--13\(H\)-dibenzo[\(b,i\)]phenothiazine

Precursor 13\(H\)-dibenzo[\(b,i\)]phenothiazine 57 is the key intermediate on the pathway to LETS compounds. Compound 57 is a linearly extended heterocyclic compound with sulfur and nitrogen positioned at the 6 and 13 sites. It is a conjugated extension of phenothiazine. Due to the similarity to the phenothiazine structure, it can be realized by modified synthetic routes towards phenothiazine.

3.2.3 First Proposed Method to Synthesize the Precursor of LETSs

Based on the traditional protocol to synthesize phenothiazine, a modified synthetic scheme to form linear dibenzophenothiazine 57 was proposed (Scheme 10). First, 2,2'-dinaphthylamine 65 can be intimately mixed with sulfur in the presence of a
catalytic amount of iodine. The resulting mixture could be heated at 180-200 °C to afford the desired product 57.

\[
\begin{align*}
\text{Scheme 10:} & \quad \text{First proposed method to form 13H-dibenzo}\{b,i\}\text{phenothiazine}
\end{align*}
\]

### 3.2.3.1 Proposed Synthetic route to Unsubstituted Precursor of LETS Compounds

Considering the structure and properties of diphenylamine, a synthetic scheme was designed starting with commercially available 2-substituted naphthalene (Scheme 11). First, the starting material could be converted to 2-naphthylamine 66, which reacts with another 2-substituted naphthalene substrate and generates 2,2’-dinaphthylamine 65. Final product 57 is obtained after treating the secondary amine with elemental sulfur and catalyst iodine.

\[
\begin{align*}
\text{Scheme 11:} & \quad \text{Synthetic scheme to unsubstituted precursor of LETS compounds}
\end{align*}
\]
3.2.3.1.1 Synthesis of 2-naphthylamine

2-naphthylamine is an aromatic amine and shows strong basicity in reactions. It is a carcinogen and has been found in tobacco smoke, which is suspected to induce bladder tumors.\textsuperscript{65} Thus, exposure should be strictly controlled when operating experiments with it. This compound is one of the requisite chemicals to carry out the synthesis of dibenzophenothiazine \textsuperscript{57} and is needed in large quantity. An efficient method must be figure out to synthesize it. Several approaches have been tried to achieve this goal.

3.2.3.1.1.1 Attempted synthesis of 2-naphthylamine using Ullmann reaction

The Ullmann amination was conducted in a sealed tube following Wei’s protocol\textsuperscript{66} with some modifications (Scheme 12). Wei reported this reaction as a facile and practical method with bromobenzene as starting material and a yield of 85\%. Upon changing bromobenzene to 2-bromonaphthalene, I saw no sign of the desired compound. The lack of reactivity is not understood.

![Scheme 12: Ullmann reaction to synthesis of 2-naphthylamine](image)

Since the copper-catalyzed, ligand-free Ullmann-type amination illustrated above is not suitable for 2-bromonaphthalene, another Ullmann-type reaction was attempted.
Ma’s group reported an efficient coupling of aryl bromides and aqueous ammonia using CuI/4-hydro-L-proline as the catalytic system (Scheme 13).67

\[
\text{Scheme 13: Ullmann reaction to synthesis of 2-naphthylamine}
\]

Although the N-coupling reaction of 2-bromonaphthalene 67 and ammonium hydroxide afforded 66, I only observed a trace of it at 60 °C under CuI/4-hydro-L-proline conditions, as monitored by TLC. A higher temperature was then applied to the reaction system in order to increase the yield of product. Unfortunately, starting material was still the main compound of the resulting mixture thus leaving the reaction incomplete (Table 3).

Table 3: Attempted experiments to synthesize 2-naphthylamine

<table>
<thead>
<tr>
<th>Entries</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Results (TLC monitored)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>24</td>
<td>SM + PDT(trace)</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>24</td>
<td>SM + PDT(trace)</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>24</td>
<td>SM + PDT(trace)</td>
</tr>
</tbody>
</table>

Reaction conditions: 2-bromonaphthalene (0.25 mmol), ammonium hydroxide (12 mmol), CuI (0.05 mmol), ligand (0.1 mmol), K₂CO₃ (0.75 mmol), DMSO (1 mL), 24 h.

Apparently, the α position is more favorable for nucleophilic substitution than the β position in this reaction because 1-naphthylamine is aminated with a yield of 76 under the same condition as reported by Ma.67
3.2.3.1.2 Synthesis of 2-naphthylamine using pressure vessel

To introduce a primary amino group to the naphthalene moiety, ammonia or ammonium hydroxide are typically utilized as the nitrogen source. High pressure can be generated during the reaction and ammonia is corrosive. To overcome these problems, a special reactor which can hold high pressure and resist basic corrosivity should be used. In this case, a modified synthetic route (Scheme 14) based on Yuan’s synthetic scheme\(^{68}\) was studied and achieved. 2-Naphthol \(68\), sodium bisulfite and a large excess of ammonium hydroxide were sealed in a pressure vessel and heated at 170 °C for 7 h. Several types of pressure vessels were utilized to run this reaction. (Table 4) These include a sealed tube (glassware) which could hold a pressure of 150 psi, a microwave tube that could sustain a pressure as high as 250 psi and a Teflon autoclave that could hold a pressure as high as 430 psi.

![Scheme 14: Synthetic route to 2-naphthylamine using pressure vessel](image)

Because of the harsh reaction conditions, the sealed glass tube could only withstand 145 °C before leakage of ammonium hydroxide. The O-ring, which creates a seal to prevent leakage, was damaged severely by the corrosive ammonia vapor. Furthermore, the yields of this reaction ranged from 0-40% depending on the performance of the O-rings. Thus, the sealed glass tube was not a reliable reactor for this reaction. A similar situation also resulted when using the microwave reactor. The
microwave reactor reacted at its pressure limit of 250 psi with liquid mixture leaking out of the tube when the temperature reached 130 °C. Neither of these pressure vessels is suitable for this amination reaction.

A Teflon autoclave, on the other hand, met the pressure requirements and showed resistance to strong basic corrosivity. It proved to be an ideal reactor to achieve the purpose. 2-Naphthylamine 66 was successfully synthesized in the autoclave heated in a furnace at 170 °C with a yield of 83%.

Table 4: Experiments to synthesize 2-naphthylamine

<table>
<thead>
<tr>
<th>Pressure Vessel</th>
<th>T_{\text{max}} (°C)^a</th>
<th>Reaction T (°C)</th>
<th>Pressure (psi)^b</th>
<th>Results/Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealed Tube (glassware)</td>
<td>145</td>
<td>145</td>
<td>150</td>
<td>0-40%</td>
</tr>
<tr>
<td>Microwave Tube</td>
<td>130</td>
<td>130</td>
<td>250</td>
<td>0%</td>
</tr>
<tr>
<td>Autoclave</td>
<td>220</td>
<td>170</td>
<td>430</td>
<td>83%</td>
</tr>
</tbody>
</table>

a: The maximum temperature that the reaction vessel can hold.
b: The maximum pressure that the reaction vessel can hold.

### 3.2.3.1.2 Synthesis of 2,2'-Dinaphthylamine

The proposed synthetic methodology to form 2,2'-dinaphthylamine 65 involves coupling reaction between 2-naphthylamine 66 and 2-naphthyl halides or pseudohalide (for example: hydroxyl, tosylate, triflate) in the presence of a catalyst. The 2-naphthylamine 66 reacts as a nucleophile and the other naphthyl compound acts as an electrophile.
3.2.3.1.2.1 Synthesis of 2,2'-dinaphthylamine under neat conditions

The reaction depicted in Scheme 15 is a neat reaction, also called a solventless reaction. As the name implies, the chemical reaction is taken up without solvent in the system. The drive for the development of neat reactions is that they are in accordance with the concept of green chemistry, satisfying the principle of human health and environment protection, while at the same time achieving commercial viability.

Compounds 66, 68 and catalysts zinc chloride, ammonium chloride, were initially mixed together and then heated at a temperature ranging from 200 to 250 °C following the procedure reported by Lieber and Somasekhara.69 It was supposed to have a higher reaction rate and higher yield because of the high concentration of reactants. However, a high yield was not achieved and it might be due to the following reasons. First, the high reaction rate and yield depend on the homogeneity of the reaction system. At temperatures above 200 °C, 2-naphthylamine 66 and 2-naphthol 68 exceed their melting points and are in molten state. However, the catalysts zinc chloride and ammonium chloride are not melted, thus it is hard to generate a completely homogenous system. Second, the reaction scale (amount of reactants and catalysts) also affects the yield. As temperature increases, there is a greater likelihood of developing side reactions and carbonization. Besides, the loss of product in the workup step also causes a difference for the calculation of the final yield. Although, the neat reaction has some merits, the low yield is unacceptable.
3.2.3.1.2.2 Attempted synthesis of 2,2'-dinaphthylamine in solvent

Pandey and coworkers\(^7\) reported a coupling reaction of 1-substituted naphthol and aniline reacting in ethanol to generate the secondary amine with a yield of 50%. A similar synthetic route to \(65\) was proposed (Scheme 16) and performed in different solvents under different temperatures (Table 5).

First, solvents methanol, ethanol and n-butanol were used, but I didn’t observe formation of \(65\) was detected in the resulting mixture. It was thought that increasing the reaction temperature would help. Thus, the solvent was switched to DMF which has the boiling point of 152 °C. Unfortunately, DMF caused the formation of unexpected by-products instead of \(65\).
Table 5: Attempted experiments to synthesize 2,2’-dinaphthylamine

<table>
<thead>
<tr>
<th>Entries</th>
<th>Solvents</th>
<th>b.p. (°C)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>65</td>
<td>No Reaction</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>78</td>
<td>No Reaction</td>
</tr>
<tr>
<td>3</td>
<td>n-Butanol</td>
<td>118</td>
<td>No Reaction</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>152</td>
<td>Byproducts</td>
</tr>
</tbody>
</table>

Ferguson and coworkers\textsuperscript{72} reported a Cu/CuI catalyzed O-coupling reaction using aryl bromides and phenols in the presence of catalyst DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and pyridine under reflux in DMF. A modified scheme (Scheme 17) with an aryl amine replacing phenol was conducted in the presence of the same ratio of catalyst, ligand, base and solvent under reflux. However, it was not working for N-coupling, and no desired compound was observed. It seems that this is a specific reaction that only works for the formation of aryl ethers, although aryl primary amines are more reactive than phenol in a nucleophilic reaction.

![Scheme 17](image)

Scheme 17: Attempted synthesis of 2,2’-dinaphthylamine under solvent condition

Another Ullmann coupling reaction reported by Buchwald\textsuperscript{73} was attempted with some modification using 2-bromonaphthalene and 2-naphthylamine as reactants, CuI as catalyst under reflux in ethylene glycol (Scheme 18). Buchwald’s scheme works well for
aryl iodide and thiol coupling. Since the aryl amine is a reactive nucleophile similar to the aryl thiol, it was assumed that the reaction would function well for N-coupling. In fact, the reaction did work and the desired compound was observed by TLC. Unfortunately, the reaction cannot be completed even when increasing the temperature to 110 °C and prolonging the reaction time to 72 h. Unreacted 2-bromonaphthalene and 2-naphthylamine are still the major components of the product mixture. Thus, this reaction is not an effective method to produce the desired product in good yield.

Scheme 18: Attempted synthesis of 2,2'-dinaphthylamine under solvent condition

3.2.3.1.2.3 Synthesis of 2,2'-dinaphthylamine under solvent condition

Since the Ullmann coupling is not suitable for this purpose, Buchwald-Hartwig coupling was employed to achieve the same goal. Using the same reactants, but changing the catalyst from CuI to Pd$_2$(dba)$_3$ with xantphos as ligand gave a satisfactory result (Scheme 19). Reactants are completely converted to the desired product with a yield of up to 90% following Bliss’s method.$^{74}$

Scheme 19: Synthesis of 2,2'-dinaphthylamine under solvent condition
3.2.3.1.3 Attempted synthesis of 13H-dibenzo[b,i]phenothiazine

The sulfur cyclization reaction with 2,2’-dinaphthylamine 65 would give three possible isomers instead of one because there are multiple reactive sites on the naphthyl moiety (Scheme 20). Both α and β positions are available to react with sulfur to afford the according products. Among the three possible isomers, the linear one 57 is the desired product because it is the precursor of LETS compounds.

![Scheme 20: Attempted synthesis of 13H-dibenzo[b,i]phenothiazine 57:](image)

The crude $^1$H-MNR spectrum of this reaction gave little information of what compound formed since the aromatic region from 6.5 to 8.5 ppm in the spectrum showed complex signals that were hard to distinguish. However, the MALDI-TOF-MS (Figure 15) base peak closely matched the exact mass of products 57, 69 and 70. Further separation and purification was carried out using silica gel chromatography. Pure and relatively clean compounds were obtained and then characterized by $^1$H-NMR, gCOSY and MALDI-TOF-MS.
Figure 15: Crude MALIDI-TOF-MS for sulfur cyclization reaction

The $^1$H-NMR spectrum (Figure 16) represents compound 69 that was isolated from chromatography. From the spectrum, four doublets and two triplets were observed, but no singlet, which suggests no possibility of 57 and 70. Thus, we assume it might be isomer 69, of which the $^1$H-NMR signal patterns match the protons. Furthermore, the integrals fit the number of protons in the compound, six aromatic protons and one attached to the nitrogen atom. The amino proton signal might be buried in the triplet with an integral of 3H. Although the $^1$H-NMR spectrum can explain the structure quite reasonably, other characterization techniques are still needed to further confirm the structure of 69.
Figure 16: $^1$H-NMR spectrum of 69, 7H-dibenzo[c,h] phenothiazine

The mass spectrum (Figure 17) was also consistent with the formation of 69 with the molecular ion peak at 298.7. The exact mass of 69 is 299.08, suggesting loss of a proton under MALDI conditions. The base peak at 266.9 corresponds to the molecular ion minus sulfur, which means that the sulfur in this compound is cleaved under MALDI-TOF-MS conditions.
The gCOSY spectrum (Figure 17) shows the expected correlations between the protons in compound 69. The two triplets correspond to protons 2 and 3, while proton 1, 4, 5 and 6 correspond to the doublet signals. The correlations between protons 1 and 2, 2 and 3, 3 and 4, 5 and 6 perfectly match the gCOSY spectrum.
In addition to isomer 69, another compound was isolated and characterized by $^1$H-NMR and MALDI-TOF-MS. The MALDI-TOF-MS (Figure 19) shows a base peak at 298.8 which closely matches the exact mass of the isomers of 299.08. However the $^1$H-NMR spectrum (Figure 20) is complicated. In the aromatic region, singlet signals that could come from isomers 57 and 70 were observed. But the entire integral of the signals neither match molecule 57 nor 70. Considering the complexity of the $^1$H-NMR signals, it is assumed that this isolated component would be a mixture of isomers 57 and 70, in which compound 70 takes a large part because 57 is a symmetric molecule and it would give a much clear $^1$H-NMR spectrum.

**Figure 19:** MALIDI-TOF-MS spectrum for another isolated constituent
All the discussions above lead to a conclusion that this synthetic method is not an efficient for the synthesis of unsubstituted LETS compounds due to the non-specificity. Although, the bent and half-bent isomers were generated, the desired compound 57 was not isolated. Even if the compound we could purify it, the yield is so low (<5%) that it is not a practical method. Compound 57 is a precursor to the desired LETS compounds (3 synthetic steps away), so a more efficient method should be found to fulfill our purpose.

Figure 20: $^1$H-NMR spectrum for another isolated constituent
3.2.3.2 Syntheses of Unsymmetrical α-Substituted Precursor of LETS Compounds

Molecules 56, 71 and 72 (Figure 21) are phenothiazine analogs with longer wavelength absorption due to the extended conjugation within the heterocyclic ring systems.\textsuperscript{75,76} Because of their different constructions, the synthetic methods used to generate these analogs vary. Compounds 71 and 72 have been reported previously to be prepared by thionation of the corresponding isomeric N-phenyl-2-naphthylamine 73 and N-phenyl-1-naphthylamine 74 with elemental sulfur in the presence of catalytic iodine as depicted in Scheme 21.\textsuperscript{77,78} The remaining isomer 56 was synthesized by direct condensation of naphthalene-2,3-diol 75 with 2-aminobenzenethiol 43 under reflux in 1,2,4-trichlorobenzene (Scheme 21 (c)).\textsuperscript{77}

![Figure 21: The structures of phenothiazine analogs](image-url)
Compound 77 is another phenothiazine analog which can also be prepared via thionation of amine 76 with elemental sulfur in the presence of iodine as catalyst under microwave irradiation (Scheme 22).\(^7\)

From the literature information depicted above, the linear phenothiazine analogs cannot be prepared directly via thionation with elemental sulfur. Thionation of an aryl secondary amine provides compounds with sulfur attached to the \(\alpha\) position of naphthyl groups, for example the formation of 71 and 77. Only when the \(\alpha\) position is occupied by other groups will the thionation occur at the \(\beta\) position (compound 72). The results show...
that the α position in naphthalene is more reactive than the β position in the thionation reaction with elemental sulfur.

In Scheme 20, the thionation of 2,2’-dinaphthylamine 65 with elemental sulfur has been attempted and only one isomer 69 has been successfully isolated. This again, demonstrates that the α position is more reactive than the β position. If we want to produce linear dibenzophenothiazine, the α position must be blocked to afford opportunity of thionation at the β position, as in the formation of 72. Based on the reactivity and selectivity of different reaction sites, a synthetic route (Scheme 23) is proposed with the α position blocked. Synthetic details will be discussed in the following sections.

![Scheme 23: Synthetic scheme to unsymmetrical substituted precursor of LETS compounds](image)

### 3.2.3.2.1 Synthesis of 1-methoxynaphthalen-2-amine

The 1-methoxy-2-nitronaphthalene 80 can be readily accessed in high yield (Scheme 24) by direct methylation of commercially available 2-nitronaphthalen-1-ol 78. Subsequent reduction of 1-methoxy-2-nitronaphthalene 79 with conventional reducing agent palladium/carbon generates the expected compound 80.
**Scheme 24**: Synthetic route to **80**: 1-methoxynaphthalen-2-amine

![Scheme 24](image)

**3.2.3.2.2 Synthesis of 1-phenynaphthalen-2-yl 4-methylbenzenesulfonate**

In **Scheme 25**, the 1-phenynaphthalen-2-ol **83** can be directly achieved by Suzuki coupling of 1-bromonaphthalen-2-ol **81** and phenylboronic acid **82** in the presence of catalyst bis(triphenylphosphine)palladium(II) dichloride under microwave irradiation, which has been reported by Janz and Kaila. Simple tosylation of **83** affords the other substrate 1-phenynaphthalen-2-yl 4-methylbenzenesulfonate **84** which is required for the following N-coupling reaction as illustrated in **Scheme 23**. The new compound **84** was purified by flash chromatography and fully characterized by $^1$H-NMR, $^{13}$C-NMR and MALDI-TOF-MS.
Scheme 25: Synthetic route to 84: 1-phenylnaphthalen-2-yl 4-methylbenzenesulfonate

3.2.3.2.3 Attempted Synthesis of 1-methoxy-N-(1-phenylnaphthalen-2-yl) naphthalen-2-amine via N-coupling reaction

Synthetic efforts by Bliss and coworkers\(^7\) allowed easy access to 2,2’-dinaphthylamine which could be used in the thionation reaction with elemental sulfur (Scheme 19). However, when this reaction is applied to N-coupling of 80 and 84, complete conversion of starting materials was not achieved under the same reaction conditions, even when increasing the temperature to 200 °C (Scheme 26).

Scheme 26: Synthetic route to 85: 1-methoxy-N-(1-phenylnaphthalen-2-yl) naphthalen-2-amine via N-coupling reaction
Compound 84 has a large phenyl group on the α position and a bulky tosyl group on the β position, neither of which can rotate freely because of steric hindrance (Figure 22). The bulky groups may hinder the insertion of palladium catalyst and prevent the attack of the aryl amine substrate to the β position.

![Figure 22: Conformer of 84: 1-phenynaphthalen-2-yl 4-methylbenzenesulfonate](image)

To investigate the steric effect on the coupling reaction, efforts were carried out using different substrates for controls (Scheme 27). The first control showed that 1-phenynaphthalen-2-yl 4-methylbenzenesulfonate 84 and 2-naphthylamine 66 hardly reacted. Even when the temperature was increased to 200 °C and the reaction time was prolonged to 20 h, the reaction could still not be completed. In contrast, when using 87 and 80 as starting materials, complete conversion to 88 was achieved under the same conditions as depicted in Scheme 19. From the control results, we can draw a conclusion that two bulky groups on the α and β positions of the same ring in naphthalene will retard the N-coupling reaction and decrease the corresponding yields. To successfully conduct the coupling reaction, small substituents should be installed into the α position and β position of the naphthyl moiety.
3.2.3.2.4 Synthesis of 1-phenynaphthalen-2-yl trifluoromethanesulfonate

Introduction of a triflate group which is smaller than tosyl group in spatial size into the reactant system may realize the N-coupling reaction due to the reduction of steric hindrance. Thus, 1-phenynaphthalen-2-yl trifluoromethanesulfonate 89 was generated via triflation\(^\text{84}\) of 83 with triflic anhydride in the presence of pyridine as a base (Scheme 28). The new compound 89 was purified by flash chromatography and fully characterized by \(^1\)H-NMR, \(^13\)C-NMR, \(^19\)F-NMR and MALDI-TOF-MS.

Scheme 27: Synthetic routes to aryl amine

Scheme 28: Synthetic route to 89: 1-phenynaphthalen-2-yl trifluoromethanesulfonate

3.2.3.2.5 Synthesis of 1-methoxy-N-(1-phenynaphthalen-2-yl)naphthalen-2-amine
Bliss and coworkers\textsuperscript{74} have developed a method allowing easy access to N-coupling compounds with various substituents or heterocyclics. 1-Methoxy-N-(1-phenynaphthalen-2-yl)naphthalen-2-amine 85 was successfully generated with both α positions unsymmetrically substituted 80 and 89 (Scheme 29). This new compound was then utilized in next step, the thionation reaction.

![Scheme 29: Synthetic route to 85: 1-methoxy-N-(1-phenynaphthalen-2-yl)naphthalen-2-amine](image)

3.2.3.2.5 Attempted Synthesis of 12-methoxy-14-phenyl-13H-dibenzo[b,i]phenothiazine

Using the same synthetic strategy as for the formation of 13H-dibenzo[b,i]phenothiazine, the synthesis of 1-methoxy-N-(1-phenynaphthalen-2-yl)naphthalen-2-amine 90 was attempted under several heating methods and different temperatures (Scheme 30). The details are outlined in Table 6.

![Scheme 30: Attempted synthetic route to 12-methoxy-14-phenyl-13H-dibenzo[b,i]phenothiazine](image)
Table 6: Attempted experiments to synthesize 1-methoxy-N-(1-phenylnaphthalen-2-yl)naphthalen-2-amine

<table>
<thead>
<tr>
<th>Entries</th>
<th>Heating Methods</th>
<th>T (°C)</th>
<th>Time</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oil Bath</td>
<td>200</td>
<td>20 min</td>
<td>Unreacted SM (majority) Unidentified by-products</td>
</tr>
<tr>
<td>2</td>
<td>Oil Bath</td>
<td>200</td>
<td>2 h</td>
<td>Unreacted SM Unidentified by-products (majority)</td>
</tr>
<tr>
<td>3</td>
<td>Oil Bath</td>
<td>222</td>
<td>15 min</td>
<td>Unreacted SM (majority) Unidentified by-products</td>
</tr>
<tr>
<td>4</td>
<td>Microwave</td>
<td>233</td>
<td>15 min</td>
<td>Unreacted SM (majority) Unidentified by-products</td>
</tr>
<tr>
<td>5</td>
<td>Sand Bath</td>
<td>275-300</td>
<td>2 h</td>
<td>Decomposed</td>
</tr>
</tbody>
</table>

The results obtained from several characterization methods such as MS, TLC and $^1$H-NMR indicated no reaction. The majority of starting material was left unreacted and unidentified by-products were formed when the temperature was kept around 200 °C. Thus, it appears that the α position in naphthylamine is vastly favored in the reaction with sulfur as compared to the β position. Also, aryl amine 85 is vulnerable to high temperatures. As shown in Table 6, the starting material was decomposed when the temperature was increased to 300 °C. Moreover, the methoxy moiety in this system might lead to side reactions due to the reactivity of the heteroatom oxygen.

3.2.3.3 Synthesis of Symmetrical α-Substituted Precursor of LETS Compounds

Since hetero substituents are apparently not a good choice for blocking the α position, a phenyl group was selected as an alternative. Phenyl substituent has been used to increase the solubility of acenes.85,86,87 It follows that the solubility will also be enhanced if a phenyl substituent is introduced to LETS compounds.
3.2.3.3.1 Synthesis of 1-phenynaphthalen-2-amine

The strategy to synthesize phenyl substituted 2-naphthylamine 92 started by methylation of commercially available starting material 78 with dimethyl sulfate in refluxing acetone. This reaction was followed by nucleophilic aromatic substitution of 79 with Grignard reagent phenylmagnesium bromide. Subsequent reduction of 2-nitro-1-phenynaphthalene 91 with Pd/C generated the expected compound 92 (Scheme 31), which was fully characterized by $^1$H-NMR, $^{13}$C-NMR and MALDI-TOF-MS.

![Scheme 31: Synthetic route to 1-phenynaphthalen-2-amine](image)

3.2.3.3.2 Synthesis of bis(1-phenynaphthalen-2-yl)amine

The synthesis of bis(1-phenynaphthalen-2-yl)amine 93 was achieved in high yield using Bliss and coworkers’s protocol (Scheme 32). This new compound was purified by chromatography and fully characterized by $^1$H-NMR, $^{13}$C-NMR and MALDI-TOF-MS.
3.2.3.3.2 Attempted Synthesis of 12,14-diphenyl-13H-dibenzo[b,i]phenothiazine

This thionation reaction was attempted under relatively harsh conditions in a microwave reactor with molten sulfur and a catalytic amount of iodine (Scheme 33). Only unreacted starting materials and by-products were separated from the crude product mixture by chromatography. This neat condition led to many complex side reactions because larger molecular weight by-products signals were observed in the mass spectrum. Again, the thionation reaction with sulfur is not specific for cyclization of bis(1-phenynaphthalen-2-yl)amine 93 at β position. Therefore, no desired compound was generated from this reaction after several attempts (Table 7).
Table 7: Attempted experiments to synthesize 12,14-diphenyl-13H-dibenzo[b,i]phenothiazine

<table>
<thead>
<tr>
<th>Entries</th>
<th>Heating Methods</th>
<th>T (°C)</th>
<th>Time</th>
<th>Results</th>
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</thead>
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<td>1</td>
<td>Microwave</td>
<td>180</td>
<td>30 min</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Unidentified by-products</td>
</tr>
<tr>
<td>2</td>
<td>Microwave</td>
<td>200</td>
<td>30min</td>
<td>Unreacted SM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Unidentified by-products</td>
</tr>
</tbody>
</table>

3.2.4 Second Method to Synthesize the Precursor of LETS Compounds

As discussed in chapter one, the second method widely used to generate phenothiazine is a C-S and C-N coupling reaction. Based on Zeng’s protocol, phenothiazine 38 is generated by beginning with 2-aminobenzenethiol 52 and 1-bromo-2-iodobenzene 53 to conduct the coupling reaction in the presence of copper iodide catalyst (Scheme 6). VanAllan and coworkers reported a protocol to synthesize 12H-benzo[b]phenothiazine 56 using 2-aminobenzenethiol 52 and naphthalene-2,3-diol 75 which were heated to reflux in 1,2,4-trichlorobenzene (Scheme 21 (c)). Both protocols provide promise for generating 13H-dibenzo[b,i]phenothiazine by a coupling reaction employing 3-aminonaphthalene-2-thiol and 2,3-substituted naphthalene (Scheme 34).

![Scheme 34: Second proposed scheme to form 13H-dibenzo[b,i]phenothiazine](image-url)
Compound 75 is a commercially available compound. The 2,3-ditosynaphthalene 96 and ditriflate 97 can be easily accessed from 75 by tosylation and triflation reactions, respectively. The readily available synthetic strategies for 2,3-dibromonaphthalene 98 have been reported by Bowles and Anthony, and Schlosser and coworkers.

The synthetic approaches for 95 that have ever been reported are few. Thus, the synthesis of compound 57 exclusively relies on the generation of 95, which is the key step to realize the coupling reaction.

3.2.4.1 First Attempted Synthesis of 3-aminonaphthalene-2-thiol

3.2.4.1.1 Proposed Synthetic route

Elemental sulfur has been frequently employed as an electrophile to react with ortho-lithiated intermediates to generate aryl thiols. Pardoe and coworkers have reported a straightforward method to synthesize aryl thiol 100 beginning with 2-naphthaldehyde 99 via directed ortho-lithiation (Scheme 35). Ortho-lithiation is a useful method and is widely used in organic synthesis.
Based on Pardoe’s protocol, a modified synthetic route to generate the desired compound 3-aminoaryl thiol was proposed, starting with α-blocked 2-nitronaphthalene which can prevent the formation of α-lithiated intermediates and generate the β-lithiated intermediates (Scheme 36). This strategy proceeds through ortho-lithiation in the presence of tetramethylethylenediamine (TMEDA) which helps accelerate the metalation reaction, followed by sulfur quenching with lithiated intermediate to afford the thiol. Subsequent reduction of the nitro group generates the amino aryl thiol.

This lithiation method is considered promising due to the possibility that the negatively charged oxygen on the nitro group can stabilize the lithiated intermediate by coordinating with lithium atom (Figure 24). Like the aldehyde, the carbonyl group functions as a directed metatation group (DMG) by generating the -OLi moiety first before the formation of lithiated intermediate (Figure 25).
3.2.4.1.2 Attempted Synthesis of α-blocked 3-aminonaphthalene-2-thiol

The metalation reaction was undertaken following Pardoe’s protocol using 1-methoxy-2-nitronaphthalene 79. Instead of generating aryl thiol 101, the n-butyl lithium reacted with the methoxy group and afforded 1-butyl-2-nitronaphthalene 102 (Scheme 37). Apparently, the ortho-proton is much less reactive than the methoxy group when reacting with organolithium reagent.
Since a new α-blocked compound was synthesized, it was undertaken the ortholithiation and sulfur substitution under the same condition (Scheme 38). However, no sign of the desired product 103 was detected in the mass spectrum.

In order to determine the exact reasons that led to the failure of this reaction, control studies (Scheme 39) were performed using 2-nitronaphthalene as starting material under similar condition as illustrated in Scheme 37. For the control studies, D₂O was
employed to quench the lithiated intermediate. In both reactions, no desired compounds were obtained but the same resulting mixture was generated, as determined by TLC, MS and $^1$H-NMR. The results indicate that the anticipated intermediate 105 was not formed in the first step. In this case, the second step makes no difference.

Scheme 39: Control studies of lithiation reaction and the intermediate structure

Although the nitro group was expected to be a good DMG, it turned out that no desired result was obtained and further literature searching shows that no nitro group has ever been reported as a DMG. One possible explanation to the failure of this reaction is reaction between the nitro group and the organolithium reagent. Therefore, the nitro group could not be used as a good DMG.

3.2.4.2 Second Attempted Synthesis of 3-aminonaphthalene-2-thiol

A variety of substituents, including CONR$, CONR_2$, SO$_2$NR$, SO_2$NR$_2$, CONR$, OCH_3$, NR$_2$, CF$_3$, CH$_2$NR$_2$, CH$_2$CH$_2$NR$_2$, Cl, F have been reported to be strong or moderate DMGs. The relative reactivity and rates in directed metalation are listed in Table 8.
The expected compound 3-aminonaphthalene-2-thiol 95 has two functional groups: a primary amino group and a thiol. In order to synthesize it, priority should be given to those starting materials having similar functional groups. In Table 8, the –N\textsuperscript{COR}, -N‘COOR, NR\textsubscript{2} and –S\textsuperscript{–} are particularly useful in the project because these groups either have a nitrogen or a sulfur moiety, which could be converted to primary amino and thiol groups.

A number of publications have reported on amides\textsuperscript{95f,97} and amines\textsuperscript{98,99} as DMGs. Therefore, new synthetic metalation schemes of this type were investigated.

2-Naphthylamine 66 was first treated with an organolithium reagent to form an ortho-lithiated intermediate, followed by sulfur quenching (Scheme 40). However, compound 95 was not synthesized because 66 showed no reactivity towards the lithiation reaction, and 90\% of starting material 66 was recovered by chromatography.
Scheme 40: Synthetic scheme to 3-aminonaphthalene-2-thiol

One possible explanation for the failure of thionation is that the -NH$_2$ group is not a good DMG. Hence, a stronger DMG-substituted compound 108 was synthesized and the same lithiation and sulfur quenching were attempted (Scheme 41). Again, no thiol product was detected and by-products were formed as evidenced by TLC and the mass spectrum.

Scheme 41: Synthetic scheme to 3-aminonaphthalene-2-thiol

Control studies were also carried out using D$_2$O and H$_2$O to quench the lithiated intermediate, and neither desired deuterated molecule 111 nor starting material 108 were detected (Scheme 42). The resulting mixture of these two reactions gave similar mass and crude $^1$H-NMR spectra. All of these experimental results suggest no formation of a lithiated intermediate and thionation with elemental sulfur was not achieved. This method is not working for the formation of an amino aryl thiol.
Scheme 42: Control studies of lithiation reaction and the intermediate structure

3.2.4.3 Third Attempted Synthesis of 3-aminonaphthalene-2-thiol

Thiol is considered to be a relatively weak DMG, but it has been widely used to synthesize a number of ortho-substituted aryl thiols.\textsuperscript{100,101} Block and coworkers\textsuperscript{101} reported a methalation reaction starting with 2-naphthenethiol 112 to generate 3-(trimethylsilyl)-2-naphthenethiol 114 (Scheme 43).

Scheme 43: Synthetic scheme to 3-(Trimethylsilyl)-2-naphthenethiol

To get 3-aminonaphthalene-2-thiol 95, nitrating agent nitronium tetrafluoroborate was selected to react with the lithiated intermediate (Scheme 44). However, the one-pot, two-step reaction shows no reaction between nitronium tetrafluoroborate and lithiated intermediate 113. Instead of obtaining the desired compound 107, an oxidized product difulfide 115 was generated.
To rule out the possibility that the nitrating agent was oxidizing the 2-naphthalenethiol, another control experiment was carried out. The intermediate was quenched with H₂O before adding nitrating agent (Scheme 45). Compound 115 was again isolated by chromatography. It turned out that the disulfide was formed in the lithiation step, which indicates that the 2-naphthalenethiol can be easily oxidized even in the presence of oxygen.

Three reasons might be responsible for the failed formation of compound 95. One is the existence of water in the reaction system because the reactive protons in water can quench the organolithium reagent or intermediate and deactivate them. No formation of lithiated intermediate might be the second reason. If no reactive intermediate was formed, it is not possible for the nitrating agent to substitute for the lithium ion. If these two

Scheme 44: Synthetic scheme of 3-nitronaphthalene-2-thiol

Scheme 45: Control experiment to test the formation of 115 in the lithiation step
reasons can be ruled out, a lack of reactivity of nitronium tetrafluoroborate may account for the failure of the strategy.

In order to determine whether the water or the formation of intermediates is responsible for the failure, all the liquid reagents were dried with molecular sieves and solid reagents were dried under vacuum before being used in the experiments. To make sure that the lithiated intermediate is formed, widely used electrophile iodomethane was utilized in a control study. The experimental results showed that the nitration was still not working although the reagents were dried before use. Therefore, the water in the system could not be responsible for the failure of reaction. Upon changing the electrophile to iodomethane, the reaction worked. However the desired compound was not obtained (Scheme 46). Not only was the β proton removed, but protons on other positions were also removed and replaced by methyl groups, as shown in the $^1$H-NMR spectrum (Figure 26). Several signals around 2.5 ppm suggest that the lithiation shows no selectivity towards naphthalene. In summary, it is not the water or lithiated intermediate, but the nitrating agent nitronium tetrafluoroborate that is responsible for the failure of nitration.

**Scheme 46:** Control studies to figure out the unsuccessful reasons
Figure 26: $^1$H-NMR spectrum of control study

3.2.5 Third Method to Synthesize the Precursor of LETS Compounds

3.2.5.1 Proposed Synthetic Route to 16$H$-dinaphtho[2,3-b:2',3'-i]phenothiazine

Like 13$H$-dibenzo[b,i]phenothiazine 57, 16$H$-dinaphtho[2,3-b:2',3'-i]phenothiazine 124 can be treated as an extended phenothiazine which is modified with symmetric naphthyl groups on both sides. Based on this theory, a new method to synthesize molecule 124 is proposed (Scheme 47). This route begins with a double Friedel-Crafts acylation of phenothiazine 38 with two equivalents of phthalic anhydride 117 in the presence of aluminum trichloride catalyst. The resulting bis-ketoacid of phenothiazine 118 will be reduced to diacid 119 using zinc-dust. Treating diacid 119 with concentrated sulfuric acid will offer the bent bis-keto compound 120. Subsequent
reduction of ketone and aromatization will afford the compound 8H-dinaphtho[2,3-c:2',3'-h]phenothiazine 121.

The bent seven-ring compound 121 is expected to be the major product but not the desired one. In order to generate linear compound 124, modifications should be applied before the cyclization step using concentrated sulfuric acid. By oxidizing the sulfide to sulfone 122, the directing effect of the functional group potentially prevents the cyclization occurring ortho to the sulfide leading, potentially, to the formation of linear bis-keto compound 123. It will be converted to the desired compound 124 by subsequent reduction of the sulfone with sodium borohydride and aromatization using tin(II) chloride in acetic acid.
Scheme 47: Proposed synthetic scheme of 16H-dinaphtho[2,3-b:2',3'-i]phenothiazine

3.2.5.2 Attempted Synthesis of 2,2'-(10H-phenothiazine-3,7-dicarbonyl)dibenzoic acid

To carry out the Friedel-Crafts acylation reaction (Scheme 48), several entries were performed (Table 9). First, a mixture of the starting material 38 and 117 was refluxed in carbon disulfide. According to the MS and $^1$H-NMR, there was a lot of unreacted starting material phenothiazine as well as unidentified by-products. In order to make sure all starting material can be converted to product, the solvent was changed to
DCE and the temperature increased to 84 °C. Again, the reaction led to unreacted starting material and by-products. It is assumed that excess anhydride might lead to side reactions. Thus, the ratio of starting material was changed, decreasing the phthalic anhydride to 2.5 equivalents, and increasing the temperature to 120 °C. Although the desired signal was not observed, M+23 and M+39 signals were observed in the mass spectrum.

Scheme 48: Synthetic scheme to 2,2’-(10H-phenothiazine-3,7-dicarbonyl)dibenzoic acid

<table>
<thead>
<tr>
<th>Entries</th>
<th>38(eq.)</th>
<th>117(eq.)</th>
<th>AlCl₃(eq.)</th>
<th>Solvent</th>
<th>Temp(°C)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5</td>
<td>12.5</td>
<td>CS₂</td>
<td>47</td>
<td>38 + unidentified byproducts</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>5</td>
<td>12.5</td>
<td>DCE</td>
<td>84</td>
<td>38 + unidentified byproducts</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2.5</td>
<td>7.2</td>
<td>PhNO₂</td>
<td>120</td>
<td>38 + unidentified byproducts MS [M+23]⁺,[M+39]⁺ (very weak)</td>
</tr>
</tbody>
</table>

In the above three experiments, phthalic anhydride is in excess and phenothiazine is the limiting reagent. In order to determine whether the acylation reaction occurs or not, two more control experiments were carried out in DCE under reflux with phenothiazine 38 as the excess reactant (Scheme 49) (Table 10).
In both cases, a molecular ion signal of 125 was observed although it was very weak. The molecular ion peaks were only observed when a sulfur matrix was used. When no sulfur employed, no molecular ion was observed in the mass spectrum.

![Scheme 49: Synthetic scheme to 2-(10H-phenothiazine-3-carbonyl)benzoic acid](image)

**Table 10:** Attempted experiments of Friedel-Crafts acylation – change the ratio

<table>
<thead>
<tr>
<th>Entries</th>
<th>38(eq.)</th>
<th>117(eq.)</th>
<th>AlCl₃(eq.)</th>
<th>Solvent</th>
<th>Temp(°C)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>DCE</td>
<td>84</td>
<td>38 + unidentified by-products + possible product MS: M⁺(very weak)</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1</td>
<td>12</td>
<td>DCE</td>
<td>84</td>
<td>38 + unidentified by-products + possible product MS: M⁺(very weak)(125)</td>
</tr>
</tbody>
</table>

Since phthalic anhydride did not function well as an electrophile, a stronger electrophilic reagent phthaloyl dichloride 127 was employed in Friedel-Crafts acylations (Scheme 50) with either CS₂ or DCE as solvent (Table 11). Again, the desired compound 118 was not successfully synthesized.
Scheme 50: Synthetic scheme to 2-(10H-phenothiazine-3-carbonyl)benzoic acid

Table 11: Attempted experiments of Friedel-Crafts acylation with phthaloyl dichloride

<table>
<thead>
<tr>
<th>Entries</th>
<th>38(eq.)</th>
<th>127(eq.)</th>
<th>AlCl₃(eq.)</th>
<th>Solvent</th>
<th>Temp(°C)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
<td>7.2</td>
<td>CS₂</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>38 (major) unidentified byproducts</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
<td>7.2</td>
<td>DCE</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>38 (major) unidentified byproducts</td>
</tr>
</tbody>
</table>

Because the above reaction with AlCl₃ as catalyst is not working, sulfuric acid, another common catalyst for acylation reactions, was applied into this reaction (Scheme 51). Again, the desired compound 128 was not detected by mass spectrometry. Instead, two by-products 129 and 130 from the oxidation of phenothiazine 38 were formed (Figure 27).

Scheme 51: Synthetic scheme to 2,2’-(10H-phenothiazine-2,8-dicarbonyl)dibenzoic acid
It seemed that phthalic anhydride 117 was not involved in this Friedel-Craft acylation reaction. A control study with phenothiazine 38 in concentrated sulfuric acid was carried out at 100 °C for 24 hours (Scheme 52). Products 129 and 130 were generated and fully characterized by NMR, MS, UV-Vis, and IR.

Compound 129 drew our attention because of its bright red color and broad, intense absorbance in UV-Vis spectrum (Figure 28). The $\lambda_{\text{max}}$ of 129 in chloroform is 502 nm, which is larger than the three-numbered ring aromatic compound anthracene (378 nm). If the conjugation can be extended, it would exhibit even smaller HOMO-LUMO gap and larger $\lambda_{\text{max}}$ of absorbance. Thus, a Knoevenagel condensation route which aimed at the extension of conjugation in 129 was proposed and proceeded (Scheme 53). Dimethyl malonate 131 and phenothiazine 38 in sodium methoxide and
methanol under reflux was supposed to generate dimethyl 2-(3H-phenothiazin-3-ylidene)malonate. However, no desired compound signal was observed in mass spectrum.

Figure 28: UV-Vis spectrum of 3H-phenothiazin-3-one 129

Scheme 53: Attempted synthesis of dimethyl 2-(3H-phenothiazin-3-ylidene)malonate 132

3.2.6 Fourth Method to Synthesize the Precursor of LETSs

3.2.6.1 Attempted Syntheses of Unsubstitued Precursor of LETS Compounds in Solvent Condition
Since the thionation with elemental sulfur under neat conditions did not offer satisfactory results, the thionation reaction performed in solvent 1,2,4-trichlorobenzene was carried out with elemental sulfur and catalytic iodine. (Scheme 54)

In the solventless thionation reaction, the compound 69 was isolated and fully characterized by NMR, gCOSY and MS, although with a low yield of 7%. In addition to 69, isomers 57 and 70 might have been generated after careful interpretation of the $^1$H-NMR and MS. However, the pure compounds 57 and 70 were not isolated from column chromatography due to the similar polarities and low yield of the two isomers.

Unlike the neat reaction, the thionation in 1,2,4-trichlorobenzene under 180-190 °C for 24 h gave a much higher yield of compound 69 (nearly 100%) but no observation of isomers 57 or 70. It means that this reaction is a regiospecific one leading to the formation of the bent isomer. The $\alpha$ position is much more reactive than $\beta$ position in the naphthyl moiety. The compound 69 was fully characterized by NMR, gCOSY, ATR-IR and MS.
3.2.6.2 Synthesis of Symmetrical $\alpha$-Substituted Precursor of LETS Compounds

Although none of the desired compound 57 was generated, the thionation reaction in solvent to produce the precursor of LETS compounds gave a high yield. The $\alpha$ site in the naphthyl group seemed more reactive than the $\beta$ site and the reaction took place firstly on $\alpha$ sites because they were available. Therefore, in order to make sure the sulfur attached to $\beta$ position, the $\alpha$-substituted compound 93 was used as starting material for the thionation reaction in solvent (Scheme 55). Several experiments were carried out under different conditions (Table 12).
Scheme 55: Synthetic route to 12,14-diphenyl-13H-dibenzo[b,i]phenothiazine

Table 12: Experiments to synthesize 1-methoxy-N-(1-phenylnaphthalen-2-yl)naphthalen-2-amine

<table>
<thead>
<tr>
<th>Amine (equiv.)</th>
<th>Sulfur (equiv.)</th>
<th>Iodine (equiv.)</th>
<th>Solvent</th>
<th>Heating Methods</th>
<th>T (°C)</th>
<th>Time</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>Catalytic amount</td>
<td>Trichloro benzene</td>
<td>Oil Bath</td>
<td>186</td>
<td>24 h</td>
<td>SM (majority) PDT signal in MS</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Catalytic amount</td>
<td>Trichloro benzene</td>
<td>Oil Bath</td>
<td>206</td>
<td>15 h</td>
<td>SM (majority) PDT signal in MS</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Catalytic amount</td>
<td>Trichloro benzene</td>
<td>Microwave</td>
<td>186</td>
<td>30 min</td>
<td>SM (majority) PDT signal in MS</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>Catalytic amount</td>
<td>Trichloro benzene</td>
<td>Microwave</td>
<td>186</td>
<td>30 min</td>
<td>SM (majority) PDT signal in MS</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Catalytic amount</td>
<td>Trichloro benzene</td>
<td>Microwave reflux</td>
<td>30 min</td>
<td></td>
<td>SM (majority) PDT signal in MS</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Catalytic amount</td>
<td>Trichloro benzene</td>
<td>Microwave</td>
<td>186</td>
<td>2 h</td>
<td>SM (majority) PDT signal in MS</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Catalytic amount</td>
<td>Xyleno</td>
<td>Microwave</td>
<td>186</td>
<td>30 min</td>
<td>SM (majority) PDT signal in MS</td>
</tr>
</tbody>
</table>

Although the majority of starting material (98%) was unreacted and recovered in all cases, signal corresponding to the desired compound was observed in the mass spectrum of crude product (Figure 29). A chromatography technique was applied to isolate the desired compound, but was not successful. The $^1$H-NMR spectrum of the isolated component was not clear enough to identify the structure due to impurities and low yield (only 1.3 mg) (Figure 30). However, the mass spectrum indicated a stronger signal corresponding to the desired compound (Figure 31). The $\lambda_{\text{max}}$ in the UV-Vis spectrum in CHCl$_3$ is at 334 nm (Figure 32) which is not far away from the maximum
absorption of phenothiazine at 315 nm (Table 2). All these studies suggest that the desired compound was obtained although it is not an efficient reaction. Further investigation and modification should be explored to enhance the yield.

**Figure 29:** The mass spectrum of crude compounds for thionation reaction in solvent

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**Figure 30:** The $^1$H-NMR spectrum of isolated component in thionation reaction
Figure 31: The mass spectrum of isolated component in thionation reaction

Figure 32: The UV-Vis spectrum of isolated component in thionation reaction
CHAPTER 4

CONCLUSIONS

A series of novel compounds, linearly extended thiazinium salts (LETS), with structures similar to methylene blue were designed due to the fact that methylene blue has several characteristics consistent with n-type semiconductors. The compound 3,9-bis(dimethylamino)dibenzo[b,i]phenothiazin-6-ium chloride is a key target. Resembling methylene blur but with five linearly fused rings, this LETS compound is calculated to have a small HOMO-LUMO gap of 0.76 eV and a maximum absorption of light around 790 nm.

Four synthetic schemes were designed to prepare LETS compounds. A solid-state thionation reaction with elemental sulfur, a coupling reaction, a Friedel-Crafts acylation / ring-closing reaction and solution-phase thionation reaction were all investigated as a means to generate a precursor of LETS compounds, 13H-dibenzo[b,i]phenothiazine. Although the pure compound was not obtained, the thionation reaction in solvent shows promise. Once this key intermediate is synthesized, oxidative aromatization, using a reagent like I$_2$ will afford the first LETS compound.
CHAPTER 5
EXPERIMENTAL SECTION

5.1 Analytical Instrumentation and Approach

$^1$H NMR Spectra

$^1$H NMR Spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 399.768 MHz or a Varian INOVA 500 FT-NMR operating at 499.763 MHz. All chemical shift ($\delta_H$) values are reported in parts per million (ppm) relative to (CH$_3$)$_4$Si (TMS) unless otherwise noted.

$^{13}$C NMR Spectra

$^{13}$C NMR Spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 100.522 MHz or a Varian INOVA 500 FT-NMR operating at 125.666 MHz. All chemical shift ($\delta_C$) values are reported in parts per million (ppm) relative to (CH$_3$)$_4$Si (TMS) unless otherwise noted.

gCOSY Spectra

gCOSY Spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 399.768 MHz. All chemical shift ($\delta_C$) values are reported in parts per million (ppm) relative to (CH$_3$)$_4$Si (TMS) unless otherwise noted.
\textbf{\textsuperscript{19}F NMR Spectra}

\textsuperscript{19}F NMR Spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 376.376 MHz. All chemical shift ($\delta_C$) values are reported in parts per million (ppm) using CDCl\textsubscript{3} as solvent.

\textbf{MALDI-TOF Mass Spectrometry}

Matrix assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF-MS) were run on a Shimadzu Kratos Axima-CFR mass spectrometer in positive ion mode and reflection mode. Some of the spectra were obtained using sulfur as the matrix.

\textbf{Chromatography}

Sand was obtained from Fisher Scientific Co.

Silica Gel (230-400 mesh) was obtained from Natland International Co.

Thin Layer Chromatography Plates were obtained from Fisher Scientific Co.

\textbf{Celite, Filter Agent} was obtained from Aldrich Chemical Co.

Chromatograms were visualized under UV light. (254 nm and 365 nm)

\textbf{UV-Vis Spectrometry}

UV-Vis spectra were obtained on Nikolet Evolution 300 Spectrometer using 1 cm quartz cell.
Fluorescence Spectrometry

Fluorescence spectra were obtained on Varian Cary Eclipse Fluorometer using 1 cm quartz cell.

Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

IR spectra were obtained on Thermo Scientific Nicolet iS10 with solid samples.

5.2 Solvents and Reagents

*All solvent were used directly without further purification unless otherwise noted.*

Anhydrous solvents of dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), toluene, N,N-dimethyl formamide (DMF), diethyl ether (Et₂O) and methanol (MeOH) were obtained by passing through a silica column in the Innovative Technology Inc. solvent delivery system.

**Acetic Acid** (CH₃COOH) was obtained from VWR Chemical Co.

**Acetone** (CH₃COCH₃) was obtained from Pharmco.

**Benzene** (C₆H₆) was obtained from EM science.

**n-Butanol** (C₄H₉OH) was obtained from Aldrich Chemical Co.

**Carbon Disulfide** (CS₂) was obtained from EM science.

**Chloroform** (CHCl₃) was obtained from Fisher Scientific Co.

**Cyclohexane** (C₆H₁₂) was obtained from Alfa Aesar Chemical Co.

**Deuterated NMR Solvents** was obtained from Cambridge Isotope Laboratories.
Dichloromethane \((\text{CH}_2\text{Cl}_2)\) was obtained from Fisher Scientific Co.

Dichloromethane \((\text{C}_2\text{H}_4\text{Cl}_2)\) was obtained from Alfa Aesar Chemical Co.

Ethane-1,2-diol \((\text{HOCH}_2\text{CH}_2\text{OH})\) was obtained from Mallinckrodt Pharmaceuticals.

\textit{N,N}-dimethylformamide \(((\text{CH}_3)_2\text{NC(O)H})\) was obtained from Fisher Scientific Co.

Dimethyl Sulfoxide \(((\text{CH}_3)_2\text{SO})\) was obtained from Alfa Aesar Chemical Co.

\textit{1,4-Dioxane} \(((\text{CH}_2\text{CH}_2)_2\text{O}_2)\) was obtained from Aldrich Chemical Co.

Ethanol \((\text{CH}_3\text{CH}_2\text{OH})\) was obtained from Pharmco Products Inc.

Ethyl Acetate \((\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3)\) was obtained from Fisher Scientific Co.

Hexane \((\text{C}_6\text{H}_{14})\) was obtained from Fisher Scientific Co.

Nitrobenzene was obtained from TCI Co.

Methanol \((\text{CH}_3\text{OH})\) was obtained from Fisher Scientific Co.

\textit{2-Propanol} \((\text{C}_3\text{H}_7\text{OH})\) was obtained from Pharmco Products Inc.

Pyridine \((\text{C}_5\text{H}_5\text{N})\) was obtained from Aldrich Chemical Co.

Tetrahydrofuran \((\text{C}_4\text{H}_8\text{O})\) was obtained from Fisher Scientific Co.

\textbf{Reagents}

Aluminum Chloride was obtained from Alfa Aesar Chemical Co.

Aluminum Foil \((\text{Al}^0)\) was obtained from Reynolds.

\textit{Amberlite® IRA-400 chloride form} was obtained from Aldrich Chemical Co.

Ammonium Chloride \((\text{NH}_4\text{Cl})\) was obtained from Fisher Scientific Co.

Ammonium Hydroxide \((\text{NH}_3\cdot\text{H}_2\text{O})\) was obtained from BDH Chemical Co.

\textit{4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene} (Xantphos) was obtained from Aldrich Chemical Co.
Bis(triphenylphosphine)palladium(II) dichloride (PdCl$_2$(PPh$_3$)$_2$) was obtained from Acros Organics Co.

2-Bromonaphthalene was obtained from Aldrich Chemical Co.

1-Bromo-2-naphthol was obtained from Aldrich Chemical Co.

n-Butyl Lithium was obtained from Aldrich Chemical Co.

Copper Powder (Cu$^0$) was obtained from Aldrich Chemical Co.

Copper(I) Iodide (CuI) was obtained from Fisher Scientific Co.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Aldrich Chemical Co.

Deuterium Oxide was obtained from Cambridge Isotope Laboratories.

Dimethylamine was obtained from Alfa Aesar Chemical Co.

Dimethyl Sulfate ((CH$_3$O)$_2$SO$_2$) was obtained from Sigma-Aldrich Chemical Co.

Diphenylamine was obtained from Fisher Scientific Co.

Di-tert-butyl dicarbonate was obtained from Aldrich Chemical Co.

4-Hydroxy-L-proline (C$_5$H$_9$NO$_3$) was obtained from Lancaster Synthesis, Inc.

Hydrogen (H$_2$) was obtained from Airgas Inc.

Hydrogen Chloride (HCl) was obtained from EM Science.

Iodine (I$_2$) was obtained from Aldrich Chemical Co.

Iodomethane was obtained from Aldrich Chemical Co.

4-Methylbenzenesulfonyl chloride was obtained from Alfa Aesar Chemical Co.

Molecular Sieves was obtained from EMD Chemical Co.

2-Naphthol was obtained from Aldrich Chemical Co.

2-Naphthylamine was obtained from Sigma-Aldrich Chemical Co.

2-Nitronaphthalene was obtained from Aldrich Chemical Co.
2-Naphthalenethiol was obtained from Alfa Aesar Chemical Co.
2-Nitro-1-naphthol was obtained from Acros Organics Co.
Nitronium tetrafluoroborate was obtained from Alfa Aesar Chemical Co.
Palladium on activated carbon (10% Pd/C) was obtained from Aldrich Chemical Co.
Phenylboronic acid (PhB(OH)₂) was obtained from Aldrich Chemical Co.
Phenylmagnesium Bromide (PhMgBr) was obtained from Aldrich Chemical Co.
Phenylthiazine was obtained from Aldrich Chemical Co.
Phthalic acid was obtained from TCI Co.
Phthalic anhydride was obtained from Aldrich Chemical Co.
Potassium Carbonate (K₂CO₃) was obtained from Fisher Scientific Co.
Potassium Hydrate (KOH) was obtained from EM Science.
Potassium Phosphate (K₃PO₄) was obtained from Acros Organics Co.
Sodium Bisulfite (NaHSO₃) was obtained from EM Science.
Sodium Chloride (NaCl) was obtained from J. T. Baker Chemical Co.
Sodium hydroxide (NaOH) was obtained from EM Science.
Sodium Sulfate (Na₂SO₄) was obtained from J. T. Baker Chemical Co.
Sulfur (S₈) was obtained from EMD Chemical Co.
Sulfurous dichloride was obtained from Aldrich Chemical Co.
Sulfuric Acid (H₂SO₄) was obtained from J. T. Baker Chemical Co.
1,2,4-Trichlorobenzene was obtained from Alfa Aesar Chemical Co.
N,N,N',N'-Tetramethylethane-1,2-diamine (TMEDA) was obtained from Aldrich Chemical Co.
Trifluoromethanesulfonic anhydride was obtained from Oakwood Products, Inc.
Tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) was obtained from Aldrich Chemical Co.

Zinc Chloride (ZnCl$_2$) was obtained from Alfa Aesar Chemical Co.

5.3 Sytheses

General Considerations

Unless otherwise noted, all reactions were carried out in oven-dried glassware and stirred with Teflon-coated magnetic stir bars. All routine solvent evaporations were conducted on a standard rotary evaporator using vacuum pump.

Phenothiazine

Diphenylamine (167 mg, 1.00 mmole) was mixed with sulfur (69 mg, 2.16 mmole) and iodine (2.7 mg, 0.01 mmole) in sealed tube and heated in sand bath at 180-200°C for 30mins. The mixture was cooled down and dissolved in ethyl acetate (5 mL) and DI (deionized) water (10 mL), then filtered to separate the filter cake. The organic solution was separated and washed with brine (10 mL) once and dried with sodium sulfate. The filtrate was treated with vacuum evaporation after removing the sodium sulfate by filtration. The crude product was further dried under vacuum yielding 125 mg of phenothiazine. Light yellow powder, yield: 63.6%; 1H-NMR (400MHz; CDCl$_3$; Me$_4$Si) $\delta_H$: 7.00 (4H, m, 4 × CH), 6.83 (2H, t, 2 × CH), 6.57 (2H, d, 2 × CH), 5.80 (1H, s, NH)

Phenothizin-5-ium tetraiodide hydrate
A solution of phenothiazine (500.2 mg) in chloroform (17.5 mL) in round bottom flask was placed in water bath at 0-5 °C with stirring and treated dropwise within an hour with a solution of iodine (1913.8 mg, 7.50 mmoles) in chloroform (40 mL). The mixture was stirred at the same temperature for an additional 30 min. The precipitate formed was filtrated and washed with chloroform (10 × 20mL) until the filtrate became colorless. The final precipitate was kept under vacuum for several hours until no further weight loss was observed. 1.406 g product was obtained. Black powder, yield: 77.4%. (It is hard to characterize due to its poor solubility, so using it directly to next step, the addition of amino groups.)

**3,7-Bis(dimethylamino)phenazothiazin-5-nium iodide**

A solution of phenothiazin-5-ium teraiodide hydrate (521.3 mg, 0.72 mmole) in methanol (10 mL) was treated dropwise with a solution of dimethylamine in methanol (4.7 mL, 2M). The mixture was stirred at room temperature for 3.5 hours. The precipitate was filtered and washed with methanol (10 × 10mL). The filtrate was evaporated and recrystallized with methanol. Finally 58.9 mg 4 was obtained. Black powder, yield: 20%; UV-Vis (MeOH), $\lambda_{max}$: 653nm; $^1$H-NMR (400MHz; CD$_3$OD) $\delta_H$: 7.97 (2H, d, 2 × CH), 7.49 (2H, dd, 2 × CH), 7.37 (2H, d, 2 × CH), 3.40 (12H, s, 4 × CH$_3$); MS (MALDI-TOF) for C$_{16}$H$_{18}$IN$_3$S, C$_{12}$H$_{18}$N$_3$S$^+$ requires 284.12, signal found: 283.8 ([M – I$^-$$]^{-1}$).

**2-Naphthylamine**

A mixture of 2-Naphthol (2018.4 mg, 14 mmole) and NaHSO$_3$ (2913.7 mg, 28 mmole) in NH$_3$·H$_2$O (60 mL) was placed in the autoclave. The autoclave was sealed and
heated to 170 °C in furnace for 7 h. The solid was filtered and washed with DI water twice to get rid of NaHSO₃, washed with 1N HCl to remove unreacted 2-naphthol. The resulting solid was filtered and vacuum dried to afford a light pink crystal (1603 mg, 80%). ¹H-NMR (400MHz; CD₃OD) δₜ: 7.68 (2H, m, 2 × CH), 7.59 (1H, d, CH), 7.36 (1H, d, CH), 7.22 (1H, d, CH), 6.98 (1H, s, CH), 6.95 (1H, d, CH), 3.83 (2H, s, NH₂); ¹³C NMR (100 MHz, CDCl₃) δₜ: 114.38, 135.17, 129.47, 128.21, 127.99, 126.62, 126.07, 122.73, 118.51, 108.84.

2-Naphthyl p-toluenesulfonate

To a solution of 2-naphthol (432 mg, 3 mmol) in pyridine (5 mL), TsCl (572 mg, 3 mmol) was added portionwise under air atmosphere and the whole mixture was stirred at 45 °C for 15 h. After cooling to room temperature, 10 mL of water was added to the mixture and then stirred for 3 h. This mixture was diluted with benzene (50 mL) and washed with water, 1N aqueous HCl (× 2), 1N NaOH, Brine and then dried over Na₂SO₄. After filtration, solvent was evaporated in vacuum to give white needle crystal 634 mg (70%) . ¹H-NMR (400MHz; CDCl₃) δₜ: 7.81 (1H, t, CH), 7.74 (3H, m, 3 × CH), 7.48 (2H, m, 2 × CH), 7.30 (2H, m, 2 × CH), 7.10 (1H, dd, CH), 2.45 (3H, d, CH₃); ¹³C NMR (125 MHz, CDCl₃) δₜ: 147.21, 145.25, 133.41, 132.49, 132.08, 129.76, 129.73, 128.57, 127.88, 127.74, 126.83, 126.36, 121.18, 121.18, 119.95, 21.72.

2, 2’-Dinaphthylamine

2-naphthol (60.8 mg, 0.42 mmole) and 2-naphthylamine (53.3 mg, 0.37 mmole) were fully mixed with catalyst anhydrous zinc chloride (69.9 mg, 0.51 mmole) and
ammonium chloride (66.2 mg, 1.24 mmole). The mixture was heated to 200-250 °C for 2 hours. The mixture was first washed with hot water to remove zinc chloride and ammonia chloride, and then washed with hot potassium hydroxide (10%) to remove unreacted 2-naphthol, and hot diluted hydrochloric acid solution to remove unreacted 2-naphthylamine. The solid then further washed with potassium hydrate and water. The crude product was dissolved in pyridine and fine product (30 mg) was precipitated with water. Yellow powder, yield: 30%; \(^{1}\)H-NMR (400MHz; CDCl\(_3\); Me\(_4\)Si) \(\delta_H\): 7.79 (4H, m, 4 × CH), 7.68 (2H, d, 2 × CH), 7.54 (2H, d, 2 × CH), 7.43 (2H, t, 2 × CH), 7.33 (4H, m, 4 × CH), 6.07 (1H, s, NH); IR (ATR), 3413, 3050, 1627, 1600cm\(^{-1}\).

2, 2’-Dinaphthylamine

A 15 mL sealed tube equipped with a magnetic stir bar and septum was purged with argon. The flask was charged with 2-naphthylamine (28.6 mg, 0.2 mmol), 2-naphthyl p-toluenesulfonate (50.7 mg, 0.17 mmol), Pd\(_2\)(dba)\(_3\) (15.6 mg, 0.017 mmol), Xantphos (29.5 mg, 0.051 mmol), anhydrous K\(_3\)PO\(_4\) (72.2 mg, 0.34 mmol) and anhydrous 1,4-dioxane (3 mL). The reaction mixture was degassed with argon, then sealed with compatible cap and stirred at 160 °C for 20 h. The reaction mixture was cooled to room temperature, diluted with water and extracted with ethyl acetate. The organic phase was dried (anhydrous sodium sulfate), filtered and concentrated under vacuum pressure. The residue was chromatographed on silica (Hexanes/EtOAc: 20:1) to yield the desired 2, 2’-dinaphthylamine 27.5 mg (60%). \(^{1}\)H-NMR (400MHz; CDCl\(_3\); Me\(_4\)Si) \(\delta_H\): 7.78 (4H, m, 4 × CH), 7.67 (2H, d, 2 × CH), 7.54 (2H, d, 2 × CH), 7.43 (2H, t, 2 × CH), 7.33 (4H, m, 2 × CH), 6.07 (1H, s, NH);
**2, 2’-Dinaphthyline**

A 15 mL sealed tube equipped with a magnetic stir bar and septum was purged with argon. The flask was charged with 2-naphthylamine (28.6 mg, 0.2 mmol), 2-bromonaphthalene (50.7 mg, 0.17 mmol), Pd$_2$(dba)$_3$ (15.6 mg, 0.017 mmol), Xantphos (29.5 mg, 0.051 mmol), anhydrous K$_3$PO$_4$ (72.2 mg, 0.34 mmol) and anhydrous 1,4-dioxane (3 mL). The reaction mixture was degassed with argon, then sealed with compatible cap and stirred at 160 °C for 20 h. The reaction mixture was cooled to room temperature, diluted with water and extracted with ethyl acetate. The organic phase was dried (anhydrous sodium sulfate), filtered and concentrated under vacuum pressure. The residue was chromatographed on silica (Hexanes/EtOAc: 20:1) to yield the desired 2, 2’-dinaphthylamine 27.5 mg (90%). $^1$H-NMR (400MHz; CDCl$_3$; Me$_4$Si) δH: 7.78 (4H, m, 4 × CH), 7.67 (2H, d, 2 × CH), 7.54 (2H, d, 2 × CH), 7.43 (2H, t, 2 × CH), 7.33 (4H, m, 2 × CH), 6.07 (1H, s, NH);

**7H-Dibenzo[c,h]phenothiazine**

In a 10 mL round-bottomed microwave tube (for 2-5 mL reaction volumes) equipped with magnetic stir bar, 2, 2’-dinaphthylamine (26.9 mg, 0.1 mmol), element sulfur (6.4 mg, 0.2 mmol) and catalytic amount of iodine were added into the tube and mixed completely. The tube was sealed and heated in a microwave reactor for 10 min at 200 °C. The reaction mixture was cooled to room temperature, and then filtered through Celite, washed with ethyl acetate and concentrated under reduced pressure. The crude product was further purified by flash chromatography over silica gel with Hexane/EtOAc
(5:1) as eluent to give a yellow solid (5.8 mg, 7% yield). $^1$H-NMR (500MHz; CDCl$_3$; Me$_4$Si) $\delta_H$: 8.11 (2H, d, 2 $\times$ CH), 7.86 (2H, d, 2 $\times$ CH), 7.73 (2H, d, 2 $\times$ CH), 7.64 (2H, t, 2 $\times$ CH), 7.46 (1H, s, NH), 7.45 (2H, t, 2 $\times$ CH), 7.12 (2H, d, 2 $\times$ CH); MS (MALDI-TOF) for C$_{20}$H$_{13}$NS, m/z calculated: 299.08, found: 298.7; m/z calculated for [M-S]$^+$: 267.10, signal found: 266.9.

1-Methoxy-2-nitronaphthalene

2-nitronaphthalen-1-ol (946 mg, 5 mmol), dimethyl sulfate (1.42 mL, 15 mmol), K$_2$CO$_3$ (2764.2 mg, 20 mmol), and acetone (20 mL) were added to a round bottom flask equipped with magnetic stir bar, septum and condenser. The reaction mixture was stirred under reflux for 20 h. The reaction mixture was cooled down to room temperature and concentrated in vacuum to remove solvent acetone. The solid residue was then dissolved in water (50 mL) and ethyl acetate (50 mL). The organic layer was separated, washed with 1N NaOH (20 mL), DI water, and Brine. The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography with Hexane/EtOAc (20:1) as an eluent to give pure 1-methoxy-2-nitronaphthalene as a yellow needle crystal (916 mg, 90%). $^1$H-NMR (400MHz; CDCl$_3$; Me$_4$Si) $\delta_H$: 8.32 (1H, d, CH), 7.90 (2H, d, 2 $\times$ CH), 7.68 (3H, m, 3 $\times$ CH), 4.15 (3H, s, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta_C$: 151.70, 139.10, 136.45, 129.44, 128.57, 128.19, 127.58, 124.32, 124.15, 121.00, 63.71.

1-Methoxynaphthalen-2-amine
To a two-neck round bottom flask equipped with magnetic stir bar, septum and nitrogen inlet, 1-methoxy-2-nitronaphthalene (486.4 mg, 2.34 mmol) was dissolved in ethyl acetate (20 mg) and stirred for 10 min under nitrogen atmosphere until all starting material was completely dissolved. Pd/C (100 mg) was added to the solution and continued stirring for another 10 min. Nitrogen gas was replaced with hydrogen gas and the reaction mixture was stirred at room temperature in hydrogen for 24 h. The reaction process was monitored by TLC. After the conversion was complete, the mixture was filtered to remove Pd/C and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography with Hexane/EtOAc (5:1) to give pure 1-methoxynaphthalen-2-amine as reddish brown solid (307 mg, 76%). \(^1\)H-NMR (400MHz; CDCl\(_3\); Me\(_4\)Si) \(\delta_H\): 7.92 (1H, d, CH), 7.71 (1H, d, CH), 7.45 (2H, m, 2 × CH), 7.24 (1H, t, CH), 7.00 (1H, d, CH), 3.95 (2H, s, NH\(_2\)), 3.88 (3H, s, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta_C\): 139.46, 135.91, 129.07, 128.77, 128.32, 126.48, 125.06, 122.77, 120.23, 118.83, 60.10. MS (MALDI-TOF) for C\(_{11}\)H\(_{11}\)NO, m/z calculated: 173.08, signal found: 173.5.

1-Phenynaphthalen-2-ol

A 10 mL round-bottomed microwave tube (for 2-5 mL reaction volumes) equipped with magnetic stir bar was used as reaction vessel and THF (4 mL) and DI water (1 mL) were used as solvent. 1-bromonaphthalen-2-ol (223 mg, 1 mmol), phenylboronic acid (183 mg, 1.5 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (35 mg, 5% ww) and K\(_2\)CO\(_3\) (276 mg, 2 mmol) were added to the reaction vessel. The tube was sealed and heated in a microwave reactor for 10 min at 130 °C. The reaction mixture was cooled to room temperature, and then filtered through Celite, washed with ethyl acetate and concentrated
under reduced pressure. The crude product was further purified by flash chromatography over silica gel with Hexane/EtOAc (12:1) as eluent to give dark yellow oil (145 mg, 65% yield). \(^1\)H-NMR (400MHz; CDCl\(_3\); Me\(_4\)Si) \(\delta\): 7.83 (2H, m, 2 \times CH), 7.61 (2H, m, 2 \times CH), 7.52 (1H, t, CH), 7.44 (3H, m, 3 \times CH), 7.36 (2H, m, 2 \times CH), 7.29 (1H, d, CH), 5.18 (1H, s, OH).

**1-Phenynaphthalen-2-yl 4-methylbenzenesulfonate**

To a solution of 1-phenynaphthalen-2-ol (125 mg, 0.57 mmol) in pyridine (5 mL), TsCl (216 mg, 1.14 mmol) was added portionwise under air atmosphere and the whole mixture was stirred at 45 °C for 15 h. After cooling to room temperature, 10 mL of water was added to the mixture and then stirred for 3 h. This mixture was diluted with ethyl acetate (50 mL). The organic phase was washed with water, 1N aqueous HCl (\(\times\) 2), 1N NaOH, Brine and then dried over Na\(_2\)SO\(_4\). After filtration, solvent was evaporated in vacuum to give off-white solid 164 mg (76%). \(^1\)H-NMR (500MHz; CDCl\(_3\); Me\(_4\)Si) \(\delta\): 7.89 (2H, m, 2 \times CH), 7.66 (1H, d, CH), 7.53 (1H, dd, CH), 7.48 (1H, m, CH), 7.37 (2H, m, 2 \times CH), 7.31 (2H, m, 2 \times CH), 7.26 (2H, m, 2 \times CH), 7.07 (4H, m, 4 \times CH), 2.39 (3H, s, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 144.85, 144.22, 134.24, 133.30, 133.08, 132.44, 132.09, 131.03, 129.73, 129.45, 128.29, 128.26, 128.13, 127.58, 126.93, 126.70, 126.29, 121.80, 21.87. MS (MALDI-TOF) for C\(_{23}\)H\(_{18}\)O\(_3\)S, m/z calculated: 374.10, signal found: 374.1.

**1-Methoxy-N-(naphthalen-2-yl)naphthalen-2-amine**
A 15 mL sealed tube equipped with a magnetic stir bar and septum was purged with argon. The tube was charged with 1-methoxynaphthalen-2-amine (34.6 mg, 0.2 mmol), naphthalen-2-yl 4-methylbenzenesulfonate (50.7 mg, 0.17 mmol), Pd$_2$(dba)$_3$ (15.6 mg, 0.017 mmol), Xantphos (29.5 mg, 0.051 mmol), anhydrous K$_3$PO$_4$ (72.2 mg, 0.34 mmol) and anhydrous 1,4-dioxane (3 mL). The reaction mixture was degassed with argon, then sealed with compatible cap and stirred at 160 °C for 11 h. The reaction mixture was cooled to room temperature, diluted with water and extracted with ethyl acetate. The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated under vacuum pressure. The residue was chromatographed on silica (Hexanes/EtOAc: 20:1) to yield the desired 1-Methoxy-N-(naphthalen-2-yl)naphthalen-2-amine 100 mg (88%). $^1$H-NMR (500MHz; CDCl$_3$; Me$_4$Si) $\delta$H: 8.04 (1H, d, CH), 7.79 (3H, m, 3 × CH), 7.76 (2H, m, 2 × CH), 7.61 (1H, d, CH), 7.51 (2H, m, 2 × CH), 7.43 (1H, t, CH), 7.35 (3H, m, 3 × CH), 6.41 (1H, s, NH), 3.94 (3H, s, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$C: 143.40, 140.92, 134.66, 132.17, 130.24, 129.41, 129.35, 128.59, 128.13, 127.72, 126.58, 126.56, 126.40, 124.54, 123.89, 123.64, 120.78, 120.32, 119.24, 111.74, 61.07. MS (MALDI-TOF) for C$_{21}$H$_{17}$NO, m/z calculated: 299.13, signal found:299.1.

1-Phenynaphthalen-2-yl trifluoromethanesulfonate

Under nitrogen, 1-phenynaphthalen-2-ol (110 mg, 0.5 mmol) was dissolved in 3 mL of anhydrous DCM in a 50 mL round bottom flask. Dry pyridine (0.32 mL, 4 mmol) was added and the solution was cooled to 0 °C using ice bath. Then triflic anhydride (0.6 mL, 1.26 mmol) was dropwise added via syringe. The reaction mixture was allowed to warm up to 25 °C and kept stirred at 25 °C for 12 h. 10 mL water and 20 mL DCM were
added to the reaction mixture and continue stirring for 2 h. The organic phase was then washed with 1 N HCl (10 mL), 10% NaOH (10 mL), Brine and dried over Na₂SO₄. After filtration, solvent was removed under reduced pressure. The crude compound was further purified by flash chromatography over silica gel with Hexane/EtOAc (10:1) as eluent to give light yellow solid (124 mg, 70%). ¹H-NMR (400MHz; CDCl₃; Me₄Si) δH: 7.94 (2H, m, 2 × CH), 7.65 (1H, d, CH), 7.52 (6H, m, 6 × CH), 7.40 (2H, m, 2 × CH); ¹³C NMR (125 MHz, CDCl₃) δC: 144.20, 133.36, 133.04, 132.63, 132.63, 130.80, 129.98, 128.57, 128.46, 128.14, 127.48, 126.94, 126.84, 119.49, CF₃: 122.24, 119.69, 117.14, 114.59 (J_CF = 320.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δC: -74.72; MS (MALDI-TOF) for C₁₇H₁₁F₃O₃S, m/z calculated: 352.04, signal found: 352.3.

**1-Methoxy-N-(1-phenynaphthalen-2-yl)naphthalen-2-amine**

A 15 mL sealed tube equipped with a magnetic stir bar and septum was purged with argon. The tube was charged with 1-methoxynaphthalen-2-amine (62.4 mg, 0.36 mmol), 1-phenynaphthalen-2-yl trifluoromethanesulfonate (105.7 mg, 0.3 mmol), Pd₂(db₃) (27.5 mg, 0.03 mmol), Xantphos (52.1 mg, 0.09 mmol), anhydrous K₃PO₄ (127.4 mg, 0.6 mmol) and anhydrous 1,4-dioxane (3 mL). The reaction mixture was degassed with argon, then sealed with compatible cap and stirred at 160 °C for 11 h. The reaction mixture was cooled to room temperature, diluted with water and extracted with ethyl acetate. The organic phase was dried over Na₂SO₄, filtered and concentrated under vacuum pressure. The residue was chromatographed on silica (Hexanes/EtOAc: 20:1) to yield the desired 1-methoxy-N-(1-phenynaphthalen-2-yl)naphthalen-2-amine 100 mg (88%). ¹H-NMR (400MHz; CDCl₃; Me₄Si) δH: 7.93 (1H, d, CH), 7.82 (2H, m, 2 × CH),
7.75 (1H, d, CH), 7.62 (1H, d, CH), 7.54 (4H, m, 4 × CH), 7.43 (5H, m, 5 × CH), 7.32 (3H, m, 3 × CH), 6.05 (1H, s, NH), 3.66 (3H, s, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) δ$_C$: 143.20, 137.62, 136.79, 133.78, 132.29, 130.80, 130.00, 129.34, 129.31, 128.50, 128.43, 127.99, 127.92, 127.85, 126.38, 126.29, 125.84, 125.00, 124.33, 123.63, 123.38, 120.62, 118.79, 118.46, 60.35. MS (MALDI-TOF) for C$_{27}$H$_{21}$NO, m/z calculated: 375.16, signal found: 375.2.

2-Nitro-1-phenyl-naphthalene

A solution of 1-methoxy-2-nitronaphthalene (203.2 mg, 1 mmol) dissolved in 3 mL benzene was added to a 15 mL sealed tube equipped with magnetic stir bar. The mixture was degassed with argon. Phenylmagnesium bromide (1.2 mL, 1.2 mmol) was dropwise added to sealed tube. The reaction mixture was stirred at room temperature for 5 h. The reaction process was monitored by TLC until all starting material was converted to product. After completion of the reaction, the reaction mixture was washed with saturated ammonium chloride, water, Brine and dried over anhydrous Na$_2$SO$_4$. After filtration, the organic phase was concentrated under reduced vacuum. The residue was further purified by flash chromatography over silica gel with Hexane/CHCl$_3$ (5:1) as eluent to give yellow solid (176 mg, 70%). $^1$H-NMR (500MHz; CDCl$_3$; Me$_4$Si) δ$_H$: 7.97 (2H, t, 2 × CH), 7.92 (1H, d, CH), 7.63 (2H, m, 2 × CH), 7.50 (4H, m, 4 × CH), 7.34 (2H, m, 2 × CH); $^{13}$C NMR (400 MHz, CDCl$_3$) δ$_C$: 146.68, 134.79, 134.65, 134.59, 132.53, 129.38, 129.05, 128.49, 128.33, 128.27, 128.10, 127.77, 119.94. MS (MALDI-TOF) for C$_{23}$H$_{18}$O$_3$S, m/z calculated: 249.09, signal found: 288.8.
1-Phenylnaphthalen-2-amine

To a two-neck round bottom flask equipped with magnetic stir bar, septum and nitrogen inlet, 2-nitro-1-phenylnaphthalene (166 mg, 0.67 mmol) was dissolved in ethyl acetate (10 mg) and stirred for 10 min under nitrogen atmosphere until all starting material was completely dissolved. Pd/C (100 mg) was added to the solution and continued stirring for another 10 min. Nitrogen gas was replaced with hydrogen gas and the reaction mixture was stirred at room temperature in hydrogen for 24 h. The reaction process was monitored by TLC. After the conversion was complete, the mixture was filtered to remove Pd/C and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography with Hexane/EtOAc (5:1) to give pure 1-methoxynaphthalen-2-amine as reddish brown solid (142 mg, 97%). $^1$H-NMR (500MHz; CDCl$_3$; Me$_4$Si) $\delta_H$: 7.81 (1H, dd, CH), 7.77 (1H, d, CH), 7.65 (2H, m, 2 $\times$ CH), 7.55 (1H, m, CH), 7.40 (2H, m, 2 $\times$ CH), 7.32 (1H, m, CH), 7.24 (2H, m, 2 $\times$ CH), 7.17 (1H, d, CH), 4.15 (2H, s, NH$_2$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta_C$: 141.02, 137.15, 133.77, 130.91, 129.26, 128.70, 127.97, 127.87, 127.51, 126.27, 124.20, 122.13, 119.89, 118.09. MS (MALDI-TOF) for C$_{16}$H$_{13}$N, m/z calculated: 219.10, signal found: 219.0.

Bis(1-phenylnaphthalen-2-yl)amine

A 15 mL sealed tube equipped with a magnetic stir bar and septum was purged with argon. The tube was charged with 1-phenylnaphthalen-2-amine (78.9 mg, 0.36 mmol), 1-phenylnaphthalen-2-yl trifluoromethanesulfonyl (105.7 mg, 0.3 mmol), Pd$_2$(dba)$_3$ (27.5 mg, 0.03 mmol), Xantphos (52.1 mg, 0.09 mmol), anhydrous K$_3$PO$_4$ (127.4 mg, 0.6 mmol) and anhydrous 1,4-dioxane (3 mL). The reaction mixture was
degassed with argon, then sealed with compatible cap and stirred at 160 °C for 11 h. The reaction mixture was cooled to room temperature, diluted with water and extracted with ethyl acetate. The organic phase was dried over Na₂SO₄, filtered and concentrated under vacuum pressure. The residue was chromatographed on silica (Hexanes/EtOAc: 20:1) to yield the desired bis(1-phenylnaphthalen-2-yl)amine as off-white solid 114 mg (90%).

\[ \text{H-NMR (500MHz; CDCl}_3; \text{ Me}_4\text{Si)} \delta \text{H: 7.78 (4H, m, 4 × CH), 7.64 (2H, d, 2 × CH), 7.38 (6H, m, 6 × CH), 7.29 (6H, m,6 × CH), 7.04 (4H, m, 4 × CH), 5.62 (1H, s, NH); ¹³C NMR (125 MHz, CDCl}_3 \delta \text{C: 137.84, 136.56, 133.64, 130.34, 129.20, 129.17, 128.28, 127.87, 127.38, 126.27, 125.72, 124.93, 123.25, 118.32. MS (MALDI-TOF) for C}_{23}\text{H}_{18}\text{O}_3\text{S, m/z calculated: 421.18, signal found: 421.9.} \]

**7H-Dibenzo[c,h]phenothiazine**

In a 15 mL sealed tube equipped with magnetic stir bar, 2, 2’-dinaphthylamine (67 mg, 0.25 mmol), element sulfur (27 mg, 0.84 mmol), catalytic amount of iodine and 1,2,4-trichlorobenzene (2 mL) were added into the sealed tube and mixed completely. The tube was sealed and heated in oil bath for 24 h at 186 °C. The reaction mixture was cooled to room temperature, and then filtered through Celite, washed with ethyl acetate and concentrated under reduced pressure. The crude product was further purified by flash chromatography over silica gel with Hexane/EtOAc (20:1) as eluent to give a yellow solid (76 mg, 99% yield). \[ \text{H-NMR (500MHz; CD}_3\text{CN) \delta H: 8.11 (2H, d, 2 × CH), 7.86 (2H, d, 2 × CH), 7.73 (2H, d, 2 × CH), 7.64 (2H, t, 2 × CH), 7.45 (2H, t, 2 × CH), 7.12 (2H, d, 2 × CH); MS (MALDI-TOF) for C}_{20}\text{H}_{13}\text{NS, m/z calculated: 299.08, found: 298.9; UV-Vis, 354 nm in CHCl}_3; \text{ IR (ATR), 3281.68 cm}^{-1}\text{for N-H stretch.} \]
3H-phenothiazin-3-one and 10H-3,10'-biphenothiazine

In a 50 mL round bottom flask with 5 mL concentrated sulfuric acid, 10H-phenothiazine (399 mg, 2 mmol) was slowly added to sulfuric acid while stirring. Temperature was slowly increased to 100 °C and heated for 24 h. The reaction mixture was cooled to room temperature, and then poured into ice water, extracted with dichloromethane. The organic phase was washed with deionized water three times to remove extra sulfuric acid. Then it was washed with Brine, dried with Na₂SO₄ and concentrated under reduced pressure to remove the solvent. The crude product was further purified by flash chromatography over silica gel with Hexane/EtOAc (10:1) as eluent to give a red solid 3H-phenothiazin-3-one (105 mg, 24% yield) and yellow solid 10H-3,10'-biphenothiazine (36 mg, 4.5% yield).

3H-phenothiazin-3-one: ¹H-NMR (400MHz; CDCl₃; Me₄Si) δ_H: 7.91 (1H, d, CH), 7.61 (1H, d, CH), 7.48 (3H, m, 3 × CH), 6.94 (1H, dd, CH), 6.76 (1H, s, CH); ¹³H-NMR (125MHz; CDCl₃; Me₄Si) δ_H: 182.51, 146.53, 139.89, 139.27, 135.36, 135.23, 134.06, 131.03, 125.06, 6.28 (3H, m, 3 × CH); MS (MALDI-TOF) for C₁₁H₇NOS, m/z calculated: 213.01, found: 213.1; UV-Vis, 502 nm in CHCl₃.

10H-3,10'-biphenothiazine: ¹H-NMR (400MHz; CDCl₃; Me₄Si) δ_H: 6.86 (12H, m, 12 × CH), 6.28 (3H, m, 3 × CH); MS (MALDI-TOF) for C₂₄H₁₆N₂S₂, m/z calculated: 396.08, found: 396.3; UV-Vis, 318 nm in CHCl₃; EPR, G factor: 2.007.
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APPENDIX

SPECTRA

NMR, MALDI-TOF-MS, UV-Vis, IR, Fluorescence, EPR
3,7-Bis(dimethylamino)phenothiazin-5-ium iodide

\[ \text{MeOD} \]

\[ \text{H}_2\text{O} \]
3,7-Bis(dimethylamino)phenothiazin-5-ium iodide

UV-Vis Spectrum

$\lambda_{\text{max}} = 653$ nm (in MeOH)
3,7-bis(dimethylamino)phenothiazin-5-ium iodide

Exact Mass: 284.12

MALDI-TOF-MS
Naphthalen-2-amine

$\text{CHCl}_3$

$^{1}\text{H-NMR (400 MHz)}$
Naphthalen-2-amine

$^{13}$C-NMR (100 MHz)
Naphthalen-2-yl 4-methylbenzenesulfonate

$\text{CHCl}_3$

$H_2O$

$^{1}H$-NMR (400 MHz)
Naphthalen-2-yl 4-methylbenzenesulfonate

$^{13}$C-NMR (125 MHz)
$2,2'$-Dinaphthylamine

$^1$H-NMR (400 MHz)

CHCl$_3$

H$_2$O

$115$
2,2′-Dinaphthylamine

ATR – IR Spectrum

N-H Stretch
7H-Dibenzoc,h]phenothiazine

H2O

CH3CN

grease

$^1$H-NMR (500 MHz)
7H-Dibenzo[c,h]phenothiazine

gCOSY (500 MHz)
7H-Dibenzo[c,h]phenothiazine

Exact Mass: 299.08
7H-Dibenzo[c,h]phenothiazine
$\lambda_{\text{max}} = 354$ nm in CHCl$_3$
7H-Dibenzo[c,h]phenothiazine

Excitation $\lambda = 350$ (nm)
Emission $\lambda_{\text{max}} = 371$ nm, 390 nm
(in CH$_3$CN)
$^{13}$C-NMR (125 MHz)

1-Methoxy-2-nitronaphthalene
1-Methoxynaphthalen-2-amine

$^1$H-NMR (400 MHz)
$^{13}$C-NMR (100 MHz)
1-Methoxynaphthalen-2-amine

Exact Mass: 173.08

MALDI-TOF-MS
1-Phenynaphthalen-2-ol

$^1$H-NMR (400 MHz)
Naphthalen-2-yl 4-methylbenzenesulfonate

\[
\text{CHCl}_3
\]

\[
\text{H}_2\text{O}
\]

\( ^1\text{H}-\text{NMR (500 MHz)} \)
Naphthalen-2-yl 4-methylbenzenesulfonate

$^{13}$C-NMR (100 MHz)
Naphthalen-2-yl 4-methylbenzenesulfonate

Exact Mass: 374.10

MALDI-TOF-MS
1-Methoxy-N-(naphthalen-2-yl)naphthalen-2-amine

$^1$H-NMR (500 MHz)
$^{13}$C-NMR (125 MHz)

1-Methoxy-N-(naphthalen-2-yl)naphthalen-2-amine

Diagram of the 13C-NMR spectrum with chemical shifts ranging from 50 to 160 ppm.
1-Methoxy-N-(naphthalen-2-yl)naphthalen-2-amine

Exact Mass: 299.13

MALDI-TOF MS

[M⁺]

299.1
1-Phenyl-naphthalen-2-yl Trifluoromethanesulfonate

$\text{CHCl}_3$

$\text{H}_2\text{O}$

$^1\text{H}-\text{NMR (400 MHz)}$
1-Phenylnaphthalen-2-yl Trifluoromethanesulfonate

$^{13}$C-NMR (125 MHz)
1-Phenyl-1-naphthyl-2-yl Trifluoromethanesulfonate
1-Phenyl-naphthalen-2-yl Trifluoromethanesulfonate

Exact Mass: 352.04

MALDI-TOF-MS
1-Methoxy-N-(1-phenyl)naphthalen-2-yl)naphthalen-2-amine

$^1$H-NMR (400 MHz)
$^{13}$C-NMR (125 MHz)

1-Methoxy-N-(1-phenylnaphthalen-2-yl)naphthalen-2-amine
1-Methoxy-N-(1-phenyl)naphthalen-2-yl)naphthalen-2-amine

Exact Mass: 375.16

MALDI-TOF-MS
$^1$H-NMR (500 MHz)

2-Nitro-1-phenylnaphthalene

HNMR spectrum with peaks at specific ppm values.
2-Nitro-1-phenynaphthalene

$^{13}$C-NMR (125 MHz)
1-Phenynaphthalen-2-amine

$^1$H-NMR (500 MHz)
$^{13}$C-NMR (125 MHz)

1-Phenyl-1-naphthalen-2-amine
1-Phenylphenanthrene-2-amine

Exact Mass: 219.10

[M+]

MALDI-TOF-MS
Bis(1-phenylnaphthalen-2-yl)amine

${}^1$H-NMR (500 MHz)
Bis(1-phenylnaphthalen-2-yl)amine

\[ \text{Bis}(1\text{-phenylnaphthalen}-2\text{-yl})\text{amine} \]

\[ ^{13}\text{C-NMR (125 MHz)} \]
Bis(1-phenylnaphthalen-2-yl)amine

Exact Mass: 421.18

MALDI-TOF-MS
1-Butyl-2-nitronaphthalene

\( \text{CHCl}_3 \)

\( \text{H}_2\text{O} \)

\( \text{grease} \)
1-Butyl-2-nitronaphthalene

Exact Mass: 229.11
1,2-Di(naphthalen-2-yl)disulfane

1H-NMR (400 MHz)

H2O

CHCl3

grease
$^{13}$C-NMR (100 MHz)

1,2-Di(naphthalen-2-yl)disulfane

Impurity
$^{1}$H-NMR (400 MHz)

1,2-Di(naphthalen-2-yl)disulfane
$^{13}$C-NMR (100 MHz)

1,2-Di(naphthalen-2-yl)disulfane

Impurity
3,7-bis(dimethylamino)phenothiazin-5-ium iodide

Exact Mass: 318.05

MALDI-TOF MS
$^1$H-NMR (400 MHz)

3H-phenothiazin-3-one

$\text{CHCl}_3$

$\text{H}_2\text{O}$
$^{13}$C-NMR (125 MHz)

3H-phenothiazin-3-one
3H-phenothiazin-3-one

Exact Mass: 213.02
3H-phenothiazin-3-one

UV-Vis Spectrum

$\lambda_{\text{max}} = 502 \text{ nm in CHCl}_3$
ATR – IR Spectrum

3H-phenothiazin-3-one

%Transmission

Wavenumbers (cm⁻¹)

3500
3000
2500
2000
1500
1000
500
0
10H-3,10'-biphenothiazine

\[ \text{CHCl}_3 \quad \text{H}_2\text{O} \]

[Diagram of the molecule]

\[^1\text{H-NMR (400 MHz)}\]
$10H-3,10'-\text{biphenothiazine}$

Exact Mass: 396.08
10H-3,10′-biphenothiazine

UV-Vis Spectrum

$\lambda_{\text{max}} = 318 \text{ nm in CHCl}_3$
Electron Paramagnetic Resonance Spectrum

G factor: 2.007

10H-3,10'-biphenothiazine

Intensity vs. Field [G]