SYNTHESIS OF NOVEL ORGANIC CHROMOPHORES
AND THEIR CHARACTERIZATION

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Nonlinear organic liquids that exhibit two-photon absorption (TPA) function as good optical limiters for sensor protection from laser pulses. L34 (4-butyl-4'-propyl-diphenylethyne) is a liquid organic compound exhibiting nonlinear optical absorption. A thiol- derivatized analog of L34 ("thiol-L34") was prepared to bind the molecules to the surface of gold nanoparticles. Surface binding is necessary to investigate synergy between nonlinear optical absorption of gold nanoparticles and thiol-L34. Thiol-L34 was prepared in a six-step organic synthesis starting from 3-(4-bromophenyl) propionic acid. Au nanoparticles with <15 nm diameter have been prepared and sensitized with the thiol-L34 compound for assessment of their nonlinear optical behavior. Diazolylmethenes a class of metal-coordinating dyes that are similar to dipyrrins with some substitutions of nitrogen atoms in place of carbon atoms. Modification in the framework of dipyrrinoid dyes via this replacement of nitrogen for carbon atoms may lead to compounds that serve as effective agents for bioimaging and/or photodynamic therapy. Several routes to the synthesis of di-(1,2,3)-triazolylmethenes, di-(1,2,4)-triazolylmethenes, and ditetrazolylmethenes are presented.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>x</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Overview and Objectives of Dissertation</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Nonlinear Organic Liquid Materials</td>
<td>1</td>
</tr>
<tr>
<td>1.3 Synthesis of Nitrogen-Enriched BODIPY Dyes</td>
<td>5</td>
</tr>
<tr>
<td>1.4 References</td>
<td>9</td>
</tr>
<tr>
<td>CHAPTER 2 PREPARATION OF A COLLOIDAL OPTICAL-LIMITING MATERIAL</td>
<td>13</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>13</td>
</tr>
<tr>
<td>2.2 Synthesis</td>
<td>17</td>
</tr>
<tr>
<td>2.2.1 General Procedures</td>
<td>17</td>
</tr>
<tr>
<td>2.2.2 Experimental Section</td>
<td>17</td>
</tr>
<tr>
<td>2.2.3 Characterization and Physical Measurements</td>
<td>23</td>
</tr>
<tr>
<td>2.3 Results and Discussion</td>
<td>25</td>
</tr>
<tr>
<td>2.4 Conclusion and Future Works</td>
<td>26</td>
</tr>
<tr>
<td>2.5 References</td>
<td>27</td>
</tr>
<tr>
<td>CHAPTER 3 SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF BODIPY</td>
<td>30</td>
</tr>
<tr>
<td>DYES- DITRIAZOLYL METHENE DYES AND THEIR DERIVATIVES</td>
<td>30</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>30</td>
</tr>
<tr>
<td>3.2 Synthesis</td>
<td>39</td>
</tr>
<tr>
<td>3.2.1 General Procedure</td>
<td>39</td>
</tr>
<tr>
<td>3.2.2 Experimental Section</td>
<td>40</td>
</tr>
<tr>
<td>3.2.3 Characterization and Physical Properties</td>
<td>46</td>
</tr>
<tr>
<td>3.3 Results and Discussions</td>
<td>50</td>
</tr>
</tbody>
</table>
CHAPTER 4 SOME OTHER ROUTES OF SYNTHESIS OF A NEW CLASS OF BODIPY
DYES- DITETRAAZOLYLMETHENE DYSES AND THEIR DERIVATIVES .................. 71
4.1 Introduction ........................................................................................................... 71
4.2 Synthesis ............................................................................................................... 71
4.2.1 General Procedure ..................................................................................... 71
4.2.3 Characterization and Physical Properties .................................................. 75
4.3 Results and Discussions ...................................................................................... 76
4.4 Conclusion and Future Works .............................................................................. 76
4.5 References ............................................................................................................. 77

CHAPTER 5 A GREENER SYNTHESIS OF 6-METHYLNAPHTHOQUINONE ............ 79
5.1 Introduction ........................................................................................................... 79
5.2 Synthesis ............................................................................................................... 81
5.2.1 General Procedure ..................................................................................... 81
5.2.2 Experimental Section ................................................................................ 81
5.3 Results and Discussions ...................................................................................... 82
5.4 Conclusion and Future Works .............................................................................. 84
5.5 References ............................................................................................................. 85

APPENDIX SUPPLEMENTAL DATA ............................................................................. 86
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Crystallography data for phenylpropanedinitrile</td>
<td>47</td>
</tr>
<tr>
<td>3.2</td>
<td>Crystallography data 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol, (21C)</td>
<td>49</td>
</tr>
<tr>
<td>3.3</td>
<td>Crystallography data for 1 – Stilbene</td>
<td>58</td>
</tr>
<tr>
<td>3.4</td>
<td>Crystallography data p-tolyl(2H-triazol-4-yl)methanone</td>
<td>63</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Schematic diagram of the nonlinear optical limiting mechanisms in a fiber array (not drawn to scale)</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Molecular structure of L34 and its linear absorption spectrum</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Energy-level diagram for the nonlinear organic fiber core liquid L34</td>
<td>4</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Structures of L34 and thiol-L34</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>Structure of s-indacene and aza-indacene analogs</td>
<td>6</td>
</tr>
<tr>
<td>Figure 1.6</td>
<td>Synthesis of first boron dipyrrin dye by Treibs and Kreuzer</td>
<td>6</td>
</tr>
<tr>
<td>Figure 1.7</td>
<td>Synthesis of unsubstituted BODIPY 59C</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.8</td>
<td>The structure of dimethylBODIPY- phenyl 01C</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.9</td>
<td>UV-vis spectrum of dimethylBODIPY-phenyl</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.10</td>
<td>Fluorescence spectrum of dimethylBODIPY-phenyl</td>
<td>8</td>
</tr>
<tr>
<td>Figure 1.11</td>
<td>Synthesis of new diazolylmethene dyes having more than three nitrogen atoms</td>
<td>9</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Predicted reaction mechanism of Sonogashira reaction</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Synthesis of 4-(4-butylphenyl)-2-methylbut-3-yn-2-ol (01B)</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Synthesis of 1-butyl-4-ethynylbenzene (02B)</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>IR spectrum of Thiol-L34</td>
<td>23</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>UV-vis spectrum of thiol-L34</td>
<td>24</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>UV-vis spectrum of L34</td>
<td>24</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>1H NMR of By product (09B) of the reduction of 05B</td>
<td>26</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>1H NMR of By product (09B) of the reduction of 05B</td>
<td>26</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>Concentration dependent nonlinear property of L34</td>
<td>27</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Mechanism of synthesis of 1,4-dialkyne from alcohol</td>
<td>35</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Oxidation of 29C using DDQ</td>
<td>46</td>
</tr>
</tbody>
</table>
Figure 3.3 Crystal structure of phenylpropanedinitrile ................................................................. 47

Figure 3.4 The crystal structure of 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol (21C) ................................................................. 49

Figure 3.5 1H NMR of 49C ........................................................................................................ 54

Figure 3.6 1H NMR of toluoyl malondialdehyde ................................................................. 55

Figure 3.7 Formation of I Stilbene instead of 44C ....................................................................... 57

Figure 3.8 The crystal structure of I - Stilbene ........................................................................ 58

Figure 3.9 The structure of (5Z)-3-methyl-5-[phenyl(1H-1,2,4-triazol-3-yl)methylene]-1,2,4-triazole (46C) ................................................. 61

Figure 3.10 UV-vis of pink compound 1H- 1,2,4 Ditriazolylmethene (expected compound (5Z)-3-methyl-5-[phenyl(1H-1,2,4-triazol-3-yl)methylene]-1,2,4-triazole (46C)) .................................................................................. 61

Figure 3.11 Synthesis of 47C ..................................................................................................... 62

Figure 3.12 Crystal structure of p-tolyl(2H-triazol-4-yl)methanone (47C) .................................... 62

Figure 4.1 Mechanism of 5-substituted 1H tetrazole from nitrile ................................................. 72

Figure 4.2 The crystal structure of (44C) .................................................................................... 75

Figure 4.3 UV-vis spectrum of ditetraazole (01D) ......................................................................... 76

Figure 5.1 Naphthacenequinone-2-carboxylic acid ................................................................. 79

Figure 5.2 Schematic diagrams of solar cell types: photogalvanic (“PSC”, left), dye-sensitized (“DSC”, center), and photogalvanic dye-sensitized (“P-DSC”, right). Within diagrams: SC = semiconductor; D = donor; A = acceptor; hv = photoexcitation; e− = electron; I−/I3− = iodide/triiodide ................................................................................................................................. 82

Figure 5.3 Laser flash photolysis of a thin film blend of 2-methylnaphthacenequinone (NeQ-2Me) and spiroMeOTAD. A: Time resolved spectra. B: Monochromatic decay rates for the radical cation spiro-MeOTAD(+) at 500 nm, and for the radical anion NeQ-2Me(−) at 603 nm. Traces are normalized with respect to ∆OD at 740 fs. Inset: overlaid decay traces for initial 9 ps ................................................................. 83

Figure 5.4 Laser flash photolysis of a ternary TiO2/naphthacenequinone-carboxylic acid /spiroMeOTAD film consisting of rutile TiO2 nanorods with surface chemisorbed naphthacenequinone-carboxylic acid and spin-coated spiroMeOTAD. A: Time resolved spectra. B: Monochromatic decay rates for the radical cation spiroMeOTAD(+) at 490 nm, and for the radical anion of naphthacenequinone-carboxylic acid(−) at 600 nm, normalized with respect to ∆OD at 605 fs. Inset: overlaid decay traces for initial 30 ps .................................................................................. 84
### LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 2.1</td>
<td>Synthesis thiol-L34</td>
<td>16</td>
</tr>
<tr>
<td>Scheme 3.1</td>
<td>Synthesis of ditriazolylmethene and its metal chelate</td>
<td>31</td>
</tr>
<tr>
<td>Scheme 3.2</td>
<td>Synthesis of penta-1,4-diyn-3-ylbenzene (06C) from α,α- dibromobenzene</td>
<td>32</td>
</tr>
<tr>
<td>Scheme 3.3</td>
<td>Synthesis of penta-1,4-diyn-3-ylbenzene (06C) The starting from 1-phenyl-2-propyn-1-ol</td>
<td>33</td>
</tr>
<tr>
<td>Scheme 3.4</td>
<td>Synthesis of ditriazolylmethane 26C</td>
<td>34</td>
</tr>
<tr>
<td>Scheme 3.5</td>
<td>Synthesis of 1-methyl-4-(penta-1,4-diyn-3-yl)benzene (34C) The starting from tolualdehyde and copper triflate</td>
<td>36</td>
</tr>
<tr>
<td>Scheme 3.6</td>
<td>Synthesis of (34C) The starting with toluoyl malondialdehyde</td>
<td>37</td>
</tr>
<tr>
<td>Scheme 3.7</td>
<td>Protection of enolic proton of toluoyl malondialdehyde</td>
<td>38</td>
</tr>
<tr>
<td>Scheme 3.8</td>
<td>Synthesis of (5Z)-3-methyl-5-[phenyl(1H-1,2,4-triazol-3-yl)methylene]-1,2,4-triazole (46C) starting from phenylpropanedinitrile</td>
<td>39</td>
</tr>
<tr>
<td>Scheme 3.9</td>
<td>Protection of enol of toluoyl malonaldehyde</td>
<td>56</td>
</tr>
<tr>
<td>Scheme 3.10</td>
<td>Synthesis of 34C The starting from protected toluoyl malondialdehyde</td>
<td>65</td>
</tr>
<tr>
<td>Scheme 4.1</td>
<td>Synthesis of ditetraazolylmethene (02D) starting from phenylpropanedinitrile</td>
<td>73</td>
</tr>
<tr>
<td>Scheme 4.2</td>
<td>Synthesis of 02D from 01D using NBS</td>
<td>77</td>
</tr>
<tr>
<td>Scheme 5.1</td>
<td>Synthesis of 6-methylnaphthoquinone</td>
<td>80</td>
</tr>
<tr>
<td>Scheme 5.2</td>
<td>Overall synthesis of naphthacenequinone-2-carboxylic acid using chromic acid to prepare the 6-methylnaphthoquinone</td>
<td>80</td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

BODIPY: Boron dipyrrin, 4,4-difluoro-4-bora-3\textsuperscript{a},4\textsuperscript{a}-diaz-a-s-indacene

CuAAC: Copper - catalyzed azide - alkyne cycloaddition

DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

DMF: \textit{N},\textit{N}-dimethylformamide

DMSO: Dimethyl sulfoxide

ESA: Excited State Absorption

IR: Infrared (light)

MS: Molecular seives

NMR: Nuclear magnetic resonance

RSA: Reverse saturable absorption

RuAAC: Ruthenium - catalyzed azide - alkyne cycloaddition

SEM: Scanning electron microscope

TBAF: Tetrabutylammonium fluoride

TFA: Trifluoroacetic acid

THF: Tetrahydrofuran

TLC: Thin layer chromatography

TMS: Trimethylsilyl

TPA: Two photon absorption

UV: Ultraviolet

UV-vis: Ultraviolet-visible light
CHAPTER 1
INTRODUCTION

1.1 Overview and Objectives of Dissertation

This dissertation represents part of the work performed by the author during her graduate study at UNT. This dissertation is a study of two major topics that involve synthetic strategies of nonlinear organic liquid material thiol-L34 and the synthesis of nitrogen-enriched derivatives of BODIPY dyes.

1.2 Nonlinear Organic Liquid Materials

Nowadays lasers are being used in different applications such as sensing, switching, medical, surveying and ranging, recreation and entertainment, communication and in military applications. Direct exposure of intense laser on human eyes or on sensors can cause temporary or permanent damage to them. When the wavelength of a laser is known, an appropriate wavelength filter can be used to protect sensors or eyes from the high intensity light of the laser. Fixed-wavelength filters cannot be used for tunable lasers since they range from the UV light to the far infrared region. Tunable filters are also not useful for short laser pulses because they respond very slowly. Usually a laser pulse ranges from picoseconds to nanoseconds in duration and the pulse energy ranges from micro joules to joules. Exposure to high-intensity pulsed laser for a very short duration can damage an optical sensor.¹

Research is being focused on non-linear absorbing materials to protect optical sensors against intense laser pulses.²⁻¹⁵,³²⁻⁴⁸ These materials have multi-photon absorption properties such as reverse saturable absorption (RSA),³⁶⁻³⁹ two photon absorption (TPA) and excited state absorption (ESA),⁴⁰⁻⁵⁰ and non-linear scattering properties.⁵¹ When the light intensity is low the absorption of light is also weak but these materials become increasingly opaque with increasing
intensity of light. The reason they become opaque with increasing intensity of light is due to multiple photon absorption. Materials which have the properties of two-photon absorption and strong excited-state absorption are in demand.

Figure 1.1. Schematic diagram of the nonlinear optical limiting mechanisms in a fiber array (not drawn to scale). There is usually a thin (0.2–0.5mm) layer of liquid between the fiber array and the front window in some of the actual constructed devices.

Most known 2PA materials are solid materials in their pure state at room temperature, and typically do not have good enough solubility to actually effect significant transmittance changes despite their non-linear absorption properties due to the dilute concentrations available. Maximum concentrations of TPA chromophores are about $10^{-3}$ to $10^{-2}$ M. TPA chromophores that are liquid in their pure form at room temperature are desired for optical limiting applications (Figure 1.1), because these chromophores can maintain their linear and nonlinear optical absorption properties at 100%. Examples of liquid TPA chromophores are L346–49, a diarylethyne compound (Figures 1.2 and 1.3), and certain liquid crystalline chromophores in their isotropic phase. Designing new TPA compounds with high solubility and/or a liquid state in pure form at ambient temperature is an important area of research.
4-propyl-4′-butyl diphenyl acetylene called as L34 is an organic compound which behaves as nonlinear liquid material. This compound was prepared by the group Khoo et.al. Figure 1.2 is the UV-vis spectrum of L34 which demonstrates the absorption between 200-300nm.

Two-photon absorbers are transparent at low intensity of light and become increasingly absorptive with increase in the intensity of light.11,14,24-27 L34 has TPA property. In figure 1.3 N₁ is the ground state of L34. When a low intensity laser is passed through L34 fiber core it absorbs one photon and goes to the lower singlet state N₄. When the intensity of the laser is high there is higher probability of two photons simultaneously striking a molecule of the nonlinear material and being absorbed at a time and it goes to the higher singlet state N₂. From higher singlet state N₂ the chromophore loses energy and goes to inter- system crossing. N₅ and N₃ are the lower and higher triplet states of the molecule. After inter system crossing it goes to N₅ where it can absorb the photon and can go to the higher triplet state N₃.
The author in her first project has targeted the synthesis of a thiol derivative of nonlinear compound L34 which will be called thiol-L34 now on. The structure of L34 and thiol-L34 is given below. Thiol group will be bonded at the one end of the L34 molecule. It is assumed that there will be no significant difference in nonlinear properties of these two compounds because the thiol group is very far from the conjugation system of the molecule hence there is no electronic interaction between them. The main purpose of synthesizing thiol-L34 is to anchor gold nanoparticles at thiol group. The reason to bond gold nanoparticles on thiol-L34 is to see a synergetic effect in optical limiting. Because thiol-L34 is a thiol derivative of L34, it is expected to show nonlinear property towards lasers and gold nanoparticles show nonlinear property towards lasers. It is expected to see enhanced TPA of thiol-L34 in the presence of Au nanoparticle due to energy transfer from thiol-L34 to Au.
1.3 Synthesis of Nitrogen-Enriched BODIPY Dyes

Aza-indacenes are rigidified cyclic cyanine dyes that resemble $s$-indacene in shape (Figure 1.5). Dipyrrolylmethenes (dipyrrins) and azadipyrrolylmethenes (aza dipyrrins) dyes are two of the most commonly known aza-indacene dyes. Dipyrrins have a carbon atom at the meso position and azadipyrrins have a nitrogen atom at the meso position. These two classes of dyes differ in their optoelectronic properties as a result of the different atom at the meso position.

Both dipyrrin and azadipyrrin dyes have strong absorbance in the visible region. Metal complexes of dipyrrins such as Zn(II), Sn(II), and Cd(II) are fluorescent. Both types of dyes are used as fluorescent probes of pH, various metal and halide ions, and for some small molecules. They are stable in physiological pH-range and their optical behavior is not strongly dependent on solvent polarity. They decompose only in strongly acidic and basic conditions. They are also used in biomolecule tagging and tissue-scale bioimaging. They have application in solar cells for harvesting solar energy.
Highly fluorescent compound 55C was synthesized accidentally in 1968 by Treibs and Kreuzer which was the first appearance of BODIPY dyes (Figure 1.6). Acylation of 2,4-dimethylpyrrole 52C was carried out with acetic anhydride and boron trifluoride to synthesize the compound 53C. In the presence of acid the condensation of pyrroles 52C and 53C took place to form dipyrrin 54C and which followed the complexation with boron difluoride to give 55C.

In 2009 three groups simultaneously reported the synthesis of unsubstituted BODIPY 59C given in figure 1.7. The synthesis of 59C gave problems while following the commonly known route because the intermediate compound 58C is not stable over -40°C. Tram et al. synthesized 58C at -78°C with the yield of 5-10%. Schmitt et al. carried out McDonald condensation from pyrrole-2-carbaldehyde 57C and pyrrole in the presence of trifluoroacetic acid and prepared unsubstituted dipyrrin 58C. Pena-Cabrera et al. reduced a thiomethyl substituted BODIPY dye 60C to form 59C. The unsubstituted dye 59C is a highly fluorescent compound and has a fluorescence quantum yield of 90% in water.
Dipyrrins (dipyrrolylmethenes) and azadipyrrins (azadipyrrolylmethenes) have strong absorbance in the visible spectrum around 500 nm. Chelation of these two dyes with boron give a strong red shift (50-60 nm) and boron chelation makes them highly emissive.\(^{71}\) UV-vis and fluorescence spectra of dimethylBODIPY-phenyl (01C) are given in figures 1.9 and 1.10 respectively.
The second project targeted the synthesis of compounds 02C, 03C, 04C and 05C to study their optoelectronic properties. BODIPY (bora-diaza-indacene) dyes are highly fluorescent molecules. When the C atom at meso position of BODIPY is replaced by N- atom its fluorescent is red-shifted. In this project the author targeted to substitute C- atom to N –atom in non-ital positions and expand the aza-indacene members including pyrazole, triazoles (1,2,3 and 1,2,4) and tetrazole rings in the structure. It is expected that this research will bring new insight in the optoelectronics, coordination and the reactivity of aza-indacene compounds with N-atom substitution in different positions. These new compounds/complexes will have different applications as ligands and as chromophores. The author has attempted to synthesize aza-indacenes in which 4-8 nitrogen atoms are substituted for carbon atoms within the indacene system. In chapter three the synthesis of the molecules 03C and 04C is discussed and in chapter 4 the synthesis of the molecule 02C is described.
1.4 References


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CHAPTER 2
PREPARATION OF A COLLOIDAL OPTICAL-LIMITING MATERIAL BASED ON DIARYLALKYNE-SENSITIZED GOLD NANOPARTICLES

2.1 Introduction

Chapter two describes the synthesis and characterization of a thiol derivative of L34 (4-propyl-4′-butyldiphenyl acetylene) compound. It is a six steps synthetic route given in Scheme 1.1. After the synthesis of thiol-L34 gold nanoparticles are grown on it. L34 is a compound that exhibits nonlinear optical absorbance which is used to prevent sensors against high intensity lasers. The purpose of synthesizing thiol-L34 is to grow gold nanoparticles at the end of thiol group. Gold also exhibits nonlinear optical absorbance. By growing gold nanoparticles on thiol-L34 a synergetic effect will be studied. It is expected to see enhanced TPA of the organic absorber in the presence of Au nanoparticle due to energy transfer from thiol-L34 to Au.

The compounds 01B and 04B are synthesized by Sonogashira cross coupling reaction. In Sonogashira cross-coupling reaction, coupling between vinyl or aryl halides and terminal alkynes takes place using Pd(0) catalyst, a copper(I) co-catalyst, and an amine base. Because it is difficult to isolate and analyze the organometallic compounds that are present as intermediates in the reaction, the reaction mechanism of the Sonogashira reaction is not completely understood. The predicted mechanism of the reaction is given below.

The compound 03B was prepared by the acid catalyzed esterification of p-bromophenyl propanoic acid and methanol.
Figure 2.1. Predicted reaction mechanism of Sonogashira reaction.\textsuperscript{3}

![Chemical reaction diagram]

Figure 2.2. Synthesis of 4-(4′-butylphenyl)-2-methylbut-3-yn-2-ol (01B)

\[
\begin{align*}
\text{HCCCOH(CH}_3)_2, \text{ CuI} & \quad \text{PdCl}_2(\text{PPh}_3)_2, \text{ PPh}_3, 80 \degree \text{C} \\
\text{Br} & \quad \text{01B} \\
\text{80\%}
\end{align*}
\]

Figure 2.3. Synthesis of 1-butyl-4-ethynylbenzene (02B)

\[
\begin{align*}
\text{HCCCOH(CH}_3)_2, \text{ CuI} & \quad \text{PdCl}_2(\text{PPh}_3)_2, \text{ PPh}_3, 80 \degree \text{C} \\
\text{Br} & \quad \text{01B} \\
\text{80\%}
\end{align*}
\]

Lithium aluminium hydride is widely used as a reducing agent. It can convert esters, carboxylic acids, acyl chlorides, aldehydes and ketones into corresponding alcohols. Compared
to sodium borohydride, LiAlH₄ is a stronger reducing agent because the Al-H bond is weaker than the B-H bond. Esters can easily be reduced by LiAlH₄ into alcohols. The reaction requires 2 equivalents of hydride (H⁻), first to reduce ester to aldehyde and second to reduce aldehyde to alcohol. The reaction is followed by an acid work up. The compound 05B will be prepared by the reduction of 04B with LiAlH₄.

The Appel reaction is used to convert an alcohol to an alkyl halide using a tetrahalomethane (CCl₄ or CBr₄) and triphenylphosphine (PPh₃). In the first step lone pair of electrons of phosphorus attack halogen atom and phosphonium halide is formed along with trihalomethyl cation. Then trihalomethyl cation attack hydrogen of alcohol group and alkoxide ion is formed. The alkoxide ion subsequently attacks the phosphorus and a halide ion is released as a leaving group. In a nucleophilic substitution reaction (SN₂), the halide (nucleophile) attacks the carbon stereocenter and SN₂ reaction takes place resulting in the formation of alkyl halide. Because of the SN₂ mechanism, inversion of the configuration takes place and the reaction gives the product with inverted stereochemistry. Triphenylphosphine oxide is the byproduct of this reaction which is favored by the strong P=O bond formation. The conversion of 05B to 06B is carried out through Appel reaction using PPh₃ and CBr₄. In the compound 05B the carbon bonded with alcohol group has no steric center hence it will not undergo any inversion of configuration after the SN₂ step.

The compound 07B can be prepared by treating 06B with potassium thioacetate. Thioacetate attacks the carbon atom containing bromine and an SN₂ reaction takes place. Bromine departs as a leaving group. Since polar aprotic solvent accelerates the rate of SN₂ reaction, acetone is used as the solvent.
Scheme 2.1. Synthesis thiol-L34
The compound 08B is synthesized from 07B by treating it with HCl and methanol. HCl reacts with methanol to form (CH$_3$OH$_2^+$)Cl$^-$. The carbonyl oxygen is protonated by CH$_3$OH$_2^+$ and an oxonium ion is formed. Then lone pair of electrons on oxygen atom of methanol attacks on carbonyl carbon atom and one of the double bond of C-O bond breaks. The proton from protonated methanol leaves. Then, the double bond is formed between C-O atoms and alkyl sulfide leaves as a leaving group. After protonation, the alkyl sulfide forms thiol (08B).

2.2 Synthesis

2.2.1 General Procedures

Manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques wherever needed. Solvents were purchased from commercial sources, dried over molecular sieves whenever needed for anhydrous conditions, and degassed by purging with argon gas. All other chemicals were reagent grade and were used as received. Glassware were oven-dried at 150°C overnight. NMR solvent CDCl$_3$ was reagent grade and stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on glass backed, pre-coated silica gel plates and visualization was accomplished with UV light. Silica gel 60 μm (average particle size) was used for column chromatography. UV-vis data were collected with a Varian Cary spectrophotometer. 400Hz was used for $^1$H and 75 MHz was used $^{13}$C NMR spectra in CDCl$_3$ unless noted otherwise.

2.2.2 Experimental Section

• Synthesis of 4-(4-butylphenyl)-2-methylbut-3-yn-2-ol (01B)

An oven-dried Schlenk flask with magnetic stir bar was charged with CuI (0.16 g, 0.86 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.60 g, 0.86 mmol) and PPh$_3$ (0.45 g, 1.7 mmol) and evacuated and purged with argon three times successively. In another oven-dried round bottom flask with magnetic stir
bar 1-bromo-4-butylbenzene (3.76 g, 17.6 mmol), 2-methyl-3-butyl-2-ol (1.48 g, 17.6 mmol) and freshly dried TEA (100 mL) was taken and purged with argon for 40 minutes. It was transferred in Schlenk flask. The reaction was left overnight at 80°C. Then mixture was extracted with hexanes and deionized water. The organic layer was separated and washed with a saturated solution of NaHCO₃ and then with brine. The organic layer was isolated and dried over anhydrous Na₂SO₄. The product was purified by column chromatography using hexanes: ethyl acetate in 6:1 ratio. The product was isolated as a transparent liquid (3.03 g, 0.02 mol, yield= 80%) , ^1H NMR (CDCl₃) δ 0.89-0.93 (t, 3H, J = 16 Hz), 1.28-1.37 (m, 2H), 1.53-1.60 (m, 8H), 1.92 (s, OH), 2.56-2.60 (t, 2H, J = 16 Hz), 7.09-7.12 (d, 2H, J = 12 Hz), 7.31-7.33 (d, 2H, J = 8Hz).

- Synthesis of 1-butyl-4-ethynylbenzene (02B)

An oven-dried round bottom flask with a magnetic stir bar was charged with 01B (0.50 g, 0.02 mol), 1-butanol (1 mL) and toluene (25 mL). Finely grounded NaOH (0.02 g, 0.46 mmol) was added and a condenser was connected. The reaction was refluxed for 6 hours. The reaction mixture was cooled at room temperature then extracted with deionized water and hexanes. The organic layer was first washed with saturated solution of NaHCO₃ then with brine. The organic layer was isolated and dried over anhydrous Na₂SO₄. It was filtered and solvent was removed by rotary evaporation. The product was purified using rotary chromatography. Hexanes was used as eluent. The product (0.25 g, 1.58 mmol, yield= 69%) , ^1H NMR (CDCl₃) δ 0.89-0.93 (t, 3H, J = 16 Hz), 1.29-1.38 (m, 2H), 1.53-1.61 (m, 2H), 2.58-2.63 (t, 2H, J = 20 Hz), 3.02 (s, 1H), 7.11-7.14 (d, 2H, J = 12 Hz), 7.39-7.41 (d, 2H, J = 8 Hz).
- Synthesis of methyl 3-(4-bromophenyl)propanoate (03B)

An oven-dried 500 mL round bottom flask was charged with a magnetic stir bar, 3-(4-bromophenyl)propanoic acid (5.33g, 23.3 mmol), methanol (250 mL) and concentrated H₂SO₄ (5 mL) and the mixture was refluxed overnight. Then, it was cooled to room temperature and dried. The mixture was extracted with deionized water and diethyl ether. The organic layer was isolated and dried over anhydrous MgSO₄. Purified product was obtained using rotary chromatography (SiO₂, hexanes:ether, 1:1). The product (5.09 g, 0.02 mol, yield = 90%), ¹H NMR (CDCl₃) δ 2.59-2.63 (t, 2H, J = 16 Hz), 2.88-2.92 (t, 2H, J = 16 Hz), 3.66 (s, 3H), 7.06-7.09 (d, 2H, J = 12 Hz), 7.39-7.41 (d, 2H, J = 8 Hz).

- Synthesis of methyl 3-{4-[(4-butylphenyl)ethynyl]phenyl}propanoate (04B)

An oven-dried Schlenk flask was charged with 2 stir bar, methyl 3-(4-bromophenyl)propanoate (0.75 g, 3.1 mmol), PdCl₂(PPh₃)₂ (0.11 g, 0.15 mmol), PPh₃ (.079 g, 0.30 mmol) and CuI (0.030 g, 0.15 mmol) and purged three times with vacuum and dry argon gas. Another oven-dried round bottom flask was charged with a stir bar, dry TEA and 1-butyl-4-ethynylbenzene and purged with dry N₂ for 30 minutes. This mixture was transferred to a Schlenk flask and heated at 80°C overnight. Then the reaction was cooled to room temperature and TEA was removed by rotary evaporation. The mixture was extracted with deionized water and hexanes. The organic layer was isolated and washed with a saturated aqueous solution of NH₄Cl. The organic layer was then isolated and dried over anhydrous Na₂SO₄. The mixture was purified in rotary chromatography (SiO₂, hexanes:ethyl acetate, 6:1). The product was obtained as pale yellow solid (0.76 g, 2.38 mmol, yield= 78%), ¹H NMR (CDCl₃) δ 0.88-0.92 (t, 3H, J = 16 Hz), 1.28-1.38 (m, 2H), 1.54-1.61 (m, 2H), 2.57-2.64 (m, 4H), 2.91-2.96 (t, 2H, J = 20 Hz), 3.65 (s, 3H), 7.12-7.16 (t,4H, J = 16 Hz), 7.39-7.43 (t, 4H, J = 16 Hz).
- Synthesis of 3-{4-[((4-butylphenyl)ethynyl]phenyl]propan-1-ol (05B)

In an oven-dried round bottom flask with a magnetic stir bar, methyl 3-{4-[((4-butylphenyl)ethynyl]phenyl]propanoate (0.51 g, 1.6 mmol), LiAlH₄ (0.11 g, 3.2 mol) and dry THF (25 mL) were combined. The mixture was stirred for 11 hours. The mixture was quenched with methanol, and extracted with deionized water and ethyl acetate. The organic layer was isolated and dried over anhydrous MgSO₄. The product was purified using rotary chromatography using the eluent hexanes: ethyl acetate in 3:1 ratio. The product was obtained as a dull white liquid (0.35 g, 1.2 mmol, yield = 77%), ¹H NMR (CDCl₃) δ 0.90-0.94 (t, 3H, J = 16 Hz), 1.30-1.39 (m, 2H), 1.45 (s, OH), 1.55-1.63 (m, 2H), 1.86-1.92 (m, 2H), 2.59-2.63 (t, 2H, J = 16 Hz), 2.70-2.74 (t, 2H, J = 16 Hz), 3.66-3.69 (t, 2H, J = 12 Hz), 7.14-7.18 (t, 4H, J = 16 Hz), 7.41-7.45 (t, 4H, J = 16 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 13.96, 22.31, 31.46, 31.98, 33.42, 34.00, 35.59, 61.99, 62.17, 89.13, 119.56, 120.48, 120.96, 128.45, 130.20, 131.43, 131.60.

Synthesis of 1-(3-bromopropyl)-4-[((4-butylphenyl)ethynyl]benzene (06B)

An oven-dried round bottom flask with a magnetic stir bar was charged with PPh₃ (0.38 g, 1.44 mmol). Another oven-dried round bottom flask with magnetic stir bar was charged with CBr₄ (0.48 g, 1.4 mmol) and 05B (0.21 g, 0.72 mmol). Both the flasks were evacuated and purged with argon for three times successively. Dry THF was added in both flasks then they were submerged in ice bath. The solution from the first flask was transferred to the second flask by cannulation. The ice bath was removed and the reaction was run for 45 minutes. The reaction mixture was extracted with hexanes and deionized water, then washed with brine and dried over anhydrous Na₂SO₄. The product was purified by rotary chromatography using the eluent hexanes: ethyl acetate in 9:1 ratio. The product (0.17 g, 0.47 mmol, yield = 65%), ¹H NMR (75 MHz, CDCl₃) δ 0.91-0.94 (t, 3H, J = 12 Hz), 1.3-1.4 (m, 2H), 1.56-1.63 (m, 2H), 2.13-2.20 (m,
2H), 2.60-2.63 (t, 2H, J = 12 Hz), 2.77-2.81 (t, 2H, J = 16 Hz), 3.37-3.41 (t, 2H, J = 16 Hz), 7.14-7.19 (t, 4H, J = 20 Hz), 7.42-7.46 (t, 4H, J = 16 Hz). 13C NMR (75 MHz, CDCl3) δ 13.91, 22.30, 30.92, 33.40, 33.85, 35.59, 88.60, 89.30, 120.46, 121.36, 128.47, 128.59, 131.46, 140.69, 143.31, 207.09.

- Synthesis of S-methyl 3-{4-[(4-butylphenyl)ethynyl]phenyl}propanethioate (07B)

An oven-dried round bottom flask with a magnetic stir bar was charged with 06B (0.16 g, 0.47 mmol), potassium thioacetate (0.070 g, 0.57 mmol) and acetone (4 mL). A septum was put on. The reaction was left stirring overnight at room temperature. The solution was then removed using rotary evaporation. The reaction mixture was extracted using deionized water and ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na2SO4. The product was purified by rotary chromatography using hexanes: ethyl acetate in 12:1 ratio. The product was isolated as a pale yellow liquid (0.14 g, 0.39 mmol, yield = 84%), 1H NMR (CDCl3) δ 0.90-0.94 (t, 3H, J = 16 Hz), 1.30-1.39 (m, 2H), 1.55-1.63 (m, 2H), 1.86-1.93 (m, 2H), 2.34 (s, 3H), 2.59-2.63 (t, 2H, J = 16 Hz), 2.67-2.71 (t, 2H, J = 16 Hz), 2.86-2.90 (t, 2H, J = 16 Hz), 7.13-7.16 (m, 4H), 7.41-7.45 (m, 4H). 13C NMR (75 MHz, CDCl3) δ 13.94, 22.31, 28.49, 30.66, 30.91, 33.41, 34.74, 35.59, 88.69, 89.18, 120.47, 121.12, 128.44, 128.46, 131.44, 131.61, 141.33, 143.26, 195.83.

- Synthesis of 3-{4-[(4-butylphenyl)ethynyl]phenyl}propane-1-thiol (08B)

An oven-dried two-necked round bottom flask with a stir bar was charged with 07B (0.11 g, 0.30 mmol) and a condenser was connected. It was purged with argon for 10 minutes. Methanol (15 mL) and HCl (5 drops) were added and the mixture was refluxed for 5 hours. The reaction was allowed to cool. The reaction mixture was concentrated using rotary evaporation. It was extracted using deionized water and ethyl acetate. The organic layer was washed with brine.
and dried over anhydrous Na₂SO₄. The product was purified by rotary chromatography using hexanes: ethyl acetate in 12:1 ratio. The product was isolated as a pale yellow liquid (0.06 g, 0.22 mmol, yield = 72%), ¹H NMR (CDCl₃) δ 0.90-0.94 (t, 3H, J = 16 Hz), 1.25 (s, SH), 1.32-1.39 (m, 2H, J = 28 Hz), 1.89-1.97 (m, 2H, J = 32 Hz), 2.50-2.56 (m, 2H, J = 24 Hz), 2.59-2.63 (t, 2H, J = 16 Hz), 2.72-2.76 (t, 2H, J = 16 Hz), 7.14-7.16 (m, 4H), 7.41-7.45 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 13.94, 22.30, 23.92, 33.40, 34.25, 35.21, 35.59, 88.68, 89.20, 120.47, 121.08, 128.45, 128.49, 131.44, 131.61, 141.46, 143.28.

• Growth of gold nanoparticles

In a conical flask HAuCl₄.3H₂O (0.070 g, 0.17 mmol) was dissolved in deionized water (5.73 mL). In another flask tetraoctyl ammonium bromide (0.43 g, 0.17 mmol) was dissolved in toluene (18.6 mL) to make a 0.04M solution. The second solution was added to the first solution and the mixture was stirred vigorously. An intense red/orange color was formed. When all the red/orange color had moved to the upper (organic) layer, 08B (0.050 g, 0.17 mmol) in toluene (4 mL) was added and stirred for 30 minutes. Then in another flask NaBH₄ (0.070 g, 0.17 mmol) was dissolved in deionized water (5.66 mL) to make 0.34 M solution and was added to the above solution. Simultaneously, the color changed to black/brown. The reaction was left stirring for 16 hours. The organic layer was separated and reduced to 5 mL using rotary evaporation. Ethanol (50 mL) was added and the mixture was centrifuged for 1 hour. The supernatant was separated with a pipette. Again, ethanol (50 mL) was added and the mixture was centrifuged for 1 hour and the supernatant was removed. The residue was dissolved in toluene, filtered and concentrated by rotary evaporation. The product (0.040 g) was collected as a black powder.
2.2.3 Characterization and Physical Measurements

C-S and C-S-H stretching vibrations give very weak absorption in the infrared spectrum. Infrared spectrum of thiol-L34 is given in figure 2.4. The weak peak around 2567 cm\(^{-1}\) is the peak for S-H stretching. Another weak peak around 644 cm\(^{-1}\) could be the peak for C-S-H stretching where the carbon atom is aliphatic. The very weak peak around 2100 cm\(^{-1}\) may be the peak for internal alkyne C-C triple bond stretching, although that region is noisy due to difficulty in accurately baselining the absorption by ambient CO\(_2\).

![Figure 2.4. IR spectrum of Thiol-L34](image)

Figure 2.4 is the UV-vis absorbance spectrum of thiol-L34. Here absorbance can be seen around 300 nm. Figure 2.5 is the UV-vis absorbance spectrum of the L34 which is copied from the article.\(^6\) While comparing between these two figures it is observed that there is a similar
pattern of absorbance around 300 nm in both the compound L34 and thiol-L34. This is what was expected because in thiol-L34 thiol group is very far from the unsaturated system within the molecule hence there is no interaction between unsaturated system and thiol group within the molecule.

Figure 2.5. UV-vis spectrum of thiol-L34

Figure 2.6. UV-vis spectrum of L346
Results and Discussion

Compounds 01B and 04B were synthesized using a Pd(0) catalyst according to the typical conditions for the Sonogashira reaction. While synthesizing 01B for the first time, the reaction was made at room temperature. There was no reaction and the starting compound was recovered. The second time, the reaction was run at 80ºC and 01B was formed and the yield was 80%. In synthesizing 04B first the reaction was ran at 80ºC and the yield was lower and when the reaction was ran at 40ºC the yield was 79%. It was seen that in Sonogashira reaction yield depends on using an optimal temperature which depends on the starting compounds.

During the synthesis of compound 02B, the yield was very low in the initial attempts. Later it was found that compound is volatile. When the reaction was refluxed overnight some of the compound escaped. After purification, the compound was kept under high vacuum and it escaped. Later it was recovered from the trap of the high vacuum. This is very important to use trap if the molecules are small in size.

05B was synthesized by reducing 04B using the reducing agent LiAlH₄. LiAlH₄ was taken in an oven-dried round bottom flask with a magnetic stir bar and purged with argon for 5 minutes. Dry THF was added. Then 05B was dissolved in dry THF and added. After two hours a TLC was done using SiO₂ plate as stationary phase and the eluent hexanes: ethyl acetate in 2:1 ratio. By assuming that LiAlH₄ is not in good condition an excess of LiAlH₄ was added and the reaction was left running for 3 days. After purification it was found that trans-alkene (09B) (the structure is given below) was formed as major product along with desired product. ¹H NMR spectrum of this product is given below.
During the synthesis of the compound 02B, dimer 10B was formed as by product. The $^1$H NMR of 10B is given in the appendix.

The compound synthesized here is thiol derivative of L34 and to enhance the optical limiter property gold nanoparticles are also grown. We expect the behavior of our compound will be similar to this compound. We are growing gold nanoparticles to improve the range of the radiation compound can absorb. We expect that our compound will only show TPA properties not the ESA property.

2.4 Conclusion and Future Works

Thiol-L34 was synthesized in a six-steps synthesis starting from 3-(4-bromophenyl)propanoic acid. Gold nanoparticles were grown on thiol-L34. Both the material
neat thiol-L34 and gold nanoparticles capped with thiol-L34 were synthesized. Gold nanoparticles capped with thiol-L34 will be characterized by SEM and/or TEM imaging.

![Concentration dependent nonlinear property of L34](image)

**Figure 2.9. Concentration dependent nonlinear property of L34**

Both the materials have already been sent to collaborator professor I. C. Khoo from Penn State University for further investigation of the properties and effectiveness of the material in controlling the intensities of the laser. Figure 2.9 shows the nonlinear property of L34 dependent on the concentration of the compound. From the figure it is seen that the nonlinear property improves as the concentration of the compound is increased. Gold nanoparticles capped with thiol-L34 will be mixed with L34 and the nonlinear optical absorption will be studied.

2.5 References


CHAPTER 3
SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF BODIPY DYES-
DITRIAZOYL METHENE DYES AND THEIR DERIVATIVES

3.1 Introduction

When C-atom from dipyrrin is replaced by an N-atom at the *meso* position, the intensity of the fluorescence was significantly red-shifted. In this chapter the attempt of replacement of C-atom by N-atom at non-*meso* positions of the dipyrrin scaffold is described. This chapter mainly describes the different routes of synthesis of ditriazolylmethene that were attempted.

In Scheme 3.1, 1,2,3-triazole synthesis is planned using $06C$ and $07C$ with ruthenium catalyst$^{10,11}$ and it will give 1,5-substitution. Among $[\text{Cp}^*\text{RuCl}]$ complexes $[\text{Cp}^*\text{RuCl}]_4$, $\text{Cp}^*\text{RuCl}($COD$)$, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$, and $\text{Cp}^*\text{RuCl}($NBD$)$, are the common catalysts used in the cycloaddition of azides with terminal alkynes which leads to regioselectivity, 1,5-disubstituted 1,2,3-triazoles. In contrast to the CuAAC, ruthenium catalyzed reaction RuAAC, gives cycloaddition reaction of azides with internal alkynes easily to produce 1,2,3-triazoles, providing access to fully substituted 1,2,3-triazoles.$^{19-25}$The compound $08C$ must be treated with TBAF to give free triazole $10C$. $10C$ can exist in two tautomeric form 1H or 3H. Further, $10C$ must be oxidized using $p$-chloranil to form $12C$. 


Scheme 3.1. Synthesis of ditriazolylmethene and its metal chelate

In Scheme 3.2, trimethylsilylacetylene is treated with n-butyllithium to form trimethylsilyl lithium acetylide. When trimethylsilyl lithium acetylide is treated with \(\alpha,\alpha\)-dibromobenzene it will form the compound \(14\) through \(S_N2\) reaction. Treating \(14\) with TBAF will result in the formation of \(06\).
Scheme 3.2. Synthesis of penta-1,4-diyn-3-ylbenzene (06C) from α,α- dibromobenzene

In Scheme 3.3, the compound 07C is oxidized to form 08C with DDQ. When 08C is treated with trimethylsilyl lithium acetylide it will attack carbonyl carbon and an intermediate of lithium alkoxide salt is formed. After quenching with NaHCO₃ it is protonated and gives 09C. The trimethylsilyl groups can be cleaved with TBAF and 10C will be formed. When 10C is treated with TFA and triethylsilane the mixture of 06C, 12C, 61C and 13C is expected to be formed.
Scheme 3.3. Synthesis of penta-1,4-diyn-3-ylbenzene (06C) The starting from 1-phenyl-2-propyn-1-ol

In Scheme 3.4, toluoyl chloride will be treated with trimethylsilyl lithium acetylide. First, trimethylsilyllithium acetylide will attack to the carbon atom of the carbonyl group and negative charge will be created on the oxygen atom. A double bond will be formed between the carbon
atom and oxygen atoms and chloride will leave. Again, another trimethylsilylithium acetylide will attack the carbon atom of carbonyl carbon atom. After quenching with NaHCO₃ 21C will be formed. Trimethylsilyl groups of 21C can be cleaved with TBAF to form 24C. Azide-Alkyne Huisgen cycloaddition is carried out between 24C and 25C in the presence of Cp*RuCl(COD) catalyst to synthesize 26C.

![Scheme 3.4. Synthesis of ditriazolylmethane 26C](image)

In Scheme 3.5, tolualdehyde is treated with triisopropylsilyllithium acetylide then quenching with NaHCO₃ to form 29C. Then 29C is treated with triisopropylsilyl acetylene in the
presence of copper triflate to form $30C$. Then $34C$ can be prepared by cleaving triisopropylsilyl group with TBAF. In the mechanism shown below (figure 3.1) propargyl alcohol 1 is activated by Lewis or Brønsted acid to form carbocation A. Now the nucleophilic attack of alkyne 2 will form alkenyl cation B. After this step two pathways are possible path I, proton elimination and path II, hydrolysis. Path I will give 1,4-diynes and path II will give $\gamma$-alkynyl ketones. Since in Scheme 3.5 $30C$ is expected to form so molecular sieves will be used in the reaction to minimize the path II.

Figure 3.1. Mechanism of synthesis of 1,4-dialkyne from alcohol$^{63}$
Scheme 3.5. Synthesis of 1-methyl-4-(penta-1,4-diyn-3-yl)benzene (34C) The starting from tolualdehyde and copper triflate
In Scheme 3.6, a Corey-Fuchs procedure is used to convert aldehyde 31C to a terminal alkyne 34C. In 1972, Corey and Fuchs published a method in which an aldehyde could be converted to a terminal alkyne with one carbon derivativeation.77-79 This is a one pot synthesis of alkyne which proceeds through two steps. In the first step CBr4 and PPh3 reagents are used to convert aldehyde into dibromoolefin with derivativeation of one carbon atom, is called Ramirez olefination.80 In the second step n-butyllithium is used followed by protonation with water to form the alkyne.

Scheme 3.6. Synthesis of 1-methyl-4-(penta-1,4-diyn-3-yl)benzene (34C) The starting with toluoyl malondialdehyde
Oxidative cyclization of nitriles can be done with amidines in the presence of CuI. Atmospheric oxygen will be used as an oxidant.\textsuperscript{73} This type of oxidative cyclization gives 1,2,4-triazole (Scheme 3.8).
Scheme 3.8. Synthesis of (5Z)-3-methyl-5-[phenyl(1H-1,2,4-triazol-3-yl)methylene]-1,2,4-triazole (46C) The starting from phenylpropanedinitrile

3.2 Synthesis

3.2.1 General Procedure

All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques wherever needed. Solvents were purchased from commercial sources, dried over molecular sieves and degassed by purging with argon gas. All other chemicals were reagent
grade and were used as received. Glassware were oven-dried at 150°C overnight. NMR solvent CDCl₃ was reagent grade and stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on glass backed, pre-coated silica gel plates and visualization was accomplished with UV light. Silica gel 60 μm (average particle size) was used for column chromatography. UV-vis data were collected with a Varian Cary spectrophotometer. 400 MHz was used for ¹H and ¹³C NMR spectra in CDCl₃ unless noted otherwise.

3.2.2 Experimental Section

- Synthesis of 1-phenylprop-2-yn-1-one (08C)

A round bottom flask with a stir bar was charged with 07C (1.88g, 14.0 mmol), DDQ (3.18 g, 14.0 mmol) and dichloromethane (140 mL). The reaction was run overnight and TLC was performed using eluent hexanes: dichloromethane in 1.5:1 ratio. The starting compound was seen in TLC. The reaction was left stirring 3 days. The reaction mixture was filtered through silica gel using dichloromethane. The filtrate was concentrated. The product was collected as a light orange liquid (1.21 g, 9.30 mmol, yield = 66%), ¹H NMR (CDCl₃) δ 3.38 (s, 1H), 7.26-7.29 (t, 2H), 7.39-7.43 (t, 1H), 7.94-7.95 (d, 2H).

- Synthesis of (09C)

An oven-dried round bottom flask with a stir bar was charged with 08C (0.10 g, 0.77 mmol) and kept under argon gas. Dry tetrahydrofuran (15 mL) was added in it. Another oven-dried round bottom flask with a stir bar was charged with trimethylsilyl lithium acetylide (0.50 M, 6.10 mL, 3.07 mmol) and dry tetrahydrofuran (10 mL) and kept under argon gas for 20 minutes. The solution of the first round bottom flask was transferred to the second round bottom flask drop by drop with an oven-dried glass syringe. A red color appeared in the mixture. After 4 hours the reaction was evaluated by thin layer chromatography using the eluent hexanes:
dichloromethane in 1:1.5 ratio and it was found that all the starting compound \textit{08C} was consumed. The reaction mixture was quenched with saturated solution of NaHCO$_3$. It was extracted with diethyl ether and deionized water. The organic layer was separated and dried over anhydrous MgSO$_4$. Then it was filtered, concentrated and purified by rotary chromatography. The product (0.05 g 0.20 mmol, yield = 26\%) \textsuperscript{1}H NMR (CDCl$_3$) $\delta$ 0.23 (s, 9H), 1.64 (s, 1H), 2.79 (s, 1H), 7.38-7.40 (d, 3H), 7.78-7.80 (d, 2H).

- Synthesis of 3-phenylpenta-1,4-diyn-3-ol (10C)

A round bottom flask with a stir bar was charged with \textit{09C} (0.84 g, 3.70 mmol), tetrabutylammonium fluoride (0.97g, 3.70 mmol) and tetrahydrofuran (25 mL). The reaction was stirred for 1 hour at ambient temperature. The reaction mixture was concentrated and filtered through silica gel and purified by rotary chromatography. The product (0.05 g, yield = 6\%), \textsuperscript{1}H NMR (CDCl$_3$) $\delta$ 2.80 (s, 2H), 2.94 (s, broad, OH), 7.37-7.43 (t, 3H), 7.80-7.82 (d, 2H).

Synthesis of 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol , (21C)

An oven-dried round bottom flask with a stir bar was purged with argon for 10 minutes. Dry THF (20 mL) was transferred with an oven-dried glass syringe and trimethylsilyl acetylene (1.01 mL, 7.10 mmol) was added to it. Then the round bottom flask was merged in isopropyl alcohol and a dry ice bath was applied to make the temperature -78$^\circ$C and n-butyllithium (4.93 mL, 7.10 mmol) was added. The reaction was run for one hour. Isopropyl alcohol and dry ice were removed. At room temperature, toluoyl chloride (0.50 g, 3.23 mmol) was added and the reaction was left running overnight. Then, it was quenched with saturated ammonium chloride solution. Then it was extracted with deionized water and ether. The organic layer was separated and dried over anhydrous magnesium sulfate. The mixture was purified by rotary chromatography using the eluent hexanes: ethyl acetate in 10:1 ratio. The product was dried
under high vacuum. The product (0.40 g, 1.26 mmol, yield = 39%), $^1$H NMR (CDCl$_3$) $\delta$ 0.22 (s, 1H), 2.37 (s, 3H), 2.78 (s, 1H), 7.18-7.20 (d, 2H), 7.66-7.69 (d, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 0.031, 21.50, 65.83, 90.18, 104.96, 126.31, 129.31, 138.84, 139.01.

Synthesis of 3-(4-methylphenyl)penta-1,4-diyn-3-ol (24C)

In a round bottom flask with a stir bar 21C (0.14g, 0.44 mmol) was dissolved in 20 mL THF and tetrabutylammonium fluoride (0.88 mL, 0.88 mmol) was added in it. The reaction was run for one hour. After one hour the mixture was concentrated and filtered through silica gel using the eluent ethyl acetate. Then the filtrate was concentrated and purified using rotary chromatography and hexanes: dichloromethane in 1.5:1 ratio. The product was dried under high vacuum. The product (0.07 g, 0.39 mmol, yield = 89%), $^1$H NMR (CDCl$_3$) $\delta$ 2.37 (s, 3H), 2.78 (s, 1H), 7.21-7.22 (d, 2H), 7.68-7.70 (d, 2H).

- Synthesis of 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol, (29C)

An oven-dried round bottom flask with a stir bar was purged with argon gas for 10 minutes. Dry THF (75 mL) was added and the vessel was purged with argon for 10 minutes. Triisopropylsilylacetylene (1.01 mL, 4.58 mmol) was added. Then, n-butyllithium (4.32 mL, 4.576 mmol) was added. The mixture changed to milky white appearance which disappeared after 2-5 minutes. The reaction was run for 1 hour then p-tolualdehyde (0.50 g, 4.2 mmol) was added in it. After 4 hours TLC was done using the eluent hexanes: dichloromethane in 1:1.5 ratio. The starting material was not consumed completely. The reaction was run overnight. Afterwards, the color was changed to pale yellow. Then the mixture was quenched with saturated solution of sodium bicarbonate. It was first extracted with hexanes and deionized water then with brine. The organic layer was separated and dried over anhydrous sodium sulfate. The organic layer was concentrated and purified using rotary chromatography and the eluent hexanes:
dichloromethane in 1:1.5 ratio. The product was concentrated and kept under high vacuum. The product (1.25 g, 4.10 mol, yield = 99%), $^1$H NMR (CDCl$_3$) δ 1.09 (s, 21H), 2.36 (s, 3H), 5.44-5.45 (d, 1H), 7.18-7.20 (d, 2H), 7.46-7.48 (d, 2H).

- **Synthesis of 1-methyl-4-(1,1,5,5-tetrabromopenta-1,4-dien-3-yl)benzene (32C)**

An oven-dried round bottom flask with a stir bar was charged with carbon tetrabromide (0.82 g, 2.48 mmol) and dry dichloromethane (40 mL) and kept under argon gas. The round bottom flask was submerged in ice bath to make the temperature 0°C. After 10 minutes PPh$_3$ (1.26 g, 4.80 mmol) was added in it. The color of the mixture changed to orange. Then toluoyl malondialdehyde (0.40 g, 2.48 mmol) was added in it and ice bath was removed. The orange color of the mixture was disappeared. The reaction mixture was evaluated by thin layer chromatography and it was noticed that all the starting compound was consumed. The reaction mixture was extracted with dichloromethane and deionized water. The organic layer was separated and dried over anhydrous Na$_2$SO$_4$. The product was purified by rotary chromatography using hexanes: dichloromethane in 1.5:1 ratio, concentrated in rotary evaporation and kept under high vacuum. The product (0.08 g, Yield = 6%), $^1$H NMR (CDCl$_3$) δ 1.59 (s, 1H), 2.43 (s, 3H), 7.19-7.21 (d, 2H), 7.65 (s, 1H), 9.66 (s, 1H).

- **Synthesis of 4,4-dibromo-2-(4-methylphenyl)but-3-enal (33C)**

An oven-dried round bottom flask with a stir bar was charged with carbon tetrabromide (CBr$_4$) (0.41 g, 1.23 mmol) and dry dichloromethane (15 mL), submerged in ice bath and kept under argon gas. PPh$_3$ (0.65 g, 2.50 mmol) was added in it. After 40 minutes triethylamine (0.39 mL) was added and the color of the mixture was changed to dark orange. After 2 hours the color was changed from dark orange to purple. Then toluoyl malondialdehyde (0.20 g, 1.23 mmol) was added and the reaction was left running overnight at ambient temperature. The reaction mixture
was extracted with deionized water and dichloromethane. The organic layer was separated and dried over anhydrous Na$_2$SO$_4$. It was filtered, concentrated and purified by rotary chromatography using hexanes: dichloromethane in 1.5:1 ratio. The product was collected, concentrated and kept under high vacuum. The product (0.03 g, yield = 7%), $^1$H NMR (CDCl$_3$) $\delta$ 2.44 (s, 3H), 6.26-6.29 (d, 1H), 7.01-7.04 (d, 1H), 7.10-7.13 (d, 2H), 7.28-7.30 (d, 2H), 9.69 (s, 1H).

- Synthesis of (2Z)-3-hydroxy-2-(4-methylphenyl)prop-2-enal (35C)

An oven-dried round bottom flask with a stir bar was charged with CBr$_4$ (0.20 g, 0.62 mmol) and dichloromethane (5 mL). It was kept under argon gas and was submerged in an ice bath to make the temperature 0°C. Then PPh$_3$ (0.33 g, 1.25 mmol) was added in it. The color changed to orange. After 10 minutes TEA (0.20 mL, 1.40 mmol) was added. The change in color from orange to purple was noticed after 35 minutes. In another oven-dried round bottom flask toluoyl malonodialdehyde (0.10 g, 0.61 mmol) was dissolved in dry dichloromethane (2.5 mL) and transferred to the first round bottom flask. The reaction was evaluated by TLC using the eluent hexanes: ethyl acetate in 3:1 ratio. The starting compound was not consumed completely. The reaction was left running overnight. Then the reaction mixture was distillated by rotary evaporation to remove the solvent. Then it was filtered through silica gel using the eluent hexanes: dichloromethane in 1.5:1 ratio, and purified by rotary chromatography using the eluent hexanes: dichloromethane in 1.5:1 ratio. The product was concentrated and kept under high vacuum. The product (0.04 g, 0.13 mmol, yield = 41%).

- Synthesis of (Z)-5-[tert-butyl(diphenyl)silyl]oxy-3-(p-tolyl)pent-4-en-2-one (42C)

An oven-dried round bottom flask with a stir bar was charged with toluoyl malonodialdehyde (0.40 g, 2.50 mmol) and kept under argon gas. Dry dichloromethane (20 mL)
was added in it. When all the toluoyl malonodialdehyde was dissolved in dichloromethane, t-butyl chlorodiphenyl silane (1.02 g, 3.70 mmol) and triethylamine (0.34 mL, 2.50 mmol) was added. The reaction was evaluated by TLC using the eluent hexanes: diethyl ether in 3:1 ratio. Hence the starting compound was not consumed completely, reaction was run overnight. Then the mixture was concentrated and purified in rotary chromatography using the eluent hexanes: diethylether in 3:1 ratio. The compound was collected, concentrated and kept under high vacuum. The product (0.36 g, 0.90 mmol, yield = 36%) 1H NMR (CDCl3) δ 1.07 (s, 9H), 2.38 (s, 3H), 5.30 (s, 1H), 7.15 (s, 1H), 7.22-7.24 (d, 2H), 7.36-7.45 (m, 5H), 7.48-7.52 (t, 3H), 7.62-7.64 (d, 3H), 7.70-7.72 (d, 1H), 9.26 (s, 1H).

- Synthesis of phenylpropanedinitrile (44C)

A two-necked oven-dried round bottom flask with a stir bar was charged with malononitrile (0.26 g, 1.96 mmol), CuI (0.04 g, 1.96 mmol) and K2CO3 (1.09 g, 1.96 mmol). An oven-dried condenser was set on it. Dry dimethyl sulfoxide (5 mL) was added. Then iodobenzene (0.40 g, 1.96 mmol) was added in it. The mixture was refluxed overnight. Then, it was cooled to room temperature and quenched with dilute hydrochloric acid. The mixture was extracted with deionized water and diethyl ether. The organic layer was separated and dried over anhydrous Na2SO4. The product was purified by rotatory chromatography using the eluent hexanes: ethyl acetate in 6:1 ratio. The second band was collected, concentrated and kept under high vacuum for 1 hour and the sample was taken for NMR. The product (0.10 g, 0.70 mmol, Yield = 36%) 1H NMR (CDCl3) δ 5.07 (s, 1H), and 7.50 (s, 5H).

- Synthesis of 1-(p-tolyl)-3-trimethylsilyl-prop-2-yn-1-one (51C)

A round-bottom flask with a stir bar was charged with 29C (1.25 g, 4.10 mmol) and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.93g, 4.10 mmol). Dichloromethane (140 mL) was
added in it. The color of the mixture changed to green. The reaction was left running for 3 days and the color changed to orange. The mixture was concentrated and filtered through silica gel to remove unreacted DDQ and purified by rotary chromatography using the eluent hexanes: dichloromethane in 1:1.5 ratio. The product (1.08 g, yield = 87%) had following data $^1$H NMR (CDCl₃) $\delta$ 1.16 (s, 21H), 2.43 (s, 3H), 7.28-7.30 (d, 2H), 8.06-8.08 (d, 2H)

![Chemical structure diagram](image)

Figure 3.2. Oxidation of 29C using DDQ

3.2.3 Characterization and Physical Properties

X-ray crystallographic data were collected by Dr. Vladimir Nesterov from the University of North Texas, who also provided the following description of the crystallographic data and details. Crystal structure determination for all complexes were carried out using a Bruker SMATR APEX2 CCD-based X-ray diffractometer equipped with a low temperature device and Mo-target X-ray tube (wavelength = 0.71073 Å). Measurements were taken at 100(2) K.

A few milligrams of phenylpropanedinitrile (44C) was dissolved in a minimum of dichloromethane to make a saturated solution. The solution was left 3 days in the dark under the fume hood. After 3 days pale yellow colored crystals were formed and the crystals were taken for crystallography. The crystal structure of phenylpropanedinitrile is given in figure 3.3 and other information is given in table 3.1 in detail.
Table 3.1 Crystallography data for phenylpropanedinitrile

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A few milligrams of 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol (21C) was dissolved in minimum dichloromethane to make a saturated solution and left in the dark under the hood for 3 days. Light orange colored crystals were formed which were taken for crystallography. The crystal structure of (21C) is given in figure 3.4 and other information are given in Table 3.2 in detail.
Figure 3.4. The crystal structure of 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol (21C)

Table 3.2. Crystallography data 3-(p-tolyl)-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol , (21C)

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To synthesize 06C, an oven-dried round bottom flask with magnetic stir bar was charged with NaNH₂ (0.31 g, 7.82 mmol) under argon gas. Dry diethyl ether (12 mL) was added in it.
Then, trimethylsilylacetylene (0.70 g, 7.10 mmol) was added. The color was changed to milky white. α,α- dibromotoluene (0.81 g, 3.23 mmol) was added and the reaction was left overnight. Then, reaction mixture was quenched with saturated solution of NaHCO₃ and extracted with diethyl ether and deionized water. The organic layer was separated and dried over anhydrous MgSO₄. Unfortunately the product 06C was not formed and the starting compound α,α- dibromotoluene was recovered. Now, an oven-dried round bottom flask with magnetic stir bar was charged with trimethylsilyllithium acetylide (7.76 mL, 3.88 mmol) and kept under argon gas. Dry tetrahydrofuran (15 mL) was added in it. Then α,α- dibromotoluene (0.50 g, 1.94 mmol) was added and reaction was left overnight. Then it was quenched with saturated solution of NaHCO₃ and extracted with diethyl ether and deionized water. The organic layer was separated and dried over anhydrous MgSO₄. The product was purified. Again, unfortunately The starting compound α,α– dibromotoluene was recovered. It was concluded that the presence of two electronegative atoms (bromine atoms) facilitate deprotonation of benzylic proton rather than the substitution of bromine by trimethylsilylsodium acetylide/ trimethylsilyl lithium acetylide.

The compound 08C was synthesized by the oxidation of 1-phenyl-2-propyn-1-ol with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone as given in experimental section. Then the compound 09C was synthesized which is also described in experimental section of this dissertation. The compound 09C was treated with tetrabutylammonium fluoride to cleave trimethylsilyl group to form the compound 10C. The compound 10C was treated with trifluoroacetic acid and triethylsilane. It was expected that the mixture of three compounds 06C, 12C and 13C will be formed. When the resulting mixture was evaluated by thin layer chromatography a very large number of compounds were seen and it was not worthwhile to purify the mixture.
To synthesize the compound 21C, n-butyllithium was titrated with diphenyl acetic acid. 
n-butyllithium was treated with trimethylsilylacetylene (TMS-acetylene) to prepare lithium 
trimethylsilylacetylide. p-toluoyl chloride was added in lithium trimethylsilyl acetylide. Then the 
mixture was quenched with saturated solution of ammonium chloride. The compound 21C was 
prepared successfully.

To synthesize the compound 23C, 21C was dissolved in dichloromethane under argon 
gas (under inert condition) and triethylsilane was added. Then trifluoroacetic acid (TFA) was 
added in it expecting to synthesize the mixture of compounds 06C, 12C, 61Cand 13C. Later, the 
reaction was planned to treat with tetrabutyl ammonium fluoride (TBAF) to get the final product 
23C. Unfortunately, the reaction did not succeed. A large number of compounds was formed in 
the mixture and it was not possible to purify the compounds formed in the mixture and identify 
them. When the synthesis of 6C, 12C, 61C and 13C did not succeed according to Scheme 3.3 
compound 22C was used as it is to proceed to further reaction as given in Scheme 3.4. The 
compound 22C was treated with tetrabutylammonium fluoride to synthesize 3-(4-
methylphenyl)penta-1,4-diyn-3-ol (24C). The detail of this reaction is given in the experimental 
section. The next step was to make the click reaction by the ruthenium catalyzed 1,3-dipolar 
azole-alkyne cycloaddition. An oven-dried round bottom flask with magnetic stir bar was 
charged with Cp*RuCl(COD) (0.01 g) and purged with argon gas three times. Another oven-
dried round bottom flask with magnetic stir bar was charged with 24C (0.18 g, 1.10 mmol) and 
25C (0.28 g, 1.10 mmol) and it was also purged with argon gas three times. Then dry toluene (5 
ml) was added in both of the flasks. The second flask’s solution was canulated to the first flask. 
The color of the mixture was changed to dark brown immediately. Progress of the reaction was 
evaluated by thin layer chromatography. A very polar spot was noticed in TLC which did not
move in very polar solvents like acetone and ethanol. It was assumed that the product might have been polymerized which is a drawback of double azide-alkyne cycloaddition. The mixture was treated with NaF and ethanol and again it was evaluated by TLC. There was no change in TLC. Now the mixture was treated with acetic acid and triethylamine and again evaluated by TLC. TLC showed the same result. It was assumed that the –OH group at benzylic position might have been reacted with Cp*RuCl(COD) catalyst. Now, it was necessary to synthesize the compound 06C or 34C and another route was followed which is given in Scheme 3.5.

In Scheme 3.5 tolualdehyde was treated with triisopropylsilyllithium acetylide to synthesize the compound 29C. An oven-dried round bottom flask with stir bar was charged with the compound 29C (0.40 g, 1.32 mmol) and dichloroethane (12 mL) and purged with argon gas for 5 minutes. Another oven-dried round bottom flask with a stir bar was charged with Cu(OTf)2 (0.05 g, 0.13 mmol) and a reflux condenser was connected. The solution from the first round bottom flask was transferred in second round bottom flask. Then trimethylsilyl acetylene (0.129 g, 0.13 mmol) was added in it. Round bottom flask was submerged in preheated oil bath (84°C). The reaction was refluxed for 5 minutes. The color of the mixture was changed to green. Then the oil bath was removed. The product was purified by rotary chromatography. Unfortunately the compound 30C was not formed. Instead, it appears that the compound 1,1'-deca-1,4,6,9-tetrayne-3,8-diyl dibenzene 49C and / or 50C was formed through Eglington coupling. The NMR spectrum of this compound is given in given below in figure 3.5.
In Scheme 3.6, Corey- Fuchs reaction was carried out to synthesize the compound 34C. When toluoyl malondialdehyde was treated with PPh$_3$ and CBr$_4$ in the presence of triethylamine in the place of 32C the compound 33C was formed. When toluoyl malondialdehyde was treated with PPh$_3$ and CBr$_4$ the compound 32C was formed but the yield was very low. It was assumed that the reason of low yield and the formation of the compound 33C was the enolic form of the starting compound toluoyl malondialdehyde as given below. There is possibility of hydrogen bonding between enolic hydrogen and the oxygen atom of aldehyde group. $^1$H NMR of the compound is given in figure 3.6.
Now, it was necessary to protect the enolic proton. To protect the enol toluoyl malondialdehyde was treated with acetic anhydride as given in Scheme 3.9. After work up and purification it was found that the compound \(36C\) was formed in a very little quantity and majority of the compound formed was \(37C\). Multiple acylation took place. The \(^1\)H NMR of these two compounds are given in the Appendix.

Now toluoyl malondialdehyde was treated with dihydropyran as given in Scheme 3.7 to form \(40C\). Again the majority of the compound was \(41C\) not \(40C\).
When the protection of enol of toluoyl malonaldehyde with acetic anhydride or dihydropyran did not give satisfactory result t-butylchlorodiphenyl silane was used for protection. To protect the enolic proton of toluoyl malondialdehyde, it was treated with t-butyl chlorodiphenyl silane and the compound 42C was synthesized. More information about the synthesis of 42C is given in experimental section and further reactions are planned and given in conclusion and future works of this chapter. 1H NMR and 13C NMR of this compound is given in appendix.

When the synthesis of 06C took long time and many routes were followed and simultaneously some other reactions were carried out to synthesize 10C and/or 12C. One of
them is given in Scheme 3.8. Several routes and attempts were carried out to synthesize phenylpropanedinitrile (44C). In the first attempt, an oven-dried round bottom flask with a stir bar was charged with KI and KCN. Dry DMF was added in it then alpha, alpha-dibromotoluene was added. The reaction was refluxed overnight. First the color changed to brownish yellow, then after 30 minutes brownish yellow color was disappeared. The reaction mixture was evaluated by thin layer chromatography using silica gel plate as stationary phase and hexanes as solvent. The starting compound (alpha, alpha-dibromotoluene) was not consumed completely. The reaction was left running overnight. Then the color of the reaction mixture was yellow. The reaction mixture was quenched with 2 M H₃PO₄. Then it was extracted with deionized water and hexanes. The organic layer was separated and dried over anhydrous Na₂SO₄. The product was purified by rotary chromatography using hexanes as solvent. The product was collected, concentrated and dried over high vacuum and taken for NMR. The crystals of the product were grown from dichloromethane solution. From the crystallography it was confirmed that the crystals have monoclinic structure and the product was not phenylpropanedinitrile but (E)-stilbene. Crystal structure of (E)–stilbene is given below in figure 3.8 and its other information are given in Table 3.3. This crystal structure is already known in the literature.

![Figure 3.7. Formation of (E) Stilbene instead of 44C](image-url)
Figure 3.8. The crystal structure of (E) - Stilbene

Table 3.3. Crystallography data for (E) - Stilbene

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<td>2232 ([R(int) = 0.0508])</td>
</tr>
<tr>
<td>Completeness to theta = 27.15°</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9988 and 0.9802</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2232 / 0 / 127</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.005</td>
</tr>
<tr>
<td>Final R indices [I&gt;2(\sigma(I))]</td>
<td>(R1 = 0.0450, wR2 = 0.0979)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R1 = 0.0800, wR2 = 0.1149)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.225 and -0.184 e.Å(^{-3})</td>
</tr>
</tbody>
</table>
When the synthesis of \textit{44C} did not succeed from alpha,alpha-dibromotoluene a new route was followed which is given in Scheme 3.8. When iodobenzene was treated with CuI, K$_2$CO$_3$ and malononitrile \textit{44C} was formed. Then, a pressure vessel with a stir bar was charged with phenylmalononitrile \textit{44C} (0.08 g, 0.53 mmol), acetamidine (0.15 g, 1.60 mmol) Cs$_2$CO$_3$ (1.03 g, 3.16 mmol), CuI (0.01 g, 0.05 mol) and dimethylsulfoxide (1 mL) and sealed tightly. It was heated in an oil bath at 120$^\circ$C for 24 hours. After 24 hours reaction was cooled to room temperature and diluted with ethyl acetate. Then it was washed with a saturated solution of NaHCO$_3$ followed by deionized water. The organic layer was separated and dried over anhydrous MgSO$_4$, then concentrated and purified by rotary chromatography. A pink colored compound was obtained. The yield of the compound was very low (< 1mg) so it could not be characterized by NMR spectroscopy. UV-vis spectroscopy of the compound was done. In UV-vis dipyrromethene gives a specific absorbance peak around 500nm which was seen in the UV-vis of the pink compound. It is expected to be the compound \textit{46C} but further characterization is needed to confirm the compound. The UV-vis spectrum of the pink compound is given below in Figure 3.10
In the synthesis of 1H-1,2,4 ditriazolylmethene (48C), an oven-dried round bottom flask with a magnetic stir bar was charged with 21C (0.05 g, 0.16 mmol) and sodium azide (0.02 g, 0.16 mmol) and kept under argon gas. Then, dry dimethyl sulfoxide (5 mL) was added and the reaction was run overnight at ambient temperature. Then, the reaction mixture was quenched with dilute hydrochloric acid. It was extracted with deionized water and ethyl acetate. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and concentrated. A few miligrams of the product were dissolved in dichloromethane to make a saturated solution and left in dark under the hood for 48 hours. Pale yellow crystals were formed and crystal structure was analyzed which is given below in Figure 3.12.
Figure 3.11. Synthesis of 47C

Figure 3.12. Crystal structure of p-tolyl(2H-triazol-4-yl)methanone (47C)
Table 3.4. Crystallography data p-tolyl(2H-triazol-4-yl)methanone

<table>
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<td>Empirical formula</td>
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</tr>
<tr>
<td>Formula weight</td>
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</tr>
<tr>
<td>Temperature</td>
<td>200(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 14.5903(11) Å, b = 11.6891(9) Å, c = 10.4713(8) Å</td>
</tr>
<tr>
<td></td>
<td>a= 90°, b= 92.4470(10)°, g = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1784.2(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.394 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
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</tr>
<tr>
<td>F(000)</td>
<td>784</td>
</tr>
<tr>
<td>Crystal size</td>
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</tr>
<tr>
<td>Theta range for data collection</td>
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</tr>
<tr>
<td>Index ranges</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>3898 [R(int) = 0.0239]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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</table>
Max. and min. transmission 0.9943 and 0.9768

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 3898 / 2 / 264

Goodness-of-fit on F² 1.045

Final R indices [I>2sigma(I)] R1 = 0.0321, wR2 = 0.0841

R indices (all data) R1 = 0.0350, wR2 = 0.0864

Largest diff. peak and hole 0.135 and -0.231 e.Å⁻³

3.4 Conclusion and Future Works

The compound 42C was synthesized successfully. Now it has to be treated with PPh₃ and CBr₄ to synthesize the compound 52C. Then 52C will be reacted first with BuLi then with H₂O to synthesize 53C. Then, 53C is to be treated with tetrabutylammonium fluoride followed by methanol to produce 54C. Next the compound 54C must be reacted with PPh₃ and CBr₄ to form 55C. After treating 55C with BuLi then with water the Compound 34C will be formed. After synthesizing the compound 34C the Scheme 3.1 will be followed replacing 34C to 06C.

Scheme 3.8 was followed to synthesize the compound 46C. In the step where reaction was set up for the synthesis of the compound 45C, a pink colored compound was obtained. The compound was not enough to do NMR spectroscopy. UV-vis of the pink compound gave the absorption around 500 nm which is the specific character of dipyrrromethene. For further characterization more amount of the compound is needed.
Scheme 3.10. Synthesis of 34C starting from protected toluoyl malondialdehyde
3.5 References


42. Bonnier, C.; Piers, W.; Al-Sheikh, A. Thompson, M. Parvez, Organometallics, 2009, 28, 4845.


CHAPTER 4
SOME OTHER ROUTES OF SYNTHESIS OF A NEW CLASS OF BODIPY DYES- DITETRAAZOXYLMETHENE DYES AND THEIR DERIVATIVES

4.1 Introduction

Aryl halides such as iodobenzene can be reacted with malononitrile in the presence of CuI and K₂CO₃ to form the compound 44C. Copper salt promotes the formation of carbon nucleophile as the anion of active methylene.¹² This carbon nucleophile attacks the carbon atom of an aryl halide where a halide (iodine in case of iodobenzene) is bonded and the halide is substituted.

Tetrazole can be prepared by Huisgen cyclization between azide and nitriles in the presence of Zn catalyst.⁷ Two reaction mechanisms are supported for this reaction, a two-steps mechanism and a concerted [2+3] cycloaddition. The studies showed that zinc has more than the role of a Lewis acid. When Lewis acids other than Zinc were used there was no or a little acceleration in the rate of the reaction. Almost 0.5 molar equivalent of the zinc salt (usually ZnBr₂) is required for fast formation of tetrazole. In this reaction hydrolysis of the nitrile to the primary amide competes with tetrazole. The two mechanisms for this reaction are given in Figure 4.1.¹³

4.2 Synthesis

4.2.1 General Procedure

Manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques wherever needed. Solvents were purchased from commercial sources, dried over molecular sieves and degassed by purging with argon gas. All other chemicals were reagent grade and were used as received. Glassware were oven-dried at 150°C overnight. NMR solvent
CDCl₃ was reagent grade and stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on glass backed, pre-coated silica gel plates and visualization was accomplished with UV light. Silica gel 60 μm (average particle size) was used for column chromatography. UV-vis data were collected with a Varian Cary spectrophotometer. 400 MHz was used for $^1$H and $^{13}$C NMR spectra in CDCl₃ unless noted otherwise.

Figure 4.1. Mechanism of 5-substituted 1H tetrazole from nitrile

Two-step Mechanism

Concerted Mechanism

$M = H, Li, Zn, other metals$

Figure 4.1. Mechanism of 5-substituted 1H tetrazole from nitrile
Scheme 4.1. Synthesis of ditetraazolylmethene (02D) starting from phenylpropanedinitrile
4.2.2 Experimental Section

- Synthesis of 5-[phenyl(2H-tetrazol-5-yl)methyl]-2H-tetrazole (01D),

A pressure vessel with magnetic stir bar was charged with phenylmalononitrile (0.02 g, 0.14 mmol), zinc bromide (0.03 g, 0.28 mmol), sodium azide (0.03 g, 0.42 mmol) and H2O (2.5 mL). The vessel was tightly closed and submerged in a preheated sand bath 170°C overnight. Then, the vessel was cooled down to room temperature. Hydrochloric acid (3N, 0.42 mL) was added to achieve the pH 1 of the aqueous layer. Then ethyl acetate (3 mL) was added and the mixture was stirred vigorously until all solid was dissolved. The organic layer was separated and aqueous layer was extracted with 3 mL of ethyl acetate twice. All the organic layers were combined and concentrated by rotary evaporation. Then, NaOH (0.25 N, 8.40 mL) was added and stirred for 30 minutes until the original precipitate was dissolved and the suspension of zinc hydroxide was formed. The suspension was filtered and the solid was washed with NaOH (1 N, 0.840 mL). HCl (3 N, 1.68 mL) was added in the filtrate and stirred vigorously until the precipitate of ditetraazolylmethane was formed. Ditetraazolylmethane was collected and washed with HCl (3N, 0.84 mL) twice. The product was kept under high vacuum to dry and the sample was taken for NMR. NMR spectra of this compound is given in Appendix. The product is collected as pale yellow solid (0.01 g, yield = 38%) ¹H NMR (DMSO-d6) δ 1.91 (s, NH), 6.51 (s, 1H), 7.36-7.43 (m, 5H).

- Synthesis of 5-[phenyl(2H-tetrazol-5-yl)methylene]tetrazole (02D)

A round bottom flask with a magnetic stir bar was charged with ditetraazolylmethane (01D) (0.03 g, 0.132 mmol), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.03 g, 0.13 mmol) and potassium phosphate monobasic (KH₂PO₄) (0.02 g, 0.13 mmol). Dichloromethane (2 mL) was added. After 30 minutes the reaction mixture turned black. The mixture was evaluated.
by thin layer chromatography (TLC) using hexanes: ethyl acetate in different ratios, 15:1, 10:1, 8:1, 6:1, 3:1, 1:1 and at last in straight ethyl acetate. Unfortunately, from TLC it was noticed that there is not a single major product in mixture and it is the mixture of many compounds which could not be collected separately.

4.2.3 Characterization and Physical Properties

A saturated solution of 44C in dichloromethane was made and left in the dark under the hood for weekend. The crystals were collected and taken for crystallography. The crystal structure of 44C is given in Figure 4.2.

![Crystal Structure](image)

Figure 4.2. The crystal structure of (44C)

The UV-vis absorbance of 01D is given in figure 4.3. The absorbance peak is seen around 225 nm.
4.3 Results and Discussions

The compound 44C was prepared using iodobenzene and malonitrile in the presence of CuI and K₂CO₃. 44C is characterized by crystallography and ¹H NMR. The compound 01D was synthesized successfully and characterized by ¹H NMR spectrum which is given in Appendix.

4.4 Conclusion and Future Works

The compound 01D was synthesized in aqueous medium. When 01D was oxidized with DDQ to form 02D a black paste was formed. In evaluating with thin layer chromatography it was a large number of compounds in very small quantity each. It seems 01D decomposed in the presence of DDQ and some mild oxidizing agent is needed to oxidize 01D to 02D. To synthesize 02D to 01D 01D will be treated with NBS to form brominated compound 03D. 03D will be treated with a mild base such TEA to form 04D. Scheme 4.2 shows the next step.
Scheme 4.2. Synthesis of 02D from 01D using NBS

4.5 References


CHAPTER 5
A GREENER SYNTHESIS OF 6-METHYLNAPHTHOQUINONE

5.1 Introduction

Naphthoquinones with substituents at the 6-position can be prepared in a two-step process that begins with the Diels-Alder reaction between benzoquinone and a butadiene compound and is completed by the oxidation of the initial product using an oxidant (Scheme 5.1).\textsuperscript{1,2} The oxidation removes the equivalent of 2 hydrogen atoms from the naphthoquinone (4e\textsuperscript{-}, 4H\textsuperscript{+}). Chromium-based oxidants such as CrO\textsubscript{3} have been previously reported to oxidize the intermediate adduct to the naphthoquinone, but chromium is a toxic element. It would be helpful to replace the chromium-based oxidation method with a method that uses non-toxic elements. This chapter describes my work to develop a greener synthesis of 6-methylnaphthoquinone that uses a nontoxic oxidant, iron trichloride (FeCl\textsubscript{3}) as an oxidation catalyst together with ambient oxygen (O\textsubscript{2}) as a stoichiometric oxidant. I did this work together with Eunsol Park, a graduate student in the Youngblood group. Each of us tried the Diels-Alder reaction and FeCl\textsubscript{3}-based oxidation method and reported our results to our professor, Dr. Youngblood. We obtained very similar results. The quantity of 6-methylnaphthoquinone that we produced was contributed to another graduate student, Seare Berhe, who used our compound in the overall synthesis of another quinone compound, naphthacenequinone-2-carboxylic acid (01E) (Figure 5.1).

![Figure 5.1. Naphthacenequinone-2-carboxylic acid](image-url)
In the previous synthesis of 6-methylnaphthoquinone, chromic acid or Na₂Cr₂O₇/H₂SO₄ was used to oxidize 6-methyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (02E) into 6-methylnaphthoquinone (03E) (Scheme 5.2).³ Chromium is a toxic element. In the new method, FeCl₃ was used as an environmentally safer oxidizing agent. The overall synthesis still uses one step with Na₂Cr₂O₇, so it is not entirely a ‘green’ synthesis. The naphthacenequinone-2-carboxylic acid (NeQ in Scheme 5.2) was used to make a new kind of solar cell called a “photogalvanic solid-state dye-sensitized solar cell” and our group published a paper on this topic that includes myself and Eunsol Park as coauthors along with Seare Berhe and Haptom Gobeze (a student in the D’Souza group).⁴ This paper included the synthesis of organic dyes, the assembly and testing of solar cells, and the time-resolved studies of photoinduced electron transfer between the dyes and an arylamine donor compound (octakis(methoxyphenyl)spirobifluorenyl-tetramine, also known as spiroMeOTAD), as well as the thermal (dark) electron transfer between the dyes and an oxide semiconductor (titanium dioxide, TiO₂). This paper was published in 2014.

Scheme 5.1. Synthesis of 6-methylnaphthoquinone.

Scheme 5.2. Overall synthesis of naphthacenequinone-2-carboxylic acid using chromic acid to prepare the 6-methylnaphthoquinone.³
5.2 Synthesis

5.2.1 General Procedure

Manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques wherever needed. Solvents were purchased from commercial sources, dried over molecular sieves and degassed by purging with argon gas. All other chemicals were reagent grade and were used as received. Glassware were oven-dried at 150°C overnight. NMR solvent CDCl₃ was reagent grade and stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on glass backed, pre-coated silica gel plates and visualization was accomplished with UV light. Silica gel 60 μm (average particle size) was used for column chromatography. UV-vis data were collected with a Varian Cary spectrophotometer. 400 MHz was used for ¹H and 75 MHz was used for ¹³C NMR spectra in CDCl₃ unless noted otherwise.

5.2.2 Experimental Section

- Synthesis of 6-methylnaphthoquinone

An oven-dried round-bottom flask with a magnetic stir bar was charged with benzoquinone (0.53 g, 7.50 mmol) and LiClO₄ (0.53 g, 5mmol). Diethyl ether (10 mL) was added and stirred until all solid was dissolved. Then, isoprene (0.75 mL, 7.5 mmol) was added. Immediately, white colored precipitate was formed. The reaction was run for 24 hours. The mixture was extracted between deionized water and ethyl acetate. The organic layer was separated and dried over anhydrous Na₂SO₄. It was filtered and concentrated. The mixture had the intermediate compound 6-methyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (02E) which was used as it is to oxidize into 6-methylnaphthoquinone (03E). In the mixture, DMF (10 mL) and FeCl₃.6H₂O (4.05 g, 15.0 mmol) were added. The mixture was heated at 110°C for 24 hours black colored mixture was formed. Then, it was cooled to room temperature and filtered through...
silica gel using chloroform. After filtration yellow color solid compound was obtained (0.67 g, yield = 52%) $^1$H NMR (CDCl$_3$) δ 2.50 (s, 3H), 6.94 (m, 2H), 7.53-7.56 (d, 1H), 7.88 (s, 1H), 7.96-7.98 (d, 1H). The proton spectrum of 03E is given in Appendix.

5.3 Results and Discussions

6-methylnaphthoquinone was synthesized in one pot starting from benzoquinone and isoprene. First, 6-methyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (02E) was synthesized and it was oxidized in the same vessel with FeCl$_3$.6H$_2$O to get 6-methylnaphthoquinone (03E). The 6-methylnaphthoquinone was used to make more of the naphthacenequinone-2-carboxylic acid, which is an electron-accepting dye compound. We explored this dye compound in photogalvanic solar cells, which was a project guided by my advisor Prof. Youngblood and most experiments were led by our former group member, Seare Berhe.

![Schematic diagrams of solar cell types: photogalvanic (“PSC”, left), dye-sensitized (“DSC”, center), and photogalvanic dye-sensitized (“P-DSC”, right).](image)

Photogalvanic cells (PSCs) produce electrochemical potential by the photoinitiated perturbation of a redox equilibrium between donor and acceptor compounds in an electrolyte (Figure 5.2-left). This is distinct from the photogeneration of charge directly across the molecule-semiconductor interface, which is the standard mechanism in dye-sensitized solar cells (DSCs, Figure 5.2-center). Some researchers had previously attempted to make a modified form
of photogalvanic solar cell that had primary charge separation between a dye that is bound to a semiconductor and an electron donating species that was dissolved in the electrolyte. This is called a photogalvanic dye-sensitized solar cell (P-DSC, Figure 5.2-right). In our paper, we explored this model of P-DSC but we replaced the liquid electrolyte with a solid state hole conductor called spiroMeOTAD. With the use of transient absorption spectroscopy, we were able to observe primary charge separation between electron accepting dyes and the SpiroMeOTAD. Figure 5.3 shows the charge separation in a blend of 2-methylnaphthacenequinone, which is the compound that is used to make naphthacenequinone-2-carboxylic acid at the last step of the overall synthesis.

Figure 5.3. Laser flash photolysis of a thin film blend of 2-methylnaphthacenequinone (NcQ-2Me) and spiroMeOTAD. A: Time resolved spectra. B: Monochromatic decay rates for the radical cation spiro-MeOTAD(•+) at 500 nm, and for the radical anion NcQ-2Me(•−) at 603 nm. Traces are normalized with respect to ΔOD at 740 fs. Inset: overlaid decay traces for initial 9 ps.4

The transient absorbance spectra in Figure 5.3 shows that the charge separation between the 2-methylnaphthacenequinone and spiroMeOTAD decays at the same rate, except for a brief decay at the early decay of the reduced form of the quinone species, which we identified as electron transfer to ambient oxygen, since this reaction was done in the open air. The fact that the majority of the decay of the signals for the two charged species has the same rate is evidence that there is only one process that is occurring: the electron is going back to the spiroMeOTAD from...
the reduced quinone species. When we prepared a ternary interface that had a naphthacenequinone bound to titanium dioxide (TiO₂), and put the spiroMeOTAD as the electron donor, we observed that the rates of the decay of the different signals for the charged molecular species are no longer the same. We infer from this evidence that there is not only one process that can happen after the primary charge separation, but more than one process. We identify that the reduced quinone can send an electron back to the spiroMeOTAD, or it can send an electron to the TiO₂. Both processes are happening in the material.

Figure 5.4. Laser flash photolysis of a ternary TiO₂/naphthacenequinone-carboxylic acid/spiro-MeOTAD film consisting of rutile TiO₂ nanorods with surface chemisorbed naphthacenequinone-carboxylic acid and spin-coated spiroMeOTAD. A: Time resolved spectra. B: Monochromatic decay rates for the radical cation spiroMeOTAD(•⁺) at 490 nm, and for the radical anion of naphthacenequinone-carboxylic acid(•⁻) at 600 nm, normalized with respect to ΔOD at 605 fs. Inset: overlaid decay traces for initial 30 ps.⁴

5.4 Conclusion and Future Works

The FeCl₃-mediated oxidation provided 6-methylnaphthacenequinone without the use of chromic acid. This naphthoquinone compound was used to make naphthacenequinone-2-carboxylic acid, which was used in a study of photogalvanic dye-sensitized solar cells. This study was the first report of a photogalvanic dye-sensitized system that actually allowed the observation of the formation and decay of the reduced form of an electron-accepting dye that was bound to an oxide semiconductor.
5.5 References


$^1$H NMR of methyl 3-(4-bromophenyl)propanoate (03B)

$^1$H NMR of 04B
$^1$H NMR of 05B

$^1$H NMR of 09B
$^1$H NMR of 1-(3-bromopropyl)-4-[(4-butylphenyl)ethynyl]benzene (06B)

$^1$H NMR of 07B
1H NMR of 08B

13C NMR of 10B
\[ ^1H \text{NMR of 08C} \]

\[ ^1H \text{NMR of 09C} \]
$^1$H NMR of 10C

$^1$H NMR of 21C
$^1$H NMR of 24C

$^1$H NMR of 29C
$^1$H NMR of 32C

$^1$H NMR 33C
$^1$H NMR of 36C

$^1$H NMR of 42C
$^1$H NMR of 44C

$^1$H NMR of 51C
$^1$H NMR of Multiple acylation of toluoyl malondialdehyde

$^1$H NMR of protected enol (42C)
$^{13}$C NMR of 42C

$^1$H spectrum of 21C
$^{13}$C NMR of 21C

$^{1}$HNMR of 49C (through Eglington coupling)
$^1$H NMR of 01D

$^1$H NMR of 03E