การสังเคราะห์พอลิเมอร์ชนิดคอนจูเกตที่มีหมู่ไตรเอโซลผ่านปฏิกิริยาคลิกพอลิเมอไรเซชัน

นายพงศ์พัฒน์ ลิมป์จรรยาวงศ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

SYNTHESIS OF TRIAZOLE-CONTAINING CONJUGATED POLYMER THROUGH CLICK POLYMERIZATION

Mr. Pongpat Limjunyawong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2014

Thesis Title	SYNTHESIS OF TRIAZOLE-CONTAINING CONJUGATED POLYMER THROUGH CLICK POLYMERIZATION
By	Mr. Pongpat Limjunyawong
Field of Study	Chemistry
Thesis Advisor	Assistant Professor Yongsak Sritana-anant, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.....Chairman
(Associate Professor Vudhichai Parasuk, Ph.D.)

.....Thesis Advisor
(Assistant Professor Yongsak Sritana-anant, Ph.D.)

.....Examiner
(Assistant Professor Sumrit Wacharasindhu, Ph.D.)

.....External Examiner
(Thanawadee Leejarkpai, Ph.D.)

พงศ์พัฒน์ ลิมป์จรรยาวงศ์ : การสังเคราะห์พอลิเมอร์ชนิดคอนจูเกตที่มีหมู่ไตรเอโซลผ่านปฏิกิริยาคลิกพอลิเมอไรเซชัน (SYNTHESIS OF TRIAZOLE-CONTAINING CONJUGATED POLYMER THROUGH CLICK POLYMERIZATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ยงศักดิ์ ศรีธนาอนันต์, 87 หน้า.

คอนจูเกตพอลิเมอร์ที่มีหมู่ไตรเอโซลได้ถูกสังเคราะห์จากมอนอเมอร์แบบหมู่ฟังก์ชันเดี่ยวและสองหมู่ฟังก์ชัน ผ่านปฏิกิริยาการเกิดพอลิเมอร์แบบคลิก ระหว่างเอไซด์และแอลไคน์ โดยมีคอปเปอร์เป็นตัวเร่งปฏิกิริยา สารตั้งต้นไดเอไซด์ทั้งสองชนิดคือ 1,4-ไดอะซิโดเบนซีน และ 2,7-ไดอะซิโดฟลูออรีน สังเคราะห์ได้จากอนุพันธ์ไดอะมิโนเบนซีนและไดไนโตรฟลูออรีน ในปริมาณ 68% และ 76% ตามลำดับ ในขณะที่ สารประกอบประเภทสองหมู่ฟังก์ชัน 5-อะซิโด-2-เอไทนิลไพริดีน นั้นได้มาจากปฏิกิริยา 5 ขั้นตอนที่เริ่มจาก 2-คลอโร-5-ไนโตรไพริดีน ในปริมาณสุทธิจากทุกขั้น 11% พอลิเมอร์ พี1 พี2 หรือ พี3 ถูกเตรียมจากปฏิกิริยาคลิกพอลิเมอไรเซชันของ 1,4-ไดเอไทนิลเบนซีนกับสารประกอบ 5, สารประกอบ 7 และ 4,4'-ไดอะซิโด-2,2'-สติลบีนไดซัลโฟเนต ในปริมาณ 91%, ใกล้เคียง 100% และ 44% ตามลำดับ ส่วนมอนอเมอร์แบบสองหมู่ฟังก์ชัน 5-อะซิโด-2-เอไทนิลไพริดีน (11) สามารถนำมาสังเคราะห์พอลิเมอร์ พี4 ได้ในทำนองเดียวกันในปริมาณ 67%

ภาควิชา เคมี ลายมือชื่อนิสิต .....

สาขาวิชา เคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

ปีการศึกษา 2557

5572051723 : MAJOR CHEMISTRY

KEYWORDS: CLICK REACTION, TRIAZOLE, CONDUCTING POLYMER

PONGPAT LIMJUNYAWONG: SYNTHESIS OF TRIAZOLE-CONTAINING CONJUGATED POLYMER THROUGH CLICK POLYMERIZATION. ADVISOR: ASST. PROF. YONGSAK SRITANA-ANANT, Ph.D., 87 pp.

Novel triazole-containing conjugated polymers from monofunctional and bifunctional monomers were synthesized via copper-catalyzed azide-alkyne cycloaddition (CuAAC) Click polymerizations. The two diazide precursors: 1,4-diazidobenzene (4) and 2,7-diazidofluorene (6) were synthesized from their corresponding diamino and dinitro derivatives in 68 and 76% yields, respectively. The bifunctional monomer 5-azido-2-ethynylpyridine (11) was obtained in five steps from 2-chloro-5-nitropyridine with an overall yield of 11%. Polymer P1, P2 or P3 were prepared from Click polymerizations of 1,4-diethynylbenzene with either compound 3, 5 or 4,4'-diazido-2,2'-stilbenedisulfonate in 91%, quantitative, or 44% yields, respectively. The bifunctional monomer 5-azido-2-ethynylpyridine (12) was also used to synthesize polymer P4 in 67% yield via similar processes.

Department: Chemistry
Field of Study: Chemistry
Academic Year: 2014

Student's Signature .....

Advisor's Signature .....

ACKNOWLEDGEMENTS

My utmost gratitude goes to my thesis advisor, Assist. Prof. Yongsak Sritana-anant, for his expertise, kindness, support, and most of all, for his patience during the course of research including completing this thesis.

I am sincerely grateful to the members of the thesis committee, Assoc. Prof.Vudhichai Parasuk, Assist. Prof. Sumrit Wacharasindhu and Dr. Thanawadee Leejarkpai for their valuable comments and suggestions.

I gratefully acknowledge the members of the YS research group on the fourteenth floor, Mahamakut building for their companionship and friendship.

Finally, I would like to take this opportunity to express my sincere appreciation and thanks to my parents and Chulalongkorn University.

CONTENTS

Page

Page

Page

Page

LIST OF FIGURES

Figure Page

LIST OF SCHEMES

Scheme Page

LIST OF ABBREVIATIONS

^{13}C NMR	: carbon-13 nuclear magnetic resonance spectroscopy
^{1}H NMR	: proton nuclear magnetic resonance spectroscopy
cm^{-1}	: unit of wavenumber (IR)
CuAAC	: copper-catalyzed azide-alkyne cycloaddition
d	: doublet (NMR), day
DMAP	: 4-dimethylaminopyridine
DMSO-d_6	: hexadeuterated dimethyl sulfoxide
equiv	: equivalent
EtOAc	: ethyl acetate
EtOH	: ethanol
g	: gram
h	: hour
HCl	: hydrochloric acid
Hz	: hertz
HOMO	: highest occupied molecular orbital
IR	: infrared spectroscopy
J	: coupling constant
LUMO	: lowest unoccupied molecular orbital
m	: multiplet (NMR)
MeOH	: methanol
min	: minute
mg	: milligram

mL	: milliliter
mol	: mole
mmol	: millimole
m.p.	: melting point
m/z	: mass per charge ratio
M	: molar
MS	: mass spectrometry
NaASC	: sodium ascorbate
NaOH	: sodium hydroxide
ppm	: parts per million (unit of chemical shift)
PTAs	: polytriazoles
q	: quartet (NMR)
RT, rt	: room temperature
s	: singlet (NMR)
st	: stretching vibration (IR)
S_N2	: bimolecular nucleophilic substitution
S/cm	: siemens per centimeter
t	: triplet (NMR)
TBDMS	: *tert*-butyldimethylsilyl
TBDMSCl	: *tert*-butylchlorodimethylsilane
TMS	: trimethylsilyl
TMSA	: trimethylsilylacetylene
TLC	: thin layer chromatography
t-BuOH	: *tert*-butyl alcohol

UV-Vis	: ultra-violet and visible spectroscopy
V	: volume (mL)
°C	: degree Celsius
Δ	: heat
δ	: chemical shift
λ_{max}	: maximum wavelength
π	: pi

CHAPTER I

INTRODUCTION

1.1 Conducting polymer

Chiang and coworkers discovered polyacetylene as the first conductive polymer in which its conductivity reached an order of 10^{-5} S/cm [1]. Then researchers also revealed that oxidation with halogen vapor made polyacetylene film 10^{9} times more conductive than the initially undoped state [2]. The discoverers were awarded the Nobel prize in chemistry in 2000 "for the discovery and development of electrically conductive polymers". Conductive polymers have distinctive properties which are remarkable for the new technology as organic electronics or plastic electronics [3]. Organic semiconductor materials offer numerous advantages over inorganic materials such as: low cost, light weight, flexibility, tunability and processability.

Conductive polymers are organic macromolecules that contain a backbone chain of alternating single and double bonds mostly between carbon-carbon or carbon-nitrogen atoms. Polymer chain of conductive polymers was made up of sp^2-hybridized orbitals of the carbon or nitrogen atoms which form the delocalized π-orbitals. The π-electrons delocalization from one bond to the others gave the polymers the semiconducting properties. Conductive polymers not only have the electronic behaviors of semiconductor but also the mechanical flexibility and ease of fabrication of plastics. Furthermore, they are good materials to be used in the production of electronic devices because we can adjusted their properties by external parameters during chemical synthesis. Whereas a certain band width and the flexibility of their polymer enables novel and low-cost manufacturing techniques of flexible sensors, flexible roll-up displays, large photovoltaic arrays and many others. These

lightweight and easily fabricated materials can be used as replacements for semiconductor chips and integrated circuits, electrode materials in fuel cells and batteries, lightweight wiring, and components in wide varieties of optoelectronic devices [4]. The conductive property of conjugated polymers is usually the key factor to determine their usages and efficiency. This property has been investigated to proportionally correlate with the HOMO-LUMO energy gap, which could be directly calculated from the experimentally measured UV-Visible spectrum of the polymer. The increase of the maximum absorption value or bathochromic shift in the spectrum corresponds to smaller energy gap, and hence the longer effective conjugation length in the polymer backbone [5], [6].

1.2 Click chemistry

"Click reaction" is the description of a reaction that occurs when two functional groups that have specific interaction were mixed together under suitable to efficiently give the corresponding product. (**Figure 1.1)** Sharpless and co-workers who discovered this reaction in 2001 described click chemistry as a '*set of powerful, highly reliable and selective reactions for the rapid synthesis of useful new compounds and combinatorial libraries through heteroatom links (C–X–C)'* [7]. Click reactions are usually high in efficiency, consistently give high yields of specific product, simple reaction conditions, readily available starting materials and reagents, simple purification methods, physiologically stable, stereospecific and wide in scope [8]. The examples of Click reactions are as follows:

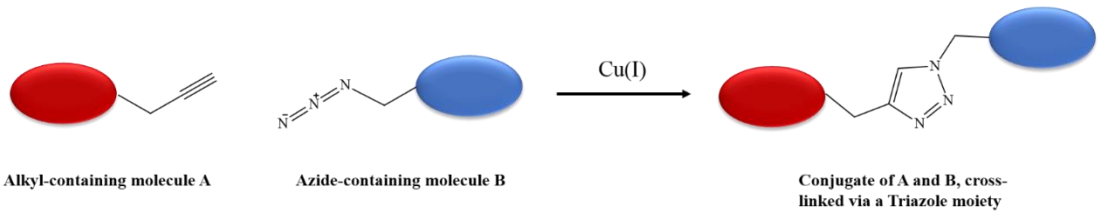


Figure 1.1 An example of Click reaction

1.2.1 Nucleophilic opening of spring-loaded rings

The S_N2 ring opening of these energetic heterocycle compounds including epoxides, aziridines, cyclic sulfates, episulfonium ions and aziridinium ions was one of the well-known types of Click chemistry [7].

Some of these ring opening reactions are shown in **Figure 1.2.** The reaction can be carried out in many solvents and type of solvent could control regioselectivity of product. The example of ring opening reaction of cis-1,4-cyclohexadiene epoxide with benzylamine is shown in **Figure 1.3**. When methanol was used as the solvent, the reaction gave the 1,4-diol product in 90% yield. While neat reaction gave a different product as the 1,3-diol in 94% yield.

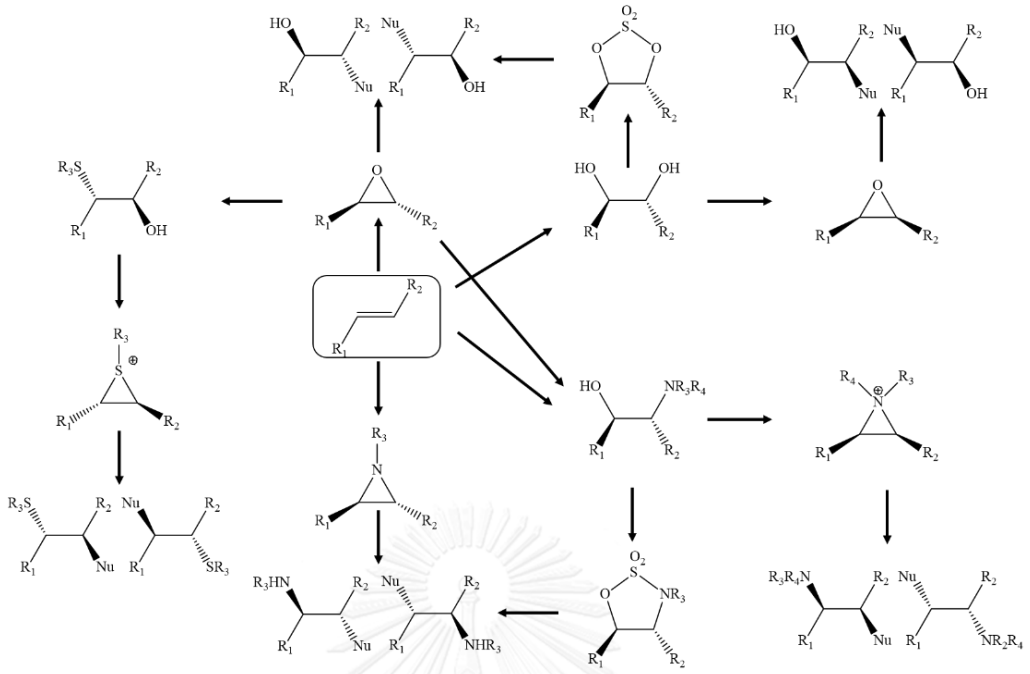


Figure 1.2 Generation and opening of spring-loaded cyclic electrophiles from olefins or their oxidation products

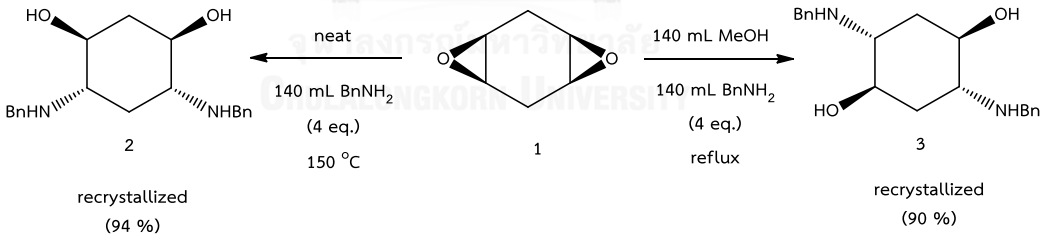


Figure 1.3 Regioselectivity of dixirane opening

1.2.2 Protecting group reaction

Most protecting and deprotecting groups reactions were developed to be highly efficient and specific and can be considered a large set of Click reactions [7]. The acid-catalyzed reactions of aldehydes or ketones obtain cyclic 1,3- dioxolane rings

in high yields. **(Figure 1.4)** Apart from being protecting groups, this protected form could have its own beneficial properties. It is generally stable at physiological pH, has already appeared as components in orally available drugs, contributes several hydrogen bond acceptor sites and interesting dipole effects, provides constrained scaffolds with well-defined projections and spatial orientations of their substituents.

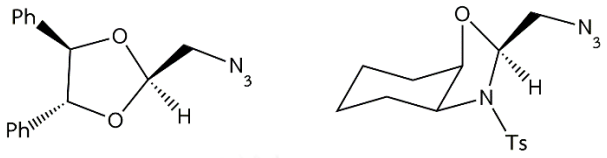


Figure 1.4 Examples of protected products

1.2.3 Cycloaddition reaction

Cycloaddition reaction was the most popular reaction of click chemistry that relates to heteroatoms such as hetero-Diels-Alder and 1,3-dipolar cycloadditions [7]. These reactions combine two unsaturated organic molecules to generate products five or six-membered heterocycles. Huisgen 1,3-dipolar cycloaddition between azides and alkynes to form triazoles was the most well-known type of cycloaddition in Click chemistry [9]. **(Figure 1.5)**

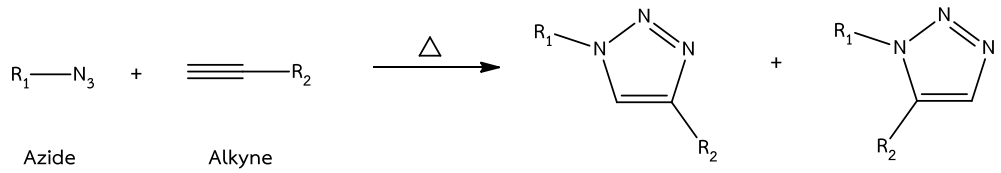


Figure 1.5 The Huisgen 1,3-dipolar cycloaddition of azides and alkynes, which gives mixture of triazole regioisomers

Classical Huisgen 1,3-dipolar cycloaddition of azides and alkynes required high temperature and generates the products as a mixture of two regioisomers of 1,4-

disubstituted and 1,5-disubstituted triazoles. It was later found that an appropriate catalyst could control regiqoselectivity of the resulted triazoles. The copper-catalyzed reaction produces the 1,4-disubstituted regioisomer of triazoles, the traditional themal cycloadditon provided the two disubstituted triazole isomers as a products [10]. **(Figure 1.6)** While the ruthenium-catalyzed reaction mostly creates the product as the 1,5-disubstituted triazoles.

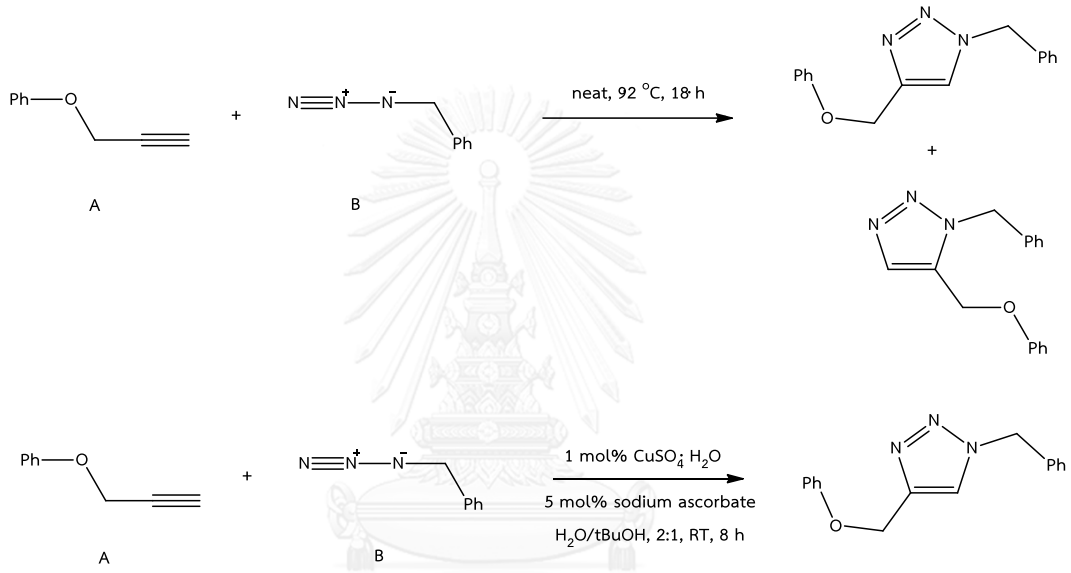


Figure 1.6 Thermal and Huisgen copper-catalyzed 1,3-dipolar cycloadditions of phenyl propargyl ether (A) with benzyl azide (B)

Sharpless and co-workers were the first group that highlighted the copper-catalyzed azide-alkyne cycloaddition (CuAAC), with the 1,4-disubstituted triazole was obtained as the main product from an azide and terminal alkyne [10]. The rate of CuAAC reaction increases greatly at 10^7-10^8 times when compared to that of the uncatalyzed 1,3-dipolar cycloaddition. CuAAC reaction uses copper (I) catalyst directly from a salt or air-oxidized copper metal, or copper (II) salts with reducing agents such as sodium ascorbate to reduce Cu from (+2) to (+1) oxidation state [11]. **(Figure 1.7)**

Diversity of solvent used in this reaction included mixture of water with a variety of miscible organic solvents including DMSO, DMF, alcohol and acetone. Simple filtration was used to isolate the product.

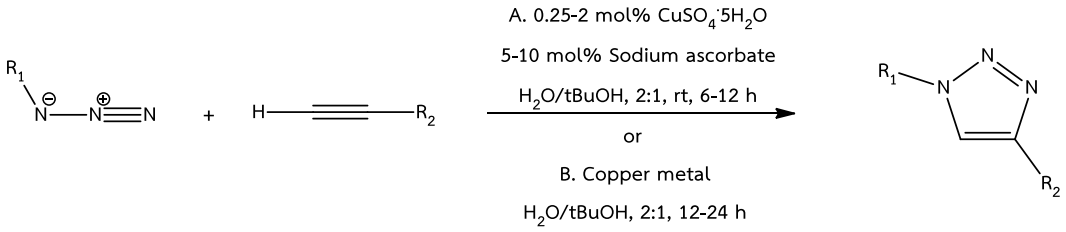


Figure 1.7 Copper (I)-Catalyzed Synthesis of 1,4-Disubstituted 1,2,3-Triazoles

CuAAC reaction mechanism is shown in **Figure 1.8** [12]. First, the copper (I) catalyst is generated in an induction period or by a reducing agent (step A). Copper (I) acetylide was formed from C-H insertion of terminal alkyne (step B). After that, the copper is bonded to the azide group to generate a copper-azide-acetylide complex (step C). The ring closing forms the six-membered matallacycle (step D). The metallacycle then converts to copper (I) triazolide (step E). Finally, reductive elimination of copper acquires the product while the copper complex catalyst was regenerated to return to the reaction cycle.

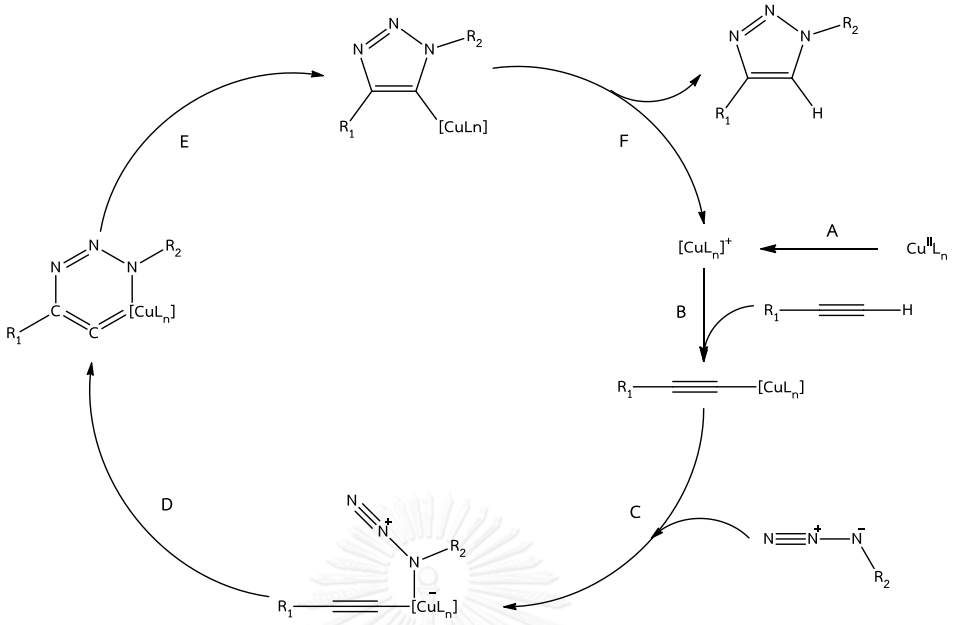


Figure 1.8 The mechanism of CuAAC L= ligand or a counterion

1.3 Advantages and applications of Click Chemistry

Click chemistry has gained much interest among researchers and has created numerous research success because of several advantages such as: [13]

- Rapid reactions
- Mild reaction conditions
- Small amount of byproducts
- Simple isolation technique
- Various applications
- High yields
- Tolerance of various functional groups
- Readily available reagent

The high efficiency of click chemistry has led to many useful products for many applications such as:

- Biotechnology
  - Modification of peptides, peptoids, oligonucleotide
  - Modification of natural products
  - Synthesis of carbohydrate clusters and conjugation
  - Protein/Peptide-Polymer conjugates
  - Labeling of DNA
  - Construction of fluorescent oligonucleotides for DNA sequencing
- Medical biotechnology
  - Drug discovery
  - Pharmaceuticals
- Nanotechnology
  - Nanoscale electronics
  - Functionalization of inorganic nanoparticles
- Materials science
  - Coating for glass, metal, plastics and other surface
  - Anti-coatings for medical implants
- Macromolecules
  - Synthesis of various polymers such as polytriazole
  - Synthesis of polymer-protein bioconjugates
  - Synthesis and modification of dendrimer
  - Reaction on surface and resin materials

1.4 Click Chemistry in Polymer and Materials Science

Functional polymers have been reportedly prepared from many new synthetic approaches. Nevertheless, these methods cannot efficiently created linear block copolymers due to these limitations: [13]

- The reactivity of each monomer is mostly quite different from one another. The more reactive monomer would then be too much incorporated in the copolymer.
- The synthesis of amphiphilic block copolymers often encounter the problem of identifying a common solvent in which both polar and nonpolar components could be dissolved.

In general, polymerization requires high efficiency chemical transformations along with the tolerance against a variety of reagents, functional groups and reaction conditions. Click chemistry is quite suitable in this regard because the character of these reactions are theoretically very fast and selective and potentially give polymer with high molecular weights in comparison to the traditional methods such as condensation and coupling polymerization, which are relatively slow and have poor atom economy [14].

In 2004, Hawker, Sharpless and co-workers were reported the preparation of triazole dendrimers that was the first time that Click chemistry has been introduced to polymer science [15]. Linear polymers as well as hyperbranched poly([1,2,3]-triazole)s were prepared by click polymerizations developed from the highly efficient Click reactions of small molecules [16].

The most popular and successful Click reactions are the CuAAC process, reactions of diazide and dialkyne monomers using copper (I) as catalyst to obtain the

triazole-containing polymer [14]. Various synthetic strategies polytriazoles (PTAs) by CuAAC click polymerizations include the linear A_2 + B_2 type **(Figure 1.9)** [17], the branched A_2 + B_3 **(Figure 1.10)** [18, 19], the linear AB and branched AB_2 **(Figure 1.11)** [20-22].

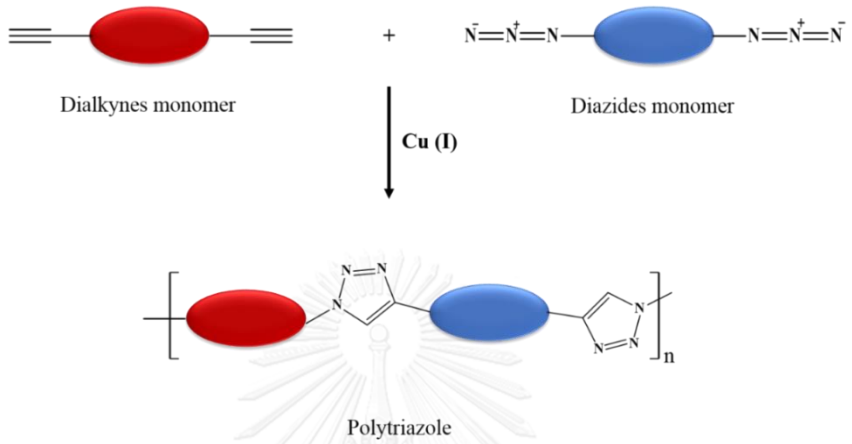


Figure 1.9 Synthesis of linear A_2 + B_2 type PTAs by Cu (I) catalyzed click polymerization

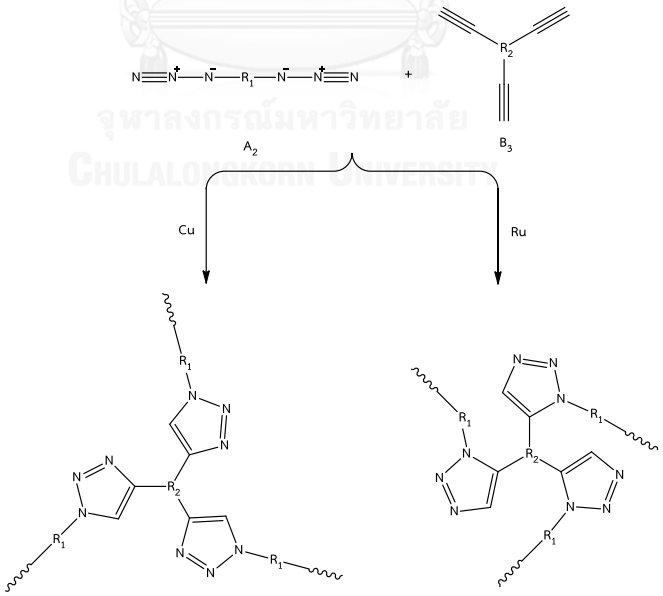


Figure 1.10 Synthesis of hyperbranched A_2 + B_3 type PTAs by Cu or Ru catalyzed Click polymerizations

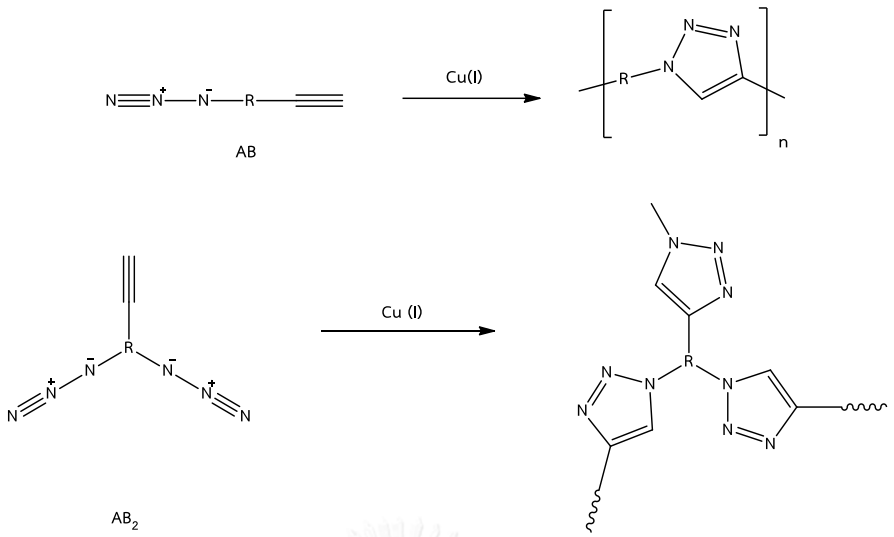


Figure 1.11 Synthesis of linear AB type and hyperbranched AB_2 type PTAs by Cu (I) catalyzed Click polymerization

1.5 Literature reviews

In 2011, Song et al. reported the synthesis of polymer electrolytes containing phenothiazine from Click polymerization for use in dye-sensitized solar cell applications. They used copper (II) acetate as catalyst to obtain the polymer in high yield (88 %yield) as shown in **Figure 1.12**. The polymer showed maximum absorption at 353 nm and exhibited the PCE value of 4.84% with thermal stability of only 5% weight loss at 298°C [23].

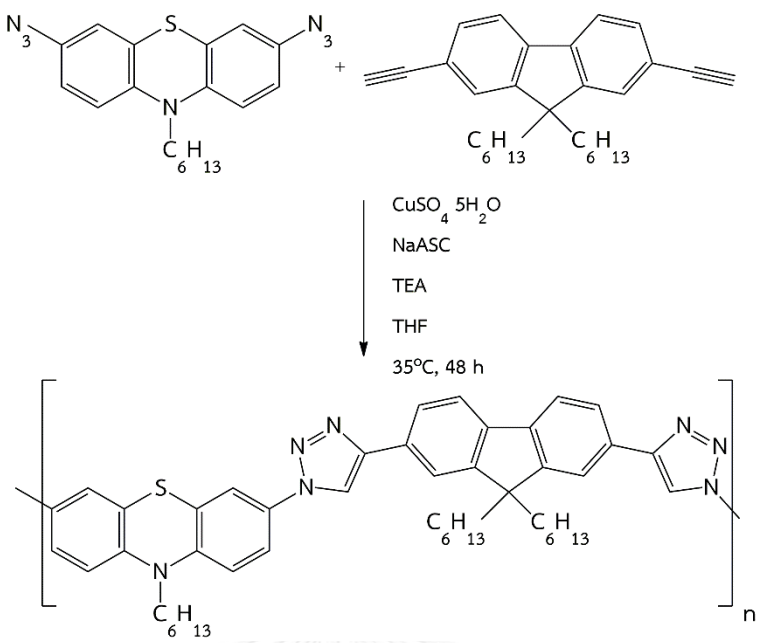


Figure 1.12 Synthesis of phenothiazine-based polymer from Click polymerization

Wu et al. reported an accomplishment on synthesizing fluorescence sensor for Hg^{2+} ion via click reaction. The reaction obtained the polymer as shown in **Figure 1.13** in 90 %yield. The obtained polymer exhibited the fluorescence wavelength at 425 nm. In the presence of Hg^{2+}, the fluorescence signal was quenched with the detection limit of $4.69x10^{-7}$ $molL^{-1}$. The fluorescence intensity of the polymer sensor was not observably affected by the addition of $Co^{2+,}$ Ni^{2+}, Na^{+}, Ag^{+}, K^{+}, Cr^{3+}, Mg^{2+}, Al^{3+}, Ca^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+} and Zn^{2+} even at high concentrations of metal ions [24].

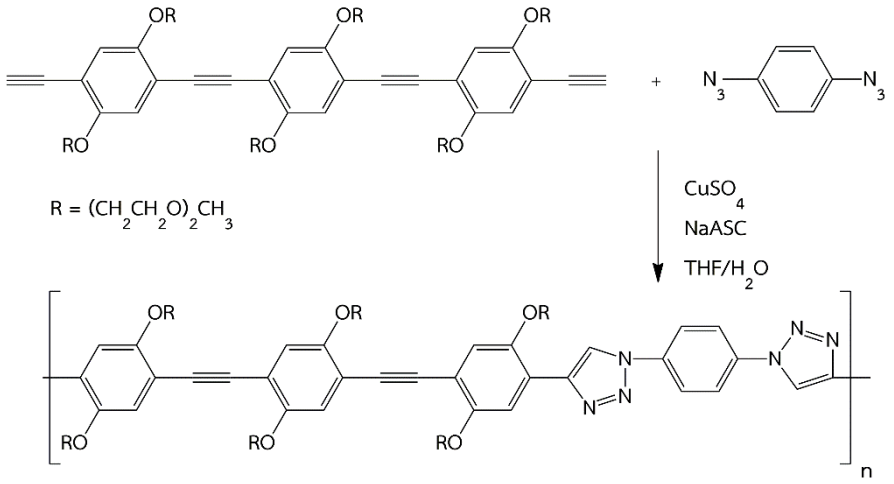


Figure 1.13 Synthesis of Hg^{2+} ion detector via click reaction

Wang et al. reported the synthesis of hyperbranched conjugated polytriazole via Click polymerization using copper (II) sulfate as catalyst. The hyperbranched polymer as shown in **Figure 1.14** was obtained in 84.4 %yield and exhibited the maximum absorption at 282 and 340 nm with 5% weight loss at 363.3 °C. The polymers can form unimolecular nanoparticles from their dilute solutions with diameters around 100 nm. This hyperbranched polymer was a novel clickable fluorescent platform, onto which various functional groups or biomolecules could be grafted efficiently for applications in biological and optoelectronic fields. [25].

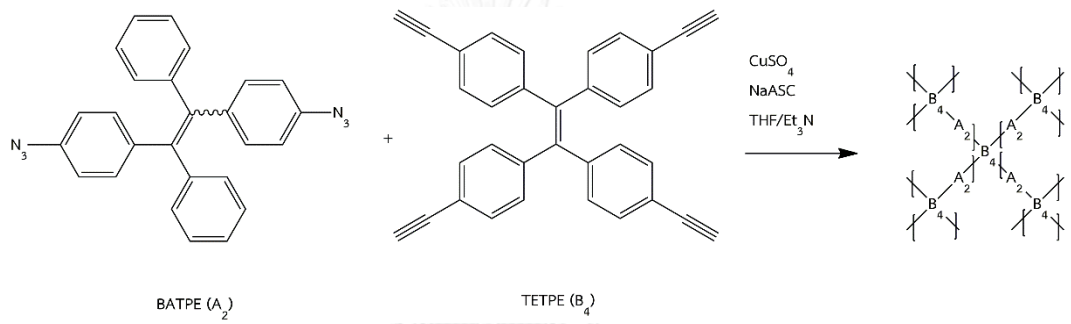


Figure 1.14 Synthesis of hyperbranched conjugated polytriazole

He et al. reported the synthesis of polymer that contained dithiazolo[5,4-b:4',5'-d]phosphole building block that can work as highly emissive electron-accepting moieties for use in molecular optoelectronics and sensors applications. The dithiazolo[5,4-b:4',5'-d]phosphole moieties could be used as stronger electron acceptor compared to the previously reported dithienophosphole system due to the lower HOMO and LUMO energy levels. The cyclic voltammetry observed quasireversible reduction process that supported electron-accepting properties [26].

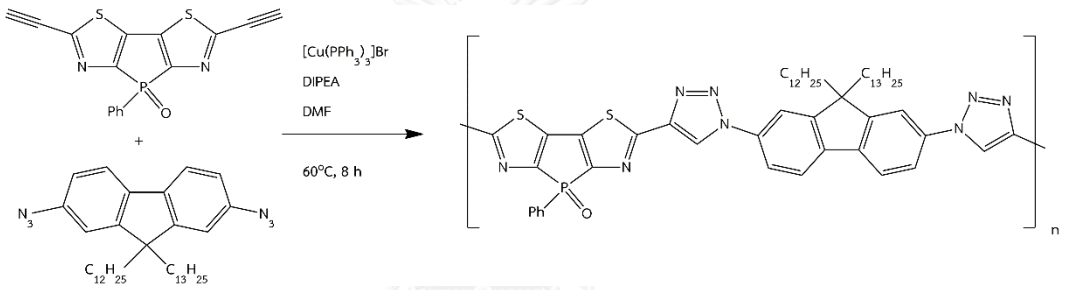


Figure 1.15 Synthesis of dithiazolo[5,4-b:4',5'-d]phosphole building block containing polymer

1.6 Synthesis of conducting polymer via Click polymerization

Although various synthetic routes to prepare conjugated polymers have been discovered, alternative synthetic routes that lead to conjugated polymers with new molecular structures might lead to new properties of materials that can be used to create new device [17]. To acquire polymers of appropriate length and purity these synthetic procedures should be highly effective and selective. Cu(I)-catalysed 1,3-dipolar ''Click'' cycloaddition between azides and alkynes could be one of the most attractive strategies that responds to such requirement because of the characters of being strategies that highly efficient, mild and selective, simple to perform in various

solvents and work-up procedures. Moreover, the 1,4-disubstituted 1,2,3-triazole products can be part of conjugated polymers. They are highly stable units, due to their conjugated system, with numerous nitrogen atoms that might be beneficial as the stabilizers of counter-cations while the electrons mobilize.

1.7 Objectives

- Synthesis of dialkyne and diazide monomers as the precursors of CuAAC click polymerization.
- Synthesis and characterization of novel conducting polymer via Click polymerization.

CHAPTER II

EXPERIMENT

2.1 Chemicals

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgel 60 F254) (Merck KgaA, Darmstadt, Germany). Column chromatography was performed using silica gel 0.06-0.2 mm or 70-230 mesh ASTM (Merck Kieselgel 60 G, Merck KgaA, Darmstadt, Germany). Solvents used in synthesis were reagent or analytical grades. Solvents used in column chromatography were distilled from commercial grade prior to use. Other reagents were purchased from the following venders:

- RCI Labscan (Bangkok, Thailand): chloroform, dimethylsulfoxide (DMSO), acetonitrile, acetone AR Grade, dichloromethane AR Grade, tetrahydrofuran
- Acrös Organics (USA): tetrakis(triphenylphosphine)palladium(0), tin(II)chloride, ethyl propiolate, 1,4-diethynylbenzene
- Carlo Erba (Milan, Italy): potassium carbonate (K_2CO_3), sodium azide (NaN_3), sodium iodide (NaI), benzoyl chloride
- Fluka Chemical (Buchs, Switzerland): triethylamine (TEA), *tert*-butyl alcohol (*t*-BuOH), methanesulfonic acid, 4-dimethylaminopyridine
- Merck Co. (Darmstadt, Germany): ethanol absolute (EtOH), , sodium hydroxide (NaOH), chloroacetyl chloride, sodium nitrite ($NaNO_2$), sodium iodide, sulphuric acid (H_2SO_4), glacial acetic acid (CH_3COOH), zinc dust, concentrated hydrochloric acid (HCl), methanol
- Cambridge Isotope Laboratories, (USA): deuterated chloroform ($CDCl_3$), deuterated dimethylsulfoxide (DMSO-d_6), deuterated acetone (Acetone-d_6)

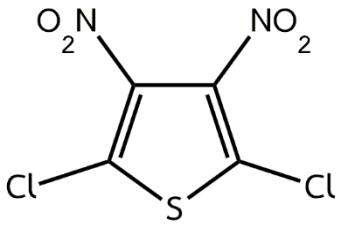
- Aldrich (USA): *p*-phenylenediamine, copper (I) iodide, 2-Chloro-5-nitropyridine, 2,7-dinitrofluorene, trimethylsilylacetylene, copper (II) acetate, phenylacetylene
- Sigma (USA): (+)-sodium L-ascorbate
- Panreac (Spain): anhydrous magnesium sulfate ($MgSO_4$)
- Ajax Finechem (Auckland, New Zealand): calcium chloride anhydrous

2.2 Instruments and equipments

Melting points were determined with a Stuart Scientific Melting Point SMP1 (Bibby Sterlin Ltd., Staffordshire, UK). The ^{1}H NMR spectra was recorded on a Varian Mercury NMR spectrometer operated at 400.00 MHz for ^{1}H and and ^{13}C NMR was recorded on a Bruker NMR spectrometer operated at 400.00 MHz for ^{13}C nuclei (Varian Company, USA). IR spectra were recorded on a Nicolet 6700 FT-IR RXI spectrometer (Perkin Elmer Instruments, USA). Mass spectra were recorded on Waters Micromass Quatto micro API ESCi Mass Spectrometer (Waters, USA). The UV-Vis absorption spectra were recorded on UV-VISIBLE Spectrometer: UV-2550 (Shimadzu Corporation, Kyoto, Japan).

2.3 Monomer synthesis

2.3.1 2,5-dichloro-3,4-dinitrothiophene (1)

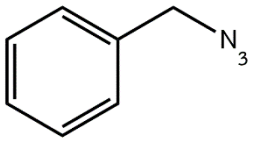


1

2,5-dichlorothiophene (2.884 g, 18.8 mmol) was dissolved in mixture of 7 mL of fuming nitric acid and 40 mL of concentrated sulfuric acid. The reaction mixture was stirred at 0 °C under N_2 atmosphere for 3 h. After that the reaction was poured into ice to precipitate crude product. Then the solid residue was filtered to obtain yellow crude product. The crude mixture was purified by silica gel column chromatography, eluting with a 8:2 mixture of hexane and ethyl acetate (R_f = 0.33), giving the product as pale yellow solid. (4.251 g, 93 %) [27]

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 137.4, 128.5 **(Figure A.1, Appendix A)**. IR (ATR, cm^{-1}): 1544, 1313 (N-O st) **(Figure A.2, Appendix A)**.

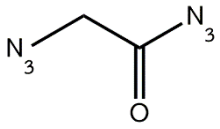
2.3.2 Benzyl azide (2)



2

Benzyl bromide (1.71 mL, 10 mmol) and sodium azide (6.500 g, 100 mmol) were mixed with 10 mL acetonitrile. The reaction mixture was stirred at room temperature for 5 d and then added 5 mL water and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed on a rotary evaporator to give the product as colorless oil. (2.426 g, 91%) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 (m, 5H), 4.36 (s, 2H) **(Figure A.3, Appendix A)**. ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 135.5, 128.8, 128.3, 127.9, 54.8 **(Figure A.4, Appendix A)**. IR (ATR, cm^{-1}): 3060 (C–H st), 2084 ($-N_3$ st) **(Figure A.5, Appendix A)**.

2.3.3 2-azidoacetylazide (3)

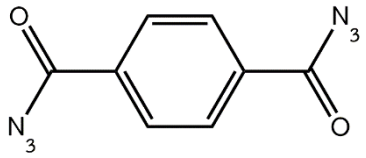


3

Chloroacetyl chloride (1.477 g, 13 mmol) was dissolved in 11 mL of acetonitrile and then added sodium azide (2.209 g, 32.5 mmol). The reaction mixture was stirred at 0 °C for 2 h and then another 22 h at room temperature. After that the reaction was extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous magnesium sulfate and evaporated. The crude mixture was purified by silica

gel column chromatography, eluting with a 4:6 mixture of hexane and ethyl acetate (R_f = 0.75), giving the product as light yellow liquid. (0.728 g, 44 %) ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 4.64 (s) **(Figure A.6, Appendix A)**. IR (ATR, cm^{-1}): 2153, 2098 (–N_3 st), 1680 (C=O st), 1193 (C-N st) **(Figure A.7, Appendix A)**.

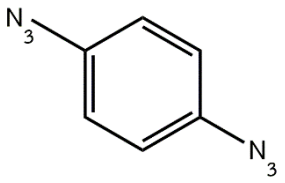
2.3.4 Terephthaloyl azide (4)



4

Terephthaloyl chloride (0.723 g, 3.5 mmol) and sodium azide (0.618 g, 9 mmol) was mixed with 10 mL of acetonitrile. The reaction was stirred at room temperature for 25 h and then extracted with ethyl acetate. The organic layer was washed with sodium bicarbonate twice and dried over anhydrous magnesium sulfate and evaporated. The crude mixture was purified by silica gel column chromatography, eluting with a 9:1 mixture of hexane and ethyl acetate (R_f = 0.44), giving the product as light yellow solid. (0.687 g, 89%) ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 8.11 (s) **(Figure A.8, Appendix A)**. IR (ATR, cm^{-1}): 2057 (C-H st), 2178, 2135 (–N_3 st), 1712 (C=O st), 1486 (C=C st) **(Figure A.9, Appendix A)**.

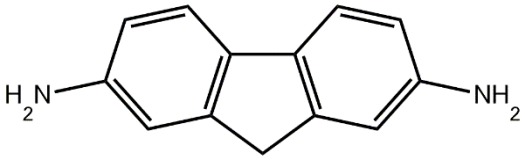
2.3.5 1,4-diazidobenzene (5)



5

Sodium nitrite (0.691 g, 10 mmol) was dissolved in 8 mL of concentrated sulfuric acid and stirred at 0 ℃. Then the solution of *p*-phenylenediamine (0.436 g, 4 mmol) in 13 mL glacial acetic acid was added dropwise to the sodium nitrite solution and stirred at 0 ℃ for 20 min. A solution of sodium azide (0.665 g, 10 mmol) in 10 mL water was then added dropwise. After 1.5 h, 100% sodium hydroxide was added slowly until the solution turned basic. The aqueous layer was extracted twice with dichloromethane, and the organic layer was separated and dried over anhydrous magnesium sulfate, filtered and evaporated to afford a brown solid. The crude product was purified by silica gel column chromatography, eluting with hexane (R_f = 0.31), giving the product as yellow solid (0.441 g, 68%). mp. = 80-82 ℃ (lit. 81.2-82.2 ℃ [28]). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 7.01 (s) **(Figure A.10, Appendix A)**. ^{13}C NMR (101 MHz, $CDCl_3$): **δ** (ppm) 136.7, 120.4 **(Figure A.11, Appendix A)**. IR (ATR, cm^{-1}): 3062, (C-H st) 2095, 2067 (–N_3 st) **(Figure A.12, Appendix A)**. [29], [30]

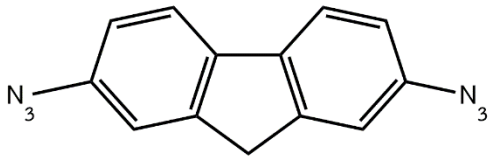
2.3.6 2,7-diaminofluorene (6)



6

2,7-dinitrofluorene (1.289 g, 5 mmol), zinc dust (8.197 g, 125 mmol) and calcium chloride (1.701 g, 15 mmol) were mixed with 45 mL ethanol and 15 mL water, and heated to reflux under N_2 atmosphere for 5 h. The reaction was filtered to remove the solid residue and extracted with dichloromethane to obtain the product as brown solid (1.009 g, quantitative). ^{1}H NMR (400 MHz, Acetone-d_6): **δ** (ppm) 7.32 (d, 2H), 6.80 (s, 2H), 6.63 (d, 2H), 4.48 (s, 4H), 3.63 (s, 2H) **(Figure A.13, Appendix A)**. ^{13}C NMR (101 MHz, Acetone-d_6): **δ** (ppm) 147.1, 144.5, 133.3, 119.4, 114.0, 112.2, 37.2. **(Figure A.14, Appendix A)**. IR (ATR, cm^{-1}): 3378, 3320 (N-H st), 3003 (C-H st), 1464 (C-H bend) **(Figure A.15, Appendix A)**. [31]

2.3.7 2,7-diazidofluorene (7)

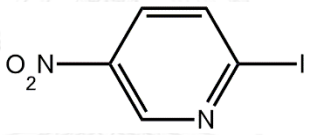


7

The solution of 2,7-diazidofluorene (0.576 g, 2.32 mmol) in 30 mL of glacial acetic acid was added dropwise to the cooled solution of sodium nitrite (0.494 g, 7 mmol) in 9 mL of concentrated sulfuric acid and stirred at 0 °C for 45 min. Then the solution of sodium azide (0.613 g, 9 mmol) in 4 mL of water was added and stirred for

3 h. When the reaction was completed, 100 % sodium hydroxide was added until basic. The mixture was extracted by dichloromethane, and the separated organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to afford a brown solid. The crude product was purified by silica gel column chromatography, eluting with hexane (R_f = 0.23), to give the pure product as yellow solid (0.554 g, 76%). mp. = 114-117 °C (lit. 111-112 °C [32]). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 7.67 (d, 2H), 7.18 (s, 2H), 7.03 (d, 2H), 3.85 (s, 2H). **(Figure A.16, Appendix A)**. ^{13}C NMR (101 MHz, $CDCl_3$): **δ** (ppm) 144.8, 138.5, 138.2, 120.6, 118.0, 115.8, 36.8. **(Figure A.17, Appendix A)**. IR (ATR, cm^{-1}): 2102, 2083 (–N_3 st) **(Figure A.18, Appendix A)**. [29], [30]

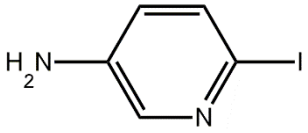
2.3.8 2-iodo-5-nitropyridine (8)



8

2-Chloro-5-nitropyridine (0.634 g, 4 mmol) and sodium iodide (3.000 g, 20 mmol) were dissolved in 10 mL of glacial acetic acid and heated to reflux for 2.5 h. The reaction mixture was poured into ice and precipitation occurred. The solid residue was filtered and re-dissolved with dichloromethane and dried over magnesium sulfate, filtered and evaporated to afford a brown product. (0.567, 57%) mp. = 164-166 °C (lit. 165-166 °C [33]). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 9.16 (s, 1H), 8.10 (d, 1H), 7.96 (d, 1H) **(Figure A.19, Appendix A)**. IR (ATR, cm^{-1}): 3024 (C-H st) 1504, 1344 (N-O st) **(Figure A.20, Appendix A)**.

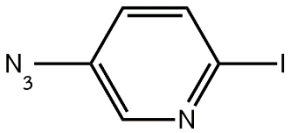
2.3.9 5-amino-2-iodopyridine (9)



9

2-iodo-5-nitropyridine (0.875 g, 3.5 mmol) was dissolved in 15 mL of ethanol. Then tin (II) chloride (3.320 g, 17.5 mmol) was added and the reaction was heated to reflux under nitrogen atmosphere for 3 h. The solvent was removed by vacuum evaporation and the crude product was re-dissolved by ethyl acetate. The organic solution was washed with water and 2 M sodium hydroxide and then dried over anhydrous magnesium sulfate, filtered and evaporated to obtain a yellow solid product. (0.688 g, 89%) mp. = 128-129 °C (lit. 132 °C [33]). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 7.85 (s, 1H), 7.35 (d, 1H), 6.65 (d, 1H), 4.06 (s, 2H). **(Figure A.21, Appendix A)**. IR (ATR, cm^{-1}): 3304, 3178 (N-H st) **(Figure A.22, Appendix A)**.

2.3.10 5-azido-2-iodopyridine (10)

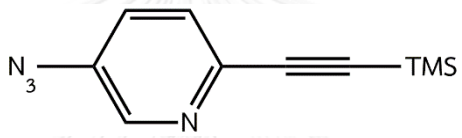


10

The solution of 5-amino-2-iodopyridine (0.423 g, 1.92 mmol) in 5 mL of 10% sulfuric acid was added dropwise to the cooled solution of sodium nitrite (0.273 g, 3.85 mmol) in 4 mL water and stirred at 0 °C for 1 h. Then the solution of sodium azide (0.250 g, 3.85 mmol) in 4 mL water was added and stirred for 1 h. When the reaction

was completed, 100 % sodium hydroxide was added until basic and the solution was extracted by dichloromethane. The separated organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to give the product as brown solid (0.452 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 8.06 (s, 1H), 7.60 (s, 1H), 6.98 (s, 1H) **(Figure A.23, Appendix A)**. ^{13}C NMR (101 MHz, $CDCl_3$): **δ** (ppm) 142.1, 137.5, 135.2, 127.9, 111.3 **(Figure A.24, Appendix A)**. IR (ATR, cm^{-1}): 2092 ($-N_3$ st) **(Figure A.25, Appendix A)**. MS: $[M+H]^+$ m/z = 247.02 **(Figure A.26, Appendix A).** [33]

2.3.11 5-azido-2-((trimethylsilyl)ethynyl)pyridine (11)

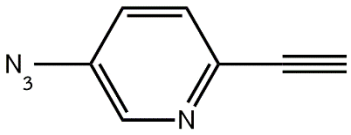


11

5-azido-2-iodopyridine (0.400 g, 1.63 mmol), trimethylsilylacetylene (0.193 g, 1.96 mmol) tetrakis(triphenylphosphine)palladium(0) (0.229 g, 0.20 mmol) and copper (I) iodide (0.019 g, 0.10 mmol) were mixed with 2 mL triethylamine and 6 mL tetrahydrofuran. The reaction was stirred at room temperature under nitrogen atmosphere for 3 h. It was then extracted by ethyl acetate and the organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered and evaporated to give a brown solid. The crude mixture was purified by silica gel column chromatography, eluting with 9:1 mixture of hexane and ethyl acetate (R_f = 0.43), to give the product as yellow solid (0.177 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 8.02 (s, 1H), 7.19 (d, 1H), 7.04 (d, 1H), 0.00 (s, 9H) **(Figure A.27, Appendix A)**. ^{13}C NMR (101 MHz, $CDCl_3$): **δ** (ppm) 141.7, 139.6, 136.7, 128.2, 126.1, 103.4, 95.5, 0.0 **(Figure A.28,**

Appendix A). IR (ATR, cm^{-1}): 2956 (C–H st), 2110 (-N_3 st) **(Figure A.29, Appendix A)**. [34]

2.3.12 5-azido-2-ethynylpyridine (12)

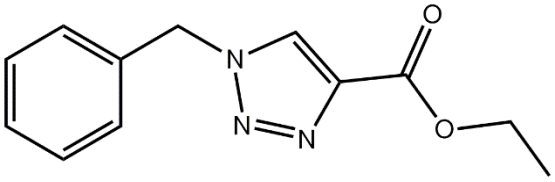


12

5-azido-2-((trimethylsilyl)ethynyl)pyridine (0.184 g, 0.85 mmol) and potassium fluoride (0.151 g, 2.556 mmol) were dissolved in 5 mL methanol and stirred at room temperature under nitrogen atmosphere for 17 h. After that the solvent was removed by vacuum evaporation and the residue was re-dissolved in ethyl acetate. The organic solution was washed by water and then dried over anhydrous magnesium sulfate, filtered and evaporated to give a brown solid. The crude mixture was purified by silica gel column chromatography, eluting with 9.5:1.5 mixture of hexane and ethyl acetate (R_f = 0.13), giving the product as yellow solid (0.177 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 8.25 (s, 1H), 7.40 (d, 1H), 7.27 (d, 1H), 3.14 (s, 1H) **(Figure A.30, Appendix A)**. ^{13}C NMR (101 MHz, $CDCl_3$): **δ** (ppm) 141.5, 138.4, 136.9, 128.0, 125.9, 82.2, 77.5 **(Figure A.31, Appendix A)**. IR (ATR, cm^{-1}): 3243 (**≡**C-H st), 2104 (C**≡**C st) **(Figure A.32, Appendix A)**. [34]

2.4 Click reactions

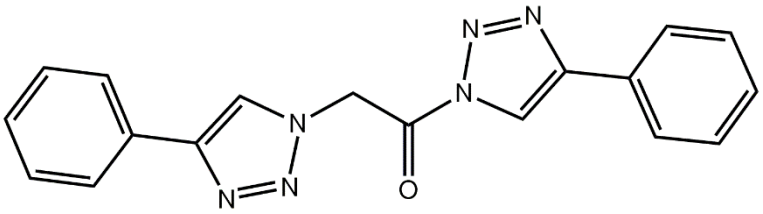
2.4.1 Click synthesis of ethyl-1-benzyltriazole-4-carboxylate (13)



13

Benzyl azide (0.266 g, 2 mmol), ethyl propiolate (0.214 g, 3 mmol) and copper (II) acetate (0.410 g, 2.27 mmol) were dissolved in 2 mL of *t*-butanol and stirred at room temperature for 23 h. After the reaction was completed, ethyl acetate was added and washed with water. The separated organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to obtain a brown solid. The crude mixture was purified by silica gel column chromatography, eluting with 8:2 mixture of hexane and ethyl acetate, giving the product as light yellow solid. (0.292 g, 63%), ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 8.03 (s, 1H), 7.20 (m, 5H), 5.46 (s, 2H), 4.20 (q, 2H), 1.20 (t, 3H). **(Figure A.33, Appendix A)** ^{13}C NMR (101 MHz, $CDCl_3$) **δ** (ppm) 160.6, 140.4, 134.1, 129.1, 128.9, 128.1, 127.6, 61.0, 54.2, 14.2. **(Figure A.34, Appendix A)**

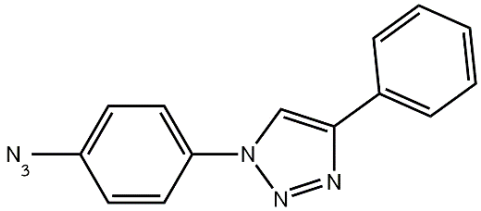
2.4.2 Click synthesis of 1,2-bis[(4-phenyl)-triazol-1-yl]-ethanone (14)



14

Azidoacetylazide (0.262 g, 2 mmol), phenylacetylene (0.613 g, 6 mmol) and copper (II) acetate (0.313 g, 1.73 mmol) were dissolved in 2 mL of *t*-butanol and stirred at room temperature for 25 h. Then ethyl acetate was added to the reaction and washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to obtain a brown solid. The crude mixture was purified by silica gel column chromatography, eluting with a 1:1 mixture of hexane and ethyl acetate, giving the product as brown solid. (0.069 g, 10%), ^{1}H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 8.44 (s, 1H), 8.37 (s, 1H), 7.91 (s, 4H), 7.44 (s, 4H), 7.35 (s, 2H), 5.82 (s, 2H). **(Figure A.35, Appendix A)**.

2.4.3 Click synthesis of 1-(4-azidophenyl)-4-phenyltriazole (15)

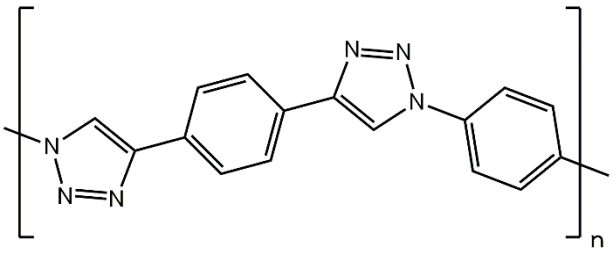


15

1,4-diazidobenzene (0.320 g, 2 mmol), phenylacetylene (0.449 g, 4.4 mmol) and copper (II) acetate (0.397 g, 2.20 mmol) were dissolved in mixture of 3 mL of *t*-butanol and 1 drop of glacial acetic acid and stirred at room temperature for 4 d. After the reaction was completed, it was added ethyl acetate, washed with water, dried over anhydrous magnesium sulfate, filtered and evaporated to obtain a brown solid. (0.132 g, 25%), ^{1}H NMR (400 MHz, acetone-d_6) **δ** (ppm) 8.99 (s, 1H), 8.01 (m, 4H), 7.49 (t, 2H), 7.37 (m, 3H). **(Figure A.36, Appendix A)** IR (ATR, cm^{-1}): 3120 (C-H st), 2135, 2092 (-N_3 st) **(Figure A.37, Appendix A)**

2.5 Polymer synthesis

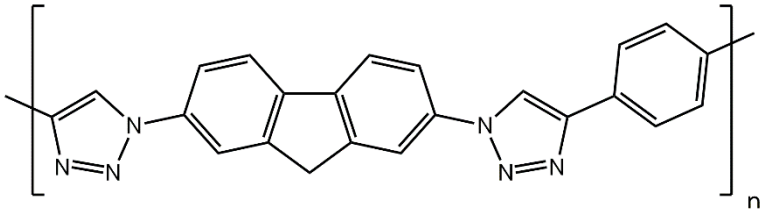
2.5.1 Click polymerization to polymer P1



P1

1,4-diazidobenzene (0.320 g, 2 mmol), 1,4-diethynylbenzene (0.268 g, 2 mmol) and copper (II) acetate (0.398 g, 2 mmol) were dissolved in 11 mL of *t*-butanol. After 9 d sodium ascorbate (0.079 g, 0.4 mmol) was added and stirred for 3 d. The reaction was added 20 mL water and filtered to obtain light brown solid, which was washed with water and ethyl acetate, and dried in desiccator overnight to afford brown product (0.522 g, 91%) ^{1}H NMR (400 MHz, (DMSO-d_6)) **δ** (ppm) 9.09 (2H), 7.87 (4H), 7.46 (2H), 7.17 (2H). **(Figure A.38, Appendix A)** IR (ATR, cm^{-1}): 2129, 2089 (-N_3 st) **(Figure A.39, Appendix A)**. Solid-UV: λ_{max} = 496 nm **(Figure A.40, Appendix A)**

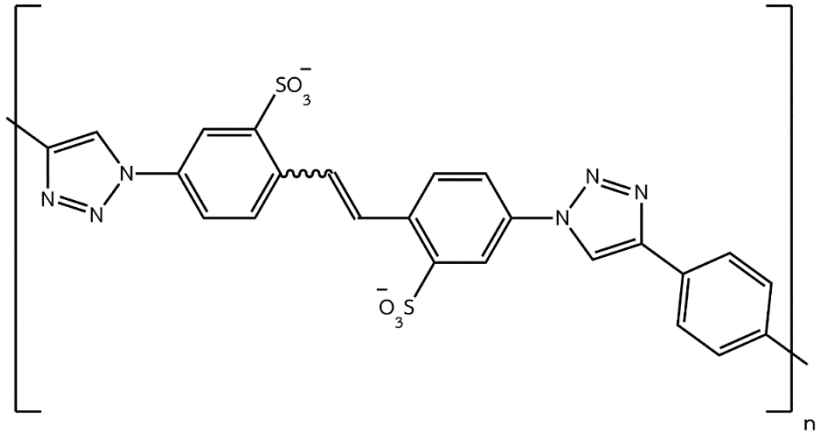
2.5.2 Click polymerization to polymer P2



P2

2,7-diazidofluorene (0.125 g, 0.5 mmol), 1,4-diethynylbenzene (0.074 g, 0.55 mmol) and copper (II) acetate (0.310 g, 1.71 mmol) were dissolved in 3 mL of *t*-butanol and stirred at room temperature for 1 h and sodium ascorbate (0.200 g, 1 mmol) was added to the reaction. After 4 d water was added and filtered. The collected solid was washed by water and acetone to obtain brown product (0.326 g, quantitative). IR (ATR, cm^{-1}): 2108 ($-N_3$ st) **(Figure A.41, Appendix A)**. Solid-UV: λ_{max} = 748 nm **(Figure A.42, Appendix A)**

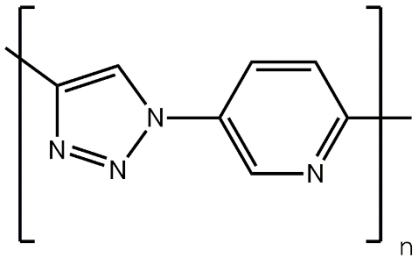
2.5.3 Click polymerization to polymer P3



P3

4,4'-diazido-2,2'-stilbenedisulfonate disodium salt tetrahydrate (0.541 g, 1 mmol), 1,4-diethynylbenzene (0.128 g, 1 mmol), copper (II) acetate (0.182 g, 1 mmol) and sodium ascorbate (0.200 g, 1 mmol) were dissolved in 3 mL of *t*-butanol and 4 mL of water and stirred at room temperature for 6 d. The reaction was added 20 mL water and filtered to obtained dark brown product. (0.240 g, 44%) ^{1}H NMR (400 MHz, (DMSO-d_6)) **δ** (ppm) 9.45 (2H), 8.42 (2H), 8.26 (2H), 8.14 (2H), 8.00 (2H), 7.86 (2H), 7.58 (2H). **(Figure A.43, Appendix A)** IR (ATR, cm^{-1}): 3387 (SO_2O-H st, broad) **(Figure A.44, Appendix A)**. Solid-UV: λ_{max} = 500-540 nm **(Figure A.45, Appendix A)**

2.5.4 Click polymerization to polymer P4



P4

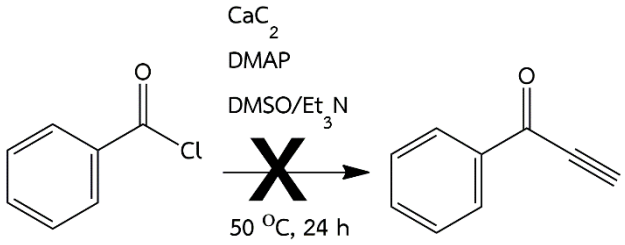
5-azido-2-ethynylpyridine (0.060 g, 0.42 mmol), copper (II) acetate (0.004 g, 0.008 mmol), sodium ascorbate (0.007 g, 0.033 mmol) and glacial acetic acid (0.028 g, 0.417 mmol) were dissolved in 3 mL of 1:2 mixture of *t*-butanol and water and stirred for 27 h. When the reaction was completed, 20 mL of 1 M sodium bicarbonate was added, followed by filtration. The solid was washed by water to obtain orange product. (0.022 g, 67%). IR (ATR, cm^{-1}): 2101 ($-N_3$ st) **(Figure A.46, Appendix A)**. Solid-UV: λ_{max} = 344-500 nm **(Figure A.47, Appendix A)**

CHAPTER III

RESULTS AND DISSCUSION

3.1 Monomer synthesis

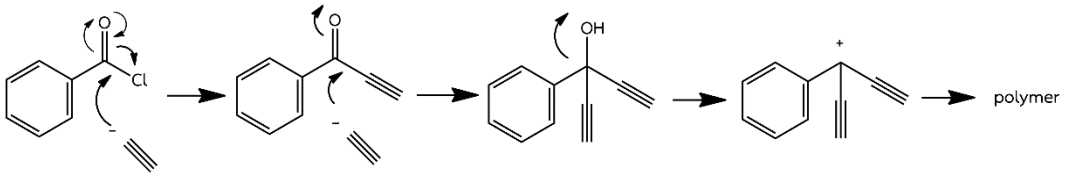
3.1.1 Carbide substitution on acid chlorides



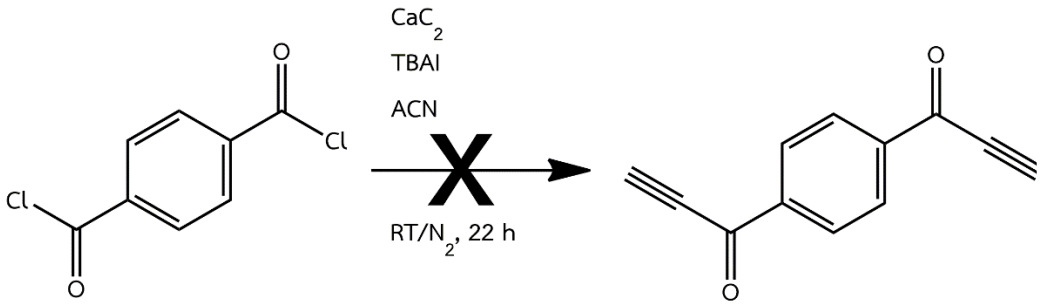
Scheme 3.1 Attempetd synthesis of propynoyl benzene

The synthesis of propynoyl benzene from benzoyl chloride was attempted via acyl substitution using calcium carbide and 4-dimethylaminopyridine (DMAP) in dimethylsulfoxide.

Unfortunately, the reaction was unsuccessful with no observable desired product. One of the reason might be because calcium carbide could re-attack on the carbonyl carbon of the product. The oversubstituted product could form a carbocation that could propagate into an unidentified polymer mixture. The final solid compound obtained had very low solubility and could not be characterized.



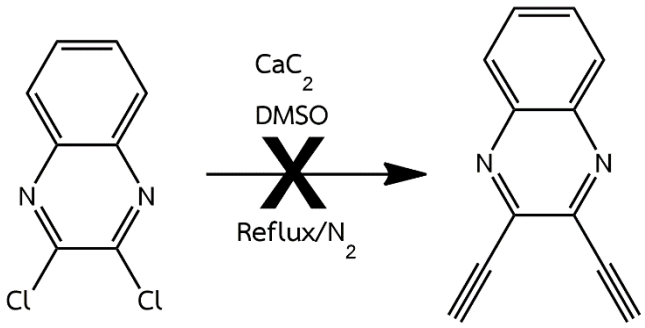
Scheme 3.2 Proposed over-substitution by calcium carbide



Scheme 3.3 Attempted synthesis of 1,4-dipropynoylbenzene

Similar synthesis of 1,4-dipropynoylbenzene by substitution terephthaloyl chloride with calcium carbide was also carried out. None of the product was detected. The only basic-aqueous soluble crude product isolated from the reaction was assumed to be terephthalic acid. The reaction might also suffer the same oversubstitution and polymerization discussed previously. Although part of the starting material remained unreact and eventually quenched during the workup to give the dicarboxylic acid by products.

3.1.2 S_NAr on chloroquinoxaline using carbide

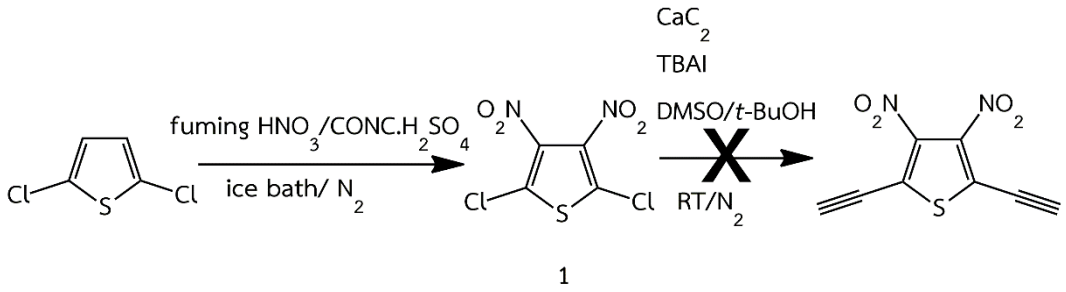


Scheme 3.4 Attempted synthesis of 2,3-diethynylquinoxaline

The synthesis of 2,3-diethynylquinoxaline was attempted from direct substitution of calcium carbide on 2,3-dichloroquinoxaline in dimethylsulfoxide. A dark

brown crude solid was obtained after work up. ^{1}H NMR of the crude product showed very complex signal. Unfortunately, none of them appeared in the region that corresponded to the terminal protons of alkyne group. It was assumed that the substitutions by calcium carbide on 2,3-dichloroquinoxaline might not occur and the staring material only decomposed in such a harsh condition.

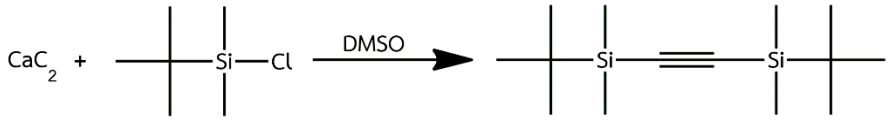
3.1.3 S_NAr on chloronitrothiophene



Scheme 3.5 Attempted synthesis of 2,5-diethynyl-3,4-dinitrothiophene

Compound **1** was synthesized from double nitrations of 2,5-dichlorothiophene using fuming nitric acid to obtain the desired product as yellow solid in 93% yield. The structure of compound **1** was confirmed by showing no signal on the spectrum, and two signals in ^{13}C NMR spectrum. **(Figure A.2, Appendix A)** and two signals of N-O stretching on IR spectrum. **(Figure A.3, Appendix A)** Compound **1** was used to react with calcium carbide to synthesize 2,5-diethynyl-3,4-dinitrothiophene. After long reaction time and crude product purification. ^{1}H and ^{13}C NMR spectrum did not showed the signal that corresponded to 2,5-diethynyl-3,4-dinitrothiophene structure.

3.1.4 Substitution on silyl chloride

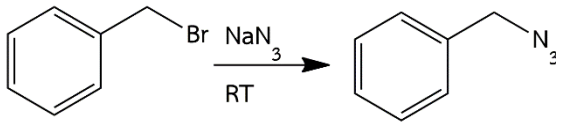


16

Scheme 3.6 Synthesis of compound **16**

Compound **16** was synthesized through substitution reaction on *tert*-butylchlorodimethylsilane (TBDMSCl) using calcium carbide in dimethylsulfoxide. The product was obtained as colorless liquid in 97% yield after purification by silica gel column chromatography, eluting with hexane (R_f = 0.75). The ^{1}H NMR spectrum showed the expected two signals of *tert*-butylsilyl group at 0.85 and 0.00 ppm. **(Figure A.48, Appendix A)**

3.1.5 Benzyl azide (2)



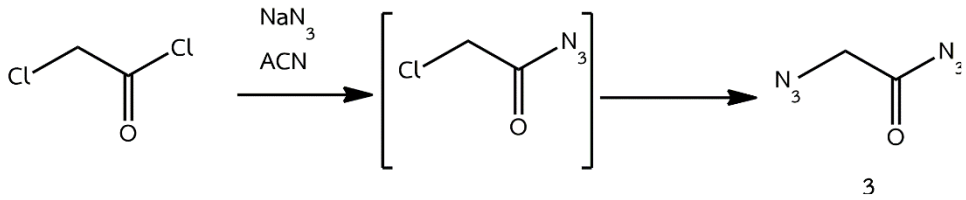
2

Scheme 3.7 Synthesis of compound **2**

Compound **2** was obtained by substitution of benzyl bromide by sodium azide to give the product as colorless oil in 91% yield. The ^{1}H NMR spectrum showed one singlet signal of methylene group at 4.36 ppm and aromatic signals at 7.40 ppm **(Figure A.3, Appendix A).** ^{13}C NMR spectrum showed four signals of aromatic carbons and one methylene carbon at **(Figure A.4, Appendix A)**. IR spectrum showed the signals of

C-H stretching of aromatic group at 3060 cm^{-1} and azido functional group at 2084 cm^{-1} **(Figure A.5, Appendix A)**.

3.1.6 2-Azidoacetyl azide (3)

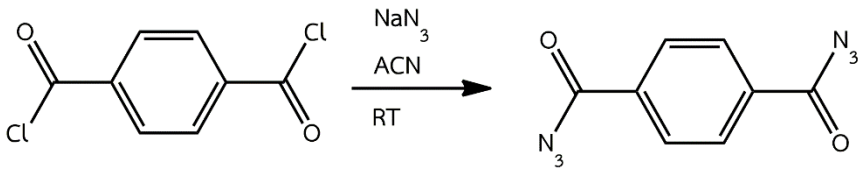


3

Scheme 3.8 Synthesis of compound **3**

2-Azidoacetyl azide **(3)** was synthesized through double nucleophilic substitutions of chloroacetyl chloride with sodium azide. The product was obtained as light yellow liquid in 44% yield. The ^{1}H NMR spectrum showed the singlet signal of methylene group at **δ** 4.64 ppm. **(Figure A.6, Appendix A)** The product was quite unstable and gave impurities upon storage as evidence in the ^{1}H NMR have impurity. IR spectrum showed the strong azide signals at 2153 and 2098 cm^{-1} and the carbonyl signal at 1680 cm^{-1}. **(Figure A.7, Appendix A)**

3.1.7 Terephthaloyl azide (4)

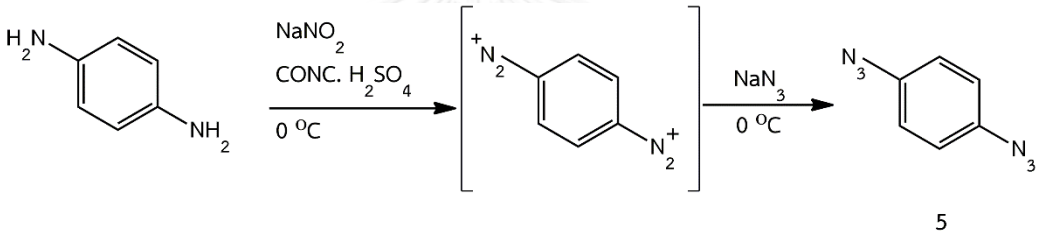


4

Scheme 3.9 Synthesis of compound **4**

The reaction of terephthaloyl chloride and sodium azide obtained terephthaloyl azide **(3)** through nucleophilic substitution reaction. The light yellow solid of compound **3** was obtained in 89% yield. ^{1}H NMR spectrum showed the singlet signal of aromatic protons at 8.11 ppm. **(Figure A.8, Appendix A)** IR spectrum appeared the signal of C-H stretching of aromatic group at 3057 cm^{-1}, the azide functional group at 2178, 2135 cm^{-1}, and the C=O stretching signal of the carbonyl groups at 1712 cm^{-1} **(Figure A.9, Appendix A)**. [27]

3.1.8 1,4-diazidobenzene (5)

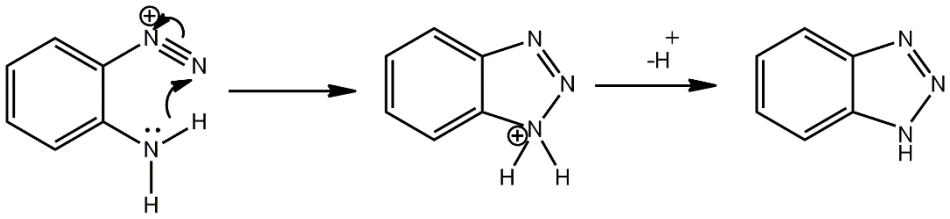


5

Scheme 3.10 Synthesis of compound **5**

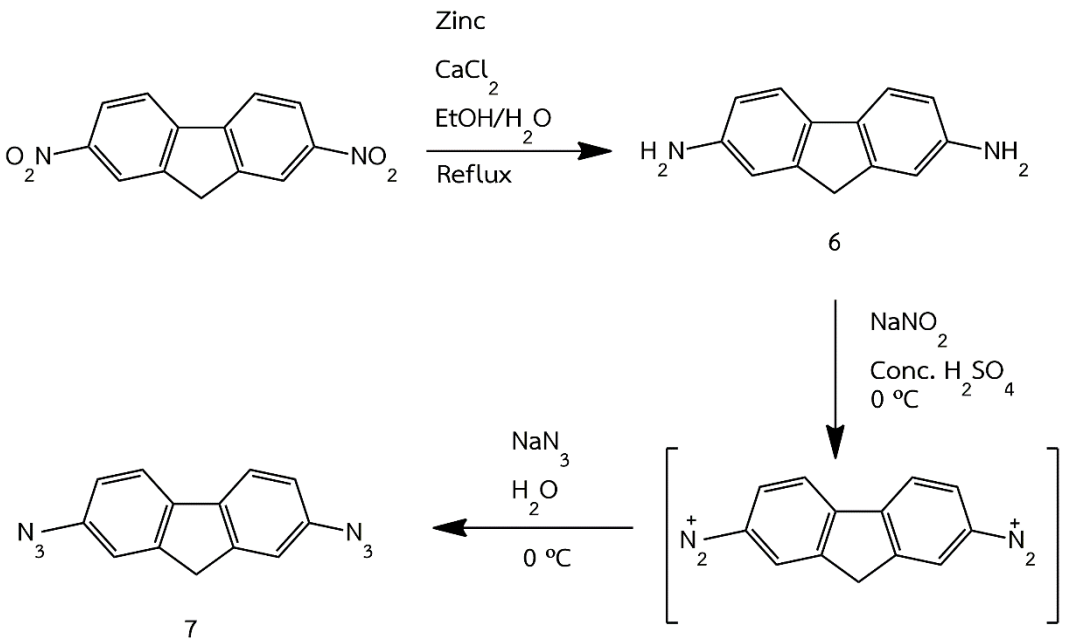
1,4-diazidobenzene **(5)** was prepared from double diazotizations of *p*-phenylenediamine with sodium nitrite, followed by double azidations with sodium azide. This compound was obtained in 68% yield. The ^{1}H NMR spectrum showed one singlet signal at 7.01 ppm. **(Figure A.10, Appendix A)** ^{13}C NMR spectrum showed two signals of aromatic carbons at 136.7 and 120.4 ppm. **(Figure A.11, Appendix A)** IR spectrum showed the signals of C-H stretching of aromatic group at 3062 cm^{-1}, and the azide functional group at 2095, 2067 cm^{-1} **(Figure A.12, Appendix A)**. These data correspond well to those in literature [28]. Another method using hydrazine instead of sodium azide had been performed [35]. However, only 17% of the product was obtained in this latter case. [29], [30]

The synthesis of 1,2-diazidobenzene was also attempted through the same procedure but unsuccessful. It was possible that the monodiazotized occurred during the process underwent intramolecular cyclization by the addjacent amino group to form the stable triazole ring as shown in **scheme 3.11**. [36]



Scheme 3.11 Ring closing mechanism of *o*-aminobenzene diazonium salt intermidiate

3.1.9 2,7-diazidofluorene (7)



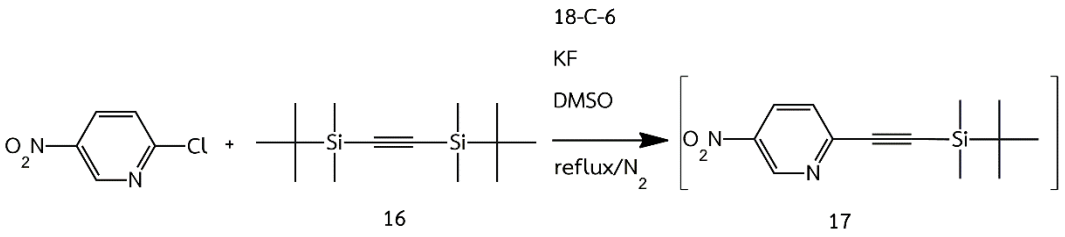
Scheme 3.12 Synthesis of compound **7**

2,7-diaminofluorene **(5)** was synthesized through reduction of 2,7-dinitrofluorene with metallic zinc. The product was obtained as brown solid in quantitative yield. The ^{1}H NMR spectrum showed a singlet signal of aromatic protons at 6.80 ppm, two doublet signals of aromatic protons at 7.32, 6.63 ppm, a proton signal of amino group at 4.48 ppm and methylene protons at 3.63 ppm **(Figure A.13, Appendix A)**. ^{13}C NMR spectrum showed the signals of six aromatic carbons at 147.1, 144.5, 133.3, 119.4, 114.0, 112.2 ppm and one methylene carbon at 37.2 ppm **(Figure A.14, Appendix A)**. IR spectrum showed the signals of N-H stretching at 3378, 3320 cm^{-1} and C-H stretching of aromatic group at 3003 cm^{-1} **(Figure A.15, Appendix A)**. [31]

Further reaction of 2,7-diaminofluorene **(6)** with sodium nitrite and sodium azide through diazotizations and subsequent azidations obtained the yellow product **(6)** in 76% yield. The ^{1}H NMR spectrum showed a singlet signal of aromatic protons at 7.18 ppm, two doublet signals of aromatic protons at 7.67, 7.18 ppm, and methylene protons at 3.85 ppm **(Figure A.16, Appendix A)**. ^{13}C NMR spectrum showed the signals of six aromatic carbons at 144.8, 138.5, 138.2, 120.6, 118.0, 115.8 ppm and one methylene carbon at 36.8 ppm **(Figure A.17, Appendix A)**. IR spectrum showed the strong signals of azide group at 2102, 2083 cm^{-1} **(Figure A.18, Appendix A)**. These data correspond well to those in literature [32]. [29], [30]

The reaction time of the last azidation step had been optimized. It was found that the best condition was at approximately 3 h, which gave the product in 76% yield. Shorter reaction time did not complete the reaction (50% yield of product) whereas longer reaction time at 4 h probably caused decomposition of the product and lowered the yield to 54%.

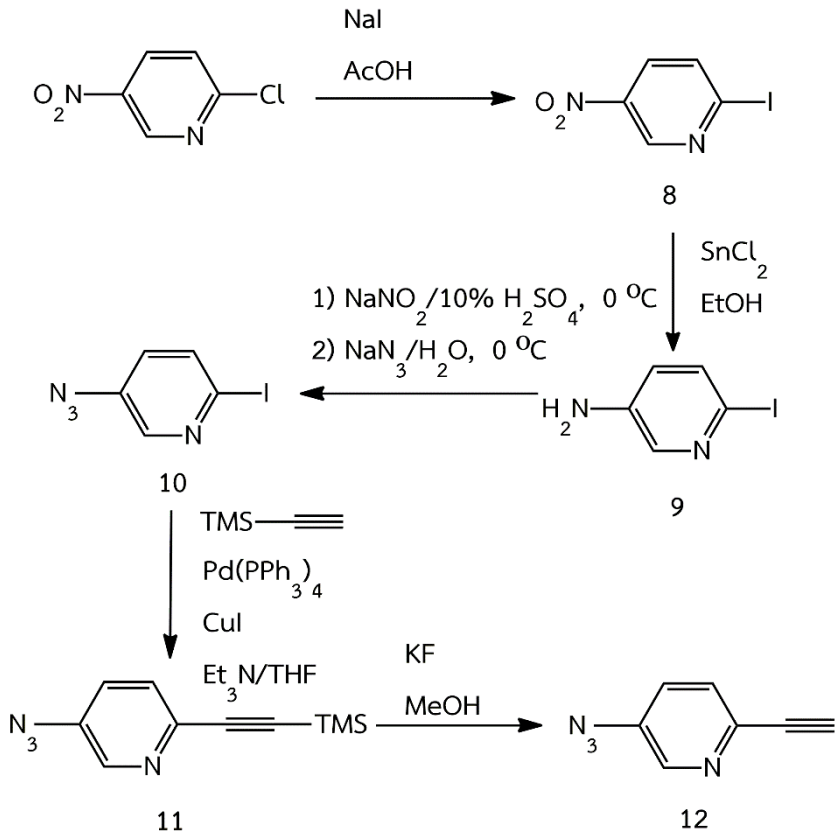
3.1.10 2-((*tert*-butyldimethylsilyl)ethynyl)-5-nitropyridine (17)



Scheme 3.13 Attempted synthesis of compound **17**

The synthesis of compound **17** had been attempted from 2-chloro-5-nitropyridine reacted with bis(*tert*-butyldimethylsilyl)ethyne in dimethyl sulfoxide through desilylation followed by nucleoplilic aromatic substitution. However, the obtained crude product was found to be soluble in 1 M NaOH showed no signal in the ^{1}H NMR spectrum that would correspond to the TBDMS group. The absence of this group indicated that the process was unsuccessful and the starting material would probably reacted with residual water to generate the corresponding phenol derivative, which could be well dissolved in aqueous base solution.

3.1.11 5-Azido-2-ethynylpyridine (12)



Scheme 3.14 Synthesis of compound **12**

2-iodo-5-nitropyridine **(8)** was obtained from iodination of 2-chloro-5-nitropyridine with sodium iodide through S_NAr processThe reaction gave the product as brown solid in 58% yield. The ^1H NMR spectrum showed one singlet signal of aromatic proton at 9.16 ppm and two doublet signals of aromatic protons at 8.10, 7.96 ppm **(Figure A.19, Appendix A).** IR spectrum showed signals of C-H stretching of aromatic group at 3024 cm^{-1}, and nitro functional group at 1504, 1344 cm^{-1} **(Figure A.20, Appendix A)**. [33]

The reduction of compound **8** by tin (II) acquire yellow solid product **9** in 89% yield. The ^1H NMR spectrum showed one singlet signal of aromatic proton at 7.85 ppm,

two doublet signals of aromatic protons at 7.35, 6.65 ppm and one singlet signal of amino group at 4.06 ppm **(Figure A.21, Appendix A).** IR spectrum showed signals of N-H stretching at 3304, 3178 cm^{-1} **(Figure A.22, Appendix A)**. [33]

Next, 5-azido-2-iodopyridine **(10)** was prepared from diazotization of the amino group on compound **7** follwed by azidation to obtain brown solid in 96% yield. The ^{1}H NMR spectrum showed one singlet signal of aromatic proton at 8.06 ppm and two doublet signals of aromatic protons at 7.60, 6.98 ppm **(Figure A.23, Appendix A).** ^{13}C NMR spectrum showed five aromatic carbons signals at 142.1, 137.5, 135.2, 127.9, 111.3 ppm **(Figure A.24, Appendix A)**. IR spectrum showed strong signal of azide at 2092 cm^{-1} **(Figure A.25, Appendix A)**. Finally, the mass spectrum exhibited the sorresponding molecular ion peak in the positive mode at 247.02 amu $[M+H]^{+}$ **(Figure A.26, Appendix A)**. [33]

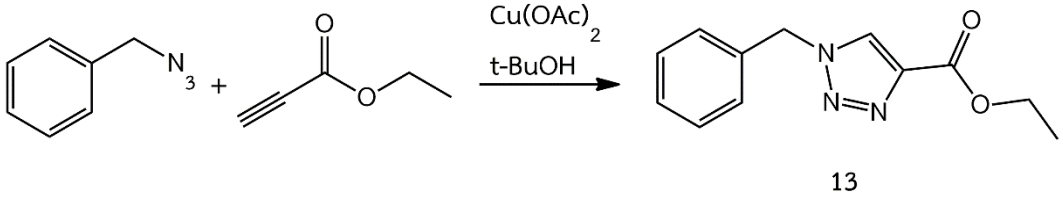
To obtain 5-azido-2-((trimethylsilyl)ethynyl)pyridine **(11)**, compound **10** was reacted with trimethylsilylacetylene by palladium catalyzed Sonogashira coupling to give yellow solid product in 40% yield. The ^{1}H NMR spectrum showed one singlet signal of aromatic proton at 8.02 ppm, two doublet signals of aromatic protons at 7.19, 7.04 ppm and one singlet signal of trimethylsilyl group at 0.00 ppm **(Figure A.27, Appendix A).** ^{13}C NMR spectrum showed five aromatic carbons signals at 141.7, 139.6, 136.7, 128.2, 126.1 ppm, two ethynyl carbons at 103.4, 95.5 ppm and one trimethylsilyl group at 0.0 ppm **(Figure A.28, Appendix A)**. IR spectrum showed the signal of C-H stretching at 2110 cm^{-1} and strong signal of azide at 2110 cm^{-1} **(Figure A.29, Appendix A)**. [34]

Compound **11** was finally removed the TMS group to obtain brown solid product **12** in 57% yield. The ^{1}H NMR spectrum showed one singlet signal of aromatic proton at 8.25 ppm, two doublet signals of aromatic protons at 7.40, 7.27 ppm and one singlet signal of terminal alkyne at 3.14 ppm **(Figure A.30, Appendix A)**. ^{13}C NMR

spectrum showed five aromatic carbons signals at 141.5, 138.4, 136.9, 128.0, 125.9 ppm and two ethynyl carbons at 82.2, 77.5 ppm **(Figure A.31, Appendix A)**. IR spectrum showed signal of C-H stretching of terminal alkyne at 3243 cm^{-1} and strong signal of C≡C stretching at 2104 cm^{-1} **(Figure A.32, Appendix A)**. [34]

3.2 Click reaction

3.2.1 Ethyl-1-benzyltriazole-4-carboxylate (13)

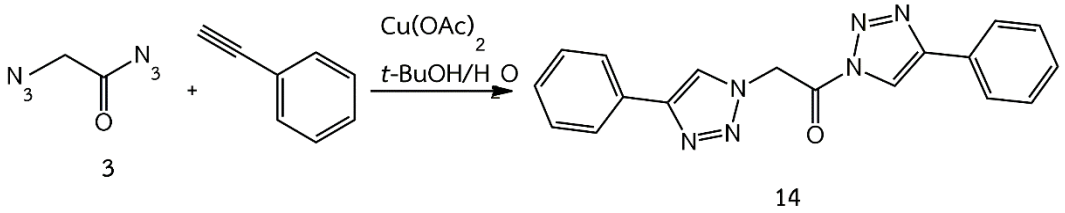


13

Scheme 3.15 Synthesis of compound **13**

The synthesis of ethyl-1-benzyltriazole-4-carboxylate **(13)** was obtained in 63% yield through CuAAC click reaction of benzyl azide with ethyl propiolate using copper (II) acetate at room temperature in *t*-BuOH. The ^{1}H NMR spectrum showed the singlet signal of the newly formed triazole proton at 8.03 ppm with the disappearance of the terminal alkyne proton of ethyl propiolate at 2.90 ppm. **(Figure A.33, Appendix A)** ^{13}C NMR spectrum indicated all the ten signals that corresponded to the expected structure. **(Figure A.34, Appendix A)** [37]

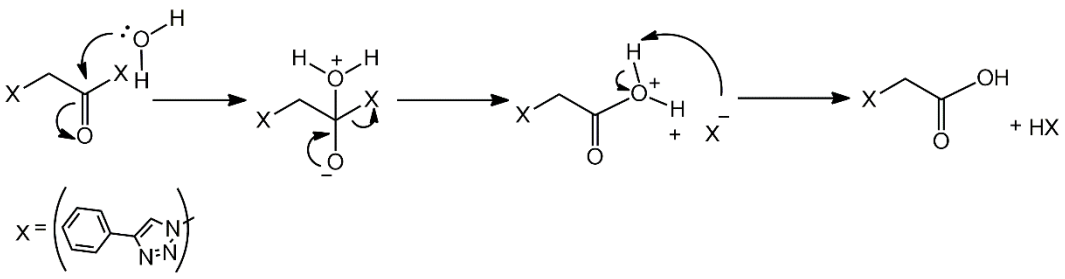
3.2.2 Click reaction of 2-Azidoacetyl azide (14)



Scheme 3.16 Synthesis of compound **14**

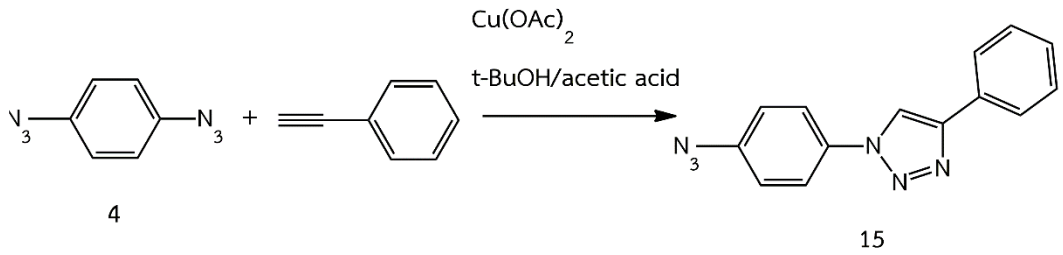
Compound **14** was synthesized by Click reaction of compound **3** and phenylacetylene using copper (II) acetate as catalyst to obtain the product as brown solid in 10% yield. The ^{1}H NMR spectrum showed one broad signal of triazole on alkyl side at 8.44 ppm, possibly with a long range coupling with the methylene protons. While the triazole proton on acyl side appeared as a sharp signal at 8.37 ppm. **(Figure A.35, Appendix A)** [37]

Furthermore, we can detected 4-phenyltriazole byproduct, assumed to come from hydrolysis of compound **13** as shown in **scheme 3.17.** Its ^{1}H NMR spectrum showed the singlet signal of triazole proton at 8.18 ppm and three aromatic proton at 7.89, 7.43 and 7.34 ppm. **(Figure A.49, Appendix A)** The presence of this byproduct illustrated that acyl triazole residue could be simply hydrolyzed in the Click condition. As a result, this acyltriazole functional group is not appropriate to be used as a precursor in Click polymerizations afterwards.



Scheme 3.17 Hydrolysis of compound **14**

3.2.3 Click reaction of 1,4-diazidobenzene (15)



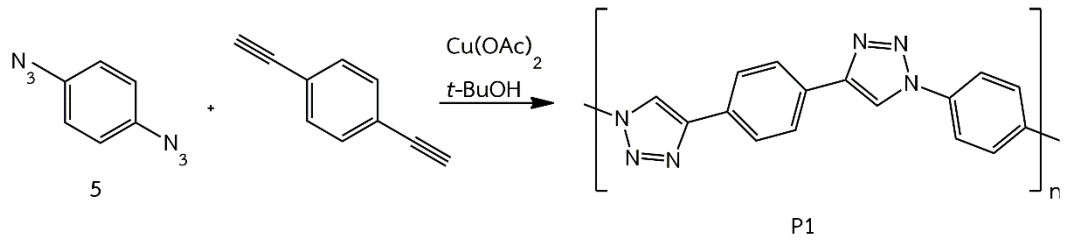
4 15

Scheme 3.18 Synthesis of compound **15**

Compound **4** and phenylacetylene were reacted via Click reaction using copper (II) acetate catalyst to acquire compound **15** as a brown solid in 25% yield. ^{1}H NMR spectrum showed the singlet signal of triazole proton at 8.99 ppm and three signals that corresponded to aromatic protons in the structure. **(Figure A.36, Appendix A)** IR spectrum showed the azide group at 2135 cm^{-1} and no terminal alkyne group. **(Figure A.37, Appendix A)**.The reaction seemed to be unusually slow and only one-side Click product was isolated as the major product. It was possible that this product has low solubility in the reaction condition and precipitate off before the second Click reaction to occur. [37]

3.3 Click polymerization

3.3.1 Synthesis of polymer P1



Scheme 3.19 Synthesis of polymer **P1**

Polymer **P1** was obtained from compound **3** and phenylacetylene through CuAAC click polymerization using copper (II) acetate as a catalyst. After the reaction completed, the solid residue was washed with ethyl acetate to afford polymer **P1** in 91% yield. ^{1}H NMR spectrum of the partially dissolved product showed triazole proton signal at 9.09 ppm with three aromatic signal at 7.87, 7.46 and 7.17 ppm. **(Figure A.38, Appendix A)** The relatively sharp peaks and the presence of unsymmetric aromatic signals indicated that the dissolved part of the product was rather short in length and still oligomer. IR spectrum showed the presence of azide and alkyne groups signals at 2129, 2089 cm^{-1}, supporting the relatively short oligomeric chains because of the still visible signals of the end groups. **(Figure A.39, Appendix A)** The solid-UV spectrum showed maximum absorption at small value of 496 nm **(Figure A.40, Appendix A)** [37]

Moreover, we could detect the 1:1 Click product **18 (Figure 3.1)** of this reaction from the filtrate washed from the solid **P1**. ^{1}H NMR spectrum of this byproduct showed triazole signal at 8.18 ppm and four aromatic protons signals corresponded to the structure. **(Figure 3.1, Figure A.50, Appendix A)** IR spectrum showed C-H stretching of terminal alkyne at 3289 cm^{-1}, and azide ad alkyne signals at 2132 and 2089 cm^{-1}. **(Figure A.51, Appendix A)**

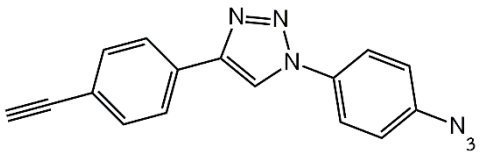
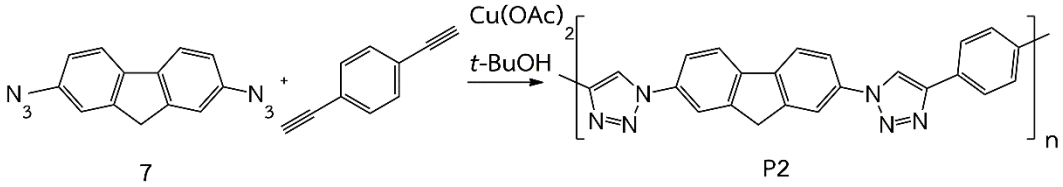


Figure 3.1 1:1 Click product **18**

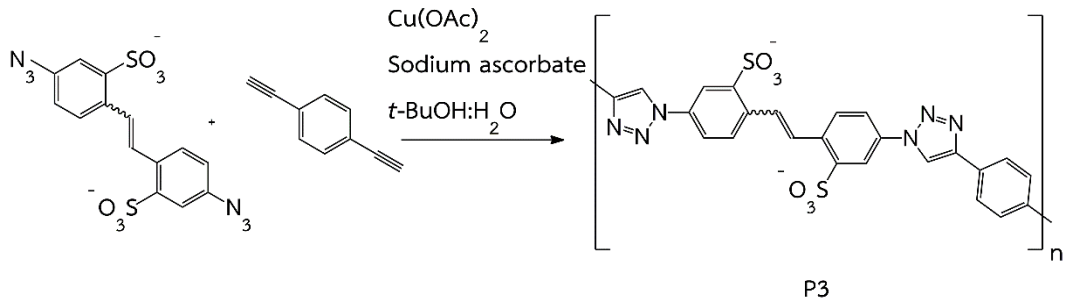
3.3.2 Synthesis of polymer P2



Scheme 3.20 Synthesis of polymer **P2**

Polymer **P2** was obtained in quantitative yield from Click reaction of compound **5** and 1,4-diethynylbenzene using copper (II) acetate as catalyst. The rather broad and complex solid-UV spectrum showed that polymer **P2** have maximum absorption at 748 nm, corresponded to a highly conjugated system in the structure**. (Figure A.42, Appendix A)** IR spectrum still showed the azide signal at 2108 cm^{-1} suggeting the presence of some short chain oligomers in the mixture. **(Figure A.41, Appendix A)** Due to the low solubility of this polymer, the characterizations by NMR spectroscopy could not be obtained. [37]

3.3.3 Synthesis of polymer P3



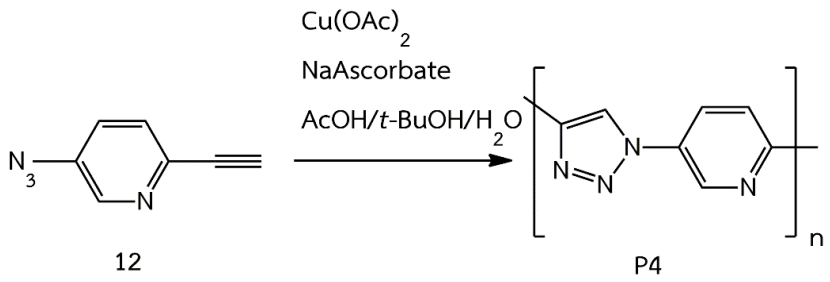
P3

Scheme 3.21 Synthesis of polymer **P3**

4,4'-diazido-2,2'-stilbenedisulfonate disodium salt tetrahydrate and 1,4-diethynylbenzene were combined to synthesize polymer **P3** via Click polymerization using copper (II) acetate as catalyst. The reaction was stirred at room temperature for 6 days to obtain the dark brown product in 44% yield. The ^{1}H NMR showed all the signals relevant to the structure, but they were broadened with no clear coupling pattern. The singlet signal of the newly formed triazole protons appeared at approximately 9.45 ppm **(Figure A.43, Appendix A)**. IR spectrum confirmed the disappearances of both azides at 2117 cm^{-1} and the remaining SO_2O-H broad signal over the range of 3650-3000 cm^{-1} after click polymerization. **(Figure A.44, Appendix A)** UV-vis spectrum showed the broad maximum absorption between 500-540 nm. **(Figure A.45, Appendix A)** [37]

3.3.4 Synthesis of polymer P4

Polymer **P4** was obtained from Click polymerization of compound **11** in presence of catalytic amount of copper (II) acetate with sodium ascorbate as reducing agent. The crude solid product was obtained as orange solid in 67% yield.



Scheme 3.22 Synthesis of polymer **P4**

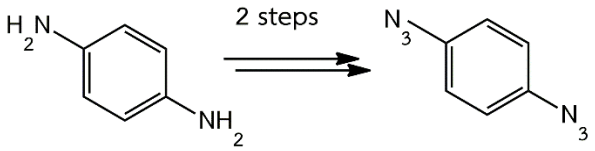
IR spectrum showed the existence of azide signals at 2110 cm^{-1}, supporting the relatively short oligomeric chains because of the still visible signals of the end groups. **(Figure A.46, Appendix A)** Solid-UV spectrum showed the broad maximum absorption between 344-500 nm. **(Figure A.47, Appendix A)** [37]

Moreover, the shorter oligomers of polymer **P4** from the acetone filtrate were characterized by IR spectroscopy, which still showed the azide group at 2132, 2102 cm^{-1} **(Figure A.52, Appendix A).**

CHAPTER IV

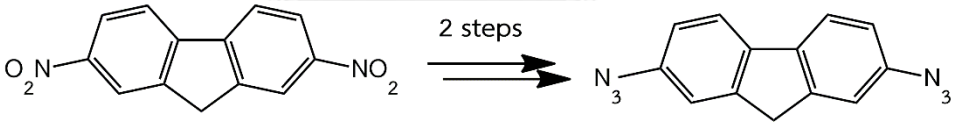
CONCLUSION

The synthesis of two diazide monomers and one bifunctional alkyne-azide monomer had been accomplished. Compound **5** was synthesized through diazotizations and azidations from *p*-phenylenediamine in 68% yield. **(Scheme 4.1)** Reduction of 2,7-dinitrofluorene followed by similar diazotizations and azidations provided compound **7** in 76% yield. **(Scheme 4.2)**



5

Scheme 4.1 Synthesis of compound **5**

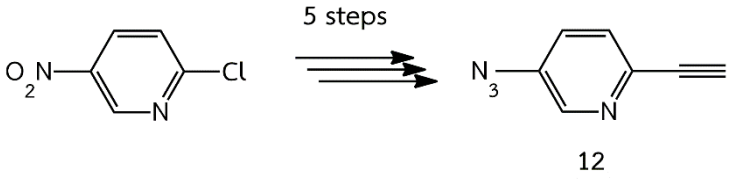


7

Scheme 4.2 Synthesis of compound **7**

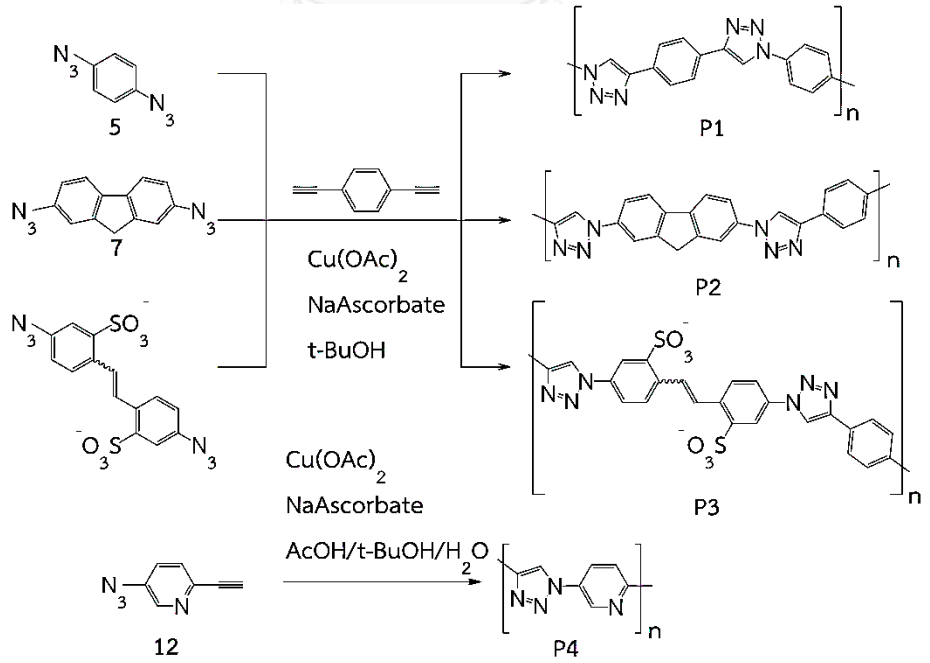
Compound **12** was obtained from five steps reactions of 2-chloro-5-nitropyridine. **(Scheme 4.3)** First, iodine substitution obtained compound **8** in 58% yield. Reduction of the nitro group gave compound **9** in 89% yield. Next, diazotization and azidation of the amino group acquired compound **10** in 96% yield. Subsequent coupling with trimethylsilylacetylene obtained compound **11** in 40% yield. Finally, compound **12** was prepared by removal of the trimethylsilyl group from compound

11 in 57% yield. When combined all five steps, the overall yield of this process was 11%.



Scheme 4.3 Synthesis of compound **12**

Polymers **P1-P3** was obtained from Click polymerizations of either 1,4-diazidobenzene, 2,7-diazidofluorene or 4,4'-diazido-2,2'-stilbenedisulfonate with 1,4-diethynylacetylene, respectively. **(Scheme 4.4)** polymer **P1** was obtained in 91% yield, while polymer **P2** was obtained in quantitative yield and polymer **P3** was obtained in 44% yield. Polymer **P4** was similarly prepared from the bifunctional monomer **12** via Click polymerization in 67% yield. The UV-vis spectra of all polymers bathochromic shift that indicated the conjugate nature of these polymers.



Scheme 4.4 Synthesis of polymer **P1-P4**

REFERENCES

[1] Chiang, C.K., Fincher Jr, C., Park, Y., Heeger, A., Shirakawa, H., Louis, E., Gau, S., and MacDiarmid, A.G. Electrical conductivity in doped polyacetylene. Physical Review Letters 39(17) (1977): 1098-1101.

[2] Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K., and Heeger, A.J. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene,$(CH)_x$. Journal of the Chemical Society, Chemical Communications (16) (1977): 578-580.

[3] Forrest, S.R. The path to ubiquitous and low-cost organic electronic appliances on plastic. Nature 428(6986) (2004): 911-918.

[4] Allcock, H.R., Lampe, F.W., and Mark, J.E. Contemporary polymer chemistry 3rd ed.: Pearson Education, Upper Saddle River, NJ, USA, 2003.

[5] Chen, P., Lalancette, R.A., and Jäkle, F. Applying the Oligomer Approach to Luminescent Conjugated Organoboranes. Journal of the American Chemical Society 133(23) (2011): 8802-8805.

[6] Hao, Q., Yu, S., Li, S., Chen, J., Zeng, Y., Yu, T., Yang, G., and Li, Y. Locked Planarity: A Strategy for Tailoring Ladder-Type **π**-Conjugated Anilido–Pyridine Boron Difluorides. The Journal of organic chemistry 79(1) (2013): 459-464.

[7] Kolb, H.C., Finn, M., and Sharpless, K.B. Click chemistry: diverse chemical function from a few good reactions. Angewandte Chemie International Edition 40(11) (2001): 2004-2021.

[8] Kolb, H.C. and Sharpless, K.B. The growing impact of click chemistry on drug discovery. Drug discovery today 8(24) (2003): 1128-1137.

[9] Huisgen, R. 1,3-dipolar cycloadditions. Past and future. Angewandte Chemie International Edition 2(10) (1963): 565-598.

[10] Rostovtsev, V.V., Green, L.G., Fokin, V.V., and Sharpless, K.B. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes. Angewandte Chemie International Edition 33(43) (2002): 45-45.

[11] Himo, F., Lovell, T., Hilgraf, R., Rostovtsev, V.V., Noodleman, L., Sharpless, K.B., and Fokin, V.V. Copper (I)-catalyzed synthesis of azoles. DFT study predicts unprecedented reactivity and intermediates. Journal of the American Chemical Society 127(1) (2005): 210-216.

[12] Bu, H.-B., Götz, G., Reinold, E., Vogt, A., Schmid, S., Segura, J.L., Blanco, R., Gómez, R., and Bäuerle, P. Efficient post-polymerization functionalization of conducting poly (3,4-ethylenedioxythiophene) (PEDOT) via 'click'-reaction. Tetrahedron 67(6) (2011): 1114-1125.

[13] Lahann, J. Click chemistry for biotechnology and materials science. Wiley, Chichester, 2009.

[14] Qin, A., Lam, J.W., and Tang, B.Z. Click polymerization: progresses, challenges, and opportunities. Macromolecules 43(21) (2010): 8693-8702.

[15] Wu, P., Feldman, A.K., Nugent, A.K., Hawker, C.J., Scheel, A., Voit, B., Pyun, J., Frechet, J.M., Sharpless, K.B., and Fokin, V.V. Efficiency and fidelity in a click-chemistry route to triazole dendrimers by the copper (I)-catalyzed ligation of azides and alkynes. Angewandte Chemie International Edition 43(30) (2004): 3928-3932.

[16] Scheel, A.J., Komber, H., and Voit, B.I. Novel Hyperbranched Poly ([1,2,3]-triazole)s Derived from AB2 Monomers by a 1,3-Dipolar Cycloaddition. Macromolecular rapid communications 25(12) (2004): 1175-1180.

[17] van Steenis, D.J.V., David, O.R., van Strijdonck, G.P., van Maarseveen, J.H., and Reek, J.N. Click-chemistry as an efficient synthetic tool for the preparation of novel conjugated polymers. Chemical communications (34) (2005): 4333-4335.

[18] Qin, A., Lam, J.W., Jim, C.K., Zhang, L., Yan, J., Haussler, M., Liu, J., Dong, Y., Liang, D., and Chen, E. Hyperbranched polytriazoles: click polymerization, regioisomeric structure, light emission, and fluorescent patterning. Macromolecules 41(11) (2008): 3808-3822.

[19] Tang, Y., Jim, C.K., Liu, Y., Ye, L., Qin, A., Lam, J.W., Zhao, C., and Tang, B.Z. Synthesis and curing of hyperbranched poly (triazole)s with click

polymerization for improved adhesion strength. ACS applied materials & interfaces 2(2) (2010): 566-574.

[20] Tsarevsky, N.V., Sumerlin, B.S., and Matyjaszewski, K. Step-growth "click" coupling of telechelic polymers prepared by atom transfer radical polymerization. Macromolecules 38(9) (2005): 3558-3561.

[21] Hartwig, S. and Hecht, S. Polypseudopeptides with Variable Stereochemistry: Synthesis via Click-Chemistry, Postfunctionalization, and Conformational Behavior in Solution. Macromolecules 43(1) (2009): 242-248.

[22] Li, Z., Yu, G., Hu, P., Ye, C., Liu, Y., Qin, J., and Li, Z. New azo-chromophore-containing hyperbranched polytriazoles derived from AB2 monomers via click chemistry under copper (I) catalysis. Macromolecules 42(5) (2009): 1589-1596.

[23] Song, M., Park, J.S., Kim, Y.H., Karim, M.A., Jin, S.-H., Ree, R.S., Cho, Y.R., Gal, Y.-S., and Lee, J.W. Synthesis and characterization of polymer electrolytes containing phenothiazine-based click polymers for dye-sensitized solar cell applications. Macromolecular Research 19(7) (2011): 654-659.

[24] Wu, Y., Dong, Y., Li, J., Huang, X., Cheng, Y., and Zhu, C. A Highly Selective and Sensitive Polymer-based Fluorescence Sensor for Hg^{2+}-Ion Detection via Click Reaction. Chemistry-an Asian Journal 6(10) (2011): 2725.

[25] Wang, J., Mei, J., Zhao, E., Song, Z., Qin, A., Sun, J.Z., and Tang, B.Z. Ethynyl-Capped Hyperbranched Conjugated Polytriazole: Click Polymerization, Clickable Modification, and Aggregation-Enhanced Emission. Macromolecules 45(19) (2012): 7692-7703.

[26] He, X., Woo, A.Y., Borau-Garcia, J., and Baumgartner, T. Dithiazolo [5, 4-b: 4′, 5′-d] phosphole: A Highly Luminescent Electron-Accepting Building Block. Chemistry-A European Journal 19(23) (2013): 7620-7630.

[27] Katritzky, A.R., Rogers, J.W., Witek, R.M., Vakulenko, A.V., Mohapatra, P.P., Steel, P.J., and Damavarapu, R. Synthesis and characterization of blowing agents and hypergolics. Journal of Energetic Materials 25(2) (2007): 79-109.

[28] Herring, D. The Reactions of 1, 4-Bis (diphenylphosphino) benzene with Phenyl Azide and 1, 4-Diazidobenzene. The Journal of Organic Chemistry 26(10) (1961): 3998-3999.

[29] Colasson, B., Save, M., Milko, P., Roithová, J., Schröder, D., and Reinaud, O. A ditopic calix [6] arene ligand with N-methylimidazole and 1,2,3-triazole substituents: Synthesis and coordination with Zn (II) cations. Organic letters 9(24) (2007): 4987-4990.

[30] Furniss, B.S., Hannaford, A.J., Smith, P.W.G., and Tatchell, A.R. Vogel's textbook of practical organic chemistry. 5th ed.: Longman Scientific & Technical, Essex, 1989.

[31] Kuhn, W. 2-Nitrofluorene and 2-Aminofluorene. Organic Syntheses 13 (1943): 74.

[32] Lee, J.W., Kim, H.J., Han, S.C., Kim, J.H., and Jin, S.-H. Synthesis and characterization of poly(amido amine) dendrimer containing fluorene as a core chromophore. Journal of nanoscience and nanotechnology 8(9) (2008): 4635-4639.

[33] Seton, A.W., Stevens, M.F., and Westwell, A.D. A revised synthesis of the antitumour antibiotic L-azatyrosine via 2-iodo-5-methoxypyridine. Journal of Chemical Research 2001(12) (2001): 546-548.

[34] Sagitullina, G., Vorontsova, M., Garkushenko, A., Poendaev, N., and Sagitullin, R. Nitropyridines: X. Palladium-catalyzed cross-coupling of 2-bromo-5-nitropyridine with terminal acetylenes. Russian journal of organic chemistry 46(12) (2010): 1830-1834.

[35] Siddiki, A.A., Takale, B.S., and Telvekar, V.N. One pot synthesis of aromatic azide using sodium nitrite and hydrazine hydrate. Tetrahedron Letters 54(10) (2013): 1294-1297.

[36] Joshi, A.A. and Viswanathan, C. Docking studies and development of novel 5-heteroarylamino-2, 4-diamino-8-chloropyrimido-[4, 5-b] quinolines as potential antimalarials. Bioorganic & medicinal chemistry letters 16(10) (2006): 2613-2617.

[37] Nagao, Y. and Takasu, A. “Click polyester”: Synthesis of polyesters containing triazole units in the main chain via safe and rapid “click” chemistry and their properties. Journal of Polymer Science Part A: Polymer Chemistry 48(19) (2010): 4207-4218.

APPENDICES

APPENDIX A

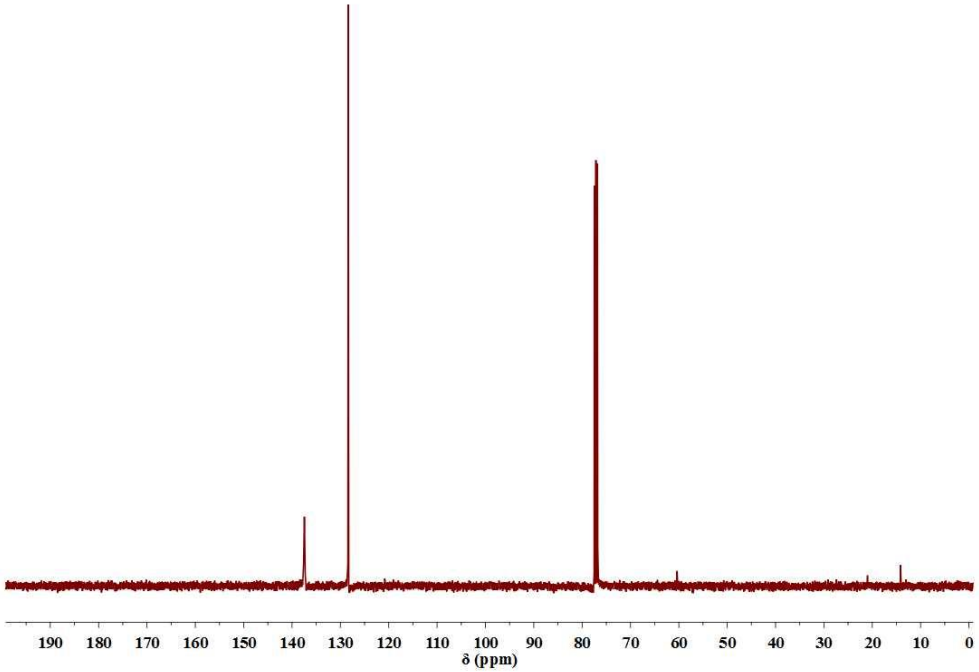


Figure A.1 ^{13}C NMR ($CDCl_3$) spectrum of 2,5-dichloro-3,4-dinitrothiophene **(1)**

Figure A.2 IR spectrum of 2,5-dichloro-3,4-dinitrothiophene **(1)**

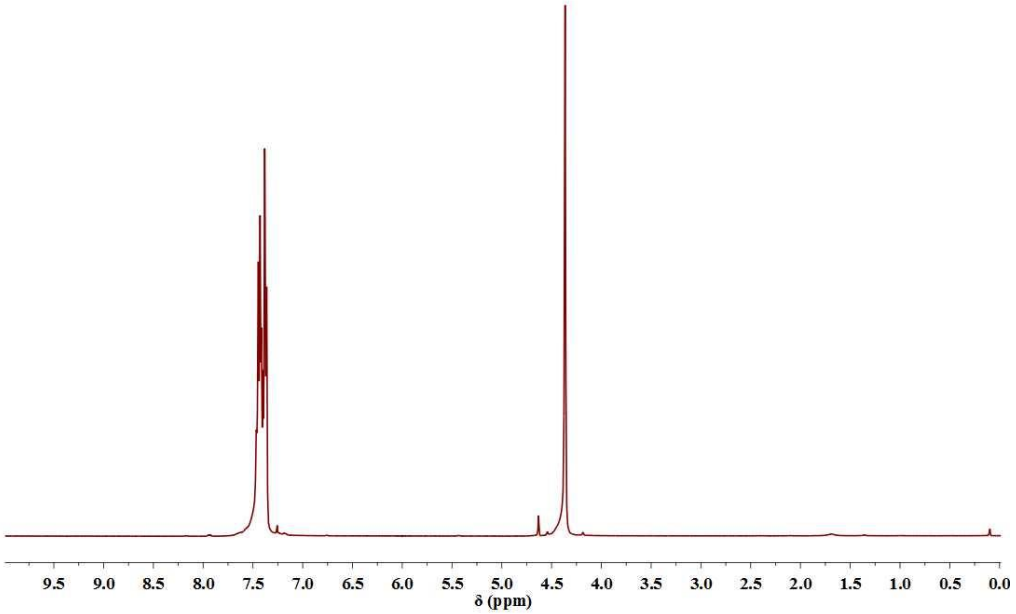


Figure A.3 ^{1}H NMR ($CDCl_3$) spectrum of benzyl azide **(2)**

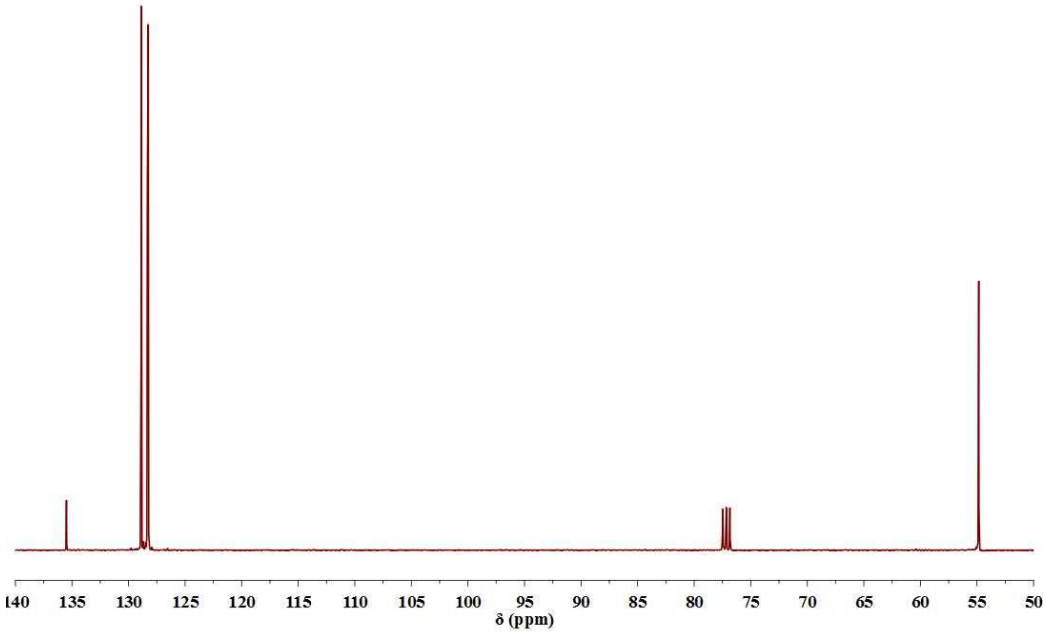


Figure A.4 ^{13}C NMR ($CDCl_3$) spectrum of benzyl azide **(2)**

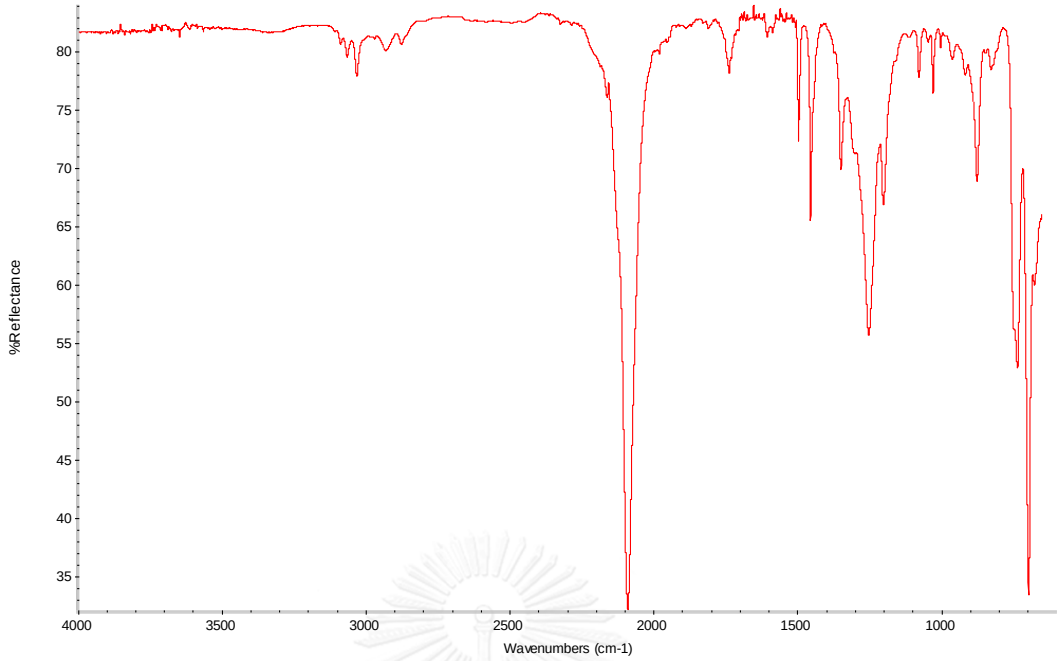


Figure A.5 IR spectrum of benzyl azide **(2)**

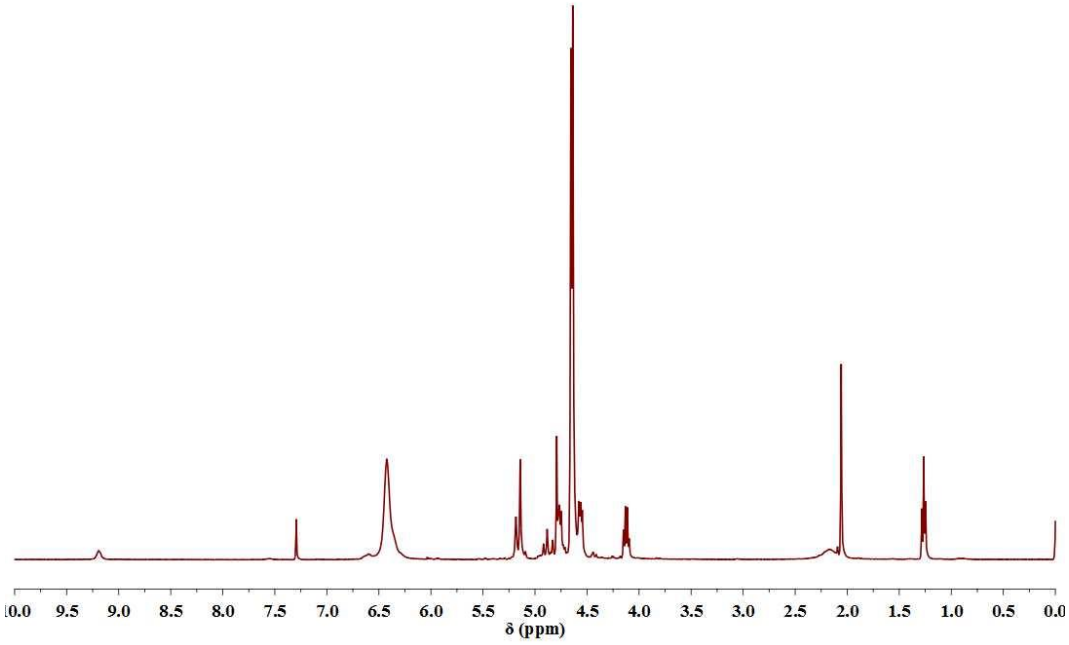


Figure A.6 ^{1}H NMR ($CDCl_3$) spectrum of azidoacetylazide **(3)**

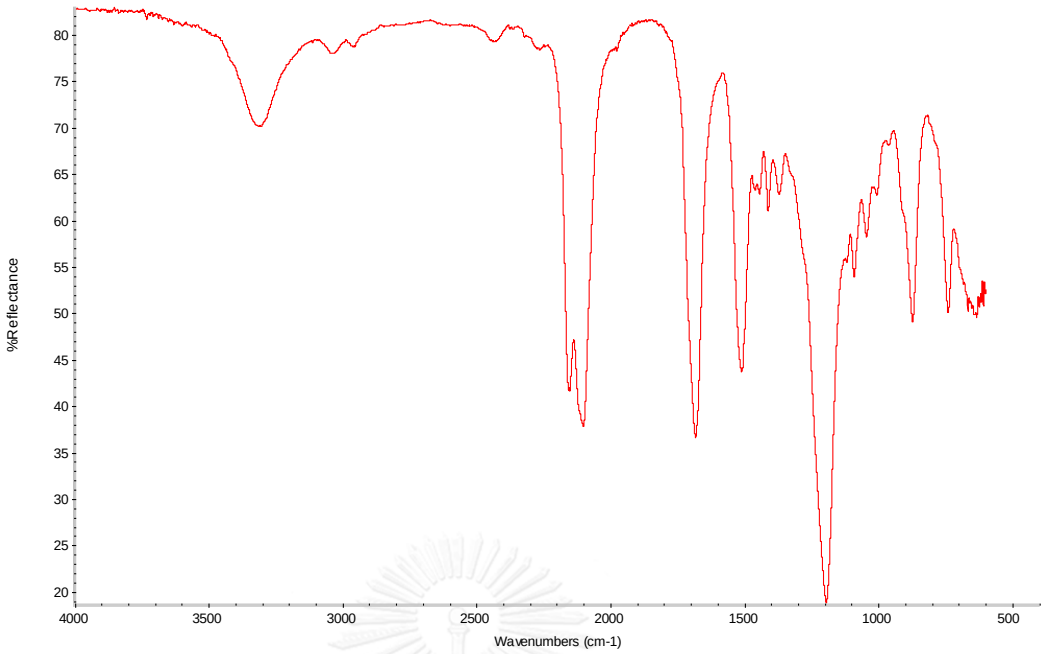


Figure A.7 IR spectrum of azidoacetylazide **(3)**

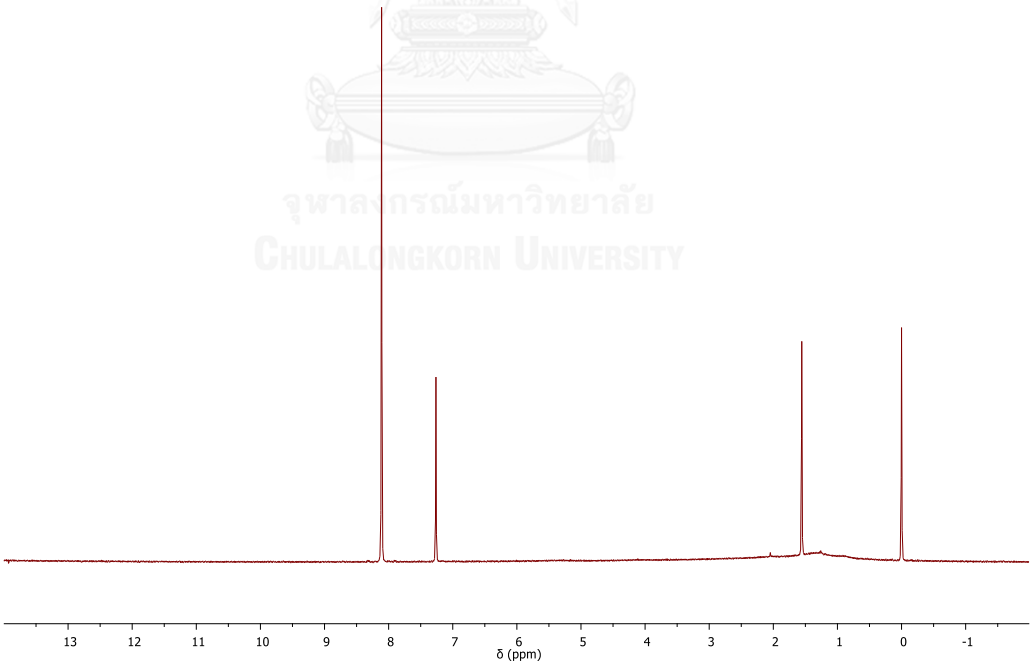


Figure A.8 ^{1}H NMR ($CDCl_3$) spectrum of terephthaloyl azide **(4)**

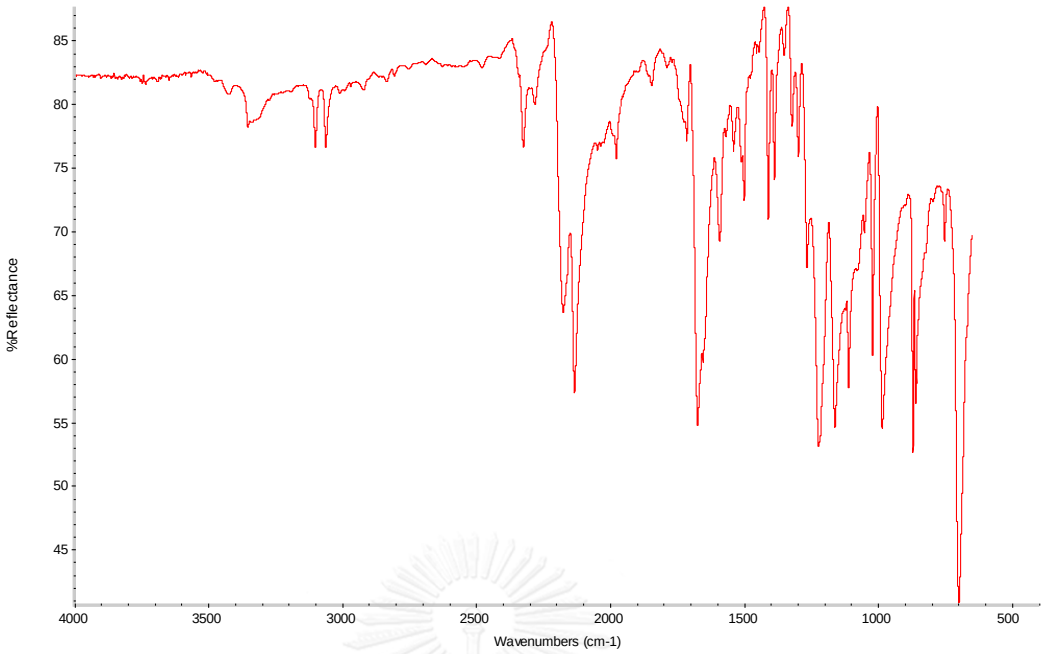


Figure A.9 IR spectrum of terephthaloyl azide **(4)**

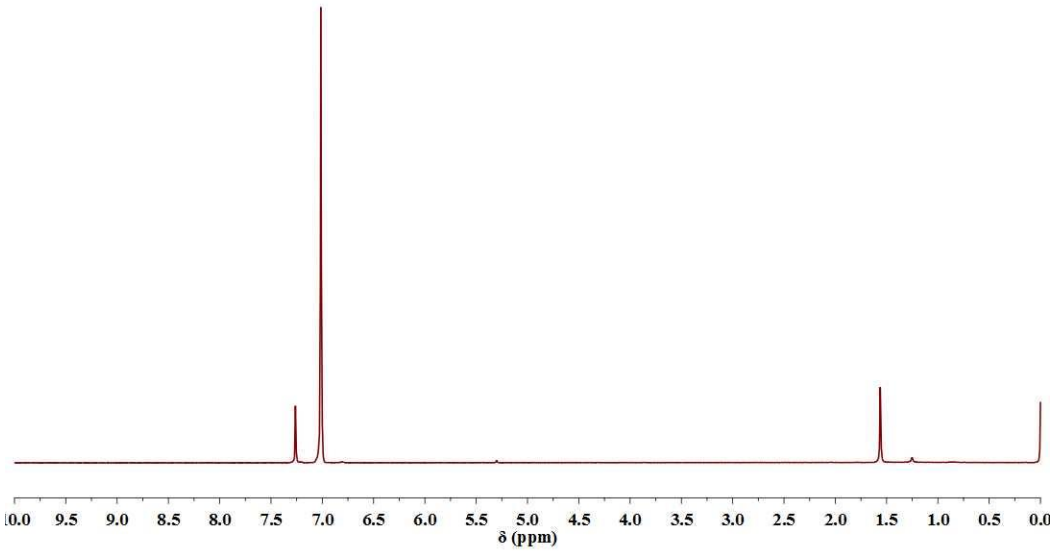


Figure A.10 ^{1}H NMR ($CDCl_3$) spectrum of 1,4-diazidobenzene **(5)**

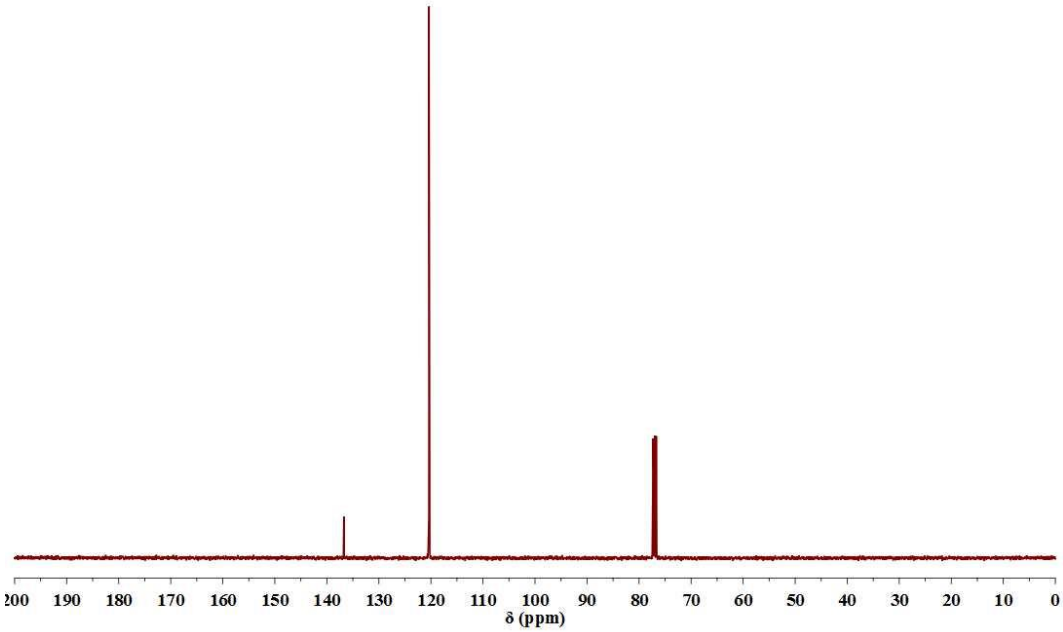


Figure A.11 ^{13}C NMR ($CDCl_3$) spectrum of 1,4-diazidobenzene **(5)**

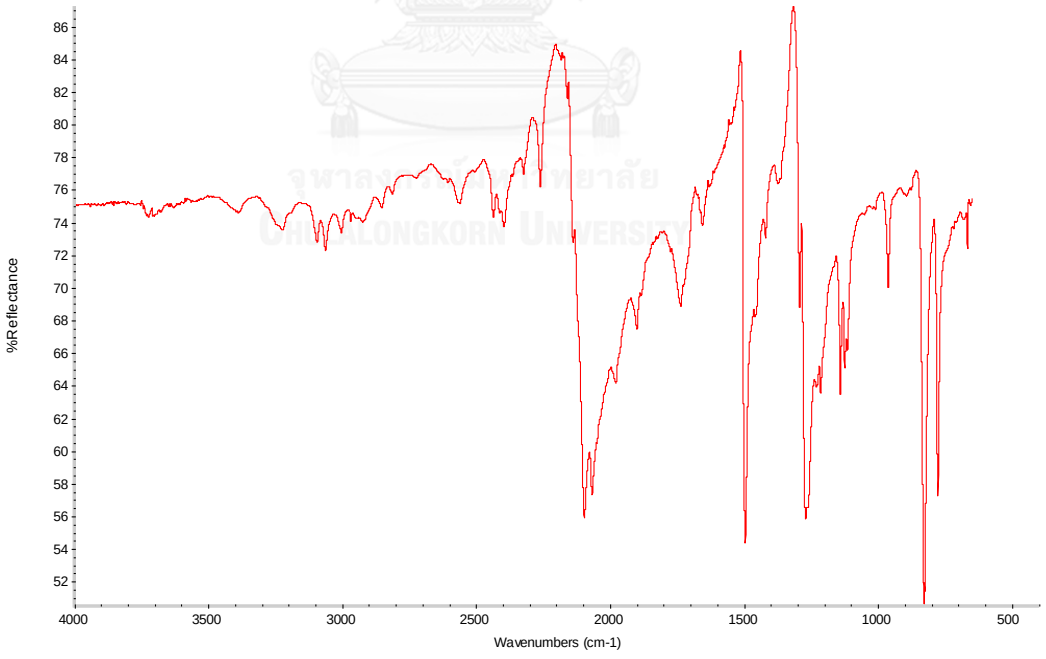


Figure A.12 IR spectrum of 1,4-diazidobenzene **(5)**

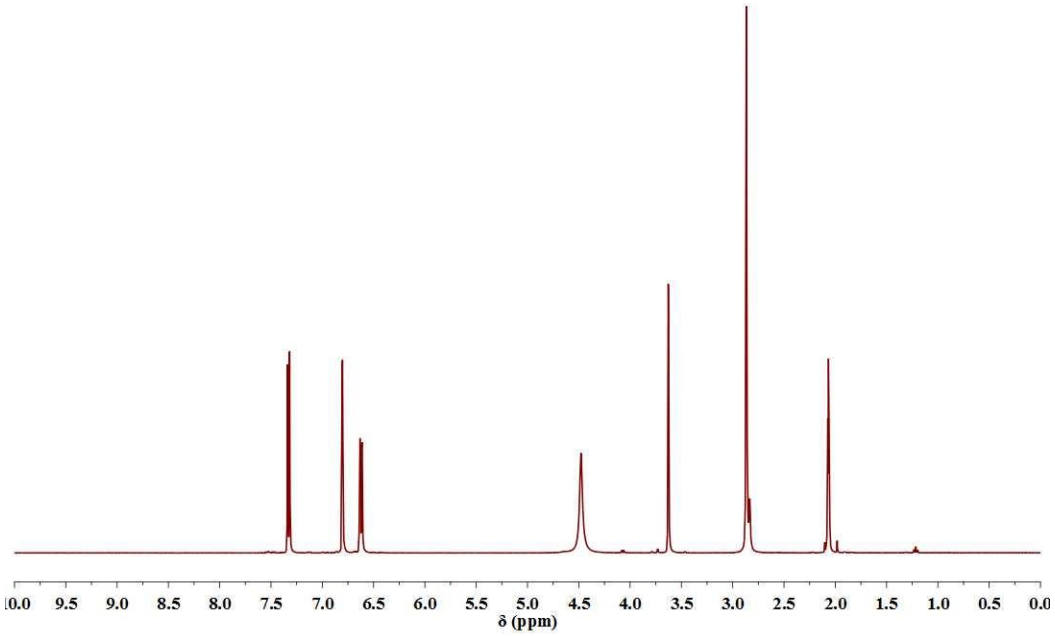


Figure A.13 ^{1}H NMR (acetone-d_6) spectrum of 2,7-diaminofluorene **(6)**

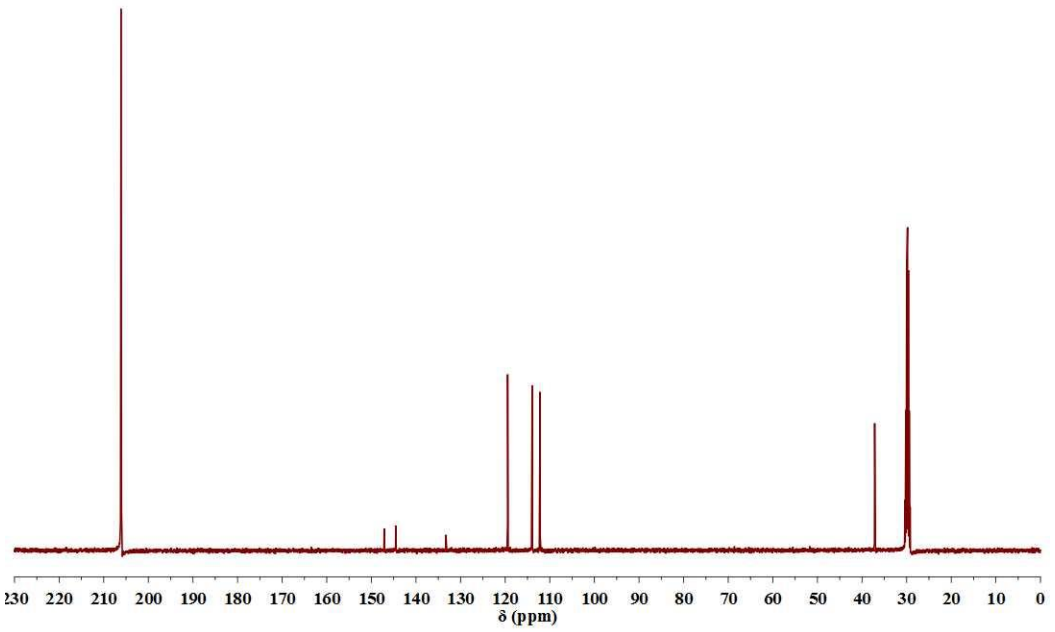


Figure A.14 ^{13}C NMR (acetone-d_6) spectrum of 2,7-diaminofluorene **(6)**

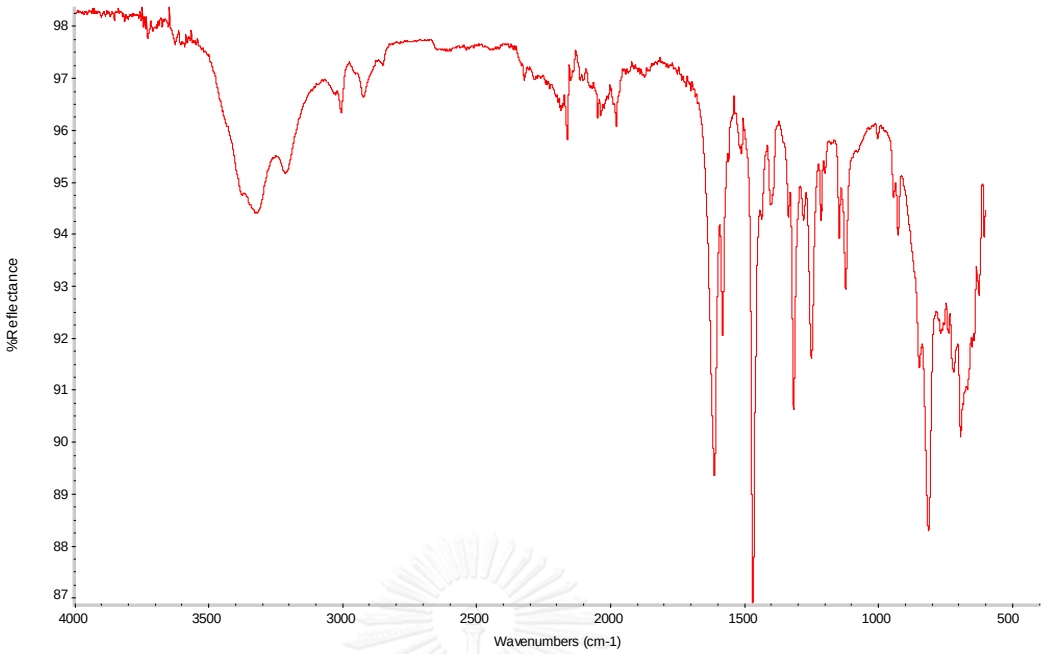


Figure A.15 IR spectrum of 2,7-diaminofluorene **(6)**

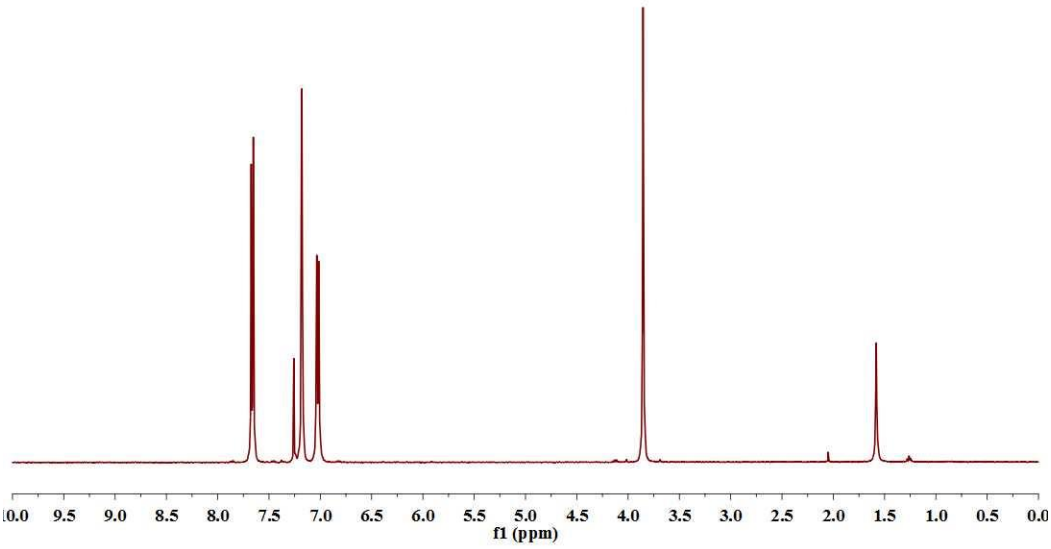


Figure A.16 ^{1}H NMR ($CDCl_3$) spectrum of 2,7-diazidofluorene **(7)**

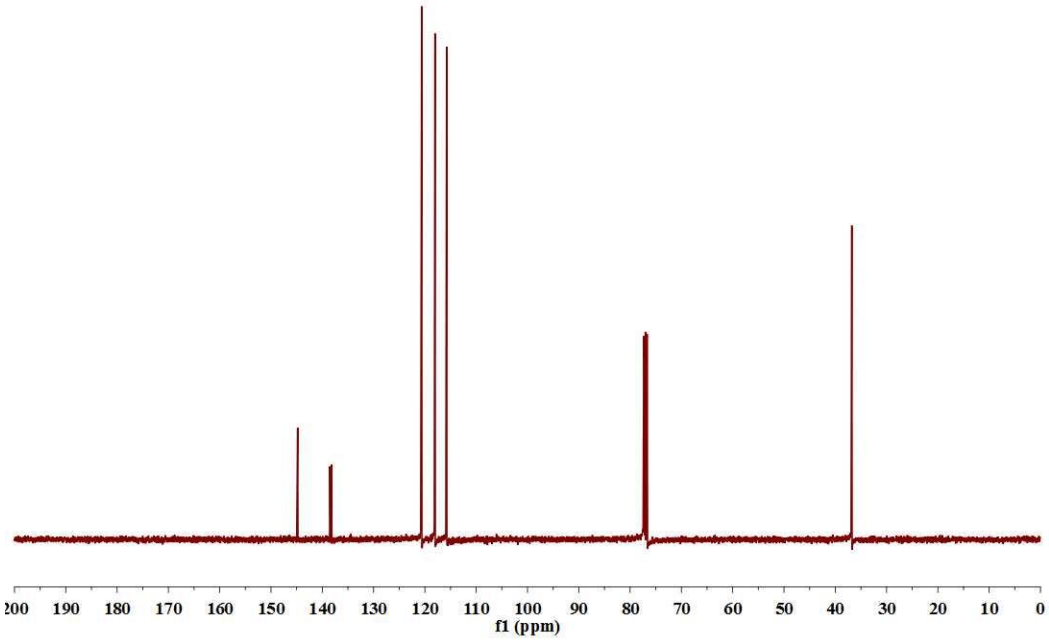


Figure A.17 ^{13}C NMR ($CDCl_3$) spectrum of 2,7-diazidofluorene **(7)**

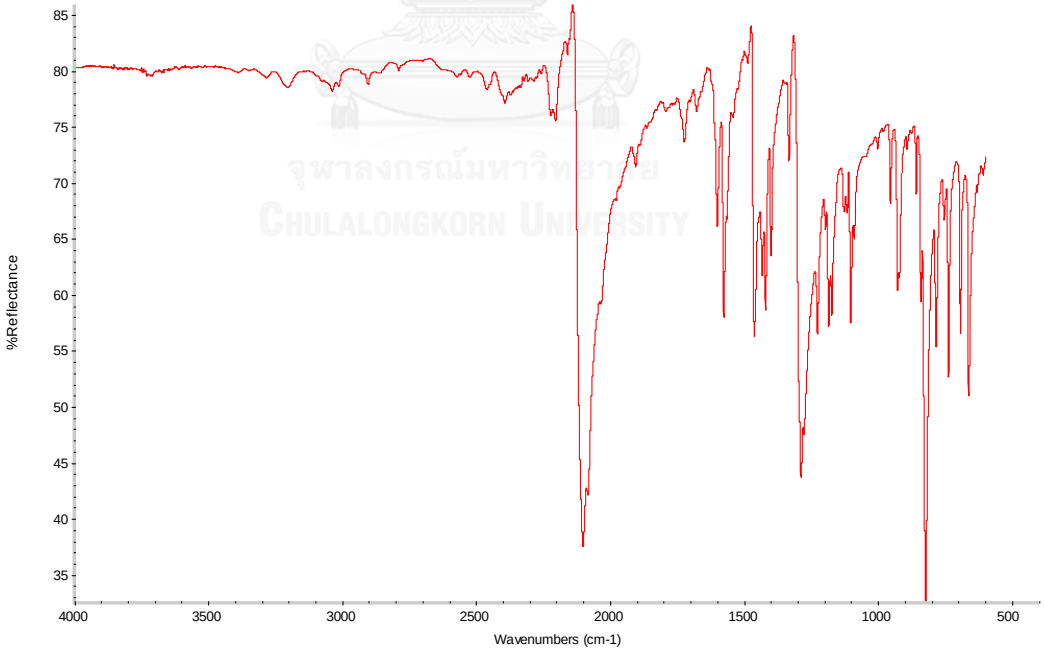


Figure A.18 IR spectrum of 2,7-diazidofluorene **(7)**

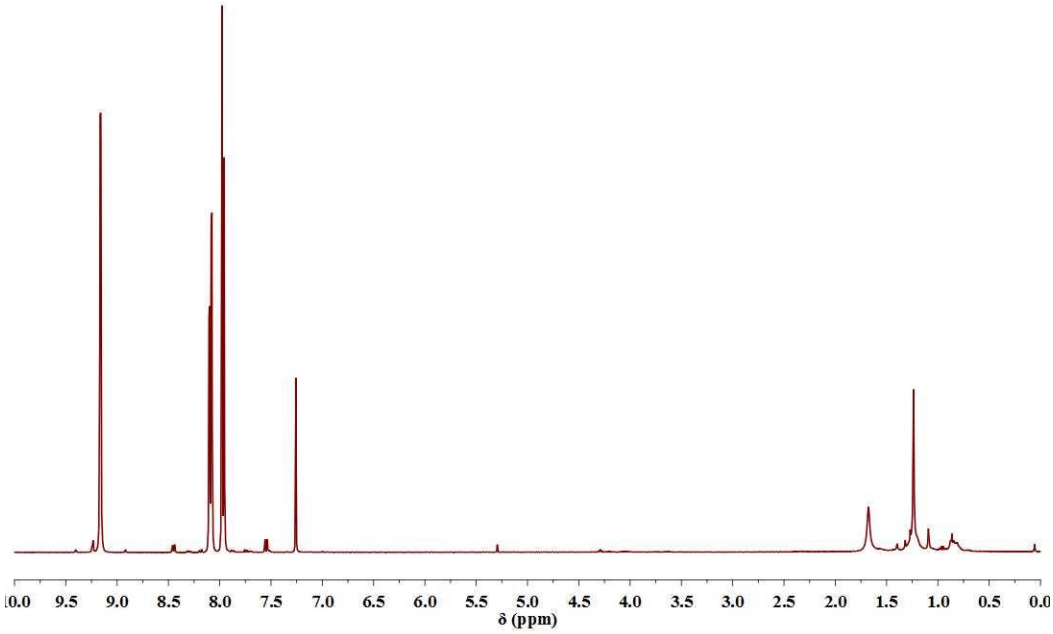


Figure A.19 ^{1}H NMR ($CDCl_3$) spectrum of 2-iodo-5-nitropyridine **(8)**

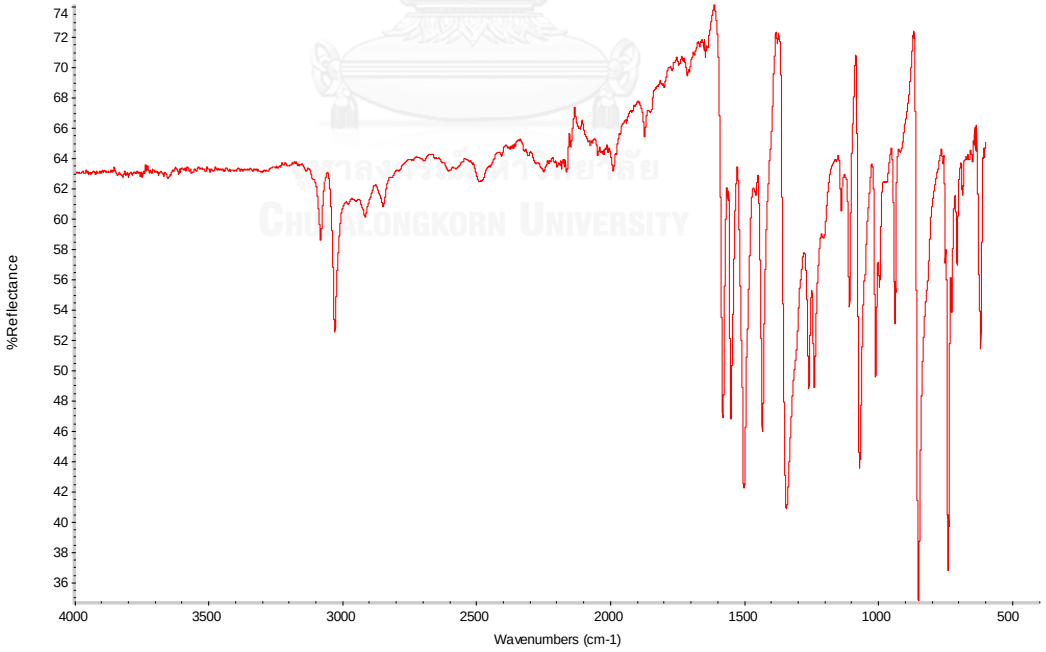


Figure A.20 IR spectrum of 2-iodo-5-nitropyridine **(8)**

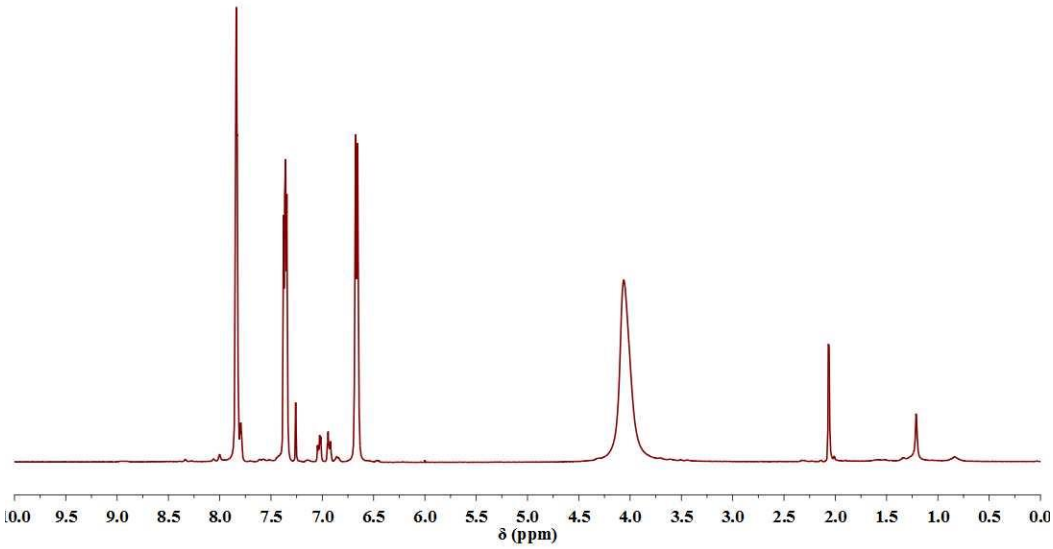


Figure A.21 ^{1}H NMR ($CDCl_3$) spectrum of 5-amino-2-iodopyridine **(9)**

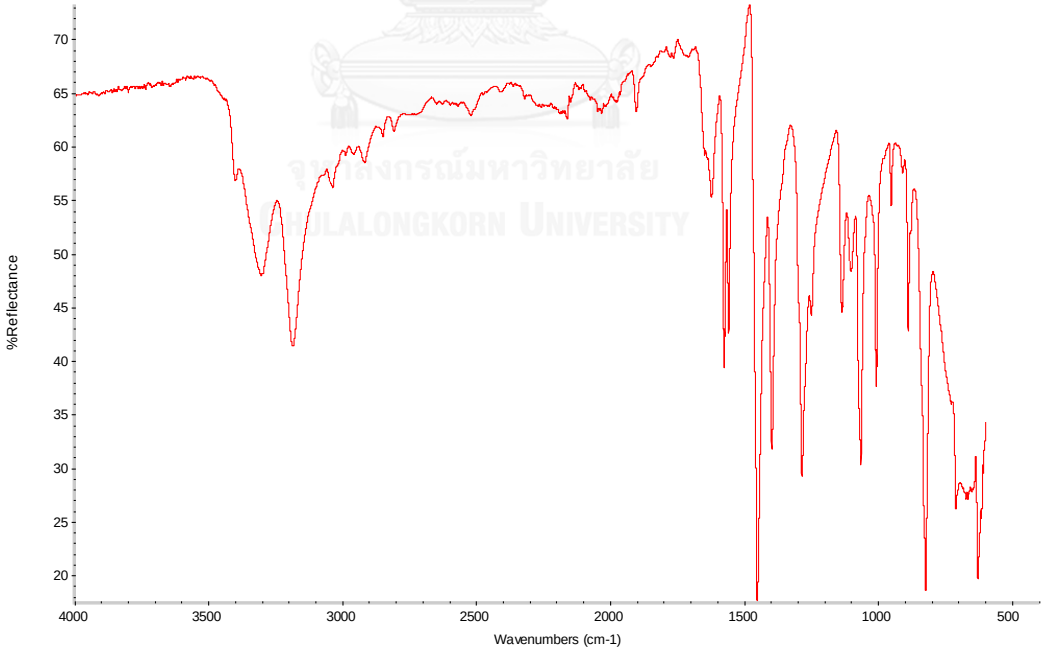


Figure A.22 IR spectrum of 5-amino-2-iodopyridine **(9)**

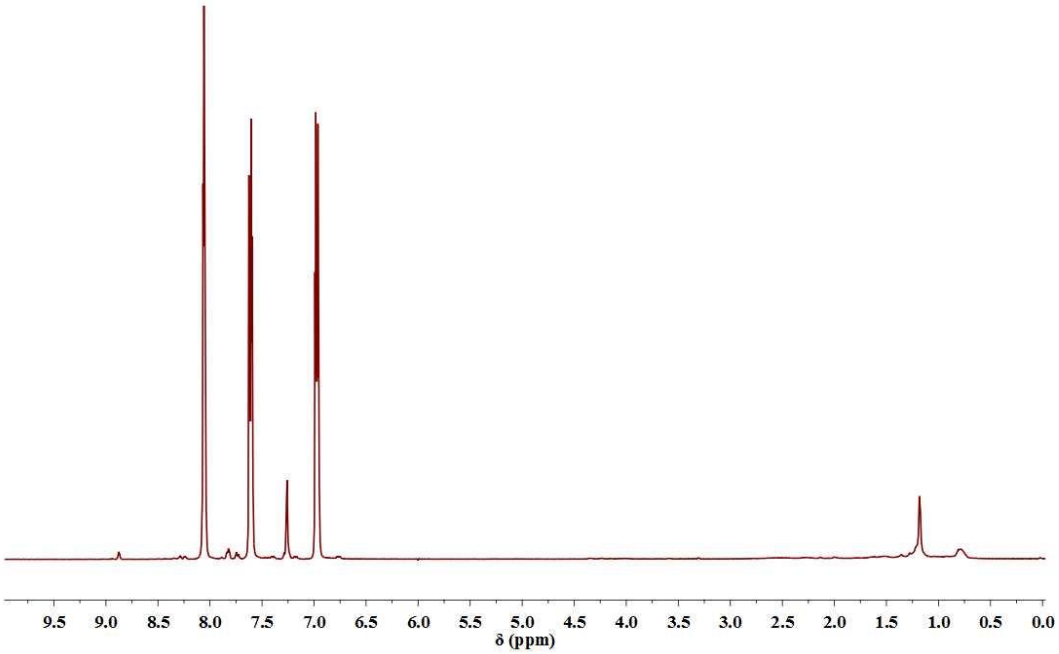


Figure A.23 ^{1}H NMR ($CDCl_3$) spectrum of 5-azido-2-iodopyridine **(10)**

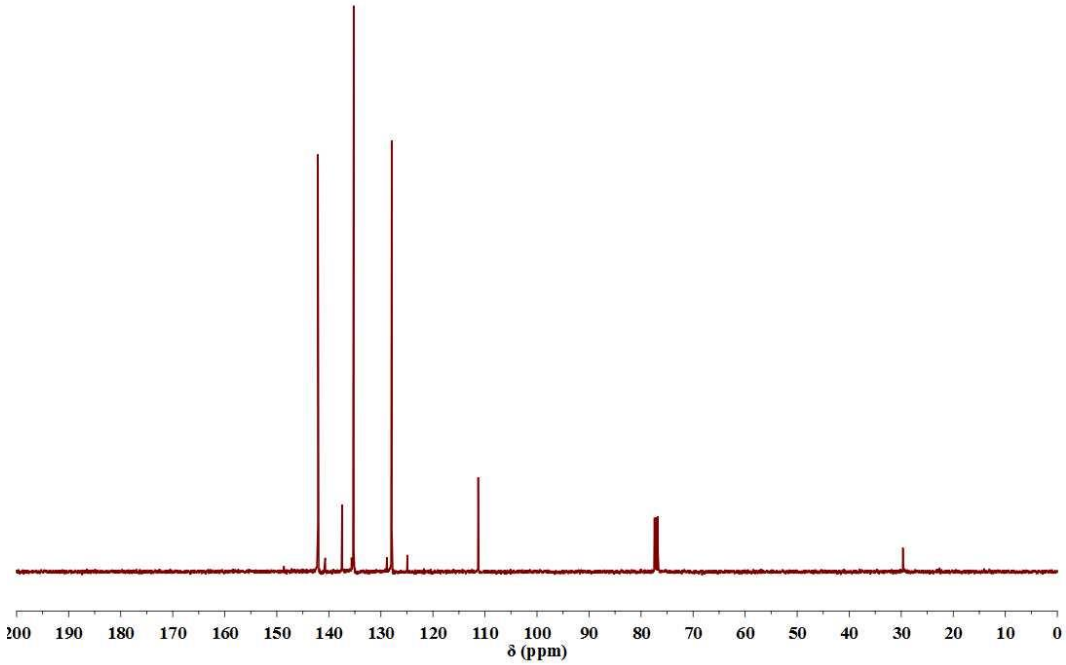


Figure A.24 ^{13}C NMR ($CDCl_3$) spectrum of 5-azido-2-iodopyridine **(10)**

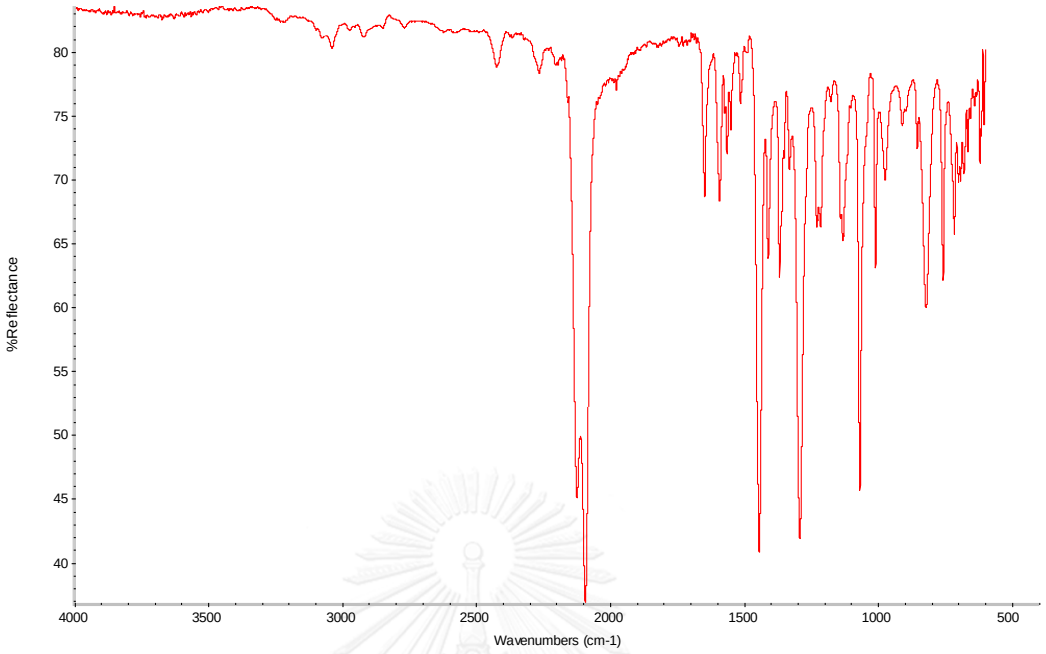


Figure A.25 IR spectrum of 5-azido-2-iodopyridine **(10)**

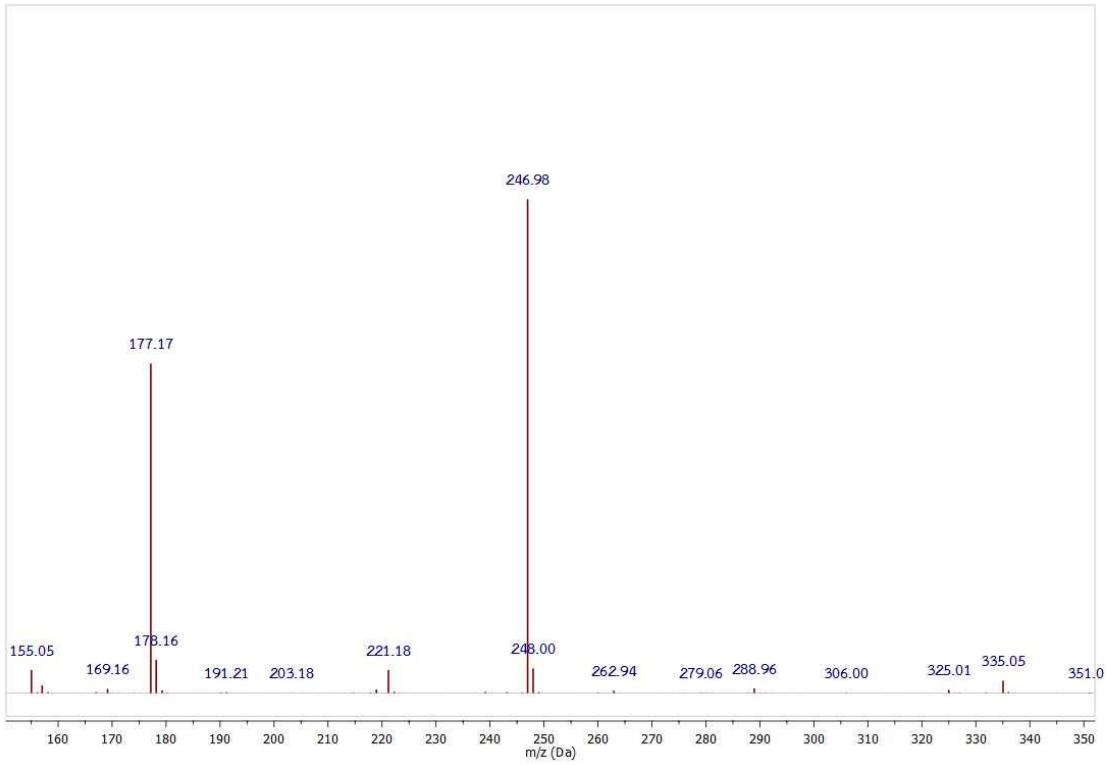


Figure A.26 Maa spectrum of 5-azido-2-iodopyridine **(10)**

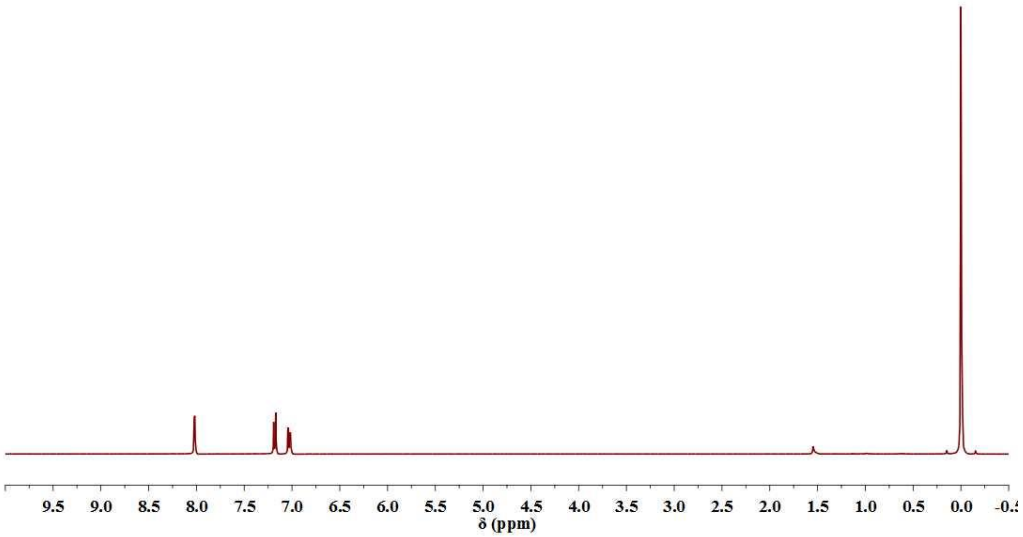


Figure A.27 ^{1}H NMR ($CDCl_3$) spectrum of 5-azido-2-((trimethylsilyl)ethynyl)pyridine **(11)**

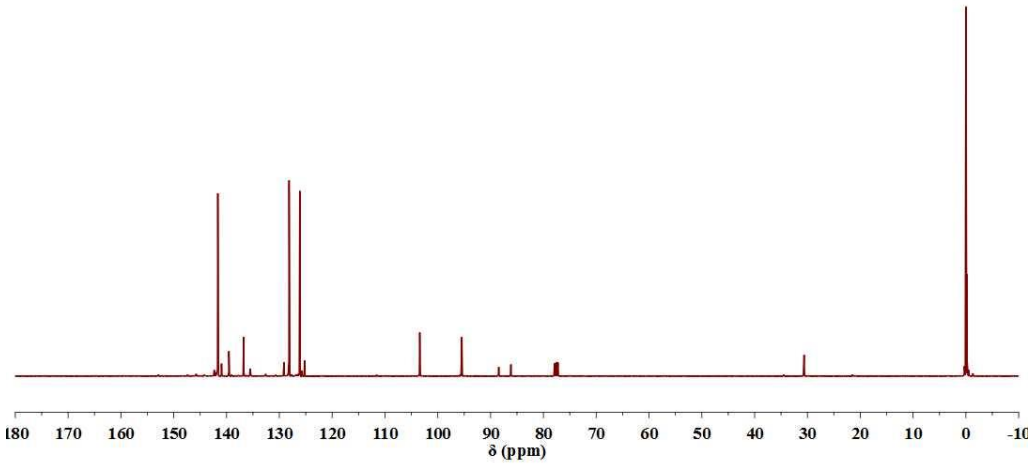


Figure A.28 ^{13}C NMR ($CDCl_3$) spectrum of 5-azido-2-((trimethylsilyl)ethynyl)pyridine **(11)**

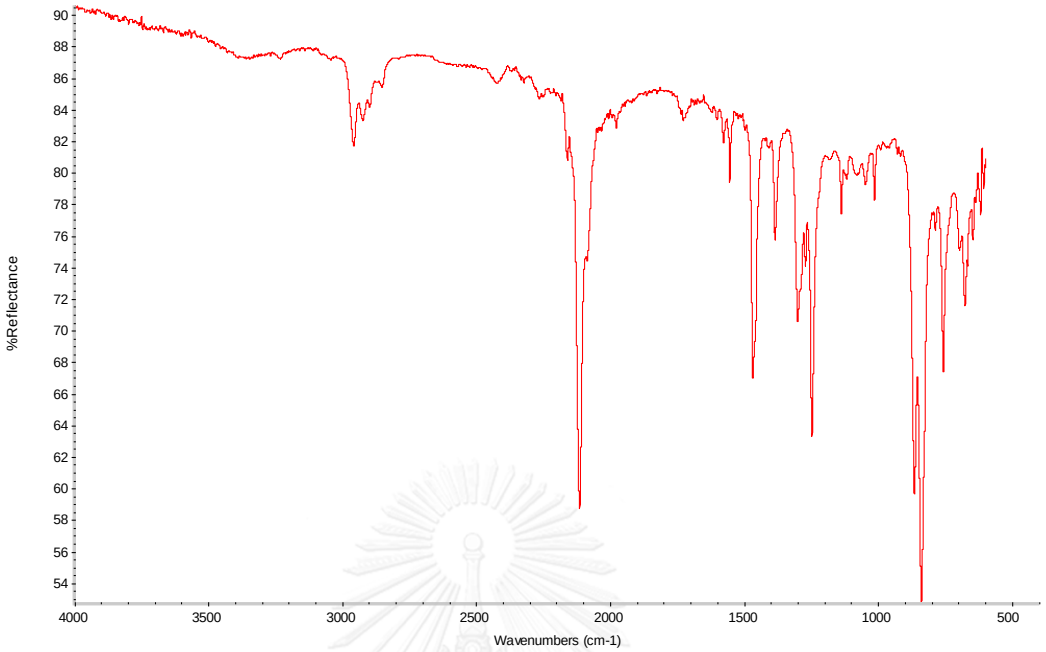


Figure A.29 IR spectrum of 5-azido-2-((trimethylsilyl)ethynyl)pyridine **(11)**

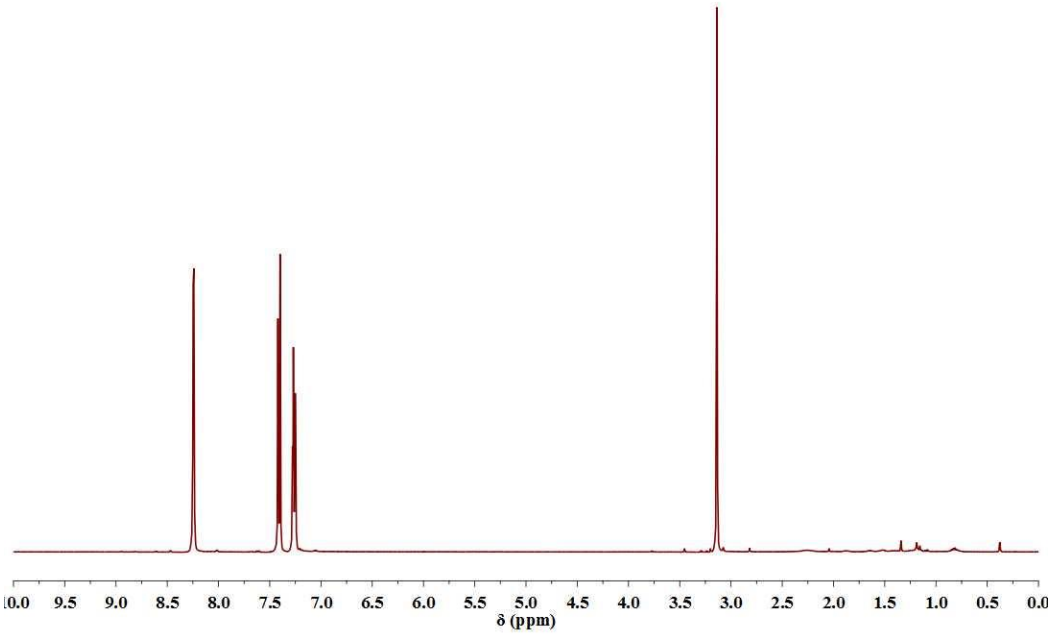


Figure A.30 ^{1}H NMR ($CDCl_3$) spectrum of 5-azido-2-ethynylpyridine **(12)**

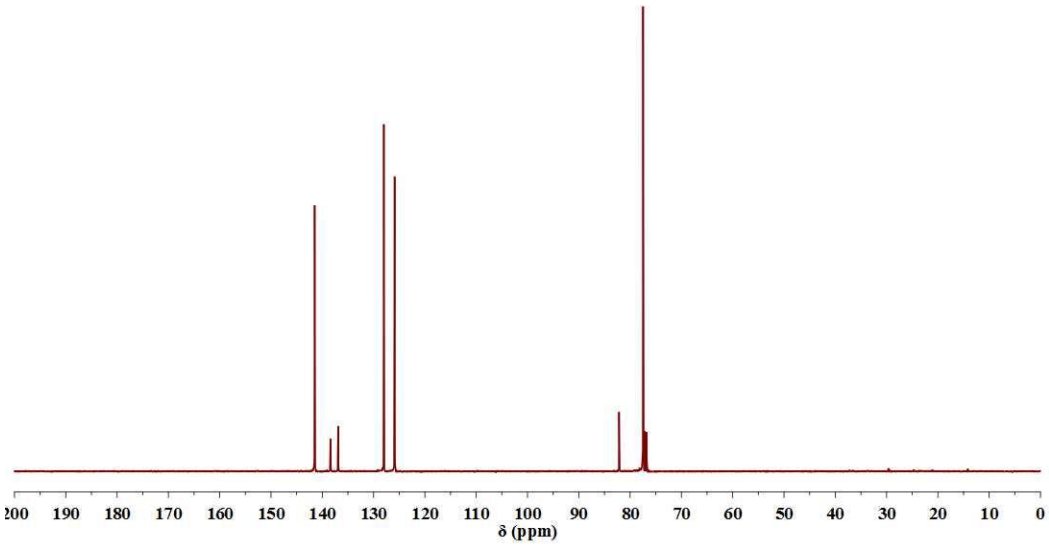


Figure A.31 ^{13}C NMR ($CDCl_3$) spectrum of 5-azido-2-ethynylpyridine **(12)**

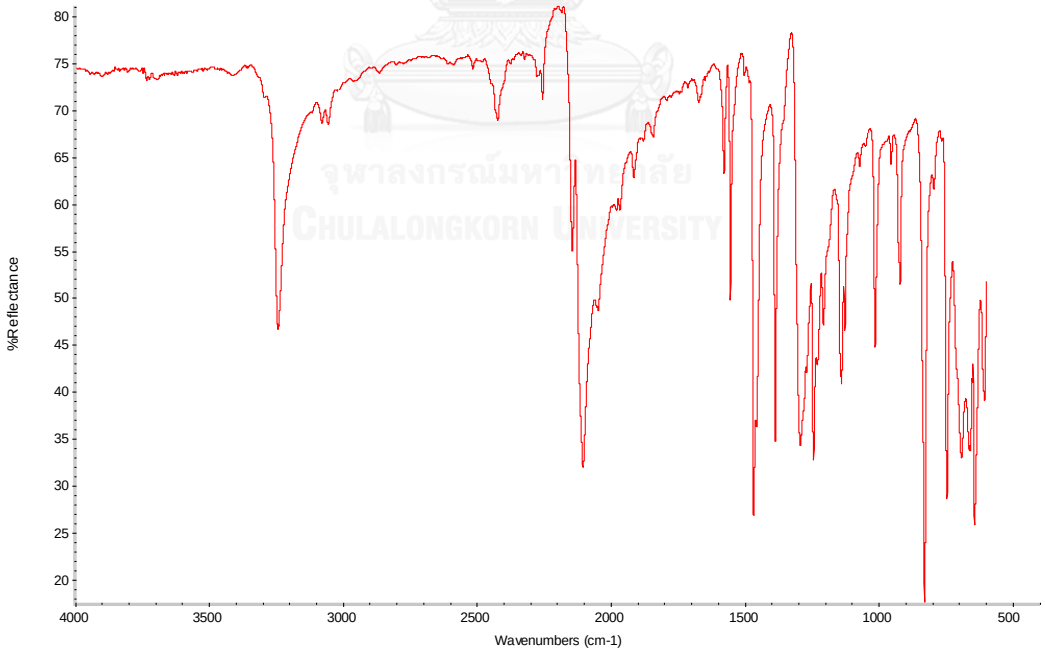


Figure A.32 IR spectrum of 5-azido-2-ethynylpyridine **(12)**

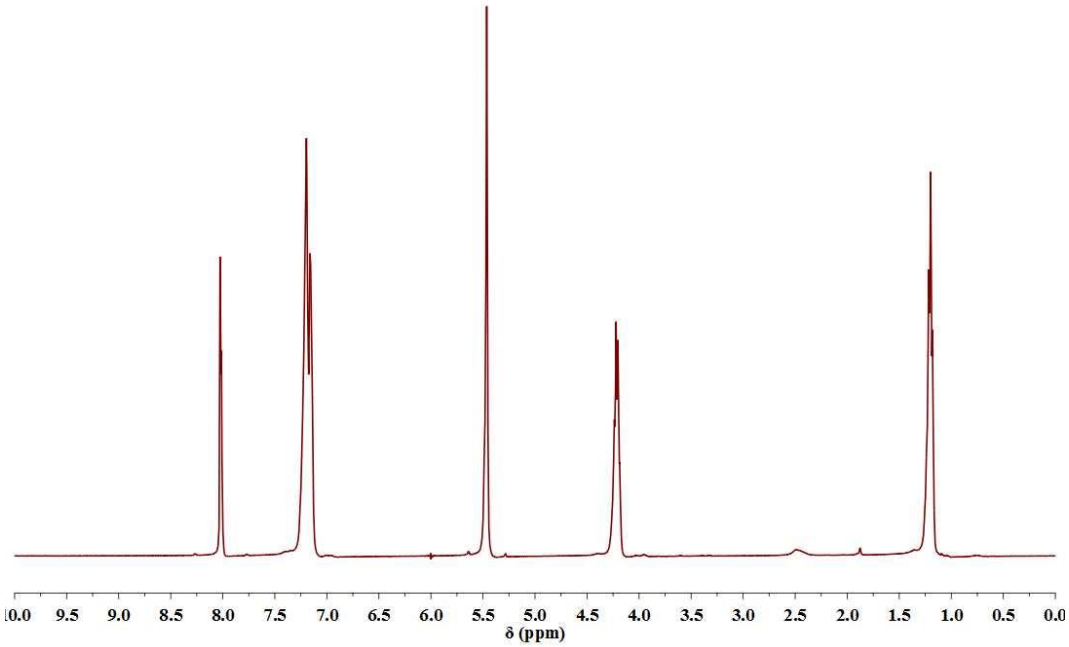


Figure A.33 ^{1}H NMR ($CDCl_3$) spectrum of ethyl-1-benzyltriazole-4-carboxylate **(13)**

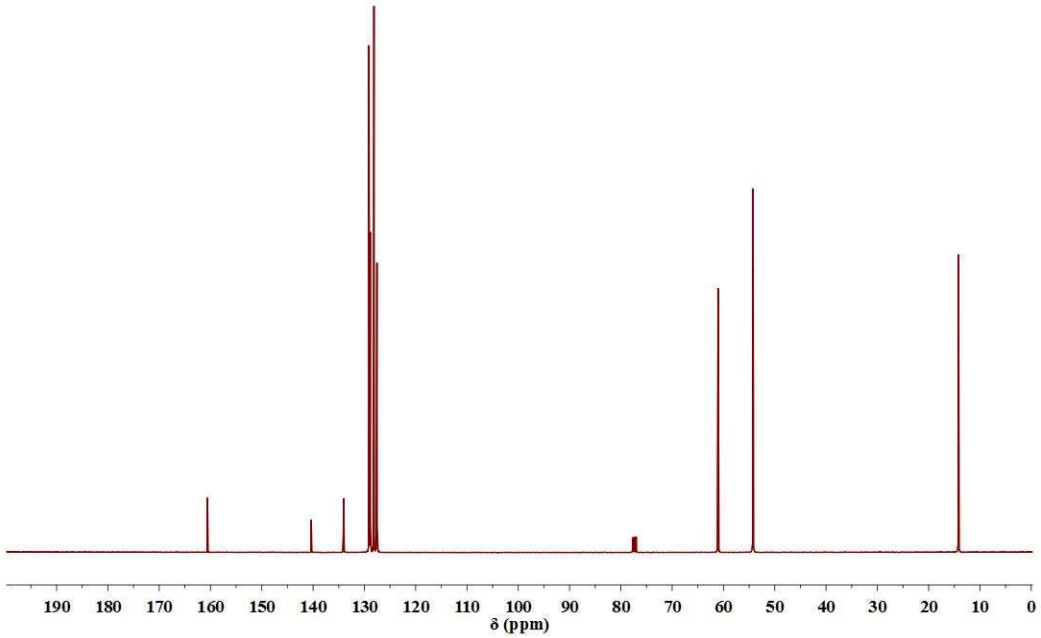


Figure A.34 ^{13}C NMR ($CDCl_3$) spectrum of ethyl-1-benzyltriazole-4-carboxylate **(13)**

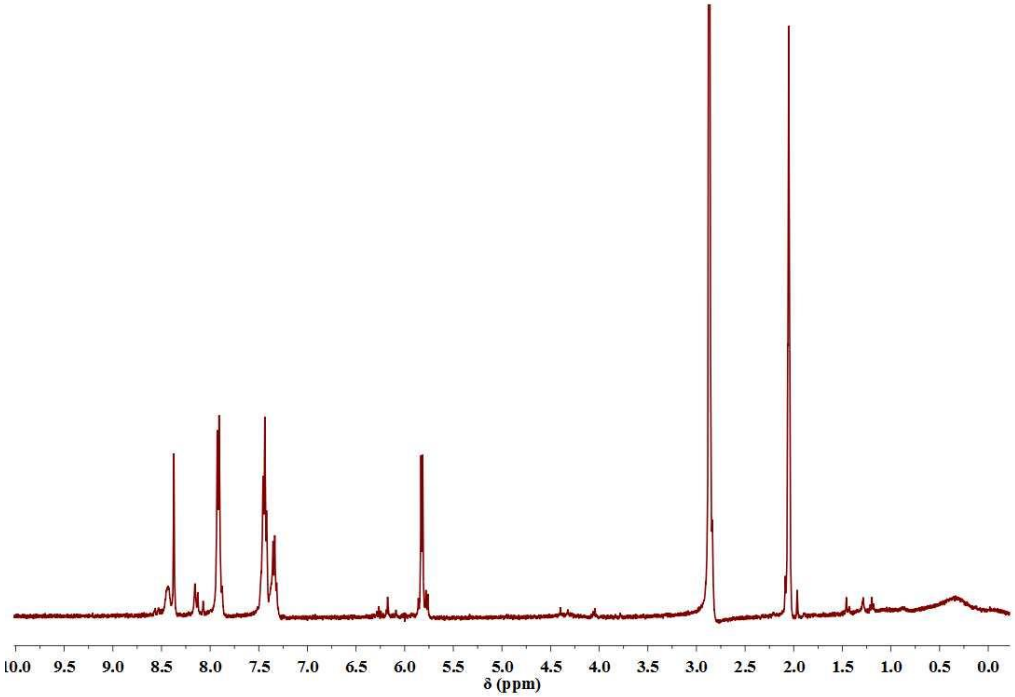


Figure A.35 ^{1}H NMR (acetone-d_6) spectrum of 1,2-bis[(4-phenyl)-triazol-1-yl]-ethanone **(14)**

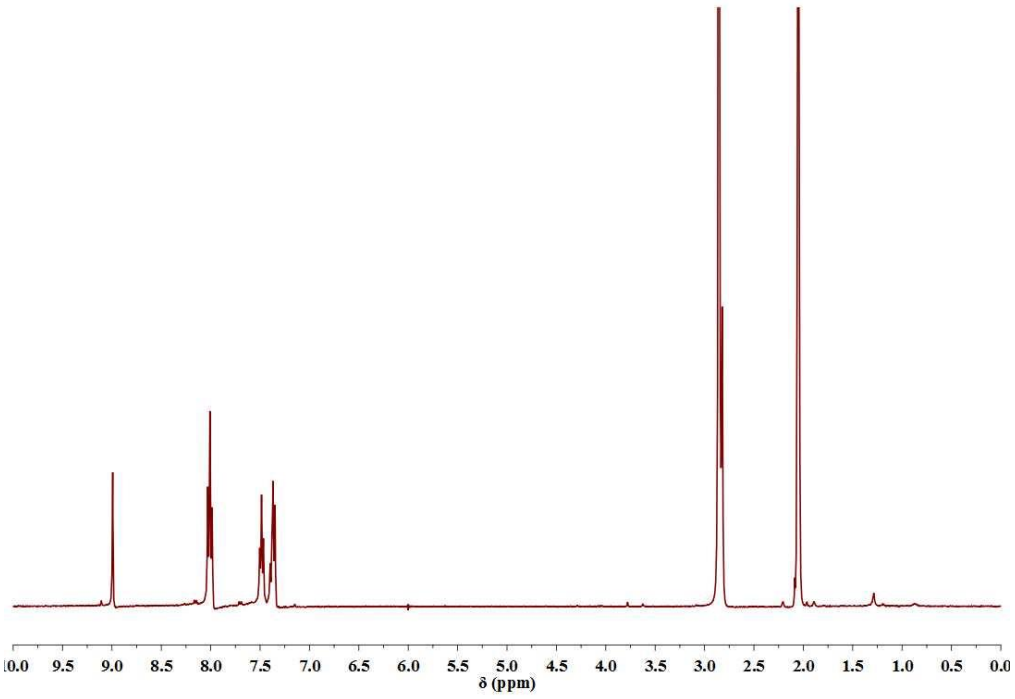


Figure A.36 ^{1}H NMR (acetone-d_6) spectrum of 1-(4-azidophenyl)-4-phenyltriazole **(15)**

Figure A.37 IR spectrum of 1-(4-azidophenyl)-4-phenyltriazole **(15)**

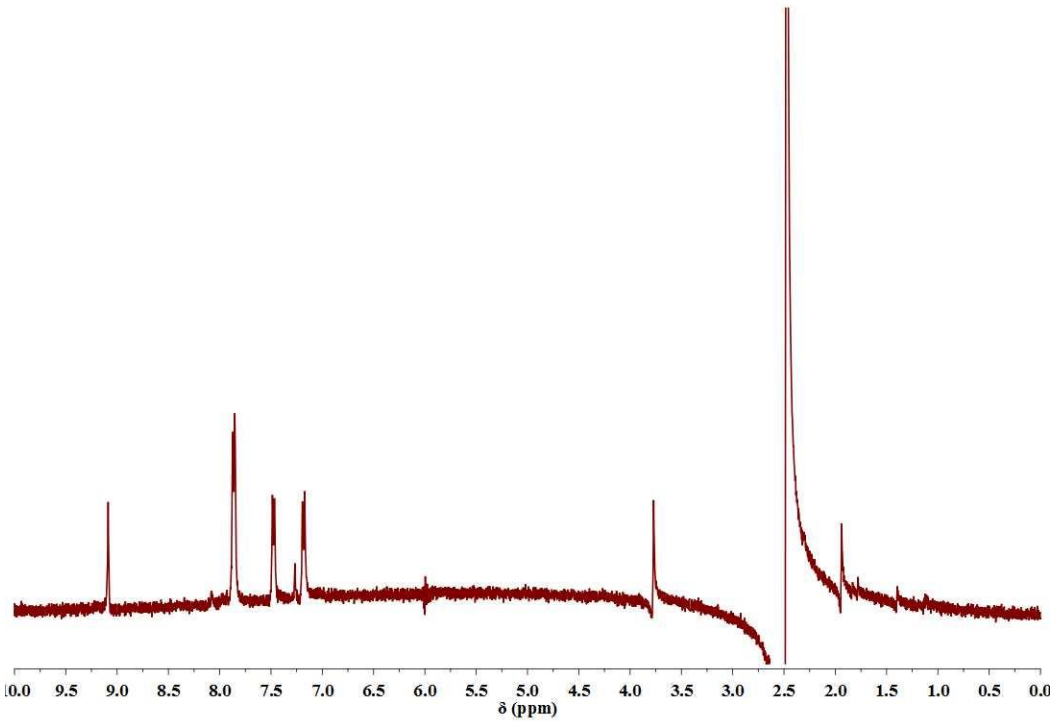


Figure A.38 ^{1}H NMR (DMSO-d_6) spectrum of polymer **P1**

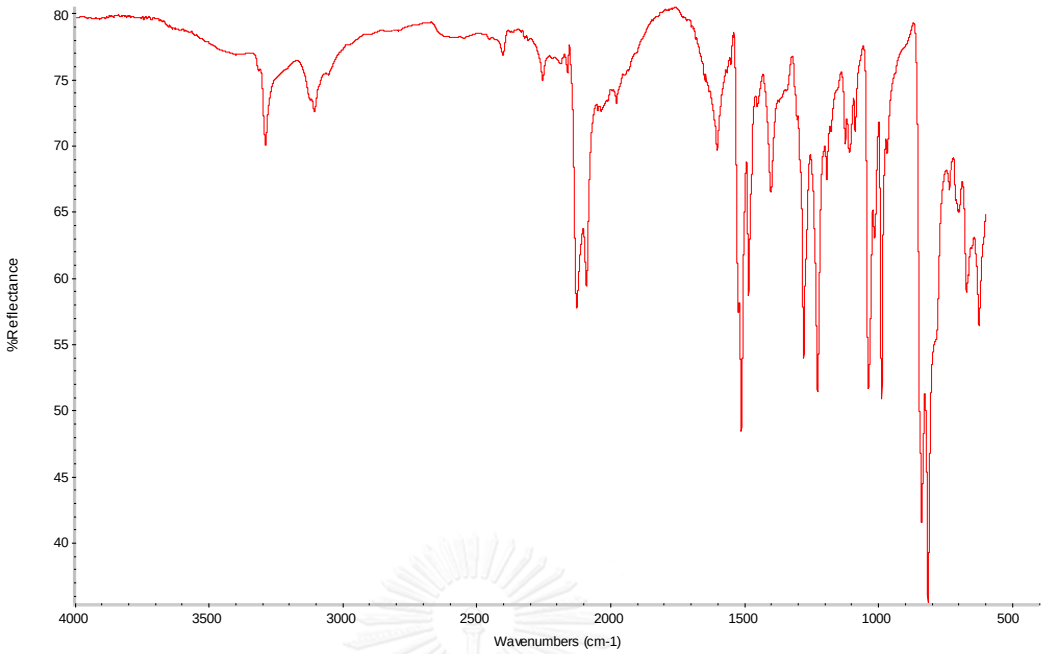


Figure A.39 IR spectrum of polymer **P1**

Figure A.40 Solid UV-visible spectra of polymer **P1**

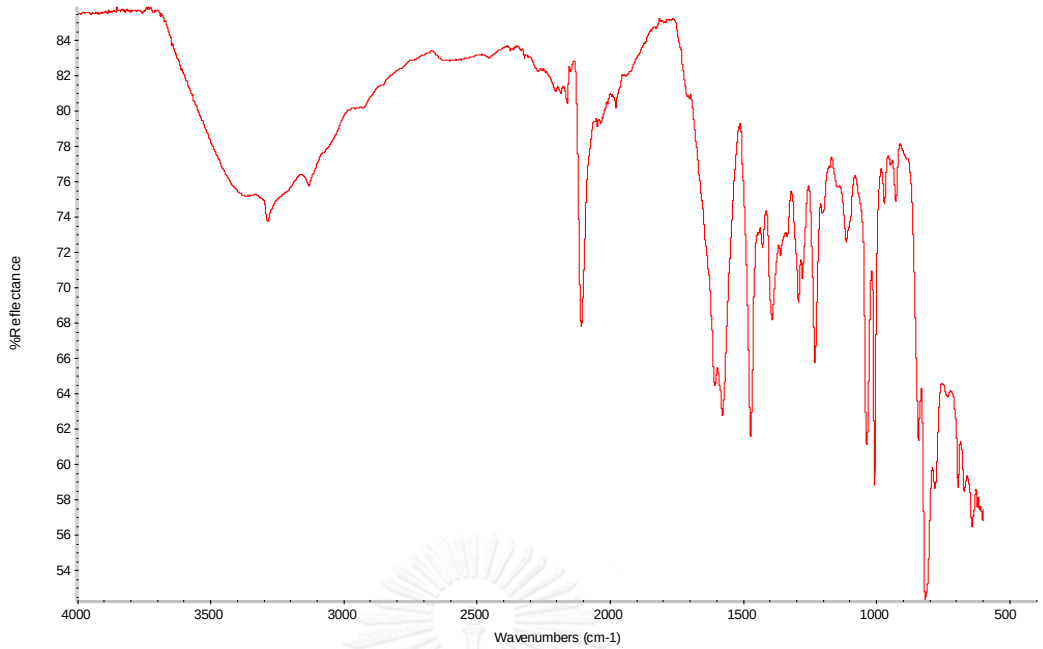


Figure A.41 IR spectrum of polymer **P2**

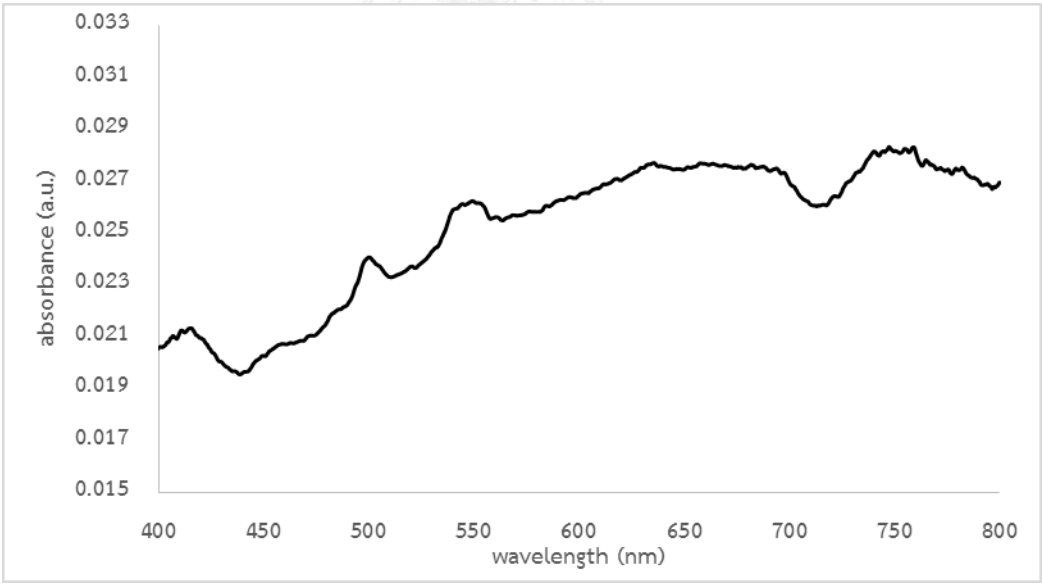


Figure A.42 Solid UV-visible spectra of polymer **P2**

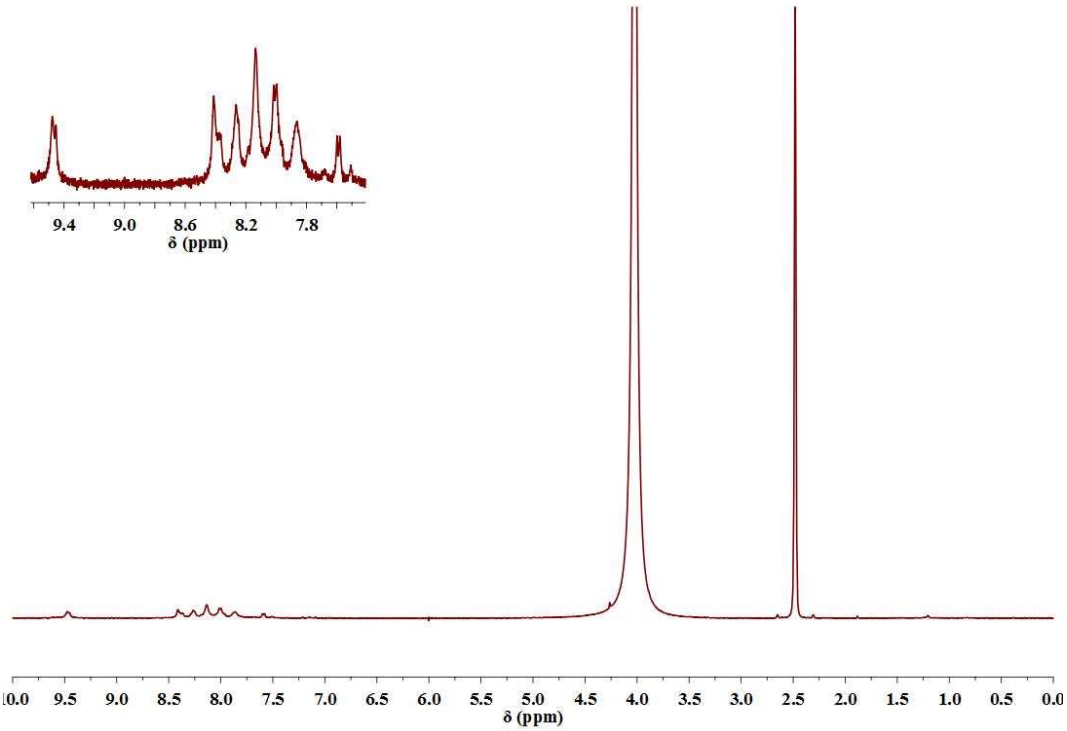


Figure A.43 ^{1}H NMR (DMSO-d_6) spectrum of polymer **P3**

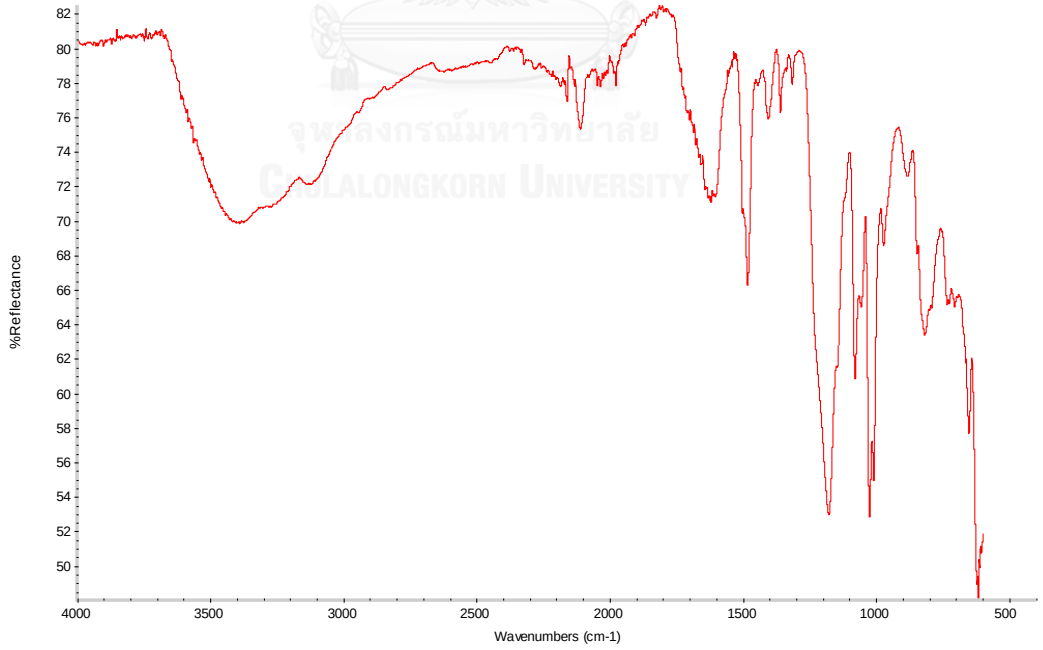


Figure A.44 IR spectrum of polymer **P3**

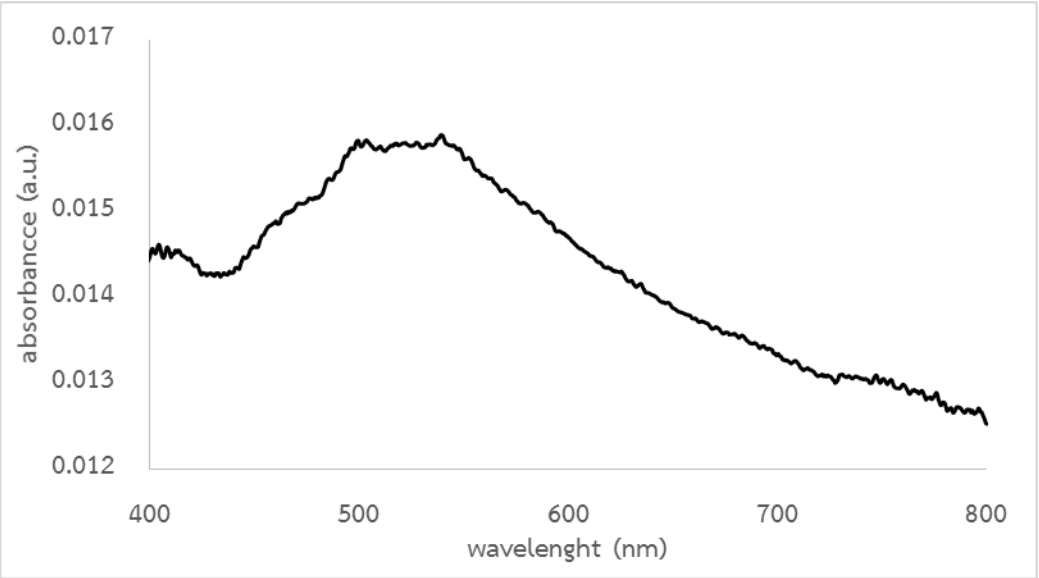


Figure A.45 Solid UV-visible spectra of polymer **P3**

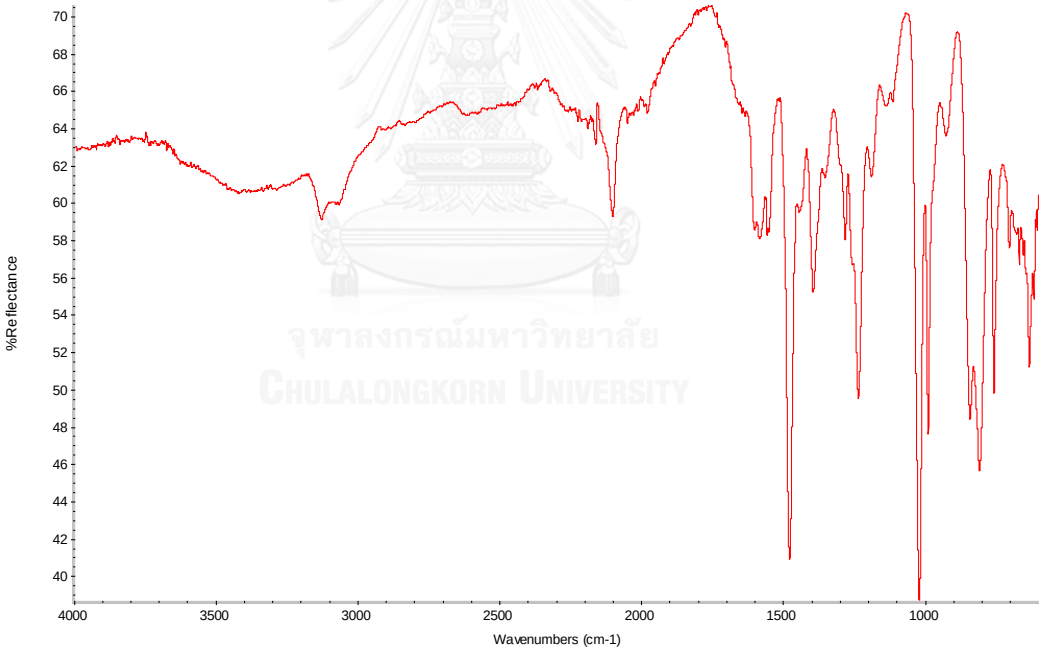


Figure A.46 IR spectrum of polymer **P4**

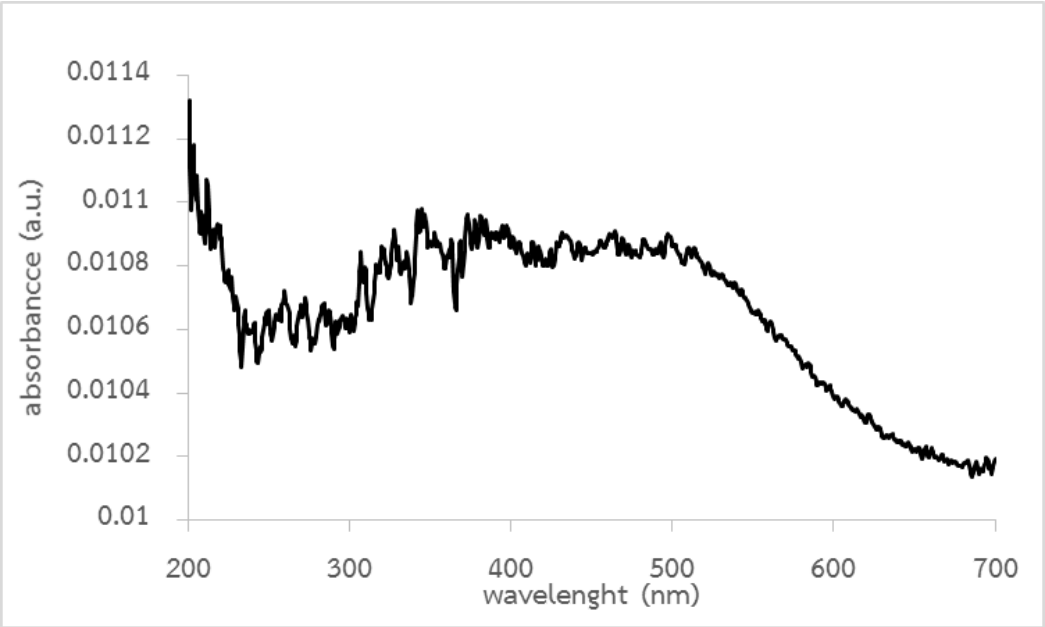


Figure A.47 Solid UV-visible spectra of polymer **P4**

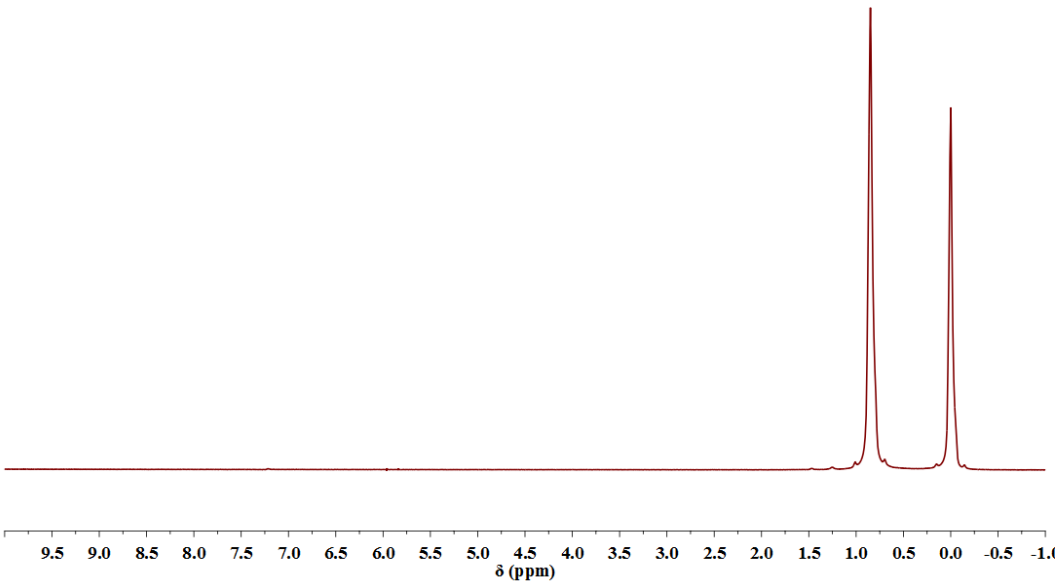


Figure A.48 ^{1}H NMR ($CDCl_3$) spectrum of compound **16**

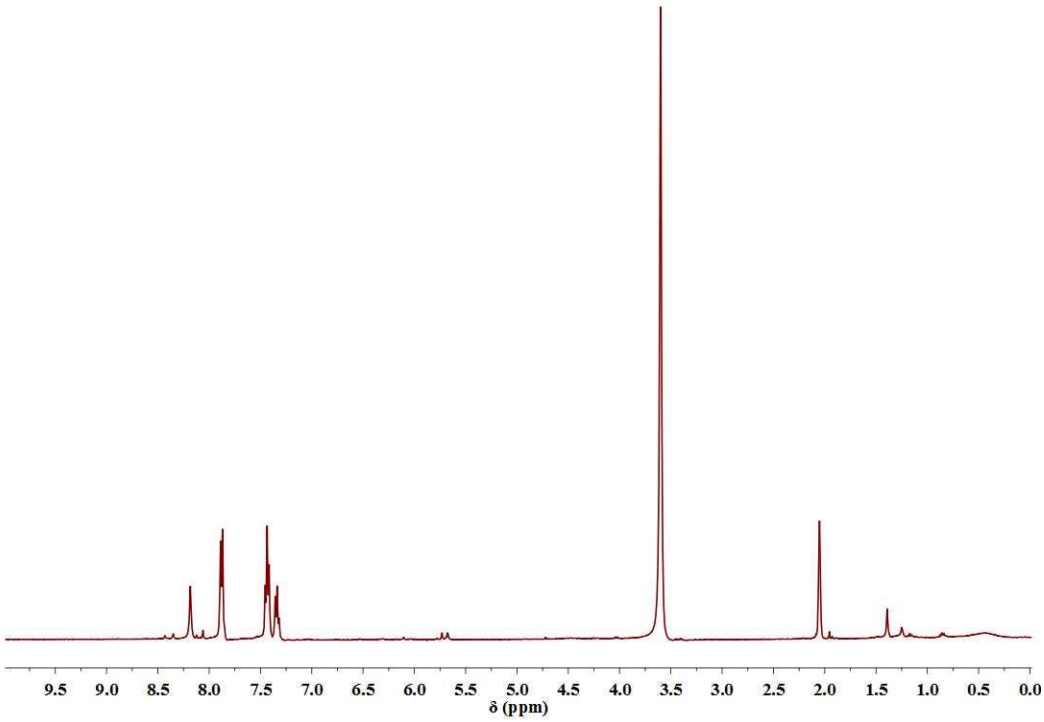


Figure A.49 ^{1}H NMR (acetone-d_6) spectrum of hydrolysis of compound **14**

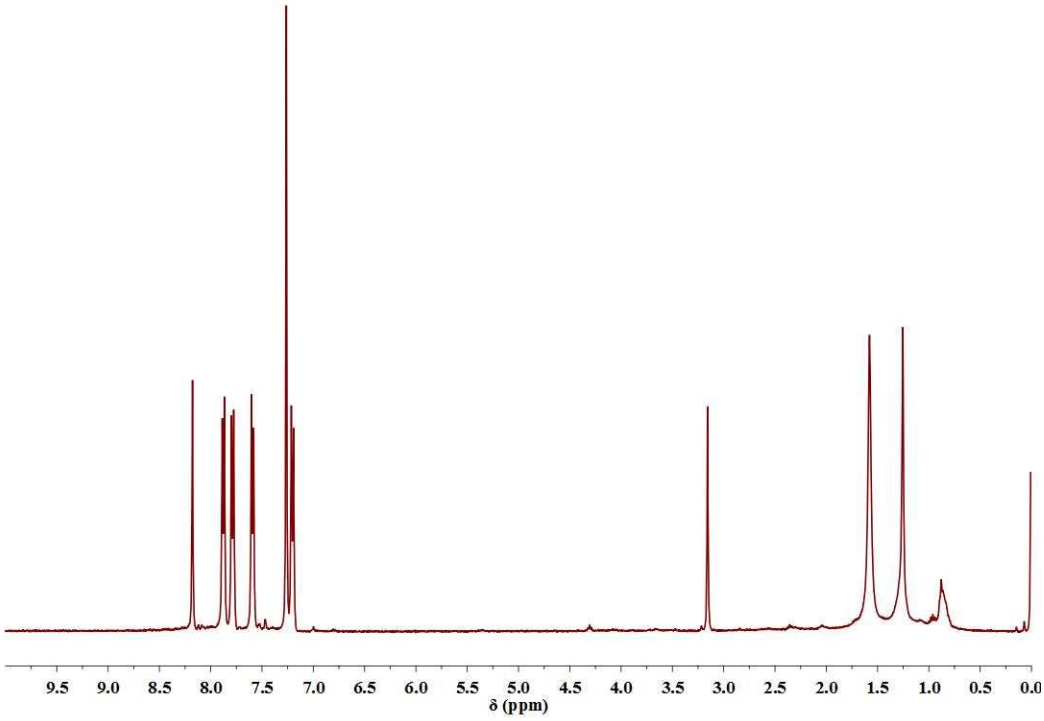


Figure A.50 ^{1}H NMR ($CDCl_3$) spectrum of compound **18**

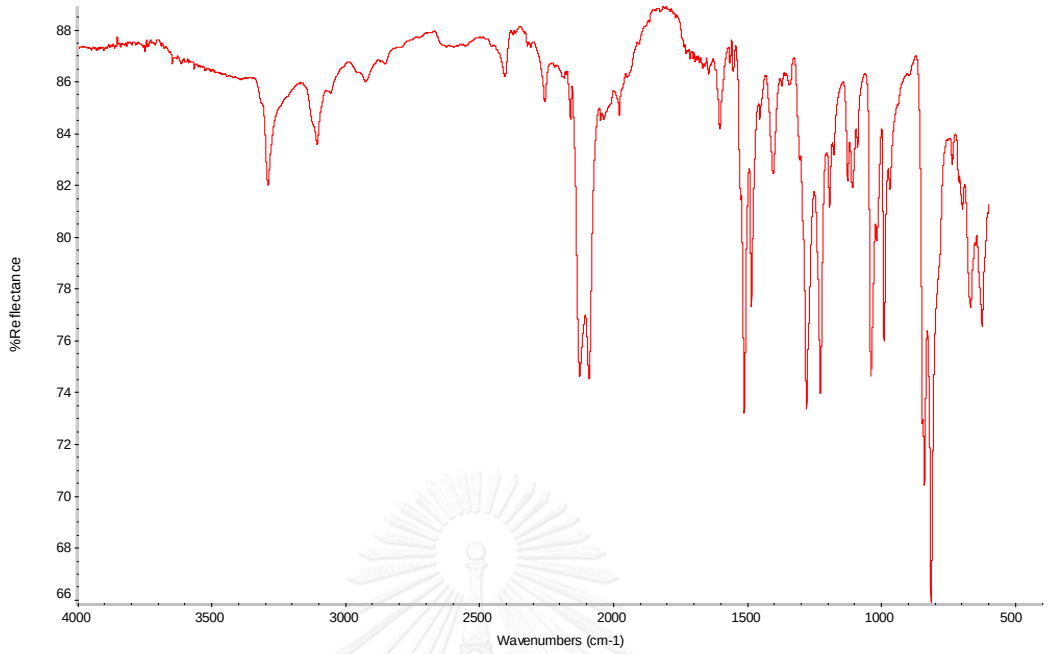


Figure A.51 IR spectrum of compound **18**

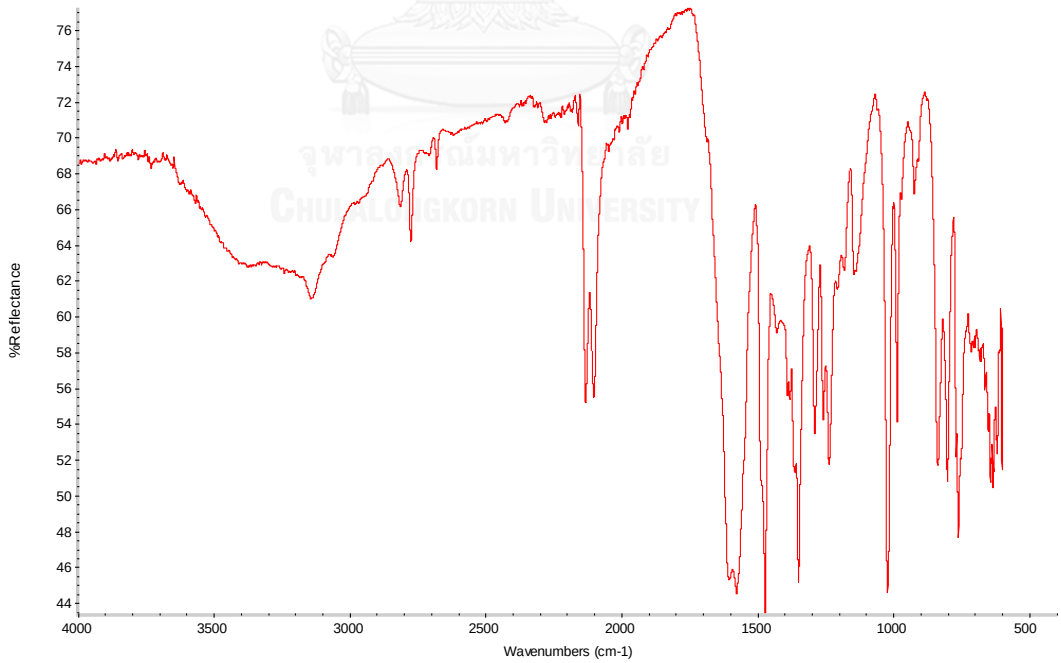


Figure A.52 IR spectrum of oligomer of polymer **P4**

VITA

Mr. Pongpat Limjunyawong was born on November 2, 1989 in Bangkok, Thailand. He received a Bachelor's degree of Science from Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand, in 2012. He was admitted to a Master's Degree Program in Chemistry, Faculty of Science, Chulalongkorn University and completed the program in 2015. His address is 790, Chan road, Thung Wat Don, Sathon, Bangkok, 10120, Thailand.