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ไฮโดรเจน



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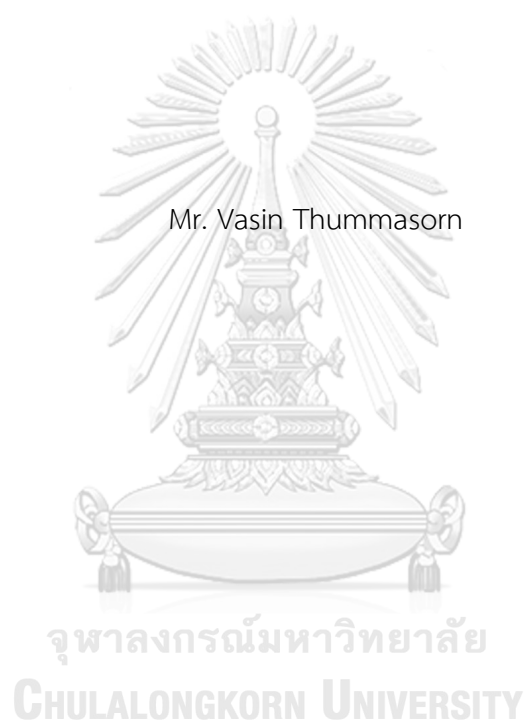
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SYNTHESIS OF ALTERNATING CONJUGATED COPOLYMERS FROM DIRECT C-H
ARYLATION



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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การสังเคราะห์คอนจูเกตพอลิเมอร์ผ่านปฏิกิริยาแอริลเลชันโดยตรงบนพันธะคาร์บอน-ไฮโดรเจน โดยใช้แพลเลเดียมเป็นตัวเร่งปฏิกิริยาในการสังเคราะห์พอลิเมอร์เป็นงานหลักที่ในงานวิจัยนี้ศึกษา ซึ่งวิธีนี้ดีกว่าวิธีดั้งเดิมคือ ลดขั้นตอนในการเตรียมหนึ่งในมอนอเมอร์ตั้งต้น ก่อนการเข้าทำปฏิกิริยาควบคู่ระหว่างกัน อันเป็นการลดการเกิดของเสียที่เป็นพิษ ลดผลิตภัณฑ์ข้างเคียง และลดค่าใช้จ่าย คณะผู้วิจัยสามารถสังเคราะห์โคพอลิเมอร์ 4 ที่เป็นประเภทตัวให้และตัวรับอิเล็กตรอน จากปฏิกิริยาแอริลเลชันโดยตรงบนพันธะคาร์บอน-ไฮโดรเจนระหว่าง 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอฟิน กับ 3,4-เอทิลีนไดออกซีไทโอฟิน ได้เป็นของแข็งสีส้มในปริมาณ 31.7% โคพอลิเมอร์ 5 สามารถสังเคราะห์ได้ด้วยวิธีเดียวกัน โดยใช้ 3,4-เอทิลีนไดออกซีไทโอฟิน กับ 1,4-ไดโบรโม-2,5-บิสออกทิลออกซีเบนซีน และเป็นสารตั้งต้นที่ใช้ทำปฏิกิริยา โดยได้ปริมาณที่ดีที่สุด คือ 86% ภาวะของปฏิกิริยาที่ปรับปรุงแล้วนี้ ได้นำมาใช้สังเคราะห์โคพอลิเมอร์ 6 (จาก 3-เฮกซิลไทโอฟิน และ 1,4-ไดโบรโม-2,5-บิสออกทิลออกซีเบนซีน), 7 (จาก ไดโบรโมออกทิลไตรอะโซล และ 3,4-เอทิลีนไดออกซีไทโอฟิน) และ 8 (จาก ออกทิลเบนโซไตรอะโซล และ 3,4-เอทิลีนไดออกซีไทโอฟิน) ในปริมาณ 65.4%, 83.2% และ 77.2% ตามลำดับ คอนจูเกตโคพอลิเมอร์ที่สังเคราะห์ได้เหล่านี้แสดงสมบัติการดูดกลืนแสงยูวี-วิสิเบิลที่มีความยาวคลื่นสูงสุดหลากหลายค่าอยู่ในช่วง 300-451 นาโนเมตร

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VASIN THUMMASORN: SYNTHESIS OF ALTERNATING CONJUGATED COPOLYMERS FROM DIRECT C-H ARYLATION. ADVISOR: ASSIST. PROF. YONGSAK SRITANA-ANANT, Ph.D., pp.

Synthesis of conjugated polymers via Direct Hetero Arylation Polycondensations (DHAPs) through palladium catalyzed cross-coupling polymerization was investigated. This synthetic method has advantages over traditional method by omitting the preactivation of one of the coupling partner, minimizing production of toxic wastes, side products, and cost. We obtained the donor-acceptor copolymer 4 from DHAPs of 2,5-dichloro-3,4-dinitrothiophene (DCDNT) and 3,4-ethylenedioxythiophene (EDOT) as orange solid in 31.7% yield. Copolymer 5 was also obtained using the same methodology from EDOT and 1,4-dibromo-2,5-bis(octyloxy)benzene (DBOB) as the precursors, in which the best result was 86% yield. The optimized DHAP condition was used to prepare copolymers 6 (from 3-hexylthiophene and DBOB), 7 (from dibromooctyltriazole and EDOT) and 8 (from octylbenzotriazole and EDOT) in 65.4%, 83.2%, and 77.2% yields, respectively. These conjugated copolymers exhibited UV-visible maximum wavelength absorption at various values in the range of 300-451 nm.

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LIST OF ABBREVIATIONS

cm^{-1}	: unit of wavenumber (IR)
CDCl_3	: deuterated chloroform
Cs_2CO_3	: cesium carbonate
$^\circ\text{C}$: degree Celsius
^{13}C NMR	: carbon-13 nuclear magnetic resonance spectroscopy
d	: doublet (NMR)
DBOB	: 1,4-Dibromo-2,5-bis(octyloxy)benzene
DBOTZ	: 3,5-Dibromo-1-octyl-1H-1,2,4-triazole
DCDNT	: 2,5-dichloro-3,4-dinitrothiophene
DCM	: dichloromethane
DMAc	: dimethylacetamide
DMF	: dimethylformamide
EDOT	: 3,4-ethylenedioxythiophene
EDTA	: ethylenediaminetetraacetic acid
EtOAc	: ethyl acetate
FeCl_3	: ferric chloride
FT-IR	: fourier-transform infrared spectroscopy
g	: gram (s)
GPC	: gel Permeation Chromatography
3-HT	: 3-hexylthiophene

h	: hour (s)
$^1\text{H NMR}$: proton nuclear magnetic resonance spectroscopy
HNO_3	: nitric acid
H_2SO_4	: sulfuric acid
Hz	: hertz (s)
Lit.	: literature
M	: molar (s)
m	: multiplet (NMR)
M_n	: the number average molecular weight
MeOH	: methanol
MgSO_4	: magnesium sulfate
min	: minute
mL	: milliliter (s)
mmol	: millimole (s)
NaOAc	: sodium acetate
Na_2CO_3	: sodium carbonate
NaOH	: sodium hydroxide
nm	: nanometer (s)
$\text{Pd}(\text{OAc})_2$: palladium acetate
PivOH	: pivalic acid
PPh_3	: triphenylphosphine
$\text{P}(\text{n-Bu})_3$: tri-n-butylphosphine

ppm	: parts per million (unit of chemical shift)
q	: quartet (NMR)
rt	: room temperature
s	: singlet (NMR)
t	: triplet (NMR)
TFA	: trifluoroacetic acid
UV-Vis	: ultra-violet and visible spectroscopy
δ	: chemical shift
λ_{max}	: maximum wavelength



CHAPTER I

INTRODUCTIONS

1.1 Conductive polymer

Conductive polymers or conjugated polymers are materials that consist of π -conjugated system on the backbone of the polymers. Electrons can delocalize along the polymer chain through these conjugated π -orbitals resulting in conducting properties. These polymers can combine the electronic properties of inorganic semiconductors and mechanical-physical properties of organic polymers including the ability to solubilize in organic solvents [1], which lead to the ease of fabrication to form thin and lightweight film using spray-coating and inkjet printing technologies[2-4]. These processing techniques are the advantages of emerging low-cost organic electronic devices for many applications such as solar cells [5, 6], transistor [7, 8], light emitting diodes (LEDs) [9, 10], memory devices [11, 12], and sensing technologies [13-15].

The difference of HOMO and LUMO energy levels of conjugated polymers, or band gap, is generally in the range of semiconductors, but the ability of conductivity of these polymers could be raised to the level of conductors when doped with doping agent [16]. The conjugated polymers with aromatic rings as the π -conjugated backbones are often functionalized with electron-donating (donor, D) or electron-withdrawing (acceptor, A) moieties in order to increase the HOMO or decrease the

LUMO levels, respectively. These functionalizations of the result in narrower band gap polymers, hence lead to better optical, electronic, and physical properties [17, 18]. However, the planarity of aromatic rings allows stronger interchain attractions and lower their solubility. The alkyl non-conjugated side chains were usually required to recover the good solubility in organic solvents [19, 20]. Connections of these electron-rich or electron-poor units yield various types of conjugated polymers known as donor-donor polymers (D-D), donor-acceptor polymers (D-A) and acceptor-acceptor polymers (A-A). The electron-rich or donor units commonly found in most conjugated polymers include 3,4-ethylenedioxythiophene (EDOT), 3-hexylthiophene (3-HT) [21], and 1,4-dibromo-2,5-bis(octyloxy)benzene (DBOB) [22]. while triazole derivatives [23], thienopyrazine derivatives [24], and thieno[3,4-c]pyrrole-4,6-dione [25] derivatives were among the examples of common electron-poor acceptor units.

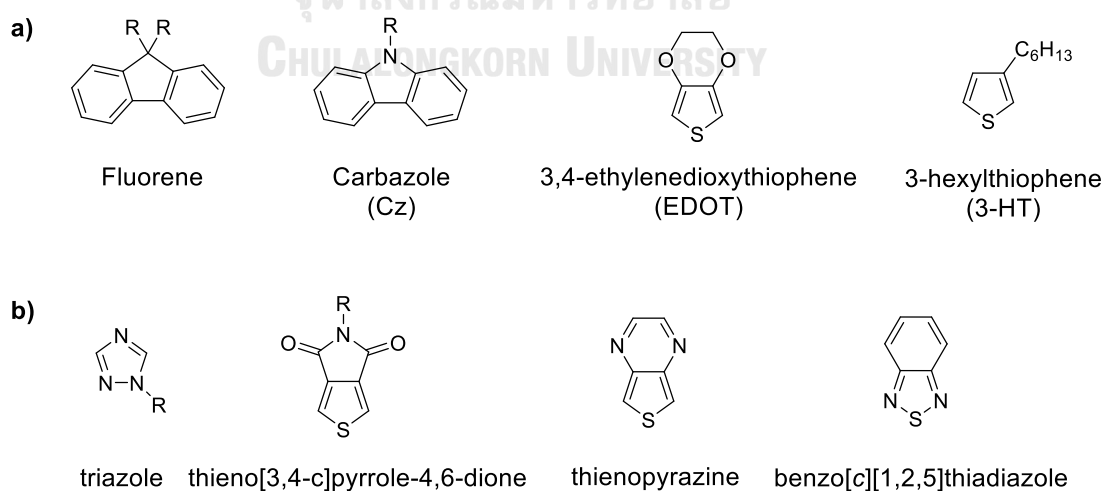


Figure 1.1: Examples of a) donor units b) acceptor units

Among these types of conjugated polymers, those composed of D-A units were of the most interest. Linking the units with large difference in polarities of electron rich and electron poor moieties together were found to increase charge-transfer properties [26], induce a coplanar polymeric backbone that increased the electron transport and interchain ordering [27], and raise the intensity and wavelength in UV-visible absorption [28]. The long alkyl side chains were usually attached to improve the solubility in common organic solvent during solution and film processing [29-32].

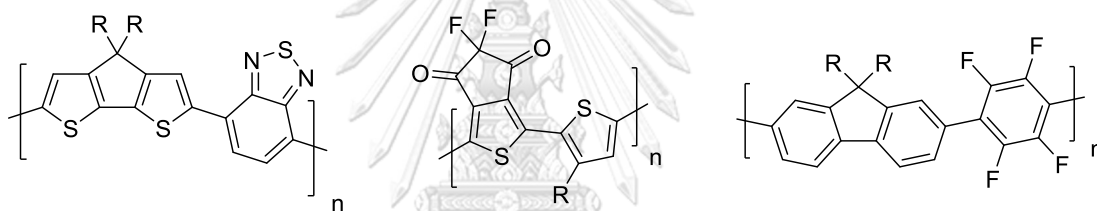


Figure 1.2: Examples of D-A polymers (R = long alkyl side chain)

Thiophene-based polymers are among the most studied and can be used as conducting polymers because of their wide range in UV visible absorption and good stability in environment while maintaining high charge mobility [33]. The most successful π -conjugated polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) [34-36], and its derivatives have been found in variety of applications such as antistatic coatings, electrochromic display, solid state ion sensors and biomedical devices [37]. These thiophene derivatives were also the most common donor units found to be incorporated in several designs of D-A polymers.

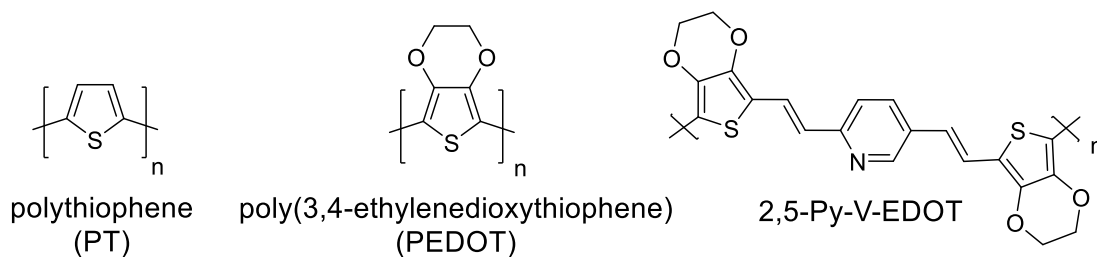


Figure 1.3: Examples of conjugated polymer containing thiophene derivatives

1.2 Overview of the synthesis of conjugated polymer

The synthesis of π -conjugated polythiophenes and other polyarenes was mostly prepared through several types of palladium catalyzed cross coupling reactions or oxidative coupling reactions. (Figure 1.4) Detailed examples of these methodologies are presented below.

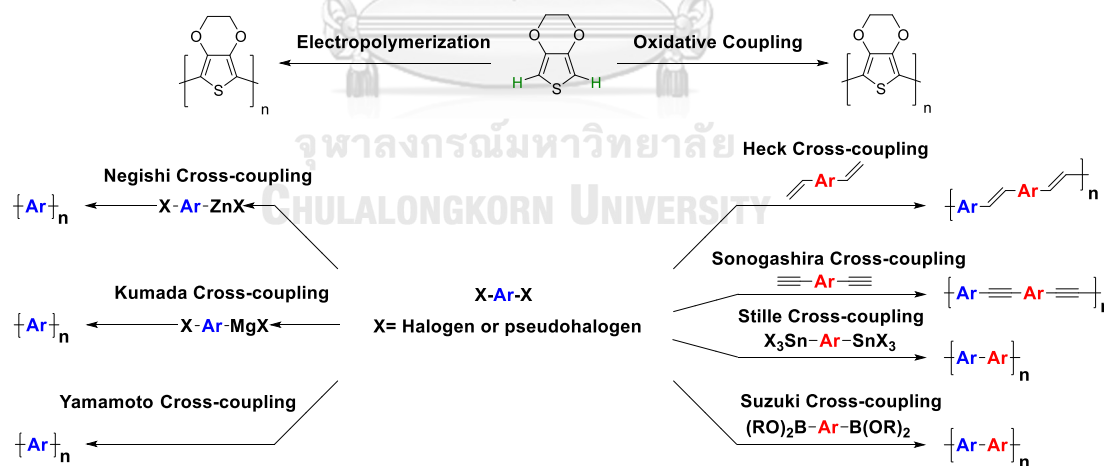
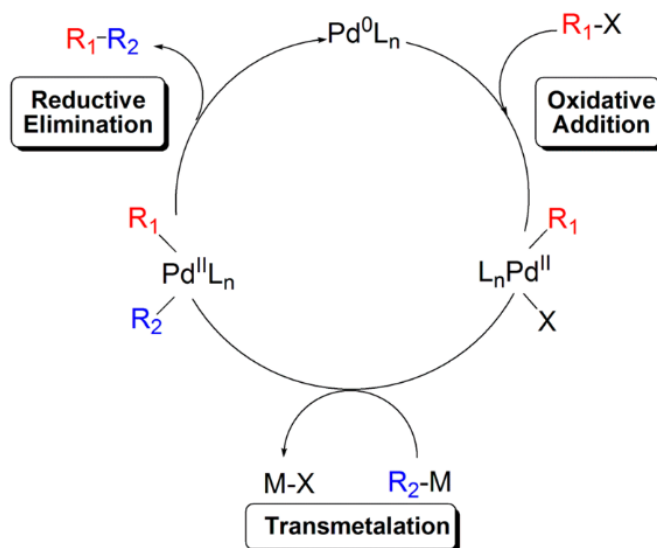


Figure 1.4: Common C-C coupling techniques for the preparations of π -conjugated polyarenes and related polymers

1.2.1 General mechanism of palladium catalyzed cross coupling reaction

Most palladium-catalyzed cross coupling reaction involving (hetero)aryl molecule followed the same general catalytic cycle of three main steps: oxidative addition, transmetalation and reductive elimination. The oxidative addition of Pd^0L_n and electrophilic aromatic compound ($\text{R}^1\text{-X}$) formed the intermediate of $\text{L}_n\text{R}^1\text{PdX}$. This step often becomes the rate determining step in palladium-catalyzed cross coupling reaction [38]. In some cases, other steps could be rate limiting such as Stille cross couplings with the rate limiting transmetalation steps [39, 40]. The palladium (II) intermediate, Pd-Ar and X-type ligands, involved with a nucleophilic organometallic aryl compound. Following the transmetalation step, the transferring of aryl group to the catalyst ($\text{L}_n\text{R}^1\text{PdR}^2$) was presumed during the elimination of M-X . The process ends with the reductive elimination of diaryl compound $\text{R}^1\text{-R}^2$ (Figure 1.5).



where, R_1 and R_2 are arene derivatives
 X represents an halogen or a pseudo-halogen
 M represents an organometallic functional compound

Figure 1.5: General mechanism of Pd-catalyzed cross coupling reactions

1.2.2 Suzuki-Miyaura cross coupling reaction

In 2003, Svensson et al. [41] synthesized an alternating polyfluorene conjugated copolymers, PFDTBT. The polymers were derived from couplings of 2,7-fluorenediboronic acid pinacol esters and dibromo derivative of benzothiadiazole based acceptor and used $Pd(PPh_3)_4$ as the catalyst and obtained this polymer at 60% yield. (Figure 1.6) The film of the polymer showed the longest wavelength absorption at 545 nm. The results gave a copolymer with low molecular weight ($M_n=4800$). Using this polymer as donor unit and PCBM as acceptor unit, the mixture was applied to be polymer solar cell device and exhibited the power conversion efficiency (%PCE) at 2.2%.

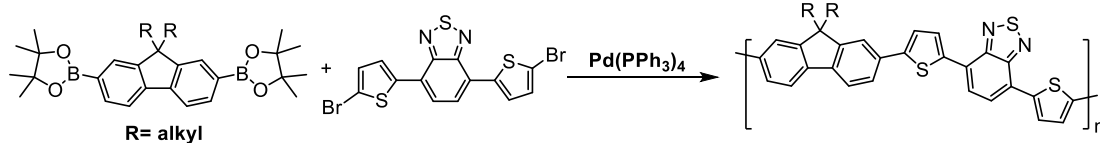


Figure 1.6: Suzuki cross coupling polymerization between 2,7-fluorenediboronic acid pinacol ester and dibromo derivative of benzothiadiazole based acceptor

In 2007, Blouin and coworkers [42] successfully synthesized conjugated polymers *via* Suzuki-cross coupling polymerization using the precursors: 2,7-carbazolediboronic acid pinacol ester and benzothiadiazole based dibromide, and Pd_2dba_3 and $\text{P}(o\text{-tol})_3$ as the catalyst of the reaction. (**Figure 1.7**) This polymer was tested for its performance as organic solar cell and got the percent of power conversion efficiency (%PCE) at 3.6%.

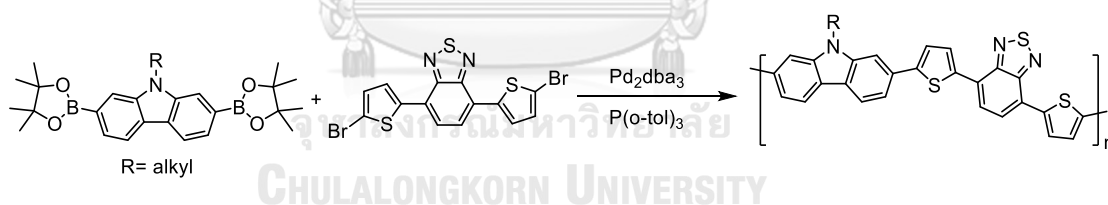


Figure 1.7: Suzuki cross coupling polymerization between 2,7-fluorenediboronic acid pinacol ester and benzothiadiazole based dibromide

1.2.3 Migita-Kosugi-Stille cross coupling reaction

In 2011, Chu and coworkers [43] synthesized new alternating D-A copolymers consisting of dithienosilole and thienopyrrole-4,6-dione units using $\text{Pd}(\text{PPh}_3)_4$ as catalyst (**Figure 1.8**). The desired copolymer was used in photovoltaic cells blended with PC_{71}BM , which gave 7.3% PCE.

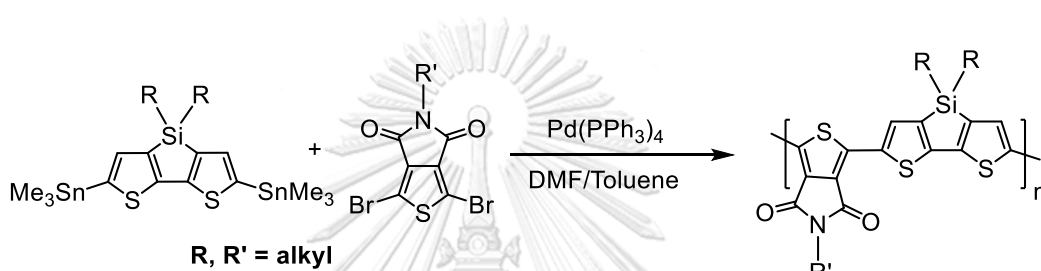


Figure 1.8: Stille cross coupling polymerization between dithienosilole and thienopyrrole-4,6-dione derivatives

In 2012, Jen and coworkers [44] prepared poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(5-fluoro-[2,1,3]-benzothiadiazole)]

PCPDTFBT) through a microwave-assisted Stille polymerization (**Figure 1.9**). The results gave a higher hole mobility than the non-fluorinated polymer (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-([2,1,3]-benzothiadiazole)], PCPDTBT) because of better π - π stacking in solution. PCE of PCPDTFBT/ PC_{71}BM as the active layer (5.51%) was much higher than PCPDTBT/ PC_{71}BM (2.75%).

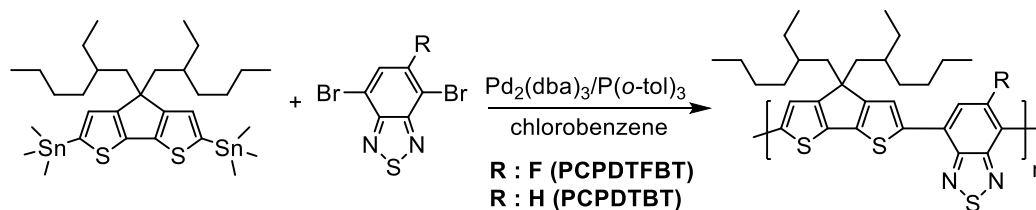


Figure 1.9: Stille cross coupling polymerization of PCPDTFBT and PCPDTBT

1.2.4 Negishi cross coupling reactions

In 2014, Tkachov and coworkers [45] used Negishi chain growth polycondensation of the Zn-organic AB type monomer under mild conditions at low loading of catalyst. The result gave a homo polymer of fluorene derivatives with high molecular weight (**Figure 1.10**).

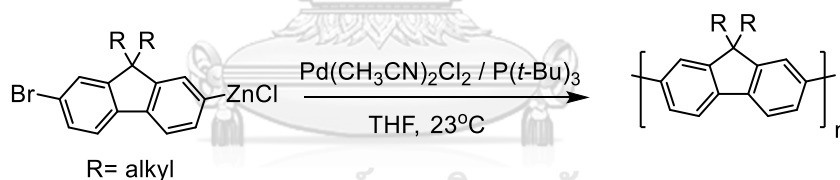


Figure 1.10: Negishi cross coupling polymerization of bromofluorenylene zinc derivatives

1.2.5 Kumada Tamao–Corriu cross coupling reactions

In 2016, Maes [46] and coworkers successfully synthesized a push-pull monomer consisting of thiophene (donor) and pyridine (acceptor) unit using Kumada catalyst-transfer polymerization with a nickel catalyst (GRIM polymerization). The conjugated block copolymers containing 3-hexylthiophenes and the alternating push-pull units were successfully prepared in one pot. (Figure 1.11)

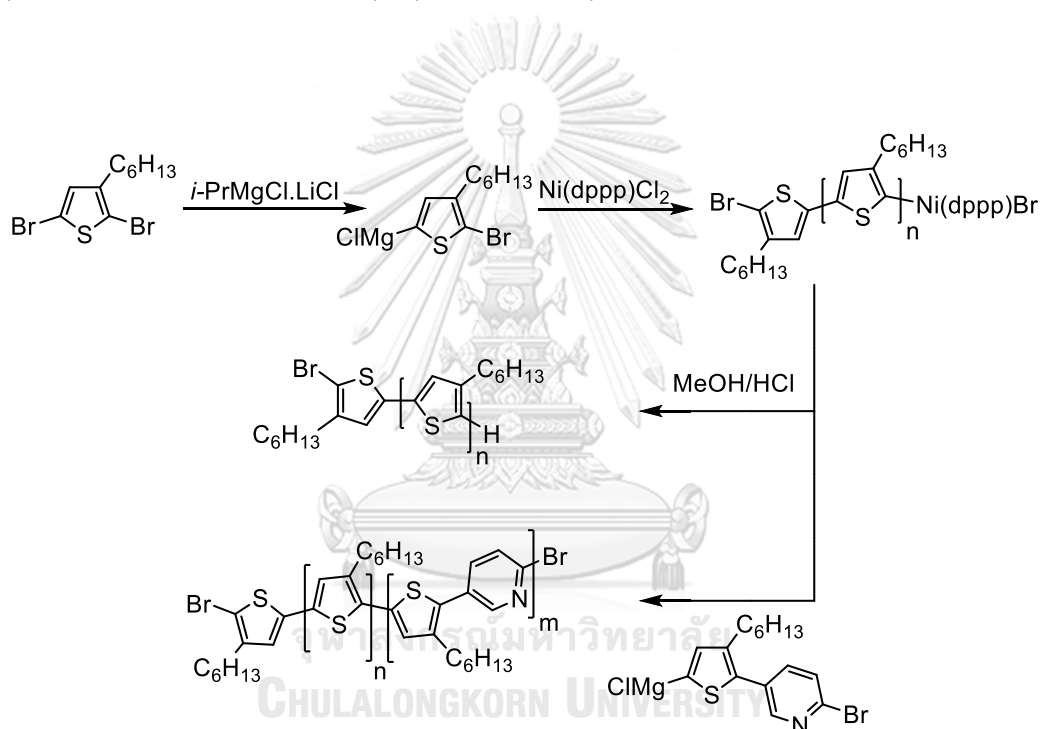


Figure 1.11: Kumada cross coupling polymerization of block copolymers of 3-hexylthiophene and pyridine units

1.3 Direct C-H arylation polymerizations (DHAPs)

Cross coupling reactions that rely on organometallic intermediates face some disadvantages especially the requirement of multiple step preparations of bifunctional organometallic precursors, which are either air sensitive, difficult to handle or expensive to make, or highly toxic. Recently, the new method of cross coupling reactions of heteroarene with aryl halides by direct C-H arylation polycondensations (DHAPs) have been introduced as the preferred method due to their advantages of fewer reaction steps and reduced metal toxic waste [47-49]. This reaction can generate C-C bonds between the two precursors with no need of preactivation step of one of them.

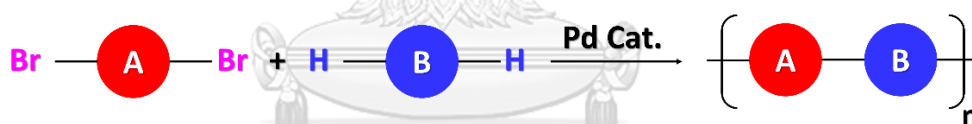


Figure 1.12: Direct C-H arylation polycondensation or DHAP

Direct (hetero) C-H arylation polymerization (DHAP) is a type of palladium-catalyzed cross coupling reaction between (hetero)-aromatic C-H and C-halogen bonds. (Figure 1.12) DHAP has been of interest because it can exhibit well-defined and high molecular weight conjugated polymer with high selectivity. The mechanism of DHAP has been investigated to improve its efficiency of the reaction.

DHAP also uses the same general catalytic cycle as other palladium catalyzed cross coupling reactions. The most studies on mechanisms were Heck-type arylation and concerted metalation deprotonation (CMD). In recent reports, the Heck-type mechanism was demonstrated in some cases that had a specific condition, thereby offering alternative reaction selectivity when compared to the CMD process [47, 50-53]. The CMD pathway for a cross coupling of small molecules had been extensively studied [54]. It is potentially involved in most direct(hetero) arylation processes. Carbonates mixed with catalytic amounts of bulky carboxylic acid were key to enhance reactivity through a proton shuttle between the carbonate base and homogenous catalytic species [55]. The proposed CMD mechanism was supported by DFT calculations and applications using a wide variety of substrates [56, 57]. In contrast, the mechanistic studies generally dismiss the S_EAr mechanism (**Figure 1.13**) because of a failure of DFT calculations to identify the key cationic Wheland intermediate [58] (**Figure 1.14**).

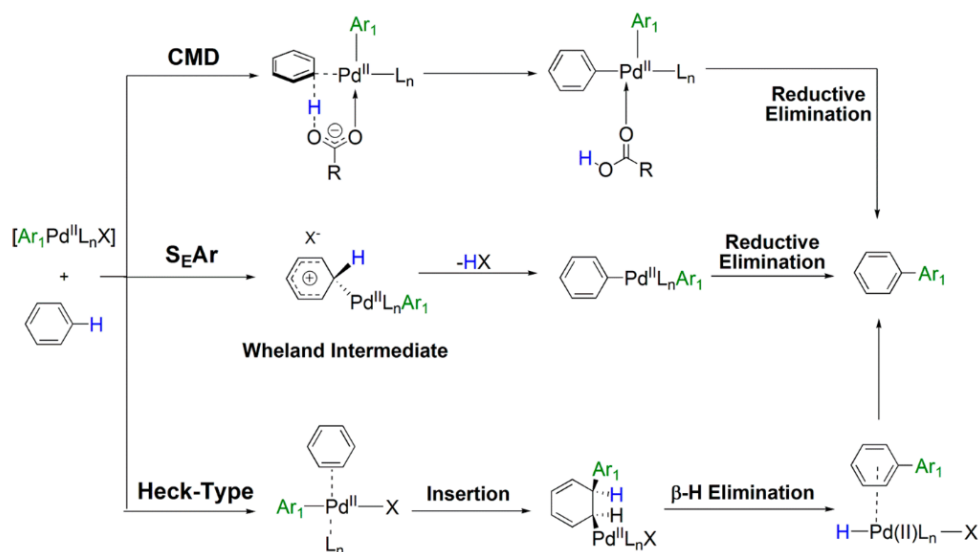


Figure 1.13: Transition states for the carboxylate-assisted concerted metalation deprotonation (CMD), aromatic electrophilic substitution (S_EAr) and Heck-type reaction mechanisms

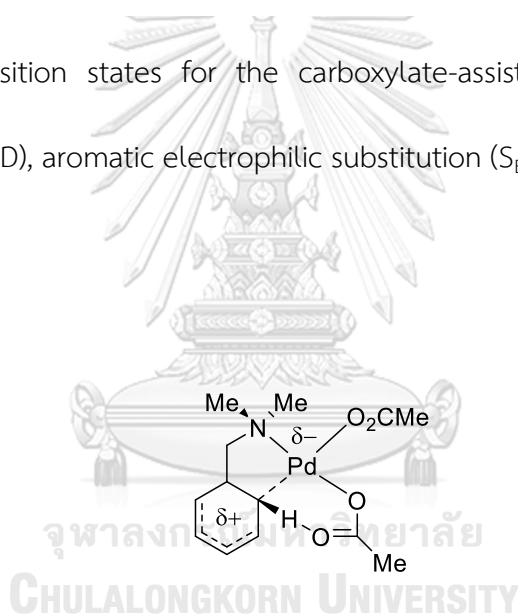


Figure 1.14: Palladium intermediate of S_EAr mechanism

The better understanding of DHAP mechanism selectivity was found by activation-strain analysis to calculate the CMD enthalpic contribution to the transition state energy interaction between substrates. The distortion factor starts from the deformation of the palladium-ligand bond ($E_{dist}[PdL]$), out of plane bending and elongation of C-H bond ($E_{dist}[ArH]$). The interaction energy (E_{int}) is determined by the

bond strength between the palladium atom and the π -orbitals of the aromatic compound. Distortion energies account for the high energy transition state, while the E_{int} counteracts this by stabilizing the transition state (**Figure 1.15**). $E_{\text{dist}}(\text{PdL})$ is generally inessential because the transition state is mainly controlled by the opponent $E_{\text{dist}}(\text{ArH})$ and E_{int} contributions. E_{int} is more important in electron-rich compounds, which explains the higher reactivity of more π -nucleophilic substrates. On the other hand, electron-poor compounds are more reactive due to a generally lower $E_{\text{dist}}(\text{ArH})$ barrier, which is linked to the acidity of the C-H bond [59, 60]

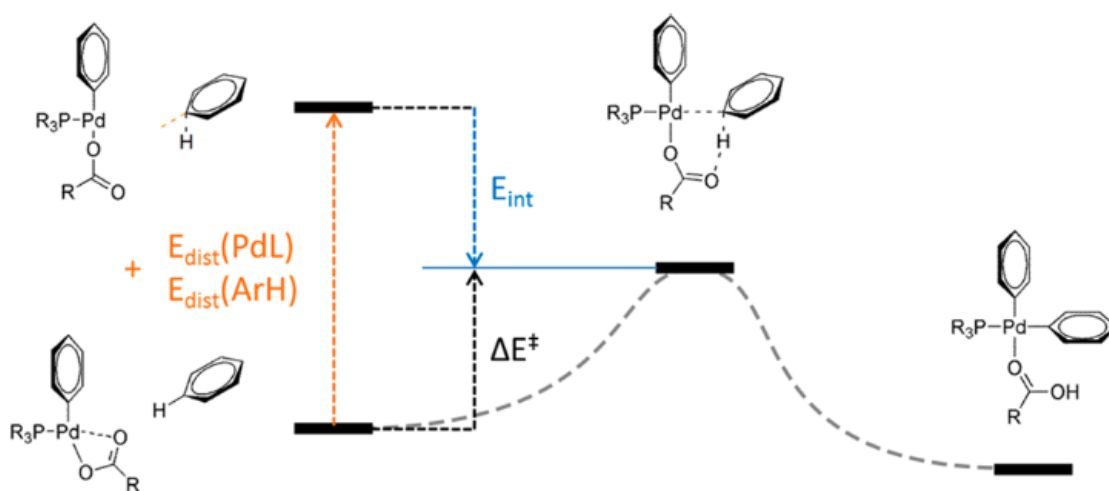


Figure 1.15: Enthalpic contributions to the CMD transition state energy, as divided into the factors of distortion (E_{dist}) and interaction (E_{int})

In the studies of cross coupling reactions of thiophene and bromobenzene [54], (Figure 1.16) the oxidative addition of carbon-halogen bond exchanged the halogen ligand with cesium salt and formed complex **1**. The thiophene substrate was partially deprotonated by carboxylate ligand and complex **1** forms a metal-carbon bond through transition state **1-TS** (pathway 1) [61]. The phosphine ligands, or solvent can regenerate complex **1** through pathway 2 [58]. But mostly, the reductive elimination was preferred to generate the product at the end of the process.

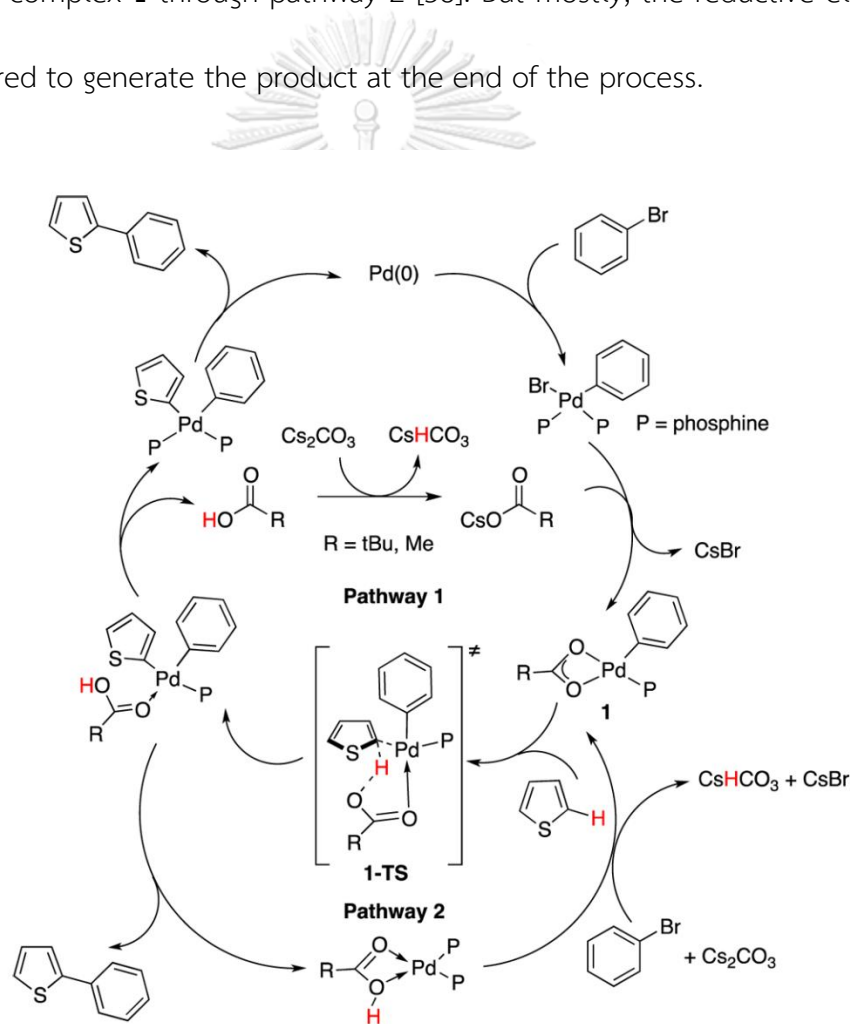
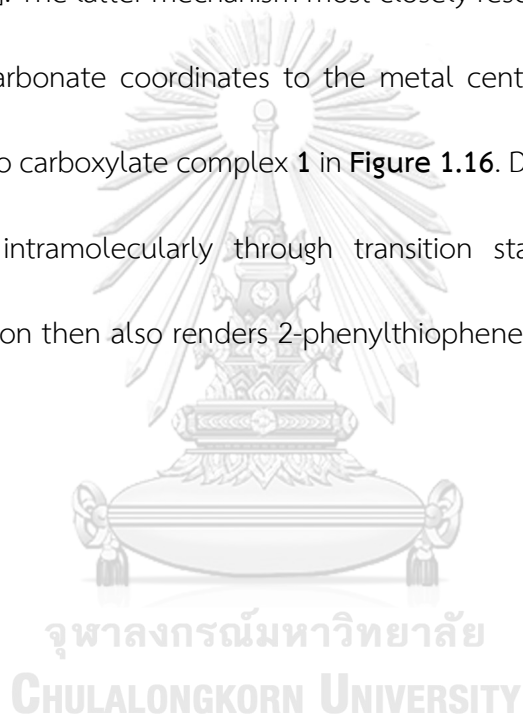


Figure 1.16: Catalytic cycle for cross coupling between thiophene and bromobenzene using a carboxylate additive

On the other hand, without using carboxylate as the additive, the product from oxidative addition of aryl bromide would follow one of two pathways as shown in **Figure.1.17**. If the phosphine was a bidentate ligand, the C-H activation of thiophene can follow pathway 1 and give the intermediate **2-TS** [54]. In some cases, when monodentate phosphine ligand was formed, the reaction may follow either pathway 1 or pathway 2 [54]. The latter mechanism most closely resembles pathway 2 in **Figure 1.16** where the carbonate coordinates to the metal center to give the zwitterionic species **1'** similar to carboxylate complex **1** in **Figure 1.16**. Deprotonation of thiophene substrate occurs intramolecularly through transition state **1'-TS** [54]. The final reductive elimination then also renders 2-phenylthiophene product.



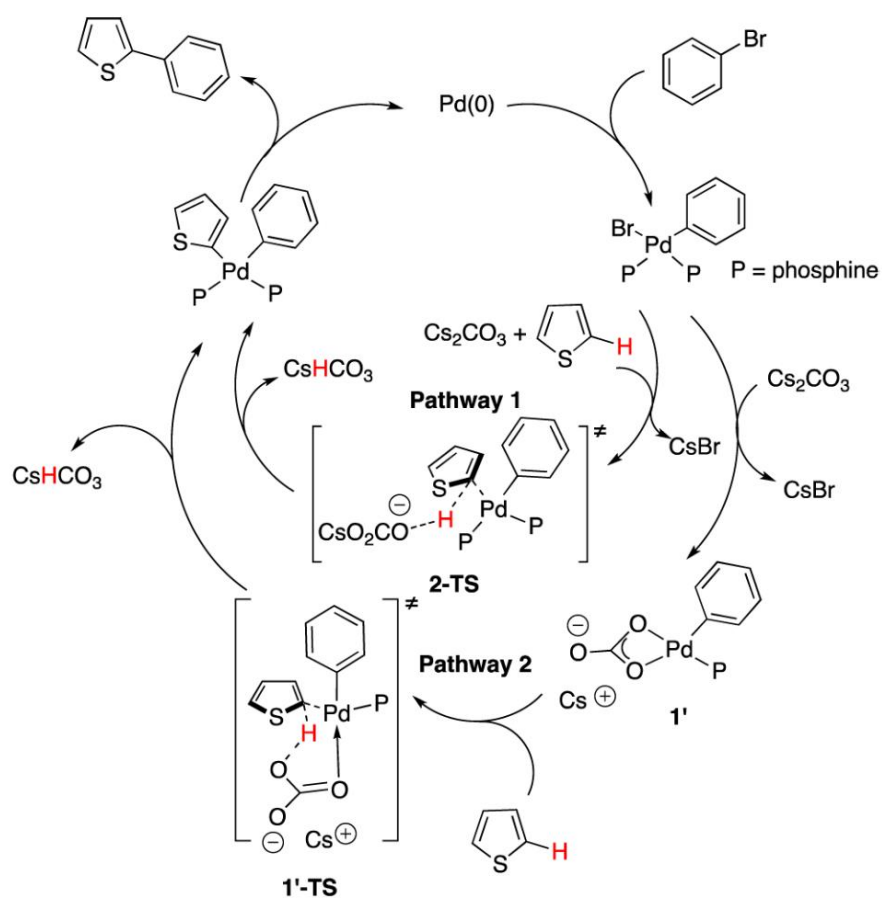


Figure 1.17: Catalytic cycle for cross coupling between thiophene and bromobenzene

without a carboxylate additive

1.4 Literature reviews

In 2012, Yu and coworkers [37] synthesized conjugated homo-polymers by direct C-H arylation using various substrates of dialkoxythiophene derivatives bearing 3,4-propylenedioxythiophenes (ProDOT) or 3,4-ethylenedioxythiophene (EDOT) as the core monomeric units (**Figure 1.18**). The effect of palladium catalyst, phosphine source, additive and functional groups were investigated. The desired copolymers were synthesized with reasonable molecular weight ($M_n = 6100-9600$) and low PDI. They demonstrated UV-visible absorption at maximum wavelength around 480-590 nm and could be reversible between oxidized state and neutral state upon applying appropriate potentials.

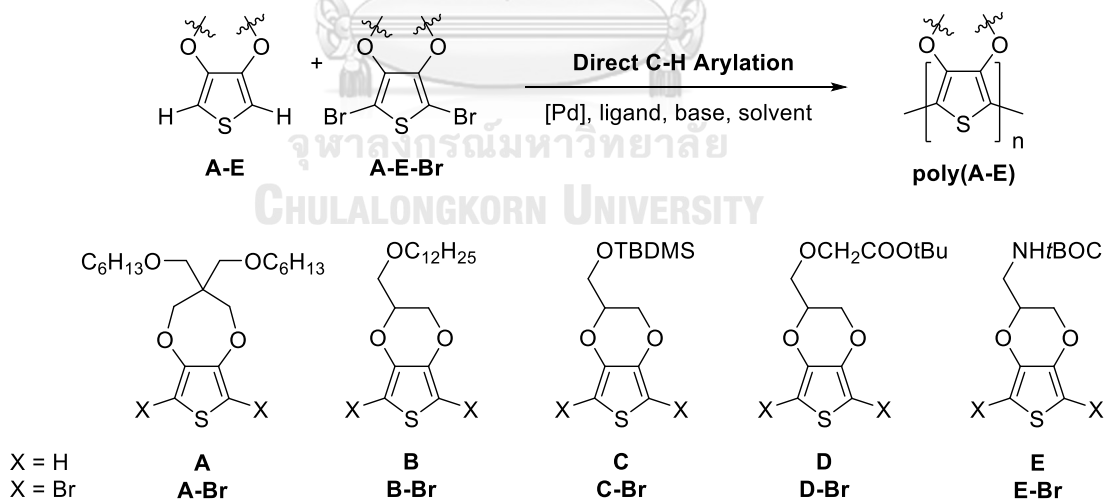


Figure 1.18: The synthesis of polydialkoxythiophene derivatives via direct C-H arylation

In 2012, Kanbara and coworkers [62] carried out polycondensations of 1,2,4,5-tetrafluorobenzene with various dibromoarenes to provide new conjugated copolymers in **Figure 1.19**. The tetrafluorobenzene unit can induce the HOMO energy level of the polymer to low level. The desired copolymer, PDOF-TP, displayed as the material for OLEDs because of the effective hole blocking property.

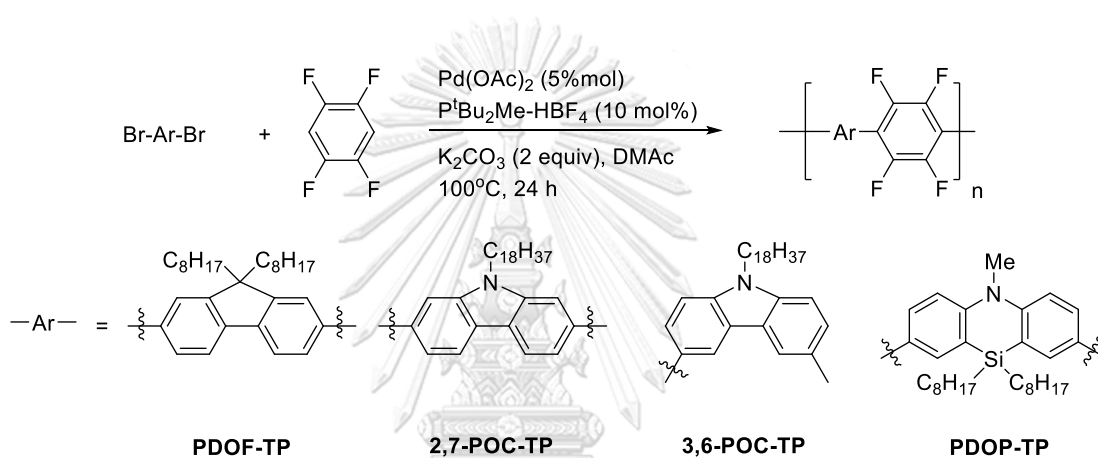


Figure 1.19: Polycondensations of 1,2,4,5-tetrafluorobenzene with various dibromoaromatic compounds

In 2013, Kanbara and coworkers [63] also performed the polymerizations between 3,4-ethylenedioxythiophene (EDOT) and 2,7-dibromo-9,9-dioctylfluorene using DHAP in **Figure 1.20**. The reaction conditions were investigated in terms of catalyst, reaction times, and additive for high performance polymerization. (**Table 1.1**) The resulted polymer exhibited high synthetic yields, and high molecular weight (89% yield, $M_n=39400$).

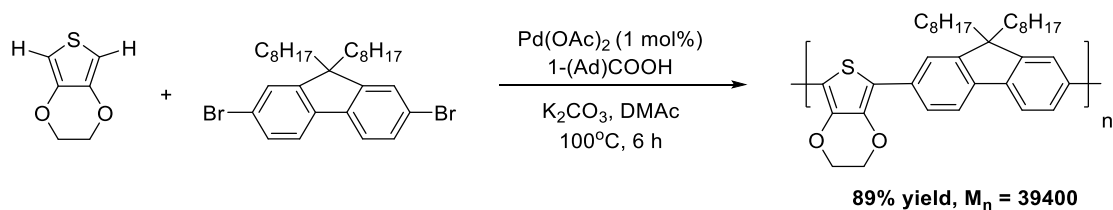


Figure 1.20: Polycondensation of EDOT and 2,7-dibromo-9,9-dioctylfluorene

Table 1.1 : The variety of reaction conditions for copolymerizations of EDOT and 2,7-dibromo-9,9-dioctylfluorene

Entry	Pd precatalyst	Time	Additive	Yield ^(b)	M_n ^(c)
1	$\text{Pd}(\text{OAc})_2$	24 h	$\text{PivOH}^{(f)}$	89	26900
2	$\text{Pd}_2(\text{dba})_3$	24 h	PivOH	57	4900
3 ^(d)	$\text{Pd}(\text{OAc})_2$	6 h	PivOH	81	28300
4	$\text{Pd}(\text{OAc})_2$	3 h	PivOH	79	14900
5	$\text{Pd}(\text{OAc})_2$	6 h	No acid	78	9600
6 ^(d)	$\text{Pd}(\text{OAc})_2$	6 h	CF_3COOH	61	9100
7 ^(d)	$\text{Pd}(\text{OAc})_2$	6 h	CH_3COOH	79	27900

^{a)}Reactions were carried out at 100°C using $\text{Pd}(\text{OAc})_2$ (2 mol%), PivOH (30 mol%), and K_2CO_3 (2.5 equiv.) in DMAc (1.67 mL); ^{b)}The products were obtained by reprecipitation from $\text{CHCl}_3/\text{MeOH}$; ^{c)}Estimated by GPC calibrated on polystyrene standards; ^{d)}Average of two runs; ^{e)} $\text{Pd}(\text{OAc})_2$ (1 mol%); ^{f)}Pivalic acid

In 2014, Wang and coworkers [64] successfully synthesized the donor-acceptor copolymer containing benzo[1,2-b:4,5-b']-dithiophene and 2,1,3-benzothiadiazole via DHAP. (**Figure 1.21**) Using 1,2-dimethylbenzene (ODMB) as a non-polar high boiling point solvent with $\text{Pd}_2\text{dba}_3/(\text{o-MeOPh})_3\text{P}$, potassium carbonate, and pivalic acid, a high-quality copolymer (PBDTBT) with high molecular weight at 60 kg/mol was obtained.

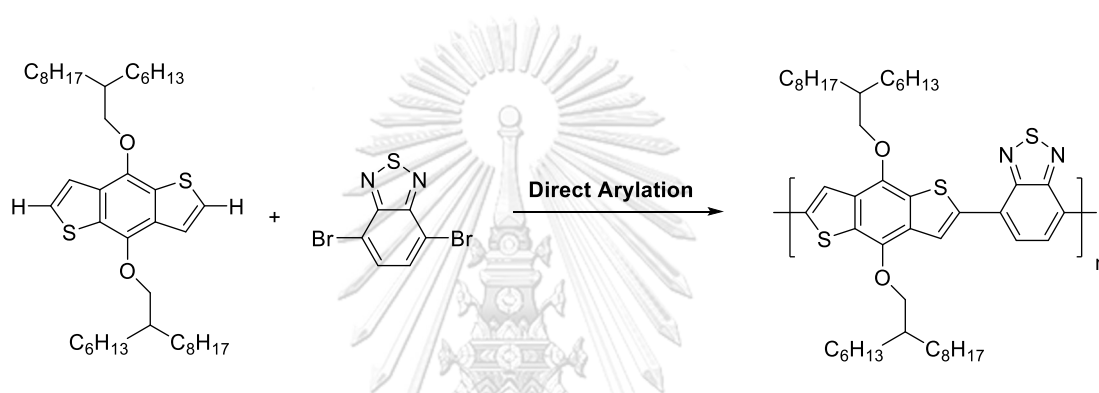


Figure 1.21: Synthesis of polymer PBDTBT using DHAP

In 2015, Sirringhaus and coworkers [65] successfully synthesized copolymers with low-bandgap energy containing diketopyrrole (DPP) and benzotriazole (BTZ) moieties (**Figure 1.22**). By comparison of the synthetic routes between Suzuki cross coupling and direct arylation, the product from direct arylation exhibited higher density of chain defect and led to lower electrical performance.

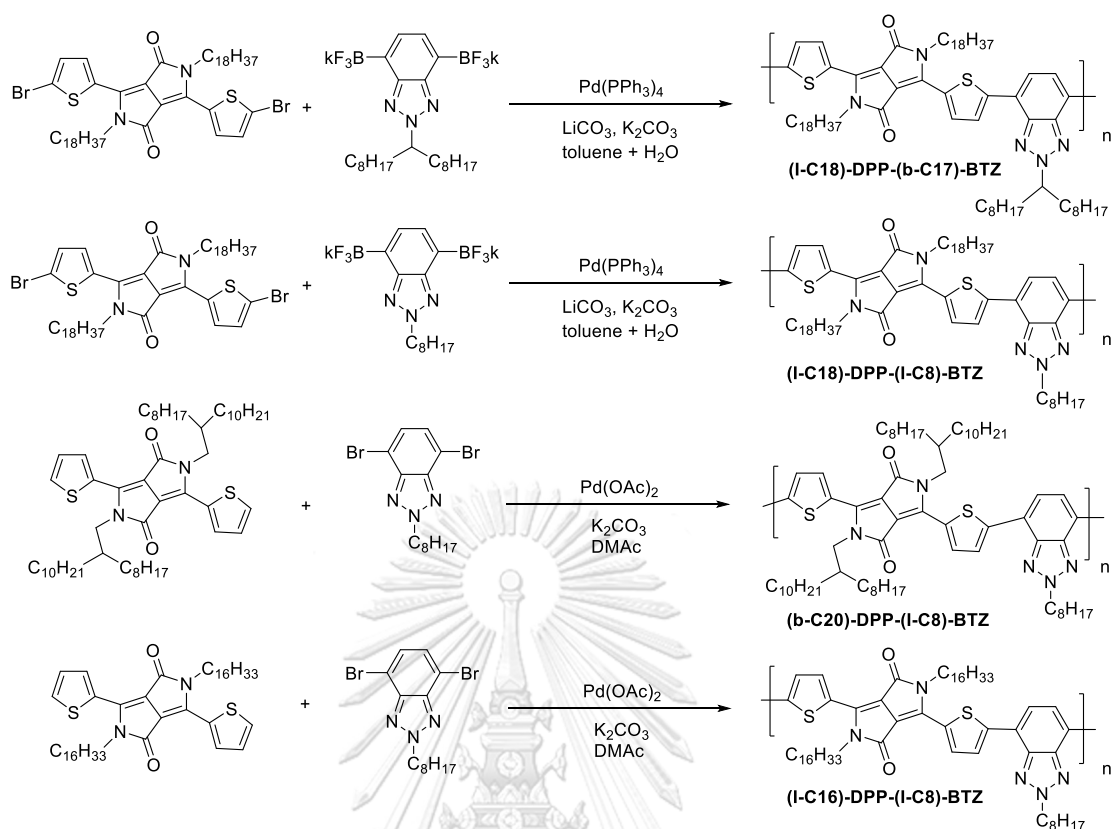


Figure 1.22: Synthesis of the four new DPP-BTZ copolymers

In 2016, Michinobu and coworker [66] achieved novel environmentally-friendly polymerizations for π -conjugated polymers via direct C-H arylation polymerization, using EDOT and a series of dibromocarbazoles (Cbzs) as monomers. (Figure 1.23) In this case, the phosphine-free and microwave-assisted polycondensations were used. The electrochromic properties were investigated and found that the thin film polymer could produce two-step color change upon increasing potentials.

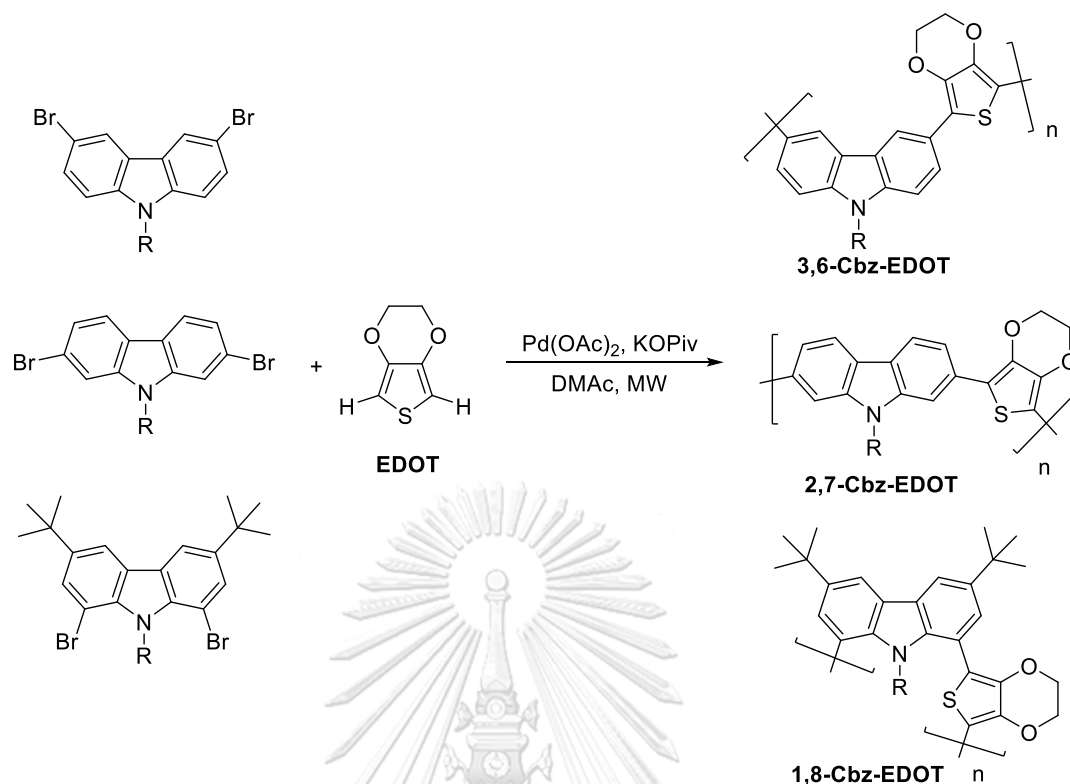


Figure 1.23: Polymerizations of EDOT and different dibromocarbazole monomers

In 2017, Gomez and coworkers [67] synthesized donor-acceptor poly(benzo[1,2-b:4,5-b']dithiophenebenzotriazole) (PBnDT-TAZ) copolymers using a series of benzotriazole (BTZ) monomers with fluorinated and non-fluorinated benzotriazole derivatives. (Figure 1.24) They found that the addition of fluorine substituents could produce a high charge transport in polymer semiconductor. The intermolecular interaction of donor part and acceptor part between polymer chains could induce stacking crystallites and reduce the energetic barrier for charge hopping.

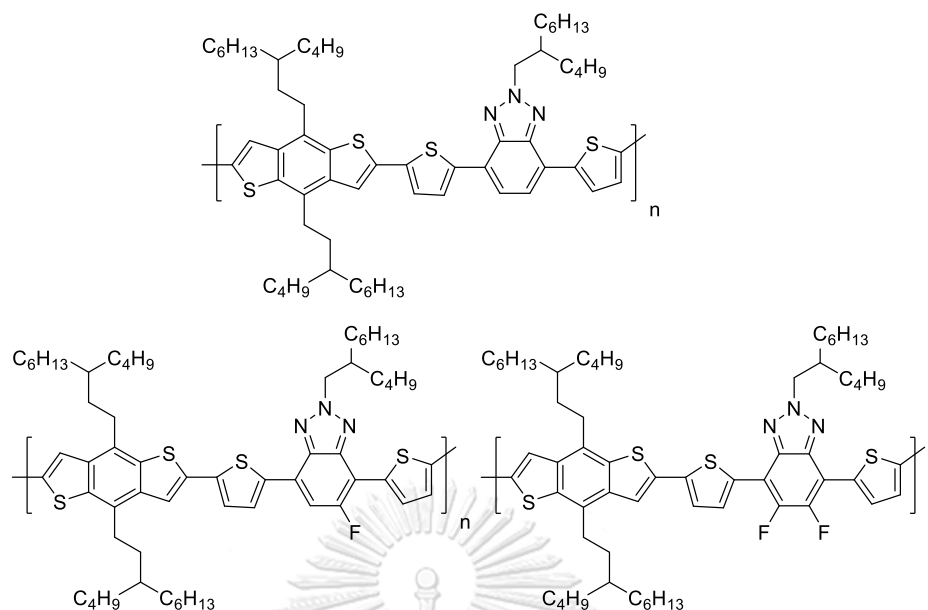


Figure 1.24: Structure of the PBnDT-TAZ copolymers

1.5 The objective of this work

Many examples of conjugated copolymers using direct (hetero) C-H arylation were reported because of the advantages of this method as earlier explained. This opens a vast opportunity to create many new and re-make conjugated copolymers easier and in higher varieties. The goal of this project is to synthesize new conjugated copolymers based on thiophene derivatives which are known to undergo direct (hetero) C-H arylation (DHAPs) with several dibromoarenes, in which improvements on the absorption of UV-visible radiation and solubility in the organic solvents were expected. Mild reaction conditions were mostly investigated together with commonly used palladium catalyst and phosphine ligand, with an aim to find a general and simple DHAP method to be applied towards other monomers.

CHAPTER II

EXPERIMENTS

2.1 Chemicals

Thin layer chromatography (TLC) was performed on aluminum sheets coated with silica gel (Merck Kieselgel 60 F₂₅₄, Merck KGaA, Darmstadt, Germany). Column chromatography used 0.040-0.060 mm or 40-60 mesh ASTM silica gel 60 (Merck Kieselgel 60 P, Merck KGaA, Darmstadt, Germany). Solvents for synthesis were reagent or analytical grades, Solvent and for column chromatography were distilled from commercial grade. Other reagents were purchased from the following vendors:

- Acros Organics (USA): dimethylacetamide (DMAc), *o*-phenylenediamine, sodium nitrite (NaNO₂)
- Cambridge Isotope Laboratories (USA): deuterated chloroform (CDCl₃), deuterated acetone (acetone-d₆)
- Carlo Erba (Italy): 1,2-dichloroethane, ethylenediaminetetraacetic acid (EDTA), potassium carbonate (K₂CO₃), potassium tert-butoxide
- Fluka Chemical (Switzerland): triphenylphosphine (PPh₃)
- Merck Co. (Germany): 1,4-dibromohydroquinone, fuming nitric acid, palladium acetate (Pd(OAc)₂), sodium acetate (NaOAc), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄)
- Panreac (Spain): sodium sulfite (Na₂SO₃)

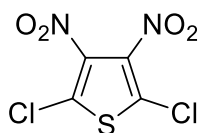
- RCI Labscan (Thailand): acetone, acetic acid, acetonitrile, dichloromethane (DCM), dimethylformamide (DMF), ethyl acetate (EtOAc), hexane, magnesium sulfate (MgSO_4), methanol, toluene
- Sigma-Aldrich (USA): cesium carbonate (Cs_2CO_3), 2,5-dichlorothiophene, 3,4-ethylenedioxythiophene (EDOT), liquid bromine (Br_2), octyl bromide
- TCI (Japan): 3,5-dibromo-1H-1,2,4-triazole, trifluoroacetic acid (TFA), pivalic acid (PivOH)

2.2 Instruments and Equipment

Melting points were determined with a Stuart Scientific Melting Point apparatus SMP10 (Bibby Sterlin Ltd., Staffordshire, UK). The FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer and Nicolet iS5. ^1H NMR spectra were obtained from Varian Mercury NMR spectrometer operated at 400.00 MHz. ^{13}C NMR spectra were obtained from Bruker Avance 400 operated at 100.00 MHz. UV-Vis absorption measurements were made with Agilent Technology G1103A UV-visible spectrophotometer. Mass data were measured with ESI-MS (Water Quattro microTM API) or Gel permeation chromatography (GPC) (Tosoh Ecosec HLC-8320GPC and Waters 2414 refractive index (RI) detector with Styragel HR5E).

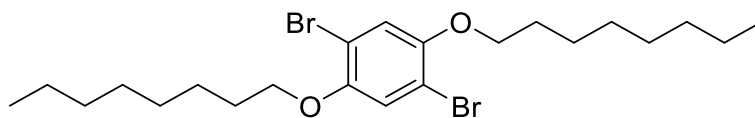
2.3 Monomer Synthesis

2.3.1 2,5-Dichloro-3,4-dinitrothiophene (DCDNT)



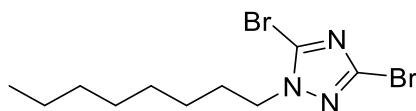
DCDNT was prepared following the modification from previous work [68]. Mixture of fuming HNO_3 (7 mL) and conc. H_2SO_4 (30 mL) was added into a round bottom flask and the solution was stirred and cooled in an ice bath. 2,5-Dichlorothiophene (2.10 mL, 20 mmol) was added dropwise. The reaction was maintained at temperature 5-10 °C until completion (3 h). The mixture was poured over large amount of ice. The solid crude was recovered by vacuum filtration. The crude product was purified by column chromatography (eluent= Hexane: EtOAc = 8:2) which gave the product as pale yellow solid (3.45 g, 71.4 %yield). (lit. mp. 81-83 °C [68]). IR (ATR, cm^{-1}): 1546, 1394 (N-O st). (Figure A.1, Appendix) ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 136.8, 127.8. (Figure A.2, Appendix)

2.3.2 1,4-Dibromo-2,5-bis(octyloxy)benzene (DBOB)



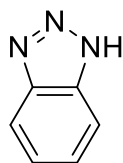
A mixture of 1,4-dibromohydroquinone (2.104 g, 8 mmol), potassium carbonate (2.756 g, 20 mmol), octyl bromide (3.870 g, 20 mmol) and sodium sulfite (2.050 g, 16 mmol) was dissolved in DMF (15 mL) and heated to 80 °C under nitrogen atmosphere for 6 h. After cooling to room temperature, the reaction was added 10 mL of water and 15 mL of ethyl acetate. The organic phase was washed three times with additional water and then dried over anhydrous magnesium sulfate. After evaporation of solvent, the crude mixture was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane= 1:9). The product was obtained as a light-yellow solid. (3.402 g, 88.0% yield), (lit. [22, 69] mp 64-66 °C). $^1\text{H NMR}$ (CDCl_3): δ (ppm) 7.06 (s, 2H), 3.92 (t, 4H), 1.80 (m, 4H), 1.48 (m, 4H), 1.35 (m, 16H), 0.88 (t, 6H). (Figure A.3, Appendix)

2.3.3 3,5-Dibromo-1-octyl-1H-1,2,4-triazole (DBOTZ)



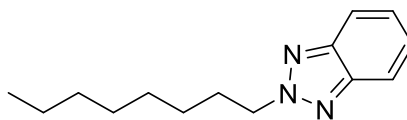
A solution of 3,5-dibromo-1H-1,2,4-triazole (0.710 g, 3.13 mmol), potassium carbonate (0.501 g, 3.63 mmol), and octyl bromide (0.886 g, 4.59 mmol) in acetonitrile (10 mL) was heated to reflux under nitrogen atmosphere for 6 h. Then the reaction was cooled down to room temperature, followed by an addition of 20 mL of water and extracted two times with ethyl acetate (20 mL). The separated organic layer was dried over anhydrous magnesium sulfate (MgSO_4). After evaporation of solvent, the crude product was purified by column chromatography on silica gel using 2:8 mixture of EtOAc:hexane as the eluent to afford the product as light yellow liquid (1.021 g, 96.5% yield). [70] ^1H NMR (CDCl_3) δ (ppm): 4.10 (t, 2H), 1.83 (m, 2H), 1.26 (br, m, 14H), 0.85 (m, 3H). (Figure A.4, Appendix) ^{13}C NMR (CDCl_3) δ (ppm): 139.9, 129.2, 50.2, 31.7, 29.2, 28.9, 28.9, 26.2, 22.6, 14.0. (Figure A.5, Appendix) FT-IR (ATR, cm^{-1}): 2953, 2925, 2853, 1457, 1432, 1257. (Figure A.6, Appendix) MS: m/z 339 (M^+). (Figure A.7, Appendix)

2.3.4 1H-Benzo[d]-1,2,3-triazole



o-Phenylenediamine (1.083 g, 10 mmol) was mixed with glacial acetic acid (35 mL). Sodium nitrite (NaNO₂) (1.060 g, 15 mmol) was dissolved in water (20 mL). The two solutions were kept in ice bath to below 5-10°C before adding the latter to the former solution dropwise. Then, the reaction was stirred for another 30 min in ice bath and then sodium hydroxide (1 M) was added until the solution turned neutral. After that, it was extracted with ethyl acetate (20 mL), which was washed with water (20 mL). The organic layer was dried over anhydrous magnesium sulfate (MgSO₄). After evaporation of solvent, the crude product was purified by column chromatography (eluent= hexane: EtOAc= 1:1) and gave the product as light-yellow solid. (0.761 g, 63.75 %yield) (lit.[71] mp 99-100 °C) ¹H NMR (CDCl₃) δ (ppm): 7.97 (d, 2H), 7.48 (dd, 2H) (Figure A.8, Appendix) FT-IR (ATR, cm⁻¹): 3338, 3244, 2790, 1206, 1005, 777, 751, 738, 704. (Figure A.9, Appendix) MS: m/z 119 (M⁺). (Figure A.10, Appendix)

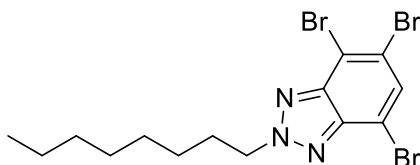
2.3.5 2-octyl-2H-benzo[d][1,2,3]triazole (2)



2

The mixture of 1H-Benzo[d]-1,2,3-triazole (0.720 g, 6 mmol), octyl bromide (1.745 g, 9 mmol), potassium tert-butoxide (1.009 g, 9 mmol) was dissolved in DMF 10 mL and heated to 140 °C for 24 h. The reaction was then cooled down at room temperature and extracted with ethyl acetate (15 mL) and water (15 mL). The separated organic layer was dried with anhydrous magnesium sulfate (MgSO₄). After evaporation of solvent, unfortunately the crude product contained two major compounds: the symmetric product (**2**) and the asymmetric product (**9**). (described in section 3.1.5) It was further purified by column chromatography (eluent= hexane: EtOAc= 9:1) to give the desired product (**2**) as yellow oil. [72] (0.548 g, 37.01%) ¹H NMR (CDCl₃) δ (ppm): 7.84, 7.36, 4.70, 2.09, 1.32, 1.23, 0.84. (Figure A.12, Appendix) ¹³C NMR (CDCl₃) δ (ppm): 132.9, 126.1, 117.9, 57.50, 56.6, 31.7, 30.1, 28.9, 26.6, 14.0 (Figure A.13, Appendix) FT-IR (ATR, cm⁻¹): 2952, 2922, 2853, 1466, 1426, 1174, 975. (Figure A.14, Appendix) MS: m/z 231 (M⁺). (Figure A.15, Appendix)

2.3.6 4,6,7-Tribromo-2-octyl-2H-benzo[d]-1,2,3-triazole (3)



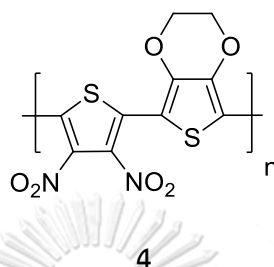
3

The mixture of compound **2** (0.548 g, 2.4 mmol), liquid Br₂ (0.72 mL, 12 mmol), FeCl₃ (1.557 g, 9.6 mmol) was dissolved in 1,2-dichloroethane (5 mL) and stirred at room temperature for 24 h. Then, excess sodium sulfite (Na₂SO₃) (0.5 g) was added to eliminate the remaining Br₂ until the solution changed from brown to light yellow. The solution was extracted by ethyl acetate (15 mL) and water (15 mL). The organic layer was dried with anhydrous magnesium sulfate (MgSO₄). After evaporation of solvent, the crude product was purified by column chromatography (eluent= hexane: EtOAc= 9:1) and gave the product as orange oil (0.879 g, 95.36 %yield). ¹H NMR (CDCl₃) δ (ppm): 7.71 (d, 2H), 4.71 (t, 2H), 2.10 (m, 4H), 1.31 (m, 4H), 1.21 (m, 4H), 0.81 (t, 3H) (**Figure A.16, Appendix**) ¹³C NMR (CDCl₃) δ (ppm): 143.0, 132.8, 126.0, 122.5, 113.7, 110.3, 31.6, 30.0, 29.00, 28.9, 26.4, 22.5, 14.0. (**Figure A.17, Appendix**) FT-IR (ATR, cm⁻¹): 2952, 2921, 2857, 1415, 1169. (**Figure A.18, Appendix**) MS: m/z 461 (M⁺). (**Figure A.19, Appendix**)

2.4 Polymer Synthesis

2.4.1 poly(3,4-ethylenedioxythiophene-co-3,4-dinitrothiophene)

(poly(EDOT-co-DNT) (4))

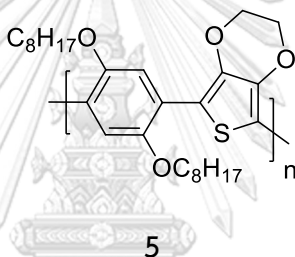


The mixture of EDOT (0.160 g, 1 mmol), DCDNT (0.202 g, 1.5 mmol), palladium acetate ($\text{Pd}(\text{OAc})_2$) (0.012 g, 0.05 mmol), cesium carbonate (0.782 g, 2.4 mmol), and triphenylphosphine (0.027 g, 0.1 mmol) was dissolved in toluene (10 mL) and refluxed for 48 h. The reaction was cooled down to room temperature and the solution was extracted by ethyl acetate (EtOAc) (15 mL) and water (15 mL). The solution was dried with anhydrous magnesium sulfate (MgSO_4). After evaporation, an orange solid product was obtained. Due to its insolubility in all solvents, this product was not characterized.

In the second attempt, the mixture of EDOT (0.148 g, 1 mmol), DCDNT (0.258 g, 1.5 mmol), palladium acetate ($\text{Pd}(\text{OAc})_2$) (0.018 g, 0.05 mmol), sodium acetate (NaOAc) (0.372 g, 2.4 mmol), and triphenylphosphine (0.029 g, 0.1 mmol) was dissolved in toluene (10 mL) and refluxed for 16 h. The reaction was cooled down to room temperature and the solution was extracted by dichloromethane (DCM) (15 mL) and water (15 mL). The solution was dried with anhydrous magnesium sulfate (MgSO_4),

filtered, and evaporated at reduced pressure, which gave the product as brown solid (0.103 g, 31.69 %yield). ^1H NMR (CDCl_3) δ ppm: 4.42. (Figure A.20, Appendix) FT-IR (ATR, cm^{-1}): 2931, 1544, 1318. (Figure A.21, Appendix) $\lambda_{\text{max}} = 419$ nm (Figure A.22, Appendix) M_n (GPC) = 1503.

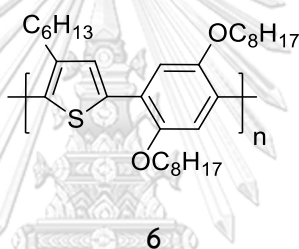
2.4.2 poly(3,4-ethylenedioxythiophene-co-1,4-(2,5-dioctoxyphenylene) (poly(EDOT-co-DOP)) (5)



The mixture of EDOT (0.085 g, 0.6 mmol), DBOB (0.2406 g, 0.49 mmol), palladium acetate ($\text{Pd}(\text{OAc})_2$) (0.006 g, 0.027 mmol), cesium carbonate (0.4035 g, 1.2 mmol), and triphenylphosphine (0.014 g, 0.05 mmol) was dissolved in toluene (4 mL). The mixture was heated at reflux for 24 h under nitrogen atmosphere. The reaction was cooled down to room temperature, added 0.5 M ethylenediaminetetraacetic acid (EDTA) at pH= 8 (15 mL) and stirred for another 12 h. The mixture was extracted with ethyl acetate (15 mL). Then, the organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure. The crude polymer was purified by column chromatography (eluent: EtOAc/ DCM= 1/1) to give the product as

a dark green solid (0.20 g, 86% yield). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 7.64, 4.34, 4.05, 1.87, 1.48, 1.26, 0.86. (Figure A.23, Appendix) FT-IR (ATR): 2923, 2845, 1457, 1426, 1354, 1204, 1082. (Figure A.24, Appendix) $\lambda_{\text{max}} = 451 \text{ nm}$ (Figure A.25, Appendix) M_n (GPC) = 5706.

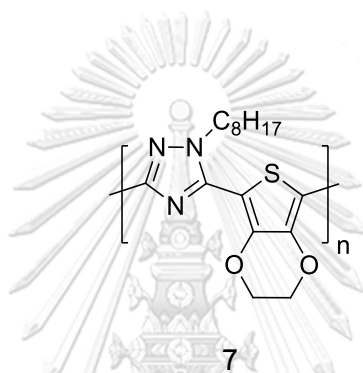
2.4.3 poly(3-hexylthiophene-co-1,4-(2,5dioctoxyphenylene)) (poly(3HT-co-DOP)) (6)



A mixture of 3-hexylthiophene (0.082 g, 0.49 mmol), DBOB (0.244 g, 0.49 mmol), palladium acetate (0.006 g, 0.027 mmol), pivalic acid (PivOH) (0.035 g, 0.34 mmol), cesium carbonate (0.40 g, 1.22 mmol), and triphenylphosphine (0.013 g, 0.05 mmol), was dissolved in toluene (4 mL) and refluxed for 24 h under nitrogen atmosphere. The reaction was cooled down to room temperature and added 0.5 M ethylenediaminetetraacetic acid (EDTA) at pH= 8 (15 mL) and stirred for another 12 h. Then, it was extracted with ethyl acetate (20 mL), and the separated organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated at a reduced pressure. Crude product was purified by column chromatography on silica gel (eluent: EtOAc/DCM= 1/1). The afforded product was yellow brown solid (0.159 g, 65.4% yield).

$^1\text{H NMR}$ (CDCl_3) δ (ppm): 7.45, 6.94, 4.06, 3.92, 2.58, 1.90, 1.68, 1.26, 0.86. (Figure A.26, Appendix) FT-IR (ATR): 2917, 2850, 1468, 1204, 1032. (Figure A.27, Appendix) $\lambda_{\text{max}} = 377$ nm (Figure A.28, Appendix) M_n (GPC) = 7431.

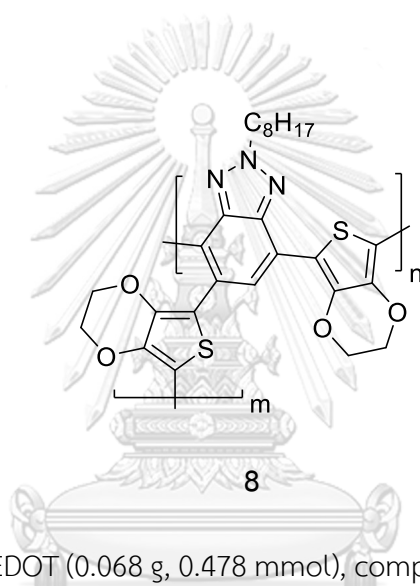
2.4.5 poly(3,4-ethylenedioxythiophene-co-3,5-(1-octyl-1,2,4-triazolene)) (poly(EDOT-co-OTZ)) (7)



DBOTZ (0.176 g, 0.51 mmol), EDOT (0.075 g, 0.53 mmol), palladium acetate (0.006 g, 0.026 mmol), cesium carbonate (0.410 g, 1.26 mmol), triphenylphosphine (0.015 g, 0.06 mmol), and pivalic acid (0.030 g, 0.29 mmol) were dissolved in 1,4-dioxane (4 mL) under nitrogen atmosphere. The mixture was heated at reflux for 24 h and then cooled down to room temperature, added 0.5 M ethylenediaminetetraacetic acid (EDTA) at pH = 8 (15 mL) and stirred for another 12 h. The reaction was extracted with ethyl acetate (20 mL), dried the separated organic layer over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure. Crude product was purified by column chromatography on silica gel eluent: EtOAc/hexane = 2/8 and gave the product as yellow brown solid (0.138 g, 83.2% yield). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 4.39,

4.24, 3.76, 2.04, 1.88, 1.73, 1.26, 0.86. (Figure A.29, Appendix) FT-IR (ATR, cm^{-1}): 2953, 2914, 2848, 1676, 1432, 1116, 1080. (Figure A.30, Appendix) $\lambda_{\text{max}} = 305 \text{ nm}$ (Figure A.31, Appendix) M_n (GPC) = 1816.

2.4.6 poly(3,4-ethylenedioxythiophene-co-4,7-(2-octyl-2H-benzo[d]-1,2,3-triazolene) (poly(EDOT-co-OBTZ)) (8)



The mixture of EDOT (0.068 g, 0.478 mmol), compound **3** (0.188 g, 0.483 mmol), palladium acetate (0.006 g, 0.025 mmol), triphenyl phosphine (0.015 g, 0.057 mmol), cesium carbonate (0.396 g, 1.21 mmol), and PivOH (0.008 g, 0.07 mmol) was dissolved in DMAc as the solvent (5 mL) and refluxed for 24 h under nitrogen atmosphere. The reaction was cooled down to room temperature, added 0.5 M ethylenediaminetetraacetic acid (EDTA) at pH = 8 (15 mL) and stirred for another 12 h. The mixture was extracted with DCM (25 mL), and the organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure. The crude solid was washed with 50% MeOH: H₂O and hexane respectively to give the

product as orange-red solid (0.290 g, 77.2%). ^1H NMR (CDCl_3) δ (ppm): 8.30, 6.41, 4.66, 4.19, 4.06, 4.04, 2.03, 1.98, 1.19, 0.77. (Figure A.32, Appendix) FT-IR (ATR): 2912, 2855, 1499, 1433, 1359, 1071. (Figure A.33, Appendix) $\lambda_{\text{max}} = 407$ nm (Figure A.34, Appendix) M_n (GPC) = 3537.

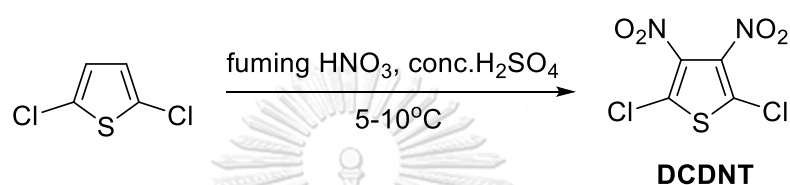


CHAPTER III

RESULTS AND DISCUSSION

3.1 Monomers Synthesis

3.1.1 2,5-Dichloro-3,4-dinitrothiophene (DCDNT)



DCDNT was synthesized through electrophilic nitration reaction from 2,5-dichlorothiophene [73]. The conditions were varied according to **Table 3.1**.

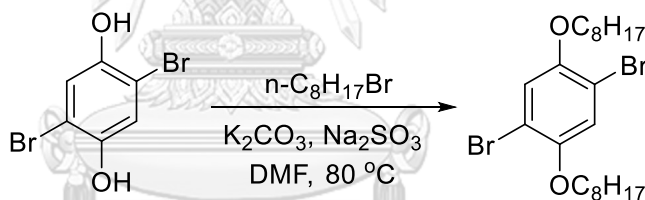
Table 3.1: The synthesis conditions for DCDNT

Entry	2,5-dichlorothiophene (mmol)	fuming HNO ₃ (mL)	conc. H ₂ SO ₄ (mL)	Time (h)	Product (%yield)
1	5	1.5	7.5	3	48.9
2	20	7	30	3	71.4
3	20	7	30	4	68.9

Following **Table 3.1**, the optimized time and scale of the reaction were investigated. High yields of the product were obtained in the larger scale. (Entries 2 and 3) The lower yield in small scale (Entry 1) was partly due to incomplete reaction

as we found the leftover reactant spot on TLC of the crude product solution after quenching the reaction. Larger amount of the nitrating agents could complete it, while the increased time of the reaction did not affect the yield of the product. The structure of the product was confirmed by strong and sharp peak of the IR signal at 1549 and 1309 cm^{-1} the nitro groups. (Figure A.1, appendix) It showed no signal in ^1H NMR spectrum as expected. The ^{13}C NMR spectrum (Figure A.2, appendix) also showed the signals peak that matched with those from the previous reported [68].

3.1.2 1,4-Dibromo-2,5-bis(octyloxy)benzene (DBOB)

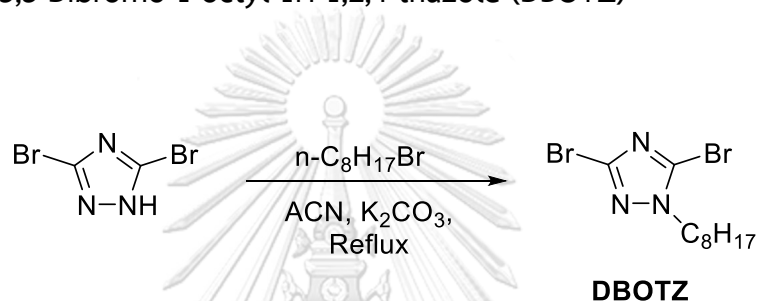


DBOB was synthesized from 2,5-dibromo-1,4-hydroquinone through excessive nucleophilic substitution on n-octyl bromide. [22] High yields of the product were obtained at larger scale of the reaction and longer time, optimized at approximately 6 h. (Table 3.2, entry 2) The product was characterized by NMR spectroscopic methods (Figure A.3, Appendix), in which all the data matched well with the expected structure and the corresponding information from literature. [22, 69, 74]

Table 3.2: Conditions for the synthesis of DBOB

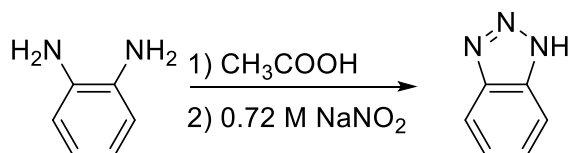
Entry	2,5-dibromo-1,4-hydroquinone (mmol)	n-C ₈ H ₁₇ Br (mmol)	Time (h)	%Yield
1	4	10	4	69.3
2	8	20	6	88.0
3	8	20	8	86.5

3.1.3 3,5-Dibromo-1-octyl-1H-1,2,4-triazole (DBOTZ)



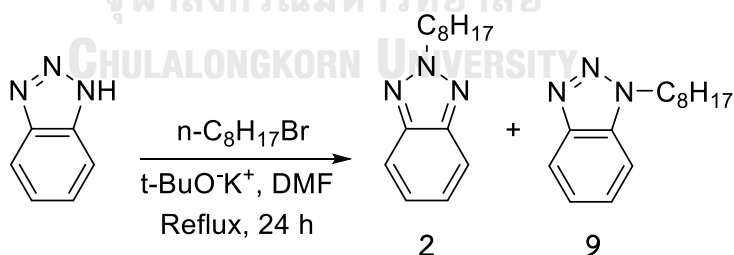
DBOTZ was successfully synthesized in high yield (96.5%) using the optimized methodology DBOB synthesis in section 3.1.2. The structure of the product was confirmed with ¹H NMR spectrum (Figure A.4, Appendix), ¹³C NMR spectrum (Figure A.5, Appendix), FT-IR spectrum (Figure A.6, Appendix) and Mass spectrum (Figure A.7, Appendix) by the appearance of proton signals of the octyl group and all the carbon signals in ¹H and ¹³C NMR spectra were well corresponded to the expected structure [70]. The fact that there were two distinct carbon signals of the triazole ring implied that the substitution reaction occurred at the 1-position rather than 4, giving the shown unsymmetrical isomer and hence two different carbon signals in ¹³C NMR spectrum.

3.1.4 1H-benzo[d]-1,2,3-triazole



The 1H-benzo[d]-1,2,3-triazole was synthesized from diazotization of o-phenylenediamine with intramolecular coupling following a method from a previous report [72]. The ^1H NMR spectrum showed the expected signals of four protons on benzo-aromatic ring at 7.97, 7.95, 7.48 and 7.46 ppm. (Figure A.8, Appendix) The product was obtained in good yield (63.8%).

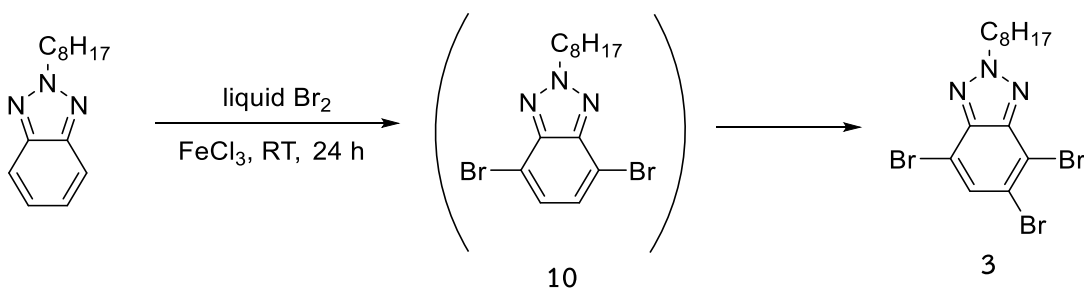
3.1.5 2-Octyl-2H-benzo[d]-1,2,3-triazole (2)



The 2-octyl-2H-benzo[d]-1,2,3-triazole (2) was synthesized through nucleophilic substitution on n-octyl bromide following a modification from literature using DMF instead of ethanol as the solvent [75]. This reaction unfortunately gave two

major products: the desired symmetric products (**2**) and the asymmetry products (**9**) in approximately equal amount. Using DMF as the solvent seemed to obtain higher amount of compound **2** than in ACN. The ^1H NMR spectrum of compound **2** showed the expected two signals of protons on benzo-aromatic ring at 7.84 and 7.36 ppm and the signal of α -protons on alkyl side chain at 4.70 ppm, (Figure A.12, Appendix) and the corresponding eleven ^{13}C NMR signals. (Figure A.13, Appendix) The asymmetric compound **9** was confirmed by its ^1H NMR spectrum, in which four proton signals from asymmetric platform of the benzo-aromatic ring structure were found at 8.04, 7.49, 7.45 and 7.35 ppm. (Figure A.35, Appendix). The reaction obtained compounds **2** and **9** in 37.0% and 32.5 %yields, respectively. They could be separated by silica gel column chromatography eluted with 10%EtOAc: hexane at R_f 0.68 and 0.45 for compound **2** and **9**, respectively.

3.1.6 4,6,7-Tribromo-2-octyl-2H-benzo[d]-1,2,3-triazole (3)

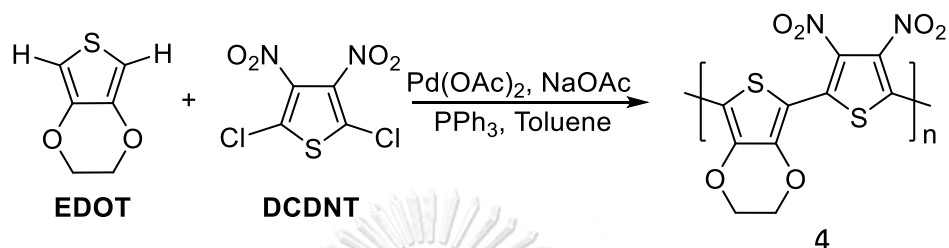


Compound **2** was then used as the starting material to prepare the dibromo derivative as one of the monomers. At first, the standard bromination was used. [76] It appeared that the aromatic ring of the starting material was too electron deficient to be directly brominated as no change in the reaction was observed. Consequently, a Lewis catalyst was added which could drive the reaction forward. Unfortunately, over-brominations on the benzene ring was obtained in this case. The unexpected tribromo product **3** was confirmed by 1H NMR spectrum that showed the one singlet signal at 7.71 ppm (Figure A.16, Appendix), which was more downfield than 7.43 ppm expected from the aromatic proton signal of the desired dibromo product **10** reported in the literature [76]. ^{13}C NMR spectrum of compound **3** also showed extra signals that did not correspond to the dibromo **10**. (Figure A.17, Appendix) Mass spectrum also confirmed compound **3**, as revealed the molecular ion at 461 (M^+). (Figure A.19, Appendix)

3.2 Polymerization of Monomers

3.2.1 poly(3,4-ethylenedioxythiophene-co-3,4-dinitrothiophene)

(poly(EDOT-co-DNT) (4))



DCDNT and EDOT were used as the starting precursors in the first attempt to use direct C-H arylation polymerization. The original condition of this reaction was first carried out using cesium carbonate (Cs₂CO₃) as the base according to **Table 3.3, entry 1**. [77] Unfortunately, no characterizable new product could be detected or isolated. Only unreacted monomers and insoluble black solid were found. It is possible that the reaction was too slow to give the copolymer and parts of the monomers decomposed or polymerized to its corresponding insoluble homopolymers instead. Surprisingly, the repeated reaction using sodium acetate (NaOAc) as base was successful and gave a partially soluble product in which the soluble part could be confirmed its structure by ¹H NMR, and IR spectra. [78] The ¹H NMR spectrum showed the signal at 4.42 ppm from the proton on ethylene bridge of EDOT units, while the IR spectrum showed N-O stretching signals of nitro groups of dinitrothiophene units at 1544, 1318 cm⁻¹. (**Figure A.20 and A.21, Appendix**) The measurement of optical property exhibited a maximum wavelength absorption (λ_{max}) at 419 nm. (**Figure A.22,**

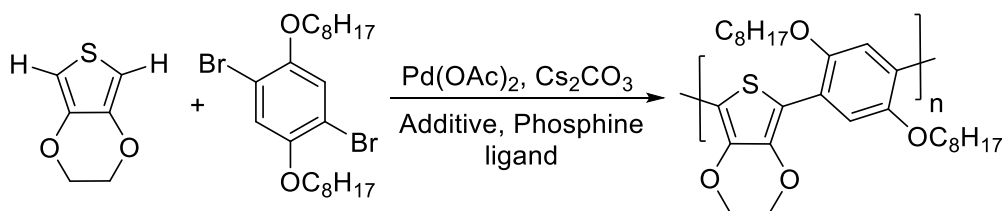
Appendix) It might be assumed that the obtained copolymer **4** was still relatively small because of its unexpected good solubility in common organic solvents despite its lack of the usually required long alkyl chains to assist in solubilization in most other large polymers.

Table 3.3: Conditions for the synthesis of copolymer **4**

Entry	Base	Solvent	Temperature	Reaction Time (h)	%Yield
1	Cs ₂ CO ₃	Toluene	reflux	48	- ^a
2	Cs ₂ CO ₃	Toluene	rt	24	- ^a
3	NaOAc	Toluene	rt	16	31.7

^aNo characterizable product was obtained

3.2.2 poly(3,4-ethylenedioxythiophene-co-2,5-dioctoxy-1,4-phenylene) (poly(EDOT-co-DOP)) (**5**)



5

The desired copolymer **5** was successfully synthesized through direct C-H arylation of EDOT with DBOB as the dibromoarene partner. The conditions of the

reaction were varied according to **Table 3.4** following a modification of a reported protocol that included the triphenylphosphine ligand and pivalic acid (PivOH) additive [79]. For this polymerization, the use of refluxing dimethylacetamide (DMAc) with 30% PivOH was not a suitable choice of the reaction (**Entry 1**), as it gave low yield and low λ_{max} value of the absorption of the resulted product. It was assumed that DMAc partially decomposed at high temperature in this condition and heavily contaminate the reaction. Reducing the temperature to 110°C in DMAc solvent (**Entry 2**) improved yield and λ_{max} of the UV-Vis absorption. On the other hand, using toluene as solvent, [80] good results were mostly obtained even without an additive. (**Entry 3-5**) 1,4-Dioxane could also be used, although with lower λ_{max} of UV-Vis absorption of the product. (**Entry 6**) Replacing the additive with trifluoroacetic acid (TFA) in toluene solvent also improved the product yield, but with low λ_{max} value. (**Entry 7**) Finally, using trialkyl phosphine as the ligand resulted in a total failure of the reaction. (**Entry 8**)

Table 3.4: The synthesis conditions of polymer **5^a**

Entry	Ligand	Additive	Solvent	Temperature (°C)	λ_{max} (nm)	Yield (%)	M_n
1	PPh ₃	30% PivOH	DMAc	reflux	330	20	621
2	PPh ₃	10% PivOH	DMAc	110	407	74.2	1908
3	PPh ₃	30% PivOH	Toluene	reflux	451	45	1815
4	PPh ₃	10% PivOH	Toluene	reflux	451	81.6	4107
5	PPh ₃	-	Toluene	reflux	450	86	2057
6	PPh ₃	30% PivOH	1,4-	Reflux	423	98.6	1790
7	PPh ₃	30% TFA	Dioxane	Reflux	420	96	1211
8	P(n- Bu) ₃	30% PivOH	Toluene Toluene	reflux	-	-	-

^aReaction time was limited at 24 h.

Despite all the successful synthetic results, the copolymers obtained so far in these cases were found to be arranged randomly, considering from unequal incorporations of two monomer units as reflected in the unequal integrations of ¹H NMR signals of -CH₂O- groups from part of either monomers. (**Figure 3.1A**). The more downfield signals are from EDOT units. Surprisingly, when no acid additive was present in the reaction, (**Entry 5 in Table 3.4**) the copolymer appeared to be derived from alternately connections of the two monomers as deduced from the equal integrations of the NMR signals from the same region (**Figure 3.1B**). Such ordered arrangement also gave the bathochromic shift of the λ_{max} to 450 nm in its UV-visible

spectrum. The reason for the apparent alternating connection might come from slower reaction in the absence of an acid additive, resulting in better selectivity.

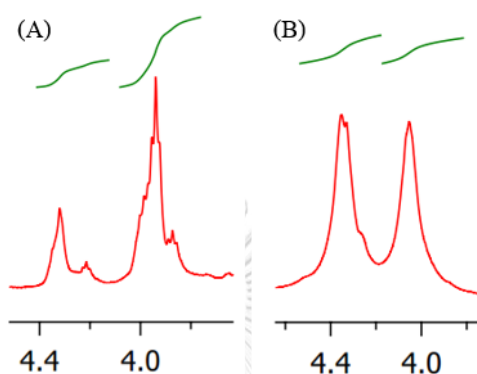
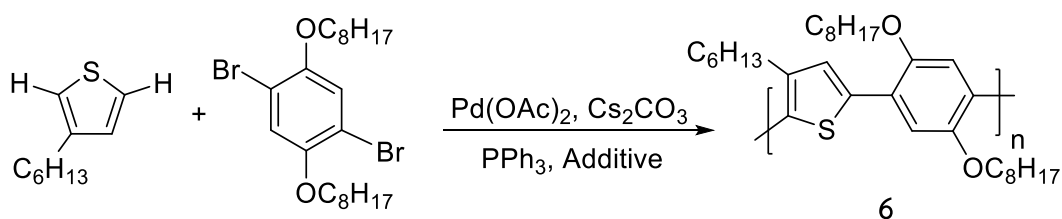


Figure 3.1: Partial ^1H NMR spectra of the synthesized poly(EDOT-co-DOP) (A) without alternating (random) connection, (B) with alternating connection

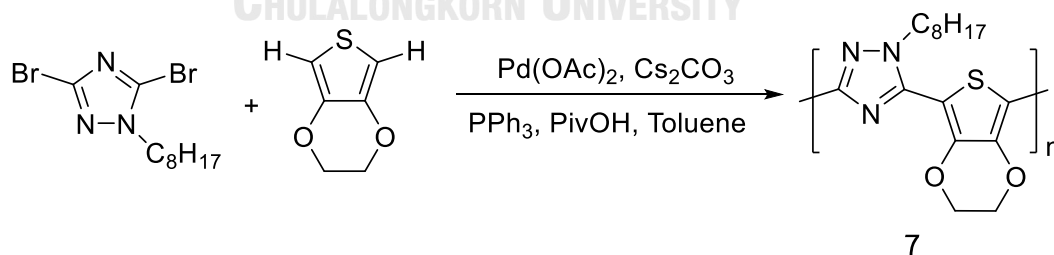
3.2.3 poly(3-hexylthiophene-co-2,5-dioctoxy-1,4-phenylene) (poly(3HT-co-DOP)) (6)



Similar copolymerization was performed between 3-HT and DBOB. The initial attempt using no-additive condition was unsuccessful, which could be due to the low reactivity of 3-HT toward C-H arylation because of lower electron density than EDOT

used in previous sections. The reaction adding PivOH was successful and obtained the desired copolymer **6** as yellow brown solid in 65.4% yield. The confirmation of the structure of the product was evidenced by the appearance of the ^1H NMR signals with chemical shift values that corresponded to the expected copolymer. (Figure A.19, Appendix) However, the alternated connection could not be clearly justified because of the overlapped signals of 3-HT units. The optical property of desired copolymer exhibited a relatively low λ_{max} of 377 nm in UV-visible spectrum. (Figure A28, Appendix) It is possible that both relatively short polymeric chain from slow reaction rate and a non-perfectly alternating connection of the obtained copolymer contributed to the disappointed results.

3.2.4 poly(3,4-ethylenedioxythiophene-co-1-octyl-3,5-triazolene) (poly(EDOT-co-OTZ)) (**7**)



The direct C-H arylation polymerization using EDOT as the electron rich monomeric unit was continued on the couple with DBOTZ electron poor unit. The conjugated copolymer **7** was successfully obtained as yellow brown solid in good yield

with well corresponding NMR signals to the expected structure. However, the UV-Vis absorption of the resulted copolymer exhibited unexpectedly low maximum wavelength absorption (λ_{max}) at 305 nm. (**Figure A.31, Appendix**) This result may be due to the rather localized π -bonds in the triazole rings that maintain their aromaticity and would not effectively participate into the π -conjugated system along the polymeric chain, hence make the resulted copolymer becomes relatively non-conjugated. This problem may be solved using the isomer of the starting DBOTZ where the alkyl group was attached at the 4-position of the triazole ring. Despite many attempts to prepare such regioisomer, only the original 2-alkylated DBOTZ was always obtained as the only product. Furthermore, the lone pair electrons of the nitrogen atoms could coordinate with the palladium and behaved as a poison to the catalyst, which slowed down the reaction and shortened the polymeric chain. There is a possible way to circumvent the non-conjugated problem, when the triazole units of the copolymer were protonated by strong acid, in which the positive charges developed on the triazole rings could shift the π -system of these rings to reconnect with the π -conjugation along the chain as shown in **Figure 3.2**.

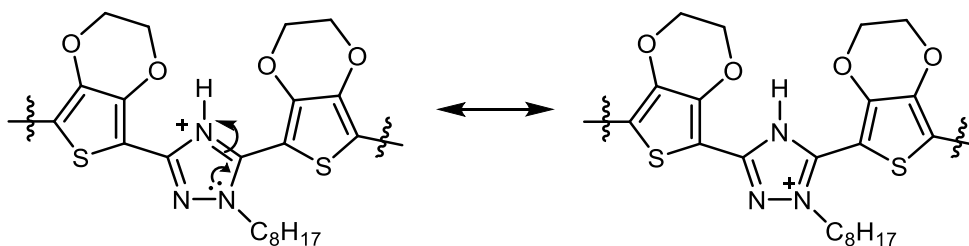


Figure 3.2: Resonance forms of the triazole rings of copolymer **7** after protonation

When we dropped TFA into the solution of copolymer **7**, the absorption of this copolymer slightly shifted to the red region (bathochromic) as shown in **Figure 3.3**. The color of the solution of this copolymer was changed from yellow to light green. When stronger acid like methanesulfonic acid was used instead of TFA, the absorption results were almost the same in term of red shifting of the λ_{max} values, and the signal baseline was increased (**Figure 3.4**), it seemed that the whole chain of the polymer was doped by the acid, not just the triazole moieties.

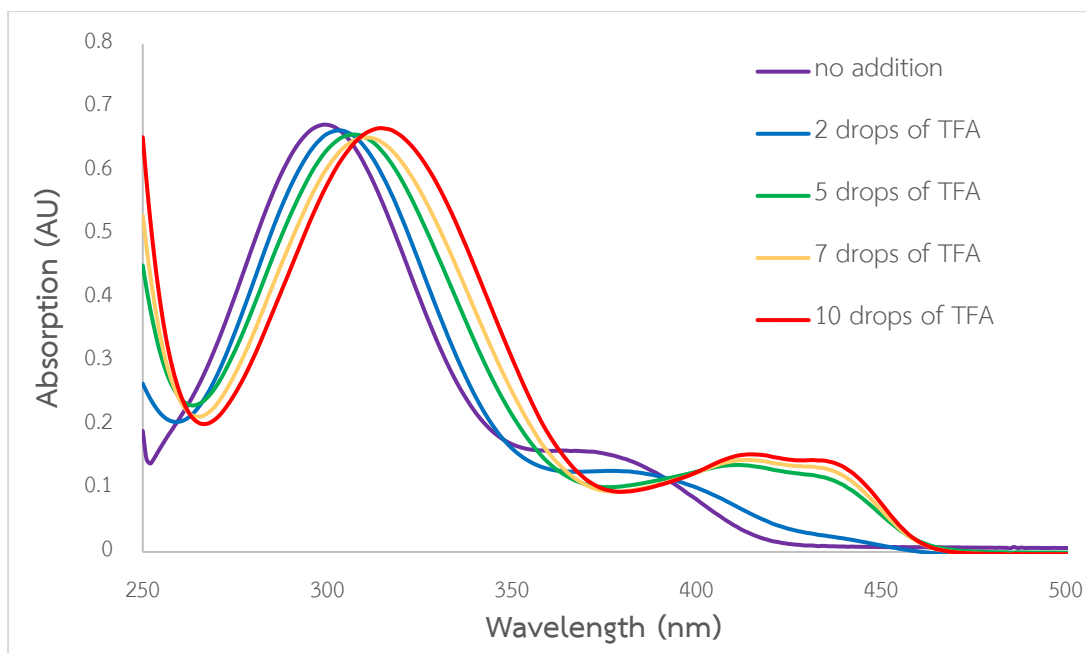


Figure 3.3: The UV-visible absorption of polymer 7 solution with addition of TFA

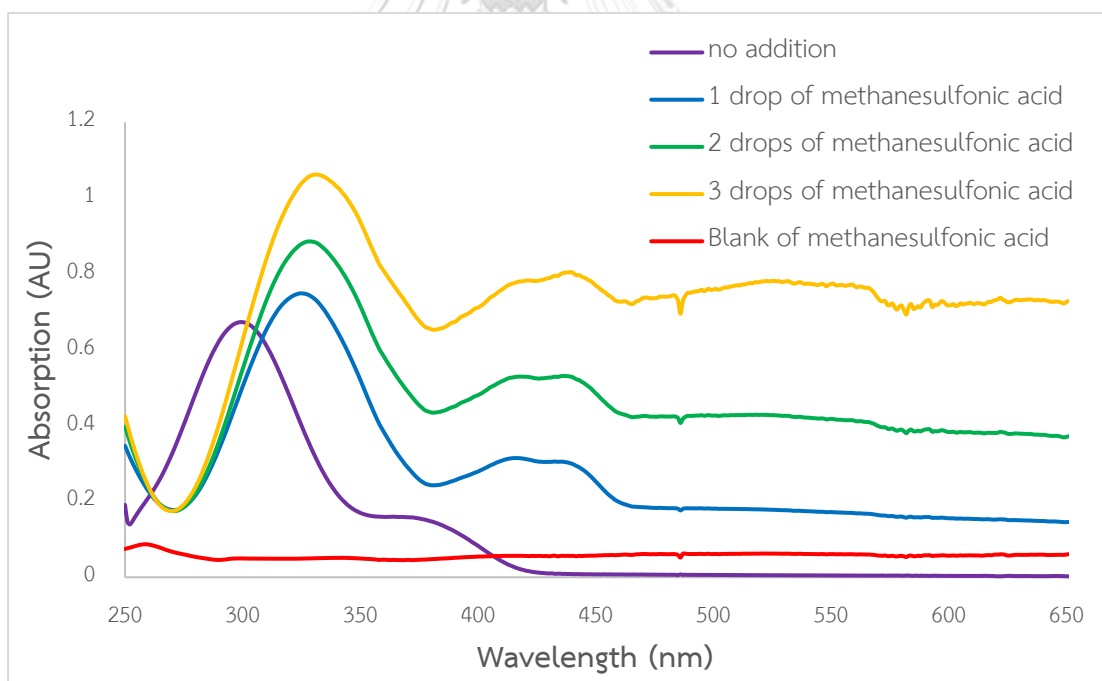
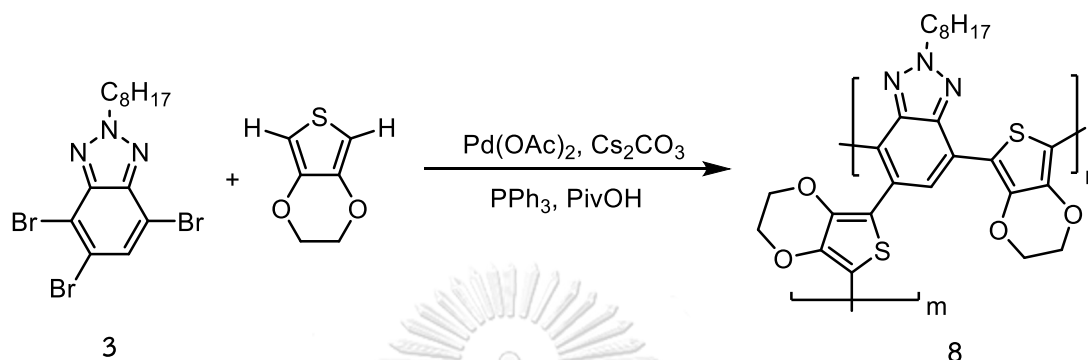


Figure 3.4: The UV-visible absorption of polymer 7 solution with addition of methanesulfonic acid

3.2.5 poly(3,4-ethylenedioxythiophene-co-2-octyl-2H-benzo[d]-1,2,3-triazolene) (poly(EDOT-co-OBTZ)) (**8**)



The donor-acceptor copolymer **8** was successfully synthesized from compound **3** and EDOT in high yield as orange solid. In this situation, we also used the same condition as the previous synthesis in either DMAc or toluene as the solvent. The copolymer **8** obtained from the reaction with DMAc solvent exhibited λ_{max} at 407 nm in UV visible spectrum and gave the product yield at 58.9% ($M_n=3537$). On the other hand, using toluene as the solvent gave slightly lower λ_{max} at 397 nm but the yield was improved to 77.2% yield ($M_n=3760$). It could also be concluded that these copolymers had relatively short polymeric chains which corresponded to low values of λ_{max} of UV-visible spectra. The desired alternating arrangements were perhaps not achieved due to the possibility of branching from the extra couplings on the tribromobenzotriazole units, as reflected in the non-corresponding ratio of integrations of 1H NMR signals from the protons on ethylene bridges of EDOT units and the protons

of -CH₂-N- of the alkylated-benzotriazole units. (Figure A.32, Appendix) It is assumed that the polymer might grow in various branched connections instead of linear chain, thus decreased the coplanarity between adjacent units and the effectiveness of the π -conjugated system of the backbone polymer.



CHAPTER IV

CONCLUSION

The synthesis of new conjugated copolymers containing 3,4-ethylenedioxythiophene (EDOT) or 3-hexylthiophene (3-HT) via direct C-H arylation polymerization had been accomplished. For monomer synthesis, 2,5-dichloro-3,4-dinitrothiophene (DCDNT) was synthesized from 2,5-dichlorothiophene using fuming HNO_3 in 71.4% yield. The 1,4-dibromo-2,5-bis(octyloxy)benzene (DBOB), 3,5-dibromo-1-octyl-1H-1,2,4-triazole (DBOTZ), and 4,6,7-tribromo-2-octyl-2H-benzo[d]-1,2,3-triazole (**3**) were also successfully synthesized from substitutions on n-octyl bromide in 88.0%, 96.5% and 95.4% yields, respectively.

1H-Benzo[d]-1,2,3-triazole was synthesized from diazotization of one of the amino groups of *o*-phenylenediamine followed by intramolecular coupling in 63.8%. It was used to make compound **2** through nucleophilic substitution reaction in 32.5% yield. After that, compound **2** was used to synthesize compound **3** through bromination reaction in 95.4% yield.

For polymer synthesis, polymer **4** was synthesized from the two precursors DCDNT and EDOT in 31.7% yield using NaOAc as the base. The ^1H NMR spectrum of partly dissolved polymer showed the expected signal at 4.42 ppm from ethylene bridge of the EDOT units, and the IR spectrum showed the expected signals at 1544

and 1318 cm^{-1} of the nitro groups of DCDNT. The optical properties showed the maximum wavelength absorption λ_{max} at 419 nm.

Polymer **5** was synthesized from DBOB and EDOT via direct C-H arylation polymerization in various yields depended on condition used. The desired alternating copolymer was obtained in toluene solution when no acid additive was added. This product also showed a relatively high value of maximum wavelength absorption (λ_{max}) at 450 nm.

On the other hand, pivalic acid was needed to achieve the synthesis of polymer **6** from 3-HT and DBOB, which was obtained in 65.4% yield. Its maximum wavelength absorption (λ_{max}) appeared lower than EDOT based copolymer at 377 nm.

Polymer **7** was synthesized from DBOTZ and EDOT via the same process in 83.2% yield. The optical absorption value (λ_{max}) was relatively low at 305 nm, due to the localized π -bonds in the triazole ring which made the resulted copolymer become non-conjugated. The chain conjugation could be reconnected by adding a strong acid such as TFA to shift π -bonds in the triazole rings. The optical properties of the copolymer were found to give red shifts of λ_{max} values upon adding the acid.

Polymer **8** was synthesized from TBOBTZ with EDOT also via direct C-H arylation polymerization in 58.9% and 77.2% yields using DMAc and toluene as the solvents, respectively. The appeared moderate maximum wavelength absorption (λ_{max}) of these

copolymers at 407 and 397 nm arised from chain branchings from the tribromobenzotriazole precursor.



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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

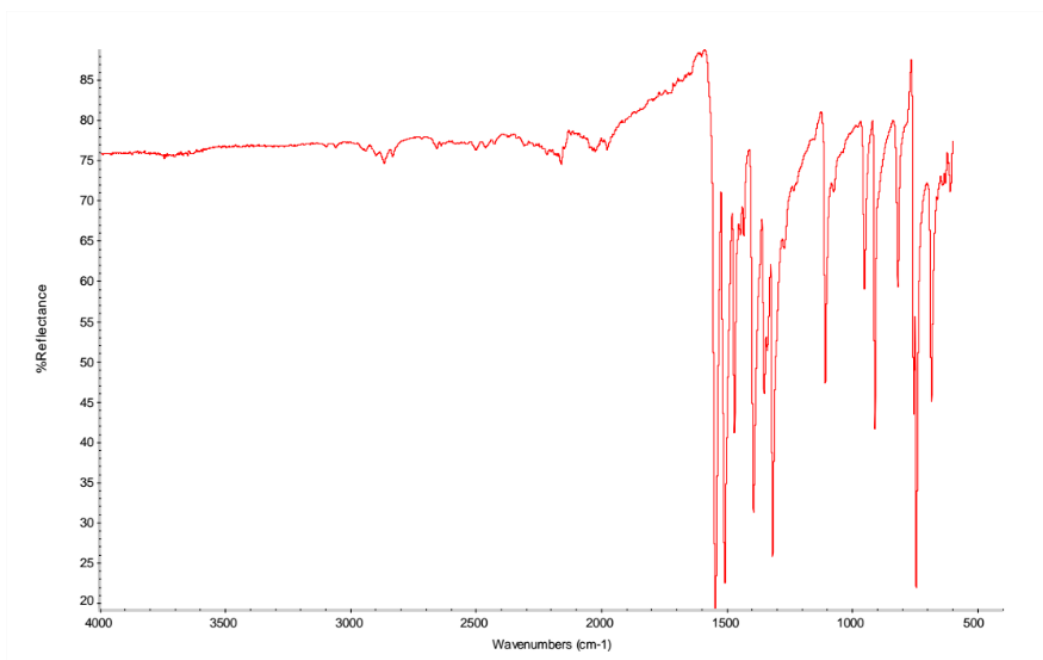


Figure A.1: IR spectrum of DCDNT

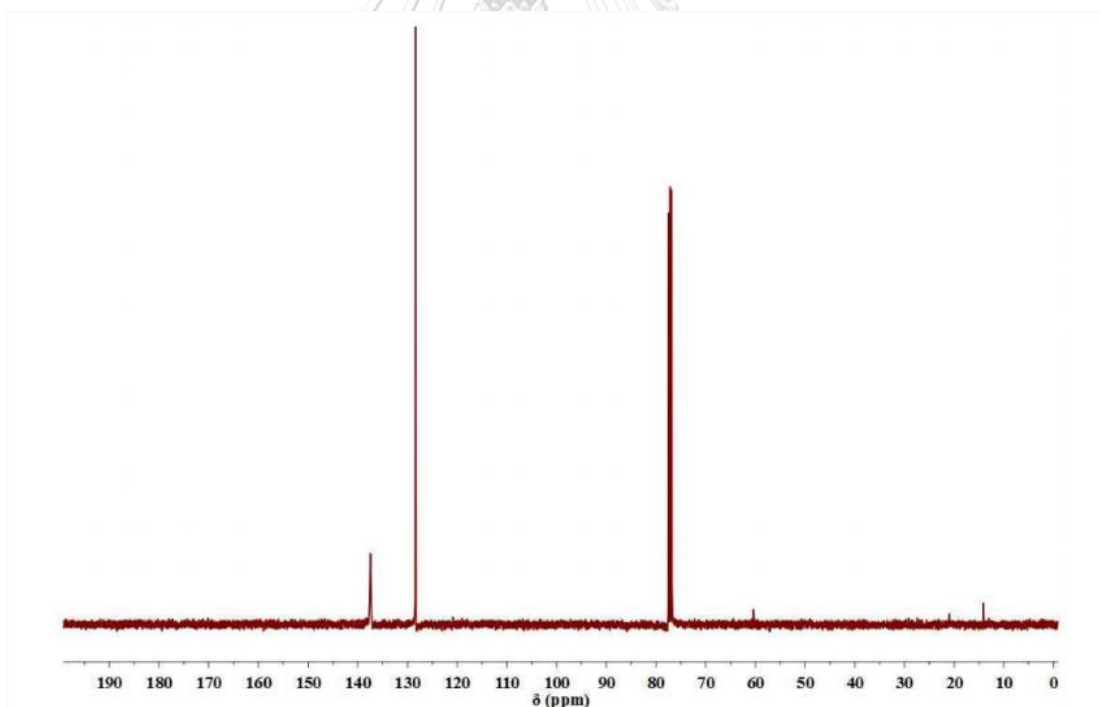


Figure A.2: ¹³C NMR (CDCl₃) spectrum of DCDNT

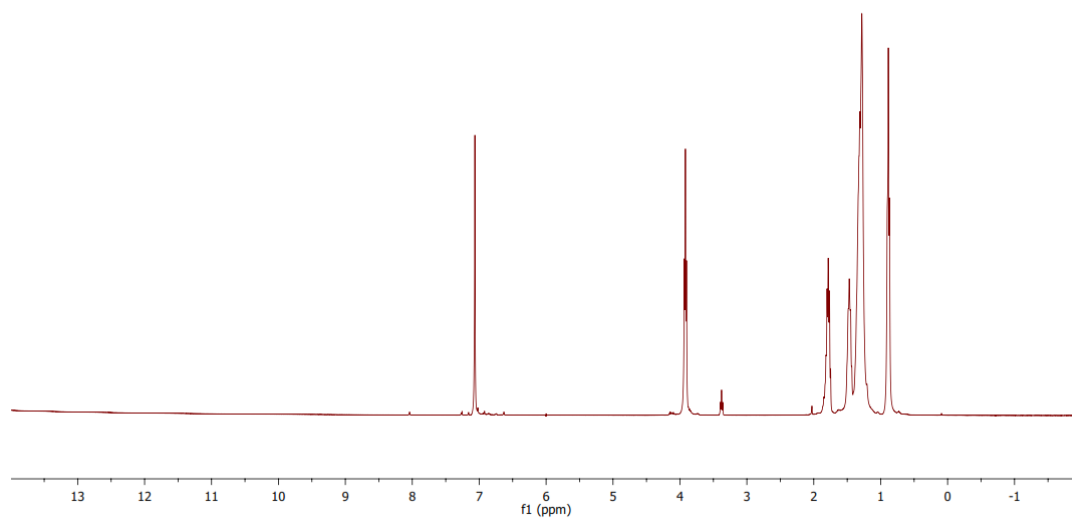


Figure A.3: ^1H NMR (CDCl_3) spectrum of DBOB



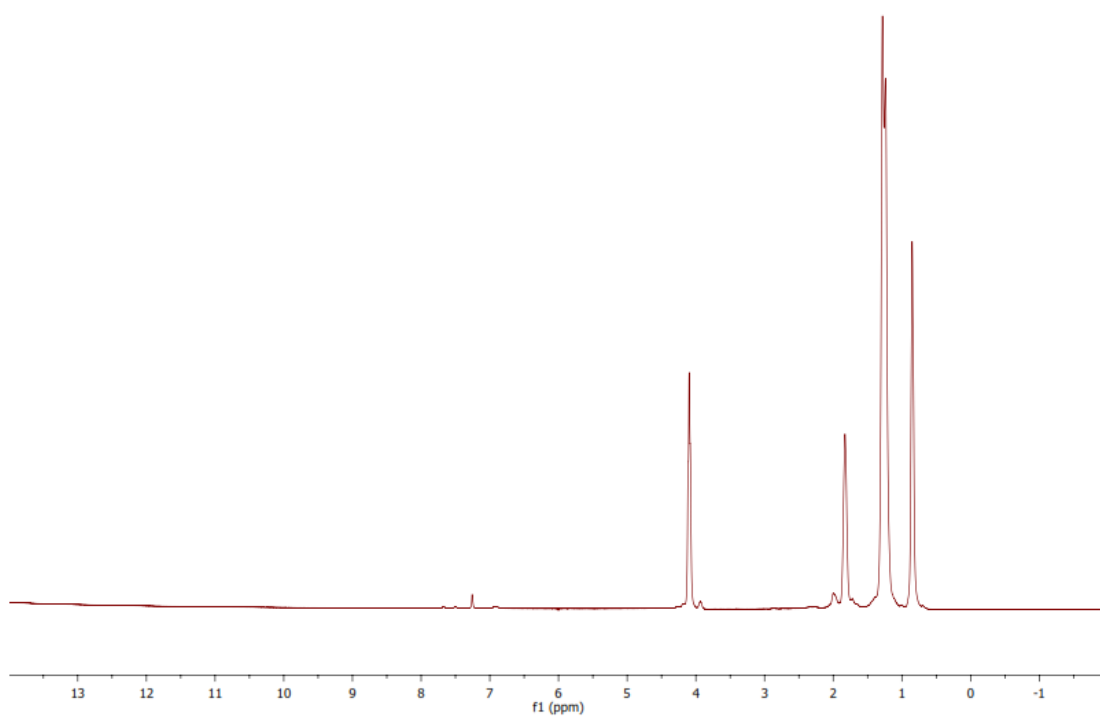


Figure A.4: ^1H NMR (CDCl_3) spectrum of DBOTZ

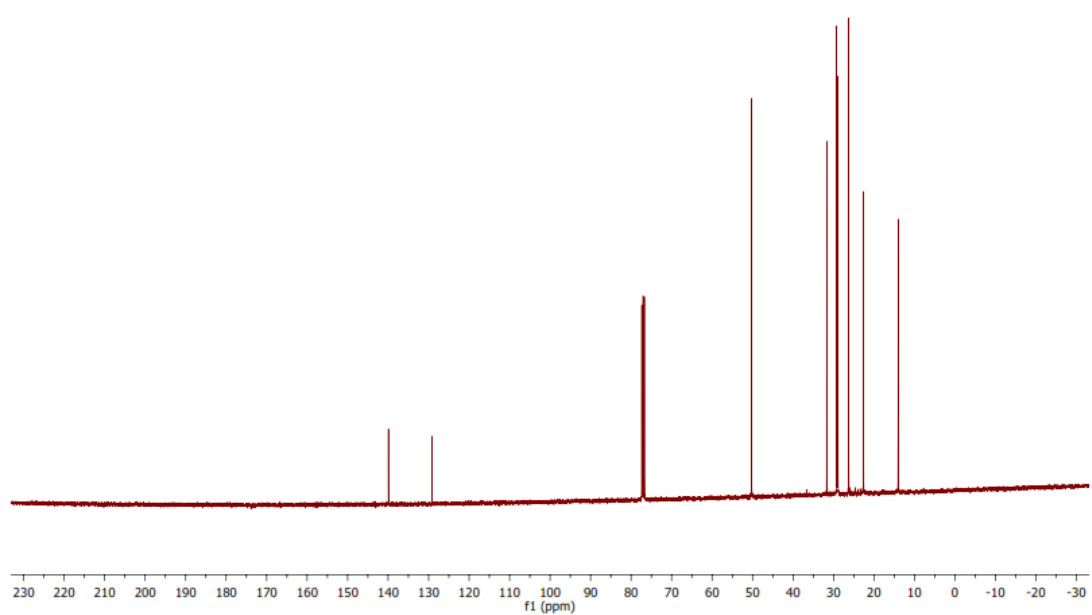


Figure A.5: ^{13}C NMR (CDCl_3) spectrum of DBOTZ

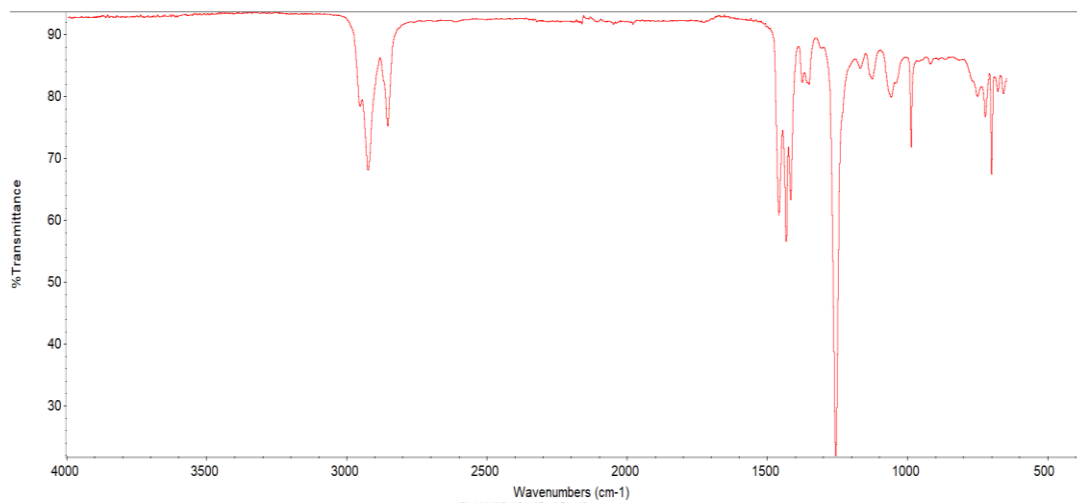


Figure A.6: IR spectrum of DBOTZ

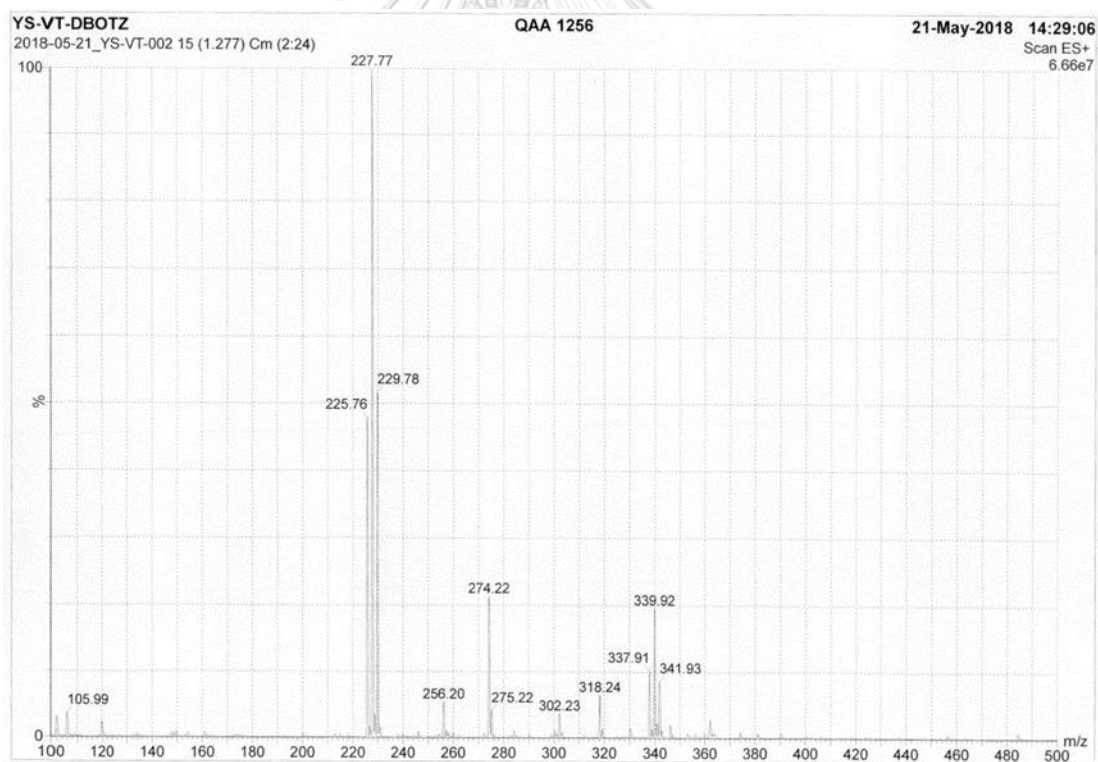


Figure A.7: Mass spectrum of DBOTZ

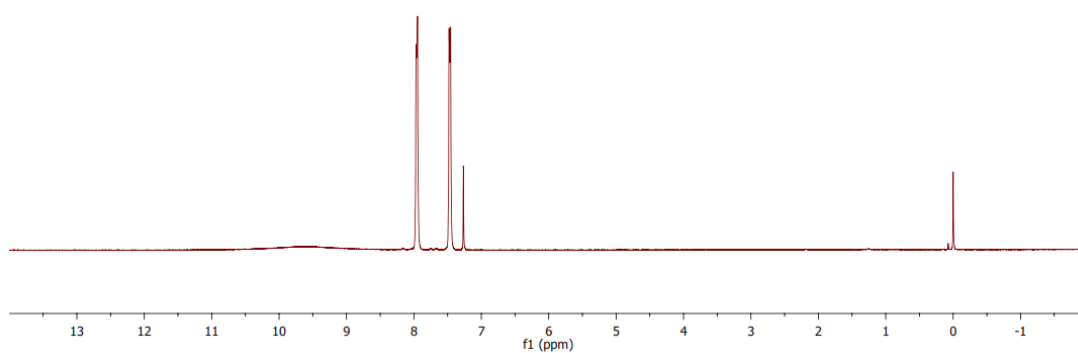


Figure A.8: ^1H NMR (CDCl_3) spectrum of 1H-Benzo[d]-1,2,3-triazole

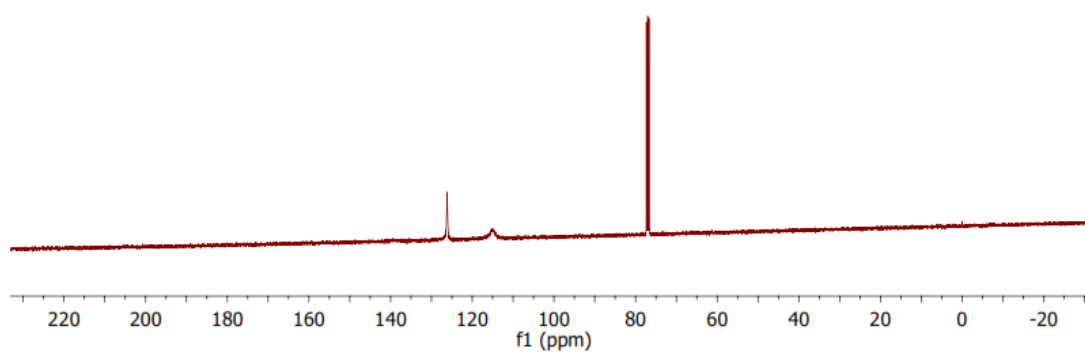


Figure A.9: ^{13}C NMR (CDCl_3) spectrum of 1H-Benzo[d]-1,2,3-triazole

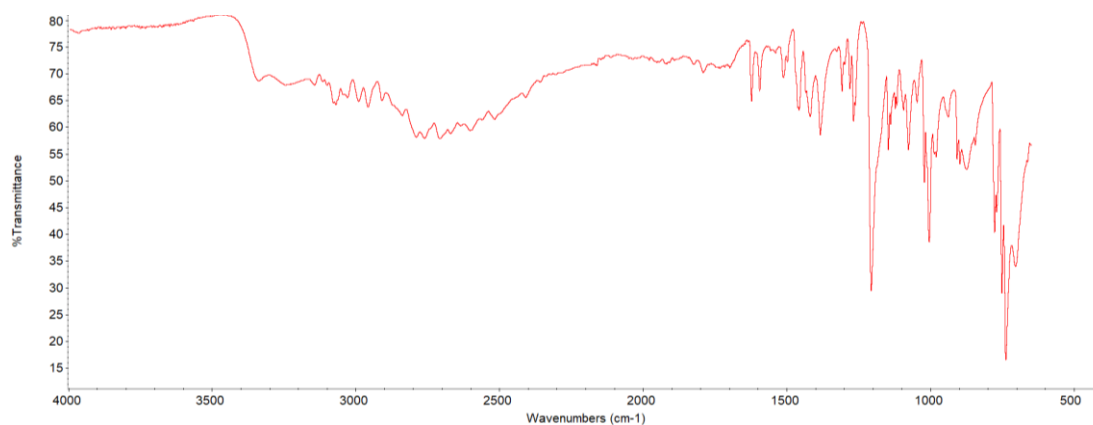


Figure A.10: IR spectrum of 1H-Benzo[d]-1,2,3-triazole

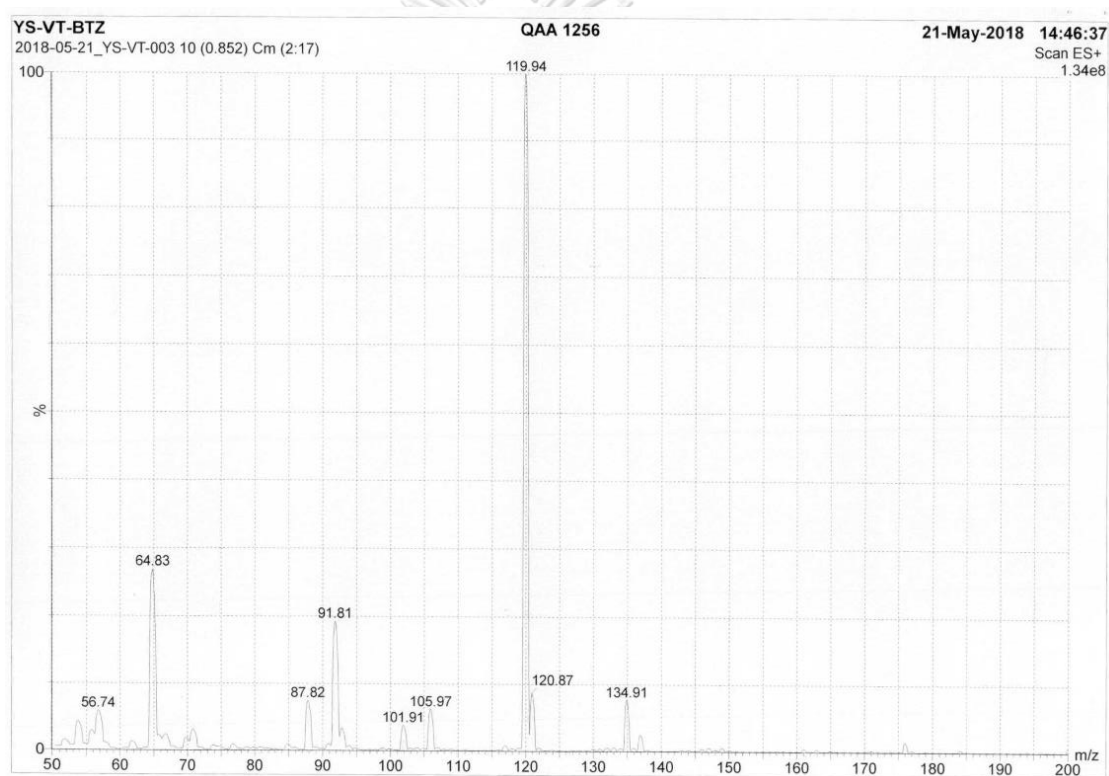


Figure A.11: Mass spectrum of 1H-Benzo[d]-1,2,3-triazole

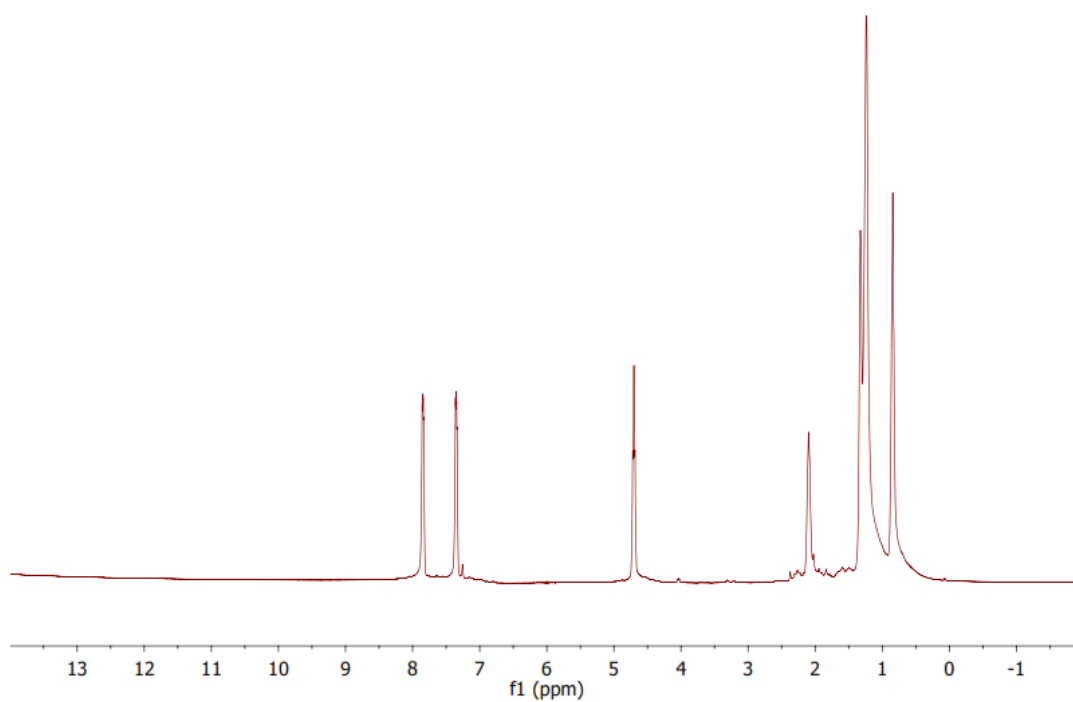


Figure A.12: ^1H NMR (CDCl_3) spectrum of compound 2

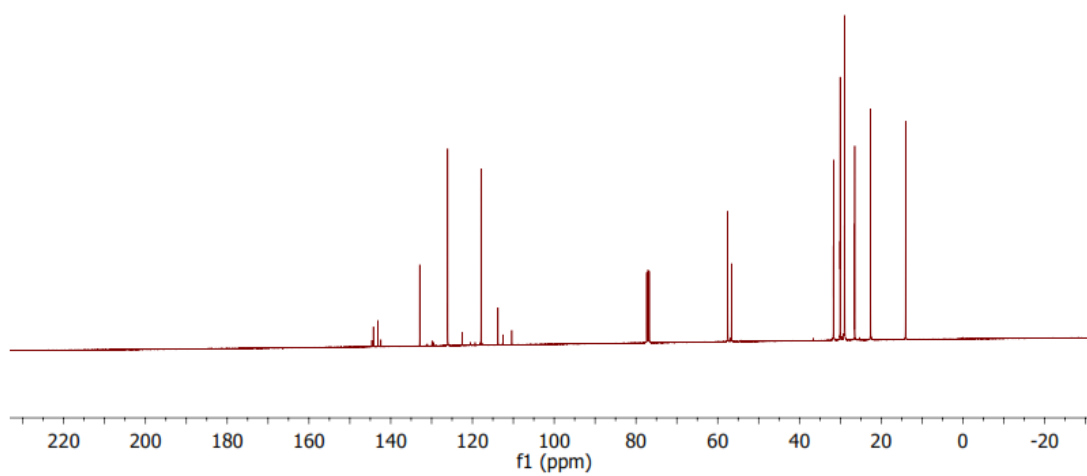


Figure A.13: ^{13}C NMR (CDCl_3) spectrum of compound 2

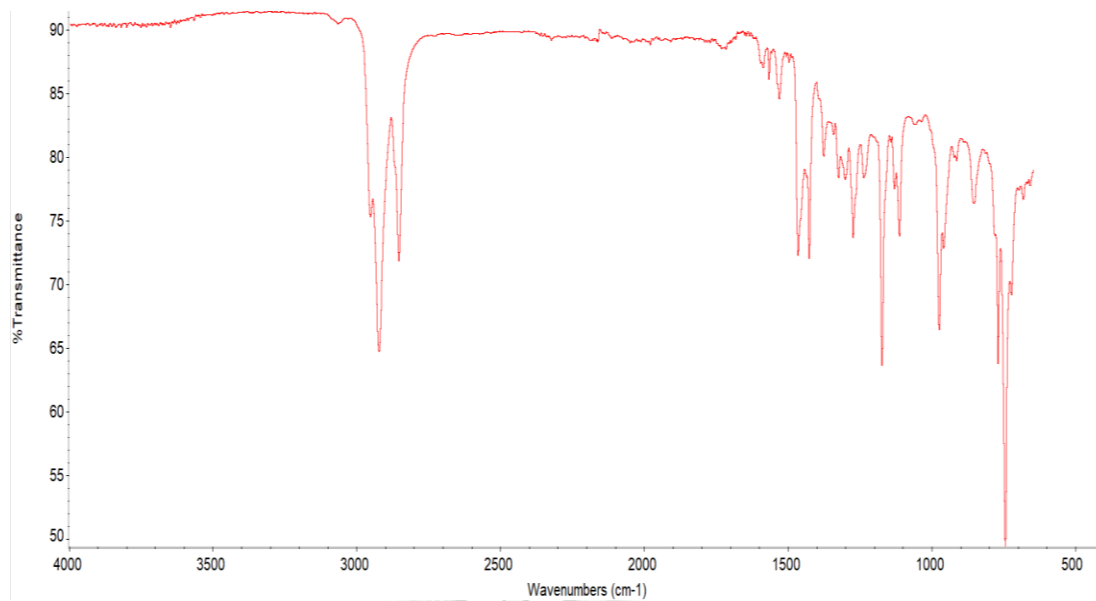


Figure A.14: IR spectrum of compound 2

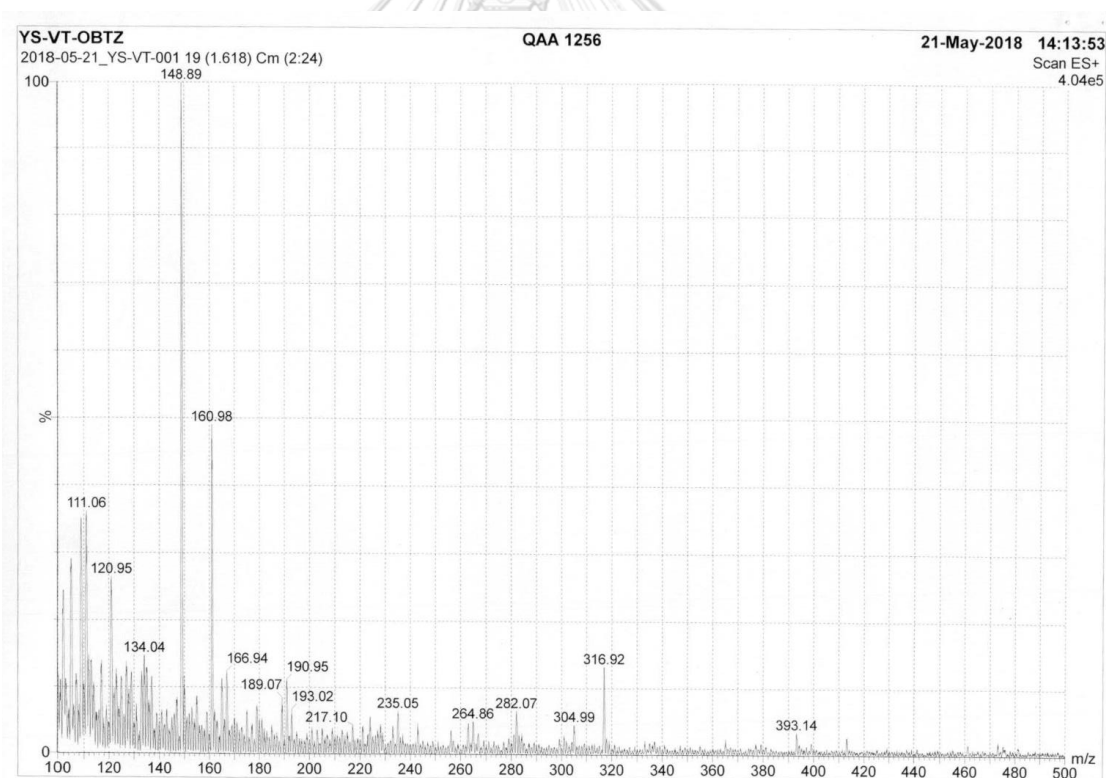


Figure A.15: Mass spectrum of compound 2

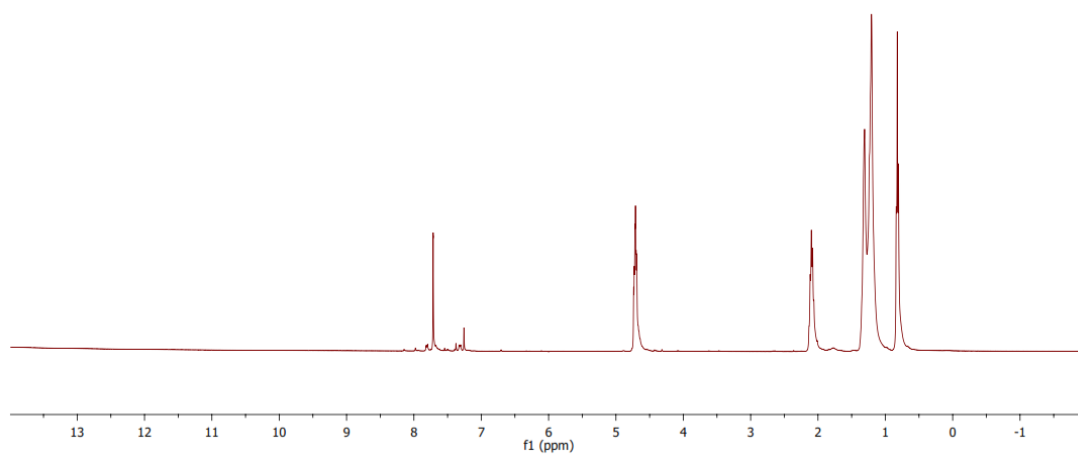


Figure A.16: ^1H NMR (CDCl_3) spectrum of compound **3**

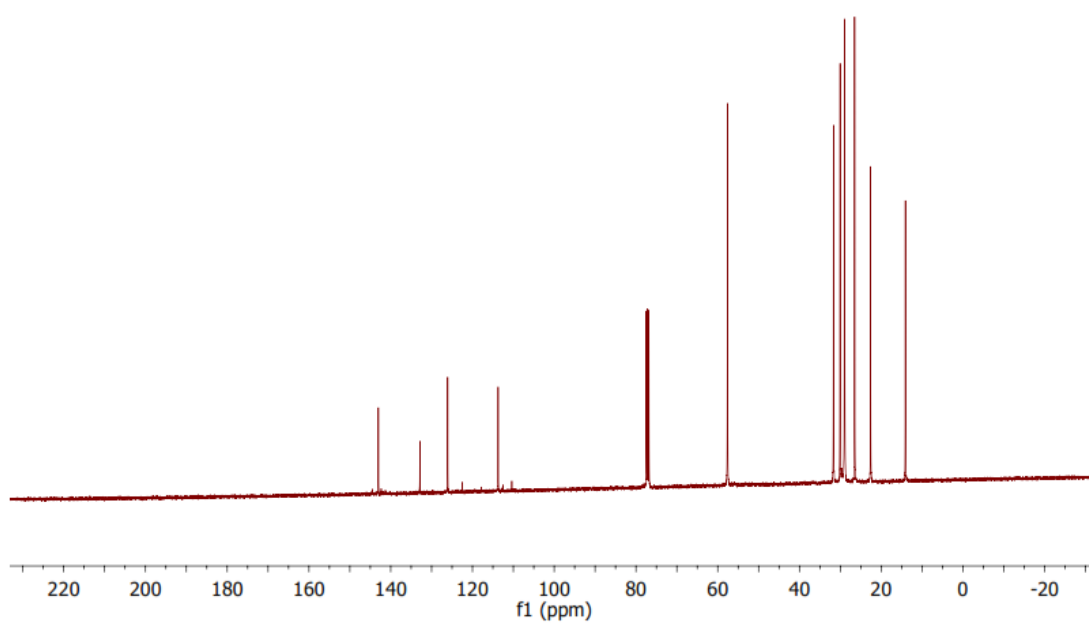


Figure A.17: ^{13}C NMR (CDCl_3) spectrum of compound **3**

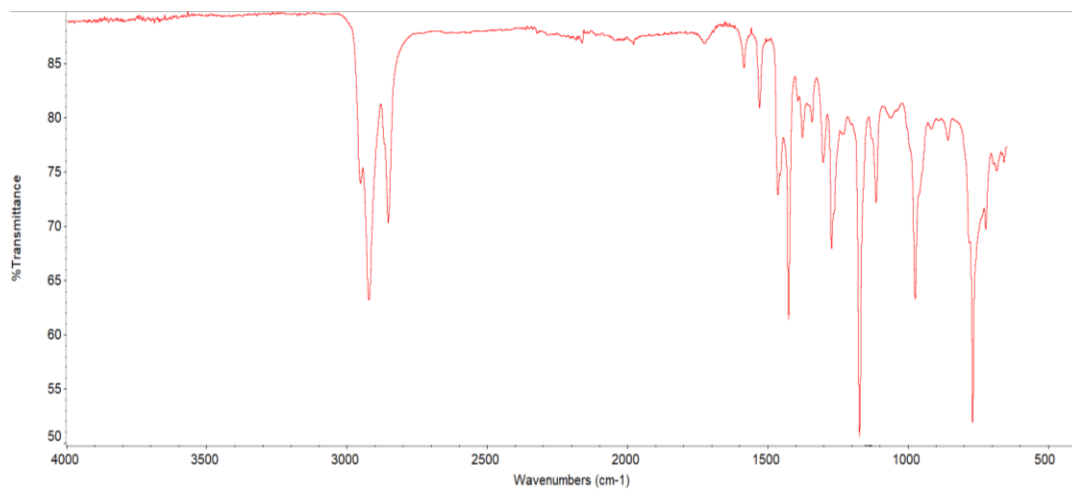


Figure A.18: IR spectrum of compound 3

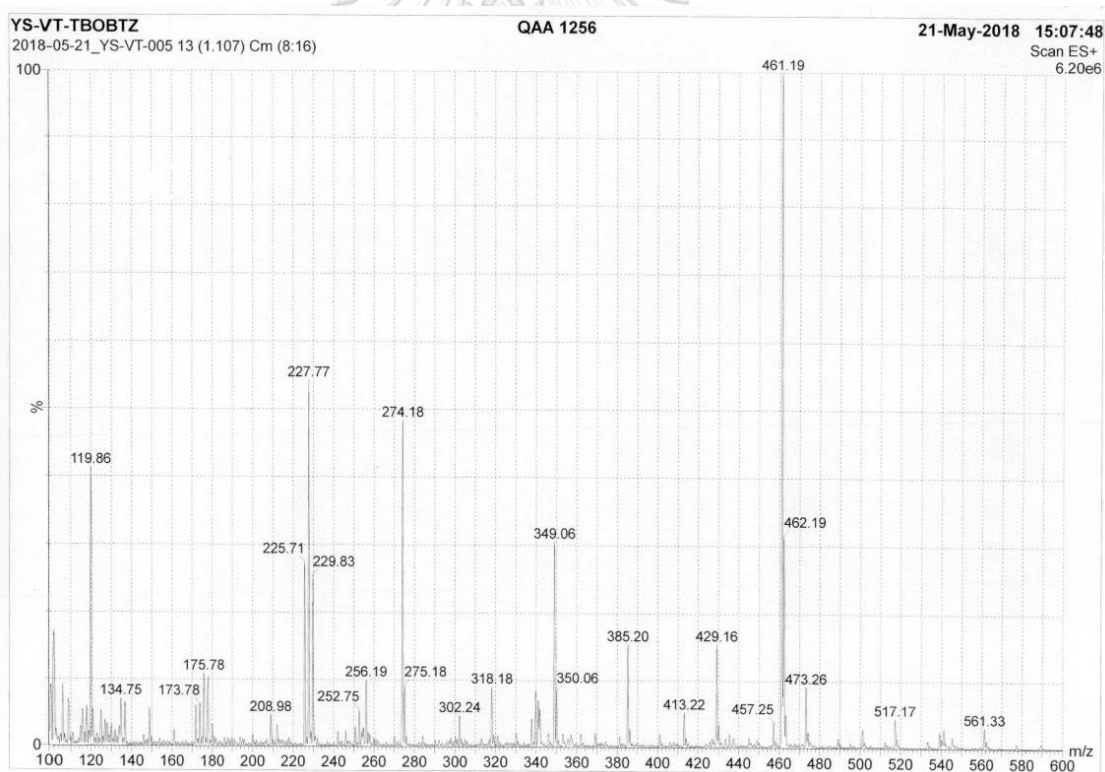


Figure A. 19: Mass spectrum of compound 3

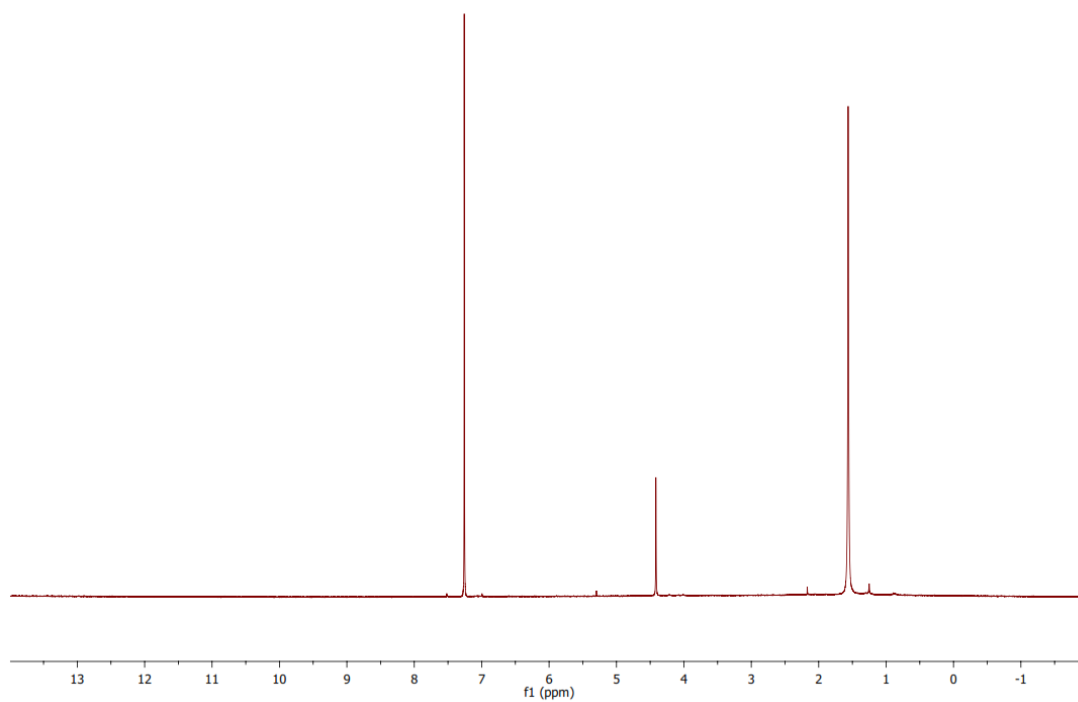


Figure A.20: ^1H NMR (CDCl_3) spectrum of polymer 4

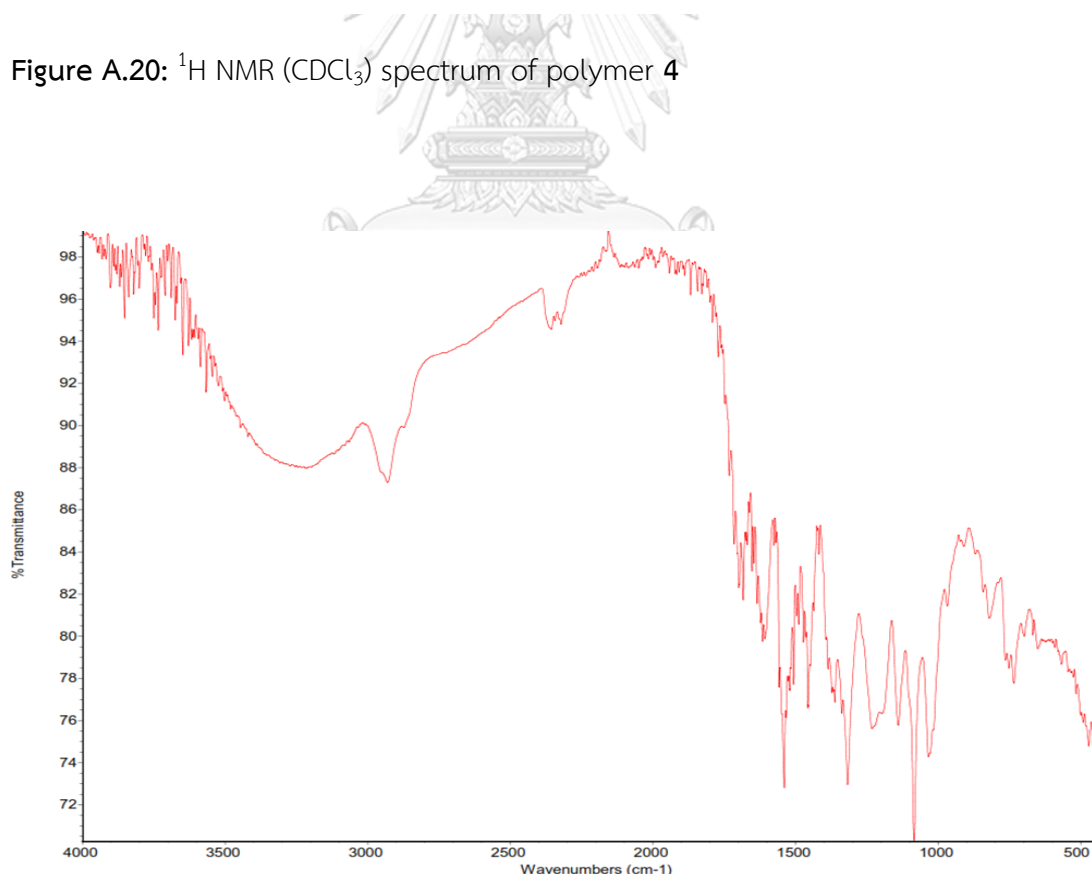


Figure A.21: IR spectrum of polymer 4

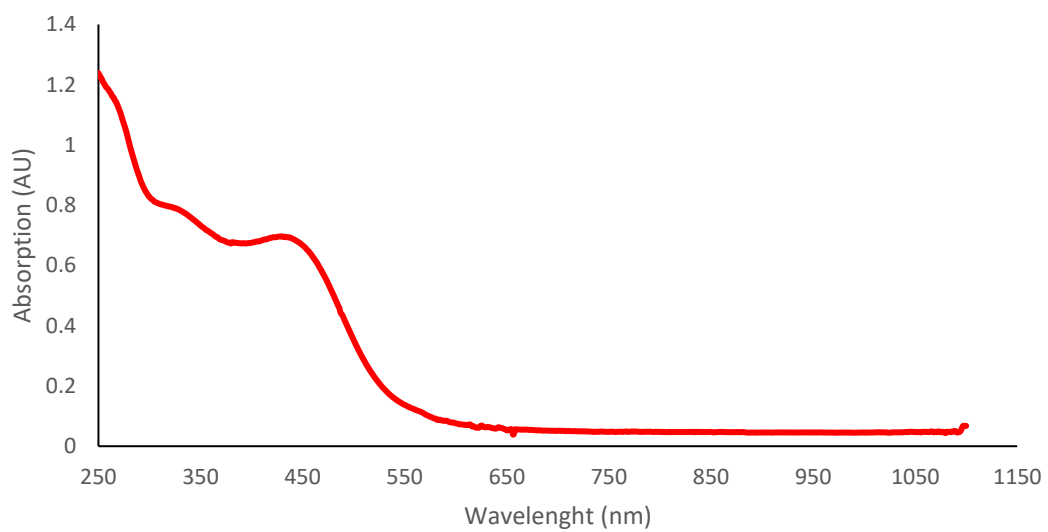


Figure A.22: UV-visible absorption spectrum of polymer 4

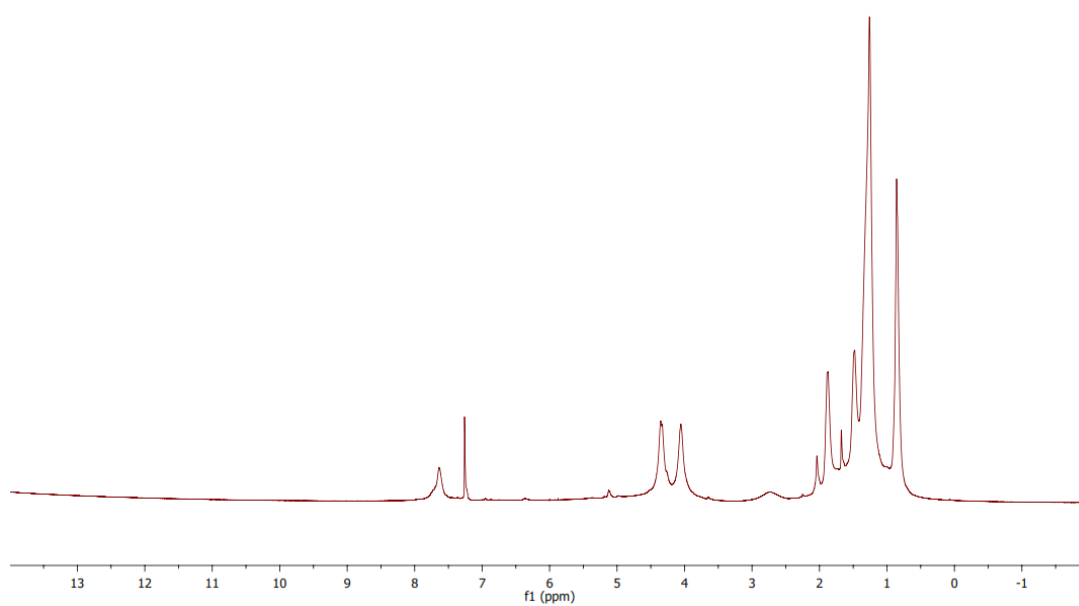


Figure A.23: ¹H NMR (CDCl₃) spectrum of polymer 5

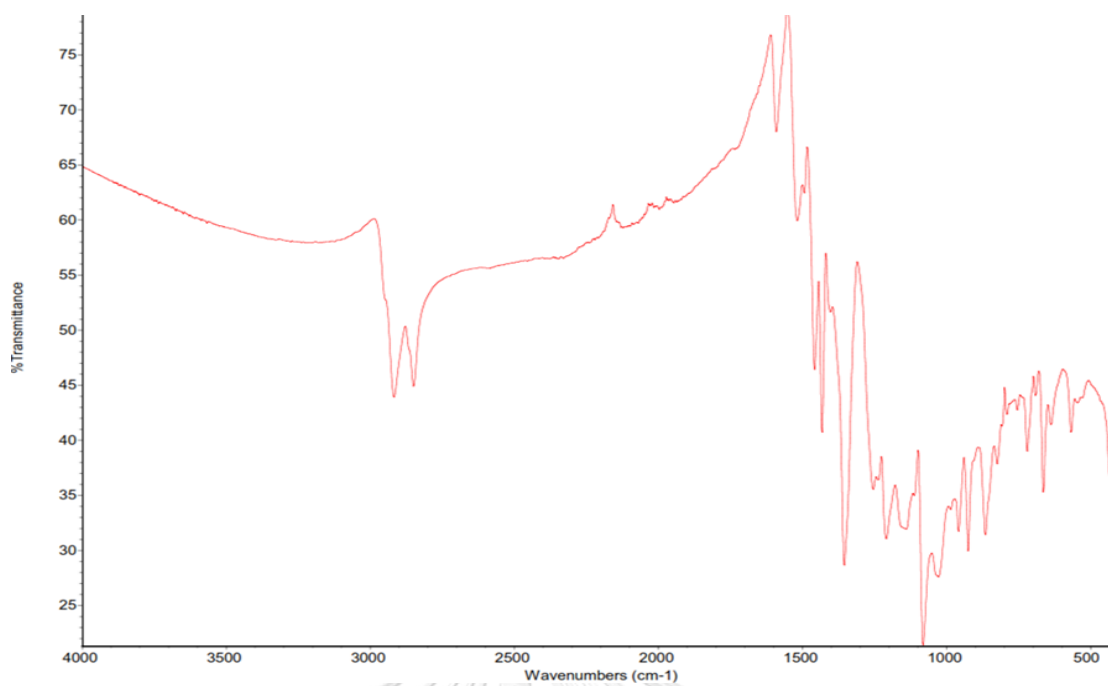


Figure A.24: IR spectrum of polymer 5

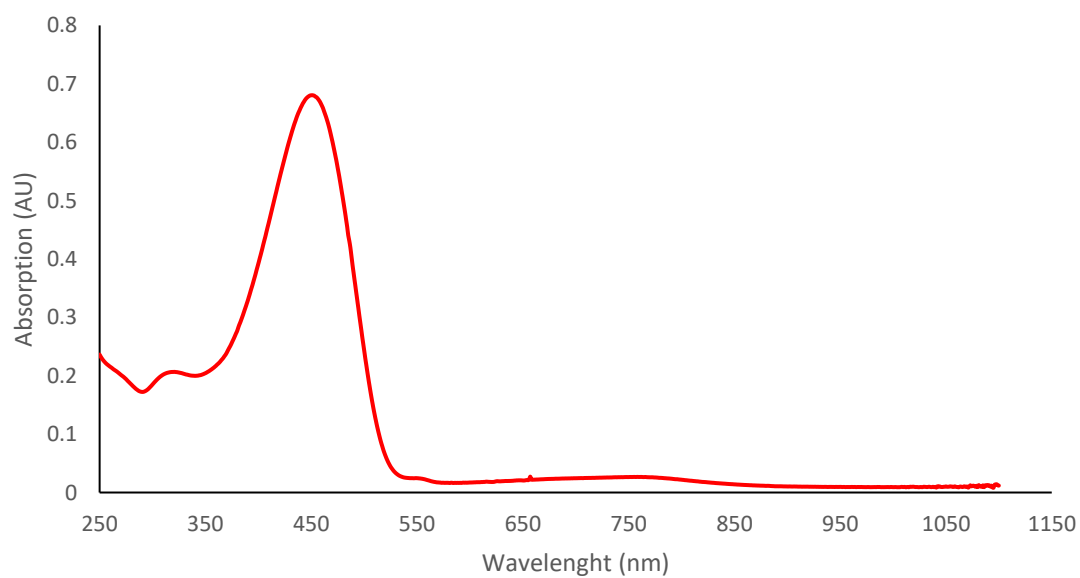
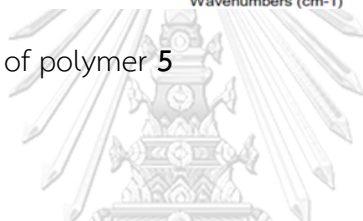


Figure A.25: UV-visible absorption spectrum of polymer 5

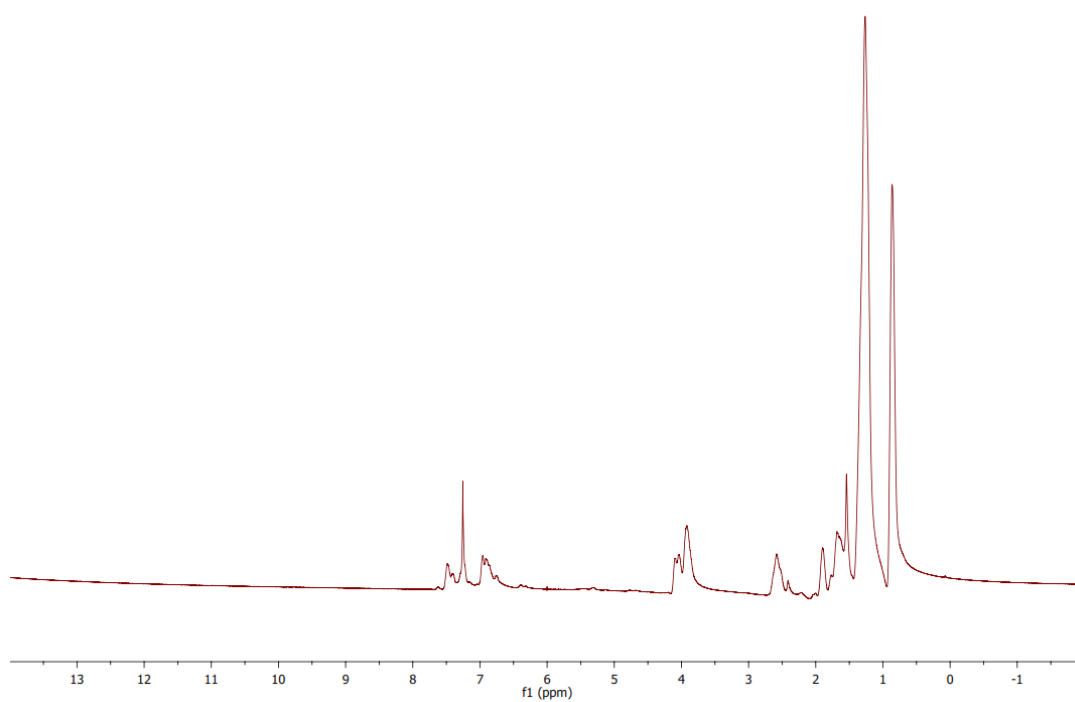


Figure A.26: ^1H NMR (CDCl_3) spectrum of polymer 6

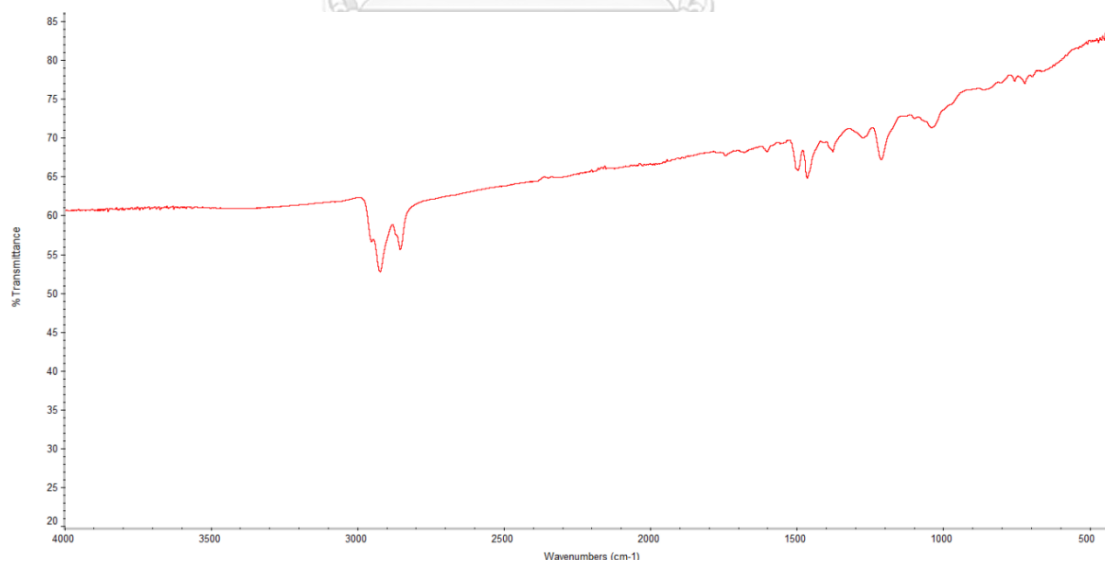


Figure A.27: IR spectrum of polymer 6

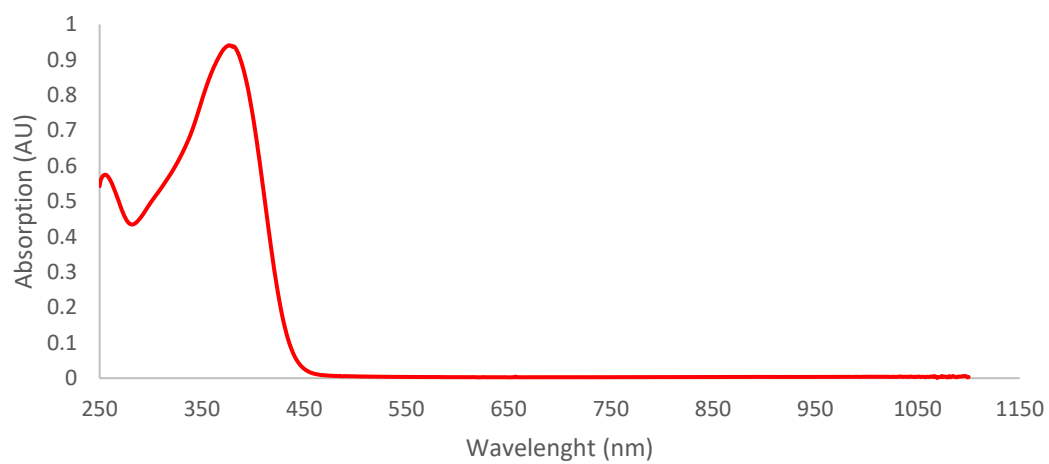


Figure A.28: UV-visible absorption spectrum of polymer 6

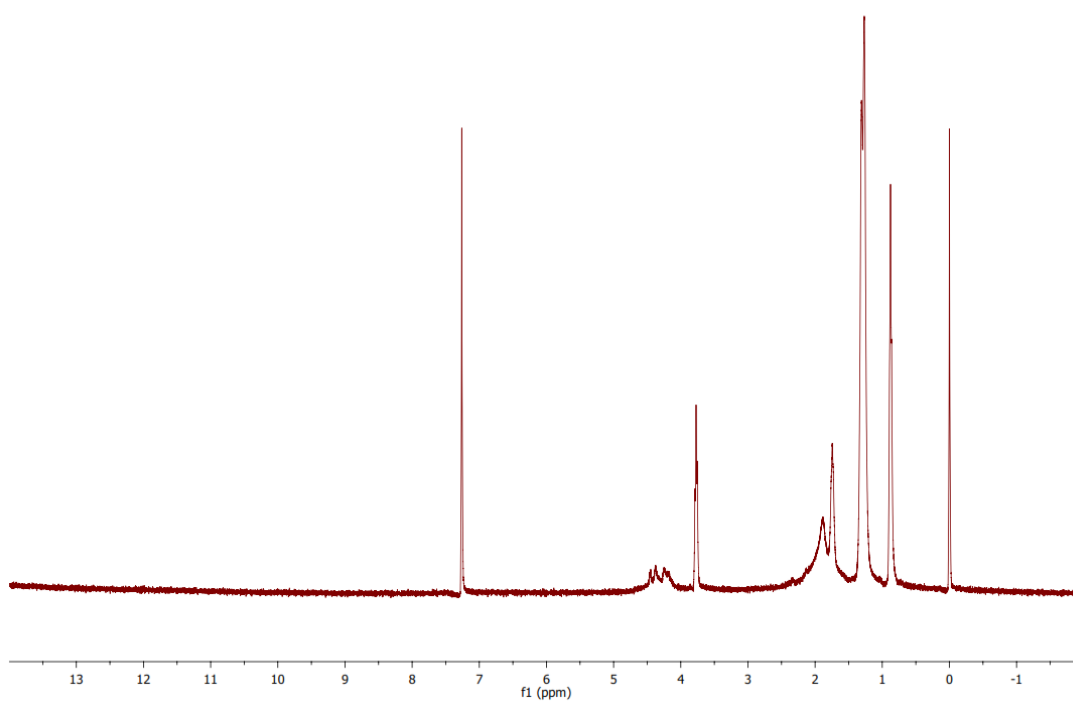


Figure A.29: ¹H NMR (CDCl₃) spectrum of polymer 7

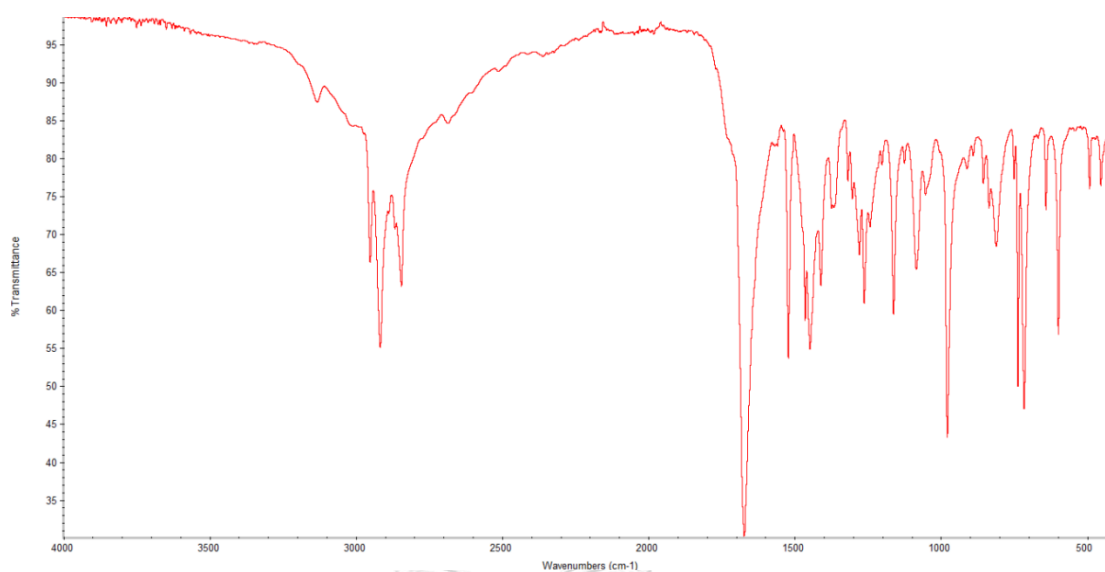


Figure A.30: IR spectrum of polymer 7

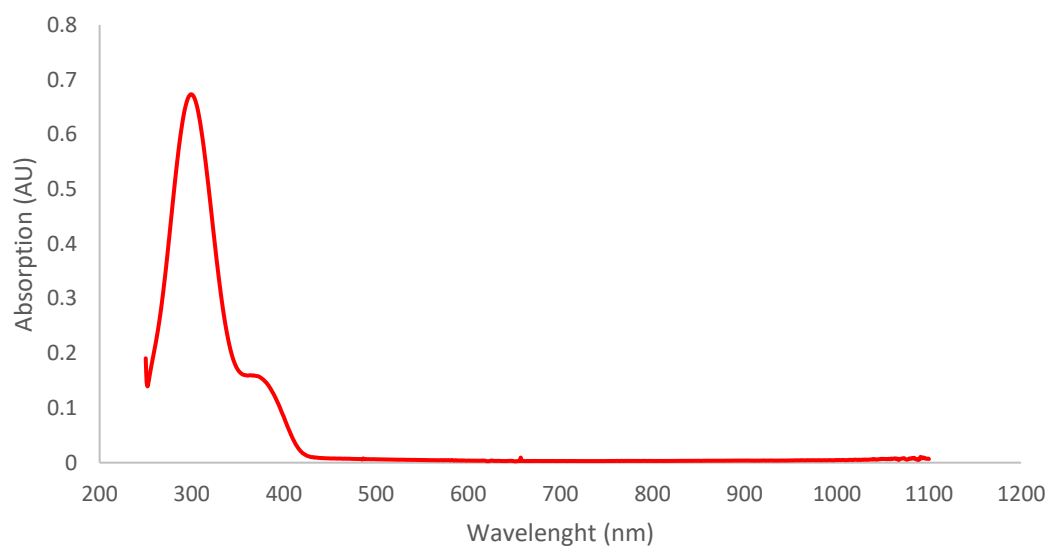
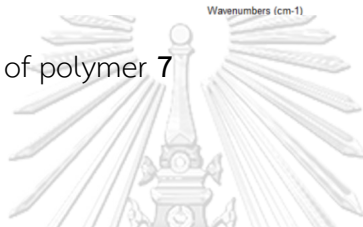


Figure A.31: UV-visible absorption spectrum of polymer 7

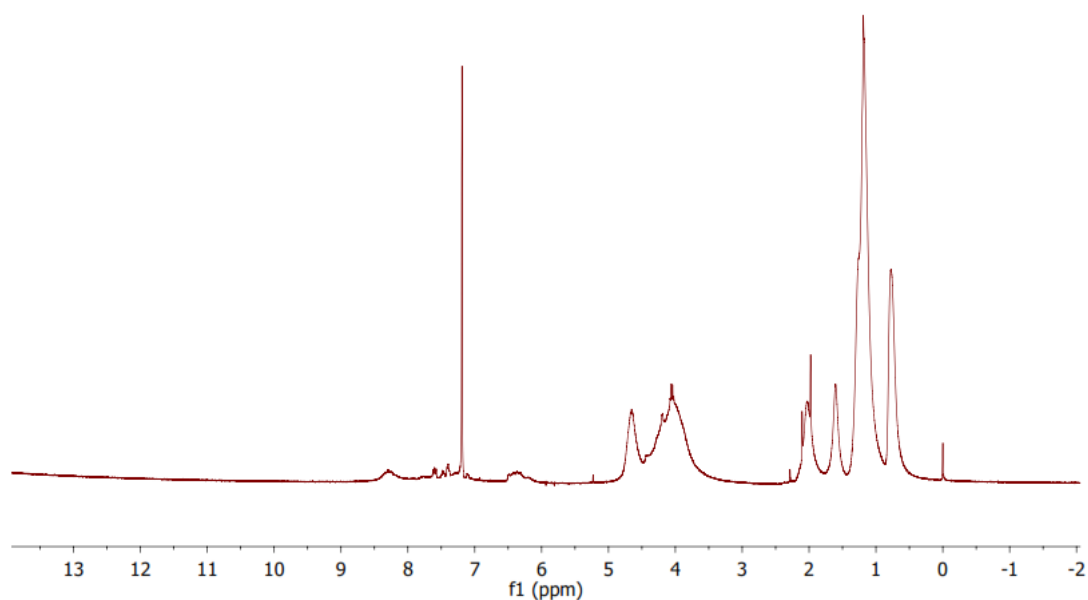


Figure A.32: ^1H NMR (CDCl_3) spectrum of polymer **8**

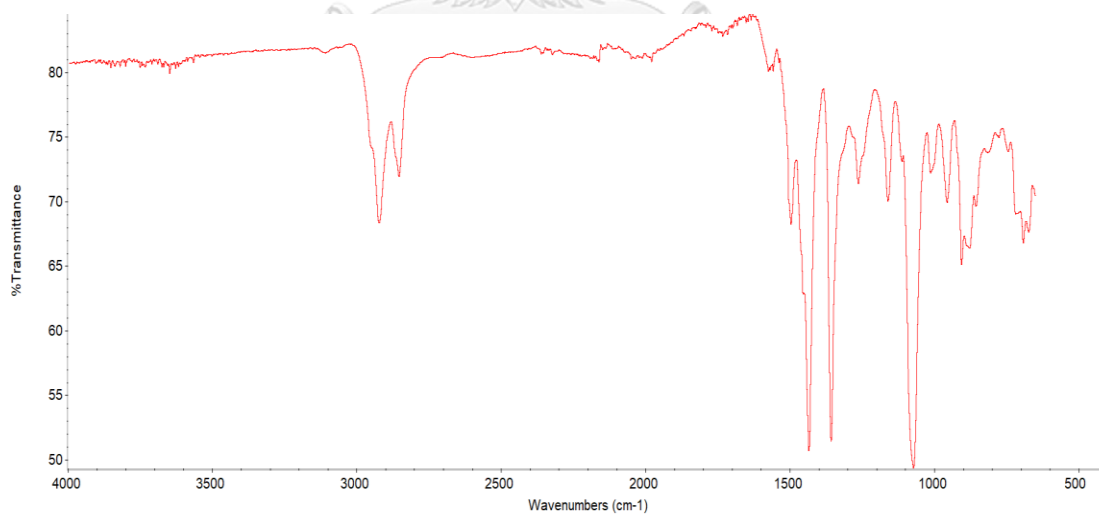


Figure A.33: IR spectrum of polymer **8**

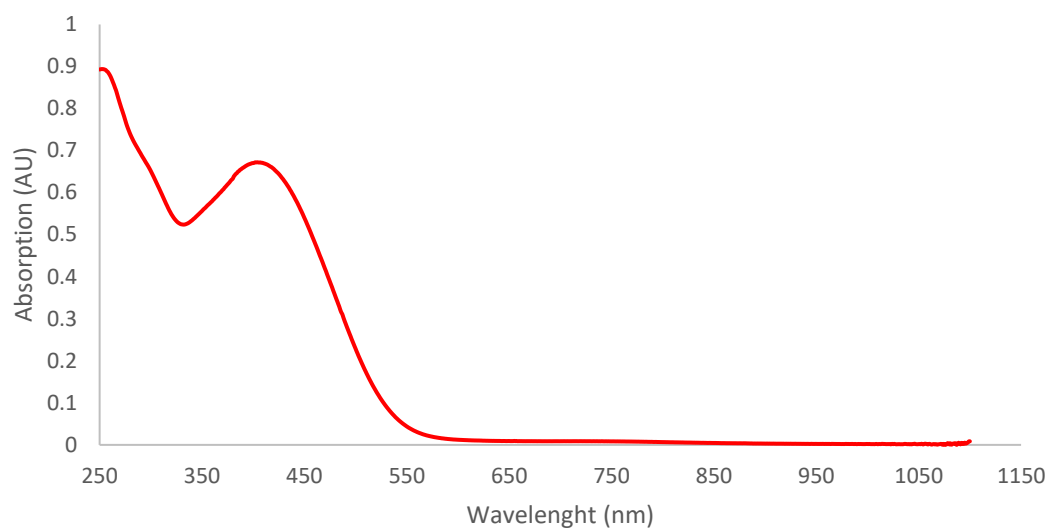


Figure A.34: UV-visible absorption spectrum of polymer 8

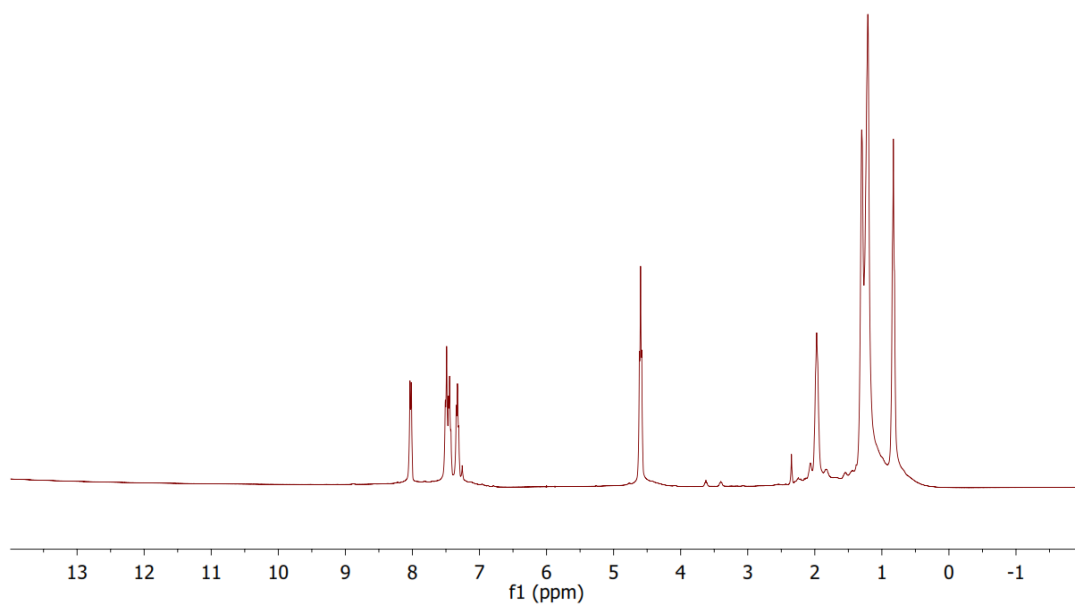


Figure A.35: ¹H NMR (CDCl₃) spectrum of compound 9

VITA

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