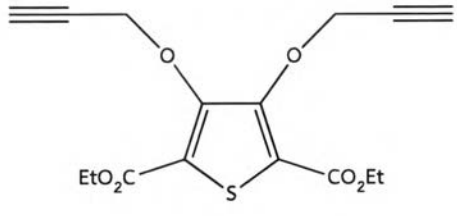
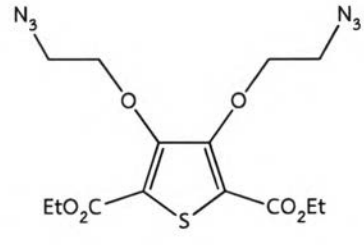
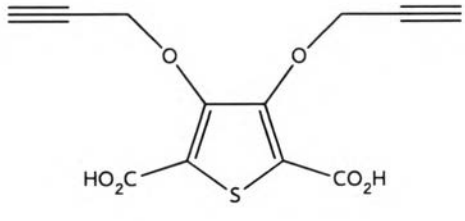
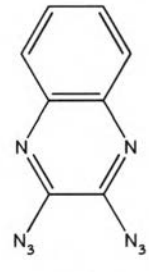
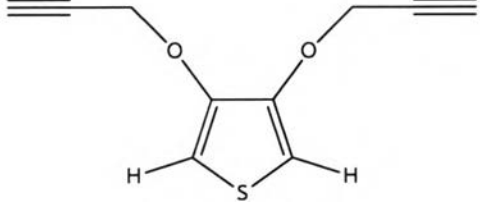
CHAPTER III

RESULTS AND DISSCUSION

3.1 Monomer Synthesis

The structures and synthetic yields of all targeted monomers are showed in **Table 3.1**

Table 3.1 Structures of alkyne and azide monomers

Alkyne monomers	Azide monomers
 **4** (76%)	 **6b** (-)
 **5** (84%)	 **7** (72%)
 **5a** (-)	**8** (83%)

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3.1.1 Synthesis of diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (3)

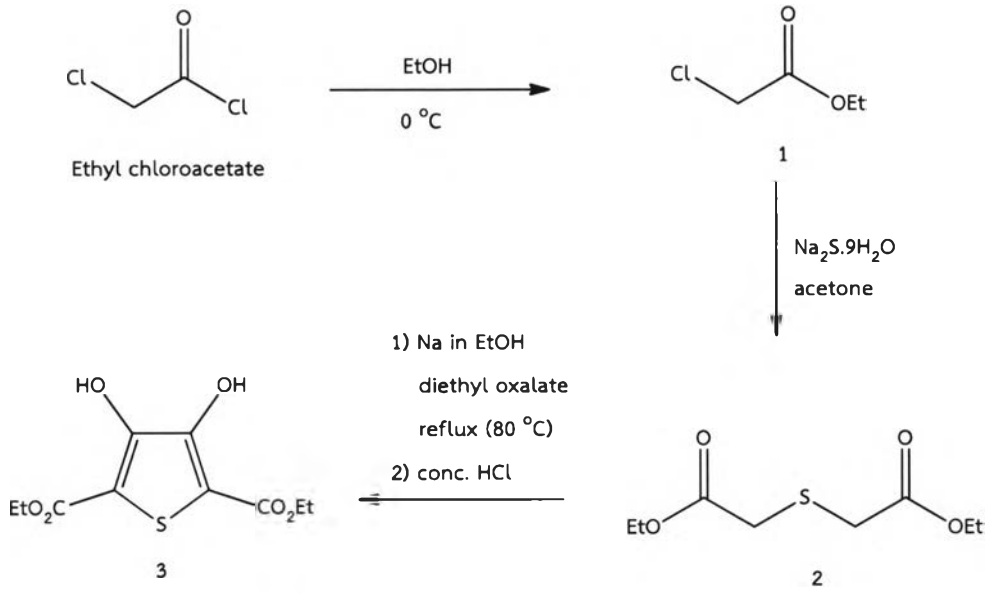

Figure 3.1 Synthesis of compound **3**

Ethyl chloroacetate **(1)** was synthesized through bimolecular nucleophilic acyl substitution of chloroacetyl chloride with ethanol. The product was obtained as colorless liquid in 99% yield. It was verified by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum showed the quartet and triplet signals of ethyl group at δ 4.24, 1.30 ppm **(Figure A.1, Appendix A)**. ^{13}C NMR spectrum showed the signals of ethyl group at 62.1 and 13.9 ppm **(Figure A.2, Appendix A)**.

The reaction of compound **1** and sodium sulfide obtained diethyl thiodiglycolate **(2)** through nucleophilic substitution reaction (S_N2). The reaction was accomplished at 60 °C for 3 h under nitrogen to give the product as colorless liquid in 60% yield. Compound **2** was verified by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR spectrum showed the singlet signal of methylene group at 3.28 ppm and the quartet and triplet signals of ethyl group at 4.09 and 1.17 ppm **(Figure A.3, Appendix A)** ^{13}C NMR spectrum showed the signal of carbonyl carbon at 169.5 ppm **(Figure A.4, Appendix A)**. These data correspond well to those in literature [41].

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Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate **(3)** was synthesized through Hinsberg reaction. This condensation of compound **2** with diethyl oxalate under basic condition obtained compound **3** as a white solid in 55% yield. The mechanism of this reaction, as shown in **Figure 3.,** indicates that the reaction involves double Claisen condensation reactions to produce a diketone intermediate that readily tautomerizes to the corresponding dihydroxythiophene [38].

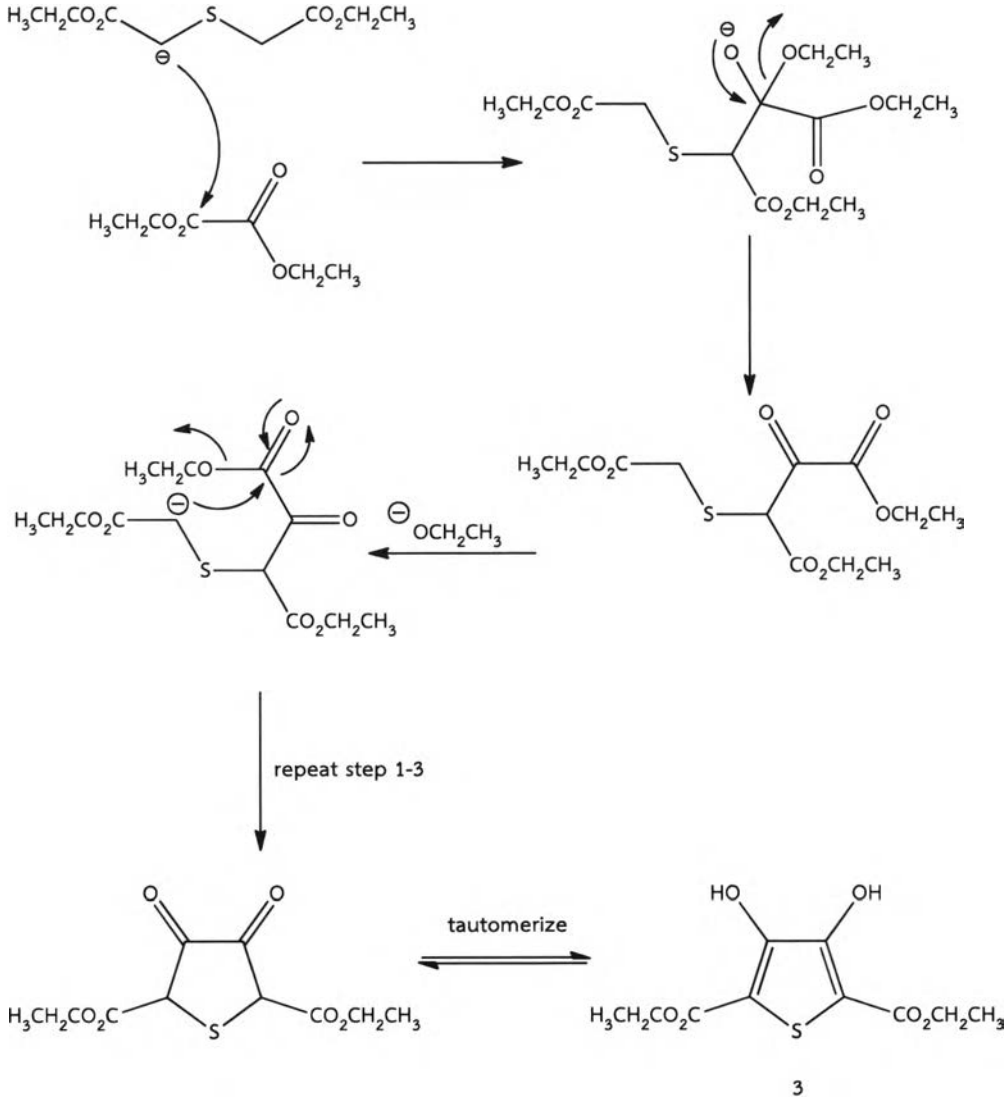

Figure 3.2 Mechanism of Hinsberg reaction

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Compound **3** was characterized by ^{1}H NMR, ^{13}C NMR, IR and MS techniques. ^{1}H NMR spectrum showed a broad singlet signal of OH groups at 9.37 ppm and the quartet and triplet signals of ethyl groups at 4.40 and 1.39 ppm **(Figure A.5, Appendix A)**. ^{13}C NMR spectrum of the carbonyl carbon and thiophene ring appeared at 165.5, 107.1 and 151.6 ppm respectively **(Figure A.6, Appendix A)**. IR spectrum showed OH stretching with the very strong broad signal of OH groups at 3293 cm^{-1} and C=C stretching, C=O stretching signal of carbonyl groups at 1661 cm^{-1} and 1508 cm^{-1} **(Figure A.7, Appendix A)**. Finally, the mass spectrum exhibited the molecular ion peak in the positive mode at 259.20 amu $[M-H]^{+}$ **(Figure A.8, Appendix A)**. These data correspond well to those in literature [38].

3.1.2 Alkyne monomers synthesis

The synthetic route of alkyne monomers (compound **4**, **5** and **5a**) were synthesized from nucleophilic substitution reaction, hydrolysis and decarboxylation respectively, as illustrated in the three step route in **Figure 3.3.**

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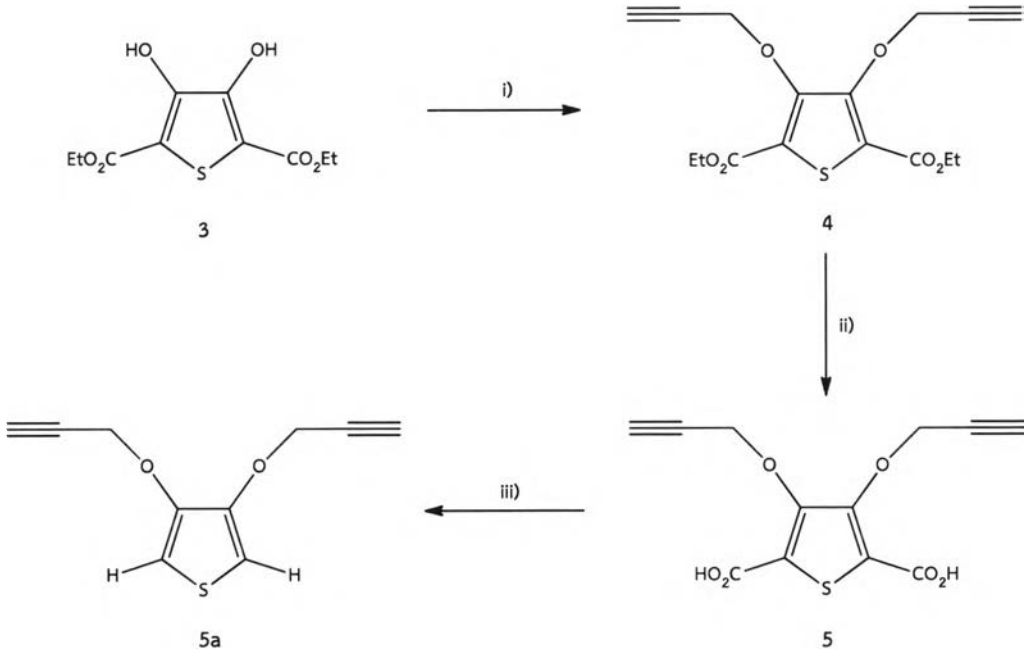

Figure 3.3 The synthesis of compound **4**, **5** and **5a** *Reagents and conditions:* i) propargyl bromide, K_2CO_3, DMAP, CH_3CN:DMF, 80 °C, 4 h; ii) NaOH, EtOH, 80 °C, 4 h; iii) Cu_2O, quinoline, 150 °C, 5 h.

3.1.2.1 Synthesis of diethyl 3,4-bis(2-propynyloxy) thiophene-2,5-dicarboxylate (4)

Compound **4** was synthesized through double nucleophilic substitution reaction of compound **3** with propargyl bromide in the presence of 4-dimethylaminopyridine (DMAP) as a nucleophilic catalyst **(Table 3.2).** Changing the solvent from CH_3CN to (5:2) DMF:CH_3CN and adding the reagent slowly gave the best yield of 76 % **(Entry 6, Table 3.2)**. Longer reaction time resulted in lower **(Entry 3, Table 3.2)** assumably due to partial decomposition of the product. This reaction failed to give the product when propargyl benzenesulfonate was used in place of propargyl bromide.

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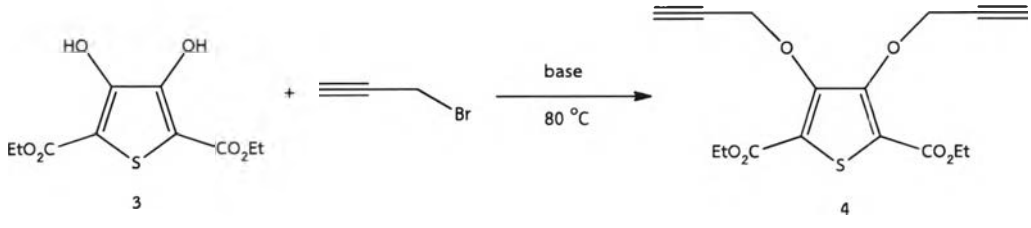
Table 3.2 Conditions for synthesis of compound **4**



Entry	Base	Solvent	DMAP (eq.)	Time (h)	yield (%)
1	K_2CO_3	CH_3CN	-	4	52
2	K_2CO_3	CH_3CN	-	5	48
3	K_2CO_3	CH_3CN	-	9	40
4	Et_3N , K_2CO_3	CH_3CN:DMF	-	6.5	41
5	K_2CO_3	CH_3CN:DMF	0.01	4	56
6[a]	K_2CO_3	CH_3CN:DMF	0.01	4	76

[a]Propargyl bromide was added dropwise.

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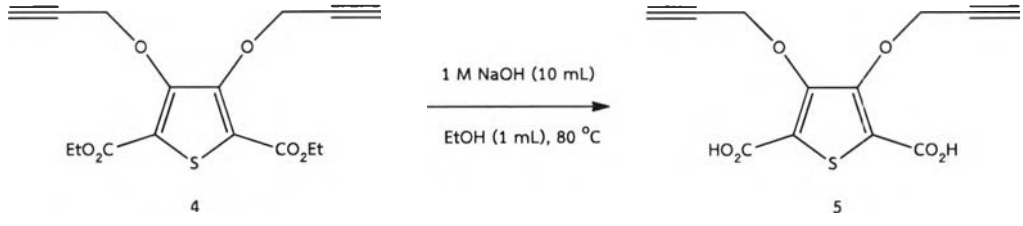
The structure of compound **4** was confirmed by ^{1}H NMR, ^{13}C NMR, IR and MS spectroscopy. ^{1}H NMR spectrum showed a singlet signal of terminal alkyne at 2.53 ppm with disappearance of broad singlet OH signal of compound **3** at 9.36 ppm, and showed the quartet and triplet signals of ethyl groups at 4.23 and 1.23 ppm **(Figure A.9, Appendix A)**. ^{13}C NMR spectrum showed the signal of terminal alkyne at 79.1 and 78.1 ppm **(Figure A.10, Appendix A)**. IR spectrum showed C≡C stretching at 2127 cm^{-1} and C–H stretching of terminal alkynes at 3304 cm^{-1} **(Figure A.11, Appendix A)**. Finally, the mass spectrum exhibited the molecular ion peak appeared in the positive mode at 359.07 $[M+Na]^+$ **(Figure A.12, Appendix A)**.

3.1.2.2 Synthesis of diethyl-3,4-bis(2-propynyloxy)thiophene-2,5-dicarboxylic acid (5)

Compound **5** was synthesized from hydrolysis of compound **4**, obtaining the product as light gray solid **(Table 3.3)**. The yield of the product improved when scaling

up the reaction with more starting material, probably because of better reparation of the product.

Table 3.3 Conditions for synthesis of compound **5**



4 5

Entry	Starting material (mmol)	Time (h)	yield (%)
1	0.41	3.5	53
2	0.75	3	70
3	1.00	4	84

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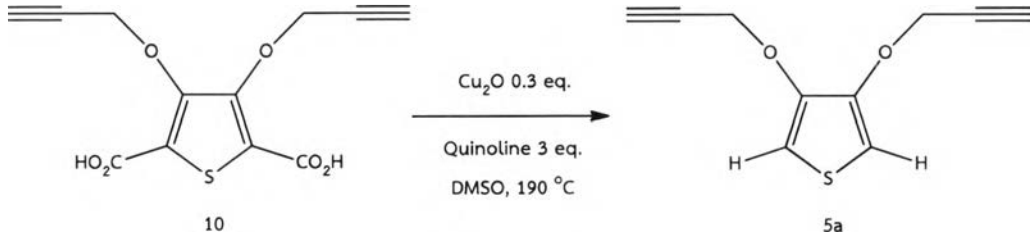
The structure of compound **5** was characterized by ^{1}H NMR, ^{13}C NMR, IR and MS spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of this compound were similar to the starting material except the disappearance of the signals of ethyl groups at 4.23, 1.23 ppm in ^{1}H NMR spectrum **(Figure A.13, Appendix A),** and 62.2, 14.4 ppm in ^{13}C NMR spectrum **(Figure A.14, Appendix A)**. The IR spectrum showed the strong carbonyl stretching signal and the very strong broad OH stretching of carboxyl group at 1652 and 2829 cm^{-1} respectively **(Figure A.15, Appendix A)**.

3.1.2.3 Synthesis of 3,4-bis(2-propynyloxy)thiophene (5a)



Attempts to decarboxylate compound **5** using Cu_2O and quinoline in DMSO at 190 °C gave only small amount of mixture. The crude product was characterized by ^1H NMR spectroscopy which showed some signals that corresponded to the structure of compound **5a**. Unfortunately, the amount of this crude product was too small and too difficult to purify.

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3.1.3 Azide monomers synthesis

Azide monomers (**6b**, **7** and **8**) were synthesized from nucleophilic substitution of azide anion with the compounding alkyl halide precursors. The precursors of **6b** vary come from two methods as showed in **Figure 3.4**.

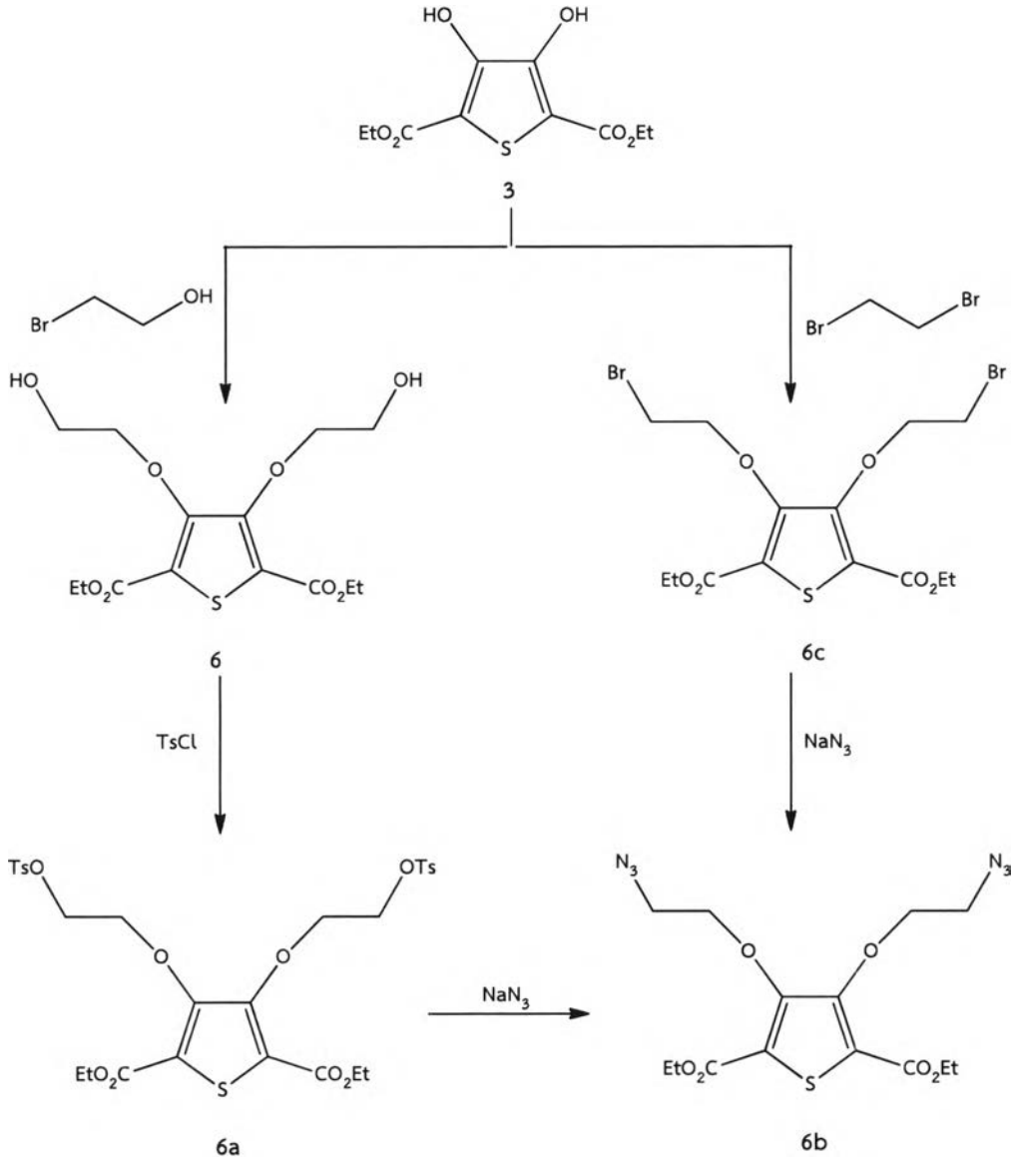
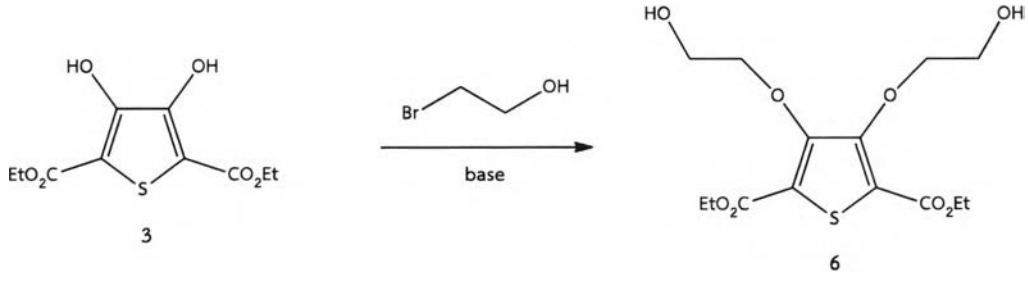


Figure 3.4 Synthesis of compound **6b**

3.1.3.1 Synthesis of diethyl 3,4-bis(2-hydroxyethoxy)thiophene-2,5-dicarboxylate (6)

Compound **6** was prepared from nucleophilic substitution reactions of compound **3** and 2-bromoethanol **(Table 3.4)**. Changing the solvent from CH_3CN to DMF allowed the reaction to be run at higher temperature, resulting in better product yield **(Entry 3, Table 3.4)**.

Table 3.4 Conditions for synthesis of compound **6**



Entry	Base (eq.)	Solvent	Time (h)	Temp (°C)	yield (%)
1	Et_3N (9)	CH_3CN	21.5	80	32
2	Et_3N (9)	DMF	9.5	75	37
3	Et_3N (9), K_2CO_3 (2)	DMF	25.5	130	74

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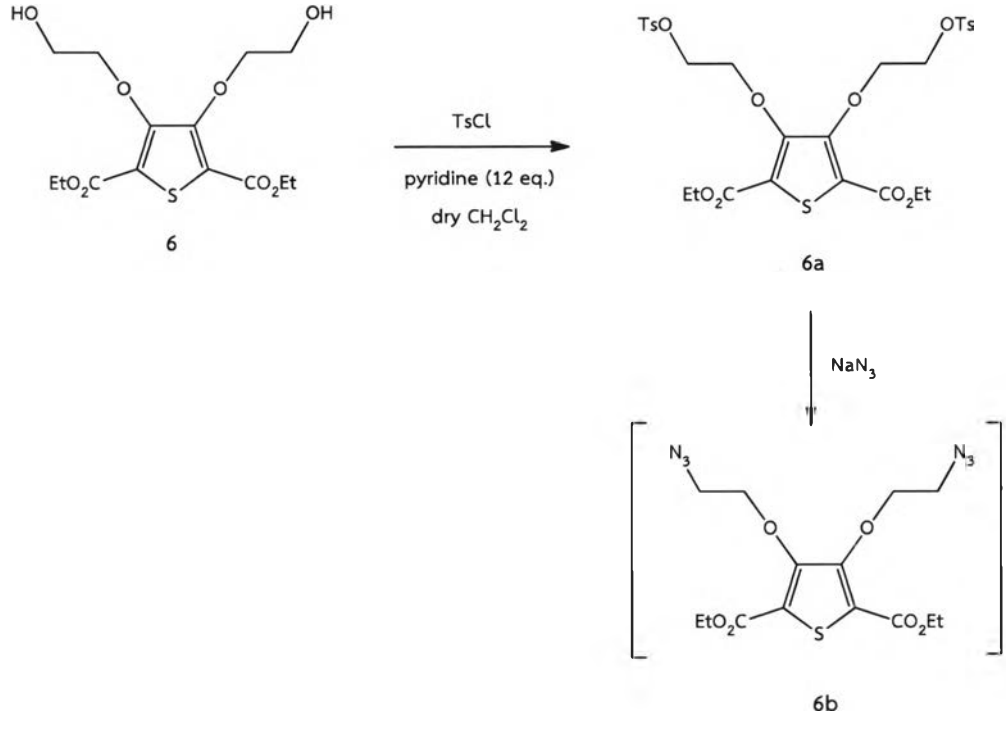
This compound was characterized by ^1H NMR, ^{13}C NMR, IR and MS spectroscopy. The NMR spectra showed two new triplet signals at 4.44 and 3.83 ppm in ^1H NMR spectrum **(Figure A.16, Appendix A)** and at 76.5 and 61.0 ppm in ^{13}C NMR spectrum **(Figure A.17, Appendix A)** assigned to CH_2–O and CH_2–OH groups. IR spectrum showed the very strong broad OH stretching at 3335 cm^{-1} **(Figure A.18, Appendix A)**. Mass spectrum exhibited the molecular ion peak appeared in the positive mode at 371.16 $[M+Na]^+$ **(Figure A.19, Appendix A)**.

3.1.3.2 Synthesis of diethyl 3,4-bis(2-(tosyloxy)ethoxy)thiophene-2,5-dicarboxylate (6a)

Diethyl 3,4-bis(2-(tosyloxy)ethoxy)thiophene-2,5-dicarboxylate **(6a)** was synthesized via tosylation of compound **6**. ^1H NMR spectrum showed that this reaction did not complete **(Figure A.20, Appendix A)**. Much longer reaction time or more reagent would be needed to complete the reaction. Because of the unsuccessful result, the planned synthesis of **6b** was not pursued.



Scheme 3.1 Synthesis route of diethyl 3,4-bis(2-(tosyloxy)ethoxy)thiophene-2,5-dicarboxylate **(6a)**

3.1.3.3 Synthesis of diethyl 3,4-bis(2-bromoethoxy)thiophene-2,5-dicarboxylate (6c)

Compound **6c** was prepared from compound **3** and 1,2-dibromoethane. The reaction instead obtained the diethyl 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarboxylate **(6d)** as a major product together with much smaller amount of compound **6c** as a minor product. The plan to make compound **6b** through **6c** was also not quite practical.

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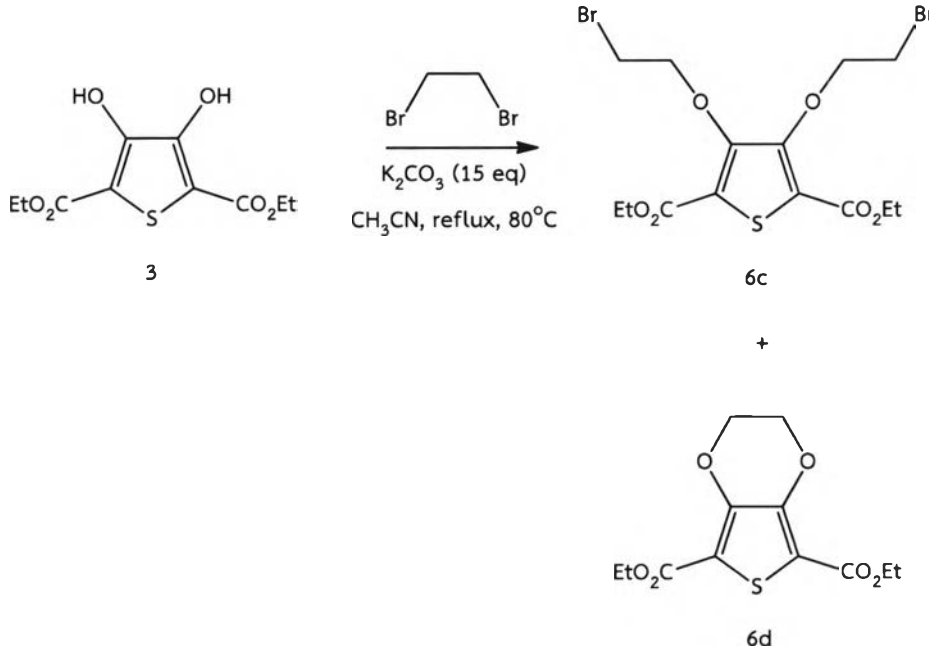
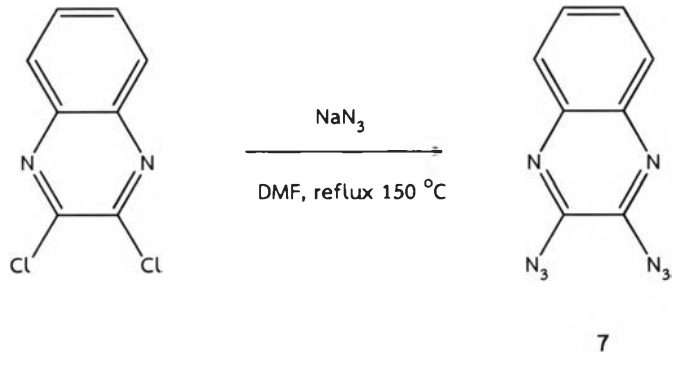


Scheme 3.2 Synthesis of diethyl 3,4-bis(2-bromoethoxy)thiophene-2,5-dicarboxylate **(6c)**

3.1.3.4 Synthesis of 2,3-diazidoquinoxaline (7)

2,3-Diazidoquinoxaline **(7)** was obtained through nucleophilic substitutions of 2,3-dichloroquinoxaline by sodium azide at 150 °C for 1 h in DMF in high yield (72%). Part of the product may be lost during the repeated aqueous washes of DMF.



Scheme 3.3 Synthesis of 2,3-diazidoquinoxaline **(7)**

Compound **7** was confirmed by ^{1}H NMR, ^{13}C NMR, IR and MS spectroscopy. ^{1}H NMR spectrum showed the multiplet signals of aromatic protons at 8.72-8.64 and 8.04-7.96 ppm which shifted relative to that of the starting material **(Figure A.21, Appendix A)**. ^{13}C NMR spectrum of compound **7** matched with the structure of this compound **(Figure A.22, Appendix A)**. IR spectrum appeared the signal of azide functional group with the strong signal at 2141 cm^{-1} and the signal of aromatic group at 3075, 3055 cm^{-1} **(Figure A.23, Appendix A)**. Finally, the mass spectrum exhibited the molecular ion peak appeared in the positive mode at 235 $[M+Na]^{+}$ **(Figure A.24, Appendix A)**.

3.1.3.5 Synthesis of 1,5-diazidopentane (8)

1,5-diazidopentane was synthesized through nucleophilic substitutions of 1,5-dibromopentane by sodium azide. in high yield as shown in **Table 3.5**. The product yield was quite comparable to that of reported procedure [40]. Changing the solvent to DMF obtained slightly less yield relative to CH_3CN due to part of the product may be lost during the repeated aqueous washes of DMF **(Entry 1, Table 3.5)**.

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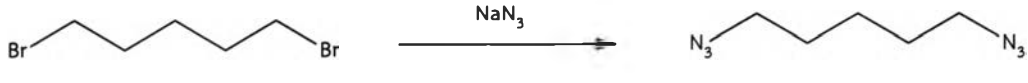
Table 3.5 Conditions for synthesis of compound **8**



8

Entry	NaN_3 (eq.)	Solvent	Temp (°C)	Time (h)	yield (%)
1	2.7	DMF	RT	24	83
2	5	CH_3CN	80	13	89

The product was characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy. The ^{1}H NMR showed that the α-CH_2 signal shifted 0.1 ppm upfield relative to that of the starting material **(Figure A.25, Appendix A)**. IR spectrum confirmed the presence of

azide functional group with the strong signal at 2090 cm^{-1} **(Figure A.27, Appendix A)**. These spectra matched well with the data from the previous report [40].

3.2 CuAAC click reaction of diazide

The trial of click reaction was attempted with the synthesized diazides using the procedure modified from the reported literature [10].

3.2.1 Synthesis of 1,5-bis(4-phenyl-1,2,3-triazolyl)pentane (9)

1,5-bis(4-phenyl-1,2,3-triazolyl)pentane **(9)** was obtained in 37% yield through CuAAC click reaction of compound **8** with phenylacetylene using copper (II) acetate at room temperature in t-BuOH.

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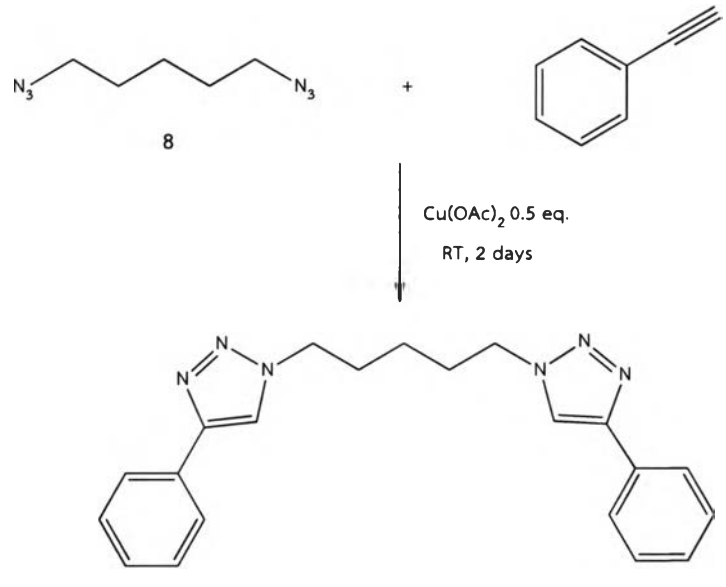

Scheme 3.4 Synthesis of 1,5-bis(4-phenyl-1,2,3-triazolyl)pentane **(9)**

The structure of compound **9** was confirmed by ^{1}H NMR, ^{13}C NMR and IR spectroscopy. The ^{1}H NMR spectrum showed the newly singlet signal of the lone triazole protons at 7.73 ppm with the disappearance of the terminal alkyne protons of phenyl acetylene at 3.06 ppm **(Figure A.28, Appendix A)**. IR spectrum showed the

disappearances of both azide groups from compound **9** at 2084 cm^{-1} and alkyne group from phenyl acetylene at 3300 cm^{-1} **(Figure A.30, Appendix A)**.

Unfortunately, compound **7** did not react with alkyne precursor through CuAAC click reaction in which no triazole proton was detected in ^{1}H NMR spectrum of the mixture. It is possible that copper may coordinate with lone pair electrons at nitrogen atoms of compound **7** to generate a stable complex and become inert. Both starting materials were recovered from the reaction.

3.3 Polymer synthesis via click polymerization and oxidative polymerization

The double strand polymer **P4** was prepared from two methods as showed in **Scheme 3.5.** Click polymerization and oxidative polymerization procedures were modified from previous reports [10, 27].

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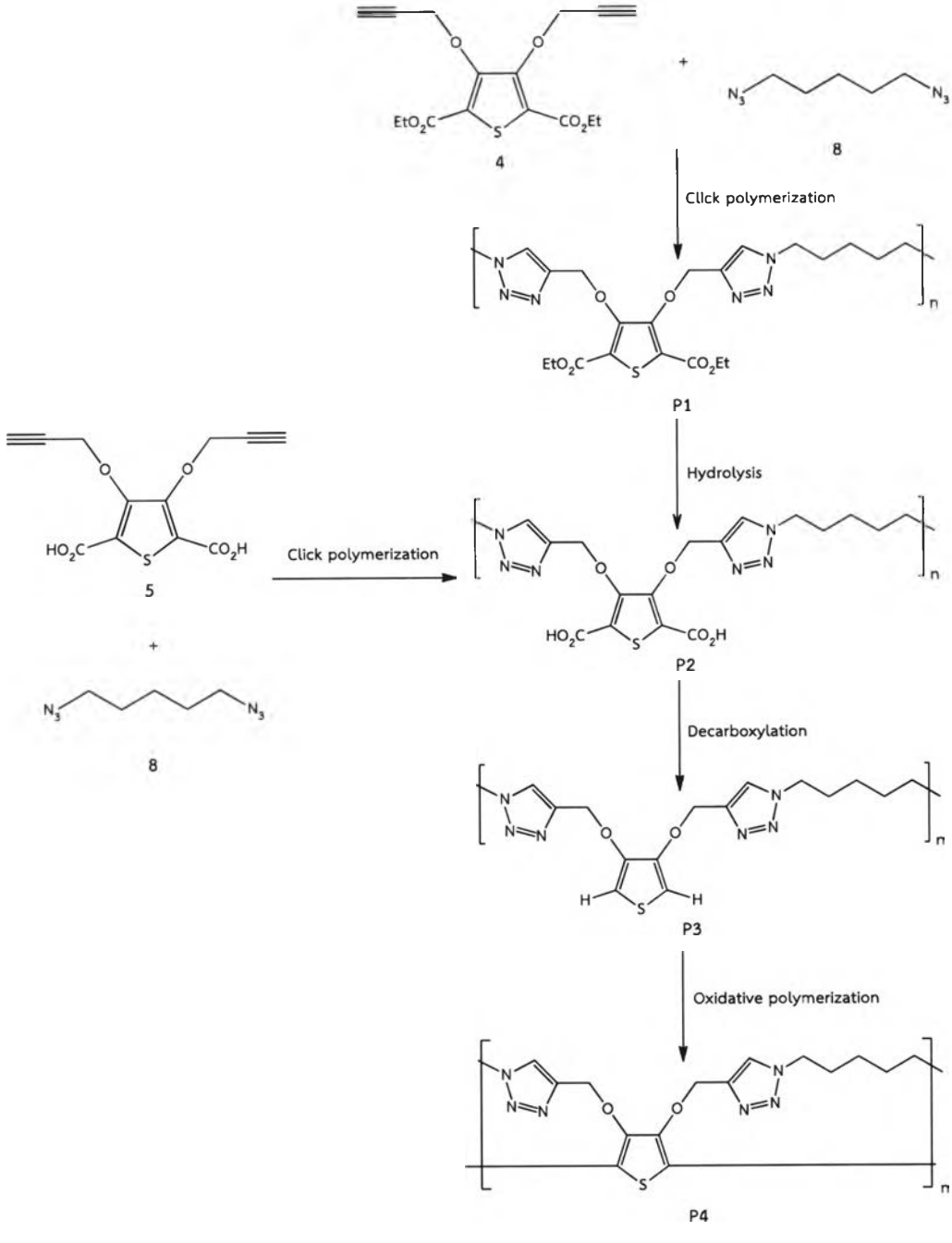

Scheme 3.5 Synthetic routes to double strand polymer **P4**

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3.3.1 Synthesis of polymer P1 via click polymerization

Polymer **P1** was obtained from compounds **4** and **8** through CuAAC click polymerization using copper (II) acetate as a catalyst. The reaction was optimized in two different conditions as shown in **Table 3.6**. The polymer was prepared mostly at room temperature with short reaction time to obtain polymer **P1 (Entry 1, Table 3.6).** At higher temperature, the catalyst was presumably more active and could promote chain propagations from reactions with monomer, resulting in higher molecular weight of this polymer. The low yield of polymer was assumed to be due to unidentified competing side reactions. Lowering the reaction temperature with extended reaction time to produce polymer slightly raised the product yield. While the size of the polymer was smaller probably because of lower activity of the catalyst, and hence less interchain reactions **(Entry 2, Table 3.6)**.

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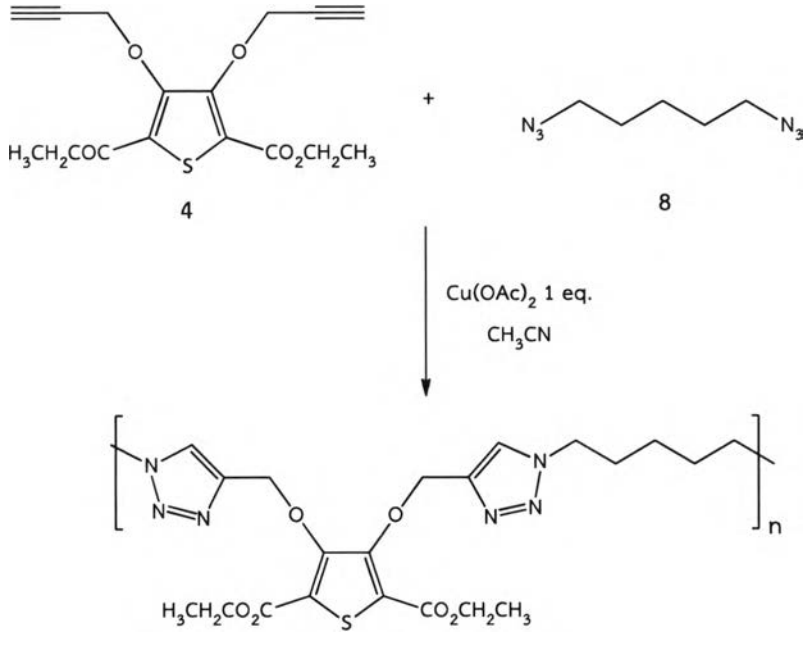
Table 3.6 Conditions for synthesis of polymer **P1**



P1

Entry	Conditions	M_n	M_w	PDI	yield (%)
1	0 °C/6 h then RT/42 h	2903	4484	1.54	27
2	0 °C/7 d	2045	3095	1.51	32

From M_w data, these results correspond to the structures of 9 units of both monomers **(Entry 1, Table 3.6)**, or 6 units **(Entry 2, Table 3.6)**. These small numbers may reflect that the reactions were unexpectedly slow, or longer portions of these polymers were too insoluble and were filtered off during preparations for GPC analysis.

The structure of polymer **P1** was verified by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR showed that all signals were broadened with no clear coupling pattern. The singlet signal of the newly formed triazole protons appeared at approximately 7.93 ppm with the disappearance of the terminal alkyne protons of compound **4** at 2.53 ppm **(Figure A.31, Appendix A)**. IR spectrum confirmed the disappearances of both azides from compound **8** at 2090 cm^{-1} and alkynes from compound **4** at 2127, 3265 and 3304 cm^{-1} after click polymerization **(Figure A.32, Appendix A)**.

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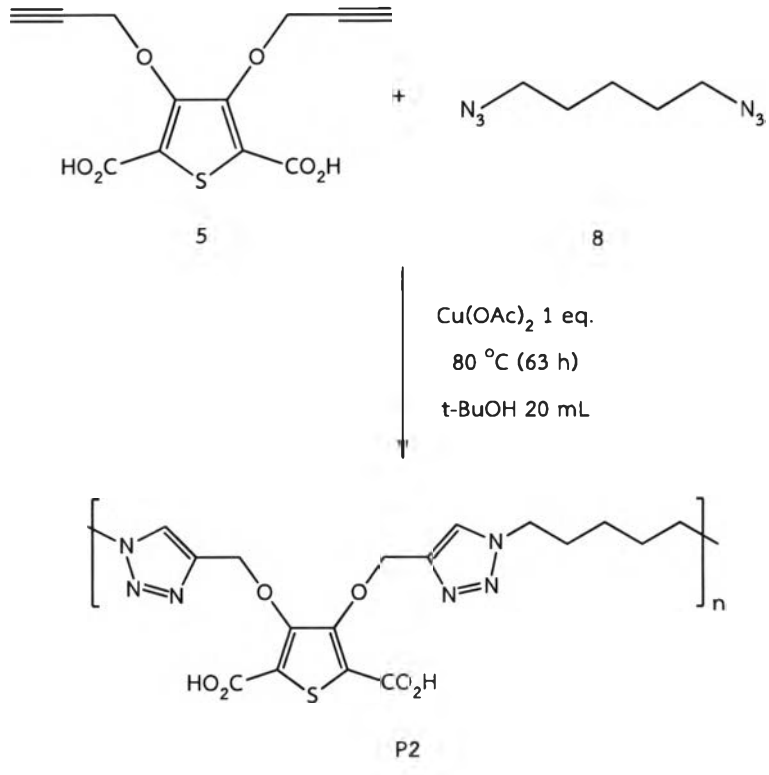
3.3.2 Synthesis of polymer P2 via click polymerization

Polymer **P2** was obtained from compounds **5** and **8** through CuAAC click polymerization using copper (II) acetate in t-BuOH at 80 °C for 63 h in moderate yield (48%). Part of compound **5** may not be dissolved in t-BuOH, resulting in slow and incomplete reaction.



Scheme 3.6 Synthesis of polymer **P2** via click polymerization

The structure of polymer **P2** was verified by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR showed that all signals were broadened with no clear coupling pattern and the singlet signal of the newly formed triazole protons appeared at approximately 8.12 ppm with the disappearance of the terminal alkyne protons of compound **5** at 2.96 ppm **(Figure A.35, Appendix A)**. The IR spectrum showed the strong carbonyl stretching signal and the very strong broad OH stretching at 1704 and 3142 cm^{-1} respectively **(Figure A.36, Appendix A)**. Polymer **P2** cannot be characterized by GPC due to insolubility in THF.

3.3.3 Synthesis of polymer P2 via hydrolysis of polymer P1

Polymer **P2** was synthesized via hydrolysis of polymer **P1** using NaOH in ethanol at 80 °C for 17 h, to obtain polymer with carboxyl groups at α-thiophene ring. The

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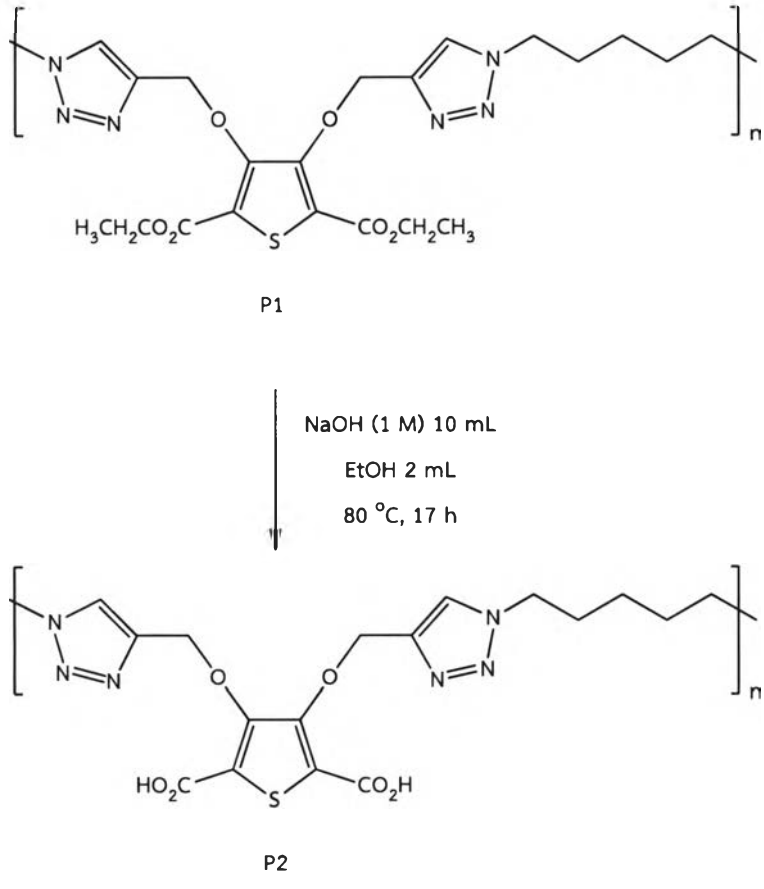
desired polymer was obtained in moderate yield (69%). Yields may be affected by low solubility of the polymer in solvent.



P1

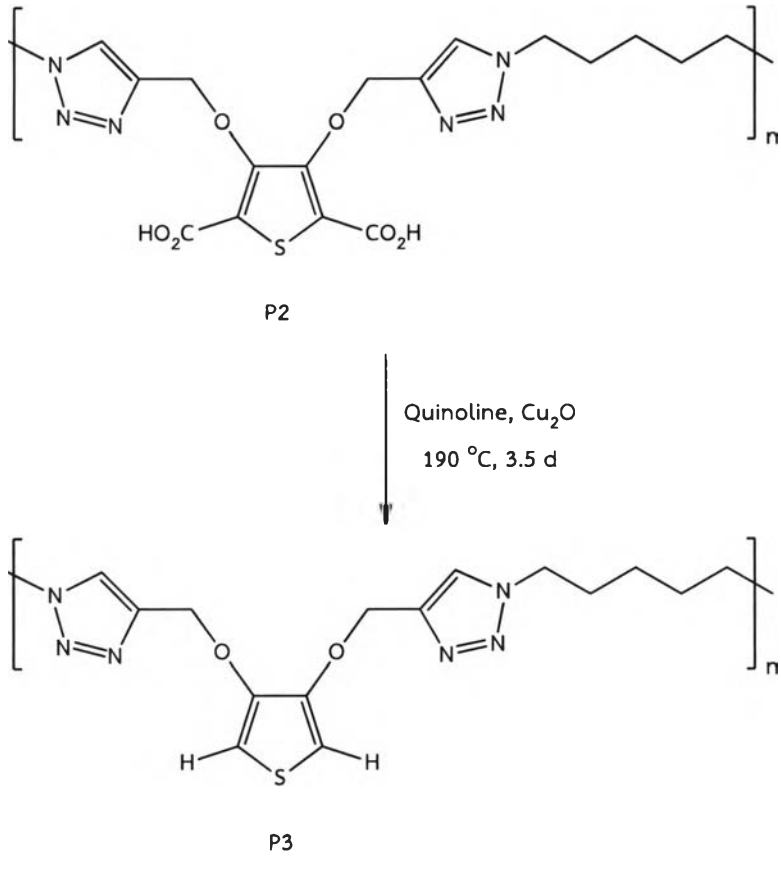
P2

Scheme 3.7 Synthesis of polymer **P2**

The structure of polymer **P2** was verified by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR showed that all signals were broadened with no clear coupling pattern The spectrum was quite similar to the starting material except the disappearance of the signals of ethyl group **(Figure A.37, Appendix A)**. The IR spectrum showed strong carbonyl stretching signal and the very strong broad OH stretching of carboxyl OH at 1774 and 2884 cm^{-1} respectively **(Figure A.38, Appendix A)**.

3.3.4 Synthesis of polymer P3 via decarboxylation of polymer P2

Polymer **P3** was synthesized through decarboxylation of polymer **P2** using cuprous oxide and quinoline in DMSO [41, 42]. The moderate yield obtained was assumed to be due to incomplete reaction on polymer.



Scheme 3.8 Synthesis of polymer **P3**

The structure of polymer **P3** was verified by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR showed that all signals were broadened with no clear coupling pattern and with the appearance of the singlet signal of α-protons of thiophene ring at 6.63 ppm **(Figure A.39, Appendix A)**. IR spectrum showed the disappearance of the carboxyl functional group signal at 2284 and 1774 cm^{-1} **(Figure A.40, Appendix A)**.

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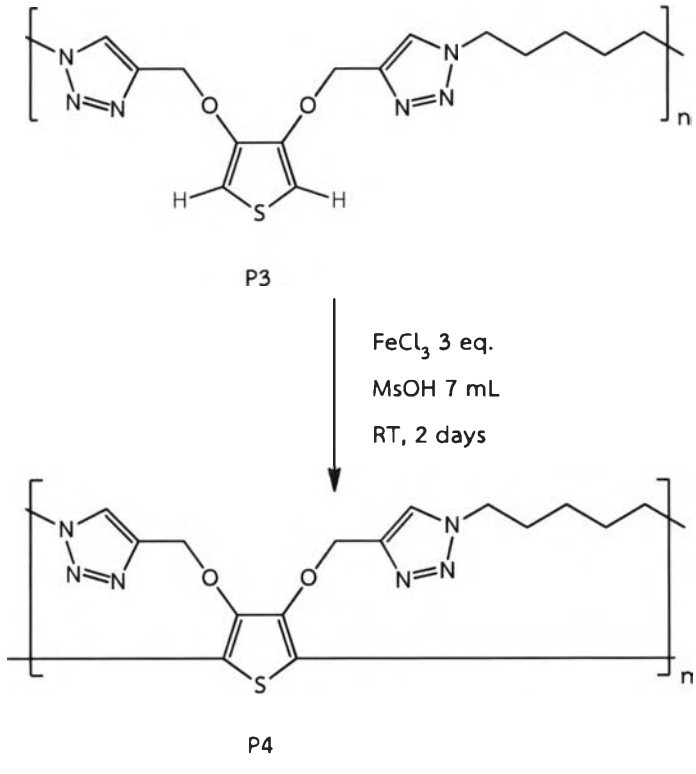
3.3.5 Synthesis of double strand polymer via oxidative polymerization P4

The synthesis of polythiophene by oxidative polymerization using ferric chloride ($FeCl_3$) was modified from the report in literature [36]. Double strand polymer **P4** was synthesized using this method from polymer **P3** in the presence of methanesulfonic acid at room temperature for 2 d as shown in **Scheme 3.9.** The desired polymer was obtained with black solid in good yield (72%). Double strand polymer **P4** was found to be mostly insoluble in common organic solvents but could be made more soluble by adding an organic acid.



Scheme 3.9 Synthesis of double strand polymer **P4**

The ^1H NMR showed that all signals were broadened with no clear coupling pattern and this spectra was similar to the starting material except the disappearance of the singlet signal of α-proton of thiophene ring at 6.63 ppm after polymerization **(Figure A.42, Appendix A)**. FT-IR spectrum showed the broad signals of C–H stretching

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at 3017, 2931 and C=C stretching at 1332 cm^{-1} **(Figure A.43, Appendix A)**. These results confirm that the chemical oxidative polymerization has occurred.

The UV-vis spectra of polymer **P3** and polymer **P4** were shown in **Figure 3.5.** The UV-vis spectrum of polymer **P4** showed various absorption bands at around 751, 552 and 504 nm which assumed to correspond to inhomogeneous mixture of several types and sizes of polymers. Double strand polymer **P4** also exhibits several absorption bands with a maximum at around 630 nm, close to that was previously reported with polythiophene [36]. Polymer **P4** showed absorption in high wavelength region, which related to polymer with low energy band gap and high conjugation length, possibility due to the high coplanarity of the polymer structure. This may be because of the connection of all thiophene units at both α and β positions that prevented the twisting of thiophene monomers on the main chain.

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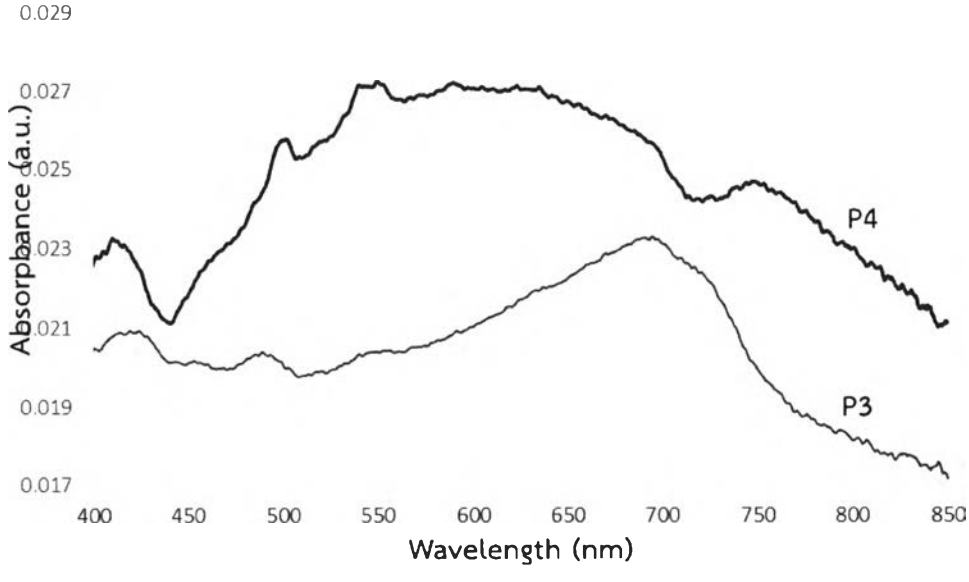

Figure 3.5 Solid UV-vis spectra of polymer **P3** and double strand polymer **P4**

The thermal properties of double strand polymer **P4** was analyzed through thermogravimetric analyzer (TGA). The TGA thermogram of the polymer was carried out under nitrogen atmosphere with the heating rate of 20 °C/min. The T_d value of this polymer could be clearly obtained from the derivative thermogravimetric (DTG) curves as shown in **Figure 3.6**. There are two major thermal decomposition ranges of this polymer, which were found to be at about 298.5 °C and 437.4 °C. The two degradations are potentially due to thermal decomposition of triazole group and the alphatic strand on this polymer. The TGA thermogram showed that only 40% mass loss was observed on this polymer at 500 °C, reflecting in its relatively high thermal stability.

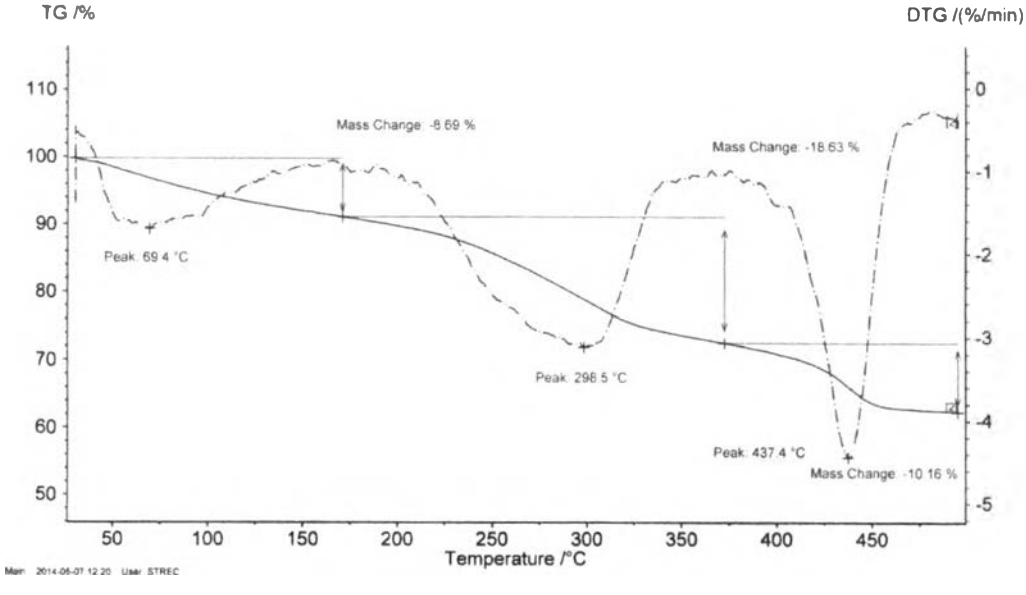

Figure 3.6 DTG thermogram of double strand polymer **P4**

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The double strand polymer **P4** could then be studied its conductivity properties to demonstrate its coplanarity that correlate to the conjugation system. This polymer is anticipated to find wide applications in electrochemical devices such as sensors, solar cells, etc.

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