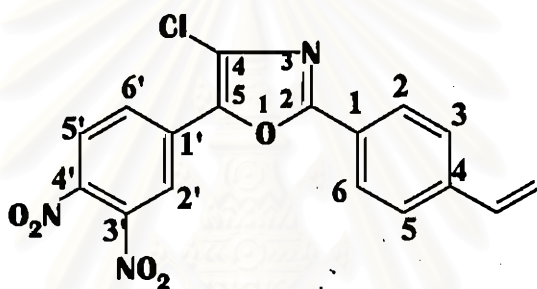# CHAPTER III

RESULTS AND DISCUSSION

The aim of this study as to synthesis 4-chloro-5-(3',4'-dinitro phenyl)-2-(4-vinylphenyl)oxazole (10) which is a new monomer for preparation of a new fluorescent polymer. The chemical structure of (10) is again shown below:
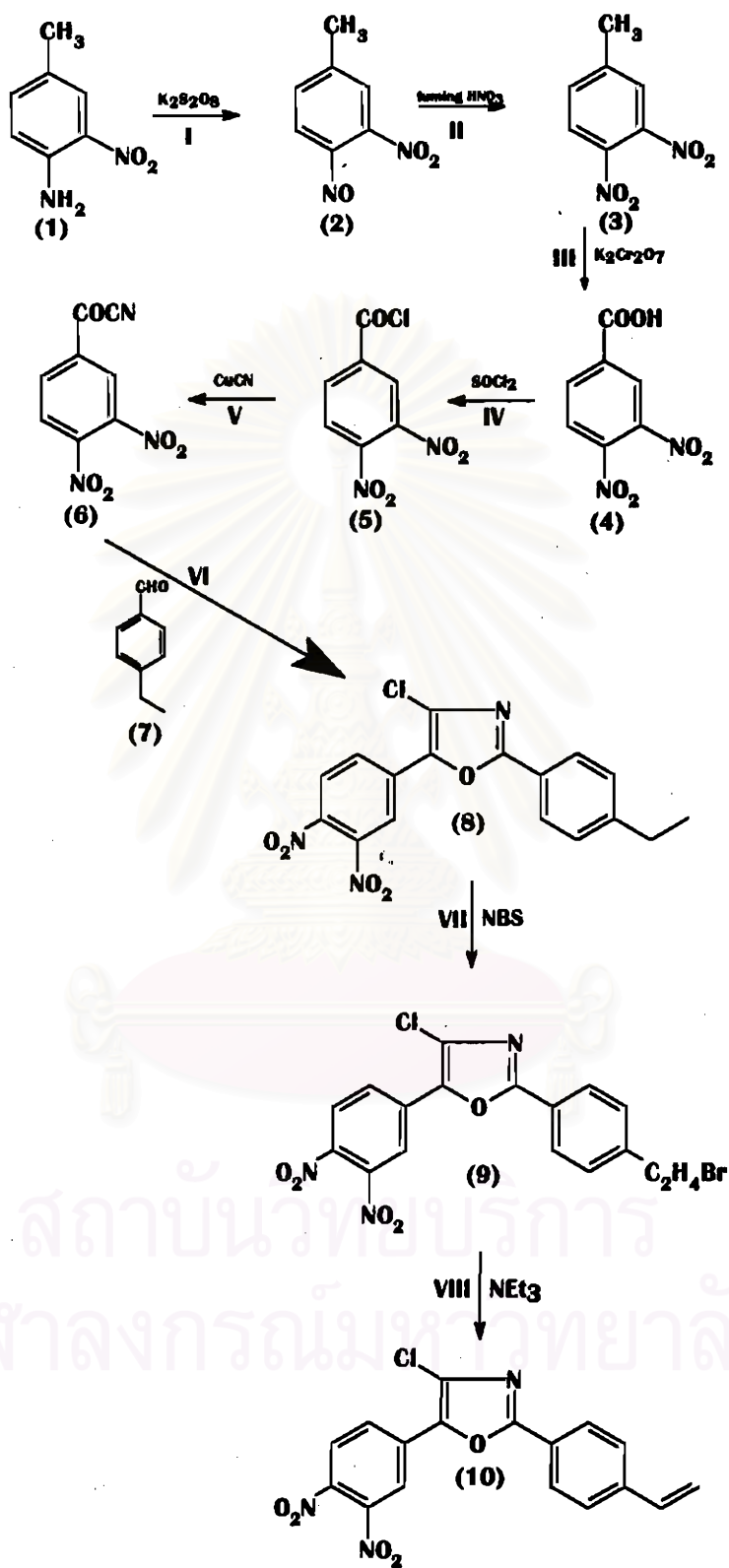

(10)

Scheme 3.1 shows the concept of structural breakdown of (10) in order to find a synthetic route as well as starting and intermediate compounds employed in this study. Scheme 3.2 shows the synthetic route carried out in this study. Detailed discussion on the synthesis of compounds (2) (10) are given subsequently.
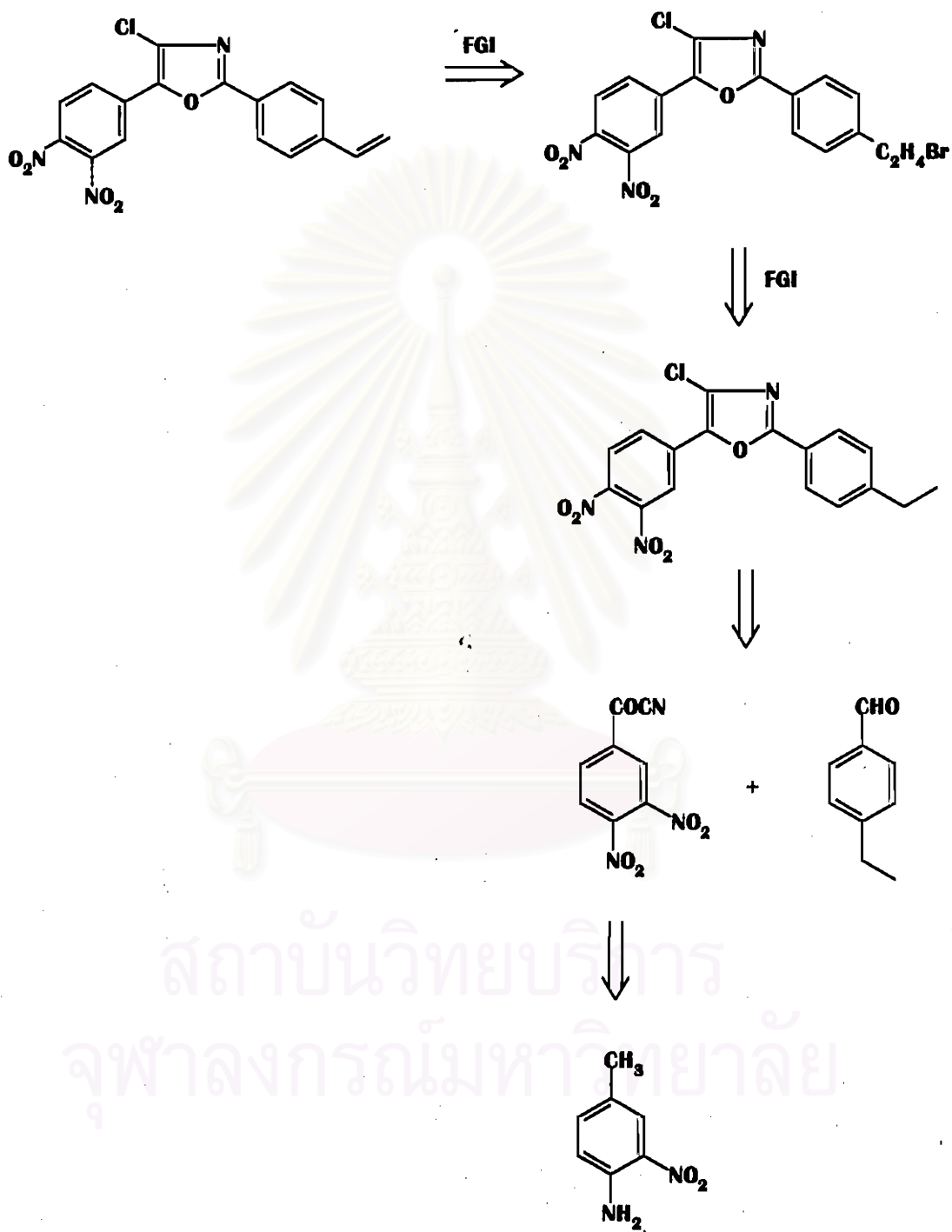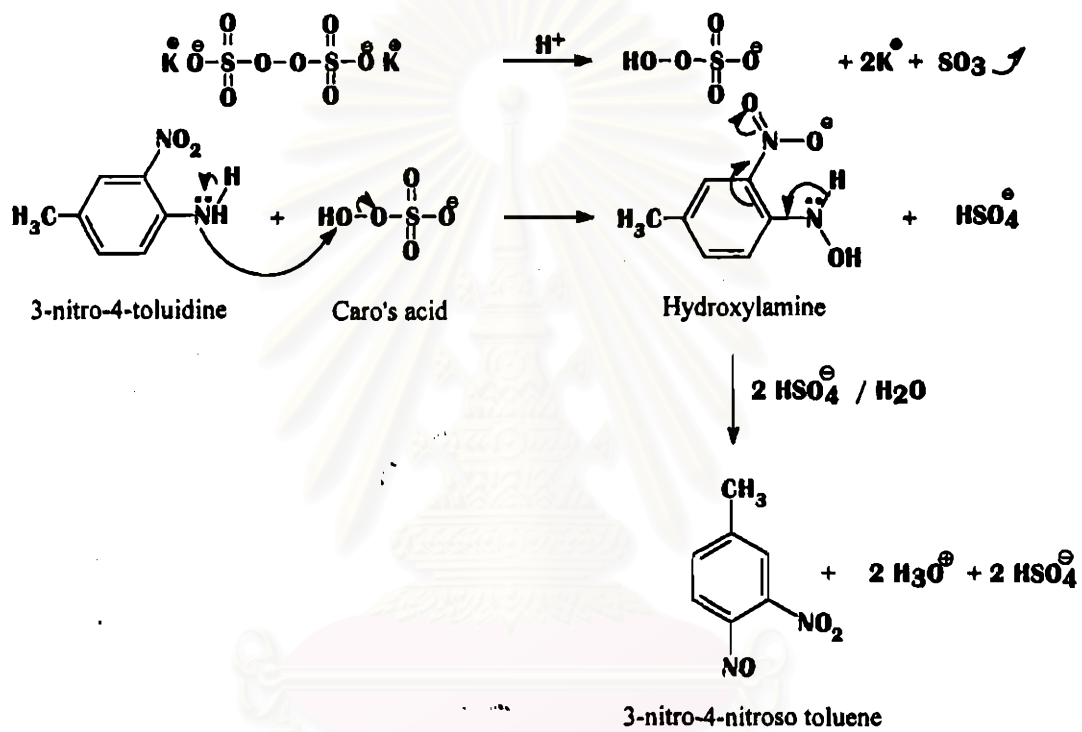
Scheme 3.1

Scheme 3.2

Conceptual synthetic method of (10)

I 17791248

3.1) Preparation of 3,4-Dinitrobenzoyl Cyanide from 3-Nitro-4-Toluidine

In preparation of the oxazole by the Ternai synthesis, the appropiate aroylcyanide was needed. However, this compound is not available commercially. Therefore, 3,4-dinitro benzoyl chloride was prepared using 3-nitro-4-toluidine [27] as the starting compound which was then converted to 3,4-dinitrotoluene, 3,4-dinitrobenzoic acid, 3,4-dinitrobenzoyl chloride and 3,4-dinitrobenzoyl cyanide, respectively (see Scheme 3.2, steps 1 to 5).
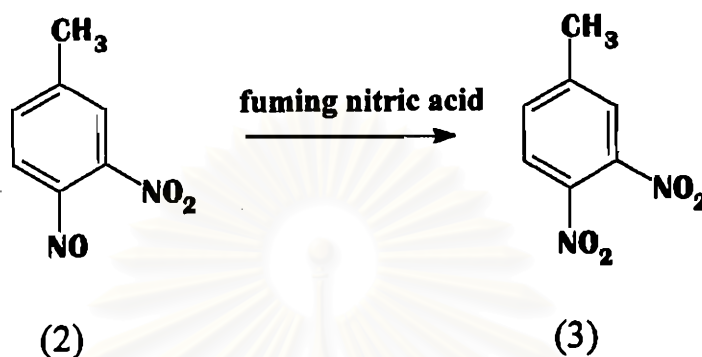
In general primary aromatic amines can be oxidized to nitro compounds via nitroso intermediate. Most often the conversion is accomplished using Caro's acid (H_2SO_5) [28, 29]. The reaction is shown in Scheme 3.3.

Scheme 3.3

Then the nitroso compound was oxidized to the nitro compound using fuming nitric acid as the oxidizing agent.

(2)   (3)

In order to get 3,4-dinitrobenzoic acid, the methyl group on the aromatic ring of 3,4-dinitrotoluene was converted to the carboxylic acid with chromic acid (chromic oxide or dichromate salt mixed with concentrated sulfuric acid). The Figure A1 - A4 (in Appendix A), Figure B1 - B5 (in Appendix B), Figure C1 - C4 (in Appendix C) and Figure D1 - D3 (in Appendix D), data have shown that 3,4-dinitrobenzoic acid has been obtained. The chemical shift values are given in Table 3.1 and 3.2, respectively, which confirm that (4) was prepared from 3,4-dinitrotoluene (3) using the previously mentioned reaction scheme.
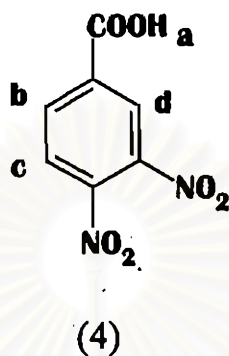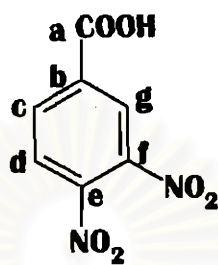
(4)

Table 3.1 Calculated and experimental chemical shifts of ^{1}H of
3,4-dinitrobenzoic acid (4) a measured by ^{1}H-NMR Spectroscopy
(200 MHz).

| ^{1}H position	Chemical shift (ppm)	
	Calculation	Found
H_a	10-13	not found
H_b	8.57d	8.39d
H_c	8.47d	8.33d
H_d	9.27s	8.56s

(4)

Table 3.2 Calculated and experimental chemical shifts of ^{13}C of 3,4-dinitrobenzoic acid (4) a measured by ^{13}C-NMR Spectroscopy (200 Mhz).

| ^{13}C position	Chemical shift (ppm)	
	Calculation	Found
C_a	162-183	164.1
C_b	138.2	135.9
C_c	137.3	135.1
C_d	125.9	126.1
C_e	149.4	144.2
C_f	145.2	14.6
C_g	126.8	126.1

3,4-Dinitrobenzoic acid (4) was then reacted with thionylchloride (SOCl$_2$) [30] using *N,N*-dimethylformamide (DMF) as a catalyst. The mechanism is shown in Scheme 3.4.
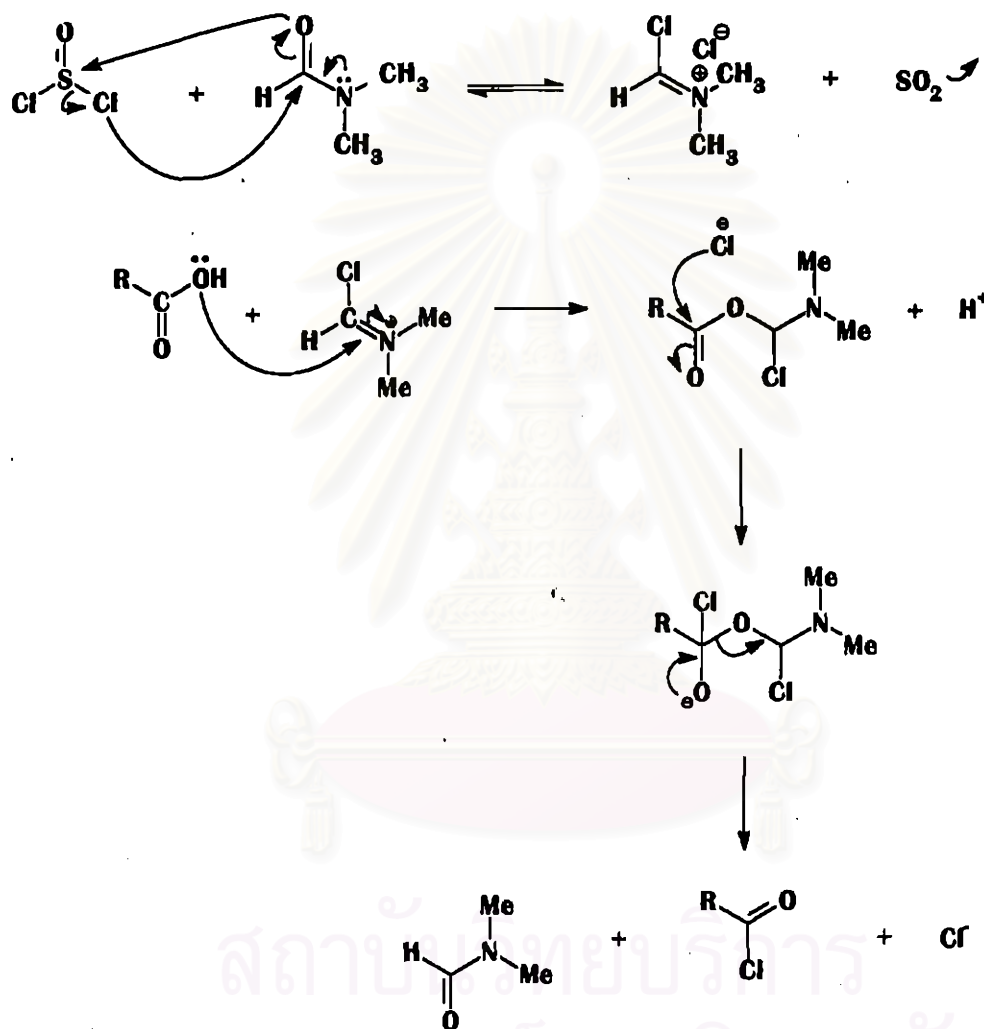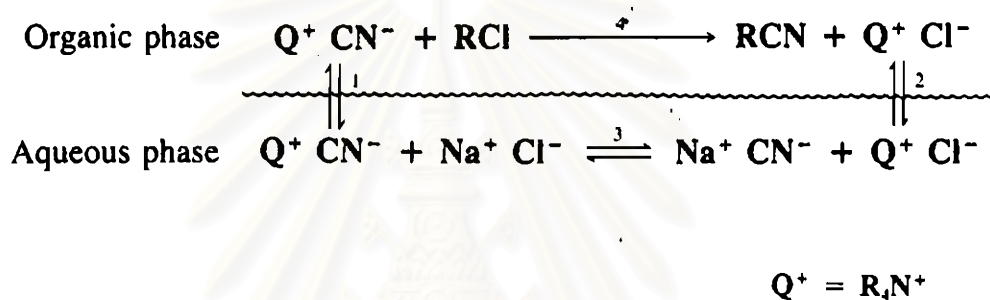

Scheme 3.4

From Figure B6 (in Appendix B), the IR band at 3400 cm^{-1} (O-H stretching) disappeared while the band at 746 cm^{-1} (C-Cl stretching) appeared. It implied that 3,4-dinitrobenzoic acid was converted to 3,4-dinitrobenzoyl chloride. Then this compound was used to prepare aroyl cyanide in the next step. 3,4-Dinitrobenzoyl cyanide was prepared by reacting 3,4-dinitrobenzoyl chloride with cuprous(I)cyanide (CuCN) or sodium cyanide (NaCN). Aroyl cyanides were prepared by three methods, including (a) direct substitution of Cl by CN at high temperature [31], (b) using acetonitrile as solvent, and (c) phase transfer catalysis [32].

Polynitro compounds easily explode at high temperature, in particular 3,4-dinitrobenzoyl chloride explodes above 225 ^{0}C, therefore the direct substitution of Cl with CN at high temperature is not suitable for this reaction. The operating temperatures of the other methods were lower, e.g. 80 ^{0}C for the second method and about 10 ^{0}C for the third one. However, the two reactions were similar to each other.
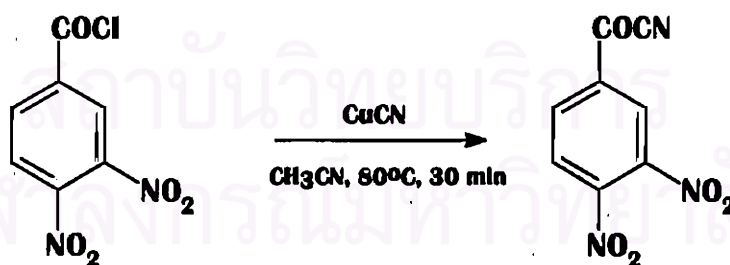
For the phase-transfer method sodium cyanide (NaCN), used as CN reservoir, was dissolved in water. The CN⁻ ions were paired with the tetrabutyl ammonium ion and crossed from the aqueous phase to the organic phase, then the chlorine atom of the 3,4-dinitrobenzoyi chloride was exchanged with the CN ion pair in the organic phase. The reaction is shown in Scheme 3.5.

Organic phase $Q^+ \ CN^- \ + \ RCl \ \xrightarrow{\quad\quad} \ RCN \ + \ Q^+ \ Cl^-$

Aqueous phase $Q^+ \ CN^- \ + \ Na^+ \ Cl^- \ \rightleftharpoons \ Na^+ \ CN^- \ + \ Q^+ \ Cl^-$

$Q^+ \ = \ R_4N^+$

Scheme 3.5

Both of these methods have been tried and found to give high yields and were very convenient. The resulting red-brown viscous liquid was 3,4-dinitrobenzoyl cyanide because its IR spectrum (Figure B7 (Appendix B)) at 2224.6 cm⁻¹ and 1692.9 cm⁻¹ showed the CN stretching and C=O stretching vibrations.

3.2) Synthesis of 4-Chloro-5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl) oxazole Using Ternai Synthesis.

A hypothetical reaction mechanism for the Ternai synthesis is shown below (see Scheme 3.6). It is interesting to note that steps 3, 4 and 5 could not take place as the expected oxazolid-4-one which did not in fact forms even in the presence of added water.
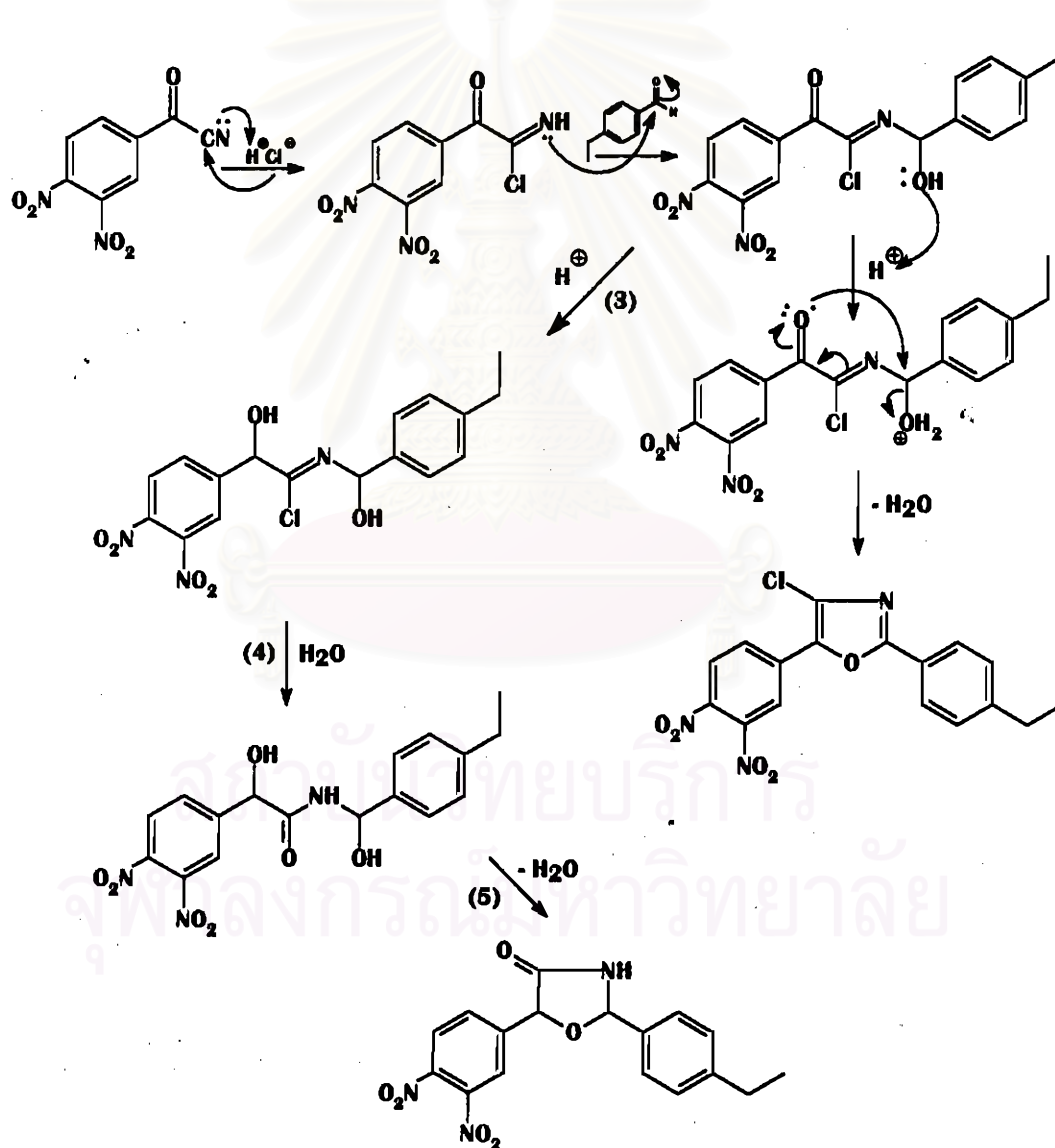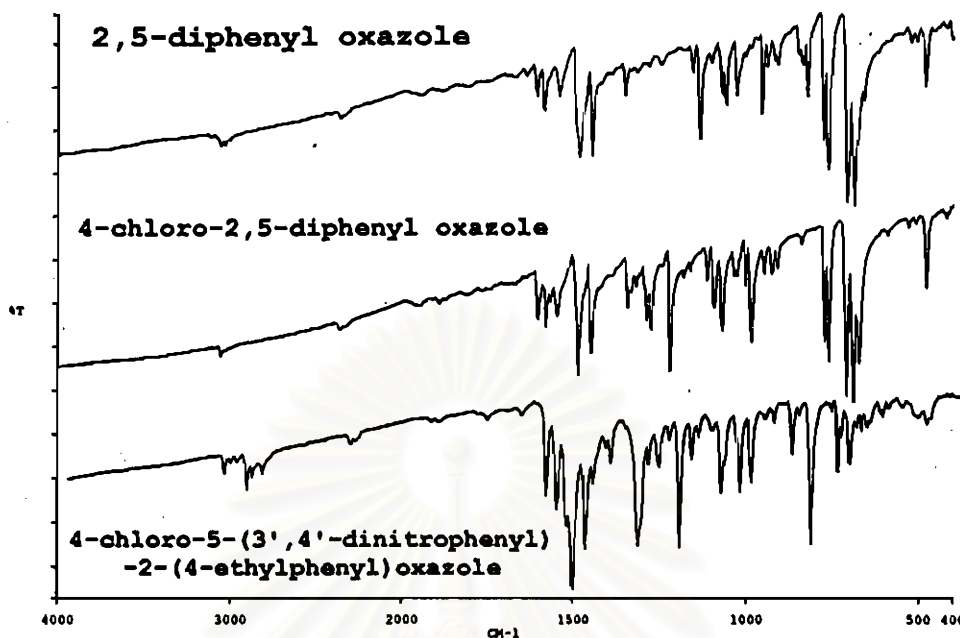

Scheme 3.6

Figure 3.1 Comparison of IR spetra of 2,5-diphenyloxazole, 4-chloro-
2,5-diphenyloxazole and 4-chloro-5-(3',4'-dinitrophenyl)-2-
(4-ethylphenyl)oxazole.

Table 3.3 Interpretation of IR spectrum of 4-chloro-5-(3',4'-dinitro
phenyl)-2-(4-ethyl phenyl)oxazole.

Wave number(cm^{-1})	Assignment
3095	C-H(st) of aromatic
2967	C-H (st) of aliphatic
1583	-N=C-O- ring [33]
1536 and 1355	-NO$_2$ (st)
842 and 884	C-H deformation of 1,3,4-trisubstitute
831	C-H deformation of 1,4-disubstitute
765	C-Cl (st)

From Figure 3.1, the IR spetrum of 4-chloro-5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl)oxazole was similar to the spectra of the parent compound, 2,5-diphenyloxazole and 4-chloro-2,5-diphenyl oxazole. It implied that the dinitrooxazole derivative might be prepared using this condition. The chemical structure of 4-chloro-5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl)oxazole was confirmed by ^{1}H-NMR (see Figure C5 in Appendix C), the chemical shift at 1.27t (CH$_3$, J$_{HH}$ 7.6Hz) was coupled to 2.70q (CH$_2$, J$_{HH}$ 7.6Hz) indicating a presence of CH$_2$CH$_3$. The chemical shift at 7.65d (J$_{HH}$= 8.62 Hz), 8.09d (J$_{HH}$= 8.56 Hz) and 8.37d (J$_{HH}$= 2.10 Hz) ppm were due to the aromatic ring with the two substituted nitro groups. The other protons of were at 7.34d (J$_{HH}$= 8.23 Hz) and 7.96d (J$_{HH}$= 8.26 Hz) other the aromatic ring (see Figure 3.2).

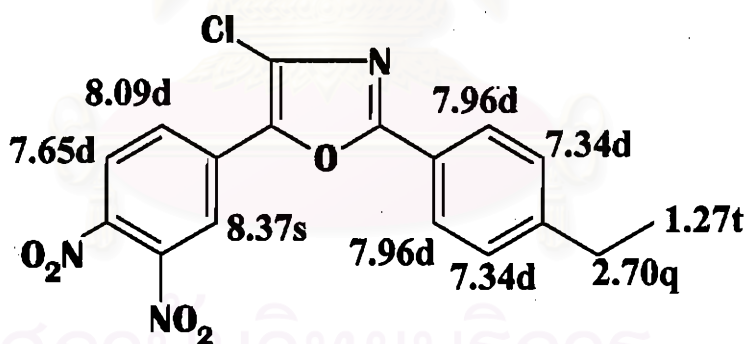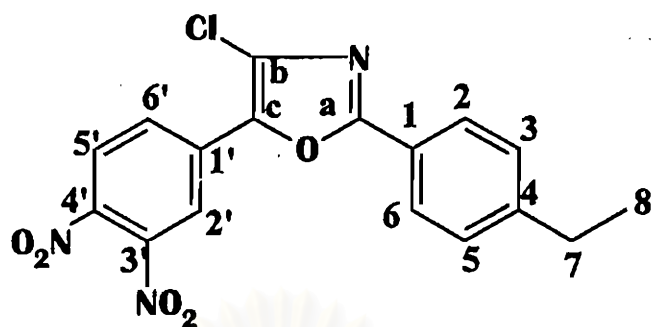Figure 3.2 ^{1}H-NMR chemical shift assignment of 4-chloro-5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl)oxazole.

1′ : 123.18C	a : 160.50C	1 : 123.18C
2′ : 132.48CH	b : 123.18C	2 : 128.63CH
3′ : 148.63C	c : 148.63C	3 : 128.63CH
4′ : 148.63C		4 : 123.18C
5′ : 121.37CH		5 : 128.63CH
6′ : 126.78CH		6 : 128.63CH
		7 : 28.94CH$_2$
		8 : 15.17CH$_3$

Figure 3.3 ^{13}C-NMR chemical shift assignment of 4-chloro-5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl)oxazole.

The ^{13}C spectra exhibited only eleven instead of the expected fifteen peaks. DEPT 90 and DEPT 135 spectra indicated that peaks 132.48, 128.63, 126.78 and 121.37 were due to carbons bearing one H. However, on a closer inspection it was found that the peak at 128.63 consisted of 2 very nearly overlapping resonances. These were assigned to carbons at the position of 2, 3, 5 and 6. Using substituent effect based rules [34], the 2′, 6′ and 5′ carbons were assigned to 132.48, 126.78 and

121.37, respectively. Based on the known (but only partially assigned) ^{13}C spectrum of 2,5-diphenyloxazole, the resonance at 160.5 was assigned to C-a. However, Carbon c has a resonance at 151.2 in 2,5-diphenyloxazole, therefore the peak at 148.63 must be due to C'-c of the dinitro compound. On the other hand, calculations based on substituent constant additivities indicate that carbons 4' and 3' shown also have the same chemical shift. It seems to be extremely that three resonances would coincide to such an extent that only a simple, unresolved resonance is seen. The resonances of the aliphatic carbons are at their expected positions. It can be concluded, that even though some carbons could not be assigned with confidence, that the compound has the expected chemical structure.

3.3)The Bromination of 4-Chloro-5-(3',4'-dinitrophenyl)-2-(4-ethyl phenyl)oxazole with *N*-Bromosuccinimide

The bromination of allylic and benzylic groups is best carried out with *N*-bromosuccinimide (NBS). NBS brominates organic molecules in excellent yield by reactions initiated by light, dibenzoyl perxide (BPO) or other radical sources. NBS and BPO were chosen to use for this case.

4-chloro-5-(3',4'-dinitrophenyl)-2-(4-ethylphenyl)oxazole was brominated with NBS and purified using recrystallization from chloroform: petroleum ether 30-60 ^{0}C (1:1). Then it was analysed by means of DSC, FTIR and ^{1}H-NMR techniques, respectively.

FTIR spectra (Figure B9 in Appendix B) indicated the presence of a C-Br bond at 592 cm^{-1}. ^{1}H-NMR (see Figure C6 in Appendix C) shows
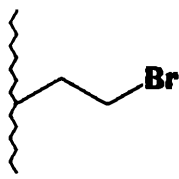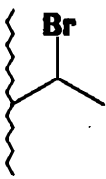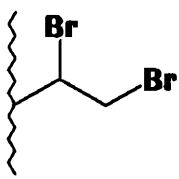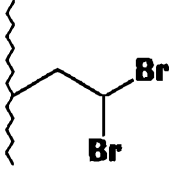
peaks at 5.23q (J_{HH} 6.94 Hz,-CHBr-) and 2.08m (J_{HH} 6.94 Hz, CH_3). In addition, the coupling constant (J) confirms that the peak at 2.07ppm is coupled with 5.23ppm (AX_3 coupling pattern).

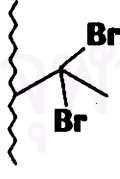Normally, the radical intermediate of the organic reaction is mixed in the reaction, but the secondary radical intermediate was more stable than the primary one. Therefore, it was predicted that α-isomer was a major product. However, when the concentration of NBS was high, the dihalogenated compound was formed. The reaction may occured as follows:
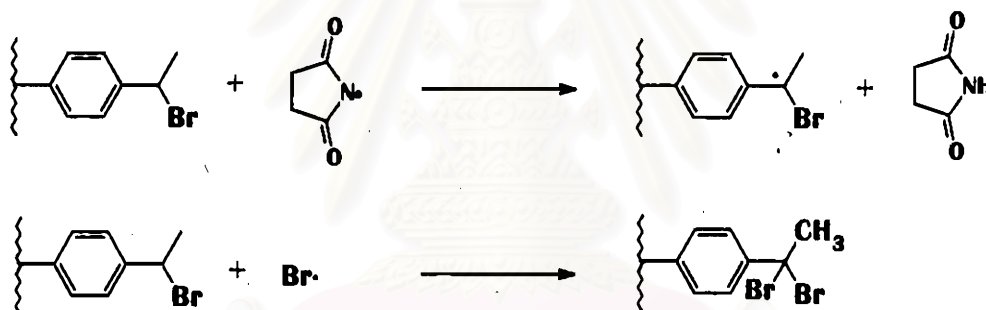
Therefore, the chemical shift at 2.99s ppm (Figure C7 in Appendix C) should be due to the H on the CH_3 group of the α,α-dibromoethyl compound. All possibility products for the bromination of this reaction are shown in Table 3.4. The ^{1}H-NMR (Figure C6 in Appendix C) indicates that the products was mixed α- and β-isomers. It has not been required to separate both isomers because these products would be dehydrobrominated in the next step.

Table 3.4 Expected ^{1}H-NMR patterns for various bromine substitutions.

Compounds	Spin-Spin Splitting Pattern		Probability
	α-position	β-position	
(structure: —CH₂CH₂Br)	triplet	triplet	minor product
(structure: —CH(Br)CH₃)	quartet	doublet	major product
(structure: —CH(Br)CH₂Br)	triplet	doublet	less
(structure: —CH₂CH(Br)Br)	doublet	triplet	less
(structure: —C(Br)₂CH₃)	—	singlet	high concentration of NBS

3.4) Synthesis of 4-Chloro-5-(3′,4′-dinitrophenyl)-2-(4-vinylphenyl) Oxazole

The vinyl group can be prepared by dehydrohalogenation of alkyl halide. The elimination of hydrohalogen (HX) from alkyl halide is a very general reaction and can be accomplished with all halogens. Hot alcoholic KOH is the most frequently used base, though stronger bases (OR⁻, NH₂⁻ etc.) or weaker one (e. g. amines) are used where warranted.

Synthesis, 4-chloro-5-(3′,4′-dinitrophenyl)-2-(4-bromoethyl phenyl)oxazole was treated using triethylamine. The IR band (Figure B10 in Appendix B) at 592 cm^{-1} (C-Br stretching) disappeared. The ¹H-NMR spectrum (Figure C8 in Appendix C) showed the chemical shift at 5.29-5.97 ppm (multiplet, 2H) and 6.52-6.86 ppm (multiplet, 1H), respectively. Moreover, the mixture in this product was presented in the ¹H-NMR spectrum also. It implied that the product should be purified with the optimum condition. It was not clear to state that the pure compound was obtained; however, there was an indication to conclude that the expected product was successfully synthesized at low yield with the presence of some impurities. Therefore, an attempt should be made to find out the optimum synthesis condition as well as the method to purify the product.