CHAPTER IV

CONCLUSION

4.1 Photoreaction of 1-methyl-3-(trifluoromethyl)pyrazole [39], 1-methyl-4-(trifluoromethyl)pyrazole [43], and 1-methyl-5-(trifluoromethyl)pyrazole [42]

Upon irradiation of 1-methyl-3-(trifluoromethyl)pyrazole **[39]**, the results indicated the generation of 1-methyl-2-(trifluoromethyl)imidazole **[45]** and 1-methyl-4-(trifluoromethyl)imidazole **[47]** as predicted products of P_7 and P_6 process ,respectively, via electrocyclic ring closure, whereas the photocleavage product was not detected. The latter product **[47]** was assumed to be the secondary product arising from 1-methyl-2-(trifluoromethyl)imidazole **[45]**. To confirm the permutation pathway for 1-methyl-3-(trifluoromethyl)pyrazole **[39]**, 4-deuterio-1-methyl-3-(trifluoromethyl)pyrazole **[39-4d$_1$]** was synthesized and irradiated. The experimental result showed that 1-methyl-2-(trifluoromethyl)imidazole **[45]** was generated from P_7 only.

The photoreaction of 1-methyl-4-(trifluoromethyl)pyrazole **[43]** afforded 1-methyl-4-(trifluoromethyl)imidazole **[47]** as predicted to form via P_4 process, whereas the phototransposition product was not detected. In this reaction the photocleavage intermediates, which were identified as cis- and trans-isomers of 3-(N-methylamino)-2-(trifluoromethyl)propenenitrile **[48]** and (N-methylamino)-1-(trifluoromethyl)ethenylisocyanide **[49]**, were as revealed in the ^{1}H-NMR spectrum of the irradiated solution comparing with the previous report on ^{1}H-NMR data of each intermediates generated from the photoreaction of phenyl-substituted 1-methylpyrazoles.[4]

When 1-methyl-5-(trifluoromethyl)pyrazole **[42]** was irradiated, it underwent photocleavage to 1-methyl-5-(trifluoromethyl)imidazole **[46]**, a predicted product of P_4 process, as well as electrocyclic ring closure to 1-methyl-2-(trifluoromethyl) imidazole **[45]** and 1-methyl-4-(trifluoromethyl)imidazole **[47]**, predicted products of P_6 and P_7 process, respectively. 1-Methyl-4-(trifluoromethyl)imidazole **[47]** was

assumed to be the secondary product arising from 1-methyl-2-(trifluoromethyl) imidazole **[45]**. By using ^{1}H-NMR spectroscopic technique, it could be identified that the photocleavage intermediates of this reaction were cis- and trans- isomers of (N-methylamino)-3-(trifluoromethyl)propenenitrile **[50]** and 2-(N-methylamino)-3-(trifluoromethyl)ethenylisocyanide **[51]**.

Trifluoromethyl-substituted 1-methylpyrazoles undergo phototransposition to trifluoromethyl-substituted 1-methylimidazoles by four distinct mechanistic pathways. The results clearly showed that ring trifluoromethyl substitution can substantially alter the extent to which each pathway operates. 3-Substituted 1-methylpyrazole restricts the phototransposition to the P4 pathway, 4-substituted 1-methylpyrazoles favor the phototransposition to the P4 pathway, and 5-substituted 1-methylpyrazoles are the least perturbed. The photocleavage *via* isocyanide and enaminonitrile intermediates for the P4 pathway is general to the pyrazoles that bear the hydrogen at the C-3 ring position.

4.2 Proposal for future work

1. The phototransposition reactions of other pyrazoles, such as phenyl-substituted 1-phenylpyrazoles and nitro-substituted 1-methylpyrazoles, should be investigated the influence of the steric and inductive effects, respectively.
2. The exact quantum yield of phtotoproducts should be determined and the mechanism for these photoreactions should be studied by computational chemistry.