CHAPTER IV

CONCLUSION

The synthesis of hexasubstituted benzene has been successfully performed by using phloroglucinol dihydrate as the starting material reacting with various acid chlorides (RCOCl; R = CH_3, Ph and C_7H_{15}) as the electrophilic reagent and medium. The desired 1,3,5-triacyl-2,4,6-trihydroxybenzene products were synthesized presumably through triple O-acylation and then underwent Fries rearrangement to *ortho* or *para*-positions to become tris(*ortho*-hydroxyacyl)aromatic molecules upon treatment with $AlCl_3$. The signal of their phenolic protons appeared as a singlet at unusually downfield chemical shift indicating that the molecule was not arranged in an *ababab* geometry, but rather in a relatively flat platform induced by three strong intramolecular hydrogen bonds between the hydroxy groups and the adjacent carbonyl groups. The larger the sizes of the α-substituents of acyl groups were, the less planar of the molecule would become due to the more congestion around the aromatic ring. Ethyl formate and *N,N*-dimethylformamide (DMF) were investigated to synthesize other derivatives of acyl groups using similar strategy. Ethyl formate did not react with phloroglucinol while DMF provided a complicate mixture that could not be characterized by ^{1}H-NMR data. Benzyl chloride was next used as the electrophile. Unfortunately large amount of unexpected product was obtained, which was most likely a polymer of benzyl groups. The reaction with allyl bromide provided the partially rearranged product during allylation process to become a pentasubstituted benzene. This product was best obtained in 35% yield using K_2CO_3 as the base in the reflux temperature of DMF for 3.5 hours.

1,3,5-triacetyl-2,4,6-trihydroxybenzene **(60)** was modified into the *ababab* geometry by functionalization to various derivatives. The functionalization had been done in two pathways: alkylations on the phenolic hydroxy groups and additions on the carbonyl of the ketone groups. The reaction of O-alkylations were found to occur yielding compounds **69** and **71** under basic condition using acetonitrile as the solvent. Compound **60** was benzylated to provide a symmetric structure of **69** in 65% yield. When switching the acetylation and benzylation steps, this product was not obtained, but appeared to be mostly the starting **60** in 46% yield and some polymers of benzyl groups. The reaction of compound **60** with ethyl iodoacetate provided a symmetric platform of trifuranyl triester **71** in 18% yield. The desired product apparently condensed immediately among the *ortho*-neighboring groups to finally gave **71** as the most stable product.

The addition on the ketone carbonyl of compound **60** was carried out by the reaction with phenylhydrazine yielding tris-hydrazone **72** in 18%. The intramolecular hydrogen bonds between the hydroxyl groups and C=N were also present. Compound **72** was found to form complexes with Fe(III) and Cu(II), evidenced by hypsochromic shift of the λ_{max} of the complexes relative to that of compound **72** in the absorption spectra. In the ^{1}H-NMR spectra of Fe and Cu-complex, the methyl protons shifted downfield to 2.8 ppm and all aromatic protons grouped at 7.3 ppm. The Cu-complex spectrum also found free acetate proton at 2.1 ppm which was released by $Cu(OAc)_2$. Phenylhydrazine, however, did not appear to react with compound **69** toward the desired hydrazone. The functionalization at α-atoms around benzene ring seemed to be too difficult to perform under the reaction condition used since these positions carried high steric crowd among the neighboring groups.