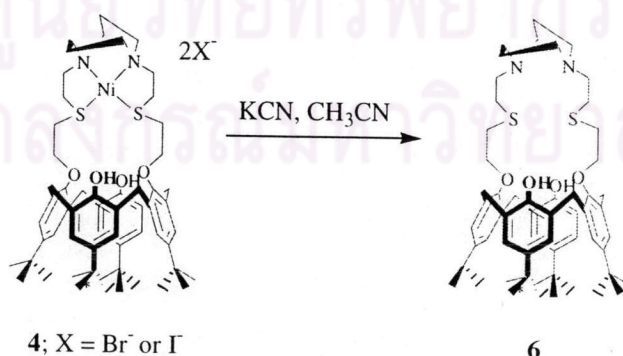


CHAPTER IV

CONCLUSION

4.1 Syntheses of diaza dioxa dithia *p*-tert-butylcalix[4]arenes as heavy metal ion receptors

Preparation of Ni(bme-daco) calix[4]arene (**4**) can be carried out in two routes. In route A, the desired product was obtained using bromoethyltosylate (**1a**) to yield dibromoethyl-calix[4]arene (**2a**) as precursor in 23% and calix[4]arene dimer (**3**) in 41%. Coupling reaction between dibromoethyl-calix[4]arene (**2a**) and Ni(bme-daco) in CH₃CN afforded the green solid of Ni(bme-daco)calix[4]arene (**4a**) having 2Br⁻ as counter anion in the yield of 18%. In terms of route B, chloroethyltosylate (**1b**) was precursor to produce dichloroethyl-calix[4]arene (**2b**) in 67% yield. For the last step, the alkylation reaction of the Ni mercaptan and dichloroethyl-calix[4]arene (**2b**) in the presence of NaI in catalytic amount provided the desired product, Ni(bme-daco)calix[4]arene (**4b**) and by-product, bis[Ni(bme-daco)]calix[4]arene (**5**) in the yield of 11% and 35%, respectively. Both products have either I⁻ or Cl⁻ as counter anions. One way to get the desired ligand is to use KCN in CH₃CN for removing Ni (II) from azathiol-calix[4]arene. The result is the slight yellow solid in the yield of 92% as shown in **Scheme 4.1** and free ligand was characterized by ¹H-NMR spectrum shown in **Figure 4.1**.



Scheme 4.1 Procedure of demetallic compound

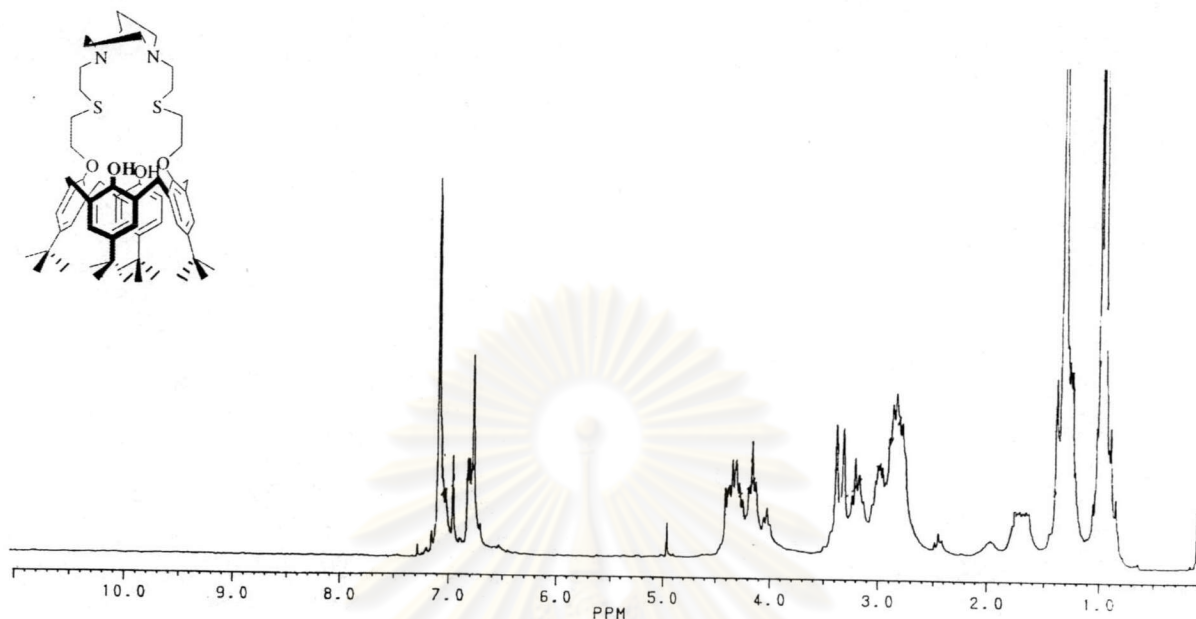


Figure 4.1 $^1\text{H-NMR}$ spectrum of demetallic(bme-daco)calix[4]arene (**6**) in CDCl_3 with 200 MHz

$^1\text{H-NMR}$ spectrum of **6** shows the broaden signals of ethylene bridge protons which were monitored the peak shift corresponding on the complex with heavy metal ions. Furthermore, $\text{Ni}(\text{bme-daco})$ was difficulty prepared due to not only air and moisture sensitive compound but also its high cost.

4.2 Anion sensory studies of amide ferrocene calix[4]arene derivatives

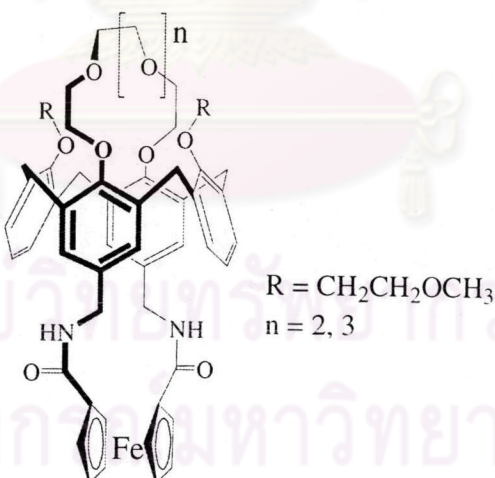
5,7-Diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**5a**), 5,7-diamide ferrocenyl-25,26,27,28-dimethoxy dimethyl ethylestercalix[4]arene (**5b**) and 5,7-diamide ferrocenyl-25,26,27,28-tetramethyl ethylestercalix[4]arene (**5c**) have been synthesized by coupling reactions between 1,1-di(chlorocarbonyl)ferrocene and tetramethoxy-diaminocalix[4]arene (**4a**), dimethoxy dimethylethylester-diaminocalix[4]arene (**4b**) and tetramethyl ethylester-diaminocalix[4]arene (**4c**), respectively. Characterizations by NMR and X-ray structures show that **5a** and **5b** are in the mixture of cone and partial cone conformation in solutions while **5c** is in cone conformation only. In the case of solid state structures, **5a** is in partial cone conformation while **5b** is in cone conformation. The stability constants measured by $^1\text{H-NMR}$ titration in CD_3CN show the **5a**, **5b** and **5c** bind acetate selectively

and display the anion binding affinity in order of **5c** > **5a** > **5b**. Electrochemical studies of the three ligands carried out by cyclic voltammetry exhibit the binding enhancement for benzoate over acetate, H_2PO_4^- and Cl^- . Binding abilities of **5c** towards cations have been investigated by electrospray ionization mass spectrometry. The results support the binding abilities of **5c** with cations such as Na^+ , K^+ , Rb^+ and Cs^+ . However, binding constants are probably low, therefore, they cannot be calculated by $^1\text{H-NMR}$ titrations. Interestingly, cyclic voltammetry can show the difference of voltammograms between the free ligand and its cation complex. This technique supports that **5c** can form a complex with Na^+ with weak interactions.

The suggestion for future works:

Future works should be aimed at:

- 1 To study a conformational interconversions of **5a** and **5b**. This can be carried out by EXSY-NMR technique.
- 2 Design and synthesize the novel amide ferrocene calix[4]arene in order to solve the problems for the cation binding ability and the conformational interconversion.



- 3 Study the effect of tetraalkylammonium salts such as $n\text{-NBu}_4\text{X}$, $t\text{-NBu}_4\text{X}$, NCH_4X , alkyl- and aryl-sulfonate to the anion binding ability of **5c** by $^1\text{H-NMR}$ titrations. They are expected to bind with ethyl ester at the lower rim of the ligand **5c**.¹⁵⁴⁻¹⁵⁷