CHAPTER III

EXPERIMENTAL SECTION

3.1 Apparatus

The temperature during extraction or stripping was controlled at 25.0 ± 1.0 ^{O}C by Bosstech control temperature model TMD/1 water bath. After extraction or stripping, the two phases (aqueous and organic phases) were separated by Heraeus Christ medifuge. The pH of the extracted aqueous solution and the initial solution of Cr(VI) was measured by Schott pH-meter CG 825 (reference electrode: Ag/AgCl). UV-vis spectra of $Cr_2O_7^{2-}$ (350 nm) and CrO_4^{2-} (373 nm) were obtained on a HP 8453 UV-vis spectrophotometer. Velp Scientifica Vortex Mixer was used for shaking the extraction glass vessel in solid-phase extraction experiments.

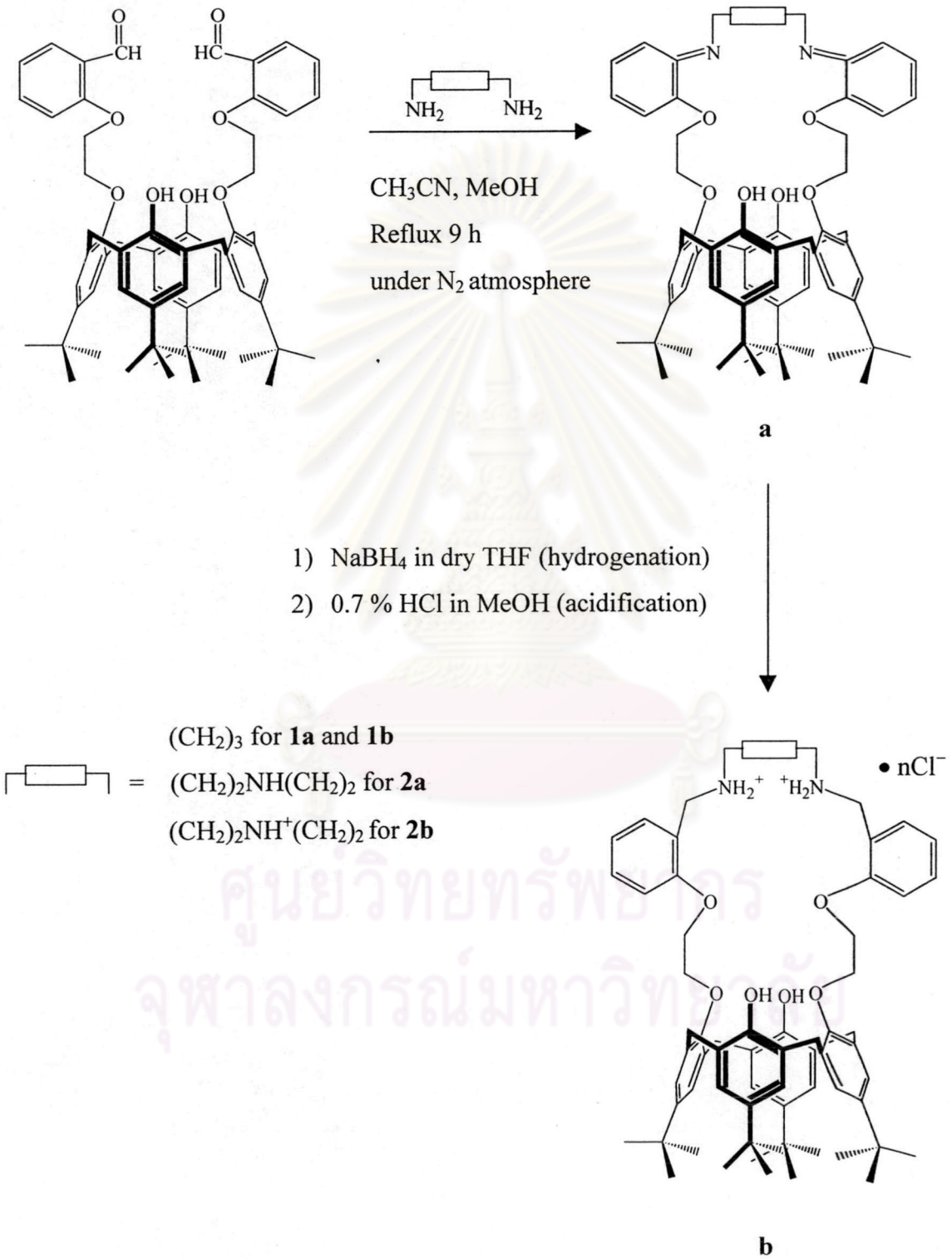
3.2 Chemicals

All materials were standard analytical grade purchased from Merck ($CHCl_3$, HNO_3, HCl, KCl, KNO_3, NaOH and SiO_2 0.063-0.200 mm) and Fluka (K_2SO_4, KH_2PO_4 and K_2CrO_4). These materials were used without further purification unless otherwise noted. All anions for extraction were used as their potassium salts (K_2CrO_4, KCl, KNO_3, K_2SO_4 and KH_2PO_4) and stored in a desiccator.

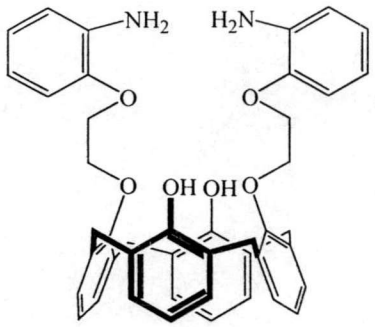
The 25,27-*N,N*-di-((2-ethoxy)benzyl) propylenediamine-*p-tert*-butylcalix[4] arene dichloride (compound **1b**) and 25,27-{2,2'-[2,2'-((2,5,8-triammonium)nonyl) diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene trichloride (compound **2b**) and inclusion of 25,27-di-((2-ethoxy)benzylamine)-calix[4]arene (compound **3**) and 3,3'-dihexylurea azobenzene (compound **4**) were used as extractant for the extraction studies of Cr(VI) anions. All of extractants were kept away from direct sunlight to avoid the decomposition and stored in a desiccator.

All of extractants employed in this research were synthesized from Supramolecular Chemistry Research Unit, Department of Chemistry, Chulalongkorn

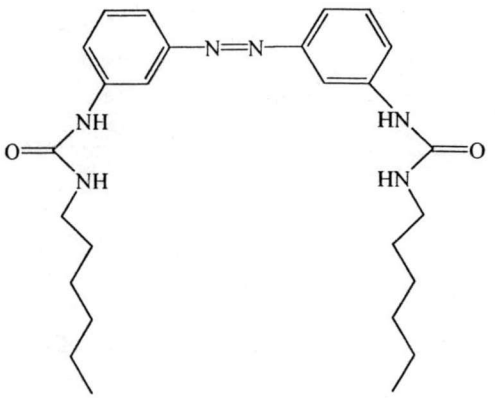
University. The synthesis of compounds **1b** and **2b** were based on the previously published procedures [52, 150, 151] (synthetic route shown in Scheme 3.1). The compounds **3** and **4** are reported for the first time [152] (Figure 3.1).



Scheme 3.1 Synthetic route of compounds **1b** and **2b**.



Compound **3**



Compound **4**

Figure 3.1 Structures of compounds **3** and **4**.

3.3 Parameters Studied and Conditions Used

3.3.1 Liquid-liquid Extraction Studies

3.3.1.1 Extraction Efficiency by Chloroform (Blank Test)

2.57×10^{-4} M (~50 ppm) K_2CrO_4 in 0.01M KCl at initial pH 2.37 and chloroform were magnetically stirred for 30 min.

3.3.1.2 Influence of Initial pH in K_2CrO_4 Solution

2.57×10^{-4} M compound **1b**, 2.56×10^{-4} M compound **2b**, 2.89×10^{-4} M compound **3** and 2.61×10^{-4} M compound **4** in chloroform were used as extractant for the extraction of 2.57×10^{-4} M K_2CrO_4 in 0.01 M KCl at different pH values: 2.26, 2.38, 2.63 and 3.23. The extraction time of 30 min was used.

3.3.1.3 Influence of Extraction Time

2.57×10^{-4} M compound **1b**, 2.58×10^{-4} M compound **2b** and 2.57×10^{-3} M compound **4** in chloroform were used as extractant for the extraction of 2.57×10^{-4} M K_2CrO_4 in 0.01 M KCl at initial pH 2.37. The extraction times of 15, 30, 45 and 60 min were individually studied.

3.3.1.4 Influence of Type and Concentration of Mediums

2.57×10^{-4} M compound **1b** and 2.58×10^{-4} M compound **2b** were used for the extraction of 2.57×10^{-4} M K_2CrO_4 in 0.01, 0.05, 0.1 and 0.5 M KCl or KNO_3 at initial pH 2.37. The extraction time was 30 min.

3.3.1.5 Influence of Competitive Anions

2.57×10^{-4} M compound **1b** and 2.58×10^{-4} M compound **2b** were used for the extraction of 2.57×10^{-4} M K_2CrO_4 in 0.01 M KCl (initial pH 2.37) which was individually added an anion of K_2SO_4, KNO_3 or KH_2PO_4. The concentration of anion in aqueous solution was maintained at 1.28×10^{-3} M. The extraction time was 30 min.

3.3.1.6 Influence of Concentration of Extractant in Various Mediums

Five concentrations of compounds **1b** and **2b** ($1.54\times10^{-4} - 5.65\times10^{-4}$ M) were used. The 2.57×10^{-4} M K_2CrO_4 in 4 mediums (0.01 M KCl at pH 2.37 and 2.76, 0.05 M KCl at pH 2.37 and 0.01 M KNO_3 at pH 2.37) were studied. The extraction time was 30 min.

3.3.1.7 Recycling of Ligand

2.57×10^{-4} M compound **1b** and 2.58×10^{-4} M compound **2b** were used for the extraction of 2.57×10^{-4} M K_2CrO_4 in 0.01M KCl at initial pH 2.37. Each extractant was used for 7 cycles of extraction. The extraction time was 30 min.

3.3.2 Solid-phase Extraction Studies

3.3.2.1 Extraction by SiO_2 (Blank Test)

2.57×10^{-4} M K_2CrO_4 in 0.01 M KCl (10.00 mL) at initial pH 2.37 were agitated with 0.01XX and 0.03XX g of SiO_2. The extraction time was 30 min.

2.57×10^{-4} M K_2CrO_4 in 0.01 M KCl (10.00 mL) at initial pH 2.37 were agitated with 0.200X and 0.500X g of SiO_2. The extraction times of 30 and 60 min were individually studied.

2.57×10^{-4} M K_2CrO_4 in 0.01 M KCl (10.00 mL) at initial pH 2.37 were agitated with 1.00XX g of SiO_2. The extraction times of 15, 30, 45 and 60 min were individually studied.

3.3.2.2 Extraction with Ligand Coated on SiO_2

The extraction of 2.57×10^{-4} M K_2CrO_4 in 0.01M KCl (5.00 mL) at initial pH 2.37 and 0.03XX g of compound **1b**-LC and **2b**-LC, and 0.01XX g of compound **1b**-HC and **2b**-HC was individually observed. The extraction times of 15, 30, 45 and 60 min were used. (LC = Low Capacity, HC = High Capacity, see section 3.4.2.2)

3.3.2.3 Recycling of Ligand Coated on SiO_2

The extractions of 2.57×10^{-4} M of K_2CrO_4 in 0.01M KCl (5.00 mL) at initial pH 2.37 and 0.03XX g of compound **1b**-LC and **2b**-LC (white powder) was individually observed at the extraction time of 30 min.

3.3.2.4 Leaching of Ligand from SiO_2 by Chloroform

An amount of 0.05XX g of compounds **1b**-HC and **2b**-HC was individually agitated with 20.00 mL of chloroform for 30, 60, 90 and 120 min.

3.4 Preparation of the Solution

3.4.1 Liquid-liquid Extraction Experiments

3.4.1.1. Preparation of K_2CrO_4 Solution

All aqueous solutions were prepared in chloroform-saturated deionized water. (Deionized water was agitated with chloroform for 30 min.).

A stock solution of K_2CrO_4 (2.57×10^{-3} M or 500 ppm) was prepared by dissolution of a weighed amount of K_2CrO_4 in 0.01 M KCl.

Unless otherwise noted, a solution of 2.57×10^{-4} M K_2CrO_4 used as initial aqueous phase of extraction was prepared by dilution of the stock solution of K_2CrO_4 in 0.01 M KCl. The desired pH was adjusted by 0.01 M HCl. (The deviation of adjusted pH was ± 0.01.)

In case of the extraction in various mediums (KCl or KNO_3), K_2CrO_4 solutions were prepared by dilution of the stock solution of K_2CrO_4 by 0.01, 0.05, 0.1 and 0.5 M KCl or KNO_3. The pH was adjusted by 0.01, 0.05, 0.1, 0.5 M HCl or HNO_3, respectively.

For the study of competitive anions, the K_2CrO_4 solution was prepared by mixing individual anion (potassium salt of SO_4^{2-}, NO_3^-, $H_2PO_4^-$) to the stock solution of K_2CrO_4 in 0.01 M KCl. The pH was adjusted by 0.01 M HCl. The concentration of anion in aqueous solution was maintained at 1.28×10^{-3} M.

Five concentrations of K_2CrO_4 (5.15×10^{-5}, 1.03×10^{-4}, 1.54×10^{-4}, 2.06×10^{-4} and 2.57×10^{-4} M) were prepared by dilution of the standard stock solution of K_2CrO_4 with 0.01 M NaOH. These solutions were used to construct a standard calibration curve.

3.4.1.2. Preparation of the Extracting Solution

The extractant in organic phase was obtained by dissolving each ligand in water-saturated chloroform. (The chloroform employed in this work was washed with deionized water just before use.)

The concentration of 0.257 ± 0.001 mM was used for compound **1b** and **2b** unless otherwise noted.

The extraction with compounds **3** and **4** at different pH were done at 2.89×10^{-4} and 2.61×10^{-4} M, respectively.

A concentration of 2.57×10^{-3} M of compounds **4** was used for the extraction time study.

3.4.2 Solid-phase Extraction Experiments

3.4.2.1. Preparation of K_2CrO_4 Solution

The aqueous phase consisted of 2.57×10^{-4} M K_2CrO_4 in a 0.01 M KCl at pH 2.37 for all of extraction studies. The solution was prepared as described in section 3.4.1.1

3.4.2.2 Preparation of Ligand Coated on SiO_2

The ligands coated on SiO_2 were prepared as follows: A weighted amount of ligand (~ 40 μmole) was dissolved in 25 mL of chloroform. 1.00XX g of SiO_2 was added. The mixture was magnetically stirred for 60 min at 25.0 ^{0}C in closed system in order to prevent a chloroform evaporation. Compounds **1b**-LC and **2b**-LC (LC = Low Capacity) were obtained from using compounds **1b** and **2b**, respectively.

In a similar manner, compounds **1b**-HC and **2b**-HC (HC = High Capacity) were prepared from ~ 100 μmole of compound **1b** and ~ 150 μmole of compound **2b**, respectively.

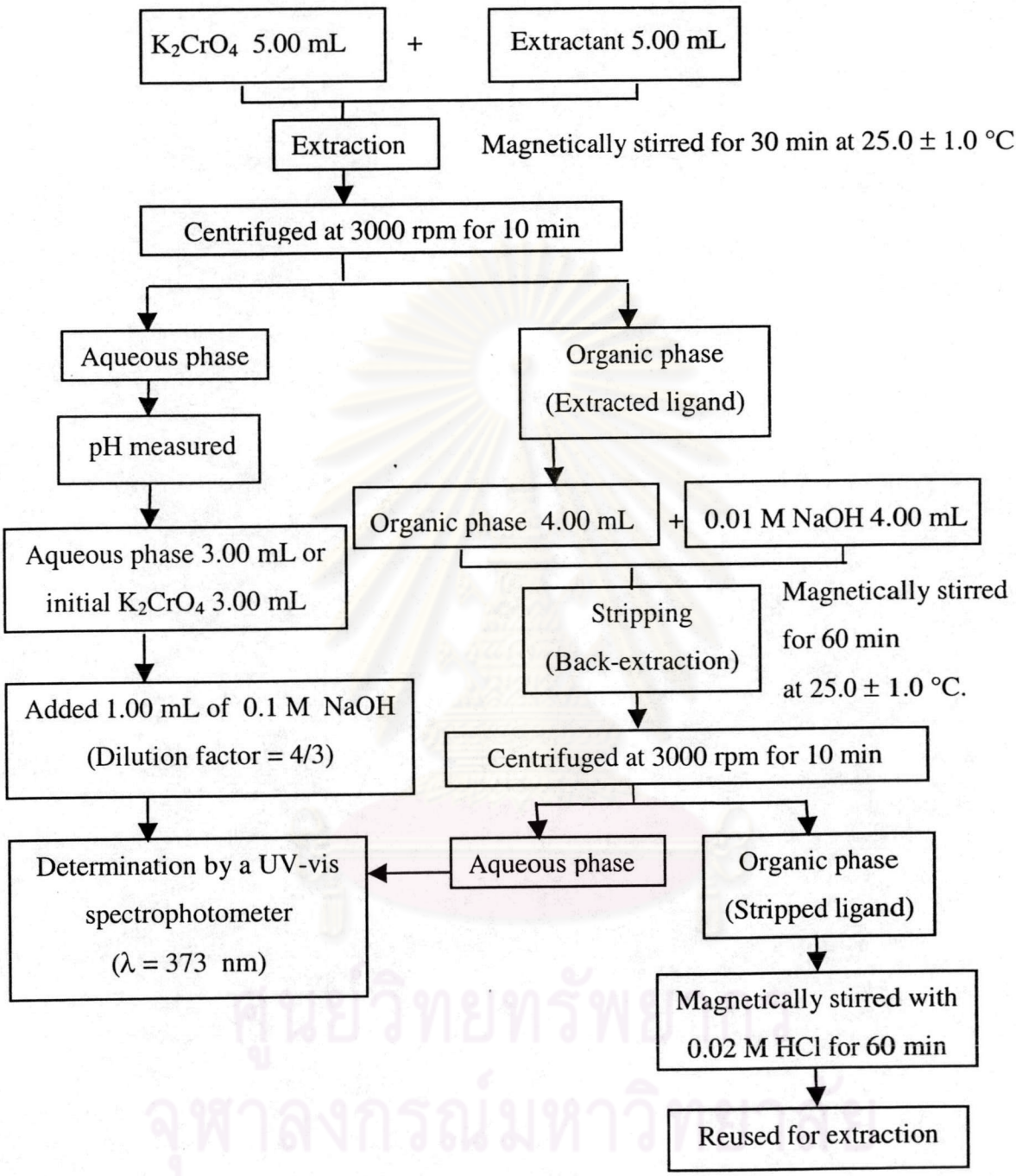
Five concentrations of compounds **1b** and **2b** (2.1×10^{-5}, 4.1×10^{-5}, 6.1×10^{-5}, 8.1×10^{-5} and 1.0×10^{-4} M) in chloroform were used to obtain a standard calibration curve.

3.5 Analytical Procedure

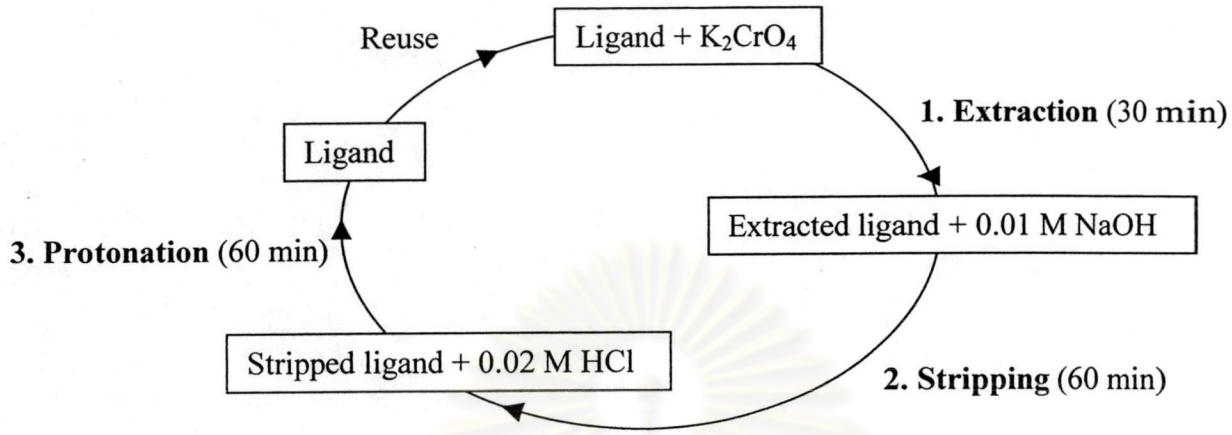
3.5.1 Liquid-Liquid Extraction Procedure

The extracting solution (5.00 mL) and the initial K_2CrO_4 solution (5.00 mL) were mixed in a stoppered round-bottle flask (extraction vessel) and magnetically stirred for 30 min at 25.0 ± 1.0 ^{0}C (with the exception of the extraction time study). After centrifugation at 3000 rpm for 10 min, the aqueous phase was separated and its pH was measured. The aqueous phase (3.00 mL) was then mixed with 0.1 M NaOH (1.00 mL) in order to obtain CrO_4^{2-} ion as main species (see Chapter II section 2.2.2.1). The organic phase (4.00 mL) was back-extracted (stripping) for 60 min at 25.0 ± 1.0 ^{0}C by 0.01 M NaOH (4.00 mL). The concentration of CrO_4^{2-} ion in the aqueous phase was measured on UV-vis spectrophotometer at 373 nm. The liquid-liquid extraction pathway is shown in Scheme 3.2.

For the study of recycling of ligand, ligand containing organic phase (24.00 mL) and K_2CrO_4 aqueous solution (24.00 mL) were used in the first cycle of extraction. The extraction step was carried out at 25.0 ± 1.0 ^{0}C for 30 min. After centrifugation, the aqueous phase was separated. The organic phase containing extracted ligand (23.00 mL) was back-extracted (stripping) for 60 min at 25.0 ± 1.0 ^{0}C by 0.01 M NaOH (23.00 mL). After centrifugation and separation of aqueous phase, 0.02 M HCl solution (22.00 mL) was added to organic phase containing stripped ligand (22.00 mL). The protonation step was carried out at 25.0 ± 1.0 ^{0}C for 60 min giving the protonated form of ligand in organic phase. This organic solution was used for the second cycle of extraction. The concentration of CrO_4^{2-} in aqueous phase was measured by a UV-vis spectrophotometer. These three steps were repeated 7 times. The recycle pathway and the volume used are summarized in Scheme 3.3 and Table 3.1, respectively.



Scheme 3.2 Liquid-liquid extraction pathway.



Scheme 3.3 Recycle pathway for liquid-liquid extraction.

Table 3.1 Volume used for each phase of 7 extraction cycles.

No. of Cycle	Volume (mL)					
	Extraction		**Stripping**		**Protonation**	
	Ligand	K_2CrO_4	Extracted ligand	0.01 M NaOH	Stripped ligand	0.02 M HCl
1	24.00	24.00	23.00	23.00	22.00	22.00
2	21.00	21.00	20.00	20.00	19.00	19.00
3	18.00	18.00	17.00	17.00	16.00	16.00
4	15.00	15.00	14.00	14.00	13.00	13.00
5	12.00	12.00	11.00	11.00	10.00	10.00
6	9.00	9.00	8.00	8.00	7.00	7.00
7	6.00	6.00	5.00	5.00	4.00	4.00

3.5.2 Solid-phase Extraction Procedure

Compounds **1b**-LC or **2b**-LC (white powder) was weighed in a stopper glass tube. 5.00 mL of K_2CrO_4 (2.57×10^{-4} M) in 0.01 M KCl at initial pH 2.37 ± 0.01 was added. The mixture was magnetically stirred for 15, 30, 45 or 60 min at 25.0 ± 1.0 ^{0}C. After centrifugation, the extracted ligand powder, which became yellow because of CrO_4^{2-} ion (the CrO_4^{2-} ion was extracted into the ligand-coated SiO_2), was precipitated at bottom of the tube. The aqueous solution was withdrawn to another tube and 3.00 mL of aqueous phase was then mixed with 1.00 mL of 0.1 M NaOH in order to obtain CrO_4^{2-} ion as main species for determination of the concentration of CrO_4^{2-} ion by UV-vis spectrophotometer.

For the study of recycling of ligand, the solid residue was rinsed twice (after the extraction step as described above) by adding 5 mL of 0.01 M HCl solution and then shaking by Vortex mixer for 2 min. In this step, the solid still maintained yellow in color because no deprotonation of ligand occurred. The back-extraction was carried out by adding 5.00 mL of 0.01 M NaOH and shaking by Vortex mixer for 5 min in order to deprotonate proton on the nitrogen atom ($-NH_2^+-$) on ligand and recover CrO_4^{2-} ion into aqueous phase. After centrifugation, the solid became white and the aqueous phase was slightly yellow. The basic aqueous solution was kept to determine the concentration of CrO_4^{2-} ion by UV-vis spectrophotometer. The solid residue was rinsed by adding 5 mL of deionized water and then shaking by Vortex mixer for 2 min. The protonation step was performed by adding 5 mL of 0.02 M HCl and then shaking by Vortex mixer for 5 min. After centrifugation, the aqueous phase was separated. The solid residue was used as extractant for next cycle. This cycle steps were repeated 3 times.

The leaching of ligand from SiO_2 performed as follows:

Compounds **1b**-HC or **2b**-HC were weighed in a stopper glass tube. 20.00 mL of chloroform was added. The mixture was agitated for 30 min at 25.0 ± 1.0 ^{0}C. The ligand-coated SiO_2 was left to precipitation by gravity. The chloroform was withdrawn to measure the concentration of the ligand by UV-vis spectrophotometer at 281 nm. After UV-vis measurement, the measured chloroform was poured in the stopper glass tube again and the mixture was then agitated for 60, 90, and 120 min. The concentration of the ligand was measured after each agitation as described above.