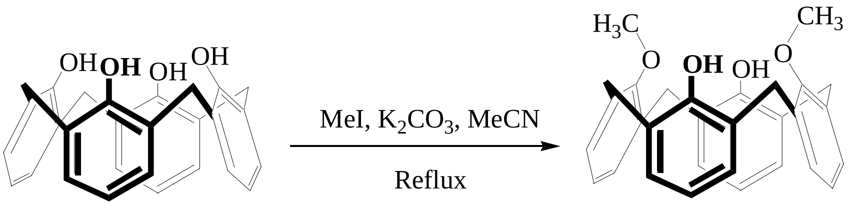
Prepatration of 26, 28-dimethoxycalix[4]arene (1a)



1a

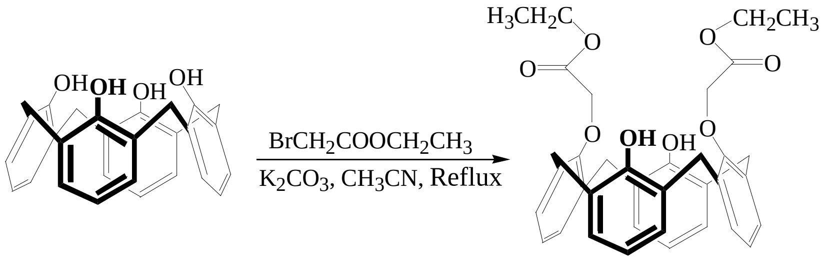
Calix[4]arene (0.425 g, 1.0 mmol) and K_2CO_3 (0.1512 g, 1.09 mmol) was suspended in CH_3CN (10 mL) and the mixture was stirred at room temperature for 1 h. Iodomethane (0.1313 g, 2.20 mmol) was then added and the mixture was heated at reflux overnight. The mixture cooled to room temperature. The reaction was filtered to take K_2CO_3 off and then the filtrate was concentrated by rotary evaporator. The residue was dissolved in dichloromethane and washed with 3 M HCl 3 times. The organic layer was dried over anhydrous $NaSO_4$. The volumn of the solvent was reduced by using a rotary evaporator. Upon adding CH_3OH, a white solid of compound **1a** precipitated (0.397 g, 87.77% yield).

Characterization data for 1a

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 7.72 (s, 2H, O*H*), 7.09-6.63 (m, 12H, Ar*H*), 4.33 and 3.42 (d, *J* = 13.2 Hz, 8H, ArCH_2Ar), 3.97 (s, 6H, OCH_3).

Preparation of 26,28-dimethylethylestercalix[4]arene (1b)



1b

Calix[4]arene (1.0 g, 2.36 mmol) and K_2CO_3 (2.50 g, 23.6 mmol) was suspended in CH_3CN (15 mL) and the mixture was stirred at room temperature for 1 h. Bromoethyl acetate (0.87 g, 5.20 mmol) was then added and the mixture was heated at reflux for 4 h. The mixture was cooled to room temperature. The reaction was filtered to take K_2CO_3 off and then the filtrate was concentrated by rotary evaporator. The residue was dissolved in dichloromethane and washed with saturated NH_4Cl 3 times. The organic layer was dried over anhydrous $NaSO_4$. The volumn of the solvent was reduced by using a rotary evaporator. Upon adding CH_3OH, a white solid of **1b** was obtained in 0.801g, 57%.

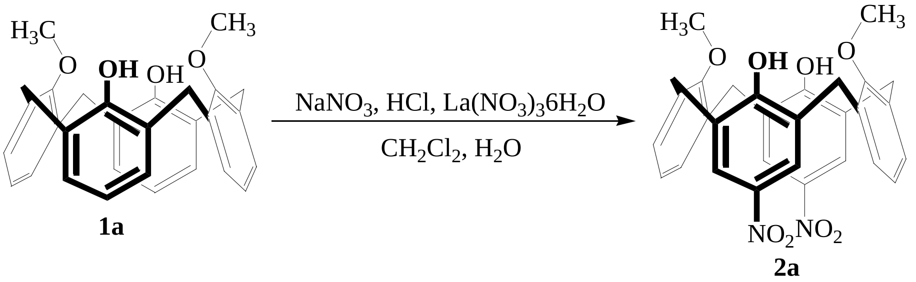
Characterization data for 1b

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 7.57 (s, 2H, O*H*), 7.04 (d, *J* = 7.47 Hz, 4H, *m*-Ar*H*OR), 6.89 (d, *J* = 7.41 Hz, 4H, *m*-Ar*H*OH), 6.76-6.60 (m, 4H, *p*-Ar*H*OR and *p*-Ar*H*OH), 4.71 (s, 4H, ArOCH_2-), 4.46 and 3.38 (dd, *J* = 13.3, ArCH_2Ar), 4.37-4.27 (q, *J* = 7.23 Hz, -OC$H_2$$CH_3$), 1.34 (t, *J* = 6.53 Hz, 6H, -OCH_2CH_3)

melting point: 180 °C

Preparation of 5,7-dinitro-26,28-dimethoxycalix[4]arene (2a)

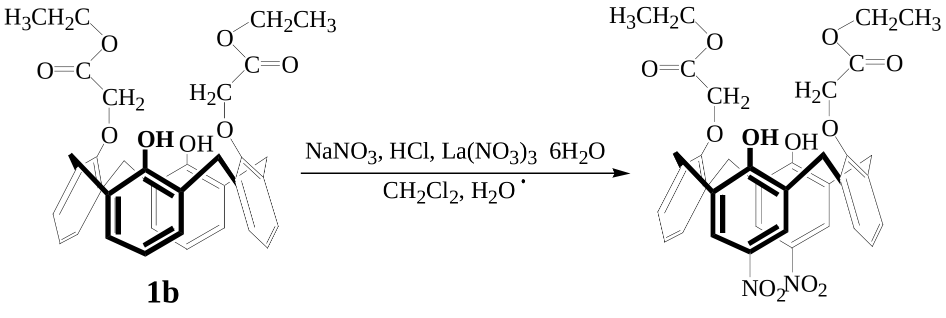


To a solution (CH2Cl2, 494 mL) of 26,28-dimethoxycalix[4]arene (**1a**) (10 g, 22.1 mmol) was added $NaNO_3$ (5.64 g ; 66.3 mmol) and a catalytic amount of $La(NO_3)_3.6H_2O$ in a mixture of H_2O (304 mL) and concentrated HCl (55 mL). The mixture was stirred overnight at room temperature. The colour of the mixture turned to yellow. The aqueous layers were then separated and extracted with CH_2Cl_2 (250x2). The organic layer was combined and washed with saturated aqueous NH_4Cl (250x2) and dried over anhydrous Na_2SO_4. The solvent was removed by a rotary evaporator and the product was crytallized by adding hexane to give a white solid (8.51 g, 71% yield). mp > 320 ^{O}C decomposed.

Characterization data for 2a

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm) δ 8.93(s, 2H, -O*H*), 8.04 (s, 4H, *H*Ar-NO_2), 6.94 (d, 4H, *m*-*H*Ar-OCH_3, *J* = 7.2 Hz), 6.85-6.77 (t, 2H, *p*-*H*Ar-OCH_3, *J* = 7.4), 4.28 and 3.52 (dd, 8H, *H*AB system, *J* = 13.3 Hz), 4.02 (s, 6H, -OCH_3).

Preparation of 5,7-dinitro-26,28-dimethylethylestercalix[4]arene (2b)



1b

2b

To a solution (CH_2Cl_2, 140 mL) of 26,28-dimethylethylestercalix[4]arene (**1b**) (3.15 g, 5.26 mmol) was added $NaNO_3$ (2.70 g, 31.74 mmol) and a catalytic amount of La $(NO_3)_3.6H_2O$ in a mixture of H_2O (88 mL) and concentrated HCl (14.3 mL). The mixture was stirred overnight at room temperature and then worked up in a similar fashion as **2a** to give a yellow solid **2b** (3.17 g, 88% yield).

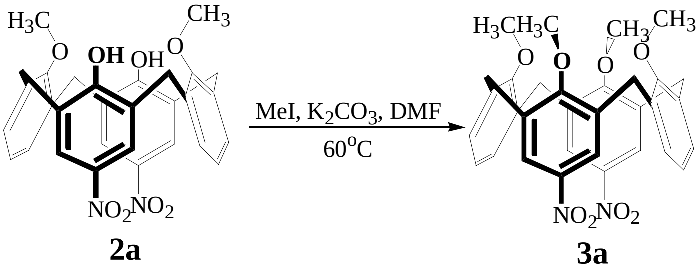
Characterization data for 2b

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 8.90 (s, 2H, -O*H*), 8.01 (s, 4H, *O*-Ar*H*-NO_2), 6.91 (d, *J* = 8.34 Hz, *m*-Ar*H*-OH), 6.84 (t, *J* = 6.44 Hz, 2H, *p*-Ar*H*-OR), 4.67 (s, 4H, OCH_2CO), 4.45, and 3.49 (dd, *J* = 13.32 Hz, 8H, AB system), 4.35 (q, *J* = 7.14 Hz, 4H, OCH_2CH_3), 1.39 (t, *J* = 8.7 Hz, 6H, -CH_2CH_3)

Melting point : 250 ^oC

Preparation of 5,7-dinitro-25,26,27,28-tetramethoxycalix[4]arene (3a)



2a

3a

A solution (DMF, 10 mL) of 5,7-dinitro-26,28-dimethoxycalix[4]arene (**2a)** (0.2713 g, 0.5 mmol) and K_2CO_3 (0.695 g, 5 mmol) was stirred at room temperature for 1 h. CH_3I (0.50 mL, 8.00 mmol) was then added and the mixture was heated at 60 ^{o}C for 7 days. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with water and brine (2x30) and then dried over anhydrous Na_2SO_4. The solvent was removed by using a rotary evaporator. Upon addition of CH_3OH, a white solid **3a** precipitated (71% yield).

Characterization data for 3a

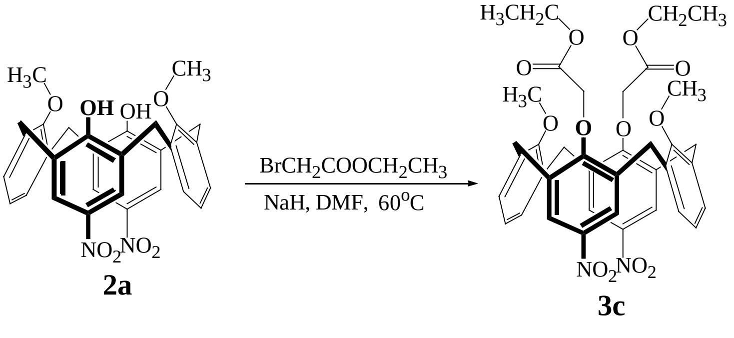
^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 8.19-6.43 (m, 10H, Ar*H*), 4.37, 4.05, 3.28 and 3.17 (d, each *J* = 13.3 Hz, 8H, ArC*H*$_2$Ar), 3.85-3.72 (m, 12H, -OC*H*$_3$).

ESI-TOF mass spectrum: $C_{32}H_{30}N_2O_8$ = 571.30 ([M+H$^+$]) m/z.

Melting point: 260 ^{o}C

Preparation of 5,7-dinitro-25,26,27,28-dimethoxydimethylethylestercalix[4]arene (3b)



A solution (DMF, 20 mL) of 5,7-dinitro-26,28-dimethoxy dimethylethyl ester calix[4]arene (**2a)** (0.543 g, 1.0 mmol) and NaH (0.12 g, 5.0 mmol was stirred at room temperature for 1 h. Bromoethyl acetate (0.40 mL, 3.0 mmol) was then added and the mixture was heated at 60 ^{o}C overnight. The reaction was worked up corresponding to the procedure of **3a** to provide the pale yellow solid of **3b** in ---g., (61%).

Characterization data for 3b

^{1}H-NMR spectrum (200 MHz, $\mathrm{CDCl_3}$): δ (in ppm)

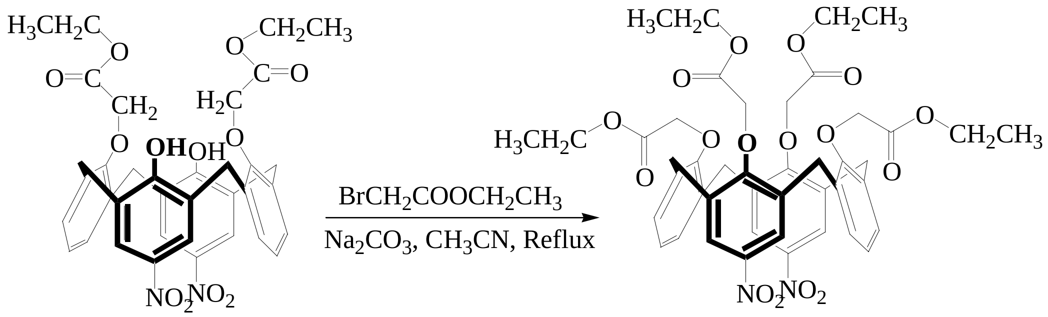
δ 7.83-7.08 (m, 10H, *H*-Aromatic), 4.45 (s, 4H, -OCH_2CO-), 4.32-4.21 (q, 4H, -OC$H_2\mathrm{CH_3}$, J = 7.2 Hz), 3.96-2.99 (m, 14H, -OCH_3 and *H*AB system), 1.34-1.27 (td, 6H, -$\mathrm{CH_2C}H_3$, J = 7.1 and 1.5 Hz).

Elemental Analysis:

Anal. Calcd for $\mathrm{C_{38}H_{38}O_{12}N_2}$: C, 63.86 ; H, 5.36 ; N, 3.92

Found : C, 63.85 ; H, 5.29 ; N, 3.88

Preparation of 5,7-dinitro-25,26,27,28-dimethylethylestercalix[4]arene (3c)



2b **3b**

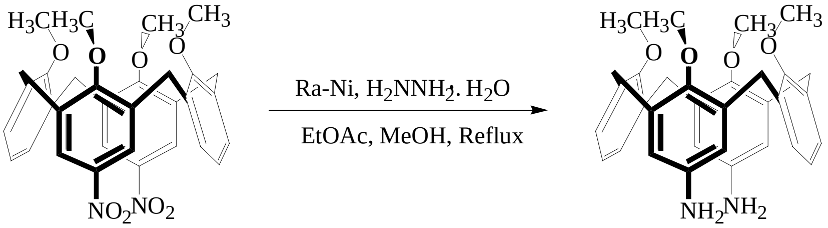
A solution ($\mathrm{CH_3CN}$, 30 mL) of 5,7-dinitro-26,28-dimethylethylestercalix[4]arene (**2b)** (0.60 g, 1.0 mmol) and $\mathrm{Na_2CO_3}$ (1.14 g, 10.4 mmol) was stirred at room temperature for 1 h. Bromoethyl acetate (1.20 mL, 1.67 mmol) was then added and the mixture was refluxed overnight. The mixture was allowed to cool to room temperature and $\mathrm{Na_2CO_3}$ was removed by filtration. The mixture was evaporated using a rotary evaporator. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (20 mL). The organic phase was then washed with saturated $\mathrm{NH_4Cl}$ 3 times. The organic layer was dried over anhydrous $\mathrm{Na_2SO_4}$. The solvent was removed under reduced pressure. Finally, compound **3c** precipitated as a yelloe solid upon addition of $\mathrm{CH_3OH}$ (0.524 g, 61%).

Characterization data for 3c

^{1}H-NMR spectrum (200 MHz, $\mathrm{CDCl_3}$): δ (in ppm) δ 8.90 (s, 2H, O*H*), 8.01 (s, 4H, *m*-Ar*H*OH), 6.99 (d, *J* = 6.97 Hz, *m*-Ar*H*OR), 6.89-6.80 (m, 2H, *p*-Ar*H*OR), 4.71 (s, 4H, -OC*H*$_2$CO-), 4.45 and 3.49 (dd, J = 13.3 Hz, 8H, ArC*H*$_2$Ar), 4.40-4.29 (q, *J* = 7.17 Hz, -OC*H*$_2$CH$_3$), 1.35 (t, *J* = 7.13 Hz, 6H, OCH$_2$C*H*$_3$)

Melting point: 190 °C

Preparation of 5,7-diamino-25,26,27,28-tetramethoxycalix[4]arene (4a)



3a **4a**

5,7-Dinitro-25,26,27,28-tetramethoxycalix[4]arene (1.3928 g, 1.95 mmol) and Raney Ni (2.0951 g) in the mixture of ethylacetate (80 mL) and CH$_3$OH (40 mL). Hydrazine (4 mL) was then added into the mixture. The mixture was refluxed for 2 h. and allowed to cool to room temperature. The solvent was subsequently removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and extracted and washed with several portions of H$_2$O. The organic layer was separated, combinded and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure to give a pale-white solid 4a (0.976 g, 98% yield).

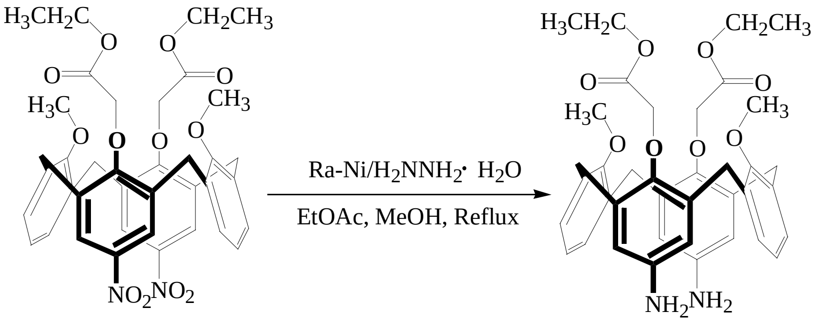
Characterization data for 4a

^{1}H-NMR spectrum (200 MHz, CDCl$_3$): δ (in ppm)

δ 7.04-6.43 (m-br, 6H, Ar*H*), 6.09 (s,br, 4H, *o*-Ar*H*-NH$_2$), 4.26-2.91 (m, br, 20H, OC*H*$_3$ and AB system).

ES-TOF mass spectrum: $C_{32}H_{34}N_2O_4$ = 511.30 ([M+H$^+$]) m/z.

Preparation of 5,7-diamino-25,26,27,28-dimethoxy dimethylethylester calix[4]arene (4b)



3c **4c**

5,7-Dinitro-25,26,27,28-dimethoxydimethylethylestercalix[4]arene (**3b**) (0.714 g, 1.0 mmol) and Raney Ni (1.0 g) were dissolved in the mixture of ethylacetate (38 mL) and CH_3OH (28 mL). Hydrazine (4 mL) was subsequently added. The mixture was refluxed for 2 h. and allowed to cool to room temperature. The reaction was worked up as described previously (**4a**). Compound **4b** was obtained as a white solid (0.628 g, 96%).

Characterization data for 4b

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 7.22 (d, 4H, *m-H*Ar-OCH_3, *J* = 6.9 Hz), 6.93-6.86 (t, 2H, *p-H*Ar-OCH_3, *J* = 7.2 Hz), 5.69 (s, 4H, *o-H*Ar-NH_2), 4.40 (d, 4H, AB system, *J* = 13.1 Hz and s, 4H, *o*-CH_2CO-), 4.30-4.20 (q, 4H, -OC$H_2$$CH_3$, *J* = 7.1 Hz), 3.96 and 3.46 (s, 6H, -OCH_3), 3.10 (d, 4H, AB system, *J* = 12.8 Hz), 1.33-1.26 (t, 6H,-OCH_2CH_3, *J* = 7.1 Hz).

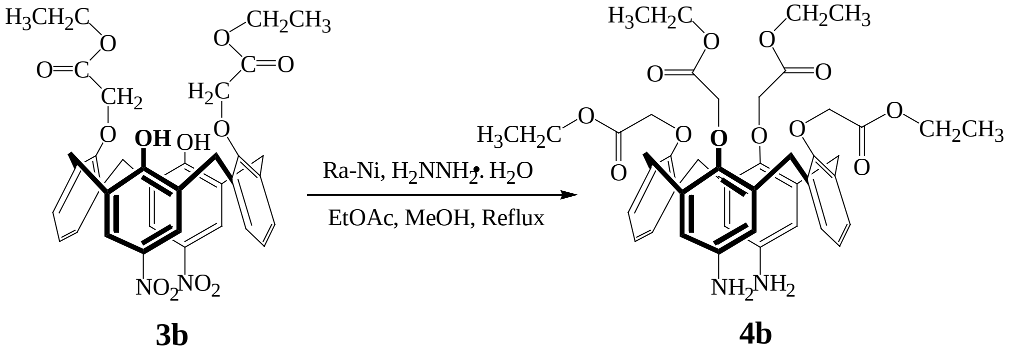
ESI-TOF mass spectrum: $C_{38}H_{42}N_2O_8$ = 655.70 ([M+H$^+$]) m/z.

Elemental Analysis:

Anal. Calcd.for $C_{38}H_{42}N_2O_8$: C, 69.71 ; H, 6.47 ; N, 4.28

Found : C, 69.71 ; H, 6.25 ; N, 4.26.

Preparation of 5,7-diamino-25,26,27,28-tetramethylethylestercalix[4]arene (4c)



5,7-Dinitro-25,26,27,28-tetramethylethylestercalix[4]arene (1.47 g, 1.52 mmol) (**3c**) and Raney Ni (1.52 g) were dissolved in the mixture of ethylacetate (58 mL) and CH_3OH (42 mL). Hydrazine (6 mL) was subsequently added. The mixture was refluxed for 2 h. and allowed to cool to room temperature. The reaction was worked up as described previously (**4a**). Compound **4c** was obtained as a white solid (1.15g, 95%).

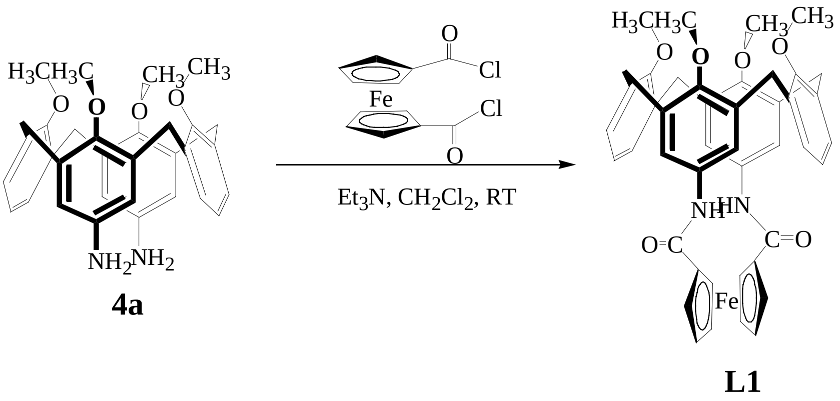
Characterization data for 4c

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 6.69-6.59 (m, 6H, m-Ar*H*-OR), 6.01 (s, 4H, *o*-Ar*H*-NH_2), 4.78 and 3.10 (d, *J* = 13.1 Hz, 8H, AB system), 4.70 (s, 4H, ArOC*H*$_2$-), 4.61 (s, 4H, NH_2-Ar-OC*H*$_2$-), 4.18 (q, *J* = 7.1 Hz, 8H, *o*-C*H*$_2$$CH_3$), 1.26 (t, *J* = 7.2 Hz, 12 H, -C*H*$_3$)

ESI-TOF mass spectrum: $C_{44}H_{50}N_2O_{12}$ = 799.13 ([M+H$^+$]) m/z.

Preparation of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (L1)



Into a two-necked round-bottomed flask, the mixture of tetramethoxy-diaminocalix[4]arene(**4a**) (0.786 g, 1.54 mmol) and triethylamine (0.5 mL) in dichloromethane (30 mL) was stirred at room temperature under N_2. 1,1-Bis (chlorocabonyl)ferrocene (0.6201g, 2.0 mmol) in dichloromethane (30 mL) was transferred into the mixture via cannula. The mixture was stirred at room temperature under N_2 for 4 h. It was then washed with several portion of H_2O. The organic layer was dried with anhydrous $NaSO_4$. The solvent was removed under reduced pressure to afford a dark red residue which was then placed on a silica gel chromotography column. Compound **L1** was eluted from the column using 10% EtOAc in CH_2Cl_2 as eluant. The yield of compound **L1** is an orange solid (0.576 g., 50%). An orange crystal **L1** was obtained by slow diffusion of hexane into CH_2Cl_2 and CH_3OH solution of compound **L1**.

Characterization data for L1

^{1}H-NMR spectrum (500 MHz, d^6-Acetone): δ (in ppm)

δ 8.09 (s, 2H, -N*H*-(pc)), 7.86 (s, 2H,-N*H*-(c)), 7.59 and 6.46 (d, *J* =3 Hz, 4H, -Ar*H*-NH-(pc)), 7.22 (d, *J* = 8 Hz, 4H, *m*-Ar*H* (c)) 7.18 and 7.10 (d, *J* = 7.5 Hz, 4H, *m*-Ar*H*, (pc)), 7.01 (t, *J* = 7.5 Hz, 2H, *p*-Ar*H* (c)), 6.93 and 6.81 (t, *J* = 7.5 Hz, 2H, *p*-Ar*H* (pc)), 6.47 (s, 4H, -NH-Ar*H*- (c)) 5.00 and 4.83 (m, 4H, *o*-Cp*H* (pc)), 4.75 (t, *J* = 2.5 Hz, 4H, *o*-Cp*H* (c)), 4.41 and 4.36 (m, 4H, m-Cp*H* (pc)), 4.36 and 3.14 (d, *J* =13.5, 8H, AB system(c)), 4.313 (t, *J* = 2 Hz, 4H-Cp*H* (c)), 4.04 and 3.06 (d, *J* = 14 Hz, 8H, AB system), 3.92-3.65 (m, 21H, -OCH_3 (pc and c)), 2.86 (s, 3H, -OCH_3 (pc)).

ESI-TOF mass spectrum: $C_{44}H_{40}N_2O_6Fe$ = 749.50 ([M+H$^+$]) m/z.

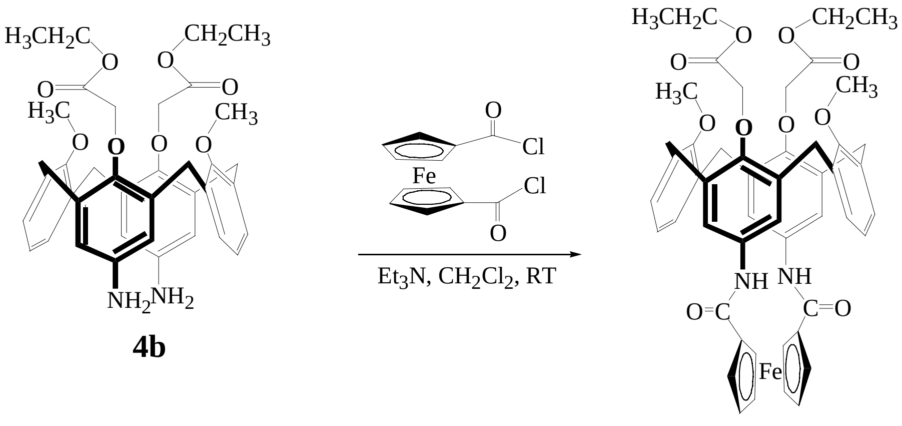
Elemental Analysis:

Anal. Calcd. for $C_{44}H_{40}N_2O_6Fe^{\bullet}0.5\ CH_2Cl_2$: C, 67.56; H, 5.22; N, 3.45.

Found : C, 67.72; H, 5.24; N, 3.55.

Melting point: 200 ^{o}C decomposed

Preparation of 5,7-diamideferrocenyl-25,26,27,28-dimethoxy dimethylethylestercalix [4] arene (L2)



4b

L2

Into a two-necked round-bottomed flask, the mixture of dimethoxy dimethyl ethylester-diaminocalix[4]arene(**4b**) (1.31 g, 2.0 mmol) and triethylamine (mL) in dichloromethane (40 mL) was stirred at room temperature under N_2. 1,1-Bis (chlorocabonyl)ferrocene (0.620g, 2.1 mmol) in dichloromethane (20 mL) was transferred into the mixture via cannula. The mixture was stirred at room temperature under N_2 for 4 h. It was then washed with several portion of H_2O. The organic layer was dried with anhydrous $NaSO_4$. The solvent was removed under reduced pressure to afford a dark red residue which was then placed on a silica gel chromotography column. Compound **L2** was eluted from the column using 10% EtOAc in CH_2Cl_2 as eluant. The yield of compound **L2** is an orange solid (0.576 g., 50%). An orange crystal **L2** was obtained by slow diffusion of hexane into CH_2Cl_2 and CH_3OH solution of compound **L2**.

Characterization data for L2

^{1}H-NMR spectrum (500 MHz, d^6-Acetane): δ (in ppm)

δ 8.10 (s, 2H, -N*H*-(pc)) and 7.88 (s, 2H, -N*H*-(c)), 7.58 and 6.45 (d, *J* = 2.5 Hz, 4H, -Ar*H*-NH-(pc)), 7.43 and 7.04 (d, *J* = 7.5 Hz, 4H, *m*-Ar*H*, (pc)), 7.12 (d, *J* = 7.5 Hz, 4H, *m*-Ar*H* (c)), 6.95 (t, *J* = 7.5 Hz, 2H, *p*-Ar*H* (c)), 6.89 and 6.82 (t, *J* = 7.5 Hz, 2H, *p*-Ar*H* (pc)), 6.46 (s, 4H, -NH-Ar*H*- (c)) 5.03 and 4.86 (m, 4H, *o*-Cp*H* (pc)), 4.78 (t, J = 2 Hz, 4H, *o*-Cp*H* (c)), 4.39-4.37 (m, 4H (m-Cp*H* (pc)), 4H (m-Cp*H* (c)), 8H (-OCH_2-CO-(c and pc)), 4H (AB system(c))), 4.26-4.21 (m, 4H, -OCH_2CH$_3$). 4.07 and 3.05 (d, J = 14 Hz, 4H, AB system (pc)), 3.83 and 3.59 (d, J = 12.5 Hz, 4H, AB system (pc)), 2.97 (s, 3H, -OCH_3), 1.28 (m, 6H, -CH_3).

ESI-TOF mass spectrum: $C_{50}H_{48}N_2O_{10}Fe$ = 893.51 ([M+H$^+$]) m/z.

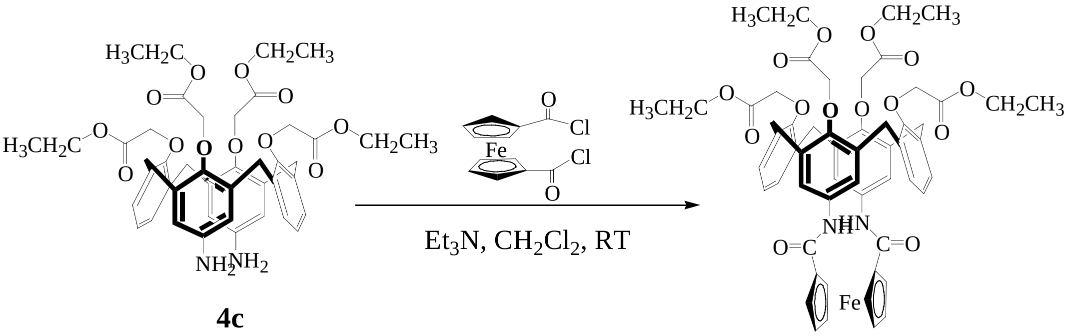
Elemental Analysis:

Anal. Calcd. for $C_{50}H_{48}N_2O_{10}Fe·0.5\ CH_2Cl_2$: C, 64.85; H, 5.28; N, 3.00.

Found: C, 65.28; H, 5.51; N, 3.19.

Melting point: 150 ^oC

Preparation of 5,7-diamideferrocenyl-25,26,27,28-tetramethyl ethylestercalix[4] arene (L3)



4c

L3

Into a two-necked round-bottomed flask, the mixture of tetramethylethylester-diaminocalix[4]arene(**4c**) (1.13 g, 1.53 mmol) and triethylamine () in dichloromethane (40 mL) were stirred at room temperature under N_2. 1,1-Bis(chlorocabonyl)ferrocene (0.481 g, 1.55 mmol) in dichloromethane (20 mL) was transferred into the mixture via cannula. The mixture was stirred at room temperature under N_2 for 4 h. The work-up procedure is similar to the procedure as described previously. Crude product was purified on a silica gel column using 10% EtOAc in CH_2Cl_2 as eluant to afford an orange solid **L3** (0.666 g, 42%).

Characterization data for L3

^{1}H-NMR spectrum (200 MHz, $CDCl_3$): δ (in ppm)

δ 7.25 (s, 2H, -NH-), 7.20 (d, *J* = 6.7 Hz, 4H, m-Ar*H*-OR), 7.09 (t, *J* = 6.4 Hz, 2H, *p*-Ar*H*OR), 6.43 (s, 4H, *o*-Ar*H*-NH-), 4.87 and 3.22 (d, *J* = 13.0, 8H, AB system), 4.90 (s, 4H, -NH-ArHOCH_2-), 4.77 (s, br, 4H,Cp*H*), 4.45 (s, 4H, ArH-OCH_2-), 4.33 (s, br, 4H, Cp*H*), 4.17 (q, *J* = 7.1 Hz, 8H, -OC$H_2$$CH_3$), 1.33-1.22 (m, 12H, -O$CH_2CH_3$).

ES-TOF mass spectrum: $C_{56}H_{56}N_2O_{14}Fe$ = 1037.20 ([M+H$^+$]) m/z.

Elemental Analysis:

Anal. Calcd. for $C_{56}H_{56}N_2O_{14}Fe$: C, 64.87; H, 5.44; N, 2.70.

Found: C, 64.84; H, 5.40; N, 2.63.

Melting point: 227 ^oC

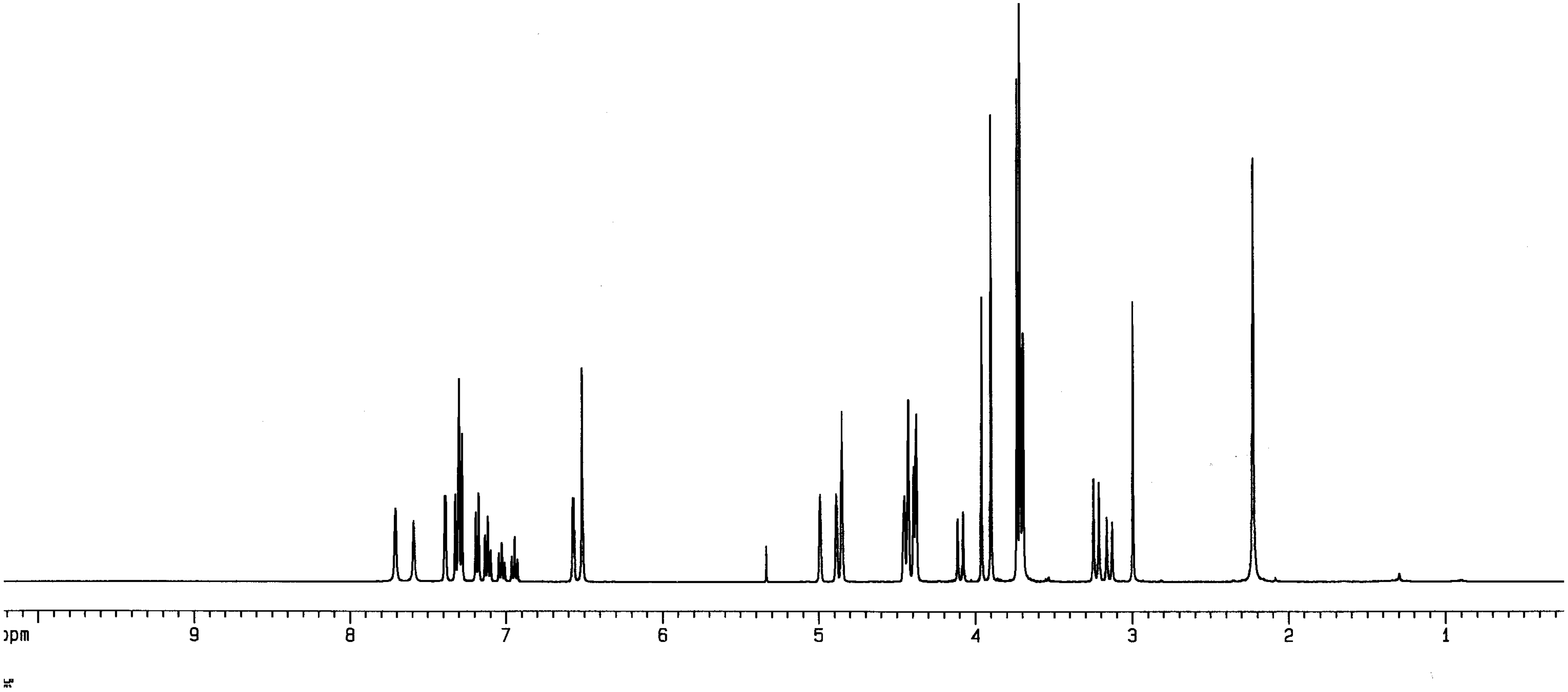


Figure 1 ^{1}H-NMR of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

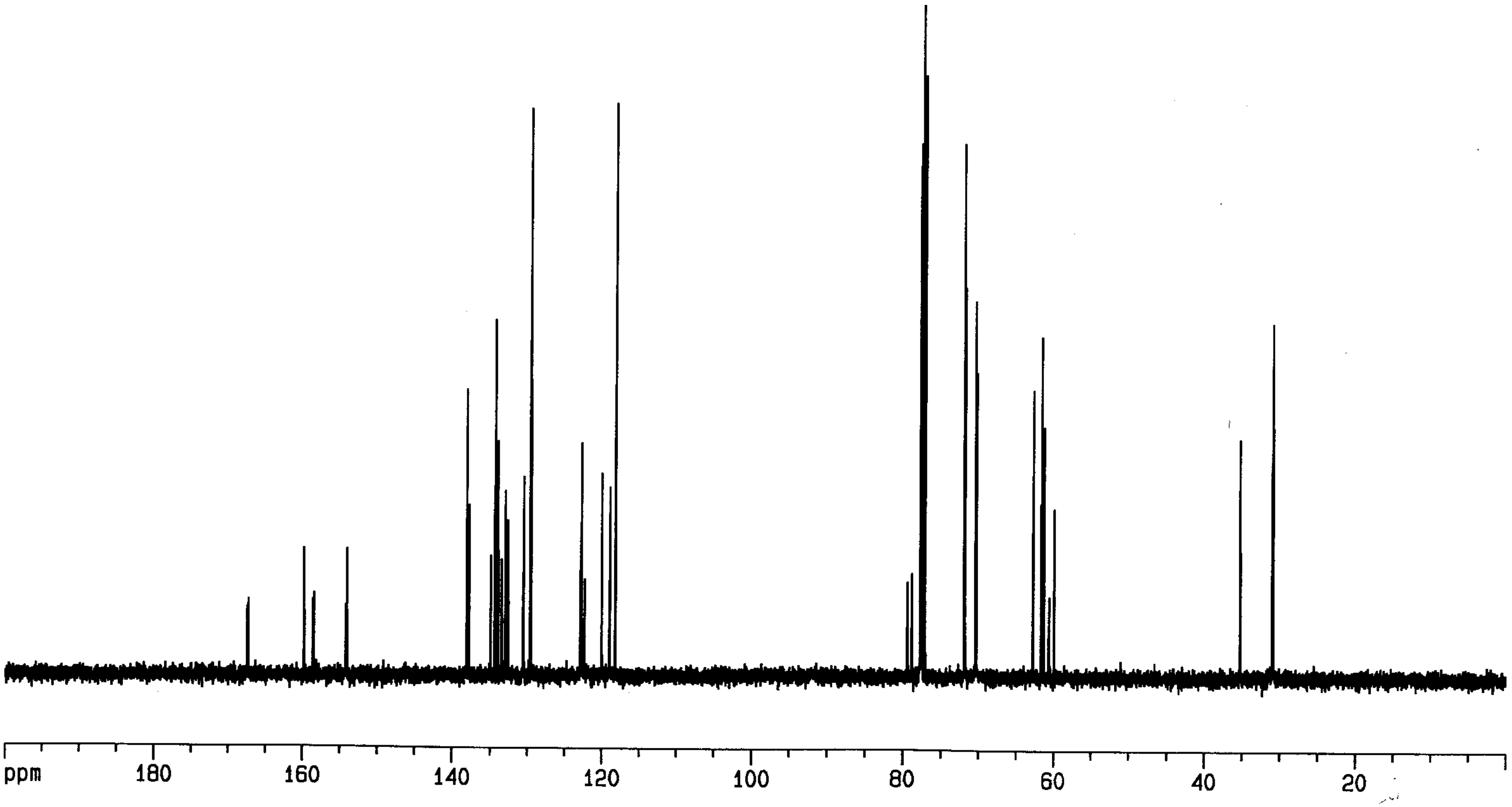


Figure 2 ^{13}C-NMR of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

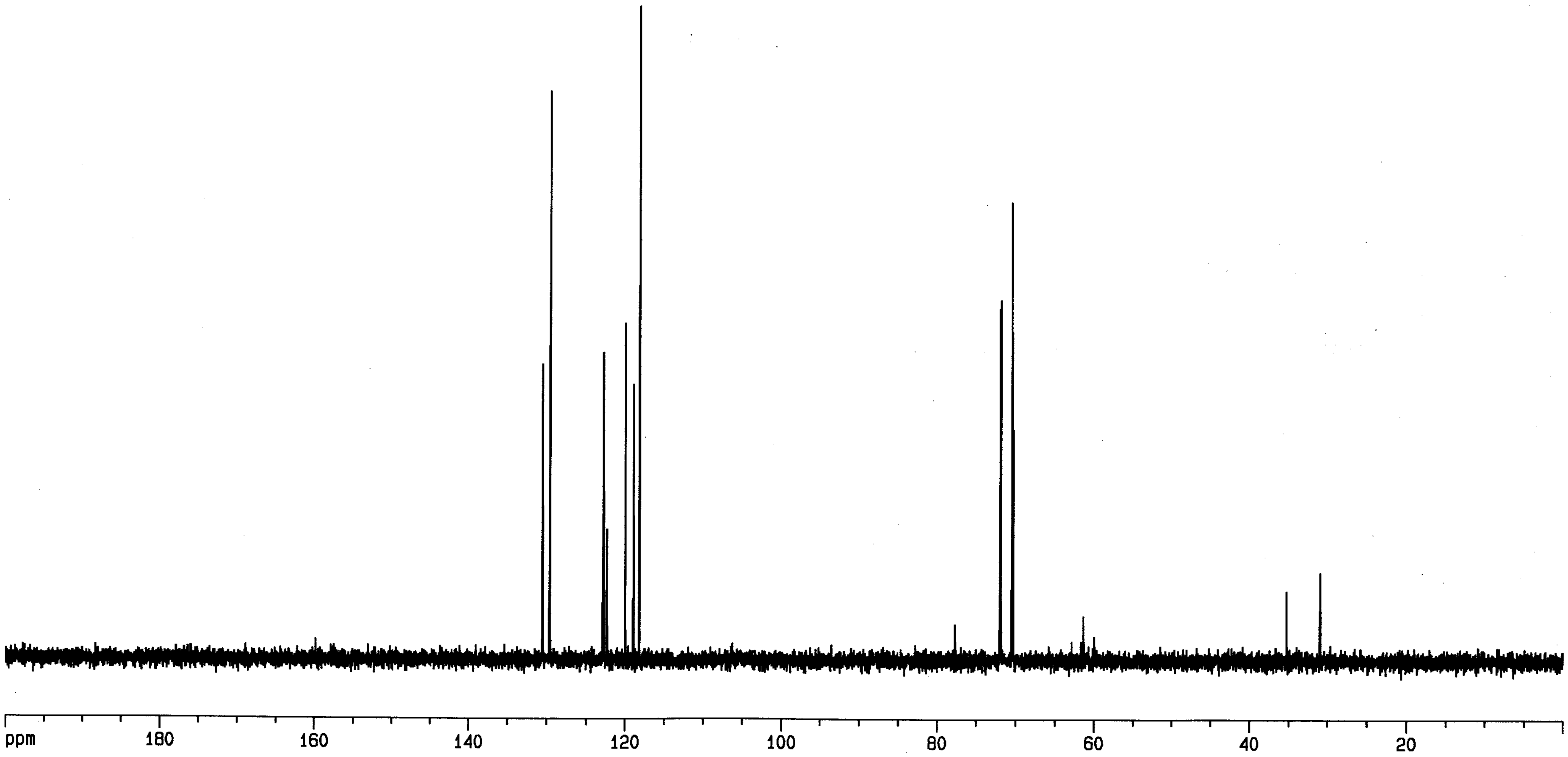
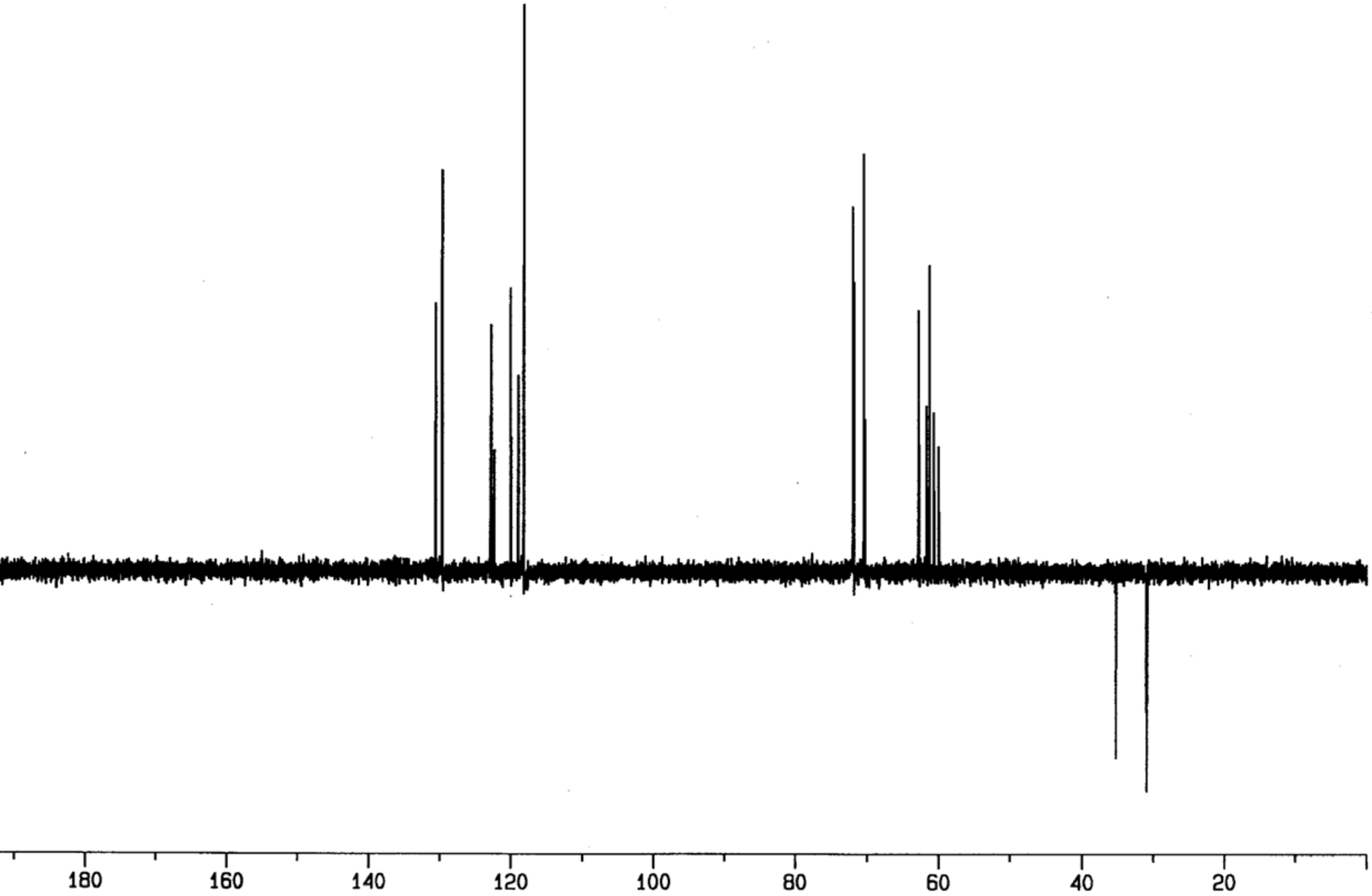


Figure 3 ^{13}C-DEPT-90 of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in CDCl$_3$ 400 MHz



gure 4 ^{13}C-DEPT-135 of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

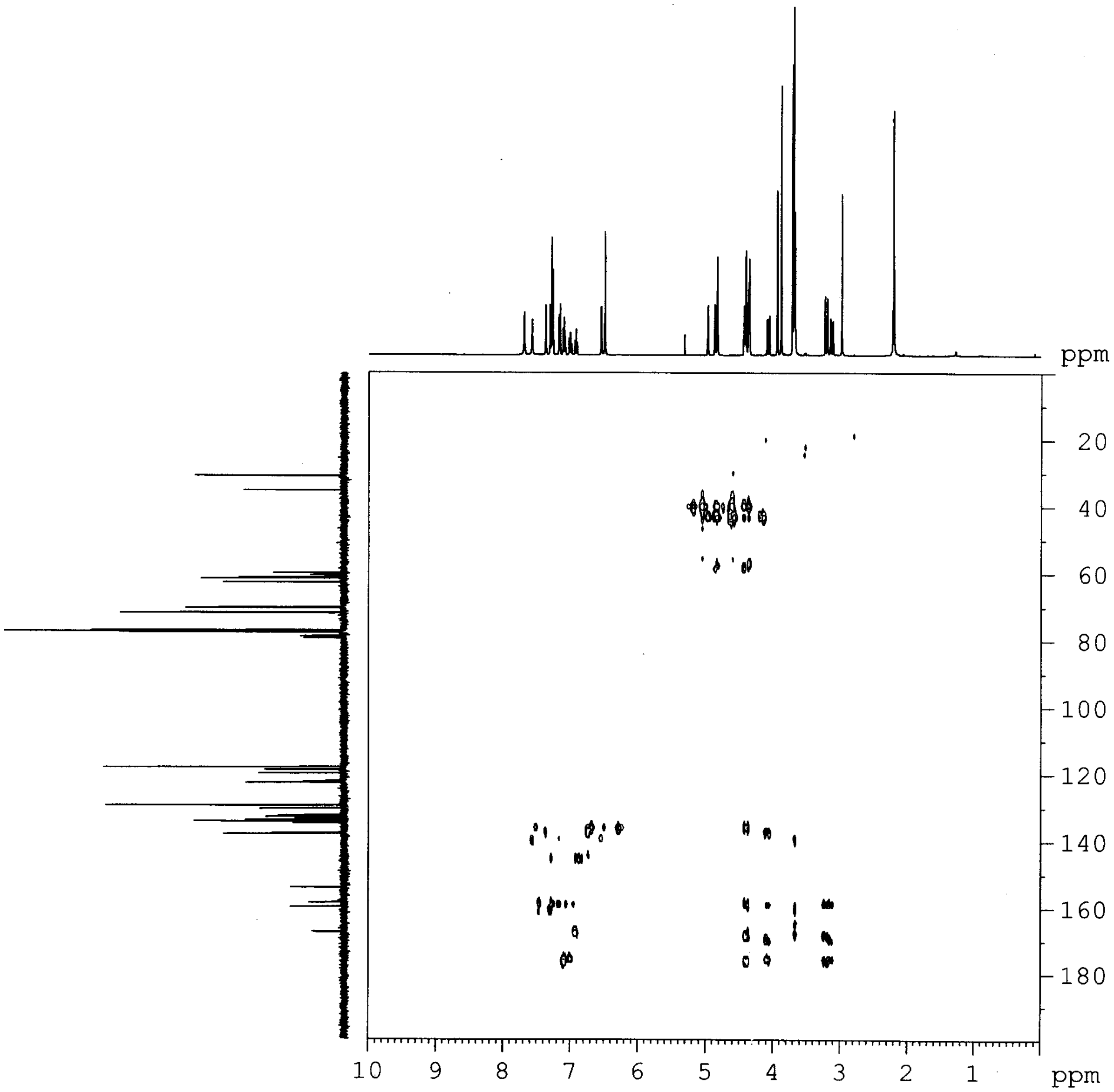


Figure 5 HMBC of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

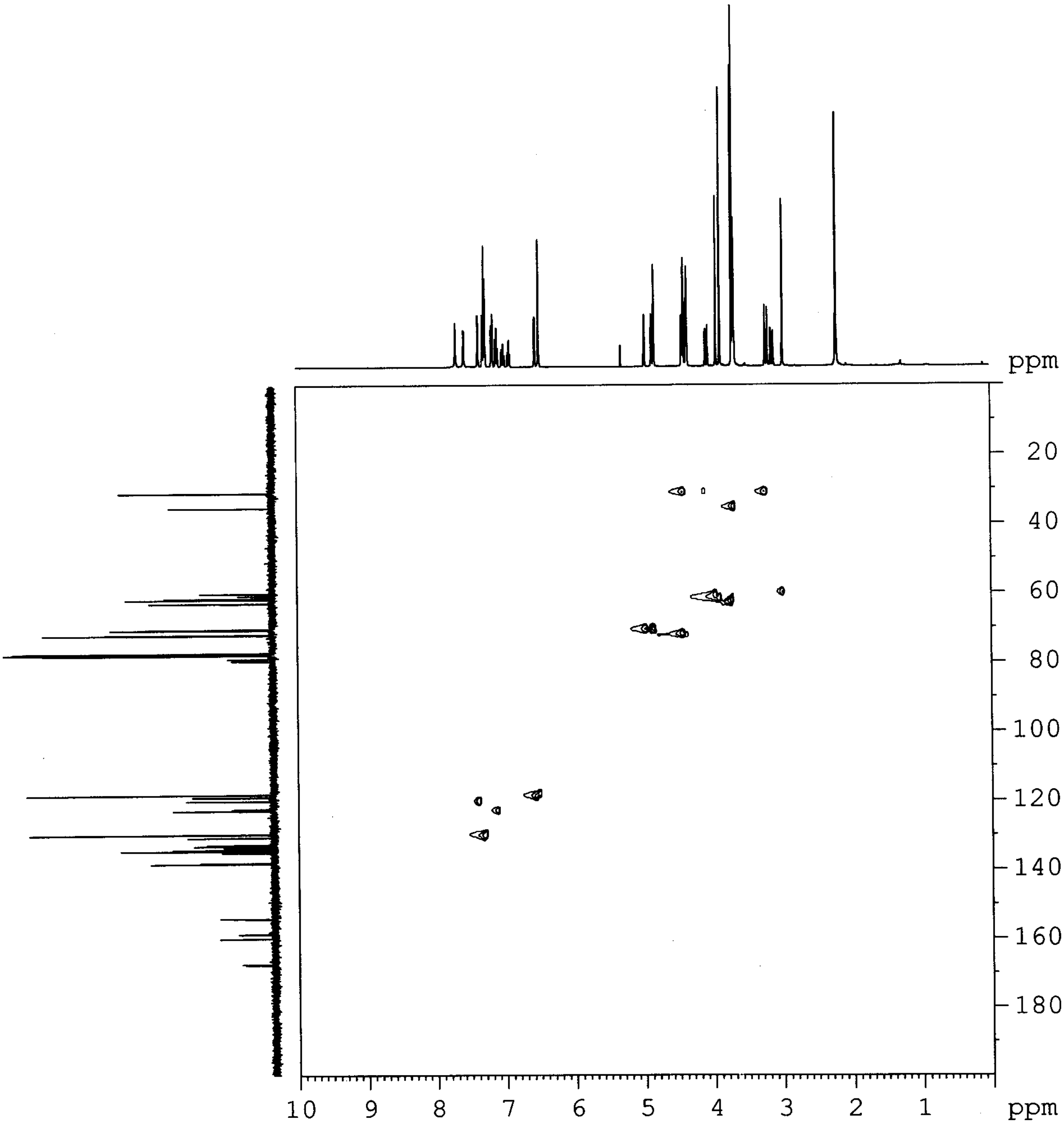


Figure 6 HMQC of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

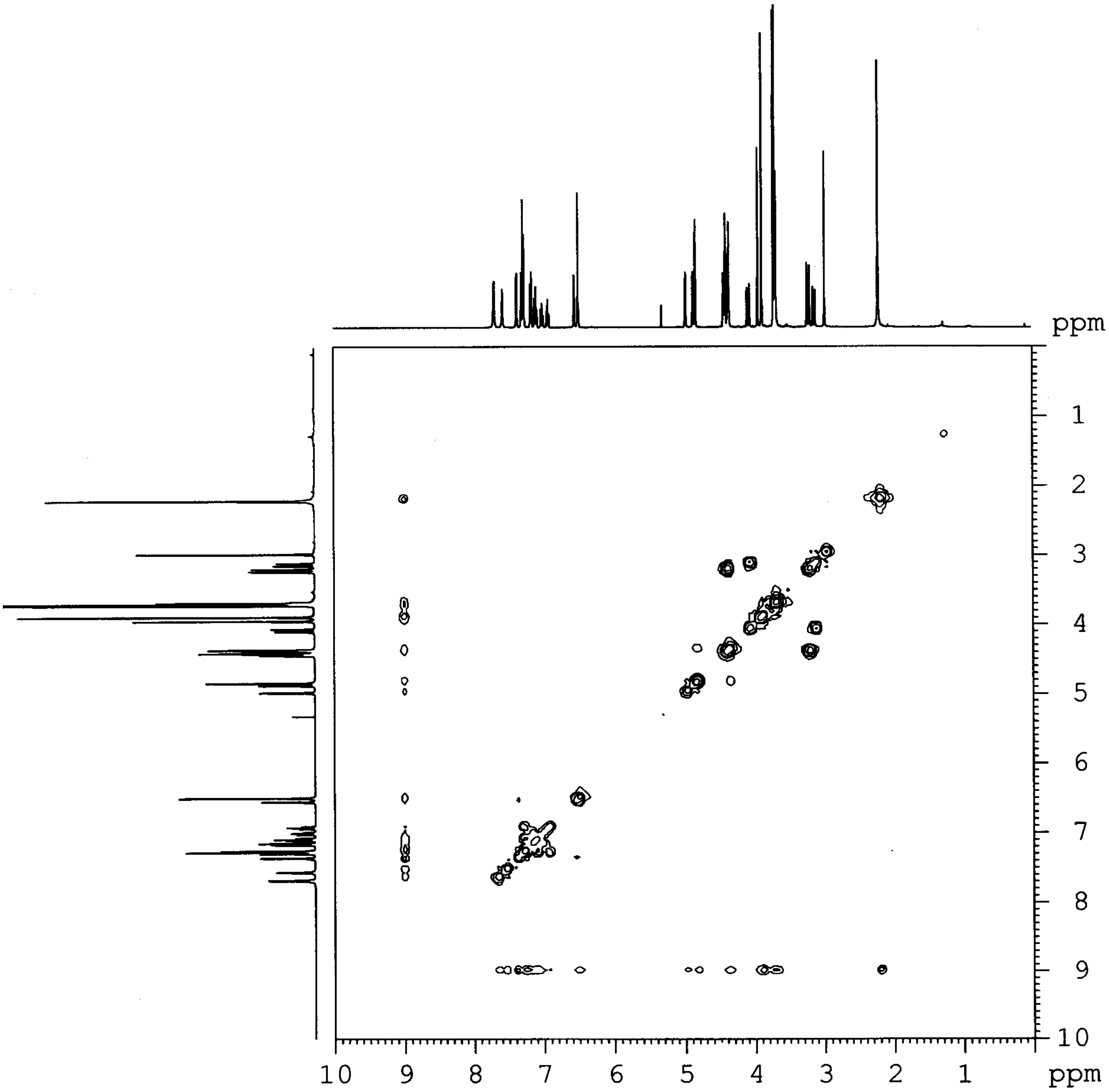


Figure 7 COSY of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

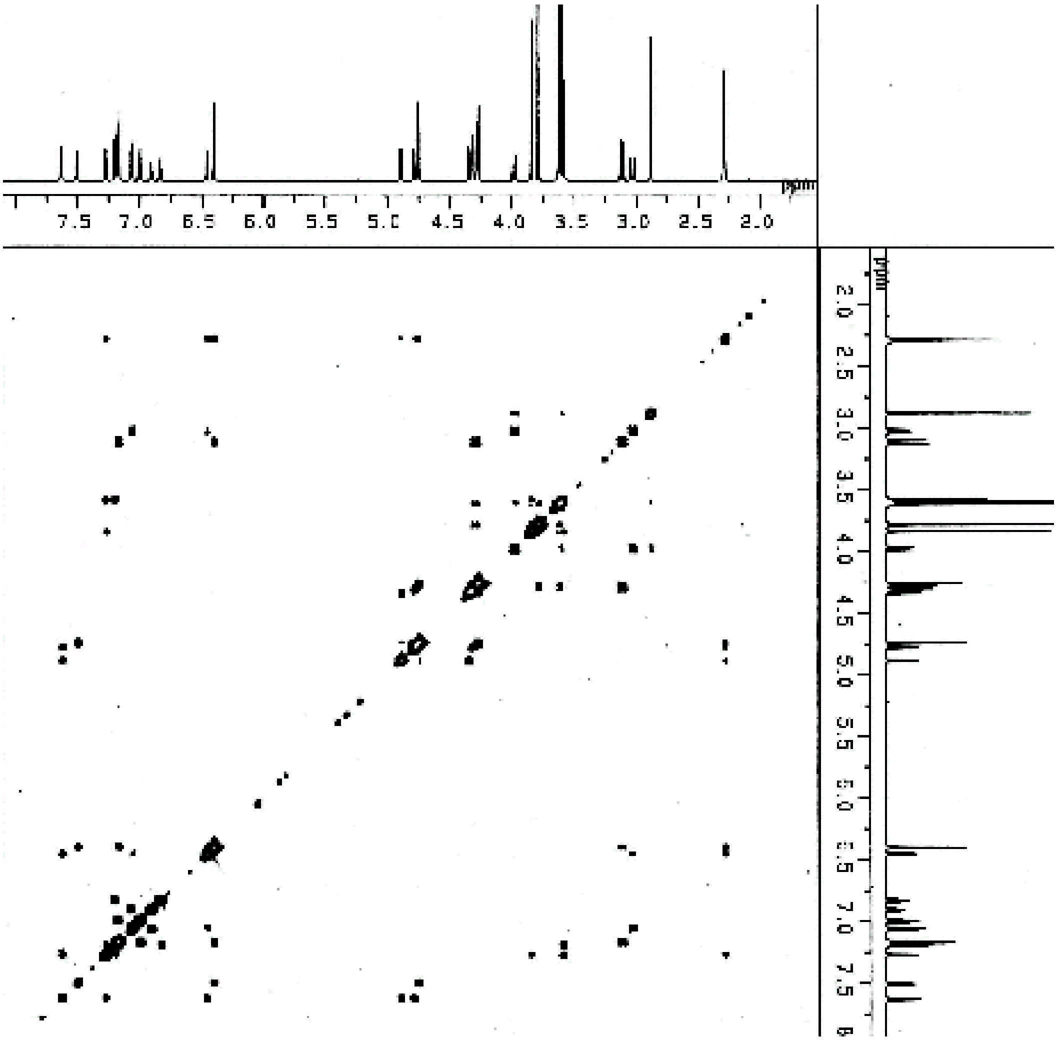


Figure 8 NOESY of 5,7-diamideferrocenyl-25,26,27,28-tetramethoxycalix[4]arene (**L1**) in $CDCl_3$ 400 MHz

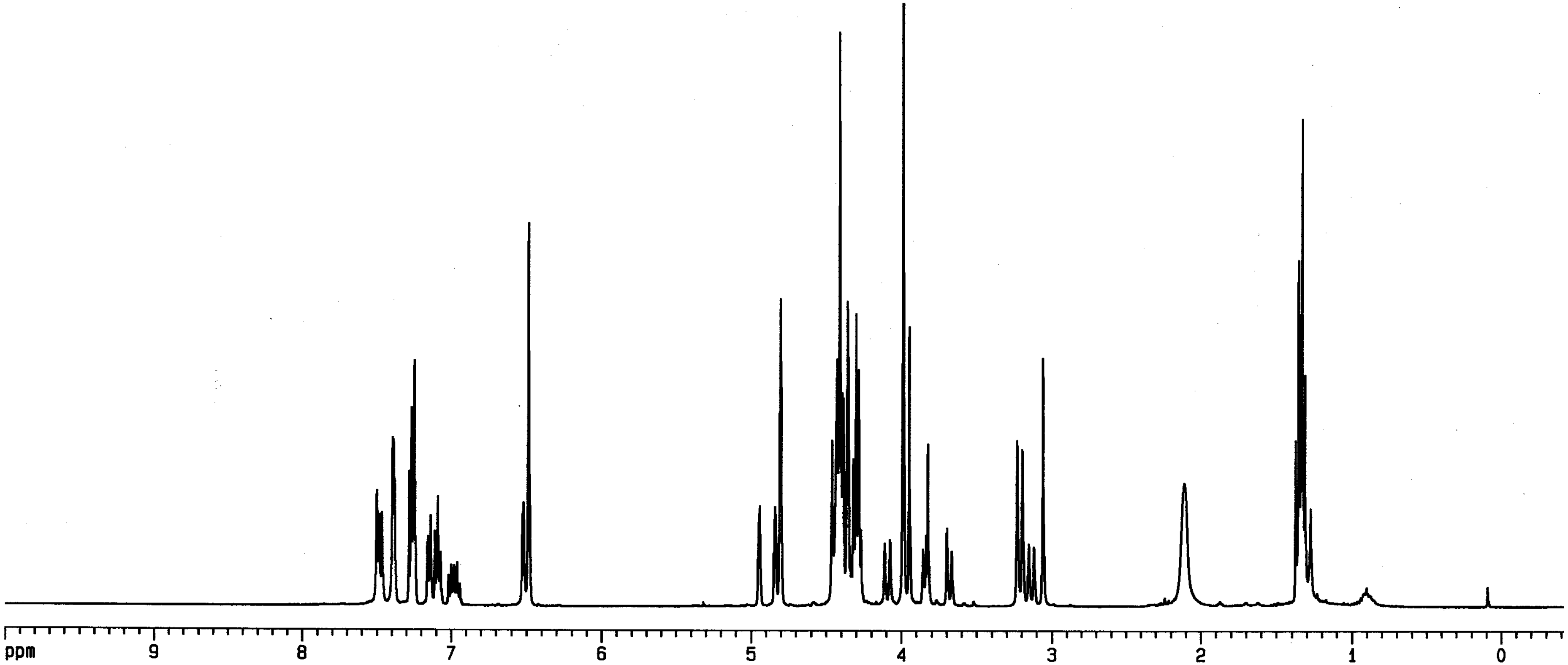


Figure 9. ^{1}H-NMR of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz.

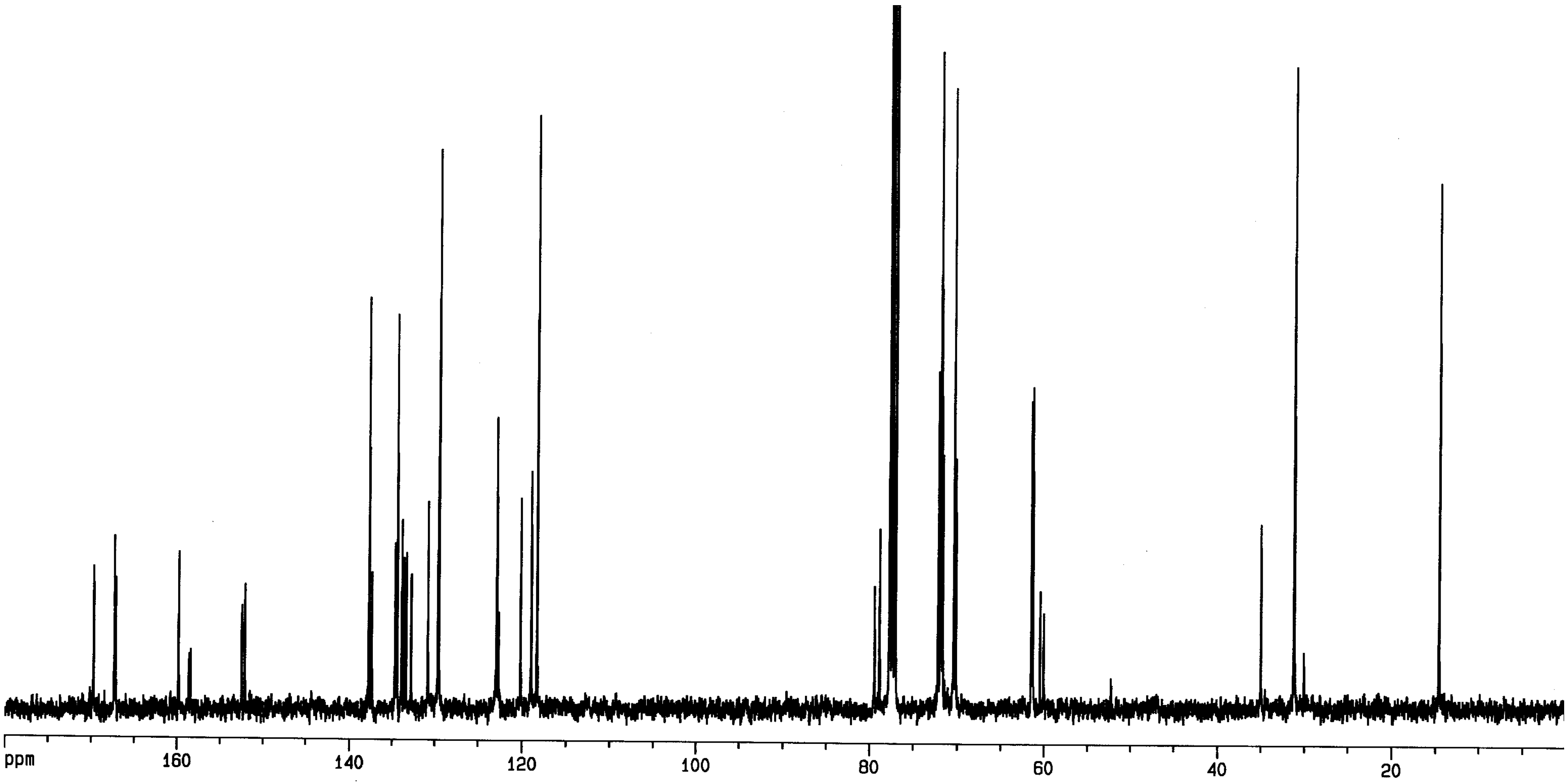


Figure 10. ^{13}C-NMR of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz.

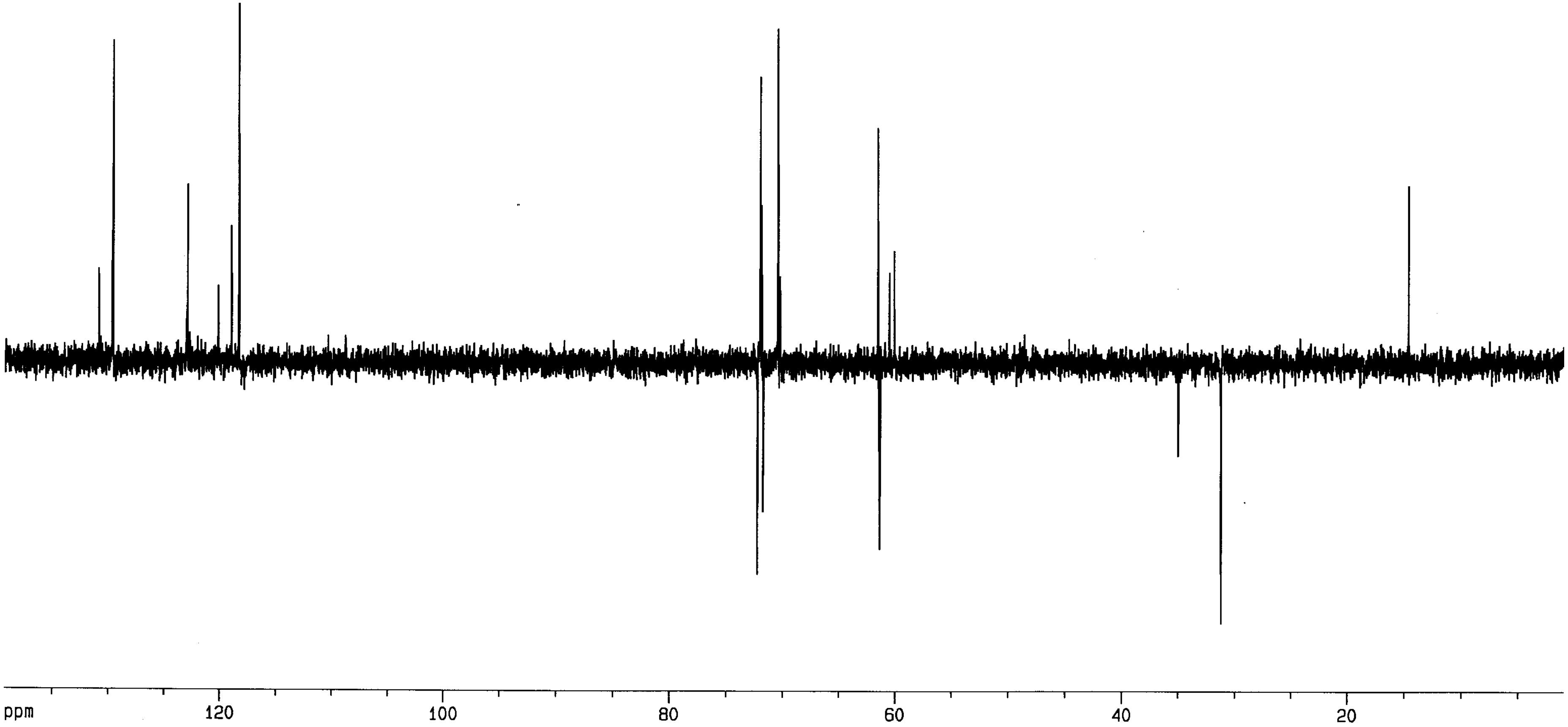


Figure 11. ^{13}C-DEPT-135 of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz.

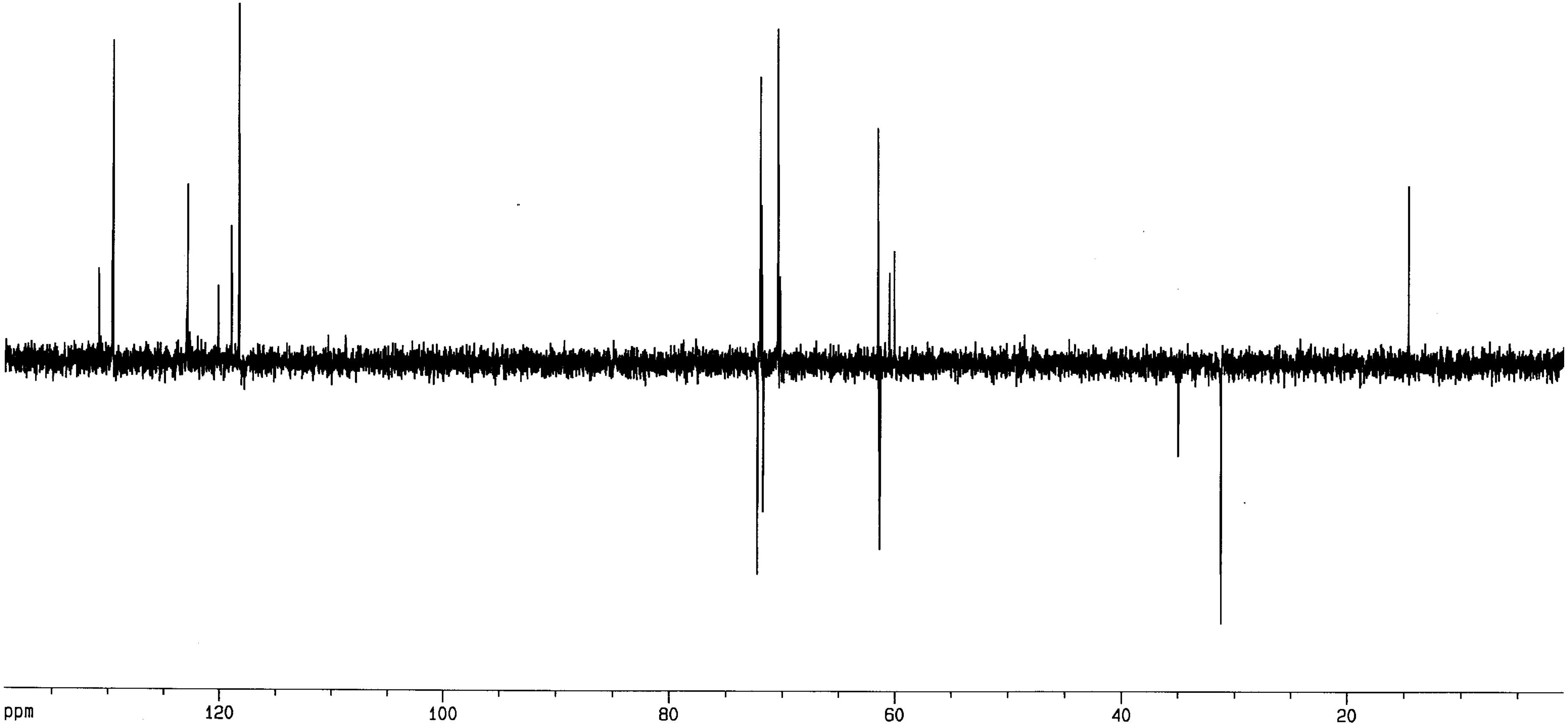


Figure 12. ^{13}C-DEPT-135 of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz.

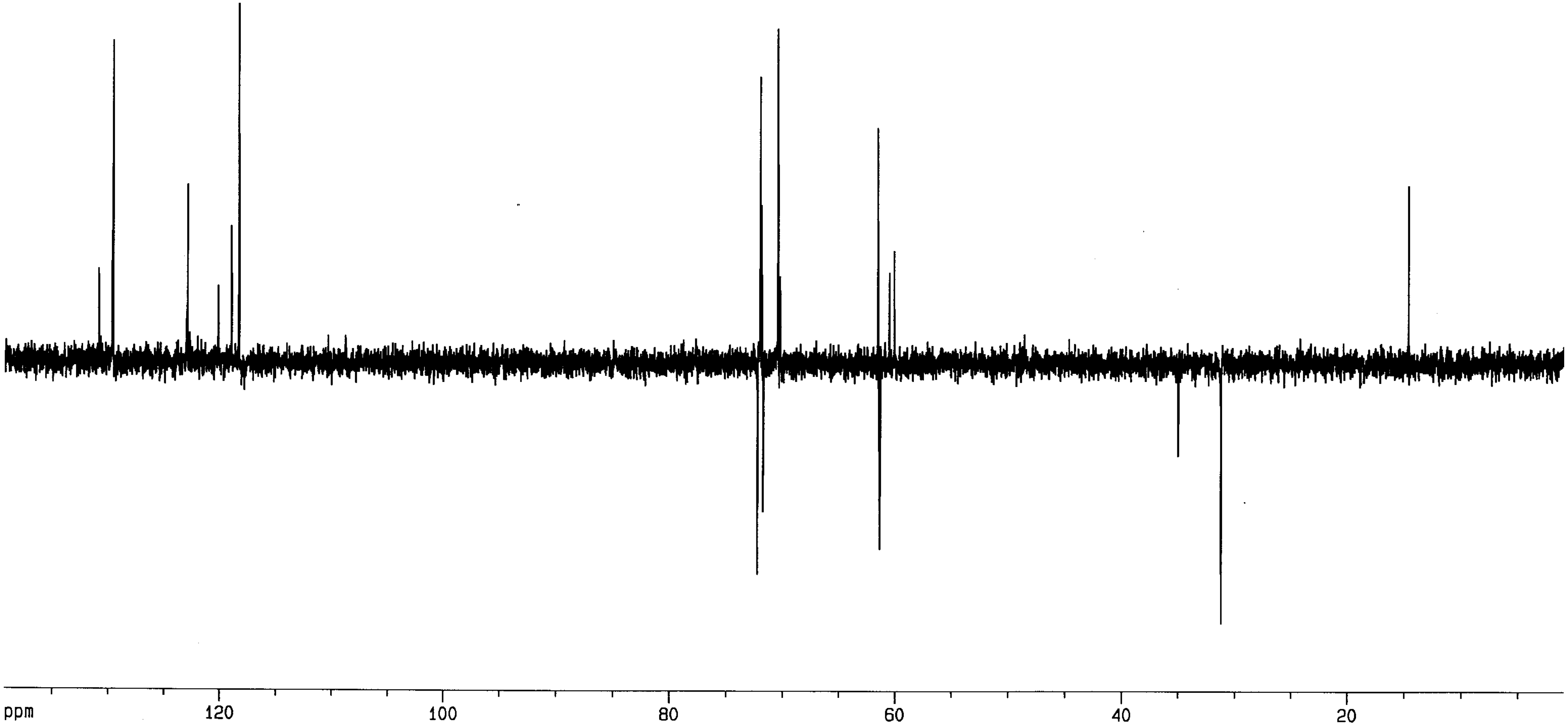


Figure 13. ^{13}C-DEPT-135 of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz.

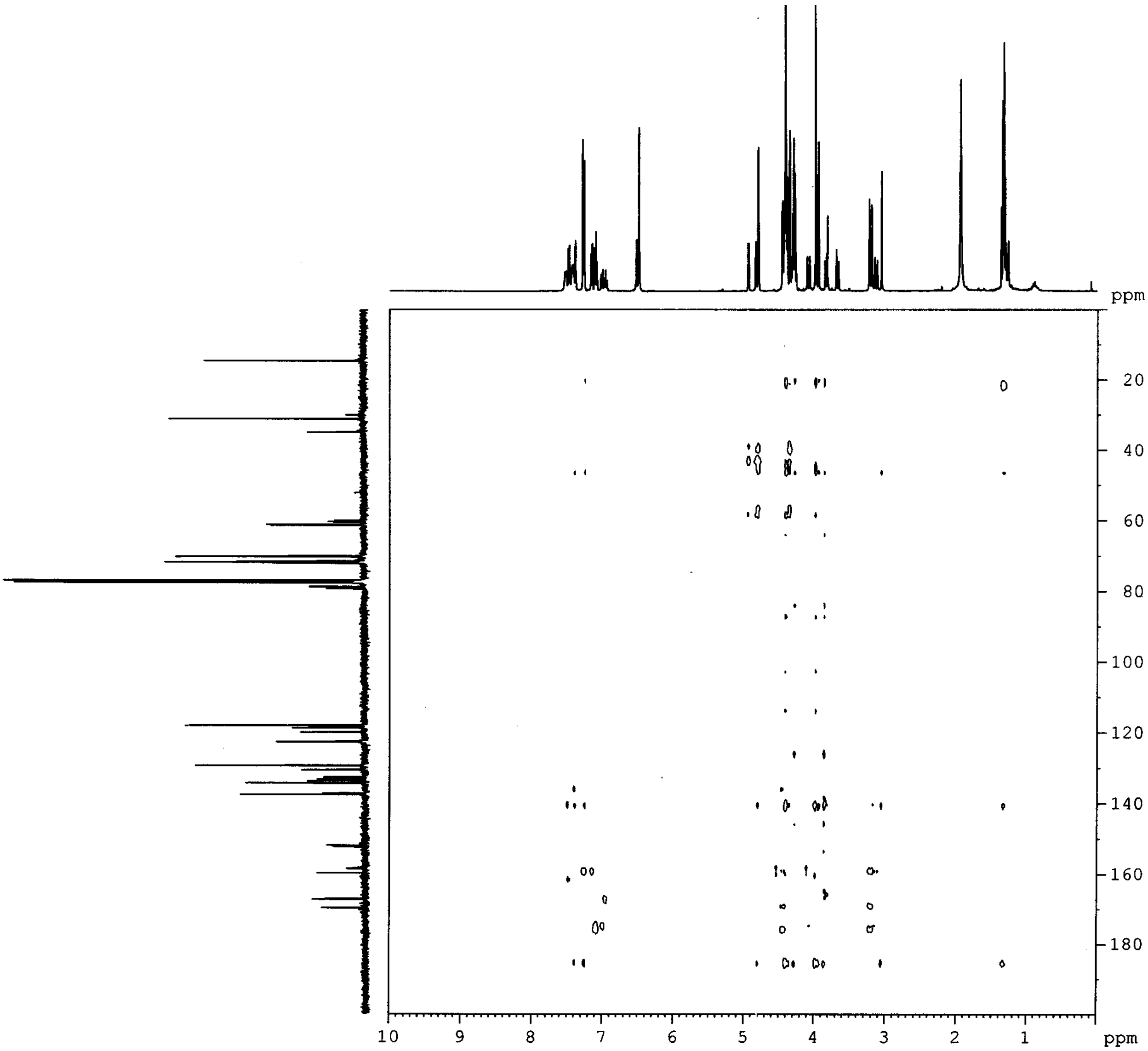


Figure 14. HMBC of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz

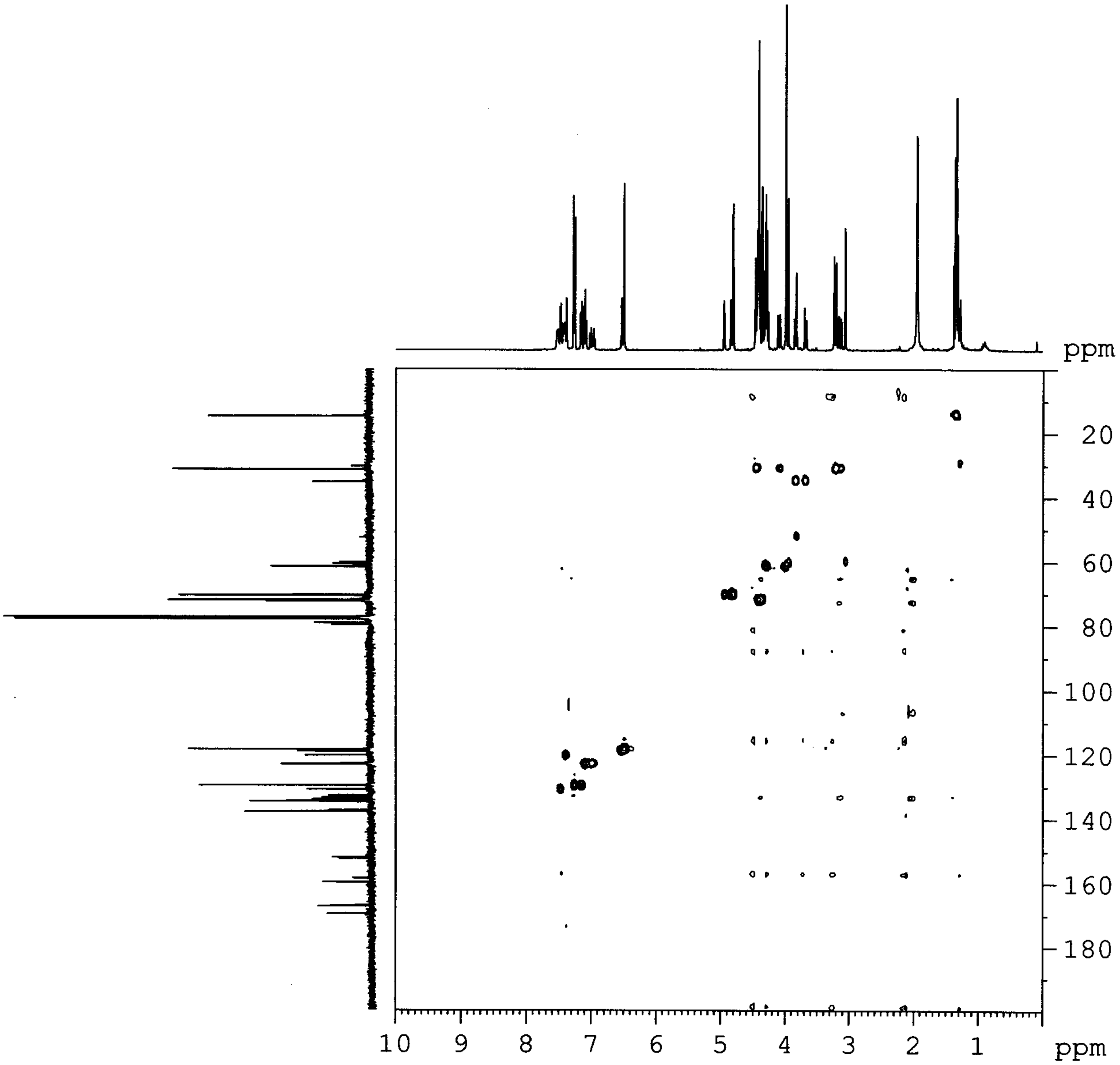


Figure 15. HMQC of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz

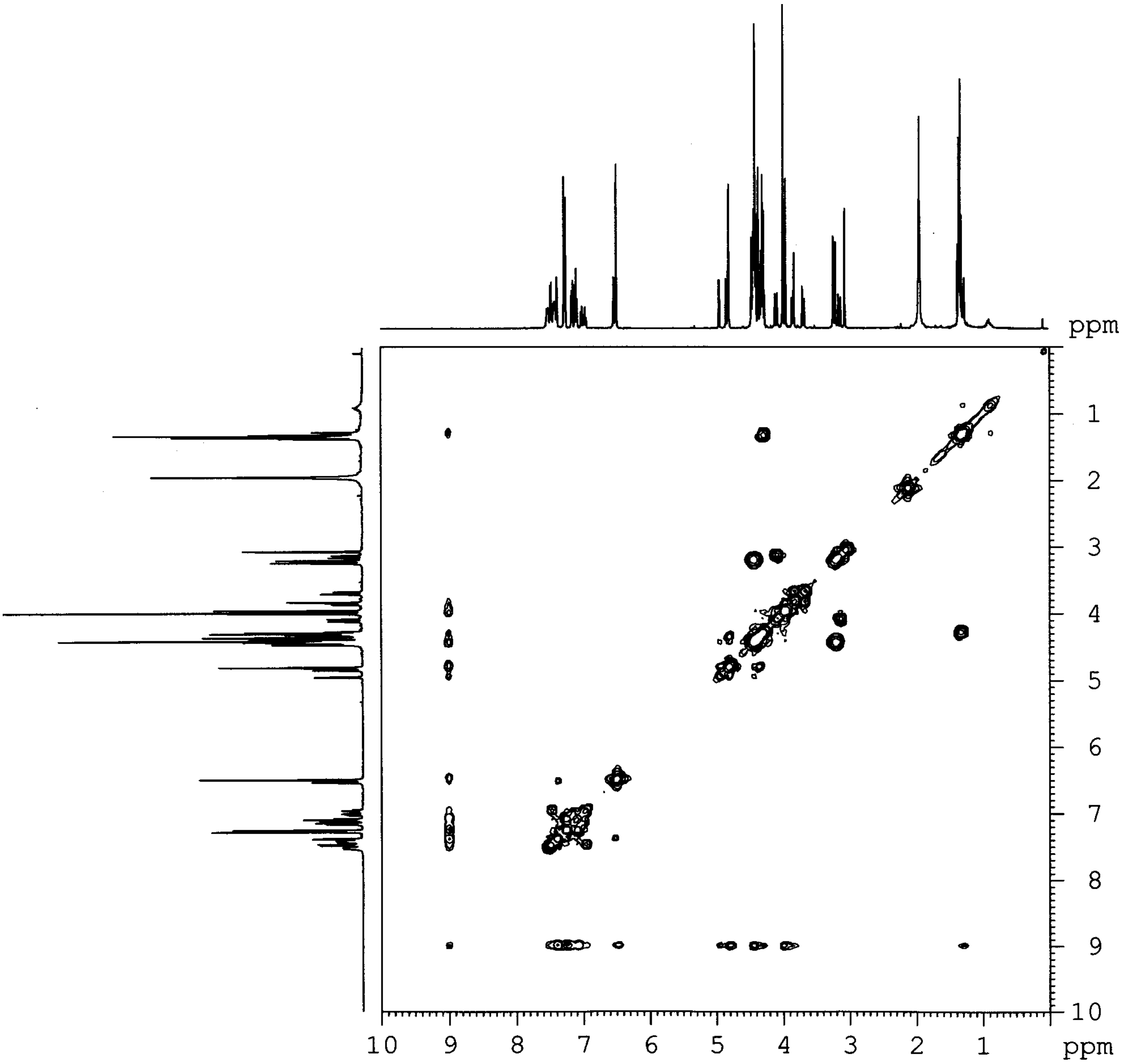


Figure 16. COSY of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz

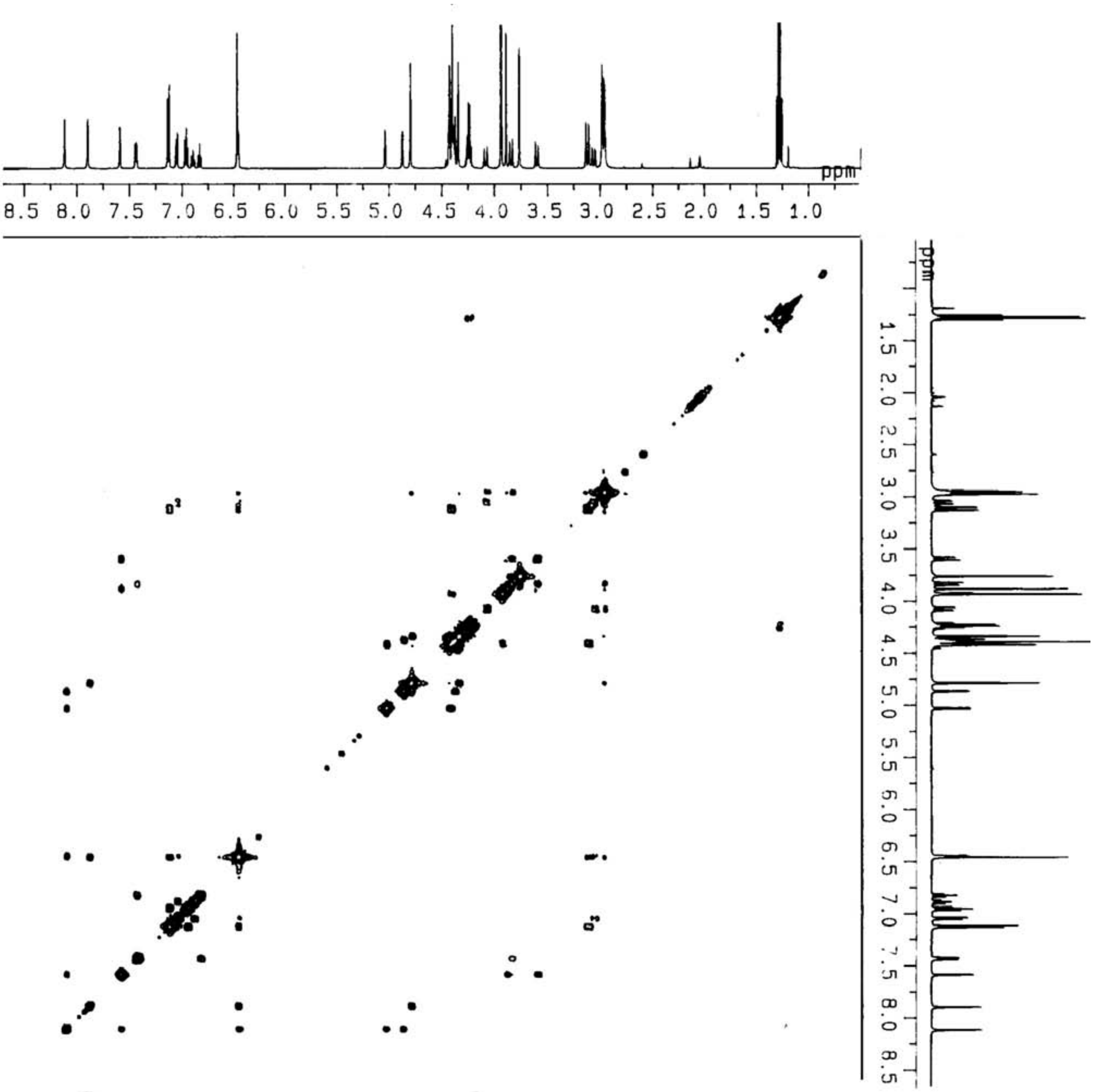


Figure 17 NOESY of 5,7-diamideferrocenyl-25,26,27,28-tetramethylethylestercalix[4]arene (**L2**) in $CDCl_3$ 400 MHz

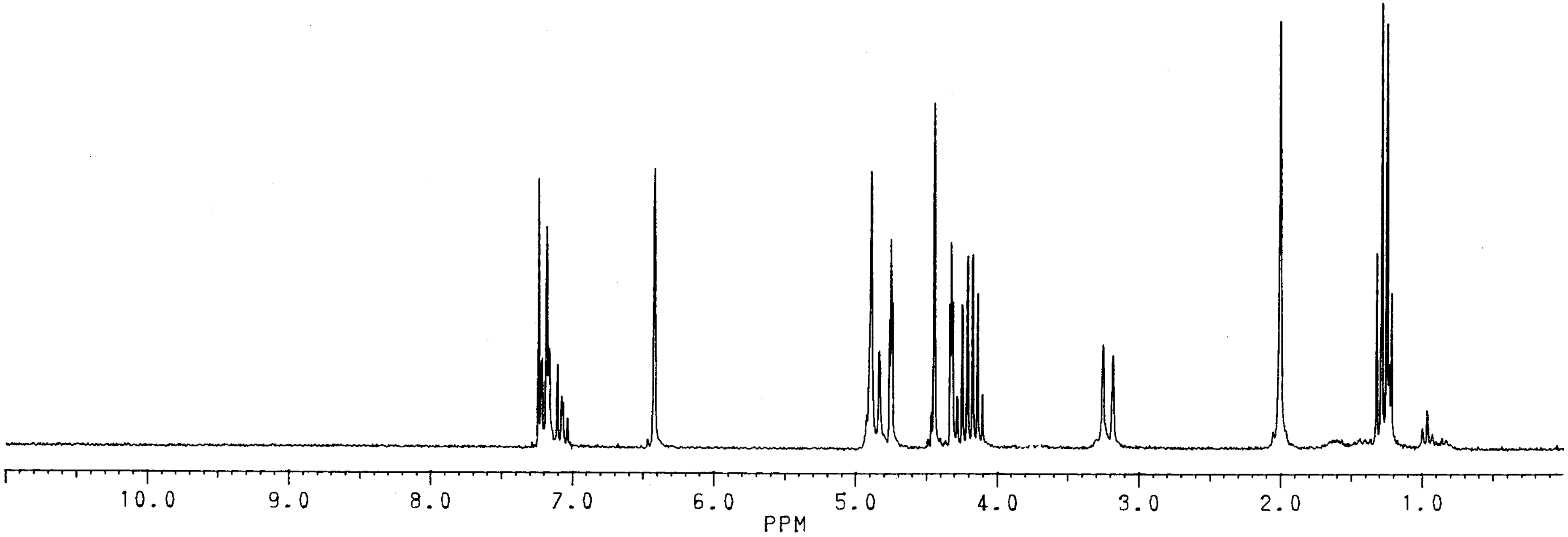
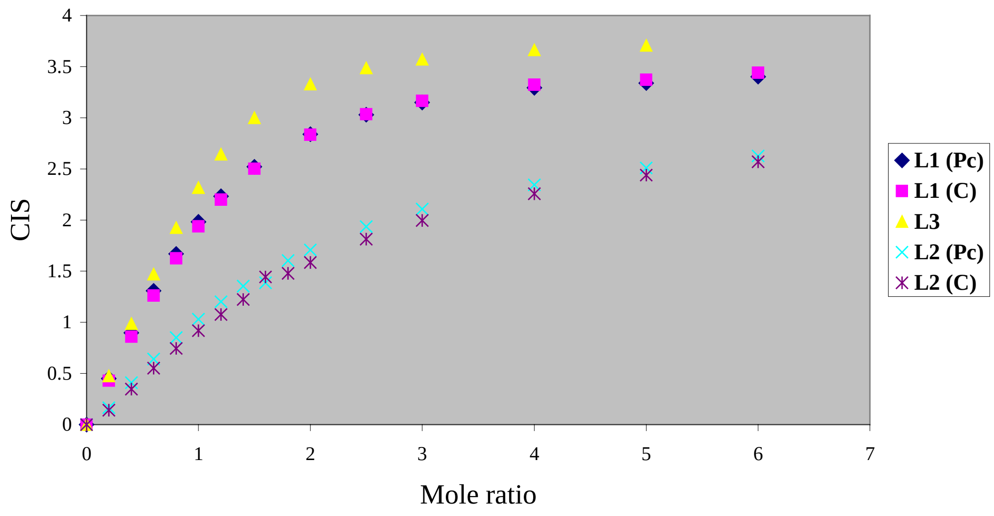


Figure 18 ^{1}H-NMR of 5,7-diamideferrocenyl-25,26,27,28-dimethoxydimethylethylestercalix[4] arene (**L3**) in $CDCl_3$ 200 MHz

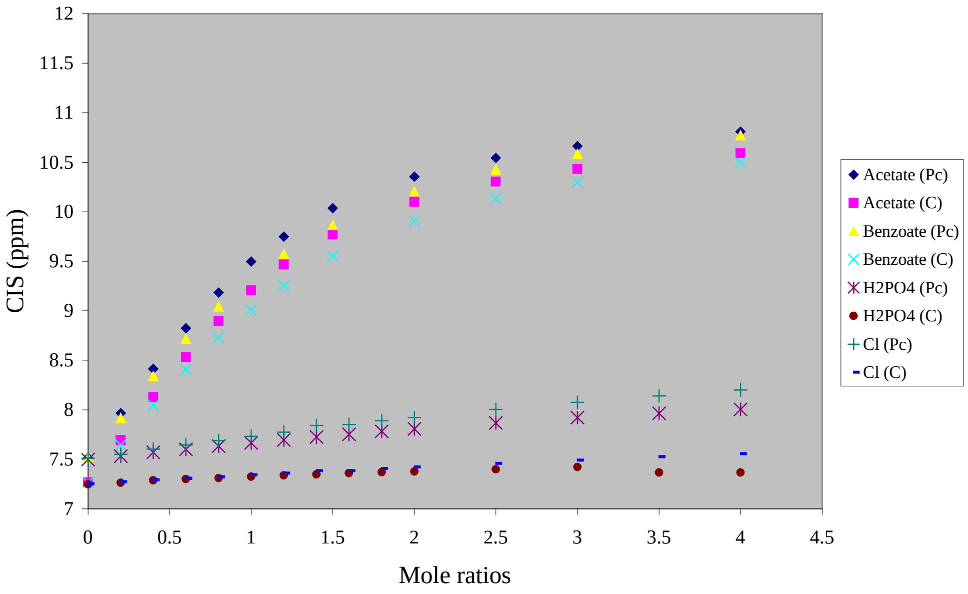
Supporting Informations

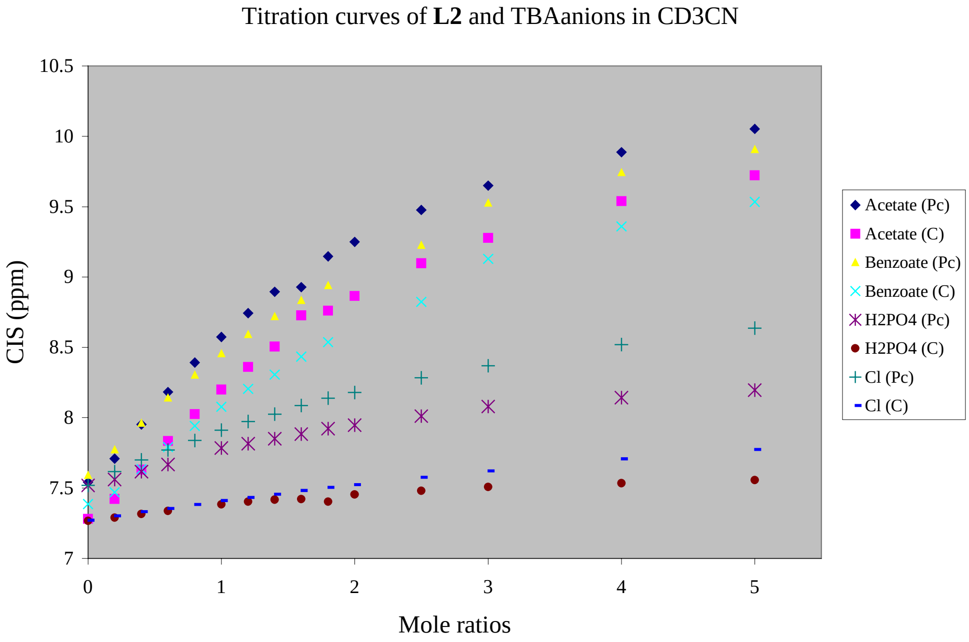
^{1}H-NMR titration techniques of **L1**, **L2** and **L3** with anions in CD$_3$CN:

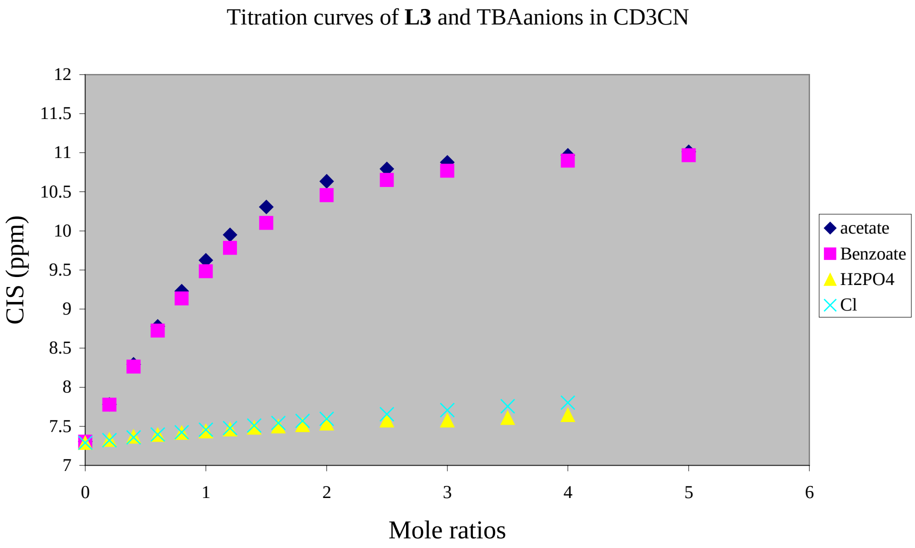
Titration curve of **L1**, **L2** and **L3** with acetate in AN-d6



Titration curves of **L1** and TBAanions in CD3CN



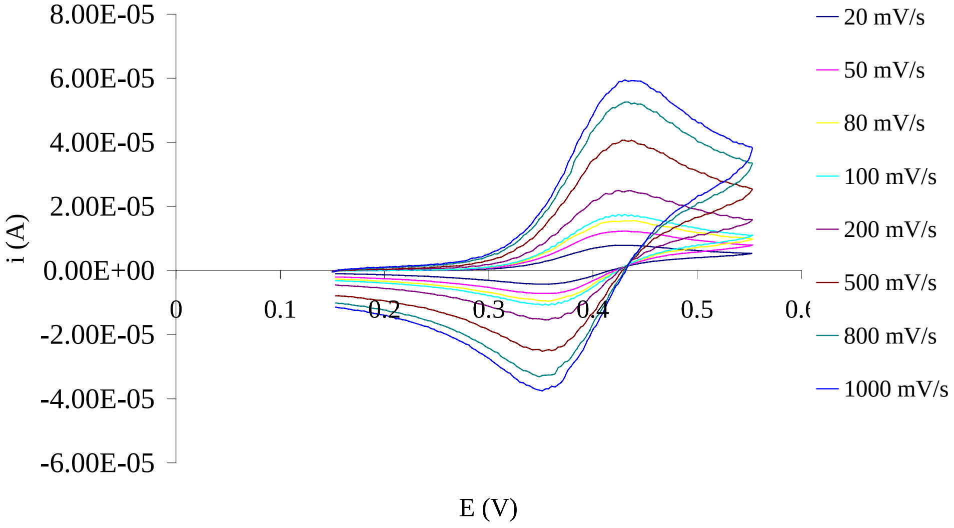

Titration curves of **L2** and TBAanions in CD3CN
CIS (ppm)
10.5
10
9.5
9
8.5
8
7.5
7
0
1
2
3
4
5
Mole ratios
Acetate (Pc)
Acetate (C)
Benzoate (Pc)
Benzoate (C)
H2PO4 (Pc)
H2PO4 (C)
Cl (Pc)
Cl (C)


Titration curves of **L3** and TBAanions in CD3CN
CIS (ppm)
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
0
1
2
3
4
5
6
Mole ratios
acetate
Benzoate
H2PO4
Cl

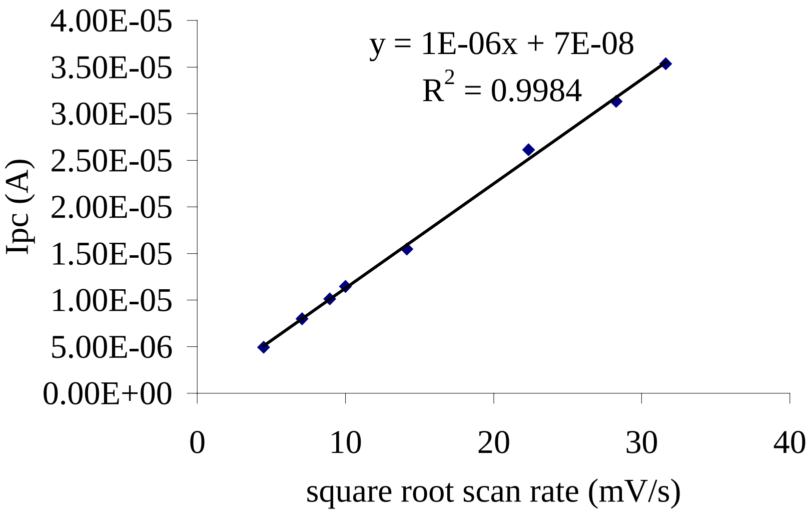
Cyclic Voltammetry Results:

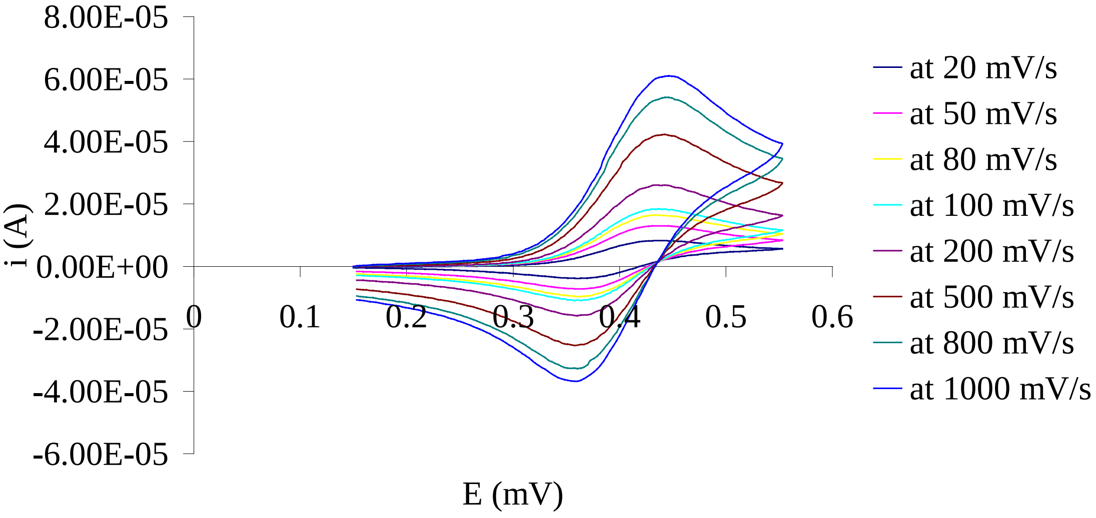
1 Ligands at various scan rates

CVs of **L1** in acetonitrile with 0.1 m. TBAPF at different scan rates

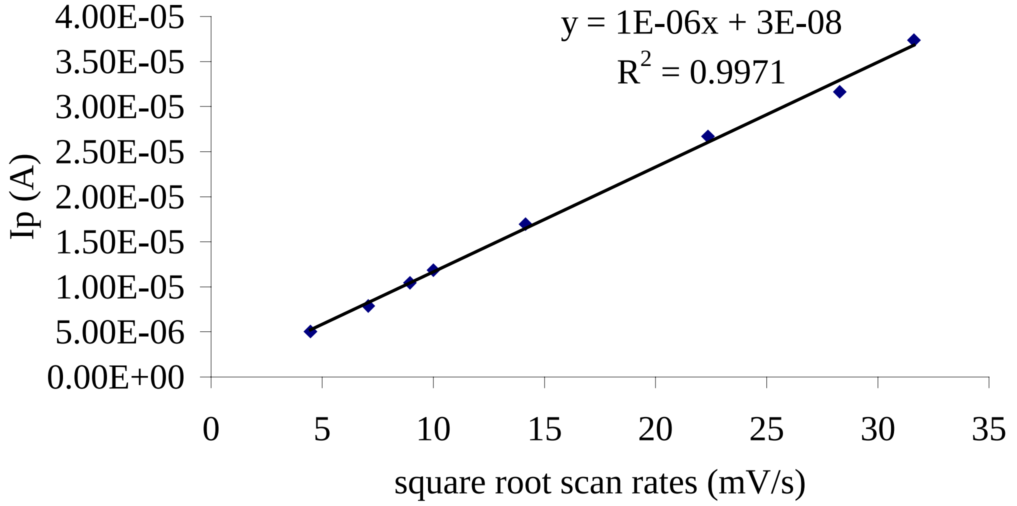


Correlation of **L1** with various scan rates



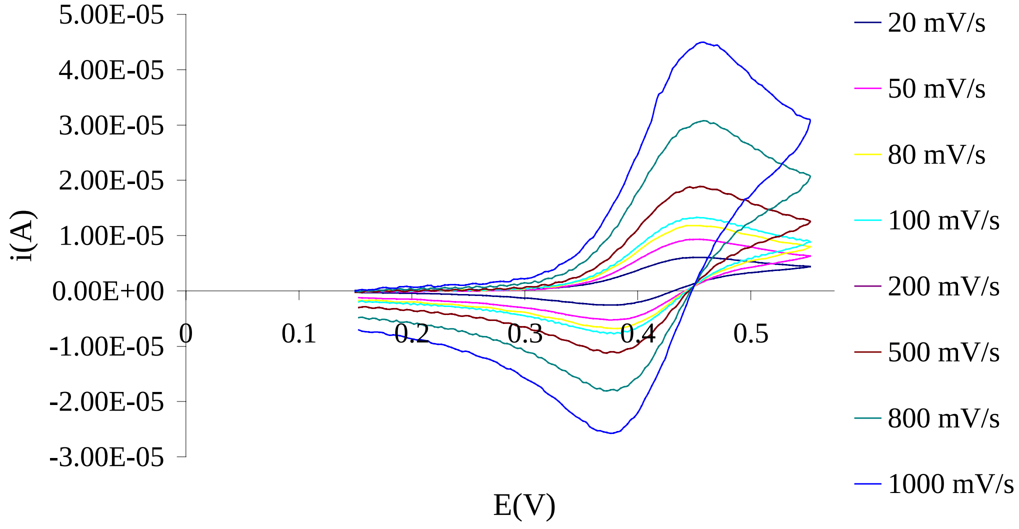


CVs of **L2** in acetonitrile with 0.1 M. TBAPF at different scan rates

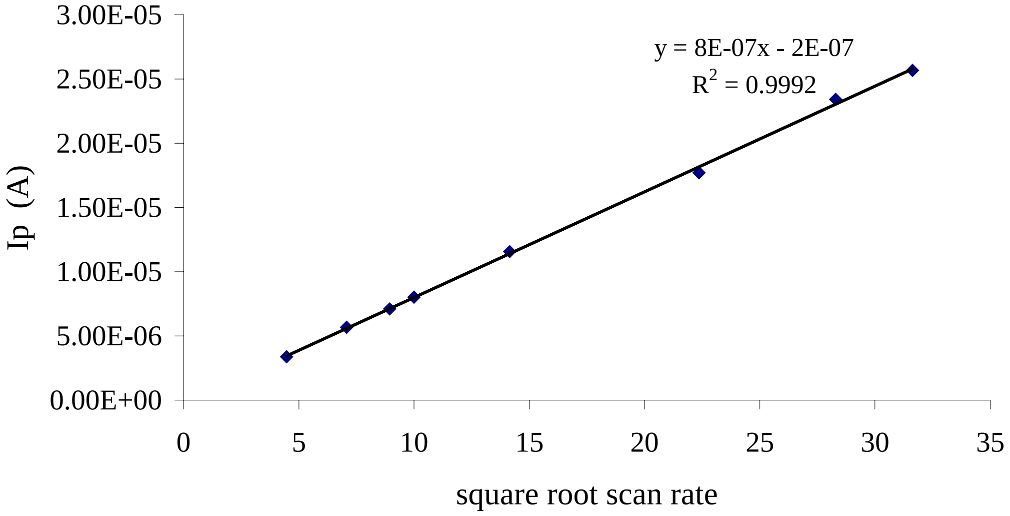


Correlation of L2 at various scan rate

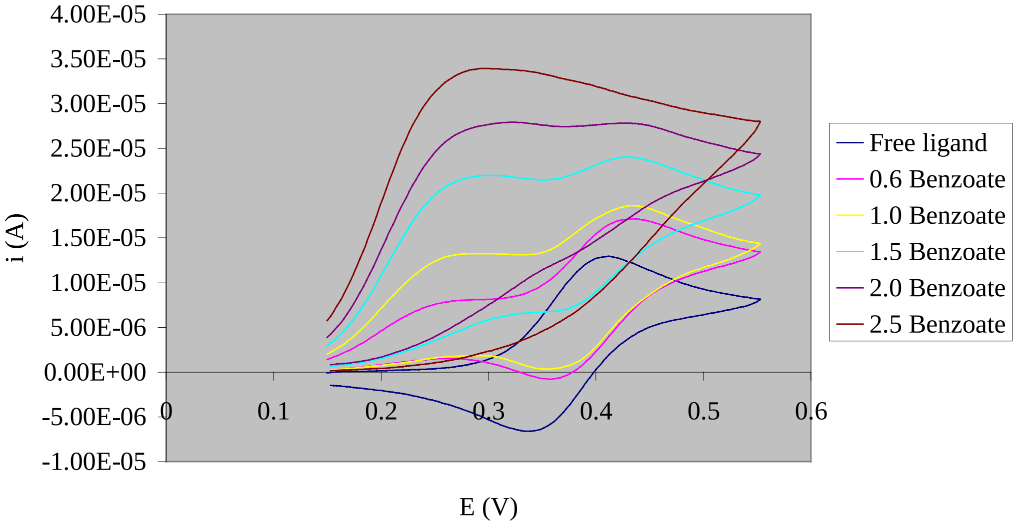
CVs of **L3** in acetonitrile with 0.1 M TABPF at different scan rates



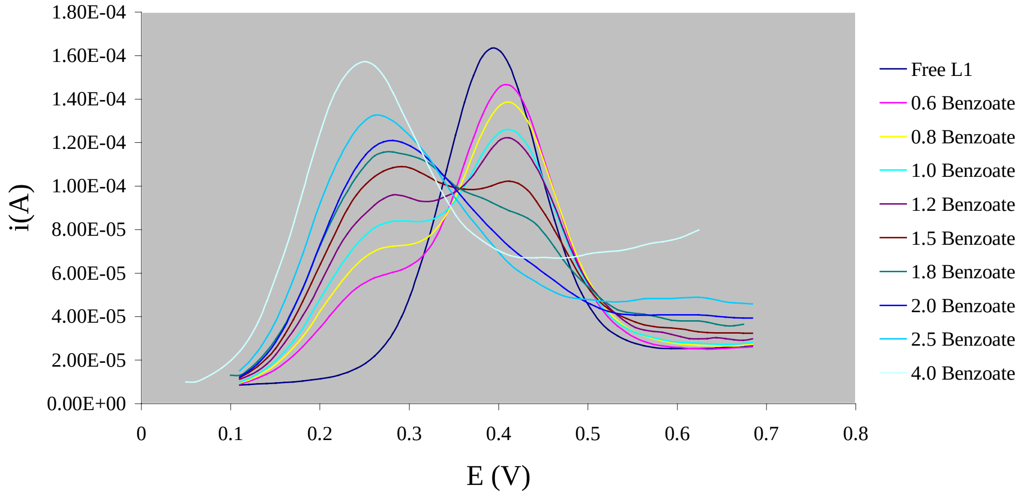
Correlation of **L3** at various scan rates



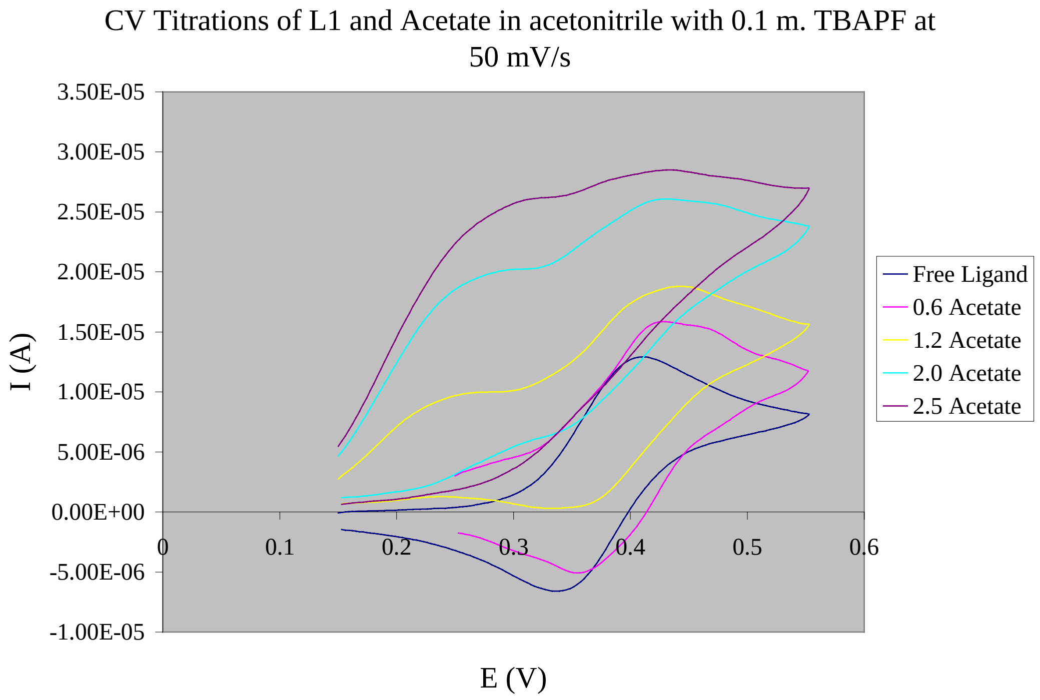
1. Cyclic Voltammetry titrations with anions.



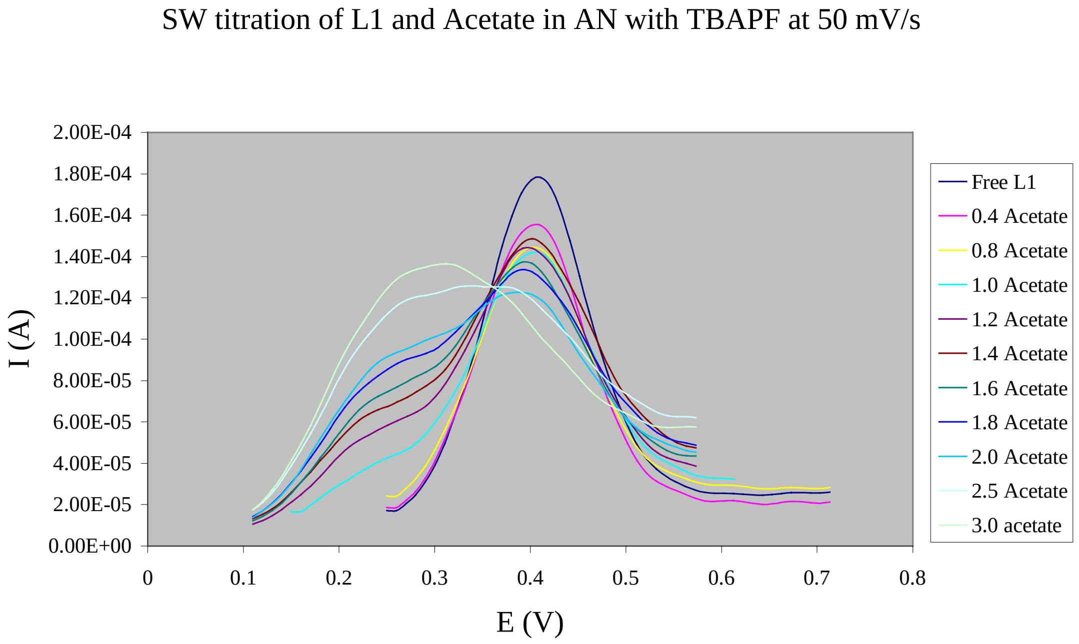
CV titrations between **L1** and Benzoate in acetonitrile with 0.1 M. TBAPF at 50 mV/s



SW titration of L1and Aenzoate in AN with 0.1 M. TBAPF at 50 mV/s

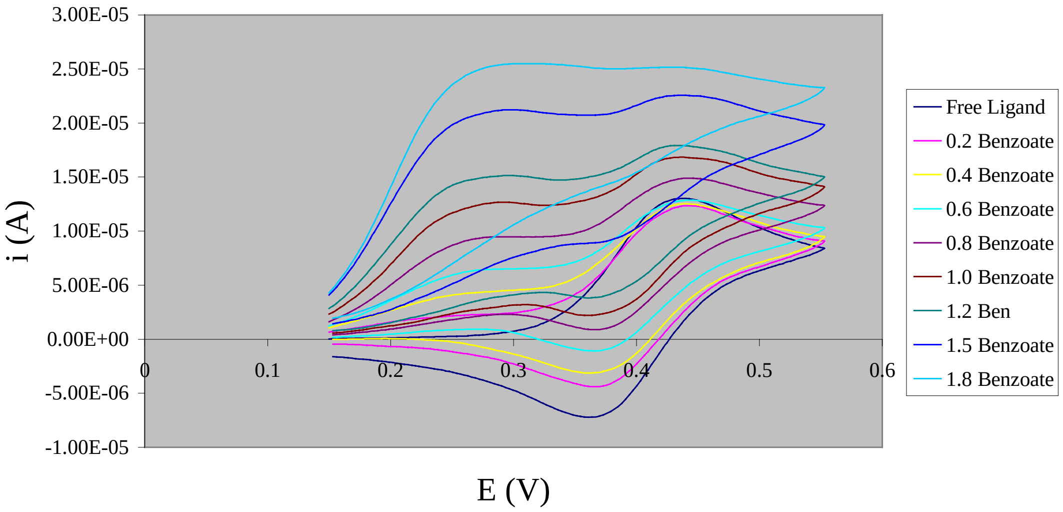


CV Titrations of L1 and Acetate in acetonitrile with 0.1 m. TBAPF at 50 mV/s

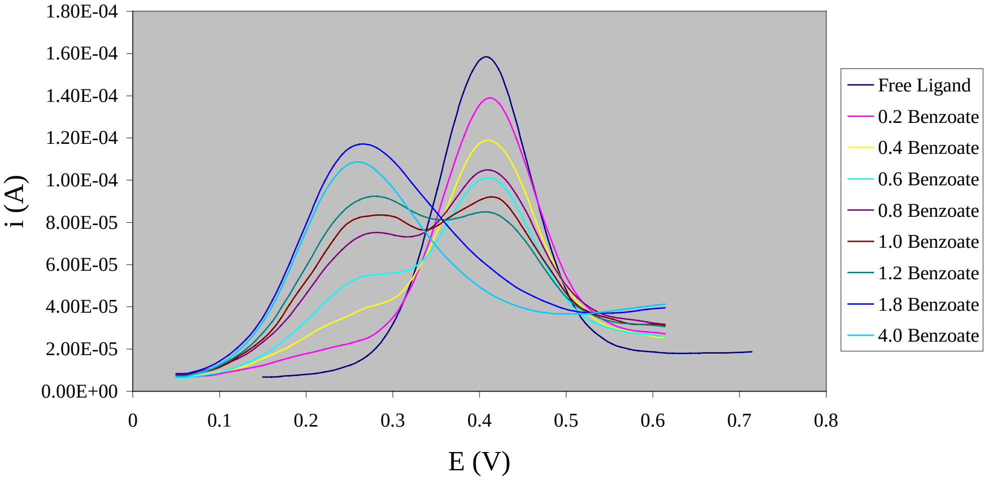


SW titration of L1 and Acetate in AN with TBAPF at 50 mV/s

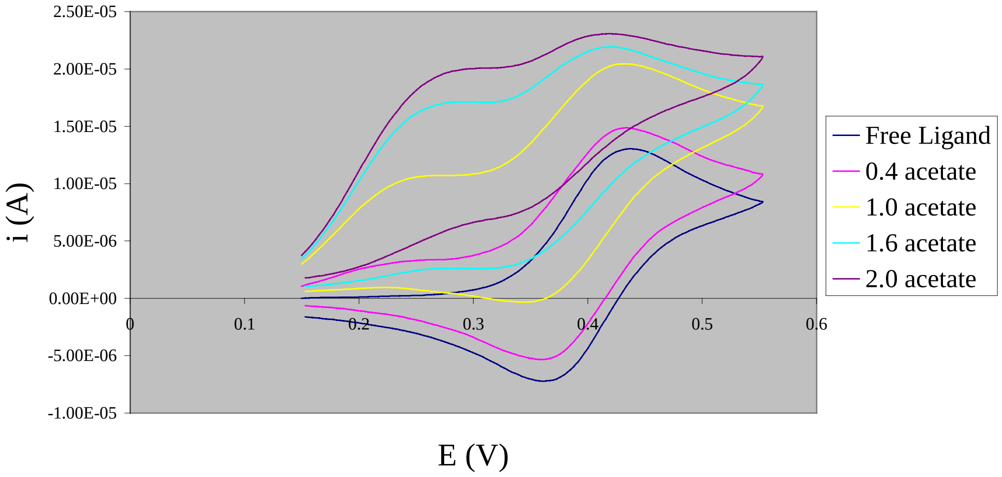
CV titration of **L2** and Benzoate in AN with 0.1 M. TBAPF at 50 mV/s



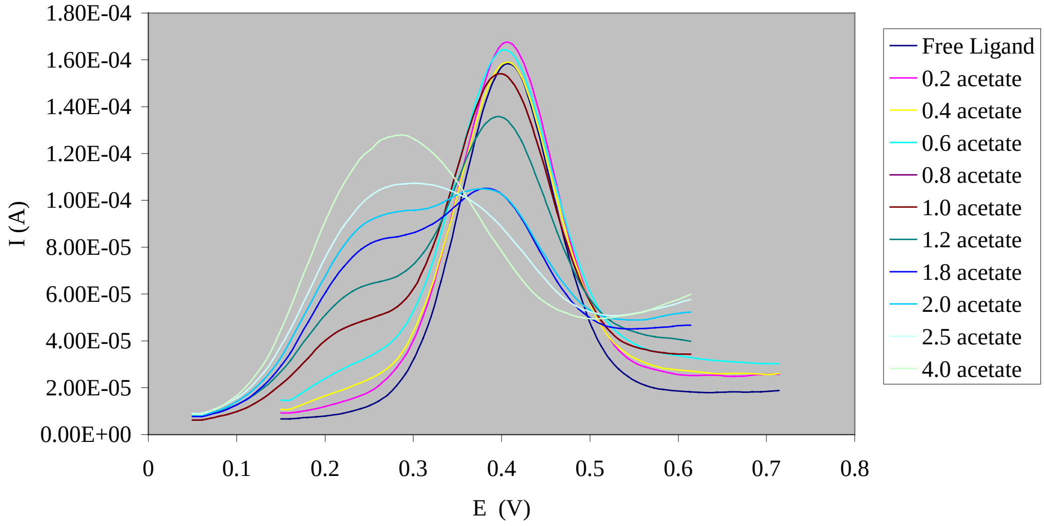
SW titration of **L2** and Benzoate in AN with 0.1 M. TBAPF at 50 mV/s

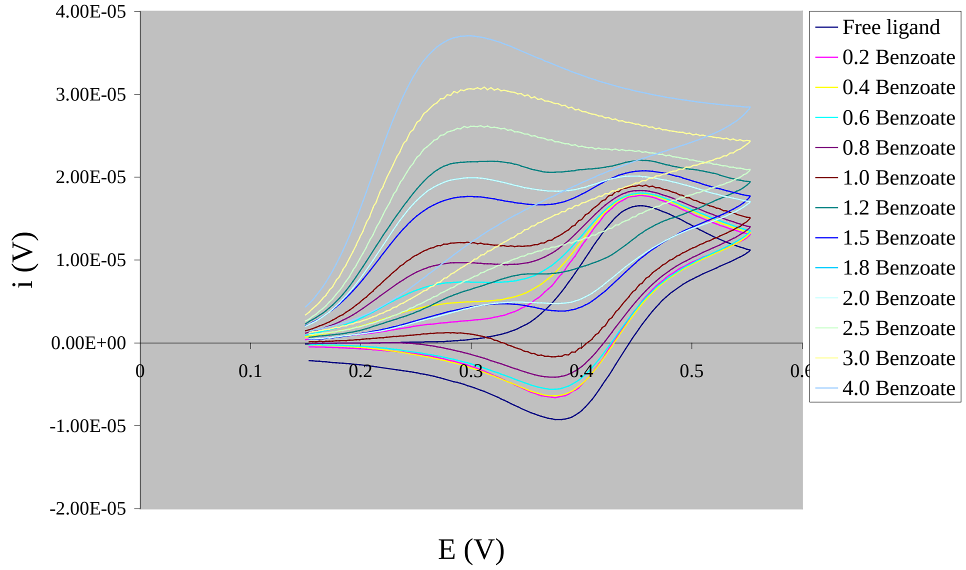


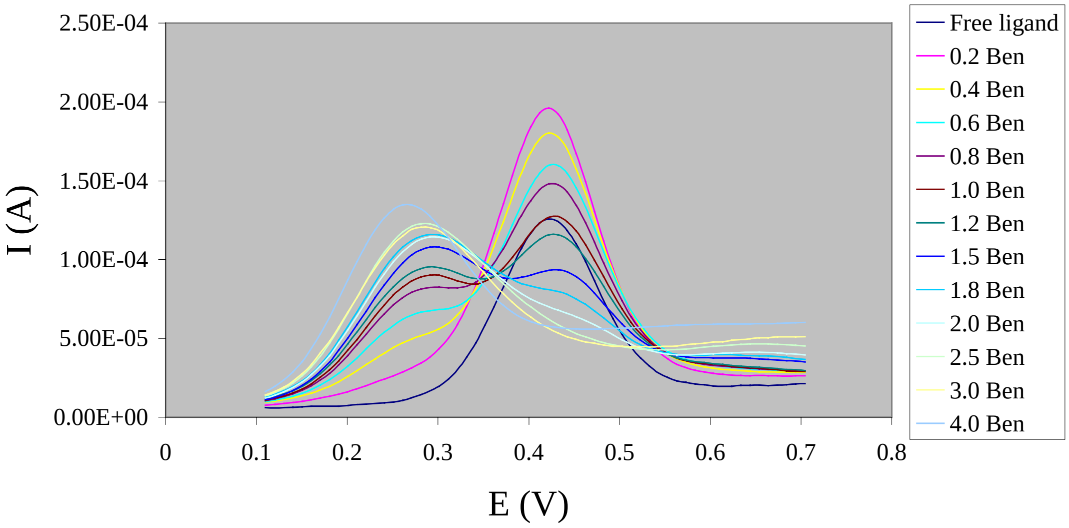
CV titrations of **L2** and Acetate in AN with 0.1 M. TBAPF6 at 50 mV/s



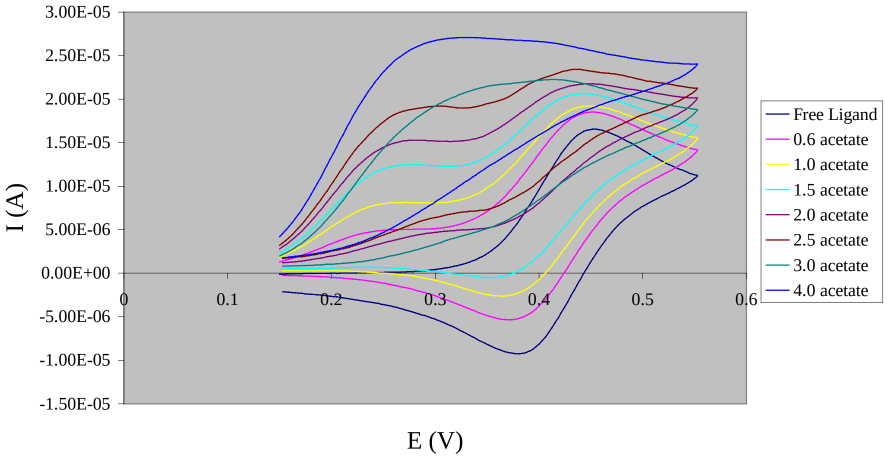
SW of **L2** and Acetate in 0.1 M. TBAPF in AN at 50 mV/s



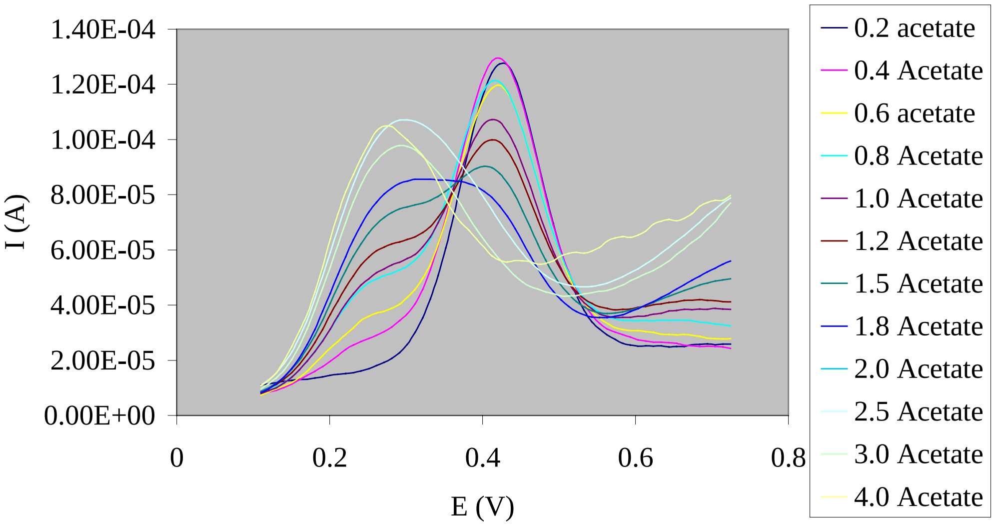

CV Titrations of **L3** and Benzoate in AN with 0.1 M. TBAPF at 50 mV/s


SW titration of **L3** and Benzoate in AN with 0.1 M. TBAPF at 50 mV/s

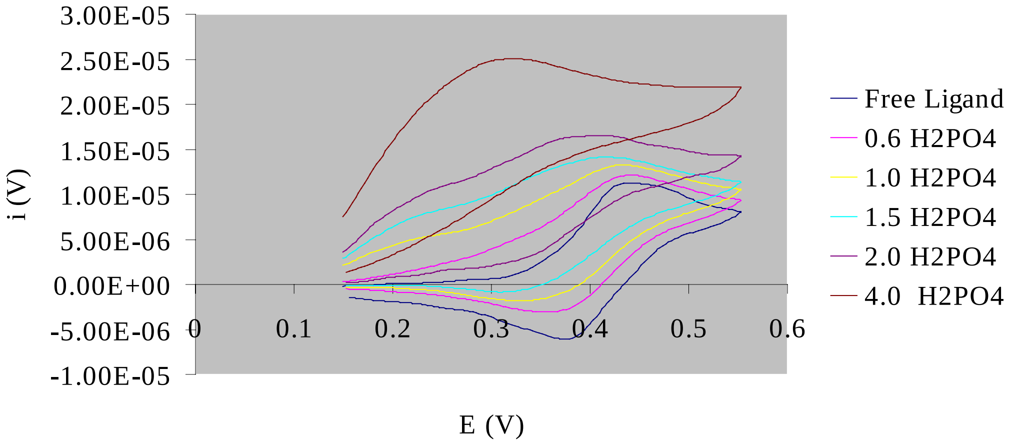
CV titrations of **L3** and acetate in AN with TBAPF at 50 mV/s



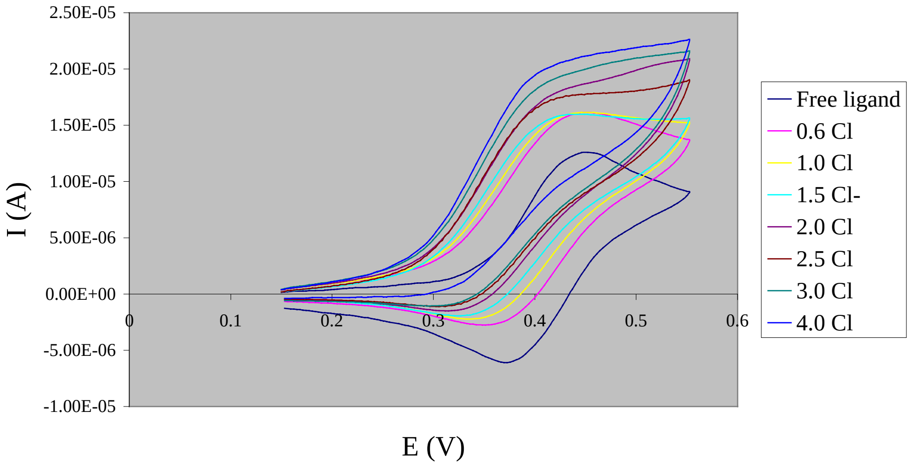
SW titration of L3 and Acetate in AN with TBAPF at 50 mV/s



CV titration of **L2** and H2PO4- in AN with 0.1 M.TBAPF at 50 mV/s



CV titrations of **L2** and Cl- in AN with TBAPF at 50 mV/s



CV titrations of **L1** and Cl in AN with TBAPF at 50 mV/s