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# Syntheses, crystal structures, and electrochemical properties of multi-ferrocenyl resorcinarenes

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**Abstract**—Tetraaryl and tetraferrocenyl resorcinarenes **1a–1c** have been synthesized by the HCl-catalyzed condensation of resorcinol with aromatic aldehydes or ferrocenecarbaldehyde, which were fully alkylated with ethyl α-chloroacetate to give the activated ethyl resorcinarylacetates **2a–2c**. Reaction of **2a–2c** with hydrated hydrazine yielded the resorcinarene acylhydrazine derivatives **3a–3c**, from which the multi-ferrocenyl functional groups were selectively and efficiently introduced on the upper rim, or on the lower rim, or both on the upper and lower rims of resorcinarenes **4a–4c** and calixarenes **4d–4f** based upon the condensation reactions of acylhydrazones with ferrocenecarboxaldehyde.


## 1. Introduction

Calixarenes and resorcinarenes have become popular templates for a number of chemical investigations because it can be produced selectively in large quantities from cheap commercial starting materials and can easily be chemically modified, leading to versatile tail-made receptors.[1–3] In order to design new types of valuable receptor molecules and supramolecular structures, various methods have been developed for complete and selective modification on the upper and lower rims of calixarenes and resorcinarenes.[4–5] Recently, molecular design of calixarenes and resorcinarenes for anion recognition and sensing has become an increasingly important research topics in supramolecular chemistry because selective binding of anions is more demanding than that of cations in view of the high free energies of solvation of anions and that the frequently occurring pH dependency of anion complexation.[6–8] The incorporation of redox-active centers, such as ferrocene into ligands of the calixarene type aimed at the development of molecular sensory devices, which allow electrochemical recognition of trapped guests, has attracted much more attention in the past years. Ferrocene does not directly interact with anions until it is oxidized to ferrocenium, when electrostatic interactions are switched on. Beer and co-workers firstly prepared metallocene amide receptors for binding and sensing anions.[9–10] From then Beer and others reported a lot of works with different strategies for introducing ferrocene[11–22] and other metallocene[23–26] units to the lower and upper rims of calixarenes and resorcinarenes, many of which include an amide hydrogen-bonding group.[27–28] Anions may be recognized in a range of environmental conditions, with some receptors even being active in aqueous solution.[29–31] The tetraferrocenyl resorcinarenes were also obtained from the condensation of resorcinol with ferrocenecarboxaldehyde.[17] In continuation of our studies on molecular design of calixarene acceptors, we are interested in constructing multi-ferrocene functional groups on *p-tert*-butylcalix[*n*]arenes and resorcinarenes. In this paper, we report a selective and efficient procedure to introduce ferrocenes on the upper rim, or on the lower rim, or both on the upper and lower rims of resorcinarenes and calixarenes based upon the condensation reactions of acylhydrazones with ferrocenecarboxaldehyde.

## 2. Results and discussion

### 2.1. Synthesis and characterization

Tetraaryl resorcinarenes, which can be easily prepared from the condensation of resorcinol with aromatic aldehydes, have received less attention compared to tetraalkyl resorcinarenes[32–34] because tetraaryl resorcinarenes have less solubility in common solvents and are much difficult for chemical modifications. But rigid aryl groups might create a more stable conformation for resorcinarenes and result in much high selective recognition. Thus resorcinarenes **1a–1c** with phenyl, *p*-hydroxyphenyl, and ferrocenyl groups were prepared in high yields from the condensation of

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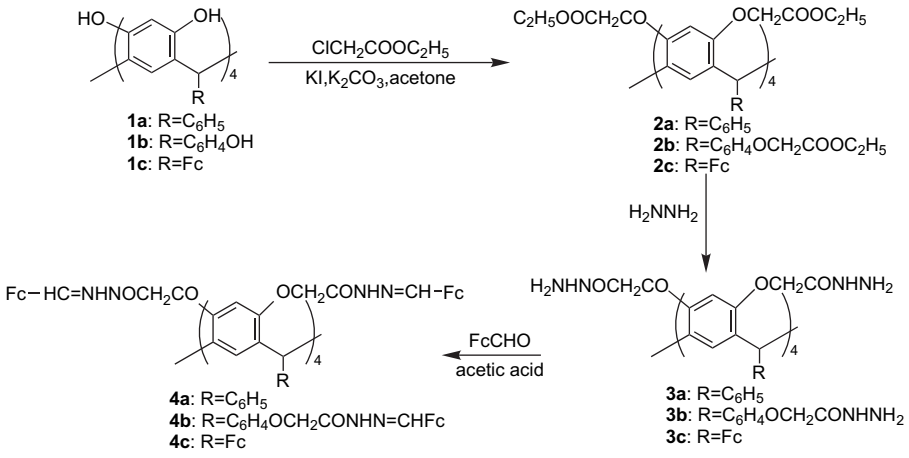



**1a**: R=$C_6H_5$
**1b**: R=$C_6H_4OH$
**1c**: R=Fc

**2a**: R=$C_6H_5$
**2b**: R=$C_6H_4OCH_2COOC_2H_5$
**2c**: R=Fc

**3a**: R=$C_6H_5$
**3b**: R=$C_6H_4OCH_2CONHNH_2$
**3c**: R=Fc

**4a**: R=$C_6H_5$
**4b**: R=$C_6H_4OCH_2CONHN=CHFc$
**4c**: R=Fc

**Scheme 1**. Synthesis of multi-ferrocenyl resorcinarenes.

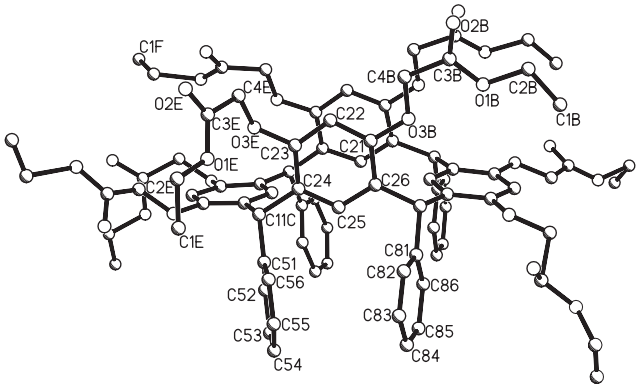



**Figure 1**. The crystal structure of **2a**.

resorcinol with benzaldehyde, *p*-hydroxybenzaldehyde, and ferrocenecarboxaldehyde according to the published method (Scheme 1).[32–34] Although having very poor solubilities in common solvents, **1a**–**1c** can still be fully O-alkylated with ethyl α-chloroacetate in $K_2CO_3$/KI/acetone system to give active ester derivatives **2a**–**2c** in 50–70% yield, which make it possible to modify resorcinarene on the upper rim. It must be noticed that there are 8, 12, or 8 active ester groups in **2a**–**2c**, respectively, for the *p*-hydroxyphenyl groups in **1b** would be also alkylated in this procedure. The structures of **2a**–**2c** were characterized by spectroscopic data and fully confirmed by the X-ray single crystal analysis.

The molecular structures are shown in Figures 1–3. The crystal structures give stronger evidence that all hydroxyl groups have been alkylated by ethyl α-chloroacetate to give fully alkylated ethyl calixarylacetate. It can be seen that in **2a**–**2c** the four resorcinol units in the ring were divided into two groups with two resorcinol rings almost perpendicular to the other two resorcinol rings, which show the resorcinarene in boat conformation, with much distorted in a propeller-like manner in **2c**. The stretching directions of two perpendicular resorcinol rings are opposite. One is upper standing and the other is upside down. It is interesting

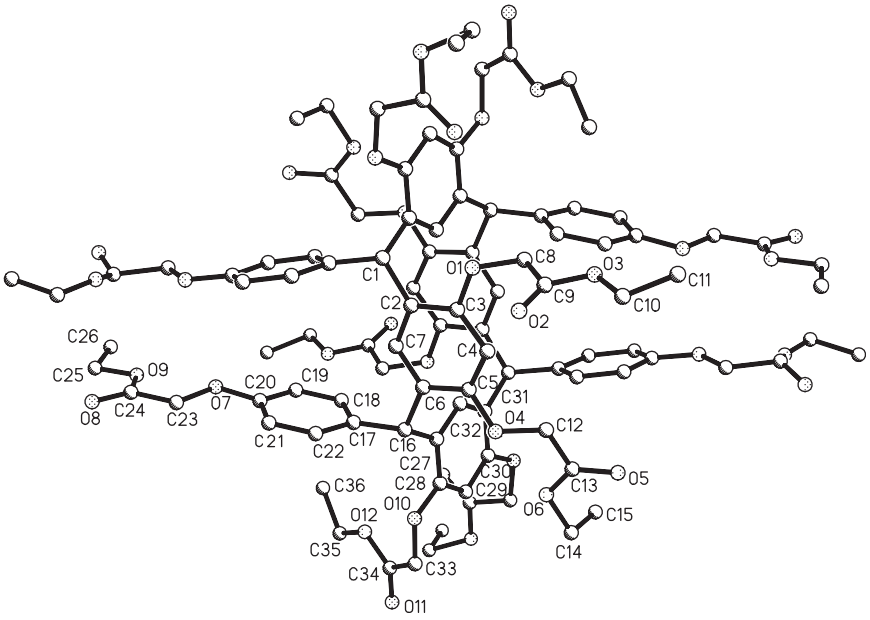



**Figure 2**. The crystal structure of **2b**.

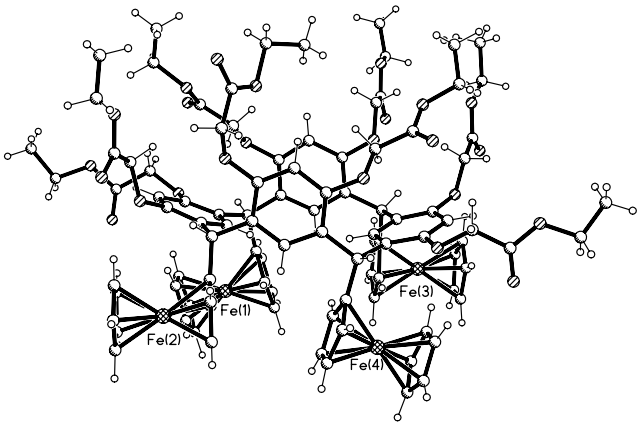



**Figure 3**. The crystal structure of **2c**.

to find that in **2a** and **2c** the four phenyl groups and ferrocenyl groups are located in the lower rim direction. Compounds **2a** and **2c** show *rccc* (all *cis*) conformation. Compound **2b** exists in *rctt* (*cis–trans–trans*) conformation, in which two neighboring *p*-hydroxyphenyl groups are located in upper rim direction with other two *p*-hydroxyphenyl groups lying at the opposite direction. Thus the 12 ethoxycarbonylmethoxy groups in the calixarene are peripherally stretched from resorcinarene core, which give a good advantage for the preparation of dendrite molecules.

Refluxing **2a–2c** or ethyl *p-tert*-butylcalix[*n*]aryl acetates **2d–2f** (*n*=4, 6, 8)[35] with excess of hydrated hydrazine in ethanol gave the corresponding calixaryl acylhydrazine derivatives **3a–3f** as white solid in excellent yields (85–92%, Scheme 2). It should be pointed out that beside **3d**, other acylhydrazine derivatives have very poor solubility in most organic solvents, which makes great difficulty to get satisfied characterization data for them. Compound **3d** has good solubility in common organic solvent because it has only four hydrazine groups, while others have 6–12 hydrazine groups. In the IR spectra of **3a–3f**, the C═O group of acylhydrazine shows stronger absorption band at 1680 $cm^{-1}$, while C═O group of ester in **2a–2f** appears at 1750 $cm^{-1}$, which indicates that all ethyl ester groups in 2**a–2f** have been transformed into acylhydrazine groups. The molecular structures of acylhydrazine derivatives **3a–3f** were fully confirmed by the X-ray single crystal analysis of one representative compound **3d** (Fig. 4). It exists in cone conformation with the four acylhydrazine groups orienting in the same direction.

Even if **3a–3f** had very poor solubility in common solvent, the suspension of acylhydrazine derivatives **3a–3f** in acetic acid at room temperature reacted smoothly with ferrocenecarbaldehyde to yield brown precipitates as the ferrocenyl hydrazone products **4a–4f** in satisfied yields (62–89%). In the IR spectra of ferrocenyl hydrazones **4a–4f**, the absorption band of C═O appears at about 1680 $cm^{-1}$ and the absorption of N═CH was observed with a strong peak at about 1610 $cm^{-1}$. Thus multi-ferrocenyl groups have been successfully introduced into the calixarene plateform.

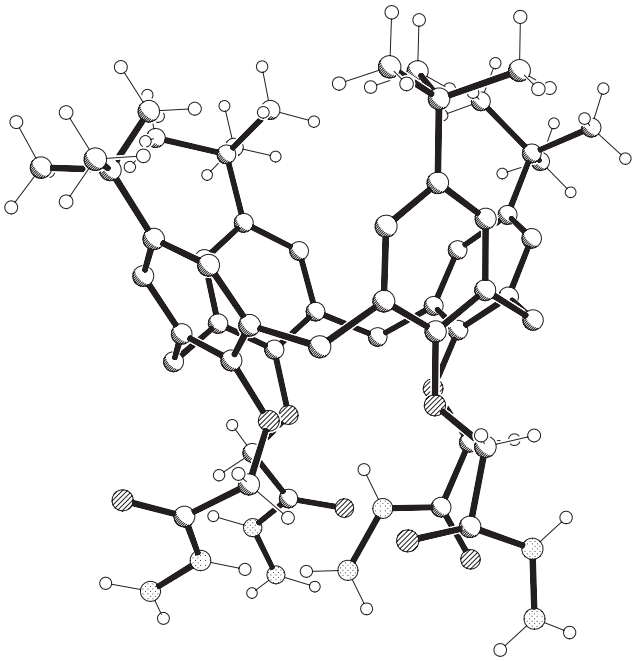
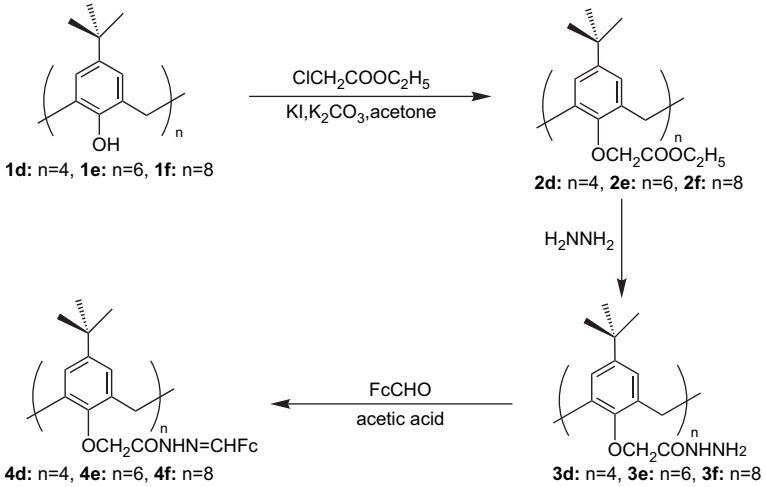
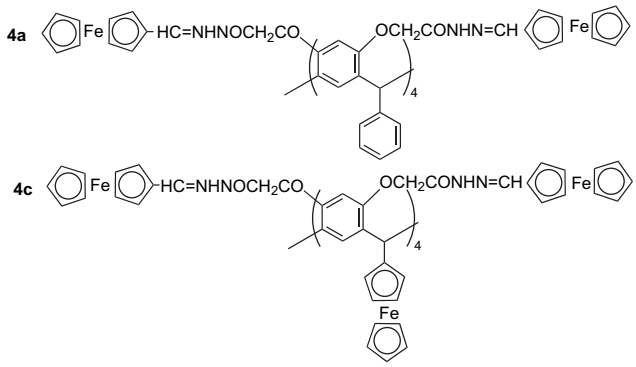


**Figure 4**. The crystal structure of **3d**.




**Scheme 2**. Synthesis of multi-ferrocenyl calixarenes.



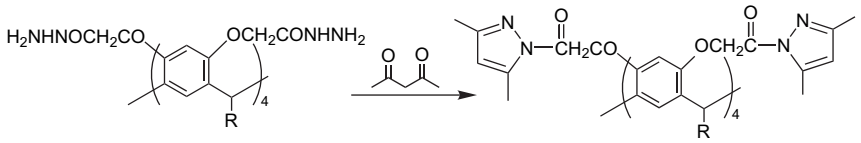

**Scheme 3**. Concise representation of molecules **4a** and **4c**.

According to the crystal structure of the ester precursors **2a**–**2c**, the ferrocenyl groups must occupy the different positions of the calixarene. In **4a** all eight ferrocenyl groups are at the upper rim. In **4c** there are eight ferrocenyl hydrazone groups at the upper rim and four ferrocenyl groups at side position of resorcinarene (Scheme 3).

Refluxing resorcinarene acylhydrazines **3a** and **3c** with excess of acetoacetone in THF caused the formation of pyrazole derivatives **5a** and **5c** in moderate yields (Scheme 4). Compounds **5a** and **5c** were characterized and gave further evidence to the structure of the resorcinarene acylhydrazine.

## 2.2. Electrochemical properties

The electrochemical properties of the resorcinarene compounds **2c** and **4a**–**4f** (Fig. 5) with the redox-active ferrocenyl groups were studied by cyclic voltammetry, which is a sensitive electrochemical method and permits the collection of excellent data at low concentration of electroactive substance.[36,37] The values obtained for the peak potentials of the anodic and cathodic waves ($E_{pa}$ and $E_{pc}$, respectively) for the oxidation processes are given in Table 1. The




**3a**: R=$C_6H_5$
**3c**: R=Fc

**5a**: R=$C_6H_5$
**5b**: R=Fc

**Scheme 4**. Synthesis of resorcinarene pyrazole derivatives **5a** and **5b**.

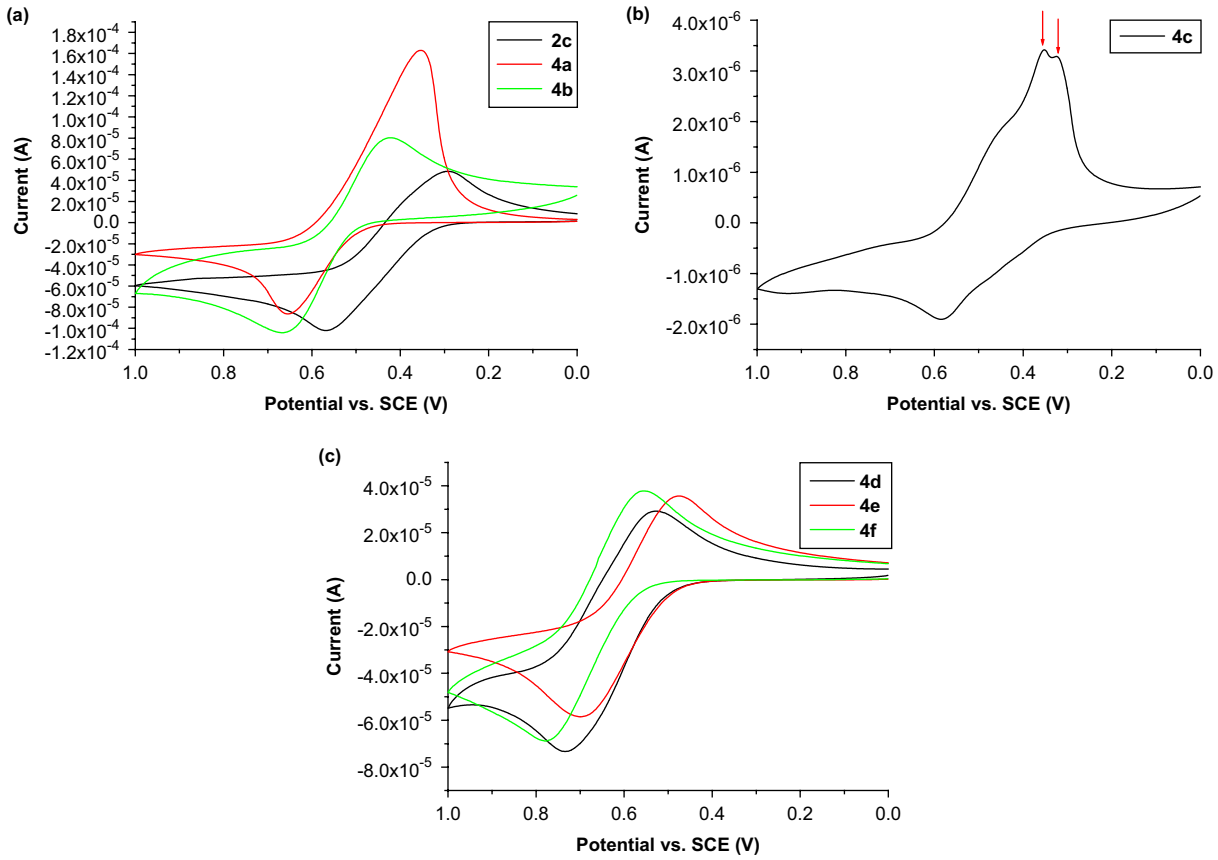



**Figure 5**. Cyclic voltammetric curves ($5\times10^{-4}$ M $CH_2Cl_2$ solution, 0.1 M $Bu_4NClO_4$ (TBAP), 298 K; scan rate 50 mV $s^{-1}$) for the ferrocene units in (a) **2c**, (b) **4a**–**4c**, and (c) **4d**–**4f**.

**Table 1**. Electrochemical data of **2c** and **4a–4f** at scan rates 50 mV $s^{-1}$

| Entry | ($Fc-e \rightarrow Fc^+$) | | | |
|---|---|---|---|---|
| | $E_{pa}$ (V) | $E_{pc}$ (V) | $\Delta E_p$ (V) | $E_{1/2}$ (V) |
| **FcH** | 0.548 | 0.441 | 0.107 | 0.494 |
| **2c** | 0.550 | 0.292 | 0.258 | 0.421 |
| **4a** | 0.655 | 0.354 | 0.301 | 0.505 |
| **4b** | 0.628 | 0.382 | 0.246 | 0.505 |
| **4c** | 0.585 | 0.352/0.324 | — | — |
| **4d** | 0.734 | 0.528 | 0.206 | 0.631 |
| **4e** | 0.700 | 0.476 | 0.224 | 0.588 |
| **4f** | 0.779 | 0.555 | 0.224 | 0.667 |

All potentials are referred to the saturated calomel electrode (SCE) in $CH_2Cl_2$ solution.

electrochemical results of the investigated compounds were compared to that of ferrocene.

The cyclic voltammetric behavior of compounds **2c** and **4a–4f** showed one redox wave in the potential range of 0–1.0 V suggesting that ferrocene units of each compound were in the same ferrocenyl environment. The separation of the anodic and the cathodic peak potentials, $\Delta E_p$, was 258, 301, 246, 206, 224, and 224 mV at 50 mV $s^{-1}$ for compounds **2c**, **4a**, **4b**, and **4d–4f**, respectively. These values were larger or smaller than that expected for a reversible 4-, 6-, 8-, and 12-electron transfer reaction, which is given by $|E_p - E_{p/2}| = 56.5/n$ mV, where $n$ is the number of electron transferred in the process,[38] indicating that the electron transfer process was irreversible under this condition. Otherwise, the larger the scan rate, the broader the observed $\Delta E_p$ would be. It is probably due to the onset of kinetic complications. The peak current of the redox couples described above is not proportional to the square root of the scan rate (50–250 mV $s^{-1}$), indicating that the electrochemical processes are adsorption-controlled.[39] Compound **4c** shows much complicated redox waves because it has two kinds of ferrocenyl subunits, which are eight ferrocenyl acylhydrazone groups and four outer ferrocenyl groups. Two reduction peaks at 0.352 and 0.324 V are observed with only one oxidation peak (Fig. 5b), which is possibly due to peak-superposition. DPV (differential pulse voltammetry) is applied to **4c** in order to distinguish two kinds of ferrocenyl groups (Fig. 6). The result is disappointing. The number of electron transferred in the process is less than the academic number, which also indicates that this electrochemical process is irreversible. The group CH=N in **4a–4f** may be contributing to electrochemical process, their strong electron-withdrawing effect causes an increase in anodic potential of **4a–4f** compared with the data of ferrocene itself.

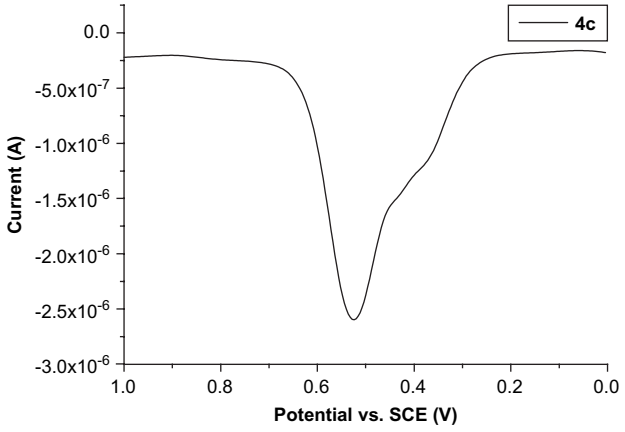



**Figure 6**. Differential pulse voltammetry of **4c**; pulse amplitude: 50 mV; pulse width: 50 ms; amplitude: 50 mV; scan rate: 0.004 V $s^{-1}$; other conditions as in Figure 5.

## 3. Experimental

### 3.1. General remarks

**3.1.1. Materials.** All reagents and solvents were commercially available with analytical grade and used as received. Further purification and drying by standard method were employed and distilled prior to use when necessary. All evaporations of organic solvents were carried out with a rotary evaporator in conjunction with a water aspirator. The plates used for thin-layer chromatography (TLC) were silica gel $GF_{254}$ (0.25 mm thickness) precoated on glass plates, and they were visualized under both long (365 nm) and short (254 nm) UV light. Flash column chromatography was performed on silica gel H (6~8 cm thickness). Tetra-*n*-butylammonium perchlorate (TBAP) was prepared by treatment of tetra-*n*-butylammonium bromide, and recrystallized three times from ethanol and dried under vacuum for 24 h. Ferrocenecarboxaldehyde,[40] resorcinarenes **1a–1c**,[32–34] *p-tert*-butylcalix[*n*]arenes[41] **1d–1f** ($n$=4, 6, 8), and ethyl calixarylacetate[35] **2d–2f** were prepared according to the published methods.

**3.1.2. Apparatus.** Melting points were taken on a hot-plate microscope apparatus and were uncorrected. $^1$H NMR spectra were recorded with a Bruker AV-600 spectrophotometer (600 MHz for $^1$H NMR). They were carried out at room temperature in deuterated trichloromethane solution unless otherwise stated. Chemical shifts are reported as parts per million (ppm) in $\delta$ units on the scale downfield from tetramethylsilane (TMS). $^1$H NMR data are reported in this order: chemical shift, multiplicity, numbers of proton, group of proton. IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). Elemental analysis was obtained on Perkin–Elmer 2400 SERIESII Instrument. X-ray data were collected on a Bruker Smart APEX-2 diffractometer. The cyclic voltammograms were recorded with a Shanghai ZhenHua CHI 660A recorder.

### 3.2. General procedure for the syntheses of 2a–2c

A suspension of **1a–1c** (3.0 mmol) and anhydrous potassium carbonate (8.28 g, 60 mmol), and potassium iodide (0.5 g, 3.0 mmol) in dry acetone (120 mL) was heated to reflux under nitrogen for at least 0.5 h. Then ethyl α-chloroacetate (5.3 mL, 50 mmol) was added. The reaction mixture was refluxed for 7 days. After removal of acetone, the residue was dissolved in water, acidified with hydrochloric acid, and then extracted with $CHCl_3$. The yellow organic layers were separated and dried with $MgSO_4$. Red oil was yielded after evaporation of the solvent, which was titrated with alcohol to give yellow products, and recrystallized from ethanol to give pure solid of **2a–2c**.

**3.2.1. Compound 2a.** White solid, 69.5%, mp 143–144 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 1760 (C=O). $^1$H NMR (600 MHz,

$CDCl_3$) $\delta$: 6.2–6.9 (m, 28H, ArH), 5.9 (s, 4H, CH), 4.25–4.30 (m, 16H, $OCH_2$), 4.1–4.2 (m, 16H, $CH_2$), 1.2–1.3 (m, 24H, $CH_3$). Anal. Calcd for $C_{84}H_{88}O_{24}$: C, 68.10; H, 5.99. Found: C, 68.25; H, 5.71.

**3.2.2. Compound 2b.** White solid, 56.5%, mp 151–153 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 1760 (C=O). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$: 6.2–6.6 (m, 24H, ArH), 5.9 (s, 4H, CH), 4.3–4.5 (m, 24H, $OCH_2$), 4.1–4.6 (m, 24H, $CH_2$), 1.2–1.3 (m, 36H, $CH_3$). Anal. Calcd for **2b**·2$CHCl_3$ ($C_{102}H_{114}O_{36}Cl_6$): C, 57.55; H, 5.40. Found: C, 57.27; H, 5.27.

**3.2.3. Compound 2c.** Yellow solid, 69.0%, mp 135 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 1758 (C=O). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$: 6.24 (s, 4H, ArH), 6.13 (s, 4H, ArH), 5.53 (s, 4H, ArCHAr), 4.23 (s, 16H, $OCH_2$), 4.05 (s, 8H, $C_5H_4$), 4.02 (s, 20H, Cp), 3.84 (s, 8H, $C_5H_4$), 1.29–1.30 (m, 16H, $CH_2$), 1.28–1.27 (m, 24H, $CH_3$). Anal. Calcd for **2c**·$H_2O$·$C_2H_5OH$ ($C_{102}H_{112}Fe_4O_{26}$): C, 61.96; H, 5.71; Found: C, 61.80; H, 5.69.

### 3.3. General procedure for the syntheses of 3a–3f

A mixture of ethyl resorcinarylacetates **2a**–**2c** or ethyl *p*-*tert*-butylcalixarylacetates **2d**–**2f** (0.50 mmol) and hydrated hydrazine (10 mL, 80%) in 15 mL of ethanol was refluxed for 24 h. After cooling to room temperature the resulting precipitate was collected by filtration and washed with absolute alcohol to give the white solid of **3a**–**3b**, **3d**–**3f** and yellow solid **3c**.

**3.3.1. Compound 3a.** White solid, 92.0%; mp >250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3397 (s), 1683 (vs), 1612 (s), 1503 (vs), 1438 (m), 1407 (m), 1299 (s), 1199 (s), 1161 (m), 1106 (s), 1061 (s), 930 (m), 709 (m). Anal. Calcd for $C_{68}H_{72}N_{16}O_{16}$: C, 56.64; H, 5.30; N, 16.37. Found: C, 57.10; H 5.52; N, 15.89.

**3.3.2. Compound 3b.** White solid, 85.0%; mp >250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3401 (s), 1680 (s), 1611 (s), 1508 (vs), 1438 (m), 1405 (m), 1296 (s), 1160 (m), 1103 (m), 1106 (s), 1030 (m), 927 (w), 827 (w). Anal. Calcd for $C_{76}H_{88}N_{24}O_{24}$: C, 53.02; H, 5.15; N, 19.53. Found: C, 52.75; H 5.38; N, 19.27.

**3.3.3. Compound 3c.** Yellow solid, 75.8%; mp 198 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 2405 (s), 1672 (vs), 1500 (vs), 1197 (s), 1060 (ms), 1145 (ms), 873 (w). Anal. Calcd for $C_{84}H_{88}Fe_4N_{16}O_{16}$: C, 56.02; H, 4.92; N, 12.44. Found: C, 56.23; H, 5.18; N, 12.65.

**3.3.4. Compound 3d.** White solid, 86.8%; mp 275 °C (decomp.). IR (KBr disc, $cm^{-1}$) $\nu$: 3316 (m), 3041 (m), 2957 (s), 2893 (m), 2858 (m), 1661 (vs), 1597 (m), 1470 (vs), 1351 (m), 1189 (s), 1111 (m). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$: 9.25 (s, 4H, NH), 6.86 (s, 8H, ArH), 4.46 (s, 8H, $OCH_2$), 4.30, 3.27 (d, d, $J$=6.4 Hz, 8H, $CH_2$), 1.08 (s, 36H, $C(CH_3)_3$). Anal. Calcd for $C_{52}H_{72}N_8O_8$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.75; H, 7.09; N, 12.23.

**3.3.5. Compound 3e.** White solid, 90.7%; mp 300 °C (decomp.). IR (KBr, $cm^{-1}$) $\nu$: 3316 (m), 3041 (m), 2950 (s), 2893 (m), 2858 (m), 1668 (vs), 1597 (m), 1470 (vs), 1351 (m), 1182 (s), 1104 (m). Anal. Calcd for $C_{78}H_{108}N_{12}O_{12}$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.27; H, 7.36; N, 12.37.

**3.3.6. Compound 3f.** White solid, 95.2%; mp 290 °C (decomp.). IR (KBr, $cm^{-1}$) $\nu$: 3316 (m), 3041 (m), 2957 (s), 2893 (m), 2858 (m), 1668 (vs), 1604 (m), 1470 (vs), 1280 (m), 1182 (s), 1104 (m). Anal. Calcd for $C_{104}H_{144}N_{16}O_{16}$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.81; H, 8.23; N, 11.73.

### 3.4. General procedure for the syntheses of 4a–4f

To a solution of calixaryl acylhydrazines **3a**–**3f** (0.1 mmol) in 5 mL of acetic acid was added dropwise ferrocenecarbaldehyde (1.1 mol for each hydrazine group) in 10 mL of ethanol in 10 min. Then the mixture was stirred under nitrogen at room temperature overnight. The precipitates were collected by filtration, washed with ethanol (until the filtrate was colorless), and dried in vacuum to give orange solid products **4a**–**4f**.

**3.4.1. Compound 4a.** Yellow-orange solid, yield: 89.7%; mp 250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3403 (m), 1686 (vs), 1609 (s), 1496 (s), 1439 (w), 1279 (m), 1189 (m), 1105 (m), 821 (m), 701 (m). $^1H$ NMR (600 MHz, DMSO-$d_6$) $\delta$: 8.10 (s, 8H, NH), 7.01 (s, 8H, CH=N), 5.97–6.34 (m, 28H, ArH), 5.75 (s, 4H, ArCHAr, CH), 4.55–4.63 (m, 16H, $CH_2$), 4.41–4.22 (m, 32H, $C_5H_4$), 4.15 (s, 40H, Cp). Anal. Calcd for $C_{156}H_{136}Fe_8N_{16}O_{16}$: C, 63.78; H, 4.67; N, 7.63. Found: C, 64.25; H, 4.79; N, 7.21.

**3.4.2. Compound 4b.** Yellow-orange solid, yield: 62.9%; mp >250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3401 (m), 1681 (vs), 1609 (s), 1507 (s), 1440 (w), 1253 (m), 1189 (m), 1105 (m), 824 (m). $^1H$ NMR (600 MHz, DMSO-$d_6$) $\delta$: 8.10 (s, 12H, NH), 6.97 (s, 12H, CH=N), 5.96–6.30 (m, 24H, ArH), 5.75 (s, 4H, ArCHAr, CH), 4.79–4.82 (m, 24H, $CH_2$), 4.30–4.40 (m, 48H, $C_5H_4$), 4.17 (s, 60H, Cp). Anal. Calcd for $C_{208}H_{184}Fe_{12}N_{24}O_{24}$: C, 61.32; H, 4.55; N, 8.25. Found: C, 61.27; H, 5.07; N, 8.57.

**3.4.3. Compound 4c.** Red-orange solid, yield: 79.0%; mp 209 °C (decomp.). IR (KBr disc, $cm^{-1}$) $\nu$: 3441 (s), 2918 (vs), 2549 (s), 1884 (vs), 1618 (m), 1487 (m), 1282 (m), 1105 (s), 1022 (w), 818 (w), 785 (m). $^1H$ NMR (600 MHz, DMSO-$d_6$) $\delta$: 7.97 (s, 8H, NH), 6.73 (s, 8H, CH=N), 6.54–6.60 (s, 8H, ArH), 5.83 (s, 4H, ArCHAr, CH), 4.54–4.62 (m, 16H, $CH_2$), 4.17–4.37 (m, 108H, $C_5H_4$). Anal. Calcd for $C_{172}H_{152}Fe_{12}N_{16}O_{16}$: C, 61.31; H, 4.54; N, 6.65. Found: C, 60.78; H, 4.83; N, 6.22.

**3.4.4. Compound 4d ($n$=4).** Yellow-orange solid, yield: 67.7%; mp >250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3441 (m), 2960 (s), 1689 (vs), 1628 (s), 1479 (s), 1244 (m), 1104 (m). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$: 8.48 (s, 4H, NH), 7.15 (s, 4H, CH=N), 6.43–6.57 (m, 8H, ArH), 4.78 (s, 8H, $C_5H_4$), 4.46 (s, 8H, $C_5H_4$), 4.23 (s, 20H, Cp), 4.15 (s, 8H, $OCH_2$), 3.45–3.49 (m, 8H, $ArCH_2Ar$, CH), 1.24 (s, 12H, $C(CH_3)_3$), 0.84 (s, 24H, $C(CH_3)_3$). Anal. Calcd for $C_{96}H_{104}Fe_4N_8O_8$: C, 66.99; H, 6.09; N, 6.51. Found: C, 66.63; H, 6.28; N, 6.39.

**3.4.5. Compound 4e ($n$=6).** Yellow-orange solid, yield: 69.0%; mp >250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3437 (m), 2960 (s), 1680 (vs), 1611 (s), 1470 (m), 1188 (m), 1107 (m). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$: 8.38 (s, 6H, NH), 7.17 (s, 6H, CH=N), 6.69–7.07 (m, 12H, ArH), 4.40–4.89 (m, 24H, $C_4H_5$), 4.21–4.28 (s, 30H, Cp), 3.98 (s, 12H, $OCH_2$), 3.79–3.86 (m, 12H, $ArCH_2Ar$, CH), 1.21–1.29 (m, 54H, $C(CH_3)_3$). Anal. Calcd for $C_{144}H_{156}Fe_6N_{12}O_{12}$: C, 66.99; H, 6.09; N, 6.51. Found: C, 66.67; H, 6.31; N, 6.31.

**3.4.6. Compound 4f ($n$=8).** Yellow-orange solid, yield: 74.4%; mp >250 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3412 (m), 2957 (s), 1689 (vs), 1621 (s), 1477 (s), 1181 (m), 1102 (m). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$: 8.35 (s, 8H, NH), 7.15 (s, 8H, CH=N), 6.69–7.07 (m, 16H, ArH), 4.44–4.73 (m, 32H, $C_4H_5$), 4.22–4.28 (s, 40H, Cp), 3.98 (s, 16H, $OCH_2$), 3.79–3.83 (m, 16H, $ArCH_2Ar$, CH), 1.22–1.31 (m, 72H, $C(CH_3)_3$). Anal. Calcd for $C_{192}H_{208}Fe_8N_{16}O_{16}$: C, 66.99; H, 6.09; N, 6.51. Found: C, 66.59; H, 6.55; N, 6.26.

### 3.5. General procedure for the syntheses of 5a and 5b

Calixaryl acylhydrazine **3a** or **3c** (0.1 mmol), an excess of acetoacetone (3.0 mL), and a little *p*-toluenesulfonic acid were added as catalysts in 30 mL of anhydrous THF. The mixture was heated under reflux for 72 h under nitrogen. The solvent was removed under reduced pressure, and the residue was dissolved in 3 mL of $CHCl_3$ and filtered, and powder was collected when 3 mL of ethanol was added into the above yellow $CHCl_3$ solution. Recrystallization from ethanol gave pure white solid for **5a** or yellow solid for **5b**.

**3.5.1. Compound 5a (R=H).** White solid, yield: 40.0%; mp 143–145 °C. IR (KBr disc, $cm^{-1}$) $\nu$: 3477 (w), 3414 (w), 1747 (vs), 1614 (w), 1585 (m), 1495 (m), 1438 (m), 1401 (s), 1328 (m), 1298 (m), 1161 (m), 1255 (m), 960 (s), 807 (m). $^1H$ NMR ($CDCl_3$) $\delta$: 6.98 (s, 8H, ArH), 6.88 (s, 4H, ArH), 6.79 (s, 8H, ArH), 6.40–6.54 (m, 8H, ArH), 6.16 (s, 4H, CH), 5.84–5.88 (m, 8H, CH), 5.11–5.36 (m, 16H, $OCH_2$), 2.43 (s, 24H, $CH_3$), 2.09–2.18 (m, 24H, $CH_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$: 13.5, 13.8, 69.5, 110.6, 125.2, 126.7, 128.3, 129.0, 129.1, 129.2, 132.4, 142.3, 144.0, 144.1, 152.1, 152.3, 154.7, 154.9, 168.4. Anal. Calcd for $C_{108}H_{104}N_{16}O_{16}$: C, 68.92; H, 5.57; N, 11.90. Found: C, 68.55; H, 5.83; N, 12.28.

**3.5.2. Compound 5b (R=Fc).** Yellow solid, yield: 35.0%; mp 188–189 °C (decomp.). IR (KBr disc, $cm^{-1}$) $\nu$: 3441 (w), 3133 (w), 2956 (m), 1746 (s), 1629 (s), 1496 (m), 1400 (vs), 1328 (s), 1255 (m), 1151 (m), 1106 (m), 962 (s), 803 (m). $^1H$ NMR ($CDCl_3$) $\delta$: 6.82 (s, 8H, ArH), 6.38 (s, 4H, CH), 5.73–5.83 (m, 8H, CH), 5.24 (s, 16H, $OCH_2$), 4.01–4.23 (m, 36H, Cp), 2.35 (s, 24H, $CH_3$), 2.05 (s, 24H,

**Table 2**. Crystal data and structure refinement details of **2a**–**2c** and **4d**

| | **2a** | **2b** | **2c** | **4d** |
|---|---|---|---|---|
| Empirical formula | $C_{84}H_{88}O_{24}$ | $C_{100}H_{112}O_{36}\cdot 2CHCl_3$ | $C_{102}H_{112}Fe_4O_{26}$ | $C_{56}H_{81}N_8O_{10}$ |
| Formula weight | 1481.54 | 2086.87 | 1977.32 | 1026.29 |
| Temperature (K) | 293(2) | 173(2) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71070 | 0.71073 | 0.71073 |
| Crystal system, space group | Triclinic, *P*-1 | Triclinic, *P*-1 | Monoclinic, $P2_1/n$ | Monoclinic, $P2(1)/c$ |
| Unit cell dimensions | $a$=12.160(0) Å, $\alpha$=78.470°, $b$=17.530(0) Å, $\beta$=77.630°, $c$=19.260(0) Å, $\gamma$=79.790° | $a$=11.0389(7) Å, $\alpha$=64.406(13)°, $b$=17.1440(6) Å, $\beta$=73.919(16)°, $c$=17.4008(6) Å, $\gamma$=71.743(16)° | $a$=13.9751(3) Å, $\alpha$=90°, $b$=27.7708(6) Å, $\beta$=100.4270(10)°, $c$=25.4590(5) Å, $\gamma$=90° | $a$=23.742(5) Å, $\alpha$=90°, $b$=13.266(3) Å, $\beta$=97.639°, $c$=20.975(4) Å, $\gamma$=90° |
| Volume ($Å^3$) | 3890.4 | 2781.6(2) | 9717.5(4) | 6080(2) |
| $Z$ | 2 | 1 | 4 | 4 |
| Calculated density ($g\,cm^{-3}$) | 1.265 | 1.246 | 1.352 | 1.121 |
| Absorption coefficient ($mm^{-1}$) | 0.093 | 0.229 | 0.661 | 0.077 |
| $F$(000) | 1568 | 1039 | 4144 | 2212 |
| Crystal size (mm) | 0.2×0.2×0.3 | 0.1×0.27×0.3 | 0.2×0.2×0.3 | 0.20×0.20×0.20 |
| $\theta$ Range for data collection | 1.10–24.99 | 3.02–25.35 | 1.68–25.00 | 1.80–25.98 |
| *hkl* Ranges | 0 to 14, −20 to 20, −20 to 22 | −12 to 13, −20 to 20, −20 to 18 | −14 to 16, −33 to 27, −30 to 30 | −26 to 29, −16 to 0, −25 to 0 |
| Reflections collected/ unique | 14,311/13,638 [$R$(int)=0.0345] | 27,350/10,121 [$R$(int)=0.0977] | 61,173/17,064 [$R$(int)=0.0809] | 12,250/11,907 [$R$(int)=0.0659] |
| Completeness to $\theta$=27.50 | 99.5% | 99.5% | 99.7% | 99.7% |
| Absorption correction | None | None | None | None |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/ parameters | 13,638/0/974 | 10,121/6/667 | 17,064/56/1188 | 11,907/26/685 |
| Goodness-of-fit on $F^2$ | 1.014 | 1.247 | 0.992 | 0.885 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$=0.0957, $wR_2$=0.2719 | $R_1$=0.1579, $wR_2$=0.3788 | $R_1$=0.0703, $wR_2$=0.1788 | $R_1$=0.0886, $wR_2$=0.2301 |
| $R$ indices (all data) | $R_1$=0.2252, $wR_2$=0.3585 | $R_1$=0.2362, $wR_2$=0.4298 | $R_1$=0.1507, $wR_2$=0.2328 | $R_1$=0.3078, $wR_2$=0.3269 |
| Largest diff. peak and hole ($eÅ^{-3}$) | 0.738 and −0.421 | 1.710 and −0.770 | 0.730 and −0.486 | 0.446 and −0.445 |

Weighting scheme: $w=1/[\sigma^2(F_o^2)+(0.1660P)^2+0.0000P]$, where $P=(F_o^2+2F_c^2)/3'$.

$CH_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$: 13.5, 13.8, 68.1, 68.3, 68.6, 68.7, 68.9, 69.0, 69.1, 69.2, 110.3, 144.0, 151.9, 168.4. Anal. Calcd for $C_{124}H_{120}Fe_4N_{16}O_{16}$: C, 64.37; H, 5.23; N, 9.69. Found: C, 64.58; H, 5.65; N, 9.41.

### 3.6. Electrochemical analysis

$E_{1/2}(E_{pa})$ versus $Fc^+$/Fc was estimated by cyclic voltammetric method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode; the solution (0.5 mM) was dissolved in $CH_2Cl_2$ using 0.1 M $Bu_4NClO_4$ (TBAP) as a supporting electrolyte with a scan rate of 50 mV $s^{-1}$ and all the potentials were calibrated and referenced with ferrocene ($E_{1/2}$ ($Fc/Fc^+$)=0.49 V vs SCE) as an internal standard.

### 3.7. X-ray structure determination

The procedure of crystal structure determination for both **2a**–**2c** and **4d** was the same. X-ray data were collected at 293(2) K on a Bruker diffractometer using Mo K$\alpha$ X-ray (0.71069 Å) source and a graphite monochromator. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25° reflections. Psi scan absorption corrections were applied. The structures were solved by direct methods using CRYSTAL STRUCTURE and refined by full-matrix least square method using SHELXL97. In the final step of refinement procedure, all non-hydrogen atoms were refined with anisotropic displacement parameters. A summary of crystallographic relevant data is given in Table 2.

### 3.8. Supplementary material

Single crystal X-ray diffraction data are deposited at CCDC (deposition numbers **2a**: 622100; **2b**: 622101; **2c**: 622102; **4d**: 622103).

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