

## Synthesis of Schiff Base Calix[4]arene Crowns

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**Abstract:** This letter reports the synthesis of Schiff base calix[4]arene crowns containing *m*-xylylene phenol subunit, in which calix[4]arene Schiff base crowns **2a**, **2b** and **2c** were formed by 1:1 condensation of calix[4]arene diamine **1** with dialdehydes (2, 6-diformyl-4-chlorophenol **3a**, 2, 6-diformyl-4-methylphenol **3b**, 2, 6-diformyl-4-*tert*-butylphenol **3c**) under high dilute condition in refluxing anhydrous ethanol in 65-70% yield.

**Keywords:** Calix[4]arene, Schiff base, 2, 6-diformyl-4-substituted phenol, 1:1 condensation.

Calixcrowns are a novel class of host compounds which have attracted increasing attention because of their much increased ability and selectivity for catching cations than crowns or calixarenes<sup>1</sup>. However, the studies of Schiff base calixcrowns are relatively rare. Recently, Huang Z.T. *et al*<sup>2-3</sup> reported the synthesis of three Schiff base calixcrowns by the condensation of calix[4]arene diamine **1** with dialdehydes. In their work, the 2:2 Schiff base condensation products were obtained. Here we wish to report the synthesis of 1:1 Schiff base calix[4]arene crowns containing *m*-xylylene phenol subunit, in which pale-yellow solids **2a**, **2b** and **2c** were obtained by the condensation of calix[4]arene diamine **1** and 2, 6-diformyl-4-substituted phenols (molar ratio 1:1) (**Scheme 1**). The general procedure is that a solution of dialdehyde (0.27 mmol) in anhydrous EtOH (100 mL) was added dropwise into the refluxing anhydrous EtOH solution (100 mL) of the calix[4]arene diamine **1** (0.27 mmol) and the mixture was kept at reflux for 10 h. The purification of the products was carried out by recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH. Yield: **2a**, 62.5 %; **2b**, 60.1 %; **2c**, 59.7 %, mp: **2a**, 264-266°C; **2b**, 238-240°C; **2c**, 250-252°C, respectively. The experimental results of solvent extraction have indicated that the novel Schiff bases calix[4]arene crowns have strong ability to complex Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup> cations.

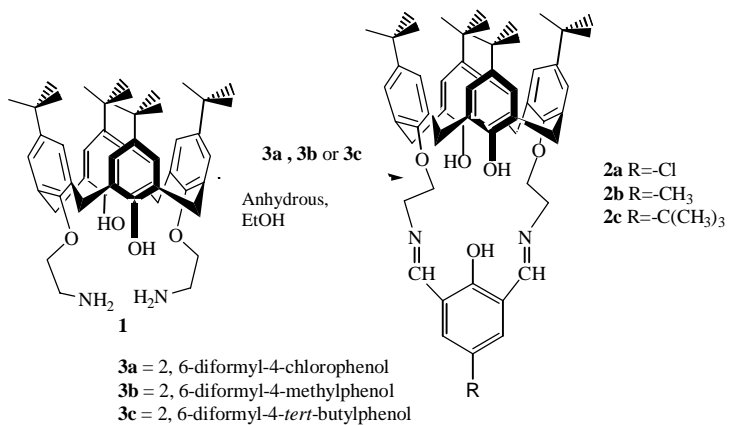
The structures of Schiff bases calix[4]arene crowns are confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, ESIMS, IR and elemental analysis. The <sup>1</sup>H NMR singlet around 8.5 ppm and the IR absorption peaks at 1640 cm<sup>-1</sup> indicate the formation of carbon-nitrogen double bond of Schiff base. In the ESIMS spectra, the *m/z* values of [M+H]<sup>+</sup> are 883.8 (calcd. 883.5), 863.6 (calcd. 863.5) and 905.7 (calcd. 905.6) for **2a**, **2b** and **2c**, respectively. It is clear that compounds **2a**, **2b** and **2c** are 1:1 Schiff base condensation products rather

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than 2:2 analogues.

**Scheme 1** Synthesis of Schiff bases calix[4]arene crowns



## References

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