

Full Paper

## Syntheses of Calix[4]Pyrroles by Amberlyst-15 Catalyzed Cyclocondensations of Pyrrole with Selected Ketones

Shive Murat Singh Chauhan\*, Bhaskar Garg and Tanuja Bisht

Bioorganic Research Laboratory, Department of Chemistry, University of Delhi, Delhi-110007, India;  
Fax : (+91)-11-27666845

\* Author to whom correspondence should be addressed. E-mail: smschauhan@chemistry.du.ac.in

Received: 1 October 2007; in revised form: 1 November 2007 / Accepted: 1 November 2007 /  
Published: 9 November 2007

---

**Abstract:** A facile and efficient protocol is reported for the synthesis of calix[4]pyrroles and *N*-confused calix[4]pyrroles in moderate to excellent yields by reaction of dialkyl or cycloalkyl ketones with pyrrole catalyzed by reusable Amberlyst™-15 under eco-friendly conditions.

**Keywords:** Calix[4]pyrrole; *N*-confused calix[4]pyrrole; Amberlyst™-15; Catalysis.

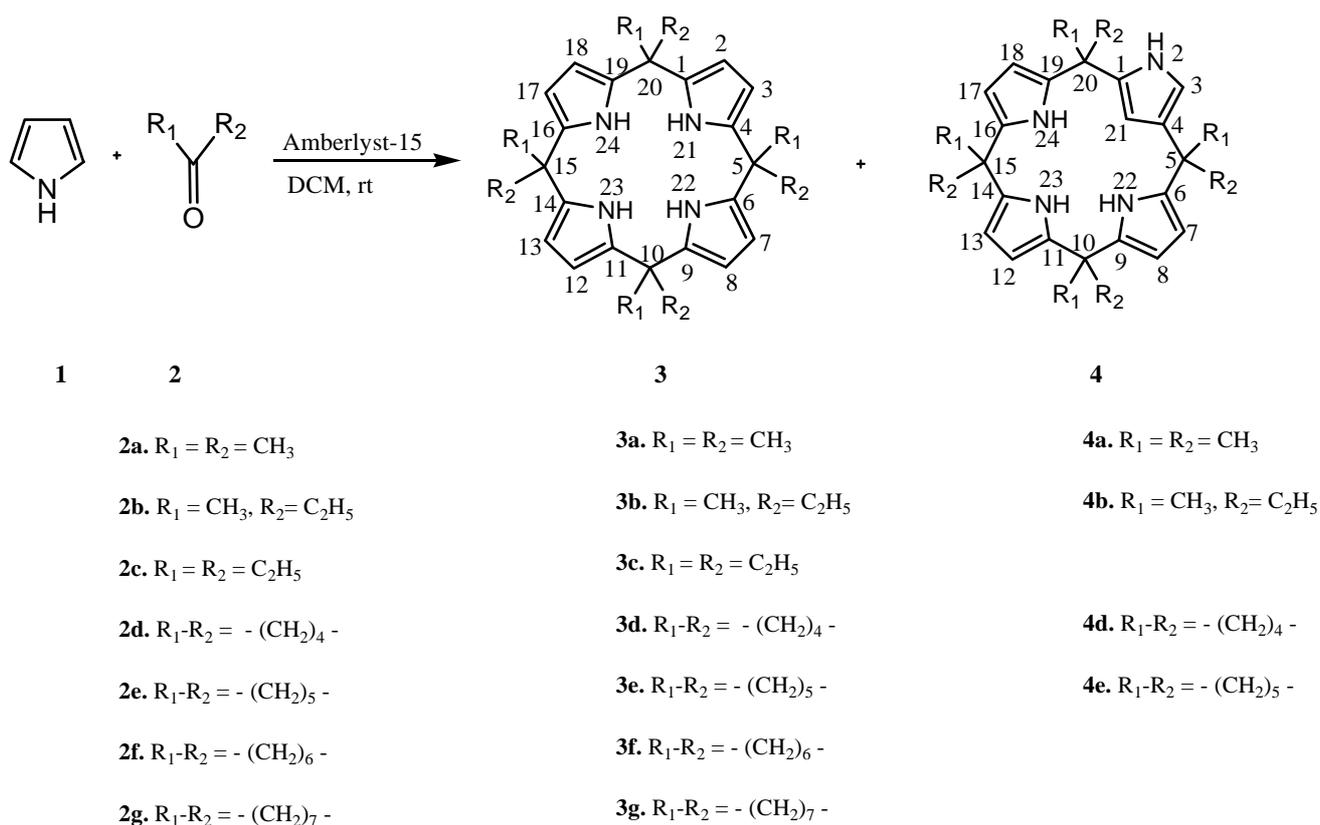
---

### Introduction

The design and synthesis of receptors to recognize, sense and bind the anions is an important area of supramolecular chemistry [1-5]. Calix[4]pyrroles are conformationally flexible macrocycles [6,7] of significant importance due to their binding under different conditions with anions [8], neutral substrates [9] and metal ions [10]. The complexation behavior of calix[4]pyrroles with anions and cations has been widely studied using fluorescent [11], colorimetric [12] and electrochemical signaling [13] devices. They find interesting applications as raw materials for transformation into novel calix[4]pyridines and calix[4]pyridinopyrroles [14], as new solid supports capable of separating anion mixtures [15], in optical recognition of organic vapors [16] and as biologically active species [17]. Porphyrinogens, bearing hydrogen atoms at meso positions, are key intermediates in biological and chemical synthesis of porphyrins [18,19]. Various attempts have been made for the development of

milder methods for the synthesis of porphyrins [20-22], N-C isomerization [23, 24] and higher homologues of porphyrins [25]. The meso-octamethylcalix[4]pyrrole **3a** has been prepared by condensation of pyrrole with acetone in the presence of aqueous hydrochloric acid or methanesulfonic acid in methanol [26, 27]. The reaction of pyrrole and acetone in the presence of trifluoroacetic acid in ethanol gave meso-octamethylcalix[4]pyrrole (**3a**) and the *N*-confused octamethylcalix[4]pyrrole (**4b**) [28]. The reactions of pyrrole with dialkyl ketones in the presence of protic acids (HCl, H<sub>2</sub>SO<sub>4</sub>), organic acids (CH<sub>3</sub>SO<sub>3</sub>H) and Lewis acids (BBr<sub>3</sub> and BF<sub>3</sub>) have also been used in the synthesis of calix[4]pyrroles [29-33]. The reaction of excess of pyrrole with dialkylketones in the presence of acid gave 5,5-dialkyldipyrromethanes which on subsequent reaction with dialkylketones in the presence of borontrifluoride-etherate formed strapped calix[4]pyrroles [34, 35]. These acids are considered hazardous and corrosive and their removal from the reaction mixtures is difficult. Recently, condensations in dichloromethane of pyrrole with dialkyl ketones in the presence of the molecular sieve Al-MCM-41 and the zeolite HY afforded dipyrromethane, calix[4]pyrroles and other linear products, but not the *N*-confused calix[4]pyrroles [36, 37].

Scheme 1.



Amberlyst<sup>TM</sup>-15 is an inexpensive and non-hazardous solid acid, useful as a catalyst. It can be easily handled and is removed from reaction mixtures by simple filtration. In recent years Amberlyst<sup>TM</sup>-15 has been explored as a powerful catalyst for various organic transformations [38]. The reaction of pyrrole with different aldehydes in dichloromethane in the presence of Amberlyst<sup>TM</sup>-15 gave dipyrromethanes, which in the presence of excess aldehydes followed by oxidation with chloronil [39] or DDQ [40] gave 5,10,15,20-tetraaryl porphyrins, whereas the reaction of pyrrole with aldehydes

in the absence of solvent followed by oxidation with DDQ gave 5,10,15-triarylcorroles [40]. Herein we report an eco-friendly synthesis of calix[4]pyrroles and related products under mild reaction conditions by the reaction between ketones and pyrrole catalyzed by Amberlyst™-15.

## Results and Discussion

The reaction in dichloromethane of pyrrole (**1**) with acetone for 8 hrs in the presence of Amberlyst™-15 (10 %, w/w) gave the calix[4]pyrrole **3a** and the *N*-confused calix[4]pyrrole **4a** in 83 and 14 % yield, respectively (Scheme 1, Table 1). On the other hand, an Amberlite™ IR-120 catalyzed reaction of pyrrole with acetone afforded **3a** and **4a** in poorer yields (61.3 and 3.7 %). The same reaction was examined using different solvents and the best yields were obtained in dichloromethane (Table 1).

**Table 1:** Amberlyst™-15 catalyzed condensation of pyrrole and acetone in different solvents <sup>a</sup>.

Entry	Solvent	Isolated yield of <b>3a</b> (%)	Isolated yield of <b>4a</b> (%)
1	EtOH (MeOH) [41]	75, (65 [28], 65 [41])	10, (26 [28], 15 [41])
2	CHCl <sub>3</sub>	65	8.6
3	C <sub>6</sub> H <sub>6</sub>	40	-
4	EtOAc	43	-
5	THF	60	-
6	DMF	33	-
7	Toluene	41	-
8	DCM	83, 77, 69 <sup>b</sup> , (70.3 [36])	14, 10, 5.8 <sup>b</sup> (0 [36])

<sup>a</sup> Reaction conditions: pyrrole (7.2 mmol) and acetone (7.2 mmol); solvent (10 mL); Amberlyst™-15 dried (10%, w/w); r.t.; 8 hrs; <sup>b</sup> Catalyst was reused over three runs.

This high yield formation of **3a** and **4a** in the presence of Amberlyst™-15 prompted us to examine the reaction in dichloromethane of other ketones **3b-3g** with pyrrole. The reaction products, yields and physical data are given in Table 2.

**Table 2:** Reaction of different ketones (**2a-2g**) with pyrrole in DCM, catalyzed by Amberlyst™-15.

Entry	<b>2</b>	Catalyst <sup>a</sup>	Time (h)	% Conversion of pyrrole	% yield <sup>b</sup> /mp °C (lit. mp °C, [ref.])	
					<b>3</b>	<b>4</b>
1	<b>2a</b>	Amberlyst™-15	8	99.0	83.0/295 (296 [27])	14.0/ 185 (184 -185 [41])
2	<b>2a</b>	Amberlite-IR-120	12	65.6	61.3/295 (296 [27])	3.7/185 (184 -185 [41])
3	<b>2b</b>	Amberlyst™-15	10	87.0	78.0/144 (146 [42])	9.0/121
4	<b>2c</b>	Amberlyst™-15	48 (32) <sup>c</sup>	72.0	68.3 (71.1) <sup>c</sup> /222 (-)	-
5	<b>2d</b>	Amberlyst™-15	8	96.7	79.7 /235 (236 [42])	13.5 /198
6	<b>2e</b>	Amberlyst™-15	8	98.5	83.5 (53.0 [43])/273 (271-272 [43])	11.3 (5.0 [43])/224 (223.2-223.6 [43])
7	<b>2f</b>	Amberlyst™-15	60 (55) <sup>c</sup>	33.0	30.2 (46.0) <sup>c</sup> /163 (-)	-
8	<b>2g</b>	Amberlyst™-15	72 (64) <sup>c</sup>	24.9	19.7 (40.0) <sup>c</sup> /223 (-)	-

<sup>a</sup> Amberlyst™-15, Amberlite™-IR-120 were dried before use; <sup>b</sup> Isolated yields; <sup>c</sup> Under reflux conditions in absolute ethanol

### Product Characterization

A strong N-H stretching peak appeared at  $3450\text{ cm}^{-1}$  in the IR spectra of calix[4]pyrrole **3a** in both  $\text{CHCl}_3$  solution and KBr pellets. In the  $^1\text{H-NMR}$  spectrum of **3a** a sharp singlet at  $\delta$  1.50 is assigned to the eight bridge methyl groups, a doublet at  $\delta$  5.89 ( $J = 2.5\text{ Hz}$ ) to the eight pyrrole ring  $\beta$ -protons and a broad peak at  $\delta$  7.01 was assigned to the four N-H protons. The ratio of the integrated peak areas are 6:2:1, in agreement with the empirical formula and  $D_4$  symmetry of **3a**. In the  $^1\text{H-NMR}$  spectrum of **4a** the appearance of a multiplet at  $\delta$  1.56-1.48 for the eight bridge methyl groups, signals at  $\delta$  6.30 and  $\delta$  5.50 corresponding to the  $\alpha$ - and  $\beta$ -pyrrole hydrogens (1H each) of the 2,4-disubstituted pyrrole, respectively, well apart from those of the 2,5-disubstituted pyrrole  $\beta$ -hydrogen atoms ( $\delta$  5.93-6.04, 6H) and three broad peaks at  $\delta$  7.75 (1H), 7.41 (1H) and 7.26 (2H) for four N-H protons indicate the reduction of symmetry as compared to **3a**. Indeed, the higher polarity and non-zero dipole moment of *N*-confused calix[4]pyrrole than calix[4]pyrrole have been attributed to this lower symmetry [50]. Calix[4]pyrrole **3a** and *N*-confused calix[4]pyrrole **4a** each gave a  $[\text{M-H}]^-$  ion peak at 427.2860 and 427.2868, respectively, along with a peaks at 462.7863 and 462.7859 for the  $[\text{M+Cl}]^-$  ion at 65V (cone voltage) in negative ion ESI-MS. A detailed ESI-MS study of these macrocycles has been reported recently [44]. The structures of calix[4]pyrroles **3a-3g** and *N*-confused calix[4]pyrroles **4a, 4b, 4d** and **4e** were all confirmed by their physical and spectroscopic data (Tables 2, 3 and 4).

In the reactions of **2a, 2d** and **2e** with pyrrole, a third isomer (1-4 %) was also observed, but due to small sample availability and poor solubility in organic solvents a detailed structural characterization was not possible [28]. The reactions of cycloheptanone (**2f**) and cyclooctanone (**2g**) with pyrrole gave the corresponding calix[4]pyrroles **3f** and **3g** in 30.2% and 19.7% yield at ambient temperature, but the time required for the conversions was considered too long. By refluxing the reaction mixtures, improved yields of 46.0 % (**3f**) and 40.0 % (**3g**) were obtained after shorter reaction times. In the reactions of pyrrole with **2c, 2f** and **2g**, the corresponding *N*-confused calix[4]pyrroles could not be isolated. This could be attributed to the steric hindrance encountered with these higher acyclic and cyclic ketones. The C-2 and C-5 atoms are more reactive than the C-3 and C-4 positions in pyrrole, hence the electrophilic reaction at C-2 and C-5 position of pyrrole with acetone in the presence of acid gave calix[4]pyrrole in preference to *N*-confused calix[4]pyrrole [28, 43]. The data presented in Tables 1 and 2 indicates that Amberlyst<sup>TM</sup>-15 is a more efficient and superior catalyst than other solid catalysts for the formation of calix[4]pyrroles in DCM [36]. The recovered catalyst was recycled twice with modest product yield loss being noted (Table 1). The catalytic activity of Amberlyst<sup>TM</sup>-15 is remarkable and it is environmentally benign. The ready commercial availability of this catalyst and its superiority over the existing methods should make the present protocol an attractive addition to the many conventional procedures.

### Conclusions

A facile and efficient method has been developed for preparing a variety of calix[4]pyrroles and *N*-confused calix[4]pyrroles in high yields by the reactions of various ketones with pyrrole in dichloromethane in the presence of a catalytic amount of Amberlyst<sup>TM</sup>-15.

**Table 3:** <sup>1</sup>H-NMR and mass spectra of meso-octaalkyl and cycloalkyl calix[4]pyrroles **3a-3g**.

Calix.	<sup>1</sup> H-NMR spectra (298 K, δ = ppm) <sup>a</sup>	HRMS (ESI-MS) <sup>b</sup>
<b>3a</b>	7.01 (4H, br s, NH), 5.89 (8H, d, <i>J</i> =2.5 Hz, β-pyrrole), 1.50 (24 H, s)	C <sub>28</sub> H <sub>36</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 427.2862, found : 427.2860.
<b>3b</b>	6.97 (4H, br s, NH), 5.80 (8H, d, <i>J</i> =2.5 Hz, β-pyrrole), 1.79-1.76 (8H, q, -CH <sub>2</sub> -), 1.45-1.18 (12H, br s, CH <sub>3</sub> ), 0.80-0.63 (12 H, t, CH <sub>3</sub> -)	C <sub>32</sub> H <sub>44</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 483.3487, found : 483.3480.
<b>3c</b>	7.05 (4H, br s, NH), 5.89 (8H, d, <i>J</i> =2.3 Hz, β-pyrrole), 1.79-1.57 (16H, q, -CH <sub>2</sub> -), 0.71-0.58 (24 H, t, CH <sub>3</sub> -)	C <sub>36</sub> H <sub>52</sub> N <sub>4</sub> [M-H] <sup>-</sup> ; calcd : 539.4113, found : 539.4120.
<b>3d</b>	7.03 (4H, br s, NH), 5.85 (8H, d, <i>J</i> =2.3 Hz, β-pyrrole), 2.21-2.00 (16H, m), 1.68-1.44 (16H, m)	C <sub>36</sub> H <sub>44</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 531.3488, found : 531.3486.
<b>3e</b>	7.25 (4H, br s, NH), 5.89 (8H, d, <i>J</i> =2.5 Hz, β-pyrrole), 1.91-1.90 (16H, m), 1.50-1.41 (24H, m),	C <sub>40</sub> H <sub>52</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 587.4114, found : 587.4112.
<b>3f</b>	6.88 (4H, br s, NH), 5.83 (8H, d, <i>J</i> =2.5 Hz, β-pyrrole), 2.01-1.94 (16H, m), 1.72-1.52 (32H, m)	C <sub>44</sub> H <sub>60</sub> N <sub>4</sub> [M-H] <sup>-</sup> Calcd: 643.4817, Found: 643.4810.
<b>3g</b>	6.99 (4H, br s, NH), 5.93 (8H, d, <i>J</i> =2.4 Hz, β-pyrrole), 1.97-1.95 (16H, m), 1.52-1.34 (32H, m), 1.23-1.21 (8H, m)	C <sub>48</sub> H <sub>68</sub> N <sub>4</sub> [M-H] <sup>-</sup> calcd : 699.5443, Found : 699.5456.

<sup>a</sup> The <sup>1</sup>H-NMR spectra of **3a-3g** were in agreement with literature data [36]; <sup>b</sup> The ESI-MS spectra were in agreement with literature data [44].

**Table 4:** <sup>1</sup>H-NMR and mass spectra of meso-octaalkyl and cycloalkyl *N*-confused calix[4]pyrroles **4a, 4b, 4d, 4e**.

Calix.	<sup>1</sup> H-NMR spectra (298 K, δ = ppm)	HRMS (ESI-MS)
<b>4a</b>	NH: 7.75 (1H, br), 7.41 (1H, br), 7.26 (2H, br); α-pyrrole: 6.30 (1H, d, <i>J</i> = 2 Hz), β-pyrrole: 6.04 (2H, br), 5.97 (2H, br), 5.93 (2H, m), 5.50 (1H, br); 1.56-1.48 (24H, m) <sup>a</sup>	C <sub>28</sub> H <sub>36</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 427.2862, found : 427.2868
<b>4b</b>	NH: 7.63 (1H, br), 7.53 (1H, br), 7.35 (2H, br); α-pyrrole: 6.40 (1H, d, <i>J</i> = 2 Hz) ; β-pyrrole: 6.03 (2H, br), 5.88 (2H, br), 5.78 (2H, m), 5.53 (1H, br); 1.92 (3H, s, -CH <sub>3</sub> ), 1.83-1.12 (29H, m)	C <sub>32</sub> H <sub>44</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 483.3487, found : 483.3482.
<b>4d</b>	NH: 7.48 (1H, br), 7.29 (1H, br), 7.00 (2H, br); α-pyrrole: 6.42 (1H, d, <i>J</i> =1.97 Hz); β-pyrrole: 6.00 (2H, br), 5.90 (2H, br), 5.88 (2H, m), 5.58 (1H, br); 2.25-1.98 (16H, m), 1.50-1.20 (16H, m)	C <sub>36</sub> H <sub>44</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 531.3488, found : 531.3480.
<b>4e</b>	NH: 7.63 (1H, br), 7.44 (1H, br), 7.10 (2H, br); α-pyrrole: 6.42 (1H, d, <i>J</i> = 1.98 Hz); β-pyrrole: 6.03 (2H, br), 5.97 (2H, br), 5.82 (2H, m), 5.50 (1H, br); 2.70-2.10 (16H, m), 1.60-1.20 (24H, m) <sup>a</sup>	C <sub>40</sub> H <sub>52</sub> N <sub>4</sub> [M-H] <sup>-</sup> : calcd : 587.4114, found : 587.4110.

<sup>a</sup> <sup>1</sup>H-NMR spectra of *N*-confused calix[4]pyrroles **4a** and **4e** are comparable to those reported in [43] and [28] respectively.

## Experimental

### General

The infrared spectra (IR) were recorded on Perkin Elmer FT-1710 spectrophotometer. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> with TMS as internal standard on a Bruker Avance 300 MHz spectrophotometer. ESI-MS spectra were recorded on KC ESI 455-TOF mass spectrometer (Micromass, Manchester, UK). The starting materials such as pyrrole, ketones, Amberlyst<sup>TM</sup>-15 and Amberlite<sup>TM</sup> IR-120 were obtained from Acros USA. Pyrrole and ketones were distilled immediately prior to use. The experimental operations were performed under ambient conditions. Neutral alumina was used for all the chromatographic purifications.

*Representative experimental procedure for the preparation of calix[4]pyrroles 3a-g and N-confused calix[4]pyrroles 4a-g: synthesis of meso-octamethylcalix[4]pyrrole (3a) and N-confused octamethyl calix[4]-pyrrole (4a)*

Equimolar amount of pyrrole (0.5 mL, 7.2 mmol) and acetone (0.52 mL, 7.2 mmol) were taken up in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). Dry Amberlyst<sup>TM</sup>-15 (10% w/w) was added to the reaction mixture, which was stirred at ambient temperature for the appropriate time (Table 2). The reaction progress was monitored by thin layer chromatography (TLC). After the completion of reaction, the catalyst was removed by filtration and washed thoroughly with CH<sub>2</sub>Cl<sub>2</sub> to dissolve all the contents. The filtrate was concentrated to give the crude product, which was subjected to column chromatography over neutral alumina eluting with petroleum ether-chloroform (9:1, v/v) to afford pure meso-octamethylcalix[4]pyrrole (**3a**). Further elution of the column with petroleum ether-chloroform (2:3, v/v) gave the N-confused isomer of octamethylcalix[4]pyrrole (**4a**). The above general method is used for the synthesis of different calix[4]pyrroles **3b-3g** and N-confused calix[4]pyrroles **4b, 4d** and **4e**.

## Acknowledgements

The authors are thankful to the Department of Science and Technology (Govt. of India) for project no. SR/S1/OC-54/2003 and the Council of Scientific and Industrial Research New Delhi for its financial assistance.

## References

1. Gale, P. A.; Sessler, J. L.; Král, V. Calixpyrroles. *Chem. Commun.* **1998**, 1-8.
2. Suksai, C.; Tuntulani, T.; Chromogenic anion sensors. *Chem. Soc. Rev.*, **2003**, 32, 192-202.
3. Stibor, I.; Zlatuskova, P.; Chiral recognition of anions. *Top. Curr. Chem.* **2005**, 255, 31-63.
4. Gale, P. A.; Quesada, R. Anion coordination and templated assembly: highlights from 2002-2004, *Coord. Chem. Rev.* **2006**, 250, 3219-3244.
5. Gale, P. A. Structural and molecular recognition studies with acyclic anion receptors. *Acc. Chem. Res.* **2006**, 39, 465-475.

6. Gale, P. A. Anion and ion-pair receptor chemistry: highlights from 2000 and 2001. *Coord. Chem. Rev.* **2003**, *240*, 191-221.
7. Sessler, J. L.; Camiolo, S.; Gale, P. A. Pyrrolic and polypyrrolic anion binding agents. *Coord. Chem. Rev.* **2003**, *240*, 17-55.
8. Gale, P. A.; Sessler, J. L.; Král, V.; Lynch, V. Calix[4]pyrroles: Old yet new anion-binding agents. *J. Am. Chem. Soc.* **1996**, *118*, 5140-5141.
9. Allen, W. E.; Gale, P. A.; Brown, C. T.; Lynch, V. M.; Sessler, J. L. Binding of neutral substrates by Calix[4]pyrroles. *J. Am. Chem. Soc.* **1996**, *118*, 12471-12472.
10. Bachmann, J.; Nocera, D. G. Multielectron redox chemistry of iron porphyrinogens *J. Am. Chem. Soc.* **2005**, *127*, 4730-4743.
11. Miyaji, H.; Anzenbacher P.; Sessler, J. L.; Bleasdale E. R.; Gale P. A. Anthracene-linked calix[4]pyrroles: fluorescent chemosensors for anions. *Chem. Commun.* **1999**, 1723-1724.
12. Gale, P. A.; Twyman, L. J.; Handlin, C. I.; Sessler, J. L. A colourimetric calix[4]pyrrole-4-nitrophenolate based anion sensor. *Chem. Commun.* **1999**, 1851-1852.
13. Gale, P. A.; Hursthouse, M. B.; Light, M. E.; Sessler, J. L.; Warriner, C. N.; Zimmerman, R. S. Ferrocene-substituted calix[4]pyrrole: a new electrochemical sensor for anions involving CH... anion hydrogen bonds. *Tetrahedron Lett.* **2001**, *42*, 6759-6762.
14. Král, V.; Gale, P. A.; Anzenbacher Jr. P.; Jursíková, K.; Lynch, V.; Sessler J. L.; Anzenbacher Jr. P. Calix[4]pyridine: a new arrival in the heterocalixarene family. *Chem. Commun.* **1998**, 9 – 10.
15. He, L. J.; Cai, Q. S.; Shao, S. J.; Jiang, S. X. Effect of calix[4]pyrrole as addition reagent on anion separation in capillary zone electrophoresis (CZE). *Chin. Chem. Lett.* **2001**, *12*, 511-512.
16. Conoci, S.; Palumbo, M.; Pignataro, B.; Rella, R.; Valli, L.; Vasapollo, G. Optical recognition of organic vapors through ultra thin calix[4]pyrrole films. *Colloid. Surf. A: Physicochem. Eng. Asp.* **2002**, *198-200*, 869-873.
17. Sessler, J. L.; Allen, W. E. Anion carriers: New tools for crossing membranes. *Chemtech* **1999**, *29*, 16-24.
18. Floriani, C. The porphyrinogen-porphyrin relationship: the discovery of artificial porphyrins. *Chem. Commun.* **1996**, 1257-1263.
19. Battersby, A. R.; Leeper, F. J. Biosynthesis of the pigments of life: mechanistic studies on the conversion of porphobilinogen to uroporphyrinogen III. *Chem. Rev.* **1990**, *90*, 1261-1274.
20. Chauhan, S. M. S.; Singh, R.; Gulati, A. Clay catalyzed synthesis of 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin and related compounds. *Ind. J. Heterocycl. Chem.* **2000**, *9*, 231-232.
21. Chauhan, S. M. S.; Sahoo, B. B.; Srinivas, K. A. Microwave assisted synthesis of 5,10,15,20-tetraarylporphyrins. *Synth. Commun.* **2001**, *31*, 33-37.
22. Ghosh, A. A perspective of one pot pyrrole-aldehyde condensation as versatile self-assembly processes. *Angew. Chem. Int. Ed.* **2004**, *43*, 1918-1931.
23. Maeda, H.; Furuta, H.; A dozen years of N-confused: from synthesis to supramolecular chemistry. *Pure Appl. Chem.* **2006**, *78*, 29-44.
24. Geier, G. R.; Haynes, D. M.; Lindsey, J. S. An efficient one-flask synthesis of N-confused tetraphenylporphyrin. *Org. Lett.* **1999**, *1*, 1455-1458.
25. Chandrashekar, T. K.; Venkatraman, S. Core-modified expanded porphyrins: new generation organic materials. *Acc. Chem. Res.* **2003**, *36*, 676-691.

26. Baeyer, A.; Ueber ein condensation product von Pyrrol mit Aceton. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 2184-2185.
27. Rothenmund, P.; Gage, C. L. Concerning the structure of acetonepyrrole. *J. Am. Chem. Soc.* **1955**, *77*, 3340-3341.
28. Depraetere, S.; Smet, M.; Dehaen, W. N-confused calix[4]pyrroles. *Angew. Chem. Int. Ed.* **1999**, *38*, 3359-3361.
29. Shao, S.; Wang, A.; Yang, M.; Jiang, S.; Xianda Yu. Synthesis of meso-aryl-substituted calix[4]pyrroles. *Synth. Commun.* **2001**, *31*, 1421-1426.
30. Chen, Q.; Wang, T.; Zhang, Y.; Wang, Q.; Ma, J. Doubly n-confused calix[4]pyrrole prepared by rational synthesis. *Synth. Commun.* **2002**, *32*, 1051-1058.
31. Wu, Y.; Wang, D.; Sessler, J. L.; Conformational features and anion binding properties of calix[4]pyrroles: A theoretical study. *J. Org. Chem.* **2001**, *66*, 3739-3746.
32. Anzenbacher Jr., P.; Jursíková, K.; Lynch, V. M.; Gale, P. A.; Sessler, J. L. Calix[4]pyrroles containing deep cavities and fixed walls. Synthesis, structural studies, and anion binding properties of the isomeric products derived from the condensation of p-hydroxyacetophenone and Pyrrole. *J. Am. Chem. Soc.* **1999**, *121*, 11020-11021.
33. Camiolo, S.; Gale, P. A. Fluoride recognition in super-extended cavity calix[4]pyrroles. *Chem. Commun.* **2000**, 1129 - 1130.
34. Miyaji, H.; Hong, S.; Jeong, D.; Yoon, D.; Na, H.; Hong, J.; Ham, S.; Sessler, J. L.; Lee, C. A binol-strapped Calix[4]pyrrole as a model chirogenic receptor for the enantioselective recognition of carboxylate anions. *Angew.Chem.Int.Ed.* **2007**, *46*, 2508-2511.
35. Jeong, S.; Yoo, J. Na, H.; Chi, D.; Lee, C. Strapped-calix[4]pyrroles bearing acridine moiety. *Supramolecular Chemistry* **2007**, *19*, 271-275.
36. Radha Kishan, M.; Srinivas, N.; Raghavan, K. V.; Kulkarni, S. J.; Sarma, J. A. R. P.; Vairamani, M. A novel, shape-selective, zeolite-catalyzed synthesis of calix[4]pyrroles. *Chem. Commun.* **2001**, 2226 - 2227.
37. Radha Kishan, M.; Radha Rani, V. ; Murty, M.R.V.S.; Sita Devi, P.; Kulkarni, S. J.; Raghavan, K.V. Synthesis of calixpyrroles and porphyrins over molecular sieve catalysts. *J. Mol. Cat. A.* **2004**, *223*, 263-267.
38. Harmer, M.A. Industrial processes using solid acid catalysts, in *Handbook of Green Chemistry and Technology*; Clark, J. H.; Macquarris, D. J.; eds.; Blackwell Publishers: London, **2002**; pp. 86-117.
39. Naik, R.; Joshi, P.; Kaiwar, S. P.; Deshpande, R. K. Facile synthesis of meso-substituted dipyrromethanes and porphyrins using cation exchange resins. *Tetrahedron*, **2003**, *59*, 2207-2213.
40. Kumari, P. *Synthesis of metallocorroles and their use in the oxidation of selected hydrocarbons*. Ph.D. Thesis, University of Delhi, **2007**; Chapter 2, pp. 55-104.
41. Nishibayyu, R.; Palacios, M. A.; Dehaen, W.; Anzenbacher, P. Jr. Synthesis, structure, anion binding and sensing by calix[4]pyrrole isomers. *J. Am. Chem. Soc.* **2006**, *128*, 11496-11504.
42. Dey, S.; Pal, K.; Sarkar, S. An efficient and eco-friendly protocol to synthesize calix[4]pyrroles. *Tetrahedron Lett.* **2006**, *47*, 5851-5854.
43. Anzenbacher Jr., P.; Nishibayyu, R.; Palacios, M. A. N-confused calix[4]pyrrole. *Coord. Chem. Rev.* **2006**, *250*, 2929-2938.

44. Bhaskar, G.; Prabhakar, S.; Ramanjaneyulu, G. S.; Vairamani, M.; Srinivasu, V. N. V.; Srinivas, K. Mass spectral studies of meso-dialkyl, alkyl aryl and cycloalkyl calix[4]pyrroles under positive and negative ion electrospray ionization conditions. *J. Mass Spectrom.* **2007**, *42*, 1194-1206.

*Sample Availability:* Limited samples of compounds **3a** and **3e** are available from the corresponding author.

© 2007 by MDPI (<http://www.mdpi.org>). Reproduction is permitted for noncommercial purposes.