

HETEROCYCLES, Vol. 85, No. 4, 2012, pp. 851 - 860. © 2012 The Japan Institute of Heterocyclic Chemistry  
Received, 8th January, 2012, Accepted, 1st March, 2012, Published online, 6th March, 2012  
DOI: 10.3987/COM-12-12423

## RECOVERABLE AND REUSABLE CATALYST FOR THE REACTION OF *N*-TOSYL IMINES WITH PYRROLE: SYNTHESIS OF *MESO*-TETRAARYLPORPHYRINS

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**Abstract** – The direct and efficient synthesis of *meso*-substituted porphyrins from the reaction of *N*-tosyl imines with pyrrole in the presence of environmentally friendly catalysts, Cu(OTf)<sub>2</sub> and Montmorillonite K-10 clay, is described. The advantages of the new method include mild reaction conditions and using environmentally friendly catalysts which can be recovered and reused after the reactions without any significant loss of catalytic activity.

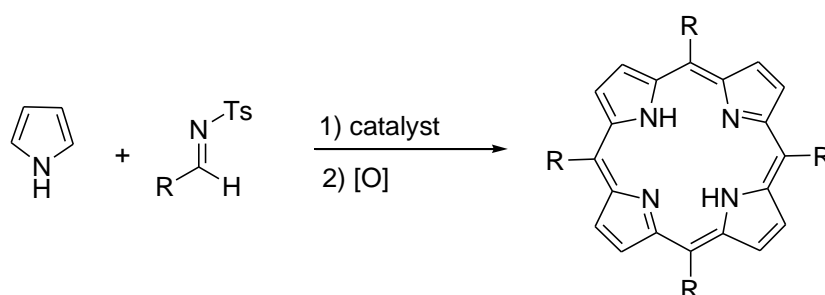
### INTRODUCTION

Porphyrins are an important class of macrocyclic aromatic compounds due to their wide range of biological properties and also applications in photodynamic therapy, catalysts, sensors and molecular electronic devices.<sup>1</sup> Variety of synthetic methods have been developed for non-natural porphyrins, especially for the tetra-*meso*-substituted porphyrins. The general method for the synthesis of this type of porphyrins depends on the reaction of pyrrole with aldehydes. This reaction was first developed by Rothmund in pyridine at 200 °C in a sealed-tube (~ 5% yield)<sup>2</sup> and then modified by Adler and Longo using propionic or acetic acid as solvent under aerobic conditions (10–30% yield).<sup>3</sup> Finally Lindsey optimized the reaction using two step procedure (i) BF<sub>3</sub> or TFA catalysed in situ formation of tetraarylporphyrinogen, (ii) oxidation of porphyrinogen to porphyrin by using DDQ (10–60% yield).<sup>4</sup> Although the condensation of pyrrole with aldehydes proves the most popular route at this time, considerable efforts have been devoted to develop alternative reagents such as Mannich reagents,<sup>5</sup> orthoesters<sup>6</sup> and catalysts including clays<sup>7</sup> and transition metal salts.<sup>8</sup>

When the catalysts used in porphyrin synthesis are considered, they have many drawbacks such as sensitivity to moisture, the use of stoichiometric or higher amounts of catalysts, the difficulty of

recovering and reusing catalysts. In the view of these drawbacks, we were motivated to investigate the development of a mild, convenient, and efficient method for the synthesis of *meso*-substituted porphyrins in the presence of environmentally friendly, recoverable and reusable catalysts.

In our recent work<sup>9a</sup> we found that the reaction of dipyrromethanes with *N*-tosyl imines affords A<sub>4</sub> and A<sub>2</sub>B<sub>2</sub> type porphyrins in the presence of Cu(OTf)<sub>2</sub>. In the light of this finding and our preliminary studies on the reaction of heteroaromatic compounds with *N*-tosyl imines,<sup>9</sup> we investigated the direct, one step synthesis of A<sub>4</sub> type *meso*-substituted porphyrins from the reaction of pyrrole with *N*-tosyl imines by using metal triflates and clays (Scheme 1), which have been widely applied in numerous organic reactions as green catalysts.<sup>10</sup>



Scheme 1

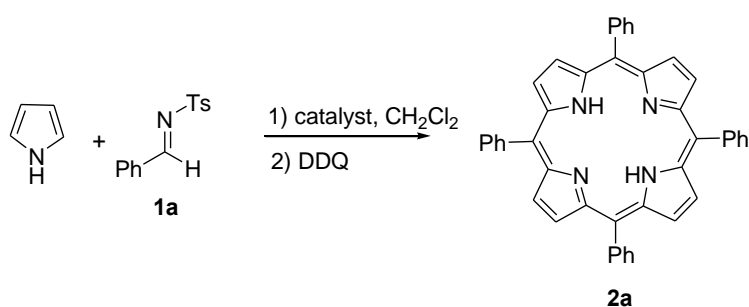
## RESULTS AND DISCUSSION

First, we examined the reaction of pyrrole with *N*-benzylidene-4-methylbenzenesulfonamide (**1a**) and applied different metal triflates, clays and other Lewis acids on the model reaction to compare their activities (Table 1). The reactions were monitored with TLC and 5,10,15,20-tetraphenylporphyrin (TPP) (**2a**) was purified by flash column chromatography after work-up. No reaction proceeded in the absence of catalyst (Table 1, entry 1). While Cu and Y- triflates catalysed the model reaction with 27 and 20% yield respectively (Table 1, entries 2 and 3), Gd and La-triflates did not give any product (Table 1, entries 4 and 5). Two clays, Montmorillonite K-10 and KSF, which are widely used in organic reactions, were tested and 18% yield of TPP (**2a**) was obtained only with Montmorillonite K-10 (Table 1, entries 6 and 7). KSF clay did not provide any product at all. This may due to the greater surface area (220-270 m<sup>2</sup>/g) of Montmorillonite K-10 than that of KSF clay (20-40 m<sup>2</sup>/g). Interestingly, common catalysts utilized in porphyrin synthesis such as TFA and BF<sub>3</sub>.OEt<sub>2</sub> were not effective (Table 1, entries 8 and 9). Only InCl<sub>3</sub> (18% yield) and FeCl<sub>3</sub> (16% yield) showed comparable catalytic activity with Y(OTf)<sub>3</sub> and Montmorillonite K-10.

Among the treated catalysts, efficient and environmentally friendly Cu(OTf)<sub>2</sub> and Montmorillonite K-10 were chosen to improve the reaction yield. The optimization reactions were carried out by using 10% mole of Cu(OTf)<sub>2</sub> and 1 gram of clay for 1 mmol of reactants. The effects of reactant concentrations are shown

in Table 2. The yield of porphyrin product increased by increasing the concentration of reagents up to 20 mM for both of the catalysts, Cu(OTf)<sub>2</sub> and Montmorillonite K-10. Further increasing the concentration caused decrease in porphyrin yield for triflate catalyst, while yields for clay catalyst remained constant.

Table 1. Effect of catalysts on the synthesis of TPP (**2a**)<sup>a</sup>



Entry	Catalyst	Yield <sup>b</sup>
1	-	-
2	Cu(OTf) <sub>2</sub>	27
3	Y(OTf) <sub>3</sub>	20
4	Gd(OTf) <sub>3</sub>	-
5	La(OTf) <sub>3</sub>	-
6	Mont. K-10 <sup>c</sup>	18
7	Mont. KSF <sup>c</sup>	-
8	TFA	-
9	BF <sub>3</sub> ·OEt <sub>2</sub>	-
10	InCl <sub>3</sub>	18
11	FeCl <sub>3</sub>	16
12	AlCl <sub>3</sub>	12
13	ZnCl <sub>2</sub>	-
14	TsOH	4

<sup>a</sup> Reaction conditions: (i) 20 mM of *N*-tosyl imine (**1a**) (1 mmol) and pyrrole (1 mmol), catalyst (10 mol %), rt, (ii) DDQ (1.5 mmol). <sup>b</sup> Yield refers to pure product after column chromatography. <sup>c</sup> 1.0 g of clay was used.

To illustrate the generality of the method, a range of *N*-tosyl imines (**1a-g**) were reacted with pyrrole in the presence of Cu(OTf)<sub>2</sub> and Montmorillonite K-10 under optimized reaction conditions. The results are shown in Table 3. Cu(OTf)<sub>2</sub>-catalysed reactions of *N*-tosyl imines with pyrrole gave higher yields than

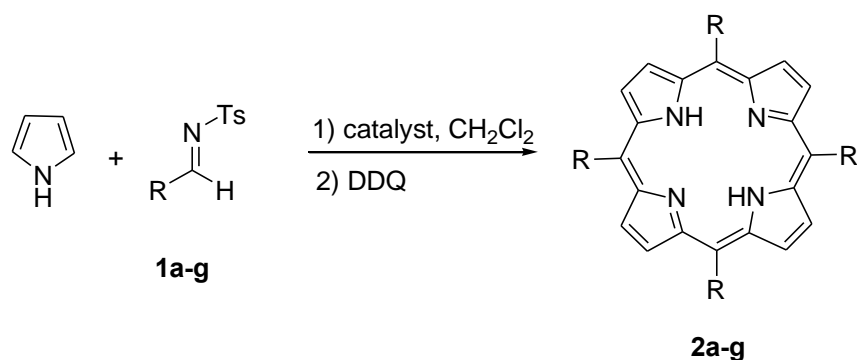
the corresponding Mont. K-10-catalysed reactions in all cases except **2d** and **2g** (Table 3, entries 7, 8, 15, 16). *Meso*-substituted porphyrin products (**2a-g**) were obtained in the range of 10-27% yields (Table 3).

Table 2. Effects of reagent concentrations in porphyrin synthesis

Concentration of Reagents (mM)	Yield of <b>2a</b> (%)	
	<u>Cu(OTf)<sub>2</sub></u>	<u>Mont. K-10</u>
1	1	-
2.5	4	3
5	11	10
10	21	15
20	27	18
40	17	18
80	9	17

In view of environmentally benign green catalyst methodologies, recovery and reuse of the catalyst is highly preferable. In this context, the recyclable character of two environmentally friendly catalysts, Cu(OTf)<sub>2</sub> and Mont. K-10 were investigated using the model reaction of **1a** with pyrrole. Cu(OTf)<sub>2</sub> was recovered in an almost quantitative amount after the work up procedure by evaporating the aqueous solution. The catalyst was dried in vacuum and reused in the next reaction. The same recovery procedure was applied in each step accordingly and the catalyst was subjected to further reaction. The results were illustrated in Table 4. Even after the fifth use, Cu(OTf)<sub>2</sub> showed almost same activity as first reaction and the catalyst was easily recovered (Table 4). The recovery of Montmorillonite K-10 catalyst was examined by filtration of catalyst and washing several times with chloroform and methanol. The catalyst was dried in vacuo. The colour of clay catalyst returned from white to black after the reaction due to oligomeric or polymeric pyrrole tar. As shown in Table 4, the clay catalyst was deactivated in the first reaction and gave no porphyrin product in the second use.

For better environmental and safety conditions, ethanol and ethanol-water mixtures were used as solvent, but very low (5% <) or no porphyrin product was obtained. Then we examined whether the oxidation step of the porphyrin synthesis could be carried out by using environmentally friendly oxidizing agents such as hydrogen peroxide, oxone and in open air reflux condition to use air as oxidant. But very low product was observed even after long reaction times (72 h).

Table 3. Cu(OTf)<sub>2</sub> and Montmorillonite K-10 catalysed reactions of *N*-tosyl imines with pyrrole<sup>a</sup>

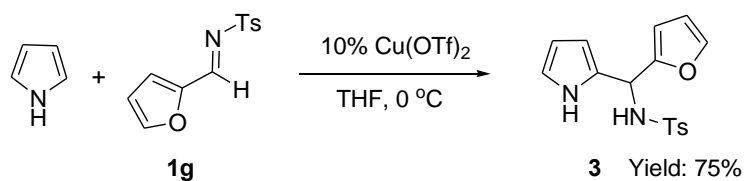
Entry	R	Product	Catalyst	Yield (%) <sup>b</sup>
1	<b>1a</b>	<b>2a</b>	Cu(OTf) <sub>2</sub>	27
2			Mont. K-10	18
3			Cu(OTf) <sub>2</sub>	25
4	<b>1b</b>	<b>2b</b>	Mont. K-10	22
5			Cu(OTf) <sub>2</sub>	23
6	<b>1c</b>	<b>2c</b>	Mont. K-10	20
7			Cu(OTf) <sub>2</sub>	21
8	<b>1d</b>	<b>2d</b>	Mont. K-10	24
9	<b>1e</b>	<b>2e</b>	Cu(OTf) <sub>2</sub>	25
10			Mont. K-10	20
11	<b>1f</b>	<b>2f</b>	Cu(OTf) <sub>2</sub>	22
12			Mont. K-10	17
15	<b>1g</b>	<b>2g</b>	Cu(OTf) <sub>2</sub>	10
16			Mont. K-10	18

<sup>a</sup> Reaction conditions: (i) 20 mM of *N*-tosyl imine (**1**) (1 mmol) and pyrrole (1 mmol), catalyst (10 mol % Cu(OTf)<sub>2</sub> or 1 gram of clay), rt, (ii) DDQ (1.5 mmol). <sup>b</sup> Yield refers to pure product after column chromatography.

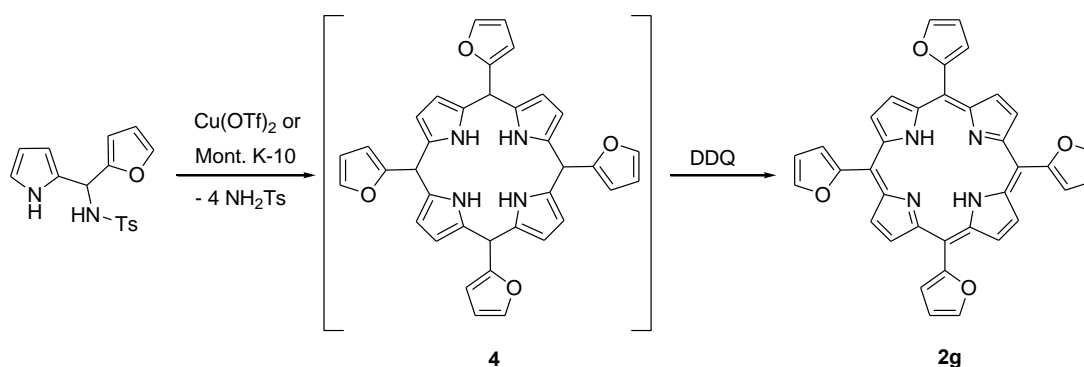
Table 4. Recycling of Cu(OTf)<sub>2</sub> and Mont. K-10 for the synthesis of TPP (**2a**)

Run	Yield of <b>2a</b> (%)	
	Cu(OTf) <sub>2</sub>	Mont. K-10
1	27	18
2	26	-
3	26	-
4	25	-
5	25	-

In order to understand the role of the catalyst in the porphyrin formation mechanism, we first synthesized the addition product **3** from the reaction of *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide **1g** with pyrrole in the presence of 10% mol of Cu(OTf)<sub>2</sub> at 0 °C (Scheme 2). The product was isolated in 75% yield and subjected to the porphyrin formation reaction without any catalyst. No porphyrin product was observed in the absence of catalyst even after 48 h. The reaction was repeated by using Cu(OTf)<sub>2</sub> and Mont. K-10 and desired porphyrin product **2g** was isolated as a sole product after the reactions. Pyrrole sulfonamide compound **3** was activated by catalyst and cyclization reaction gave porphyrinogen **4** which was oxidized by DDQ in the reaction medium to form *meso*-5,10,15,20-tetrakis(2-furyl)porphyrin **2g** (Scheme 3).



Scheme 2



Scheme 3

## CONCLUSION

In conclusion, we developed a new procedure for the preparation of *meso*-substituted tetraarylporphyrins through the reaction of *N*-tosyl imines with pyrrole in the presence of Cu(OTf)<sub>2</sub> and Montmorillonite K-10 catalysts. The main advantage of this method is that it replaces highly hazardous, corrosive and air sensitive catalysts with an environmentally friendly catalyst, Cu(OTf)<sub>2</sub>, that can be recovered and reused without any significant loss of activity. The method provides also an alternative route to the existing porphyrin synthesis methodologies with applicability of variety of porphyrins, reasonably good yields and mild reaction conditions.

## EXPERIMENTAL

**General remarks.** Commercially available reagents and solvents were used without further purification. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded using SiMe<sub>4</sub> as an internal reference with Bruker Ultrashield FT NMR spectrometer. Coupling constants are expressed as *J* values in hertz. Infrared spectra were taken by Unicam Mattson 1000 FTIR spectrophotometer. Reactions were monitored by thin layer chromatography using 60F silica gel plates. Flash column chromatography was performed on silica gel 60 F254 (230–400 mesh). The spots were visualized with UV light (λ 254 nm). Mass spectra were recorded on Agilent Technologies 6224 TOF LC/MS. *N*-Tosyl imines (**1a–g**) are synthesized in high yields by the reaction of *p*-toluenesulfonamide and aldehydes in the presence of *p*-toluenesulfonic acid.

**General procedure for the synthesis of *meso*-substituted porphyrins **2a–g**.** *N*-Tosyl imine (**1a–g**) (1 mmol) and catalyst (0.1 mmol of Cu(OTf)<sub>2</sub> or 1 gram of Montmorillonite K-10) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and stirred for 30 min at room temperature under nitrogen atmosphere. A solution of pyrrole (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added dropwise into the reaction mixture shielded from light with aluminium foil. After 2 h, DDQ (1.5 mmol) was added and the reaction mixture was further stirred for 2 h. Water (10 mL) was added to the mixture and aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL). The combined organic phases were dried over magnesium sulphate and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>.

**Cu(OTf)<sub>2</sub> recovery and reuse.** The recovery and reusability of Cu(OTf)<sub>2</sub> was investigated in the synthesis of 5,10,15,20-tetraphenylporphyrin (**2a**) by using pyrrole (10 mmol), *N*-benzylidene-4-methylbenzenesulfonamide (**1a**) (10 mmol) and Cu(OTf)<sub>2</sub> (1 mmol). After completion of the reaction, water (100 mL) was added to the mixture and aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x100 mL). Cu(OTf)<sub>2</sub> in the aqueous phase was concentrated under reduced pressure to give a crystalline residue,

which was dried at 150 °C for 6 h in vacuo. The recovered Cu(OTf)<sub>2</sub> was reused in another reaction.

**5,10,15,20-Tetraphenylporphyrin (2a)**<sup>11a,b</sup> Purple crystal; mp >300 °C; R<sub>f</sub> 0.95 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 416, 514, 548, 590, 646; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: -2.71 (bs, 2H, NH), 7.78-7.80 (m, 12H), 8.26 (d, *J* = 5.9, 8H), 8.89 (s, 8H); HRMS (APCI) calcd for C<sub>44</sub>H<sub>31</sub>N<sub>4</sub> (M+H)<sup>+</sup> 615.2543, found 615.2562.

**5,10,15,20-Tetrakis(4-fluorophenyl)porphyrin (2b)**<sup>11a</sup> Purple crystal; mp >300 °C; R<sub>f</sub> 0.56 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 416, 514, 548, 590, 646; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: -2.75 (bs, 2H), 7.45-7.59 (m, 8H), 8.16-8.21 (m, 8H), 8.90 (s, 8H); HRMS (APCI) calcd for C<sub>44</sub>H<sub>27</sub>F<sub>4</sub>N<sub>4</sub> (M+H)<sup>+</sup> 687.2166, found 687.2165.

**5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin (2c)**<sup>11a</sup> Purple crystal, mp >300 °C; R<sub>f</sub> 0.95 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 418, 514, 548, 590, 646; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ -2.83 (bs, 2H), 7.77 (d, *J* = 8.2, 8H), 8.16 (d, *J* = 8.2, 8H), 8.87 (s, 8H); HRMS (APCI) calcd for C<sub>44</sub>H<sub>27</sub>Cl<sub>4</sub>N<sub>4</sub> (M+H)<sup>+</sup> 751.0984, found 751.0978.

**5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (2d)**<sup>11b</sup> Purple crystal, mp >300 °C; R<sub>f</sub> 0.95 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 418, 514, 548, 590, 646; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ -2.85 (bs, 2H), 7.93 (d, *J* = 8.2, 8H), 8.09 (d, *J* = 8.2, 8H), 8.87 (s, 8H); HRMS (APCI) calcd for C<sub>44</sub>H<sub>27</sub>Br<sub>4</sub>N<sub>4</sub> (M+H)<sup>+</sup> 926. 8964, found 926.9021.

**5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (2e)**<sup>11a</sup> Purple crystal, mp >300 °C; R<sub>f</sub> 0.74 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 416, 512, 546, 588, 648; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ -2.72 (bs, 2H), 4.16 (s, 12H), 7.27-7.32 (m, 8H), 8.15 (d, *J* = 8.6, 8H), 8.89 (s, 8H); HRMS (APCI) calcd for C<sub>48</sub>H<sub>39</sub>N<sub>4</sub>O<sub>4</sub> (M+H)<sup>+</sup> 735.2966, found 735.2986.

**5,10,15,20-Tetrakis(4-methylphenyl)porphyrin (2f)**<sup>11a</sup> Purple crystal, mp >300 °C; R<sub>f</sub> 0.95 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 416, 514, 546, 590, 646; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ -2.73 (bs, 2H), 2.73 (s, 12H), 7.57 (d, *J* = 8.0, 8H), 8.12 (d, *J* = 8.0, 8H), 8.88 (s, 8H); HRMS (APCI) calcd for C<sub>48</sub>H<sub>39</sub>N<sub>4</sub> (M+H)<sup>+</sup> 671.3169, found 671.3178.

**5,10,15,20-Tetrakis(2-furyl)porphyrin (2g)**<sup>11c</sup> Purple crystal, mp >300 °C; R<sub>f</sub> 0.95 (CH<sub>2</sub>Cl<sub>2</sub>); UV-vis (λ<sub>max</sub> / CH<sub>2</sub>Cl<sub>2</sub>): 418, 514, 548, 590, 646; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ -2.68 (bs, 2H), 7.17-7.27 (m,

8H), 8.03 (s, 4H), 9.06 (s, 8H); HRMS (APCI) calcd for C<sub>36</sub>H<sub>23</sub>N<sub>4</sub>O<sub>4</sub> (M+H)<sup>+</sup> 575.1714, found 575.1716.

**Synthesis of *N*-(furan-2-yl(1*H*-pyrrol-2-yl)methyl)-4-methylbenzenesulfonamide (3)** A mixture of *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (**1g**) (2 mmol) and Cu(OTf)<sub>2</sub> (0.2 mmol) was stirred in 20 mL THF for 30 min. The mixture was cooled to 0 °C and a solution of pyrrole (2 mmol) in 10 mL of THF was added dropwise. The reaction was monitored by TLC and the reaction was completed in 6 h. The mixture was passed through a short column packed with silica gel by using EtOAc to remove the catalyst. The eluent was evaporated under reduced pressure and the crude product was purified by flash column chromatography.

***N*-(Furan-2-yl(1*H*-pyrrol-2-yl)methyl)-4-methylbenzenesulfonamide (3)** White solid; mp 113–114 °C; IR (KBr): 3492, 2975, 2923, 1142, 788, 560 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.32 (s, 3H), 5.38 (d, *J* = 8.0, 1H), 5.56 (d, *J* = 8.0, 1H), 5.70 (s, 1H), 5.93 (s, 1H), 6.10 (s, 1H), 7.08–7.11 (m, 3H), 7.70 (d, *J* = 8.2, 2H), 8.59 (bs, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 20.4, 48.6, 106.6, 106.9, 107.2, 109.1, 117.6, 126.0, 128.3, 128.5, 136.2, 141.2, 141.9, 150.0; HRMS (APCI) calcd for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S (M-H)<sup>-</sup> 315.0809, found 315.0814.

## ACKNOWLEDGEMENTS

Financial support from Hacettepe University (BAP Project 010D05601004 and BAP Project 07A601004) is gratefully acknowledged.

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