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# Green synthesis of dipyrromethanes in aqueous media catalyzed by $SO_3H$-functionalized ionic liquid†

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A mild, efficient and metal-free method was described for the green synthesis of dipyrromethanes from aldehydes and unsubstituted pyrrole catalyzed by $SO_3H$-functionalized ionic liquids ($SO_3H$-ILs) in aqueous media at room temperature. Notably, $SO_3H$-ILs, 1-butylsulfonic-3-methylimidazolium hydrogen sulfate ([bsmim][$HSO_4$]) was the most efficient catalyst for moderate to good yields of the corresponding desired products.

## Introduction

Dipyrromethanes are important precursors for porphyrin syntheses,[1,2] particularly for the preparation of asymmetric polypyrrolic compounds, and are used in a wide range of applications in materials science, medicine and optics.[1–4] Furthermore, dipyrromethanes are the structural skeletons of some critical biological compounds,[5] especially prodigiosin and heme analogues (Fig. 1). Recently, dipyrromethanes and their derivatives have shown promising biological activity as anti-inflammatory agents.[6]

Generally, dipyrromethanes are synthesized by the condensation of aldehydes with pyrroles *via* double Friedel–Crafts reaction.[1a–f,2,7] Imines[8] and 1,3-oxazinanes[9] are used alternatively as carbonyl equivalents to react with pyrroles. Most of the methods require metal catalysts as well as strong acid catalysts for stimulating the reactions such as $TiCl_4$,[1d] cation exchange resin,[1e] trifluoroacetic acid (TFA),[1f,j,2,4a,7e–f,9] HCl/$H_2O$,[7a,h] ionic liquid,[7i] $InCl_3$,[7j] iodine,[7k] $H_2SO_4$–$SiO_2$,[7l] Amberlyst 15,[7m] and metal triflates[8] (Scheme 1).

High yields of desirable products have been achieved under conditions that include substituted pyrrole,[7i–j] excess pyrrole[1e,j,7e] and/or harsh conditions.[7h,k,m] Unsubstituted pyrrole reduces yield due to instability of intermediates and desirable products and easily generates oligomeric by-products. However, due to the versatile applications of these dipyrromethane derivatives derived from unsubstituted pyrrole,[2–4]

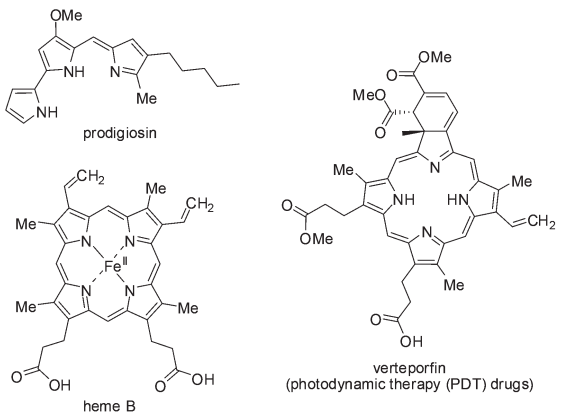
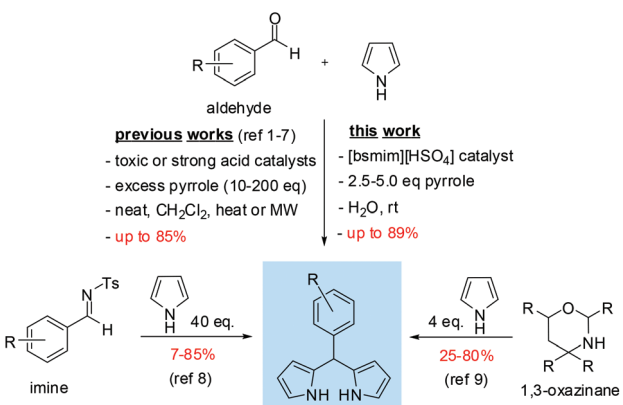



**Fig. 1** Examples of biologically active compound containing dipyrromethane moiety.




**Scheme 1** Strategies for synthesis of dipyrromethane.

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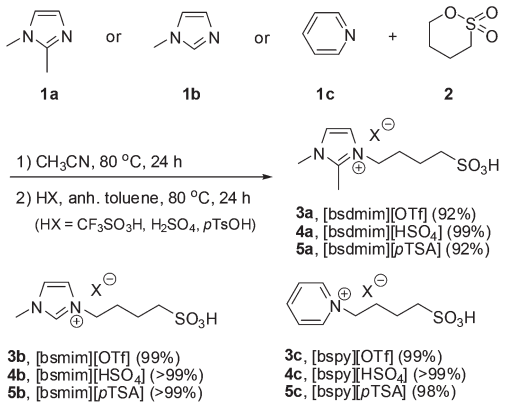
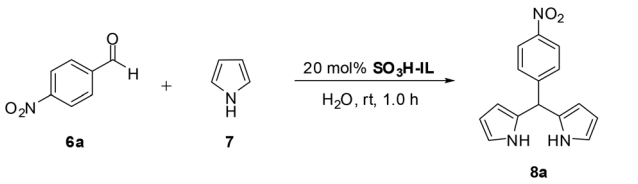
alternative more efficient syntheses continue to be sought to provide high selectivity and yields. To date, the synthetic processes under green context are increasing rapidly in response to biological applications. Furthermore, process reactions that take place in water represent an interesting approach for the green chemistry group.[10] With these concerns and those for the environment, our challenge was to synthesize dipyrromethanes using a metal-free method in aqueous media.

Ionic liquids (ILs)[11] are salts usually existing in a liquid form at room temperature. They have unique properties including wide temperature range of liquid state, non-volatility, non-flammable, high thermal stability, high solubility and are recyclable. These qualities make them desirable as green solvents, reagents and catalysts in many useful reactions. Since, ILs are widely utilized for environmentally friendly benign processes, well-designed ionic liquids as task-specific ionic liquids (TSILs) have emerged as activity enhancers. One of the TSILs, Brønsted acidic ionic liquid (BAIL)[12] has received attention as an efficient acidic catalyst due to high performance under a wide range of reaction conditions. Additionally, they are miscible in water, water-tolerant and suitable for reactions that need to proceed in water[12l,m–o] and can be reused allowing products to be easily separated from water by simple extraction. There are many reports on the use of BAILs as catalysts in versatile organic reactions such as esterification,[12a,b,d,e,t] Mannich reaction,[12c,f] nitration,[12h,q] Beckmann rearrangement,[12j] Friedlander reaction,[12l] Michael addition reaction[12r] and other one-pot multicomponent reactions.[12i,m–o,s] Recently, Ishikawa group[1g] has reported the use of BAILs for the synthesis of symmetric porphyrins from aldehydes and pyrrole in one-pot process using $CH_2Cl_2$ as a solvent. Herein, we first report the use of reusable BAIL as a catalyst for the green synthesis of dipyrromethanes from aldehydes and pyrrole in water *via* double Friedel–Crafts reaction.




**Scheme 2** Preparations of $SO_3H$-functionalized ionic liquids.

**Table 1** Optimization of Friedel–Crafts alkylation in water using various $SO_3H$-IL catalysts[a]




| Entry | $SO_3H$-IL | Yield **8a**[b] (%) |
|---|---|---|
| 1 | **3a**, [bsdmim][OTf] | 58 |
| 2 | **4a**, [bsdmim][$HSO_4$] | 53 |
| 3 | **5a**, [bsdmim][*p*TSA] | 37 |
| 4 | **3b**, [bsmim][OTf] | **64** |
| 5 | **4b**, [bsmim][$HSO_4$] | **65** |
| 6 | **5b**, [bsmim][*p*TSA] | 46 |
| 7 | **3c**, [bspy][OTf] | 55 |
| 8 | **4c**, [bspy][$HSO_4$] | **64** |
| 9 | **5c**, [bspy][*p*TSA] | 51 |

[a] All reactions were conducted with 1.0 mmol of **6a** and 5.0 mmol of **7** using 20 mol% of $SO_3H$-IL in 3.0 mL $H_2O$ at rt for 1.0 h. [b] Isolated yield.

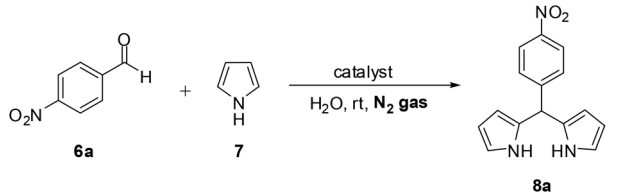
## Results and discussion

A series of $SO_3H$-functionalized ionic liquids ($SO_3H$-ILs) bearing imidazolium and pyridinium cations with three different anions was investigated. According to a previous report,[12a] the preparation of these $SO_3H$-ILs was achieved in a two-step synthesis using inexpensive materials. Reactions were completely converted to $SO_3H$-ILs (**3a–c**, **4a–c** and **5a–c**) providing excellent yields (Scheme 2).

The production of dipyrromethanes from 4-nitrobenzaldehyde (**6a**) with 5.0 equivalents of pyrroles (**7**) in the double Friedel–Crafts reaction was initially investigated using 20 mol% of various synthesized $SO_3H$-ILs in water under air atmosphere at room temperature for 1.0 h (Table 1). The yield of dipyrromethanes was the highest with [bsmim][OTf] (**3b**), [bsmim] [$HSO_4$] (**4b**), and [bspy][$HSO_4$] (**4c**) as catalysts (entries 4, 5 and 8, respectively). The lowest yield was found in the case of *p*TSA anion (entries 3, 6 and 9). By-products were observed same as in the earlier study[7i] which include tripyrranes and other oligomeric compounds, likely due to the presence of oxygen.

When this reaction was performed in degassed water and under a nitrogen atmosphere with 20 mol% of each of the three most efficient $SO_3H$-ILs (**3b**, **4b**, and **4c**) for 1.0 h (Table 2, entries 5–7), yields increased to 72 and 73% for catalysts (**4b**) and (**4c**), respectively and remained unchanged for catalyst (**3b**). This discloses that the activity of $SO_3H$-ILs depends on the counter-anion, and the $HSO_4$ anion exhibited better catalytic activity for the double Friedel–Crafts process than OTf and *p*TSA anions under oxygen-free conditions. The order of catalytic activity for this protocol is [bsmim][$HSO_4$] > [bsmim][OTf] > [bsmim][*p*TSA].[13]

Table 2 Optimization of Friedel–Crafts reaction in water using $SO_3H$-IL catalyst under a nitrogen atmosphere[a]




| Entry | Catalyst | Catalyst (mol%) | Pyrrole 7 (equiv.) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | — | — | 5.0 | 1.0 | 0 (25)[c] |
| 2 | $CF_3SO_3H$ | 20 | 5.0 | 1.0 | 62 |
| 3 | $H_2SO_4$ | 20 | 5.0 | 1.0 | 66 |
| 4 | *p*TsOH | 20 | 5.0 | 1.0 | 49 |
| 5 | **3b**, [bsmim][OTf] | 20 | 5.0 | 1.0 | 65 |
| 6 | **4b**, [bsmim][$HSO_4$] | 20 | 5.0 | 1.0 | 73 |
| 7 | **4c**, [bspy][$HSO_4$] | 20 | 5.0 | 1.0 | 72 |
| 8 | **4b**, [bsmim][$HSO_4$] | 10 | 5.0 | 1.0 | 84 (90)[d] |
| 9 | **4c**, [bspy][$HSO_4$] | 10 | 5.0 | 1.0 | 78 |
| 10 | **4b**, [bsmim][$HSO_4$] | 10 | 5.0 | 1.5 | **89** |
| 11[e] | **4b**, [bsmim][$HSO_4$] | 10 | 5.0 | 1.5 | 31 |
| 12 | **4b**, [bsmim][$HSO_4$] | 10 | 2.5 | 1.5 | 31 |
| 13 | **4b**, [bsmim][$HSO_4$] | 10 | 2.5 | 3.0 | 59 |
| 14[f] | **4b**, [bsmim][$HSO_4$] | 10 | 2.5 | 1.5 | 73 |
| 15[f] | **4b**, [bsmim][$HSO_4$] | 5 | 5.0 | 3.0 | 81 |
| 16[f] | **4b**, [bsmim][$HSO_4$] | 5 | 2.5 | 3.0 | 65 |
| 17 | **4b**, [bsmim][$HSO_4$] | 50 | 5.0 | 0.5 | 53 |

[a] All reactions were conducted with 1.0 mmol of **6a** and 5.0 mmol of 7 using 0–50 mol% of acid-IL in 3.0 mL $H_2O$ at rt for 1.0–3.0 h. [b] Isolated yield. [c] Performed for 24 h. [d] Conversion yield. [e] Performed at 10 °C. [f] Performed with 1.5 mL of $H_2O$.

The reaction with no catalyst was also performed (Table 2, entry 1). We found no reaction within 1.0 h, while 25% yield of the desired product (**8a**) was produced with a longer reaction period (24 h). In addition, general acids such as $CF_3SO_3H$, $H_2SO_4$, and *p*TsOH, were employed, which resulted in lower yields of the desired product (**8a**) than with our synthesized $SO_3H$-ILs (Table 2, entries 2–4). Surprisingly, the reaction generated a higher yield after 1.0 h when the amount of $SO_3H$-IL catalysts (**4b** and **4c**) was reduced to 10 mol% (Table 2, entries 8 and 9). This was especially the case for $SO_3H$-IL (**4b**) with 84% increase in the yield of the desired product (**8a**) (90% conversion yield). However, the highest yield of the desired product (**8a**), 89%, occurred when the reaction time was slightly increased to 1.5 h under the same conditions (Table 2, entry 10).

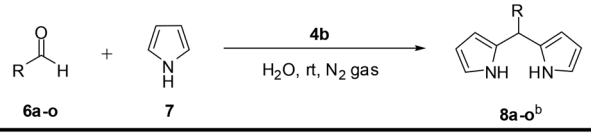
The other effects of the most efficient catalyst (**4b**) (10 mol%) in concert with reaction temperature and the amount of pyrrole (7) used on the yield of the desired product (**8a**) were also explored (Table 2, entries 11–17). At 10 °C, some of the remaining initial aldehydes were observed on the TLC, indicating that the reaction was incomplete and the isolated yield of the desired product (**8a**) was only 31% (Table 2, entry 11). On decreasing pyrrole (7) to 2.5 equivalents, the desired product (**8a**) was obtained in lower yields, 31 and 59% (**8a**) after 1.5 and 3.0 h, respectively (Table 2, entries 12 and 13, respectively). Highly concentrated reaction volume could improve the yield of the desired product (**8a**) to 73% after 1.5 h (Table 2, entry 14). However this result indicates that a reduction in the amount of pyrrole (7) to 2.5 equivalents resulted in lower yield of the desired product (**8a**) than that when pyrrole (7) was present at 5.0 equivalents. It is obvious that 2.5 equivalents of pyrrole (7) were not sufficient to produce the desired product (**8a**) in highest yield using this protocol. Nonetheless, the yield was higher than that in previous studies with a similar amount of pyrrole (7).[6,7j,l] The catalyst (**4b**) was tested with 5 mol% under high concentration conditions with both 5.0 and 2.5 equivalents of pyrrole (7), the desired product (**8a**) was obtained in acceptable yields after 3.0 h with 81 and 65% yields, respectively (Table 2, entries 15 and 16). In addition, the desired product yield was the lowest, 53%, when the catalyst was increased to 50 mol% (Table 2, entry 17). This is likely due to too strong acidic conditions created by the large amount of acid catalyst causing the production of oligomers as complex mixtures.

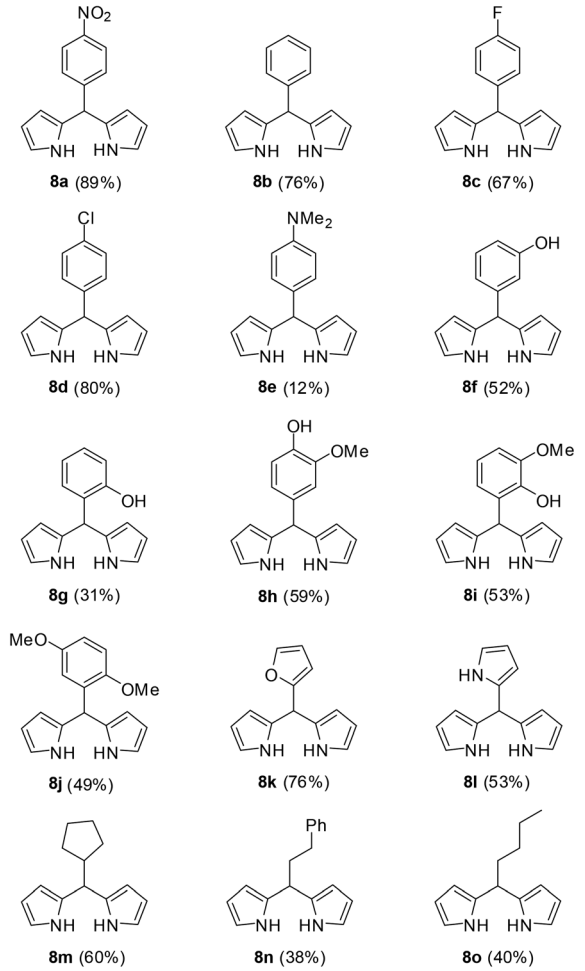
The recycling performance of the catalyst (**4b**) was also investigated using the 4-nitrobenzaldehyde substrate. After the completion of the reaction (Table 2, entry 10), the product (**8a**) was isolated from the catalytic system by simple extraction, and then 4-nitrobenzaldehyde (**6a**) and pyrrole (7) were directly added into the catalytic system (water layer containing catalyst) for next runs. The results showed that the catalyst could be reused without significant loss of activity; the yields remained unchanged even after four cycles (89, 89, 88 and 87%, respectively) and the used catalyst retained its structure as confirmed by NMR analysis.

The chemical suitability of the substrate for the green synthesis of dipyrromethane derivatives *via* $SO_3H$-IL catalyzed Friedel–Crafts reaction was investigated under these optimized reaction conditions (Table 2, entry 10). A variety of either aromatic or aliphatic aldehydes were tested with respect to moderate and good product yields (Table 3). The corresponding desirable products were yielded depending on electronic and steric effects of the aldehyde substrates. However, this new protocol is tolerant of various functional groups of aldehydes including both electron donating and electron withdrawing groups. Aldehyde substrates with an electron withdrawing group (**6a**, **6c**, and **6d**) including benzaldehyde (**6b**) produced good yield of products (**8a–8d**; 67–89% yields), while aldehyde substrates with an electron donating group (**6f–6j**) provided the products (**8i–8j**) in moderate yields (31–59% yields). In contrast the high electron-rich 4-(*N*,*N*-dimethylamino)benzaldehyde (**6e**) produced very low product yield, 12%, (**8e**) in the same time due to incomplete reaction. Moreover, heteroaromatic aldehydes such as furan-2-carbaldehyde (**6k**) and pyrrole-2-carbaldehyde (**6l**) also produced the product (**8k**) in good yields (76% yield) and the product (**8l**) in moderate yield (53% yield), respectively. Interestingly, this protocol also works well with aliphatic aldehydes (**6m**, **6n**, and **6o**) and gave the desired products (**8m**, **8n**, and **8o**) in moderate yields (38–60%).

Table 3 Synthesis of dipyrromethanes with various substances[a]




[a] All reactions were conducted with 1.0 mmol of aldehyde **6** and 5.0 mmol of pyrrole **7** using 10 mol% of **4b**, [bsmim][$HSO_4$] in 3.0 mL $H_2O$ at rt for 1.5 h. [b] Isolated yield. [bsmim][$HSO_4$] = 1-butylsulfonic-3-methylimidazolium bisulfate.

## Conclusions

In summary, we have demonstrated a green method for the synthesis of dipyrromethanes under mild and metal-free conditions in aqueous media. The reaction was performed by using a catalytic amount of $SO_3H$-IL, which consisted of an imidazolium cation and a $HSO_4$ anion, named [bsmim][$HSO_4$]. The desired products were successfully obtained in moderate to good yields with a wide range of aldehyde substrates. The corresponding products are easily separated from the reaction system by simple extraction and catalyst recycling was possible for subsequent reactions. This protocol may offer green chemistry from the aspect of avoiding toxic catalysts and solvents.

## Experimental section

### General methods

All chemicals were purchased from commercial sources and used without further purification. Proton NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer. All spectra were recorded in $CDCl_3$ or $CD_3OD$ solvent and chemical shifts are reported as $\delta$ values in parts per million (ppm) relative to tetramethylsilane ($\delta$ 0.00), $CDCl_3$ ($\delta$ 7.26) or $CD_3OD$ ($\delta$ 3.34) as internal standard. Carbon NMR spectra were recorded on a Bruker Avance (100 MHz) spectrometer. All spectra were recorded in $CDCl_3$ or $CD_3OD$ solvent and chemical shifts are reported as $\delta$ values in parts per million (ppm) relative to $CDCl_3$ ($\delta$ 77.0) or $CD_3OD$ ($\delta$ 49.0) as internal standard. High-resolution mass spectra (HRMS) data were obtained with a Bruker Daltonics - micrOTOF-Q spectrometer. Infrared spectra were recorded on a Perkin Elmer FT/IR-2000S spectrophotometer and are reported in wave number ($cm^{-1}$). Open-column chromatography was carried out using silica gel 60 PF254 [E. Merck, Darmstadt, Germany]. Melting points were measured using a melting point apparatus (Griffin) and are uncorrected.

### General procedure for synthesis of 1-butylsulfonic-2,3-dimethylimidazolium salts (3a, 4a and 5a)

To a solution of 1,2-dimethylimidazole **1a** (5.00 g, 52.0 mmol) in $CH_3CN$ (25.0 mL) was added 1,4-butanesultone **2** (7.79 g, 57.2 mmol) in portions at room temperature. The reaction mixture was heated to 80 °C with stirring for 24 h, and then cooled to room temperature resulting in a white precipitate. The white precipitate was filtered and washed with ethanol (3 × 5 mL) to remove any unreacted starting materials, and then the precipitate was dried in a vacuum to give the zwitterionic compound as a white solid in 81% yield (9.7403 g). M.p. 197–200 °C; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.83 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.01 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.67 (s, 3H, $CH_3$), 2.87 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.84 (s, 3H, $CH_3$), 4.23 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.50 (d, 1H, $J$ = 2.0 Hz, CH), 7.57 (d, 1H, $J$ = 2.0 Hz, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 9.48, 22.83, 29.44, 35.35, 51.39, 122.26, 123.63, 146.01. A mixture of zwitterionic compound (1.50 g, 6.46 mmol) in anhydrous toluene (3.00 mL) was added to a stoichiometric amount of acid HX (1 eq.) in portions at room temperature. The reaction mixture was then stirred at 80 °C for 24 h. After the white solid was fully dissolved, the reaction mixture was cooled to room temperature, the toluene layer was removed and extracted with ethyl acetate (3 × 10 mL) to remove the remaining organic compounds. The insoluble residue was dried under high vacuum to give the products in 92–99% yields.

**1-Butylsulfonic-2,3-dimethylimidazolium trifluoromethanesulfonate (3a).** 92% yield (2.4253 g) as a brown color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.84 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.02 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.67 (s, 3H, $CH_3$), 2.90 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.85 (s, 3H, $CH_3$), 4.23 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.50 (d, 1H, $J$ = 2.0 Hz, CH), 7.56 (d, 1H,

$J$ = 2.0 Hz, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 9.49, 22.76, 29.40, 35.37, 48.97, 51.43, 122.20, 123.63, 145.98.

**1-Butylsulfonic-2,3-dimethylimidazolium hydrogen sulfate (4a).** 99% yield (2.1152 g) as a brown color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.84 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.02 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.68 (s, 3H, $CH_3$), 2.91 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.86 (s, 3H, $CH_3$), 4.23 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.51 (d, 1H, $J$ = 2.0 Hz, CH), 7.57 (d, 1H, $J$ = 2.0 Hz, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 9.52, 22.72, 29.38, 35.40, 48.93, 51.47, 122.17, 123.63, 145.96.

**1-Butylsulfonic-2,3-dimethylimidazolium *p*-toluenesulfonate (5a).** 92% yield (2.4195 g) as a yellow color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.83 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.00 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.40 (s, 3H, $CH_3$), 2.64 (s, 3H, $CH_3$), 2.90 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.82 (s, 3H, $CH_3$), 4.20 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.28 (d, 2H, $J$ = 8.0 Hz, $H_{Ar}$), 7.48 (d, 1H, $J$ = 2.0 Hz, CH), 7.54 (d, 1H, $J$ = 2.0 Hz, CH), 7.72 (d, 2H, $J$ = 8.0 Hz, $H_{Ar}$); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 9.49, 21.29, 22.71, 29.37, 35.37, 48.92, 51.45, 122.16, 123.61, 126.93 (2C), 129.90 (2C), 142.01, 143.08, 145.92.

### General procedure for synthesis of 1-butylsulfonic-3-methylimidazolium salts (3b, 4b and 5b)

To a solution of 1-methylimidazole **1b** (5.00 g, 60.9 mmol) in $CH_3CN$ (25.0 mL) was added 1,4-butanesultone **2** (9.12 g, 67.0 mmol) in portions at room temperature. The reaction mixture was heated to 80 °C with stirring for 24 h, and then cooled to room temperature resulting in a white precipitate. The white precipitate was filtered and washed with ethanol (3 × 5 mL) to remove any unreacted starting materials, and then the precipitate was dried in a vacuum to give the zwitterionic compound as a white solid in 71% yield (9.4700 g). M.p. 193–196 °C; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.81 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.08 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.88 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.97 (s, 3H, $CH_3$), 4.30 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.61 (brs, 1H, CH), 7.70 (brs, 1H, CH), 9.00 (s, 1H, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 22.72, 29.83, 36.47, 50.31, 51.41, 123.72, 124.99, 138.05. A mixture of zwitterionic compound (1.50 g, 6.87 mmol) in anhydrous toluene (3.00 mL) was added to a stoichiometric amount of acid HX (1 eq.) in portions at room temperature. The reaction mixture was then stirred at 80 °C for 24 h. After the white solid was fully dissolved, the reaction mixture was cooled to room temperature, the toluene layer was removed and extracted with ethyl acetate (3 × 10 mL) to remove the remaining organic compounds. The insoluble residue was dried under high vacuum to give the products in most-quantitative yields.

**1-Butylsulfonic-3-methylimidazolium trifluoromethanesulfonate (3b).** 98% yield (2.5211 g), as an orange color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.82 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.08 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.90 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.96 (s, 3H, $CH_3$), 4.29 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.60 (brs, 1H, CH), 7.68 (brs, 1H, CH), 8.97 (s, 1H, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 22.67, 29.79, 36.48, 50.32, 51.40, 123.69, 124.99, 137.98.

**1-Butylsulfonic-3-methylimidazolium hydrogen sulfate (4b).** Quantitative yield (2.3228 g) as an orange color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.82 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.08 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.90 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.97 (s, 3H, $CH_3$), 4.30 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.61 (brs, 1H, CH), 7.69 (brs, 1H, CH), 8.99 (s, 1H, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 22.68, 29.80, 36.51, 50.32, 51.43, 123.68, 124.99, 137.96.

**1-Butylsulfonic-3-methylimidazolium *p*-toluenesulfonate (5b).** Quantitative yield (2.6970 g) as a brown color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.81 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.06 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.41 (s, 3H, $CH_3$), 2.89 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 3.95 (s, 3H, $CH_3$), 4.28 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.28 (d, 2H, $J$ = 8.0 Hz, $H_{Ar}$), 7.59 (brs, 1H, CH), 7.67 (brs, 1H, CH), 7.73 (d, 2H, $J$ = 8.0 Hz, $H_{Ar}$), 8.97 (s, 1H, CH); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 21.29, 22.38, 29.59, 36.41, 49.92, 51.45, 123.33, 124.66, 126.64, 126.69, 129.92, 129.97, 137.66, 142.01, 142.78.

### General procedure for synthesis of 1-butylsulfonic pyridinium salts (3c, 4c and 5c)

To a solution of 1-methylimidazole **1c** (5.00 g, 63.3 mmol) in $CH_3CN$ (25.0 mL) was added 1,4-butanesultone **2** (9.47 g, 69.6 mmol) in portions at room temperature. The reaction mixture was heated to 80 °C with stirring for 24 h, and then cooled to room temperature resulting in a white precipitate. The white precipitate was filtered and washed with ethanol (3 × 5 mL) to remove any unreacted starting materials, and then the precipitate was dried in a vacuum to give the zwitterionic compound as a white solid in 57% yield (7.7744 g). M.p. 193–196 °C; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.88 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.24 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.92 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 4.73 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 8.16 (bst, 2H, $J$ = 7.0 Hz, $H_{Ar}$), 8.63 (t, 1H, $J$ = 8.0 Hz, $H_{Ar}$), 9.07 (bsd, 2H, $J$ = 6.0 Hz, $H_{Ar}$); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 22.70, 31.16, 51.28, 62.52, 129.52 (3C), 146.06, 146.85. A mixture of zwitterionic compound (1.50 g, 6.97 mmol) in anhydrous toluene (3.00 mL) was added to a stoichiometric amount of acid HX (1 eq.) in portions at room temperature. The reaction mixture was then stirred at 80 °C for 24 h. After white solid was fully dissolved, the reaction mixture was cooled to room temperature, the toluene layer was removed and extracted with ethyl acetate (3 × 10 mL) to remove the remaining organic compounds. The insoluble residue was dried under high vacuum to give products in 98% to quantitative yields.

**1-Butylsulfonic pyridinium trifluoromethanesulfonate (3c).** 94% yield (2.3853 g) as an orange color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.88 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.23 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.93 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 4.72 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 8.16 (brt, 2H, $J$ = 6.5 Hz, $H_{Ar}$), 8.63 (t, 1H, $J$ = 7.5 Hz, $H_{Ar}$), 9.05 (brd, 2H, $J$ = 6.0 Hz, $H_{Ar}$); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 22.63, 31.09, 51.27, 62.53, 129.53 (3C), 146.00, 146.88.

**1-Butylsulfonic pyridinium hydrogen sulfate (4c).** Quantitative yield (2.3695 g) as an orange color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.88 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.24 (quint, 2H,

$J$ = 7.5 Hz, $CH_2$), 2.94 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 4.73 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 8.16 (brt, 2H, $J$ = 6.5 Hz, $H_{Ar}$), 8.64 (t, 1H, $J$ = 7.5 Hz, $H_{Ar}$), 9.06 (brd, 2H, $J$ = 6.0 Hz, $H_{Ar}$): $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 22.64, 31.11, 51.29, 62.52, 129.54 (3C), 146.03, 146.88.

**1-Butylsulfonic pyridinium toluenesulfonate (5c).** 98% yield (2.6732 g) as a yellow color oil; $^1$H-NMR (400 MHz, $CD_3OD$): $\delta$ 1.87 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.22 (quint, 2H, $J$ = 7.5 Hz, $CH_2$), 2.41 (s, 3H, $CH_3$), 2.92 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 4.71 (t, 2H, $J$ = 7.5 Hz, $CH_2$), 7.28 (d, 2H, $J$ = 8.0 Hz, $H_{Ar}$), 7.73 (d, 2H, $J$ = 8.0 Hz, $H_{Ar}$), 8.14 (brt, 2H, $J$ = 6.5 Hz, $H_{Ar}$), 8.62 (t, 1H, $J$ = 8.0 Hz, $H_{Ar}$), 9.05 (brd, 2H, $J$ = 6.0 Hz, $H_{Ar}$); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 21.28, 22.63, 31.08, 51.25, 62.53, 126.92 (2C), 129.52 (3C), 129.83 (2C), 141.78, 143.43, 145.97, 146.85.

### General procedure for the synthesis of dipyrromethanes

To a suspension of [bsmim][$HSO_4$] (**4b**)* (10 mol%) in degassed water (3.0 mL) was added an aldehyde (1.0 mmol) and a pyrrole (5.0 mmol) at room temperature under nitrogen gas. The mixture suspension was stirred at room temperature for 1.5 h. Then, the mixture was extracted with ethyl acetate (3 × 2 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous sodium sulfate. The solvent was removed by using a rotary evaporator and concentrated under reduced pressure. The residue was purified by column chromatography to give the desired products (**8**).

**Recycling experiment*. After completion of the reaction, the remaining catalyst in aqueous solution could be reused directly by adding aldehyde and pyrrole substrates in the next run without purification.

***meso*-(4-Nitrophenyl)dipyrromethane (8a).**[1e,j,6,7b,e,h,k,l,8a,9a] 89% yield (0.2388 g) as a yellow solid; m.p. 135–138 °C; $R_f$ = 0.17 (10% EtOAc/*n*-hexane); IR (neat): 3391, 1594, 1515, 1346, 1028, 728, 556 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.58 (s, 1H, $H_{1'}$), 5.85–5.89 (m, 2H, 2 × $H_3$), 6.16–6.20 (m, 2H, 2 × $H_4$), 6.73–6.77 (m, 2H, 2 × $H_5$), 7.37 (2H, d, $J$ = 8.5 Hz, 2 × $H_{Ar}$), 8.00 (brs, 2H, 2 × $H_1$), 8.17 (d, 2H, $J$ = 8.5 Hz, 2 × $H_{Ar}$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 43.78, 107.80 (2C), 108.77 (2C), 117.95 (2C), 123.77 (2C), 129.22 (2C), 130.79 (2C), 146.89, 149.64; HRMS (ESI) $m/z$ $C_{15}H_{13}N_3O_2$ [M + Na]$^+$ calcd 290.0905, found 290.0907.

***meso*-(Phenyl)dipyrromethane (8b).**[1b,e,j,f,6,7b,e,g,h,k,l,m,8a,9a] 76% yield (0.1682 g) as a white solid; m.p. 91–101 °C; $R_f$ = 0.32 (10% EtOAc/*n*-hexane); IR (neat): 3379, 3100, 1559, 1495, 1451, 1090, 1027, 722, 550 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.47 (s, 1H, $H_{1'}$), 5.89–5.93 (m, 2H, 2 × $H_3$), 6.14–6.17 (m, 2H, 2 × $H_4$), 6.67–6.70 (m, 2H, 2 × $H_5$), 7.19–7.34 (m, 5H, 5 × $H_{Ar}$), 7.19 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 43.92, 107.20 (2C), 108.38 (2C), 117.20 (2C), 126.94, 128.36 (2C), 128.61 (2C), 132.47 (2C), 142.03; HRMS (ESI) $m/z$ $C_{15}H_{14}N_2$ [M + Na]$^+$ calcd 245.1055, found 245.1050.

***meso*-(4-Fluorophenyl)dipyrromethane (8c).**[1e,7e,8a] 67% yield (0.1606 g) as a brown solid; m.p. 96 °C; $R_f$ = 0.30 (20% EtOAc/*n*-hexane); IR (neat): 3378, 1603, 1561, 1506, 1222, 1158, 1092, 1028, 720, 541 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.46 (s, 1H, $H_{1'}$), 5.87–5.90 (m, 2H, 2 × $H_3$), 6.14–6.18 (m, 2H, 2 × $H_4$), 6.69–6.72 (m, 2H, 2 × $H_5$), 6.96–7.04 (m, 2H, 2 × $H_{Ar}$), 7.14–7.20 (m, 2H, 2 × $H_{Ar}$), 7.92 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 43.16, 107.29 (2C), 108.46 (2C), 115.35 (2C, $J$ = 21.0 Hz), 117.38 (2C), 129.83 (2C, $J$ = 8.0 Hz), 132.31 (2C), 137.80, 161.75 ($J$ = 244.0 Hz); HRMS (ESI) $m/z$ $C_{15}H_{13}FN_2$ [M + H]$^+$ calcd 241.1141, found 241.1143.

***meso*-(4-Chlorophenyl)dipyrromethane (8d).**[1e,7b,m,8a] 80% yield (0.2061 g) as a bark brown solid; m.p. 96–98 °C; $R_f$ = 0.30 (10% EtOAc/*n*-hexane); IR (neat): 3378, 1560, 1489, 1255, 1089, 1027, 723, 511 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.45 (s, 1H, $H_{1'}$), 5.87–5.91 (m, 2H, 2 × $H_3$), 6.14–6.19 (m, 2H, 2 × $H_4$), 6.69–6.73 (m, 2H, 2 × $H_5$), 7.15 (d, 2H, $J$ = 8.0 Hz, 2 × $H_{Ar}$), 7.29 (d, 2H, $J$ = 8.0 Hz, 2 × $H_{Ar}$), 7.94 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$); $\delta$ 43.23, 107.36 (2C), 108.44 (2C), 117.44 (2C), 128.61 (2C), 129.65 (2C), 131.94 (2C), 132.61, 140.59; HRMS (ESI) $m/z$ $C_{15}H_{13}ClN_2$ [M + Na]$^+$ calcd 279.0665, found 279.0669.

***meso*-(4-(*N*,*N*-Dimethylamino)phenyl)dipyrromethane (8e).**[7b,l] 12% yield (0.0306 g) as a brown solid; m.p. 111–117 °C; $R_f$ = 0.44 (10% EtOAc/*n*-hexane); IR (neat): 3397, 1611, 1519, 1349, 1026, 717, 534 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 2.94 (s, 6H, 2 × $CH_3$), 5.40 (s, 1H, $H_{1'}$), 5.91–5.96 (m, 2H, 2 × $H_3$), 6.13–6.18 (m, 2H, 2 × $H_4$), 6.66–6.69 (m, 2H, 2 × $H_5$), 6.71 (d, 2H, $J$ = 8.0 Hz, 2 × $H_{Ar}$), 7.09 (d, 2H, $J$ = 8.0 Hz, 2 × $H_{Ar}$), 7.93 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$); $\delta$ 40.63 (2C), 43.18, 106.90 (2C), 108.44 (2C), 112.91 (2C), 116.80 (2C), 129.09 (2C), 130.10, 133.37 (2C), 149.81; HRMS (ESI) $m/z$ $C_{17}H_{19}N_3$ [M + H]$^+$ calcd 266.1657, found 266.1650.

***meso*-(3-Hydroxyphenyl)dipyrromethane (8f).** 52% yield (0.1229 g) as a brown solid; m.p. 105–107 °C; $R_f$ = 0.23 (20% EtOAc/*n*-hexane); IR (neat): 3383, 1599, 1456, 1265, 1092, 1027, 723, 549 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.41 (s, 1H, $H_{1'}$), 5.91–5.95 (m, 2H, 2 × $H_3$), 6.14–6.18 (m, 2H, 2 × $H_4$), 6.58 (brs, 1H, $H_{Ar}$), 6.67–6.70 (m, 2H, 2 × $H_5$), 6.72 (dd, 1H, $J$ = 7.5, 2.0 Hz, $H_{Ar}$), 6.81 (d, 1H, $J$ = 7.5 Hz, $H_{Ar}$), 7.19 (t, 1H, $J$ = 7.5 Hz, $H_{Ar}$), 7.94 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$); $\delta$ 43.64, 107.21 (2C), 108.30 (2C), 113.97, 115.25, 117.33, 117.35, 120.94, 129.84, 132.32 (2C), 143.84, 155.64; HRMS (ESI) $m/z$ $C_{15}H_{14}N_2O$ [M + Na]$^+$ calcd 261.1004, found 261.1003.

***meso*-(2-Hydroxyphenyl)dipyrromethane (8g).**[7l,8a] 31% yield (0.0749 g) as a brown solid; m.p. 103–105 °C; $R_f$ = 0.18 (20% EtOAc/*n*-hexane); IR (neat): 3407, 1594, 1599, 1456, 1276, 1087, 1027, 722, 534 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.22 (brs, 1H, OH), 5.54 (s, 1H, $H_{1'}$), 5.99–6.02 (m, 2H, 2 × $H_3$), 6.15–6.18 (m, 2H, 2 × $H_4$), 6.70–6.73 (m, 2H, 2 × $H_5$), 6.86 (d, 1H, $J$ = 7.5 Hz, $H_{Ar}$), 6.91 (t, 1H, $J$ = 7.5 Hz, $H_{Ar}$), 7.08 (dd, 1H, $J$ = 7.5, 1.5 Hz, $H_{Ar}$), 7.19 (td, 1H, $J$ = 7.5, 1.5 Hz, $H_{Ar}$), 8.18 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 40.01, 106.97 (2C), 108.44 (2C), 117.33, 117.87 (2C), 121.42, 128.34, 128.62, 130.02, 130.98 (2C), 153.54; HRMS (ESI) $m/z$ $C_{15}H_{14}N_2O$ [M + Na]$^+$ calcd 261.1004, found 261.1008.

***meso*-(3-Methoxy-4-hydroxyphenyl)dipyrromethane (8h).** 59% yield (0.1583 g) as a brown solid; m.p. 113–115 °C; $R_f$ = 0.23 (20% EtOAc/*n*-hexane); IR (neat): 3380, 1603, 1512, 1463, 1431, 1273, 1230, 1028, 721, 550 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$):

$\delta$ 3.80 (s, 3H, OMe), 5.40 (brs, 1H, O*H*), 5.56 (s, 1H, $H_{1'}$), 5.92 (brs, 2H, $H_3$), 6.16 (dd, 2H, $J$ = 5.5, 2.5 Hz, $H_4$), 6.66–6.72 (m, 4H, $H_5$, $H_{Ar}$), 6.85 (d, 1H, $J$ = 8.0 Hz, $H_{Ar}$), 7.94 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 43.53, 55.82, 106.99 (2C), 108.28 (2C), 111.02, 114.25, 117.09 (2C), 120.97, 132.73 (2C), 133.97, 144.42, 146.54; HRMS (ESI) $m/z$ $C_{16}H_{16}N_2O_2$ $[M + H]^+$ calcd 269.1290, found 269.1290.

***meso*-(2-Hydroxy-3-methoxy)dipyrromethane (8i).** 53% yield (0.1434 g) as a brown solid; $R_f$ = 0.22 (20% EtOAc/*n*-hexane); IR (neat): 3402, 2938, 1478, 1441, 1274, 1223, 1067, 1026, 721, 550 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): 3.88 (s, 3H, OMe), 5.71 (s, 1H, $H_{1'}$), 5.91 (brs, 1H, O*H*), 5.94–5.98 (m, 2H, 2 × $H_3$), 6.13–6.16 (m, 2H, 2 × $H_4$), 6.67–6.70 (m, 2H, 2 × $H_5$), 6.75–6.85 (m, 3H, 3 × $H_{Ar}$), 8.27 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$); $\delta$ 38.80, 55.99, 106.58 (2C), 108.10 (2C), 109.32, 116.80 (2C), 119.90, 121.91, 127.96, 132.05 (2C), 142.78, 146.59; HRMS (ESI) $m/z$ $C_{16}H_{16}N_2O_2$ $[M + H]^+$ calcd 269.1290, found 269.1294.

***meso*-(2,5-Dimethoxyphenyl)dipyrromethane (8j).**[7m] 49% yield (0.1374 g) as a brown solid; m.p. 117–127 °C; $R_f$ = 0.19 (10% EtOAc/*n*-hexane); IR (neat): 3381, 1559, 1497, 1428, 1223, 1026, 271, 566 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 3.70 (s, 3H, OMe), 3.71 (s, 3H, OMe), 5.74 (s, 1H, $H_{1'}$), 5.89–5.93 (m, 2H, 2 × $H_3$), 6.11–6.15 (m, 2H, 2 × $H_4$), 6.64–6.68 (m, 2H, 2 × $H_5$), 6.70 (d, 1H, $J$ = 3.0 Hz, $H_{Ar}$), 6.75 (dd, 1H, $J$ = 8.0, 3.0 Hz, $H_{Ar}$), 6.85 (d, 1H, $J$ = 9.0 Hz, $H_{Ar}$), 8.14 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$); $\delta$ 38.07, 55.53, 56.56, 106.69 (2C), 108.13 (2C), 112.13, 112.73, 115.91, 116.75 (2C), 132.27 (3C), 150.96, 153.82; HRMS (ESI) $m/z$ $C_{17}H_{18}N_2O_2$ $[M + H]^+$ calcd 283.1447, found 283.1446.

***meso*-(Furan-2-yl)dipyrromethane (8k).**[7d,l,m,8b] 76% yield (0.1602 g) as a pale gray solid; m.p. 73–77 °C; $R_f$ = 0.52 (20% EtOAc/*n*-hexane); IR (neat): 3383, 3117, 1727, 1558, 1505, 1466, 1427, 1403, 1250, 1090, 1028, 1010, 768, 721, 553 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.52 (s, 1H, $H_{1'}$), 5.97–6.01 (m, 2H, 2 × $H_3$), 6.13–6.18 (m, 3H, 2 × $H_4$, $H_{3'}$), 6.32–6.35 (m, 1H, $H_{4'}$), 6.68–6.72 (m, 2H, 2 × $H_5$), 7.37–7.41 (m, 1H, $H_{5'}$), 8.10 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 37.67, 106.72 (2C), 106.90, 108.33 (2C), 110.24, 117.51 (2C), 129.92 (2C), 142.02, 154.26; HRMS (ESI) $m/z$ $C_{13}H_{12}N_2O$ $[M + Na]^+$ calcd 235.0847, found 235.0845.

**Tripyrromethane (8l).**[7m,8b] 53% yield (0.1128 g) as a brown-yellow solid; m.p. 113–117 °C; $R_f$ = 0.22 (10% EtOAc/*n*-hexane); IR (neat): 3366, 1554, 1401, 1113, 1091, 1026, 722, 537 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.53 (s, 1H, $H_{1'}$), 6.02–6.06 (m, 3H, 3 × $H_3$), 6.15–6.19 (m, 3H, 3 × $H_4$), 6.65–6.69 (m, 3H, 3 × $H_5$), 7.93 (brs, 3H, 3 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 37.16, 106.74 (3C), 108.39 (3C), 117.34 (3C), 131.14 (3C); HRMS (ESI) $m/z$ $C_{13}H_{13}N_3$ $[M + Na]^+$ calcd 234.1007, found 234.1008.

***meso*-(Cyclopentyl)dipyrromethane (8m).** 60% yield (0.1289 g) as a pale orange solid; m.p. 65–69 °C; $R_f$ = 0.38 (10% EtOAc/*n*-hexane); IR (neat): 3378, 3078, 3002, 2868, 1558, 1429, 1090, 1026, 718, 563 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 1.25–1.35 (m, 2H, Hc-pentyl), 1.49–1.62 (m, 4H, Hc-pentyl), 1.73–1.82 (m, 2H, Hc-pentyl), 2.38–2.50 (m, 1H, Hc-pentyl), 3.79 (d, 1H, $J$ = 9.5 Hz, $H_{1'}$), 6.06–6.09 (m, 2H, 2 × $H_3$), 6.12–6.15 (m, 2H, 2 × $H_4$), 6.58–6.62 (m, 2H, 2 × $H_5$), 7.74 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 25.23 (2C), 29.67, 31.77 (2C), 43.42, 105.71 (2C), 107.85 (2C), 116.75 (2C), 133.47 (2C); HRMS (ESI) $m/z$ $C_{14}H_{18}N_2$ $[M + H]^+$ calcd 215.1548, found 215.1543.

***meso*-(3-Phenylpropyl)dipyrromethane (8n).** 38% yield (0.0948 g) as a yellow oil; $R_f$ = 0.58 (20% EtOAc/*n*-hexane); IR (neat): 3378, 2926, 2861, 1559, 1496, 1545, 1092, 1026, 720, 566 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 2.28 (q, 2H, $J$ = 7.5 Hz, $H_{2'}$), 2.63 (t, 2H, $J$ = 7.5 Hz, $H_{3'}$), 3.98 (t, 1H, $J$ = 7.5 Hz, $H_{1'}$), 6.09–6.13 (m, 2H, 2 × $H_3$), 6.14–6.19 (m, 2H, 2 × $H_4$), 6.62–6.66 (m, 2H, 2 × $H_5$), 7.10–7.22 (m, 3H, $H_{Ar}$), 7.26–7.32 (m, 2H, $H_{Ar}$), 7.78 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 33.42, 35.88, 36.79, 105.57 (2C), 107.94 (2C), 117.16 (2C), 125.81, 128.31 (2C), 128.46 (2C), 133.11 (2C), 141.78; HRMS (ESI) $m/z$ $C_{17}H_{18}N_2$ $[M + H]^+$ calcd 251.1548, found 251.1545.

***meso*-(Butyl)dipyrromethane (8o).** 40% yield (0.0810 g) as a pale orange solid; m.p. 58 °C; $R_f$ = 0.61 (20% EtOAc/*n*-hexane); IR (neat): 3377, 2956, 2931, 2860, 1559, 1467, 1087, 1026, 721, 565 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.89 (t, 3H, $J$ = 7.0 Hz, $H_{5'}$), 1.23–1.40 (m, 4H, $H_{3'}$, $H_{4'}$), 1.94 (q, 2H, $J$ = 7.5 Hz, $H_{2'}$), 3.95 (t, 1H, $J$ = 7.5 Hz, $H_{1'}$), 6.06–6.10 (m, 2H, 2 × $H_3$), 6.14–6.17 (m, 2H, 2 × $H_4$), 6.59–6.62 (m, 2H, 2 × $H_5$), 7.68 (brs, 2H, 2 × $H_1$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 14.00, 22.54, 29.72, 34.14, 37.51, 105.42 (2C), 107.87 (2C), 117.03 (2C), 133.66 (2C); HRMS (ESI) $C_{13}H_{18}N_2$ $[M + Na]^+$ calcd 225.1368, found 225.1365.

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