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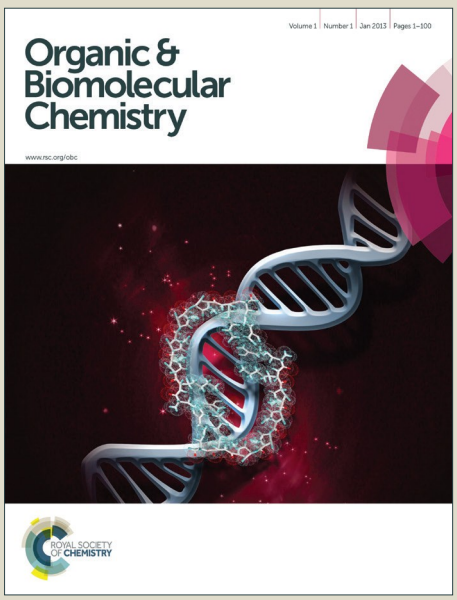

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ARTICLE

Green synthesis of dipyrromethanes in water media catalyzed by SO_3H-functionalized ionic liquid

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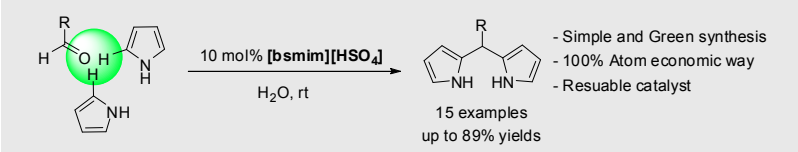
A mild, efficient and metal-free method was described for the green synthesis of dipyrromethanes from aldehydes and unsubstituted pyrrole catalyzed by SO_3H-functionalized ionic liquids (SO_3H-ILs) in water media at room temperature. Notably, SO_3H-ILs, 1-butylsulfonic-3-methylimidazolium hydrogen sulfate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



Introduction

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

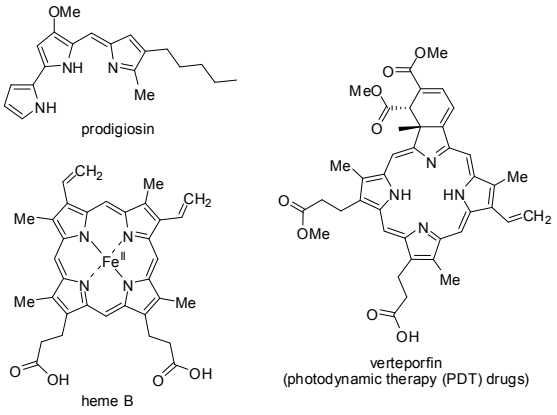
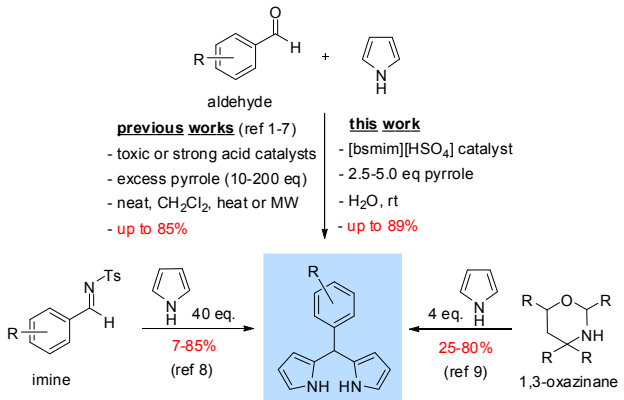


Figure 1. Examples of biologically active compound containing diprromethane moiety



Scheme 1. Strategies for Synthesis of dipyrromethane

Generally, dipyrromethanes are synthesized by 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 requires 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,1j,2,4a,7e-f,9] HCl/H_2O,[7a,7h] 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 with conditions that include substituted pyrrole,[7i-j] excess pyrrole[1e,1j,7e] and/or harsh conditions.[7h,7k,7m] 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,[2,3,4] alternative more efficient syntheses

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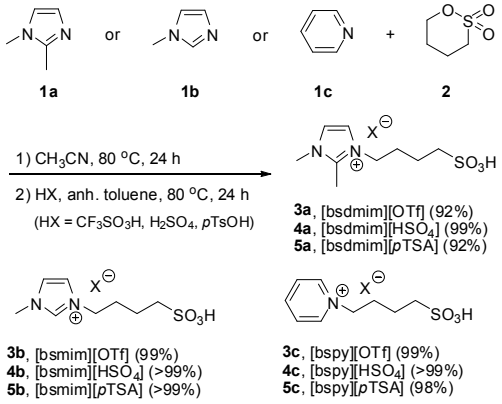
continue to be sought to provide high selectivity and yields. To date, the synthetic processes under green context are increasing rapidly in response to biological applications. Furthermore, process reactions that take place in water represent an interesting approach for the green chemistry group.[10]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

Ionic liquids (ILs)[11] are salts usually existing as a liquid at room temperature. They have unique properties including; wide temperature range of liquid state, non-volatile, non-flammable, high thermal stability, high solubility and recyclable. These qualities confer 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, Brönsted acidic ionic liquids (BAILs)[12] has received attention as an efficient acidic catalysts 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,n,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,n,o,s] In recently, Ishikawa group[1g] 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 on 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.

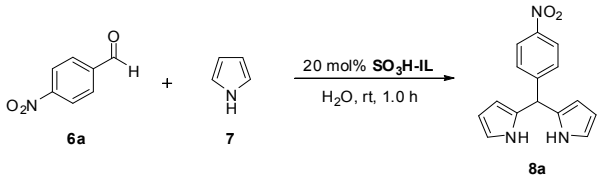
Results and discussion

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 in excellent yields (Scheme 2).



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

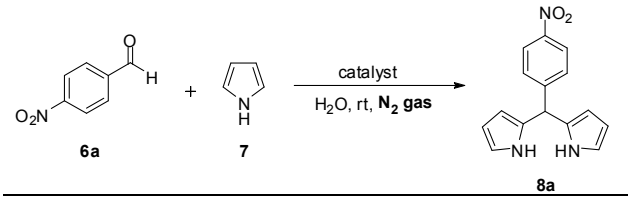
[a] All reactions were conducted with 1.0 mmol of **6a** and 5.0 mmol of **7** using 20 mol% of SO_3H-IL in 3.0 mL H_2O at rt for 1.0 h. [b] Isolated yield.

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). Yield of dipyrromethanes was highest with [bsmim][OTf] (**3b**), [bsmim][HSO_4] (**4b**), and [bspy][HSO_4] (**4c**) as catalysts (entries 4, 5 and 8, respectively). Lowest yield was found in case of *p*TSA anion (entries 3, 6 and 9). By-products were observed same as earlier study[7i] to include tripyrranes and other oligomeric compounds, likely due to the presence of oxygen.

When this reaction was performed in degas water and under 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**). These disclosed that the activity of SO_3H-ILs depends on counter-anion, and HSO_4 anion exhibited better catalytic activity for double Friedel-Crafts process than OTf and *p*TSA anions under oxygen-free condition. The order of catalytic activity for this protocol is [bsmim][HSO_4]>[bsmim][OTf]>[bsmim][*p*TSA].[13]

The reaction with no catalyst was also performed (Table 2, entry 1). We found no reaction within 1.0 h, while 25% yield of 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, and resulted in lower yields of desired product (**8a**) than our synthesized SO_3H-ILs (Table 2, entries 2-4). Surprisingly, the reaction generated a higher yield after 1.0 h when 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 yield of desired product (**8a**) (90% conversion yield). However, the highest yield of desired product (**8a**), 89%, occurred when reaction time was slightly increased to 1.5 h under the same conditions (Table 2, entry 10).

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

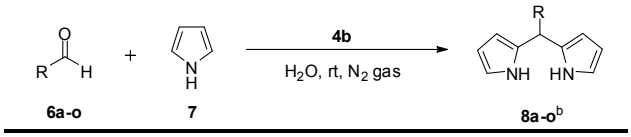


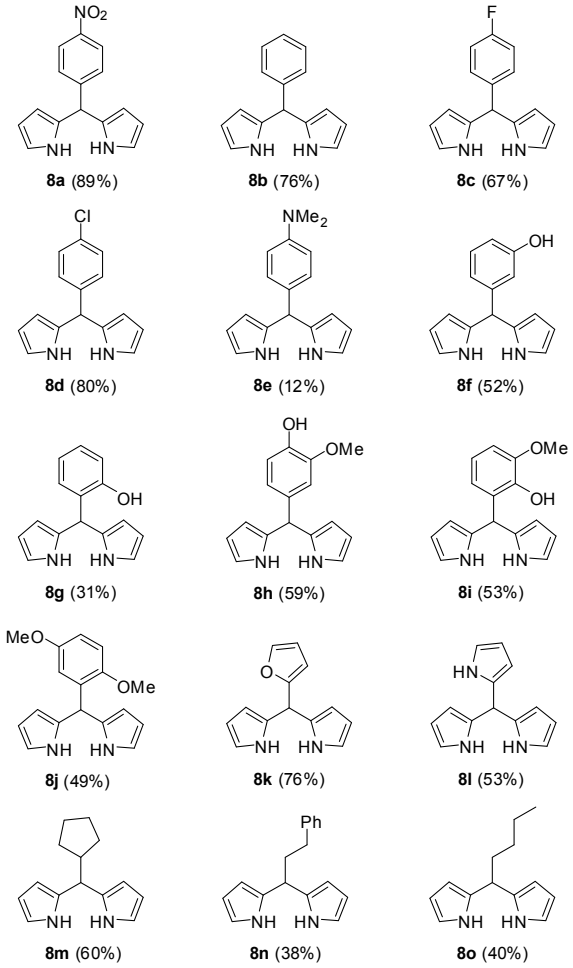
Entry	Catalyst	Catalyst (mol%)	Pyrrole **7** (equiv.)	Time (h)	Yield (%)[b]
1	-	-	5.0	1.0	0(25)[c]
2	CF_3SO_3H	20	5.0	1.0	62
3	H_2SO_4	20	5.0	1.0	66
4	*p*TsOH	20	5.0	1.0	49
5	**3b**, [bsmim][OTf]	20	5.0	1.0	65
6	**4b**, [bsmim][HSO_4]	20	5.0	1.0	73
7	**4c**, [bspy][HSO_4]	20	5.0	1.0	72
8	**4b**, [bsmim][HSO_4]	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 other effects of the most efficient catalyst (**4b**) (10 mol%) in concert with reaction temperature and amount of pyrrole (**7**) on yield of desired product (**8a**) were explored (Table 2, entries 11-17). At 10 °C, some of the remaining initial aldehyde was observed on the TLC, indicating the reaction was incompleted and isolated yield of desired product (**8a**) was only 31% (Table 2, entry 11). With decreasing pyrrole (**7**) to 2.5 equivalents, the desired product (**8a**) were obtained in lower yields, 31 and 59 % (**8a**) after 1.5 and 3.0 h, respectively (Table 2, entries 12 and 13, respectively). High concentrated reaction volume could improve yield of desired product (**8a**) to 73% after 1.5 h (Table 2, entry 14). However this result indicated that a reduction in amount of pyrrole (**7**) to 2.5 equivalents resulted in lower yield of desired product (**8a**) than that when pyrrole (**7**) was present at 5.0 equivalents. It is obvious that 2.5 equivalent of pyrrole (**7**) was not sufficient to produce the desired product (**8a**) in highest yield using this protocol. Nonetheless, yield was higher than that in previous studies with a similar amount of pyrrole (7).[6,7j,7l] The catalyst (**4b**) was tested with 5 mol% under high concentration condition 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, desired product

Table 3 Synthesis of dipyrrolemethanes 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.

yield was lowest, 53%, when 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 4-nitrobenzadehyde substrate. After completion of the reaction (Table 2, entry 10), the product (**8a**) was isolated from 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.

The chemical suitability of the substrate for the green synthesis of diprromethane derivatives *via* SO_3H-IL catalyzed Friedel-Crafts reaction was investigated under this optimized reaction condition (Table 2, entry 10). A variety of either aromatic or aliphatic aldehydes were tested with respect to moderate and good product yields (Table 3). Corresponding desirable products were yielded depending on electronic and steric effects of 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 electron withdrawing group (**6a**, **6c**, and **6d**) including benzadehyde (**6b**) produced good yield of products (**8a-8d**; 67-89% yields). While aldehyde substrates with electron donating group (**6f-6j**) provided the products (**8i-8j**) in moderate yields (31-59% yields). In contrast high electron-rich 4-(*N*,*N*-dimethylamino)benzaldehyde (**6e**) produced very low product yield, 12%, (**8e**) for 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%).

Conclusions

In summary, we have demonstrated a green method for synthesis of dipyrromethanes under mild and metal-free condition in water media. The reaction was performed by using catalytic amount of SO_3H-IL, which consisted of imidazolium cation and HSO_4 anion, named as [bsmim][HSO_4]. The desired products were successfully obtained in moderate to good yields with a wide range of aldehyde substrates. Corresponding products are easily separated from reaction system by simple extraction and catalyst recycling was possible for subsequent reactions. This protocol may offer the 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 AVANC (400 MHz). All spectra were measured in $CDCl_3$ or CD_3OD solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (δ 0.00), $CDCl_3$ (δ 7.26) or CD_3OD (δ 3.34) as internal standard. Carbon NMR spectra were recorded on a BRUKER AVANC (100 MHz). All spectra were measured in $CDCl_3$ or CD_3OD solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to $CDCl_3$ (δ 77.0) or CD_3OD (δ 49.0) as internal standard. High-resolution mass spectra (HRMS) data were obtained with a Bruker Daltonics - micrOTOF-Q. Infrared spectra were determined 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 portion at room temperature. The reaction mixture was heated to 80 ^oC with stirring for 24 h, and then cooled to room temperature resulting precipitate white solid. The white solid was filtered and washed with ethanol (3×5 mL) to remove any unreacted starting materials, and then the solid was dried in vacuum to give the zwitterion compound as white solid in 81% yield (9.7403 g). mp. 197-200 ^oC; ^{1}H-NMR (400 MHz, CD_3OD): δ 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): δ 9.48, 22.83, 29.44, 35.35, 51.39, 122.26, 123.63, 146.01. A mixture of zwitterion compound (1.50 g, 6.46 mmol) in anhydrous toluene (3.00 mL) was added stoichiometric amount of acid HX (1 eq.) in portion at room temperature. The reaction mixture was then stirred at 80 ^oC for 24 h. After white solid was all soluble, the reaction mixture was cooled to room temperature, removed toluene layer and extracted with ethyl acetate (3×10 mL) to remove 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): δ 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): δ 9.49, 22.76, 29.40, 35.37, 48.97, 51.43, 122.20, 123.63, 145.98.

1-Butylsulfonic-2,3-dimethylimidazoluium hydrogen sulfate (4a). 99% yield (2.1152 g) as a brown color oil; ^{1}H-NMR (400 MHz, CD_3OD): δ 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): δ 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): δ 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): δ 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 portion at room temperature. The reaction mixture was heated to 80 °C with stirring for 24 h, and then cooled to room temperature resulting precipitate white solid. The white solid was filtered and washed with ethanol (3×5 mL) to remove any unreacted starting materials, and then the solid was dried in vacuum to give the zwitterion compound as white solid in 71% yield (9.4700 g). mp. 193-196 °C; ^{1}H-NMR (400 MHz, CD_3OD): δ 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): δ 22.72, 29.83, 36.47, 50.31, 51.41, 123.72, 124.99, 138.05. A mixture of zwitterion compound (1.50 g, 6.87 mmol) in anhydrous toluene (3.00 mL) was added stoichiometric amount of acid HX (1 eq.) in portion at room temperature. The reaction mixture was then stirred at 80 °C for 24 h. After white solid was all soluble, the reaction mixture was cooled to room temperature, removed toluene layer and extracted with ethyl acetate (3×10 mL) to remove 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): δ 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): δ 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): δ 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): δ 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): δ 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): δ 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 portion at room temperature. The reaction mixture was heated to 80 °C with stirring for 24 h, and then cooled to room temperature resulting precipitate white solid. The white solid was filtered and washed with ethanol (3×5 mL) to remove any unreacted starting materials, and then the solid was dried in vacuum to give the zwitterion compound as white solid in in 57% yield (7.7744 g). Mp. 193-196 °C; ^{1}H-NMR (400 MHz, CD_3OD): δ 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): δ 22.70, 31.16, 51.28, 62.52, 129.52 (3C), 146.06, 146.85. A mixture of zwitterion compound (1.50 g, 6.97 mmol) in anhydrous toluene (3.00 mL) was added stoichiometric amount of acid HX (1 eq.) in portion at room temperature. The reaction mixture was then stirred at 80 °C for 24 h. After white solid was all soluble, the reaction mixture was cooled to room temperature, removed toluene layer and extracted with ethyl acetate (3×10 mL) to remove 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): δ 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): δ 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): δ 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): δ 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): δ 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): δ 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 degas water (3.0 mL) was added aldehyde (1.0 mmol) and 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 sodium sulfate anhydrous. The solvent was removed by rotary 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,1j,6,7b,7e,7h,7k,7l,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, $CDCl_3$): δ 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, $CDCl_3$): δ 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,1e,1j,1f,6,7b,7e,7g,7h,7k,7l,7m,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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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,7m,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, $CDCl_3$): δ 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, $CDCl_3$); δ 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,7l] 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, $CDCl_3$): δ 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, $CDCl_3$); δ 40. 63(2C), 43.18, 106. 90(2C), 108. 44(2C), 112. 91(2C), 116.8 0(2C), 129.0 9(2C), 130.10, 133. 37(2C), 149.81; HRMS (ESI) *m/z* $C_{17}H_{19}N_3$ $[M+H]^+$ calcd 266.1657, found 0266.1650.

***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, $CDCl_3$): δ 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, $CDCl_3$); δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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 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, $CDCl_3$); δ 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, $CDCl_3$): δ 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, $CDCl_3$); δ 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,7l,7m,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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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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Notes and references

1 (*a*) C.-H. Lee, J. H. Lindesey, *Tetrahedron*, 1994, **50**, 11427-11440; (*b*) T. Mizutani, T. Ema, T. Tomita, Y. Kuroda, H. Ogoshi, *J. Am. Chem. Soc.*, 1994, **116**, 4240-4250; (*c*) C.-H. Lee, F. Li, K. Iwamoto, J. Dadok, A. A. Bothner-By, J. S. Lindsey, *Tetrahedron*, 1995, **51**, 11645-11672; (*d*) J-i. Setsune, M. Hashimoto, K. Shiozawa, J-y. Hayakawa, T. Ochi and R. Masuda, *Tetrahedron*, 1998, **54**, 1407-1424; (*e*) R. Naik, P. Joshi, S. P. Kaiwar, R. K. Deshpande, *Tetrahedron*, 2003, **59**, 2207-2213; (*f*) G. R. Geier, J. S. Lindsey, *Tetrahedron*, 2004, **60**, 11435-11444; (*g*) S. Kitaoka, K. Nobuoka, Y. Ishikawa, *Chem. Commun*., 2004, 1902-1903; (*h*) S.-J. Hong, M.-H. Lee, C.-H. Lee, *Bull. Korean Chem. Soc.*, 2004, **25**, 1545-1550; (*i*) S. J. Lee, R. A. Jensen, C. D. Malliakas, M. G. Kanatzidis, J. T. Hupp, S. T. Nguyen, *J. Mater. Chem*., 2008, **18**, 3640-3642; (*j*) Z. Abada, L. Ferrié, B. Akagah, A. T. Lormier, B. Figadère, *Tetrahedron Lett*., 2011, **52**, 3175-3178; (*k*) M. H. Beyzavi, C. Nietzold, H.-U. Reissig, *Adv. Synth. Catal*., 2013, **355**, 1409-1422; (*l*) Y. Terazono, E. J. North, A. L. Moore, T. A. Moore, D. Gust, *Org. Lett*., 2012, **14**, 1776-1779; (*m*) H. R. A. Golf, H.-U. Reissig, A. Wiehe, *Org. Lett*., 2015, **17**, 982-985; (*n*) H. R. A. Golf, H.-U. Reissig, A. Wiehe, A. *J. Org. Chem.*, 2015, **80**, 5133-5143. (*o*) K. Singh, S. Sharma, P. Kaur, C.-H. Lee, *Tetrahedron*, 2015, **71**, 8373-8390.

2 M. Ak, V. Gancheva, L. Terlemezyan, C. Tanyeli, L. Toppare, *Eur. Polym. J.*, 2008, **44**, 2567-2573.

3 (*a*) T. P. Wijesekera, *Can. J. Chem*., 1996, **74**, 1868-1871; (*b*) P. A. Liddell, D. Kuciauskas, J. P. Sumida, B. Nash, D. Nguyen, A. L. Moore, T. A. Moore, D. Cust, *J. Am. Chem. Soc.*, 1997, **119**, 1400-1405; (*c*) L. Ruhlmann, S. Lobstein, M. Gross, A. Giraudeau, *J. Org. Chem*., 1999, **64**, 1352-1355; (*d*) C. M. Drain, J. T. Hupp, K. S. Suslick, M. R. Wasielewski, X. Chen, *J. Porphyrins Phthalocyanines*, 2002, **6**, 243-258; (*e*) H. Imahori, *Org. Biomol. Chem.*, 2004, **2**, 1425-1433; (*f*) A. Wiehe, Y. M. Shaker, J. C. Brandt, S. Mebs, M. O. Senge, *Tetrahedron*, 2005, **61**, 5535-5564; (*g*) S. Fox, R. W. Boyle, *Tetrahedron*, 2006, **62**, 10039-10054; (*h*) J. L. Sessler, E. Tomat, *Acc. Chem. Res*., 2007, **40**, 371-379; (*i*) M. Fazekas, M. Pintea, M. O. Senge, M. Zawadzka, *Tetrahedron Lett*., 2008, **49**, 2236-2239; (*j*) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res*., 2009, **42**, 1890-1898; (*k*) H. Song, M. Taniguchi, J. R. Diers, C. Kirmaier, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Phys. Chem. B*, 2009, **113**, 16483-16493; (*l*) N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res*., 2009, **42**, 1922-1934; (*m*) M. G. Walter, A. B. Rudine, C. C. Wamser, *J. Porphyrins Phthalocyanines*, 2010, **14**, 759-792; (*n*) S.-H. Lee, A. G.

Larsen, K. Ohkubo, Z.-L. Cai, J. R. Reimers, S. Fukuzumi, M. Crossley, *J. Chem. Sci.*, 2012, **3**, 257-269.

4 (*a*) N. Nishino, R. W. Wagner, J. S. Lindsey, *J. Org. Chem*., 1996, **61**, 7534-7544; (*b*) S. Banfi, E. Caruso, S. Caprioil, L. Mazzagatti, G. Canti, R. Ravizza, M. Gariboldi, E. Monti, *Bioorg. Med. Chem*., 2004, **12**, 4853-4860; (*c*) M. R. Detty, S. L. Gibson, S. J. Wagner, *J. Med. Chem*., 2004, **47**, 3897-3915; (*d*) S. Banfi, E. Caruso, L. Buccafurni, R. Murano, E. Monti, M. Gariboldi, E. Papa, P. Gramatica, *J. Med. Chem.*, 2006, **49**, 3293-3304; (*e*) H. Tamiaki, Y. Kotegawa, K. Mizutani, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 6037-6040.

5 (*a*) C. T. Walsh, S. Garneau-Tsodikova, A. R. Howard-Jones, *Nat. Prod. Rep.*, 2006, **23**, 517-531. (*b*) J. Regourd, A. A.-S. Ali, A. Thompson, *J. Med. Chem.*, 2007, **50**, 1528-1536; (*c*) R. I. SáezDíaz, J. Regourd, P. V. Santacroce, J. T. Davis, D. L. Jakeman, A. Thompson, *Chem. Commun*., 2007, 2701–2703; (*d*) K. Papireddy, M. Smilkstein, J. X. Kelly, Shweta, S. M. Salem, M. Alhamadsheh, S. W. Haynes, G. L. Challis, K. A. Reynolds, *J. Med. Chem*., 2011, **54**, 5296-5306.

6 J. Jaratjaroonphong, S. Tuengpanya, R. Saeeng, S. Udompong, K. Srisook, *Eur. J. Med. Chem*., 2014, **83**, 561-568.

7 (*a*) J. P. Nagarkatti, K. R. Ashley, *Synthesis*, 1974, 186-187. (*b*) S. J. Vigmond, M. C. Chang, K. M. R. Kallury, M. Thompson, *Tetrahedron Lett.*, 1994, **35**, 2455-2458; (*c*) C. Brückner, V. Karunaratne, S. J. Rettig, D. Dolphin, *Can. J. Chem.*, 1996, **74**, 2182-2193; (*d*) M. D'Auria, E. De Luca, V. Esposito, G. Mauriello, R. Racioppi, *Tetrahedron*, 1997, **53**, 1157-1166; (*e*) B. J. Littler, M. A. Miller, C.-H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle, J. S. Lindsey, *J. Org. Chem*., 1999, **64**, 1391-1396; (*f*) J.-W. Ka, C.-H. Lee, *Tetrahedron Lett*., 2000, **41**, 4609-4613; (*g*) J. K. Laha, S. Dhanalckshmi, M. Taniguchi, A. Ambroise, J. S. Lindscy, *Org. Process Res. Dev*., 2003, **7**, 799-812; (*h*) A. J. F. N. Sobral, N. G. C. L. Rebanda, M. D. Silva, S. H. Lampreia, M. R. Silva, A. M. Beja, J. A. Paixao, A. M. d'A. R. Gonsalves, *Tetrahedron Lett*., 2003, **44**, 3971-3973; (*i*) C. Biaggi, M. Benaglia, L. Raimondi, F. Cozzi, *Tetrahedron*, 2006, **62**, 12375-12379; (*j*) P. Thamyongkit, A. D. Bhise, M. Taniguchi, J. S. Lindsey, *J. Org. Chem.*, 2006, **17**, 903-910; (*k*) P.-A. Faugeras, B. Boëns, P-H. Elchinger, J. Vergnaud, K. Teste, R. Zerrouki, *Tetrahedron Lett*., 2010, **51**, 4630-4632; (*l*) Z. Yan, L. Jun, S. Zhical, *Chin. J. Chem.*, 2010, **28**, 259-262; (*m*) K. Singh, S. Sharma, A. Sharma, *J. Mol. Catal. A: Chem.*, 2011, **347**, 34-37. (*n*) D. T. Gryko, D. Gryko, C.-H. Lee, *Chem. Soc. Rev.*, 2012, **41**, 3780-3789.

8 (*a*) B. Temelli, C. Unaleroglu, *Tetrahedron*, 2006, **62**, 10130-10135; (*b*) B. Temelli, D. I. Tasgin, C. Unalerogu, *Tetrahedron*, 2010, **66**, 6765-6768.

9 (*a*) K. Singh, S. Behal, M. S. Hundal, *Tetrahedron*, 2005, **61**, 6614-6622; (*b*) K. Singh, S. Behal, P. K. Deb, *Synth. Commun*., 2005, **35**, 929-934.

10 (*a*) K. Manabe, Y. Mori, S. Kobayashi, *Tetrahedron*, 2001, **57**, 2537-2544; (*b*) C.-J. Li, *Chem. Rev*., 2005, **105**, 3095-3165; (*c*) V. Mévellec, B. Leger, M. Mauduit, A. Roucoux, *Chem. Commun*., 2005, 2838-2839; (*d*) S. Shirakawa, S. Kobayashi, *Org. Lett*., 2006, **8**, 4939-4942; (*e*) Y. Ye, Q. Ding, J. Wu, *Tetrahedron*, 2008, **64**, 1378-1382; (*f*) F. Dong, F. Zhenghao, L. Zuliang, *Catal. Commu.*, 2009, **10**, 1267-1270; (*g*) L.-M. Wang, N. Jiao, J. Qiu, J.-J. Yu, J.-Q. Liu, F.-L. Guo, Y. Liu, *Tetrahedron*, 2010, **66**, 339-343; (*h*) L. Lin, Y. Li, S. Zhang, S. Li, *Synlett*, 2011, 1779-1783; (*i*) R. Sharma, A. K. Pandey, P. M. S. Chauhan, *Synlett.*, 2012, **23**, 2209-2214; (*j*) K. Pradhan, S. Paul, A. R. Das, *Tetrahedron Lett*., 2013, **54**, 3105-3110.

11 (*a*) T. Welton, *Chem. Rev*., 1999, **99**, 2071-2083; (*b*) V. I. Pârvulescu, C. Hardacre, *Chem. Rev*., 2007, **107**, 2615-2665; (*c*) J. Pavlinac, M. Zupan, K. K. Laali, S. Stavber, *Tetrahedron*, 2009, **65**, 5625-5662.

12 (*a*) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. D. Jr, *J. Am. Chem. Soc.*, 2002, **124**, 5962-5963; (*b*) Y. Gu, F. Shi, Y. Deng, *J. Mol. Catal A: Chem*., 2004, **212**, 71-75; (*c*) G. Zhao, T. Jiang, H. Gao, B. Han, J. Huang, D. Sun, *Green Chem*., 2004, **6**, 75-77; (*d*) H. Xing, T. Wang, Z. Zhou, Y. Dai, *Ind. Eng. Chem. Res*., 2005, **44**, 4147-4150; (*e*) Z. Duan, Y. Gu, J. Zhang, L. Zhu, Y. Deng, *J. Mol. Catal. A: Chem*., 2006, **250**, 163-168; (*f*) S. Sahoo, T. Joseph, S. B. Halligudi, *J. Mol. Catal. A: Chem*., 2006, **250**, 179-182; (*g*) V. I. Pârvulescu, C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615-2665; (*h*) D. Fang, Q.-R. Shi, J. Cheng, K. Gong, Z.-L. Liu, *Appl. Catal. A: Gen*., 2008, **345**, 158-163; (*i*) A. R. Hajipour, Y. Ghayeb, N. Sheikhan, A. E. Ruoho, *Tetrahedron Lett*., 2009, **50**, 5649-5651; (*j*) X. Lui, L. Xiao, H. Wu, Z. Li, J. Chen, C. Xia, *Catal. Commun*., 2009, **10**, 424-427; (*k*) A. S. Smarasekara, O. S. Owereh, *Catal. Commun*., 2010, **11**, 1072-1075; (*l*) J. Akbari, A. Heydari, H. R. Kalhor, S. A. Kohan, *J. Comb. Chem*., 2010, **12**, 137-140; (*m*) P. P. Salvi, A. M. Mandhare, A. S. Sartape, D. K. Pawar, S. H. Han, S. S. Kolekar, *C. R. Chimie*, 2011, **14**, 883-886; (n) R. Kore, R. Srivastava, *J. Mol. Catal. A: Chem.*, 2011, **345**, 117-126; (*o*) Z. Chen, Q. Zhu, W. Su, *Tetrahedron Lett*., 2011, **52**, 2601-2604; (*p*) X. Liang, C. Qi, *Catal. Commun.*, 2011, **12**, 808-812; (*q*) M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare, H. G. Kruger, Z. Asgari, V. Khakyzadeh, M. Kazem-Rostami, *J. Org. Chem.*, 2012, **77**, 3640-3645; (*r*) F. Han, L. Yang, Z. Li, C. Xia, *Org. Biomol. Chem*., 2012, **10**, 346-354; (*s*) A. Zare, F. Abi, A. R. Moosavi-Zare, M. H. Beyzavi, M. A. Zolfigol, *J. Mol. Liq*., 2013, **178**, 113-121; (*t*) L. He, S. Qin, T. Chang, Y. Sun, X. Gao, *Catal. Sci. Technol.*, 2013, **3**, 1102-1107.

13 (a) H. Xing, T. Wang, Z. Zhou, Y. Dai, *Ind. Eng. Chem. Res*., 2005, **44**, 4147-4150; (*b*) H. Xing, T. Wang, Z. Zhou, Y. Dai, *J. Mol. Catal. A: Chem*., 2007, **264**, 53-59.