Note

1-Butyl-3-methylimidazolium Hydrogen Sulfate [bmim]HSO_4: An Efficient Reusable Acidic Ionic Liquid for the Synthesis of 1,8-Dioxo-octahydroxanthenes

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1-Butyl-3-methylimidazolium hydrogen sulfate [bmim]HSO_4 as an acidic ionic liquid was prepared and used as a catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes in excellent yields and short reaction times at 80 °C. The ionic liquid was easily separated from the reaction mixture by water extraction and was recycled four times without any loss in activity.

Keywords: Acidic ionic liquids; [bmim][HSO_4]; Xanthenes; Dimedone; Aldehydes.

INTRODUCTION

Ionic liquids (ILs) are now well known as salts with melting points below 100 °C, and typically have broad liquid ranges, low vapor pressures, and may be both non-coordinating and highly polar. They are receiving considerable global attention because they offer a unique environment for chemistry, biocatalysts, separation science, material synthesis, and electrochemistry.[1] These ionic liquids have several interesting properties such as excellent chemical and thermal stability, non-volatility, a non-coordinating nature, good solvating capability, a wide liquid range, and ease of recycling. Furthermore, their hydrophobicities/hydrophilicities can be tuned by appropriate modification of the cation or anion.[1,2] Therefore, room temperature ionic liquids have found wide use in catalytic and non-catalytic reactions.[3] In addition, the synthesis of task-specific ionic liquids, which have a functional group in their framework, may expand the application of ionic liquids in organic chemistry.[4-6] Recently, acidic ionic liquids have been successfully used in these reactions due to their unique properties such as being vapor-less and their reusability.[5-9]

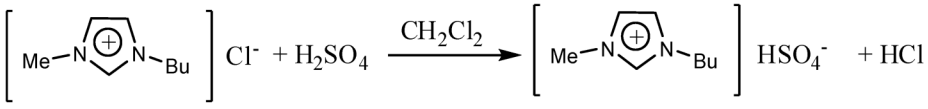
Xanthenes are an important class of organic compounds that find use as dyes, fluorescent material for visualization of biomolecules and in laser technologies due to their useful spectroscopic properties.[10] Xanthenes have also received significant attention from many pharmaceutical and organic chemists essentially because of the broad spectrum of their biological and pharmaceutical properties such as their antiviral,[11] antibacterial,[12] and antinociceptive activities[13] as well as their efficiency in photodynamic therapy[14] and anti-inflammatory activities.[15] There are several reports in the literature for the synthesis of 1,8-dioxooctahydroxanthene derivatives employing aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione; these include $InCl_3.4H_2O$ in ionic liquid,[16] solid-state condensation by grinding at room temperature,[17] diammonium hydrogen phosphate,[18] *p*-dodecylbenzenesulfonic acid in water,[19] Fe^{3+}-montmorilonite,[20] $NaHSO_4$-SiO_2 or silica chloride,[21] amberlyst-15,[22] silica sulfuric acid,[23] tetrabutylammonium hydrogen sulfate,[24] trimethylsilylchloride (TMSCl),[25] 1-methylimidazolium trifluroacetate,[26] and montmorillonite K-10-supported.[27] Each of these methods have their own advantages but also some of them often suffer from one or more disadvantages such as prolonged reaction time, tedious work-up processes, low yield, lack of easy availability/preparation of starting materials, expensive reagents and hazardous reaction conditions. Hence, a more realistic catalyzed condensation between active methylene carbonyl compound and aldehyde is needed for contemporary chemical synthesis with less waste and more facile isolation of products, perhaps with reuse of the catalysts as well.

Recently, 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim]HSO_4) as an acidic ionic liquid (Scheme I) has been used as an efficient IL catalyst for many organic transformations.[6-7,28]

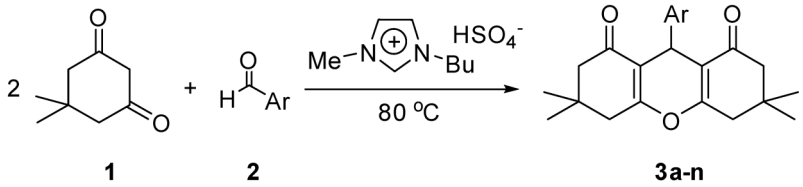
RESULTS AND DISCUSSION

In our continued interest in the development of a highly expedient methodology[29-32] for the synthesis of fine chemicals and heterocyclic compounds of biological im-

Scheme I Preparation of 1-butyl-3-methylimidazolium hydrogen sulfate [bmim][HSO_4]



Scheme II Synthesis of 1,8-dioxo-octahydroxanthene using [bmim][HSO_4] as catalyst



portance, we report here the synthesis of 1,8-dioxo-octahydroxanthenes in the presence of 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim]HSO_4) as an acidic ionic liquid (Scheme II).

We first studied a reaction between 5,5-dimethyl-1,3-cyclohexanedione (**1**) and benzaldehyde by screening the reaction conditions. In order to determine the optimum conditions, we examined the influence of the reaction temperature, the reaction time, and the amounts of IL (Table 1). In all reactions the conditions were optimized for a 100% conversion. It can be seen that the best result was obtained with 0.1 g of [bmim]HSO_4 at 80 ºC (Table 1, entry 5).

After optimizing the conditions, we next examined the generality of these conditions to other substrates using several aromatic aldehydes (Scheme II). The results are summarized in Table 2.

It can be seen that [bmim]HSO_4 as environmentally benign acidic IL catalyzed the condensation of dimedone and a wide range of aromatic aldehydes at 80 ºC. As indicated in Table 2, in all cases the reaction gives the products in good yields and prevents problems which many associate with solvent use such as cost, handling, safety and pollution.

To make this method more suitable we examined the reusability of the [bmim]HSO_4 using 5,5-dimethyl-1,3-cyclohexanedione and benzaldehyde as model substrates. For this aim, after completion of the reaction (monitored by TLC), water was added to the reaction mixture and then the solid was isolated by filtration. The IL in water could be recovered easily by evaporation at 80 ºC in a vacuum. The recovered IL was washed with diethyl ether. After evaporation at 80 ºC in a vacuum for 1 h, IL was assessed by ^{1}H NMR spectroscopy and no traces of 5,5-dimethyl-1,3-cyclohexanedione and benzaldehyde were detected. Investigations proved the successive reuse of the recovered ionic liquid. It could be seen that no considerable change in activity of [bmim]HSO_4 was observed even after four consecutive runs (Table 2, product **3a**).

Table 1. Optimization of the reaction conditions on the condensation reaction of dimedone (1 mmol), benzaldehyde (1 mmol) in the presence of IL

Entry	Temperature (°C)	Time (h)	Yield (%)[a]
1	25	20	Trace
2	30	16	40
3	50	9	75
4	70	5	85
5	80	3	85
6	90	3	85
7	100	4	80
8	80	15	41[b]

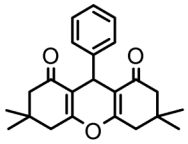
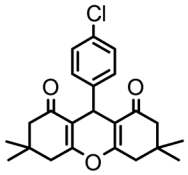
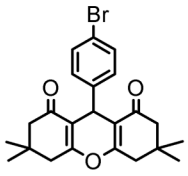
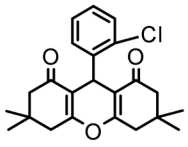
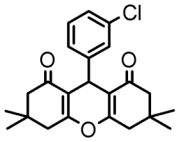
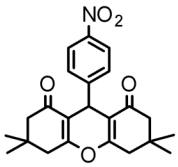
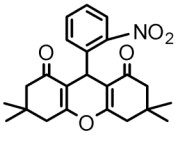
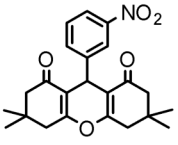
[a] In all reactions the conditions were optimized for a 100% conversion.
[b] The reaction was performed without IL.

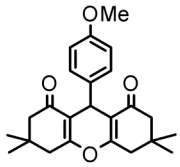
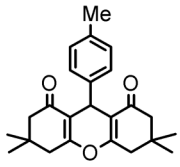
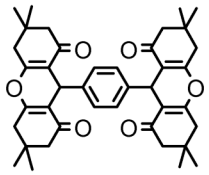
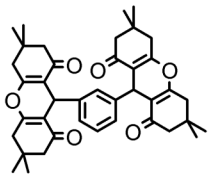
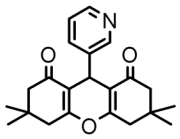
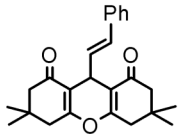
The practical synthetic efficiency of this reaction was highlighted by the reaction of terephthaldehyde (**4**) and isophthaldehyde (**5**) with dimedone (**1**) to give structurally complex xanthenone derivatives (**3k**, and **3l**) (Scheme III).

An important feature of this method is that the acid-sensitive functionality present in the molecule remains unaffected. This fact was amply demonstrated by the reaction of pyridine-3-caboxaldehyde (**6**) with dimedone (**1**), which gave 9-(pyridine-3-yl)-1,8-dioxo-octahydroxanthene (**3m**) in excellent yield (Scheme IV).

In conclusion, we have developed a novel and efficient method for the synthesis of 1,8-dioxo-octahydroxanthenes in high yields employing [bmim]HSO_4 as an acidic

Table 2. Synthesis of 1,8-dioxo-octahydroxanthenes by the reaction of dimedone and aromatic aldehydes in the presence of [bmim]HSO_4 at 80 °C

Entry	Ar	Product	Time (h)	Yield[a]%
1	C_6H_5	 **3a**	3.0	85, 83, 82, 80[b]
2	4-Cl-C_6H_4	 **3b**	3.5	95
3	4-Br-C_6H_4	 **3c**	3.5	90
4	2-Cl-C_6H_4	 **3d**	3.5	89
5	3-Cl-C_6H_4	 **3e**	3.0	78
6	4-NO_2-C_6H_4	 **3f**	1.5	85
7	2-NO_2-C_6H_4	 **3g**	3.5	76
8	3-NO_2-C_6H_4	 **3h**	3.0	87

9	4-MeO-C_6H_4	 **3i**	3.5	89
10	4-Me-C_6H_4	 **3j**	6.0	91
11	4-OHC-C_6H_4	 **3k**	6.0	80
12	3-OHC-C_6H_4	 **3l**	7.0	82
13	3-Pyridyl	 **3m**	3.0	89
14	C_6H_5-CH=CH-	 **3n**	1.5	94

[a] Isolated yield.
[b] Isolated yield by using reused IL for four runs.

IL. The application of an inexpensive, easily available and reusable IL makes this method simple, clean, practical and economically viable. In contrast to other acids, storage and handling of this compound do not need special precautions and it can be stored on the bench top for weeks without losing its activity.

EXPERIMENTAL SECTION

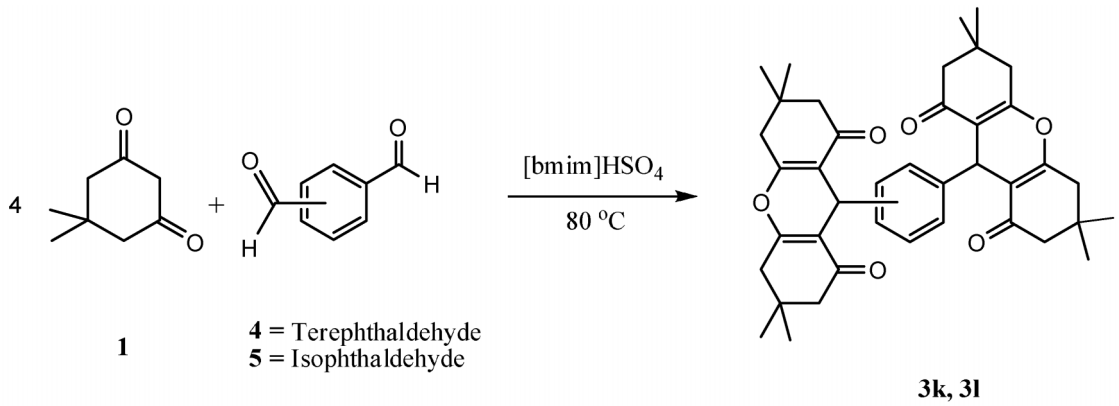
General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The products were characterized by comparison of their spectral (IR, ^{1}H NMR), TLC and physical data with those reported in the literature. The 1-butyl-3-methylimidazolium hydrogen sulfate [bmim][HSO_4] was synthesized according to a reported procedure for 1-hexyl-3-methylimidazolium hydrogen sulfate ([hmim][HSO_4]).[5,6]

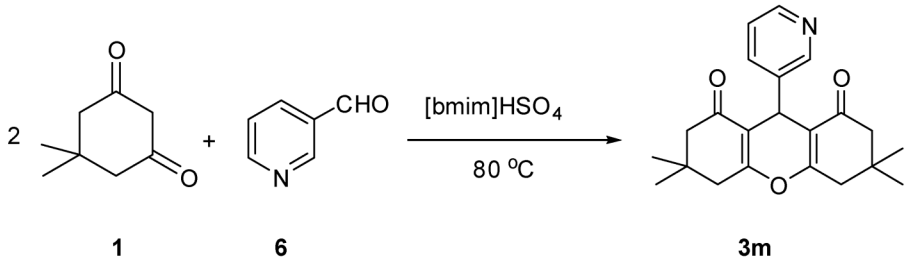
General procedure for the synthesis of 1,8-dioxo-octahydroxanthene derivatives

To a mixture of an aromatic aldehyde (1 mmol) and

Scheme III Synthesis of bis(1,8-dioxo-octahydroxanthenes)



Scheme IV Synthesis of 9-(pyridine-3-yl)-1,8-dioxo-octahydroxanthene



5,5-dimethyl-1,3-cyclohexanedione (2 mmol) in a round bottomed flask, [bmim]HSO_4 (0.1 g) was added. The mixture was heated at 80 ºC and the reaction was monitored by TLC. After completion of the reaction, water was added to the mixture and then filtered. The solid residue was recrystallized from ethanol.

Spectral data

3a: mp 203-204 °C, (Lit.:[24] 204-206 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.02 (s, 6H), 1.13 (s, 6H), 2.19 (d, 2H, J = 16.2 Hz), 2.26 (d, 2H, J = 16.2 Hz), 2.50 (s, 4H), 4.78 (s, 1H), 7.12 (t, 1H, J = 7.2 Hz), 7.24 (t, 2H, J = 7.5 Hz), 7.32 (d, 2H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.75, 29.69, 32.26, 32.61, 41.29, 51.18, 116.07, 126.76, 128.45, 128.80, 144.54, 162.70, 196.76.

3b: mp 230-232 °C, (Lit.:[25] 230-232 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.03 (s, 6H), 1.14 (s, 6H), 2.20 (d, 2H, J = 16.3 Hz), 2.27 (d, 2H, J = 16.3 Hz), 2.50 (s, 4H), 4.75 (s, 1H), 7.22 (d, 2H, J = 8.5 Hz), 7.27 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.72, 29.68, 31.89, 32.61, 41.28, 51.13, 115.69, 128.63, 130.19, 132.45, 143.13, 162.83, 196.71.

3c: mp 240-241 °C, (Lit.:[25] 240-242 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.03 (s, 6H), 1.14 (s, 6H), 2.20 (d, 2H, J = 16.3 Hz), 2.27 (d, 2H, J = 16.3 Hz), 2.50 (s, 4H), 4.74 (s, 1H), 7.21 (d, 2H, J = 8.4 Hz), 7.37 (d, 2H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.73, 29.69, 31.98, 32.62, 41.28, 51.12, 115.63, 120.66, 130.60, 131.57, 143.64, 162.82, 196.69.

3d: mp 225-227 °C, (Lit.:[24] 225-227 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.05 (s, 6H), 1.13 (s, 6H), 2.19 (d, 2H, J = 16.2 Hz), 2.26 (d, 2H, J = 16.2 Hz), 2.48 (s, 4H), 5.03 (s, 1H), 7.09 (dt, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.19 (dt, 1H, J_1 = 7.6 Hz, J_2 = 1.1 Hz), 7.26 (dd, 1H, J_1 = 7.9 Hz, J_2 = 1.0 Hz),), 7.46 (d, 1H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.79, 29.69, 32.28, 32.43, 41.25, 51.14, 114.13, 126.74, 128.20, 130.56, 133.34, 133.88, 140.32, 163.37, 196.84.

3e: mp 184-186 °C, (Lit.:[24] 182-184 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.99 (s, 6H), 1.09 (s, 6H), 2.17 (d, 2H, J = 16.2 Hz), 2.22 (d, 2H, J = 16.2 Hz), 2.46 (s, 4H), 4.71 (s, 1H), 7.06 (dt, 1H, J_1 = 9.1 Hz, J_2 = 1.5 Hz), 7.13 (t, 1H, J = 7.9 Hz), 7.21 (d, 1H, J = 1.2 Hz), 7.23 (t, 1H, J = 1.3 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.79, 29.62, 32.16, 32.63, 41.27, 51.13, 115.51, 127.05, 127.40, 128.75, 129.65, 134.28, 146.54, 162.99, 196.67.

3f: mp 222-223 °C, (Lit.:[24] 221-223 °C; ^{1}H NMR

($CDCl_3$, 500 MHz), δ: 1.02 (s, 6H), 1.15 (s, 6H), 2.20 (d, 2H, J = 16.3 Hz), 2.29 (d, 2H, J = 16.3 Hz), 2.53 (s, 4H), 4.86 (s, 1H), 7.51 (dd, 2H, J_1 = 7.0 Hz, J_2 = 1.7 Hz), 8.12 (dd, 2H, J_1 = 7.0 Hz, J_2 = 1.7 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.70, 29.64, 32.64, 32.79, 41.27, 51.03, 114.96, 123.83, 129.78, 146.92, 151.94, 163.36, 196.63.

3g: mp 252-254 °C, (Lit.:[24] 248-249 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H), 1.07 (s, 6H), 2.13 (d, 2H, J = 16.2 Hz), 2.21 (d, 2H, J = 16.2 Hz), 2.45 (s, 4H), 5.51 (s, 1H), 7.21 (dt, 1H, J_1 = 7.7 Hz, J_2 = 1.4 Hz), 7.34 (d, 1H, J = 7.5 Hz), 7.41 (dt, 1H, J_1 = 7.5 Hz, J_2 = 1.2 Hz), 7.73 (d, 1H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 28.00, 29.16, 29.36, 32.48, 41.26, 51.04, 114.60, 125.03, 127.59, 131.46, 132.40, 138.46, 150.27, 163.44, 196.73.

3h: mp 170-172 °C, (Lit.:[24] 170-172 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H), 1.10 (s, 6H), 2.15 (d, 2H, J = 16.3 Hz), 2.24 (d, 2H, J = 16.3 Hz), 2.49 (s, 4H), 4.82 (s, 1H), 7.38 (t, 1H, J = 7.9 Hz), 7.79 (d, 1H, J = 7.7 Hz), 7.96 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.9 Hz), 8.02 (t, 1H, J = 1.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.72, 29.61, 32.52, 32.66, 41.23, 51.06, 114.96, 122.06, 123.02, 129.21, 136.07, 146.74, 148.73, 163.46, 196.76.

3i: mp 242-244 °C, (Lit.:[24] 240-242 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H), 1.08 (s, 6H), 2.15 (d, 2H, J = 16.3 Hz), 2.21 (d, 2H, J = 16.3 Hz), 2.44 (s, 4H), 3.71 (s, 3H), 4.68 (s, 1H), 6.74 (dd, 2H, J_1 = 6.8 Hz, J_2 = 1.9 Hz), 7.19 (dd, 2H, J_1 = 6.8 Hz, J_2 = 1.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.76, 29.69, 31.38, 32.61, 41.29, 51.20, 55.52, 113.89, 116.21, 129.73, 136.98, 158.38, 162.48, 196.86.

3j: mp 215-217 °C, (Lit.:[24] 217-218 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.98 (s, 6H), 1.09 (s, 6H), 2.15 (d, 2H, J = 16.3 Hz), 2.20-2.23 (m, 5H), 2.45 (s, 4H), 4.70 (s, 1H), 7.00 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 21.47, 27.80, 29.69, 31.86, 32.62, 41.30, 51.20, 116.19, 128.66, 129.20, 136.17, 141.63, 162.51, 196.80.

3k: mp > 300 °C (dec.); IR (KBr): 3010, 2950, 2881, 1660, 1620, 1462, 1425, 1365, 1200, 1162, 1003, 808 (cm^{-1}); ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.87 (s, 12H), 0.99 (s, 12H), 2.07 (d, 4H, J = 16.2 Hz), 2.11 (d, 4H, J = 16.2 Hz), 2.33 (d, 4H, J = 17.6 Hz), 2.39 (d, 4H, J = 17.6 Hz), 4.59 (s, 2H), 6.99 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.80, 29.41, 31.03, 32.57, 41.12, 51.10, 115.91, 128.16, 142.15, 162.93, 196.73; MS (*m/z*): 624 (M^{+2}) (1.6), 623 (M^{+1}) (8.8), 622 (M^+) (19.2), 416 (9.6), 350 (85.6), 349 (base peak), 311 (9.6), 273 (76.0), 217 (31.2), 161 (20.0), 83 (10.4); Anal. Calc. C, 77.14; H, 7.44; O, 15.41; Found C, 76.98; H, 7.29; O, 15.26.

3l: mp 238-240 °C, (Lit.:[24] 236-238 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.03 (s, 12H), 1.11 (s, 12H), 2.16 (d, 4H, J = 16.2 Hz), 2.21 (d, 4H, J = 16.2 Hz), 2.46 (d, 4H, J = 17.4 Hz), 2.56 (d, 4H, J = 17.4 Hz), 4.72 (s, 2H), 7.07-7.09 (m, 3H), 7.15 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 28.02, 29.57, 31.76, 32.56, 41.27, 51.27, 116.01, 126.84, 128.18, 128.66, 144.04, 162.72, 196.66.

3m: mp 184-186 °C; IR (KBr): 3012, 2960, 1608, 1572, 1424, 1364, 1272, 1236, 1124, 1084, 856 (cm^{-1}); ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.01 (s, 6H), 1.12 (s, 6H), 2.18 (d, 2H, J = 16.3 Hz), 2.26 (d, 2H, J = 16.3 Hz), 2.50 (s, 4H), 4.73 (s, 1H), 7.16-7.18 (m, 1H), 7.72-7.75 (dt, 1H, J_1 = 7.8 Hz, J_2 = 1.9 Hz), 8.36 (dd, 1H, J_1 = 4.7 Hz, J_2= 1.5 Hz), 8.45 (d, 1H, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 27.79, 29.58, 32.63, 41.20, 51.03, 115.11, 123.44, 136.96, 140.07, 148.04, 149.90, 163.24, 196.73; MS (*m/z*): 353 (M^{+2}) (22.2), 352 (M^{+1}) (95.2), 351 (M^+) (base peak), 273 (73.8), 217 (19.8), 161 (11.9), 78 (10.3); Anal. Calc. C, 75.19; H, 7.17; N, 3.99; O, 13.66; Found C, 74.99; H, 6.98; N, 3.77; O, 13.49.

3n: mp 174-176 °C, (Lit.:[24] 176-178 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 1.16 (s, 12H), 2.31 (d, 2H, J = 16.3 Hz), 2.35 (d, 2H, J = 16.3 Hz), 2.45 (d, 2H, J = 18.7 Hz), 2.50 (d, 2H, J = 17.8 Hz), 4.44 (d, 1H, J = 6.0 Hz), 6.30 (d, 1H, J = 16.0 Hz), 6.36 (dd, 1H, J_1 = 16.0 Hz, J_2 = 6.0 Hz), 7.17-7.20 (m, 1H), 7.26 (t, 2H, J = 7.5 Hz), 7.31 (dd, 2H, J_1 = 7.1 Hz, J_2 = 1.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 28.02, 28.32, 29.66, 32.62, 41.38, 51.28, 114.95, 126.77, 127.51, 128.70, 130.84, 131.76, 137.69, 163.44, 196.91.

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