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3,3-(Butane-1,4-diyl)bis(1,2-dimethyl-1*H*-imidazole-3-ium)bromide–Cerium(IV) Ammonium Nitrate: A Novel Reagent for Mild Synthesis of 12-Aryldibenzo[*i*,*b*]pyrano[4,3-*b*]chromenone of Benzyl Alcohols[1]

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Abstract—A novel and efficient procedure for the synthesis of pyrano[4,3-*b*]chromene derivatives via three-component condensation reaction of benzyl alcohol, β-naphthol, and 4-hydroxycoumarin using a catalytical amount of cerium(IV) ammonium nitrate (CAN) and a reusable ionic liquid as a catalyst at room temperature is presented. The method provides several advantages such as simple work-up, environmental friendliness and shorter reaction time along with high yields. All synthesized compounds were elucidated by comparison with authentic samples, IR, ^{1}H, and ^{13}C NMR spectroscopy, and elemental analysis.

Keywords: pyrano[4,3-*b*]chromene, 4-hydroxycoumarin, β-naphthol, benzyl alcohol

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INTRODUCTION

Chromenes attract close attention as biologically active compounds [1, 2] and reagents in organic synthesis [3, 4]. Fused chromenes demonstrate anti-tumor [5], anti-cancer [6], anti-coagulant [6], anti-Alzheimer [7], anti-bacterial [8, 9], anti-malaria [10], diuretic [11], and spasmolytic [12–14] activities.

The typical approach to pyrano[4,3-*b*]chromene involves a one-pot reaction of tetrahydro-chromeno [4,3-*b*]chromene-6,8-dione with tetrahydropyrano[4,3-*b*]chromene-1,9-dione derivatives under solvent-free conditions [15]. Recently some original approaches to new chromenes were presented [16–18]. Among those were 7-tetrahydropyran-2-yl chromanes: β-site amyloid precursor protein cleaving enzyme 1 (BACE1) inhibitors that reduced amyloid β-protein (Aβ) in the central nervous system [18].

The use of ionic liquids as reaction media and catalysts [19–21] could solve the problems of the earlier approaches to pyrano[4,3-*b*]chromenes: solvents emission and catalysts recycling.

RESULTS AND DISCUSSION

Following the earlier studies of synthesis of heterocyclic pharmaceutically sound compounds [22–26], we present herein the experimental data on the synthesis of pyrano[4,3-*b*]chromenes, using various benzyl alcohols, 2-naphthol and 4-hydroxycoumarin in the presence of bis ionic liquid, 3,3-(butane-1,4-diyl)-bis(1,2-dimethyl-1*H*-imidazole-3-ium)bromide ([BDBDMIm]Br), and CAN at room temperature (Scheme 1).

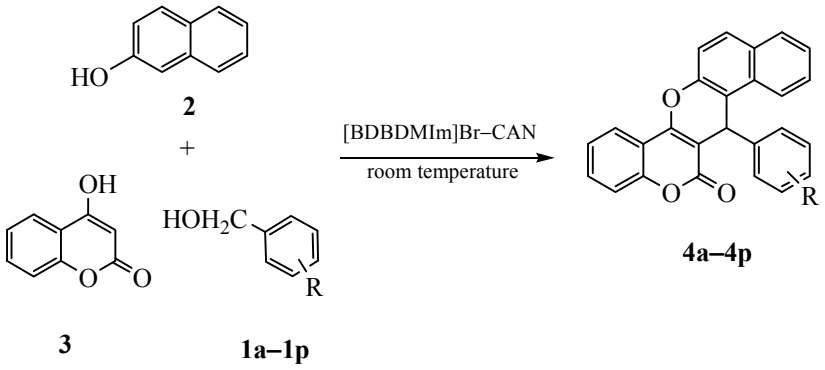
The effect of various acidic catalysts was tested in the model reaction (Table 1).

The ionic liquid [BDBDMIm]Br was determined to be the most efficient for the synthesis of pyrano[4,3-*b*]-chromenes (Table 1).

Efficiency of the reaction was tested by using various benzyl alcohols combined with 2-naphthol and 4-hydroxycoumarin in the presence of [BDBDMIm]Br–CAN at room temperature (Table 2). According to the experimental data the electron withdrawing substituents could facilitate the reaction by decreasing reaction time and increasing yields in comparison with benzyl alcohols that contained electron donating substituents.

[1] The text was submitted by the authors in English.

Scheme 1. Synthesis of pyrano[4,3-*b*]chromenes using [BDBDMIm]Br.



On the basis of the above data a possible mechanism for the synthesis of pyrano[4,3-*b*]chromene derivatives was proposed (Scheme 2) according to which the reaction started with full activation by polarization of benzyl alcohols with [BDBDMIm]Br forming the intermediate **5** which was followed by benzyl alcohols conversion to benzaldehydes **6** by oxidation with CAN $[(NH_4)_2Ce(NO_3)_6]$. The nucleophilic addition of 4-hydroxycoumarin to intermediate **6** led to **7**. Finally, nucleophilic attack of 2-naphthol in compound **7** and dehydration led to compound **4**.

The proposed mechanism was supported by the experiment in which 4-nitrobenzyl alcohol (1 mmol) was treated with 4 mmol % of [BDBDMIm]Br and 0.05 g of CAN at room temperature in the absence of another reagent. 4-Nitrobenzaldehyde was isolated in 15 min with the yield 99%. The ionic liquid was easily recovered by separation from the reaction medium by washing with distilled H_2O after which it could be reuse in subsequent reactions. In five successive runs the recycled ionic liquid demonstrated nearly no loss of activity (Table 3).

EXPERIMENTAL

Materials and measurements. Chemicals were purchased from Merck and Fluka and used without further purification. Elemental analysis was carried out on a Carlo-Erba EA1110CNNO-S analyzer. Melting

Table 1. Effect of catalysts on the synthesis of **4a**[a,b]

Entry no.	Catalyst	Catalyst amount/1 mmol of aldehyde	Reaction condition	Time, min	Yield, %
1	HCl	4 drops	Reflux	840	52
2	SiO_2	0.2 mmol	Reflux	360	65
3	Montmorillonite K10	0.2 g	Reflux	240	71
4	Montmorillonite KSF	0.2 g	Reflux	210	68
5	Fe_3O_4	0.2 mmol	Reflux	720	48
6	$ZnCl_2$	0.2 mmol	Reflux	360	63
7	[BMIm]Br	0.04 mmol	Neat, room temperature	180	80
8	[BMIm]OH	0.04 mmol	Neat, room temperature	170	79
9	$[BMIm]HSO_4$	0.04 mmol	Neat, room temperature	175	82
10	[BDBDIm]Br	0.02 mmol	Neat, room temperature	90	87
11	[BDBDIm]Br	0.04 mmol	Neat, room temperature	60	96
12	[BDBDIm]Br	0.06 mmol	Neat, room temperature	60	96

[a] The solvent in entries 1–6 was water [b] 0.05 g of CAN was used in all reactions.

Table 2. Synthesis of pyrano[4,3-*b*]chromenes **4a–4p** using [BDBDIm]Br

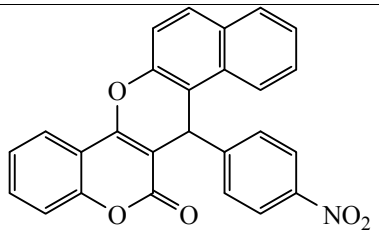
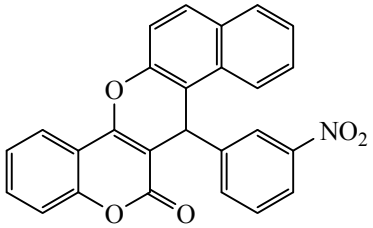
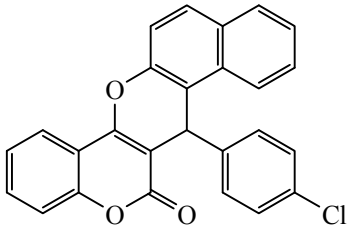
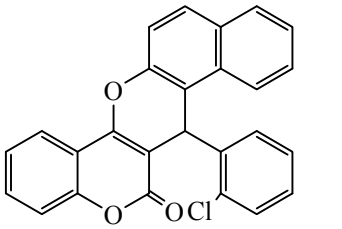
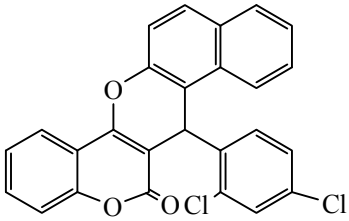
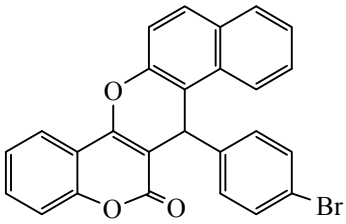
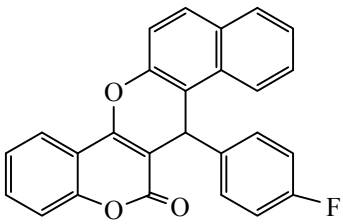
Comp. no.	Product	Time, min	Yield, %[a]	mp, °C	
				found	calculated
4a		60	96	258–260	257–258 [12]
4b		75	91	231–233	237–238 [14]
4c		60	89	267–269	267–268 [12]
4d		120	89	238–240	240–241 [14]
4e		120	92	267–269	267–268 [12]
4f		75	92	287–289	281–282 [14]
4g		60	92	241–243	245–246 [14]

Table 2. (Contd.)

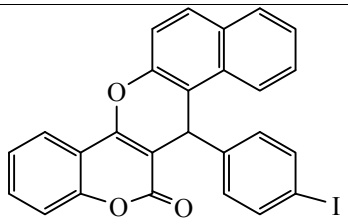
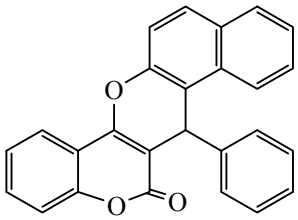
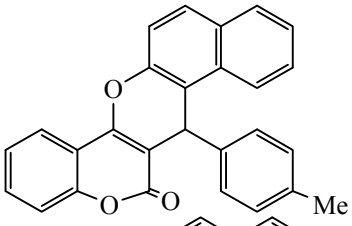
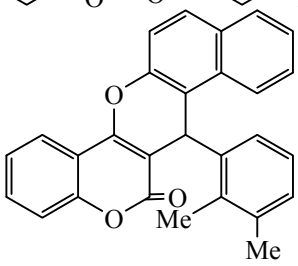
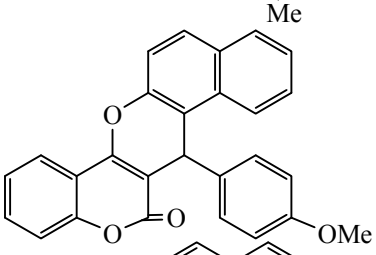
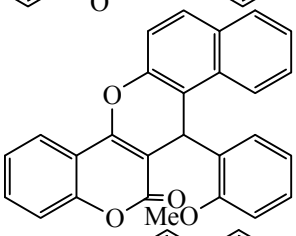
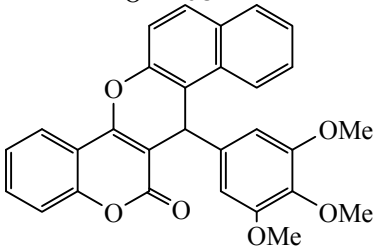
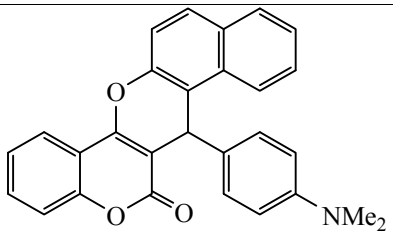
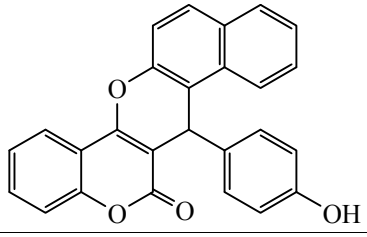
Comp. no.	Product	Time, min	Yield, %[a]	mp, °C	
				found	calculated
4h		60	94	276–278	282–283 [14]
4i		75	88	276–278	280–282 [12]
4j		120	85	225–227	230–231 [12]
4k		120	83	257–258	267–268 [14]
4l		135	82	211–213	214–215 [12]
4m		150	80	214–216	211–212 [14]
4n		120	83	201–203	196–197 [14]

Table 2. (Contd.)

Comp. no.	Product	Time, min	Yield, %[a]	mp, °C	
				found	calculated
4o		135	84	255–257	257–258 [12]
4p		150	85	298–300	299–300 [14]

[a] Isolated yield.

points were measured on an Electro-thermal 9100 apparatus. FT-IR spectra were recorded (KBr discs) on a Shimadzu FT-IR-8400S spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX 500 Avance spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard.

Scheme 2. A possible mechanism of synthesis of pyrano[4,3-*b*]chromene.

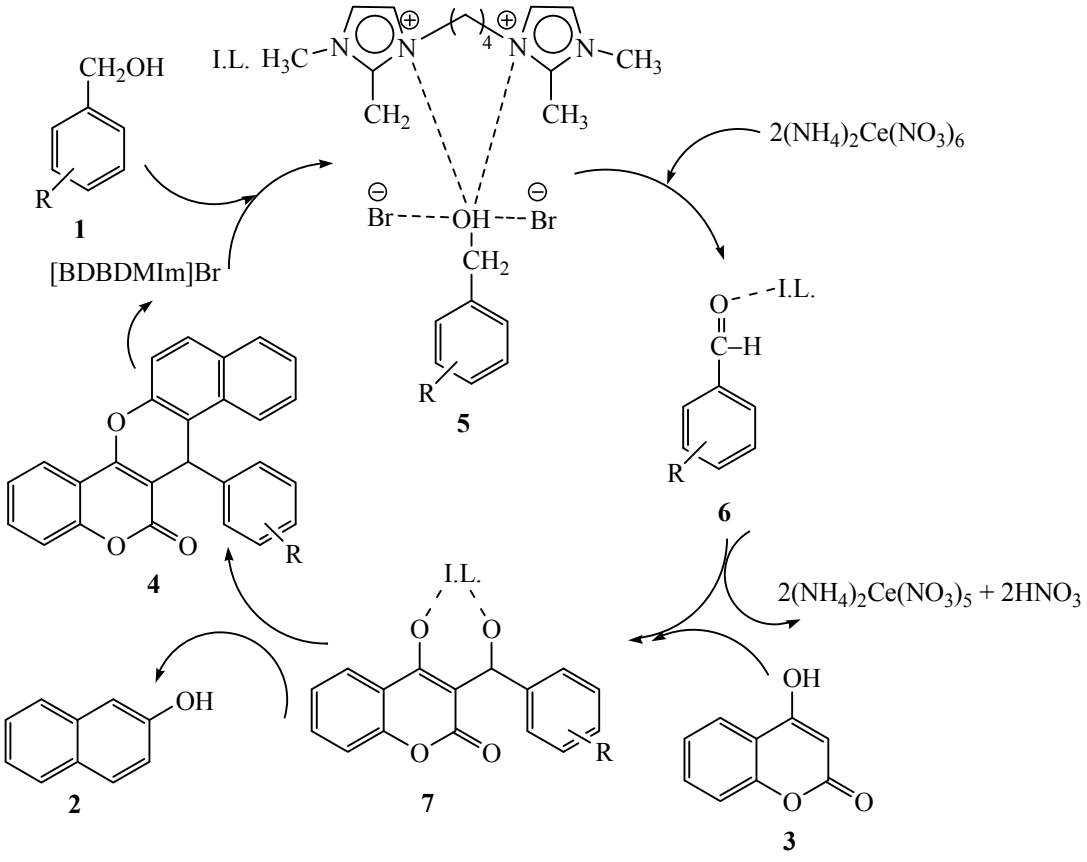


Table 3. Evaluation of reusability of ionic liquid for the synthesis of **4a**

Run no.	Time, min	Yield, %
1	60	96
2	60	96
3	60	96
4	60	95
5	60	92

Synthesis of [BDBDMIm]Br. A mixture of 1,4-dibromobutane (10 mmol) or 1,4-dibromopentane (10 mmol) and 1,2-dimethylimidazole (20 mmol) was loaded in a pressure tube and mixed well. The sealed pressure tube was irradiated at 180W and 75°C under 3–4 psi pressure for 2 min three times in a microwave oven with intervals of 2 min. Upon completion of the reaction (TLC) the ionic liquid was separated from the reaction mixture by extraction with 2×15 cm^3 of water. The aqueous phase was evaporated under vacuum to give the desired ionic liquid.

General procedure for synthesis of pyrano[4,3-*b*]-chromenes. A mixture containing benzyl alcohol (1 mmol), β-naphthol (1 mmol), 4-hydroxycoumarin (1 mmol), 4 mmol % of [BDBDMIm]Br, and 0.05 g of CAN was stirred at room temperature for the required reaction times. Progress of the reaction was monitored by TLC (EtOAc : petroleum ether, 1 : 3). Upon completion of the process the product was extracted with $CHCl_3/H_2O$. The organic phases was separated and the solvent evaporated. Crystallization of the residue gave the pure product. The aqueous phase was concentrated under reduced pressure, washed with Et_2O, and evaporated under reduced pressure to recover the ionic liquid for subsequent use.

12-(4-Nitrophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4a). White solid, mp 258–260°C. IR spectrum, ν, cm^{-1}: 3016, 1729, 1480, 1538, 1250, 1341. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.24 s (1H), 7.34–7.51 m (5H), 7.61–7.70 m (3H), 7.81–7.92 m (3H), 8.09 d (2H, *J* = 8.6 Hz), 8.19 d (1H, *J* = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.9, 98.3, 116.2, 116.7, 117.5, 123.3, 123.4, 123.8, 125.8, 125.9, 126.7, 127.3, 128.5, 129.8, 130.2, 130.7, 131.6, 133.5, 146.6, 148.0, 150.7, 153.2, 160.4, 177.3. Found, %: C 74.03; H 3.65; N 3.21. $C_{26}H_{15}NO_5$. Calculated, %: C 74.10; H 3.59; N 3.32.

12-(3-Nitrophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4b). White solid, mp 251–253°C. IR spectrum, ν, cm^{-1}: 3070, 2931, 1714, 1485, 1573, 1269, 1523, 1350 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.23 s (1H), 7.41–7.54 m (6H), 7.70 m (1H), 7.88 d (1H, *J* = 1.2 Hz), 7.92 d (2H, *J* = 4.8 Hz), 7.94 d (2H, *J* = 8.4 Hz), 8.19 d (2H, *J* = 1.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.2, 99.1, 115.9, 116.7, 117.5, 122.0, 122.9, 123.1, 123.3, 125.5, 125.7, 125.9, 127.8, 128.8, 129.2, 130.4, 130.6, 131.9, 133.7, 134.9, 145.7, 147.5, 148.4,153.0, 160.0, 176.8. Found,%: C 74.18; H 3.62; N 3.27. $C_{26}H_{15}NO_5$. Calculated, %: C 74.10; H 3.59; N 3.32.

12-(4-Cholorophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4c). White solid, mp 267–269°C. IR spectrum, ν, cm^{-1}: 3072, 1708, 1637, 1488, 1506, 1577, 1267, 1226, 1093, 813. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.10 s (1H), 7.20 d.d (2H, *J* = 8.8, 2.8 Hz), 7.42–7.50 m (6H), 7.67 t (1H, *J* = 8.4 Hz), 7.86–7.98 m (3H), 8.10 d (1H, *J* = 8.4 Hz), 8.20 d.d (1H, *J* = 8.0, 6.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.9, 99.8, 117.0, 117.4, 122.7, 123.3, 123.4, 124.3, 125.4, 125.6, 126.0, 127.5, 128.6, 129.8, 130.0, 130.9, 131.8, 132.5, 133.5, 142.2, 147.4, 153.0, 160.0, 176.9. Found, %: C 76.05; H 3.71. $C_{26}H_{15}ClO_3$. Calculated, %: C 76.01; H 3.68.

12-(2-Cholorophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4d). White solid, mp 238–240°C. IR spectrum, ν, cm^{-1}: 3056, 2929, 1714, 1643, 1465, 1560, 1612, 1224, 1035, 742. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.40 s (1H), 7.05–7.12 m (2H), 7.35–7.57 m (7H), 7.67 t (1H, *J* = 9.2 Hz), 7.82–7.88 m (12H), 8.20 d.d (1H, *J* = 8.0, 1.2 Hz), 8.27 d (1H, *J* = 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 34.6, 99.5, 116.5, 117.3, 123.2, 123.8, 124.1, 125.3, 125.4, 126.0, 127.1, 127.5, 128.1, 128.6, 129.8, 130.1, 131.3, 131.6, 133.4, 141.1, 147.2, 152.9, 160.3, 176.7. Found, %: C 75.93; H 3.61. $C_{26}H_{15}ClO_3$. Calculated, %: C 76.01; H 3.68.

12-(4-Bromophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4f). White solid, mp 287–289°C. IR spectrum (KBr), ν, cm^{-1}: 3072, 1708, 1635, 1463, 1546, 1226, 1267. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.02 s (1H), 7.41 s (4H), 7.47–7.57 m (3H), 7.64 d (1H, *J* = 8.8 Hz), 7.71–7.74 m (1H), 7.80–7.86 m (1H), 8.0–8.09 m (4H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.8, 105.2, 113.4, 116.1, 116.9, 117.0, 117.1, 118.3, 120.9, 123.8, 125.2, 125.5, 128.0, 129.2, 130.9, 131.0, 131.6, 131.9, 133.8, 141.3, 152.5,

153.9, 160.1, 176.0. Found, %: C 68.65; H 3.26. $C_{26}H_{15}BrO_3$. Calculated, %: C 68.59; H 3.32.

12-(4-Fluorophenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4g). White solid, mp 241–243°C. IR spectrum, ν, cm^{-1}: 3132, 1700, 1600, 1650, 1481, 1508, 1564, 1240, 1255. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.11 s (1H), 6.88-6.92 m (2H), 7.41–7.50 m (7H), 7.64–7.69 m (1H), 7.85–7.90 m (2H), 7.97 d (1H, *J* = 8.0 Hz), 8.22 d.d (1H, *J* = 8.0, 1.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.5, 115.1, 115.3, 116.5, 117.3, 122.7, 123.9, 125.3, 125.5, 125.9, 127.5, 128.6, 129.7, 129.9, 130.0, 130.9, 131.8, 133.4, 139.5, 147.3, 152.9, 176.9. Found, %: C 79.13; H 3.79. $C_{26}H_{15}FO_3$. Calculated, %: C 79.18; H 3.83.

12-Phenyldibenzo[*i,b*]pyrano[4,3-*b*]chromen-11(12*H*)-one (4i). White solid, mp 276–278°C. IR spectrum, ν, cm^{-1}: 3056, 3022, 2920, 1718, 1641, 1463, 1575, 1610, 1222, 1271, 746. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.0 s (1H), 7.10 t (1H, *J* = 7.2 Hz), 7.22 t (2H, *J* = 7.6 Hz), 7.49 d.d (2H, *J* = 7.2 Hz,), 7.52–7.57 m (4H), 7.62 d (1H, *J* = 9.2 Hz), 7.72 d (1H, *J* = 9.2 Hz), 7.82 t (1H, *J* = 6.8 Hz), 7.99–8.12 m (3H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.7, 106.0, 113.6, 116.7, 117.0, 117.3, 117.4, 118.2, 119.0, 120.2, 122.3, 124.2, 124.5, 127.5, 129.5, 130.0, 130.1, 131.2, 133.7, 138.8, 152.7, 153.4, 160.2, 173.2. Found, %: C 83.02; H 4.21. $C_{26}H_{16}O_3$. Calculated, %: C 82.96; H 4.28.

12-(4-Methylphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4j). White solid, mp 225–227°C. IR spectrum, ν, cm^{-1}: 3018, 2920, 1714, 1639, 1463, 1510, 1566, 1224. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.16 s (3H), 5.73 s (1H), 7.0–7.04 m (2H), 7.27–7.30 m (2H), 7.46–7.55 m (4H), 7.74 d (2H, *J* = 9.2 Hz), 8.01–8.08 m (3H), 8.17 d.d (1H, *J* = 7.6, 0.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 31.2, 34.6, 105.9, 114.2, 116.0, 117.1, 117.3, 117.4, 118.0, 120.0, 122.1, 124.3, 125.0, 127.2, 128.8, 130.0, 130.5, 131.4, 132.0, 135.0, 140.2, 153.3, 154.4, 161.4, 174.7. Found, %: C 83.12; H 4.61. $C_{27}H_{18}O_3$. Calculated, %: C 83.06; H 4.65.

12-(2,3-Dimethylphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4k). White solid, mp 257–258°C. IR spectrum, ν, cm^{-1}: 3018, 1682, 1636, 1543, 1452, 1319, 1242. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.78 s (3H), 2.32 s (3H), 6.63 s (1H), 7.06–7.08 m (3H), 7.11 d (1H, *J* = 8.6 Hz), 7.32–7.37 m (2H), 7.42 d (1H, *J* = 8.2 Hz), 7.51 t (1H, *J* = 8.2 Hz), 7.65 t (1H, *J* = 8.4 Hz), 7.79 d (1H, *J* = 8.4 Hz), 7.89 d (1H, *J* = 8.4 Hz), 7.92 d (1H, *J* = 8.2 Hz), 8.11 d (1H, *J* = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 15.2, 20.6, 36.5, 98.8, 105.7, 112.9, 116.1, 116.3, 118.7, 119.6, 122.9, 122.3, 123.6, 124.2, 125.6, 126.0, 127.6, 128.1, 129.5, 132.6, 133.2, 134.2, 136.6, 139.5, 151.3, 162.6, 176.9. Found, %: C 83.03; H 5.06. $C_{28}H_{20}O_3$. Calculated, %: C 83.15; H 4.98.

12-(4-Methoxyphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4l). White solid, mp 211–213°C. IR spectrum, ν, cm^{-1}: 3064, 2941, 1712, 1641, 1461, 1508, 564, 1174, 1240, 811. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.35 s (3H), 5.92 s (1H), 6.77 t (2H, *J* = 8.8 Hz), 7.29–7.32 m (2H), 7.48–7.55 m (3H), 7.60 d (1H, *J* = 9.2 Hz), 7.68–7.72 m (2H), 7.96–8.09 m (3H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.8, 62.2, 105.8, 113.8, 115.5, 116.5, 117.8, 118.1, 118.7, 121.4, 123.0, 124.4, 125.0, 127.5, 128.5, 129.9, 130.7, 132.6, 133.9, 138.1, 146.3, 154.5, 155.6, 160.3, 175.5. Found, %: C 79.85; H 4.41. $C_{27}H_{18}O_4$. Calculated, %: C 79.79; H 4.46.

12-(3,4,5-Trimethoxyphenyl)dibenzo[*i,b*]pyrano-[4,3-*b*]chromen-11(12*H*)-one (4n). White solid, mp 201–203°C. IR spectrum, ν, cm^{-1}: 3054, 1704, 1639, 1538, 1472, 1352, 1242. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.56 s (3H), 3.61 s (6H), 5.75 s (1H), 6.69 d (2H, *J* = 8.6 Hz), 7.42–7.58 m (4H), 7.70–7.76 m (2H), 8.02 d (1H, *J* = 8.2 Hz), 8.11 d (1H, *J* = 8.6 Hz), 8.24 t (2H, *J* = 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.4, 56.25, 56.8, 56.3, 98.9, 115.3, 116.5, 117.5, 121.2, 122.5, 123.4, 125.6, 127.2, 128.9, 129.0, 130.2, 131.4, 134.5, 135.1, 145.3, 146.7, 147.1, 152.9, 159.2, 175.4. Found, %: C 74.78; H 4.83. $C_{29}H_{22}O_6$. Calculated, %: C 74.67; H 4.75.

12-(4-Dimethylaminophenyl)dibenzo[*i,b*]pyrano-[4,3-*b*]chromen-11(12*H*)-one (4o). White solid, mp 255–257°C. IR spectrum, ν, cm^{-1}: 3074, 2914, 1656, 1521, 1560, 1660, 1346, 1191, 810. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s (6H), 5.60 s (1H), 7.22–7.39 m (8H), 7.50–7.52 m (1H), 7.63–7.68 m (1H), 7.80–7.84 m (3H), 8.01 d (1H, *J* = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.0, 52.4, 105.7, 113.0, 115.2, 116.1, 117.2, 117.9, 118.2, 121.9, 123.4, 125.0, 126.8, 128.6, 129.0, 132.1, 133.0, 133.6, 136.2, 137.0, 142.3, 154.2, 155.0, 158.5, 173.4. Found, %: C 80.24; H 4.99; N 3.29. $C_{28}H_{21}NO_3$. Calculated, %: C 80.17; H 5.05; N 3.34.

12-(4-Hydroxyphenyl)dibenzo[*i,b*]pyrano[4,3-*b*]-chromen-11(12*H*)-one (4p). White solid, mp 298–300°C. IR spectrum, ν, cm^{-1}: 3281, 3012, 1706, 1635, 1551, 1462, 1301, 1203. ^1H NMR spectrum ($CDCl_3$),

δ, ppm: 5.72 s (1H), 7.60 d (1H, *J* = 8.6 Hz), 7.63–7.70 m (3H), 7.87 t (1H, *J* = 8.6 Hz), 7.90 d (*J* = 8.4 Hz, 3H), 8.05 d (*J* = 8.2 Hz, 3H), 8.13 t (2H, *J* = 8.2 Hz), 8.21 d (1H, *J* = 8.2 Hz), 9.31 s (1H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.8, 98.4, 112.5, 116.2, 118.4, 122.5, 123.3, 123.7, 126.2, 127.8, 128.5, 128.9, 130.4, 130.8, 131.3, 131.9, 135.0, 140.3, 140.4, 149.6, 151.98, 152.5, 156.0, 162.3, 175.2. Found, %: C 79.66; H 4.03. $C_{26}H_{16}O_4$. Calculated, %: C 79.58; H 4.11.

3,3-(Butane-1,4-diyl)bis(1,2-dimethyl-1*H*-imidazole-3-ium)bromide ([BDBDMIm]Br). IR spectrum, ν, cm^{-1}: 3075, 2909, 1610, 1520, 1486, 1324. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.45 t (4H), 2.28 s (6H), 2.72 s (6H), 3.01 t (4H), 6.65 d (1H, *J* = 7.5 Hz), 6.72 d (1H, *J* = 7.5 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 23.2, 41.0, 52.2, 56.1, 127.9, 129.0, 133.0. Found, %: C 41.04; H 6.02; N 13.85. $C_{14}H_{24}Br_2N_4$. Calculated, %: C 41.20; H 5.93; N 13.73.

3,3'-(Pentane-1,5-diyl)bis(1,2-dimethyl-1*H*-imidazol-3-ium)bromide ([PDBMDIm]Br). IR spectrum, ν, cm^{-1}: 3026, 2927, 1639, 1695, 1367. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.71 s (6H), 2.75 s (6H), 3.80 br (6H), 3.90 br (4H), 7.11 s (2H), 7.13 d (2H, *J* = 1.6 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 23.6, 41.4, 42.1, 52.6, 56.7, 128.4, 129.3, 132.4. Found, %: C 42.54; H 6.32; N 13.32. $C_{15}H_{26}Br_2N_4$. Calculated, %: C 42.67; H 6.21; N 13.27.

2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-*a*]azepineium acetate (DBU–OAc). IR spectrum, ν, cm^{-1}: 2949, 1745, 1563, 1371, 1303. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.63–1.67 m (2H), 1.74–1.75 m (2H), 1.98–2.0 m (7H), 2.82–2.87 m (2H), 3.40–3.48 m (6H), 7.10 s (NH, 1H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.2, 22.9, 23.4, 24.0, 25.8, 41.6, 43.5, 42.7, 48.3, 159.2, 162.5. Found, %: C 62.15; H 9.62; N 13.15. $C_{11}H_{20}N_2O_2$. Calculated, %: C 62.23; H 9.50; N 13.20.

CONCLUSIONS

We have developed an efficient, green, fast, and convenient procedure for the multicomponent synthesis of pyrano[4,3-*b*]chromenes via a tandem reaction, in which benzyl alcohols were converted to benzaldehydes using the novel oxidant system [BDBDMIm]Br–CAN followed by cyclocondensation reaction of β-naphthol, aldehydes and 4-hydroxycoumarin. To the best of our knowledge, that was the first report on synthesis of pyrano[4,3-*b*]chromenes derivatives using 3,3-(butane-1,4-diyl)bis(1,2-dimethyl-1*H*-imidazole-3-ium)bromide–CAN.

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