Synthesis of Some Novel *N*-Alkyl/Acyl/Aroyl 2-(Chroman/6-bromochroman-2-yl)-1*H*-benzimidazoles Using Ionic Liquids and Their Antibacterial Activity

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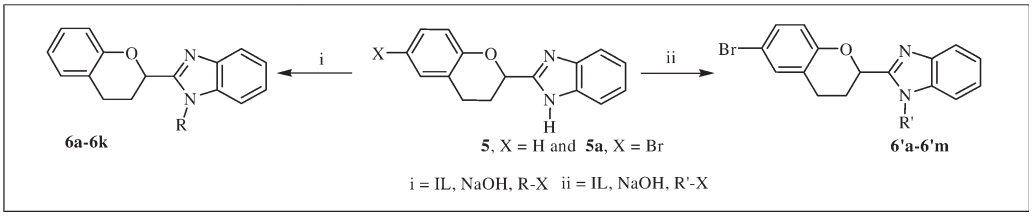

Synthesis of some novel *N*-substituted 2-(chroman/6-bromochroman-2-yl)-1*H*-benzimidazoles by the condensation of 3,4-dihydro-2*H*-chroman-2-carboxylic acid and 6-bromo-3,4-dihydro-2*H*-chroman-2-carboxylic acid with *o*-phenylenediamine in ionic liquid (IL) [bmim]BF_4 and subsequent reactions at the benzimidazole-NH with different types of electrophiles in ILs [bmim]BF_4 = 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]PF_6 = 1-butyl-3-methylimidazolium hexafluorophosphate and [buPy]BF_4 = butylpyridinium tetrafluoroborate in the presence of sodium hydroxide as a base have been reported. All the synthesized compounds were screened for their antibacterial activity. Some compounds exhibited promising antibacterial activity against *Staphylococcus aureus* and *Salmonella typhimurium* when compared to Cephalexin as a reference standard.

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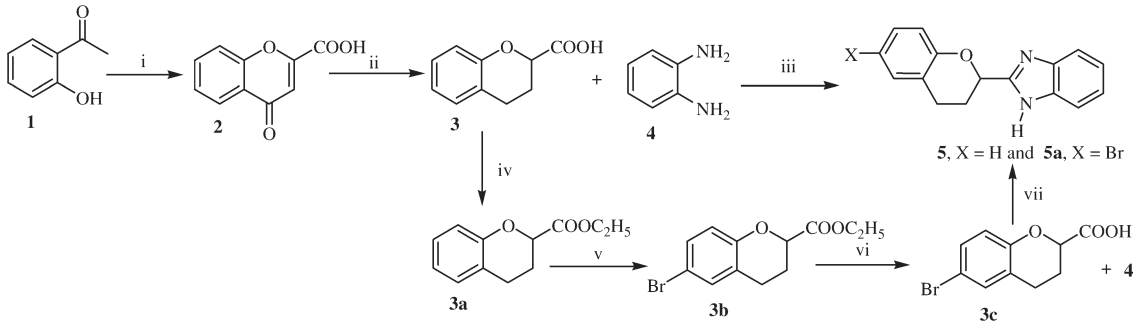
INTRODUCTION

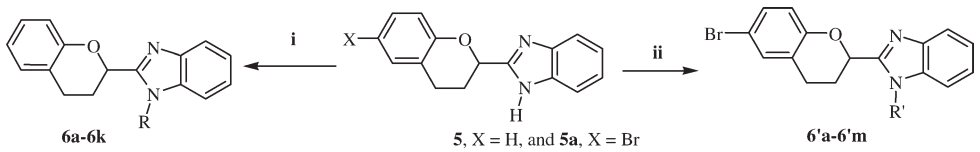
There are a vast number of pharmacologically active heterocyclic compounds, many of which are in regular clinical use. Of the wide variety of heterocyclic systems known till date, the nitrogen heterocycles are of great importance and benzimidazole is one amongst such important heterocycles because of its synthetic utility and broad spectrum of pharmacological activity [1–10]. Various substituted benzimidazoles are known to have varied biological activities and among these, 2-substituted benzimidazoles are found to be more potent [11]. The biological activities of benzimidazoles containing compounds have been well documented [12–13]. Despite their wide applicability, available routes for their synthesis are limited. The reported synthesis of benzimidazoles included reactions of aryl acid with *o*-phenylenediamine (OPDA) in conventional [14,15], microwave-assisted [16], and ionic liquids (ILs) [17] methods. The *N*-alkylation and acylation of benzimidazoles has been reported to be accomplished by treatment with an appropriate base such as sodium hydride, sodium hydroxide, potassium carbonate, pyridine, etc. followed by reaction of the resulting salt with an alkylating reagent in various solvents, e.g. acetone, acetonitrile, pyridine, DMF, THF, etc. [18–20].

In the rapidly developing field of synthetic organic chemistry, an efficient, simple, and highly selective synthetic method for widely used organic compounds from readily available reagents is one of the major challenges. ILs are proving to be increasingly promising as viable media not only for potentially 'green' synthesis and separations, but also for novel applications. The unique property set of the IL materials provides new options based on different chemical and physical properties. The room temperature ILs are of special interest as 'green' recyclable alternative to the classical molecular solvents in the synthetic organic chemistry [21–24]. ILs are the best choice for *N*-alkylation of heterocyclic compounds bearing an acidic hydrogen attached to nitrogen. The reports on great improvement in the yields and rates of reaction using ILs [25] prompted us to study the *N*-alkylation and acylation of benzimidazoles in ILs. Hence it was thought that it would be worthwhile to design and synthesize the *N*-substituted benzimidazoles in ILs under environment-friendly conditions and screen them for potential biological activity.

Scheme 1. Reagents, i) Diethyl Oxalate, NaOEt, aq.HCl ii) AcOH, H_2, Pd/C, 175psi iii) [bmim]BF_4, 100°C iv) Ethanolic-HCl v) AcOH, Br_2 vi) EtOH/NaOH vii) [bmim]BF_4,100°C



Scheme 2



i) IL, NaOH, R-X ii) IL, NaOH, R'-X

RESULTS AND DISCUSSION

Compound **3** was synthesized according to literature procedure in good yield [26]. Condensation of 3,4-dihydro-2*H*-chroman-2-carboxylic acid **(3)** with OPDA **(4)** was carried out in IL [bmim]BF_4 at 100°C for 6 h to obtain compound **5** in excellent yield (scheme 1).

For the synthesis of compound **3c**, 3,4-dihydro-2*H*-chroman-2-carboxylic acid **(3)** was treated with ethanolic-HCl at 85°C for 3 h to afford the corresponding ethyl ester derivative **3a** in a reasonable yield. Compound **3a** was brominated using bromine in glacial acetic acid at 25°C for 2 h to obtain 6-bromo-3,4-dihydro-2*H*-chroman-2-carboxylic acid ethyl ester **(3b)**, which

Table 1a

Reaction conditions, physical and analytical data of synthesized compounds.

Sr. No	Substrate	R/R′	Ionic liquid	Reaction conditions	Product	Yield (%)	Mp (°C)
1	**5**	CH_3—O—CO—	[bmim]PF_6	50°C, 3 h	**6a**	75	132–133
2	**5**	C_2H_5—O—CO—	[bupy]BF_4	50°C, 3 h	**6b**	71	105–107
3	**5**	$(CH_3)_2$—CH—CH_2—O—CO—	[bmim]BF_4	50°C, 3 h	**6c**	77	90–92
4	**5**	C_6H_5—O—CO—	[bmim]PF_6	50°C, 3 h	**6d**	85	120–121
5	**5**	CH_3—SO_2—	[bmim]BF_4	60°C, 2 h	**6e**	82	190–192
6	**5**	(*p*)—CH_3—C_6H_4—SO_2—	[buPy]BF_4	60°C, 2 h	**6f**	73	172–173
7	**5**	C_6H_5—CH_2—	[bmim]BF_4	75°C, 5 h	**6g**	80	128–130
8	**5**	(*p*)F—C_6H_4—CH_2—	[buPy]BF_4	75°C, 6 h	**6h**	75	120–122
9	**5**	(*p*)Br—C_6H_4—CH_2—	[bmim]PF_6	75°C, 5 h	**6i**	76	155–157
10	**5**	(*p*)CH_3—C_6H_4—CH_2—	[bmim]BF_4	75°C, 6 h	**6j**	82	176–178
11	**5**	(*p*)Tert.butyl—C_6H_4—CH_2—	[bmim]BF_4	75°C, 5 h	**6k**	68	150–151
12	**5a**	CH_3	[bmim]BF_4	50°C, 5 h	**6′a**	70	138–140
13	**5a**	C_2H_5	[bmim]BF_4	50°C, 5 h	**6′b**	80	125–127
14	**5a**	CH_3—O—CO—	[bmim]PF_6	50°C, 3 h	**6′c**	73	140–141
15	**5a**	C_2H_5—O—CO—	[buPy]BF_4	50°C, 3 h	**6′d**	78	148–150
16	**5a**	Isobutyl—O—CO—	[bmim]BF_4	50°C, 3 h	**6′e**	75	120–121
17	**5a**	CH_3—SO_2—	[bmim]PF_6	60°C, 2 h	**6′f**	89	115–116
18	**5a**	(*p*) CH_3—C_6H_4—SO_2—	[bupy]BF_4	60°C, 2 h	**6′g**	86	140–141
19	**5a**	C_6H_5—CH_2—	[bmim]BF_4	75°C, 5 h	**6′h**	78	180–182
20	**5a**	(*p*) F—C_6H_4—CH_2—	[buPy]BF_4	75°C, 6 h	**6′i**	85	210–212
21	**5a**	(*p*) Br—C_6H_4—CH_2—	[bmim]PF_6	75°C, 5 h	**6′j**	80	178–180
22	**5a**	(*p*) CH_3—C_6H_4—CH_2—	[bmim]BF_4	75°C, 6 h	**6′k**	84	225–226
23	**5a**	(*p*)Tert.butyl—C_6H_4—CH_2—	[bmim]BF_4	75°C, 5 h	**6′l**	78	166–167
24	**5a**	C_6H_5—O—CO—	[bmim]BF_4	50°C, 3 h	**6′m**	82	170–172

Table 1b

Recycling of [bmim]BF_4 for the compound **6g**.

Number of cycles	Yield (%)
1	78
2	75
3	71

was further hydrolyzed in ethanol, sodium hydroxide, and 5*N* HCl to give 6-bromo-3,4-dihydro-2*H*-chroman-2-carboxylic acid **(3c)** as a brownish solid. Condensation of **3c** with **4** was carried out in IL [bmim]BF_4 at 100°C for 6 h yielded compound **5a** as a white solid.

The *N*-alkylation and acylation of **5** and **5a** with various electrophilic reagents in ILs to obtain the *N*-alkylated/acylated derivatives **6a-6k** and **6′a-6′m** (Scheme 2). The recovered IL was reused successfully with only a slight loss in yield (Table 1b). The structures of newly synthesized compounds were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry. The physical and spectral data of the compounds **6a-6k** and **6′a-6′m** is presented in experimental section. The synthesized compounds were tested for their antimicrobial activity against two different bacterial species namely, *Staphylococcus aureus* NCIM 5021 and *Salmonella typhimurium* NCIM 2501.

Table 2

Antibacterial activity of synthesized compounds **5, 5a, 6a–6k**, and **6′a–6′m** against *S. aureus* NCIM 5021.

Compound No.	Concentration (μg/mL)						
	0.1	1	10	100	200	500	App. MIC
5	++	++	+	P	−	−	10
6a	++	+	+	P	−	−	10
6b	++	++	++	+	−	−	100
6c	++	++	+	+	−	−	10
6d	++	++	+	P	−	−	10
6e	++	++	++	+	−	−	100
6f	++	++	++	+	−	−	100
6g	++	++	+	P	−	−	10
6h	++	++	++	+	P	−	100
6i	++	++	+	+	−	−	100
6j	++	++	+	P	−	−	10
6k	++	++	++	+	−	−	100
5a	++	++	+	+	P	−	10
6′a	++	++	++	+	P	−	100
6′b	++	++	++	+	P	−	100
6′c	++	++	++	+	P	−	100
6′d	++	++	++	+	P	−	100
6′e	++	++	++	+	P	−	100
6′f	++	++	+	+	P	−	10
6′g	++	+	+	P	P	−	1
6′h	++	++	+	+	P	−	10
6′i	++	++	+	+	P	−	10
6′j	++	+	P	−	−	−	1
6′k	++	++	++	+	P	−	100
6′l	++	++	+	+	P	−	10
6′m	++	+	+	+	P	−	1
Cephalexin	+	−	−	−	−	−	0.1

Table 3

Antibacterial activity of synthesized compounds **5, 5a, 6a–6k**, and **6′a–6′m** against *S. typhimurium* NCIM 2501.

Compound No.	Concentration (μg/mL)						
	0.1	1	10	100	200	500	App. MIC
5	++	++	+	P	−	−	10
6a	++	++	+	+	−	−	10
6b	++	++	++	+	−	P	100
6c	++	++	++	+	−	−	100
6d	++	++	++	+	−	−	100
6e	++	++	++	+	−	−	100
6f	++	++	++	+	−	−	100
6g	++	++	+	P	−	−	10
6h	++	++	++	+	−	−	100
6i	++	++	++	+	−	−	100
6j	++	++	++	+	−	−	100
6k	++	++	+	P	−	−	10
5a	++	++	++	++	+	−	200
6′a	++	++	++	+	−	−	100
6′b	++	++	++	+	−	−	100
6′c	++	++	++	++	+	−	200
6′d	++	++	++	+	−	−	100
6′e	++	++	++	+	P	−	100
6′f	++	++	+	P	−	−	10
6′g	++	++	++	+	−	−	100
6′h	++	++	++	+	P	−	100
6′i	++	++	++	++	+	−	200
6′j	++	++	++	+	P	−	100
6′k	++	++	++	+	P	−	100
6′l	++	++	++	+	P	−	100
6′m	++	++	++	+	P	−	100
Cephalexin	+	−	−	−	−	−	0.1

−, Total inhibition, no growth of organism; P, Poor growth compared to controls; +, Medium growth compared to controls; ++, Confluent growth, no inhibition.

BIOLOGICAL ACTIVITY

All the compounds prepared herein were screened for their antibacterial activity against *Staphylococcus aureus* NCIM 5021 (Gram positive) and *Salmonella typhimurium* NCIM 2501 (Gram negative) bacterial strains. Cephalexin was used as a reference standard. Antibacterial activity result of compounds **5**, **5a, 6a-6k,** and **6′a-6′m** is summarized in Table 2 and 3. Some of the compounds found to have good antibacterial activity against *S. aureus*; however, they were found to have less activity against *S. typhimurium* when compared to Cephalexin as a reference standard.

CONCLUSION

In conclusion, we have successfully synthesized a novel series of *N*-substituted 2-(chroman/6-bromo-chroman-2-yl)-1*H*-benzimidazole derivatives by the

condensation of 3,4-dihydro-2*H*-chroman-2-carboxylic acid and 6-bromo-3,4-dihydro-2*H*-chroman-2-carboxylic acid with OPDA and subsequent reactions at the benzimidazole-NH with different electrophilic reagents under different reaction conditions in ILs and tested for antibacterial activity. Some of the compounds **6′g**, **6′j**, 6′m showed the most potent inhibition at 1 μg/mL, where as compounds **5, 6a–6d**, **6g**, **6j** and **5a**, **6′f**, **6′h**, **6′i**, **6′l** were found to possess good activity at 10 μg/mL against *S. aureus* and compounds **5**, **6a**, **6g**, **6k**, **6′f** showed the good activity at 10 μg/mL, where as other compounds showed minimal activity against a *S. typhimurium*.

EXPERIMENTAL

All the solvents were of commercial grade and OPDA, alkylating and acylating agents were obtained from Aldrich. Melting points were recorded on a MRVIS series, Lab India Instrument and are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer in potassium bromide pellets unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VX SWBB 300 MHz spectrometer. Elemental analysis was carried out on a PerkinElmer Series-II C H N S O Analyzer 2400. Chemical shifts are reported in ppm from internal tetramethylsilane (TMS) standard and are given δ units. The solvent for NMR spectra was $CDCl_3$ unless otherwise mentioned. Mass spectra were recorded on *hp* 1100 LC/MSD mass spectrometer (positive and negative APCI ion source, 50–200 V, nitrogen). ILs [bmim]BF_4, [bmim]PF_6, and [buPy]BF_4 were synthesized in the laboratory according to reported procedures [27].

Synthesis of 6-bromo-3,4-dihydro-2*H*-chroman-2-carboxylic acid (3c). A solution of (34 mmol) of **3a** dissolved in glacial acetic acid (50 mL) was cooled to 10–15°C. The compound **3a** was brominated by slowly adding a solution of bromine (33 mmol) in glacial acetic acid (25 mL). After the addition was complete, the solution was stirred at 25–30°C for 3 h. The reaction mass was then diluted with water (100 mL). The product was isolated by extraction with ethyl acetate (50 mL × 3). The ethyl acetate layer was washed with 5% aqueous sodium bicarbonate solution (50 mL × 2) and water (50 mL × 2). The ethyl acetate layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure to obtain 6-bromo-3,4-dihydro-2*H*-chroman-2-carboxylic acid ethyl ester **(3b)**.

A solution of (67 mmol) of **3b** dissolved in ethanol (25 mL) was hydrolysed by 0.5*M* sodium hydroxide solution (25 mL) at 25–30°C for 1 h. The solution was concentrated to about its half volume and acidified with 5*N* hydrochloric acid. The resultant solid was filtered to give **3c,** 4.5 g, Yield 85%; mp 170–172°C; ^{1}H NMR ($CDCl_3$) (300 MHz): δ 2.13–2.25 (m, 2H, CH_2), 2.29–2.37 (m, 1H, CH), 2.72–2.91 (m, 2H, CH_2), 4.79 (dd, 1H, J = 7.8, 7.8 Hz, CH), 6.81 (d, 1H, J = 9 Hz, Ar-H), 7.19–7.26 (m, 2H, Ar-H), 11.63 (s, 1H, COOH).

Synthesis of 2-(chroman-2-yl)-1*H*-benzimidazole using IL (5). A solution of (10 mmol) of **3** in IL [bmim]BF_4 (2 mL) and (12 mmol) of OPDA **(4)** was heated at 100°C for 6 h (as monitored by TLC). After 6 h the mixture was cooled to 25°C and diluted with water (10 mL). The product was extracted with ethyl acetate (10 mL × 2). The ethyl acetate layer was washed with 5*N* HCl (10 mL), 5% aqueous sodium bicarbonate solution (10 mL) and water (10 mL). The ethyl acetate layer was dried over sodium sulfate and evaporated under reduced pressure to afford crude product, which was recrystallized from ethyl acetate to obtain as a white solid compound **5**. After isolation of the product in ethyl acetate IL was in aqueous layer, which was further washed with ethyl acetate (10 mL) and dried under vacuum. The suspension was filtered to remove insoluble and the recovered IL was recycled.

2-(Chroman-2-yl)-1*H*-benzimidazole (5). mp 225–227°C; ir (KBr): 3434, 2950, 1487, 1231 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.20–2.35 (m, 2H, CH_2), 2.81–3.04 (m, 2H, CH_2), 5.47 (dd, J = 8.6, 8.9 Hz, 1H, CH), 6.87–6.91 (m, 4H, Ar-H), 7.08–7.18 (m, 2H, Ar-H), 7.46 (d, J = 7.4 Hz, 1H, Ar-H), 7.71 (d, J = 7.6 Hz, 1H, Ar-H), 9.7 (bs, 1H, NH); ms: *m*/*z* 249.1 (M^++1); Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.52; H, 5.52; N, 11.36.

Synthesis of 2-(6-bromochroman-2-yl)-*1H*-benzimidazole using IL (5a). A mixture of **3c** (10 mmol), OPDA **(4)** (12 mmol) and IL [bmim]BF_4 (2 mL) was heated to 100°C for 6 h (as monitored by TLC). The reaction mixture was then cooled to room temperature and diluted with water (10 mL). The product was extracted with ethyl acetate (10 mL × 2) and ethyl acetate layer was washed with 5*N* HCl (10 mL), 5% aqueous sodium bicarbonate solution (10 mL) and water (10 mL). The ethyl acetate layer was dried over sodium sulfate and solvent was evaporated under reduced pressure to obtain crude product, which was recrystallized from ethyl acetate to yield the pure compound **5a**. The IL was recovered by the procedure described earlier.

2-(6-Bromochroman-2-yl)-*1H*-benzimidazole (5a). mp 210–211°C; ir (KBr): 3428, 2919, 1476, 1232 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.26–2.38 (m, 2H, CH_2), 2.86–3.01 (m, 2H, CH_2), 5.46 (dd, J = 8.7, 8.7 Hz, 1H, CH), 6.86 (d, J = 9 Hz, 1H, Ar-H), 7.15–7.34 (m, 4H, Ar-H), 7.48 (d, J = 6.9 Hz, 1H, Ar-H), 7.62 (d, J = 6.9 Hz, 1H, Ar-H) 12.62 (bs, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6) (75 MHz): δ 23.36 (CH_2), 25.60 (CH_2), 72.25 (OCH), 111.77, 112.11, 119,01, 119.24, 121.64, 122.63, 125.01, 130.18, 132.18, 134.43, 142.95, 153.02, 153.23 (aromatic carbons) ppm; ms: *m*/*z* 329.32 (M^++1); Anal. Calcd. for $C_{16}H_{13}BrN_2O$: C, 58.38; H, 3.98; N, 8.51. Found: C, 58.26; H, 3.75; N, 8.66.

General procedure for the synthesis of compound 6′a-6′b using IL. A solution (2 mmol) of **5a,** IL (2 mL), sodium hydroxide (4 mmol) and followed by the addition of respective alkylting reagents (3 mmol) at 25–30°C. After the addition was complete, the solution was heated to 50°C for 5 h (as monitored by TLC). The reaction mixture was then cooled to 25°C and diluted with water (10 mL). The product was extracted with ethyl acetate (10 mL × 2) and ethyl acetate layer was washed with water (10 mL × 2). The organic layer was dried over sodium sulfate and the solvent was evaporated under reduced pressure to obtain the corresponding *N*-substituted derivatives. The crude products were recrystallized from ethanol to give pure compounds **6′a** and **6′b,** respectively. The IL was recovered by the procedure described earlier.

Methyl 2-(6-bromochroman-2-yl)-1H-benzimidazole (6′a). ir (KBr): 3435, 2948, 1474, 1231 cm^{-1}; 1H NMR (DMSO-d_6): δ 2.40–2.46 (m, 2H, CH_2), 2.97–3.01 (m, 2H, CH_2), 3.91

(s, 3H, CH_3), 5.63 (dd, J = 8.1, 8.4 Hz, 1H, CH), 6.81(d, J = 8.4 Hz, 1H, Ar-H), 7.28–7.35 (m, 4H, Ar-H), 7.59–7.66 (m, 2H, Ar-H) ppm; ^{13}C NMR (DMSO-d_6) (75 MHz): δ 23.07 (CH_2), 23.59 (CH_2), 29.41 (NCH_3), 70.10 (CH), 108.11, 111.84, 117.24, 118.84, 121.01, 121.89, 122.08, 128.93, 130.95, 134.91, 140.60, 149.96, 151.55 (aromatic carbons) ppm; ms: m/z 343.61 (M^++1); Anal. Calcd. for $C_{17}H_{15}BrN_2O$: C, 59.49; H, 4.41; N, 8.56. Found: C, 59.38; H, 4.62; N, 8.32.

Ethyl 2-(6-bromochroman-2-yl)-1H-brenzimidazole (6′b). ir (KBr): 3435, 2983, 1473, 1234 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 1.4 (t, J = 6.9 Hz, 3H, CH_3), 2.42–2.50 (m, 2H, CH_2), 3.03–3.07 (m, 2H, CH_2), 4.41 (q, J = 6.8 Hz, 2H, CH_2), 5.62 (dd, J = 8.1, 8.3 Hz, 1H, CH), 6.78 (d, J = 9 Hz, 1H, Ar-H), 7.24–7.36 (m, 4H, Ar-H), 7.61–7.67 (m, 2H, Ar-H) ppm; ^{13}C NMR (DMSO-d_6) (75 MHz): δ 15.25 (CH_3), 24.25 (CH_2), 24.86 (CH_2), 39.23 (NCH_2), 71.24 (CH), 109.61, 113.08, 118.51, 120.24, 122.23, 123.12, 124.08, 130.22, 132.27, 135.11, 142.18, 150.80, 152.93 (aromatic carbons) ppm; ms: m/z 357.66 (M^++1); Anal. Calcd. for $C_{18}H_{17}BrN_2O$: C, 60.52; H, 4.80; N, 7.84. Found: C, 60.38; H, 4.97; N, 7.63.

General procedure for the synthesis of compound (6a-6f, 6′c-6′g, and 6′m) using ILs. To a solution of **5** and **5a** (2 mmol) in ILs (2 mL), pyridine (10 mmol), followed by the addition of appropriate acyl or arylsulfonyl chloride (3 mmol) were stirred (for reaction conditions, Table 1a). The reaction mixture was then cooled to 25°C and diluted with water (10 mL). The product was extracted with ethyl acetate (10 mL × 2), ethyl acetate layer was washed with 5% aqueous sodium bicarbonate solution (10 mL) followed by washed with water (10 mL). The ethyl acetate layer was dried over sodium sulfate and the solvent was evaporated to obtain the crude products, which were recrystallized from ethanol, to afford pure compounds (**6a-6f**), (**6′c-6′g** and **6′m**), respectively. The ILs was recovered by the procedure described earlier.

Methyl 2-(chroman-2-yl)-1H-benzimidazole-1-carboxylate (6a). ir (KBr): 3453, 2922, 1759, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.40–2.51 (m, 2H, CH_2), 2.92–3.07 (m, 2H, CH_2), 4.13 (s, 3H, CH_3), 5.86 (dd, J = 8.4, 8.6 Hz, 1H, CH), 6.87–6.94 (m, 2H, Ar-H), 7.12 (d, J = 6.9 Hz, 2H, Ar-H), 7.37–7.38 (m, 2H, Ar-H), 7.82 (d, J = 6.9, Hz, 1H, Ar-H), 7.95 (d, J = 7.2 Hz, 1H, Ar-H); ms: m/z 309.1 (M^++1); Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.23; H, 5.35; N, 9.25.

Ethyl 2-(chroman-2-yl)-1H-benzimidazole-1-carboxylate (6b). ir (KBr): 3453, 2972, 1744, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.53 (t, J = 7.2 Hz, 3H, CH_3), 2.40–2.51 (m, 2H, CH_2), 2.92–3.06 (m, 2H, CH_2), 4.57 (q, 2H, CH_2), 5.89 (dd, J = 8.7 Hz, 1H, CH), 6.87–6.95 (m, 2H, Ar-H), 7.1 (d, J = 6.9 Hz, 2H, Ar-H), 7.36–7.39 (m, 2H, Ar-H), 7.82 (d, J = 8.1 Hz, 1H, Ar-H), 7.98 (d, 1H, J = 6 Hz, Ar-H); ms: m/z 323.1 (M^++1); Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.92, H, 5.48; N, 8.85.

Isobutyl 2-(chroman-2-yl)-1H-benzimidazole-1-carboxylate (6c). ir (KBr): 3272, 1738, 1456 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.57 (d, J = 6.6 Hz, 6H, CH_3), 2.16–2.19 (m, 1H, CH), 2.44–2.52 (m, 2H, CH_2), 2.91–3.06 (m, 2H, CH_2), 4.32 (d, J = 6.6 Hz, 2H, CH2), 5.91 (dd, J = 8.1, 8.1 Hz, 1H, CH), 6.89–6.94 (m, 2H, Ar-H), 7.11 (d, J = 6.6 Hz, 2H, Ar-H), 7.39 (m, 2H, Ar-H), 7.82 (d, J = 6 Hz, 1H, Ar-H), 7.97 (d, J = 5.7 Hz, 1H, Ar-H); ms: m/z 351.2 (M^++1); Anal. Calcd. for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found: C, 71.86; H, 6.43; N, 8.10.

Phenyl 2-(chroman-2-yl)-1H-benzimidazole-1-carboxylate (6d). ir (KBr): 3460, 2938, 1762 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.52–2.57 (m, 2H, CH_2), 2.99–3.05 (m, 2H, CH_2), 5.92 (dd, J = 8.6, 8.7 Hz, 1H, CH), 6.86–6.97 (m, 2H, Ar-H), 7.12 (d, J = 7.5 Hz, 2H, Ar-H), 7.26–7.52 (m, 7H, Ar-H), 7.87 (d, J = 6.3 Hz, 1H, Ar-H), 8.09 (d, J = 5.7 Hz ,1H, Ar-H); ms: m/z 371.1 (M^++1); Anal. Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56. Found: C, 74.69; H, 4.78; N, 7.66.

2-(Chroman-2-yl)-1-methanesulfonyl-1H-benzimidazole (6e). ir (KBr): 3436, 1583, 1489 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.59–2.69 (m, 2H, CH_2), 3.02–3.08 (m, 2H, CH_2), 3.56 (s, 3H, CH_3), 5.82 (dd, J = 7.9, 8.1 Hz, 1H, CH), 6.76 (d, J = 8.1 Hz, 2H, Ar-H), 6.89–6.94 (m, 2H, Ar-H), 7.41–7.44 (m, 2H, Ar-H), 7.82 (d, J = 7.8 Hz, 1H, Ar-H), 7.97 (d, J = 6.3 Hz, 1H, Ar-H); ms: m/z 329.1 (M^++1); Anal. Calcd. for $C_{17}H_{16}N_2O_3S$: C, 62.18; H, 4.91; N, 8.53. Found: C, 62.32; H, 4.80; N, 8.49.

2-(Chroman-2-yl)-1-tosyl-1H-benzimidazole (6f). ir (KBr): 3399, 1485, 1374 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H, CH_3), 2.53–2.61 (m, 2H, CH_2), 2.96–3.10 (m, 2H, CH_2), 5.97 (dd, J = 7.7, 7.9 Hz, 1H, CH), 6.7 (d, J = 9 Hz, 1H, Ar-H), 6.88–6.93 (m, 1H, Ar-H), 7.08–7.15 (m, 2H, Ar-H), 7.3–7.40 (m, 4H, Ar-H), 7.76 (d, J = 7.8 Hz, 1H, Ar-H), 7.97 (d, J = 8.1 Hz, 2H, Ar-H), 8.05 (d, J = 8.1 Hz, 1H, Ar-H); ms: m/z 405.1 (M^++1); Anal. Calcd. for $C_{23}H_{20}N_2O_3S$: C, 60.30; H, 4.98; N, 6.93. Found: C, 60.15; H, 5.20; N, 6.78.

Methyl-2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (6′c). ir (KBr): 3434, 2926, 1753, 1481, 1357 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.42–2.52 (m, 2H, CH_2), 2.95–3.08 (m, 2H, CH_2), 4.13 (s, 3H, CH_3), 5.88 (dd, J = 8.4, 8.4 Hz, 1H, CH), 6.83 (d, J = 8.7 Hz, 1H, Ar-H), 7.19–7.4 (m, 4H, Ar-H), 7.80–7.95 (m, 2H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 23.22 (CH_2), 23.87 (CH_2), 53.52 (NCH_3), 70.76 (OCH), 111.55, 113.68, 117.56, 119.39, 122.77, 123.47, 128.85, 130.66, 130.95, 131.31, 140.59, 149.28, 151.85, 152.26 (aromatic carbons) ppm; ms: m/z 389.52 (M^++1); Anal. Calcd. for $C_{18}H_{15}BrN_2O_3$: C, 55.83; H, 3.90; N, 7.23. Found: C, 55.94; H, 3.78; N, 7.34.

Ethyl-2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (6′d). ir (KBr): 3436, 2945, 1745, 1480, 1330 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.51 (t, J = 7.2 Hz, 3H, CH_3), 2.45–2.50 (m, 2H, CH_2), 2.94–3.02 (m, 2H, CH_2), 4.58 (q, J = 5.4 Hz, 2H, CH_2), 5.88, (dd, J = 8.7 and 8.7 Hz, 1H, CH), 6.82 (d, J = 8.4 Hz, 1H, Ar-H), 7.19–7.39 (m, 4H, Ar-H), 7.8–7.97 (m, 2H, Ar-H) ppm; ^{13}C NMR (DMSO-d_6) (75 MHz): δ 13.1 (CH_3), 63.52 (NCH_2), 23.29 (CH_2), 24.94 (CH_2), 70.87 (OCH), 111.58, 113.78, 117.62, 119.44, 122.76, 123.43, 128.90, 130.71, 130.98, 131.52, 140.66, 148.78, 151.89, 152.29 (aromatic carbons) ppm; ms: m/z 403.46 (M^++1); Anal. Calcd. for $C_{19}H_{17}BrN_2O_3$: C, 56.87; H, 4.27; N, 6.98. Found: C, 56.70; H, 4.38; N, 7.15.

Isobutyl-2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (6′e). ir (KBr): 3429, 2927, 1730, 1663, 1474 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 1.07 (d, J = 6.6 Hz, 6H, CH_3), 1.50–1.58 (m, 1H, CH), 2.17–2.24 (m, 2H, CH_2), 2.98–3.04 (m, 2H, CH_2), 4.32 (d, J = 6.6 Hz, 2H, CH_2), 5.9 (dd, J = 8.9, 8.9 Hz, 1H, CH), 6.82 (d, J = 8.4 Hz, 1H, Ar-H), 7.18–7.26 (m, 2H, Ar-H), 7.37–7.39 (m, 2H, Ar-H), 7.81 (d, J = 7.8 Hz, 1H, Ar-H), 7.96 (d, J = 6.6 Hz, 1H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 19.21, 19.21, 24.38 (CH_3), 26.06 (CH_2), 27.81, 71.92 (CH_3), 74.46, 112.65, 114.80, 118.73, 120.59,

123.83, 124.52, 125.32, 129.98, 131.79, 132.59, 141.79, 150.10, 153.10, 153.38 (aromatic carbons) ppm; ms: *m/z* 429.51 (M^++1); Anal. Calcd. for $C_{21}H_{21}BrN_2O_3$: C, 58.75; H, 4.93; N, 6.53. Found: C, 58.82; H, 4.83; N, 6.64.

2-(6-Bromochroman-2-yl)-1-methanesulfonyl-1H-benzimidazole (6′f). ir (KBr): 3435, 3030, 2927, 1475, 1372 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.58–2.66 (m, 2H, CH_2), 2.96–3.04 (m, 2H, CH_2), 3.52 (s, 3H, CH_3), 5.8 (dd, *J* = 8.7, 8.9 Hz, 1H, CH), 6.65 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.18–7.44 (m, 4H, Ar-H), 7.82 (d, *J* = 5.4 Hz, 1H, Ar-H), 7.96 (d, *J* = 6.3 Hz, 1H, Ar-H) ppm; ^{13}C NMR (DMSO-d_6) (75 MHz): δ 24.25 (CH_2), 24.83 (CH_2), 42.62 (SCH_3), 70.69 (OCH), 113.32, 116.09, 117.88, 120.99, 124.17, 125.02, 126.03, 129.82, 130.11, 132.30, 141.04, 150.75, 152.76 (aromatic carbons) ppm; ms: *m/z* 409.23 (M^++1); Anal. Calcd. for $C_{17}H_{15}BrN_2O_3S$: C, 50.13; H, 3.71; N, 6.88. Found: C, 50.30; H, 3.59; N, 7.11.

2-(6-Bromochroman-2-yl)-1-tosyl-1H-benzimidazole (6′g). ir (KBr): 3432, 2938, 1474, 1370 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.41 (s, 3H, CH_3) 2.42–2.52 (m, 2H, CH_2), 2.92–3.01 (m, 2H, CH_2), 5.96 (dd, *J* = 8.4 and 8.4 Hz, 1H, CH), 6.56 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.18 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.26–7.42 (m, 4H, Ar-H), 7.76 (d, *J* = 6.9 Hz, 1H, Ar-H), 7.94 (d, *J* = 8.1 Hz, 2H, Ar-H), 8.04 (d, *J* = 7.8 Hz, 2H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 21.70 (CH_3), 24.38 (CH_2), 26.08 (CH_2), 70.77 (OCH), 112.98, 113.78, 118.35, 120.95, 124.07, 124.94, 125.83, 127.29, 127.29, 130.04, 130.04, 130.09, 132.17, 132.91, 135.21, 141.46, 146.12, 151.62, 153.21 (aromatic carbons) ppm; ms: *m/z* 483.38 (M^++1); Anal. Calcd. for $C_{23}H_{19}BrN_2O_3S$: C, 57.15; H, 3.96; N, 5.80. Found: C, 57.31; H, 3.85; N, 5.62.

General procedure for the synthesis of compound (6g-6k and 6′h-6′l) using ILs. A solution of (2 mmol) of **5** and **5a**, (4 mmol) of sodium hydroxide in ILs (2 mL), followed by the addition of appropriate (3 mmol) benzyl bromides at 25–30°C. After the addition was complete, the solution was heated to 75°C for 5–6 h (as monitored by TLC). The reaction mass was then cooled to 25°C and diluted with water (25 mL). The resultant solid was filtered and washed with water (10 mL) to afford crude products. The crude products were recrystallized from ethanol, to obtain pure compounds **6g-6k** and **6′h-6′l**, respectively. The aqueous layer contains the ILs, which was recovered as described earlier procedure.

2-(Chroman-2-yl)-1-benzyl-1H-benzimidazole (6g). ir (KBr): 3432, 2930, 1583, 1487, 1232 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.55–2.63 (m, 2H, CH_2), 2.94–3.01 (m, 2H, CH_2), 5.36 (dd, *J* = 9.3, 9.4 Hz, 1H, CH), 5.62 (s, 2H, CH_2), 6.64 (d, *J* = 8.1 Hz, 1H, Ar-H), 6.85–6.90 (m, 1H, Ar-H), 7.03–7.13 (m, 4H, Ar-H), 7.26–7.28 (m, 6H, Ar-H), 7.83 (d, *J* = 6, 6 Hz, 1H, Ar-H); ms: *m/z* 341.2 (M^++1); Anal. Calcd. for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.27; H, 5.82; N, 8.35.

2-(Chroman-2-yl)-1-(4-fluorobenzyl)-1H-benzimidazole (6h). ir (KBr): 3454, 2945, 1485 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.56–2.60 (m, 2H, CH_2), 2.90–3.02 (m, 2H, CH_2), 5.35 (dd, *J* = 8.7, 9.0 Hz, 1H, CH), 5.58 (s, 2H, CH_2), 6.62 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.86–6.91 (m, 1H, Ar-H), 6.99–7.11 (m, 5H, Ar-H), 7.24–7.28 (m, 4H, Ar-H), 7.82 (d, *J* = 6.6 Hz, 1H, Ar-H); ms: *m/z* 360.2 (M^++1); Anal. Calcd. for $C_{23}H_{19}FN_2O$: C, 77.08; H, 5.34; N, 7.82. Found: C, 77.26; H, 5.42; N, 7.68.

2-(Chroman-2-yl)-1-(4-bromobenzyl)-1H-benzimidazole (6i). ir (KBr): 3432, 2926, 1584, 1459, 1231cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.54–2.60 (m, 2H, CH_2), 2.99–3.04 (m, 2H, CH_2), 5.34 (dd, *J* = 7.8, 8.4 Hz, 1H, CH), 5.56 (s, 2H, CH_2), 6.59 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.88 (m, 2H, Ar-H), 6.99–7.11 (m, 2H, Ar-H), 7.19–7.31 (m, 4H, Ar-H), 7.42 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.83 (d, *J* = 7.2 Hz, 1H, Ar-H); ms: *m/z* 421.1 (M^++1); Anal. Calcd. for $C_{23}H_{19}BrN_2O$: C, 65.88; H, 4.57; N, 6.68. Found: C, 65.98; H, 4.45; N, 6.78.

2-(Chroman-2-yl)-1-(4-methylbenzyl)-1H-benzimidazole (6j). ir (KBr): 3431, 1582, 1456, 1230 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.31 (s, 3H, CH_3), 2.55–2.61 (m, 2H, CH_2), 2.91–3.01 (m, 2H, CH_2), 5.33 (dd, *J* = 7.5 Hz, 1H, CH), 5.57 (s, 2H, CH_2), 6.7 (d, *J* = 8.1 Hz, 1H, 5′ Ar-H), 6.86–6.90 (m, 1H, Ar-H), 7.01–7.11 (m, 6H, Ar-H), 7.30–7.32 (m, 3H, Ar-H), 7.82 (d, *J* = 7.2 Hz, 1H, Ar-H); ms: *m/z* 355.2 (M^++1); Anal. Calcd. for $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90. Found: C, 81.19; H, 6.37; N, 8.11.

2-(Chroman-2-yl)-1-(4-tert-butylbenzyl)-1H-benzimidazole (6k). ir (KBr): 3428, 2958, 1581, 1463 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.28 (s, 9H, *tert* butyl), 2.55–5.62 (m, 2H, CH_2), 2.97–3.01 (m, 2H, CH_2), 5.34 (dd, *J* = 9.1, 9.1 Hz, 1H, CH), 5.52–5.65 (s, 2H, CH_2), 6.63–6.66 (m, 1H, Ar-H), 6.85–6.90 (m, 1H, Ar-H), 7.03–7.10 (m, 3H, Ar-H), 7.26–7.31 (m, 6H, Ar-H), 7.82 (d, *J* = 6.2 Hz, 1H, Ar-H); ms: *m/z* 397.2 (M^++1); Anal. Calcd. for $C_{27}H_{28}N_2O$: C, 81.78; H, 7.12; N, 7.06. Found: C, 81.69; H, 7.31; N, 7.20.

2-(6-Bromochroman-2-yl)-1-benzyl-1H-benzimidazole (6′h). ir (KBr): 3446, 2926, 1574, 1482, 1234 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.46–2.55 (m, 2H, CH_2), 2.94–3.01 (m, 2H, CH_2), 5.38 (dd, *J* = 7.2, 8.1 Hz, 1H, CH), 5.60 (s, 2H, CH_2), 6.47 (d, *J* = 9 Hz, 1H, Ar-H), 7.02–7.15 (m, 2H, Ar-H), 7.21–7.28 (m, 8H, Ar-H), 7.86 (d, *J* = 7.8 Hz, 1H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 22.99 (CH_2), 23.68 (CH_2), 46.54 (NCH_2), 70.08 (OCH), 108.89, 111.84, 117.25, 118.97, 121.24, 122.23, 122.73, 125.07, 125.07, 126.51, 127.57, 127.57, 128.87, 130.88, 134.55, 134.89, 140.74, 150.15, 151.41 (aromatic proton) ppm; ms: *m/z* 421.60 (M^++1); Anal. Calcd. for $C_{23}H_{19}BrN_2O$: C, 65.88; H, 4.57; N, 6.68. Found: C, 65.70; H, 4.68; N, 6.77.

2-(6-Bromochroman-2-yl)-1-(4-fluorobenzyl)-1H-benzimidazole (6′i). ir (KBr): 3435, 2928, 1605, 1484, 1227 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.54–2.58 (m, 2H, CH_2), 2.96–3.04 (m, 2H, CH_2), 5.38 (dd, *J* = 8.4, 8.4 Hz, 1H, CH), 5.56 (s, 2H, CH_2), 6.47 (d, *J* = 9 Hz, 1H, Ar-H), 6.96–6.99 (m, 2H, Ar-H), 7.12–7.22 (m, 3H, Ar-H), 7.26–7.44 (m, 4H, Ar-H), 7.85 (d, *J* = 9 Hz, 1H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 24.02 (CH_2), 24.72 (CH_2), 47.07 (NCH_2), 71.28 (OCH), 110.01, 113.17, 115.63, 115.92, 118.39, 120.29, 122.60, 123.57, 123.98, 128.03, 128.14, 130.18, 131.91, 132.22, 135.64, 142.03, 151.33, 152.62, 160.58 (aromatic carbons) ppm; ms: *m/z* 437.7 (M^++1); Anal. Calcd. for $C_{23}H_{18}BrFN_2O$: C, 63.17; H, 4.15; N, 6.41. Found: C, 63.28; H, 4.31; N, 6.28.

2-(6-Bromochroman-2-yl)-1-(4-bromobenzyl)-1H-benzimidazole (6′j). ir (KBr): 3444, 2932, 1574, 1480, 1234 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.51–2.57 (m, 2H, CH_2), 2.92–3.02 (m, 2H, CH_2), 5.36 (dd, *J* = 9, 9 Hz, 1H, CH), 5.54 (s, 2H, CH_2), 6.46 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.44 (d, *J* = 9 Hz, 2H, Ar-H), 6.97 (d, *J* = 7.8 Hz, 2H, Ar-H) 7.19 (m, 3H, Ar-H), 7.44 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.83 (d, *J* = 7.8 Hz, 1H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 23.95 (CH_2), 24.96 (CH_2), 47.11 (NCH_2), 71.13 (OCH), 109.81, 113.05, 118.19, 120.09, 121.48, 122.49, 123.45, 123.76, 127.88, 127.88, 129.96, 131.71,

131.71, 131.91, 134.97, 135.34, 141.74, 151.06, 152.34 (aromatic carbons) ppm; ms: *m*/*z* 499.64 (M^++1); Anal. Calcd. for $C_{23}H_{18}Br_2N_2O$: C, 55.45; H, 3.64; N, 5.62. Found: C, 55.34; H, 3.76; N, 5.49.

2-(6-Bromochroman-2-yl)-1-(4-methylbenzyl)-1H-benzimidazole (6′k). ir (KBr): 3427, 2929, 1513, 1262 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.51–2.55 (m, 2H, CH_2), 2.94–3.0 (m, 2H, CH_2), 5.41 (dd, *J* = 8.6, 8.6 Hz, 1H, CH), 5.56 (s, 2H, CH_2), 6.55 (d, *J* = 8.7 Hz, 1H, Ar-H), 6.98–6.70 (m, 2H, Ar-H), 7.09–7.16 (m, 4H, Ar-H), 7.22–7.29 (s, 3H, Ar-H), 7.85 (d, *J* = 7.2 Hz, 1H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 21.16 (CH_3), 24.19 (CH_2), 24.88 (CH_2), 47.52 (NCH_2), 71.25 (OCH), 110.12, 112.99, 118.46, 119.9, 120.10, 122.35, 123.33, 123.93, 126.26, 129.39, 129.39, 130.04, 132.05, 132.97, 135.46, 137.46, 141.90, 151.28, 152.67 (aromatic carbons) ppm; ms: *m*/*z* 435.75 (M^++1); Anal. Calcd. for $C_{24}H_{21}BrN_2O$: C, 66.52; H, 4.88; N, 6.46. Found: C, 66.40; H, 5.13; N, 6.58.

2-(6-Bromochroman-2-yl)-1-(4-tert-butylbenzyl)-1H-benzi-midazole (6′l). ir (KBr): 3446, 2962, 1475, 1411, 1219 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.28 (s, 9H, *tert*. butyl), 2.50–2.54 (m, 2H, CH_2), 2.94–2.99 (m, 2H, CH_2), 5.36 (dd, *J* = 9.9 Hz, 1H, CH), 5.57 (s, 2H, CH_2), 7.02 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.11–7.13 (m, 1H, Ar-H), 7.21–7.29 (m, 8H, Ar-H), 7.85 (d, *J* = 7.8 Hz, 1H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$) (75 MHz): δ 24.06 (CH_2), 24.75 (CH_2), 31.30, 31.30, 31.30 (CH_3), 34.51 (*tert*.butyl), 47.29 (NCH_2), 71.06, (OCH), 110.04, 112.90, 118.39, 120.05, 122.27, 123.25, 123.87, 125.56, 125.56, 125.91, 125.91, 129.91, 131.95, 133.03, 135.73, 141.86, 150.57, 151.24, 152.56 (aromatic carbons) ppm; ms: *m*/*z* 477.40 (M^++1); Anal. Calcd. for $C_{27}H_{27}BrN_2O$: C, 68.21; H, 5.72; N, 5.89. Found: C, 68.10; H, 5.80; N, 6.10.

Phenyl-2-(6-bromochroman-2-yl)-1H-benzimidazole-1-carboxylate (6′m). ir (KBr): 3435, 2925, 1766, 1475, 1355, 1232 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.50–2.54 (m, 2H, CH_2), 2.95–3.05 (m, 2H, CH_2), 5.60 (s, 2H, CH_2), 5.94 (dd, *J* = 9.0, 9.1 Hz, 1H, CH), 6.90 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.09–7.14 (m, 2H, Ar-H), 7.26–7.52 (m, 5H, Ar-H), 7.86–7.88 (m, 1H, Ar-H), 8.07–8.09 (m, 1H, Ar-H) ppm; ms: *m*/*z* 421.72 (M^++1); Anal. Calcd. for $C_{23}H_{17}BrN_2O_3$: C, 61.48; H, 3.81; N, 6.23. Found: C, 61.58; H, 3.92; N, 6.31.

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