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A simple and efficient one-pot synthesis of novel benzimidazo[1,2-*a*]-chromeno[4,3-*d*] pyrimidinones catalyzed by $[Et_3NH][HSO_4]$

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A simple and efficient one-pot synthesis of novel polyheterocyclic benzimidazo[1,2-*a*]- chromeno[4,3-*d*]pyrimidinones **4** *via* a three-component condensation of 2-aminobenzimidazole **1**, aromatic aldehydes **2** and 4-hydroxy coumarin **3** catalyzed by Bronsted acid ionic liquid triethyl ammonium hydrogen sulphate $[Et_3NH][HSO_4]$ under solvent-free conditions is reported. The main advantages of this protocol are short reaction time, easy work-up, operational simplicity, and excellent yields with high purity, without intervention of chromatography.

Keywords: Multi-component synthesis, benzimidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidinones, polyheterocycles, triethyl ammonium hydrogen sulphate [TEAHS], solvent-free conditions

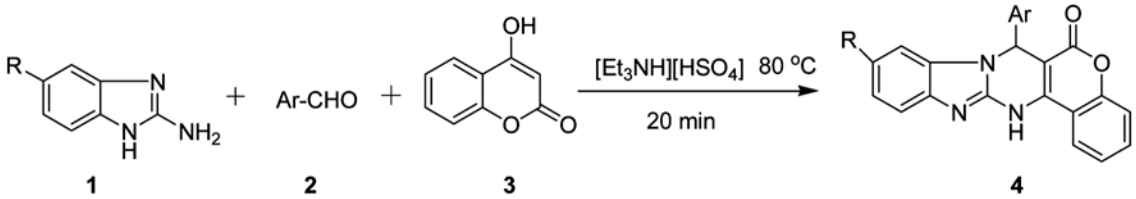
Multi-component reactions (MCRs) have proved to be remarkably successful in generating products in a single synthetic operation[1,2], and are important owing to their synthetic efficiency[3,4]. In times, where a premium is put on speed, diversity, and efficiency in drug discovery process[5], MCR strategies offer significant advantages over conventional linear-type syntheses. MCRs contribute to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption and waste production. Besides this, MCRs have their inherent advantages of atom economy, short reaction time, operational simplicity, and structural diversity to get the goal of an ideal organic synthesis[6,7].

Heterocycles containing nitrogen atom are abundant in nature, and exhibit diverse and promising biological activities[8]. Nitrogen-bridged polyheterocycles are frequently found in natural products and pharmaceutical agents. Fused pyrimidine core structures have wide applications as pharmacophores, and exhibited antibacterial[9], antiparasitic[10], antiviral[11], and anti-inflammatory activities[12]. On the other hand, chromene is a ubiquitous heterocyclic scaffold and important pharmacophore that displays several biological properties such as antioxidant[13], antimicrobial[14], antitumor[15], anticoagulant[16] and antivascular activities[17]. Similarly, benzimidazole is an important nucleus that has been extensively used in medicinal chemistry, notable examples being the antihistaminic asterizole and the antiulcerative omeprazole[18,19]. Benzimidazoles are also known for their anti-inflammatory[20], antibiotic[21], anthelmintic[22], anticancer[23], and antiviral activities[24]. Prompted by these reports, and as a sequel to our interest in developing more efficient methodologies for the synthesis of fused polyheterocyclic compounds[25-27], we report herein a simple, and high-yielding one-pot efficient protocol for the synthesis of novel benzimidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidinones by using $[Et_3NH][HSO_4]$ as a reusable catalyst under solvent-free conditions.

Results and Discussion

The synthesis of title compounds has been accomplished by synthetic sequence shown in Scheme I. The three-component reaction of 2-amino benzimidazole (**1**), substituted aromatic aldehydes (**2**), and 4-hydroxy coumarin (**3**) in presence of 20 mol% of Bronsted acid ionic liquid triethyl ammonium hydrogen sulphate $[Et_3NH][HSO_4]$ (TEAHS) at 80^0C for 20 min under solvent-free reaction conditions furnished novel 7-aryl-7,14-dihydro-6*H*-benzo [4,5]imidazo- [1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-ones **(4)** in excellent yields (Scheme I).

The above reaction was initially carried out in the presence of triethyl amine, and subsequently with



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	R	Ar		R	Ar
a	H	C_6H_5	**h**	CH_3	C_6H_5
b	H	4-$CH_3C_6H_4$	**i**	CH_3	4-$OCH_3C_6H_4$
c	H	4-$OCH_3C_6H_4$	**j**	CH_3	4-ClC_6H_4
d	H	4-$N(CH_3)_2C_6H_4$	**k**	CH_3	4-BrC_6H_4
e	H	4-ClC_6H_4	**l**	Cl	C_6H_5
f	H	4-BrC_6H_4	**m**	Cl	4-$CH_3C_6H_4$
g	H	4-$NO_2C_6H_4$	**n**	Br	C_6H_5
			o	Br	4-$OCH_3C_6H_4$

Scheme I

piperidine, and *P*TSA catalyst at 80°C in ethanol. The product was isolated in 40, 35, and 55% yields respectively, and it took more time (100-120 min). Consequently, we conducted the reaction by using ionic liquid $[Et_3NH][HSO_4]$ in ethanol solvent at 80 °C. The product was isolated in 75% yield, and it also required more time (100 min). Then, the reaction was carried out with $[Et_3NH][HSO_4]$ catalyst in the absence of solvent at 80°C. To our surprise, the product yield increased to 95% under solvent-free reaction conditions, and the reaction completed within 20 min.

The reaction was also explored by using different ionic liquids *viz*., $[bmIm]BF_4$, [bmIm]OH, [bmIm]Br and $[HMim]BF_4$. Among all the ionic liquids screened, $[Et_3NH][HSO_4]$ was found to be superior with respect to the reaction time and product yield. Utilization of other ionic liquids was found to be quite unsatisfactory. TEAHS is playing the dual role of solvent as well as catalyst in this reaction.

To establish the feasibility of the strategy, and optimize reaction conditions, the reaction was further studied by increasing the catalyst loading from 20 mol% to 30 mol%. We found that, there is no noticeable improvement in the yield of the desired product (95%), even after increasing the catalyst loading to 30%. We also examined the reaction by decreasing the catalyst loading to 10 mol%. The reaction resulted in low yield (85%) compared to 20 mol % reaction (95%). The effect of temperature on the reaction was also observed. It is noticed that by increasing the temperature to 100°C, the yields are not improved. When the reaction was run at 60^0C, decrease in the yield (80%) was observed. Therefore, based on the above results, we concluded that 80 ^{0}C temperature, 20 min time, and 20 mol % of the TEAHS catalyst under solvent-free conditions is sufficient and optimum for the complete conversion of reactants into the products (Table I).

Having established that, the best solvent and catalyst is TEAHS for this transformation, the another advantage is, it can easily be recovered after the completion of the reaction, and can be used in subsequent runs (five runs) without loss of efficiency, and product yield. The recovery and reusability of TEAHS was also investigated. After completion of the reaction, cold water was added to the reaction mixture, and the products were isolated by filtration. The IL was recovered by removing water under reduced pressure, and was reused at least for five times without appreciable loss of catalyst, and product yield (Table II).

The effect of different substituents on the benzene ring of aromatic aldehydes and amines are also investigated. We found that, different substituted aromatic aldehydes, and amines take part in this one-pot condensation, and provided the corresponding products in excellent yields. It has also been observed that, this method has the ability to tolerate a variety of functional groups such as electron donating methyl, methoxy, dimethylamino, and electron withdrawing chloro, bromo and nitro groups substituted on the aromatic ring of the aldehyde as well as on the amine. In all these cases, the product yields are excellent.

A plausible mechanism for the synthesis of novel benzimidazo[1,2-*a*]chromeno- [4,3-*d*]pyrimidinones is depicted in Scheme II. The first step is the

Table I — Effect of different catalysts and ionic liquids on the synthesis of benzimidazo[1,2-*a*]-chromeno[4,3-*d*]pyrimidinones **4**

Entry	Catalyst	Catalyst loading (mol%)	Solvent	Temp(°C)	Time (min)	Yield(%)[a]
1	Et_3N	20	EtOH	80	120	40
2	Piperidine	20	EtOH	80	100	35
3	*p*-TSA	20	EtOH	80	100	55
4	$[Et_3NH]HSO_4$	20	EtOH	80	100	75
5	$[Et_3NH]HSO_4$	20	solvent- free	80	20	95
6	$[bmIm]BF_4$	20	solvent- free	80	40	58
7	[bmIm]OH	20	solvent- free	80	25	45
8	[bmIm]Br	20	solvent- free	80	50	30
9	$[HMIm]BF_4$	20	solvent -free	80	20	65
10	$[Et_3NH][HSO_4]$	30	solvent- free	80	20	95
11	$[Et_3NH][HSO_4]$	10	solvent -free	80	20	85
12	$[Et_3NH][HSO_4]$	20	solvent -free	100	20	95
13	$[Et_3NH][HSO_4]$	20	solvent -free	60	20	80

[a] Optimized and isolated yields.

Table II — Recycling of IL $[Et_3NH][HSO_4]$

Run	IL recycled (in mL)	Yield (%) [a]
1	5	95
2	5	95
3	4.7	94
4	4.5	92
5	4.0	90

[a] Isolation yields

Knoevenagel condensation between aldehyde (**2)** and 4-hydroxy coumarin (**3)** catalyzed by TEAHS. The resulting intermediate (**5),** then undergoes Michael type addition with 2-aminobenzimidazole (**1)** to afford the adduct (**6)**. Subsequently, **6** undergoes intramolecular ring- closure followed by dehydration to afford title compounds (**4**).

Fifteen new benzimidazo[1,2-*a*]chromeno[4,3-*d*] pyrimidinones **(4a-o)** are reported for the first time. The structures of all the newly synthesized compounds **(4)** are confirmed by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. Elemental analyses confirmed the elemental composition and purity of the newly synthesized compounds.

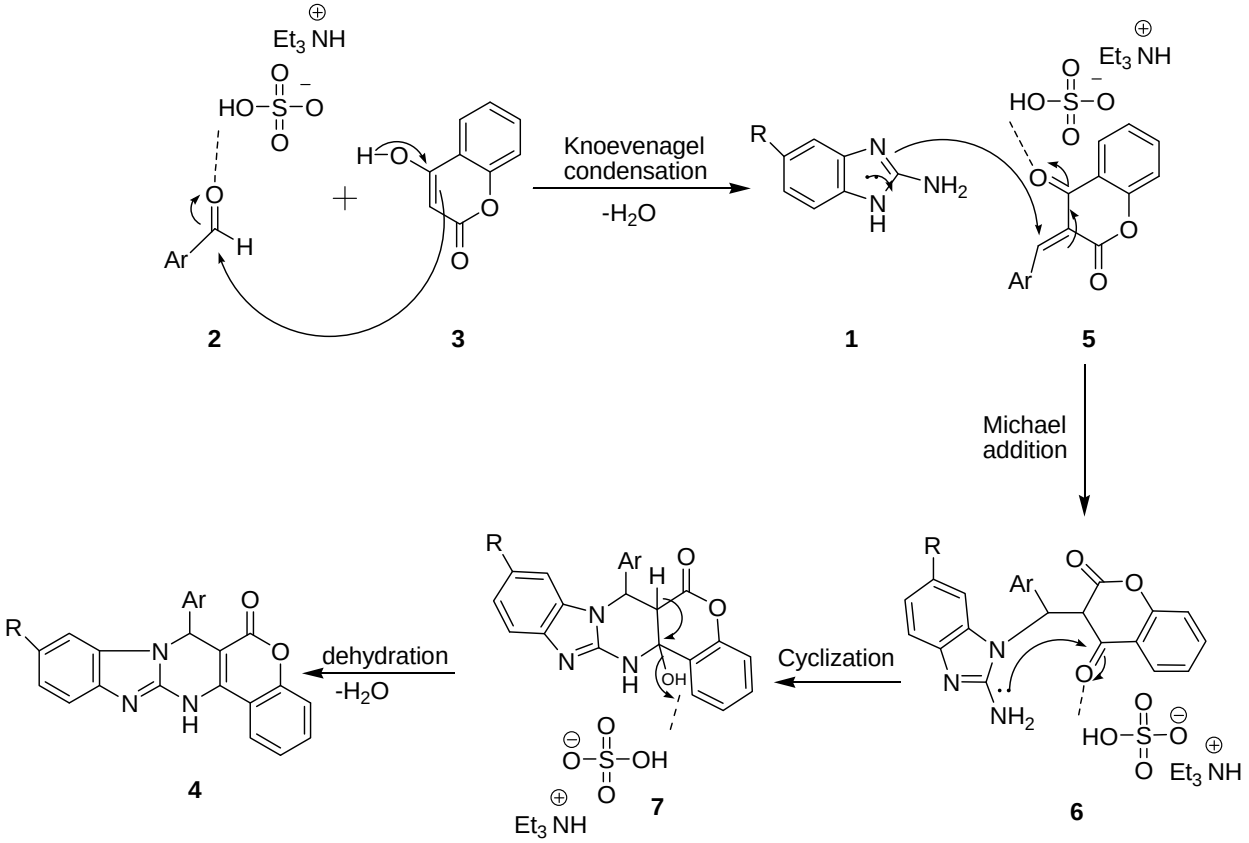
IR spectrum of compound **4a** exhibited strong absorption bands at 3450, 1670, 1620 and 1130 cm^{-1} for NH, C=O, C=N and C-O-C functional groups respectively. ^{1}HNMR spectrum of **4a** displayed a prominent peak at δ 5.66 due to ArCH proton. The NH proton appeared as a broad singlet at δ 8.76, which is D_2O exchangeable. All the aromatic protons appeared as a complex multiplet between δ 7.00-7.83. In ^{13}C NMR spectrum of **4a,** ArCH carbon signal appeared at δ 49.34 confirming the cyclization. The mass spectrum of **4a** displayed the molecular ion $[M+H]^+$ peak at *m/z* 366, supporting the formation of benzimidazo [1,2-*a*]chromeno[4,3-*d*]pyrimidinone (**4a)**.

Experimental Section

Melting points have been determined on a Fisher-Johns melting point apparatus and are uncorrected. Analytical TLC has been performed on Merck precoated 60 F_{254} silica gel plates. Visualization is carried out by exposure to iodine vapour. IR spectra (KBr pellet) have been recorded on a Perkin-Elmer BX series FT-IR spectrometer. ^{1}H NMR spectra are recorded on a Bruker 300 MHz spectrometer. ^{13}C NMR spectra are recorded on a Bruker 75 MHz spectrometer. Chemical shift values are given in δ ppm with tetramethyl silane as an internal standard. ESI mass spectra are recorded on a Agilent LC-MSD mass spectrometer. Elemental analyses are performed on a Carlo Erba 106 and Perkin-Elmer model 240 analyzers.

General procedure for the synthesis of 7-aryl-7,14-dihydro-6*H*-benzo[4,5]imidazo [1,2-*a*] chromeno [4,3-*d*]pyrimidin-6-ones (4a-o)

To a mixture of 2-amino benzimidazole (**1a**, 1 mmol), aromatic aldehyde (**2a**, 1 mmol) and 4-hydroxy coumarin (**3a**, 1 mmol), 20 mol % $[Et_3NH][HSO_4]$ was added, and the reaction mixture was stirred at 80°C under solvent-free conditions for 20 min. The termination of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, water was added, and the contents are stirred for 5 min. The solid thus obtained was removed by filtration, and recrystallized from ethanol to afford the pure product **4a**. The water was removed from filtrate under



Scheme II — Plausible mechanism for the synthesis of novel benzimidazo[1,2-*a*]chromeno-[4,3-*d*]pyrimidinones

reduced pressure to recover $[Et_3NH][HSO_4]$, which was then reused in subsequent cycles. Compounds (**4b-4o)** have been synthesized by adopting similar procedure.

7-Phenyl-7,14-dihydro-*6H*-benzo[4,5]imidazo [1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4a) Orange solid, yield 95%, m.p. 192-94°C, IR (KBr): 3450 (NH), 1670 (CO), 1620 (C=N), 1130 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.66 (s, 1H, CH), 7.00-7.83 (m, 13H, Ar-H), 8.76 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 49.34, 99.45, 114.35, 115.43, 115.98, 121.76, 123.10, 123.68,125.24, 125.98, 126.98, 127.89, 128.03, 128.98, 129.05, 129.87, 134.65, 137.45, 138.97, 149.56, 150.45, 152.76, 165.45; ESI-MS: *m/z* 366 $[M+H]^+$. Anal.cacld for $C_{23}H_{15}N_3O_2$: C, 75.61; H, 4.10; N, 11.50 % Found: C, 75.64; H, 4.13; N, 11.52 %.

7-(*P*-Tolyl)-7,14-dihydro-6*H*-benzo[4,5]imidazo [1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4b)

Orange solid, yield 95%, m.p. 182-84°C, IR (KBr): 3456 (NH), 1674 (CO), 1626 (C=N), 1135 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 5.68 (s, 1H, CH), 7.06-7.86 (m, 12H, Ar-H), 8.76 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 24.12, 49.37, 99.49, 114.69, 115.49, 116.45, 122.16, 123.23, 123.72,125.24, 126.01, 126.99, 127.92, 128.09, 129.01, 129.55, 130.02, 134.65, 137.55, 139.02, 149.89, 150.85, 152.36, 166.02; ESI-MS: *m/z* 380 $[M+H]^+$. Anal.cacld for $C_{24}H_{17}N_3O_2$: C, 75.98; H, 4.48; N, 11.08 % Found: C, 75.95; H, 4.45; N, 11.05 %.

7-(4-Methoxyphenyl)-7,14-dihydro-6*H*-benzo [4,5]imidazo[1,2-*a*]chromeno [4,3-*d*]pyrimidin-6-one, (4c)

Orange solid, yield 95%, m.p. 187-89°C, IR (KBr): 3454 (NH), 1673 (CO), 1625 (C=N), 1133 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, OCH_3), 5.66 (s, 1H, CH), 7.06-7.89 (m, 12H, Ar-H), 8.78 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 49.39, 63.46, 99.99, 114.76, 115.59, 117.47, 122.56, 123.65, 123.92,125.54, 126.11,127.23, 127.92, 128.19, 129.10, 129.68, 130.12, 134.76, 137.98, 139.02, 150.02, 150.85, 152.66, 166.12; ESI-MS: *m/z* 396 $[M+H]^+$. Anal. cacld for $C_{24}H_{17}N_3O_3$: C, 72.91; H, 4.30; N, 10.63 % Found: C, 72.94; H, 4.33; N, 10.60 %.

7-(4-(Dimethylamino)phenyl)-7,14-dihydro-6*H*-benzo[4,5]imidazo[1,2-*a*]chromeno [4,3-*d*] pyrimidin-6-one, (4d)

Orange solid, yield 95%, m.p. 215-17°C, IR (KBr): 3460 (NH), 1672 (CO), 1625 (C=N), 1138 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.54 (s, 6H, $N(CH_3)_2$), 5.66 (s, 1H, CH), 7.06-7.90 (m, 12H, Ar-H), 8.78 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 48.32, 50.10, 51.79, 100.13, 114.91, 115.86, 117.88, 122.81, 123.98, 124.02, 125.87, 126.53,127.51, 127.98, 128.43, 129.30, 130.12, 130.45, 134.76, 138.01, 139.32, 150.08, 150.80, 154.16, 166.22; ESI-MS: *m/z* 409. $[M+H]^+$. Anal.cacld for $C_{25}H_{20}N_4O_2$: C, 73.52; H, 4.90; N, 13.72 % Found: C, 73.56; H, 4.93; N, 13.75 %.

7-(4-Chlorophenyl)-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4e)

Orange solid, yield 94%, m.p. 238-40°C, IR (KBr): 3459 (NH), 1672 (CO), 1626 (C=N), 1134 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.69 (s, 1H, CH), 7.06-7.94 (m, 12H, Ar-H), 8.78 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 50.10, 100.13, 114.89, 115.87, 118.07, 122.76, 123.88, 123.90,125.87, 126.33,127.85, 127.99, 128.55, 129.39, 130.20, 130.62, 134.89, 138.01, 139.32, 150.12, 150.95, 153.79, 166.30; ESI-MS: *m/z* 400 $[M+H]^+$. Anal.cacld for $C_{23}H_{14}ClN_3O_2$: C, 69.17; H, 3.50; N, 10.52 % Found: C, 69.14; H, 3.53; N, 10.55%.

7-(4-Bromophenyl)-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4f)

Brown solid, yield 94%, m.p. 272-74°C, IR (KBr): 3458 (NH), 1669 (CO), 1621 (C=N), 1136 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.68 (s, 1H, CH), 7.06-7.92 (m, 12H, Ar-H), 8.75 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 50.02, 100.03, 114.86, 115.79, 117.67, 122.76, 123.78, 123.92,125.67, 126.43,127.45, 127.92, 128.35, 129.30, 130.02, 130.22, 134.76, 137.98, 139.32, 150.02, 150.85, 153.76, 166.32; ESI-MS: *m/z* 444 $[M+H]^+$. Anal.cacld for $C_{23}H_{14}BrN_3O_2$: C, 62.30; H, 3.16; N, 9.48 % Found: C, 62.33; H, 3.13; N, 9.44 %.

7-(4-Nitrophenyl)-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4g)

Orange solid, yield 94%, m.p. 250-52°C, IR (KBr): 3461 (NH), 1671 (CO), 1625 (C=N), 1136 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.68 (s, 1H, CH), 7.02-7.90 (m, 12H, Ar-H), 8.79 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 50.13, 101.03, 113.89, 115.47, 118.67, 123.06, 123.90, 124.10,125.97, 126.13,128.05, 128.99, 129.15, 129.79, 130.00, 131.32, 135.19, 138.11, 139.52, 150.42, 151.15, 154.09, 166.51; ESI-MS: *m/z* 411 $[M+H]^+$. Anal.cacld for $C_{23}H_{14}N_4O_4$: C, 67.31; H, 3.41; N, 13.65 % Found: C, 67.34; H, 3.45; N, 13.62 %.

10-Methyl-7-phenyl-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4h)

Orange solid, yield 95%, m.p. 208-10°C, IR (KBr): 3458 (NH), 1672 (CO), 1623 (C=N), 1132 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 5.69 (s, 1H, CH), 7.02-7.96 (m, 12H, Ar-H), 8.78 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 24.22, 49.48, 99.89, 115.09, 115.89, 116.65, 122.86, 123.13, 123.94, 126.04, 126.11, 127.09, 127.98, 128.19, 129.11, 130.05, 130.82, 134.85, 137.95, 139.12, 149.89, 151.01, 152.36, 167.02; ESI-MS: *m/z* 380 $[M+H]^+$. Anal.cacld for $C_{24}H_{17}N_3O_2$: C, 75.98; H, 4.48; N, 11.08 % Found: C, 75.94; H, 4.50; N, 11.06 %.

7-(4-Methoxyphenyl)-10-methyl-7,14-dihydro-6*H*-benzo[4,5]imidazo[1,2-*a*]chromeno [4,3-*d*] pyrimidin-6-one, (4i)

Orange solid, yield 95%, m.p. 221-23°C, IR (KBr): 3457 (NH), 1676 (CO), 1626 (C=N), 1135 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 5.67 (s, 1H, CH), 7.09-7.93 (m, 11H, Ar-H), 8.79 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 25.16, 49.69, 63.36, 100.01, 114.46, 115.39, 116.87, 123.16, 123.85, 124.12, 125.64, 126.19, 127.13, 127.98, 128.29, 129.10, 129.81, 131.10, 134.88, 138.08, 139.22, 150.22, 151.15, 152.76, 166.32; ESI-MS: *m/z* 410 $[M+H]^+$. Anal.cacld for $C_{25}H_{19}N_3O_3$: C, 73.34; H, 4.64; N, 10.26 % Found: C, 73.31; H, 4.67; N, 10.24 %.

7-(4-Chlorophenyl)-10-methyl-7,14-dihydro-6*H*-benzo[4,5]imidazo[1,2-*a*]chromeno [4,3-*d*] pyrimidin-6-one, (4j)

Orange solid, yield 94%, m.p. 260-62°C, IR (KBr): 3458 (NH), 1676 (CO), 1628 (C=N), 1137 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 5.69 (s, 1H, CH), 7.03-7.90 (m, 11H, Ar-H), 8.78 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 24.32, 49.77, 100.02, 114.75, 115.29, 117.25, 122.36, 123.13, 123.92, 125.14, 126.21, 127.02, 127.95, 128.19, 129.23, 129.75, 131.02, 134.65, 137.35, 140.01, 149.80, 151.05, 152.39, 166.12; ESI-MS: *m/z* 414 $[M+H]^+$. Anal.cacld for $C_{24}H_{16}ClN_3O_2$: C, 69.73; H, 3.87; N, 10.16 % Found: C, 69.76; H, 3.84; N, 10.14%.

7-(4-Bromophenyl)-10-methyl-7,14-dihydro-6*H*-benzo[4,5]imidazo[1,2-*a*]chromeno [4,3-*d*]pyrimidin-6-one, (4k)

Brown solid, yield 94%, m.p. 280-82°C, IR (KBr): 3457 (NH), 1675 (CO), 1625 (C=N), 1135 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 5.68 (s, 1H, CH), 7.01-7.85 (m, 11H, Ar-H), 8.76 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 24.29, 49.67, 99.89, 114.54, 115.20, 117.15, 122.26, 122.93, 123.32, 125.25, 126.11, 127.22, 128.01, 128.59, 129.34, 129.85, 131.32, 134.87, 137.41, 140.21, 149.80, 151.35, 152.55, 166.38; ESI-MS: *m/z* 458 $[M+H]^+$. Anal.cacld for $C_{24}H_{16}BrN_3O_2$: C, 63.01; H, 3.50; N, 9.19% Found: C, C, 63.04; H, 3.53; N, 9.15%.

10-Chloro-7-phenyl-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4l)

Orange solid, yield 94%, m.p. 243-45°C, IR (KBr): 3456 (NH), 1673 (CO), 1625 (C=N), 1133 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.67 (s, 1H, CH), 7.04-7.98 (m, 12H, Ar-H), 8.79 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 50.12, 100.23, 114.92, 115.77, 118.58, 122.91, 123.25, 124.02, 125.37, 126.33, 127.65, 128.01, 128.65, 129.58, 131.00, 130.91, 134.79, 138.11, 139.55, 150.22, 151.21, 153.85, 166.56; ESI-MS: *m/z* 400 $[M+H]^+$. Anal.cacld for $C_{23}H_{14}ClN_3O_2$: C, 69.17; H, 3.50; N, 10.52 % Found: C, 69.19; H, 3.50; N, 10.50%.

10-Chloro-7-(p-tolyl)-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4m)

Orange solid, yield 94%, m.p. 266-68°C, IR (KBr): 3461 (NH), 1672 (CO), 1625 (C=N), 1137 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 5.69 (s, 1H, CH), 7.06-8.04 (m, 11H, Ar-H), 8.80 (s, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 24.87, 49.39, 99.59, 114.65, 115.61, 116.87, 122.21, 123.45, 123.87,125.34, 126.34, 126.99, 127.99, 128.10, 129.32, 129.59, 130.08, 134.35, 137.55, 139.22, 149.91, 150.86, 152.36, 166.32; ESI-MS: *m/z* 414 $[M+H]^+$. Anal.cacld for $C_{24}H_{16}ClN_3O_2$: C, 69.73; H, 3.87; N, 10.16 % Found: C, 69.71; H, 3.89; N, 10.13 %.

10-Bromo-7-phenyl-7,14-dihydro-6*H*-benzo[4,5] imidazo[1,2-*a*]chromeno[4,3-*d*]pyrimidin-6-one, (4n)

Brown solid, yield 94%, m.p. 276-78°C, IR (KBr): 3456 (NH), 1667 (CO), 1623 (C=N), 1134 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.66 (s, 1H, CH), 7.04-7.96 (m, 12H, Ar-H), 8.74 (bs, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 50.21, 100.23, 114.79, 116.79, 117.47, 121.76, 122.78, 123.42,125.69, 126.43, 127.76, 128.01, 128.39, 129.31, 130.02, 130.52, 135.16, 138.01, 139.22, 150.22, 151.32, 153.56, 166.39; ESI-MS: *m/z* 444 $[M+H]^+$. Anal.cacld for $C_{23}H_{14}BrN_3O_2$: C, 62.30; H, 3.16; N, 9.48 % Found: C, 62.28; H, 3.18; N, 9.45 %.

10-Bromo-7-(4-methoxyphenyl)-7,14-dihydro-6*H*-benzo[4,5]imidazo[1,2-*a*]chromeno [4,3-*d*]pyrimidin-6-one, (4o)

Brown solid, yield 94%, m.p. 286-88°C, IR (KBr): 3456 (NH), 1674 (CO), 1628 (C=N), 1137 (COC) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 5.68 (s, 1H, CH), 7.06-7.94 (m, 11H, Ar-H), 8.78 (s, 1H, NH, D_2O exchangeable); ^{13}C NMR (75MHz, $CDCl_3$): δ 50.02, 63.79, 100.01, 114.91, 115.39, 117.57, 123.01, 123.69, 124.05,125.59, 126.18, 127.43, 127.93, 128.29, 129.45, 129.78, 130.02, 134.57, 138.05, 139.06, 150.12, 150.80, 152.77, 166.52; ESI-MS: *m/z* 474 $[M+H]^+$. Anal.cacld for $C_{24}H_{16}BrN_3O_3$: C, 60.88; H, 3.38; N, 8.87 % Found: C, 60.86; H, 3.35; N, 8.89 %.

Conclusion

In conclusion, the present procedure that uses ionic liquid$[Et_3NH][HSO_4]$ provides a fast and highly efficient methodology for the synthesis of novel polyheterocyclic benzimidazo[1,2-*a*]- chromeno[4,3-*d*]pyrimidinones under solvent-free conditions. This protocol avoids the usage of hazardous organic solvents, and has several advantages such as high yields, convenient operation, easy-workup, catalytic reusability, and no by-products formation. The products are isolated in pure form by recrystallization, without intervention of chromatography, making the technology practical, easy to perform and facile.

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