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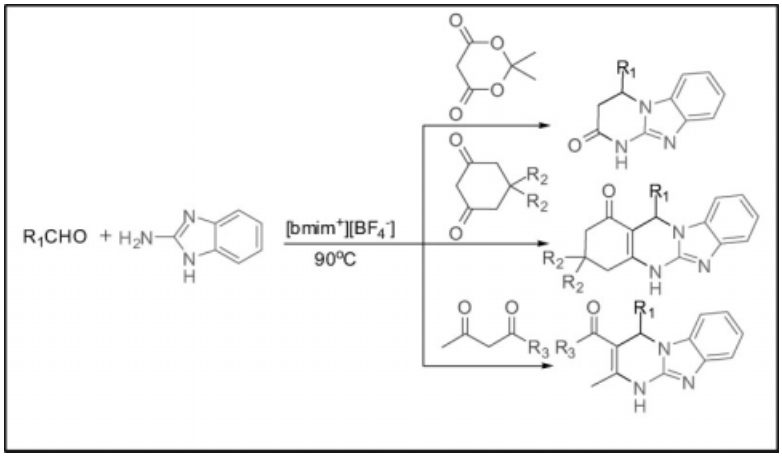

A green and simple synthesis of 4-ayrl-3,4-dihydro-1*H*-pyrimido[1,2-*a*]benzimidazole derivatives was accomplished in excellent yields via the reaction of aryl aldehyde, 1,3-dicarbonyl compounds and 1*H*-benzo[*d*]imidazol-2-amine in ionic liquid of [bmim$^+$][BF_4^-]. This protocol has the advantages of easier work-up, mild reaction conditions, high yields, and an environmentally benign procedure compared with the reported methods.

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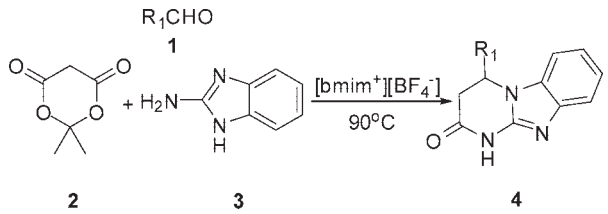
INTRODUCTION

The small organic molecules, such as, the fused nitrogen-containing heterocycles receive a large amount of attention in the literature due to their exciting biological properties and their roles as pharmacophores of considerable historical importance. For example, the derivatives of pyrimido[1,2-*a*]benzimidazol-2-one can be used as inhibitor of cell proliferation [1], lymphocyte specific kinase [2], DNA-topoisomerase I [3], and protein kinase [4]. Hence, the preparation of this important heterocyclic core unit has gained much importance. However, only one method reported to synthesize these compounds was via the reaction of α, β-unsaturated esters, which could be prepared via the condensation reaction, with 1*H*-benzo [*d*]imidazol-2-amine in the presence of organic solvents or under solvent-free conditions at high temperature [5–9]. Furthermore, most of the synthetic protocols in literature so far have many drawbacks, including prolonged reaction time, drastic reaction conditions, the use of some toxic organic solvents, such as, nitrobenzene, and low yields. Therefore, the development of simple, convenient, and environmentally benign approaches for the synthesis of these compounds is still desirable.

A multicomponent reaction (MCR) can create highly complex molecules from readily available starting materials without the complicated purification operations; thus, MCRs are resource- and time-effective and economically favorable processes in diversity generation [10–13]. Recently, there have been tremendous development in three- and four-component reactions and great efforts continue to be made to develop new MCRs [14–19]. Besides, the ionic liquids have been widely used as environmentally benign reaction media in organic synthesis because of their unique properties of nonvolatility, nonflammability, and recyclability. Many organic reactions, including MCRs, were carried out efficiently in ionic liquids [20–28]. To continue our work on the synthesis of heterocyclic compounds via MCR in ionic liquids [29–31], we report herein the three-component synthesis of 4-aryl-3,4-dihydro-1*H*-pyrimido[1,2-*a*]benzimidazol-2-one in ionic liquid (Scheme 1).

Scheme 1



RESULTS AND DISCUSSION

The effect of solvent on the reaction was initially examined by reacting phenyl aldehyde (1 mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (1 mmol), and 1*H*-benzo[*d*]imidazol-2-amine (1 mmol) at room temperature. The results in Table 1 show that only in ionic liquids the expected product **4a** was given with moderate yield (60–75%) by the three-component reaction. Furthermore, the reaction accomplished in [bmim$^+$][BF$_4^-$] exhibited higher yield (75%) than other counterparts. Therefore, we carried out the three-component reaction in [bmim$^+$][BF$_4^-$] to synthesize the desired products.

To find the optimal reaction temperature, the synthesis of (**4a**) was studied at different temperatures. The results are summarized in Table 2. As shown in Table 2, the reaction at 90°C proceeded in highest yield among the six reaction temperatures tested. Therefore, 90°C was chosen for this reaction.

Based on the optimized reaction conditions, a series of 4-aryl-3,4-dihydro-1*H*-pyrimido[1,2-*a*]benzimidazol-2-one were synthesized. The results, summarized in Table 3, show that the three-component reaction in [bmim$^+$][BF$_4^-$] gave the corresponding products in moderate to good yields. This methodology can be applied to aromatic aldehydes either with electron-withdrawing groups (such as, a nitro group, halogen) or electron-donating groups (such as, a methoxy) with excellent yields under the same conditions. Therefore, we conclude that the electronic nature of substituents of the aromatic aldehyde had no significant effect on the reaction. Even the heterocyclic aldehyde could be used in this reaction (**4h**). However, when the aliphatic aldehyde was applied to this reaction, no expected product was obtained.

All of the compounds were characterized by HRMS(ESI), FTIR, and ^{1}H NMR. To further elucidate the structure of products, a single crystal of compound **4a** was prepared and its structure was determined by X-ray diffraction (Fig. 1).

The recovery and reuse of solvent and/or catalyst are highly preferable in terms of green synthetic process. Therefore, with the success of the above reactions, we continued our research by studying the reuse of the solvent. It turned out that the recovery and reuse of [bmim$^+$][BF$_4^-$] is not only convenient but also efficient. Thus, at completion monitored by TLC, the reaction mixture was cooled to room temperature and poured into water. The solid product was collected by filtration and recrystallized from ethanol to give the pure product. The filtrate was washed with acetic ester, concentrated under reduced pressure, and dried *in vacuo* at 100°C for several hours to give the reusable solvent. Studies by using phenyl aldehyde, 2,2-dimethyl-1,3-dioxane-4,6-dione and 1*H*-benzo[*d*]imidazol-2-amine as model substrates shows that the recovered solvent could be successively recycled in subsequent reactions without almost

Table 1

Solvent effect on the synthesis of **4a**.

Entry	Solvent[a]	Temperature (°C)	Time (h)	Yield (%)
1	[byp$^+$][Br$^-$]	r.t.	10	60
2	[byp$^+$][BF$_4^-$]	r.t.	10	62
3	[bmim$^+$][Br$^-$]	r.t.	10	70
4	[bmim$^+$][BF$_4^-$]	r.t.	10	75
5	Ethanol	r.t.	10	Trace
6	CH_3CN	r.t.	12	Trace
7	CH_3COOH	r.t.	12	Trace
8	$CHCl_3$	r.t.	12	Trace
9	H_2O	r.t.	15	Trace

[a] [byp$^+$][Br$^-$], 1-butylpyridinium bromide; [byp$^+$][BF$_4^-$], 1-butylpyridinium tetrafluoroborate; [bmim$^+$][Br$^-$], 3-butyl-1-methyl-1*H*-imidazol-3-ium bromide; [bmim$^+$] [BF$_4^-$], 3-butyl-1-methyl-1*H*-imidazol-3-ium tetrafluoroborate.

Table 2

Temperature optimization for the synthesis of **4a**.

Entry	Temperature (°C)	Time (h)	Yield (%)
1	20	10	75
2	40	9	80
3	60	8	86
4	80	7	88
5	90	6	90
6	100	6	85

Table 3

Synthesis of **4** in ionic liquid ([bmim$^+$][BF$_4^-$]).

Compound no.	R_1	Time (h)	Yield (%)	M.p. (°C)
4a	C_6H_5	7	90	291–293 (ref. 32, 289–290)
4b	4-BrC_6H_4	7	85	294–296
4c	3,4,5-$(OCH_3)_3C_6H_2$	8	82	273–275
4d	3-$NO_2C_6H_4$	8	85	283–285
4e	2-FC_6H_4	7	88	284–285
4f	3,4-$(OCH_2O)C_6H_3$	8	83	236–238
4g	4-$NO_2C_6H_4$	8	82	>300 (ref. 6, >300)
4h	2-SC_4H_3	7	80	285–287

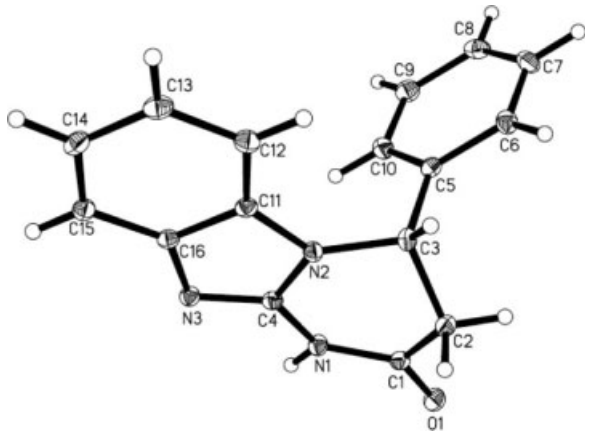


Figure 1. The crystal structure of **4a**.

any decrease in its efficiency. The results of the reuse of the ionic liquid are summarized in Table 4. Even in the fourth round, the yield of the product **4a** is fairly high.

A plausible mechanism of the reaction was presented in Scheme 2. Product **4** may be synthesized via sequential Knoevenagel condensation, Michael addition, cyclization, and elimination mechanism (Scheme 2). The condensation between aldehyde and Meldrum's acid gave 5-arylidene substituted Meldrum's acid **5**. Michael addition between **5** and 1*H*-benzo[*d*]imidazol-2-amine **3** then furnished the intermediate **6**, which isomerized to **7**. After that, intramolecular cyclization of **7** gave **8**, which finally afforded **4** by loosing acetone and carbon dioxide.

To test the proposed reaction pathway, compound **5a** was synthesized in [bmim$^+$][BF$_4^-$] and it could react with **3** smoothly and gave product **4a** with yield similar to the three-component reaction in ionic liquid. The fact supported the supposed reaction mechanism.

To extend the scope of this protocol for the synthesis of the derivatives of pyrimido[1,2-*a*]benzimidazole, other cyclic 1,3-dicarbonyl compounds (Scheme 3) and acyclic 1,3-dicarbonyl compounds (Scheme 4) were applied in the three-component synthesis as the surrogates of 2,2-dimethyl-1,3-dioxane-4,6-dione. The results, listed in Tables 5 and 6, show that these three-component reactions in ionic liquid gave the desired products, **10** and **12**, successfully.

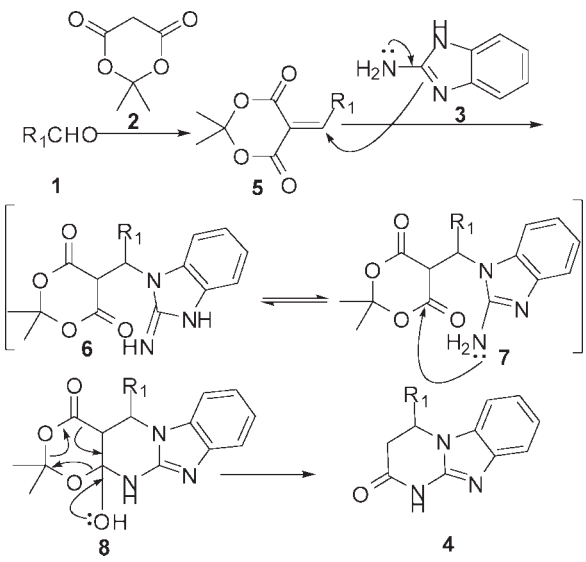
In summary, we have developed an efficient, economical, safe, and environmentally benign procedure for

Table 4

Study on the reuse of ionic liquid ([bmim$^+$][BF$_4^-$]).

Round	1	2	3	4
4a Yield (%)	90	88	87	87

Scheme 2



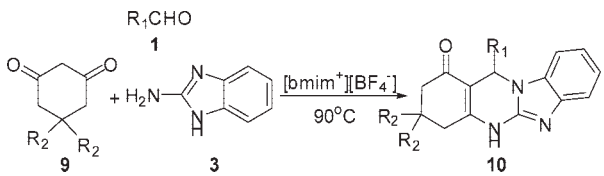
synthesizing 4-aryl-1*H*-pyrimido[1,2-*a*]benzimidazole derivatives in ionic liquid medium [bmim$^+$][BF$_4^-$]. Meanwhile, the ionic liquid was chosen as a kind of green solvent, which could be reused for several rounds without significant loss of activity.

EXPERIMENTAL

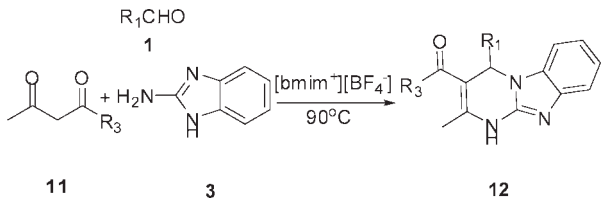
Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. NMR spectra were recorded on a Bruker DPX 400; data for ^{1}H are reported as follows: chemical shift (ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad), coupling constant (Hz), and number. Infrared (IR) spectra were recorded on a TENSOR 27 spectrophotometer in KBr pellet and are reported in terms of frequency of absorption (cm^{-1}). HRMS (ESI) were determined by using micrOTOF-QIIHRMS/MS instrument (BRUKER). Melting points were determined in open capillaries and are uncorrected. The single crystal diffraction data were gathered on a Rigaku Saturn diffractometer.

General procedure for the synthesis of 4-Aryl-1*H*-pyrimido[1,2-*a*]benzimidazol derivatives. Aryl aldehyde **1** (1.0 mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione **2** (0.14 g, 1.0 mmol), and 1*H*-benzo[*d*]imidazol-2-amine **3** (0.13 g, 1.0 mmol) were mixed in 3 mL [bmim$^+$][BF$_4^-$]. Then, the mixture was stirred for a certain time (monitored by TLC) at 90°C. The result mixture was cooled to room temperature and poured into 20 mL of water. The solid product was collected by

Scheme 3



Scheme 4



filtration and recrystallized from ethanol to give the pure compound **4**. The filtrate was washed with acetic ester for several times, concentrated under reduced pressure, and dried *in vacuo* at 100°C for several hours to give the reusable solvent. A similar procedure was used in preparing the following compounds **10** and **12**.

4-Phenyl-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4a). IR (potassium bromide): 3059, 3034, 2912, 1730, 1649, 1590, 1458, 1363, 1323, 1287, 1245, 1168, 926, 890, 766, 743, 700 cm^{-1}; ^1H NMR (DMSO-d_6): δδ11.66 (s, 1H, NH), 7.83 (d, J = 8.0 Hz, 1H, ArH), 7.46–7.40 (m, 2H, ArH), 7.35–7.32 (m, 3H, ArH), 7.08–7.03 (m, 3H, ArH), 5.94 (q, J = 4.0 Hz, 1H, CH), 3.52 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 1H, CH_2), 2.94 (dd, J_1 = 3.2 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 264.1131 $[M+H]^+$, found: 264.1132.

4-(4-Bromophenyl)-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4b). IR (potassium bromide): 3054, 2996, 2929, 2849, 2698, 1694, 1634, 1583, 1505, 1455, 1420, 1359, 1324, 1263, 1239, 1150, 1076, 1010, 974, 894, 843, 817, 759, 741, 677 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.74 (s, 1H, NH), 7.56 (d, J = 7.2 Hz, 2H, ArH), 7.47 (d, J = 8.0 Hz, 1H, ArH), 7.10–7.02 (m, 5H, ArH), 6.00 (dd, J_1 = 3.2 Hz, J_2 = 7.2 Hz, 1H, CH), 3.54 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 1H, CH_2), 2.93 (dd, J_1 = 3.2 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 342.0237 $[M+H]^+$, found: 342.0252.

4-(3,4,5-Trimethoxyphenyl)-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4c). IR (potassium bromide): 2939, 2846, 2761, 1704, 1633, 1594, 1509, 1460, 1427, 1343, 1331, 1283, 1241, 1129, 1143, 1002, 898, 847, 823, 766, 744, 689 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.76 (s, 1H, NH), 7.45 (d, J = 8.0 Hz, 1H, ArH), 7.20–6.98 (m, 3H, ArH), 6.50–6.46 (m, 2H, ArH), 5.80 (dd, J_1 = 4.4 Hz, J_2 = 6.8 Hz, 1H, CH), 3.65 (s, 6H, 2 × OCH_3), 3.63 (s, 3H, OCH_3), 3.40 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H, CH_2), 3.03 (dd, J_1 = 4.4 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 354.1448 $[M+H]^+$, found: 354.1439.

4-(3-Nitrophenyl)-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4d). IR (potassium bromide): 3065, 2866, 2729, 1696, 1637, 1586, 1532, 1506, 1458, 1351, 1284, 1246, 1161, 1130, 1085, 921, 873, 813, 731 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.82 (s, 1H, NH), 8.20 (d, J = 8.0 Hz, 1H, ArH), 8.02 (s, 1H, ArH), 7.70–7.66 (m, 1H, ArH), 7.50 (d, J = 4.0 Hz, 2H, ArH), 7.13–7.05 (m, 3H, ArH), 6.17 (dd, J_1 = 3.2 Hz, J_2 = 7.2 Hz, 1H, CH), 3.57 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 1H, CH_2), 3.03 (dd, J_1 = 3.2 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 309.0983 $[M+H]^+$, found: 309.0985.

4-(2-Fluorophenyl)-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4e). IR (potassium bromide): 3061, 3006, 2923, 2864, 2702, 1687, 1637, 1584, 1486, 1456, 1423, 1377, 1354, 1311, 1286, 1244, 1226, 1160, 1095, 898, 762, 746 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.77 (s, 1H, NH), 7.48 (d, J = 8.0 Hz, 1H, ArH), 7.40–7.30 (m, 2H, ArH), 7.13–7.04 (m, 4H, ArH), 6.68 (t, J = 7.6 Hz, 1H, ArH), 6.17 (dd, J_1 = 2.8 Hz, J_2 = 7.6 Hz, 1H, CH), 3.60 (dd, J_1 = 7.6 Hz, J_2 = 16.4 Hz, 1H, CH_2), 2.86 (dd, J_1 = 2.8 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 282.1037 $[M+H]^+$, found: 282.1034.

4-Benzo[1,3]dioxol-5-yl-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4f). IR (potassium bromide): 3051, 2888, 2725, 1686, 1639, 1585, 1504, 1490, 1456, 1445, 1350, 1241, 1037, 931, 891, 810, 728 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.67 (s, 1H, NH), 7.46 (d, J = 8.0 Hz, 1H, ArH), 7.11–7.09 (m, 1H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 6.86 (d, J = 8.0 Hz, 1H, ArH), 6.77 (s, 1H, ArH), 6.50 (q, J = 4.0 Hz, 1H, ArH), 6.00 (s, 2H, OCH_2O), 5.82 (dd, J_1 = 3.6 Hz, J_2 = 6.8 Hz, 1H, CH), 3.42 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H, CH_2), 2.94 (dd, J_1 = 3.6 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 308.1029 $[M+H]^+$, found: 308.1029.

4-(4-Nitrophenyl)-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4g). IR (potassium bromide): 3050, 2859, 2750, 1702, 1636, 1584, 1524, 1486, 1456, 1412, 1346, 1318, 1286, 1246, 1105, 965, 927, 896, 851, 741, 698 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.82 (s, 1H, NH), 8.22 (d, J = 8.0 Hz, 2H, ArH), 7.50 (d, J = 8.0 Hz, 1H, ArH), 7.33 (d, J = 8.0 Hz, 2H, ArH), 7.14 (d, J = 7.6 Hz, 2H, ArH), 7.05 (d, J = 7.6 Hz, 1H, ArH), 6.17 (dd, J_1 = 2.4 Hz, J_2 = 7.2 Hz, 1H, CH), 3.60 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 1H, CH_2), 3.00 (dd, J_1 = 2.4 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): m/z cal. for: 309.0982 $[M+H]^+$, found: 309.0985.

4-Thiophen-2-yl-3,4-dihydro-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4h). IR (potassium bromide): 3098, 2996, 2848, 2696, 1699, 1634, 1602, 1587, 1504, 1456, 1410, 1368, 1343,

Table 5

Synthesis of **10** in ionic liquid ([bmim$^+$][BF_4^-]).

Compound no.	R_1	R_2	Time (h)	Yield (%)	M.p. (°C)
10a	C_6H_5	H	7	85	291–293 (ref. 33, >300)
10b	3-$NO_2C_6H_4$	H	6	82	289–291 (ref. 33, >300)
10c	3-BrC_6H_4	H	7	83	>300 (ref. 33, >300)
10d	4-$CH_3C_6H_4$	H	7	84	293–295 (ref. 33, >300)
10e	C_6H_5	CH_3	7	86	>300 (ref. 34, 368)
10f	3,4-(OCH_2O)C_6H_3	CH_3	7	85	294–296 (ref. 33, >300)
10g	3-BrC_6H_4	CH_3	6	84	294–296 (ref. 33, >300)
10h	4-$OCH_3C_6H_4$	CH_3	7	83	>300 (ref. 34, 389)

Table 6

Synthesis of **12** in ionic liquid ([bmim$^+$][BF_4^-]).

Compound no.	R_1	R_3	Time (h)	Yield (%)	M.p. (°C)
12a	C_6H_5	CH_3	6	80	294–296 (ref. 35, >300)
12b	3-$NO_2C_6H_4$	CH_3	5	82	287–289 (ref. 35, 290–292)
12c	4-$OCH_3C_6H_4$	CH_3	6	83	286–288 (ref. 35, 279–282)
12d	4-FC_6H_4	CH_3	7	84	>300 (ref. 35, >300)
12e	C_6H_5	OC_2H_5	6	83	294–296 (ref. 35, 294–297)
12f	4-$NO_2C_6H_4$	OC_2H_5	6	84	>300 (ref. 35, >300)
12g	4-BrC_6H_4	OC_2H_5	6	82	>300 (ref. 35, >300)
12h	4-FC_6H_4	OC_2H_5	6	86	>300 (ref. 35, >300)

1295, 1263, 1235, 1154, 1013, 974, 894, 843, 720 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.72 (s, 1H, NH), 7.44 (t, J = 7.6 Hz, 2H, ArH), 7.34–7.36 (m, 1H, thiophene-H), 7.12–7.09 (m, 2H, ArH), 6.99–6.94 (m, 2H, thiophene-H), 6.28 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 1H, CH), 3.58 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H, CH_2), 3.00 (dd, J_1 = 2.0 Hz, J_2 = 16.4 Hz, 1H, CH_2). HRMS (ESI): *m/z* cal. for: 270.0696 $[M+H]^+$, found: 270.0709.

5-Phenyl-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10a). IR (potassium bromide): 3226, 3029, 2957, 1653, 885, 749 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.10 (s, 1H, NH), 7.38–7.31 (m, 3H, ArH), 7.25–7.22 (m, 3H, ArH), 7.15 (t, J = 7.6 Hz, 1H, ArH), 7.04 (t, J = 7.6 Hz, 1H, ArH), 6.95 (t, J = 7.6 Hz, 1H, ArH), 6.42 (s, 1H, CH), 2.74–2.70 (m, 2H, CH_2), 2.32–2.20 (m, 2H, CH_2), 2.00–1.86 (m, 2H, CH_2). HRMS (ESI): *m/z* cal. for: 316.1444 $[M+H]^+$, found: 316.1459.

5-(3-Nitrophenyl)-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10b). IR (potassium bromide): 3220, 3040, 2950, 1652, 1514, 1020, 744 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.30 (s, 1H, NH), 8.27 (s, 1H, ArH), 8.04 (d, J = 8.4 Hz, 1H, ArH), 7.70 (d, J = 7.6 Hz, 1H, ArH), 7.55 (t, J = 8.0 Hz, 1H, ArH), 7.40 (d, J = 7.6 Hz, 1H, ArH), 7.27 (d, J = 7.6 Hz, 1H, ArH), 7.06 (t, J = 7.2 Hz, 1H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 6.67 (s, 1H, CH), 2.73–2.70 (m, 2H, CH_2), 2.36–2.19 (m, 2H, CH_2), 1.99–1.85 (m, 2H, CH_2). HRMS (ESI): *m/z* cal. for: 361.1295 $[M+H]^+$, found: 361.1298.

5-(3-Bromophenyl)-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10c). IR (potassium bromide): 3220, 3048, 2891, 1647, 1571, 996, 890 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.16 (s, 1H, NH), 7.55 (s, 1H, ArH), 7.36–7.31 (m, 2H, ArH), 7.24–7.13 (m, 3H, ArH), 7.02 (t, J = 7.6 Hz, 1H, ArH), 6.94 (t, J = 7.6 Hz, 1H, ArH), 6.41 (s, 1H, CH), 2.66–2.63 (m, 2H, CH_2), 2.28–2.18 (m, 2H, CH_2), 1.95–1.80 (m, 2H, CH_2). HRMS (ESI): *m/z* cal. for: 394.0531 $[M+H]^+$, found: 394.0558.

5-p-Tolyl-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10d). IR (potassium bromide): 3224, 3038, 2950, 1645, 1514, 977, 829 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.04 (s, 1H, NH), 7.31 (d, J = 7.6 Hz, 1H, ArH), 7.20–7.14 (m, 3H, ArH), 7.01–6.98 (m, 3H, ArH), 6.90 (t, J = 7.6 Hz, 1H, ArH), 6.33 (s, 1H, CH), 2.65–2.61 (m, 2H, CH_2), 2.29–2.19 (m, 2H, CH_2), 2.17 (s, 3H, CH_3), 1.93–1.80 (m, 2H, CH_2). HRMS (ESI): *m/z* cal. for: 330.1601 $[M+H]^+$, found: 330.1637.

8,8-Dimethyl-5-phenyl-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10e). IR (potassium bromide): 3228, 2956, 1658, 1106, 891, 838, 759 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.13 (s, 1H, NH), 7.38–7.33 (m, 3H, ArH), 7.28–7.23 (m, 3H, ArH), 7.18–7.14 (m, 1H, ArH), 7.05 (t, J = 8.0 Hz, 1H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 6.42 (s, 1H, CH), 2.67–2.50 (m, 2H, CH_2), 2.29–2.04 (m, 2H, CH_2), 1.06 (s, 3H, CH_3), 0.93 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 344.1757 $[M+H]^+$, found: 344.1786.

5-Benzo[1,3]dioxol-5-yl-8,8-dimethyl-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10f). IR (potassium bromide): 3228, 3095, 2966, 1644, 850, 791 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.09 (s, 1H, NH), 7.38–7.31 (m, 2H, ArH), 7.06 (t, J = 7.2 Hz, 1H, ArH), 6.98 (t, J = 7.6 Hz, 1H, ArH), 6.89 (s, 1H, ArH), 6.82–6.76 (m, 2H, ArH), 6.35 (s, 1H, CH), 5.93 (s, 2H, OCH_2O), 2.64–2.53 (m, 2H, CH_2), 2.28–2.06 (m, 2H, CH_2), 1.06 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 388.1656 $[M+H]^+$, found: 388.1685.

5-(3-Bromophenyl)-8,8-dimethyl-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10g). IR (potassium bromide): 3222, 3048, 2944, 1650, 887, 743 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.17 (s, 1H, NH), 7.61 (s, 1H, ArH), 7.38 (t, J = 8.0 Hz, 2H, ArH), 7.31–6.98 (m, 3H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.00 (t, J = 7.6 Hz, 1H, ArH), 6.46 (s, 1H, CH), 2.66–2.50 (m, 2H, CH_2), 2.29–2.07 (m, 2H, CH_2), 1.07 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 422.0845 $[M+H]^+$, found: 422.0851.

5-(4-Methoxyphenyl)-8,8-dimethyl-5,8,9,10-tetrahydro-7H-4b,10,11-triaza-benzo[b]fluoren-6-one (10h). IR (potassium bromide): 3231, 3099, 2957, 2866, 1645, 838, 737 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.08 (s, 1H, NH), 7.36 (d, J = 7.6 Hz, 1H, ArH), 7.28–7.24 (m, 3H, ArH), 7.04 (t, J = 7.6 Hz, 1H, ArH), 6.96 (t, J = 8.0 Hz, 1H, ArH), 6.76 (d, J = 8.4 Hz, 2H, ArH), 6.36 (s, 1H, CH), 3.66 (s, 3H, OCH_3), 2.65–2.51 (m, 2H, CH_2), 2.28–2.03 (m, 2H, CH_2), 1.06 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 374.1863 $[M+H]^+$, found: 374.1853.

1-(2-Methyl-4-phenyl-1,4-dihydro-benzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)-ethanone (12a). IR (potassium bromide): 3273, 3103, 3053, 1645, 1536, 1471, 1292, 1158, 806 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.83 (s, 1H, NH), 7.42 (d, J = 8.0 Hz, 3H, ArH), 7.35–7.26 (m, 3H, ArH), 7.20–7.16 (m, 1H, ArH), 7.06–6.95 (m, 2H, ArH), 6.60 (s, 1H, CH), 2.49 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 304.1444 $[M+H]^+$, found: 304.1471.

1-[2-Methyl-4-(3-nitrophenyl)-1,4-dihydro-benzo[4,5] imidazo[1,2-a]pyrimidin-3-yl]-ethanone (12b). IR (potassium bromide): 3215, 3087, 2881, 1649, 1560, 1458, 1267, 1059, 959, 888, 737, 690 cm^{-1}; ^1H NMR (DMSO-d_6): δ 11.01 (s, 1H, NH), 8.28 (s, 1H, ArH), 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH), 7.58 (t, J = 7.6 Hz, 1H, ArH), 7.45 (d, J = 8.0 Hz, 1H, ArH), 7.37 (d, J = 8.0 Hz, 1H, ArH), 7.06 (t, J = 7.2 Hz, 1H, ArH), 6.99 (t, J = 7.6 Hz, 1H, ArH), 6.77 (s, 1H, CH), 2.53 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 349.1295 $[M+H]^+$, found: 349.1326.

1-[4-(4-Methoxyphenyl)-2-methyl-1,4-dihydro-benzo[4,5]imidazo[1,2-a]pyrimidin-3-yl]-ethanone (12c). IR (potassium bromide): 3227, 3099, 3002, 2832, 1654, 1628, 1590, 1514, 1459, 1335, 1228, 958, 807, 744, 659 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.75 (s, 1H, NH), 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.05–6.97 (m, 4H, ArH), 6.83 (d, J = 8.0 Hz, 2H, ArH), 6.57 (s, 1H, CH), 3.67 (s, 3H, OCH_3), 2.47 (s, 3H, CH_3), 2.22 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 334.1550 $[M+H]^+$, found: 334.1565.

1-[4-(4-Fluorophenyl)-2-methyl-1,4-dihydro-benzo[4,5]imidazo[1,2-a]pyrimidin-3-yl]-ethanone (12d). IR (potassium bromide): 3227, 3100, 3022, 2914, 2840, 1653, 1627, 1565, 1459, 1330, 1229, 1006, 954, 854, 747 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.85 (s, 1H, NH), 7.48–7.42 (m, 3H, ArH), 7.35 (d, J = 8.0 Hz, 1H, ArH), 7.12–6.98 (m, 4H, ArH), 6.62 (s, 1H, CH), 2.49 (s, 3H, CH_3), 2.24 (s, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 322.1350 $[M+H]^+$, found: 322.1389.

2-Methyl-4-phenyl-1,4-dihydro-benzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylic acid ethyl ester (12e). IR (potassium bromide): 3234, 3103, 3026, 2928, 2865, 1698, 1615, 1572, 1365, 1255, 1092, 893, 794, 730 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.82 (s, 1H, NH), 7.35 (t, J = 6.8 Hz, 3H, ArH), 7.27 (t, J = 8.0 Hz, 3H, ArH), 7.20–7.16 (m, 1H, ArH), 7.04 (t, J = 8.0 Hz, 1H, ArH), 6.95 (t, J = 7.6 Hz, 1H, ArH), 6.43 (s, 1H, CH), 4.02 (q, J = 7.2 Hz, 2H, CH_2), 2.46 (s, 3H, CH_3), 1.14 (t, J = 7.2 Hz, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 334.1550 $[M+H]^+$, found: 334.1607.

2-Methyl-4-(4-nitrophenyl)-1,4-dihydro-benzo[4,5]imidazo [1,2-a]pyrimidine-3-carboxylic acid ethyl ester (12f). IR (potassium bromide): 3234, 3105, 2978, 2861, 1697, 1619, 1572, 1518, 1458, 1235, 870, 755, 715, 608 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.99 (s, 1H, NH), 8.15 (d, J = 8.4 Hz, 2H, ArH), 7.66 (d, J = 8.8 Hz, 2H, ArH), 7.37 (d, J = 7.6 Hz, 1H, ArH), 7.28 (d, J = 7.6 Hz, 1H, ArH), 7.06 (t, J = 7.2 Hz, 1H, ArH), 6.96 (t, J = 7.2 Hz, 1H, ArH), 6.62 (s, 1H, CH), 4.03 (q, J = 7.2 Hz, 2H, CH_2), 2.48 (s, 3H, CH_3), 1.16 (t, J = 7.2 Hz, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 379.1401 $[M+H]^+$, found: 379.1422.

4-(4-Bromophenyl)-2-methyl-1,4-dihydro-benzo[4,5]imidazo [1,2-a]pyrimidine-3-carboxylic acid ethyl ester (12g). IR (potassium bromide): 3233, 3101, 3023, 2978, 2849, 1698, 1618, 1571, 1487, 1385, 1234, 1010, 893, 801, 730 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.87 (s, 1H, NH), 7.47 (d, J = 8.4 Hz, 2H, ArH), 7.36–7.32 (m, 3H, ArH), 7.26 (d, J = 8.0 Hz, 1H, ArH), 7.06 (t, J = 7.6 Hz, 1H, ArH), 6.96 (t, J = 8.0 Hz, 1H, ArH), 6.45 (s, 1H, CH), 4.02 (q, J = 7.2 Hz, 2H, CH_2), 2.46 (s, 3H, CH_3), 1.16 (t, J = 7.2 Hz, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 412.0655 $[M+H]^+$, found: 412.0663.

4-(4-Fluorophenyl)-2-methyl-1,4-dihydro-benzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylic acid ethyl ester (12h). IR (potassium bromide): 3235, 3039, 2929, 1697, 1617, 1458, 1303, 1096, 792, 637 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.84 (s, 1H, NH), 7.43–7.40 (m, 2H, ArH), 7.35 (d, J = 8.0 Hz, 1H, ArH), 7.28 (d, J =7.6 Hz, 1H, ArH), 7.12–7.03 (m, 3H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 6.46 (s, 1H, CH), 4.02 (q, J = 7.2 Hz, 2H, CH_2), 2.46 (s, 3H, CH_3), 1.15 (t, J = 7.2 Hz, 3H, CH_3). HRMS (ESI): *m/z* cal. for: 352.1456 $[M+H]^+$, found: 352.1486.

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[36] The single-crystal growth was carried out in ethanol at room temperature. X-ray crystallographic analysis was performed using a Rigaku Saturn diffractometer. Crystal data for **4a**: $C_{16}H_{13}N_3O$, crystal dimension 0.18 mm × 0.16 mm × 0.12 mm, Orthorhombic, space group *P*bca, $a = 13.606(3)$, $b = 7.5674(15)$, $c = 24.578(5)$ Å, $V = 2530.6(9)$ Å^3, $M_r = 263.29$, $Z = 8$, $D_c = 1.382$ g/cm^3, $\lambda = 0.71073$ Å, μ (Mokα) = 0.090 mm^{-1}, $F(000) = 1104$, $S = 1.151$, $R_1 = 0.0366$, $wR_2 = 0.0976$.