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FACILE AND EFFICIENT ACCESS TO TETRAHYDROBENZO[*b*]-PYRANS CATALYZED BY *N*,*N*-DIMETHYLBENZYLAMINE

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Abstract – The *N,N*-dimethylbenzylamine (DMBA) has been used as an efficient, inexpensive, and commercially available organocatalyst for the one-pot, three-component synthesis of tetrahydrobenzo[*b*]pyrans in good to high yields. It was found that the one-pot Knoevenagel-Michael-Thorpe-Ziegler cyclization sequence of dimedone, malononitrile/ethyl cyanoacetate, and various aldehydes was efficiently implemented in ethanol at 45 °C. This procedure offers attractive several features: mild reaction conditions, use of ethanol as a green solvent, reusability the reaction media, shorter reaction times, and the ease of the work-up.

INTRODUCTION

The multicomponent reactions (MCRs) are highly efficient tools in modern organic synthesis chemistry for the construction of several bonds in a one-step operation, which leads to biologically and pharmaceutically active compounds. In this category of reactions, the desired products are formed by association more than three chemical species. MCRs have many benefits, such as high atom economy, the avoidance of time-consuming, simplicity in processing, high efficacy in constructing libraries of heterocyclic molecules from simple and readily available materials without isolation of any intermediate, minimal waste generation, shorter reaction times, the avoidance of changing the conditions during the implementation of the reaction, energy saving, the possible structural variations, high yields and the simplicity of a one-pot procedure.[1-5] The tetrahydrobenzo[*b*]pyrans are unique classes of 4*H*-pyran-annulated heterocyclic frameworks represent a “drug-like” structural motif with a broad spectrum of applications in organic synthesis and medicinal chemistry. A series of these six-membered oxygen-containing heterocyclic compounds exhibited a wide range of biological and pharmaceutical activities including, anticancer,[6] antibacterial,[7] cytotoxicity,[8] and the human excitatory amino acid transporter subtype1 (EAAT1) inhibitory activity.[9] They can also be used as cognitive enhancers for the

treatment of schizophrenia, Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, and Down's syndrome.[10] Some exemplary biologically active tetrahydrobenzo[*b*]pyran-containing compounds are shown in Figure 1.

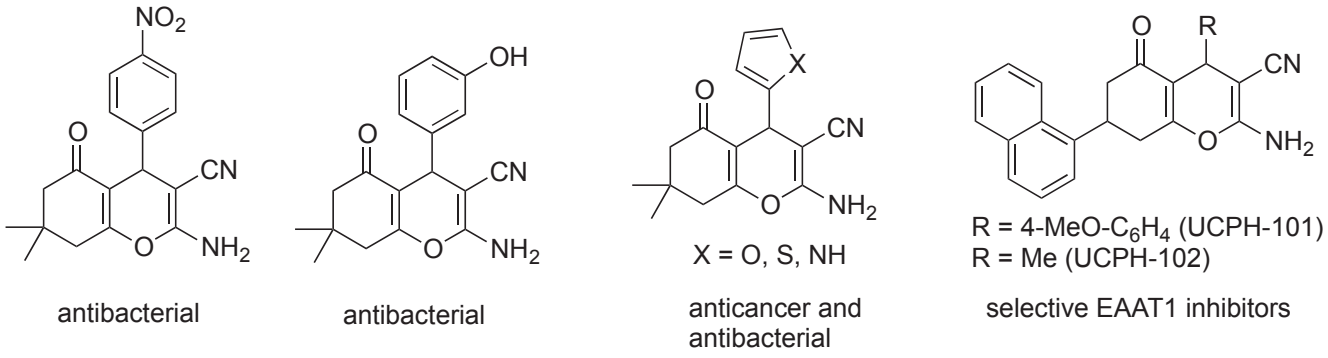


Figure 1. Selected examples of synthetically drug-like tetrahydrobenzo[*b*]pyrans

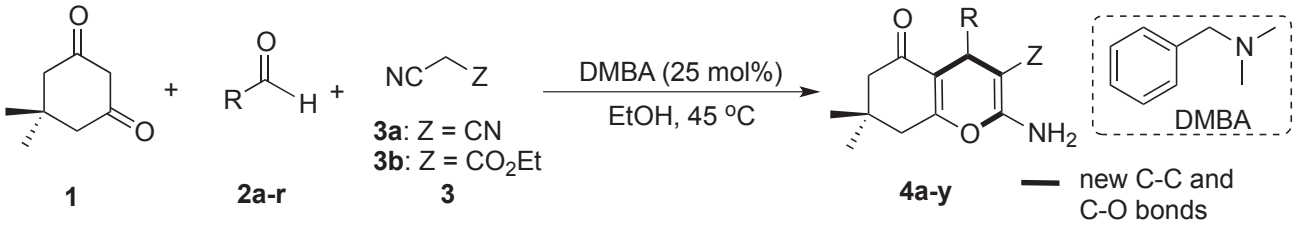
In recent years, considering the aforementioned properties, it is expected that the multicomponent synthesis of tetrahydrobenzo[*b*]pyrans and their derivatives has received much attention from researchers interested in organic synthetic chemistry. To date, various synthetic approaches have been reported in the literature for the preparation of these eye-catching heterocyles by one-pot, three-component annulation (3CA) of different aldehydes, malononitrile and 5,5-dimethylcyclohexane-1,3-dione (dimedone) using a variety of catalysts such as nanoparticles,[11,12] ionic liquids,[13,14] carbohydrates,[15] solid acids,[16-21] solid bases,[22,23] organocatalysts,[24-28] and iodine/DMSO system.[29] Microwave[30,41] and ultrasound[32] irradiations, ball milling,[33] and electrosynthesis[34] techniques have also been used to the promoting synthesis of tetrahydrobenzo[*b*]pyrans. Furthermore, uncatalyzed versions in aqueous media,[35] and 2,2,2-trifluoroethanol (TFE)[36] have been utilized for this 3CA. Substituted tetrahydrobenzo[*b*]pyran-containing compounds have also been obtained using the reaction of 1,3-oxazines with dimedone and malononitrile in refluxing acetonitrile:acetic acid (10:1).[37] We have recently used the potassium phthalimide[38-40] and potassium hydrogen phthalate[41] as catalysts for the synthesis of diverse 4*H*-pyran-annulated molecules.

Each of above-mentioned procedures has their own merits. However, some of the methods required the use of organic solvents such as DMSO and TFE, reflux conditions, relatively low yields, tedious work-up procedures, expensive catalysts, special apparatus (ultrasound, microwave, and ball milling) or electrosynthesis system. In consequence, using an inexpensive, mild, and efficient catalyst leading to the tetrahydrobenzo[*b*]pyran scaffold *via* a simple MCR remains an issue of interest.

The *N,N*-dimethylbenzylamine (DMBA) has been broadly utilized as a useful *ortho*-metalated ligand in organometallic chemistry for the synthesis of a number of transition metallocycles.[42,43] This *tert*-amine

was also used as the directing group to *ortho*-functionalizations such as, *ortho* arylation,[44] *ortho* olefination,[45] borylation of arenes,[46] *ortho* carbonylation,[47] and *ortho*-silylation.[44] It is noteworthy to mention that the *N*,*N*-dimethylaminomethyl group present in the functionalized *N*,*N*-dimethylbenzylamines can be easily converted to various and useful functional groups including, amide,[48] aldehyde,[49] alkene,[50] as well as chloromethyl substituent.[51] In addition, DMBA has been employed as a promoter for the process production of heat-cured epoxy systems[52] and polyurethanes,[53] as well as the reaction of oils with maleic anhydride to functionalize the tri-glycerides.[54]

As above-mentioned, there are a plethora of catalysts about the synthesis of pyran-annulated heterocycles, but we have not seen any publication about catalytic effect of DMBA on the preparation of these heterocyclic scaffolds and this work is the first report on the use of DMBA for the preparation of them (Scheme 1).



Scheme 1. DMBA-Catalyzed 3CA towards the synthesis of tetrahydrobenzo[*b*]pyrans (**4a**-**y**) at 45 °C in EtOH

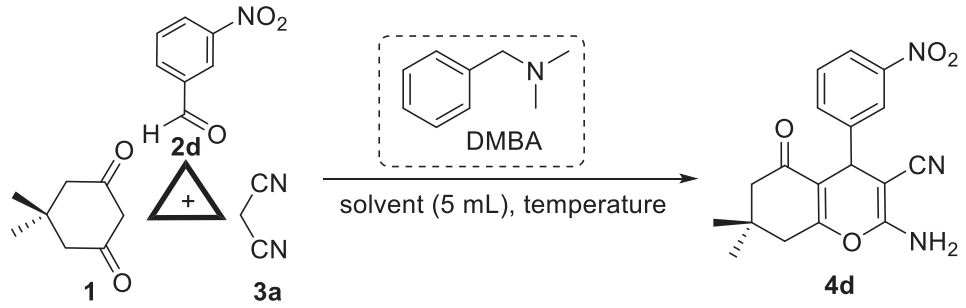
RESULTS AND DISCUSSION

To find out the best experimental conditions for the preparation of tetrahydrobenzo[*b*]pyrans, a model reaction, involving the 3-component annulation (3CA) between dimedone (**1**), 3-nitrobenzaldehyde (**2d**) and malononitrile (**3a**) was selected (Table 1).

The initial studies were carried out on the model reaction using 25 mol% DMBA as the catalyst in benign solvent ethanol (EtOH) at various temperatures (Table 1, entries 1-8). The model reaction was implemented in the presence of 25 mol% loading of DMBA catalyst and 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4d**) was isolated in good yield after 54 min at rt (Table 1, entry 1). In this stage, formation of the desired product (**4d**) revealed that the reaction proceeded efficiently by adding the catalyst. The chemical yields were improved by increasing the reaction temperatures from rt to 30, 40 and 45 °C, and the reaction times were significantly shortened (Table 1, entries 2-4). The reaction was also carried out at temperatures above 45 °C and did not achieve any improvement in the yields and reaction times (Table 1, entries 5-8). The best results were obtained when the model reaction was conducted at 45 °C, and hence this temperature was chosen as the optimum

temperature. Increasing the amount of the catalyst beyond 25 mol% did not increase the yield noticeably (Table 1, entry 9). We investigated the model reaction without any added the catalyst at rt and optimum temperature; the product (**4d**) was formed in low yield even after prolonged reaction times (Table 1, entries 10 and 11) indicating that the catalyst is necessary for the 3CA. Next, the amount of DMBA was

Table 1. Optimization of the reaction conditions for the 3CA of dimedone (1, 1 mmol), 3-nitrobenzaldehyde (**2d**, 1 mmol), and malononitrile (**3a**, 1 mmol) for the synthesis of 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4d**)[a]



Entry	Solvent	Catalyst amounts (mol%)	Time (min)	Temp. (°C)	Isolated yields (%)[b]
1	EtOH	25	54	rt	86
2	EtOH	25	30	30	88
3	EtOH	25	5	40	91
4[c]	**EtOH**	**25**	**4**	**45**	**96**
5	EtOH	25	9	50	90
6	EtOH	25	10	55	90
7	EtOH	25	10	60	92
8	EtOH	25	12	70	92
9	EtOH	30	15	45	92
10	EtOH	none	300	rt	25
11	EtOH	none	300	45	40
12	EtOH	5	30	45	81
13	EtOH	10	14	45	83
14	EtOH	15	11	45	84
15	EtOH	20	6	45	85
16	*n*-hexane	25	60	45	20
17	CH_2Cl_2	25	50	45	94
18	EtOAc	25	60	45	79
19	MeOH	25	23	45	75
20	H_2O	25	60	45	20

[a] All substrates and catalyst stirred at various temperatures. [b] Isolated yields after recrystallization. [c] The optimal conditions are specified in bold.

decreased and it was observed that lower yield of the corresponding product (**4d**) was obtained and progress of the reaction was slow (Table 1, entries 12-15). Hence, the efficacy of the reaction is affected mainly by the amount of DMBA catalyst. It was concluded that 25 mol% DMBA loading and 45 °C was the best catalyst amount and reaction temperature, respectively. Under these optimized conditions, the efficacy of the solvent system was also examined using various solvents such as *n*-hexane, dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), methanol (MeOH) and water (H_2O) (Table 1, entries 16-20). Under these conditions EtOH was again found to be superior to the other solvents. Due to the

Table 2. The scope synthesis of tetrahydrobenzo[*b*]pyran derivatives (**4a-y**) catalyzed by DMBA[a]

Entry	*R*	*Z*	Product	Time (min)	Yield (%)[b]	Mp (°C)	
						Found	Reported [ref.]
1	C_6H_5/**2a**	CN (**3a**)	**4a**	32	89	228-230	230-232[21]
2	2-NO_2-C_6H_4/**2b**	CN (**3a**)	**4b**	10	98	229-230	222-224[19]
3	4-NO_2-C_6H_4/**2c**	CN (**3a**)	**4c**	6	95	183-185	183-185[24]
4	3-NO_2-C_6H_4/**2d**	CN (**3a**)	**4d**	4	96	209-211	213-215[21]
5	4-Cl-C_6H_4/**2e**	CN (**3a**)	**4e**	8	98	209-211	210-213[21]
6	2,4-di-ClC_6H_3/**2f**	CN (**3a**)	**4f**	6	98	192-194	192-194[35]
7	2-Cl-C_6H_4/**2g**	CN (**3a**)	**4g**	35	88	210-213	215-217[24]
8	4-Me-C_6H_4/**2h**	CN (**3a**)	**4h**	20	97	217-219	215-218[20]
9	4-MeO-C_6H_4/**2i**	CN (**3a**)	**4i**	18	98	199-201	199-201[19]
10	4-HO-C_6H_4/**2j**	CN (**3a**)	**4j**	35	88	213-215	213-216[20]
11	3-HO-C_6H_4/**2k**	CN (**3a**)	**4k**	32	94	226-227	226-227[41]
12	4-Me_2N-C_6H_4/**2l**	CN (**3a**)	**4l**	60	84	223-224	215-217[20]
13	3-MeO-4-HO-C_6H_3/**2m**	CN (**3a**)	**4m**	30	95	239-240	235-237[19]
14	3,4-di-MeO-C_6H_3/**2n**	CN (**3a**)	**4n**	50	92	174-176	171-173[19]
15	2-Furyl/**2o**	CN (**3a**)	**4o**	60	90	222-224	224-226[24]
16	2-Thienyl/**2p**	CN (**3a**)	**4p**	65	92	215-218	217-220[41]
17	C_6H_5-CH=CH/**2q**	CN (**3a**)	**4q**	50	84	209-210	207-209[20]
18	Propyl/**2r**	CN (**3a**)	**4r**	90	72	179-181	178-180[20]
19	C_6H_5/**2a**	CO_2Et (**3b**)	**4s**	60	83	156-158	155-158[27]
20	3-NO_2-C_6H_4/**2d**	CO_2Et (**3b**)	**4t**	50	92	181-183	182-183[27]
21	4-Cl-C_6H_4/**2e**	CO_2Et (**3b**)	**4u**	45	93	155-157	156-158[27]
22	2-Cl-C_6H_4/**2g**	CO_2Et (**3b**)	**4v**	80	93	180-182	183-185[27]
23	4-Me_2N-C_6H_4/**2l**	CO_2Et (**3b**)	**4w**	85	82	155-157	156-157[41]
24	4-Me-C_6H_4/**2h**	CO_2Et (**3b**)	**4x**	70	86	157-159	155-156[35]
25	4-MeO-C_6H_4/**2i**	CO_2Et (**3b**)	**4y**	75	85	188-190	186-188[17]

[a] Reaction conditions: substrates 1 mmol; EtOH (5 mL); DMBA (25 mol%); stirred at 45 °C.
[b] Yields refer to those of pure isolated products.

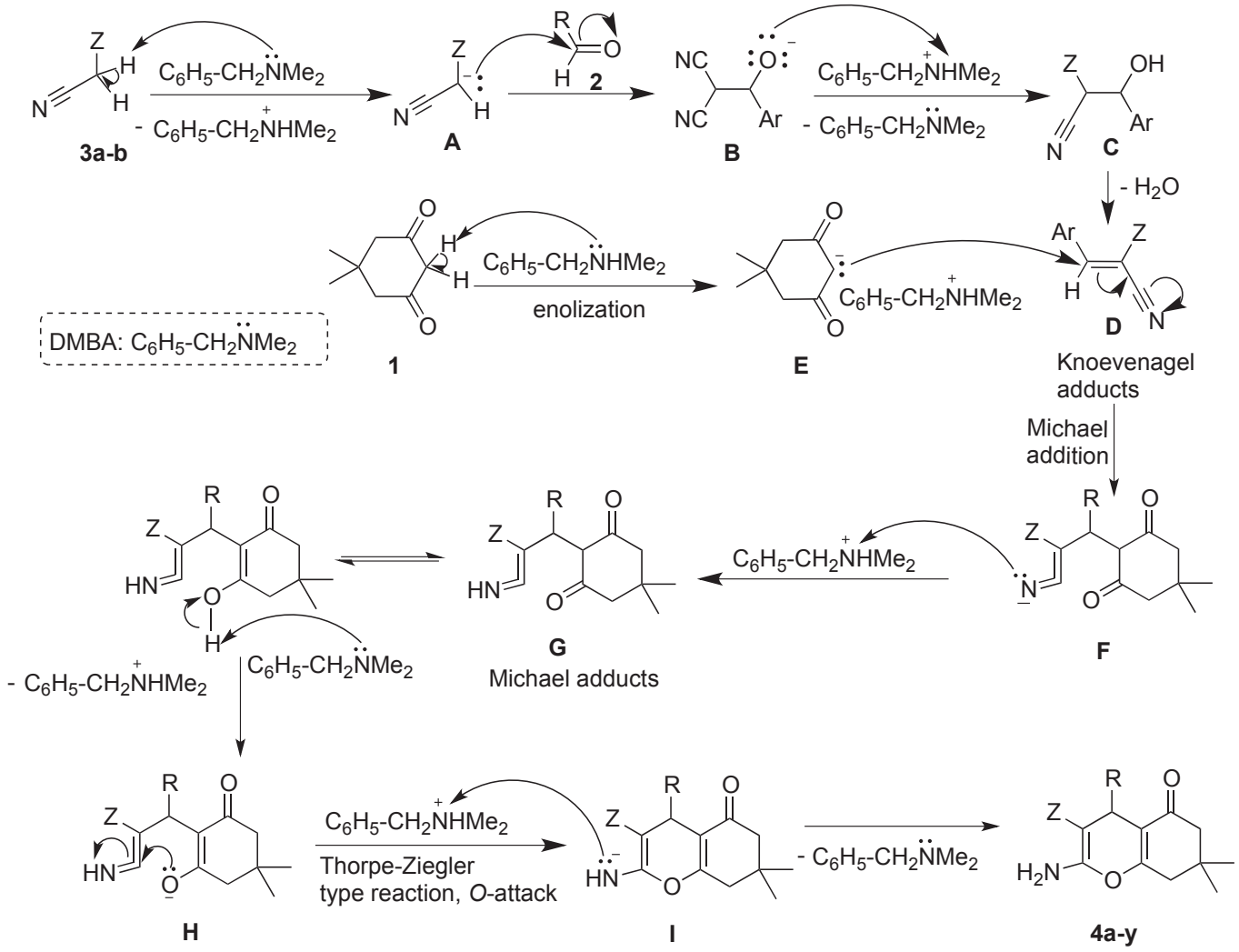
shorter reaction time and high yield the optimum conditions for further reactions were selected as EtOH solvent with 25 mol% of DMBA and heating to 45 °C.

Using with optimized reaction conditions in hand, the reactions of various aryl, heteroaryl, and aliphatic aldehydes (**2a-j**) as well as the cyano substrates (**3a-b**) with dimedone (**1**) were tested to investigate the generality of the reaction. The results are summarized in Table 2. All aryl aldehydes substituted with either electron-withdrawing (Table 2, entry 2-7) or electron-donating (Table 2, entries 8-14) functional groups and heteroaryl aldehydes (Table 2, entries 15 and 16) reacted smoothly with dimedone (**1**) and malononitrile (**3a**) to produce the desired annulated products in good to excellent yields. The annulation process with α,β-unsaturated aldehydes such as cinnamaldehyde (**2q**) and butyraldehyde (**2r**) as an aliphatic aldehyde was also proceeded smoothly under the same optimized reaction conditions and the corresponding products (**4q-r**) were isolated in good yields (Table 2, entries 17 and 18). In these two cases, lower yields than that of the other aldehydes is probably owing to the high electron density of these two aldehydes.

Based on the results indicated in Table 2, the electronic nature of the substituents on the benzaldehydes did not significantly influence the chemical yields of the corresponding annulated products; however the reaction times are affected. When aromatic aldehydes with electron-withdrawing groups (**2b-f**) as substrates were used, the reaction time was shorter and the reaction proceeded well at faster rate compared with aromatic aldehydes with electron-donating groups (**2h-n**). Substitutions at the *ortho* positions of the benzaldehydes resulted in a slight decrease in the yield of the reaction in addition to a lower reaction rate (Table 2, entries 2, 7 and 22). It was observed that when the malononitrile (**3a**) replaced with a less reactive methylene compound such as ethyl cyanoacetate (**3b**), the corresponding products (**4s-y**) were isolated in small lower yields and required longer reaction times (Table 2, entries 19-25), which may be ascribed to the competency of the cyanide group in stabilizing the reaction intermediates compared to the ester group. In all cases, the reaction media can be reused for further reactions. Reusability of the reaction media was carried out using the model reaction for the synthesis of **4d**. After completion of the reaction, the resulting solid product was collected by filtration. To the filtrate that containing DMBA, dimedone (**1**), 3-nitrobenzaldehyde (**2d**), and malononitrile (**3a**) were added in the same molar ratio devoid of extra load of catalyst. The reaction mixture was stirred at 45 °C for the required time. It showed a slight decrease of yield in first three runs (92%, 84%, and 80%), while in fourth run the yield dropped to 45%.

Based on the proposed mechanisms in the literature,[27] a reasonable mechanism for the DMBA-catalyzed one-pot, three-component synthesis of the corresponding pyran-annulated heterocycles is depicted in Scheme 2. Probably, the malonate carbanions **A** were formed *via* deprotonation of the active methylene nitriles (**3a-b**), which is likely; facilitate the Knoevenagel condensation between these carbanions and

aldehydes (**2**) to afford the arylidene nitrile intermediates **D** (Knoevenagel adducts). On the other hand, the role of DMBA in aiding enol-keto tautomerism in the C—H enolizable compounds (**1** and **5**) to **E** is also envisioned, which undergoes Michael-type addition with the Knoevenagel adducts **D** to give intermediates **F**, which is protonated to in-situ yield ketenimine intermediates **G** (Michael adducts). Furthermore, the intramolecular *O*-attack heterocyclization (Thorpe-Ziegler type reaction) of **H** results in the give intermediates **I**, followed protonation afford the final heterocyclic products **4**.



Scheme 2

A comparative study on the catalytic performance of DMBA with other reported catalysts for the one-pot, three-component synthesis of **4d** as typical example are shown in Table 3. The present method is better or comparable with others in terms of the yields and reaction times.

Table 3. Comparative study of DMBA with other reported catalysts for the one-pot, three-component synthesis of **4d**

Entry	Catalyst/conditions	Time (min)	Yield (%)[Ref.]
1	lactose/H_2O-EtOH, 60 °C	30	97[15]
2	nano-TiO_2/SF, 70 °C	35	95[12]
3	urea/H_2O-EtOH, rt	120	90[24]
4	CBSA/EtOH, reflux	10	90[16]
5	K_3PO_4/H_2O-EtOH, rt	45	89[22]
6	no catalyst/TFE, reflux	300	92[36]
7	DABCO/H_2O, reflux	120	88[27]
8	APSG/H_2O, 70 °C	60	92[23]
9	CA-SiO_2/H_2O-EtOH, reflux	20	94[18]
10	PFPA/H_2O-EtOH, rt	80	89[28]
11	I_2/DMSO, 120 °C	240	86[29]
12	PPI/H_2O, reflux	10	97[38]
13	KHP/H_2O, 50 °C	180	93[41]
14	DMBA/EtOH, 45 °C	4	96[current work]

SF solvent-free; *rt* room temperature; *CBSA* carbon-based solid acid; *TFE* 2,2,2-trifluoroethanol; *DABCO* 1,4-diazabicyclo[2.2.2]octane; *APSG* aminopropylated silica gel; *CA-SiO₂* Caro's acid-SiO_2; *PFPA* pentafluoropropionic acid; *PPI* potassium phthalimide; *KHP* potassium hydrogen phthalate; *HMT*, hexamethylenetetramine.

EXPERIMENTAL

All the reagents were obtained from commercial sources and used without further purification. Melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a BRUKER AVANCE DRX-400 and 500 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. The purity of synthesized compounds as well as a the development of the reactions was monitored by thin layer chromatography (TLC) analysis on Merck pre-coated silica gel 60 F_{254} aluminum sheets, visualized by UV light. Elemental microanalyses were performed on an Elementar Vario EL III analyzer. All of the targeted products are reported in the literature and are characterized by comparison of their spectral and physical data on the basis of literature descriptions.

General Procedure for the synthesis of tetrahydrbenzo[*b*]pyrans (4a-y). To a magnetically stirring mixture of aldehyde (**2**, 1 mmol), dimedone (**1**, 1 mmol), malononitrile/ethyl cyanoacetate (**3**, 1 mmol) in EtOH (5 mL), DMBA (25 mol%) was added. The mixture was heated at 45 °C for the required time indicated in Table 2. The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the reaction mixture was gradually cooled to room temperature and the resulting precipitates were collected by filtration, washed with cold EtOH and air-dried to give the pure corresponding products.

The filtrate containing DMBA was used as such for exploring the reusability of the catalyst. If necessary, the solid products can be recrystallized from hot EtOH. The identity of the known products was confirmed by comparison of their spectroscopic data and physical properties with those described in the respective literature. Spectral data for **4a**, **4d** and **4o** were as follows:

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4a). IR (KBr, cm^{-1}): ν = 3385, 3315, 2971, 2195, 1670, 1372, 1215; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 3H), 1.15 (s, 3H), 2.22-2.30 (m, 2H), 2.49 (m, 2H), 4.44 (s, 1H), 4.59 (s, 2H), 7.22-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4, 29.2, 32.1, 35.8, 41.4, 51.1, 63.8, 114.3, 119.8, 127.5, 127.9, 129.1, 143.8, 158.1, 162.3, 199.5. Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.42; H, 6.19; N, 9.50.

2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4d). IR (KBr, cm^{-1}): ν = 3361, 3340, 2945, 2208, 1675, 1655, 1520, 1330, 1195; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.09 (s, 3H), 1.16 (s, 3H), 2.27 (m, 2H), 2.54 (m, 2H), 4.56 (s, 1H), 4.79 (s, 2H), 7.52 (t, J = 7.9 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 8.07-8.13 (m, 2H). Anal. Calcd for $C_{18}H_{17}N_3O_4$ (%): C, 63.71; H, 5.05; N, 12.38. Found: C, 63.74; H, 5.08; N.

2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4o). IR (KBr, cm^{-1}): ν = 3352, 3205, 2940, 2208, 1680, 1650, 1195; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.01 (s, 3H), 1.05 (s, 3H), 2.20 (m, 2H), 2.48 (m, 2H), 4.35 (s, 1H), 6.07 (d, J = 3.9 Hz, 1H), 6.31 (dd, J = 3.9, 1.8 Hz, 1H), 7.06 (s, 2H), 7.50 (d, J = 3.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.3, 29.5, 31.2, 32.7, 50.9, 58.8, 114.0, 120.5, 124.6, 125.2, 127.8, 150.3, 159.8, 163.5, 196.4. Anal. Calcd for $C_{16}H_{16}N_2O_3$ (%): C, 67.59; H, 5.67; N, 9.85. Found: C, 67.77; H, 5.66; N, 9.83.

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