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AN EFFICIENT ONE POT SYNTHESIS OF 2-AMINO-4*H*-BENZO [*B*] PYRAN CATALYZED BY TETRABUTYL AMMONIUM HYDROGEN SULPHATE IN AQUEOUS MEDIA

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ABSTRACT:
A green, efficient and environmentally benign procedure has been developed for the synthesis of Tetrahydro benzo [*b*] pyran derivatives from one-pot three component condensation reactions of Aromatic aldehyde, malononitrile and dimedone in tetrabutyl ammonium hydrogen sulphate (TBAHS) and aqueous ethanol.

KEYWORDS:
TBAHS, Dimedone, Aromatic Aldehyde , MCRs.

INTRODUCTION:

As an important class of oxygen containing heterocycles, tetrahedrobenzo [*b*] pyran are widely employed as potential biodegradable agrochemicals[i], anti coagulant, antiancaphylactin, and anticancer activity[ii-iii], photoactive material[iv], cosmetic and pigments[v] . They can also be used as cognitive enhancer not only for the treatment of neurodegnrative disease. For example Alzhaimer's disease, Huntington's disease, Parkinson's disease, amyotropiclatera Sclerosis, AIDS associated dementia and Down syndrome but also for the treatment of Schizophrenia and Myoclonus[vi]. The versatile utilization of the pyran derivatives in the field of organic synthesis and medicinal chemistry, many researchers have been encouraged to develop highly efficient procedure for the preparation of this kind of compound.

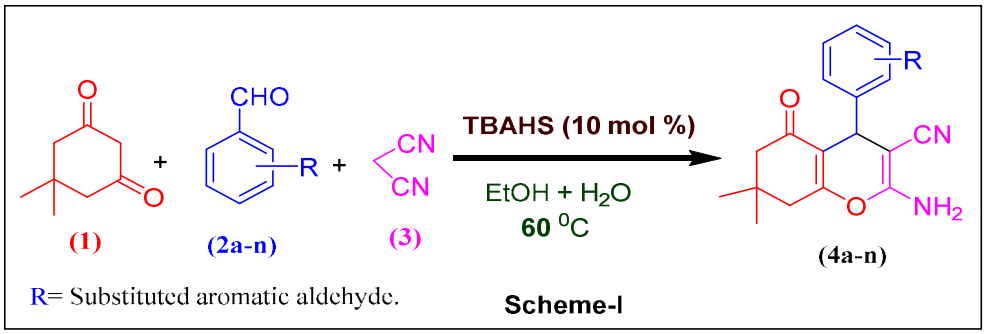
Hence, considering the fascinating advantages of MCRs some methodologies for the synthesis of tetrahedrobenzo [*b*] pyran via three component one pot reaction catalyzed by N-methylimidazole[vii], 1,4-diazabicyclo [2.2.2] octane[viii], $(NH_4)_2HPO_4$ [ix] , ZnO-beta Zeolite[x], K_3PO_4 [xi], nanosized $Ce_1MgXZr_{1-x}O_2$ [xii], Ru (II) complex[xiii], Na_2SeO_4 [xiv], S-Proline[xv], L-Proline[xvi] , 1,8-

diazabicyclo [5.4.0] undec-7-ene[xvii], sulfonic acid silica[xviii], phenylboronic acid[xix], Caro's acid-silica gel[xx] and cesium (III) chloride [xxi] have been reported. In addition, procedure of catalyst-free and 2, 2, 2-trifluoro ethanol as a reaction medium[xxii], microwave and ultrasonic irradiation [xxiii-xxiv] and ionic liquid mediated [xxv] synthesis have also been reported. Some of the reported methods were also reported expensive catalysts, strong acidic conditions, higher temperature, require longer reaction time, resulting cumbersome product isolation procedure.

Acidic TBAHS act as a Phase transfer catalyst (PTC) and it perform much organic transformation under mild condition. The one-pot multicomponent synthesis of 2,4,6-triaryl pyridine [xxvi], N-monosubstituted α-ketoamide[xxvii], 3-alkylated indole derivatives[xxviii] and benzopyran annulated pyrano[2,3-*c*] pyrazole by using TBAHS as a catalyst. Thus new route utilizing a MCR protocol, for the synthesis of benzo [*b*] pyran can attract considerable attention in the search of method for rapid entry of these heterocycles. Consequently, we thought that there is scope for further innovation towards milder reaction condition, short reaction time and better yield in choosing TBAHS for this multicomponent reaction (MCRs).

RESULT AND DISCUSSION:

Here, we reported the synthesis of tetrahydro benzo [*b*] pyran derivatives (**4a-n**) via Knoevenagel-Michael condensation pathways (Table **3**). Initially, a model reaction was examined using dimedone (**1**), benzaldehyde (**2**), and malononitrile (**3**) were refluxed in aqueous ethanol using Tetrabutyl ammonium hydrogen sulphate (TBAHS) (10 mol%) (Scheme **1**). After 4 h, 85% of tetrahydro benzo [*b*] pyran (**4**) product was obtained. When the amount of Tetrabutyl ammonium hydrogen sulphate (TBAHS) was gradually increased to 20 mol % , the yield was remain same. Therefore, TBAHS (10 mol%) catalyst is good for the yields of benzo [*b*] pyran derivatives (**4a-n**). Further, we investigated on the systematic evaluation of different solvent, such as toluene, DCM, THF, DMF, water, ethanol and ethanol: water, (Table1, entry **1-7**), for model reaction in presence of Tetrabutyl ammonium hydrogen sulphate (TBAHS) (10 mol%) catalyst (Scheme **1**). The results indicated that the solvent has significant effect on the product yield and reaction time. The best conversation was found, when the reaction carried out in aqueous ethanol (EtOH:H_2O) (Table**1**, entry **7**). The use of aqueous ethanol as solvent in reaction protocol exhibit remarkable benefits like environmentally safe, comparatively cheaper to operate and easy work up. We have carried out the model reaction using different amount of catalyst. The catalyst screening result are summarized in (Table **2**). It was observed that the excellent yield was obtained by using 10 mol% of Tetrabutyl ammonium hydrogen sulphate (Table **2**, entry **5**).



Scheme-I

Table 1. Optimization of the reaction conditions using different solvents.[a]

Entry	Solvent	Reaction Time (h)	Yield (%)[b]
1	Toluene	7.0	35
2	DCM	8.0	40
3	THF	9.0	45
4	DMF	6.5	50
5	Water	5.5	75
6	Ethanol	4.5	75
7	Ethanol-Water(1:1)	4.0	85

[a] ***Reaction conditions:*** dimedone (1) (2.0 mmol), substituted aromatic aldehydes (2) (2.0 mmol), and malononitrile (3) (2.0 mmol) in aqueous ethanol and Tetrabutyl ammonium hydrogen sulphate were refluxed at 60□.
[b] Isolated yields.

Table 2: Optimization Study for the amount of Tetrabutyl ammonium hydrogen sulphate.[a]

Entry	**Catalyst (mole %)**	**Temperature (^{0}C)**	**Reaction Time (h)**	**Yield %[b]**
1	01	60	3.0	42
2	02	60	3.0	50
3	05	60	3.0	60
4	08	60	3.0	71
5	10	60	3.0	85
6	15	60	3.0	85
7	20	60	3.0	85

[a] ***Reaction conditions:*** dimedone (1) (2.0 mmol), substituted aromatic aldehydes (2) (2.0 mmol), and malononitrile (3) (2.0 mmol) in aqueous ethanol and Tetrabutyl ammonium hydrogen sulphate were refluxed at 60□. [b] Isolated yields.

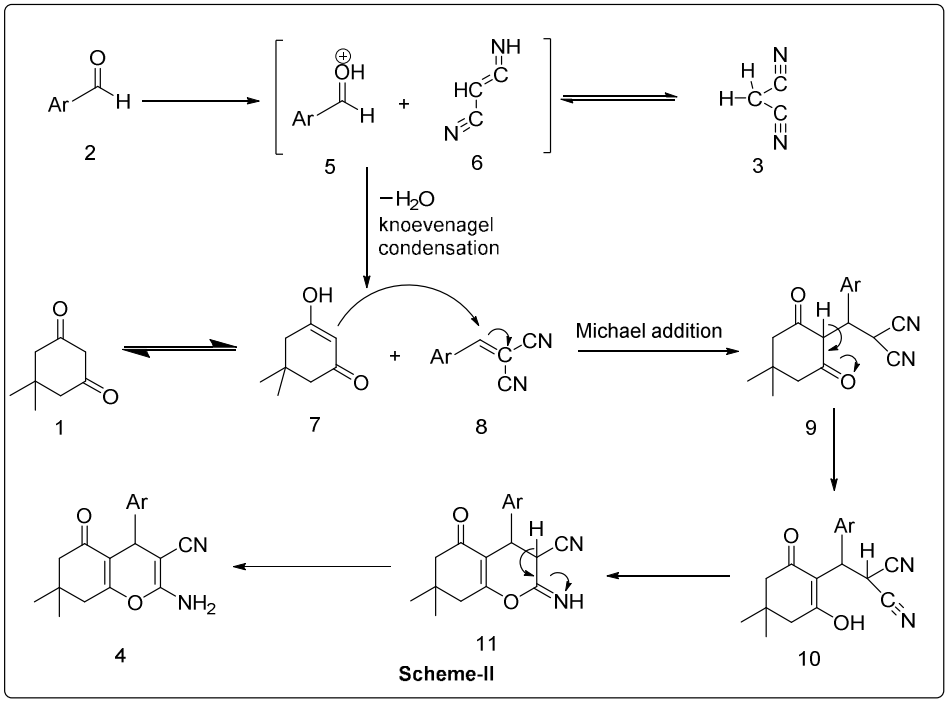
Table 3: Three component reaction of dimedone (1) (2.0 mmol), substituted aromatic aldehydes (2) (2.0 mmol), and malononitrile (3) (2.0 mmol) for the synthesis of **(4a-4n).**[a]

Entry	Aldehydes	Time (Hrs)	Yield (%)[b]	Mp (^{0}C)	
				Found	Lit.[Ref]
4a	-C_6H_5	2.5	75	226-228	228-230[xxii]
4b	4'-OCH_3 -C_6H_4	3.0	85	199-201	198-200[xxii]
4c	4'-CH_3 -C_6H_4	3.0	80	213-215	212-214[xxiii]
4d	4'-Br -C_6H_4	3.0	78	200-201	201-203[xxiv]
4e	4'-Cl -C_6H_4	3.5	70	199-201	201-203[xxiii]
4f	4'-NO_2 -C_6H_4	3.5	63	235-237	236-238[xxiii]
4g	4'-OH -C_6H_4	2.0	75	199-201	201-203[xxv]
4h	4'-F -C_6H_4	4.0	59	196-198	200-201[xxiii]
4i	4'-OCH_3, 3'-OCH_3-C_6H_3	2.0	79	210-212	211-213[xxiii]
4j	3'- Br -C_6H_4	3.5	67	227-229	229-231[xxiii]
4k	3'- NO_2 -C_6H_4	4.5	59	202-204	201-203[xxvi]
4l	3'- OH -C_6H_4	2.0	70	210-212	213-215[xxvii]
4m	2'- Cl -C_6H_4	3.5	68	221-223	222-224[xxviii]
4n	-C_4H_3O	3.5	66	202-204	200-202[xxviii]

[a] *Reaction conditions:* dimedone (1) (2.0 mmol), substituted aromatic aldehydes (2) (2.0 mmol), and malononitrile (3) (2.0 mmol) in aqueous ethanol and Tetrabutyl ammonium hydrogen sulphate were refluxed at 60□.
[b] Isolated yields.

After investigating the influence of different parameters on the model reaction, we turned our attention towards the tetrahydro benzo [*b*] pyran derivatives **(4a-n)**, using dimedone (**1**), different substituted Aromatic aldehydes **(2a-n)**, and malononitrile (**3**) were refluxed in the presence of Tetrabutyl ammonium hydrogen sulphate (TBAHS) (10 mol%) in aqueous ethanol (Scheme **1**), and the result are summarized in Table **3**. The desired products (**4a-n**) were obtained to excellent yields.

These synthesized products **(4a-n)** were completely characterized from IR, ^{1}H-NMR, Mass and ^{13}C-NMR spectroscopic technique and also elemental analysis. We proposed tentative plausible mechanism for the formation of tetrahydro benzo [*b*] pyran derivatives **(4a-n)** in the presence of Tetrabutyl ammonium hydrogen sulphate (TBAHS). The overall, mechanism takes place according to Knoevenagels-Micheal reaction **(Scheme-II).**



EXPERIMENTAL:

Open capillary tubes were used for melting points of isolated synthesized compounds and are uncorrected. Perkin-Elmer FTIR spectrophotometer was used for IR (KBr) spectra of compounds. Mass spectral data were recorded on liquid chromatography mass spectrometer (Shimadzu 2010Ev) using ESI probe. The ^{1}H and ^{13}C NMR spectra were recorded on various spectrometers at 300 & 400MHz using TMS as an internal standard.

General procedure for the synthesis of 2-Amino-3-Cyano-7,7-dimethyl-oxo-5, 6,7,8-tetrahydro-4*H*- benzopyran (4a-4n):

A mixture of Dimedone or 5, 5-dimethyl-1,3-cyclohexanedione **(1)** (2.0 mmol), different substituted Aromatic aldehydes **(2a-n)** (2.0 mmol), Malononitrile **(3)**, (2.0 mmol) and Tetrabutyl ammonium hydrogen sulphate (TBAHS) (10 mol %) was refluxed in the presence 10 ml ethanol and 10 ml water for three hours. The progress of reaction was monitored by TLC. The reaction mixture was cooled to room temperature and separated solid product was filtered,

washed with water and recrystallized from ethanol to form **(4a-n).** These synthesized products **(4a-n)** were characterized from IR, ^{1}H-NMR, Mass and ^{13}C-NMR spectroscopic technique and also elemental analysis.

SPECTRAL ANALYSIS:

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-phenyl-5-oxo-4*H* benzopyran (4a) :

IR (KBr / cm^{-1}) 3394,3213 (-NH_2), 2198 (-CN), 1681 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.95 -1.03 (2s, 6H, -2CH_3), 2.07-2.12 & 2.22-2.28 (2d, 2H, -CH_2), 2.50 (s, 2H, -CH_2), 2.51 (s, 1H, -CH), 6.90 (bs,2H,-NH_2) 7.01-7.89 (m, 5 H, Ar-H) ; EI-MS (m/z: RA %): 295 ($M^{+\cdot}$, 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 195(C=O), 162, 158, 144, 128, 127,126,119 (-CN),112, 58, 50, 39, 35, 31, 28, 26. Elemental analysis calculated data for $C_{18}H_{18}N_2O_2$; C, 73.53 ; N, 09.92. Found: C, 73.50; N, 09.90.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7, 7-dimethyl-4-(4'-methoxy phenyl)-5- oxo-4*H*-benzopyran (4b) :

IR (KBr / cm^{-1}): 3375,3305 (-NH_2), 2190 (-CN), 1685 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.95 -1.03 (2s, 6H, -2CH_3), 2.05-2.11 & 2.21-2.27 (2d, 2H, -CH_2), 2.49 (s, 2H,-CH_2), 3.70 (s,3H,- Ar–OCH_3), 4.11 (s, 1H, -CH), 6.95 (bs, 2H,-NH_2) 6.82-6.85 & 7.03-7.06 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 323 ($M^{+\cdot}$, 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 195(C=O), 162, 158, 157, 128, 121(-CN), 58, 54, 50, 39, 34,31, 28, 26. Elemental analysis calculated data for $C_{19}H_{20}N_2O_3$; C, 70.37 ; N, 08.64. Found: C, 70.35; N, 08.62.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4'-methylphenyl)-5-oxo-4*H* benzopyran(4c) :

IR (KBr / cm^{-1}): 3426, 3325 (-NH_2), 2191 (-CN), 1682 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.95 -1.03 (2s, 6H, -2CH_3), 2.10 & 2.23 (2d, 2H, -CH_2), 2.25 (s, 3H,-CH_3), 2.51 (s, 2H, -CH_2), 4.12 (s, 1H, -CH), 6.96 (bs, 2H,-NH_2) 7.02- 7.10 (m, 4 H, Ar-H); EI-MS (m/z: RA %): 308 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 196(C=O), 162, 158, 142, 136,129, 127, 120(-CN), 113, 58, 50, 40, 39, 32, 28, 27, 21. Elemental analysis calculated data for $C_{19}H_{20}N_2O_2$; C, 74.03 ; N, 09.09. Found: C, 74.00; N, 09.09.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4'-bromophenyl)-5-oxo-4*H* benzopyran (4d) :

IR (KBr / cm^{-1}): 3390, 3286 (-NH_2), 2187 (-CN), 1677 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.94 -1.03 (2s, 6H, -2CH_3), 2.10 & 2.20 (2d, 2H, -CH_2), 2.50 (s, 2H, -CH_2), 4.17 (s, 1H, -CH), 7.06 (bs, 2H,-NH_2) 7.12 & 7.49 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 373 (M+2, 98%), 371($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 196(C=O), 164, 158, 157, 128,120(-CN), 126, 58, 50, 39, 31, 28, 26. Elemental analysis calculated data for $C_{18}H_{17}BrN_2O_2$; C, 65. 85 ; N, 08.54. Found: C, 65.83; N, 08.52.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4'-chlorophenyl)-5-oxo-4*H*-benzopyran (4e) :

IR (KBr / cm^{-1}): 3469, 3320 (-NH_2), 2190 (-CN), 1685 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.98 -1.07 (2s, 6H, -2CH_3), 2.09 & 2.27 (2d, 2H, -CH_2), 2.53 (s, 2H, -CH_2), 4.70 (s, 1H, -CH), 7.03 (bs, 2H,-NH_2) 7.16 - 7.38 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 328 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 195(C=O), 163, 159, 142, 130, 129,128, 119(-CN), 112, 57, 50, 40, 39, 32,28, 27. Elemental analysis calculated data for $C_{18}H_{17}ClN_2O_2$; C, 65.85 ; N, 08.54. Found: C, 65.82; N, 08.51.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4'-nitrophenyl)-5-oxo-4*H*-benzopyran (4f) :

IR (KBr / cm^{-1}): 3407, 3325 (-NH_2), 2180 (-CN), 1672 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.95 -1.04 (2s, 6H, -2CH_3), 2.13 & 2.28 (2d, 2H, -CH_2), 2.56 (s, 2H, -CH_2), 4.36 (s, 1H, -CH), 7.18 (bs, 2H,-NH_2) 7.43- 8. 19 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 339 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 192(C=O), 163, 159, 146, 129,124, 119(-CN), 112, 57, 50, 40, 39, 32, 28, 27. Elemental analysis calculated data for $C_{18}H_{17}N_3O_4$; C, 63.72 ; N, 08.26. Found: C, 63.70; N, 08.24.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4'-hydroxyphenyl)-5-oxo-4*H*-benzopyran (4g) :

IR (KBr / cm^{-1}): 3465 (-OH), 3365, 3201 (-NH_2), 2198 (-CN), 1661 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.98 -1.07 (2s, 6H, -2CH_3), 2.09 & 2.27 (2d, 2H, -CH_2), 2.53 (s, 2H, -CH_2), 4.26 (s, 1H, -CH), 5.73 (bs, 2H,-NH_2) 6.63- 7.09 (m, 4 H, Ar-H) 8.70 (s, 1H, Ar-OH); EI-MS (m/z: RA %): 310 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 195(C=O), 156, 159, 132, 130,129, 128, 119(-CN), 112, 57, 50, 40, 39, 28, 27. Elemental analysis calculated data for $C_{18}H_{18}N_2O_3$; C, 65.85 ; N, 08.54. Found: C, 65.83; N, 08.52.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4'-fluorophenyl)-5-oxo-4*H*-benzopyran(4f) :

IR (KBr / cm^{-1}): 3345, 3310 (-NH_2), 2191 (-CN), 1687 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.94 -1.03 (2s, 6H, -2CH_3), 2.12 & 2.26 (2d, 2H, -CH_2), 2.50 (s, 2H, -CH_2), 4.20 (s, 1H, -CH), 7.03 (bs, 2H,-NH_2), 7.09-7.13 (d, 2H, Ar-H), δ 7.17-7. 20.(d, 2H, Ar-H); EI-MS (m/z: RA %): 312 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 196(C=O), 163, 159, 141, 129,120(-CN), 115,113, 58, 50, 40, 39, 32, 28, 27. Elemental analysis calculated data for $C_{18}H_{17}FN_2O_2$; C, 69.23; N, 08.97. Found: C, 69.20; N, 08.92.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3,4'-dimethoxyphenyl)-5-oxo-4*H*-benzopyran (4i) :

IR (KBr / cm^{-1}): 3390, 3320 (-NH_2), 2193 (-CN), 1682 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.98 -1.04 (2s, 6H, -2CH_3), 2.12 & 2.24 (2d, 2H, -CH_2), 2.50 (s, 2H, -CH_2), 3.77 (2s, 6H,(-2-OCH_3), 4.13 (s, 1H, -CH), 6.95 (bs, 2H,-NH_2) 6.63-6.66 (dd, 1H, Ar-H), 6.69-6.70(d, 1H, Ar-H), 6.85-6.87(d, 1H, Ar-H) ; EI-MS (m/z: RA %): 354 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 195(C=O), 162, 158, 148, 137, 119(-CN), 113, 58, 54, 39, 31, 28, 26. Elemental analysis calculated data for $C_{20}H_{22}N_2O_4$; C, 67.81; N, 07.89. Found: C, 67.79; N, 07.87.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3'-bromophenyl)-5-oxo-4*H*-benzopyran (4j) :

IR (KBr / cm^{-1}): 3343, 3310 (-NH_2), 2191 (-CN), 1687 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.97 -1.03 (2s, 6H, -2CH_3), 2.12 & 2.24 (2d, 2H, -CH_2), 2.53 (s, 2H, -CH_2), 4.20 (s, 1H, -CH), 7.09 (bs, 2H,-NH_2) 7.15- & 7.40 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 373 (M+2, 98%), 371($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 196(C=O), 163, 159, 147, 131, 129,127, 119(-CN), 112, 58, 50, 40, 39,32, 28, 27. Elemental analysis calculated data for $C_{18}H_{17}BrN_2O_2$; C, 57. 91 ; N, 07.51. Found: C, 57.89; N, 07.50.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3'-nitrophenyl)-5-oxo-4*H*-benzopyran (4k) :

IR (KBr / cm^{-1}): 3420, 3325 (-NH_2), 2187 (-CN), 1654 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.96 -1.04 (2s, 6H, -2CH_3), 2.13 & 2.30 (2d, 2H, -CH_2), 2.55 (s, 2H, -CH_2), 4.42 (s, 1H, -CH), 7.14 (bs, 2H,-NH_2) 7.61- 8.09 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 339 ($M^{+\cdot}$

100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 196(C=O), 163, 159, 146, 134,130, 122, 120(-CN), 112, 57, 50, 40, 39, 28, 27. Elemental analysis calculated data for $C_{18}H_{17}N_3O_4$; C, 63.72 ; N, 08.26. Found: C, 63.70; N, 08.24.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3'-hydroxyphenyl)-5-oxo-4*H*-benzopyran(4l) :

IR (KBr / cm^{-1}): 3465 (-OH), 3469, 3320 (-NH_2), 2176 (-CN), 1685 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.98 -1.07 (2s, 6H, -2CH_3), 2.09 & 2.27 (2d, 2H, -CH_2), 2.53 (s, 2H, -CH_2), 4.26 (s, 1H, -CH), 5.73 (bs, 2H,-NH_2) 6.63- 7.09 (m, 4 H, Ar-H) 8.70 (s, 1H, Ar-OH); EI-MS (m/z: RA %): 310 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 195(C=O), 156, 159, 132, 130,129, 128, 119(-CN), 112, 57, 50, 40, 39, 28, 27. Elemental analysis calculated data for $C_{18}H_{18}N_2O_3$; C, 65.85 ; N, 08.54. Found: C, 65.83; N, 08.52.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(2'-chlorophenyl)-5-oxo-4*H*-benzopyran (4m) :

IR (KBr / cm^{-1}): 3469, 3325 (-NH_2), 2185 (-CN), 1680 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.96 -1.08 (2s, 6H, -2CH_3), 2.06 & 2.29 (2d, 2H, -CH_2), 2.54 (s, 2H, -CH_2), 4.72 (s, 1H, -CH), 7.01 (bs, 2H,-NH_2) 7.16 - 7.40 (m, 4 H, Ar-H) ; EI-MS (m/z: RA %): 328 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ ppm) δ: 192(C=O), 161, 159, 140, 130, 129,128, 120(-CN), 112, 55, 50, 40, 38, 32,28. Elemental analysis calculated data for $C_{18}H_{17}ClN_2O_2$; C, 65.80 ; N, 08.50. Found: C, 65.78; N, 08.48.

2-Amino-3-Cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(furan-2-yl)--5-oxo-4*H*-benzopyran(4n) :

IR (KBr / cm^{-1}): 3469, 3320 (-NH_2), 2176 (-CN), 1685 (C=O); ^{1}H NMR (300MHz, DMSO-d_6 / ppm) δ 0.96 -1.06 (2s, 6H, -2CH_3), 2.05 & 2.29 (2d, 2H, -CH_2), 2.29 (s, 2H, -CH_2), 4.19 (s, 1H, -CH), 6.80 (bs, 2H,-NH_2), 6.40-7.52 (m, 3H, furan-H); EI-MS (m/z: RA %): 285 ($M^{+\cdot}$ 100%). ^{13}C NMR (300 MHz, DMSO–d_6 / ppm) δ: 197(C=O), 159, 155, 152, 142, 129,119(-CN), 115,113, 56, 50, 40, 39, 32, 28, 27. Elemental analysis calculated data for $C_{16}H_{16}N_2O_3$; C, 67.59; N, 09.85. Found: C, 67.57; N, 09.82.

CONCLUSION:

In Conclusion, we have developed a novel efficient and eco-friendly synthesis for the preparation of tetrahydro benzo[*b*] pyran derivatives by one-pot three component condensation reactions of Aromatic aldehyde, Malononitrile and Dimedone in Tetrabutyl ammonium hydrogen sulphate (TBAHS) and aqueous ethanol. The product can be easily isolated by simple work up procedure such as dilution and filtration of the precipitated product. The ambient condition, ecofriendly solvent, short reaction time, excellent isolated yields and easy work up make this methodology for the synthesis of benzo[*b*] pyran.

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