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Vitamin B_{12}, A Natural and Green Catalyst for the One-pot Three-Component Synthesis of 4H-Pyran Annulated Systems

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Abstract

Vitamin B_{12} was found as a natural and efficient catalyst for the one-pot three-component synthesis of 4H-pyran annulated systems from the condensation between aryl aldehydes, malononitril and 1,3 dicarbonil compounds in aqueous media at ambient and thermal condition. Vitamin B_{12} is an organometallic compound that can play the catalytic role in the organic reactions. It has many active sites that make this catalyst affect significantly in spite of its very low amount (0.00017g). This methodology has number of advantages such as: use of very small amount of catalyst, easy access, short reaction times, high yields, easy work up and use of non-toxic and hazardous catalyst and solvents. Although, all products were obtained just with a simple filtration and no need to column chromatography.

Keywords: Vitamin B_{12}; 4H-pyrane annulated systems; High yields; Non-toxic; Hazardous catalyst; Solvents

Introduction

The word "Vitamin B_{12}" is generally used for cyanocobalamin that is a water-soluble substance. Vitamin B_{12} is the first organometallic compound that naturally occurs. In addition, it is a crucial nutrient for human growth and cell development [1]. Vitamin B_{12} (molecular weight 1355.4) is stable in aqueous solution between pH 4 and 7 can be heated at 120˚C without significant loss [2]. The B_{12} not only has biological function in nervous system, but also diminishes the risk of heart diseases. This vitamin plays an essential role in human biological system, include DNA synthesis and regulation, enzymatic reaction, red blood cell formation and etc. [3]. Moreover, It has a complex organometallic cofactor with a central cobalt (III) atom to coordinate with coring ring consisting of six donor ligands [3, 4] **(Figure 1).** The performed studies about the vitamin B_{12}'s structure and biochemistry in the areas of chemistry, psychology and medicine have awarded four Noble [4]. Vitamin B_{12} has been already used for many organic reactions such as: methyltransferases [5], the asymmetric catalyst for the enantioselective cyclopropanation of alkenes [6], catalyzed carbon-carbon bond forming reaction [7] and catalyzed dehydrogenation reaction [8].

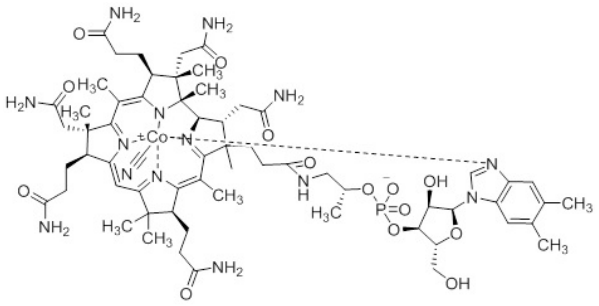
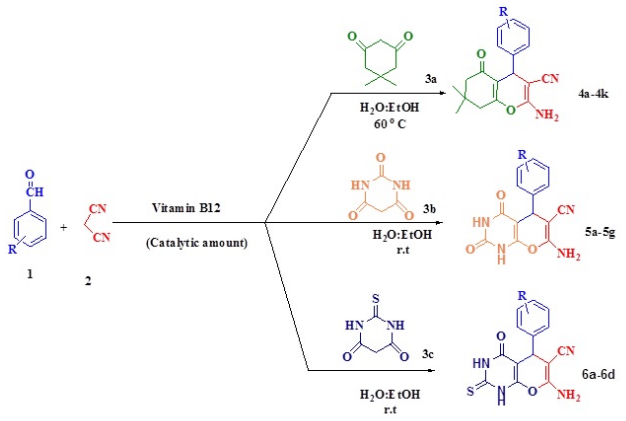


Figure 1: The structure of Vitamin B_{12}.

Tetrahydrobenzopyran, and their derivatives are of considerable interest as they includes a wide range of biological properties [9], such as spasmolytic, diuretic, anticoagulant, anticancer, and anti-anaphylactic activity [10]. In addition, they can be used as cognitive enhancers for the treatment of neurodegenerative diseases, containing amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS-associated dementia, Alzheimer's disease, and Down's syndrome, as well as for the treatment of schizophrenia and myoclonus [11]. In addition, a number of 2-amino-4H-pyrans are useful as photoactive materials [12]. These molecules are biologically active and find application in pharmacological properties such as anticoagulant, spasmolytic, diuretic, anti-anaphylactic, and anticancer agents [10]. Some of the 2-aminobenzochromene derivatives are useful cosmetics and pigments [13] and are utilized as potential biodegradable agrochemicals [14]. Some methods have been reported for the preparing of tetrahydrobenzopyran, and pyrano [2,3-d] pyrimidine derivatives [15-29]. However, some of these methods have drawbacks, such as long reaction times, use of expensive reagents, low yields, harsh reaction conditions, effluent pollution, and tedious work-up procedures. In continue of our research on multi-component reactions [30-37], herein we

report easy and green synthesis of 4H-pyran annulated systems from the reaction between aromatic aldehydes, malononitrile and dimedone/barbituric acid and thiobarbituric acid in the presence of vitamin B_{12} as catalyst in aqueous media at ambient and thermal conditions **(Scheme 1).**



Scheme 1: Synthesis of 2-amino-4H-pyran derivatives in the presence of vitamin B_{12} as catalyst in aqueous media.

Methodology

Melting points and IR spectra were measured with an Electro-thermal 9100 apparatus and a JASCO FT-IR-460 plus spectrometer, respectively. The 1H NMR spectra were obtained on Bruker DRX-400 & 300 Advance instruments with DMSO as a solvent. All reagents and solvents are obtained from Fluka and Merck and used without further purification. The Vitamin B_{12} was purchased from the Sigma-Aldrich company. TLC was performed on Silica–gel Polygram SILG/UV 254 plates.

General procedure for the synthesis of 2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromenes

Vitamin B_{12} (0.00017g) dissolved in H_2O: Et-OH (3:1 mL), then a mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol), and 1,3-dicarbonyl compounds (1 mmol) was added to above solution and stirred at 60°C for products (4a-4h) and ambient temperature for other products (5a-5g, 6a-6d). After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered and residue was washed with ethanol (3 × 5 mL) to separate catalyst. The crude product was recrystallized from ethanol to afford the pure product. The desired pure products were characterized by comparison of their physical data (melting points, IR and 1H NMR) with those of known compounds in the literature.

Spectral data for selected products

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4b).

IR (KBr, cm-): 3329, 3394,3215, 2204, 1681; 1H NMR (400 MHz, DMSO-d6): δ (ppm): 1.02 (s, 3H),1.14 (s,3H), 2.13 (d, J = 16.1 Hz, 1H), 2.28 (d, J = 16.2 Hz, 1H),2.56 (s, 2H),4.30 (s, 1H), 6.25 (s, 2H, br), 7.17–7.32 (5H, Ar).

2-Amino-5,6,7,8-tetrahydro-4-(4-methyl)-7,7-dimethyl-5-oxo-4H-chromene-3- carbonitrile (4f)

IR (KBr, cm-): 3466, 3322, 2954, 2191, 1675, 1248; 1H NMR (400 MHz, DMSO-d6): δ (ppm): 1.09 (s, 3H), 1.12 (s, 3H), 2.22 (dd, J = 16.4 Hz, 2H), 2.31 (s, 3H), 2.46 (dd, J = 17.6, 2H), 4.53(s, 2H), 4.71(s, 1H), 6.713–6.808 (m, 2H), 6.971 (t, 1H).

2-Amino-5,6,7,8-tetrahydro-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-4Hchromene-3-carbonitrile (4h)

IR (KBr, cm-): 3,287, 3,165, 2,962, 2,184, 1,672, 1,208; 1H NMR (400 MHz, DMSO-d6): δ (ppm): 1.051(s, 3H), 1.11 (s, 3H), 2.26 (dd, J = 16.4 Hz, 2H), 2.465 (s, 2H), 4.34 (s, 1H), 4.51(s, 2H), 5.24 (s, 1H), 6.725–7.104 (dd, J = 8.4, 4H).

2-Amino-5,6,7,8-tetrahydro-4-(2,3-dimethoxyphenyl)-7,7-dimethyl-5-oxo-4Hchromene-

3-carbonitrile (4j)

IR (KBr, cm-1): 3,304, 3,205, 2,947, 2,172, 1,674, 1,213; 1H NMR (400 MHz, DMSO-d6): δ (ppm): 1.07 (s, 3H), 1.13 (s, 3H), 2.24 (dd, J = 16 Hz, 2H), 2.44 (dd, J = 17.6, 2H), 3.83 (s, 3H), 3.94 (s, 3H), 4.52(s, 2H), 4.77(s, 1H), 6.712–6.807 (dd, J = 8, 2H), 6.973 (t, J = 8, 1H).

7-amino-5-(4-nitrophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (5a)

1H NMR (300 MHz, DMSO-d6): δ (ppm): 4.43 (s, 1H, CH), 7.30-8.45 (m, 6H, Ar & NH_2), 11.15 (s, 1H, NH), 12.20 (s, 1H, NH).

7-amino-5-(4-bromophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (5b)

1H NMR (300 MHz, DMSO-d6): δ (ppm): 4.24 (s, 1H, CH), 7.18-7.85 (m, 6H, Ar & NH_2), 11.14 (s, 1H, NH), 12.12 (s, 1H, NH).

7-amino-5-(4-chlorophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (5d)

1H NMR (300 MHz, DMSO-d6): δ (ppm): 4.25 (s, 1H, CH), 7.18 (s, 2H, NH_2), 7.24-7.34 (m, 4H, Ar), 11.11 (s, 1H, NH), 12.11 (s, 1H, NH).

7-amino-5-(4-fluorophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (5e)

1H NMR (300 MHz, DMSO-d6): δ (ppm): 4.25 (s, 1H, CH), 7.08-7.16 (m, 6H, Ar & NH_2), 11.01 (s, 1H, NH), 12.10 (s, 1H, NH).

7-amino-5-(3-chlorophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (5g)

1H NMR (300 MHz, DMSO-d6): δ (ppm): 4.27 (s, 1H, CH), 7.18-7.34 (m, 6H, Ar & NH_2), 11.10 (s, 1H, NH), 12.30 (s, 1H, NH).

7-amino-5-(4-bromophenyl)-2,3,4,5-tetrahydro-4-oxo-2-thioxo-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (6b)

1H NMR (300 MHz, DMSO-d6): δ(ppm): 4.93 (s, 1H, CH), 5.91 (s, 2H, NH_2), 6.94-7.37 (m, 4H, Ar), 11.66 (s, 1H, NH), 12.26 (s, 1H, NH).

Results and Discussions

In order to be able to synthesis of 2-amino-4H-pyran derivatives in a more efficient way, minimizing the time and amount of catalyst, the reaction of 4-nitrobenzaldehyde, malononitrile and dimedone/barbituric acid/thiobarbituric acid was selected as a model system. The reaction was carried out in different solvents, and temperatures. The best results were obtain in H_2O: Et-OH (3:1 mL) at ambient temperature for the 5a and 6a and 60°C for the 4a **(Table 1).** As can be seen in **Table 2**, 12.54 µmol %) of vitamin B_{12} (0.00017 g) was the most effective amount to catalyze the reactions.

Table 1: Optimization of solvent and temperature in synthesis of compound 4a, 5a and 6a.

Entry	product	Solvent	Catalyst	Temperature	Isolated yield %
1	4a	H_2O	Vitamin B_{12}	60	70
2	4a	H_2O:EtOH (2:1)	Vitamin B_{12}	60	71
3	4a	H_2O:EtOH (3:1)	Vitamin B_{12}	60	86
4	4a	H_2O:EtOH (4:1)	Vitamin B_{12}	60	65
5	4a	H_2O:EtOH (3:1)	Vitamin B_{12}	r.t	-
6	4a	H_2O:EtOH (3:1)	Vitamin B_{12}	40	45
7	4a	H_2O:EtOH (3:1)	Vitamin B_{12}	50	70
8	5a	H_2O:EtOH (3:1)	Vitamin B_{12}	r.t	94
9	5a	H_2O:EtOH (3:1)	Vitamin B_{12}	50	60
10	5a	H_2O:EtOH (1:1)	Vitamin B_{12}	r.t	65
11	6a	H_2O:EtOH (3:1)	Vitamin B_{12}	r.t	80
12	6a	H_2O:EtOH (3:1)	Vitamin B_{12}	50	66
13	6a	H_2O:EtOH (1:1)	Vitamin B_{12}	r.t	70

Table 2: Optimization catalyst in synthesis of compound 4a, 5a and 6a.

Entry	product	Catalyst µ (mol %)	Time (min)	Yield(%)
1	4a	2.21	80	60
2	4a	3.7	35	71
3	4a	8.12	29	82
4	4a	12.54	15	86
5	4a	15.5	20	86
6	4a	70.38	20	86
7	5a	2.21	15	70
8	5a	3.7	13	76
9	5a	8.12	10	80
10	5a	12.54	4	94
11	5a	15.5	5	94

12	5a	70.38	5	94
13	6a	2.21	15	68
14	6a	3.7	10	70
15	6a	8.12	8	75
16	6a	12.54	5	80
17	6a	15.5	5	80
18	6a	70.38	5	80

Using these optimized reaction, the scope and efficiency of the reaction were explored for the synthesis of a wide variety of 4H-pyrans annulated systems using aromatic aldehydes, malononitriles and 1,3-dicarbonyl compounds. The results are summarized in **Table 3** [38-50].

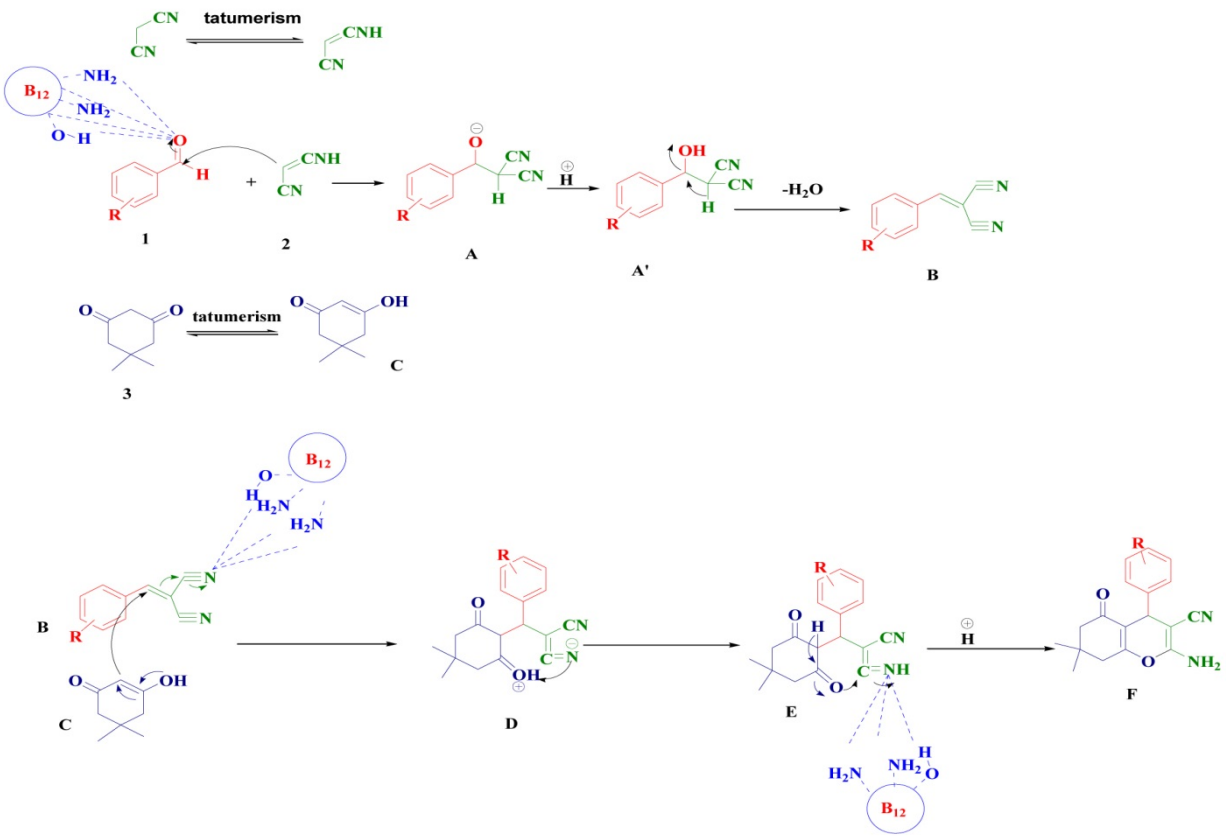
Table 3: Preparation of 4H-pyran substitutes.

Entry	Ar	1,3-dicarbonil compounds	Product	Time (min)	Yeild%	MP(Obs) (°C)	MP(Lit) (°C) [ref]
1	4-NO_2 C_6H_4	3a	4a	15	86	180-181	183-185 [38]
2	C_6H_5	3a	4b	20	85	229-230	233-235 [38]
3	4-Cl C_6H_4	3a	4c	26	79	219-220	218 [38]
4	4-F C_6H_4	3a	4d	39	80	205-206	208-210 [39]
5	4-Br C_6H_4	3a	4e	18	75	207-208	207-209 [40]
6	4-Me C_6H_4	3a	4f	20	85	214-215	215-218 [41]
7	2-NO_2 C_6H_4	3a	4g	19	85	221-222	223-225 [42]
8	4-OH C_6H_4	3a	4h	30	85	212-213	214-215 [43]
9	3-NO_2 C_6H_4	3a	4i	120	88	208-209	208-211 [44]
10	2,3-$(OMe)_2$ C_6H_4	3a	4j	42	88	217-218	214-216 [45]
11	3-Cl C_6H_4	3a	4k	53	82	221-222	226-227 [36]
12	4-NO_2 C_6H_4	3b	5a	4	94	245-246	245 [46]
13	4-Br C_6H_4	3b	5b	3	91	240-241	235–236 [47]
14	C_6H_5	3b	5c	5	89	220-222	223 [48]
15	4-Cl C_6H_4	3b	5d	3	89	244-245	242-244 [46]
16	4-F C_6H_4	3b	5e	3	96	232-233	225-226 [46]
17	4-Me C_6H_4	3b	5f	2	90	226-227	225 [48]
18	3-Cl C_6H_4	3b	5g	3	85	237-238	240-241 [47]
19	4-NO_2 C_6H_4	3c	6a	5	80	232-233	233–235 [49]
20	4-Br C_6H_4	3c	6b	5	90	236-237	236 [49]
21	3-Cl C_6H_4	3c	6d	22	85	237-238	237-238 [49]
22	3-NO_2 C_6H_4	3c	6e	20	93	238-239	235-236 [50]

Interestingly, a variety of aryl aldehydes including electron withdrawing or releasing substituents (ortho-, meta-, and para-substituted) participated well in this reaction and gave the product in good to excellent yield.

A mechanism was proposed for this reaction. As can be seen in **scheme 2,** First, Knoevenagal condensation between 1 and 2 produced 2-benzylidenemalononitrile B, Michael addition of B with C (1,3-dicarbonyl compound), and followed cyclization and tautomerization afforded the corresponding product F. There are many reactive sites in the vitamin B_{12} molecule that can active carbonyl group **(Figure 1).**

In order to assess the efficiency and generality of this methodology, the obtained result from the reaction of 4-nitrobenzaldehyde and malononitrile with substrate 3a, 3b and 3c by this method has been compared with those of the previously reported methods **(Table 4).** It was found that the present method is convincingly superior to the reported methods with respect to reaction time, yield of the product and amount of the catalyst.



Scheme 2: Proposed mechanism for the one-pot three-component synthesis of 4H-pyran substitutes in the presence of vitamin B_{12}.

Table 4: Comparison of the efficiency of vitamin B_{12} with other reported catalysts in literature.

Entry	product	Catalyst/Condition	Time	Yield (%)	Reference
1	4a	Melt/130°C	1 h	100	[38]
2	4a	Urea (10 mol%)/ EtOH:H_2O/ r.t	5 h	92	[39]
3	4a	$(NH_4)_2.HPO_4$/ H_2O/r.t	2 h	78	[40]
4	4a	Phenylboronic acid/ EtOH.H_2O/reflux	30 min	88	[41]
5	4a	Vitamin B_{12}/ H_20:EtOH, 60°C	15 min	86	Present work
6	5a	Zn|(L) prline|$_2$/ EtOH/reflux	30min	90	[48]
7	5a	L-proline/EtOH/r.t	45 min	73	[49]
8	5a	Triethanolamine/Choline chloride Zncl2/ 75°C/EtOH	92 sec	67	[50]
9	5a	Vitamin B_{12}/H_2O:EtOH/r.t	4 min	94	Present work
10	6a	L-proline/EtOH/r.t	90 min	76	[49]
11	6a	Triethanolamine/Choline chloride Zncl$_2$/ 75°C/EtOH	240 sec	42	[50]
12	6a	Vitamin B_{12}/H_2O:EtOH/r.t	5 min	80	Present work

Conclusion

In conclusion, Vitamin B_{12} can be used as a promising eco-friendly catalyst for the synthesis of 4H-pyrans annulated system. Moreover, this method has several other advantages such as, high yields, operational simplicity, clean and neutral reaction conditions, which makes it a useful and attractive process for the synthesis of a wide variety of biologically active compounds.

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References

1. Banerjee R (1999) Chemistry and Biochemistry of B_{12}. John Wiley & Sons.
2. Sherma J, Fried B (2003) Handbook of thin-layer chromatography. CRC press 89.
3. Giedyk M, Goliszewska K, Gryko D (2015) Vitamin B_{12} catalyzed reactions. Chem Soc Rev 44: 3391-3404.
4. Pozharskii AF, Soldatenkov AT, Katritzky AR (1997) Front Matter. John Wiley & Sons, Ltd.
5. Matthews RG (2001) Cobalamin-dependent methyltransferases. Acc chem res 34: 681-689.
6. Chen Y, Zhang XP (2004) Vitamin B_{12} derivatives as natural asymmetric catalysts: enantioselective cyclopropanation of alkenes. J org chem 69: 2431-2435.
7. Shey J, McGinley CM, McCauley KM, Dearth AS, Young BT, et al. (2002). Mechanistic investigation of a novel vitamin B_{12}-catalyzed carbon-carbon bond forming reaction, the reductive dimerization of arylalkenes. Jorgchem 67: 837-846.
8. Pratt DA, Van der DWA (2006) On the role of alkylcobalamins in the vitamin B_{12}-catalyzed reductive dehalogenation of perchloroethylene and trichloroethylene. Chemcomm 5: 558-560.
9. Shitole NV, Shelke KF, Sadaphal SA, Shingate BB, Shingare MS (2010) PEG-400 remarkably efficient and recyclable media for one-pot synthesis of various 2-amino-4 H-chromenes. Green Chem Letters Rev 3: 83-87.
10. Zavar S (2012) A novel three component synthesis of 2-amino-4H-chromenes derivatives using nano ZnO catalyst. Arab J Chem.
11. Bonsignore L, Loy G, Secci D, Calignano A (1993) Synthesis and pharmacological activity of 2-oxo-(2H) 1-benzopyran-3-carboxamide derivatives. Eur J Med Chem 28: 517-520.
12. Konkoy CS, Fick DB, Cai SX, Lan NC, Keana JF, et al. (2004) Substituted 5-oxo-5, 6, 7, 8-tetrahydro-4H-1-benzopyrans and benzothiopyrans and the use thereof as potentiators of AMPA. U.S. Patent 6,680,332.
13. Armesto D, Horspool WM, Martin N, Ramos A, Seoane C (1989) Synthesis of cyclobutenes by the novel photochemical ring contraction of 4-substituted 2-amino-3, 5-dicyano-6-phenyl-4H-pyrans. J Org Chem 54: 3069-3072.
14. Kumar BS, Srinivasulu N, Udupi RH, Rajitha B, Reddy YT, et al. (2006) An efficient approach towards three component coupling of one pot reaction for synthesis of functionalized benzopyrans. J Heterocycl Chem 43: 1691-1693.
15. Azath IA, Puthiaraj P, Pitchumani K (2012) One-pot multicomponent solvent-free synthesis of 2-amino-4 H-benzo [b] pyrans catalyzed by per-6-amino-β-cyclodextrin. ACS Sus Chem & Eng. 1: 174-179.
16. Hafez EAA, Elnagdi MH, Elagamey AGA, EL-Taweel FMAA (1987) Nitriles in heterocyclic synthesis: novel synsthesis of benzo [c]-coumarin and of benzo [c] pyrano [3, 2-c] quinoline derivatives. Heterocycles, 26: 903-907.
17. Heber D, Heers C, Ravens U (1993) Positive inotropic activity of 5-amino-6-cyano-1, 3-dimethyl-1, 2, 3, 4-tetrahydropyrido [2, 3-d] pyrim idine-2, 4-dione in cardiac muscle from guinea-pig and man. Part 6: Compounds with positive inotropic activity. Die Pharmazie 48: 537-541.
18. Grivsky EM, Lee S, Sigel CW, Duch DS, Nichol CA (1980) Synthesis and antitumor activity of 2, 4-diamino-6-(2, 5-dimethoxybenzyl)-5-methylpyrido [2, 3-d] pyrimidine. J Med Chem 23: 327-329.
19. Ghorab MM, Hassan AY (1998) Synthesis and antibacterial properties of new dithienyl containing pyran, pyrano [2, 3-b] pyridine, pyrano [2, 3-d] pyrimidine and pyridine derivatives. Phosphorus, Sulfur Silicon Relat. Elem 141: 251-261.
20. Devi I, Borah HN, Bhuyan PJ (2004) Studies on uracils: a facile one-pot synthesis of oxazino [4, 5-d]-, pyrano [2, 3-d]-, pyrido [2, 3-d]-and pyrimido [4, 5-d] pyrimidines using microwave irradiation in the solid state. Tetrahedron letters, 45: 2405-2408.
21. Davoll, J, Clarke J, Elslager EF (1972). Antimalarial substances. 26. Folate antagonists. 4. Antimalarial and antimetabolite effects of 2, 4-diamino-6-[(benzyl) amino] pyrido [2, 3-d] pyrimidines. J Med Chem 15: 837-839.
22. Kretzschmar E (1980) On derivatives of 4-oxo-3, 4-dihydropyrido [2, 3-d] pyrimidine. Pharmazie, 35: 253-256.
23. Lian XZ, Huang YQ, Li WJ, Zheng Y (2007) Monatsh Chem 139: 129-131.
24. Jin TS, Wang AQ, Shi F, Han LS, Liu LB, et al. (2006) Hexadecyldimethyl benzyl ammonium bromide: an efficient catalyst for a clean one-pot synthesis of tetrahydrobenzopyran derivatives in water. Arkivoc 14: 78-86.
25. Devi I, Bhuyan PJ (2004) Sodium bromide catalysed one-pot synthesis of tetrahydrobenzo [b] pyrans via a three-component cyclocondensation under microwave irradiation and solvent free conditions. Tetrahedron Letters, 45(47), 8625-8627.
26. Balalaie S, Sheikh-Ahmadi M, Bararjanian M (2007) Tetra-methyl ammonium hydroxide: An efficient and versatile catalyst for the one-pot synthesis of tetrahydrobenzo [b] pyran derivatives in aqueous media. Catal Comm 8: 1724-1728.
27. Abdolmohammadi S, Balalaie S (2007) Novel and efficient catalysts for the one-pot synthesis of 3, 4-dihydropyrano [c] chromene derivatives in aqueous media. Tetrahedron Letters 48: 3299-3303.
28. Davoodnia A, Allameh S, Fazli S, Tavakoli-Hoseini N (2011). One-pot synthesis of 2-amino-3-cyano-4-arylsubstituted tetrahydrobenzo [b] pyrans catalysed by silica gel-supported polyphosphoric acid (PPA-SiO2) as an efficient and reusable catalyst. Chemical Papers 65: 714-720.

29. Mobinikhaledi A, Fard MB (2010) Tetrabutylammonium Bromide in Water as a Green Media for the Synthesis of Pyrano [2, 3-d] pyrimidinone and Tetrahydrobenzo [b] pyran Derivatives. Acta Chim Slov 57: 931-935.

30. Sadeh FN, Maghsoodlou MT, Hazeri N, Kangani M (2015) A facile and efficient synthesis of tetrahydrobenzo [b] pyrans using lactose as a green catalyst. Res Chem Intermed 41: 5907-5914.

31. Kangani M, Maghsoodlou MT, Hazeri N (2016) Vitamin B_{12}: An efficient type catalyst for the one-pot synthesis of 3, 4, 5-trisubstituted furan-2 (5H)-ones and N-aryl-3-aminodihydropyrrol-2-one-4-carboxylates. Chin Chem Lett 27: 66-70.

32. Vafajoo Z, Veisi H, Maghsoodlou MT, Ahmadian H (2014) Electrocatalytic multicomponent assembling of aldehydes, 4-hydroxycoumarin and malononitrile: An efficient approach to 2-amino-5-oxo-4, 5-dihydropyrano (3, 2-c) chromene-3-carbonitrile derivatives. Comptes Rendus Chimie 17: 301-304.

33. Adrom B, Maghsoodlou MT, Hazeri N, Lashkari M (2015) Solvent-free synthesis of 1-(benzothiazolylamino) methyl-2-naphthols with maltose as green catalyst. Res Chem Intermed 41: 7553-7560.

34. Abadi AYE, Maghsoodlou MT, Heydari R, Mohebat R (2015) An efficient four-component domino protocol for the rapid and green synthesis of functionalized benzo [a] pyrano [2, 3-c] phenazine derivatives using caffeine as a homogeneous catalyst. Res. Chem. Intermed.1-9.

35. Sajadikhah SS, Maghsoodlou MT (2014) A simple and green approach for the synthesis of polyfunctionalized mono-and bis-dihydro-2-oxopyrroles catalyzed by trityl chloride. RSC Advances, 4: 43454-43459.

36. Hazeri N, Maghsoodlou MT, Mir F, Kangani M, Saravani H, et al. (2014). An efficient one-pot three-component synthesis of tetrahydrobenzo [b] pyran and 3, 4-dihydropyrano [c] chromene derivatives using starch solution as catalyst. Chin J Cata 35: 391-395.

37. Hazeri N, Maghsoodlou MT, Mousavi MR, Aboonajmi J, Safarzaei M (2015) Potassium sodium tartrate as a versatile and efficient catalyst for the one-pot synthesis of pyran annulated heterocyclic compounds in aqueous media. Res Chem Intermed 41: 169-174.

38. Kaupp G, Naimi-Jamal MR, Schmeyers J (2003) Solvent-free Knoevenagel condensations and Michael additions in the solid state and in the melt with quantitative yield. Tetrahedron 59: 3753-3760.

39. Brahmachari G, Banerjee B (2013) Facile and one-pot access to diverse and densely functionalized 2-amino-3-cyano-4 H-pyrans and pyran-annulated heterocyclic scaffolds via an eco-friendly multicomponent reaction at room temperature using urea as a novel organo-catalyst. ACS Sus Chem & Eng 2: 411-422.

40. Balalaie S, Bararjanian M, Sheikh-Ahmadi M, Hekmat S, Salehi P (2007) Diammonium Hydrogen Phosphate: An Efficient and Versatile Catalyst for the One-Pot Synthesis of Tetrahydrobenzo [b] pyran Derivatives in Aqueous Media. Synthetic Commu 37: 1097-1108

41. Nemouchi S, Boulcina R, Carboni B, Debache A (2012) Phenylboronic acid as an efficient and convenient catalyst for a three-component synthesis of tetrahydrobenzo [b] pyrans. Comptes Rendus Chimie 15: 394-397.

42. Sarrafi Y, Mehrasbi E, Vahid A, Tajbakhsh M (2012) Well-ordered mesoporous silica nanoparticles as a recoverable catalyst for one-pot multicomponent synthesis of 4H-chromene derivatives. Chin J Catal 33: 1486-1494.

43. Katkar SS, Lande MK, Arbad BR, Gaikwad ST (2011) A Recyclable and Highly Effective ZnO-beta Zeolite as a Catalyst for One-pot Three-Component Synthesis of Tetrahydrobenzo [b] pyrans. Chin J Chem 29: 199-202.

44. Jin TS, Wang AQ, Wang X, Zhang JS, Li TS (2004) A clean one-pot synthesis of tetrahydrobenzo [b] pyran derivatives catalyzed by hexadecyltrimethyl ammonium bromide in aqueous media. Synlett 871-873.

45. Devi I, Bhuyan PJ (2004) Sodium bromide catalysed one-pot synthesis of tetrahydrobenzo [b] pyrans via a three-component cyclocondensation under microwave irradiation and solvent free conditions. Tetrahedron Letters 45: 8625-8627.

46. Yu J, Hanqing W (2005) Green synthesis of pyrano [2, 3-d]-pyrimidine derivatives in ionic liquids. Synthetic comm 35: 3133-3140.

47. Ziarani GM, Faramarzi S, Asadi S, Badiei A, Bazl R, et al. (2013) Three-component synthesis of pyrano [2, 3-d]-pyrimidine dione derivatives facilitated by sulfonic acid nanoporous silica (SBA-Pr-SO 3 H) and their docking and urease inhibitory activity. DARU Journal of Pharmaceutical Sciences 21: 1.

48. Heravi MM, Ghods A, Bakhtiari K, Derikvand F (2010) Zn [(L) proline] 2: an efficient catalyst for the synthesis of biologically active pyrano [2, 3-d] pyrimidine derivatives. Synthetic Comms 40: 1927-1931.

49. Bararjanian M, Balalaie S, Movassag B, Amani AM (2009) One-pot synthesis of pyrano [2, 3-d] pyrimidinone derivatives catalyzed by L-proline in aqueous media. J Iran Chem Soc 6: 436-442.

50. Kumar YD, Quraishi MA (2014) Choline chloride. ZnCl2: green, effective and reusable ionic liquid for synthesis of 7-amino-2, 4-dioxo-5-phenyl-2, 3, 4, 5-tetrahydro-1H-pyrano [2, 3-d] pyrimidine-6-carbonitrile derivative. J Mater Environ Sci 5: 1075-1078.