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Synthetic studies on biologically novel pyrimidinones and related heterocyclic compounds

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ABSTRACT

The thesis is constructed in four different parts. The first part describes the $Yb(OTf)_3$ catalyzed/greener protocol for the synthesis of β-ketoesters *via* transesterification reaction and its applications. The second part deals with synthesis of pyrimidinones and pyrimidines derivatives using N-halo reagent [N,N'-dichlorobis(2,4,6-trichlorophenyl)urea] *via* Biginelli reaction. A five-component reaction involving transesterification/Biginelli/click reaction for the construction of glycoside annulated dihydropyrimidinone derivatives with 1,2,3-triazole linkage analogues was discussed in third part. Finally the fourth fraction engages with ZnO nanoparticles as a heterogeneous catalyst for the synthesis of naphthoxazinone derivatives through Biginelli like reaction.

Keywords: Biginelli Reacion, Pyrimidinones and Pyrimidines, Transesterificaion, β-Ketoesters, ZnO-Nanoparticles, Naphthoxazinones, Click Chemistry.

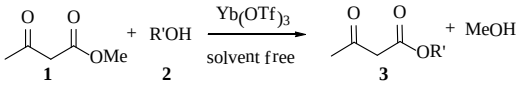
Introduction

Dihydropyrimidinones (DHPMs) have been extensively explored in the past twelve decades owing their potential pharmacological and biological activities like, calcium channel blockers, mitotic kinesine inhibitor, adrenergic receptor antagonist, antibacterial and antiviral activities.[1] Therefore, the synthesis of this core nucleus has gained significance in medicinal chemistry. Such a medicinally significant DHPMs was pioneered by Italian chemist Pietro Biginelli (University of Florence) in 1893 for the synthesis of 3,4-dihydropyrimidinones (DHPMs),[2] which involves one-pot three component condensation of β-ketoester, arylaldehyde and urea under strong acidic circumstances. However, the yields of the products were modest. Besides this, an impressive number of reports[1] for the synthesis of DHPMs were now available to improve the reaction conditions and product yields along with variation in precursors to obtain the multi-functionalized dihydropyrimidinone derivatives.

Section I: $Yb(OTf)_3$ catalyzed/greener protocol for the synthesis of β-ketoesters and its application

β-Ketoester, the one of precursors out of the three construction blocks in the Biginelli reaction, was prepared through transesterification[3] as an dominant organic conversion and it also occupied a protuberant position in industrial laboratories.[4] The chemistry expounded in transesterification is the exchange of alkoxy moiety of ester with alcohol to form a new ester. Transesterification is an equilibrium driven procedure and it can be controlled by acidic and basic catalysts[3] or usage of excess of one of the precursor to get quantitative yield.

tert-Butylacetoacetate could also be rehabilitated simply into its corresponding esters in catalyst-free condition,[5] which was basically due to the existence of a better departure group. Moreover, great deal of consideration has been paid towards *trans*-acetoacylation (transesterification) of lower homologue to higher homologue. So, herein we report a $Yb(OTf)_3$ catalyzed (0.3 mmol) *trans*-acetoacetylation transformation[6] (Scheme 1) using 1: 1 mmol ratio of methyl β-ketoester **1** and alcohol **2** under solvent free condition at 110°C to afford the corresponding new β-ketoester **3** derivatives (Table 1).



1 **2** **3**

Scheme 1

With an intention to progress a sustainable and greener protocol of transesterification, the reaction (Scheme 1) was re-examined under solvent-free and catalyst-free conditions to achieve a number of β-ketoesters by a simple and usual method of transesterification from readily accessible methyl β-ketoester **1**. Herein, we report a realistic process for the synthesis of β-ketoester using 1:1.5 mole ratio of methyl β-ketoester **1** with different functionalized alcohols **2** under solvent-free and catalyst-free conditions[7] at 110°C and results are appended in Table 1.

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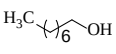
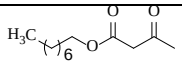
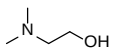
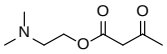
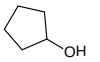
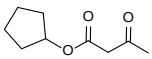
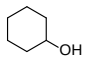
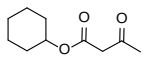
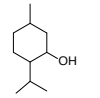
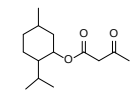
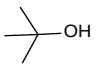
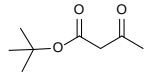
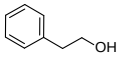
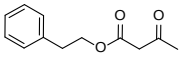
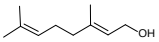
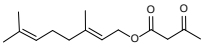
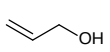
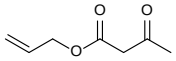
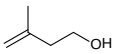
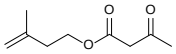
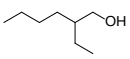
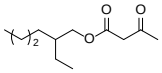
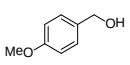
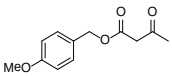
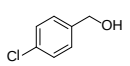
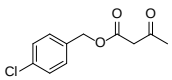
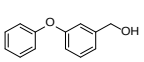
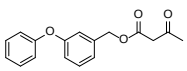
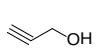
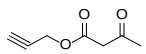
Highlights

1. The transesterification transformation has been developed using $Yb(OTf)_3$ as a catalyst and greener protocol for the synthesis of non-commercial β-ketoesters.
2. A novel N-halo reagent (CC-2) has been introduced for the construction of pyrimidinone and pyrimidine derivatives.
3. A newfangled one-pot five-component synthesis of glycoside annulated dihydropyrimidinone derivatives with 1,2,3-triazole linkage has been demonstrated *via* transesterification/Biginelli/click reactions.
4. The applicability of ZnO NPs as catalyst for the synthesis of naphtha[1,2-e]oxazinone derivatives has been developed under solvent free condition.

Table 1. $Yb(OTf)_3$ catalyzed/Greener protocol for *trans*-acetoactylation transformation

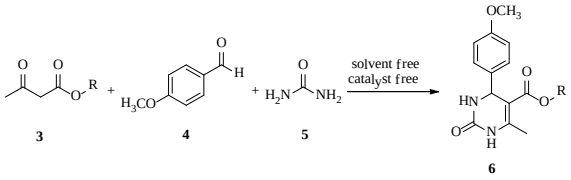
S. No.	Alcohol (2)	Product (3)	Time (h)[a/b]	Yield (%)[a/b]
1			3/3	92/85
2			3/3	90/90
3			3/NT	89/--
4			3/3	91/85
5			3/NT	85/--
6			4.5/5.5	65/60
7			3/3	87/83
8			4/NT	80/--
9			3/3	80/80
10			4/4	82/76
11			NT/3	--/85
12			NT/3	--/90
13			NT/4	--/85
14			NT/4	--/80
15			NT/3	--/75

[a]Yb(OTf)3 catalyzed *trans*-acetoacetylation,[b]greener protocol for *trans*-acetoacetylation, NT= Not Tried.

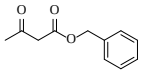
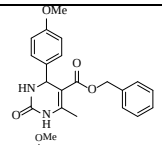
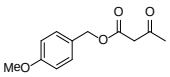
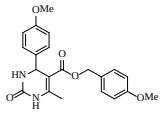
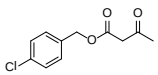
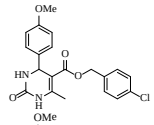
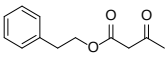
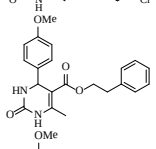
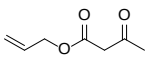
The newly formed non-commercial β-ketoester as stated above is used to achieve assortment at C-5 position of DHPMs **6** using 1: 1: 1.2 moleratio of β-ketoester **3**, *p*-methoxy arylaldehyde **4** and urea **5** under greener conditions at 110°C *via* Biginelli reaction[7] and all results are tabulated in Table 2.

In summary, we have developed and demonstrated a new and highly efficient viable procedure for the synthesis of non-commercial β-ketoester *via* transesterification transformation (catalytic/greener protocol) and its function as precursor in synthesis of dihydropyrimidinone C-5 ester derivatives over straight forward Biginelli reaction under solvent-free, catalyst-free conditions.

Table 2: Synthesis of dihydropyrimidinone C-5 ester derivatives using non-commercial β-ketoester under greener conditions



3 4 5 6

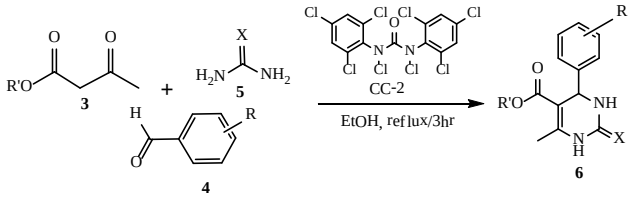
S. No.	β-Ketoester	Product (6)	M.P (°C)	%Yield
1			190-192	92
2			178-180	92
3			200-202	90
4			140-142	89
5			152-154	90
6			128-130	87
7			194-196	85
8			158-160	82

Section II: Synthesis of pyrimidinones and pyrimidines using N-halo reagent under solvent free condition

N,N'-dichlorobis(2,4,6-trichlorophenyl)urea also known as 2-chlorocarbinol (CC-2)[8] belong to N-halo group and has 14.54% high active chlorine. The CC-2 is a simple, steady,

harmless N-halo reagent and has been used for various organic conversions.[9-10] CC-2 releases active chlorine and get transformed into unsolvable solid form of 1,3-bis(2,4,6-trichlorophenyl)urea. The insoluble mass can be easily separated by simple filtration and re-converted to CC-2 by reaction with AcOH/ Cl_2/ NaOH.[11] Due to these advantages; herein we attempted the N-halo reagent (CC-2) for the Biginelli reaction using aryl aldehydes **4**, β-ketoester **3**, urea **5** and CC-2 were used in the ratio of 1: 1: 1.2: 0.3 in ethanol solvent at 70°C to afford the corresponding dihydropyrimidinone derivatives **6** (Table 3).

Table 3: Synthesis of dihydropyrimidinone derivatives[12] using CC-2 (N-halo reagent).



S.No	R	R'	X	%Yield	M. P (°C)
1	H	C_2H_5	O	93	200-202
2	4-OH	C_2H_5	O	88	200-202
3	4-F	C_2H_5	O	85	180-182
4	4-N(CH_3)$_2$	C_2H_5	O	91	228-230
5	4-CH_3	C_2H_5	S	82	194-196
6	4-OH	CH_3	O	84	242-244
7	4-OCH_3	CH_3	S	80	152-154
8	4-NO_2	CH_3	O	90	233-235
9	4-F	CH_3	O	85	193-195
10	3-OCH_3	CH_3	O	80	204-206

In addition, various pyrimidine derivatives **8** were also synthesized[12] by using 2-aminobenzimidazole/ 2-aminobenzothioazole **7** as alternatives to urea. The same optimized reaction conditions were applied in synthesis of pyrimidine derivatives using CC-2 in Biginelli like reaction (Table 4).

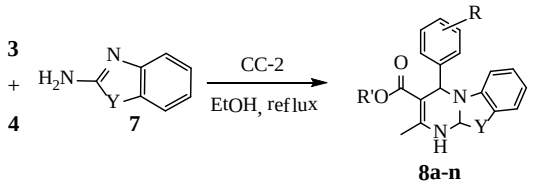
In swift, we have demonstrated the application of CC-2 for the synthesis of diversified pyrimidones and pyrimidines by three component coupling *via* Biginelli reaction in one-pot.

Section III: One-pot five-component synthesis of glycoside annulated dihydropyrimidinone derivatives with 1,2,3-triazole linkage

Click chemistry is the Huisgen 1,3-dipolar cycloaddition mediated by Cu(I) catalyst of alkyne and azides reaction[13] has become a greatest ubiquitous example to achieve 1,2,3-triazole, which is an significant class of biologically active N-heterocycles.[14] On other hand, 1,2,3-triazole can mimic natural peptides and heterocyclic in geometrical shape and interaction function.[15]

The most copious molecules in nature are the glycosides and show very vital role in cellular metabolism, physiology, single transduction.[16] All cell surfaces are coated with complex glycosides where they act as recognition molecules

Table 4: Synthesis of pyrimidine derivatives using CC-2



S. No	R	R'	Y	Product	T (h)	Yield %
1	4-OCH_3	C_2H_5	N	8a	5	82
2	4-OC_2H_5-	C_2H_5	N	8b	5	78
3	4-C_2H_5-	C_2H_5	N	8c	5.5	76
4	4-Me_2CH-	C_2H_5	N	8d	6.5	72
5	4-F-	C_2H_5	N	8e	6	68
6	4-NO_2-	C_2H_5	N	8f	6	70
7	3-NO_2-	CH_3	N	8g	7	68
8	4-OH-	C_2H_5	N	8h	6	71
9	4-OCH_3	C_2H_5	S	8i	6.5	75
10	3-OH-	C_2H_5	S	8j	6.5	66
11	4-Me_2N-	C_2H_5	S	8k	6.5	65
12	4-CF_3-	C_2H_5	S	8l	8	58
13	3,4,5-(OMe)$_3$-	CH_3	N	8m	8	55
14	Indol-	CH_3	N	8n	10	55

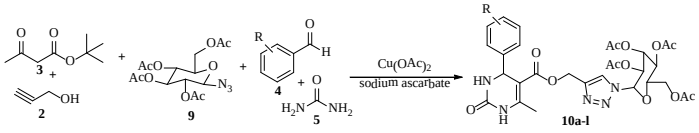
for other cells. However, glycosides are more water soluble than the respective aglycons. Attaching of the glycosidic core unit into the molecule enhances its hydrophilicity and reduces its toxicity.

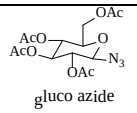
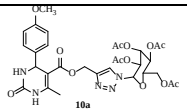
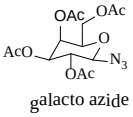
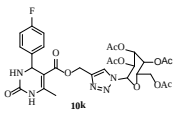
tert-Butyl β-ketoester underwent transesterification transformation with alcohol to form the corresponding new β-ketoester in presence of toluene/xylene as solvent under catalyst-free condition[5] due to presence of better leaving group. By taking the advantage of bulkier group of *tert*-butyl β-ketoester and above observations (Section 1) herein, we knock a feasible protocol for the synthesis of glycoside annulated dihydropyrimidinone derivatives with 1,2,3-triazole linkage[17] by the *in situ* formation of propargyl β-ketoester by the transesterification between *tert*-butyl β-ketoester **3** (1.0 mmol) and propargyl alcohol **2** (1.5 mmol) followed by Biginelli and click reactions using arylaldehyd **4** (1.0 mmol), urea **5** (1.5 mmol) and glycosyl azide **9** (1.0 mmol) with catalytic amount of $Cu(OAc)_2$ (0.1 mmol) and sodium ascorbate (0.2 mmol) in water (2 ml) as a solvent at 110°C (Table 5).

In conclusion, we have documented a simple, environmentally benign and straight forward protocol for the effective synthesis of glycoside annulated

dihydropyrimidinone derivatives with 1,2,3-triazole linkage *via* transesterification, Biginelli and click reactions in one-pot using water, an environmentally benign solvent.

Table 5: Glycoside annulated dihydropyrimidinone derivatives with 1,2,3-triazole linkage.



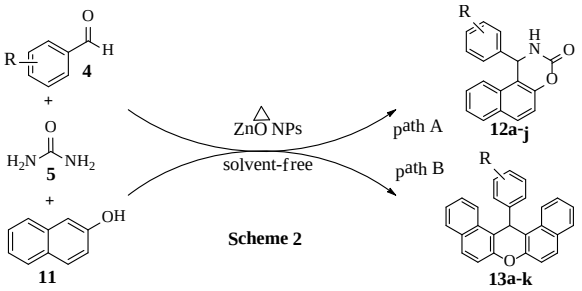
S. No.	Aldehyde (R)	Azide (9)	Product	%yield
1	4-OCH_3	 gluco azide	 10a	78
2	4-OC_2H_5	gluco azide	10b	72
3	4-CF_3	gluco azide	10c	70
4	4-NO_2	gluco azide	10d	60
5	4-F	gluco azide	10e	78
6	3-Cl	gluco azide	10f	61
7	4-F	 galacto azide	 10k	75
8	4-CF_3	galacto azide	10h	72

Section IV: ZnO nanoparticles catalyzed synthesis of naphtha[1,2-e]oxazinone and 14-substituted -14*H*-dibenzo[*a,j*]xanthene derivatives.

Aryl-condensed oxazinones analogues are very significant class of heterocyclic moieties and have received considerable attention, due to its wide range of biological activities.[18-19] for example naphthalene condensed oxazinone derivatives have broad spectrum of antibacterial properties[20] and the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one which involves 2-naphthol, arylaldehyde and urea a three-component Biginelli like condensation reaction in one-pot.

Recent advances in nanotechnology have led to an increasing demand for multifunctional materials due to their unique properties.[21]. Highly ordered materials function as excellent heterogeneous catalysts in organic transformations owing to their high surface area and surface functionalities. Thus, synthesis of ordered nano materials has attracted great deal of research interest in the last few years. Zinc oxide nanoparticles (ZnO-NPs) is one such heterogeneous catalyst and extensively used in cosmetics, paints, and fibers. It can also play a role of Lewis acid in numerous organic reactions.[22-23]

We synthesized naphtha[1,2-e]oxazinone derivatives[24] (Scheme 2, Path A) by the union of 2-naphthol (1.0 mmol) **11**, arylaldehyde (1.0 mmol) **4** and urea (2.0 mmol) **5** in presence of catalytic amount of ZnO-NPs (0.3 mmol) as an environmentally benign solvent-free reaction at 150^{o}C (Table 6). By the random addition of reactants **11**, **5** and **4** (Scheme 2, Path B) we found xanthene derivative (Table 7, 13a-g) as a major product. This might be due to the very reactive nature of benzaldehyde with 2-naphthol than urea. So, the sequential addition of reactants like **4**, **5** and catalyst



Scheme 2

Path A: **aldehyde** + **urea** + **2-naphthol** sequence addition

Path B: **aldehyde**, **urea**, **2-naphthol** random addition

Table 6: ZnO-NPs catalyzed synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes derivatives (12a-h).

S. No	Aldehyde (R)	Product	Time (min)	Yield (%)	M.P (^{o}C)
1	4-CH_3-	12a	90	85	164-166
2	4-F-	12b	60	92	198-200
3	3-F-	12c	50	92	218-220
4	3-Cl-	12d	60	88	194-196
5	4-OC_2H_5-	12e	80	80	216-218
6	4-CF_3-	12f	50	94	234-236
7	4-OCF_3-	12g	45	90	168-170
8	4-$(CH_3)_3C$-	12h	120	76	180-182

Table 7: ZnO-NPs catalyzed synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes derivatives (13a-g).

S. No.	Aldehyde (R)	Product	Time (min)	Yield (%)	M.P (^{o}C)
1	4-OCH_3 -	13a	60	82	202-204
2	4-Cl-	13b	40	92	288-290
3	3-Cl-	13c	60	90	210-212
4	3-F -	13d	45	90	258-260
5	4-C_2H_5-	13e	70	88	186-188
6	3-C_5H_4N-CHO	13f	60	85	202-204
7	$(CH_3)_2CH$-CHO	13g	80	86	156-158

followed by **11** played a crucial role and influenced towards the course of desired naphthoxazinone derivatives **12a-h**.

In summary, we have described a simple one-pot procedure for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one and 14-substituted-14*H*-dibenzo[*a,j*]xanthenes derivatives by using catalytic amount of ZnO-NPs under thermal and solvent-free conditions.

Finally the conclusion of the thesis is, we have established the synthesis of non-commercial β-ketoesters *via* transesterifications reaction under catalytic $[Yb(OTf)_3]$/greener conditions, we introduced the new N-halo reagent (CC-2) for the synthesis of pyrimidinones and pyrimidines through Biginelli reaction, we also demonstrate the application of transesterification and Biginelli reactions in synthesis of 1,2,3-triazole fused dihydropyrimidinone derivatives and finally we study the catalytic activity of ZnO-NPs in synthesis of naphthoxizinone derivatives.

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Thesis Details

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Supplementary Material

Spectroscopic data for compounds **3** (Table 1, S. No. 12, 13), **6** (Table 2, S. No. 2, 3), **8f**, **8i**, **10b**, **10e**, **12e**, **12g** along with ^{1}H and ^{13}C spectra are accessible online from article page.

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