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First vinyl acetate mediated organocatalytic transesterification of Phenols: A step towards sustainability

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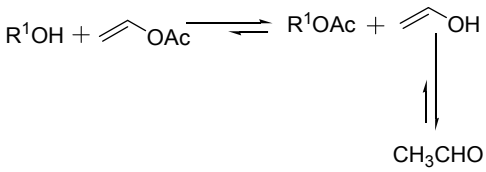
The present report outlines our efforts toward a simple yet elegant protocol for O-acylation of wide variety of phenols. This highly enabling and solventless method relies on vinyl acetate as innocuous acyl donor and DABCO as an organocatalyst. Operational simplicity, excellent yields, higher and faster conversion rate without excess reagent, simple work up and essentially no need of column are some of the salient features of the reported protocol.

Introduction

Acylation of alcohols, phenols and amines is a transformation of fundamental interest. Acetic anhydride and acyl halide in the presence of basic[1] (tertiary amines, pyridine, DMAP, PBu_3), acidic[2] (Lewis/protic) and other catalysts[3] are usually employed for this purpose. No doubt, most of these catalysts ensure good conversion however they still suffer from many disadvantages[3d] such as poor selectivity, cleavage of acid sensitive groups such as acetal, diene, epoxide (with strong acid catalyst), toxicity (Pyridine, DMAP), low air stability and flammability (PBu_3).

Transesterification (acylation by esters) is an important alternative way.[4] However, lower reactivity of ester carbonyl functionality and the reversible nature of the reaction equilibrium resulting in partial conversion, are two major limitations associate with this class of reactions. Here also, a wide range of acidic, basic and other catalysts (sulfuric acid,[5] *p*-toluenesulfonic acid,[6,7] DMAP,[8] ZnO,[9] sodium alkaoxide,[10] solid K_2CO_3,[11] KCN[12], Rasta Resin-TBD[13] etc) have been employed to enhance reactivity of ester carbonyl. These catalysts act by either coordinating acyl carbonyl or by enhancing the nucleophilicity of the attacking species. Meanwhile, reversibility issue is customarily overcome either by using excess starting alcohol or by continuously removing the product alcohol which is neither trivial nor economical.[14,15]

An effective replacement to the above is the use of enol esters such as vinyl acetate (**Caution! Carcinogenic A3 and 2B**) as acylating agent, since enol alcohols formed in the product side rapidly turn into corresponding aldehyde or ketone, enabling the system to escape from equilibrium (**Scheme 1**).[14,15] Moreover, the reactivity profile of enol esters is also better than ordinary esters.



Scheme 1 Vinyl acetate based transesterification reaction. Tautomerization of vinyl alcohol to acetaldehyde drive the equilibrium toward product side.

Several catalysts, promoters and additives have been put forth for enol ester based acylation such as Cp_2-Sm(thf)$_2$,[14] SmI_2,[14] distannoxane,[15] diethyl Zinc + N-substituted diethanolamine (as a ligands),[16] binuclear zinc,[17] iminophosphoranes,[18] $PdCl_2$,[19] Al(OTf)$_3$,[20] ytterbium complexes such as $Y_5(O^t\text{-pr})_{13}O$,[21] [$RuCl_2$(*p*-cymene)]$_2$,[22] molecular iodine,[23] N-heterocyclic carbenes,[24] nucleophilic Fe catalyst,[25] lipases[26] and antibody[27] etc. Despite several advantages, these methods also suffer from one or the

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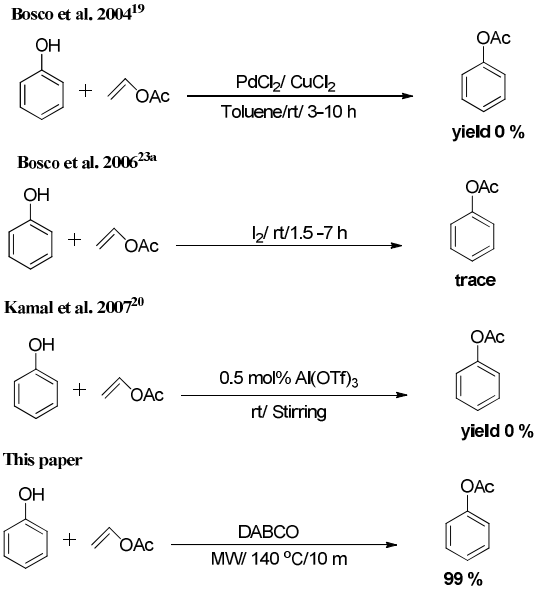
other drawback such as use of expensive catalyst,[14,21,22] requirement of delicate reaction condition,[14] use of obnoxious solvents[16,18,19] and long reaction time.[15,17,18]

It is strange that most of these methods have remained limited to non-aromatic primary and secondary alcohols.[14-25] To the best of our knowledge, there are only a few reports of vinyl acetate based acylation of phenol and in all the cases, it resulted in a failure (**Scheme 2**).[19,20,23a] It was assumed that deprived nucleophilic properties of the phenol could be a possible reason for these failures.[28] Secondly, the catalytic systems exploited so far comprised either enzymes[21] or metals/organometallic compounds.[14-17,19-22] Interestingly, we could not find any report of organocatalysts being ever used for entitled esterification. Organocatalysts, which in many occasions are viewed as filler between metal- and enzyme-catalysis[29a] and have shown general superiority for many similar transformations,[29b] seem to be a logical choice for such studies. Other inherent advantages associates with organocatalysts are their easy and cheaper commercial availability, easy procedure and separation and environment friendliness etc.[29,30]



Scheme 2 Comparison of various methods attempted for vinyl acetate based transesterification of phenols.

Considering all these fact, we were keen to device an effective yet practical protocol for vinyl ester based esterification particularly suited for phenols under organocatalytic conditions. After a careful survey of number of conditions and catalysts and assessment of results on the basis of yield, efficiency, time, cost and greenness; we report herein a DABCO catalyzed vinyl ester based esterification of phenols under microwave condition.

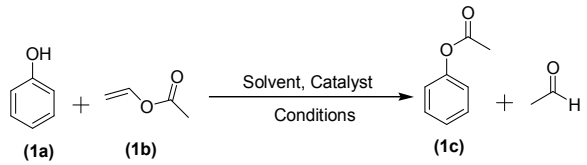
Results and discussion

In all the scouting experiments, 1 mmol of phenol (**1a**) and 1.2 mmols of vinyl acetate (**1b**) were taken as model substrates. Before all else, role of catalyst was determined by performing a reaction between **1a** and **1b** in acetonitrile at 60 °C without any catalyst. Even after 15 h of continuous heating, nothing new was spotted on TLC and the starting material remained intact, indicating that a suitable catalyst system was mandatory for the reaction to occur (**Table 1**, entry 1). Initially, pyridine was used as a catalyst in the above reaction which unfortunately resulted in a black unidentifiable viscous mixture and multiple spots on the TLC (**Table 1**, entry 2). By replacing pyridine with secondary amine catalysts such as morpholine and piperidine created a marked change in reaction profile with the formation of desired product. However, some of the catalyst itself got converted into the corresponding amine acetate (confirmed by Mass spectroscopy) and this might be a reason for unsatisfactory yield of **1c** (**Table 1**, entries 3, 4). This prompted us to use tertiary amines such as DIPEA, DMAP and DBU as catalysts which resulted in further improvements in the yield of **1c** (**Table 1**, entries 5-7). Gratifyingly, employment of DABCO in catalytic amount increased the yield up to 67% (**Table 1**, entry 8). Since DMAP, DBU and DABCO are quite hygroscopic compounds so traces of water or moisture in the reaction system could adversely affect the outcome, so these experiments were also duplicated under anhydrous conditions with special care. No significant changes were noticed in reaction outcomes. Since DABCO was found better than all other catalysts, probably because of its "higher nucleophilicity"[27] therefore, all further optimization reactions were carried out using DABCO as catalyst.

Because of the relatively low boiling point of vinyl acetate, next set of experiments were performed under closed microwave conditions in anticipation of better availability of the ester to the reacting atmosphere. Comparable results were obtained at relatively higher temperature (100°C) however, notable improvement in the yield occurred at 140 °C (**Table 1**, entries 11 and 12). Further optimization involving a temperature of 140 °C, holding time of 10 minutes and 30% catalytic loading increased the yield of **1b** up to

90% (**Table 1**, entries 12-18). The reaction yield was seemed to be independent of the solvent used (**Table 1**, entries 19-21) and this prompted us to perform a reaction under solvent-free conditions. Gratifyingly, the reaction under neat conditions resulted in 95% of **1b** (**Table 1**, entry 22) and hence this was selected as optimized protocol for the ensuing course. It becomes apparent that "solvent effects" reported in some previous cases for acylation of alcohols vanished under microwave condition in the present reaction.[16]

Table 1 Optimization of reaction conditions[a]



(1a) **(1b)** **(1c)**

Entry	Solvent	Catalyst (mol %)	Condition	Temp (°C)	Time	Yield[b] %
1	ACN		heating	60	15h	0
2	ACN	Pyridine (10)	heating	60	3h	nd
3	ACN	Morpholine	heating	60	3h	37[c]
4	ACN	Piperidine (10)	heating	60	3h	30[c]
5	ACN	DIPEA (10)	heating	60	3h	34
6	ACN	DMAP (10)	heating	60	3h	48
7	ACN	DBU (10)	heating	60	3h	55
8	ACN	DABCO (10)	heating	60	3h	67
9	ACN	DABCO (10)	heating	60	5h	68
10	ACN	DABCO (10)	heating	60	8h	68
11	ACN	DABCO (10)	MW	100	5m	68
12	ACN	DABCO (10)	MW	140	5m	75
13	ACN	DABCO (10)	MW	180	5m	75
14	ACN	DABCO (10)	MW	140	10m	79
15	ACN	DABCO (10)	MW	140	15m	80
16	ACN	DABCO (20)	MW	140	10m	87
17	ACN	DABCO (30)	MW	140	10m	95
18	ACN	DABCO (50)	MW	140	10m	90
19	Toluene	DABCO (30)	MW	140	10m	86
20	Hexane	DABCO (30)	MW	140	10m	85
21	THF	DABCO (30)	MW	140	10m	86
22		**DABCO (30)**	**MW**	**140**	**10m**	**95**

h = hours, m = minutes, MW = Anton Paar Monowave 300 Microwave reactor. Irradiation Power: 850 W;

Ramp time: 1 min. 60 °C, ACN = Acetonitrile, DIPEA = *N*,*N*-Diisopropylethylamine,

DMAP = 4-Dimethylaminopyridine**,** DBU **=**1,8-Diazabicyclo[5.4.0]undec-7-ene,

DABCO = 1,4-diazabicyclo[2.2.2]octane

[a]General condition: Phenol **1a** (1 mmol); vinyl acetate **1b** (1.2mmol).

[b]Isolated yield; nd = not determined.[c]Corresponding amine acetate is formed (confirmed by mass spectra of the reaction mixture)

We also examined the effectiveness of other enol esters such as isopropenyl acetate (**2b**), 1-acetoxy-1,3-butadiene (**3b**), 1-(trifluoromethyl)vinyl acetate (**4b**) on the above mentioned transesterification reaction. As expected other enol esters proved equally good acyl donors with nearly quantitative conversions illustrating the generality of the method. (**Table 2**, entries 1 to 4). However, we decided to continue with vinyl acetate in our work due to economical reasons.[31]

Table 2 Effect of nature of acylating agent on Tranesterification reaction[a]

Entry	Enol ester	Yield[b] %
1	Vinyl acetate (1b)	95
2	Isopropenyl acetate (2b)	93
3	1-Acetoxy-1,3-butadiene (3b)	96
4	1-(Trifluoromethyl)vinyl acetate (4b)	96

[a]General condition: phenol **1a** (1 mmol); Enol ester **1b-4b** (1.2 mmol); DABCO (30 mol %); Solvent-less, Anton Paar Monowave 300 microwave reactor. Irradiation Power: 850 W; Ramp time: 1 min. 60 °C, holding time: 10 min. 140 °C

[b]Isolated Yield.

With optimized condition in hand, the substrate scope and generality of the protocol was explored and results are summarized in **Table 3**. A wide variety of substituted phenols underwent facile and nearly quantitative conversions. Substrates bearing both electron-rich (such as 4-methoxy, 4-methyl and 4-*tert* butylphenol) and electron-deficient (4-chloro and 3-trifluoromethylphenols) groups smoothly got converted into corresponding acetates. Reaction worked well with *ortho-, meta-, para-* methoxyphenols (**Table 3**, entries 2-4) and hydroxyphenols such as catechol, resorcinol, hydroquinone, 2,3-dihydroxy naphthol and 1,6- and 1,5-dihydroxy naphthol (**Table 3**, entries 14-16, 19, 20, 22) and afforded the respective product in excellent yields under standard conditions. In our hands, 4-methoxyphenol resulted in better yield than the one reported previously.[20]Present methodology was further extended to O-benzoylation of phenols using vinyl benzoate as evident from **Table 4**.

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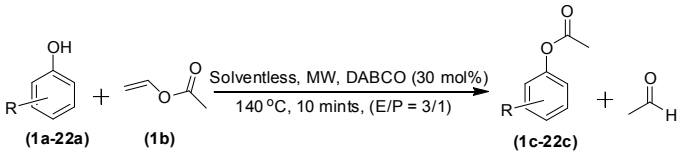
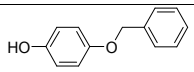
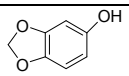
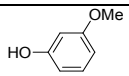
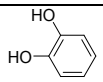
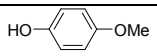
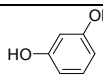
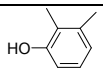
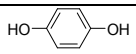
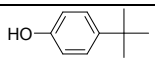
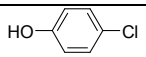
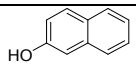
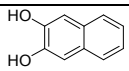
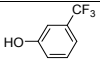
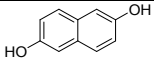
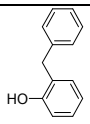
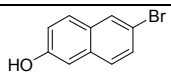
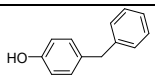
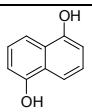
Table 3 Scope of the Transesterification reaction[a].



Entry	Substrate	Product	Yield[b] %	Entry	Substrate	Product	Yield[b] %
1		1c	99	12		12c	96
2		2c	98	13		13c	98
3		3c	97	14		14c	92[c]
4		4c	98	15		15c	94[c]
5		5c	98	16		16c	92[c]
6		6c	99	17		17c	90
7		7c	96	18		18c	99
8		8c	96	19		19c	98[c]
9		9c	97	20		20c	97[c]
10		10c	95	21		21c	96
11		11c	94	22		22c	99[c]

[a]General condition: Substrate **1a-22a** (1 mmol); Vinyl acetate **1b** (1.2 mmol); DABCO Catalyst loading (30 mol %), Anton Paar Monowave 300 reactor. Irradiation Power: 850 W; Ramp time: 1 min. 70 °C. Holding time: 10 min. 140 °C.[b]Isolated yield.[c]2.5 mmols of vinyl acetate was used

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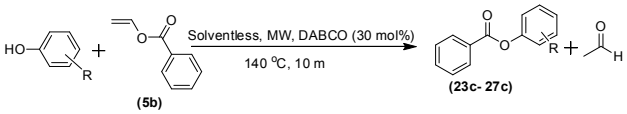
Table 4 Benzoylation of phenol using vinyl bezoate[a].



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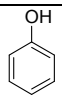
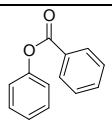
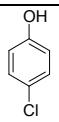
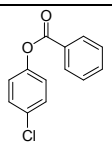
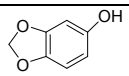
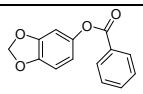
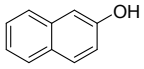
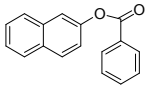
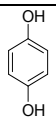
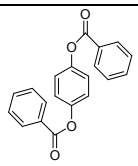
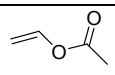
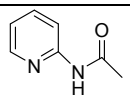
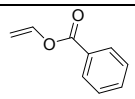
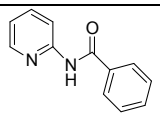
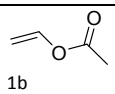
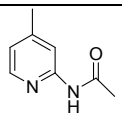
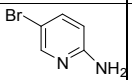
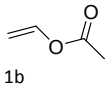
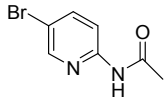
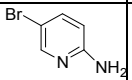
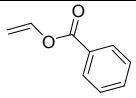
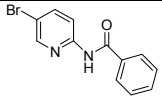
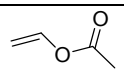
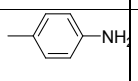
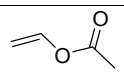
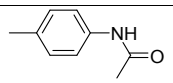
1	 1a	 23c	97
2	 7a	 24c	95
3	 13a	 25c	95
4	 18a	 26c	98
5	 16a	 27c	93[c]

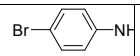
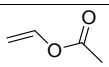
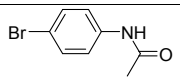
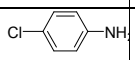
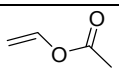
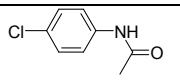
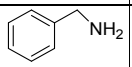
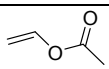
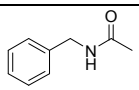
General condition: Substrate phenol (1 mmol); Vinyl benzoate **1b** (1.2 mmol); DABCO Catalyst loading (30 mol %), Anton Paar Monowave 300 reactor. Irradiation Power: 850 W; Ramp time: 1 min. 70 °C. Holding time: 10 min. 140 °C.

[b]Isolated yield.[c]2.5 mmols of vinyl benzoate were used.

Having achieved success with phenols, we next turned our attention toward acylation of anilines. As apparent from **Table 5,** presented method worked equally well with aminoazines such as 2-aminopyridine, 2-amino-4-methylpyridine and 2-amino-5-bromopyridine (**Table 5**, enteries 1-5). However crude and unidentifiable mixtures were obtained with unsubstituted aniline, *p*-toluidine and benzylamine. We reasoned that enolate half (and ensuing aldehyde) generated from the cleavage of vinyl ester might be interacting with unsubstituted aniline, *p*-toluidine and benzylamine. The reactive imines thus formed, had a chance to undergo a series of reactions. The presence of imine was also confirmed by GC-MS and by similar TLC profile of a standard reaction between acetaldehyde and aniline under similar set of conditions. It was however surprising that 4-bromo and 4-chloroanilinedid not react under the given conditions and only starting material was recovered (**Table 5**, entries 6-10).

Table 5 Transesterification of amines using vinyl esters[a].

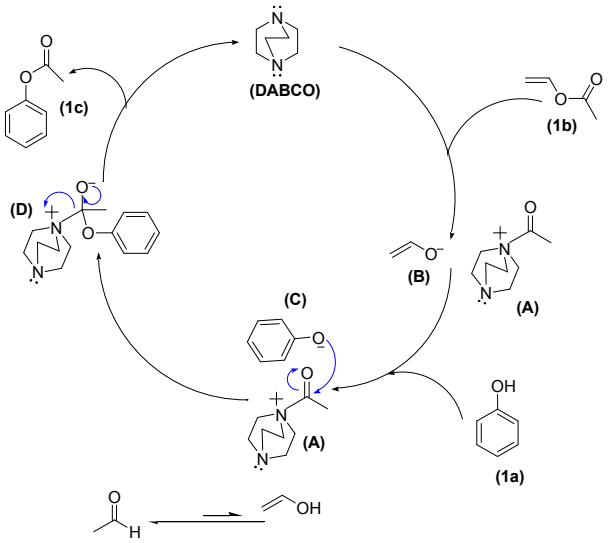
Entry	Substrate	Enol ester	Product	Yield[b]
1	 23a	 1b	 28c	97
2	 23a	 5b	 29c	96
3	 24a	 1b	 30c	98
4	 25a	 1b	 31c	92
5	 25a	 5b	 32c	90
6.	 26a	 1b	33c	nd
7.	 27a	 1b	 34c	nd

8.	 28a	 1b	 35c	0
9.	 29a	 1b	 36c	0
10..	 30a	 1b	 37c	nd

[a]General condition: Substrate amine **23a-30a** (1 mmol); Vinyl ester **1b** or **5b** (1.2 mmol); DABCO Catalyst loading (30 mol %), Anton Paar Monowave 300 reactor. Irradiation Power: 850 W; Ramp time: 1 min. 70 °C. Holding time: 10 min. 140 °C.

[b]Isolated yield; nd = not determined.

A plausible mechanism that is also in agreement with the previous reports of DABCO catalyzed transformations[30] is outlined in **Scheme 3**. Enolester is activated by an initial nucleophilic attack from DABCO and forms intermediate 'A' and enolate 'B'. This enolate abstracts a proton from phenol and subsequently tautomerises to corresponding aldehyde. The phenolate thus generated attacks the nucleophilic carbon of intermediate 'A' forming a tetrahedral complex 'C' , which eventually produces O-acylated product and regenerates DABCO for the next cycle.



Scheme 3 Proposed mechanism of the reaction.

In summary, this is the first successful report of organocatalytic transesterification of wide ranging phenols using vinyl acetate. In addition, solventless condition, inexpensive catalyst, operational simplicity, simple and column free workup, faster and quantitative conversions and exclusive formation of O-acylated product without excess reagent are some of the salient features of the presented protocol which renders significant greenness to the method. Considering the bulk scale applicability, further work is currently underway in our laboratory to extend the scope and scale of this reaction.

Experimental Section General Experimental Detail

All NMR spectra were recorded on a Jeol Resonance ECX-400II. Chemical shifts are reported in parts per million and are referenced to TMS. Spectra were processed using MestReNova[6] software. Mass spectrometry (HRMS) was performed using a Bruker daltronics microTOF-QII® spectrometer using ESI ionization, with less than 5 ppm error for all HRMS analyses. Analytical Thin layer chromatography (TLC) was performed on a silica gel plate (Merck® $60F_{254}$). All solvent were distilled prior to use and all chemicals were purchased from sigma-Aldrich® and used without further purification.

Microwave Irradiation Experiment

All microwave experiments were carried out in a dedicated Anton-Paar Monowave 300 reactor®, operating at a frequency of 2.455 GHz with continuous irradiation power of 0 to 300 W. The reactions were performed in a G-4 Borosilicate glass vial sealed with Teflon septum and placed in a microwave cavity. Initially, microwave of required power was used and temperature was being ramped from room temperature to a desired temperature. Once this temperature was attained, the process vial was held at this temperature for required time. The reactions were continuously stirred. Temperature was measured by an IR sensor. After the experiments a cooling jet cooled the reaction vessel to ambient temperature.

General procedure for the vinyl acetate based transesterification of phenols

In a solvent-free condition, phenol **1a** (1.0 mmol), vinyl acetate **1b** (1.2 mmols) and 1,4-diazabicyclo[2.2.2]octane (30 mol%) were mixed well in a G-4 process vial capped with Teflon septum. After a pre-stirring of 1 or 2 minutes, the vial was subjected to microwave

irradiation with the initial ramp time of 1 minute at 70 °C. The temperature was then raised to 140 °C with the holding time of 10 minutes. The reaction mixture was brought to room temperature by cooling jet and dissolved in 10 ml of ethyl acetate. This organic layer was washed with water, saturated brine solution, and dried over anhydrous $MgSO_4$ and finally evaporated under reduced pressure to give corresponding ester **1c.** The product **1c** was pure enough for spectral elucidation by ^{1}H NMR, ^{13}C NMR and HRMS.

Phenyl acetate (1c). Yield: 99%; whitish yellow solid; mp: 52 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.29 (s, 3H), 7.01 (dd, 2H, *J* = 6.0 & 1.0 Hz), 7.14 (tt, 1H, *J* = 6.0 & 1.1 Hz), 7.23 (t, 2H, *J* = 5.9 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.9, 121.0, 125.2, 129.9, 150.5, 169.7. HRMS (ESI) m/z calcd. for ($C_8H_8O_2$) [M+ Na]$^+$: 159.0422, found: 159.0419.

2-methoxyphenyl acetate (2c). Yield: 98%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.30 (s, 3H), 2.80 (s, 3H), 6.91-6.97 (m, 2H), 7.05 (dd, 1H, *J* = 7.8 & 1.8 Hz), 7.16-7.23 (m, 1H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.7, 55.9, 112.5, 120.8, 122.9, 127.0, 139.9, 151.3, 169.1. HRMS (ESI) m/z calcd. for ($C_9H_{10}O_3$) [M+ Na]$^+$: 189.0528, found: 189.0522.

3-methoxyphenyl acetate (3c). Yield: 97%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.22 (s, 3H), 2.31 (s, 3H), 6.81-6.92 (m, 2H), 7.0 (d, 1H, *J* = 7.6 Hz), 7.21 (t, 1H, *J* = 7.7 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.0, 60.4, 118.6, 122.2, 126.6, 129.2, 139.5, 150.7, 169.6. HRMS (ESI) m/z calcd. for ($C_9H_{10}O_3$) [M+ Na]$^+$: 189.0528, found: 189.0525.

4-methoxyphenyl acetate (4c). Yield: 98%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.24 (s, 3H), 3.75 (s, 3H), 6.86 (dt, 2H, *J* = 9.1 & 3.6 Hz), 6.98 (dt, 2H, *J* = 9.2 & 3.5 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.1, 55.6, 114.5, 122.4, 144.3, 157.3, 170.0. HRMS (ESI) m/z calcd. for ($C_9H_{10}O_3$) [M+ Na]$^+$: 189.0528, found: 189.0523.

2,3-dimethylphenyl acetate (5c). Yield: 98%; brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.26 (d, 6H, *J* = 6.0 Hz), 2.29 (s, 3H), 6.84 (dd, 1H, *J* = 8.0 & 2.4 Hz), 6.90 (br s, 1H), 7.14 (d, 2H, *J* = 8.1 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 19.3, 20.0, 21.2, 118.7, 122.6, 130.5, 134.3, 138.0, 148.7, 170.0. HRMS (ESI) m/z calcd. for ($C_{10}H_{12}O_2$) [M+ Na]$^+$: 187.0735, found: 187.0730.

4-tert-butylphenyl acetate (6c). Yield: 99%; brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.25 (s, 9H), 2.22 (s, 3H), 6.90-6.99 (m, 2H), 7.28-7.38 (m, 2H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 14.2, 31.4, 34.5, 120.9, 126.3, 148.4, 171.5. HRMS (ESI) m/z calcd. for ($C_{12}H_{16}O_2$) [M+ Na]$^+$: 215.1048, found: 215.1041.

4-chlorophenyl acetate (7c). Yield: 96%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.21 (s, 3H), 6.97 (dt, 2H, *J* = 8.7 & 3.2 Hz), 7.27 (dt, 2H, *J* = 8.8 & 3.2 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.1, 123.0, 129.5, 131.1, 149.2, 169.2. HRMS (ESI) m/z calcd. for ($C_8H_7ClO_2$) [M+ Na]$^+$: 193.0033, found: 193.0028.

2,6-dichlorophenyl acetate (8c). Yield: 96%; yellow solid; mp: 108-110 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)2.32 (s, 3H), 7.05 (d, 1H, *J* = 8.7 Hz), 7.23 (dd, 1H, *J* = 8.7 & 2.4 Hz), 7.43 (d, 2H, *J* = 2.4 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.6, 124.7, 128.0, 129.2, 130.2, 132.0, 135.8, 168.4. HRMS (ESI) m/z calcd. for ($C_8H_6Cl_2O_2$) [M+ Na]$^+$: 226.9643, found: 226.9638.

3-(trifluromethyl)phenyl acetate (9c). Yield: 97%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.30 (s, 3H), 7.24-7.30 (m, 1H), 7.37 (br s, 1H), 7.48 (d, 2H, *J* = 5.2 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.0, 119.0 (q, *J* = 3.8 Hz), 122.3, 122.7 (q, *J* = 3.8 Hz), 125.0, 125.3 (q, *J* = 1.0 Hz), 130.1, 150.8, 169.2. HRMS (ESI) m/z calcd. for ($C_9H_7F_3O_2$) [M+ Na]$^+$: 227.0296, found: 227.0290.

2-benzylphenyl acetate (10c). Yield: 95%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.25 (s, 3H), 3.99 (s, 2H), 7.14 (d, 1H, *J* = 8.2 Hz), 7.22-7.24 (m, 1H), 7.24-7.26 (m, 3H), 7.27-7.33 (m, 2H), 7.35 (dt, 2H, *J* = 7.6 & 0.6 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.0, 36.6, 115.6, 120.6, 122.7, 126.4, 126.5, 127.8, 128.7, 129.0, 131.2, 133.1, 139.8, 149.2, 169.7. HRMS (ESI) m/z calcd. for ($C_{15}H_{14}O_2$) [M+ Na]$^+$: 249.0892, found: 249.0882.

4-benzylphenyl acetate (11c). Yield: 94%; brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.35 (s, 3H), 4.08 (s, 2H), 7.15 (dt, 2H, *J* = 8.6 & 2.7 Hz), 7.29-7.36 (m, 5H), 7.39-7.45 (m, 2H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.3, 41.5, 115.6, 121.8, 126.5, 128.8, 129.2, 130.1, 139.0, 141.0, 149.2, 170.0. HRMS (ESI) m/z calcd. for ($C_{15}H_{14}O_2$) [M+ Na]$^+$: 249.0892, found: 249.0887.

4-(benzyloxy)phenyl acetate (12c). Yield: 96%; whitish solid; mp: 120 ^{o}C (decomp); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.29 (s, 3H), 5.05 (s, 2H), 7.0 (qt, 4H, *J* = 10.1 & 2.9 Hz), 7.34 (tt, 1H, *J* = 7.0 &

1.6 Hz), 7.37-7.47 (m, 4H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.2, 70.5, 115.5, 122.5, 127.6, 128.1, 128.7, 136.9, 144.5, 156.5, 170.0. HRMS (ESI) m/z calcd. for ($C_{15}H_{14}O_3$) [M+ Na]$^+$: 263.0841, found: 263.0836.

Benzo*[d][1,3]*dioxol-5-yl acetate (13c). Yield: 98%; brown solid; mp: 106-109 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.19 (s, 3H), 5.88 (s, 2H), 6.48 (dd, 1H, *J* = 8.4 & 2.4 Hz), 6.58 (d, 1H, *J* = 2.32 Hz), 6.72 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.0, 101.8, 103.8, 108.0, 114.0, 145.1, 145.4, 148.1, 169.8. HRMS (ESI) m/z calcd. for ($C_9H_8O_4$) [M+ Na]$^+$: 203.0321, found: 203.0318.

1,2-benzenediol 1,2-diacetate (14c). Yield: 92%; brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.25 (s, 6H), 7.13-7.19 (m, 2H), 7.19-7.25 (m, 2H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.7, 123.5, 126.5, 142.2, 168.4. HRMS (ESI) m/z calcd. for ($C_{10}H_{10}O_4$) [M+ Na]$^+$: 217.0477, found: 217.0470.

1,3-benzenediol 1,3-diacetate (15c). Yield: 94%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.27 (s, 6H), 6.86 (t, 1H, *J* = 1.1 Hz), 6.92 (dd, 2H, *J* = 6.0 & 1.2 Hz), 7.22 (t, 1H, *J* = 6.0 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.9, 115.4, 119.2, 131.2, 151.6, 169.7. HRMS (ESI) m/z calcd. for ($C_{10}H_{10}O_4$) [M+ Na]$^+$: 217.0477, found: 217.0471.

1,4-benzenediol 1,4-diacetate (16c). Yield: 92%; brown liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.26 (s, 6H), 7.07 (s, 4H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.1, 122.5, 148.1, 169.4. HRMS (ESI) m/z calcd. for ($C_{10}H_{10}O_4$) [M+ Na]$^+$: 217.0477, found: 217.0468.

Naphthalen-1-yl acetate (17c). Yield: 90%; brown solid; mp: 88 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.48 (s, 3H), 7.31 (d, 1H, *J* = 8.0 Hz), 7.50 (t, 1H, *J* = 8.0 Hz), 7.52-7.60 (m, 2H), 7.78 (d, 1H, *J* = 8.2 Hz), 7.92 (t, 2H, *J* = 7.3 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.2, 118.3, 121.3, 125.6, 126.2, 126.6, 126.9, 128.2, 134.7, 146.7, 169.7. HRMS (ESI) m/z calcd. for ($C_{12}H_{10}O_2$) [M+ Na]$^+$: 209.0579, found: 209.0573.

Naphthalen-2-yl acetate (18c). Yield: 99%; brown solid; mp: 96-98 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.37 (s, 3H), 7.26 (dd, 1H, *J* = 6.5 & 2.4 Hz), 7.45-7.54 (m, 2H), 7.59 (d, 1H, *J* = 2.2 Hz), 7.80-7.90 (m, 3H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.3, 118.7, 121.3, 125.9, 126.7, 127.8, 127.9, 129.6, 131.6, 133.9, 148.4, 169.9. HRMS (ESI) m/z calcd. for ($C_{12}H_{10}O_2$) [M+ Na]$^+$: 209.0579, found: 209.0574.

2,3-naphthalenediol-2,3-diacetate (19c). Yield: 98%; white solid; mp: 110-112 ^{o}C;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.34 (s, 6H), 7.45-7.50 (m, 2H), 7.68 (s, 2H), 7.76-7.82 (m, 2H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.9, 121.1, 126.6, 127.6, 131.7, 141.1, 168.8. HRMS (ESI) m/z calcd. for ($C_{14}H_{12}O_4$) [M+ Na]$^+$: 267.0634, found: 267.0621.

2,6-naphthalenediol-2,6-diacetate (20c). Yield: 97%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.34 (s, 6H), 7.24 (dd, 2H, *J* = 6.6 & 2.1 Hz), 7.56 (d, 2H, *J* = 2.3 Hz), 7.80 (d, 2H, *J* = 8.8 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.2, 118.6, 122.1, 129.2, 131.8, 148.4, 169.7. HRMS (ESI) m/z calcd. for ($C_{14}H_{12}O_4$) [M+ Na]$^+$: 267.0634, found: 267.0630.

6-bromonaphthalen-2-yl acetate (21c). Yield: 96%; white solid; mp: 112 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.35 (s, 3H), 7.22 (dd, 1H, *J* = 8.9 & 2.3 Hz), 7.49-7.54 (m, 2H), 7.62 (d, 1H, *J* = 8.9 Hz), 7.71 (d, 1H, *J* = 8.9 Hz), 7.96 (d, 1H, *J* = 1.8 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.3, 118.8, 119.7, 122.4, 128.6, 129.4, 129.9, 130.1, 132.2, 132.5, 148.6, 169.7. HRMS (ESI) m/z calcd. for ($C_{12}H_9BrO_2$) [M+ Na]$^+$: 286.9684, found: 286.9682.

1,5-naphthalenediol-1,5-diacetate (22c). Yield: 99%; white solid; mp: 128-130 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.27 (s, 6H), 6.82 (dd, 2H, *J* = 6.0 & 1.1 Hz), 7.25 (t, 2H, *J* = 6.0 Hz), 7.44 (dd, 2H, *J* = 5.9 & 1.1 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.9, 117.5, 121.2, 125.1, 125.6, 145.4, 170.2. HRMS (ESI) m/z calcd. for ($C_{14}H_{12}O_4$) [M+ Na]$^+$: 267.0634, found: 267.0630.

Phenyl benzoate (23c). Yield: 97%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.03 (tt, 1H, *J* = 5.9 & 1.3 Hz), 7.17 (dd, 2H, *J* = 6.1 & 1.2 Hz), 7.30 (t, 2H, *J* = 6.0 Hz), 7.42 (t, 2H, *J* = 6.1 Hz), 7.50 (tt, 1H, *J* = 5.9 & 1.2 Hz), 8.10 (dd, 2H, *J* = 6.0 & 1.0 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 123.7, 128.1, 132.0, 132.6, 132.7, 133.8, 136.5, 153.9, 170.0. HRMS (ESI) m/z calcd. for ($C_{13}H_{10}O_2$) [M+ Na]$^+$: 221.0579, found: 221.0575.

4-chlorophenyl benzoate (24c). Yield: 95%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.13 (d, 2H, *J* = 6.0 Hz), 7.39 (d, 2H, *J* = 6.0 Hz), 7.50 (t, 2H, *J* = 6.0 Hz), 7.57 (tt, 1H, *J* = 6.0 & 1.1 Hz), 8.17 (dd, 2H, *J* = 5.9 & 1.2 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm)

123.5, 131.0, 131.5, 131.7, 132.9, 133.3, 135.6, 152.1, 169.1. HRMS (ESI) m/z calcd. for ($C_{13}H_9ClO_2$) [M+ Na]$^+$: 255.0189, found: 255.0183.

Benzo[d][1,3]dioxol-5-yl benzoate (25c). Yield: 95%; brown solid; mp: 120-121 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 5.90 (s, 2H), 6.67 (dd, 1H, *J* = 6.0 & 1.1 Hz), 6.72 (d, 1H, *J* = 1.2 Hz), 6.76 (d, 1H, *J* = 6.0 Hz), 7.43 (t, 2H, *J* = 6.0 Hz), 7.50 (tt, 1H, *J* = 6.0 & 1.1 Hz), 8.11 (dd, 2H, *J* = 5.9 & 1.2 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 102.1, 102.6, 110.9, 115.3, 129.1, 129.7, 131.0, 133.6, 146.8, 147.8, 149.8, 167.2. HRMS (ESI) m/z calcd. for ($C_{14}H_{10}O_4$) [M+ Na]$^+$: 265.0477, found: 265.0472.

Naphthalen-2-yl benzoate (26c). Yield: 98%; brown solid; mp: 126-127 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.2 (t, 1H, *J* = 1.1 Hz), 7.36-7.48 (m, 5H), 7.53 (tt, 1H, *J* = 6.0 & 1.1 Hz), 7.58 (dd, 1H, *J* = 6.0 & 1.0 Hz), 7.78 (tt, 2H, *J* = 5.3 & 1.2 Hz), 8.14 (dd, 2H, *J* = 5.9 & 1.2 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 117.9, 122.7, 125.4, 128.6, 128.7, 130.1, 130.5, 130.6, 131.1, 132.3, 132.5, 133.0, 136.5, 151.7, 168.6. HRMS (ESI) m/z calcd. for ($C_{17}H_{12}O_2$) [M+ Na]$^+$: 271.0735, found: 271.0730.

1,4-benzenediol 1,4-dibenzoate (27c). Yield: 93%; yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.19 (s, 4H), 7.44 (t, 4H, *J* = 6.0 Hz), 7.52 (tt, 2H, *J* = 6.0 & 1.2 Hz), 8.03 (dd, 4H, *J* = 6.0 & 1.0 Hz). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 123.0, 129.8, 130.5, 131.7, 134.4, 149.9, 167.9. HRMS (ESI) m/z calcd. for ($C_{20}H_{14}O_4$) [M+ Na]$^+$: 341.0790, found: 341.0784.

N-(pyridine-2yl)acetamide (28c). Yield: 97%; brown solid; mp: 108-109 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.17 (s, 3H), 6.97-7.06 (m, 1H), 7.68 (td, 1H, *J* = 7.9 & 2.0 Hz), 8.15-8.32 (m, 2H), 9.38 (s, 1H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 24.7, 114.6, 119.8, 138.7, 147.5, 151.9. HRMS (ESI) m/z calcd. for ($C_7H_8N_2O$) [M+ Na]$^+$: 159.0535, found: 159.0529.

N-(pyridine-2yl)benzamide (29c). Yield: 96%; brown solid; mp: 118 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.55 (td, 1H, *J* = 6.0 & 1.1 Hz), 7.73 (t, 2H, *J* = 5.5 Hz), 7.78 (tt, 1H, *J* = 5.8 & 1.4 Hz), 7.99 (td, 1H, *J* = 6.0 & 1.1 Hz), 8.15 (dd, 2H, *J* = 5.9 & 1.2 Hz), 8.35 (dd, 1H, *J* = 6.0 & 1.1 Hz), 8.73 (dd, 1H, *J* = 6.0 & 1.3 Hz), 9.38 (s, 1H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 116.9, 120.0, 129.2, 129.6, 132.7, 136.0, 140.7, 148.9, 153.2, 168.5. HRMS (ESI) m/z calcd. for ($C_{12}H_{10}N_2O$) [M+ Na]$^+$: 221.0691, found: 221.0687.

N-(4-methylpyridine-2yl)actamide (30c). Yield: 98%; brown solid; mp: 122-124 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.63 (s, 3H), 2.85 (s, 3H), 7.47 (dd, 1H, *J* = 6.0 & 1.1 Hz), 8.65 (d, 1H, *J* = 1.1 Hz), 8.82 (d, 1H, *J* = 6.0 Hz), 9.38 (s, 1H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 21.2, 23.8, 114.8, 121.8, 149.4, 155.2, 170.5. HRMS (ESI) m/z calcd. for ($C_8H_{10}N_2O$) 173.0691 [M+ Na]$^+$, found: 173.0689.

N-(5-bromopyridine-2yl)actamide (31c). Yield: 92%; brown solid; mp: 126 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.21 (s, 3H), 8.25 (dd, 1H, *J* = 6.0 & 1.1 Hz), 8.54 (d, 1H, *J* = 6.0 Hz), 8.59 (d, 1H, *J* = 1.1 Hz), 9.38 (s, 1H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 20.2, 106.9, 115.3, 134.9, 147.3, 148.9, 166.8. HRMS (ESI) m/z calcd. for ($C_7H_7BrN_2O$) [M+ Na]$^+$: 236.9640, found: 236.9636.

N-(5-bromopyridine-2yl)benzamide (32c). Yield: 90%; brown solid; mp: 132-134 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.44 (t, 2H, *J* = 5.8 Hz), 7.49 (tt, 1H, *J* = 5.8 & 1.2 Hz), 7.86 (dd, 2H, *J* = 5.8 & 1.0 Hz), 8.09 (dd, 1H, *J* = 6.0 & 1.1 Hz), 8.32 (d, 1H, *J* = 6.0 Hz), 8.54 (d, 1H, *J* = 1.1 Hz), 9.44 (s, 1H). ^{13}C NMR: (100 MHz, DMSO-d_6): δ (ppm) 113.2, 121.8, 128.5, 128.8, 132.0, 135.2, 139.7, 150.4, 151.7, 167.7. HRMS (ESI) m/z calcd. for ($C_{12}H_9BrN_2O$) [M+ Na]$^+$: 298.9796, found: 298.9792.

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Table of content

First vinyl acetate mediated organocatalytic transesterification of Phenols: A step towards sustainability

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A practical and efficient method for vinyl ester based transesterification of phenols under organocatalytic conditions has been described.