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The 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 a wide variety of phenols. This highly enabling and solventless method relies on vinyl acetate as an innocuous acyl donor and DABCO as an organocatalyst. Operational simplicity, excellent yields, higher and faster conversion rates without excess reagents, a simple workup and essentially no need of columns are some of the salient features of the reported protocol.

Introduction

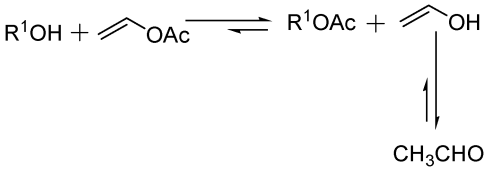
Acylation of alcohols, phenols and amines is a transformation of fundamental interest. Acetic anhydride and acyl halide in the presence of basic[1] (tertiary amines, pyridine, DMAP, PBu_3), acidic[2] (Lewis/protic) and other catalysts[3] are usually employed for this purpose. No doubt, most of these 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 catalysts), toxicity (pyridine, DMAP), low air stability and flammability (PBu_3).

Transesterification (acylation by esters) is an important alternative method.[4] However, lower reactivity of the ester carbonyl functionality and the reversible nature of the reaction equilibrium resulting in partial conversion are two major limitations associated 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 alkoxide,[10] solid K_2CO_3,[11] KCN,[12] Rasta resin-TBD,[13] *etc.*) have been employed to enhance the reactivity of ester carbonyl. These catalysts act either by coordinating acyl carbonyl or by enhancing the nucleophilicity of the attacking species. Meanwhile, the reversibility issue is customarily overcome either by using excess starting alcohols or by continuously removing the product alcohols which are neither trivial nor economical.[14,15]

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

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 catalysts,[25] lipases[26] and antibodies[27] *etc.* Despite several advantages, these methods also suffer from one or the other drawback such as the use of expensive catalysts,[14,21,22] requirement of delicate reaction conditions,[14] the use of obnoxious solvents[16,18,19] and long reaction times.[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 phenols and in all the cases, it resulted in failure (Scheme 2).[19,20,23a] It was assumed that deprived nucleophilic properties of the phenols could be a possible reason for the failure.[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



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

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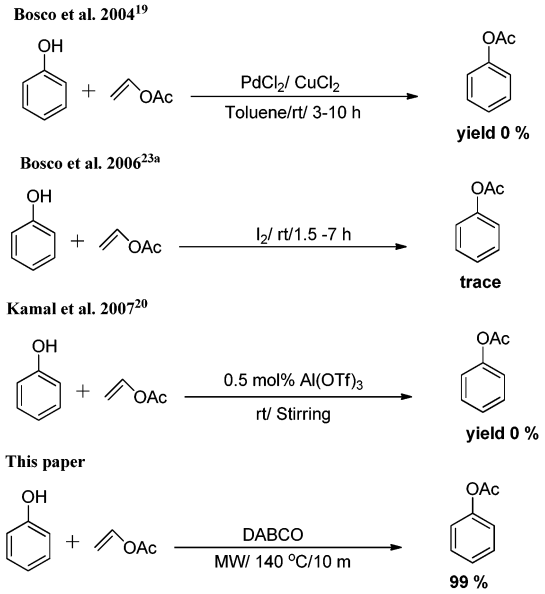
† Electronic supplementary information (ESI) available: General experimental details, the microwave irradiation experiment, the general procedure, ^{1}H, ^{13}C NMR and HRMS spectral data and the recorded spectra. See DOI: 10.1039/c5nj01436k



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

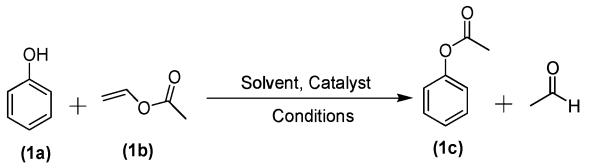
report of organocatalysts being ever used for entitled esterification. The use of organocatalysts, which in many occasions are viewed as fillers between metal- and enzyme-catalysis[29a] and have shown general superiority in many similar transformations,[29b] seem to be a logical choice for such studies. Other inherent advantages associated with organocatalysts are their easy and cheaper commercial availability, easy procedure and separation and environmental friendliness, *etc.*[29,30]

Considering all these facts, 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 a number of conditions and catalysts and assessment of the 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 conditions.

Results and discussion

In all the scouting experiments, 1 mmol of phenol (**1a**) and 1.2 mmol of vinyl acetate (**1b**) were taken as model substrates. Before anything else, the role of a 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 the 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). Replacing pyridine with secondary amine catalysts such as morpholine and piperidine created a marked change in the reaction profile with the formation of the desired product. However, some of the catalysts themselves got converted into the corresponding

Table 1 Optimization of reaction conditions[a]



Entry	Solvent	Catalyst (mol%)	Condition	Temp. (°C)	Time	Yield[b] (%)
1	ACN		Heating	60	15 h	0
2	ACN	Pyridine (10)	Heating	60	3 h	nd
3	ACN	Morpholine	Heating	60	3 h	37[c]
4	ACN	Piperidine (10)	Heating	60	3 h	30[c]
5	ACN	DIPEA (10)	Heating	60	3 h	34
6	ACN	DMAP (10)	Heating	60	3 h	48
7	ACN	DBU (10)	Heating	60	3 h	55
8	ACN	DABCO (10)	Heating	60	3 h	67
9	ACN	DABCO (10)	Heating	60	5 h	68
10	ACN	DABCO (10)	Heating	60	8 h	68
11	ACN	DABCO (10)	MW	100	5 m	68
12	ACN	DABCO (10)	MW	140	5 m	75
13	ACN	DABCO (10)	MW	180	5 m	75
14	ACN	DABCO (10)	MW	140	10 m	79
15	ACN	DABCO (10)	MW	140	15 m	80
16	ACN	DABCO (20)	MW	140	10 m	87
17	ACN	DABCO (30)	MW	140	10 m	95
18	ACN	DABCO (50)	MW	140	10 m	90
19	Toluene	DABCO (30)	MW	140	10 m	86
20	Hexane	DABCO (30)	MW	140	10 m	85
21	THF	DABCO (30)	MW	140	10 m	86
22		**DABCO (30)**	**MW**	**140**	**10 m**	**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 conditions: phenol **1a** (1 mmol); vinyl acetate **1b** (1.2 mmol). [b] Isolated yields; nd = not determined. [c] The corresponding amine acetate is formed (confirmed by mass spectroscopy of the reaction mixture).

amine acetates (confirmed by mass spectroscopy) and this might be a reason for an unsatisfactory yield of **1c** (Table 1, entries 3 and 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 a catalytic amount increased the yield up to 67% (Table 1, entry 8). Since DMAP, DBU and DABCO are quite hygroscopic, compounds traces of water or moisture in the reaction system could adversely affect the outcome, therefore, these experiments were also conducted in duplicates under anhydrous conditions with special care. No significant changes were noticed in reaction outcomes. Since DABCO was found to be better than all other catalysts probably because of its higher nucleophilicity,[27] therefore, all further optimization reactions were carried out using DABCO as the catalyst.

Because of the relatively low boiling point of vinyl acetate, the next set of experiments was 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, a 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 seemed to be independent of the solvent used (Table 1, entries 19–21) and this prompted us to perform the 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 the optimized protocol for the ensuing course. It becomes apparent that the solvent effects reported in some previous cases for acylation of alcohols vanished under microwave conditions in the present reaction.[16]

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 to be 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]

With optimized conditions in hand, the substrate scope and generality of the protocol were explored and the 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 the corresponding acetates. The 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 and 22) and afforded the respective products in excellent yields under standard conditions. In our hands, 4-methoxyphenol resulted in a better yield than the one reported previously.[20] The present methodology was further extended to *O*-benzoylation of phenols using vinyl benzoate as evident from Table 4.

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

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

In summary, this is the first successful report of organocatalytic transesterification of a wide range of phenols using vinyl acetate. In addition, solventless conditions, inexpensive catalysts, operational simplicity, a simple and column free workup, faster and quantitative conversions and the exclusive formation of *O*-acylated products without excess reagents 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.

Table 2 Effect of the nature of the acylating agent on the transesterification 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 conditions: 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 yields.

Experimental section

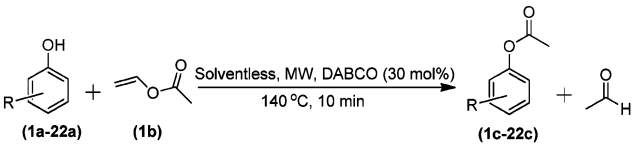
General experimental details

All NMR spectra were recorded on a Jeol Resonance ECX-400II. The chemical shifts are reported in parts per million and are referenced to TMS. The 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.

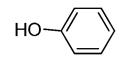
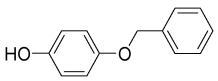
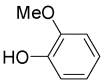
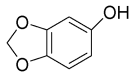
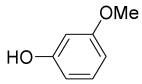
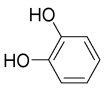
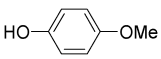
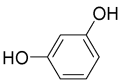
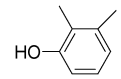
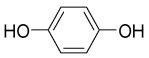
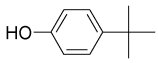
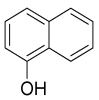
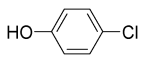
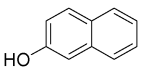
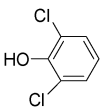
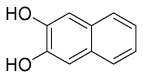
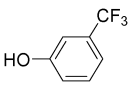
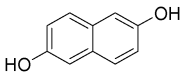
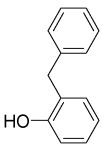
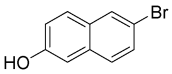
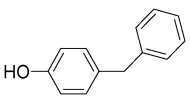
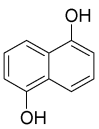
Microwave irradiation experiment

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

Table 3 Scope of the transesterification reaction[a]



(1a-22a) (1b) (1c-22c)

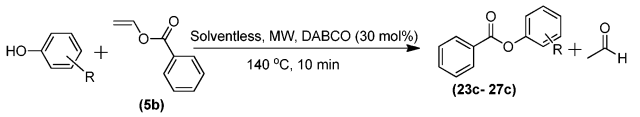
Entry	Substrate	Product	Yield[b] (%)	Entry	Substrate	Product	Yield[b] (%)
1		**1c**	99	12		**12c**	96
2		**2c**	98	13		**13c**	98
3		**3c**	97	14		**14c**	92[c]
4		**4c**	98	15		**15c**	94[c]
5		**5c**	98	16		**16c**	92[c]
6		**6c**	99	17		**17c**	90
7		**7c**	96	18		**18c**	99
8		**8c**	96	19		**19c**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

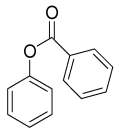
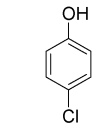
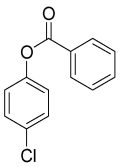
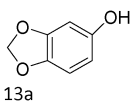
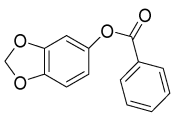
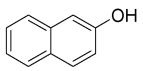
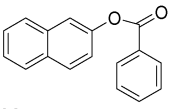
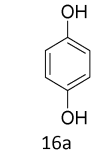
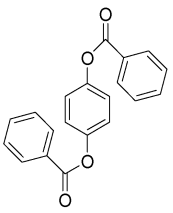
[a] General conditions: substrate **1a–22a** (1 mmol); vinyl acetate **1b** (1.2 mmol); DABCO catalyst loading (30 mol%), Anton Paar Monowave 300 reactor. Irradiation power: 850 W; ramp time: 1 min. 70 °C. Holding time: 10 min. 140 °C. [b] Isolated yield. [c] 2.5 mmols of vinyl acetate were used.

General procedure for the vinyl acetate based transesterification of phenols

Under solvent-free conditions, 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 a Teflon septum. After pre-stirring for 1 or 2 minutes, the vial was subjected to microwave irradiation with an initial ramp time of 1 minute at 70 °C. The temperature was then increased to 140 °C with a 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**. Product **1c** was pure enough for spectral elucidation by ^{1}H NMR, ^{13}C NMR and HRMS.

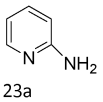
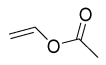
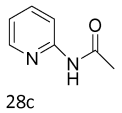
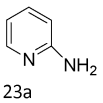
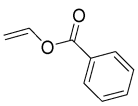
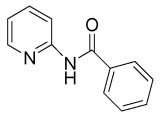
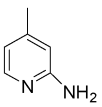
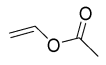
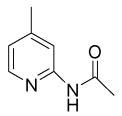
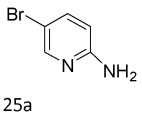
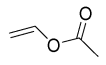
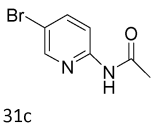
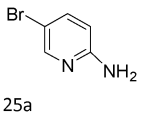
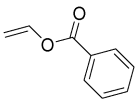
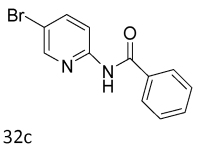
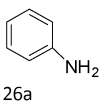
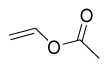
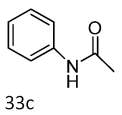
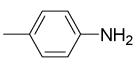
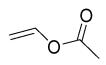
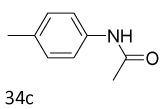
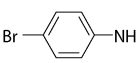
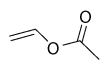
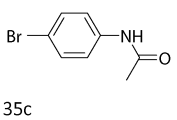
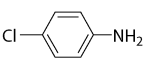
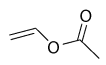
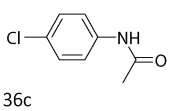
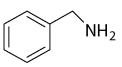
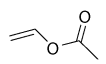
Table 4 Benzoylation of phenol using vinyl benzoate[a]



Entry	Substrate	Product	Yield[b] (%)
1	 1a	 23c	97
2	 7a	 24c	95
3	 13a	 25c	95
4	 18a	 26c	98
5	 16a	 27c	93[c]

[a] General conditions: 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.

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

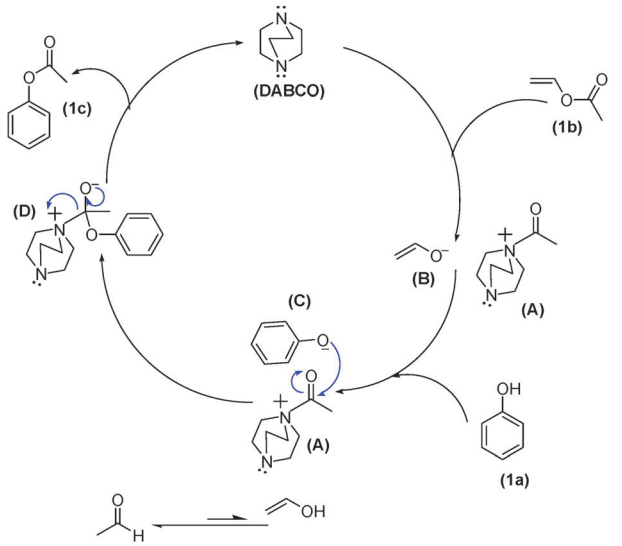
[a] General conditions: substrate amine **23a–30a** (1 mmol); vinyl ester **1b** or **5b** (1.2 mmol); DABCO catalyst loading (30 mol%), Anton Paar Monowave 300 reactor. Irradiation power: 850 W; ramp time: 1 min. 70 °C. Holding time: 10 min. 140 °C. [b] Isolated yields; nd = not determined.

Phenyl acetate (1c). Yield: 99%; whitish yellow solid; mp: 52 °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,



Scheme 3 Proposed mechanism of the reaction.

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 °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-(Trifluoromethyl)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 °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 °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 °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 °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 °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 °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 °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 °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 °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 °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 °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 °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 °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 °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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