



## Research Article

# Water hyacinth ash: an efficient green catalyst for the synthesis of $\beta$ -amino carbonyl/nitrile compounds by *aza*-Michael reaction at room temperature

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## Abstract

Water hyacinth ash is found to be an efficient and reusable catalyst for the synthesis of  $\beta$ -amino carbonyl/nitrile compounds by *aza*-Michael reaction of amines with  $\alpha,\beta$ -unsaturated compounds at room temperature under solvent free condition. Due to low cost of the catalyst, good activity, ease of handling and easy recovery with high yields of the products in short reaction time, easy workup procedure, mild reaction condition, the protocol is highly applicable in synthetic organic chemistry.

**Keywords** *Aza*-Michael · Water hyacinth ·  $\beta$ -amino carbonyl ·  $\beta$ -amino nitrile · Solvent free

## 1 Introduction

Development of simple, green and cost effective synthetic procedure is the main focus of the modern synthetic chemist. In this context, biomass-derived heterogeneous catalysts play a key role due to wide range of advantages such as low cost, high activity, easy recovery and reusability. Recently, the water extracts of various agro-waste ashes have been successfully employed as green and non-conventional solvent or as green catalysts in a number of organic reactions viz. Suzuki–Miyaura [1–7] and Sonogashira cross-coupling [8, 9], Dakin reaction [10], *ipso*-hydroxylation of arylboronic acid [11], Knoevenagel reaction [12], Henry reaction [13], 3-carboxycoumarins synthesis [14], peptide bond synthesis [15], etc. Additionally, many researchers have reported the ash based heterogeneous catalysts derived from different agricultural wastes as the promising green catalysts for biodiesel production. Some

of the reported heterogeneous catalysts from agro-wastes for biodiesel productions are *Musa balbisiana* [16–18], *Lemna perpusilla* [19], coconut husk [20], rice husk [21], cocoa pod husk [22], *Carica papaya* stem [23], *Tectona grandis* leaves [24], etc.

Water hyacinth is an aquatic weed which is naturally available across the globe in fresh water wet lands. Water hyacinth ash (WHA) has been found an efficient basic heterogeneous catalyst for organic transformations [25, 26]. Its high stability, ease of handling, reusability, non-toxicity and eco-friendliness make it a catalyst of choice.

The  $\beta$ -amino carbonyl/nitrile compounds have found a wide range of applications for the synthesis of a variety of bioactive natural products [27], antibiotics [28], heterocyclic compounds [29], chiral auxiliaries [30] etc. Further, its presence as structural constituents in biologically active natural products and use in the synthesis of chemicals [31] and pharmaceuticals [32] have elevated its

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synthetic importance. Among the various methods, the *aza*-Michael addition is a straightforward route for the generation of carbon–nitrogen bonds in the synthesis of  $\beta$ -amino carbonyl or nitrile compounds. *Aza*-Michael reaction is reportedly catalyzed by a couple of transition metal salts like  $\text{InCl}_3$  [33],  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  [34],  $\text{Yb}(\text{OTf})_3$  [35],  $\text{Bi}(\text{NO}_3)_3$  [36],  $\text{Cu}(\text{OTf})_2$  [37],  $\text{LiClO}_4$  [38],  $\text{SmI}_2$  [39],  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  [40], cerium(IV) ammonium nitrate [41]. Heterogeneous catalysts like  $\text{SiO}_2\text{-H}_2\text{SO}_4$  [42],  $\text{SiO}_2\text{-HClO}_4$  [43] have also been found to effectively catalyze the reaction. However, most of the protocols are associated with one or more limitations such as harsh reaction condition, high temperature, use of expensive catalyst, toxic organic solvent and tedious workup procedure. Therefore, the development of a simple, efficient and cost-effective methodology under mild reaction condition is highly desirable. In continuation of our research in the application of bio-mass derived heterogeneous catalysts in organic synthesis, herein we are reporting a simple and environmentally benign catalyst derived from the waste biomass of water hyacinth to catalyze *aza*-Michael addition of amines (**1**) to  $\alpha,\beta$ -unsaturated compounds (**2**) at room temperature under solvent free condition (Scheme 1).

## 2 Experimental

All commercially available chemicals and reagents were purchased from Aldrich and used without further purification. IR spectra were recorded on a SHIMADZU FT-IR instrument as KBr pellets and the adsorption expressed in  $\text{cm}^{-1}$ .  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$ -NMR (75 MHz) spectra were recorded on a Bruker NMR spectrometer at ambient temperature. Chemical shifts are given in  $\delta$  relative to tetramethylsilane (TMS), the coupling constants  $J$  are given in Hz. The spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  as solvent at ambient temperature, TMS served as internal standard ( $\delta = 0$  ppm) for  $^1\text{H}$  NMR. Mass spectra were recorded on Waters ZQ 4000 equipped with ESI source. Elemental analysis was done on Perkin Elmer Series II Analyser 2400. Column chromatography was performed on silica gel (60–120

mesh) using ethyl acetate:petroleum ether as the eluent. For TLC, precoated silica gel plates (Merck 60 F254) were used and compounds were visualized by irradiating with UV light or in an iodine chamber.

### 2.1 General procedure for the synthesis of $\beta$ -amino carbonyl compounds

A mixture of aliphatic amine (3 mmol),  $\alpha,\beta$ -unsaturated compound (3.3 mmol), and 10 mg of the WH ash was stirred at ambient temperature for a certain period of time. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and the mixture was extracted with ethyl acetate thrice (25 mL $\times$ 3). The combined extract was dried over anhydrous sodium sulfate and the solvent was removed in a rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica-gel with different ratios of petroleum ether/ethyl acetate as the eluent. The recovered catalyst was washed repeatedly with ethyl acetate and acetone, dried in hot air oven and reused for subsequent experiments.

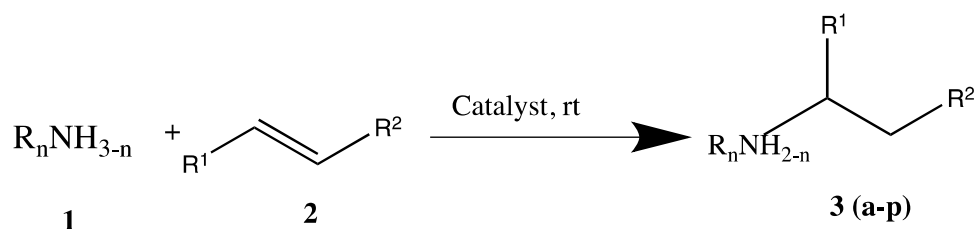
### 2.2 Preparation of the catalyst

Roots were separated from the plant stems and were cut into small pieces and dried under sun for about 15 days. The dry mass was burnt in an earthen pot in the presence of air. The ash was allowed to cool down to ambient temperature in its own and preserved in an air tight container. The water hyacinth ash (WHA) was further heated in a furnace at 500 °C for 3 h and kept in a desiccator before use. From proximate analyses it was found that the ash contains 48.87 wt% moisture at 110 °C and 7 wt% volatile matters at 350 °C [26].

#### 2.2.1 Catalyst composition

The chemical composition of the catalyst was examined by chemical analysis and different standard laboratory techniques such as SEM–EDX, XRF, TEM, atomic absorption spectroscopy and flame photometry. Potassium and

**Scheme 1** *Aza*-Michael addition of amines to  $\alpha,\beta$ -unsaturated carbonyl/nitrile compounds



$n = 1$ ,  $R = \text{akyl, heteroaryl}$

$R^1 = \text{H}$ ,  $R^2 = \text{COOMe, CN}$

calcium are present as the major components along with eleven other metals viz. Na, Fe, Mg Cr, Mn, Co, Ni, Cu, Zn, Pb and Ti which are present only in trace amounts (ppm level). Metals are present in the form of carbonates, chlorides, sulfates, phosphates and oxides [26, 44].

### 3 Results and discussion

In significance, this methodology proves to be operationally simple affording high yields in short reaction time. Further, achieving the synthesis under solvent free condition and at room temperature makes it cost and energy efficient. The application of water hyacinth ash (WHA) as a heterogeneous catalyst further expands wider scope of the less explored biomass derived natural catalysts in organic synthesis. Moreover, simple purification process along with reusability of the catalyst up to three times increases the applicability of the methodology.

Initially, methyl acrylate and benzylamine were chosen to optimize the catalyst loading at ambient temperature (Table 1) to generate the corresponding Michael adduct as shown in Scheme 1. The reaction was carried out in the presence of 0.01 g of ash in solvent free condition at ambient temperature. After 20 min complete disappearance of starting material was observed (monitored by TLC). On increasing the catalyst loading from 0.01 to 0.02 g, reaction time was decreased to 10 min with 95% yield. The reaction was attempted in different solvents such as dichloromethane, methanol and ethanol, but the yield was found to be better in absence of the solvents. Under the optimized conditions, we then explored the scope of the reaction. As shown in Table 3, a wide range of  $\beta$ -amino carbonyl and nitrile compounds were prepared from the reactions of different primary and secondary amines (both acyclic and cyclic), and various  $\alpha,\beta$ -unsaturated compounds and Baylis–Hillman adducts. When amine and alkene ratio was 1:2, doubly substituted products were isolated (Table 3, entry 10).

Having optimized the reaction condition we then proceeded to examine the efficiency of the catalyst. The efficiency of WHA as a catalyst was compared to common bases like  $K_2CO_3$ ,  $Na_2CO_3$  and Lewis acids such as  $FeCl_3 \cdot 6H_2O$  and  $SnCl_4$  with results as shown in Table 2. WHA shows better catalytic activity as compared to  $K_2CO_3$ ,  $Na_2CO_3$ ,  $FeCl_3$  and  $SnCl_4$ .

Under optimized reaction conditions, all the amines afforded the desired product in good yield (Table 3). After completion of the reaction, the catalyst could be easily recovered from the reaction mixture and reused in several runs.

The reusability of the catalyst was studied through a model reaction of 2-aminoethanol and methyl acrylate under the optimized conditions, where the catalyst was

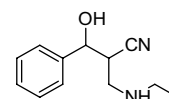
separated by simple filtration, washed with ethyl acetate and acetone for several times and dried in a hot air oven and reused. It was observed that WHA was reusable but with a bit of sacrifice in yield in every subsequent run (Fig. 1).

### 4 Conclusion

In conclusion, water hyacinth ash is an efficient catalyst for Michael addition of amines with different Michael acceptors including Baylis–Hillman products under solvent-free condition. The procedure avoids the use of organic solvent to carry out the reaction, and the catalyst can be separated from the product quite easily and reused. The catalyst is inexpensive, environment-friendly and can be disposed off without affecting the environment.

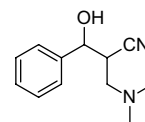
### 5 Spectral data

**Compound 3a (Entry 1, Table 3): 2-[(Ethylamino)methyl]-3-hydroxy-3-phenylpropanenitrile,**



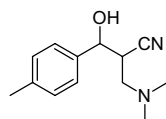
**droxy-3-phenylpropanenitrile,  $C_{12}H_{16}N_2O$**  0.188 g; yield 92%; colourless solid; m.p. 68 °C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 1.12 (t, 3H), 2.68 (q, 2H), 2.74 (m, 2H), 3.77 (m, 2H), 5.02(1H), 7.38 (m, 5H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 140.64, 128.45, 125.73, 118.41, 75.13, 39.98, 38.36, 14.77; MS (ESI)  $m/z$  204.27( $M^+$ ); Elemental analysis: calculated: C, 70.56, H 7.90, N, 13.71; found: C, 70.63, H 7.82, N, 13.61.

**Compound 3b (Entry 2, Table 3): 2-[(Dimethylamino)methyl]-3-hydroxy-3-phenylpropanenitrile,**

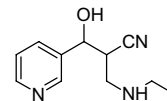


**$C_{12}H_{16}N_2O$**  0.192 g; yield 94%; colourless solid; 46 °C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 2.37, 2.72 (d, 1H), 2.79 (d, 1H), 3.08 (broad peak, 1H -OH), 5.08 (s, 1H), 7.33–7.46 (m, 5H, Ar H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 139.95, 128.44, 128.39, 128.15, 128.36, 125.94, 118.59, 73.72, 58.69, 45.83, 37.08MS (ESI)  $m/z$  204.27( $M^+$ ); Elemental analysis: calculated: C, 70.56, H, 7.90, N, 13.71; found: C, 70.46, H, 7.80, N, 13.66.

**Compound 3c (Entry 3, Table 3): 2-[(Dimethylamino)methyl]-3-hydroxy-3-(*p*-tolyl)propanenitrile,**

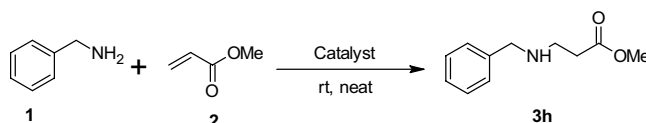


**C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O** 0.198 g; yield 91%; Colourless solid; 38 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 2.36(s, 9H), 2.68(d, 1H), 2.74 (d, 1H), 3.06 (broad peak, –OH), 5.03 (s, 1H), 7.18(d, 2H Ar), 7.31(s, 2H Ar); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 137.89, 137.02, 129.14, 129.09, 126.28, 125.87, 118.78, 73.54, 58.64, 45.82, 45.33, 37.23, 36.70, 21.08; MS (ESI) m/z 218.14(M<sup>+</sup>); Elemental analysis: calculated: C, 71.53, H, 8.31, N, 12.83; found: C, 71.41, H, 8.20, N, 12.71.



**C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O** 0.168 g; yield 82%; dark brown oily compound; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 1.06 (q, 3H), 1.87 (s, 1H), 2.65 (m, 3H), 3.05 (m, 1H), 3.36 (m, 2H), 5.04 (s, 1H), 7.19 (d, 1H), 7.54 (d, 1H), 7.72 (d, 1H), 8.48 (dd, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 159.38, 148.69, 137.40, 121.82, 74.21, 44.17, 39.06, 15.12;

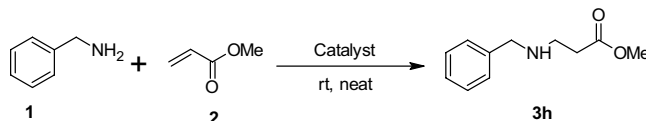
**Table 1** Optimization of reaction conditions<sup>a</sup>



Entry	Catalyst (g)	Solvent	Time (min)	Yield (%) <sup>b</sup>
1	–	–	180	Trace
2	0.002	Ethanol	180	30
3	0.004	Ethanol	180	50
4	0.006	Ethanol	120	65
5	0.008	Ethanol	90	80
6	0.01	Ethanol	20	91
7	0.01	Methanol	30	94
8	0.01	Dichloromethane	60	45
9	0.01	No solvent	20	95
10	0.02	No solvent	10	95

<sup>a</sup>Reaction conditions: benzylamine (1 mmol), methyl acrylate (1 mmol), <sup>b</sup>Isolated yields

**Table 2** Effect of various catalysts on the model reaction of benzylamine and methyl acrylate<sup>a</sup>



Entry	Catalyst	Yield <sup>b</sup> (%)
1	K <sub>2</sub> CO <sub>3</sub>	60
2	Na <sub>2</sub> CO <sub>3</sub>	50
3	FeCl <sub>3</sub>	58
4	SnCl <sub>4</sub>	87
5	WHA	96

<sup>a</sup>Reaction conditions: benzyl amine (1 mmol), methyl acrylate (1 mmol), WHA (10 mg), <sup>b</sup>Isolated yields

**Table 3** Aza-Michael addition of amines to  $\alpha,\beta$ -unsaturated compounds (Scheme 1)<sup>a</sup>


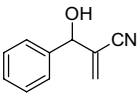
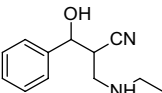

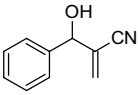
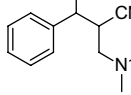

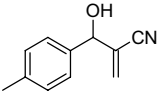
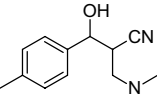

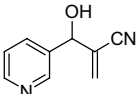
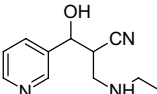

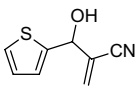
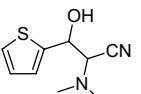
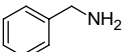

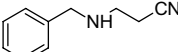


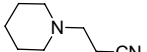
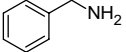
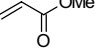
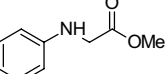

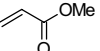
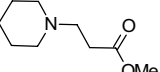
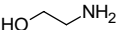

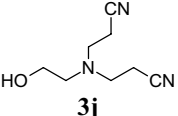
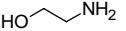

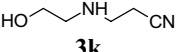
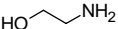
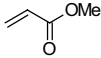
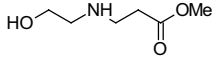
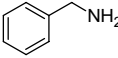
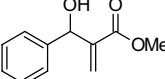
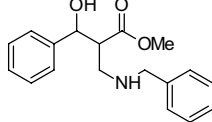
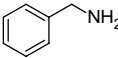
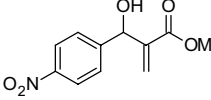
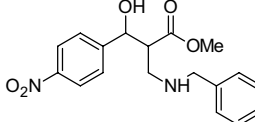
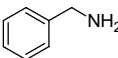
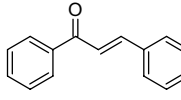
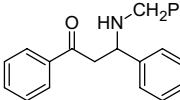

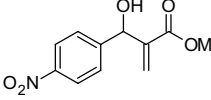
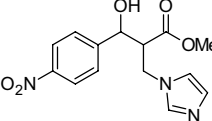
Entry	1	2	Product	Time (min)	Yield <sup>b</sup> (%)
1			 <b>3a</b>	120	96
2			 <b>3b</b>	150	95
3			 <b>3c</b>	150	94
4			 <b>3d</b>	180	82
5			 <b>3e</b>	30	85
6			 <b>3f</b>	15	94
7			 <b>3g</b>	15	96
8			 <b>3h</b>	15	97
9			 <b>3i</b>	15	96
10			 <b>3j</b>	15	96
11			 <b>3k</b>	20	96

Table 3 (continued)

12				24	95
13				120	91
14				180	90
15				300	85
16				420	87

<sup>a</sup>The products are characterized by their spectral data (IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, Mass spectra); <sup>b</sup>Isolated yield.

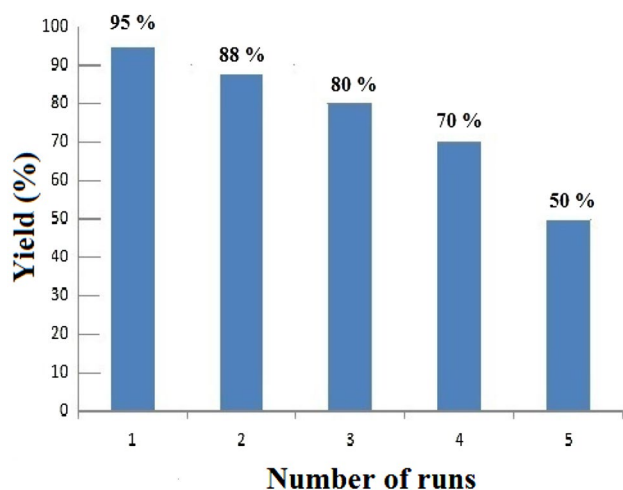
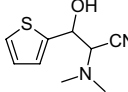


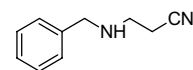
Fig. 1 Recyclability of WHA

MS (ESI)  $m/z$  205.26( $M^+$ ); Elemental analysis: calculated: C, 64.37, H 7.37, N, 20.47; found: C, 64.26, H 7.24, N, 20.40.

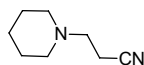
**Compound 3e (Entry 5, Table 3):** 2-[(Ethylamino)methyl]-3-hydroxy-3-(thiophen-2-yl)propanenitrile,

  
 $C_{10}H_{14}N_2OS$  0.179 g; yield 85%; black oily compound; <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 2.26 (m, 6H), 2.45 (m, 2H), 4.28 (m, 2H), 6.94–7.46 (m, 4H); <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 138.16, 127.36, 125.15, 124.08, 62.55, 45.05, 37.37; MS (ESI)  $m/z$  210.30( $M^+$ ); Elemental analysis: calculated: C, 57.11, H, 6.71, N13.32; found: C, 57.08, H, 6.66, N, 13.21.

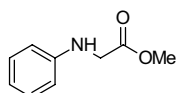
**Compound 3f (Entry 6, Table 3):** 3-(Benzylamino)propaneni-



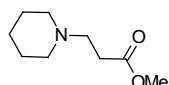
**trile,  $C_{10}H_{12}N_2$**  Yield 95%; white solid; mp 46 °C; <sup>1</sup>H NMR ( $CDCl_3$ , 300 MHz)  $\delta_H$ : 7.34 (m, 5H), 3.85 (s, 2H), 2.97 (t,  $J=6.3$  Hz, 2H), 2.58 (t,  $J=6.27$  Hz, 2H), 1.69 (br s, 1H); <sup>13</sup>C NMR ( $CDCl_3$ , 75 MHz)  $\delta_C$ : 139.35, 128.59, 128.09, 127.33, 118.74, 53.18, 44.30, 18.78; MS (ESI,  $m/z$ ) 161.8 ( $M^++1$ ). Elemental analysis: calculated: C, 74.97, H, 7.55, N, 17.48; found: C, 75.23, H, 7.84, N, 16.10.

**Compound 3 g (Entry 7, Table 3): 3-(Piperidin-1-yl)propanenitrile**

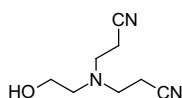
**nitrile**,  $C_8H_{14}N_2$  0.133 g; yield 96%; yellow oily compound;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 1.43 (m, 2H), 1.55 (m, 4H), 2.39 (m, 4H), 2.45 (m, 2H), 2.64 (m, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 118.96, 53.96, 53.81, 25.61, 23.89, 15.43. MS (ESI)  $m/z$  139.1 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 69.52, H, 10.21, N, 20.27; found: C, 57.46, H, 7.84, N, 25.13.

**Compound 3 h (Entry 8, Table 3): Methyl 3-(benzylamino)propanoate**

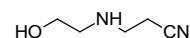
**propanoate**,  $C_{11}H_{15}NO_2$  0.175 g (90%); colourless oily liquid;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 2.45(t, 2H), 2.47(s, -NH), 2.80(q, 2H), 3.58(s, 3H), 3.71(s, 2H), 7.21(m, Ar H);  $^{13}C$  NMR (75 MHz, DMSO)  $\delta_C$ : 172.65, 139.33, 127.96, 127.70, 126.57, 53.11, 51.10, 43.83, 33.83, 33.83; MS(ESI)  $m/z$ : 194.3 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 68.37, H, 7.82, N, 7.25; found: C, 68.32, H, 7.69, N, 7.20.

**Compound 3i (Entry 9, Table 3): Methyl 3-(piperidin-1-yl)propanoate**

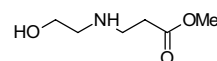
**propanoate**,  $C_9H_{17}NO_2$  0.159 g (90%), yellow liquid;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 1.06 (s, 1H), 1.32 (d, 2H), 1.43 (d, 4H), 2.28 (s, 3H), 2.39 (m, 2H), 2.49(m, 2H), 3.55(s, 3H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 172.18, 54.03, 40.06, 31.74, 25.71, 24.36; MS (ESI)  $m/z$  172.3 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 63.13, H, 10.01, N, 8.18; found: C, 63.08, H, 10.00, N, 8.10.

**Compound 3j (Entry 10, Table 3): 3,3-[(2-Hydroxyethyl)azanediyl]dipropanenitrile**

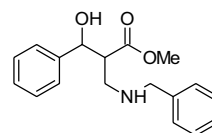
**azanediyl]dipropanenitrile**,  $C_8H_{13}N_3O$  0.151 g (90%), yellow oily compound;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 2.45 (t, 2H), 2.59 (t, 2H), 2.75 (t, 2H), 3.46 (q, 2H), 3.67 (m, 5H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 120.91, 76.81, 58.82, 49.28, 42.47, 16.61. MS (ESI)  $m/z$  168.2 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 57.46, H, 7.84, N, 25.13; found: C, 57.32, H, 7.70, N, 25.09.

**Compound 3 k (Entry 11, Table 3): 3-(2-hydroxyethylamino)propanenitrile**

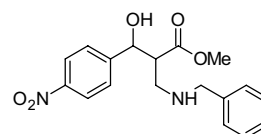
**propanenitrile** 0.151 g (90%), brown oily compound;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 2.13 (s, 2H), 2.48 (t, 2H), 2.74 (t, 2H), 2.87(t, 2H), 3.6 (t, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta_C$ : 118.74, 60.41, 52.03, 44.28, 23.29. MS (ESI)  $m/z$  168.2 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 57.46, H, 7.84, N, 25.13; found: C, 57.32, H, 7.70, N, 25.09.

**Compound 3 l (Entry 12, Table 3): Methyl 4-((2-hydroxyethylamino)butanoate**

**ethylamino)butanoate**,  $C_7H_{15}NO_3$  0.146 g (90%); brown oily compound;  $^1H$  NMR (300 MHz, DMSO)  $\delta_H$ : 2.54(m, 7H), 2.71(m, 2H), 3.42(t, 1H), 3.57(m, 3H);  $^{13}C$  NMR (75 MHz, DMSO)  $\delta_C$ : 173.74, 58.24, 54.19, 49.18, 31.45. MS (ESI)  $m/z$  162.1 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 52.16, H, 9.38, N, 8.69; found: C, 52.10, H, 9.26, N, 8.46.

**Compound 3 m (Entry 13, Table 3): Methyl 2-[(benzylamino)ethyl]-3-hydroxy-3-phenylpropanoate**

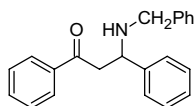
**methyl]-3-hydroxy-3-phenylpropanoate**,  $C_{18}H_{21}NO_3$  0.270 g (90%); white solid; melting point 45 °C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 2.91(s, 2H), 3.01(m, 2H), 3.62(s, 3H), 3.74(d, 2H), 5.12(d, 1H), 7.30(m, Ar H);  $^{13}C$  NMR (75 MHz, DMSO)  $\delta_C$ : 173.61, 141.75, 139.39, 128.54, 128.24, 128.03, 127.68, 127.25, 126.03, 125.73, 74.98, 53.82, 51.76, 48.34; MS(ESI)  $m/z$ : 300.01 ( $M^+ + 1$ ); Elemental analysis: calculated: C, 72.22, H, 7.07, N, 4.68; found: C, 72.16, H 7.01, N, 4.62.

**Compound 3n (Entry 14, Table 3): Methyl 2-[(benzylamino)ethyl]-3-hydroxy-3-(4-nitrophenyl)propanoate**

**$C_{18}H_{22}N_2O_5$**  0.345 g (90%), sticky compound;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta_H$ : 3.5(m, 3H), 3.46(m, 5H), 5.30(d, 1H), 5.68(s, 2H), 7.25–8.19(m, ArH).  $^{13}C$  NMR (75 MHz, DMSO)  $\delta_C$ : 171.97, 148.99, 128.79, 73.05, 53.02; (ESI)  $m/z$ : 345.14

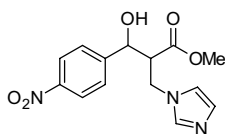
(M<sup>+</sup>+1); Elemental analysis: calculated C, 62.78, H, 5.85, N, 8.13; found C, 62.48, H, 5.76, N, 8.10.

**Compound 3o (Entry 15, Table 3): 3-(Benzylamino)-1,3-di-**



**phenylpropan-1-one, C<sub>22</sub>H<sub>21</sub>NO** 0.265 g; yield 84% white solid; mp 47 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub>: 8.41 (s, 1H), 7.80 (m, 15 H), 4.8 (s, 2H), 4.45 (t, *J* = 6.27 Hz, 1H), 3.9 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub>: 195.53, 136.62, 136.09, 134.83, 133.90, 132.88, 130.63, 129.00, 128.88, 128.53, 128.50, 126.65, 56.51, 55.76, 44.24, 77.2, 117.3, 119.7, 145.4, 242.0, 295.2, 302.7, 341.8; MS (ESI), *m/z*: 316.13 (M<sup>+</sup>+1); Elemental analysis: calculated C, 83.78, H, 6.71, N, 4.44; found C, 83.84, H, 6.16, N, 4.78.

**Compound 3p (Entry 16, Table 3): 3-Hydroxy-2-(imidazol-1-ylmethyl)-3-(4-nitrophenyl)propanoic acid methyl ester,**



**C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>** 0.273 g; yield 89%; white solid; mp 168 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub>: 8.12 (d, *J* = 3.6 Hz, 2H), 8.09 (m, 3H), 6.87 (m, 2H), 6.75 (s, 1H), 4.89 (d, *J* = 7.2 Hz, 1H), 4.44–4.12 (m, 3H), 4.20 (d, *J* = 3.3 Hz, 2H), 3.11 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub>: 175.76, 152.79, 132.04, 131.77, 128.24, 123.96, 59.54, 56.70, 44.99, 44.16, 75.7, 85.6, 108.0, 122.3, 124.4, 135.3, 144.6, 151.4, 151.4, 163.4, 173.7, 285.1, 295.9, 311.2, 342.6; MS (ESI), *m/z*: 305.99 (M<sup>+</sup>+1); Elemental analysis: calculated C, 55.08, H, 4.95, N, 13.76; found C, 55.10, H, 4.92, N, 13.78.

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### Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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