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Microwave-assisted one-pot synthesis of tetrahydrobenzo[*b*]pyrans in the presence of WEWFPA and their electrochemical studies

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Abstract: The present work described one-pot three-component synthesis of tetrahydro benzo[b]pyran derivatives using Water Extract of Watermelon Fruit Peel Ash (WEWFPA) as a inexpensive grener catalyst. The title compounds were synthesized *via* the condensation reaction of aromatic aldehyde, dimedone, and ethyl cyanoacetate under microwave irradiation in agro-waste solvent medium and ethanol as a co-solvent. The developed method is simple, rapidity, high yields, pure, low cost, mild reaction condition, evading use of toxic metals and solvent, and the catalyst reusability are the main advantages. The resulting products were isolated by simple workup and recrystallization gave pure compounds. Further, the oxidation and reduction potential of the selected tetrahydrobenzo[b]pyran derivatives were studied using cyclic voltammetry.

Keywords: Tetrahydrobenzo[*b*]pyrans; ethyl cyanoacetate; microwave irradiation; agro-waste; cyclic voltametry. © 2022 ACG Publications. All rights reserved.

1. Introduction

Heterocyclic compounds play a pivotal role in the biological systems for a wide range of pharmacological applications.[1] Most of the presently available drug molecules and potent agrochemicals possess at least one or more heterocyclic skeletons. The heterocycles are also found in other applications in reprography, information storage devices, cosmetics, switching devices, photocatalysts, and plastics are main dependent on the heterocyclic core structure.[2] The organic compound possessing heteroatoms in the benzene ring are emerged important field in chemistry, due to their vast applications, heteroatom presence, and acting as a nucleus to the various bio-active scaffolds. Thus, in this regard, the oxygen-containing heterocyclic core structure has attracted the attention of the organic chemists, due to its wide range of pharmacological applications (Figure S1). Among them, 2-amino-4*H*-pyrans has been recognized as a highly potent bioactive compound in cosmetics, dyes, and pigments, and utilized in agrochemicals, because of their biodegradable

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properties.[3-5] Natural products structurally similar to the polyfunctionalized 4*H*-pyrans[6,7] have reported several pharmacological activities[8] such as antibacterial,[9-13] antitumor,[14] and calcium channel antagonists[15] (Figure 1). Also, numerous organic reactions have been done in the water as a green solvent reaction medium. Water has several advantages such as abundance, non-polluting, inexpensive, safety and green chemistry protocol, but have a limitation of solubility.[16]

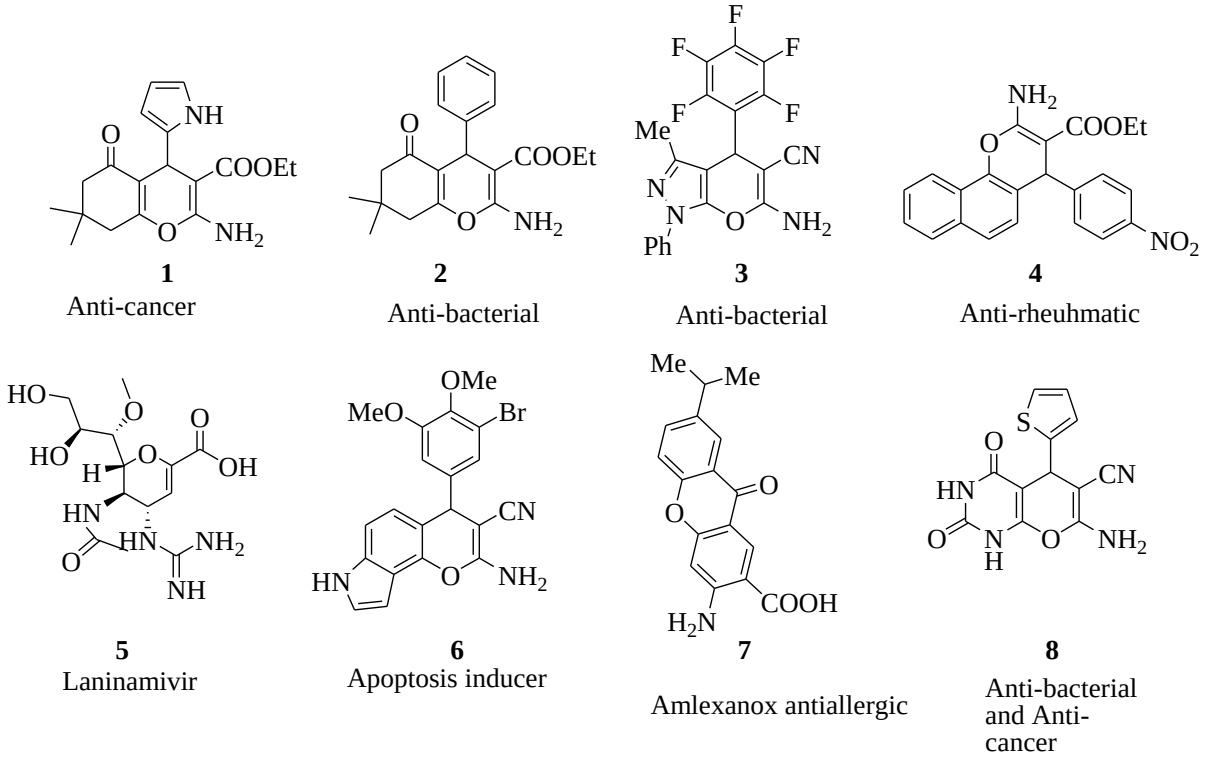


Figure 1. Selected pharmacologically prominent 4*H*-pyran scaffolds

Due to the distinct aforementioned good properties of the 4H-pyrans, different synthetic protocol have been reported for the synthesis of 4H-pyrans in the presence of several catalysts reported such as TiO_2-CNTs nanocomposite,[17] Graphene oxide,[18] Magnetic Fe_3O_4@MCM-41 core-shell nanoparticles,[19] Ammonium chloride,[20] [Bmim]PF_6,[21] Quaternary ammonium-functionalized MCM-48 mesoporous silica,[22] MCM-41/Poly(Ionic Liquids),[23-24] [BMIm]BF_4,[25] Na_2CO_3,[26] SBPPSP,[27] $SnCl_2$/Nano SiO_2,[28] Nano-TiO_2/$H_{14}[NaP_5W_{30}O_{110}]$,[29] Nano-ZnO,[31] [HMIM]$C(CN)_3$,[32] TFE,[33] Supported-KF,[34] Urea,[35] Nanozeolit,[36] Fe_3O_4@SiO_2-imid–PMA,[37] Aminopropylated silica gel,[38] and potassium phthalimide (POPI).[39] The heating method to expedite some of the organic reactions is continuously modified from last three decades.[40] In 1855, Robert Bunsen discovered a burner,[41] which acts as a heating energy source for the various reactions in the vessel, this was later overruled by oil bath heating,[42] hot plates,[43] but the drawback of heating by these methods are remains the same. To eliminate some of these limitations of the traditional method of heating, Microwave-Assisted Organic Synthesis (MAOS) is demonstrated and considered to be superior to the conventional method of heating.[44] The use of microwave ovens in the late 1980's started in chemistry labs just to heat leftover food or to warm frozen items for a late-night snack.[45] Later, organic chemists had figured out the advantage of microwaves to faster and uniformly heat organic reaction mixtures in a synthetic process.[46] However, some of the synthetic methods reported have limitations such as toxic, expensive, use of the organic solvent, high catalyst loading, harsh reaction condition, use of heavy metals, low yields, long reaction times, and tedious workup are the associated with many of the reported catalytic methods for the synthesis of 4*H*-pyran derivatives. Moreover, in many of the reported methods, catalysts are not recycled. Therefore organic chemists have utterly focused on the establishment of agro-waste sourced catalytic solvent media emerged alternative catalytic media for various organic transformations. Some of the reported pineapple juice,[47, 48] water extract of orange fruit shell ash,[49,50] water extract of rice straw ash (WERSA)[51–53] water extract of papaya bark ash (WEPBA),[54–58] water

extract of banana (WEB),[59-62] onion peel,[63] bael fruit extract (BFE),[64] water hyacinth,[65] water extract of muskmelon fruit shell ash (WEMFSA),[66] water extract of pomegranate peel ash (WEPPA),[67] water extract of nilgiri bark ash (WENBA),[68] calcinated burnt peel ash (CBPA) from *Musa balbisiana colla* peels,[69] calcinated tectona grandis leaves (CTGL),[70] calcinated caprica papaya stem (CCPS)[71], eggshell powder (ESP)[72], and more. To replace hazardous catalysts and use organic solvents in the chemical reaction, the feedstock extract endows the reaction with eco-friendly, inexpensive, abundant and hazardous-free as a green chemistry protocol. In the present work, we have selected recently developed agro-waste-derived catalyst WEWFPA (manuscript submitted) developed by our group. The extracted solvent media is used for the synthesis of tetrahydrobenzo[*b*]pyrans by the condensation of aromatic aldehyde, dimedone and ethylcyanoacetate under microwave irradiation. Further, the selected tetrahydrobenzo[*b*]pyrans are subjected to the electrochemical behavior studies and observed molecules behaving well in oxidizing and reducing properties due to the presence of donor-acceptor heteroatom present on it.

2. Experimental

2.1. Materials and Methods

All the reagents used in the synthesis are purchased from the Avra chemicals and were used without further purification. Custom-made microwave oven having the facility to fit reflux condenser and the magnetically stirring facility is used for the irradiation reaction at the power of 300 W. FT-IR Spectrometer measured in Thermo scientific using KBr pellet method. ^{1}H- and ^{13}C-NMR spectra were collected in DMSO-d_6 on an Agilent spectrometer at 400 MHz. The chemical shifts are reported in ppm (δ) relative to tetramethylsilane as an internal standard. LC-MS spectra were recorded in a Waters synapt G2 high detection mass spectrometry The electrochemical behavior was studied using CHI6005E Electrochemical Analyzer. The melting points were determined by the open capillary method and are uncorrected.

2.2. Preparation and Characterization of WEWFPA

The watermelon (*Citrullus lanatus*) fruits are collected from the local market, Belagavi, Karnataka, India and were authenticated. The peel of the fruit was manually separated from the pulp and kept for drying under sunlight for about 3-4 days. The dried peels (rinds) are subjected directly on a Bunsen flame containing wire gauze and produced ash (10g) was suspended in 100 mL of deionized water in a 250 mL conical flask, stirred for about one hour at room temperature. The suspension was then filtered, and a light yellow colored filtrate is denominated as a Water Extract of Watermelon Fruit Peel Ash (WEWFPA).

*2.3. General Procedure for theSynthesis of Tetrahydrobenzo[b]pyran derivatives (**4a-4s**)*

Aromatic aldehyde (1mmole), dimedone (1mmole) and ethylcyanoaceatate (1mmole) in 4 mL of WEWFPA and ethanol (2 mL) was taken in a 50 mL round bottom flask, and the reaction mixture is subjected to microwave irradiation, which has the facility of magnetic stirring and reflux condenser fitting. The microwave irradiation was carried out for a specific period of time with a power output of 300 W. After reaction completion (TLC control, mobile phase: $CHCl_3$: MeOH), the reaction mixture is cooled, diluted with cold water (10 mL), and the separated solid filtered and washed repeatedly with water, and recrystallization from ethanol gave chromatographically pure product with excellent yields. The prepared compounds are confirmed by FT-IR, ^{1}H- & ^{13}C-NMR, and mass spectrometry techniques. The obtained melting point of the products synthesized in this method is very much comparable with the literature data.

2.4. Spectral Data of Representative Compounds

Ethyl-2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate ***(4a)****:* White solid; m.p. 151–153°C; 92% yield; FT-IR (KBr cm^{-1}) : 3403 (N-H), 3290 (N-H), 3027 (HC=H), 1693 (C=O), 1655 (C-N), 1524 (C=C), 1202 (Estes C=O); ^{1}H NMR (DMSO-d_6) δ : (ppm) 0.89 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, t, *J* =7.2 Hz CH_3), 2.06 (1H, d, *J* = 16.0 Hz, C-H), 2.26 (1H, d, *J* = 16.0 Hz, C-H), 2.46 (1H, d, *J* = 17.6 Hz, C-H), 2.55 (1H, d, *J* = 17.6 Hz, C-H), 3.94 (2H, q, *J* = 7.2 Hz, CH_2O), 4.50 (1H, s, C-H), 7.02-7.22 (5H, m, Ar-H), 7.54 (2H, s NH_2); LC-MS: *m/z* found: 282.12 $[M+H]^+$, Calcd. ($C_{20}H_{23}NO_4$): 281.10.

Ethyl-2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate ***(4c)****:* Yellow solid; m.p. 153-154 °C; 89% yield; FT-IR (KBr cm^{-1}) : 3480 (N-H), 3327 (N-H), 2976 (HC=H), 1681 (C=O), 1665 (C-N), 1524 (C=O), 1202 (Ester C=O); ^{1}H NMR (DMSO-d_6) δ: (ppm) 0.89 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, t, *J* = 7.2 Hz CH_3), 2.06 (1H, d, *J* = 16.0 Hz, C-H), 2.26 (1H, d, *J* =16.0 Hz, C-H), 2.46 (1H, d, *J* = 17.6 Hz, C-H), 2.55 (1H, d, *J* =17.6 Hz, C-H), 3.94 (2H, q, *J* = 7.2 Hz, CH_2O), 4.50 (1H, s, C-H), 7.12– 7.22 (5H, m, Ar-H), 7.56 (2H, s NH_2); LC-MS: *m/z* found: 376.58 $[M+H]^+$, Calcd. ($C_{20}H_{22}ClNO_4$): 375.12.

Ethyl-2-amino-7,7-dimethyl-5-oxo-4-p-tolyl-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate ***(4f)****:* Light yellow solid; m.p. 165-166°C; 90% yield; FT-IR (KBr cm^{-1}): 3408 (N-H), 3289 (N-H), 2976 (HC=H), 1692 (C=O),1692 (C-N), 1520 (C=C), 1202 (Ester,C=O); ^{1}H NMR (DMSO-d_6) δ: (ppm) 0.89 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.09 (3H, t, *J* = 7.2 Hz CH_3), 2.06 (1H, d, *J* =16.0 Hz, C-H), 2.20 (3H, s, CH_3), 2.26 (1H, d, *J* = 16.0 Hz, C-H), 2.46 (1H, d, *J* = 17.6 Hz, C-H), 2.55 (1H, d, *J* = 17.6 Hz, C-H), 2.53 (1H, d, *J* = 17.6 Hz, C-H), 3.94 (2H, q, *J* =7.2 Hz, CH_2O), 4.50 (1H, s, C-H), 6.92-7.02 (4H, m, Ar-H), 7.50 (2H, s, NH_2); LC-MS: *m/z* found 356.67, $[M+H]^+$, Calcd. ($C_{21}H_{25}NO_4$): 355.12.

Ethyl-2-amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate ***(4k):*** Light brown solid; m.p. 196-198 °C; 92% yield; FT-IR (KBr cm^{-1}) : 3402 (N-H), 3278 (N-H), 2980 (HC=H), 1691 (C=O), 1691 (C-N), 1529 (C=C), 1207 (Ester C=O); ^{1}H NMR (DMSO-d_6) δ: (ppm) 1.11 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.38 (3H, t, *J* = 7.2 Hz CH_3), 1.50 (2H, d, *J* =16.0 Hz, CH_2), 2.52 (2H, s, *J* = 16.0 Hz, CH_2), 4.05 (1H, d, *J* = 17.6 Hz, CH), 4.33 (2H, *J* = 17.6 Hz, CH_2), 5.90 (1H, d, *J* = 17.6 Hz, C-H), 6.19 (1H, q, *J* = 7.2 Hz, CH), 7.3 (1H, s, C-H), 8.08 (2H, s, NH_2); ^{13}C NMR (DMSO-d_6): (ppm) 14.80, 25.64, 26.5, 27.4, 32.4, 43.2, 50.6, 59.6, 75.5, 105.1, 111.1, 113.6, 141.1, 152.2, 157.8, 160.2, 168.5, 196.03; LC-MS: *m/z* found 332.13, $[M+H]^+$, Calcd ($C_{18}H_{21}NO_5$): 331.14.

Ethyl-2-amino-4-(6-methoxynaphthalen-2-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate ***(4q)****:* Yellow solid; m.p. 289-291 °C; 90% yield; FT-IR (KBr cm^{-1}): 3430 (N-H), 3317 (N-H), 2956 (HC=H), 1720 (C=O), 1689 (C-N), 1585 (C=C), 1199 (Ester C=O); ^{1}H NMR (DMSO-d_6) δ : (ppm) 1.03 (3H, s, CH_3), 1.22 (3H, s, CH_3), 1.50 (3H, t, *J* = 7.2 Hz CH_3), 1.95 (1H, d, *J* = 16.0 Hz, C-H), 2.0 (3H, s, CH_3), 2.55 (1H, d, *J* = 16.0 Hz, C-H), 3.36 (1H, d, *J* = 17.6 Hz, C-H), 3.82 (1H, d, *J* = 17.6 Hz, C-H), 4.91 (1H, d, *J* = 17.6 Hz, C-H), 6.55 (2H, q, *J* = 7.2 Hz, CH_2O), 7.12-7.52 (4H, m, Ar-H), 8.11 (2H, s NH_2). ^{13}C NMR (DMSO-d_6): (ppm) 14.8, 26.2, 27.8, 31.9, 33.7, 43.1, 50.0, 55.1, 62.5, 77.8, 105.5, 115.6, 126.6, 123.6, 125.2, 125.8, 129.1, 135.6, 154.8, 156.1, 162.07, 165.7, 196.8; LC-MS: *m/z* found 422.16, $[M+H]^+$, Calcd. ($C_{25}H_{27}NO_5$): 421.14.

Ethyl-2-amino-4-(6-chloropyridin-3-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate ***(4r)****:* White solid; m.p. 263-265 °C; 89% yield; FT-IR (KBr cm^{-1}) : 3474 (N-H), 3333 (N-H), 2977 (HC=H), 1690 (C=O), 1654 (C-N), 1528 (C=C) 1208 (Ester C=O); ^{1}H NMR (DMSO-d_6) δ : (ppm) 1.05 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.50 (3H, t, *J* = 7.4 Hz, CH_3), 1.91 (2H, d, CH_2), 2.51 (2H, s, CH_2), 3.89 (1H, t, CH), 4.31 (2H, d, *J* =16.0 Hz, CH_2), 7.55 (1H, s, CH), 7.89 (1H, s, CH), 8.15 (1H, d, CH), 8.43 (2H, s, NH_2); ^{13}C NMR (DMSO-d_6): (ppm) 24.9, 26.7, 28.9, 31.5, 37.4, 46.3, 50.8, 59.5, 76.59, 114.2, 123.6, 132.6, 138.6, 142.2, 149.7, 155.1, 163.5, 167.7, 196.0; LC-MS:*m/z* found.377.10, $[M+H]^+$, Calcd ($C_{19}H_{21}ClN_2O_4$): 376.12.

*Ethyl 4-(4-(methoxycarbonyl)phenyl)-2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carboxylate (**4t**):* White powder; m.p. 228-30 °C; 88% yield; FT-IR (KBr cm^{-1}): 3421(N-H), 2962 (HC=H), 1715(C=O), 1662 (C-N), 1518 (C=C), 1210 (Ester C=O); ^{1}H NMR (DMSO-d_6): δ : (ppm) 0.98 (3H, s, CH_3), 1.13 (3H, s, CH_3), 1.42 (3H, t, *J* = 7.2 Hz, CH_3), 2.12 (1 H, d, *J* = 15.2 Hz, Ar-H), 2.22 (1H, d, *J* =15.2 Hz, Ar-H), 2.49 (2H, s, C-H), 3.98 (3H, s, OCH_3), 4.41 (2H, q, *J* = 7.2 Hz, OCH_2), 4.80 (1H, s, C-H), 7.36 (2H, d, *J* =7.6 Hz, ar-H), 7.85 (2H, d, *J* =7.7 Hz, ar-H); ^{13}C NMR (DMSO-d_6): (ppm) 15.47, 27.24, 29.29, 32.12, 32.21, 40.79, 50.52, 51.80, 52.56, 116.02, 128.25, 128.44, 129.53, 149.26, 153.48, 163.23, 166.11, 167.86, and 197.22; LC-MS:*m/z* found.399.10, $[M+H]^+$, Calcd. ($C_{22}H_{25}NO_6$): 398.12.

2.5. Electrodes Used for the Electrochemical Measurements

Cyclic voltammetry is the most commonly used technique for the electrochemical behavior investigation of molecules on the electrode surface. The oxidation reaction is obtained from the cathodic region, whereas the reduction reaction is take place in anodic region. All cyclic voltammetric experiments were carried out using three-electrode system with a standard electrode set-up consisting of GCE as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode used for the electrochemical studies.

3. Result and Discussion

3.1. Characterization of WEWFPA Catalyst

In continuation of our research studies to develop a green chemistry protocol for the synthesis of bioactive heterocyclic molecules, herein, we presented another agro-waste-derived catalytic solvent media for the homogeneous synthesis of tetrahydrobenzo[b]pyran derivatives. For this purpose, firstly, the agro-waste extract was prepared by watermelon (*Citrullus lanatus*) fruit peel collected from the local area. Then, the peel was cleaned with distilled water, dried in sunlight and burnt to ash on the Bunsen burner. Taken 10 g of the resulting ash in 100 mL of deionized water, and stirred for about 1 h, filtered and the filtered solution was labeled as a WEWFPA (Figure 3). The pH of the solution was measured and found to be 11.8. To analyze the cause for the basic nature of the WEWFPA solution, the powdered ash was subjected to elemental analyses using XRF (not reported earlier, Table 1). These data revealed that, the extracted solution is basic in nature due to the presence of oxide and carbonate forms of K and Ca, and it serves as a convenient basic catalyst alternative to the present chemical catalysts used in the organic transformation.

Watermelon peel, the green outer portion is the tough layer of a watermelon. As in the inner part of the fruit itself, the peel of the fruit contains a high percentage of the bionutrients too. The fruit peel contains certain minerals, antioxidants, potassium, vitamins, and active ingredients. The peel also contain some nutrients such as chlorophyll, lycopene, amino acids, polyphenols, flavonoids and citrulline.[73] Herein, we also examined direct hot water extraction of the dried peel of watermelon. For this purpose, a mixture of 50 g of the dried peels in 100 mL of deionized water was heated at about 90 °C for about 3 h, then cooled to rt, filtered and pH measured was found 7.2. After filtration, the extracted solution (hot boiled water) was used for the catalytic action on a model reaction of aromatic aldehyde, dimedone and ethylcyanoaceatate in ethanol. Unfortunately, the product yield was too low. The reason for the lowness of catalytic activity of direct water extracts may be attributed to the pH. In the case of ash water, burning all the organic and complex materials affords basic alkali or transition metal oxides or carbonates with higher pH of the solution (Table 1).

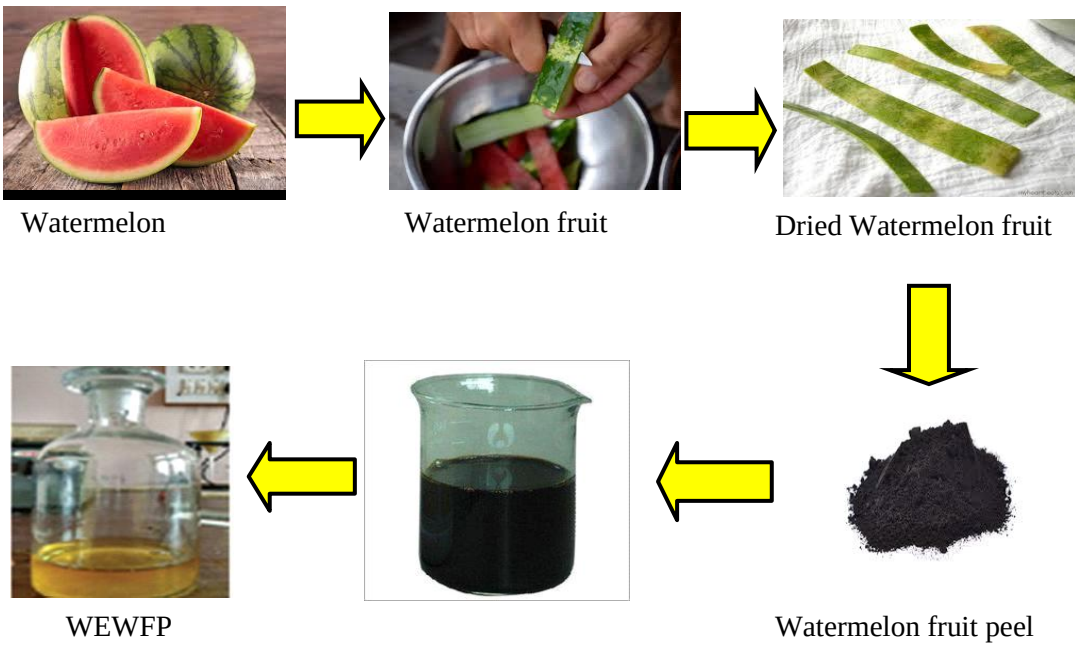


Figure 3. Preparation of WEWFPA

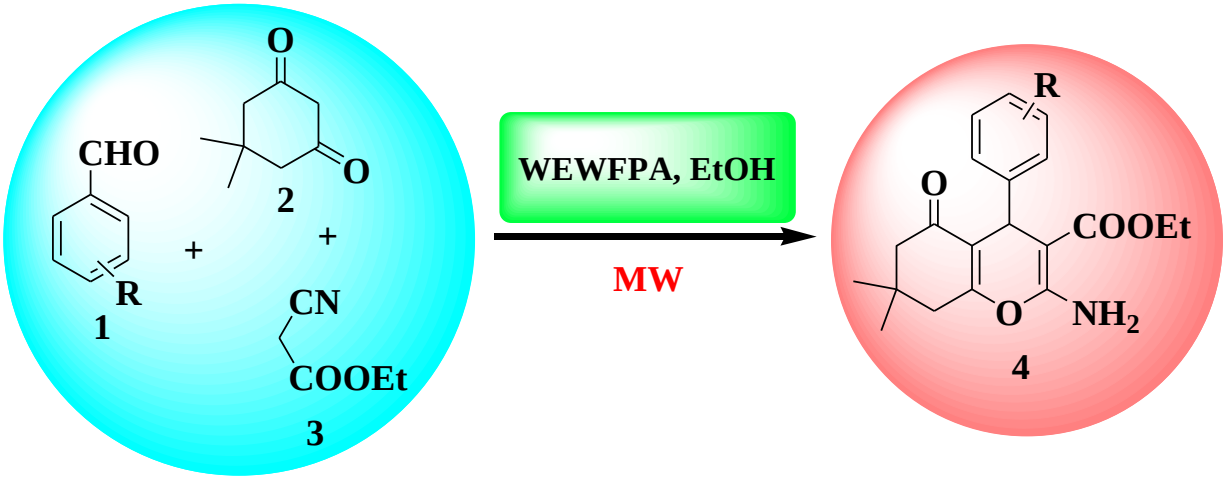
Table 1. XRF Data of WEWFPA

S. No.	Elements	Quantity (%)
1	K_2O	69.8
2	P_2O	14.5
3	CaO	8.9
4	SiO_2	4.2
5	Fe_2O_3	1.72
6	MgO	0.75
7	CuO	0.40
8	TiO_2	0.29
9	ZnO	0.10
10	MnO	0.07
11	Br	0.05
12	Rb_2O	0.04
13	Nb_2O_5	0.03
14	SrO	0.03

3.2. Optimization of Reaction Conditions

To optimize the developed synthetic protocol for tetrahydrobenzo[*b*]pyrans synthesis at first, a mixture of benzaldehyde (**1**) (1 mmol), dimedone (**2**) (1 mmol) and ethylcyanoaceatate **(3)** (1 mmol) in WEWFPA under room temperature stirring condition about 1 hr (Scheme 1). After completion of the reaction (monitored by TLC), the reaction mixture was diluted with water and separated solid product was filtered, washed with water gave moderate yield. Further, we thought of accelerating the reaction rate using custom-made microwave irradiation. As expected, microwave irradiation accelerated the reaction rate with improved yield. During isolation of the product, observed presence of the starting materials, this inspires us to use eco-friendly solvent ethanol for complete solubility of the reactants and performed reaction in a model reaction gave excellent product yield isolation under microwave irradiation. To optimize the required agro-waste solvent media for 1 mmol model reaction, carried out

series of reaction starting with 0, 1, 2, 3, 4, and 5 mL under microwave irradiation at 300 W power (Table 2). The experimental data revealed that, the gradual increase of the volume of WEWFPA from 1 to 4 mL increases gradually product yield isolation (entries 2, 3, 4 and 5, Table 2), but further increasing WEWFPA to 5 mL, surprisingly no affect on the reaction rate as well yield isolation compared to 4 mL of WEWFPA ((entry 6, Table 2).



Scheme 1. Three-component reaction of aryl aldehyde (**1**), dimedone (**2**) and ethylcyanoacetate (**3**) catalyzed WEWFPA.

Table 2. Optimization of the volume of WEWFPA in a model reaction*

Entry	Catalyst volume (mL)	Time (min)	Yield (%)
1	0	10	30
2	1	5	42
3	2	5	50
4	3	5	71
5	**4**	**5**	**92**
6	5	5	92

*Reaction condition: Benzaldehyde (1 mmol), Dimedone (1 mmol) and Ethylcyanoacetate (1 mmol) under MWI.

Despite low yield, a reaction that occurred without use of the WEWFPA may be attributed due to use of the microwave (entry 1, Table 2). To understand the most suitable microwave power for the reaction acceleration and better product isolation. In this context, we studied the required MW power for the best-suited reaction using 4 mL of optimized WEWEPA solvent media with varying microwave power starting with 100, 180, 300, 450 and 600 W (Table 3). This microwave power experiments revealed that, the reaction carried out at a power of 300 W emerged with the highest yield isolation in a short reaction time of 5 min. Therefore, these optimized experiments gave us the use of MW power 300 W and 4 mL of solvent media in 5 min reaction time achieved the best tetrahydrobenzo[b]pyran product isolation. Further, to check the different techniues available in the laboratory for the acceleartion of the reaction rate under various methods are examined (Table 4).

Table 3. Optimization of microwave power

Entry	MW Power (W)	Time (min)	Yield (%)
1	100	5	41
2	180	5	72
3	300	5	92
4	450	5	92
5	600	5	92

The experimental methods used are tabulated in Table 4 are microwave with stirring, grindstone, room temperature stirring and ultrasonic irradiation. Among tested techniques, the MW irradiation excelled better techniques to achieve excellent product yield isolation with faster rate of the raection in 4-5 min (Table 4, entry 4).

Table 4. Optimization of reaction condition

Entry	Condition	Time (min)	Yield (%)
1	Mechanochemical grinding	35	33
2	Room temperature stirring	76	60
3	Ultrasonication	65	66
4	Microwave irradiation	4-5	93

To check the developed synthetic method compatibility with aliphatic aldehyde, we examined the reaction conditions using acetaldehyde (CH_3CHO) in place of aromatic aldehyde to get the product under 4 mL solvent media and 300 W MWI. Unfortunately, there was no product formation even after 12 min irradiation noticed. To understand the tolerance of the present method to other aromatic benzaldehyde containing electron-donating group (EDG) and electron-withdrawing group (EWG). We performed synthesis of series of tetrahydrobenzo[*b*]pyrans derivatives containing various substitutents **(**Table 5). In Table 5 difference product yield in percentage with difference of very small or little for both EDG and EWG on the aromatic aldehyde observed, and not observed any major accountable difference in product yield isolation. Further, the method is extended to heterocycle containing aldehydes (entries, Table 5), and found similar type product yield isolation under MWI. The final products were isolated in pure form by simple recrystallization in ethanol and not required further chromatographic purification. The isolated products were characterized by FT-IR, ^{1}H- and ^{13}C-NMR, and mass spectrometry techniques.

To demonstrate the advantages and efficiency of the present developed procedure for the synthesis of tetrahydrobenzo[*b*] pyrans derivatives are compared with those of the previously reported procedures (Table 6). Thus, the present protocol using WEWFPA have some added advantages like higher catalytic activity, inexpensive, environmentally friendly in comparison to several of the other reported methods, evading the use of toxic transition metals, and avoiding use of toxic solvents.

Table 5. Synthesis of and physical data of tetrahydrobenzo[*b*] pyrans

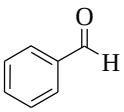
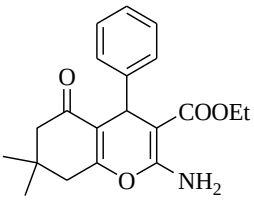
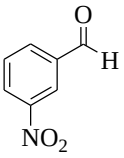
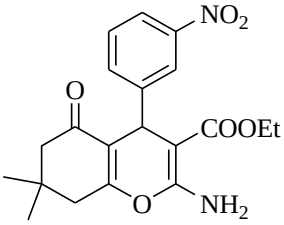
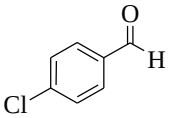
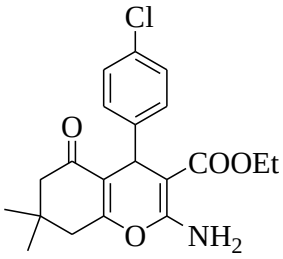
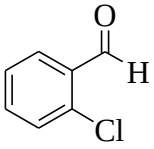
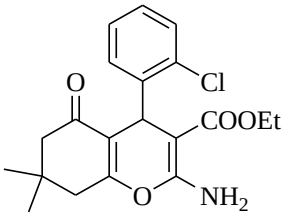
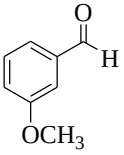
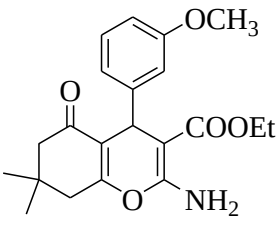
Entry	Aldehyde	Products[a]	Time (min)	Yield[b] (%)	m.p. (ºC)	
					Obs.	Rep.
1		 **4a**	5	92	151- 153	153-155[74]
2		 **4b**	5	87	183-185	185-187[83]
3		 **4c**	5	89	258-260	261-263[83]
4		 **4d**	5	88	236-238	239-241[84]
5		 **4e**	4	86	203-205	201-203[84]

Table 5 continued..

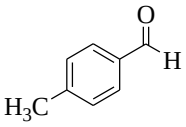
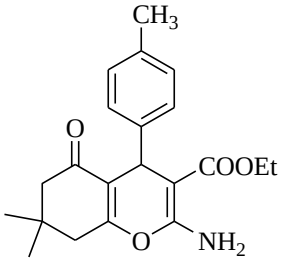
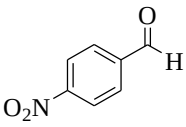
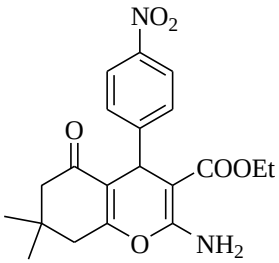
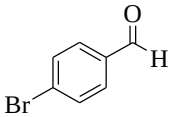
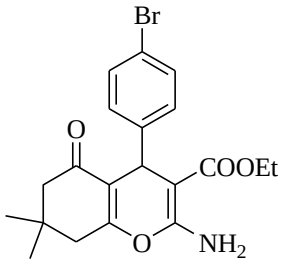
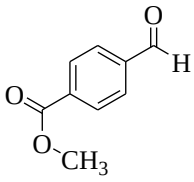
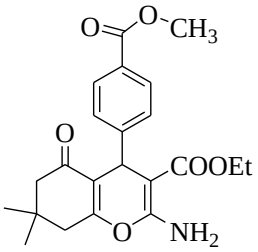
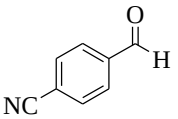
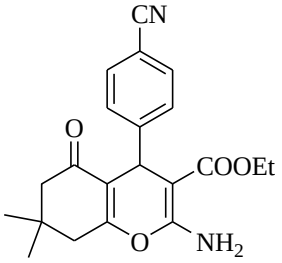
6		 **4f**	5	90	224-226	226-228[85]
7		 **4g**	4	87	182-184	180-182[83]
8		 **4h**	5	88	286-288	286-288[84]
9		 **4i**	4	85	228-230	130-232[83]
10		 **4j**	4	86	262-264	265-267[83]

Table 5 continued..

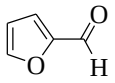
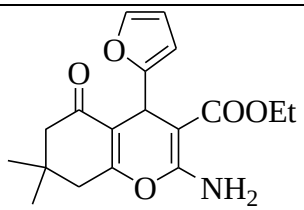
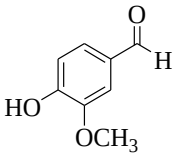
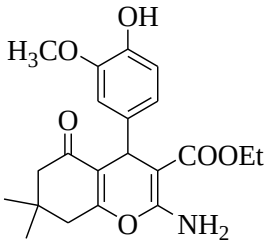
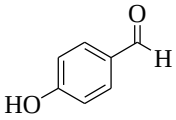
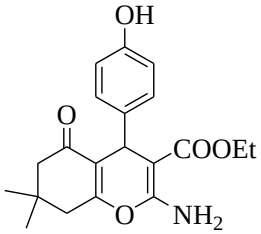
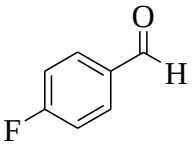
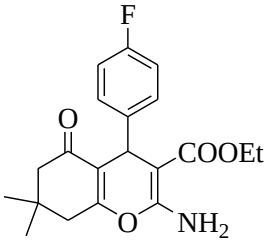
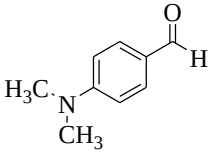
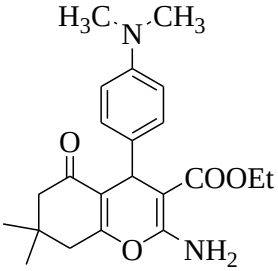
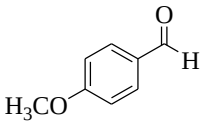
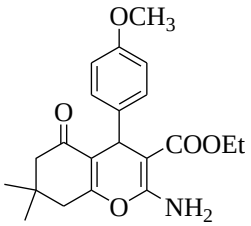
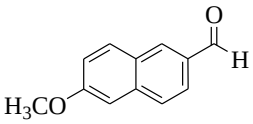
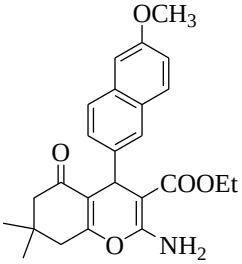
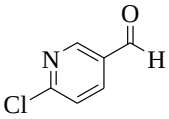
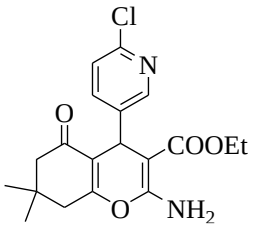
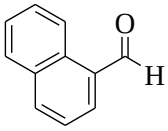
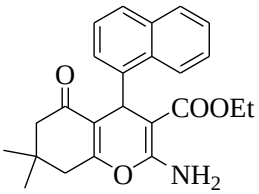
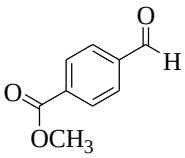
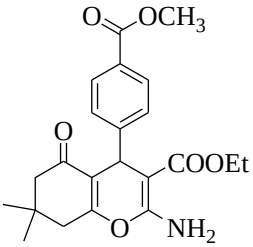
11		 **4k**	5	92	196-198	new
12		 **4l**	5	90	258-260	new
13		 **4m**	5	89	236-238	234-236[83]
14		 **4n**	4	88	216-218	219-221[84]
15		 **4o**	4	89	248-250	250-252[83]

Table 5 continued..

16		 **4p**	4	90	209-211	208-210[84]
17		 **4q**	5	90	289-291	New
18		 **4r**	5	89	263-265	new
19		 **4s**	5	90	249-251	New
20		 **4t**	5	88	228-230	230-232[83]

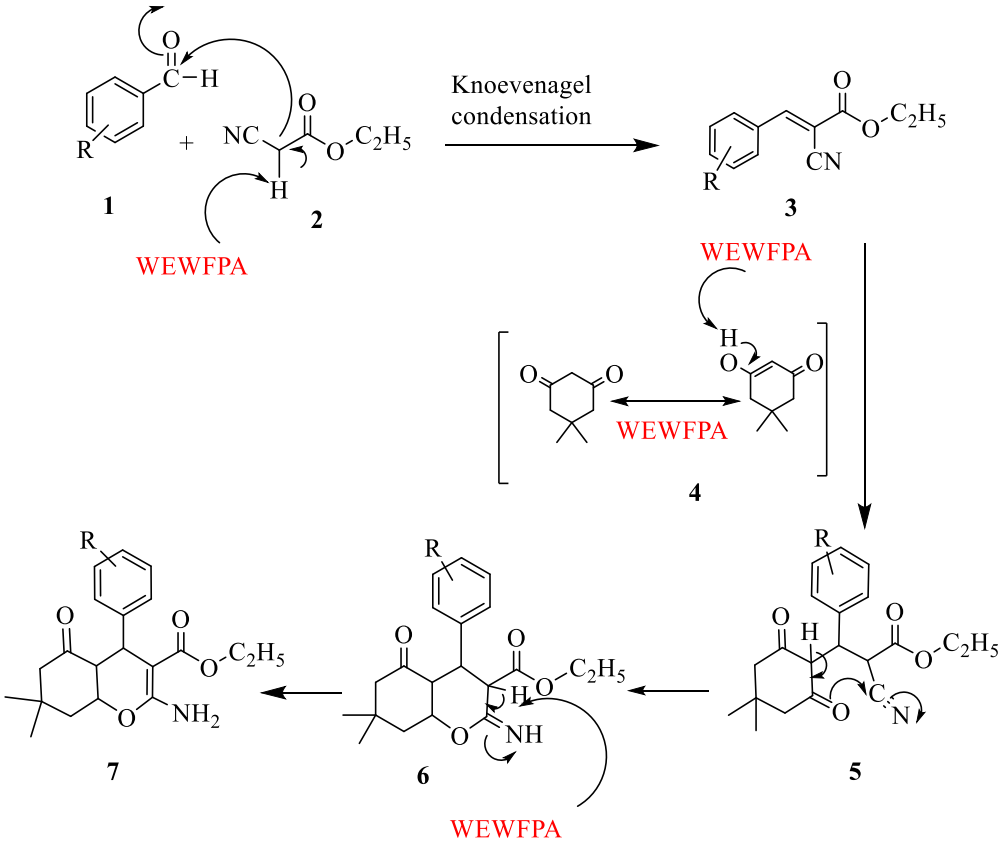
[a]All the products were characterized by FT-IR, ^{1}H and ^{13}C NMR, and LC-MS.
[b]Yields refer to the isolated yields.

Table 6. Comparison of the catalytic efficiency of WEWFPA with other reported methods

Entry	Catalyst	Solvent/ method	Condition	Time (min)	Yield[b] (%)
1	Alumina supported KF	EtOH	Reflux	120	92[68]
2	Urea	Water-EtOH	r.t	7h	93[69]
3	Nano-TiO2/$H_{14}[NaP_5W_{30}O_{110}]$	EtOH	US[a] 40°C	15	94[70]
4	Borax	EtOH	Reflux	10	82[71]
7	Nano-ZnO	Water	Heat 80°C	30	95[72]
5	Aminopropylated silica gel	Water	Heat 70°C	90	92[71]
6	NaBr	Neat	MWI	15	92[73]
8	S-proline	H_2O	rt	2 hr	94[74]
9	TMAH	H_2O	rt	2 hr	92[78]
10	ZnO NPs	EtOH	reflux	10	89[76]
11	PEG	H_2O	rt	45	94[79]
12	PbO NPs	Neat, grinding	rt	20	91[77]
13	NSB-DBU	H_2O	Heat 50ºC	20	94[78]
14	MNPs@Cu	Neat	Heat 90ºC	25	94[80]
15	WEWFPA	EtOH	MWI	5	[Present work]

[a]US = Ultrasound, [b]Isolated yields, MWI =Microwave irradiation

The probable mechanisitic pathway for the agro-waste catalyzed synthesis of tetrahydrobenzo[*b*]pyran (**7**) is shown in Scheme 2. In the first step, the reaction proceeds *via* Knoevenagel condensation resulted in ethyl-2-cyano-3-phenylacrylate (**3**) by the reaction of benzaldehyde (**1**) with ethylcyanoacetate (**2**) in the presence of agro-waste solvent medium, this helps in withdrawing one of the active hydrogen from the active methylene site. The formed Knoevenagel product undergoes nucleophilic addition by enolizable dimedone (**4**) followed by intramolecular cyclization to produce the title compound **7**.[63] From our observation, the developed agro-waste solvent medium will be serving as a basic catalyst, and it stands as a better alternative to the reported methods, and it does not have any measurable adverse effect to environment and fall under the green chemistry protocol for the organic transformation.



Scheme 2. A possible mechanism for the synthesis of product **7**

3.3. Studies of Electrochemical Behavior

We studied the electrochemical behavior of the prepared tetrahydrobenzo[*b*] pyrans by cyclic voltammetry experiments[81] (Figure 4) using a CHI6005E Electrochemical Analyzer with general-purpose electrochemical system software. A three-electrode cell system was employed with the silver electrode (Ag/AgCl) as a reference, GC (Glassy Carbon) as a working electrode & a platinum wire as a counter electrode, and experiments were carried out in an inert atmosphere by purging nitrogen gas (99.99 % pure) for 20 min before every experiment to start. The electrochemical characterization was performed using 0.1mM of the complex TBAP with supporting electrolyte in DMSO. Inlaid glassy carbon (GC) disks of surface area 0.071 cm^2 are employed as electrodes in the electrochemical characterization. The GCEs are polished by polishing cloth (Buehler, Micro Cloth,) using sequentially 1.0 µm and 0.5 µm alumina in a water slurry. They were repeatedly washed with 1:1 HNO_3, acetone and water respectively, and subjected to ultrasonication for about 5 min alternatively in water and ethanol.[82] Herein, we first carried out the electrochemical behavior study of the bare electrode, and the derivatives dissolved in water by neat sonication then 0.1 mM of TBAB in DMSO was added. The selected tetrahydrobenzo[*b*]pyrans derivatives are subjected to electrochemical behavior studies. The anodic peaks of these derivatives observed at almost 0.8 V are probably due to the oxidation of the amine groups present on these derivatives and showed both oxidation and reduction potential reactions. This study revealed that, compounds **4k, 4p, 4r** and **4s** are electrochemically active and exhibited intensive oxidation and reduction potential peaks, and act as a good oxidation and reducing properties. The derivatives **4a** and **4b** showed moderate oxidation and reduction potential values,

while these redox peaks were not observed in the spectra of bare GCE. The compound **4k** exhibits better anodic and cathodic peaks, because of the influence of the furan ring present on it.

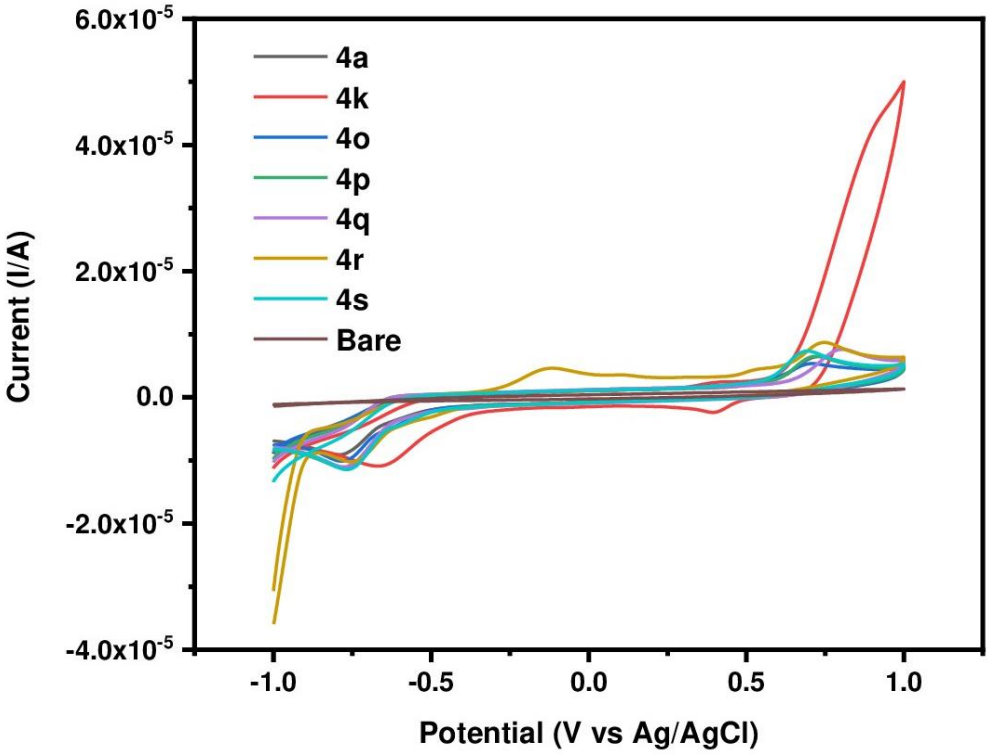


Figure 4. Electrochemical behavior of tetrahydrobenzo[*b*]pyran derivatives

4. Conclusion

Present work, we have demonstarted agro-waste WEWFPA catalysed one-pot synthesis of tetrahydrobenzo[b]pyrans derivatives by the reaction of aromatic aldehyde, dimedone and ethylcyanoaceate under MWI. The advantages of this procedure are the medium not required hazardous organic solvent, mild reaction condition, greener catalyst, inexpensive and simple. Further synthesized derivatives are subjected to CV behavior studies, and revealed that tetrhydro pyrans have a good oxidation and reduction behaviour propeties, and may be acted as a antioxidant agents. In the near future, the author group is extending the agro-waste catalytic medium to more bioactive and complex scaffolds drug molecule synthesis under green chemistry thematic.

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Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/organic-communications

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