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Poly Ethylene Glycols as Efficient Media for the Synthesis of *β*-Nitro Styrenes from *α*, *β*-Unsaturated Carboxylic Acids and Metal Nitrates under Conventional and Non-Conventional Conditions

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Abstract

Poly ethylene glycols (PEG-200, 400, 600, 4000 and 6000) supported reactions were conducted with certain *α*, *β*-unsaturated acids in presence of metal nitrates under solvent free (solid state) and mineral acid free conditions. The reactants were ground in a mortar with a pestle for about 30 minutes. The aromatic acids underwent nitro decarboxylation and afforded *β*-nitro styrene derivatives in very good yield while *α*, *β*-unsaturated aliphatic carboxylic acids gave corresponding nitro derivatives. Addition of PEG accelerated rate of the reaction enormously. Reaction times substantially decreased from several hours to few minutes followed by highly significant increase in the product yield. Among the several PEGs PEG-300 has been found to be much more effective than other PEGs.

Keywords: Poly Ethylene Glycols (PEG), Rate Accelerations, *α*, *β*-Unsaturated Acids, Metal Nitrates, Solvent Free (Solid State), *β*-Nitro Styrene Derivatives, *α*, *β*-Unsaturated Aliphatic Acids, Nitro Derivatives

1. Introduction

The use of non volatile solvents is an essential ingredient in a large number of organic synthesis protocols, which may be toxic, hazardous and also cause environmental pollution. Therefore the use of environmentally safe and non-toxic solvents and more specifically removal of organic solvents in chemical synthesis are important in the drive towards benign chemical technologies. Solvent-free organic reactions make synthesis simpler, save energy, and prevent solvent wastes, hazards, and toxicity. The development of solvent-free organic synthetic methods has thus become an important and popular research area. Reports on solvent-free reactions between solids, gases and solids, solids and liquid, between liquids, and on solid inorganic supports have become increasingly frequent in recent years. A mortar and pestle is a tool used to crush, grind, and mix solid substances. Solvent less preparation of organic compounds in the solid state and via microwave irradiation has been the subject of interest for the past one decade which has the advantage of being eco-friendly, easy to handle, employ shorter reaction times and solvent less conditions. Reactions performed under solvent-free conditions have gained much attention because of their enhanced selectivity, mild reaction conditions and associated ease of manipulation. The recent reviews and publications [1-6] in this field prove the importance of solvent free organic synthesis and highlights that, this process is not only simple but also satisfies both economical and environmental demands by replacing the toxic solvents. Since more than a decade our group is also actively working on exploiting the use of a variety of eco friendly materials such as metal ions and surfactants as catalysts and non-conventional energy sources (such as microwave and ultra sound) to assist organic transformations such as Vilsmeier-Haack [7-9], Hunsdiecker [10] and nitration reactions [11-13]. The classical Hunsdiecker-Borodin reaction [14,15] is an important halo decarboxylation reaction, which is used for the synthesis of *β*-halo styrenes from *α*, *β*-unsaturated Cinnamic acid. This reaction has been modified by several workers with a view to overcome the toxicity factors arising from the use of molecular bromine and metal salt catalysts [16-25]. The use of solid acid catalysis has been found potentially more attractive because of the ease of removal and recycling of the catalyst and the possibility that the solid might influence the selectivity. In one of the recent reports Das and coworkers [26] reported that nitro styrenes can be achieved from *α*, *β*-unsaturated carboxylic acids using nitric acid (3 equiv) and catalytic amount of AIBN (2 mol%) in acetonitrile medium. In another report Rao *et al.* [27] enlightened the use of ceric ammonium nitrate (CAN) in nitro Hunsdiecker-Borodin reactions. Recently we have concentrated on developing new methodologies using non-conventional energy sources and eco-friendly materials as catalysts in organic transformations, and reported a methodology in metal ion mediated nitration of organic compounds in presence of small amount of HNO_3 under solvent free (solid state) conditions [28]. Polyethylene glycol (PEG-400) is a biologically acceptable inexpensive polymer and an eco-friendly reagent [29], which is widely used in many organic reactions for conversion of oxiranes to thiiranes [30], asymmetric aldol reactions [31], cross-coupling reactions [18], Baylis-Hillman reaction [32,33] and ring opening of epoxides [34]. Encouraged by these results, we want to explore, the use of Polyethylene glycols (PEGs) as efficient catalyst in this study. We have studied PEG triggered Hunsdiecker-Borodin reactions for the synthesis of *β*-nitro styrenes from *α*, *β*-unsaturated carboxylic acids under conventional and non-conventional (solvent free mortar-pestle and microwave) conditions.

2. Experimental Details

Cinnamic acid, metal nitrates, nitric acid and polyethylene glycols were obtained from SD Fine Chemicals or Loba. Substituted Cinnamic acid were prepared by Perkins reaction as cited in literature [35].

2.1. General Procedure for PEG Mediated Synthesis of *β*-Nitro Styrenes in MeCN Medium

In a typical solid state synthesis, Cinnamic acid (0.01 mol), PEG (0.02 mmol) and metal nitrate (0.12 mmol) are placed in a clean two necked R. B. flask and stirred for certain time. Ground with a pestle for about 30 to 60 minutes until the mixture is homogeneous and particles are no longer getting smaller. Progress of the reaction is periodically monitored by TLC. After completion, the reaction mixture is treated with 2% sodium carbonate solution, followed by the addition dichloro methane (DCM) or dichloro ethane (DCE). The organic layer was separated, dried over Na2SO4 and the solvent is recollected by distillation using Rotavapor. The resultant compound is further purified with column chromatogram-phy using ethyl acetate: hexane (3:7) as eluent to get pure product. Hexane and ethyl acetate are also separated using Rotavapor according to standard procedures [35-37].

2.2. General Procedure for the Synthesis of *β*-Nitro Styrenes in Acetonitrile Medium under Continuously Stirred Conditions

In a typical synthesis, Cinnamic acid (0.01 mol), PEG (0.02 mmol) and metal nitrate (0.12 mmol) are placed in a clean mortar and ground with a pestle for about 30 to 60 minutes until the mixture is homogeneous, the particles are no longer getting smaller. Progress of the reaction is periodically monitored by TLC. After completion, the reaction mixture is treated with 2% sodium bicarbonate solution, followed by the addition dichloro methane (DCM) or dichloro ethane (DCE). The organic layer was further treated in a similar manner discussed in the earlier section to get pure product.

2.3. General Procedure for the Synthesis of *β*-Nitro Styrenes under Microwave Irradiated Conditions

Cinnamic acid (0.01 mol), PEG (0.02 mmol) and metal nitrate (0.12 mmol) were dissolved in minimum amount of MeCN, and mixed with silica gel (10 g) and the mixture was transfered into a test tube and subjected to microwave irradiation (BPL make, BMO 700T, 650 W, power 80%) for a specified period. Reaction was monitored by TLC (hexane-ethyl acetate, 7:3). After completion of the reaction, products are isolated as discussed in the above section.

2.4. General Procedure for the Synthesis of *β*-Nitro Styrenes under Solvent-Free Conditions

A mortar was charged with Cinnamic acid (0.01 mol), PEG (0.02 mmol) and metal nitrate (0.12 mmol). The mixture was ground at room temperature with a pestle until TLC showed complete disappearance of the starting material. After completion, the reaction mixture is treated with 2% sodium bicarbonate solution, followed by addition of dichloro methane (DCM) or dichloro ethane

(DCE). The organic layer was further treated in a similar manner discussed in the earlier section to get pure product.

3. Results and Discussion

The *α*, *β*-unsaturated aromatic carboxylic acids such as Cinnamic acid afforded *β*-nitro styrenes when they are taken along with PEG in presence of metal nitrates in a mortar and ground with a pestle for about half a hour. The reactions afforded good yield of products with high regio selectivity. The yields of major products are compiled in **Tables 1-3**. The products were characterized by

Table 1. NMR and Mass Spectral data for selected reaction products.

Entry	Substrate	Product	Spectral data	
			m/z	^{1}HNMR
1	CA	*β*–Nitro Styrene	149	δ 6.4 (d 1H, *β*-CH), δ 7.3 - 7.65 (m 5H, Ar-H) δ 7.8(d 1H, *α*-CH)
2	4-ClCA	4-Chloro *β*–Nitro Styrene	184	δ 6.6 (d 1H, *β*-CH) δ 7.2 (d 2H, Ar-H) δ 7.6 (d 2H, Ar-H) δ 8.3 (d 1H, *α*-CH)
3	4-OMeCA	4-Methoxy *β*–Nitro Styrene	179	δ 3.8 (s 3H, OCH_3) δ 6.4 (d 1H, *β*-CH) δ 7.32 - 7.7 (m 4H, Ar-H) δ 7.9 (d 1H, *α*-CH)
4	4-MeCA	4-Methyl *β*–Nitro Styrene	163	δ 3.0 (s 3H, CH_3) δ 6.6 (d 1H, , *β*-CH) δ 7.4 - 7.7 (m 4H, Ar-H δ 7.9 (d 1H, *α*-CH)
5	4-NO_2CA	4-Nitro *β*–Nitro Styrene	194	δ 6.6 (d 1H, *β*-CH) δ 7.4 (d 2H, Ar-H) δ 7.8 (d 2H, Ar-H) δ8.2 (s 1H, *α*-CH)
6	4-OHCA	4-Hydroxy *β*–Nitro Styrene	165	δ 6.5 (d 1H, *β*-CH) δ 7.3 (d 2H, Ar-H) δ 7.8 (d 2H, Ar-H) δ 8.1 (d 1H, *α*-CH) δ 10.5 (s 1H, Ar-OH)
7	AA	1–Nitro Ethene	73	δ 5.92 (d 1H, *β*-CH) δ 6.6 (d 1H, trans *β*-CH) δ 7.25 (q 1H, *α*-CH)
8	CRA	1–Nitro Propene	87	δ 2.12 (d 3H, CH_3) δ 7.0 (d 1H, *α*-CH) δ 7.15 (m 1H, *β*-CH)
9	3-PhCRA	3- Phenyl 1–Nitro Propene	163	δ 3.3 (d 2H, CH_2) δ 7.23 - 7.33 (m 5H, Ar-H) δ 8.2 (d 1H, *α*-C-H)
10	2-ClCA	2-Chloro *β*–Nitro Styrene	183	δ 6.6 (d 1H, *β*-CH) δ 7.3 - 7.7 (m 4H, Ar-H) δ 8.2 (d 1H, *α*- C-H)
11	2-MeCA	2-Methyl *β*–Nitro Styrene	163	δ 2.9 (s 3H, CH_3) δ 6.7 (d 1H, *β*-CH) δ 7.1 - 7.8 (m 4H, Ar-H) δ 8.2 (d 1H, *α*-CH)

Table 2. Effect of different PEGs on nitro Hunsdiecker reactions (Solution phase) with Cinnamic acid.

S.No	Metal Nitrate	PEG-200		PEG-300		PEG-400		PEG-600		PEG-4000		PEG-6000	
		RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1	$Ni(NO_3)_2$	1.75	75	1.75	88	1.75	85	1.75	80	2.75	85	2.75	81
2	$Zn(NO_3)_2$	1.75	80	1.75	85	1.75	86	1.75	85	2.75	87	2.75	86
3	$ZrO(NO_3)_2$	1.75	75	1.75	85	1.75	88	1.75	87	2.75	82	2.75	82
4	$Cd(NO_3)_2$	1.75	80	1.75	85	1.75	84	1.75	86	2.75	84	2.75	84
5	$Hg(NO_3)_2$	1.75	80	1.75	85	1.75	82	1.75	85	2.75	78	2.75	70
6	$Mg(NO_3)_2$	1.75	85	1.75	90	1.75	87	1.75	88	2.75	85	2.75	86
7	$Sr(NO_3)_2$	1.75	88	1.75	90	1.75	92	1.75	94	2.75	88	2.75	90
8	$Al(NO_3)_2$	1.75	83	1.75	89	1.75	85	1.75	86	2.75	83	2.75	83
9	$UO_2(NO_3)_2$	1.75	88	1.75	90	1.75	90	1.75	91	2.75	88	2.75	89
10	$Th(NO_3)_2$	1.75	88	1.75	88	1.75	86	1.75	90	2.75	85	2.75	90
11	$AgNO_3$	1.75	70	1.75	80	1.75	80	1.75	86	2.75	78	2.75	80
12	$NH_4(NO_3)_2$	1.75	75	1.75	80	1.75	80	1.75	78	2.75	75	2.75	75
13	$Ca(NO_3)_2$	1.75	80	1.75	85	1.75	84	1.75	86	2.75	84	2.75	84

Table 3. Effect of different PEGs on (Solvent free-Mortar Pestle) nitro Hunsdiecker reactions with Cinnamic acid.

S. No	Metal Nitrate	PEG-200		PEG-300		PEG-400		PEG-600		PEG-4000		PEG-6000	
		RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1	$Ni(NO_3)_2$	30	80	30	90	30	83	30	85	60	75	60	78
2	$ZrO(NO_3)_2$	30	85	30	88	30	86	30	88	60	80	60	76
3	$Cd(NO_3)_2$	30	82	30	85	30	85	30	87	60	85	60	75
4	$Ca(NO_3)_2$	30	81	30	86	30	84	30	86	60	78	60	80
5	$Hg(NO_3)_2$	30	79	30	89	30	85	30	84	60	78	60	75
6	$Mg(NO_3)_2$	30	90	30	95	30	90	30	90	60	85	60	86
7	$Sr(NO_3)_2$	30	85	30	92	30	90	30	94	60	88	60	90
8	$Al(NO_3)_2$	30	90	30	90	30	87	30	89	60	83	60	83
9	$Th(NO_3)_2$	30	88	30	90	30	90	30	91	60	88	60	89
10	$UO_2(NO_3)_2$	30	85	30	90	30	88	30	90	60	85	60	90
11	$Ag NO_3$	30	70	30	80	30	75	30	78	60	75	60	80
12	$NH_4(NO_3)_2$	30	75	30	85	30	80	30	80	60	75	60	75
13	$Zn(NO_3)_2$	30	72	30	83	30	80	30	78	60	78	60	84

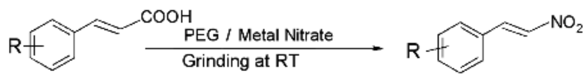
IR, 1H-NMR, Mass spectra and physical data with authentic samples and found to agree well with earlier reports [26-28]. Here we used simple mortar and pestle for grinding purpose to complete the reaction [28]. Grinding, milling, shearing, scratching and polishing provide mechanical impact for mechanical breakage of intramolecular bonds by external force and must be differentiated from molecular solid-state chemistry. Further, it appears clearly that in mortar pestle reactions mechanical energy is converted to thermal energy which is utilized to break intramolecular chemical bonds to causing chemical change [38].

3.1. Effect of Structure on Reactivity

To check the generality of the reaction an array of substituted Cinnamic acid and metal nitrates are used under varied reaction conditions, as shown in **Schemes 1 and 2**. In order to have a closer look into the effect of structural variation on nitro decarboxylation the study has been taken up extensively the following variable (in solution phase and under solvent-free) conditions:

$$\text{Ar- CH = CH-COOH} \xrightarrow[\text{(i) MeCN (ii) MWI}]{\text{PEG/Metal Nitrate}} \text{Ar- CH = CH-NO}_2$$

Scheme 1. Decarboxylative nitration of *α*, *β*-unsaturated acid under Microwave irradiation. Metal Nitrate = $Mg(NO_3)_2$, $Sr(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$, $Zn(NO_3)_2$, $Hg(NO_3)_2$, $AgNO_3$, $ZrO(NO_3)_2$, $UO_2(NO_3)_2$, Th $(NO_3)_2$, NH_4NO_3; PEG = PEG-200, 300, 400, 600, 4000 and 6000.



Scheme 2. Decarboxylative nitration of *α*, *β*-unsaturated acid under Solvent-free conditions (Grinding). Metal Nitrate = $Mg(NO_3)_2$, $Sr(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$, $Zn(NO_3)_2$, $Hg(NO_3)_2$, $AgNO_3$, $ZrO(NO_3)_2$, $UO_2(NO_3)_2$, $Th(NO_3)_2$, NH_4NO_3; PEG = PEG-200, 300, 400, 600, 4000 and 6000.

1) Different *α*, *β*-unsaturated aromatic and aliphatic carboxylic acids.

2) Different metal nitrates belonging to s-block, p-block, d-block and f-block ($Mg(NO_3)_2$, $Sr(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$, $Zn(NO_3)_2$, $Hg(NO_3)_2$, $AgNO_3$, $ZrO(NO_3)_2$, $UO_2(NO_3)_2$, $Th(NO_3)_2$, NH_4NO_3.

3) Different Poly ethylene glycols (PEG-200, 300, 400, 600, 4000 and 6000).

Data presented in **Tables 2-4** and **Tables 5-22** of electronic supplementary data) indicate the reaction times and yield of reaction products under different conditions, which revealed that the reaction is sensitive to the structural variation of Cinnamic acid, PEGs and also the nature of metal nitrate. Reaction rates accelerated with the introduction of electron donating groups and retarded with electron withdrawing groups. In order to have clarity, kinetic data for Cinnamic acid conversion are separately shown in **Tables 5-7** and **Figures 1** and **2**. **Figure 1** depicts that addition of PEG gradually decreases the reaction times (RT) gradually with an increase in the molecular weight of PEG. Among the several PEGs,

Table 4. Effect of different PEGs on microwave irradiated nitro Hunsdiecker reactions with Cinnamic acid.

S. No	Metal Nitrate	PEG-200		PEG-300		PEG-400		PEG-600		PEG-4000		PEG-6000	
		RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1	$Ni(NO_3)_2$	180	70	90	86	90	82	90	84	180	80	180	82
2	$Zn(NO_3)_2$	180	77	90	89	90	84	90	85	180	82	180	80
3	$ZrO(NO_3)_2$	180	77	90	86	90	83	90	84	180	85	180	84
4	$Cd(NO_3)_2$	180	78	90	84	90	85	90	85	180	80	180	82
5	$Hg(NO_3)_2$	180	74	90	82	90	82	90	80	180	78	180	82
6	$Mg(NO_3)_2$	180	82	90	88	90	85	90	86	180	80	180	85
7	$Sr(NO_3)_2$	180	83	90	90	90	88	90	86	180	82	180	84
8	$Al(NO_3)_2$	180	80	90	86	90	82	90	84	180	82	180	84
9	$UO_2(NO_3)_2$	180	84	90	86	90	85	90	90	180	85	180	86
10	$Th(NO_3)_2$	180	83	90	90	90	88	90	86	180	85	180	86
11	$AgNO_3$	180	62	90	76	90	70	90	74	180	78	180	80
12	$NH_4(NO_3)_2$	180	75	90	80	90	80	90	80	180	80	180	80
13	$Ca(NO_3)_2$	180	78	90	82	90	80	90	82	180	76	180	78

Table 5. Nitro decarboxylation of Cinnamic acid in presence of PEG-200 and metal nitrates under Solution phase.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1a	1.75	70	1.75	75	1.75	72	1.75	71	1.75	69	1.75	85	1.75	88	1.75	83	1.75	88	1.75	88	1.75	60	1.75	75
1b	2.00	66	2.00	69	2.00	68	2.00	62	2.00	67	2.00	78	2.00	82	2.00	85	2.00	90	2.00	88	2.00	62	2.00	77
1c	1.50	74	1.50	82	1.50	76	1.50	76	1.50	80	1.50	87	1.50	88	1.50	85	1.50	88	1.50	89	1.50	65	1.50	70
1d	1.50	78	1.50	75	1.50	76	1.50	70	1.50	77	1.50	83	1.50	86	1.50	85	1.50	84	1.50	83	1.50	62	1.50	68
1e	2.00	64	2.00	62	2.00	70	2.00	62	2.00	75	2.00	78	2.00	81	2.00	78	2.00	80	2.00	80	2.00	60	2.00	66
1f	1.50	85	1.50	80	1.50	88	1.50	78	1.50	76	1.50	77	1.50	85	1.50	87	1.50	86	1.50	90	1.50	60	1.50	68
1g	1.50	66	1.50	62	1.50	65	1.50	64	1.50	61	1.50	76	1.50	73	1.50	80	1.50	80	1.50	80	1.50	63	1.50	68
1h	2.00	67	2.00	69	2.00	68	2.00	68	2.00	68	2.00	78	2.00	77	2.00	78	2.00	76	2.00	78	2.00	64	2.00	69
1i	1.50	62	1.50	64	1.50	64	1.50	65	1.50	66	1.50	79	1.50	82	1.50	77	1.50	74	1.50	80	1.50	64	1.50	61
1j	2.00	66	2.00	62	2.00	61	2.00	64	2.00	65	2.00	68	2.00	73	2.00	69	2.00	66	2.00	66	2.00	60	2.00	70
1k	1.50	74	1.50	71	1.50	74	1.50	71	1.50	71	1.50	74	1.50	74	1.50	74	1.50	70	1.50	74	1.50	67	1.50	75

Table 6. Nitro decarboxylation of Cinnamic acid in presence of PEG-300 and metal nitrates under Solution phase.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1a	1.75	71	1.75	75	1.75	83	1.75	72	1.75	70	1.75	85	1.75	90	1.75	85	1.75	88	1.75	87	1.75	63	1.75	74
1b	2.00	68	2.00	70	2.00	70	2.00	75	2.00	68	2.00	78	2.00	84	2.00	87	2.00	90	2.00	89	2.00	64	2.00	78
1c	1.50	75	1.50	83	1.50	76	1.50	78	1.50	81	1.50	86	1.50	90	1.50	87	1.50	88	1.50	92	1.50	68	1.50	72
1d	1.50	80	1.50	76	1.50	76	1.50	72	1.50	78	1.50	85	1.50	88	1.50	87	1.50	84	1.50	85	1.50	65	1.50	67
1e	2.00	67	2.00	84	2.00	71	2.00	65	2.00	76	2.00	80	2.00	82	2.00	78	2.00	80	2.00	82	2.00	63	2.00	68
1f	1.50	87	1.50	82	1.50	88	1.50	79	1.50	77	1.50	88	1.50	87	1.50	87	1.50	86	1.50	92	1.50	63	1.50	70
1g	1.50	68	1.50	65	1.50	67	1.50	66	1.50	63	1.50	76	1.50	75	1.50	82	1.50	82	1.50	82	1.50	66	1.50	70
1h	2.00	70	2.00	72	2.00	70	2.00	70	2.00	70	2.00	80	2.00	78	2.00	80	2.00	78	2.00	80	2.00	67	2.00	71
1i	1.50	65	1.50	66	1.50	66	1.50	67	1.50	68	1.50	80	1.50	83	1.50	78	1.50	75	1.50	82	1.50	67	1.50	63
1j	2.00	71	2.00	64	2.00	63	2.00	66	2.00	67	2.00	70	2.00	73	2.00	70	2.00	68	2.00	68	2.00	62	2.00	72
1k	1.50	78	1.50	72	1.50	77	1.50	72	1.50	72	1.50	77	1.50	78	1.50	78	1.50	72	1.50	78	1.50	68	1.50	77

Table 7. Nitro decarboxylation of Cinnamic acid in presence of PEG-400 and metal nitrates under Solution phase.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1a	1.75	73	1.75	76	1.75	75	1.75	74	1.75	72	1.75	87	1.75	92	1.75	87	1.75	90	1.75	88	1.75	65	1.75	76
1b	2.00	70	2.00	72	2.00	72	2.00	68	2.00	70	2.00	80	2.00	88	2.00	89	2.00	92	2.00	91	2.00	67	2.00	80
1c	1.50	77	1.50	85	1.50	78	1.50	82	1.50	84	1.50	88	1.50	91	1.50	89	1.50	90	1.50	93	1.50	70	1.50	74
1d	1.50	83	1.50	78	1.50	79	1.50	76	1.50	80	1.50	87	1.50	88	1.50	89	1.50	86	1.50	88	1.50	67	1.50	70
1e	2.00	69	2.00	66	2.00	74	2.00	68	2.00	79	2.00	83	2.00	84	2.00	80	2.00	82	2.00	84	2.00	64	2.00	70
1f	1.50	88	1.50	85	1.50	91	1.50	83	1.50	80	1.50	90	1.50	91	1.50	89	1.50	88	1.50	94	1.50	64	1.50	72
1g	1.50	70	1.50	68	1.50	69	1.50	70	1.50	65	1.50	78	1.50	78	1.50	84	1.50	85	1.50	85	1.50	67	1.50	72
1h	2.00	73	2.00	75	2.00	73	2.00	74	2.00	74	2.00	73	2.00	80	2.00	82	2.00	81	2.00	82	2.00	69	2.00	73
1i	1.50	67	1.50	69	1.50	68	1.50	70	1.50	72	1.50	83	1.50	85	1.50	80	1.50	78	1.50	84	1.50	69	1.50	65
1j	2.00	74	2.00	67	2.00	75	2.00	68	2.00	71	2.00	73	2.00	75	2.00	72	2.00	69	2.00	70	2.00	63	2.00	74
1k	1.50	80	1.50	74	1.50	78	1.50	74	1.50	76	1.50	78	1.50	78	1.50	80	1.50	74	1.50	78	1.50	70	1.50	79

Table 8. Nitro decarboxylation of Cinnamic acid in presence of PEG-600 and metal nitrates under Solution phase.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1a	1.75	75	1.75	78	1.75	77	1.75	76	1.75	74	1.75	89	1.75	94	1.75	89	1.75	91	1.75	90	1.75	66	1.75	78
1b	2.00	72	2.00	75	2.00	76	2.00	70	2.00	72	2.00	83	2.00	90	2.00	92	2.00	93	2.00	93	2.00	68	2.00	82
1c	1.50	78	1.50	88	1.50	81	1.50	84	1.50	87	1.50	91	1.50	93	1.50	92	1.50	91	1.50	96	1.50	71	1.50	76
1d	1.50	85	1.50	80	1.50	82	1.50	79	1.50	84	1.50	89	1.50	90	1.50	92	1.50	87	1.50	91	1.50	68	1.50	71
1e	2.00	72	2.00	69	2.00	76	2.00	70	2.00	83	2.00	87	2.00	87	2.00	82	2.00	83	2.00	87	2.00	66	2.00	71
1f	1.50	90	1.50	88	1.50	93	1.50	86	1.50	84	1.50	93	1.50	93	1.50	92	1.50	89	1.50	96	1.50	66	1.50	74
1g	1.50	73	1.50	71	1.50	72	1.50	72	1.50	68	1.50	80	1.50	81	1.50	88	1.50	86	1.50	88	1.50	69	1.50	75
1h	2.00	75	2.00	78	2.00	75	2.00	77	2.00	77	2.00	87	2.00	83	2.00	86	2.00	82	2.00	86	2.00	70	2.00	74
1i	1.50	69	1.50	73	1.50	71	1.50	73	1.50	75	1.50	87	1.50	87	1.50	88	1.50	79	1.50	87	1.50	71	1.50	67
1j	2.00	77	2.00	71	2.00	69	2.00	71	2.00	74	2.00	77	2.00	78	2.00	80	2.00	72	2.00	73	2.00	65	2.00	76
1k	1.50	84	1.50	79	1.50	80	1.50	77	1.50	80	1.50	80	1.50	81	1.50	82	1.50	77	1.50	81	1.50	73	1.50	70

Table 9. Nitro decarboxylation of Cinnamic acid in presence of PEG-4000 and metal nitrates under Solution phase.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1a	2.75	70	2.75	75	2.75	72	2.75	71	2.75	69	2.75	85	2.75	88	2.75	83	2.75	88	2.75	8	2.75	60	2.75	75
1b	3.00	66	3.00	70	3.00	68	3.00	62	3.00	67	3.00	78	3.00	82	3.00	85	3.00	90	3.00	88	3.00	62	3.00	77
1c	2.50	74	2.50	73	2.50	76	2.50	76	2.50	80	2.50	87	2.50	88	2.50	85	2.50	88	2.50	89	2.50	65	2.50	70
1d	2.50	78	2.50	74	2.50	76	2.50	70	2.50	77	2.50	83	2.50	86	2.50	85	2.50	84	2.50	83	2.50	62	2.50	68
1e	3.00	84	3.00	62	3.00	70	3.00	62	3.00	75	3.00	78	3.00	81	3.00	78	3.00	80	3.00	80	3.00	60	3.00	66
1f	2.50	85	2.50	60	2.50	88	2.50	78	2.50	76	2.50	87	2.50	85	2.50	87	2.50	86	2.50	90	2.50	60	2.50	68
1g	2.50	66	2.50	63	2.50	65	2.50	64	2.50	61	2.50	76	2.50	73	2.50	80	2.50	80	2.50	80	2.50	63	2.50	68
1h	3.00	67	3.00	69	3.00	68	3.00	68	3.00	68	3.00	78	3.00	77	3.00	78	3.00	76	3.00	78	3.00	64	3.00	69
1i	2.50	62	2.50	64	2.50	64	2.50	65	2.50	66	2.50	79	2.50	82	2.50	77	2.50	74	2.50	80	2.50	64	2.50	61
1j	3.00	66	3.00	62	3.00	61	3.00	64	3.00	65	3.00	68	3.00	73	3.00	69	3.00	66	3.00	66	3.00	60	3.00	70
1k	2.50	74	2.50	71	2.50	74	2.50	71	2.50	71	2.50	74	2.50	74	2.50	74	2.50	70	2.50	74	2.50	67	2.50	75

Table 10. Nitro decarboxylation of Cinnamic acid in presence of PEG-6000 and metal nitrates under Solution phase.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)	RT (hrs)	Yield (%)
1a	2.75	71	2.75	76	2.75	72	2.75	72	2.75	50	2.75	86	2.75	90	2.75	83	2.75	89	2.75	90	2.75	60	2.75	75
1b	3.00	67	3.00	70	3.00	68	3.00	66	3.00	68	3.00	80	3.00	84	3.00	85	3.00	91	3.00	90	3.00	62	3.00	77
1c	2.50	75	2.50	73	2.50	76	2.50	78	2.50	80	2.50	89	2.50	90	2.50	85	2.50	81	2.50	81	2.50	65	2.50	70
1d	2.50	79	2.50	75	2.50	77	2.50	72	2.50	78	2.50	85	2.50	88	2.50	85	2.50	85	2.50	84	2.50	62	2.50	88
1e	3.00	65	3.00	63	3.00	71	3.00	63	3.00	76	3.00	80	3.00	83	3.00	78	3.00	81	3.00	82	3.00	60	3.00	66
1f	2.50	85	2.50	81	2.50	89	2.50	75	2.50	77	2.50	89	2.50	87	2.50	87	2.50	88	2.50	92	2.50	60	2.50	68
1g	2.50	66	2.50	64	2.50	86	2.50	65	2.50	63	2.50	78	2.50	75	2.50	80	2.50	82	2.50	84	2.50	63	2.50	68
1h	3.00	67	3.00	69	3.00	69	3.00	69	3.00	70	3.00	80	3.00	79	3.00	78	3.00	78	3.00	80	3.00	64	3.00	69
1i	2.50	62	2.50	65	2.50	65	2.50	67	2.50	68	2.50	81	2.50	83	2.50	77	2.50	76	2.50	82	2.50	64	2.50	61
1j	3.00	66	3.00	63	3.00	62	3.00	66	3.00	66	3.00	70	3.00	73	3.00	69	3.00	68	3.00	68	3.00	60	3.00	70
1k	2.50	74	2.50	72	2.50	76	2.50	63	2.50	73	2.50	76	2.50	74	2.50	74	2.50	72	2.50	76	2.50	67	2.50	75

Table 11. Nitro decarboxylation of Cinnamic acid in presence of PEG-200 and metal nitrates under Solvent free conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
1a	45	80	45	82	45	81	45	81	45	78	45	85	45	86	45	83	45	87	45	87	45	60	45	75
1b	60	76	60	75	60	72	60	77	60	76	60	78	60	80	60	85	60	87	60	88	60	64	60	74
1c	30	78	30	81	30	84	30	83	30	82	30	86	30	84	30	84	30	88	30	87	30	66	30	70
1d	30	80	30	78	30	84	30	82	30	80	30	83	30	82	30	85	30	82	30	84	30	65	30	68
1e	60	74	60	72	60	78	60	77	60	78	60	79	60	78	60	78	60	75	60	80	60	64	60	66
1f	30	88	30	84	30	90	30	90	30	86	30	88	30	85	30	87	30	88	30	85	30	65	30	68
1g	30	76	30	68	30	75	30	76	30	69	30	76	30	70	30	81	30	80	30	80	30	66	30	68
1h	60	74	60	70	60	78	60	83	60	78	60	78	60	75	60	80	60	78	60	76	60	67	60	70
1i	30	72	30	70	30	76	30	78	30	75	30	79	30	80	30	78	30	76	30	78	30	68	30	64
1j	60	78	60	68	60	68	60	76	60	76	60	68	60	70	60	70	60	65	60	66	60	66	60	72
1k	30	82	30	81	30	88	30	87	30	84	30	76	30	75	30	76	30	73	30	76	30	78	30	68

Table 12. Nitro decarboxylation of Cinnamic acid in presence of PEG-300 and metal nitrates under Solvent free conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
1a	45	90	45	88	45	85	45	86	45	80	45	88	45	88	45	86	45	90	45	90	45	75	45	85
1b	60	86	60	80	60	76	60	80	60	78	60	83	60	82	60	88	60	88	60	88	60	74	60	84
1c	30	88	30	86	30	88	30	88	30	84	30	87	30	85	30	86	30	88	30	86	30	78	30	80
1d	30	86	30	83	30	88	30	86	30	82	30	85	30	84	30	88	30	82	30	85	30	76	30	78
1e	60	76	60	76	60	82	60	80	60	80	60	80	60	80	60	82	60	76	60	80	60	75	60	75
1f	30	92	30	90	30	90	30	90	30	88	30	88	30	86	30	90	30	88	30	86	30	76	30	78
1g	30	80	30	72	30	78	30	78	30	71	30	78	30	72	30	84	30	82	30	82	30	78	30	76
1h	60	78	60	75	60	82	60	86	60	80	60	78	60	76	60	84	60	80	60	78	60	78	60	78
1i	30	76	30	75	30	80	30	82	30	78	30	80	30	82	30	82	30	78	30	82	30	76	30	75
1j	60	82	60	72	60	72	60	76	60	78	60	70	60	72	60	77	60	70	60	65	60	76	60	76
1k	30	86	30	86	30	90	30	88	30	86	30	78	30	76	30	80	30	76	30	80	30	80	30	80

Table 13. Nitro decarboxylation of Cinnamic acid in presence of PEG-400 and metal nitrates under Solvent free conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
1a	45	84	45	85	45	82	45	84	45	85	45	86	45	90	45	84	45	90	45	88	45	70	45	80
1b	60	82	60	77	60	73	60	78	60	78	60	81	60	80	60	86	60	86	60	86	60	70	60	80
1c	30	84	30	83	30	85	30	86	30	82	30	85	30	82	30	83	30	85	30	85	30	74	30	75
1d	30	82	30	80	30	84	30	84	30	80	30	82	30	80	30	85	30	80	30	82	30	72	30	72
1e	60	72	60	73	60	80	60	78	60	82	60	78	60	82	60	80	60	72	60	78	60	70	60	70
1f	30	88	30	87	30	86	30	86	30	88	30	86	30	85	30	90	30	86	30	83	30	72	30	73
1g	30	76	30	70	30	75	30	76	30	70	30	76	30	70	30	82	30	80	30	80	30	73	30	71
1h	60	75	60	72	60	80	60	84	60	80	60	75	60	74	60	80	60	78	60	76	60	74	60	73
1i	30	72	30	72	30	78	30	80	30	78	30	78	30	80	30	80	30	76	30	80	30	72	30	70
1j	60	78	60	68	60	78	60	74	60	78	60	68	60	70	60	74	60	68	60	62	60	72	60	74
1k	30	82	30	82	30	88	30	85	30	86	30	76	30	75	30	76	30	74	30	78	30	76	30	75

Table 14. Nitro decarboxylation of Cinnamic acid in presence of PEG-600 and metal nitrates under Solvent free conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
1a	45	85	45	86	45	84	45	84	45	80	45	88	45	88	45	85	45	90	45	88	45	74	45	82
1b	60	83	60	78	60	74	60	78	60	73	60	82	60	78	60	86	60	84	60	85	60	72	60	82
1c	30	85	30	84	30	84	30	84	30	78	30	84	30	80	30	84	30	86	30	84	30	75	30	76
1d	30	83	30	80	30	85	30	82	30	75	30	82	30	78	30	86	30	80	30	82	30	72	30	74
1e	60	73	60	74	60	82	60	78	60	78	60	78	60	80	60	80	60	74	60	78	60	70	60	72
1f	30	88	30	86	30	86	30	86	30	85	30	86	30	82	30	90	30	86	30	84	30	75	30	75
1g	30	77	30	72	30	76	30	76	30	68	30	77	30	70	30	82	30	80	30	80	30	73	30	72
1h	60	76	60	74	60	82	60	84	60	75	60	76	60	72	60	82	60	78	60	76	60	74	60	73
1i	30	73	30	74	30	80	30	80	30	76	30	78	30	80	30	80	30	74	30	80	30	72	30	70
1j	60	78	60	68	60	78	60	76	60	76	60	70	60	72	60	75	60	68	60	64	60	74	60	74
1k	30	82	30	82	30	88	30	86	30	84	30	78	30	74	30	76	30	75	30	78	30	80	30	76

Table 15. Nitro decarboxylation of Cinnamic acid in presence of PEG-4000 and metal nitrates under Solvent free conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
1a	90	82	90	84	90	85	90	80	90	78	90	82	90	84	90	83	90	86	90	85	90	75	90	78
1b	120	81	120	76	120	74	120	74	120	71	120	78	120	74	120	84	120	80	120	82	120	73	120	78
1c	60	82	60	82	60	83	60	80	60	76	60	78	60	76	60	82	60	82	60	80	60	76	60	72
1d	60	81	60	80	60	84	60	80	60	75	60	76	60	75	60	82	60	76	60	80	60	73	60	70
1e	120	70	120	72	120	82	120	74	120	76	120	70	120	76	120	78	120	70	120	72	120	71	120	68
1f	60	86	60	85	60	86	60	84	60	82	60	80	60	79	60	88	60	82	60	80	60	76	60	72
1g	60	74	60	70	60	75	60	76	60	68	60	71	60	65	60	80	60	76	60	78	60	74	60	70
1h	120	75	120	72	120	80	120	80	120	72	120	70	120	78	120	80	120	74	120	75	120	75	120	71
1i	60	71	60	72	60	80	60	78	60	75	60	68	60	78	60	78	60	70	60	78	60	73	60	70
1j	120	76	120	68	120	78	120	72	120	76	120	65	120	68	120	72	120	65	120	62	120	75	120	75
1k	60	80	60	80	60	86	60	84	60	82	60	70	60	70	60	72	60	72	60	75	60	80	60	77

Table 16. Nitro decarboxylation of Cinnamic acid in presence of PEG-6000 and metal nitrates under Solvent free conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)	RT (min)	Yield (%)
1a	90	78	90	80	90	82	90	80	90	78	90	86	90	85	90	84	90	86	90	86	90	80	90	78
1b	120	77	120	72	120	71	120	74	120	72	120	80	120	74	120	84	120	80	120	83	120	78	120	76
1c	60	78	60	80	60	80	60	82	60	76	60	80	60	76	60	82	60	82	60	82	60	78	60	74
1d	60	78	60	78	60	82	60	82	60	74	60	78	60	76	60	80	60	76	60	80	60	76	60	72
1e	120	68	120	70	120	80	120	75	120	76	120	72	120	78	120	76	120	72	120	74	120	76	120	68
1f	60	85	60	82	60	83	60	84	60	82	60	82	60	80	60	88	60	82	60	81	60	78	60	74
1g	60	72	60	68	60	72	60	75	60	68	60	75	60	66	60	82	60	76	60	78	60	75	60	72
1h	120	72	120	70	120	78	120	80	120	74	120	72	120	78	120	82	120	75	120	76	120	76	120	72
1i	60	68	60	70	60	78	60	78	60	76	60	70	60	80	60	78	60	72	60	78	60	76	60	74
1j	120	73	120	65	120	80	120	74	120	76	120	68	120	68	120	74	120	66	120	64	120	78	120	76
1k	60	80	60	78	60	85	60	82	60	82	60	72	60	72	60	76	60	74	60	76	60	80	60	78

Table 17. Nitro decarboxylation of Cinnamic acid in presence of PEG-200 and metal nitrates under microwave conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)
1a	180	70	180	77	180	77	180	78	180	74	180	82	180	83	180	80	180	84	180	83	180	62	180	75
1b	180	66	180	70	180	68	180	73	180	72	180	75	180	77	180	82	180	84	180	85	180	64	180	74
1c	180	88	180	66	180	80	180	79	180	78	180	82	180	81	180	81	180	85	180	82	180	66	180	70
1d	180	70	180	73	180	80	180	78	180	76	180	80	180	79	180	82	180	78	180	81	180	65	180	68
1e	180	64	180	67	180	74	180	73	180	74	180	75	180	75	180	75	180	72	180	78	180	64	180	66
1f	120	78	120	80	120	86	120	85	120	82	120	85	120	82	120	84	120	85	120	82	120	66	120	70
1g	180	66	180	63	180	71	180	73	180	65	180	73	180	66	180	78	180	78	180	77	180	66	180	68
1h	200	64	200	65	200	74	200	80	200	74	200	75	200	72	200	78	200	75	200	73	200	68	200	70
1i	180	62	180	65	180	72	180	74	180	72	180	76	180	76	180	75	180	73	180	75	180	68	180	65
1j	240	68	240	63	240	64	240	72	240	72	240	65	240	67	240	67	240	64	240	64	240	65	240	72
1k	200	72	200	68	200	84	200	82	200	80	200	73	200	72	200	73	200	70	200	75	200	78	200	70

Table 18. Nitro decarboxylation of Cinnamic acid in presence of PEG-300 and metal nitrates under microwave conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)
1a	90	86	90	89	90	86	90	84	90	82	90	88	90	90	90	86	90	86	90	90	90	76	90	80
1b	120	82	120	80	120	76	120	80	120	78	120	84	120	84	120	88	120	85	120	86	120	74	120	82
1c	90	84	90	85	90	86	90	86	90	82	90	85	90	82	90	86	90	86	90	84	90	78	90	78
1d	60	82	60	84	60	88	60	86	60	80	60	86	60	85	60	86	60	80	60	82	60	75	60	76
1e	90	72	90	76	90	84	90	82	90	82	90	80	90	80	90	84	90	78	90	78	90	75	90	72
1f	60	90	60	90	60	90	60	90	60	88	60	86	60	85	60	90	60	88	60	86	60	78	60	76
1g	120	78	120	74	120	78	120	78	120	70	120	78	120	72	120	84	120	80	120	80	120	76	120	74
1h	120	76	120	75	120	80	120	86	120	80	120	76	120	75	120	80	120	78	120	76	120	78	120	75
1i	120	76	120	75	120	80	120	80	120	78	120	80	120	82	120	82	120	76	120	80	120	76	120	72
1j	180	82	180	70	180	72	180	76	180	76	180	72	180	74	180	76	180	72	180	68	180	76	180	70
1k	120	86	120	85	120	86	120	88	120	85	120	78	120	78	120	78	120	78	120	80	120	80	120	76

Table 19. Nitro decarboxylation of Cinnamic acid in presence of PEG-400 and metal nitrates under microwave conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)
1a	90	82	90	84	90	83	90	85	90	82	90	85	90	88	90	82	90	85	90	88	90	70	90	80
1b	120	80	120	76	120	72	120	78	120	78	120	82	120	78	120	84	120	82	120	85	120	70	120	82
1c	90	82	90	82	90	84	90	85	90	80	90	84	90	80	90	81	90	81	90	84	90	74	90	75
1d	60	80	60	80	60	82	60	84	60	82	60	81	60	78	60	83	60	76	60	80	60	72	60	74
1e	90	70	90	72	90	78	90	78	90	78	90	76	90	80	90	78	90	68	90	78	90	70	90	70
1f	60	88	60	86	60	85	60	86	60	88	60	84	60	84	60	88	60	84	60	84	60	74	60	76
1g	120	74	120	68	120	74	120	75	120	70	120	78	120	70	120	80	120	76	120	80	120	73	120	71
1h	120	72	120	70	120	78	120	82	120	82	120	76	120	74	120	78	120	75	120	75	120	74	120	73
1i	120	70	120	70	120	76	120	80	120	78	120	78	120	80	120	80	120	72	120	80	120	72	120	70
1j	180	76	180	66	180	75	180	75	180	76	180	68	180	70	180	72	180	66	180	64	180	70	180	72
1k	120	80	120	80	120	84	120	84	120	85	120	78	120	76	120	74	120	75	120	78	120	76	120	76

Table 20. Nitro decarboxylation of Cinnamic acid in presence of PEG-600 and metal nitrates under microwave conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)
1a	90	84	90	85	90	84	90	85	90	80	90	86	90	86	90	84	90	90	90	86	90	74	90	80
1b	120	82	120	76	120	75	120	78	120	72	120	80	120	76	120	85	120	82	120	83	120	76	120	82
1c	90	83	90	82	90	84	90	82	90	78	90	82	90	78	90	82	90	84	90	82	90	75	90	78
1d	60	82	60	79	60	86	60	80	60	74	60	78	60	76	60	84	60	80	60	80	60	72	60	76
1e	90	74	90	72	90	80	90	78	90	78	90	76	90	78	90	80	90	74	90	76	90	70	90	72
1f	60	88	60	85	60	86	60	86	60	84	60	83	60	80	60	90	60	85	60	84	60	76	60	78
1g	120	76	120	70	120	78	120	76	120	68	120	76	120	68	120	80	120	80	120	78	120	73	120	72
1h	120	75	120	72	120	82	120	82	120	75	120	75	120	70	120	82	120	78	120	75	120	75	120	73
1i	120	74	120	72	120	80	120	80	120	76	120	76	120	78	120	78	120	75	120	78	120	72	120	70
1j	180	76	180	66	180	76	180	75	180	78	180	72	180	70	180	74	180	68	180	66	180	74	180	78
1k	120	80	120	80	120	86	120	84	120	82	120	76	120	76	120	75	120	76	120	78	120	80	120	80

Table 21. Nitro decarboxylation of Cinnamic acid in presence of PEG-4000 and metal nitrates under microwave conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		Th $(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)
1a	180	80	180	82	180	85	180	80	180	78	180	80	180	82	180	82	180	85	180	85	180	78	180	80
1b	180	78	180	74	180	74	180	74	180	72	180	76	180	72	180	82	180	80	180	80	180	74	180	78
1c	180	80	180	80	180	80	180	79	180	76	180	78	180	74	180	80	180	82	180	82	180	75	180	75
1d	120	78	120	78	120	82	120	81	120	75	120	75	120	72	120	79	120	76	120	78	120	72	120	70
1e	180	72	180	70	180	80	180	74	180	76	180	70	180	75	180	78	180	70	180	74	180	70	180	68
1f	120	85	120	86	120	82	120	85	120	80	120	80	120	78	120	86	120	82	120	80	120	78	120	74
1g	180	72	180	68	180	72	180	75	180	68	180	69	180	65	180	78	180	76	180	78	180	74	180	70
1h	220	74	220	70	220	78	220	80	220	72	220	70	220	76	220	80	220	74	220	75	220	75	220	71
1i	180	72	180	72	180	80	180	78	180	75	180	68	180	78	180	78	180	70	180	78	180	74	180	70
1j	240	74	240	70	240	76	240	74	240	70	240	66	240	68	240	75	240	68	240	68	240	75	240	76
1k	220	80	220	80	220	82	220	82	220	80	220	70	220	74	220	76	220	74	220	76	220	80	220	78

Table 22. Nitro decarboxylation of Cinnamic acid in presence of PEG-6000 and metal nitrates under microwave conditions.

Entry	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k
Substrate	CA	4-ClCA	4-OMeCA	4-MeCA	4-NO_2CA	4-OHCA	AA	CRA	3-PhCRA	2-ClCA	2-MeCA

Entry	$Ni(NO_3)_2$		$Zn(NO_3)_2$		$ZrO(NO_3)_2$		$Cd(NO_3)_2$		$Hg(NO_3)_2$		$Mg(NO_3)_2$		$Sr(NO_3)_2$		$Al(NO_3)_3$		$UO_2(NO_3)_2$		$Th(NO_3)_2$		$AgNO_3$		NH_4NO_3	
	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)	RT (sec)	Yield (%)
1a	180	82	180	80	180	84	180	82	180	82	180	85	180	84	180	84	180	86	180	86	180	80	180	80
1b	180	77	180	76	180	73	180	72	180	74	180	82	180	73	180	84	180	81	180	84	180	75	180	76
1c	180	80	180	82	180	82	180	80	180	78	180	80	180	75	180	80	180	84	180	82	180	78	180	78
1d	120	78	120	78	120	80	120	80	120	76	120	78	120	76	120	78	120	76	120	80	120	76	120	72
1e	180	68	180	72	180	78	180	76	180	75	180	74	180	78	180	75	180	74	180	75	180	74	180	68
1f	120	85	120	84	120	85	120	86	120	82	120	85	120	80	120	88	120	84	120	82	120	78	120	80
1g	180	72	180	68	180	70	180	75	180	70	180	76	180	68	180	80	180	76	180	78	180	75	180	72
1h	220	72	220	70	220	78	220	80	220	74	220	74	220	78	220	82	220	75	220	76	220	76	220	74
1i	180	68	180	72	180	78	180	78	180	75	180	70	180	80	180	78	180	74	180	78	180	76	180	76
1j	240	73	240	68	240	80	240	76	240	78	240	72	240	70	240	75	240	68	240	68	240	78	240	76
1k	220	82	220	82	220	83	220	80	220	80	220	75	220	76	220	80	220	78	220	80	220	80	220	78

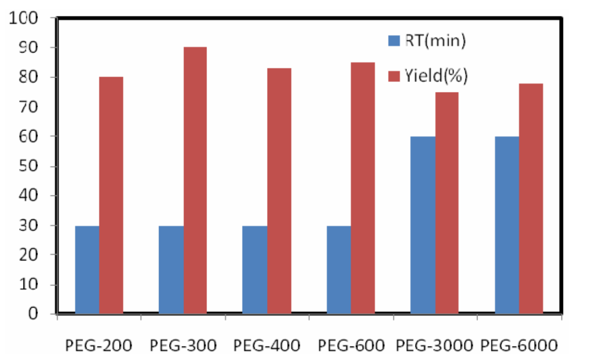


Figure 1. Effect of different Poly ethylene glycols (PEG) on RT versus Yield (%) in presence of Nickel Nitrate.

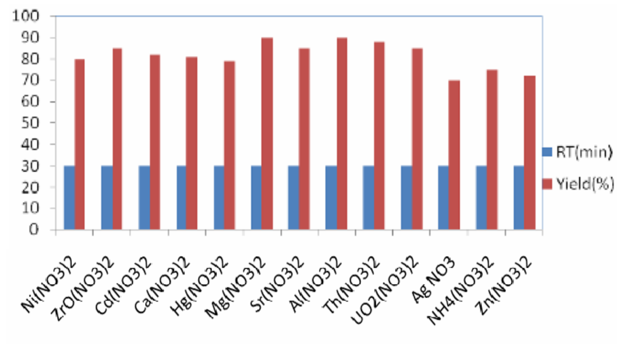
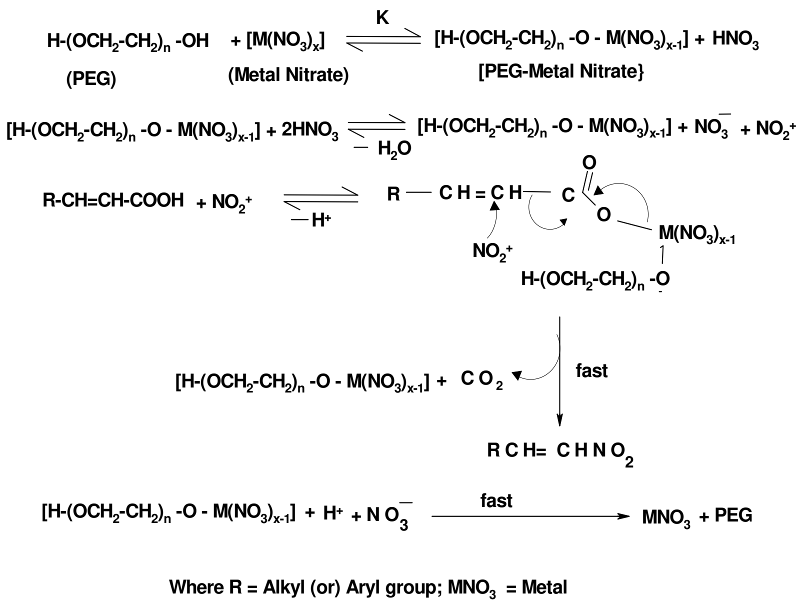


Figure 2. Effect of different Metal nitrates on RT versus Yield (%) in presence of PEG-300.

PEG-300 has been found to be much more effective than other PEGs. The catalytic activity was found to be in the increasing order: PEG-300 > PEG-400 > PEG-600 > PEG-200. The plot of RT versus PEG type indicated that reaction time decreases with an increase in molecular weight of PEG as could be seen from the data presented in **Figure 1**.

A comparative data profile given in **Figure 2** clearly shows remarkable rate enhancements in presence of a variety of metal nitrates.

However, the metal nitrates belonging to s and p -blocks such as $Mg(NO_3)_2$, $Sr(NO_3)_2$, $Al(NO_3)_3$, found to be much more reactive than other metal nitrates, which could be attributed to their hardness compared to d- and f-block metal nitrate species. Similar trends are shown in other systems. When PEG is added to the reaction system Metal nitrate is capable to form PEG bound Metal nitrates due to complexation according to the following reaction. The species thus formed could act as an effecttive catalyst to accelerate the reaction by generating nitronium ion. Nitronium thus formed converts Cinnamic acid into beta nitro styrene as shown in the following sequence of steps shown in **Scheme 3**.



Scheme 3. The formation of Nitronium converts Cinnamic acid into beta nitro styrene.

4. Conclusions

Poly ethylene glycols (PEG-200, 300, 400, 600, 4000 and 6000) supported reactions were conducted with certain α, β-unsaturated acids in presence of metal nitrates under mineral acid free and solvent free microwave irradiated (MWI) and grinding (mortar –pestle) conditions. The aromatic acids underwent nitro decarboxylation and afforded β-nitro styrene derivatives in very good yield while α, β-unsaturated aliphatic carboxylic acids gave corresponding nitro derivatives. Addition of PEG accelerated the rate of the reaction enormously. Reaction times substantially decreased from several hours to few minutes followed by highly significant increase in the product yield. Among the several PEGs, PEG-300 has been found to be much more effective than other PEGs.

5. Electronic Supplementary Material

Elaborated data pertains to nitro decarboxylation of certain α, β-unsaturated acids in presence of metal nitrates under mineral acid free and solvent free MWI and grinding (mortar-pestle) conditions are presented separately in **Tables 5-22**, which is furnished as supplementary data.

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