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Green Synthesis of N-benzylidene-5-(styryl)-1,3,4-thiadiazol-2-amine and 4-(2-(5-(benzylideneamino)-1,3,4-thiadiazol-2-yl)vinyl)-2-methoxyphenol in Ionic Liquid

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ABSTRACT

An eco-friendly synthesis of N-benzylidene-5-(styryl)-1,3,4-thiadiazol-2-amine and 4-(2-(5-(benzylideneamino)-1,3,4-thiadiazol-2-yl)vinyl)-2-methoxyphenol starting from easily available reactant molecule. In the first step we synthesized substituted cinnamic acid and ferulic acid 3 from various types of aldehyde with malonic acid catalyzed by sodium acetate. In second step of reaction, multicomponent approach cyclization followed by Schiff base formation 6 a-j from prepared acids 3 a-j, thiosemicarbazide and aldehydes, solvent free catalyzed by ionic liquid [Et₃N H₂SO₄] under conventional method.

Keywords: Ionic liquid, Sodium acetate, Thiosemicarbazide, 1,3,4-thiadiazol, Conventional method

INTRODUCTION

Sulfur and nitrogen containing heterocyclic compound particular 1,3,4-thiadiazole and its derivatives endure to a great interest of researchers owing to their great pharmaceutical and industrial fields. 1,3,4-thiadiazole was first described in 1882 by Fischer, Busch and his coworkers. The true environment of the ring system was established first in 1956 by Goerdler et al [1]. The beginning of sulphur drugs and the later discovery of mesoionic compound greatly accelerated the rate of progress in the field of thiadiazole. It carrying mercapto and amino substituents can exist in many tautomeric forms. The 1,3,4-thiadiazoles are conveniently divided into three subclasses: (I) Aromatic systems which include the neutral thiadiazole 1 and constitute a major part of this review. (II) Mesoionic systems 2 which is defined as five-membered heterocycles which are not covalent or polar and possess a sextet of electrons in association with the five atoms comprising the ring [2]. (III) Non aromatic systems such as the 1,3,4-thiadiazolines 3, 4 and the tetrahydro 1,3,4-thiadiazolidines 5 (Figure 1).

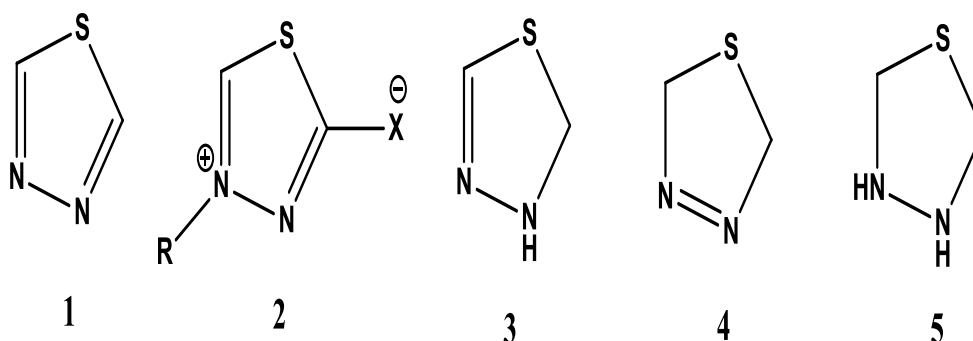


Figure 1: Mesoionic structure of 1,3,4-thiadiazole

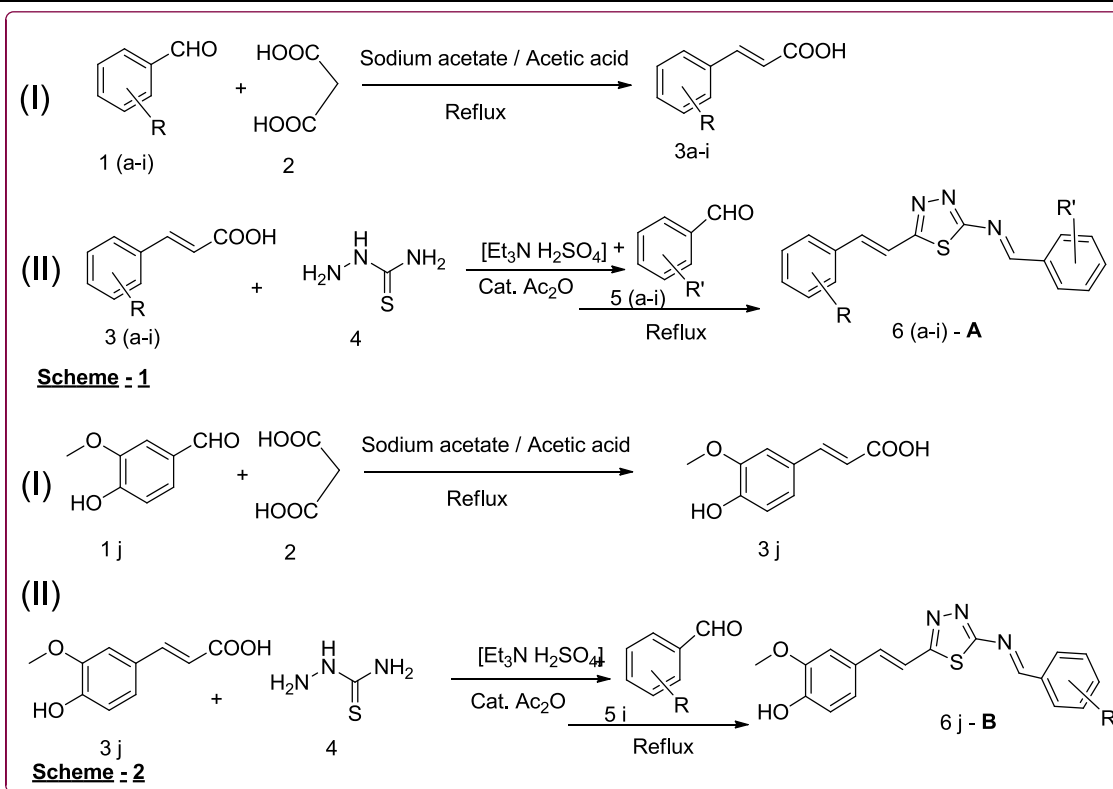


Figure 2: Synthesis of N-benzylidene-5-(styryl)-1,3,4-thiadiazol-2-amine and 4-(2-(5-(N-benzylideneamino)-1,3,4-thiadiazol-2-yl)vinyl)-2-methoxyphenol

Thiadiazole derivatives possessed a wide range of therapeutic activities such as antimicrobial [3], anti-fungal [4], antileishmanial [5], antimycobacterial [6], analgesic, anti-inflammatory [7] antidepressant [8], antipsychotic [9] and anticonvulsant [9,10]. 1,3,4-thiadiazole derivatives exhibited interesting *in vitro* [11-13] and *in vivo* [14-17] antitumor activities. Inhibition of DNA and RNA synthesis specifically without appreciably affecting protein synthesis [18], inhibition of carbonic anhydrase [19], phosphodiesterase-7 [20], histone deacetylase [21] or as adenosine A3 receptor antagonists [22]. Analgesic, anti-inflammatory and anti-bacterial activity of Schiff Bases of 2-amino-5-aryl-1,3,4-thiadiazoles [23]. In past, some 1,3,4-thiadiazole and its derivatives has been studied and investigated [24-36].

The interesting properties of ionic liquids room-temperature, organic salts that are liquid temperature below 100°C, have received considerable attention as substitutes for volatile organic solvents, non-flammable, non-volatile and recyclable, they are classified as green solvents. Owing to their remarkable properties, such as outstanding solvating potential, thermal stability [37,38] and their tunable properties by suitable choices of cations and anions [39]. ILs as they simultaneously possess the proton acidity and the characteristic properties of an ionic liquid [40,41]. Keeping in mind the biological significance of 4-((E)-2-(5-(E)-benzylideneamino)-1,3,4-thiadiazol-2-yl)vinyl)-2-methoxyphenol and the utility of ionic liquids for organic transformation [42-61], and in continuation of our earlier green approach research work [37] to exploring this research for the synthesis of Schiff base of 2-amino 1,3,4-thiadiazole containing Cinnamic and ferulic acid Figure 2. Herein we report synthesis of cinnamic acid and ferulic acid containing 1,3,4-thiadiazol derivatives using sodium acetate, acetic acid and [Et₃N H₂SO₄] ionic liquid as a catalyst (Figure 2).

EXPERIMENTAL SECTION

Materials

The chemicals with high purity, playing important role in the present synthesis of functionalized 1,3,4-thiadiazole starting from easily available cinnamic acid, aromatic acid, malonic acid and various aromatic aldehyde, amine in presence of ionic liquid.

The ionic liquid [Et₃N H₂SO₄] is prepared using reported method [38]. An appropriate molar proportion of starting materials was taken and the protocols of standard techniques were followed for the *in situ* multi-component synthesis of acid containing Schiff base of 2-amino 1,3,4-thiadiazole (Figure 2). Melting points of synthesized product were recorded with the help of capillary tube and thermometer apparatus and were uncorrected. The IR spectra were recorded on a Fourier Transform Infra-Red (FTIR) spectroscopy (Bruker). ¹H-NMR spectra were recorded on a 400 MHz Bruker spectrometer in solvent Deuterated Dimethyl Sulfoxide (DMSO-d₆) and Deuterated Chloroform (CDCl₃) as Part Per Million (ppm) downfield from a Tetramethylsilane (TMS) internal standard.

Preparation of ionic liquid

Procedure for the synthesis of triethyl ammonium hydrogen sulfate [Et₃NH][HSO₄]ILs

In a small round-bottom flask (100 ml), immersed in water-bath and fitted with a reflux condenser. Sulfuric acid, (1.96 g, 0.02 mol) was drop wise added into triethylamine (2.02 g, 0.02 mol) at 60-65°C for one hour. After completion of addition, the reaction mixture was stirred for an additional period of one hour at 65-70°C. The residue was heated and removed water molecule from reaction mixture under a high vacuum until the weight of the residue remained constant. The obtained yield of [Et₃NH][HSO₄] was 96%. Having characterization data: FTIR cm⁻¹ 3022 (N-H stretch), 2818 (C-H stretch), 1236 (C-N stretch); ¹H-NMR (400 MHz, DMSO-d₆), δ(ppm)=1.13-1.27 (t, 9H, 3×9 CH₃), 3.02-3.18 (q, 6H, 3×9 CH₂) and 8.84 (s, 1H, NH); ¹³C-NMR (75 MHz, DMSO-d₆), δ (ppm)=11.06 (CH₃) and 52.8 (CH₂).

General procedure for the synthesis of compound 3

A mixture of malonic acid (0.073 mol) in of sodium acetate and acetic acid (0.073 mol) (1:1) were mechanically stirr become to homogeneous (sticky solid) then substituted aromatic aldehyde (0.073 mol) was added in the reaction mixture and were reflux 85-90 min (TLC). The reaction became a honey-colored viscous liquid with the formation of bubbles during the reaction. The viscous liquid quickly solidified on cooling at room temperature to give a solid. The product were isolated, by dissolved in a minimum amount of ethanol and glacial acetic acid and were filtered and washed (three-four time) by cold 95% ethanol and instantly purified by recrystallization or air dried.

(E)-3-(4-methoxyphenyl)acrylic acid (3): A spectroscopic quality product was obtained by purifying the compound through recrystallization from 98% or absolute ethanol. off-white to orange crystalline solid (needles); Yield: 93%; Melting point, 180-182°C; IR (FTIR): 2550 cm⁻¹, 1672 cm⁻¹, 821 cm⁻¹ (δ ppm); ¹H-NMR (DMSO-d₆, 90 MHz, δ ppm)=3.81 (s, 3H), 6.40 (d, *J*=16 Hz, 1H), 6.98 (d, *J*=8.7 Hz, 2H, CH), 7.58 (d, *J*=16 Hz, 1H) 7.65 (d, *J*=8.7 Hz, 2H, CH); ¹³C-NMR (75 MHz, DMSO-d₆), δ =167.9, 161.0, 143.6, 130.1, 126.9, 116.5, 114.5, 55.2.; Mol. Formula: C₁₀H₁₀O₃; MS (ESI): *m/z* (%) 179.06 (M+H); HRMS-EI: found: 178.0560, calculated: 178.0630.

3-(3-Hydroxy-4-methoxy-phenyl)-acrylic acid/Ferulic acid (3): Yield: 93%; Melting point: 171-172°C; IR (FTIR): 1060 cm⁻¹, 1490 cm⁻¹, 1628 cm⁻¹, 2802 cm⁻¹, 2834 cm⁻¹, 2845 cm⁻¹, 2916 cm⁻¹, 2935 cm⁻¹, 2970 cm⁻¹, 3025 cm⁻¹, 3260 cm⁻¹; ¹H-NMR (200 MHz, DMSO-d₆), δ =12.17 (brs, 1H), 9.15 (brs, 1H), 7.43 (dd, *J*=15.8, 6.6 Hz, 1H), 6.99 (m, 3H), 6.23 (dd, *J*=15.8, 6.8 Hz, 1H), 3.79 ppm (s, 3H); ¹³C-NMR (75 MHz, DMSO-d₆), δ =168.29, 150.25, 147.09, 144.67, 127.53, 121.45, 116.70, 114.53, 112.33, 55.96; Formula: C₁₀H₁₀O₄; MS (ESI): *m/z* (%) 195.06 (M+H); HRMS-EI: found: 194.0500., calculated: 194.0570.

General procedure for the synthesis of compound 6

A mixture substituted cinnamic acid or ferulic acid (0.1 mol), Thiosemicarbazide (0.1 mol) in [Et₃N H₂SO₄] ILs (20 mol %) and catalytic amount of acetic anhydride were added and heat at 80°C (TLC). To this Aromatic aldehyde (0.1 mol) was added and continuous heated at 85-90°C for the appropriate time. Progress the reaction was monitored on TLC. After completion of reaction the reaction mixture was extracted with ethyl acetate/Et₂O, the ethereal layer was concentrated by rotary evaporator and the crude product was purified by the preparative thin-layer chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluent to provide the corresponding pure products 6 (83-90%)

(E)-N-benzylidene-5-(E-styryl)-1,3,4-thiadiazol-2-amine (6a): Yield: 90%; IR (FTIR): 1040 cm⁻¹, 1470 cm⁻¹, 1545 cm⁻¹, 1560 cm⁻¹, 1628 cm⁻¹, 2802 cm⁻¹, 2832 cm⁻¹, 2843 cm⁻¹, 2928 cm⁻¹, 2932 cm⁻¹, 2970 cm⁻¹, 3025 cm⁻¹, 3078 cm⁻¹, 3260 cm⁻¹; ¹H-NMR (200 MHz, DMSO-d₆), δ =6.96 (2H, *dd*), 8.34 (1H, *s*), 7.62 (2H, *d*), 7.31-7.42 (3H, *m*), 7.53-7.82 (5H, *m*); ¹³C-NMR (75 MHz, DMSO-d₆), δ =6.95, 6.99, 7.33, 7.40, 7.40, 7.60, 7.60, 7.52, 7.52, 7.52, 7.83, 7.83, 8.36; Formula: C₁₇H₁₃N₃S; MS (ESI): *m/z* (%) 292.08 (M+H); HRMS-EI: found: 291.0780, calculated: 291.0830.

4-(E)-2-(5-(E)-benzylideneamino)-1,3,4-thiadiazol-2-yl)vinyl)-2-methoxyphenol (6j): Yield: 90%; IR (FTIR): 1040 cm⁻¹, 1470 cm⁻¹, 1545 cm⁻¹, 1560 cm⁻¹, 1628 cm⁻¹, 2802 cm⁻¹, 2832 cm⁻¹, 2843 cm⁻¹, 2928 cm⁻¹, 2932 cm⁻¹, 2970 cm⁻¹, 3025 cm⁻¹, 3078 cm⁻¹, 3260 cm⁻¹; ¹H-NMR (200 MHz, DMSO-d₆), δ =6.96 (2H, *dd*), 8.34 (1H, *s*), 7.15 (1H, *s*), 7.11 (1H, *d*), 6.97 (1H, *d*), 5.34 (1H, *s*), 3.81 (3H, *s*), 7.51-7.83 (5H, *m*); ¹³C-NMR (75 MHz, DMSO-d₆), δ =3.83, 5.35, 6.95, 6.99, 6.99, 7.12, 7.16, 7.52, 7.52, 7.52, 7.83, 7.83, 8.36.; Formula: C₁₈H₁₅N₃O₂S; MS (ESI): *m/z* (%) 338.08 (M+H); HRMS-EI: found: 337.0794, calculated: 337.0854.

RESULTS AND DISCUSSION

Aim to prepare multi-component synthesis of acid containing Schiff base of 2-amino 1,3,4-thiadiazole (Figure 2) starting from easily available chemicals.

At first, we optimized different base catalyst and catalyst free Table 1 for the model reaction of malonic acid (0.073 mol) and benzaldehyde (0.073 mol) in different bases such as Et₃N, pyridine, piperidine, NaOAc, NaHCO₃ and mixture of NaOAc+AcOH buffer solution under reflux condition Table 1. Herein we observed that in sodium acetate gave better yield at 100 min (Table 1, entry 5). If we added acetic acid in sodium acetate, the yield of products was increases as excellent in 90 min (Table 1). Thus all the chalcones derivatives were prepared from various aromatic aldehyde and vanillin in the mixture of sodium acetate and acetic acid (1:1) under reflux condition Table 2.

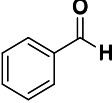

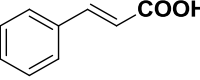
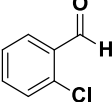

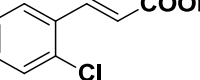
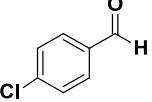

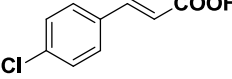
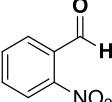
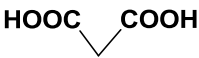
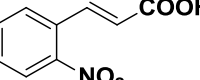
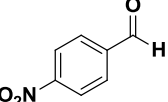

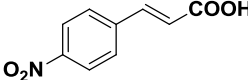
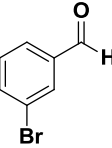
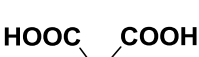
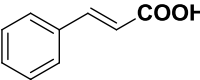
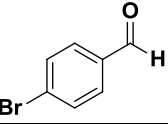
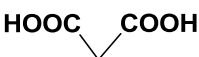
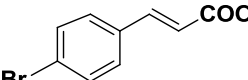
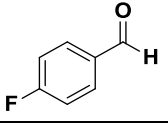

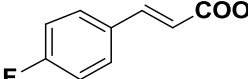
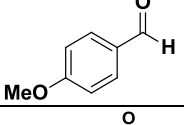

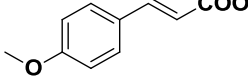
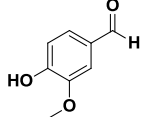
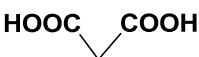
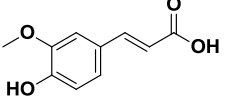
Secondly, we screened various solvent like MeOH, EtOH, Tert. BuOH, Iso-pr. alcohol, H₂O, THF, Toluene, CH₃CN and also solvent free condition Table 3 for the model multicomponent reaction of cinnamic acid or ferulic acid (0.1 mol), thiosemicarbazide (0.1 mol), aromatic aldehyde (0.1 mol) in [Et₃N H₂SO₄] ILs (20 mol%) and catalytic amount of acetic anhydride were heated at 80°C to reflux condition for the appropriate time (Table 3). Herein, we observed that at solvent free condition gave well to excellent yield with increasing temperature at 60-90 or 100°C (Table 3 entry 9-13). Thus, all the derivatives of ferulic and cinnamic acids were synthesized under solvent free condition at 90°C in [Et₃N H₂SO₄] ILs (20 mol %) at 50-55 min (Table 4). Progress the reaction was monitored on TLC. After completion of reaction the reaction mixture was extracted with ethyl acetate/Et₂O, the ethereal layer was concentrated by rotary evaporator and the crude product was purified by the preparative thin-layer chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluent to provide the corresponding pure products 6 (83-90%) shown in Table 4.

Table 1: Optimization of catalyst for the synthesis of compound 3a

Entry	Catalyst	Time (min)			Yield ^a (%)		
		I	II	III	I	II	III
1	Without	50	80	120	0	0	0
2	Et ₃ N	50	80	100	0	40	40
3	Pyridine	50	80	100	0	48	50
4	Piperidine	50	80	100	0	35	40
5	NaOAc	50	80	100	0	52	68
6	NaOAc+AcOH	50	80	90	0	78	93
7	NaHCO ₃	50	80	100	0	38	40

^aReaction Condition: Malonic acid (0.073 mol); sodium acetate and acetic acid (0.073 mol) (1:1) were mechanically stirr become to homogeneous (sticky solid) then substituted aromatic aldehyde (0.073 mol) was added and were reflux

Table 2: Synthesis of compound 3(a-j)

S. No.	Reactant	Reactant	Product	Time (min)	Yield ^a (%)
1				90	93
2				92	92
3				90	92
4				95	90
5				90	93
6				95	90
7				95	92
8				95	90
9				90	93
10				90	93

^aReaction Condition: Malonic acid (0.073 mol), sodium acetate and acetic acid (0.073 mol) (1:1) were mechanically stir become to homogeneous (sticky solid) then substituted aromatic aldehyde (0.073 mol) was added and were reflux.; Yield: 90-93%

Table 3: Optimization of solvent for the synthesis of compound 6

S. No.	Solvent	Temperature (°C)	Yield ^b (%)
1.	MeOH	Reflux	45
2.	EtOH	Reflux	48
3.	Tert-BuOH	Reflux	53
4.	Iso-pr. alcohol	Reflux	50
5.	H ₂ O	Reflux	30
6.	THF	Reflux	38
7.	Toluene	Reflux	53
8.	CH ₃ CN	Reflux	49
9.	Solvent free	60	50
10.	Solvent free	70	68
11.	Solvent free	80	82
12.	Solvent free	90	90
13.	Solvent free	100	90

^bReaction condition: Cinnamic acid or ferulic acid (0.1 mol); Thiosemicarbazide (0.1 mol) in [Et₃N H₂SO₄] ILs (20 mol %) and catalytic amount of acetic anhydride were added and heat to (TLC); To this Aromatic aldehyde (0.1 mol)

Table 4: Synthesis of compound 6 (a-j)

S. No.	Reactant	Reactant	Reactant t	Product	Time (min)	Yield ^b (%)
1					50	90
2					55	89
3					52	86
4					50	90
5					50	90
6					55	89
7					50	86
8					55	83
9					50	90
10					55	90

^bReaction condition: Cinnamic acid or ferulic acid (0.1 mol); Thiosemicarbazide (0.1 mol) in [Et₃N H₂SO₄] ILs (20 mole %) and catalytic amount of acetic anhydride were added and heat to (TLC); To this aromatic aldehyde (0.1 mol) was added and continuous heated at 85-90°C

CONCLUSION

We have successfully developed an easy green approach synthesis of N-benzylidene-5-(styryl)-1,3,4-thiadiazol-2-amine and 4-(2-(5-(benzylideneamino)-1,3,4-thiadiazol-2-yl)vinyl)-2-methoxyphenol under the solvent free condition in Ionic Liquid (ILs) under conventional technique. The starting chemicals were easily available as aromatic aldehyde, acid, malonic acid and thiosemicarbazide. Further research is ongoing in our laboratory for the facile and eco-friendly synthesis of bioactive 'Nitrogen' and 'Sulfur' containing heterocyclic compounds and its derivative under the conventional and non-conventional technique.

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