

Synthesis of 3,4-Dihydropyrano[c]Chromene Derivatives Using Sulfonic Acid Functionalized Silica (SiO₂PrSO₃H)

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ABSTRACT: 3,4-Dihydropyrano[c]chromene derivatives were synthesized using sulfonic acid functionalized silica (SiO₂-Pr-SO₃H) as a highly efficient heterogenous solid acid catalyst via one-pot three-component condensation of aromatic aldehydes with malononitrile and 4-hydroxycoumarin in excellent yields.

KEY WORDS: 3,4-Dihydropyrano[c]chromenes, Sulfonic acid functionalized silica (SiO₂-Pr-SO₃H), 4-hydroxycoumarin, Malononitrile, Acid catalyst.

INTRODUCTION

Recently, the syntheses of 4H-chromene and its derivatives have attracted great interest due to their biological and pharmacological activities [1]. The 4H-chromene derivatives show various pharmacological properties such as spasmolytic [2], diuretic [3], anti-coagulant, anti-cancer [1], anti-HIV [4], antitumor [5], anti-malarial activities [6], anti-alzheimer [7], anti-leukemic [8-9], antibacterial [10], anti-malarial activities [11], emetic [12], and anti-anaphylactic activities [13]. Moreover, they can also be employed

as cosmetics and pigments [2] and utilized as potential biodegradable agrochemicals [14].

In literature, few methods have been reported for the synthesis of dihydropyrano[c]chromene derivatives. Some of these compounds have been already prepared in the presence of piperidine [15], diammonium hydrogen phosphate (DAHP), s-proline [16], K₂CO₃ under microwave irradiation [17], H₆P₂W₁₈O₆₂.18H₂O [18], MgO [19] and Tetrabutylammonium bromide (TBAB) [20]. Each method has own advantages and disadvantages.

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Therefore for the development of more effective methods and in continuation of our studies [21-23] on the application of nanoporous heterogeneous solid catalyst in organic synthesis [24], we have decided to explore the catalytical activity of sulfonic acid functionalized silica ($\text{SiO}_2\text{-Pr-SO}_3\text{H}$) as highly efficient heterogeneous acid catalyst towards the synthesis of dihydropyrano[c]chromene derivatives. In literature, there are just a few methods about the application of this catalyst [25].

EXPERIMENTAL SECTION

IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The ^1H NMR (250 MHz) was run on a Bruker DPX, 250 MHz. Weight change curve in nitrogen was measured on a TA instrument of TGA Q50 V6.3 with maximum heating rate of $20^\circ\text{C}/\text{min}$. Nitrogen adsorption and desorption isotherms were measured at -196°C using a Japan Belsorb II system after the samples were vacuum dried at 150°C overnight.

Preparation of catalyst

Synthesis of 3-mercaptopropylsilica (MPS) and its oxidation

To 20g of SiO_2 in dry toluene, 25mL of (3-mercaptopropyl)trimethoxysilane was added, and the mixture of reaction was refluxed for 24 h. After this period, the mixture was filtered to obtain 3-MercaPtopropylSilica (MPS) which was washed with acetone and dried. 3-MercaPtopropylSilica (MPS) was oxidized with H_2O_2 (excess) in methanol (20 mL) for 24h at room temprature and then the mixture was filtered and washed with H_2O , and then acetone to obtain $\text{SiO}_2\text{-Pr-SO}_3\text{H}$ catalyst. The modified $\text{SiO}_2\text{-Pr-SO}_3\text{H}$ was dried and used as solid acid catalyst in the organic synthesis.

General procedure for the preparation of 3,4-dihydropyrano[c]chromene derivatives

A mixture of aryl aldehyde (1mmol), malononitril (1.2 mmol), 4-hydroxycoumarin (1 mmol), and $\text{SiO}_2\text{-Pr-SO}_3\text{H}$ (0.05 g) in H_2O (4mL), and EtOH (1mL) was stirred at reflux. After completion of the reaction (monitored by TLC), the mixture was cooled and filtered. The crude product was heated in ethanol and then the catalyst was removed by filtration. The filtrate was cooled and concentrated to provide

the pure crystals of 3,4-dihydropyrano[c]chromene derivatives. The products are known compounds and were characterized by IR and NMR spectroscopy data for new compounds. Their melting points are compared with reported values.

Recycling of the catalyst

The catalyst could be washed subsequently with diluted acid solution, water and then acetone. After drying, it can be reused without noticeable loss of reactivity. It can be reused for several times.

Spectral Data for Selected Products

2-Amino-4-(4-chlorophenyl) -3- cyano -5- oxo -4H,5H-pyrano-[3,2-c]chromene 4d: white solid, IR (KBr, cm^{-1})

$\nu_{\text{max}} = 3380, 3258, 3188, 2190, 1713, 1676, 1606, 1376, 1059, 758$. ^1H NMR (250 MHz, DMSO, ppm): $\delta = 4.5$ (s, 1H, H-4), 7.3 (d, 2H, $J = 8.5$ Hz, H_{Ar}), 7.36 (br s, 2H, NH_2), 7.39 (br s, 2H, H_{Ar}), 7.45 (d, 1H, $J = 7.75$ Hz, H_{Ar}), 7.48 (t, 1H, $J = 7.75$ Hz, H_{Ar}), 7.72 (dt, 1H, $J = 7.25, 1.5$ Hz, H_{Ar}), 7.89 (dd, 1H, $J = 7.75, 1.25$ Hz, H_{Ar}).

2-Amino-4-(2,4-dichlorophenyl)-3-cyano -5-oxo- 4H,5H-pyrano-[3,2-c]-chromene 4e: white solid, IR (KBr, cm^{-1}):

$\nu_{\text{max}} = 3460, 3293, 3163, 3068, 2197, 1716, 1672, 1587, 1374, 1058, 758$. ^1H NMR (250 MHz, DMSO, ppm): $\delta = 4.98$ (s, 1H, H-4), 7.36 (dd, 1H, $J = 8.5, 2$ Hz, H_{Ar}), 7.38 (d, 1H, $J = 8.25$ Hz, H_{Ar}), 7.41 (br s, 2H, NH_2), 7.46 (d, 1H, $J = 8.3$ Hz, H_{Ar}), 7.50 (t, 1H, $J = 8.25$ Hz, H_{Ar}), 7.58 (d, 1H, $J = 7.75$ Hz, H_{Ar}), 7.73 (dt, 1H, $J = 7.5, 1.5$ Hz, H_{Ar}), 7.89 (dd, 1H, $J = 7.0, 1.5$ Hz, H_{Ar}).

2-Amino -4- (4-florophenyl) -3- cyano -5- oxo- 4H,5H-pyrano-[3,2-c]chromene 4i: IR (KBr, cm^{-1})

$\nu_{\text{max}} = 3378, 3291, 3190, 2192, 1715, 1676, 1605, 1505, 1378, 1505, 1605, 1378, 1219, 1059, 848, 754$. ^1H NMR (250 MHz, DMSO, ppm): $\delta = 4.5$ (s, 1H, H-4), 7.14 (d, 2H, $J = 8.5$ Hz, H_{Ar}), 7.32 (t, 2H, $J = 7.25$ Hz, H_{Ar}), 7.35 (br s, 2H, NH_2), 7.47 (d, 1H, $J = 7.25$ Hz, H_{Ar}), 7.53 (1H, t, $J = 7.5$ Hz, H_{Ar}), 7.72 (1H, dt, $J = 5, 1.5$ Hz, H_{Ar}), 7.92 (dd, 1H, $J = 7.7, 1.25$ Hz, H_{Ar}).

2-Amino -4- (2-methoxyphenyl) -3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene 4k: IR (KBr, cm^{-1})

$\nu_{\text{max}} = 3384, 3296, 3187, 2189, 1708, 1675, 1603, 1491, 1378, 1250, 1059, 755$. ^1H NMR (250 MHz, DMSO, ppm): $\delta = 3.34$ (s, 3H, OCH_3), 4.71 (s, 1H, H-4), 6.87 (t, 1H, $J = 7.25$ Hz, H_{Ar}), 7.00 (d, 1H, $J = 6.5$ Hz, H_{Ar}), 7.1

Table 1. The Optimization of reaction conditions in the synthesis 2-amino-4-(phenyl)-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene 4a.

Entry	Solvent	Time (min)	Yield (%)
1	H ₂ O	190	85
2	EtOH	180	77
3	EtOH/H ₂ O (1:1)	120	97
4	EtOH/H ₂ O (1:4)	30	100

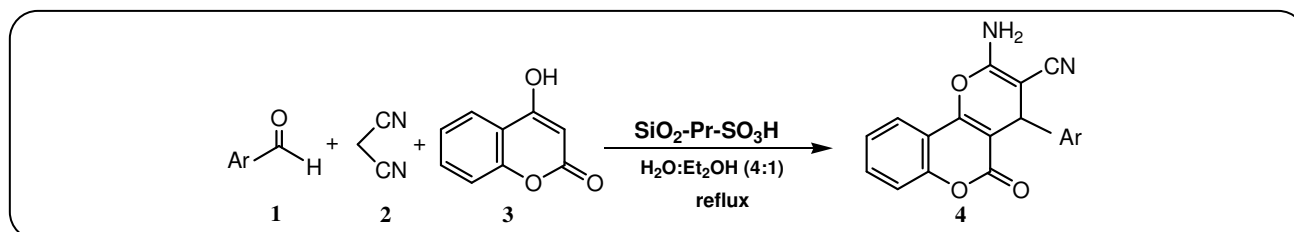


Fig. 1: The synthesis of 3,4-dihydropyrano[c]chromene derivatives.

(dd, 1H, $J = 1.5, 1.5$ Hz, H_{Ar}), 7.19 (d, 1H, $J = 7.5$ Hz, H_{Ar}), 7.25 (br s, 2H, NH_2), 7.53 (t, 2H, $J = 7.5$ Hz, H_{Ar}), 7.71 (dt, 1H, $J = 7.25, 1.5$ Hz, H_{Ar}), 7.9 (dd, 1H, $J = 7.25, 1.5$ Hz, H_{Ar}).

2-Amino-4-(2,4-dimethoxyphenyl)-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]-chromene 4l: IR (KBr, cm^{-1})

$\nu_{max} = 3553, 3388, 3342, 3211, 2191, 1713, 1675, 1607, 1381, 1298, 1207, 1054, 763$. 1H NMR (250 MHz, DMSO, ppm): $\delta = 3.70$ (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 4.61 (s, 1H, H-4), 6.44 (dd, 1H, $J = 7.5, 2.25$ Hz, H_{Ar}), 6.54 (d, 1H, $J = 7.5$ Hz, H_{Ar}), 7.03 (d, 1H, $J = 8.5$ Hz, H_{Ar}), 7.21 (br s, 2H, NH_2), 7.52 (dd, 2H, $J = 7.5, 1.5$ Hz, H_{Ar}), 7.7 (dt, 1H, $J = 7.5, 1.25$ Hz, H_{Ar}), 7.92 (dd, 1H, $J = 7.5, 1.5$ Hz, H_{Ar}).

2-Amino-4-(3-methoxyphenyl)-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene 4m: IR (KBr, cm^{-1})

$\nu_{max} = 3389, 3321, 3185, 2198, 1704, 1673, 1602, 1377, 1060, 763$. 1H NMR (250 MHz, DMSO, ppm): $\delta = 2.27$ (s, 3H, OCH_3), 4.40 (s, 1H, H-4), 7.05 (ds, 3H, $J = 7.5$ Hz, H_{Ar}), 7.23 (t, H, $J = 7.5$ Hz, H_{Ar}), 7.38 (br s, 2H, NH_2), 7.48 (dd, 2H, $J = 7.7, 5$ Hz, H_{Ar}), 7.75 (dt, 1H, $J = 7.25, 1.5$ Hz, H_{Ar}), 7.92 (dd, 1H, $J = 7.5, 1.25$ Hz, H_{Ar}).

2-Amino-4-(2-methylphenyl)-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene 4n: IR (KBr, cm^{-1})

$\nu_{max} = 3397, 3280, 3177, 2201, 1708, 1674, 1638, 1489, 1455, 1376, 1057, 750$. 1H NMR (250 MHz,

DMSO, ppm): $\delta = 2.50$ (s, 3H, CH_3), 4.76 (s, 1H, H-4), 7.06 (dd, 2H, $J = 7.5, 3.25$ Hz, H_{Ar}), 7.15 (dd, 2H, $J = 7.5, 3.5$ Hz, H_{Ar}), 7.37 (br s, 2H, NH_2), 7.53 (dd, 2H, $J = 7.5, 7.5$ Hz, H_{Ar}), 7.71 (dt, 1H, $J = 7.5, 1.25$ Hz, H_{Ar}), 7.93 (dd, 1H, $J = 7.5, 1.5$ Hz, H_{Ar}).

2-Amino-4-(4-methylphenyl)-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene 4o: IR (KBr, cm^{-1})

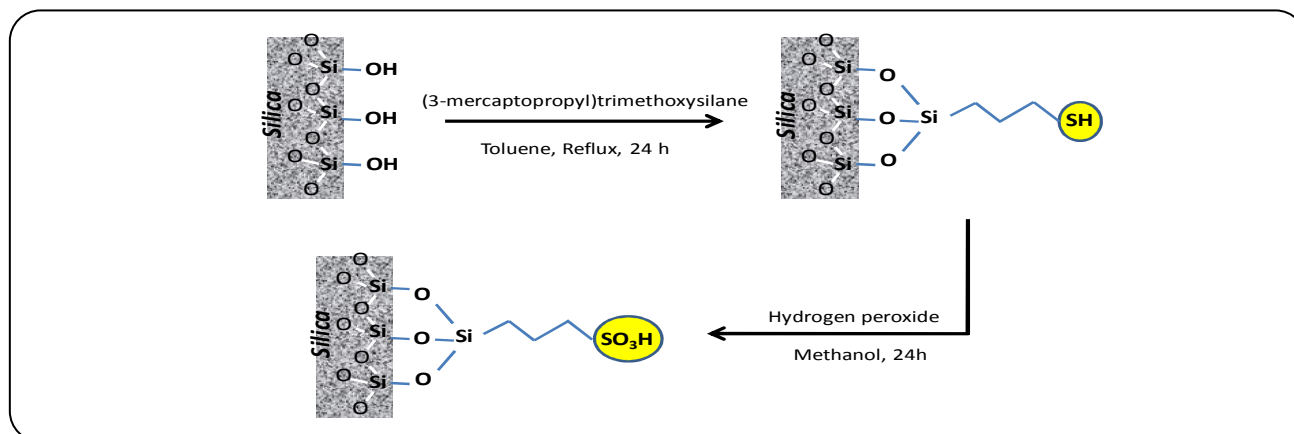
$\nu_{max} = 3387, 3312, 3191, 2192, 1713, 1674, 1606, 1372, 1055, 753$. 1H NMR (250 MHz, DMSO, ppm): $\delta = 2.66$ (s, 3H, CH_3), 4.40 (s, 1H, H-4), 7.09 (s, 2H, $J = 7.5$ Hz, H_{Ar}), 7.13 (s, 2H, $J = 7.5$ Hz, H_{Ar}), 7.39 (br s, 2H, NH_2), 7.52 (dd, 2H, $J = 7.5, 4.5$ Hz, H_{Ar}), 7.71 (t, 1H, $J = 7.5$ Hz, H_{Ar}), 7.92 (dd, 1H, $J = 7.5, 1.25$ Hz, H_{Ar}).

RESULTS AND DISCUSSION

The synthesis of 2-amino-4-aryl-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene derivatives were achieved by the one-pot, three-component condensation of an aromatic aldehyde, malonitrile, and 4-hydroxycoumarin in the presence of SiO_2 -Pr- SO_3H in the mixture of ethanol and H_2O at reflux to give products in excellent yields (Fig. 1). For optimization of reaction conditions, 2-amino-4-Phenyl-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene 4a was synthesized in different solvents. As shown results in Table 1, the mixture of water and ethanol (4:1) is the most effective solvent for this reaction. In this condition, the reaction was occurred very fast.

Table 2: $\text{SiO}_2\text{-Pr-SO}_3\text{H}$ catalyzed the synthesis of 2-amino-4-aryl-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromenes.

Entry	Aldehyde	Product	Time (min)	Yield (%)	M.p ($^{\circ}\text{C}$)	Ref
1	Ph	4a	25	100	256-257	256-258 [16]
2	4- $\text{NO}_2\text{C}_6\text{H}_4$	4b	30	100	257-260	258-260 [16]
3	3- $\text{NO}_2\text{C}_6\text{H}_4$	4c	30	100	260-263	262-264 [16]
4	4- ClC_6H_4	4d	30	100	266-267	263-265 [16]
5	2,4- $\text{Cl}_2\text{C}_6\text{H}_4$	4e	30	100	257-259	257-259 [16]
6	2,3- $\text{Cl}_2\text{C}_6\text{H}_4$	4f	30	100	287-289	287-289 [16]
7	2,6- $\text{Cl}_2\text{C}_6\text{H}_4$	4g	30	100	300-301	299-301 [16]
8	4- OHC_6H_4	4h	30	100	262-266	264-266 [16]
9	4- FC_6H_4	4i	30	100	278-282	-
10	4- $\text{OCH}_3\text{C}_6\text{H}_4$	4j	37	99	242-244	240-242 [16]
11	2- $\text{OCH}_3\text{C}_6\text{H}_4$	4k	37	99	274-276	-
12	2,4-(OCH_3) $_2\text{C}_6\text{H}_4$	4l	37	99	236-238	-
13	3- $\text{OCH}_3\text{C}_6\text{H}_4$	4m	37	99	242-244	-
14	2- $\text{CH}_3\text{C}_6\text{H}_4$	4n	37	99	279-282	-
15	4- $\text{CH}_3\text{C}_6\text{H}_4$	4o	37	99	265-267	-

Fig. 2: Preparation of silica based sulfonic acid ($\text{SiO}_2\text{-Pr-SO}_3\text{H}$).

By dissolving of crude product in hot ethanol, heterogeneous solid catalyst was removed easily by simple filtration, and after cooling of filtrate, the pure crystals of products were obtained. The results were summarized in Table 2. The acid catalyst can be reactivated by simple washing subsequently with diluted acid solution, water and acetone, and then reused without noticeable loss of reactivity.

For the preparation of catalyst, acid sites have been incorporated into silica surface by grafting method [26-27]. The surface of silica was first grafted with

(3-MercaptoPropyl)TrimethoxySilane (MPTS) [28] and then the thiol functionalities were oxidized into sulfonic acid groups by hydrogen peroxide to give $\text{SiO}_2\text{-Pr-SO}_3\text{H}$ as solid heterogeneous catalyst (Fig. 2).

Table 3 shows the obtained results from the nitrogen adsorption studies at 200 K. The surface area (BET), pore volume and average pore diameter (BJH) of silica based sulfonic acid ($\text{SiO}_2\text{-Pr-SO}_3\text{H}$) are smaller than those of SiO_2 . It was shown that the organic groups (propyl sulfonic acid) were immobilized into the pores.

Table 3: Textural properties of silica gel and SiO₂-Pr-SO₃H.

Name	Surface area* (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter** (nm)
Silica gel	499	0.737	6.4
SiO ₂ -Pr-SO ₃ H	440	0.430	5.9

*) The BET (Brunauer-Emmet-Teller) surface area.

**) The average pore diameter was obtained by using the BJH (Barrett, Joyner and Halenda) model.

Table 4: Comparison of efficiency of various catalysts in synthesis of 2-amino-4-(phenyl)-3-cyano-5-oxo-4H,5H-pyrano-[3,2-c]chromene.

Entry	Catalyst	Condition	Time	Yield (%)	Ref.
1	(S)-proline	Reflux (H ₂ O: EtOH, 1: 1)	3 h	72-88	[16]
2	H ₆ [P ₂ W ₁₈ O ₆₂].18H ₂ O	Reflux (H ₂ O: EtOH, 1: 1)	30-85 min	80-90	[18]
3	MgO	Reflux (H ₂ O: EtOH, 4: 1)	30-35 min	87-92	[19]
4	TBAB	H ₂ O	45-60 min	84-93	[20]
5	SiO ₂ -Pr-SO ₃ H	Reflux (H ₂ O: EtOH, 4: 1)	25-37 min	99-100	This work

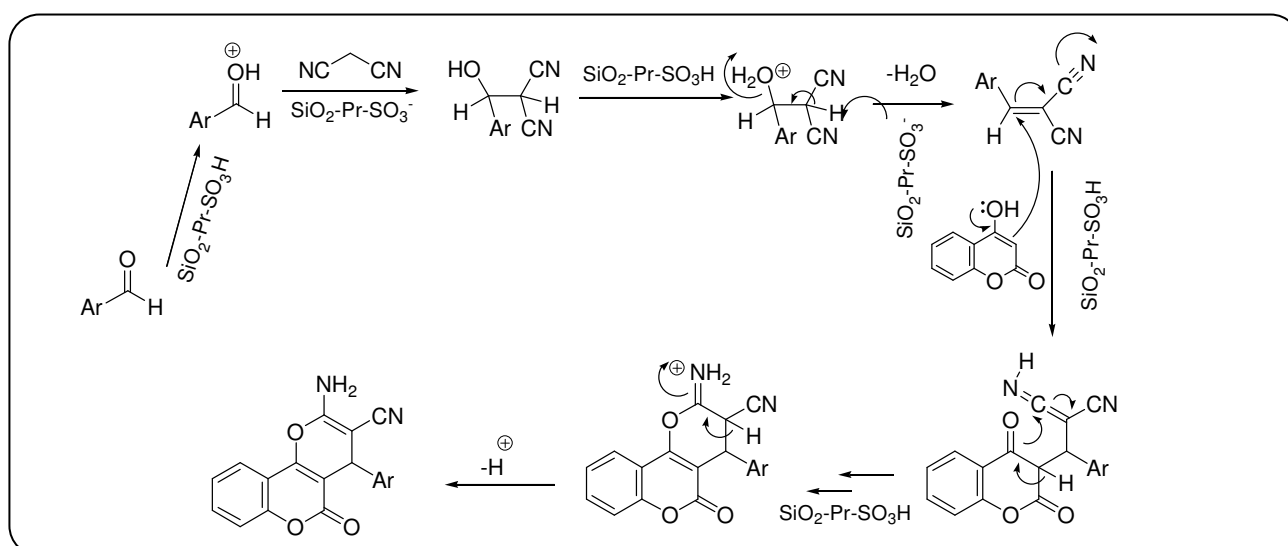


Fig. 4: Proposed mechanism.

The thermogravimetric analysis (TGA) of SiO₂-Pr-SO₃H was demonstrated the total weight loss about 20% due to loss of chemisorbed water and decomposition of organic groups.

A reasonable mechanism is outlined in Fig 3. The Knoevenagel reaction occurs in the presence of catalyst via an initial formation of α -cyanocinnamionitrile derivatives 5 by the condensation of protonated aromatic aldehydes 1 and malononitrile 2. Then, Michael addition of intermediate 5 with 4-hydroxy coumarin followed by cyclization and rearrangement provides desired products.

The efficiency of various catalysts in synthesis of 2-amino-4-(phenyl) -3- cyano -5- oxo-4H,5H-pyrano

-[3,2-c]chromene 4a as the model reaction has been compared in Table 4. The high yields of products and short reaction time were attributed to the nano pore size of about 5.9 nm in which the catalyst could act as a nanoreactor.

CONCLUSIONS

In conclusion, an efficient synthesis of 3,4-dihydropyrano[c]chromene derivatives has been achieved via a one-pot three-component reaction of an aromatic aldehyde, malonitrile, and 4-hydroxycoumarin using the reusable and environmentally benign SiO₂-Pr-SO₃H as a solid catalyst. The key advantages of this method are the very short reaction time, high yields, simple workup,

the non-chromatographic purification of products, i.e., simple recrystallization from Ethanol. The present method does not involve any hazardous organic solvent. Therefore, this procedure could be classified in green chemistry.

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