PEG-SO\textsubscript{3}H promoted one pot grinding method for the synthesis of 2-amino-4\textit{H}-chromene-3-carboxylates

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**Abstract**  
There is a crucial medical need for the synthesis of 4\textit{H}-chromene compounds via simple efficient methods. 4\textit{H}-chromene compounds are stated to have a wide range of medicinal applications such as anti-bacterial, anti-cancer (EPC2407 and MX58151), antimalarial, antifungal, anti-rheumatic and antiviral properties depending up on the substituents which is present on the heterocyclic compounds. Nowadays multi component protocols shows a better advantages such as better yield, less reaction time and no usage of different solvents for synthesis of biological important heterocyclic compounds over other synthetic approaches. The operational simplicity and applicability of this protocol to various analogues make it an alternative to previous reported methods. Therefore, this work was to prepare a series of 4\textit{H}-chromene analogues via simple method with short time. Here, we reported the synthesis of 2-amino-4\textit{H}-chromene-3-carboxylates using green solvent (water) under grinding method by one pot three component reaction of substituted aldehydes, dimedone and cyano acetates. This reaction was catalysed by catalytic amount of PEG-SO\textsubscript{3}H at room temperature. This catalyst proved the efficient for synthesis of many heterocyclic compounds. This reaction proceeds with very short time i.e. 5 mins. The 2-amino-4\textit{H}-chromene derivatives (4a-i) was obtained with excellent yields (85-94%).

**INTRODUCTION**

Organic chemistry utilizes substance and energy. Now a day’s selection of solvent in the organic reactions is the problematic aspect. The use of solvents in the chemical reactions shows a significant impact for the achieving novel compounds. It is well known that 4\textit{H}-chromenes and their derivatives are useful compounds. They have used as intermediates because of their medicinal applications and biological properties (Figure 1). 4\textit{H}-chromenes are very important structural backbones found in several biologically active compounds. The oxygen containing heterocycles of 4\textit{H}-chromenes shows pharmacological applications such as antioxidant (Symeonidis \textit{et al.}, 2009), anticancer (Jain \textit{et al.}, 2014), antifungal (Alvey \textit{et al.}, 2009) and antimicrobial (Kathrotiya and Patel, 2012). The 4\textit{H}-chromene derivatives are used as substrates for the synthesis of medicinal compounds and some of the natural products. EPC2407, HA14-1 and MX58151 showing good cytotoxic activity against the cancercells (Doshi \textit{et al.}, 2006; Patil \textit{et al.}, 2013). In recent years several synthetic approaches reported for the synthesis of 2-amino-4\textit{H}-chromene compounds. Earlier 2-amino-4\textit{H}-chromene com-
pounds was reported using potassium pthalimide catalyst (Kiyani and Ghorbani, 2014). Shuijiang reported the derivatives of 4H-chromenes under microwave irradiation without catalyst. In addition, several homo and heterogeneous catalysts (Figure 2) such as Ferric hydrogen sulphate (Eshghi et al., 2011), silicagel supported phosphoric acid (Davoodnia et al., 2011), Ba(otf)2 (Kumar and Rao, 2012), CuSO4·5H2O (Behbahani and Maryam, 2013), DABCO (Jain et al., 2014), DMAP (Khan et al., 2011), Lithium bromide (Sun et al., 2010), Amberlyst A-21 (Yadav et al., 2007) and amino acids like Glycine (Datta and Pasha, 2012), L-proline (Guo et al., 2007) also used to synthesized the 4H-chromene compounds. However, these protocols are suitable for the synthesis of compounds but facing some limitations such as reaction time, reaction conditions, difficult workup, product yields, costly organic solvents and highly expensive catalysts. To overcome these limitations we used PEG-SO3H in aqueous media by grinding method to achieve good to excellent yields at short time. In recent decades grinding method shows a vital role in the formation of C-C bond in organic synthesis over microwave and conventional methods. Grinding method has more applications over the other methods because it does not require the harsh conditions and equipment’s. Several biological important organic compounds have been synthesized by using grinding protocol. This method is used for the synthesis of Indolyl quinolines from indole corbaldehyde, substituted aniline and phenylacetylene under the catalyst of silicagel (Yadav et al., 2018), synthesis of pyrans and pyrano pyrazole derivatives from malononitrile, aldehydes and dimedone with 94% yields.

It also proved the efficient method for the synthesis of coumarin derivatives in one pot from aldehydes, dimedone and 1,3-dioxane-4,6-diones under solvent free conditions (Rong et al., 2007) and synthesis of 3,4-dihydropyranono chromenes from aldehydes and 4-Hydroxy coumarins under catalyst of ionic liquids (Patel et al., 2016). Synthesis of 2,4,5-triaryl substituted imidazole’s from 1,2diketones, aromatic aldehydes and ammonium acetate in presence of I2catalyst (Parveen et al., 2007).

PEG-SO3H is a stable, recyclable and biodegradable catalyst and used for the several reactions without losing catalytic activity. Nasseri reported the synthesis of quinazoline derivatives by Knoevenagel condensation of aldehydes with diones (Nasseri et al., 2007). Xicun used PEG-SO3H catalyst for the synthesis of Di-hydropyrimidiones via biginelli reaction under solvent free conditions (Xicum et al., 2005). It is previously used for the synthesis of B-hydroxy thiocyanates via regioselective ring opening of epoxides (Kiasat and Mehrjardi, 2008) and synthesis of triazoloindazole-triones, spiro triazoloindazole-tetraones (Hasaninejad et al., 2011). PEG-SO3H in aqueous media proved a good catalyst for the synthesis of Bis-indolyl and Tris-indolymethanes by condensation of indole with aldehydes (Rani et al., 2012). Recently several methods have been employed for carried out reactions in water irrespective usage of organic solvents because water is very cheap, less cost, on-flammable, and environmentally eco-friendly solvent.

MATERIALS AND METHODS

All the chemicals were procured from Alfa Aesar, Sigma-Aldrich and Avra synthesis used without purification. Thin Layer chromatography is used for the completion of all the reactions. Calibrated, dried glasswares are used to carry out all the reactions. The 1H NMR 13CNMR spectra was recorded in Bruker Advance-400MHz spectrometer in CDCl3 solvent.

Procedure for the synthesis of PEG-SO3H catalyst

The catalyst PEG-SO3H was prepared by using previous reported protocols. Initially PEG-6000 (1mmol) was taken in 10ml of dichloromethane and stirred these two solutions for some time. Then add chlorosulfonic acid (10mmol) at 0°C. The mixture was kept 12h at normal temperature by continuous stirring. Add ether to the solution, formed precipitate was filtered, followed by wash with ether thrice to afford catalyst as a white powder.

General protocol for synthesized compounds (4a-i)

Benzaldehydes (1) (1mmol), Ethyl cyanatoacetate (2) (1mmol), cyclohexane-1,3-dione (3) (1mmol), water(5ml) and catalytic amount of catalyst (50mg) were transferred into a mortar and pulverized with pestle for 5 mins. After the completion of reaction confirmed by thin layer chromatography, the obtained solid was filtered, followed by recrystallization from ethanol afforded pure products.

Compound (4a)

1H NMR (400 MHz, CDCl3); δ 7.28-7.09 (m, 9H), 6.18(s,2H), 4.73(s,1H), 4.05-4.00 (m, 2H), 2.59-2.53(m,2H), 2.35-2.30(m,2H), 2.03-1.92(m,2H), 1.14(t, J=7.2Hz, 3H); 13CNMR (100 MHz, CDCl3); δ 196.51, 169.12, 162.98, 158.35, 146.01, 128.27, 127.80, 126.05, 118.16, 80.80, 59.66, 36.88, 33.79, 26.97, 20.23, 14.21. Isolated yield: 94%.

Compound (4b)

1H NMR (400 MHz, CDCl3); δ 7.32(d, J=8.4Hz, 2H), 7.28-7.09(m,9H), 6.18 (s, 2H), 4.73(s,1H), 4.05-4.00 (m, 2H), 2.59-2.53(m,2H), 2.35-2.30(m,2H), 2.03-1.92(m,2H), 1.14(t, J=7.2Hz, 3H);

13CNMR (100 MHz, CDCl3); δ 196.51, 169.12, 162.98, 158.35, 146.01, 128.27, 127.80, 126.05, 118.16, 80.80, 59.66, 36.88, 33.79, 26.97, 20.23, 14.21. Isolated yield: 94%.

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Figure 1: Highly functionalized biological active 4H-chromenes

Table 1: Optimization of Reaction Conditions

| Entry | Catalyst loading (mg) | Solvent      | Time (Min) | Yield (%) |
|-------|-----------------------|--------------|------------|-----------|
| 1     | -                     | -            | 60         | NR        |
| 2     | 20                    | -            | 30         | 60        |
| 3     | 50                    | -            | 22         | 62        |
| 4     | 25                    | Water        | 15         | 81        |
| 5     | 40                    | Water        | 10         | 84        |
| 6     | 50                    | Water        | 05         | 94        |
| 7     | 50                    | MeOH         | 16         | 72        |
| 8     | 50                    | DMF          | 20         | 47        |
| 9     | 50                    | 1,4-Dioxane  | 30         | 12        |
| 10    | 50                    | Acetonitrile | 20         | 22        |
| 11    | 50                    | DMSO         | 15         | 42        |

Scheme 1: Synthesis of 2-amino 4H-chromene-3-carboxylates
Table 2: One pot synthesis of 4H-Chromene Derivatives by Using Different Catalysts

| Entry | Catalyst                        | Condition | Solvent   | Time   | Yield  |
|-------|---------------------------------|-----------|-----------|--------|--------|
| 1     | Ionic liquid                    | 80°C      | —         | 15-30min | 60-90  |
| 2     | K2CO3                           | Microwave | C2H5OH    | 3.5min | 87-93  |
| 3     | Na2CO3-30mol%                   | RT        | H2O       | 10h    | 75-83  |
| 4     | CuSO4·5H2O                      | Reﬂux    | H2O       | 1h     | 95     |
| 5     | Amberlyst-21                    | RT        | C2H5OH    | 4h     | 85     |
| 6     | H14(NaP5W300100)                | Reﬂux    | H2O       | 5h     | 91     |
| 7     | NH4OAc                          | Microwave | C2H5OH    | 4-5h   | 85     |
| 8     | PEG-400                         | 100°C     | –         | 2h     | 90     |
| 9     | Glycerine                       | Sonication| H2O      | 10min  | 91     |
| 10    | PPA-Sio2                        | Reﬂux    | H2O       | 10min  | 84     |
| 11    | Yb(OTf)3                        | Reﬂux    | PEG-H2O   | 30min  | 83     |
| 12    | Methane sulfonic acid           | Reﬂux    | H2O       | 3h     | 91     |
| 13    | Al2O3                           | RT        | C2H5OH    | 3h     | 71     |
| 14    | Triethyl amine                  | Microwave | C2H5OH    | 10min  | 76     |
| 15    | PEG-SO3H                        | Grinding  | H2O       | 5min   | 94     |

Figure 2: Physical data of the synthesized compounds (4a-i)
7.14(d, J = 8.4 Hz, 2H), 6.20(s,2H), 4.65(s,1H), 4.03(d, J = 7.2 Hz, 2H), 2.42(s,2H), 2.19(m, J = 16.4 Hz, 2H), 1.15(t, J = 7.2 Hz, 3H), 1.09(s,3H), 0.97(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.33, 168.92, 161.49, 158.32, 144.96, 130.85, 130.09, 119.79, 116.32, 80.25, 59.77, 50.69, 40.65, 33.55, 32.24, 29.11, 27.38, 14.23. Isolated yield: 89%.

Compound (4c)
1H NMR (400 MHz, CDCl3); δ 7.20(m,4H), 6.20(s,2H), 4.67(s,1H), 4.08-3.97(m,2H), 2.25-2.13(m,2H), 1.15(t, J = 7.2 Hz, 3H), 1.09(s,3H), 0.97(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.37, 168.95, 161.47, 158.32, 143.14, 131.62, 129.67, 127.91, 116.40, 80.34, 59.76, 50.69, 40.65, 33.46, 32.25, 29.11, 27.37, 14.23. Isolated yield: 87%.

Compound (4d)
1H NMR (400 MHz, CDCl3); δ 7.17(d, J = 8.8 Hz, 2H), 6.74(d, J = 8.8 Hz, 2H), 6.15(s,2H), 4.65(s,1H), 4.10-3.97(m,2H), 2.45(d, J = 2.4 Hz, 2H), 2.27-2.13(m,2H), 1.13(m, J = 7.2 Hz, 3H), 1.11(s,3H), 0.96(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.27, 168.60, 162.00, 158.42, 153.47, 146.32, 129.27, 123.11, 115.58, 79.37, 59.90, 50.59, 40.65, 34.29, 32.27, 29.08, 27.32, 14.22. Isolated yield: 90%.

Compound (4e)
1H NMR (400 MHz, CDCl3); δ 7.17(d, J = 8.8 Hz, 2H), 6.74(d, J = 8.8 Hz, 2H), 6.15(s,2H), 4.65(s,1H), 4.10-3.97(m,2H), 2.45(d, J = 2.4 Hz, 2H), 2.27-2.13(m,2H), 1.17(t, J = 7.2 Hz, 3H), 1.09(s,3H), 0.98(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.49, 169.18, 161.14, 158.26, 157.79, 138.29, 129.16, 116.99, 113.18, 81.05, 59.66, 55.14, 50.77, 40.66, 32.97, 32.24, 29.10, 27.44, 14.26. Isolated yield: 89%.

Compound (4f)
1H NMR (400 MHz, CDCl3); δ 7.32(d, J = 8.4 Hz, 2H), 7.14(d, J = 8.4 Hz, 2H), 6.20(s,2H), 4.66(s,1H), 3.59(s,3H), 2.41(s,2H), 2.25-2.13(m,2H), 1.09(s,3H), 0.96(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.26, 169.28, 161.50, 158.51, 144.85, 130.98, 129.89, 119.86, 116.43, 80.10, 51.02, 50.68, 40.64, 33.36, 32.25, 29.12, 27.35. Isolated yield: 86%.

Compound (4g)
1H NMR (400 MHz, CDCl3); δ 7.21-7.16(m,4H), 6.20(s,2H), 4.68(s,1H), 3.60(s,3H), 2.41(s,2H), 2.25-2.13(m,2H), 1.10(s,3H), 0.95(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.30, 169.31, 161.50, 158.51, 144.32, 131.69, 129.47, 128.04, 116.51, 80.18, 51.02, 40.64, 33.27, 32.25, 29.12, 27.34. Isolated yield: 85%.

Compound (4h)
1H NMR (400 MHz, CDCl3); δ 8.08(d, J = 8.8 Hz, 2H), 7.44(d, J = 8.4 Hz, 2H), 6.30(s,2H), 4.80(s,1H), 3.59(s,3H), 2.45(d, J = 3.6 Hz, 2H), 2.20(m, J = 16.4 Hz, 2H), 1.11(s,3H), 0.95(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.19, 168.97, 162.03, 158.58, 153.34, 146.35, 129.04, 123.32, 115.65, 79.25, 51.10, 50.58, 40.64, 34.13, 32.27, 29.10, 27.29. Isolated yield: 88%.

Compound (4i)
1H NMR (400 MHz, CDCl3); δ 7.16(d, J = 8.8 Hz, 2H), 6.75(d, J = 8.4 Hz, 2H), 6.16(s,2H), 4.66(s,1H), 3.74(s,3H), 3.60(s,3H), 2.40(s,2H), 2.19(m, J = 16.4 Hz, 2H), 1.09(s,3H), 0.97(s,3H); 13 CNMR (100 MHz, CDCl3); δ 196.42, 169.55, 161.17, 158.49, 157.82, 138.07, 128.96, 117.12, 113.30, 80.85, 55.13, 50.96, 50.75, 40.65, 32.77, 32.55, 29.11, 27.41. Isolated yield: 86%.

MATERIALS AND METHODS
Earlier several methods have been developed for the synthesis of 4H-chromene derivatives By using several catalysts such as Ionic liquids, Potassium carbonate, Copper sulphate, Amberlyst-21, Ammonium acetate, Zinc chloride, PEG-400, Glycerin, PPA-SiO2, Yb(otf)3. Methane sulphonic acid, Al2O3 and Triethyl amine (Table 2) but shows some demerits such as reaction time, solvent, catalyst, tedious workup and reaction condition. Here with reported using grinding method to synthesize the derivatives of chromene compounds with high yields in a very short time. In recent decades water is used as a green solvent for the synthesis of many biological important heterocyclic compounds and natural products due to its advantages such as costless, easily availability, nonflammable and environmentally eco-friendly nature. Here we synthesized the chromene derivatives by using water as a green solvent.

In this protocol we report the Knoevenagel condensation of 1,3-cyclohexane dione with aldehyde using water as a solvent under catalytic amount of PEG-SO3H (Scheme 1). Initially benzaldehyde (compound1), ethyl cyanoacetate (compound2), dime-done (compound3) was taken into a mortar, pulverized with pestle for 1hr without a catalyst and solvent, there is no progress of reaction was observed (Table 1). After that the same reaction was conducted for 30mins by using 20mg of catalyst the reaction proceed with 60% yield. It shows increase of catalyst concentration plays a significant effect on product yield(4a). Then we conducted the trail with increased the catalyst concentration from 20mg to 50mg afford desired product yield with 62% it shows there is no comparable yield. Later we monitored the reactions with changing the parameters such of usage of different solvents, reaction time...
and catalyst concentration. The reaction was conducted by using 5ml of water with 25mg of catalyst produced the desired product(4a) with 81% yield due to the increase solubility of catalyst in water. Finally compound(4a) was obtained with excellent yield 94% by using 50mg of catalyst in water solvent (Scheme 1). Later we assessed the effect of solvent on the product yields we carried out the reactions with different solvents such as methanol, DMF, 1,4-Dioxane, DMSO and ACN (Table 1). Reaction in presence of methanol produced good yield when compared to reaction proceeds with other solvents. Finally we synthesized the chromene derivatives(4a-i)with high yields under grinding method in a short time (Figure 2).

CONCLUSIONS

In conclusion we demonstrated an efficient and simple protocol for the synthesis of 2-amino 4H-chromene derivatives(4a-i)by taking aldehydes, methyl (or) ethyl cyano acetic ester and 5,5 dimethyl 1,3-cyclohexane diones using PEG-SO3H as an efficient catalyst. This protocol offers several applications such as excellent yields, short time and green solvent and no usage of organic solvents.

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Conflict of Interest

The authors declare that they have no conflict of interest for this study.

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