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Nano polypropylenimine dendrimer (DAB-PPI-G₁): as a novel nano basic-polymer catalyst for one-pot synthesis of 2-amino-2-chromene derivatives

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Abstract:

Nano polypropylenimine dendrimer (DAB-PPI-G₁) Lewis base catalyst was found to be a highly efficient and recoverable catalyst for the rapid and convenient synthesis of 2-amino-2-chromene derivatives of three-component condensation of aromatic aldehyde, malononitrile or ethyl cyanoacetate and phenols under solvent-free conditions in excellent yields and short reaction times.

Keywords: 2-Amino-2-chromene; Nano polypropylenimine dendrimer; Aldehyde; Malononitrile; Phenols; Solvent-free

Introduction

Dendrimers are monodisperse and usually highly symmetric, spherical compounds. Nano polypropylenimine is an important class of dendrimers. In fact, dendrimers are polymer nanostructures with unique capabilities. First generation of polypropylenimine dendrimer consists of four free NH₂ terminal groups.¹ These groups could be polyvalent of PPI and also increase basic property. Polypropylenimine dendrimers are used as agents for targeted drug delivery and gene transfer.² The physical characteristics of dendrimers, including their monodispersity, water solubility, encapsulation ability, and large number of functionalizable peripheral groups, make these macromolecules appropriate candidates for evaluation as drug delivery vehicles (Fig. 1).

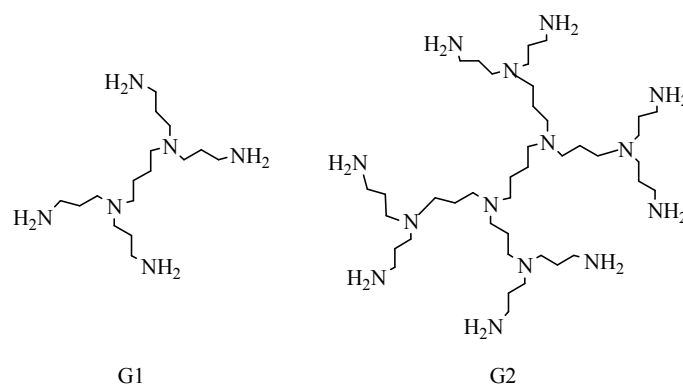


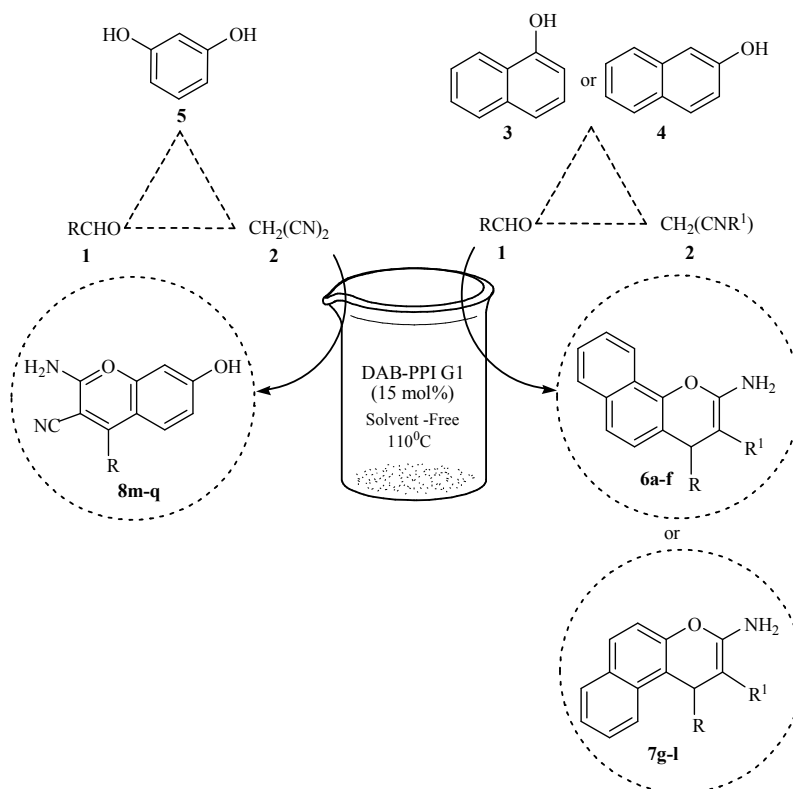
Fig. 1 Schematic representations of dendrimeric structures.

2-Amino-2-chromen derivatives have attracted extensive interest owing to their biological activities.³ There is a widespread interest in the synthesis of chromene and its derivatives owing to their diverse range of biological properties such as antimicrobial,⁴ TNF- α inhibitor,⁵ antifungal,⁶ estrogenic,⁷ anticancer,⁸ anti-HIV,⁹ anti-bacterial,¹⁰ compound applies in pigments¹¹ and pesticides and insecticides.¹² Among several methods reported for the synthesis of 2-amino-2-chromen derivatives, three-component reaction between aldehydes, malononitrile or ethylcyanoacetate and phenol is particularly popular. Catalysts that have been used for this conversion include basic ionic liquid [1-(*n*-butyl)-3-methylimidazolium hydroxide ([bmim]OH)],¹³ *p*-Dimethylaminopyridine (DMAP),¹⁴ Triton B,¹⁵ K₂CO₃,¹⁶ MCM-41-NH₂,¹⁷ cetyltrimethylammonium chloride (CTACl),¹⁸ cetyltrimethylammonium bromide (CTABr),¹⁹ K₃PO₄·3H₂O,²⁰ piperazine,²¹ tetramethylguanidine,²² H₁₄[Na P₅W₃₀O₁₁₀],²³ CuSO₄·5H₂O,²⁴ methanesulfonic acid,²⁵ KF-Al₂O₃,²⁶ potassium phthalimide-*N*-oxyl,²⁷ nanostructured diphosphate Na₂CaP₂O₇,²⁸ DBU,²⁹ and Ca(OH)₂,³⁰ However, most of the reported methods suffer from one or more of the following drawbacks: low yields, long reaction times, harsh reaction conditions, and tedious work-up leading to the generation of large amounts of toxic waste, and the use of unrecyclable, hazardous, catalysts. Therefore, use of eco-friendly and non-toxic catalysts with high efficiency in the synthesis of these compounds is highly regarded.

Result and discussions

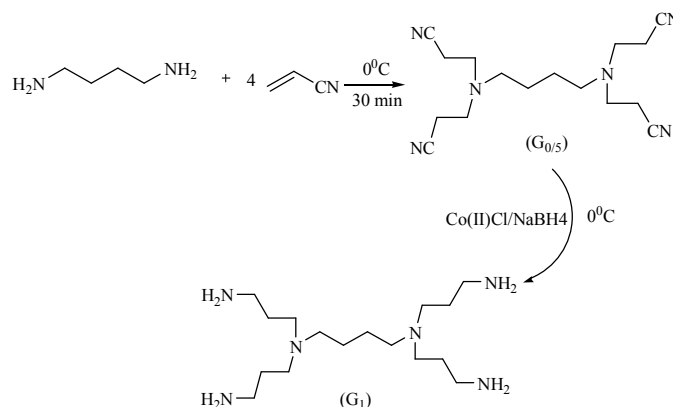
During the course of our recent studies directed toward the development of practical safe and environmentally friendly procedures for some important transformations,³¹ we hoped to report a

simple and efficient procedure for the synthesis of 2-amino-chromenes using nano polypropylenimine dendrimer (DAB-PPI-G₁) under solvent-free conditions (Scheme 1).



Scheme 1 One-pot synthesis of 2-amino-2-chromen derivatives.

The core of PPI is a diamine (commonly 1,4-diaminobutane). The reaction began with the increase of four molecules of acrylonitrile to central core 1,4-diaminobutane, and produced generation 0.5 of polypropylenimine dendrimer by four groups terminal nitrile. In the next step, we reduced nitrile groups by NaBH₄ in the presence of catalyst anhydrous chloride cobalt and produced generation 1 of nano polypropylenimine dendrimer by four groups terminal amine (Scheme 2).



Scheme 2 Synthesis of nano polypropylenimine dendrimer (DAB-PPI-G₁).

In the bottom are shown images of nano polypropylenimine dendrimer (Fig. 2A). Morphology indicates agglomeration of dendrimer particles and porous structure. Pictures are shown in Fig. 2B have been prepared by optical microscope nano focus, they Show approximate size of the particles of dendrimer PPI that have been sprayed on the glass with the use of colors (Fig. 2B).

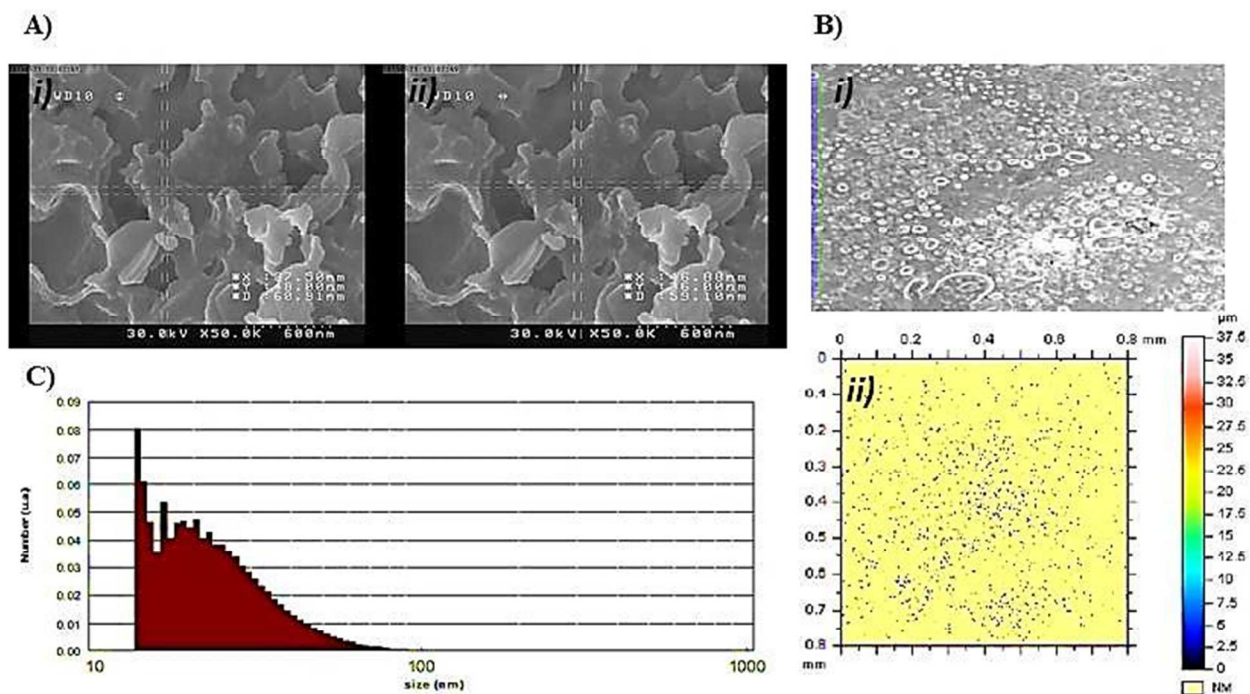


Fig. 2 (A) Scanning electron microscopy images of dendrimer PPI G₁ (i-ii); (B) Optical microscope nano focus images of dendrimer PPI G₁ i) Image of dendrimer PPI spray on the glass (film of PPI G₁) ii) Image obtained from the particle size of PPI G₁ film on the glass; (C) Particle size dispersion of PPI by method dynamic light scattering (DLS).

The dispersion size of the synthesized PPI by proposed method and dynamic light scattering (DLS) of them was shown in Fig. 2C. As it can be seen, the nanoparticle size is between 13-53 nm and mean diameter is 24 nm.

Creation of molecular functionality and diversity³² from common starting materials while combining economic³³ and environmental³⁴ aspects constitutes a great challenge in modern organic chemistry.³⁵ In these contexts, multicomponent reactions (MCRs) under solvent-free conditions are valuable procedures in organic synthesis because a multistep reaction may produce considerable amounts of environmentally unfavorable wastes mainly due to a series of complex isolation procedures, which often needs expensive, toxic, and hazardous solvents after each step. Malononitrile is one of the most versatile reagents to be used in MCRs because of the high reactivity of both the methylene and the cyano groups.³⁶ From this perspective, we used malononitrile (1.5 mmol) as the active reagent to react with benzaldehyde (1 mmol) and 1-naphthol (1 mmol) to optimize the reaction conditions at first. A summary of the optimization experiment is provided in Table 1.

Initially, we operated the three-component reaction in using nano polypropylenimine dendrimer (PPI) as the catalyst under solvent-free condition at 110⁰C, and exhilaratingly obtained the target product with 95% yield for 3 min (Table 1, entry 1). To further optimize the reaction conditions, a series of catalysts such as ethylenediamine (EDA), 1,4-diamino butane (DAB), triethanol amine (TEA), diethanol amine (DEA), and poly (amido amine) (PAMAM) dendrimers were investigated (entries 2-6). Compared with other catalysts, PPI was the best catalyst in terms of the yield and the reaction time (entry 1). Next, we screened the proper temperature for the model reaction (entry 7-8). Afterward, the loading of PPI was selected, and 15 mol % of PPI was the optimal (entries 9-10). To evaluate the effect of PPI, the reaction was examined in the absence PPI under solvent-free condition at 110⁰C; no product was formed after 20 min at 110⁰C (entry 11).

Table 1 Optimization of reaction conditions

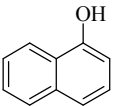
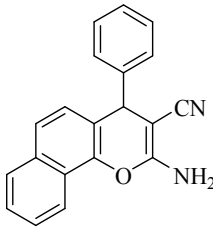
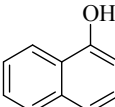
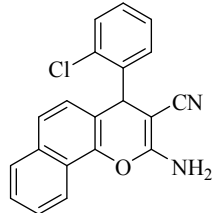
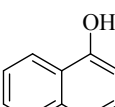
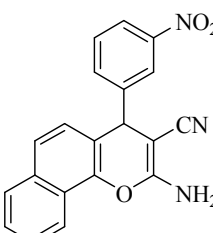
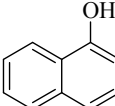
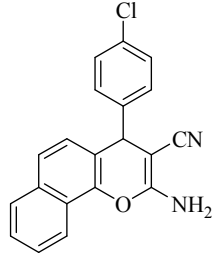
Entry	Catalysts	Conditions	Time (min)	Yield ^a (%)
1	PPI (15 mol%)	Solvent-Free/110 ⁰ C	3	95
2	EDA (5 drops)	Solvent-Free/110 ⁰ C	3	70
3	DAB (5 drops)	Solvent-Free/110 ⁰ C	3	45
4	TEA (5 drop)	Solvent-Free/110 ⁰ C	7	85
5	DEA (5 drop)	Solvent-Free/110 ⁰ C	5	86
6	PAMAM (5 drops)	Solvent-Free/110 ⁰ C	3	trace
7	PPI (15 mol%)	Solvent-Free/120 ⁰ C	3	90
8	PPI (15 mol%)	Solvent-Free/100 ⁰ C	3	74
9	PPI (10 mol%)	Solvent-Free/110 ⁰ C	3	86
10	PPI (20 mol%)	Solvent-Free/110 ⁰ C	3	89
11	--	Solvent-Free/110 ⁰ C	20	-- ^b

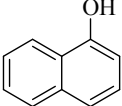
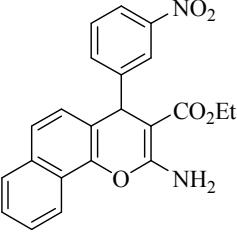
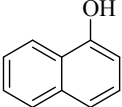
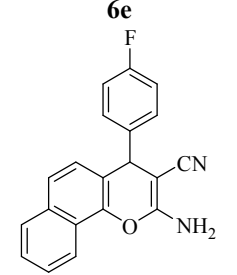
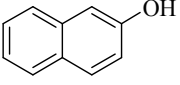
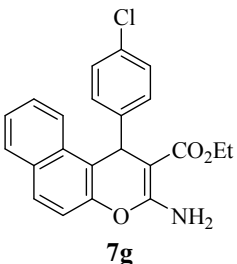
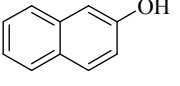
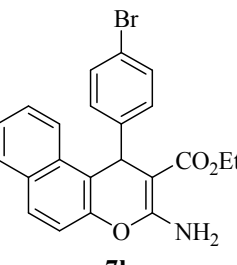
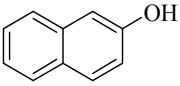
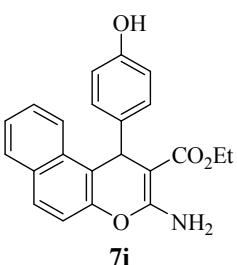
^aIsolated yields; ^bNo reaction;

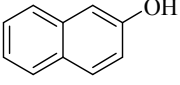
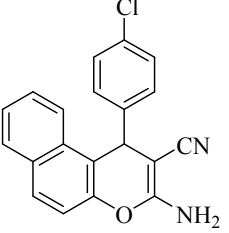
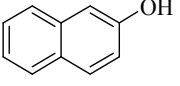
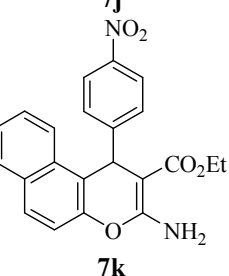
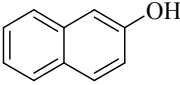
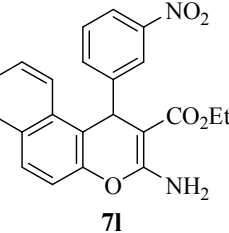
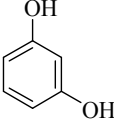
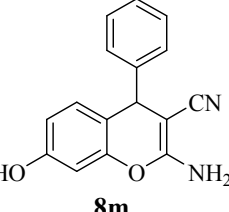
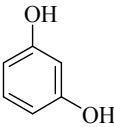
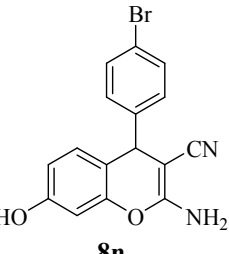
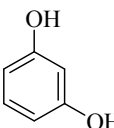
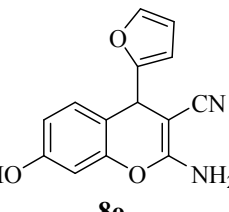
In recent years, various nano-materials have been used as suitable catalysts for synthesis of various organic compounds.³⁷ They increase efficiency at time consuming reactions toward regular catalysts. One efficient approach to enhance the catalytic activity of catalyst is their nanostructure construction. Favorable properties of nano polypropylenimine dendrimer (PPI) including increased surface area, saving of materials, and cost efficiency make them more efficient catalyst than their counterparts. In our quest for the proof of efficiency of nano polypropylenimine dendrimer (PPI), where nanostructures play an important role at catalytic properties, the synthesis of **6a** was investigated by similar non nanostructures (Table 1, entries 2-6). As it can be seen, better efficiency for the nano polypropylenimine dendrimer (PPI) is found in the synthesis of **6a**.

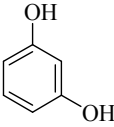
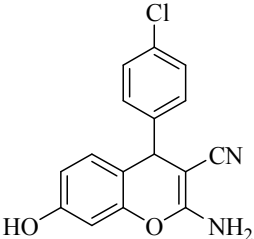
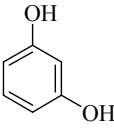
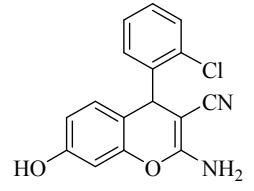
Based on the optimized reaction conditions, the reactions of 1 or 2- naphthol or resorcinol, malonitrile, and various aromatic (heterocyclic) aldehydes were investigated. As shown in Table 2, aromatic aldehydes carrying either electron-withdrawing or electron-donating substituents afforded excellent yields of products with high purity at 110⁰C under solvent-free conditions.

Table 2 One-pot synthesis of 2-amino-2-chromen derivatives

Entry	R	Phenols	R ¹	Products	Time (min)	Yield ^a % (ref.)
1	C ₆ H ₅		CN	 6a	3	95 (ref. 24)
2	2-ClC ₆ H ₅		CN	 6b	4	95 (ref. 24)
3	3-NO ₂ C ₆ H ₅		CN	 6c	12	94 (ref. 24)
4	4-ClC ₆ H ₅		CN	 6d	4	96 (ref. 24)

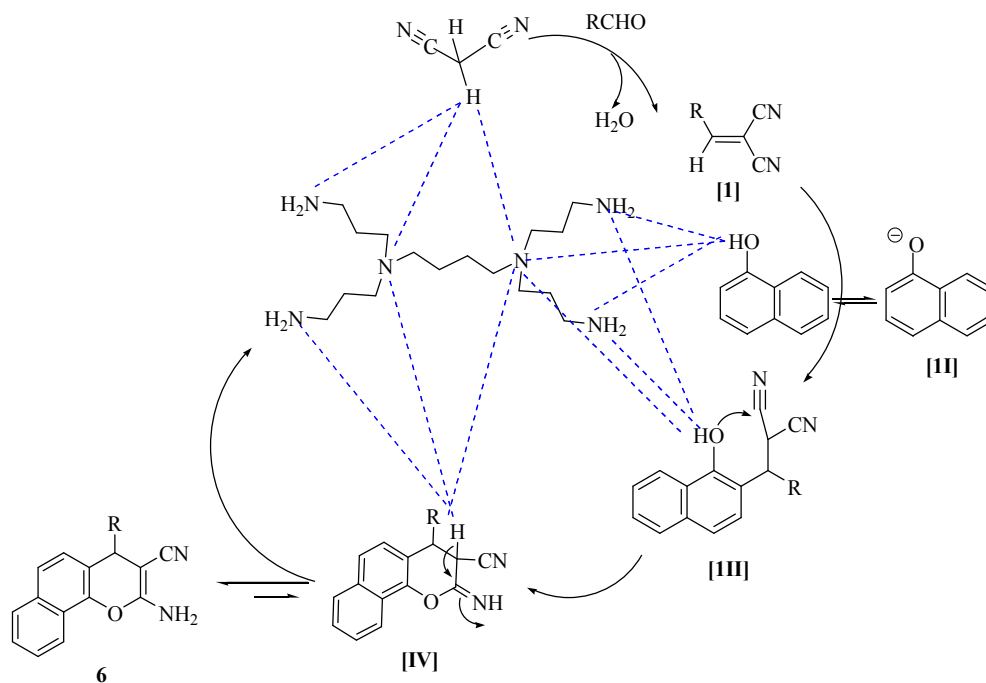
5	3-NO ₂ C ₆ H ₅		CO ₂ Et		20	88 (ref. 25)
6	4-FC ₆ H ₅		CN		15	78 (ref. 26)
7	4-ClC ₆ H ₅		CO ₂ Et		30	95 (ref. 26)
8	4-BrC ₆ H ₅		CO ₂ Et		30	89 (new)
9	4-OHC ₆ H ₅		CO ₂ Et		50	88 (new)

10	4-ClC ₆ H ₅		CN		15	92 (ref. 27)
11	4-NO ₂ C ₆ H ₅		CO ₂ Et		20	89 (new)
12	3-NO ₂ C ₆ H ₅		CO ₂ Et		20	90 (ref. 15)
13	C ₆ H ₅		CN		20	82 (ref. 27)
14	4-BrC ₆ H ₅		CN		25	85 (ref. 27)
15	2-Furyl		CN		30	76 (ref. 27)

16	4-ClC ₆ H ₅		CN		20	87 (ref. 27)
17	2-ClC ₆ H ₅		CN		20	89 (ref. 27)

^aIsolated Yields.

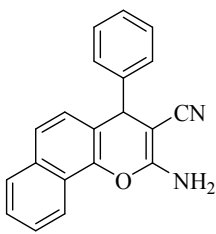
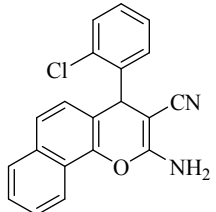
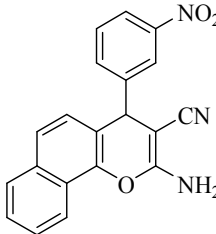
The possible reaction mechanism is proposed in Scheme 3. We presume that the reaction proceeds via initial formation of **I** through Knoevenagel condensation of aryl aldehyde and malononitrile. Then, 1-naphthol loses a hydrogen atom under the action of PPI. Subsequently, the Michael addition between **II** and **I** produces intermediate **III**, followed by intramolecular cyclization to form **IV**. The isomerization of **IV** gives the final product **6**.



Scheme 3 Proposed mechanism.

Table 3 summarizes and compares with the results obtained by other groups. Based on this comparison, our method is simpler, more efficient for the synthesis of 2-amino-2-chromene derivatives. These results clearly demonstrate that the polypropylenimine dendrimer catalyst is better and in all cases much more efficient for this reaction than the other catalysts (including acidic and basic catalysts).

Table 3 Comparison of methods for the synthesis of 2-amino-2-chromene including acidic and basic catalysts

Entry	Compounds	Conditions	Time (min)	Yield (%)
1	 7a	Solvent-free/110°C/PPI (present work)	3	95
		MCM-41-NH ₂ /H ₂ O/70°C (ref. 17)	30	69
		CTABr/H ₂ O/Ultrasonic/rt (ref. 19)	150	92
		Piperazine/MWI/solvent-free (ref. 21)	7	88
		CuSO ₄ ·5H ₂ O/water/reflux (ref. 24)	60	95
		Methanesulfonicacid/CH ₃ CN/ reflux (ref. 25)	180	90
		Na ₂ CaP ₂ O ₇ /water/reflux (ref. 28)	300	81
2	 7b	Solvent-free/110°C/PPI (present work)	4	95
		DMAP/Solvent-free/MWI (ref. 14)	60	95
		CTABr/H ₂ O/Ultrasonic/rt (ref. 19)	150	80
		CuSO ₄ ·5H ₂ O/water/reflux (ref. 24)	30	85
		KF-Al ₂ O ₃ /EtOH/80°C/reflux (ref. 26)	300	86
3	 7c	Solvent-free/110°C/PPI (present work)	12	94
		CTABr/H ₂ O/Ultrasonic/rt (ref. 19)	40	93
		K ₃ PO ₄ ·3H ₂ O/100°C/solvent-free (ref. 20)	60	77
		Methanesulfonicacid/CH ₃ CN/reflux (ref. 25)	240	90
		Na ₂ CaP ₂ O ₇ /water/reflux (ref. 28)	300	84

Experimental

General

All the chemicals required were purchased from Merck or Aldrich. Melting points were determined by using an Electrothermal 9100 apparatus. FT-IR spectra were recorded on a Shimadzu FT IR-8400S instrument (the samples as KBr disks for the range 400-4000 cm^{-1}). ^1H and ^{13}C NMR spectra were determined on a Bruker DRX-300 Avance spectrometer in DMSO-d_6 or CDCl_3 , and shifts are given in δ downfield from tetramethylsilane (TMS) as an internal standard. Optical microscope was performed with nano focus AG lindner strabe 98 D-46149 Oberhausen.

1. Synthesis of Nano polypropylenimine dendrimer (PPI)

1.1. Synthesis of polypropylenimine dendrimer Generation 0.5 (DAB-PPI- $G_{0.5}$)

To a mixture of 1,4-diaminobutane (10 ml) was added dropwise acrylonitrile (35 ml) at 0°C for 30 min. Then, the additional acrylonitrile was removed by rotary vacuum at 0.1mm and temperature of 45°C . The polypropylenimine dendrimer Generation 0.5 (DAB-PPI- $G_{0.5}$) was obtained oily viscous solution as a light yellow in 95% yields.

1.2. Synthesis of polypropylenimine dendrimer Generation 1 (DAB-PPI- G_1)

To a mixture of polypropylenimine dendrimer Generation 0.5 (10 g) in methanol (35 ml) at 0°C , was added NaBH_4 (6.23 gr) and anhydrous chloride cobalt (0.0002 gr). The reaction mixture is stirred for 60 min at this temperature. Then, the mixture was filtered, washed with methanol (30 ml), and then dried at room temperature to give polypropylenimine dendrimer Generation 1 (DAB-PPI- G_1) as a white powder (92% yields).

2. General procedure for synthesis of 2-amino-2-chromene

PPI (15 mol %) was added to a mixture of the aromatic aldehydes (1 mmol), methylene active (malononitrile or ethyl cyanoacetate) (1 mmol), phenols (α or β - naphthol or resorcinol) (1 mmol) in a 10 mL flask at room temperature. The temperature was then raised to 110°C and maintained for the appropriate time (see Table 2) with stirring. After the completion of the reaction as indicated by TLC (hexane-ethyl acetate, 4:1), hot EtOH (96%, 5 ml) was added and the mixture was stirred for 2 min.

Next, the resulting crude product was poured into crushed ice cold water and to get pure 2-amino-2-chromene derivatives, the solid product, which was separated, was filtered, recrystallized from EtOH (3 ml).

Spectral Data for New Compounds:

Ethyl-3-amino-1-(4-bromo phenyl)-1H-benzo[f]chromene-2-carboxylate (7h):

White solid, m.p 204-206°C; IR (KBr, cm^{-1}): 3328, 3463, 3082, 2977, 1670, 1635, 1504, 1222, 1072; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.19 (t, 3H, CH_3), 4.67 (m, 2H, CH_2), 5.35 (s, 1H, CH), 6.13 (br, 2H, NH_2 , D_2O exchangeable), 7.19-7.76 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 14.6, 36.7, 59.7, 79.8, 116.7, 118.5, 119.8, 123.3, 124.9, 127.0, 128.6, 129.0, 130.0, 130.8, 131.2, 131.3, 145.5, 147.0, 159.9, 169.0; *Anal.* Calcd for $\text{C}_{22}\text{H}_{18}\text{BrNO}_3$: C, 62.25; H, 4.27; N, 3.30. Found: C, 62.13; H, 4.35; N, 3.18.

Ethyl-3-amino-1-(4-hydroxy phenyl)-1H-benzo[f]chromene-2-carboxylate (7i):

White solid, m.p 129-130°C; IR (KBr, cm^{-1}): 3332, 3463, 3062, 2981, 1662, 1593, 1512, 1222, 1076; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.39 (t, 3H, CH_3), 4.24 (m, 2H, CH_2), 5.62 (s, 1H, CH), 6.33 (br, 2H, NH_2 , D_2O exchangeable), 7.05-7.89 (m, 10H), 10.21 (s, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 14.6, 36.7, 59.7, 79.9, 116.7, 118.5, 123.3, 124.8, 127.0, 128.2, 128.6, 129.0, 129.5, 130.9, 131.3, 131.7, 145.0, 147.0, 159.9, 169.0; *Anal.* Calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4$: C, 73.10; H, 5.30; N, 3.87. Found: C, 72.95; H, 5.46; N, 3.79.

Ethyl-3-amino-1-(4-nitro phenyl)-1H-benzo[f]chromene-2-carboxylate (7k):

Yellow solid, m.p 180-182 °C. IR (KBr, cm^{-1}): 3301, 3448, 3070, 2990, 1678, 1639, 1515, 1390, 1224, 1072; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.39 (t, 3H, CH_3), 4.25 (m, 2H, CH_2), 5.71 (s, 1H, CH), 6.44 (br, 2H, NH_2 , D_2O exchangeable); 7.08-8.06 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 14.6, 37.2, 59.9, 78.9, 116.7, 117.5, 123.0, 123.6, 125.1, 127.2, 128.8, 129.0, 129.5, 130.7, 131.3, 146.2, 147.1, 153.8, 160.0, 168.7; *Anal.* Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_5$: C, 67.66; H, 4.65; N, 7.18. Found: C, 67.57; H, 4.81; N, 7.02.

Polypropylenimine dendrimer generation 0.5: Yellow solution. IR (KBr, cm^{-1}): 2250 (C-N), 720 (CH_2 -DAB), 1220, 1315 (C-N).

Polypropylenimine dendrimer generation 1: Yellow solid. IR (KBr, cm^{-1}): 3400 (N-H), 1668 (N-H), 1219, 1315 (C-N), 1130 (C-C).

Conclusion

In conclusion, we have reported the green and eco- friendly synthesis 2-amino-2-chromene derivatives by using highly efficient catalyst nano material polymeric (PPI). PPI is classification dendrimers with special properties such as being antimicrobial, antibacterial, non-toxic, and environmentally friendly. The most important advantages of this reaction include mild, green synthesis; avoidance of the use of toxic organic solvents, excellent yield and short reaction times and simple work up procedure.

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Graphical Abstract

Nano polypropylenimine dendrimer (DAB-PPI-G₁): as a novel nano basic-polymer catalyst for one-pot synthesis of 2-amino-2-chromene derivatives

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- ✓ For the first time, a novel nano basic-polymer catalyst for 2-amino-2-chromene derivatives is proposed.
- ✓ Synthesis of new 2-amino-2-chromenes
- ✓ Avoiding of any metal, or acid catalysts
- ✓ Green chemistry

