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ORIGINAL RESEARCH ARTICLE

Sustainable synthesis of chromene derivatives catalysed by magnetite nanoparticle cored polyamine dendrimer

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ABSTRACT

Chromene derivatives are naturally occurring heterocyclic compounds used as cosmetic agents, food additives, and potential biodegradable agrochemicals. Normally, its synthesis is carried out with three component/substrates with a suitable base. Dendrimer with amine functionality has several applications in catalysis, more specifically, dendrimers having enriched amino groups with accessible void makes a significant impact in base catalysis. Moreover, polar periphery of the dendrimers may enhance the solubility of material in the reaction medium. Therefore, herein we report the base catalytic efficiency of magnetite nanoparticle supported polyamine dendrimer with enriched amine groups and peripheral carboxyl groups. Actually, magnetite supported polyamine dendrimer synthesis involves the synthesis of PAMAM G3 on magnetite nanoparticle core, followed by reduction of amide group with subsequent functionalization of carboxylic acid terminals. Further, it is used as versatile polyvalent base for the synthesis of chromene derivatives. The magnetite supported dendritic scaffold has accessible voids and polar periphery which enables them dispersible in the reaction medium. The recycle efficiency study confirms, the competency of the material to work in industrial catalysis.

keywords: magnetite nanoparticle; polyamine dendrimer; base catalysis; chromene derivatives; recycle efficiency

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1. Introduction

Dendrimers such as PAMAM, PPI, PEI, DPA, PEG, etc., were employed as base catalyst in condensation reactions[1], addition reactions[2], hydrogenation reactions[3] and many more. Amine enriched dendrimers emerged as base catalyst to wide variety of reactions such as aldol condensation and Michael addition reaction. PAMAM dendrimer are widely employed, as they can be easily tunable to synthesis other class of dendrimers. The peripheral amine groups and the interior amide groups can be modified and utilized as catalyst. Chromenes are important class of compound with biological significance such as anticoagulant, antifungal, antiglycemic, antioxidant, etc.[4,5]. Several supported base catalysts such as $Ni_{0.5}Zn_{0.5}Fe_2O_3$@hydroxyapatite[6], Fe_3O_4@D-NH_2-HPA dendrimer[7], Poly Ionic Liquid Functionalized Mn (III)[8], 1-Methylimidazolium tricyanomethanide[9], piperazine@graphene oxide hydrotalcite[10], Fe_3O_4[11–14]. Fe_3O_4@SiO_2-NH_2, MgO[15], etc., have been reported for the synthesis of chromene derivatives. Hence, structurally modified PAMAM dendrimer with enriched amino groups on silica coated magnetite nanoparticle can serve as a base catalyst for the synthesis of chromene derivatives, a biologically important compound for various applications.

Therefore, we have developed a simple strategy to synthesis and structurally modify the PAMAM to afford polyamine dendrimer with increased nitrogen content as well as the amphiphilic nature which will be more competent than the existing PAMAM in the high throughput applications[16]. This newly developed magnetic dendrimer material with enriched active amino groups and carboxylic acid groups will show remarkable efficiency as catalyst in the synthesis of chromene derivatives

2. Materials and methods

All the reagents and solvents were purchased from commercial sources. Ferrous sulphate heptahydrate (98%), anhydrous ferric chloride (98%), acrylonitrile (99%), sodium metal was purchased from Spectrochem. Oleic acid, Polyvinylpyrrolidone (Mol. Wt. 40,000 Da) were purchased from LOBA. Tetraethoxysilane (TEOS, 98%), 3-aminopropyltriethoxysilane (APTES, 98%) were purchased from Alfa Aesar. Methylacrylate (99%) and sodium metal was purchased from Spectrochem. Lithium aluminum hydride (LAH, powder reagent, 95%) was purchased from Sigma Aldrich. Solvents such as methanol, ethanol, THF, toluene (HPLC grade), DCM, DMF were purchased from Fischer, THF and DCM were distilled and used. Deionized water has been used for the reactions wherever is applicable. All the reactions were carried out using Remi digital overhead stirrer with digital rpm controller provided with Teflon blade.

2.1. Synthesis of magnetite cored polyamine dendrimer catalyst

Magnetite core dendrimer template was synthesized by using our previously reported method[14], which involves the synthesis of polyamidoamine (PAMAM) dendrimer up to third generation on silica coated magnetite nanomaterial by microwave assisted method. The synthesized PAMAM dendrimer was modified into polyamine dendrimer (PNPEDA) through reduction using LAH. The peripheral amino groups were functionalized with succinic anhydride to yield carboxyl terminated PNPEDA-COOH@Fe_3O_4/SiO_2 nanomaterial.

2.2. Synthesis of chromene derivatives using PNPEDA-COOH@Fe_3O_4/SiO_2 catalyst

Aryl aldehyde (1 mmol), active methylene compound (1 mmol) and aryl hydroxy compound (1 mmol) were dissolved in 6 mL of the solvent (1:1 v/v of ethanol and water) taken in a 100 mL round bottomed flask. To this dispersion 20 mg of the catalyst was added and dispersed well via sonication. The solution was stirred at 60 °C for particular time. Completion of the reaction was monitored through TLC using hexane and ethyl acetate as eluent (9:1). After completion of the reactions, the catalyst was isolated using an external magnet and the mixture was extracted with water and ethyl acetate. Then dried over anhydrous Na_2SO_4 and the solvent was evaporated, chromene products were purified by recrystallisation using ethanol. All the isolated products were analyzed through ^{13}C and ^{1}H NMR studies.

3. Results and discussion

In our previous report, we have synthesised magnetite nanoparticle supported polyamine dendrimer with enriched amine groups and peripheral carboxyl groups[16]. Silica coated magnetite nanoparticles by co-precipitation method. Microwave assisted synthesis of PAMAM G_3 dendrimer on the silica coated magnetite core have been achieved in a shorter reaction time at the maximum of 6 h; whereas the classical synthetic method is time consuming process. The amide groups of PAMAM G_3@Fe_3O_4/SiO_2 was reduced using LAH to yield the amine groups which enables polyamides into polyamine dendrimer viz., poly (N-propylethane-1,2-diamine) G_3 (i.e., PNPEDA G_3@Fe_3O_4/SiO_2). It was further functionalised with carboxylic acid terminal groups using succinic anhydride to yield PNPEDA-COOH@Fe_3O_4/SiO_2 (**Figure 1**).

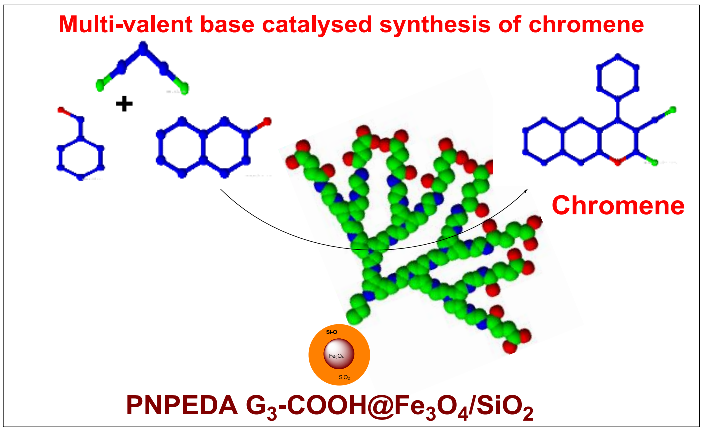


Figure 1. Magnetite cored catalyst PNPEDA-COOH@Fe_3O/SiO_2 for the synthesis of chromene derivatives.

3.1. Catalysis of PNPEDA-COOH@Fe_3O_4/SiO_2 for the synthesis of chromene derivatives

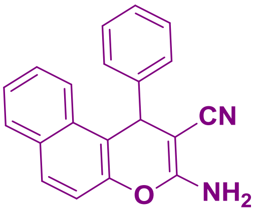
This material has meritorious characteristics like rapid synthesis via microwave method, enriched amino groups obtained by reduction of polyamide dendrimer into polyamine dendrimer and improved amphiphilicity by modifying the terminal amino groups into carboxylic acid group. PNPEDA-COOH@Fe_3O_4/SiO_2 nanomaterial was exploited as base catalyst for the synthesis of chromene derivatives (**Table 1**). One pot synthesis of chromene compounds were prepared from benzaldehyde (1 mmol), malanonitrile (1 mmol) and 2-napthol (1 mmol), which is the model reaction for the optimisation of reaction conditions. Solvent, temperature and catalyst quantity affect the reaction time and product yield. 20 mg of PNPEDA-COOH@Fe_3O_4/SiO_2 nanomaterial in 5 mL of ethanol and water (1:1 by volume) at 60 °C is the optimized reaction conditions to obtain chromene in better yield.

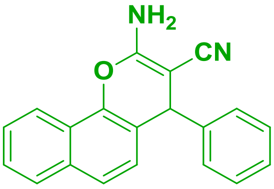
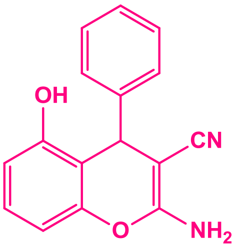
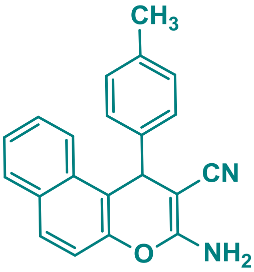
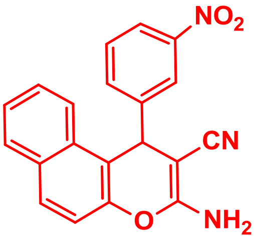
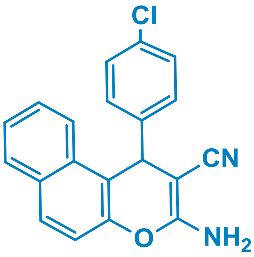
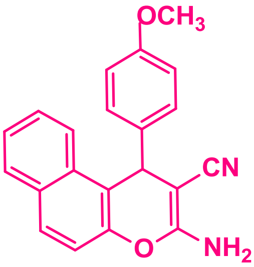
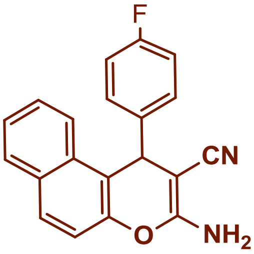
Table 1. Catalysis of PNPEDA-COOH@Fe_3O_4/SiO_2 for validating chromene synthesis.

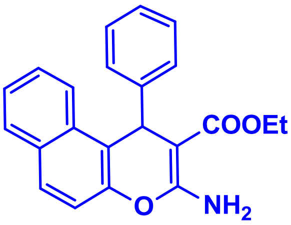
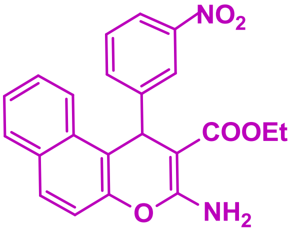
S. No.	Solvent	Temperature	Time (min)	Yield [b] %
1	Without catalyst	60	360	NR
2	H_2O	60	60	69
3	EtOH	60	30	80
4	H_2O/EtOH	50	60	81
5	H_2O/EtOH	80	20	92
6a	H_2O/EtOH	60	75	75
7b	H_2O/EtOH	60	35	83
8	H_2O/EtOH	60	20	92

Substrate 1: aldehyde (1 mmol), Substrate 2: malanonitrile (1 mmol), Substrate 3: naphthol (1 mmol), catalyst PNPEDA COOH@Fe_3O_4/ SiO_2 (20 mg), [a] catalyst PNPEDA COOH @Fe_3O_4/SiO_2 (10 mg), [b] catalyst PNPEDA COOH @Fe_3O_4/SiO_2 (15 mg).

Table 2. Synthesis of chromene using PNPEDA-COOH@Fe_3O_4/SiO_2 catalyst.

S. No	Substrate 1	Substrate 3	Product	Time (min)	Yield (%)	Ref
1	4-H	2-naphthol		20	92	[17]

S. No	Substrate 1	Substrate 3	Product	Time (min)	Yield (%)	Ref
2	4-H	1-naphthol		20	89	[18]
3	4-H	resorcinol		20	90	[19]
4	4-CH_3	2-naphthol		30	87	[20]
5	3-NO_2	2-naphthol		30	85	[21]
6	4-Cl	2-naphthol		20	87	[22]
7	4-OCH_3	2-naphthol		30	82	[18]
8	4-F	2-naphthol		20	83	[22]

S. No	Substrate 1	Substrate 3	Product	Time (min)	Yield (%)	Ref
9[a]	4-H	2-naphthol		45	79	[20]
10[a]	3-NO_2	2-naphthol		45	77	[20]

Substrate 1: aldehyde (1mmol), Substrate 2: malanonitrile (1mmol), Substrate 3: naphthol (1 mmol), catalyst PNPEDA COOH@Fe_3O_4/ SiO_2 (20 mg); [a] Substrate 2: ethylcyanoacetate (1mmol).

One pot three component chromene synthesis using PNPEDA-COOH@Fe_3O_4/SiO_2 nanomaterial catalyst involves two steps, Knoevenagel condensation between benzaldehyde and malononitrile followed by Michael addition between condendsed product and 2-napthol. Reactions using various substrates were carried out resulting in good yield of chromene derivatives. Among, 2-naphthol, 1-naphthol and resornicol (**Table 2,** entry 1,2,3) in the reaction with benzaldehyde and malononitrile, 2-naphthol gave better yield than others. Several substituted aromatic aldehydes such as methyl, nitro, chloro, methoxy, fluoro were employed and the products obtained were in good yields (**Table 2** entry 4,5,6,7,8). 2-ethyl cyanoacetate along with benzaldehyde and 2-naphthol (**Table 2,** entry 9,10**)** gave chromene products in lesser yield compared to product yield using malononitrile. PNPEDA-COOH@Fe_3O_4/SiO_2 with enriched amine groups favours the shorter reaction time compared to other supported base catalysed reactions. All the synthesised products were extracted, recrystallised and confirmed through ^{1}H NMR and ^{13}C NMR studies.

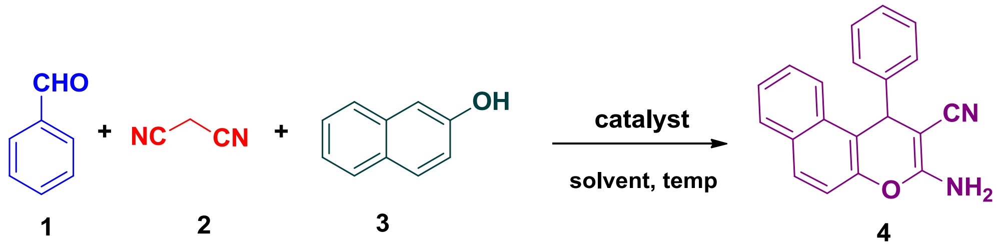
The rationally synthesised magnetite cored polyamine dendrimer was compared with other reported base catalyst for the synthesis of chromene (**Table 3**). PNPEDA-COOH@ Fe_3O/SiO_2 catalyst has been proved to be better and efficient catalyst than the other reported catalysts.

Table 3. Comparison of the catalytic activities of various catalysts for chromene synthesis.

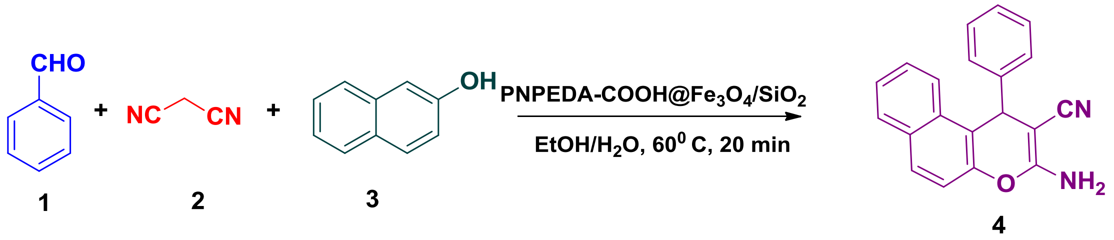
S. No	Catalyst	Reaction condition	Time (min)	Yield (%)
1	MgO	DMF, reflux	240	70[15]
2	Urea	EtOH: H_2O, RT	120	90[23]
3	Hydrotalcite	H_2O, reflux	240	95[10]
4	Fe_3O_4@SiO_2@NH-NH_2-PW	H_2O, reflux	40	90[23]
5	Amine-functionalized hyper-crosslinked polyphenanthrene	Solvent free	60	92[24]
6	Amine functionalised MOF	EtOH	240	92[25]
7	amino-appended β-cyclodextrins	H_2O	300	93[26]
8	PNPEDA-COOH@Fe_3O/SiO_2	EtOH: H_2O, 60 °C	20	92

Table 3 data reveals the merit of magnetite supported dendrimer in the chromene synthesis. Even though other catalysts in **Table 3** had good yield, their reaction conditions vary from the present catalyst, especially solvent, temperature and reaction time for the synthesis of chromene (**Scheme 1**). NH_2 functionalised MOF catalysts (**Table 3**, entry 5) yields 90% chromene but reactions take place in ethanol medium for 60 min, similarly, MgO (**Table 3**, entry 1) yields 70% chromene only under reflux conditions with DMF and the

reaction time is also prolonged. Amino-appended β-cyclodextrins catalyst give better yield but reaction time is too longer (300 min) (**Table 3**, entry 7). All other catalysts in **Table 3** were compared with PNPEDA G3@Fe_3O_4/SiO_2, which seems to be superior in terms of reaction conditions, solvent and high yield at low reaction time. The better catalytic efficiency was attributed by the multivalent interaction of basic nitrogen atoms available in the dendrimer molecule. Further, the dendrimer voids can accommodate the substrate molecules which facilitates faster reaction time. The amphiphilic nature of catalyst molecules disperses them in the reaction medium which favours the chemical reaction faster to yield the product. This material has been used in eight cycles for chromene synthesis (**Scheme 2**) without any significant decline in their catalytic activity. It assures the better stability of the catalyst for the industrial process in a greener way.



Scheme 1. Base catalysis for the synthesis of chromene.



Scheme 2. Synthesis of chromene using PNPEDA-COOH@Fe_3O_4/SiO_2 catalyst.

3.2. Recycle efficiency of the catalyst PNPEDA-COOH@ Fe_3O/SiO_2

Synthesised magnetite supported polyamine dendrimer was efficiently recycled, regenerated and reused. The nanomaterial was proved to be sustainable and effective catalyst up to eight catalytic cycles for the synthesis of chromene (**Scheme 2**) without any significant loss in weight and product yield. **Figure 2** shows the recycling efficiency of the catalyst by simple magnetic separation. The regenerated catalyst from the first cycle was employed in new chromene synthesis reaction (**Scheme 2)** and the yield was calculated at time 20 min. Since, at each cycle the yield of the chromene varies for a constant reaction time of 20 min. Magnetically separated catalyst was regenerated by washing thrice with ethanol, acetone, dried and reused for several catalytic cycles.

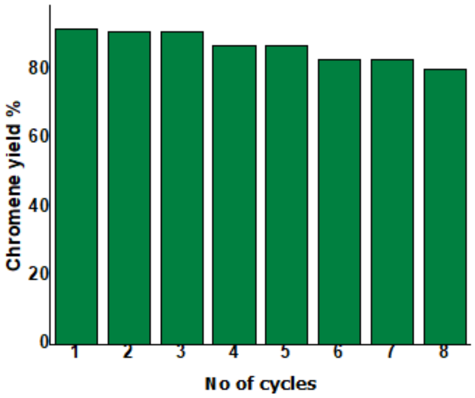


Figure 2. Recycle plot of the magnetite cored catalyst PNPEDA-COOH@Fe_3O/SiO_2.

4. Conclusion

As we had an objective to develop a rational magnetite supported polyamine dendrimer, the PAMAM G_3 has been converted into PNPEDA G_3 with enriched amino groups satisfactorily. Likewise, the aqueous dispersibility of the dendritic nanomaterial has been simply achieved by grafting with succinic anhydride to attain carboxylic acid terminated dendritic nanomaterial. The multivalent basic amino and hydroxy groups catalytic activities were enlightened through organic reaction for the synthesis of chromene derivatives. The magnetic cored dendritic nanomaterial being inexpensive can be recovered by magnetic separation and also regenerated by acid treatment for further use.

5. NMR spectroscopic data of the chromene products (Table 2)

(1) **3-Amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile, (Table 2, entry 1), $C_{20}H_{14}N_2O$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 8.03–7.17 (m, 11H), 7.10 (2H), 4.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 160.0, 146.4, 145.3, 130.9, 130.7, 130.1, 128.9, 128.5, 127.4, 126.5, 126.3, 125.1, 123.7, 120.5, 117.8, 116.6, 113.7, 112.5, 57.8, 38.8. mp- 280–281 °C.

(2) **2-Amino-4-phenyl-4H-benzo[h]chromene-3-carbonitrile, (Table 2, entry 2), $C_{20}H_{14}N_2O$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.88–7.17 (m, 11H), 6.21 (s, 2H), 4.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 160.0, 146.2, 141.7, 134.1, 132.5, 128.9, 128.5, 127.6, 126.7, 126.4, 125.2, 123.1, 120.6, 117.8, 116.6, 115.1, 55.8, 38.8.

(3) **2-Amino-5-hydroxy-4-phenyl-4H-chromene-3-carbonitrile, (Table 2, entry 3), $C_{16}H_{12}N_2O_2$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 9.84 (s, 1H), 7.30–6.42 (m, 8H), 6.86 (s, 2H), 4.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 161.0, 157.3, 148.9, 146.3, 131.3, 129.0, 128.8, 128.0, 121.1, 114.1, 112.6, 102.7, 56.6, 39.7.

(4) **3-Amino-1-(p-tolyl)-1H-benzo[f]chromene-2-carbonitrile, (Table 2, entry 4), $C_{21}H_{16}N_2O$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.94–7.08 (m, 10H), 6.86 (s, 2H), 4.62 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 162.6, 145.2, 143.4, 134.6, 130.7, 130.2, 129.8, 129.3, 129.1, 128.9, 128.3, 127.7, 126.5, 126.3, 123.6, 123.5, 117.8, 115.5, 60.8, 37.9, 24.7.

(5) **3-Amino-1-(3-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile, (Table 2, entry 5), $C_{20}H_{13}N_3O_3$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.95–7.40 (m, 10H), 7.19 (s, 2H), 5.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 158.3, 147.1, 143.2, 134.6, 130.6, 130.0, 129.9, 129.8, 129.1, 128.9, 128.5, 127.7, 126.5, 126.3, 123.6, 123.4, 117.8, 116.5, 58.2, 38.2.

(6) **3-Amino-1-(4-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (Table 2, entry 6), $C_{20}H_{13}ClN_2O$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.98–7.19 (m, 10H), 7.04 (s, 2H), 4.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 160.5, 148.8, 143.2, 130.9, 130.4, 130.4, 129.9, 128.8, 128.4, 128.2, 126.5, 125.4, 123.5, 120.1, 117.8, 116.8, 61.07, 38.72; mp- 219–220 °C.

(7) **3-Amino-1-(4-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (Table 2, entry 7), $C_{21}H_{16}N_2O_2$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.98–6.81 (m, 10H), 7.09 (s, 2H), 5.36 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 159.0, 157.4, 146.8, 134.6, 130.9, 130.2, 129.8, 128.9, 127.7, 126.5, 124.0, 123.5, 120.7, 117.8, 115.1, 114.4, 58.2, 55.8, 37.3.

(8) **3-Amino-1-(4-fluorophenyl)-1H-benzo[f]chromene-2-carbonitrile (Table 2, entry 8), $C_{20}H_{13}FN_2O$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.98–7.19 (m, 10H), 7.04 (s, 2H), 4.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 161.8, 160.1, 146.3, 141.2, 130.9, 130.1, 129.3, 128.9, 128.3, 127.7, 124.8, 123.5, 120.1, 116.8, 115.5, 115.3, 58.2, 38.1.

(9) **Ethyl 3-amino-1-phenyl-1H-benzo[f]chromene-2-carboxylate (Table 2, entry 9), $C_{22}H_{19}NO_3$-**^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm), 7.90–7.01 (m, 11H), 6.98 (m, 2H), 4.56 (s, 1H), 3.89 (s, 2H), 1.18 (m, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$); δ (ppm) 158.5, 153.7, 151.9, 148.5, 135.1, 134.6, 132.8, 130.5, 129.8, 128.8, 127.5, 126.9, 126.4, 126.3, 125.6, 123.5, 117.7, 113.5,79.2, 60.9, 38.4, 13.8.

(10) **Ethyl 3-amino-1-(3-nitrophenyl)-1H-benzo[f]chromene-2-carboxylate (Table 2, entry 10), $C_{22}H_{18}N_2O_5$:** ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) 8.19–7.14 (m, 10H), 7.05 (m, 2H), 4.36 (m, 2H), 4.62 (s, 1H), 1.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 159.5, 153.5, 152.1, 148.5, 135.1, 134.7, 131.8, 130.5, 129.7, 128.6, 127.7, 127.1, 126.6, 126.3, 125.6, 122.5, 117.8, 114.5,80.1, 63.5, 37.8, 14.13.

Author contributions

Conceptualization, RR; methodology, RR; software, KL; validation, KL; formal analysis, KL; investigation, KL; resources, KL; data curation, KL; writing—original draft preparation, KL; writing—review and editing, RR and KL; visualization, KL; supervision, RR; project administration, RR; funding acquisition, RR. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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