

Cyclohexylamine – An efficient organocatalyst for the synthesis of 2-amino-4*H*-chromene derivatives by multicomponent reactions of salicylaldehydes, active methylene compounds and nitroalkanes

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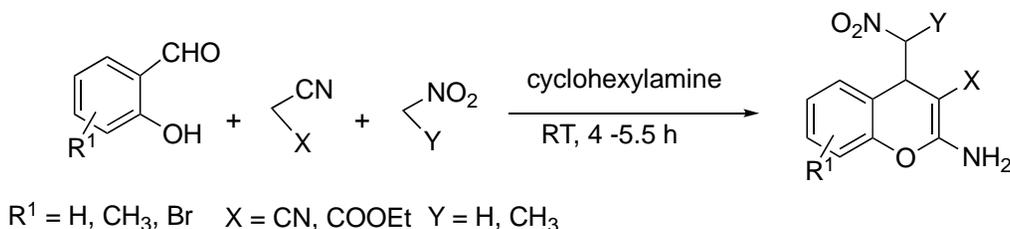
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Abstract

Cyclohexylamine was found to be an efficient organocatalyst for the synthesis of structurally diverse 2-amino-4*H*-chromenes by multicomponent reaction of (substituted) salicylaldehydes, active methylene compounds and nitroalkanes at ambient temperature and under solvent-free conditions. The synthesis of a variety of 2-amino-4*H*-chromenes was achieved using the reaction of (substituted) salicylaldehydes with two different C-H acids. The present protocol, which employed commercially available cyclohexylamine as an organocatalyst, offered the advantages of operational simplicity and avoidance of conventional purification methods and the obtained products were essentially pure.



Keywords: 2-Amino-4*H*-chromene, cyclohexylamine, organocatalyst, active methylene compound

Introduction

The chromene and pyran moieties are frequently found as central structural components in biologically active molecules and natural products. For instance, hepialone - the pheromone isolated from hairpencils of the male moth - possesses a pyran nucleus.¹ Likewise, chromene framework appears in natural products such as (+)-brazillin, myristinin-B and dracoflavin B²⁻⁴ (Figure 1). Furthermore, substituted chromenes play a pivotal role in development of synthetic methodologies for biologically active molecules. Diversely functionalized chromene derivatives and their biological activities are well documented in the field of biomedical chemistry (Figure 2).^{5,6} Recently, 4*H*-chromenes bearing a nitrile functionality have received a great deal of attention as they exhibit potential applications in the treatment of human inflammatory TNF α -mediated diseases such as rheumatoid and psoriatic arthritis and they are also reported to be useful in cancer therapy.⁷⁻⁹ Chromenes with a nitrile functionality such as (4*H*-chromen-4-yl) malononitriles were found to inhibit mitogen-activated protein kinase, protein kinase 2 (MK-2) and to suppress the expression of the TNF α in U937 cells.¹⁰⁻¹¹

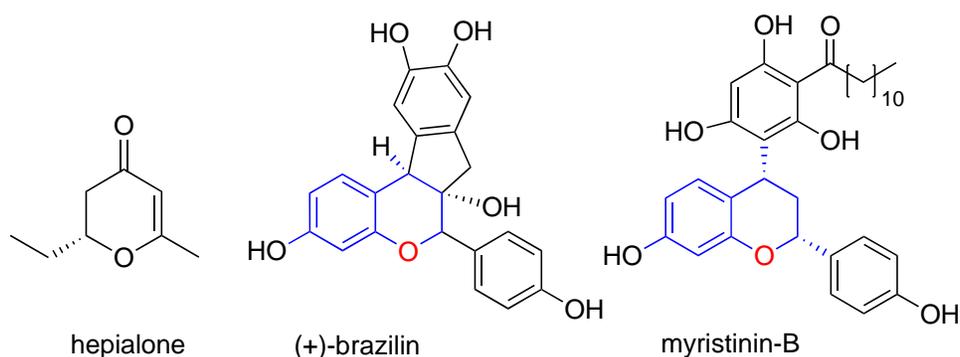


Figure 1. Some chromene and pyran natural products.

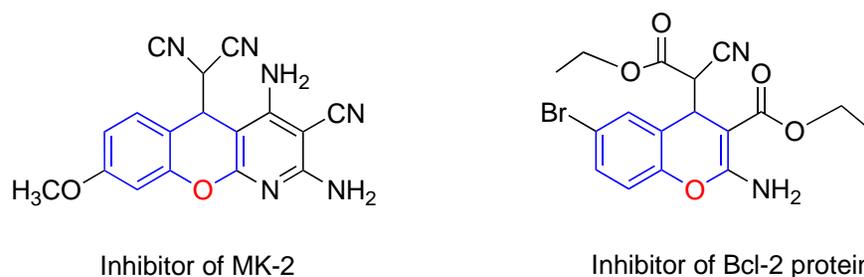


Figure 2. Some biologically active chromenes.

Considering the potential utility of structurally and functionally diverse chromenes in various pharmaceuticals and biological applications, it is of practical interest to design efficient and greener protocols for the synthesis 2-amino-4*H*-chromenes.

In the past three decades, the concept of sustainability has taken a center stage in chemical industry.¹² Consequently, there is a heightened interest in the evaluation of simple organic molecules as organocatalysts.^{13,14} Notably, a literature survey with regard to synthesis of chromenes using salicylaldehyde and two different acids found to only two reports by Elinson et al.^{15,16} The first report dealt with electrochemically induced chain transformation of salicylaldehydes and alkyl cyanoacetates into substituted 4*H*-chromenes¹⁵ whereas the second report demonstrated the use of sodium acetate or potassium fluoride as

a base catalyst for direct multicomponent assembly of 2-amino-4*H*-chromene scaffold from salicylaldehyde, malononitrile or cyanoacetate and nitroalkanes under solvent-free conditions. To the best of our knowledge, protocols for synthesis of chromenes using organocatalysts have not been reported to date.

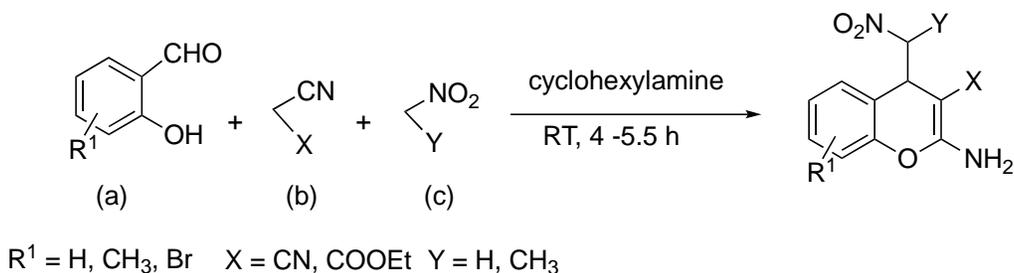
Inspired by our earlier work on evaluation of the catalytic potential of simple organocatalysts like diethylamine in organic transformations^{17,18} and also by considering the fact that the pKa values of cyclohexylamine (18.36) and diethylamine (18.75) are comparable¹⁹ we set out to test the catalytic efficacy of cyclohexylamine in the synthesis of chromenes. The results of these studies are reported herein.

Results and Discussion

The base-catalyzed synthesis 2-amino-4*H*-chromenes by reaction between an aldehyde and active methylene compounds follows a cascade Knoevenagel-carba-Michael cyclization pathway. With the use of cyclohexylamine as the base catalyst we planned to carry out the reaction of (substituted) salicylaldehydes with two different active methylene compounds, namely malononitrile and nitromethane as C-H acids.

A model reaction between salicylaldehyde, malononitrile and nitromethane was performed at ambient temperature under solvent-free conditions using cyclohexylamine as an organocatalyst. Upon addition of cyclohexylamine (10 mol %) to an equimolar mixture of salicylaldehyde, malononitrile and nitromethane, a slightly exothermic reaction took place. After stirring the reaction mixture for 4.5 hours, a solid mass was obtained. However, with use of substituted salicylaldehydes it was observed that due to limited miscibility of aldehydes with other reactants the yields were low. In order to improve the yields, the protocol was modified and it was observed that addition of ethyl alcohol (2 mL) to the reaction mixture after addition of catalyst, resulted in a homogenous reaction system and improved yields were obtained. Further, it was observed that after completion of reaction (TLC), addition of water (20 mL) to the reaction mixture and stirring for 30 minutes followed by simple filtration, washing by water and petroleum ether gave pure product and further purification by column chromatography was not required. Under the established reaction conditions with a view to broaden the scope of the developed protocol, nitroethane was selected as C-H acid in place of nitromethane. The reaction worked equally well and the desired products were obtained in high yields.

Encouraged with this success, we then planned to demonstrate the generality of the reaction conditions and to expand its scope to the synthesis of structurally diverse 2-amino-4*H*-chromene derivatives. Accordingly, reactions were performed between various substituted salicylaldehydes, malononitrile / ethyl cyanoacetate and nitromethane / nitroethane under the established reaction conditions. The results are summarized in Table 1. All the synthesized compounds were characterized by physical and spectroscopic methods. When nitroethane was used C-H acid, a mixture of diastereoisomeric products was obtained. The ratio of two diastereoisomers was calculated by ¹H-NMR spectroscopy. Compared to earlier reported protocols the present protocol offered the advantages of operational simplicity and higher yields.

Table 1. Cyclohexylamine-catalyzed synthesis of 2-amino-4*H*-chromenes

Entry	Aldehyde (a)	X	Y	Product (d)	Time (h)	Yield (%)
1.		CN	H		4.0	92
2.		CN	CH ₃		4.5	90
3.		COOEt	H		5.0	82
4.		COOEt	CH ₃		5.0	80
5.		CN	H		4.5	91
6.		CN	CH ₃		5.0	93
7.		COOEt	H		5.5	84
8.		COOEt	CH ₃		5.5	81
9.		CN	H		4.5	84
10.		CN	CH ₃		5.0	86
11.		COOEt	H		5.0	82
12.		COOEt	CH ₃		5.5	80

a: Reaction conditions: (substituted) salicylaldehyde, malononitrile/ethyl cyanoacetate and nitromethane/nitroethane (2 mmol each), cyclohexylamine (10 mol %), ethanol (2 mL), RT

Conclusions

In conclusion, we have demonstrated the utility of commercially available cyclohexylamine as an efficient organocatalyst for the synthesis of a variety of 2-amino-4*H*-chromene derivatives at ambient temperature by the reaction of (substituted) salicylaldehyde with two different C-H acids under solvent-free conditions. The clean reaction profile, simple work-up procedure and high yields make the present protocol attractive for the synthesis of 2-amino-4*H*-chromenes.

Experimental Section

General. ¹H NMR spectra were recorded in DMSO-*d*₆ using a BRUKER 400 MHz spectrometer or Varian 300 MHz spectrometer at 400 or 300 MHz respectively, ¹³C spectra were recorded on BRUKER spectrometer or Varian spectrometer at 100 MHz or 75 MHz, respectively. The chemical shifts (δ) and coupling constants (*J*)

are expressed in ppm and Hz, respectively. Reagents and starting materials were directly used as received from commercial sources.

General experimental procedure. To a well-stirred mixture of (substituted) salicylaldehyde (2 mmol), malononitrile/ethyl cyanoacetate (2 mmol) and nitromethane/nitroethane (2 mmol) was added cyclohexylamine (10 mol %) and ethanol (2 mL). The stirring was continued at room temperature and the progress of the reaction was monitored by TLC (The solvent system used was the mixture of n-hexane and ethyl acetate (8:2, v/v)). Upon completion of the reaction, water (20 mL) was added and the resultant solid was filtered off, washed with water, dried in air, washed with petroleum ether and dried. The resultant products were found to be essentially pure and did not require any further purification. Melting points were recorded on 'Kumar Melting Point Apparatus' - model number KI-11-02(A).

2-Amino-4-(nitromethyl)-4H-chromene-3-carbonitrile (1d). Solid; Yield 92%; mp 143-144 °C (lit. mp¹⁶ 139-140 °C); IR (KBr): 3436.94, 3332.10, 3217.99, 2919.40, 2201.82, 1659.98, 1604.61, 1535.30, 1420.13, 1213.89, 1048.81, 999.73, 859.92, 763.97, 596.77 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 4.36 (dd, 1H, *J* 5.7 Hz), 4.52 (dd, 1H, *J* 12.0 and 6.6 Hz), 4.60 (dd, 1H, *J* 11.7 and 5.1 Hz), 4.89 (br s, NH₂), 7.03 (d, 1H, *J* 12 Hz), 7.04- 7.19 (m, 2H, ArH), 7.29- 7.33 (m, 1H, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 35.25 (CH), 50.98 (=C-CN), 80.71 (CH₂-NO₂), 116.67 (ArCH), 119.35 (ArC), 119.68 (CN), 125.00, 127.98, 129.18 (ArCH), 149.69 (ArC), 162.57 (=C-NH₂) ppm. HRMS: (MH⁺) 232.0723, 223.0946, 215.1065; for C₁₁H₉N₃O₃ (231.21).

2-Amino-4-(1-nitroethyl)-4H-chromene-3-carbonitrile (2d). Solid; Yield 90%; mp 166-168 °C; IR (KBr): 3432.81, 3318.58, 3202.03, 2930.15, 2195.30, 1642.34, 1538.76, 1419.13, 1223.47, 1182.91, 1105.13, 1033.83, 870.98, 759.05, 622.37, 497.41, 450.28 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.35 (d, 2H, *J* 6.8 Hz), 1.60 (t, 5H, *J* 6.6 Hz), 4.19 (d, 1H, *J* 6.8 Hz), 4.42 (d, 0.65 H, *J* 3.3 Hz), 4.69 (m, 1H, *J* 6.8 Hz), 4.71 (d, 0.68 H, *J* 6.8 Hz), 4.99 (br s, NH₂), 6.96- 6.98 (m, 0.70 H), 6.99-7.02 (m, 1.66 H), 7.06 -7.13 (m, 2.72 H), 7.30 (d, 1.69 H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 13.72 & 14.21 (CH₃), 48.92 (=C-CN), 87.08 & 87.59 (CHNO₂), 116.42 (ArCH), 120.20 & 120.28 (CN), 124.92 (ArCH), 125.02 (ArCH), 128.38 (ArCH), 129.31, (ArCH), 150.27 & 150.46 (ArC); 163.34 & 163.65 (=C-NH₂) ppm; HRMS: (MH⁺) 246.0879, 237.0799, 216.1140, 209.0117; for C₁₂H₁₁N₃O₃ (245.24).

Ethyl- 2-amino-4-(nitromethyl)-4H-chromene-3-carboxylate (3d). Solid; Yield 82%; mp 108-110 °C; IR (KBr): 3403.03, 3301.99, 2989.92, 2949.26, 2906.78, 1671.51, 1616.86, 1538.36, 1480.34, 1414.63, 1374.13, 1304.86, 1215.06, 1084.52, 1051.88, 768.76, 505.43, cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.34 (t, 3H, *J* 7.2 Hz), 4.24 (dq, 2H, *J* 6.9 and 2.7 Hz, COOCH₂), 4.39 (dd, 1H, *J* 10.5 and 7.8 Hz, CH), 4.62 (m, 2H, CH₂NO₂), 7.01 (d, 1H, *J* 8.0 Hz, ArH), 7.12 (t, 1H, *J* 7.2 Hz, ArH), 7.16 (d, 1H, ArH), 7.27 (t, 1H, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 14.59 (CH₃), 34.43 (CH), 59.14 (OCH₂), 71.52 (=C-COOEt), 81.25 (CH₂NO₂), 116.17 (ArCH), 121.99 (ArC), 124.68, 128.18, 128.70 (ArCH), 149.98 (ArC), 162.42 (=C-NH₂), 167.93 (COOEt) ppm; HRMS: (MH⁺) 279.0983, 264.1236, 256.0377, 218.0819, for C₁₃H₁₄N₂O₅ (278.27).

Ethyl -2-amino-4-(1-nitroethyl)-4H-chromene-3-carboxylate (4d). Solid; Yield 80%; mp 195-146 °C; IR (KBr): 3433.45, 3318.91, 3203.34, 2928.44, 2196.87, 1641.67, 1540.18, 1420.14, 1261.33, 1225.23, 1184.81, 1106.91, 1035.10, 872.01, 760.62, 646.42, 462.70 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.35 (d, 1.74 H, *J* 6.8 Hz), 1.24 - 1.45 (t, 7H, *J* 6.8 Hz), 4.18 - 4.19 (d, 1.22 H), 4.41 - 4.53 (m, 1.25H), 4.56 - 4.59 (m, 0.75 H), 4.88-4.91 (br s, NH₂), 6.91 (dd, 1.88 H, *J* 9.0 and 4.2 Hz), 7.06 - 7.15 (m, 2.5H), 7.46 (d, 0.5H, *J* 7.4 Hz); ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 12.03, 14.10, 14.18, 14.51 (CH₃), 39.26 & 39.35 (CH), 59.89 & 60.00 (CH₂), 71.99 & 73.56 (=C-COOEt), 85.49 & 87.59 (CH₂NO₂), 117.02, 117.46 (ArCH), 124.25 (ArC), 128.26, 128.36, 128.38, 128.56 (ArC), 128.68, 128.94 (ArCH), 129.95, 130.06 (ArC), 133.97, 146.86, 149.15 & 149.25 (=C-NH₂), 162.17 & 168.26 (COOEt) ppm.; HRMS: (MH⁺) 293.1750, 292.0975, 291.1959; for C₁₄H₁₆N₂O₅ (292.29).

2-Amino-6-bromo-4-(nitromethyl)-4H-chromene-3-carbonitrile (5d). Solid; Yield 91%; mp 217-219 °C; IR (KBr): 3446.17, 3326.52, 3205.32, 3047.20, 2917.55, 2203.77, 1733.51, 1654.37, 1604.96, 1539.47, 1478.89, 1417.85, 1231.19, 1185.55, 1127.44, 1052.15, 959.65, 883.65, 825.21, 759.44, 658.67, 605.58, 443.76 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 4.29-4.32 (dd, 1H, *J* 8 and 8 Hz), 4.50-4.55 (dd, 1H, *J* 8 and 8 Hz), 4.59-4.63 (dd, 1H, *J* 8 and 8 Hz), 4.92 (br s, NH₂), 6.93 (d, 1H, *J* 8 Hz), 7.35-7.38 (t, 1H, ArH), 7.42 (d, 1H, *J* 8 Hz); HRMS: (MH⁺) 311.1159, 309.9831, 301.1419; for C₁₁H₈BrN₃O₃ (310.11).

2-Amino-6-bromo-4-(1-nitroethyl)-4H-chromene-3-carbonitrile (6d). Solid; Yield 93%; mp 170-172 °C; IR (KBr): 3435.13, 3324.44, 3216.28, 2937.35, 2191.56, 1732.54, 1648.81, 1544.12, 1475.57, 1409.31, 1241.72, 1179.79, 1117.38, 1031.62, 871.66, 820.25, 624.03 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.41 (d, 2.3H, *J* 6.8 Hz), 1.57 (d, 3.7H, *J* 6.8 Hz), 4.16 (d, 1.10 H, *J* 6.4 Hz), 4.33 (d, 0.9 H, *J* 3.6 Hz), 4.53 (m, 0.9 H, *J* 6.8 Hz), 4.69 (m, 1.10 H, *J* 6.8 Hz), 4.95 (br s, NH₂), 6.92-6.96 (m, 0.90 H), 7.15-7.29 (m, 1.10 H), 7.30-7.32 (m, 0.90 H), 7.42-7.44 (m, 1.10 H), 7.48-7.53 (m, 0.90 H), 7.79-7.82 (m, 1.10 H); HRMS: (MH⁺) 325.9966, 317.1159, 311.1652, for C₁₂H₁₀BrN₃O₃ (324.14).

Ethyl 2-amino-6-bromo-4-(nitromethyl)-4H-chromene-3-carboxylate (7d). Solid; Yield 84%; IR (KBr): 3458.05, 3307.07, 2980.61, 2919.87, 2194.49, 1675.44, 1614.63, 1531.34, 1475.39, 1408.51, 1376.09, 1304.73, 1226.57, 1085.83, 1045.03, 878.60, 816.62, 604.52, 519.25, 454.45 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.31-1.34, 3H (t, *J* 8 Hz), 4.20-4.26, 2H (m, *J* 8 Hz), 4.29, 1H (t, *J* 4 Hz), 4.39-4.52, 1H (dd, *J* 4 Hz), 4.53-4.57, 1H (dd, *J* 4 Hz), 6.89-6.91, 1H (d, *J* 8 Hz), 7.33, 1H (d, *J* 8 Hz), 7.38, 1H (t, *J* 4 Hz); HRMS: (MH⁺) 358.0089, 338.3424, 317.9744, 305.9564, 295.9924, for C₁₃H₁₃BrN₂O₅ (357.16).

Ethyl 2-amino-6-bromo-4-(1-nitroethyl)-4H-chromene-3-carboxylate (8d). Solid; Yield 81%; IR (KBr): 3437.24, 3319.07, 2982.78, 2926.85, 2193.87, 1679.54, 1636.63, 1539.59, 1472.72, 1406.20, 1291.09, 1230.35, 1081.52, 1021.79, 873.84, 821.82, 647.17, 497.40, 446.23 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.17-1.19, 1H (d, *J* 8 Hz), 1.26-1.30, 3H (t, *J* 8 Hz), 1.33-1.36, 3H (t, *J* 8 Hz), 4.11-4.16, 1.6H (m), 4.24-4.26, 0.5H (t, *J* 8 Hz), 4.51-4.72, 1.6H (m), 4.72-4.74, 0.5H (d, *J* 4 Hz), 6.89-6.92, 1.3H (dd, *J* 4 Hz), 7.10-7.12, 0.3H (d, *J* 4 Hz), 7.35-7.38, 2H (d, *J* 4 Hz); HRMS: (MH⁺) 371.0247, 365.1063, 359.0067, 351.2521, for C₁₄H₁₅BrN₂O₅ (371.19).

2-Amino-7-methyl-4-(nitromethyl)-4H-chromene-3-carbonitrile (9d). Solid; Yield 84%; mp 131-132 °C; IR (KBr): 3436.75, 3310.90, 3186.84, 2911.10, 2201.32, 1648.43, 1537.55, 1421.78, 1303.13, 1230.37, 1186.79, 1151.96, 1048.46, 1001.15, 809.46, 692.08, 614.21, 496.67, 449.01, 430.85 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.39, 3H (s), 4.31-4.34, 1H (dd, *J* 4 Hz), 4.44-4.49, 1H (dd, *J* 4 Hz), 4.57-4.62, 1H (dd, *J* 4 Hz), 4.85, 2H (br s -NH₂), 6.84, 1H (s), 6.97-6.98, 1H (d, *J* 3 Hz), 7.00-7.02, 1H (dd, *J* 4 Hz); HRMS: (MH⁺) 246.0880, 237.0799, 223.0947, 218.1392, 207.0535, for C₁₂H₁₁N₃O₃ (245.24).

2-Amino-7-methyl-4-(nitroethyl)-4H-chromene-3-carbonitrile (10d). Solid; Yield 86; mp 143-144 °C; IR (KBr): 3425.69, 3322.29, 2929.03, 2195.75, 1644.45, 1541.26, 1416.28, 1262.44, 1136.56, 1044.23, 951.44, 872.94, 811.73, 621.20, 481.41, 447.39 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.33, 1H (d, *J* 8 Hz), 1.56, 2H (d, *J* 8 Hz), 2.34, 3H (s), 4.14, 0.6H (d, *J* 8 Hz), 4.36, 0.3H (d, *J* 4 Hz), 4.49-4.52, 0.6H (t, *J* 4 Hz), 4.67-4.70, 0.3H (m), 4.92, 2H (br s -NH₂), 6.82-6.85, 1.3H (t, *J* 8 Hz), 6.93-6.97, 1H (m), 7.00-7.02, 0.7H (m).

Ethyl 2-amino-7-methyl-4-(1-nitromethyl)-4H-chromene-3-carboxylate (11d). Solid; mp 130-131 °C; Yield 82%; mp 121-123 °C; IR (KBr): 3461.44, 3316.03, 2978.19, 2918.44, 1752.75, 1682.79, 1631.11, 1537.09, 1417.19, 1302.47, 1255.04, 1214.81, 1150.59, 1075.62, 864.30, 795.75, 643.82, 583.42, 476.84, 451.28 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.33, 3H (t, *J* 8 Hz), 2.32, 3H (s), 4.19-4.27, 2H (m), 4.33-4.38, 1H (dd, *J* 8 Hz, 4 Hz), 4.49-4.57, 1H (dd, *J* 8 Hz, 4 Hz), 4.58-4.60, 1H (t, *J* 4 Hz), 6.82, 1H, (s), 6.91, 1H, (t, *J* 4 Hz), 7.02-7.04, 1H, (d, *J* 8 Hz).

Ethyl 2-amino-7-methyl-4-(1-nitroethyl)-4H-chromene-3-carboxylate (12d). Gummy Solid; Yield 80%; IR (KBr): 3433.22, 3317.11, 2983.72, 2928.85, 2189.81, 1680.54, 1632.53, 1537.59, 1477.72, 1409.20, 1287.09, 1230.35,

1081.52, 1022.79, 877.83, 821.82, 647.17, 497.40, 446.23 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.09-1.11, 3H (d, *J* 4 Hz), 1.22-1.26, 6H (t, *J* 4 Hz), 2.25, 3H (s), 2.24, 1H (s), 3.34-3.46, 0.5H (m), 4.06-4.16, 1.6H (m), 4.24-4.26, 0.5H (t, *J* 8 Hz), 4.17-4.20, 1.6H (m), 4.22-4.27, 0.8H (d, *J* 4 Hz), 4.32-4.38, 1H, (m), 4.50-4.70, 1H (m), 6.74-6.89, 2H (dt, *J* 4 Hz), 7.05-7.07, 1.6H (d, *J* 4 Hz), 7.09-7.26, 1.2H (t, *J* 4 Hz), 7.42-7.44, 0.3H(d, *J* 4 Hz).

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Supplementary Material

Copies of IR spectra, ¹H NMR spectra and HRMS spectra of compounds are provided in the supplementary material file associated with this paper.

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