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# Potassium-Exchanged Zirconium Hydrogen Phosphate [α-Zr(KPO$_4$)$_2$]-Catalyzed Synthesis of 2-Amino-4*H*-pyran Derivatives under Solvent-Free Conditions

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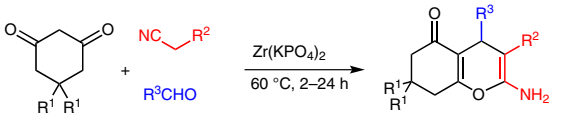


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**Abstract** A high-yielding, one-pot, three-component synthesis of functionalized 2-amino-4*H*-pyrans from β-dicarbonyl compounds, activated cyanomethylene compounds, and aldehydes, mediated by potassium-exchanged zirconium hydrogen phosphate [α-Zr(KPO$_4$)$_2$], is reported. The protocol shows excellent versatility, as it can be applied to aromatic, aliphatic, or α,β-unsaturated aldehydes under solvent-free conditions.

**Key words** pyrans, amines, heterogeneous catalysis, solvent-free synthesis, multicomponent reactions, cyclizations

The pyran moiety is a well-known motif in synthetic, medicinal, and natural-product chemistry,[1] as illustrated by the selected structures shown in Figure 1.

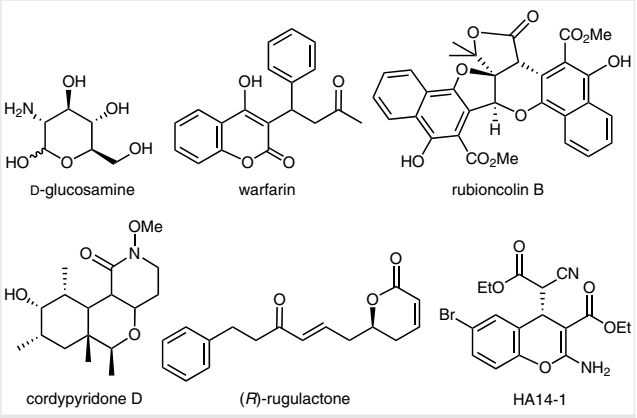



**Figure 1** Examples of compounds containing a pyran moiety

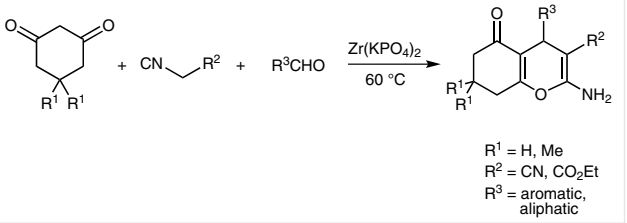
The presence of an amino or nitrile group on the 4*H*-pyran core[2] broadens the range of applications of these heterocycles; such compounds have been used as pigments,[3] agrochemicals,[4] or versatile synthetic scaffolds.[5] The importance of these compounds is further demonstrated by the numerous recent efforts made to synthesize them.[6] A closer examination of the preparative methods available indicates that the three-component coupling of an aldehyde, a β-dicarbonyl derivative, and an activated methylene donor is the method of choice for obtaining the 4*H*-pyran nucleus. Kaupp and co-workers reported a catalyst-free synthesis of 2-amino-4*H*-pyran derivatives from Michael adducts at high temperatures (97–130 °C).[7] Evidently, this procedure requires Michael adducts that need to be synthesized in advance, and the harsh conditions for the reaction are not amenable to the safe use of volatile aldehydes.

In this respect, the use of heterogeneous processes is particularly desirable because of the simplicity of the synthetic operations that are required.[8] Although the use of catalyst can be avoided by performing the reactions in glycerol,[9] the difficulties associated with the extraction of the products from the water-miscible phase cannot be neglected, and these lessen the synthetic appeal of the overall transformation.

In recent years, there has been increasing interest in the use of acidic or basic solids in liquid organic synthesis.[10] Among the obvious advantages of their use in preparative processes are their uniformly good yields, high regio- and chemoselectivities, and short reaction times, which are in accord with Anastas and Eghbali's philosophical principles for green chemistry.[11] In this context, our group has introduced the use of layered potassium-exchanged zirconium hydrogen phosphate [α-Zr(KPO$_4$)$_2$][12] as an excellent heterogeneous catalyst for C–C bond-forming processes through Michael-type, Henry, or Knoevenagel chemistries.[13] Inter-

estingly, we were able to employ this effective species for a straightforward synthesis of 2-amino-4*H*-chromene derivatives under solvent-free conditions.[14]

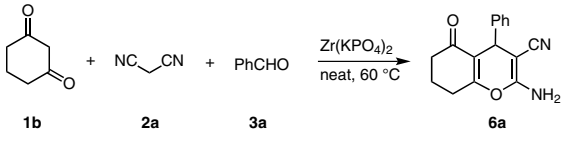
As a consequence of these successful precedents, and as part of our continuing interest in developing the synthesis of derivatives with pyran as a core moiety,[15] we wondered whether α-$Zr(KPO_4)_2$ might be used as a heterogeneous catalyst for the preparation of 2-amino-4*H*-pyrans from combinations of β-dicarbonyl compounds, cyano derivatives, and aldehydes. Here, we report the results of our investigations (Scheme 1).




**Scheme 1** General scheme for the reaction of β-dicarbonyl compounds, cyano derivatives, and aldehydes catalyzed by α-$Zr(KPO_4)_2$

To explore the generality and feasibility of the α-$Zr(KPO_4)_2$-catalyzed synthesis of 2-amino-4*H*-pyran derivatives, we selected the condensation of benzaldehyde, cyclohexane-1,3-dione, and malononitrile as a model reaction under solvent-free conditions. To ensure mild conditions during the process, the reaction mixtures were heated to only 60 °C. As shown in Table 1, the use of 10 mol% of the catalyst was optimal, affording the desired compound **6a** in an excellent 93% isolated yield (Table 1, entry 2). The beneficial effect of the catalyst can be deduced from the control reaction run in its absence (entry 4), which gave the target product in a markedly decreased yield after a prolonged reaction time (12 h).

**Table 1** Optimization of the Catalyst Loading for the Reaction of Benzaldehyde, Malononitrile, and Cyclohexane-1,3-dione at 60 °C




**1b** **2a** **3a** **6a**

| Entry | $Zr(KPO_4)_2$ (mol%) | Time (h) | Yield (%) |
|---|---|---|---|
| 1 | 20 | 2 | 82 |
| 2 | 10 | 2 | 93 |
| 3 | 5 | 2 | 78 |
| 4 | 0 | 12 | 47 |

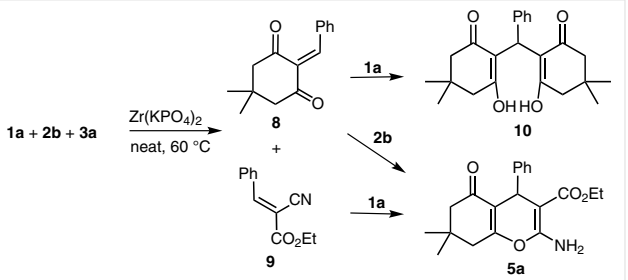
To evaluate the effects of various solvents, the reactions of benzaldehyde (**3a**) or hexanal (**3e**) with cyclohexane-1,3-dione (**1b**) and malononitrile (**2a**) were performed in ethanol or acetonitrile. As shown in Table 2, the reactions under solvent-free conditions gave slightly higher yields, regardless of the electronic nature of the aldehyde.

**Table 2** Effects of Solvents on the Reaction of Benzaldehyde or Hexanal with Malononitrile and Cyclohexane-1,3-dione at 60 °C for 2 Hours

| | Yield (%) | | |
|---|---|---|---|
| | Neat | EtOH | MeCN |
| PhCHO (**3a**) | 93 | 85 | 75 |
| $Me(CH_2)_4CHO$ (**3e**) | 89 | 88 | 83 |

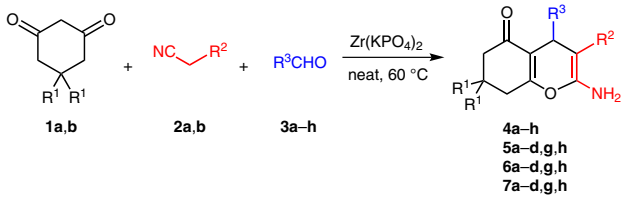
To determine the scope of the reaction, two 1,3-dicarbonyl compounds [cyclohexane-1,3-dione (**1b**) and 5,5-dimethylcyclohexane-1,3-dione (**1a**)] and two cyano derivatives [malononitrile (**2a**) and ethyl cyanoacetate (**2b**)] were condensed with various aromatic or aliphatic aldehydes **3a**–**h** under the optimized conditions (Table 3).

One point merits attention: the reaction of ethyl cyanoacetate (**2b**), benzaldehyde (**3a**), and 5,5-dimethylcyclohexane-1,3-dione (**1a**) gave 2,2′-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (**10**) as a byproduct and, after 12 hours, the tetrahydrochromene **5a** was obtained in only 53% yield (Table 3, entry 9). A plausible rationale for this intriguing result arises from the fact that adducts **8** and **9** are formed at comparable, if not similar, rates, suggesting that the competition between 5,5-dimethylcyclohexane-1,3-dione (**3a**) with ethyl cyanoacetate (**2b**) for condensation with the Knoevenagel adduct **8** might occur (Scheme 2). This behavior was not observed when malononitrile (**2a**) was used instead of ethyl cyanoacetate (**2b**). The greater reaction rate of malononitrile (**2a**) towards benzaldehyde (**1a**), compared with that of ethyl cyanoacetate (**2b**), decreases the possibility of formation of the Knoevenagel adduct **8** and, subsequently, the Michael adduct **10**.




**Scheme 2** Possible pathways for the reaction of 5,5-dimethylcyclohexane-1,3-dione (**1a**), ethyl cyanoacetate (**2b**), and benzaldehyde (**3a**) in the presence of α-$Zr(KPO_4)_2$

**Table 3** Reactions of Aldehydes, Malononitrile or Ethyl Cyanoacetate, and Cyclohexane-1,3-dione or 5,5-Dimethylcyclohexane-1,3-dione at 60 °C in the Presence of 10 mol% of α-Zr(KPO$_4$)$_2$




| Entry | Product | | $R^2$ | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | | **4a** | Ph | 2 | 93 |
| 2 | | **4b** | 3-ClC$_6$H$_4$ | 2 | 90 |
| 3 | | **4c** | 4-O$_2$NC$_6$H$_4$ | 2 | 91 |
| 4 | | **4d** | 4-MeO$_2$CC$_6$H$_4$ | 2 | 71 |
| 5 | | **4e** | 4-Tol | 2 | 92 |
| 6 | | **4f** | 3-HO-4-MeOC$_6$H$_3$ | 2 | 90 |
| 7 | | **4g** | (CH$_2$)$_4$Me | 2 | 89 |
| 8 | | **4h** | (*E*)-CH=CHPh | 2 | 42 |
| 9 | | **5a** | Ph | 12 (20)[a] | 53 (71)[a] |
| 10 | | **5b** | 3-ClC$_6$H$_4$ | 20 | 62 |
| 11 | | **5c** | 4-O$_2$NC$_6$H$_4$ | 24 | 82 |
| 12 | | **5d** | 4-MeO$_2$CC$_6$H$_4$ | 20 | 87 |
| 13 | | **5g** | (CH$_2$)$_4$Me | 5 | 50 |
| 14 | | **5h** | (*E*)-CH=CHPh | 12 | – |
| 15 | | **6a** | Ph | 4 | 92 |
| 16 | | **6b** | 3-ClC$_6$H$_4$ | 2 | 86 |
| 17 | | **6c** | 4-O$_2$NC$_6$H$_4$ | 3 | 93 |
| 18 | | **6d** | 4-MeO$_2$CC$_6$H$_4$ | 2 | 88 |
| 19 | | **6g** | (CH$_2$)$_4$Me | 1 | 89 |
| 20 | | **6h** | (*E*)-CH=CHPh | 4 | 33 |
| 21 | | **7a** | Ph | 18 | 69 |
| 22 | | **7b** | 3-ClC$_6$H$_4$ | 20 | 80 |
| 23 | | **7c** | 4-O$_2$NC$_6$H$_4$ | 24 | 87 |
| 24 | | **7d** | 4-MeO$_2$CC$_6$H$_4$ | 22 | 84 |
| 25 | | **7g** | (CH$_2$)$_4$Me | 24 | 51 |
| 26 | | **7h** | (*E*)-CH=CHPh | 12 | – |

[a] Two-step one-pot reaction

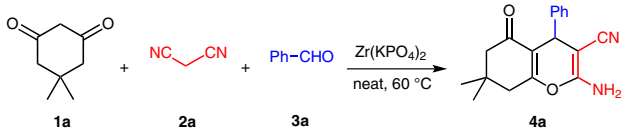
It is noteworthy that Michael adduct **10** was obtained in a quantitative yield after two hours when benzaldehyde (**3a**) was treated with two equivalents of 5,5-dimethylcyclohexane-1,3-dione (**1a**) under the optimized reaction conditions.

To avoid the formation of byproduct **10**, a two-step one-pot reaction was carried out by treating benzaldehyde (**3a**) with ethyl cyanoacetate (**2b**), with subsequent addition of 5,5-dimethylcyclohexane-1,3-dione (**1a**) after 14 hours. By using this modified procedure, it was possible to obtain compound **5a** in 71% yield after a total of 20 hours (Table 3, entry 9).

As shown in Table 3, the reactions carried out with malononitrile (**2a**) were faster and more efficient than those involving ethyl cyanoacetate (**2b**). For example, hexanal (**3e**) reacted in higher yield with malononitrile (Table 3, entries 7 and 19) than with the ethyl cyanoacetate (entries 13 and 25). In contrast, cinnamaldehyde (**3h**) gave a moderate yield with malononitrile (**1b**) (entries 8 and 20) but failed to give a product with ethyl cyanoacetate (**2b**) in the presence of either 5,5-dimethylcyclohexane-1,3-dione (**1a**) or cyclohexane-1,3-dione (**1b**) (entries 14 and 26). The presence of electron-withdrawing or electron-donating groups on aromatic aldehydes was well tolerated, and good yields were obtained in both cases (entries 2–6).

To evaluate the efficiency and capability of our protocol, we compared the reaction of **1a**, **2a**, and **3a** to give tetrahydrochromene **4a** with other reported methods and catalysts. The results, reported in Table 4, demonstrate the effectiveness of our protocol. The use of α-Zr(KPO$_4$)$_2$ as a solid catalyst under neat conditions gave results that were comparable or better than those of the other protocols. Moreover, in many of these protocols the reactions were limited to the use of malononitrile and aromatic aldehydes, and the use of aliphatic aldehydes or the less-reactive ethyl cyanoacetate as an activated methylene compound were not considered.

**Table 4** Comparison of Syntheses of Tetrahydro-4H-Chromene 4a by Various Protocols




| Entry | Catalyst | mol% | Reaction conditions | Yield (%) |
|---|---|---|---|---|
| 1 | α-$Zr(KPO_4)_2$[a] | 10 | neat, 60 °C, 2 h | 93 |
| 2 | $CoFe_2O_4$[a,16] | 1 | $H_2O$–EtOH (1:3), 60 °C, 7 min | 93 |
| 3 | ZnO[6e] | 10 | $H_2O$–EtOH (1:1), r.t., 3.5 h | 86 |
| 4 | NaBr[8f] | 20 | neat, MW, 70 °C, 10 min | 95 |
| 5 | meglumine[a,8a] | 5 | $H_2O$–EtOH (1:1), r.t., 5 min | 97 |
| 6 | glycerol[a,9] | – | glycerol, 80 °C, 1 h | 93 |
| 7 | electrogenerated base[6f] | – | MeCN, r.t., 4–5 h | 96 |

[a] The authors describe the possibility of reusing the catalyst.

Finally, we examined the recycling of the solid catalyst by a simple washing–drying sequence. The activity of the catalyst was substantially preserved after five consecutive condensations of benzaldehyde (**3a**), malononitrile (**2a**), and 5,5-dimethylcyclohexane-1,3-dione (**1b**), giving yields of 91, 90, 91, 89, and 87%, respectively. This valuable characteristic of the catalyst is an important advantage in terms of the sustainability of the process, which would be welcome for the purposes of scaling up.

We have reported the use of layered potassium-exchanged zirconium hydrogen phosphate [α-$Zr(KPO_4)_2$] as a heterogeneous catalyst for high-yielding multicomponent reactions that give 2-amino-4*H*-pyran derivatives under solvent-free conditions. This process tolerates various functionalities, which gives it a remarkably wide scope and is particularly attractive from the perspective of sustainability. The thermal and chemical stability of the catalyst and the possibility of recovering it by simple filtration ensure that the process is simple to perform and that it results in the formation of negligible amounts of chemical wastes. To optimize the use of less-reactive ethyl cyanoacetate, a two-step one-pot multicomponent reaction was also investigated

All chemicals were purchased in the highest purity grade from major chemical suppliers and were used without further purification. Column chromatography was performed on Merck silica gel 60 (70–230 mesh ASTM) with $CH_2Cl_2$–EtOAc or $CH_2Cl_2$–MeOH. $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ or DMSO-$d_6$ with a Bruker Avance DRX 200 spectrometer at frequencies of 200.1 and 50 MHz, respectively, or with a Bruker Avance DPX 400 spectrometer at frequencies of 400.13 and 100.62 MHz, respectively. IR spectra were recorded with a Jasco model 410 spectrometer with a diffuse-reflectance sampling cell; only significant absorption maxima are reported. Melting points were determined on a Kofler Hot Stage apparatus, and are uncorrected. Elemental analyses were performed by a Fisons EA1108CHN analyzer, and the results for C, H, and N were all within 0.4% of the theoretical values (≥95% purity). Physical data (mp, solid state, etc.) for known compounds matched those already reported. Full and unambiguous characterization by spectroscopic methods ($^1H$ NMR, $^{13}C$ NMR, FT-IR) is reported for all the synthesized compounds.

### 2-Amino-5-oxotetrahydro-4*H*-chromene Derivatives 4–7; General Procedure

$Zr(KPO_4)_2$ (10 mol%) was added to a neat mixture of malononitrile or ethyl cyanoacetate (1 mmol), the appropriate1,3-dicarbonyl compound (1 mmol), and the appropriate aldehyde (1 mmol). The mixture was heated to 60 °C, and the progress of the reaction was monitored by TLC. After the appropriate time, the mixture was diluted with $CH_2Cl_2$ and filtered under reduced pressure. To obtain the pure ethoxycarbonyl derivatives **5a**–**d**,**g**, and **7a**–**d**,**g**, the solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel.

The 3-carbonitrile derivatives **4a**–**h** and **6a**–**d**,**g**,**h** have very low solubilities; consequently, the treatment with $CH_2Cl_2$ was useful for eliminating unreacted material and byproducts. The solid residue was treated with hot MeOH or acetone, and the solid catalyst was recovered by filtration at reduced pressure. The filtrate was concentrated under vacuum to obtain products **4a**–**h** and **6a**–**d**,**g**,**h** in high purity.

### 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4a)

White solid; yield: 274 mg (93%); mp 227–228 °C (Lit.[8a] 225–226 °C).

FT-IR: 2200, 1679, 1661 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.35–7.05 (m, 5 H, PhH), 7.02 (br s, 2 H, $NH_2$), 4.19 (s, 1 H, CH), 2.52 (br s, 2 H, $CH_2$), 2.26 and 2.11 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.04 (s, 3 H, $CH_3$), 0.96 (s, 3 H, $CH_3$).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 196.4, 163.2, 159.3, 145.5, 129.1 (2 C), 127.9 (2 C), 127.3, 120.4, 113.5, 59.1, 50.7, 40.5, 36.3, 32.5, 29.1, 27.6.

Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.61; H, 6.03; N, 9.40.

### 2-Amino-4-(3-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4b)

White solid; yield: 296 mg (90%); mp 234–236 °C (Lit.[8a] 235–236 °C).

FT-IR: 2190, 1682, 1656 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.33 (t, $J$ = 8 Hz, 1 H, PhH), 7.27 (d, $J$ = 8.Hz, 1 H, PhH), 7.17 (s, 1 H, PhH), 7.13 (d, $J$ = 8 Hz, 1 H, PhH), 7.10 (br s, 2 H, $NH_2$), 4.22 (s, 1 H, CH), 2.53 (br s, 2 H, $CH_2$), 2.26 and 2.13 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.04 (s, 3 H, $CH_3$), 0.96 (s, 3 H, $CH_3$).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 196.4, 163.6, 159.3, 148.0, 133.6, 131.0, 127.8, 127.4, 126.7, 120.2, 112.8, 58.4, 50.7, 40.4, 36.1, 32.6, 29.0, 27.6.

Anal. Calcd for $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 5.21; N, 8.52. Found: C, 65.68; H, 5.17; N, 8.41.

### 2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4c)

White solid; yield: 309 mg (91%); mp 184–185 °C (Lit.[8a] 185–186 °C).

FT-IR: 2192, 1713, 1687 $cm^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.18 (d, $J$ = 8.6 Hz, 2 H, PhH), 7.45 (d, $J$ = 8.6 Hz, 2 H, PhH), 7.17 (br s, 2 H, $NH_2$), 4.38 (s, 1 H, CH), 2.54 (br s, 2 H, $CH_2$), 2.26 and 2.12 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.04 (s, 3 H, $CH_3$), 0.96 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 196.4, 163.8, 159.3, 153.0, 147.0, 129.4 (2 C), 124.4 (2 C), 120.0, 112.5, 57.8, 50.6, 40.5, 36.4, 32.6, 29.0, 27.7.

Anal. Calcd for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38. Found: C, 63.82; H, 4.94; N, 12.30.

**Methyl 4-(2-Amino-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-4-yl)benzoate (4d)**

White solid; yield: 250 mg (71%); mp 278–280 °C (Lit.[17] 280–282 °C).

FT-IR: 2193, 1718, 1684, 1651, 1606 cm$^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.90 (d, $J$ = 8.1 Hz, 2 H, PhH), 7.31 (d, $J$ = 8.1 Hz, 2 H, PhH), 7.08 (br s, 2 H, $NH_2$), 4.27 (s, 1 H, CH), 3.83 (s, 3 H, $OCH_3$), 2.48–2.61 (m, 2 H, $CH_2$), 2.27 and 2.09 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.04 (s, 3 H, $CH_3$), 0.95 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 196.4, 166.8, 163.6, 159.3, 150.8, 130.1 (2 C), 128.8, 128.4 (2 C), 120.2, 112.9, 58.2, 52.8, 50.6, 40.4, 36.4, 32.5, 29.1, 27.5.

Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.27; H, 5.81; N, 7.84.

**2-Amino-7,7-dimethyl-5-oxo-4-(4-tolyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4e)**

White solid; yield: 284 mg (92%); mp 215–217 °C (Lit.[8a] 211–212 °C).

FT-IR: 2192, 1675, 1639, 1602 cm$^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.09 (d, $J$ = 8.0 Hz, 2 H, PhH), 7.02 (d, $J$ = 8.0 Hz, 2 H, PhH), 6.97 (br s, 2 H, $NH_2$), 4.13 (s, 1 H, CH), 2.51 (m, 2 H, $CH_2$), 2.25 (s, 3 H, $CH_3$), 2.25 and 2.09 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.04 (s, 3 H, $CH_3$), 0.95 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 196.4, 163.0, 159.2, 142.6, 136.4, 129.6 (2 C), 127.8 (2 C), 120.5, 113.6, 52.2, 50.7, 40.4, 35.9, 32.5, 29.2, 27.5, 21.3.

Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.87; H, 6.78; N, 9.19.

**2-Amino-4-(3-hydroxy-4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4f)**

White solid; yield: 306 mg (90%); mp 238–240 °C (Lit.[18] 237–239 °C).

FT-IR: 2191, 1674, 1600 cm$^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.87 (s, 1 H, OH), 6.92 (br s, 2 H, $NH_2$), 6.79 (d, $J$ = 8.2 Hz, 1 H, PhH), 6.55 (d, $J$ = 2.0 Hz, 1 H, PhH), 6.51 (dd, $J$ = 8.2, 2.0 Hz, 1 H, PhH), 4.01 (s, 1 H, CH), 3.70 (s, 3 H, $OCH_3$), 2.51 and 2.44 (AB system, $J$ = 16.6 Hz, 2 H, $CH_2$), 2.24 and 2.08 (AB system, $J$ = 16.2 Hz, 2 H, $CH_2$), 1.02 (s, 3 H, $CH_3$), 0.95 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 196.0, 162.4, 158.8, 146.7, 146.6, 137.8, 120.2, 118.1, 114.9, 113.5, 112.4, 59.0, 56.0, 50.4, 40.1, 35.2, 32.1, 28.8, 27.2.

Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 67.05; H, 5.92; N, 8.23. Found: C, 66.89; H, 5.78; N, 8.32.

**2-Amino-7,7-dimethyl-5-oxo-4-pentyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4g)**

Pale-yellow solid; yield: 257 mg (89%); mp 149–151 °C (Lit.[19] 150–153 °C).

FT-IR: 2189, 1682, 1652, 1604 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 4.53 (br s, 2 H, $NH_2$), 3.44 (t, $J$ = 6.0 Hz, 1 H, CH), 2.37 (br s, 2 H, $CH_2$), 2.29 (br s, 2 H, $CH_2$), 1.71–1.48 (m, 2 H, $CH_2$), 1.42–1.16 (m, 6 H, 3 × $CH_2$), 1.12 (s, 3 H, $CH_3$), 1.10 (s, 3 H, $CH_3$), 0.86 (t, $J$ = 6.3 Hz, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.9, 163.0, 159.1, 119.6, 114.3, 61.5, 51.1, 40.9, 34.9, 32.3, 32.0, 29.6, 29.4, 27.7, 24.8, 22.9, 14.3.

Anal. Calcd for $C_{17}H_{24}N_2O_2$: C, 70.80; H, 8.39; N, 9.71. Found: C, 70.72; H, 8.29; N, 9.62.

**2-Amino-7,7-dimethyl-5-oxo-4-[(*E*)-2-phenylvinyl]-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4h)**

White solid; yield: 135 mg (42%); mp 187–189 °C (Lit.[16] 185–188 °C).

FT-IR: 2184, 1687, 1652 cm$^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.38 (d, $J$ = 7.3 Hz, 2 H, PhH), 7.30 (t, $J$ = 7.3 Hz, 2 H, PhH), 7.22 (t, $J$ = 7.3 Hz, 1 H, PhH), 7.05 (br s, 2 H, $NH_2$), 6.37 (d, $J$ = 15.7 Hz, 1 H, CHCH=CHPh), 6.09 (dd, $J$ = 7.4, 15.7 Hz, 1 H, CHCH=CHPh), 3.82 (d, $J$ = 7.4 Hz, 1 H, CHCH=CH), 2.44 (br s, 2 H, $CH_2$), 2.29 and 2.21 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.03 (s, 3 H, $CH_3$), 1.01 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 196.6, 163.2, 160.0, 137.2, 131.9, 130.0, 129.3 (2 C), 128.2, 127.0 (2 C), 120.6, 112.6, 56.0, 50.8, 40.5, 33.5, 32.6, 29.0, 27.7.

Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.85; H, 6.21; N, 8.62.

**Ethyl 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (5a)**

White solid; yield: 242 mg (71%); mp 152–154 °C (Lit.[16] 150–152 °C).

FT-IR: 1667, 1661, 1612 cm$^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.57 (br s, 2 H, $NH_2$), 7.37–7.06 (m, 5 H, PhH), 4.50 (s, 1 H, CH), 3.95 (q, $J$ = 7 Hz, 2 H, $OCH_2$), 2.57 and 2.46 (AB system, $J$ = 18 Hz, 2 H, $CH_2$), 2.27 and 2.05 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.09 (t, $J$ = 7 Hz, 3 H, $CH_3$), 1.03 (s, 3 H, $CH_3$), 0.89 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 196.2, 168.4, 162.5, 159.5, 146.7, 128.1 (2 C), 128.0 (2 C), 126.2, 115.9, 78.2, 59.1, 50.3, 39.9, 33.6, 32.3, 29.0, 26.8, 14.6.

Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.23; H, 6.86; N, 4.21.

**Ethyl 2-Amino-4-(3-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (5b)**

White solid; yield: 233 mg (62%); mp 129–131 °C.

FT-IR: 1692, 1667, 1525 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.07 (m, 4 H, PhH), 6.23 (br s, 2 H, $NH_2$), 4.69 (s, 1 H, CH), 4.05 (q, $J$ = 7 Hz, 2 H, $OCH_2$), 2.46 (s, 2 H, $CH_2$), 2.24 and 2.20 (AB system, $J$ = 16 Hz, 2 H, $CH_2$), 1.18 (t, $J$ = 7 Hz, 3 H, $CH_3$), 1.11 (s, 3 H, $CH_3$), 1.00 (s, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.6, 169.2, 161.9, 158.6, 148.2, 133.9, 129.3, 128.7, 126.9, 126.5, 116.4, 80.4, 60.1, 50.9, 40.9, 34.1, 32.5, 29.3, 27.7, 14.5.

Anal. Calcd for $C_{20}H_{22}ClNO_4$: C, 63.91; H, 5.90; N, 3.73. Found: C, 63.76; H, 5.98; N, 3.81.

**Ethyl 2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (5c)**

Yellow solid; yield: 317 mg (82%); mp 179–181 °C (Lit.[8a] 180–181 °C).

FT-IR: 1695, 1652, 1520 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 8.11 (d, *J* = 8.4 Hz, 2 H, PhH), 7.69 (br s, 2 H, $NH_2$), 7.42 (d, *J* = 8.4 Hz, 2 H, PhH), 4.62 (s, 1 H, CH), 3.94 (q, *J* = 7.1 Hz, 2 H, $OCH_2$), 2.54 (d, *J* = 19 Hz, 1 H, HCH), 2.44 (d, *J* = 19 Hz, 1 H, HCH), 2.28 and 2.06 (AB system, *J* = 16 Hz, 2 H, $CH_2$), 1.07 (t, *J* = 7.1 Hz, 3 H, $CH_3$), 1.04 (s, 3 H, $CH_3$), 0.88 (s, 3 H, $CH_3$).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 196.5, 168.4, 163.4, 159.9, 154.9, 146.4, 129.9 (2 C), 123.8 (2 C), 115.1, 77.3, 59.7, 50.6, 40.3, 34.6, 32.6, 29.3, 27.3, 14.9.

Anal. Calcd for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.31; H, 5.63; N, 7.35.

**Ethyl 2-Amino-4-[4-(methoxycarbonyl)phenyl]-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (5d)**

White solid; yield: 348 mg (87%); mp 163–165 °C.

FT-IR: 1719, 1689, 1657, 1608 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8 Hz, 2 H, ArH), 7.35 (d, *J* = 8 Hz, 2 H, ArH), 6.27 (br s, 2 H, $NH_2$), 4.75 (s, 1 H, CH), 4.02 (q, *J* = 7.1 Hz, 2 H, $OCH_2$), 3.88 (s, 3 H, $OCH_3$), 2.44 (s, 2 H, $CH_2$), 2.25 and 2.14 (AB system, *J* = 16 Hz, 2 H, $CH_2$), 1.14 (t, *J* = 7.1 Hz, 3 H, $CH_3$), 1.10 (s, 3 H, $CH_3$), 0.96 (s, 3 H, $CH_3$).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 196.2, 168.8, 167.1, 161.6, 158.3, 151.1, 129.2 (2 C), 128.3 (2 C), 127.8, 116.0, 79.9, 59.7, 51.9, 50.5, 40.6, 34.0, 32.1, 29.1, 27.2, 14.1.

Anal. Calcd for $C_{22}H_{25}NO_6$: C, 66.15; H, 6.31; N, 3.51. Found: C, 66.28; H, 6.17; N, 3.71.

**Ethyl 2-Amino-7,7-dimethyl-5-oxo-4-pentyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (5g)**

Yellow oil; yield: 168 mg (50%).

FT-IR: 1688, 1667, 1615 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 6.15 (br s, 2 H, $NH_2$), 4.26–4.09 (m, 2 H, $OCH_2$), 3.72 (t, *J* = 4.5 Hz, 1 H, CH), 2.34 (br s, 2 H, $CH_2$), 2.26 (br s, 2 H, $CH_2$), 1.57–1.39 (m, 2 H, $CH_2$), 1.26 (t, *J* = 7.1 Hz, 3 H, $CH_3$), 1.37–0.96 (m, 6 H, 3 × $CH_2$), 1.09 (s, 3 H, $CH_3$), 1.05 (s, 3 H, $CH_3$), 0.81 (t, *J* = 6.4 Hz, 3 H, $CH_3$),

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.2, 169.5, 163.0, 159.4, 116.3, 78.9, 59.4, 50.8, 40.7, 34.9, 32.0, 31.9, 29.3, 27.2, 27.1, 24.3, 22.6, 14.4, 13.9.

Anal. Calcd for $C_{19}H_{29}NO_4$: C, 68.03; H, 8.71; N, 4.18. Found: C, 68.21; H, 8.93; N, 4.01.

**2-Amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6a)**

White solid; yield: 245 mg (92%); mp 235–236 °C (Lit.[16] 234–235 °C).

FT-IR: 2192, 1682, 1645 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.44–7.07 (m, 5 H, PhH), 7.00 (br s, 2 H, $NH_2$), 4.20 (s, 1 H, CH), 2.72–2.54 (m, 2 H, $CH_2$), 2.48–2.34 (m, 2 H, $CH_2$), 2.15–1.97 (m, 2 H, $CH_2$).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 196.6, 165.2, 159.2, 145.5, 129.1 (2 C), 127.9 (2 C), 127.3, 120.5, 114.5, 59.0, 37.1, 36.2, 27.2, 20.5.

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.33; H, 5.42; N, 10.38.

**2-Amino-4-(3-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6b)**

White solid; yield: 259 mg (80%); mp 224–224 °C (Lit.[20] 223–224 °C).

FT-IR: 2196, 1687, 1644 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.33 (t, *J* = 7.5 Hz, 1 H, PhH), 7.26 (d, *J* = 7.5 Hz, 1 H, PhH), 7.19 (s, 1 H, PhH), 7.14 (d, *J* = 7 Hz, 1 H, PhH), 7.10 (br s, 2 H, $NH_2$), 4.22 (s, 1 H, CH), 2.73–2.55 (m, 2 H, $CH_2$), 2.41–2.23 (m, 2 H, $CH_2$), 1.83–2.02 (m, 2 H, $CH_2$).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 196.6, 165.6, 159.3, 148.0, 133.6, 131.0, 127.8, 127.3, 126.7, 120.3, 113.9, 58.3, 37.0, 36.0, 27.2, 20.5.

Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31. Found: C, 64.04; H, 4.31; N, 9.42.

**2-Amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6c)**

Yellowish crystals; yield: 290 mg (93%); mp 234–236 °C (Lit.[6d] 234–236 °C).

FT-IR: 2194, 1681, 1650 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 8.17 (d, *J* = 8.6 Hz, 2 H, PhH), 7.47 (d, *J* = 8.6 Hz, 2 H, PhH), 7.18 (br s, 2 H, $NH_2$), 4.37 (s, 1 H, CH), 2.72–2.57 (m, 2 H, $CH_2$), 2.39–2.20 (m, 2 H, $CH_2$), 2.05–1.85 (m, 2 H, $CH_2$).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 196.6, 165.9, 159.3, 153.1, 147.0, 129.3 (2 C), 124.4 (2 C), 120.1, 113.5, 57.6, 36.9, 36.3, 27.3, 20.5.

Anal. Calcd for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50. Found: C, 61.60; H, 4.08; N, 13.59.

**Methyl 4-(2-Amino-3-cyano-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-4-yl)benzoate (6d)**

White solid; yield: 286 mg (88%); mp 234–235 °C.

FT-IR: 2192, 1725, 1681, 1646, 1606 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.89 (d, *J* = 8 Hz, 2 H, PhH), 7.32 (d, *J* = 8 Hz, 2 H, PhH), 7.10 (br s, 2 H, $NH_2$), 4.27 (s, 1 H, CH), 3.83 (s, 3 H, $OCH_3$), 2.72–2.55 (m, 2 H, $CH_2$), 2.41–2.20 (m, 2 H, $CH_2$), 2.07–1.82 (m, 2 H, $CH_2$).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 196.6, 166.8, 165.6, 159.2, 150.9, 130.1 (2 C), 128.7, 128.4 (2 C), 120.2, 113.9, 58.2, 52.8, 37.0, 36.3, 27.2, 20.5.

Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.45; H, 4.83; N, 8.77.

**2-Amino-5-oxo-4-pentyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6g)**

White solid; yield: 232 mg (89%); mp 122–123 °C.

FT-IR: 2186, 1678, 1646, 1606 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 4.52 (br s, 2 H, $NH_2$), 3.43 (t, *J* = 4.6 Hz, 1 H, CH), 2.59–2.33 (m, 4 H, 2 × $CH_2$), 2.16–1.94 (m, 2 H, $CH_2$), 1.68–1.41 (m, 2 H, $CH_2$), 1.35–1.14 (m, 6 H, 3 × $CH_2$), 0.87 (t, *J* = 6.4 Hz, 3 H, $CH_3$).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 196.7, 164.2, 158.7, 119.4, 115.1, 61.0, 36.9, 34.8, 31.6, 29.2, 26.9, 24.3, 22.5, 20.2, 14.0.

Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.20; H, 7.74; N, 10.76. Found: C, 69.05; H, 7.53; N, 10.87.

**2-Amino-5-oxo-4-[(*E*)-2-phenylvinyl]-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (6h)**

Yellow solid; yield: 97 mg (33%); mp 193–195 °C (Lit.[16] 195–198 °C).

FT-IR: 2190, 1679, 1648, 1608 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.15 (m, 5 H, PhH), 6.52 (d, *J* = 16 Hz, 1 H, CHCH=CHPh), 6.12 (dd, *J* = 7.0, 16.0 Hz, 1 H, CHCH=CH), 4.68 (br s, 2 H, $NH_2$), 4.11 (d, *J* = 7 Hz, 1 H, CH), 2.64–2.36 (m, 4 H, 2 × $CH_2$), 2.17–1.98 (m, 2 H, $CH_2$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.5, 163.7, 158.6, 137.1, 131.2, 130.1, 128.7 (2 C), 127.8, 126.8 (2 C), 119.1, 114.7, 60.8, 37.1, 32.7, 27.3, 20.4.

Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.15; H, 5.40; N, 9.67.

**Ethyl 2-Amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (7a)**

White solid; yield: 216 mg (69%); mp 188–190 °C.

FT-IR: 1684, 1653, 1613 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.08 (m, 5 H, PhH), 6.20 (br s, 2 H, $NH_2$), 4.75 (s, 1 H, CH), 4.18–4.03 (m, 2 H, $OCH_2$), 2.69–2.51 (m, 2 H, $CH_2$), 2.46–2.28 (m, 2 H, $CH_2$), 2.13–1.91 (m, 2 H, $CH_2$), 1.16 (t, *J* = 7.1 Hz, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.8, 169.4, 163.3, 158.6, 146.3, 128.5 (2 C), 128.1 (2 C), 126.3, 118.4, 81.1, 59.9, 37.2, 34.1, 27.2, 20.5, 14.5.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.14; H, 6.23; N, 4.34.

**Ethyl 2-aAmino-4-(3-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (7b)**

Yellow solid; yield: 278 (80%); mp 181–183 °C.

FT-IR: 1685, 1654, 1614 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.08 (m, 4 H, PhH), 6.25 (br s, 2 H, $NH_2$), 4.71 (s, 1 H, CH), 4.05 (q, *J* = 7.1 Hz, 2 H, $OCH_2$), 2.70–2.51 (m, 2 H, $CH_2$), 2.46–2.30 (m, 2 H, $CH_2$), 2.14–1.92 (m, 2 H, $CH_2$), 1.16 (t, *J* = 7.1 Hz, 3 H, $CH_3$),

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.7, 169.2, 163.6, 158.6, 148.4, 133.8, 129.3, 128.7, 127.0, 126.5, 117.7, 80.4, 60.0, 37.1, 34.1, 27.2, 20.5, 14.5.

Anal. Calcd for $C_{18}H_{18}ClNO_4$: C, 62.16; H, 5.22; N, 4.03. Found: C, 62.05; H, 5.34; N, 4.17.

**Ethyl 2-Amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (7c)**

White solid; yield: 312 mg (87%); mp 179–181 °C (Lit.[6d] 181–182 °C).

FT-IR: 1689, 1658, 1613 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.7 Hz, 2 H, PhH), 7.46 (d, *J* = 8.7 Hz, 2 H, PhH), 6.17 (br s, 2 H, $NH_2$), 4.82 (s, 1 H, CH) 4.11–3.97 (m, 2 H, $OCH_2$), 2.70–2.54 (m, 2 H, $CH_2$), 2.42–2.30 (m, 2 H, $CH_2$), 2.15–1.92 (m, 2 H, $CH_2$), 1.13 (t, *J* = 7.1 Hz, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.7, 168.9, 163.9, 158.7, 153.9, 146.6, 129.5 (2 C), 123.5 (2 C), 117.1, 79.6, 60.1, 37.0, 34.5, 27.3, 20.4, 14.5.

Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.44; H, 5.16; N, 7.74.

**Ethyl 2-Amino-4-[4-(methoxycarbonyl)phenyl]-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (7d)**

White solid; yield: 311 mg (84%); mp 167–169 °C.

FT-IR: 1687, 1663, 1610 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.2 Hz, 2 H ArH), 7.36 (d, *J* = 8.2 Hz, 2 H ArH), 6.24 (br s, 2 H, $NH_2$), 4.83 (s, 1 H, CH), 3.96–4.11 (m, 2 H, $OCH_2$), 3.88 (s, 3 H, $OCH_3$), 2.69–2.50 (m, 2 H, $CH_2$), 2.43–2.28 (m, 2 H, $CH_2$), 2.12–1.86 (m, 2 H, $CH_2$), 1.13 (t, *J* = 7.1 Hz, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.7, 169.1, 167.4, 163.6, 158.6, 151.6, 129.5 (2 C), 128.7 (2 C), 128.2, 117.7, 80.2, 60.0, 52.2, 37.1, 34.4, 27.2, 20.5, 14.5.

Anal. Calcd for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.88; H, 5.83; N, 3.56.

**Ethyl 2-Amino-5-oxo-4-pentyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (7g)**

Yellow oil; yield: 157 mg (51%).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.12 (br s, 2 H, $NH_2$), 4.23–4.04 (m, 2 H, $OCH_2$), 3.68 (t, *J* = 4.5 Hz, 1 H, CH), 2.58–2.24 (m, 4 H, 2 × $CH_2$), 2.10–1.83 (m, 2 H, $CH_2$), 1.21 (t, *J* = 7.1 Hz, 3 H, $CH_3$), 1.47–0.92 (m, 8 H, 4 × $CH_2$), 0.76 (t, *J* = 6.9 Hz, 3 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.7, 169.7, 165.0, 159.7, 117.8, 79.1, 59.7, 37.2, 35.4, 32.2, 27.4, 27.2, 24.5, 22.9, 20.7, 14.7, 14.3.

Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.55; H, 8.01; N, 4.37.

## Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560411.

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