RSC Advances

PAPER

View Article Online
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Cite this: *RSC Adv.*, 2014, **4**, 14501

Synthesis of amidoalkyl chromen-2-ones by one pot three component reaction under solvent free conditions†

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Received 8th January 2014
Accepted 11th March 2014

DOI: 10.1039/c4ra00166d

www.rsc.org/advances

A mild and efficient method for the functionalization of chromen-2-ones with amidoalkyl derivatives have been developed starting from 4-trifluoromethyl substituted chromen-2-ones, aromatic aldehydes and acetamide promoted by stannous chloride dihydrate in a one pot three component reaction under solvent free condition. Simple reaction conditions, high yields and environmentally benign procedure are the advantage of this protocol.

1. Introduction

Chromen-2-ones are ubiquitous structural motifs that represent a very important class of naturally occurring compounds.[1] They are reported to exhibit wide range of valuable biological activity properties including anti-oxidant, antibacterial, antifungal and anti-inflammatory activities.[2] Additionally, chromen-2-ones or coumarins also found to have substantial application in photo sensitizers, fluorescent, laser dyes[3] and represent very useful synthetic building blocks in organic and medicinal chemistry (Fig. 1). Further, strategically positioned fluorine in organic molecule can lead to distinctive modifications in their biological properties owing to the strong electron withdrawing nature and large hydrophobic domain. These factors modify the bioavailability and stability of the molecule. Because of these reasons, they have become the popular building blocks in the design and synthesis of various agrochemicals,[4] selective antibacterial agents, enzyme inhibitors, and enzyme receptor antagonists or agonists.[5] On the other hand multicomponent reactions (MCRs) constitute a significant group of methods in organic synthesis[6] and became very popular tools to form heterocyclic structures including complex structures when combined with subsequent transformations. They incorporate portions of three or more reactants into new products in a one pot reaction through powerful transformations.

Furthermore, solvent free multicomponent reactions gained popularity and it is often claimed that the best solvent in organic synthesis is no solvent.[7] These protocols effectively answer the harmful effects of organic solvents to the environment and also provide a cleaner, safer, and economical,[8] pollution free organic syntheses at source.

In the recent past a number of reports have appeared in the literature on synthesis of fused coumarins such as pyranocoumarins,[9] pyranochalcones,[10] and 7-hydroxy substituted fluorinated coumarins as fluorogenic analogues.[11]

However, to the best of our knowledge, there are no reports available on the functionalization of chromen-2-ones with amidoalkyl derivatives. Whereas numerous reports[12] are available on the functionalization of naphthols with amidoalkyl derivatives which reported to exhibit depressor and bradycardia effects in humans[13] and also important precursors of heterocycles.[14] Based on the importance of chromen-2-one compounds in various ways and our continuous efforts to develop the new methodologies to synthesize the novel chromene compounds and study the biological activity aspects[15] herein, we report the synthesis of so far unreported amidoalkyl trifluoromethyl substituted chromen-2-ones (**6**) by one pot three component reaction under solvent free condition.

2. Results and discussions

Initially, 7-hydroxy-4-trifluoromethyl chromen-2-one derivatives (**3a–c**) were prepared independently starting from the reaction

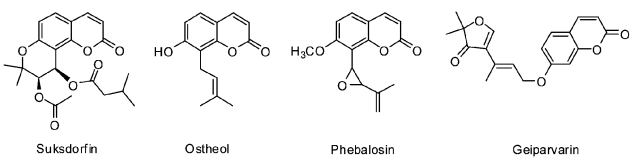

Fig. 1 Some of the potent molecules with chromen-2-one skeleton.

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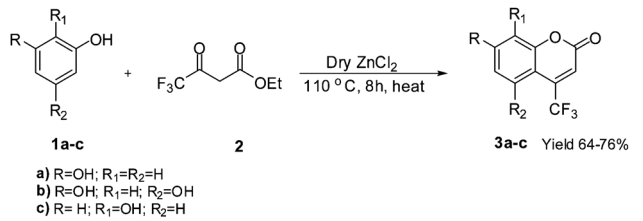
† CCDC 929729. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra00166d



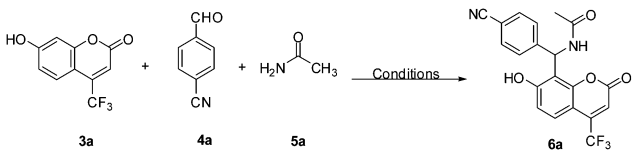
Scheme 1

of substituted phenols (**1**) and ethyltrifluoroacetoacetate (**2**) by Pechmann condensation promoted by dry $ZnCl_2$.[16] (Scheme 1).

Subsequently a model reaction was attempted to prepare **6a** (Table 1) by reacting **3a** with *p*-cyanobenzaldehyde (**4a**) and acetamide (**5a**) in presence of catalytic amount of stannous chloride dihydrate under solvent free conditions. Interestingly, exclusive formation of **6a** was observed in moderate yields. To scrutinize the catalyst ratio, same reaction was carried out with 10 mol%, 20 mol%, and 30 mol% of stannous chloride dihydrate at 125 °C. Further, the reaction was also studied by employing various other acid catalysts as indicated in Table 1. However, it was observed that 20 mol% stannous chloride dihydrate at 125 °C gave the highest yield among all. Increasing the reaction temperature to 140 °C didn't improve the yields (entry2, Table 1). Poor yields were observed when the reaction was carried out in absence of catalyst.

Encouraged by exclusive formation of **6a** with 20 mol% of stannous chloride dihydrate in high yields, a similar reaction was conducted with **3b**, **3c** and 4-cyano benzaldehyde (**4a**), acetamide (**5**) independently under identical reaction conditions and obtained the desired products **6n**, **6r** in equally good yields. However, it is observed that formation of **6r** required 140 °C temperature. With the optimized reaction conditions in hand, we set out to explore the scope and generality of this protocol. Thus compound **3a–c** was reacted with variety of aromatic aldehydes containing different substituents on the aromatic ring and acetamide. The electronic properties of the groups on the phenyl ring of aldehyde had varied the yields of the desired product **6**. Electron withdrawing groups at either *ortho* or *para* position to aldehyde afforded the corresponding products **6a**, **6c**, **6i**, **6p**, **6q**, **6r**, **6s** in high yields compared to the electron releasing groups. Unfortunately, this method didn't work for aliphatic aldehydes. Furthermore, compound **3c** reacted with *p*-cyanobenzaldehyde (**4a**), benzamide (**5b**) and found the formation of the desired product **6v** in good yields. Results of products **6a–v** depicted in Scheme 2.

Table 1 Optimization[b] of reaction conditions for synthesis of **6a**



Entry	Catalyst (mol%)	T (°C)	Time (h)	Yield[c] (%) (**6a**)
1	$SnCl_2 \cdot 2H_2O$ (20)	125	1	72
2	$SnCl_2 \cdot 2H_2O$ (20)	140	1	68
3	$SnCl_2 \cdot 2H_2O$ (10)	125	1	60
4	$SnCl_2 \cdot 2H_2O$ (30)	125	1	69
5	$InCl_3$ (20)	130	2	55
6	$FeCl_3$ (20)	125	2	43
7	$CeCl_3$ (20)	130	2	40
8	PTSA (20)	130	2	48
9	CuCl (20)	125	2	35
10	$HClO_4 \cdot SiO_2$ (20)	130	2	52
11	—[a]	140	4	30
12	Acetic acid (200)	130	8	38

[a] No catalyst. [b] 7-Hydroxy coumarin (**3a**) (0.5 mmol), *p*-cyanobenzaldehyde (**4a**) (0.55 mmol), acetamide (0.75 mmol) and catalyst were heated under solvent free condition at above mentioned temperature. [c] Yield refers to pure products after column chromatography.

Structure of the products **6** was established by their ^{1}H-NMR spectra, where the significant methine proton was coupled with adjacent –NH and appeared at δ 7.04 as a doublet and became singlet after D_2O exchange. Further, structure of a representative compound (**6d**) was unambiguously confirmed by single crystal X-ray diffraction analysis[17] (Fig. 2).

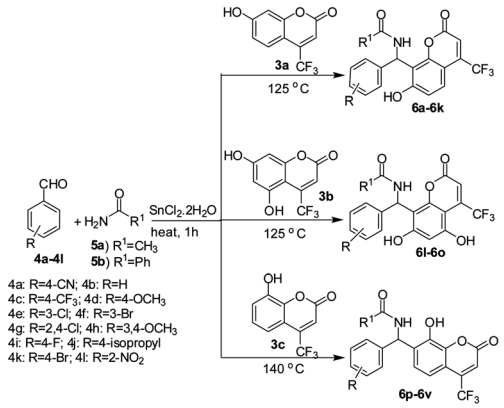
A plausible mechanism for the formation of amidoalkyl 7-hydroxy-2-oxo-4-trifluoromethyl-2*H*-chromene (**6**) is illustrated in Scheme 3, where it is reasonable to assume that the reaction may proceed through the formation of *ortho* quinone methide by addition of 7-hydroxy 4-trifluoromethyl chromene 2-one (**3a**) to the aromatic aldehyde (**4**) and subsequently dehydration in the presence of acidic catalyst followed by Michael addition of the amide (**5**) leads to the formation of amidoalkyl 7-hydroxy-2-oxo-4-trifluoromethyl-2*H*-chromene (**6**).

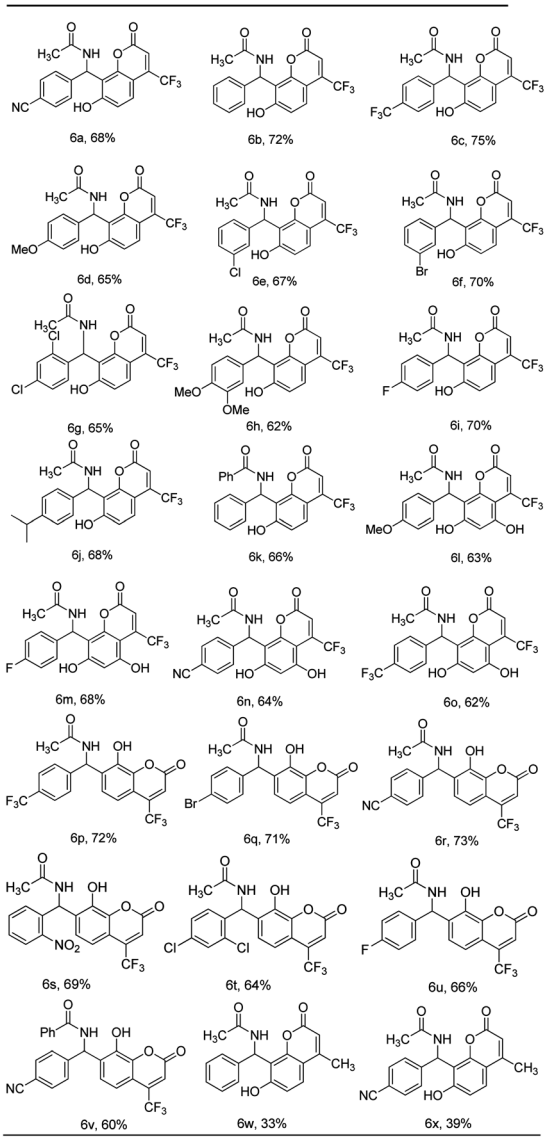
Exclusive formation of **6l–o** presumably attributable in part to the *o*, *p*-directing electronic effect of 5,7-dihydroxyfunctional on the chromen-2-one. On the other hand, formation **6p–v** is in agreement with the related reports.[18] On the other hand this protocol was also verified with methyl derivative of **3a** *in lieu* of CF_3 with varying aldehydes under identical reaction conditions as in Table 1 and obtained the products **6w** and **6x** in poor yields.

3. Experimental

3.1 General information

All reactions were carried out under air and monitored by TLC using Merck 60 F_{254} pre coated silica gel plates (0.25 mm thickness) and the products were visualized by UV detection. Flash chromatography was carried out with silica gel (60–120 mesh). IR spectra were obtained on a Perkin-Elmer FTIR spectrophotometer neat or as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance (III) 300 & 500 MHz spectrometer. Data for ^{1}H NMR are reported as a chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant J (Hz), integration, and assignment, data for ^{13}C are reported as a chemical shift. Mass spectra were recorded in ESI spectrometers. All high resolution mass spectra were recorded on QSTAR XL hybrid ms/ms system (Applied Bio systems/MDS sciex, Foster city, USA), equipped with an ESI source (IICT, Hyderabad).





Scheme 2 $SnCl_2 \cdot 2H_2O$ catalyzed synthesis of trifluoromethyl amidoalkyl chromen-2-ones under solvent free conditions. All the products were characterized by NMR, IR and mass spectroscopy. Yield refers to pure products after column chromatography.

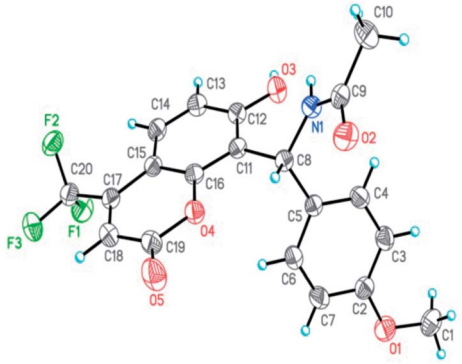
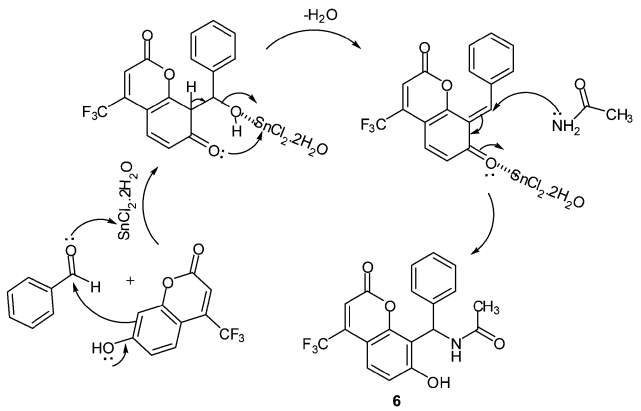


Fig. 2 The molecular structure of **6d** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.



Scheme 3 Plausible reaction mechanism to the synthesis of compound **6**.

3.1.1 General experimental procedure for the synthesis of *N*-((hydroxyl-2-oxo-4-(trifluoromethyl)-2*H*-chromenyl) (aryl) methyl) amide derivatives (6). A mixture of hydroxy coumarin (**3a**/**3b**/**3c**) (1 mmol), aldehyde (**4**) (1.1 mmol), amide (**5**) (1.5 mmol) and $SnCl_2 \cdot 2H_2O$ (20 mol%) was heated to 125 °C (in case of **3c** 140 °C) for 1 h. As the reaction completed (by TLC), the reaction mixture was allowed to cool to room temperature and added H_2O (20 mL) and ethyl acetate (20 mL) followed by 5% HCl (10 mL). Then the mixture was extracted with ethyl acetate (3 × 20 mL), washed with water, brine respectively and dried over anhydrous Na_2SO_4. The organic phase was evaporated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel using hexane and ethyl acetate as eluent to furnish the pure product **6**.

3.1.2 *N*-((4-Cyanophenyl)(7-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6a). Mp 204–205 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 7.86 (m, 1H), 7.66–7.44 (m, 5H), 7.16–6.99 (m, 2H), 6.56 (s, 1H), 2.09 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.3, 161.9, 159.6, 158.0, 153.0, 146.2, 141.1 (q, $^2J_{C-F}$ = 32.4 Hz), 131.4, 127.6, 126.7, 125.2, 121.1 (q, $^1J_{C-F}$ = 275 Hz), 118.3, 114.3, 110.7 (q, $^3J_{C-F}$ = 6.0 Hz), 109.7, 105.6, 46.3, 22.5 ppm; IR (KBr): 3396, 2925, 2229, 1739, 1677, 1283, 1138, 1079,

668 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{13}F_3N_2NaO_4$ *m/z* 425.0719 $[M + Na]^+$, found 425.0717.

3.1.3 *N*-((7-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8yl)phenyl)methyl)acetamide) (6b). Mp 251–253 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 7.80 (d, J = 9.4 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.36–7.16 (m, 5H), 7.08–6.98 (m, 2H), 6.54 (s, 1H), 2.06 (s, 3H) ppm; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) (D_2O exchange): δ 7.50 (d, J = 8.9 Hz, 1H), 7.38–7.17 (m, 5H), 7.04 (d, J = 9.4 Hz, 1H), 7.0 (d, J = 9.1 Hz, 1H), 6.55 (s, 1H), 2.08 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.9, 159.8, 158.1, 153.0, 140.9 (q, $^2J_{C-F}$ = 33 Hz), 140.4, 127.7, 126.3, 125.8, 124.7, 121.1 (q, $^1J_{C-F}$ = 276 Hz), 114.5, 113.7, 110.7 (q, $^3J_{C-F}$ = 4.6 Hz), 105.5, 46.4, 22.6 ppm; IR (KBr): 3414, 1735, 1576, 1284, 1145, 826 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{15}F_3NO_4$ *m/z* 378.0947 $[M + H]^+$, found 378.0957.

3.1.4 *N*-((7-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(4-(trifluoromethyl)phenyl)methyl) acetamide (6c). Mp 186–187 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 11.08 (br s, 1H), 7.93 (d, J = 10.1 Hz, 1H), 7.54–7.46 (m, 5H), 7.06 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 10.1 Hz, 1H), 6.55 (s, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.0, 159.4, 157.9, 152.9, 144.7, 141.0 (q, $^2J_{C-F}$ = 32.4 Hz), 126.2, 125.0, 124.9, 124.4 (q, $^3J_{C-F}$ = 3.8 Hz), 121.1 (q, $^1J_{C-F}$ = 275.6 Hz), 114.6, 113.6, 110.7 (q, $^3J_{C-F}$ = 6.0 Hz), 105.6, 46.2, 22.6 ppm; IR (KBr): 3359, 2927, 1728, 1654, 1579, 1328, 1280, 1148, 869, 675 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{13}F_6NNaO_4$ *m/z* 468.0641 $[M + Na]^+$, found 468.0641.

3.1.5 *N*-((7-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(4-methoxyphenyl)methyl)acetamide (6d). Mp 123–124 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 9.2 Hz, 1H), 7.45 (d, J = 8.7 Hz, 1H), 7.24 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.9 Hz, 1H), 6.90 (d, J = 9.2 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 6.53 (s, 1H), 3.74 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.7, 159.5, 158.2, 157.9, 152.8, 141.1 (q, $^2J_{C-F}$ = 32.4 Hz), 132.2, 127.0, 124.5, 124.5, 121.1 (q, $^1J_{C-F}$ = 276 Hz), 115.6, 113.7, 113.0, 110.6, 110.5 (q, $^3J_{C-F}$ = 6.0 Hz), 105.6, 54.6, 46.2, 22.7 ppm; IR (KBr): 3378, 2928, 1741, 1578, 1511, 1280, 1142, 822 cm^{-1}; ESI (MS): *m/z* 430 $[M + Na]^+$.

3.1.6 *N*-((3-Chlorophenyl)(7-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6e). Mp 249–250 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.98 (br s, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.56–7.49 (m, 1H), 7.33 (s, 1H), 7.29–7.15 (m, 3H), 7.08–6.99 (m, 2H), 6.56 (s, 1H), 2.08 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.2, 159.7, 158.1, 143.2, 140.8 (q, $^2J_{C-F}$ = 34 Hz), 133.0, 129.37, 126.3, 125.8, 125.0, 124.5, 121.2 (q, $^1J_{C-F}$ = 274 Hz), 115.0, 113.6, 111.1 (q, $^3J_{C-F}$ = 4.3 Hz), 105.4, 45.9, 22.5 ppm; IR (KBr): 3413, 2923, 1745, 1644, 1511, 1400, 1286, 1078, 825, 547 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{13}ClF_3NNaO_4$ *m/z* 434.0377 $[M + Na]^+$, found 434.0378.

3.1.7 *N*-((3-Bromophenyl)(7-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6f). Mp 258–259 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 7.82 (d, J = 9.1 Hz, 1H), 7.55–7.48 (m, 2H, Ar-H, NH), 7.35–7.25 (m, 2H), 7.17 (d, J = 7.7 Hz, 1H), 7.05–6.98 (m, 2H), 6.56 (s, 1H), 2.08 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.9, 159.8, 157.8, 152.9, 143.2, 140.7 (q, $^2J_{C-F}$ = 32.4 Hz), 129.7, 129.3, 129.1, 128.6, 125.9, 124.8, 124.7, 122.9, 121.4, 121.3 (q, $^1J_{C-F}$ = 275.6 Hz), 114.7, 113.6, 110.7 (q, $^3J_{C-F}$ = 5.8 Hz), 105.3, 45.9, 22.5 ppm; IR (KBr): 3412, 1745, 1587, 1511, 1284, 1134, 826 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{13}BrF_3NNaO_4$ *m/z* 477.9872 $[M + Na]^+$, found 477.9875.

3.1.8 *N*-((2,4-Dichlorophenyl)(7-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6g). Mp 250–251 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.77 (br s, 1H), 7.58–7.48 (m, 3H), 7.32 (d, J = 2.1 Hz, 1H), 7.20 (dd, J = 8.5, 2.1 Hz, 1H), 7.02 (d, J = 8.9 Hz, 1H), 6.98 (d, J = 9.1 Hz, 1H), 6.52 (s, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.2, 160.23, 158.2, 153.7, 141 (q, $^2J_{C-F}$ = 31.9 Hz), 136.7, 133.0, 132.4, 130.5, 128.5, 125.9, 125.2, 121.3 (q, $^1J_{C-F}$ = 275 Hz), 113.6, 113.4, 110.5 (q, $^3J_{C-F}$ = 5.0 Hz), 105.4, 45.2, 22.3 ppm; IR (KBr): 3367, 2925, 1725, 1575, 1278, 1152, 1078, 866 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{12}Cl_2F_3NNaO_4$ *m/z* 467.9987 $[M + Na]^+$, found 467.9991.

3.1.9 *N*-((3,4-Dimethoxyphenyl)(7-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6h). Mp 150–152 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 10.45 (br s, 1H), 7.55 (d, J = 9.4 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.02–6.94 (m, 2H), 6.91–6.83 (m, 2H), 6.76 (d, J = 8.5 Hz, 1H), 6.55 (s, 1H), 3.83 (s, 6H), 2.17 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.8, 159.4, 158.2, 152.9, 148.2, 147.5, 141.1 (q, $^2J_{C-F}$ = 35.5 Hz), 132.9, 124.5, 121.3 (q, $^1J_{C-F}$ = 275 Hz), 118.2, 115.5, 113.7, 110.5 (q, $^3J_{C-F}$ = 5.8 Hz), 110.0, 105.7, 55.3, 55.3, 46.7, 22.8 ppm; IR (KBr): 3364, 2924, 1724, 1577, 1280, 1142, 1075 cm^{-1}; HRMS (ESI) anal. calcd for $C_{21}H_{18}F_3NNaO_6$ *m/z* 460.0978 $[M + Na]^+$, found 460.0977.

3.1.10 *N*-((4-Fluorophenyl)(7-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6i). Mp 236–237 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 7.76 (d, J = 9.2 Hz, 1H), 7.54–7.47 (m, 1H), 7.39–7.29 (m, 2H), 7.07–6.91 (m, 4H), 6.55 (s, 1H), 2.06 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.0, 162.6, 159.6, 159.3, 158.2, 152.9, 141.3 (q, $^2J_{C-F}$ = 31.3 Hz), 136.3, 136.2, 127.6, 127.5, 124.8, 121.1 (q, $^1J_{C-F}$ = 276.5 Hz), 115.2, 114.5, 114.2, 113.7, 110.6 (q, $^3J_{C-F}$ = 5.5 Hz), 105.6, 46.0, 22.6 ppm; IR (KBr): 3414, 3079, 2924, 1737, 1577, 1286, 1149, 1084, 830 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{13}F_4NNaO_4$ *m/z* 418.0672 $[M + Na]^+$, found 418.0672.

3.1.11 *N*-((7-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(4-isopropylphenyl)methyl)acetamide (6j). Mp 210–211 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.43 (br s, 1H), 7.54 (d, J = 9.1 Hz, 1H), 7.46 (dd, J = 9.1, 2.2 Hz, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 6.98 (d. J = 9.1 Hz, 1H), 6.87 (d, J = 9.1 Hz, 1H), 6.54 (s, 1H), 2.93–2.79 (m, 1H), 2.15 (s, 3H), 1.20 (d, J = 6.8 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.8, 159.5, 158.3, 152.9, 146.9, 140.8 (q, $^2J_{C-F}$ = 31 Hz), 137.4, 125.8, 125.7, 124.6, 121.1 (q, $^1J_{C-F}$ = 275 Hz), 115.5, 113.7, 110.5 (q, $^3J_{C-F}$ = 6.0 Hz), 105.7, 46.6, 32.9, 23.4 (2C), 22.8 ppm; IR (KBr): 3412, 2964, 1740, 1581, 1282, 1139, 1078 cm^{-1}; HRMS (ESI) anal. calcd for $C_{22}H_{20}F_3NNaO_4$ *m/z* 442.1236 $[M + Na]^+$, found 442.1237.

3.1.12 *N*-((7-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(phenyl)methyl)benzamide (6k). Mp 104–106 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 8.45 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 7.0 Hz, 2H), 7.57–7.37 (m, 6H), 7.32–7.21 (m, 4H), 7.05 (d, J = 9.1 Hz, 1H), 6.59 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 165.6, 159.6, 158.1, 152.9, 141.0 (q, $^2J_{C-F}$ = 32.4 Hz), 140.3, 133.8, 132.1, 131.0, 129.0, 128.0, 127.8, 127.7, 126.5, 126.6, 125.9,

124.8, 121.1 (q, $^1J_{C-F}$ = 275 Hz), 115.1, 113.8, 110.8 (q, $^3J_{C-F}$ = 4.9 Hz), 105.7, 47.2 ppm; IR (KBr): 3418, 2926, 1743, 1577, 1279, 1143, 695 cm^{-1}; ESI (MS): *m*/*z* 440 [M + H]$^+$.

3.1.13 *N*-((5,7-Dihydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(4-methoxyphenyl)methyl) acetamide (6l). Mp 165–166 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.53 (br s, 1H), 7.71 (d, *J* = 9.4 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 9.4 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.58 (s, 1H), 6.53 (br s, 1H), 3.80 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.9, 159.9, 158.9, 157.8, 154.9, 153.7, 140.9 (q, $^2J_{C-F}$ = 33.5 Hz), 133.1, 127.0, 126.5, 121.1 (q, $^1J_{C-F}$ = 275 Hz), 113.0, 109.6 (q, $^3J_{C-F}$ = 8.2 Hz), 107.3, 99.9, 96.9, 54.7, 46.2, 22.9 ppm; IR (KBr): 3106, 2922, 1723, 1614, 1512, 1389, 1273, 1143 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{17}F_3NO_6$ *m*/*z* 424.1002 [M + H]$^+$, found 424.1005.

3.1.14 *N*-((5, 7-Dihydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(4-fluorophenyl)methyl)acetamide (6m). Mp 166–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.76 (br s, 1H), 10.63 (br s, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.34–7.38 (m, 2H), 6.99–6.92 (m, 2H), 6.89 (d, *J* = 9.4 Hz, 1H), 6.55 (s, 1H), 6.48 (br s, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.8, 161.7, 160.0, 159.8, 158.4, 153.9, 154.8, 140.4 (q, $^2J_{C-F}$ = 34 Hz), 137.4, 127.6, 127.5, 121.4 (q, $^1J_{C-F}$ = 276 Hz), 114.3, 114.1, 109.7 (q, $^3J_{C-F}$ = 7.5 Hz) 107.0, 99.5, 96.6, 45.7, 22.6 ppm; IR (KBr): 3198, 2925, 1723, 1615, 1389, 1273, 1143, 864 cm^{-1}; ESI (MS): *m*/*z* 412 [M + H]$^+$.

3.1.15 *N*-((4-Cyanophenyl)(5,7-dihydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)methyl)acetamide (6n). Mp 160–161 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6): δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.53 (s, 1H), 6.46 (br s, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.3, 159.9, 158.5, 155.2, 154.0, 147.2, 140.6 (q, $^2J_{C-F}$ = 35 Hz), 131.3, 126.7, 126.5, 126.4, 121.0 (q, $^1J_{C-F}$ = 274 Hz), 118.5, 109.8 (q, $^3J_{C-F}$ = 6.5 Hz), 109.4, 106.1, 99.6, 96.8, 46.3, 22.6 ppm; IR (KBr): 3334, 2925, 2231, 1725, 1613, 1385, 1273, 1145 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{13}F_3N_2NaO_5$ *m*/*z* 441.0665 [M + Na]$^+$, found 441.0666.

3.1.16 *N*-((5, 7-Dihydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-8-yl)(4-(trifluoromethyl)phenyl)methyl)acetamide (6o). Mp 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.89 (br s, 1H), 10.78 (br s, 1H), 8.10–7.99 (m, 1H), 7.58–7.36 (m, 4H), 6.92–6.81 (m, 1H), 6.53 (s, 1H), 6.47 (br s, 1H), 2.06 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.8, 159.8, 158.2, 154.9, 153.9, 146.1, 140.2 (q, $^2J_{C-F}$ = 33 Hz), 127.3 (q, $^2J_{C-F}$ = 32 Hz), 126.2, 124.2 (q, $^3J_{C-F}$ = 3.3 Hz), 124.0 (q, $^1J_{C-F}$ = 272 Hz), 121.1 (q, $^1J_{C-F}$ = 275 Hz), 109.7 (q, $^3J_{C-F}$ = 7.7 Hz), 106.4, 99.4, 96.5, 45.9, 22.5 ppm; IR (KBr): 3331, 2924, 1730, 1619, 1327, 1159, 863 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{14}F_6NO_5$ *m*/*z* 462.0770 [M + H]$^+$, found 462.0769.

3.1.17 *N*-((8-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl) (4-(trifluoromethyl) phenyl) methyl) acetamide (6p). Mp 230–232 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.13 (br s, 1H), 8.40–8.26 (m, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.35–7.28 (m, 1H), 7.21–7.15 (m, 1H), 6.74 (s, 1H), 6.66–6.59 (m, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.4, 157.6, 144.6, 142.7, 142.2, 140.9 (q, $^2J_{C-F}$ = 33 Hz), 132.6, 128.3 (q, $^2J_{C-F}$ = 32.4 Hz), 127.2, 125.3, 124.6, 124.5 (q, $^3J_{C-F}$ = 3.8 Hz), 123.5 (q, $^1J_{C-F}$ = 271 Hz) 123.5, 120.8 (q, $^1J_{C-F}$ = 275 Hz), 114.8 (q, $^3J_{C-F}$ = 5.5 Hz), 114.5, 112.5, 51.0, 22.3 ppm; IR (KBr): 3420, 3307, 2926, 1750, 1655, 1328, 1283, 1166, 1067 cm^{-1}; ESI (MS): *m*/*z* 468 [M + Na]$^+$.

3.1.18 *N*-((4-Bromophenyl)(8-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl)methyl)acetamide (6q). Mp 216–218 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.14 (br s, 1H), 8.41 (d, *J* = 8.1 Hz, 1H), 7.44–7.30 (m, 3H), 7.22–7.13 (m, 3H), 6.75 (s, 1H), 6.58–6.51 (m, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.5, 157.7, 142.6, 142.1, 141.1 (q, $^2J_{C-F}$ = 33 Hz), 139.3, 132.8, 130.7, 128.6, 123.5, 120.9 (q, $^1J_{C-F}$ = 276 Hz), 120.3, 114.7 (q, $^3J_{C-F}$ = 5.5 Hz), 114.5, 112.5, 51.2, 22.4 ppm; IR (KBr): 3293, 2926, 1747, 1650, 1283, 1146 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{13}BrF_3NNaO_4$ *m*/*z* 477.9872 [M + Na]$^+$, found 477.9875.

3.1.19 *N*-((4-Cyanophenyl)(8-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl)methyl)acetamide (6r). Mp 249–250 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 8.18–8.04 (m, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.22–7.17 (m, 1H), 6.75 (s, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 2.09 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.5, 157.7, 146.1, 142.8, 142.2, 140.9 (q, $^2J_{C-F}$ = 31.9 Hz), 132.5, 131.6, 127.7, 122.8, 123.7, 120.9 (q, $^1J_{C-F}$ = 275.6 Hz), 118.2, 115.1 (q, $^3J_{C-F}$ = 5.5 Hz), 114.7, 114.6, 112.7, 110.1, 51.0, 22.4 ppm; IR (KBr): 3297, 2239, 1750, 1651, 1285, 1171, 1143, 888 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{14}F_3N_2O_4$ *m*/*z* 403.0900 [M + H]$^+$, found 403.0903.

3.1.20 *N*-((8-Hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl)(2-nitrophenyl)methyl)acetamide (6s). Mp 267–268 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 8.26–8.13 (m, 1H), 7.93–9.88 (m, 1H), 7.64–7.43 (m, 3H), 7.17–7.04 (m, 3H), 6.76 (s, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.5, 157.9, 142.6, 142.6, 140.7 (q, $^2J_{C-F}$ = 32.9 Hz), 136.5, 134.0, 133.1, 131.7, 129.4, 128.8, 126.4, 123.6, 122.8, 121.0 (q, $^1J_{C-F}$ = 275 Hz), 115.0 (q, $^3J_{C-F}$ = 6.5 Hz), 114.2, 112.7, 48.8, 22.2 ppm; IR (KBr): 3277, 2924, 1749, 1529, 1283, 1140, 886 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{13}F_3N_2NaO_6$ *m*/*z* 445.0617 [M + Na]$^+$, found 445.0618.

3.1.21 *N*-((2,4-Dichlorophenyl)(8-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl)methyl)acetamide (6t). Mp 278–279 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 8.10–8.18 (m, 1H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.26–7.13 (m, 4H), 6.77 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 168.7, 157.6, 148.6, 142.6, 142.4, 140.2 (q, $^2J_{C-F}$ = 34.2 Hz) 134.7, 132.6, 129.4, 128.2, 124.1, 123.0, 120.8 (q, $^1J_{C-F}$ = 275 Hz), 115.7 (q, $^3J_{C-F}$ = 4.9 Hz), 114.1, 112.7, 47.1, 22.1 ppm; IR (KBr): 3402, 3084, 2923, 1744, 1652, 1286, 1143, 897 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{13}Cl_2F_3NO_4$ *m*/*z* 446.0168 [M + H]$^+$, found 446.0166.

3.1.22 *N*-((4-Fluorophenyl)(8-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl)methyl)acetamide (6u). Mp 225–227 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.49 Hz, 1H), 7.32–7.22 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.99–6.91 (m, 2H), 6.71 (s, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 2.08 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 169.7, 162.9, 159.7, 158.0, 142.8, 142.2, 141.0 (q, $^2J_{C-F}$ = 33.0 Hz), 136.9, 136.4, 132.5, 131.9, 131.7, 131.5, 131.4, 128.9, 128.8, 128.3, 128.2, 123.4, 121.0

(q, $^1J_{C-F}$ = 275 Hz), 115.0 (q, $^3J_{C-F}$ = 6.0 Hz), 114.8, 114.5, 112.5, 50.5, 22.4 ppm; IR (KBr): 3366, 2924, 1752, 1509, 1284, 1152, 881 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{14}F_4NO_4$ *m*/*z* 396.08535 $[M + H]^+$, found 396.08531.

3.1.23 *N*-((4-Cyanophenyl)(8-hydroxy-2-oxo-4-(trifluoromethyl)-2*H*-chromen-7-yl)methyl)benzamide (6v). Mp 266–267 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6): δ 10.35 (br s, 1H), 8.61 (d, *J* = 7.4 Hz, 1H), 7.90 (d, *J* = 6.6 Hz, 2H), 7.67–7.36 (m, 8H), 7.25 (d, *J* = 5.8 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 166.0, 157.6, 146.2, 142.7, 142.2, 140.2 (q, $^2J_{C-F}$ = 33.6 Hz), 133.7, 132.6, 131.6, 130.9, 128.1, 127.7, 127.3, 123.7, 121.1 (q, $^1J_{C-F}$ = 274 Hz) 118.1, 115.5 (q, $^3J_{C-F}$ = 5.5 Hz), 114.3, 112.6, 109.9, 50.7 ppm; IR (KBr): 3423, 3284, 2922, 2228, 1750, 1638, 1283, 1139, 697 cm^{-1}; HRMS (ESI) anal. calcd for $C_{25}H_{16}F_3N_2O_4$ *m*/*z* 465.1056 $[M + H]^+$, found 465.1057.

3.1.24 *N*-((7-Hydroxy-4-methyl-2-oxo-2*H*-chromen-8-yl)-(phenyl)methyl)acetamide (6w). Mp 265–270 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6): δ 10.57 (br s, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.34–7.29 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 9.3 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H) 6.06 (s, 1H), 2.39 (s, 3H), 2.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO-d_6): δ 168.7, 159.5, 158.2, 152.3, 151.3, 140.6, 120.5, 126.1, 125.6, 124.2, 114.4, 112.5, 112.2, 110.2, 46.4, 22.1, 18.2 ppm; IR (KBr): 3372, 2960, 1704, 1649, 1511, 1246, 1067 cm^{-1}; HRMS (ESI) anal. calcd for $C_{19}H_{18}NO_4$ *m*/*z* 324.1230 $[M + H]^+$, found 324.1230.

3.1.25 *N*-((4-cyanophenyl)(7-hydroxy-4-methyl-2-oxo-2*H*-chromen-8-yl)methyl)acetamide (6x). Mp 260–266 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6): δ 10.76 (br s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.07 (s, 1H), 2.38 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO-d_6): δ 168.5, 159.3, 158.2, 152.6, 151.2, 146.6, 131.2, 126.7, 124.9, 124.8, 118.2, 113.3, 112.3, 112.0, 110.2, 109.2, 46.1, 22.4, 18.1 ppm; IR (KBr): 3372, 2960, 1704, 1649, 1511, 1246, 1067 cm^{-1}; HRMS (ESI) anal. calcd for $C_{20}H_{16}N_2NaO_4$ *m*/*z* 371.1002 $[M + Na]^+$, found 371.1008.

4. Conclusions

In conclusion, we have developed an efficient methodology to synthesize a series of amidoalkyl based trifluoromethyl substituted chromen-2-ones, in a one pot three component reaction under solvent free condition. Higher yields, simple reaction condition, and environmentally benign procedure are the advantages of this protocol.

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