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Reaction of chromone-3-carboxaldehydes with TOSMIC: synthesis of 4-(2-hydroxybenzoyl)pyrroles

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Abstract—Chromone-3-carboxaldehydes **1** react with tosylmethylisocyanide (TOSMIC) in the presence of DBU in THF at room temperature to furnish, after in situ deformylation, good yields of 2-tosyl-4-(2-hydroxybenzoyl)pyrroles **2**. When the same reaction is performed with potassium carbonate in methanol under reflux pyrroles **2** are again isolated, but in lower yields. Finally, from the reaction of **1a** in the presence of a stronger base (NaOH) only a small amount of the 3-substituted derivative **3a** along with polymeric material is isolated.

1. Introduction

Besides forming the basic nucleus of an entire class of natural products, i.e. flavones,[1] the chromone moiety forms the important component of pharmacophores of a large number of molecules of medicinal significance.[2] Consequently, considerable attention is being devoted to isolation from natural resources, chemistry and synthesis of chromone derivatives, and evaluation of their biological activity with emphasis on their potential medicinal applications.[2–4] Because chromone-3-carboxaldehyde (**1**) has been extensively used in the formation of various heterocyclic systems since its convenient synthesis was reported in the 1970s, the synthesis and reactivity of this versatile compound has been the subject of numerous reviews.[5–8] Chromone-3-carboxaldehyde represents a very reactive system owing to the presence of an unsaturated keto function, a conjugated second carbonyl group at C-3 and above all of a center at C-2, which is very reactive toward Michael addition of nucleophiles with opening of the γ-pyrone ring followed by a new cyclization. So, compound **1** can be readily converted into a broad range of heterocyclic systems, e.g. xanthones[9] and pyranobenzopyranones[10] by cycloaddition strategies, pyrazolopyrimidines,[11] pyridopyrimidines,[12] pyrimidopyrimidines,[13] benzopyranobenzo-thiazepines, -oxazepines, -diazepines,[14] furobenzopyranones,[15] *o*-hydroxyphenyl substituted pyrazoles,[16] and pyrimidines[16,17] through reaction with several nucleophiles, and particularly bis-nucleophiles. The reaction of **1** with amino esters leading to mixtures of 4-(2-hydroxybenzoyl)pyrroles and 6-benzopyranopyridines[18] and very recently with α-amino acids leading to (2-hydroxybenzoyl)-pyrroles have also been studied.[19]

In the present work our objective was to study the reaction between compounds **1** and TOSMIC speculating, on account of the above mentioned reactions with nucleophiles,[11–19] that the unsaturated aldehyde moiety of **1** would rather react as a Michael acceptor to generate disubstituted benzoylpyrroles, and would not be involved in van Leusen's oxazole synthesis,[20] namely a base catalyzed reaction of TOSMIC with aldehydes. Considering that the pyrrole ring is an important heterocycle in biological systems being incorporated into the porphyrin ring systems of chlorophyll, heme, vitamin B_{12}, and the bile pigments, but also there are a number of pyrrole-containing small molecules that exhibit useful biological activities,[21,22] novel synthesis of this type of compounds is always of interest. Moreover, benzoylpyrroles show antibacterial[23] and anti-inflammatory activities[24] and act as aldose–reductase inhibitors.[25] In that way, the pyrrole derivatives described here are potential biologically active agents.

2. Results and discussion

When chromone-3-carboxaldehydes (**1a**–**1e**) were allowed to react with equimolar amounts of TOSMIC in the presence of the mild base 1,8-diazabicyclo-[5.4.0]undecane-7 (DBU), in the aprotic nonpolar solvent THF at room temperature for 2 h the 2-tosyl-4-(2-hydroxybenzoyl)pyrroles (**2a**–**2e**) were isolated in good yields (50–65%, Table 1). Because of the earlier[26] reported contrasting behavior of 2-formylindole and 2-formylimidazole toward their base induced reaction with TOSMIC but also because of the dependence of the

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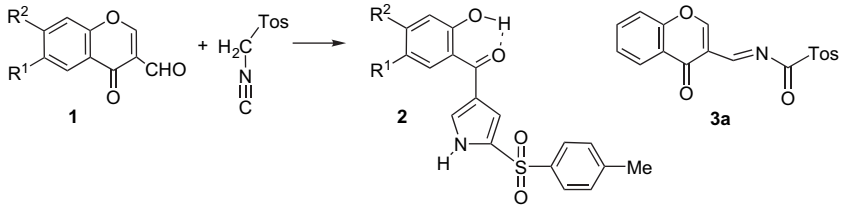
Table 1. Conditions and products during the reaction of chromone-3-carboxaldehydes **1** with TOSMIC



Chromone	Substituents	Reaction conditions	Product	Yield (%)
1a	R^1=R^2=H	DBU, 1 equiv, THF, rt, 2–3 h	**2a**	56
1b	R^1=Me, R^2=H	DBU, 1 equiv, THF, rt, 2–3 h	**2b**	51
1c	R^1=Cl, R^2=H	DBU, 1 equiv, THF, rt, 2–3 h	**2c**	65
1d	R^1=Cl, R^2=Me	DBU, 1 equiv, THF, rt, 2–3 h	**2d**	52
1e	R^1=NO_2, R^2=H	DBU, 1 equiv, THF, rt, 2–3 h	**2e**	50
1a	R^1=R^2=H	K_2CO_3, 1 equiv, MeOH, reflux, 2–3 h	**2a**	30
1b	R^1=Me, R^2=H	K_2CO_3, 1 equiv, MeOH, reflux, 2–3 h	**2b**	31
1c	R^1=Cl, R^2=H	K_2CO_3, 1 equiv, MeOH, reflux, 2–3 h	**2c**	35
1a	R^1=R^2=H	NaOH, 1 equiv, DMF, reflux, 2–3 h	**3a**	13

reaction outcome from the reaction conditions,[27] the reactions of **1a**, **1b**, and **1c** were repeated with equimolar amounts of TOSMIC in the presence of potassium carbonate in methanol under reflux, to furnish again the same pyrroles **2a**, **2b**, and **2c**, though in lower yield (30–35%). When an even stronger base, NaOH, was used compound **3a** was the only product in small yield (13%) along with polymeric material, whereas with NaH only polymeric material was formed.

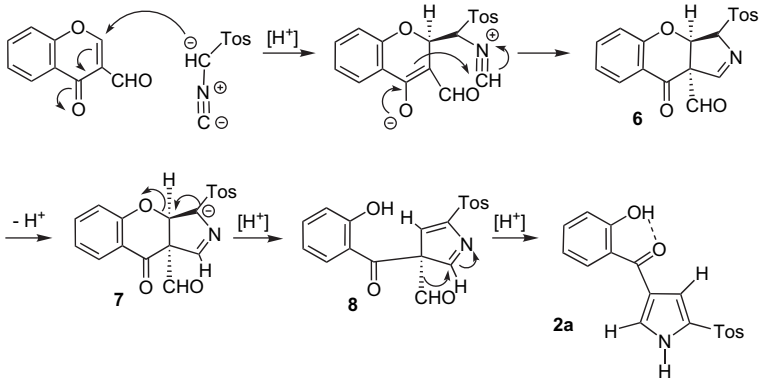
Although deformylation of chromone derivatives has been previously reported on several occasions[19,28] the fact that in all cases the formyl group leaves preferentially over the tosyl group is extremely remarkable. For the formation of products **2** a plausible mechanism depicted in Scheme 1 can be proposed. The reaction is most probably initiated by an attack of the base-activated nucleophilic TOSMIC to the C-2 double bond chromone carbon, being a Michael acceptor, followed by ring closure, which gives rise to the intermediate **6**. Subsequent formation of intermediate **7** is followed by chromone ring opening to give intermediate **8**, from which by loss of the formyl instead the tosyl group the more stable aromatic pyrrole derivatives **2** can be formed.

Concerning the formation of compound **3a** a reasonable mechanism cannot be proposed at this time.

2.1. Structure assignments of the new compounds

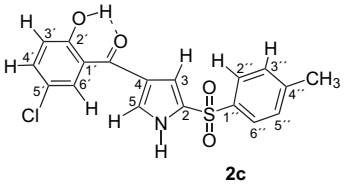
The assigned molecular structures of all new compounds **2** and **3** are based on rigorous spectroscopic analyses including IR, NMR (^{1}H, ^{13}H, COSY, NOESY, HETCOR, and COLOC), MS, and elemental analysis data.

Regarding the structure of pyrroles **2a**–**2e** the assignment of **2c** is described, because the aromatic proton signals are well separated and easily defined. The elemental analysis and mass spectra unequivocally established the reaction of one molecule of chromone-aldehyde **1c** with one molecule of TOSMIC with the loss of a formyl group, a fact that was also confirmed from the ^{13}C NMR spectrum, where 16 different signals were observed. Moreover, in the IR spectra (see Section 4) the two chromone carbonyls (1695 and 1650 cm^{-1}) were replaced by one, most probably hydrogen bonded, at 1623 cm^{-1}. From the H–H COSY spectrum three distinguishable proton groups were defined corresponding to the three aromatic rings. In the ^{1}H NMR the presence of the tosyl group was identified from the three proton singlet at δ 2.41 (with the corresponding carbon at 21.55 ppm) and the *p*-substituted phenyl moiety ($H_{2'',6''}$=7.85 ppm, $H_{3'',5''}$=7.32 ppm, with coupling constants $J_{2'',3''}$=8.4 Hz, $J_{2'',6''}$=2.0 Hz, and $J_{3'',5''}$=2.2 Hz with carbons at 127.4 and 130.3 ppm, respectively).[29] In addition, the methyl group



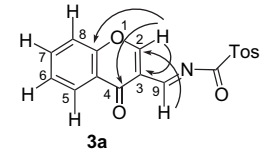
Scheme 1. Plausible mechanism for the reaction of TOSMIC with chromone-3-carboxaldehydes yielding compounds **2**.

protons gave COLOC correlations with the carbon at 130.3 ppm and also with the quaternary carbon at 145.0 ppm, whereas the protons at δ 7.32 gave correlations with the quaternary carbon at 138.7 ppm, so the whole sequence of the tosyl group was identified (Fig. 1). Concerning the hydroxybenzoyl moiety the assignment of the aromatic protons was obvious from their splitting pattern, with protons resonating as a doublet at δ 6.97 with J=8.9 Hz, as a double of doublets at δ 7.40 (J_1=8.9 Hz, J_2=2.6 Hz), and as a doublet at δ 7.73 (J=2.6 Hz) and their carbons resonating at 120.2, 135.7, and 130.6 ppm, respectively. Moreover, the hydroxyl proton appears in the ^{1}H NMR as a singlet at δ 11.60 correlating with the quaternary carbons at 120.8 and 161.3 ppm and also with the protonated carbon at 120.2 ppm. The proton at δ 7.73 shows COLOC correlations with the C=O at 192.0 ppm, the C-2′ and the C-4′ via $^3J_{CH}$ coupling and with the C-5′ via $^2J_{CH}$ coupling. Proton at C-3′ shows a low intensity COLOC correlation with C-5′, whereas proton at C-4′ does not show any COLOC correlation. This can be attributed to the combined effects of the three substituents resulting in a decrease of the $^3J_{CH}$ couplings to small values deviating thus very much from the optimized values of 10 Hz for COLOC correlations. Concerning the pyrrole ring the NH proton appears as a broad singlet at δ 9.77 and the two ring protons appear as doublet of doublets at δ 7.52 (J_1=3.1 Hz, J_2=1.6 Hz) and at δ 7.24 (J_1=2.4 Hz, J_2=1.6 Hz) with their carbons resonating at 127.5 and at 116.0 ppm, respectively. The above J_1 couplings are originated from the interaction of NH proton with the corresponding CH pyrrole ring protons.[29] The proton resonating at δ 7.52 correlates in COLOC spectrum with the quaternary carbons at 125.4 ppm and 131.9 ppm, whereas the proton resonating at δ 7.24 correlates with the carbons at 131.9 and 127.5 ppm. To elucidate the assignment of the above signals to 3- and 5-positions of pyrrole ring the C–H coupled spectrum was obtained, because chemical shifts are more sensitive on substitution than coupling constants. It is known[30] that pyrrole has chemical shifts and coupling constants for C-2 118.0 ppm and $^1J_{CH}$=182 Hz, and for C-3 107.7 ppm and $^1J_{CH}$=170 Hz. The measured $^1J_{CH}$ couplings were 181.0 Hz and 164.7 Hz for carbons resonating at 116.0 and 127.5 ppm, respectively, so the signal at 116.0 ppm corresponds to C-5 and the signal at 127.5 ppm to C-3 (Fig. 1).



2c

Proton	COLOC to Carbon
H-3	C-2, C-4
H-5	C-3, C-4
H-6′	C-2′, C-4′, C-5′, C=O
OH	C-1′, C-2′, C-3′
H-2″,6″	C-4″
H-3″,5″	C-1″, CH_3
CH_3	C-3″,5″, C-4″



3a

Figure 1. Diagnostic COLOC correlations observed for compounds **2c** and **3a** and atom numbering of the products **2** and **3a**.

Finally, the ^{1}H and ^{13}C NMR spectra of compound **3a** show the characteristic resonances of the chromone ring in addition to the TOSMIC moiety. Moreover, the C-2 chromone proton at δ 8.84 appears as a doublet (J=0.7 Hz) due to long-range coupling with the 3-position substituent methinic proton (δ 8.13, d, J=0.7 Hz). This proton attached to carbon resonating at 126.0 ppm has COLOC correlation with C-2 at 158.0 ppm, thus proving its position (Fig. 1).

3. Conclusions

The present work demonstrates the versatility of TOSMIC in bringing about one-pot synthetic procedures. Thus the synthesis of disubstituted pyrroles with two distinct substituents, namely the hydroxybenzoyl and the tosyl, was possible. Subsequent replacement of tosyl group by an appropriate substituent is a promising method to develop new routes to new pyrrole derivatives.

4. Experimental

4.1. General

Melting points were measured on a Kofler hot-stage and are uncorrected. Column chromatography was carried out using Merck silica gel. TLC was performed using precoated silica gel glass plates of 0.25 mm containing fluorescent indicator UV_{254} purchased from Macherey–Nagel using a 3:1 mixture of petroleum ether–ethyl acetate. Petroleum ether refers to the fraction boiling between 60 and 80 °C. NMR spectra were recorded at room temperature (rt) on a Bruker AM 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, respectively, using $CDCl_3$ as solvent. Chemical shifts are expressed in δ values (ppm) relative to TMS as an internal standard for ^{1}H and relative to TMS (0.00 ppm) or to $CDCl_3$ (77.05 ppm) for ^{13}C NMR spectra. Coupling constants ^nJ are reported in Hertz. IR spectra were recorded on a Perkin–Elmer 297 spectrometer or on a Perkin–Elmer 1600 series FTIR spectrometer and are reported in wave numbers (cm^{-1}). Low-resolution electron impact mass spectra were recorded on a 6890N GC/MS system (Agilent Technology) and elemental analyses performed with a Perkin–Elmer 2400-II CHN analyzer. Structural assignments of the derived compounds were established by analysis of their IR, MS, and NMR spectra (^{1}H, ^{13}C, COSY, NOESY, HETCOR, and COLOC).

4.2. General procedure for the reaction of chromone-3-carboxaldehydes (1a–1e) with TOSMIC: method A

To a stirred solution of aldehyde **1** (1.0 mmol) in THF (2 mL), anhydrous DBU (0.17 mL, 1.1 mmol) and TOSMIC (0.22 g, 1.1 mmol) were added and the reaction mixture was stirred at rt until aldehyde **1** was consumed completely

(followed by TLC, approximately 2–3 h). The reaction mixture was diluted with AcOEt (60 mL), washed with water, dried (Na_2SO_4), the solvent was distilled off, and the resulting residue was subjected to column chromatography on silica gel using petroleum ether–AcOEt (7:1) as an eluent, slowly increasing the polarity up to 4:1 to give the 4-(2-hydroxybenzoyl)-2-[(4-methylphenyl)sulfonyl]pyrroles (**2**).

4.2.1. 4-(2-Hydroxybenzoyl)-2-[(4-methylphenyl)sulfonyl]pyrrole (2a). R_f=0.19; 0.191 g, 56% yield, white solid, mp 177–179 °C (CH_2Cl_2–petroleum ether); IR (Nujol) ν_{max}: 1623 cm^{-1}. ^1H NMR: 2.41 (s, 3H, CH_3), 6.92 (ddd, J=8.1, 7.3, 1.2 Hz, 1H, C(5′)), 7.03 (dd, J=8.3, 1.2 Hz, 1H, C(3′)), 7.29–7.32 (m, 3H, C(5) and C(3″,5″)), 7.49 (ddd, J=8.3, 7.3, 1.6 Hz, 1H, C(4′)), 7.56 (dd, J=3.0, 1.6 Hz, 1H, C(3)), 7.81 (dd, J=8.1, 1.6 Hz, 1H, C(6′)), 7.85 (dt, J=8.3, 1.8 Hz, 2H, C(2″,6″)), 10.8 (br s, 1H, NH), 11.9 (s, 1H, OH). ^{13}C NMR: 21.7 (CH_3), 116.4 (C-5), 118.4 (C-3′), 119.0 (C-5′), 119.8 (C-1′), 125.3 (C-4), 127.2 (C-2″), 128.2 (C-3), 130.2 (C-3″, 5″), 130.7 (C-2), 131.7 (C-6′), 136.0 (C-4′), 138.1 (C-1″), 145.0, (C-4″), 162.5 (C-2′), 193.1 (C═O). EIMS *m/z* (%) 341 (29, $M^{+\bullet}$), 186 (100). Anal. Calcd for $C_{18}H_{15}NO_4S$ (341.38): C, 63.33; H, 4.43; N, 4.10%. Found: C, 63.16; H, 4.40; N, 4.08%.

4.2.2. 4-(2-Hydroxy-5-methyl-benzoyl)-2-[(4-methylphenyl)sulfonyl]pyrrole (2b). R_f=0.20; 0.181 g, 51% yield, white solid, mp 168–169 °C (CH_2Cl_2–petroleum ether); IR (Nujol) ν_{max}: 3260, 1628 cm^{-1}. ^1H NMR: 2.29 (s, 3H, 5′-CH_3), 2.39 (s, 3H, 4″-CH_3), 6.92 (d, J=8.7 Hz, 1H, C(3′)), 7.29 (d, J=8.4 Hz, 2H, C(3″,5″)), 7.30 (m, 2H, C(5) and C(4′)), 7.56 (d, J=2.0 Hz, 1H, C(6′)), 7.58 (d, J=1.8 Hz, 1H, C(3)), 7.86 (d, J=8.4 Hz, 2H, C(2″,6″)), 10.91 (br s, 1H, NH), 11.72 (s, 1H, OH). ^{13}C NMR: 20.5 (5′-CH_3), 21.6 (4″-CH_3), 116.4 (5), 118.1 (3′), 119.5 (1′), 125.2 (4), 127.1 (2″,6″), 128.1 (5′), 128.3 (3), 130.1 (3″,5″), 130.7 (2), 131.3 (6′), 136.9 (4′), 138.2 (1″), 144.8 (4″), 160.3 (2′), 193.1 (C═O). EIMS *m/z* (%) 355 (59, $M^{+\bullet}$), 200 (73), 134 (100). Anal. Calcd for $C_{19}H_{17}NO_4S$ (355.44): C, 64.21; H, 4.82; N, 3.94%. Found: C, 64.01; H, 4.71; N, 3.89%.

4.2.3. 4-(5-Chloro-2-hydroxy-benzoyl)-2-[(4-methylphenyl)sulfonyl]pyrrole (2c). R_f=0.22; 0.243 g, 65% yield, white solid, mp 203–204 °C (CH_2Cl_2–ether); IR (Nujol) ν_{max}: 3250, 1623 cm^{-1}. ^1H NMR: 2.41 (s, 3H, CH_3), 6.97 (d, J=8.9 Hz, 1H, C(3′)), 7.24 (dd, J=2.4, 1.6 Hz, C(5)), 7.32 (dt, J=8.4, 2.2 Hz, 2H, C(3″,5″)), 7.40 (dd, J=8.9, 2.6 Hz, 1H, C(4′)), 7.52 (dd, J=3.1, 1.6 Hz, 1H, C(3)), 7.73 (d, J=2.6 Hz, 1H, C(6′)), 7.85 (dt, J=8.4, 2.0 Hz, 2H, C(2″,6″)), 9.77 (br s, 1H, NH), 11.6 (s, 1H, OH). ^{13}C NMR: 21.6 (CH_3), 116.0 (5), 120.2 (3′), 120.8 (1′), 123.8 (5′), 125.4 (4), 127.4 (2″,6″), 127.5 (3), 130.3 (3″,5″), 130.6 (6′), 131.9 (2), 135.7 (4′), 138.7 (1″), 145.0 (4″), 161.3 (2′), 192.0 (C═O). EIMS *m/z* (%) 375/377 (67, $M^{+\bullet}$), 220/222 (100). Anal. Calcd for $C_{18}H_{14}ClNO_4S$ (375.83): C, 57.52; H, 3.75; N, 3.73%. Found: C, 57.59; H, 3.63; N, 3.60%.

4.2.4. 4-(5-Chloro-2-hydroxy-4-methyl-benzoyl)-2-[(4-methylphenyl)sulfonyl]pyrrole (2d). R_f=0.21; 0.202 g, 52% yield, white solid, mp 205–206 °C (CH_2Cl_2–ether); IR (Nujol) ν_{max}: 3250, 1632 cm^{-1}. ^1H NMR: 2.38 (s, 3H, 4′-CH_3), 2.42 (s, 3H, 4″-CH_3), 6.91 (s, 1H, C(3′)), 7.27 (d, J=1.5 Hz, C(5)), 7.33 (d, J=8.3 Hz, 2H, C(3″,5″)), 7.53 (d, J=1.5 Hz, 1H, C(3)), 7.73 (s, 1H, C(6′)), 7.86 (d, J=8.3 Hz, 2H, C(2″,6″)), 10.22 (br s, 1H, NH), 11.77 (s, 1H, OH). ^{13}C NMR: 20.8 (4′-CH_3), 21.6 (4″-CH_3), 116.0 (5), 118.6 (1′), 120.5 (3′), 124.3 (5′), 125.0 (4), 127.2 (2″,6″), 127.6 (3), 130.2 (3″,5″), 130.9 (6′), 131.2 (2), 138.1 (1″), 144.9 (4″), 145.1 (4′), 161.0 (2′), 191.6 (C═O). EIMS *m/z* (%) 389/391 (91, $M^{+\bullet}$), 234/236 (100), 168 (86). Anal. Calcd for $C_{19}H_{16}ClNO_4S$ (389.85): C, 58.54; H, 4.14; N, 3.59%. Found: C, 58.56; H, 4.02; N, 3.58%.

4.2.5. 4-(2-Hydroxy-5-nitro-benzoyl)-2-[(4-methylphenyl)sulfonyl]pyrrole (2e). R_f=0.11; 0.193 g, 50% yield, white solid, mp 266–267 °C (ethanol); IR (Nujol) ν_{max}: 3470, 1623 cm^{-1}. ^1H NMR: 2.43 (s, 3H, CH_3), 7.12 (d, J=9.2 Hz, 1H, C(3′)), 7.28 (d, J=1.5 Hz, 1H, C(5)), 7.35 (d, J=8.2 Hz, 2H, C(3″,5″)), 7.57 (d, J=1.5 Hz, 1H, C(3)), 7.88 (d, J=8.2 Hz, 2H, C(2″,6″)), 8.32 (dd, J=9.2, 2.6 Hz, 1H, C(4′)), 8.69 (d, J=2.6 Hz, 1H, C(6′)), 12.4 (br s, 1H, NH), 13.0 (br s, 1H, OH). ^{13}C NMR: 20.9 (CH_3), 115.3 (5), 118.3 (3′), 119.7 (1′), 122.9 (4), 126.6 (2″,6″), 126.5 (6′), 126.8 (3), 129.1 (4′), 129.4 (3″,5″), 131.4 (2), 138.0 (5′), 138.9 (1″), 143.8 (4″), 165.7 (2′), 190.5 (C═O). EIMS *m/z* (%) 386 (28, $M^{+\bullet}$), 231 (100). Anal. Calcd for $C_{18}H_{14}N_2O_6S$ (386.38): C, 55.95; H, 3.65; N, 7.25%. Found: C, 55.95; H, 3.42; N, 7.14%.

4.3. General procedure for the reaction of chromone-3-carboxaldehydes (1a–1c) with TOSMIC: method B

To a stirred solution of aldehyde **1** (1.0 mmol) in dry MeOH (10 mL), anhydrous K_2CO_3 (0.16 g, 1.1 mmol) and TOSMIC (0.22 g, 1.1 mmol) were added and the reaction mixture was stirred under reflux until chromone-3-carboxaldehyde was consumed completely (followed by TLC, approximately 2–3 h). The reaction mixture was cooled, diluted with AcOEt (60 mL), washed with water until free of alkali, dried (Na_2SO_4), the solvent was distilled off, and the resulting residue was subjected to column chromatography on silica gel using petroleum ether–AcOEt (7:1) as an eluent, slowly increasing the polarity up to 4:1 to give compounds **2**.

4.3.1. Compound 2a. As described above in 30% yield.

4.3.2. Compound 2b. As described above in 31% yield.

4.3.3. Compound 2c. As described above in 35% yield.

4.4. General procedure for the reaction of chromone-3-carboxaldehyde 1a with TOSMIC: method C

To a stirred solution of aldehyde **1a** (1.0 mmol) in dry DMF (10 mL), solid NaOH (0.16 g, 1.1 mmol) and TOSMIC (0.22 g, 1.1 mmol) were added and the reaction mixture was stirred under reflux until chromone-3-carboxaldehyde was consumed completely (followed by TLC, approximately 2–3 h). The reaction mixture was cooled, diluted with AcOEt (60 mL), and after work up as above gave compound **3a**.

4.4.1. 3-[(4-Methylphenyl)sulfonyl]-*N*-[(*E*)-(4-oxo-4*H*-1-benzopyran-3-yl)methylidene]-carboxamide (3a). R_f=0.41; 0.046 g, 13% yield, white solid, mp 180–181 °C

(CH_2Cl_2–petroleum ether). ^{1}H NMR: 2.48 (s, 3H, CH_3), 7.42 (ddd, J=8.4, 2.0, 0.6 Hz, 2H, C(3′,5′)), 7.50 (ddd, J=8.0, 7.2, 0.9 Hz, 1H, C(6)), 7.53 (ddd, J=8.4, 0.9, 0.5 Hz, 1H, C(8)), 7.77 (ddd, J=8.4, 7.2, 1.8 Hz, 1H, C(7)), 7.91 (ddd, J=8.4, 1.6, 0.6 Hz, 2H, C(2′,6′)), 8.13 (d, J=0.7 Hz, 1H, C(9)), 8.27 (ddd, J=8.0, 1.8, 0.5 Hz, 1H, C(5)), 8.84 (d, J=0.7 Hz, 1H, C(2)). ^{13}C NMR: 21.8 (CH_3), 116.3 (3), 118.5 (8), 123.4 (4a), 126.0 (9), 126.57 (5), 126.62 (6), 129.3 (2′,6′), 130.4 (3′,5′), 133.3 (1′), 135.0 (7), 146.3 (4′), 155.8 (8a), 158.0 (2), 174.2 (4), 179.7 (N–C═O). Anal. Calcd for $C_{18}H_{13}NO_5S$ (355.37): C, 60.84; H, 3.69; N, 3.94%. Found: C, 60.97; H, 3.53; N, 3.82%.

References and notes

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