Synthesis V. A. Osyanin et al. Paper

Catalyst-Free Synthesis of Chromane-Type N,O-Acetals via Intramolecular Addition of Phenols to Enamines

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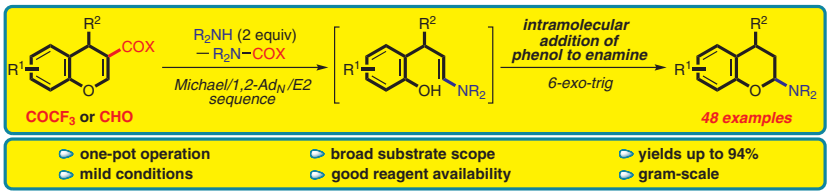

Received: 17.01.2020
Accepted after revision: 19.06.2020
Published online: 27.07.2020
DOI: 10.1055/s-0040-1707209; Art ID: ss-2020-c0037-op

Abstract A new strategy to 2-aminochromanes through catalyst-free cascade reaction of 3-trifluoroacetyl-4*H*-chromenes and 4*H*-chromene-3-carbaldehydes with cyclic secondary amines is presented. The reaction proceeds through subsequent 1,4- and 1,2-additions of amine, bimolecular elimination of trifluoroacetamide or formamide, and 6-*exo*-*trig* cyclization. The latter stage is a very rare example of addition of phenols to enamines. The obtained semicyclic N,O-acetals were applied as useful precursors for the synthesis of other chromanes.

Key words chromanes, 4*H*-chromenes, cascade reactions, enamines, cyclic secondary amines, N,O-acetals

N,O-Acetals, also called N,O-aminals, represent an interesting class of organic compounds, which is a common structural element in various pharmaceuticals and biologically active natural products, for example, alkaloids.[1] Besides, N,O-acetals are useful reagents and building blocks since they are relatively stable, but readily generate unstable N-imines, which are attacked by nucleophiles to produce complex highly functionalized molecules.[2] For example, they have been well recognized as key intermediates for the iminium ion-mediated carbon–carbon bond-formation reaction, particularly under protonic or Lewis acid conditions.[3]

One of the type of semicyclic N,O-acetals with an exocyclic N-atom are 2-aminochromanes. Among 2-aminochromanes and their areno- and heterocondensed analogues, compounds with antiplatelet,[4] anticancer activity[5] and non-steroidal glucocorticoid receptor antagonists[6] were identified. Tetracyclic alkaloid, perinadine A, isolated from the cultured broth of the fungus *Penicillium citrinum*, also contains an aminochromane fragment.[7] In addition, compounds of this type are effective precursors of 2-(3-aminopropyl)phenols, which can be obtained by hydrogenation of 2-aminochromanes.[8] This approach was used in the synthesis of the drug tolterodine and its analogues, which are antagonists of muscarinic receptors and are used in the treatment of urological diseases (Figure 1).[9]

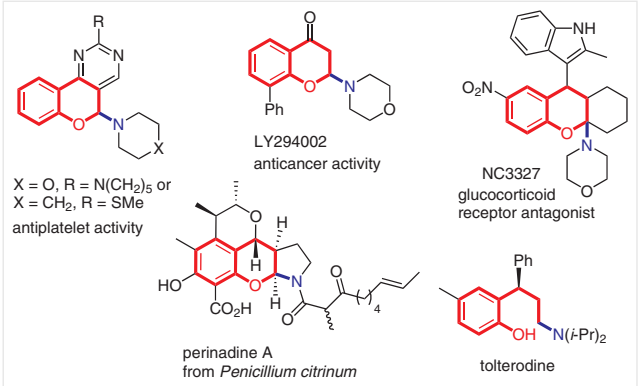

Figure 1 Selection of relevant 2-aminochromane derivatives

Unlike acyclic N,O-acetals, there are significantly fewer methods for the preparation of chromane-type N,O-acetals, such as the reaction of chroman-2-ols with secondary amines,[4,9] three-component condensation of 2-naphthol, 3-hydroxy-2,2-dialkylpropanal and secondary amines in the presence of *p*-TSA,[10] the Diels–Alder reaction of *o*-quinone methide precursors with substituted enamines,[5a,11] as well as the reaction of enamines with *o*-hydroxy-ω-nitrostyrenes[12] or 2-hydroxybenzaldehydes,[13] and a three-component condensation of phenols or 2-naphthol, α,β-unsaturated aldehydes and amines.[14] In these cases, the obtained chromane-type N,O-acetals, as a rule, contain various substituents at the C-3 and/or C-4 carbons of the dihydropyran ring. For this reason, to access 2-aminochromanes unsubstituted at mentioned positions remains difficult. One of the obvious approaches to their preparation could be [4+2]

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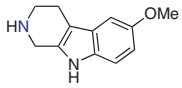
cycloaddition between N-vinylamines and precursors of *o*-quinone methides.[15] However, most N-vinylamines are not commercially available, their synthesis is fraught with a number of difficulties,[16] or they are not known. In addition, enamines of this type are often thermally unstable and undergo polymerization.[16b]

Table 1 Synthesized Benzo[*f*]chroman-3-amines[a]

G	HNR_2		Product[b]
H (**1a**)		(**2**)	**8a**, 79%
Br (**1b**)			**8b**, 83%
t-Bu (**1c**)			**8c**, 87%
Ad (**1d**)			**8d**, 93%
H (**1a**)		(**3**)	**9a**, 89%
Br (**1b**)			**9b**, 91%
		CX_2:	
H (**1a**)		CH_2 (**4a**)	**10a**, 79%
		CHMe (**4b**)	**10b**, 84%
		CHBn (**4c**)	**10c**, 80%
		CHPh (**4d**)	**10d**, 81%
		C(OH)Ph (**4e**)	**10e**, 70%
		C(OH)H (**4f**)	**10f**, 70%
		C=O (**4g**)	**10g**, 71%
		Y:	
H (**1a**)		Me (**5a**)	**11a**, 73%
		CH_2CH_2OH (**5b**)	**11b**, 69%
		cinnamyl (**5c**)	**11c**, 83%
		Bn (**5d**)	**11d**, 74%
		$CH(4\text{-}FC_6H_4)_2$ (**5e**)	**11e**, 89%
		CO_2Et (**5f**)	**11f**, 90%
		Boc (**5g**)	**11g**, 94%
		Ph (**5h**)	**11h**, 75%
		$2\text{-}MeC_6H_4$ (**5i**)	**11i**, 80%
		$3\text{-}MeC_6H_4$ (**5j**)	**11j**, 82%
		$4\text{-}MeC_6H_4$ (**5k**)	**11k**, 94%
		$2,6\text{-}Me_2C_6H_3$ (**5l**)	**11l**, 71%
		$2\text{-}ClC_6H_4$ (**5m**)	**11m**, 83%
		$4\text{-}ClC_6H_4$ (**5n**)	**11n**, 80%
		$4\text{-}O_2NC_6H_4$ (**5o**)	**11o**, 82%
		$2\text{-}MeOC_6H_4$ (**5p**)	**11p**, 78%
		$2\text{-}EtOC_6H_4$ (**5q**)	**11q**, 82%
		$4\text{-}HOC_6H_4$ (**5r**)	**11r**, 80%

Table 1 (continued)

G	HNR_2		Product[b]
		$4\text{-}AcC_6H_4$ (**5s**)	**11s**, 90%
		pyrimidin-2-yl (**5t**)	**11t**, 85%
H (**1a**)		(**6**)	**12**, 74%
H (**1a**)		(**7**)	**13**, 71%

[a] Reaction conditions: **1a–d** (1 mmol) and amine (2 mmol) in MeOH (3 mL) at rt for 1 h.
[b] Isolated yields.

The trifluoroacetyl group has the property of unusually greatly increasing the reactivity of electrophilic substrates and affecting the regiodirection of reactions involving nucleophiles. Its introduction into a molecule often makes possible to easily proceed reactions that do not occur even under the most severe conditions in the absence of this substituent. The presence of a trifluoroacetyl group in the β-position of the pyran ring increases its susceptibility to various nucleophiles and makes these compounds valuable building blocks for the synthesis of a wide variety of heterocyclic compounds. 3-Trifluoroacetyl-4*H*-chromenes and their benzofused analogues can be easily obtained via reaction of *o*-quinone methide precursors and 1,1,1-trifluoro-4-morpholinobut-3-en-2-one.[17] In continuation of our interest in the chemistry of 3-trifluoroacetyl-4*H*-chromenes,[18] we have studied their reaction with cyclic secondary amines.

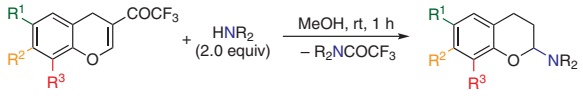
We have shown that the reaction of 2-trifluoroacetyl-1*H*-benzo[*f*]chromenes **1a–d** with 2.0 equivalents of cyclic secondary amines **2–7** in a methanol solution at room temperature leads to 3-amino-substituted 2,3-dihydro-1*H*-benzo[*f*]chromenes **8–13** (Table 1). We initially studied the effect of the nature of the solvent on the yield of the product **8a** in the reaction of chromene **1a** (G = H) with morpholine. We have found that the yield of chromane **8a** was 58% in acetonitrile, 65% in THF, 67% in ethyl acetate, 75% in benzene, and 79% in methanol. Thus, we have chosen methanol as a solvent for further studying the scope and generality of the reaction. The synthesis of chromane **8a** was repeated on several different scales (up to 20 mmol), all with comparable yields. A variety of cyclic secondary amines, such as pyrrolidine (**3**), piperidines **4a–f**, 4-piperidone (**4g**), piperazines **5**, homopiperidine (**6**), and 6-methoxy-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (**7**) were examined, and the results are summarized in Table 1. The target products precipitate directly from the reaction mixture and, as a rule, do not require additional purification. A full conversion was usually obtained after only 1 hour or less to give 3-aminobenzochromanes **8–13** in high yields. The second isolated

product in the reaction is *N*-trifluoroacetylmorpholine or morpholin-4-ium trifluoroacetate as a result of the hydrolysis of amide. This reaction works extremely well under mild conditions, which allows the use of various functionally substituted amines and chromenes. The reaction of chromene **1a** and tetrahydrocarboline derivative **7** proceeds selectively at the more nucleophilic nitrogen atom of the six-membered ring (product **13**). A characteristic feature of ^{13}C NMR spectra of aminobenzochromanes indicated in Table 1 is the presence of a strongly unshielded signal of the α-carbon atom of the dihydropyran ring in the range of 91.8–94.4 ppm. In the ^{1}H NMR spectra, a semiaminal hydrogen atom is usually detected in the form of a doublet of doublets or a multiplet in the range of 4.54–4.86 ppm.

Acyclic secondary amines were also introduced in the reaction. Unfortunately, we were not able to isolate the corresponding aminochromanes in the reaction of chromene **1a** with such amines as diethylamine, dibenzylamine, diisopropylamine, and methylcyclohexylamine. We observed rapid conversion of starting materials into a complex mixture of unidentified products.[19] Apparently, the presence of a nitrogen atom in the composition of the cycle is a key requirement for the formation of aminochromanes. Besides, less nucleophilic 1*H*-azoles (imidazole, pyrazole) do not react with trifluoroacetylchromenes.

When using 3-trifluoroacetyl-4*H*-chromenes **1e–h** in the reaction with cyclic secondary amines, a number of chroman-2-amines was produced under similar conditions (Table 2).

Table 2 Synthesized Chroman-2-amines[a]

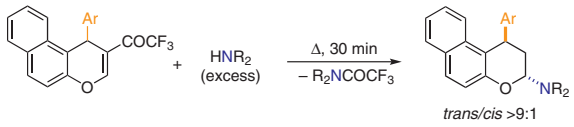


R^1, R^2, R^3	HNR_2		Product[b]
Cl, H, H (**1e**)	HN O	(**2**)	**8e**, 70%
Me, Me, H (**1f**)			**8f**, 73%
Me, H, Ad (**1g**)			**8g**, 82%
Br, H, Br (**1h**)	HN NY	Y = cinnamyl (**5c**)	**11u**, 87%
Me, Me, H (**1f**)		Y = 4-FC_6H_4 (**5u**)	**11v**, 77%

[a] Reaction conditions: **1e–h** (1 mmol) and amine (2 mmol) in MeOH (3 mL) at rt for 1 h.
[b] Isolated yields.

This reaction was also extended to 1,3-disubstituted 2-trifluoroacetyl-1*H*-benzo[*f*]chromenes. The corresponding aminochromanes **8h–j** and **10h** were obtained in good yields when carrying out the reaction in an excess of secondary amine without any additional solvent under reflux (Table 3). In spite of the presence of two asymmetric centers, only *trans*-isomers of **8h–j** and **10h** were isolated from the reaction mixture in crystalline form. This is, probably, due to ability of these cyclic N,O-acetals to epimerize at C-3 via phenoxyimmonium zwitterion[12] and, even if *cis*-isomers were initially formed, only the less soluble *trans*-1,3-disubstituted products were obtained.

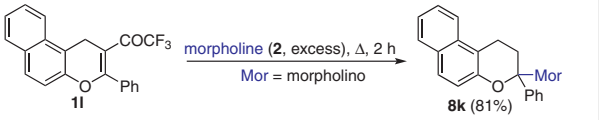
Table 3 Synthesized 1-(Het)arylbenzo[*f*]chroman-3-amines[a]



Ar	HNR_2		Product[b,c]
Ph (**1i**)	HN O	(**2**)	**8h**, 84%
3-$O_2NC_6H_4$ (**1j**)			**8i**, 59%
2-thienyl (**1k**)			**8j**, 81%
Ph (**1i**)	HN	(**4a**)	**10h**, 85%

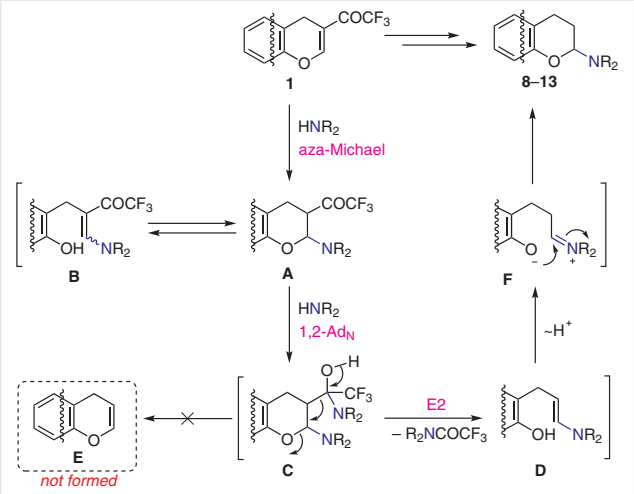
[a] Reaction conditions: **1i–k** (1 mmol), and amine (3 mL) under reflux for 30 min.
[b] Diastereomeric ratio were determined by ^{1}H NMR analysis of the unpurified material.
[c] Isolated yields.

The reaction between 3-phenyl-substituted 2-trifluoroacetyl-1*H*-benzo[*f*]chromene **1l** and an excess of morpholine under reflux leads to the expected N,O-acetal **8k** (Scheme 1).



Scheme 1 Reaction of chromene **1l** and morpholine

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2. We suppose that the mechanism includes the conjugate addition of a secondary amine to trifluoroacetylchromene **1** to form chroman **A**, which may be in equilibrium with enaminoketone **B**. Next, a second molecule of amine is attached at the carbonyl carbon atom to give intermediate **C**, which undergoes decomposition into enamine **D** and N,N-disubstituted trifluoroacetamide. Since the O-atom in chromane **C** is a better (phenolic) leaving group than the N-atom, the formation of chromene **E** is not observed. The mechanism of cyclization of enamine **D** into aminochromane, probably, includes its isomerization into phenoxyimmonium zwitterion **F**, which collapses via 6-*exo*-*trig* cyclization to give semicyclic N,O-acetals **8–13**. The initiator protons are generated in the medium of methanol by the dissociation of the phenol. It should be noted that very few examples of inter- and intramolecular addition of phenols to enamines are described in the literature.[20]



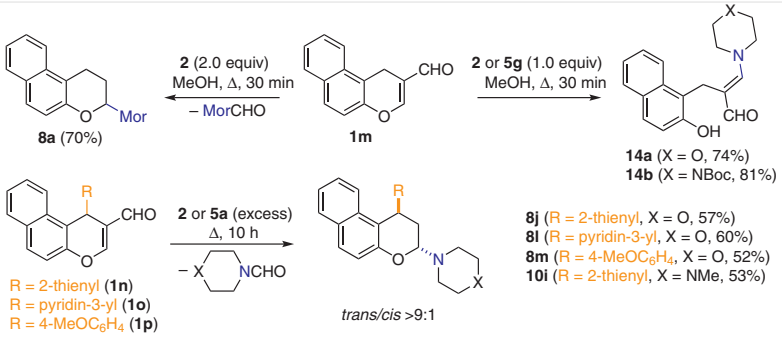
Scheme 2 Proposed mechanism

Attempts to extend the reaction of trifluoroacetylchromenes **1** with cyclic secondary amines to 3-aroyl-4*H*-chromenes, however, failed to furnish the expected N,O-acetals. Nevertheless, it turned out that the presence of formyl group in the β-position to the O-atom of the pyran ring is sufficient for the reaction to proceed. For example, chromane **8a** was obtained in 70% yield from 1*H*-benzo[*f*]chromene-2-carbaldehyde **1m** and morpholine (2.0 equiv) (Scheme 3) but the reaction was completed in 2 days at room temperature, although usually no more than 1 hour was required in the case of trifluoroacetyl derivatives. This fact can be explained by a lower electrophilicity of aldehydes. It is interesting to note that when using only 1.0 equivalent of a cyclic secondary amine in the reaction with aldehyde **1m**, enaminals **14a**,**b** were isolated as individual *E*-isomers. The preparation of enaminals supports the mechanism presented in Scheme 1. It should be noted that attempts to prepare enaminoketones **B** (Scheme 2) from 3-trifluoroacetylchromenes and 1.0 equivalent of a secondary amine did not succeed, only half of starting chromene got converted into aminochroman, while the other half remained unchanged.

1-Aryl- and 1-hetaryl-substituted 1*H*-benzo[*f*]chromene-2-carbaldehydes also react with cyclic secondary amines but under more severe conditions. For example, the yield of **8j** after boiling for 25 hours in methanol even with excess of morpholine (5.0 equiv) was 41%, and the yield of **8l** after 40 hours was 48%. Higher yields of 1,3-disubstituted 3-aminobenzochromanes were achieved by prolonged heating of aldehydes **1n–p** in an excess of secondary amine without any additional solvent under reflux.

The relative *trans* configurations of the C-1 and C-3 substituents of compounds **8h–j**,**l**,**m** and **10h**,**i** were assigned on the basis of ^{1}H NMR spectra. They were deduced from the chemical shift values and coupling constants of the protons attached to C-1 and C-3 of the dihydropyran ring that exists in a half-chair conformation. The protons attached to C-1 give rise to a doublet of doublets with two small coupling constants ^3J = 1.8 and 5.3–5.4 Hz at δ = 4.73–5.03. Thus, H-1 is *pseudo-equatorial* and the aryl moiety occupies the *pseudo-axial* position. The proton H-3 resonates at δ = 4.51–4.80 as a doublet of doublets with two coupling constants ^3J = 1.8 and 11.0–11.4 Hz. Thus, H-3 is in the *pseudo-axial* position and the amine moiety occupies the *pseudo-equatorial* position.[21] In the NOESY spectra of **10i** and **8m**, there are cross peaks corresponding to the interaction between the H-1 proton and the H_{ax}-2 and H_{eq}-2 protons (see the Supporting Information). The proton H-3 has a cross peak only with H_{eq}-2. As shown in Figure 2, in the *cis*-isomers H-1 and H-3 protons must be spatially close in the **I** conformer (showing an appreciable NOE), whereas in the *trans*-isomers a weak or non-existent NOE effect is to be expected.

The reaction between of homopiperazine and 2-formyl-1*H*-benzo[*f*]chromenes **1p–r** proceeds in an unusual way and leads to benzo[*f*]chroman-3-ol derivatives **15a–c** containing 1,5-diazabicyclo[3.2.1]octane core (Scheme 4). This cascade reaction is a rare example of synthesis of 1,5-diazabicyclo[3.2.1]octane core via double aza-Michael addition[22] and includes the following main steps: aza-Michael addition of homopiperazine to chromenes, opening of the dihydropyran ring in the intermediate **K** with formation of the enaminone **L**, repeated aza-Michael addition and he-



Scheme 3 Reactions of 1*H*-benzo[*f*]chromene-2-carbaldehyde with cyclic secondary amines

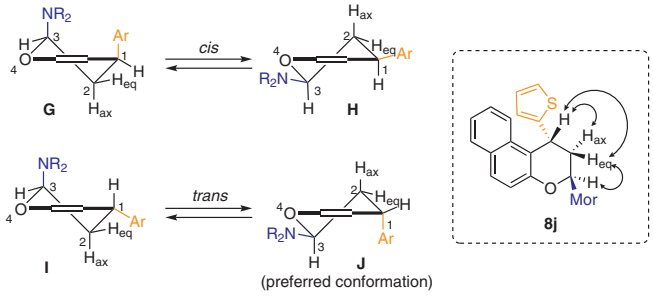
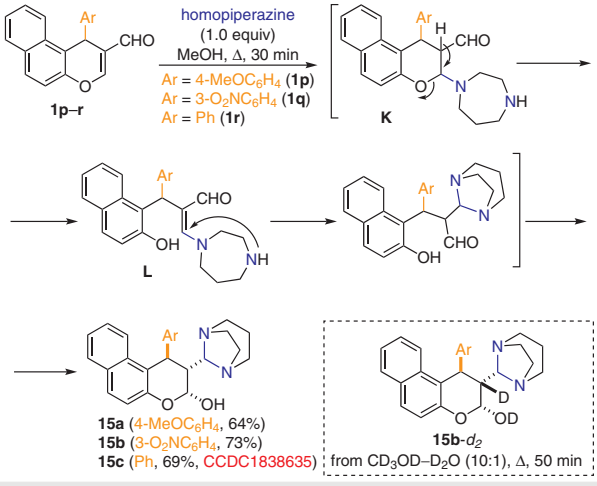


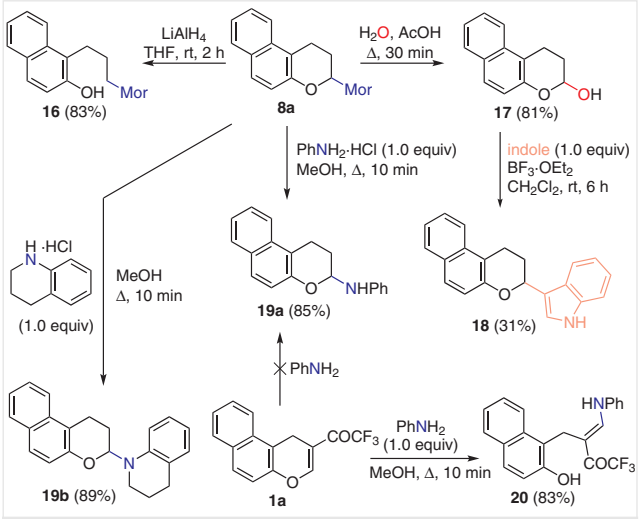
Figure 2 Possible conformations of *cis*- and *trans*-isomers of **8h–j**,**l**,**m** and **10h**,**i** and selected NOESY ^{1}H–^{1}H correlations of compound **8j**

miketalization. In the additional experiment for the reaction of chromene **1q** and homopiperazine in deuterated methanol as a reaction media in the presence of deuterium oxide (10:1 CD_3OD/D_2O), a product **15b**-d_2 containing deuterium atom at the β-position of the pyran ring and OD-group instead of hydroxyl was obtained. This fact confirms the formation of the intermediate **L**, which is further deuterated by a solvent as a result of the aza-Michael reaction. At the same time, the experimental data do not completely exclude another mechanism in which homopiperazine condenses on the exocyclic formyl carbon to form the aminal without ring-opening, while subsequent enol hydration leads to the products **15**.



Scheme 4 Synthesis of benzochromanols **15** and plausible mechanism

The synthetic applicability of aminochromanes as valuable precursors for further transformations was studied. The chromane-type N,O-acetals can be transformed in a number of different ways (Scheme 5). For instance, treatment of compound **8a** with $LiAlH_4$ in THF resulted in C–O bond cleavage and the formation of 1-(3-morpholinopropyl)naphthalen-2-ol **16** in 83% yield. In aqueous acetic acid, the morpholinyl product **8a** was hydrolyzed to a benzochromanol **17**. The proposed sequence of transformations starting from trifluoroacetylchromenes can become the basis of a new method of synthesis of 2-chromanols widely used in organic synthesis.[23] The usefulness of this approach was demonstrated on the example of the synthesis of hybrid heterocycle **18** containing benzochromane and indole fragments.[24] The reaction of compound **8a** with aniline and 1,2,3,4-tetrahydroquinoline hydrochlorides proceeds with the substitution of morpholine moiety and formation of aminochromanes **19a**,**b**. It should be noted that the attempt to the direct synthesis of **19a** from trifluoroacetylchromene **1a** and aniline leads to ring-opening product **20**.

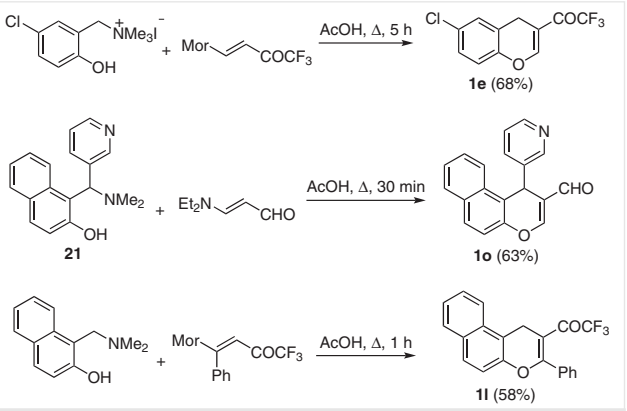


Scheme 5 Synthetic transformations of 4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine **8a**

In conclusion, we have offered an alternative approach to 2-substituted chromanes, a class of privileged structures with a broad range of interesting biological activities. The developed transformation proceeds through subsequent Michael and 1,2-nucleophilic additions of amine to 4*H*-chromene, bimolecular elimination of trifluoroacetamide or formamide and very rare intramolecular addition of phenol to enamine as the key step of this cascade reaction. The advantages of our method include 1) the use of readily prepared starting materials, 2) simple operation and workup

procedures, 3) generally good yields, and 4) scalability and good functional group tolerance due to in general mild reaction conditions.

Melting points were determined by capillary method on a SRS OptiMelt MPA100 apparatus and are uncorrected. FTIR-spectra were taken on a Shimadzu IR Affinity-1 spectrophotometer with single-reflection ATR accessory and are reported in cm^{-1}. ^1H, ^{19}F, and ^{13}C NMR spectra (including DEPT-135, HMBC, HMQC, and NOESY experiments) were recorded on a JEOL JNM-ECX 400 spectrometer (400, 376, and 100 MHz, respectively) in DMSO-d_6 or $CDCl_3$ solutions at ambient temperature, unless otherwise noted, relative to residual solvent signal [$CHCl_3$ δ = 7.26 (^1H), $CDCl_3$ δ = 77.0 (^{13}C); DMSO-d_6 δ = 2.50 (^1H), δ = 39.5 (^{13}C)] of $CFCl_3$ (^{19}F) as internal standard. Chemical shifts and coupling constants were recorded in units of parts per million and hertz (Hz), respectively. Mass spectra were recorded on a Finnigan Trace DSQ chromato mass spectrometer (EI, 70 eV, mass-selective detector). Elemental analyses were carried out on a Euro Vector EA-3000 automatic CHNS analyzer. High-resolution mass spectra (HRMS) were recorded on an Agilent 6230 TOF using an electrospray (ESI) ionization source. The reaction progress was monitored by TLC on aluminum foil-backed silica gel plates (Merck, Kiesgel 60 F254), visualization under UV light and in I_2 vapor, eluent CH_2Cl_2. Organic solutions were concentrated under reduced pressure on a rotary evaporator. All commercial solvents and reagents were used without additional purification. The reported trifluoroacetylchromenes and 1*H*-benzo[*f*]chromene-2-carbaldehydes were prepared according to literature procedures or Scheme 6.[17,25]



Scheme 6 Synthesis of unknown 4*H*-chromenes

1-(6-Chloro-4*H*-chromen-3-yl)-2,2,2-trifluoroethan-1-one (1e)

A solution of 1-(5-chloro-2-hydroxyphenyl)-*N*,*N*,*N*-trimethylmethanaminium iodide (4.00 g, 12.2 mmol) and (*E*)-1,1,1-trifluoro-4-morpholinobut-3-en-2-one (2.55 g, 12.2 mmol) in AcOH (15 mL) was heated under reflux for 5 h. The reaction mixture was cooled to rt, and the formed precipitate was collected. The crude product was purified by recrystallization from MeOH; yield: 2.18 g (68%); colorless solid; mp 94–95 °C.

IR (ATR): 1684, 1630, 1614, 1574, 1508, 1481, 1425, 1412, 1360, 1315, 1259, 1238, 1184, 1175, 1149, 1109, 1084, 933, 912, 903, 870, 856, 829, 754 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 3.57 (s, 2 H), 6.96 (d, *J* = 8.2 Hz, 1 H), 7.14–7.18 (m, 2 H), 7.80 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.6 (CH_2), 109.9 (CH), 116.4 (q, $^1J_{C,F}$ = 291.4 Hz, CF_3), 118.3 (C), 120.9 (CH), 128.5 (C), 129.4 (CH), 130.8 (C), 147.5 (C), 156.4 (q, $^3J_{C,F}$ = 4.8 Hz, CH), 178.9 (q, $^2J_{C,F}$ = 36.4 Hz, C).

^{19}F NMR ($CDCl_3$, 376 MHz): δ = –70.4 (3 F, CF_3).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_7{}^{35}ClF_3O_2$: 263.0087; found: 263.0075.

1-[(Dimethylamino)(pyridin-3-yl)methyl]naphthalen-2-ol (21)

Dimethylamine (11 mL of a 33% aq solution, 0.073 mol) and nicotinaldehyde (7.73 g, 0.069 mol) were added to a solution of naphthalen-2-ol (10 g, 0.069 mol) in MeOH (35 mL) at rt. The solvent was distilled off, the residue was dissolved in MeOH by heating, and the solution was kept for 2 days at rt and then 1 day at –30 °C. The precipitate was collected by filtration, washed with ice-cold MeOH, and purified by recrystallization from cyclohexane; yield: 11.8 g (61%); colorless solid; mp 117–118 °C.

IR (ATR): 3200–2400, 1622, 1599, 1578, 1522, 1474, 1460, 1427, 1329, 1269, 1242, 1179, 1142, 1032, 997, 953, 943, 833, 816, 806, 745, 714 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ = 2.26 (s, 6 H), 5.27 (s, 2 H), 7.08 (d, *J* = 8.9 Hz, 1 H), 7.19–7.23 (m, 1 H), 7.27 (dd, *J* = 7.8, 4.8 Hz, 1 H), 7.36–7.40 (m, 1 H), 7.68–7.73 (m, 2 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 8.7 Hz, 1 H), 8.39 (d, *J* = 4.8 Hz, 1 H), 8.84 (s, 1 H), 13.43 (br s, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 44.0 (2 × CH_3), 68.7 (CH), 116.5 (C), 120.1 (CH), 121.7 (CH), 123.1 (CH), 124.5 (CH), 127.2 (CH), 128.6 (C), 129.2 (CH), 130.1 (CH), 132.1 (C), 136.0 (CH), 137.0 (C), 149.7 (CH), 150.1 (CH), 155.5 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}N_2O$: 279.1497; found: 279.1490.

1-(Pyridin-3-yl)-1*H*-benzo[*f*]chromene-2-carbaldehyde (1o)

A solution of **21** (417 mg, 1.5 mmol) and 3-(diethylamino)acrolein (190 mg, 1.5 mmol) in AcOH (5 mL) was heated under reflux for 30 min. The solvent was distilled off and the residue was purified by recrystallization from EtOH; yield: 271 mg (63%); colorless solid; mp 202–203 °C.

IR (ATR): 2854, 2754, 1665, 1647, 1616, 1589, 1576, 1510, 1477, 1462, 1422, 1383, 1300, 1260, 1229, 1213, 1198, 1061, 1026, 989, 957, 895, 837, 808, 779, 750, 714, 704, 681 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.67 (s, 1 H), 7.11 (dd, *J* = 7.8, 4.8 Hz, 1 H), 7.35 (d, *J* = 9.0 Hz, 1 H), 7.37–7.46 (m, 2 H), 7.55 (s, 1 H), 7.60 (dt, *J* = 7.8, 1.8 Hz, 1 H), 7.77–7.82 (m, 3 H), 8.34 (dd, *J* = 4.8, 1.6 Hz, 1 H), 8.59 (d, *J* = 2.1 Hz, 1 H), 9.43 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 32.8 (CH), 115.0 (C), 117.2 (CH), 122.1 (C), 123.4 (CH), 123.5 (CH), 125.5 (CH), 127.6 (CH), 128.8 (CH), 130.0 (CH), 131.0 (C), 132.0 (C), 135.9 (CH), 139.4 (C), 148.1 (CH), 148.3 (C), 150.0 (CH), 157.9 (CH), 189.0 (CH).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}NO_2$: 288.1025; found: 288.1015.

2,2,2-Trifluoro-1-(3-phenyl-1*H*-benzo[*f*]chromen-2-yl)ethan-1-one (1l)

A mixture of 1,1,1-trifluoro-4-morpholino-4-phenylbut-3-en-2-one (2.00 g, 7 mmol) and 1-[(dimethylamino)methyl]naphthalen-2-ol (1.41 g, 7 mmol) in AcOH (30 mL) was heated under reflux for 1 h. The solvent was distilled off, the residue was purified by column chromatography (silica gel, CCl_4), and recrystallized from EtOH; yield: 1.44 g (58%); colorless solid; mp 105–106 °C.

IR (ATR): 1703, 1583, 1568, 1526, 1468, 1402, 1234, 1196, 1177, 1148, 1121, 1074, 1011, 930, 879, 862, 773, 762, 741, 710, 694, 625 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ = 4.09 (s, 2 H), 7.33 (d, *J* = 8.7 Hz, 1 H), 7.47–7.59 (m, 6 H), 7.61–7.66 (m, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 7.88 (d, *J* = 9.1 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.1 (CH_2), 105.3 (C), 111.9 (C), 116.8 (q, $^1J_{C,F}$ = 290.8 Hz, C), 117.0 (CH), 122.7 (CH), 125.4 (CH), 127.4 (CH), 128.6 (CH), 128.7 (2 × CH), 129.0 (CH), 129.1 (2 × CH), 131.1 (CH), 131.2 (C), 131.3 (C), 134.0 (C), 147.3 (C), 163.3 (C) 183.7 (q, $^2J_{C,F}$ = 35.3 Hz, C=O).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{14}F_3O_2$: 355.0946; found: 355.0952.

4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine (8a)

To a suspension of 1-(1*H*-benzo[*f*]chromen-2-yl)-2,2,2-trifluoroethan-1-one (**1a**; 278 mg, 1 mmol) in a solvent (MeCN, THF, EtOAc, benzene, or MeOH; 4 mL) was added morpholine (0.172 mL, 174 mg, 2 mmol) at rt. The resulting mixture was kept at rt for 1 h and then evaporated to dryness in vacuo. The residue was recrystallized from MeOH (3 mL); yield: 156 mg (58%) in MeCN; 175 mg (65%) in THF; 180 mg (67%) in EtOAc; 202 mg (75%) in benzene; 213 mg (79%) in MeOH; colorless solid; mp 151–152 °C (MeOH).

IR (ATR): 2957, 2911, 2889, 2849, 1618, 1595, 1512, 1468, 1435, 1406, 1391, 1377, 1296, 1265, 1240, 1207, 1186, 1159, 1115, 1066, 1037, 1022, 970, 920, 887, 841, 814, 802, 772, 754 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.14–2.25 (m, 2 H), 2.80–2.84 (m, 2 H), 3.05–3.13 (m, 3 H), 3.19–3.25 (m, 1 H), 3.73–3.82 (m, 4 H), 4.65 (dd, *J* = 8.9, 3.2 Hz, 1 H), 7.06 (d, *J* = 8.9 Hz, 1 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 7.62 (d, *J* = 8.9 Hz, 1 H), 7.74–7.79 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.6 (CH_2), 25.0 (CH_2), 47.9 (2 × CH_2), 67.3 (2 × CH_2), 92.0 (CH), 113.4 (C), 119.2 (CH), 122.0 (CH), 123.3 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 132.9 (C), 152.7 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{20}NO_2$: 270.1494; found: 270.1499.

N-Trifluoroacetylmorpholine described in the literature was also isolated from the mother liquor by column chromatography as a colorless liquid.

^1H NMR ($CDCl_3$, 400 MHz): δ = 3.65–3.76 (m, 8 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 43.6 (CH_2), 46.4 (CH_2), 66.6 (2 × CH_2), 116.7 (q, $^1J_{C,F}$ = 297.7 Hz, C), 155.8 (q, $^2J_{C,F}$ = 35.3 Hz, C).

2,3-Dihydro-1*H*-benzo[*f*]chromen-3-amines and Chroman-2-amines; General Procedure

To a suspension of 3-trifluoroacetyl-4*H*-chromene or 2-trifluoroacetyl-1*H*-benzo[*f*]chromene (1 mmol) in MeOH (4 mL) was added cyclic secondary amine (2 mmol) at rt. The resulting mixture was heated under reflux for 1–2 min until the trifluoroacetylchromene was completely dissolved (in case of poor solubility) and then kept at rt for 1 h and at –30 °C for 30 min. The precipitate formed was collected by filtration, washed with ice-cold MeOH (1 mL), and purified by recrystallization, if necessary.

4-(8-Bromo-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine (8b)

Yield: 289 mg (83%); colorless solid; mp 207–208 °C (DMF–MeOH).

IR (ATR): 2855, 1614, 1585, 1495, 1462, 1445, 1389, 1310, 1292, 1263, 1236, 1194, 1179, 1159, 1115, 1067, 1038, 1022, 966, 918, 883, 839, 827, 808, 777 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.14–2.25 (m, 2 H), 2.78–2.83 (m, 2 H), 3.01–3.10 (m, 3 H), 3.14–3.19 (m, 1 H), 3.72–3.81 (m, 4 H), 4.65 (dd, *J* = 8.7, 3.4 Hz, 1 H), 7.05 (d, *J* = 8.9 Hz, 1 H), 7.50–7.53 (m, 2 H), 7.62 (d, *J* = 8.9 Hz, 1 H), 7.88 (d, *J* = 2.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.6 (CH_2), 24.9 (CH_2), 47.8 (2 × CH_2), 67.3 (2 × CH_2), 92.1 (CH), 113.6 (C), 116.9 (C), 120.4 (CH), 123.8 (CH), 127.0 (CH), 129.6 (CH), 130.1 (C), 130.4 (CH), 131.5 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}{}^{79}BrNO_2$: 348.0599; found: 348.0603.

4-[8-(*tert*-Butyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]morpholine (8c)

Yield: 283 mg (87%); colorless solid; mp 177–178 °C (EtOH).

IR (ATR): 2961, 1597, 1474, 1462, 1450, 1416, 1393, 1373, 1360, 1263, 1234, 1196, 1169, 1113, 1069, 1020, 966, 920, 887, 843, 820, 808 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.40 (s, 9 H), 2.12–2.26 (m, 2 H), 2.78–2.84 (m, 2 H), 3.02–3.11 (m, 3 H), 3.18–3.24 (m, 1 H), 3.71–3.81 (m, 4 H), 4.64 (dd, *J* = 8.8, 3.1 Hz, 1 H), 7.02 (d, *J* = 9.0 Hz, 1 H), 7.55–7.60 (m, 2 H), 7.68 (d, *J* = 1.4 Hz, 1 H), 7.72 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.6 (CH_2), 25.1 (CH_2), 31.4 (3 × CH_3), 34.6 (C), 47.9 (2 × CH_2), 67.4 (2 × CH_2), 91.9 (CH), 113.1 (C), 119.0 (CH), 121.8 (CH), 123.6 (CH), 125.2 (CH), 127.9 (CH), 128.8 (C), 130.9 (C), 145.8 (C), 152.2 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{28}NO_2$: 326.2120; found: 326.2115.

4-[8-(Adamantan-1-yl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]morpholine (8d)

The synthesis was carried out in MeOH (15 mL); yield: 376 mg (93%); colorless solid; mp 229–230 °C (DMF–MeOH).

IR (ATR): 2847, 1682, 1626, 1597, 1504, 1477, 1450, 1391, 1298, 1269, 1240, 1192, 1169, 1117, 1069, 1024, 972, 918, 887, 847, 822, 800 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.76–1.85 (m, 6 H), 1.99–2.01 (m, 6 H), 2.12–2.24 (m, 5 H), 2.78–2.84 (m, 2 H), 3.03–3.11 (m, 3 H), 3.17–3.24 (m, 1 H), 3.72–3.81 (m, 4 H), 4.63 (dd, *J* = 9.0, 3.2 Hz, 1 H), 7.01 (d, *J* = 8.9 Hz, 1 H), 7.55–7.60 (m, 2 H), 7.63 (d, *J* = 1.8 Hz, 1 H), 7.73 (d, *J* = 8.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.5 (CH_2), 25.1 (CH_2), 29.1 (3 × CH), 36.1 (C), 37.0 (3 × CH_2), 43.3 (3 × CH_2), 47.9 (2 × CH_2), 67.3 (2 × CH_2), 91.9 (CH), 113.1 (C), 118.9 (CH), 121.7 (CH), 123.6 (CH), 124.5 (CH), 128.0 (CH), 129.0 (C), 131.1 (C), 146.1 (C), 152.2 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{34}NO_2$: 404.2590; found: 404.2598.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)pyrrolidine (9a)

Yield: 225 mg (89%); colorless solid; mp 86–87 °C (MeOH).

IR (ATR): 1620, 1595, 1514, 1468, 1435, 1404, 1389, 1260, 1231, 1215, 1177, 1155, 1146, 1126, 1059, 1033, 1024, 961, 843, 818, 770, 743 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.82–1.90 (m, 4 H), 2.10–2.20 (m, 1 H), 2.25–2.31 (m, 1 H), 2.93–2.99 (m, 2 H), 3.04–3.12 (m, 3 H), 3.20 (ddd, *J* = 16.5, 6.1, 2.6 Hz, 1 H), 4.89 (dd, *J* = 10.1, 1.8 Hz, 1 H), 7.04 (d, *J* = 8.7 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1 H), 7.47 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.6 (CH_2), 24.5 (2 × CH_2), 27.4 (CH_2), 47.2 (2 × CH_2), 89.0 (CH), 113.5 (C), 119.4 (CH), 122.0 (CH), 123.1 (CH), 126.3 (CH), 127.8 (CH), 128.4 (CH), 128.8 (C), 133.0 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{20}NO$: 254.1545; found: 254.1549.

1-(8-Bromo-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)pyrrolidine (9b)

Yield: 302 mg (91%); colorless solid; mp 149–150 °C (DMF–MeOH).

IR (ATR): 2965, 2821, 1611, 1585, 1495, 1462, 1445, 1435, 1412, 1387, 1356, 1342, 1310, 1258, 1206, 1190, 1173, 1159, 1128, 1063, 1034, 968, 961, 883, 808 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.82–1.90 (m, 4 H), 2.08–2.18 (m, 1 H), 2.23–2.29 (m, 1 H), 2.92–2.98 (m, 2 H), 3.00–3.16 (m, 4 H), 4.88 (dd, *J* = 10.1, 1.8 Hz, 1 H), 7.04 (d, *J* = 8.9 Hz, 1 H), 7.48–7.52 (m, 2 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.87 (d, *J* = 1.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.5 (CH_2), 24.5 (2 × CH_2), 27.2 (CH_2), 47.1 (2 × CH_2), 89.1 (CH), 113.7 (C), 116.7 (C), 120.5 (CH), 123.9 (CH), 126.9 (CH), 129.4 (CH), 130.0 (C), 130.3 (CH), 131.6 (C), 153.4 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}{}^{79}BrNO$: 332.0650; found: 332.0646.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperidine (10a)

Yield: 211 mg (79%); colorless solid; mp 113–114 °C (MeOH).

IR (ATR): 2936, 2824, 1622, 1599, 1514, 1466, 1410, 1381, 1350, 1306, 1231, 1206, 1196, 1177, 1113, 1076, 1057, 1036, 1013, 970, 959, 910, 851, 804, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.52–1.72 (m, 6 H), 2.14–2.29 (m, 2 H), 2.74–2.80 (m, 2 H), 3.02–3.12 (m, 3 H), 3.21 (ddd, *J* = 16.5, 5.5, 2.0 Hz, 1 H), 4.69 (dd, *J* = 10.1, 1.8 Hz, 1 H), 7.05 (d, *J* = 8.9 Hz, 1 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 1 H), 7.61 (d, *J* = 8.7 Hz, 1 H), 7.73–7.79 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.1 (CH_2), 24.8 (CH_2), 25.5 (CH_2), 26.4 (2 × CH_2), 48.6 (2 × CH_2), 93.1 (CH), 113.5 (C), 119.3 (CH), 122.0 (CH), 123.1 (CH), 126.4 (CH), 127.8 (CH), 128.5 (CH), 128.8 (C), 133.0 (C), 153.2 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}NO$: 268.1701; found: 268.1698.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-methylpiperidine (10b)

Yield: 236 mg (84%); colorless solid; mp 99–100 °C (MeOH).

IR (ATR): 2947, 2922, 2868, 2830, 1624, 1597, 1514, 1466, 1447, 1408, 1394, 1379, 1231, 1206, 1190, 1167, 1128, 1117, 1070, 1032, 1020, 982, 968, 953, 849, 802, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.97 (d, *J* = 6.4 Hz, 3 H), 1.17–1.34 (m, 2 H), 1.42–1.54 (m, 1 H), 1.69–1.73 (m, 2 H), 2.13–2.29 (m, 2 H), 2.58 (td, *J* = 11.9, 2.5 Hz, 1 H), 2.94–2.98 (m, 2 H), 3.04–3.25 (m, 3 H), 4.71 (dd, *J* = 10.1, 2.1 Hz, 1 H), 7.04 (d, *J* = 8.9 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.46 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.2 (CH_3), 23.1 (CH_2), 25.6 (CH_2), 31.2 (CH), 34.6 (CH_2), 34.9 (CH_2), 44.9 (CH_2), 51.0 (CH_2), 92.8 (CH), 113.5 (C), 119.3 (CH), 122.0 (CH), 123.1 (CH), 126.4 (CH), 127.8 (CH), 128.5 (CH), 128.8 (C), 133.0 (C), 153.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{24}NO$: 282.1858; found: 282.1855.

4-Benzyl-1-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperidine (10c)

Yield: 286 mg (80%); colorless solid; mp 135–137 °C (MeOH).

IR (ATR): 1624, 1595, 1514, 1495, 1466, 1447, 1410, 1387, 1261, 1232, 1209, 1174, 1153, 1138, 1070, 1039, 1028, 1022, 970, 943, 845, 808, 791, 762, 746, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.25–1.41 (m, 2 H), 1.60–1.78 (m, 3 H), 2.13–2.28 (m, 2 H), 2.53–2.62 (m, 3 H), 2.90–3.00 (m, 2 H), 3.03–3.25 (m, 3 H), 4.71 (dd, *J* = 10.1, 2.0 Hz, 1 H), 7.02 (d, *J* = 9.0 Hz, 1 H), 7.16–7.22 (m, 3 H), 7.27–7.34 (m, 3 H), 7.46 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1 H), 7.60 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.76 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.0 (CH_2), 25.5 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 38.2 (CH_3), 43.4 (CH_2), 44.9 (CH_2), 50.9 (CH_2), 92.7 (CH), 113.4 (C), 119.3 (CH), 122.0 (CH), 123.1 (CH), 125.9 (CH), 126.4 (CH), 127.8 (CH), 128.3 (2 × CH), 128.5 (CH), 128.8 (C), 129.3 (2 × CH), 133.0 (C), 140.8 (C), 153.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{28}NO$: 358.2171; found: 358.2168.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-phenylpiperidine (10d)

Yield: 278 mg (81%); colorless solid; mp 170–172 °C (MeOH).

IR (ATR): 2936, 2824, 1624, 1597, 1514, 1493, 1410, 1379, 1261, 1232, 1205, 1180, 1151, 1140, 1067, 1036, 1009, 968, 959, 849, 808, 756, 741, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.73–1.99 (m, 4 H), 2.18–2.33 (m, 2 H), 2.64 (tt, *J* = 12.1, 3.7 Hz, 1 H), 2.77 (td, *J* = 12.1, 1.8 Hz, 1 H), 3.07–3.18 (m, 3 H), 3.23–3.32 (m, 2 H), 4.78 (dd, *J* = 9.8, 1.6 Hz, 1 H), 7.08 (d, *J* = 8.7 Hz, 1 H), 7.20–7.35 (m, 6 H), 7.46–7.50 (m, 1 H), 7.63 (d, *J* = 8.9 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.1 (CH_2), 25.6 (CH_2), 33.8 (CH_2), 33.9 (CH_2), 43.0 (CH), 45.2 (CH_2), 51.6 (CH_2), 92.7 (CH), 113.5 (C), 119.3 (CH), 122.0 (CH), 123.2 (CH), 126.3 (CH), 126.4 (CH), 127.0 (2 × CH), 127.9 (CH), 128.49 (CH), 128.54 (2 × CH), 128.9 (C), 133.0 (C), 146.5 (C), 153.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{26}NO$: 344.2014; found: 344.2018.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-phenylpiperidin-4-ol (10e)

Yield: 251 mg (70%); colorless solid; mp 176–177 °C (MeOH).

IR (ATR): 3300–3100, 2959, 2934, 2885, 1622, 1595, 1514, 1500, 1491, 1464, 1448, 1435, 1402, 1387, 1306, 1261, 1267, 1205, 1176, 1151, 1126, 1065, 1043, 1012, 978, 966, 943, 862, 814, 760 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.77 (br s, 1 H), 1.84 (d, *J* = 13.1 Hz, 2 H), 2.15–2.34 (m, 4 H), 2.91–2.96 (m, 1 H), 3.06–3.16 (m, 3 H), 3.22–3.28 (m, 1 H), 3.46 (td, *J* = 12.4, 2.5 Hz, 1 H), 4.77 (dd, *J* = 10.1, 2.1 Hz, 1 H), 7.10 (d, *J* = 8.7 Hz, 1 H), 7.27–7.41 (m, 4 H), 7.48 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1 H), 7.54–7.58 (m, 2 H), 7.63 (d, *J* = 9.0 Hz, 1 H), 7.76 (d, *J* = 7.8 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.9 (CH_2), 25.4 (CH_2), 38.8 (CH_2), 38.9 (CH_2), 41.3 (CH_2), 46.5 (CH_2), 71.8 (C), 92.5 (CH), 113.4 (C), 119.4 (CH), 122.0 (CH), 123.2 (CH), 124.7 (2 × CH), 126.4 (CH), 127.1 (CH), 127.9 (CH), 128.5 (3 × CH), 128.9 (C), 133.0 (C), 148.5 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{26}NO_2$: 360.1964; found: 360.1966.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperidin-4-ol (10f)

Yield: 198 mg (70%); colorless solid; mp 180–181 °C (MeOH).

IR (ATR): 3450–3300, 2943, 2830, 1624, 1599, 1514, 1466, 1406, 1368, 1231, 1219, 1206, 1180, 1136, 1096, 1063, 1036, 1020, 988, 968, 932, 849, 804, 724 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.55–1.68 (m, 2 H), 1.79 (br s, 1 H), 1.94–2.02 (m, 2 H), 2.14–2.26 (m, 2 H), 2.63–2.70 (m, 1 H), 2.98–3.01 (m, 2 H), 3.04–3.13 (m, 1 H), 3.17–3.26 (m, 2 H), 3.75–3.82 (m, 1 H), 4.72 (dd, *J* = 9.6, 2.5 Hz, 1 H), 7.03 (d, *J* = 8.9 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1 H), 7.47 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.60 (d, *J* = 8.9 Hz, 1 H), 7.73–7.78 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.0 (CH_2), 25.7 (CH_2), 34.8 (CH_2), 35.1 (CH_2), 43.4 (CH_2), 47.2 (CH_2), 68.5 (CH), 92.3 (CH), 113.4 (C), 119.2 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 133.0 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}NO_2$: 284.1651; found: 284.1648.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperidin-4-one (10g)

Yield: 200 mg (71%); colorless solid; mp 117–119 °C (MeOH).

IR (ATR): 2828, 1730, 1713, 1624, 1599, 1514, 1468, 1408, 1375, 1348, 1298, 1233, 1209, 1194, 1177, 1159, 1140, 1070, 1038, 1016, 997, 974, 945, 860, 853, 806, 737 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.21–2.27 (m, 2 H), 2.54 (t, *J* = 6.2 Hz, 4 H), 3.08–3.19 (m, 3 H), 3.26 (dt, *J* = 16.5, 4.0 Hz, 1 H), 3.32–3.39 (m, 2 H), 4.86 (dd, *J* = 6.4, 6.0 Hz, 1 H), 7.01 (d, *J* = 9.0 Hz, 1 H), 7.34 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.48 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1 H), 7.62 (d, *J* = 8.7 Hz, 1 H), 7.75 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8 (CH_2), 26.0 (CH_2), 42.0 (2 × CH_2), 47.7 (2 × CH_2), 92.1 (CH), 113.3 (C), 119.1 (CH), 122.0 (CH), 123.4 (CH), 126.5 (CH), 128.0 (CH), 128.5 (CH), 129.0 (C), 132.9 (C), 152.6 (C), 209.3 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{20}NO_2$: 282.1494; found: 282.1495.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-methylpiperazine (11a)

Yield: 206 mg (73%); colorless solid; mp 138–140 °C (MeOH).

IR (ATR): 1620, 1595, 1514, 1470, 1445, 1433, 1410, 1391, 1373, 1360, 1290, 1260, 1236, 1211, 1200, 1182, 1169, 1144, 1134, 1080, 1063, 1032, 1013, 970, 932, 847, 826, 810, 745 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.14–2.21 (m, 2 H), 2.36 (s, 3 H), 2.54 (br s, 4 H), 2.85–2.90 (m, 2 H), 3.02–3.23 (m, 4 H), 4.69 (dd, *J* = 8.9, 3.4 Hz, 1 H), 7.02 (d, *J* = 8.9 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1 H), 7.46 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1 H), 7.59 (d, *J* = 8.9 Hz, 1 H), 7.73–7.77 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.2 (CH_2), 46.2 (CH_3), 47.3 (br, 2 × CH_2), 55.4 (2 × CH_2), 91.8 (CH), 113.3 (C), 119.3 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 132.9 (C), 152.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{23}N_2O$: 283.1810; found: 283.1814.

2-[4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazin-1-yl]ethan-1-ol (11b)

After completion of the reaction, the solvent was distilled off, and the residue was purified by recrystallization from MeOH; yield: 215 mg (69%); colorless solid; mp 148–150 °C (MeOH).

IR (ATR): 3500–2600, 1620, 1595, 1512, 1470, 1408, 1391, 1377, 1335, 1294, 1261, 1234, 1182, 1165, 1130, 1065, 1042, 1016, 974, 945, 858, 831, 800, 768, 750 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.13–2.25 (m, 2 H), 2.60–2.73 (m, 6 H), 2.86–2.91 (m, 2 H), 3.03–3.25 (m, 4 H), 3.50 (br s, 1 H), 3.66–3.69 (m, 2 H), 4.70 (dd, *J* = 9.2, 3.2 Hz, 1 H), 7.04 (d, *J* = 8.9 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1 H), 7.47 (ddd, *J* = 8.0, 6.9, 1.4 Hz, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.73–7.77 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.3 (CH_2), 47.1 (br, 2 × CH_2), 53.2 (2 × CH_2), 57.7 (CH_2), 59.5 (CH_2), 91.8 (CH), 113.3 (C), 119.2 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 132.9 (C), 152.7 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{25}N_2O_2$: 313.1916; found: 313.1919.

1-Cinnamyl-4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine (11c)

Yield: 319 mg (83%); colorless solid; mp 149–150 °C (EtOH).

IR (ATR): 1620, 1595, 1514, 1503, 1495, 1468, 1452, 1433, 1410, 1393, 1375, 1331, 1290, 1263, 1234, 1207, 1167, 1132, 1099, 1070, 1059, 1026, 1005, 968, 918, 847, 812, 768, 745, 691 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.14–2.26 (m, 2 H), 2.63 (br s, 4 H), 2.88–2.93 (m, 2 H), 3.03–3.20 (m, 4 H), 3.23 (d, *J* = 5.7 Hz, 2 H), 4.71 (dd, *J* = 8.7, 3.2 Hz, 1 H), 6.34 (dt, *J* = 15.8, 6.9 Hz, 1 H), 6.56 (d, *J* = 15.8 Hz, 1 H), 7.03 (d, *J* = 8.9 Hz, 1 H), 7.22–7.27 (m, 1 H), 7.30–7.35 (m, 3 H), 7.39–7.42 (m, 2 H), 7.47 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.74–7.78 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.2 (CH_2), 47.2 (br, 2 × CH_2), 53.5 (2 × CH_2), 61.2 (CH_2), 91.8 (CH), 113.3 (C), 119.3 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 126.5 (3 × CH), 127.7 (CH), 127.9 (CH), 128.5 (CH), 128.7 (2 × CH), 128.9 (C), 133.0 (C), 133.4 (CH), 137.0 (C), 152.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{29}N_2O$: 385.2280; found: 385.2278.

1-Benzyl-4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine (11d)

Yield: 265 mg (74%); colorless solid; mp 113–115 °C (MeOH).

IR (ATR): 1620, 1595, 1514, 1493, 1470, 1454, 1433, 1414, 1391, 1379, 1333, 1310, 1294, 1260, 1238, 1209, 1186, 1167, 1130, 1078, 1026, 1007, 841, 822, 808, 748, 704 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.15–2.22 (m, 2 H), 2.57 (br s, 4 H), 2.84–2.90 (m, 2 H), 3.03–3.25 (m, 4 H), 3.59 (s, 2 H), 4.70 (dd, *J* = 8.9, 3.4 Hz, 1 H), 7.04 (d, *J* = 9.0 Hz, 1 H), 7.26–7.40 (m, 6 H), 7.47 (ddd, *J* = 8.0, 6.7, 1.4 Hz, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.74–7.78 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.3 (CH_2), 47.3 (2 × CH_2), 53.4 (2 × CH_2), 63.2 (CH_2), 91.9 (CH), 113.4 (C), 119.3 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.2 (CH), 127.9 (CH), 128.4 (2 × CH), 128.5 (CH), 128.9 (C), 129.4 (2 × CH), 133.0 (C), 138.0 (C), 152.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}N_2O$: 359.2123; found: 359.2120.

1-[Bis(4-fluorophenyl)methyl]-4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine (11e)

Yield: 419 mg (89%); colorless solid; mp 141–143 °C (EtOH).

IR (ATR): 1624, 1601, 1503, 1468, 1445, 1435, 1412, 1391, 1323, 1294, 1279, 1219, 1192, 1153, 1136, 1094, 1036, 1024, 1009, 974, 957, 849, 826, 810, 783, 743 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.12–2.24 (m, 2 H), 2.40–2.56 (m, 4 H), 2.82–2.90 (m, 2 H), 3.03–3.24 (m, 4 H), 4.27 (s, 1 H), 4.69–4.72 (m, 1 H), 6.96–7.02 (m, 4 H), 7.08 (d, *J* = 8.9 Hz, 1 H), 7.31–7.42 (m, 5 H), 7.47 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1 H), 7.63 (d, *J* = 9.0 Hz, 1 H), 7.74–7.78 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8 (CH_2), 25.3 (CH_2), 47.5 (2 × CH_2), 52.0 (2 × CH_2), 74.6 (CH), 91.8 (CH), 113.4 (C), 115.5 (d, $^2J_{o\text{-}C,F}$ = 21.0 Hz, 4 × CH), 119.2 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 129.4 (d, $^3J_{m\text{-}C,F}$ = 6.7 Hz, 4 × CH), 133.0 (C), 138.3 (2 C), 152.8 (C), 161.9 (d, $^1J_{ipso\text{-}CF}$ = 244.1 Hz, 2 C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{29}F_2N_2O$: 471.2248; found: 471.2253.

Ethyl 4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine-1-carboxylate (11f)

Yield: 306 mg (90%); colorless solid; mp 129–130 °C (MeOH).

IR (ATR): 1695, 1622, 1601, 1431, 1412, 1389, 1325, 1310, 1248, 1231, 1217, 1209, 1198, 1179, 1144, 1121, 1094, 1036, 1020, 997, 974, 953, 854, 806, 768, 745 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.28 (t, *J* = 7.1 Hz, 3 H), 2.14–2.27 (m, 2 H), 2.75–2.81 (m, 2 H), 3.02–3.14 (m, 3 H), 3.19–3.26 (m, 1 H), 3.50–3.58 (m, 4 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 4.70 (dd, *J* = 9.2, 2.9 Hz, 1 H), 7.01 (d, *J* = 9.0 Hz, 1 H), 7.33 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1 H), 7.47 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.73–7.78 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.8 (CH_3), 22.7 (CH_2), 25.3 (CH_2), 44.0 (br, 2 × CH_2), 47.4 (2 × CH_2), 61.5 (CH_2), 92.1 (CH), 113.3 (C), 119.1 (CH), 122.0 (CH), 123.3 (CH), 126.5 (CH), 128.0 (CH), 128.5 (CH), 128.9 (C), 132.9 (C), 152.6 (C), 155.6 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{25}N_2O_3$: 341.1865; found: 341.1861.

***tert*-Butyl 4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine-1-carboxylate (11g)**

Yield: 346 mg (94%); colorless solid; mp 122–123 °C (EtOH).

IR (ATR): 1690, 1622, 1595, 1418, 1408, 1366, 1281, 1231, 1163, 1123, 1020, 1001, 972, 953, 862, 854, 808, 768, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.48 (s, 9 H), 2.14–2.27 (m, 2 H), 2.73–2.79 (m, 2 H), 3.00–3.13 (m, 3 H), 3.20–3.26 (m, 1 H), 3.45–3.54 (m, 4 H), 4.70 (dd, *J* = 9.2, 3.0 Hz, 1 H), 7.02 (d, *J* = 8.9 Hz, 1 H), 7.33 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1 H), 7.47 (ddd, *J* = 8.0, 6.9, 1.4 Hz, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.73–7.78 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.3 (CH_2), 28.6 (3 × CH_3), 43.1 (br, CH_2), 44.2 (br, CH_2), 47.5 (2 × CH_2), 79.8 (C), 92.1 (CH), 113.3 (C), 119.2 (CH), 122.0 (CH), 123.3 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 132.9 (C), 152.7 (C), 154.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{29}N_2O_3$: 369.2178; found: 369.2181.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-phenylpiperazine (11h)

Yield: 258 mg (75%); colorless solid; mp 212–213 °C (MeOH).

IR (ATR): 2882, 2833, 1620, 1593, 1503, 1466, 1449, 1408, 1387, 1323, 1313, 1279, 1263, 1230, 1209, 1190, 1146, 1072, 1038, 1020, 959, 922, 845, 812, 748, 685 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.21–2.31 (m, 2 H), 2.96–3.03 (m, 2 H), 3.07–3.17 (m, 1 H), 3.22–3.32 (m, 7 H), 4.77 (dd, *J* = 9.2, 3.0 Hz, 1 H), 6.89 (t, *J* = 7.4 Hz, 1 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.9 Hz, 1 H), 7.27–7.36 (m, 3 H), 7.46–7.51 (m, 1 H), 7.63 (d, *J* = 8.9 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.3 (CH_2), 47.5 (2 × CH_2), 49.7 (2 × CH_2), 91.9 (CH), 113.4 (C), 116.4 (2 × CH), 119.2 (CH), 119.9 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 129.2 (2 × CH), 133.0 (C), 151.6 (C), 152.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{25}N_2O$: 345.1967; found: 345.1970.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(*o*-tolyl)piperazine (11i)

Yield: 287 mg (80%); colorless solid; mp 175–176 °C (MeOH).

IR (ATR): 1620, 1595, 1574, 1512, 1463, 1464, 1445, 1408, 1393, 1375, 1306, 1263, 1227, 1206, 1184, 1159, 1140, 1020, 976, 949, 932, 845, 816, 806, 764, 745, 721 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20–2.33 (m, 2 H), 2.37 (s, 3 H), 2.97–3.30 (m, 10 H), 4.78 (dd, *J* = 8.9, 3.0 Hz, 1 H), 7.00 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 7.10 (d, *J* = 8.9 Hz, 1 H), 7.17–7.21 (m, 2 H), 7.34 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1 H), 7.48 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1 H), 7.63 (d, *J* = 8.9 Hz, 1 H), 7.76 (d, *J* = 7.8 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.0 (CH_3), 22.9 (CH_2), 25.4 (CH_2), 47.9 (br, 2 × CH_2), 52.1 (2 × CH_2), 92.1 (CH), 113.4 (C), 119.1 (CH), 119.3 (CH), 122.0 (CH), 123.22 (CH), 123.24 (CH), 126.4 (CH), 126.7 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 131.2 (CH), 132.8 (C), 133.0 (C), 151.7 (C), 152.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}N_2O$: 359.2123; found: 359.2121.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(*m*-tolyl)piperazine (11j)

Yield: 294 mg (82%); colorless solid; mp 189–191 °C (MeOH).

IR (ATR): 2955, 2837, 1620, 1599, 1582, 1514, 1493, 1466, 1452, 1433, 1410, 1381, 1354, 1342, 1323, 1307, 1273, 1229, 1207, 1188, 1142, 1096, 1074, 1037, 1024, 993, 974, 953, 853, 835, 810, 772, 745, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22–2.28 (m, 2 H), 2.37 (s, 3 H), 2.97–3.03 (m, 2 H), 3.08–3.16 (m, 1 H), 3.23–3.30 (m, 7 H), 4.77 (dd, *J* = 8.9, 3.4 Hz, 1 H), 6.73 (d, *J* = 7.6 Hz, 1 H), 6.79–6.82 (m, 2 H), 7.08 (d, *J* = 8.7 Hz, 1 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 7.36 (ddd, *J* = 8.0, 6.8, *J* = 0.9 Hz, 1 H), 7.50 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1 H), 7.64 (d, *J* = 8.9 Hz, 1 H), 7.77–7.82 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.9 (CH_3), 22.8 (CH_2), 25.3 (CH_2), 47.5 (2 × CH_2), 49.8 (2 × CH_2), 91.9 (CH), 113.4 (C), 113.5 (CH), 117.2 (CH), 119.3 (CH), 120.8 (CH), 122.0 (CH), 123.3 (CH), 126.5 (CH), 128.0 (CH), 128.5 (CH), 129.0 (C), 129.1 (CH), 133.0 (C), 138.9 (C), 151.6 (C), 152.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}N_2O$: 359.2123; found: 359.2125.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(*p*-tolyl)piperazine (11k)

Yield: 337 mg (94%); colorless solid; mp 233–235 °C (EtOH–DMF).

IR (ATR): 2824, 1620, 1595, 1562, 1514, 1466, 1450, 1435, 1414, 1383, 1319, 1269, 1207, 1198, 1188, 1018, 924, 843, 810, 746 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20–2.31 (m, 5 H), 2.94–3.02 (m, 2 H), 3.07–3.28 (m, 8 H), 4.76 (dd, *J* = 9.0, 2.9 Hz, 1 H), 6.89 (d, *J* = 8.2 Hz, 2 H), 7.04 (d, *J* = 8.9 Hz, 1 H), 7.09 (d, *J* = 8.2 Hz, 2 H), 7.31–7.35 (m, 1 H), 7.46–7.50 (m, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5 (CH_3), 22.7 (CH_2), 25.3 (CH_2), 47.5 (2 × CH_2), 50.2 (2 × CH_2), 91.9 (CH), 113.4 (C), 116.7 (2 × CH), 119.2 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 129.4 (C), 129.7 (2 × CH), 133.0 (C), 149.5 (C), 152.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}N_2O$: 359.2123; found: 359.2122.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(2,6-dimethylphenyl)piperazine (11l)

Yield: 264 mg (71%); colorless solid; mp 147–148 °C (MeOH).

IR (ATR): 3061, 2934, 2837, 1620, 1597, 1516, 1466, 1408, 1395, 1375, 1306, 1271, 1261, 1236, 1206, 1173, 1165, 1138, 1067, 1025, 972, 845, 808, 764, 745 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.24–2.27 (m, 2 H), 2.40 (s, 6 H), 2.90–2.96 (m, 2 H), 3.10–3.25 (m, 8 H), 4.76–4.80 (m, 1 H), 6.96–7.04 (m, 3 H), 7.13 (d, *J* = 9.0 Hz, 1 H), 7.33–7.37 (m, 1 H), 7.47–7.51 (m, 1 H), 7.65 (d, *J* = 9.0 Hz, 1 H), 7.77 (d, *J* = 8.2 Hz, 1 H), 7.80 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.9 (2 × CH_3), 22.9 (CH_2), 25.4 (CH_2), 48.9 (2 × CH_2), 50.1 (2 × CH_2), 92.6 (CH), 113.5 (C), 119.3 (CH), 122.0 (CH), 123.2 (CH), 125.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 129.1 (2 × CH), 133.0 (C), 137.1 (2 C), 148.5 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{29}N_2O$: 373.2280; found: 373.2284.

1-(2-Chlorophenyl)-4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine (11m)

Yield: 314 mg (83%); colorless solid; mp 169–170 °C (MeOH).

IR (ATR): 1620, 1589, 1514, 1479, 1466, 1449, 1412, 1396, 1377, 1261, 1229, 1207, 1188, 1153, 1138, 1123, 1069, 1018, 970, 955, 928, 847, 812, 766, 745 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20–2.32 (m, 2 H), 3.00–3.33 (m, 10 H), 4.76 (dd, *J* = 9.2, 3.0 Hz, 1 H), 7.00 (td, *J* = 7.8, 1.4 Hz, 1 H), 7.07 (m, 2 H), 7.22–7.27 (m, 1 H), 7.32–7.37 (m, 1 H), 7.39 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.49 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.64 (d, *J* = 8.9 Hz, 1 H), 7.76–7.80 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8 (CH_2), 25.3 (CH_2), 47.7 (2 × CH_2), 51.6 (2 × CH_2), 92.0 (CH), 113.4 (C), 119.3 (CH), 120.5 (CH), 122.0 (CH), 123.2 (CH), 123.8 (CH), 126.4 (CH), 127.7 (CH), 127.9 (CH), 128.5 (CH), 129.0 (2C), 130.8 (CH), 133.0 (C), 149.5 (C), 152.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}{}^{35}ClN_2O$: 379.1577; found: 379.1580.

1-(4-Chlorophenyl)-4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazine (11n)

Yield: 303 mg (80%); colorless solid; mp 256–257 °C (EtOH–DMF).

IR (ATR): 2833, 1620, 1593, 1466, 1447, 1410, 1385, 1358, 1344, 1312, 1234, 1207, 1146, 1018, 957, 847, 810, 750 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18–2.31 (m, 2 H), 2.94–3.01 (m, 2 H), 3.07–3.28 (m, 8 H), 4.76 (dd, *J* = 9.2, 3.0 Hz, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 7.03 (d, *J* = 8.9 Hz, 1 H), 7.21 (d, *J* = 9.0 Hz, 2 H), 7.31–7.35 (m, 1 H), 7.45–7.50 (m, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.3 (CH_2), 47.3 (2 × CH_2), 49.7 (2 × CH_2), 91.8 (CH), 113.3 (C), 117.5 (2 × CH), 119.2 (CH), 122.0 (CH), 123.3 (CH), 124.7 (C), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 129.1 (2 × CH), 132.9 (C), 150.1 (C), 152.7 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}{}^{35}ClN_2O$: 379.1577; found: 379.1575.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(4-nitrophenyl)piperazine (11o)

Yield: 319 mg (82%); yellow solid; mp 222–223 °C (DMF).

IR (ATR): 1618, 1595, 1504, 1491, 1466, 1449, 1412, 1389, 1323, 1279, 1244, 1227, 1207, 1190, 1165, 1146, 1115, 1092, 1018, 959, 922, 818, 754 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz, 120 °C): δ = 2.11–2.25 (m, 2 H), 2.86–2.95 (m, 3 H), 3.01–3.18 (m, 3 H), 3.48–3.52 (m, 4 H), 4.80 (d, *J* = 9.4 Hz, 1 H), 6.95–7.00 (m, 3 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 8.02 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (DMSO-d_6, 100 MHz, 120 °C): δ = 22.1 (CH_2), 25.3 (CH_2), 47.2 (2 × CH_2), 47.6 (2 CH_2), 92.1 (CH), 113.3 (2 × CH), 114.1 (C), 119.3 (CH), 122.4 (CH), 123.5 (CH), 126.1 (2 × CH), 126.8 (CH), 128.0 (CH), 128.6 (CH), 129.2 (C), 133.2 (C), 138.1 (C), 152.8 (C), 155.4 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}N_3O_3$: 390.1818; found: 390.1819.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(2-methoxyphenyl)piperazine (11p)

Yield: 292 mg (78%); colorless solid; mp 172–173 °C (MeOH).

IR (ATR): 1620, 1595, 1503, 1466, 1445, 1412, 1391, 1379, 1335, 1317, 1306, 1250, 1207, 1190, 1140, 1119, 1070, 1059, 1020, 974, 953, 924, 845, 822, 806, 752, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22–2.32 (m, 2 H), 3.00–3.36 (m, 10 H), 3.90 (s, 3 H), 4.77 (dd, *J* = 8.4, 3.7 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.93–7.08 (m, 4 H), 7.32–7.36 (m, 1 H), 7.48 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1 H), 7.62 (d, *J* = 8.9 Hz, 1 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.79 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.2 (CH_2), 47.7 (2 × CH_2), 51.0 (2 × CH_2), 55.5 (CH_3), 92.0 (CH), 111.3 (CH), 113.3 (C), 118.4 (CH), 119.3 (CH), 121.1 (CH), 122.0 (CH), 123.1 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 133.0 (C), 141.5 (C), 152.4 (C), 152.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}N_2O_2$: 375.2073; found: 375.2070.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-4-(2-ethoxyphenyl)piperazine (11q)

Yield: 318 mg (82%); colorless solid; mp 153–154 °C (MeOH).

IR (ATR): 1620, 1595, 1503, 1488, 1451, 1406, 1385, 1337, 1308, 1236, 1207, 1188, 1155, 1140, 1123, 1040, 1022, 974, 949, 937, 912, 843, 816, 762, 741 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (t, *J* = 6.9 Hz, 3 H), 2.18–2.32 (m, 2 H), 3.02–3.34 (m, 10 H), 4.10 (q, *J* = 6.9 Hz, 2 H), 4.77 (dd, *J* = 8.0, 3.9 Hz, 1 H), 6.86–6.89 (m, 1 H), 6.91–7.02 (m, 3 H), 7.07 (d, *J* = 8.7 Hz, 1 H), 7.34 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1 H), 7.49 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1 H), 7.63 (d, *J* = 8.9 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.1 (CH_3), 22.7 (CH_2), 25.3 (CH_2), 47.7 (2 × CH_2), 50.9 (2 × CH_2), 63.7 (CH_2), 92.0 (CH), 112.6 (CH), 113.4 (C), 118.3 (CH), 119.3 (CH), 121.1 (CH), 122.0 (CH), 122.9 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 133.0 (C), 141.6 (C), 151.7 (C), 152.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{29}N_2O_2$: 389.2229; found: 389.2232.

4-[4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazin-1-yl]phenol (11r)

Yield: 288 mg (80%); colorless solid; mp 193–195 °C (DMF).

IR (ATR): 3500–2500, 1620, 1593, 1514, 1466, 1452, 1433, 1410, 1391, 1306, 1261, 1229, 1206, 1188, 1157, 1144, 1099, 1072, 1020, 974, 959, 922, 851, 827, 808, 772, 750 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz, 120 °C): δ = 2.10–2.23 (m, 2 H), 2.72–3.20 (m, 10 H), 4.74 (d, *J* = 8.2 Hz, 1 H), 6.66 (d, *J* = 7.3 Hz, 2 H), 6.77 (d, *J* = 7.3 Hz, 2 H), 6.99 (d, *J* = 8.7 Hz, 1 H), 7.27–7.31 (m, 1 H), 7.42–7.47 (m, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.73–7.79 (m, 2 H), 8.31 (br s, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz, 120 °C): δ = 22.2 (CH_2), 25.4 (CH_2), 47.7 (2 × CH_2), 51.1 (2 × CH_2), 92.3 (CH), 114.1 (C), 116.3 (2 × CH), 118.6 (2 × CH), 119.4 (CH), 122.4 (CH), 123.4 (CH), 126.8 (CH), 128.0 (CH), 128.6 (CH), 129.1 (C), 133.3 (C), 145.2 (C), 151.7 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{25}N_2O_2$: 361.1916; found: 361.1919.

1-{4-[4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazin-1-yl]phenyl}ethan-1-one (11s)

Yield: 348 mg (90%); light-yellow solid; mp 239–240 °C (DMF–MeOH).

IR (ATR): 2841, 1659, 1618, 1595, 1510, 1389, 1360, 1277, 1227, 1188, 1144, 1018, 955, 924, 847, 812, 770, 754 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.21–2.28 (m, 2 H), 2.53 (s, 3 H), 2.94–3.00 (m, 2 H), 3.07–3.16 (m, 1 H), 3.20–3.29 (m, 3 H), 3.38–3.46 (m, 4 H), 4.76 (dd, *J* = 9.1, 3.1 Hz, 1 H), 6.90 (d, *J* = 8.9 Hz, 2 H), 7.02 (d, *J* = 8.9 Hz, 1 H), 7.34 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.48 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.61 (d, *J* = 8.9 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.89 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.7 (CH_2), 25.3 (CH_2), 26.2 (CH_3), 47.2 (2 × CH_2), 47.8 (2 × CH_2), 91.8 (CH), 113.3 (C), 113.6 (2 × CH), 119.1 (CH), 122.0 (CH), 123.3 (CH), 126.5 (CH), 127.7 (C), 128.0 (CH), 128.5 (CH), 128.9 (C), 130.5 (2 × CH), 132.9 (C), 152.6 (C), 154.3 (C), 196.6 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{27}N_2O_2$: 387.2073; found: 387.2073.

2-[4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)piperazin-1-yl]pyrimidine (11t)

Yield: 294 mg (85%); colorless solid; mp 142–143 °C (MeOH).

IR (ATR): 1622, 1585, 1545, 1514, 1466, 1449, 1408, 1389, 1362, 1310, 1260, 1231, 1207, 1192, 1179, 1153, 1138, 1020, 980, 970, 955, 939, 837, 814, 783, 768, 743 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.19–2.31 (m, 2 H), 2.85–2.92 (m, 2 H), 3.06–3.17 (m, 3 H), 3.20–3.27 (m, 1 H), 3.86–3.96 (m, 4 H), 4.76 (dd, *J* = 9.2, 3.0 Hz, 1 H), 6.49 (t, *J* = 4.8 Hz, 1 H), 7.01 (d, *J* = 8.9 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.47 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1 H), 7.60 (d, *J* = 8.7 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 8.32 (d, *J* = 4.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8 (CH_2), 25.3 (CH_2), 44.0 (2 × CH_2), 47.5 (2 × CH_2), 92.1 (CH), 109.9 (CH), 113.4 (C), 119.2 (CH), 122.0 (CH), 123.2 (CH), 126.4 (CH), 127.9 (CH), 128.5 (CH), 128.9 (C), 132.9 (C), 152.7 (C), 157.8 (2 × CH), 161.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}N_4O$: 347.1872; found: 347.1876.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)azepane (12)

Yield: 208 mg (74%); colorless solid; mp 78–79 °C (MeOH).

IR (ATR): 2926, 2847, 1622, 1597, 1514, 1468, 1449, 1431, 1416, 1383, 1229, 1207, 1186, 1163, 1140, 968, 947, 818, 745 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.63–1.75 (m, 8 H), 2.17–2.23 (m, 2 H), 2.90–2.97 (m, 2 H), 3.04–3.23 (m, 4 H), 4.80–4.83 (m, 1 H), 7.05 (d, *J* = 8.9 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1 H), 7.47 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1 H), 7.60 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 8.5 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.4 (CH_2), 26.7 (CH_2), 27.5 (2 × CH_2), 29.9 (2 × CH_2), 50.2 (2 × CH_2), 94.4 (CH), 113.2 (C), 119.6 (CH), 122.0 (CH), 123.0 (CH), 126.3 (CH), 127.7 (CH), 128.4 (CH), 128.8 (C), 133.1 (C), 153.7 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{24}NO$: 282.1858; found: 282.1861.

2-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-6-methoxy-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (13)

To a suspension of 2-trifluoroacetyl-1*H*-benzo[*f*]chromene (**1a**; 278 mg, 1 mmol) in MeOH (8 mL) was added 6-methoxy-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (404 mg, 2 mmol) at rt. The resulting mixture was heated under reflux for 15 min and then kept at rt for 1 h and at –30 °C for 30 min. The precipitate formed was collected by filtration, washed with ice-cold MeOH (1 mL) and purified by recrystallization; yield: 273 mg (71%); colorless solid; mp 211–213 °C (DMF–MeOH).

IR (ATR): 3381, 1620, 1595, 1512, 1483, 1466, 1454, 1433, 1401, 1389, 1304, 1219, 1209, 1179, 1155, 1126, 1113, 1067, 1032, 966, 916, 835, 810, 800, 770, 752 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.18–2.32 (m, 2 H), 2.64–2.75 (m, 2 H), 3.02–3.20 (m, 3 H), 3.26–3.32 (m, 1 H), 3.72 (s, 3 H), 3.97 (d, *J* = 14.9 Hz, 1 H), 4.12 (d, *J* = 14.9 Hz, 1 H), 4.99 (d, *J* = 9.6 Hz, 1 H), 6.62 (dd, *J* = 8.7, 2.1 Hz, 1 H), 6.86 (d, *J* = 2.1 Hz, 1 H), 7.00 (d, *J* = 9.0 Hz, 1 H), 7.14 (d, *J* = 8.5 Hz, 1 H), 7.29–7.33 (m, 1 H), 7.45–7.49 (m, 1 H), 7.64 (d, *J* = 9.0 Hz, 1 H), 7.77–7.80 (m, 2 H), 10.54 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 22.5 (CH_2), 22.7 (CH_2), 25.7 (CH_2), 44.0 (CH_2), 47.4 (CH_2), 55.8 (CH_3), 92.5 (CH), 100.3 (CH), 107.2 (C), 110.4 (CH), 112.0 (CH), 114.0 (C), 119.5 (CH), 122.5 (CH), 123.6 (CH), 127.0 (CH), 127.6 (C), 128.1 (CH), 128.7 (CH), 128.9 (C), 131.6 (C), 133.1 (C), 133.9 (C), 153.0 (C), 153.5 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{25}N_2O_2$: 385.1916; found: 385.1912.

4-(6-Chlorochroman-2-yl)morpholine (8e)

Yield: 178 mg (70%); colorless solid; mp 100–101 °C (MeOH).

IR (ATR): 2940, 2864, 2843, 1574, 1479, 1449, 1408, 1263, 1238, 1213, 1190, 1177, 1115, 1082, 1072, 1015, 968, 920, 914, 872, 831, 820, 797, 770, 642 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.93–2.09 (m, 2 H), 2.70–2.79 (m, 3 H), 2.84–2.92 (m, 1 H), 2.95–3.01 (m, 2 H), 3.68–3.77 (m, 4 H), 4.57 (dd, *J* = 9.8, 2.3 Hz, 1 H), 6.71 (d, *J* = 8.5 Hz, 1 H), 6.99 (d, *J* = 2.5 Hz, 1 H), 7.01 (dd, *J* = 8.5, 2.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.8 (CH_2), 25.6 (CH_2), 47.8 (2 × CH_2), 67.2 (2 × CH_2), 92.3 (CH), 118.1 (CH), 123.4 (C), 124.7 (C), 127.3 (CH), 128.7 (CH), 153.8 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{17}{}^{35}ClNO_2$: 254.0948; found: 254.0951.

4-(6,7-Dimethylchroman-2-yl)morpholine (8f)

Yield: 180 mg (73%); colorless solid; mp 94–95 °C (MeOH).

IR (ATR): 2967, 2930, 2866, 2828, 1622, 1572, 1503, 1454, 1402, 1294, 1273, 1260, 1218, 1200, 1165, 1111, 1092, 1069, 1043, 1020, 1006, 957, 918, 908, 885, 853, 785 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.92–2.09 (m, 2 H), 2.15 (s, 3 H), 2.18 (s, 3 H), 2.70–2.77 (m, 3 H), 2.81–2.90 (m, 1 H), 2.96–3.02 (m, 2 H), 3.69–3.78 (m, 4 H), 4.54 (dd, *J* = 10.1, 2.0 Hz, 1 H), 6.62 (s, 1 H), 6.79 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.8 (CH_3), 19.5 (CH_3), 25.3 (CH_2), 25.4 (CH_2), 47.8 (2 × CH_2), 67.3 (2 × CH_2), 92.0 (CH), 117.6 (CH), 118.9 (C), 128.1 (C), 130.0 (CH), 135.7 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{22}NO_2$: 248.1651; found: 248.1647.

4-[8-(Adamantan-1-yl)-6-methylchroman-2-yl]morpholine (8g)

Yield: 301 mg (82%); colorless solid; mp 174–176 °C (MeOH).

IR (ATR): 2901, 2849, 1462, 1447, 1408, 1373, 1342, 1315, 1298, 1261, 1211, 1202, 1179, 1157, 1113, 1092, 1078, 1040, 995, 976, 943, 918, 889, 847, 816, 783 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.71 (br s, 6 H), 1.80 (dd, *J* = 12.8, 6.1 Hz, 1 H), 1.92 (dd, *J* = 12.8, 5.6 Hz, 1 H), 2.01 (br s, 9 H), 2.12 (s, 3 H), 2.63–2.70 (m, 3 H), 2.82–2.91 (m, 1 H), 2.96–3.02 (m, 2 H), 3.55–3.64 (m, 4 H), 4.55 (d, *J* = 9.6 Hz, 1 H), 6.65 (s, 1 H), 6.69 (s, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 21.0 (CH_3), 25.2 (CH_2), 26.5 (CH_2), 29.0 (3 × CH), 36.9 (CH), 37.2 (3 × CH_2), 40.7 (3 × CH_2), 48.6 (2 × CH_2), 67.1 (2 × CH_2), 92.3 (CH), 121.9 (C), 125.1 (CH), 127.8 (CH), 128.0 (C), 137.5 (C), 152.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{34}NO_2$: 368.2590; found: 368.2592.

1-Cinnamyl-4-(6,8-dibromochroman-2-yl)piperazine (11u)

Yield: 428 mg (87%); colorless solid; mp 131–132 °C (MeOH).

IR (ATR): 2943, 2810, 1554, 1454, 1419, 1348, 1313, 1278, 1251, 1230, 1197, 1180, 1134, 1085, 1058, 1039, 1006, 964, 927, 910, 858, 837, 790, 775, 736, 717, 688, 659 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97–2.13 (m, 2 H), 2.57 (br s, 4 H), 2.74–2.96 (m, 4 H), 3.10–3.15 (m, 2 H), 3.19 (d, *J* = 6.9 Hz, 2 H), 4.74 (dd, *J* = 9.9, 2.1 Hz, 1 H), 6.30 (dt, *J* = 15.8, 6.9 Hz, 1 H), 6.53 (d, *J* = 15.8 Hz, 1 H), 7.09 (d, *J* = 2.1 Hz, 1 H), 7.22 (t, *J* = 7.3 Hz, 1 H), 7.28–7.32 (m, 2 H), 7.37 (d, *J* = 7.4 Hz, 2 H), 7.44 (d, *J* = 2.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.1 (CH_2), 26.1 (CH_2), 47.4 (br, 2 × CH_2), 53.4 (2 × CH_2), 61.2 (CH_2), 93.6 (CH), 111.6 (C), 112.2 (C), 125.2 (C), 126.4 (2 × CH), 126.6 (CH), 127.6 (CH), 128.6 (2 × CH), 130.7 (CH), 133.1 (CH), 133.2 (CH), 137.0 (C), 151.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{25}Br_2N_2O$: 491.0334; found: 491.0335.

1-(6,7-Dimethylchroman-2-yl)-4-(4-fluorophenyl)piperazine (11v)

Yield: 262 mg (77%); colorless solid; mp 147–148 °C (MeOH).

IR (ATR): 2853, 1622, 1574, 1518, 1501, 1449, 1406, 1387, 1310, 1294, 1263, 1246, 1233, 1202, 1165, 1142, 1078, 1045, 1007, 951, 920, 868, 860, 818, 787, 750, 716, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97–2.13 (m, 2 H), 2.17 (s, 3 H), 2.19 (s, 3 H), 2.73–2.79 (m, 1 H), 2.85–2.97 (m, 3 H), 3.12–3.20 (m, 6 H), 4.65 (d, *J* = 9.2 Hz, 1 H), 6.63 (s, 1 H), 6.82 (s, 1 H), 6.88–6.92 (m, 2 H), 6.95–7.00 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.9 (CH_3), 19.6 (CH_3), 25.5 (CH_2), 25.7 (CH_2), 47.4 (2 × CH_2), 50.6 (2 × CH_2), 91.9 (CH), 115.6 (d, $^2J_{C,F}$ = 21.9 Hz, 2 × CH), 117.7 (CH), 118.0 (d, $^3J_{C,F}$ = 7.6 Hz, 2 × CH), 118.9 (C), 128.1 (C), 130.0 (CH), 135.8 (C), 148.3 (C), 153.1 (C), 157.3 (d, $^1J_{C,F}$ = 237.4 Hz, C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}FN_2O$: 341.2029; found: 341.2033.

1-Aryl(hetaryl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-amines; General Procedure

A solution of the corresponding 2-trifluoroacetyl-1*H*-benzo[*f*]chromene or 1*H*-benzo[*f*]chromene-2-carbaldehyde (1 mmol) in cyclic secondary amine (morpholine, *N*-methylpiperazine, or piperidine) (3 mL) was heated under reflux for 30 min (for 2-trifluoroacetyl-1*H*-benzo[*f*]chromenes) or 10 h (for 1*H*-benzo[*f*]chromene-2-carbaldehydes). The reaction mixture was poured into H_2O (10 mL) to yield a solid product, which was collected by filtration, washed with H_2O, dried, and purified by recrystallization.

4-(*trans*-1-Phenyl-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine (8h)

Yield: 289 mg (84%) (from 2-trifluoroacetyl-1*H*-benzo[*f*]chromene); colorless solid; mp 184–185 °C (MeOH–DMF).

IR (ATR): 2855, 1620, 1595, 1508, 1491, 1454, 1302, 1236, 1211, 1192, 1113, 1059, 1024, 1011, 982, 920, 862, 849, 822, 746, 700 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.16 (dt, *J* = 13.3, 1.8 Hz, 1 H), 2.55 (ddd, *J* = 13.3, 11.3, 5.4 Hz, 1 H), 2.73–2.79 (m, 2 H), 3.00–3.06 (m, 2 H), 3.65–3.71 (m, 4 H), 4.65 (dd, *J* = 11.3, 1.8 Hz, 1 H), 4.77 (dd, *J* = 5.4, 1.8 Hz, 1 H), 7.11–7.30 (m, 8 H), 7.43–7.46 (m, 1 H), 7.70–7.75 (m, 2 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 33.3 (CH_2), 38.7 (CH), 47.7 (2 × CH_2), 67.3 (2 × CH_2), 87.6 (CH), 113.6 (C), 119.1 (CH), 123.1 (CH), 123.2 (CH), 126.5 (CH), 126.6 (CH), 128.50 (CH), 128.54 (2 × CH), 128.6 (2 × CH), 129.2 (CH), 132.8 (C), 145.3 (C), 153.7 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_2$: 346.1807; found: 346.1795.

4-[*trans*-1-(3-Nitrophenyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]morpholine (8i)

Yield: 230 mg (59%) (from 2-trifluoroacetyl-1*H*-benzo[*f*]chromene); colorless solid; mp 169–170 °C (MeOH).

IR (ATR): 1618, 1528, 1341, 1265, 1260, 1236, 1203, 1192, 1119, 1059, 1036, 1022, 1013, 984, 918, 878, 849, 826, 781, 754, 733, 698 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.19 (dt, *J* = 13.0, 1.8 Hz, 1 H), 2.65 (ddd, *J* = 13.0, 11.2, 5.4 Hz, 1 H), 2.74–2.79 (m, 2 H), 3.01–3.07 (m, 2 H), 3.65–3.75 (m, 4 H), 4.56 (dd, *J* = 11.2, 1.8 Hz, 1 H), 4.87 (dd, *J* = 5.4, 1.8 Hz, 1 H), 7.16 (d, *J* = 8.9 Hz, 1 H), 7.25–7.42 (m, 5 H), 7.75–7.78 (m, 2 H), 8.05–8.09 (m, 2 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 33.3 (CH_2), 38.5 (CH), 47.7 (2 × CH_2), 67.2 (2 × CH_2), 87.3 (CH), 111.9 (C), 119.3 (CH), 121.9 (CH), 122.5 (CH), 123.3 (CH), 123.4 (CH), 126.9 (CH), 128.8 (CH), 129.4 (C), 129.6 (CH), 130.0 (CH), 132.3 (C), 134.8 (CH), 147.6 (C), 148.7 (C), 153.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}N_2O_4$: 391.1658; found: 391.1650.

4-[*trans*-1-(Thiophen-2-yl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]morpholine (8j)

Yield: 200 mg (57%) (from 1*H*-benzo[*f*]chromene-2-carbaldehyde); 284 mg (81%) (from 2-trifluoroacetyl-1*H*-benzo[*f*]chromene); colorless solid; mp 158–159 °C (EtOH).

IR (ATR): 2855, 1622, 1595, 1508, 1468, 1454, 1435, 1416, 1393, 1302, 1263, 1236, 1211, 1200, 1188, 1153, 1144, 1113, 1059, 1032, 1024, 999, 982, 918, 976, 860, 849, 822, 746, 708, 692 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.25 (dt, *J* = 13.1, 1.8 Hz, 1 H), 2.51 (ddd, *J* = 13.1, 11.4, 5.3 Hz, 1 H), 2.76–2.82 (m, 2 H), 3.01–3.06 (m, 2 H), 3.70–3.76 (m, 4 H), 4.80 (dd, *J* = 11.4, 1.8 Hz, 1 H), 4.98 (dd, *J* = 5.3, 1.8 Hz, 1 H), 6.58 (d, *J* = 3.5 Hz, 1 H), 6.84 (dd, *J* = 5.0, 3.5 Hz, 1 H), 7.11 (d, *J* = 8.9 Hz, 1 H), 7.15 (d, *J* = 5.0 Hz, 1 H), 7.25–7.29 (m, 1 H), 7.32–7.36 (m, 1 H), 7.63 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.9 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 33.7 (CH_2), 34.2 (CH), 47.8 (2 × CH_2), 67.3 (2 × CH_2), 88.0 (CH), 114.0 (C), 119.2 (CH), 122.9 (CH), 123.2 (CH), 124.2 (CH), 126.1 (CH), 126.7 (CH), 127.0 (CH), 128.5 (CH), 129.1 (C), 129.5 (CH), 132.7 (C), 149.3 (C), 153.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{22}NO_2S$: 352.1371; found: 352.1369.

1-(*trans*-1-Phenyl-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)piperidine (10h)

Yield: 292 mg (85%) (from 2-trifluoroacetyl-1*H*-benzo[*f*]chromene); colorless solid; mp 193–195 °C (EtOH).

IR (ATR): 2928, 1622, 1597, 1491, 1464, 1450, 1410, 1314, 1261, 1231, 1209, 1190, 1165, 1126, 1117, 1053, 1020, 1011, 972, 839, 822, 812, 745, 696 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.48–1.65 (m, 6 H), 2.16 (dt, *J* = 13.0, 1.8 Hz, 1 H), 2.59 (ddd, *J* = 13.0, 11.0, 5.5 Hz, 1 H), 2.64–2.75 (m, 2 H), 2.94–3.05 (m, 2 H), 4.67 (dd, *J* = 11.0, 1.8 Hz, 1 H), 4.77 (dd, *J* = 5.5, 1.8 Hz, 1 H), 7.10–7.28 (m, 8 H), 7.45 (d, *J* = 8.7 Hz, 1 H), 7.68–7.75 (m, 2 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 24.8 (CH_2), 26.3 (2 × CH_2), 33.6 (CH_2), 38.9 (CH), 48.6 (2 × CH_2), 88.5 (CH), 113.7 (C), 119.2 (CH), 122.9 (CH), 123.2 (CH), 126.4 (CH), 126.5 (CH), 128.4 (CH), 128.5 (2 × CH), 128.6 (2 × CH), 129.0 (CH), 129.1 (C), 132.9 (C), 145.5 (C), 154.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{26}NO$: 344.2014; found: 344.2009.

1-Methyl-4-[*trans*-1-(thiophen-2-yl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]piperazine (10i)

Yield: 193 mg (53%) (from 1*H*-benzo[*f*]chromene-2-carbaldehyde); colorless solid; mp 152–154 °C (MeOH). In the NMR assignments, pip = piperazine and thi = thiophenyl.

IR (ATR): 1620, 1599, 1464, 1456, 1412, 1398, 1375, 1352, 1321, 1287, 1261, 1227, 1200, 1190, 1155, 1142, 1130, 1078, 1059, 1013, 997, 978, 851, 833, 810, 785, 748, 710, 696 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.02 (dt, *J* = 13.3, 1.8 Hz, 1 H, H_{eq}-2), 2.12 (s, 3 H, CH_3), 2.28 (br s, 4 H, 2 × CH_{2pip}-2,6), 2.51 (ddd, *J* = 13.3, 11.3, 5.4 Hz, 1 H, H_{ax}-2), 2.61–2.66 (m, 2 H, CH_{2pip}-3,5), 2.92–2.97 (m, 2 H, CH_{2pip}-3,5), 4.72 (dd, *J* = 11.3, 1.8 Hz, 1 H, H-3), 5.03 (dd, *J* = 5.4, 1.8 Hz, 1 H, H-1), 6.65 (d, *J* = 3.4 Hz, 1 H, H_{thi}-3), 6.86 (dd, *J* = 5.0, 3.5 Hz, 1 H, H_{thi}-4), 7.05 (d, *J* = 8.9 Hz, 1 H, H-5), 7.22–7.26 (m, 1 H, H-8), 7.29–7.34 (m, 2 H, H_{thi}-5, H-9), 7.56 (d, *J* = 8.5 Hz, 1 H, H-10), 7.74 (d, *J* = 8.9 Hz, 1 H, H-6), 7.77 (d, *J* = 8.0 Hz, 1 H, H-7).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 33.8 (CH-1), 34.2 (CH_2-2), 46.4 (CH_3), 47.2 (br, 2 × CH_{2pip}-3,5), 55.4 (2 × CH_{2pip}-2,6), 88.4 (CH-3), 114.7 (C-10b), 119.5 (CH-5), 123.2 (CH-10), 123.5 (CH-8), 125.1 (CH_{thi}-5), 126.0 (CH_{thi}-3), 127.1 (CH-9), 127.6 (CH_{thi}-4), 128.9 (CH-7), 129.1 (C-6a), 129.8 (CH-6), 132.8 (C-10a), 150.1 (C_{thi}-2), 153.1 (C-4a).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{25}N_2OS$: 365.1688; found: 365.1689.

4-[*trans*-1-(Pyridin-3-yl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]morpholine (8l)

Yield: 208 mg (60%) (from 1*H*-benzo[*f*]chromene-2-carbaldehyde); colorless solid; mp 202–203 °C (MeOH–$CHCl_3$).

IR (ATR): 2859, 2839, 1620, 1597, 1572, 1481, 1466, 1414, 1391, 1337, 1300, 1294, 1261, 1231, 1200, 1167, 1153, 1144, 1109, 1069, 1061, 1024, 1011, 978, 972, 920, 872, 858, 843, 833, 820, 787, 745, 725, 712 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.03 (dt, *J* = 13.5, 1.8 Hz, 1 H), 2.55–2.66 (m, 3 H), 2.88–2.94 (m, 2 H), 3.50–3.57 (m, 4 H), 4.51 (dd, *J* = 11.4, 1.8 Hz, 1 H), 4.89 (dd, *J* = 5.3, 1.8 Hz, 1 H), 7.13 (d, *J* = 8.9 Hz, 1 H), 7.21–7.28 (m, 3 H), 7.36–7.38 (m, 2 H), 7.76–7.80 (m, 2 H), 8.35–8.38 (m, 2 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 33.1 (CH_2), 35.8 (CH), 47.7 (2 × CH_2), 66.9 (2 × CH_2), 87.8 (CH), 113.0 (C), 119.5 (CH), 123.2 (CH), 123.6 (CH), 124.0 (CH), 127.2 (CH), 129.0 (CH), 129.3 (C), 129.8 (CH), 132.5 (C), 136.3 (CH), 141.2 (C), 148.1 (CH), 150.1 (CH), 153.9 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{23}N_2O_2$: 347.1760; found: 347.1757.

4-[*trans*-1-(4-Methoxyphenyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl]morpholine (8m)

Yield: 193 mg (52%) (from 1*H*-benzo[*f*]chromene-2-carbaldehyde); colorless solid; mp 188–190 °C (MeOH).

IR (ATR): 1620, 1611, 1597, 1582, 1506, 1466, 1435, 1414, 1395, 1317, 1298, 1285, 1261, 1234, 1202, 1186, 1144, 1115, 1061, 1022, 1007, 980, 918, 876, 862, 853, 837, 820, 812, 746 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.95 (dt, *J* = 13.1, 1.8 Hz, 1 H, H_{eq}-2), 2.44–2.54 (m, 1 H, H_{ax}-2), 2.59–2.65 (m, 2 H, CH_2N), 2.89–2.96 (m, 2 H, CH_2N), 3.52 (br s, 4 H, 2 × CH_2O), 3.64 (s, 3 H, CH_3O), 4.51 (dd, *J* = 11.0, 1.8 Hz, 1 H, H-3), 4.73 (dd, *J* = 5.4, 1.8 Hz, 1 H, H-1), 6.78 (d, *J* = 8.7 Hz, 2 H, $H_{o\text{-MeO}}$), 6.96 (d, *J* = 8.7 Hz, 2 H, $H_{m\text{-MeO}}$), 7.09 (d, *J* = 8.9 Hz, 1 H, H-5), 7.19–7.27 (m, 2 H, H-8,9), 7.39 (d, *J* = 8.0 Hz, 1 H, Ar), 7.72–7.78 (m, 2 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 33.7 (CH_2-2), 37.3 (CH-1), 47.8 (2 × CH_2N), 55.5 (CH_3O), 66.9 (2 × CH_2O), 88.0 (CH-3), 114.4 (2 × $CH_{o\text{-MeO}}$), 114.5 (C-10b), 119.4 (CH-5), 123.4 (2 × CH-8,10), 126.9 (CH-9), 128.9 (CH-7), 129.2 (C-6a), 129.4 (CH-6), 129.7 (2 × $CH_{m\text{-MeO}}$), 132.8 (C-10a), 137.9 ($C_{p\text{-MeO}}$), 153.6 (C-4a), 158.2 (*C*–OMe).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{26}NO_3$: 376.1913; found: 376.1917.

4-(3-Phenyl-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine (8k)

A solution of 2,2,2-trifluoro-1-(3-phenyl-1*H*-benzo[*f*]chromen-2-yl)ethan-1-one (354 mg, 1 mmol) in morpholine (3 mL) was heated under reflux for 2 h. The reaction mixture was poured into H_2O (10 mL) to yield a solid product, which was collected by filtration, washed with H_2O, dried, and purified by recrystallization; yield: 280 mg (81%); light-yellow solid; mp 145–146 °C (DMF–MeOH).

IR (ATR): 2845, 1620, 1595, 1512, 1466, 1445, 1396, 1352, 1277, 1240, 1196, 1152, 1117, 1022, 972, 918, 885, 851, 818, 772, 756, 746, 700 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.24–2.38 (m, 2 H), 2.54–2.71 (m, 3 H), 3.00–3.10 (m, 3 H), 3.64–3.74 (m, 4 H), 7.19–7.43 (m, 8 H), 7.64 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.9 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.2 (CH_2), 29.3 (CH_2), 46.1 (2 × CH_2), 67.6 (2 × CH_2), 94.8 (C), 113.9 (C), 118.7 (CH), 122.0 (CH), 123.1 (CH), 126.3 (CH), 126.9 (2 × CH), 127.5 (CH), 128.2 (3 × CH), 128.5 (CH), 128.8 (C), 132.8 (C), 141.2 (C), 152.6 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_2$: 346.1807; found: 346.1803.

(*E*)-2-[(2-Hydroxynaphthalen-1-yl)methyl]-3-morpholinoacrylaldehyde (14a)

To a suspension of 1*H*-benzo[*f*]chromene-2-carbaldehyde (**1m**; 210 mg, 1 mmol) in MeOH (3 mL) was added a solution of morpholine (87 mg, 1 mmol) in MeOH (2 mL) dropwise with stirring at rt for 10 min. The mixture was stirred additionally for 30 min, stored at –30 °C for 1 h, the formed product was collected by filtration, and recrystallized from MeOH; yield: 220 mg (74%); colorless solid; mp 144–145 °C.

IR (ATR): 3300–2500, 1626, 1584, 1558, 1506, 1458, 1437, 1404, 1358, 1290, 1273, 1234, 1157, 1115, 1067, 1026, 982, 922, 889, 876, 812, 748 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ = 3.23–3.26 (m, 4 H), 3.37–3.40 (m, 4 H), 3.95 (s, 2 H), 6.86 (s, 1 H), 7.10 (d, *J* = 8.9 Hz, 1 H), 7.17–7.21 (m, 1 H), 7.24–7.28 (m, 1 H), 7.58 (d, *J* = 8.7 Hz, 1 H), 7.66–7.70 (m, 2 H), 8.87 (s, 1 H), 9.77 (br s, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 18.6 (CH_2), 51.1 (2 × CH_2), 66.8 (2 × CH_2), 111.9 (C), 118.8 (CH), 119.7 (C), 122.9 (CH), 124.4 (CH), 126.0 (CH), 128.1 (CH), 128.7 (CH), 129.0 (C), 133.9 (C), 152.2 (C), 159.7 (CH), 191.1 (CH).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{20}NO_3$: 298.1443; found: 298.1439.

***tert*-Butyl (*E*)-4-[2-Formyl-3-(2-hydroxynaphthalen-1-yl)prop-1-en-1-yl]piperazine-1-carboxylate (14b)**

The title compound was prepared similarly to compound **14a** from 1*H*-benzo[*f*]chromene-2-carbaldehyde (**1m**; 210 mg, 1 mmol) and *tert*-butyl piperazine-1-carboxylate (186 mg, 1 mmol) in MeOH (3 mL); yield: 321 mg (81%); colorless solid; mp 171–172 °C (DMF–MeOH).

IR (ATR): 3329, 2903, 2849, 1647, 1593, 1560, 1454, 1369, 1342, 1317, 1292, 1244, 1211, 1140, 1105, 1067, 980, 864, 791 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ = 1.33 (s, 9 H, *t*-C_4H_9), 2.98 (br s, 4 H, CH_2NBoc), 3.34 (br s, 4 H, CH_2N), 3.96 (s, 2 H, CH_2), 6.88 (s, 1 H, =CHN), 7.12 (d, *J* = 8.9 Hz, 1 H, H-3), 7.16–7.20 (m, 1 H, H-6), 7.23–7.27 (m, 1 H, H-7), 7.59 (d, *J* = 8.7 Hz, 1 H, H-4), 7.66 (d, *J* = 8.5 Hz, 1 H, H-5), 7.69 (d, *J* = 7.6 Hz, 1 H, H-8), 8.88 (s, 1 H, CHO), 9.82 (s, 1 H, OH).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 18.5 (CH_2), 28.5 (3 × CH_3), 43.9 (br, CH_2NBoc), 44.2 (br, CH_2, CH_2NBoc), 50.4 (br, 2 × CH_2, CH_2N), 79.8 (CMe_3), 112.1 (C–CHO), 118.7 (CH-3), 119.6 (C-1), 122.9 (CH-6), 124.4 (C-8), 126.0 (CH-7), 128.2 (CH-4), 128.8 (CH-5), 129.0 (C-4a), 133.9 (C-8a), 152.2 (C-2), 154.0 (C=O), 159.7 (=CHN), 191.2 (HC=O).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{29}N_2O_4$: 397.2127; found: 397.2130.

(1*R,2*R**,3*R**)-1-Aryl-2-(1,5-diazabicyclo[3.2.1]octan-8-yl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-ols 15a–c; General Procedure**

To a suspension of 1-aryl-1*H*-benzo[*f*]chromene-2-carbaldehyde **1p–r** (1 mmol) in MeOH (4 mL for **15a**, 7 mL for **15b**,**c**) was added homopiperazine (200 mg, 2 mmol) at rt. The resulting mixture was heated under reflux for 30 min and then kept at rt for 24 h. H_2O (2 mL for **15a**, 1 mL for **15b**,**c**) was added, the precipitate formed was collected by filtration, washed with 60% aq MeOH (1 mL) and purified by recrystallization.

(1*R,2*R**,3*R**)-2-(1,5-Diazabicyclo[3.2.1]octan-8-yl)-1-(4-methoxyphenyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-ol (15a)**

Yield: 266 mg (64%); colorless solid; mp 176–177 °C (MeOH).

IR (ATR): 3100–2900, 1622, 1599, 1508, 1464, 1244, 1231, 1177, 1138, 1111, 1074, 1059, 1049, 1030, 1005, 947, 893, 835, 812, 787, 758, 746, 725 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.09 (dt, *J* = 14.6, 4.3 Hz, 1 H), 1.82–1.98 (m, 2 H), 2.82–2.94 (m, 3 H), 3.00–3.26 (m, 5 H), 3.72 (s, 3 H), 4.10 (d, *J* = 11.2 Hz, 1 H), 4.89 (s, 1 H), 5.38 (d, *J* = 2.1 Hz, 1 H), 6.74 (d, *J* = 8.9 Hz, 1 H), 6.95 (d, *J* = 8.9 Hz, 2 H), 7.24–7.27 (m, 4 H), 7.49–7.52 (m, 1 H), 7.72–7.76 (m, 2 H) (hydroxyl proton does not appear in the ^1H NMR spectrum).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.5 (CH_2), 39.7 (CH), 42.2 (CH), 49.7 (CH_2), 51.0 (CH_2), 55.1 (CH_2), 56.1 (CH_2), 55.3 (CH_3), 87.4 (CH), 93.5 (CH), 112.7 (C), 114.1 (2 × CH), 119.2 (CH), 123.4 (CH), 124.1 (CH), 126.5 (CH), 128.4 (CH), 129.2 (CH), 129.3 (2 × CH), 129.8 (C), 133.0 (C), 138.0 (C), 152.1 (C), 158.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{29}N_2O_3$: 417.2178; found: 417.2182.

(1*R,2*R**,3*R**)-2-(1,5-Diazabicyclo[3.2.1]octan-8-yl)-1-(3-nitrophenyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-3-ol (15b)**

Yield: 315 mg (73%); light-yellow solid; mp 196–197 °C (DMF–MeOH).

IR (ATR): 3088, 2951, 2895, 1624, 1601, 1523, 1464, 1391, 1344, 1323, 1308, 1263, 1234, 1140, 1111, 1072, 1049, 1001, 949, 889, 829, 785, 752, 698, 679 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (dt, *J* = 14.6, 4.3 Hz, 1 H), 1.85–1.98 (m, 2 H), 2.84–2.95 (m, 3 H), 3.03–3.27 (m, 5 H), 4.13 (d, *J* = 11.2 Hz, 1 H), 5.07 (s, 1 H), 5.32 (d, *J* = 1.6 Hz, 1 H), 7.23–7.31 (m, 4 H), 7.34–7.38 (m, 2 H), 7.76–7.80 (m, 2 H), 8.01–8.04 (m, 2 H), 9.66 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.4 (CH_2), 40.5 (CH), 41.9 (CH), 49.7 (CH_2), 51.0 (CH_2), 55.1 (CH_2), 56.2 (CH_2), 87.2 (CH), 93.1 (CH), 110.8 (C), 119.3 (CH), 121.8 (CH), 123.2 (CH), 123.4 (CH), 123.8 (CH), 126.9 (CH), 128.8 (CH), 129.7 (CH), 130.0 (C), 130.1 (CH), 132.5 (C), 134.5 (CH), 148.2 (C), 148.8 (C), 152.4 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{26}N_3O_4$: 432.1923; found: 432.1920.

(1*R,2*R**,3*R**)-2-(1,5-Diazabicyclo[3.2.1]octan-8-yl)-1-(3-nitrophenyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-2-*d*-3-ol-*d* (15b-d_2)**

A suspension of 1-(3-nitrophenyl)-1*H*-benzo[f]chromene-2-carbaldehyde (150 mg, 0.45 mmol) and homopiperazine (75 mg, 0.75 mmol) in a mixture of CD_3OD (5 mL) and of D_2O (0.5 mL) was heated under reflux for 50 min under argon atmosphere. After 40 min, the solution became homogeneous. The precipitated light-yellow crystals were collected by filtration and washed with ice-cold MeOH; yield: 0.115 g (59%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.09–1.14 (m, 1 H), 1.88–1.96 (m, 1 H), 2.84–2.96 (m, 3 H), 3.03–3.28 (m, 5 H), 4.12 (s, 1 H), 5.07 (s, 1 H), 5.31 (d, *J* = 1.1 Hz, 1 H), 7.23–7.30 (m, 4 H), 7.34–7.38 (m, 2 H), 7.76–7.80 (m, 2 H), 8.01–8.04 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.4 (CH_2), 40.4 (CH), 41.5 (t, *J* = 18.2 Hz, CD), 49.7 (CH_2), 51.0 (CH_2), 55.1 (CH_2), 56.1 (CH_2), 87.1 (CH), 92.9 (CH), 110.8 (C), 119.3 (CH), 121.8 (CH), 123.1 (CH), 123.4 (CH), 123.8 (CH), 126.9 (CH), 128.8 (CH), 129.7 (CH), 130.0 (C), 130.1 (CH), 132.5 (C), 134.5 (CH), 148.1 (C), 148.8 (C), 152.4 (C).

(1*R,2*R**,3*R**)-2-(1,5-Diazabicyclo[3.2.1]octan-8-yl)-1-phenyl-2,3-dihydro-1*H*-benzo[*f*]chromen-3-ol (methanol solvate) (15c)**[26]

Yield: 289 mg (69%); colorless solid; mp 131–132 °C (MeOH).

IR (ATR): 3400–2800, 1622, 1599, 1466, 1389, 1265, 1233, 1134, 1109, 1072, 1059, 1030, 1011, 949, 893, 814, 799, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.09 (dt, *J* = 14.7, 4.4 Hz, 1 H), 1.41 (br s, 1 H), 1.83–1.94 (m, 1 H), 1.97 (d, *J* = 11.2 Hz, 1 H), 2.83–2.94 (m, 3 H), 3.00–3.28 (m, 5 H), 3.46 (s, 3 H), 4.12 (d, *J* = 11.2 Hz, 1 H), 4.95 (s, 1 H), 5.40 (s, 1 H), 7.04 (d, *J* = 7.3 Hz, 2 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 7.19–7.28 (m, 5 H), 7.49 (dd, *J* = 7.3, 1.8 Hz, 1 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 9.67 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.5 (CH_2), 40.7 (CH), 42.0 (CH), 49.7 (CH_2), 50.88 (CH_3), 50.95 (CH_2), 55.1 (CH_2), 56.1 (CH_2), 87.4 (CH), 93.5 (CH), 112.4 (C), 119.2 (CH), 123.5 (CH), 124.0 (CH), 126.5 (CH), 126.6 (CH), 128.4 (3 × CH), 128.8 (2 × CH), 129.4 (CH), 129.8 (C), 132.9 (C), 145.9 (C), 152.2 (C).

Anal. Calcd for $C_{25}H_{26}N_2O_2$·CH_3OH: C, 74.61; H, 7.23; N, 6.69. Found: C, 74.55; H, 7.20; N, 6.61.

1-(3-Morpholinopropyl)naphthalen-2-ol Hydrochloride (16·HCl)

To a solution of 4-(2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine (**8a**; 269 mg, 1 mmol) in anhyd THF (10 mL) was added $LiAlH_4$ (115 mg, 3 mmol) in one portion. The resulting mixture was stirred at rt for 2 h, and then quenched with sat. aq NH_4Cl. The solvent was removed under reduced pressure. The residue was extracted with EtOAc (3 × 10 mL), and the combined organic layers were washed with H_2O (10 mL) and brine (10 mL), and dried (anhyd Na_2SO_4). The solvent was again removed under reduced pressure, the residue was treated with EtOAc (2 mL) saturated with gaseous HCl, and the product was isolated by filtration; yield: 274 mg (89%); colorless solid; mp 242–243 °C.

IR (ATR): 3163, 2926, 2668, 2558, 2471, 1626, 1605, 1582, 1514, 1477, 1439, 1358, 1267, 1119, 1094, 970, 818, 741 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.92–2.02 (m, 2 H), 2.94–3.20 (m, 4 H), 3.15 (t, *J* = 7.9 Hz, 2 H), 3.28–3.35 (m, 2 H), 3.72–3.88 (m, 4 H), 7.21–7.26 (m, 2 H), 7.39–7.43 (m, 1 H), 7.61 (d, *J* = 8.7 Hz, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.88 (d, *J* = 8.5 Hz, 1 H), 9.81 (br s, 1 H), 11.14 (br s, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 22.1 (CH_2), 23.8 (CH_2), 51.4 (2 × CH_2), 56.4 (CH_2), 63.7 (2 × CH_2), 118.2 (C), 118.6 (CH), 122.7 (CH), 122.9 (CH), 126.7 (CH), 128.0 (CH), 128.7 (C), 129.0 (CH), 133.5 (C), 153.0 (C).

Anal. Calcd for $C_{17}H_{21}NO_2$·HCl: C, 66.33; H, 7.20; N, 4.55. Found: C, 66.28; H, 7.17; N, 4.46.

1-(3-Morpholinopropyl)naphthalen-2-ol (16)

1-(3-Morpholinopropyl)naphthalen-2-ol hydrochloride (200 mg, 0.65 mmol) was dissolved in MeOH (2 mL), treated with sat. aq $NaHCO_3$ (5 mL), and the free base was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with H_2O (5 mL) and brine (5 mL), dried (anhyd Na_2SO_4), and concentrated; yield: 164 mg (93%); colorless solid; mp 87–88 °C.

IR (ATR): 3462, 3410, 3287, 3065, 2949, 1558, 1452, 1425, 1352, 1248, 1229, 1163, 1146, 1107, 1053, 1034, 984, 953, 895, 876, 856, 731, 710 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.03–2.09 (m, 2 H), 2.26–2.30 (m, 2 H), 2.54 (br s, 4 H), 3.12–3.15 (m, 2 H), 3.87 (t, *J* = 4.5 Hz, 4 H), 7.18 (d, *J* = 8.7 Hz, 1 H), 7.29–7.33 (m, 1 H), 7.44–7.48 (m, 1 H), 7.65 (d, *J* = 8.7 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 11.18 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.3 (CH_2), 24.3 (CH_2), 52.8 (2 × CH_2), 54.5 (CH_2), 66.4 (2 × CH_2), 117.4 (C), 120.2 (CH), 122.5 (CH), 122.6 (CH), 126.2 (CH), 128.2 (CH), 128.8 (CH), 129.3 (C), 133.5 (C), 154.4 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{22}NO_2$: 272.1651; found: 272.1654.

2,3-Dihydro-1*H*-benzo[*f*]chromen-3-ol (17)

4-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)morpholine (**8a**; 2.69 g, 10 mmol) was dissolved in AcOH (27 mL) and H_2O (13 mL) was added. The resulting solution was heated under reflux for 30 min. The solution was cooled to rt, H_2O (40 mL) was added, and the resulting suspension was kept at 5 °C for 1 h. The formed precipitate was collected by filtration, washed with H_2O, and recrystallized from MeOH; yield: 1.62 g (81%); colorless solid; mp 90–92 °C.

IR (ATR): 3400–3100, 2935, 1626, 1595, 1514, 1464, 1431, 1418, 1400, 1350, 1307, 1296, 1263, 1234, 1225, 1174, 1122, 1053, 1024, 980, 960, 881, 870, 806, 768, 737 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.09–2.24 (m, 2 H), 3.05–3.20 (m, 2 H), 3.34 (br s, 1 H), 5.66 (dd, *J* = 3.9, 2.5 Hz, 1 H), 7.06 (d, *J* = 8.9 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.4 (CH_2), 27.1 (CH_2), 92.1 (CH), 113.9 (C), 119.0 (CH), 122.1 (CH), 123.6 (CH), 126.5 (CH), 128.1 (CH), 128.5 (CH), 129.3 (C), 132.8 (C), 149.3 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_2$: 201.0916; found: 201.0918.

3-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-1*H*-indole (18)

To a solution of **17** (269 mg, 1 mmol) and indole (117 mg, 1 mmol) in CH_2Cl_2 (4 mL) was added boron trifluoride etherate (1 drop) and the solution was kept at rt for 6 h. The solvent was distilled off, the residue was purified by column chromatography (silica gel, CH_2Cl_2), and recrystallized from MeOH; yield: 93 mg (31%); colorless solid; mp 143–145 °C.

IR (ATR): 3410, 3352, 1620, 1597, 1555, 1512, 1458, 1431, 1393, 1346, 1261, 1231, 1211, 1096, 1042, 972, 868, 806, 768, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.41–2.48 (m, 2 H), 3.13–3.16 (m, 2 H), 5.42 (dd, *J* = 8.0, 3.7 Hz, 1 H), 6.99 (t, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 9.0 Hz, 1 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.37 (d, *J* = 8.3 Hz, 1 H), 7.42 (s, 1 H), 7.48 (t, *J* = 7.7 Hz, 1 H), 7.64–7.68 (m, 2 H), 7.79 (d, *J* = 8.3 Hz, 1 H), 7.83 (d, *J* = 8.5 Hz, 1 H), 11.09 (s, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.9 (CH_2), 27.8 (CH_2), 72.3 (CH), 112.2 (CH), 114.1 (C), 115.4 (C), 119.3 (CH), 119.6 (CH), 119.8 (CH), 121.8 (CH), 122.5 (CH), 123.7 (CH), 123.8 (CH), 126.4 (C), 127.0 (CH), 128.0 (CH), 128.8 (CH), 129.0 (C), 133.3 (C), 136.9 (C), 153.1 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}NO$: 300.1388; found: 300.1390.

N-Phenyl-2,3-dihydro-1*H*-benzo[*f*]chromen-3-amine (19a)

A mixture of **8a** (269 mg, 1 mmol) and aniline hydrochloride (130 mg, 1 mmol) in MeOH (5 mL) was stirred under reflux for 10 min and cooled to rt. The formed precipitate was collected by filtration, washed with MeOH, and recrystallized from EtOH–DMF; yield: 234 mg (85%); colorless solid; mp 151–153 °C.

IR (ATR): 3393, 1620, 1595, 1510, 1466, 1433, 1391, 1304, 1261, 1221, 1209, 1179, 1157, 1140, 1117, 1069, 1042, 966, 858, 824, 743, 689 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.10–2.18 (m, 1 H), 2.21–2.31 (m, 1 H), 3.06–3.28 (m, 2 H), 5.49–5.56 (m, 1 H), 6.63–6.63 (m, 1 H), 6.74 (d, *J* = 8.7 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 6.94 (d, *J* = 8.9 Hz, 1 H), 7.12 (t, *J* = 7.8 Hz, 2 H), 7.30–7.33 (m, 1 H), 7.46–7.50 (m, 1 H), 7.62 (d, *J* = 8.9 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.81 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 20.4 (CH_2), 27.0 (CH_2), 80.8 (CH), 113.9 (C), 114.0 (2 × CH), 118.1 (CH), 119.7 (CH), 122.5 (CH), 123.7 (CH), 126.9 (CH), 128.1 (CH), 128.7 (CH), 129.0 (C), 129.5 (2 × CH), 133.1 (C), 146.8 (C), 151.5 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}NO$: 276.1388; found: 276.1392.

1-(2,3-Dihydro-1*H*-benzo[*f*]chromen-3-yl)-1,2,3,4-tetrahydroquinoline (19b)

A mixture of **8a** (269 mg, 1 mmol) and 1,2,3,4-tetrahydroquinoline hydrochloride (170 mg, 1 mmol) in MeOH (5 mL) was stirred under reflux for 10 min and cooled to rt. The formed precipitate was collected by filtration, washed with MeOH, and recrystallized from EtOAc; yield: 280 mg (89%); colorless solid; mp 154–156 °C.

IR (ATR): 1620, 1597, 1574, 1497, 1464, 1395, 1344, 1302, 1288, 1258, 1229, 1211, 1190, 1063, 1034, 1024, 968, 895, 856, 843, 818, 756, 745 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.91–2.00 (m, 1 H), 2.02–2.12 (m, 1 H), 2.30–2.35 (m, 1 H), 2.42–2.53 (m, 1 H), 2.70–2.90 (m, 2 H), 3.18–3.38 (m, 2 H), 3.46–3.58 (m, 2 H), 5.67 (d, *J* = 10.1 Hz, 1 H), 6.72–6.76 (m, 1 H), 6.93 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 7.06–7.10 (m, 2 H), 7.34–7.38 (m, 1 H), 7.48–7.52 (m, 1 H), 7.64 (d, *J* = 9.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.9 (CH_2), 23.4 (CH_2), 25.9 (CH_2), 28.2 (CH_2), 42.2 (CH_2), 86.4 (CH), 113.1 (CH), 113.3 (C), 118.3 (CH), 119.5 (CH), 122.0 (CH), 123.4 (CH), 125.2 (C), 126.5 (CH), 127.2 (CH), 128.0 (CH), 128.6 (CH), 129.1 (CH, C), 132.9 (C), 144.4 (C), 153.0 (C).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{22}NO$: 316.1701; found: 316.1689.

(*E*)-1,1,1-Trifluoro-3-[(2-hydroxynaphthalen-1-yl)methyl]-4-(phenylamino)but-3-en-2-one (20)

A mixture of chromene **1a** (278 mg, 1 mmol) and aniline (93 mg, 1 mmol) in MeOH (3 mL) was heated under reflux for 10 min, and kept at rt for 30 min. The formed precipitate was collected by filtration and recrystallized from EtOH; yield: 308 mg (83%); colorless solid; mp 175–176 °C.

IR (ATR): 3400–2800, 1655, 1628, 1601, 1558, 1512, 1493, 1450, 1439, 1404, 1335, 1296, 1265, 1246, 1234, 1188, 1173, 1153, 1126, 1057, 995, 930, 907, 810, 748 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.12 (s, 2 H, CH_2), 7.09 (t, *J* = 7.6 Hz, 1 H, $H_{p\text{-Ph}}$), 7.14 (d, *J* = 7.8 Hz, 2 H, $H_{o\text{-Ph}}$), 7.23–7.27 (m, 2 H, H-3,6), 7.34–7.41 (m, 3 H, H-7, $H_{m\text{-Ph}}$), 7.68 (d, *J* = 8.9 Hz, 1 H, H-4), 7.74 (d, *J* = 8.0 Hz, 1 H, H-5), 7.95 (d, *J* = 13.8 Hz, 1 H, =CHN), 7.99 (d, *J* = 8.9 Hz, 1 H, H-8), 9.99 (d, *J* = 13.8 Hz, 1 H, NH), 11.21 (s, 1 H, OH).

^{13}C NMR (DMSO-d_6, 100 MHz): δ = 19.1 (CH_2), 108.8 (*C*–$COCF_3$), 116.9 (2 × $CH_{o\text{-Ph}}$), 117.1 (C-1), 117.9 (CH-3), 118.6 (q, $^1J_{C,F}$ = 290.8 Hz, CF_3), 123.5 (CH-6), 124.0 (CH-8), 124.9 ($CH_{p\text{-Ph}}$), 127.0 (CH-7), 128.97 (CH-5), 129.05 (CH-4), 129.4 (C-4a), 130.5 (2 × $CH_{m\text{-Ph}}$), 133.9 (C-8a), 139.9 (C_{Ph}), 146.7 (q, $^4J_{C,F}$ = 3.8 Hz, CHN), 151.3 (C-2), 176.0 (q, $^2J_{C,F}$ = 30.5 Hz, C=O).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}F_3NO_2$: 372.1211; found: 372.1201.

Funding Information

The work was supported by Russian Science Foundation (Grant No. 19-13-00421).

Acknowledgment

We thank Dr. V. B. Rybakov (Moscow State University) for the X-ray diffraction analysis, which was fulfilled using a STOE STADI VARI PILATUS-100K diffractometer purchased by MSU Development Program.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707209.

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