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Reactivity of α-arylidene benzoheteracyclanone dibromides toward azide ion: an effective approach to 3-(α-substituted-benzyl)chromones and -1-thiochromones

Tamás Patonay,* Zoltán Dinya, Albert Lévai and Dénes Molnár

Department of Organic Chemistry, University of Debrecen, P.O. Box 20, H-4010 Debrecen, Hungary

Dedicated to Professor Miklós Hollósi on the occasion of his 60th birthday

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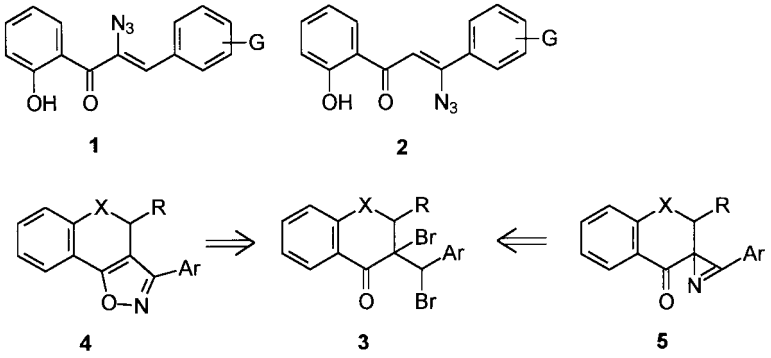
Abstract—Treatment of dibromides of 3-arylidenechromanones and -1-thiochromanones with sodium azide resulted in the formation of 3-(α-azidobenzyl)chromones and -1-thiochromones whereas dibromides having no antiperiplanar vicinal hydrogen in the ring such as flavanone, 1-thioflavanone and benzosuberone derivatives afforded only the parent enones by bromine elimination. Evidence supported the intermediacy of 3-(α-bromobenzyl)chromones and -1-thiochromones in this reaction. These postulated intermediates were prepared in an independent way and transformed into azides in high yield.

1. Introduction

Vinyl azides are valuable synthetic building blocks and have attracted considerable interest because of their manifold transformations.[1–6] Important subclasses of vinyl azides, namely α- and β-azidovinyl ketones, have also been studied thoroughly. The most effective methods for the synthesis of these latter compounds are the iodine azide addition to α,β-unsaturated ketones[5–9] and the eliminative azidation of α,β-dibromo ketones and esters.[2,5,6,10,11] Very recently, a CAN-mediated addition of azide leading to α-azidocinnamates and α-azido-α,β-unsaturated ketones via α-azido-β-nitrato esters and ketones was reported.[12] We have reported on the reaction of 2′-hydroxychalcone dibromides and related derivatives with sodium azide which gives α-azido-2′-hydroxychalcones **1** and several secondary products derived from the unstable regioisomeric β-azido-2′-hydroxychalcones **2**. The ratio of azide **1** and the products from azide **2**, i.e. the participation of the competing pathways, was highly dependent on the substituent G[13,14] (Scheme 1).

As a part of our interest in the synthetic applications of azido ketones, we have examined the analogous azidation reaction of dibromides **3** derived from exocyclic α,β-unsaturated ketones. In these substrates the lack of an α-hydrogen excludes the formation of any α-azidovinyl ketones. Consequently, they may serve as possible precursors of



Scheme 1.

Keywords: azides; chromones; dehalogenation; elimination reaction.

* Corresponding author. Tel.: +36-52-512-900; fax: +36-52-453-836; e-mail: tpatonay@tigris.klte.hu

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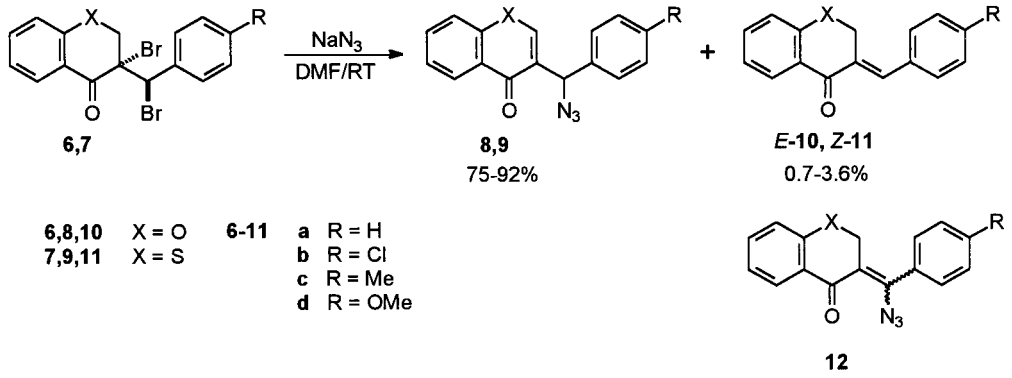


Scheme 2.

the tricyclic oxazoles **4** and spiroazirines **5** (Scheme 1). Herein, we summarize the results of our study.

2. Results and discussion

Treatment of (3*R**,α*S**)-3-bromo-3-(α-bromobenzyl)chromanones **6a**–**c**[†] and (3*R**,α*R**)-3-bromo-3-(α-bromobenzyl)-1-thiochromanones **7a**,**c**,**d**[†] with 3.3 equiv. of sodium azide in DMF solution led to the formation of 3-(α-azido-4-substituted-benzyl)chromones **8a**–**c** and 3-(α-azido-4-substituted-benzyl)-1-thiochromones **9a**,**c**,**d** in good yields (75–92%). A small amount (0.7–3.6%) of the parent 3-arylidenechromanones *E*-**10** and 3-arylidene-1-thiochromanones *Z*-**11** were also isolated but no formation of any expected 3-(α-azidoarylidene)benzoheteracyclanones **12** could be detected (Scheme 2).

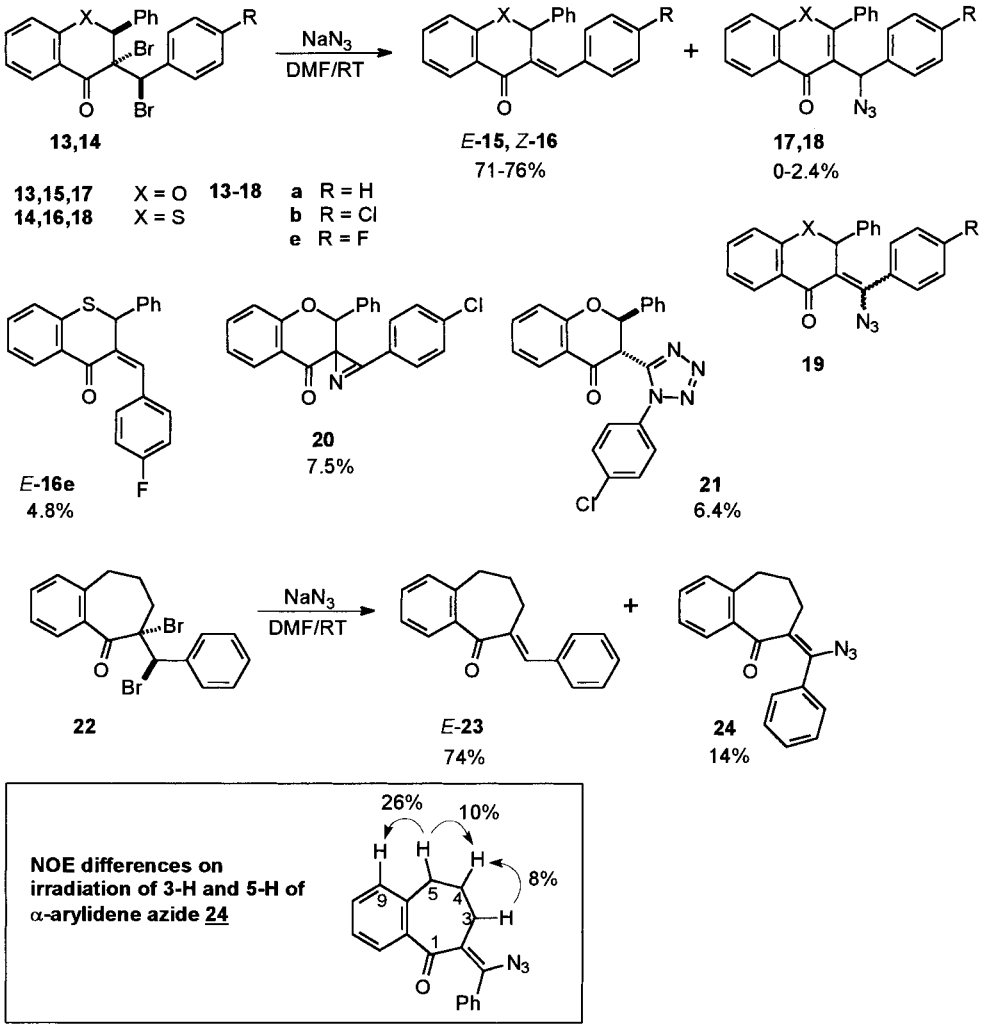
The position of the double bond in products **8** and **9** was unequivocally proven by the C=O bonds, located at relatively low wavenumbers (1610–1640 cm^{-1}) in their IR spectra which is characteristic for the highly conjugated chromone-type systems. The appearance of 2-H and α-H signals at low field (7.90–8.00 and ca. 6.00 ppm) in the ^1H NMR spectra, and the tertiary carbon C_α signal at 60–63 ppm in ^{13}C NMR spectra also supported the chromone structure. Finally, a small but characteristic long-range coupling (^4J~1 Hz) between protons 2-H and H_α was also observed in both series, which provided an additional proof for the allylic structure. In contrast with the similar reaction of chalcone dibromides, no marked effect of substituent *R* on the product ratio was observed.

Incorporation of a phenyl substituent into the 2-position of the (thio)chromanone skeleton resulted in a dramatic change in the product distribution. When (2*R**,3*R**,α*S**)-3-bromo-3-(α-bromobenzyl)flavanones **13a**,**c** and (2*R**,3*S**,α*S**)-3-bromo-3-(α-bromo-4-fluorobenzyl)flavanones **14e** were similarly reacted with sodium azide, the debrominated parent compounds *E*-**15a**,**c** and *Z*-**16e** were isolated as major products (71–76%) as well as some minor components (Scheme 3). The 3-(α-azidobenzyl)chromone-type derivative, which was the major product in the 2-unsubstituted chromanone series, was isolated in only one case, reaction of dibromide **13a** afforded a small amount (2.4%) of azide **17a**. The low yield indicates that this pathway is not preferred for these substrates.

In addition to the major product *Z*-**16e**, its diastereomer *E*-**16e** was also isolated from the reaction mixture of dibromide **14e**, and *E* diastereomers were detected by TLC in other cases as well. The appearance of these thermodynamically less stable diastereomers in the products could be rationalized in terms of either incomplete diastereoselectivity in the debromination step or a subsequent photoisomerization of the α,β-enones *E*-**15**, *Z*-**16** during column chromatography. Similar isomerization has already been observed in the field of aurones.[15]

As in the chromanone series, no α-azidoarylidene intermediate **19** was detected or isolated in any case of flavanone derivatives **13**,**14** but two interesting by-products were obtained from dibromide **9c**. The first, which was obtained in 7.5% yield, proved to be 2′-(4-chlorophenyl)-2-phenyl-spiro[chroman-3,3′-azirine]-4-one (**20**). The most characteristic NMR evidences for its structure were the flavanone-type 2-H at δ=5.90 ppm and C-2 signal at δ=81.9 ppm, the presence of a quaternary C(CO) type signal at δ=43.8 ppm and the appearance of a new quaternary C=N signal (δ=159.3 ppm) in place of the benzylic C_α signal which had disappeared from the spectrum. An IR band at 1762 cm^{-1} is characteristic for 1-azirines[16] and the loss of 4-chlorobenzonitrile identified in the MS spectrum furnished additional support for the constitution of the molecule. The other minor product obtained in 6.4% yield was identified as *trans*-3-[1-(4-chlorophenyl)-5-tetrazolyl]flavanone (**21**) on the basis of the following structural evidence. Doublets at δ=5.39 and 6.11 ppm with a large coupling constant (^3J=12.1 Hz) in the ^1H NMR spectrum together with the signals of two tertiary carbon signals at δ=65.3 and 81.8 ppm in the ^{13}C NMR spectrum, and the characteristic *m*/*z*=120 fragment in MS proved the presence of a *trans*-3-substituted flavanone moiety. The slight upfield shift of the 2′′,6′′-H signals in relation to the parent flavanone indicated the presence of an electron-donating substituent in the 3-position. The disappearance of the benzylic C_α signal and the appearance of a new quaternary carbon at δ=155.7 ppm, as well as the strong upfield shift of

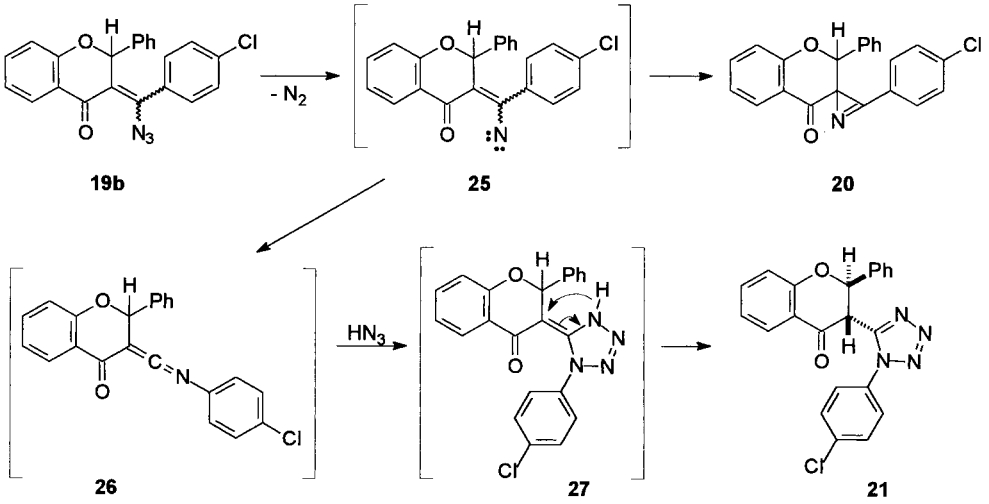
[†] Dibromides **3**,**9** with oxygen atom and derivatives **4**,**10** with sulfur atom in position 1 possess the same relative configuration, the difference in nomenclature is due to the change in the priority of the substituents at C-3 with the oxygen/sulfur change.



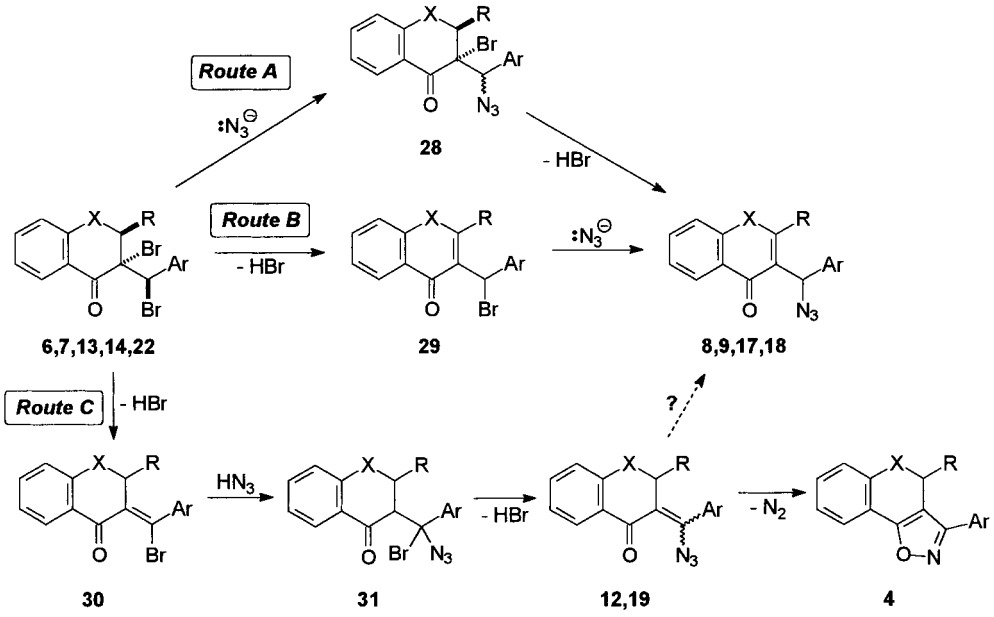
Scheme 3.

C-3 signal in relation to that of flavanone, also supported the structure. In spite of their low percentage yields, these compounds are of high importance since both of them should be derived from an intermediate vinyl azide **19b** (Scheme 4).

The formation of 1-azirines from either α-azidocinnamates[17,18] or β-azidovinyl aldehydes, ketones and esters,[1,2,4,5,19–22] and β-azido-α,β-unsaturated phosphorus derivatives[23] is well-documented. Tetrazole **21** may result from a keteneimine **26** by 1,3-dipolar cycloaddition and a



Scheme 4.



Scheme 5.

subsequent hydrogen migration. Formation of keteneimines from vinylazides including β-azidovinyl ketones and β-azido-α,β-unsaturated esters under photolytic or thermolytic conditions have been reported.[4,5,16,24] Recently, we observed the formation of 1-aryl-5-(2-chromonylmethyl)tetrazoles as by-products from *E*- and *Z*-2-α-bromostyrylchromones and sodium azide in hot DMF which could also be explained by an azide addition to an intermediate keteneimine.[25]

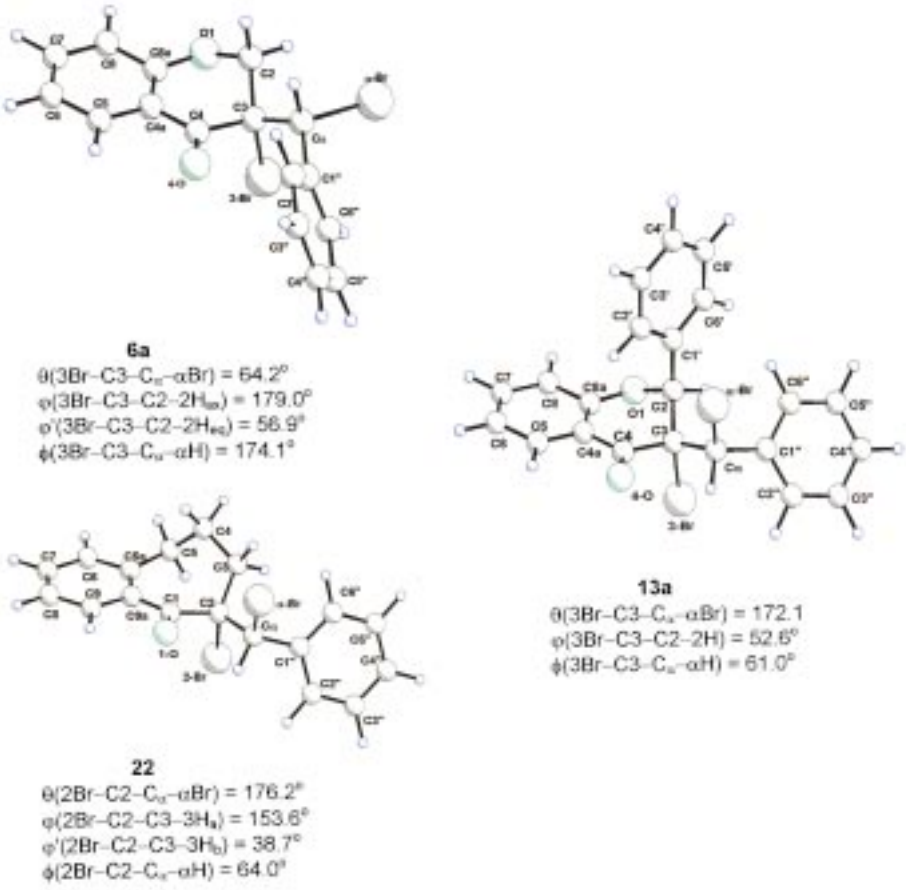
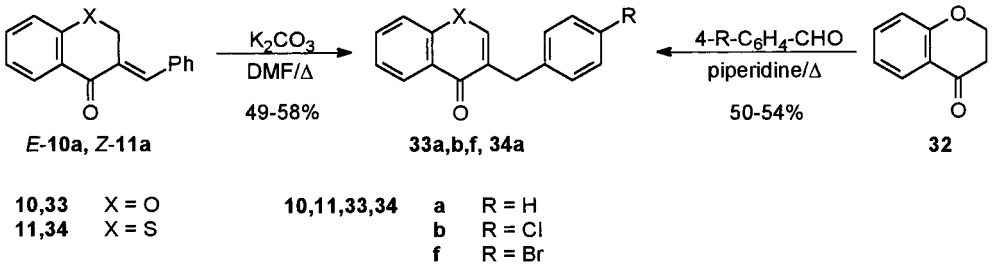


Figure 1. Optimized geometry of (3*R**,αS*)-3-bromo-3-(α-bromobenzyl)chromanone (**3a**), (2*R**,3*R**,α*S**)-3-bromo-3-(α-bromobenzyl)flavanone (**9a**) and (2*R**,αS*)-2-bromo-2-(α-bromobenzyl)-1-benzosuberone (**17**).



Scheme 6.

Our assumption that α-azidoarylidene derivatives **19** could be minor products in the reactions of dibromides **13**,**14** with azide ion, was also supported by the treatment of (2*R**,α*S**)-2-bromo-2-(α-bromobenzyl)-1-benzosuberone (**22**) with sodium azide. In this case, the major product (74%) parent α,β-enone (*E*-23) was accompanied by a smaller amount (14%) of *E*-2-(α-azidobenzylidene)-1-benzosuberone (**24**). The exocyclic double bond was unequivocally demostrated by the three adjacent CH_2 signals observed in the ^1H and ^{13}C NMR spectra. Relative configuration of azide **24** was determined by $^1H-\{^1H\}$ NOE experiments. Irradiation of 5-H gave a marked difference in the signals of both 6-H and 4-H while irradiation of 3-H gave an effect on 4-H only indicating a long distance between 3-H and the hydrogens of 2-phenyl group (Scheme 3). This relative configuration is in accordance with the reported[5,17,26] higher thermal stability of *trans*-β-azidovinyl ketones and esters in relation to their *cis* diastereomers.

On the basis of their products and product ratios, dibromides **3** could be divided into two subclasses. In the first group, the major products are α-azidobenzyl derivatives **8**,**9** while in the second, the debromination leading to formation of the parent enones **15**,**16**,**23** dominates. Elimination of Br_2 from *vic*-dibromides is a well-documented procedure. Variously substituted chalcone dibromides have been reported to give chalcones in the presence of soft nucleophiles such as iodides,[27] thiourea,[28,29] thiocarbanilide,[30] sodium hydrogen sulfide,[31] sodium hydrogen selenide,[32] and also with potassium fluoride–alumina under microwave irradiation[33] or tin(II)chloride,[34] hot pyridine[35] or even hot DMF.[36,37] Previously, we have also observed the formation of 2′-hydroxy-4-methoxychalcone among other products in the reaction of 2-hydroxy-4-methoxychalcone dibromide and sodium azide in DMF at room temperature.[14] It is very likely that the azide ion and not the DMF itself acts as nucleophile in the reaction of dibromides **3** since only an extremely slow conversion was observed for **3a** in pure DMF solution and the completion of the Br_2 elimination in the absence of azide ion required 7 weeks at room temperature.

The origin of 3-(α-azidobenzyl)-chromones **8**,**9** and -1-thiochromones **17**,**18** is a much more intriguing question, the possible routes leading to these derivatives are shown in Scheme 5.

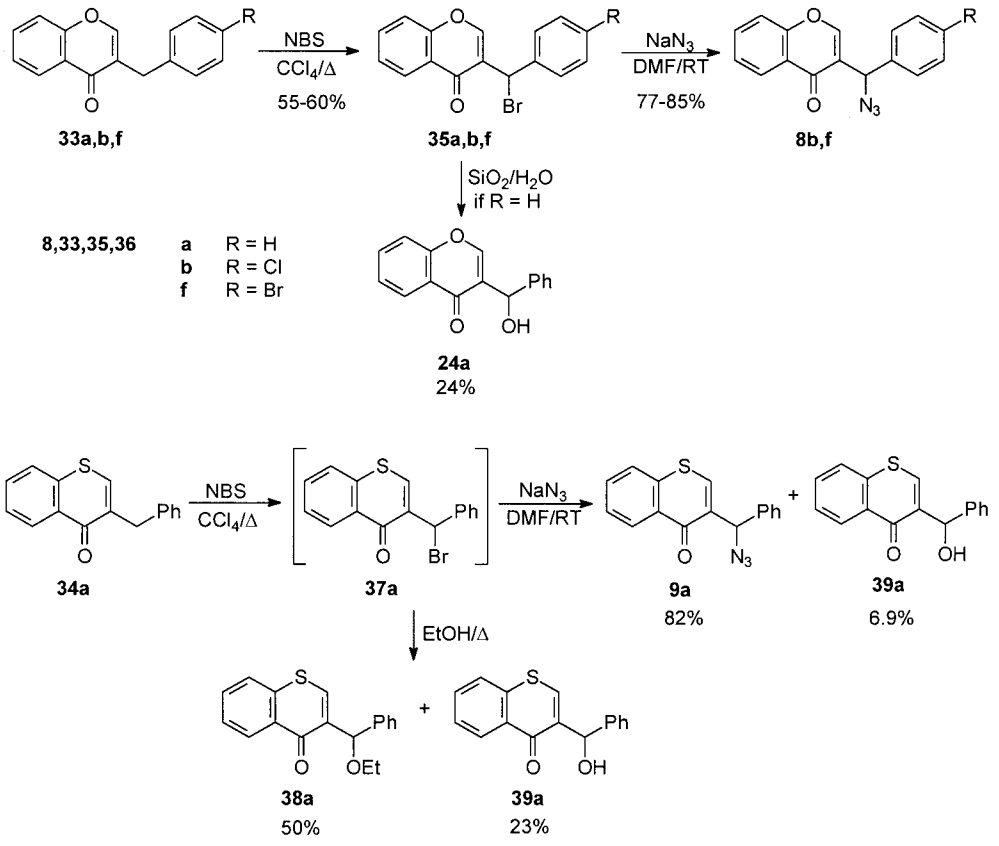
We can exclude route C since neither intermediate **30** nor **31** could be detected or isolated in any case and a **12**→**8**,**9**,**17**,**18** rearrangement at room temperature is very improbable in the light of literature data.[38–43] The observed lack of any marked substituent effect on the product ratio contradicts route A since its first S_N step should be sensitive to the electron-donating/withdrawing character of the substituent of the benzyl group. The intermediate **29** in route B with a doubly activated (allylic and benzylic) center at C_α is expected to be highly reactive and, therefore, to be less dependent on the electronic effects. At the same time, both routes A and B involve an HBr elimination step which requires an antiperiplanar[44] position of bromine and hydrogen atoms in the (hetero)ring to give the endocyclic double bond. The optimized[45] geometry of substrates **6**,**7**,**13**,**14** and **22** was determined and some selected results are shown in Fig. 1.

These calculations indicated antiperiplanar hydrogen and bromine atoms only in chromanones **6** and **7**. On the other hand, dibromides **13**,**14** and **22** contain nearly antiperiplanar bromine atoms as exemplified by substrates **13a** and **22**. As a consequence, dibromides **6** and **7** should afford 3-substituted chromones by HBr elimination whereas Br_2 elimination should be preferred for dibromides **13**,**14** and **22**, a reactivity pattern that fits well with the experimental facts.

To obtain more indirect proof for the intermediacy of bromide **29**, we decided to synthesize 3-(α-bromobenzyl)-chromones **35** and their thio analogues **37** and to study their reactivity. Since our attempts to obtain chromones **35** from dibromides **6** upon treatment with non-nuclophilic bases such as DABCO or DBU failed to give a single product, we explored another approach based on the bromination of the corresponding 3-benzyl derivatives **33**,**34**. Substrates **33b**,**f** with electron-withdrawing substituents in their benzyl group were prepared by a one-pot procedure[41] from chromanone (**32**) whereas chromones **33a** and **34a** were synthesized by the base-induced rearrangement of enones *E*-**10a** and *Z*-**11a** reported first by Donnelly et al.[38] (Scheme 6).

Treatment of 3-benzylchromones **33a**,**b**,**f** and **34a** with *N*-bromosuccinimide (NBS) furnished the corresponding bromides **35a**,**b**,**f** and **37a** but only products **35b**,**f** with electron-poor benzyl groups were sufficiently stable to be isolated in moderate (55–60%) yields (Scheme 7).

The presence of **35a** in the reaction mixture was supported by TLC but it disappeared during chromatography and only 3-(α-hydroxybenzyl)chromone (**36a**) was isolated as a product of hydrolysis. The solvolytic origin of **36a** was demonstrated by an experiment where thiochromone **34a** was brominated and the reaction mixture was directly

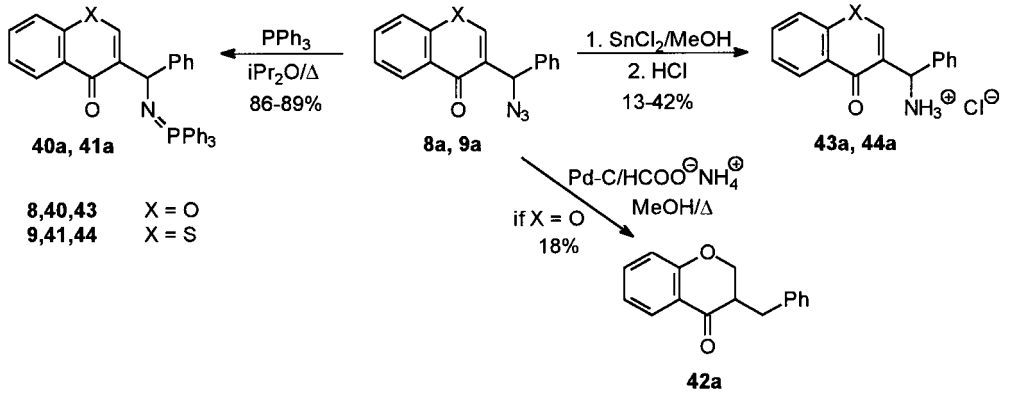


Scheme 7.

treated with excess of ethanol yielding 3-(α-ethoxybenzyl)-1-thiochromone (**38a**) and a small amount of alcohol **39a**. This is in accordance with the expected high reactivity of the bromides **35**,**37** which can be decreased by electron-withdrawing groups. It is noteworthy that Mallik and co-workers[46] have reported the formation of 3-(α-hydroxybenzyl)flavones in the reaction of 3-arylideneflavanones and NBS without any mechanistic details. Treatment of these alcohols with NaN_3 in TFA solution resulted in rearranged products, 3-(α-azidobenzyl)flavone was obtained only in a single case when the corresponding carbocation was destabilized by a nitro group.[47]

When bromides **35b**,**f**,**36a** (either in their isolated form or as a reaction mixture containing them) were reacted with sodium azide in DMF, the azides **8b**,**f** and **9a** were obtained in excellent (77–85%) yields. This result offers another easy entry to azides **8** and **9** starting from chromanones. The observed high reactivity of bromides **35**,**37** in conjunction with the above-mentioned lack of substituent effect on the product ratio in the azidolysis of dibromides **6** and **7** prompt us to favor route B (Scheme 5) over the route A.

3-(α-Azidobenzyl)chromones and thiochromones **8**,**9** are considered compounds of great synthetic value. Although no systematic studies have been conducted in this field, as a demonstration we transformed compounds **8a**,**9a** into iminophosphoranes **40a**,**41a** in excellent (86–89%) yields, the usefulness of iminophosphoranes is well-documented and reviewed.[48–53] Selective reduction of the azide functionality



Scheme 8.

to give the highly unstable allylic amines **43a**,**44a** was performed by treatment with $SnCl_2$/methanol.[54] Surprisingly, transfer hydrogenation of azide **8a** resulted in a complete reductive elimination of the azide functionality and 3-benzylchromanone (**42a**) was obtained as a sole product in poor yield (Scheme 8).

In conclusion, we have devised two simple, efficient and convenient methods for the synthesis of 3-(α-azidobenzyl)-chromones and -1-thiochromones **8**,**9**. Synthesis starting from dibromides **6**,**7** requires an antiperiplanar 2-H in the heteroring otherwise Br_2 elimination leading to the parent exocyclic α,β-enones occurs. Evidence supports the intermediacy of 3-(α-bromobenzyl)chromones and -1-thiochromones **35**,**37** in this approach. Bromides **35**,**37** were prepared in an independent way and transformed into azides **8**,**9** in high yields.

3. Experimental

3.1. General

Melting points were determined on a Boetius hot-stage apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer 16 PC FT-IR instrument in KBr pellets unless otherwise specified. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded with a Bruker WP 200 SY, ^{1}H NMR (360 MHz) spectra were measured with a Bruker AM 360 instrument in $CDCl_3$ solution (internal standard TMS, δ=0 ppm) unless otherwise stated.^{13}C NMR assignments were supported by J-echo technique. MS spectra were recorded with a VG 7035 GC-MS-DS system or VG Trio-2 (EI, 70 eV). Elemental analyses were performed in-house with a Carlo Erba 1106 EA instrument. $MgSO_4$ was used as drying agent, column chromatography was performed on Silica 60 (0.063–0.2 mm). Thin-layer chromatography (TLC) was performed on Kieselgel 60 F_{254} (Merck) sheets using toluene–ethyl acetate (4:1, v/v) or hexane–ethyl acetate (6:1, v/v) as developing systems. Dibromides **3**,**4**,**9**,**10** and **19** were prepared as described.[55]

3.1.1. Reaction of (3*R,α*S**)-3-bromo-3-(α-bromobenzyl)chromanone (6a) with sodium azide.** A solution of (3*R**,α*S**)-3-bromo-3-(α-bromobenzyl)chromanone (**6a**) (1.980 g, 4.999 mmol) and NaN_3 (1.076 g, 16.55 mmol) in abs. *N*,*N*-dimethylformamide (DMF) (20 mL) was stirred for 2 h at room temperature. The mixture was poured into crushed ice, the precipitation was filtered off and submitted to column chromatography (hexane–ethyl acetate (6:1, v/v)) to yield 9 mg (0.8%) of *E*-3-benzylidenechromanone[40] (*E*-**10a**) and 1.275 g (92%) of 3-(α-azidobenzyl)chromone (**8a**). **8a**. Colourless platelets. Mp 113–115°C (methanol). IR: 2102 (N_3), 1643 (C=O), 1624 (C=C), 1613, 1470, 1398, 1356, 1163, 760 cm^{-1}. ^{1}H NMR: 6.03 (brs, 1H, α-H), 7.30–7.45 (m, 7H, 6,8-H+Ph), 7.65 (ddd, *J*=8.0, 7.8, 1.9 Hz, 1H, 7-H), 7.91 (d, *J*=1.0 Hz, 1H, 2-H), 8.18 (dd, *J*=8.6, 1.9 Hz, 1H, 5-H). ^{13}C NMR: 60.4 (C_α), 118.1 (C-8), 123.7 (C-4a), 123.9 (C-3), 125.3 (C-6), 125.9 (C-5), 127.3 (C-2″,6″), 128.4 (C-4″), 128.8 (C-3,5″), 133.7 (C-1″), 133.8 (C-7), 154.2 (C-2), 156.3 (C-8a), 175.8 (C-4). MS: 249 (76, $M^{+\cdot}-N_2$), 248 (20, $M^{+\cdot}-N_3$), 235 (15), 221 (8), 220 (10), 207 (4), 191 (3), 172 (33), 165 (6), 146 (100, chromone skeleton), 128 (8), 120 (55, $C_7H_4O_2$), 118 (26), 104 (86), 92 (26), 90(30), 77 (30), 76 (16). Anal. calcd for $C_{16}H_{11}N_3O_2$ (277.28): C, 69.31; H, 4.00; N, 15.15%. Found: C, 69.14; H, 3.87; N, 15.33%.

3.1.2. Reaction of (3*R,α*S**)-3-bromo-3-(α-bromo-4-chlorobenzyl)chromanone (6b) with sodium azide.** (3*R**,α*S**)-3-Bromo-3-(α-bromo-4-chlorobenzyl)chromanone (**6b**) (2.150 g, 4.994 mmol) was reacted as given for dibromide **6a**. Work-up and column chromatography afforded 10 mg (0.7%) of *E*-3-(4-chlorobenzylidene)chromanone[40] (*E*-**10b**) and 1.324 g (85%) of 3-(α-azido-4-chlorobenzyl)-chromone (**8b**). **8b**. Colourless needles. Mp 82–84°C (methanol). IR: 2102 (N_3), 1640 (C=O), 1622 (C=C), 1612, 1490, 1466, 1400, 1356, 1320, 1242, 1164, 1088 (Ar–Cl), 800, 768, 756 cm^{-1}. ^{1}H NMR: 5.99 (s, 1H, α-H), 7.37 (m, 5H, 6,2″,3″,5″,6″-H), 7.45 (d, *J*=8.3 Hz, 1H, 8-H), 7.69 (ddd, *J*=8.8, 8.5, 1.5 Hz, 1H, 7-H), 7.97 (d, *J*=1.0 Hz, 1H, 2-H), 8.18 (dd, *J*=7.9, 1.4 Hz, 1H, 5-H). ^{13}C NMR: 59.9 (C_α), 118.1 (C-8), 123.9 (C-3, C-4a), 125.4 (C-6), 126.0 (C-5), 128.7 (C-2″,6″), 129.0 (C-3″,5″), 133.9 (C-7), 134.4 (C-1″), 136.4 (C-4″), 153.9 (C-2), 156.3 (C-8a), 175.6 (C-4). MS: 283 (17, $M^{+\cdot}-N_2$)+285 (6, isotope peak), 269 (6), 172 (14), 149 (11), 146 (100, chromone skeleton), 120 (23, $C_7H_4O_2$), 111 (9), 104 (28), 92 (19), 89 (14), 79 (10), 77 (14), 76 (10). Anal. calcd for $C_{16}H_{10}ClN_3O_2$ (311.73): C, 61.65; H, 3.23; N, 13.48%. Found: C, 61.75; H, 3.16; N, 13.22%.

3.1.3. Reaction of (3*R,α*S**)-3-bromo-3-(α-bromo-4-methylbenzyl)chromanone (6c) with sodium azide.** (3*R**,α*S**)-3-Bromo-3-(α-bromo-4-methylbenzyl)chromanone (**3c**) (2.050 g, 4.999 mmol) was reacted as given for dibromide **6a**. Work-up and column chromatography afforded 46 mg (3.6%) of *E*-3-(4-methylbenzylidene)chromanone[40] (*E*-**10c**) and 1.137 g (78%) of 3-(α-azido-4-methylbenzyl)-chromone (**8c**). **8c**. Colourless needles. Mp 126–128°C (hexane–ethyl acetate). IR: 3034, 2098 (N_3), 1640 (C=O), 1622 (C=C), 1468, 1400, 1358, 1164, 762 cm^{-1}. ^{1}H NMR: 2.32 (s, 3H, 4″-Me), 5.98 (brs, 1H, α-H), 7.17 (d, *J*=8.0 Hz, 2H, 3″,5″-H), 7.32 (d, *J*=8.0 Hz, 2H, 2″,6″-H), 7.36 (m, 1H, 6-H), 7.42 (d, *J*=8.6 Hz, 1H, 8-H), 7.63 (m, 1H, 7-H), 7.94 (d, *J*=1.0 Hz, 2-H), 8.17 (dd, *J*=7.9, 1.4 Hz, 1H, 5-H). ^{13}C NMR: 21.0 (4″-Me), 60.3 (C_α), 118.0 (C-8), 123.9 (C-4a), 124.2 (C-3), 125.2 (C-6), 126.0 (C-5), 127.2 (C-2″,6″), 129.4 (C-3″,5″), 133.7 (C-7), 134.6 (C-1″), 138.2 (C-4″), 154.0 (C-2), 156.3 (C-8a), 175.7 (C-4). MS: 263 (53, $M^{+\cdot}-N_2$), 262 (14), 249 (17, $M^{+\cdot}-N_3$), 248 (12), 234 (10), 220 (4), 172 (20), 146 (100, chromone skeleton), 129 (23), 120 (35, $C_7H_4O_2$), 118 (13), 104 (57), 92 (20), 91 (24), 90 (20), 77 (9), 76 (8). Anal. calcd for $C_{17}H_{13}N_3O_2$ (291.31): C, 70.09; H, 4.50; N, 14.42%. Found: C, 70.43; H, 4.47; N, 14.46%.

3.1.4. Reaction of (3*R,α*R**)-3-bromo-3-(α-bromobenzyl)-1-thiochromanone (7a) with sodium azide.** (3*R**,α*R**)-3-Bromo-3-(α-bromobenzyl)-1-thiochromanone (**7a**) (2.060 g, 4.998 mmol) was reacted as given for dibromide **6a**. Work-up and column chromatography afforded 40 mg (3.2%) of *Z*-3-benzylidene-1-thiochromanone[40] (*Z*-**11a**) and 1.221 g (83%) of 3-(α-azidobenzyl)-1-thiochromone (**9a**). **9a**. Off-white prisms. Mp 85–87.5°C

(hexane–ethyl acetate). IR: 2107 (N_3), 1613 (C=O+C=C), 1590, 1451, 1439, 1377, 1258, 1239, 748, 710 cm^{-1}. ^1H NMR: 6.19 (brs, 1H, α-H), 7.33 (m, 1H, 4″-H), 7.30–7.51 (m, 5H, 6,7,8,3″,5″-H), 7.57 (m, 2H, 2″,6″-H), 7.97 (d, J=0.8 Hz, 1H, 2-H), 8.52 (dd, J=7.8, 1.9 Hz, 1H, 5-H). ^{13}C NMR: 63.6 (C_α), 126.5, 127.8, 128.3, 129.0 (C-5,6,8,4″), 127.4, 128.7 (C-2″,3″,5″,6″), 131.4 (C-7), 131.6 (C-4a), 134.6 (C-3), 135.6 (C-2), 136.7 (C-8a), 137.8 (C-1″), 177.6 (C-4). MS: 265 (37, $M^{+\cdot}-N_2$), 264 (6, $M^{+\cdot}-N_2$–H), 251 (4), 237 (7), 236 (6), 188 (12, $M^{+\cdot}-N_2$–Ph), 162 (100, 1-thiochromone skeleton), 149 (3), 136 (15), 134 (67, 1-thiochromone–CO), 108 (14), 104 (41), 89 (17), 77 (17). Anal. calcd for $C_{16}H_{11}N_3OS$ (293.35): C, 65.51; H, 3.78; N, 14.32%. Found: C, 65.77; H, 3.65; N, 14.44%.

3.1.5. Reaction of (3*R,α*R**)-3-bromo-3-(α-bromo-4-methylbenzyl)-1-thiochromanone (7c) with sodium azide.** (3*R**,α*R**)-3-Bromo-3-(α-bromo-4-methylbenzyl)-1-thiochromanone (**7c**) (2.130 g, 4.998 mmol) was reacted as given for dibromide **6a**. Work-up and column chromatography afforded 10 mg (0.8%) of *Z*-3-(4-methylbenzylidene)-1-thiochromanone[40] (*Z*-**11c**) and 1.190 g (78%) of 3-(α-azido-4-methylbenzyl)-1-thiochromone (**9c**). **9c**. Yellowish oil. IR (neat): 3028, 2922, 2104 (N_3), 1614 (C=O+C=C), 1590, 1550, 1512, 1438, 1372, 1302, 1238, 1180, 1144, 1114, 820, 762, 746 cm^{-1}. ^1H NMR: 2.31 (s, 3H, 4″-Me), 6.15 (s, 1H, H_α), 7.16 (d, J=8.0 Hz, 2H, 3″,5″-H), 7.30 (d, J=8.0 Hz, 2H, 2″,6″-H), 7.45–7.62 (m, 3H, 6,7,8-H), 7.98 (s, 1H, 2-H), 8.51 (dd, J=7.5, 1.5 Hz, 1H, 5-H). MS: 279 (23, $M^{+\cdot}-N_2$), 265 (3), 188 (5, $M^{+\cdot}-N_2$–Bn), 162 (100, 1-thiochromone skeleton), 134 (26, 1-thiochromone–CO), 108 (10), 104 (18), 89 (15). Anal. calcd for $C_{17}H_{13}N_3OS$ (307.36): C, 66.43; H, 4.26; N, 13.67%. Found: C, 66.78; H, 4.07; N, 13.64%.

3.1.6. Reaction of (3*R,α*R**)-3-bromo-3-(α-bromo-4-methoxybenzyl)-1-thiochromanone (7d) with sodium azide.** (3*R**,α*R**)-3-Bromo-3-(α-bromo-4-methoxybenzyl)-1-thiochromanone (**7d**) (2.210 g, 4.998 mmol) was reacted as given for dibromide **6a**. Work-up and column chromatography afforded 48 mg (3.4%) of *Z*-3-(4-methoxybenzylidene)-1-thiochromanone[40] (*Z*-**11d**) and 1.217 g (75%) of 3-(α-azido-4-methoxybenzyl)-1-thiochromone (**9d**). **9d**. Yellowish oil. IR (neat): 3034, 2956, 2836, 2104 (N_3), 1614 (C=O+C=C), 1590, 1550, 1512, 1462, 1438, 1372, 1304, 1250 (C–O–C), 1176, 1112, 1034 (C–O–C), 834, 748 cm^{-1}. ^1H NMR: 3.78 (s, 3H, 4″-OMe), 6.13 (s, 1H, H_α), 6.90 (d, J=8.7 Hz, 2H, 3″,5″-H), 7.34 (d, J=8.7 Hz, 2H, 2″,6″-H), 7.47–7.60 (m, 3H, 6,7,8-H), 8.01 (s, 1H, H-2), 8.51 (dd, J=7.8, 1.2 Hz, 1H, 5-H). MS: 295 (35, $M^{+\cdot}-N_2$), 281 (7), 188 (5, $M^{+\cdot}-N_2$–$MeOC_6H_4$), 162 (100, 1-thiochromone skeleton), 134 (30, 1-thiochromone–CO), 108 (10), 104 (18), 89 (16). Anal. calcd for $C_{17}H_{13}N_3O_2S$ (323.36): C, 63.14; H, 4.05; N, 12.99%. Found: C, 63.36; H, 3.92; N, 13.12%.

3.1.7. Reaction of (2*R,3*R**,α*S**)-3-bromo-3-(α-bromobenzyl)flavanone (13a) with sodium azide.** (2*R**,3*R**,α*S**)-3-Bromo-3-(α-bromobenzyl)flavanone (**13a**) (2.360 g, 4.998 mmol) was reacted for 30 h as given for dibromide **6a**. Work-up and column chromatography afforded 1.186 g (76%) of *E*-3-benzylideneflavanone[56,57] (*E*-**15a**) and 41 mg (2.3%) of 3-(α-azidobenzyl)flavone (**17a**). **17a**. Colourless oil. IR (neat): 3062, 3030, 2098 (N_3), 1644 (C=O), 1622 (C=C), 1568, 1494, 1464, 1384, 1304, 1222, 1148, 1110, 1028, 760, 730, 698 cm_{-1}. ^1H NMR: 5.90 (s, 1H, α-H), 7.25–7.49 (m, 12H, 6,8-H+2xPh), 7.69 (ddd, J=8.6, 8.0, 1.6 Hz, 1H, 7-H), 8.26 (dd, J=7.9, 1.6 Hz, 1H, 5-H). ^{13}C NMR: 61.0 (C_α), 117.9 (C-8), 119.7 (C-3), 123.5 (C-4a), 125.4 (C-6), 126.2 (C-5), 126.4, 128.2, 128.5, 128.7 (C-2′,3′,5′,6′,2″,3″,5″,6″), 127.3 (C-4″), 130.8 (C-4′), 132.2 (C-1″), 134.0 (C-7), 137.9 (C-1′), 156.0 (C-8a, C-2),165.4 (C-2), 176.9 (C-4). MS: 325 (34, $M^{+\cdot}-N_2$), 324 (100), 312 (19), 311 (16), 248 (18), 233 (15), 222 (10), 221 (17), 207 (5), 194 (8), 191 (21), 165 (21), 121 (36, 2-$HOC_6H_4CO^{\oplus}$), 120 (28, $C_7H_4O_2$), 115 (5), 105 (6), 92 (20), 84 (13), 77 (11). Anal. calcd for $C_{22}H_{15}N_3O_2$ (353.38): C, 74.78; H, 4.28; N, 11.89%. Found: C, 74.51; H, 4.39; N, 11.65%.

3.1.8. Reaction of (2*R,3*R**,α*S**)-3-bromo-3-(α-bromo-4-chlorobenzyl)flavanone (13c) with sodium azide.** (2*R**,3*R**,α*S**)-3-Bromo-3-(α-bromo-4-chlorobenzyl)flavanone (**13c**) (2.000 g, 3.948 mmol) was reacted for 2 h as given for dibromide **6a**. Work-up and column chromatography (hexane–ethyl acetate (4:1, v/v)) afforded 967 mg (71%) of *E*-3-(4-chlorobenzylidene)flavanone[57] (*E*-**15c**), 107 mg (7.5%) of 2′-(4-chlorophenyl)-2-phenylspiro[chroman-3,3′-azirine]-4-one (**20**) and 102 mg (6.4%) of *trans*-3-[1-(4-chlorophenyl)-5-tetrazolyl]flavanone (**21**).

20. White crystal powder. Mp 182–187°C (hexane–ethyl acetate). IR: 1762 (C=N), 1684 (C=O), 1606, 1594, 1486, 1472, 1462, 1454, 1314, 1300, 1222 (C–O–C), 1100, 1018, 764, 700 cm^{-1}. ^1H NMR: 5.90 (s, 1H, 2-H), 7.07–7.21 (m, 2H, 6,8-H), 7.26 (m, 3H, 3‴,4‴,5‴-H), 7.33 (m, 2H, 2‴,6‴-H), 7.50 (d, J=8.5 Hz, 2H, 2″,6″-H), 7.57 (m, 1H, 7-H), 7.71 (d, J=8.5 Hz, 2H, 3″,5″-H), 7.95 (dd, J=7.8, 1.5 Hz, 1H, 5-H). ^{13}C NMR: 43.8 (C-3), 81.9 (C-2), 118.7 (C-8), 120.6, 122.7 (C-4a, C-4‴), 122.1 (C-6), 127.2 (C-5), 127.5, 128.5 (C-2″,3″,5″,6″), 128.7 (C-4″), 129.8 (C-2‴,6‴), 131.4 (C-3‴,5‴), 134.8 (C-1″), 136.5 (C-7), 140.1 (C-1‴), 159.3 (C-2′), 161.2 (C-8a). MS: 359 (45, $M^{+\cdot}$)+361 (16, isotope peak), 358 (84)+360 (34), 282 (39, $M^{+\cdot}-Ph$)+284 (15), 238 (8), 221 (100, $M^{+\cdot}-1-4$-ClC_6H_4CN), 194 (8), 165 (14), 150 (7), 137 (57, 4-$ClC_6H_4CN^{+\cdot}$)+139 (22), 121 (13, 2-$HOC_6H_4CO^{\oplus}$), 120 (25, $C_7H_4O_2$), 102 (51), 92 (25), 76 (22). Anal. calcd for $C_{22}H_{14}ClNO_2$ (359.81): C, 73.44; H, 3.92; N, 3.89%. Found: C, 73.12; H, 4.02; N, 3.97%.

21. White needles. Mp 168–171°C (hexane–ethyl acetate). IR: 3064, 2898, 1702 (C=O), 1608, 1430, 1326, 1300, 1228, 1110, 1092, 1024, 840, 760, 700 cm^{-1}. ^1H NMR: 5.39 (d, J=12.1 Hz, 1H, 3-H), 6.11 (d, J=12.1 Hz, 1H, 2-H), 6.93 (d, J=7.1 Hz, 2H, 2″,6″-H), 7.01–7.32 (m, 7H, 6,8-H+Ph), 7.65 (m, 1H, 7-H), 8.04 (d, 1H, J=7.8 Hz, 1H, 5-H). ^{13}C NMR: 65.3 (C-3), 81.8 (C-2), 118.4 (C-8), 119.4 (C-4″), 121.3 (C-4a), 123.0 (C-6), 126.5 (C-2″,6″), 128.0 (C-5), 129.0, 129.5, 130.1 (C-2′,3′,5′,6′,3′,6′), 129.9 (C-4″), 134.4 (C-1′), 137.7 (C-7), 137.9 (C-1″), 155.7 (tetrazole C), 161.2 (C-8a), 185.1 (C-4). MS: 402 (32, $M^{+\cdot}$)+404 (11, isotope peak), 374 (11, $M^{+\cdot}-CO$), 373 (13), 332 (83, $M^{+\cdot}-CO-N_3$)+334 (32), 253 (72)+255 (24), 222 (77, flavone skeleton), 209 (21), 181 (66), 152 (11), 121 (66, 2-$HOC_6H_4CO^{\oplus}$), 120 (100, $C_7H_4O_2$), 117 (28), 93

(23), 90 (36). Anal. calcd for $C_{22}H_{14}ClNO_2$ (402.84): C, 65.59; H, 3.75; N, 13.91%. Found: C, 65.23; H, 3.72; N, 13.57%.

3.1.9. Reaction of (2*R,3*S**,α*S**)-3-bromo-3-(α-bromo-4-fluorobenzyl)-1-thioflavanone (14e) with sodium azide.** A mixture of (2*R**,3*S**,α*S**)-3-bromo-3-(α-bromo-4-fluorobenzyl)-1-thioflavanone (**14e**) (1.518 g, 2.999 mmol), NaN_3 (646 mg, 9.933 mmol) and abs. DMF (12 mL) was stirred at room temperature for 3 h, a slightly exothermic reaction and some gas evolution was observed in the first 10 min. The mixture was poured on water, the precipitate was filtered off and crystallized from methanol to give 778 mg (75%) of *Z*-3-(4-fluorobenzylidene)-1-thiochromanone[56] (*Z*-**16e**). The evaporated mother liquor was submitted to column chromatography (eluent: toluene) and two fractions were collected. The more polar fraction was re-chromatographed on silica gel (eluent: hexane–acetone (4:1, v/v)) to give 14 mg (1.2%) of 3-(α-azido-4-fluorobenzyl)-1-thioflavone (**18e**). **18e**. Pale yellow oil. IR (neat): 3062, 2924, 2096 (N_3), 1626 (C=O), 1614 (C=C), 1592, 1538, 1510, 1436, 1338, 1226, 1158, 830, 746, 700 cm^{-1}. ^1H NMR: 5.96 (s, 1H, α-H), 6.90 (m, 2H, 6,8-H), 7.14–7.65 (m, 10H, 7-H+2″,3″,5″,6″-H+Ph), 8.54 (dd, *J*=7.9, 2.0 Hz, 1H, 5-H). ^{13}C NMR: 61.6 (C_α), 114.9 (d, $J_{C-F,\ ortho}$=21.4 Hz, C-3″,5″), 125.5, 128.0, 129.4 (C-5,6,8), 127.7 (d, $J_{C-F,\ meta}$=8.1 Hz, C-2″,6″), 128.5, 128.7 (C-2′,3′,5′,6′), 130.0 (C-4′), 131.2, 131.5 (C-4a,1′), 131.9 (C-7), 134.3 (C-1″), 135.1, 136.9 (C-3,8a), 154.8 (C-2), 161.7 (d, $J_{C-F,\ ipso}$=246 Hz, C-4″), 178.7 (C-4). Anal. calcd for $C_{22}H_{14}FN_3OS$ (387.43): C, 68.20; H, 3.64; N, 10.85%. Found: C, 68.43; H, 3.39; N, 10.59%.

The less polar fraction was re-chromatographed on silica gel (eluent: toluene-1,2-dichloroethane (2:1, v/v)) to afford 50 mg (4.8%) of *E*-3-(4-fluorobenzylidene)-1-thiochromanone[56] (*E*-**16e**) and 45 mg (4.3%) of *Z*-isomer (*Z*-**16e**). *E*-**16e**. Yellow oil. IR (neat): 3060, 2926, 1660 (C=O), 1614 (C=C), 1600, 1504, 1434, 1294, 1224, 1158, 1072, 970, 834, 742, 728 cm^{-1}. ^1H NMR: 5.26 (s, 1H, 2-H), 6.71 (s, 1H, α-H), 6.97 (m, 2H, 6,8-H), 7.15–7.62 (m, 10H, 7-H+2″,3″,5″,6″-H+Ph), 8.10 (d, *J*=8.0 Hz, 5-H). ^{13}C NMR: 45.4 (C-2), 116.0 (d, $J_{C-F,\ ortho}$=21.4 Hz, C-3″,5″), 126.0 (C-6), 127.7, 128.6 (C-2′,3′,5′,6′), 128.2 (d, $J_{C-F,\ meta}$= 4.5 Hz, C-3″,5″), 129.6, 131.2, 131.4 (C-5,8,4′), 130.9 (C-4a), 132.1 (C-3)*, 135.0 (C-1‴), 136.7 (C-1')*, 137.3 (C_α), 139.4 (C-8a), 163.0 (d, $J_{C-F,\ ipso}$=252 Hz, C-4″), 186.0 (C-4). *Interchangeable signals. MS: 346 (100, $M^{+\cdot}$), 345 (17, $M^{+\cdot}-1$), 332 (12), 317 (7, $M^{+\cdot}-HCO$), 282 (9), 237 (12, $M^{+\cdot}-FC_6H_4CH^{\oplus}$), 210 (45, RDA fragment), 209 (52, RDA fragment-1), 183 (14), 137 (26, $2\text{-}HSC_6H_4CO^{\oplus}$), 136 (24, C_7H_4OS), 108 (19, C_7H_4OS-CO), 83 (91, $FC_5H_4^{\oplus}$). Anal. calcd for $C_{22}H_{15}FOS$ (346.41): C, 76.28; H, 4.36%. Found: C, 76.02; H, 4.40%.

3.1.10. Reaction of (2*R,α*S**)-2-bromo-2-(α-bromobenzyl)-1-benzosuberone (22) with sodium azide.** (2*R**,α*S**)-2-Bromo-2-(α-bromobenzyl)-1-benzosuberone (**22**) (1.020 g, 2.499 mmol) was reacted as given for dibromide **6a**. Work-up and column chromatography (eluent: 1,2-dichloroethane–toluene (3:1, v/v)) afforded 462 mg (74%) of *E*-2-benzylidene-1-benzosuberone[58] (*E*-23) and 102 mg (14%) of *E*-2-(α-azidobenzylidene)-1-benzosuberone (**24**). **24**. Yellowish oil. IR (neat): 3060, 2942, 2860, 2106 (N_3), 1668 (C=O), 1596, 1448, 1304, 1266, 1246, 972, 958, 766 cm^{-1}. ^1H NMR: 2.13 (m, 2H, 4-H), 2.74 (t, 2H, 3-H), 3.06 (t, 2H, 5-H), 7.23–7.39 (m, 7H, 7,9-H+Ph), 7.47 (m, 1H, 8-H), 7.80 (dd, *J*=7.7, 1.4 Hz, 1H, 9-H). ^{13}C NMR: 23.5 (C-4), 30.8, 32.1 (C-3,5), 127.0 (C-8), 128.1, 128.5 (C-2″,3″,5″,6″), 128.7, 129.6, 130.1 (C-6,9,4″), 133.3 (C-7), 133.8 (C-1″), 136.5 (C-9a), 140.6, 141.0, 141.6 (C-2,5a, C_α), 193.5 (C-1). Anal. calcd for $C_{18}H_{15}N_3O$ (289.33): C, 74.72; H, 5.23; N, 14.52%. Found: C, 74.29; H, 5.21; N, 14.77%.

3.1.11. *N*,*N*-Dimethylformamide-induced elimination of (3*R,α*S**)-3-bromo-3-(α-bromo-benzyl)chromanone (6a).** A solution of (3*R**,α*S**)-3-bromo-3-(α-bromobenzyl)-chromanone (**6a**) (800 mg, 2.020 mmol) in abs. DMF (15 mL) allowed to stand at room temperature. The reaction was monitored by TLC for the disappearence of starting material. After 7 weeks, the mixture was poured into 0.5% Na_2SO_3 solution (100 mL) and extracted with dichloromethane (3×20 mL). The dried solution was concentrated in vacuo and submitted to column chromatography (eluent: toluene–ethyl acetate (4:1, v/v)) to give 203 mg (43%) of *E*-3-benzylidenechromanone[56] (*E*-**10a**) and 153 mg (30%) of 3-(α-hydroxybenzyl)chromone (**36a**). **36a**. Mp 121–123°C (hexane–ethyl acetate), lit.[59] mp 120°C. IR: 3420 (OH), 1636 (C=O), 1618, 1606, 1570, 1466, 1420, 1402, 1350, 1318, 1158, 1142, 1036, 862, 762, 742, 728, 704 cm^{-1}. ^1H NMR: 3.01 (brs, 1H, α-OH), 5.93 (s, 1H, α-H), 7.32–7.50 (m, 7H, 6,8-H+Ph), 7.64 (s, 1H, 2-H), 7.66 (m, 1H, 7-H), 8.21 (dd, *J*=8.1, 1.6 Hz, 5-H). ^{13}C NMR: 70.4 (C_α), 118.1 (C-8), 123.8, 126.4 (C-3,4a), 125.3, 125.7 (C-5,6), 126.6 (C-4″), 127.9, 128.5 (C-2″,3″,5″,6″), 134.0 (C-7), 140.6 (C-1″), 153.7 (C-2), 156.0 (C-8a), 178.2 (C-4). MS: 252 (100, $M^{+\cdot}$), 251 (29, $M^{+\cdot}-1$), 234 (17, $M^{+\cdot}-H_2O$), 233 (16, $M^{+\cdot}-1-H_2O$), 222 (24, $M^{+\cdot}-CH_2O$), 221 (28, $M^{+\cdot}-CH_2O-1$), 205 (37, $M^{+\cdot}-1-H_2O-CO$), 173 (48, $M^{+\cdot}-1-PhH$), 146 (22. chromone skeleton), 121 (41, $2\text{-}HOC_6H_4CO^{\oplus}$), 105 (24, $PhCO^{\oplus}$), 92 (20), 90 (20), 77 (69). Anal. calcd for $C_{16}H_{12}O_3$ (252.26): C, 76.18; H, 4.79%. Found: C, 76.33; H, 4.77%.

3.1.12. 3-Benzylchromone (33a). A mixture of *E*-3-benzylidenechromanone[56] (*E*-**10a**) (1.665 g, 7.047 mmol), anh. K_2CO_3 (1.665 g, 12.048 mmol) and abs. DMF (85 mL) was refluxed for 5 h, then poured into brine and extracted with ethyl acetate (5×50 mL). After drying, the solvent was removed under reduced pressure and the residue was submitted to column chromatography (eluent: toluene–ethyl acetate (8:1, v/v)) to afford 808 mg (49%) of pure **33a** as brownish prisms, Mp 110–111°C (methanol), lit.[60] mp 109–111°C. IR: 1646 (C=O), 1611 (C=C), 1466, 1398, 1355, 1318, 1143, 762, 758 cm^{-1}. ^1H NMR: 3.82 (d, *J*=0.8 Hz, 2H, α-H), 7.25 (m, 1H, 6-H), 7.31 (s, 1H, Ph), 7.40 (d, *J*=7.1 Hz, 1H, 8-H), 7.61 (d, *J*=0.8 Hz, 1H, 2-H), 7.63 (m, 1H, 7-H), 4.54 (dd, *J*=7.8, 1.5 Hz, 1H, 5-H). ^{13}C NMR: 31.5 (C_α), 118.1 (C-8), 124.0, 124.7 (C-3,4a), 125.0, 126.1 (C-5,6), 126.6 (C-4″), 128.7, 129.1 (C-2″,3″,5″,6″), 133.5 (C-7), 138.77 (C-1″), 153.3 (C-2), 156.6 (C-8a), 177.6 (C-4). Anal. calcd for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12%. Found: C, 81.09; H, 4.97%.

3.1.13. 3-(4-Chlorobenzyl)chromone (33b). A mixture of 4-chromanone (**32**) (7.400 g, 49.946 mmol), 4-chlorobenzaldehyde (7.025 g, 49.976 mmol) and piperidine (3.0 mL, 34.281 mmol) was heated at 150°C for 5 h. The solidified residue was treated with methanol, filtered off and recrystallized to give 6.768 g (50%) of pure chromone **33b** as colourless needles. Mp 140.5–141.5°C (methanol), lit.[61] mp 140°C. IR: 1643 (C=O), 1608 (C=C), 1490, 1463, 1399, 1362, 1318, 1148, 1087, 1014, 764, 758 cm^{-1}. ^1H NMR: 3.78 (s, 2H, α-H), 7.25 (s, 4H, 2″,3″,5″,6″-H), 7.36–7.43 (overlapping m's, 2H, 6,8-H), 7.65 (m, 1H, 7-H), 7.66 (s, 1H, 2-H), 8.22 (d, *J*=8.0, 1.8 Hz, 1H, 5-H). ^{13}C NMR: 31.1 (C_α), 118.0 (C-8), 123.8, 124.1 (C-3,4a), 125.0, 125.9 (C-5,6), 128.6 (C-2″,6″), 130.2 (C-3″,5″), 132.3 (C-4″), 133.5 (C-7), 137.2 (C-4″), 152.9 (C-2), 156.4 (C-8a), 177.3 (C-4).

3.1.14. 3-(4-Bromobenzyl)chromone (33f). 4-Chromanone (**32**) (3.702 g, 24.986 mmol) and 4-bromobenzaldehyde (4.630 g, 25.023 mmol) were reacted as given for chromone **33b** to afford 4.253 g (54%) of product **33f** as off-white prisms. Mp 152–154°C (methanol), lit.[43] mp 155.0–156.9°C. IR: 1641 (C=C), 1609 (C=C), 1571, 1488, 1463, 1398, 1351, 1310, 1147, 1010, 764, 757 cm^{-1}. ^1H NMR: 3.76 (s, 2H, α-H), 7.19 (d, *J*=8.4 Hz, 2H, 2″,6″-H), 7.40 (overlapping d and m's, 4H, 6,8,3″,5″-H), 7.65 (m, 1H, 7-H), 7.66 (s, 1H, 2-H), 8.22 (dd, *J*=8.0, 1.7 Hz, 1H, 5-H). ^{13}C NMR: 31.1 (C_α), 118.1 (C-8), 120.5 (C-4″), 124.0, 124.2 (C-3,4a), 125.2, 126.1 (C-5,6), 130.8 (C-2″,6″), 131.8 (C-3″,5″), 133.7 (C-7), 137.9 (C-1″), 153.2 (C-2), 156.7 (C-8a), 177.5 (C-4). Anal. calcd for $C_{16}H_{11}BrO_2$ (315.16): C, 60.98; H, 3.52%. Found: C, 61.21; H, 3.37%.

3.1.15. 3-Benzyl-1-thiochromone (34a). *Z*-3-Benzylidene-1-thiochromanone[40] (*Z*-**11a**) (3.500 g, 13.871 mmol) was reacted as given for chromone **33a** (reaction period: 2 h) to afford 2.017 g (58%) of thiochromone **34a** as off-white prisms. Mp 59–61°C (diisopropyl ether). IR: 1614 (C=O+C=C), 1588, 1546, 1436, 1374, 1262, 1074, 948, 752, 744, 704 cm^{-1}. ^1H NMR: 4.00 (s, 2H, α-H), 7.19–7.39 (m, 7H, 6,8-H+Ph), 7.52 (m, 1H, 7-H), 7.54 (s, 1H, 2-H), 8.60 (dd, *J*=7.5, 1.3 Hz, 1H, 5-H). ^{13}C NMR: 37.7 (C_α), 126.4, 126.5 (C-6,4″), 127.4 (C-2), 128.6, 129.5 (C,2″,3″,5″,6″), 129.0, 131.0 (C-5,8), 131.6 (C-4a), 134.1 (C-7), 136.7, 137.2 (C-3,8a), 138.7 (C-1″), 179.0 (C-4). Anal. calcd for $C_{16}H_{12}OS$ (252.33): C, 76.16; H, 4.79%. Found: C, 76.35; H, 4.59%.

3.1.16. NBS Bromination of 3-benzylchromone (33a). A solution of 3-benzylchromone (**33a**) (808 mg, 3.420 mmol), *N*-bromosuccinimide (NBS) (730 mg, 4.101 mmol) and dibenzoyl peroxide (50 mg, 0.206 mmol) in carbon tetrachloride (30 mL) was refluxed for 6 h. The precipitated succinimide was filtered off, the filtrate was washed with satd $NaHCO_3$ solution and water, and dried. The solvent was removed under reduced pressure and residue was submitted to column chromatography (eluent: toluene–ethyl acetate (8:1, v/v)) to afford 203 mg (24%) of 3-(α-hydroxybenzyl)-chromone (**36a**). Mp 122–123°C.

3.1.17. 3-(α-Bromo-4-chlorobenzyl)chromone (35b). A solution of 3-(4-chlorobenzyl)chromone (**33b**) (1.360 g, 5.024 mmol), NBS (1.070 g, 6.012 mmol) and benzoyl peroxide (60 mg, 0.248 mmol) in carbon tetrachloride (50 mL) was refluxed for 2 h and 30 min. The precipitated succinimide was filtered off, the filtrate was washed with satd $NaHCO_3$ solution and water, and dried. The solvent was removed under reduced pressure and residue was crystallized from hexane–ethyl acetate (1:1, v/v) to give 1.023 g (58%) of chromone **35b** as colourless platelets. Mp 151–153°C. IR: 1644 (C=O), 1620 (C=C), 1466, 1398, 1354, 1318, 1142, 1090, 762, 756 cm^{-1}. ^1H NMR: 6.40 (s, 1H, α-H), 7.33 (d, *J*=8.7 Hz, 2H, 2″,6″), 7.34 (m, 1H, 6-H), 7.45 (overlapping d and dd, 3H, 8,3″,5″-H), 7.70 (m, 1H, 7-H), 8.14 (d, *J*=0.8 Hz, 1H, 2-H), 8.22 (dd, *J*=8.1, 1.8 Hz, 1H, 5-H). ^{13}C NMR: 44.5 (C_α), 118.1 (C-8), 123.5 (C-4a), 125.1 (C-3), 125.6, 126.1 (C-5,6), 128.9, 129.5 (C-2″,3″,5″,6″), 134.1 (C-7), 134.3 (C-4″), 137.8 (C-1″), 156.2 (C-8a), 156.3 (C-2), 174.9 (C-4). MS: 269 (100, $M^{+\cdot}-Br$)+271 (36, Cl isotope peak), 234 (14, $M^{+\cdot}-Br-Cl$), 205 (5), 178 (7), 176 (5), 149 (65, $M^{+\cdot}-Br$–RDA fragment [$C_7H_4O_2$]), 121 (13, 2-$HOC_6H_4CO^{\oplus}$), 117 (15), 114 (10), 92 (11). Anal.calcd for $C_{16}H_{10}BrClO_2$ (349.61): C, 54.97; H, 2.88%. Found: C, 54.58; H, 2.95%.

3.1.18. 3-(α,4-Dibromobenzyl)chromone (35f). 3-(4-Bromobenzyl)chromone (**33f**) (2.835 g, 8.995 mmol) was reacted as given for chromone **35b**. Work-up and crystallization from hexane–ethyl acetate (1:1, v/v) afforded 1.949 g (55%) of chromone **35f** as colourless needles. Mp 139–141°C. IR: 1640 (C=O), 1609 (C=C), 1466, 1401, 1356, 1165, 1105, 766, 740, 707 cm^{-1}. ^1H NMR: 6.38 (s, 1H, α-H), 7.40–7.52 (m, 6H, 6,8,2″,3″,5″,6″-H), 7.70 (m, 1H, 7-H), 8.14 (d, *J*=1.0 Hz, 1H, 2-H), 8.22 (dd, *J*=8.2, 1.9 Hz, 1H, 5-H). ^{13}C NMR: 44.5 (C_α), 118.0 (C-8), 122.4 (C-4″), 123.4, 125.0 (C-3,4a), 125.5, 126.0 (C-5,6), 129.7 (C-2″,6″), 129.7 (C-2″,6″), 131.8 (C-3″,5″), 134.0 (C-7), 138.3 (C-1″), 156.2 (C-8a), 156.3 (C-2), 175.0 (C-4). Anal. calcd for $C_{16}H_{10}Br_2O_2$ (394.06): C, 48.77; H, 2.56%. Found: C, 48.98; H, 2.43%.

3.1.19. 3-(α-Ethoxybenzyl)-1-thiochromone (38a) and 3-(α-hydroxybenzyl)-1-thiochromone (39a). 3-Benzyl-1-thiochromone (**34a**) (566 mg, 2.243 mmol), NBS (480 mg, 2.697 mmol), dibenzoyl peroxide (33 mg, 0.136 mmol) in carbon tetrachloride (20 mL) was refluxed for 105 min. The precipitated succinimide was filtered off, the filtrate was washed with satd $NaHCO_3$ solution and water, and dried. After removal of the solvent under reduced pressure, abs. ethanol (5 mL) was added and the mixture was refluxed for 1 h, then concentrated and submitted to column chromatography (eluent: toluene–ethyl acetate (8:1, v/v)) to afford 330 mg (50%) of 3-(α-ethoxybenzyl)-1-thiochromone (**38a**) and 140 mg (23%) 3-(α-hydroxybenzyl)-1-thiochromone (**39a**).

38a. Off-white prisms. Mp 96–97.5°C (hexane–ethyl acetate). IR: 3056, 2973, 2892, 1584, 1566, 1456, 1437, 1382, 1093, 1072, 745, 707 cm^{-1}. ^1H NMR: 1.20 (t, *J*=7.2 Hz, 3H, CH_2CH_3), 3.49 (q, *J*=7.2 Hz, 2H, CH_2CH_3), 5.74 (s, 1H, α-H), 7.16–7.53 (m, 8H, 6,7,8-H+Ph), 8.09 (d, *J*=0.6 Hz, 1H, 2-H), 8.45 (dd, *J*=9.1, 1.1 Hz, 1H, 5-H). ^{13}C NMR: 15.3 (CH_2CH_3), 64.6 (CH_2CH_3), 77.7 (C_α), 126.4 (C-6), 127.2 (C-2″,6″), 127.5 (C-4″), 128.2 (C-3″,5″), 128.9, 131.1 (C-5,8), 131.9 (C-4a), 137.0, 137.3 (C-3,8a), 140.7 (C-1″), 177.9 (C-4). MS: 267 (100,

$M^{+\cdot}-HCO$), 252 (10, $M^{+\cdot}-C_2H_4O$), 221 (8,, $M^{+\cdot}-HCO-EtOH$), 189 (87, $M^{+\cdot}-HCO-PhH$), 133 (12, $C_8H_5S^{\oplus}$), 115 (22), 89 (18), 77 (33). MS (Thermospray): 297 (36, M+1), 283 (7), 251 (100, M+1−EtOH), 223 (19). Anal. calcd for $C_{18}H_{16}O_2S$ (296.38): C, 72.95; H, 5.44%. Found: C, 73.12; H, 5.40%.

39a. Off-white needles. Mp 130–133°C (hexane–diisopropyl ether). IR: 3446 (OH), 1610 (C=O+C=C), 1588, 1438, 1410, 1018, 864, 752, 714 cm^{-1}. ^1H NMR: 4.05 (brs, 1H, α-OH), 5.94 (s, 1H, α-H), 7.12–7.56 (m, 8H, 5,6,7-H+Ph), 7.64 (s, 1H, 2-H), 8.49 (dd, *J*=7.7, 0.9 Hz, 1H, 5-H). ^{13}C NMR: 73.3 (C_α), 126.4 (C-6), 126.8 (C-2″,6″), 127.7 (C-4″), 128.4 (C-3″,5″), 128.8, 131.4 (C-5,8), 131.6 (C-4a), 135.5 (C-7), 137.1, 137.7 (C-3,8a), 141.0 (C-1″), 179.5 (C-4). Anal. calcd for $C_{16}H_{12}O_2S$ (268.33): C, 71.62; H, 4.51%. Found: C, 71.59; H, 4.78%.

3.1.20. 3-(α-Azido-4-chlorobenzyl)chromone (8b). A solution of 3-(α-bromo-4-chlorobenzyl)chromone (**35b**) (524 mg, 1.499 mmol) and NaN_3 (293 mg, 4.507 mmol) in abs. DMF (20 mL) was stirred for 3 and 30 min, poured into water, extracted with dichloromethane (3×50 mL), the combined organic phases were washed with water (2×50 mL) and dried ($CaCl_2$). The solvent was removed under reduced pressure and the residues were crystallized from hexane to give 390 mg (77%) of azide **8b**. Mp 83–84°C.

3.1.21. 3-(α-Azido-4-bromobenzyl)chromone (8f). 3-(α,4-Dibromobenzyl)chromone (**35f**) (394 mg, 1.000 mmol) was reacted as given for **35b**. Work-up and crystallization from hexane afforded 304 mg (85%) of azide **8f** as colourless prisms. Mp 96–97.5°C. IR: 2102 (N_3), 1640 (C=C), 1622 (C=C), 1468, 1400, 1358, 1320, 1274, 1240, 1164, 1072, 1012, 856, 798, 766 cm^{-1}. ^1H NMR: 6.00 (s, 1H, α-H), 7.36 (d, *J*=8.7 Hz, 2H, 2″,6″-H), 7.40 (m, 1H, 6-H), 7.45 (m, 1H, 8-H), 7.53 (d, *J*=8.7 Hz, 2H, 3″,5″-H), 7.71 (ddd, *J*=8.6, 7.1, 1.5 Hz, 7-H), 7.98 (d, *J*=0.9 Hz, 1H, 2-H), 8.20 (dd, *J*=8.0, 1.8 Hz, 1H, 5-H). ^{13}C NMR: 59.8 (C_α), 118.1 (C-8), 122.5 (C-4″), 123.5, 123.6 (C-3,4a), 125.4, 125.8 (C-5,6), 129.0 (C-2″,6″), 131.9 (C-3″,5″), 134.0 (C-7), 136.6 (C-1″), 153.8 (C-2), 156.2 (C-8a), 175.8 (C-4). Anal. calcd for $C_{16}H_{10}BrN_3O_2$ (356.17): C, 53.95; H, 2.83; N, 11.80%. Found: C, 54.11; H, 2.66; N, 11.59%.

3.1.22. 3-(α-Azidobenzyl)-1-thiochromone (9a) and 3-(α-hydroxybenzyl)-1-thiochromone (39a). 3-Benzyl-1-thiochromone (**34a**) (505 mg, 2.001 mmol), NBS (428 mg, 2.405 mmol), dibenzoyl peroxide (30 mg, 0.124 mmol) in carbon tetrachloride (18 mL) was refluxed for 1 and 45 min. The precipitated succinimide was filtered off, the filtrate was washed with satd $NaHCO_3$ solution and water, then dried and concentrated. The residue was dissolved in abs. DMF (25 mL), NaN_3 (391 mg, 6.013 mmol) was added and the mixture was stirred for 3 h and 30 min at room temperature, then poured into water and extracted with dichloromethane (3×50 mL). After drying and evaporation, the oily residue was submitted to column chromatography (eluent: toluene–ethyl acetate (8:1, v/v)) to afford 487 mg (82%) of azide **9a**, mp 79.5–80°C (hexane) and 37 mg (6.9%) of alcohol **39a**, mp 131–132.5°C (hexane).

3.1.23. 3-[α-[(Triphenylphosphoranylidene)amino]benzyl]-chromone (40a). A solution of 3-(α-azidobenzyl)chromone (**8a**) (416 mg, 1.500 mmol) and triphenylphosphine (500 mg, 1.906 mmol) in diisopropyl ether (15 mL) was refluxed for 90 min and gave 608 mg (89%) of phosphimine **40a** as colourless plates on cooling. Mp 147–148°C (diisopropyl ether–ethyl acetate), IR: 3054, 1630 (C=O), 1608, 1465, 1436 (P–Ph), 1392, 1344, 1312, 1286, 1214 (N=P), 1136, 1028, 1108, 760, 720 cm^{-1}. ^1H NMR (DMSO-d_6): 5.48 (d, $^3J_{P-H\alpha}$=20.8 Hz, 1H, α-H), 7.05–7.17 (m, 2H, 6,8-H), 7.37–7.61 (m, 20H, Ph), 7.73 (m, 1H, 7-H), 7.90 (dd, *J*=7.9, 1.4 Hz, 1H, 5-H), 8.66 (brs, 1H, 2-H). Anal. calcd for $C_{34}H_{26}NO_2P$ (511.55): C, 79.83; H, 5.12; N, 2.74%. Found: C, 79.55; H, 4.83; N, 2.57%.

3.1.24. 3-[α-[(Triphenylphosphoranylidene)amino]benzyl]-1-thiochromone (41a). 3-(α-Azidobenzyl)-1-thiochromone (**9a**) (880 mg, 3.000 mmol) was reacted for 3 h as given for **40a** to afford 1.355 g (86%) of phosphimine **41a** as white microcrystalline powder. Mp 144–146.5°C (diisopropyl ether–ethyl acetate). IR: 3054, 3022, 1608 (C=O), 1588, 1546, 1482, 1436 (P–Ph), 1346, 1208 (N=P), 1180, 1108, 744, 722, 712 cm^{-1}. ^1H NMR (DMSO-d_6): 5.67 (d, $^3J_{P-H\alpha}$=21.2 Hz, 1H, α-H), 7.01–7.15 (m, 2H, 6,8-H), 7.33–7.82 (m, 20H, Ph), 7.65 (m, 1H, 7-H), 8.22 (dd, *J*=8.0, 1.4 Hz, 1H, 5-H), 8.93 (s, 1H, 2-H). Anal. calcd for $C_{34}H_{26}NOPS$ (527.62): C, 77.40; H, 4.97; N, 2.65%. Found: C, 77.41; H, 4.64; N, 2.43%.

3.1.25. 3-Benzylchromanone (42a). A mixture of 3-(α-azidobenzyl)chromone (**8a**) (372 mg, 1.342 mmol), ammonium formate (315 mg), palladium on charcoal (50 mg) and methanol (15 mL) was refluxed and the reaction was monitored by TLC (hexane-acetone (6:1, v/v)). After 2 and 5 h, new batches of ammonium formate (400 mg each) were added and the heating was continued until the completion of the reduction (7 h and 30 min). The catalyst was filtered off, washed with methanol, the combined filtrates were concentrated and submitted to column chromatography (eluent: hexane–acetone (6:1, v/v)) to give chromanone **42a** (59 mg, 18%) as the sole product. Colourless needles, Mp 55–57°C, lit.[62] mp 58°C. IR (neat): 2924, 1714, 1690 (C=O), 1604, 1478, 1454, 1324, 1302, 1220, 754 cm^{-1}. ^1H NMR: 2.70 (dd, *J*=13.5, 10.3 Hz, 1H, one of CH_2Ph), 2.93 (m, 1H, 3-H), 3.29 (dd, *J*=13.5, 3.9 Hz, 1H, other of CH_2Ph), 4.16 (dd, *J*=11.3, 8.0 Hz, 1H, 2-H_{ax}), 4.37 (dd, *J*=11.3, 4.5 Hz, 1H, 2-H_{eq}), 6.94–7.06 (m, 2H, 6,8-H), 7.22–7.32 (m, 5H, Ph), 7.47 (ddd, *J*=8.7, 8.4, 1.8 Hz, 1H, 7-H), 7.94 (dd, *J*=8.1, 1.8 Hz, 1H, 5-H). ^{13}C NMR: 32.3 (C_α), 47.6 (C-3), 69.3 (C-2), 117.8 (C-8), 120.5 (C-4a), 121.4 (C-6), 126.6, 127.5, 128.7, 129.1 (C-5,2″,3″,4″,5″,6″), 135.9 (C-7), 138.2 (C-1″), 161.6 (C-8a), 193.7 (C-4).

3.1.26. 3-(α-Aminobenzyl)chromone hydrochloride (43a). A mixture of 3-(α-azidobenzyl)chromone (**8a**) (416 mg, 1.500 mmol), tin(II)-chloride monohydrate (762 mg, 3.670 mmol) and methanol (17 mL) was stirred for 5 days at room temperature, then poured into 4% NaOH solution and extracted with chloroform. The solvent was removed under reduced pressure, the residue was dissolved in abs. diethyl ether and satd solution of hydrogen chloride in abs. diethyl ether was added dropwise. The yellowish precipitate was filtered off and crystallized from hexane–abs.

ethanol (3:1, v/v) mixture to give 58 mg (13%) of pure salt **43a** as white microcrystalline powder. Mp 191–196°C (dec.). IR: 2868 (br, $NH_3^{\oplus}$), 1644 (C=O), 1610 (C=C), 1506, 1466, 1355, 1112, 762, 697 cm^{-1}. ^1H NMR (DMSO-d_6): 5.60 (s, 1H, H_α), 7.39–7.58, 7.64–7.74 (m, 7H, 6,8-H+Ph), 7.88 (ddd, J=8.6, 8.4, 1.6 Hz, 1H, 7-H), 8.07 (dd, J=7.9, 1.4 Hz, 1H, 5-H), 9.26 (brs, 3H, $NH_3^{\oplus}$). ^{13}C NMR (DMSO-d_6): 56.0 (C_α), 118.8 (C-8), 121.3 (C-3), 123.2 (C-4a), 125.2 (C-6), 126.2 (C-5), 127.7, 128.8 (C-2″,3″,5″,6″), 128.6 (C-4″), 135.1, 136.5 (C-7,1″), 156.0, 156.2 (C-2,8), 175.4 (C-4). Anal. calcd for $C_{16}H_{14}ClNO_2$ (287.74): C, 66.79; H, 4.90; N, 4.87. Found: C, 66.95; H, 5.10; N, 4.59.

3.1.27. 3-(α-Aminobenzyl)-1-thiochromone hydrochloride (44a). 3-(Azidobenzyl)-1-thiochromone (**9a**) (293 mg, 0.999 mmol) was treated with $SnCl_2 \cdot H_2O$ as given for **43a** to yield 126 mg (42%) of pure salt **44a** as white prisms. Mp 198–203°C. IR: 2832 (br, $NH_3^{\oplus}$), 1607 (C=O+C=C), 1590, 1438, 1384, 1093, 928, 771, 741, 705 cm^{-1}. ^1H NMR (DMSO-d_6): 5.79 (s, 1H, H_α), 7.36–7.48 (m, 3H, 3″,4″,5″-H), 7.61–7.84 (m, 3H, 6,2″,6″-H), 7.97 (d, J=7.0 Hz, 1H, 7-H), 8.40 (dd, J=7.9, 1.3 Hz, 1H, 5-H), 8.91 (s, 1H, 2-H), 9.24 (brs, 1H, $NH_3^{\oplus}$). ^{13}C NMR (DMSO-d_6): 53.8 (C_α), 127.6, 127.8, 128.6, 128.7 (C-5,6,8,4″), 128.3, 128.8 (C-2″,3″,5″,6″), 130.9 (C-4a), 132.1, 132.5 (C-3,7), 136.6 (C-2), 136.8 (C-8a), 139.7 (C-1″), 177.2 (C-4). Anal. calcd for $C_{16}H_{14}ClNOS$ (303.80): C, 63.26; H, 4.64; N, 4.61. Found: C, 61.99; H, 4.66; N, 4.52.

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