Base-Induced Coupling of α-Azido Ketones with Aldehydes − An Easy and Efficient Route to Trifunctionalized Synthons 2-Azido-3-hydroxy Ketones, 2-Acylaziridines, and 2-Acylspiroaziridines[‡]

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Dedicated to Prof. Pál Sohár on the occasion of his 60th birthday

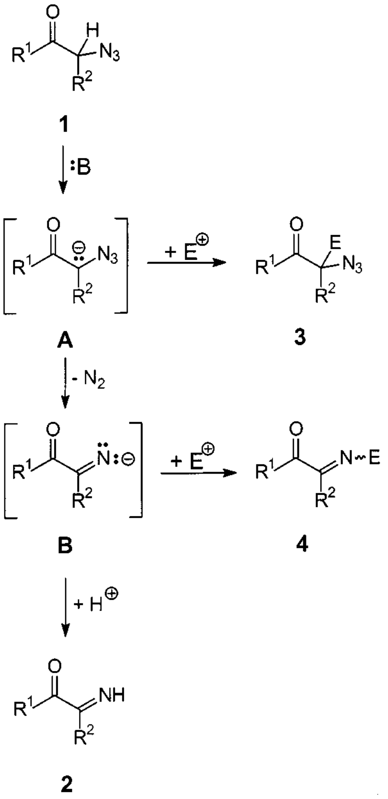
Keywords: Aldol reactions / Azides / Aziridines / Ketones / Spiro compounds

An improved synthesis of α-azido ketones under phase-transfer conditions has been developed. The transformation of α-azido ketones into acyclic and heterocyclic 2-azido-3-hydroxy ketones has been demonstrated and the relative configurations of the chromanone derivatives have been determined by X-ray analysis. Treatment of the aldol-type products with triphenylphosphane afforded 2-acylaziridines and the hitherto unknown spiro[chroman-3,2′-aziridin]-4-ones. The relative configuration of the spiroaziridines was determined by NOE measurements.

Introduction

α-Azido ketones **1** with at least one α-hydrogen atom have been found to be highly base-sensitive and to undergo loss of nitrogen from carbanion **A**, followed by protonation of imino anion **B** to give imine **2** (Scheme 1).[1,2] Recently, we suggested a possible synthetic methodology, based on the trapping of anions **A** and **B** with electrophiles, that could furnish ketone derivatives **3** and **4**.[3]

This kind of trapping was completely unknown in the literature, the only related transformation has been reported by Eguchi and co-workers,[4] who synthesized β-(acyloxy)vinyl azide by deprotonation of α-azido ketones with LDA and subsequent treatment with acid chlorides or anhydrides. The product obviously derived from the enolate form of anion **A**. In our previous paper[3] we demonstrated that anions **A** and **B**, generated from azides **1** by treatment with amines, could be trapped with aldehydes or ketones to yield 2-azido-3-hydroxy ketones or 2,5-dihydro-5-hydroxyoxazoles, depending on the conditions and techniques. Some examples of the synthetic utility of 2-azido-3-hydroxy ketones were also presented; these valuable 1,2,3-trifunctionalized synthons can be transformed easily and selectively in many ways, even without protecting groups.



Scheme 1. Trapping of the anions generated from α-azido ketones **1** by electrophiles

In this contribution we wish to present further results in the synthesis and transformations of 2-azido-3-hydroxy ketones and their α-azido ketone precursors.

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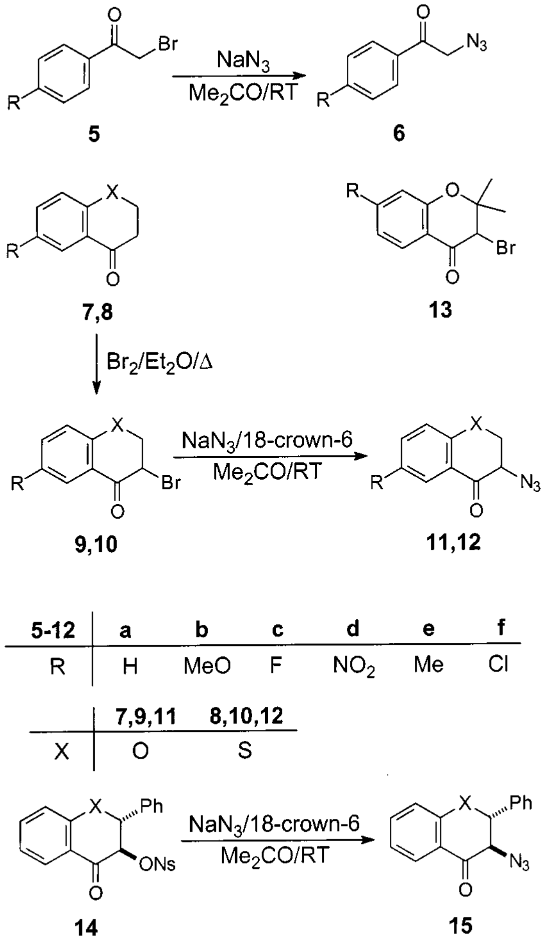
Results and Discussion

Two sets of α-azido ketone substrates were studied. 2-Azido-1-(4-substituted phenyl)ethanones (phenacyl azides) **6** were chosen to investigate the electronic effect of the substituents on the deprotonation and coupling reaction of azido ketones. In the cases of 3-azidochromanones **11** and **15** and -1-thiochromanones **12** we wished to survey the possible extension of the reactions to more complex heterocyclic systems.

A number of methods to synthesize α-azido ketones have been developed. The most obvious and frequently used approach utilizes the nucleophilic substitution of a ketone containing a good leaving group, such as halogeno[2,4,5] or sulfonyloxy,[6] at the α-position. The main drawback of this method is the lability of the formed azide under basic conditions; substrates with β-hydrogen atoms, and in particular with a conjugating group at the β-position, give α-azido ketones in low yields and the major product is the tautomerized form of the imine **2**.[5e–5j] New preparative methods to overcome this difficulty have been developed,[7–10] but these approaches also suffer from lack of regioselectivity and laborious synthesis required for the starting material and/or the substrate. Another solution is to enhance nucleophilic substitution, increasing the rate of displacement under less basic conditions. The use, in acetone solution, of α-nosyloxy ketones with a leaving group of greater nucleofugacity has been demonstrated.[6d]

We have now established that acetone can also be used advantageously in the transformations of phenacyl bromides **5a–d** and **5f** with sodium azide to afford the corresponding azides **6a–d** and **6f** in excellent (81–94%) yields (Scheme 2).



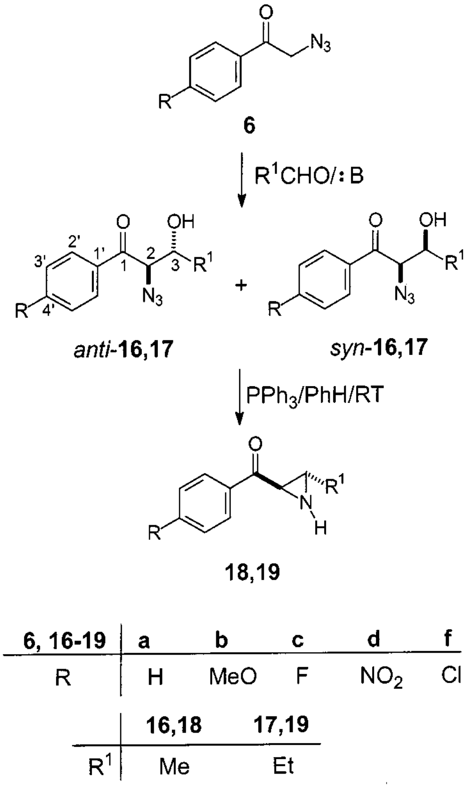
5-12	a	b	c	d	e	f
R	H	MeO	F	NO$_2$	Me	Cl

	7,9,11	8,10,12
X	O	S

Scheme 2. Synthesis of α-azido ketones **6**, **11**, **12**, and **15**

At the same time, merely changing the solvent was insufficient to solve the problem of lability in the case of more sensitive azido ketones. It was found that the reaction between sodium azide and 3-bromochromanones **9a**, **9e**, and **9f**, prepared by the bromination of the corresponding chromanones **7a**, **7e**, and **7f** (Scheme 2), takes place very slowly in acetone, due to the steric hindrance of the S_N2 displacement, with considerable amount of secondary products also being detected. In the presence of 10 mol % of 18-crown-6, the reaction was accelerated thanks to the higher concentration of azide ions, and the 3-azidochromanones **11a**, **11e**, and **11f** were obtained in good to excellent yields (73–95%). Even the very sensitive 3-azido-1-thiochromanone (**12a**) became available in modest yield (26%) by this methodology. Earlier attempts to prepare azides **11** and **12** by nucleophilic substitution of 3-bromochromanones **9** and 3-bromo-1-thiochromanones **10** in more polar solvents such as DMF, DMSO, alcohols, and mixtures of these with water had failed to give any azide, affording only 3-aminochromones and -1-thiochromones,[5e–5g] and so our technique has notable synthetic value. The use of crown ethers in combination with acetone as solvent also enabled *trans*-3-azidoflavanone (**15**) to be synthesized from nosylate **14**. Previously, azide **15** had been prepared in poor yield by quenching the reaction between *trans*-3-mesyloxyflavananone and sodium azide in DMF at low levels of conversion.[6a] On the other hand, when 3-bromo-2,2-dimethylchromanones **13a** and **13b** were treated with sodium azide under the standard conditions, no reaction was observed, even after longer periods or at elevated temperatures, due to the steric hindrance exerted by the axial methyl group in the β-position on the rear-side attack of the nucleophile at C-3. This has so far been the only observed limitation of our new method.

With both sets of α-azido ketones in hand, we systematically investigated their reactions with aldehydes. In continuation of our previous work,[3] we treated phenacyl azide **6a** with acetaldehyde in the presence of various bases, but all attempts to find a deprotonating agent more effective than the previously used DBU failed. No reaction took place in the presence of triethylamine or 4-(dimethylamino)pyridine; only the use of 1,4-diazabicyclo[2.2.2]octane (DABCO) resulted in the formation of the desired **16a** in low yield after an extremely long reaction period (10 d). It is noteworthy that the 1,2-azido alcohol **16a** was also obtained in moderate yield by use of tetrabutylammonium fluoride (TBAF) trihydrate as a base, meaning that the generation of the carbanion and the subsequent coupling reaction tolerated the presence of small amounts of water. Next, the 2-azido-4′-substituted acetophenone series **6a–d** and **6f** was treated with acetaldehyde and propionaldehyde under the optimized conditions (8 equiv. of electrophile, 0.08 equiv. of DBU) and the corresponding aldol products *syn*- and *anti*-**16a−d**, **16f**, **17a**, and **17f** were obtained in good yields (Scheme 3, Table 1).



6, 16-19	a	b	c	d	f
R	H	MeO	F	NO_2	Cl

	16,18	17,19
R^1	Me	Et

Scheme 3. Synthesis of azido alcohols **16** and **17** and their transformation into aziridines **18** and **19**

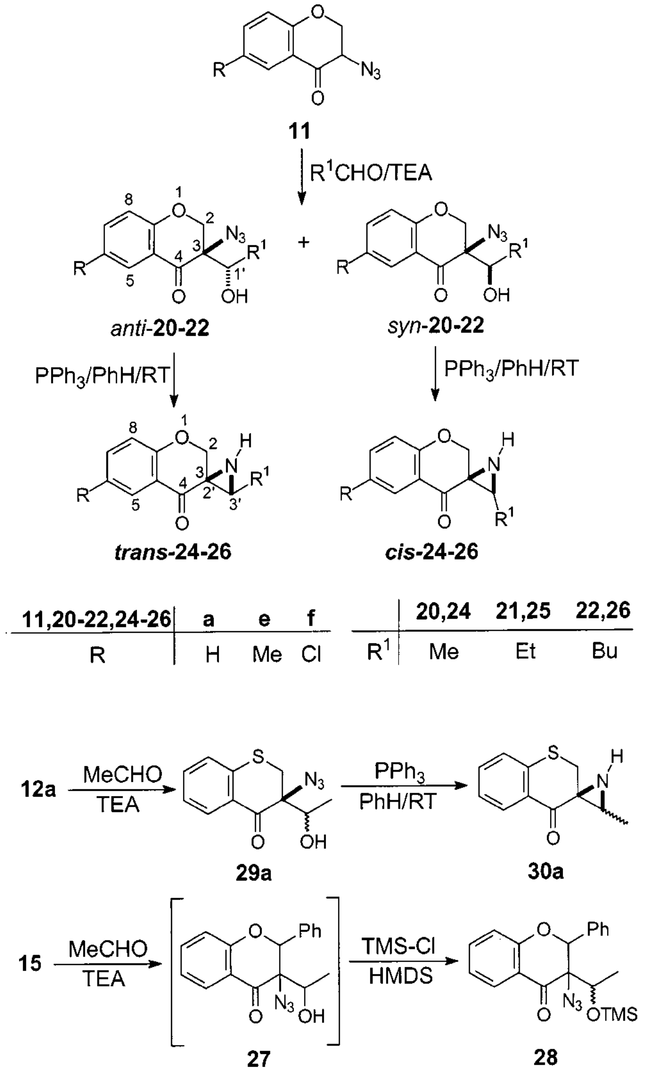
Table 1. Reaction between phenacyl azides **6** and aldehydes

Product[a]	R	R^1	*t* [h]	Conversion (%)[b]	Yield (%)	*syn*/*anti*
16a	H	Me	6.5	100	76	56:44
16b	MeO	Me	6.5	90	80	66:34
16c	F	Me	7	89	82	54:41
16d	NO_2	Me	17	100	30	59:41
16f	Cl	Me	22	100	67	50:50
17a	H	Et	6.5	100	56	65:35
17f	Cl	Et	4	100	35	63:37

[a] Reactions performed at 0 °C, with the exceptions of **17a** and **17f** (room temperature). [b] Determined by ^1H NMR analysis of the reaction mixture.

Incorporation of electron-withdrawing substituents, particularly the nitro group, into position 4′ resulted in a significant decrease in the yield. This phenomenon may be explained in terms of the increased stability, and hence the lower reactivity, of the carbanion **A**. In accordance with our previous report,[3] a low diastereoselectivity (0−32% *de*) with a *syn* preference was observed in the formation of products **16** and **17**.

Analogous treatment of 3-azidochromanones **11a**, **11e**, and **11f** and 3-azido-1-thiochromanone (**12a**) with aliphatic aldehydes in the presence of 1 equiv. of triethylamine afforded the desired 3-azido-3-(1-hydroxyalkyl)chromanones **20a**, **21a**, **21e**, **21f**, **22a**, and 3-azido-3-(1-hydroxyallyl)-1-thiochromanone **29a** in good (60−74%) yields (Scheme 4, Table 2).



11,20-22,24-26	a	e	f
R	H	Me	Cl

	20,24	21,25	22,26
R^1	Me	Et	Bu

Scheme 4. Synthesis of heterocyclic azido alcohols **20−22**, **27**, and **29a** and their transformation into aziridines **24−26** and **30a**

Table 2. Treatment of 3-azidochromanones **11** and 3-azido-1-thiochromanone **12a** with aldehydes

Starting material[a]	Product	*t* [h]	Yield (%)	*syn*/*anti*
11a	**20a**	5	67	56:44
11a	**21a**	3	62	58:42
11a	**22a**	24	60	67:33
11e	**21e**	22	74	57:43
11f	**21f**	2	62	57:43
12a	**29a**	23	65	78:22

[a] Reactions were performed at 0 °C.

Products **20**, **21**, **22**, and **29** were isolated as mixtures of *syn* and *anti* diastereomers, but the determination of their relative configurations in this case was more troublesome due to the lack of $^3J_{H,H}$ coupling constant in the 1,2-azido alcohol unit, and our original tentative assignment[3] based on ^{13}C chemical shifts had been tenuous because of the conflicting spectroscopic data. Now, repeated column chromatography of the products afforded *syn*-**21a**, *anti*-**21a**, *syn*-**21f**, *anti*-**21f**, and *syn*-**22a** in diastereopure forms and the stereochemistry of *syn*-**21a** was unequivocally determined by X-ray analysis of its *p*-nitrobenzoate **23** (Figure 1).

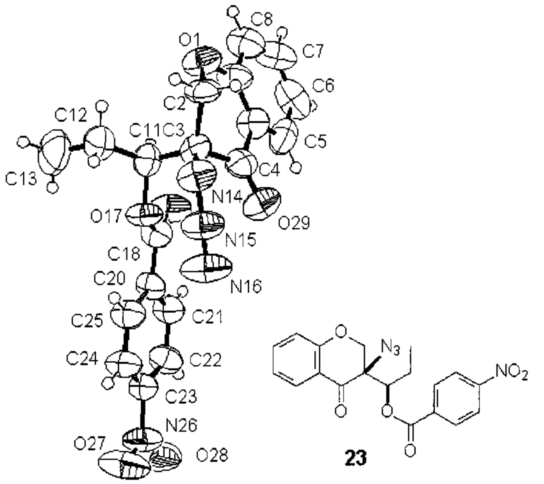


Figure 1. Crystal structure of *p*-nitrobenzoate **23**

This allowed us to assign the isomers in the whole series, on the basis of their characteristic spectral differences. The characteristic feature in the ^{1}H NMR spectra of the more polar *anti* diastereomers was the well-separated AX doublets of the 2-methylene group of the chromanone ring (δ = 4.32−4.36 and 4.66−4.70, respectively), whereas the less polar *syn* isomers showed a very tight AB system ($\Delta\delta_{AB}$ = 0.02−0.03). Another diagnostic tool was the chemical shift of the C-1′ carbon signal, which appeared at lower field ($\Delta\delta$ = 1.8−2.1) in the ^{13}C NMR spectrum of the *syn* isomer than in that of the *anti* diastereomer.

As before, low diastereoselectivity with *syn* preference was observed in most cases, the diastereomeric excesses varying between 12 and 16% for products **20a**, **21a**, **21e**, and **21f**. However, the selectivity depended significantly on steric factors, since 1,2-azido alcohol **22a**, obtained from valeraldehyde, with a longer alkyl chain, and aldol product **29a**, obtained from 3-azido-1-thiochromanone (**12a**), a substrate with a more distorted heterocycle, afforded higher *syn*/*anti* ratios (34 and 56% *de*, respectively).

Treatment of *trans*-3-azidoflavanone (**15**) with acetaldehyde yielded the anticipated but highly unstable product **27**, which decomposed by retro-aldol reaction during the attempted purification by silica gel chromatography. Treatment of the crude reaction mixture with trimethylsilyl chloride afforded the protected derivative **28** in 13% overall yield.

These results clearly show the generality of this new C−C bond-forming reaction, both for aliphatic and for cyclic α-azido ketones. 2-Azido-3-hydroxy ketones, available from the reaction between various α-azido ketones and aldehydes, are useful trifunctionalized synthons. We have reported[3] some preliminary results on the transformation of 2-azido-3-hydroxy-1-phenylbutanone (**16a**) and 2-azido-3-hydroxy-1-phenylpentanone (**17a**) into 2-acylaziridines **18a** and **19a** on treatment with triphenylphosphane (TPP). The transformation of *vic*-azido alcohols into aziridines by trivalent phosphorous reagents is well documented in the literature[11] − examples include the preparation of 1*H*-aziridine-2-carboxylates,[11d,11j] aziridine-2,3-dicarboxylates,[11c,11f,11h] and 2-[2-(ethoxycarbonyl)ethenyl]aziridines[11i] − but our method was the first report of the synthesis of 1-unsubstituted-2-acylaziridines. More recently, an alternative method, based on the base-induced cyclization of β-(methoxyamino) ketones,[11i] has also been published. Related aziridine-2-carboxamides have been prepared from α,β-unsaturated amides and diaziridine.[12] 1-Sulfonyl-2-acyl- or 1,2-diacylaziridines have been obtained by electrophilic amination of α,β-unsaturated ketones with (*N*-tosylimino)phenyliodinane[13] and by treatment of monocarbonyl iodonium ylides with sulfonyl- or acylimines.[14] Since 2-acylaziridines and related derivatives are useful synthetic building blocks,[11−14] we investigated the transformation of our 2-azido-3-hydroxy ketones **16**, **17**, **20−22**, and **29** into these valuable compounds.

Treatment of 1,2-azido alcohols **16a−d**, **16f**, and **17a** with TPP in benzene solution yielded the corresponding *trans*-aziridines **18a−c**, **18f**, and **19a** in poor (3.1−21%) yields (Scheme 3), and all attempts (change of stoichiometry and solvent, use of other phosphanes or triethyl phosphite instead of TPP) failed to improve the yields. A marked substituent effect was observed; the presence of an electron-withdrawing substituent in position 4′ significantly lowered the yield of the ring-closure and the nitro derivative **18d** was unavailable in this way. However, much better (29−63%) yields were achieved for the analogous treatment of *syn*- and *anti*-3-azido-3-(1-hydroxyalkyl)chromanones and -1-thiochromanone **20a**, **21a**, **21e**, **21f**, **22a**, and **29a**, which afforded the desired *cis*- and *trans*-aziridines **24a**, **25a**, **25e**, **25f**, **26a**, and **30a** (Scheme 4). The relative configurations of the aziridine rings were determined by 2D {^{1}H}-^{1}H NOE measurements. Irradiation of the chromanone ring 2-H_{eq} hydrogen atom resulted in an NOE difference on the 3′-methyl group of *trans*-**24a**, but on the 3′-methine proton in the case of the isomeric *cis*-**24a**. This type of spiroaziridines (**24−26**, **30**) was almost unknown in the literature, the only synthesis, reported by Piva,[15] being based on the photoinduced cyclization of 2-aminocyclohexenone derivatives.

The stereochemical outcome of the cyclization was another point of interest. The phosphane-induced transformation of 1,2-azido alcohols into aziridines is generally regarded[11] as a diastereospecific and diastereoselective reaction with inversion at the carbon atom bearing the hydroxy group, although some controversial data have also been published by Zwanenburg et. al.[11c] In our case, the reactions of diastereomerically pure chromanone derivatives *syn*-**21a**, *anti*-**21a**, and *syn*-**22a** displayed complete diastereospecificity and diastereoselectivity. The *syn*-1,2-azido alcohols yielded *cis*-aziridines, and the *anti*-1,2-azido alcohol a *trans*-aziridine exclusively, in accordance with the earlier findings and the proposed mechanism.[11] At the same time, treatment of a *syn*/*anti* mixture of acyclic derivatives **16** and **17** gave *trans*-aziridines **18** and **19** as the only products, with no *cis*-aziridines detected or isolated. Surprisingly, treatment of *syn*-**16f** with TPP resulted in the formation of the *trans*-**18f**, although the yield was considerably lower (7.3%) than that of the analogous ring-closure of *anti*-**16f** (32%). The reason for this anomaly is unclear. Fast decomposition of *cis*-aziridines may explain the lack of this isomer in the reaction mixtures, but formation of the *trans*-aziridine in the reaction of the *syn*-1,2-azido alcohol remains unexplained. Its relative configuration, which contradicts the suggested mechanism,[11] may indicate incomplete diastereoselectivity in the ring-forming step. However, we cannot rule out epimerization of the starting material in a preequilibrium either through α-deprotonation−reprotonation or even by a retro-aldol−aldol reaction sequence.

Conclusion

We have improved the synthesis of α-azido ketones and demonstrated the usefulness of the obtained azides in the synthesis of acyclic and heterocyclic 2-azido-3-hydroxy ketones, which are valuable trifunctionalized synthons. Treatment of 2-azido-3-hydroxy ketones with triphenylphosphane resulted in the formation of 2-acylaziridines. The hitherto unknown spiro[chroman-3,2′-aziridin]-4-ones have also been prepared in moderate to good yields and with complete diastereoselectivity.

Experimental Section

General: All chemicals were used as purchased unless otherwise stated. THF was distilled from benzophenone ketyl, triethylamine was distilled from LAH. Column chromatography was performed on Kieselgel 60 or Kieselgel 40, TLC was performed on Kieselgel 60 F_{254} (Merck) plates. Melting points: Boetius hot-stage, uncorrected values. IR: Perkin−Elmer 16 PC-FT-IR; KBr pellets unless otherwise stated. NMR: Varian Gemini 200, Bruker WP 200 SY, Bruker AM 360 (200 or 360 MHz for ^{1}H; 50 or 90 MHz for ^{13}C). Recorded in $CDCl_3$ solution unless otherwise stated. Chemical shifts are given in δ relative to an internal standard TMS (δ = 0) or to the residual $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Elemental analysis: Carlo−Erba 1108 CHN analyzer.

General Procedure for the Synthesis of Phenacyl Bromides 5: After dropwise addition, at room temperature over 5 min, of a solution of bromine (1.7 mL, 33.00 mmol) in diethyl ether (40 mL) to a stirred solution of the corresponding acetophenone (30.30 mmol) in dioxane (50 mL), the reaction mixture was heated and stirred at 40 °C for 1−2 h, and then allowed to cool to room temperature. The mixture was washed with water (5 × 50 mL), and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Recrystallization gave pure **5**.

2-Bromo-1-(4-methoxyphenyl)ethanone (5b): This compound was produced from 1-(4-methoxyphenyl)ethanone (4.55 g), giving 4.89 g (71%) of **5b**. White crystals. M.p. 66−69 °C (diethyl ether; ref.[16] 70−72 °C). ^{1}H NMR: δ = 3.89 (s, 3 H, 4′-OMe), 4.41 (s, 2 H, 2-H), 6.97 (d, J = 9.0 Hz, 2 H, 3′,5′-H), 7.98 (d, J = 9.0 Hz, 2 H, 2′,6′-H).

2-Bromo-1-(4-fluorophenyl)ethanone (5c): This compound was produced from 1-(4-fluorophenyl)ethanone (3.16 g), giving 3.25 g (66%) of **5c**. White crystals. M.p. 43−45 °C (hexane; ref.[17] 49 °C). ^{1}H NMR: δ = 4.42 (s, 2 H, 2-H), 7.18 (dd, J_{ortho} = 8.9 Hz, J_{HF} = 8.7 Hz, 2 H, 3′,5′-H), 7.18 (dd, J_{ortho} = 8.9 Hz, J_{HF} = 5.3 Hz, 2 H, 2′,6′-H).

2-Bromo-1-(4-chlorophenyl)ethanone (5f): This compound was produced from 1-(4-chlorophenyl)ethanone (4.50 g), giving 4.52 g (66%) of **5f**. White crystals. M.p. 92−94 °C (hexane; ref.[17] 78 °C, ref.[18] 77−79 °C). ^{1}H NMR: δ = 4.41 (s, 2 H, 2-H), 7.48 (d, J = 8.8 Hz, 2 H, 3′,5′-H), 7.94 (d, J = 8.8 Hz, 2 H, 2′,6′-H).

General Procedure for the Synthesis of Phenacyl Azides 6: A mixture of the appropriate α-bromoacetophenone **5** (14.00 mmol) and sodium azide (1.82 g, 28.00 mmol) in acetone (250 mL) was stirred at room temperature until completion of the reaction (TLC). The mixture was poured into water and extracted with CH_2Cl_2 (3 × 80 mL), and the organic layer was dried ($MgSO_4$), concentrated under reduced pressure, and purified by crystallization or column chromatography.

2-Azido-1-phenylethanone (6a): Compound **6a** (2.61 g, 81%) was obtained from **5a** (3.98 g). Purification was by column chromatography (eluent: hexane/ethyl acetate, 4:1, v/v). Yellow oil which solidifies in the refrigerator (ref.[19] 17 °C). Spectroscopic data have been reported previously.[6d]

2-Azido-1-(4-methoxyphenyl)ethanone (6b): Compound **6b** (3.61 g, 94%) was obtained from **5b** (4.60 g). Purification was by crystallization from hexane. Yellowish-white crystals. M.p. 68−69 °C. IR: $\tilde{\nu}$ = 2124 (N_3), 1684 (C=O), 1600, 1240 (C−O−C), 1178, 826 cm^{-1}. ^{1}H NMR: δ = 3.89 (s, 3 H, 4′-OMe), 4.52 (s, 2 H, 2-H), 6.98 (d, J = 9.0 Hz, 2 H, 3′,5′-H), 7.90 (d, J = 9.0 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 54.4 (C-2), 55.4 (4′-OMe), 114.0 (C-3′,5′), 127.2 (C-1′), 130.1 (C-2′,6′), 164.1 (C-4′), 191.5 (C-1). $C_9H_9N_3O_2$ (191.2): C 56.54, H 4.74, N 21.98; found C 56.39, H 4.70, N 22.09.

2-Azido-1-(4-fluorophenyl)ethanone (6c): Compound **6c** (2.30 g, 93%) was obtained from **5c** (3.00 g). Purification was by crystallization from hexane. Yellow crystals. M.p. 47.5−48.5 °C. IR: $\tilde{\nu}$ = 2100 (N_3), 1689 (C=O), 1594, 1226, 1217, 834 cm^{-1}. ^{1}H NMR: δ = 4.54 (s, 2 H, 2-H), 7.18 (dd, J_{ortho} = 9.0 Hz, J_{HF} = 8.9 Hz, 2 H, 3′,5′-H), 7.97 (dd, J_{ortho} = 9.0 Hz, J_{HF} = 5.4 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 54.7 (C-2), 116.3 (d, J_{CF} = 22.2 Hz, C-3′,5′), 130.8 (d, J_{CF} = 9.5 Hz, C-2′,6′), 130.9 (C-1′), 166.5 (d, J_{CF} = 256 Hz, C-4′), 192.0 (C-1). $C_8H_6FN_3O$ (179.2): C 53.63, H 3.38, N 23.45; found C 53.49, H 3.22, N 23.22.

2-Azido-1-(4-nitrophenyl)ethanone (6d): Compound **6d** (2.12 g, 93%) was obtained from **5d** (2.70 g). Purification was by crystallization from a hexane/ethyl acetate mixture (10:1, v/v). Pale brownish crystals. M.p. 91−93 °C. IR: $\tilde{\nu}$ = 2114 (N_3), 1706 (C=O), 1524 (NO_2), 1344 (NO_2), 1212, 854 cm^{-1}. ^{1}H NMR: δ = 4.62 (s, 2 H, 2-H), 8.10 (d, J = 8.8 Hz, 2 H, 2′,6′-H), 8.37 (d, J = 8.8 Hz, 2 H, 3′,5′-H). ^{13}C NMR: δ = 55.2 (C-2), 124.3 (C-3′,5′), 129.2 (C-2′,6′), 138.9 (C-1′), 151.1 (C-4′), 192.3 (C-1). $C_8H_6N_4O_3$ (206.2): C 46.61, H 2.93, N 27.18; found C 46.88, H 3.07, N 26.99.

2-Azido-1-(4-chlorophenyl)ethanone (6f): Compound **6f** (3.22 g, 89%) was obtained from **5f** (4.30 g). Purification was by crystallization from hexane. Yellow crystals. M.p. 60−64 °C. IR: $\tilde{\nu}$ = 2107 (N_3), 1694 (C=O), 1595, 1220, 1093 (Ar-Cl) cm^{-1}. ^{1}H NMR: δ = 4.53 (s, 2 H, 2-H), 7.48 (d, J = 8.6 Hz, 2 H, 3′,5′-H) 7.86 (d, J = 8.6 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 54.7 (C-2), 129.2 (C-2′,3′,5′,6′) 132.6 (C-1′), 140.5 (C-4′), 192.0 (C-1). $C_8H_6ClN_3O$

(195.6): C 49.12, H 3.09, N 21.48; found C 48.92, H 3.25, N 21.32.

General Procedure for the Synthesis of 3-Bromochroman-4-ones 9 and 13: Bromine (1.6 mL, 31.20 mmol) was added at reflux temperature to a stirred solution of the appropriate chromanone **7** (26.00 mmol) in diethyl ether (22 mL) and the mixture was heated for 3 h. It was then stirred overnight and extracted with water (5 × 25 mL), and the organic layer was dried (MgSO$_4$) and concentrated in vacuo. The residue was either purified by crystallization or submitted to column chromatography.

3-Bromo-4-chromanone (9a): Compound **9a** (4.63 g, 75%) was obtained from **7a** (4.00 g). Purification was by crystallization from hexane. White crystals. M.p. 66−68 °C (ref.[20] 70 °C). ^{1}H NMR: δ = 4.57−4.69 (m, 2 H, 2,3-H), 7.04 (d, J = 8.6 Hz, 1 H, 8-H), 7.09 (dd, J = 7.8, 6.9 Hz, 1 H, 6-H), 7.54 (dd, J = 8.6, 6.9 Hz, 1 H, 7-H), 7.95 (d, J = 7.8 Hz, 1 H, 5-H).

3-Bromo-6-methyl-4-chromanone (9e): Compound **9e** (3.96 g, 82%) was obtained from **7e** (3.24 g). Purification was by column chromatography (eluent: toluene/hexane, 2:3, v/v). Pale yellow crystals. M.p. 68−70 °C (ref.[21] 74 °C). ^{1}H NMR: δ = 2.33 (s, 3 H, Me), 4.50−4.69 (m, 3 H, 2,3-H), 6.94 (d, J = 8.3 Hz, 1 H, 8-H), 7.36 (dd, J = 8.3, 1.7 Hz, 1 H, 7-H), 7.72 (br. s, 1 H, 5-H).

3-Bromo-6-chloro-4-chromanone (9f): Compound **9f** (4.41 g, 85%) was obtained from **7f** (3.65 g). Purification was by crystallization from hexane. Yellow crystals. M.p. 93−96 °C. IR: $\tilde{\nu}$ = 1698 (C=O), 1473, 1419, 1269, 1182, 1163, 1012, 830 cm^{-1}. ^{1}H NMR: δ = 4.57−4.71 (m, 3 H, 2,3-H), 7.01 (d, J = 8.8 Hz, 1 H, 8-H), 7.48 (dd, J = 8.8, 2.5 Hz, 1 H, 7-H), 7.88 (d, J = 2.5 Hz, 1 H, 5-H). ^{13}C NMR: δ = 44.5 (C-3), 71.3 (C-2), 119.6 (C-4a), 119.8 (C-8), 127.5 (C-5), 128.6 (C-6), 136.7 (C-7), 159.3 (C-8a), 184.4 (C-4). C$_9$H$_6$BrClO$_2$ (261.5): C 41.34, H 2.31; found C 41.11, H 2.42.

3-Bromo-2,2-dimethyl-4-chromanone (13a): Compound **13a** (906 mg, 57%) was obtained from 2,2-dimethyl-4-chromanone (1.00 g). Purification was by column chromatography (eluent: hexane/ethyl acetate, 5:1, v/v). Pale yellow crystals. M.p. 56−58 °C (ref.[22] 62−63 °C). ^{1}H NMR: δ = 1.54, 1.63 (2 × s, 2 × 3 H, 2,2-Me$_2$), 4.39 (s, 2 H, 3-H), 6.98 (d, J = 8.3 Hz, 1 H, 8-H), 7.05 (m, 1 H, 6-H), 7.53 (m, 1 H, 7-H), 7.92 (d, J = 7.2 Hz, 1 H, 5-H).

3-Bromo-7-methoxy-2,2-dimethyl-4-chromanone (13b): Compound **13b** (254 mg, 37%) was obtained from 7-methoxy-2,2-dimethyl-4-chromanone (500 mg). Purification was by column chromatography (eluent: toluene). White crystals. M.p. 37−38 °C (hexane; ref.[23] 40−41 °C). ^{1}H NMR: δ = 1.52, 1.62 (2 × s, 2 × 3 H, 2,2-Me$_2$), 3.84 (s, 3 H, 7-OMe), 4.33 (s, 2 H, 3-H), 6.42 (d, J = 2.1 Hz, 1 H, 8-H), 6.61 (dd, J = 8.9, 2.1 Hz, 1 H, 6-H), 7.84 (d, J = 8.9 Hz, 1 H, 5-H).

3-Bromo-1-thiochroman-4-one (10a): Bromine (1.03 mL, 19.99 mmol) was added dropwise to a stirred solution of 1-thiochroman-4-one (3.28 g, 20.00 mmol) in chloroform (80 mL) and the mixture was stirred for 3 h at room temperature. It was washed with 10% NaHCO$_3$ solution (50 mL) and water (30 mL), and then dried (MgSO$_4$). Concentration and crystallization from hexane afforded pure **10a** (4.42 g, 91%) as yellow crystals. M.p. 70−73 °C (ref.[24] 76 °C). ^{1}H NMR: δ = 3.50 (dd, J = 14.1, 8.5 Hz, 1 H, 2-H$_{ax}$), 3.67 (dd, J = 14.1, 3.1 Hz, 1 H, 2-H$_{eq}$), 4.98 (dd, J = 8.5, 3.1 Hz, 1 H, 3-H), 7.21−7.30 (m, 2 H, 6,8-H), 7.44 (m, 1 H, 7-H), 8.15 (dd, J = 7.9, 1.5 Hz, 1 H, 5-H).

General Procedure for the Synthesis of 3-Azidochromanones 11 and Thio Derivative 12a: A mixture of the appropriate bromide **9** or **10a** (1.76 mmol), sodium azide (229 mg, 3.52 mmol), 18-crown-6 (47 mg, 0.18 mmol), and acetone (20 mL) was stirred at room temperature until completion of the reaction (TLC). It was then poured into water, extracted with CH$_2$Cl$_2$ (3 × 40 mL), dried (MgSO$_4$), and concentrated in vacuo. The residue was purified by column chromatography (eluent: hexane/ethyl acetate, 6:1, v/v).

3-Azido-4-chromanone (11a): Compound **11a** (364 mg, 73%) was obtained from **9a** (600 mg). Spectroscopic data have been reported previously.[6d]

3-Azido-6-methyl-4-chromanone (11e): Compound **11e** (1.20 g, 95%) was obtained from **9e** (1.50 g). Pale yellow crystals. M.p. 57−58.5 °C. IR: $\tilde{\nu}$ = 2138 (N$_3$), 1696 (C=O), 1616, 1490, 1220, 822 cm^{-1}. ^{1}H NMR: δ = 2.32 (s, 3 H, 6-Me) 4.21 (dd, J = 11.4, 10.5 Hz, 1 H, 2-H$_{ax}$), 4.35 (dd, J = 10.5, 4.5 Hz, 1 H, 3-H), 4.47 (dd, J = 11.4, 4.5 Hz, 1 H, 2-H$_{eq}$), 6.89 (d, J = 8.6 Hz, 1 H, 8-H), 7.33 (d, J = 8.6 Hz, 1 H, 7-H), 7.70 (br. s, 1 H, 5-H). ^{13}C NMR: δ = 20.3 (Me), 60.1 (C-3), 68.8 (C-2), 117.6 (C-8), 118.9 (C-4a), 127.0 (C-5), 131.7 (C-6), 137.8 (C-7), 159.4 (C-8a), 188.6 (C-4). C$_{10}$H$_9$N$_3$O$_2$ (203.2): C 59.11, H 4.46, N 20.68; found C 59.34, H 4.32, N 20.43.

3-Azido-6-chloro-4-chromanone (11f): Compound **11f** (690 mg, 81%) was obtained from **9f** (1.00 g). Yellow crystals. M.p. 85−86 °C. IR: $\tilde{\nu}$ = 2133, 2100 (N$_3$), 1683 (C=O), 1650, 1558, 1287, 830 cm^{-1}. ^{1}H NMR: δ = 4.40 (m, 3 H, 2,3-H), 6.97 (d, J = 8.7 Hz, 1 H, 8-H), 7.47 (dd, J = 8.7, 2.5 Hz, 1 H, 7-H), 7.88 (d, J = 2.5 Hz, 1 H, 5-H). ^{13}C NMR: δ = 59.7 (C-3), 68.9 (C-2), 119.6 (C-8), 120.1 (C-4a), 126.7 (C-5), 127.7 (C-6), 136.5 (C-7), 159.7 (C-8a), 187.4 (C-4). C$_9$H$_6$ClN$_3$O$_2$ (223.6): C 48.34, H 2.70, N 18.79; found C 48.53, H 2.55, N 18.57.

3-Azido-1-thiochroman-4-one (12a): Compound **12a** (433 mg, 26%) was obtained from **10a** (2.00 g). Toluene/ethyl acetate (9:1, v/v) was used as eluent. Yellow crystals. M.p. 85−86 °C. IR: $\tilde{\nu}$ = 2108 (N$_3$), 1678 (C=O), 1436, 1266, 1216, 736 cm^{-1}. ^{1}H NMR: δ = 3.15 (dd, J = 13.2, 4.4 Hz, 1 H, 2-H$_{eq}$), 3.38 (dd, J = 13.2, 12.5 Hz, 1 H, 2-H$_{ax}$), 4.54 (dd, J = 12.5, 4.4 Hz, 1 H, 3-H), 7.20−7.29 (m, 2 H, 6,8-H), 7.44 (m, 1 H, 7-H), 8.14 (dd, J = 8.1, 1.6 Hz, 1 H, 5-H). ^{13}C NMR: δ = 30.7 (C-2), 63.5 (C-3), 125.4 (C-6), 127.2 (C-8), 130.0 (C-5), 133.9 (C-7), 141.0 (C-8a), 190.3 (C-4). C$_9$H$_7$N$_3$OS (205.2): calcd. C 52.67, H 3.44, N 20.47; found C 52.82, H 3.19, N 20.70. 1-Thiochromone (599 mg, 45%), m.p. 72−73 °C (ref.[6d] 74−76 °C) and 3-amino-1-thiochromone (60 mg, 8.7%), m.p. 125−128 °C (ref.[24] 127−129 °C) were isolated from the fractions eluting subsequently.

***trans*-3-Azidoflavanone (15):** A mixture of 3-nosyloxyflavanone (**14**)[6a] (2.50 g, 5.50 mmol), sodium azide (715 mg, 11.00 mmol), and 18-crown-6 (145 mg, 0.55 mmol) in dry acetone (150 mL) was stirred at room temperature for 100 h, poured into water, extracted with CH$_2$Cl$_2$ (3 × 30 mL), dried (MgSO$_4$), and concentrated in vacuo. The residue was purified by column chromatography (eluent: hexane/ethyl acetate, 3:1, v/v) to give 733 mg (50%) of azide **15** as pale yellow crystals. M.p. 77−80 °C (hexane). IR: $\tilde{\nu}$ = 2114 (N$_3$), 1698 (C=O), 1608, 1464, 1278, 1232, 760 cm^{-1}. ^{1}H NMR: δ = 4.55 (d, J = 12.0 Hz, 1 H, 2-H), 5.15 (d, J = 12.0 Hz, 1 H, 3-H), 7.02−7.20 (m, 2 H, 6,8-H) 7.45−7.69 (m, 6 H, 7-H, Ph) 7.96 (dd, J = 7.6, 1.9 Hz, 1 H, 5-H). C$_{15}$H$_{11}$N$_3$O$_2$ (265.3): C 67.92, H 4.18, N 15.84; found C 67.85, H 4.02, N 15.62.

General Procedure for the Synthesis of 1-Aryl-2-azido-3-hydroxy-1-alkanones 16 and 17: A mixture of α-azido ketone **6** (6.21 mmol), the appropriate aldehyde (24.74 mmol), and DBU (77.8 µL, 0.52 mmol) in dry THF (50 mL) was stirred for 1 h. Another batch of aldehyde (24.74 mmol) was then added and the mixture was stirred until completion of the reaction (TLC). The mixture was poured into water, extracted with CH_2Cl_2 (6 × 40 mL), and dried ($MgSO_4$), the solvent was evaporated under reduced pressure, and the residue was submitted to column chromatography.

2-Azido-3-hydroxy-1-phenyl-1-butanone (16a): Compound **16a** (960 mg, 76%) was obtained from **6a** (1.00 g) (reaction period: 6.5 h; temperature: 0 °C). Spectroscopic data have been reported previously.[3] Compound **16a** (40 mg, 28%) was also obtained from **6a** (112 mg) with 0.08 equiv. of DABCO as base (reaction period: 10 d; temperature: 0 °C). Compound **16a** (50 mg, 37%) was also obtained from **6a** (106 mg) with 0.085 equiv. of TBAF·$3H_2O$ as base (reaction period: 5 h; temperature: 0 °C).

2-Azido-3-hydroxy-1-(4-methoxyphenyl)-1-butanone (16b): Compound **16b** (445 mg, conversion: 90%; yield: 80%, normalized to 100% conversion) was obtained from **6b** [500 mg, reaction period: 6.5 h; temperature: 0 °C; elution with hexane/ethyl acetate (3:1, v/v) mixture]. Yellow oil, 66:34 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3462 (OH), 2104 (N_3), 1680 (C=O), 1598, 1512, 1310, 1264, 1174, 1028, 848 cm^{-1}. ^{1}H NMR: ***anti*-16b:** δ = 4.48 (d, *J* = 6.2 Hz, 1 H, 2-H), 7.98 (d, *J* = 8.7 Hz, 2 H, 2′,6′-H); ***syn*-16b**: δ = 7.97 (d, *J* = 8.7 Hz, 2 H, 2′,6′-H); inseparable signals: δ = 1.33 (d, *J* = 6.7 Hz, 3 H, 4-H), 3.89 (s, 3 H, 4′-OMe), 4.32−4.38 [m, 1 H, 3-H (*anti*) + m, 2 H, 2,3-H (*syn*)], 6.95−7.00 (m, 2 H, 3′,5′-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: ***anti*-16b:** δ = 19.1 (C-4), 66.7, 68.1 (C-2,3), 128.1 (C-1′), 194.2 (C-1); ***syn*-16b**: δ = 19.8 (C-4), 66.8, 68.5 (C-2,3), 127.6 (C-1′), 194.5 (C-1); inseparable signals: δ = 55.4 (4′-OMe), 114.0 (C-3′,5′), 131.1 (C-2′,6′), 164.3 (C-4′); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{11}H_{13}N_3O_3$ (235.2): C 56.16, H 5.57, N 17.86; found C 55.98, H 5.71, N 17.76.

2-Azido-1-(4-fluorophenyl)-3-hydroxy-1-butanone (16c): Compound **16c** (450 mg; conversion: 89%; yield: 82%, normalized to 100% conversion) was obtained from **6c** [500 mg, reaction period: 7 h; temperature: 0 °C; elution with hexane/ethyl acetate (3:1, v/v) mixture]. Yellow oil, 59:41 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3444 (OH), 2104 (N_3), 1682 (C=O), 1598, 1504, 1410, 1300, 1234, 1160, 1104, 852 cm^{-1}. ^{1}H NMR: ***anti*-16c:** δ = 4.48 (d, *J* = 6.5 Hz, 1 H, 2-H); inseparable signals: δ = 1.38 (d, *J* = 6.2 Hz, 3 H, 4-H), 4.40−4.46 [m, 1 H, 3-H (*anti*) + m, 2 H, 2,3-H (*syn*)], 7.12−7.28 (m, 2 H, 3′,5′-H), 7.98−8.10 (m, 2 H, 2′,6′-H). NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: ***anti*-16c:** δ = 19.5 (C-4), 67.0, 68.0 (C-2,3); ***syn*-16c:** δ = 19.9 (C-4), 67.3, 68.5 (C-2,3); inseparable signals: δ = 116.1 (d, J_{CF} = 22.0 Hz, 3′,5′-C), 131.6 (d, J_{CF} = 9.9 Hz, 2′,6′-C), 131.1 (C-1′), 166.3 (d, J_{CF} = 258 Hz, 4′-C), 194.6 (C-1). NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{10}H_{10}FN_3O_2$ (223.2): C 53.81, H 4.52, N 18.83; found C 54.00, H 4.25, N 18.62.

2-Azido-3-hydroxy-1-(4-nitrophenyl)-1-butanone (16d): Compound **16d** [181 mg, 30%; reaction period: 17 h; temperature: 0 °C; elution with toluene/ethyl acetate (4:1, v/v) mixture] was obtained from **6d** (500 mg). Brownish oil, 59:41 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3446 (OH), 2114 (N_3), 1652 (C=O), 1522 (NO_2), 1348 (NO_2), 852 cm^{-1}. ^{1}H NMR: ***anti*-16d:** δ = 4.50 (d, *J* = 6.4 Hz, 1 H, 2-H); ***syn*-16d:** δ = 4.45 (d, *J* = 3.8 Hz, 1 H, 2-H); inseparable signals: δ = 1.37 (d, *J* = 6.3 Hz, 3 H, 4-H), 4.38 (m, 1 H, 3-H), 8.13 (overlapping d's, *J* = 8.4 Hz, 2 H, 2′,6′-H), 8.34 (d, *J* = 8.4 Hz, 2 H, 3′,5′-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: ***anti*-16d:** δ = 19.8 (C-4), 67.6, 68.0 (C-2,3), 140.0 (C-1′), 195.3 (C-1); ***syn*-16d:** δ = 20.1 (C-4), 68.3, 68.5 (C-2,3), 139.5 (C-1′), 195.0 (C-1); inseparable signals: δ = 124.0 (C-3′,5′), 129.8 (C-2′,6′), 150.6 (C-4′); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{10}H_{10}N_4O_4$ (250.2): calcd. C 48.00, H 4.03, N 22.39; found C 48.21, H 3.79, N 22.23.

2-Azido-1-(4-chlorophenyl)-3-hydroxy-1-butanone (16f): Compound **16f** [1.17 g, 67%; reaction period: 22 h; temperature: 0 °C; elution with toluene/ethyl acetate (8:1, v/v) mixture] was obtained from **6f** (1.42 g). Yellow oil, 50:50 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3452 (OH), 2112 (N_3), 1684 (C=O), 1588, 1284, 1252, 1216, 822 cm^{-1}. Fractional crystallization from diisopropyl ether afforded pure diastereomers. ***anti*-16f:** White prisms. M.p. 100−103 °C. ^{1}H NMR: δ = 1.35 (d, *J* = 6.3 Hz, 3 H, 4-H), 2.03 (br. s, 1 H, OH), 4.35 (m, 1 H, 3-H), 4.48 (d, *J* = 6.2 Hz, 1 H, 2-H), 7.49 (d, *J* = 8.6 Hz, 2 H, 3′,5′-H), 7.93 (d, *J* = 8.6 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 19.5 (C-4), 67.0, 68.0 (C-2,3), 129.2 (C-3′,5′), 130.2 (C-2′,6′), 133.6 (C-1′), 140.8 (C-4′), 195.0 (C-1). $C_{10}H_{10}ClN_3O_2$ (239.7): calcd. C 50.12, H 4.21, N 17.53; found C 50.21, H 4.23, N 17.39. ***syn*-16f:** Yellowish prisms. M.p. 37−41 °C. ^{1}H NMR: δ = 1.35 (d, *J* = 6.5 Hz, 3 H, 4-H), 2.20 (br. s, 1 H, OH), 4.33−4.41 (m, 2 H, 2,3-H), 7.49 (d, *J* = 9.0 Hz, 2 H, 3′,5′-H), 7.92 (d, *J* = 9.0 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 19.9 (C-4), 67.5, 68.4 (C-2,3), 129.2 (C-3′,5′), 130.1 (C-2′,6′), 133.1 (C-1′), 140.7 (C-4′), 195.0 (C-1). $C_{10}H_{10}ClN_3O_2$ (239.7): calcd. C 50.12, H 4.21, N 17.53; found C 50.26, H 4.18, N 17.43.

2-Azido-3-hydroxy-1-phenyl-1-pentanone (17a): Compound **17a** [766 mg, 56%; reaction period: 6.5 h; temperature: 25 °C; elution with hexane/ethyl acetate (3:1, v/v) mixture] was obtained from **6a** (1.00 g). Spectroscopic data have been reported previously.[3]

2-Azido-1-(4-chlorophenyl)-3-hydroxy-1-pentanone (17f): Compound **17f** [455 mg, 35%; reaction period: 4 h; temperature: 25 °C; elution with toluene/ethyl acetate (4:1, v/v) mixture] was obtained from **6f** (1.00 g). Yellow oil, 63:37 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3444 (OH), 2108 (N_3), 1682 (C=O), 1588, 1402, 1210, 1180, 1012, 984, 822 cm^{-1}. ^{1}H NMR: ***anti*-17f:** δ = 4.48 (d, *J* = 6.6 Hz, 1 H, 2-H), 7.93 (d, *J* = 8.1 Hz, 2 H, 2′,6′-H); ***syn*-17f:** δ = 4.47 (d, *J* = 3.0 Hz, 1 H, 2-H), 7.90 (d, *J* = 7.8 Hz, 2 H, 2′,6′-H); inseparable signals: δ = 1.03 (t, *J* = 7.3 Hz, 3 H, 5-H), 1.66 (m, 2 H, 4-H), 2.35 (br. s, 1 H, OH), 4.08 (m, 1 H, 3-H), 7.49 (d, *J* = 8.9 Hz, 2 H, 3′,5′-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: ***anti*-17f:** δ = 9.7 (C-5), 26.5 (C-4), 65.3 (C-2), 73.1 (C-3), 133.8 (C-1′); ***syn*-17f:** δ = 10.1 (C-5), 27.1 (C-4), 66.0 (C-2), 73.8 (C-3), 133.1 (C-1′); inseparable signals: δ = 129.3, 130.2 (C-2′,3′,5′,6′), 140.8 (C-4′), 195.1 (C-1); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{11}H_{12}ClN_3O_2$ (253.7): calcd. C 52.08, H 4.77, N 16.56; found C 51.99, H 4.72, N 16.52.

General Procedure for the Synthesis of 3-Azido-3-(1-hydroxyalkyl)chromanones 20−22 and Thio Derivative 29a: A mixture of the appropriate α-azido ketone (1.48 mmol), aldehyde (143 mmol), and TEA (0.21 mL, 1.48 mmol) was allowed to stand at 0 °C until completion of the reaction (TLC). The mixture was poured into water and extracted with CH_2Cl_2 (4 × 40 mL), the organic layer was dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue was submitted to column chromatography.

3-Azido-3-(1-hydroxyethyl)-4-chromanone (20a): Compound **20a** (230 mg, 67%) was obtained from **11a** (280 mg; reaction period: 5 h; elution with hexane/ethyl acetate (3:1, v/v) mixture]. Yellow oil, 56:44 mixture of the *syn*/*anti* diastereomers[26] (based on ^{1}H NMR). ^{1}H NMR: ***anti*-20a:** δ = 1.30 (d, *J* = 6.6 Hz, 3 H, 2′-H), 2.28

(deuterable s, 1 H, OH), 4.36, 4.68 (AB q, *J* = 11.6 Hz, 2 H, 2-H); ***syn*-20a:** δ = 1.34 (d, *J* = 6.2 Hz, 3 H, 2′-H), 2.98 (br. deuterable s, 1 H, OH), 4.29 (s, 2 H, 2-H); detailed spectroscopic data have been reported previously.[3]

3-Azido-3-(1-hydroxypropyl)-4-chromanone (21a): Compound **21a** (1.63 g, 62%) was obtained from **11a** [2.00 g; reaction period: 3 h; elution with toluene/ethyl acetate (9:1, v/v) mixture]. Yellow oil, 58:42 mixture of the *syn*/*anti* diastereomers[26] (based on ^{1}H NMR). Pure diastereomers were obtained by repeated column chromatography, with a toluene/ethyl acetate (9:1, v/v) mixture as eluent. ^{1}H NMR: ***anti*-21a:** δ = 1.03 (t, *J* = 7.3 Hz, 3 H, 3′-H), 1.39−1.72 (m, 2 H, 2′-H), 4.11 (m, 1 H, 1′-H), 4.34, 4.68 (AB q, *J* = 12.0 Hz, 2 H, 2-H); ***syn*-21a:** δ = 1.06 (t, *J* = 7.2 Hz, 3 H, 3′-H), 1.40−1.74 (m, 2 H, 2′-H), 4.10 (m, 1 H, 1′-H), 4.31, 4.35 (AB q, *J* = 12.2 Hz, 2 H, 2-H); detailed spectroscopic data have been reported previously.[3]

3-Azido-3-(1-hydroxypropyl)-6-methyl-4-chromanone (21e): Compound **21e** (761 mg, 74%) was obtained from **11e** [800 mg; reaction period: 22 h; elution with toluene/ethyl acetate (9:1, v/v) mixture]. Yellow oil, 57:43 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): ṽ = 3456 (OH), 2110 (N_3), 1682 (C=O), 1616, 1494, 1418, 1294, 1220, 1138, 824 cm^{-1}. ^{1}H NMR: ***anti*-21e:** δ = 1.04 (t, *J* = 7.2 Hz, 3 H, 3′-H), 4.32, 4.66 (AB q, *J* = 11.5 Hz, 2 H, 2-H), 6.91 (d, *J* = 8.4 Hz, 1 H, 8-H); ***syn*-21e:** δ = 1.07 (t, *J* = 7.4 Hz, 3 H, 3′-H), 4.29, 4.33 (AB q, *J* = 12.1 Hz, 2 H, 2-H), 6.90 (d, *J* = 8.1 Hz, 1 H, 8-H); inseparable signals: δ = 1.48−1.68 (m, 2 H, 2′-H), 2.33 (s, 3 H, 6-Me), 4.08 (m, 1 H, 1′-H), 7.36 (overlapping d's, 1 H, 7-H), 7.73 (overlapping d's, 1 H, 5-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: ***anti*-21e**: δ = 10.8 (C-3′), 23.7 (C-2′), 68.0 (C-3), 69.3 (C-2), 72.1 (C-1′), 117.8 (C-8), 119.2 (C-4a), 127.3 (C-5), 131.7 (C-6), 189.3 (C-4); ***syn*-21e**: δ = 10.6 (C-3′), 24.1 (C-2′), 67.4 (C-3), 69.8 (C-2), 74.1 (C-1′), 117.7 (C-8), 118.9 (C-4a), 127.4 (C-5), 131.9 (C-6), 190.3 (C-4); inseparable signals: δ = 20.4 (6-Me), 138.2 (C-7), 159.1 (C-8a); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{13}H_{15}N_3O_3$ (261.3): C 59.76, H 5.79, N 16.08; found C 59.89, H 5.55, N 16.05.

3-Azido-6-chloro-3-(1-hydroxypropyl)-4-chromanone (21f): Compound **21f** (236 mg, 62%) was obtained from **11f** [300 mg; reaction period: 2 h; elution with toluene/ethyl acetate (9:1, v/v) mixture]. Yellow oil, 57:43 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): ṽ = 3438 (OH), 2112 (N_3), 1682 (C=O), 1606, 1470, 1418, 1270, 1100, 824 cm^{-1}. Pure diastereomers were obtained by repeated column chromatography with toluene/ethyl acetate (9:1, v/v) mixture as eluent. ***anti*-21f:** Yellow oil. ^{1}H NMR: δ = 1.06 (t, *J* = 7.2 Hz, 3 H, 3′-H), 1.46−1.68 (m, 2 H, 2′-H), 4.09 (dd, *J* = 10.6, 2.6 Hz, 1 H, 1′-H), 4.36, 4.70 (AB q, *J* = 12.1 Hz, 2 H, 2-H), 6.98 (d, *J* = 8.7 Hz, 1 H, 8-H), 7.48 (dd, *J* = 8.7, 2.6 Hz, 1 H, 7-H), 7.89 (d, *J* = 2.6 Hz, 1 H, 5-H). ^{13}C NMR: δ = 10.8 (C-3′), 23.7 (C-2′), 67.6 (C-3), 69.4 (C-2), 72.0 (C-1′), 119.8 (C-8), 120.4 (C-4a), 127.1 (C-5), 127.8 (C-6), 136.9 (C-7), 159.5 (C-8a), 188.1 (C-4). $C_{12}H_{12}ClN_3O_3$ (281.7): C 51.17, H 4.29, N 14.92; found C 51.09, H 4.42, N 14.83. ***syn*-21f:** Yellow oil. ^{1}H NMR: δ = 1.07 (t, *J* = 7.4 Hz, 3 H, 3′-H), 1.51−1.72 (m, 2 H, 2′-H), 4.06 (dd, *J* = 9.4, 3.3 Hz, 1 H, 1′-H), 4.30, 4.35 (AB q, *J* = 12.3 Hz, 2 H, 2-H), 6.95 (d, *J* = 8.6 Hz, 1 H, 8-H), 7.46 (dd, *J* = 8.6, 2.3 Hz, 1 H, 7-H), 7.88 (d, *J* = 2.3 Hz, 1 H, 5-H). ^{13}C NMR: δ = 10.5 (C-3′), 24.2 (C-2′), 67.3 (C-3), 69.8 (C-2), 73.8 (C-1′), 119.6 (C-8), 120.1 (C-4a), 127.1 (C-5), 127.9 (C-6), 136.7 (C-7), 159.4 (C-8a), 189.1 (C-4). $C_{12}H_{12}ClN_3O_3$ (281.7): C 51.17, H 4.29, N 14.92; found C 51.02, H 4.51, N 15.11.

3-Azido-3-(1-hydroxypentyl)-4-chromanone (22a): Compound **22a** (450 mg, 60%) was obtained from **11a** [520 mg; reaction period: 24 h; elution with hexane/acetone (12:1, v/v) mixture]. Yellow oil, 67:33 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): ṽ = 3478 (OH), 2112 (N_3), 1682 (C=O), 1608, 1480, 1466, 1312, 1270, 1218, 1148, 1038, 760 cm^{-1}. The pure *syn* diastereomer was obtained by repeated column chromatography with toluene/ethyl acetate (9:1, v/v) mixture as eluent. ***syn*-22a:** Yellow oil. ^{1}H NMR: δ = 0.92 (t, *J* = 7.0 Hz, 3 H, 5′-H), 1.20−1.61 (m, 6 H, 2′,3′,4′-H), 4.18 (m, 1 H, 1′-H), 4.35 (s, 2 H, 2-H), 7.00 (d, *J* = 8.4 Hz, 1 H, 8-H), 7.11 (m, 1 H, 6-H), 7.56 (m, 1 H, 7-H), 7.97 (dd, *J* = 7.6, 1.6 Hz, 1 H, 5-H). ^{13}C NMR: δ = 13.8 (C-5′), 22.3, 28.1, 30.7 (C-2′,3′,4′), 67.4 (C-3), 69.6 (C-2), 72.3 (C-1′), 117.8 (C-8), 119.2 (C-4a), 122.2 (C-6), 127.9 (C-5), 136.8 (C-7), 160.9 (C-8a), 190.1 (C-4). $C_{14}H_{17}N_3O_3$ (275.3): C 61.08, H 6.22, N 15.26; found C 60.90, H 6.25, N 15.34. ***anti*-22a:** ^{1}H NMR: δ = 4.19 (m, 1 H, 1′-H), 4.35, 4.70 (AB q, *J* = 12.1 Hz, 2 H, 2-H), 7.01 (d, *J* = 8.4 Hz, 1 H, 8-H), 7.09 (t, *J* = 8.4 Hz, 1 H, 6-H); inseparable signals: δ = 0.88−0.93 (m, 3 H, 5′-H), 1.34−1.67 (m, 6 H, 2′,3′,4′-H), 7.55 (m, 1 H, 7-H), 7.94 (d, *J* = 8.1, 1.7 Hz, 1 H, 5-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: δ = 13.8 (C-5′), 22.3, 28.3, 30.1, (C-2′,3′,4′), 67.8 (C-3), 69.1 (C-2), 70.2 (C-1′), 117.9 (C-8), 119.5 (C-4a), 122.0 (C-6), 127.9 (C-5), 136.8 (C-7), 160.9 (C-8a), 189.1 (C-4); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{14}H_{17}N_3O_3$ (275.3): C 61.08, H 6.22, N 15.26; found C 60.95, H 6.26, N 15.03.

3-Azido-3-(1-hydroxyethyl)-1-thiochroman-4-one (29a): Compound **29a** (198 mg, 65%) was obtained from **12a** [250 mg; reaction period: 23 h; elution with hexane/ethyl acetate (3:1, v/v) mixture]. Yellow oil, 78:22 mixture of the *syn*/*anti* diastereomers (based on ^{1}H NMR). IR (neat): ṽ = 3479 (OH), 2109 (N_3), 1695 (C=O), 1590, 1436, 1267, 903, 738 cm^{-1}. ^{1}H NMR: ***anti*-29a:** δ = 1.24 (d, *J* = 6.4 Hz, 3 H, 2′-H), 3.37, 3.58 (AB q, *J* = 13.6 Hz, 2 H, 2-H); ***syn*-29a:** δ = 1.36 (d, *J* = 6.3 Hz, 3 H, 2′-H), 3.08, 3.41 (AB q, *J* = 14.0 Hz, 2 H, 2-H); inseparable signals: δ = 4.59 (overlapping q's, 1 H, 1′-H), 7.20−7.24 (m, 2 H, 6,8-H), 7.41 (m, 1 H, 7-H), 8.09 (m, 1 H, 5-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. ^{13}C NMR: ***anti*-29a:** δ = 17.2 (C-2′), 31.3 (C-1′), 69.1 (C-2), 125.5 (C-6), 127.3 (C-8), 130.7 (C-5), 134.2 (C-7), 141.6 (C-8a), 191.1 (C-4); ***syn*-29a:** δ = 17.6 (C-2′), 32.1 (C-1′), 69.0 (C-2), 125.7 (C-6), 127.1 (C-8), 131.0 (C-5), 134.1 (C-7), 141.0 (C-8a), 192.0 (C-4); inseparable signals: δ = 66.8 (C-3), 129.6 (C-4a); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{11}H_{11}N_3O_2S$ (249.3): C 53.00, H 4.45, N 16.86; found C 53.21, H 4.57, N 14.88.

***syn*-3-Azido-3-[1-(*p*-nitrobenzoyloxy)propyl]-4-chromanone (23):** *p*-Nitrobenzoyl chloride (295 mg, 1.59 mmol) was added to a stirred and cooled (0 °C) solution of *syn*-3-azido-3-(1-hydroxypropyl)-4-chromanone (*syn*-**21a**; 328 mg, 1.33 mmol) in dry pyridine (9 mL) and the reaction mixture was allowed to warm to ambient temperature. After 18 h, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure, and purified by short column chromatography (eluent: hexane/ethyl acetate, 3:1, v/v) to give 420 mg (80%) of ester **23** as colorless crystals. M.p. 78−80 °C. IR: ṽ = 2114 (N_3), 1732 (C=O, ester), 1696 (C=O, ketone), 1608, 1524 (NO_2), 1478, 1344 (NO_2), 1260 (C−O−C), 1098, 718 cm^{-1}. ^{1}H NMR: δ = 1.02 (t, *J* = 7.3 Hz, 3 H, 3′-H), 1.99 (m, 2 H, 2′-H), 4.22, 4.40 (AB q, *J* = 12.0 Hz, 2 H, 2-H), 5.78 (dd, *J* = 7.7, 5.5 Hz, 1 H, 1′-H), 6.98 (d, *J* = 8.1 Hz, 1 H, 8-H), 7.10 (m, 1 H, 6-H), 7.55 (m, 1 H, 7-H), 7.85 (dd, *J* = 7.6, 1.5 Hz, 1 H, 5-H), 8.16 (d, J = 8.8 Hz, 2 H, 2′′,6′′-H), 8.28 (d, J = 8.8 Hz, 2 H, 3′′,5′′-H). ^{13}C NMR: δ = 10.1 (C-3′), 22.8 (C-2′), 66.6 (C-3), 70.1 (C-2), 75.8 (C-1′), 117.8 (C-8), 119.2 (C-4a), 122.7 (C-6), 123.6 (C-3′′,5′′), 128.0 (C-5), 131.0 (C-2′′,6′′), 134.4 (C-1′′), 136.9 (C-7), 150.7 (C-4′′), 160.7 (C-8a), 163.8 (C=O, ester), 189.5 (C-4). $C_{19}H_{16}N_4O_6$ (396.4): C 57.58, H 4.07, N 14.14; found C 57.41, H 4.11, N 14.19.

Crystal Data of 23: Colorless hexagonal block of twinned crystals (0.65 × 0.3 × 0.12 mm) of $C_{19}H_{16}N_4O_6$, M = 396.36, trigonal, a = 15.8076(10) Å, b = 15.8076(10) Å, c = 14.0709(10) Å, α = 90°, V = 3045.0(3) Å^3, Z = 6, space group: P3bar, $\rho_{calcd.}$ = 1.297 g cm^{-3}. Data were collected at 293(1) K, Enraf−Nonius MACH3 diffractometer, Mo-K_α radiation λ = 0.71073 Å, ω-2θ motion, θ_{max} = 25.23°, 3677 measured, unique reflections of which 1141 with $I > 2\sigma(I)$, decay: 7%. The structure was solved by SIR-92 software[27] and refined on F^2 with the SHELX-97[28] program, publication material was prepared with the WINGX-97 suite,[29] $R(F)$ = 0.1453 and $wR(F^2)$ = 0.4475 for 3677 reflections, 263 parameters. Residual electron density: 1.266/−0.268 e/Å^3. Crystal structure data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144756. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

3-Azido-3-(1-trimethylsilyloxyethyl)flavanone (28): A mixture of *trans*-3-azido-flavanone (**15**, 198 mg, 0.74 mmol), acetaldehyde (5.00 mL, 88.6 mmol), and TEA (0.10 mL, 0.74 mmol) was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and hexamethyldisilazane (0.05 mL, 0.25 mmol) was then added to the stirred solution of the residue in hexane (2 mL). A solution of chlorotrimethylsilane (0.03 mL, 0.25 mmol) in hexane (5 mL) was added dropwise over 15 min at room temperature. The reaction mixture was refluxed and stirred. Two batches of HMDS (0.25 mmol) and TMSCl (0.25 mmol) were added to the reaction mixture after 4 and 17 h. When the reaction was complete (29 h), the mixture was filtered and the precipitate was washed with hexane (2 × 10 mL). The combined organic layers were concentrated in vacuo and the residue was purified by column chromatography (eluent: hexane/ethyl acetate, 3:1, v/v) to give pure **28** (51 mg, 13%) as a yellow oil, 74:26 mixture of the diastereomers **28/28′** (based on ^{1}H NMR). IR (neat): ṽ = 2112 (N_3), 1694 (C=O), 1606, 1252, 1464, 842 cm^{-1}. ^{1}H NMR: **28**: δ = 0.19 (s, 9 H, **Me**$_3$Si), 1.04 (d, J = 6.5 Hz, 1 H, 2′-H), 4.61 (q, J = 6.5 Hz, 1 H, 1′-H), 5.81 (s, 1 H, 2-H), 7.00 (d, J = 8.3 Hz, 1 H, 8-H), 7.09 (m, 1 H, 6-H), 7.93 (dd, J = 8.2, 1.6 Hz, 1 H, 5-H). **28′**: δ = −0.06 (s, 9 H, **Me**$_3$Si), 1.52 (d, J = 6.0 Hz, 1 H, 2′-H), 4.53 (q, J = 6.0 Hz, 1 H, 1′-H), 5.35 (s, 1 H, 2-H), 6.98 (d, J = 8.3 Hz, 1 H, 8-H), 7.08 (m, 1 H, 6-H), 7.91 (dd, J = 8.0, 1.7 Hz, 1 H, 5-H); inseparable signals: δ = 7.26−7.44 (m, 5 H, 2-Ph), 7.55 (m, 1 H, 7-H); NMR spectroscopic data were taken from the spectra of the diastereomeric mixture. $C_{20}H_{23}N_3O_3Si$ (381.5): C 62.97, H 6.08, N 11.01; found C 62.83, H 5.96, N 10.93.

General Procedure for the Synthesis of Aziridines 18, 19, 24−26, 30a: A mixture of the appropriate α-azido-β-hydroxy ketone **16**, **17**, **20−22**, or **29a** (0.90 mmol) and triphenylphosphane (236 mg, 0.90 mmol) in dry benzene (10 mL) was stirred at room temperature until completion of the reaction (TLC). The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography.

***trans*-2-Benzoyl-3-methylaziridine (18a):** Compound **18a** (27 mg, 20%) was obtained from a 56:44 mixture of the *syn*/*anti* diastereomers of **16a** [170 mg; reaction period: 24 h; elution with hexane/ethyl acetate (1:3, v/v) mixture]. Spectroscopic data have been reported previously.[3]

***trans*-2-(4-Methoxybenzoyl)-3-methylaziridine (18b):** Compound **18b** (34 mg, 21%) was obtained from a 66:34 mixture of the *syn*/*anti* diastereomers of **16b** [200 mg; reaction period: 7 h; elution with hexane/ethyl acetate (1:3, v/v) mixture]. Yellow oil. IR (neat): ṽ = 3264 (NH), 1660 (C=O), 1600, 1512, 1424, 1254, 1172, 942, 848, 722 cm^{-1}. ^{1}H NMR: δ = 1.35 (d, J = 5.4 Hz, 3 H, 3-Me), 2.12−2.21 (m, 2 H, NH, 3-H), 3.18 (d, J = 2.1 Hz, 1 H, 2-H), 3.89 (s, 3 H, 4′-MeO), 6.98 (d, J = 8.6 Hz, 2 H, 3′,5′-H), 8.01 (d, J = 8.6 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 18.4 (3-Me), 37.6 (C-3), 40.1 (C-2), 55.4 (4′-MeO), 114.0 (C-3′,5′), 129.4 (C-1′), 130.6 (C-2′,6′), 164.2 (C-4′), 195.7 (C=O). $C_{11}H_{13}NO_2$ (191.2): C 69.09, H 6.85, N 7.32; found C 69.23, H 7.01, N 7.31.

***trans*-2-(4-Fluorobenzoyl)-3-methylaziridine (18c):** Compound **18c** (5 mg, 3.1%) was obtained from a 59:41 mixture of the *syn*/*anti* diastereomers of **16c** [200 mg; reaction period: 23 h; elution with hexane/ethyl acetate (1:3, v/v) mixture]. Yellow oil. IR (neat): ṽ = 3268 (NH), 1670 (C=O), 1598, 1422, 1258, 1232, 852 cm^{-1}. ^{1}H NMR: δ = 1.36 (d, J = 5.4 Hz, 3 H, 3-Me), 2.16−2.37 (m, 2 H, NH, 3-H), 3.22 (d, J = 2.2 Hz, 1 H, 2-H), 7.16−7.24 (m, 2 H, 3′,5′-H), 8.08 (dd, J_{ortho} = 8.7 Hz, J_{HF} = 5.5 Hz, 2 H, 2′,6′-H). $C_{10}H_{10}FNO$ (179.2): C 67.03, H 5.62, N 7.82; found C 66.80, H 5.79, N 8.02.

***trans*-2-(4-Chlorobenzoyl)-3-methylaziridine (18f):** Compound **18f** (26 mg, 32%) was obtained from *anti*-**16f** [100 mg; reaction period: 18 h; elution with hexane/ethyl acetate (1:3, v/v) mixture]. Yellow oil. IR (neat): ṽ = 3255, 3186 (NH), 1682 (C=O), 1588, 1402, 1226, 1092, 1012, 850 cm^{-1}. ^{1}H NMR: δ = 1.36 (d, J = 5.8 Hz, 3 H, 3-Me), 2.24 (dq, J = 5.8, 2.7 Hz, 1 H, 3-H), 2.40 (br. s, 1 H, NH), 3.18 (d, J = 2.7 Hz, 1 H, 2-H), 7.48 (d, J = 8.4 Hz, 2 H, 3′,5′-H), 7.95 (d, J = 8.4 Hz, 2 H, 2′,6′-H). $C_{10}H_{10}ClNO$ (195.6): C 61.39, H 5.15, N 7.16; found C 61.12, H 4.98, N 7.32. When the reaction was repeated with *syn*-**16f** (100 mg; reaction period: 26 h), 6 mg (7.3%) of *trans*-aziridine **18f** was obtained.

***trans*-2-Benzoyl-3-ethylaziridine (19a):** Compound **19a** (15 mg, 9.4%) was obtained from a 65:35 mixture of the *syn*/*anti* diastereomers of **17a** [200 mg; reaction period: 29 h; elution with hexane/ethyl acetate (1:3, v/v) mixture]. Yellow oil. IR (neat): ṽ = 3270 (NH), 1668 (C=O), 1450, 1258, 700 cm^{-1}. ^{1}H NMR: δ = 1.07 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.50−1.72 (m, 2 H, CH_2CH_3), 2.09−2.29 (m, 2 H, NH, 3-H), 3.28 (d, J = 2.2 Hz, 1 H, 2-H), 7.40−7.70 (m, 3 H, 3′,4′,5′-H), 7.98−8.10 (dd, J = 8.0, 1.6 Hz, 2 H, 2′,6′-H). ^{13}C NMR: δ = 11.0 (CH_2CH_3), 26.3 (CH_2CH_3), 39.5 (C-3), 44.5 (C-2), 128.3, 128.8, 128.9 (C-2′,3′,5′,6′), 133.8 (C-4′), 196.8 (C=O). $C_{11}H_{13}NO$ (175.2): C 75.40, H 7.48, N 7.99; found C 75.41, H 7.29, N 8.05.

3′-Methylspiro[chroman-3,2′-aziridin]-4-one (24a): Compound **24a** (65 mg, 37%) was obtained from a 56:44 mixture of the *syn*/*anti* diastereomers of **20a** [220 mg; reaction period: 4d; elution with hexane/ethyl acetate (1:3, v/v) mixture] as a 51:49 mixture of the *cis*/*trans* diastereomers (based on ^{1}H NMR). Analytical samples of pure *cis* and *trans* diastereomers were obtained by repeated column chromatography with a hexane/ethyl acetate (1:3, v/v) mixture as eluent. ***trans*-24a:** Yellowish oil. IR (neat): ṽ = 3269 (NH), 1684 (C=O), 1608, 1477, 1317, 1212, 1100, 792 cm^{-1}. ^{1}H NMR: δ = 1.36 (d, J = 5.3 Hz, 3 H, CH_3), 2.08 (s, 1 H, NH), 2.45 (q, J = 5.3 Hz, 1 H, 3′-H), 4.27, 4.68 (AB q, J = 11.9 Hz, 2 H, 2-H), 6.99−7.09 (m, 2 H, 6,8-H), 7.52 (m, 1 H, 7-H), 7.89 (dd, J = 7.5, 1.6 Hz, 1 H, 5-H). ^{13}C NMR: δ = 14.2 (CH_3), 41.8 (C-3′), 42.9 (C-

3/2′), 67.9 (C-2), 118.3 (C-8), 120.9 (C-4a), 121.7 (C-6), 127.0 (C-5), 136.5 (C-7), 162.1 (C-8a), 192.2 (C-4). $C_{11}H_{11}NO_2$ (189.2): C 69.83, H 5.86, N 7.40; found C 69.66, H 5.99, N 7.23. ***cis*-24a:** Yellowish oil. ^{1}H NMR: δ = 1.26 (d, *J* = 5.5 Hz, 3 H, CH_3), 2.04 (s, 1 H, NH), 2.54 (q, *J* = 5.5 Hz, 1 H, 3′-H), 3.99, 4.74 (AB q, *J* = 11.7 Hz, 2 H, 2-H), 6.99−7.09 (m, 2 H, 6,8-H), 7.52 (m, 1 H, 7-H), 7.92 (dd, *J* = 7.4, 1.9 Hz, 1 H, 5-H). ^{13}C NMR: δ = 13.0 (CH_3), 43.7 (C-3/2′), 44.6 (C-3′), 73.0 (C-2), 118.2 (C-8), 121.6 (C-6), 126.9 (C-5), 136.4 (C-7), 162.0 (C-8a), 190 3 (C-4). $C_{11}H_{11}NO_2$ (189.2): C 69.83, H 5.86, N 7.40; found C 70.11, H 5.69, N 7.47.

***cis*-3′-Ethylspiro[chroman-3,2′-aziridin]-4-one (*cis*-25a):** Compound ***cis*-25a** (68 mg, 62%) was obtained from *syn*-**21a** [133 mg; reaction period: 7 d; elution with hexane/ethyl acetate (1:1, v/v) mixture]. Yellow oil. IR (neat): ṽ = 3254 (NH), 1682 (C=O), 1606, 1470, 1288, 1210, 760 cm^{-1}. ^{1}H NMR: δ = 0.38 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 1.28−1.71 (m, 2 H, CH_2CH_3), 1.80 (br. s, 1 H, NH), 2.34 (m, 1 H, 3′-H), 3.92, 4.71 (AB q, *J* = 11.6 Hz, 2 H, 2-H), 6.96−7.05 (m, 2 H, 6,8-H), 7.48 (m, 1 H, 7-H), 7.90 (dd, *J* = 7.7, 1.9 Hz, 1 H, 5-H). ^{13}C NMR: δ = 11.8 (CH_2CH_3), 20.8 (CH_2CH_3), 43.5 (C-3/2′), 51.0 (C-3′), 73.0 (C-2), 118.2 (C-8), 121.6 (C-6), 126.9 (C-5), 136.5 (C-7), 162.1 (C-8a), 190.7 (C-4). $C_{12}H_{13}NO_2$ (203.2): C 70.92, H 6.45, N 6.89; found C 70.73, H 6.69, N 6.63.

***trans*-3′-Ethylspiro[chroman-3,2′-aziridin]-4-one (*trans*-25a):** Compound ***trans*-25a** (17 mg, 26%) was obtained from *anti*-**21a** [80 mg, reaction period: 7 d; elution with hexane/ethyl acetate (1:1, v/v) mixture]. Yellow oil. IR: (neat): ṽ = 3269 (NH), 1676 (C=O), 1608, 1457, 1325, 1212, 757 cm^{-1}. ^{1}H NMR: δ = 1.06 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.47−1.77 (m, 2 H, CH_2CH_3), 2.34 (br. s, 2 H, 3′-H, NH), 4.23, 4.66 (AB q, *J* = 12.1 Hz, 2 H, 2-H), 7.00−7.10 (m, 2 H, 6,8-H), 7.53 (m, 1 H, 7-H), 7.90 (dd, *J* = 8.1, 1.9 Hz, 1 H, 5-H). ^{13}C NMR: δ = 11.3 (CH_2CH_3), 22.2 (CH_2CH_3), 42.8 (C-3/2′), 48.5 (C-3′), 68.0 (C-2), 118.4 (C-8), 121.0 (C-4a), 121.8 (C-6), 127.2 (C-5), 136.6 (C-7), 162.4 (C-8a), 192.6 (C-4). $C_{12}H_{13}NO_2$ (203.2): C 70.92, H 6.45, N 6.89; found C 71.07, H 6.31, N 6.77.

3′-Ethylspiro[6-methylchroman-3,2′-aziridin]-4-one (25e): Compound **25e** (303 mg, 63%, normalized to 100% conversion) was obtained from a 57:43 mixture of the *syn*/*anti* diastereomers of **21e** [700 mg; reaction period: 6 d; elution with hexane/ethyl acetate (2:1, v/v) mixture; conversion: 83%] as a 58:42 mixture of the *cis*/*trans* diastereomers (based on ^{1}H NMR). Analytical samples of the pure *cis* and *trans* diastereomers were obtained by repeated column chromatography with hexane/ethyl acetate (2:1, v/v) mixture as eluent. ***trans*-25e:** Yellowish-brown oil. IR (neat): ṽ = 3268 (NH), 1683 (C=O), 1618, 1492, 1299, 876 cm^{-1}. ^{1}H NMR: δ = 1.06 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 1.72−1.94 (m, 2 H, CH_2CH_3), 2.32 (overlapping s and t, 5 H, 6-Me, 3′-H, NH), 4.20, 4.62 (AB q, *J* = 12.2 Hz, 2 H, 2-H), 6.91 (d, *J* = 8.3 Hz, 1 H, 8-H), 7.33 (dd, *J* = 8.3, 2.9 Hz, 1 H, 7-H), 7.68 (d, *J* = 2.9 Hz, 1 H, 5-H). ^{13}C NMR: δ = 11.4 (CH_2CH_3), 20.2 (6-Me), 22.3 (CH_2CH_3), 42.8 (C-3/2′), 48.4 (C-3′), 67.9 (C-2), 117.9 (C-8), 120.4 (C-4a), 126.5 (C-5), 131.1 (C-6), 137.4 (C-7), 160.1 (C-8a), 192.3 (C-4). $C_{13}H_{15}NO_2$ (217.3): C 71.87, H 6.96, N 6.45; found C 71.99, H 7.12, N 6.24. ***cis*-25e:** Brownish oil. IR (neat): ṽ = 3254 (NH), 1680 (C=O), 1618, 1492, 1286, 873 cm^{-1}. ^{1}H NMR: δ = 0.87 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.35−1.67 (m, 2 H, CH_2CH_3), 2.07 (br. s, 1 H, NH), 2.32 (s, 3 H, 6-Me), 2.38 (t, *J* = 6.8 Hz, 1 H, 3′-H) 3.92, 4.71 (AB q, *J* = 11.7 Hz, 2 H, 2-H), 6.91 (d, *J* = 8.3 Hz, 1 H, 8-H), 7.33 (dd, *J* = 8.3, 2.2 Hz, 1 H, 7-H), 7.70 (s, 1 H, 5-H). ^{13}C NMR: δ = 12.0 (CH_2CH_3), 20.3 (6-Me), 20.9 (CH_2CH_3), 43.6 (C-3/2′), 51.0 (C-3′), 73.0 (C-2), 117.8 (C-8), 121.0 (C-4a), 126.2 (C-5), 130.9 (C-6), 137.3 (C-7), 160.0 (C-8a), 190.4 (C-4). $C_{13}H_{15}NO_2$ (217.3): C 71.87, H 6.96, N 6.45; found C 71.66, H 7.00, N 6.58.

3′-Ethylspiro[6-chlorochroman-3,2′-aziridin]-4-one (25f): Compound **25f** (63 mg, 44%) was obtained from a 57:43 mixture of the *syn*/*anti* diastereomers of **21f** [170 mg; reaction period: 4 d; elution with hexane/ethyl acetate (2:1, v/v) mixture] as a 66:34 mixture of the *cis* and *trans* diastereomers (based on ^{1}H NMR). Analytical samples of pure *cis* and *trans* diastereomers were obtained by repeated column chromatography with hexane/ethyl acetate (2:1, v/v) mixture as eluent. ***trans*-25f:** Yellow oil. IR (neat): ṽ = 3271 (NH), 1684 (C=O), 1605, 1474, 1260, 860 cm^{-1}. ^{1}H NMR: δ = 1.06 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 1.44−1.73 (m, 2 H, CH_2CH_3), ≈1.8 (br. s, 1 H, NH), 2.35 (br. s, 1 H, 3′-H), 4.24, 4.65 (AB q, *J* = 12.4 Hz, 2 H, 2-H), 6.99 (d, *J* = 8.3 Hz, 1 H, 8-H), 7.46 (dd, *J* = 8.3, 2.7 Hz, 1 H, 7-H), 7.86 (d, *J* = 2.7 Hz, 1 H, 5-H). ^{13}C NMR: δ = 11.4 (CH_2CH_3), 22.4 (CH_2CH_3), 42.8 (C-3/2′), 48.9 (C-3′), 68.1 (C-2), 120.0 (C-8), 121.7 (C-4a), 126.3 (C-5), 127.3 (C-6), 136.2 (C-7), 160.5 (C-8a), 191.4 (C-4). $C_{12}H_{12}ClNO_2$ (237.7): C 60.64, H 5.09, N 5.89; found C 60.43, H 4.97, N 5.64. ***cis*-25f:** Pale yellow oil. IR (neat): ṽ = 3257 (NH), 1684 (C=O), 1604, 1474, 1261, 859 cm^{-1}. ^{1}H NMR: δ = 0.87 (t, *J* = 7.7 Hz, 3 H, CH_2CH_3), 1.35 (m, 1 H, one of CH_2CH_3), 1.63 (m, 1 H, other CH_2CH_3), 1.76 (br. s, 1 H, NH), 2.39 (br. t, *J* = 6.1 Hz, 1 H, 3′-H) 3.95, 4.72 (AB q, *J* = 11.5 Hz, 2 H, 2-H), 6.98 (d, *J* = 8.9 Hz, 1 H, 8-H), 7.45 (dd, *J* = 8.9, 2.6 Hz, 1 H, 7-H), 7.87 (d, *J* = 2.6 Hz, 1 H, 5-H). ^{13}C NMR: δ = 12.1 (CH_2CH_3), 21.1 (CH_2CH_3), 43.5 (C-3/2′), 51.5 (C-3′), 73.2 (C-2), 119.9 (C-8), 122.2 (C-4a), 126.1 (C-5), 127.2 (C-6), 136.2 (C-7), 160.4 (C-8a), 189.4 (C-4). $C_{12}H_{12}ClNO_2$ (237.7): C 60.64, H 5.09, N 5.89; found C 60.63, H 5.05, N 5.98.

***cis*-3′-Butylspiro[chroman-3,2′-aziridin]-4-one (*cis*-26a):** Compound ***cis*-26a** (46 mg, 39%) was obtained from *syn*-**22a** [140 mg; reaction period: 14 d; elution with hexane/ethyl acetate (2:1, v/v) mixture]. Yellow oil. IR (neat): ṽ = 3255 (NH), 1684 (C=O), 1607, 1477, 1283, 1211, 1027, 760 cm^{-1}. ^{1}H NMR: δ = 0.78 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.19−1.57 (m, 6 H, $(CH_2)_3CH_3$), 1.99 (br. s, 1 H, NH), 2.38 (t, *J* = 6.3 Hz, 1 H, 3′-H), 3.95, 4.74 (AB q, *J* = 11.7 Hz, 2 H, 2-H), 7.00−7.09 (m, 2 H, 6,8-H), 7.52 (m, 1 H, 7-H), 7.92 (dd, *J* = 8.0, 1.4 Hz, 1 H, 5-H). ^{13}C NMR: δ = 13.7 (CH_3), 22.0, 27.1, 29.8 ($CH_2CH_2CH_2CH_3$), 43.5 (C-3/2′), 49.8 (C-3′), 73.1 (C-2), 118.1 (C-8), 121.5 (C-6), 126.7 (C-5), 136.3 (C-7), 161.9 (C-8a), 190.4 (C-4). $C_{14}H_{17}NO_2$ (231.3): C 72.70, H 7.41, N 6.06; found C 72.58, H 7.65, N 5.92.

3′-Butylspiro[chroman-3,2′-aziridin]-4-one (26a): Compound **26a** (122 mg, 52%) was obtained from a 67:33 mixture of the *syn*/*anti* diastereomers of **22a** [280 mg; reaction period: 9 d; elution with hexane/ethyl acetate (2:1, v/v) mixture], as a 70:30 mixture of the *cis*/*trans* diastereomers (based on ^{1}H NMR). Analytical samples of the pure *cis* and *trans* diastereomers were obtained by repeated column chromatography with hexane/ethyl acetate (2:1, v/v) mixture as eluent. ***trans*-26a:** Yellow oil. IR (neat): ṽ = 3268 (NH), 1683 (C=O), 1607, 1477, 1324, 1034, 759 cm^{-1}. ^{1}H NMR: δ = 0.89 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.34−1.59 (m, 6 H, $(CH_2)_3CH_3$), 2.34 (overlapping t and s, *J* = 6.2 Hz, 2 H, 3′-H, NH), 4.23, 4.65 (AB q, *J* = 12.0 Hz, 2 H, 2-H), 6.98−7.08 (m, 2 H, 6,8-H), 7.49 (m, 1 H, 7-H), 7.89 (dd, *J* = 8.4, 1.3 Hz, 1 H, 5-H). ^{13}C NMR: δ = 13.8 (CH_3), 22.4, 28.6, 29.4 ($CH_2CH_2CH_2CH_3$), 42.8 (C-3/2′), 47.1 (C-3′), 68.0 (C-2), 118.2 (C-8), 120.8 (C-4a), 121.6 (C-6), 127.0 (C-5), 136.4 (C-7), 162.0 (C-8a), 192.2 (C-4). $C_{14}H_{17}NO_2$ (231.3): C 72.70, H 7.41, N 6.06; found C 72.79, H 7.69, N 6.24.

3′-Methylspiro[1-thiochroman-3,2′-aziridin]-4-one (30a): Compound **30a** (26 mg, 44%, normalized to 100% conversion) was obtained from a 78:22 mixture of the *syn*/*anti* diastereomers of **29a** [110 mg; reaction period: 10 d; elution with hexane/ethyl acetate (1:1, v/v) mixture; conversion: 65%] as a 65:35 mixture of the *cis*/

trans diastereomers (based on ^{1}H NMR). Analytical samples of the pure *cis* and *trans* diastereomers were obtained by repeated column chromatography with hexane/ethyl acetate (1:1, v/v) mixture as eluent. ***trans*-30a:** Yellow oil. IR (neat): $\tilde{\nu}$ = 3262 (NH), 1666 (C=O), 1588, 1438, 1306, 1212, 744 cm^{-1}. ^{1}H NMR: δ = 1.42 (d, J = 5.9 Hz, 3 H, CH_3), 2.31 (q, J = 5.4 Hz, 1 H, 3′-H), 2.79, 3.87 (AB q, J = 14.1 Hz, 2 H, 2-H), 7.20−7.41 (m, 3 H, 6,7,8-H), 8.08 (dd, J = 9.5, 1.4 Hz, 1 H, 5-H). $C_{11}H_{11}NOS$ (205.3): C 64.36, H 5.40, N 6.82; found C 64.04, H 5.29, N 6.52. ***cis*-30a:** Yellow oil. IR (neat): $\tilde{\nu}$ = 3250 (NH), 1666 (C=O), 1590, 1438, 1350, 1212, 1082, 914, 744 cm^{-1}. ^{1}H NMR: δ = 1.19 (d, J = 5.5 Hz, 3 H, CH_3), 2.55 (q, J = 5.8 Hz, 1 H, 3′-H), 2.49, 3.94 (AB q, J = 14.1 Hz, 2 H, 2-H), 7.17−7.42 (m, 3 H, 6,7,8-H), 8.13 (dd, J = 8.0, 1.2 Hz, 1 H, 5-H). $C_{11}H_{11}NOS$ (205.3): C 64.36, H 5.40, N 6.82; found C 64.29, H 5.45, N 6.63.

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