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Investigations on Peri-, Regio- and Stereoselectivities in Thermal Cycloadditions Involving *C*-(4-Oxo-4*H*[1]benzopyran-3-yl)-*N*-phenylnitrones: Role of Steric Factors and Secondary Interactions in 1,3-Dipolar Cycloadditions

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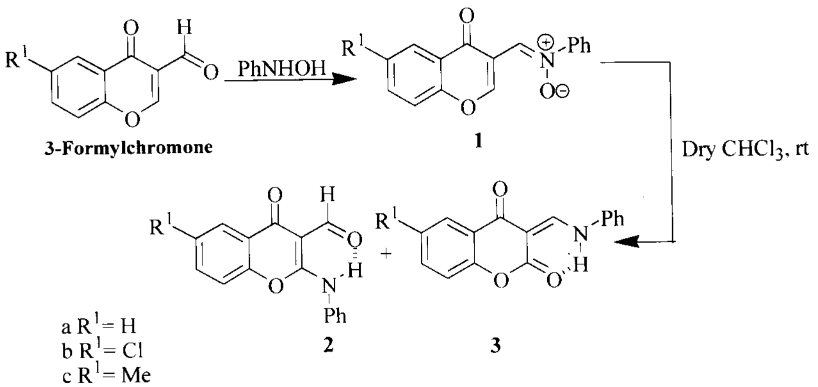
Abstract—Complete peri-, regio- and stereoselectivities in thermal reactions of C-(4-oxo-4*H*[1]benzopyran-3-yl)-*N*-phenylnitrones with both electron-rich and electron-deficient olefins have been investigated. This conjugated nitrone undergoes frontier-orbital (LUMO-dipole HOMO-dipolarophile) controlled *exo*-selecitve 1,3-dipolar cycloadditions; the stereo-chemical outcome is influenced predominantly by steric factors, besides secondary orbital and/or polar interactions. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The chromone moiety is a component of a number of biologically active substances of both synthetic and natural origin having medicinal significance,[1] and the 3-formylchromone has emerged as the most valuable synthon for the incorporation of the chromone moiety.[2] We have recently reported[3] thermal cycloadditions involving c-(4-oxo-4*H*[1]benzopyran-3-yl)-*N*-phenylnitrones (**1a**–**c**) and allenic esters, and have also observed[4] that these 3-formylchromone derived nitrones undergo tandem intramolecular cyclization-rearrangements yielding 2-(*N*-phenylamino)-4-oxo-4*H*[1]-benzopyran-3-carboxaldehydes(**2a**–**c**,) and 3-(phenyliminomethylene)-chroman-2,4-diones (**3a**–**c**, Scheme 1).

A perusal of literature[5] revealed that although nitrone **1a** has been shown to undergo 1,3-dipolar cycloadditions to acrylonitrile and styrene, the reported spectroscopic data, the regio- and stereochemical assignments as well as discussion thereof are limited.[6] On the contrary the above nitrones have been reported[7] to add as a heterodiene ($4\pi^{+}+2\pi$ cycloadditions) to electron rich alkenes like ethoxyethylene and isobutoxy-ethylene. We have investigated the complete



Scheme 1.

Keywords: nitrone; 1,3-dipolar cycloaddition; regioselectivity; stereoselectivity; steric hindrance; secondary orbital interactions.

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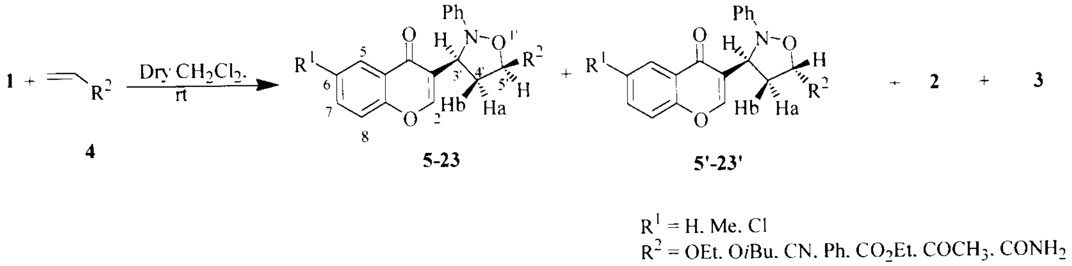


Scheme 2.

peri-, regio- and stereoselectivities in thermal additions of nitrones (**1a**–**c**) to a number of both electron rich and electron deficient olefinic systems, and report that nitrones (**1a**–**c**) exist only in (*Z*)-form, adding only as 1,3-dipole under all conditions. The regiochemistry of addition is frontier molecular orbital controlled and the additions are highly *exo*-selective, controlled mainly by steric factors, and *endo*- mode of addition is obtained only in cases wherein secondary orbital/dipolar interactions become operative or steric factors force an *endo*-mode of addition. Steric constraints on approach of dipole to dipolarophile, particularly in the case of additions to disubstituted olefins, also have a limiting influence on the feasibility of a reaction as reflected in yields of cycloadducts.

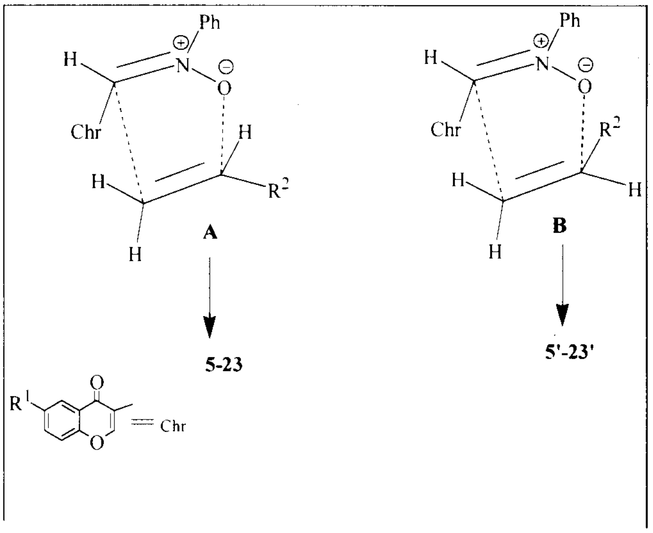
Results and Discussion

Initially the reactions of nitrones (**1a**–**c**) with monosubstituted dipolarophiles (**4**, Scheme 2) were examined; the reaction conditions and product composition are summarised in Table 1.

The assigned structures are based on rigorous spectroscopic analysis (UV, IR, ^{1}H and ^{13}C NMR including extensive ^{1}H homodecouplings, recording of off-resonance and DEPT ^{13}C NMR, 2D NMR correlations, and Mass) and microanalytical data. A comparison of the spectroscopic, in particular, NMR spectral data with the data reported[8] for isoxazolidines obtained by 1,3-dipolar cycloadditions of various nitrones to a variety of olefins indicated that the presently obtained cycloadducts are also derived from 1,3-dipolar cycloaddition. This was further corroborated by UV and NMR spectral data which clearly indicated[9] that the chromone moiety is intact in the obtained cycloadducts (**5**–**23** and **5′**–**23′**), including the ones derived from reactions with electron rich olefins, thereby ruling out any involvement of the heterodiene moiety of **1** in cycloadditions. The assigned regiochemistry of addition is based on ^{1}H NMR couplings which clearly indicated that methylene hydrogens (C4′–Hs) are coupled with both C3′–H and C5′–H, and is also corroborated by ^{13}C NMR chemical shifts of various carbons of isoxazolidine moiety. For instance the ^{13}C resonance of the methylene carbon (C4′) in **5**–**23** appears in the range $\sim\delta$ 36–45, clearly indicating that it is not attached to any hetero atom. The assigned sterochemistry in cycloadducts (**5**–**23** and **5′**–**23′**) is also based on NMR spectral evidence. The *cis* relationship between chromone moiety at C3′ and substituent at C5′ in **5**–**23** are based on ^{1}H NMR couplings involving C3′–, C4′– and C5′–Hs and follows from the consistent observation[8,10] that *cis* vicinal ^{1}H couplings are always higher (5–9 Hz) than the *trans* (0–6 Hz) in case of isoxazolidines (e.g. in **5** $J_{3',4'a}$=9.66 Hz; $J_{3',4'b}$=2.92 Hz; $J_{5',4'a}$=6.31 and $J_{5',4'b}$=1.27 Hz); thus in case of **5**–**23** both C3′–H– and C5′–H show higher coupling and hence *cis* relationship with C4′–Ha. The ^{1}H chemical shifts and couplings constants involving C3′–H, C5′–H. C4′–Ha, C4′–Hb and variation

Table 1. Reaction conditions, reaction times, and yields of various products for reactions of nitrones (**1a**–**c**) with dipolarophiles (**4a**–**g**)

Serial no.	Nitrone **1**	Dipolarophile **4**	Reaction time (h)	Yield (%) of various products			
				2	**3**	*exo*-Adducts	*endo*-Adducts
1	**1a** (R^1=H)	**4a** (R^2=OEt)	48	15	3	**5** (80)	–
2	**1a**	**4b** (R^2=O*i*Bu)	48	15	2	**6** (78)	**6′** (3)
3	**1a**	**4c** (R^2=CN)	60	6	Trace	**7** (47)	**7′**(40)
4	**1a**	**4d** (R^2=Ph)	48	15	2	**8** (80)	**8′**(trace)
5	**1a**	**4e** (R^2=CO$_2$Me)	68	4	Nil	**9** (65)	**9′**(25)
6	**1a**	**4f** (R^2=COMe)	72	10	6	**10** (45)	**10′**(35)
7	**1a**	**4g** (R^2=CONH$_2$)	72	30	15	**11** (50)	–
8	**1b** (R^1=Cl)	**4a**	48	15	Trace	**12** (80)	**12′**(trace)
9	**1b**	**4b**	48	15	Trace	**13** (80)	**13′**(trace)
10	**1b**	**4c**	60	10	Trace	**14** (50)	**14′**(35)
11	**1b**	**4d**	50	14	2	**15** (77)	–
12	**1b**	**4e**	72	5	Nil	**16** (70)	**16′**(20)
13	**1b**	**4f**	72	20	3	**17** (45)	**17′**(30)
14	**1c** (R^1=Me)	**4a**	50	9	6	**18** (80)	**18′**(trace)
15	**1c**	**4b**	50	6	6	**19** (75)	**19′**(6)
16	**1c**	**4c**	60	5	3	**20** (45)	**20′**(40)
17	**1c**	**4d**	55	8	5	**21** (80)	–
18	**1c**	**4e**	72	3	3	**22** (70)	**22′**(25)
19	**1c**	**4f**	72	6	9	**23** (45)	**23′**(40)



Scheme 3.

of these values in going from *cis*-(**5–23**) to *trans*-adducts (**5′–23′**) are in consonance cf.[8,10] with the stereochemical assignments.

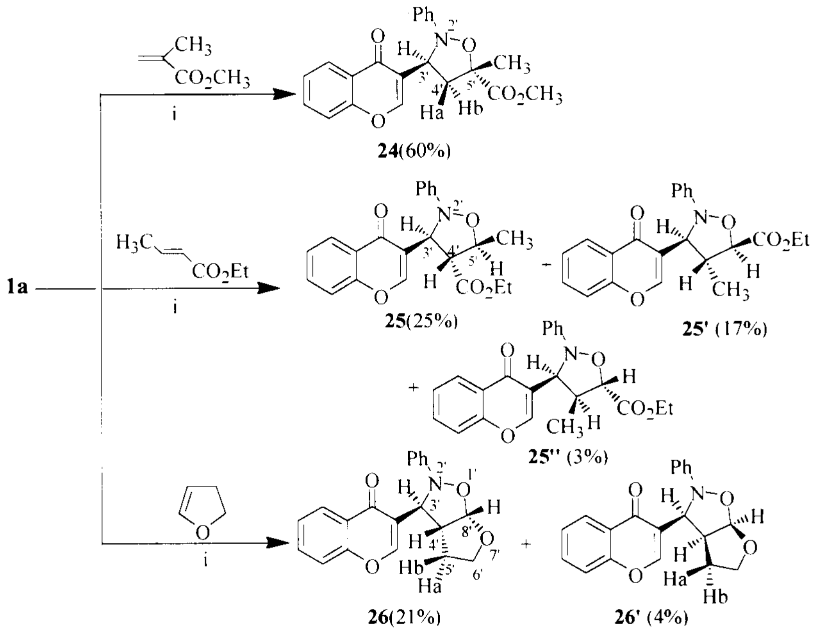
The obtained regiochemistry of addition can be rationalised in terms of frontier molecular orbital control, i.e. the reactions are controlled by LUMO (dipole)-HOMO (dipolarophile) interaction.[11] Our earlier observations[4] that nitrones (**1a–c**) undergo facile intramolecular cyclization — rearrangement on refluxing in benzene or stirring a chloroform solution at ambient temperature and even in the solid state (when stored at ambient temperature) have indicated clearly that these nitrones exist in the *Z*-form under these conditions. This is also corroborated by comparison of ^{1}H and ^{13}C NMR data for **1a–c** with the data reported for the (*E*)- and (*Z*)-aldonitrones,[12] particularly, with *C*-benzoyl-*N*-phenylnitrone which is reported to exist only in (*Z*)-form; apparently the corresponding (*E*)-form of **1a–c** should be highly disfavoured for steric reasons. Therefore, if these nitrones react in the (*Z*)-form only, the *cis*-cycloadducts (**5–23**) originate from an *exo*-mode of addition as depicted in **A** and the corresponding *trans*-adducts (**5′–23′**) are derived from an *endo*-approach (**B**) (Scheme 3).

The formation of the *exo*-adduct is apparently dictated by steric factors and significant amounts of *endo*-adducts are obtained only in the case of the dipolarophiles bearing polar substituents (Table 1); these substituents can also undergo secondary orbital interactions. Though secondary orbital interaction has been invoked to explain *endo*-selectivities in the case of 1,3-dipolar cycloadditions involving nitrones,[11,13] the contribution of secondary orbital interaction to *endo*-selectivity in 1,3-dipolar cycloadditions and cycloadditions in general has been disputed,[14] and observed *endo*-selectivity in the case of polar substituents on dipolarophiles has been attributed to some sort of dipolar stacking in the transition state.[14,15] We would like to mention here that observable amounts of *endo*-adducts have been also obtained in the case of nitrone additions to vinylic ethers (**4a**,**b**, Table 1) and their formation can be attributed to either attractive van der Waal interactions[11c,14,16] or secondary orbital interactions involving etheral oxygen; such secondary orbital interactions involving ethereal/hydroxy oxygens have been also resorted to for explaining the *endo*-selectivity in certain cases.[13b]

To unravel the possible influence of steric factors on 1,3-dipolar cycloadditions involving these nitrones, particularly in the light of our assumptions that these nitrones exist and react in the (*Z*)-form, the investigations were extended to reactions of nitrone **1a** with 1,1-disubstituted, 1,2-disubstituted, and cyclic dipolarophiles. The results are summarised in Scheme 4.

The assigned structures are again based on rigorous spectroscopic analysis. The structure of compound (**24**), a 1:1 adduct (mass), has been arrived at by comparison of NMR spectroscopic data with the reported data for the 1,3-dipolar cycloadduct of α-benzoyl-*N*-phenylnitrone with methyl methacrylate;[10c] the NMR spectral conclusions were also aided by known substituent effects on proton chemical shifts for isoxazolidines.[10d] Thus, the hydrogen, which is *cis* to C5-methyl in **7** (C4–Ha), appears upfield (δ 2.14) and its *trans* relationship with C3–H is indicated by its lower vicinal coupling constant value $J_{3',4'a}$=6.05 Hz as compared to $J_{3',4'b}$=7.90 Hz.[10] The obtained pattern of coupling is also in consonance with the assigned regiochemistry of addition; the overall structural assignment is corroborated by ^{13}C NMR spectral data.

The reaction of **1a** with ethyl crotonate afforded a pure compound (**25**, 25%) along with a mixture (6:1, 20%) of **25′** and **25″**. The assigned structure of **25** follows directly from the comparison of the spectroscopic, in particular NMR, data with the data reported for 1,3-dipolar cycloadducts of various nitrones with crotonates.[10a,c,17] The *trans* relationship between C3′–H and C4′–H in **25** is based on the lower value of $J_{3',4'}$=5.20 Hz.[10a,c,17] The regioisomers of **25**, i.e. **25′** and **25″** have been isolated for the first time by the reaction of a nitrone with a crotonate. The assigned regiochemistry of addition in the case of these 1:1 adducts is based on the chemical shift value and multiplicity of C4′–H (m at δ 3.36–3.29 in **25″** and at δ 2.84–2.70 in **25′**); the corresponding proton resonance,



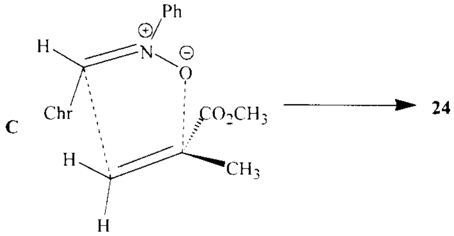
(i) **1a** and excess dipolarophile in 10 mL dry benzene.
heated in sealed tube at 90° for 24h

Scheme 4.

which is coupled to the methyl group in regioisomer (**25**), appeared at δ 4.35 (assigned as C5′–H in the latter case). In the case of **25′**, the major component of the mixture, the C5′–H was located as a doublet at δ 4.78 and C3′–H as a doublet at δ 4.32; the *trans* relationship between C3′–H and C4′–H is again based on the low value of $J_{3',4'}$=3.59 Hz. Here, the relative upfield shifted position of C3′–H and C5′–H (relative to their chemical shift value in other adducts, e.g. in adducts of **1a** with acrylate) is corroborative of their *cis*relationship with the C4′-methyl.[10d] The assigned structure of **25″** is based on similar inferences involving chemical shifts and coupling constants of C3′–H, C4′–H and C5′–H, and corroborated by ^{13}C NMR spectral data.

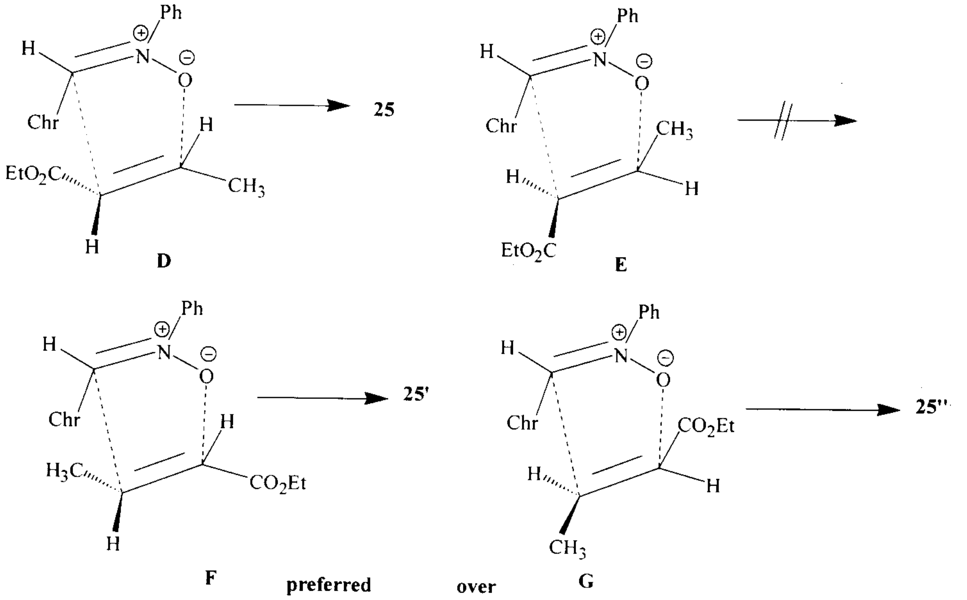
The structures of adducts (**26** and **26′**) derived from addition of nitrone **1a** to dihydrofuran are again based on a detailed spectroscopic analysis. The major product (**26**) has been assigned as the *endo*-adduct based on the appearance of C3′–H as a broad singlet at δ 4.90; its low coupling constant value ($J_{3',4'}\sim$ zero) being indicative of its *trans* relationship with C4′–H. In the stereoisomeric adduct (**26′**) the C8′–H is obtained as a doublet at δ 5.65 (J=3.81 Hz) and as anticipated it is upfield shifted as compared with C8′–H in the *endo*-adduct (δ 5.79). C3′–H in **26′** is obtained as a double doublet at δ 5.40 (J=6.42 and 0.85 Hz); here the 0.85 Hz splitting, probably, arises from a W relationship between C3′–H and C5′–Hb. The obtained variations in the chemical shift values in going from *endo*-(**26**) to *exo*-adduct (**26′**) are in keeping with the observation recorded in the case of adducts derived from mono-substituted olefins. The assigned ^{13}C chemical shift values are in consonance with the assigned structures.

As recorded earlier the main factors favouring an *exo*-mode of addition are steric in nature and only in the case of polar substituents, which are also capable of entering into a secondary orbital interaction does the *endo*-mode of addition become significant. In the case of methyl methacrylate, a 1,1-disubtituted olefin, interplay of both these factors, i.e. methyl group in *exo*-orientation caters for the steric influences and ester moiety is preferably accommodated in the *endo*-orientation (**C**) leading to **24**, complete stereoslectivity is observed and a single adduct (**24**) is obtained. The results are contrary to the stereoselectivities obtained in the case of Diels–Alder additions of dienes to such 1,1-disubstituted olefins.[16]

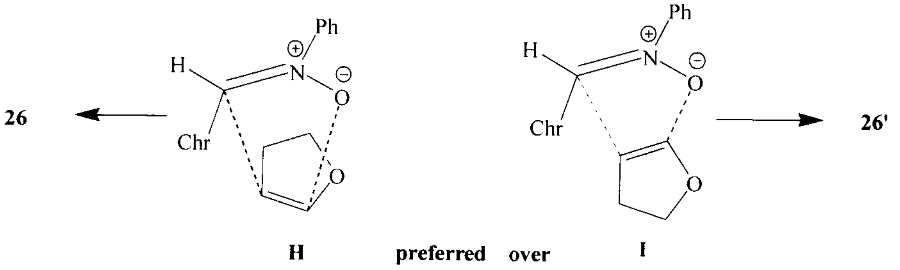


The major product (**25**) from addition of **1a** to ethyl crotonate is anticipated as far as the regiochemistry of addition is concerned,[10a,c,17] however, the obtained complete steroselectivity of addition is dictated by steric considerations, i.e. in the approach of the dipole, in the (Z)-form, the ester function takes up *endo*-orientation to avoid proximity to chromone moiety (**D**) and the alternative approach (**E**) is sterically prohibited (Scheme 5).

The other products of this reaction (**25′** and **25″**), are characterized only in the mixture and this mode of addition (regiochemistry) has been obtained for the first time as far as addition of a nitrone to crotonate is concerned, and is indicative of a loss of regioselectivity. Here again the major isomer (**25′**) has been derived from approach of the nitrone



Scheme 5.



Scheme 6.

as depicted in **F** and the controlling factors, apparently, are again steric in nature. It may be mentioned here that overall yields of adducts in the case of addition to crotonate are low which may be again attributed to steric factors.[11f]

The obtaining of the *endo*-adduct as major product in the case of addition of **1a** to dihydrofuran represents a very interesting and clear case of very high *endo*-selectivity on account of steric factors. It also clearly establishes our initial conclusions regarding the geometric preferences of nitrone (**1**). The two approaches of dipole to dihdyrofuran are depicted in **H** and **I** (Scheme 6).

The investigations have clearly established that the nitrone (**1**) undergoes frontier controlled 1,3-dipolar cycloadditions. It adds preferably in the (*Z*)-form and reactions are *exo*-selective with monosubstituted dipolarophiles; *endo* mode of addition is obtained only in the case of polar substituents on the dipolarophiles, and such substituents are also capable of entering into secondary orbital interactions. In the case of cyclic dipolarophiles which can be regarded as a *cis*-disubstituted olefin, steric factors force a preferential *endo*-mode of addition. The effect of the C6-substituent on the reactivity behaviour of dipoles (**1a–c**) is not very apparent, though the C6-methyl substituted dipole (**1c**) seems to be relatively less selective and also has reduced reactivity. In general the relative yields of side products (non-adducts, **2** and **3**) is more in the reactions involving less reactive dipolarophiles, particularly the disubstituted ones. There also appears to be a pattern in the relative yields of **2** and **3** i.e., the yield of **2** is more form **1c** and more of **3** is produced from **1b**. This may be attributed to the C6-substituent effects in the intermediates postulated[4] to intervein the conversion of **1** to **2** and **3**, and shall be elaborated elsewhere after more detailed investigations. Synthetically, these cycloadditions provide a simple route for incorporating the medicinally significant chromone moiety on to an isoxazolidine ring; the latter heterocyclic systems have also been recently ascribed some valuable medicinal properties.[19]

Experimental

All melting points are uncorrected. NMR spectra were recorded on Bruker AC-200FT (200 MHz) and Bruker-F 300 MHz NMR spectrometers, using TMS as internal standard. IR spectra were recorded on Shimadzu DR 2001 FT-IR spectrometer and mass spectra were recorded on Shimadzu GCMS-QP-2000A spectrometer. Nitrones (**1a–c**) were obtained by reacting *N*-phenylhydroxylamine with corresponding 3-formylchromones (Aldrich) as described earlier[4] and characterized spectroscopically[4,18] (**1b** mp 149–150°C, Lit.[18] mp 151–152°C; **1c** mp

173–175°C, Lit.[18] mp 175–176°C). All dipolarophiles were procured commercially and distilled before use.

General reaction procedure

Reactions of nitrones with monosubstituted olefins were carried out by mixing nitrone (**1a–c,** 0.75 mmol) with olefin (**4a–g**, 2.25 mmol) in dry CH_2Cl_2 (40 ml) and the mixture was stirred, under exclusion of moisture, until all the nitrone was consumed (TLC). The solvent was removed under vacuum and the residues were separated by column chromatography using 100–200 mesh silica and 1% EtOAc in hexane as eluent. The reactions with disubstituted/cyclic olefins were carried out by heating a dry benzene solution (5–8 ml) of **1a** (0.75 mmol) and olefin (2.25 mmol) in a sealed glass tube at 90° C for 24 h; the products have been similarly isolated by column chromatography. The reported yields are based on isolated pure products and relative proportions in mixtures determined by ^{1}H NMR spectroscopy.

Reaction of 1a with ethyl vinyl ether. Reaction of **1a** with ethyl vinyl ether afforded *exo*-adduct (**5**, 80%) light yellow solid (benzene/pet. ether 1:10); mp 78–79°C; [Found C, 71.30; H, 5.71; N, 4.13%. $C_{20}H_{19}O_4N$ requires C, 71.21; H, 5.63; N, 4.15%]; λ_{max} (MeOH): 362, 304, 298, 248 (inf.) and 227 nm; ν_{max} (CHCl$_3$): 1645(s), 1600(s), 1580(s), 1500(s), 1460(s), 1428(m), 1400(s), 1350(m), 1298(s), 1229(m), 1210(s), 1158(s), 1100(s) and 1050(s) cm^{-1}; δ_H (300 MHz, CDCl$_3$): 8.33 (br s, 1H, C2–H), 8.26 (dd, 1H, J=9.5, 1.7 Hz, C5–H), 7.67 (dt, 2H, J=6.5, 1.7 Hz), 7.50–7.40 (m, 2H), 7.25 (broad t, 2H, J=8.7 Hz), 7.06–6.88 (m, 3H), 5.45 (dd, 1H, J=6.3, 1.2 Hz, C5′–H), 4.93 (dd, 1H, J=9.6, 2.9 Hz, C3′–H), 3.93 (dq, 1H, J=9.6, 7.0 Hz), 3.61 (dq, 1H, J=9.6, 7.0 Hz), 2.90 (ddd, 1H, J=13.3, 9.6, 6.3 Hz, C4′–Ha), 2.27 (ddd, 1H, J=13.3, 2.9, 1.2 Hz, C4′–Hb), 1.23 (t, 3H, J=7.0 Hz); δ_C (75 MHz, CDCl$_3$): 176.39 (C4), 156.34 (C8a), 154.82 (C2), 150.34 (quat. arom.), 133.29 (C7), 128.63 (CH, arom.), 125.60 (C6), 124.88 (C5), 124.57 (C4a), 123.89 (C3), 122.09 (CH, arom.), 118.07 (C8), 115.10 (CH, arpm.), 101.86 (C5′), 63.54 (OCH_2), 59.98 (C3′), 41.67 (C4′), 15.27 (CH$_3$); m/z 338 (2, M$^+$+1), 337 (10, M$^+$), 265 (10), 229 (100). **2** (R^1=H, 15%)[4]. **3** (R^1=H, 3%).[4]

Reaction of 1a with isobutyl vinyl ether. Reaction of **1a** with isobutyl vinyl ether afforded *exo*-adduct (**6**, 78%) as light yellow solid (benzene/pet. ether 1:10); mp 84–85°C; [Found C, 72.35; H, 6.28; N, 3.80%. $C_{22}H_{23}O_4N$ requires C, 72.32; H, 6.30; N, 3.83%]; λ_{max} (MeOH): 361, 306, 247 (inf), 227 nm; ν_{max} (CHCl$_3$): 1650(s), 1610(s), 1600(m), 1460(s), 1430(s), 1400(m), 1360(s), 1300(m), 1250(m), 1200(s), 1145(s), 1100(s), 1050(m) cm^{-1}; δ_H (200 MHz, CDCl$_3$): 8.34 (d, 1H, J=0.9 Hz, C2–H), 8.27 (dd, 1H, J=7.6, 1.9 Hz, C5–H), 7.67 (dt, 1H, J=6.6, 1.7 Hz), 7.56 (m, 2H), 7.29 (t, 2H, J=6.9 Hz), 7.07–6.82 (m, 3H), 5.43 (dd, 1H, J=5.8, 1.1 Hz, C5′–H), 4.95 (dd, 1H, J=9.5, 1.7 Hz, C3′–H), 3.64 (dd, 1H, J=9.2, 6.8 Hz), 3.25 (dd, 1H, J=9.2, 6.3 Hz), 2.86 (ddd, 1H, J=13.1, 9.5, 5.8 Hz, C4′–Ha), 2.31 (ddd, 1H, J=13.1, 1.7, 1.1 Hz, C4′–Hb), 1.86 (m, 1H), 0.88 (d, 6H, J=6.5 Hz, 2×CH$_3$); δ_C (50 MHz, CDCl$_3$): 176.77 (C4), 156.49 (C8a), 155.08 (C2), 150.64 (quat., arom.), 133.56 (C7), 128.80 (CH, arom.), 125.70 (C6), 125.10 (C5), 124.60 (C4a), 123.95 (C3), 122.26 (CH, arom.), 118.24 (C8), 115.31 (CH, arom.), 102.36 (C5′), 75.22 (–OCH_2), 60.16 (C3′), 41.58 (C4′), 28.46 (CH), 19.38 (CH$_3$); m/z366 (1, M$^+$+1), 365 (8, M$^+$), 292 (10), 265 (4). *endo*-Adduct (**6′**, ~3%) obtained only in mixture with **6**, critical NMR spectral data: δ_H (CDCl$_3$): 8.20 (s, C2–H), 5.29 (d, J=3.24 Hz, C5′–H), 5.10 (dist.t, J~7.25 Hz, C3′–H), 3.49 (dd, C4′–Ha), 3.12 (dd, C4′–Hb), 1.66 (m), 0.76 (d, –CH$_3$); δ_C (CDCl$_3$): 153.15 (C2), 103.88 (C5′), 74.65 (–OCH$_2$–), 58.86 (C3′), 43.55 (C4′), 28.32 (CH), 19.11 (–CH$_3$). **2** (R^1=H, 15%) and **3** (R^1=H, ~2%).

Reaction of 1a with acrylonitrile. Reaction of **1a** with acrylonitrile afforded *exo*-adduct (**7**, 47%) as a yellowish white solid (benzene/pet. ether 1:10); mp 74–75°C; [Found C, 71.70; H, 4.51; N, 8.68%. $C_{19}H_{14}O_3N_2$ requires C, 71.69; H, 4.40; N, 8.80%]; λ_{max} (MeOH): 364, 301, 248(sh) and 229 nm; ν_{max} (CHCl$_3$): 2320(w), 1645(s), 1600(s), 1575(m), 1525(s), 1490(s), 1480(s), 1472(s), 1425(s), 1340(s) 1225(b s), 1050(s), 1030(s) cm^{-1}; δ_H (200 MHz, CDCl$_3$): 8.34 (d, 1H, J=1.2 Hz, C2–H), 8.25 (dd, 1H, J=7.9, 2.4 Hz, C5–H), 7.72 (dt, 1H, J=6.5, 1.7 Hz, C7–H), 7.54–7.42 (m, 2H), 7.25 (broad t, 2H, J=6.9 Hz), 7.14–6.92 (m, 3H), 5.11 (dd, 1H, J=8.9, 2.9 Hz, C5′–H), 5.01 (dd, 1H, J=9.0, 3.4 Hz, C3′–H), 3.11 (dt, 1H, J=13.4, 8.9 Hz, C4′–Ha), 2.70 (dt, 1H, J=13.4, 3.0 Hz, C4′–Hb); δ_C (CDCl$_3$): 124.99 (C5), 123.48 (C4a), 123.38 (CH, arom.), 122.62 (C3), 118.60 (C8), 117.37 (CN), 115.17 (CH, arom.), 63.85 (C5′), 61.32 (C3′), 39.95 (C4′); m/z 319 (5, M$^+$+1), 318 (48, M$^+$), 317 (100, M$^+$−1), 290(15), 289(90), 288(87), 264(5), 263(70), 162(78). *endo*-Adduct (**7′**, 40%) obtained as a semisolid (slightly contaminated with **7**); δ_H (200 MHz, CDCl$_3$): 8.32 (dd, 1H, J=7.8, 2.3 Hz, C5–H), 8.22 (s, 1H C2–H), 7.76–7.71 (m, 1H), 7.55–7.22 (m, 4H), 7.17–6.92 (m,3H), 5.31 (dd, 1H, J=6.7, 3.0 Hz, C5′–H), 4.77 (t, 1H, J=7.4 Hz, C3′–H), 3.08–2.84 (m, 2H); δ_C (CDCl$_3$): 176.27 (C4), 156.05 (C8a), 153.37 (C2), 149.43 (quat. arom.), 133.66 (C7), 129.21 (CH, arom.), 126.16 (CH), 125.42 (CH, arom.), 123.37 (C4a), 122.43 (C3), 121.70 (CH, arom.), 118.079 (C8), 117.88 (CN), 115.04 (CH, arom.), 64.65 (C5′), 62.49 (C3′), 39.20 (C4′); m/z 319(5, M$^+$+1), 318(25, M$^+$), 274(5), 273(3). **2** (R^1=H, 6%). **3** (R^1=H, trace).

Reaction of 1a with styrene. Reaction of **1a** with styrene afforded *exo*-adduct (**8**, 80%) as a yellowish solid (benzene/pet. ether 1:10); mp 52–53°C; [Found C, 78.20; H, 5.16; N, 3.87%. $C_{24}H_{19}O_3N$ requires C, 78.04; H, 5.14; N, 3.79%]; λ_{max} (MeOH): 362, 306, 299 and 229 nm; ν_{max} (CHCl$_3$): 1653.7(S), 1615(s), 1607(m), 1585(m), 1495.5(s), 1470(s), 1410(m), 1350(m), 1320(m), 1271(m), 1226(s), 1200.7(s), 1175(m), 1149(m), 1102(s), 1034(s)cm^{-1}; δ_H (200 MHz, CDCl$_3$): 8.42 (bs, 1H, C2–H), 8.25 (bd, 1H, J=7.18 Hz, C5–H), 7.69 (bt, 1H, J=7.04 Hz, C7–H), 7.52–7.25(m, 8H), 7.09 (d, 2H, J=8.08 Hz), 6.97 (t, 1H, J=7.04 Hz), 5.20 (m, 2H, C3′–H and C5′–H), 3.40 (dt, 1H, J=12.57, ~7.9 Hz, C4′–Ha), 2.35–2.21 (ddd, 1H, J=12.6, 3.62, ~2.40 Hz, C4′–Hb); δ_C (50 MHz, CDCl$_3$): 176.21 (C4), 156.21 (C8a), 152.79 (C2), 151.36 (quat. arom.), 133.67 (quat. arom.), 133.16 (C7), 128.86 (CH, arom.), 128.20 (CH, arom.), 127.86 (CH), 126.44

(C6), 125.39 (C5),124.70 (CH, overlapping with C4a), 123.63 (C3), 121.45 (CH), 117.89 (C8), 113.66 (CH), 79.85 (C5′), 63.44 (C3′), 45.06 (C4′); *m/z* 369(2, M$^+$), 310(2), 283(10), 265(8), 264(9), 249(33). **2** (R^1=H, 15%). **3** (R^1=H).

Reaction of 1a with methyl acrylate. Reaction of **1a** with methyl acrylate afforded mixture of cycloadducts (**9** and **9′**, 2.6:1, 90%) as a light yellow semisolid; λ_{max} (MeOH): 363, 310, 299, 248(sh) and 228 nm; ν_{max} (CHCl$_3$):1743(b,s), 1649.5(s), 1615.8(m), 1602.5(m), 1581(m), 1496(m), 1474(s), 1444(sh), 1414(m), 1355(km), 1320(m), 1222(m), 1187(m), 1145(m), 1046(m), 1016(w) cm^{-1}; δ_{H} (200 MHz, CDCl$_3$): 8.36 (s, C2–H in **9**), 8.28 (s, C2–H in **9′**), 8.22 (bd, 1H, *J*=7.7 Hz, C5–H), 7.67 (bt, 1H, *J*~7.2 Hz, C7–H), 7.49–7.31 (m, 2H), 7.27–7.12 (m, 2H), 7.09–6.92 (m, 3H), 5.16–5.02 (m, C5′–H in both **9** and **9′**), 4.79 (dd, 1H, *J*=9.3, 5.8 Hz, C3′–H in **9**), 4.61 (t, 1H, *J*~7.8 Hz, C3′–H in **9′**), 3.71 (bs, 3H, –OCH$_3$), 3.03 (dt, 1H, *J*=12.9, ~8.7 Hz, C4′–Ha in **9**), 2.90 (dt, 1H, *J*=12.7, 7.7 Hz, C4′–Ha in **9′**), 2.58–2.58 (m, C4′–Hb in both isomers); δ_{C} (50 MHz, CDCl$_3$): δ 176.52 and 176.42 (C4 in **9** and **9′** respectively), 170.51 and 170.15 (–CO$_2$– in **9′** and **9** respectively), 156.42 (C8a), 154.37 and 153.74 (C2 in **9** and **9′**), 150.55 and 150.18 (quat. arom. Cs), 133.59 (C7 in **9′**), 133.46 (C7 in **9**), 129.01 and 128.61 (CH in **9** and **9′**), 125.68 and 125.62 (C6 in **9** and **9′**), 125.11 and 125.00 (C5), 123.75 and 123.64 (C4a in **9** and **9′**), 122.84 and 122.42 (C3 in **9′** and **9**), 122.66 (CH, arom.), 118.18 (C8), 115.41 and 114.85 (CH, arom. **9′** and **9**), 76.18 (C5′ in **9′**), 75.21 (C5′ in **9**), 62.17 and 61.93 (C3′ in **9′** and **9**, respectively), 52.14(–OCH$_3$), 36.87 and 37.70 (C4′ in **9** and **9′** respectively); *m/z* 353 (0.8, M$^+$+2), 352 (1, M$^+$+1), 351 (5, M$^+$), 292 (13), 275 (10), 265 (10), 264 (13), 263 (19), 262 (33), 77 (100). **2** (R^1=H, 4%).

Reaction of 1a with methyl vinyl ketone. Reaction of **1a** with methyl vinyl ketone afforded *exo*-adduct (**10**, 45%) as an off white solid (benzene/pet. ether 1:10); mp 88–89°C; [Found C, 71.86; H, 5.14; N, 4.19%. C$_{20}$H$_{17}$O$_4$N requires C, 71.64; H, 5.07; N, 4.17%.]; λ_{max} (MeOH): 364, 304, 299, 248(sh), 228 nm; ν_{max} (CHCl$_3$): 1726(s), 1649.5(s), 1619.5(m), 1602(sh), 1581(m), 1495.6(m), 1474(s), 1410(m), 1354.6(m), 1320.4(m), 1222(m), 1175(m), 1145(m), 1059.6(w), 1038(w) cm^{-1}; δ_{H} (300 MHz, CDCl$_3$): 8.24 (bd, 1H, *J*=7.8 Hz, C5–H), 8.15 (bs, 1H, C2–H), 7.65 (bt, 1H, *J*=8.0 Hz, C7–H), 7.45–7.35 (m, 2H), 7.30–7.19 (m, 2H), 7.07–6.89 (m, 3H), 4.98 (dd, 1H, *J*=8.4, 3.8 Hz, C5′–H), 4.62 (dd, 1H, *J*=9.0, 5.6 Hz, C3′–H), 3.00 (dt, 1H, *J*=12.9, ~8.8 Hz, C4′–Ha), 2.61–2.44 (m, 1H, C4′–Hb), 2.34 (s, 3H, –COC*H*$_3$). δ_{C} (75 MHz, CDCl$_3$): 205.67(–C=O), 176.13 (C4), 156.24 (C8a), 153.29 (C2), 149.91 (quat. arom.), 133.57 (C7), 128.97 (CH), 125.59 (C6), 125.05 (C5), 123.96 (C4a) 122.81 (CH), 122.34 (C3), 118.07 (C8), 115.24 (CH), 81.76 (C5′), 61.52 (C3′), 38.02 (C4′), 26.49 (–CO*C*H$_3$); *m/z* 336(0.1, M$^+$+1), 335(0.9, M$^+$), 320(0.4), 265(12), 250(15). *endo*-Adduct (**10′**, 35%) was obtained only as mixture (2:1) with **10**; critical NMR data of **10′**: δ_{H} (200 MHz, CDCl$_3$): 5.16 (bd, 1H, *J*=7.6 Hz, C5′–H), 4.51 (t, 1H, *J*~7.8 Hz, C3′–H), 2.84 (dt, 1H, *J*=13.0, ~8.8 Hz, C4′–Ha), 2.29 (s, 3H, –COC*H*$_3$); δ_{C} (50 MHz, CDCl$_3$): 205.33(–C=O), 153.75 (C2), 149.53 (quat., arom.), 128.73 (CH, arom.), 123.69 (C4a), 123.05 (C3), 122.33 (CH, arom.), 115.55 (CH, arom.), 82.02 (C5′), 60.23 (C3′), 37.34 (C4′), 26.00(–CO*C*H$_3$). **2** (R^1=H, 10%) and **3** (R^1=H, 6%).

Reaction of 1a with acrylamide. Reaction of **1a** with acrylamide afforded *exo*-adduct (**11**, 50%) as a colourless solid (CHCl$_3$/Hexane 3:1); mp 152°C; [Found C, 67.81; H, 4.67; N, 8.20%. C$_{19}$H$_{16}$O$_4$N$_2$ requires C, 67.85; H, 4.76; N, 8.33%]; λ_{max} (MeOH): 365, 303, 248(sh) and 231 nm; ν_{max} (CHCl$_3$): 3432(b), 3047(m), 1685(s), 1649(s), 1620(s), 1581(m), 1496(m), 1474 (s), 1410(m), 1380(m), 1355(w), 1316(m), 1239(s), 1214(s), 1150(m), 1051(m) cm^{-1}; δ_{H} (300 MHz, CDCl$_3$): 8.22 (dd, 1H, *J*=8.2, 1.5 Hz, C5–H), 8.17 (d, 1H, *J*=0.9 Hz, C2–H), 7.64 (split t, 1H, *J*=7.7, 1.6 Hz, C7–H), 7.47–7.24 (m, 4H), 7.08–7.00 (m, 3H), 6.60 and 5.54 (b, 1H each, –NH$_2$), 4.98 (dd, 1H, *J*=7.2, 2.8 Hz, C5′–H), 4.76 (dd, 1H, *J*=9.5, 4.8 Hz, C3′–H), 3.10 (ddd, 1H, *J*=12.8, 9.5, 7.2 Hz, C4′–Ha), 2.70–2.62 (m, 1H, C4′–Hb). δ_{C} (75 MHz, CDCl$_3$): 176.87(–*C*ONH$_2$), 173.28 (C4), 156.45 (C8a), 153.40 (C2), 149.95 (quat. arom.), 133.87 (C7), 129.15 (CH, arom.), 125.77 (C6), 125.36 (C5), 123.64 (C4a), 123.40 (CH, arom.), 122.85 (C3), 118.18 (C8), 115.53 (CH, arom.), 76.68 (C5′), 62.25 (C3′), 38.84 (C4′). *m/z* 338(0.6, M$^+$+2), 337(0.8, M$^+$+1), 336(1, M$^+$). **2** (R^1=H, 30%) and **3** (R^1=H, 15%).

Reaction of 1b with ethyl vinyl ether. Reaction of **1b** with ethyl vinyl ether afforded *exo*-adduct (**12**, 80%) as a light yellow solid (benzene/pet. ether 1:10); mp 82–83°C; [Found C, 64.71; H, 4.85; N, 3.96%. C$_{20}$H$_{18}$O$_4$NCl requires C, 64.69; H, 4.85; N, 3.77%]; λ_{max} (MeOH): 361, 307, and 231 nm. ν_{max} (CHCl$_3$): 1653.7(s), 1615.3(s), 1576.8(m), 1495.6(m), 1474.2(s), 1452.9(m), 1396(m), 1346(m), 1316.1(s), 1269.1(m), 1217.8(m), 1161128(s), 1102.4(s) cm^{-1}. δ_{H} (200 MHz, CDCl$_3$): 8.26 (s, 1H, C2–H), 8.19 (d, 1H, *J*=2.5 Hz, C5–H), 7.56 (dd, 1H, *J*=8.7, 2.5 Hz, C7–H), 7.40 (d, 1H, *J*=8.8 Hz, C7–H), 7.26–7.16 (m, 2H), 6.95–6.87 (m, 3H), 5.40 (d, 1H, *J*=5.7 Hz, C5′–H), 4.84 (dd, 1H, *J*=8.5, 2.0 Hz, C3′–H), 3.88 (dq, 1H, *J*=9.8, 7.0 Hz), 3.55 (dq, 1H, *J*=9.8, 7.0 Hz), 2.82 (ddd, 1H, *J*=13.5, 8.5, 5.7 Hz, C4′–Ha), 2.24 (dd, 1H, *J*=13.5, ~2.0 Hz, C4′–Hb), 1.23 (t, 3H, *J*=7.0 Hz). δ_{C} (50 MHz, CDCl$_3$): 176.71 (C4), 155.01 (C8a), 154.75 (C2), 150.64 (quat. arom.), 133.37 (C7), 130.95 (C6), 128.71 (CH, arom.), 125.56 (C5), 125.17 (C4a), 124.01 (C3), 122.19 (CH, arom.), 119.77 (C8), 115.19 (CH, arom.), 101.85 (C5′), 63.56(–O*C*H$_2$–), 60.21 (C3′), 41.57 (C4′), 15.51 (CH$_3$); *m/z* 373(3, M$^+$+2), 371(7, M$^+$), 286(28), 285(24), 284(82), 281(44), 265(18), 263(48), 207(54), 205(62), 181(20), 112(35), 93(48), 77(52), 71(54), 58(100). **2** (R^1=Cl,15%) as yellow crystalline solid (CHCl$_3$/pet.ether 4:1), mp 158°C; [Found C, 64.28; H, 3.40; N, 4.65%. C$_{16}$H$_{10}$O$_3$NCl requires C, 64.21; H, 3.34; N, 4.68%]; λ_{max} (CH$_3$OH): 320, 303(sh), 288, 238 and 213 nm. ν_{max} (KBr): 3345(NH), 1659(HC=O), 1625 (C=O), 1602 (sh), 1565(m), 1488(m), 1455(s), 1368(m), 1320(m), 1196(m), 950(m), 753(s); δ_{H} (200 MHz, CDCl$_3$): 12.46 (bs, 1H, NH), 10.25 (s, 1H, CH=O), 8.16 (d, 1H, *J*=2.4 Hz, C5–H), 7.58–7.23 (ms, 7H, Arom.-Hs). δ_{C} (50 MHz, CDCl$_3$): 189.38 (CH=O), 173.45 (C4), 161.85 (C2), 151.35 (C8a), 134.51 (quat. arom.), 133.64 (C7), 131.87 (C6), 129.49 (CH, arom.), 126.80 (C5), 125.71 (CH, arom.), 124.08 (C4a), 122.96 (CH, arom.), 118.35 (C8), 99.24 (C3). *m/z* 302(M$^+$+3, 2), 301(M$^+$+2, 12), 300(M^++1, 37), 299(M^+, 30), 298(M^+-1, 89), 273(6), 272(40), 271(27), 270(100). **3** (R^1=Cl, <1%) as a white crystalline solid ($CHCl_3$), mp 208–209°C; [Found C, 64.25; H, 3.35; N, 4.65%. $C_{16}H_{10}O_3ClN$ C, 64.21; H, 3.34; N, 4.68%]; λ_{max} (CH_3OH): 365, 312.1, 284.5 nm; ν_{max} (KBr): 3307 and 3250 (NH), 1688 (O-$C{=}O$), 1655 (C4=O), 1616, 1595, 1580. δ_H (200 MHz, $CDCl_3$): δ 13.43 and 11.95 (broad doublets, together 1H, –NH in isomeric structures), 9.01 and 8.87 (doublets, together 1H, J=14.6, 14.3 Hz respectively, C9–H in isomeric structures), 8.07 and 8.01 (doublets, together 1H, J=2.6 Hz, C5–H in isomers), 7.85–7.19 (m, 7H); m/z 300(20, M^++1), 299 (48, M^+), 252 (18), 273 (16).

Reaction of 1b with isobutyl vinyl ether. Reaction of **1b** with isobutyl vinyl ether afforded *exo*-adduct (**13**, 80%), as light yellow solid (benzene/pet. ether 1:10); mp 89–90°C; [Found C, 66.12; H, 5.46; N, 3.42%. $C_{22}H_{22}O_4ClN$ requires C, 66.16; H, 5.51; N, 3.50%]; λ_{max} (MeOH): 365, 317, 306 and 231 nm. ν_{max} ($CHCl_3$): 1653.7(s), 1615.3(m), 1606.7(m), 1576.8(m), 1512.7(m), 1495.6(s), 1474.1(s), 1448.6(s), 1388.7(m), 1341.7(m), 1311.8(m), 1265(m), 1205(m), 1162(m), 1128(w), 1102.4(m), 1059(m), 1046.8(m). δ_H (200 MHz, $CDCl_3$): 8.28 (s, 1H, C2–H), 8.16 (d, 1H, J=2.5 Hz, C5–H), 7.55 (dd, 1H, J=8.9, 2.5 Hz, C7–H), 7.37 (d, 1H, J=8.9 Hz, C8–H), 7.21 (bt, 1H, J=9.6 Hz), 6.98–6.88 (m, 3H), 5.39 (d, 1H, J=5.6 Hz, C5′–H), 4.86 (bd, 1H, J=7.9 Hz, C3′–H), 3.60 (dd, 1H, J=9.1, 6.8 Hz), 3.22 (dd, 1H, J=9.1, 6.3 Hz), 2.80 (ddd, 1H, J=13.3, 7.9, 5.6 Hz, C4′–Ha), 2.27 (dd, 1H, J=13.3, 1.8 Hz, C4′–Hb), 1.92–1.73 (m, 1H), 0.86 (d, 6H, J=6.7 Hz, 2×CH_3). δ_C (50 MHz, $CDCl_3$): 175.07 (C4), 154.86 (C2), 154.64 (C8a), 150.58 (quat. arom.), 133.47 (C7), 130.86 (C6), 126.64 (CH, arom.), 125.11 (C5), 124.82 (C4a), 124.71 (C3), 122.16 (CH, arom.), 119.70 (C8), 115.12 (CH, arom.), 102.29 (C5′), 75.03 (–OCH_2), 60.23 (C3′), 41.19 (C4′), 28.37 (CH), 19.32 (CH_3). m/z 402 (1, M^++3), 401 (3, M^++2), 400 (2, M^++1), 399 (8, M^+), 291 (47), 235 (90), 207 (100). **2** (R^1=Cl, 15%). **3** (R^1=Cl, <1%).

Reaction of 1b with acrylonitrile. Reaction of **1b** with acrylonitrile afforded *exo*-adduct (**14**, 50%) as light yellow solid (benzene/pet. ether 1:10), mp 73–74°C; [Found C, 64.92; H, 3.60; N, 7.91%. $C_{19}H_{13}O_3N_2Cl$ requires C, 64.77; H, 3.69; N, 7.95%]; λ_{max} (MeOH): 362, 312, 232 and 209 nm. ν_{max} ($CHCl_3$): 2316(w), 1649.5(s), 1619.5(m), 1606.7(m), 1576.8(m), 1495.6(m), 1470(s), 1448.6(m), 1393(m), 1346(m), 1316.1(m), 1149.4(m), 1123.7(m), 1085(m), 1068.2(w), 1034.0(w). δ_H (200 MHz, $CDCl_3$): 8.30 (d, 1H, J=0.9 Hz, C2–H), 8.19 (d, 1H, J=2.5 Hz, C5–H), 7.64 (dd, 1H, J=8.9, 2.5 Hz, C7–H), 7.46 (d, 1H, J=8.8 Hz, C8–H), 7.33–7.25 (m, 2H), 7.08–6.98 (m, 3H), 5.09 (dd, 1H, J=8.2, 1.6 Hz, C5′–H), 4.96 (dd, 1H, J=9.3, 3.4 Hz, C3′–H), 3.04 (ddd, 1H, J=13.2, 9.3, 8.2 Hz, C4′–Ha), 2.65 (dt, 1H, J=13.2, ~3.0 Hz, C4′–Hb). δ_C (50 MHz, $CDCl_3$): 175.41 (C4), 154.88 (C8a), 154.43 (C2), 147.77 (quat. arom.), 134.18 (C7), 131.52 (C6), 129.26 (CH), 125.13 (C5), 124.66 (C4a), 123.89 (CH), 122.77 (C3), 120.10 (C8), 117.25 (CN), 115.50 (CH), 64.07 (C5′), 61.61 (C3′), 40.03 (C4′); m/z 355 (0.5, M^++3), 354 (0.4, M^++2), 352 (1, M^+), 298 (12), 296 (16), 285 (18). *endo*-Adduct (**14′**, 35%) as a light yellow semisolid (contaminated with 14), ν_{max} ($CHCl_3$): 2363.3 (w), 1658 (sh), 1645.2 (br), 1615 (s), 1602 (m), 1572.5 (s), 1491.3 (s), 1470.0 (s), 1452.9 (s), 1393.0 (m), 1341.7 (m), 1311.8 (s), 1256.2 (w), 1149.4 (s), 1123.7 (m), 1076.7 (m), 1063.9 (m) cm^{-1}. δ_H (200 MHz, $CDCl_3$): 8.33 (bs, 1H, C2–H), 8.22 (d, 1H, J=2.3 Hz, C5–H), 7.64 (dd, 1H, J=8.6, 2.5 Hz, C7–H), 7.48 (d, 1H, J=8.4 Hz, C8–H), 7.35–7.25 (m, 2H), 7.14 -6.94 (m, 3H), 5.30 (dd, 1H, J=7.0, 2.5 Hz, C5′–H), 4.77 (t, 1H, J=7.6 Hz, C3′–H), 3.11–2.99 (m, 1H, C4′–Ha), 2.82 (ddd, 1H, J=13.2, 7.6, 2. 8 Hz, C4′–Hb). **2** (R^1=Cl, 10%). **3** (R^1=Cl, <1%).

Reaction of 1b with styrene. Reaction of **1b** with styrene afforded *exo*-adduct (**15**, 77%) as an offwhite solid (benzene/pet. ether 1:10); mp 54–55°C; [Found C, 71.50; H, 4.42; N, 3.40%. $C_{24}H_{18}O_3NCl$ requires C, 71.46; H, 4.46; N, 3.47%]; λ_{max} (MeOH): 367, 317, 307 and 220 nm. ν_{max} ($CHCl_3$): 1658(s), 1607(m), 1576(m), 1500(s), 1474(s), 1449(s), 1393(m), 1346(s), 1312(s), 1261(m), 1222(m), 1170(s), 1128(m), 1081(m), 1038(m), 1000(w) cm^{-1}. δ_H (200 MHz, $CDCl_3$): 8.39 (s, 1H, C2–H), 8.16 (d, 1H, J=2.5 Hz, C5–H), 7.56 (dd, 1H, J=8.8, 2.5 Hz, C7–H), 7.44–7.23 (m, 8H), 7.06 (d, 2H, J=8.0 Hz), 6.95 (t, 1H, J=7.2 Hz), 5.24–5.16 (m, 2H, C3′–H and C5′–H), 3.37 (dt, 1H, J=12.6, ~7.8 Hz, C4′–Ha), 2.23 (ddd, 1H, J=12.6, 6.2, 5.8 Hz). δ_C (50 MHz,$CDCl_3$): 175.46 (C4), 154.90 (C8a), 154.21 (C2), 153.41 (quat. arom.), 137.92 (quat. arom.), 133.78 (C7), 131.12 (C6), 129.24 (CH), 128.78 (CH, arom.), 128.59 (CH, arom.), 126.77 (CH, arom.), 125.82 (C4a), 125.15 (C5), 124.88 (C3), 121.94 (CH, arom.), 119.99 (C8), 114.01 (CH, arom.), 80.19 (C5′), 63.65 (C3′), 44.44 (C4′). m/z 405(1.5, M^++2), 404(1.3, M^++1), 403(4, M^+), 387(1), 298(18), 77 (100). **2** (R^1=Cl, 14%). **3** (R^1=Cl, 2%).

Reaction of 1b with methyl acrylate. Reaction of **1b** with methyl acrylate afforded mixture (3.5:1) of adducts (**16** and **16′**, 90%) as a light yellow viscous material, λ_{max} (MeOH): 362, 310, 306 and 231 nm. ν_{max} ($CHCl_3$): 1742 (b,s), 1649.5(s), 1611(s), 1576.8(s), 1576.8(s), 1496.6(s), 1474.2(s), 1448.6(m), 1393(m), 1346(s), 1316.1(s), 1217.8(s), 1183.6(m), 1149.4(m), 1128(m), 1081(m), 1055.4(m); δ_H (200 MHz, $CDCl_3$): 8.25 (d, 1H, J=0.7 Hz, C2–H), 8.05 (d, 1H, J=2.4 Hz, C5–H), 7.49 (dd, 1H, J=8.9, 2.4 Hz, C7–H), 7.32 (d, 1H, J=8.9 Hz, C8–H), 7.21–7.05 (m, 2H), 7.04–6.85 (m, 3H), 5.18 (d, 1H, J=5.3 Hz, C5′–H in, **16′**), 5.03 (dd, 1H, J=8.1, 2.2 Hz, C5′–H **16**), 4.68 (dd, 1H, J=9.4, 5.6 Hz, C3′–H in **16**), 4.51 (t, 1H, J~7.1 Hz, C3′–H in **16′**), 3.61 and 3.60 (singlets, –OCH_3 in **16′** and **16**, respectively), 2.90 (dt, 1H, J=13.0, ~8.8 Hz, C4′–Ha in **16**), 2.86–2.74 (m, 1H, C4′–Ha in **16′**), 2.62- 2.46 (m, C4′–H in **16′**), 2.40 (ddd, 1H, J=12.9, 5.6, 2.2 Hz, C4′–Hb in **16**); δ_C (50 MHz, $CDCl_3$): 174.83 (C4), 170.03(–CO_2– in**16′**), 169.71(–CO_2– in **16**), 154.87 (C8a in **16′**), 154.35 (C8a in **16**), 154.23 (C2 in **16**), 153.58 (C2 in **16′**), 150.24 and 149.84 (quat. arom. Cs in **16** and **16′**), 133.44 (C7 in **16′**), 133.34 (C7 in **4**), 130.73 (C6 in **16′**), 130.62 (C6 in **16**), 128.73 and 128.31 (CH in **16** and **16′**, respectively), 124.62 and 124.34 (CH in **16** and **16′**, respectively), 124.02 (C4a in **16′**), 123.51 (C4a in **16**), 122.77 (C3 in **16′**), 122.45 (CH), 122.13 (C3 in **16**), 121.27 (C8), 115.10 and 114.44 (CH in **16′** and **16** respectively), 75.89 (C5′ in **16′**), 74.88 (C5′

in **16**), 61.84 (C3′ in **16′**), 61.57 (C3′ in **16**), 51.79 (–OMe in **16**), 49.94(–OMe in **16′**), 38.26 and 37.19 (C4′ in **16** and **16′**, respectively); *m/z* 387(1.5, M$^+$+2), 386 (1, M$^+$+1), 385 (2.5, M$^+$), 357 (1), 356 (2). **2** (R^1=Cl, 5%).

Reaction of 1b with methyl vinyl ketone. Reaction of **1b** with methyl vinyl ketone afforded *exo*-adduct (**17**, 45%) as an offwhite solid (benzene/pet. ether 1.5:10), mp 82–82.5°C; [Found C, 65.22; H, 4.46; N, 3.83%. $C_{20}H_{16}O_4NCl$ requires C, 65.04; H, 4.33; N, 3.79%]; λ_{max} (MeOH): 363, 318, 306 and 232 nm; ν_{max} (CHCl$_3$): 1722(s), 1649.5(s), 1611(s), 1577(s), 1496(s), 1474(s), 1449(s), 1393(m), 1346(s), 1316(s), 1218(s), 1184(m), 1149(m), 1128(m), 1081(m), 1055(m) cm^{-1}; δ_H (200 MHz, CDCl$_3$): 8.11 (bs, 1H, C2–H), 8.09 (bs, 1H, C5–H), 7.54 (dd, 1H, *J*=8.9, 2.5 Hz, C7–H), 7.34 (d, 1H, *J*~8.9 Hz, C8–H), 7.25–7.17 (m, 2H), 6.99–6.90 (m, 3H), 4.96 (dd, 1H, *J*=8.4, 3.6 Hz, C5′–H), 4.57 (dd, 1H, *J*=9.1, 5.4 Hz, C3′–H), 2.92 (dt, 1H, *J*=12.9, 8.4 Hz, C4′–Ha), 2.47–2.30 (m, 1H, C4′–Hb), 2.23 (s, 3H, –CH$_3$); δ_C (50 MHz, CDCl$_3$): 205.08 (C═O), 174.82 (C4), 154.42 (C8a), 153.26 (C2), 149.42 (quat. arom.), 133.57 (C7), 130.95 (C6), 128.78 (CH, arom.), 124.91 (C5), 124.45 (C4a), 123.92 (C3), 122.77 (CH, arom.), 119.56 (C8), 115.34 (CH, arom.), 81.50 (C5′), 61.12 (C3′), 37.57 (C4′), 25.81(–CH$_3$); *m/z* 369(0.5, M$^+$), 208(10), 207(40), 206(18), 205(90). *endo*-Adduct **17′** (30%), obtained only in mixture with **17**, Critical NMR data, δ_H (200 MHz, CDCl$_3$): 5.12 (dd, *J*=7.6, 0.9 Hz, C5′–H), 4.49 (bt, 1H, *J*~7.8 Hz, C3′–H), 2.82–2.68 (m, C4′–Ha), 2.47–2.30 (m, C4′–Hb), 2.21(–C*H*$_3$); δ_C (50 MHz, CDCl$_3$): 205.82 (C═O), 153.67 (C2), 149.02 (quat. arom.), 124.01 (C3), 82.76 (C5′), 59.64 (C3′), 37.26 (C4′), 26.21 (–CH$_3$). **2** (R^1=Cl, 20%). **3** (R^1=Cl, 3%).

Reaction of 1c with Ethyl vinyl ether. Reaction of **1c** with ethyl vinyl ether afforded *exo*-adduct (**18**, 80%) as a faint yellow solid (benzene/pet. ether 1:10), mp 76°C; [Found C, 71.83; H, 5.99; N 3.95%. $C_{21}H_{21}O_4N$ requires C, 71.79; H, 5.98; N, 3.98%]; λ_{max} (MeOH): 361.5, 308 and 233, and 214 nm; ν_{max} (CHCl$_3$): 1653.7(s), 1619(s), 1607(sh), 1491(s), 1444(m), 1395(m), 1350(m), 1320(s), 1273(m), 1239(m), 1218(s), 1166(m), 1102(s), 1051(s); δ_H (300 MHz, CDCl$_3$): δ 8.29 (s, 1H, C2–H), 8.03 (bs, 1H, C5–H), 7.47 (dd, 1H, *J*=8.7, 1.2 Hz, C7–H), 7.30 (d, 1H, *J*=8.6 Hz, C8–H), 7.20 (bt, 2H), 7.02–6.90 (m, 3H), 5.43(broad d, 1H, *J*=5.5 Hz, C5′–H), 4.91 (dd, 1H, *J*=9.6, 2.7 Hz, C3′–H), 3.92 (dq, 1H, *J*=10.2, 7.0 Hz,), 3.57 (dq, 1H, *J*=10.2, 7.0 Hz), 2.89 (ddd, 1H, *J*=13.2, 9.6, 5.5 Hz, C4′–Ha), 2.49 (s, 3H, C6-C*H*$_3$), 2.27 (dd, 1H, *J*=13.2, 2.7 Hz, C4′–Hb), 1.25 (t, 3H, *J*=7.0 Hz); δ_C (75 MHz, CDCl$_3$): 176.49 (C4), 154.74 (C2 and C8a), 150.49 (quat. arom.), 134.76 (C6), 134.57 (C7), 128.64 (CH, arom.), 124.99 (C5), 124.34 (C4a), 123.59 (C3), 122.09 (CH,arom.), 117.87 (C8), 115.23 (CH, arom.), 101.75 (C5′), 63.55 (OCH$_2$–), 59.96 (C3′), 41.80 (C4′), 20.88 (C6–*C*H$_3$), 15.28 (CH$_3$); *m/z* 352 (3, M$^+$+1), 351 (7, M$^+$), 304 (3), 289 (5), 288 (6), 277 (14), 264 (80), 243 (47), 187 (35), 186 (48), 185 (100). **2** (R^1=Me, 9%) as a yellow crystalline solid (CHCl$_3$/Hexane 4:1) mp 156°C; [Found C, 73.21; H, 4.69; N, 4.99%. $C_{17}H_{13}O_3N$ requires C, 73.11; H, 4.65; N, 5.01%]; ν_{max} (KBr): 3308(NH), 1663 (HC═O), 1645(br), 1625 (C═O), 1596(sh), 1585(m), 1470(s), 1446(br), 1381(m), 1352(m), 1300(s), 1215(m), 1157(w), 1030(w), 922(m), 898(m), 759(s); δ_H (300 MHz, CDCl$_3$): 12.47 (broad s, 1H, NH), 10.27 (s, 1H, CH═O), 8.02 (broad s, 1H, C5–H), 7.47–7.27 (m, 5H), 7.20 (d, 2H, *J*=8.4 Hz), 2.46 (s, 3H, Me); δ_C (75 MHz, CDCl$_3$): 189.19(HC═O), 175.09 (C4) 161.59 (C2), 151.01 (C8a), 135.58 (C6), 134.71 (quat.), 134.36 (C7), 129.21 (CH), 126.12 (CH), 125.54 (C5), 122.31 (overlapping C4a and a CH), 116.29 (C8), 99.15 (C3), 20.59(Me); *m/z*280 (5, M$^+$+2), 279(28, M$^+$), 278(100, M$^+$−1). **3** (R^1=Cl, 3%) as a white fluffy solid mp 212°C;. [Found C, 73.29; H, 4.80; N, 5.25%. $C_{17}H_{13}O_3N$ requires C, 73.11; H, 4.65; N, 5.01%]; λ_{max} (MeOH): 363.5, 249(sh), 244 and 213 nm; ν_{max} (KBr): 3310 and 3267 (NH), 1683(s), 1640(m), 1617(m), 1580(s), 1548(sh), 1495(sh), 1475(m), 1442(s), 1370(w), 1315(s), 1285(m), 1265(br), 1242(w), 1220(sh), 1210(m), 1155(m), 1135(m), 1109(m), 1010(br), 952(r), 898(m), 812(s), 760(m), 748(sh); δ_H (200 MHz, CDCl$_3$): 13.70 and 11.98 (broad doublets, together 1H, NH in isomers), 9.01 and 8.87 (doublets, together 1H, *J*=14.4 and 13.1 Hz respectively, C9–H in isomers), 7.89 and 7.82(b singlets together 1H, C5–H in isomeric structures), 7.52–7.11 (m, 7H), 2.42 (s, 3H); *m/z* 279(6, M$^+$), 213(5), 199(5), 197(14).

Reaction of 1c with isobutyl vinyl ether. Reaction of **1c** with isobutyl vinyl ether afforded *exo*-adduct (**19**, 75%) as a faint yellow solid (benzene/pet. ether 1:10), mp 87–89°C; [Found C, 72.95; H, 6.75; N, 3.68%. $C_{23}H_{25}O_4N$ requires C, 72.82; H, 6.59; N, 3.69%]; λ_{max} (MeOH): 367, 309, 250, 232 nm; ν_{max} (CHCl$_3$): 1653.4(s), 1628.1(s), 1606.7(s), 1491.3(s), 1443(s), 1393(m), 1346(m), 1320.4(s), 1273.4(m), 1239.4(m), 1213.5(w), 1207(w), 1196(w), 1170.8(m), 1149.4(w), 1102.4(s), 1055.4(s), 1021.2(w); δ_H (300 MHz, CDCl$_3$): 8.22 (s, 1H, C2–H), 7.95 (bs, 1H, C5–H), 7.39 (dd, 1H, *J*=8.5, 1.9 Hz, C7–H), 7.28 (d, 1H, *J*=8.5 Hz, C8–H), 7.20–7.07 (m, 2H), 6.95–6.83 (m, 3H), 5.33 (d, 1H, *J*=5.6 Hz, C5′–H), 4.84 (dd, 1H, *J*=9.5, 2.4 Hz, C3′–H), 3.55 (dd, 1H, *J*=9.1, 6.8 Hz), 3.17 (dd, 1H, *J*=9.1, 6.3 Hz), 2.79 (ddd, 1H, *J*=13.1, 9.5, 5.6 Hz, C4′–Ha), 2.42 (bs, 3H, C6–CH$_3$), 2.23 (dd, 1H, *J*=13.1, 2.4 Hz, C4′–Hb), 1.77 (m, 1H), 0.82 (d, 6H, *J*=6.6 Hz, 2×–CH$_3$); δ_C (75 MHz, CDCl$_3$): 176.51 (C4), 154.73 (C2), 153.15 (C8a), 150.69 (quat. arom.), 134.75 (C6), 134.58 (C7), 128.71 (CH, arom.), 125.17 (C5), 124.46 (C4a), 123.74 (C3), 122.13 (CH, arom.), 119.16 (C8), 115.52 (CH, arom.), 102.77 (C5′), 75.11(–OCH$_2$–), 60.20 (C3′), 41.68 (C4′), 28.48 (CH), 21.50 (C6–Me), 20.20(–CH$_3$); *m/z*378(1.5, M$^+$+2), 380 (2.5, M$^+$+1), 379 (7.5, M$^+$), 277 (10), 276 (28), 273 (10), 272 (36), 265 (18), 263 (28), 264 (100). *endo*-Adduct (**19′**, 6%) obtained only in mixture with **19**, Critical NMR data: δ_H (300 MHz, CDCl$_3$): 8.09 (C2–H), 5.22 (d, *J*=4.5 Hz, C5′–H), 4.98 (t, *J*=7.7 Hz, C3′–H), 3.43 (dd, 1H, OC*H*$_2$), 3.22–32.99(m), 2.42–2.16(m), 1.64(m), 0.75(d); δ_C (75 MHz, CDCl$_3$): 153.48 (C2), 151.24 (quat. arom.), 128.47 (CH, arom.), 121.89 (C3), 104.22 (C5′), 74.75 (–OCH$_2$), 59.55 (C3′), 43.63 (C4′), 28.23 (CH), 19.09 (–CH$_3$). **2** (R^1=Me, 6%). **3** (R^1=Me, 6%).

Reaction of 1c with acrylonitrile. Reaction of **1c** with acrylonitrile afforded *exo*-adduct (**20**, 45%) as an off-white solid (benzene/pet. ether 1:10), mp 74–75°C;

[Found C, 72.32; H, 4.99; N, 8.49%. $C_{20}H_{16}O_3N_2$ requires C, 72.28; H, 4.81; N, 8.43%]; λ_{max} (MeOH): 364, 320, 247, 231 and 210 nm. ν_{max} ($CHCl_3$): 2321(w), 1652(s), 1624(m), 1599(m), 1460(m), 1339(w), 1288(m-s), 1265(m-s), 1197(w), 1174(w) cm^{-1}; δ_H (200 MHz, $CDCl_3$): 8.31 (s, 1H, C2–H), 8.00 (s, 1H, C5–H), 7.51 (dd, 1H, *J*=8.5, 1.5 Hz, C7–H), 7.40 (d, 1H, *J*=8.5 Hz, C8–H), 7.33–7.25 (m, 2H), 7.12–7.01 (m, 3H), 5.11 (dd, 1H, *J*=7.9, 2.5 Hz, C5′–H), 4.97 (dd, 1H, *J*=9.2, 3.4 Hz, C3′–H), 3.04 (ddd, 1H, *J*=12.3, 9.2, 7.9 Hz, C4′–Ha), 2.68 (dt, 1H, *J*=12.3, 2.8 Hz, C4′–Hb); δ_C (75 MHz, $CDCl_3$): 176.67 (C4), 154.92 (C8a), 154.13 (C2), 148.92 (quat. arom.), 135.33 (C6), 135.22 (C7), 129.23 (CH), 124.98 (C5), 123.77 (CH, arom.), 123.60 (C4a), 122.38 (C3), 118.21 (C8), 117.37 (CN), 115.54 (CH, arom.), 64.07 (C5′), 61.68 (C3′), 40.32 (C4′), 21.06 (CH_3); *m/z* 333 (0.5, M$^+$+1), 332 (1.5, M$^+$), 305(1), 276(33), 264(20), 263(54), 262(20), 187(12), 186(64), 185(100). *endo*-Adduct **20′** (40%) obtained only in mixture with **20**, selected NMR data: δ_H (200 MHz, $CDCl_3$): 5.32 (dd, 1H, *J*=7.02, 3.45 Hz, C5′–H), 4.76 (t, *J*=7.6 Hz, C3′–H), 2.96–2.76 (m,2H); δ_C (50 MHz, $CDCl_3$): 154.74 (C2), 150.01 (quat., arom.), 128.98 (CH, arom.), 123.44 (C3), 118.04 (CN), 115.29 (CH), 64.88 (C5′), 62.97 (C3′), 39.51 (C4′). **2** (R^1=Me,5%). **3** (R^1=Me, 3%).

Reaction of 1c with styrene. Reaction of **1c** with styrene afforded *exo*-adduct (**21**, 80 light yellow semisolid, [Found C, 78.53; H, 5.54; N, 3.77%. $C_{25}H_{21}O_3N$ C, 78.32; H, 5.48; N, 3.65%]; λ_{max} (MeOH): 364, 313, 235 and 213 nm; ν_{max} ($CHCl_3$): 1649.7(s), 1616(s), 1600(s), 1570(m), 1508(s), 1474(s), 1449(s), 1393(m), 1346(s), 1313.7(s), 1169(s) cm^{-1}; δ_H (200 MHz, $CDCl_3$): 8.37 (d, 1H, *J*~0.8 Hz, C2–H), 8.02 (bs, 1H, C5–H), 7.45–7.22 (m, 9H, arom.-Hs), 7.09 (d, 2H, *J*=7.7 Hz), 6.95 (t, 1H, *J*=7.2 Hz), 5.25–5.13 (m, 2H, C3′–H and C5′–H), 3.38 (dt, 1H, *J*=12.8, ~7.4 Hz, C4′–Ha), 2.47 (s, 3H, C6-CH_3), 2.34–2.25 (ddd, 1H, *J*=12.8, 5.6, 3.8 Hz, C4′–Hb); δ_C (50 MHz, $CDCl_3$): 176.86 (C4), 154.95 (C8a),153.17 (C2), 151.62 (quat. arom.), 137.87(q), 134.97 (C6), 134.65 (C7), 128.55 (CH, arom.), 128.49 (CH, arom.), 128.27 (CH, arom.), 126.83 (CH, arom.), 125.37 (C5), 125.03 (C4a), 123.63 (C3), 121.78 (CH, arom.), 118.04 (C8), 113.95 (CH, arom.), 80.26 (C5′), 63.81 (C3′), 45.41 (C4′), 21.05(–CH_3); *m/z* 383(10, M$^+$), 292(5), 266(10), 265(45), 264(15), 263(14), 244(8), 187(18), 186(32), 185(34), 135(21), 134(15), 128(15), 117(10), 106(18), 105(38), 104(21), 93(15), 92(8), 91(4), 78(32), 77(100). **2** (R^1=Me, 8%). **3** (R^1=Me, 5%).

Reaction of 1c with methyl acrylate. Reaction of **1c** with methyl acrylate afforded mixture (2.8:1.0) of *exo*- and *endo*-adduct (**22** and **22′**, 95%) a light yellow semisolid, λ_{max} (MeOH): 364, 312, 233 and 210 nm; ν_{max} ($CHCl_3$): 1741(s), 1649.0(s), 1624(s), 1602.5(s), 1581(m), 1496(s), 1444(s), 1397(s), 1346(w), 1320(s), 1286(w), 1218(s), 1188(m), 1150(w), 1146(w), 1044(m) cm^{-1}; δ_H (200 MHz, $CDCl_3$): 8.34 (s, 1H, C2–H in **22**), 8.23 (s, C2–H in **22′**), 8.01 (bs, 1H, C5–H), 7.47–6.96 (m, 7H, arom.-Hs), 5.17–5.12 (m, C5′–H in **22** and **22′**), 4.80 (dd, 1H, *J*=9.3, 5.8 Hz, C3′–H in **22**), 4.61 (t, *J*=6.6 Hz, C3′–H **22′**), 3.71 and 3.70 (singlets, –OCH_3 **22′** and **22**, respectively), 3.05 (dt, *J*=12.8, ~8.0 Hz C4′–Ha in **22**), 2.88–2.74 (m, C4′–Ha in **22′**), 2.78–2.48 (m, 4H with a sharp singlet at δ 2.46, C4′–Hb and C6–Me); δ_C (50 MHz, $CDCl_3$): 176.51 and 176.41 (C4 in **22** and **22′**), 170.58 and 170.20 (ester C=O in **22′** and **22**), 154.95 (C8a in **22′**), 154.71 (C8a in **22**), 154.19 (C2 in **22**), 153.62 (C2 in **22′**), 150.66 and 150.30 (quat. arom. Cs in **22′** and **22**), 135.00 (C6 in **22′**), 134.86 (C6 in **22**), 134.75 and 134.50 (C7 in **22** and **22′**), 129.00 (CH, arom.), 128.60 (CH, arom.), 124.86 (C5), 123.42 (C8a), 122.65 (CH, arom.), 122.37 (C3 in **22′**), 122.02 (C3 in **22′**). 118.19 (C8), 115.46 and 114.90 (CH, arom.), 76.22 (C5′ in **22′**), 75.25 (C5′ in **22**), 62.21 and 62.00 (C3′ in **22′** and **22**), 52.13 and 50.51(–OCH_3 in **22** and **22′**), 38.86 and 37.75 (C4′ in **22** and **22′**), 20.89 (C6-CH_3). *m/z* 365 (3, M$^+$), 304(10), 277(12), 276(24), 264(23), 263(75), 262(23), 213(26), 187(22), 186(74), 185(72). **2** (R^1=Me, 3%). **3** (R^1=Me, 3%).

Reaction of 1c with methyl vinyl ketone. Reaction of **1c** with methyl vinyl ketone afforded *exo*-adduct (**23**, 45%) as a light yellow solid (benzene/pet. ether 1:5); mp 81–82°C; [Found C, 72.00; H, 5.41; N, 3.98%. $C_{21}H_{19}O_4N$ requires C, 72.20; H, 5.44; N, 4.01%]; λ_{max} (MeOH): 364, 310, 232 and 212 nm; ν_{max} ($CHCl_3$): 1722(s), 1649 (s), 1624(s), 1440(s), 1393(m), 1320(s) cm^{-1}; δ_H (200 MHz, $CDCl_3$): 8.07 (bs, 1H, C2–H), 7.93 (bs, 1H, C5–H), 7.40 (dd, 1H, *J*=8.7, 1.9 Hz C7–H), 7.26 (d, 1H, *J*~8.6 Hz, C8–H), 7.16 (bt, 2H, *J*=7.2 Hz), 6.98 (bd, 2H, *J*=6.2 Hz), 6.88 (t, 1H, *J*=7.2 Hz), 4.93 (dd, 1H, *J*=8.4, 3.9 Hz, C5′–H), 4.54 (dd, 1H, *J*=9.1, 5.6 Hz, C3′–H), 2.95 (dt, 1H, *J*=12.9, 8.8 Hz, C4′–Ha), 2.54–2.37 (m, 4H, with an overlapping singlet at δ 2.41, C4′–Hb and C6-C*H*$_3$), 2.26 (s, 3H, CO-C*H*$_3$); δ_C (50 MHz, $CDCl_3$): 205.63 (C=O), 176.36 (C4), 154.59 (C8a), 153.68 (C2), 149.37 (quat. arom. C), 134.97 (C6), 134.84 (C7), 128.75 (CH, arom.), 124.99 (C5), 123.71 (C4a), 123.43 (C3), 122.40 (CH, arom.), 117.86 (C8), 115.57 (CH, arom.), 81.50 (C5′), 61.50 (C3′), 38.19 (C4′), 25.99(–CO–*C*H$_3$), 20.90 (C6-*C*H$_3$); *m/z* 349 (2, M$^+$), 331(10), 278(12), 263(12), 212(10), 187(20), 186(30), 185(100). *endo*-Adduct (**23′**, 40%) obtained only in mixture with **23**; critical NMR data: δ_H (200 MHz, $CDCl_3$): 5.11 (dd, *J*=7.7, 2.08 Hz, C5′–H), 4.44 (bt, 1H, *J*~8.1 Hz, C3′–H), 2.77 (dt, 1H, *J*=13.0, ~8.1 Hz, C4′–Ha), 2.50–2.37 (m, 4H, with an overlapping singlet at δ 2.41, C4′–Hb and C6–C*H*$_3$), 2.23(–COC*H*$_3$); δ_C (50 MHz, $CDCl_3$): 205.93 (C=O), 154.65 (C8a), 153.22 (C2), 149.80 (quat. arom. C), 128.98 (CH), 122.86 (C3), 115.25 (CH), 83.11 (C5′), 60.10 (C3′), 37.64 (C4′), 26.50 (–CO*C*H$_3$). **2** (R^1=Me, 6%). **3** (R^1=Me, 9%).

Reaction of 1a with methyl methacrylate. Reaction of **1a** with methyl methacrylate afforded adduct (**24**, 60%) as a colorless solid ($CHCl_3$), mp 143°C; [Found C, 69.09; H, 5.15; N, 3.73%. $C_{21}H_{19}O_5N$ requires C, 69.04; H 5.20; N 3.83%]; λ_{max} (MeOH): 367, 308, 248(sh) and 231.5 nm; ν_{max} (KBr): 1743.5(s), 1649.5(s), 1602.5(s), 1495.6(s), 1474.2(s), 1397.3(b), 1358.8(s), 1324.6(s), 1290.4(s), 1260.5(s), 1213.5(s), 1184(s), 1140(s), 1098(m), 1025(s) cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.24 (dd, 1H, *J*=7.8, 1.6 Hz, C5–H), 8.21 (bs, 1H, C2–H), 7.67(split t, 1H, *J*=7.0, 1.7 Hz, C7–H), 7.47–7.37 (m, 2H), 7.22–7.14 (m, 2H), 7.02–6.86 (m, 3H), 5.13 (distorted t, *J*~7.6 Hz, C3′–H), 3.62 (dd, 1H, *J*=12.8, 7.9 Hz, C4′–Hb), 3.46 (s,3H, –OCH_3), 2.14 (dd, 1H, *J*=12.8, 6.0 Hz, C4′–Ha), 1.56 (s, 3H, C4′–CH$_3$); δ_C (75 MHz, CDCl$_3$): 176.37 (C4), 172.40 (–*C*O$_2$–), 156.46 (C8a), 153.17 (C2), 150.40 (quat. arom. C), 133.47 (C7), 128.52 (CH, arom.), 125.77 (C6), 125.02 (C5), 124.33 (C4a), 123.87 (C3), 121.35 (CH, arom.), 118.08 (C8), 113.83 (CH, arom.), 83.58 (C5′), 61.58 (C3′), 51.94 (–O*CH*$_3$), 45.72 (C4′), 22.78 (C5′–*C*H$_3$); *m*/*z* 366 (2, M$^+$+1), 365 (12, M$^+$), 323(18), 318(16), 306(40), 291(18), 265(20), 264(100). **2** (R^1=H, 30%). **3** (R^1=H, 10%).

Reaction of 1a with ethyl crotonate. Reaction of **1a** with ethyl crotonate afforded adduct (**25**, 25%) as a light yellow solid (benzene/pet. ether 1:2); mp 90°C; [Found C, 69.77; H, 5.65; N, 3.78%. C$_{22}$H$_{21}$O$_5$N requires C, 69.65; H, 5.54; N, 3.69%]; λ_{max} (MeOH): 362, 306, 298 and 228.5 nm; ν_{max} (CHCl$_3$): 1736.4(m), 1653.7(s), 1619.5(m), 1564.3(s), 1551.2(s), 1517(s), 1495.6(s), 1470(s), 1401.6(m), 1346(m), 1320.4(m), 1264.8(s), 1132.3(m), 1029.7(s) cm^{-1}; δ_H (200 MHz, CDCl$_3$): 8.32 (s, 1H, C2–H), 8.22 (d, 1H, *J*=7.8 Hz, C5–H), 6.67 (bt, 1H, *J*=7.6 Hz, C7–H), 7.49–7.16 (m, 4H), 7.02–6.93 (m, 3H), 5.43 (d, 1H, *J*=5.2 Hz, C3′–H), 4.35 (dq, 1H, *J*=6.8, 6.1 Hz, C5′–H), 4.18 (q, 2H, *J*=7.1, OC*H*$_2$–), 3.98 (dd, 1H, *J*=6.8, 5.2 Hz, C4′–H), 1.44 (d. 3H, *J*=6.1 Hz, C5′–C*H*$_3$), 1.21 (t, 3H, *J*=7.1 Hz, –CH$_3$); δ_C (50 MHz, CDCl$_3$): 176.48 (C4), 169.57(*C*O$_2$Et), 156.54 (C8a), 153.42 (C2), 150.62 (quat. arom. C), 133.62 (C7), 129.17 (CH. arom.), 125.99 (C6), 125.19 (C5), 124.56 (C4a), 124.01 (C3), 121.89 (CH, arom.), 118.28 (C8), 113.99 (CH, arom.), 78.69 (C5′), 66.92 (C3′), 63.48 (C4′), 61.27 (–O*C*H$_2$–), 17.64 (C5′–CH$_3$), 14.26 (–CH$_3$); *m*/*z* 379 (2, M$^+$), 290(11), 289(10), 288(10), 285(12), 253(18), 252(20), 250(22), 249(70), 248(28). A mixture (6:1) of adducts (**25′**, **25″**, 20%) as a yellow viscous mass; λ_{max} (MeOH): 362, 306, 298 and 228.5 nm; ν_{max} (CHCl$_3$): 1743.5 (s), 1649.5 (s), 1615.3 (s), 1602.5 (w), 1585.4 (w), 1495.6 (s), 1474.2 (s), 1431.5 (s), 1410.1 (s), 1350.3 (w), 1316.1 (w), 1269.1 (s), 1239(w), 1106 (s), 1021.2 (s) cm^{-1}; δ_H (200 MHz, CDCl$_3$): 8.29 (s, C2–H in **25″**), 8.28 (s, C2–H in **25′**), 8.17 (bd, 1H, *J*=6.8, C5–H), 7.69–7.55 (m, 1H, C7–H), 7.51–7.33 (m, 2H), 7.29–7.13 (m, 2H), 7.06–6.89 (m, 3H), 5.34 (d, *J*=6.5, C5′–H in **25″**), 4.78 (d, 1H, *J*=3.5 Hz, C5′–H in **25′**), 4.68 (d, *J*=7.2 Hz, C3′–H in **25″**), 4.32 (d, 1H, *J*=6.0 Hz, C3′–H in **25′**), 4.14 (q, *J*=7.1 Hz, –OC*H*$_2$– in **25′**), 3.86 (q, *J*=7.1 Hz, –OC*H*$_2$– in **25″**), 3.36–3.29 (m, C4′–H in **25″**), 2.84–2.70 (m, C4′–H in **25′**), 1.40 (d, *J*=6.2 Hz, C4′–CH$_3$ in **25″**), 1.32 (d, *J*=6.5 Hz, C4′–CH$_3$ in **25′**), 1.19 (t, *J*=7.1 Hz, OCH$_2$C*H*$_3$ in **25′**), 0.98 (t, *J*=7.0 Hz, OCH$_2$C*H*$_3$ in **25″**); δ_C (50 MHz, CDCl$_3$): 176.31C4), 168.34 (*C*O$_2$Et), 154.35 (C2), 150.10 (quat. arom.), 134.71 (C7), 129.16 and 129.04 (CH, arom.), 126.57 and 126.45 (C6 in **25′** and **25″**), 125.84 and 125.19 (C5 in **25″** and **25′**), 124.45 (C4a), 122.30 (C3), 120.57 (CH, arom.), 118.50 and 118.36 (C8 in **25′** and **25″**), 114.47 (CH, arom.), 82.55 (C5′ in **25′**), 68.79 (C3′), 61.32(–O*C*H$_2$–), 51.43 (C4′ in **25′**), 20.58 and 19.19 (C4′–CH$_3$ in **25′** and **25″**), 14.27 (–CH$_3$); *m*/*z* 379 (22, M$^+$), 350 (23), 307 (20), 306 (3), 304 (15), 301 (25), 265 (38), 250 (15), 249 (54), 58 (100). **2** (R^1=H, 30%). **3** (R^1=H, 10%).

Reaction of 1a with dihydrofuran. Reaction of **1a** with dihydrofuran afforded a mixture (7:1)of *endo*-adduct **26** and exoadduct **26′** (25%) as an off-white semisolid; λ_{max} (MeOH): 330, 288, 245(sh), 220 nm; ν_{max} (CHCl$_3$): 1653.7 (s), 1619.5 (sh), 1581.1 (sh), 1495.6(w), 1474.2(s), 1354.6(s), 1324.6 (s), 1260.5 (s), 1222.1 (s), 1179.4 (s), 1153.7 (m), 1119.5 (m), 1085.3 (s), 1029.7 (s) cm^{-1}; δ_H (300 MHz, CDCl$_3$): 8.16 (dd, 1H, *J*=7.8, 1.3 Hz, C5–H), 8.10 (bs, 1H, C2–H), 7.60 (split t, 1H, *J*=7.8, 1.4 Hz, C7–H), 7.46–7.32 (m, 2H), 7.19–7.11 (m, 2H), 6.94 (bd, 2H, *J*=7.9 Hz), 6.80 (t, 1H, *J*=7.2 Hz), 5.79 (d, 1H, *J*=5.2 Hz, C8′–H in **26**), 5.65 (d, *J*=3.8, C8′–H in **26′**), 5.40 (dd, *J*=6.4, 0.8 Hz, C3′–H in **26′**), 4.90 (bs, 1H, C3′–H in **26**), 4.20 (td, 1H, *J*=7.0, 2.7 Hz, C6′–H in **26′**), 4.03–3.95 (m, 1H, C6′–H in **26′**), 3.82–3.69 (m, 1H, C6′–H in **26**), 3.41 (dt, 1H, *J*=12.1, 8.3 Hz, C6′–H in **26**), 3.16–3.08 (m, 1H, C4′–H in **26**), 2.90–2.78 (m, C4′–H in **26** C4′–H in **26′**), 2.25–2.01 (m, 2H, C5′–Hs); δ_C (75 MHz, CDCl$_3$): 177.17 (C4), 155.54 (C8a), 153.42 (C2), 150.98 (quat. arom.), 133.71 (C7), 128.80 (CH, arom.), 125.74 (C6), 125.27 (C5), 124.32 (C4a), 122.13 (C3), 121.29 (CH, arom.), 118.33 (C8), 114.16 (CH, arom.), 108.84 (C8′ in **26**), 104.75 (C8′ in **26′**), 71.02 (C3′ in **26′**), 68.75 (C6′ in **26′**), 68.32 (C6′ in **26**), 67.76 (C3′, in **26**), 59.58 (C4′ in **26′**), 55.44 (C4′ in **26**), 32.08 (C5′ in **26**), 32.08 (C5′ in **26′**); *m*/*z* 336 (1.3, M$^+$+2), 335 (4, M$^+$), 287(12), 250(40), 249(18), 227(35). **2** (R^1=H, 70%). **3** (R^1=H, 10%).

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