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3-Nitrochromene derivatives as 2π components in 1,3-dipolar cycloadditions of azomethine ylides

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Abstract—The 1,3-dipolar cycloaddition of 2-aryl-3-nitrochromenes with various azomethine ylides has been investigated. The structure and stereochemistry of cycloadducts were studied in detail by NMR spectroscopic methods.

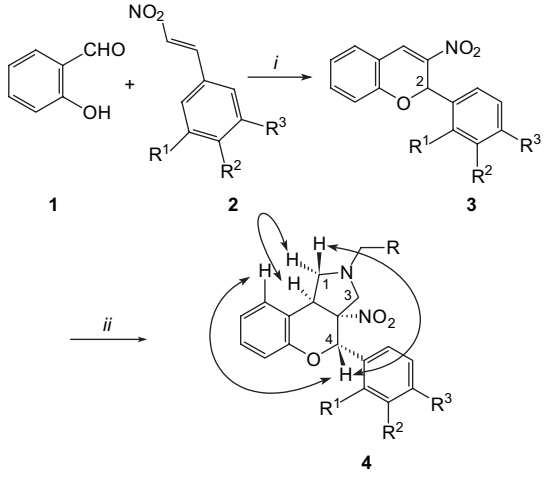
1. Introduction

1,3-Dipolar cycloadditions delineate one of the simplest approaches for the construction of five-membered heterocyclic rings.[1] The ease of generation of 1,3-dipoles, coupled with the often observed highly regio- and stereoselective nature of their cycloaddition reactions has led to a number of syntheses, which utilize such a reaction as the key step.[2] Recently, we have demonstrated the usefulness of the intermolecular 1,3-dipolar cycloaddition of azomethine ylides in the synthesis of aza-cephalotaxine analogues[3] or alkaloid derivatives with a spiro-indolenine framework.[4] This method gives rapid access to the pyrrolo[3,2-*c*]quinoline ring system of martinellines[5] and to pyrrolo[3,4-*c*]quinolines.[6] The abundance of naturally occurring chromene and chromane derivatives, and their interesting physiological properties along with the known selective dopamine D_3 receptor antagonist action of some benzopyrano[3,4-*c*]pyrrolidine derivatives,[7] suggested the study of easily available 2-aryl-3-nitrochromene derivatives as 2π components in 1,3-dipolar cycloadditions of azomethine ylides.

To our knowledge, 3-nitrochromenes[8] have never been used as 2π components in cycloaddition reactions, although they are promising starting materials for the synthesis of functionalized heterocyclic frameworks. Some examples involving coumarins such as 3-nitro-,[9] 3-cyano-[10] and 4-phenylsulfonyl-[11] derivatives have been reported. With the intention to develop a new procedure for the synthesis of benzopyrano[3,4-*c*]pyrrolidine derivatives in this paper, we report the 1,3-dipolar cycloadditions of azomethine ylides with 2-aryl-3-nitrochromenes.[12]

2. Results and discussion

The 3-nitrochromene derivatives (**3a–j**) were prepared by modification of the method described by Yao[8b] from the corresponding 2-aryl-nitroethylenes (**2a–j**)[13] by the treatment with salicylaldehyde, in the presence of DABCO, without any solvent, in a single step (Scheme 1).



Scheme 1. Reagents and conditions: (i) DABCO, 40 °C; (ii) $CH_3NHCH_2CO_2H$ (R=H) or $BnNHCH_2CO_2H$ (R=Ph), $(CH_2O)_n$, toluene, reflux.

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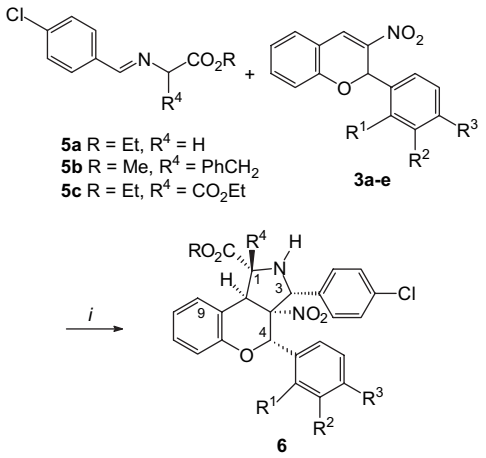
In the first set of experiments, we used the most simple non-stabilized azomethine ylides, which were generated from paraformaldehyde and sarcosine or *N*-benzyl-glycine using the decarboxylation method.[10] The reaction of 3-nitrochromenes (**3a–j**) with these unstable intermediates in refluxing toluene proceeds smoothly, to give the expected 3a-nitro-4-aryl-benzopyrano[3,4-*c*]-pyrrolidines (**4a–q**) (Scheme 1). The results, summarized in Table 1, showed that dipolarophiles (**2**) with more electron-donating substituents on the 2-aryl group are less reactive than those either without electron-donating groups or with electron-withdrawing substituents. This result is similar to our earlier experiments with β-nitro-styrenes.[14]

The structures of compounds **4** were elucidated by NMR spectroscopy using ^{1}H, ^{13}C, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMQC techniques. The relative stereochemistry of these cycloadducts (**4**) was established on **4a** and **4n** mostly by $^{1}H\{^{1}H\}$ NOE studies. The most important proof of their stereochemistry was the NOE enhancements indicated with arrows in Scheme 1.

Thermally generated dipoles from the imines of glycine or other α-amino acid esters undergo stereoselective cycloadditions with highly activated cyclic dipolarophiles such as maleimides leading to the exclusive formation of *endo*-adducts of *E*,*E*-ylides.[15] However, their cycloadditions with less reactive olefin dipolarophiles such as maleates and fumarates were found to be no longer stereoselective.[16] Activation with a wide range of metal salt/tertiary amine combinations proved to be effective for increasing the rate of cycloaddition of aryl imines to less reactive dipolarophiles, allowing the reaction to run at room temperature with excellent regio- and stereocontrol.[17] The cycloaddition of **3** with the azomethine ylides derived from the imines of ethyl glycinate, phenylalanine ethylester or diethyl aminomalonate in the presence of AgOAc and Et_3N occurred smoothly at room temperature giving pure benzopyrano[3,4-*c*]-pyrrolidine derivatives **6a–k** in 60–77% yield (Scheme 2, Table 2). Representative ^{1}H and ^{13}C NMR data for compounds **6c** and **6f**, which verify the structure are collected in Tables 3 and 4. Assignments and stereochemistry were confirmed as noted above in the case of compounds **4**.



Scheme 2. Reagents and conditions: AgOAc, Et_3N, toluene, rt.

The condensation of various aldehydes with *N*-alkyl or *N*-aryl α-amino esters leads to *N*-substituted azomethine ylides. These ylides can be trapped smoothly by the added dipolarophiles, since there are no other reactive reagents (e.g., base, Lewis acids) in the reaction mixture.[18] The cycloaddition of **3** with the azomethine ylides derived from methyl sarcosinate and benzaldehyde in refluxing toluene under Dean–Stark conditions resulted in the formation of cycloadducts **7a–f** in moderate yield (Scheme 3, Table 5). Selected NMR data for cycloadduct **7a** are collected in Table 6.

Table 2. Products of the cycloaddition of **3** with the azomethine ylides derived from the imines **5a–c**

Entry	R^1	R^2	R^3	Starting material	R	R^4	Product	Yield (%)
1	H	H	H	**3a**	Et	H	**6a**	72
2	H	H	H	**3a**	Me	$PhCH_2$	**6b**	75
3	H	H	MeO	**3c**	Et	H	**6c**	60
4	H	H	MeO	**3c**	Me	$PhCH_2$	**6d**	65
5	H	H	Cl	**3f**	Et	H	**6e**	70
6	H	H	Cl	**3f**	Me	$PhCH_2$	**6f**	72
7	Cl	H	H	**3e**	Me	$PhCH_2$	**6g**	60
8	H	MeO	MeO	**3h**	Et	H	**6h**	61
9	H	MeO	MeO	**3h**	Me	$PhCH_2$	**6i**	62
10	H	NO_2	H	**3j**	Me	$PhCH_2$	**6j**	75
11	H	H	H	**3a**	Et	CO_2Et	**6k**	48

Table 1. Reaction times and yields of compounds **4a–q**

Entry	R^1	R^2	R^3	Nitro-chromene	R	Product	Time (h)	Yield (%)
1	H	H	H	**3a**	H	**4a**	3	93
2	H	H	H	**3a**	Ph	**4b**	5	72
3	MeO	H	H	**3b**	H	**4c**	7	79
4	H	H	MeO	**3c**	H	**4d**	5	94
5	H	H	MeO	**3c**	Ph	**4e**	5	85
6	H	MeO	H	**3d**	H	**4f**	7	76
7	H	MeO	H	**3d**	Ph	**4g**	11	68
8	Cl	H	H	**3e**	H	**4h**	7	71
9	H	Cl	H	**3f**	H	**4i**	5	89
10	H	Cl	H	**3f**	Ph	**4j**	5	83
11	H	OBn	H	**3g**	H	**4k**	5	96
12	H	OBn	H	**3g**	Ph	**4l**	5	83
13	H	MeO	MeO	**3h**	H	**4m**	12	75
14	H	MeO	MeO	**3h**	Ph	**4n**	16	68
15	H	OCH_2O		**3i**	H	**4o**	12	66
16	H	H	NO_2	**3j**	H	**4p**	1	84
17	H	H	NO_2	**3j**	Ph	**4q**	1	79

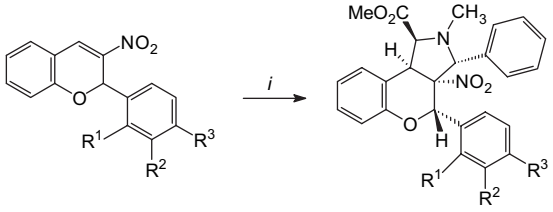
Table 3. ^{1}H and ^{13}C NMR chemical shifts, selected H–H couplings and measured NOE and HMQC connectivities for compound **6c**

	δ_H	$J_{H,H}$ (Hz)	$^1H\{^1H\}$ NOE connections	δ_C	HMQC correlations
1	4.12, br s		H-9, H-4, H-3, H-9b, OCH_2, H-3	68.3	H-9b
3	4.94, d	7.4	H-4, H-1, Ar^3-2′ and 6′H	69.4	Ar^3-2′ and 6′H, H-4
3a	—			96.6	H-3, H-4, H-9b
4	5.49, s		Ar^3-2′ and 6′H, Ar^4-2′ and 6′H, H-9b	75.2	Ar^4-2′ and 6′H, H-9b
9b	4.79	3.8	H-9, Ar^3-2′ and 6′H, Ar^4-2′ and 6′H, H-1	45.6	H-9, H-4, H-1

Table 4. ^{1}H and ^{13}C NMR chemical shifts, selected H–H couplings and measured NOE and HMBC connectivities for compound **6f**

	δ_H	$J_{H,H}$ (Hz)	$^1H\{^1H\}$ NOE[a]	δ_C	HMQC
1	—			72.2	CH_2, H-9b, H-2
2 (NH)	2.94, d	7.8	Ar^3-2′,6′H, Bn-2′,6′H, H-3, H-9b	—	—
3[a]	5.09, d	7.8	H-9, Ar^3-2′,6′H, Ar^4-2′,6′H, H-4, *O*Me, H-2	67.4	Ar^3-2′,6′H, H-4, H-9b
3a	—			98.5	H-4, H-3, H-2, H-9b.
4	5.55, s		Ar^3-2′,6′H, Ar^4-2′,6′H, H-3, β-CH_2; H-6	77.0	Ar^4-2′ and 6′H, H-9b
CH_2-α	2.81, d	13.7	H-9, Bn-2′,6′H, *O*Me, β-CH_2		
CH_2-β	2.37, d	13.7	Bn-2′,6′H, H-4, H-3, H-9b, *O*Me, α-CH_2	42.2	H-9b
9b[a]	5.10, s		H-9, Ar^3-2′,6′H, Ar^4-2′,6′H, H-4, OMe, H-2, β-CH_2	49.8	H-9, H-4

[a] H-3 and H-9b were irradiated together.



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Scheme 3. Reagents and conditions: $CH_3NHCH_2CO_2Me$, PhCHO, toluene, reflux.

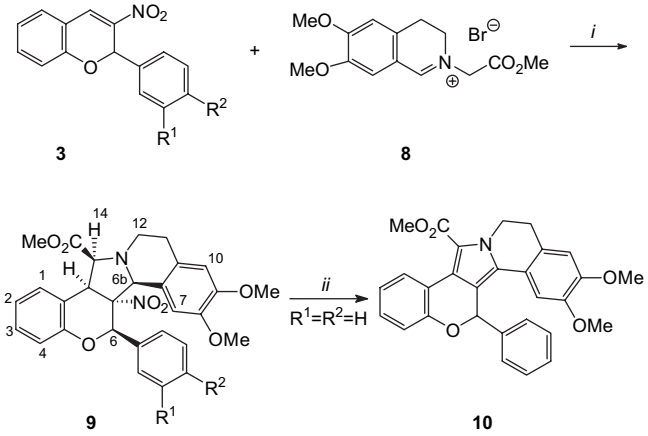
Table 5. Products of the cycloaddition of **3** with the azomethine ylides derived from methyl sarcosinate and benzaldehyde

Entry	R^1	R^2	R^3	Starting material	Product	Yield (%)
1	H	H	H	**3a**	**7a**	57
2	OMe	H	H	**3b**	**7b**	44
3	Cl	H	H	**3e**	**7c**	50
4	H	H	Cl	**3f**	**7d**	63
5	H	MeO	MeO	**3h**	**7e**	47
6	H	OCH_2O		**3i**	**7f**	38

Table 6. ^{1}H and ^{13}C NMR chemical shifts, selected H–H couplings and measured NOE and HMBC connectivities for compound **7a**

	δ_H	$^1H\{^1H\}$ NOE	δ_C	HMQC
1	3.88, d[a]	H-3, H-9b, NMe	73.3	H-9b, H-9a, NMe
3	3.85, s	H-1, H-4, NMe, Ph^3-2′ and 6′H	81.8	H-3a, H-4, NMe
3a	—	—	95.6	H-3, H-4, H-9b
4	5.16, s	H-3, Ph^4-2′ and 6′H, Ph^3-2′ and 6′H	76.8	H-3, Ph^4-2′ and 6′H
9b[a]	5.02, s	H-1, Ph^4-2′ and 6′H, H-9	43.1	H-9, H-4, H-2

1,3-Dipolar cycloadditions of azomethine ylides derived from isoquinolinium salt **8** by deprotonation have previously been studied in detail by us.[19] Reaction with suitably active dipolarophiles afford pyrrolo[2,1-*a*]isoquinoline cycloadducts in practically quantitative yield as single diastereoisomers. The cycloaddition of **3** with the azomethine ylide derived from isoquinolinium salt **8** at ambient temperature with the exclusion of air gave rise to the formation of cycloadducts **9a–c** in virtually quantitative yield as a single diastereoisomer (Scheme 4, Table 7). However, as observed during the earlier experiments, the solution of **9a** in the presence of oxygen transforms into pyrrole derivative **10** at room temperature in a short period of time.



Scheme 4. Reagents and conditions: (i) Et_3N, EtOH, rt; (ii) O_2, $CDCl_3$, rt.

Table 7. Cycloaddition of **3** with azomethine ylide derived from isoquinolinium salt **8**

Entry	R^1	R^2	Nitro-chromene	Product	Yield (%)
1	H	H	**3a**	**9a**	92
2	H	MeO	**3c**	**9b**	95
3	MeO	MeO	**3h**	**9c**	93

The structures of compounds **9** were elucidated again by NMR spectroscopy: the ^{1}H–^{1}H NOE experiments proved the all-cis relationship of the 6, 6b, 14, 14a protons. The strongly shielded aromatic H-7 proton, probably result as a consequence of the anisotropy of the aromatic ring connected at C-6 exhibiting a chemical shift of 6.10 ppm, further corroborated the proposed structure. Selected NMR data are collected in Table 8.

Table 8. ^{1}H and ^{13}C NMR chemical shifts, selected H–H couplings and measured NOE and HMQC connectivities for compound **9c**

	δ_H	$J_{H,H}$ (Hz)	$^{1}H\{^{1}H\}$ NOE connections	δ_C	HMQC correlations
6	5.77, s	—	Ar^6-2′ and 6′H, H-7, H-6b, H-14, H-14a	75.8	Ar^6-2′ and 6′H, H-6b
6a	—	—	—	90.4	H-6b
6b	4.86, s	—	H-7, H-6, H-14, H-14a, H-12α	65.7	H-7, H-12, H-14
7	6.10, s	—	H-6, H-6b, 8-OMe	109.8	H-6b
14	4.11, d	11.3	—	67.7	H-12, H-14a
14a	4.12, d	11.3	—	47.2	H-1, H-14

In summary, the use of 3-nitrochromene derivatives as 2π components in 1,3-dipolar cycloadditions of azomethine ylides allows the assembly of polysubstituted benzopyrano[3,4-*c*]-pyrrolidines from simple precursors in one-pot reaction.

3. Experimental

3.1. General

Melting points were determined on a Gallenkamp apparatus and are uncorrected. Column chromatography was performed using Merck Kieselgel 60 (70–230 mesh), TLC on aluminium sheets coated with Kieselgel 60 F_{254}. Plates were stained with anisaldehyde solution (100 ml glacial acetic acid, 2 ml concd sulfuric acid and 1 ml anisaldehyde) and heated at ca. 150 °C. IR spectra were obtained on a Bruker VECTOR 22 FT-IR instrument. NMR spectra were obtained on Varian INOVA 500, Bruker DRX-500 and Bruker 250 instruments. Chemical shifts are given relative to δ_{TMS}. All solvents were purified according to standard procedures.

3.1.1. Synthesis of 2-methyl- and 2-benzyl-3a-nitro-4-aryl-benzopyrano[3,4-*c*]-pyrrolidines (4). General procedure. A mixture of sarcosine (2.5 equiv) or *N*-benzylglycine (2.5 equiv), paraformaldehyde (6 equiv) and the corresponding 3-nitrochromene (1 equiv) was heated under reflux in toluene (10 ml for 1 mmol of dipolarophile). The water formed was removed by the aid of a Dean–Stark trap. After completion of the reaction, the reaction mixture was filtered through a pad of Celite and the solvent was evaporated in vacuo. The residue was crystallized from ether to give the title products. The reaction times and yields (based on the dipolarophiles) are summarized in Table 1.

3.1.1.1. 2-Methyl-3a-nitro-4-phenyl-benzopyrano[3,4-*c*]-pyrrolidine (4a). White powder, mp 138–139 °C; [Found: C, 69.9; H, 5.8; N, 9.0. $C_{18}H_{18}N_2O_3$ requires C, 69.7; H, 5.9; N, 9.0%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.44 (5H, m, Ph-H), 7.23 (2H, m, H-7 and H-9), 7.04 (2H, m, H-6 and H-8), 5.01 (1H, s, H-4), 4.03 (1H, t, *J* 8.5 Hz, H-9b), 3.62 (1H, d, *J* 11.4 Hz, H-3), 3.50 (1H, t, *J* 8.5 Hz, H-1), 2.85 (1H, d, *J* 11.4 Hz, H-3), 2.71 (1H, t, *J* 8.5 Hz, H-1), 2.41 (3H, s, NMe); ^{13}C NMR (62.5 MHz, $CDCl_3$): 154.0 (q), 134.0 (q), 129.4 (CH), 128.5 (2×CH), 128.3 (CH), 127.8 (CH), 126.8 (2×CH), 122.6 (q), 122.5 (CH), 117.6 (CH), 95.9 (q), 80.1 (CH), 62.8 (CH_2), 61.8 (CH_2), 43.3 (CH), 41.3 (CH_3); IR (KBr, cm^{-1}): 2976, 2947, 2823, 1535, 1489, 1479, 1452, 1371, 1254, 1238, 1149, 1045, 1024.

3.1.1.2. 2-Benzyl-3a-nitro-4-phenyl-benzopyrano[3,4-*c*]-pyrrolidine (4b). White powder, mp 144 °C; [Found: C, 74.5; H, 5.7; N, 7.0. $C_{24}H_{22}N_2O_3$ requires C, 74.6; H, 5.7; N, 7.2%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.43 (10H, m, Ar-H), 7.28 (1H, t, *J* 7.5 Hz, H-7), 7.23 (1H, d, *J* 7.5 Hz, H-9), 7.12 (2H, m, H-6 and H-8), 5.13 (1H, s, H-4), 4.08 (1H, t, *J* 7.5 Hz, H-9b), 3.80 (1H, d, *J* 12.5 Hz, C*H*$_2$Ph), 3.69 (1H, d, *J* 12.5 Hz, C*H*$_2$Ph), 3.56 (2H, m, H-3 and H-1), 3.03 (1H, d, *J* 11.5 Hz, H-3), 2.9.0 (1H, t, *J* 7.5 Hz, H-1); ^{13}C NMR (62.5 MHz, $CDCl_3$): 154.3 (q), 137.7 (q), 134.2 (q), 129.5 (CH), 128.8 (2×CH), 128.7 (2×CH), 128.65 (2×CH), 128.6 (CH), 128.0 (CH), 127.7 (CH), 127.1 (2×CH), 123.1 (q), 122.7 (CH), 117.8 (CH), 95.1 (q), 80.3 (CH), 60.7 (CH_2), 59.3 (CH_2), 59.2 (CH_2), 42.8 (CH); IR (KBr, cm^{-1}): 3029, 2926, 2839, 2808, 1534, 1488, 1452, 1370, 1306, 1231, 1048, 1028.

3.1.1.3. 2-Methyl-4-(2-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4c). White powder, mp 152–153 °C; [Found: C, 67.1; H, 5.7; N, 8.2. $C_{19}H_{20}N_2O_4$ requires C, 67.0; H, 5.9; N, 8.2%]; ^{1}H NMR (500 MHz, DMSO-d_6): 7.41 (1H, t, *J* 7.5 Hz, Ar^4-5′H), 7.32 (1H, d, *J* 7.5 Hz, Ar^4-6′H), 7.21 (1H, t, *J* 7.5 Hz, H-7), 7.14 (1H, d, *J* 7.5 Hz, H-9), 7.12 (1H, d, *J* 7.5 Hz, H-8), 7.07 (1H, t, *J* 7.5 Hz, H-6), 6.99 (1H, d, *J* 7.5 Hz, Ar^4-3′H), 6.95 (1H, d, *J* 7.5 Hz, Ar^4-4′H), 5.49 (1H, s, H-4), 3.99 (1H, t, *J* 8.3 Hz, H-9b), 3.83 (3H, s, OMe), 3.51 (1H, t, *J* 8.3 Hz, H-3), 3.39 (1H, d, *J* 11.1 Hz, H-1), 2.86 (1H, d, *J* 11.1 Hz, H-3), 2.59 (1H, t, *J* 8.3 Hz, H-1), 2.29 (3H, s, NMe); ^{13}C NMR (125 MHz, DMSO-d_6): 156.1 (q), 154.2 (q), 130.6 (q), 129.9 (CH), 127.7 (CH), 127.1 (CH), 123.5 (CH), 122.65 (q), 122.6 (CH), 120.8 (CH), 117.1 (CH), 111.5 (CH), 96.9 (q), 73.1 (CH), 62.4 (CH_2), 61.4 (CH_2), 55.8 (CH_3), 43.4 (CH), 41.1 (CH_3); IR (KBr, cm^{-1}): 2944, 2841, 2824, 2761, 1585, 1532, 1494, 1456, 1365, 1289, 1256, 1232, 1115, 1045.

3.1.1.4. 2-Methyl-4-(3-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4d). White powder, mp 141–142 °C; [Found: C, 67.2; H, 6.0; N, 8.1. $C_{19}H_{20}N_2O_4$ requires C, 67.0; H, 5.9; N, 8.2%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.30 (1H, t, *J* 7.5 Hz, H-7), 7.23 (4H, m, H-6, H-8, H-9 and Ar^4-6′H), 7.03 (1H, d, *J* 7.8 Hz, Ar^4-4′H), 6.90 (2H, m, Ar^4-2′ and 5′H), 4.96 (1H, s, H-4), 4.01 (1H, t, *J* 8.1 Hz, H-9b), 3.77 (3H, s, OMe), 3.62 (1H, d, *J* 11.5 Hz, H-1), 3.50 (1H, t, *J* 8.5 Hz, H-3), 2.85 (1H, d, *J* 11.5 Hz, H-3), 2.70 (1H, t, *J* 8.6 Hz, H-1), 2.40 (3H, s, NMe); ^{13}C NMR (125 MHz, $CDCl_3$): 159.7 (q, Ar^4-1′C), 152.3 (q, C-5a), 135.0 (q), 129.6 (CH), 128.4 (CH, C-7), 127.9 (CH, C-9), 123.1 (CH, C-8), 122.6 (q, C-9a), 119.2 (CH), 117.7 (CH), 116.9 (CH, C-6), 112.5 (CH), 94.8 (q, C-3a), 79.1 (CH, C-4), 63.0 (CH_2), 62.1 (CH_2), 55.3 (OMe), 43.5 (CH, H-9b), 41.5 (NCH_3); IR (KBr, cm^{-1}): 2990, 2920, 2830, 1601, 1543, 1486, 1458, 1358, 1261, 1206, 1173, 1036.

3.1.1.5. 2-Benzyl-4-(3-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4e). White powder, mp 149 °C; [Found: C, 71.9; H, 6.0; N, 6.7. $C_{25}H_{24}N_2O_4$ requires C,

72.1; H, 5.8; N, 6.7%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.25 (8H, m, Ph-H and H-6, H-7, H-8), 7.03 (2H, m, H-9 and Ar^4-6′H), 6.88 (3H, m, Ar^4-2′, 4′ and 5′H), 5.02 (1H, s, H-4), 4.00 (1H, t, *J* 7.6 Hz, H-9b), 3.79 (1H, d, *J* 12.3 Hz, C*H*$_2$Ph), 3.78 (3H, s, OMe), 3.74 (1H, d, *J* 12.3 Hz, C*H*$_2$Ph), 3.62 (1H, t, *J* 8.1 Hz, H-3), 3.48 (1H, d, *J* 11.3 Hz, H-1), 2.98 (1H, d, *J* 11.3 Hz, H-3), 2.86 (1H, t, *J* 8.1 Hz, H-1); ^{13}C NMR (125 MHz, $CDCl_3$): 159.7 (q), 153.3 (q), 135.0 (q), 130.8 (q), 129.7 (2×CH), 129.6 (CH), 128.6 (2×CH), 127.5 (CH), 128.5 (CH), 127.9 (CH), 123.1 (CH), 122.6 (q), 119.2 (CH), 118.9 (CH), 116.9 (CH), 112.3 (CH), 88.7 (q), 80.0 (CH), 60.6 (CH_2), 59.3 (CH_2), 59.1 (CH_2), 55.3 (CH_3), 42.7 (CH); IR (KBr, cm^{-1}): 3020, 2961, 2810, 1600, 1543, 1486, 1457, 1358, 1261, 1206, 1173, 1137, 1035, 1016.

3.1.1.6. 2-Methyl-4-(4-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4f). White powder, mp 135–136 °C; [Found: C, 67.1; H, 5.9; N, 8.2. $C_{19}H_{20}N_2O_4$ requires C, 67.0; H, 5.9; N, 8.2%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.22 (2H, s, *J* 8.6 Hz, Ar^4-3′ and 5′H), 7.20 (1H, t, *J* 7.5 Hz, H-7), 7.14 (1H, d, *J* 7.5 Hz, H-9), 7.00 (1H, t, *J* 7.5 Hz, H-8), 6.97 (1H, d, *J* 7.5 Hz, H-6), 6.86 (2H, s, *J* 8.6 Hz, Ar^4-2′ and 6′H), 4.90 (1H, s, H-4), 3.95 (1H, t, *J* 8.3 Hz, H-9b), 3.75 (3H, s, *O*Me), 3.54 (1H, d, *J* 11.3 Hz, H-3), 3.43 (1H, t, *J* 8.3 Hz, H-1), 2.74 (1H, d, *J* 11.3 Hz, H-3), 2.63 (1H, t, *J* 8.5 Hz, H-1), 2.33 (3H, s, *N*Me); ^{13}C NMR (62.5 MHz, $CDCl_3$): 160.3 (q), 154.1 (q), 128.3 (CH), 128.1 (2×CH), 127.8 (CH), 125.9 (q), 122.6 (q), 122.5 (CH), 117.6 (CH), 114.0 (2×CH), 95.9 (q), 79.9 (CH), 62.9 (CH_2), 61.9 (CH_2), 55.2 (CH_3), 43.3 (CH), 41.4 (CH_3); IR (KBr, cm^{-1}): 2949, 2822, 1537, 1515, 1475, 1454, 1307, 1253, 1231, 1176, 1045, 1034.

3.1.1.7. 2-Benzyl-4-(4-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4g). White powder, mp 158 °C; [Found: C, 72.2; H, 5.7; N, 6.8. $C_{25}H_{24}N_2O_4$ requires C, 72.1; H, 5.8; N, 6.7%]; ^{1}H NMR (500 MHz, DMSO-d_6+MeOD): 7.31 (5H, m, Ar-H), 7.27 (2H, m, H-9 and H-7), 7.18 (2H, d, *J* 8.0 Hz, Ar^4-3′ and 5′H), 7.02 (1H, t, *J* 8.0 Hz, H-8), 6.96 (1H, d, *J* 8.0 Hz, H-6), 6.89 (2H, s, *J* 8.0 Hz, Ar^4-2′ and 6′H), 5.18 (1H, s, H-4), 3.85 (1H, t, *J* 8.5 Hz, H-9b), 3.79 (1H, d, *J* 13.4 Hz, C*H*$_2$Ph), 3.76 (1H, d, *J* 13.4 Hz, C*H*$_2$Ph), 3.74 (3H, s, *O*Me), 3.57 (1H, t, *J* 8.5 Hz, H-1), 3.43 (1H, d, *J* 11.0 Hz, H-3), 2.84 (1H, d, *J* 11.0 Hz, H-3), 2.70 (1H, t, *J* 8.5 Hz, H-1); ^{13}C NMR (125 MHz, DMSO-d_6+MeOD): 160.3 (q), 154.3 (q), 138.6 (q), 129.2 (CH), 128.8 (2×CH), 128.7 (2×CH), 128.5 (CH), 128.4 (2×CH), 128.0 (CH), 126.5 (q), 123.4 (q), 122.7 (CH), 117.4 (CH), 114.1 (2×CH), 95.9 (q), 79.2 (CH), 60.3 (CH_2), 58.9 (CH_2), 58.5 (CH_2), 55.3 (CH_3), 43.1 (CH); IR (KBr, cm^{-1}): 3030, 2964, 2940, 2802, 1613, 1584, 1534, 1515, 1488, 1452, 1370, 1255, 1238, 1179, 1054, 1046, 1026.

3.1.1.8. 4-(2-Chlorophenyl)-2-methyl-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4h). White powder, mp 143–144 °C; [Found: C, 62.7; H, 4.9; N, 8.1. $C_{18}H_{17}ClN_2O_3$ requires C, 62.7; H, 5.0; N, 8.1%]; ^{1}H NMR (500 MHz, DMSO-d_6): 7.59 (1H, d, *J* 7.8 Hz, Ar^4-3′H), 7.48 (1H, t, *J* 7.8 Hz, Ar^4-4′H), 7.42 (1H, t, *J* 7.8 Hz, Ar^4-5′H), 7.34 (1H, d, *J* 7.6 Hz, H-9), 7.26 (1H, d, *J* 7.8 Hz, Ar^4-6′H), 7.22 (1H, t, *J* 7.6 Hz, H-7), 7.10 (1H, t, *J* 7.6 Hz, H-8), 6.98 (1H, d, *J* 7.6 Hz, H-6), 5.61 (1H, s, H-4), 4.08 (1H, t, *J* 7.5 Hz, H-9b), 3.45 (1H, t, *J* 8.9 Hz, H-1), 3.31 (1H, d, *J* 10.9 Hz, H-3), 2.97 (1H, d, *J* 10.9 Hz, H-3), 2.80 (1H, t, *J* 8.9 Hz, H-1), 2.30 (3H, s, NMe); ^{13}C NMR (125 MHz, DMSO-d_6): 153.6 (q), 132.4 (q), 132.3 (q), 131.3 (CH), 129.9 (CH), 129.2 (CH), 128.7 (q), 128.4 (CH), 127.9 (CH), 127.85 (CH), 122.9 (CH), 117.1 (CH), 96.1 (q), 75.3 (CH), 62.3 (CH_2), 60.1 (CH_2), 42.8 (CH), 40.8 (CH_3); IR (KBr, cm^{-1}): 2943, 2843, 2828, 2793, 2765, 1585, 1532, 1489, 1479, 1455, 1363, 1301, 1280, 1268, 1256, 1237, 1161, 1134, 1114, 1093, 1061, 1048, 1038, 1025.

3.1.1.9. 4-(4-Chlorophenyl)-2-methyl-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4i). White powder, mp 150 °C; [Found: C, 62.4; H, 4.8; N, 8.3. $C_{18}H_{17}ClN_2O_3$ requires C, 62.7; H, 5.0; N, 8.1%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.35 (2H, d, *J* 8.5 Hz, Ar^4-2′ and 6′H), 7.27 (2H, d, *J* 8.5 Hz, Ar^4-3′ and 5′H), 7.17 (2H, m, H-7 and H-9), 7.05 (1H, t, *J* 7.5 Hz, H-8), 6.99 (1H, d, *J* 7.5 Hz, H-6), 4.97 (1H, s, H-4), 4.00 (1H, t, *J* 8.4 Hz, H-9b), 3.54 (1H, d, *J* 11.1 Hz, H-3), 3.43 (1H, t, *J* 8.4 Hz, H-1), 2.80 (1H, d, *J* 11.1 Hz, H-3), 2.70 (1H, t, *J* 8.4 Hz, H-1), 2.37 (3H, s, *N*Me); ^{13}C NMR (62.5 MHz, $CDCl_3$): 154.0 (q), 135.6 (q), 132.9 (q), 129.0 (2×CH), 128.6 (CH), 128.4 (2×CH), 128.1 (CH), 123.0 (CH), 122.9 (q), 117.8 (CH), 96.0 (q), 79.7 (CH), 63.1 (CH_2), 62.1 (CH_2), 43.4 (CH), 41.6 (CH_3); IR (KBr, cm^{-1}): 2948, 2843, 2793, 1534, 1490, 1456, 1366, 1254, 1227, 1152, 1090, 1060, 1014.

3.1.1.10. 2-Benzyl-4-(4-chlorophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4j). White powder, mp 155–157 °C; [Found: C, 68.8; H, 4.9; N, 6.6. $C_{24}H_{21}ClN_2O_3$ requires C, 68.5; H, 5.0; N, 6.7%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.37–7.23 (8H, m, Ph-H, Ar^4-2′ and 6′H and H-9), 7.21 (1H, t, *J* 7.5 Hz, H-7), 7.16 (2H, d, *J* 8.5 Hz, Ar^4-3′ and 5′H), 7.02 (1H, t, *J* 7.5 Hz, H-8), 7.00 (1H, d, *J* 7.5 Hz, H-6), 5.03 (1H, s, H-4), 3.97 (1H, t, *J* 8.4 Hz, H-9b), 3.71 (1H, d, *J* 12.9 Hz, CH_2Ph), 3.57 (1H, d, *J* 12.9 Hz, CH_2Ph), 3.46 (1H, t, *J* 8.4 Hz, H-1), 3.41 (1H, d, *J* 11.4 Hz, H-3), 2.87 (1H, d, *J* 11.4 Hz, H-3), 2.86 (1H, t, *J* 8.4 Hz, H-1); ^{13}C NMR (62.5 MHz, $CDCl_3$): 154.0 (q), 137.6 (q), 135.5 (q), 132.8 (q), 129.1 (CH), 128.9 (2×CH), 128.8 (2×CH), 128.7 (2×CH), 128.4 (2×CH), 128.1 (CH), 127.8 (CH), 123.1 (CH), 122.9 (q), 117.8 (CH), 94.9 (q), 79.6 (CH), 60.7 (CH_2), 59.2 (CH_2), 59.1 (CH_2), 42.6 (CH); IR (KBr, cm^{-1}): 3061, 3025, 2968, 2920, 2824, 1537, 1490, 1455, 1380, 1260, 1233, 1210, 1153, 1092, 1057, 1014.

3.1.1.11. 4-(4-Benzyloxyphenyl)-2-methyl-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4k). White powder, mp 139–140 °C; [Found: C, 72.1; H, 5.9; N, 6.6. $C_{25}H_{24}N_2O_4$ requires C, 72.1; H, 5.8; N, 6.7%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.42 (2H, d, *J* 7.2 Hz, Bn-2′ and 6′H), 7.38 (2H, t, *J* 7.2 Hz, Bn-3′ and 5′H), 7.32 (1H, t, *J* 7.2 Hz, Bn-4′H), 7.26 (2H, d, *J* 8.5 Hz, Ar^4-2′ and 6′H), 7.17 (2H, m, H-9 and H-7), 7.04 (1H, t, *J* 7.4 Hz, H-8), 7.01 (1H, d, *J* 7.4 Hz, H-6), 6.98 (2H, d, *J* 8.5 Hz, Ar^4-2′ and 6′H), 5.05 (2H, s, OCH_2), 4.94 (1H, s, H-4), 4.00 (1H, t, *J* 8.3 Hz, H-9b), 3.58 (1H, d, *J* 11.2 Hz, H-3), 3.47 (1H, t, *J* 8.7 Hz, H-1), 2.80 (1H, d, *J* 11.2 Hz, H-3), 2.69 (1H, t, *J* 8.7 Hz, H-1), 2.38 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 159.6 (q), 154.1 (q), 136.6 (q), 128.6 (2×CH), 128.4 (CH), 128.2 (2×CH), 128.0 (q), 127.8 (CH), 127.5 (2×CH), 126.3 (CH), 122.7 (q), 122.5 (CH), 117.6 (CH), 114.9 (2×CH),

95.9 (q), 79.9 (CH), 70.0 (CH_2), 63.0 (CH_2), 62.0 (CH_2), 43.4 (CH), 41.4 (CH_3); IR (KBr, cm^{-1}): 3026, 2937, 2910, 2796, 1614, 1588, 1533, 1514, 1457, 1423, 1395, 1372, 1331, 1233, 1178, 1117, 1095, 1056, 1040, 1027.

3.1.1.12. 2-Benzyl-4-(4-benzyloxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4l). White powder, mp 139–140 °C; [Found: C, 75.6; H, 5.9; N, 5.6. $C_{31}H_{28}N_2O_4$ requires C, 75.6; H, 5.7; N, 5.7%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.43–7.27 (10H, m, Ar-H), 7.17 (4H, m, Ar-H), 7.03 (1H, t, *J* 7.6 Hz, H-8), 7.00 (1H, d, *J* 7.4 Hz, H-6), 6.93 (2H, d, *J* 8.2 Hz, Ar^4-2′ and 6′H), 5.04 (2H, s, OCH_2), 5.00 (1H, s, H-4), 3.99 (1H, t, *J* 7.9 Hz, H-9b), 3.71 (1H, d, *J* 12.9 Hz, NCH_2), 3.62 (1H, d, *J* 12.9 Hz, NCH_2), 3.46 (2H, m, H-3 and H-1), 2.90 (1H, d, *J* 11.1 Hz, H-3), 2.84 (1H, t, *J* 7.7 Hz, H-1); ^{13}C NMR (125 MHz, $CDCl_3$): 159.6 (q), 154.2 (q), 137.5 (q), 137.1 (q), 136.7 (q), 128.65 (2×CH), 128.6 (2×CH), 128.5 (2×CH), 128.2 (2×CH), 128.0 (CH), 127.9 (CH), 127.51 (CH), 127.5 (2×CH), 126.2 (CH), 122.9 (q), 122.5 (CH), 117.6 (CH), 114.9 (2×CH), 94.9 (q), 79.8 (CH), 70.0 (CH_2), 60.6 (CH_2), 59.2 (CH_2), 59.1 (CH_2), 42.6 (CH); IR (KBr, cm^{-1}): 3050, 3020, 2930, 2800, 1612, 1539, 1513, 1490, 1455, 1235, 1177, 1027.

3.1.1.13. 4-(3,4-Dimethoxyphenyl)-2-methyl-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4m). White powder, mp 129–130 °C; [Found: C, 64.5; H, 5.9; N, 7.5. $C_{20}H_{22}N_2O_5$ requires C, 64.8; H, 6.0; N, 7.6%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.04 (1H, t, *J* 7.8 Hz, H-7), 7.02 (1H, d, *J* 7.8 Hz, H-9), 6.89 (1H, t, *J* 7.8 Hz, H-8), 6.87 (1H, d, *J* 7.8 Hz, H-6), 6.70 (3H, m, Ar^4-H), 4.77 (1H, s, H-4), 3.83 (1H, t, *J* 8.2 Hz, H-9b), 3.72 (3H, s, OMe), 3.71 (3H, s, OMe), 3.45 (1H, d, *J* 11.2 Hz, H-3), 3.32 (1H, t, *J* 8.2 Hz, H-1), 2.64 (1H, d, *J* 11.2 Hz, H-3), 2.52 (1H, t, *J* 8.2 Hz, H-1), 2.23 (3H, s, *N*Me); ^{13}C NMR (62.5 MHz, $CDCl_3$): 154.0 (q), 149.8 (q), 149.1 (q), 128.9 (CH), 128.3 (CH), 126.2 (q), 122.6 (q), 122.5 (CH), 119.7 (CH), 117.6 (CH), 110.6 (CH), 109.4 (CH), 95.8 (q), 80.1 (CH), 62.9 (CH_2), 61.9 (CH_2), 55.9 (CH_3), 55.7 (CH_3), 43.4 (CH), 41.4 (CH_3); IR (KBr, cm^{-1}): 2959, 2844, 2785, 1536, 1518, 1492, 1456, 1365, 1266, 1230, 1147, 1052, 1020.

3.1.1.14. 2-Benzyl-4-(3,4-dimethoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4n). White powder, mp 134 °C; [Found: C, 69.7; H, 5.9; N, 6.5. $C_{26}H_{26}N_2O_5$ requires C, 69.9; H, 5.9; N, 6.3%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.34 (5H, m, Bn-H), 7.23 (1H, t, *J* 7.6 Hz, H-7), 7.18 (1H, d, *J* 7.6 Hz, H-9), 7.06 (1H, t, *J* 7.6 Hz, H-8), 7.05 (1H, d, *J* 7.6 Hz, H-6), 6.82 (2H, m, Ar^4-5′H and 6′H), 6.76 (1H, s, Ar^4-2′H), 5.03 (1H, s, H-4), 4.00 (1H, t, *J* 8.0 Hz, H-9b), 3.88 (3H, s, *O*Me), 3.78 (3H, s, *O*Me), 3.78 (1H, d, *J* 12.8 Hz, CH_2Ph), 3.59 (1H, d, *J* 12.8 Hz, CH_2Ph), 3.49 (1H, t, *J* 8.0 Hz, H-1), 3.44 (1H, d, *J* 11.1 Hz, H-3), 2.98 (1H, d, *J* 11.1 Hz, H-3), 2.94 (1H, t, *J* 8.0 Hz, H-1); ^{13}C NMR (125 MHz, $CDCl_3$): 154.0 (q), 149.8 (q), 149.0 (q), 137.6 (q), 128.6 (2×CH), 128.5 (2×CH), 128.2 (CH), 127.8 (CH), 127.4 (CH), 126.3 (q), 122.9 (q), 122.5 (CH), 119.6 (CH), 117.6 (CH), 110.7 (CH), 109.7 (CH), 94.7 (q), 79.9 (CH), 60.8 (CH_2), 59.03 (CH_2), 59.01 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 42.4 (CH); IR (KBr, cm^{-1}): 2956, 2933, 2825, 1537, 1515, 1489, 1455, 1378, 1266, 1232, 1160, 1143, 1057, 1024.

3.1.1.15. 2-Methyl-4-(3,4-methylenedioxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4o). White powder, mp 122–124 °C; [Found: C, 64.7; H, 4.9; N, 7.9. $C_{19}H_{18}N_2O_5$ requires C, 64.4; H, 5.1; N, 7.9%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.20 (1H, t, *J* 7.5 Hz, H-7), 7.17 (1H, d, *J* 7.5 Hz, H-9), 7.05 (1H, t, *J* 7.5 Hz, H-8), 7.01 (1H, d, *J* 7.5 Hz, H-6), 6.82 (3H, m, Ar^4-H), 6.98 (2H, s, OCH_2O), 4.92 (1H, s, H-4), 4.00 (1H, t, *J* 8.2 Hz, H-9b), 3.60 (1H, d, *J* 11.4 Hz, H-3), 3.47 (1H, t, *J* 8.2 Hz, H-1), 2.82 (1H, d, *J* 11.4 Hz, H-3), 2.70 (1H, t, *J* 8.2 Hz, H-1), 2.39 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 154.0 (q), 148.5 (q), 148.0 (q), 128.4 (CH), 127.9 (CH), 127.7 (q), 122.7 (q), 122.6 (CH), 120.8 (CH), 117.6 (CH), 108.3 (CH), 107.1 (CH), 101.3 (CH_2), 95.9 (q), 80.1 (CH), 63.0 (CH_2), 62.1 (CH_2), 43.4 (CH), 41.4 (CH_3); IR (KBr, cm^{-1}): 2984, 2943, 2898, 2843, 2776, 1588, 1542, 1505, 1491, 1445, 1336, 1295, 1263, 1251, 1231, 1180, 1166, 1103, 1086, 1060, 1041.

3.1.1.16. 2-Methyl-4-(3-nitrophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4p). White powder, mp 152–153 °C; [Found: C, 60.7; H, 4.8; N, 11.9. $C_{18}H_{17}N_3O_5$ requires C, 60.8; H, 4.8; N, 11.8%]; ^{1}H NMR (250 MHz, $CDCl_3$+DMSO-d_6): 8.03 (1H, d, *J* 7.6 Hz, Ar^4-4′H), 8.01 (1H, s, Ar^4-2′H), 7.52 (1H, d, *J* 7.6 Hz, Ar^4-6′H), 7.40 (1H, t, *J* 7.6 Hz, Ar^4-5′H), 7.01 (1H, d, *J* 8.0 Hz, H-9), 6.99 (1H, t, *J* 8.0 Hz, H-7), 6.86 (1H, t, *J* 8.0 Hz, H-8), 6.78 (1H, d, *J* 8.0 Hz, H-6), 5.01 (1H, s, H-4), 3.82 (1H, t, *J* 8.3 Hz, H-9b), 3.34 (1H, d, *J* 11.2 Hz, H-3), 3.30 (1H, t, *J* 8.3 Hz, H-1), 2.68 (1H, d, *J* 11.2 Hz, H-3), 2.52 (1H, t, *J* 8.2 Hz, H-1), 2.20 (3H, s, *N*Me); ^{13}C NMR (62.5 MHz, $CDCl_3$+DMSO-d_6): 152.8 (q), 147.4 (q), 135.9 (q), 132.3 (CH), 129.0 (CH), 127.8 (CH), 127.3 (CH), 123.4 (CH), 122.3 (CH), 121.9 (q), 121.1 (CH), 116.7 (CH), 95.5 (q), 80.0 (CH), 61.8 (CH_2), 60.9 (CH_2), 42.5 (CH), 40.5 (CH_3); IR (KBr, cm^{-1}): 3104, 3042, 2949, 2840, 2793, 1527, 1485, 1455, 1353, 1224, 1168, 1092, 1053.

3.1.1.17. 2-Benzyl-4-(3-nitrophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine (4q). White powder, mp 155 °C; [Found: C, 66.7; H, 4.8; N, 9.9. $C_{24}H_{21}N_3O_5$ requires C, 66.8; H, 4.9; N, 9.7%]; ^{1}H NMR (250 MHz, $CDCl_3$): 8.19 (1H, d, *J* 8.0 Hz, Ar^4-4′H), 8.11 (1H, s, Ar^4-2′H), 7.57 (1H, d, *J* 8.0 Hz, Ar^4-6′H), 7.48 (1H, t, *J* 8.0 Hz, Ar^4-5′H), 7.34 (5H, m, Bn-H), 7.20 (1H, t, *J* 8.1 Hz, H-7), 7.17 (1H, d, *J* 8.1 Hz, H-9), 7.06 (1H, t, *J* 8.1 Hz, H-8), 7.02 (1H, d, *J* 8.1 Hz, H-6), 5.18 (1H, s, H-4), 4.03 (1H, t, *J* 8.5 Hz, H-9b), 3.78 (1H, d, *J* 12.9 Hz, CH_2Ph), 3.58 (1H, d, *J* 12.9 Hz, CH_2Ph), 3.49 (1H, t, *J* 8.5 Hz, H-1), 3.38 (1H, d, *J* 11.1 Hz, H-3), 2.95 (1H, d, *J* 11.1 Hz, H-3), 2.93 (1H, t, *J* 8.5 Hz, H-1); ^{13}C NMR (62.5 MHz, $CDCl_3$): 153.6 (q), 148.2 (q), 137.4 (q), 136.6 (q), 133.0 (CH), 129.8 (CH), 128.9 (CH), 128.8 (CH), 128.7 (2×CH), 128.2 (CH), 127.9 (CH), 125.8 (CH), 124.4 (CH), 123.2 (CH), 122.9 (q), 122.3 (CH), 117.7 (CH), 94.9 (q), 79.1 (CH), 60.6 (CH_2), 59.05 (CH_2), 59.0 (CH_2), 42.4 (CH); IR (KBr, cm^{-1}): 2802, 1536, 1489, 1455, 1356, 1265, 1234, 1212, 1144, 1091, 1054.

3.1.2. Synthesis of 3-(4-chlorophenyl)-3a-nitro-4-aryl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylates (6). General procedure. The appropriate 3-nitro-2*H*-chromene (**3**) (1 mmol) was dissolved in dry toluene (15 ml), and ethyl (4-chlorobenzylideneamino)acetate (**5a**) (0.25 g,

1.1 mmol) or ethyl 2-[1-(4-chlorophenyl)methylideneamino]-3-phenylpropanoate (**5b**) (0.35 g, 1.1 mmol) or diethyl 2-[1-(4-chlorophenyl)methylideneamino]malonate (**5c**) (0.33 g, 1.1 mmol), silver acetate (0.25 g, 1.5 mmol) and triethylamine (0.11 g, 0.16 ml, 1.1 mmol) were added. The reaction mixture was stirred at room temperature for 12 h. After the completion of the reaction (judged by TLC) saturated NH_4Cl solution (15 ml) was added to the reaction mixture and this was washed with water (2×10 ml) and brine (10 ml). The combined organic fractions were dried over magnesium sulfate, evaporated and the residue was trituated with ether. The crystallized product was collected to yield white powder, which could be recrystallized from ethanol. The yields (based on the dipolarophiles) are summarized in Table 2.

3.1.2.1. Ethyl 3-(4-chlorophenyl)-3a-nitro-4-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6a). White powder, mp 137–138 °C; [Found: C, 65.4; H, 4.8; N, 5.9. $C_{26}H_{23}N_2O_5Cl$ requires C, 65.2; H, 4.8; N, 5.8%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.51 (1H, d, *J* 7.6 Hz, H-9), 7.35 (2H, d, *J* 8.7 Hz, Ar^3-3′ and 5′H), 7.27 (2H, d, *J* 8.7 Hz, Ar^3-2′ and 6′H), 7.12 (7H, m, Ar-H), 6.77 (1H, d, *J* 7.5 Hz, H-6), 5.48 (1H, s, H-4), 4.88 (1H, br m, H-3), 4.74 (1H, d, *J* 3.6 Hz, H-9b), 4.43 (2H, q, *J* 7.1 Hz, OCH_2), 4.05 (1H, br s, H-1), 2.99 (1H, br s, H-2), 1.41 (3H, t, *J* 7.1 Hz, CH_2CH_3); ^{13}C NMR (62.5 MHz, $CDCl_3$): 171.8 (q), 149.7 (q), 135.4 (q), 134.7 (q), 129.1 (2×CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.5 (2×CH), 128.4 (q), 128.3 (2×CH), 128.2 (2×CH), 124.8 (CH), 123.2 (CH), 118.2 (CH), 96.4 (q), 75.5 (CH), 69.4 (CH), 68.3 (CH), 62.2 (CH_2), 45.6 (CH), 14.3 (CH_3); IR (KBr, cm^{-1}): 3334, 2979, 1733, 1586, 1540, 1487, 1453, 1368, 1298, 1228, 1212, 1114, 1094, 1015.

3.1.2.2. Methyl 1-benzyl-3-(4-chlorophenyl)-3a-nitro-4-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6b). White powder, mp 162–163 °C; [Found: C, 69.4; H, 4.8; N, 4.9. $C_{32}H_{27}N_2O_5Cl$ requires C, 69.2; H, 4.9; N, 5.0%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.84 (1H, d, *J* 7.5 Hz, H-9), 7.40 (2H, d, *J* 8.5 Hz, Ar^3-3′ and 5′H), 7.35 (2H, d, *J* 8.5 Hz, Ar^3-2′ and 6′H), 7.23 (9H, m, Ar-H), 7.13 (1H, t, *J* 7.5 Hz, H-8), 7.05 (2H, m, Bn-H), 6.83 (1H, d, *J* 7.5 Hz, H-6), 5.67 (1H, s, H-4), 5.21 (1H, s, H-9b), 5.20 (1H, d, *J* 7.2 Hz, H-3), 3.84 (3H, s, *O*Me), 3.01 (1H, br d, *J* 7.2 Hz, H-2), 2.89 (1H, d, *J* 14.0 Hz, α-CH_2), 2.45 (1H, d, *J* 14.0 Hz, β-CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): 174.6 (q), 152.5 (q), 136.3 (q), 135.5 (q), 134.5 (q), 133.8 (q), 130.7 (CH), 130.7 (CH), 130.2 (2×CH), 129.3 (2×CH), 129.2 (q), 129.1 (CH), 128.6 (2×CH), 128.5 (4×CH), 128.3 (2×CH), 127.2 (CH), 123.1 (CH), 122.7 (q), 118.9 (CH), 98.8 (q), 78.0 (CH), 72.4 (q), 67.6 (CH), 52.8 (CH_3), 50.2 (CH), 42.5 (CH_2); IR (KBr, cm^{-1}): 3373, 3059, 3032, 2954, 1725, 1541, 1533, 1488, 1456, 1361, 1337, 1260, 1245, 1187, 1110, 1096, 1033, 1015.

3.1.2.3. Ethyl 3-(4-chlorophenyl)-4-(4-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6c). White powder, mp 145–146 °C; [Found: C, 63.4; H, 4.8; N, 5.5. $C_{27}H_{25}N_2O_6Cl$ requires C, 63.7; H, 4.9; N, 5.5%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.57 (d, 1H, *J* 7.5 Hz, H-9), 7.40 (2H, d, *J* 8.8 Hz, Ar^3-3′ and 5′H), 7.33 (2H, d, *J* 8.8 Hz, Ar^3-2′ and 6′H), 7.17 (1H, t, *J* 7.5 Hz, H-7), 7.09 (1H, t, *J* 7.5 Hz, H-8), 7.08 (2H, d, *J* 8.7 Hz, Ar^4-2′ and 6′H), 6.84 (d, 1H, *J* 7.5 Hz, H-6), 6.70 (2H, d, *J* 8.7 Hz, Ar^4-3′ and 5′H), 5.49 (1H, s, H-4), 4.94 (1H, d, *J* 7.4 Hz, H-3), 4.79 (1H, d, *J* 3.8 Hz, H-9b), 4.48 (2H, q, *J* 7.1 Hz, OCH_2), 4.12 (1H, br s, H-1), 3.69 (3H, s, *O*Me), 3.02 (1H, br s, H-2), 1.48 (3H, t, *J* 7.1 Hz, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 171.8 (q), 159.8 (q), 149.9 (q), 135.4 (q), 132.7 (q), 129.6 (2×CH), 129.1 (2×CH), 128.9 (CH), 128.7 (CH), 128.3 (2×CH), 126.9 (q), 124.9 (q), 123.2 (CH), 118.3 (CH), 113.8 (2×CH), 96.6 (q), 75.2 (CH), 69.4 (CH), 68.3 (CH), 62.1 (CH_2), 55.1 (CH_3), 45.6 (CH), 14.3 (CH_3); IR (KBr, cm^{-1}): 3331, 2936, 2837, 1733, 1612, 1586, 1539, 1515, 1489, 1457, 1300, 1253, 1212, 1185, 1111, 1036, 1015.

3.1.2.4. Methyl 1-benzyl-3-(4-chlorophenyl)-4-(4-methoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6d). White powder, mp 159–160 °C; [Found: C, 67.7; H, 4.8; N, 4.9. $C_{33}H_{29}N_2O_6Cl$ requires C, 67.7; H, 5.00; N, 4.8%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.90 (1H, d, *J* 8.0 Hz, H-9), 7.70 (2H, d, *J* 8.3 Hz, Ar^3-3′ and 5′H), 7.45 (2H, d, *J* 8.3 Hz, Ar^3-2′ and 6′H), 7.35 (8H, m, Ar-H), 7.18 (1H, t, *J* 8.0 Hz, H-8), 7.07 (2H, m, Bn-H), 6.77 (1H, d, *J* 7.5 Hz, H-6), 5.65 (1H, s, H-4), 5.22 (1H, s, H-9b), 5.21 (1H, d, *J* 7.0 Hz, H-3), 3.84 (3H, s, *O*Me), 3.70 (3H, s, *O*Me), 3.00 (1H, br d, *J* 7.0 Hz, H-2), 2.89 (1H, d, *J* 14.0 Hz, CH_2), 2.46 (1H, d, *J* 14.0 Hz, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): 174.4 (q), 159.6 (q), 152.7 (q), 137.3 (q), 136.1 (q), 133.6 (q), 130.5 (CH), 129.9 (2×CH), 129.7 (2×CH), 129.6 (2×CH), 129.1 (CH), 128.8 (2×CH), 128.4 (CH), 128.3 (2×CH), 126.6 (q), 122.9 (CH), 122.5 (q), 118.8 (CH), 113.6 (2×CH), 98.8 (q), 77.5 (CH), 72.1 (q), 67.4 (CH), 55.1 (CH_3), 52.3 (CH_3), 49.9 (CH), 42.3 (CH_2); IR (KBr, cm^{-1}): 3436, 2954, 1746, 1544, 1513, 1490, 1455, 1244, 1184, 1112, 1028, 1014.

3.1.2.5. Ethyl 3,4-bis-(4-chlorophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6e). White powder, mp 144 °C; [Found: C, 60.7; H, 4.6; N, 5.4. $C_{26}H_{22}N_2O_5Cl_2$ requires C, 60.8; H, 4.3; N, 5.5%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.54 (d, 1H, *J* 8.1 Hz, H-9), 7.38–7.22 (6H, m, Ar-H), 7.18–7.04 (4H, m, Ar-H), 6.82 (1H, d, *J* 8.1 Hz, H-6), 5.49 (1H, s, H-4), 4.91 (1H, s, H-3), 4.71 (1H, d, *J* 3.7 Hz, H-9b), 4.43 (2H, q, *J* 7.1 Hz, OCH_2), 4.12 (1H, d, *J* 3.7 Hz, H-1), 3.11 (1H, br s, H-2), 1.44 (3H, t, *J* 7.1 Hz, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 171.6 (q), 149.5 (q), 137.8 (q), 135.4 (q), 133.3 (q), 132.5 (q), 129.5 (2×CH), 129.1 (2×CH), 129.0 (CH), 128.7 (CH), 128.7 (2×CH), 128.2 (2×CH), 124.5 (q), 123.4 (CH), 118.2 (CH), 96.3 (q), 74.7 (CH), 69.3 (CH), 68.1 (CH), 62.1 (CH_2), 45.4 (CH), 14.2 (CH_3); IR (KBr, cm^{-1}): 2981, 2903, 1734, 1587, 1543, 1490, 1456, 1371, 1208, 1092, 1013.

3.1.2.6. Methyl 1-benzyl-3,4-bis-(4-chlorophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6f). White powder, mp 168–169 °C; [Found: C, 65.0; H, 4.6; N, 4.4. $C_{32}H_{26}N_2O_5Cl_2$ requires C, 65.2; H, 4.4; N, 4.7%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.76 (1H, dd, *J* 1.7 and 7.8 Hz, H-9), 7.35 (2H, d, *J* 8.6 Hz, Ar^3-3′ and 5′H), 7.27 (2H, d, *J* 8.6 Hz, Ar^3-2′ and 6′H), 7.15 (4H, m, Bn-H and H-7), 7.14 (2H, d, *J* 8.5 Hz, Ar^4-3′ and 5′H), 7.10 (1H, dt, *J* 1.7 and 7.8 Hz, H-8), 7.05 (2H, d, *J* 8.5 Hz, Ar^4-2′ and 6′H), 6.96 (2H, m, Bn-H), 6.76 (1H, dd, *J* 1.7 and 7.8 Hz, H-6), 5.55 (1H, s, H-4), 5.10 (1H, s, H-9b), 5.09

(1H, d, *J* 7.8 Hz, H-3), 3.78 (3H, s, *O*Me), 2.94 (1H, br d, *J* 7.8 Hz, H-2), 2.81 (1H, d, *J* 13.7 Hz, CH_2), 2.37 (1H, d, *J* 13.7 Hz, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): 174.4 (q), 152.1 (q), 136.0 (q), 135.4 (q), 134.9 (q), 133.3 (q), 132.9 (q), 130.6 (CH), 129.9 (2×CH), 129.6 (2×CH), 129.3 (CH), 129.2 (2×CH), 128.5 (2×CH), 128.3 (2×CH), 128.1 (2×CH), 127.0 (CH), 123.1 (CH), 122.2 (q), 118.7 (CH), 98.5 (q), 77.0 (CH), 72.2 (q), 67.4 (CH), 52.7 (CH_3), 49.8 (CH), 42.2 (CH_2); IR (KBr, cm^{-1}): 3341, 3031, 1751, 1601, 1542, 1491, 1456, 1436, 1239, 1208, 1130, 1111, 1096, 1079, 1042, 1014, 1006.

3.1.2.7. Methyl 1-benzyl-3-(4-chlorophenyl)-4-(2-chlorophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6g). White powder, mp 151–152 °C; [Found: C, 65.3; H, 4.2; N, 4.6. $C_{32}H_{26}N_2O_5Cl_2$ requires C, 65.2; H, 4.4; N, 4.7%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.75 (1H, d, *J* 7.6 Hz, H-9), 7.36 (5H, m, Bn-H), 7.17 (3H, m, Ar^3-3′ and 5′H, Ar^4-3′H), 7.11 (2H, m, H-7 and Ar^4-4′H), 7.08 (1H, t, *J* 7.6 Hz, H-8), 6.98 (2H, d, *J* 7.7 Hz, Ar^3-2′ and 6′H), 6.89 (1H, t, *J* 7.6 Hz, Ar^4-5′H), 6.78 (1H, d, *J* 7.6 Hz, H-6), 6.75 (1H, d, *J* 7.6 Hz, Ar^4-6′H), 6.18 (1H, s, H-4), 5.21 (1H, d, *J* 8.5 Hz, H-3), 5.13 (1H, s, H-9b), 3.82 (3H, s, *O*Me), 3.01 (1H, d, *J* 8.5 Hz, H-2), 2.75 (1H, d, *J* 13.6 Hz, CH_2), 2.40 (1H, d, *J* 13.6 Hz, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): 174.2 (q), 152.0 (q), 136.1 (q), 135.5 (q), 135.3 (q), 131.8 (q), 130.3 (CH), 130.2 (CH), 130.0 (CH), 127.0 (q), 129.9 (2×CH), 129.3 (CH), 129.2 (2×CH), 128.25 (2×CH), 128.2 (CH), 128.1 (2×CH), 128.0 (CH), 126.1 (CH), 123.3 (CH), 123.0 (q), 118.7 (CH), 99.1 (q), 73.8 (CH), 72.6 (q), 68.0 (CH), 52.7 (CH_3), 50.5 (CH), 41.6 (CH_2); IR (KBr, cm^{-1}): 3364, 3021, 1723, 1542, 1535, 1489, 1472, 1439, 1261, 1209, 1186, 1112, 1094, 1052, 1034, 1014.

3.1.2.8. Ethyl 3-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6h). White powder, mp 137–139 °C; [Found: C, 62.5; H, 4.9; N, 5.4. $C_{28}H_{27}N_2O_7Cl$ requires C, 62.4; H, 5.0; N, 5.2%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.54 (1H, d, *J* 7.5 Hz, H-9), 7.38 (2H, d, *J* 8.4 Hz, Ar^3-3′ and 5′H), 7.31 (2H, d, *J* 8.4 Hz, Ar^3-2′ and 6′H), 7.16 (1H, t, *J* 7.5 Hz, H-7), 7.07 (1H, t, *J* 7.5 Hz, H-8), 6.83 (1H, d, *J* 8.1 Hz, H-6), 6.70 (1H, s, Ar^4-2′H), 6.61 (2H, m, Ar^4-5′ and 6′H), 5.46 (1H, s, H-4), 4.92 (1H, s, H-3), 4.76 (1H, d, *J* 3.6 Hz, H-9b), 4.45 (2H, q, *J* 7.1 Hz, OCH_2), 4.09 (1H, d, *J* 3.7 Hz, H-1), 3.73 (3H, s, OMe), 3.70 (3H, s, OMe), 3.00 (1H, br s, H-2), 1.45 (3H, t, *J* 7.1 Hz, CH_2CH_3); ^{13}C NMR (62.5 MHz, $CDCl_3$): 172.0 (q), 150.1 (q), 149.6 (q), 148.9 (q), 135.5 (q), 132.9 (q), 129.3 (2×CH), 129.1 (CH), 128.8 (CH), 128.5 (2×CH), 127.3 (q), 125.2 (q), 123.4 (CH), 120.3 (CH), 118.5 (CH), 112.3 (CH), 110.7 (CH), 96.8 (q), 75.5 (CH), 69.5 (CH), 68.3 (CH), 62.3 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 45.7 (CH), 14.5 (CH_3); IR (KBr, cm^{-1}): 3336, 2981, 2935, 2836, 1737, 1589, 1543, 1519, 1490, 1453, 1366, 1261, 1245, 1210, 1146, 1092, 1020.

3.1.2.9. Methyl 1-benzyl-3-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6i). White powder, mp 143–144 °C; [Found: C, 66.5; H, 4.9; N, 4.3. $C_{34}H_{31}N_2O_7Cl$ requires C, 66.4; H, 5.1; N, 4.5%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.77 (1H, d, *J* 8.0 Hz, H-9), 7.35 (2H, d, *J* 8.5 Hz, Ar^3-3′ and 5′H), 7.30 (2H, d, *J* 8.5 Hz, Ar^3-2′ and 6′H), 7.26 (4H, m, H-7 and Bn-H), 7.19 (1H, t, *J* 7.5 Hz, H-8), 7.06 (2H, m, Bn-H), 6.87 (1H, d, *J* 7.5 Hz, H-6), 6.75 (1H, s, Ar^4-2′H), 6.67 (2H, m, Ar^4-5′ and 6′H), 5.62 (1H, s, H-4), 5.23 (1H, s, H-9b), 5.23 (1H, d, *J* 7.0 Hz, H-3), 3.88 (3H, s, *O*Me), 3.83 (3H, s, *O*Me), 3.82 (3H, s, *O*Me), 3.00 (1H, br d, *J* 7.0 Hz, H-2), 2.92 (1H, d, *J* 13.5 Hz, CH_2), 2.47 (1H, d, *J* 13.5 Hz, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): 174.5 (q), 152.3 (q), 149.3 (q), 148.6 (q), 136.1 (q), 135.3 (q), 133.5 (q), 130.4 (CH), 129.9 (2×CH), 129.2 (CH), 129.1 (2×CH), 128.4 (2×CH), 128.1 (2×CH), 127.0 (CH), 126.6 (q), 122.9 (CH), 122.7 (q), 120.7 (CH), 118.9 (CH), 111.8 (CH), 110.3 (CH), 98.9 (q), 77.7 (CH), 72.3 (q), 67.4 (CH), 55.8 (CH_3), 55.6 (CH_3), 52.7 (CH_3), 49.9 (CH), 42.1 (CH_2); IR (KBr, cm^{-1}): 3337, 2986, 2950, 1747, 1545, 1515, 1490, 1454, 1261, 1240, 1209, 1113, 1030, 1010.

3.1.2.10. Methyl 1-benzyl-3-(4-chlorophenyl)-4-(3-nitrophenyl)-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (6j). White powder, mp 165 °C; [Found: C, 64.1; H, 4.2; N, 6.9. $C_{32}H_{26}N_3O_7Cl$ requires C, 64.1; H, 4.4; N, 7.0%]; ^{1}H NMR (250 MHz, DMSO-d_6): 8.29 (1H, s, Ar^3-2′H), 8.11 (1H, d, *J* 8.1 Hz, Ar^3-4′H), 7.81 (1H, d, *J* 7.0 Hz, H-9), 7.59 (1H, d, *J* 8.1 Hz, Ar^4-6′H), 7.51–7.38 (5H, m, Ar-H), 7.28–7.11 (5H, m, Ar-H), 7.03 (2H, m, Bn-H), 6.82 (1H, d, *J* 7.5 Hz, H-6), 5.97 (1H, s, H-4), 5.27 (1H, d, *J* 9.0 Hz, H-3), 5.28 (1H, s, H-9b), 3.82 (3H, s, *O*Me), 3.26 (1H, br d, *J* 9.0 Hz, H-2), 2.65 (1H, d, *J* 13.5 Hz, CH_2), 2.52 (1H, d, *J* 13.5 Hz, CH_2); ^{13}C NMR (62.5 MHz, DMSO-d_6): 173.6 (q), 151.8 (q), 148.1 (q), 136.8 (q), 136.1 (q), 134.1 (q), 134.0 (CH), 133.7 (q), 130.5 (CH), 130.1 (2×CH), 129.6 (CH), 129.3 (CH), 129.1 (CH), 129.0 (2×CH), 128.7 (2×CH), 127.7 (2×CH), 126.6 (CH), 123.7 (CH), 123.0 (CH), 122.4 (q), 118.0 (CH), 98.9 (q), 76.0 (CH), 71.9 (q), 66.7 (CH), 52.7 (CH_3), 50.4 (CH), 41.0 (CH_2); IR (KBr, cm^{-1}): 3370, 3097, 2952, 1730, 1585, 1534, 1488, 1456, 1356, 1288, 1241, 1208, 1187, 1112, 1094, 1040, 1013.

3.1.2.11. Diethyl 3-(4-chlorophenyl)-4-phenyl-3a-nitro-benzopyrano[3,4-*c*]-pyrrolidine-1,1-dicarboxylate (6k). White powder, mp 126–127 °C; [Found: C, 63.1; H, 5.0; N, 5.9. $C_{29}H_{27}N_2O_7Cl$ requires C, 63.2; H, 4.9; N, 5.1%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.54 (1H, d, *J* 7.5 Hz, H-9), 7.27 (4H, s, Ar^3-H), 7.18 (5H, m, Ar^4-H), 7.05 (1H, t, *J* 7.5 Hz, H-7), 6.93 (1H, t, *J* 7.5 Hz, H-8), 6.72 (1H, d, *J* 7.5 Hz, H-6), 5.71 (1H, s, H-9b), 5.57 (1H, s, H-4), 5.54–5.57 (1H, s, H-3), 4.45 (1H, m, OCH_2), 4.37 (1H, m, OCH_2), 3.74 (1H, m, OCH_2), 3.60 (1H, m, OCH_2), 3.30 (1H, br s, H-2), 1.35 (3H, t, *J* 7.1 Hz, CH_2CH_3), 0.89 (3H, t, *J* 7.1 Hz, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 170.5 (q), 169.4 (q), 151.9 (q), 134.9 (q), 134.8 (q), 134.1 (q), 130.0 (CH), 129.0 (CH), 128.7 (2×CH), 128.6 (2×CH), 128.2 (2×CH), 128.1 (2×CH), 128.05 (CH), 122.1 (CH), 121.1 (q), 118.0 (CH), 96.7 (q), 77.3 (CH), 76.3 (q), 67.8 (CH), 62.5 (CH_2), 62.0 (CH_2), 47.1 (CH), 13.9 (CH_3), 13.3 (CH_2); IR (KBr, cm^{-1}): 3340, 3067, 3037, 2985, 2899, 1739, 1586, 1546, 1490, 1456, 1367, 1271, 1255, 1215, 1174, 1143, 1120, 1092, 1038, 1016.

3.1.3. Synthesis of methyl 4-aryl-3-phenyl-3a-nitro-2-methyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylates (7). General procedure. Methyl sarcosinate hydrochloride

(0.23 g, 2 mmol), the corresponding 3-nitrochromene (**3**) (1 mmol), benzaldehyde (0.15 g, 1.4 mmol) and triethylamine (0.20 g, 0.29 ml, 2 mmol) were heated under reflux in toluene (20 ml). The water formed was continuously removed by the aid of a Dean–Stark trap. After the completion of reaction, the mixture was poured into saturated NH_4Cl solution (20 ml) and was extracted with ethyl acetate (2×15 ml). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated in vacuo. The residue was recrystallized from ethanol to yield the title products. The reaction yields (based on the dipolarophiles) are summarized in Table 5.

3.1.3.1. Methyl 3,4-diphenyl-3a-nitro-2-methyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (7a). White powder, mp 112–113 °C; [Found: C, 70.2; H, 5.4; N, 6.1. $C_{26}H_{24}N_2O_5$ requires C, 70.3; H, 5.4; N, 6.3%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.45 (5H, m, Ph^3-H), 7.09 (1H, m, Ph^4-4′H), 7.08 (1H, dd, *J* 1.5 and 7.5 Hz, H-9), 7.05 (1H, dt, *J* 1.5 and 7.5 Hz, H-7), 7.02 (2H, t, *J* 8.7 Hz, Ph^4-3′ and 5′H), 6.90 (1H, dt, *J* 1.5 and 7.5 Hz, H-8), 6.85 (2H, d, *J* 8.7 Hz, Ph^4-2′ and 6′H), 6.66 (1H, dd, *J* 1.5 and 7.5 Hz, H-6), 5.16 (1H, s, H-4), 5.02 (1H, d, *J* 6.5 Hz, H-9b), 3.88 (1H, d, *J* 6.5 Hz, H-1), 3.85 (1H, s, H-3), 3.69 (3H, s, *O*Me), 2.18 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 169.4 (q), 151.9 (q), 134.9 (q), 134.4 (q), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.2 (4×CH), 128.15 (4×CH), 127.7 (CH), 122.5 (q), 121.9 (CH), 118.7 (CH), 95.6 (q), 81.8 (CH), 76.8 (CH), 73.3 (CH), 51.8 (CH_3), 43.1 (CH), 39.9 (CH_3); IR (KBr, cm^{-1}): 2848, 2807, 1761, 1588, 1543, 1490, 1454, 1386, 1280, 1240, 1211, 1197, 1132, 1116, 1084, 1072.

3.1.3.2. Methyl 4-(2-methoxyphenyl)-3a-nitro-2-methyl-3-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (7b). White powder, mp 118–119 °C; [Found: C, 68.2; H, 5.4; N, 6.0. $C_{27}H_{26}N_2O_6$ requires C, 68.3; H, 5.5; N, 5.9%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.33 (2H, br s, Ph^3-3′ and 5′H), 7.14 (1H, t, *J* 7.5 Hz, H-7), 7.00–7.10 (4H, m, H-8, H-9, Ar^4-H, Ph^3-4′H), 6.88 (1H, d, *J* 7.5 Hz, H-6), 6.84 (1H, d, *J* 7.9 Hz, Ar^4-H), 6.78 (1H, t, *J* 7.9 Hz, Ar^4-H), 6.67 (2H, d, *J* 7.9 Hz, Ph^3-2′ and 6′H), 6.53 (1H, t, *J* 7.9 Hz, Ar^4-H), 5.67 (1H, s, H-4), 5.06 (1H, d, *J* 6.7 Hz, H-9b), 3.91 (1H, d, *J* 6.5 Hz, H-1), 3.84 (1H, s, H-3), 3.69 (3H, s, *O*Me), 3.61 (3H, s, *O*Me), 2.19 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 170.2 (q, C═O), 158.4 (q), 153.1 (q), 135.3 (q), 131.0 (q), 130.8 (CH), 129.9 (CH), 129.6 (2×CH), 129.2 (CH), 128.4 (2×CH), 128.3 (CH), 124.3 (CH), 122.6 (CH), 121.2 (q), 120.6 (CH), 119.6 (CH), 112.0 (CH), 96.2 (q), 83.2 (CH), 75.5 (CH), 74.5 (CH), 56.5 (CH_3), 52.5 (CH_3), 44.5 (CH), 40.7 (CH_3); IR (KBr, cm^{-1}): 2964, 2840, 1763, 1723, 1588, 1545, 1492, 1457, 1295, 1252, 1225, 1213, 1173, 1107, 1073, 1030.

3.1.3.3. Methyl 4-(2-chlorophenyl)-3a-nitro-2-methyl-3-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (7c). White powder, mp 111–112 °C; [Found: C, 65.2; H, 5.0; N, 6.0. $C_{26}H_{23}ClN_2O_5$ requires C, 65.2; H, 4.8; N, 5.8%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.49 (4H, m, Ph), 7.25 (2H, m, Ph and Ar^4-6′H), 7.11 (1H, d, *J* 7.8 Hz, H-9), 7.04 (1H, t, *J* 7.8 Hz, H-7), 7.03 (1H, d, *J* 7.7 Hz, Ar^4-4′H), 6.92 (1H, t, *J* 7.8 Hz, H-8), 6.83 (1H, t, *J* 7.7 Hz, Ar^4-5′H), 6.71 (2H, m, H-6 and Ar^4-3′H), 5.83 (1H, s, H-4), 5.06 (1H, d, *J* 6.9 Hz, H-9b), 3.96 (1H, d, *J* 6.9 Hz, H-1), 3.87 (1H, s, H-3), 3.69 (3H, s, *O*Me), 2.23 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 169.2 (q), 151.9 (q), 135.6 (q), 134.0 (q), 132.5 (q), 130.2 (CH), 129.8 (CH), 129.4 (CH), 129.2 (CH), 128.3 (CH), 127.7 (CH), 127.2 (2×CH), 126.1 (2×CH), 122.8 (q), 122.1 (CH), 118.9 (CH), 94.9 (q), 82.4 (CH), 73.8 (CH), 72.2 (CH), 51.8 (CH_3), 43.7 (CH), 39.9 (CH_3); IR (KBr, cm^{-1}): 3335, 2977, 2905, 1727, 1542, 1507, 1489, 1456, 1359, 1300, 1275, 1232, 1215, 1130, 1114, 1097, 1052, 1016.

3.1.3.4. Methyl 4-(4-chlorophenyl)-3a-nitro-2-methyl-3-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (7d). White powder, mp 131–132 °C; [Found: C, 65.1; H, 5.1; N, 5.9. $C_{26}H_{23}ClN_2O_5$ requires C, 65.2; H, 4.8; N, 5.8%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.48 (2H, d, *J* 8.1 Hz, Ar^4-H), 7.41 (2H, d, *J* 8.1 Hz, Ar^4-H), 7.44 (1H, d, *J* 7.6 Hz, H-9), 7.25 (3H, m, Ph^3-C), 7.17 (1H, t, *J* 7.6 Hz, H-7), 7.05 (2H, m, Ph^3-C), 7.03 (1H, t, *J* 7.6 Hz, H-8), 6.91 (1H, d, *J* 7.6 Hz, H-6), 5.85 (1H, s, H-4), 5.14 (1H, d, *J* 9.8 Hz, H-9b), 4.87 (1H, s, H-3), 4.76 (1H, d, *J* 6.5 Hz, H-1), 3.44 (3H, s, *O*Me), 2.31 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 171.9 (q), 154.5 (q), 135.7 (q), 134.9 (q), 133.9 (q), 129.9 (2×CH), 129.5 (CH), 128.7 (CH), 128.6 (CH), 128.5 (3×CH), 128.3 (q), 128.0 (2×CH), 122.0 (CH), 119.1 (CH), 117.4 (CH), 97.8 (q), 78.6 (CH), 71.9 (CH), 69.7 (CH), 51.5 (CH_3), 44.3 (CH), 35.6 (CH_3); IR (KBr, cm^{-1}): 2950, 2811, 1739, 1588, 1541, 1491, 1457, 1438, 1372, 1261, 1233, 1219, 1179, 1089, 1014.

3.1.3.5. Methyl 4-(3,4-dimethoxyphenyl)-3a-nitro-2-methyl-3-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (7e). White powder, mp 125–126 °C; [Found: C, 66.6; H, 5.6; N, 5.5. $C_{28}H_{28}N_2O_7$ requires C, 66.7; H, 5.6; N, 5.5%]; ^{1}H NMR (300 MHz, $CDCl_3$): 7.29 (1H, d, *J* 7.5 Hz, H-9), 7.24 (3H, m, Ph-H and H-9), 7.15 (1H, t, *J* 7.5 Hz, H-7), 7.04 (3H, m, Ph-H), 7.00 (1H, d, *J* 7.5 Hz, H-6), 6.95 (1H, s, Ar^4-2′H), 6.89 (1H, d, *J* 8.1 Hz, Ar^4-5′H), 6.87 (1H, d, *J* 8.1 Hz, Ar^4-6′H), 5.77 (1H, s, H-4), 5.10 (1H, d, *J* 9.9 Hz, H-9b), 4.90 (1H, s, H-3), 4.72 (1H, d, *J* 9.6 Hz, H-1), 3.91 (3H, s, *O*Me), 3.86 (3H, s, *O*Me), 3.40 (3H, s, *O*Me), 2.27 (3H, s, *N*Me); ^{13}C NMR (125 MHz, $CDCl_3$): 171.9 (q), 154.6 (q), 149.6 (q), 148.5 (q), 135.9 (q), 129.5 (CH), 128.6 (CH), 128.5 (4×CH), 128.4 (q), 127.5 (CH), 121.8 (q), 121.3 (CH), 119.6 (CH), 117.6 (CH), 111.7 (CH), 110.0 (CH), 97.8 (q), 79.2 (CH), 76.6 (CH), 72.1 (CH), 56.0 (CH_3), 55.9 (CH_3), 51.5 (CH_3), 44.5 (CH), 35.6 (CH_3); IR (KBr, cm^{-1}): 2952, 2838, 1735, 1588, 1545, 1519, 1491, 1465, 1261, 1236, 1209, 1145, 1027.

3.1.3.6. Methyl 4-(3,4-methylenedioxyphenyl)-3a-nitro-2-methyl-3-phenyl-benzopyrano[3,4-*c*]-pyrrolidine-1-carboxylate (7f). White powder, mp 119–120 °C; [Found: C, 66.5; H, 5.1; N, 5.6. $C_{27}H_{24}N_2O_7$ requires C, 66.4; H, 4.9; N, 5.7%]; ^{1}H NMR (500 MHz, DMSO-d_6): 7.42 (1H, d, *J* 7.5 Hz, H-9), 7.31 (3H, m, Ph-H and H-9), 7.18 (3H, m, Ph-H), 7.05 (1H, t, *J* 7.5 Hz, H-7), 7.00 (1H, d, *J* 8.2 Hz, Ar^4-5′H), 6.93 (1H, d, *J* 7.5 Hz, H-6), 6.89 (1H, d, *J* 8.2 Hz, Ar^4-6′H), 6.79 (1H, s, Ar^4-2′H), 6.09 (1H, s, OCH_2O), 6.07 (1H, s, OCH_2O), 5.86 (1H, s, H-4), 5.21 (1H, d, *J* 10.2 Hz, H-9b), 4.75 (1H, s, H-3), 4.73 (1H, d, *J* 10.2 Hz, H-1), 3.31 (3H, s, *O*Me), 2.14 (3H, s, *N*Me); ^{13}C NMR (125 MHz, DMSO-d_6): 171.8 (q), 153.7 (q), 148.0 (q), 147.2 (q), 135.5 (q), 130.1 (CH), 128.65

(5×CH), 128.6 (CH), 128.5 (q), 122.1 (q), 121.8 (CH), 119.9 (CH), 116.8 (CH), 107.95 (CH), 107.9 (CH), 101.5 (CH_2), 96.7 (q), 78.2 (CH), 71.6 (CH), 69.4 (CH), 51.6 (CH_3), 43.2 (CH), 35.6 (CH_3); IR (KBr, cm^{-1}): 2949, 2867, 2808, 1733, 1544, 1506, 1491, 1457, 1443, 1391, 1368, 1334, 1305, 1250, 1240, 1211, 1173, 1112, 1096, 1040.

3.1.4. Synthesis of methyl 8,9-dimethoxy-6a-nitro-6-aryl-6a,6b,11,12,14,14a-hexahydro-6*H*-chromeno[3′,4′:3,4]-pyrrolidino[2,1-*a*]isoquinoline-14-carboxylates (9). General procedure. The corresponding 3-nitrochromene (**3**) (0.8 mmol) and 6,7-dimethoxy-(2-methoxycarbonylmethyl)-3,4-dihydroisoquinolinium bromide (**8**) (0.29 g, 0.85 mmol) were dissolved in dry methanol (10 ml) and triethylamine (0.14 ml, 0.10 g, 1 mmol) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo and the residue was suspended in ether (20 ml). The ethereal solution was washed with water (10 ml) and brine (5 ml), dried over $MgSO_4$ and evaporated in vacuo to yield a white solid, which was recrystallized from ethanol. The reaction yields (based on the dipolarophiles) are summarized in Table 7.

3.1.4.1. Methyl 8,9-dimethoxy-6a-nitro-6-phenyl-6a,6b,11,12,14,14a-hexahydro-6*H*-chromeno[3′,4′:3,4]-pyrrolidino[2,1-*a*]isoquinoline-14-carboxylate (9a). White powder, mp 152–153 °C; [Found: C, 67.5; H, 5.3; N, 5.3. $C_{29}H_{28}N_2O_7$ requires C, 67.4; H, 5.5; N, 5.4%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.22 (1H, t, *J* 7.5 Hz, H-3), 7.12 (1H, d, *J* 7.5 Hz, H-1), 7.06 (1H, d, *J* 7.5 Hz, H-4), 7.02 (1H, t, *J* 7.5 Hz, H-2), 6.95 (5H, m, Ph-H), 6.51 (1H, s, H-10), 6.05 (1H, s, H-7), 5.81 (1H, s, H-6), 4.88 (1H, s, H-6b), 4.18 (1H, d, *J* 11.2 Hz, H-14a), 4.12 (1H, d, *J* 11.2 Hz, H-14), 3.83 (3H, s, *O*Me), 3.37 (3H, s, *O*Me), 3.25 (3H, s, *O*Me), 3.20 (1H, m, H-11), 3.03 (1H, dd, *J* 6.6 and 10.8 Hz, H-12), 2.74 (1H, dd, *J* 3.2 and 11.1 Hz, H-12), 2.64 (1H, m, H-11); ^{13}C NMR (125 MHz, $CDCl_3$): 170.5 (q), 153.5 (q), 147.9 (q), 146.5 (q), 135.9 (q), 129.9 (CH), 129.5 (CH), 128.9 (2×CH), 128.4 (CH), 128.2 (q), 127.4 (q), 127.4 (2×CH), 123.2 (q), 120.7 (CH), 117.1 (CH), 110.8 (CH), 109.8 (CH), 90.4 (q), 76.4 (CH), 67.8 (CH), 65.9 (CH), 55.8 (CH_3), 54.8 (CH_3), 51.9 (CH_3), 47.4 (CH), 46.9 (CH_2), 29.7 (CH_2); IR (KBr, cm^{-1}): 3019, 2949, 2886, 2843, 1754, 1615, 1586, 1537, 1518, 1493, 1454, 1390, 1357, 1290, 1265, 1249, 1234, 1213, 1178, 1152, 1119, 1041, 1024.

3.1.4.2. Methyl 8,9-dimethoxy-6a-nitro-6-(4-methoxyphenyl)-6a,6b,11,12,14,14a-hexahydro-6*H*-chromeno[3′,4′:3,4]pyrrolidino[2,1-*a*]isoquinoline-14-carboxylate (9b). White powder, mp 159–160 °C; [Found: C, 65.9; H, 5.5; N, 5.1. $C_{30}H_{30}N_2O_8$ requires C, 65.9; H, 5.5; N, 5.1%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.18 (1H, t, *J* 7.5 Hz, H-3), 7.06 (1H, d, *J* 7.5 Hz, H-1), 6.93 (1H, d, *J* 7.5 Hz, H-4), 6.90 (1H, t, *J* 7.5 Hz, H-2), 6.85 (2H, d, *J* 8.2 Hz, Ar^6-2′ and 6′H), 6.51 (1H, s, H-10), 6.46 (2H, d, *J* 8.2 Hz, Ar^6-3′ and 5′H), 6.10 (1H, s, H-7), 5.77 (1H, s, H-6), 4.86 (1H, s, H-6b), 4.12 (1H, d, *J* 11.3 Hz, H-14a), 4.11 (1H, d, *J* 11.3 Hz, H-14), 3.83 (3H, s, *O*Me), 3.70 (3H, s, *O*Me), 3.36 (3H, s, *O*Me), 3.32 (3H, s, *O*Me), 3.18 (1H, m, H-11), 3.01 (1H, m, H-12), 2.70 (1H, m, H-12), 2.62 (1H, m, H-11); ^{13}C NMR (125 MHz, $CDCl_3$): 170.4 (q), 159.6 (q), 153.6 (q), 147.8 (q), 146.7 (q), 129.9 (2×CH), 129.4 (CH), 128.8 (CH), 128.0 (q), 127.5 (q), 127.4 (q), 123.4 (q), 120.5 (CH), 116.2 (CH), 113.2 (CH), 112.9 (2×CH), 109.8 (CH), 90.4 (q), 75.8 (CH), 67.7 (CH), 65.7 (CH), 55.8 (CH_3), 55.2 (CH_3), 54.6 (CH_3), 51.7 (CH_3), 47.2 (CH), 46.8 (CH_2), 29.7 (CH_2); IR (KBr, cm^{-1}): 2990, 2945, 2913, 2835, 1749, 1612, 1585, 1552, 1519, 1490, 1459, 1437, 1353, 1249, 1212, 1193, 1150, 1117, 1076, 1042, 1021.

3.1.4.3. Methyl 8,9-dimethoxy-6a-nitro-6-(3,4-dimethoxyphenyl)-6a,6b,11,12,14,14a-hexahydro-6*H*-chromeno[3′,4′:3,4]pyrrolidino[2,1-*a*]isoquinoline-14-carboxylate (9c). White powder, mp 146–147 °C; [Found: C, 64.6; H, 5.4; N, 5.0. $C_{31}H_{32}N_2O_9$ requires C, 64.6; H, 5.6; N, 4.9%]; ^{1}H NMR (500 MHz, $CDCl_3$): 7.19 (1H, t, *J* 7.5 Hz, H-3), 7.07 (1H, d, *J* 7.5 Hz, H-1), 6.96 (1H, d, *J* 7.5 Hz, H-4), 6.92 (1H, t, *J* 7.5 Hz, H-2), 6.58 (1H, s, Ar^6-2′H), 6.51 (1H, s, H-10), 6.43 (1H, d, *J* 8.3 Hz, Ar^6-5′H), 6.37 (1H, d, *J* 8.3 Hz, Ar^6-6′H), 6.12 (1H, s, H-7), 5.75 (1H, s, H-6), 4.86 (1H, s, H-6b), 4.13 (1H, d, *J* 11.2 Hz, H-14a), 4.10 (1H, d, *J* 11.2 Hz, H-14), 3.82 (3H, s, *O*Me), 3.78 (3H, s, *O*Me), 3.69 (3H, s, *O*Me), 3.38 (3H, s, *O*Me), 3.34 (3H, s, *O*Me), 3.18 (1H, m, H-11), 3.03 (1H, dd, *J* 6.0 and 10.5 Hz, H-12), 2.71 (1H, m, H-12), 2.64 (1H, m, H-11); ^{13}C NMR (125 MHz, $CDCl_3$): 170.4 (q), 153.5 (q), 149.1 (q), 148.2 (q), 147.8 (q), 146.5 (q), 129.4 (CH), 128.8 (CH), 128.2 (q), 127.6 (q), 127.2 (q), 123.5 (q), 121.6, 120.6 (CH), 117.0 (CH), 116.2 (CH), 111.4 (CH), 110.8 (CH), 110.3 (CH), 109.8 (CH), 90.4 (q), 76.1 (CH), 67.6 (CH), 65.7 (CH), 55.9 (CH_3), 55.7 (CH_3), 55.3 (CH_3), 54.5 (CH_3), 51.7 (CH_3), 47.3 (CH), 46.9 (CH_2), 29.7 (CH_2); IR (KBr, cm^{-1}): 2995, 2953, 2908, 2834, 2797, 1733, 1610, 1589, 1540, 1520, 1458, 1324, 1266, 1234, 1143, 1027.

3.1.4.4. Methyl 8,9-dimethoxy-6a-nitro-6-phenyl-11,12-dihydro-6*H*-chromeno[3′,4′:3,4]pyrrolidino[2,1-*a*]isoquinoline-14-carboxylate (10). Compound **10** was prepared analogously to **9a** from **3a** but *not under argon atmosphere*. The product was isolated after column chromatography (eluent: hexanes–acetone 3:1 v/v) as a white powder (0.13 g, 32%); mp 133–134 °C; [Found: C, 74.7; H, 5.6; N, 3.0. $C_{29}H_{25}NO_5$ requires C, 74.5; H, 5.4; N, 3.0%]; ^{1}H NMR (250 MHz, $CDCl_3$): 7.95 (1H, d, *J* 7.5 Hz, H-1), 7.40 (2H, m, Ph-H), 7.29 (3H, m, Ph-H), 6.95 (1H, t, *J* 7.5 Hz, H-3), 6.84 (1H, t, *J* 7.5 Hz, H-2), 6.74 (1H, d, *J* 7.5 Hz, H-4), 6.66 (1H, s, H-10), 6.43 (1H, s, H-7), 6.31 (1H, s, H-6), 5.06 (1H, ddd, *J* 13.4, 5.4 and 2.7 Hz, H-12), 3.83 (3H, s, OMe), 3.81 (3H, s, OMe), 3.79 (1H, m, H-12), 3.75 (3H, s, OMe), 3.00 (1H, m, H-11), 2.80 (1H, m, H-11); ^{13}C NMR (125 MHz, $CDCl_3$): 162.1 (q), 151.7 (q), 148.2 (q), 147.8 (q), 138.5 (q), 129.6 (q), 128.4 (2×CH), 128.3 (2×CH), 128.1 (CH), 126.5 (q), 125.6 (q), 122.2 (q), 121.4 (CH), 120.7 (q), 119.9 (q), 118.3 (CH), 116.1 (q), 114.7 (q), 110.8 (CH), 74.2 (CH), 55.8 (CH_3), 55.3 (CH_3), 51.2 (CH_3), 43.0 (CH_2), 28.9 (CH_2); IR (KBr, cm^{-1}): 2949, 2886, 2843, 1754, 1615, 1586, 1537, 1518, 1493, 1390, 1265, 1235, 1178, 1055.

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