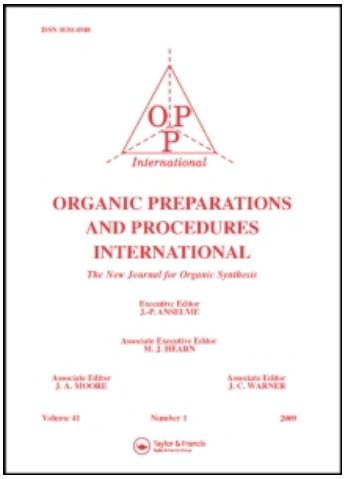

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SYNTHESIS OF 6*H*-*bis*-[1]-BENZOPYRANO[2,3-*b*:3',4'-e]PYRIDIN-8(8*H*)ONES AND 3-(2'-HYDROXYBENZOYL)-5*H*-[1]BENZOPYRANO[4,3-*b*]PYRIDINES AND THEIR DERIVATIVES

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SYNTHESIS OF 6*H*-*bis*-[1]-BENZOPYRANO[2,3-*b*:3',4'-e]PYRIDIN-8(8*H*)ONES AND 3-(2'-HYDROXYBENZOYL)-5*H*-[1]BENZOPYRANO[4,3-*b*]PYRIDINES AND THEIR DERIVATIVES

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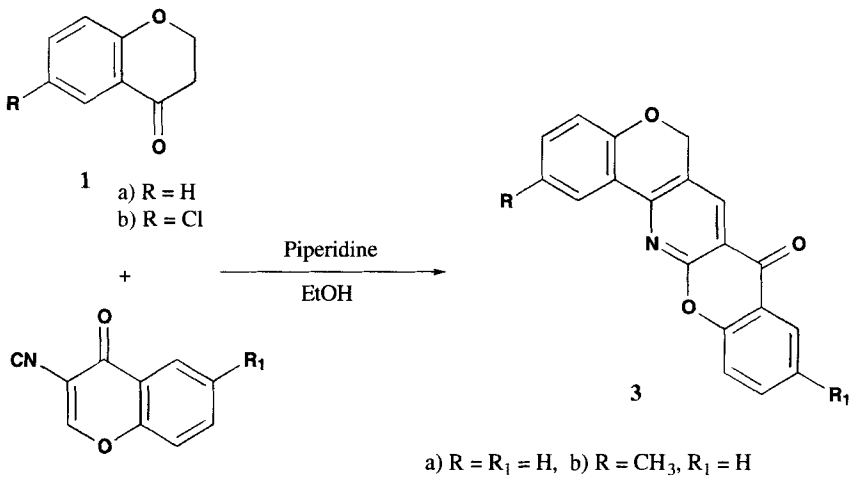
4-Chromanone (**1**) [1] is an attractive synthon for the elaboration of a variety of heterocycles fused at 3,4 of benzopyran moiety.[2] Such a feature is encountered in several physiologically important heterocyclic systems.[3] We now describe, the synthesis of 6*H*-*bis*-[1]-benzopyrano[2,3-*b*:3',4'-e] pyridin-8(8*H*)-ones and 3-(2'-hydroxybenzoyl)-5*H*-[1]-benzopyrano[4,3-*b*]pyridines, making use of 4-chromanone (**1**) by reaction with 3-cyanochromone (**2**),[4] and 3-formylchromone (**4**).[5] These compounds (**2** and **4**) posses active reaction sites in the pyrone ring suitable for the construction of fused heterocyclic molecules by nucleophilic addition-cyclization reaction.[6-8]

Reaction of **1** with 3-cyanochromone (**2**) in refluxing ethanol in the presence of a catalytic amount of piperidine proceeds as shown in Scheme 1. Michael addition of **1** on the pyrone ring, with concomitant opening of the pyrone ring, followed by double cyclization and loss of a molecule of



water results in the formation of 6-H-bis-[1]-benzopyrano[2,3-*b*:3',4'-e]pyridin-8(8*H*)-ones (**3a-h**) (Table 1). The ^{1}H NMR (**3a,b,d**)[9] and mass spectra of all the compounds are consistent with the assigned structures. Reaction of **1** with 3-formylchromone (**4**) gives 3-(4-oxo-4*H*-[1]-benzopyrano-3-methynyl)-2,3-dihydro-4*H*-1-benzopyran-4-ones (**5a-j**) (Table 2). These compounds react with ammonium acetate in acetic acid or with ammonia in aqueous methanolic medium to give 3-(2'-hydroxybenzoyl)-5*H*-[1]-benzopyrano[4,3-*b*]pyridines (**6a-j**) (Table 2); the former method however gives unsatisfactory yields due to the poor solubility of the reactants (**5a-j**) in acetic acid. The *o*-hydroxybenzoyl moiety of this system may be exploited further in building up 3-phenylcoumarins and 2-benzoylbenzofuran ring systems. Thus, reaction of **6** with phenylacetyl chloride in the presence of aqueous K_2CO_3 in a two -phase system using tetrabutylammonium hydrogen sulfate ($TBAHSO_4$) as the phase transfer catalyst and dichloromethane (DCM) as organic solvent gives 3-(2-oxo-3-phenyl-2*H*-[1]-benzopyran-4-yl)-5*H*-[1]-benzopyrano[4,3-*b*]pyridines **7a-j** (Table 3).

Similar reaction of 6 with *p*-chlorophenacyl bromide gives 3-(2-benzoylbenzo[*b*]furan-3-yl)-5*H*-[1]-benzopyrano[4,3-*b*]pyridines, **8a-e** (Table 2) in good yields. The spectral data of all these compounds supports the assigned structures.

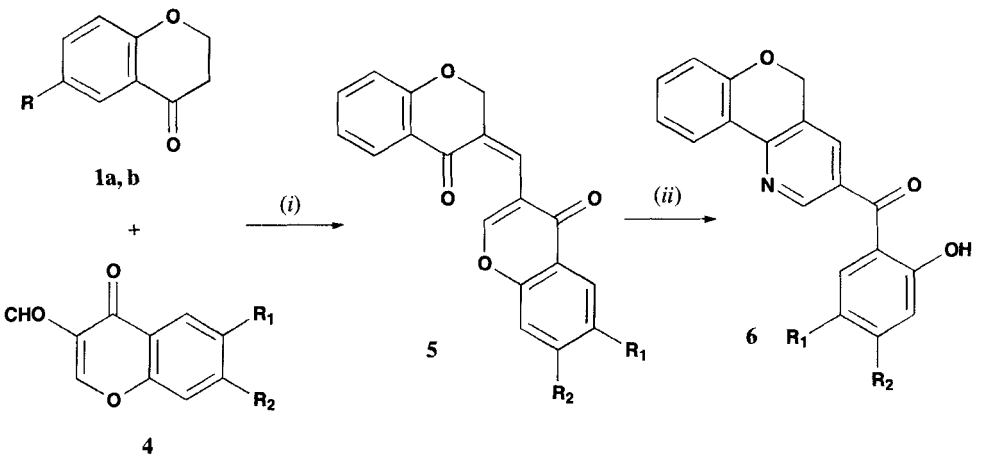
TABLE 1. Yields, Mps and Elemental Analyses of compounds **3a-h**

Cmpd.	Yield (%)	mp (°C)	Elemental Analyses Calcd (Found) C	H	N
3a	66	218-223	75.74 (76.04)	3.68 (3.91)	4.65 (4.84)
3b	75	246-248	76.18 (76.43)	4.16 (4.34)	4.44 (4.66)
3c	60	295-297	67.97 (67.96)	3.00 (3.15)	4.17 (4.01)
3d	68	282-286	60.02 (59.72)	2.65 (2.45)	3.68 (3.58)
3e	70	230-236	67.97 (68.26)	3.00 (3.19)	4.17 (4.33)
3f	83	250-257	68.68 (68.40)	3.46 (3.23)	4.01 (3.90)
3g	65	285-290	61.64 (61.34)	2.45 (2.23)	3.78 (3.56)
3h	78	290-294	55.04 (55.35)	2.19 (2.37)	3.38 (3.60)

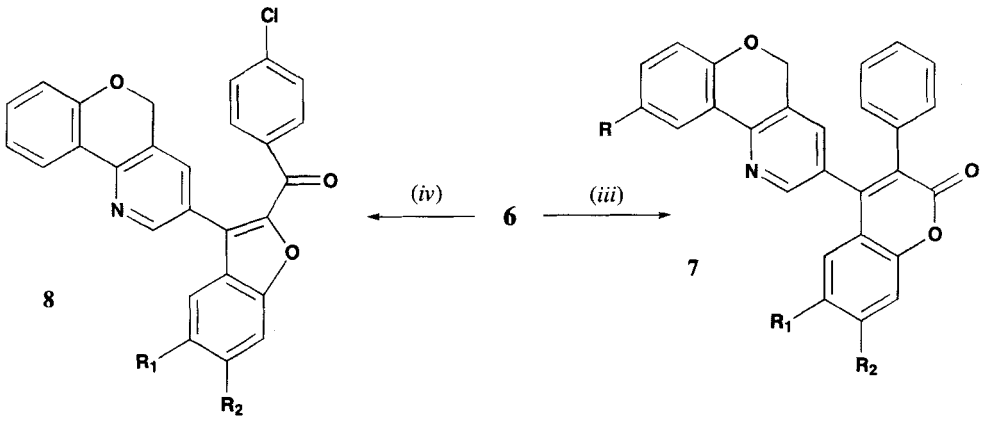
EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H NMR spectra were determined on Varian Gemini 200 MHz spectrometer (Internal Me_4Si). Mass spectra were recorded on a VG Micromass 70-70H instrument. Thin layer chromatography (TLC) was performed on Merck silica gel 60F254 precoated plates (0.2mm).

6*H*-*bis*-[1]-benzopyrano[2,3-*b*:3',4'-e]pyridin-8(8*H*)-ones (3a-h). General Procedure.- A mixture of 4-chromanone (**1a-b**) (30 mmol) and 3-cyanochromone (**2a-d**) (25 mmol) was refluxed in ethanol (50 mL) in the presence of piperidine (1 mL) for 4 hrs. The reaction mass was cooled to room temperature and the resulting solid was collected and crystallized from ethanol to give **3a-h** in 60-83% yield (Table 1).



a) $R_1 = R_2 = H$, b) $R_1 = CH_3$, $R_2 = H$
c) $R_1 = Cl$, $R_2 = H$, d) $R_1 = Br$, $R_2 = H$
e) $R_1 = Cl$, $R_2 = CH_3$



a) $R = R_1 = H$, b) $R = CH_3$, $R_1 = H$
c) $R = Cl$, $R_1 = H$, d) $R = Br$, $R_1 = H$,
e) $R = Cl$, $R_1 = CH_3$

5, 6, 7	a	b	c	d	e	f	g	h	i	j
R	H	H	H	H	H	Cl	Cl	Cl	Cl	Cl
R_1	H	CH_3	Cl	Br	Cl	H	CH_3	Cl	Br	Cl
R_2	H	H	H	H	CH_3	H	H	H	H	CH_3

i) EtOH, Et_3N (67-80%) *ii)* MeOH, aq. NH_4OH (50-63%) *iii)* $PhCH_2COCl/TBAHSO_4$, DCM, aq. K_2CO_3 (48-70%) *iv)* 4-Chlorophenacyl bromide, $TBAHSO_4$, DCM, aq. K_2CO_3 (60-84%)

TABLE 2. Yields, mps and Elemental Analyses of Compounds **5a-j, 6a-j, 7a-j and 8a-e**

Cmpd	Yield[a] (%)	mp (°C)	Elemental Analyses Calcd (Found) C	H	N
5a	75	180-185	74.99 (75.23)	3.98 (4.17)	
5b	80	170-174	75.46 (75.21)	4.43 (4.52)	
5c	70	198-200	67.37 (67.64)	3.28 (3.13)	
5d	68	203-205	*59.55* (59.41)	2.89 (2.77)	
5e	78	205-208	68.09 (68.04)	3.71 (3.77)	
5f	77	219-221	67.37 (67.50)	3.27 (3.48)	
5g	79	225-227	68.09 (68.37)	3.71 (3.86)	
5h	67	250-253	61.15 (61.30)	2.70 (2.70)	
5i	69	258-260	54.64 (54.54)	2.41 (2.32)	
5j	72	250-252	62.03 (62.29)	3.12 (3.30)	
6a	63	108-110	75.24 (75.07)	4.32 (4.20)	4.62 (4.50)
6b	60	118-122	75.69 (75.54)	4.76 (4.64)	4.41 (4.23)
6c	51	124-126	67.56 (67.82)	3.58 (3.41)	4.15 (4.31)
6d	54	148-150	59.70 (59.60)	3.17 (3.03)	3.66 (3.26)
6e	62	151-153	68.28 (68.53)	4.01 (4.09)	3.98 (3.76)
6f	61	140-145	67.56 (67.31)	3.58 (3.39)	4.15 (4.05)
6g	59	146-149	68.28 *(68.55)*	4.01 (4.20)	3.98 (3.80)
6h	52	188-191	61.31 (61.05)	2.98 (2.89)	3.76 (3.66)
6i	50	180-183	54.77 (54.88)	2.66 (2.78)	3.36 (3.56)
6j	55	174-176	62.19 (62.27)	3.39 (3.48)	3.63 (3.65)
7a	66	198-200	80.38 (80.63)	4.25 (4.55)	3.47 (3.71)
7b	68	232-235	80.56 (80.89)	4.59 (4.89)	3.56 (3.56)
7c	60	238-240	74.06 (74.35)	3.68 (3.38)	3.20 (3.10)
7d	58	238-242	67.23 (67.62)	3.34 (3.66)	2.90 (2.74)
7e	70	240-245	74.42 (74.04)	4.01 (4.19)	3.10 (3.39)
7f	62	253-266	74.06 (74.41)	3.68 (3.99)	3.20 (3.45)
7g	61	188-190	74.42 (74.04)	4.01 (3.71)	3.10 (3.31)
7h	50	223-226	68.66 (68.51)	3.20 (3.04)	2.97 (2.84)
7i	48	239-242	62.75 (62.86)	2.93 (3.12)	2.71 (2.91)
7j	58	*253-255*	69.15 (69.40)	3.52 (3.74)	2.88 (3.08)
8a	60	143-145	74.06 (74.43)	3.68 (3.92)	3.20 (3.38)
8b	65	178-180	74.42 (74.16)	4.01 (4.30)	3.10 (3.25)
8c	69	166-168	68.66 (68.90)	3.20 (3.00)	2.97 (2.70)
8d	72	186-190	62.75 (62.38)	2.93 (2.61)	2.71 (2.47)
8e	80	198-202	69.15 (69.01)	3.52 (3.20)	2.88 (2.90)

a) After recrystallization

TABLE 3. Spectroscopic Data of Compounds **5a-j** and **6a-j**

Cmpd	^{1}H NMR ($CDCl_3$, DMSO-d_6), δ, J (Hz)
5a	5.15 (s, 2H), 6.80-7.09 (m, 2H), 7.38-7.55 (m, 4H) 7.65-7.75 (m, 1H), 7.92 (s, 1H), 7.96 (dd, 1H, J = 2.0, 8.5), 8.21 (d, 1H, J = 8.5).
5b	2.42 (s, 3H), 5.13 (s, 2H), 6.88-7.06 (m, 2H), 7.34-7.60 (m, 4H), 7.89 (s, 1H), 7.96 (dd, 1H, J = 2.0, 8.5), 8.02 (d, 1H, J = 8.5).
5c	5.18 (s, 2H), 6.94-7.12 (m, 2H), 7.44-7.70 (m, 4H), 7.92 (s, 1H), 8.02 (d, 1H, J = 8.5), 8.26 (d, 1H, J = 8.5).
5d	5.18 (s, 2H), 6.96-7.14 (m, 2H), 7.40-7.60 (m, 3H), 7.82 (dd, 1H, J = 2.0, 8.5), 7.96 (s, 1H), 8.04 (dd, 1H, J = 2.5, 8.5), 8.40 (d, 1H, J = 8.5).
5e	2.41 (s, 3H), 5.16 (s, 2H), 6.87-7.10 (m, 2H), 7.32-7.59 (m, 4H), 7.88 (s, 1H), 7.95 (dd, 1H, J = 2.0, 8.5), 8.04 (d, 1H, J = 8.5).
5f	5.15 (s, 2H), 6.98 (d, 1H, J = 8.5), 7.09 (d, H, J = 8.5), 7.43-7.70 (m, 4H), 7.93 (s, 1H), 8.04 (dd, 1H, J = 2.0, 8.5), 8.23 (d, 1H, J = 8.5).
5g	2.49 (s, 3H), 5.20 (s, 2H), 6.92 (d, 1H, J = 8.5), 7.38-7.49 (m, 2H), 7.53-7.68 (m, 2H), 7.98 (dd, 2H, J = 2.0, 8.5), 8.06 (s, 1H).
5h	5.15 (s, 2H), 6.89-7.10 (m, 2H), 7.43-7.69 (m, 3H), 7.96 (s, 1H), 8.03 (d, 1H, J = 2.5), 8.28 (d, 1H, J = 8.5).
5i	5.18 (s, 2H), 6.96-7.12 (m, 2H), 7.44-7.70 (m, 2H), 7.80 (dd, 1H, J = 2.0, 8.5), 7.98 (s, 1H), 8.06 (dd, 1H, J = 2.0, 8.5), 8.39 (d, 1H, J = 8.5).
5j	2.48 (s, 3H), 5.15 (s, 2H), 7.02-7.60 (m, 4H), 7.92 (s, 1H), 8.04 (d, 1H, J = 8.5), 8.32 (d, 1H, J = 2.5).
6a	5.25 (s, 2H), 6.88-7.64 (m, 7H), 7.80 (s, 1H), 8.28 (dd, 1H, J = 2.0, 8.5), 8.84 (d, 1H, J = 2.0), 11.82 (s, 1H).
6b	2.30 (s, 3H), 5.30 (s, 2H), 6.88 (s, 1H), 7.05 (s, 1H), 7.10-7.55 (m, 4H), 7.78 (s, 1H), 8.30 (d, 1H, J = 10.0), 8.86 (d, 1H, J = 2.0), 11.62 (s, 1H).
6e	5.23 (s, 2H), 6.92-7.59 (m, 6H), 7.76 (s, 1H), 8.35 (dd, 1H, J = 2.0, S.5), 8.82 (d, 1H, J = 2.0) 11.67 (s, 1H).
6d	5.28 (s, 2H), 6.72-7.78 (m, 7H), 8.25 (dd, 1H, J = 2.5, 8.5), 8.82 (d, 1H, J = 2.0), 11.64 (s, 1H).
6e	2.42 (s, 3H), 5.35 (s, 2H), 7.0 (s, 1H), 7.06-7.48 (m, 3H), 7.60 (s, 1H), 7.78 (s, 1H), 8.30 (d, 1H, J = 10.0), 8.82 (d, 1H, J = 2.0), 11.75 (s, 1H).
6f	5.23 (s, 2H), 6.86-7.60 (m, 6H), 7.78 (s, 1H), 8.20 (d, 1H, J = 2.0), 8.82 (d, 1H, J = 2.0), 1.72 (s, 1H).
6g	2.30 (s, 3H), 5.30 (s, 2H), 6.90-7.02 (m, 2H), 7.25-7.40 (m, 3H), 7.80 (s, 1H), 8.25 (d, 1H, J = 2.0), 8.82 (d, 1H, J = 2.0), 11.60 (s, 1H).
6h	5.28 (s, 2H), 6.98 (d, 1H, J = 8.5), 7.10 (d, 1H, J = 8.5), 7.36-7.60 (m, 3H), 7.80 (s, 1H), 8.30 (d, 1H, J = 2.0), 8.88 (d, 1H, J = 2.0), 11.70 (s, 1H).
6i	5.35 (s, 2H), 6.98 (d, 1H, J = 8.5), 7.02 (d, 1H, J = 8.5), 7.36-7.75 (m, 3H), 7.80 (s, 1H), 8.30 (d, 1H, J = 2.0), 8.90 (d, 1H, J = 2.0), 11.70 (s, 1H).
6j	2.44 (s, 3H), 5.16 (s, 2H), 6.96-7.02 (m, 2H), 7.28 (dd, 1H, J = 2.0, 8.5), 7.48 (s, 1H), 7.80 (s, 1H), 8.25 (d, 1H, J = 2.0), 8.95 (d, 1H, J = 2.0), 11.65 (s, 1H).

TABLE 4. Spectroscopic Data of Compounds **7a-j** and **8a-e**

Cmpd	^{1}H NMR ($CDCl_3$, DMSO-d_6), δ, J (Hz)
7a	5.1 (d, 2H, J = 10.0), 6.95 (d, 1H, J = 10.0), 7.05-7.65 (m, 12H), 8.18 (dd, 1H, J = 2.5, 10.0), 8.4 (d, 1H, J = 2.5).
7b	2.33 (s, 3H), 5.1 (d, 2H, J = 10.0), 6.9-7.38 (m, 12H), 8.18 (dd, 1H, J = 2.5, 10.0), 8.39 (d, 1H, J = 2.5).
7c	5.1 (d, 2H, J = 10.0), 6.96 (d, 1H, J = 10.0), 7.08-7.48 (m, 10H), 7.53 (dd, 1H, J = 2.5, 10.0), 8.18 (dd, 1H, J = 2.5, 10.0), 8.35 (d, 1H, J = 2.5).
7d	5.15 (d, 2H, J = 10.0), 6.94 (d, 1H, J = 10.0), 7.05-7.40 (m, 10H), 7.68 (dd, 1H, J = 2.5, 10.0), 8.2 (dd, 1H, J = 2.5, 10.0), 8.4 (d, 1H, J = 2.5).
7e	2.50 (s, 3H), 5.12 (d, 2H, J = 10.0), 6.91 (d, 1H, J = 10.0), 7.13-7.41 (m, 10H), 8.17 (dd, 1H, J = 2.5, 10.0), 8.42 (d, 1H, J = 2.5).
7f	5.10 (d, 2H, J = 10.0), 6.69 (d, 1H, J = 10.0), 7.1-7.32 (m, 8H), 7.45-7.65 (m, 3H), 8.14 (d, 1H, J = 4.5), 8.39 (d, 1H, J = 2.5).
7g	2.31 (s, 3H), 5.1 (d, 2H, J = 10.0), 6.89-7.40 (m, 11H), 8.16 (d, 1H, J = 4.5), 8.40 (d, 1H, J = 2.5).
7h	5.15 (d, 2H, J = 10.0), 6.93 (d, 1H, J = 10.0), 7.1-7.62 (m, 10H), 8.19 (d, 1H, J = 4.5), 8.40 (d, 1H, J = 2.5).
7i	5.14 (d, 2H, J = 10.0), 6.91 (d, 1H, J = 10.0), 7.10-7.40 (m, 9H), 7.70 (dd, 1H, J = 2.5, 10.0), 8.19 (d, 1H, J = 4.5), 8.40 (d, 1H, J = 2.5).
7j	2.5 (s, 3H), 5.12 (d, 2H, J = 10.0), 6.90 (d, 1H, J = 10.0), 7.10-7.38 (m, 9H), 8.16 (d, 1H, J = 4.5), 8.40 (d, 1H, J = 2.5).
8a	5.21 (s, 2H), 6.95 (d, 1H, J = 10.0), 7.06-7.70 (m, 9H), 7.90 (d, 1H, J = 10.0), 7.98 (d, 1H, J = 8.5), 8.23 (dd, 1H, J = 2.0, 8.5), 8.78 (d, 1H, J = 2.5).
8b	2.49 (s, 3H), 5.29 (s, 2H), 6.98 (d, 1H, J = 10.0), 7.10-7.56 (m, 7H), 7.80 (s, 1H), 7. 98 (s, 1H), 8.02 (s, 1H), 8.3 (dd, 1H, J = 2.0, 8.5), 8.84 (d, 1H, J = 2.5).
8c	5.22 (s, 2H), 6.95 (d, 1H, J = 10.0), 7.05-7.58 (m, 6H), 7.65 (d, 1H, J = 10.0), 7.73 (d, 1H, J = 10.0), 7.89 (d, 1H, J = 8.5), 7.94 (d, 1H, J = 8.5), 8.24 (dd, 1H, J = 2.0, 8.5), 8.78 (d, 1H, J = 2.5).
8d	8.23 (s, 2H), 6.96 (d, 1H, J = 10.0), 7.08-7.60 (m, 6H), 7.69 (d, 1H, J = 10.0), 7.78 (d, 1H, J = 10.0), 7.91 (d, 1H, J = 8.5), 7.98 (d, 1H, J = 8.5), 8.25 (dd, 1H, J = 2.0, 8.5), 8.80 (d, 1H, J = 2.5).
8e	2.58 (s, 3H), 5.29 (s, 2H), 6.99 (d, 1H, J = 10.0), 7.1-7.74 (m, 7H), 7.95 (s, 1H), 8.05 (s, 1H), 8.26 (dd, 1H, J = 2.0, 8.5), 8.78 (d, 1H, J = 2.5).

3-(4-Oxo-4H-[1]-benzopyrano-3-methynyl)-2,3-dihydro-4H-[1]-benzopyran-4-ones (5a-j). General Procedure.- A mixture of 3-formylchromone (**4a-e**) (25 mmol), 4-chromanone (**1a-b**) (30 mmol) and triethylamine (30 mmol) in ethanol (50 mL) was refluxed for 3 hrs. and cooled. The resulting pale yellow crystalline solid was filtered, washed with cold ethanol (20 mL) and recrystallized from ethanol to give **5a-j** in 67-80% yield (Table 2).

3-(2'-Hydroxybenzoyl)-5*H*-[1]-benzopyrano[4,3-*b*]pyridines (6a-j). General Procedure.- A mixture of **5a-j** (5g) methanol (155 mL) and aqueous ammonia (25% w/w, 25 mL) was refluxed for 2 hrs. Methanol was distilled off, and the reaction mass was diluted with cold water. It was then acidified with conc. HCl to give a yellow solid. The solid was collected, washed with cold water and crystallized from alcohol to give **6a-j** in 50-63% yield (Table 2).

3-(2-Oxo-3-phenyl-2*H*-[1]-benzopyran-4-yl)-5*H*-[1]-benzopyrano[4,3-*b*]pyridines (7a-j). General Procedure.- To a stirred mixture of the compound **6a-j** (7 mmol) in dichloromethane (30 mL) and aqueous K_2CO_3 (30% *w/v*, 30 mL), tetrabutylammonium hydrogen sulfate (50 mg) was added. A solution of phenylacetyl chloride (15 mL) was added dropwise to the above mixture under stirring during 15 min. The reaction mass was stirred at room temperature for 6-8 hrs. The organic layer was separated, washed with water (2 X 20 mL), dried (Na_2SO_4) and the solvent distilled off. The residue was crystallized from ethanol to give **7a-j** in 48-70% yield (Table 2).

3-(2-Benzoylbenzo[b]furan-3-yl)-5*H*-[1]-benzopyrano[4,3-b]pyridines (8a-e). General Procedure.- To a stirred mixture of **6a-e** (7 mmol) in dichloromethane (30 mL) and aqueous K_2CO_3 (30% w/v, 30 mL), tetrabutylammonium hydrogen sulfate (50 mg) was added, followed by dropwise addition of 4-chlorophenacyl bromide (8 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 8-10 hrs. Usual work up gave **8a-e** in 60-84% yield (Table 2).

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9. ^{1}H NMR of **3c**, **3e**, **3f**, **3g** and **3h** could not be recorded because of their insolubility.

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