Tetrahedron 66 (2010) 7625–7632

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Substituent-controlled domino-Knoevenagel-hetero Diels–Alder reaction—a one-pot synthesis of polycyclic heterocycles

Sourav Maiti, Suman Kalyan Panja, Chandrakanta Bandyopadhyay *

Department of Chemistry, R.K. Mission Vivekananda Centenary College, Rahara, Kolkata 700 118, West Bengal, India

ARTICLE INFO

Article history:
Received 1 June 2010
Received in revised form 13 July 2010
Accepted 13 July 2010
Available online 21 July 2010

Keywords:
2-Aminochromone-3-carbaldehyde
Intramolecular Diels–Alder reaction
Knoevenagel reaction
1-Benzopyran
Domino reaction

ABSTRACT

The reaction of 2-(*N*-alkenyl-*N*-aryl)amino-4-oxo-4*H*-1-benzopyran-3-carbaldehyde with dimedone/Meldrum's acid/4-hydroxycoumarin by heating in ethanol in the presence of pyridine produces polycyclic heterocycles bearing pyridine and pyran rings in a one-pot reaction. The effect of substituents on N-atom of the amino function controls the mode of reaction. Terminal alkenes prefer intramolecular Michael type reaction, but non-terminal alkenes favour Diels–Alder reaction, whereas, under similar condition, 2-(*N*-alkyl-*N*-allyl)amino-4-oxo-4*H*-1-benzopyran-3-carbaldehyde undergoes domino-Knoevenagel-hetero Diels–Alder reaction.

1. Introduction

Domino-Knoevenagel-hetero Diels–Alder (DKHDA) reaction has now become a popular tool for the synthesis of polycyclic heterocycles.[1–3] Compounds having an aldehyde functionality and a suitably placed alkene or alkyne[4] moiety can be made to undergo DKHDA reaction. The active methylene components used for the Knoevenagel reaction are usually either in the form of 1,3-dicarbonyl compounds or as a part of suitable heterocycles. The widely studied substrates for DKHDA reaction are *O*-alkenylated salicylaldehydes,[5–7] but *N*-alkenylated analogues are studied a little. *N*-Alkenylated-2-formylindole[8] and *N*-alkenylated-α-aminoacetaldehyde[9] have been employed in DKHDA reaction.

2-Arylamino-4-oxo-4*H*-1-benzopyran-3-carbaldehyde (**1**)[10–12] has proved itself to be a very good synthon for the synthesis of various heterocycles. Although compound **1** was earlier utilized by converting it into tertiary amines, followed by substitution with suitable bisnucleophiles,[13–16] we have reported deformylative Mannich reaction on **1** for the synthesis of bischromones,[17,18] reactions of different amines with **1**,[19] and conversion of **1** into 1-benzopyrano[2,3-*b*]pyridines with different substitutions at their 3-positions.[20] *N*-Alkenylated derivatives **3**, obtained by the reaction of **1** with **2** in the presence of K_2CO_3, have been utilized for the synthesis of 1-benzopyrano[2,3-*b*]pyridines,[16] and also used in intramolecular [3+2] nitrone-olefin cycloaddition reaction.[21] We report herein the DKHDA reaction involving **3**, which is controlled by the substituents on the amine part of **3**.

2. Results and discussion

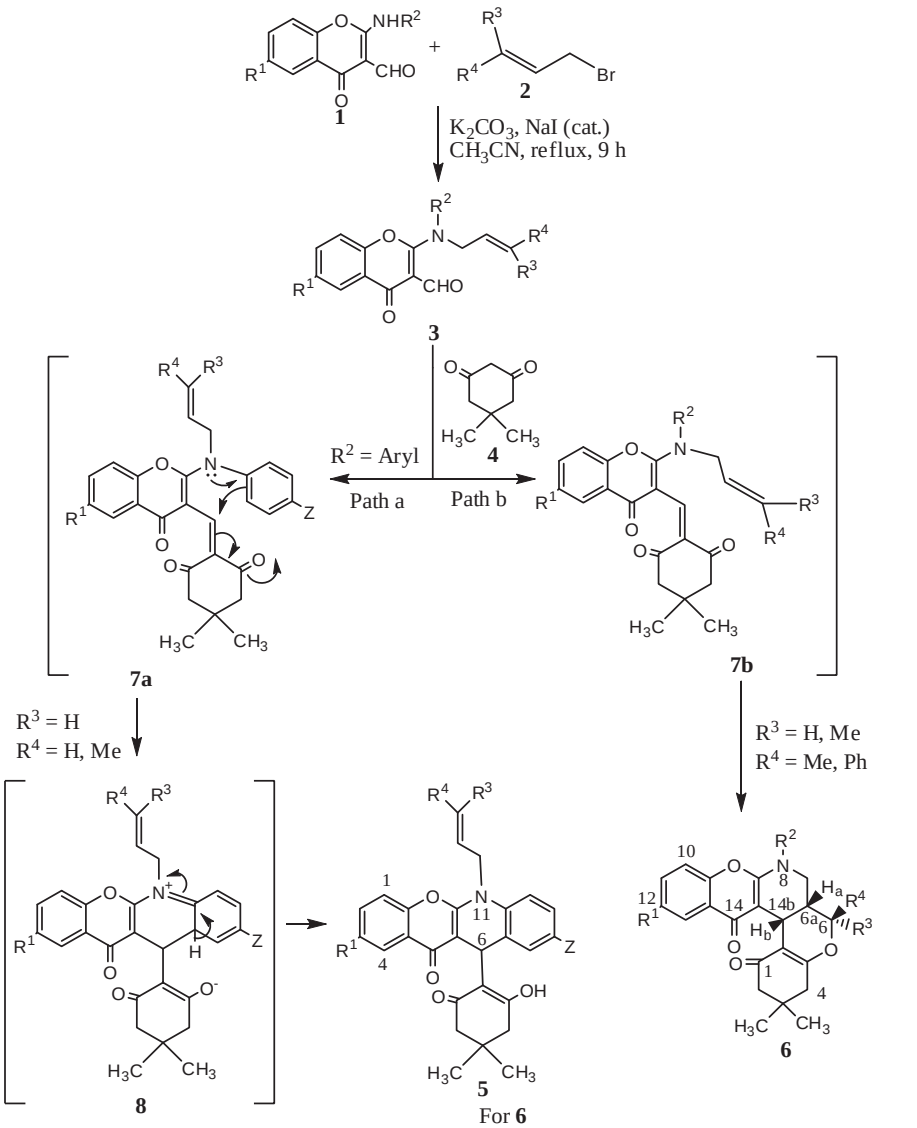
On heating an equimolar mixture of **3** (R^2=aryl; R^3=R^4=H) and dimedone (**4**) in ethanol for 4-5 h in the presence of catalytic amount of pyridine produced compound **5** in good yields (Table 1, entries 1–4). Formation of **5** may be rationalized by considering the formation of intermediate **7a**, which undergoes intramolecular Michael type addition of the activated aromatic ring (**8**) (path a, Scheme 1). Similar cyclisation process involving the aldehyde group[10,11,18,22] or using the Knoevenagel condensate[23] has been reported earlier. Literature survey revealed that DKHDA reactions involving allyl moieties having terminal double bond are scarce. Reaction of 2-allylbenzaldehyde with *N*,*N*'-dimethylbarbituric acid in the presence of EDDA,[6] and α,β-unsaturated thiocarbonyl generated from *O*-allylsalicylaldehyde[5] are reported.

To check the effect of the substituent in the allyl part in the intramolecular hetero Diels–Alder (IHDA) reaction, compound **1** was alkenylated with cinnamyl bromide **2** (R^3=H, R^4=Ph) to form **3** (R^3=H, R^4=Ph). It was then heated with equimolar amount of **4** in ethanol in the presence of catalytic amount of pyridine, when a pentacyclic compound **6** (R^3=H, R^4=Ph) was obtained in moderate yields (entries 5 and 6).

To examine the effect of alkyl group in the dienophile part of IHDA reaction system, compound **3** (R^3=R^4=Me) admixed with dimedone

* Corresponding author. Tel.: +91 03325682049; e-mail address: kantachandra@rediffmail.com (C. Bandyopadhyay).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.07.028



Scheme 1.

was heated under reflux in ethanol in the presence of pyridine and surprisingly, compound **6** (R^3=R^4=Me) was obtained in good yield (entries 7 and 8). For examining the effect of alkyl group in the allyl part more precisely in a IHDA reaction, compound **3** (R^3=H, R^4=Me) was synthesized, and an equimolar mixture of **3** (R^3=H, R^4=Me) and **4** was reacted similarly. The reaction mixture produced two compounds **5e**–**f** (15–17%) and **6e**–**f** (55–60%) (entries 9 and 10).

In an attempt to use the terminal alkene in compound **3** (R^3=R^4=H) as a dienophile in the IHDA reaction, *N*-aryl moiety was replaced by *N*-alkyl group and indeed the reaction of **3** (R^2=Me or Et; R^3=R^4=H) with **4** produced **6g** or **6h** (entries 11 and 12). The above results clearly demonstrate the occurrence of two competitive reactions (path a and b, Scheme 1), which are substituent-dependent. Although ene-reaction was found to be a competitive reaction with DKHDA reaction,[1] to the best of our knowledge here is the first example where intramolecular Michael reaction competes with DKHDA reaction.

Formation of **6** from **3** and dimedone may be rationalized by considering the in situ formation of Knoevenagel condensate **7b**, which undergoes intramolecular Diels–Alder reaction. The presence of alkyl or aryl group increases the energy of HOMO of the dienophile and facilitates inverse electron demand Diels–Alder reaction by interacting with the LUMO of the in situ formed heterodiene (path b, Scheme 1).

The cis-stereochemistry of the C/D ring juncture in **6** was considered on the basis of the small coupling constant values (J_{Ha}–J_{Hb}=3–4 Hz). It is reported in the literature[1] that the aromatic

Table 1
Reaction of **3** with dimedone (**4**)/Meldrum's acid (**9**)/4-hydroxycoumarin (**15**) in ethanol under reflux in the presence of catalytic amount of pyridine

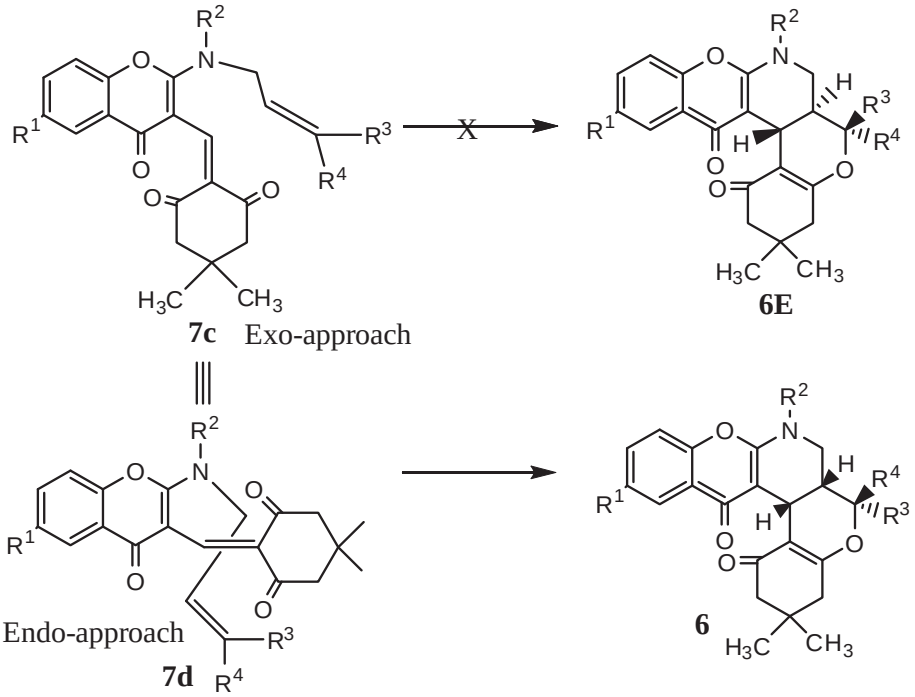
Entry	**3**				Active methylene component	Time	Products (% yield[a])	Mp (°C)
	R^1	R^2	R^3	R^4				
1	Me	Ph	H	H	**4**	4.5 h	**5a** (85)	186–188
2	H	Ar	H	H	**4**	5 h	**5b** (80)	212–214
3	Me	Ar	H	H	**4**	5 h	**5c** (70)	228–230
4	H	Ph	H	H	**4**	5 h	**5d** (80)	236–238
5	Me	Ar	H	Ph	**4**	4 h	**6a** (63)	238–240
6	H	Ph	H	Ph	**4**	4 h	**6b** (58)	260–262
7	Me	Ph	Me	Me	**4**	4 h	**6c** (74)	256–258
8	H	Ph	Me	Me	**4**	4.5 h	**6d** (72)	268–270
9	Me	Ph	H	Me	**4**	5 h	**5e** (15) and	240–242
							6e (55)	140–142
10	H	Ph	H	Me	**4**	5 h	**5f** (17) and	254–256
							6f (60)	92–94
11	H	Me	H	H	**4**	5 h	**6g** (50)	196–198
12	Me	Et	H	H	**4**	5 h	**6h** (55)	80–82
13	Me	Ph	Me	Me	**9**	5 h	**10a** (68)	230–232
14	H	Ph	Me	Me	**9**	5 h	**10b** (55)	254–256
15	H	Ph	H	Ph	**9**	5 h	**10c** (58)	198–200
16	Me	Ar	H	Ph	**9**	5 h	**10d** (46)	184–186
17	Me	Ar	H	Ph	**15**	5 h	**16a** (52) and	216–218
							17a (25)	268–270
18	H	Ph	H	Ph	**15**	4.5 h	**16b** (45) and	290–292
							17b (27)	286–288
19	H	Ar	H	H	**15**	5 h	**19a** (80)	234–236
20	Me	Ph	H	H	**15**	4.5 h	**19b** (76)	226–228

'Ar' stands for 4-C_6H_4(Me).
[a] isolated yields.

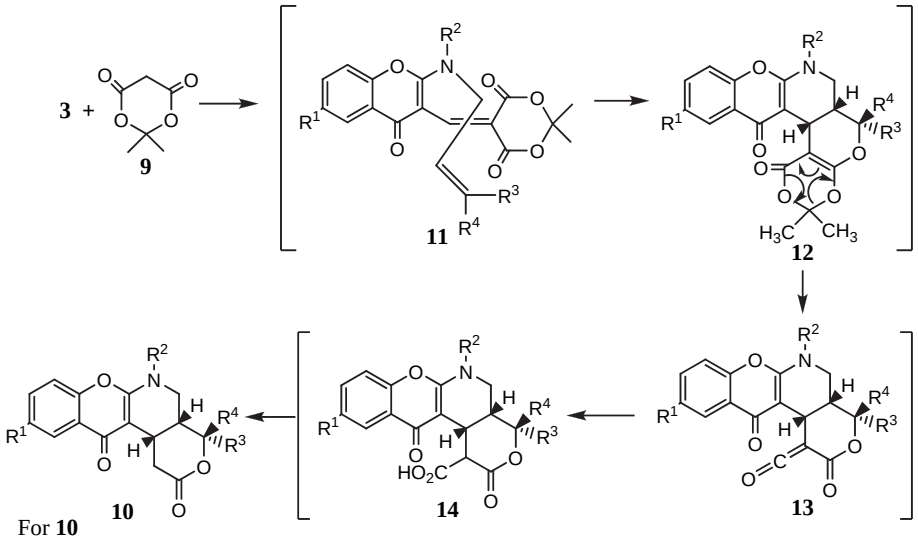
aldehydes and α,β-unsaturated aliphatic aldehydes give *cis* product and aliphatic aldehydes prefer *trans* product in DKHDA reaction. *exo*-Approach of dienophile in the Knoevenagel adduct **7c** (Scheme 2) leads to the trans-isomer **6E**, but *endo*-approach (**7d**) gives the *cis*-fused product **6** (Scheme 2).

The above reaction was then extended using other active methylene compounds. Compound **3** yielded **10**, when Meldrum's acid (**9**) was used in place of dimedone (Table 1, entries 13–16) (Scheme 3). The reaction proceeds through the same pathway as in the case of the reaction of **3** with **4**. Compound **3** and **9** reacted to give **12** via the condensate **11**. Under the reaction condition compound **12** undergoes retro Diels–Alder reaction to form ketene **13**, which traps water to form β-ketoacid **14** and decarboxylates to form **10**.[6]

Use of 4-hydroxycoumarin (**15**) as an active methylene compound, the above reaction produced **16** and **17** (entries 17 and 18) by IDKHDA reaction[8] (path a, Scheme 4). As in the previous cases, the Knoevenagel condensate is formed first, which then interacts with the dienophile in two ways as shown in **18a** and **18b**. Compound **16** was formed when α,β-unsaturated ketone moiety in **18a** acted as the heterodiene and **17** was formed when α,β-unsaturated ester moiety in **18b** acted as the heterodiene. Compound **18a** acts as better heterodiene than **18b**, which is reflected into the higher yield

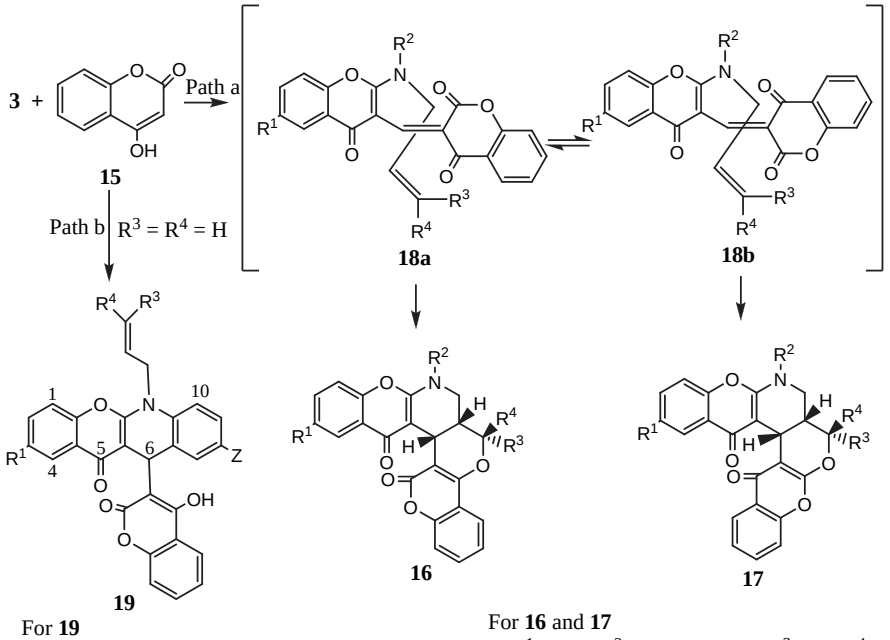


Scheme 2.



For **10**
a: $R^1 = R^3 = R^4 = Me$; $R^2 = Ph$
b: $R^1 = H$; $R^2 = Ph$; $R^3 = R^4 = Me$
c: $R^1 = R^3 = H$; $R^2 = R^4 = Ph$
d: $R^1 = Me$; $R^2 = p\text{-}C_6H_4(Me)$; $R^3 = H$; $R^4 = Ph$

Scheme 3.



For **19**
a: $R^1 = R^3 = R^4 = H$; Z = Me
b: $R^1 = Me$; $R^3 = R^4 = Z = H$

For **16** and **17**
a: $R^1 = Me$; $R^2 = p\text{-}C_6H_4(Me)$; $R^3 = H$; $R^4 = Ph$
b: $R^1 = R^3 = H$; $R^2 = R^4 = Ph$

Scheme 4.

of **16** over **17**. However, when **3** (R^3=R^4=H) was treated with **15** by heating in ethanol in presence of pyridine, compound **19** was produced following the involvement of the aromatic ring (entries 19 and 20) (path b, Scheme 4).

3. Conclusions

In summary, we have reported domino-Knoevenagel-hetero Diels–Alder reaction of 2-*N*,*N*-disubstitutedaminochromone-3-carbaldehyde **3** with various active methylene compounds to produce hitherto unreported polycyclic heterocycles. The substituents on the amino function control the mode of the reaction.

4. Experimental

4.1. General

The recorded mps are uncorrected. IR spectra were recorded in KBr on a Beckman IR 20a, ^{1}H NMR spectra on a Bruker 300 MHz spectrometer in $CDCl_3$ unless stated otherwise, mass spectra on a Qtof Micro YA 263 instrument and elemental analysis on

a Perkin–Elmer 240c elemental analyzer. Light petroleum refers to the fraction with 60–80 °C. All chemicals used are of commercial grade and are used as such.

4.2. General procedure for synthesis of 5 and/or 6

An ethanolic solution of a mixture of **3** (1 mmol) and **4** (1 mmol) was heated under reflux for 4–5 h in the presence of catalytic amount of pyridine (two drops). The reaction mixture was concentrated to obtain a solid, which was crystallized from benzene/light petroleum mixture (60:40) to obtain **5a**–**d** or **6a**–**d** as faint yellow or white crystalline solids. But the above reaction with **3** (R^3=H; R^4=Me) under similar conditions produced two compounds, which were separated by column chromatography over silica gel (100–200 mesh). Compounds **5e**–**f** were obtained using benzene and compounds **6e**–**f** were obtained using 10% ethyl acetate in benzene as eluent. On similar treatment, compound **3** (R^2=alkyl, R^3=R^4=H) produced **6g**–**h**, which were purified by chromatography using 50% ethyl acetate in benzene as eluent.

*4.2.1. 11-Allyl-6,11-dihydro-6-(5,5-dimethyl-3-hydroxy-2-cyclohexenone-2-yl)-3-methyl-1-benzopyrano[2,3-b]quinoline-5H-5-one (**5a**).* Faint yellow crystals, mp 186–188 °C; [found: C, 76.09; H, 6.11; N, 3.12. $C_{28}H_{27}NO_4$ requires C, 76.17; H, 6.16; N, 3.17%]; R_f (5% EtOAc/C_6H_6) 0.49; ν_{max} (KBr) 3458, 2952, 2871, 1645, 1608 cm^{-1}; δ_H 12.65 (1H, br s, exchangeable, OH), 7.94 (1H, br s, 4-H), 7.39 (1H, br d, *J* 8.4 Hz, 2-H), 7.28–7.26 (1H, m, ArH), 7.20–7.15 (1H, m, ArH), 7.09 (1H, br d, *J* 7.2 Hz, 10-H), 7.01–6.98 (2H, m, ArH), 6.17–6.08 (1H, m, vinylic-H), 5.41 (1H, d, *J* 17.4 Hz, R^3), 5.33 (1H, d, *J* 10.8 Hz, R^4), 5.31 (1H, s, 6-H), 4.93 (1H, br d, *J* 16.2 Hz, *N*–CH_2), 4.69 (1H, br d, *J* 16.2 Hz, *N*–CH_2), 2.42 (3H, s, $ArCH_3$), 2.42–2.29 (2H, m, CH_2–CMe_2), 1.97 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.90 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.01 (3H, s, CH_3), 0.98 (3H, s, CH_3); δ_C 197.2, 175.8, 172.0, 157.5, 151.2, 138.6, 134.9, 133.6, 132.2, 128.3, 126.9, 126.8, 124.7, 123.6, 121.3, 120.8, 117.1, 116.3, 113.9, 97.9, 50.5, 47.0, 43.4, 31.6, 30.6, 30.2, 26.1, 20.8; *m*/*z* 442 ($M+H^+$), 464 ($M+Na^+$).

*4.2.2. 11-Allyl-6,11-dihydro-6-(5,5-dimethyl-3-hydroxy-2-cyclohexenone-2-yl)-8-methyl-1-benzopyrano[2,3-b]quinoline-5H-5-one (**5b**).* Faint yellow crystals, mp 212–214 °C; [found: C, 76.12; H, 6.05; N, 3.13. $C_{28}H_{27}NO_4$ requires C, 76.17; H, 6.16; N, 3.17%]; R_f (5% EtOAc/C_6H_6) 0.46; ν_{max} (KBr) 3460, 3014, 2892, 1652, 1614 cm^{-1}; δ_H 12.61 (1H, br s, exchangeable, OH), 8.13 (1H, br d, *J* 7.5 Hz, 4-H), 7.60–7.55 (1H, m, ArH), 7.36–7.34 (2H, m, ArH), 6.97 (1H, d, *J* 8.1 Hz, 10-H), 6.90–6.87 (2H, m, ArH), 6.16–6.07 (1H, m, vinylic-H), 5.41 (1H, d, *J* 17.1 Hz, R^3), 5.32 (1H, d, *J* 10.5 Hz, R^4), 5.27 (1H, s, 6-H), 4.91 (1H, br d, *J* 17.7 Hz, *N*–CH_2), 4.68 (1H, br d, *J* 17.7 Hz, *N*–CH_2), 2.50–2.33 (2H, m, CH_2–CMe_2), 2.24 (3H, s, $ArCH_3$), 2.03–1.85 (2H, m, CH_2–CMe_2), 0.99 (6H, s, 2×CH_3).

*4.2.3. 11-Allyl-6,11-dihydro-3,8-dimethyl-6-(5,5-dimethyl-3-hydroxy-2-cyclohexenone-2-yl)-1-benzopyrano[2,3-b]quinoline-5H-5-one (**5c**).* Faint yellow crystals, mp 228–230 °C; [found: C, 76.38; H, 6.35; N, 3.02. $C_{29}H_{29}NO_4$ requires C, 76.46; H, 6.42; N, 3.07%]; R_f (5% EtOAc/C_6H_6) 0.50; ν_{max} (KBr) 3450, 2932, 2850, 1660, 1622 cm^{-1}; δ_H 12.69 (1H, br s, exchangeable, OH), 7.93 (1H, br s, 4-H), 7.37 (1H, br d, *J* 8.4 Hz, 2-H), 7.24 (1H, br d, *J* 9.0 Hz, 9-H), 6.98–6.86 (3H, m, ArH), 6.16–6.05 (1H, m, vinylic-H), 5.40 (1H, d, *J* 17.4 Hz, R^3), 5.30 (1H, d, *J* 10.7 Hz, R^4), 5.27 (1H, s, 6-H), 4.90 (1H, br d, *J* 15.6 Hz, *N*–CH_2), 4.67 (1H, br d, *J* 15.6 Hz, *N*–CH_2), 2.42 (3H, s, $ArCH_3$), 2.41–2.33 (2H, m, CH_2–CMe_2), 2.23 (3H, s, $ArCH_3$), 1.97 (1H, d, *J* 17.7 Hz, CH_2–CMe_2), 1.91 (1H, d, *J* 17.7 Hz, CH_2–CMe_2), 1.10 (3H, s, CH_3), 0.98 (3H, s, CH_3).

*4.2.4. 11-Allyl-6,11-dihydro-6-(5,5-dimethyl-3-hydroxy-2-cyclohexenone-2-yl)-1-benzopyrano[2,3-b]quinoline-5H-5-one (**5d**).* Faint yellow crystals, mp 236–238 °C; [found: C, 75.79; H, 5.95; N, 3.24. $C_{27}H_{25}NO_4$ requires C, 75.86; H, 5.89; N, 3.28%]; R_f (5% EtOAc/C_6H_6) 0.44; ν_{max} (KBr) 3455, 2957, 2870, 1648, 1610 cm^{-1}; δ_H 12.59 (1H, br s, exchangeable, OH), 8.14 (1H, br d, *J* 7.8 Hz, 4-H), 7.61–7.56 (1H, m, ArH), 7.38–7.36 (2H, m, ArH), 7.20–7.15 (1H, m, ArH), 7.09 (1H, br d, *J* 6.9 Hz, 10-H), 7.00–6.98 (2H, m, ArH), 6.18–6.09 (1H, m, vinylic-H), 5.42 (1H, d, *J* 17.4 Hz, R^3), 5.33 (1H, d, *J* 11.1 Hz, R^4), 5.31 (1H, s, 6-H), 4.96 (1H, br d, *J* 16.5 Hz, *N*–CH_2), 4.70 (1H, br d, *J* 16.5 Hz, *N*–CH_2), 2.39 (1H, d, *J* 18.6 Hz, CH_2–CMe_2), 2.30 (1H, d, *J* 18.6 Hz, CH_2–CMe_2) 1.98 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.90 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.01 (3H, s, CH_3), 0.98 (3H, s, CH_3).

*4.2.5. 11-(But-2-en-1-yl)-6,11-dihydro-6-(5,5-dimethyl-3-hydroxy-2-cyclohexenone-2-yl)-3-methyl-1-benzopyrano[2,3-b]quinoline-5H-5-one (**5e**).* White crystalline solid, mp 240–242 °C; [found: C, 76.59; H, 6.51; N, 3.00. $C_{29}H_{29}NO_4$ requires C, 76.46; H, 6.42; N, 3.07%]; R_f (5% EtOAc/C_6H_6) 0.51; ν_{max} (KBr) 3467, 3016, 2890, 1670, 1620 cm^{-1}; δ_H 12.68 (1H, br s, exchangeable, OH), 7.94 (1H, br d, *J* 7.8 Hz, 4-H), 7.41–7.36 (1H, m, ArH), 7.29–7.28 (1H, m, ArH), 7.20–7.15 (1H, m, ArH), 7.01–6.97 (3H, m, ArH), 5.90–5.82 (1H, m, vinylic H), 5.81–5.71 (1H, m, R^3), 5.30 (1H, s, 6-H), 4.89 (1H, br d, *J* 17.1 Hz, *N*–CH_2), 4.57 (1H, br d, *J* 17.1 Hz, *N*–CH_2), 2.43 (3H, s, $ArCH_3$), 2.38 (1H, d, *J* 18.6 Hz, CH_2–CMe_2), 2.32 (1H, d, *J* 18.6 Hz, CH_2–CMe_2) 1.96 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.89 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.74 (3H, d, *J* 5.4 Hz, R^4), 1.00 (3H, s, CH_3), 0.98 (3H, s, CH_3).

*4.2.6. 11-(But-2-en-1-yl)-6,11-dihydro-6-(5,5-dimethyl-3-hydroxy-2-cyclohexenone-2-yl)-1-benzopyrano[2,3-b]quinoline-5H-5-one (**5f**).* White crystalline solid, mp 254–256 °C; [found: C, 76.29; H, 6.23; N, 3.10. $C_{28}H_{27}NO_4$ requires C, 76.17; H, 6.16; N, 3.17%]; R_f (5% EtOAc/C_6H_6) 0.49; ν_{max} (KBr) 3470, 3016, 2890, 1670, 1625 cm^{-1}; δ_H 12.63 (1H, br s, exchangeable, OH), 8.15 (1H, br d, *J* 7.8 Hz, 4-H), 7.59 (1H, br t, *J* 7.5 Hz, 2-H), 7.40–7.35 (2H, m, ArH), 7.21–7.16 (1H, m, ArH), 7.10–6.98 (3H, m, ArH), 5.91–5.83 (1H, m, vinylic H), 5.82–5.71 (1H, m, R^3), 5.30 (1H, s, 6-H), 4.91 (1H, br d, *J* 16.8 Hz, *N*–CH_2), 4.60 (1H, br d, *J* 16.8 Hz, *N*–CH_2), 2.43 (1H, d, *J* 19.2 Hz, CH_2–CMe_2), 2.36 (1H, d, *J* 19.2 Hz, CH_2–CMe_2), 1.97 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.90 (1H, d, *J* 16.8 Hz, CH_2–CMe_2), 1.75 (3H, d, *J* 5.4 Hz, R^4), 1.01 (3H, s, CH_3), 0.98 (3H, s, CH_3).

*4.2.7. 8-(4-Methylphenyl)-6-phenyl-1,2,3,4,6,6a,7,8-octahydro-3,3,12-trimethyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6a**).* White crystalline solid, mp 238–240 °C; [found: C, 78.98; H, 6.19; N, 2.58. $C_{35}H_{33}NO_4$ requires C, 79.07; H, 6.26; N, 2.63%]; R_f (10% EtOAc/C_6H_6) 0.12; ν_{max} (KBr) 3034, 2926, 1665, 1633, 1613, 1542 cm^{-1}; δ_H 7.93 (1H, br s, 13-H), 7.37–7.25 (6H, m, ArH), 7.20 (2H, d, *J* 7.5 Hz, ArH), 7.05 (2H, d, *J* 7.5 Hz, ArH), 6.87 (1H, d, *J* 8.1 Hz, 10-H), 5.20 (1H, d, *J* 9.9 Hz, 6-H), 4.39 (1H, br s, H_b), 3.85 (1H, br d, *J* 12.0 Hz, *N*–CH_2), 3.21 (1H, br d, *J* 12.0 Hz, *N*–CH_2), 2.81–2.76 (1H, m, H_a), 2.47 (1H, d, *J* 17.1 Hz, 2-CH_2), 2.40 (1H, d, *J* 17.1 Hz, 2-CH_2), 2.38 (3H, s, $ArCH_3$), 2.36 (1H, d, *J* 17.1 Hz, 4-CH_2), 2.35 (3H, s, $ArCH_3$), 2.25 (1H, d, *J* 17.1 Hz, 4-CH_2), 1.17 (3H, s, CH_3), 1.13 (3H, s, CH_3); δ_C 197.8, 174.7, 164.1, 157.4, 150.7, 139.4, 136.8, 134.0, 132.5, 129.9, 129.0, 128.8, 128.3, 127.2, 125.8, 125.5, 123.0, 115.7, 112.9, 96.5, 77.8, 51.4, 50.7, 42.3, 36.2, 32.3, 29.6, 27.8, 25.5, 21.0, 20.7; *m*/*z* 532 ($M+H^+$), 554 ($M+Na^+$).

*4.2.8. 3,3-Dimethyl-6,8-diphenyl-1,2,3,4,6,6a,7,8-octahydrodi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6b**).* White crystalline solid, mp 260–262 °C; [found: C, 78.77; H, 5.85; N, 2.83. $C_{33}H_{29}NO_4$ requires C, 78.71; H, 5.80; N, 2.78%]; R_f (10% EtOAc/C_6H_6) 0.09; ν_{max} (KBr) 3030, 2935, 1670, 1640, 1612, 1545 cm^{-1}; δ_H 8.14 (1H, br d, *J* 7.2 Hz, 13-H), 7.40–7.16 (12H, m, ArH), 6.96 (1H, br d, *J* 7.8 Hz, 10-H), 5.22 (1H, d, *J* 9.6 Hz, 6-H), 4.40 (1H, br s, H_b), 3.89 (1H, br d, *J* 12.0 Hz, *N*–CH_2), 3.26 (1H, br d, *J* 12.0 Hz, *N*–CH_2), 2.77 (1H,

br d, *J* 9.6 Hz, H_a), 2.47 (1H, d, *J* 17.1 Hz, 2-CH_2), 2.41 (1H, d, *J* 17.1 Hz, 2-CH_2), 2.36 (1H, d, *J* 17.4 Hz, 4-CH_2), 2.27 (1H, d, *J* 17.4 Hz, 4-CH_2), 1.17 (3H, s, CH_3), 1.14 (3H, s, CH_3).

*4.2.9. 1,2,3,4,6,6a,7,8-Octahydro-3,3,6,6,12-pentamethyl-8-phenyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6c**).* White crystalline solid, mp 256–58 °C; [found: C, 76.65; H, 6.58; N, 2.91. $C_{30}H_{31}NO_4$ requires C, 76.73; H, 6.65; N, 2.98%]; R_f (10% EtOAc/C_6H_6) 0.06; ν_{max} (KBr) 3000, 2925, 1650, 1646, 1615, 1548 cm^{-1}; δ_H 8.07 (1H, br s, 13-H), 7.43–7.36 (2H, m, ArH), 7.28 (1H, br d, *J* 8.1 Hz, ArH), 7.20–7.17 (3H, m, ArH), 6.86 (1H, d, *J* 8.1 Hz, 10-H), 4.52 (1H, br s, H_b), 3.89 (1H, dd, *J* 11.7, 5.4 Hz, *N*–CH_2), 3.68 (1H, t, *J* 11.7 Hz, *N*–CH_2), 2.39 (3H, s, $ArCH_3$), 2.39–2.05 (5H, m, 2×CH_2+H_a), 1.47 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.02 (3H, s, CH_3), 0.94 (3H, s, CH_3); δ_C 195.8, 175.8, 167.2, 155.5, 151.3, 142.3, 133.7, 132.3, 129.2, 126.2, 125.8, 125.4, 122.7, 115.9, 109.7, 98.6, 77.6, 51.6, 48.8, 43.2, 37.9, 31.4, 29.2, 26.7, 26.5, 25.8, 23.3, 20.7; *m*/*z* 470 ($M+H^+$), 492 ($M+Na^+$).

*4.2.10. 1,2,3,4,6,6a,7,8-Octahydro-8-phenyl-3,3,6,6-tetramethyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6d**).* White crystalline solid, mp 268–270 °C; [found: C, 76.54; H, 6.38; N, 2.95. $C_{29}H_{29}NO_4$ requires C, 76.46; H, 6.42; N, 3.07%]; R_f (10% EtOAc/C_6H_6) 0.05; ν_{max} (KBr) 3015, 2946, 1674, 1629, 1619, 1573 cm^{-1}; δ_H 8.29 (1H, dd, *J* 7.2, 1.2 Hz, 13-H), 7.44–7.36 (3H, m, ArH), 7.31–7.25 (2H, m, ArH), 7.20 (2H, br d, *J* 7.5 Hz, ArH), 6.96 (1H, br d, *J* 8.4 Hz, 10-H), 4.53 (1H, br s, H_b), 3.89 (1H, dd, *J* 11.7, 5.7 Hz, *N*–CH_2), 3.80 (1H, t, *J* 11.7 Hz, *N*–CH_2), 2.33–2.06 (5H, m, 2×CH_2+H_a), 1.48 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.03 (3H, s, CH_3), 0.95 (3H, s, CH_3).

*4.2.11. 1,2,3,4,6,6a,7,8-Octahydro-8-phenyl-3,3,6,12-tetramethyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6e**).* White crystalline solid, mp 140–142 °C; [found: C, 76.39; H, 6.48; N, 2.96. $C_{29}H_{29}NO_4$ requires C, 76.46; H, 6.42; N, 3.07%]; R_f (10% EtOAc/C_6H_6) 0.08; ν_{max} (KBr) 3155, 2923, 1650, 1632, 1613, 1556 cm^{-1}; δ_H 7.94 (1H, br s, 13-H), 7.47–7.42 (2H, m, ArH), 7.35–7.30 (1H, m, ArH), 7.23–7.17 (3H, m, ArH), 6.82 (1H, d, *J* 8.4 Hz, 10-H), 4.45–4.40 (1H, m, 6-H), 4.34 (1H, br s, H_b), 3.99 (1H, dd, *J* 12.3, 3.0 Hz, *N*–CH_2), 3.66 (1H, dd, *J* 12.3, 5.1 Hz, *N*–CH_2), 2.58–2.53 (1H, m, H_a), 2.35 (3H, s, $ArCH_3$), 2.32 (1H, d, *J* 15.9 Hz, 2-CH_2), 2.27 (1H, d, *J* 15.9 Hz, 2-CH_2), 2.22 (1H, d, *J* 16.5 Hz, 4-CH_2), 2.17 (1H, d, *J* 16.5 Hz, 4-CH_2), 1.45 (3H, d, *J* 6.3 Hz, 6-CH_3), 1.09 (3H, s, CH_3), 1.06 (3H, s, CH_3).

*4.2.12. 1,2,3,4,6,6a,7,8-Octahydro-8-phenyl-3,3,6-trimethyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6f**).* White crystalline solid, mp 92–94 °C; [found: C, 76.10; H, 6.07; N, 3.24. $C_{28}H_{27}NO_4$ requires C, 76.17; H, 6.16; N, 3.17%]; R_f (10% EtOAc/C_6H_6) 0.06; ν_{max} (KBr) 3115, 2932, 1645, 1628, 1610, 1525 cm^{-1}; δ_H 8.15 (1H, br d, *J* 7.2 Hz, 13-H), 7.45–7.42 (2H, m, ArH), 7.38–7.33 (2H, m, ArH), 7.25–7.21 (3H, m, ArH), 6.92 (1H, br d, *J* 8.1 Hz, 10-H), 4.45–4.41 (1H, m, 6-H), 4.36 (1H, br s, H_b), 3.99 (1H, br d, *J* 11.7 Hz, *N*–CH_2), 3.66 (1H, dd, *J* 11.7, 4.8 Hz, *N*–CH_2), 2.63–2.53 (1H, m, H_a), 2.36 (1H, d, *J* 18.6 Hz, 2-CH_2), 2.27 (1H, d, *J* 18.6 Hz, 2-CH_2), 2.23 (1H, d, *J* 16.5 Hz, 4-CH_2), 2.19 (1H, d, *J* 16.5 Hz, 4-CH_2), 1.46 (3H, d, *J* 6.0 Hz, 6-CH_3), 1.09 (3H, s, CH_3), 1.06 (3H, s, CH_3).

*4.2.13. 1,2,3,4,6,6a,7,8-Octahydro-3,3,8-trimethyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6g**).* White crystalline solid, mp 196–198 °C; [found: C, 72.40; H, 6.29; N, 3.76. $C_{22}H_{23}NO_4$ requires C, 72.31; H, 6.34; N, 3.83%]; R_f (50% EtOAc/C_6H_6) 0.09; ν_{max} (KBr) 2912, 1665, 1650, 1618, 1548 cm^{-1}; δ_H 8.15 (1H, br d, *J* 7.8 Hz, 13-H), 7.55–7.35 (1H, m, ArH), 7.27–7.20 (2H, m, ArH), 4.22–4.10 (3H, m, 6-CH_2+H_b), 3.63 (1H, br d, *J* 9.3 Hz, *N*–CH_2), 3.27 (1H, br d, *J* 9.3 Hz, *N*–CH_2), 3.16 (3H, s, *N*–CH_3), 2.55–2.53 (1H, m, H_a), 2.35 (1H, d, *J* 16.8 Hz, 2-CH_2), 2.30 (1H, d, *J* 16.8 Hz, 2-CH_2), 2.25 (1H, d, *J* 17.4 Hz, 4-CH_2), 2.15 (1H, d, *J* 17.4 Hz, 4-CH_2), 1.08 (3H, s, CH_3), 1.04 (3H, s, CH_3); δ_C 197.3, 174.0, 164.8, 157.7, 152.5, 131.1, 126.0, 124.2, 123.3, 115.7, 112.2, 95.0, 66.4, 50.9, 49.5, 42.4, 35.9, 32.0, 29.0, 27.9, 24.7; *m*/*z* 366 ($M+H^+$), 388 ($M+Na^+$).

*4.2.14. 8-Ethyl-1,2,3,4,6,6a,7,8-octahydro-3,3,12-trimethyldi[1-benzopyrano][2,3-b:4′,3′-d]pyridine-14H,14bH-1,14-dione (**6h**).* White crystalline solid, mp 80–82 °C; [found: C, 73.42; H, 6.82; N, 3.48. $C_{24}H_{27}NO_4$ requires C, 73.26; H, 6.92; N, 3.56%]; R_f (50% EtOAc/C_6H_6) 0.12; ν_{max} (KBr) 2915, 1670, 1646, 1630, 1545 cm^{-1}; δ_H 7.93 (1H, br s, 13-H), 7.26 (1H, br d, *J* 8.4 Hz, 11-H), 7.10 (1H, d, *J* 8.4 Hz, 10-H), 4.20–4.03 (3H, m, 6-CH_2+H_b), 3.66 (1H, br d, *J* 9.6 Hz, *N*–CH_2), 3.56 (2H, q, *J* 6.3 Hz, *N*–CH_2Me), 3.28 (1H, br d, *J* 9.6 Hz, *N*–CH_2), 2.57–2.52 (1H, m, H_a), 2.37 (3H, s, $ArCH_3$), 2.41–2.13 (4H, m, 2×CH_2), 1.24 (3H, t, *J* 6.3 Hz, *N*–CH_2CH_3), 1.08 (3H, s, CH_3), 1.04 (3H, s, CH_3).

4.3. General procedure for the synthesis of 10

An equimolar mixture of **3** and **9** was heated under reflux in ethanol in the presence of catalytic amount of pyridine (two drops) for 5 h (Table 1). The solvent from the reaction mixture was removed under reduced pressure and ice-water (10 g) was added to the residue to afford a solid, which was filtered out. The solid mass was chromatographed over silica gel using 10% ethyl acetate in benzene as eluent to obtain **10** as white crystalline solid.

*4.3.1. 1,2,4,4a,5,6-Hexahydro-6-phenyl-4,4,10-trimethyl-1-benzopyrano[2,3-b]pyrano[4′,3′-d]pyridine-12H,12bH-2,12-dione (**10a**).* White crystalline solid, mp 230–232 °C; [found: C, 73.87; H, 5.88; N, 3.50. $C_{24}H_{23}NO_4$ requires C, 74.02; H, 5.95; N, 3.60%]; R_f (10% EtOAc/C_6H_6) 0.08; ν_{max} (KBr) 2979, 2928, 1724, 1611, 1554, 1482 cm^{-1}; δ_H 7.94 (1H, br s, 11-H), 7.51–7.46 (2H, m, ArH), 7.38 (1H, br d, *J* 8.4 Hz, 9-H), 7.31–7.27 (3H, m, ArH), 6.94 (1H, d, *J* 8.4 Hz, 8-H), 4.07–3.99 (1H, m, 12b-H), 3.90–3.73 (2H, m, *N*–CH_2), 3.41 (1H, dd, *J* 19.2, 8.0 Hz, 1-CH_2), 2.41 (3H, s, $ArCH_3$), 2.43–2.37 (1H, m, 1-CH_2), 2.30–2.23 (1H, m, 4a-H), 1.65 (3H, s, CH_3), 1.45 (3H, s, CH_3); δ_C 174.4, 169.8, 157.2, 151.2, 141.6, 134.6, 133.1, 129.5, 127.2, 126.0, 125.0, 122.2, 116.2, 99.1, 81.2, 47.9, 36.9, 32.6, 29.1, 26.5, 24.4, 20.8; *m*/*z* 390 ($M+H^+$), 412 ($M+Na^+$).

*4.3.2. 4,4-Dimethyl-1,2,4,4a,5,6-hexahydro-6-phenyl[1-benzopyrano][2,3-b]pyrano[4′,3′-d]pyridine-12H,12bH-2,12-dione (**10b**).* White crystalline solid, mp 254–256 °C; [found: C, 73.68; H, 5.55; N, 3.67. $C_{23}H_{21}NO_4$ requires C, 73.58; H, 5.64; N, 3.73%]; R_f (10% EtOAc/C_6H_6) 0.08; ν_{max} (KBr) 3025, 2910, 1728, 1618, 1575, 1496 cm^{-1}; δ_H 8.16 (1H, dd, *J* 8.7, 1.2 Hz, 11-H), 7.52–7.44 (3H, m, ArH), 7.41–7.27 (4H, m, ArH), 7.04 (1H, br d, *J* 8.1 Hz, 8-H), 4.07–4.00 (1H, m, 12b-H), 3.89–3.79 (2H, m, *N*–CH_2), 3.41 (1H, dd, *J* 19.5, 8.1 Hz, 1-CH_2), 2.39 (1H, dd, *J* 19.5, 9.6 Hz, 1-CH_2), 2.31–2.23 (1H, m, 4a-H), 1.65 (3H, s, CH_3), 1.45 (3H, s, CH_3).

*4.3.3. 4,6-Diphenyl-1,2,4,4a,5,6-hexahydro[1-benzopyrano][2,3-b]pyrano[4′,3′-d]pyridine-12H,12bH-2,12-dione (**10c**).* White crystalline solid, mp 198–200 °C; [found: C, 76.70; H, 4.91; N, 3.23. $C_{27}H_{21}NO_4$ requires C, 76.58; H, 5.00; N, 3.31%]; R_f (10% EtOAc/C_6H_6) 0.15; ν_{max} (KBr) 3030, 2900, 1717, 1620, 1584, 1516 cm^{-1}; δ_H 8.13 (1H, dd, *J* 8.7, 0.9 Hz, 11-H), 7.50–7.43 (3H, m, ArH), 7.36–7.29 (7H, m, ArH), 7.26–7.24 (2H, m, ArH), 7.06 (1H, br d, *J* 8.1 Hz, 8-H), 5.36 (1H, d, *J* 5.7 Hz, 4-H), 3.83–3.78 (2H, m, *N*–CH_2), 3.77–3.69 (1H, m, 12b-H), 3.59 (1H, dd, *J* 17.4, 7.2 Hz, 1-CH_2), 2.73–2.69 (1H, m, 4a-H), 2.53 (1H, dd, *J* 17.4, 9.3 Hz, 1-CH_2); δ_C 174.8, 170.8, 157.5, 152.9, 143.3,

137.8, 132.2, 129.3, 128.8, 128.2, 126.6, 126.0, 125.3, 124.9, 124.8, 116.5, 112.6, 99.7, 80.5, 49.9, 38.3, 33.8, 25.2.

*4.3.4. 1,2,4,4a,5,6-Hexahydro-10-methyl-6-(4-methylphenyl)-4-phenyl[1-benzopyrano][2,3-b]pyrano[4′,3′-d]pyridine-12H,12bH-2,12-dione (**10d**).* White crystalline solid, mp 184–186 °C; [found: C, 76.98; H, 5.54; N, 3.02. $C_{29}H_{25}NO_4$ requires C, 77.14; H, 5.58; N, 3.10%]; R_f (10% EtOAc/C_6H_6) 0.16; ν_{max} (KBr) 3140, 2980, 1712, 1615, 1612, 1540 cm^{-1}; δ_H 7.91 (1H, br s, 11-H), 7.33–7.27 (4H, m, ArH), 7.25–7.18 (4H, m, ArH), 7.13 (2H, d, *J* 8.1 Hz, ArH), 6.95 (1H, d, *J* 8.4 Hz, 8-H), 5.35 (1H, d, *J* 5.1 Hz, 4-H), 3.77–3.68 (3H, m, 12b-H+*N*–CH_2), 3.57 (1H, dd, *J* 17.7, 7.2 Hz, 1-CH_2), 2.72–2.68 (1H, m, 4a-H), 2.53 (1H, dd, *J* 17.7, 9.3 Hz, 1-CH_2), 2.41 (3H, s, $ArCH_3$), 2.39 (3H, s, $ArCH_3$); *m*/*z* 452 ($M+H^+$), 474 ($M+Na^+$).

4.4. General procedure for the synthesis of 16 and 17

A mixture of **3** (1 mmol) and 4-hydroxycoumarin (**15**) (1 mmol) was heated under reflux in ethanol in the presence of catalytic amount of pyridine (two drops). The completion of the reaction was monitored by TLC (Table 1). The reaction mixture was concentrated under reduced pressure and the residual mass was treated with ice-water (10 g) to afford a solid, which was chromatographed over silica gel using 10% ethyl acetate in benzene as eluent to produce **16** and **17** as white crystalline solid.

*4.4.1. 14-Methyl-10-(4-methylphenyl)-8-phenyl-8,8a,9,10-tetrahydro-1-benzopyrano[2,3-b]1-benzopyrano[3′,4′:5″,6″]pyrano[4″,3″-d]pyridine-1H,16H,16bH-1,16-dione (**16a**).* White crystalline solid, mp 216–218 °C; [found: C, 78.21; H, 4.90; N, 2.46. $C_{36}H_{27}NO_5$ requires C, 78.10; H, 4.92; N, 2.53%]; R_f (10% EtOAc/C_6H_6) 0.16; ν_{max} (KBr) 3035, 2923, 1725, 1637, 1612, 1542 cm^{-1}; δ_H 7.92 (1H, br s, 15-H), 7.68 (1H, br d, *J* 8.4 Hz, 3-H), 7.48–7.42 (7H, m, ArH), 7.22–7.12 (6H, m, ArH), 6.85 (1H, d, *J* 8.4 Hz, 12-H), 5.48 (1H, d, *J* 9.9 Hz, 8-H), 4.59 (1H, d, *J* 3.6 Hz, 16b-H), 3.99 (1H, dd, *J* 12.6, 3.3 Hz, *N*–CH_2), 3.34 (1H, br d, *J* 12.6 Hz, *N*–CH_2), 2.55–2.53 (1H, m, 8a-H), 2.40 (3H, s, $ArCH_3$), 2.32 (3H, s, $ArCH_3$); δ_C 174.7, 164.0, 157.2, 156.2, 152.5, 150.7, 139.1, 137.8, 137.0, 134.1, 132.6, 131.0, 129.9, 129.2, 128.9, 128.2, 127.1, 125.8, 125.5, 123.3, 122.8, 122.4, 116.6, 115.6, 104.3, 95.6, 78.2, 51.1, 35.7, 28.0, 21.0, 20.7; *m*/*z* 554 ($M+H^+$).

*4.4.2. 8,10-Diphenyl-8,8a,9,10-tetrahydro-1-benzopyrano[2,3-b]1-benzopyrano[3′,4′:5″,6″]pyrano[4″,3″-d]pyridine-1H,16H,16bH-1,16-dione (**16b**).* White crystalline solid, mp 290–292 °C; [found: C, 77.82; H, 4.47; N, 2.61. $C_{34}H_{23}NO_5$ requires C, 77.70; H, 4.41; N, 2.67%]; R_f (10% EtOAc/C_6H_6) 0.14; ν_{max} (KBr) 3022, 2936, 1720, 1642, 1602, 1552 cm^{-1}; δ_H 8.12 (1H, br d, *J* 6.6 Hz, 15-H), 7.68 (1H, br d, *J* 6.6 Hz, 3-H), 7.42–7.37 (11H, m, ArH), 7.27–7.16 (4H, m, ArH), 6.94 (1H, br d, *J* 7.8 Hz, 12-H), 5.50 (1H, d, *J* 9.6 Hz, 8-H), 4.61 (1H, br s, 16b-H), 4.04 (1H, br d, *J* 12.3 Hz, *N*–CH_2), 3.39 (1H, br d, *J* 12.3 Hz, *N*–CH_2), 2.59–2.57 (1H, m, 8a-H).

*4.4.3. 14-Methyl-10-(4-methylphenyl)-8-phenyl-8,8a,9,10-tetrahydro-1-benzopyrano[2,3-b]1-benzopyrano[3′,2′:5″,6″]pyrano[4″,3″-d]pyridine-1H,16H,16bH-1,16-dione (**17a**).* White crystalline solid, mp 268–270 °C; [found: C, 77.96; H, 4.87; N, 2.45. $C_{36}H_{27}NO_5$ requires C, 78.10; H, 4.92; N, 2.53%]; R_f (10% EtOAc/C_6H_6) 0.34; ν_{max} (KBr) 3038, 2924, 1718, 1634, 1609, 1550 cm^{-1}; δ_H 7.93 (1H, br s, 15-H), 7.71 (1H, br d, *J* 7.8 Hz, 2-H), 7.51–7.38 (7H, m, ArH), 7.22–7.19 (4H, m, ArH), 7.09 (2H, d, *J* 8.1 Hz, ArH), 6.89 (1H, d, *J* 8.4 Hz, 12-H), 4.85 (1H, d, *J* 10.2 Hz, 8-H), 3.86 (1H, d, *J* 10.5 Hz, 16b-H), 3.49–3.44 (1H, m, *N*–CH_2), 3.36–3.28 (1H, m, *N*–CH_2), 2.80–2.74 (1H, m, 8a-H), 2.38 (3H, s, $ArCH_3$), 2.34 (3H, s, $ArCH_3$); *m*/*z* 554 ($M+H^+$).

*4.4.4. 8,10-Diphenyl-8,8a,9,10-tetrahydro-1-benzopyrano[2,3-b]1-benzopyrano[3′,2′:5″,6″]pyrano[4″,3″-d]pyridine-1H,16H,16bH-1,16-dione (**17b**).* White crystalline solid, mp 286–288 °C; [found: C, 77.78; H, 4.35; N, 2.71. $C_{34}H_{23}NO_5$ requires C, 77.70; H, 4.41; N, 2.67%]; R_f (10% EtOAc/C_6H_6) 0.31; ν_{max} (KBr) 3046, 2922, 1712, 1645, 1621, 1574 cm^{-1}; δ_H 8.14 (1H, br d, *J* 7.8 Hz, 15-H), 7.72 (1H, br d, *J* 7.8 Hz, 2-H), 7.52–7.36 (10H, m, ArH), 7.30–7.27 (2H, m, ArH), 7.22–7.20 (3H, m, ArH), 6.89 (1H, br d, *J* 8.4 Hz, 12-H), 4.85 (1H, d, *J* 10.2 Hz, 8-H), 3.87 (1H, d, *J* 10.5 Hz, 16b-H), 3.56–3.50 (1H, m, *N*–CH_2), 3.38–3.30 (1H, m, *N*–CH_2), 2.85–2.76 (1H, m, 8a-H).

4.5. General procedure for the synthesis of 19

An ethanolic solution of **3** (R^3=R^4=H) (1 mmol) and 4-hydroxycoumarin (**15**) (1 mmol) was heated under reflux for 4–5 h in the presence of catalytic amount of pyridine. The reaction mixture was concentrated to obtain a solid, which was further purified by crystallization from benzene/light petroleum mixture (60:40) to obtain **19** as white crystalline solid (Table 1).

*4.5.1. 11-Allyl-6,11-dihydro-6-(4-hydroxy-2-oxo-2H-1-benzopyran-3-yl)-8-methyl-1-benzopyrano[2,3-b]quinolin-5H-5-one (**19a**).* White crystalline solid, mp 234–236 °C; [found: C, 75.28; H, 4.48; N, 2.97. $C_{29}H_{21}NO_5$ requires C, 75.15; H, 4.57; N, 3.02%]; R_f (5% EtOAc/C_6H_6) 0.57; ν_{max} (KBr) 3415, 3012, 2857, 1645, 1610 cm^{-1}; δ_H 13.35 (1H, br s, exchangeable, OH), 8.10 (1H, br d, *J* 7.8 Hz, 4-H), 8.06 (1H, br d, *J* 8.1 Hz, 5′-H), 7.62–7.56 (1H, m, ArH), 7.46–7.34 (3H, m, ArH), 7.28–7.23 (1H, m, ArH), 7.15 (1H, br d, *J* 8.1 Hz, ArH), 7.02 (1H, br d, *J* 8.4 Hz, ArH), 6.94 (1H, d, *J* 9.0 Hz, 1-H), 6.93 (1H, br s, 7-H), 6.17–6.06 (1H, m, vinylic-H), 5.69 (1H, s, 6-H), 5.44 (1H, d, *J* 17.4 Hz, R^3), 5.33 (1H, d, *J* 10.5 Hz, R^4), 4.88 (1H, ddd, *J* 17.4, 3.9, 1.8 Hz, *N*–CH_2), 4.75 (1H, ddd, *J* 17.4, 4.2, 1.8 Hz, *N*–CH_2), 2.22 (3H, s, $ArCH_3$).

*4.5.2. 11-Allyl-6,11-dihydro-6-(4-hydroxy-2-oxo-2H-1-benzopyran-3-yl)-3-methyl-1-benzopyrano[2,3-b]quinolin-5H-5-one (**19b**).* White crystalline solid, mp 226–228 °C; [found: C, 75.04; H, 4.52; N, 2.99. $C_{29}H_{21}NO_5$ requires C, 75.15; H, 4.57; N, 3.02%]; R_f (5% EtOAc/C_6H_6) 0.58; ν_{max} (KBr) 3424, 3022, 2848, 1656, 1618 cm^{-1}; δ_H 13.40 (1H, br s, exchangeable, OH), 8.05 (1H, dd, *J* 7.8, 0.9 Hz, 5′-H), 7.95 (1H, br s, 4-H), 7.46–7.40 (2H, m, ArH), 7.31–7.20 (3H, m, ArH), 7.16–7.12 (2H, m, ArH), 7.07–6.99 (2H, m ArH), 6.20–6.08 (1H, m, vinylic-H), 5.73 (1H, s, 6-H), 5.45 (1H, d, *J* 17.1 Hz, R^3), 5.34 (1H, d, *J* 10.5 Hz, R^4), 4.90 (1H, ddd, *J* 17.4, 4.2, 2.1 Hz, *N*–CH_2), 4.76 (1H, ddd, *J* 17.4, 4.5, 1.2 Hz, *N*–CH_2), 2.42 (3H, s, $ArCH_3$).

Acknowledgements

We gratefully acknowledge CSIR, New Delhi [Project no. 01 (2206)/07/EMR-II] for financial assistance; Indian Institute of Chemical Biology, Jadavpur and Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032 for instrumental help; the college authority for providing research facilities. SM is thankful to Subhankar Santra for encouragement.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.07.028.

References and notes

1. Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115–136.
2. Tietze, L. F.; Rackelmann, N. *Pure Appl. Chem.* **2004**, *76*, 1967–1983.
3. Tietze, L. F.; Brasche, G.; Gericke, K. M. *Domino Reactions in Organic Synthesis*; Wiley-VCH Verlag GmbH & Co.: Weinheim, 2006.
4. Majumdar, K. C.; Taher, A.; Ponra, S. *Tetrahedron Lett.* **2010**, *51*, 147–150.

5. Matiychuk, V. S.; Lesyk, R. B.; Obushak, M. D.; Gzella, A.; Atamanyuk, D. V.; Ostapiuk, Y. V.; Kryshchyshyn, A. P. *Tetrahedron Lett.* **2008**, *49*, 4648–4651.
6. Kim, I.; Kim, S. G.; Choi, J.; Lee, G. H. *Tetrahedron* **2008**, *64*, 664–671.
7. Lee, Y. R.; Kim, Y. M.; Kim, S. H. *Tetrahedron* **2009**, *65*, 101–108.
8. Manian, R. D. R. S.; Jayasankaran, J.; Raghunathan, R. *Tetrahedron Lett.* **2007**, *48*, 1385–1389.
9. Jayagobi, M.; Raghunathan, R. *Tetrahedron Lett.* **2009**, *50*, 6886–6890.
10. Bandyopadhyay, C.; Sur, K. R.; Patra, R.; Banerjee, S. *J. Chem. Res., Synop.* **2003**, 459–460; *J. Chem. Res., miniprint* **2003**, 847–856.
11. Ishar, M. P. S.; Kumar, K.; Singh, R. *Tetrahedron Lett.* **1998**, *39*, 6547–6550.
12. Ghosh, T.; Bandyopadhyay, C. *Tetrahedron Lett.* **2004**, *45*, 6169–6172.
13. Singh, G.; Singh, L.; Ishar, M. P. S. *Tetrahedron* **2002**, *58*, 7883–7890.
14. Sattofattori, E.; Anzaldi, M.; Balbi, A.; Artali, R.; Bombieri, G. *Helv. Chim. Acta* **2002**, *85*, 1698–1705.
15. Singh, G.; Singh, G.; Ishar, M. P. S. *Synlett* **2003**, 256–258.
16. Singh, G.; Singh, G.; Ishar, M. P. S. *Helv. Chim. Acta* **2003**, *86*, 169–180.
17. Panja, S. K.; Maiti, S.; Drew, M. G. B.; Bandyopadhyay, C. *Tetrahedron* **2009**, *65*, 1276–1280.
18. Maiti, S.; Panja, S. K.; Bandyopadhyay, C. *Tetrahedron Lett.* **2009**, *50*, 3966–3969.
19. Maiti, S.; Panja, S. K.; Bandyopadhyay, C. *Indian J. Chem.* **2009**, *48B*, 1447–1452.
20. Maiti, S.; Panja, S. K.; Bandyopadhyay, C. *J. Heterocycl. Chem.* **2010**, *47*, 973–981.
21. Singh, G.; Ishar, M. P. S.; Gupta, V.; Singh, G.; Kalyan, M.; Bhella, S. S. *Tetrahedron* **2007**, *63*, 4773–4778.
22. Singh, G.; Singh, R.; Girdhar, N. K.; Ishar, M. P. S. *Tetrahedron* **2002**, *58*, 2471–2480.
23. Mahoney, S. J.; Moon, D. T.; Hollinger, J.; Fillion, E. *Tetrahedron Lett.* **2009**, *50*, 4706–4709.