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Synthesis of novel fluorescent benzo[*a*]pyrano[2,3-*c*]phenazine and benzo[*a*]chromeno[2,3-*c*]phenazine derivatives via facile four-component domino protocol

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ABSTRACT

An efficient and practical route to novel fluorescent benzo[*a*]pyrano[2,3-*c*]phenazine framework has been developed by one-pot, four-component reaction of 2-hydroxynaphthalene-1,4-dione, 1,2-phenylenediamines, aromatic aldehydes, and Meldrum's acid in glacial acetic acid at 70 °C. Photophysical studies of these compounds have been reported. Reactions involving cyclohexane-1,3-dione/5-methylcyclohexane-1,3-dione/dimedone in the place of Meldrum's acid yielded corresponding benzo[*a*]chromeno[2,3-*c*]phenazine derivatives. Crystal structure of **3k** established the regioisomer formed. Mild reaction conditions, good yields, short reaction time, and easy separation are some of the salient features of the present protocol.

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The development of convergent, atom-economic, expedient, and eco-friendly chemical methods is of utmost interest in modern synthetic chemistry. In particular, single-step or cascade reactions, such as multi-component reactions (MCRs)[1] often provide an inherently more efficient approach to chemical synthesis than conventional bimolecular reactions. MCRs provide a powerful tool for the discovery of new chemical entities required by pharmaceutical and agrochemical industries.[2] Therefore, designing of novel MCRs for the synthesis of diverse biologically active compounds has commanded great attention.[3]

Phenazines are present in natural and synthetic products showing a variety of biological functions, including antibiotic, antimicrobial, antimalarial and antiparasitic activities.[4–7] By virtue of their DNA intercalating ability, they exhibit antitumor activity in leukemia and solid tumors. For example, pyridophenazinediones and pyridazinophenazinedione derivatives are known for their antitumor activities.[8,9]

Fluorescent phenazine derivatives both natural and synthetic, are also of interest because of their rapidly expanding applications as emitters for electroluminescence devices,[10] organic semiconductors,[11] photo-sensitizers in photodynamic therapy,[12] promoter for proliferation,[13] electrochemical, and biosensors.[14] Though phenazine derivatives are well reported, pyranophenazines incorporating both phenazine and pyran moieties have not received as much attention.[15] We therefore sought to develop a simple and versatile procedure for the synthesis of a new class of pyranophenazine derivatives namely, benzo[*a*]pyrano[2,3-*c*]phenazines.

This is the first report on the glacial acetic acid catalyzed four-component condensation for the synthesis of highly functionalized novel benzo[*a*]pyrano[2,3-*c*]phenazines (Scheme 1) and their photophysical studies. The protocol could also be extended for the synthesis of benzo[*a*]chromeno[2,3-*c*]phenazines (Scheme 2). Recently synthesis of novel benzo[*a*]chromeno[2,3-*c*]phenazine annulated heterocycles had been reported by our group.[16] The optimization of the reaction conditions was evolved after attempting model reactions of 2-hydroxynaphthalene-1,4-dione (1.0 mmol), 1,2-phenylenediamine (1.0 mmol), 4-chlorobenzaldehyde (1.0 mmol), and Meldrum's acid (1.0 mmol) using different catalysts, different solvents, and also under solvent less conditions. Initially, reactions were carried out in EtOH–H_2O (1:1, v/v) as solvent at 80 °C with catalytic amount (10 mol %) of *p*-TSA, HCl, H_2SO_4, and $InCl_3$. All the reactions were sluggish and discarded. The reaction carried out in H_2O at 100 °C using Gl. AcOH (10 mol %) as catalyst went to completion and yielded a mixture of products. The desired product 1-(4-chlorophenyl)-1*H*-benzo[*a*]pyrano[2,3-*c*]phenazin-3(2*H*)-one (**2a**), characterized by spectroscopic analysis was obtained in only 25% yield (Table 1, entry 1).

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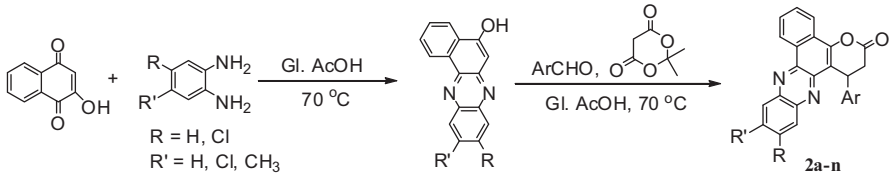
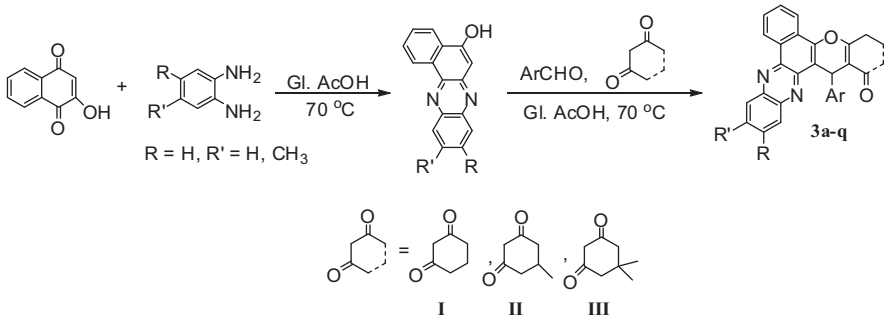


Scheme 1.



Scheme 2.

Table 1
Optimization of reaction conditions for the synthesis of 1-(4-chlorophenyl)-1*H*-benzo[*a*]pyrano[2,3-*c*]phenazin-3(2*H*)-one (**2a**)

Entry	Solvent	Catalyst	Catalyst (mol %)	Temp (°C)	Time (h)	Yield (**2a**) (%)
1	H_2O	Gl. AcOH	10	100	5	25[a,c]
2	H_2O	Gl. AcOH	10	100	6	40[b,d]
3	EtOH–H_2O	Gl. AcOH	10	80	6	53[b,d]
4	EtOH	Gl. AcOH	10	80	6	71[b]
5	CH_3CN	Gl. AcOH	10	70	6	50[b,d]
6	—	Gl. AcOH	10	70	3	82[b]
7	—	Gl. AcOH	5	70	6	68[b,d]
8	—	Gl. AcOH	20	70	3	90[b]

[a] 2-Hydroxynaphthalene-1,4-dione (1.0 mmol), 1,2-phenylenediamine (1.0 mmol), 4-chlorobenzaldehyde (1.0 mmol), Meldrum's acid (1.0 mmol), and catalyst (0.1 mmol) were added simultaneously.
[b] 2-Hydroxynaphthalene-1,4-dione (1.0 mmol), 1,2-phenylenediamine (1.0 mmol), and catalyst were first allowed to stir in solvent at appropriate temp for 30 min, followed by addition of 4-chlorobenzaldehyde (1.0 mmol) and Meldrum's acid (1.0 mmol).
[c] Mixture of products.
[d] Incomplete reaction.

The above reaction was attempted by stepwise addition to minimize formation of by-products. Therefore, a reaction of 2-hydroxynaphthalene-1,4-dione (1.0 mmol) and 1,2-phenylenediamine (1.0 mmol) was carried out initially in H_2O at 100 °C using Gl. AcOH (10 mol %) as catalyst followed by addition of 4-chlorobenzaldehyde (1.0 mmol) and Meldrum's acid (1.0 mmol) in the same pot. The reaction was incomplete after 6 h, but afforded 40% of **2a** after separation (Table 1, entry 2). Subsequently, the reactions catalyzed by Gl. AcOH attempted in EtOH–H_2O (1:1, v/v), EtOH, and CH_3CN, resulted in the formation of the desired product **2a** in 53%, 71%, and 50% yield, respectively (Table 1, entries 3–5). The reaction attempted using Gl. AcOH (10 mol %) as catalyst in the absence of any solvent at 70 °C was complete in 3 h and afforded the desired product **2a** in 82% yield after a simple work-up (Table 1, entry 6 and Scheme 1).

The above reaction performed using 5 mol % of Gl. AcOH at 70 °C was incomplete even after 6 h while a higher yield of **2a** was obtained using 20 mol % Gl. AcOH in the absence of any solvent (Table 1, entries 7 and 8). The reactions carried out with 20 mol % Gl. AcOH at room temperature and also in the absence of catalyst were not satisfactory even after 24 h. Therefore, a one pot domino reaction of equimolar amounts of 2-hydroxynaphthalene-1,4-dione, 1,2-phenylenediamine, aldehyde, and Meldrum's acid using 20 mol % of Gl. AcOH as catalyst in the absence of any solvent at 70 °C proved to be the optimum condition, wherein Meldrum's acid serves as ketene equivalent.

The optimized reaction conditions were then applied to reactions of equimolar amounts of 2-hydroxynaphthalene-1,4-dione, 1,2-phenylenediamine, and Meldrum's acid with different aldehydes having electron withdrawing and electron releasing groups. All the reactions proceeded smoothly to yield the novel benzo[*a*]pyrano[2,3-*c*]phenazines (**2b–i**) in high yields (78–91%) (Table 2, entries 1–9). Reactions carried out with 4,5-dichlorobenzene-1,2-diamine and 4-methylbenzene-1,2-diamine instead of 1,2-phenylenediamine also afforded the corresponding benzo[*a*]pyrano-[2,3-*c*]phenazines (**2j–n**) in high yields (80–92%) (Table 2, entries 10–15 and Scheme 1). However no reactions were observed with aliphatic aldehydes.

Further we explored the above optimized sequential four-component domino protocol for the condensation of equimolar amounts of 2-hydroxynaphthalene-1,4-dione, 1,2-phenylenediamines, active methylene cyclic 1,3-diketones (I–III) instead of Meldrum's acid with different aldehydes in the presence of 20 mol % of Gl. AcOH at 70 °C. All the reactions were complete in 2–3.5 h and resulted in the formation of the corresponding benzo[*a*]chromeno-phenazine derivatives (**3a–q**) (Scheme 2 and Table 3 entries

Table 2
Synthesis of benzo[*a*]pyrano[2,3-*c*]phenazine derivatives (**2a–n**) using Gl. AcOH as catalyst at 70 °C

Entry	Product	Ar	R	R′	Time (h)	Yield (%)
1	**2a**	4-ClC_6H_4	H	H	3	90
2	**2b**	4-$(NO_2)C_6H_4$	H	H	3	85
3	**2c**	3-$(NO_2)C_6H_4$	H	H	3	84
4	**2d**	4-$(CH_3)C_6H_4$	H	H	3	80
5	**2e**	4-$(OCH_3)C_6H_4$	H	H	3.5	78
6	**2f**	4-FC_6H_4	H	H	2.5	90
7	**2g**	4-$(F_3C)C_6H_4$	H	H	2	91
8	**2h**	2-$(CH_3)C_6H_4$	H	H	3.5	81
9	**2i**	C_6H_5	H	H	3	84
10	**2j**	4-FC_6H_4	H	CH_3	2	91
11	**2k**	4-$(F_3C)C_6H_4$	H	CH_3	2	92
12	**2l**	4-$(CH_3)C_6H_4$	H	CH_3	2.5	82
13	**2m**	3,4,5-$(CH_3O)_3C_6H_2$	H	CH_3	3	84
14	**2n**	4-$(NO_2)C_6H_4$	Cl	Cl	3	80

1–17). There is no significant effect of substituents both electron withdrawing and donating on the reaction time and yield of the products as evident from Table 3. Structural assignments have been made on the basis of IR, ^{1}H NMR, ^{13}C NMR, and mass spectra.

The structure of the synthesized novel benzo[*a*]chromeno[2,3-*c*]phenazine derivative (**3k**) has been confirmed by the single crystal X-ray diffraction analysis to assign the position of the aromatic methyl group when 4-methylbenzene-1,2-diamine was used instead of symmetrical 1,2-phenylenediamine as two different regioisomers are possible. All our attempts to obtain single crystals of compounds **2** were not successful. Single crystal of **3k** suitable for X-ray diffraction was obtained by evaporation of $CHCl_3$/heptane solutions at ambient temperature. The structural resolution of **3k** showed that two disordered molecules of $CHCl_3$ crystallization solvent are located in channels in the crystal. The molecular structure of **3k** with atom labeling is reported in Figure 1. It crystallizes in the P-1 space group. All bond lengths and angles are normal and in agreement with similar compounds.[17,18] The calculated structure provides accurate molecular shapes, with the pyran ring of **3k** in pseudo boat conformation with atomic displacement of 0.133 Å (for O1) and 0.257 Å (for C24) from mean plane of C11, C10, C23, and C18. Chiral carbon C20 deviates 0.777 Å from mean plane of C19, C18, C23, C22, and C21. The angle between the two planes containing C10, C11, C23, C18 and C25, C26, C27, C28, C29, C30 is 86.24°. Compound **3k** owns two chiral centers, with 'R' configuration at C20 and 'S' at C24 as revealed from the crystal structure (Fig. 2).

The regioselectivity in the reaction arises due to initial attack of more nucleophilic NH_2 group which is *para* to the methyl group of 4-methylbenzene-1,2-diamine on the more electrophilic carbon of 2-hydroxynaphthalene-1,4-dione thus leading to the formation of only one favorable regioisomer, which subsequently reacts with aldehyde and Meldrum's acid to give desired phenazine derivative. Also, the synthesized phenazine derivatives were found to be optically inactive and thus believed to be racemic mixtures.

The synthesis of benzo[*a*]pyranophenazine (2) is believed to be proceeding via sequential condensation, Michael addition, cyclization, and elimination (Scheme 3). Initially, 2-hydroxynaphthalene-1,4-dione and 1,2-phenylenediamine undergo condensation to afford benzo[*a*]phenazin-5-ol (A). Simultaneously the Knoevenagel condensation between an aldehyde and Meldrum's acid yields the arylidene Meldrum's acid (B). Subsequently benzo[*a*]phenazin-5-ol (A) undergoes Michael type addition to arylidene Meldrum's acid (B) to give intermediate (C) which undergoes cyclization with loss of acetone and carbon dioxide simultaneously to afford the desired compound **2**.

The formation of **A** was observed in the reaction. Also, the reaction of pre-formed intermediates benzo[*a*]phenazin-5-ol (A) and Knoevenagel adduct (B) independently under identical conditions gave the product **2a** thus supporting the proposed reaction pathway (Scheme 4).

Photophysical studies

Electronic absorption and photoluminescent properties of all new benzo[*a*]pyranophenazine derivatives (**2a–n**) were studied in $CHCl_3$. The 1.0×10^{-5} mol L^{-1} solution of compounds (**2a–n**) showed three absorption maxima, a strong band I in the region of 275–290 nm and two weak bands II and III in the region of 380–430 nm (Fig. S1). Moreover, when these compounds were excited at 280 nm (λ_{max}), they exhibited strong photoluminescent emissions with the emission maxima ranging from peaks varying from 428 to 449 nm (Fig. S2). The spectrophotometric properties of the compounds such as absorption maxima (λ_{max}), emission maxima (λ_{em}), molar extinction coefficient (ε), and stokes shift are listed in Table S1. The large magnitude of Stokes shift was observed for all the benzo[*a*]pyranophenazine derivatives (**2a–n**) which indicates that the excited state geometry could be different from that of the ground state. Fluorescent compounds with particularly high Stokes shift possess application in fields, where long optical path are required like sunlight collection,[19] scintillation,[20] and various biological applications. It can also be observed from Table S1 that there is only a slight change in λ_{em} and the Stokes

Table 3
Synthesis of benzo[*a*]chromeno[2,3-*c*]phenazine derivatives (**3a–q**) using Gl. AcOH as catalyst at 70 °C

Entry	Product	Ar	R	R′	1,3-Dicarbonyl compound	Time (h)	Yield (%)
1	**3a**	4-$(CH_3O)C_6H_4$	H	H	I	2	85
2	**3b**	3,4,5-$(CH_3O)_3C_6H_2$	H	H	I	2.5	88
3	**3c**	Thien-2-yl	H	H	I	3	80
4	**3d**	2-Naphthyl	H	H	I	2.5	82
5	**3e**	C_6H_5	H	H	I	2	86
6	**3f**	4-FC_6H_4	H	CH_3	I	2.5	90
7	**3g**	4-(OH),3-$(CH_3O)C_6H_3$	H	CH_3	I	3	85
8	**3h**	3,4-$(CH_3O)_2C_6H_3$	H	H	II	2.5	81
9	**3i**	3,4,5-$(CH_3O)_3C_6H_2$	H	H	II	2.5	84
10	**3j**	2-Naphthyl	H	H	II	2	80
11	**3k**	3,4,5-$(CH_3O)_3C_6H_2$	H	CH_3	II	2.5	86
12	**3l**	2-Naphthyl	H	CH_3	II	2	84
13	**3m**	3,4-$(CH_3O)_2C_6H_3$	H	H	III	3	80
14	**3n**	4-(OH),3-$(CH_3O)C_6H_3$	H	H	III	3	81
15	**3o**	2-Naphthyl	H	H	III	2.5	80
16	**3p**	3,4,5-$(CH_3O)_3C_6H_2$	H	CH_3	III	2.5	85
17	**3q**	2-Naphthyl	H	CH_3	III	2	82

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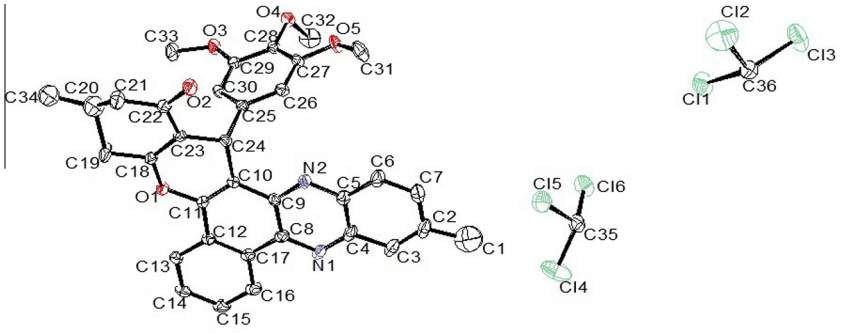


Figure 1. X-ray crystallographic structure of **3k**.

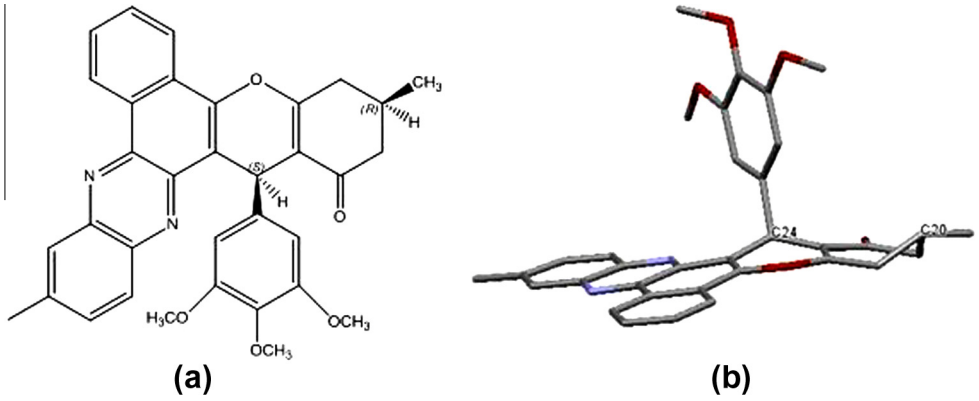
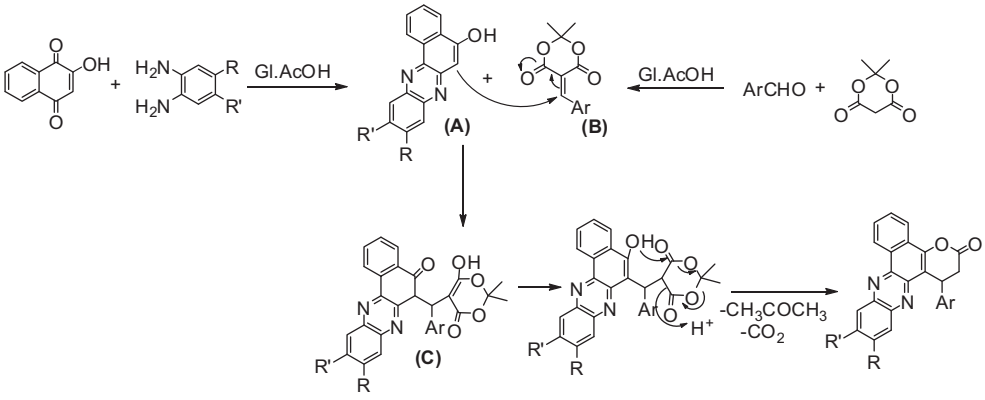
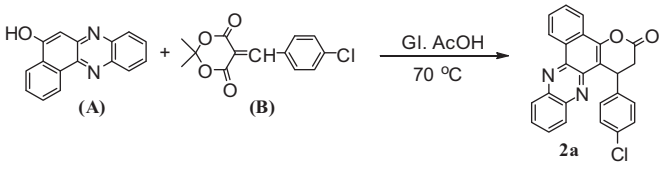


Figure 2. (a) Chemical structure of compound **3k** showing stereochemistry; (b) a perspective view of compound **3k**.



Scheme 3.



Scheme 4.

shift with changing substituents on the phenyl ring. Therefore, it can be inferred that the luminescence of the products (**2a**–**n**) is a result of their phenazine framework.

The absorption maxima (λ_{max}), emission maxima (λ_{em}), and stokes shift of **2c** were studied in solvents of different polarities and the data are listed in Table S2. No significant shift was observed in absorption spectra with varying solvent polarity. The emission spectra were found to be more sensitive to the nature of the solvents polarity, and hence a significant increase in Stokes shift was observed with increasing solvent polarity (Table S2), which indicates a larger charge transfer taking place in the excited state in comparison to the ground state. The Stokes shifts of **2c** in solvents of different polarity have been correlated with solvent polarity parameter Δf in order to obtain an insight about specific solvent–fluorophore interaction (Fig. S3). The Lippert–Mataga plot of the Stokes shift ($\Delta \nu$) as a function of solvent polarity parameter (Δf) shows linear relationship suggesting that dipole–dipole interactions and dipole-induced dipole interactions are involved between solvent and fluorophore.

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In conclusion, we have developed an efficient, clean, and confluent approach for the synthesis of novel benzo[*a*]pyrano[2,3-*c*]phenazines and the protocol could be extended to benzo[*a*]chromeno[2,3-*c*]phenazines via the reaction of 2-hydroxynaphthalene-1,4-dione, 1,2-phenylenediamines, aromatic aldehydes, and Meldrum's acid/cyclic-1,3-dicarbonyl compounds in the presence of Gl. AcOH at 70 °C in high yields.[21] The diversified phenazine derivatives are of great interest due to their fluorescent and biological properties.

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Supplementary data

Supplementary data (Figs. S1–S3, Tables S1–S2, spectral data, description of the crystal data and copies of ^{1}H NMR and ^{13}C NMR spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.04.072.

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21. *General procedure for the synthesis of benzo[a]pyrano[2,3-c]phenazine (**2a–n**) and benzo[a]chromeno[2,3-c]phenazine (**3a–q**) derivatives:* A mixture of 2-hydroxynaphthalene-1,4-dione (1.0 mmol), 1,2-phenylenediamine/4-methylbenzene-1,2-diamine/4,5-dichlorobenzene-1,2-diamine (1.0 mmol) and Gl. AcOH (20 mol %) was placed in a 50 mL round-bottomed flask and the contents were stirred magnetically in an oil-bath maintained at 70 °C. An orange solid of benzo[*a*]phenazin-5-ol was obtained after 30 min and TLC showed complete disappearance of diamine. Aldehyde (1.0 mmol) and Meldrum's acid/cyclohexane-1,3-dione/5-methylcyclohexane-1,3-dione/dimedone (1.0 mmol) were then added to the above reaction mixture which was heated further for an appropriate time as shown in Tables 2 and 3. The progress of the reaction was monitored by TLC (eluent: methanol–chloroform, 10:90, v/v). After completion of the reaction, the reaction mixture was allowed to cool at room temperature and was quenched with water (~5 mL). The precipitate formed was collected by filtration at pump and washed with water to remove residual AcOH. The crude product so obtained was dissolved in chloroform: ethyl acetate (3:1 v/v) and heated. After complete dissolution, petroleum ether was added dropwise to precipitate out the pure phenazine derivatives (**2** and **3**). The products were identified by spectral data. ^{13}C NMR data of all benzo[*a*]pyrano[2,3-*c*]phenazine derivatives (**2a–n**) could not be recorded due to their low solubility. ^{13}C NMR data of representative products **2b** and **2d** were recorded with very high number of scans.