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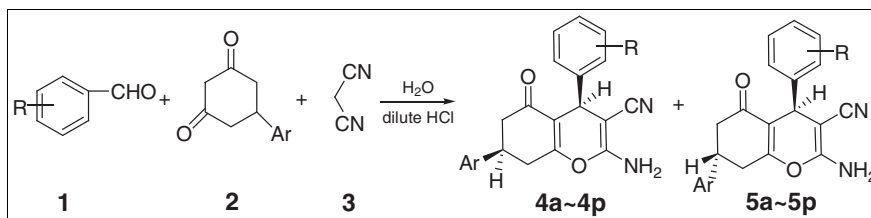
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A green and convenient approach to the synthesis of a series of 4,7-diaryl-5-oxo-4*H*-benzo[*b*]pyran derivatives from appropriate aromatic aldehydes and 5-aryl-1,3-cyclohexanedione with malononitrile in the presence of dilute HCl as catalyst (30 mmol/L) is described. This method provides several advantages such as environmental friendliness, low cost, high yields, and simple work up procedure. The structures of all compounds were characterized by infrared (IR), mass spectrometry (MS), ^1H NMR, and elemental analysis. The crystal structure of *trans/cis*-2-amino-3-cyano-7-(4'-methoxy-phenyl)-4-phenyl-5-oxo-4*H*-benzo[*b*]pyran, **g**, was determined by single crystal X-ray diffraction analysis. The crystal of compound **g** belongs to monoclinic with space group *P* 21/*c*, *a* = 8.477(3) nm, *b* = 18.948(6) nm, *c* = 24.915(7) nm, α = 90.00°, β = 107.388(11)°, γ = 90.00°, *Z* = 8, *V* = 3.819(2) nm³, *R*₁ = 0.0754, *wR*₂ = 0.2042.

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INTRODUCTION

Benzopyran, as the parent ring of many natural products, is widely found in the nature. Its derivatives have been approved to possess good biological activity and also exhibit antitumoractivity, desensitization, antispasmodic, diuresis, and so on. In addition, benzopyran derivatives could serve as the moderators for the potassium ion channel [1–3].

Recently, the synthesis of benzopyran has received much more attention. Various methods have been reported for the synthesis of benzopyran, among which the conventional method for the synthesis of benzopyran is the azeotropic removal of water by refluxing aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione with malononitrile [4]. Several other improved methods for the preparation of benzopyran have been reported to use microwaves [5,6] in distinct solution including Ac₂O [7], Acetonitrile–Ac₂O [8], toluene [9], dichloromethane [10], and so on.

However, most of the methods suffer from certain drawbacks such as long reaction time, unsatisfactory yields, expensive catalysts, hazardous solvents, complex process, low selectivity, co-occurrence of several side reactions, and needing of chromatography for purification of adducts. In this article, we report here, a simple procedure and high efficient synthesis of benzopyran starting from 5-aryl-1,3-cyclohexanedione and aromatic aldehydes with malononitrile using dilute

HCl (30 mmol/L) as a reusable, inexpensive, and efficient catalyst in a solvent-free media.

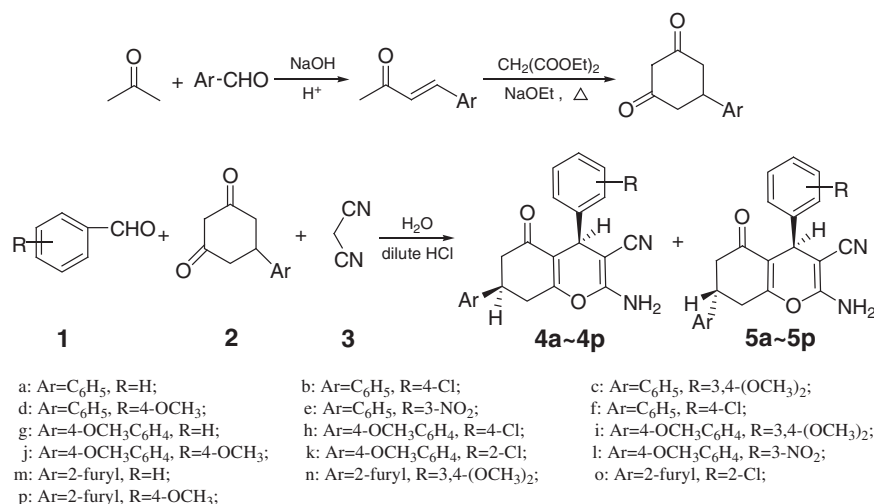
RESULT AND DISCUSSION

The synthetic route was shown in Scheme 1. A series of 4,7-diaryl-5-oxo-4*H*-benzo[*b*]pyran derivatives were prepared from appropriate aromatic aldehydes and 5-aryl-1,3-cyclohexanediones with malononitrile in the presence of dilute HCl as catalyst in water. As shown in Table 1, the reaction proceeded smoothly to afford the corresponding products in good yields. Most importantly, aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents reacted very well to afford the corresponding 4*H*-benzo[*b*]pyran derivatives in moderate to excellent yields with high purity.

To optimize the effect of the catalyst on the reaction, we increased the amount of catalyst gradually. It was found that the reaction was difficult to carry out without the catalyst, and while using two drops of concentrated HCl (about 0.1 mL) in 40 mL of water at 70–80°C for 2 h, the reaction could afford the corresponding products in good yields. But with the catalyst increased, the yields show a decreasing trend. These data indicated that two drops of concentrated HCl in 40 mL of water is quite suitable for this reaction.

Each of the compounds should be as a diastereomeric mixture because of the two chiral carbon atoms 4-C and

Scheme 1



7-C. The data of ¹H NMR, MS, and IR as shown in the experimental section are in accordance with the chemical structures of the target compounds. All standard adducts comprised a pair of epimers such as **4a** and **5a** and their certain chemical shifts appeared in pairs in distinct intensities. In the ¹H NMR spectrum of compounds **4a** and **5a**, the two broad single proton peaks at 4.65 and 4.68, which are equal to two H and disappeared after D₂O exchanging, were attributed to the two N—H of the amino group. The chemical shifts of the protons linked in C4-position were found at δ 4.46 and 4.48 ppm, whereas the two gem-carbon protons of C6- and C8-position appeared at δ 2.80–2.99 and 2.54–2.71 ppm, respectively. The two heptet peaks at 3.48–3.53 are equal to one H corresponding to the proton attached to C7-position. According to this dates, we

concluded that the compounds should be as a diastereomeric mixture.

The structures of these compounds were further supported by their IR spectra. Several typical absorption bands at 1604 cm⁻¹ for (C=O), 2196 cm⁻¹ for (C≡N), and 3383 cm⁻¹ for (N—H) were observed, respectively.

CRYSTAL STRUCTURE

A summary of the crystal data and structure refinement is presented in Table 2. A perspective view of compound **g** with atomic numbering scheme was shown in Figure 1. In the crystal structure of compound **g**, the central cyclohexyl ring in the chromene core shows a half-boat conformation. Because of the two chiral carbon atoms [C(7) or

Table 1
Synthesis of 4,7-diaryl-5-oxo-4*H*-benzo[*b*]pyran derivatives.

Entry	Ar	R	M.P. (°C)	Yield (%)	Approximate ratio (4:5) ^a
4a+5a	C ₆ H ₅	H	178–180	85	55:45
4b+5b	C ₆ H ₅	4-Cl	202–204	82	67:33
4c+5c	C ₆ H ₅	3,4-(OCH ₃) ₂	188–189	91	65:35
4d+5d	C ₆ H ₅	4-OCH ₃	212–214	87	62:38
4e+5e	C ₆ H ₅	3-NO ₂	194–196	80	47:53
4f+5f	C ₆ H ₅	2-Cl	176–178	85	58:42
4g+5g	4-OCH ₃ C ₆ H ₄	H	199–201	89	54:46
4h+5h	4-OCH ₃ C ₆ H ₄	4-Cl	236–238	79	64:36
4i+5i	4-OCH ₃ C ₆ H ₄	3,4-(OCH ₃) ₂	212–213	83	61:39
4j+5j	4-OCH ₃ C ₆ H ₄	4-OCH ₃	168–170	84	57:43
4k+5k	4-OCH ₃ C ₆ H ₄	2-Cl	170–172	82	58:42
4l+5l	4-OCH ₃ C ₆ H ₄	3-NO ₂	222–224	90	45:55
4m+5m	2-furyl	H	180–182	82	52:48
4n+5n	2-furyl	3,4-(OCH ₃) ₂	192–194	85	63:37
4o+5o	2-furyl	2-Cl	198–200	86	61:39
4p+5p	2-furyl	4-OCH ₃	202–204	88	60:40

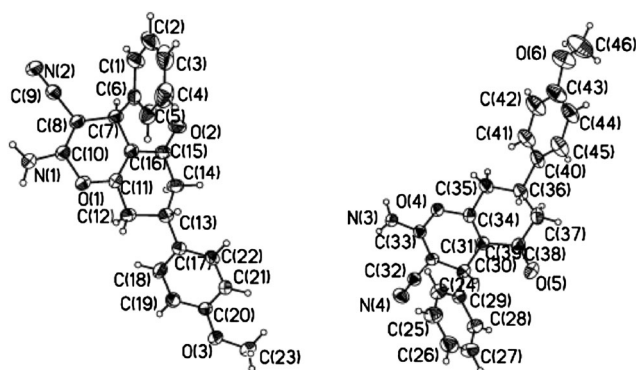
^aIt was speculated from the integration area of the special position H in the ¹H NMR spectrum.

Table 2

Crystallographic data for complex **g**.

Empirical formula	C ₂₃ H ₂₀ N ₂ O ₃
Formula weight	372.41
Wavelength (nm)	0.071073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (nm)	8.477 (3)
<i>b</i> (nm)	18.948 (6)
<i>c</i> (nm)	24.915 (7)
α (°)	90.00
β (°)	107.388 (11)
γ (°)	90.00
Volume (nm ³)	3.819 (2)
<i>Z</i>	8
Calculated density (g cm ⁻³)	1.295
Absorption coefficient (mm ⁻¹)	0.087
<i>F</i> (000)	1568
Final <i>R</i> indices [<i>I</i> > 2 sigma(<i>I</i>)]	<i>R</i> ₁ = 0.0754, <i>wR</i> ₂ = 0.2042
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1456, <i>wR</i> ₂ = 0.2338

C(30), C(13), or C(36)] in the molecules, there exist two isomer molecules in an asymmetric unit. In one molecule, the configurations of C(7) and C(13) are Sinister and Rectus, respectively, and the dihedral angles between the cyclohexyl ring and the two outer phenyl rings are 87.32 (11)° and 52.64 (10)°. However, the configurations of C(30) and C(36) in the other molecular are Rectus and Sinister, respectively, and its dihedral angles are 72.48 (11)° and 53.56 (13)°. The packing diagram of the **g** in a unit cell was shown in Figure 2. X-ray analysis reveals that there are intramolecular and intermolecular hydrogen bonds in the crystal. The length of intermolecular hydrogen bonds, N(1)-H(1B...N(4), N(1)-H(1C...O(3), N(3)-H(3B...N(2), and N(3)-H(3C...O(2) are 2.16 Å, 2.37 Å, 2.30 Å, and 3.030 Å, respectively. The structural analysis indicates that these molecular interactions play the role of further stabilizing the structure. The bond lengths and bond angles of primary hydrogen bonds were listed in Table 3.

Figure 1. Packing diagram of compound **g** in unit-cell.

CONCLUSION

In summary, we described an efficient, environmentally friendly, and convenient method for the synthesis of benzopyran by treatment of 5-aryl-1,3-cyclohexanedione, aromatic aldehydes, and malononitrile with dilute HCl (30 mmol/L) as catalyst in a solvent-free media. Moreover, the procedure possesses several advantages such as high yields, low cost, simple operation, clean reactions, and minimal environmental effects. We expect the procedure to be used for large-scale, eco-friendly preparation for these compounds.

EXPERIMENTAL

Melting points were determined on an electrothermal apparatus and uncorrected. Microanalysis was performed on Perkin-Elmer 2400 Microanalytical Service. IR spectra were recorded on a Perkin-Elmer 1700 spectrophotometer. The ¹H NMR was obtained (CDCl₃, δ 7.27 ppm) from a Bruker ARX-300 spectrometer. Mass spectra were recorded on JMS-DX300 at 70 eV.

All chemical reagents were commercially available and purified with standard operation before use. Solvents were dried in routine ways and redistilled. 5-Aryl-1,3-cyclohexanedione was obtained from aromatic aldehyde, acetone, and diethyl malonate, according to the literature [11] method with slight modification.

General procedure. A mixture of aromatic aldehydes (**1**, 5 mmol), 5-aryl-1,3-cyclohexanedione (**2**, 5 mmol), malononitrile (**3**, 5 mmol), and 30 mmol/L dilute hydrochloric acid (40 mL) was stirred at 70–80°C for 2 h. Then the mixture was cooled to room temperature and then the solid was collected and washed with water. The crude products were recrystallized from ethanol (95%).

Data of compounds are shown below. **4a+5a** ¹H NMR (CDCl₃, 300 MHz) δ : 2.54–2.71 (m, 2H, 8-H), 2.80–2.99 (m, 2H, 6-H), 3.48–3.53 (m, 1H, 7-H), 4.46 and 4.48 (each s, 1H, 4-H), 4.65 and 4.68 (each s, 2H, N—H), 7.17–7.37 (m, 10H, Ph-H). IR (KBr) ν : 3383, 3255, 2196, 1683, 1604, 1489, 1454 cm⁻¹; MS (70 eV) *m/z* (%): 343.2 (*M*⁺+1, 100). *Anal.* calcd for C₂₂H₁₈N₂O₂: C 77.17, H 5.30, N 8.18; found C 77.27, H 5.35, N 8.24.

4b+5b ¹H NMR (CDCl₃, 300 MHz) δ : 2.58–2.73 (m, 2H, 8-H), 2.83–2.98 (m, 2H, 6-H), 3.35–3.58 (m, 1H, 7-H), 4.43 and 4.44 (each s, 1H, 4-H), 4.64 and 4.66 (each s, 2H, N—H), 7.10–7.46 (m, 9H, Ph-H). IR (KBr) ν : 3395, 3251, 2200, 1670, 1604, 1492, 1413 cm⁻¹. MS (70 eV) *m/z* (%): 399.6 (*M*⁺+Na, 100). *Anal.* calcd for C₂₂H₁₇ClN₂O₂: C 70.12, H 4.55, N 7.43; found C 70.07, H 4.45, N 7.35.

4c+5c ¹H NMR (CDCl₃, 300 MHz) δ : 2.54–2.72 (m, 2H, 8-H), 2.83–2.90 (m, 2H, 6-H), 3.32–3.49 and 3.50–3.59 (each m, 1H, 7-H), 3.84 and 3.86 (each s, 3H, OCH₃), 3.95 and 3.99 (each s, 3H, OCH₃), 4.43 and 4.45 (each s, 1H, 4-H), 4.55 and 4.57 (each s, 2H, N—H), 6.69–7.17 (m, 8H, Ph-H). IR (KBr) ν : 3376, 3259, 2195, 1681, 1605, 1480, 1456 cm⁻¹. MS (70 eV) *m/z* (%): 425.7 (*M*⁺+Na, 100). *Anal.* calcd for C₂₄H₂₂N₂O₄: C 71.63, H 5.51, N 7.04.

4d+5d ¹H NMR (CDCl₃, 300 MHz) δ : 2.53–2.72 (m, 2H, 8-H), 2.75–2.95 (m, 2H, 6-H), 3.28–3.37 and 3.46–3.52 (each m, 1H,

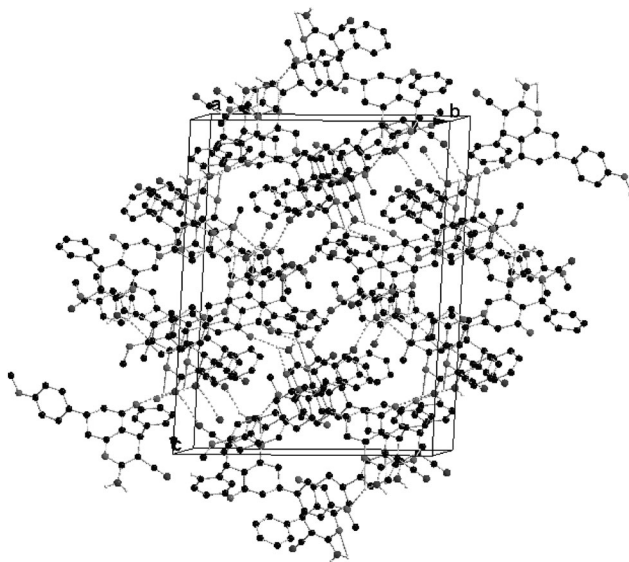
Figure 2. Molecular structure of compound **g**.

Table 3

Intermolecular and intramolecular interaction distances (Å) and the bond angle (°) of compound **g**.

D-H...A	D-H	H...A	D...A	D-H...A	Symmetry
N(1)-H(1B)...N(4)	0.86	2.16	2.943(5)	151.0	-x+1, y-1/2, -z+1/2
N(1)-H(1C)...O(3)	0.86	2.37	3.030(4)	134.2	-x+1, -y+1, -z; c-x+1
N(3)-H(3B)...N(2)	0.86	2.30	3.039(5)	143.8	-x+1, y+1/2, -z+1/2
N(3)-H(3C)...O(2)	0.86	2.14	2.980(4)	165.6	x, -y+1/2, z+1/2

7-H), 3.78 and 3.79 (each s, 3H, OCH₃), 4.42 and 4.44 (each s, 1H, 4-H), 4.58 and 4.61 (each s, 2H, N—H), 6.79–7.33 (m, 9H, Ph-H). IR (KBr) ν : 3366, 3212, 2185, 1681, 1625, 1490, 1436 cm⁻¹. MS (70 eV) m/z (%): 373.1 (M⁺+1, 100). *Anal.* calcd for C₂₃H₂₀N₂O₃: C 74.18, H 5.41, N 7.52; found C 74.27, H 5.35, N 7.43.

4e+5e ¹H NMR (CDCl₃, 300 MHz) δ : 2.56–2.70 (m, 2H, 8-H), 2.75–2.87 (m, 2H, 6-H), 3.33–3.49 (m, 1H, 7-H), 4.58 and 4.60 (each s, 1H, 4-H), 4.76 and 4.78 (each s, 2H, N—H), 7.16–8.10 (m, 9H, Ph-H). IR (KBr) ν : 3376, 3259, 2195, 1681, 1605, 1480, 1456 cm⁻¹. MS (70 eV) m/z (%): 388.1 (M⁺+1, 100). *Anal.* calcd for C₂₂H₁₇N₃O₄: C 68.21, H 4.42, N 10.85; found C 68.29, H 4.34, N 10.78.

4f+5f ¹H NMR (CDCl₃, 300 MHz) δ : 2.54–2.71 (m, 2H, 8-H), 2.76–2.91 (m, 2H, 6-H), 3.34–3.41 and 3.42–3.53 (each m, 1H, 7-H), 4.63 and 4.65 (each s, 1H, 4-H), 4.90 and 4.92 (each s, 2H, N—H), 7.14–7.40 (m, 9H, Ph-H). IR (KBr) ν : 3406, 3249, 2175, 1688, 1623, 1476, 1422 cm⁻¹. MS (70 eV) m/z (%): 377.1 (M⁺+1, 100). *Anal.* calcd for C₂₂H₁₇ClN₂O₂: C 70.12, H 4.55, N 7.43; found C 70.19, H 4.62, N 7.36.

4g+5g ¹H NMR (CDCl₃, 300 MHz) δ : 2.60–2.95 (m, 4H, 8-H +6-H), 3.20–3.35 and 3.38–3.55 (m, 1H, 7-H), 3.67 and 3.68 (each s, 3H, OCH₃), 4.25 and 4.66 (each s, H, 4-H), 4.45 and 4.47 (each s, 2H, N—H), 6.87 (m, 9H, Ph-H). IR (KBr) ν : 3413, 3315, 2176, 1659, 1610, 1511, 1504 cm⁻¹. MS (70 eV) m/z (%): 372.4 (M⁺, 100). *Anal.* calcd for C₂₃H₂₀N₂O₃: C 74.18, H 5.41, N 7.52; found C 74.27, H 5.35, N 7.46.

4h+5h ¹H NMR (CDCl₃, 300 MHz) δ : 2.63–2.92 (m, 4H, 8-H +6-H), 3.18–3.31 (m, 1H, 7-H), 3.69 and 3.70 (each s, 3H, OCH₃), 4.23 and 4.25 (each s, 1H, 4-H), 4.49 and 4.51 (each s, 2H, N—H), 7.12–7.39 (m, 8H, Ph-H). IR (KBr) ν : 3301, 3242, 2188, 1608, 1512, 1458 cm⁻¹. MS (70 eV) m/z (%): 406.1 (M⁺, 100). *Anal.* calcd for C₂₉H₁₉ClN₂O₃: C 67.90, H 4.71, N 8.71; found C 67.81, H 4.78, N 8.64.

4i+5i ¹H NMR (CDCl₃, 300 MHz) δ : 2.65–2.99 (m, 4H, 8-H +6-H), 3.23–3.45 (m, 1H, 7-H), 3.66 and 3.68 (each s, 3H, OCH₃), 3.71 and 3.73 (each s, 3H, OCH₃), 3.73 and 3.75 (each s, 3H, OCH₃), 4.16 and 4.18 (each s, 1H, 4-H), 4.53 and 4.56 (each s, 2H, N—H), 6.57–7.32 (m, 7H, Ph-H). IR (KBr) ν : 3314, 3259, 2194, 1605, 1517, 1456 cm⁻¹. MS (70 eV) m/z (%): 455.8 (M⁺+Na, 100). *Anal.* calcd for C₂₅H₂₄N₂O₅: C 69.43, H 5.59, N 6.48; found C 69.36, H 5.52, N 6.56.

4j+5j ¹H NMR (CDCl₃, 300 MHz) δ : 2.49–2.90 (m, 4H, 8-H +6-H), 3.28–3.39 and 3.40–3.49 (m, 1H, 7-H), 3.75 and 3.77 (each s, 3H, OCH₃), 3.80 and 3.82 (each s, 3H, OCH₃), 4.42 and 4.43 (each s, 1H, 4-H), 4.59 and 4.62 (each s, 2H, N—H), 6.58–7.21 (m, 8H, Ph-H). IR (KBr) ν : 3352, 3275, 2176, 1665, 1607, 1521, 1502 cm⁻¹. MS (70 eV) m/z (%): 403.2 (M⁺+1, 100). *Anal.* calcd for C₂₄H₂₂N₂O₄: C 71.63, H 5.51, N 6.96; found C 71.57, H 5.45, N 7.03.

4k+5k ¹H NMR (CDCl₃, 300 MHz) δ : 2.49–2.86 (m, 4H, 8-H +6-H), 3.27–3.49 (m, 1H, 7-H), 3.80 and 3.81 (each s, 3H, OCH₃), 4.62 and 4.63 (each s, 1H, 4-H), 4.89 and 4.91 (each s,

2H, N—H), 6.85–7.31 (m, 8H, Ph-H). IR (KBr) ν : 3401, 3282, 2208, 1623, 1522, 1468 cm^{-1} . MS (70 eV) m/z (%): 407.1 ($M^+ + 1$, 100). *Anal.* calcd for $\text{C}_{29}\text{H}_{19}\text{ClN}_2\text{O}_3$: C 67.90, H 4.71, N 8.71; found C 67.98, H 4.78, N 8.65.

4l+5l ^1H NMR (CDCl_3 , 300 MHz) δ : 2.54–2.98 (m, 4H, 8-H +6-H), 3.27–3.39 and 3.40–3.49 (m, 1H, 7-H), 3.79 and 3.81 (each s, 3H, OCH_3), 4.58 and 4.60 (each s, 1H, 4-H), 4.67 and 4.69 (s, 2H, N—H), 6.82–8.11 (m, 8H, Ph-H). IR (KBr) ν : 3324, 3253, 2182, 1611, 1526, 1465 cm^{-1} . MS (70 eV) m/z (%): 418.2 ($M^+ + 1$, 100). *Anal.* calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_5$: C 66.18, H 4.59, N 10.07; found C 66.27, H 4.55, N 10.01.

4m+5m ^1H NMR (CDCl_3 , 300 MHz) δ : 2.59–2.97 (m, 4H, 8-H +6-H), 3.57–3.67 (m, 1H, 7-H), 4.53 and 4.54 (each s, 1H, 4-H), 4.90 and 4.91 (each s, 2H, N—H), 5.94–5.95 (d, $J = 3.18$ Hz, 1H, Furyl-H), 6.27–6.29 (t, $J = 2.43$ Hz, 1H, Furyl-H), 6.92–6.95 (d, $J = 4.47$ Hz, 1H, Furyl-H), 6.92–7.30 (m, 5H, Ph-H). IR (KBr) ν : 3403, 3333, 2167, 1655, 1601, 1515, 1503 cm^{-1} . MS (70 eV) m/z (%): 333.1 ($M^+ + 1$, 100). *Anal.* calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3$: C 72.28, H 4.85, N 8.43; found C 72.35, H 4.80, N 8.37.

4n+5n ^1H NMR (CDCl_3 , 300 MHz) δ : 2.52–2.98 (m, 4H, 8-H +6-H), 3.40–3.51 (m, 1H, 7-H), 3.82 and 3.83 (each s, 3H, OCH_3), 3.88 and 3.89 (each s, 3H, OCH_3), 4.20 and 4.18 (each s, 1H, 4-H), 4.57 and 4.62 (each s, 2H, N—H), 6.07–6.08 (d, $J = 3.12$ Hz, 1H, Furyl-H), 6.31–6.33 (t, $J = 2.16$ Hz, 1H, Furyl-H), 6.68–6.69 (d, $J = 1.89$ Hz, 1H, Furyl-H), 6.70–7.36 (m, 3H, Ph-H). IR (KBr) ν : 3331, 3232, 2178, 1609, 1515, 1455 cm^{-1} . MS (70 eV) m/z (%): 393.1 ($M^+ + 1$, 100). *Anal.* calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_5$: C 67.34, H 5.14, N 7.14; found C 67.27, H 5.20, N 7.20.

4o+5o ^1H NMR (CDCl_3 , 300 MHz) δ : 2.59–2.97 (m, 4H, 8-H +6-H), 3.49–3.61 (m, 1H, 7-H), 4.53 and 4.54 (each s, 1H, 4-H), 4.90 and 4.91 (each s, 2H, N—H), 5.93–5.94 (d, $J = 3.24$ Hz, 1H, Furyl-H), 6.27–6.29 (t, $J = 2.22$ Hz, 1H, Furyl-H), 6.92–6.93 (d, $J = 4.80$ Hz, 1H, Furyl-H), 7.10–7.35 (m, 4H, Ph-H). IR (KBr) ν : 3345, 3223, 2149, 1605, 1551, 1435 cm^{-1} . MS (70 eV) m/z (%): 367.1 ($M^+ + 1$, 100). *Anal.* calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_2\text{O}_3$: C 65.49, H 4.12, N 7.64; found C 65.57, H 4.19, N 7.70.

4p+5p ^1H NMR (CDCl_3 , 300 MHz) δ : 2.52–2.97 (m, 4H, 8-H +6-H), 3.35–3.51 and 3.52–3.70 (m, 4H, 7-H), 3.47 (s,

3H, OCH_3), 4.45 and 4.46 (each s, 1H, 4-H), 4.67 and 4.70 (each s, 1H, N—H), 5.92–5.93 (d, $J = 3.21$ Hz, 1H, Furyl-H), 6.32–6.33 (d, $J = 1.86$ Hz, 1H, Furyl-H), 7.073–7.079 (d, $J = 1.71$ Hz, 1H, Furyl-H), 7.07–7.36 (m, 4H, Ph-H). IR (KBr) ν : 3295, 3212, 2166, 1601, 1508, 1433 cm^{-1} . MS (70 eV) m/z (%): 363.1 ($M^+ + \text{Na}$, 100). *Anal.* calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4$: C 69.60, H 5.01, N 7.73; found C 69.67, H 4.95, N 7.80.

Determination of crystal structure. A colorless transparent crystal of size $0.30 \times 0.20 \times 0.20 \text{ mm}^3$ was selected for the crystal structure measurement. The X-ray diffraction intensities were recorded on a Bruker SMART APEX CCD automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071073 \text{ nm}$) at 291(2)K. In the range of $2.05 < \theta < 25.99$, 2049 independent reflections were obtained. The structures were solved by direct methods using SHELXL-97 program. All the nonhydrogen atoms were refined on F^2 anisotropically with the full-matrix least squares method. Hydrogen atoms were added according to the theoretical methods.

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