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Synthesis and antimicrobial investigation of some novel phenyl pyrazole, azetidinone and diazenyl ethanone derivatives of benzofurans

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Salicylaldehyde and 2-hydroxy acetophenone on reaction with chloroacetone afford corresponding benzofurans **2a**, **2b** respectively. The compounds **2a** and **2b** on treatment with phenyl hydrazine in ethanol give **3a-d**. The products **3a-d** on treatment with DMF/$POCl_3$ underwent cyclization to produce substituted pyrazoles **4a-d**. The compounds **2a-b** on treatment with aromatic amines in ethanol afford the corresponding Schiff's bases **5a-h**, which on treatment with chloroacetyl chloride in dioxane produced azetidinones **6a-h**. Further, the compounds **2a** and **2b** on reaction with various diazotized aromatic amines produce phenyl diazenyl benzofurans **7a-h**. The structure of all newly synthesized compounds are established by elemental analysis and spectral studies. Their antimicrobial activities have been evaluated.

Keywords: Substituted phenyl pyrazole, azetidinone, diazenyl ethanone derivatives, benzofuran, antimicrobial activity

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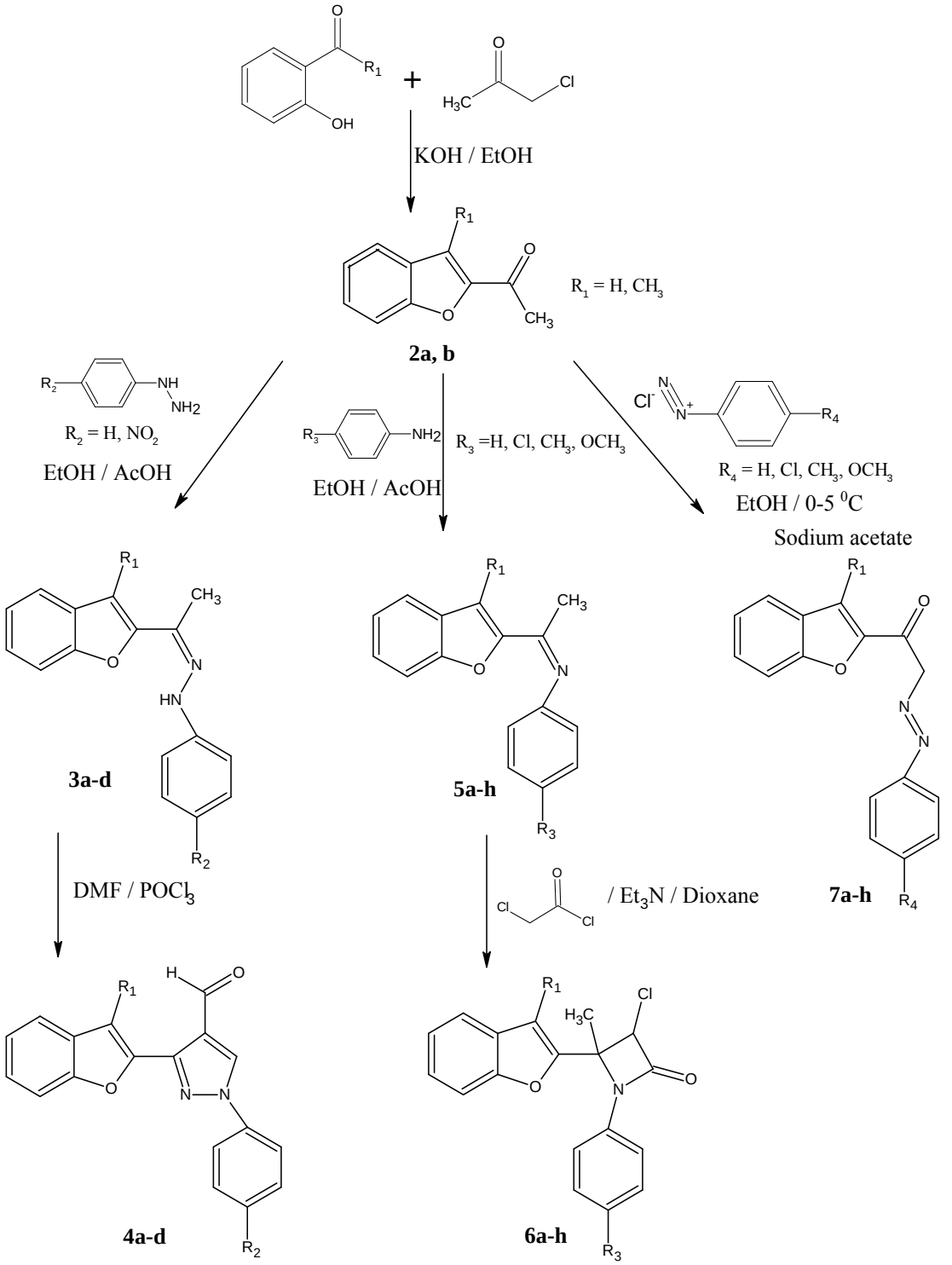
Benzofuran derivatives are known to present in natural products[1] reported to possess sedative and hypnotic[2], anticonvulsant[3], CNS stimulant[4], antibacterial[5-7] and antifungal activities[8]. Benzofurans are building blocks of optical brighteners[9]. Many of the natural benzofurans have physiological, pharmacological and toxic properties, as a result there is continuing interest in their chemical synthesis. Cyclization reactions of various types have been used to produce substituted benzofurans[10,11].

Nitrogen and oxygen containing heterocycles are compounds of biological interest. The development and design of new synthetic approach is a challenge for the organic chemist. The aldehydes and ketones on treatment with phenyl hydrazines form corresponding Schiff's bases. The Schiff's bases of aldehydes and ketones on treatment with DMF and $POCl_3$ undergo cyclization reaction forming pyrazole derivatives and get formylated on to the pyrazole ring[12]. Pyrazoles are well documented to possess antihypertensive[13], antibacterial[14, 15], anti-inflammatory[16,17], anti-tumor activities[18] and have wide applications as pharmaceutical, agrochemical agents[19,20]. Hence, in the first series of compounds the synthesis of the pyrazole derivatives of benzofuran are reported. Many azetidinone derivatives are also reported to possess significant anticonvulsant[21,22], antibacterial activity[23,24], anti-inflammatory[25], herbicidal[26], anti-degenerative, fungicidal[27] and antibiotic activity[28]. In view of the various biological activities of the azetidinone, a new series of azetidinone derivatives involving benzofuran by the reaction of benzofuran Schiff's bases with chloroacetyl chloride in dioxane are synthesized. In the third series, the modification of the side chain in benzofuran to produce a new series of benzofuran phenyldiazenyl derivatives is reported.

Results and Discussion

The synthesis of the key starting materials 2-acetylbenzofuran **2a** and 2-acetyl, 3-methylbenzofuran **2b** from salicylaldehyde and 2-hydroxyacetophenone has been well established[29].



Scheme I

The compounds **3a-d** and **3e-h** were synthesized by the reaction of **2a** and **2b** with phenyl hydrazine and 4-nitrophenylhydrazine in ethanol in presence of catalytic amount of acetic acid (**Scheme I**). The IR spectrum of **3a** exhibited the absence of the carbonyl absorption band, appearance of a band at 1595 cm^{-1} due to C=N and a broad band at 3250-3450 cm^{-1} due to N-H stretching respectively. The compounds **3a** on treatment with $DMF/POCl_3$ underwent cyclization and formylation producing 4-formyl-3-(benzofuro) *N*-phenylpyrazole carbaldehyde **4a**. Further, IR spectrum of **4a** showed absorption band at 1692 cm^{-1}

Table I—Antimicrobial and antifungal activity of compounds **4**, **6** and **7a-h**

Compd	Antimicrobial activity		Antifungal activity	
	P.aerugenosa	*S. aureus*	*A. niger*	*Curvularia*
4a	12	10	11	12
4b	11	12	10	11
4c	15	16	14	15
4d	15	16	18	17
6a	15	14	14	13
6b	13	12	13	14
6c	12	11	12	11
6d	14	15	11	12
6e	13	14	17	18
6f	15	16	18	16
6g	16	18	16	15
6h	14	15	15	14
7a	09	11	17	16
7b	12	13	15	14
7c	13	12	13	12
7d	14	15	12	13
7e	16	14	16	14
7f	13	15	13	13
7g	11	12	13	14
7h	14	13	16	17
Standard	24	26	22	24
DMF	+ve	+ve	+ve	+ve

+ve indicates growth of microbes,
Zone of inhibition expressed in mm.
Chloramphenicol, flucanazole were used as standards for antimicrobial and antifungal activity respectively.
DMF used as control.

attributed to aldehydic group and the absence of the N-H band confirms the cyclization to pyrazole ring. In the ^{1}H NMR spectrum ($CDCl_3$), a singlet appeared at δ 9.30 corresponds to aldehydic proton, one proton of the pyrazole ring appeared at 8.2 as singlet, multiplet at 6.68-7.20 integrated for 5 aromatic protons of the phenyl ring, at 7.56 (d, J = 8 Hz, 1H, C_7-H), 7.50 (d, J = 8.5 Hz, 1H, C_4-H), 7.21 (dd, J = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), and 6.62 (s, 1H, furan-H). The mass spectrum of **4a** gave a molecular ion peak at *m/z* 288, which confirmed the structure assigned to the compound. Similarly, the compounds **4b-d** were synthesized by treating the compounds **3b-d** with phenylhydrazine and 4-nitrophenylhydrazin respectively. The IR, ^{1}H NMR and the mass spectra of **4b-d** were in agreement with their structures. The compound **2a** was treated with aniline to get corresponding Schiff's base **5a**. This on further reaction with chloroacetyl chloride in presence of triethylamine in dioxane produced substituted azetidinone derivative **6a**. The IR spectrum of **6a** showed an absorption peak at 1648 due to carbonyl group of azetidinone ring and band at 685 cm^{-1} due to C-Cl stretching. In the ^{1}H NMR spectrum ($CDCl_3$) of **6a** showed a multiplet at δ 6.80-7.20 due to 5 aromatic protons of the phenyl ring, 7.65 (d, J = 8 Hz, 1H, C_7-H), 7.54 (d, J = 8.5 Hz, 1H, C_4-H), 7.28 (dd, J = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.65 (s, 1H, furan-H), a singlet at 2.89 attributed to single proton at the two position of the azetidinone ring and a singlet at 1.29 was due to-CH_3 protons. The mass spectrum of **6a** exhibited a molecular ion peak at *m/z* 312 confirmed the structure assigned to **6a**. Following the similar procedure compounds **6b-h** were synthesized by treating compounds **5b-h** with various aromatic amines. The IR, ^{1}H NMR and the mass spectra of the compounds **6b-h** were consistent with their structures.

Further, the compounds **2a** and **2b** on reaction with various diazotized aromatic amines in ethanol in presence of sodium acetate between 0-5 ºC, resulted in the formation of substituted phenyldiazenyl derivatives of benzofuran **7a-h**. The IR spectrum of **7a** showed absorption band at 1648 due to the carbonyl stretching frequency, and a band at 1600 cm^{-1} due to N=N stretching. In its ^{1}H NMR spectrum ($CDCl_3$) multiplets at δ 6.80-7.20 due to 5 aromatic protons of the phenyl ring, 7.60 (d, J = 8 Hz, 1H, C_7-H), 7.53 (d, J = 8.5 Hz, 1H, C_4-H), 7.27 (dd, J = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.66 (s, 1H, furan-H), and a singlet at 2.87 corresponds to two protons of-CH_2 were observed. In its mass spectrum molecular ion peak at *m/z* 264 confirmed the structure assigned to the molecule. The IR, ^{1}H NMR and mass spectra of **7b-h** were in good agreement with their assigned structures.

The antibacterial activity results of the newly synthesized compounds are shown in **Table I**, which confirms the compounds **6e-g** have shown significant inhibitory activity against all the microbes and fungi. All the other newly synthesized compounds have shown moderate inhibitory activity against the microbes and the fungi.

Experimental Section

All the chemicals used were of analytical grade. Melting points were uncorrected, determined in open capillary. Purity of the compounds was checked by TLC on silica gel and were purified using column chromatography. ^{1}H NMR spectra were recorded on a

Bruker supercon FT NMR (300 MHz) spectrometer using $CDCl_3$-d_1 as solvent, TMS as internal standard and the chemical shifts are expressed in δ units. IR spectra were recorded by using JASCO FT/IR-300E spectrophotometer from a KBr pelleted sample. Mass spectral data were obtained on a Jeol JMS-D 300 mass spectrometer operating at 70 eV.

Antimicrobial activity

The *in vitro* antimicrobial activity was carried out against 24 hr old cultures of two bacteria and two fungi by cup-plate method[30]. All the newly synthesized compounds were screened for the growth inhibitory activity against *Pseudomonas aerugenosa* and *Staphylococcus aureus* and antifungal activity against *Aspergillus niger* and *Curvularia.* Chloramphenicol and flucanazole were used as standards for antimicrobial and antifungal activity respectively. The compounds were tested at a concentration of 0.001 mole/mL in DMF against all organisms. The zone of inhibition was compared with the standard drug after 24 hr of incubation at 25°C for antibacterial activity and 48 hr at 30°C for antifungal activity. All compounds showed comparable antimicrobial activities. Results are reported in **Table I**.

Synthesis of 3-(1-benzofuran-2-yl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde 4a. The compound 1-(1-benzofuran-2-yl)ethanone **2a** (0.01 mole, 1.60 g) was taken in a round bottom flask dissolved in 25 mL ethanol and catalytic amount of acetic acid was added. To the above solution, phenyl hydrazine (0.01 mole, 1.10 g) was added dropwise. The mixture was stirred at room temp for about 1 hr. After the completion of the reaction as indicated by TLC, the Schiff's base **3a** formed was isolated and recrystallized from ethanol. Similarly, the compounds **3b-d** were synthesized using the above procedure. To the Vilsmeier Haack reagent, prepared from dimethyl formamide (10 mL) and phosphorous oxychloride (1.1 mL), the hydrazone **3a** (0.01 mole, 2.5 g) was added portion wise and the reaction mixture was heated to 60°C for about 4 hr and poured into crushed ice. The mixture was then neutralized with NaOH, heated to 50-60°C, cooled and acidified to *p*H-6 with 10 *M* HCl. The solid thus separated was filtered and recrystallised from methanol. The compounds **4b-d** were synthesized by following the similar procedure.

Synthesis of 4-(1-benzofuran-2-yl)-3-chloro-4-methyl-1-phenylazetidin-2-one 6a. 1-(1-benzofuran-2-yl) ethanone **2a** (0.01 mole, 1.6 g) was treated with aniline (0.01 mole, 1 g) in ethanol (25 mL), in presence of catalytic amount of AcOH producing *N*-[1-(1-benzofuran-2-yl)ethylidene]-*N*-phenyl amine **5a**. The product was isolated and recrystallized from ethanol. The compound **5a** (0.01mole, 2.5 g) in dioxane (25 mL**)** in presence of triethylamine (0.01 mole, 0.2 mL) was refluxed with chloroacetyl chloride (2 mL) for 4-5 hr. After the completion of the reaction by confirmation with TLC, the reaction mixture was cooled, poured into crushed ice, the solid obtained was recrystallised from ethanol. Similarly the compounds **6b-h** were synthesized.

Synthesis of 1-(1-benzofuran-2-yl)-2-(phenyl-diazenyl)ethanone 7a. The substituted diazonium salts of the different aromatic amines were prepared according to the reported procedure[31]. The compound 1-(1-benzofuran-2-yl) ethanone **2a** (0.01 mole, 1.6 g) in 25 mL ethanol and anhydrous sodium acetate (1g) cooled to 0 ºC. To the above mixture, the diazonium salt of the aniline was added dropwise (0.01 mole) and the reaction mixture was stirred for 2 hr. The reaction mixture was poured into water, red solid separated out was extracted with chloroform, dried over anhydrous sodium sulphate. Similarly, the compounds **7b-h** were synthesized by following the above procedure.

1-(1-Benzofuran-2-yl)ethanone phenylhydrazone 3a: Yield 67%, m.p. 85-87°C. IR (KBr): 3250-3450 (N-H), 1595 (C=N), 1095-1105 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 8.30 (s, 1H,-NH), 7.57 (d, J = 8 Hz, 1H, C_7-H), 7.51 (d, J = 8.5 Hz, 1H, C_4-H), 7.25 (dd, J = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.68 (s, 1H, furan-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 1.30 (s, 3H,-N=C-CH_3); MS: *m/z* 250 (M^+); (Found: C, 76.71; H, 5.61; N, 11.11. Calcd for $C_{16}H_{14}N_2O$:C, 76.78; H, 5.64; N, 11.19%)

1-(1-Benzofuran-2-yl)ethanone (4-nitrophenyl)-hydrazone 3b: Yield 72%, m.p. 97-99°C. IR (KBr): 3250-3450 (N-H), 1608 (C=N), 1090-1100 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 8.29 (s, 1H, NH), 7.56(d, J = 8 Hz, 1H, C_7-H), 7.50 (d, J = 8.5 Hz, 1H, C_4-H), 7.24 (dd, J = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.67 (s, 1H, furan-H), 7.21 (d, J = 8 Hz, 4H, phenyl Ar-H), 1.29 (s, 3H, N=C-CH_3); MS: *m/z* 295(M^+); (Found: C, 65.00; H, 4.42; N, 14.17. Calcd for $C_{16}H_{13}N_3O_3$: C, 65.08; H, 4.44; N, 14.23%)

1-(3-Methyl-1-benzofuran-2-yl)ethanone phenyl-hydrazone 3c: Yield 65%, m.p. 90-92°C. IR (KBr): 3250-3450 (N-H), 1605 (C=N), 1097-1108 cm^{-1}

(C-O-C); ^{1}H NMR ($CDCl_3$): δ 8.30 (s, 1H, NH), 7.56 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.25 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 1.75 (s, 3H, furan-CH_3), 1.31 (s, 3H, N=C-CH_3); MS: *m/z* 264 (M^+); (Found: C, 77.19; H, 6.04; N, 10.55. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60%)

1-(3-Methyl-1-benzofuran-2-yl)ethanone (4-nitrophenyl)hydrazone 3d: Yield 68%, m.p. 105-107°C. IR (KBr): 3250-3450 (N-H), 1609 (C=N), 1092-1107 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 8.32 (s, 1H, NH), 7.56 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.15 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 1.81 (s, 3H, furan-CH_3), 1.28 (s, 3H,-N=C-CH_3); MS: *m/z* 309 (M^+); (Found: C, 65.95; H, 4.77; N, 13.51. Calcd for $C_{17}H_{15}N_3O_3$: C, 66.01;H, 4.89; N, 13.58%)

3-(1-Benzofuran-2-yl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde 4a: Yield 73%, m.p. 116-18°C. IR (KBr): 1692 (CHO), 1605 (C=N), 1100-1110 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 9.30 (s, 1H,-CHO), 8.20 (s, 1H, pyrazole-H), 7.56 (d, *J* = 8 Hz, 1H, C_7-H), 7.50 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.21 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.62 (s, 1H, furan-H), 6.68-7.20 (m, 5H, phenyl Ar-H); MS: *m/z* 288 (M^+); (Found: C, 74.94; H, 4.15; N, 9.68. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72%)

3-(1-Benzofuran-2-yl)-1-(4-nitrophenyl)-1H-pyrazole-4-carbaldehyde 4b: Yield 76%, m.p. 125-27°C. IR (KBr): 1685 (CHO), 1612 (C=N), 1089-1105 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 9.33 (s, 1H,-CHO), 8.14 (s, 1H, pyrazole-H), 7.58 (d, *J* = 8 Hz, 1H, C_7-H), 7.50 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.65 (s, 1H, furan-H), 7.16 (d, *J* = 8 Hz, 4H, phenyl Ar-H); MS: *m/z* 333 (M^+); (Found: C, 64.82; H, 3.26; N, 12.54, Calcd for $C_{18}H_{11}N_3O_4$: C, 64.86; H, 3.33; N, 12.61%)

3-(3-Methyl-1-benzofuran-2-yl) -1 - phenyl-1*H*-pyrazole-4-carbaldehyde 4c: Yield 71%, m.p. 133-35°C. IR (KBr): 1687 (CHO), 1607 (C=N), 1100-1110 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 9.35 (s, 1H,-CHO), 8.07 (s, 1H, pyrazole-H), 7.58 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.24 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 1.80 (s, 3H, furan-CH_3); MS: *m/z* 302 (M^+); (Found: C, 75.43; H, 4.62; N, 9.22. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48;H, 4.67; N, 9.27%)

4-Methyl-3-(3-methyl-1-benzofuran-2-yl)-1-(4-nitrophenyl)-1*H*-pyrazol 4d: Yield 70%, m.p. 141-43°C. IR (KBr): 1678 (CHO), 1603 (C=N), 1103-1115 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 9.30 (s, 1H,-CHO), 8.10 (s, 1H, pyrazole-H), 7.58 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.17 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 1.77 (s, 3H, furan-CH_3); MS: *m/z* 347 (M^+); (Found: C, 65.68; H, 3.71; N, 11.96. Calcd for $C_{19}H_{13}N_3O_4$: C, 65.70; H, 3.77; N, 12.01%)

***N*-[1-(1-Benzofuran-2-yl)ethylidene]-*N*-phenylamine 5a**:Yield 65%, m.p. 111-13°C. IR (KBr): 1605 (C=N), 1095-1105 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 7.59 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.65 (s, 1H, furan-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 1.28 (s, 3H, N=C-CH_3); MS: *m/z* 235 (M^+); (Found: C, 81.62; H, 5.50; N, 5.90. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95%)

N-[1-(1-Benzofuran-2-yl)ethylidene]-N-(4-methoxyphenyl)amine 5b: Yield 68%, m.p. 121-23°C. IR (KBr): 1607 (C=N), 1100-1110 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 7.58 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.67 (s, 1H, furan-H), 7.10 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 3.86 (s, 3H, OCH_3), 1.31 (s, 3H, N=C-CH_3); MS: *m/z* 265 (M^+); (Found: C, 76.91; H, 5.63; N, 5.21. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%)

N-[1-(1-Benzofuran-2-yl)ethylidene]-N-(4-methylphenyl)amine 5c: Yield 65%, m.p. 132-33°C. IR (KBr): 1609 (C=N), 1096-1110 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 7.58 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.66 (s, 1H, furan-H), 7.12 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.34 (s, 3H, Ar-CH_3),1.28 (s, 3H, N=C-CH_3); MS: *m/z* 249 (M^+); (Found: C, 81.85; H, 6.00; N, 5.56. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62%)

N-[1-(1-Benzofuran-2-yl)ethylidene]-N-(4-chlorophenyl)amine 5d: Yield 72%, m.p. 142-44°C. IR (KBr): 1608(C=N), 1095-1110 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.28 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.68 (s, 1H, furan-H), 7.15 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 1.33 (s, 3H, N=C-CH_3); MS: *m/z* 270 (M^+); (Found: C, 71.22; H, 4.41; N, 5.13. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19%)

***N*-[1-(3-Methyl-1-benzofuran-2-yl)ethylidene]-*N*-phenylamine 5e**: Yield 69%, m.p. 153-55°C. IR (KBr): 1595 (C=N), 1095-1115 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.54 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz,

2H, $C_{5,6}$-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 1.79 (s, 3H, furan-CH_3), 1.32 (s, 3H, N=C-CH_3); MS: *m/z* 249 (M^+); (Found: C, 81.82; H, 6.00; N, 5.57. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62%)

***N*-(4-Methoxyphenyl)-*N*-[1-(3-methyl-1-benzofuran-2-yl)ethylidene]amine 5f**: Yield 69%, m.p. 137-39°C. IR (KBr): 1610 (C=N), 1090-1107 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.61 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.18 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 3.86 (s, 3H, OCH_3), 1.81 (s, 3H, furan-CH_3), 1.31 (s, 3H, N=C-CH_3); MS: *m/z* 279 (M^+); (Found: C, 77.35; H, 6.09; N, 4.96. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01%)

***N*-[1-(3-Methyl-1-benzofuran-2-yl)ethylidene]-*N*-(4-methylphenyl)amine 5g**: Yield 70%, m.p. 150-52°C. IR (KBr): 1607 (C=N), 1095-1110 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.58 (d, *J* = 8 Hz, 1H, C_7-H), 7.50 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.15 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.36 (s, 3H, Ar-CH_3), 1.80 (s, 3H, furan-CH_3), 1.30 (s, 3H, N=C-CH_3); MS: *m/z* 263 (M^+); (Found: C, 81.95; H, 6.45; N, 5.25. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%)

N-(4-Chlorophenyl)-N-[1-(3-methyl-1-benzofuran-2-yl)ethylidene]amine 5h: Yield 64%, m.p. 147-49°C. IR (KBr): 1605 (C=N), 1095-1105 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.61 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.16 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 1.83 (s, 3H, furan-CH_3), 1.28 (s, 3H, N=C-CH_3); MS: *m/z* 283 (M^+); (Found: C, 71.89; H, 4.89; N, 4.90. Calcd for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94%)

4-(1-Benzofuran-2-yl)-3-chloro-4-methyl-1-phenylazetidin-2-one 6a: Yield 73%, m.p. 133-35°C. IR (KBr): 1648 (C=O), 1610 (C=N), 1090-1100 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.65 (d, *J* = 8 Hz, 1H, C_7-H), 7.54 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.28 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.65 (s, 1H, furan-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 2.89 (s, 1H, CH-Cl), 1.29 (s, 3H,-N-C-CH_3); MS: *m/z* 312 (M^+); (Found: C, 69.25; H, 4.48; N, 4.43. Calcd for $C_{18}H_{14}ClNO_2$: C, 69.35; H, 4.53; N, 4.49%)

4-(1-Benzofuran-2-yl)-3-chloro-1-(4-methoxyphenyl)-4-methylazetidin-2-one 6b: Yield 67%, m.p. 144-46°C. IR (KBr): 1653 (C=O), 1605 (C=N), 1095-1110 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$):δ 7.63 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.67 (s, 1H, furan-H), 7.20 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 3.88 (s, 3H, OCH_3), 2.85 (s, 1H, CH-Cl), 1.30 (s, 3H,-N-C-CH_3); MS: *m/z* 341 (M^+); (Found: C, 66.71; H, 4.65; N, 4.06. Calcd for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10%)

4-(1-Benzofuran-2-yl)-3-chloro-4-methyl-1-(4-methylphenyl)azetidin-2-one 6c: Yield 75%, m.p. 165-66°C. IR (KBr): 1655 (C=O), 1600 (C=N), 1096-1105 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.59(d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.68 (s, 1H, furan-H), 7.10 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.87 (s, 1H, CH-Cl), 2.23 (s, 3H, Ar-CH_3), 1.31 (s, 3H,-N-C-CH_3); MS: *m/z* 326 (M^+); (Found: C, 69.87; H, 4.87; N, 4.25. Calcd for $C_{19}H_{16}ClNO_2$: C, 70.05; H, 4.95; N, 4.30%)

4-(1-Benzofuran-2-yl)-3-chloro-1-(4-chlorophenyl)-4-methylazetidin-2-one 6d: Yield 72%, m.p. 167-69°C. IR (KBr): 1647 (C=O), 1605 (C=N), 1095-1107 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.66 (s, 1H, furan-H), 7.15 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.86 (s, 1H, CH-Cl), 1.28 (s, 3H,-N-C-CH_3); MS: *m/z* 346 (M^+); (Found: C, 62.32; H, 3.71; N, 4.00. Calcd for $C_{18}H_{13}Cl_2NO_2$: C, 62.45; H, 3.78; N, 4.05%)

3-Chloro-4-methyl-4-(3-methyl-1-benzofuran-2-yl)-1-phenylazetidin-2-one 6e: Yield 66%, m.p. 171-73°C. IR (KBr): 1650 (C=O), 1615 (C=N), 1100-1115 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.63 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.80-7.20 (m, 5H, phenyl Ar-H) 2.89 (s, 1H, CH-Cl), 1.81 (s, 3H, furan-CH_3), 1.29 (s, 3H,-N-C-CH_3); MS: *m/z* 326 (M^+); (Found: C, 69.96; H, 4.88; N, 4.24. Calcd for $C_{19}H_{16}ClNO_2$: C, 70.05; H, 4.95; N, 4.30%)

3-Chloro-1-(4-methoxyphenyl)-4-methyl-4-(3-methyl-1-benzofuran-2-yl)azetidin-2-one 6f: Yield 67%, m.p. 162-64°C. IR (KBr): 1650 (C=O), 1607 (C=N), 1095-1110 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.60(d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.24 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.16 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 3.88 (s, 3H, OCH_3), 2.90 (s, 1H, CH-Cl), 1.81 (s, 3H, furan-CH_3), 1.29 (s, 3H,-N-C-CH_3); MS: *m/z* 356 (M^+); (Found: C, 67.37; H, 5.03; N, 3.87. Calcd for $C_{20}H_{18}ClNO_3$: C, 67.51; H, 5.10; N, 3.94%)

3-Chloro-4-methyl-4-(3-methyl-1-benzofuran-2-yl)-1-(4-methylphenyl)azetidin-2-one 6g: Yield 73%, m.p. 167-69°C. IR (KBr): 1648 (C=O), 1605

(C=N), 1096-1110 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$): δ 7.61 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.14 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.85 (s, 1H, CH-Cl), 2.25 (s, 3H, Ar-CH_3), 1.78 (s, 3H, furan-CH_3), 1.31 (s, 3H,-N-C-CH_3); MS: *m/z* 340 (M^+); (Found: C, 70.45; H, 5.27; N, 4.07. Calcd for $C_{20}H_{18}ClNO_2$: C, 70.61; H, 5.34; N, 4.12%)

3-Chloro-1-(4-chlorophenyl)-4-methyl-4-(3-methyl-1-benzofuran-2-yl)azetidin-2-one 6h: Yield 71%, m.p. 180-82°C. IR (KBr): 1650 (C=O), 1610 (C=N), 1095-1110 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$):δ 7.59 (d, *J* = 8 Hz, 1H, C_7-H), 7.50 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.15 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 1.79 (s, 3H, furan-CH_3), 2.89 (s, 1H, CH-Cl), 1.29 (s, 3H,-N-C-CH_3); MS: *m/z* 360 (M^+); (Found: C, 63.23; H, 4.13; N, 3.82. Calcd for $C_{19}H_{15}Cl_2NO_2$: C, 63.35; H, 4.20; N, 3.89%)

1-(1-Benzofuran-2-yl)-2(-phenyldiazenyl)ethanone 7a: Yield 70%, m.p. 95-97°C. IR (KBr): 1648 (C=O), 1600 (C=N), 1095-1110 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.66 (s, 1H, furan-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 2.87 (s, 2H, CH_2); MS: *m/z* 264 (M^+); (Found: C, 72.56; H, 4.51; N, 10.55. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60%)

1-(1-Benzofuran-2-yl)-2-(4-methoxyphenyl) diazenylethanone 7b: Yield 72%, m.p. 197-109°C. IR (KBr): 1650 (C=O), 1605 (C=N), 1097-1112 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.59 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.65 (s, 1H, furan-H), 7.12 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 3.87 (s, 3H, OCH_3), 2.87 (s, 2H, CH_2); MS: *m/z* 293 (M^+); (Found: C, 69.25; H, 4.70; N, 9.47. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52%)

1-(1-Benzofuran-2-yl)-2-(4-methylphenyl)diazenyl ethanone 7c: Yield 75%, m.p. 87-89°C. IR (KBr): 1648 (C=O), 1595 (C=N), 1090-1105 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.27 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.68 (s, 1H, furan-H), 7.18 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.33 (s, 3H, Ar-CH_3), 2.86 (s, 2H, CH_2); MS: *m/z* 278 (M^+); (Found: C, 73.21; H, 5.00; N, 10.00. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07%)

1-(1-Benzofuran-2-yl)-2-(4-chlorophenyl)diazenylethanone 7d: Yield 68%, m.p. 124-26°C. IR (KBr): 1647 (C=O), 1605 (C=N), 1095-1110 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.65 (s, 1H, furan-H), 7.16 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.85 (s, 2H, CH_2); MS: *m/z* 299 (M^+); (Found: C, 64.24; H, 3.67; N, 9.31, Calcd for $C_{16}H_{11}ClN_2O_2$: C, 64.33; H, 3.71; N, 9.38%)

1-(3-Methyl-1-benzofuran-2-yl)-2-[-phenyldiazenyl]ethanone 7e: Yield 65%, m.p. 102-104°C. IR (KBr): 1655 (C=O), 1607 (C=N), 1100-1115 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.61 (d, *J* = 8 Hz, 1H, C_7-H), 7.53 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.24 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 6.80-7.20 (m, 5H, phenyl Ar-H), 2.84 (s, 2H, CH_2), 1.76 (s, 3H, furan-CH_3); MS: *m/z* 278 (M^+); (Found: C, 73.31; H, 5.00; N, 10.00. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07%)

2-[-(4-Methoxyphenyl)diazenyl]-1-(3-methyl-1-benzofuran-2-yl)ethanone 7f: Yield 66%, m.p. 114-16°C. IR (KBr): 1648 (C=O), 1604 (C=N), 1095-1110 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.63 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.25 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.18 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 3.85 (s, 3H, OCH_3), 2.86 (s, 2H, CH_2), 1.81 (s, 3H, furan-CH_3); MS: *m/z* 308 (M^+); (Found: C, 70.05; H, 5.19; N, 9.03. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09%)

1-(3-Methyl-1-benzofuran-2-yl)-2-[-(4-methylphenyl)diazenyl]ethanone 7g: Yield 67%, m.p. 108-10°C. IR (KBr): 1650 (C=O), 1605 (C=N), 1100-1115 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 1H, C_7-H), 7.50 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.24 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.16 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.26 (s, 3H, Ar-CH_3), 2.85 (s, 2H, CH_2), 1.79 (s, 3H, furan-CH_3); MS: *m/z* 292 (M^+); (Found: C, 73.82; H, 5.45; N, 9.52. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58%)

2-[-(4-Chlorophenyl)diazenyl]-1-(3-methyl-1-benzofuran-2-yl)ethanone 7h: Yield 70%, m.p. 125-27°C. IR (KBr): 1652 (C=O), 1595 (C=N), 1098-1115 (C-O-C); ^1H NMR ($CDCl_3$): δ 7.61 (d, *J* = 8 Hz, 1H, C_7-H), 7.52 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.26 (dd, *J* = 7.6, 8.5 Hz, 2H, $C_{5,6}$-H), 7.18 (d, *J* = 8 Hz, 4H, phenyl Ar-H), 2.87 (s, 2H, CH_2), 1.81 (s, 3H, furan-CH_3); MS: *m/z* 312 (M^+); (Found: C, 65.07; H, 4.16; N, 8.91. Calcd for $C_{17}H_{13}ClN_2O_2$: C, 65.19; H, 4.19; N, 8.96%).

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