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A SIMPLE APPROACH TO THE SYNTHESIS OF FUROFURANS AND FUROPYRROLES USING 3-PHENACYLATED TETRAHYDRO-2-IMINO-3-FURANCARBONITRILES

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Abstract – A new and easy synthetic route to furo[2,3-*b*]furans **7a–d** and furo[2,3-*b*]pyrroles **8a–d** has been achieved by the *C*-phenacylation/cyclization reactions of 2-amino-4,5-dihydro-3-furancarbonitrile (**5**). Thermal treatment of the key intermediate 3-phenacylated tetrahydro-2-imino-3-furancarbonitriles **6a–d**, which were prepared from compound **5** and phenacyl bromides, *e.g.* phenacyl bromide, 4-chlorophenacyl bromide, 4-methylphenacyl bromide and 4-methoxyphenacyl bromide, with acetic anhydride caused intramolecular cyclization to yield the corresponding furo[2,3-*b*]furans **7a–d**. On the other hand, methanolic sodium methoxide-assisted cyclocondensation of compounds **6a–d** gave the corresponding furo[2,3-*b*]pyrroles **8a–d**.

INTRODUCTION

The fused heterocyclic systems represent important building blocks due to their aromaticity. Aromaticity is considered as one of the most important concepts in modern organic chemistry. The quantitative relationships among the magnetic, energetic and geometric criteria of aromaticity have been demonstrated recently for a wide ranging set of five-membered heterocycles.[1–6] There are four possible modes of 5:5 fusion of the simple five-membered heterocycles leading to structures **1–4**, wherein X and Y may be the same or different heteroatoms and represent O, NR, S, Se and very rarely Te (Figure 1). The positional isomers **1–4** have interesting features and their stabilities and properties are related to the positions of heteroatoms.

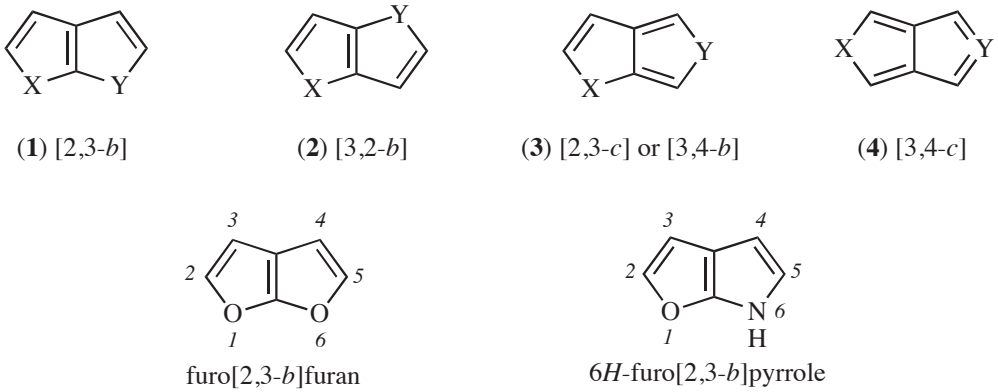


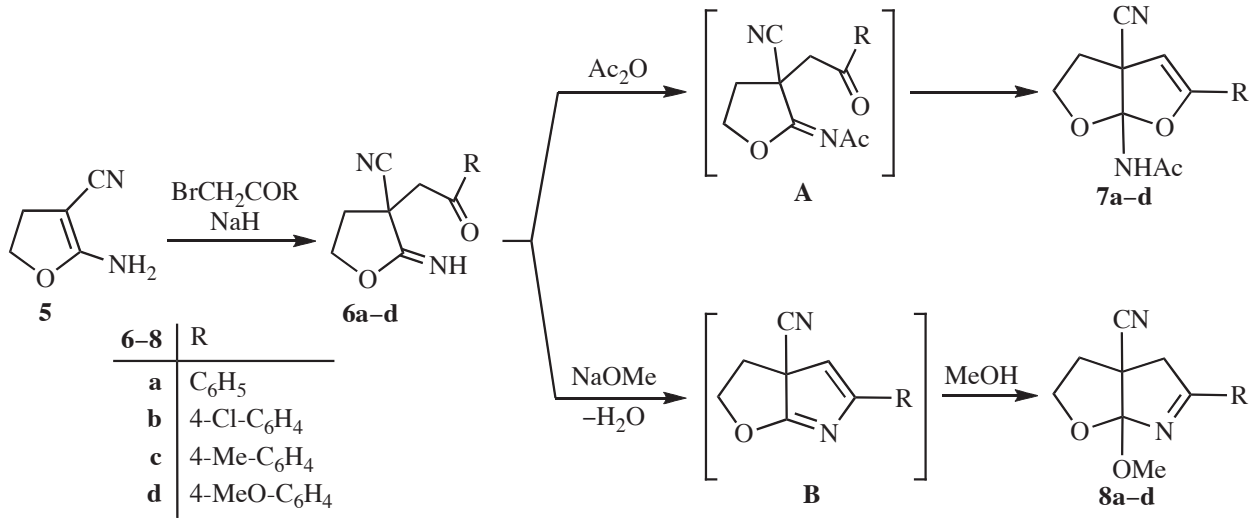
Figure 1. Typical heterobicycles: bicyclic 5-5 systems

On the other hand, hydrogenated heterobicycles are an important class of natural products and have potential uses in many fields. For example it is known that the partially hydrogenated furo[2,3-*b*]furan ring is embodied in large number of natural products, particularly in some insect antifeeding compounds such as clerodin and azadirachtin.[7–12] For this reason, the synthesis of hydrogenated heterobicycles continues to attract attention and provides an interesting challenge. Although many synthetic methods for such furo[2,3-*b*]furans have been reported,[13–18] there are relatively few methods in the literature describing the preparation of furo[2,3-*b*]pyrroles.[19] Therefore, there is still a need for synthetic methods suitable for their analogues. In the course of our studies on heterocyclic β-enaminonitriles, we have discussed the synthesis of fused heterocyclic compounds such as furo[2,3-*d*]pyrimidines,[20,21] furo[2,3-*b*]pyridines[22] and thieno[3,4-*b*]pyrroles.[23] In this context, we have been interested in the development of the methods for the synthesis of heterobicycles, such as furofurans and furopyrroles. Thus, we herein wish to report a simple and efficient method for preparing furo[2,3-*b*]furan and furo[2,3-*b*]pyrrole derivatives **7a–d** and **8a–d**.

RESULTS AND DISCUSSION

Firstly, we investigated the reaction of 3-phenacylated tetrahydro-2-imino-3-furancarbonitrile **6a** and acetic anhydride (Scheme 1). 3-Phenacylated compound **6a** was easily prepared by treatment of 2-amino-4,5-dihydro-3-furancarbonitrile (**5**) and phenacyl bromide according to our previous procedure.[24] In addition, we have also shown the *C*-phenacylation reaction of 4,5-dihydro-2-(substituted amino)-3-furancarbonitriles with phenacyl bromides.[25] Hence, we tried the intramolecular cyclization of 3-phenacylated tetrahydro-2-imino-3-furancarbonitriles as the key intermediates. As a consequence, when compound **6a** was treated with acetic anhydride at 80 °C for 3 h, furo[2,3-*b*]furan **7a** was obtained in 89% yield (Scheme 1). This compound **7a** was characterized by spectroscopic analysis (see experimental section). For example, the IR spectrum of **7a** displays bands at 3179 cm^{-1} due to an amido group and at 1668 and 1649 cm^{-1} due to an amido carbonyl groups. The ^1H NMR spectrum of **7a** exhibits a three-proton singlet at δ 1.92 attributable to the *N*-acetyl protons, a one-proton singlet at δ 5.79

attributable to the olefin proton and a one-proton singlet at δ 9.42 due to the acetylamino proton. The ^{13}C NMR spectrum of **7a** shows a signal at δ 22.7 due to the methyl carbon of the *N*-acetyl function, a signal at δ 95.8 due to the olefin carbon, and a signal at δ 169.3 due to the amido carbonyl carbon. Formation of **7a** is assumed to proceed *via* *N*-acetylation of **6a** to yield the non-isolable intermediate **A**, which subsequently cyclized to **7a**.



Scheme 1

Table 1. One-pot synthesis of furo[2,3-*b*]furan and furo[2,3-*b*]pyrrole derivatives **7a–d** and **8a–d** starting from **5**

Entry	Substrate	Product	Yield (%)	Entry	Substrate	Product	Yield (%)
1	**5**	**7a**	56	5	**5**	**8a**	40
2	**5**	**7b**	57	6	**5**	**8b**	25
3	**5**	**7c**	42	7	**5**	**8c**	24
4	**5**	**7d**	70	8	**5**	**8d**	54

Next, we also studied the behavior of **6a** under the basic conditions using sodium methoxide. Thus, **6a** reacted in methanolic sodium methoxide at 60 °C for 2 h to afford the furo[2,3-*b*]pyrrole **8a** in 65% yield most likely *via* the nucleophilic addition of methanol to the intermediate **B**, which would be probably formed by cyclocondensation *via* dehydration (Scheme 1). The ^{1}H NMR spectrum of **8a** exhibits a three-proton singlet at δ 3.75 attributable to the methoxy protons. The ^{13}C NMR spectrum of **8a** shows a signal near δ 52.7 due to the methyl carbon of the methoxy function and a signal at δ 170.7 due to the C-5 carbon (see experimental section). In these cyclization reactions, none of the possible *N*-acetylated product **A** and condensed compound **B** could be detected, and this could be explained by the instability structure of **A** and **B**. In fact, furofuran **7a** and furopyrrole **8a** were the only isolable products.

On the basis of these results, we have tried to directly construct furofuran and furopyrrole derivatives **7a–d** and **8a–d** starting from compound **5** and phenacyl bromides in a one-pot process (Scheme 1). The best results are shown in Table 1. Indeed, when a mixture of **5** and phenacyl bromides, *e.g*. phenacyl bromide, 4-chlorophenacyl bromide, 4-methylphenacyl bromide and 4-methoxyphenacyl bromide, in the presence of sodium hydride in DMF was stirred at room temperature for 1 h and then the reaction mixture was treated with acetic anhydride at 80 °C for 3 h, the desired furo[2,3-*b*]furans **7a–d** were obtained in moderate yields (entries 1–4 and see experimental section). Similarly, after the *C*-phenacylation of **5**, the resulting mixture was treated with sodium methoxide in refluxing methanol for 2 h, the furo[2,3-*b*]pyrroles **8a–d** were obtained in moderate yields (entries 5–8). By comparison of the IR spectra, NMR spectra, mass spectra and elemental analyses of **7b–d** and **8b–d** it seems that the structural assignments given to these compounds are correct.

In conclusion, we have developed a simple method for the synthesis of furofuran and furopyrrole derivatives **7a–d** and **8a–d**, proceeding by *C*-phenacylation and subsequent intramolecular cyclization when 2-amino-4,5-dihydro-3-furancarbonitrile (**5**) is treated with phenacyl bromides. This methodology offers significant advantages with regard to the simplicity of operation. Functionalized furofuran and furopyrrole derivatives are important synthons in organic synthesis and for the preparation of biologically active compounds with interest in medicinal chemistry.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-A500 spectrometer at 500.00 and 125.65 MHz, respectively. The ^{1}H and ^{13}C chemical sifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard. Positive FAB mass spectra were obtained on a JEOL JMS-700T spectrometer. Elemental analyses were performed on YANACO MT-6 CHN analyzer. The starting compound, 2-amino-4,5-dihydro-3-furancarbonitrile (**5**), was prepared in this laboratory according to the procedure reported in literature.[26]

General procedure for the preparation of furofurans 7a–d from 5, phenacyl bromides and acetic anhydride.

To an ice-cooled and stirred solution of **5** (1.10 g, 10 mmol) in DMF (10 mL) was added 60% NaH (0.40 g, 10 mmol). The stirring was continued at rt until evolution of gas ceased. To the obtained mixture was added phenacyl bromide (1.99 g, 10 mmol), 4-chlorophenacyl bromide (2.33 g, 10 mmol), 4-methylphenacyl bromide (2.13 g, 10 mmol) or 4-methoxyphenacyl bromide (2.29 g, 10 mmol) with stirring and then the mixture was stirred at rt for 1 h. After removal of the solvent *in vacuo*, acetic anhydride (3 mL) was added to the residue. The resulting mixture was stirred at 80 °C for 3 h and then

cold water was added to the reaction mixture. The precipitate was isolated by filtration, washed with water, dried and recrystallized from an appropriate solvent to give **7a–d**.

***N*-(3a-Cyano-2,3,3a,6a-tetrahydro-5-phenylfuro[2,3-*b*]furan-6a-yl)acetamide (7a)**

Colorless needles (1.50 g, 56%), mp 167–169 °C (acetone/petroleum ether); IR (KBr): 3179 (NH), 2247, 2234 (CN), 1668, 1649 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): 1.92 (s, 3H, $COCH_3$), 2.44 (dd, J = 4.6, 7.9 Hz, 1H, 3-H), 2.74–2.81 (m, 1H, 3-H), 3.70–3.76 (m, 1H, 2-H), 4.21 (t, J = 7.9 Hz, 1H, 2-H), 5.79 (s, 1H, 4-H), 7.42–7.45 (m, 3H, aryl H), 7.59–7.61 (m, 2H, aryl H), 9.42 (br s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 22.7 ($COCH_3$), 37.5 (C-3), 53.8 (C-3a), 66.5 (C-2), 95.8 (C-4), 118.7 (CN), 120.3 (C-6a), 125.3, 128.1, 128.5, 129.8 (C aryl), 155.8 (C-5), 169.3 (CO); ms: m/z 271 $[M+H]^+$; Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36; Found: C, 66.68; H, 5.26; N, 10.35.

***N*-[5-(4-Chlorophenyl)-3a-cyano-2,3,3a,6a-tetrahydrofuro[2,3-*b*]furan-6a-yl]acetamide (7b)**

Colorless needles (1.72 g, 57%), mp 188–190 °C (acetone/petroleum ether); IR (KBr): 3306 (NH), 2244 (CN), 1695 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.92 (s, 3H, $COCH_3$), 2.44 (dd, J = 4.6, 12.2 Hz, 1H, 3-H), 2.72–2.79 (m, 1H, 3-H), 3.70–3.76 (m, 1H, 2-H), 4.22 (t, J = 7.9 Hz, 1H, 2-H), 5.86 (s, 1H, 4-H), 7.49–7.52 (m, 2H, aryl H), 7.60–7.63 (m, 2H, aryl H), 9.44 (br s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 22.7 ($COCH_3$), 37.6 (C-3), 53.8 (C-3a), 66.5 (C-2), 96.6 (C-4), 118.5 (CN), 120.4 (C-6a), 127.0, 127.1, 128.7, 134.3 (C aryl), 154.7 (C-5), 169.3 (CO); ms: m/z 305 $[M+H]^+$; Anal. Calcd for $C_{15}H_{13}ClN_2O_3$: C, 59.12; H, 4.30; N, 9.19; Found: C, 59.38; H, 4.57; N, 8.95.

***N*-[3a-Cyano-2,3,3a,6a-tetrahydro-5-(4-methylphenyl)furo[2,3-*b*]furan-6a-yl]acetamide (7c)**

Colorless needles (1.18 g, 42%), mp 204–205 °C (acetone); IR (KBr): 3179 (NH), 2246, 2232 (CN), 1668 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.91 (s, 3H, $COCH_3$), 2.33 (s, 3H, CH_3), 2.39–2.43 (m, 1H, 3-H), 2.75–2.81 (m, 1H, 3-H), 3.69–3.74 (m, 1H, 2-H), 4.20 (t, J = 7.9 Hz, 1H, 2-H), 5.71 (s, 1H, 4-H), 7.23–7.26 (m, 2H, aryl H), 7.48–7.50 (m, 2H, aryl H), 9.40 (br s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 20.8 (CH_3), 22.7 ($COCH_3$), 37.4 (C-3), 53.8 (C-3a), 66.6 (C-2), 94.9 (C-4), 118.7 (CN), 120.3 (C-6a), 125.3, 125.4, 129.1, 139.6 (C aryl), 155.9 (C-5), 169.3 (CO); ms: m/z 285 $[M+H]^+$; Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85; Found: C, 67.63; H, 5.71; N, 9.86.

***N*-[3a-Cyano-2,3,3a,6a-tetrahydro-5-(4-methoxyphenyl)furo[2,3-*b*]furan-6a-yl]acetamide (7d)**

Colorless needles (2.10 g, 70%), mp 186–188 °C (acetone/petroleum ether); IR (KBr): 3176 (NH), 2246, 2233 (CN), 1667 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.91 (s, 3H, $COCH_3$), 2.40 (dd, J = 4.6, 11.9 Hz, 1H, 3-H), 2.76–2.80 (m, 1H, 3-H), 3.71–3.75 (m, 1H, 2-H), 3.79 (s, 3H, OCH_3), 4.18–4.21 (m, 1H, 2-H), 5.61 (s, 1H, 4-H), 6.97–7.01 (m, 2H, aryl H), 7.53–7.56 (m, 2H, aryl H), 9.38 (br s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 22.7 ($COCH_3$), 37.5 (C-3), 53.8 (C-3a), 55.2 (OCH_3), 66.6 (C-2), 93.7 (C-4), 114.0 (C aryl), 118.8 (CN), 120.2 (C aryl), 120.6 (C-6a), 127.0 (C aryl), 155.7 (C-5), 160.4 (C aryl), 169.3 (CO); ms: m/z 301 $[M+H]^+$; Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33; Found: C, 63.98; H, 5.45; N, 9.23.

General procedure for the preparation of furopyrroles 8a–d from 5 and phenacyl bromides in the presence of sodium methoxide.

To an ice-cooled and stirred solution of **5** (1.10 g, 10 mmol) in DMF (10 mL) was added 60% NaH (0.40 g, 10 mmol). The stirring was continued at rt until evolution of gas ceased. To the obtained mixture was added phenacyl bromide (1.99 g, 10 mmol), 4-chlorophenacyl bromide (2.33 g, 10 mmol), 4-methylphenacyl bromide (2.13 g, 10 mmol) or 4-methoxyphenacyl bromide (2.29 g, 10 mmol) with stirring and then the mixture was stirred at rt for 1 h. After removal of the solvent *in vacuo*, a solution of sodium (0.35 g, 15 mmol) in anhydrous methanol (20 mL) was added to the residue and then the resulting mixture was refluxed for 2 h. After removal of the solvent *in vacuo*, cold water was added to the residue. The precipitate was isolated by filtration, washed with water, dried and purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to afford **8a–d**.

3,3a,4,6a-Tetrahydro-6a-methoxy-5-phenylfuro[2,3-*b*]pyrrole-3a(2*H*)-carbonitrile (8a)

Colorless columns (0.98 g, 40%), mp 141–142 °C (acetone/petroleum ether); IR (KBr): 2238 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.09–2.15 (m, 1H, 3-H), 2.70–2.76 (m, 1H, 3-H), 3.30 (d, *J* = 18.0 Hz, 1H, 4-H), 3.71 (d, *J* = 18.0 Hz, 1H, 4-H), 3.75 (s, 3H, OCH_3), 3.88–3.93 (m, 1H, 2-H), 4.15–4.20 (m, 1H, 2-H), 7.42–7.46 (m, 2H, aryl H), 7.50–7.54 (m, 1H, aryl H), 7.85–7.88 (m, 2H, aryl H); ^{13}C NMR ($CDCl_3$): δ 40.1 (C-3), 46.5 (C-3a), 46.8 (C-4), 52.7 (OCH_3), 66.4 (C-2), 120.1 (CN), 128.2, 128.7, 132.3 (C aryl), 132.6 (C-6a), 170.7 (C-5); ms: *m/z* 243 $[M+H]^+$; Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56; Found: C, 69.54; H, 5.87; N, 11.54.

5-(4-Chlorophenyl)-3,3a,4,6a-tetrahydro-6a-methoxyfuro[2,3-*b*]pyrrole-3a(2*H*)-carbonitrile (8b)

Colorless columns (0.70 g, 25%), mp 99–100 °C (Et_2O/petroleum ether); IR (KBr): 2236 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.10–2.16 (m, 1H, 3-H), 2.71–2.76 (m, 1H, 3-H), 3.26 (d, *J* = 18.0 Hz, 1H, 4-H), 3.68 (d, *J* = 18.0 Hz, 1H, 4-H), 3.74 (s, 3H, OCH_3), 3.90–3.94 (m, 1H, 2-H), 4.15–4.20 (m, 1H, 2-H), 7.41–7.44 (m, 2H, aryl H), 7.79–7.82 (m, 2H, aryl H); ^{13}C NMR ($CDCl_3$): δ 40.1 (C-3), 46.6 (C-3a), 46.7 (C-4), 52.7 (OCH_3), 66.5 (C-2), 119.9 (CN), 129.1, 129.5, 130.7 (C aryl), 132.5 (C-6a), 138.6 (C aryl), 169.6 (C-5); ms: *m/z* 277 $[M+H]^+$; Anal. Calcd for $C_{14}H_{13}ClN_2O_2$: C, 60.77; H, 4.74; N, 10.12; Found: C, 60.77; H, 4.77; N, 10.11.

3,3a,4,6a-Tetrahydro-6a-methoxy-5-(4-methylphenyl)furo[2,3-*b*]pyrrole-3a(2*H*)-carbonitrile (8c)

Colorless prisms (0.62 g, 24%), mp 110–111 °C (Et_2O); IR (KBr): 2242 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.08–2.14 (m, 1H, 3-H), 2.40 (s, 3H, CH_3), 2.69–2.74 (m, 1H, 3-H), 3.27 (d, *J* = 17.9 Hz, 1H, 4-H), 3.68 (d, *J* = 17.9 Hz, 1H, 4-H), 3.74 (s, 3H, OCH_3), 3.87–3.92 (m, 1H, 2-H), 4.14–4.19 (m, 1H, 2-H), 7.23–7.25 (m, 2H, aryl H), 7.74–7.76 (m, 2H, aryl H); ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_3), 40.2 (C-3), 46.4 (C-3a), 46.8 (C-4), 52.7 (OCH_3), 66.3 (C-2), 120.2 (CN), 128.2, 129.4, 129.6 (C aryl), 132.6 (C-6a), 142.9 (C aryl), 170.6 (C-5); ms: *m/z* 257 $[M+H]^+$; Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N,

10.93; Found: C, 70.31; H, 6.35; N, 10.91.

3,3a,4,6a-Tetrahydro-6a-methoxy-5-(4-methoxyphenyl)furo[2,3-*b*]pyrrole-3a(2*H*)-carbonitrile (8d)

Colorless prisms (1.48 g, 54%), mp 138–139 °C (acetone/petroleum ether); IR (KBr): 2246 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.08–2.14 (m, 1H, 3-H), 2.69–2.74 (m, 1H, 3-H), 3.26 (d, *J* = 17.7 Hz, 1H, 4-H), 3.67 (d, *J* = 17.7 Hz, 1H, 4-H), 3.73 (s, 3H, 6a-OCH_3), 3.86 (s, 3H, PhOCH_3), 3.86–3.91 (m, 1H, 2-H), 4.14–4.19 (m, 1H, 2-H), 6.92–6.95 (m, 2H, aryl H), 7.80–7.83 (m, 2H, aryl H); ^{13}C NMR ($CDCl_3$): δ 40.2 (C-3), 46.4 (C-3a), 46.7 (C-4), 52.6 (6a-OCH_3), 55.4 (PhOCH_3), 66.3 (C-2), 114.1 (C aryl), 120.3 (CN), 124.9, 130.1 (C aryl), 132.7 (C-6a), 162.9 (C aryl), 170.0 (C-5); ms: *m/z* 273 $[M+H]^+$; Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29; Found: C, 66.17; H, 5.91; N, 10.31.

The preparation of furofuran 7a from 6a and acetic anhydride.

A mixture of **6a** (2.28 g, 10 mmol) and acetic anhydride (3 mL) was stirred at 80 °C for 3 h and then cold water was added to the reaction mixture. The precipitate was isolated by filtration, washed with water, dried and recrystallized from an appropriate solvent to yield the furo[2,3-*b*]furan **7a** (2.40 g, 89%). The melting point and IR spectrum of this compound coincided with that of a sample (entry 1 in Table 1) prepared from **5** and phenacyl bromide.

The preparation of furopyrrole 8a from 6a and sodium methoxide.

To a solution of sodium (0.35 g, 15 mmol) in anhydrous methanol (20 mL) was added **6a** (2.28 g, 10 mmol) with stirring and then the mixture was refluxed for 2 h. After removal of the solvent *in vacuo*, cold water was added to the residue. The precipitate was isolated by filtration, washed with water, dried and purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to give the furo[2,3-*b*]pyrrole **8a** (1.57 g, 65%). This compound was identical with a sample (entry 5 in Table 1) prepared from **5** and phenacyl bromide on the basis of a mixed melting point determination and comparison of the IR spectrum.

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