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One-pot three-component reaction of aromatic isocyanides and dialkyl acetylene dicarboxylates in the presence of aryl aldehydes: A convenient synthesis of highly hinderanced aminofurans

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Abstract: The reactive 1:1 intermediate produced from the reaction between 2,6-dimethyl phenylisocyanide or alkyl isocyanide and dialkyl acetylenedicarboxylates which was trapped with aromatic aldehydes to yield highly hinderanced and functionalized rare aminofuran derivatives in simple and one-pot method with excellent yields.

Keywords: Acetylenic esters, Aromatic aldehyde, 2-aminofurans, Isocyanides, Three-component reaction.

Introduction

The addition of isocyanides to dialkyl acetylenedicarboxylates has been investigated in detail [1-5]. Isocyanide-base multicomponent reactions (IMCRs) now occupy a position of importance in synthetic organic chemistry [6-11], manily due to the contributions of Ugi and co-workers [12]. These reactions have been the subject of detailed investigation by a number research groups [13-17].

One of the classic themes in the chemistry of isocyanides is heterocyclic Synthesis [18, 19]. Polysubstituted furans play an important role in organic chemistry, not only due to their presence as key structural units in many natural products [20] and in important pharmaceuticals [21], but they can also be employed in synthetic chemistry as building blocks [22, 23]. At that time, being interested in the preparation of furan derivatives, we were attracted by this new reaction, which would have made available in a clean, fast and straightforward way furans with an amino function in position 2 [24]. Indeed 2-aminofurans are quite rare [25] and according to the previous literature, rather difficult to prepare.

For these reasons the syntheses of polysubstituted furans have attracted tremendous interest. A highly reactive zwitterionic intermediate formed during the addition of isocyanide to DMAD (Scheme 1), could be trapped by aromatic aldehydes to generate 2-aminofuran derivatives. In the current work the reaction of aryl aldehydes as trapping agents, was employed for synthesis of new arylated 2-aminofurans with highly hinderanced.

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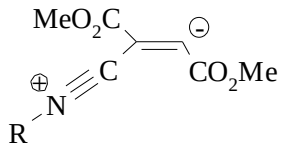


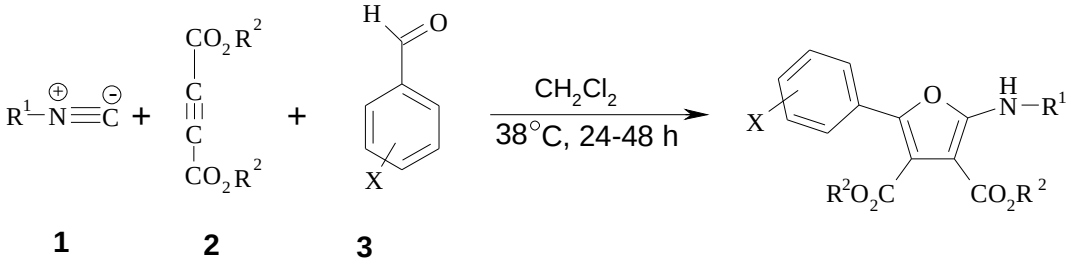
Scheme 1

This type of reaction is interesting because it provides eventually, after proper functionalization, a possibility for preparation of highly hinderanced arylated furans.

Results and Discussion

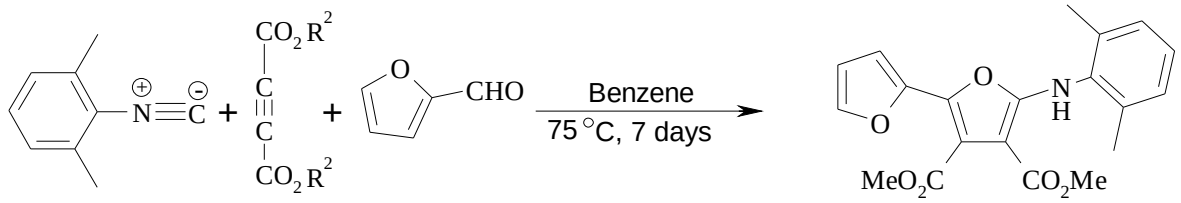
The reaction of 2,6-dimethylphenyl isocyanide with dimetyl acetylenedicarboxylate (DMAD) in the presence of 3-chlorobenzaldehyde afforded polysubstituted aminofurans in excellent yields (Scheme 2). Similar results were obtained with 4-nitrobenzaldehyde and they are reported in Table 1.

The structures of (4a-h and 6) were assigned to the isolated products on the basis of their IR, ^{1}H NMR, and ^{13}C NMR and Mass spectral data. The ^{1}H NMR spectrum of compound **4a** exhibited four singlet sharp lines, readily recognizable as arising from $2CH_3$ of 2,6-dimetylphenyl isocyanide (at δ=2.35 ppm), methoxy group (at δ=3.90 and 4.00 ppm) and NH proton (at δ= 8.13 ppm). The ^{13}C NMR spectrum of **4a** showed nineteen distinct resonance in agreement with 2-aminofuran structure. In the ^{13}C NMR spectrum two ester carbonyls resonated at δ = 164.8 and 165.40 ppm. The structural assignments of compound (**4a-h** and **6**) made on the basis of their NMR spectra were supported by their IR spectra of special interest is the fairly strong NH peak for example for **4a**, that is about 3355 cm^{-1}.



1 **2** **3**

4	R^1	R^2	X	t (*h*)	Yield (%)
a	2,6-dimethylphenyl	Me	3-chloro	24	95
b	2,6-dimethylphenyl	Et	3-chloro	48	92
c	2,6-dimethylphenyl	Me	4-nitro	24	90
d	2,6-dimethylphenyl	Et	4-nitro	48	92
e	2,6-dimethylphenyl	*t*-butyl	4-nitro	48	95
f	cyclohexyl	Me	4-nitro	24	90
g	cyclohexyl	Et	4-nitro	48	95
h	cyclohexyl	*t*-butyl	4-nitro	48	96

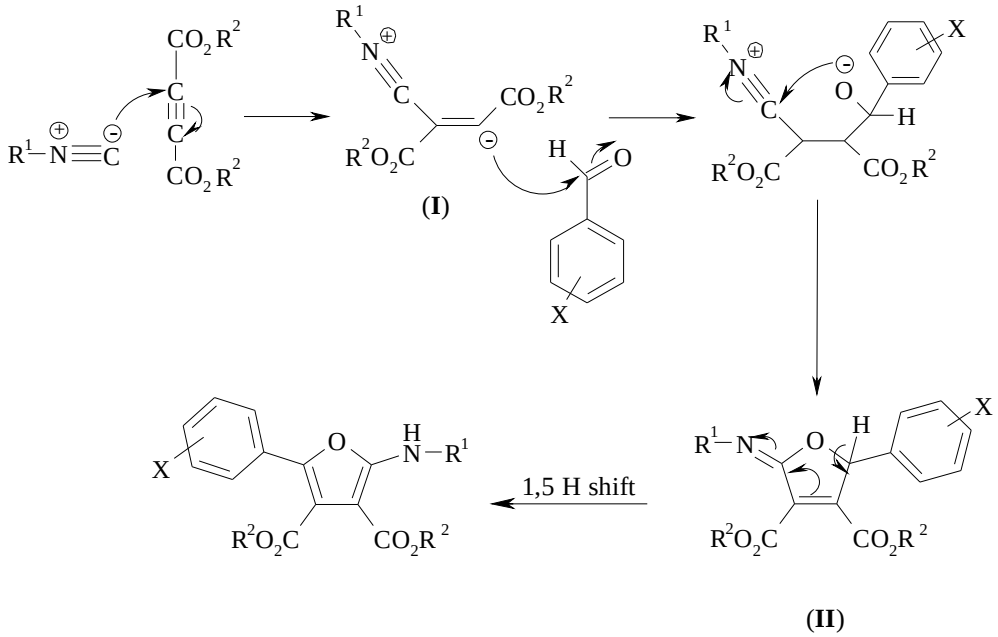


5 **6**

The ^{1}H NMR spectrum of compound **4f** exhibited two singlet sharp lines, readily recognizable as arising from two methoxy groups (at δ =3.81 and 3.97 ppm) and NH proton resonated at δ =6.74 ppm supporting the IR absorption at 3440 cm^{-1}. The ^{13}C NMR spectrum of **4f** showed sixteen distinct resonances in agreement with proposed structure. Two signal resulting from two ester carbonyl was discernible at δ =164.43 and 165.42 ppm in the ^{13}C NMR spectrum.

Partial assignments of these resonances are given in the experimental data. The ^{1}H and ^{13}C NMR spectra of **4g** and **4h** are similar to those of **4f** with the exception of the carbomethoxy groups, also in the case of (**4a**-**e**) besides of this so by virtue of the applied various aldehydes are different (see the experimental data). The IR spectrum of compounds (**4a**-**h** and **6**) at the carbonyl region displayed two distinct absorption bands for each compound. The mass spectrum of these compounds (**4a**-**h** and **6**) displayed molecular ion peaks at appropriate *m/z* value. A mechanistic rationale for the formation of the aminofurans is presented in Scheme 3.

It is conceivable that, the initial event is the formation of a 1,3–dipolar intermediate **(I)** from 2,6-dimethyl phenylisocyanide and DMAD, then nucleophilic addition of **(I)** to the aldehyde group of 3–chlorobenzaldehyde occurs. The intermediate **(II)** thus formed can, in principal, cyclize to give a five–membered aminofuran.



Scheme 3

In further investigations, similar reactivity was observed with furfuraldehyde when it was treated with dimethyl acetylenedicarboxylates in the presence of 2,6-dimethylphenyl isocyanide to yield 2-aminofurans in excellent yields. In summary, a three-component condensation reaction was observed as a convenient and one-pot synthesis of aminofurans. This method is particulary effective for the preparation of a polyfunctionalized and highly hinderanced aminofurans.

Experimental

2,6-dimethylphenyl and cyclohexyl isocyanides, dialkyl acetylenedicaboxylates and aromatic aldehydes were purchased from Merck and used without further purification. Melting points and IR spectra were measured on an Electrothermal 9100 apparatus and a Shimadzu IR–470 spectrometer respectively. The ^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX–300 AVANCE instrument with $CDCl_3$ as an applied solvent at 300.1 and 75.1 MHz, respectively. Mass spetra were recorded on a Shimadzu GC/MS QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyser.

General Procedure (exemplified by 4a)

The solution of 2,6–dimethylphenyl isocyanide (0.157 g or 1.2 mmol) in 3 mL of CH_2Cl_2 solvent was slowly added dropwise to the mixture of 3–chloro benzaldehyde (0.141g or 1mmol) and DMAD (0.171g or 1.2 mmol) in 20 mL of CH_2Cl_2 solvent for 3 min at room temperature. After the addition, the solution was heated to 38˚C for 24 h. Then, the solvent was removed under reduced pressure, and the solid product washed with cold diethyl ether (2×5 mL).

Dimethyl-2-(2,6-dimethylphenylamino)-5-(3-chlorophenyl)-3,4-furan dicarboxylate (**4a**): Pale white solid, yield: 0.39 g (95%), mp 124-126˚C, IR (KBr) (ν_{max}, cm^{-1}): 3355 (N-H), 1730 and 1669 (2 C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.35 (6H, s, CH_3), 3.90 (3H, s, OCH_3), 4.00 (3H, s, OCH_3), 7.20–7.24 (3H, m, Ar-H), 7.25–7.31 (3H, m, Ar-H), 7.37 (1H, s, Ar-H), 8.13 (1H, s, N-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 18.43 (Ar-*Me*$_2$), 51.46 and 52.80 (2 OCH_3), 88.84, 114.526, 122.62, 124.45, 127.43, 127.69, 128.55, 129.91, 130.52, 134.01, 134.61, 135.44, 139.96, 160.08 (C=$C_{aminofuran\ ring}$ and C_{arom}), 164.81 and 165.40 (2 C=O). MS (*m/z*, %): 415 (M^++2, 25), 414 (M^++1, 19), 413 (M^+, 70), 381 (26), 266 (12), 141 (34), 139 (100), 111 (76), 77 (65), 59 (35).

Diethyl -2- (2,6-dimethylphenylamino) -5- (3-chlorophenyl)-3,4-furan dicarboxylate (**4b**): Pale white solid, yield: 0.40 g (92%), mp 141-144˚C, IR (KBr) (ν_{max}, cm^{-1}): 3335 (N-H), 1728 and 1661 (2 C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.37 (3H, t, J = 7.1 Hz, CH_3), 1.43 (3H, t, J = 7.1 Hz, CH_3), 2.32 (6H, s, Ar-*Me*$_2$), 4.34 (2H, q, *J*= 7.1 Hz, OCH_2), 4.44 (2H, q, J =

7.1 Hz, OCH_2), 7.18-7.19 (3H, m, Ar-H), 7.22-7.27 (3H, m, Ar-H), 7.35 (1H, s, Ar-H), 8.11 (1H, s, N-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 14.10 and 14.41 ($2CH_3$), 18.50 (Ar-*Me*$_2$), 60.15 and 61.98 (2 OCH_2), 89.02, 114.89, 122.48, 124.30, 127.34, 127.53, 128.54, 129.90, 130.61, 134.05, 134.57, 135.38, 139.51, 159.97 (C=$C_{aminofuran\ ring}$ and C_{arom}), 164.54 and 165.04 (2 C=O). MS (*m/z*, %): 443 (M^++2, 37), 442 (M^++1, 30), 441 (M^+, 100), 395 (42), 349 (13), 294 (18), 139 (44), 105 (35), 77 (32), 53 (15). *Anal*. Calcd. for $C_{24}H_{24}ClNO_5$ (441.89): C, 65.23; H, 5.47; N, 3.17%. Found: C, 63.86; H, 5.47; N, 3.01%.

Dimethyl-2-(2,6-dimethylphenylamino)-5-(4-nitrophenyl)-3,4-furan dicarboxylate (**4c**): yellow solid, yield: 0.38 g (90%), mp 222-225˚C, IR (KBr) (ν_{max}, cm^{-1}): 3300 (N-H), 1726 and 1675 (2 C=O). ^1H NMR (300 MHz, $CDCl_3$): δ_H 2.32 (6H, s, Ar-*Me*$_3$), 3.89 (3H, s, OCH_3), 4.01 (3H, s, OCH_3), 7.20 (3H, m, Ar-H), 7.45 (2H, d, *J*=9.0 Hz, Ar-H), 8.14 (2H, d, J = 9.0 Hz, Ar-H), 8.18 (1H, s, NH). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 18.45 (Ar-*Me*$_2$), 51.71 and 53.14 (2 OCH_3), 89.74, 117.38, 124.17, 124.24, 127.71, 128.65, 133.62, 134.59, 135.40, 138.59, 146.10, 160.44 (C = $C_{aminofuran\ ring}$ and C_{arom}), 164.52 and 165.24 (2 C=O). MS (*m/z*, %): 426 (M^++2, 5), 425 (M^++1, 25), 424 (M^+, 100), 392 (45), 377 (2), 345 (4), 332 (13), 286 (4), 259 (17), 231 (8), 202 (3), 182 (19), 150 (37), 105 (37), 77 (42). *Anal*. Calcd. for $C_{22}H_{20}N_2O_7$ (424.40): C, 62.26; H, 4.75; N, 6.60%. Found: C, 61.81; H, 4.71; N, 6.72%.

Diethyl-2-(2,6-dimethylphenylamino)-5-(4-nitrophenyl)-3,4-furan dicarboxylate **(4d):** Yellow solid, yield: 0.41 g (92%), mp 191-194˚C, IR (KBr) (ν_{max}, cm^{-1}): 3295 (N-H), 1718 and 1669 (2 C=O). ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.38 (3H, t, CH_3), 1.44 (3H, t, CH_3), 2.32 (Ar-*Me*$_2$), 4.34 (2H, q, OCH_2), 4.47 (2H, q, OCH_2), 7.20 (3H, m, Ar-H), 7.46 (2H, d, *J*=8.8 Hz, Ar-H), 8.15 (2H, d, *J*=8.8 Hz, Ar-H), 8.21 (1H, s, N-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 14.09 and 14.39 (2 CH_3), 18.47 (Ar-*Me*$_2$), 60.39 and 62.32 (2 OCH_2), 89.96, 117.86, 123.99, 124.24, 127.62, 128.63, 133.69, 134.73, 135.35, 138.23, 145.99, 160.42 (C=$C_{aminofuran\ ring}$ and C_{arom}), 164.24 and 164.84 (2C=O). MS (*m/z*, %): 454 (M^++2, 4), 453 (M^++1, 29), 452 (M^+, 79), 423 (5), 406 (44), 377 (8), 332 (17), 305 (29), 286 (4), 259 (13), 231 (19), 156 (31), 150 (55), 105 (93), 77 (100), 53 (26). *Anal*. Calcd. for $C_{24}H_{24}N_2O_7$ (452.45): C, 63.71; H, 5.35; N, 6.19%. Found: C, 62.89; H, 5.30; N, 6.29%.

Di-*tert*-buthyl-2-(2,6-dimethylphenylamino)-5-(4-nitrophenyl)-3,4-furan dicarboxylate **(4e):** Light orange solid, yield: 0.48 g (95%), mp 180-183˚C, IR (KBr) (ν_{max}, cm^{-1}): 3300 (N-H), 1725 and 1665 (2 C=O). ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.62 and 1.63 (18H, 2s, 2 C*Me*$_3$), 2.32 (6H, s, Ar-*Me*$_2$), 7.18 (3H, m, Ar-H), 7.50 (2H, d, *J*=8.8 Hz, Ar-H), 8.14 (2H, d, *J*=8.8 Hz, Ar-H), 8.18 (1H, s, N-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 18.54 (Ar-*Me*$_2$), 28.18 and 28.70 (2 C*Me*$_3$), 81.69 and 83.27 (2 O*C*Me$_3$), 91.40, 119.58, 124.00, 124.31, 127.33, 128.57, 134.08, 135.15, 135.21, 138.11, 145.84, 160.01 (C=$C_{aminofuran\ ring}$ and C_{arom}), 163.36 and 163.69 (2 C=O). MS (*m/z*, %): 509 (M^++1, 5), 508 (M^+, 14), 452 (5), 396 (100), 378 (25), 277 (5), 132 (14), 105 (16), 57 (83), 41 (38). *Anal*. Calcd. for $C_{28}H_{32}N_2O_7$ (508.56): C, 66.12; H, 6.34; N, 5.51%. Found: C, 65.62; H, 6.40; N, 5.65%.

Dimethyl-2-(cyclohexylamino)-5-(4-nitrophenyl)-3,4-furan dicarboxylate **(4f):** orange solid, yield: 0.36 g (90%), mp 149-152˚C, IR (KBr) (ν_{max}, cm^{-1}): 3440 (N-H), 1727 and 1676 (2 C=O). ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.28-2.08 (10H, m, cyclohexyl), 3.77 (1H, m, CH), 3.81 and 3.97 (6H, s, 2 CO_2CH_3), 6.74 (1H, d, *J*=7.9 Hz, N-H), 7.62 (2H, d, *J*=9.0 Hz, Ar-H), 8.23 (2H, d, *J*=9.0 Hz, Ar-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 24.50, 25.32, 33.37 (5 CH_2 of cyclohexyl), 51.40 (CH of cyclohexyl), 51.70 and 53.03 (2 OCH_3), 88.76, 117.80, 123.95, 124.3, 134.97, 137.88, 145.91, 161.56 (C = $C_{aminofuran\ ring}$ and C_{arom}), 164.43 and 165.42 (2 C=O). MS (*m/z*, %): 402 (M^+, 24), 288 (21), 150 (28), 104 (21), 83 (30), 55 (100), 41 (76). *Anal*. Calcd. for $C_{20}H_{22}N_2O_7$ (402.40): C, 59.69; H, 5.51; N, 6.96%. Found: C, 59.64; H, 5.23; N, 7.05%.

Diethyl-2-(cyclohexylamino)-5-(4-nitrophenyl)-3,4-furan dicarboxylate **(4g):** Light orange solid, yield: 0.41 g (95%), mp 150-153˚C, IR (KBr) (ν_{max}, cm^{-1}): 3425 (N-H), 1719 and 1673 (2 C=O). ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.33 (3H, t, CH_3), 1.41 (3H, t, CH_3), 1.43-2.08 (10H, m, cyclohexyl), 3.77 (1H, m, CH), 4.26 (2H, q, OCH_2), 4.43 (2H, q, OCH_2), 6.78 (1H, d, *J*=8.1 Hz, N-H), 7.62 (2H, d, *J*=9.0 Hz, Ar-H), 8.22 (2H, d, *J*=9.0 Hz, Ar-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 14.04, 14.37 (2 CH_3), 24.46, 25.34, 33.34 (5 CH_2 of cyclohexyl), 51.60 (CH of cyclohexyl), 59.99 and 62.14 (2 OCH_2), 88.95, 118.29, 123.73, 124.26, 135.07, 137.50, 145.73, 161.58 (C=$C_{aminofuran\ ring}$ and C_{arom}), 164.11 and 164.96 (2 C=O). MS (*m/z*, %): 432 (M^++2, 2), 431 (M^++1, 8), 430 (M^+, 35), 247 (20), 150 (22), 83 (26), 55 (99), 41 (69). *Anal*. Calcd. for $C_{22}H_{26}N_2O_7$

(430.45): C, 61.38; H, 6.09; N, 6.51%. Found: C, 61.30; H, 6.09; N, 6.66%.

Di-*tert*-buthyl-2-(cyclohexylamino)-5-(4-nitrophenyl)-3,4-furan dicarboxylate **(4h):** Dark orange solid, yield: 0.46 g (96%), mp 151-154˚C, IR (KBr) (ν_{max}, cm^{-1}): 3415 (N-H), 1730 and 1703 (2 C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.37-2.12 (10H, m, cyclohexyl), 1.56 and 1.6 (18H, 2s, 2 C*Me*$_3$), 3.74 (1H, m, CH), 6.75 (1H, d, *J*=8.0 Hz, N-H), 7.64 (2H, d, *J*=9.0 Hz, Ar-H), 8.22 (2H, d, *J*=9.0 Hz, Ar-H). ^{13}C NMR (75.1 MHz, $CDCl_3$): δ_C 24.55, 25.40, 33.48 (5 CH_2 of cyclohexyl), 28.16 and 28.67 (2 C*Me*$_3$), 51.52 (CH of cyclohexyl), 81.08 and 83.03 (2 *C*Me$_3$), 90.27, 120.06, 124.02, 124.08, 135.51, 137.35, 145.59, 161.34 (C=$C_{aminofuran\ ring}$ and C_{arom}), 163.34 and 163.64 (2 C=O). MS (*m/z*, %): 486 (M^+, 2), 374 (5), 292 (12), 274 (25), 83 (5), 57 (100), 55 (15), 41 (28). *Anal*. Calcd. for $C_{26}H_{34}N_2O_7$ (486.55): C, 64.18; H, 7.04; N, 5.76%. Found: C, 63.16; H, 7.00; N, 5.82%.

Dimethyl-2-(2,6-dimethylphenylamino)-5-(2-furyl)-3,4-furan dicarboxylate **(6):** orange solid, yield: 0.34 g (92%), mp 67-69˚C, IR (KBr) (ν_{max}, cm^{-1}): 3455 (N-H), 1727 and 1662 (2C=O).^{1}H NMR ($CDCl_3$): δ_H 2.31 (6H, s, $2CH_3$), 3.87 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 6.39 (1H, m, CH), 6.47 (1H, d, ^{3}J = 3 Hz, CH), 7.18 (3H, m, Ar-H), 7.38 (1H, s, CH), 8.15 (1H, s, N-H). ^{13}C NMR ($CDCL_3$): δ_C 18.45 (Ar-Me_2), 51.44 and 52.48 ($2OCH_3$), 87.82, 107.84, 111.28, 112.43, 134.61, 142.69, 143.79, 160.03 (C = $C_{aminofuran\ ring}$ and C_{furyl}), 127.25, 128.48, 134.08, 135.42 (ArH), 164.45 and 165.05 (2C=O). MS (*m/z*, %): 369 (M^+, 100), 337 (30), 277 (5), 249 (5), 182 (5).

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