Regio- and Stereoselectivity of Aromatic and Heteroaromatic Nitrilimines in 1,3-Dipolar Cycloadditions

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The preparation of aromatic and heteroaromatic nitrilimines and the regio- and stereoselectivity of their subsequent 1,3-dipolar cycloadditions to various dipolarophiles (electron-rich or electron-poor mono- or disubstituted alkenes) are discussed. The cycloadditions to monosubstituted alkenes were highly regioselective and afforded only 5-substituted pyrazoles/pyrazolines, or mixtures of both, depending upon the nature of the dipolarophile, the type of substitution on nitrogen in nitrilimines, and the reaction conditions in each case.

1,3-Dipolar cycloadditions of nitrilimines to olefins have been utilized extensively to synthesize pyrazoles and pyrazolidines [1—4]. Despite the fact that reactions of this type have been known for over a century there were no reported 1,3-dipolar cycloaddition reactions involving nitrilimines prior to 1960 when *Huisgen* and his coworkers reported the cycloadditions of diphenylnitrilimine [1, 2, 5]. Many procedures have been reported for the preparation of reactive nitrilimines as they are notoriously unstable [5]; hence, 1,3-dipolar cycloadditions of nitrilimines are most commonly performed by *in situ* generation of the dipole from hydrazonoyl halides and triethylamine in the excess of dipolarophile [1—5]. A huge variety of hydrazonoyl halides have been described in literature, mainly because of their pesticidal activity [6, 7]. They are the most commonly used precursors of nitrilimines due to their stability and their easy accessibility from different precursors. Furyl-substituted nitrilimines as useful 1,3-dipoles received much less attention than their aryl analogues or furyl-substituted nitrile oxides or nitrones. In fact, only a few papers that deal specifically with 2-furannitrilimines have been published [8—10]. This situation most likely reflects the instability of available precursors and presents a relatively unexplored area suitable for study. Few years ago some preliminary reports have been already published [11, 12] and now a detailed investigation of the reactivity and regioselectivity of 1,3-cycloaddition of some *in situ* generated aryl- and especially heteroaryl-substituted nitrilimines *Ia*—*Ig* with different dipolarophiles is reported (Formula 1).

$$R^1—C\equiv\overset{\oplus}{N}—\overset{\ominus}{N}—R^2$$

Ia—*Ig*

	R^1	R^2
a	4-nitrophenyl	phenyl
b	4-nitrophenyl	methyl
c	4-chlorophenyl	phenyl
d	4-chlorophenyl	methyl
e	4-tolyl	phenyl
f	5-nitro-2-furyl	phenyl
g	5-nitro-2-furyl	methyl

Formula 1

Initially, we attempted to prepare *N*-methyl- and *N*-phenyl-*C*-(5-nitro-2-furyl)-substituted nitrilimines *If* and *Ig* by using the classical method reported previously by *Huisgen et al.* [4]. The attempts to prepare the requisite hydrazonoyl halides (chlorides or bromides) resulted similarly as referred by *Sasaki* [8] only in the formation of intractable tars accompanied by trace quantities of the desired products. Similarly, our attempts to repeat the work of *Sasaki* [8] who prepared the 2-furyl-substituted nitrilimines by $Pb(OAc)_4$-promoted dehydrogenation [13] of the corresponding aldehyde hydrazone also were not successful. The method reported by *Lee* [14] for *in situ* generation of diphenylnitrilimines, which involves treatment of the corresponding hydrazone with aqueous sodium hypochlorite solution in an inert, water-immiscible organic solvent in the presence of a catalytic amount of triethylamine, gave disappointing results; the yields of

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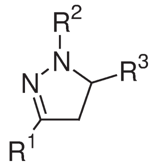
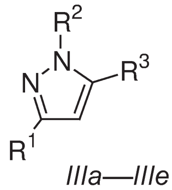


IIa—IIi



IIIa—IIIe

	R^1	R^2	R^3
a	4-nitrophenyl	phenyl	$COOC_2H_5$
b	4-chlorophenyl	phenyl	$COOC_2H_5$
c	4-tolyl	phenyl	$COOC_2H_5$
d	5-nitro-2-furyl	phenyl	$COOC_2H_5$
e	phenyl	phenyl	$COOC_2H_5$
f	4-nitrophenyl	phenyl	phenyl
g	5-nitro-2-furyl	phenyl	phenyl
h	5-nitro-2-furyl	methyl	phenyl
i	5-nitro-2-furyl	methyl	$COOCH_3$

	R^1	R^2	R^3
a	4-nitrophenyl	methyl	$COOC_2H_5$
b	5-nitro-2-furyl	methyl	$COOC_2H_5$
c	5-nitro-2-furyl	methyl	$COOCH_3$
d	4-nitrophenyl	phenyl	$COOC_2H_5$
e	5-nitro-2-furyl	methyl	phenyl

Formulae 2

the desired products thereby obtained were < 25 %.

Finally, we observed that the very simple and elegant method published by *Rai* and *Hassner* [15] for generating diphenylnitrilimine *in situ* by treatment of chloramine-T on arylaldehyde hydrazones in the presence of the dipolarophile is perfectly suited for preparing 2-furylnitrilimines and we used it successfully in the synthesis of spiroheterocycles [9, 10]. Moreover, this one-pot cycloaddition is superior to the other methods noted above because i) starting materials are readily available, ii) the procedure is straightforward and easy to apply, and iii) any contact with allergenic and skin-irritating hydrazonoyl halides is easily avoided.

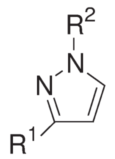
Nitrilimines *Ia—Ig* were generated *in situ* from the appropriate aldehyde hydrazone by refluxing a mixture of chloramine-T trihydrate (*N*-chloro-*N*-sodio-4-methylbenzene sulfonamide, CAT) and the dipolarophile in an appropriate solvent. The following dipolarophiles were used: ethyl/methyl acrylate, ethyl 5-nitro-2-furylacrylate, ethyl cinnamoate, vinyl acetate, styrene, dimethyl 7-oxabicyclo[2,2,1]heptadiene-2,3-dicarboxylate (*VII*), and 7-oxabicyclo[2,2,1]hept-5-ene-2,3-dicarboxylate (*X*) (Formulae 3). Dipolar cycloaddition of nitrilimines *Ia—Ig* to the monosubstituted alkenes proceeded with complete regioselectivity, thereby affording only 1,3,5-trisubstituted-4,5-dihydropyrazoles *IIa—IIh* in very good yields. Cycloaddition to acrylic esters was completed in 20 min (Formulae 2).

The corresponding regioisomers (1,3,4-trisubstituted pyrazolines) have not been detected in the crude reaction mixture by ^{1}H NMR spectroscopy. The assignment of the regiochemistry in 1,3,5-trisubstituted-4,5-dihydropyrazoles *IIa—IIi* was confirmed on the basis of ^{1}H and ^{13}C NMR spectral data. Reaction of *N*-methyl-*C*-(5-nitro-2-furyl)nitrilimine (*Ig*) with methyl acrylate afforded methyl 1-methyl-3-(5-nitro-2-furyl)pyrazol-5-carboxylate (*IIIc*) as the major reaction product together with its corresponding 4,5-dihydro analogue *IIi*, which could not be separated from *IIIc* by column chromatography. Subsequently, this mixture was treated with 2,3-dicyano-5,6-dichloroquinone (DDQ), thereby affording pure pyrazole *IIIc*. Similarly, spontaneous dehydrogenation of pyrazolines to pyrazoles occurred in the case of the corresponding cycloadditions of nitrilimines *Ib* and *Ig* to acrylic esters. The use of a large excess of CAT and longer reaction times resulted in increased pyrazole *vis-à-vis* 4,5-dihydropyrazole formation (maximum amount of substance ratio 1 : 3). However, the corresponding cycloadditions of nitrilimines *Ie—Ig* to vinyl acetate proceeded regioselectively with surprisingly complete deacetylation, thereby affording only 1,3-disubstituted pyrazoles *VI* as the sole reaction products (Formulae 3).

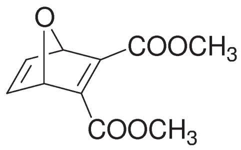
Similarly, spontaneous dehydrogenation was also observed in the cycloaddition of nitrilimine *Ig* to methyl 3-(5-nitro-2-furyl)propenoate. In this case the cycloaddition gave two regioisomers, *i.e.* 1-methyl-3,4-di(5-nitro-2-furyl)pyrazole-5-carboxylate (*IVa*) and 1-methyl-3,4-di(5-nitro-2-furyl)pyrazole-4-carboxylate (*IVb*), in the amount of substance ratio 40 : 60 (Formulae 4). The formation of corresponding 4,5-dihydro derivative was not observed in this reaction.

The assignment of regiochemistry to *IVa* and *IVb* cannot be differentiated by analysis of standard ^{1}H and ^{13}C NMR spectra. For this reason, series 1D selective INEPT experiments were performed. Here, we sought to observe coherence transfer from N—CH, H-4′, and H-4″ to the neighbouring carbons *via* their long-range spin-spin interactions.

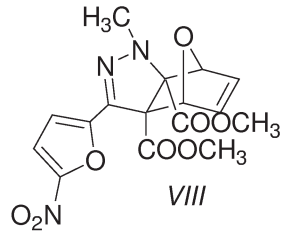
Similarly, reaction of nitrilimine *Ig* with ethyl cinnamoate produced two regioisomers, *Va* and *Vb*, in the amount of substance ratio 33 : 67. Once again, the 4-carboxylate *Vb* was obtained preferentially (Formu-



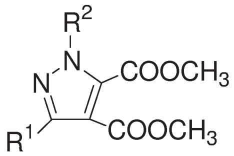
VIa—VIc



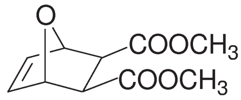
VII



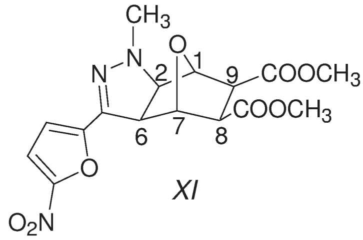
VIII



IXa—IXe



X



XI

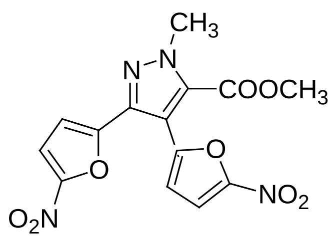
For *VIa—VIc*

	R^1	R^2
a	4-tolyl	phenyl
b	5-nitro-2-furyl	phenyl
c	5-nitro-2-furyl	methyl

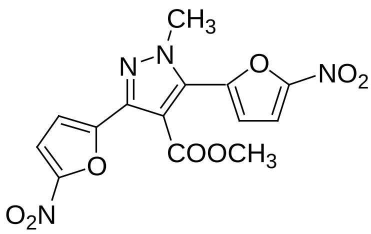
For *IXa—IXe*

	R^1	R^2
a	4-nitrophenyl	phenyl
b	4-chlorophenyl	phenyl
c	4-chlorophenyl	methyl
d	5-nitro-2-furyl	phenyl
e	5-nitro-2-furyl	methyl

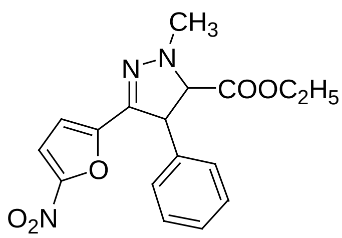
Formulae 3



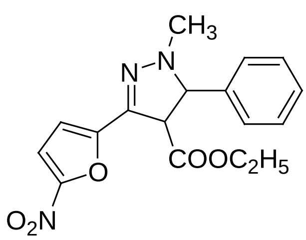
IVa



IVb



Va



Vb

Formulae 4

lae 4). Surprisingly, in this case no trace of the corresponding dehydrogenated product was found. The product ratio was determined *via* integration of the C-4 and C-5 pyrazoline methine protons in the ^{1}H NMR spectrum of the crude reaction mixture. The structure of each regioisomer *Va* and *Vb* was assigned on the basis of the relative chemical shifts and coupling constants of the C-4 and C-5 methine doublets. The major isomer *Vb* exhibits two closely spaced doublets (δ = 4.18 and 4.77, $J_{4,5}$ = 12.9 Hz), while the minor isomer *Va* exhibits two widely spaced doublets (δ = 3.99 and 4.83, $J_{4,5}$ = 9.7 Hz). More conclusive information was obtained from NOE difference experiments by the observation of an interaction between protons H-5, H-4, and H-phenyl in cycloadduct *Vb*. Irradiation of N-CH_3 (δ = 2.98) caused only the enhancement of H-5 ($\delta = 4.77$) and H-phenyl, the signal of H-4 ($\delta = 4.18$) rested without any change.

Next, we have also investigated the reactivity of the selected heterocyclic compounds *VII* and *X* as the dipolarophiles with the aforementioned nitrilimines. The outcome of the cycloadditions of the nitrilimines *Ia*, *Ic*, *Id*, *If*, *Ig* to the dimethyl 7-oxabicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate (*VII*), the diene possessing two double bonds of the different reactivity, was rather unexpected. The remarkable feature of the whole process was its total *site* selectivity. The cycloaddition only took place at the deactivated double bond. The primarily formed cycloadduct *VIII* was unstable under reaction conditions and underwent a retro-Diels—Alder reaction leading to the substituted pyrazole-4,5-dicarboxylates *IXa—IXe* (Formulae 4). The exclusive cycloadditions to the deactivated double bond of the dipolarophile *VII* can be interpreted in terms of HOMO-LUMO frontier orbitals interaction, HOMO dipole—LUMO dipolarophile interaction being the dominant one. Probably, the used nitrilimines mentioned above have higher nucleophilicity, similar to *e.g.* that of 2,5-dimethyl-3-furylnitrile oxide; there we have observed the same exclusive *site* selectivity [16]. The exclusive *exo*-stereoselective cycloaddition of nitrilimine *Ig* to dipolarophile *X* has been observed and the corresponding adduct *XI* has been formed in 81 % yield (Formulae 4).

In conclusion, a very simple and elegant method for the *in situ* generation of the aryl- and furyl-substituted nitrilimines *Ia—Ig* by treatment of chloramine-T on the corresponding arylaldehyde hydrazones in the presence of the dipolarophile was found. The cycloadditions of aromatic and heteroaromatic nitrilimines *Ia—Ig* to the monosubstituted alkenes were strictly regioselective and afforded only 5-substituted pyrazoles/pyrazolines, or mixture of both, in dependence of the used dipolarophile, substitution on nitrogen atom of nitrilimines, and reaction conditions. The cycloadditions of the nitrilimines *Ia*, *Ic*, *Id*, *If*, *Ig* to the dimethyl 7-oxabicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate (*VII*) proceeded with exclusive *site* selectivity.

EXPERIMENTAL

All commercially available starting materials and reagents (Fluka, Merck, Avocado or Aldrich) were used without further purification. Solvents were dried before use. Thin-layer chromatography (TLC, on glass plates coated with silica $60F_{254}$, Merck) was used for monitoring of reaction courses, eluents are given in the procedure. For column chromatography the flash chromatography technique was employed using silica 60 (0.040—0.063 mm, Merck). Melting points were determined on a Kofler hot-plate apparatus.

The ^{1}H and ^{13}C NMR spectra of deuterochloroform solutions were recorded on Varian VXR-300 (300 MHz) spectrometer, tetramethylsilane (TMS) being the internal standard. Methyl, methylene, and methine groups, and quaternary carbons, were discriminated in the ^{13}C NMR spectra by DEPT experiments. The IR spectra were taken on Philips analytical PU 9800 FTIR spectrometer in KBr pellets. Mass spectral data were recorded on AEI spectrometer MS 902 S with direct inlet and ionizing energy of 70 eV, capture current 100 μA and temperature of ionizing chamber 80—215 ℃. Elemental analyses were carried out on Carlo Erba CHNS-O 1108 apparatus and were in good accord with theoretical data. Substituted hydrazones were prepared according to generally used methods.

General Procedure for the Preparation of Pyrazolines and Pyrazoles by 1,3-Dipolar Cycloaddition

The mixture of 4 mmol of hydrazone and 4.5—5 mmol of chloramine-T in ethanol (40 cm^3) was added at room temperature to the excess of dipolarophile (6—30 mmol) in ethanol (25 cm^3). The reaction mixture was heated to 80 ℃ and kept under reflux for 1—8 h (TLC). Inorganic salts were filtered off, filtrate was evaporated *in vacuo* and crude reaction mixture was separated by column chromatography using chloroform or hexane—ethyl acetate ($\varphi_r = 80 : 20$) as eluent. Obtained products were crystallized from ethanol or methanol.

Treatment of 1,3-Disubstituted R-Alkyl-4,5-dihydropyrazole-5-carboxylates with DDQ

Mixture of 1 mmol of 1,3-disubstituted R-alkyl-4,5-dihydropyrazole-5-carboxylate *IIa—II*e and 0.5 g of DDQ in benzene (20 cm^3) was refluxed for 4 h. After cooling, reaction mixture was diluted with 50 cm^3 of diethyl ether, washed with solution of 2 M-NaOH, brine (30 cm^3) and dried over anhydrous sodium sulfate. Solvents were removed *in vacuo* and products *IIIa—IIIe* were crystallized from ethanol.

Ethyl 1-Phenyl-3-(4-nitrophenyl)-4,5-dihydropyrazole-5-carboxylate (IIa)

Dark orange plates; yield: 72 %, m.p. = 141—143 ℃. For $C_{18}H_{17}N_3O_4$ (M_r = 339.3) w_i(calc.): 63.71 % C, 5.05 % H, 12.38 % N; w_i(found): 63.89 % C, 5.21 % H, 12.14 % N. ^{1}H NMR spectrum, δ : 1.22 (t, 3H, CH_3), 3.48 (dd, 1H, $J_{A,B}$ = 17.3 Hz, H_A-4), 3.69 (dd, 1H, J = 17.2 Hz, H_B-4), 4.22 (q, 2H, OCH_2), 4.93 (dd, 1H, $J_{4,5}$ = 12.9 Hz, H-5), 6.93 (dd, 1H, J = 6.9 Hz, H_{Ph}), 7.14 (d, 2H, J = 7.8 Hz, H_{Ph}), 7.29 (d, 2H, J = 8.0 Hz, H_{Ph}), 7.80 (d, 2H, J = 9.0 Hz, H_{Ph}), 8.21 (d, 2H, J = 9.0 Hz, H_{Ph}); ^{13}C NMR, δ : 14.27 (CH_3), 38.47 (C-4), 61.92 (C-5), 62.14 (OCH_2), 110.37, 113.28, 119.95, 126.05, 128.76, 129.07, 129.31, 132.23, 144.94 (C_{Ph}), 147.08 (C-3), 171.64 (C═O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1741 (CO), 1647 (C═N), 1554 $(NO_2)_{as}$, 1338 $(NO_2)_s$. Mass spectrum, m/z (I_r/%): $339^{+\bullet}$ (30), 266 (100), 236 (29), 220 (44), 117 (11), 77 (19), 28 (34).

Ethyl 1-Phenyl-3-(4-chlorophenyl)-4,5-dihydropyrazole-5-carboxylate (IIb)

Yellowish solid; yield: 43 %, m.p. = 76—78 ℃. For $C_{18}H_{17}N_2O_2Cl$ (M_r = 328.8) w_i(calc.): 65.74 % C, 5.21 % H, 8.52 % N; w_i(found): 65.58 % C, 5.04 % H, 8.58 % N. ^{1}H NMR spectrum, δ : 1.21 (t, 3H, CH_3), 3. 51 (dd, 1H, $J_{A,B}$ = 16.41 Hz, H_A-4), 3.82 (dd, 1H, J = 16.68 Hz, H_B-4), 4.21 (q, 2H, OCH_2), 4.81 (dd, 1H, $J_{4,5}$ = 9.65 Hz, H-5), 7.15—7.40 (m, 5H, H_{Ph}), 7.28 (d, 2H, J = 8.31 Hz, H_{Ph}), 7.72 (d, 2H, H_{Ph}); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1723 (CO), 1655 (C═N).

Ethyl 1-Phenyl-3-(4-tolyl)-4,5-dihydropyrazole-5-carboxylate (IIc)

Yellow solid; yield: 80 %, m.p. = 118—120 ℃. For $C_{19}H_{20}N_2O_2$ (M_r = 308.4) w_i(calc.): 73.99 % C, 6.53 % H, 9.08 % N; w_i(found): 74.11 % C, 6.32 % H, 8.99 % N. ^{1}H NMR spectrum, δ: 1.22 (t, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.43 (dd, 1H, $J_{A,B}$ = 17.10 Hz, H_A-4), 3.80 (dd, J = 17.0 Hz, H_B-4), 4.15 (q, OCH_2), 4.85 (dd, 1H, $J_{4,5}$= 9.32 Hz, H-5), 7.10 (d, 2H, J = 8.1 Hz, H_{Ph}), 7.30—7.52 (m, 5H, H_{Ph}), 7.65 (d, 2H, J = 8.0 Hz, H_{Ph}); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1716 (CO), 1672 (C═N).

Ethyl 1-Phenyl-3-(5-nitro-2-furyl)-4,5-dihydropyrazole-5-carboxylate (IId)

Dark orange solid; yield: 88 %, m.p. = 96—98 ℃. For $C_{16}H_{15}N_3O_5$ (M_r = 329.3) w_i(calc.): 58.35 % C, 4.59 % H, 12.76 % N; w_i(found): 58.47 % C, 4.23 % H, 12.80 % N. ^{1}H NMR spectrum, δ : 1.22 (t, 3H, CH_3), 3.48 (dd, 1H, $J_{A,B}$ = 16.80 Hz, H_A-4), 3.69 (dd, 1H, J = 16.92 Hz, H_B-4), 4.22 (q, 2H, OCH_2), 4.95 (dd, 1H, $J_{4,5}$ = 13.20 Hz, H-5), 6.90 (d, 1H, J = 3.9 Hz, H_{Fu}-3), 6.95—7.33 (m, 5H, H_{Ph}), 7.40 (d, 1H, J = 3.9 Hz, H_{Fu}-4); ^{13}C NMR, δ: 14.2 (CH_3), 37.0 (C-4), 61.9 (C-5), 62.32 (OCH_2), 110.37, 113.79, 114.30, 121.53, 129.53, 129.47, 136.59, 143.01 (C_{Ph} and C_{Fu}), 150.94 (C-3), 171.60 (C═O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1725 (CO), 1647 (C═N), 1558 $(NO_2)_{as}$, 1336 $(NO_2)_s$. Mass spectrum, m/z (I_r/%): $329^{+\bullet}$ (30), 257 (15), 256 (100), 224 (16), 181 (21), 145 (18), 77 (37), 51 (20), 39 (14).

Ethyl 1,3-Diphenyl-4,5-dihydropyrazole-5-carboxylate (IIe)

Light orange plates; yield: 80 %, m.p. = 98—99 ℃, Ref. [15, 17] gives m.p. = 99—101 ℃. For $C_{18}H_{18}N_2O_2$ (M_r = 294.29) w_i(calc.): 73.76 % C, 6.12 % H, 9.51 % N; w_i(found): 73.89 % C, 6.28 % H, 9.36 % N. ^{1}H NMR spectrum, δ : 1.19 (t, 3H, CH_3), 3.43 (dd, 1H, $J_{A,B}$ = 14.0 Hz, H_A-4), 3.58 (dd, 1H, J = 14.0 Hz, H_B-4), 4.20 (q, 2H, OCH_2), 4.78 (dd, 1H, $J_{4,5}$ = 8.10 Hz, H-5), 6.86 (t, 1H, H_{Ph}), 7.12 (d, 2H, J = 8.7 Hz, H_{Ph}), 7.24—7.39 (m, 4H, H_{Ph}), 7.7 (d, 2H, J = 8.7 Hz, H_{Ph}); ^{13}C NMR, δ: 14.27 (CH_3), 38.37 (C-4), 62.02 (C-5), 62.14 (OCH_2), 113.28, 119.94, 126.05, 128.76, 129.07, 129.31, 132.23, 144.94 (C_{Ph}), 147.08 (C═N), 171.63 (C═O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1740 (CO), 1568 (C═N).

1,5-Diphenyl-3-(4-nitrophenyl)-4,5-dihydropyrazole (IIf)

Orange solid; yield: 67 %, m.p. = 118—120 ℃. For $C_{21}H_{17}N_3O_2$ (M_r = 343.4) w_i(calc.): 73.44 % C, 4.99 % H, 12.53 % N; w_i(found): 73.58 % C, 5.10 % H, 12.18 % N. ^{1}H NMR spectrum, δ: 3.20 (dd, 1H, $J_{A,B}$ = 13.7 Hz, H_A-4), 3.91 (dd, 1H, $J_{A,B}$ = 13.6 Hz, H_B-4), 5.45 (dd, 1H, $J_{4,5}$ = 7.82 Hz, H-5), 6.90 (t, 1H, H_{Ph}), 7.05 (d, 2H, J = 8.2 Hz, H_{Ph}), 7.14—7.88 (m, 9H, H_{Ph}), 8.23 (d, 2H, J = 8.12 Hz, H_{Ph}).

1,5-Diphenyl-3-(5-nitro-2-furyl)-4,5-dihydropyrazole (IIg)

Red solid; yield: 65 %, m.p. = 160—162 ℃. For $C_{19}H_{15}N_3O_3$ (M_r = 333.3) w_i(calc.): 68.46 % C, 4.53 % H, 12.60 % N; w_i(found): 68.61 % C, 4.28 % H, 12.66 % N. ^{1}H NMR spectrum, δ: 3.21 (dd, 1H, $J_{A,B}$ = 13.0 Hz, H_A-4,), 3.90 (dd, 1H, $J_{A,B}$ = 13.0 Hz, H_B-4), 5.48 (dd, 1H, $J_{4,5}$ = 6.2 Hz, H-5), 6.85 (t, 1H, H_{Ph}), 7.15 (d, 1H, J = 3.4 Hz, H_{Fu}-3), 7.20—7.51 (m, 9H, H_{Ph}), 7.60 (d, 1H, J = 3.4 Hz, H_{Fu}-4).

1-Methyl-3-(5-nitro-2-furyl)-5-phenyl-4,5-dihydropyrazole (IIh)

Light red solid; yield: 74 %, m.p. = 136—137 ℃. For $C_{14}H_{13}N_3O_3$ (M_r = 271.2) w_i(calc.): 61.99 % C, 4.83 % H, 15.49 % N; w_i(found): 61.72 % C, 4.98 % H, 15.35 % N. ^{1}H NMR spectrum, δ: 2.91 (s, 3H, N-CH_3), 3.03 (dd, 1H, $J_{A,B}$ = 16.5 Hz, H_A-4), 3.54 (dd, 1H, J = 16.5 Hz, H_B-4), 4.35 (dd, 1H, $J_{4,5}$ = 14.1 Hz, H-5), 6.75 (d, 1H, J = 3.9 Hz, H_{Fu}-3), 7.37 (d, 1H, J = 3.9 Hz, H_{Fu}-4), 7.38—7.40 (m, 5H, H_{Ph}); ^{13}C NMR, δ : 40.28 (N-CH_3), 41.88 (C-4), 72.81 (C-5), 109.47, 114.99, 128.31, 128.93, 134.84, 139.04, 151.56 (C_{Ph} and C_{Fu}); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1588 (C═N), 1544 $(NO_2)_{as}$, 1339 $(NO_2)_s$. Mass spectrum, m/z (I_r/%): $271^{+\bullet}$ (100), 197 (42), 194 (28), 224 (16), 118 (13), 91(16), 77 (15), 51 (12), 43 (17).

Ethyl 1-Methyl-3-(4-nitrophenyl)pyrazole-5-carboxylate (IIIa)

Light yellow needles; yield: 89 %, m.p. = 167—169 ℃. For $C_{13}H_{13}N_3O_4$ (M_r = 275.26) w_i(calc.): 56.73 % C, 4.76 % H, 15.27 % N; w_i(found): 56.48 % C, 4.58 % H, 15.49 % N. ^{1}H NMR spectrum, δ: 1.42 (t, 3H, CH_3), 4.26 (s, 3H, N-CH_3), 4.39 (q, 2H, OCH_2), 7.22 (s, 1H, H-4), 7.95 (d, 2H, J = 7.2 Hz, H_{Ph}), 8.26 (d, 2H, J = 7.2 Hz, H_{Ph}); ^{13}C NMR, δ: 14.27 (CH_3), 40.0 (N-CH_3), 61.37 (OCH_2), 108.84 (C-4), 124.18, 125.9, 134.42, 138.8, 147.27 (C_{Ph}, C-5), 147.37 (C-3), 159.50 (C=O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1730 (CO), 1590 (C=N), 1541 $(NO_2)_{as}$, 1320 $(NO_2)_s$.

Ethyl 1-Methyl-3-(5-nitro-2-furyl)pyrazole-5-carboxylate (IIIb)

Light yellow solid; yield: 90 %, m.p. = 138—139 ℃. For $C_{11}H_{11}N_3O_5$ (M_r = 265.23) w_i(calc.): 49.81 % C, 4.18% H, 15.84 % N; w_i(found): 50.22 % C, 4.15 % H, 15.89 % N. ^{1}H NMR spectrum, δ: 1.41 (t, 3H, CH_3), 4.24 (s, 3H, N-CH_3), 4.40 (q, 2H, OCH_2), 6.89 (d, 1H, J = 3.14 Hz, H_{Fu}-3), 7.25 (s, 1H, H-4), 7.41 (d, 1H, J = 3.14 Hz, H_{Fu}-4); ^{13}C NMR, δ: 14.21, (CH_3), 40.13 (N-CH_3), 61.55 (OCH_2), 108.31, 109.35 (C_{Fu}-3, C_{Fu}-4), 113.84 (C-4), 134.26 (C_{Fu}), 139.7 (C-5), 150.81 (C-3), 151.48 (C_{Fu}), 160.19 (C=O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1734 (CO), 1603 (C=N), 1552 $(NO_2)_{as}$, 1315 $(NO_2)_s$.

Methyl 1-Methyl-3-(5-nitro-2-furyl)pyrazole-5-carboxylate (IIIc)

Dark yellow solid; yield: 61 %, m.p. = 151—153 ℃. For $C_{10}H_9N_3O_5$ (M_r = 251.2) w_i(calc.): 47.81 % C, 3.61 % H, 16.72 % N; w_i(found): 47.95 % C, 3.72 % H, 16.65 % N. ^{1}H NMR spectrum, δ: 3.94 (s, 3H, N-CH_3), 4.26 (s, 3H, OCH_3), 6.90 (d, 1H, J = 3.5 Hz, H_{Fu}-3), 7.21 (s, 1H, H-4), 7.41 (d, 1H, J = 3.5 Hz, H_{Fu}-4); ^{13}C NMR, δ: 40.15 (N-CH_3), 52.34 (OCH_3), 108.44, 109.41 (C_{Fu}), 116.81 (C-4), 133.88 (C_{Fu}), 139.72 (C-5), 150.61 (C-3), 159.54 (C_{Fu}), 171.60 (C=O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1740 (CO), 1645 (C=N), 1556 $(NO_2)_{as}$, 1332 $(NO_2)_s$.

Ethyl 1-Phenyl-3-(4-nitrophenyl)pyrazole-5-carboxylate (IIId)

Light orange needles; yield: 88 %, m.p. = 168—169 ℃. For $C_{18}H_{15}N_3O_4$ (M_r = 337.33) w_i(calc.): 64.09 % C, 4.48 % H, 12.46 % N; w_i(found): 63.79 % C, 4.58 % H, 12.59 % N. ^{1}H NMR spectrum, δ: 1.27 (t, 3H, CH_3), 4.28 (q, 2H, OCH_2), 7.42 (s, 1H, H-4), 7.36—7.50 (m, 5H, H_{Ph}), 8.04 (d, 2H, J = 8.7 Hz, H_{Ph}), 8.28 (d, 2H, J = 8.7 Hz, H_{Ph}); ^{13}C NMR, δ: 14.02 (CH_3), 61.50 (OCH_2), 110.14 (C-4), 124.17, 126.01, 126.27, 128.32, 128.71, 135.36, 138.39, 140.04, 147.27, 147.54 (C_{Ph}, C-5), 149.1 (C-3), 158.71 (C=O); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1734 (CO), 1603 (C=N), 1541 $(NO_2)_{as}$, 1346 $(NO_2)_s$. Mass spectrum, m/z (I_r/%): 337$^{+\bullet}$ (100), 292 (18), 265 (11), 219 (14), 77 (28).

1-Methyl-3-(5-nitro-2-furyl)-5-phenylpyrazole (IIIe)

Dark yellow solid; yield: 89 %, m.p. = 142—144 ℃. For $C_{14}H_{11}N_3O_3$ (M_r = 269.26) w_i(calc.): 62.45 % C, 4.12 % H, 15.61 % N; w_i(found): 62.67 % C, 3.98 % H, 15.83 % N. ^{1}H NMR spectrum, δ: 3.95 (s, 3H, N-CH_3), 6.76 (s, 1H, H-4), 6.89 (d, 1H, J = 3.8 Hz, H_{Fu}-3), 7.41 (d, 1H, J = 3.8 Hz, H_{Fu}-4), 7.45—7.49 (m, 5H, H_{Ph}); ^{13}C NMR, δ: 38.06 (N-CH_3), 104.71 (C-4), 109.07, 110.45 (C_{Fu}-3), 114.06 (C_{Fu}-4), 126.04, 128.76, 128.99, 129.17, 129.47, 140.37 (C_{Fu}-2), 145.57 (C_{Fu}-5), 151.93 (C-3).

Methyl 1-Methyl-3,4-bis(5-nitro-2-furyl)pyrazole-5-carboxylate (IVa)

Colourless solid; yield: 31 %, m.p. = 176—178 ℃. For $C_{14}H_{10}N_4O_8$ (M_r = 362.2) w_i(calc.): 46.42 % C, 2.78 % H, 15.46 % N; w_i(found): 56.48 % C, 4.58 % H, 15.49 % N. ^{1}H NMR spectrum, δ: 3.88 (s, 3H, OCH_3), 4.27 (s, 3H, N-CH_3), 6.92 (d, 1H, J = 3.8 Hz, H_{Fu}-4′), 6.96 (d, 1H, J = 3.7 Hz, H_{Fu}-4″), 7.35 (d, 1H, J = 3.8 Hz, H_{Fu}-3′), 7.46 (d, 1H, J = 3.7 Hz, H_{Fu}-3″); ^{13}C NMR, δ : 40.92 (N-CH_3), 52.81 (OCH_3), 112.7 (C-4), 135.25 (C-5), 138.96 (C-3), 111.0, 111.13, 112.45, 112.54, 114.68, 114.77, 146.53, 148.49 (C_{Fu}), 158.9 (CO); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1580 (C=N), 1560 $(NO_2)_{as}$, 1344 $(NO_2)_s$.

Methyl 1-Methyl-3,5-bis(5-nitro-2-furyl)pyrazole-4-carboxylate (IVb)

Colourless solid; yield: 47 %, m.p. =173—174 ℃. For $C_{14}H_{10}N_4O_8$ (M_r = 362.2) w_i(calc.): 46.42 % C, 2.78 % H, 15.46 % N; w_i(found): 46.53 % C, 2.86 % H, 15.40 % N. ^{1}H NMR spectrum, δ: 3.72 (s, 3H, OCH_3), 4.01 (s, 3H, N-CH_3), 7.25 (d, 1H, J = 3.8 Hz, H_{Fu}-4′), 7.29 (d, 1H, J = 3.8 Hz, H_{Fu}-4″), 7.64 (d, 1H, J = 3.8 Hz, H_{Fu}-3′), 7.72 (d, 1H, J = 3.8 Hz, H_{Fu}-3″). ^{13}C NMR, δ: 39.38 (N-CH_3), 52.17 (OCH_3), 113.0 (C-4), 134.13 (C-5), 139.55 (C-3), 114.14 (C-3′), 114.02 (C-4′), 148.11 (C-5′), 151.5 (C-2′), 113.51 (C-4″), 117.23 (C-3″), 142.77 (C-5″), 152.4 (C-2″), 162.02 (CO).

Ethyl 1-Methyl-3-(5-nitro-2-furyl)-4-phenyl-4,5-dihydropyrazole-5-carboxylate (Va)

Yellow solid; yield: 24 %, m.p. = 121—123 ℃. For $C_{16}H_{15}N_3O_5$ (M_r = 329.3) w_i(calc.): 58.36 % C, 4.59 % H, 12.76 % N; w_i(found): 58.49 % C, 4.21 % H, 12.55 % N. ^{1}H NMR spectrum, δ: 1.39 (t, 3H, CH_3), 3.23 (s, 3H, N-CH_3), 3.99 (d, 1H, J = 10.1 Hz, H-4), 4.26 (q, 2H, OCH_2), 4.83 (d, 1H, J = 10.0 Hz, H-5), 6.16 (d, 1H, J = 3.8 Hz, H_{Fu}-3), 7.15 (d, 1H, J =

3.8 Hz, H_{Fu}-4), 7.29—7.34 (m, 5H, H_{Ph}); ^{13}C NMR, δ: 14.17 (CH_3), 41.43 (N-CH_3), 55.87 (C-4), 61.98 (OCH_2), 77.70 (C-5), 111.07, 113.27, 138.40, 149.84 (C_{Fu}), 127.97, 128.15, 128.44, 129.27, 129.72, 129.96 (C_{Ph}), 139.69 (C-3), 169.1 (CO).

Ethyl 1-Methyl-3-(5-nitro-2-furyl)-5-phenyl-4,5-dihydropyrazole-4-carboxylate (Vb)

Yellowish solid; yield: 49 %, m.p. = 109—110 ℃. For $C_{16}H_{15}N_3O_5$ (M_r = 329.3) w_i(calc.): 58.36 % C, 4.59 % H, 12.76 % N; w_i(found): 58.45 % C, 4.22 % H, 12.70 % N. ^{1}H NMR spectrum, δ: 1.31 (t, 3H, CH_3), 2.98 (s, 3H, N-CH_3), 4.17 (d, 1H, J = 13.0 Hz, H-4), 4.30 (q, 2H, OCH_2), 4.77 (d, 1H, J = 12.9 Hz, H-5), 6.81 (d, 1H, J = 3.9 Hz, H_{Fu}-3), 7.35 (d, 1H, J = 3.9 Hz, H_{Fu}-4), 7.37—7.39 (m, 5H, H_{Ph}); ^{13}C NMR, δ: 14.01 (CH_3), 39.85 (N-CH_3), 60.27 (C-5), 62.38 (OCH_2), 76.61 (C-4), 109.81, 113.79, 133.59, 150.49 (C_{Fu}), 127.24, 128.86, 129.13, 133.59 (C_{Ph}), 137.39 (C-3), 169.92 (CO).

1-Phenyl-3-(4-tolyl)pyrazole (VIa)

Yellow plates; yield: 78 %, m.p. = 170—171 ℃. For $C_{16}H_{14}N_2$ (M_r = 234.29) w_i(calc.): 82.02 % C, 6.02 % H, 11.96 % N; w_i(found): 81.83 % C, 6.19 % H, 11.76 % N. ^{1}H NMR spectrum, δ: 2.26 (s, 3H, CH_3), 5.78 (d, 1H, J = 5.8 Hz, H-4), 7.06 (d, 1H, J = 5.8 Hz, H-5), 7.50 (d, 2H, J = 7.6 Hz, H_{Ph}), 7.54 (d, 2H, J = 7.7 Hz, H_{Ph}), 7.30—7.35 (m, 5H, H_{Ph}); ^{13}C NMR, δ: 21.14 (CH_3), 85.51, 129.08 (C-4, C-5), 122.26, 128.74, 128.87, 129.08, 130.37, 130.40, 133.91, 134.45, 137.27, 137.29 (C_{Ph}), 152.22 (C-3); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 3057 (C-H_{Ph}), 2920 $(CH_3)_{as}$, 1595 (C=N). Mass spectrum, m/z (I_r/%): $234^{+\bullet}$ (19), 91(100), 65 (36).

1-Phenyl-3-(5-nitro-2-furyl)pyrazole (VIb)

Light yellow needles; yield: 74 %, m.p. = 188—189 ℃. For $C_{13}H_9N_3O_3$ (M_r = 255.2) w_i(calc.): 61.18 % C, 3.55 % H, 16.46 % N; w_i(found): 61.43 % C, 3.36 % H, 16.29 % N. ^{1}H NMR spectrum, δ: 6.86 (d, 1H, J = 2.6 Hz, H-4), 6.93 (d, 1H, J = 4.0 Hz, H_{Fu}-3), 7.41 (d, 1H, J = 4.0 Hz, H_{Fu}-4), 7.93 (d, 1H, J = 2.6 Hz, H-5), 7.18—7.64 (m, 5H, H_{Ph}).

1-Methyl-3-(5-nitro-2-furyl)pyrazole (VIc)

Yellow solid; yield: 86 %, m.p. = 165—166 ℃. For $C_8H_7N_3O_3$ (M_r = 193.15) w_i(calc.): 49.74 % C, 3.65 % H, 21.75 % N; w_i(found): 50.19 % C, 3.52 % H, 21.83 % N. ^{1}H NMR spectrum, δ: 3.92 (s, 3H, N-CH_3), 6.76 (d, 1H, J = 2.3 Hz, H-4), 7.06 (d, 1H, J = 4.0 Hz, H_{Fu}-3), 7.75 (d, 1H, J = 4.0 Hz, H_{Fu}-4), 7.84 (d, 1H, J = 2.2 Hz, H-5); ^{13}C NMR, δ: 38.98 (CH_3), 104.64, 132.99 (C-4, C-5), 108.92, 115.44 (C_{Fu}-3, C_{Fu}-4), 140.04 (C_{Fu}-5), 150.76 (C-3), 151.78 (C_{Fu}-2).

Dimethyl 1-Phenyl-3-(4-nitrophenyl)pyrazole-4,5-dicarboxylate (IXa)

Colourless needles; yield: 81 %, m.p. = 127—129 ℃. For $C_{19}H_{15}N_3O_6$ (M_r = 381.34) w_i(calc.): 59.84 % C, 3.96 % H, 11.02 % N; w_i(found): 59.53 % C, 3.94 % H, 10.95 % N. ^{1}H NMR spectrum, δ: 3.84 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 7.49—7.53 (m, 5H, H_{Ph}), 7.99 (d, 2H, J = 9.0 Hz, H_{Ph}), 8.29 (d, 2H, J = 9.0 Hz, H_{Ph}); ^{13}C NMR, δ: 52.37, 53.38 (OCH_3), 114.1 (C-4), 123.37, 124.39, 129.39, 129.50, 129.87 (C_{Ph}), 139.79, 137.84, 138.72, 148.02, 149.92 (C-3, C-5, C_{Ph}), 160.46, 162.73 (CO); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1736 (CO), 1603 (C=N), 1535 $(NO_2)_{as}$, 1344 $(NO_2)_s$.

Dimethyl 1-Phenyl-3-(4-chlorophenyl)-pyrazole-4,5-dicarboxylate (IXb)

Colourless solid; yield: 73 %, m.p. = 101—102 ℃. For $C_{19}H_{15}ClN_2O_4$ (M_r = 370.78) w_i(calc.): 61.55 % C, 4.08 % H, 7.56 % N; w_i(found): 61.29 % C, 3.85 % H, 7.49 % N. ^{1}H NMR spectrum, δ: 3.82 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 7.30 (d, 2H, J = 9.0 Hz, H_{Ph}), 7.40—7.51 (m, 5H, H_{Ph}), 7.71 (d, 2H, J = 9.0 Hz, H_{Ph}); ^{13}C NMR, δ: 52.18, 53.17 (OCH_3), 113.7 (C-4), 124.37, 128.15, 129.23, 130.22, 134.16, 137.24, 138.82, 150.99, 155.27, 156.67 (C-3, C-5, C_{Ph}), 160.59, 163.04 (CO).

Dimethyl 1-Methyl-3-(4-chlorophenyl)-pyrazole-4,5-dicarboxylate (IXc)

Yellowish solid; yield: 78 %, m.p. = 132—134 ℃. For $C_{14}H_{13}ClN_2O_4$ (M_r = 308.71) w_i(calc.): 54.47 % C, 4.24 % H, 9.07 % N; w_i(found): 54.18 % C, 4.39 % H, 8.97 % N. ^{1}H NMR spectrum, δ: 3.69 (s, 3H, N-CH_3), 3.81 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 7.38 (d, 2H, J = 8.5 Hz, H_{Ph}), 7.72 (d, 2H, J = 8.5 Hz, H_{Ph}).

Dimethyl 1-Phenyl-3-(5-nitro-2-furyl)pyrazole-4,5-dicarboxylate (IXd)

Colourless needles; yield: 82 %, m.p. = 145—147 ℃. For $C_{17}H_{13}N_3O_7$ (M_r = 371.3) w_i(calc.): 54.99 % C, 3.53 % H, 11.32 % N; w_i(found): 54.60 % C, 3.47 % H, 11.21 % N. ^{1}H NMR spectrum, δ: 3.88 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.40 (d, 1H, J = 3.8 Hz, H_{Fu}-3), 7.42 (d, 1H, J = 3.8 Hz, H_{Fu}-4), 7.28—7.41 (m, 5H, H_{Ph}); ^{13}C NMR, δ: 52.31, 53.08 (OCH_3), 112.48, 113.36, 114.23, 124.28, 129.04, 129.44, 137.13, 138.19, 140.20, 147.63, 150.8, 169.59, 161.67 (CO); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1741 (CO), 1597 (C=N), 1547 $(NO_2)_{as}$, 1350 $(NO_2)_s$.

Dimethyl 1-Methyl-3-(5-nitro-2-furyl)pyrazole-4,5-dicarboxylate (IXe)

Yellow needles; yield: 80 %, m.p. = 170—172 ℃. For $C_{12}H_{11}N_3O_7$ (M_r = 309.23) w_i(calc.): 46.61 % C, 3.59 % H, 13.59 % N; w_i(found): 46.43 % C, 3.60 % H, 13.42 % N. ^{1}H NMR spectrum, δ: 3.95 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.17 (s, 3H, N-CH_3), 7.09 (d, 1H, J = 3.8 Hz, H_{Fu}-3), 7.37 (d, 1H, J = 3.8 Hz, H_{Fu}-4); ^{13}C NMR, δ: 40.01 (N-CH_3), 52.85, 53.0 (OCH_3), 111.47, 112.93 (C_{Fu}-3, C_{Fu}-4), 115.75 (C-4), 130.20, 133.99 (C_{Fu}-2), 138.16, 148.38 (C_{Fu}-5), 150.8 (C-3), 159.14, 162.99 (CO); IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ = 1745 (CO), 1579 (C=N), 1537 $(NO_2)_{as}$, 1363 $(NO_2)_s$.

Dimethyl 3-Methyl-5-(5-nitro-2-furyl)-10-oxa-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene-8,9-dicarboxylate (XI)

Light red needles; yield: 81 %, m.p. = 226—227 ℃. For $C_{16}H_{17}N_3O_8$ (M_r = 379.3) w_i(calc.): 50.65 % C, 4.51 % H, 11.07 % N; w_i(found): 50.88 % C, 4.56 % H, 11.12 % N. ^{1}H NMR spectrum, δ: 3.03 (d, 1H, J = 9.5 Hz, H-8), 3.24 (d, 1H, J = 9.45 Hz, H-9), 3.17 (s, 3H, N-CH_3), 3.72 (s, 6H, OCH_3), 3.85 (d, 1H, J = 9.6 Hz, H-6), 4.01 (d, 1H, J = 9.6 Hz, H-2), 5.09 (d, 2H, J = 2.4 Hz, H-1, H-7), 6.75 (d, 1H, J = 3.9 Hz, H_{Fu}-3), 7.39 (d, 1H, J = 3.9 Hz, H_{Fu}-4); ^{13}C NMR, δ : 39.39 (N-CH_3), 47.88, 50.74 (OCH_3), 52.43, 55.83 (C-8, C-9), 72.91 (C-2), 81.15, 81.96 (C-1, C-7), 108.87, 114.53 (C_{Fu}-3, C_{Fu}-4), 134.51 (C-5), 148.5, 151.57 (C_{Fu}), 170.22, 170.40 (CO).

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