Synthesis of Novel 4-Pyrazolyl-2-oxo-1,2,3,4-tetrahydropyrimidines Promoted by Phosphotungstic Acid

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Phosphotungstic acid, a keggin's type heteropoly acid catatalysed Biginelli reaction was carried out using pyrazole aldehyde, ethyl acetoacetate and urea to synthesis novel 4-pyrazolyl -2-oxo-1,2,3,4-tetrahydropyrimidines.

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Introduction.

The synthesis of tetrahydropyrimidines by Biginelli reaction [1] is a multicomponent reaction and offers significant advantages over conventional linear type reactions [2]. The multifunctionalised tetrahydropyrimidines are found as core units in Batzelladine and Crambine alkaloids derived from marine sources [3] that have been found to be potent HIVgp -120 inhibitors [4]. They also emerged as potent calcium channel blockers [5], antihypertensive agents [6], α_{1a}-adrenergic antagonists [7] and neuropeptide antagonists. Since the originally reported method by Biginelli suffers low yields and high yields could be achieved by following multistep procedures [8] which lack the simplicity of one-pot Biginelli protocol, Biginelli reaction attracted the attention of researchers for the discovery of milder and efficient procedure for the synthesis of tetrahydropyrimidines. A wide variety of catalysts such as HCl, AcOH [9] (protic acids), $BF_3.OEt_2$, $InCl_3$, $BiCl_3$, $LiClO_4$, $ZrCl_4$, $La_9(OTf)_3$, $NiCl_2.6H_2O$, $FeCl_3.6H_2O$ (Lewis acids) and ionic liquids [10] and iodotrimethylsilane [11], were used in the Biginelli reaction. Many of these catalysts are expensive or less readily available or demanding anhydrous condition or non recoverable. A need still exists for versatile, simple and environmentally friendly processes whereby tetrahydropyrimidines may be obtained under milder conditions [12].

In this paper we report the synthesis of 4-pyrazolyl-2-oxo-1,2,3,4-tetrahydropyrimidines using readily available phosphotungstic acid, Keggins type heteropoly acid. They have strong Bronsted acidity [13] and exhibit "pseudoliquid phase" [14]. Heteropolyanions can stabilize cationic organic intermediates [15] and have very weak basicity and great softness [16]. Heteropoly acids lack side reactions [17]. Heteropoly acids are stable, relatively nontoxic, crystalline and preferable with regard to safety and ease of handling. The heteropoly acids are efficient catalyst for the synthesis of vitamins E, K1 and C [18], Prins reaction [15], Beckman rearrangement under mild conditions [19], pinacol rearrangement [20], esterification [21], cyclotrimerisation of aldehydes [22] and Friedel-Crafts reaction. Silica supported phosphotungstic acid were found to be an active and recyclable catalyst for the Diels - Alder reaction [23].

Results and Discussion.

A mixture of the corresponding pyrazole aldehyde **1**, ethyl acetoacetate **2**, urea **3** and phosphotungstic acid in methanol was stirred at reflux temperature for 7 hours (Scheme 1). The product obtained was column chromatographed to get pure tetrahydropyrimidine **4**. The Biginelli reaction was carried out successfully for a variety of substituted pyrazole aldehydes using phosphotungstic acid and the results are summarized in Table 1.

The mechanism of Biginelli reaction was reinvestigated by Kappe and the key step involving the acid-catalysed formation of an N-acyliminium ion intermediate from

Scheme 1

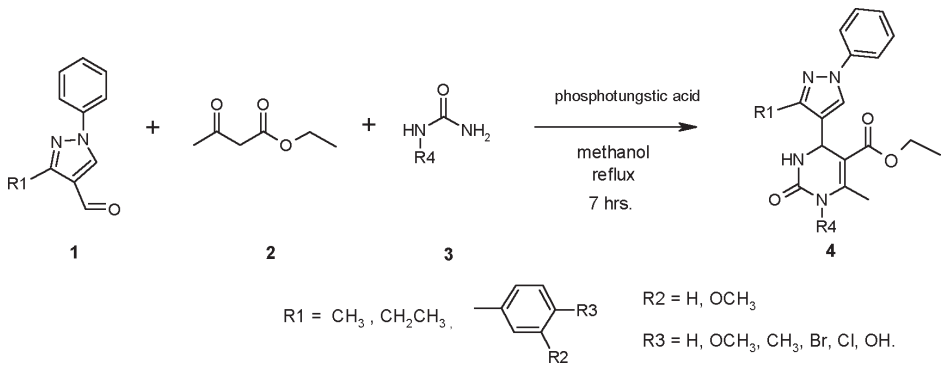


Table 1

Phosphotungstic acid catalysed synthesis of 4-pyrazolyl-2-oxo-1,2,3,4-tetrahydropyrimidines.

S.No. [a]	Product	R1	R2	R3	R4	Yield %
1	**4a**	-	H	H	-	67
2	**4b**	-	H	H	CH_3	72
3	**4c**	-	-	Cl	-	65
4	**4d**	-	-	Cl	CH_3	69
5	**4e**	-	H	OCH_3	CH_3	71
6	**4f**	-	H	OH	-	68
7	**4g**	-	H	CH_3	-	74
8	**4h**	-	OCH_3	H	-	64
9	**4i**	-	H	Br	-	68
10	**4j**	CH_3	-	-	-	73
11	**4k**	CH_2CH_3	-	-	-	71

[a] The yield is based on isolation by column chromatography and the products were characterized by IR, NMR and Mass spectrum.

aldehyde and urea precursors was established. Interception of the iminium ion by ethyl acetoacetate in enol form produces an open chain ureid, which subsequently cyclizes to hexahydropyrimidine, which on acid catalysed elimination of water, gives tetrahydropyrimidine. He also found that polyphosphate ester (PPE) is an excellent reaction mediator for the Biginelli tetrahydropyrimidine synthesis, because it specifically stabilizes the iminium ion intermediate. Since the heteropolyanions can stabilize cationic organic intermediates, the mechanism for phosphotungstic acid catalysed reaction is given in Scheme 2.

Conclusion.

In conclusion we have developed a simple and general method for the synthesis of 4-pyrazolyl-2-oxo-1,2,3,4-tetrahydropyrimidines using safe, stable, readily available and easy to handle phosphotungstic acid. This method does not require anhydrous condition. Unlike other Lewis acid catalysts, phosphotungstic acid is stable towards moisture and can be recovered and reused. The usage of phosphotungstic acid, a heteropoly acid makes this method economical and environmentally attractive.

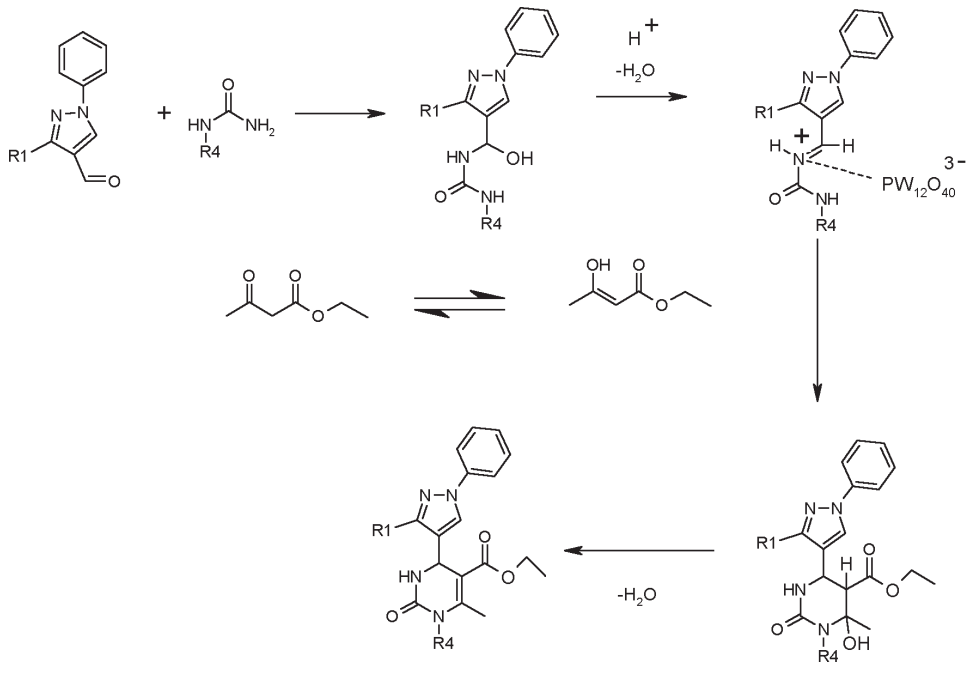
EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Analytical TLC was performed on pre-coated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Machery-Nagel, Germany). IR spectra were taken as KBr pellets on a Perkin Elmer RXI FT-IR spectrometer. ^1H NMR spectra were obtained on a JEOL instrument at 500 MHz in DMSO-d_6 and ^{13}C NMR spectra were recorded at 125 MHz in DMSO-d_6 using TMS as internal standard. Column chromatography was performed on silica gel (60 – 120 mesh, SRL, India). Mass spectra were recorded using JEOL DX-303 in EI ionization mode at 70 eV.

General Procedure for the Synthesis of 4-Pyrazolyl-2-oxo-1,2,3,4-tetrahydropyrimidines.

A mixture of the corresponding pyrazole aldehyde (1 mmol), ethyl acetoacetate (1.2 mmol), urea (1.2 mmol) and phosphotungstic acid (0.1 mmol) in methanol was stirred at reflux temperature for 7 hours. After completion of the reaction, as indicated by TLC, the solvent was removed under reduced pressure. The residue was poured on crushed ice, stirred for some time and

Scheme 2



filtered to give the crude product which was column chromatographed with a mixture of ethyl acetate and petroleum ether (1:2) using silica gel to afford pure 4-pyrazolyl-2-oxo-1,2,3,4-tetrahydropyrimidines.

Ethyl-4-(1,3-dipheyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4a**).

This compound was obtained as colourless solid, mp 218-220 °C; IR (KBr): 3427, 2953, 1696, 1648, 1454, 1233, 1095 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.77 (t, 3H), 2.20 (s, 3H), 3.80 (m, 2H), 5.32 (d, 1H, tetrahydropyrimidine-CH), 7.28 (t, 1H), 7.40 (t, 1H), 7.45 (d, 2H), 7.48 (d, 2H), 7.70 (d, 2H), 7.85 (d, 2H), 7.99 (broad s, 1H, NH), 8.22 (s, 1H, pyrazole-CH), 9.12 (broad s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.15, 16.46, 44.12, 59.81, 103.70, 118.89, 125.78, 126.89, 127.64, 128.47, 128.89, 128.93, 130.00, 133.53, 139.83, 150.80, 151.00, 153.50, 165.83; MS: *m/z* 402 (M^+).

Anal. Calcd for $C_{23}H_{22}N_4O_3$: C, 68.64; H, 5.51; N, 13.92. Found: C, 68.67; H, 5.50; N, 13.94.

Ethyl-4-(1,3-dipheyl-1*H*-pyrazol-4-yl)-1,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4b**).

This compound was obtained as colourless solid, mp 192-194°C; IR (KBr): 3218, 3089, 2953, 1680, 1636, 1446, 1261, 1090 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.76 (t, 3H), 2.43 (s, 3H), 3.12 (s, 3H), 3.78 (m, 2H), 5.34 (d, 1H, tetrahydropyrimidine-CH), 7.27 (t, 1H), 7.39 (t, 1H), 7.43 (d, 2H), 7.46 (d, 2H), 7.68 (d, 2H), 7.83 (d, 2H), 7.97 (broad s, 1H, NH), 8.29 (s, 1H, pyrazole-CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.15, 16.46, 30.27, 44.63, 59.81, 103.70, 118.89, 125.78, 126.89, 127.64, 128.47, 128.89, 128.93, 130.00, 133.53, 139.83, 150.80, 151.00, 153.50, 165.83; MS: *m/z* 416(M^+).

Anal. Calcd for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.81; N, 13.45. Found: C, 69.23; H, 5.82; N, 13.44.

Ethyl-4-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4c**).

This compound was obtained as colourless solid, mp 210-212 °C; IR (KBr): 3352, 3227, 3107, 2967, 1692, 1645, 1446, 1229, 1095 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.80 (t, 3H), 2.21 (s, 3H), 3.77 (q, 2H), 5.33 (d, 1H, tetrahydropyrimidine-CH), 7.27 (t, 1H), 7.45 (t, 2H), 7.51 (d, 2H), 7.73 (d, 2H), 7.76 (broad s, 1H, NH), 7.83 (d, 2H), 8.34 (s, 1H, pyrazole-CH), 9.16 (broad s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.29, 18.34, 48.26, 59.56, 100.18, 118.86, 126.92, 126.99, 127.99, 128.94, 130.04, 130.62, 132.48, 133.26, 139.77, 148.76, 149.68, 152.27, 165.91; MS: *m/z* 437(M^+).

Anal. Calcd for $C_{23}H_{21}ClN_4O_3$: C, 63.23; H, 4.84; N, 12.82. Found: C, 63.24; H, 4.85; N, 12.81.

Ethyl-4-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-1,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4d**).

This compound was obtained as colourless solid, mp 180-181 °C; IR (KBr): 3346, 3221, 3094, 2953, 1685, 1637, 1444, 1261 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.81 (t, 3H), 2.23 (s, 3H), 3.30 (s, 3H), 3.77 (q, 2H), 5.33 (d, 1H, tetrahydropyrimidine-CH), 7.27 (t, 1H), 7.45 (t, 2H), 7.51 (d, 2H), 7.72 (d, 2H), 7.77 (broad s, 1H, NH), 7.85 (d, 2H), 8.35 (s, 1H, pyrazole-CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.30, 18.43, 31.37, 45.97, 59.54, 99.81, 118.87, 126.96, 127.90, 128.97, 130.01, 130.65, 132.51, 132.60, 133.26, 139.77, 148.86, 149.75, 152.32, 166.18; MS: *m/z* 451(M^+).

Anal. Calcd. for $C_{24}H_{23}ClN_4O_3$: C, 63.93; H, 5.14; N, 12.43. Found: C, 63.92; H, 5.13; N, 12.44.

Ethyl-4-(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-1,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4e**).

This compound was obtained as colourless solid, mp 172-174 °C; IR (KBr): 3368, 3213, 3103, 2930, 1683, 1638, 1455, 1254, 1086 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.80 (t, 3H), 2.44 (s, 3H), 3.12 (s, 3H), 3.77 (s, 3H), 3.84 (m, 2H), 5.31 (d, 1H, tetrahydropyrimidine-CH), 6.99 (d, 2H), 7.26 (t, 1H), 7.45 (t, 2H), 7.60 (d, 2H), 7.81 (d, 2H), 7.93 (broad s, 1H, NH), 8.24 (s, 1H, pyrazole-CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.20, 16.49, 30.27, 44.66, 55.70, 59.84, 103.78, 114.32, 118.78, 125.49, 125.93, 126.74, 127.46, 129.98, 130.17, 139.86, 150.72, 150.83, 153.53, 159.68, 165.87; MS: *m/z* 446(M^+).

Anal. Calcd for $C_{25}H_{26}N_4O_4$: C, 67.25; H, 5.87; N, 12.55. Found: C, 67.27; H, 5.88; N, 12.54.

Ethyl-4-(3-(4-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4f**).

This compound was obtained as orange coloured solid, mp 202-204 °C; IR (KBr): 3490, 3363, 3224, 3118, 2981, 1707, 1662, 1458, 1242, 1088 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.82 (t, 3H), 2.22 (s, 3H), 3.77 (q, 2H), 5.32 (d, 1H, tetrahydropyrimidine-CH), 6.81 (d, 2H), 7.24 (t, 1H), 7.44 (t, 2H), 7.53 (d, 2H), 7.66 (broad s, 1H, NH), 7.81 (d, 2H), 8.25 (s, 1H, pyrazole-CH), 9.12 (broad s, 1H, NH), 9.56 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.32, 18.31, 45.98, 59.48, 95.94, 100.39, 115.64, 118.61, 124.40, 126.39, 126.57, 129.98, 130.14, 138.01, 148.52, 150.11, 151.07, 152.49, 165.73; MS: *m/z* 418 (M^+).

Anal. Calcd for $C_{23}H_{22}N_4O_4$: C, 66.02; H, 5.30; N, 13.39. Found: C, 66.01; H, 5.29; N, 13.40.

Ethyl-4-(3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4g**).

This compound was obtained as yellow coloured solid, mp 201-203 °C; IR (KBr): 3218, 3089, 2953, 1680, 1636, 1446, 1261, 1090 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.82 (t, 3H), 2.22 (s, 3H), 2.33 (s, 3H), 3.77 (q, 2H), 5.32 (d, 1H, tetrahydropyrimidine-CH), 7.26 (m, 3H), 7.44 (t, 2H), 7.63 (d, 2H), 7.70 (broad s, 1H, NH), 7.83 (d, 2H), 8.25 (s, 1H, pyrazole-CH), 9.12 (broad s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.34, 18.29, 21.43, 45.94, 59.49, 95.97, 100.38, 115.63, 118.63, 124.50, 126.41, 126.56, 129.97, 130.16, 138.03, 148.55, 150.07, 151.09, 152.48, 165.71; MS: *m/z* 416 (M^+).

Anal. Calcd. for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.81; N, 13.45. Found: C, 69.24; H, 5.83; N, 13.44.

Ethyl-4-(3-(3-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4h**).

This compound was obtained as colourless solid, mp 140-141 °C; IR (KBr): 3365, 3210, 3106, 2933, 1686, 1637, 1458, 1254, 1081 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.79 (t, 3H), 2.19 (s, 3H), 3.77 (s, 3H), 3.80 (q, 2H), 5.36 (d, 1H, tetrahydropyrimidine-CH), 6.94 (dd, 1H), 7.24 (s, 1H), 7.27 (d, 2H), 7.35 (t, 2H), 7.45 (t, 2H), 7.75 (broad s, 1H, NH), 7.83 (d, 2H), 8.31 (s, 1H, pyrazole-CH), 9.29 (broad s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.20, 16.49, 44.66, 55.70, 59.84, 103.78, 114.32, 118.78, 125.49, 125.93, 126.74, 127.46, 129.98, 130.17, 135.96, 139.86, 148.02, 150.72, 150.83, 153.53, 159.68, 165.87; MS: *m/z* 432 (M^+).

Anal. Calcd for $C_{24}H_{24}N_4O_4$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.63; H, 5.58; N, 12.97.

Ethyl-4-(3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4i**).

This compound was obtained as orange coloured solid, mp 176-178 °C; IR (KBr): 3352, 3231, 3113, 2962, 1691, 1644, 1445, 1228, 1096 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 0.81 (t, 3H), 2.21 (s, 3H), 3.77 (q, 2H), 5.33 (d, 1H, tetrahydropyrimidine-CH), 7.28 (t, 1H), 7.45 (t, 2H), 7.63 (d, 2H), 7.67 (d, 2H), 7.74 (broad s, 1H, NH), 7.84 (d, 2H), 8.34 (s, 1H, pyrazole-CH), 9.14 (broad s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.32, 18.36, 45.94, 59.53, 100.02, 118.87, 121.87, 126.94, 126.98, 128.01, 130.03, 130.91, 131.85, 132.86, 148.75, 149.67, 150.23, 152.31, 165.68; MS: *m/z* 481 (M^+).

Anal. Calcd for $C_{23}H_{21}BrN_4O_3$: C, 57.39; H, 4.40; N, 11.64. Found: C, 57.38; H, 4.39; N, 11.64.

Ehyl-6-methyl-4-(3-methyl-1-phenyl-1*H*-pyrazol-4-yl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4j**).

This compound was obtained as colourless solid, mp 204-206 °C; IR (KBr): 3223, 3106, 2963, 1700, 1642, 1460, 1222 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 1.06 (t, 3H), 2.22 (s, 3H), 2.25 (s, 3H), 3.94 (q, 2H), 5.16 (d, 1H, tetrahydropyrimidine-CH), 7.19 (t, 1H), 7.40 (t, 2H), 7.61 (broad s, 1H, NH), 7.71 (d, 2H), 8.09 (s, 1H, pyrazole-CH), 9.16 (broad s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 12.40, 14.64, 18.31, 46.08, 59.66, 99.09, 118.13, 126.09, 126.51, 129.93, 139.99, 147.99, 148.63, 152.57, 165.78; MS: *m/z* 340 (M^+).

Anal. Calcd for $C_{18}H_{20}N_4O_3$: C, 63.52; H, 5.92; N, 16.46. Found: C, 63.53; H, 5.93; N, 16.47.

Ethyl-4-(3-ethyl-1-phenyl-1*H*-pyrazol-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4k**).

This compound was obtained as red coloured solid, mp 148-149 °C; IR (KBr): cm^{-1}. 3220, 3103, 2961, 1703, 1645, 1461, 1223; ^1H NMR (500 MHz, DMSO-d_6): δ = 1.05 (t, 3H), 1.19 (t, 3H), 2.24 (s, 3H), 2.64 (q, 2H), 3.94 (q, 2H), 5.18 (d, 1H, tetrahydropyrimidine-CH), 7.20 (t, 1H), 7.40 (t, 2H), 7.59 (broad s, 1H, NH), 7.72 (d, 2H), 8.05 (s, 1H, pyrazole-CH), 9.13 (broad s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 12.40, 14.64, 18.31, 21.10, 46.08, 59.66, 99.09, 118.13, 126.09, 126.51, 129.93, 139.99, 147.95, 148.63, 150.32, 152.57, 165.78; MS: *m/z* 354 (M^+).

Anal. Calcd. for $C_{19}H_{22}N_4O_3$: C, 64.39; H, 6.26; N, 15.81. Found: C, 64.38; H, 6.27; N, 15.80.

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