

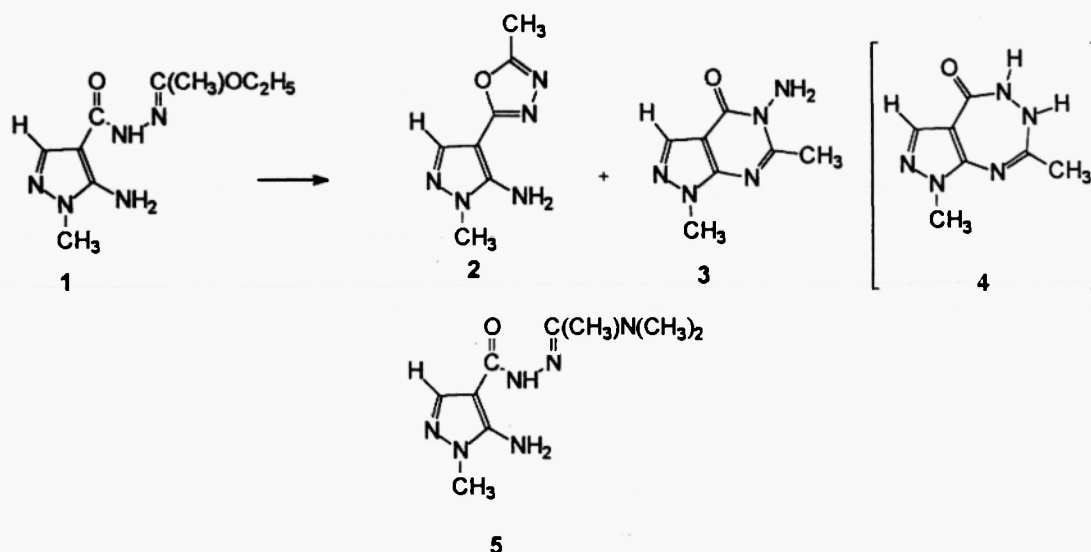
A SIMPLE ROUTE TO NOVEL 3-(5-AMINO-1H-PYRAZOL-4-YL)-5-METHYL-4H-1,2,4-TRIAZOLES

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Abstract: The title compounds can readily be prepared from β -(1'-ethoxyethylidene) 5-amino-1H-pyrazole-4-carboxhydrazides and primary amines under organic solvent free conditions. Their conformational features were deduced from the ^1H NMR data.

Introduction

Previous results (1 – 6) indicated that 5-amino-1H-pyrazole-4-carboxhydrazides are convenient precursors for the preparation of various heterocyclic systems among which 4,5-dihydropyrazolo[3,4-d]pyrimidin-4-ones, (2-6) 3,4-dihydropyrazolo[3,4-d][1,2,3]triazin-4-ones, (6) 5,6-dihydro-4H-pyrazolo[3,4-e][1,2,3]triazepin-4-ones, (1, 4, 5) and 2-(aminopyrazolyl)-1,3,4-oxadiazoles. (2, 4, 5). In particular (5) we observed that β -(1'-ethoxyethylidene) 5-amino-1-methylpyrazole-4-carboxhydrazide **1** (Scheme 1) readily cyclizes to give a mixture of the pyrazoloxadiazole **2** and the pyrazolopyrimidine **3** (which arises (1, 2, 7) probably from the rearrangement of the pyrazolotriazepinone **4**). In contrast, oxadiazole formation is exclusive from the β -[1'-(dimethylamino)ethylidene] derivative **5**.

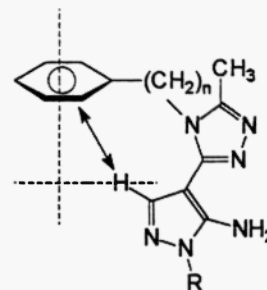


Scheme 1

The aminopyrazolecarboxhydrazides **6** and **7** (Scheme 2) were prepared according to procedures described in the literature. They react with triethyl orthoacetate in refluxing acetonitrile to afford the β -(1'-ethoxyethylidene) derivatives **1** and **8**. As indicated by ^1H NMR, formation of 5-[(1'-ethoxyethylidene)amino]pyrazole-4-carboxhydrazides does not occur (no signal around 4 - 4.5 ppm, the expected position for the signal due to the protons attached to the β -hydrazide nitrogen atom (4, 5)). Such a selectivity is related to the conjugation between the amino group at the 5-position and the carbonyl function in the starting heterocycles **6** and **7**.

Substitution of the ethoxy moiety in **1** and **8** could be achieved by thermal treatment with a primary aromatic or aliphatic amine in the absence of organic solvent. However the intermediate aminoethylidene compounds (**9**) were not isolated: they react intramolecularly, by loss of water, to yield the (aminopyrazolyl)triazoles **10** - **21** rather than the dihydropyrazolotriazepinones **22**, which have been demonstrated to be rather elusive (1, 2, 7), or the oxadiazoles **23** (Scheme 2). That can reasonably be explained by the higher nucleophilicity of the nitrogen atom of the aminoethylidene function in **9**, as compared to the other potential reactive sites (O of the carbonyl group and N of the 5-amino group).

Inspection of the ^1H NMR data of compounds **10** - **21** is revealing of their spatial conformation. For 5-aminopyrazole-4-carboxylic acid derivatives (e.g. **1**, **6** - **8**) as well for (aminopyrazolyl)-oxadiazoles **23** the signal due to the proton at the 3-position of the pyrazole ring appears around 7.5 - 8.0 ppm. (4, 5) A similar situation applies for the pyrazolyltriazoles **13** - **15** and **19** - **21**, bearing an alkyl group at position 4 of the triazole ring. On the other hand, for the pyrazolyltriazoles **10** - **12** and **16** - **18**, bearing an aryl group at the 4-position of the triazole ring, the ^1H NMR spectra indicate the predominance of a particular conformer in solution. Indeed the signal of the H(3) proton of the pyrazole group is shifted upfield to 6 ppm. This suggests that that proton is located in the vicinity of the aryl group, and the shielding occurs as, due to steric hindrances, the N(4) aryl group is *anti* to the amino moiety and is almost perpendicular to a plane consisting of the heterocycles.



Conclusions

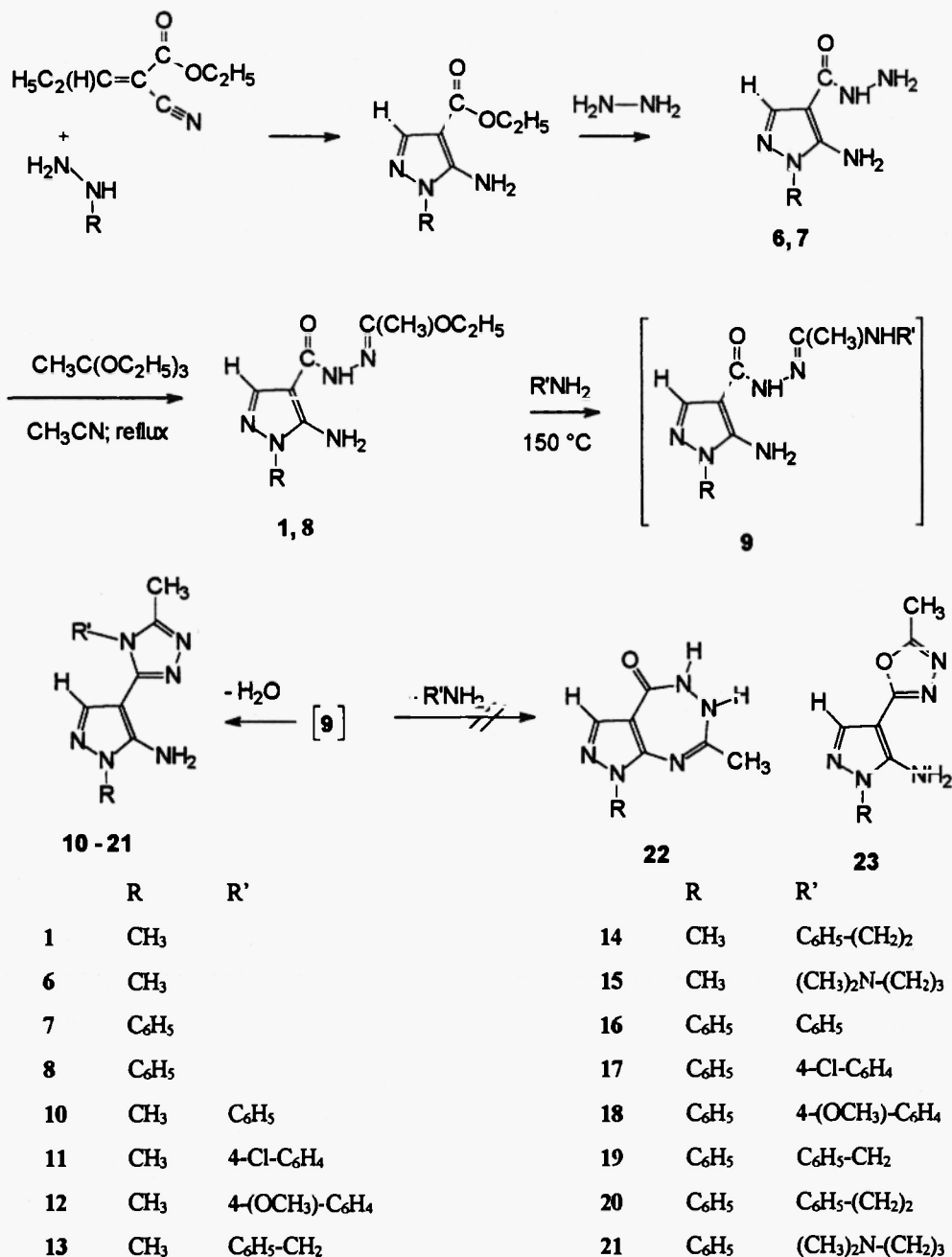
In this paper we disclose a simple procedure for the preparation of novel 3-pyrazolyl-4*H*-1,2,4-triazoles and it appeared that the spatial structures of the title compounds are highly dependent on the nature of the substituent on the N(4) atom of the triazole ring: when it is a aryl group, its position with respect to the five membered rings is frozen in a preferential conformation, a restriction that is suppressed by incorporating methylene units on the N(4) atom of the triazole system. Our results also illustrate a further synthetic capability of the β -[1'-heteroalkylidene] 5-aminopyrazole-4-carboxhydrazides and demonstrate that the chemical behavior of such compounds is dramatically determined by the distribution of the electronic charges on the heteroalkylidene moiety.

Experimental

Melting points (not corrected) were recorded on a hot-stage microscope. All compounds were characterized by infrared spectra (Perkin-Elmer FTIR 1760K spectrophotometer) and NMR spectra (TMS as internal reference; Varian EM-360 L spectrometer, 60 MHz for ^1H or Bruker AMX spectrometer, 300 MHz for ^1H ; 75 MHz for ^{13}C). Elemental analyses were performed at the Station de Haute Belgique (Libramont-Chevigny, Belgium).

In order to study the possibility of controlling the orientation of the cyclization step (ratio 2:3), we decided to modify the electronic density of the C1' atom of β -(1'-hydroxyethylidene) 5-aminopyrazole-4-carboxhydrazides by introducing various amino moieties at that position. We assumed that this could be possible by reacting 1 with primary aliphatic and aromatic amines. The results of this investigation are reported hereafter and illustrate, in fact, a further synthetic possibility of those aminopyrazolecarboxhydrazides.

Results



Scheme 2

Compounds 1, (5) 6. (3. 8) and 7 (9. 10) have been described in the literature.

β -(1'-Ethoxyethylidene) 5-amino-1-phenyl-1H-pyrazole-4-carboxhydrazide (8)

A mixture of 5-amino-1-phenyl-1H-pyrazole-4-carboxhydrazide (7 : 4.34 g ; 20 mmol), triethyl orthoacetate (4 mL : 22 mmol), and acetonitrile (10 mL) was heated under reflux for 5 hours. After cooling, the precipitate was filtered, washed with ether, and recrystallized. Yield : 85 %. M. p. (EtOH/H₂O : 1/1) : 142 - 144 °C. I. R. (KBr) : 3477 ; 3333 ; 3177 ; 1657 ; 1613 ; 1532 ; 1466 ; 1456 ; 1334 ; 1299 ; 745 cm⁻¹. ¹H NMR (DMSO d₆) : 9.9 (1 H ; NH ; br) ; 8.0 (1 H ; H(3) ; s) ; 7.6 - 7.4 (5 H ; Ar ; c) ; 6.3 (2 H ; NH₂ ; br) ; 4.1 (2 H ; CH₂ ; q ; J = 7 Hz) ; 1.9 (3 H ; =C-CH₃ ; s) ; 1.2 (3 H ; CH₂-CH₃ ; t) ppm. ¹³C NMR (DMSO d₆) : 166.8 ; 160.9 ; 149.5 ; 141.0 ; 138.4 ; 129.6 ; 127.3 ; 123.4 ; 96.6 ; 62.0 ; 15.2 ; 14.4 ppm. C₁₄H₁₁N₅O₂ (287.32). Anal. Calc. : C, 58.53 ; H, 5.96 ; N, 24.38. Found : C, 58.63 ; H, 5.89 ; N, 24.18.

Synthesis of the 3-(5-amino-1H-pyrazol-4-yl)-5-methyl-4H-1,2,4-triazoles 10 - 21. General procedure.

A mixture of the β -(1'-ethoxyethylidene) 5-amino-1H-pyrazole-4-carboxhydrazide (10 mmol) and an amine (30 mmol) was heated under stirring in an open flask at 150 °C for 3 hours. After cooling, the mixture was triturated with ether, the solid was filtered and recrystallized.

3-(5-Amino-1-methyl-1H-pyrazol-4-yl)-5-methyl-4-phenyl-4H-1,2,4-triazole 10.

Yield : 75 %. M. p. (C₆H₆) : 195 - 197 °C. I. R. (KBr) : 3389 ; 3296 ; 3161 ; 1653 ; 1646 ; 1588 ; 1565 ; 1536 ; 1501 ; 696 ; 587 cm⁻¹. ¹H NMR (DMSO d₆) : 7.6 - 7.5 (5 H ; Ar ; c) ; 6.4 (2 H ; NH₂ ; br) ; 6.0 (1 H ; H(3 pyraz) ; s) ; 3.6 (3 H ; N-CH₃ ; s) ; 2.2 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 149.4 ; 149.1 ; 146.9 ; 134.7 ; 132.9 ; 130.1 ; 130.0 ; 127.8 ; 89.8 ; 34.2 ; 10.4 ppm. C₁₃H₁₄N₆ (254.29). Anal. Calc. : C, 61.14 ; H, 5.55 ; N, 33.05. Found : C, 61.16 ; H, 5.53 ; N, 33.10.

3-(5-Amino-1-methyl-1H-pyrazol-4-yl)-4-(4-chlorophenyl)-5-methyl-4H-1,2,4-triazole 11.

Yield : 70 %. M. p. (C₆H₆) : 222 - 225 °C. I. R. (KBr) : 3388 ; 3295 ; 3165 ; 1646 ; 1624 ; 1588 ; 1564 ; 1539 ; 1498 ; 1440 ; 1421 ; 1320 ; 1094 ; 946 ; 838 ; 738 ; 584 cm⁻¹. ¹H NMR (DMSO d₆) : 7.7 - 7.5 (4 H ; Ar ; c) ; 6.3 (2 H ; NH₂ ; br) ; 6.1 (1 H ; H(3 pyraz) ; s) ; 3.6 (3 H ; N-CH₃ ; s) ; 2.2 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 149.2 ; 149.1 ; 147.0 ; 134.7 ; 135.5 ; 132.9 ; 130.2 ; 129.8 ; 89.6 ; 34.2 ; 10.3 ppm. C₁₃H₁₃N₆Cl (288.74). Anal. Calc. : C, 54.08 ; H, 4.54 ; N, 29.11. Found : C, 54.07 ; H, 4.20 ; N, 29.34.

3-(5-Amino-1-methyl-1H-pyrazol-4-yl)-4-(4-methoxyphenyl)-5-methyl-4H-1,2,4-triazole 12.

Yield : 80 %. M. p. (C₆H₆) : 218 - 221 °C. I. R. (KBr) : 3411 ; 3312 ; 1619 ; 1583 ; 1553 ; 1515 ; 1466 ; 1452 ; 1442 ; 1323 ; 1304 ; 1253 ; 1181 ; 1171 ; 1035 ; 939 ; 839 ; 618 ; 583 cm⁻¹. ¹H NMR (DMSO d₆) : 7.4 (2 H ; H(2), H(6) Ar ; d ; J = 9 Hz) ; 7.2 (2 H ; H(3), H(5) Ar ; d) ; 6.3 (2 H ; NH₂ ; br) ; 6.0 (1 H ; H(3 pyraz) ; s) ; 3.9 (3 H ; O-CH₃ ; s) ; 3.6 (3 H ; N-CH₃ ; s) ; 2.1 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 160.0 ; 149.6 ; 149.4 ; 146.8 ; 132.9 ; 129.0 ; 127.0 ; 115.1 ; 89.9 ; 55.5 ; 34.1 ; 10.3 ppm. C₁₄H₁₆N₆O (284.32). Anal. Calc. : C, 59.14 ; H, 5.67 ; N, 29.56. Found : C, 58.78 ; H, 5.78 ; N, 29.90.

3-(5-Amino-1-methyl-1H-pyrazol-4-yl)-5-methyl-4-phenylmethyl-4H-1,2,4-triazole 13.

Yield : 75 %. M. p. (C₆H₆) : 120 - 123 °C. I. R. (KBr) : 3398 ; 3274 ; 1625 ; 1588 ; 1538 ; 1455 ; 1424 ; 734 cm⁻¹. ¹H NMR (DMSO d₆) : 7.4 - 7.0 (6 H ; Ar, H(3 pyraz) ; c) ; 6.4 (2 H ; NH₂ ; br) ; 5.4 (2 H ; CH₂ ; s) ; 3.6 (3 H ; N-CH₃ ; s) ; 2.3 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 150.0 ; 149.5 ; 146.9 ; 136.0 ; 133.6 ; 128.9 ; 127.5 ; 125.6 ; 89.6 ; 46.2 ; 34.3 ; 10.1 ppm. C₁₄H₁₆N₆ (268.32). Anal. Calc. : C, 62.67 ; H, 6.01 ; N, 31.32. Found : C, 63.07 ; H, 5.94 ; N, 30.95.

3-(5-Amino-1-methyl-1H-pyrazol-4-yl)-5-methyl-4-(2-phenylethyl)-4H-1,2,4-triazole 14.

Yield : 65 %. M. p. (C₆H₆) : 178 - 180 °C. I. R. (KBr) : 3365 ; 3277 ; 3149 ; 1632 ; 1587 ; 1561 ; 1537 ; 1437 ; 1427 ; 951 ; 705 cm⁻¹. ¹H NMR (DMSO d₆) : 7.6 (1 H ; H(3 pyraz) ; s) ; 7.4 - 7.0 (5 H ; Ar ; c) ; 6.4 (2 H ; NH₂ ; br) ; 4.3 (2 H ; N-CH₂ ; t ; J = 4 Hz) ; 3.7 (3 H ; N-CH₃ ; s) ; 3.0 (2 H ; Ph-CH₂ ; t) ; 2.0 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 149.9 ; 149.1 ; 147.2 ; 137.8 ; 133.8 ; 129.1 ; 128.7 ; 127.0 ; 90.2 ; 45.0 ; 34.7 ; 34.6 ; 10.0 ppm. C₁₅H₁₃N₆ (282.35). Anal. Calc. : C, 63.81 ; H, 6.43 ; N, 29.77. Found : C, 64.17 ; H, 6.27 ; N, 29.40.

3-(5-Amino-1-methyl-1H-pyrazol-4-yl)-4-[3-(dimethylamino)propyl]-5-methyl-4H-1,2,4-triazole 15.

Yield : 75 %. M. p. (C₆H₆) : 165 - 168 °C. I. R. (KBr) : 3388 ; 3284 ; 3159 ; 2941 ; 1627 ; 1587 ; 1558 ; 1533 ; 1452 ; 1422 ; 1317 cm⁻¹. ¹H NMR (DMSO d₆) : 7.6 (1 H ; H(3 pyraz) ; s) ; 6.3 (2 H ; NH₂ ; br) ; 4.1 (2 H ; N-CH₂ ; t ; j = 7 Hz) ; 3.6 (3 H ; N(1 pyraz)-CH₃ ; s) ; 2.4 (3 H ; C-CH₃ ; s) ; 2.2 (2 H ; Ph-CH₂ ; t ; J = 6 Hz) ; 2.1 (6 H ; N(CH₃)₂ ; s) ; 1.8 (2 H ; CH₂ ; m) ppm. ¹³C NMR (DMSO d₆) : 149.6 ; 148.9 ; 146.9 ; 133.5 ; 90.0 ; 55.5 ; 45.1 ; 41.4 ; 34.3 ; 27.0 ; 10.0 ppm. C₁₂H₂₁N₇ (263.35). Anal. Calc. : C, 54.73 ; H, 8.04 ; N, 37.23. Found : C, 54.48 ; H, 7.85 ; N, 37.14.

3-(5-Amino-1-phenyl-1H-pyrazol-4-yl)-5-methyl-4-phenyl-4H-1,2,4-triazole 16.

Yield : 70 %. M. p. (AcOEt) : 212 - 214 °C. I. R. (KBr) : 3353 ; 3288 ; 1619 ; 1597 ; 1577 ; 1538 ; 1500 cm⁻¹. ¹H NMR (DMSO d₆) : 7.7 - 7.4 (10 H ; Ar ; c) ; 6.6 (2 H ; NH₂ ; br) ; 6.2 (1 H ; H(3 pyraz) ; s) ; 2.2 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 149.4 ; 149.0 ; 146.6 ; 138.2 ; 135.0 ; 134.5 ; 130.2 ; 129.3 ; 127.9 ; 127.0 ; 123.6 ; 123.0 ; 90.9 ; 10.4 ppm. C₁₈H₁₆N₆ (316.37). Anal. Calc. : C, 68.34 ; H, 5.10 ; N, 26.56. Found : C, 68.00 ; H, 5.40 ; N, 26.40.

3-(5-Amino-1-phenyl-1H-pyrazol-4-yl)-4-(4-chlorophenyl)-5-methyl-4H-1,2,4-triazole 17.

Yield : 50 %. M. p. (AcOEt) : 246 - 249 °C. I. R. (KBr) : 3459 ; 3333 ; 1619 ; 1584 ; 1576 ; 1541 ; 1506 ; 1492 ; 1420 ; 1094 ; 850 ; 772 cm⁻¹. ¹H NMR (DMSO d₆) : 7.9 - 7.1 (9 H ; Ar ; c) ; 6.5 (2 H ; NH₂ ; br) ; 6.3 (1 H ; H(3 pyraz) ; s) ; 2.2 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 149.8 ; 149.2 ; 146.9 ; 138.4 ; 135.4 ; 135.2 ; 133.7 ; 130.6 ; 130.2 ; 129.6 ; 127.4 ; 123.3 ; 91.0 ; 10.6 ppm. C₁₈H₁₅ClN₆ (350.81). Anal. Calc. : C, 61.63 ; H, 4.31 ; N, 23.96. Found : C, 61.40 ; H, 3.98 ; N, 24.07.

3-(5-Amino-1-phenyl-1H-pyrazol-4-yl)-4-(4-methoxyphenyl)-5-methyl-4H-1,2,4-triazole 18.

Yield : 75 %. M. p. (C₆H₆) : 235 - 237 °C. I. R. (KBr) : 3419 ; 3336 ; 1620 ; 1578 ; 1540 ; 1515 ; 1506 ; 1460 ; 1420 ; 1258 ; 846 ; 769 cm⁻¹. ¹H NMR (DMSO d₆) : 7.6 - 7.4 (7 H ; Ph, H(2) and H(6) Ph-OCH₃ ; c) ; 7.2 (2 H ; H(3) and H(5) Ph-OCH₃ ; d ; J = 9 Hz) ; 6.6 (2 H ; NH₂ ; br) ; 6.3 (1 H ; H(3 pyraz) ; s) ; 3.9 (3 H ; O-CH₃ ; s) ; 2.2 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 160.2 ; 149.8 ; 149.4 ; 146.5 ; 138.2 ; 135.1 ; 129.3 ; 129.1 ; 127.1 ; 126.9 ; 123.0 ; 115.3 ; 91.0 ; 55.5 ; 10.3 ppm. C₁₉H₁₈N₆O (346.39). Anal. Calc. : C, 65.88 ; H, 5.24 ; N, 24.26. Found : C, 65.50 ; H, 5.23 ; N, 24.18.

3-(5-Amino-1-phenyl-1H-pyrazol-4-yl)-5-methyl-4-phenylmethyl-4H-1,2,4-triazole 19.

Yield : 70 %. M. p. (C₆H₆) : 209 - 211 °C. I. R. (KBr) : 3441 ; 3316 ; 1617 ; 1599 ; 1578 ; 1543 ; 1505 ; 1496 ; 1454 ; 1422 ; 725 ; 692 cm⁻¹. ¹H NMR (DMSO d₆) : 7.7 - 7.4 (11 H ; Ar, H(3 pyraz) ; c) ; 6.7 (2 H ; NH₂ ; br) ; 5.5 (2 H ; Ph-CH₂ ; s) ; 2.4 (3 H ; C-CH₃ ; s) ppm. ¹³C NMR (DMSO d₆) : 150.6 ; 149.4 ; 146.8 ; 138.5 ; 136.2 ; 129.6 ; 129.2 ; 128.5 ; 127.8 ; 125.9 ; 123.4 ; 123.3 ; 90.9 ; 46.5 ; 10.4 ppm. C₁₉H₁₈N₆ (330.39). Anal. Calc. : C, 69.07 ; H, 5.49 ; N, 25.44. Found : C, 68.70 ; H, 5.68 ; N, 25.34.

3-(5-Amino-1-phenyl-1H-pyrazol-4-yl)-5-methyl-4-(2-phenylethyl)-4H-1,2,4-triazole 20.

Yield : 55 %. M. p. (C₆H₆) : 184 - 186 °C. I. R. (KBr) : 3362 ; 3273 ; 1619 ; 1576 ; 1543 ; 1536 ; 1501 ; 1421 ; 768 ; 756 ;

703 cm^{-1} . ^1H NMR ($\text{DMSO } d_6$) : 8.0 (1 H; H(3 pyraz) : s) ; 7.8 - 7.1 (10 H; Ar : c) ; 6.6 (2 H; NH_2 : br) ; 4.3 (2 H; N-CH_2 : t; $J = 7$ Hz) ; 3.0 (2 H; Ph-CH_2 : t) ; 2.0 (3 H; C-CH_3 : s) ppm. ^{13}C NMR ($\text{DMSO } d_6$) : 149.9 ; 148.5 ; 146.6 ; 138.4 ; 137.5 ; 136.0 ; 129.3 ; 128.9 ; 128.5 ; 127.0 ; 126.7 ; 123.1 ; 90.9 ; 44.8 ; 35.0 ; 9.7 ppm. $\text{C}_{20}\text{H}_{20}\text{N}_6$ (344.42). Anal. Calc. : C, 69.75 ; H, 5.85 ; N, 24.40. Found : C, 69.42 ; H, 5.57 ; N, 24.28.

3-(5-Amino-1-phenyl-1H-pyrazol-4-yl)-4-[3-(dimethylamino)propyl]-5-methyl-4H-1,2,4-triazole 21.

Yield : 80 %. M. p. (C_6H_6) : 159 - 161 $^\circ\text{C}$. I. R. (KBr) : 3422 ; 3311 ; 2825 ; 1612 ; 1576 ; 1544 ; 1502 ; 1476 ; 1454 ; 1423 ; 774 ; 768 cm^{-1} . ^1H NMR ($\text{DMSO } d_6$) : 7.8 (1 H; H(3 pyraz) : s) ; 7.6 - 7.3 (5 H; Ar : c) ; 6.5 (2 H; NH_2 : br) ; 4.0 (2 H; N-CH_2 : t; $J = 7$ Hz) ; 2.3 (3 H; C-CH_3 : s) ; 2.2 (2 H; Ph-CH_2 : t; $J = 7$ Hz) ; 2.0 (6 H; $\text{N}(\text{CH}_3)_2$: s) ; 1.7 (2 H; CH_2 : m) ppm. ^{13}C NMR ($\text{DMSO } d_6$) : 149.9 ; 148.7 ; 146.6 ; 138.5 ; 136.0 ; 129.4 ; 127.2 ; 123.2 ; 91.0 ; 55.5 ; 45.2 ; 27.1 ; 10.2 ppm. $\text{C}_{17}\text{H}_{23}\text{N}_7$ (325.42). Anal. Calc. : C, 62.75 ; H, 7.12 ; N, 30.13. Found : C, 63.01 ; H, 7.19 ; N, 29.80.

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