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SYNTHESIS OF NEW HETEROCYCLIC SYSTEMS: SPIROTHIADIAZOLEPYRAZOLO[1,5,4-*ef*][1,5]BENZODIAZEPINES

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Abstract- New derivatives spiro type of pyrazolo-1,5-benzodiazepines have been synthesized by 1,3-dipolar cycloaddition of nitrile imines with pyrazolo[1,5,4-*ef*][1,5]benzodiazepin-6-thione. When the nitrile oxide was used the corresponding pyrazolobenzodiazepin-6-one was obtained from the intermediate spirooxathiazole by elimination of isothiocyanate group. These cycloadditions are peri- and regioselectives.

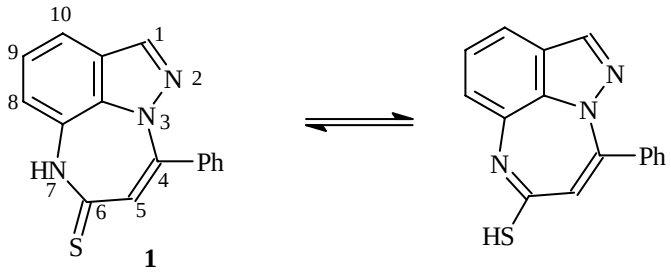
INTRODUCTION

With an aim of developing our research on the reactivity and the synthesis of new heterocyclic systems by 1,3-dipolar cycloaddition reaction, we report the behaviour of pyrazolo[1,5,4-*ef*][1,5]benzodiazepin-6-thione (**1**)[1,2] (HOMO) in the presence of 1,3-dipoles (LUMO) such as diarylnitrile imines,[3-6] *N*-aryl-*C*-ethoxycarbonylnitrile imines[7] and mesitonitrile oxide.[8]

The reaction allowed the synthesis of new spiro-type compounds as an important target in chemical synthesis because of their expecting biological activities,[9,10] and the study of the peri- and regioselectivity of this reaction. The pirazolo-1,5-benzodiazepin-6-thione (**1**) has three potential dipolarophilic sites: C4=C5 double bond, C6=S thiocarbonyl double bond or C6=N7 double bond of the benzodiazepin ring (tautomeric form) and C1=N2 double bond of the pyrazolic ring (Scheme 1).

RESULTS AND DISCUSSION

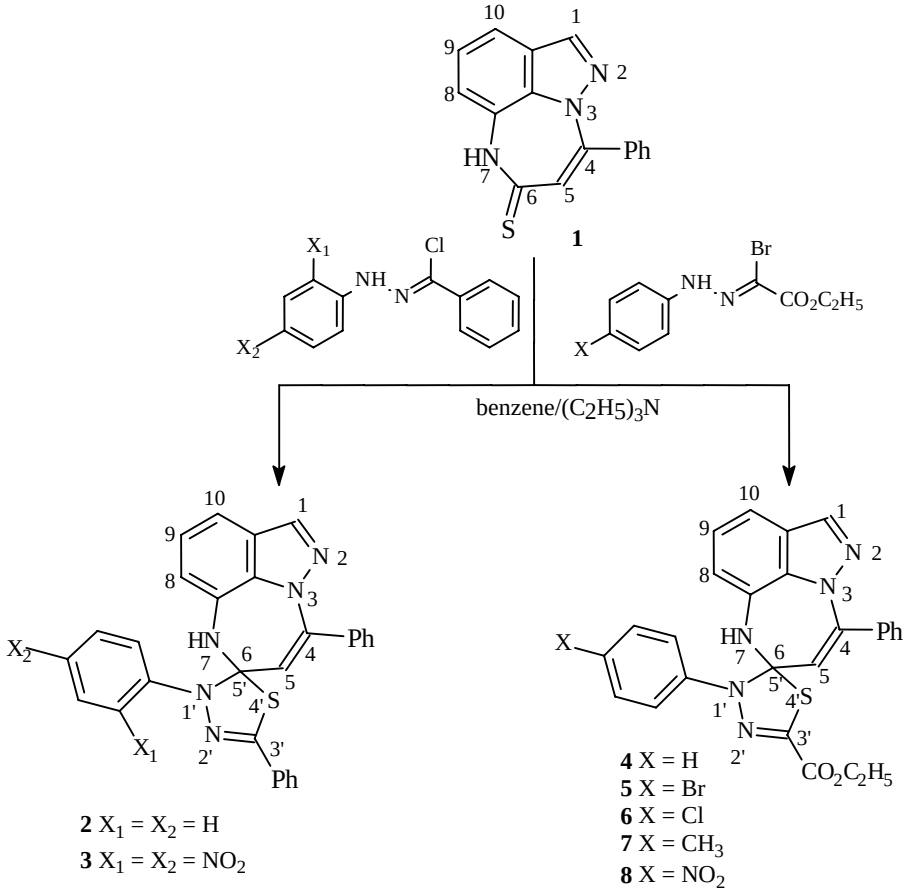
The condensation of diarylnitrile imines and *N*-aryl-*C*-ethoxycarbonylnitrile imines with pyrazolo[1,5,4-*ef*][1,5]benzodiazepin-6-thione (**1)** led in all the cases to only one spiro-type compound (thiadiazolepyrazolo-1,5-benzodiazepine) resulting from an addition of 1,3-dipoles on thioxo C6=S double bond in 30-45 % yields (Scheme 2). No adduct resulting from a condensation on one of the double bonds C4=C5, C6=N7 and C1=N2 was identified under the identical conditions. The results indicate that the reaction is periselective.



Scheme 1

It should be noted that in all 1,5-benzodiazepines series, the literature shows that, double bonds C=N or C=C were affected by the 1,3-dipoles.[11,12] No spiro-type monoadduct resulting from an addition on the C=S or C=O group was observed.

It seems that the introduction of a pyrazolic cycle on 1,5-benzodiazepine modifies the reactivity of 1,5-benzodiazepines toward the 1,3-dipoles (only the exocyclic double bond C6=S is affected) (Scheme 2).



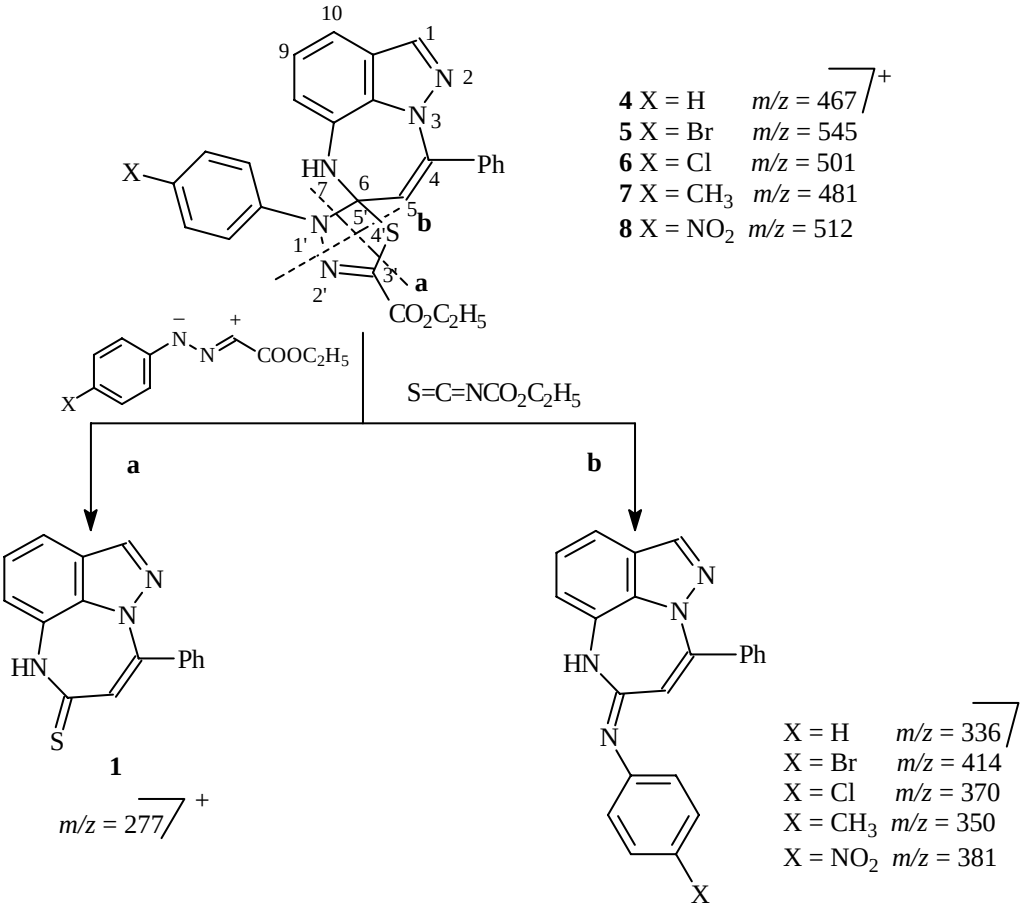
Scheme 2

The ^{1}H NMR spectra ($CDCl_3$) of the compounds (**2-8**), show in particular, a signal at 5.74-6.09 ppm, slightly desihielded assigned to the vinyl proton at position 5, a broard signal at 5.02-5.30 ppm corresponding to a proton of the NH group and a signal at 7.88-8.08 ppm due to the pyrazolic proton.

This excludes the addition of 1,3-dipoles to the double bonds C4=C5, C6=N7 and C1=N2.

The ^{13}C NMR spectra of the compounds (**2-8**) show in particular a signal at 95.7-99.5 ppm (C) due to the C-6, a signal at 112.4-114.4 ppm (CH), slightly dishielded, corresponding to carbon C-5 and a signal at 136.1-137.1 ppm (CH) assigned to C-1, which confirms the addition of *N*-arylnitrile imines and *N*-aryl-*C*-

ethoxycarbonylnitrile imines to the double bond C6=S and excludes the addition to the other centers. These results demonstrate the periselectivity of the double bond C6=S towards the 1,3-dipoles.

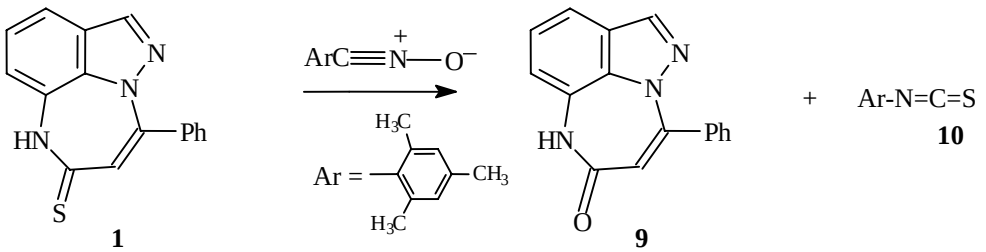


Scheme 3

The direction of the addition can also be deduced from the ^{13}C NMR spectra: the C-6 signal at 95.7-99.5 ppm (C), dishielded, rules out any other direction of the addition on the double bond C6=S; otherwise, the C-6 signal would appear upfield (the value would be between 50 and 60 ppm).[13,14] The reaction is thus regioselective.

This result was confirmed by mass spectrometry. We note in particular, in addition to the molecular ion of medium intensity, a loss of the isothiocyanate compound (**b**) and the principal fragmentation of the cycloaddition reaction corresponding to the retrocycloaddition reaction, which regenerates the dipole and the dipolarophile (**a**) (*m/z* = 277) (Scheme 3).

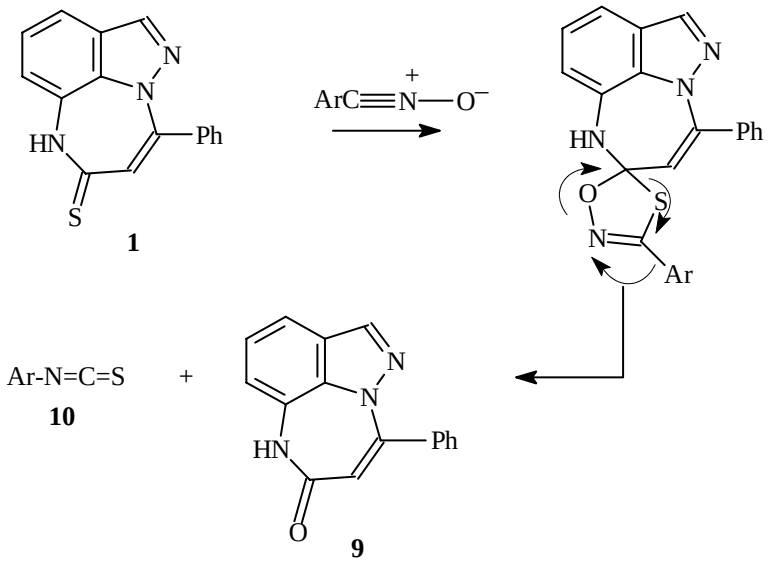
In contrast to diarylnitrile imines and *N*-aryl-*C*-ethoxycarbonylnitrile imines, the action of 2,4,6-trimethylbenzonitrile oxide on the pyrazolo[1,5,4-*ef*][1,5]benzodiazepin-6-thione (**1**) led to a mixture of two products: pyrazolo[1,5,4-*ef*][1,5]benzodiazepin-6-one (**9**) and 2,4,6-trimethylphenylisothiocyanate (**10)** (Scheme 4). The monoadduct spiro-type was not identified.



Scheme 4

The physical and spectral characteristics of compound (**9**) are the same as to those described in the literature.[15] The structure of (**10**) was checked on the basis of ^{1}H NMR, IR and mass spectroscopies. The IR spectrum showed a very broad intense band at 2100 cm^{-1} incompatible with a structure of the isomeric Ar-S-CN.

To explain the production of compounds (**9**) and (**10**), we propose the following mechanism: the initial phase of the reaction leads to a spiro-type cycloadduct resulting from the addition of a dipole on the double bond thioxo C=S; the spirooxathiazole thus formed is not stable. The heterocyclic ring is easily opened and the aryl group migrates towards the nitrogen (similar to Beckmann rearrangement) which finally leads to the oxo compound (**9**) by elimination of isothiocyanate (**10**) (Scheme 5).



Scheme 5

Thus, the results obtained during the reaction of [3+2] cycloaddition of the *N*-arylnitrile imines and the *N*-aryl-*C*-ethoxycarbonylnitrile imines with the pyrazolo-1,5-benzodiazepin-6-thione (**1**) suggest the following:

- Exocyclic dipolarophilic site C6=S is more reactive than the double bonds C4=C5, C1=N2 and C6=N7; this can be explained by the fact that these double bonds are engaged in conjugation of the tricyclic system.
- These reactions are periselective (only the double bond C6=S is affected) and also regioselective (the addition direction of the dipole with dipolarophilic site is single).

EXPERIMENTAL SECTION

General. Melting points were determined using a Büchi-Tottoli apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 577 spectrometer using KBr disks, only noteworthy IR absorptions are listed (cm^{-1}). ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution (unless otherwise specified) with TMS as an internal reference using a Bruker AM 200 (^{1}H) or 50.32 MHz (^{13}C) and AC 250 (250 or 62.89 MHz) instruments, chemical shifts are given in δ ppm downfield from TMS; for ^{13}C NMR, the multiplicities were determined through DEPT sequence. MS were performed on the kratos Concept IS at CSMUB (Centre de Spectroscopie moléculaire de l'Université de Bourgogne) using EI. Column chromatography was carried out on SiO_2 (silica gel 60 Merck 0.063-0.200 mm). TLC was carried out on SiO_2 (silica gel 60, F 254 Merck 0.063-0.200 mm) and the spots located with UV light. Elemental analyses were obtained from the Service Central d'Analyse du CNRS. All solvents were dried or purified

by standard methods. All reagents were of commercial quality from freshly opened containers. Evaporation of solvents was accomplished with a rotatory evaporator.

Preparation of Spiro[1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*][1,5]benzodiazepine] (2-8)

General procedure: A solution of Et_3N (2 mL, 9 mmol) in dry benzene was slowly added to a solution of pyrazolo[1,5,4-*ef*][1,5]benzodiazepin-6-thione (**1**) (0.8 g, 2.9 mmol) and the corresponding diarylnitrile imine (2.9 mmol) in dry benzene (80 mL). The resulting mixture was refluxed for 24 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane and petroleum ether as eluents (in a ratio indicated for every one).

1',3',4-Triphenylspiro[1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*][1,5]benzodiazepine] (2)

Following the general procedure, the compound (**2**) was obtained as a yellow solid in a yield of 45 % (0.6 g, eluents CH_2Cl_2:petroleum ether in a ratio 70:30); **mp** 184-186ºC (recrystallized from hexane). **IR**: 1620 and 1650 (CN); 3290 (NH). **^{1}H NMR** (250 MHz): δ 5.00 (s, 1H, NH); 6.01 (s, 1H, H-5); 6.73-7.88 (m, 18H, H-Ph); 8.08 (s, 1H, H-1). **^{13}C NMR** (125 MHz): 95.7 (C-6); 113.5 (C-5); 114.0 (C-8); 115.2 (C-9); 116.7 (CH); 122.1 (C-10); 123.8 (CH); 126.6 (CH); 127.4 (C); 128.0 (C); 128.1 (CH); 128.7 (CH); 129.0 (CH); 129.4 (C); 129.5 (CH); 129.7 (CH); 130.2 (CH); 134.7 (C); 135.2 (C); 136.1 (C-1); 136.3 (C); 139.5 (C-4); 141.4 (C-3'). **MS**(EI): *m/z* (relative intensity) 471 (14), 336 (66), 277 (13). **Anal.Calcd** for $C_{29}H_{21}N_5S$: C, 73.88; H, 4.46; N, 14.86. Found: C, 73.80; H, 4.45; N, 14.82.

1'-(2,4-dinitrophenyl)-3',4-diphenylspiro[1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*]-[1,5]benzodiazepine] (3)

Following the general procedure, the compound (**3**) was obtained as a yellow solid in a yield of 40 % (0.65 g, eluents CH_2Cl_2:petroleum ether in a ratio 80:20); **mp** 218-220ºC (recrystallized from hexane). **IR**: 1337/1512 (NO_2), 1600 and 1637 (CN); 3340 (NH). **^{1}H NMR** (500 MHz): δ 5.28 (s, 1H, NH); 6.09 (s, 1H, H-5); 6.67 (dd, J_{H8H9}= 7.0 Hz, J_{H8H10}= 0.6 Hz, 1H, H-8); 7.05-7.82 (m, 14H, H-Ph); 7.88 (s, 1H, H-1); 8.00 (dd, *J*ortho = 9.2 Hz, *J*meta = 2.6 Hz, 1H, H-Ph(NO_2)$_2$). **^{13}C NMR** (62.89 MHz): 99.5 (C-6); 113.4 (C-5); 113.9 (C-8); 114.4 (C-9); 121.3 (C-10); 125.4 (CH); 126.4 (CH); 126.5 (C); 128.4 (CH); 128.9 (C); 129.2 (CH); 129.3 (CH); 129.6 (CH); 129.9 (CH); 131.2 (C); 131.5 (CH); 133.9 (CH); 135.9 (C); 137.2 (C-1); 141.8 (C-4); 145.5 (C-3'); 147.4 (CH); 153.3 (C). **MS**(EI): *m/z* (relative intensity) 561 (3), 426 (8), 277 (88). **Anal.Calcd** for $C_{29}H_{19}N_7O_4S$: C, 62.03; H, 3.09; N, 17.47. Found: C, 61.95; H, 3.40; N, 17.50.

3'-Ethoxycarbonyl-1',4-diphenylspiro[1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*]-[1,5]benzodiazepine] (4)

Following the general procedure, the compound (**4**) was obtained as a yellow solid in a yield of 35 % (0.47 g, eluents CH_2Cl_2:petroleum ether in a ratio 90:10); **mp** 168-170ºC (recrystallized from toluene). **IR**: 1600 and 1640 (CN); 1715 (CO); 3230 (NH); **^{1}H NMR** (200 MHz): δ 1.25 (t, *J* = 7.0 Hz, 3H, CH_3); 4.32 (q, *J* = 7.0 Hz, 2H, CH_2); 5.17 (s, 1H, NH); 5.81 (s, 1H, H-5); 6.82 (dd, J_{H8H9} = 7.3 Hz, J_{H8H10} = 0.8 Hz, 1H, H-8); 6.94-7.41 (m, 12H, H-Ph); 8.06 (s, 1H, H-1). **^{13}C NMR** (50.32 MHz): 14.9 (CH_3); 63.3 (CH_2O); 97.4 (C-6); 112.6 (C-5); 114.0 (C-8); 115.1 (C-9); 119.8 (C); 124.6 (C-10); 126.4 (C); 128.2 (C); 128.6 (CH); 129.2 (CH); 129.7 (CH); 130.0 (CH); 131.0 (C); 132.6 (CH); 136.3 (C); 136.5 (C-1); 139.7 (C-4); 140.2 (C-3'); 160.7 (CO). **MS**(EI): *m/z* (relative intensity) 467 (11), 336 (34), 277 (87). **Anal.Calcd** for $C_{26}H_{21}N_5O_2S$: C, 66.78; H, 4.49; N, 14.98. Found: C, 66.76; H, 4.49; N, 14.97.

3'-Ethoxycarbonyl-4-phenyl-1'-(*p*-bromophenyl)spiro [1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*] [1,5]benzodiazepine] (5)

Following the general procedure, the compound (**5**) was obtained as a pale yellow solid in a yield of 42 % (0.66 g, eluents CH_2Cl_2:petroleum ether in a ratio 80:20); **mp** 180-182ºC (recrystallized from hexane). **IR**: 1653 (CN); 1711 (CO); 3247 (NH); **^{1}H NMR** (250 MHz): δ 1.32 (t, *J* = 7.2 Hz, 3H, CH_3); 4.32 (q, *J* = 7.2 Hz, 2H, CH_2); 5.12 (s, 1H, NH); 5.76 (s, 1H, H-5); 6.80 (dd, J_{H8H9} = 7.3 Hz, J_{H8H10} = 0.9 Hz, 1H, H-8); 7.13-7.57 (m, 11H, H-Ph); 8.05 (s, 1H, H-1). **^{13}C NMR** (62.89 MHz): 14.8 (CH_3); 63.2 (CH_2O); 97.4 (C-6); 112.9 (C-5); 115.1 (C-8); 116.3 (C-9); 117.3 (C); 119.9 (CH); 124.6 (C-10); 128.3 (C); 128.7 (CH); 128.8 (CH); 129.8 (CH); 130.1 (CH); 131.1 (C); 134.2 (C); 136.5 (C); 137.1 (C-1); 139.7 (C-4); 140.2 (C-3'); 160.7 (CO). **MS**(EI): *m/z* (relative intensity) 545/547 (4); 414 (44); 277 (100). **Anal.Calcd** for $C_{26}H_{20}N_5O_2BrS$: C, 57.23; H, 3.67; N, 12.84. Found: C, 57.20; H, 3.66; N, 12.83.

3'-Ethoxycarbonyl-4-phenyl-1'-(*p*-chlorophenyl)spiro [1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*] [1,5]benzodiazepine] (6)

Following the general procedure, the compound (**6**) was obtained as a yellow solid in a yield of 30 % (0.43 g, eluents CH_2Cl_2:petroleum ether in a ratio 80:20); **mp** 154-156ºC (recrystallized from hexane). **IR**: 1644 (CN); 1729 (CO); 3332 (NH); **^{1}H NMR** (250 MHz): δ 1.31 (t, *J* = 7.2 Hz, 3H, CH_3); 4.30 (q, *J* = 7.2 Hz, 2H, CH_2); 5.02 (s, 1H, NH); 5.80 (s, 1H, H-5); 6.80 (dd, J_{H8H9} = 7.3 Hz, J_{H8H10} = 0.9 Hz, 1H, H- 8); 7.15-7.23 (m, 2H, H-9 and H-10); 7.38-7.50 (m, 9H, H-Ph); 8.08 (s, 1H, H-1). **^{13}C NMR** (62.89 MHz): 14.2 (CH_3); 62.7 (CH_2O); 96.7 (C-6); 112.3 (C-5); 114.3 (C-8); 115.6 (C-9); 118.8 (CH); 123.9 (C-10); 127.5 (C); 128.1 (CH); 128.9 (CH); 129.1 (CH); 129.3 (CH); 130.3 (C); 134.4 (C); 135.6 (C); 135.9 (C); 136.4 (C-1); 139.1 (C-4); 139.5 (C-3'); 160.0 (CO). **MS**(EI): *m/z* (relative intensity) 501/503 (3), 370 (27), 277 (52). **Anal.Calcd** for $C_{26}H_{20}N_5O_2ClS$: C, 62.27; H, 3.99; N, 13.97. Found: C, 62.20; H,3.90; N, 13.95.

3'-Ethoxycarbonyl-4-phenyl-1'-(*p*-tolyl)spiro [1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo-[1,5,4-*ef*] [1,5]benzodiazepine] (7)

Following the general procedure, the compound (**7**) was obtained as a solid in a yield of 38 % (0.53 g, eluents CH_2Cl_2:petroleum ether in a ratio 70:30); **mp** 185-187ºC (recrystallized from toluene). **IR**: 1660 (CN); 1724 (CO); 3309 (NH); **^{1}H NMR** (200 MHz): δ 1.33 (t, *J* = 7.3 Hz, 3H, CH_3); 2.29 (s, 3H, CH_3); 4.32 (q, *J* = 7.3 Hz, 2H, CH_2); 5.06 (s, 1H, NH); 5.83 (s, 1H, H-5); 6.76 (dd, J_{H8H9} = 7.6 Hz, J_{H8H10} = 0.6 Hz, 1H, H-8); 7.02-7.45 (m, 11H, H-Ph); 8.04 (s, 1H, H-1). **^{13}C NMR** (50.32 MHz): 14.8 (CH_3); 21.3 (CH_3Ph); 63.0 (CH_2O); 97.7 (C-6); 113.6 (C-5); 114.9 (C-8); 116.1 (C-9); 118.6 (CH); 124.5 (C-10); 126.3 (C); 128.2 (C); 128.7 (CH); 129.7 (CH); 130.1 (CH); 130.3 (CH); 134.3 (C); 135.2 (C); 136.9 (C-1); 138.3 (C-4); 140.0 (C-3'); 159.6 (CO). **MS**(EI): *m/z* (relative intensity) 481 (7), 350 ((38); 277 (53). **Anal.Calcd** for $C_{27}H_{23}N_5O_2S$: C, 67.33; H, 4.78; N, 14.55. Found: C, 67.31; H, 4.78; N, 14.54.

3'-Ethoxycarbonyl-4-phenyl-1'-(*p*-nitrophenyl)spiro [1'*H*-4,1,2-thiadiazole-(6,5')-6,7-dihydropyrazolo[1,5,4-*ef*] [1,5]benzodiazepine] (8)

Following the general procedure, the compound (**8**) was obtained as a yellow solid in a yield of 40 % (0.59 g, eluents CH_2Cl_2:petroleum ether in a ratio 70:30); **mp** 202-204ºC (recrystallized from hexane). **IR**: 1302/1488 (NO_2); 1645 (CN); 1728 (CO); 3306 (NH); **^{1}H NMR** (200 MHz): δ 1.31 (t, *J* = 7.1 Hz, 3H, CH_3); 4.30 (q, *J* = 7.1 Hz, 2H, CH_2); 5.28 (s, 1H, NH); 5.75 (s, 1H, H-5); 6.84 (dd, J_{H8H9} = 6.9 Hz, J_{H8H10} = 1.0 Hz, 1H, H-8); 7.07-7.50 (m, 11H, H-Ph); 8.05 (s, 1H, H-1). **^{13}C NMR** (50.32 MHz): 14.2 (CH_3); 62.6 (CH_2O); 96.9 (C-6); 112.4 (C-5); 114.4 (C-8); 115.7 (C-9); 118.9 (CH); 123.4 (C); 124.0 (C-10); 127.7 (C); 128.1 (CH); 128.2 (C); 129.0 (CH); 129.2 (CH); 129.5 (CH); 130.5 (C); 135.6 (C); 136.4 (C-1); 138.6 (C-4); 139.6 (C-3'); 160.1 (CO). **MS**(EI): *m/z* (relative intensity) 512 (12), 381 (6); 277 (1). **Anal.Calcd** for $C_{26}H_{20}N_6O_4S$: C, 60.92; H, 3.90; N, 16.40. Found: C, 60.89; H, 3.90; N, 16.36.

Reaction of 2,4,6-trimethylbenzonitrile oxide with pyrazolo-1,5-benzodiazepin-6-thione (1) for the production of compounds (9) and (10)

General procedure: In a 250 mL round bottomed flask equipped with thermometer and condenser was placed the pyrazolo-1,5-benzodiazepine-6-thione (1) (1 mmol) in dry benzene (80 mL). To the resulting

solution was added the 2,4,6-trimethylbenzonitrile oxide (0.3 g, 1.8 mmol) and the mixture was refluxed for 4 h. After evaporation of solvent the residue was purified by column chromatography on silica gel (eluent; dichoromethane/ether in a ratio 90:10).

4-Phenyl-5,7-dihydropyrazolo[1,5,4-*ef*] [1,5]benzodiazepine-6-one (9)
This compound was obtained as a white solid in a yield of 74 % (0.34 g). **mp** 300-302ºC (recrystallized from hexane-ethyl acetate). **IR**: 1670 (CO); **^{1}H NMR** (250 MHz, DMSO-d_6): δ, 5.04 (s, 1H, H-5); 6.77 (dd, J_{H8H9} = 7.2 Hz, J_{H8H10} = 1.2 Hz, 1H, H-8); 7.06 (d, J_{H9H8} = 7.2 Hz, J_{H9H10} = 7.5 Hz, 1H, H-9); 7.18 (dd, J_{H10H9} = 7.5 Hz, J_{H10H8} = 1.2 Hz, 1H, H-10); 8.08 (s, 1H, H-1). **^{13}C NMR** (62.89 MHz, DMSO-d_6): 104.4 (C-5); 112.2 (C-8); 113.3 (C-9); 124.8 (C-10); 125.1 (CH); 126.2 (CH); 127.3 (CH); 127.5 (C); 128.5 (C); 128.7 (C); 134.8 (C-4); 136.4 (C-1); 146.3 (C-7a); 163.4 (CO). **MS**(EI): *m/z* (relative intensity) 261 (12). **Anal.Calcd** for $C_{16}H_{11}N_3O$: C,73.54; H, 4.25; N, 16.09. Found: C, 73.75; H, 4.31; N, 15.76.

2,4,6-Trimethylphenyl isothiocyanate (10)
This compound was obtained as a white solid in a yield of 65 % (0.21 g). **mp** 62-63ºC (recrystallized from hexane-ethyl acetate). **IR**: 2100 (CN); **^{1}H NMR** (250 MHz): δ, 2.25 (s, 6H, CH_3); 2.36 (s, 3H, CH_3); 7.20 (s, 2H, H-Ph). **MS**(EI): *m/z* (relative intensity) 177 (9). **Anal.Calcd** for $C_{10}H_{11}NS$: C, 67.77; H, 6.21; N, 7.91. Found: C, 67.78; H, 6.19; N, 7.89.

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