Synthesis of new 1,1'-di(4-nitro or 2-nitrophenyl)-5,5'-disubstituted-3,3'-bipyrazoles under microwave irradiation and classical heating conditions

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Abstract
Ten new 1,1'-di(4-nitro or 2-nitrophenyl)-5,5'-disubstituted-3,3'-bipyrazoles have been prepared in one step by N,N-arylation of 5,5'-disubstituted-3,3'-bipyrazoles with 4-fluoro and 2-fluoronitrobenzene. The reaction was carried out under microwave irradiation for 5 min and under classical heating conditions for one to two hours, affording high yields of diarylbipyrazole derivatives.

Keywords: Bipyrazole, N,N-arylation, microwave irradiation, classical heating.

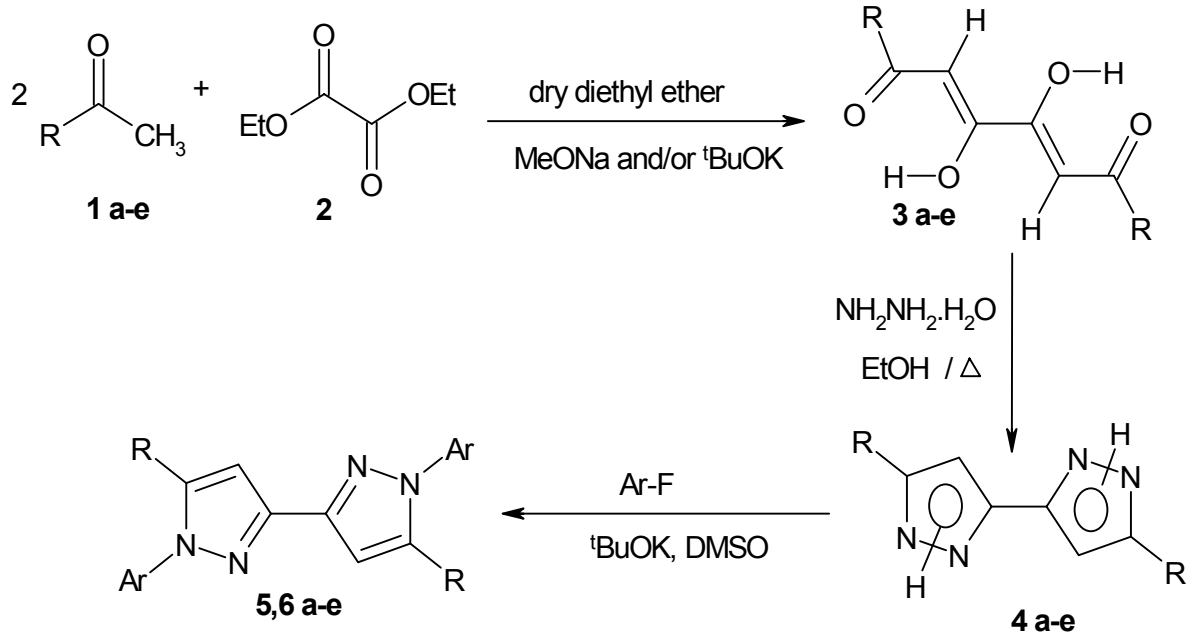
Introduction

Since Claisen's[1, 2] synthesis, many bipyrazole derivatives have been prepared for biological, medical and industrial purposes. They have been found to possess anti-inflammatory,[2-4] cytoxic[2,5] and anti-microbial[4] properties. They are also useful as insecticides,[2,6] herbicides,[2,7] fungicides[2,8] and in the synthesis of heat resistant polymers.[9] Other authors[10] reported bipyrazole derivatives as active components in capturing active oxygen and they are useful as agents for preventing or treating various diseases induced by active oxygen. Some bipyrazoles found application as agents for detecting singlet oxygen.[11] The reaction of 3,3'-dichloro-5,5'-bipyrazole with Ni(0)Lm, gives new poly(bipyrazoles) with high thermal stability.[12]

In this paper, we report two comparative approaches for the preparation of some new bipyrazole derivatives, by N,N-arylation reactions under microwave irradiation and classical heating conditions hoping to get improved catalytic and biologic activities. The compounds were obtained in excellent yields by a three-steps procedure.

Results and Discussion

Our strategy was to develop a simple and high yielding procedure, in few steps, to prepare the desired bipyrazolic compounds. The result of our investigation was given below (Scheme 1).



a : R = $CH(CH_3)_2$; **b** : R = $CH_2CH_2CH_3$; **c** : R = $CH_2C(CH_3)_3$;
d : R = $C(CH_3)_3$; **e** : R = C_6H_5; **5** : Ar = p-$NO_2C_6H_4$; **6** : Ar = o-$NO_2C_6H_4$

Scheme 1. *N,N*-arylation of 5,5'-disubstituted-3,3'-bipyrazoles with 4- and 2-fluoronitrobenzene.

The first step involves the synthesis of tetraketones **3a-e**[13,14,15] by condensation of methyl ketones **1a-e** with diethyl oxalate **2**. The second step consists of the condensation of these compounds with hydrazine hydrate in refluxing ethanol yielding the corresponding bipyrazole derivatives **4a-e**.[15,16] These compounds have high melting points and low solubility properties in organic solvents. In the last step, the N,N-arylation of bipyrazoles **4a-e** with 4-fluoronitrobenzene and 2-fluoronitrobenzene under classical heating conditions using potassium tert-butoxide as a base and DMSO as a solvent at 70°C affords after 60 to 120 min novel 1,1'-di(4-nitro or 2-nitrophenyl)-5,5'-disubstituted-3,3'-bipyrazoles **5, 6 (a-e)** in good yields (62 - 95 %).

The same reaction was then repeated using microwave irradiation, which has recently been used as an efficient technique to increase reaction rates. Thus, we have attempted to take advantage of it to decrease the reaction time of the previous N-arylation reaction, which was optimized with **4a** bipyrazole in order to obtain the best yield and until complete consumption of the starting materials. The mixture of 5,5'-di(1-methylethyl)-3,3'-bipyrazole **4a,** potassium tert-

butoxide and 4-fluoronitrobenzene or 2-fluoronitrobenzene was introduced into a Pyrex tube, which was then placed under microwave irradiation (single-mode, Prolabo Maxidigest MX 350). However, under these reaction conditions compound **5a** was isolated in poor yield and compound **6a** was not obtained. In view of this poor reactivity, these reactions were performed with some drops of DMSO solvent. Indeed, the mixture of 5,5'-disubstituted-3,3'-bipyrazoles **4 (a-e),** potassium tert-butoxide, 4-fluoronitrobenzene or 2-fluoronitrobenzene and some drops of DMSO solvent was introduced into a Pyrex tube which was then placed under microwave irradiation. Then the mixture was quenched with water. The precipitate was collected by filtration and was finally purified by column chromatography, if necessary, to afford regioselectively pure products **5, 6 (a-d)** in good yields (83-98%). The disfavoured arylation of **4e** to afford **5e** and **6e** may be attributable to the steric hindrance of the non-twisted aryl ring that prohibits access to the nitrogen atom next to the aromatic ring.[17] This method appeared to be rapid and economical, with a wide range of applications. The reaction was found to proceed smoothly under microwave irradiation within 5 min whereas under classical heating conditions, 60-120 min were required (**Table 1**).

Table 1. Comparison between microwave irradiation and classical heating conditions of synthesis of 1,1'-di(4-nitro or 2-nitrophenyl)-5,5'-disubstituted-3,3'-bipyrazole **5, 6 (a-e)**

Entry	R	m. p. (°C)	Classical heating		Microwave irradiation	
			Yield (%)	Time (min)	Yield (%)	Time (min)
5a	$-CH(CH_3)_2$	> 260	95	60	96	5[a]
5b	$-CH_2CH_2CH_3$	262 - 263	85	60	98	5[a]
5c	$-CH_2C(CH_3)_3$	>260	82	60	95	5[b]
5d	$-C(CH_3)_3$	>260	72	60	94	5[a]
5e	$-C_6H_5$	260-261	80	120	15	5[b]
6a	$-CH(CH_3)_2$	239 - 240	87	120	83	5[a]
6b	$-CH_2CH_2CH_3$	208 - 209	86	120	89	5[a]
6c	$-CH_2C(CH_3)_3$	258 - 259	96	60	86	5[a]
6d	$-C(CH_3)_3$	176 - 177	62	60	92	5[b]
6e	$-C_6H_5$	211 - 212	65	120	0	5[c]

[a] 30 W ; [b] 60 W ; [c] 180 W.

The higher regioselectivity suggests stereoelectronic effects. In general, pyrazoles with more electron-deficient aromatic substituents gave higher regioselectivity. The spectral characteristics of new bipyrazoles are in good agreement with symmetrical 3,3'-regioisomers forms.[18]

In conclusion, we have developed an efficient access to new bidendate compounds. Essentially the N,N-arylation of some bipyrazole derivatives which have the nitro group, using two methods: microwave irradiation and classical heating conditions in DMSO. The present

work is an important addition to microwave-assisted synthetic methodologies. Further developments on this subject are currently in progress, particularly, the examination of molecular conformations of the new N-aryled bipyrazole derivatives.

Experimental Section

General Procedures. Melting points were determined in open glass capillaries using BUCHI 510 Melting Point apparatus and are uncorrected. The infrared (IR) spectra were recorded on PERKIN-ELMER 1310 infrared spectrophotometer using the KBr disk technique. NMR spectra (^{1}H, ^{13}C) were recorded on a BRUKER 300 NMR spectrometer (operating at 300 MHz for ^{1}H, 75 MHz for ^{13}C). Chemical shifts are listed in ppm and are reported relative to tetramethylsilane (TMS) as an internal standard. Splitting patterns were designed as follows: s: singlet; d: doublet; t: triplet; m: multiplet. Mass spectra were obtained an a VG7070E spectrometer.

Synthesis of 5,5'-disubstituted-3,3'-bipyrazole

To a solution of tetraketones **3c,d** (8 mmol) in absolute ethanol was added the hydrazine hydrate (16 mmol) and the mixture was refluxed for one hour. The solvent was removed *in vacuo* at reduced pressure. The residue was washed with water (2x10 mL) and filtered to give the appropriate bipyrazoles **4c,d**.

5,5'-di(2-dimethylpropyl)-3,3'-bipyrazole (4c). Yield : 80% ; m. p. > 250°C; IR (cm^{-1} ; KBr Disk): 3143 (ν_{N-H}), 2954 ($\nu_{C-H,\ CH3}$), 2864, 1617, 1569, 1473, 1450, 1430, 1410, 1391, 1361, 1320, 1285, 1258, 1243, 1134, 1110, 1075, 949, 882, 797, 780, 753, 673, 520; HRMS ($C_{16}H_{26}N_4$): calcd 274.21575; found 274.2148; ^{1}H-NMR (300 MHz; DMSO-d_6, δ, ppm): 1.05 (s, 18 H, C<u>H</u>$_3$); 2.45 (s, 4 H, C<u>H</u>$_2$); 6.65 (s, 2 H, C4-<u>H</u>).

5,5'-di(1,1-dimethylethyl)-3,3'-bipyrazole (4d). Yield : 75% ; m. p. > 250°C; IR (cm^{-1} ; KBr Disk): 3470 (ν_{N-H}), 3120, 3000, 2945 ($\nu_{C-H,\ CH3}$), 2884, 2820, 1670, 1600, 1560, 1450, 1380, 1350, 1270, 1230, 1180, 1110, 1060, 1000, 910, 820, 750 ; HRMS ($C_{14}H_{22}N_4$): calcd 246.18445; found 246.1845; ^{1}H-NMR (300 MHz; $CDCl_3$, δ, ppm): 1.25 (s, 18 H, C<u>H</u>$_3$,); 6.15 (s, 2 H, C4-<u>H</u>), 8.21 (s; 2 H; N-<u>H</u>).

General methods for synthesis of 1,1'-di(4-nitro or 2-nitrophenyl)-5,5'-disubstituted-3,3'-bipyrazoles: 5, 6 (a-e)

Classical heating method. To a solution of 5,5'-disubstituted-3,3'-bipyrazoles **4 (a-e)** (0.5 mmol) in DMSO (2 mL) was added solid potassium tert-butoxide (1.1 mmol) followed by addition of 4-fluoronitrobenzene or 2-fluoronitrobenzene (1.05 mmol) in DMSO (1 mL) through a syringe. The resulting mixture was heated to 70°C and kept at this temperature for one to two hours. Then the mixture was cooled to room temperature and quenched with water (10 mL). The precipitate was collected by filtration and was passed through a short silica gel column (CH_2Cl_2) to give bipyrazole derivatives **5, 6 (a-e)** in good yield.

Microwave irradiation with solvent method. The mixture of 5,5'-disubstituted-3,3'-bipyrazoles **4(a-e)** (0.5 mmol), potassium tert-butoxide (1.1 mmol), 4- or 2-fluoronitrobenzene (1.05 mmol) and some drops of DMSO was introduced into a Pyrex tube which was then placed

under microwave irradiation. The mixture was then quenched with water. The precipitate was collected by filtration and was passed through a short silica gel column (CH_2Cl_2).

Characteristic data of new compounds 5, 6 (a-e)

1,1'-Bis(4-nitrophenyl)-5,5'-di(1-methylethyl-3,3'-bipyrazole (5a). Yield : 95 %; mp : > 260°C; IR (cm^{-1}, KBr Disk): 3060 ($\nu_{C-H,\ arom.}$), 2980, 2942 ($\nu_{C-H,\ CH3}$), 2893 ($\nu_{C-H,\ CH(CH3)2}$), 1610 ($\nu_{C=N}$), 1600 ($\nu_{C=C}$), 1530 ($\nu_{a\ NO2}$), 1366 ($\nu_{s\ NO2}$), 1180, 1110, 1030, 970, 880, 820, 710 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.35 (d, 4 H, H3', J = 9 Hz), 7.71 (d, 4 H, H2', J = 8.7 Hz), 6.76 (s, 2 H, C4-H), 3.14 (m, 2 H, CH(CH_3)$_2$), 1.25 (d, 12 H, CH(CH_3)$_2$, J = 6.9 Hz) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 152.6 (C3), 148.0 (C4'), 146.9 (C1'), 145.6 (C5), 126.0 (C3'), 125.2 (C2'), 103.0 (C4), 26.1 (CH(CH_3)$_2$), 22.9 (CH(CH_3)$_2$) ; Anal. Calcd for $C_{24}H_{24}N_6O_4$: C 62.61, H 5.21, N 18.26, Found: C 62.40, H 5.30, N 18.35; MS (EI): 460, 445, 415, 399, 260, 232, 200, 169, 109, 76, 57, 40.

1,1'-Bis(2-nitrophenyl)-5,5'-di(1-methylethyl-3,3'-bipyrazole (6a). Yield : 87 %; mp : 239-240°C; IR (cm^{-1}, KBr Disk): 3140 ($\nu_{C-H,\ arom.}$), 2939, 2894 ($\nu_{C-H,\ CH3}$), 2822 ($\nu_{C-H,\ CH(CH3)2}$), 1650 ($\nu_{C=N}$), 1598 ($\nu_{C=C}$), 1582 ($\nu_{a\ NO2}$), 1443 ($\nu_{s\ NO2}$), 1433, 1424, 1194, 1163, 1081, 1013, 954, 881, 873, 845, 812, 761; ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 8.16 (d, 4 H, H3', J = 7.5 Hz), 7.89 (m, 2 H, H4'), 7.80 (m, 4 H, H6', H5'), 6.54 (s, 2 H, C4-H), 2.85 (m, 2 H, CH(CH_3)$_2$), 1.14 (d, 12 H, CH(CH_3)$_2$, J = 6.9 Hz) ; ^{13}C-NMR (75 MHz, DMSO-d_6, δ, ppm): 153.0 (C3), 147.3 (C2'), 146.9 (C5'), 134.9 (C5), 132.8 (C1'), 131.3 (C4'), 130.2 (C3'), 126.2 (C6'), 101.7 (C4), 25.9 (CH(CH_3)$_2$), 23.0 (CH(CH_3)$_2$) ; MS (EI): 460, 445, 414, 398, 367, 324, 292, 168, 139, 122, 77, 43.

1,1'-Bis(4-nitrophenyl)-5,5'-dipropyl-3,3'-bipyrazole (5b). Yield : 85 %; mp : 262-263°C; IR (cm^{-1} ; KBr Disk): 3080 ($\nu_{C-H,\ arom.}$), 2940 ($\nu_{C-H,\ CH3}$), 2883, 2825 ($\nu_{C-H,\ CH2}$), 1601 ($\nu_{C=N}$), 1570 ($\nu_{C=C}$), 1485 ($\nu_{a\ NO2}$), 1333 ($\nu_{s\ NO2}$), 1315, 1230, 1154, 1126, 1100, 1060, 1014, 934, 854, 790, 750, 700 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.34 (d, 4 H, H3', J = 9.3 Hz), 7.72 (d, 4 H, H2', J = 9 Hz), 6.75 (s, 2 H, C4-H), 2.73 (t, 4 H, C$H_2$$CH_2CH_3$, J = 7.8 Hz), 1.71 (m, 4 H, CH_2C$H_2$$CH_3$), 0.79 (t, 6 H, CH_2CH_2CH_3 , J = 7.2 Hz) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 147.6 (C3), 146.6 (C4'), 145.9 (C1'), 145.3 (C5), 125.3 (C3'), 125.1 (C2'), 105.6 (C4), 29.2 (C$H_2$$CH_2CH_3$), 22.3 ($CH_2CH_2$$CH_3$), 14.2 ($CH_2CH_2CH_3$) ; MS (EI): 460, 445, 432, 353, 260, 230, 168, 139, 92, 76, 40.

1,1'-Bis(2-nitrophenyl)-5,5'-dipropyl-3,3'-bipyrazole (6b). Yield: 86 %; mp: 208-209°C; IR (cm^{-1}, KBr Disk): 3100 ($\nu_{C-H,\ arom.}$), 2962 ($\nu_{C-H,\ CH3}$), 2936, 2870 ($\nu_{C-H,\ CH2}$), 1595 ($\nu_{C=N}$), 1520 ($\nu_{C=C}$), 1493 ($\nu_{a\ NO2}$), 1422, 1350 ($\nu_{s\ NO2}$), 1304, 1132, 1012, 933, 854, 783, 750, 700 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.01 (d, 2 H, H3', J = 8.1 Hz), 7.67 (m, 2 H, H4'), 7.58 (m, 2 H, H5'), 7.49 (d, 2 H, H6', J = 7.8 Hz), 6.62 (s, 2 H, C4-H), 2.44 (t, 4 H, C$H_2$$CH_2CH_3$, J = 7.5 Hz), 1.62 (m, 4 H, CH_2C$H_2$$CH_3$), 0.89 (t, 6 H, CH_2CH_2CH_3 , J = 7.2 Hz) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 147.8 (C3), 146.6 (C2'), 146.6 (C5'), 133.7 (C1'), 133.6 (C5), 130.4 (C4'), 130.0 (C3'), 125.6 (C6'), 103.8 (C4), 28.1 (C$H_2$$CH_2CH_3$), 21.8 ($CH_2CH_2$$CH_3$), 14.1 ($CH_2CH_2CH_3$) ; MS (EI): 460, 432, 414, 373, 339, 311, 282, 256, 230, 193, 169, 117, 77, 43.

1,1'-Bis(4-nitrophenyl)-5,5'-di(2-dimethylpropyl)-3,3'-bipyrazole (5c). Yield : 82 %; mp : > 260°C; IR (cm^{-1}, KBr Disk): 3080, 3087 ($\nu_{C-H,\ arom.}$), 2940, 2900 ($\nu_{C-H,\ CH3}$), 2860 ($\nu_{C-H,\ CH2}$),

1615 ($\nu_{C=N}$), 1600 ($\nu_{C=C}$), 1520, 1500 ($\nu_{a\ NO2}$), 1350 ($\nu_{s\ NO2}$), 1250, 1130, 1020, 940, 860, 820, 760, 710 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.35 (d, 4 H, H3', J = 9 Hz), 7.65 (d, 4 H, H2', J = 8.7 Hz), 6.74 (s; 2 H; C4-H), 2.70 (s, 4 H, $CH_2C(CH_3)_3$), 0.79 (s, 18 H, $CH_2C(CH_3)_3$); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 147.2 (C3), 147.0 (C4'), 145.8 (C1'), 143.4 (C5), 127.3 (C3'), 125.0 (C2'), 107.1 (C4), 39.7 ($CH_2C(CH_3)_3$), 32.9 ($CH_2C(CH_3)_3$), 29.8 ($CH_2C(CH_3)_3$) ; MS (EI): 516, 515, 485, 459, 442, 412, 355, 309, 259, 168, 129, 76, 57, 41.

1,1'-bis(2-nitrophenyl)-5,5'-di(2-dimethylpropyl)-3,3'-bipyrazole (6c). Yield : 96 %; mp : 258-259°C; IR (cm^{-1}, KBr Disk): 3070, 3000 ($\nu_{C-H,\ arom.}$), 2940 ($\nu_{C-H,\ CH3}$), 2900 ($\nu_{C-H,\ CH2}$), 1613 ($\nu_{C=N}$), 1545 ($\nu_{C=C}$), 1515 ($\nu_{a\ NO2}$), 1500, 1433, 1385 ($\nu_{s\ NO2}$), 1303, 1240, 1131, 1020, 942, 864, 821, 800, 770, 725, 660 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.04 (d, 2 H, H3', J = 6.6 Hz), 7.71 (m, 2 H, H4'), 7.54 -7.61 (m, 4 H, H5', H6'), 6.68 (s, 2 H, C4-H), 2.43 (s, 4 H, $CH_2C(CH_3)_3$), 0.84 (s, 18 H, $CH_2C(CH_3)_3$) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 147.6 (C3), 146.5 (C2'), 144.3 (C5'), 133.8 (C5), 133.7 (C1'), 131.3 (C4'), 130.0 (C3'), 125.7 (C6'),), 105.7 (C4), 39.8 ($CH_2C(CH_3)_3$), 32.4 ($CH_2C(CH_3)_3$), 29.85 ($CH_2C(CH_3)_3$) ; MS (EI): 516, 501, 460, 430, 400, 372, 292, 230, 183, 149, 111, 97, 71, 57, 43.

1,1'-Bis(4-nitrophenyl)-5,5'-di(1,1-dimethylethyl)-3,3'-bipyrazole (5d). Yield: 72 %; mp : > 260°C; IR (cm^{-1}, KBr Disk): 3025 ($\nu_{C-H,\ arom.}$), 2980, 2840, 2865, 2825 ($\nu_{C-H,\ CH3}$), 1630 ($\nu_{C=N}$), 1593 ($\nu_{C=C}$), 1512 ($\nu_{a\ NO2}$), 1501, 1343 ($\nu_{s\ NO2}$), 1253, 1105, 1032, 965, 891, 833, 775, 721 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.35 (d, 4 H, H3', J = 8.4 Hz), 7.65 (d, 4 H, H2', J = 8.4 Hz), 6.74 (s, 2 H, C4-H), 0.79 (s, 18 H, $C(CH_3)_3$) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 147.2 (C3), 147.0 (C4'), 145.8 (C1'), 143.4 (C5), 127.3 (C3'), 125.0 (C2'), 107.1 (C4), 32.9 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$) ; MS (EI): 488, 460, 443, 404, 353, 260, 244, 230, 184, 168, 139, 92, 76, 57, 41.

1,1'-Bis(2-nitrophenyl)-5,5'-di(1,1-dimethylethyl)-3,3'-bipyrazole (6d). Yield: 62 %; mp : 176-177°C; IR (cm^{-1}, KBr Disk): 3030 ($\nu_{C-H,\ arom.}$), 2934, 2870, 2840 ($\nu_{C-H,\ CH3}$), 1580 ($\nu_{C=N}$), 1563 ($\nu_{C=C}$), 1504 ($\nu_{a\ NO2}$), 1461, 1332 ($\nu_{s\ NO2}$), 1250, 1223, 1134, 1093, 1055, 993, 905, 831, 763, 735 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.06 (m, 2 H, H3'), 7.70 (m, 2 H, H4'), 7.62 - 7.54 (m, 4 H, H5', H6'), 6.68 (s, 2 H, C4-H), 0.84 (s, 18 H, $C(CH_3)_3$); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 135.0 (C3), 133.7 (C2'), 131.3 (C5'), 129.9 (C5), 126.5 (C1'), 125.7 (C4'), 125.1 (C3'), 121.3 (C6'), 105.7 (C4), 32.4 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$) ; MS (EI): 488, 460, 430, 395, 339, 309, 292, 260, 218, 198, 170, 139, 122, 106, 92, 57, 40.

1,1'-Bis(4-nitrophenyl)-5,5'-diphenyl-3,3'-bipyrazole (5e). Yield : 80 %; mp : 260-261°C; IR (cm^{-1}, KBr Disk): 3020 ($\nu_{C-H,\ arom.}$), 1605 ($\nu_{C=N}$), 1520 ($\nu_{C=C}$), 1515 ($\nu_{a\ NO2}$), 1463, 1345 ($\nu_{s\ NO2}$), 1271, 1252, 1160, 1120, 1080, 1035, 960, 943, 860, 783, 708 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 8.01 (d, 4 H, H3', J = 7.2 Hz), 7.92 (d, 4 H, o-H, J = 6.6 Hz), 7.51-7.39 (m, 6 H, m-H, p-H), 7.18 (d, 4 H, H2', J = 6.9 Hz), 7.12 (s, 2 H, C4-H) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 154.3 (C3), 146.2 (C4'), 144.1 (C1'), 133.3 (C5), 131.6 (C1''), 129.6 (C4''), 129.3 (C3''), 126.3 (C2''), 124.8 (C3'), 123.1 (C2'), 109.4 (C4) ; MS (EI): 528, 498, 481, 435, 379, 332, 305, 241, 203, 166, 140, 104, 77, 40.

1,1'-Bis(2-nitrophenyl)-5,5'-diphenyl-3,3'-bipyrazole (6e). Yield : 65 %; mp : 211-212°C; IR (cm^{-1}, KBr Disk): 3060 ($\nu_{C-H,\ arom.}$), 1620, 1602, 1525 ($\nu_{C=N}$), 1505 ($\nu_{C=C}$), 1460 ($\nu_{a\ NO2}$), 1393, 1352 ($\nu_{s\ NO2}$), 1143, 1104, 1104, 1055, 944, 774, 704 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm):

8.50 (m, 2 H, H3'), 8.02 (d, 4 H, o-H, J = 7.2 Hz), 7.52 -7.39 (m, 12 H, H4', H5', H6', p-H, m-H), 7.10 (s, 2 H, C4-H) ; ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 154.0 (C3), 132.8 (C2'), 131.8 (C5'), 129.2 (C3''), 129.1 (C5), 126.6 (C2''), 126.3 (C3'), 116.8 (C6'), 98.3 (C4) ; MS (EI): 528, 482, 453, 360, 332, 283, 256, 229, 180, 154, 127, 102, 77, 51.

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