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Pyrazole and quinoxaline: synthesis and X-ray structural characterization of new tridentate (N,N,N) and bidentate (N,N or N,O) ligands

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Abstract

Herein we report the synthesis of new tridentate (N,N,N) compounds **3-6** and bidentate (N,N or N,O) compounds **8-10** based on pyrazole moieties and quinoxaline, with the opportunity to change easily structure and substituents. These methods take advantage of the vast number of commercially available starting materials containing functional and aliphatic or aromatic amines. X-ray structures for two compounds were investigated.

Keywords: Nitrogen rich compounds, pyrazole, quinoxaline, X-ray analysis.

Introduction

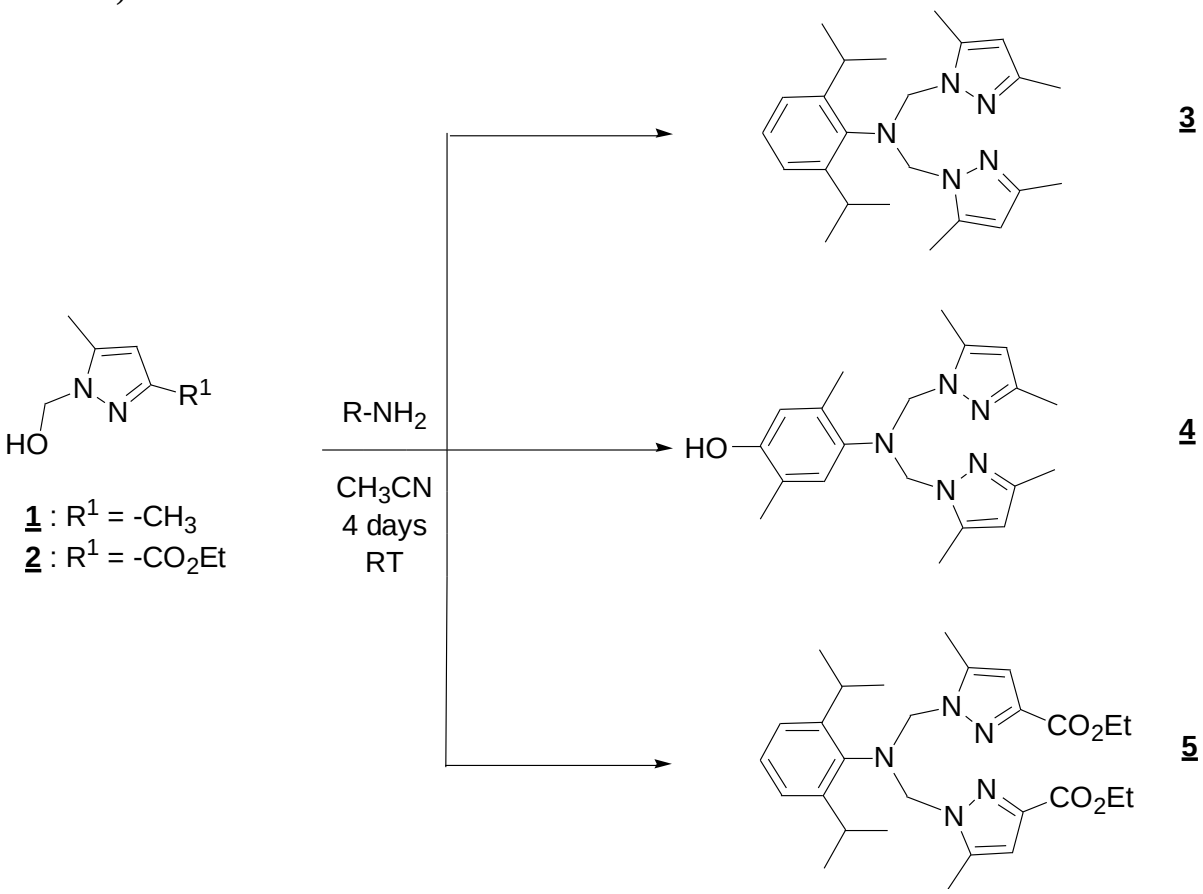
The chemistry of nitrogen containing multipodal molecules is attracting current interest in the scientific life due to their specificity for biological targets.[1] These compounds are also of great importance for building polynuclear complexes [2] as models for bioinorganic systems[3-7] as well as for the discovery of new catalyst precursors. The pyrazol ring seems to play a key role as it is involved in several types of chelating ligands,[8] which were used in models that mimic active sites of copper proteins.[9-11] Meanwhile, the researches concerning the properties of the nitrogen ligand complexes increased in an exponential way,[12-14] largely because of their possible use as photo-catalysts during the conversion of the solar energy.[15-19] These heterocyclic compounds

have been proven to be useful as potential anti-inflammatory agents,[20] cytotoxic agents,[21] insecticides,[22] herbicides,[23] fungicides[24] and in the synthesis of heat resistant polymers.[25] Herein, we report our contribution in this topic by the synthesis of some new materials based on heterocyclic chemistry especially pyrazole and quinoxaline, in different form like tridentate or bidentate ligands.

Results and discussion

Synthesis and characterization

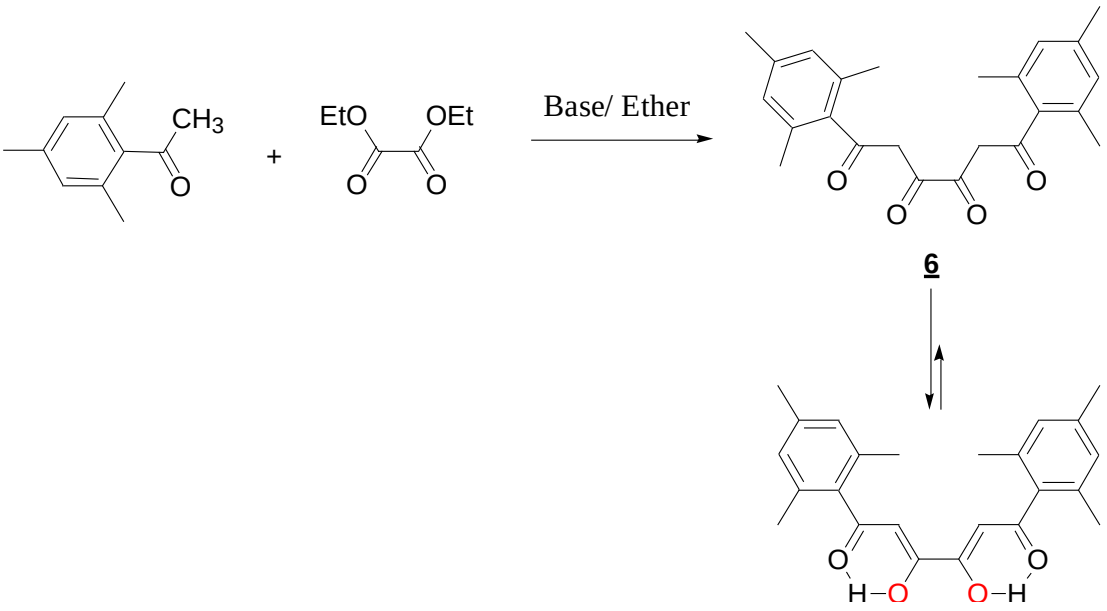
To achieve these compounds we used the condensation of two equivalent of hydroxymethyl substituted pyrazole **1**-**2** [26] with one equivalent of amines, by stirring for 4 days at 25°C in the presence of acetonitrile as solvent. We got these compounds **3**-**5** with good to excellent yields (**Scheme 1**).



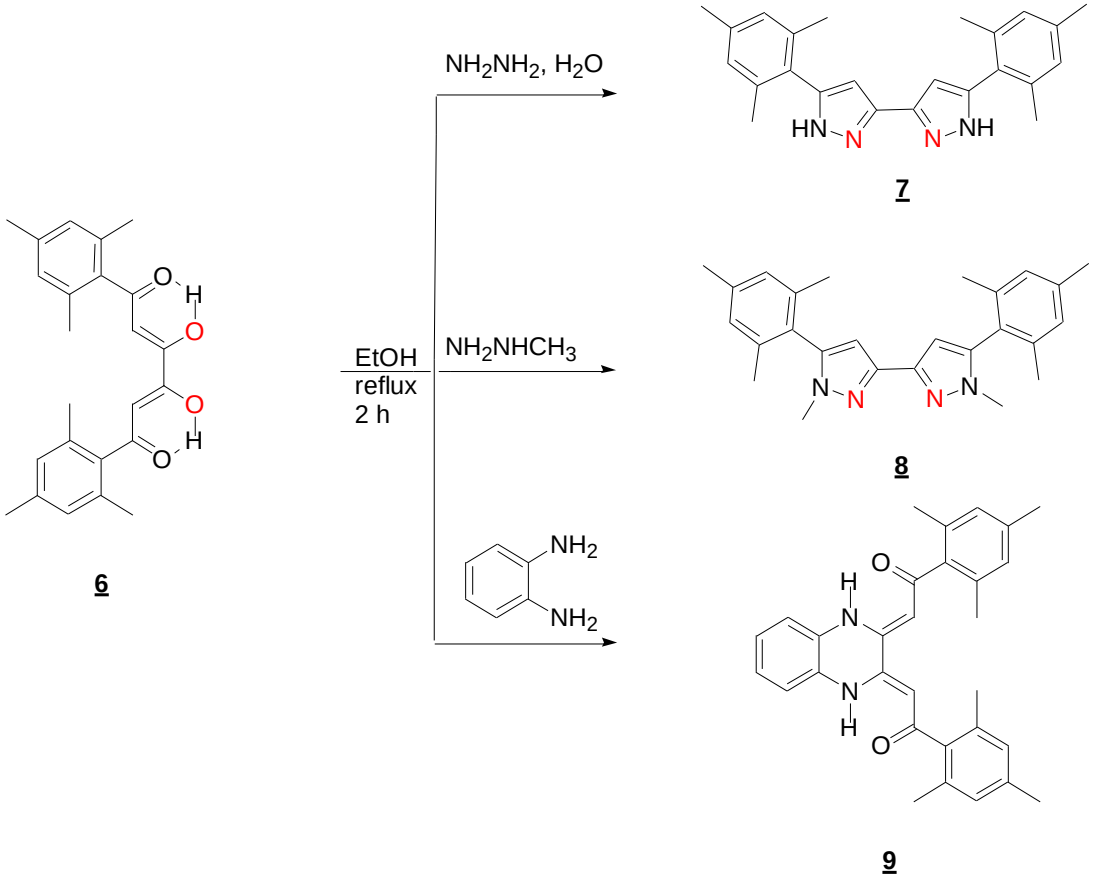
Scheme 1: Synthesis of new tridentate pyrazole ligands

We have synthesised new symmetric 5,5'-disubstitued-3,3'-bipyrazole ligands by varying the nature of hydrazine substituents. It is carried out in ethanol by two steps: the first step aims to elaborate new tetraone compound **6** (**Scheme 2**). In the second step we condensate the precursor

with two equivalents of the hydrazine producing compound **7** or methylhydrazine to get **8**, or 1,2-o-phenylenediamine to get **9** in good yields (**Scheme 3**).



Scheme 2: Preparation of tetraone **6**



Scheme 3: Preparation of bidentate compounds **7**-**9**

Crystal structure of compound 7

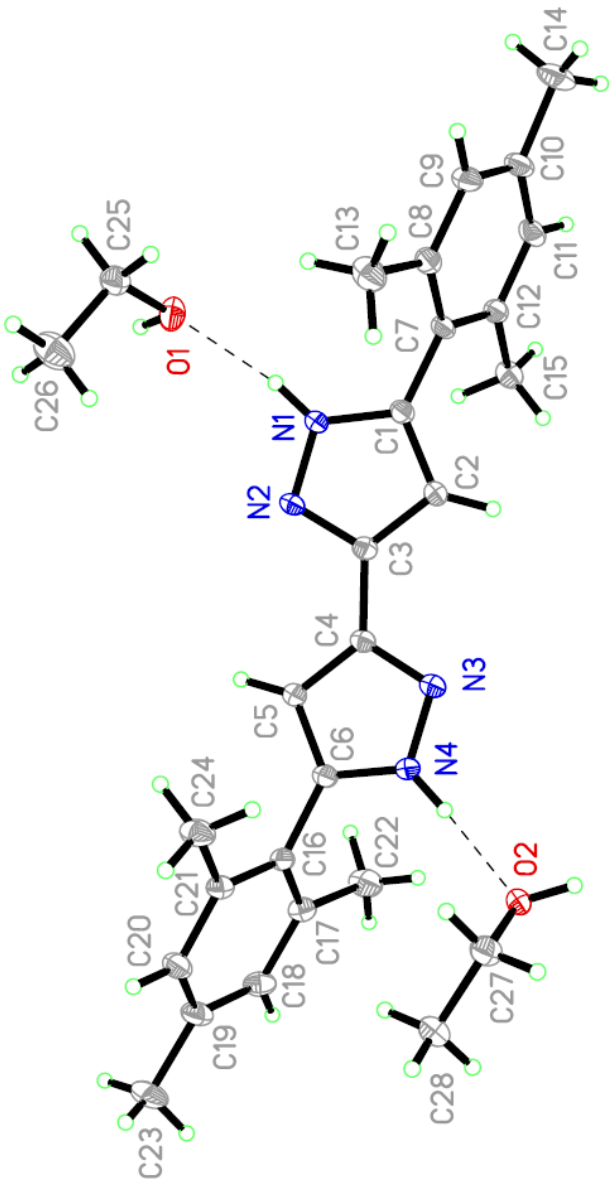


Figure 1: ORTEP diagram of compound **7** showing the atom numbering scheme. Ellipsoid probability level is 50%. Hydrogen atoms are omitted for clarity

Table 1. Crystal data and structure refinement for compound **7**.

Identification code	tr15	
Empirical formula	C28 H38 N4 O2	
Formula weight	462.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1080(10) Å	□= 90.357(2)°.
	b = 8.1980(10) Å	□= 98.143(2)°.
	c = 21.962(3) Å	□ = 116.129(2)°.
Volume	1293.5(3) $Å^3$	
Z	2	
Density (calculated)	1.188 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	500	
Crystal size	.21 x .18 x .07 mm^3	
Theta range for data collection	1.88 to 29.57°.	
Index ranges	-11<=h<=11, -11<=k<=11, -30<=l<=30	
Reflections collected	14544	
Independent reflections	7178 [R(int) = 0.0263]	
Completeness to theta = 29.57°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.709	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7178 / 0 / 331	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1373	
R indices (all data)	R1 = 0.0756, wR2 = 0.1518	
Largest diff. peak and hole	0.486 and -0.293 e.$Å^{-3}$	

Table 2 Selected bond lengths (Å) and angles (°) for compound **7**

N(1)-N(2)	1.3499(15)	C(8)-C(9)	1.3908(19)
N(1)-C(1)	1.3527(17)	C(8)-C(13)	1.503(2)
N(1)-H(1N)	0.887(19)	C(9)-C(10)	1.384(2)
N(2)-C(3)	1.3358(17)	C(9)-H(9)	0.9300
N(3)-C(4)	1.3342(17)	C(10)-C(11)	1.391(2)
N(3)-N(4)	1.3518(15)	C(10)-C(14)	1.5065(19)
N(4)-C(6)	1.3461(17)	C(11)-C(12)	1.3884(18)
N(4)-H(4N)	0.88(2)	N(2)-N(1)-C(1)	112.83(11)
C(1)-C(2)	1.3848(18)	N(2)-N(1)-H(1N)	117.2(12)
C(1)-C(7)	1.4763(17)	C(1)-N(1)-H(1N)	129.7(12)
C(2)-C(3)	1.4030(18)	C(3)-N(2)-N(1)	104.83(10)
C(2)-H(2)	0.9300	C(4)-N(3)-N(4)	104.90(11)
C(3)-C(4)	1.4607(18)	C(6)-N(4)-N(3)	112.54(11)
C(4)-C(5)	1.4077(18)	C(6)-N(4)-H(4N)	128.4(12)
C(5)-C(6)	1.3786(18)	N(3)-N(4)-H(4N)	118.9(13)
C(5)-H(5)	0.9300	N(1)-C(1)-C(2)	105.92(11)
C(6)-C(16)	1.4833(17)	N(1)-C(1)-C(7)	122.40(12)
C(7)-C(8)	1.4051(19)		
C(7)-C(12)	1.4100(18)		

Crystal structure of compound 9

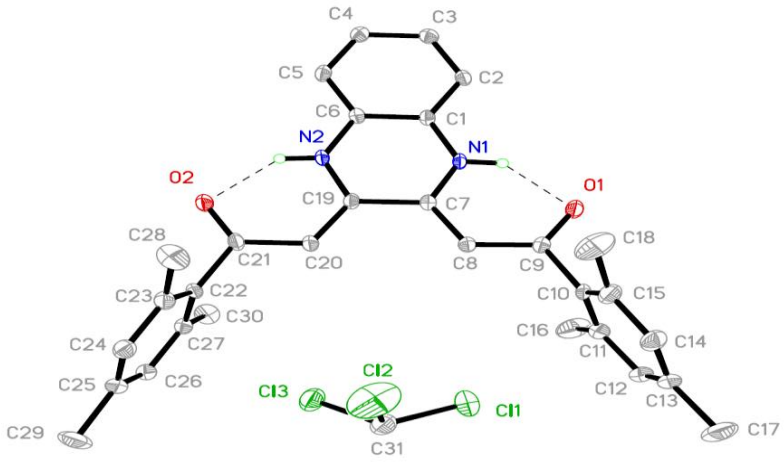


Figure 2: ORTEP diagram of compound **9** showing the atom numbering scheme. Ellipsoid probability level is 50%. Hydrogen atoms are omitted for clarity

Table 3. Crystal data and structure refinement for compound **9**.

Identification code	tr19prm_ia	
Empirical formula	C30 H30 N2 O2	
Formula weight	450.56	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Ia	
Unit cell dimensions	a = 13.2530(15) Å	□= 90°.
	b = 6.9589(8) Å	□= 103.907(1)°.
	c = 27.570(3) Å	□ = 90°.
Volume	2468.2(5) $Å^3$	
Z	4	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	960	
Crystal size	0.25 x 0.03 x 0.015 mm^3	
Theta range for data collection	1.52 to 23.31°.	
Index ranges	-14<=h<=14, -7<=k<=7, -30<=l<=30	
Reflections collected	6732	
Independent reflections	3459 [R(int) = 0.0761]	
Completeness to theta = 23.31°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7449 and 0.6249	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3459 / 2 / 313	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.1020, wR2 = 0.2229	
R indices (all data)	R1 = 0.1430, wR2 = 0.2494	
Absolute structure parameter	-2(5)	
Largest diff. peak and hole	0.795 and -0.248 e.$Å^{-3}$	

Table 4 Selected bond lengths (Å) and angles (°) for compound **9**

N(1)-C(7)	1.349(10)	C(3)-C(2)-H(2)	120.8
N(1)-C(1)	1.390(9)	C(1)-C(2)-H(2)	120.8
N(1)-H(1N)	0.8800	C(2)-C(3)-C(4)	120.7(8)
N(2)-C(8)	1.350(10)	C(2)-C(3)-H(3)	119.6
N(2)-C(6)	1.409(9)	C(4)-C(3)-H(3)	119.6
N(2)-H(2N)	0.8800	C(3)-C(4)-C(5)	122.2(8)
O(1)-C(10)	1.215(9)	C(3)-C(4)-H(4)	118.9
O(2)-C(21)	1.208(9)	C(5)-C(4)-H(4)	118.9
C(1)-C(6)	1.370(10)	C(6)-C(5)-C(4)	117.6(7)
C(1)-C(2)	1.403(10)	C(6)-C(5)-H(5)	121.2
C(2)-C(3)	1.366(11)	C(4)-C(5)-H(5)	121.2
C(2)-H(2)	0.9500	C(5)-C(6)-C(1)	121.2(7)
C(3)-C(4)	1.362(10)	C(5)-C(6)-N(2)	121.8(6)
C(3)-H(3)	0.9500	C(1)-C(6)-N(2)	116.9(6)
C(4)-C(5)	1.363(11)	N(1)-C(7)-C(9)	120.5(7)
C(4)-H(4)	0.9500	N(1)-C(7)-C(8)	116.0(7)
C(7)-N(1)-C(1)	126.2(6)	C(9)-C(7)-C(8)	123.3(7)
C(7)-N(1)-H(1N)	116.9	N(2)-C(8)-C(20)	118.7(7)
C(1)-N(1)-H(1N)	116.9	N(2)-C(8)-C(7)	116.4(7)
C(8)-N(2)-C(6)	126.0(6)	C(20)-C(8)-C(7)	124.8(7)
C(8)-N(2)-H(2N)	117.0	C(7)-C(9)-C(10)	122.8(7)
C(6)-N(2)-H(2N)	117.0	C(7)-C(9)-H(9)	118.6
C(6)-C(1)-N(1)	118.4(6)	C(10)-C(9)-H(9)	118.6
C(6)-C(1)-C(2)	119.7(7)	O(1)-C(10)-C(9)	123.1(7)
N(1)-C(1)-C(2)	121.9(6)		
C(3)-C(2)-C(1)	118.5(7)		

Experimental

Materials and instrumentation

All reagents except **1** and **2** ligands were commercially available and used without further purification. H-NMR spectra were recorded at 400 MHz on a Bruker WH400 DS spectrometer. Mass spectra (MS) were obtained by using electrospray ionization (ESI).

Synthesis of compounds 3-5

General procedure : A solution of hydroxymethylpyrazole **1** or **2** (10 mmole) in 20 ml of CH_3CN, was added an appropriate primary amine (5 mmole) in 20 mL of CH_3CN, then the reaction mixture was stirred at room temperature for 4 days. The reaction finished, we filter the precipitate and we wash our solid by CH_3CN and dried.

***N,N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2,6-diisopropylaniline* 3**:

Yield = 79%; **^{1}HNMR ($CDCl_3$, 400 MHz, ppm):** 7,11 (t, 1H, -CHBz; J= 7.8Hz); 6,96 (d, 2H, -CHBz, J= 7.6 Hz) ; 5,60 (s, 2H, -CHpz); 5,35 (s, 4H, -NCH_2N-); 2,70(m, 2H, -$CH(CH_3)_2$, J = 6,8 Hz); 2,16 (s, 6H, -CH_3); 2,09 (s, 6H, -CH_3); 0,9 (d, 12H, -$CH(CH_3)_2$, J = 6,8Hz). **^{13}CNMR ($CDCl_3$, 100 MHz, ppm):** 148,49; 148,18; 140,72, 138,72; 127,65; 124,58; 123,50; 105,60(-CHpz); 66,75 (-NCH_2N-); 28,15 (-$CH(CH_3)_2$) ; 24,91 (-CH_3); 24,25 (-CH_3); 13,85 (-CH_3); 11,00(-CH_3). **Mass Electro-spray in MeOH**: 394 (100%); 298 (50%) 202 (10%).

***4-(bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)-2,5-dimethylphenol* 4**:

Yield = 84%; **^{1}HNMR ($CDCl_3$, 400 MHz, ppm):** 9,03 (s, 1H, -OH); 6,48 (s, 1H, -CHBz) ; 6,17(s, 1H, -CHBz); 5,71 (s, 2H, -CHpz); 5,16 (s, 4H, -NCH_2N-); 2,04 (s, 6H, -CH_3); 1,89 (s, 6H, -CH_3); 1,82 (s, 3H, -CH_3Bz); 1,74 (s, 3H, -CH_3Bz). **^{13}CNMR ($CDCl_3$, 100 MHz, ppm):** 158,50; 151,41; 144,63; 141,21; 139,19; 134,50; 126,96; 121,35; 110,28 (-CHpz); 70,94 (-NCH_2N-); 22,16 (-CH_3) ; 21,05 (-CH_3); 18,84 (-CH_3); 15,42 (-CH_3). **Mass Electro-spray in MeOH**: 354 (25%); 297,3 (100%) ; 258,2 (25%); 191 (21%); 181 (27%).

***Diethyl 1,1'-(((2,6-diisopropylphenyl)azanediyl)bis(methylene))bis(5-methyl-1H-pyrazole-3-carboxylate)* 5**:

Yield = 79%; **^{1}HNMR (DMSOd_6, 400 MHz, ppm):** 7,21 (t, 1H, -CHBz; J= 7.8Hz); 7,06 (d, 2H, -CHBz, J= 5,2 Hz) ; 6,42 (s, 2H, -CHpz); 5,57 (s, 4H, -NCH_2N-); 4,37 (q, 4H, -OCH_2CH_3, J = 7Hz); 2,63 (m, 2H, -$CH(CH_3)_2$, J = 6,8 Hz); 1,85 (s, 6H, -CH_3); 1, 38 (t, 6H, -OCH_2CH_3, J = 7,2 Hz); 1,06 (d, 12H, -$CH(CH_3)_2$, J = 6,8Hz). **^{13}CNMR (DMSOd_6, 100 MHz, ppm):** 162,94; 148,02; 143,49; 139,80; 128,22; 124,87; 123,65; 67,47; 60,84; 28,20; 24,94; 14,54; 10,99. **Mass Electro-spray in DMSOd_6**: 532,3 (100%, M +Na); 509,9 (83%); 356,2(40%); 202,2 (10%).

***1,6-dimesitylhexane-1,3,4,6-tetraone* 6:**

Experimental procedure: In three neck flask, we add at zero degree Celsius, 10g (0,061 mole) of 1-mesitylethanone mixed with 4,5g (0,03 mole) of Diethyl oxalate in 30 mL of Ether to a sodium ethanol ate 5g in 30 mL of Ether. The addition should be slowly. When it finished we leave the reaction mixture under stirring at room temperature for two days. Yellow precipitate was gotten filtered and neutralized using acetic acid at Ph = 7; we got yellow compound filtered and dried.

Yield = 90%; **^{1}HNMR ($CDCl_3$, 400 MHz, ppm):** 6, 89 (s, 4H, -CHBz); 6,56(s, 2H, -CH=) ; 2,30 (s, 6H, -2CH3); 2,28 (s, 12H, -CH_3Bz).; **^{13}CNMR ($CDCl_3$, 100 MHz, ppm):** 198,92;

173,31; 139,73; 135,7; 134,63; 128,90; 128,73; 101,85; 51,09; 21,368; 19,90. **Mass Electro-spray in MeOH**: 798,9 (10%; 2M+ 2Na); 771(50%) ; 723,1 (100%); 373,2 (10%).

5,5'-dimesityl-1H,1'H-3,3'-bipyrazole 7:

General procedure: In bottom flask, we mixed, 2g (0,005 mole) of tetraketone **6** with appropriate diamine (0,01 mole) in 30 mL of ethanol. The reaction mixture leaved under stirring at reflux for two hours. We remove solvent under reduce pressure and we got solid.

Yield = 90%; **^{1}HNMR (DMSOd$_6$, 400 MHz, ppm):** 6, 96 (s, 4H, -CHBz); 6,45(s, 2H, -CHBz) ; 2,25 (s, 6H, -2CH3); 2,06 (s, 12H, -CH_3Bz).; **^{13}CNMR (DMSOd$_6$, 100 MHz, ppm):** 137,67; 128,634; 103,10; 21,37; 20,85. **Mass Electro-spray in DMSOd$_6$**: 763 (50%, 2M+ Na); 741,1 (100%, 2M); 371,4 (40%, M).

5,5'-dimesityl-1,1'-dimethyl-1H,1'H-3,3'-bipyrazole 8:

Yield = 80%; **^{1}HNMR (CDCl$_3$, 400 MHz, ppm):** 6, 96 (s, 2H, -CHBz); 6.53(s, 2H, -CHpz) ; 3,56 (s, 6H, -NCH_3); 2,33 (s, 6H, -CH_3Bz); 2,01 (s, 12H, -CH_3Bz).**^{13}CNMR (CDCl$_3$, 100 MHz, ppm):** 145,91; 142,8; 138,99; 128,5; 128,41; 127,4; 103,5; 36,37; 21,38; 20,28. **Mass Electro-spray in MeOH**: 819,2 (100%, 2M+ Na).

***(2Z,2'Z)-2,2'-(quinoxaline-2,3(1H,4H)-diylidene)bis(1-mesitylethanone)* 9:**

Yield = 90%; **^{1}HNMR (CDCl$_3$, 400 MHz, ppm):** 7,23-7,22 (m, 1H, -CHBz, J = 3,6 Hz); 7.18-7,16 (m, 1H, -CHHBz, J = 3,6 Hz); 6,83 (s, 4H, -CHBz); 5,75(s, 2H, -CH=); 2,27(s, 6H, -CH_3); 2,25 (s, 12H, -CH_3). **^{13}CNMR (CDCl$_3$, 100 MHz, ppm):** 196,61; 145,43; 139,66; 138,24; 133,83; 128,56; 126,39; 125,17; 117,08; 93,06; 21,26; 19,80. **Mass Electro-spray in MeOH**: 451,2 (50%, M); 359,4 (20%); 253,1 (40%).

X-ray Structure Determination.

After one day of refrigeration, yellow cube-like crystals of the compound **7** formed from a saturated THF solution. For the compound **9** red yellow needle-like crystals in the fridge after three days and the solvent used is ethanol for compound **7** and $CDCl_3$ for compound **9**. Data were collected on a Bruker-AXS Smart APEX CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073Å) at 100K. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a multi-scan (SADABS) method.[27] The structures were solved by Patterson or direct-methods (SHELXS86).[28] All non-hydrogen atoms were refined (SHELXL97)[29] based upon F_{obs}.[28] All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (f_O, f', f'') are as described in SHELXL97. Crystal data for the structures have been deposited in the Cambridge Crystallographic Data Center with number (compound number) CCDC 816346 and CCDC 816347.

Conclusion

We have prepared a tridentate (N,N,N) and bidentate (N,N and N,O) ligands in good to excellent yields. X-ray structures were also studied and potential applications such as corrosion inhibition, catalysis, liquid-liquid extraction, biological and computational calculations will be investigated.

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Appendix A. Supplementary data

Supplementary information includes all crystallographic data for compounds **7** and **9** (CCDC 816346 and CCDC 816347).

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