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REVIEW: SYNTHETIC NITROGEN COMPOUNDS AS EFFICIENT CORROSION INHIBITORS FOR METALLIC MATERIALS IN AGGRESSIF MEDIUM

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Abstract

Pluridisciplinary research by chemists, physics, biologists and mathematics is a primordial task to find and discover new molecules which are beneficial for humanity in many areas such as the inhibition of corrosion of materials in drastic medium. The nitrogen heterocyclic coumpounds based on pyrazole, bipyrazole, bispyrazole, imidazole and triazole, constitute a large bank of compounds with chemical, and industrial interest. In this context, we decided to present a review about the preparation of a series of heterocyclic compounds from literature and our group works (20 years experiences in this area). Then we focused on their anti-corrosion activities in drastic mediums.

1. Introduction

Corrosion universal problem [1-3] which is the main cause for the materials damage by it dysfunction and deterioration which conduct too many crucial issues as commercial losses [4-6], There are a huge diversity of corrosions types including galvanic corrosion [7], uniform corrosion [8], corrosion of cracks [9], intergranular corrosion pitting [10], and erosion [11]. It is the presence of water and fluid chemicals containing dissolved oxygen are the most identified corrosion agents [12]. To protect the materials from such problem we can use organic inhibitors such as nitrogen compounds and their derivatives. Nitrogen Heterocyclic compounds based on five membered ones as pyrazole [13-15], 1,3-thiazole [16-21], Benzotriazole [22, 23], 1,2,4-Triazole [24-27] and/or six membered ones as Pyridine [28], Pyrimidine [17, 29, 30] are known for their numerous applications especially as organic inhibitors of corrosion [31]. Here, we have discussed the synthesis of nitrogen heterocyclic compounds, properties and anticorrosion applications [32-34]. In our research we focus on the synthesis of N-alkylated heterocyclic compounds containing pyrazole derivatives or triazole moiety as the main core [35]. We are also interested in the other heterocycles compounds by developing a fast, clean and easy method for the preparation of such heterocyclic compounds.

2. Literature review

2.1 Preparation of heterocyclic ligands with huge interests

In particular, the heterocyclic compounds have an interesting attention as bioactive molecules in the drug discovery with polypharmacological activity. In our study, diversity of heterocyclic moieties was studied as:

- Pyrazole [36-41] five membered heterocyclic rings with two adjacent nitrogens which is very common in many commercial compounds used in many industrial fields.
- 1,2,4-Triazole [42-48] is also five membered heterocyclic ring with the presence of three nitrogen atoms in the positions 1,2 and 4 of the ring, and its widely used as pharmacophore core linked with other compounds to give different applications.

2. 2 N-alkylation of heterocyclic amines with primary alcohols

In **1950**, I. Dvoretzky and coll. [49] based on the work of M. Landua [50] who works in 1948 on the chloromethylation of 3,5-dimethylpyrazole (**1**), was the first one to prepare carbinol derivatives: 3,5-dimethylpyrazole-l-carbinol (**2**) prepared at room temperature by the condensation of 3,5-diméthylpyrazole with formaldehyde to have 71% yield, while the effect of higher temperature and the use of paraformaldehyde at 110-120 °C increase the yield to 90%, 3,5-dimethylpyrazole-1,4-dicarbinol (**3**) prepared by condensation of 1-carbinol, paraformaldehyde and hydrochloric acid to have the final product in a yield of 24%. 3,5-dimethylpyrazole-4-carbinol (**4**) found as traces with the products (**2** and **3**) in the mixture products from the reaction of 3,5-dimethylpyrazole with paraformaldehyde and hydrochloric acid at room temperature (**Figure 1**).

In **1981**, A. Ramdani and G. Tarrago [51, 52] prepared poly pyrazolic compounds (**Figure**) by polycondensation of dipyrazolyl methane in neutral conditions as DMF in KI (**Figure**) or basic conditions as the use of a phase transfer catalysis conditions identical in the presence and absence of catalyst to prepare the compound **2**, where they conclude that:

- All the pyrazolyl species has remained in the organic phase with same intensity values
- The species formed is stable in benzene even after removing the aqueous phase.
- When organic solution is washed with water the spectrum of the original pyrazole **3** is regenerated, while the changes are not due to degradation of the pyrazole system.
- The aqueous titration with 0.1 N hydrochloric acid shows that one molecule of NaOH reacted with one molecule of pyrazolyl pyrazole.
- The importance of the pyrazolyl pyrazole unit in the polycondensation reaction is because of the non-formation of an anion, where it does not require a phase-transfer catalyst and that it must be dependent on the alkaline hydroxide used.

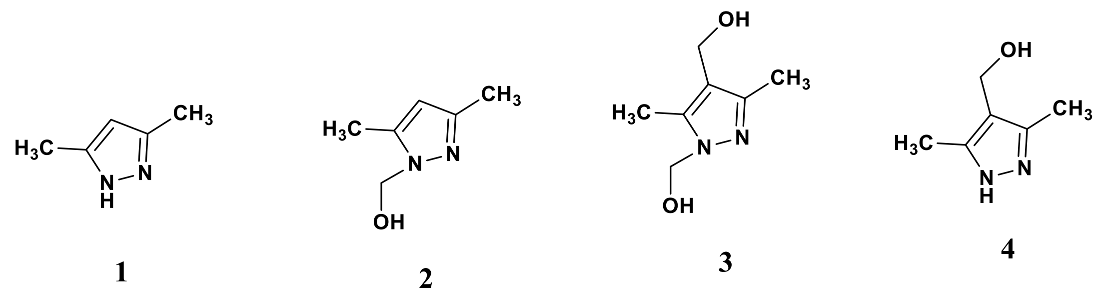


Figure 1. The chemical structure of the prepared pyrazole compounds (**1-4**) by Dvoretzky [91].

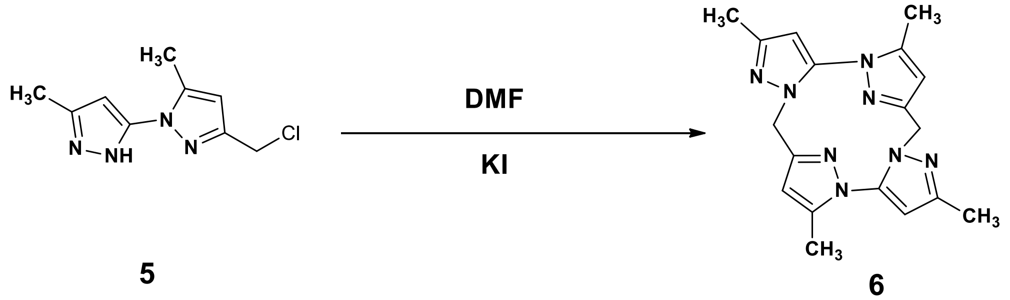


Figure 2. Polycondensation in dimethylformamide in the presence of KI by Ramdani [51, 52].

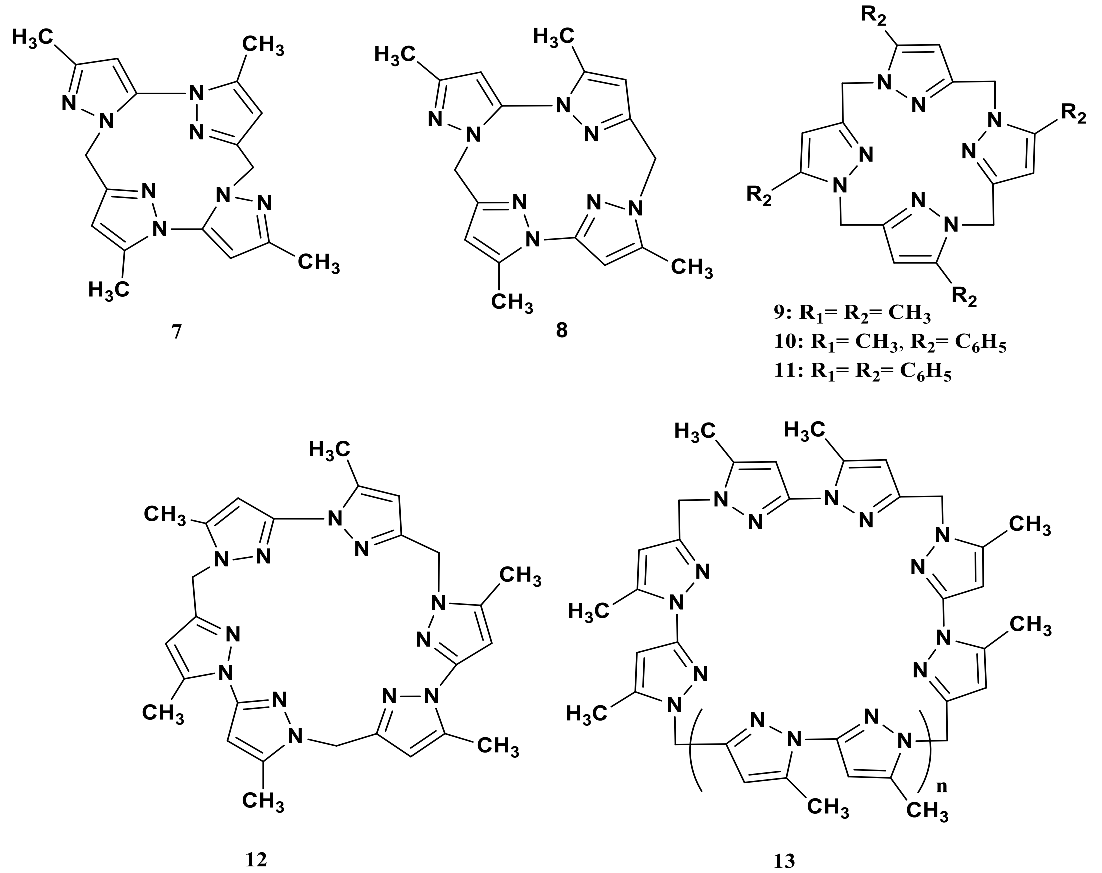


Figure 3. Chemical structure of the pyrazolic compounds prepared by Ramdani [51, 52].

In **1982**, Wiliem L. Driessen and coll. [53] prepared eighteen compounds 1a-9a and 1b-9b (**Figure**) by two-step procedure where the first one consists for preparing 1-hydroxymethyl) pyrazole (**la**) and of l- (hydroxymethyl)-3,5-dimethylpyrazole (**lb**); From 3,5-dimethyl pyrazole prepared using the method of Wiley and Hexner [54]; which already reported by I. Dvoretzky [55] while the second step is their condensation with different primary and second amines and with ammonia.

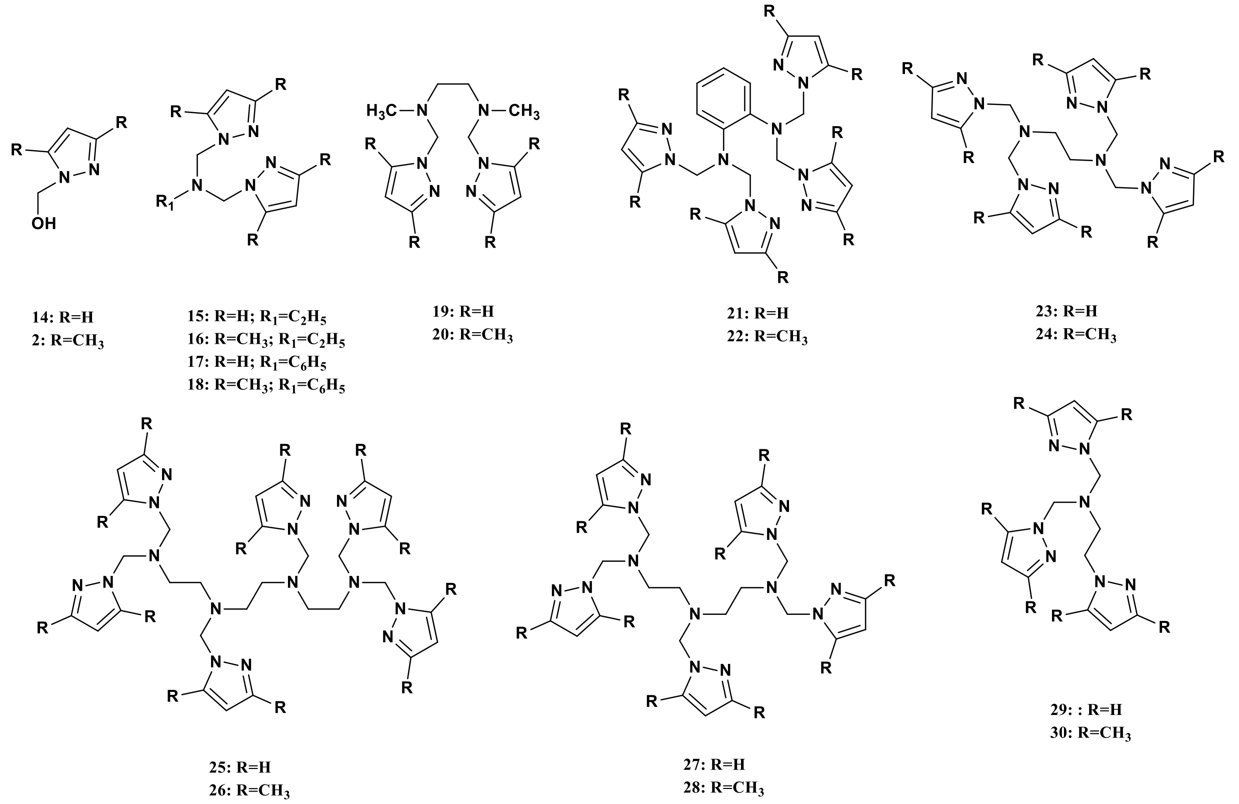
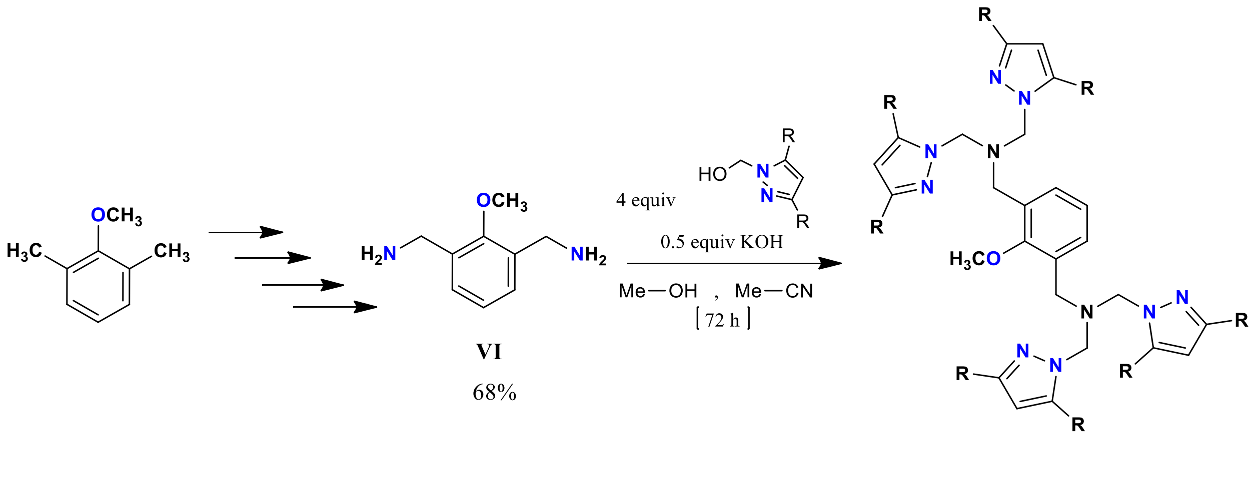


Figure 4. The chemical structure of the compounds **2** and **14-30** prepared by Driessen [53].

In **1992**, M. R. Malachowski and coll. [56] prepared two tetradentate pyrazole ligands (**Figure 5**) by multi-step reaction from 2-methoxy-1,3-dimethylbenzene to get two tetradentate pyrazole ligands **35** and **36** with 61 and 68% yields, respectively.



31: R = H, **yield** = 61%
32: R = CH_3, **yield** = 68%

Figure 5. Synthesis of the tetradentate pyrazole ligands **31** and **32** by Malachowski [56].

In **1995**, S. C. Sheu and coll. [57] prepared N, N-bis (pyrazolyl-1-methyl) benzylamine (**33**) (**Figure**) from Hydroxymethyl pyrazole and benzylamine in acetonitrile stirred in a closed vessel at room temperature for four days, after that the solution was treated using anhydrous $MgSO_4$, filtered then the solvent removed by the rotary evaporator, yielding to a yellow liquid with 72%.

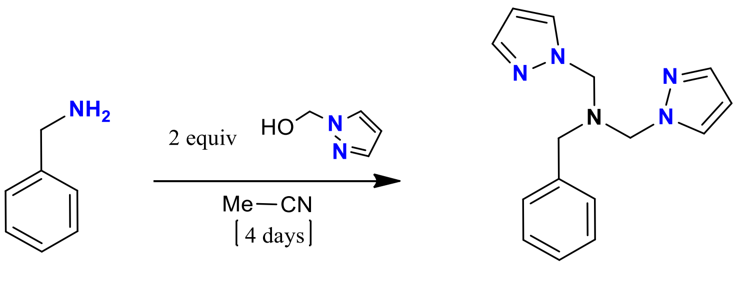


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Figure 6. Synthesis of N, N-bis (pyrazolyl-1-methyl) benzylamine **33** by Sheu [57].

In **2003**, M. Daoudi and coll. [58] prepared N, N, N', N'- tetra -[(3,5 -dimethyl-1-pyrazolyl) methyl]-para-phenylenediamine (**Figure 7**) from (Z)-4-hydroxypent-3-en-2-one by stirring p-phenylenediamine with 1-(hydroxymethyl)-3,5-dimethylpyrazole under room temperature, atmospheric pressure for 4-7 days by the modification of the method described in the literature [49, 53, 57, 59, 60].

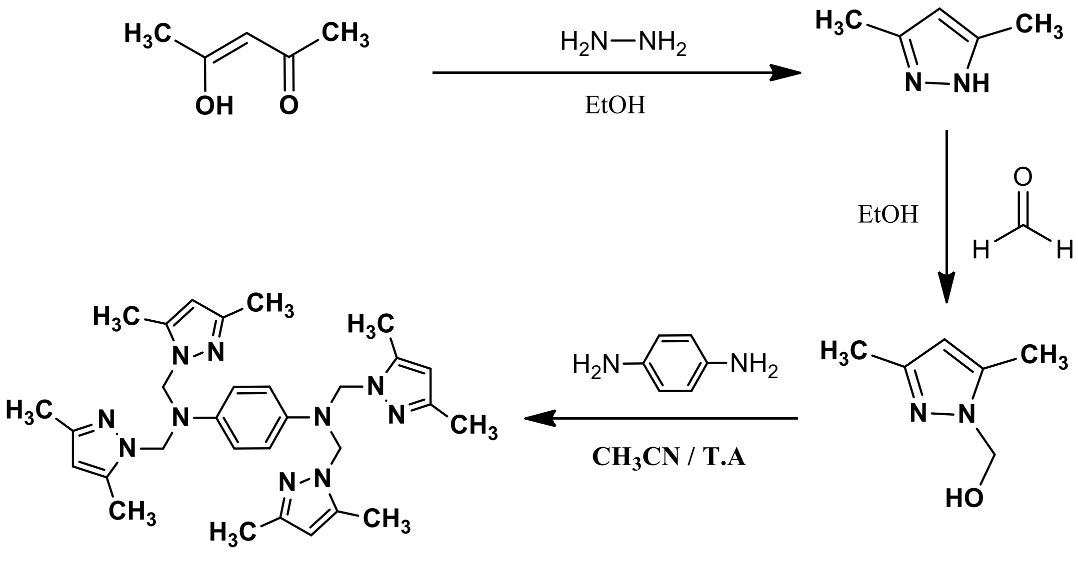

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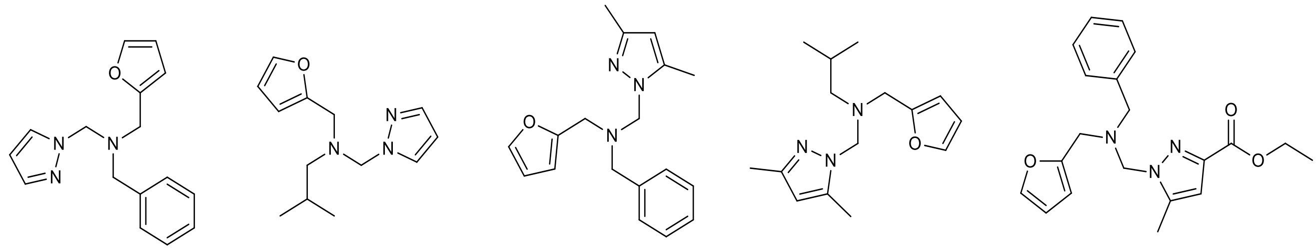
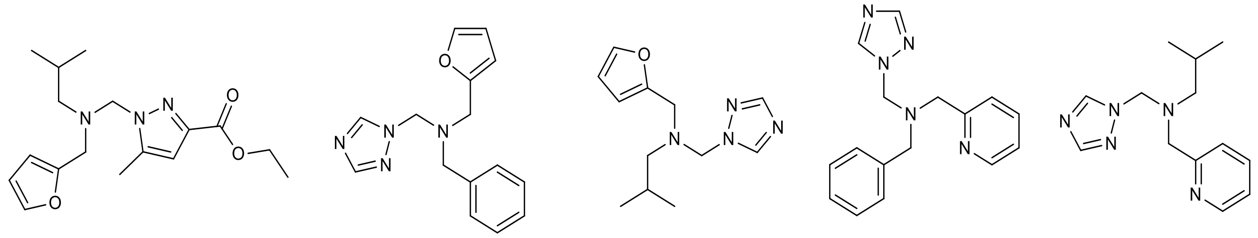
Figure 7. Synthesis of N, N, N', N'- tetra- [(3,5 -dimethyl-1-pyrazolyl) methyl]-para-phenylenediamine by Daoudi [58].

In **2003**, R. Touzani and coll. [59] prepared a library of fourteen pyrazole and triazole containing compounds using combinatorial chemistry; Reaction conditions fully automated from mixing the starting products till their purification; with yield from 52% to 90% (**Figure 88**).



35 36 37 38 39



40 41 42 43 44

Figure 8. Chemical structure of the compounds **35-44** prepared by Touzani [61].

In **2003**, M. El Kodadi and coll. [62] prepared [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethan] by condensation of 1-hydroxymethyl-3,5-dimethylpyrazole with 2-aminoethanol in a closed vessel at room temperature for 4 days (**Method A**; **Figure** 9), while this reaction requires 4 hours at 60°C without solvent (**Method B; Figure**) or under microwave irradiation (60 W) for 20 min (**Method C; Figure**) where the compound yielded in 80-90%.

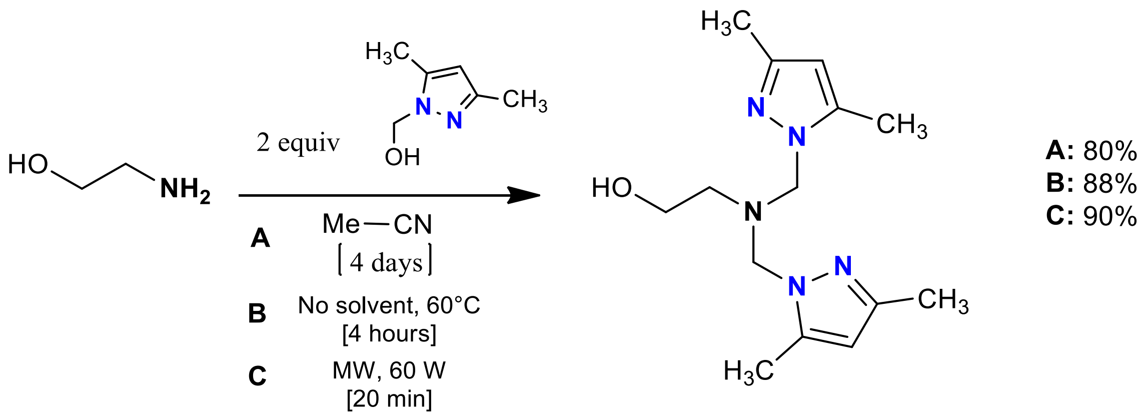


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Figure 9. Synthesis of [N, N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane] by El Kodadi [62]

In **2004**, M. El Kodadi and coll. [63] synthesized 1-(4-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl) amino) phenyl) ethenone from (3,5-dimethyl-1H-pyrazol-1-yl)methanol and 4-amino-acetophenone stirred in a closed vessel contained acetonitrile at room temperature for 6 days (**Figure 2**). In **2011**, R. Touzani and coll. [64] Prepared 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol by stirring 4-aminophenol with two equivalents of 3,5-dimethyl-1H-pyrazol-1-yl)methanol in CH_3CN at room temperature for four days (**Figure 31**).

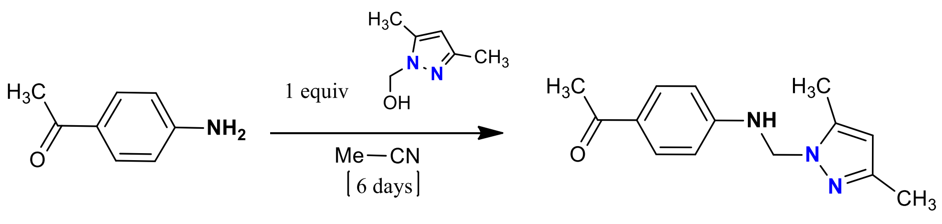

Figure 2. Synthesis of 1-(4-(((3,5-dimethyl-1H-pyrazol-1-yl) methyl) amino) phenyl) ethenone by El Kodadi [63].

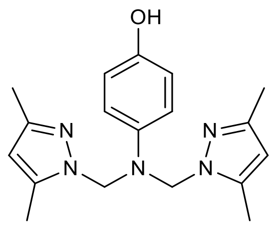

Figure 3. Chemical structure of 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol by Touzani [64]

In **2012**, S. Radi and coll. [65] Prepared new bipyrazolic tripodal derivatives (Figure 4) by stirring (Aniline, Pyridin-2-amine, 2-nitrobenzenamine and 2-methylbenzenamine to 1-hydroxymethyl-3,5-dimethylpyrazole or 3-methyl-5-esterpyrazole) in Acetonitrile at room temperature for 4-5 days.

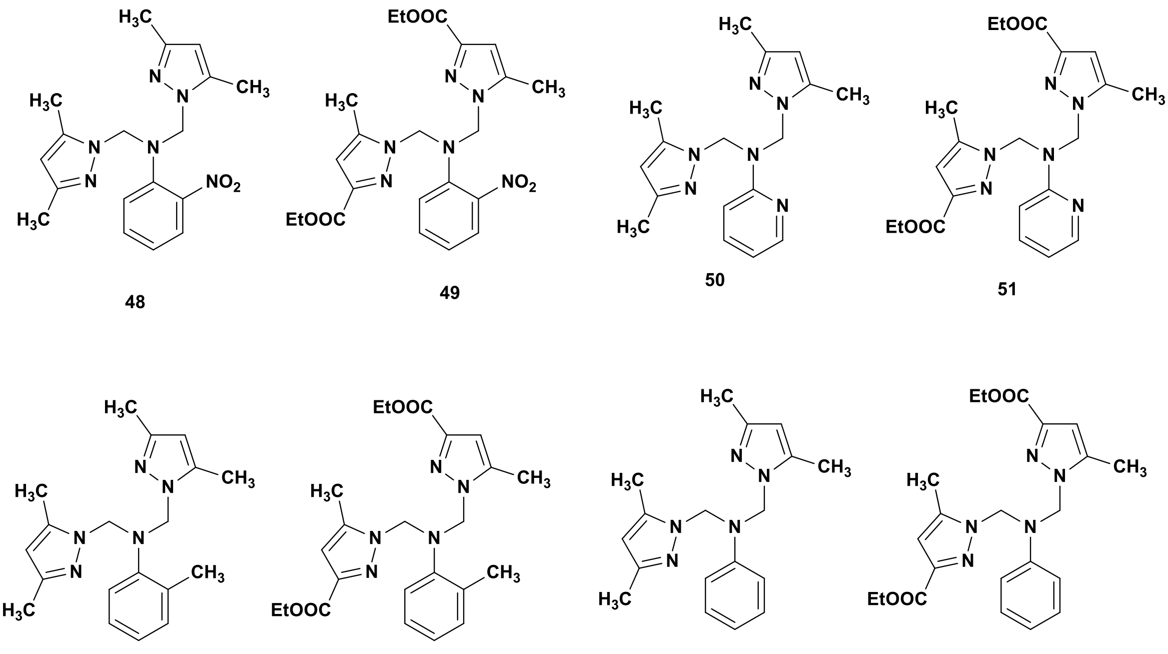

Figure 42.Chemical structure of new Bipyrazolic Tripodal Derivatives prepared by Radi [65].

In **2014**, F. Abrigach and coll. [66] Prepared fourteen N-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridin-4- amine derivatives (1-14) (Figure 5) by the condensation of (3, 5-dimethyl-1H-pyrazol-1-yl) methanol((1H-pyrazol-1-yl) methanol) with one equivalent of an amine in 20 ml of acetonitrile as solvent, stirring for 4 hours and the resulted compound dried over $MgSO_4$, filtered and concentered in vacuum (**Figure 13**).

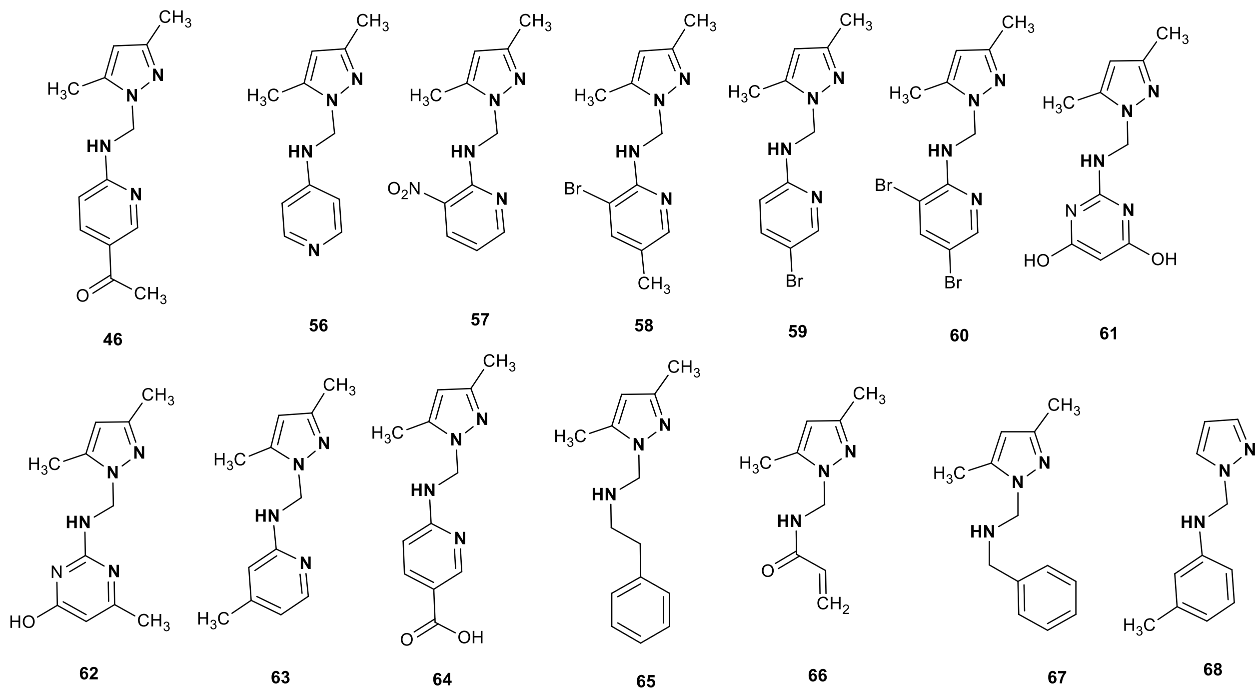

Figure 53. Chemical structure of N-((3,5-dimethyl-1H-pyrazol-1-yl) methyl) pyridin-4- amine derivatives prepared by Abrigach [66].

In **2013**, N. Boussalah and coll. [67] Prepared seven new amino acid ester functional pyrazolyl compounds (Figure) by stirring diethylosopropylamine with amine ester hydrochloride in anhydrous DMF or CH3CN under nitrogen for 5 min, then for four to six days adding a solution of (3,5-dimethyl-1H-pyrazol-1-yl)methanol in anhydrous DMF or CH_3CN was added dropwise.

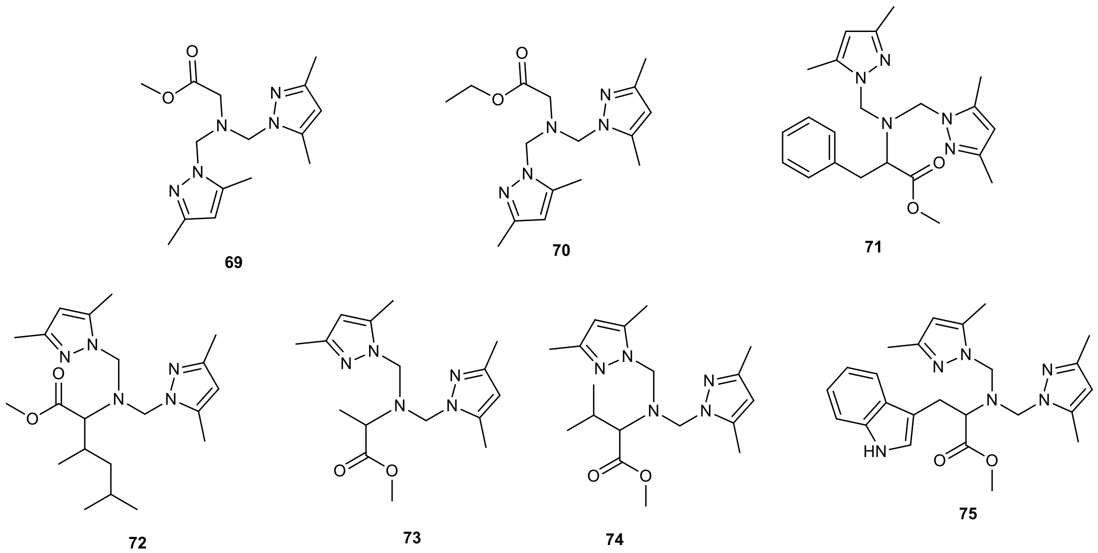

Figure 14. chemical structure of amino acid ester functional pyrazolyl compounds prepared by Boussalah [67].

In **2015**, M. El-Youbi and coll. [68] Prepared pyrazolic compounds which are already described by F. Abrigach and coll. [66] while only the new compound presented in **Figure 65**.

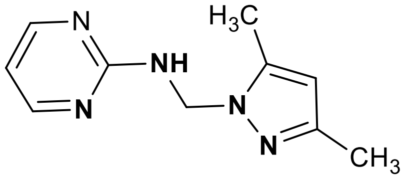

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Figure 6. Chemical structure of N-((3,5-dimethyl-1H-pyrazol-1-yl) methyl) pyrimidin-2-amine by El Youbi [68].

In **2016**, M. Lamsayah and coll. [69] Prepared N,N-bis (1H-pyrazol-1-yl) derivatives (**Figure 16**) in anhydrous acetonitrile for 4 hours under reflux.

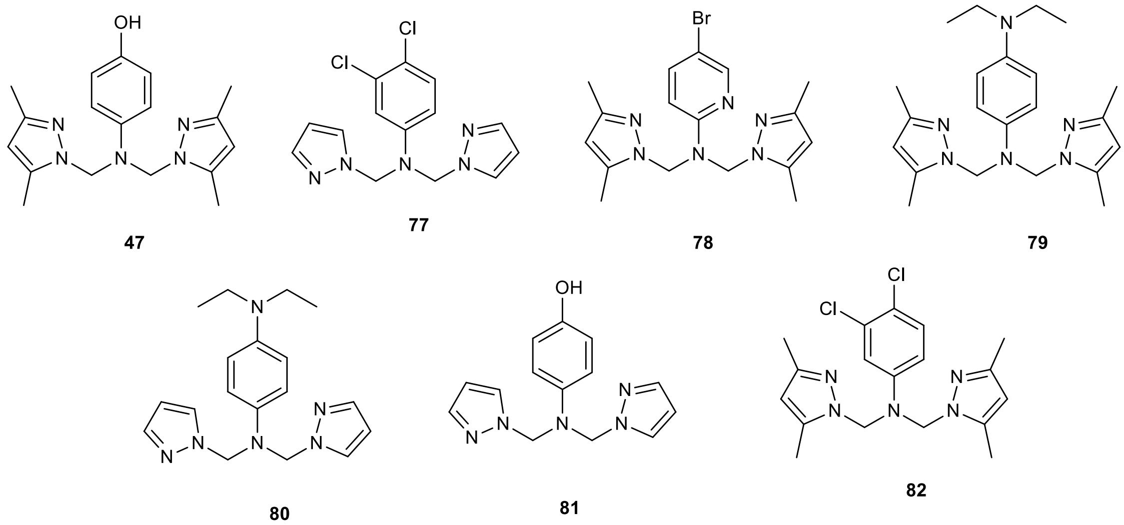
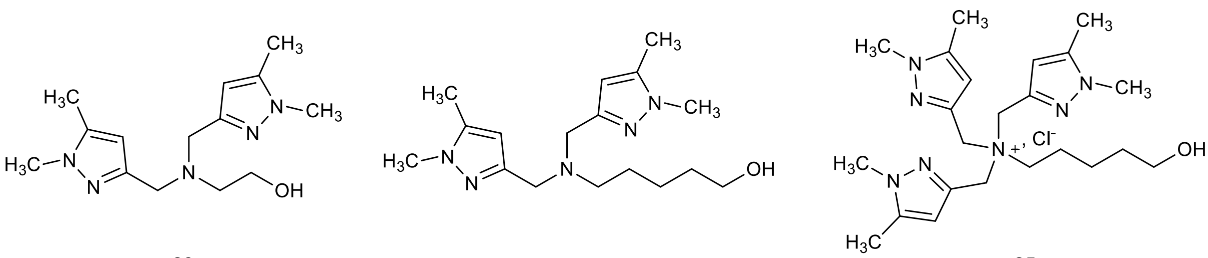


Figure 16. Chemical structure of N, N-bispyrazolyl ligands by Lamsayah [69].

In **2017**, M. El Kodadi and coll. [70] Prepared 3 pyrazole tripods by stirring 2-aminoethanol and 5(amino-1-pentanol with 3-chloromethyl-1,5-dimethylpyrazole in acetonitrile with the presence of sodium carbonate (**Figure 77**).



83 **84** **85**

Figure 7. Synthesis of tripodal ligands by El Kodadi [70].

In **2018**, I. Bouabdallah and coll. [71] prepared new tripods based on pyrazole by condensation of N,N-dimethyl-paraphenylenediamine with two equivalents of 3-chloromethyl-1,5-dimethylpyrazole in acetonitrile with the use of sodium carbonate for three hours (**Figure1818**).

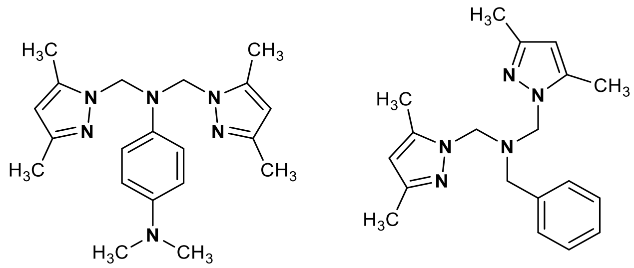


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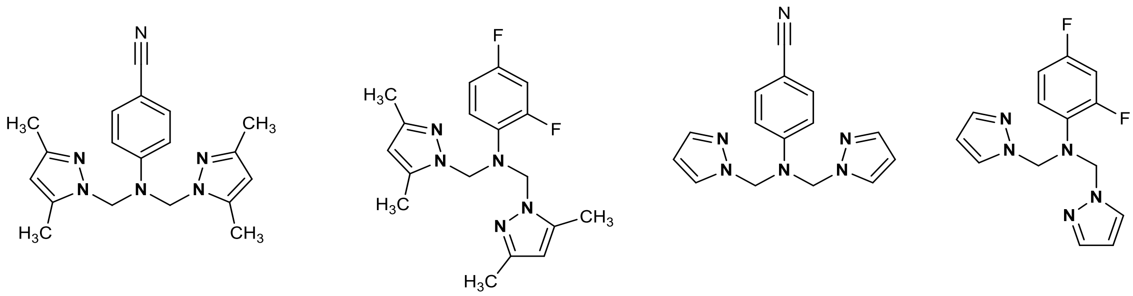
Figure18. Synthesis of these compounds prepared by Bouabdallah [71].

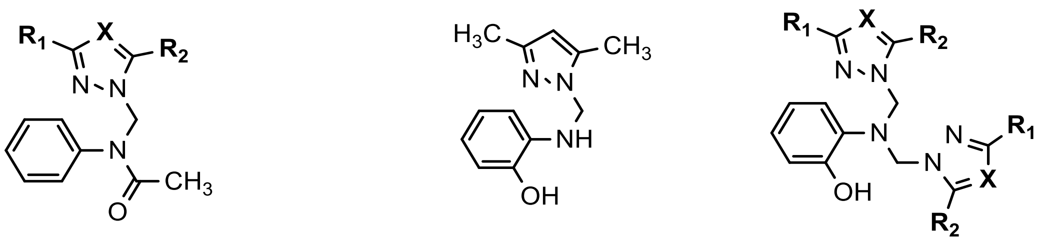
In **2017**, Y. Kaddouri and coll. [72] Prepared four tridentate pyrazolic ligands (Figure 89) by the condensation of (1H-pyrazol-1-yl)methanol or (3,5-dimethyl-1H-pyrazol-1-yl)methanol with 4-aminobenzonitrile or 2,4-difluoroaniline heated at 70°C in acetonitrile for four hours, while the compounds 1,3 purified in DCM/water, the compounds 2 and 4 purified in diethyl ether.



88 89 90 91

Figure 89. Chemical structure of tridentate pyrazolic ligands prepared by Kaddouri [72].

In **2019**, Y. Kaddouri and coll. [73] prepared nine N-alkylated 2-aminophenol and Aniline with Pyrazole and Triazole methanol derivatives (Figure 20).



92: R_1=R_2=H; X=CH
93: R_1=R_2= CH_3; X=CH
94: R_1= CH_3; R_2= COOEt; X=CH
95: R_1=R_2=H; X=N

96

97: R_1=R_2= CH_3; X=CH
98: R_1=R_2=H; X=N
99: R_1=R_2=H; X=CH
100: R_1= CH_3; R_2= COOEt; X=CH

Figure 20. Chemical structure of tridentate pyrazolic ligands prepared by Kaddouri [73].

In **2019**, H. Allali and coll. [74] Prepared 7 new tridentate pyrazole compounds (**Figure 921**) by the condensation of certain monoamines with 1-hydroxymethyl-3,5-dimethylpyrazole, 1-hydroxymethyl-pyrazole or 3-methyl-5-esterpyrazole in acetonitrile for 4 hours.

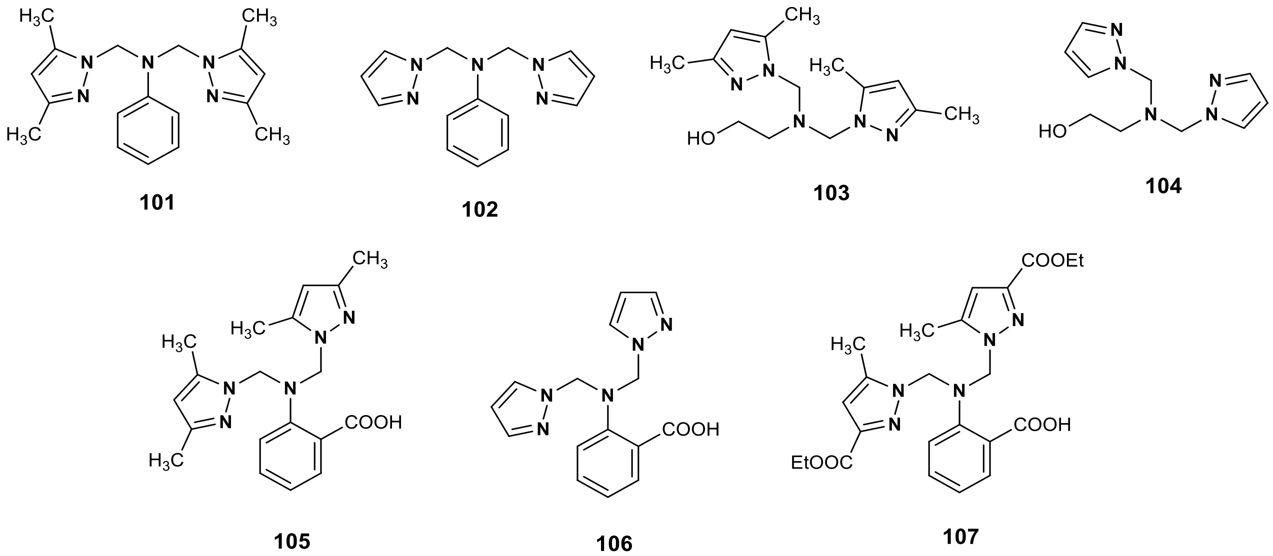


Figure 9. Chemical structure of tridentate pyrazole ligands prepared by Allali [74].

3. ANTI-CORROSION ACTIVITIES

3.1 Corrosion inhibition of copper in 3% NaCl

In **2002,** A. Dafali and coll. [75, 76] studied the inhibition of the copper corrosion in aerated 3 per cent sodium chloride solution by electrochemical polarization, weight loss and impedance measurements in the presence of bispyrazolic compounds (**Figure 22**).

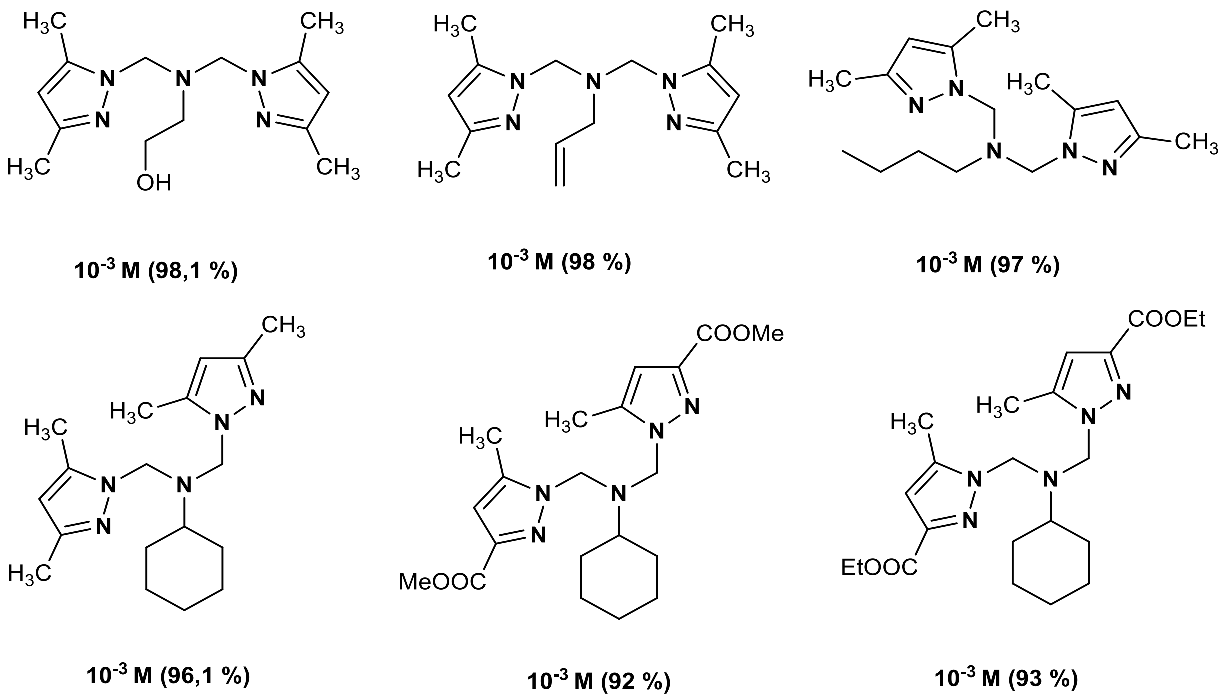
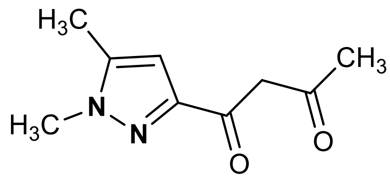


Figure 22. Inhibition efficiency of 6 bispyrazoles by Dafali in NaCl 3% for Copper [75-76].

3.2 Corrosion inhibitor for steel in 0.5M H_2SO_4

In **2007,** A. Ouchrif and coll. [77], they proofed the effect of newly synthesised 1-(1,5 dimethyl-1H-pyrazol-3-yl)-butane-1,3-dione (DPBD) on the corrosion of steel in 0.5M sulphuric acid is studied by weight-loss and electrochemical polarisation measurements. The results obtained showed that DPBD is a good inhibitor. The inhibition efficiency increases with the inhibitor concentration to attain 89% (**Figure 23**).

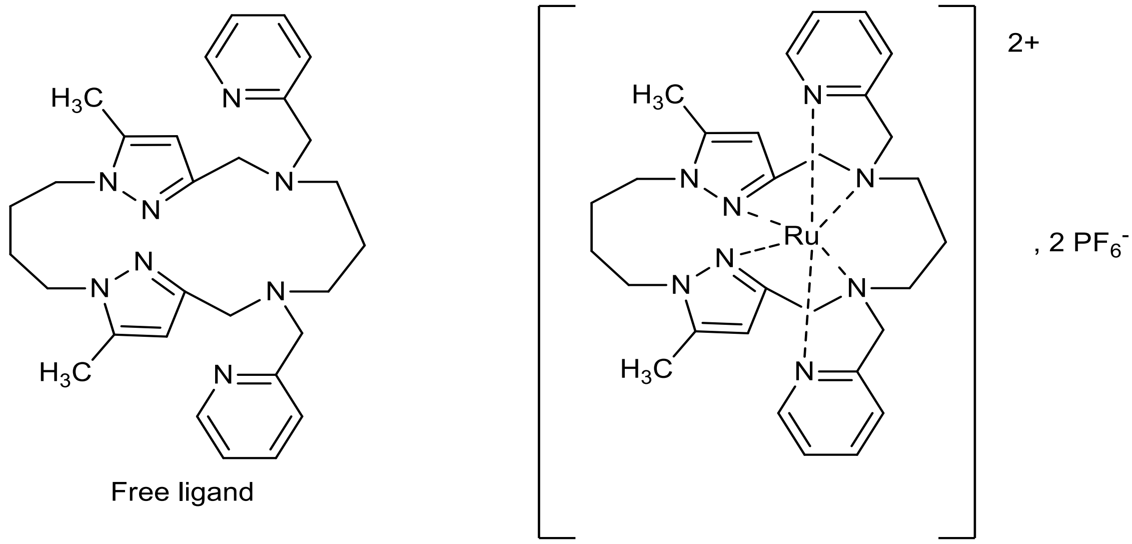


10^{-3} M (89 %)

Figure 23. Inhibition efficiency of 1-(1,5-dimethyl-1H-pyrazol-3-yl)butane-1,3-dione for steel in 0.5M H_2SO_4 [77].

3.3 Corrosion inhibitor for steel in 2M, H_3PO_4

In the same year **2007,** M. Benabdellah and coll. [78], they studied the effect of a ruthenium–ligand complex (RuLC) on the corrosion of steel in 2 M H3PO4 has been investigated at various temperatures using electrochemical techniques (impedance spectroscopy (EIS), polarisation curves) and weight loss measurements. Inhibition efficiency (E%) increases with RuLC concentration to attain 90% at 5×10^{-4} M. EIS measurements show that the dissolution process of steel occurs under activation control (**Figure 24**).



5×10^{-4} M (89%)

Figure 24. Inhibition efficiency of Ruthenium macrocyclic complex for steel in 2M H_3PO_4 [78].

3.4 Corrosion inhibitor for steel in 1M, HCl

In **2009**, A. Attayibat and coll. [79], presented a study about some possible relationship between the experimental inhibition corrosion in acidic media and the theoretical energy calculations for four series of compounds containing pyrazoles: (A) the first series of compounds, comprises only one pyrazole ring, (B) the second series has two pyrazoles (bipyrazole), (C) the third one contains one pyrazole and one pyridine (pyridylpyrazole) and (D) the last series concerns tripodal pyrazoles. These sets of compounds have been tested for their corrosion inhibition properties of steel in low concentration of hydrochloric acid medium (**Figure 25**). In **2017**, Y. Louadi and coll. [80] investigated the inhibition performance and mechanism of N1,N1,N3,N3-tetrakis((3,5-dimethyl-1Hpyrazol-1-yl)methyl)propane-1,3-diamine and N1,N1,N2,N2-tetrakis((3,5-dimethyl-1H-pyrazol-1-yl)methyl) benzene-1,2-diamine for the corrosion of mild steel in 1.0 M HCl were investigated using weight loss method and electrochemical measurements (**Figure 26**).

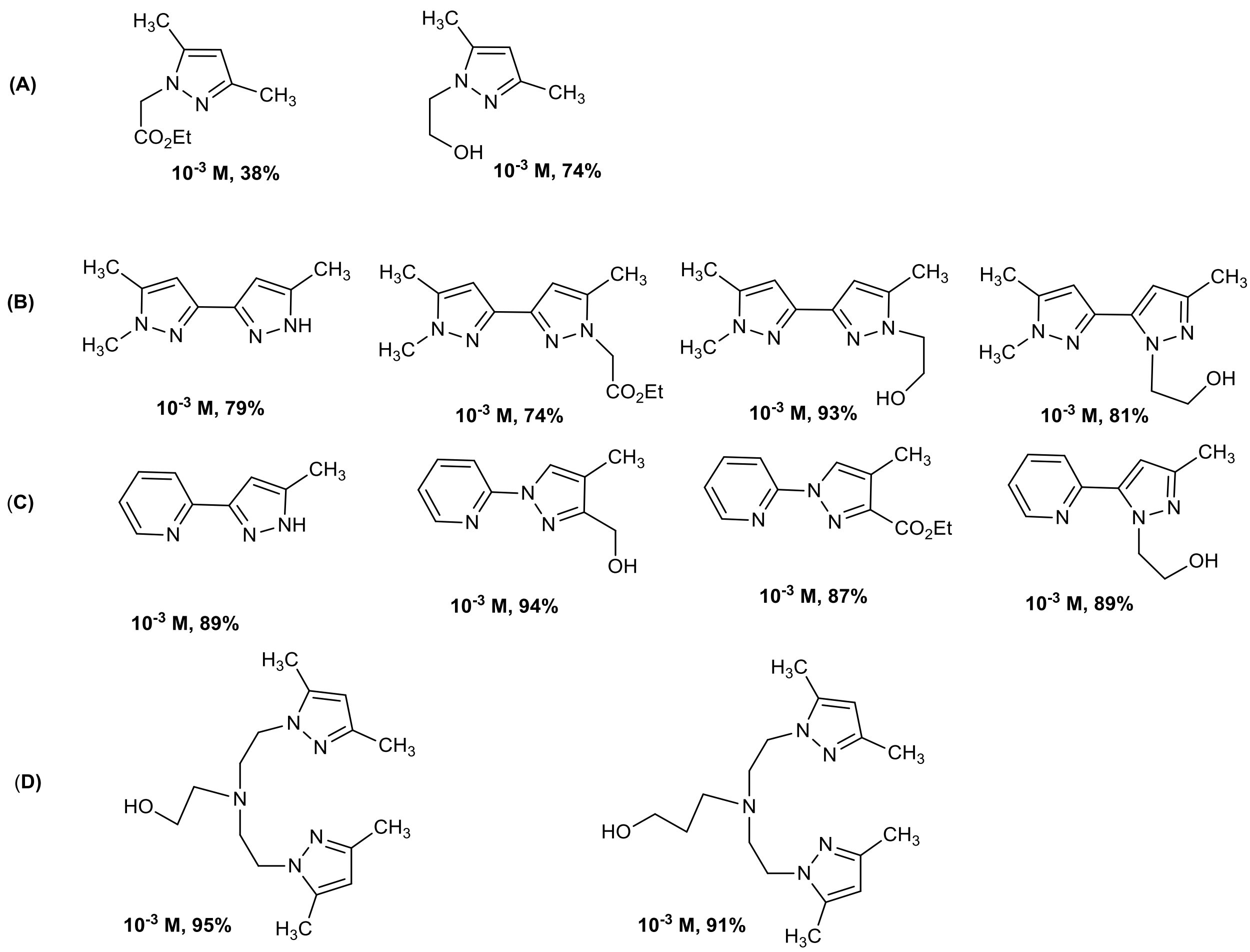


Figure 25. List of ligands used as corrosion inhibitors of steel in 1 M HCl medium [79]

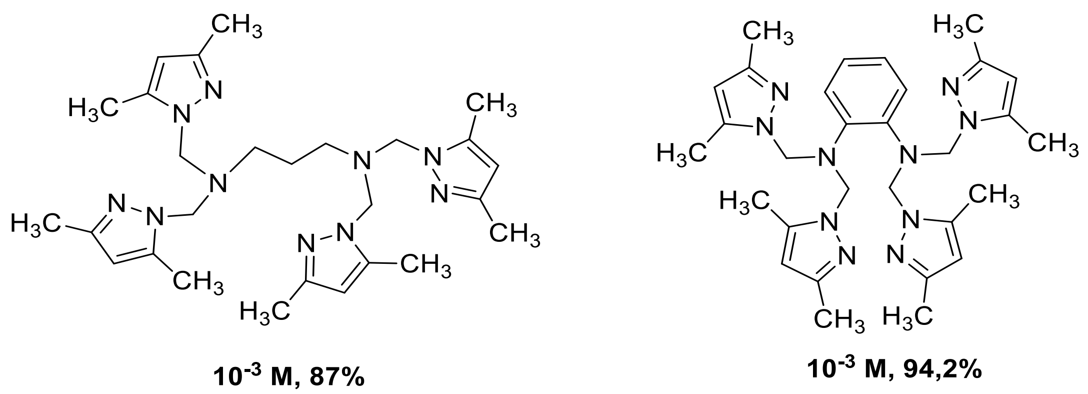


Figure 26: Chemical molecular structures of tetrakis pyrazole derivatives and their inhibition efficiency in 1M, HCl [80].

Azole-based heterocycles have a wide range of biological activities and also used as herbicides, fungicides, pesticides, insecticides and dyes as well as inhibitors of metal corrosion [81-83].

Conclusion

The following main conclusions are drawn from the present review:

➢ the investigated nitrogen compounds and their derivatives showed good performance as corrosion inhibitors in aggressive medium for all metals.

➢ the synthesis of other nitrogen compounds is the key to find the best and the ideal inhibitor of corrosion for steel, copper, aluminum and other materials.

➢ the challenges are huge still here, such as temperature, medium, economy, environmental friendly and not harmful to any one and why not biological inhibitors?

We are proud to be a chemist, proud of our students, proud of colleagues, proud of our collaborators and proud of our family supports. Thanks to all for the support and the help.

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