New 8-Hydroxyquinoline-Bearing quinoxaline derivatives as effective corrosion inhibitors for mild steel in HCl: Electrochemical and computational investigations

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3. Results and discussion

3.1. Chemical part

1-((8-hydroxyquinolin-5-yl)methyl)quinoxalin-2(1H)-one (Q2)

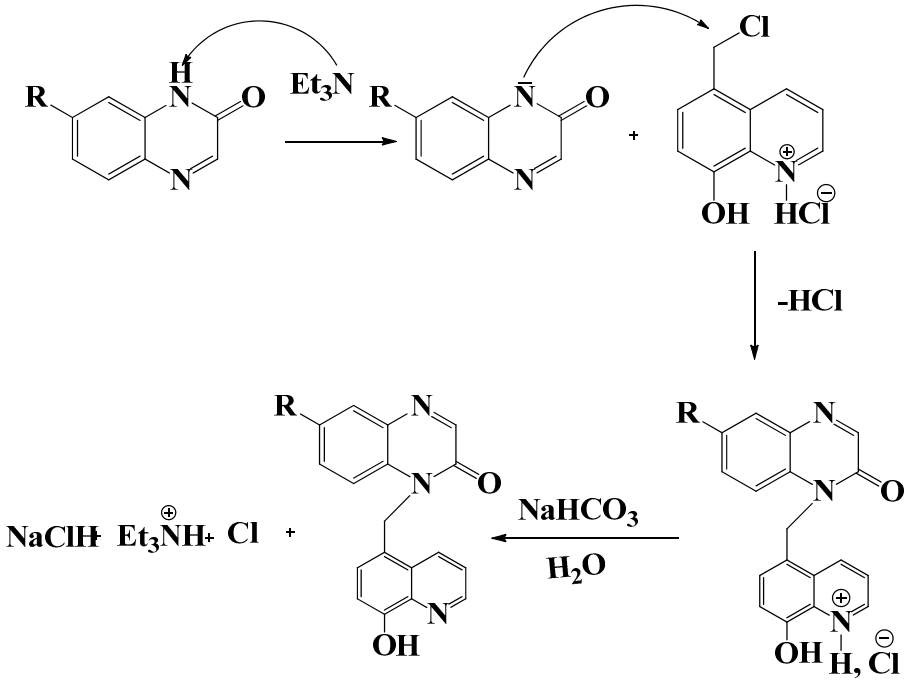
Yield 85 %, **Aspect** : Yellow solid, **Mp** = 198-200 ° C, **Fr** = 0.55 (hexane/dichloromethane, 5: 5), M = 303.31 (g / mole). **^{1}H-NMR (DMSO-d$_6$) :**δ_{ppm} = 4.68 (s, 1 H, OH), 4.55 (s, 2 H, CH_2), 7.04-7.23-7.60-8.83-9.08 (m, 5 H, ArH-quinoline), 7.18-7.19-7.21-7.51 (m, 4 H, ArH-quinoxaline).**^{13}C-NMR (DMSO-d$_6$) :**δ_{ppm} =52.39 (CH_2), 151.16 (ArC-OH), 151.36 (C=O), 114.08-123.38-129.23-130.12-144.99 (ArCH-quinoxaline), 130.26-144.54 (ArC-quinoxaline), 111.14-117.70-126.57-128.92-144.99 (ArCH-quinoline), 126.30-128.41-135.55 (ArC-quinoline).
EA (%) : Calculated : C, 71.28 ; H, 4.32 ; N, 13.85. **Find** : C, 71.13 ; H, 4.99 ; N, 13.10.

1-((8-hydroxyquinolin-5-yl)methyl)-3,6-dimethylquinoxalin-2(1H)-one (Q1)
Yield 72 %, **Aspect** : Red solid, **Mp** = 201-203 ° C, **Fr** = 0.57 (hexane / dichloromethane, 5 : 5), **M** = 317.34 (g / mole). **^{1}H-NMR:** δ_{ppm} = 1.11 (s, 3 H, CH_3), 6.99 (s, 1 H, OH), 4.73 (s, 2 H, CH_2), 7.02-7.34-7.53-7.58-7.61 (m, 10 H, ArH-quinoline), 7.19-7.20-7.50-7.57 (m, 3 H, ArH-quinoxaline).**^{13}C-NMR:** δ_{ppm}= 23.64 (CH_3), 152.49 (ArC-OH), 168.62 (C=O), 127.47-132.09-133.51-148.12 (ArCH-benzene), 127.57-138.21-139.38 (ArC-benzene), 111.05-122.06-126.28-130.54-134.88 (ArCH-quinoline), 125.60-128.73-137.20 (ArC-quinoline).**EA (%) : Calculated** : C, 71.91 ; H, 4.76 ; N, 13.24. **Find** : C, 71.32 ; H, 4.19 ; N, 13.37.

The ^{1}H-NMR spectra of the compounds **Q1** and **Q2** taken in DMSO-d6 show in particular the signals relating to the alkyl groups, thus highlighting the disappearance of the signals attributable to the **NH** groups, which attests to their involvement in the reaction.

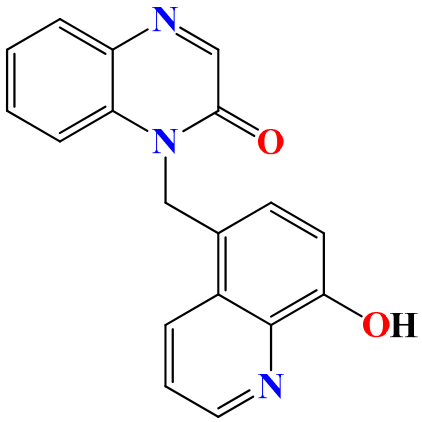
The ^{13}C-NMR spectra of compounds **Q1** and **Q2** taken in DMSO-d6, show the appearance of signals relating to the secondary carbon bound to the nitrogen atom, which shows that the nitrogen atoms of the quinoxaline compounds are well bound to the carbon of the 8-hydroxyquinoline unit.

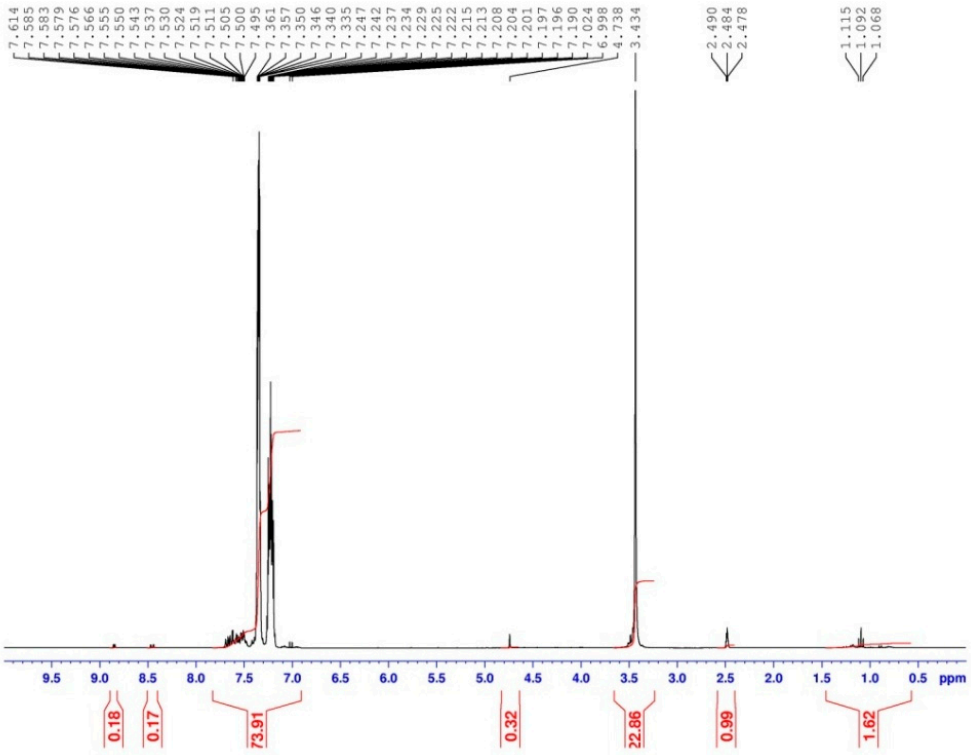
The secondary nitrogen atom of quinoxaline compounds (**A** and **B**) is δ^- polarized, it has a non-binding nucleophilic doublet which can easily attack the chlorine atom of compound **C**, according to the following reaction mechanism (**Scheme S1**).

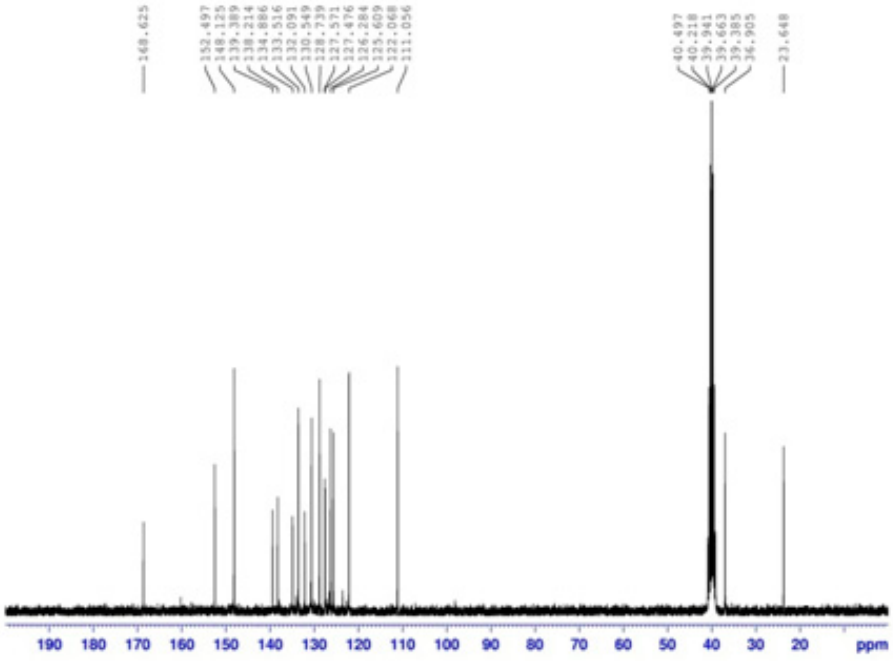


Scheme S1. Mechanism of the N-alkylation of 5-chloromethyl-8-hydroxyquinoline hydrochloride by 6-alkylquinoxalin-2 (1H) -ones derivatives

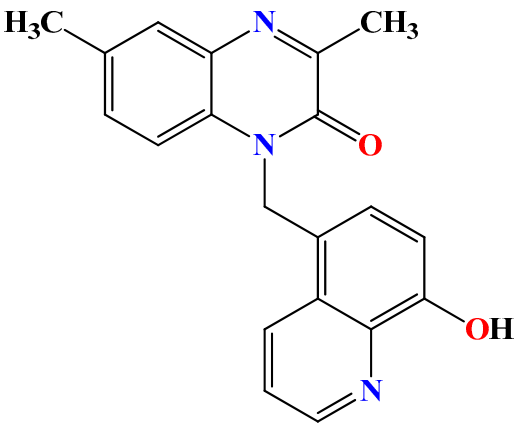
1-((8-hydroxyquinolin-5-yl)methyl)quinoxalin-2(1H)-one (Q2) :

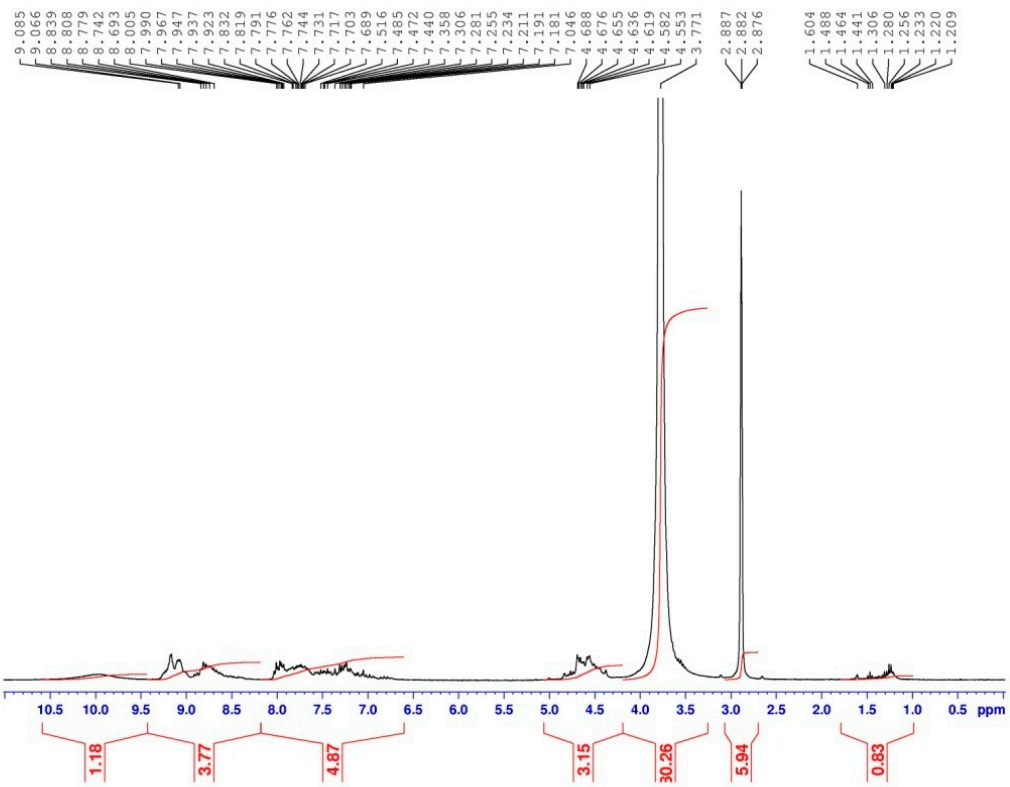






1-((8-hydroxyquinolin-5-yl)methyl)-3,6-dimethylquinoxalin-2(1H)-one (Q1):




9.085
9.066
8.839
8.808
8.779
8.742
8.693
8.005
7.990
7.967
7.947
7.937
7.923
7.832
7.819
7.791
7.776
7.762
7.744
7.731
7.717
7.703
7.689
7.516
7.485
7.472
7.440
7.358
7.306
7.281
7.255
7.234
7.211
7.191
7.181
7.046
4.688
4.676
4.655
4.636
4.619
4.582
4.553
3.771
2.887
2.882
2.876
1.604
1.488
1.464
1.441
1.306
1.280
1.256
1.233
1.220
1.209
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.18
3.77
4.87
3.15
30.26
5.94
0.83

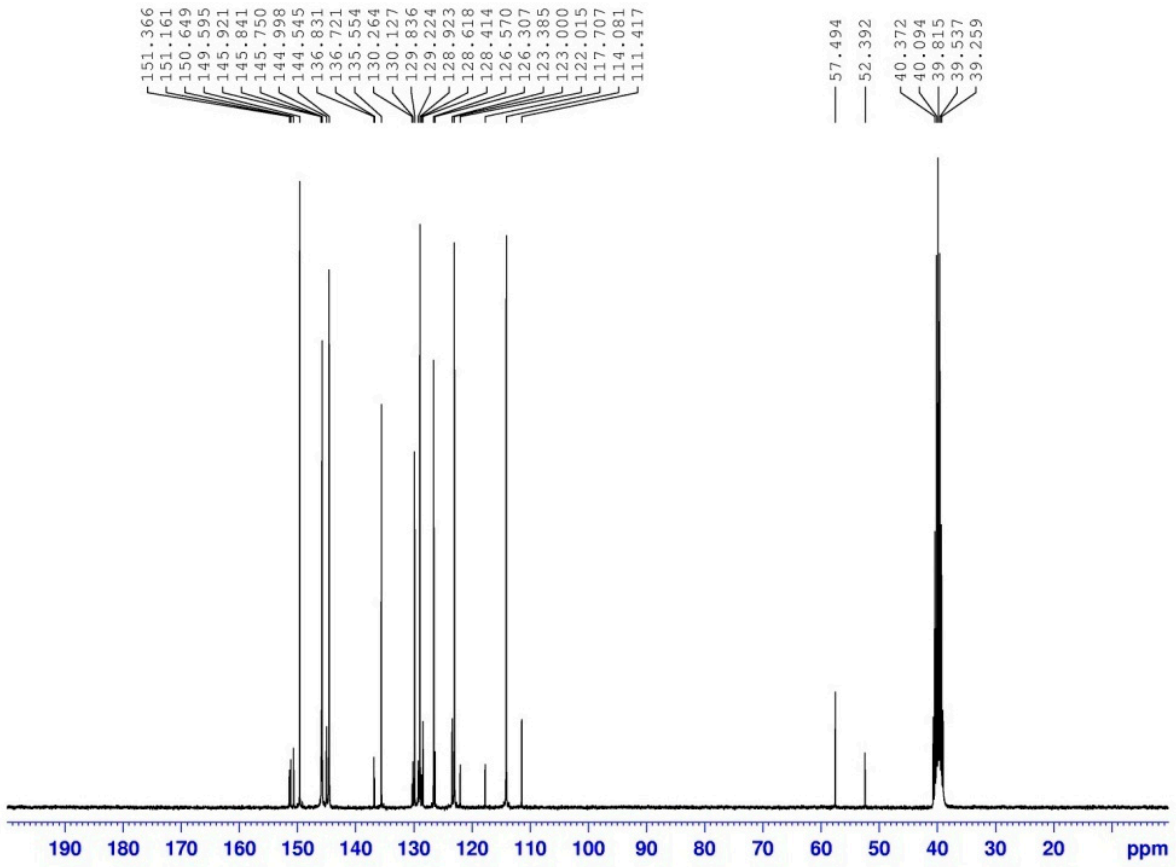
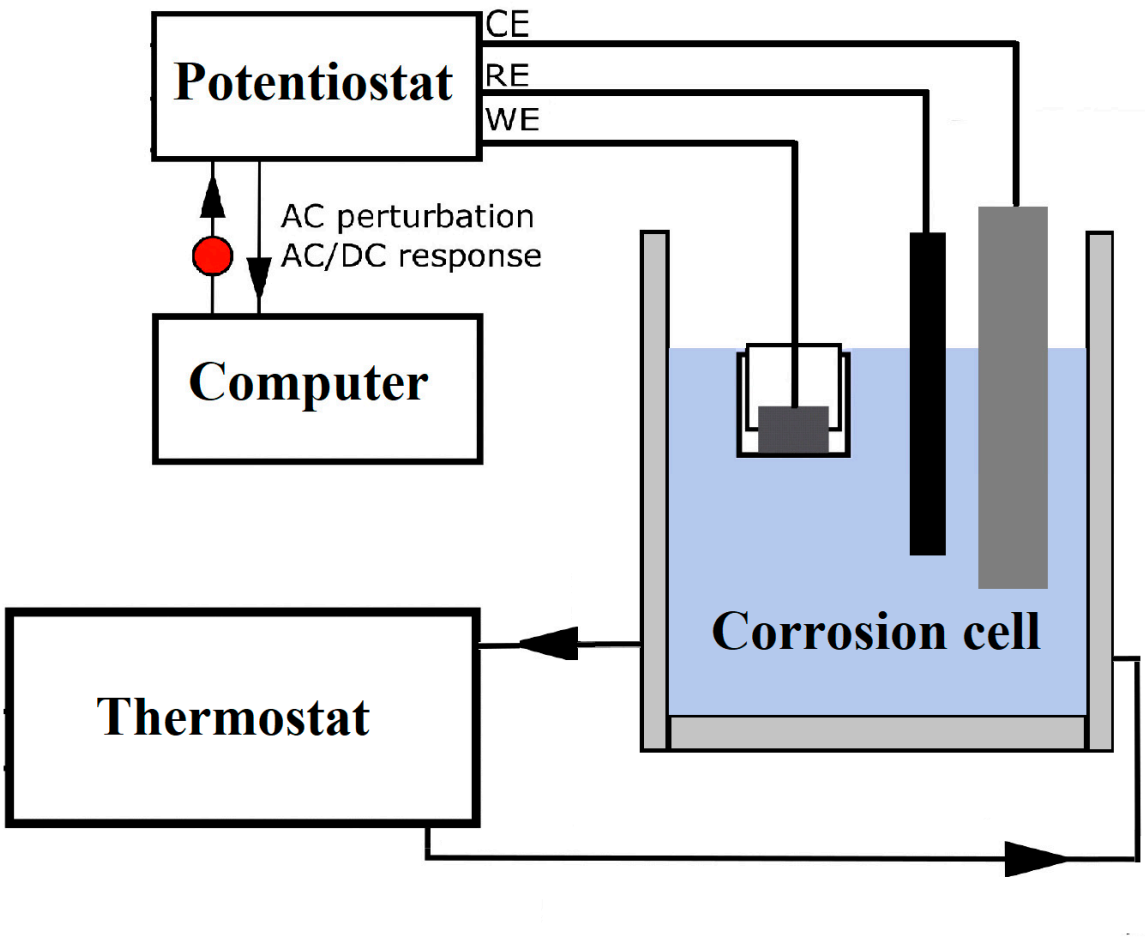


Fig.S1. Spectra IR, ^{1}H and ^{13}C NMR of compounds (**Q1** and **Q2**)



Scheme S2. Schematic representation of the corrosion measurement setup.

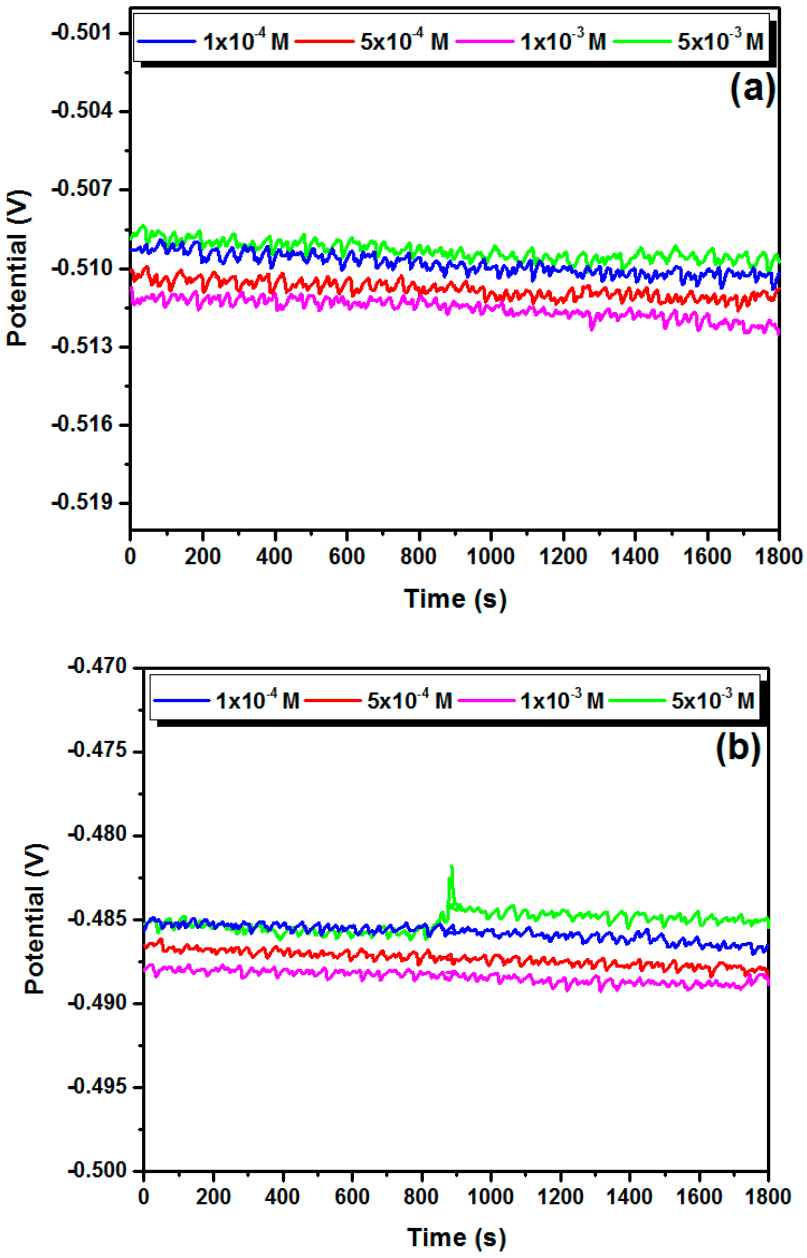


Fig.S2: OCP–time plots of MS in 1.0 M HCl with different concentrations of (a) Q1 and (b) Q2 at 303K.

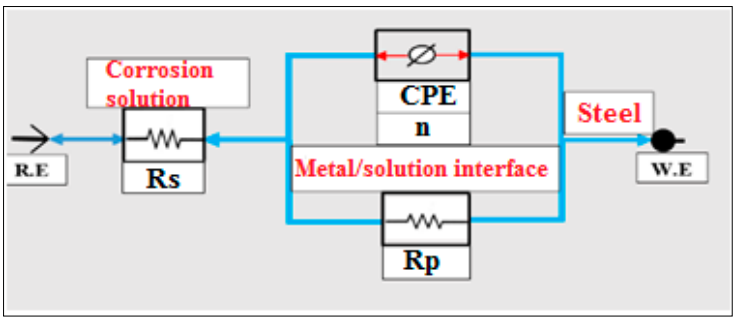


Fig. S3: Equivalent circuit model applied to fit and simúlate the impedance data.

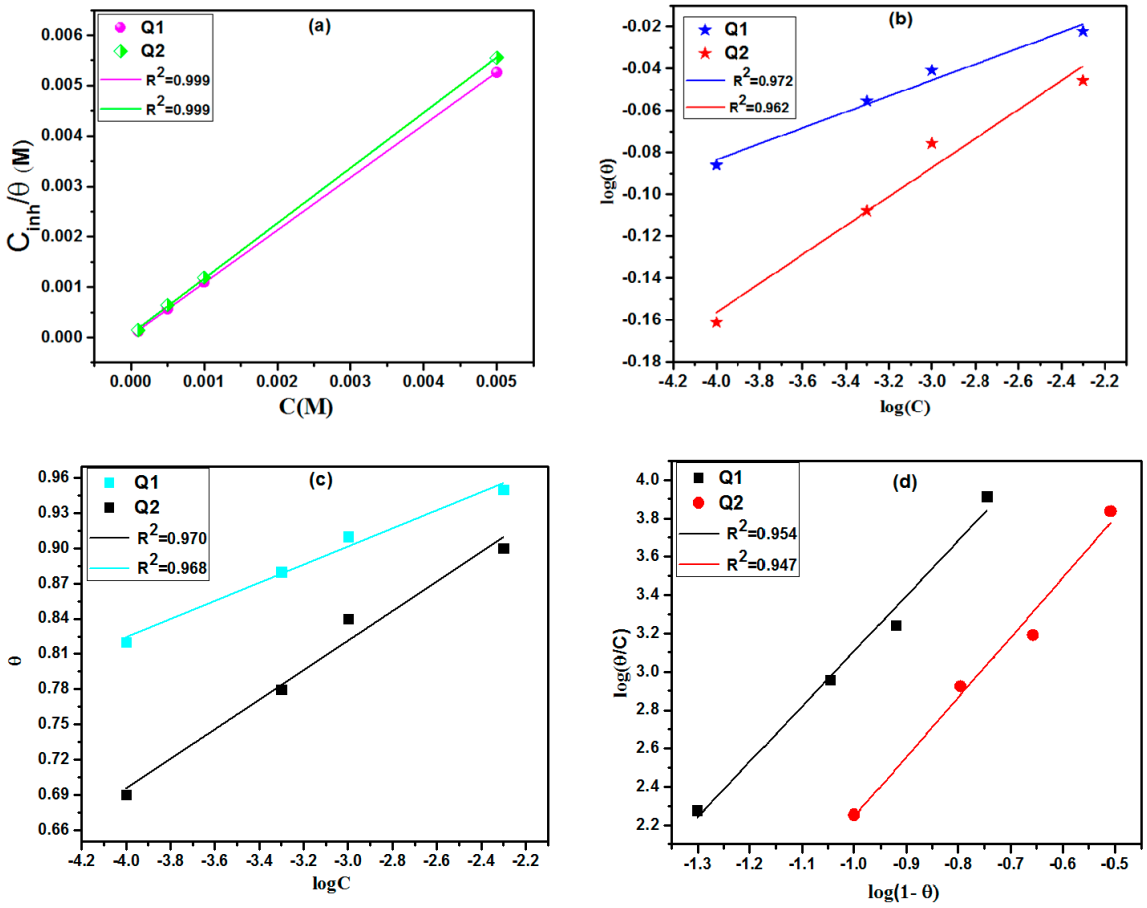


Figure S4. Adsorption isotherm models for the adsorption of Q1 and Q2 molecules on mild steel in 1.0 M HCl at 303 K (a) Langmuir, (b) Frumkin, (c) Temkin, and (d) Flory-Huggins.

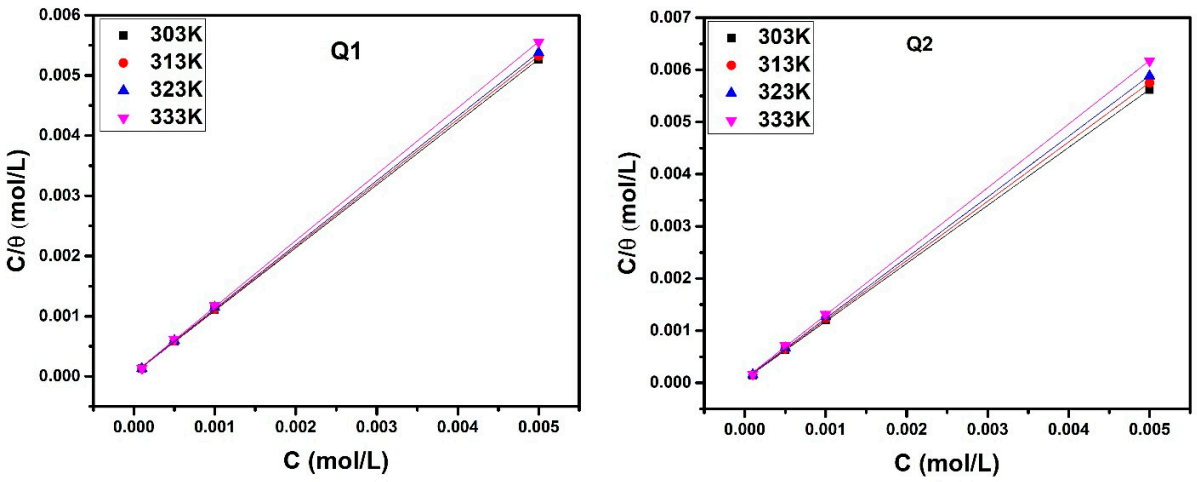


Figure S5. Langmuir adsorption isotherm models for the adsorption of Q1 and Q2 molecules on mild steel in 1.0 M HCl at different temperatures.

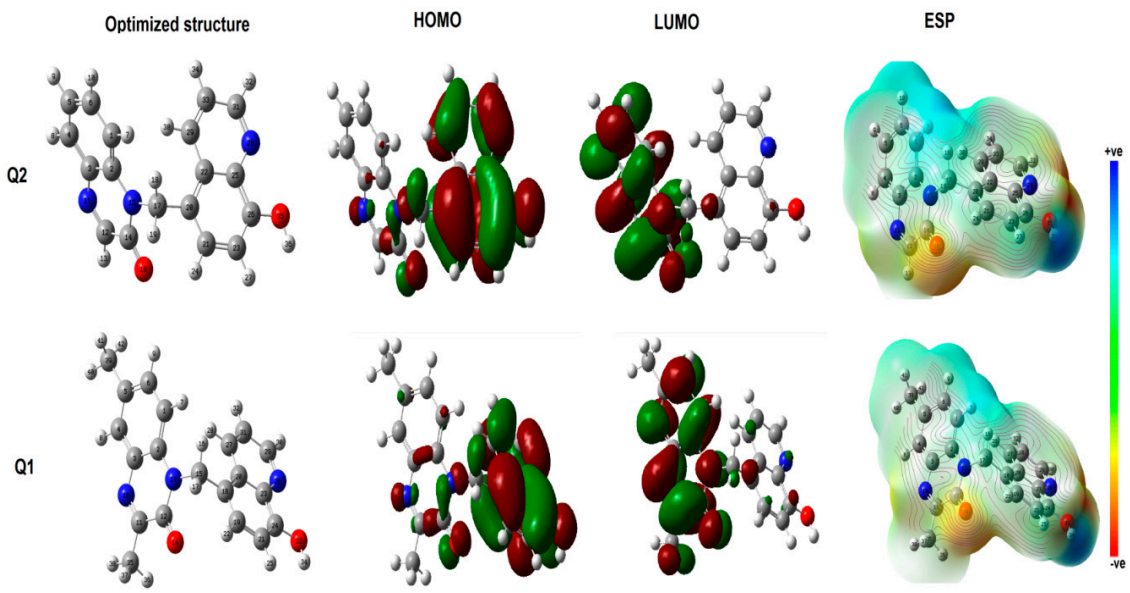


Fig. S6: Optimized structures, HOMO, LUMO and ESP of Q1 and Q2 in their neutral forms obtained by DFT/B3LYP/6-31+G(d,p) in aqueous solution.

TableS1. Mulliken atomic charges for Q1and Q2.

Q1 atoms	Mulliken atomic charges	Q2atoms	Mulliken atomic charges
C (1)	-0.014	C (1)	-0.002
C (2)	0.352	C (2)	0.330
C (3)	0.220	C (3)	-0.007
C (4)	-0.056	C (4)	0.055
C (5)	0.116	C (5)	0.017
C (6)	-0.025	C (6)	0.030
N (10)	-0.541	N (11)	-0.290
C (11)	0.237	C (12)	0.150
C (12)	0.585	C (14)	0.361
N (13)	-0.579	N (15)	-0.409
O (14)	**-0.656**	**O (16)**	**-0.462**
C (15)	0.148	C (17)	0.212
C (18)	0.073	C (20)	-0.091
C (19)	-0.014	C (21)	0.072
C (20)	0.085	C (22)	-0.076
C (21)	-0.038	C (23)	0.002
C (23)	0.194	C (25)	0.065
C (24)	0.325	C (26)	0.183
N (26)	-0.541	N (28)	-0.356
C (27)	0.017	C (29)	0.197
C (29)	0.204	C (31)	0.185
C (31)	-0.007	C (33)	-0.080
O (33)	-0.219	O (35)	-0.087
C (35)	0.039		
C (39)	-0.000		

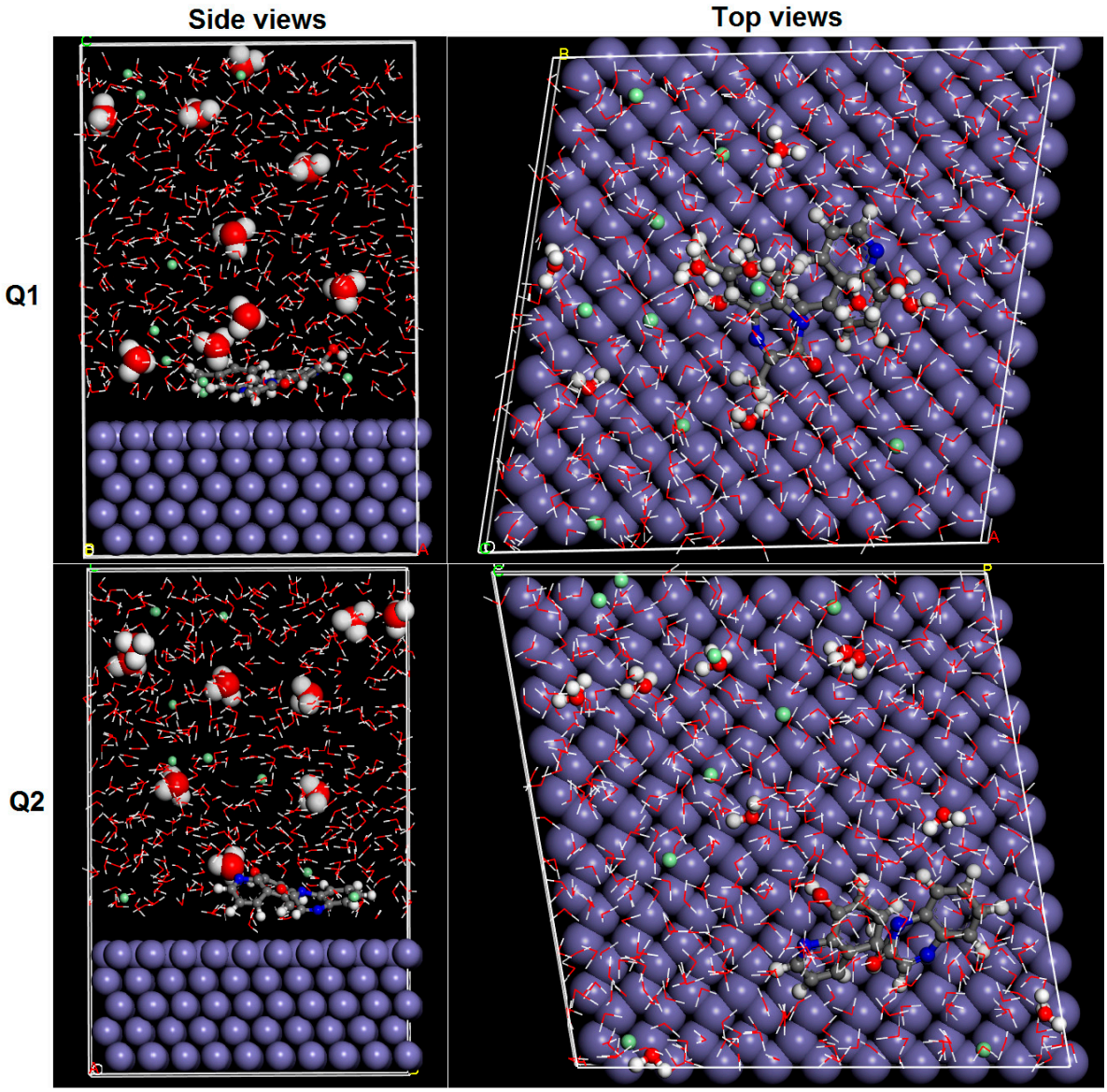


Fig.S7: Side and top views of the final adsorption of Q1 and Q2 inhibitors in their neutral forms on the Fe (110) surface in presence of solvent species.

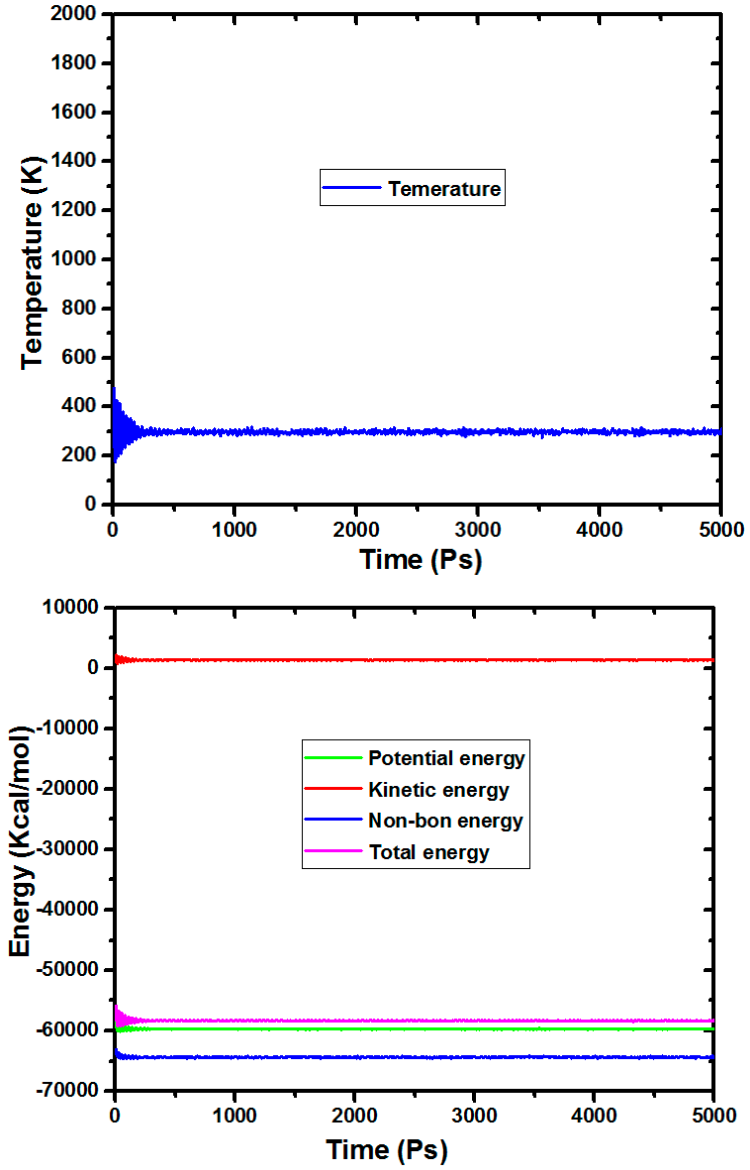


Fig.S8: Temperature and energy equilibrium curves of the investigated inhibitors adsorbed on the Fe (110) surface in solution.