The Development of a Novel Bio-based Corrosion Inhibitor: Using Biomass-Derived 5-Hydroxymethylfurfural (5-HMF) as Starting Materials

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Contents

Section A. Materials and Methods

Deuterated solvents were obtained from Cambridge Isotope Laboratories. Other routine chemicals were purchased from commercial suppliers with purity >95% and used without further purification. High-resolution accurate mass measurements (HRMS) were generated by using Agilent Technologies instrument. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker 400 MHz spectrometer. Referring to deuterated solvents, chemical changes are reported in ppm.

Section B. Synthetic Procedures

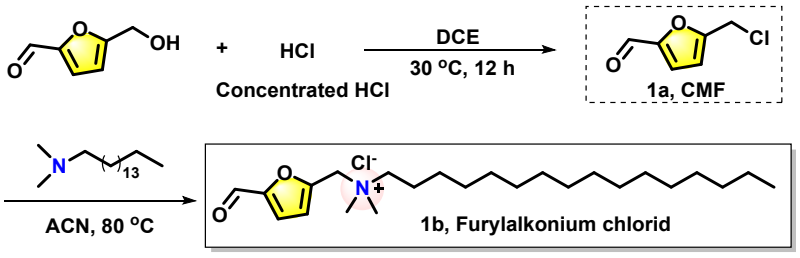
N,N-dimethylhexadecan-1-amine, acetonitrile, and $SOCl_2$ were purchased from Heowns. 5-Hydroxymethylfurfural was purchased from Zhejiang Sugar Energy Technology Co., Ltd.. All the other solvents were purchased from Heowns and used as received without further purification.

The synthetic procedure of 5-CMF

The important intermediate 5-CMF was prepared from 5-HMF (1g, 8 mmol) through a substitution step. To the solution of 5-HMF in 1,2-dichloroethane (35 mL), was added con. HCl (20 mL) dropwise at 0 °C. And then the solution was stirred at room temperature for 12 h. The reaction was quenched by water (100 mL). The organic phase was dried by Na_2SO_4, and then concentrated in vacuum to give the crude product **1a**, which can be used directly in the next step.

The synthetic procedure of target product Furylalkonium chlorid

To the solution of **1a** (1g, 772μl, 7mmol) in acetonitrile, was added N,N-dimethylhexadecan-1-amine at room temperature, and then the reaction was stirred at 80 °C for 1h. After that, the solution was concentrated directly to generate the crude product, which was subjected to column chromatography to give the target bio-based corrosion inhibitor Furylalkonium chlorid (the yield of these two steps is 85%).



Scheme S1 The synthetic route and structural formula of **1a** and Furylalkonium chlorid.

Section C. Supporting Figures

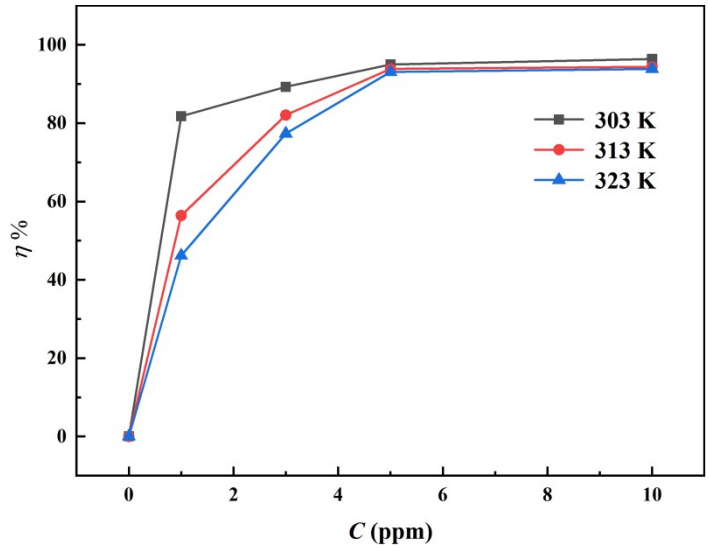


Figure S1. (a) The corrosion inhibition efficiency for the mild steel in 0.5 M HCl containing different concentrations of inhibitor Furylalkonium chlorid with at 303 K, 313 K and 323 K, respectively.

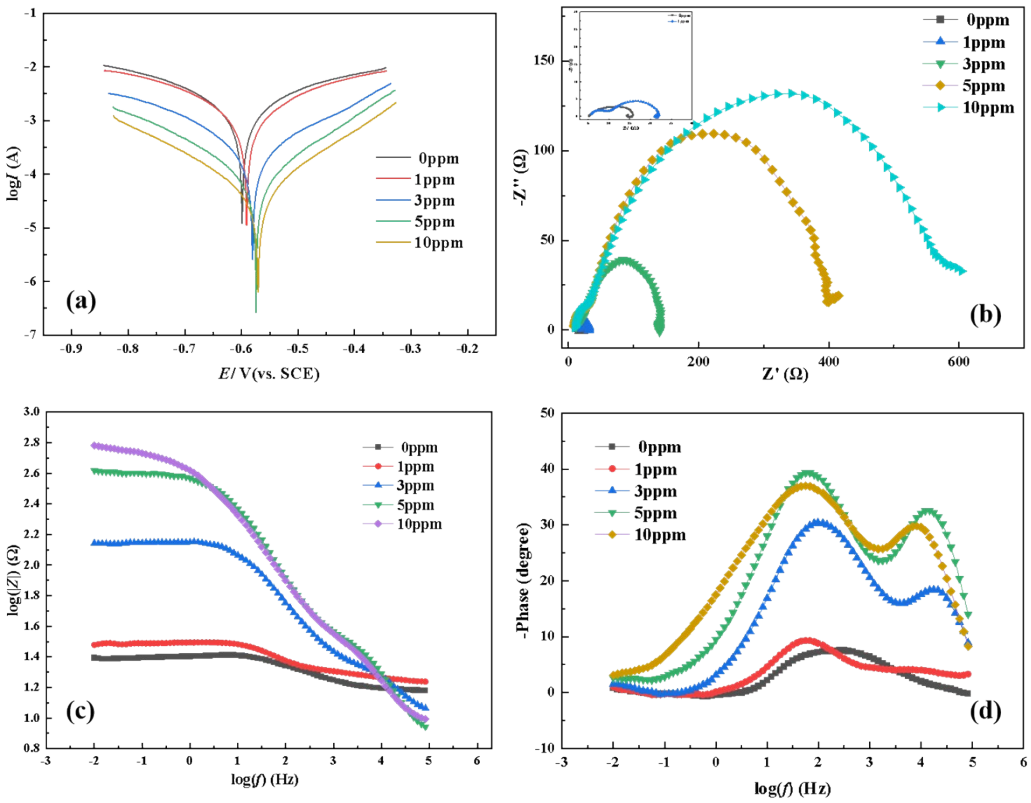


Figure S2. Potentiodynamic polarization curves (a), Nyquist plots (b), and Bode plots (c and d) for mild steel in 0.5 M HCl solution with different concentrations of Furylalkonium chlorid at 303K.

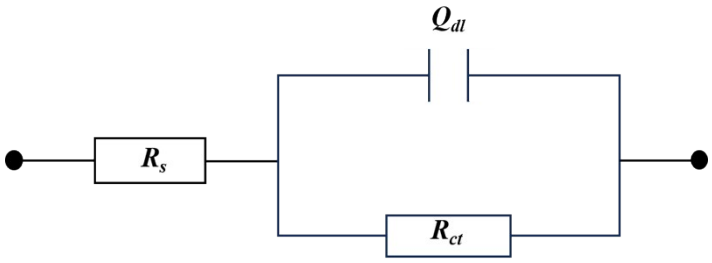


Figure S3. Simulated equivalent circuit.

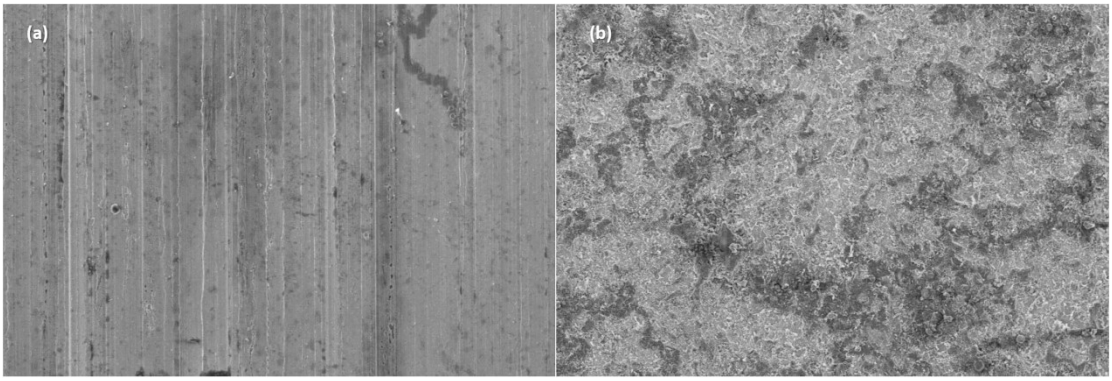


Figure S4 SEM images of the mild steel surface after corrosion in 0.5 M HCl solution with 10 ppm Furylalkonium chlorid (a), and without inhibitor for 4 h at 303 K (b).

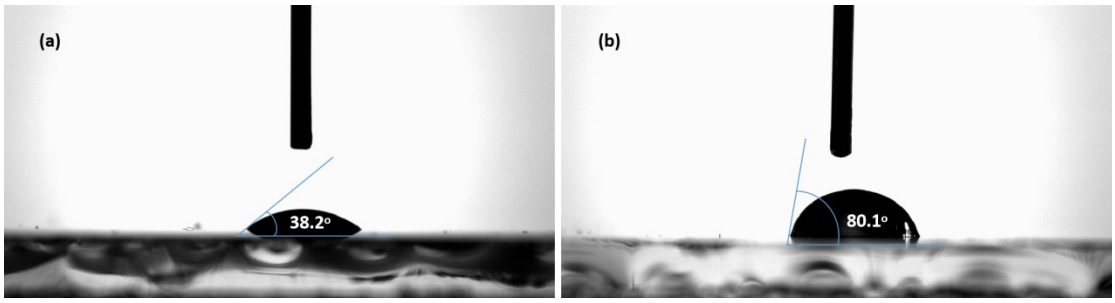


Figure S5 WCA images of glass surface (immersed in water) without inhibitor (a), and with 0.75 M inhibitor (b).

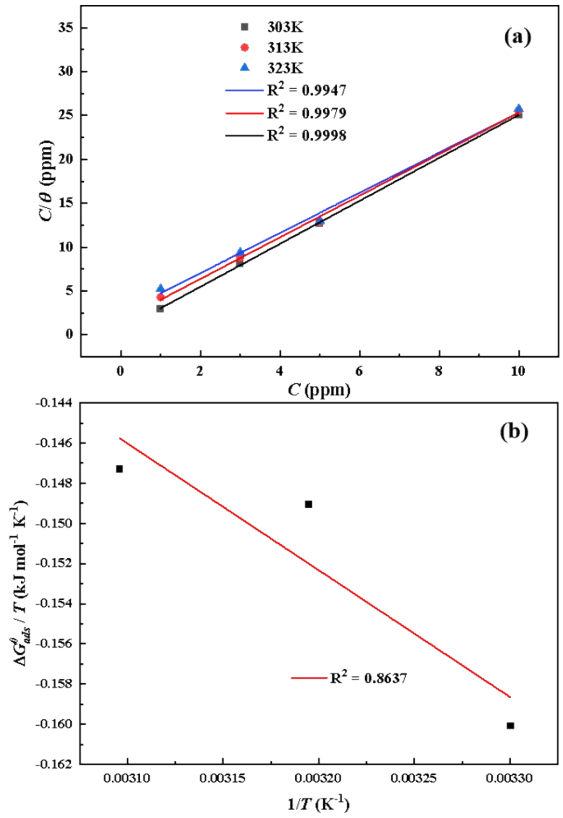


Figure S6 (a) Langmuir adsorption isotherm plots of the inhibitor Furylalkonium chlorid on metal steel surface; (b) Curves of ΔG^{0}_{ads}/T versus 1/T.

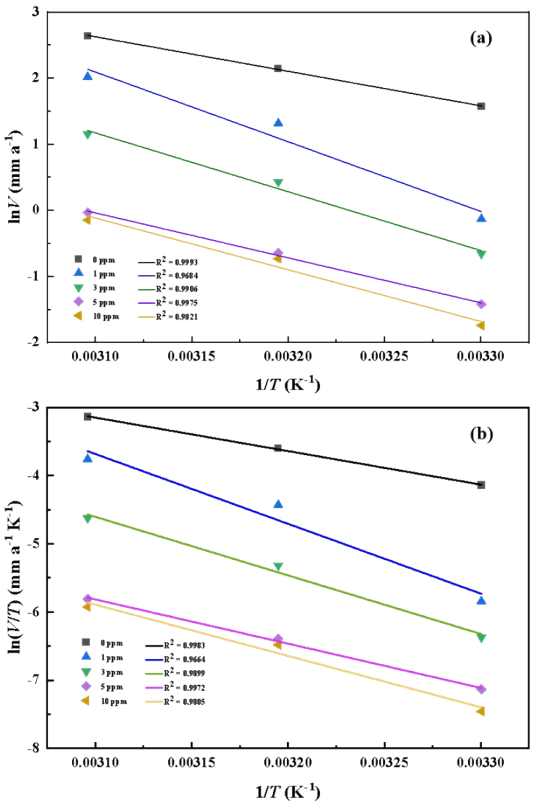


Figure S7 Arrhenius plots (a) and transition state plots (b) for metal steel in 0.5 M HCl solution with different concentrations of Furylalkonium chlorid.

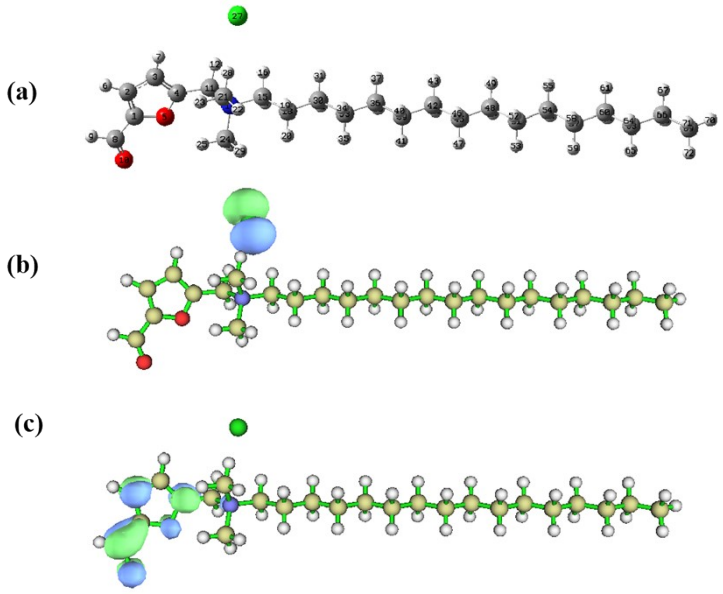


Figure S8 Optimized geometric structure (a) and the distributions of HOMO (b) and LUMO (c) for inhibitor Furylalkonium chlorid.

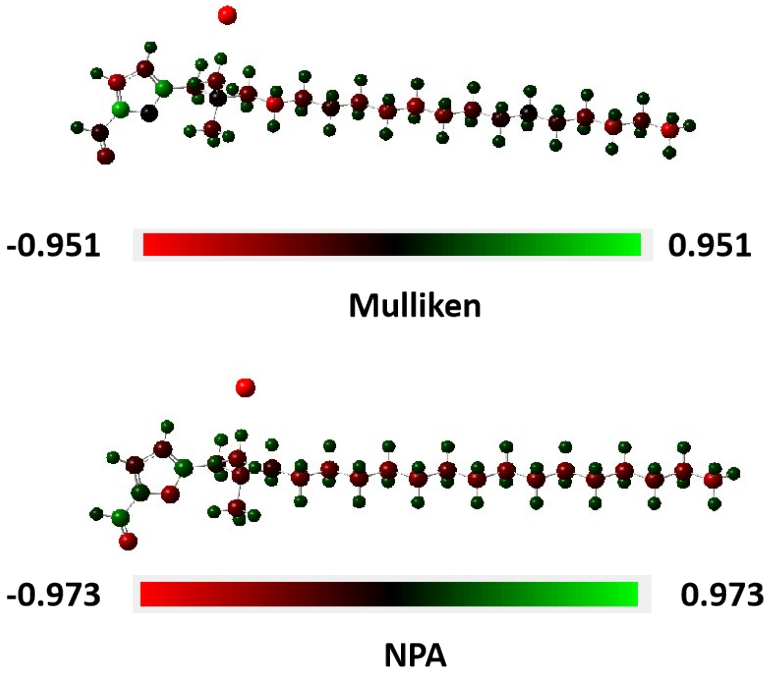


Figure S9 Mulliken and NPA charge distribution on bio-based inhibitor Furylalkonium chlorid.

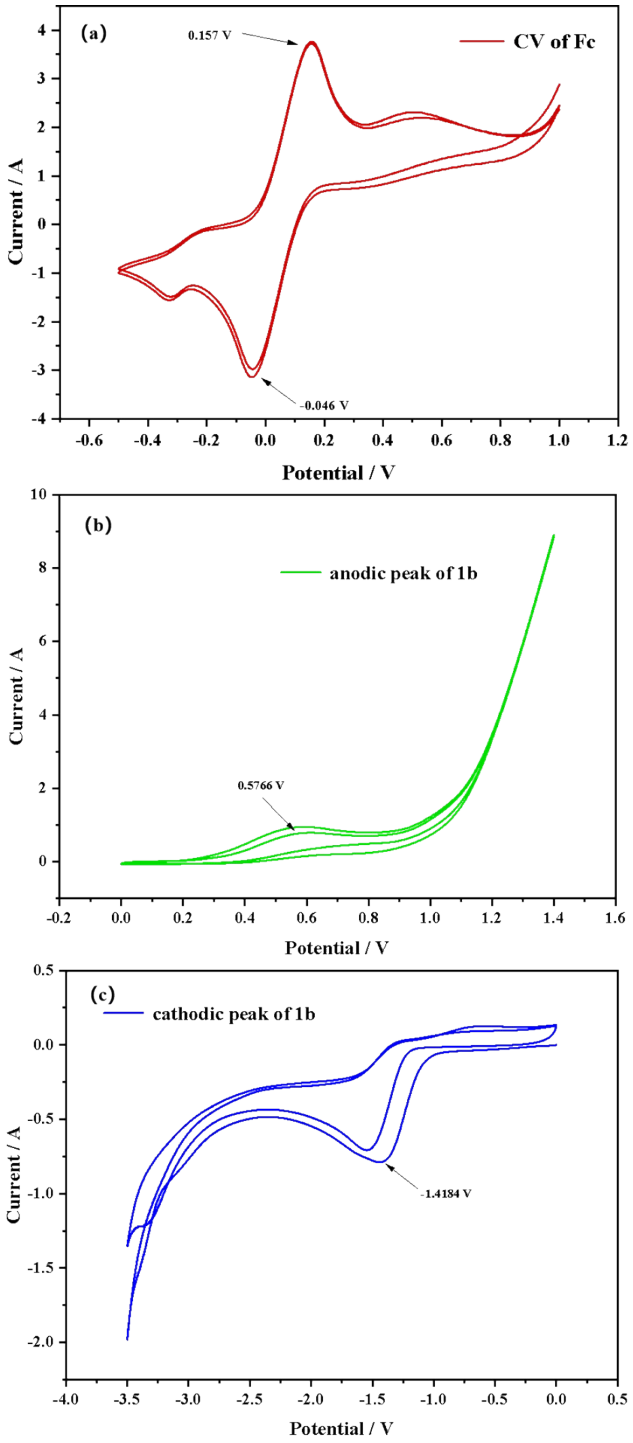


Figure S10 The cyclic voltammetry experiments of ferrocene (Fc) and bio-based inhibitor Furylalkonium chlorid.

Section D. Supporting Tables

Table S1 Weight loss results of mild steel in 1 M HCl without and with Furylalkonium chlorid at 30°C.

Inhibitor	*C* (ppm)	*r*(mm • a^{-1})	η%
-	0	1.9756	-
1b	1	0.9656	51.12
	3	0.4993	74.72
	5	0.4015	79.67
	10	0.3142	84.09
	20	0.2320	88.26

Table S2 Electrochemical parameters for steel specimens in the 0.5 M HCl solution containing different concentrations of Furylalkonium chlorid.

C (ppm)	E_{corr} (V)	I_{corr} (mA)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	η_{Tafel}%
0	-0.5990	1.590	187.8640	203.3347	-
1	-0.5905	0.7513	136.7802	93.6768	52.7
3	-0.5803	0.2569	153.8462	176.5225	83.8
5	-0.5907	0.0806	150.1276	136.3884	94.9
10	-0.5701	0.0451	146.8644	137.5327	99.7

Table S3 The EIS parameters for mild steel in 0.5 M HCl solution with different concentration of Furylalkonium chlorid at 303 K.

C	R_s	Q_{dl}		R_{ct}	η_{Rct}%
(ppm)	(Ω)	Y_0 (μF cm^{-2})	*n*	(Ω)	
0	7.679	13.23×10^{-4}	0.6940	4.962	-
1	17.91	0.1508×10^{-4}	0.6203	13.53	63.3

3	12.79	4.308×10^{-4}	0.5478	138.2	96.4
5	6.602	4.038×10^{-4}	0.4827	459.3	98.9
10	7.375	5.353×10^{-4}	0.4697	658.9	99.2

Table S4 Thermodynamic parameters for the adsorption of Furylalkonium chlorid on metal steel.

T (K)	K ($mol^{-1}L$)	ΔG_{ads}^{0} (kJ mol^{-1})	ΔH_{ads}^{0} (kJ mol^{-1})	ΔS_{ads}^{0} (J mol^{-1} K^{-1})
303	4.1506×10^{6}	-48.5064		-48.0262
313	1.1008×10^{6}	-46.6534	-63.0584	-52.4119
323	0.8911×10^{6}	-47.5764		-47.9318

Table S5 Activation parameters for mild steel in 0.5 M HCl solution with different concentrations of Furylalkonium chlorid.

C (ppm)	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (kJ mol^{-1} K^{-1})
0	43.4002	40.80013	-174.75397
1	87.6674	85.06732	-41.96085
3	73.9497	71.34965	-92.14341
5	56.5101	53.91	-156.27137
10	65.0541	62.45407	-130.42564

Table S6 The HOMO and LUMO energies of Furylalkonium chlorid obtained from CV experiments and DFT quantum chemical calculations.

Method	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
DFT	-6.82	-2.53	4.29
CV	-5.32	--3.33	1.99

Table S7 Mullikan charge and NPA charge of the various atoms present in **1b**.

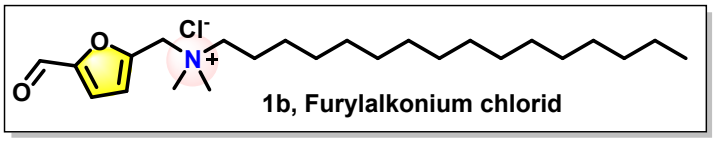
	NPA	Mulliken
Atoms	**1b**	**1b**

1C	0.17843	0.632827
2C	-0.19872	-0.51097
3C	-0.2585	-0.19606
4C	0.29952	0.313799
5O	-0.45211	-0.02475
6H	0.24849	0.177502
7H	0.25128	0.168944
8C	0.37734	-0.12815
9H	0.14474	0.144434
10O	-0.57818	-0.33486
11C	-0.23296	-0.29151
12H	0.27984	0.248792
13H	0.2474	0.252879
14N	-0.33746	-0.14243
15C	-0.1649	-0.28024
16H	0.24336	0.187143
17H	0.21923	0.196362
18C	-0.4087	-0.66139
19H	0.2108	0.182688
20H	0.20911	0.160237
21C	-0.3664	-0.30302
22H	0.2246	0.211387
23H	0.22518	0.20636
24C	-0.3561	-0.31923
25H	0.22813	0.212522
26H	0.22711	0.219303
27Cl	-0.97273	-0.8962

28H	0.24536	0.215044
29H	0.22696	0.209228
30C	-0.37467	-0.02267
31H	0.1994	0.165951
32H	0.19755	0.147729
33C	-0.37677	-0.22589
34H	0.19292	0.149747
35H	0.1924	0.147003
36C	-0.38276	-0.31792
37H	0.19049	0.146857
38H	0.19001	0.145276
39C	-0.40206	-0.37817
40H	0.18884	0.144359
41H	0.1886	0.143566
42C	-0.2904	-0.45884
43H	0.18457	0.144152
44H	0.18435	0.143332
45C	-0.40206	-0.37676
46H	0.18809	0.143644
47H	0.18796	0.143077
48C	-0.38248	-0.27196
49H	0.18827	0.143459
50H	0.18814	0.143007
51C	-0.37762	-0.12587
52H	0.18841	0.143118
53H	0.18833	0.14288
54C	-0.37723	-0.03052

55H	0.1885	0.142756
56H	0.18842	0.142501
57C	-0.37709	-0.11742
58H	0.18853	0.142581
59H	0.18847	0.142505
60C	-0.37805	-0.29749
61H	0.18865	0.142106
62H	0.18859	0.141945
63C	-0.37996	-0.47061
64H	0.18829	0.140528
65H	0.18825	0.140503
66C	-0.38322	-0.31181
67H	0.1882	0.137999
68H	0.18817	0.1379
69C	-0.57542	-0.59769
70H	0.19962	0.137746
71H	0.19339	0.133368
72H	0.19337	0.133362

Section E. ^{1}H NMR, ^{13}C NMR and HRMS Spectra of bio-based corrosion inhibitors



The bio-based corrosion inhibitor Furylalkonium chlorid: White solid; 89% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.68 (s, 1H), 7.41 (d, *J* = 3.2 Hz, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 5.42 (s, 2H), 3.52-3.50 (m, 2H), 3.40 (s, 6H), 1.25 (s, 28H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.79, 154.18, 148.39, 122.05, 119.89, 64.97, 59.24, 51.05, 32.01, 29.78, 29.75, 29.70, 29.57, 29.50, 29.45, 29.28, 26.40, 23.03, 22.77, 14.21. **HRMS m/z (ESI)** calcd for $C_{24}H_{44}NO_2^+$ $(M\text{-}Cl)^+$ 378.3367, found 378.3408.

Section F. Copies of NMR Spectra