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Upgrading of Biomass-Derived Platform Compound 5-Hydroxymethylfurfural to High-Valued Chemicals: An Environment-Friendly Corrosion Inhibitor

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Contents

Section A. Materials and Methods

Deuterated solvents were purchased from Cambridge Isotope Laboratories. The other regular chemicals were obtained from commercial suppliers with purity over 95% and used without further purification. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using a Bruker 400 MHz spectrometer. The chemical shifts were reported in ppm referenced to the deuterated solvents. High resolution exact mass measurements (HRMS) were obtained on an Agilent Techonologies instrument.

Section B. Synthetic Procedures

2-Octanone, EtOH, CaO, and triethylamine (TEA) 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.

Synthesis of the bio-based corrosion inhibitor 1a

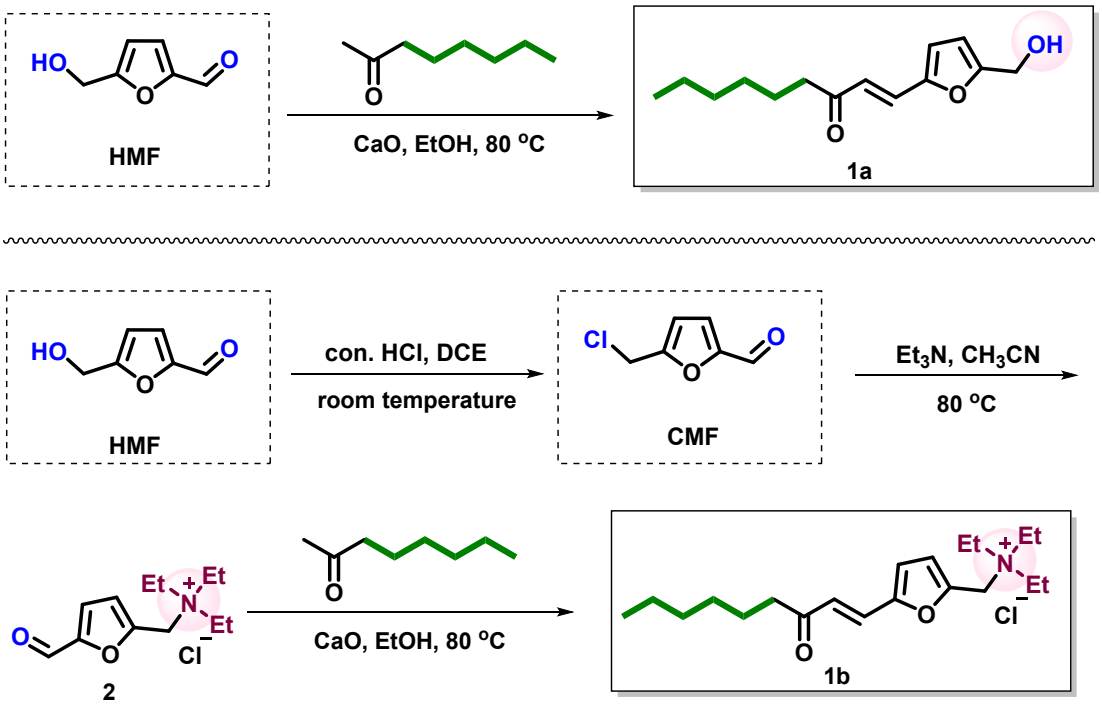
The bio-based corrosion inhibitor **1a** was synthesized from 5-HMF through Aldol condensation. To the solution of 2-octanone (384 mg, 528 μL, 3 mmol) in EtOH (2 mL) was added CaO (28 mg, 0.5 mmol), followed by solution of 5-HMF (126 mg, 1 mmol) in EtOH (2 mL). The reaction mixture was stirred at 80 °C for 24 h. Then the solution was filtered and concentrated. The generated residue was diluted with brine and extracted with EtOAc. After that, the organic phase was dried over Na_2SO_4 and concentrated under vacuum. The residue was then subjected to column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (8:1) to give the corrosion inhibitor **1a** as yellow oil (189 mg, 80 %).

Synthesis of the bio-based corrosion inhibitor 1b

The bio-based corrosion inhibitor **1b** was synthesized from **HMF** through three substitution reactions. To the solution of **HMF** (126 mg, 1 mmol) in DCE (5 mL) was added con. HCl (2.5 mL) dropwised, then the reaction mixture was stirred at room temperature for 12 h. Then water was added into the reaction solution. The organic phase was dried by Na_2SO_4 and concentrated under vacuum. The residue (chlorinated compound **CMF**) was used directly in next step.

The residue produced from the previous step was diluted with acetonitrile, and then triethylamine (121.4 mg, 167 μL, 1.2 mmol) was added to the solution. The reaction mixture was refluxed for 10 h. After cooling, the solvent of the solution was removed under vacuum, and the generated residue was subjected to column chromatography on silica gel, eluting with EtOAc/MeOH (1:4) to afford compound **2** (215 mg, the yield of two steps is 76%).

Then the bio-based corrosion inhibitor **1b** was generated from compound **2** through Aldol condensation with 2-octanone referring to the synthetic method of compound **1a**. The yield of **1b** in this step is 78%.



Scheme S1 The synthetic route and structural formula of HMF, **1a** and **1b**.

Section C. Supporting Figures

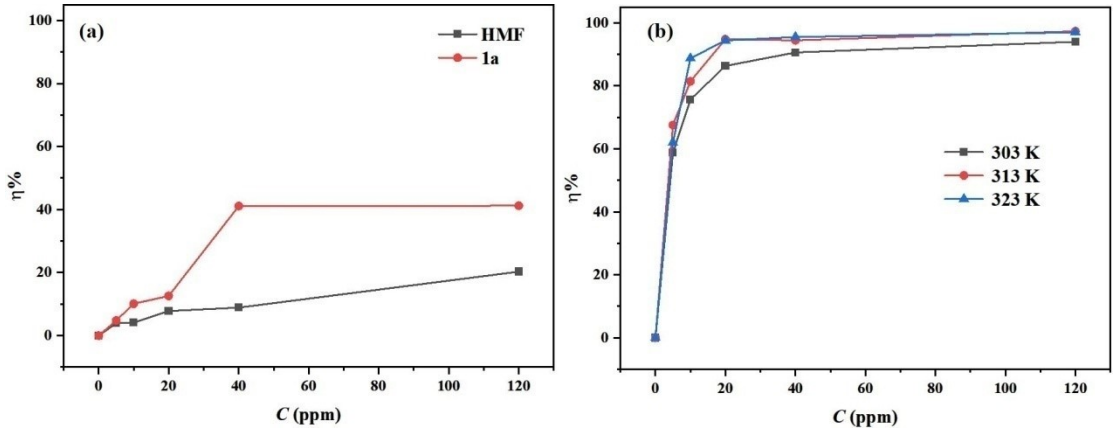


Figure S1. (a) The corrosion rate of HMF and **1a** in corrosive media with different concentrations at 303 K; (b) the corrosion inhibition efficiency of **1b** with different concentrations at 303 K, 313 K and 323 K, respectively.

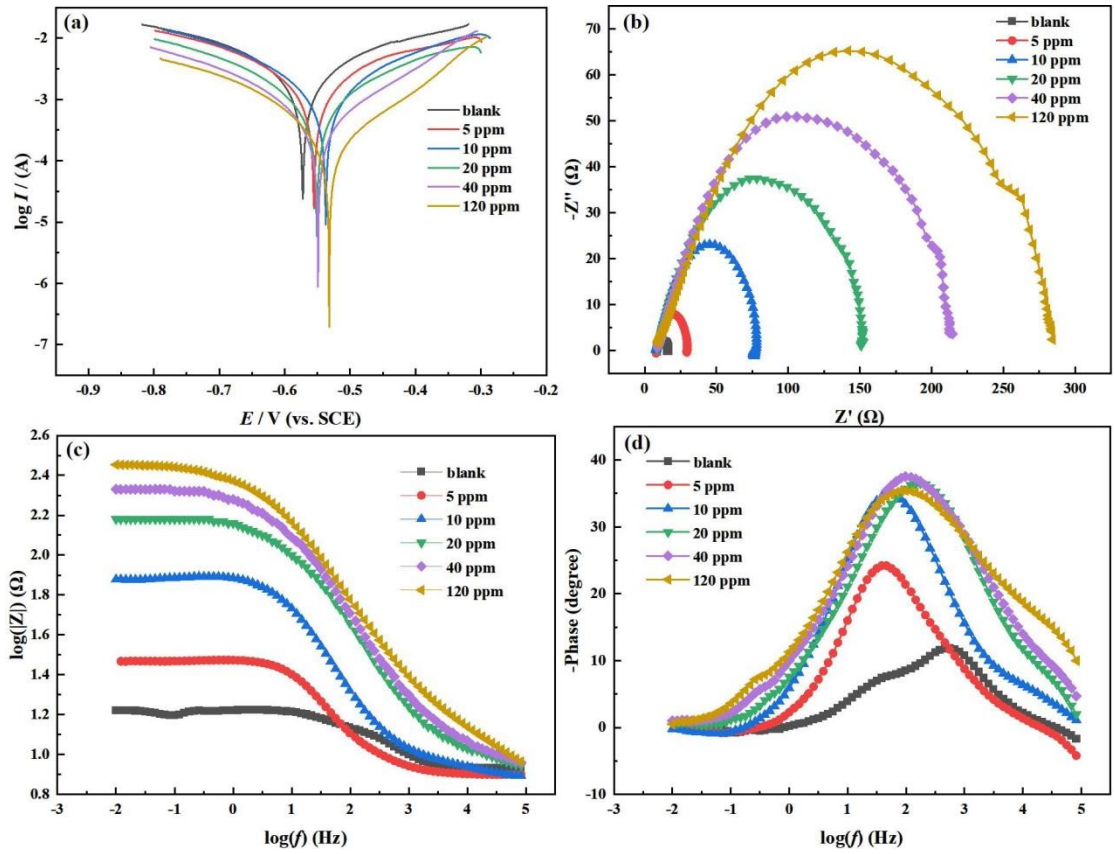


Figure S2. Potentiodynamic polarization curves (a), Nyquist plots (b) and Bode plots (c and d) for mild steel in 1 M HCl solution with different concentrations of **1b** at 303K.

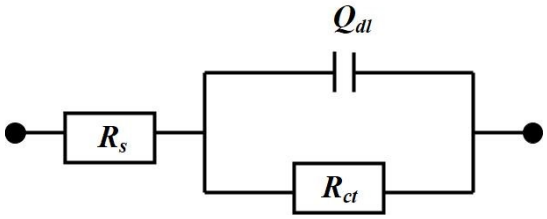


Figure S3. Electrical equivalent circuit used to fit the impedance data.

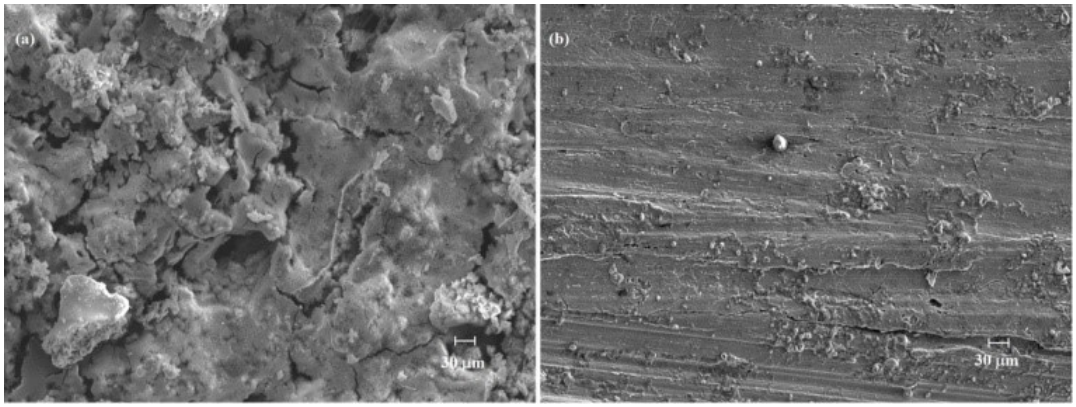


Figure 4 SEM images of the mild steel surface after immersed in 1 M HCl solution without (a) and with 120 ppm **1b** (b) for 4 h at 303 K.

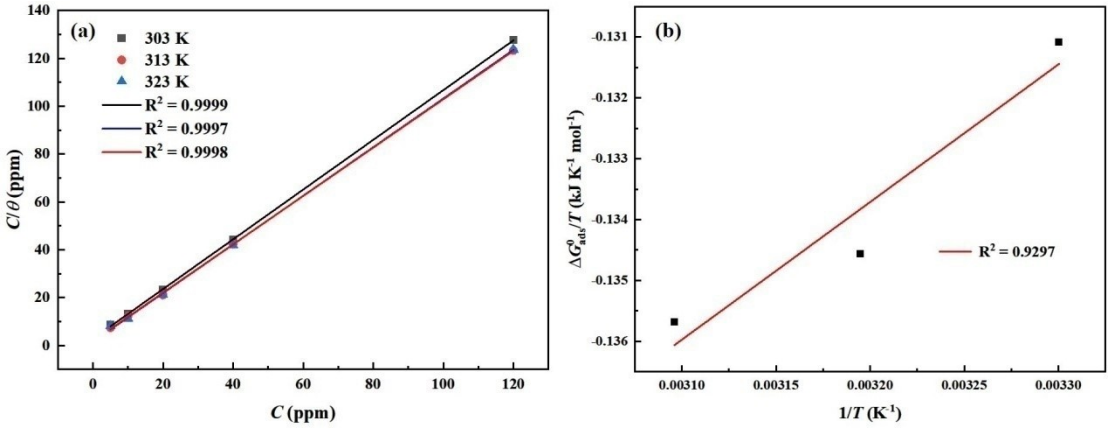


Figure S5 (a) Langmuir adsorption isotherm plots of the bio-based corrosion inhibitor **1b** on metal steel surface; (b) Curves of $\Delta G^{0}_{ads}/T$ vs.$1/T$.

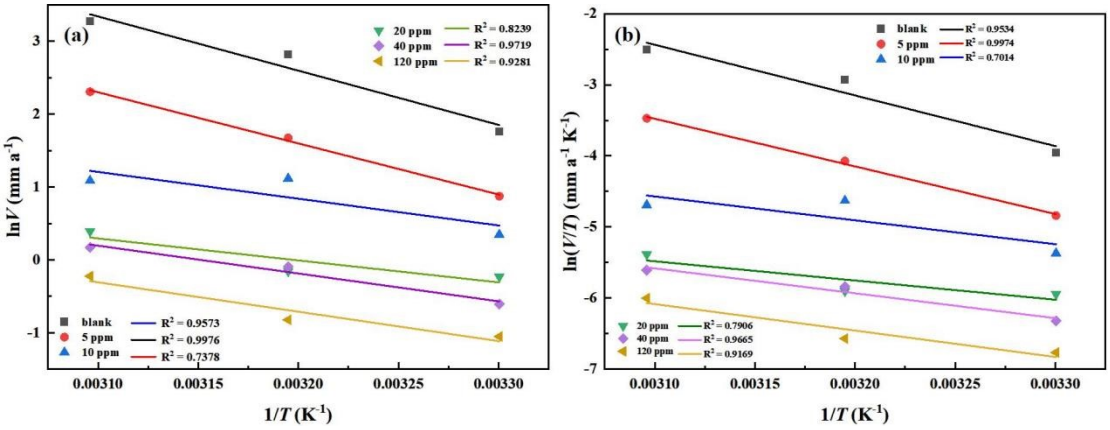


Figure S6 (a) Arrhenius plots and Transition state plots (b) for mild steel in 1 M HCl with different concentrations of **1b**.

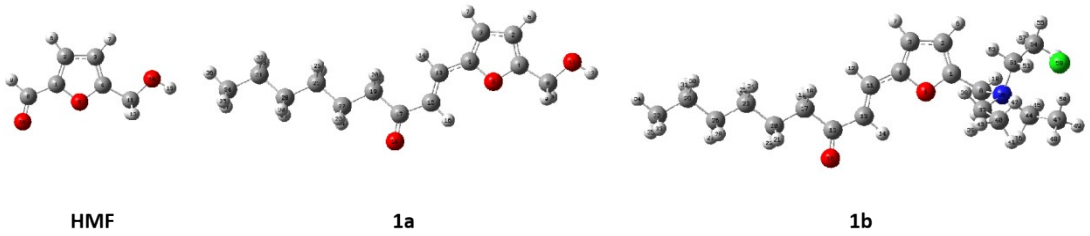


Figure S7 Optimized geometric structures of HMF, **1a** and **1b**.

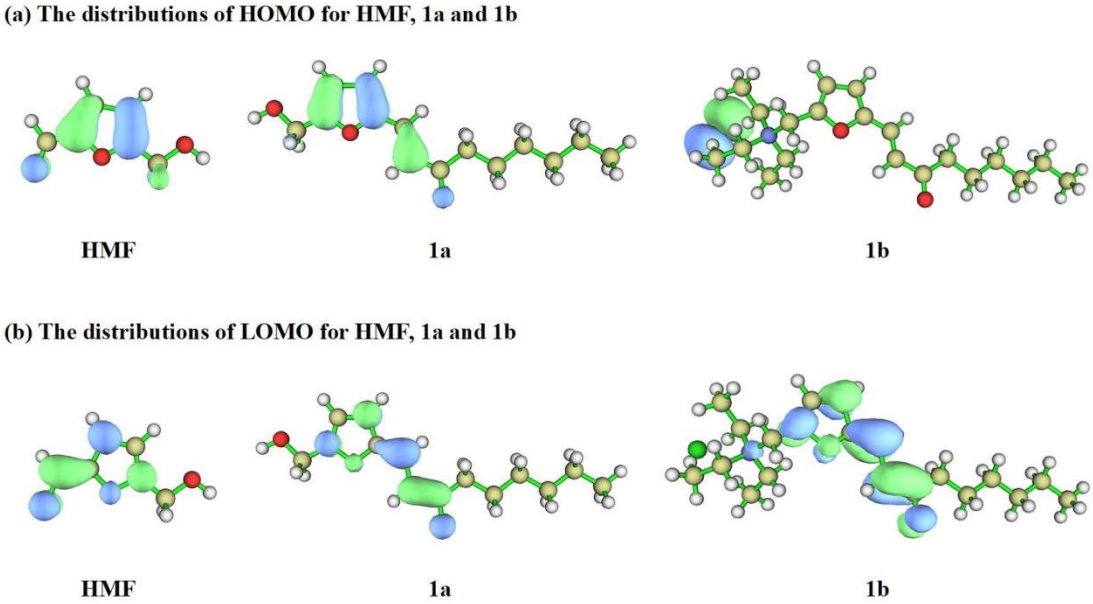


Figure S8 Electron density isosurfaces of HOMO (a) and LUMO (b) for HMF, **1a** and **1b**.

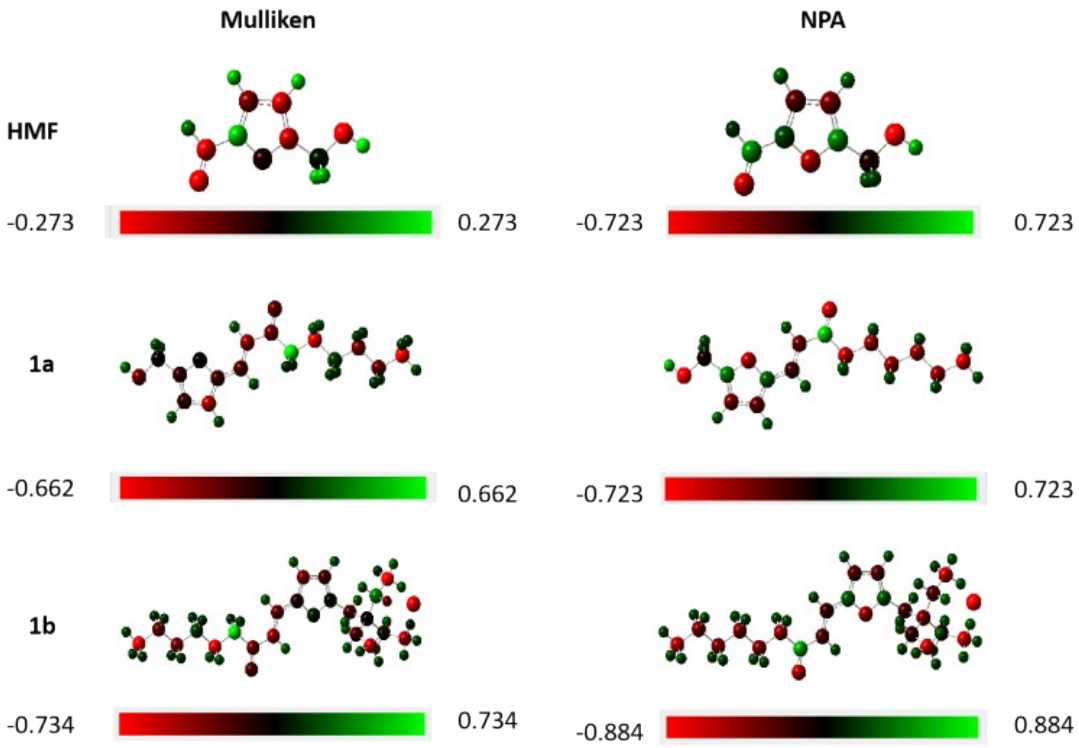


Figure S9 Mulliken and NPA charge distribution on HMF, **1a**, and **1b.**

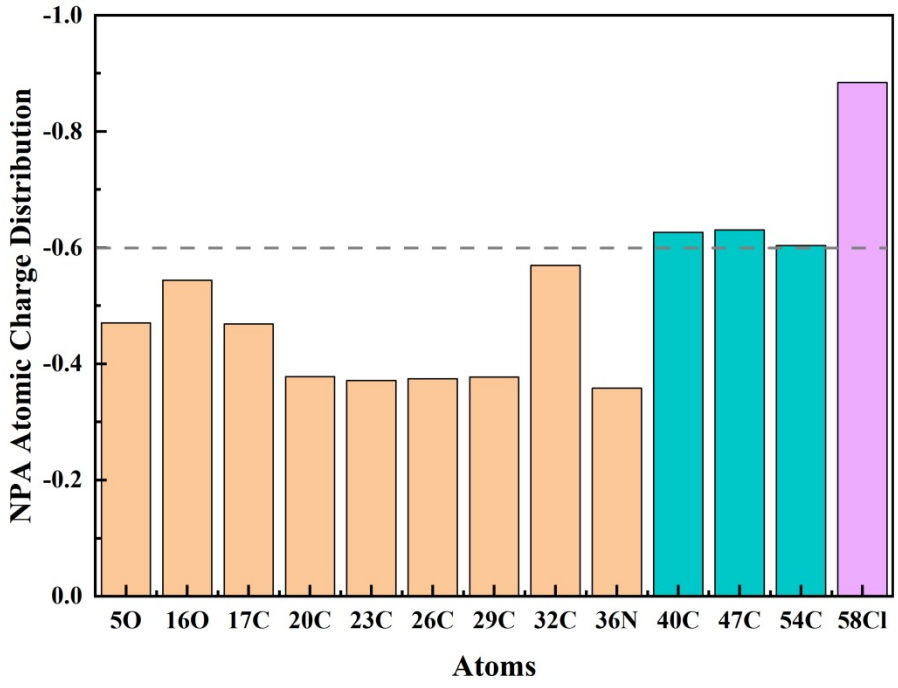


Figure S10 Negative atomic charge (above -0.3 eV) distribution of **1b**.

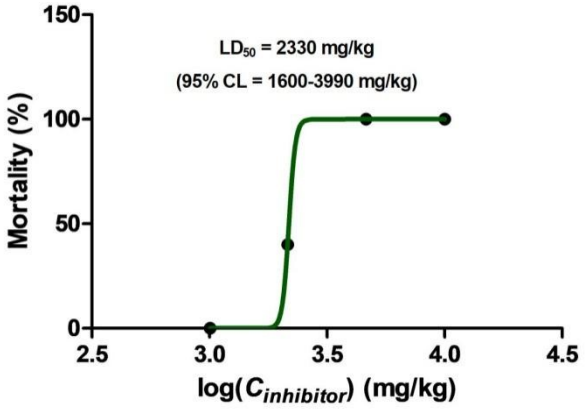


Figure S11 Dose-response mortality curve of **1b** after acute oral administration in mice.

Section D. Supporting Tables

Table S1. Weight loss results of mild steel corrosion without and with different concentrations of **1b** in 1 M HCl.

T(℃)	*C* (ppm)	**1b**		
		r(mm a^{-1})	*η*%	*θ*
30	0	5.81008	/	/
	5	2.39772	58.73172	58.73172
	10	1.41343	75.6729	75.6729
	20	0.79457	86.32437	86.32437
	40	0.54518	90.61667	90.61667
	120	0.34958	93.98329	93.98329
40	0	16.75598	/	/
	5	5.33304	67.59215	67.59215
	10	3.053	81.44689	81.44689
	20	0.85548	94.80142	94.80142
	40	0.91344	94.44918	94.44918
	120	0.43934	97.33021	97.33021
50	0	26.39655	/	/
	5	10.03948	61.96661	61.96661
	10	2.96788	88.75653	88.75653
	20	1.47887	94.39749	94.39749
	40	1.18634	95.5057	95.5057
	120	0.80008	96.96899	96.96899

Table S2 Electrochemical parameters for mild steel samples in the 1 M HCl solutions with different concentrations of **1b**.

C (ppm)	E_{corr} (V)	I_{corr} (mA)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	η_{Tafel}%
blank	-0.5653	1.992	211.1486	122.7747	-
5	-0.5498	1.122	166.7500	97.34255	44
10	-0.5354	0.8851	135.3913	106.3490	56
20	-0.5510	0.5883	116.3061	125.5020	70
40	-0.5485	0.4082	137.0990	138.9275	80
120	-0.5279	0.2278	150.5344	133.7793	89

Table S3 The EIS parameters for mild steel in 1 M HCl solution with different concentration of **1b** at 303 K.

C (ppm)	R_s (Ω)	Q_{dl}		R_{ct} (Ω)	η_{Rct}%
		Y_0 (μF cm^{-2})	n		
blank	8.401	8.36×10^{-4}	0.7006	8.155	-
5	8.011	10.37×10^{-4}	0.7539	22.12	63.1
10	8.326	6.351×10^{-4}	0.7015	71.27	88.6
20	8.837	4.003×10^{-4}	0.6195	146.6	94.4
40	9.021	4.276×10^{-4}	0.5911	210.5	96.1
120	8.835	5.091×10^{-4}	0.5311	289.4	97.2

Table S4 Thermodynamic parameters for the adsorption of **1b** 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	1.269×10^{5}	-39.72	22.60	205.67
313	1.926×10^{5}	-42.12		206.76
323	2.205×10^{5}	-43.83		205.65

Table S5 Activation parameters for mild steel in 1 M HCl with different concentrations of **1b**.

C (ppm)	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
blank	61.82	59.22	-111.716
5	58.31	55.71	-131.241
10	30.52	27.92	-226.495
20	25.06	22.46	-250.990
40	31.73	29.13	-231.134
120	33.51	30.91	-229.790

Table S6 Quantum chemical parameters for HMF, **1a** and **1b**.

Corrosion inhibitors	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	ΔE (a.u.)	μ (D)
HMF	-0.252026	-0.073398	0.178628	4.0242
1a	-0.226781	-0.079549	0.147232	4.0223
1b	-0.18082	-0.111109	0.069711	13.9467

Table S7 The global softness, global hardness and molecular volume for HMF, **1a** and **1b**.

Corrosion inhibitors	σ	η	□
HMF	0.1192	8.391	153.83482
1a	0.1527	6.55	333.68566
1b	0.2212	4.520	511.08814

Table S8 Mullikan charge and NPA charge of the various atoms present in HMF.

	Mulliken	NPA
Atoms	HMF	HMF
1C	0.189341	0.16576
2C	-0.123297	-0.21418
3C	-0.209473	-0.30134
4C	-0.192464	0.33782
5O	-0.030742	-0.44667
6H	0.185262	0.22605
7H	0.198161	0.24051

8C	-0.224894	0.36173
9H	0.106516	0.11332
10O	-0.2612	-0.52795
11C	0.017378	-0.06241
12H	0.182433	0.18274
13H	0.182429	0.18274
14O	-0.272653	-0.72324
15H	0.253204	0.46511

Table S9 Mullikan charge and NPA charge of the various atoms present in **1a**.

	Mulliken	NPA
Atoms	**1a**	**1a**
1C	0.118861	0.32077
2C	-0.10839	-0.29426
3C	-0.417055	-0.2345
4C	-0.14106	0.24367
5O	0.002409	-0.47371
6H	0.197817	0.23849
7H	0.180495	0.22222
8C	-0.016828	-0.05983
9H	0.18119	0.17918
10H	0.180561	0.17866
11O	-0.266247	-0.72291
12H	0.250817	0.464
13C	-0.191454	-0.16666
14H	0.186039	0.21315
15C	-0.349253	-0.27409
16H	0.224052	0.21817
17C	-0.263933	0.52696
18O	-0.230961	-0.56143
19C	0.6003	-0.46672
20H	0.098377	0.21014
21H	0.114359	0.21241
22C	-0.585209	-0.37827
23H	0.188033	0.20076
24H	0.191335	0.20405
25C	0.137181	-0.37069
26H	0.123589	0.18283
27H	0.121941	0.18314
28C	-0.29297	-0.37377
29H	0.116272	0.1868
30H	0.116015	0.18654

31C	-0.231834	-0.37674
32H	0.125483	0.18428
33H	0.125391	0.18437
34C	-0.661784	-0.56913
35H	0.135717	0.19217
36H	0.1421	0.19771
37H	0.136362	0.19228

Table S10 Mullikan charge and NPA charge of the various atoms present in **1b**.

	Mulliken	NPA
Atoms	**1b**	**1b**
1C	0.035031	0.26759
2C	-0.17694	-0.25521
3C	-0.315358	-0.24512
4C	-0.065976	0.27291
5O	0.08019	-0.47036
6H	0.197433	0.23348
7H	0.210008	0.23333
8C	-0.186671	-0.21057
9H	0.246512	0.23306
10H	0.203983	0.2359
11C	-0.262702	-0.17988
12H	0.219417	0.21918
13C	-0.374467	-0.24452
14H	0.223541	0.21704
15C	-0.298339	0.52991
16O	-0.201511	-0.54413
17C	0.656842	-0.46849
18H	0.111936	0.21391
19H	0.109699	0.21399
20C	-0.625826	-0.37827
21H	0.193465	0.2036
22H	0.194274	0.20356
23C	0.13769	-0.37113
24H	0.123661	0.18409
25H	0.123426	0.18362
26C	-0.303802	-0.37403
27H	0.116771	0.18719
28H	0.117605	0.18758
29C	-0.237546	-0.37691
30H	0.126789	0.18505
31H	0.125758	0.18461

32C	-0.659888	-0.56934
33H	0.136993	0.19292
34H	0.144371	0.19904
35H	0.136309	0.19257
36N	-0.022107	-0.35792
37C	-0.189921	-0.15139
38H	0.223299	0.21129
39H	0.200405	0.19926
40C	-0.52188	-0.62643
41H	0.147203	0.19834
42H	0.077466	0.27821
43H	0.168174	0.21993
44C	-0.156083	-0.15513
45H	0.194051	0.20235
46H	0.171806	0.2007
47C	-0.407294	-0.63076
48H	0.151622	0.21085
49H	0.154826	0.21451
50H	0.063178	0.27744
51C	0.314509	-0.23847
52H	0.201088	0.20426
53H	-0.223403	0.29995
54C	-0.73415	-0.60365
55H	0.212915	0.25016
56H	0.206673	0.214
57H	0.099484	0.18046
58Cl	-0.594542	-0.88407

Table S11 Lethality of mice after acute oral administration of **1b**.

Group of treatment	Dose (mg/kg)	ICR mice	Lethality	Mortality (%)
Control	0.9% saline	10	0	0
1b	1006.3	10	0	0
	2150.3	10	4	40
	4640.2	10	10	100
	10004.6	10	10	100

Table S12 The EIS corrosion inhibition efficiency (η_{Rct}%) of some typical bio-based corrosion inhibitors and quaternary ammonium salt type corrosion inhibitors reported in past three years.

Entry	Inhibitors	Concentration	Corrosive medium	*T*	η_{Rct}%	Ref.
1	Nutmeg Oil (Bio-based inhibitor)	1000 ppm	1 M HCl	303 K	94.73	(1)
2	Cinnamaldehyde (Bio-based inhibitor)	1000 ppm	1 M HCl	~300 K	99.37	(2)
3	Mint extract (Bio-based inhibitor)	800 ppm	1 M HCl	303 K	91	(3)
4	11-((2-((2-aminoethyl)amino) ethyl)amino)-11-oxo-N,N,N tripropylundecan-1-aminium bromide (Quaternary ammonium salt type corrosion inhibitor)	200 ppm	1 M HCl	303 K	92.9	(4)
5	TQD (Quaternary ammonium salt type corrosion inhibitor)	1000 ppm	1 M HCl	298 K	94.47	(5)
6	SMIF (Quaternary ammonium salt type corrosion	4000 ppm	1 M HCl	298 K	90.69	(6)

	inhibitor)				
7	This work	120 ppm	1 M HCl	303 K	97.2

References:

(1) *Journal of Molecular Liquids*, **2021**, *323*, 115036.

(2) *Corrosion Science*, **2022**, *208*, 110623.

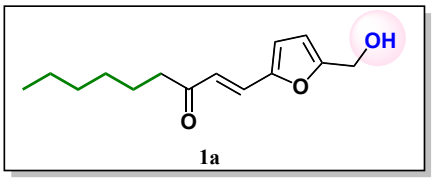
(3) *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2023**, *656*, 130540.

(4) *Journal of Molecular Liquids*, **2020**, *317*, 113917.

(5) *Journal of Molecular Structure*, **2023**, *1290*, 135914.

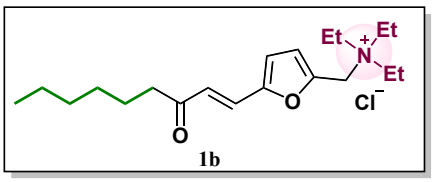
(6) *Arabian Journal of Chemistry*, **2021**, *14*, 102952.

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



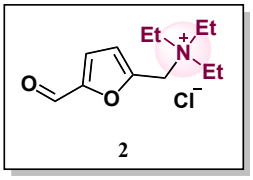
1a

The bio-based corrosion inhibitor 1a: Yellow oil; 89% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (dd, *J* = 15.6, 5.4 Hz, 1H), 6.64 (dt, *J* = 8.8, 4.1 Hz, 2H), 6.39 (d, *J* = 2.8 Hz, 1H), 4.66 (d, *J* = 4.4 Hz, 2H), 2.58 (dd, *J* = 9.7, 5.0 Hz, 2H), 2.24 (brs, 1H), 1.64 (d, *J* = 6.8 Hz, 2H), 1.31 (s, 6H), 0.89 (t, *J* = 5.3 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.43, 156.70, 150.96, 128.41, 123.22, 116.48, 110.34, 57.52, 41.51, 31.57, 28.94, 24.37, 22.45, 13.97. **HRMS m/z (ESI)** calcd for $C_{14}H_{21}O_3^+$ $(M + H)^+$ 237.1485, found 237.1488.



1b

The bio-based corrosion inhibitor 1b: Brown oil; 89% yield (two steps); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27-7.23 (m, 1H), 7.15 (d, *J* = 3.4 Hz, 1H), 6.70 (d, *J* = 3.4 Hz, 1H), 6.58-6.54 (m, 1H), 5.11 (s, 2H), 3.49 (q, *J* = 7.2 Hz, 6H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 9H), 1.38-1.16 (m, 19H), 0.94-0.79 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.83, 153.32, 144.29, 127.43, 125.66, 119.84, 115.85, 77.32, 77.00, 76.68, 53.90, 41.13, 31.66, 29.21, 29.06, 27.19, 24.20, 22.58, 14.05, 8.30. **HRMS m/z (ESI)** calcd for $C_{20}H_{34}NO_2^+$ $(M - Cl)^+$ 320.2584, found 320.2596.

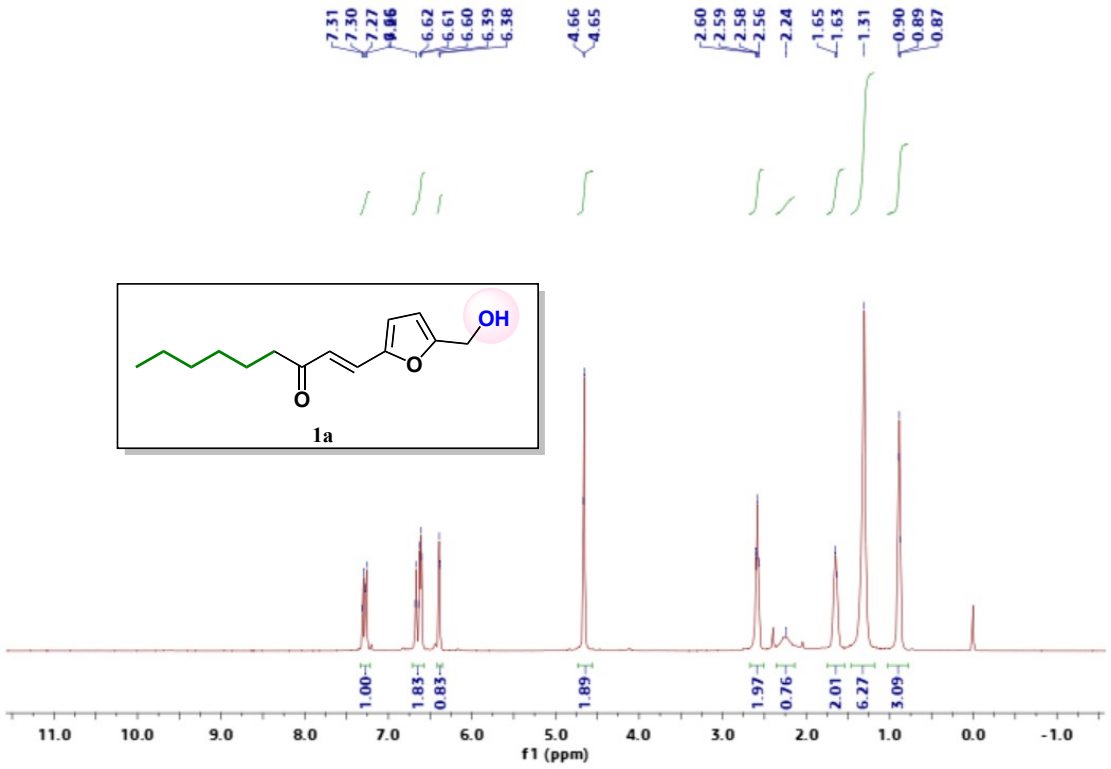


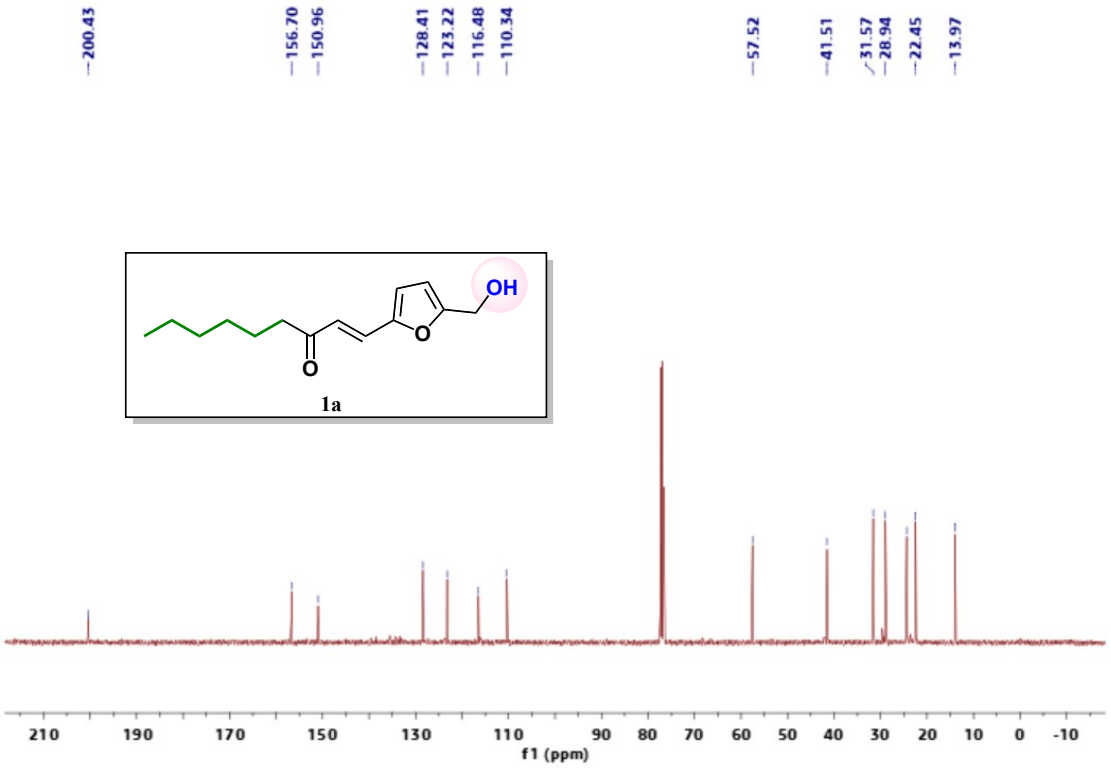
2

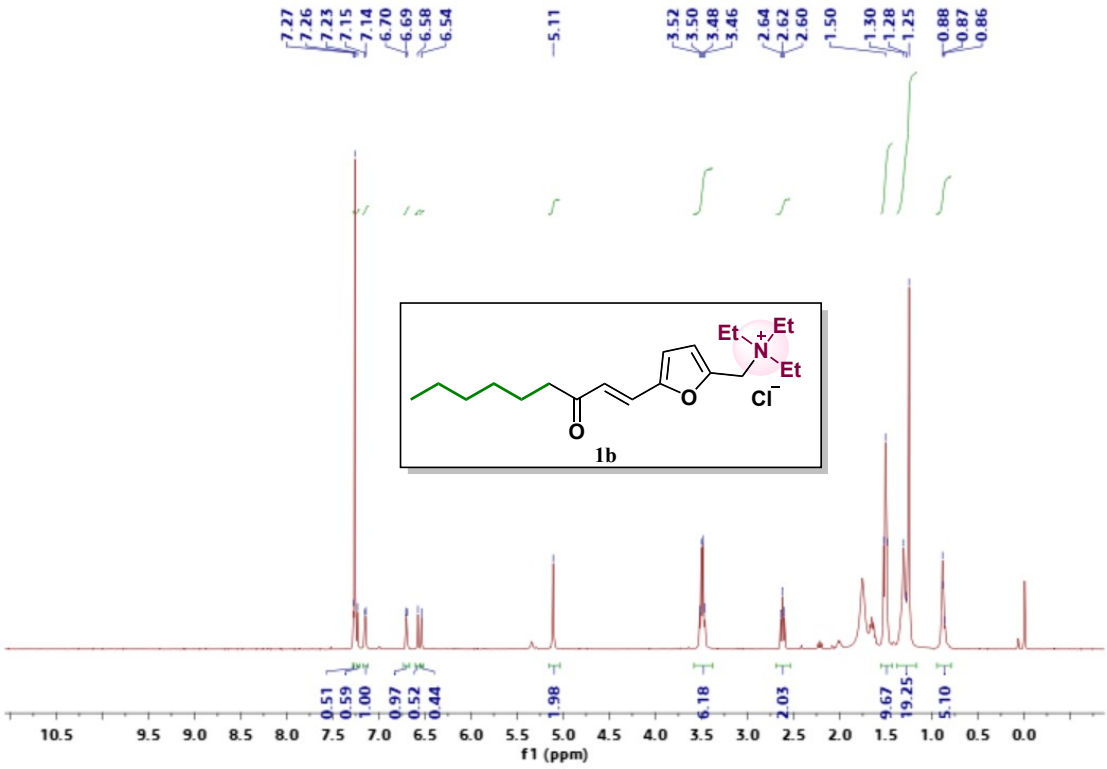
The intermediate 2: Brown oil; 81% yield (two steps); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.66 (s, 1H), 7.45 (d, *J* = 3.5 Hz, 1H), 7.28 (d, *J* = 3.5 Hz, 1H), 5.26 (s, 2H), 3.52 (q, *J* = 7.2 Hz, 6H), 1.49 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.43,

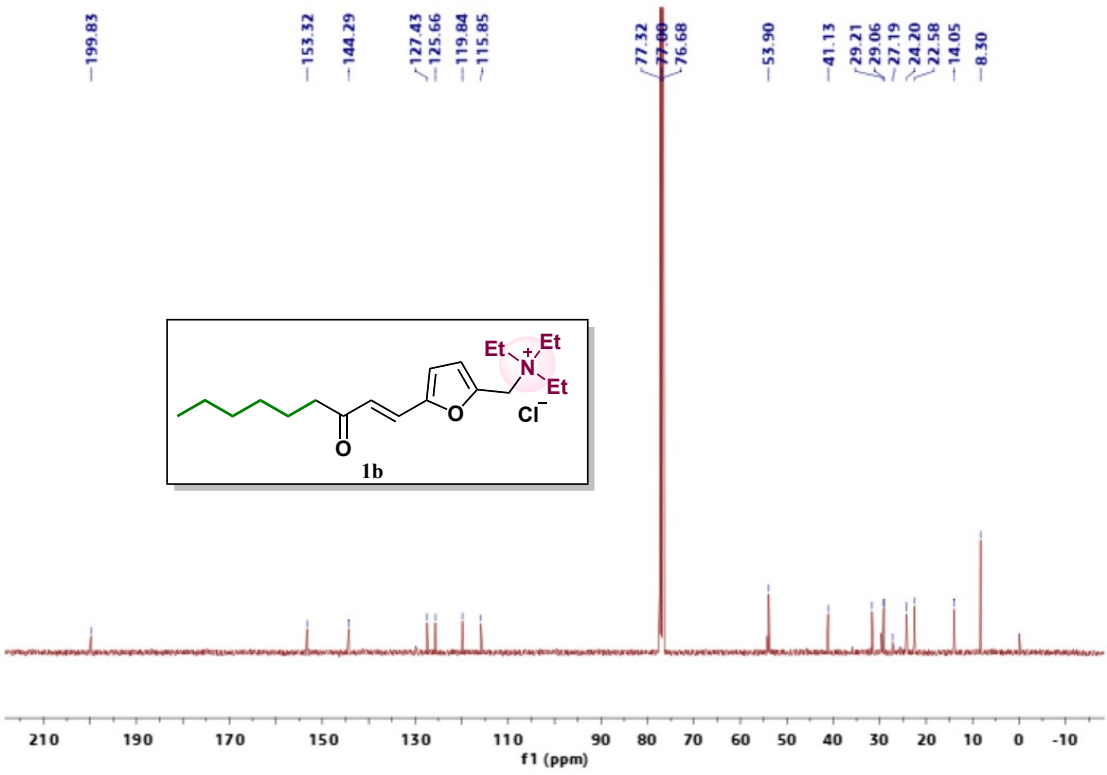
153.93, 148.06, 122.14, 119.76, 54.42, 54.03, 8.32. **HRMS m/z (ESI)** calcd for $C_{12}H_{20}NO_2^+$ $(M - Cl)^+$ 210.1489, found 210.1492.

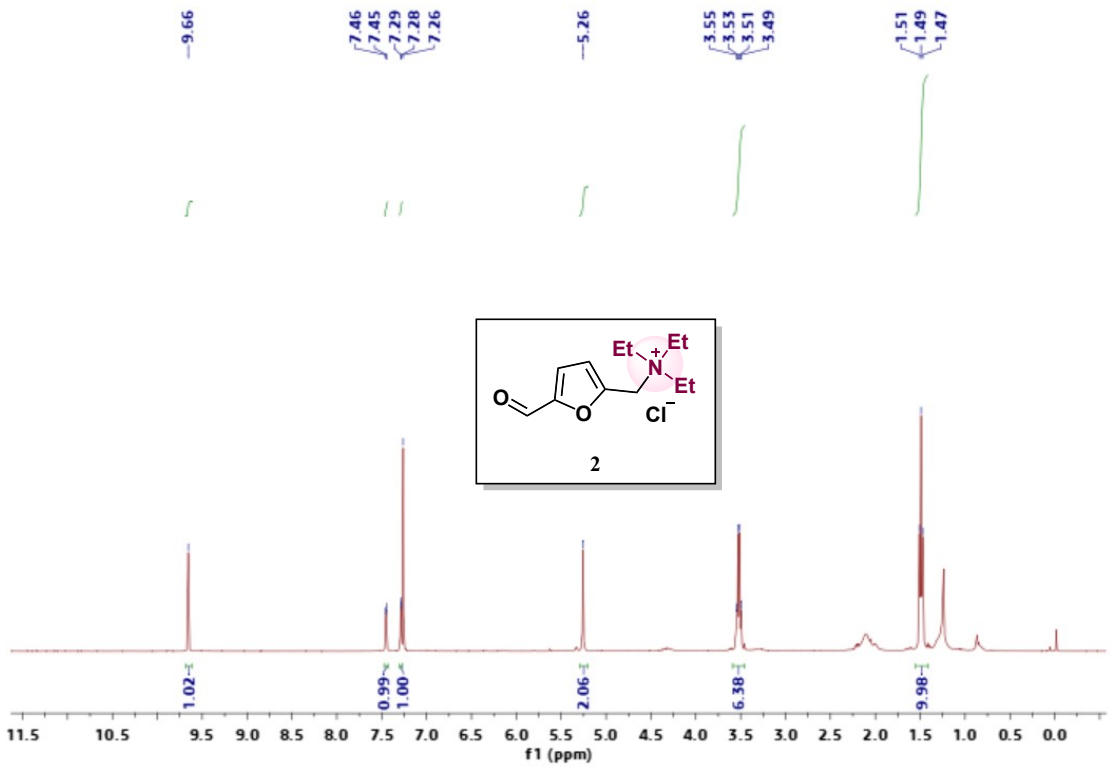
Section F. Copies of NMR Spectra

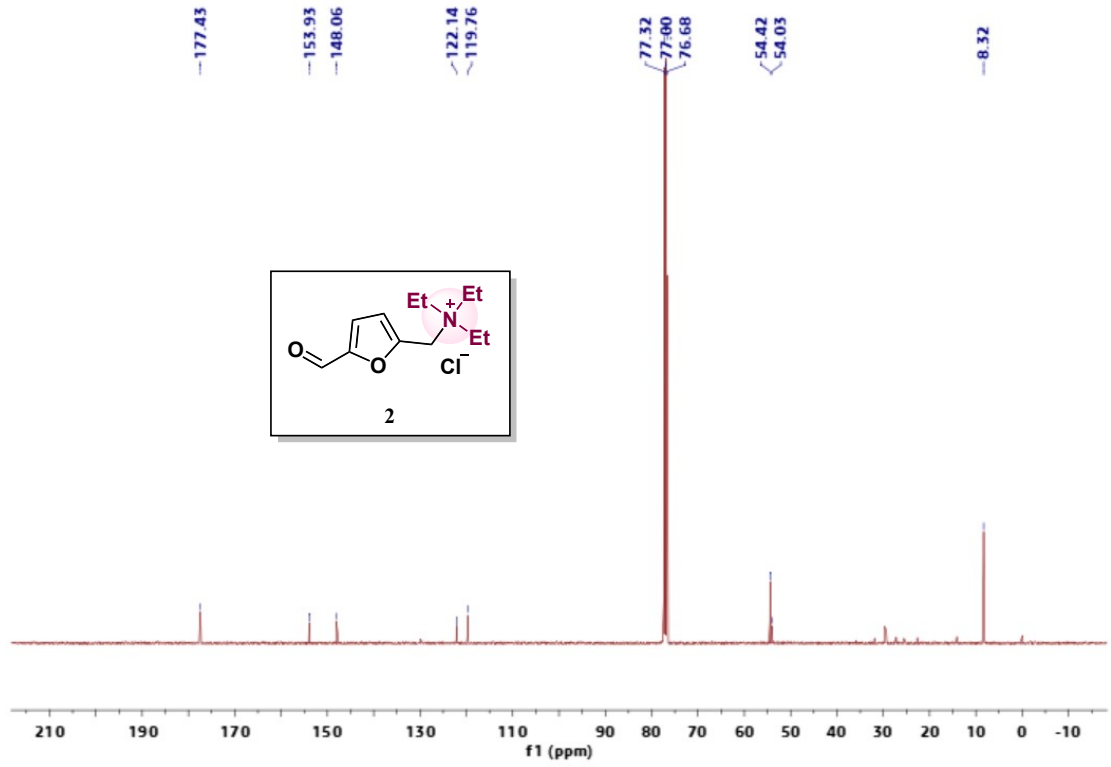





7.27
7.26
7.23
7.15
7.14
6.70
6.69
6.58
6.54
5.11
3.52
3.50
3.48
3.46
2.64
2.62
2.60
1.50
1.30
1.28
1.25
0.88
0.87
0.86
Et
Et
N
Et
O
Cl
O
1b
0.51
0.59
1.00
0.97
0.52
0.44
1.98
6.18
2.03
9.67
19.25
5.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


199.83
153.32
144.29
127.43
125.66
119.84
115.85
77.32
77.00
76.68
53.90
41.13
29.21
29.06
27.19
24.20
22.58
14.05
8.30
Et
Et
N
Et
O
Cl
O
1b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.66
7.46
7.45
7.29
7.28
7.26
5.26
3.55
3.53
3.51
3.49
1.51
1.49
1.47
Et
Et
N
Et
O
O
Cl⁻
2
1.02
0.99
1.00
2.06
6.38
9.98
11.5
10.5
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
0.0
f1 (ppm)


177.43
153.93
148.06
122.14
119.76
77.32
77.00
76.68
54.42
54.03
8.32
Et
Et
N
Et
O
O
Cl⁻
2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)