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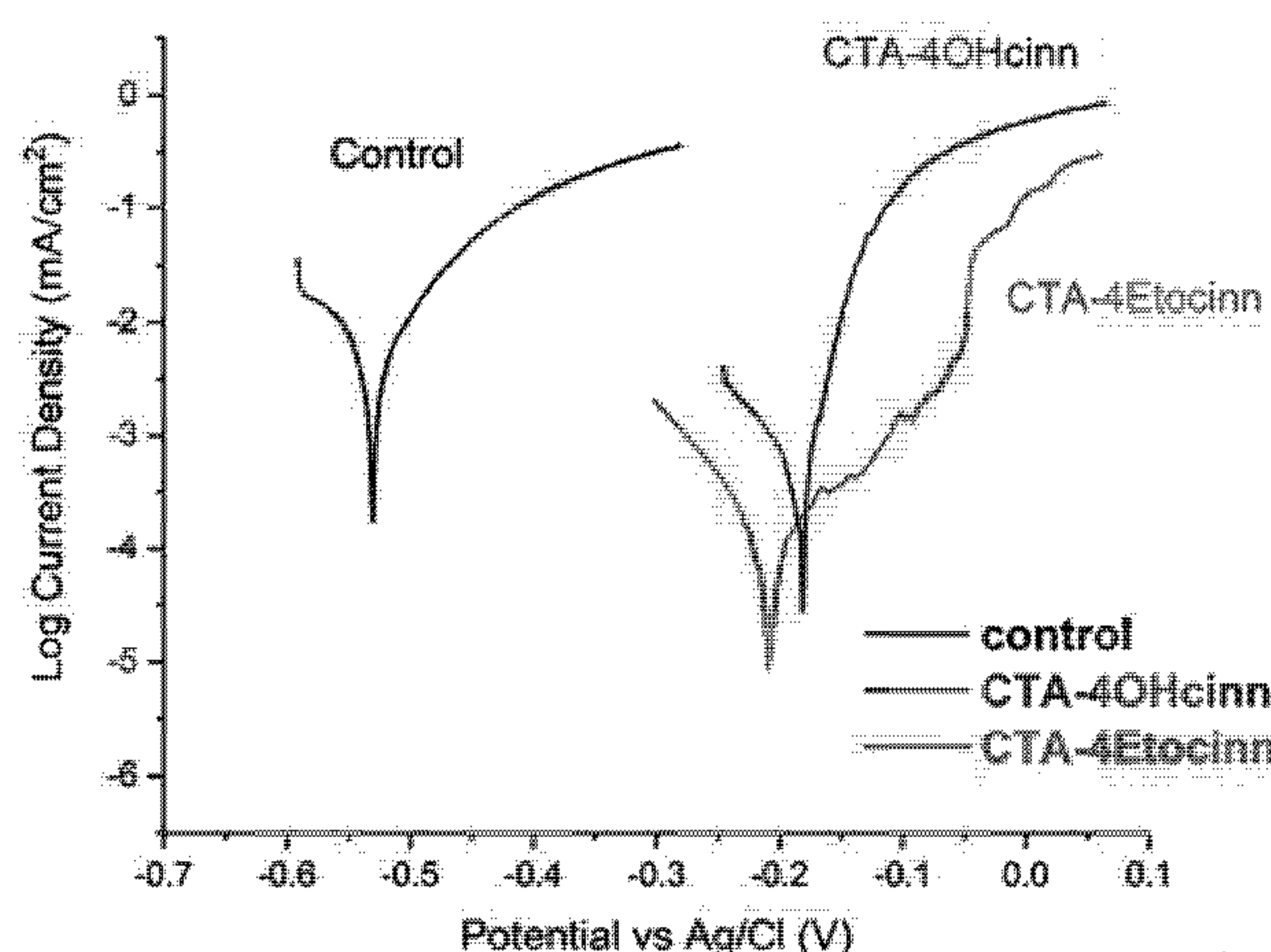


Figure 20a

(57) Abstract: The present disclosure generally relates to organic corrosion inhibitors including compositions, formulations, coatings, and methods of making and use thereof. The present disclosure also relates to a method for inhibiting corrosion on a substrate. The present disclosure provides coatings comprising an organic corrosion inhibitor comprising onium cation groups and aromatic carboxylate counter-anion groups.

## ORGANIC CORROSION INHIBITORS

### FIELD

The present disclosure generally relates to organic corrosion inhibitors, and to compositions, formulations, coatings, and methods of making and use thereof.

### 5 BACKGROUND

Corrosion of metals is a significant worldwide problem for various industries. Protective coatings used to prevent corrosion typically provide at least one of barrier protection, sacrificial (galvanic) protection and corrosion inhibition, in which each disrupt the electrochemical reaction causing corrosion. Barrier protection acts to  
10 prevent migration of electrolytes, sacrificial pigments corrode preferentially to that of the surface being protected, and corrosion inhibitors act in various mechanisms to prevent corrosion including reactions to passivate metal surfaces by forming thin inert films on metal surfaces. Coating systems may contain various resins, solvents, additives, and/or pigments, that provide corrosion protection to substrates. Coating  
15 systems are designed for coating onto substrates to provide a protective layer having good mechanical properties such as adhesion, impact resistance and ductility, and which may also include additional corrosion inhibitors for added corrosion protection. Corrosion inhibitors may be provided as pigments including inorganic pigments, organic pigments and metallic pigments. Inorganic pigments include various metal  
20 phosphates, molybdates, and silicates, such as zinc molybdate. Organic pigments include various aromatic acids and carbon based polymers including graphite and conducting polymers such as polyaniline. Metallic pigments include metal salts such as metallic zinc, which typically acts as a sacrificial pigment.

There is a need for alternative or improved corrosion inhibitors and coatings  
25 that can provide various desirable properties such as effective corrosion inhibition, mechanical properties, formulation properties and/or antimicrobial resistance.

### SUMMARY

The present disclosure relates to organic corrosion inhibitors, and to compositions, formulations, coatings, and methods of making and use thereof. The

organic corrosion inhibitors of the present disclosure comprise onium cations and aromatic carboxylate anions. The aromatic carboxylate groups can provide counter anions for the onium cations, which can provide organic corrosion inhibitors effective for providing various properties including corrosion inhibition.

5           In one aspect, there is provided a method for inhibiting corrosion on a substrate by providing one or more coatings on the substrate, wherein at least one coating comprises an organic corrosion inhibitor comprising onium cation groups and aromatic carboxylate counter-anion groups.

10           In another aspect, there is provided use of a coating comprising an organic corrosion inhibitor for inhibiting corrosion on a substrate, wherein the organic corrosion inhibitor comprises onium cation groups and aromatic carboxylate counter-anion groups.

15           In another aspect, there is provided a coated metal substrate comprising a metal substrate coated with one or more coating layers, wherein at least one of the coating layers comprises an organic corrosion inhibitor, and wherein the organic corrosion inhibitor comprises onium cation groups and aromatic carboxylate counter-anion groups.

          In another aspect, there is provided a coating applied to an optionally coated substrate, wherein the coating comprises or consists of:

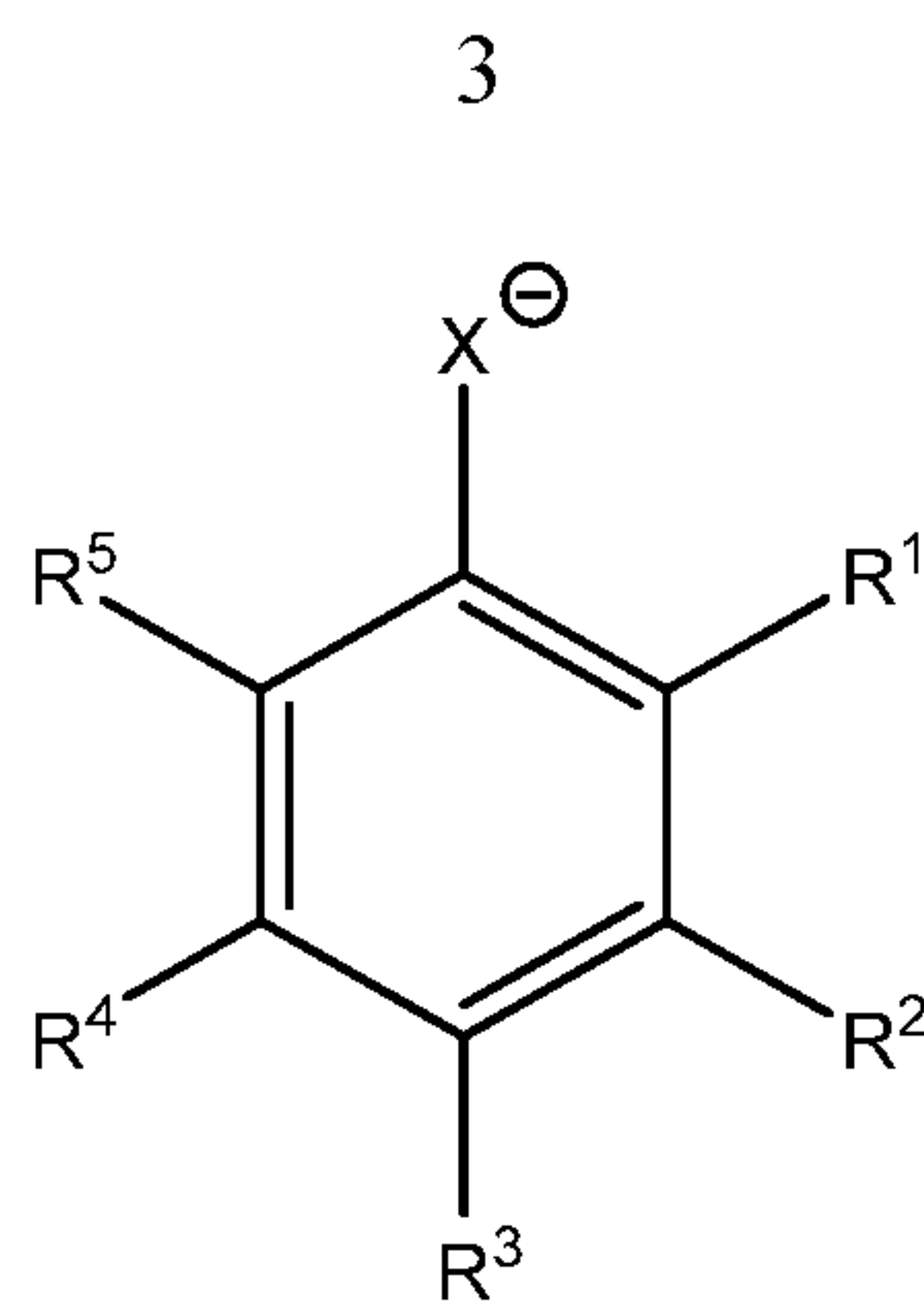
          (a) at least one organic corrosion inhibitor according to any aspects, embodiments or examples as described herein; and

20           (b) optionally one or more additives selected from a solvent, an organic film former, a curing agent, an adhesion promoter, an inorganic filler, a wetting agent, and an organic crosslinker.

          In another aspect, there is provided a coating system comprising:

- 25           (i) an optionally coated metal substrate;
- (ii) one or more optional post coating layers; and
- (iii) one or more corrosion protection layers located between (i) and (ii) comprising an organic corrosion inhibitor, wherein the organic corrosion inhibitor comprises onium cation groups and aromatic carboxylate counter-anion groups.

30           In another aspect, there is provided an organic corrosion inhibitor comprising or consisting of an aromatic carboxylate of Formula 1 and an onium cation:



Formula 1

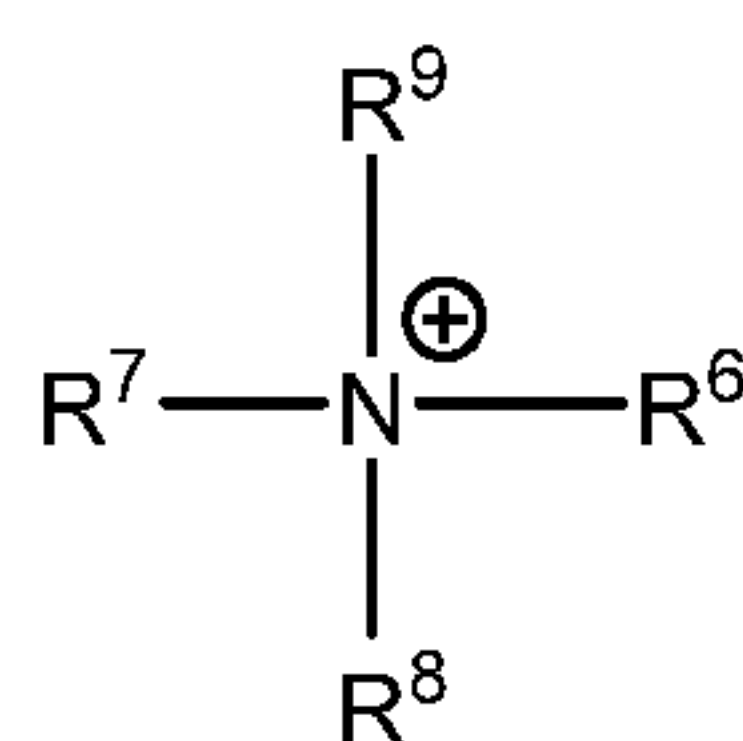
wherein

X is an optionally linked carboxylate anion group; and

- 5 R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup>, are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

10 In an embodiment, the onium cations are quaternary onium cations. In another embodiment, the onium cations are selected from ammonium cation groups, pyridinium cation groups, imidazolium cation groups, pyrazolium cation groups, pyrrolidinium cation groups, and phosphonium cation groups. In another embodiment, the onium cations are quaternary ammonium cations.

15 In another embodiment, the onium cations are ammonium cation groups of Formula 2a:



Formula 2a

wherein

- 20 R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl.

In another aspect, there is provided a coating composition comprising an organic corrosion inhibitor, wherein the organic corrosion inhibitor comprises onium cation groups and aromatic carboxylate counter-anion groups. In one embodiment, the coating composition is a curable coating composition comprising or consisting of an organic film former and an organic corrosion inhibitor, wherein the organic corrosion inhibitor comprises onium cation groups and aromatic carboxylate counter-anion groups.

25

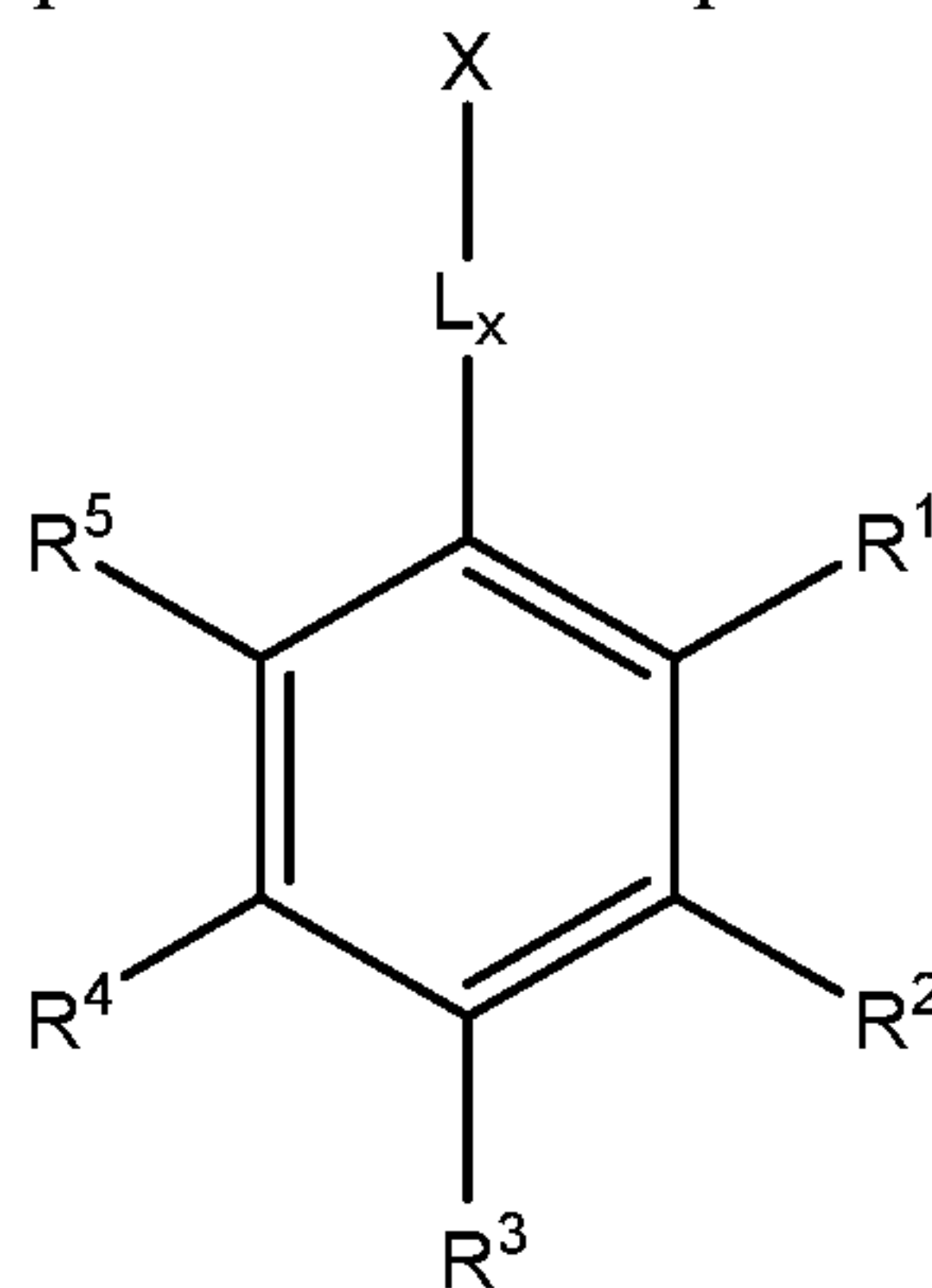
In another aspect, there is provided a process for preparing a coating system comprising:

applying the organic corrosion inhibitor or composition thereof according to any aspects, embodiments or examples as described herein, to an optionally coated substrate;

5 and

optionally applying one or more post coating layer to the coating present on the optionally coated substrate.

In another aspect, there is provided a compound of Formula 1a or salt thereof:



Formula 1a

wherein

X is a carboxylic acid or carboxylate group;

L<sub>x</sub> is an optional divalent linking group selected from alkyl, alkenyl, heteroalkyl, and heteroalkenyl;

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup>, are each independently selected from hydrogen, halo, hydroxyl, C<sub>1-12</sub>alkyl, C<sub>1-12</sub>alkenyl, C<sub>1-12</sub>heteroalkyl, C<sub>1-12</sub>heteroalkenyl, O-C<sub>1-12</sub>alkyl, O-C<sub>1-12</sub>alkenyl, O-C<sub>1-12</sub>heteroalkyl and O-C<sub>1-12</sub>heteroalkenyl;

with the proviso that R<sup>3</sup> is not hydrogen, hydroxyl or methoxyl, when R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, and R<sup>5</sup>, are hydrogen and L<sup>1</sup>-Z is -CH=CH-C(=O)OH.

Any embodiment herein shall be taken to apply *mutatis mutandis* to any other embodiment unless specifically stated otherwise.

The present disclosure is not to be limited in scope by the specific embodiments described herein, which are intended for the purpose of exemplification only. Functionally-equivalent products, compositions and methods are clearly within the scope of the disclosure, as described herein.

Throughout this specification, unless specifically stated otherwise or the context requires otherwise, reference to a single step, composition of matter, group of steps or group of compositions of matter shall be taken to encompass one and a plurality (i.e. one

or more) of those steps, compositions of matter, groups of steps or groups of compositions of matter.

## BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the present disclosure will be further described and illustrated, by way of example only, with reference to the accompanying drawings in which:

**Figure 1** shows Tafel plots at pH 7 for mild steel immersed in the control solution and the inhibitor (CTA-4OHcinn) solution.

**Figure 2** shows Nyquist plots of mild steel immersed for 2 h in the control solution (**Figure 2(a)**) and the inhibitor (CTA-4OHcinn) solution (**Figure 2(b)**).

**Figure 3** shows Bode plots of mild steel immersed for 2 h in the control solution (**Figure 3(a)**) and the inhibitor (CTA-4OHcinn) solution (**Figure 3(b)**).

**Figure 4** shows phase angle plot of mild steel immersed for 2 h in the control solution (**Figure 4(a)**) and the inhibitor (CTA-4OHcinn) solution (**Figure 4(b)**).

**Figure 5** shows cyclic polarisation curves of mild steel immersed for 2 h in the control solution (**Figure 5(a)**) and the inhibitor (CTA-4OHcinn) solution (**Figure 5(b)**).

**Figure 6** shows images of mild steel following immersion for 2 h in the control solution (**Figure 6(a)**) and the inhibitor (CTA-4OHcinn) solution (**Figure 6(b)**).

**Figure 7(a)** shows SEM image of mild steel immersed for 12 days in inhibitor solution. **Figure 7(b)** shows the EDS analysis of zone 1 and zone 2.

**Figure 8** shows trend of Nyquist plot for mild steel immersed for 2 h in control solution (**Figure 8(a)**) and inhibitor (CTA-4OHcinn) solution (**Figure 8(b)**).

**Figure 9** shows 2 h time trend of the Bode and phase angle plot for mild steel immersed for 2 h in control solution (**Figure 9(a)**) and the inhibitor (CTA-4OHcinn) solution (**Figure 9(b)**).

**Figure 10** shows optical images of the surface of mild steel with AS1030 samples with the corrosion product intact after immersion at pH 7 for 24 h in control solution (**Figure 10(a)** and **Figure 10(b)**) and inhibitor solution (**Figure 10(c)**).

**Figure 11** shows SEM and mapping images after corrosion production removal of the surface of mild steel samples immersed in inhibitor solution at pH 7 after 24 h, including a selected pit (**Figure 11(a)**), Fe map (**Figure 11(b)**), oxygen map (**Figure 11(c)**), and chloride map (**Figure 11(d)**).

**Figure 12** shows EDX spectra for spots 1 and 2 in **Figure 11**.

**Figures 13a-e** shows XPS elemental analysis following immersion testing results at various times for CTA-4OHcinn as a corrosion inhibitor.

**Figure 14** shows the deconvolution of the XPS region scans for oxygen, iron, and nitrogen at the different immersion times for CTA-4OHcinn as a corrosion inhibitor.

5 **Figure 15** shows Tafel plots for the control solution and inhibitor solution for CTA-4Etocinnas a corrosion inhibitor according to one example of the present disclosure.

10 **Figure 16** shows optical images of the sample immersed for 24 h in control solution (Figure 16(a)) and inhibitor solution (Figure 16(b)) for CTA-4Etocinn as a corrosion inhibitor according to one example of the present disclosure.

**Figure 17** shows the SEM image of mild steel after 24 h of immersion in control (Figure 17(b)) and the inhibitor (Figure 17(a)) solutions for CTA-4Etocinn as a corrosion inhibitor according to one example of the present disclosure.

15 **Figure 18** shows a higher magnification image of one of these deposits, accompanied by elemental information from EDX analysis of the sites labelled for CTA-4Etocinn as a corrosion inhibitor according to one example of the present disclosure.

20 **Figure 19** shows (a) Tafel plots for a control solution and inhibitor solution after 30 minutes immersion and (b) Tafel plots for a control solution and inhibitor solution after 24 hours immersion, for 10 mM CTA-4Etocinn and 10 mM CTA-4OHcinn as corrosion inhibitors with and without ethanol according to one example of the present disclosure.

25 **Figure 20** shows (a) Tafel plots for the control solution and both inhibitor solutions after 30 minutes immersion and (b) shows the Tafel plots for the control solution and both inhibitor solutions after 24 hours immersion, for 10 mM CTA-4Etocinn and 10 mM CTA-4OHcinn as corrosion inhibitors with 6.5% ethanol according to one example of the present disclosure.

**Figure 21** shows Tafel plots for 10 mM CTA-4Etocinn inhibitor solution with 6.5% ethanol in 0.01M NaCl at pH 7 after 30 minutes and 24 hours of immersion.

30 **Figure 22** shows (a) Tafel plots for control solution and inhibitor solution after 30 minutes immersion at pH2, (b) Tafel plots for the control solution and inhibitor solution after 24 hours immersion at pH2, and (c) combined Tafel plots comparing the effect between 30 minute and 24 hour immersions, for 0.1 mM CTA-4Butcinn as a corrosion inhibitor according to one example of the present disclosure at pH 2.

35 **Figure 23** shows optical images of the sample immersed at pH2 for 24 h in control solution (Figure 23(a)(i) and (ii) at different magnification) and inhibitor solution (Figure

23(b)) for 0.1 mM CTA-4Butcinn as a corrosion inhibitor according to one example of the present disclosure.

**Figure 24** shows the SEM image of mild steel after 24 h of immersion at pH2 in control (Figure 24(b)) and the inhibitor (Figure 24(a)) solutions for 0.1 mM CTA-4Butcinn as a corrosion inhibitor according to one example of the present disclosure.

## DETAILED DESCRIPTION

The present disclosure describes the following various non-limiting examples, which relate to investigations undertaken to identify alternative and improved corrosion inhibitors including organic corrosion inhibitors. The organic corrosion inhibitors, compositions, coatings, and coated substrates thereof in the present disclosure can provide corrosion inhibition, and in some aspects, embodiments or examples, additional properties such as antimicrobial properties, formulation processability, and/or improved barrier protection from water. It was surprisingly found that a coating composition comprising an organic corrosion inhibitor could provide an effective coating on a substrate with properties including at least one of corrosion inhibition and antimicrobial resistance. The coating compositions and coatings as described herein have been found suitable for various uses, and in particular use in protecting metal based infrastructure and conduits from corrosion in marine environments and/or oil and gas industry.

### General Definitions and Terms

In the following description, reference is made to the accompanying drawings which form a part hereof, and which is shown, by way of illustration, several embodiments. It is understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present disclosure.

With regards to the definitions provided herein, unless stated otherwise, or implicit from context, the defined terms and phrases include the provided meanings. Unless explicitly stated otherwise, or apparent from context, the terms and phrases below do not exclude the meaning that the term or phrase has acquired by a person skilled in the relevant art. The definitions are provided to aid in describing particular embodiments, and are not intended to limit the claimed invention, because the scope of the invention is limited only by the claims. Furthermore, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

All publications discussed and/or referenced herein are incorporated herein in their entirety.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present disclosure. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present disclosure as it existed before the priority date of each claim of this application.

Throughout this disclosure, unless specifically stated otherwise or the context requires otherwise, reference to a single step, composition of matter, group of steps or group of compositions of matter shall be taken to encompass one and a plurality (i.e., one or more) of those steps, compositions of matter, groups of steps or groups of compositions of matter. Thus, as used herein, the singular forms “a”, “an” and “the” include plural aspects unless the context clearly dictates otherwise. For example, reference to “a” includes a single as well as two or more; reference to “an” includes a single as well as two or more; reference to “the” includes a single as well as two or more and so forth.

Those skilled in the art will appreciate that the disclosure herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the disclosure includes all such variations and modifications. The disclosure also includes all of the examples, steps, features, methods, compositions, coatings, processes, and coated substrates, referred to or indicated in this specification, individually or collectively, and any and all combinations or any two or more of said steps or features.

The term “and/or”, e.g., “X and/or Y” shall be understood to mean either “X and Y” or “X or Y” and shall be taken to provide explicit support for both meanings or for either meaning.

Unless otherwise indicated, the terms “first,” “second,” etc. are used herein merely as labels, and are not intended to impose ordinal, positional, or hierarchical requirements on the items to which these terms refer. Moreover, reference to a “second” item does not require or preclude the existence of lower-numbered item (e.g., a “first” item) and/or a higher-numbered item (e.g., a “third” item).

As used herein, the phrase “at least one of”, when used with a list of items, means different combinations of one or more of the listed items may be used and only one of the items in the list may be needed. The item may be a particular object, thing, or category. In other words, “at least one of” means any combination of items or number of items may be used from the list, but not all of the items in the list may be required. For example, “at least one of item A, item B, and item C” may mean item A; item A and item B; item B; item A, item B, and item C; or item B and item C. In some cases, “at least one

of item A, item B, and item C” may mean, for example and without limitation, two of item A, one of item B, and ten of item C; four of item B and seven of item C; or some other suitable combination.

5 It is to be appreciated that certain features that are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination.

10 Throughout the present specification, various aspects and components of the invention can be presented in a range format. The range format is included for convenience and should not be interpreted as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range, unless specifically indicated. For example, description of a range such as from 1 to 5 should be considered to have specifically disclosed sub-ranges such as  
15 from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 5, from 3 to 5 etc., as well as individual and partial numbers within the recited range, for example, 1, 2, 3, 4, 5, 5.5 and 6, unless where integers are required or implicit from context. This applies regardless of the breadth of the disclosed range. Where specific values are required, these will be indicated in the specification.

20 Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

25 As used herein “curable” or “cured” is descriptive of a material or composition that has or can be cured (e.g., polymerized or crosslinked) by heating to induce polymerization and/or crosslinking; irradiating with actinic irradiation to induce polymerization and/or crosslinking; and/or by mixing one or more components to induce polymerization and/or crosslinking. "Mixing can be performed, for example, by combining two or more parts and mixing to form a homogeneous composition.  
30 Alternatively, two or more parts can be provided as separate layers that intermix (e.g., spontaneously or upon application of shear stress) at the interface to initiate polymerization.

The reference to “substantially free” generally refers to the absence of that compound or component in the composition other than any trace amounts or impurities  
35 that may be present, for example this may be an amount by weight % in the total composition of less than about 1%, 0.1%, 0.01%, 0.001%, or 0.0001%. The compositions

as described herein may also include, for example, impurities in an amount by weight % in the total composition of less than about 5%, 4%, 3%, 2%, 1%, 0.5%, 0.1%, 0.01%, 0.001%, or 0.0001%.

The term “alkyl” includes straight-chained, branched, and cyclic alkyl groups and includes both unsubstituted and substituted alkyl groups. Unless otherwise indicated, the alkyl groups typically contain from 1 to 20 carbon atoms. The alkyl groups may for example contain carbon atoms from 1 to 12, 1 to 10, or 1 to 8. Examples of “alkyl” as used herein include, but are not limited to, methyl, ethyl, n-propyl, n-butyl, n-pentyl, isobutyl, t-butyl, isopropyl, n-octyl, n-heptyl, ethylhexyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and norbornyl, and the like. Unless otherwise noted, alkyl groups may be mono- or polyvalent.

As used herein, the terms “halo” or “halogen”, whether employed alone or in compound words such as haloalkyl, means fluorine, chlorine, bromine or iodine.

As used herein, the term “haloalkyl” means an alkyl group having at least one halogen substituent, the terms “alkyl” and “halogen” being understood to have the meanings outlined above. Similarly, the term “monohaloalkyl” means an alkyl group having a single halogen substituent, the term “dihaloalkyl” means an alkyl group having two halogen substituents and the term “trihaloalkyl” means an alkyl group having three halogen substituents. Examples of monohaloalkyl groups include fluoromethyl, chloromethyl, bromomethyl, fluoromethyl, fluoropropyl and fluorobutyl groups; examples of dihaloalkyl groups include difluoromethyl and difluoroethyl groups; examples of trihaloalkyl groups include trifluoromethyl and trifluoroethyl groups.

As used herein, the term “alkenyl” encompasses both straight and branched chain unsaturated hydrocarbon groups with at least one carbon-carbon double bond. Examples of alkenyl groups include ethenyl, propenyl, butenyl, pentenyl and hexenyl. Preferred alkenyl groups include ethenyl, 1-propenyl, 2-propenyl and but-2-enyl.

As used herein, the term “alkynyl” encompasses both straight and branched chain unsaturated hydrocarbon groups with at least one carbon-carbon triple bond. Examples of alkynyl groups include ethynyl, propynyl, butynyl, pentynyl and hexynyl. Preferred alkynyl groups include ethynyl, 1-propynyl and 2-propynyl.

The term “heteroalkyl” includes both straight-chained, branched, and cyclic alkyl groups with one or more heteroatoms (e.g. 1-3) independently selected from S, O, and N with both unsubstituted and substituted alkyl groups. Unless otherwise indicated, the heteroalkyl groups typically contain from 1 to 20 carbon atoms. The heteroalkyl groups may for example contain carbon atoms from 1 to 12, 1 to 10, or 1 to 8. Examples of “heteroalkyl” as used herein include, but are not limited to, methoxy, ethoxy, propoxy,

3,6-dioxaheptyl, 3-(trimethylsilyl)-propyl, 4-dimethylaminobutyl, and the like. Unless otherwise noted, heteroalkyl groups may be mono- or polyvalent.

The term “heteroarylalkyl” means a group comprising a heteroalkyl and aryl according to any examples independently thereof as described herein.

5       The term "heteroalkenyl" includes both straight-chained, branched, and cyclic alkenyl groups as described herein with one or more heteroatoms (e.g. 1-3) independently selected from S, O, and N with both unsubstituted and substituted alkenyl groups. Unless otherwise indicated, the heteroalkenyl groups typically contain from 1 to 20 carbon atoms. The heteroalkenyl groups may for example contain carbon atoms from 1 to 12, 1  
10 to 10, or 1 to 8. Unless otherwise noted, heteroalkenyl groups may be mono- or polyvalent.

As used herein, the terms "carbocyclic" and "carbocyclyl" represent a ring system wherein the ring atoms are all carbon atoms, e.g., from 3 to 20 carbon ring atoms, and which may be aromatic, non-aromatic, saturated, or unsaturated. The terms encompass  
15 single ring systems, e.g. cycloalkyl groups such as cyclopentyl and cyclohexyl, aromatic groups such as phenyl, and cycloalkenyl groups such as cyclohexenyl, as well as fused-ring systems such as naphthyl and fluorenyl.

As used herein, the terms “heterocyclic” and “heterocyclyl” represent an aromatic or a non-aromatic cyclic group of carbon atoms wherein from one to three of the carbon  
20 atoms is/are replaced by one or more heteroatoms independently selected from nitrogen, oxygen or sulfur. A heterocyclyl group may, for example, be monocyclic or polycyclic, and contain for example from 3 to 20 ring atoms. In a bicyclic heterocyclyl group there may be one or more heteroatoms in each ring, or only in one of the rings. Examples of heterocyclyl groups include piperidinyl, tetrahydrofuranyl, tetrahydropyranyl, pyridyl,  
25 pyrimidinyl and indolyl.

As used herein, the term “cycloalkyl” represents a ring system wherein the ring atoms are all carbon atoms, e.g., from 3 to 20 carbon ring atoms, and which is saturated. A cycloalkyl group can be monocyclic or polycyclic. A bicyclic group may, for example, be fused or bridged. Examples of monocyclic cycloalkyl groups include cyclopropyl,  
30 cyclobutyl and cyclopentyl. Other examples of monocyclic cycloalkyl groups are cyclohexyl, cycloheptyl and cyclooctyl. Examples of bicyclic cycloalkyl groups include bicyclo[2.2.1]hept-2-yl.

As will be understood, an “aromatic” group means a cyclic group having  $4m+2$   $\pi$  electrons, where  $m$  is an integer equal to or greater than 1. As used herein, "aromatic"  
35 is used interchangeably with "aryl" to refer to an aromatic group, regardless of the valency of aromatic group.

As used herein, the terms “aromatic carbocyclyl” or “aromatic carbocycle” represent a ring system which is aromatic and in which the ring atoms are all carbon atoms, e.g. having from 6-14 ring atoms. An aromatic carbocyclyl group may be monocyclic or polycyclic. Examples of aromatic carbocyclyl groups include phenyl, naphthyl and fluorenyl. Polycyclic aromatic carbocyclyl groups include those in which only one of the rings is aromatic, such as for example indanyl.

The term “aryl” or “aromatic” group or moiety includes 6-18 ring atoms and can contain optional fused rings, which may be saturated or unsaturated. Examples of aromatic groups include phenyl, naphthyl, biphenyl, phenanthryl, and anthracyl. The aromatic group may optionally contain 1-3 heteroatoms such as nitrogen, oxygen, or sulfur and can contain fused rings. Examples of aromatic group having heteroatoms include pyridyl, furanyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, imidazolyl, indolyl, benzofuranyl, and benzthiazolyl. Unless otherwise noted the aromatic group may be mono- or polyvalent. In an example, the “aromatic” group may be a monocyclic aromatic group, for example a benzene group that may be unsubstituted or substituted.

The term “arylalkyl” means a group comprising an aryl and an alkyl according to any examples independently thereof as described herein.

As used herein, the terms “aromatic heterocycle” or “aromatic heterocyclyl” represent an aromatic cyclic group of carbon atoms wherein from one to three of the carbon atoms is/are replaced by one or more heteroatoms independently selected from nitrogen, oxygen or sulphur, e.g. having from 5-14 ring atoms. The term “aromatic heterocyclyl” is used interchangeably with “heteroaryl”. An aromatic heterocyclyl group may be monocyclic or polycyclic. Examples of monocyclic aromatic heterocyclyl groups (also referred to as monocyclic heteroaryl groups) include furanyl, thienyl, pyrrolyl, imidazolyl, pyridyl and pyrimidinyl. Examples of polycyclic aromatic heterocyclyl groups (also referred to as bicyclic heteroaryl groups) include benzimidazolyl, quinolinyl and indolyl. Polycyclic aromatic heterocyclyl groups include those in which only one of the rings is an aromatic heterocycle.

As used herein, the term “cyano” represents a -CN moiety.

As used herein, the term “hydroxyl” represents a -OH moiety.

As used herein, the term “alkoxy” represents an -O-alkyl group in which the alkyl group is as defined supra. Examples include methoxy, ethoxy, n-propoxy, iso-propoxy, and the different butoxy, pentoxy, hexyloxy and higher isomers.

As used herein, the term “aryloxy” represents an -O-aryl group in which the aryl group is as defined supra. Examples include, without limitation, phenoxy and naphthoxy.

As used herein, the term “carboxyl” represents a -CO<sub>2</sub>H moiety.

As used herein, the term "nitro" represents a -NO<sub>2</sub> moiety.

The term "optionally fused" means that a group is either fused to another ring system or unfused, and "fused" refers to one or more rings that share at least two common ring atoms with one or more other rings. Fusing may be provided by one or more carbocyclic or heterocyclic rings, as defined herein, or be provided by substituents of rings being joined together to form a further ring system. The fused ring may be a 5, 6 or 7-membered ring of between 5 and 10 ring atoms in size. The fused ring may be fused to one or more other rings, and may for example contain 1 to 4 rings.

The term "optionally substituted" means that a functional group is either substituted or unsubstituted, at any available position. The term "substituted" as referred to above or herein may include, but is not limited to, groups or moieties such as halogen, hydroxyl, alkyl, or haloalkyl.

The term "optionally linked" means a group may be attached to another group via a linker group (e.g. divalent linking group such as an alkyl, heteroatom, or heteroalkyl) or may be directly attached to another group without a linker group.

### **Organic Corrosion Inhibitors**

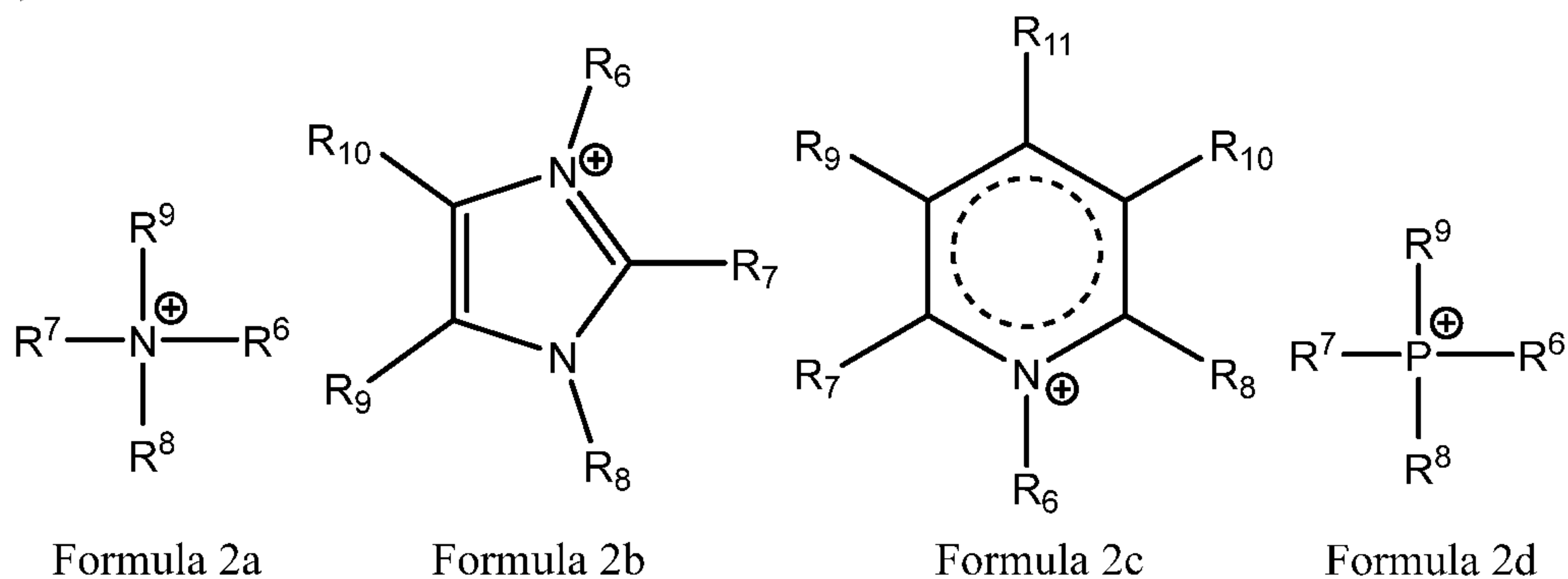
The present disclosure provides various organic corrosion inhibitors comprising onium cation groups and aromatic carboxylate counter-anion groups. The onium cation groups and aromatic carboxylate counter-anion groups can coordinate together to form an ionic compound, for example a salt. The ionic compound (e.g. salt) provides an organic corrosion inhibitor. In another example, the organic corrosion inhibitor may be an ionic liquid.

The organic corrosion inhibitors may be provided by any combination of Onium Cation Groups and Aromatic Carboxylate Groups as described below or herein.

#### **Onium Cation Groups**

The onium cations may be selected from ammonium cation groups, pyridinium cation groups, imidazolium cation groups, pyrazolium cation groups, pyrrolidinium cation groups, and phosphonium cation groups. In one embodiment, the onium cations are quaternary onium cations. In another embodiment, the onium cations are nitrogen cations, such as ammonium cations. In another embodiment, the quaternary onium cations are quaternary onium nitrogen cations, for example quaternary cations selected from ammonium cation groups, pyridinium cation groups, imidazolium cation groups, pyrazolium cation groups, and pyrrolidinium cation groups. In one example, the quaternary onium cations are quaternary ammonium cation groups.

The onium cations may be selected from any of the onium cations of Formula 2a, 2b, 2c, or 2d:

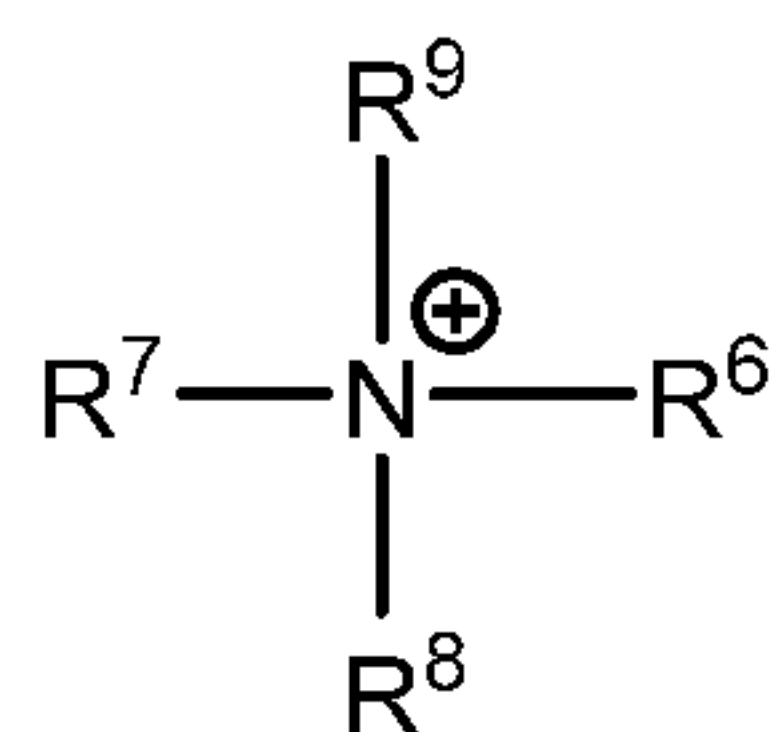


wherein

- 5  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, heteroalkenyl, aryl, arylalkyl, heteroaryl, and heteroarylalkyl. Each alkyl or alkenyl may be optionally substituted, or optionally interrupted by one or more heteroatoms selected from O, N and S.

- In another example of any of the onium cations of Formula 2a, 2b, 2c, or 2d, the groups  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, heteroalkenyl, aryl, arylalkyl, heteroaryl, and heteroarylalkyl. In another example, the groups  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl. In another example,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from hydrogen, alkyl, and heteroalkyl. In another example,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from alkyl and heteroalkyl. In another example,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from hydrogen and alkyl. In another example,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ , and  $R^{11}$ , are each independently selected from alkyl.

- In another embodiment, the onium cations are selected from quaternary onium nitrogen cations of Formula 2a:



Formula 2a

wherein

- 25  $R^6$ ,  $R^7$ ,  $R^8$ , and  $R^9$ , are each independently selected from alkyl, alkenyl, heteroalkyl, heteroalkenyl, aryl, arylalkyl, heteroaryl, and heteroarylalkyl, and wherein two or more groups may join together to provide an aromatic or aliphatic ring. Each alkyl

or alkenyl may be optionally substituted, or optionally interrupted by one or more heteroatoms selected from O, N and S.

In examples of any of the onium cations of Formula 2a, the groups R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl. In another example, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from hydrogen, alkyl, and heteroalkyl. In another example, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from hydrogen and alkyl. In another example, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from alkyl and heteroalkyl. In another example, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from alkyl. In one example, the onium cation of Formula 2a is cetrimonium.

The following Table 1 provides some further specific examples of cations, which may be provided with any other anion as described herein for forming an organic corrosion inhibitor of the present disclosure:

Table 1: Onium Cation Examples

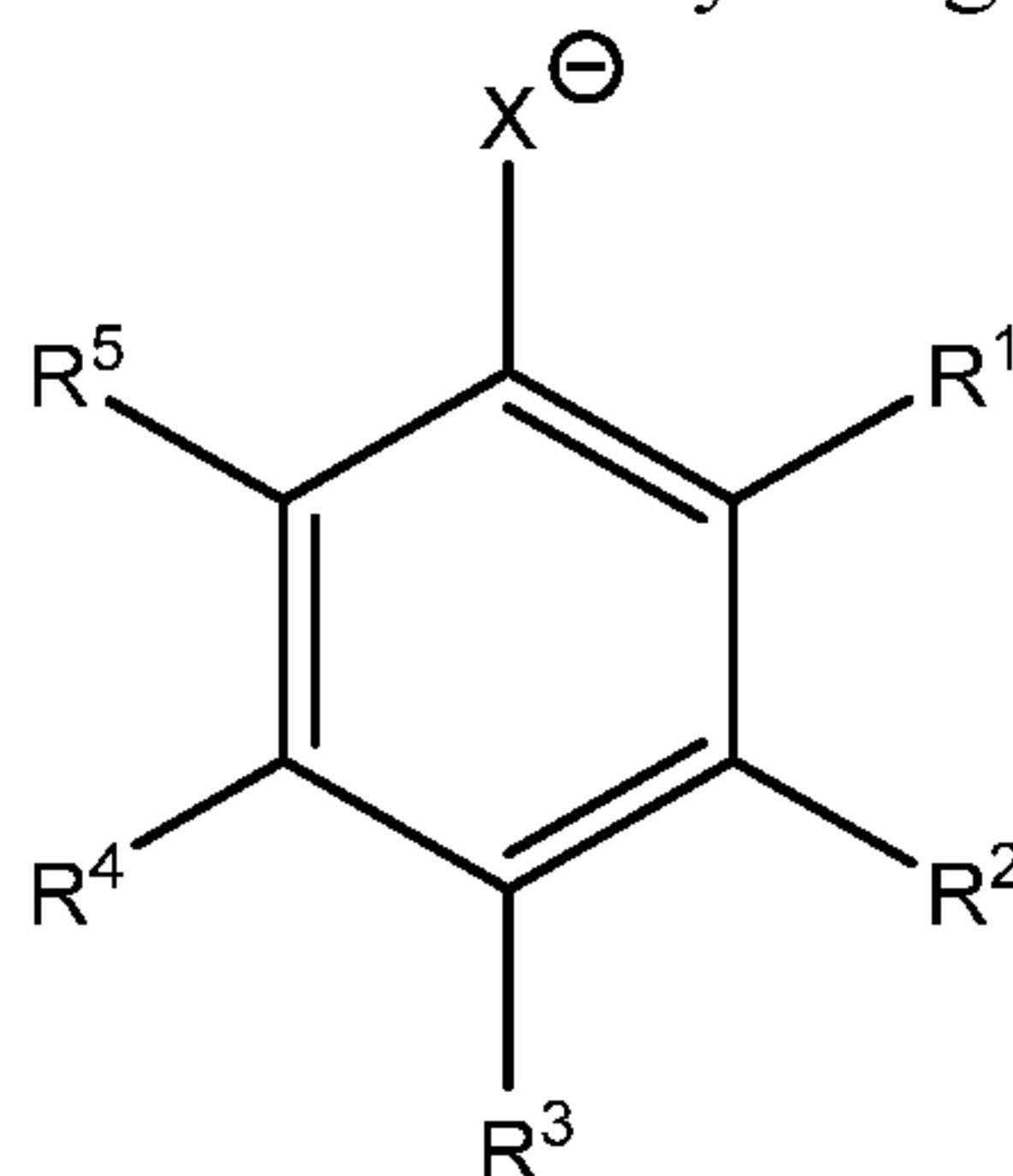
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Aromatic Carboxylate Groups

It will be appreciated that the aromatic carboxylate group provides a counter anion to the cation groups in the organic corrosion inhibitor. The aromatic carboxylate group may be an optionally linked, optionally substituted, monocyclic or polycyclic aromatic (Ar) group. The counter-anion group may be provided by its respective conjugate acid,

which in-situ may form the carboxylate anion. In one example, the aromatic carboxylate group may be provided by a benzene group (Ar) substituted with an optionally linked (L) carboxylate group ( $^-\text{OC}(=\text{O})$ ), which may be referred to by the formulae  $\text{Ar}-\text{C}(=\text{O})\text{O}^-$  or  $\text{Ar}-\text{L}-\text{C}(=\text{O})\text{O}^-$ . It will be appreciated that the aromatic (Ar) group, for example  
 5 benzene, may be further optionally substituted at one or more of its ring atoms, such as meta, ortho and/or para substituted with respect to the carboxylate substituent.

In one embodiment, the aromatic carboxylate group is a group of Formula 1:



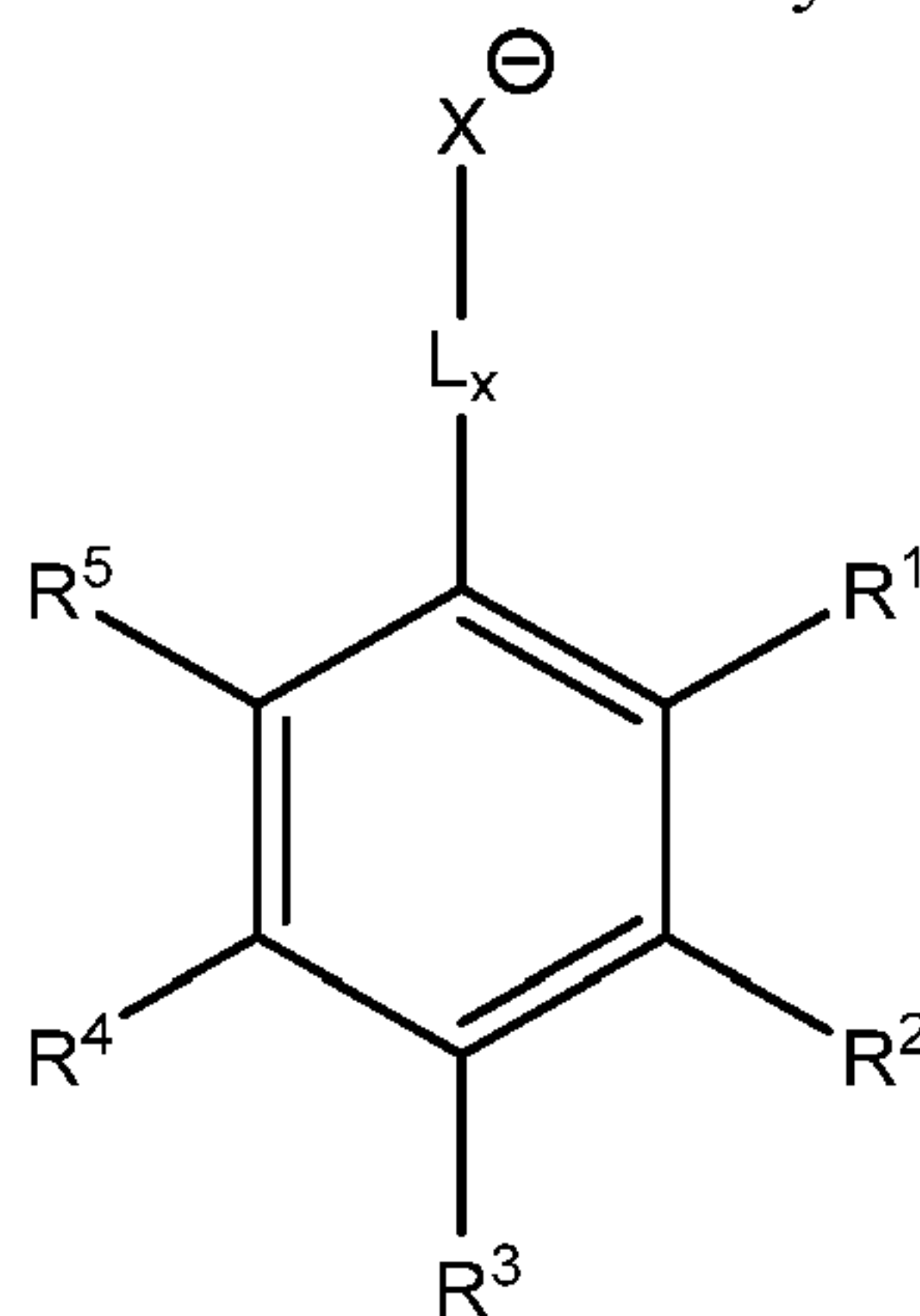
Formula 1.

10

In the above Formula 1, X is an optionally linked carboxylate group. For example, X may be defined as  $-\text{L}_x-\text{X}$  wherein  $\text{L}_x$  is an optional linking group and X is the carboxylate anion moiety. R<sup>1</sup> to R<sup>5</sup> may be each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-  
 15 heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

In one example, X is an alkenyl carboxylate, such as an ethylenyl carboxylate (i.e.  $-\text{CH}=\text{CH}-\text{C}(\text{O})-\text{OH}$ ).

In another embodiment, the aromatic carboxylate groups may be of Formula 1a:



Formula 1a.

20

In the above Formula 1a, X is a carboxylate group. Lx is an optional divalent linking group, which may be selected from alkyl, alkenyl, heteroalkyl, and heteroalkenyl. R<sup>1</sup> to R<sup>5</sup> may be each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

In one example, Lx is an alkenyl group, such as an ethylenyl group wherein -Lx-X is an ethylenyl carboxylate (i.e. -CH=CH-C(O)-OH).

In one example, for Formula 1 or Formula 1a, R<sup>1</sup> to R<sup>5</sup> may be each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl. In another example, for Formula 1 or Formula 1a, R<sup>1</sup> to R<sup>5</sup> may be each independently selected from hydrogen, halo, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl. In another example, for Formula 1 or Formula 1a, R<sup>1</sup> and R<sup>5</sup> are hydrogen, and R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, and O-heteroalkenyl. In another example, for Formula 1 or Formula 1a, R<sup>1</sup> and R<sup>5</sup> are hydrogen, and at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-alkyl, O-alkenyl, O-heteroalkyl, and O-heteroalkenyl.

In another example, for Formula 1 or Formula 1a, R<sup>1</sup> to R<sup>5</sup> may each be independently selected from hydrogen, O-alkyl and O-heteroalkyl, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-alkyl and O-heteroalkyl. For example, R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, and R<sup>5</sup>, can be hydrogen and R<sup>3</sup> can be selected from O-alkyl and O-heteroalkyl.

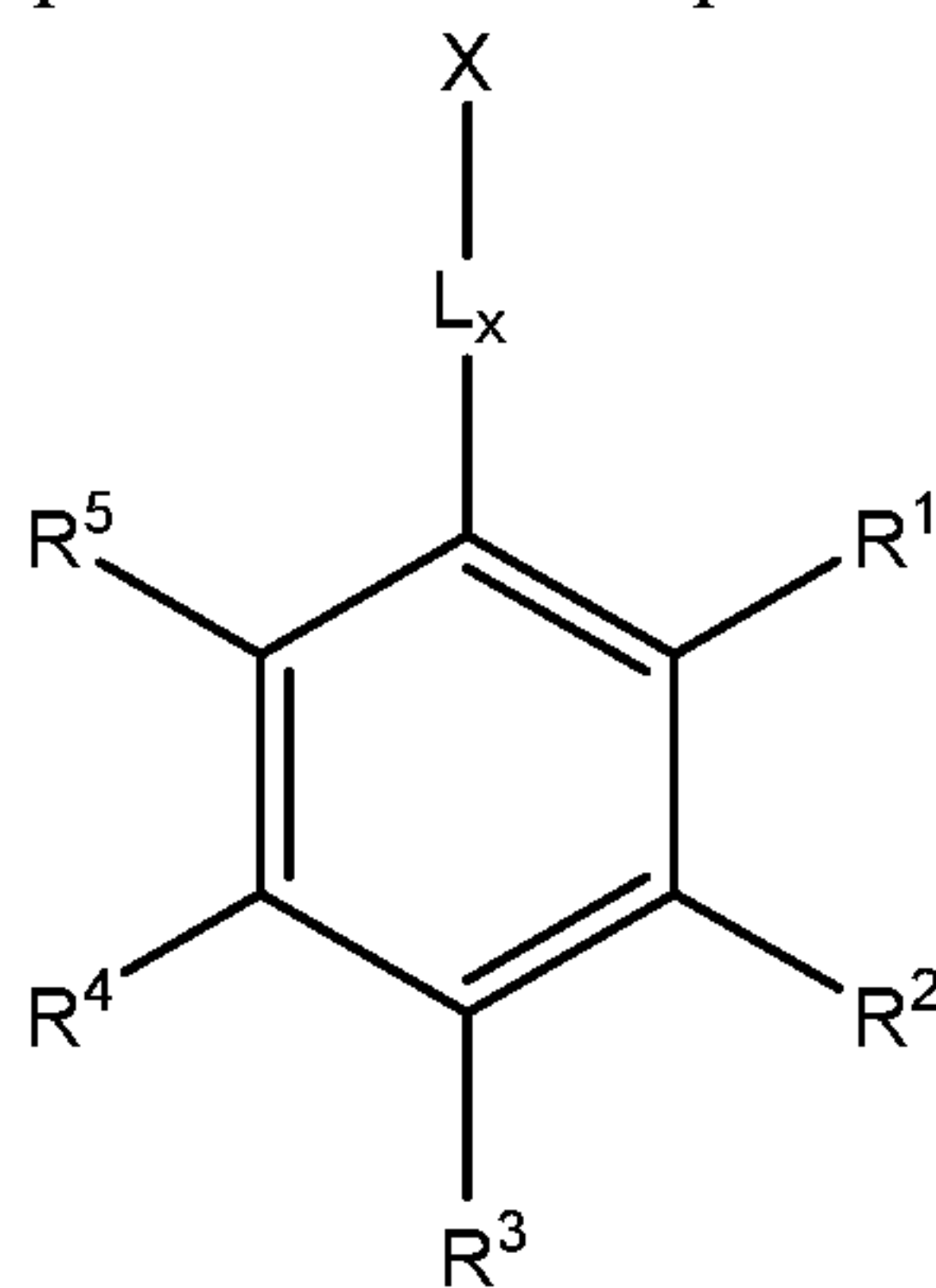
In another example, for Formula 1 or Formula 1a, R<sup>1</sup> and R<sup>5</sup> are hydrogen, and R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, are each independently selected from hydrogen and O-C<sub>1-12</sub>alkyl, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is O-C<sub>1-12</sub>alkyl. In another example, for Formula 1 or Formula 1a, R<sup>1</sup> and R<sup>5</sup> are hydrogen, and R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, are each independently selected from hydrogen and O-C<sub>2-12</sub>alkyl, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-C<sub>2-12</sub>alkyl. In another example, for Formula 1 or Formula 1a, R<sup>1</sup> and R<sup>5</sup> are hydrogen, and R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, are each independently selected from hydrogen and O-C<sub>2-8</sub>alkyl, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-C<sub>2-8</sub>alkyl. In another example, for Formula 1 or Formula 1a, R<sup>1</sup> and R<sup>5</sup> are hydrogen, and R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, are each independently selected from hydrogen and O-C<sub>3-6</sub>alkyl, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-C<sub>3-6</sub>alkyl.

In another example, for Formula 1 or Formula 1a, each of R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, and R<sup>5</sup>, are hydrogen, and R<sup>3</sup> is O-C<sub>1-12</sub>alkyl. In another example, for Formula 1 or Formula 1a, each

of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is O-C<sub>2-12</sub>alkyl. In another example, for Formula 1 or Formula 1a, each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is O-C<sub>3-6</sub>alkyl.

Aromatic Carboxylic Acid and Carboxylate Compounds

In another aspect, there is provided a compound of Formula 1a or salt thereof:



Formula 1a

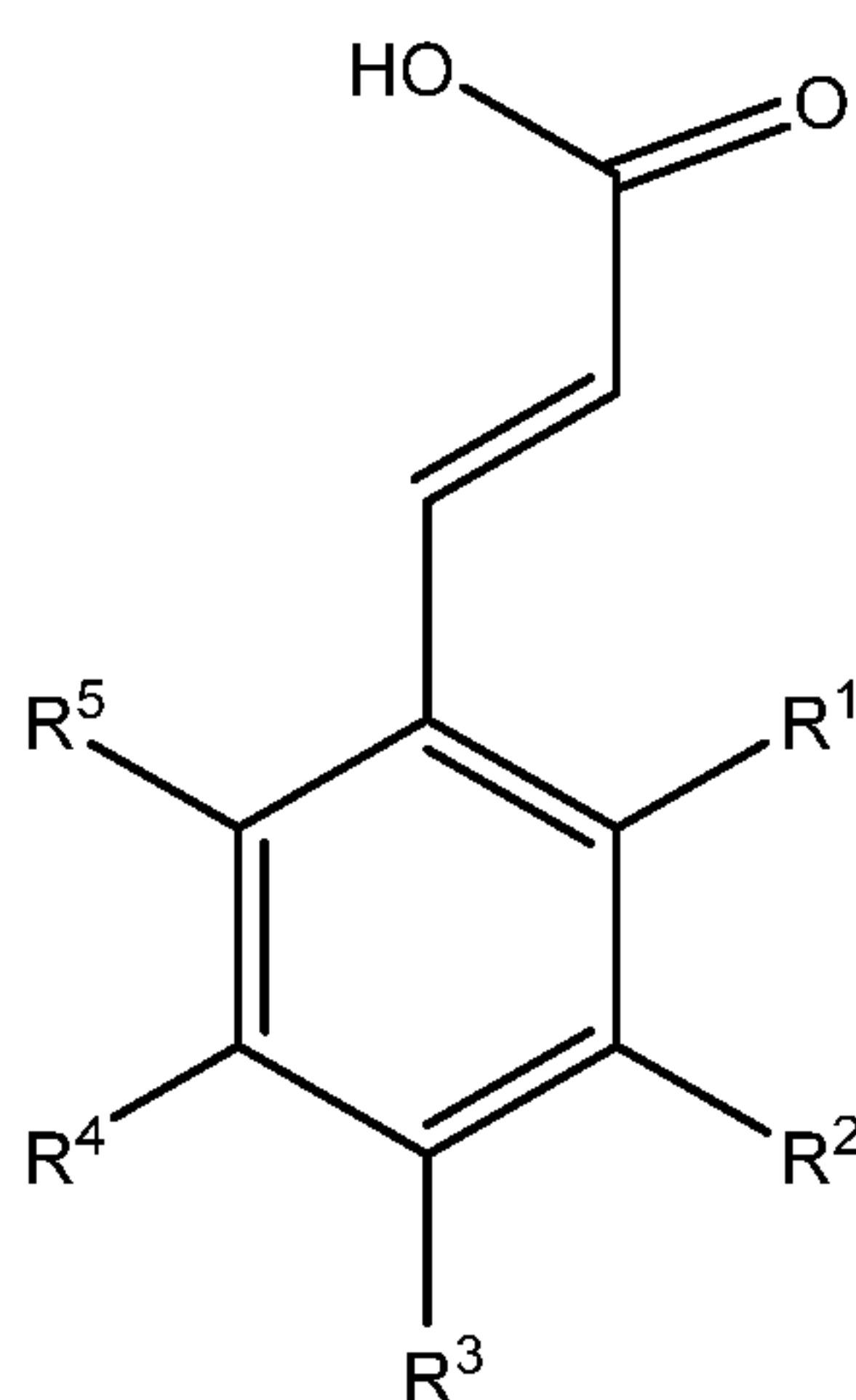
wherein

$X$  is a carboxylic acid or carboxylate group;

$L_x$  is an optional divalent linking group selected from alkyl, alkenyl, heteroalkyl, and heteroalkenyl;

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$ , are each independently selected from hydrogen, halo, hydroxyl, C<sub>1-12</sub>alkyl, C<sub>1-12</sub>alkenyl, C<sub>1-12</sub>heteroalkyl, C<sub>1-12</sub>heteroalkenyl, O-C<sub>1-12</sub>alkyl, O-C<sub>1-12</sub>alkenyl, O-C<sub>1-12</sub>heteroalkyl and O-C<sub>1-12</sub>heteroalkenyl.

In another embodiment, there is provided a compound of Formula 1a(i) or salt thereof:



Formula 1(a)(i)

wherein

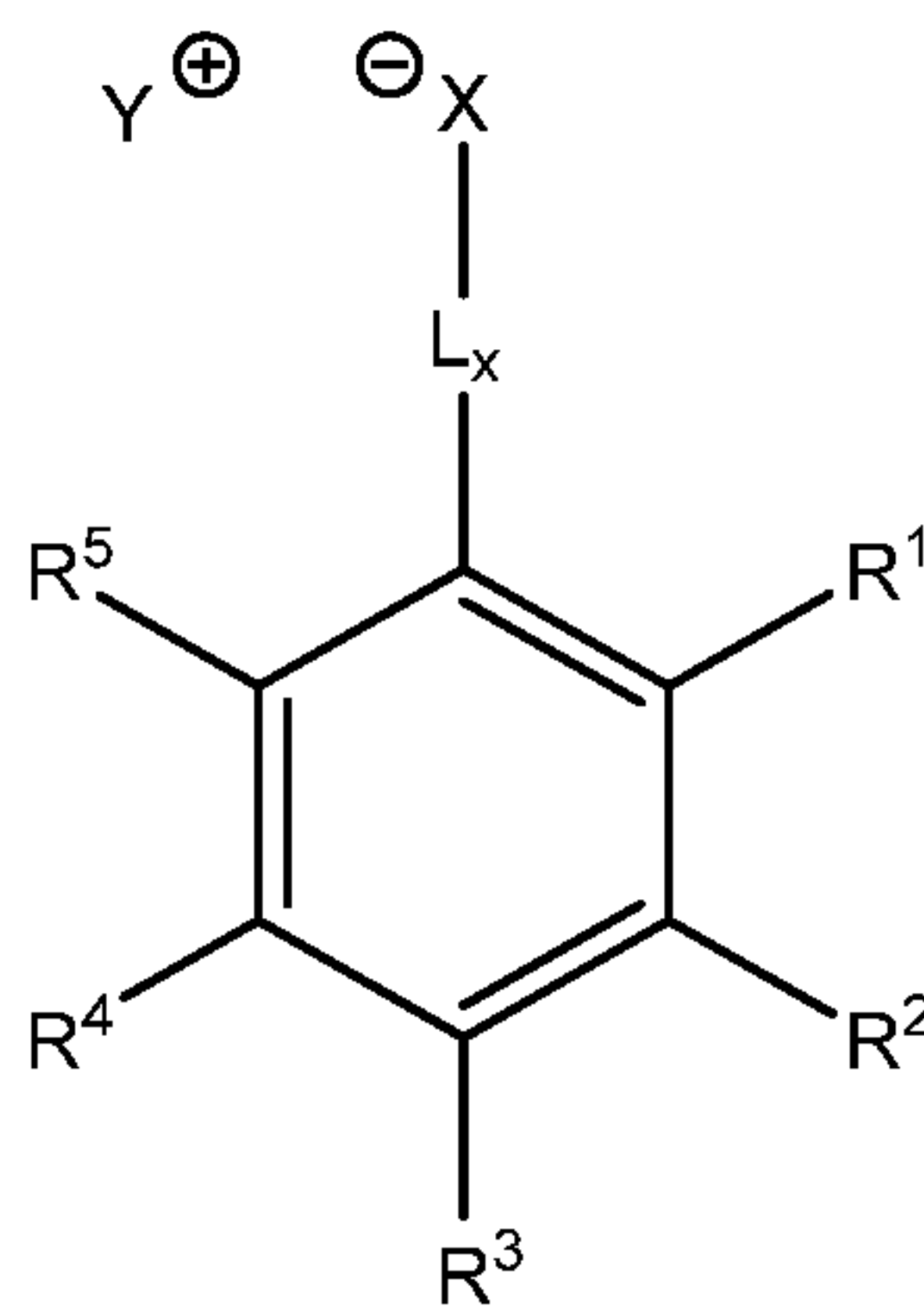
$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$ , are each independently selected from hydrogen, halo, hydroxyl,  $C_{1-12}$ alkyl,  $C_{1-12}$ alkenyl,  $C_{1-12}$ heteroalkyl,  $C_{1-12}$ heteroalkenyl,  $O-C_{1-12}$ alkyl,  $O-C_{1-12}$ alkenyl,  $O-C_{1-12}$ heteroalkyl and  $O-C_{1-12}$ heteroalkenyl.

In an embodiment of Formula 1a or Formula 1a(i), there is provided a proviso that  $R^3$  is not hydrogen, hydroxyl or methoxyl, when  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen and  $L^1-Z$  is  $-CH=CH-C(=O)OH$ . In another embodiment of Formula 1a or Formula 1a(i),  $R^3$  is  $O-C_{1-12}$ alkyl,  $O-C_{2-12}$ alkyl, or  $O-C_{3-8}$ alkyl.

In another example, for Formula 1a or Formula 1a(i),  $R^1$  and  $R^5$  are hydrogen, and at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from  $O-C_{1-12}$ alkyl. In another example, for Formula 1a or Formula 1a(i),  $R^1$  and  $R^5$  are hydrogen, and at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from  $O-C_{2-12}$ alkyl. In another example, for Formula 1a or Formula 1a(i),  $R^1$  and  $R^5$  are hydrogen, and at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from  $O-C_{2-8}$ alkyl. In another example, for Formula 1a or Formula 1a(i),  $R^1$  and  $R^5$  are hydrogen, and at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from  $O-C_{3-6}$ alkyl.

In another example, for Formula 1a or Formula 1a(i), each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is  $O-C_{1-12}$ alkyl. In another example, for Formula 1a, each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is  $O-C_{2-12}$ alkyl. In another example, for Formula 1a, each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is  $O-C_{3-6}$ alkyl.

In another aspect, there is provided an ionic compound of Formula 1(a) or salt thereof:



Formula 1(a)

wherein

$X$  is a carboxylate group;

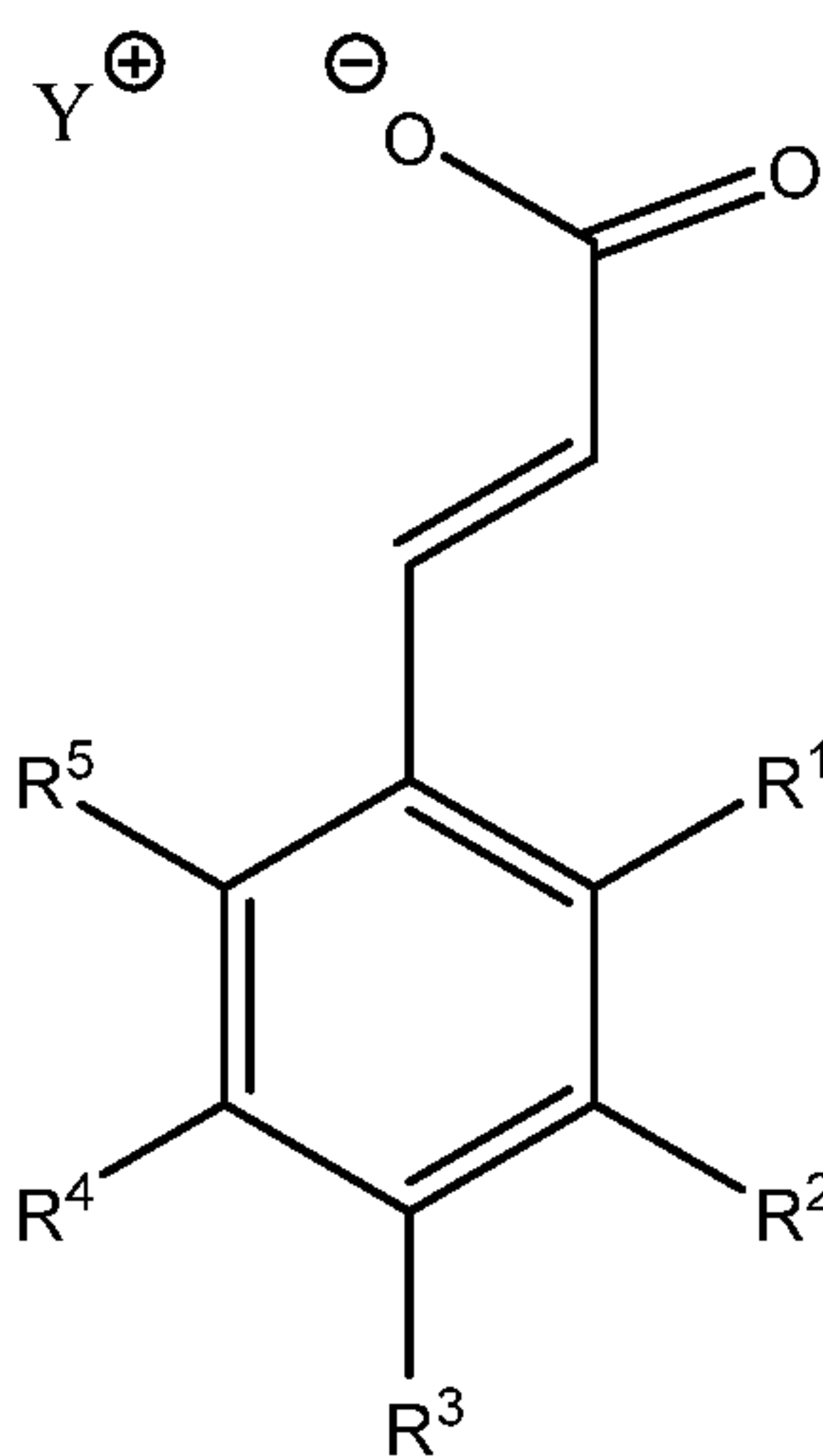
$L_x$  is an optional linking group selected from alkyl, alkenyl, heteroalkyl, and heteroalkenyl;

$Y$  is a cation;

$R^4$  and  $R^8$  are hydrogen;

$R^5$ ,  $R^6$ , and  $R^7$ , are each independently selected from hydrogen,  $C_{1-12}$ alkyl,  $C_{1-12}$ heteroalkyl,  $O-C_{1-12}$ alkyl, and  $O-C_{1-12}$ heteroalkyl.

In another embodiment, there is provided an ionic compound of Formula 1a(i) or salt thereof:



Formula 1a(i)

wherein

$Y$  is a cation;

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$ , are each independently selected from hydrogen, halo, hydroxyl,  $C_{1-12}$ alkyl,  $C_{1-12}$ alkenyl,  $C_{1-12}$ heteroalkyl,  $C_{1-12}$ heteroalkenyl,  $O-C_{1-12}$ alkyl,  $O-C_{1-12}$ alkenyl,  $O-C_{1-12}$ heteroalkyl and  $O-C_{1-12}$ heteroalkenyl.

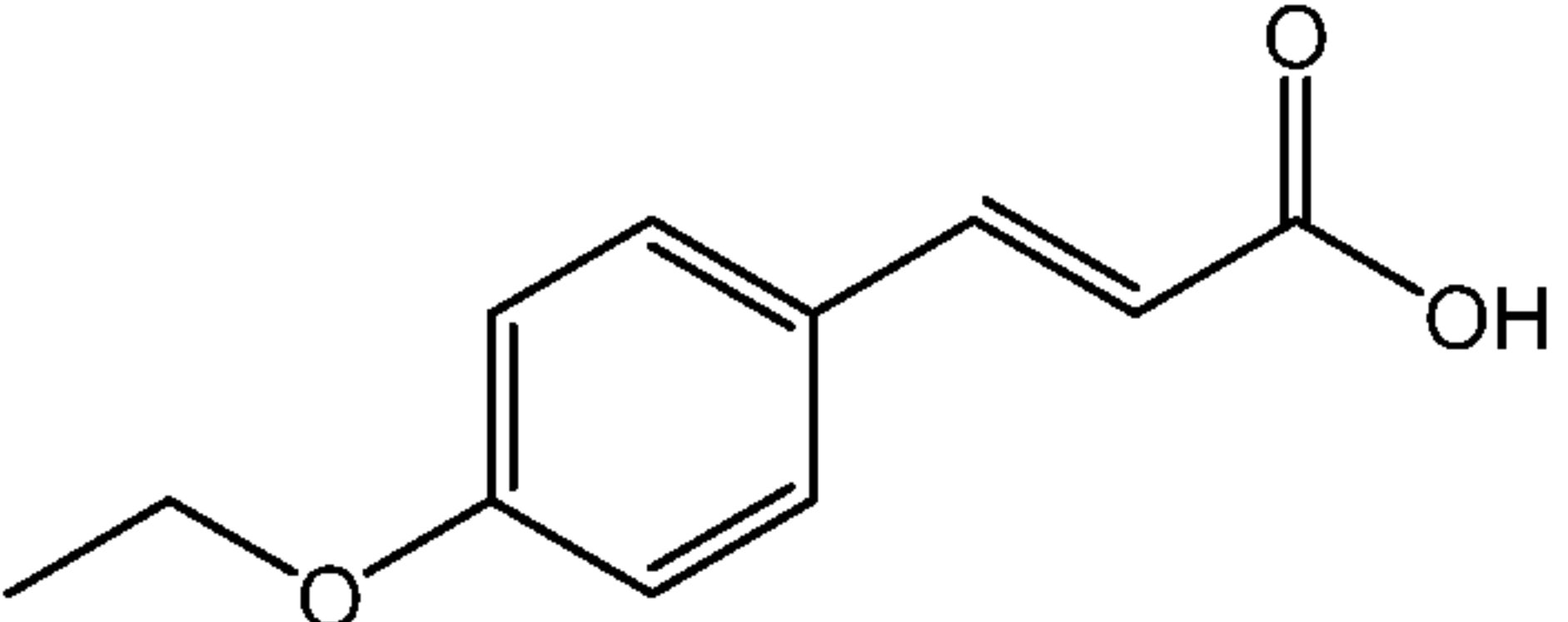
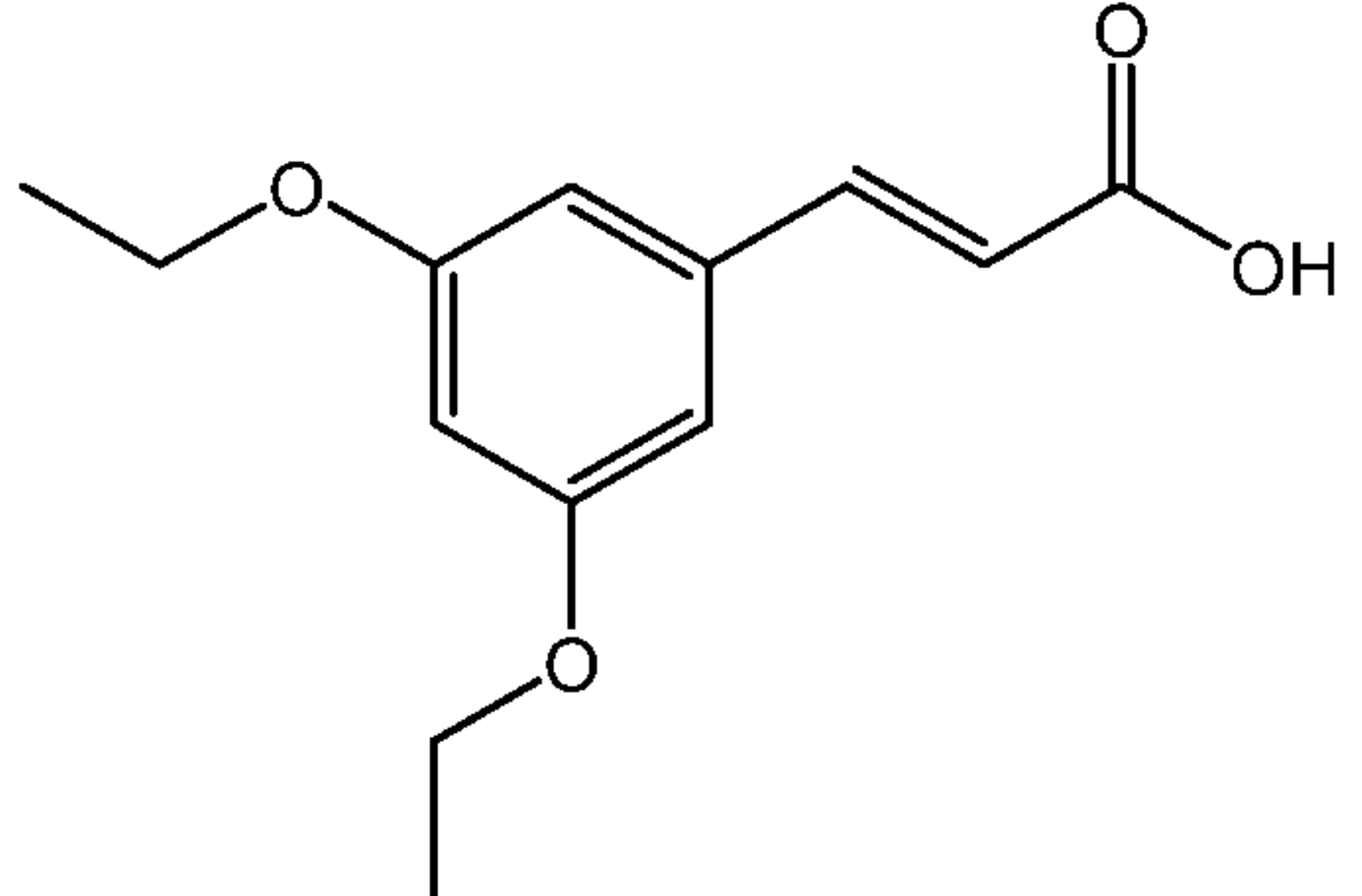
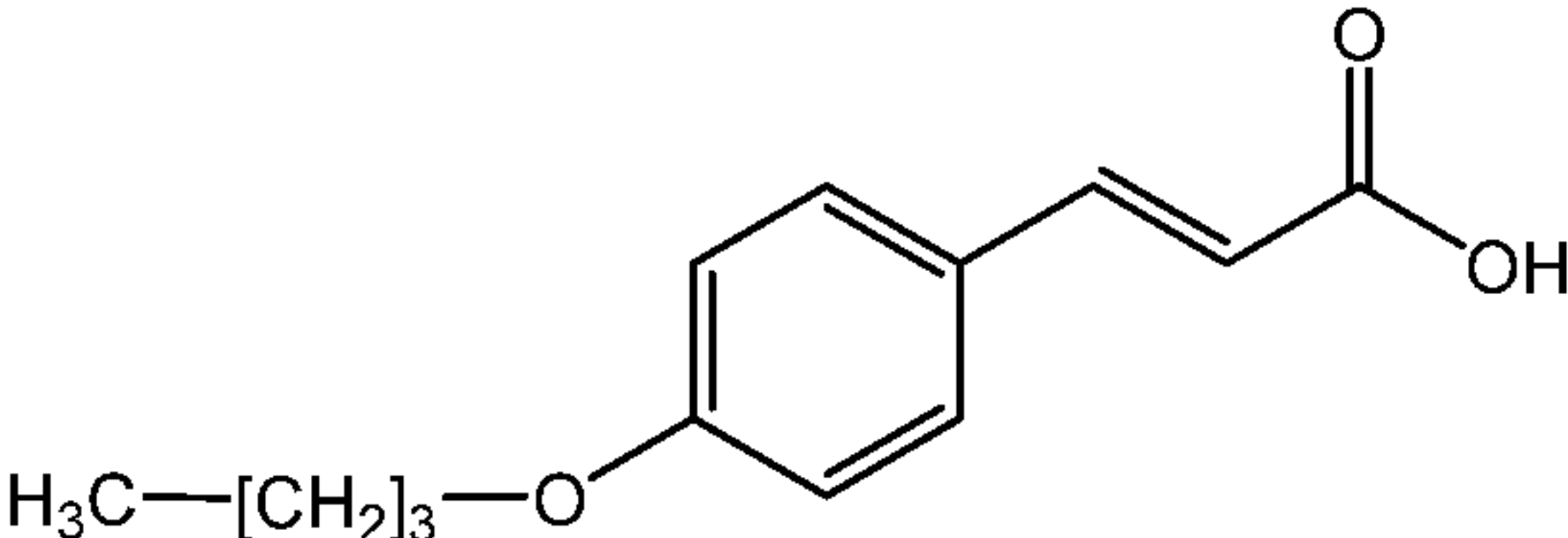
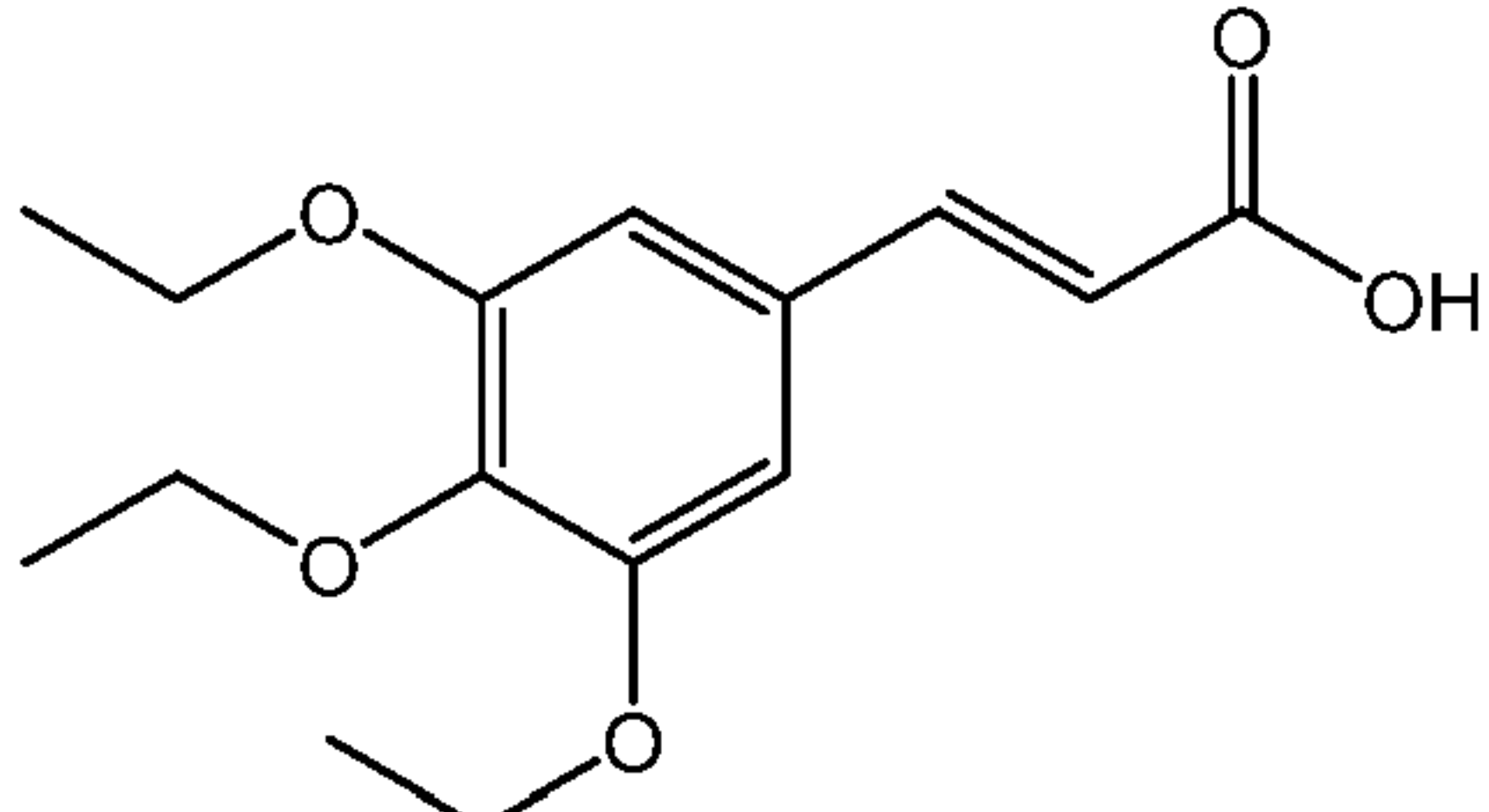
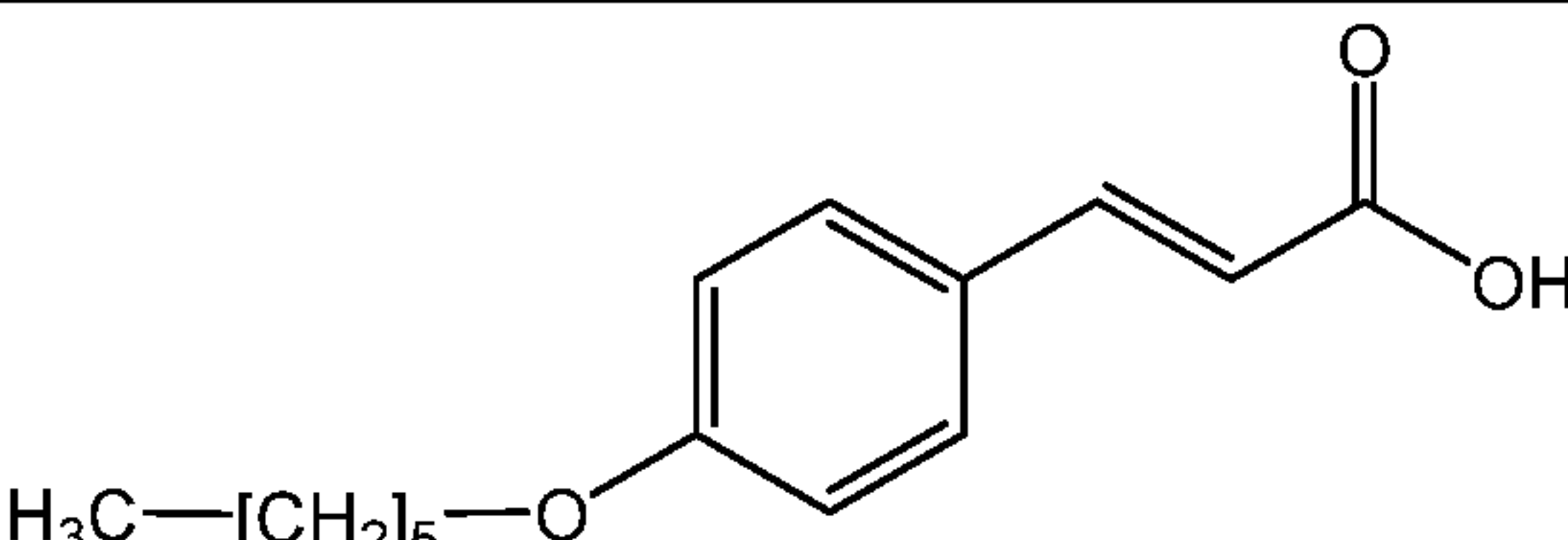
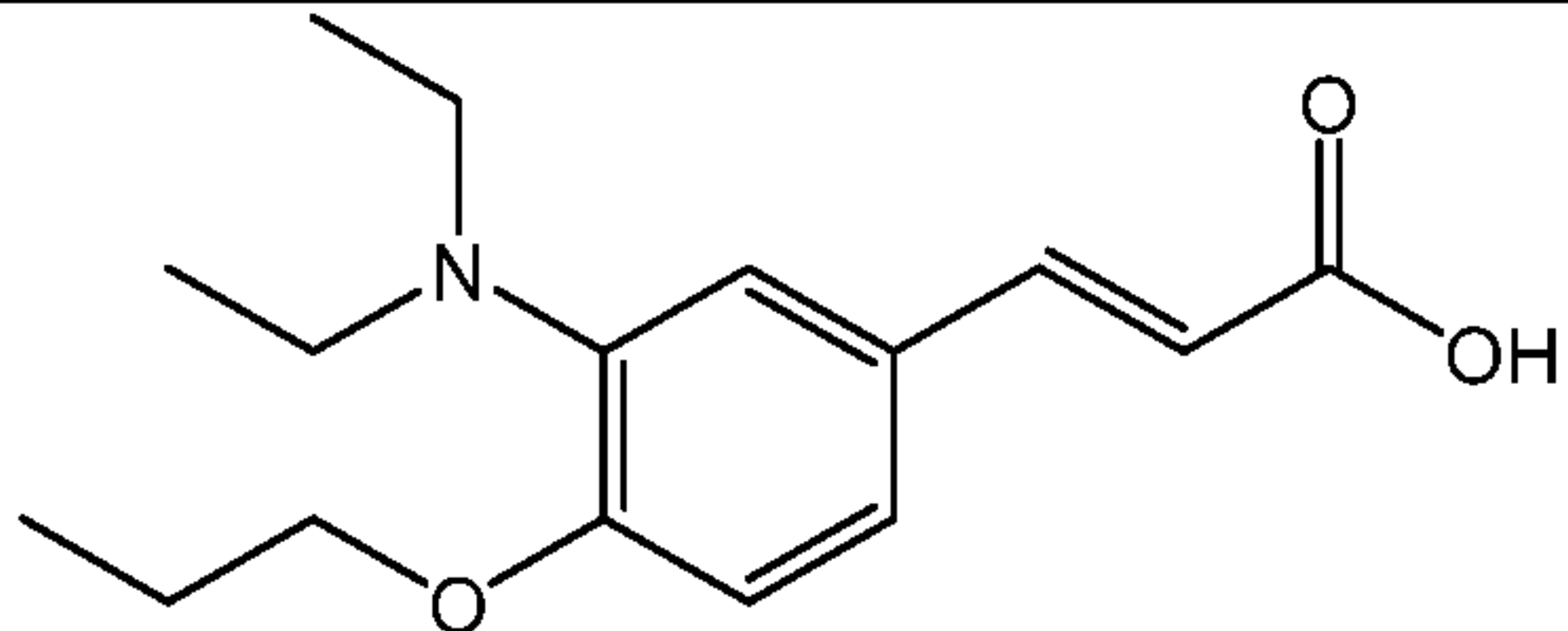
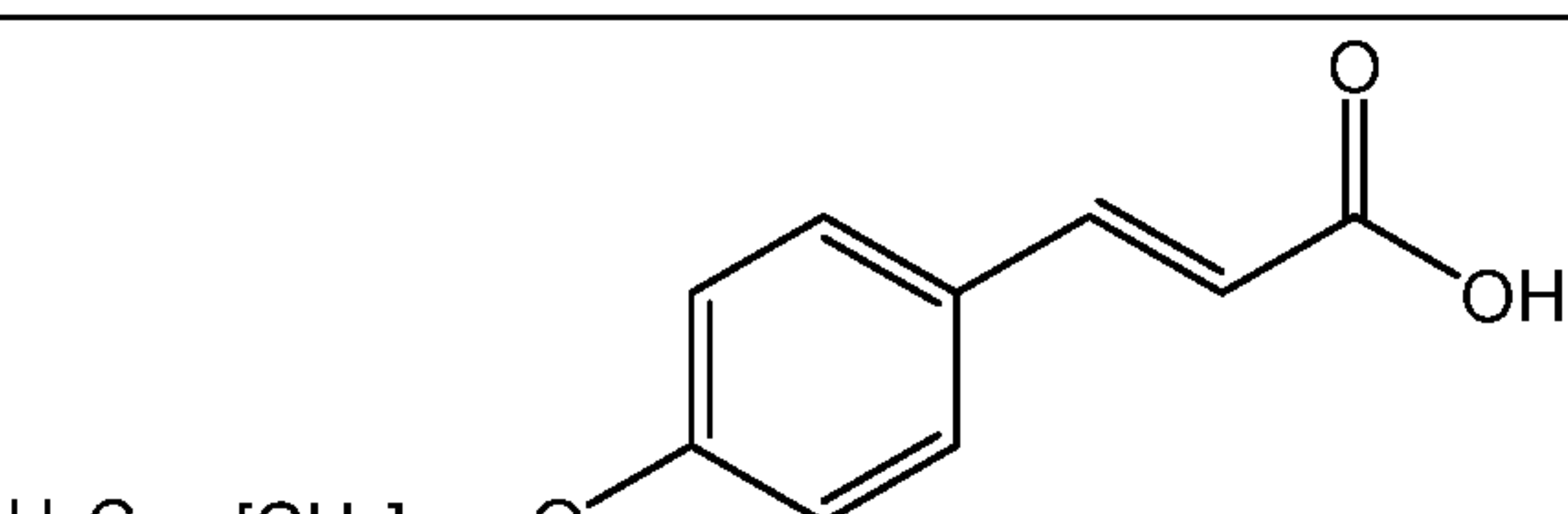
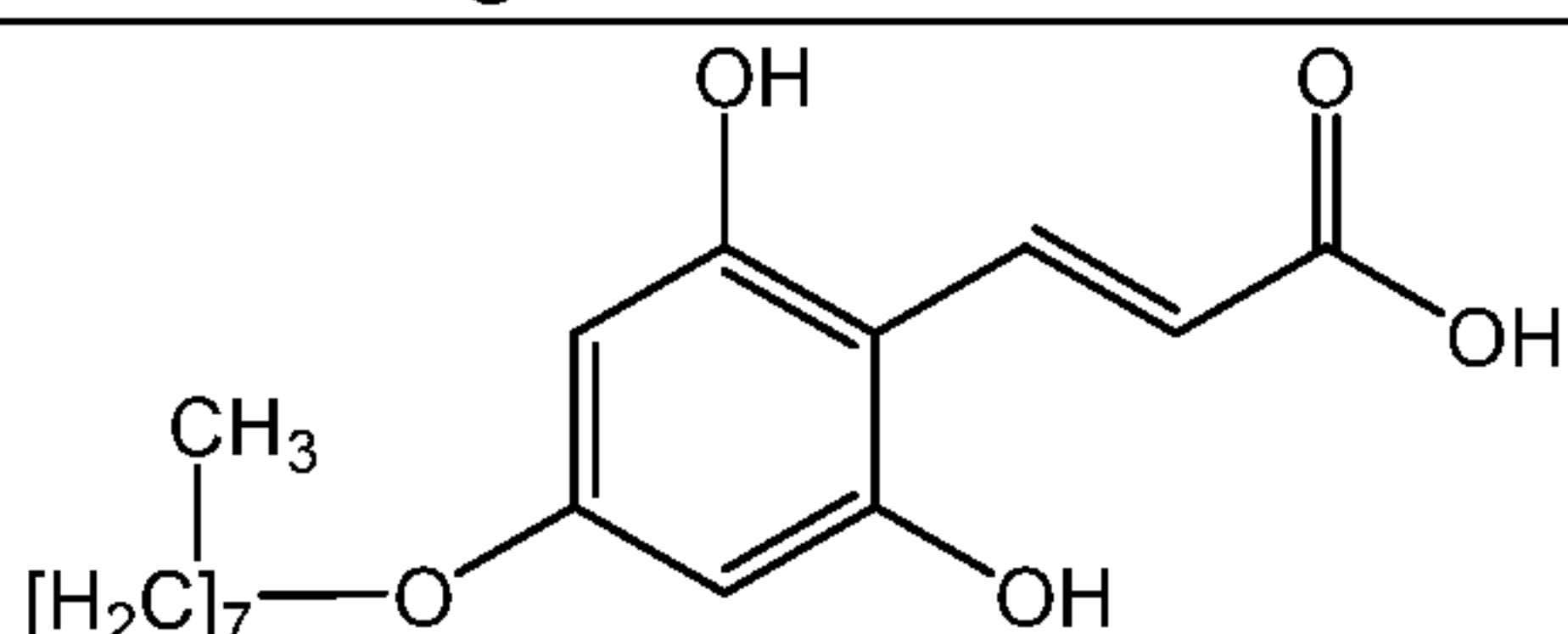
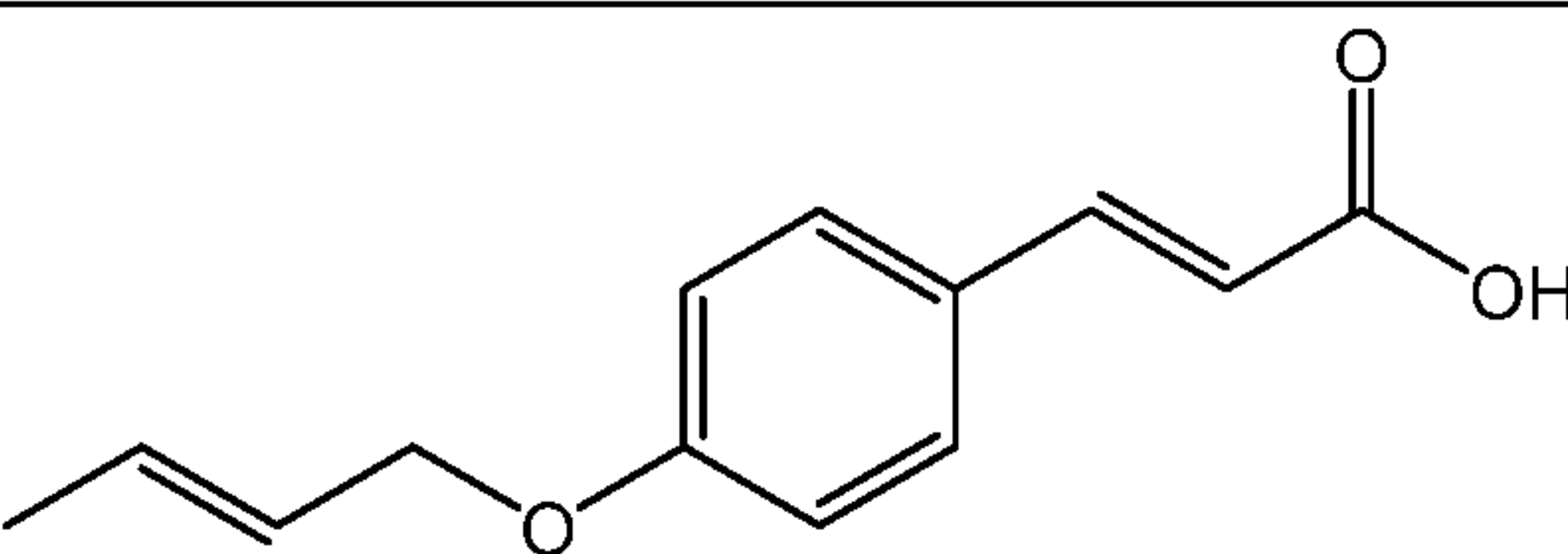
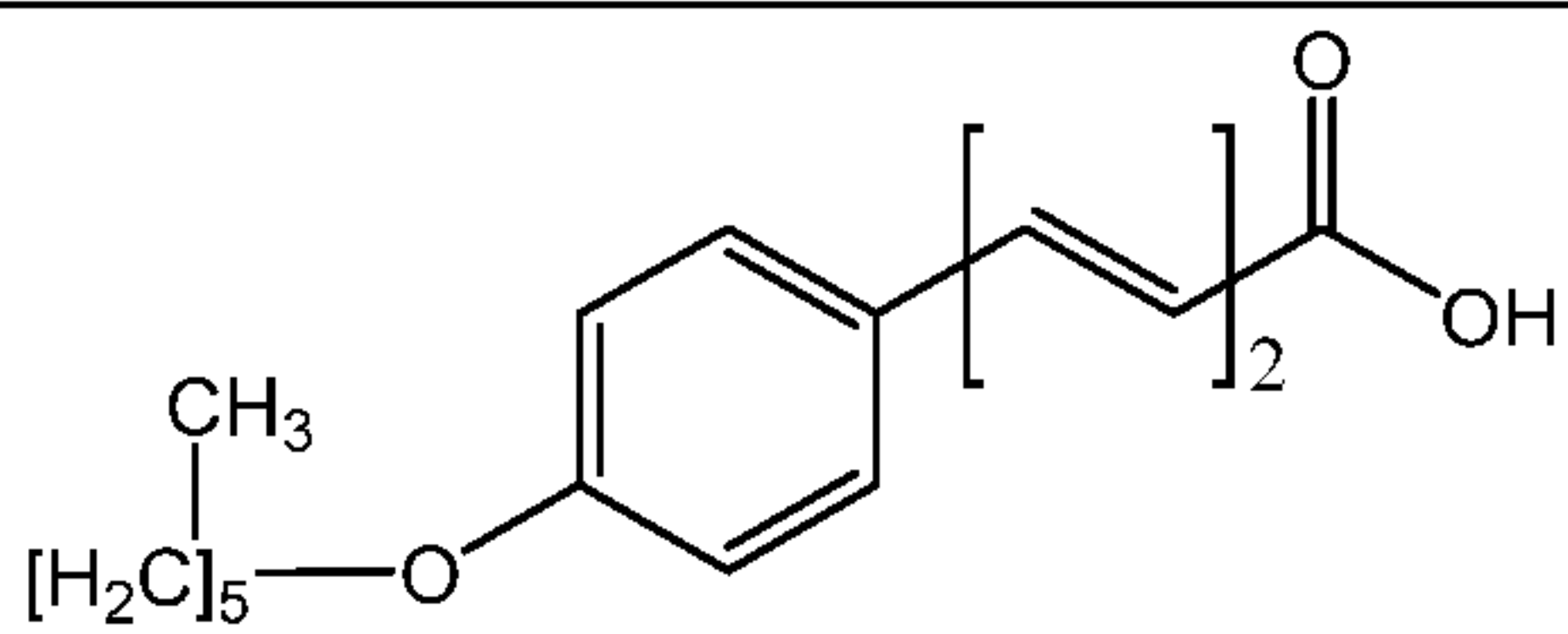
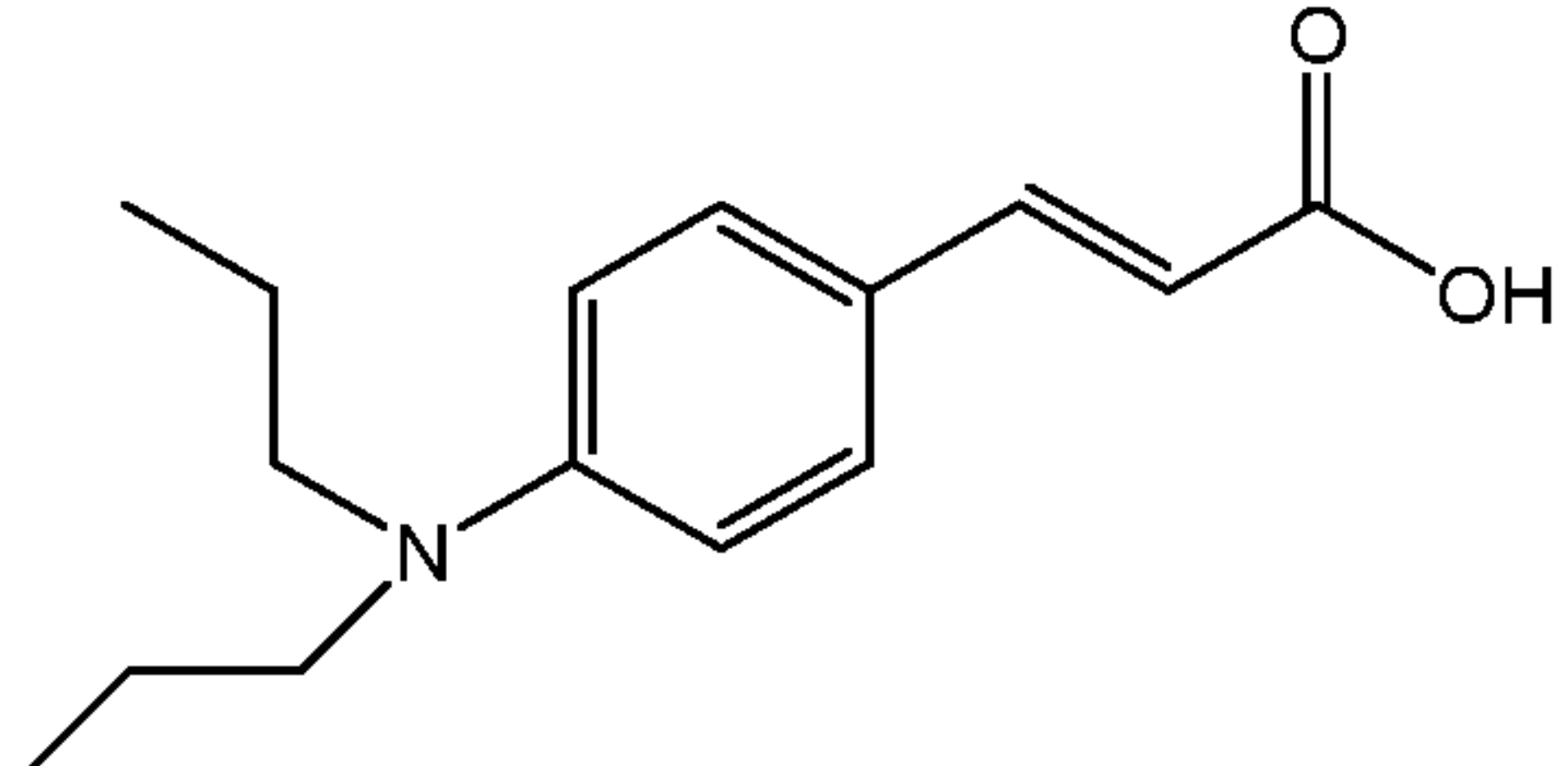
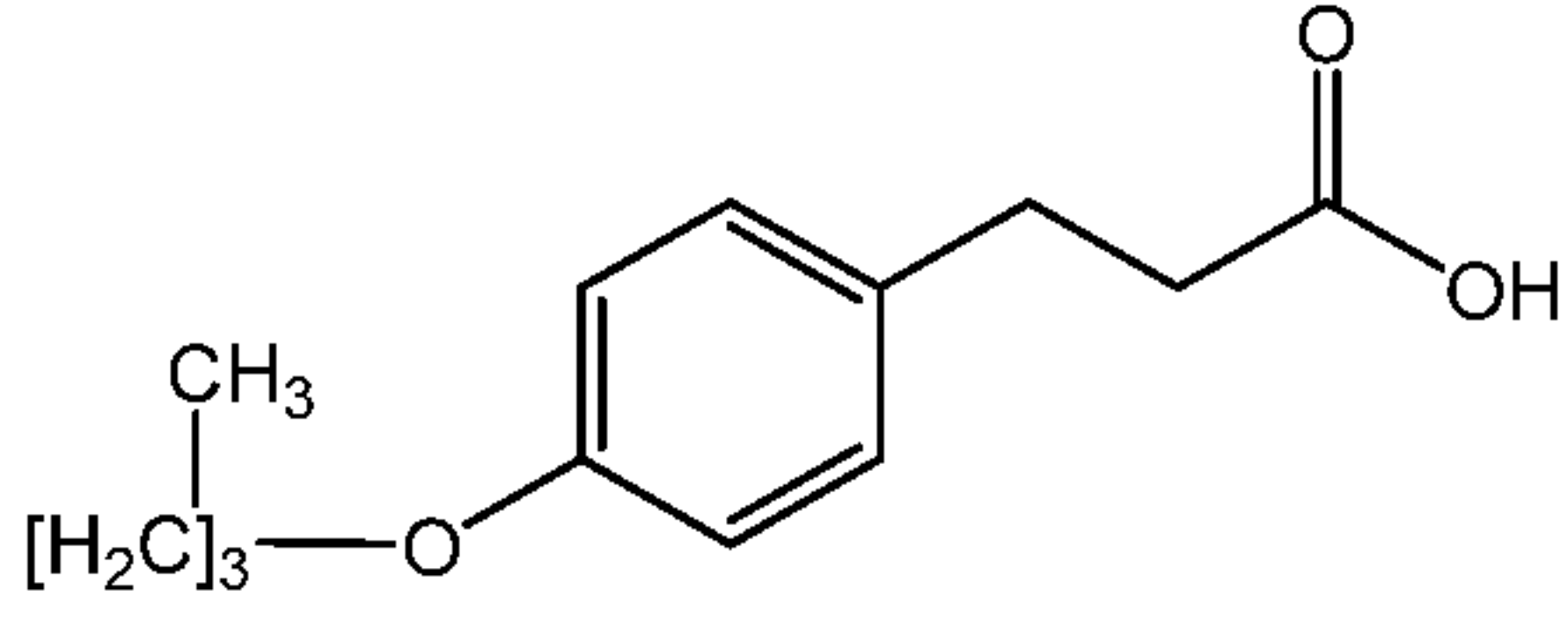
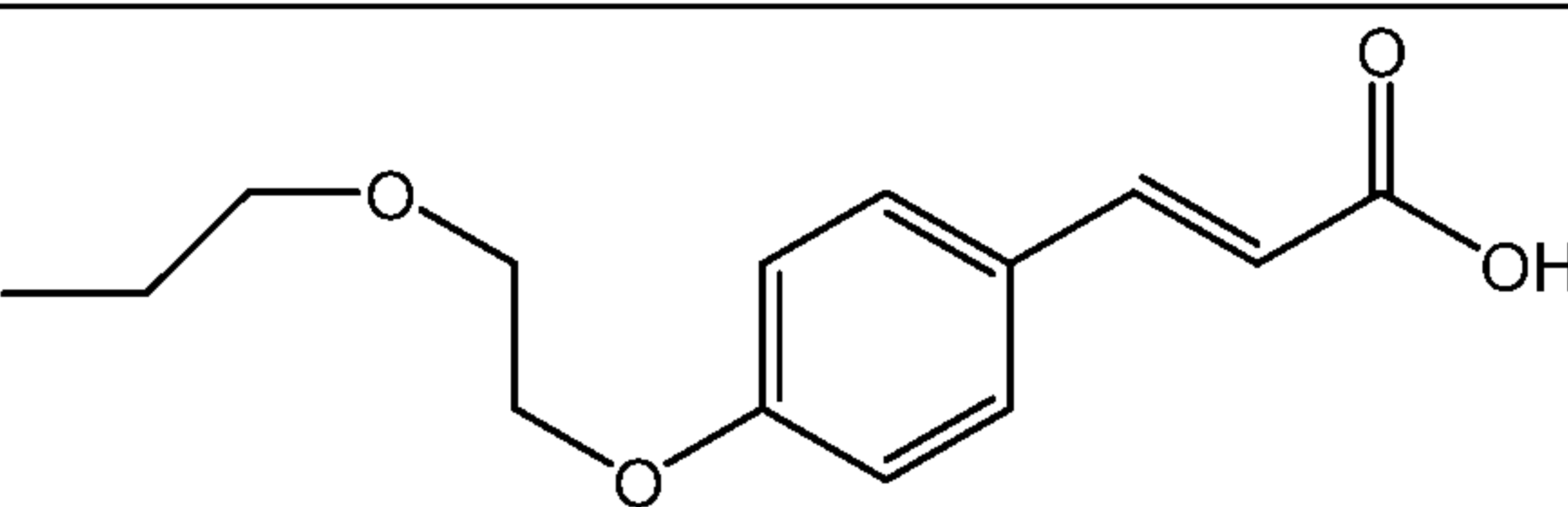
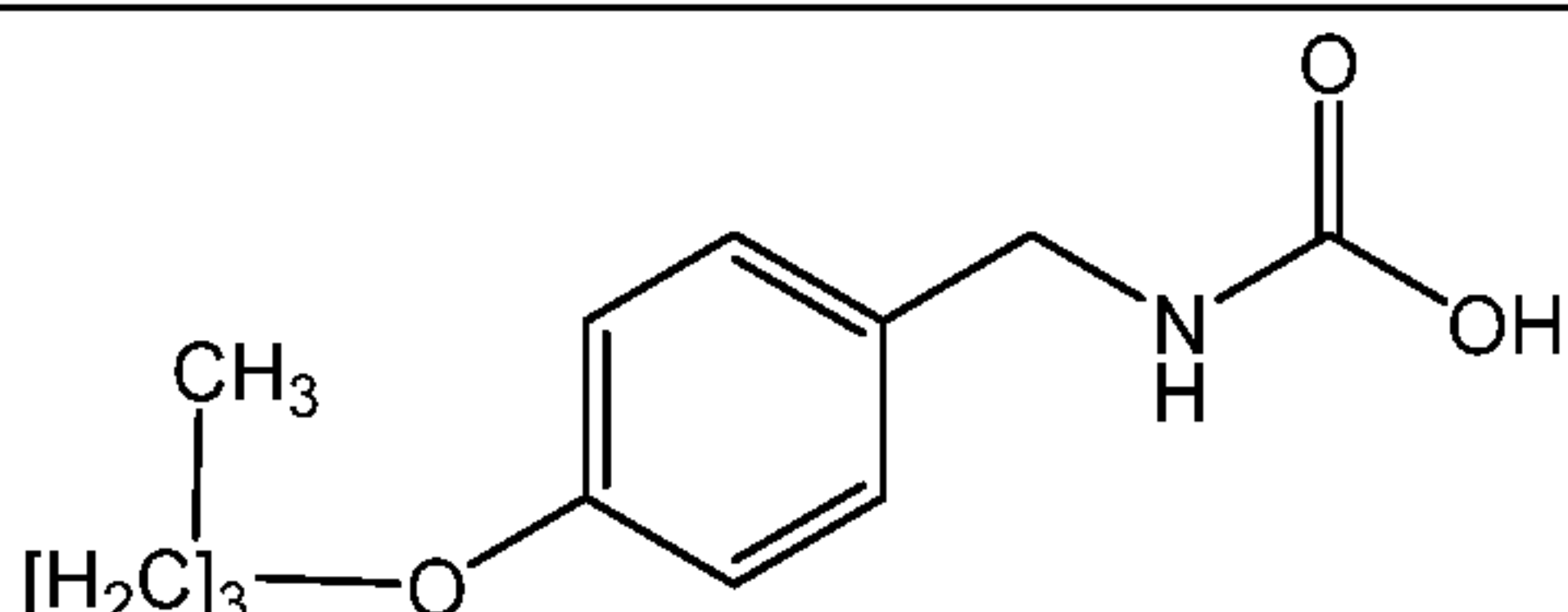
It will be appreciated that any of the above previous embodiments or examples for the carboxylic acid of Formula 1a or Formula 1a(i) in relation to  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$ , may also apply to the salt form as described above.

In one example,  $Y$  is an onium cation. In another example,  $Y$  may be selected from any of the onium cations as described herein.

The following Table 2 provides some further examples of carboxylic acids, which may be provided in a carboxylate form and/or used as a counter-anion with any other cation as described herein for forming an organic corrosion inhibitor of the present disclosure:

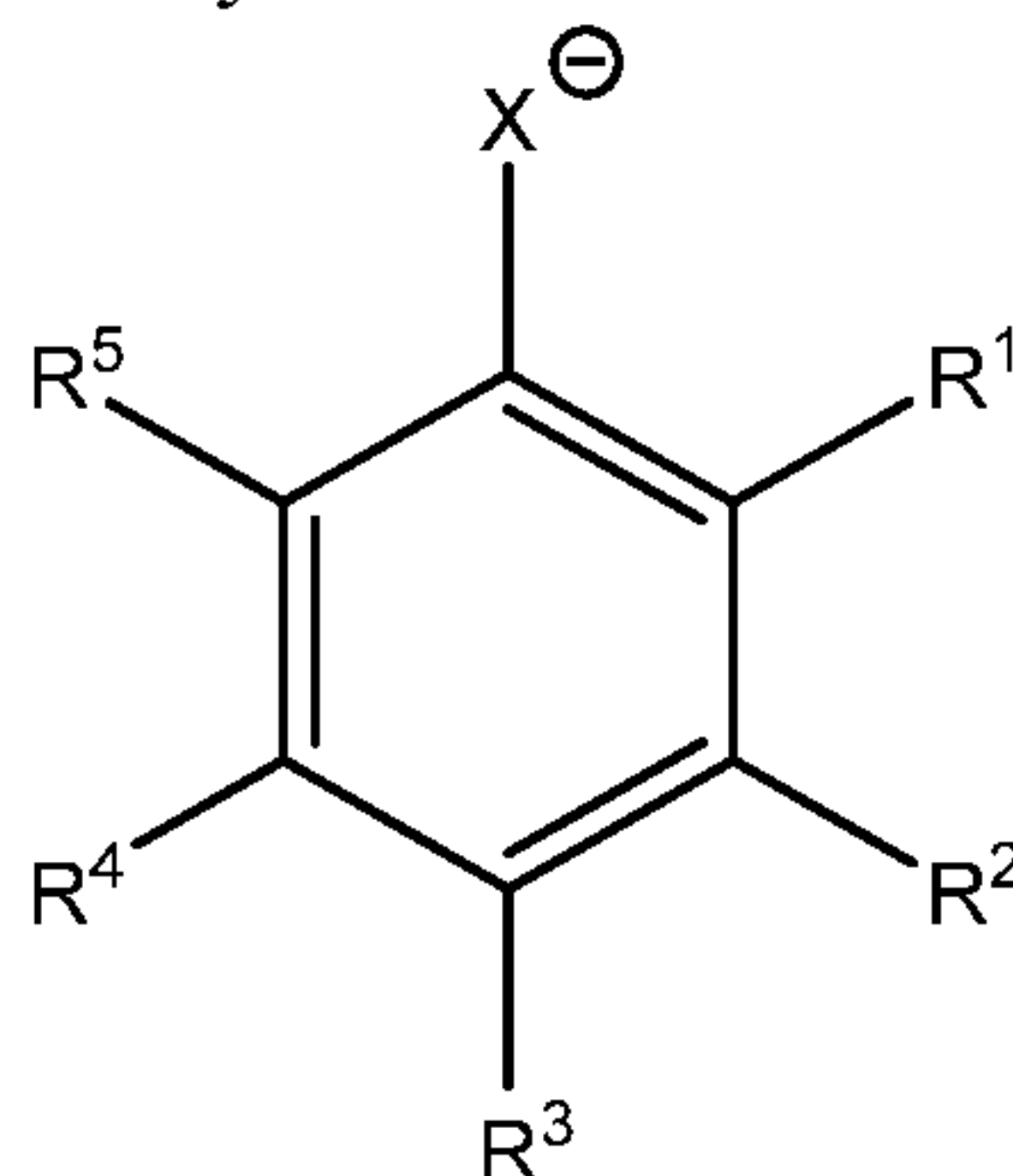
Table 2: Aromatic Carboxylic Acid and Carboxylate Examples

|                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                              |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>Chemical structure of 4-hydroxy-3-(4-hydroxyphenyl)acrylic acid: A benzene ring with a hydroxyl group (<math>HO-</math>) at the para position and a <math>trans</math>-alkene side chain (<math>-CH=CH-COOH</math>) at the other para position.</p> | <p>Chemical structure of 3-(3-hydroxyphenyl)acrylic acid: A benzene ring with a hydroxyl group (<math>HO-</math>) at the meta position and a <math>trans</math>-alkene side chain (<math>-CH=CH-COOH</math>) at the other meta position.</p> |
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Organic Corrosion Inhibitors

In another example, an organic corrosion inhibitor may comprise or consist of an onium cation and an aromatic carboxylate of Formula 1:



Formula 1

wherein

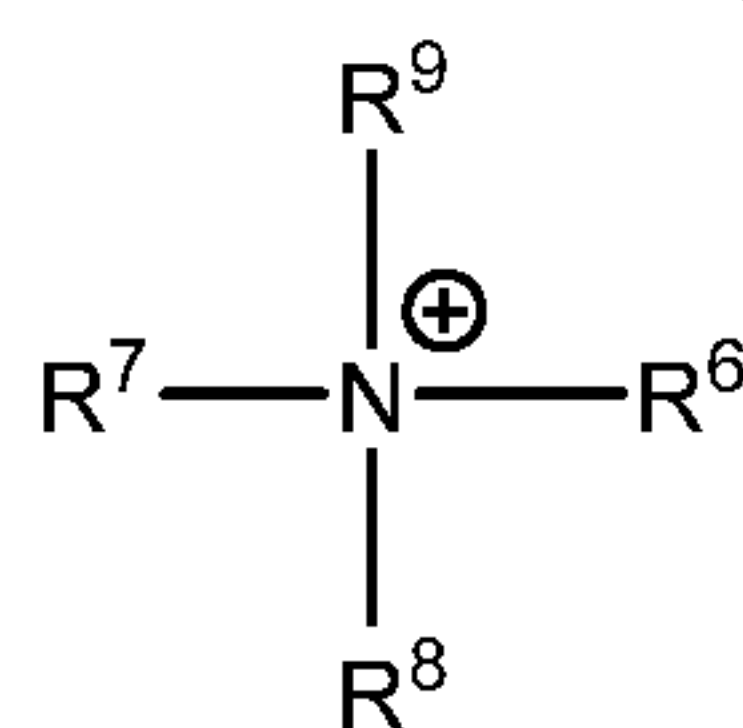
X is a carboxylate anion group;

R<sup>1</sup> and R<sup>5</sup> are hydrogen; and

R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

The onium cations may be selected from ammonium cation groups, pyridinium cation groups, imidazolium cation groups, pyrazolium cation groups, and pyrrolidinium cation groups. The onium cations may be quaternary onium cations. The onium cations may be quaternary ammonium cations.

In one embodiment, the ammonium cation groups may be of Formula 2a:



Formula 2a

wherein

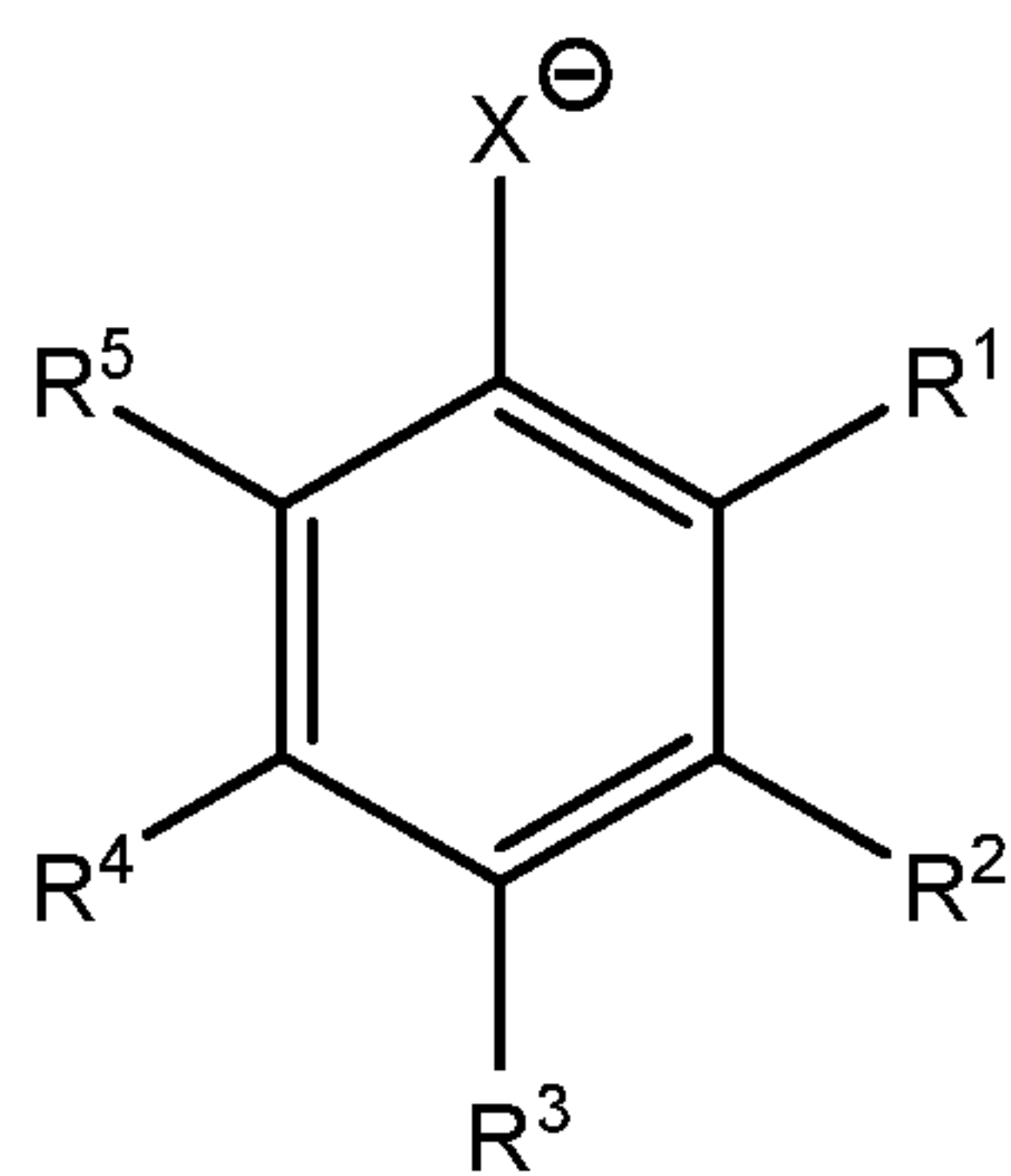
R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, heteroalkenyl, and wherein two or more groups may join together to provide an aromatic or aliphatic ring. Each alkyl or alkenyl may be optionally substituted, or optionally interrupted within one or more heteroatoms selected from O, N and S.

In another embodiment of Formula 2a, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from alkyl, alkenyl, heteroalkyl, heteroalkenyl and wherein two or more groups may join together to provide an aromatic or aliphatic ring. Each alkyl or alkenyl may be

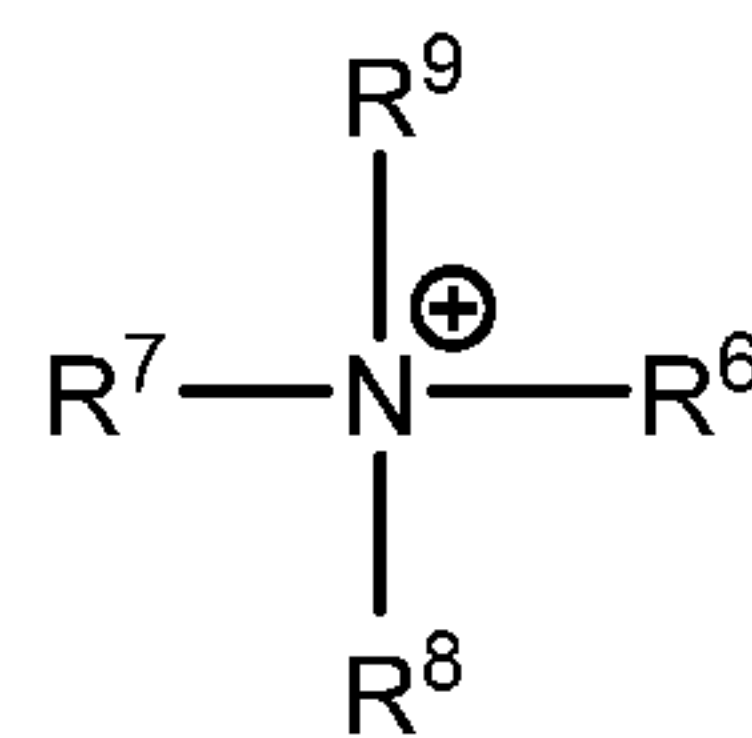
optionally substituted, or optionally interrupted within one or more heteroatoms selected from O, N and S.

In other embodiments, an organic corrosion inhibitor or ionic compound may be provided according to any combination of “Onium Cation Groups” with “Aromatic Carboxylate Groups” as described individually above for each of those groups.

In another embodiment, the organic corrosion inhibitor is provided by an ionic compound formed by an aromatic carboxylate counter-anion of Formula 1 and an onium cation of Formula 2a:



Formula 1



Formula 2a

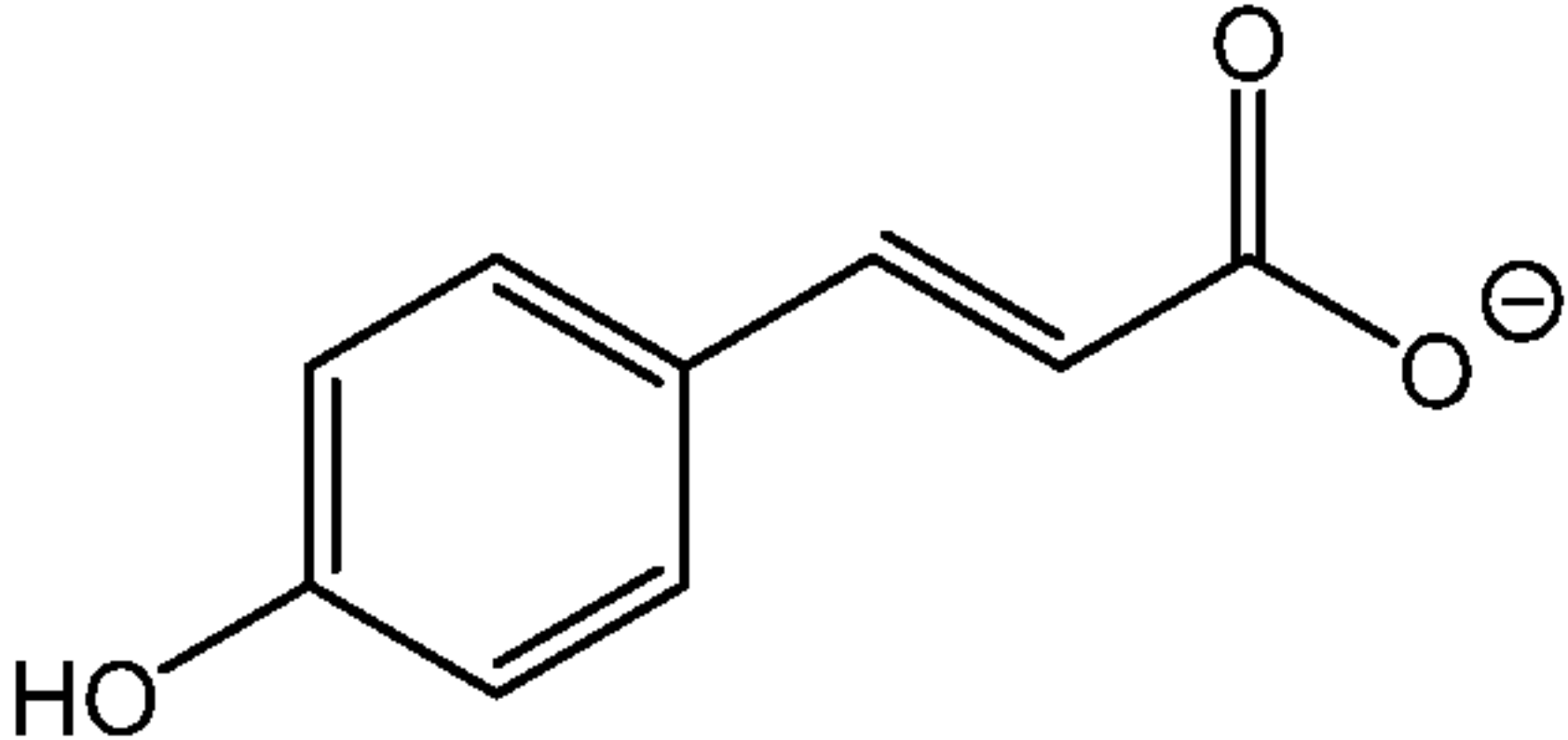
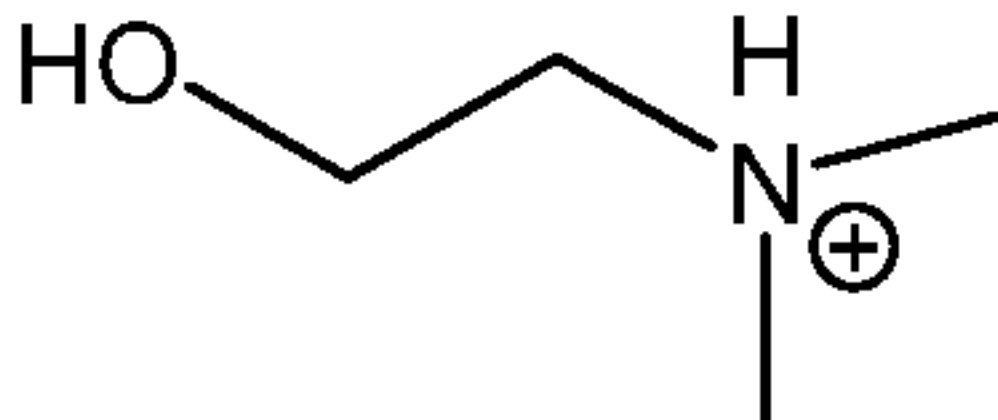
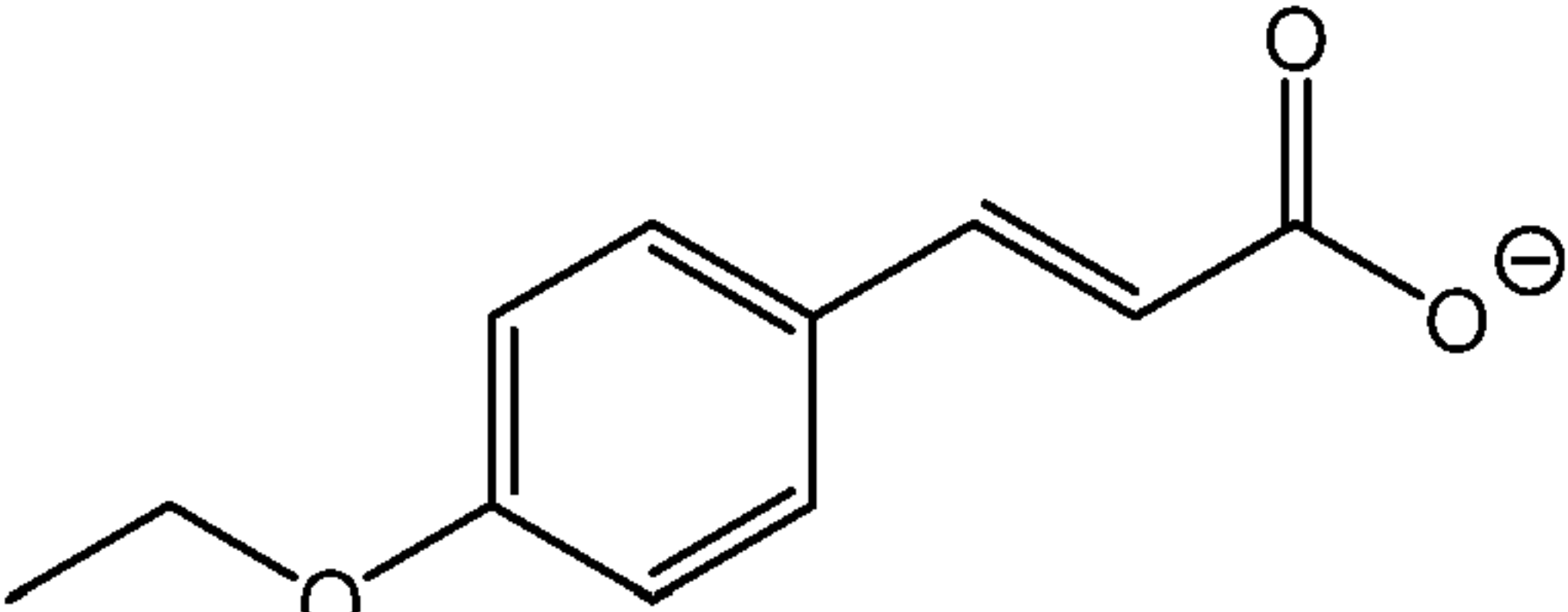
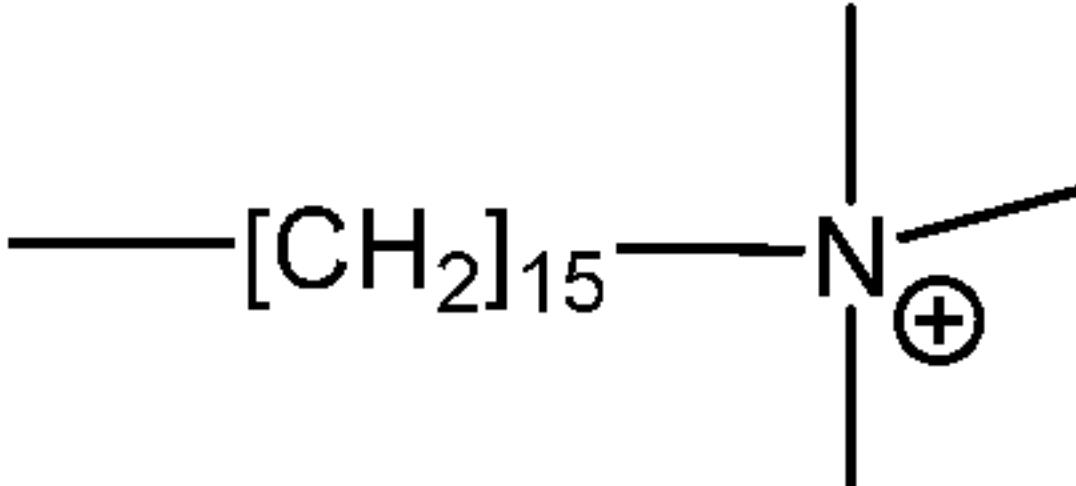
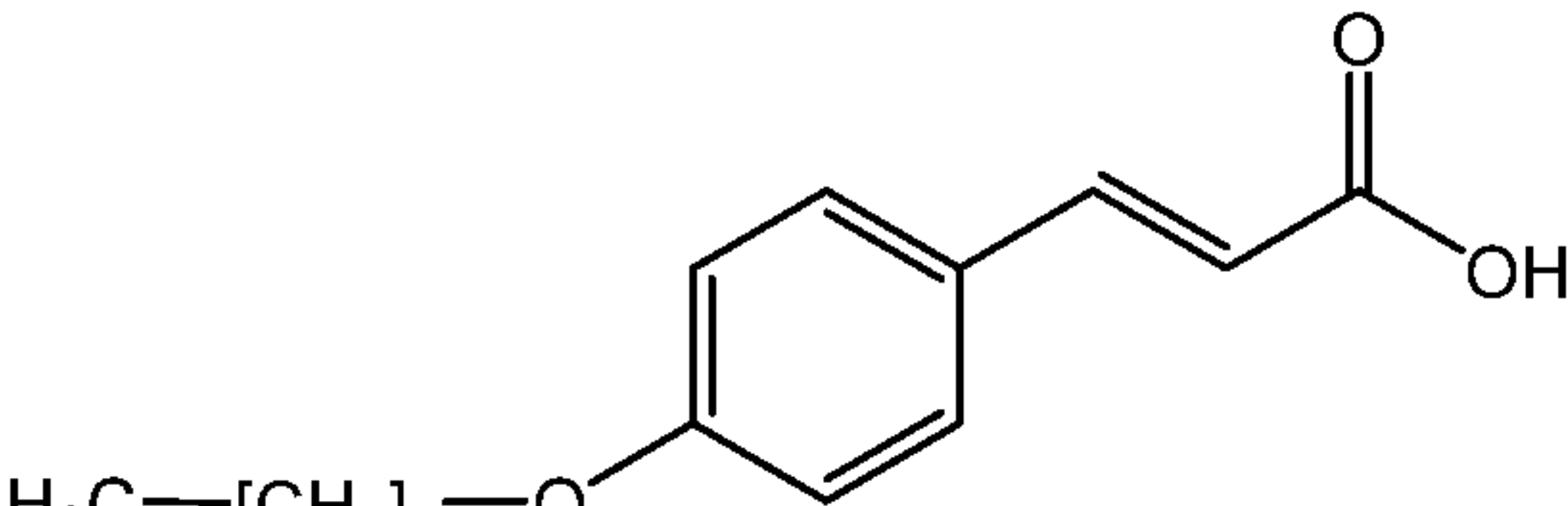
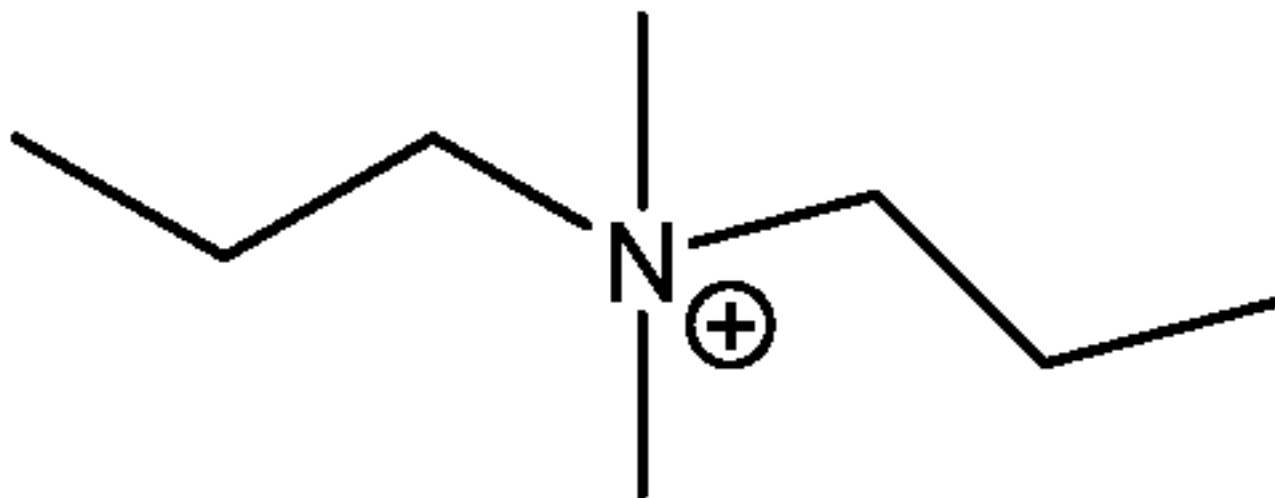
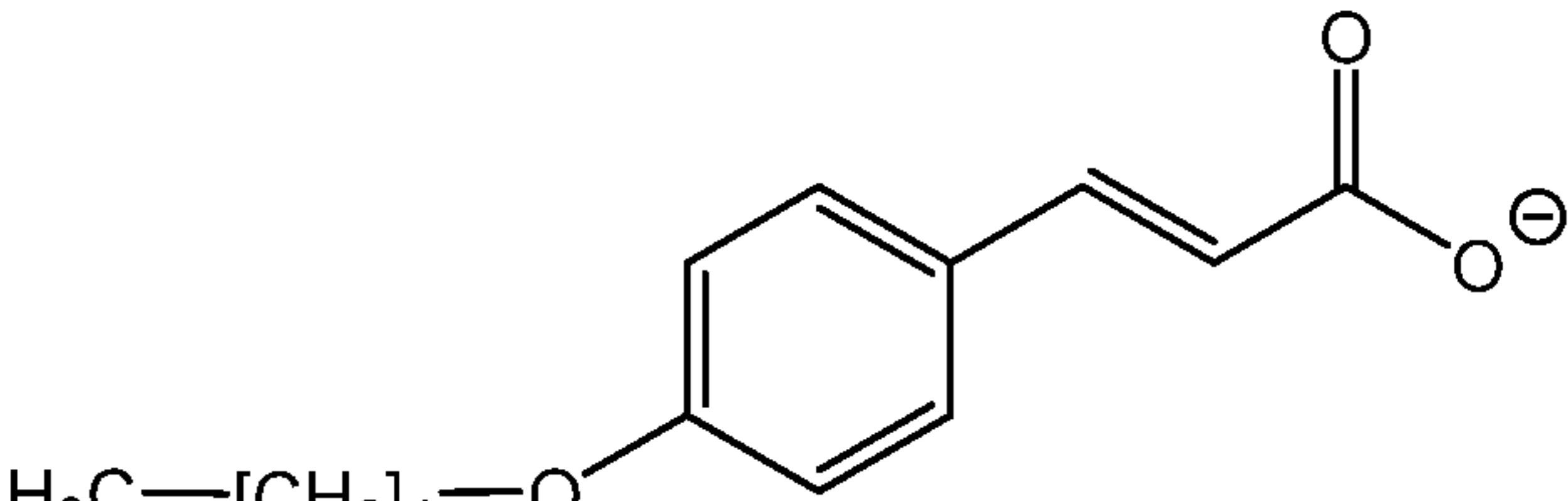
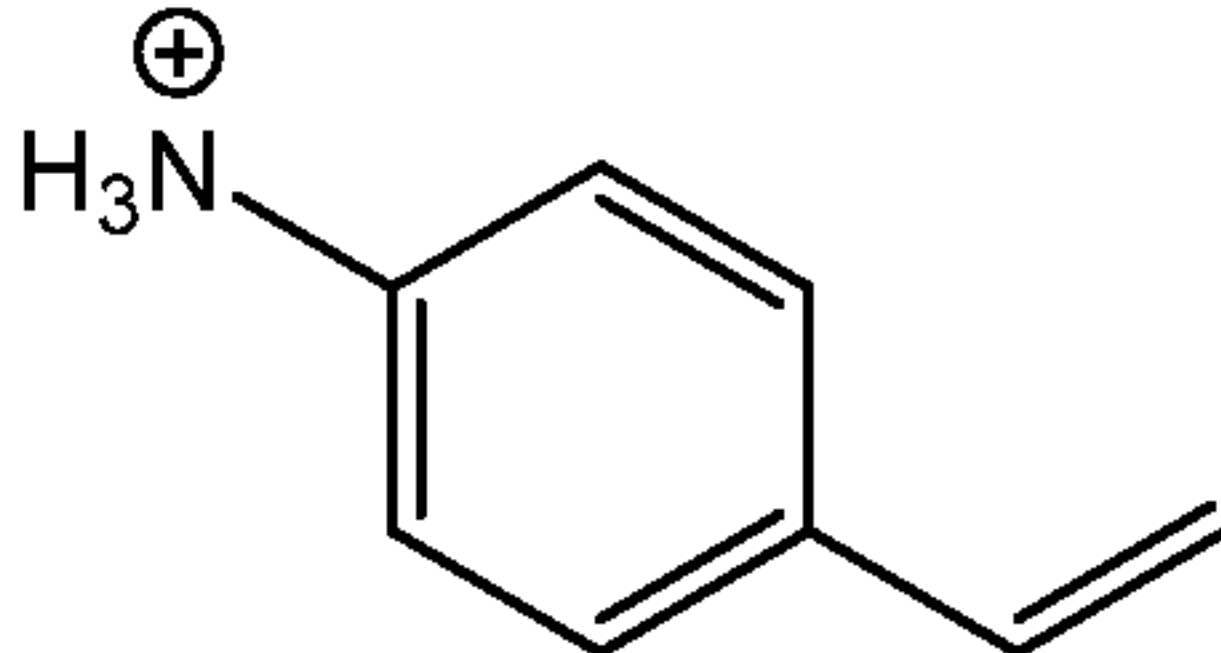
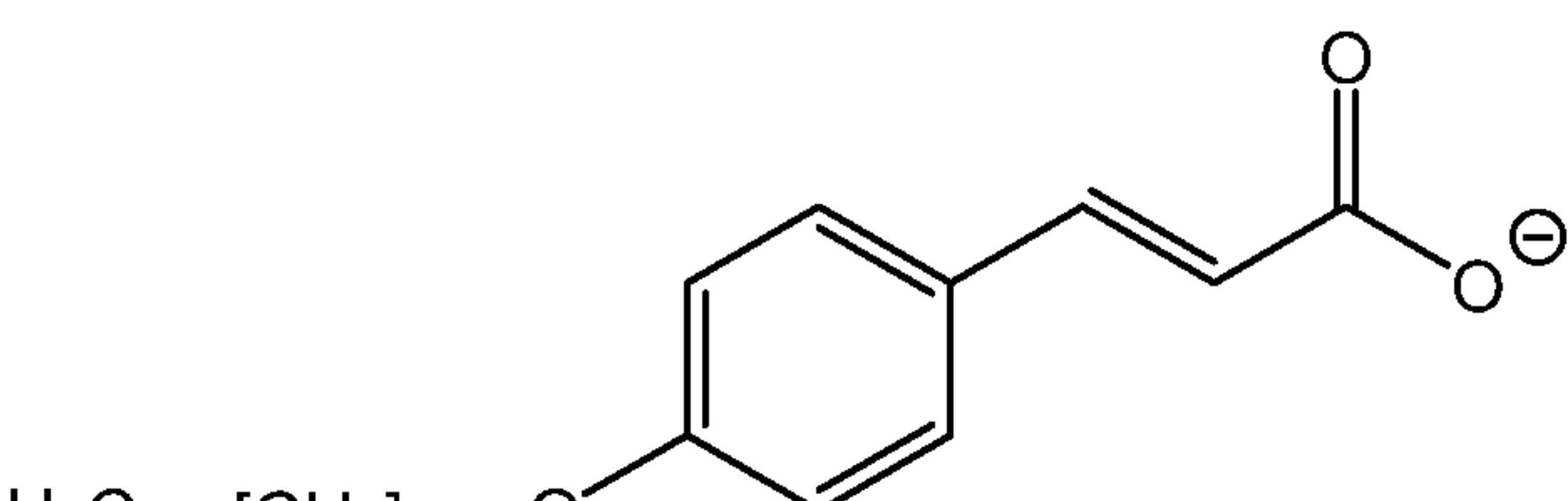
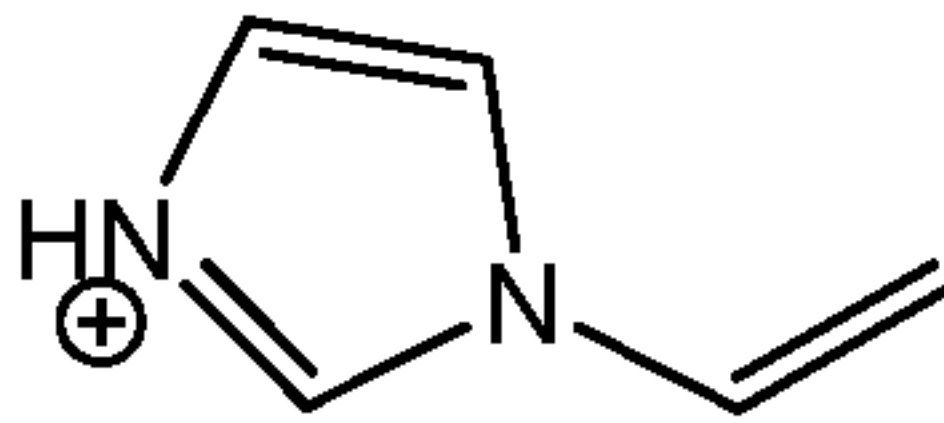
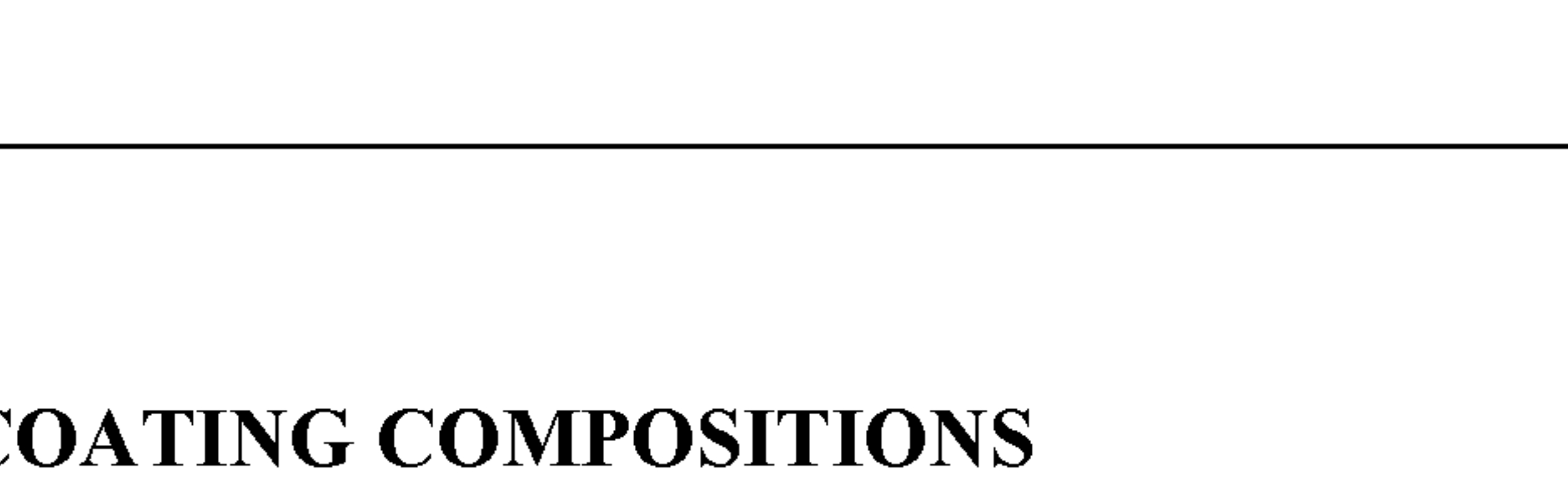
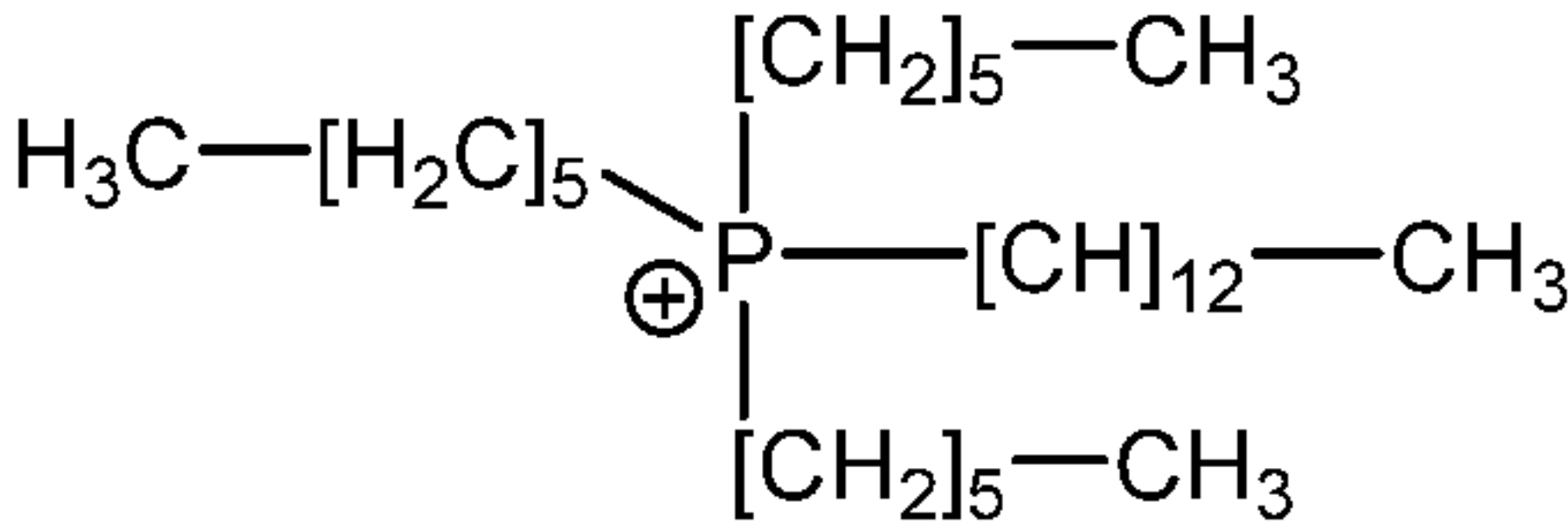
10

In some embodiments of the above organic corrosion inhibitor, Formula 1 and Formula 2 may be provided by any individual embodiments thereof as described herein. For example, X may be an optionally linked carboxylate anion group, R¹ and R⁵ may be hydrogen, R², R³, and R⁴ may each be independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl; and R⁶, R⁷, R⁸, and R⁹, may each be independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl.

20

The following Table 3 provides further specific examples of cation and anion combinations, where any one of the anions can be combined with any one of the cations that can be used in forming an organic corrosion inhibitor of the present disclosure:

Table 3: Anion and Cation Combination Examples

| ANIONS                                                                               | CATIONS                                                                               |
|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|     |    |
|   |    |
|  |  |
|  |  |
|  |  |
|  |  |

COATING COMPOSITIONS

A composition may comprise or consist of one or more organic corrosion inhibitors according to any embodiments or examples thereof as described herein, and optionally one or more additives.

The composition may be a coating composition such as a curable coating composition. A curable coating composition may comprise or consist of an organic film

former, one or more organic corrosion inhibitors according to any embodiments or examples thereof as described herein, and optionally one or more additives.

The composition may be a liquid formulation. In one example, there is provided a composition comprising or consisting of one or more solvents, one or more organic corrosion inhibitors according to any embodiments or examples thereof as described herein, and optionally one or more additives. The optional additives may also be provided according any of the embodiments or examples as described below. The organic corrosion inhibitor may be a solid, for example provided as a suspension in the liquid formulation.

The composition may be a solid formulation. In one example, there is provided a composition comprising or consisting of one or more solvents, one or more organic corrosion inhibitors according to any embodiments or examples thereof as described herein, and optionally one or more additives. The optional additives may also be provided according any of the embodiments or examples as described below.

The above formulations may be used for introduction or dosing into a pipe or conduit for providing corrosion protection. For example, an oil or gas pipe or conduit may be dosed with a formulation comprising the organic corrosion inhibitor. Another example is a water tank, such as a bilge water tank, which may be dosed with a formulation comprising the organic corrosion inhibitor. The compositions and formulations may be used in various industrial applications, for example water treatment processes, or industrial processes having acidic or low pH environments.

#### Organic Film Former

It will be appreciated that the “organic film former” comprises or consists of one or more polymeric constituents. The organic film former may comprise one or more organic corrosion inhibitors according to any embodiments or examples thereof as described herein.

Any polymeric constituents may consist of any polymers (e.g. copolymers) or polymerizable components, such as reactive monomers (e.g. resins) that can form polymers in the coatings. The polymeric constituents may consist of polymers, copolymers, resins, monomers and comonomers. Some examples of polymeric constituents include any one or more of polyolefins, polyurethanes, polyacrylic acids, polyacrylates, polyethers, polyesters, polyketides, polyamides, or any copolymers thereof.

The organic film former does not itself cover any additive as described below (e.g. inorganic filler, or wetting agent etc.). For example, if any monomers, co-monomers,

resins, copolymers, and polymers, are present in the composition, formulation or coating thereof, then it is understood those prospective constituents are encompassed by the term “organic film former”. In examples where the organic film former “consists of” one or more specified constituents, then it will be appreciated that the absence of a prospective  
 5 polymeric constituent being explicitly specified in the organic film former means the absence of that polymeric constituent from the composition, formulation or coating thereof. In other words, when the term “consists of” is used so only those polymeric constituents specified to consist in the organic film former are present in the composition, formulation or coating thereof.

10 The organic film former (in wt % of the total composition or coating) may comprise between about 40 and 99, 50 and 95, or 60 and 90. The organic film former (in wt % of the total composition or coating) may comprise at least 30, 35, 40, 45, 50, 60, 65, 70, 75, 80, 85, 90, 95, or 98. The organic film former (in wt % of the total composition or coating) may comprise less than about 99, 98, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50,  
 15 45, 40, or 35. The organic film former (in wt % of the total composition or coating) may be in a range provided by any two of these upper and/or lower values.

The organic corrosion inhibitor (in wt % of the total composition or coating) may comprise between about 1 and 50, 5 and 45, or 10 and 30. The organic corrosion inhibitor (in wt % of the total composition or coating) may comprise at least 1, 5, 10, 15, 20, 25,  
 20 30, 35, 40, 45, or 50. The organic corrosion inhibitor (in wt % of the total composition or coating) may comprise less than about 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5. The organic corrosion inhibitor (in wt % of the organic film former) may be in a range provided by any two of these upper and/or lower values.

### Optional Additives

25 In some embodiments or examples, the above compositions or formulations further comprises or further consists of one or more optional additive(s).

Other than solvents, the additive(s) are usually present in an amount of less than about 15% based on the weight of the composition.

The additive(s) are usually present in an amount of less than about 15% based on  
 30 the weight of the composition or the organic film former. For example, the amount of all additives combined, if present, may be provided in an amount of less than about 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, 0.5%, 0.1%, or 0.05%. The additives may be provided in an amount of greater than about 0.01%, 0.05%, 0.1%, 0.5%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, or 9%. The amount of all additive(s),  
 35 if present, may be provided in an amount (based on the total weight of composition) of a

range between any two of the above values, for example between about 0.01% and 10%, between about 0.05% and 5 %, between about 0.1% and about 3%, or between about 0.5% and 2%.

Any reference to “substantially free” generally refers to the absence of a compound in the composition other than any trace amounts or impurities that may be present, for example this may be an amount by weight % in the total composition of less than about 1%, 0.1%, 0.01%, 0.001%, or 0.0001%. The compositions as described herein may also include, for example, impurities in an amount by weight % in the total composition of less than about 5%, 4%, 3%, 2%, 1%, 0.5%, 0.1%, 0.01%, 0.001%, or 0.0001%.

As further described below in relation to the process conditions for application, in at least some examples the present coating compositions are configured to provide a minimum film forming temperature (MFT) for ambient conditions. For example, the MFT of various coating compositions may be provided at about 0 to 40 °C, 5 to 35 °C, 10 to 30 °C, 15 to 25 °C, or about 20 °C.

It will be appreciated that all the additives are optional and may be added to further enhance application of the coating compositions and/or further enhance performance characteristics of the completed coating system (e.g. composition, substrate, or coating). Examples of suitable additives may include any one or more of the following:

- i. polymerisation initiators;
- ii. adhesion promoters;
- iii. solvents;
- iv. organic cross-linkers;
- v. inorganic fillers;
- vi. wetting agents;
- vii. rheology modifiers;
- viii. surfactants;
- ix. dispersants;
- x. anti-foaming agents;
- xi. anti-corrosion reagents;
- xii. stabilizers;
- xiii. levelling agents;
- xiv. pigments; and
- xv. colorants.

Each of the individual additives are described in further detail below, and may be independently provided in the composition according to any examples or embodiments

as described herein. As mentioned, the composition may be a formulation, such as a liquid formulation, for which the following examples and embodiments may apply.

The coating composition can be provided as a coating formulation for commercial and industrial application. A coating formulation can be prepared by dissolving or  
5 dispersing the coating compositions, in an appropriate solvent and then mixing them together optionally with one or more additives or dissolving the compositions into a suitable solvent under suitable processing conditions. The coating formulation can be prepared from a multi-part composition which can be pre dissolved in suitable solvents, and which can then be pre-mixed together prior to application of the coating composition  
10 to the coated substrate. In an alternative embodiment, the coating composition can be formulated into a one-part stable dispersion, which for example would not require premixing before application. For example, the composition as described herein may be a liquid formulation, such as liquid suspension formulation or liquid dispersion formulation.

15 The coating composition may be applied in different physical forms such as a solution, dispersion, suspension, mixture, aerosol, emulsion, paste or combination thereof, solutions or dispersions or emulsions are preferred.

#### Polymerisation Initiators

20 A polymerisation initiator may be used. Herein “initiator” or “polymerisation initiator” refers to a chemical compound that reacts with a monomer to form an intermediate compound which capable of linking successively with a large number of other monomers into a polymeric compound. The terms “initiator” and “polymerisation initiator” may be used interchangeably within the context of this application.

25 Depending on the techniques used for preparing the polymers, different initiator agents can be used. In some embodiments a free radical initiator may be used, wherein free radicals are generated by chemical and/or radiation means. Several types of compounds can initiate polymerisation reactions by decomposing to form free radicals. These compounds include: azo-containing compounds, carboxylic peroxyacids and  
30 peroxyesters, alkyl hydroperoxides, and dialkyl and diacyl peroxides, among others. Examples of initiators have been described (Reference: W. D. Cook, G. B. Guise, eds. “Polymer Update: Science & Engineering”, Australian Polymer Science Series Volume 2, Polymer Division, Royal Australian Chemical Institute, printed by Adams Printers, Victoria, Australia, 1989, Chapter 2, pp. 19-66). In one embodiment an initiator is  
35 selected from a peroxide or an aliphatic azo compound. The polymerisation initiator may be provided in the composition in an amount (based on wt % of composition) of at least

about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. In an embodiment, the polymerisation initiator is provided in the composition in an amount (based on wt % of composition) of about 0.1 to 10, 0.5 to 6, 1 to 5, or 2 to 4.

#### 5 Adhesion Promoter

Various adhesion promoters may be used. In one example, there is provided an acid based adhesion promoter, for example siloxane. The adhesion promoter may be provided in the composition in an amount (based on wt % of composition) of at least about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. In an embodiment, the adhesion promoter is  
10 provided in the composition in an amount (based on wt % of composition) of about 0.1 to 10, 0.5 to 6, 1 to 5, or 2 to 4.

#### Solvent

The organic corrosion inhibitor and one or more optional additive may be dissolved or otherwise dispersed in a solvent to obtain the composition. The solvent may  
15 be a single solvent or a mixture of solvents. Useful solvents include water and/or an organic solvent. Organic solvents can be selected from but not limited to solvents containing groups selected from ketones such as methyl propyl ketone and methyl ethyl ketone; alcohols such as ethanol, isopropanol, tert-butyl alcohol, benzyl alcohol and tetrahydrofurfuryl alcohol; ethers such as glycol ethers, for example di(propylene  
20 glycol)dimethyl ether; and/or esters.

Organic solvents such as ethylene glycol ethers or propylene glycol ether can be added to assist in reducing the surface tension and improving the wetting and film forming. Examples include Dow glycol ethers including Cellosolve™ family solvents (such as ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethylene  
25 glycol monohexyl ether), Carbitol™ family solvents (diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether or diethylene glycol monohexyl ether), Ecosoft™ and Dowanol™ such as propylene glycol propyl ether (PnP), propylene glycol butyl ether (PnB), dipropylene glycol propyl ether (DPnP) dipropylene glycol methyl ether (DPM).

30 The solvent may be provided in the composition in an amount (based on wt % of composition) of at least about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 98, or 99. In an embodiment, the solvent is provided in the composition in an amount (based on wt % of composition) of about 50 to 99, 80, to 98, 85 to 97, or 90 to 95.

### Organic Crosslinker

The coating and composition as described herein may also include an organic crosslinker. The organic crosslinker may be incorporated into the composition prior to application on a coated substrate. Suitable crosslinkers are organic compounds or  
5 oligomers comprising of at least two groups capable of reacting with the acid functionalities of the organic polymer. Examples of organic crosslinkers include, but are not limited to aziridine, carbodiimide, epoxy, isocyanate and anhydride. In some embodiments, the composition comprises between 1 and 15 wt % crosslinker.

### Inorganic Fillers

10 The coatings and compositions described herein may comprise an optional inorganic filler. The inorganic filler is selected from but not limited to silica, alumina oxide, titania oxide, clays such as Montmorillonite, laponite and layered double hydroxide. The particle size of an inorganic filler varies from micro meter to sub micro meter, and in one embodiment can be from 0.5 to 500 nanometre or from 1 to 100 nm.  
15 In one example the particle size is from 1 to 50 nm.

### Wetting Agent

Surface finish can be important for the successful application of decorative coatings, and surface wetting agents can provide further advantages to the coatings or coating compositions. Addition of a wetting agent can also be useful in industrial  
20 application for improved control of drying time and obtaining a broader operation window.

Accordingly, the coating or coating composition as described herein may further include a wetting agent. The wetting agent may be incorporated into the coating composition prior to application on a coated substrate. Suitable wetting agents include,  
25 but are not limited to, ethers including glycol ethers (e.g. propylene glycol methyl ether (Dowanol PM) or propylene glycol propyl ether (Dowanol PnP), dipropylene glycol propyl ether (DPnP), propylene glycol butyl ether (PnB), dipropylene glycol butyl ether (DPnB), propylene glycol phenyl ether (PPh)).

### Rheology Modifiers

30 Rheology modifiers may include hydroxypropyl methyl cellulose (e.g. Methocel 311), modified urea (e.g. Byk 411, 410), cellulose acetate butyrates (e.g. Eastman<sup>TM</sup> CAB-551-0.01, CAB-381-0.5, CAB-381-20), and polyhydroxycarboxylic acid amides (e.g. Byk 405).

Surfactants

Surfactants may include fatty acid derivatives (e.g. AkzoNobel, Bermadol SPS 2543), quaternary ammonium salts, ionic and non-ionic surfactants.

Dispersants

- 5 Dispersants may include non-ionic surfactants based on primary alcohols (e.g. Merpol 4481, DuPont) and alkylphenol-formaldehyde-bisulfide condensates (e.g. Clariants 1494).

Anti-Foaming Agents

Anti-foaming agents may include BKY®-014, BKY®-1640.

10 Anti-Corrosion Reagents

- Examples of additional anti-corrosion agents include metal salts including rare earth metals, such as salts of zinc, molybdate, and barium (e.g. phosphates, chromates, molybdates, or metaborate of the rare earth metals). Anti-corrosion reagents may include phosphate esters (e.g. ADD APT, Anticor C6), alkylammonium salt of (2-  
15 benzothiazolythio), succinic acid (e.g. BASF, Irgacor 153), triazine dithiols, and thiadiazoles.

Stabilisers

Stabilizers may include various biocides.

Levelling Agents

- 20 Levelling agents such as fluorocarbon-modified polymers (e.g. EFKA 3777).

Colorants and Pigments

- Colorants may be dyes or pigments and include organic and inorganic dyes such as fluorescents (Royale Pigments and Chemicals LLC) (e.g. to enhance visibility of the reactivation treatment and where it has been applied), fluorescein, and phthalocyanines.  
25 Pigments may include organic phthalocyanine, quinaridone, diketopyrrolopyrrole (DPP), and diarylide derivatives and inorganic oxide pigments (for example to enhance visibility and where it has been applied). The addition of small amount of colorants (for example pigments and dyes) may change the colours of the coating distinguishing from the original substrate and is an useful tool servicing for quality control purpose.  
30 In some embodiments, the colorant may be a dye. Dyes may be organic, soluble in the surrounding medium, and black or chromatic substances. The optional additives may for example be selected from those as described in the book "Coating Additives" by

Johan Bielemann, Wiley-VCH, Weinheim, New York, 1998. The dyes may include organic and inorganic dyes. The dyes may be organic dyes, such as azo dyes (e.g. monoazo such as arylamide yellow PY73, diazo such as diarylide yellows, azo condensation compounds, azo salts such as barium red, azo metal complexes such as nickel azo yellow PG10, benzimidazole). The dyes may be fluorescents (e.g. Royale Pigment and chemicals, to enhance visibility of the reactivation treatment and where it has been applied), fluorescein, phthalocyanines, porphyrins. In some examples, the colorant may be a UV fluorescent dye. The colorants such as fluorescent dyes could for example be used with UV goggles to look for fluorescence after spraying to insure coverage. It will be appreciated that dyes may be organic soluble for improved compatibility or miscibility with the solvents. Peak absorption may be below about 295 nm, for example, which is the natural cut-on for sunlight. Further examples of fluorescent dyes may include acridine dyes, cyanine dyes, fluorine dyes, oxazine dyes, phenanthridine dyes, and rhodamine dyes.

In some examples, the colorant may be a pigment. Pigments may be in powder or flake-form and can provide colorants which, unlike dyes may be insoluble in the surrounding medium (see "Römpp Lexikon Lacke und Druckfarben", Georg Thieme Verlag Stuttgart / New York 1998, page 451). Pigments are typically composed of solid particles less than about 1  $\mu\text{m}$  in size to enable them to refract light, for example within light wavelengths of between about 0.4 and 0.7  $\mu\text{m}$ . The pigments may be selected from organic and inorganic pigments including color pigments, effect pigments, magnetically shielding, electrically conductive, anticorrosion, fluorescent and phosphorescent pigments. Further examples of suitable pigments may, for example, be as described in German Patent Application DE-A-2006053776 or EP-AO 692 007. Organic pigments may include polycyclic pigments (e.g. phthalocyanide such as copper phthalocyanine, anthraquinones such as dibrom anthanthrone, quinacridones such as quinacridone red PV19, dioxazine such as dioxazine violet PV23, perylene, thionindigo such as tetrachloro), nitro pigments, nitroso pigments, quinoline pigments, and azine pigments. The pigments may be inorganic. The inorganic pigments may be selected from carbon black (e.g. black), titanium dioxide (e.g. white), iron oxides (e.g. yellows, reds, browns, blacks), zinc chromates (e.g. yellows), azurites (e.g. blues), chromium oxides (e.g. greens and blues), cadmium sulphoxides (e.g. greens, yellows, reds), lithopones (e.g. whites). Examples of pigments used in aerospace paint compositions may include organic phthalocyanine, quinacridone, diketopyrrolopyrrole (DPP), and diarylide derivatives and inorganic oxide pigments (for example to enhance visibility and where it has been applied).

**COATING SYSTEM**

In some embodiments, a coating layer provided by the compositions as described herein, may form part of a coating system.

- 5 A coating system may be provided comprising:
- (i) an optionally coated metal substrate;
  - (ii) one or more optional post coating layers; and
  - (iii) one or more corrosion protection layers located between (i) and (ii) comprising an organic corrosion inhibitor according to any embodiments
- 10 or examples thereof as described herein.

**COATED SUBSTRATE**

Suitable substrates include metals and metal alloys (e.g. steel or aluminium), and composites.

- 15 It will be appreciated that there may be provided at least one coating layer provided on a substrate comprising or consisting of an organic corrosion inhibitor according to any embodiments or examples thereof as described herein.

For example, a coating may be applied to an optionally coated substrate, wherein the coating comprises or consists of:

- 20 (a) at least one organic corrosion inhibitor according to any embodiments or examples thereof as described herein; and
- (b) optionally one or more additives selected from a solvent, a curing agent, an adhesion promoter, an inorganic filler, a wetting agent, and an organic crosslinker.

- 25 In one example, there is provided a coated metal substrate comprising a metal substrate coated with one or more coating layers, wherein at least one of the coating layers comprises or consists of an organic corrosion inhibitor according to any embodiments or examples thereof as described herein.

**PROCESS FOR PREPARING AND APPLYING COMPOSITIONS**

- A process for preparing a coating system as described herein may comprise:
- 30 applying a coating composition according to any embodiments or examples thereof as described herein to an optionally coated substrate to form a coating; and
- optionally applying at least one post coating layer to the coating present on the optionally coated substrate.

In one example, a process for preparing a coating system may comprise:

applying the organic corrosion inhibitor according to any embodiments or examples thereof as described herein or coating composition thereof, to an optionally coated substrate; and

optionally applying one or more post coating layer to the coating present on the  
5 optionally coated substrate.

The coating composition as described herein can be applied onto a coated substrate to form a coating layer by any method known in the coating industry including spray, drip, dip, roller, brush or curtain coating, especially spray.

The dry thickness of the coating depends on the application. In some  
10 embodiments, the dry thickness of the coating layer (in microns) is less than about 300, 250, 200, 150, 100, 75, 50, 25, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1.

The coating layer provides effective adhesion on the coated substrate and between any primer, intermediate or post coating layers if present on the coating.

Any suitable method known to those skilled in the art may be used to assess  
15 whether the adhesive linkage between the coating layer and other layers (e.g. coated substrate or post coating layer). Methods may include but are not limited to ASTM and ISO standards.

Properties include corrosion inhibition, and may include any one or more of low toxicity, environmentally friendly, good processability, miscibility with coating systems,  
20 high stability, and improved barrier protection from water.

In another embodiment, there is provided a process for protecting a substrate from corrosion by applying the organic corrosion inhibitor or composition thereof according to any embodiments or examples as described herein, to the substrate. The substrate may be a tank, conduit or pipe. The substrate may be used in various industrial applications  
25 such as water treatment, or acidic environments. The composition may be a formulation according to any examples as described herein, such as a liquid or solid formulation. The solid or liquid formulation may be introduced or dosed into the tank, conduit or pipe, for example.

## EXAMPLES

The present disclosure will now be described with reference to the following non-limiting examples and with reference to the accompanying Figures.

### 5 1. Materials and Methods

#### *Reagents*

*p*-Coumaric acid (also referred to as para-hydroxy cinnamic acid), N-methyldiethanolamine, 2-bromoethanol, 2-bromoethane, 2-(dimethylamino)ethyl  
10 methacrylate, potassium hydroxide, 4-vinylaniline, Darocur® (Speedcure 73), Amberlist® A-26 (OH form) and 1-vinylimidazole were obtained from Sigma Aldrich. 1-Bromobutane and 1-bromohexane were obtained from Acros. Oxybis(propane-1,2-diyl) diacrylate, dipropylene glycol diacrylate, trimethylpropyl triacrylate, cyclic trimethylolpropane formal acrylate, and acid-based adhesion promoters were obtained  
15 from Arkema/Sartomer. Mild Steel 1020, NaCl aqueous solution, MiliQ water, methanol and ethanol were used without further purification.

#### *NMR*

NMR spectra were recorded on a Bruker AC-400 spectrometer under the  
20 following experimental conditions: spectral width 15 ppm with 32k data points, flip angle 90°, relaxation delay of 1 second, digital resolution of 0.24 Hz/pt.

#### *DSC*

DSC spectra were recorded on a DSC Q2000 instrument (TA Instruments) under  
25 N<sub>2</sub> atmosphere. Samples (5 mg) sealed in aluminium pans were heated from 25 °C to 100 °C at the heating rate of 20 K min<sup>-1</sup> then were left at 100 °C for 3 min in order to eliminate the thermal history. Samples were cooled down to -70 °C at the rate of 2 K min<sup>-1</sup> and were left at 70 °C for 3 min. Samples were heated again to 100 °C at the rate of 20 K min<sup>-1</sup>.

### ATR-FTIR

ATR-FTIR measurements were performed on Bruker Alpha-P equipment. Spectra were recorded from 350 to 4000  $\text{cm}^{-1}$  at the resolution of 2  $\text{cm}^{-1}$ .

### 5 Potentiodynamic Polarization (PP)

A BioLogic VMP3 multi-channel potentiostat and EC Lab V10.44 software were used for PP experiments. A three-electrode cell was used with the steel rod as the working electrode, a titanium mesh counter electrode and Ag/AgCl reference electrode. The reference electrode was placed in a Luggin capillary that was positioned close to the working electrode surface. Open Circuit Voltage (OCV) was monitored for 30 min followed by a PP scan at the scan rate of 0.167  $\text{mV s}^{-1}$ , with the scan range of from 150 mV below OCV to 250 mV above OCV. Three PP curves were obtained for each test solution.

### 15 Corrosion Current Density ( $i_{\text{corr}}$ ) and Corrosion Potential ( $E_{\text{corr}}$ )

Specific  $i_{\text{corr}}$  and  $E_{\text{corr}}$  values were extracted from the PP curves using Tafel extrapolation. The curves were approximately linear over the range of 10-25 mV on either side of  $E_{\text{corr}}$ , and so the Tafel extrapolations were made over the data in this range. A value for  $i_{\text{corr}}$  was taken as the point where the linear section of the anodic and cathodic sections of the PP curves intersected the value for  $E_{\text{corr}}$ .

From the  $i_{\text{corr}}$  values, inhibitor efficiencies (IE) were calculated according to Equation 1 below:

$$IE(\%) = \frac{i_{\text{corr (control)}} - i_{\text{corr (inhibited)}}}{i_{\text{corr (control)}}} \times 100 \quad (1)$$

25 Electrochemical impedance spectroscopy (EIS) was carried out over a test period of 24 h in order to characterise the electrochemical properties of AS1020 mild steel electrodes immersed in the control solution, solution containing the inhibitor compound, or solution containing polymer coatings. BioLogic VMP3 multi-channel potentiostat was used for the EIS tests. OCV was monitored over the frequency range of 100 kHz to 10

mHz with 6 points per decade and a sinusoidal amplitude of 10mV. Impedance responses were monitored after each hour.

#### *Immersion test and SEM*

5           Immersion tests were conducted over 24 h in control solution (0.01 M NaCl) and in control solution containing the inhibitor compound (10 mM) to determine long-term performance of the inhibitor compound. A 1 cm diameter mild steel sample mounted in epoxy resin was polished to P1200 grit, washed with distilled water, and dried with a stream of N<sub>2</sub>. The sample was then placed in a desiccator for 1 h before being immersed  
10 in 60 mL of solution, and the resulting solution was covered to minimize evaporation. After 24 h, the samples were removed from solution, washed with distilled water, and dried with a stream of N<sub>2</sub>. The corrosion product was then observed with SEM/EDXS using a JEOL JSM-IT300 scanning electron microscope with attached Oxford X-Max 50mm<sup>2</sup> EDXS detector, at the accelerating voltage of 20 kV.

15

#### *Optical microscopy*

A Leica MZ 7 optical microscope in combination with LAS V4.0 software was used to observe surfaces after 24 h of immersion.

#### 20   *Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)*

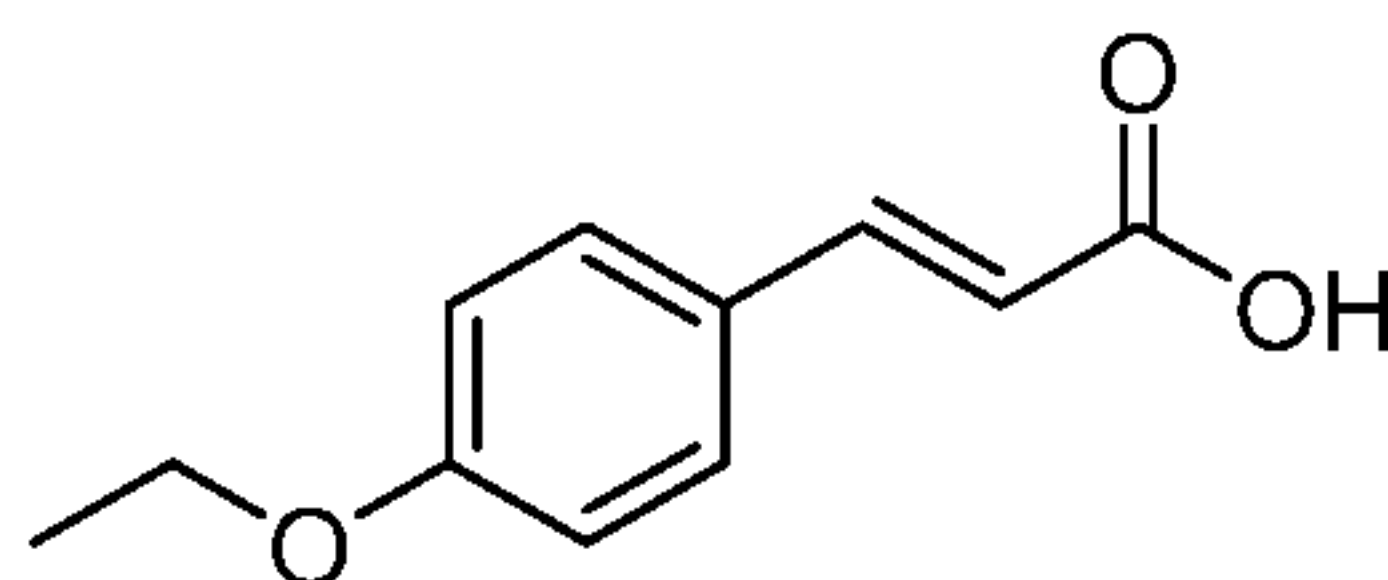
SEM and EDS were used to observe mild steel surfaces after the immersion test. A JSM-IT300 LV SEM instrument with attached Oxford instrument X-Max 50 mm<sup>2</sup> EDS detector at 15kV was used at the accelerating voltage of 20 kV. EDS spectra collected for 60 s were processed using AZtec software.

25

## 2. Synthesis

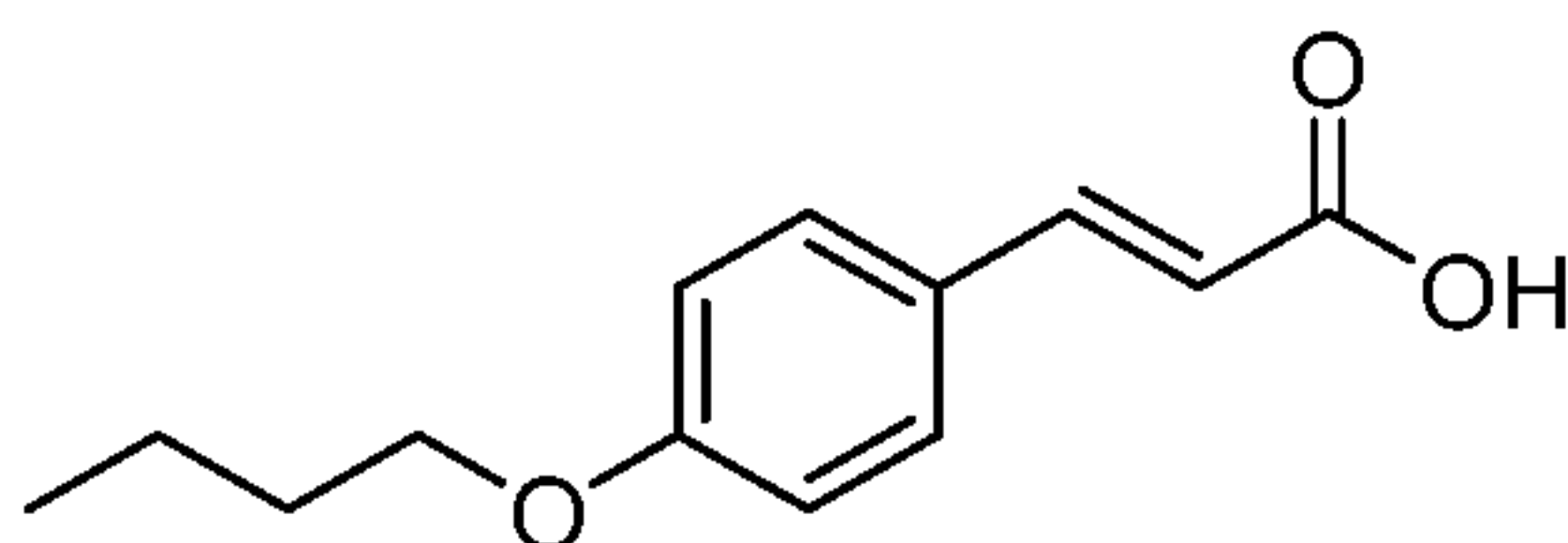
### 2.1 Synthesis of Aromatic Carboxylate Counter Anion Compounds

#### 5 2.1.1 Para-4-ethyloxycinnamic acid



An exemplary synthesis of para-4-ethyloxycinnamic acid, which may also referred to as para-ethoxy coumaric acid, is provided as follows. p-Coumaric acid (100 mmol), KOH (300 mmol), and KI (cat., 20 mol%) was dissolved in a mixture of ethanol/water (75/25) and stirred at reflux temperature for 1 h. Then the solution cool down to the room temperature and ethyl bromide (100 mmol) was added and the reaction mixture was stirred at reflux temperature for a further 24 h. The solution cool down to the room temperature and acidified with concentrated HCl. The pH was monitored by pH paper until acidified. The precipitate was filtered and washed with deionised water (DI) 4-5 times and recrystallized from a mixture of ethanol/water (75/25). The collected precipitate was dried under vacuum for 48 h at 50 °C, to yield the title compound.

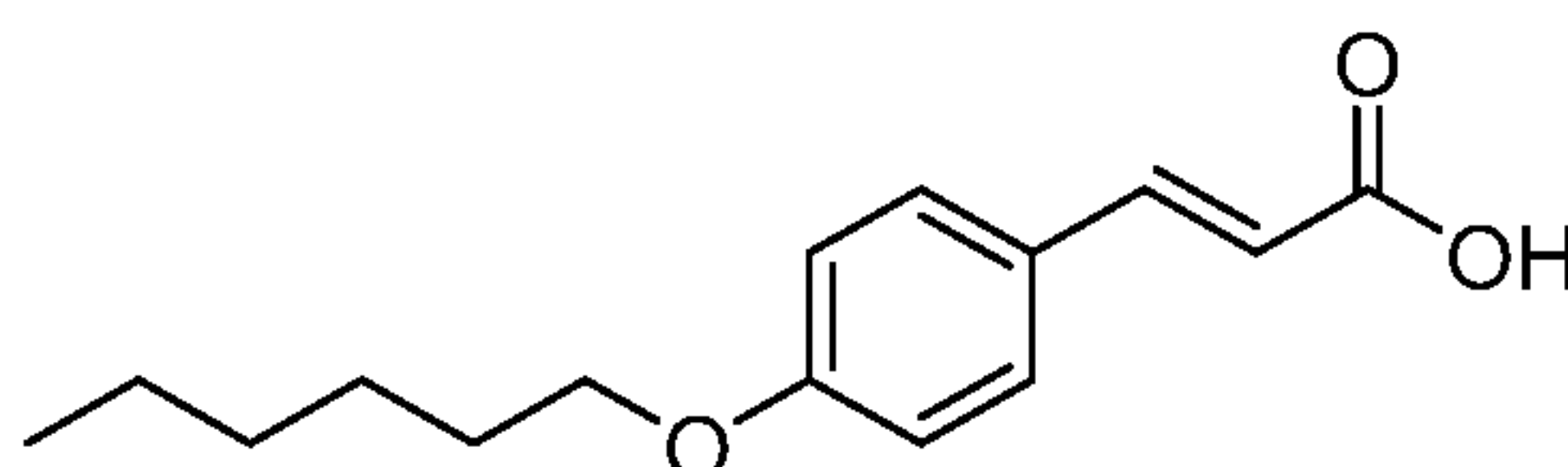
#### 2.1.2 Para-4-butyloxycinnamic acid



An exemplary synthesis of para-4-butyloxycinnamic acid, which may also be referred to as para-butoxy coumaric acid, is provided as follows. p-Coumaric acid (1 mol), KOH (3 mol) and KI (cat., 20 mol%) was dissolved in a mixture of ethanol/water (75/25) and refluxed for 1 h. Then the solution cool down to the room temperature and butyl bromide (1 mol) was added and the reaction mixture was refluxed for a further 24 hours. The solution cool down to the room temperature and acidified with concentrated

HCl. The pH was monitored by pH paper until acidified. The solvent was removed and the precipitate was acidified with concentrated HCl. The crude product was filtered, washed with DI water 4-5 times and recrystallized from a mixture of ethanol/water (75/25). The final product was dried under vacuum for 48 h at 50 °C, to yield the title compound as a white powder. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 7.57, 7.56, 7.55, 7.55, 7.35, 7.31, 7.01, 7.01, 7.00, 6.99, 6.98, 6.40, 6.40, 6.36, 6.36, 4.85, 4.79, 4.73, 4.11, 4.09, 4.07, 1.77, 1.75, 1.74, 1.73, 1.72, 1.70, 1.48, 1.46, 1.45, 1.43, 1.41, 1.39, 0.94, 0.92, 0.92, 0.90.

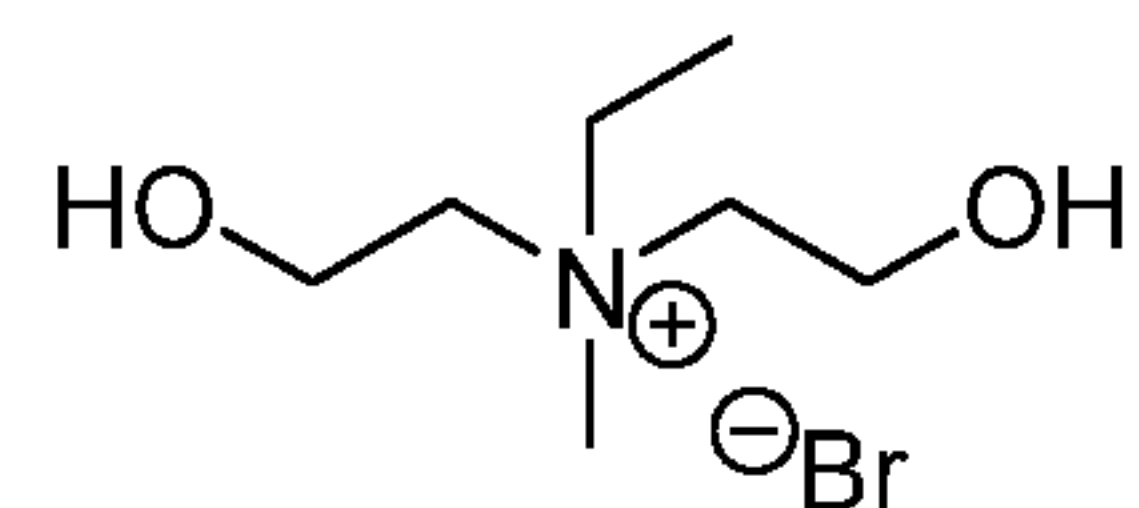
### 2.1.3 Para-4-hexyloxy cinnamic acid



An exemplary synthesis of para-4-hexyloxy cinnamic acid, which may also referred to as para-hexyloxy coumaric acid, is provided as follows. p-Coumaric acid (1 mol), KOH (3 mol) and KI (cat., 20 mol%) was dissolved in a mixture of ethanol/water (75/25) and refluxed for 1 h. Then the solution cool down to the room temperature and hexyl bromide (1 mol) was added and the reaction mixture was refluxed for a further 24 hours. The solution cool down to the room temperature and acidified with concentrated HCl. The pH was monitored by pH paper until acidified.. The crude product was filtered, washed with DI water 4-5 times and recrystallized from a mixture of ethanol/water (75/25). The final product was dried under vacuum for 48 h at 50 °C, to yield the title compound as a white powder. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 7.57, 7.57, 7.56, 7.55, 7.54, 7.35, 7.31, 7.01, 7.01, 6.99, 6.99, 6.98, 6.40, 6.40, 6.36, 6.36, 4.85, 4.85, 4.79, 4.75, 4.73, 4.10, 4.09, 4.08, 4.08, 4.06, 4.06, 1.78, 1.76, 1.74, 1.73, 1.71, 1.44, 1.42, 1.40, 1.38, 1.32, 1.31, 1.30, 1.29, 1.29, 1.28, 0.87, 0.85, 0.85, 0.84, 0.83.

## 2.2 Synthesis of Onium Cation Compounds

### 2.2.1 *N-methyl N-ethyl diethanolammonium bromide*



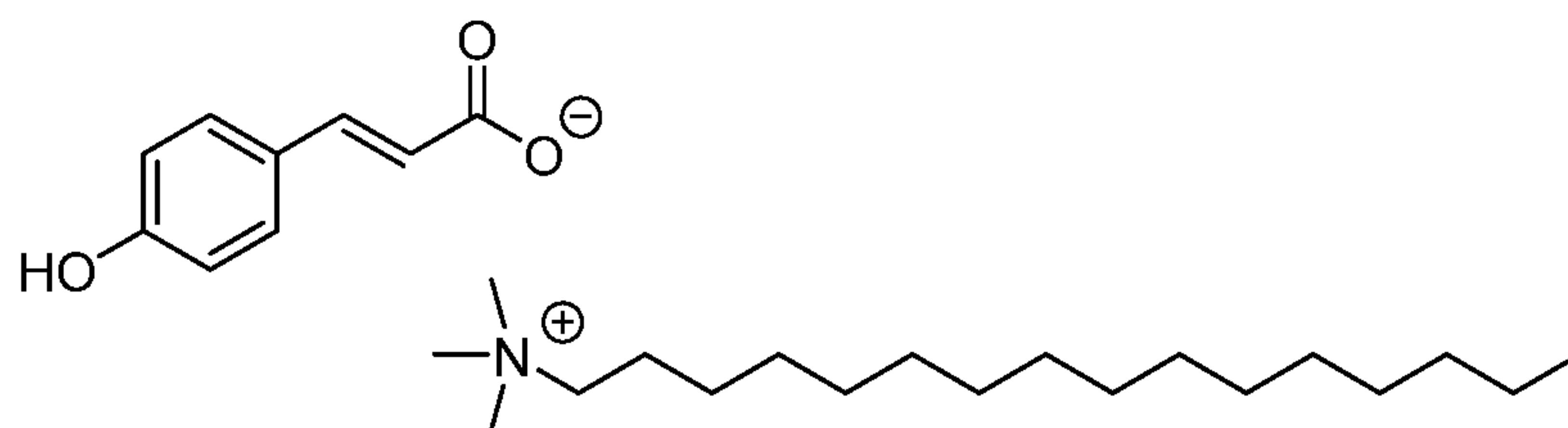
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N-methyl N-ethyl diethanolammonium bromide was obtained by quaternizing N-methyl diethanolamine using 2-bromoethane as described as follows. N-methyl diethanolamine was treated dropwise with 2-bromoethane at room temperature. After the addition of the 2-bromoethane, the reaction mixture was then stirred for 24 hours at 50 °C. The product was obtained as a solid and purified by dissolving the solid in a minimum amount of methanol and then precipitating the product in a large excess of ethyl acetate. The precipitate was washed three times with ethyl acetate and dried under vacuum at 40 °C. The final product was obtained as a white powder and stored under inert gas until further use. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 4.08, 4.07, 4.07, 4.06, 4.05, 4.04, 4.03, 3.59, 3.59, 3.57, 3.57, 3.56, 3.55, 3.54, 3.52, 3.16, 1.40, 1.37, 1.35.

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## 2.3 Synthesis of Ionic Liquids

### 2.3.1 *Cetrimonium-para-4-hydroxy-cinnamate*



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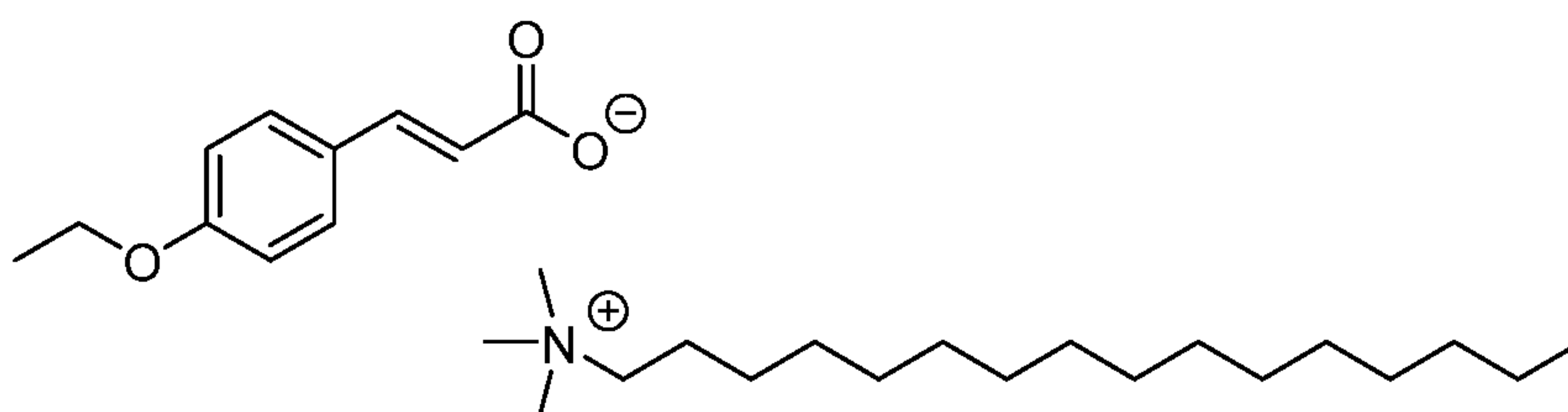
A solution of p-coumaric acid (100 mmol, 16.4 g) in ethanol (150 ml) was slowly added to a stirred solution of sodium hydroxide (100 mmol, 4 g) in ethanol (100 ml) at room temperature. After completion of the addition, the reaction was allowed to stir for approximately 2 h. The solution was then filtered, and the resulting product was dried to obtain the intermediate sodium salt. Sodium cinnamate (67 mmol, 12.46 g) was then

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dissolved in an amount of DI water then slowly added to a stirred solution of silver nitrite (67 mmol, 11.39 g) in DI water. After the completion of addition, the reaction was allowed to stir for 1 h in dark. The product was then filtered off, washed with DI water 3-4 times, and was added to methanol (100 ml). The resulting solution was slowly added to a stirred solution of cetrimonium bromide (44.75 mmol, 16.3 g) in methanol (100 ml). The reaction was stirred at 80 °C for 48 h in dark for a week. Then, AgBr and any unreacted silver cinnamate were filtered off, and methanol was evaporated using rotary evaporator to yield the title compound.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD); δ 7.27 (d, *J* = 16 Hz, -CH=CH-, 1H), 7.28 (d, *J* = 8.5 Hz, ring, -HC=CH 2H), 6.67 (d, *J* = 8.74 Hz, ring, 2H), 6.23 (d, *J* = 15.80 Hz, HC=CH, 1H), 3.18 (m, NCH<sub>2</sub>, 2H), 3.00 (s, N(CH<sub>3</sub>)<sub>3</sub>, 9H), 1.66 (m, NCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.19 (m, CH<sub>2</sub>, 26H), 0.81 (t, *J* = 7 Hz, CH<sub>2</sub>CH<sub>3</sub>, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD); δ 174.1 (COO), 158.5 (ring carbon attached to OH), 140.2 (ring C), 128.8 (ring C, C-C(OH)-C), 127.2 (C=CH-COO), 121.1 (C=C-COO), 115.2 (ring C), 66.5 (NCH<sub>2</sub>), 52.1 (N(CH<sub>3</sub>)<sub>3</sub>), 31.7 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 22.53 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 13.0 (CH<sub>3</sub>) ppm. ES<sup>+</sup> *m/z* 285.3 ((CH<sub>3</sub>)<sub>3</sub>N(C<sub>16</sub>H<sub>33</sub>)<sup>+</sup>, ES<sup>-</sup> *m/z* 163.0 (*trans*-4-hydroxycinnmate)<sup>-</sup>. Anal. Calculated for C<sub>28</sub>H<sub>50</sub>N<sub>1</sub>O<sub>3.5</sub>; C, 73.64; H, 11.04; N, 3.06. Found: C, 73.74; H, 10.71; N, 2.66.

### 2.3.2 Cetrimonium-*para*-4-ethoxy-cinnamate



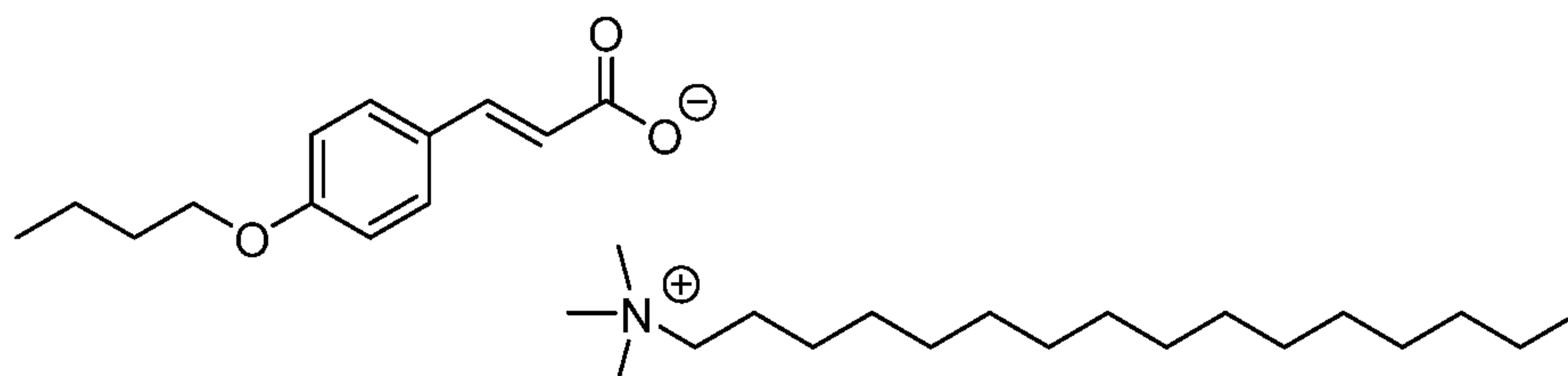
*Trans* 4-Hydroxy-cinnamic acid (100 mmol, 16.415 g), KOH (300 mmol, 16.833 g) and a catalytic amount of KI (20 mol%, 6.65 g) were dissolved in a mixture of ethanol/water (75/25%) and refluxed (80 °C) for 1 h. The reaction was cooled to room temperature (r.t) and alkyl bromide (ethyl bromide (10.897 g) was added and again the reaction mixture was refluxed (80 °C) for 24 h. After the completion of the reaction it was cooled and the product was acidified with concentrated HCl. The pH was monitored

by pH paper until acidified. The product was filtered off and then washed with DI water 4-5 times. *trans*-4 ethoxy cinnamic acid was collected and dried.

A stirring solution of *trans*-4-ethoxycinnamic acid (50 mmol, 9.6 g) in ethanol 95% (100 mL) was then slowly added to a solution of sodium hydroxide (50 mmol, 2 g) in ethanol 95% (50 mL) at room temperature. After the completion of addition the reaction was allowed to stir for around two hours. The solution was then filtered off, then washed with ethanol 95% 4-5 times and the product was dried to collect the intermediate salt, sodium *trans*-4-ethoxy cinnamate. Sodium 4-ethoxycinnamate was then dissolved in an amount of DI water then slowly added to a stirred solution of silver nitrite (equimolar amount to sodium 4-ethoxycinnamate) in DI water. After the completion of addition, the reaction was allowed to stir for 1 h in dark. The product was then filtered off, washed with DI water 3-4 times and was added to methanol (100 ml). The resulting solution was slowly added to a stirred solution of cetrimonium bromide ( $0.67 \times$  molar amount of sodium 4-ethoxycinnamate) in methanol (100 ml). The reaction was stirred at 80 °C for 48 h in dark for a week. Then, AgBr and any unreacted silver cinnamate were filtered off, and methanol was evaporated using rotary evaporator to yield the title compound.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ );  $\delta$  7.46 (d,  $J = 8.66$  Hz, ring, 2H), 7.36 (d,  $J = 15.32$  Hz,  $-\text{HC}=\text{CH}$  1H), 6.90 (d,  $J = 8.74$  Hz, ring, 2H), 6.38 (d,  $J = 16.35$  Hz,  $\text{HC}=\text{CH}$ , 1H), 4.06 (q,  $J = 7.04$ ,  $-\text{OCH}_2\text{CH}_3$ , 2H) 3.13 (s,  $\text{N}(\text{CH}_3)_3$ , 9H), 1.80 (m,  $\text{NCH}_2\text{CH}_2$ , 2H), 1.19 (m,  $\text{CH}_2$ , and  $\text{OCH}_2\text{CH}_3$ , 29H), 0.92 (t,  $J = 7.14$  Hz,  $\text{CH}_2\text{CH}_3$ , 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ );  $\delta$  174.1 (COO), 159.8 (ring carbon attached to OH), 139.2 (ring C), 128.6 (ring C,  $\text{C}-\text{C}(\text{OH})-\text{C}$ ), 128.4 ( $\text{C}=\text{CH}-\text{COO}$ ), 122.8 ( $\text{C}=\text{C}-\text{COO}$ ), 114.3 (ring C), 66.5 ( $\text{NCH}_2$ ), 63.1 ( $\text{OCH}_2\text{CH}_3$ ), 52.1 ( $\text{N}(\text{CH}_3)_3$ ), 31.7 ( $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 29.38 ( $\text{CH}_2$ ), 29.35 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.17 ( $\text{CH}_2$ ), 29.1 ( $\text{CH}_2$ ), 28.8 ( $\text{CH}_2$ ), 26 ( $\text{CH}_2$ ), 22.5 ( $\text{CH}_2$ ), 22.4 ( $\text{CH}_2$ ), 13.8 ( $\text{OCH}_2\text{CH}_3$ ), 13.1 ( $\text{CH}_3$ ) ppm.  $\text{ES}^+ m/z$  284.4 ( $(\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})^+$ ),  $\text{ES}^- m/z$  191.1 (*trans*-4-ethoxycinnmate).

## 2.3.3 Cetrimonium-para-4-butoxy-cinnamate



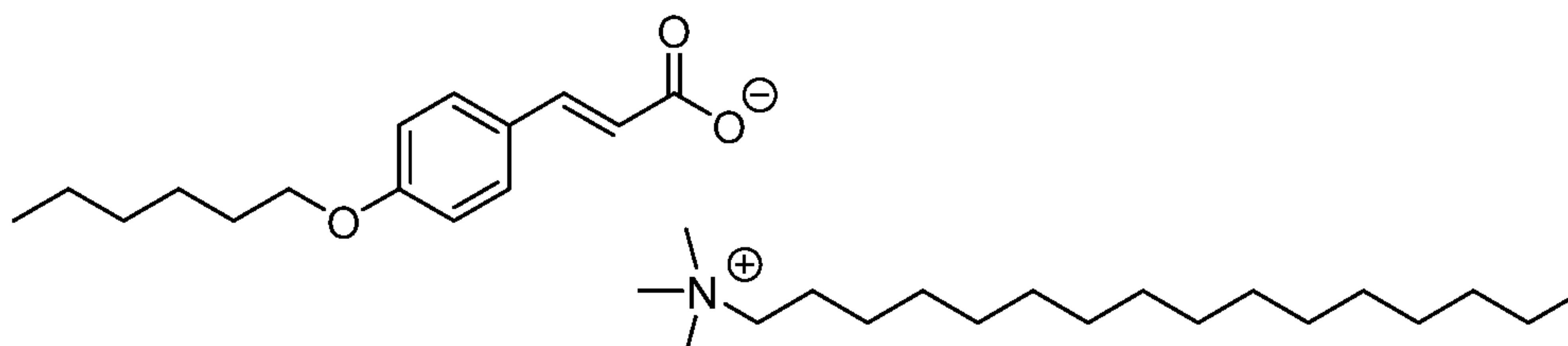
A solution of 4-butoxycinnamic acid (100 mmol) in ethanol (150 ml) was slowly  
 5 added to a stirred solution of sodium hydroxide (100 mmol, 4 g) in ethanol (100 ml) at  
 room temperature. After completion of the addition, the reaction was allowed to stir for  
 approximately 2 h. The solution was then filtered, and the resulting product was dried to  
 obtain the intermediate sodium salt. Sodium 4-butoxycinnamate was then dissolved in  
 an amount of DI water then slowly added to a stirred solution of silver nitrite (equimolar  
 10 amount to sodium 4-butoxycinnamate) in DI water. After the completion of addition, the  
 reaction was allowed to stir for 1 h in dark. The product was then filtered off, washed  
 with DI water 3-4 times and was added to methanol (100 ml). The resulting solution was  
 slowly added to a stirred solution of cetrimonium bromide ( $0.67 \times$  molar amount of  
 sodium 4-butoxycinnamate) in methanol (100 ml). The reaction was stirred at 80 °C for  
 15 48 h in dark for a week. Then, AgBr and any unreacted silver cinnamate were filtered  
 off, and methanol was evaporated using rotary evaporator to yield the title compound.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ );  $\delta$  7.46 (d,  $J = 8.54$  Hz, ring, 2H), 7.36 (d,  $J = 16$   
 Hz,  $-\text{HC}=\text{CH}$  1H), 6.90 (d,  $J = 8.96$  Hz, ring, 2H), 6.39 (d,  $J = 15.91$  Hz,  $\text{HC}=\text{CH}$ , 1H),  
 4.01 (t,  $J = 6.49$ ,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , 2H) 3.30 (m,  $\text{NCH}_2$ , 2H), 3.13 (s,  $\text{N}(\text{CH}_3)_3$ , 9H),  
 20 1.78 (m,  $\text{NCH}_2\text{CH}_2$  and  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , 4H), 1.53 (sextet,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , 2H)  
 1.35 (m,  $\text{CH}_2$ , 26H), 1.01 (t,  $J = 7.33$  Hz,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , 3H), 0.92 (t,  $J = 7.01$  Hz,  
 $\text{CH}_2\text{CH}_3$ , 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ );  $\delta$  174.5 (COO), 160 (ring carbon  
 attached to OH), 139.2 (ring C), 128.5 (ring C, C-C(OH)-C), 128.4 (C=CH-COO), 122.8  
 (C=C-COO), 114.3 (ring C), 67.4 ( $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 66.5 ( $\text{NCH}_2$ ), 63.1 ( $\text{OCH}_2\text{CH}_2$   
 25  $\text{CH}_2\text{CH}_3$ ), 52.1 ( $\text{N}(\text{CH}_3)_3$ ), 31.7 ( $\text{CH}_2$ ), 31.1 ( $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ),  
 29.1 ( $\text{CH}_2$ ), 29.06 ( $\text{CH}_2$ ), 28.8 ( $\text{CH}_2$ ), 26 ( $\text{CH}_2$ ), 22.5 ( $\text{CH}_2$ ), 22.3 ( $\text{CH}_2$ ), 18.8  
 ( $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13 ( $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 12.7 ( $\text{CH}_3$ ) ppm.  $\text{ES}^+$   $m/z$  284.6

$((\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})^+, \text{ES}^- m/z 219.0$  (*trans*-4-butoxycinnamate) $^-$ . Anal. Calculated for  $\text{C}_{32}\text{H}_{59}\text{N}_1\text{O}_{3.5}$ ; C, 74.81; H, 11.57; N, 2.73. Found: C, 75.09; H, 11.1; N, 2.4.

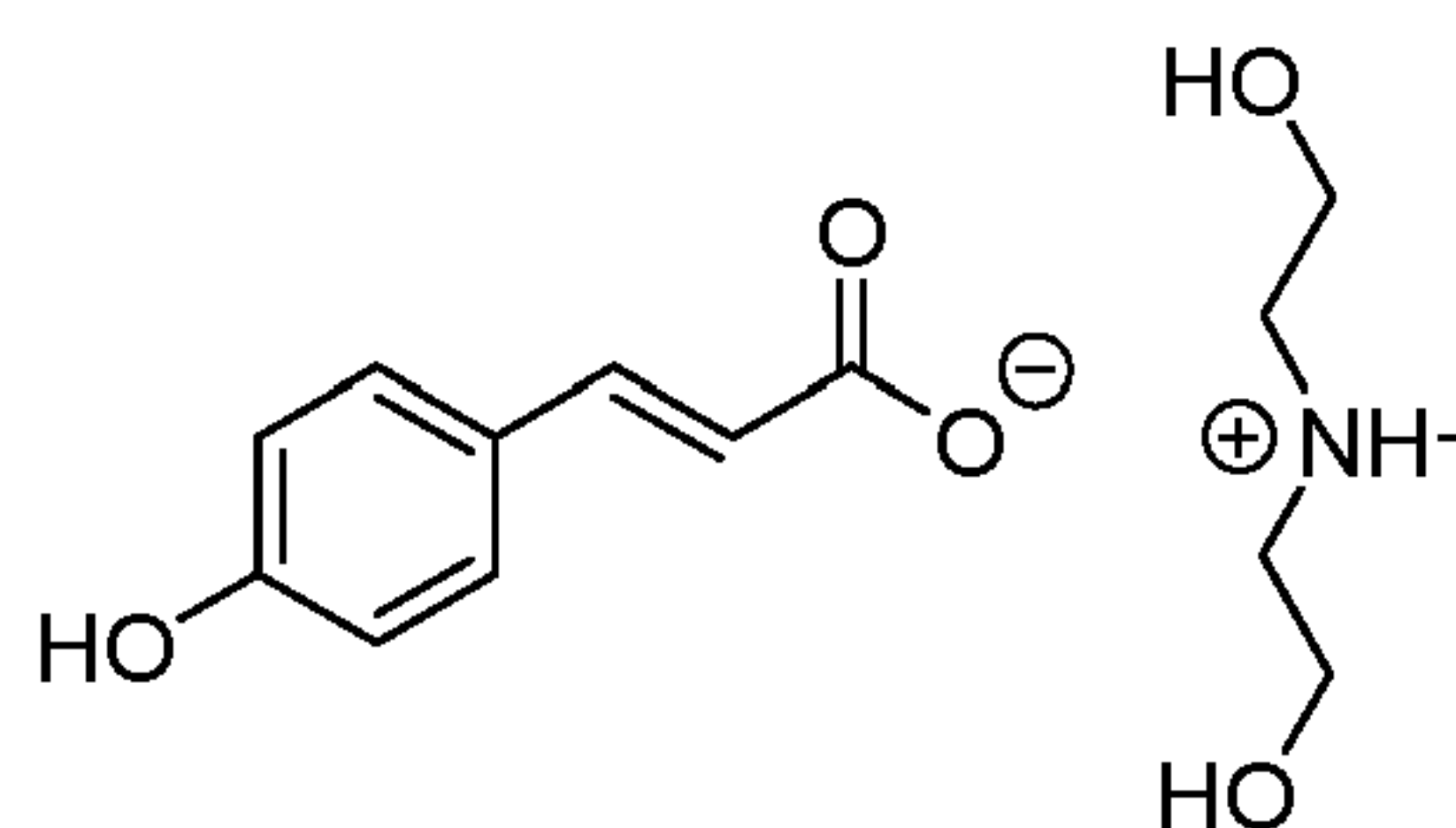
#### 2.3.4 Cetrimonium-para-4-hexyloxy-cinnamate

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A solution of 4-hexyloxycinnamic acid (100 mmol) in ethanol (150 ml) was slowly added to a stirred solution of sodium hydroxide (100 mmol, 4 g) in ethanol (100 ml) at room temperature. After completion of the addition, the reaction was allowed to stir for approximately 2 h. The solution was then filtered, and the resulting product was dried to obtain the intermediate sodium salt (sodium 4-hexyloxycinnamate) which was dried under vacuum. Sodium 4-hexyloxycinnamate was then dissolved in an amount of DI water then slowly added to a stirred solution of silver nitrite (equimolar amount to sodium 4-hexyloxycinnamate) in DI water. After the completion of addition, the reaction was allowed to stir for 1 h in dark. The product was then filtered off, washed with DI water 3-4 times and was added to methanol (100 ml). The resulting solution was slowly added to a stirred solution of cetrimonium bromide ( $0.67 \times$  molar amount of silver 4-hexyloxycinnamate) in methanol (100 ml). The reaction was stirred at  $80^\circ\text{C}$  for 48 h in dark for a week. Then, AgBr and any unreacted silver cinnamate were filtered off, and methanol was evaporated using rotary evaporator to yield the title compound.

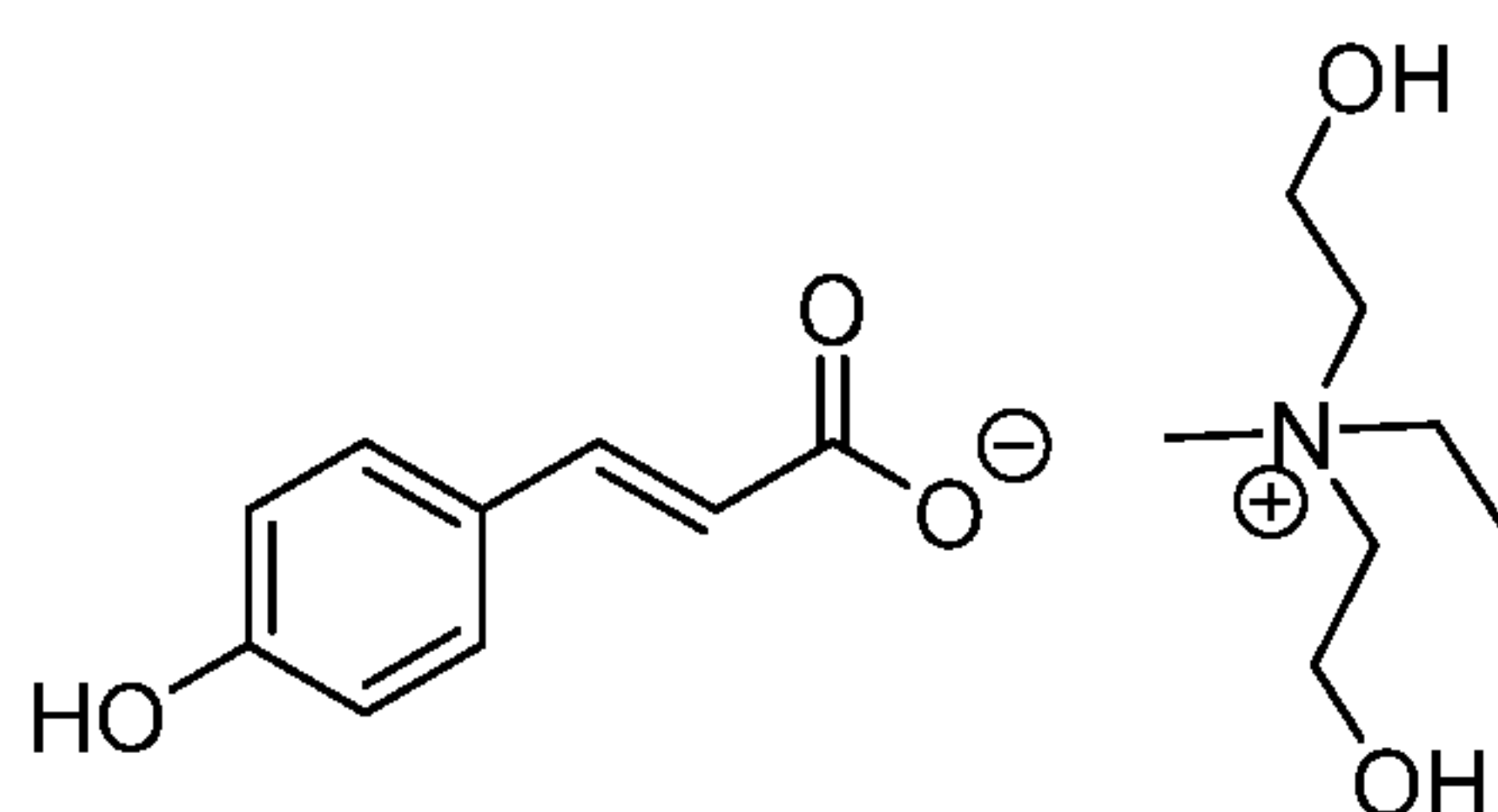
#### 2.3.5 N-Methyl diethanolammonium para-4-hydroxy-cinnamate



An exemplary synthesis of N-methyl diethanolammonium para-4-hydroxy-cinnamate, which may also be referred to as N-methyl diethanolammonium p-coumarate, is provided as follows. N-methyl diethanolamine and *p*-coumaric acid were weighed and mixed in an equimolar amount. The product was obtained instantly as a viscous liquid.

<sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  7.50, 7.47, 7.42, 6.81, 6.78, 6.31, 6.26, 5.58, 3.51, 3.49, 3.47, 3.18, 2.55, 2.53, 2.51, 2.27, 2.09.

### 2.3.6 N-methyl N-ethyl diethanolammonium para-4-hydroxy-cinnamate

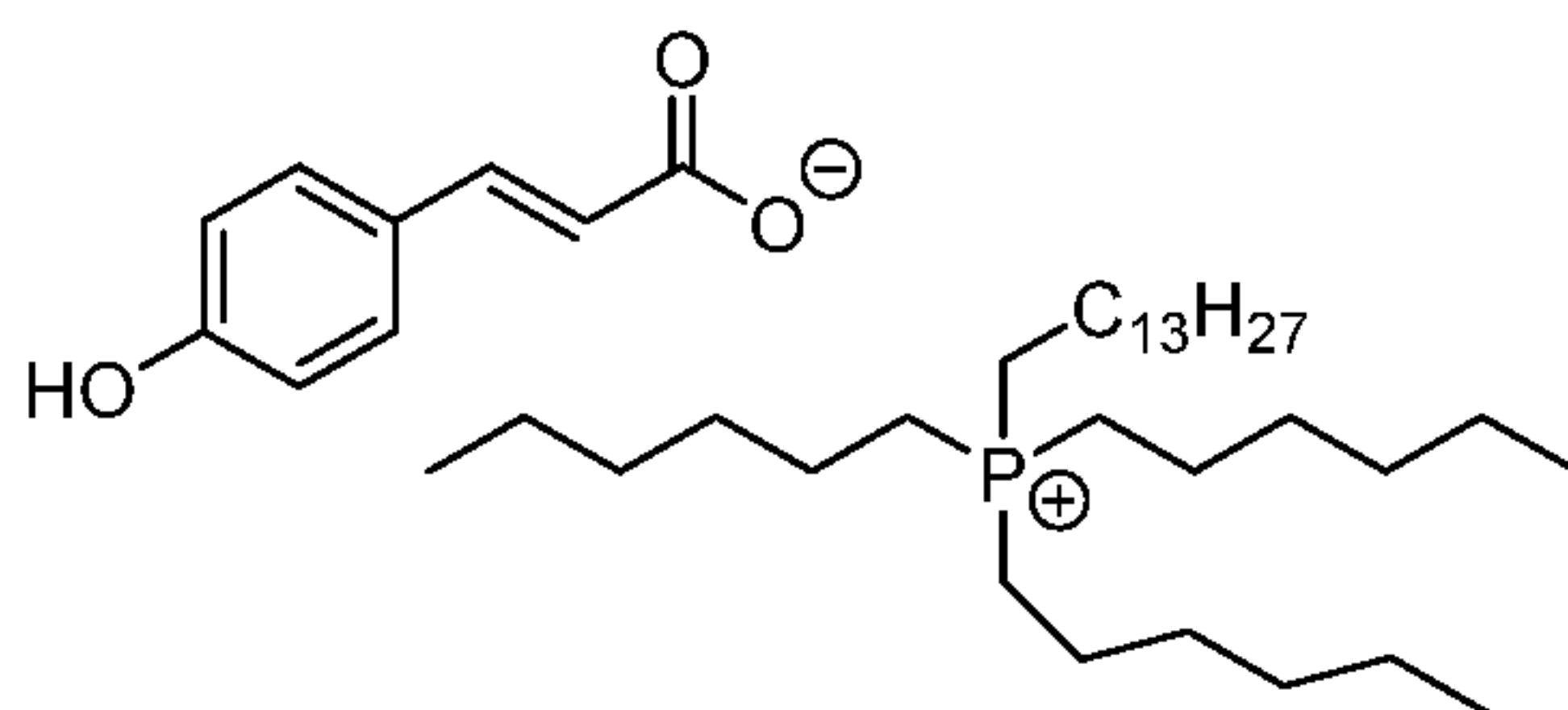


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Anion exchange resin Amberlist A-26 (OH form) was used in order to obtain bromide exchange for the p-coumarate anion in N-methyl N-ethyl diethanolammonium bromide. A column was filled with the aforementioned resin. *p*-Coumaric acid (aqueous solution, 0.01M) was passed through the column. The acid-based reaction with hydroxides occurred, resulting in the retention of the p-coumarate anion in the resin and the displacement of the formed water together with the eluted solution. N-methyl N-ethyl diethanolammonium bromide solution was passed through the column containing the A-26 (R-p-coumarate form), and 2-(dimethyl ethanol amino)ethyl methacrylate p-coumarate was obtained after evaporation of methanol. The product was obtained as a viscous liquid. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  7.22, 7.22, 7.20, 7.20, 7.08, 7.04, 6.68, 6.67, 6.66, 6.13, 6.09, 5.43, 3.86, 3.85, 3.84, 3.52, 3.50, 3.48, 3.47, 3.46, 3.45, 3.43, 3.41, 3.19, 3.09, 2.52, 2.52, 2.52, 2.51, 2.51, 2.09, 1.26, 1.24, 1.22.

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### 2.3.7 Trihexyltetradecylphosphonium-para-4-hydroxy-cinnamate



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A stirred solution of trihexyltetradecylphosphonium chloride (20 mmol, 10.38 g) in toluene (25 mL) was treated with a solution of para-4-hydroxy-cinnamic acid (20 mmol, 3.28 g) in warm DI water (50 ml) at room temperature for 3 h. Then, NaOH (20 mmol, 0.8 g) was added and the reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, a third oily yellow layer was evident between toluene (top phase) and DI water (bottom phase). The toluene and DI water were decanted and the oily layer was washed five times with toluene and DI water separately. The product was dried under high vacuum at 50 °C for 48 h to yield the title compound.

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### 3. Corrosion Inhibitor Testing of CTA-4OHcinn

#### 3.1 Potentiodynamic polarisation of CTA-4OHcinn

The efficiency of CTA-4OHcinn as a corrosion inhibitor was investigated. Mild steel was immersed at pH 7 in (a) a 0.01 M NaCl solution (“control solution”), and (b) a 10 mM CTA-4OHcinn and 0.01 M NaCl solution (“inhibitor solution”).

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Figure 1 shows the Tafel plots for the control solution (Figure 1(a)) and inhibitor solution (Figure 1(b)).

Table 4 shows corrosion current densities ( $i_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), and inhibition efficiency of CTA-4OHcinn as extracted from Tafel plots in Figure 1.

**Table 4.** Corrosion Potential ( $E_{\text{corr}}$ ), Corrosion Current Density ( $i_{\text{corr}}$ ), and Inhibitor Efficiency (IE) at pH 7.

|                                                             | $E_{\text{corr}}$ (mV) | $I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ ) | IE(%) |
|-------------------------------------------------------------|------------------------|-------------------------------------------------|-------|
| 0.01 M NaCl (“control solution”)                            | -553                   | 1.8                                             |       |
| 10 mM CTA-4OHcinn,<br>0.01 M NaCl<br>(“inhibitor solution”) |                        |                                                 |       |
| 1 <sup>st</sup> run                                         | -210                   | 0.09                                            | 95    |
| 2 <sup>nd</sup> run                                         | -206                   | 0.1                                             | 94    |
| 3 <sup>rd</sup> run                                         | -185                   | 0.07                                            | 96    |

The results demonstrate that CTA-4OHcinn at 10 mM concentration significantly reduced the corrosion process in comparison with the control sample. CTA-4OHcinn shifted the  $E_{\text{corr}}$  towards more anodic potentials, from -553 mV for the control to -200 mV. The first set of analyses highlighted the impact of the corrosion inhibitor on mild steel, with an efficiency of 95%. The Tafel plots (**Figure 1**) display transient current fluctuations. This may correspond to the breakdown and re-creation of a passivate film on the metal surface.

### 3.2 EIS results of immersion test with CTA-4OHcinn

EIS results of the mild steel immersed in control solution and inhibitor solution are shown in Figures 2, 3 and 4. The control solutions are depicted in (a), and the inhibitor solutions in (b).

Figure 2(a) shows an almost constant impedance where the arc is below 1000 ohm.cm<sup>2</sup> at all times, in the imaginary axis. On the contrary, Figure 2(b) shows an increasing trend on the impedance, reaching a maximum value of 16000 ohm.cm<sup>2</sup> in the imaginary axis.

Figure 3 shows the Bode plot for the sample immersed in the control solution (Figure 3(a)) and inhibitor solution (Figure 3(b)). Figure 3(a) shows a slight decrease at lower frequencies, whereas Figure 3(b) shows a clear increase in the impedance against time, which is more notorious at lower frequencies.

Figure 4 shows the phase angle plots of the sample immersed in the control solution (Figure 4(a)) and saturated inhibitor solution (Figure 4(b)). Figure 4(a) shows that the maximum phase angle of the control solution is below 40°, and it shifts to lower frequencies against time. Figure 4(b) shows that as time goes by, the maximum phase angle increases, reaching a maximum value of 68°. There is also a broadening with time on the curve peak of the maximum phase angle. In addition, the phase angle of the inhibitor test presents two peaks, each one representing a time constant.

Figure 5 shows the cyclic polarization curves as a result of the CPP test on the sample immersed in the control solution and the inhibitor solution. The control solution test presents a smooth cathodic curve without sharp changes, and a resulting corrosion potential around -0.410 V. Regarding the inhibitor solution test, its anodic curve occurs

at lower currents than the control test, which results in a shift of the corrosion potential to more noble values. The results also show a sudden increase in the current at a potential around 0.3 V. This critical point is the pitting potential. Finally, the reverse polarization of the inhibitor test shows a more noble corrosion potential than the original.

5        Figure 6 shows the images of the sample immersed for 24 h in control solution (Figure 6(a)) and inhibitor solution (Figure 6(b)). The sample immersed in control solution showed a significant metal dissolution on approximately 50% of its surface with some oxide deposits. On the contrary, the sample immersed in inhibitor solution showed only two pits surrounded by oxide material.

10        Figure 7(a) shows the SEM image of mild steel after 12 days of immersion in inhibitor solution. Figure 7(b) shows the elemental composition, from the EDS analysis of the sections indicated in the SEM image. The EDS analysis shows a significant difference in the composition between the film (blue frame) and the exposed metal (green frame). The film is composed of 39% carbon, while the exposed metal is mostly iron.  
15        There is no evidence of pitting corrosion or metal dissolution on the exposed iron surface.

Overall, the results show electrochemical, morphological, and compositional differences between those samples exposed to the control solution and those samples exposed to the inhibitor solution. The Nyquist plot of mild steel immersed for 2 h in control solution, Figure 2(a) showed a slight decrease in impedance with time, evidenced  
20        by a decrease in size of the semicircles with time. This trend is clearer in Figure 8(a), where the red arrows point the decreasing trend of the semicircle with time. The exposed microstructure of the steel after immersion in control solution indicates a selective dissolution mechanism. Figure 9(a) shows the 2 h time trend of the phase angle and impedance of the sample immersed in the control solution. Regarding the sample  
25        immersed in the saturated inhibitor solution, the increase of the semicircles in the Nyquist plot in Figure 2(b) suggests a rapid interaction between the mild steel and the inhibitor since there is an immediate rise in the overall resistance as soon as the sample deeps in the solution. The 2 h time trend, shown in Figure 8(b), shows this increasing trend. Figure  
9(b) shows the increase in impedance at low frequencies of the sample immersed in  
30        inhibitor solution, and suggests the formation of a protective outer layer that increases

the dielectric constant of the fluid near the interphase, as depicted by the red arrow on the impedance curves.

### 3.3 SEM/EDXS test with CTA-4OHcinn

5        Following the immersion tests, SEM images of the inhibited surface were taken and are shown in Figure 10(a)-(d). While most of the surface did not show any signs of corrosion, four pits can be seen in the optical image (Figure 10(c)).

      An SEM image showing one of these pits and the surrounding area is shown in Figure 11. To determine the elements present on the surface and the possible protection  
10       mechanisms, EDSX maps for Fe, O and Cl are shown for the area (Figures 11(b) and (c)), while Figure 12 shows EDX spectra for points 1 and 2 labelled in Figure 11(a).

      Figure 11 shows a pit surrounded by corrosion product with a background mostly clear of corrosion. From the mapping, it can be seen that O and Cl are concentrated around the pit. This is due to the formation of corrosion product, such as FeOH and the  
15       formation of FeCl<sub>2</sub>. Generally Fe(OH)<sub>2</sub> can form more easily than FeCl<sub>2</sub> due to its energy formation, however the activity of chloride specie is able to affect the cathodic mechanisms. This result is due to adsorbed Cl<sup>-</sup> specie on the interface layer where Fe-Cl forms.

      From the EDX spectra in Figure 12 for spot 1 and 2, it can be seen that the area  
20       surrounding the pit (Spot 2), which is typical of the vast majority of the surface, contains far less oxygen, while chloride is undetected. This suggests that very little corrosion has occurred on the majority of the surface, most likely due to the formation of a protective film. Accordingly, the inhibitor solution is responsible for the formation of this protective layer. As the inhibitor solution contains nitrogen, it would be expected that nitrogen  
25       should be present on the surface, however it was not detected using EDX at an accelerating voltage of 20kV. The lack of nitrogen detected is most probably a consequence of how thin the film formed on the surface is, as EDX is not a particularly surface sensitive technique, with interaction depths in the order of microns, while these protective films have been shown to be in the order of 10's of nanometers (reference).  
30       XPS has been used in to more accurately determine the elements present on the surface.

### 3.4 XPS analysis with CTA-4OHcinn

Mild steel samples were immersed in control solution (0.01M NaCl) and solution containing 10mM of CTA-4OHcinn for 15 minutes, 45 minutes, 2 hours and 24 hours. Figure 13 shows the atomic composition of oxygen, carbon, iron, nitrogen, and chlorine as a function of immersion time, as determined by the XPS elemental analysis. The decrease in the concentration of oxygen and iron, as well as the increase of carbon and nitrogen, indicate the formation of an organic film. Also, there is a slight increase in the concentration of oxygen and iron after 2 hours of immersion, which could be due to a defect in the protective film, exposing the underlying steel, which could be the result of film breakage.

In general, XPS shows the formation of a film on the metal surface whose composition stabilizes in the first 45 minutes. Also, notice that the film capacitance of the metal sample after immersion in 10 mM inhibitor solution reaches a steady-state around the first 40 minutes (Figure 2). Therefore, the constant composition of the film, as well as the constant capacitance, could indicate the film covers all the metal surface effectively in the first 45 minutes. In addition, after 2 hours of immersion, the signal of iron begins to appear again, which is in agreement with the SEM images of the sample immersed for 24 hours in 10 mM inhibitor solution (Figure 10), that shows the presence of pits. Also, the presence of nitrogen, confirms the adsorption of the cetrimonium group on the metal surface.

Figure 14 shows the deconvolution of the XPS region scans for oxygen, iron, and nitrogen at the different immersion times. In the case of oxygen, Figure 14a, the control test shows two peaks which correspond to the hydroxide and oxide states. However, after inhibitor interaction, a third peak appears, which corresponds to an oxygen-carbon single-bond. Also, the green peak represents oxygen double-bonded to a carbon atom as well as hydroxide. The oxide peak (red), decreases with the immersion time up to two hours. However, it appears again after 24 hours, which could be related to the breakdown of the protective film. In the case of the iron analysis, Figure 14b; the green and red peaks correspond to the 2p doublet for the  $Fe^{3+}$  state. These peaks decrease with the immersion time and eventually disappear almost completely after two hours of immersion. However, they appear again after 24 hours, which agrees with the previous

explanation about the film breakage. In addition, the blue peak corresponds to the elemental iron state, which could indicate the formation of an organic ultrathin layer that does not shield the iron beneath it completely from the X-rays. Since the depth of penetration for XPS analysis is estimated to be 10 nm, this suggests that the oxide/hydroxide layer on the control is greater than 10nm thick, while the protective layer formed with inhibitor present is less than 10 nm thick. Regarding the nitrogen (Figure 14c), two peaks were observed on the inhibitor exposed samples, with the blue peak corresponding to the amino group C-NH<sub>2</sub> of the inhibitor cation, which disappears after two hours of immersion. Regarding the red peak, it could correspond to a complex formation between the nitrogen atom and the iron surface.

#### 4 Corrosion Inhibitor Testing of CTA-4Etocinn

##### 4.1 Potentiodynamic polarisation of CTA-4Etocinn

The efficiency of CTA-4Etocinn as a corrosion inhibitor was investigated. Mild steel was immersed at pH 7 for 24 hours in (a) a 0.01 M NaCl solution with 6.5% ethanol (“control solution”), and (b) a 10 mM CTA-4Etocinn and 0.01 M NaCl solution with 6.5% ethanol (“inhibitor solution”).

Figure 15 shows the Tafel plots for the control solution and inhibitor solution.

Table 5 shows corrosion current densities ( $i_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), and inhibition efficiency of CTA-4OHcinn as extracted from Tafel plots in Figure 15.

**Table 5.** Corrosion Potential ( $E_{\text{corr}}$ ), Corrosion Current Density ( $i_{\text{corr}}$ ), and Inhibitor Efficiency (IE) at pH 7 for control and 10 mM CTA-4Etocinn with 6.5% ethanol.

|                                                                      | $E_{\text{corr}}$ (mV) | $I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ ) | IE(%) |
|----------------------------------------------------------------------|------------------------|-------------------------------------------------|-------|
| 0.01 M NaCl with 6.5% ethanol (“control solution”)                   | -524                   | 1.85                                            |       |
| 10 mM CTA-4Etocinn, 0.01 M NaCl, 6.5% ethanol (“inhibitor solution”) |                        |                                                 |       |
| 1 <sup>st</sup> run                                                  | 208                    | 0.033                                           | 98    |
| 2 <sup>nd</sup> run                                                  | 205                    | 0.058                                           | 97    |
| 3 <sup>rd</sup> run                                                  | 208                    | 0.074                                           | 96    |

The results demonstrate that CTA-4Etocinn at 10 mM concentration significantly reduced the corrosion process in comparison with the control sample. CTA-4Etocinn shifted the  $E_{\text{corr}}$  towards more anodic potentials, from -524 mV for the control to -207 mV. The first set of analyses highlighted the impact of the corrosion inhibitor on mild steel, with an efficiency of 97%. The Tafel plots (Figure 15) display transient current fluctuations. This may correspond to the breakdown and re-creation of a passivate film on the metal surface. The pitting potential (point of rapid current increase on anodic arm) has also been increased as compared to CTA-4Etocinn (Figure 1), from around -0.1 V to 0 V vs Ag/AgCl.

#### 4.2 Optical and SEM/EDXS test with CTA-4Etocinn

Figure 16 shows optical images of the sample immersed for 24 h in control solution (Figure 16(a)) and inhibitor solution (Figure 16(b)). The sample immersed in control solution showed a significant metal dissolution on approximately 50% of its surface with some oxide deposits. As compared to the control and the CTA-4OHcinn (Figure 10(c)), the sample immersed in the CTA-4Etocinn inhibitor solution showed no obvious signs of corrosion after 24 hours.

Figure 17 shows the SEM image of mild steel after 24 h of immersion in control (Figure 17(a)) and the inhibitor (Figure 17(b)) solutions. Extensive damage can be seen on the control sample, while small deposits are visible on the inhibitor sample.

Figure 18 shows a higher magnification image of one of these deposits, accompanied by elemental information from EDX analysis of the sites labelled. The EDS analysis shows a significant difference in the composition between the general background film (Site 20) and the deposits formed (Sites 18 and 19). As evidenced by the appearance of significant amounts of O, the deposits appear to be areas at which corrosion has started and a protective film has formed. The presence of N on these sites indicates the presence of the inhibitor in this protective film. Similar to the results for CTA-4OHcinn, the absence of N in the background film does not mean it is not there, but is below the detection limit of the EDX technique, a more surface sensitive technique such as XPS would be required to confirm, or not, the presence of N. However, the fact

that N consistently showed up on the deposits means that the inhibitor preferentially attaches to these areas and is intimately involved in the protective film that limits the corrosion.

Overall, the results show electrochemical, morphological, and compositional differences between those samples exposed to the control solution and those samples exposed to the organic corrosion inhibitor solution.

## 5 Corrosion Inhibitor Testing of CTA-4Etocinn compared with Cet-trans-4-OH-Cinnamate

10

### 5.1 *Potentiodynamic polarisation of CTA-4Etocinn compared with CTA-4OHcinn*

The efficiency of CTA-4Etocinn as a corrosion inhibitor was compared with CTA-4OHcinn. Mild steel was immersed at pH 7 for 30 minutes in (a) a 0.01 M NaCl solution with 6.5% ethanol (“control solution/6.5% ethanol”) and without ethanol (“control solution/no ethanol”), and (b) a 10 mM CTA-4Etocinn and 0.01 M NaCl solution with 6.5% ethanol (“inhibitor solution/6.5% ethanol”) and without ethanol (“inhibitor solution/no ethanol”). Mild steel was also immersed at pH 7 for 24 hours in (a) a 0.01 M NaCl solution with 6.5% ethanol (“control solution/6.5% ethanol”) and without ethanol (“control solution/no ethanol”), and (b) a 10 mM CTA-4Etocinn and 0.01 M NaCl solution with 6.5% ethanol (“inhibitor solution/6.5% ethanol”) and without ethanol (“inhibitor solution/no ethanol”).

Figure 19a shows the Tafel plots for the control solution and inhibitor solution after 30 minutes immersion and Figure 19b shows the Tafel plots for the control solution and inhibitor solution after 24 hours immersion. The inventors found that additional alkyl chain length, e.g. from a hydroxy group to an ethoxy group on the aromatic carboxylate anion can increase the corrosion protection on the metallic surface of mild steel alloy. The inventors also found that over time the inhibitor provides increased interaction with the surface of the substrate thereby creating an improved protective film layer evident from the shift of the pitting potential (point of rapid current increase on anodic arm) to a more positive value and increased corrosion inhibition efficiency.

A comparison between 10 mM CTA-4Etocinn and 10 mM CTA-4OHcinn each in 0.01 M NaCl solution with 6.5% ethanol was also investigated. Figure 20a shows the Tafel plots for the control solution and both inhibitor solutions after 30 minutes immersion and Figure 20b shows the Tafel plots for the control solution and both inhibitor solutions after 24 hours immersion. The CTA-4Etocinn demonstrates up to approximately 3 orders of magnitude reductions in the current density of the anodic arm, suggesting significant inhibition of the metal oxidation reaction, when compared to the CTA-4OHcinn inhibitor. Additionally, the  $i_{\text{corr}}$  value is approximately 1 order of magnitude smaller for the CTA-4Etocinn inhibitor, suggesting a slower corrosion rate when compared to the CTA-4OHcinn inhibitor. At 30 minutes there is some reduction of the cathodic current densities, suggesting a mixed mode of inhibition, and it appears that this reduction of the cathodic current density may linger after 24 hours. Figure 20 suggests that the addition of ethanol to the inhibitor solution may have a significant effect on micellar structure and/or speciation of inhibitor in solution. And an overall improved corrosion inhibition efficiency for the the CTA-4Etocinn inhibitor solution.

Figure 21 shows the Tafel plots for the 10 mM CTA-4Etocinn inhibitor solution with 6.5% ethanol in 0.01M NaCl at pH 7 after 30 minutes and 24 hours of immersion. Over time the inhibitor interaction with the surface of the substrate increases to form a protective film layer and thus moving the pitting potential (point of rapid current increase on anodic arm) to more positive values and increasing the inhibitor efficiency.

## 6 Corrosion Inhibitor Testing of CTA-4Butcinn

### 6.1 Potentiodynamic polarisation of CTA-4Butcinn

The efficiency of CTA-4Butcinn as a corrosion inhibitor was investigated. Mild steel was immersed at pH 2 for 24 hours in (a) a 0.01 M NaCl solution with 6.5% ethanol (“control solution”), and (b) a 0.1 mM CTA-4Butcinn and 0.01 M NaCl solution (“inhibitor solution”). Mild steel was immersed at pH 2 for 24 hours in (a) a 0.01 M NaCl solution with 6.5% ethanol (“control solution”), and (b) a 0.1 mM CTA-4Butcinn and 0.01 M NaCl solution (“inhibitor solution”).

Figure 22a shows the Tafel plots for the control solution and inhibitor solution after 30 minutes immersion, Figure 22b shows the Tafel plots for the control solution and inhibitor solution after 24 hours immersion, and Figure 22c shows a combined plot comparing the effect between 30 minute and 24 hour immersions.

The results demonstrate that CTA-4Butcinn at 0.1 mM concentration reduced the corrosion process in comparison with the control sample. CTA-4Butcinn shifted the  $E_{\text{corr}}$  towards more anodic potentials. At 30 minutes there is some reduction of the cathodic current densities, suggesting a mixed mode of inhibition, and it appears that this reduction of the cathodic current density may linger after 24 hours.

## 6.2 Optical and SEM/EDXS test with CTA-4Butcinn

Figure 23 shows optical images of the sample immersed for 24 h in control solution (Figure 23(a)(i) and (ii)) and inhibitor solution (Figure 23(b)). The sample immersed in inhibitor solution showed a significant less corrosion, indicating that protection of the alloy surfaces can occur and may suggest organic film formation on the surface of alloy.

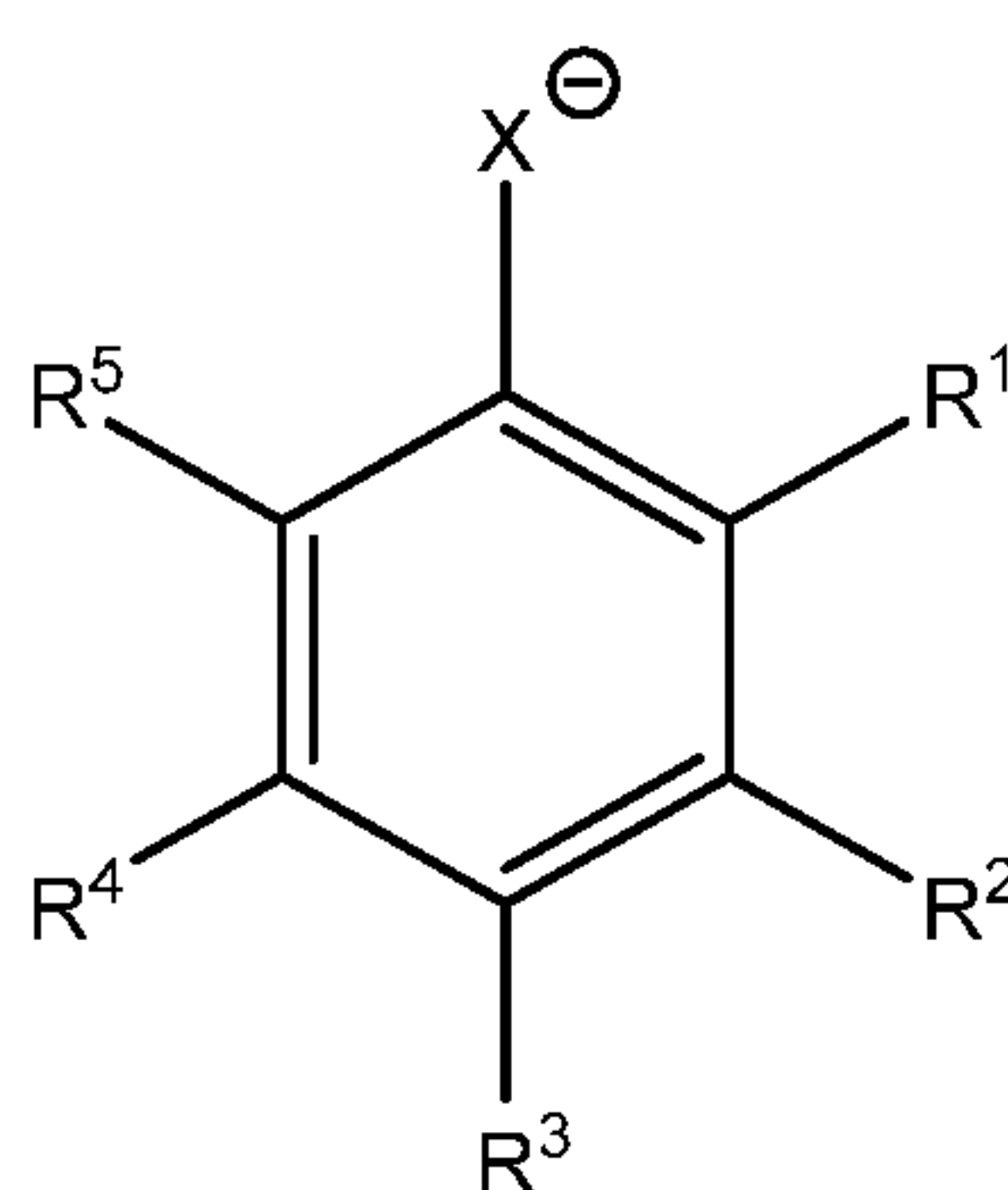
Figure 24 shows the SEM image of mild steel after 24 h of immersion in control (Figure 24(b)) and the inhibitor (Figure 24(a)) solutions. Extensive damage can be seen on the control sample, while small deposits are visible on the inhibitor sample

Overall, the results show electrochemical and morphological differences between those samples exposed to the control solution and those samples exposed to the organic corrosion inhibitor solution.

**CLAIMS:**

1. A method for inhibiting corrosion on a substrate by providing one or more coatings on the substrate, wherein at least one coating comprises an organic corrosion inhibitor comprising onium cation groups and aromatic carboxylate counter-anion groups.

2. The method of claim 1, wherein the aromatic carboxylate counter-anion groups are of Formula 1:



Formula 1

wherein

X is an optionally linked carboxylate anion group; and

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup>, are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

3. The method of claim 2, wherein:

R<sup>1</sup> and R<sup>5</sup> are hydrogen; and

R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, and O-heteroalkenyl.

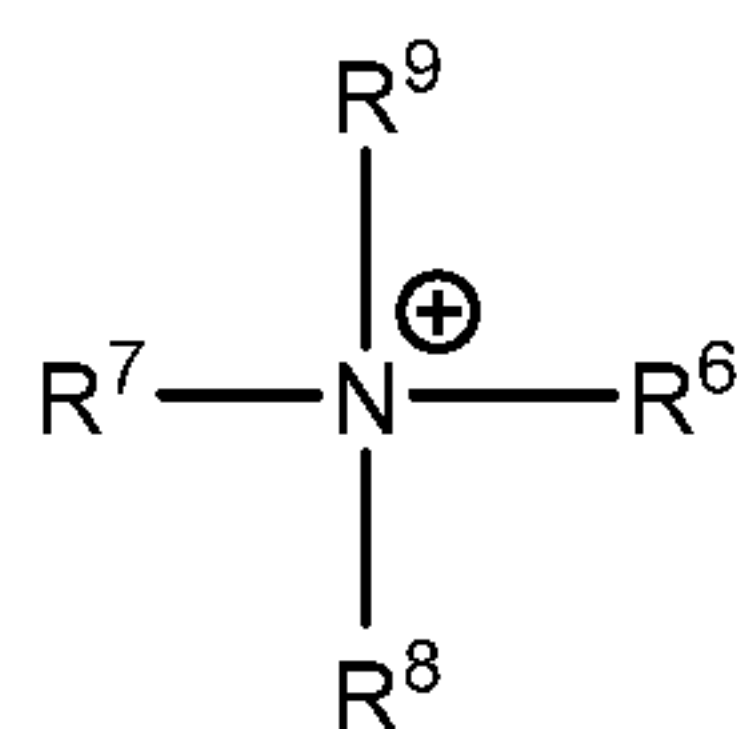
4. The method of claim 2 or claim 3, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-alkyl, O-alkenyl, O-heteroalkyl, and O-heteroalkenyl.

5. The method of any one of claims 2 to 4, wherein at least one of R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup>, is selected from O-C<sub>1-12</sub>alkyl, O-C<sub>2-12</sub>alkyl, or O-C<sub>3-6</sub>alkyl.

6. The method of any one of claims 2 to 5, wherein each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is selected from O-C<sub>1-12</sub>alkyl, O-C<sub>2-12</sub>alkyl, or O-C<sub>3-6</sub>alkyl.

7. The method of any one of claims 1 to 6, wherein the onium cation groups are polymerizable quaternary onium cation groups selected from ammonium cation groups, pyridinium cation groups, imidazolium cation groups, pyrazolium cation groups, and pyrrolidinium cation groups.

8. The method of any one of claims 1 to 7, wherein the onium cation groups are quaternary nitrogen cation groups of Formula 2a:



Formula 2a

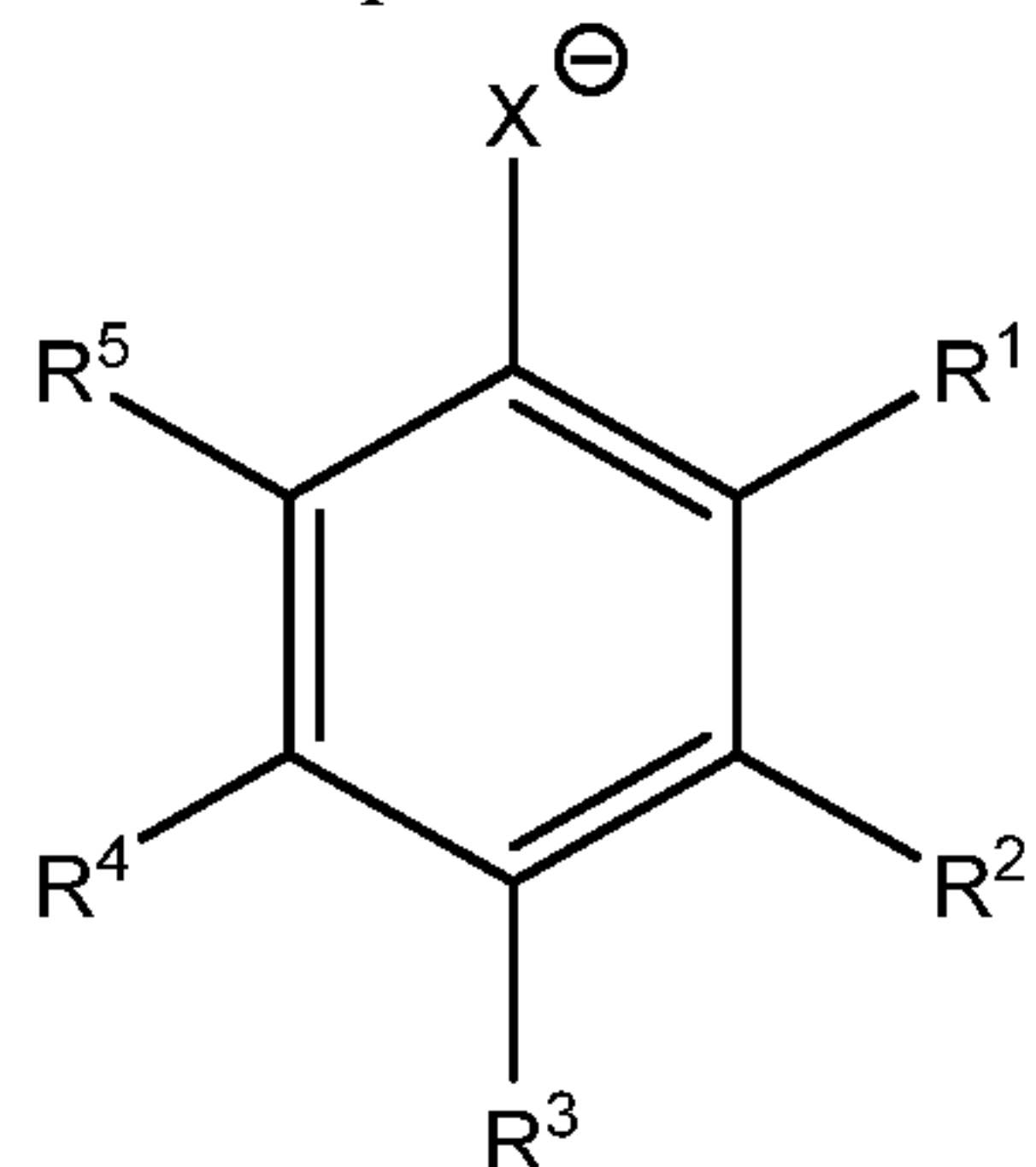
wherein

$R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$ , are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, heteroalkenyl, aryl, arylalkyl, heteroaryl, and heteroarylalkyl, and wherein two or more of  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$ , may join together to provide an aromatic or aliphatic ring.

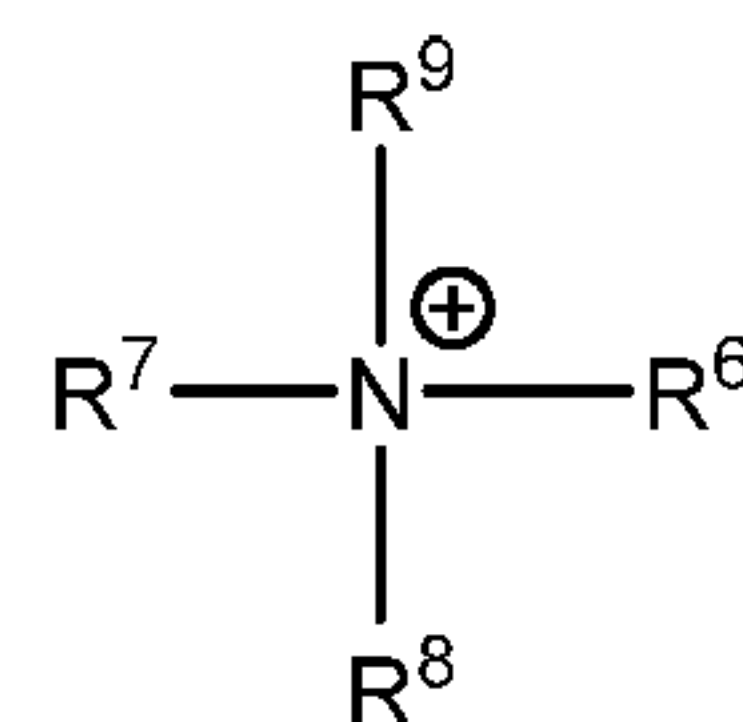
9. The method of claim 8, wherein  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$ , are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl.

10. The method of any one of claims 1 to 9, wherein the substrate is a metal substrate.

11. The method of any one of claims 1 to 10, wherein the coating comprises an aromatic carboxylate compound of Formula 1 and ammonium compound of Formula 2a:



Formula 1



Formula 2a

wherein

X is an optionally linked carboxylate anion group;

$R^1$  to  $R^5$  are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl;

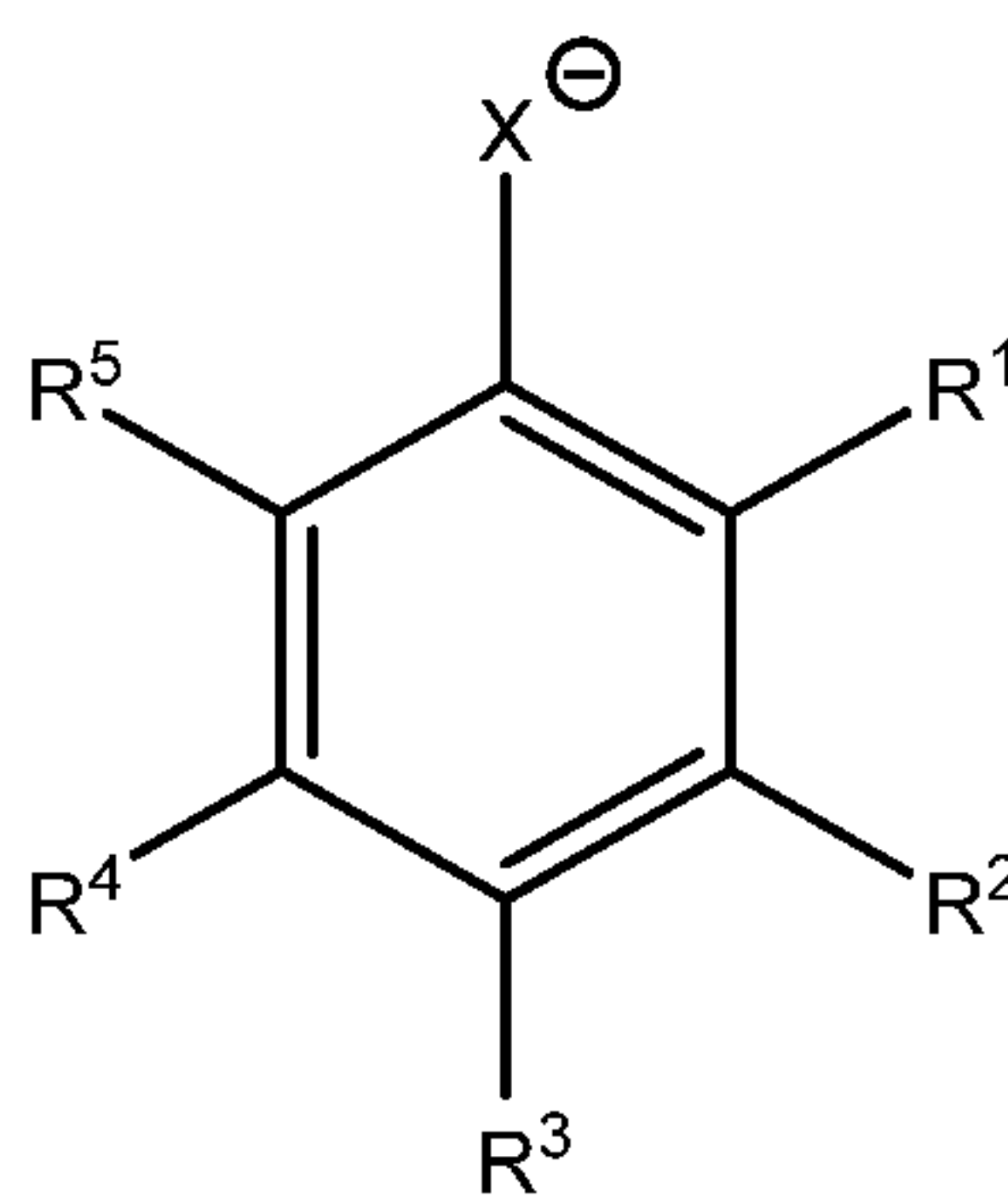
$R^6$ ,  $R^7$ ,  $R^8$ , and  $R^9$ , are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl.

12. A coated metal substrate comprising a metal substrate coated with one or more coating layers, wherein at least one of the coating layers comprises an organic corrosion inhibitor as defined in any one of claims 1 to 11.

13. A coating system comprising:

- (i) an optionally coated metal substrate;
- (ii) one or more optional post coating layers; and
- (iii) one or more corrosion protection layers located between (i) and (ii) comprising comprises an organic corrosion inhibitor as defined in any one of claims 1 to 11.

14. An organic corrosion inhibitor comprising or consisting of an aromatic carboxylate of Formula 1 and an onium cation:



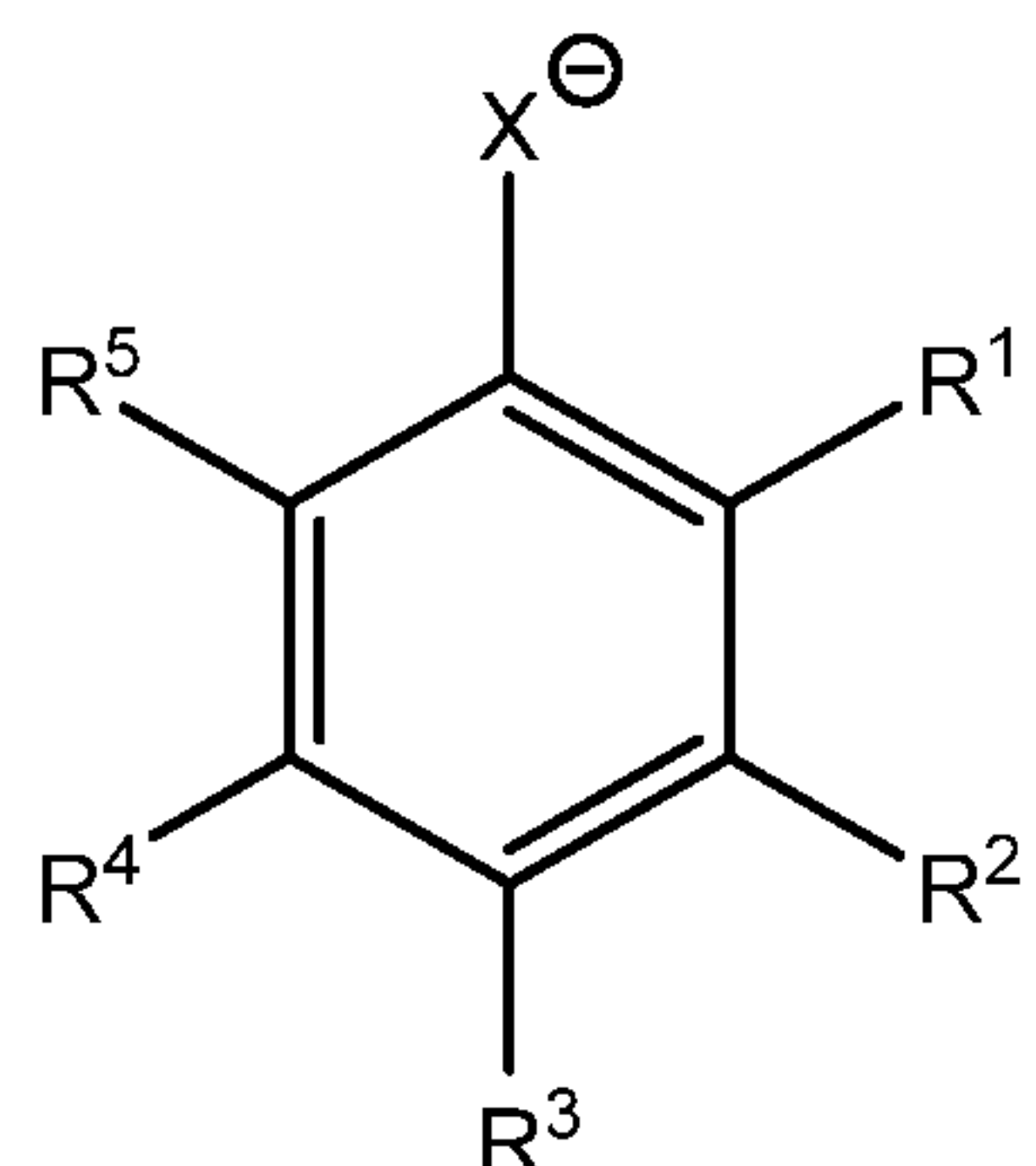
Formula 1

wherein

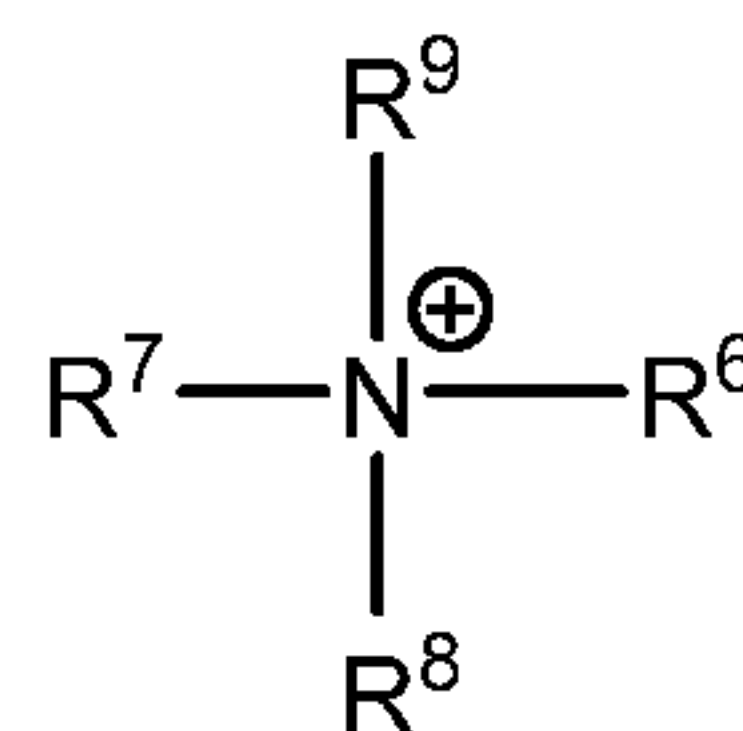
X is an optionally linked carboxylate anion group; and

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$ , are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

15. The organic corrosion inhibitor of claim 14, wherein the aromatic carboxylate counter-anions are of Formula 1 and the onium cations are of Formula 2a:



Formula 1



Formula 2a

wherein

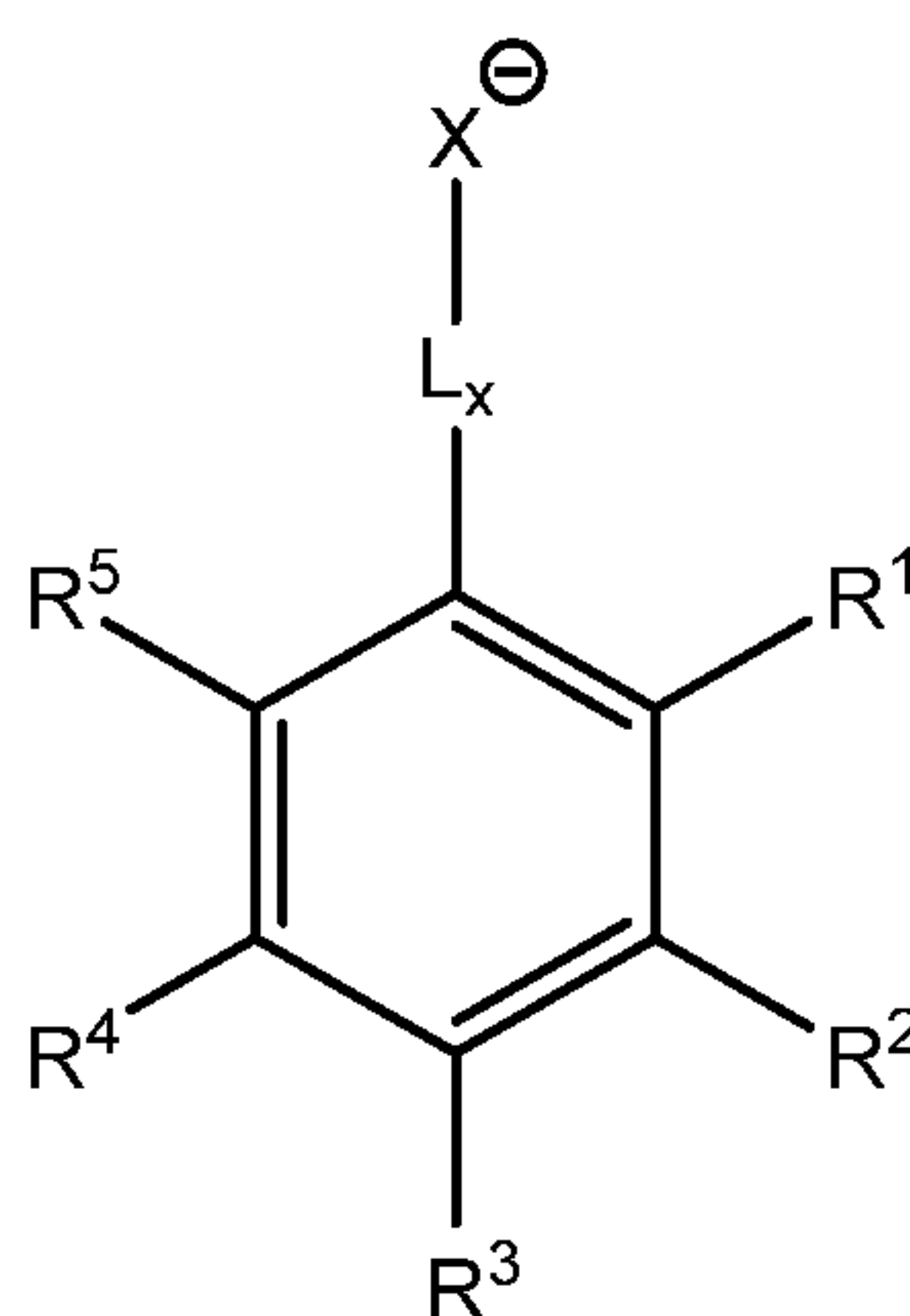
X is an optionally linked carboxylate anion group;

R<sup>1</sup> and R<sup>5</sup> are hydrogen;

R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl;

R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup>, are each independently selected from hydrogen, alkyl, alkenyl, heteroalkyl, and heteroalkenyl.

16. The organic corrosion inhibitor of claim 14 or claim 15, wherein the aromatic carboxylate counter-anions are of Formula 1a:



Formula 1a

wherein

X is a carboxylate group;

$L_x$  is an optional divalent linking group selected from alkyl, alkenyl, heteroalkyl, and heteroalkenyl;

$R^1$  and  $R^5$  are hydrogen;

$R^2$ ,  $R^3$ , and  $R^4$  are each independently selected from hydrogen, halo, hydroxyl, alkyl, alkenyl, heteroalkyl, heteroalkenyl, O-alkyl, O-alkenyl, O-heteroalkyl, O-heteroalkenyl, O-C(=O)-alkyl, O-C(=O)-alkenyl, O-C(=O)-heteroalkyl, and O-C(=O)-heteroalkenyl.

17. The organic corrosion inhibitor of any one of claims 14 to 16, wherein at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from O-alkyl, O-alkenyl, O-heteroalkyl, and O-heteroalkenyl.

18. The organic corrosion inhibitor of any one of claims 14 to 17, wherein at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from O-C<sub>1-12</sub>alkyl, O-C<sub>2-12</sub>alkyl, or O-C<sub>3-6</sub>alkyl.

19. The organic corrosion inhibitor of any one of claims 14 to 18, wherein each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is selected from O-C<sub>1-12</sub>alkyl, O-C<sub>2-12</sub>alkyl, or O-C<sub>3-6</sub>alkyl.

20. A composition comprising or consisting of an organic corrosion inhibitor as defined in any one of claims 14 to 19.

21. The composition of claim 20, wherein the composition is a liquid formulation comprising one or more liquid carriers.

22. The composition of claims 20 or claim 21, wherein the composition further comprises at least one film former selected from a polymerizable monomer, oligomer, and polymer.

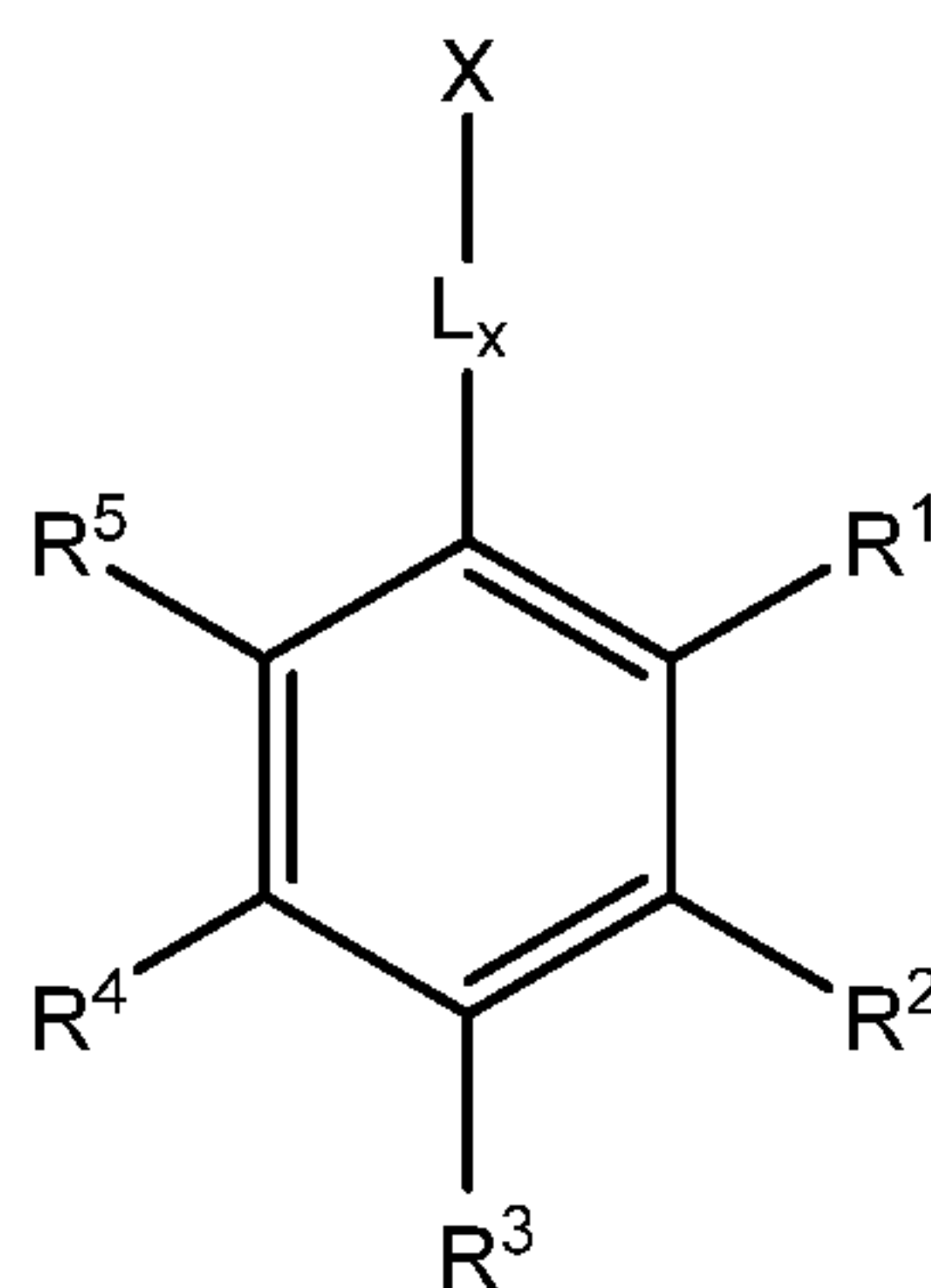
23. The composition of any one of claims 20 to 22, wherein the composition comprises one or more additives selected from a solvent, a curing agent, an adhesion promoter, an inorganic filler, a wetting agent, and an organic crosslinker.

24. A process for preparing a coating system comprising:

applying the organic corrosion inhibitor or coating composition thereof according to any one of claims 14 to 19 to an optionally coated substrate; and

optionally applying one or more post coating layer to the coating present on the optionally coated substrate.

25. A compound of Formula 1a or salt thereof:



Formula 1a

wherein

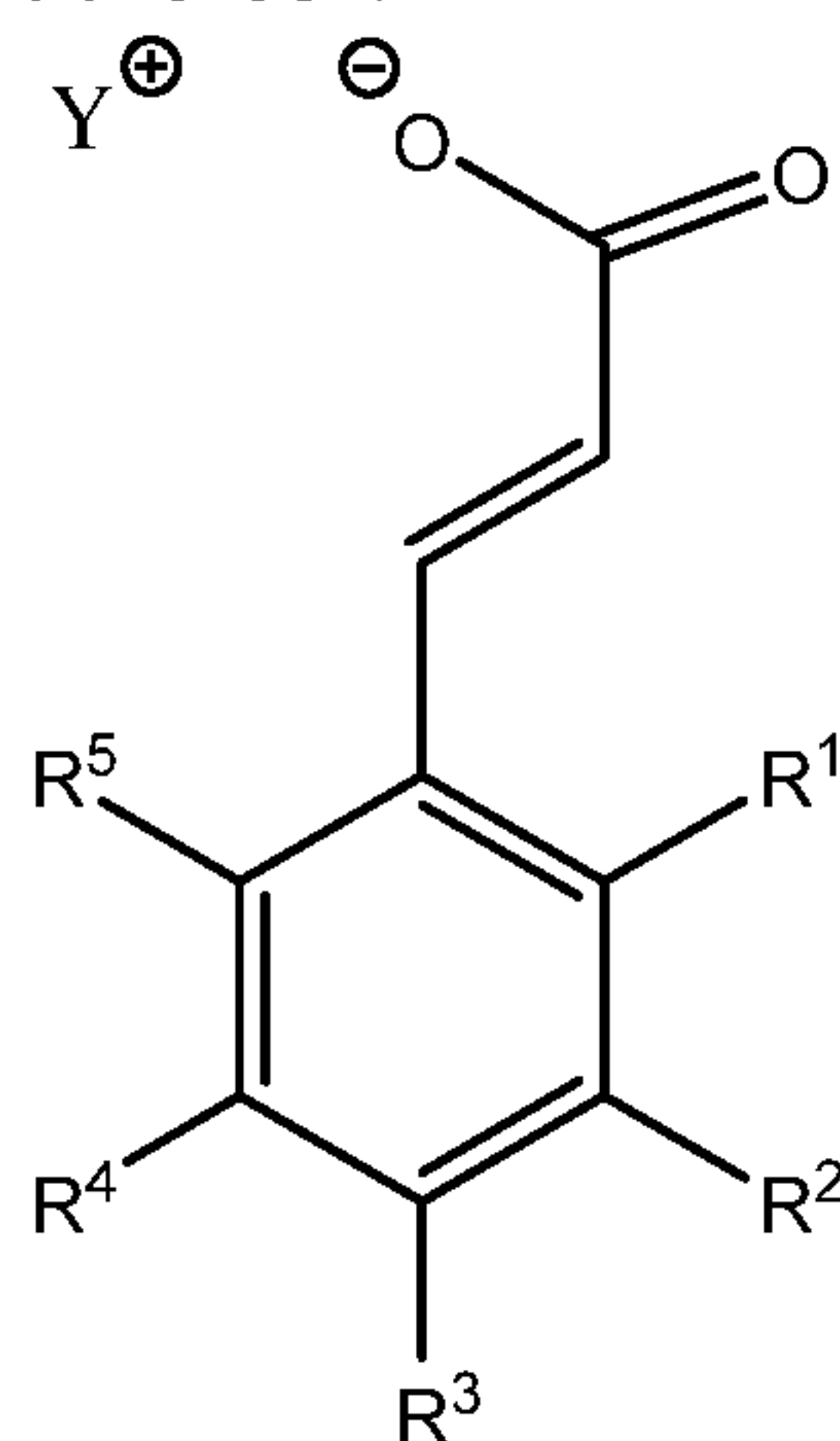
X is a carboxylic acid or carboxylate group;

L<sub>x</sub> is an optional divalent linking group selected from alkyl, alkenyl, heteroalkyl, and heteroalkenyl;

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup>, are each independently selected from hydrogen, halo, hydroxyl, C<sub>1-12</sub>alkyl, C<sub>1-12</sub>alkenyl, C<sub>1-12</sub>heteroalkyl, C<sub>1-12</sub>heteroalkenyl, O-C<sub>1-12</sub>alkyl, O-C<sub>1-12</sub>alkenyl, O-C<sub>1-12</sub>heteroalkyl, and O-C<sub>1-12</sub>heteroalkenyl;

with the proviso that R<sup>3</sup> is not hydrogen, hydroxyl or methoxyl, when R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, and R<sup>5</sup>, are hydrogen and L<sub>x</sub>-X is -CH=CH-C(=O)OH.

26. The compound of claim 25, wherein the compound of Formula 1a is an ionic compound of Formula 1a(i) or salt thereof:



Formula 1a(i)

wherein

Y is a cation;

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$ , are each independently selected from hydrogen, halo, hydroxyl,  $C_{1-12}$ alkyl,  $C_{1-12}$ alkenyl,  $C_{1-12}$ heteroalkyl,  $C_{1-12}$ heteroalkenyl, O- $C_{1-12}$ alkyl, O- $C_{1-12}$ alkenyl, O- $C_{1-12}$ heteroalkyl, and O- $C_{1-12}$ heteroalkenyl.

27. The compound of claim 25 or claim 26, wherein at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from O-alkyl, O-alkenyl, O-heteroalkyl, and O-heteroalkenyl.

28. The compound of any one of claims 25 to 27, wherein at least one of  $R^2$ ,  $R^3$ , and  $R^4$ , is selected from O- $C_{1-12}$ alkyl, O- $C_{2-12}$ alkyl, or O- $C_{3-6}$ alkyl.

29. The compound of any one of claims 25 to 28, wherein each of  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$ , are hydrogen, and  $R^3$  is selected from O- $C_{1-12}$ alkyl, O- $C_{2-12}$ alkyl, or O- $C_{3-6}$ alkyl.

30. The compound of any one of claims 25 to 29, wherein Y is selected from any onium cation as defined in any one of claims 14 to 19.

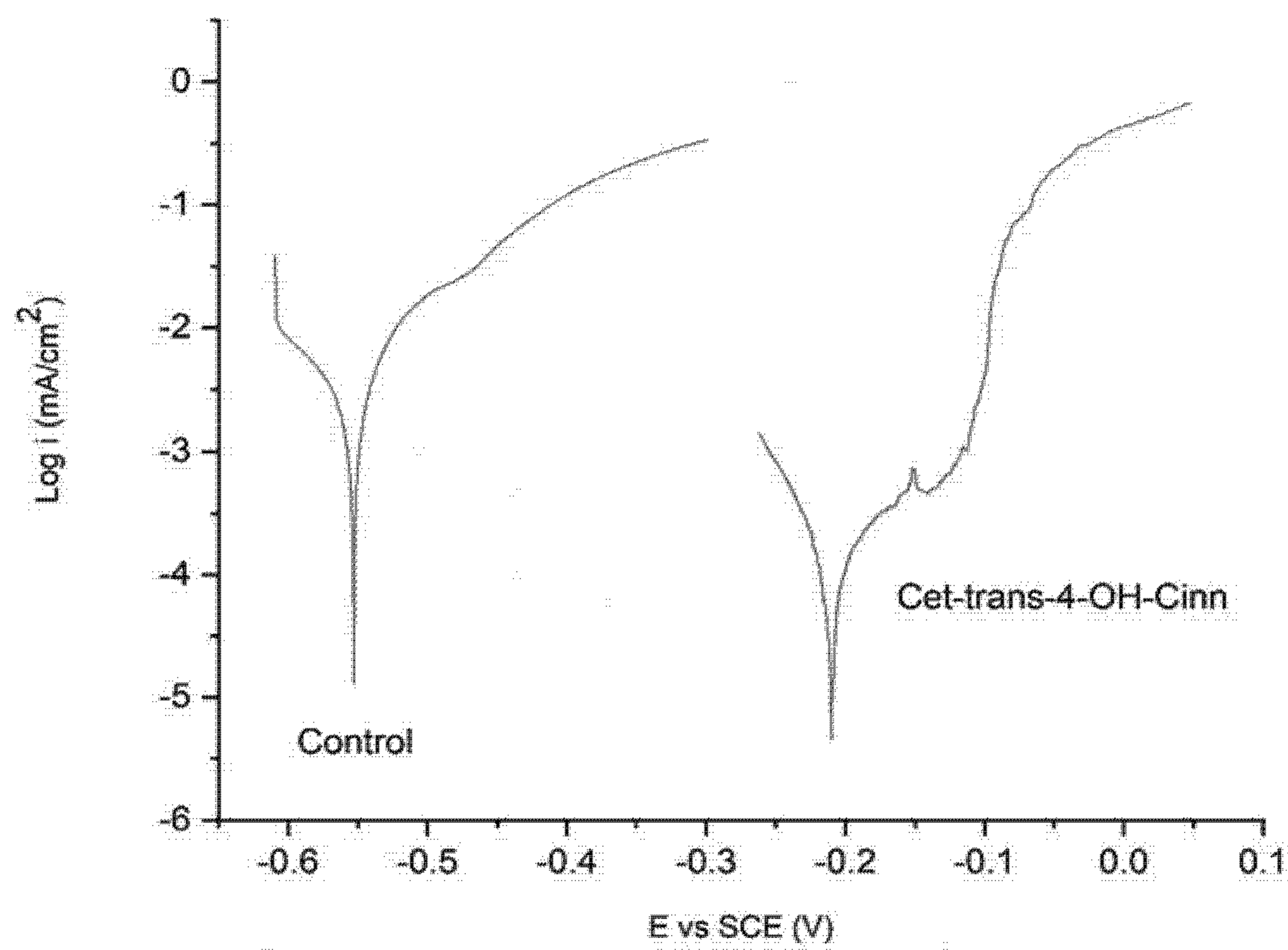


Figure 1

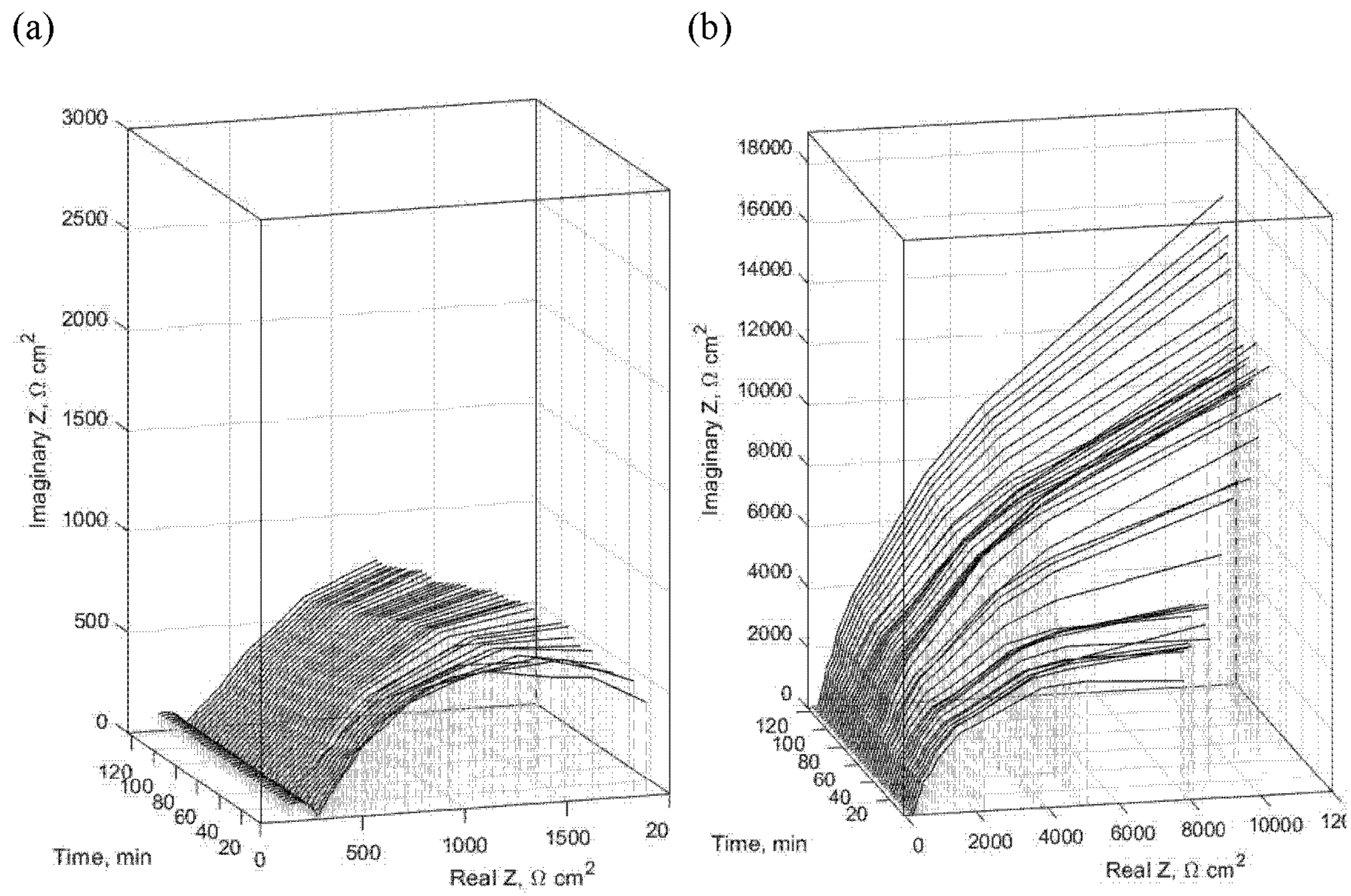


Figure 2

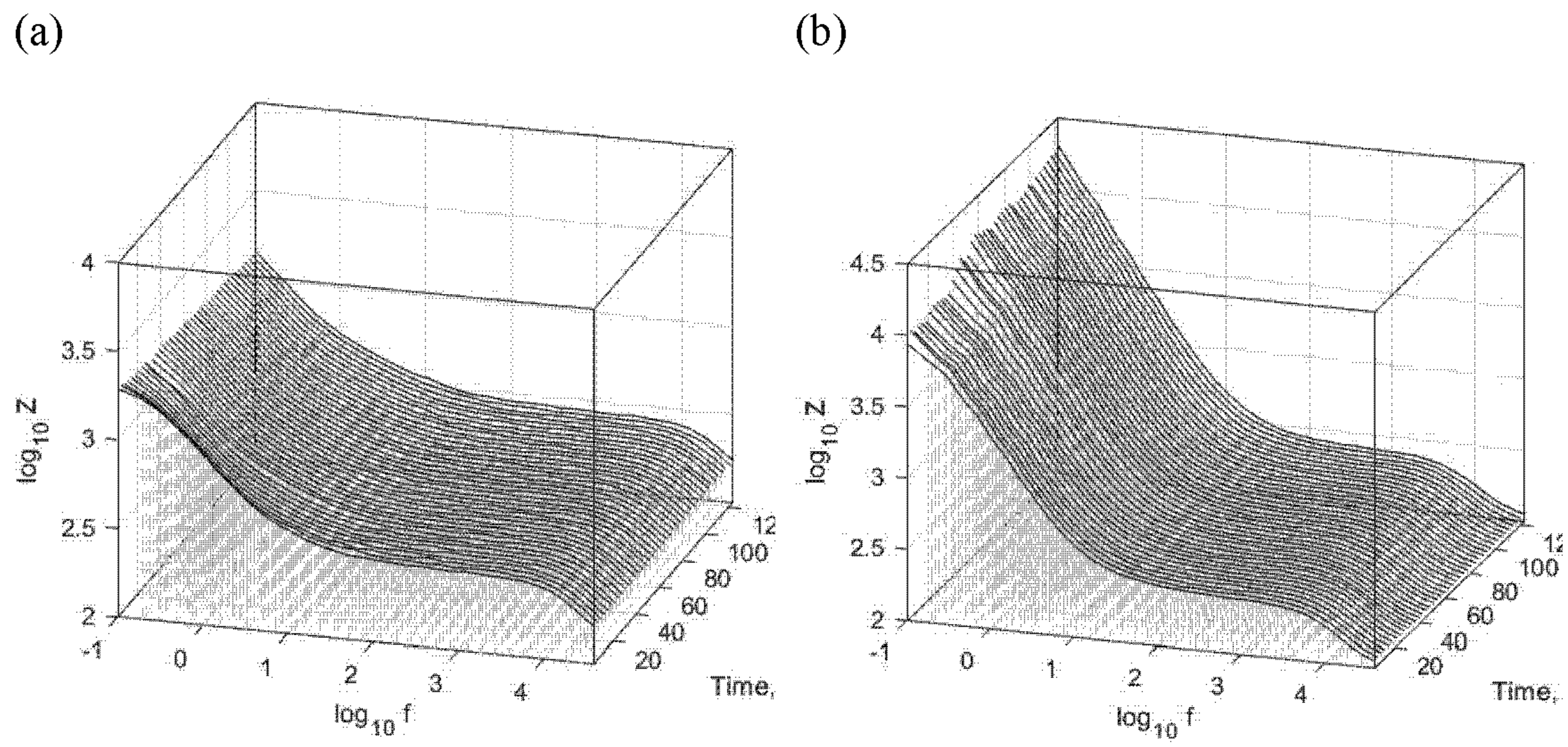


Figure 3

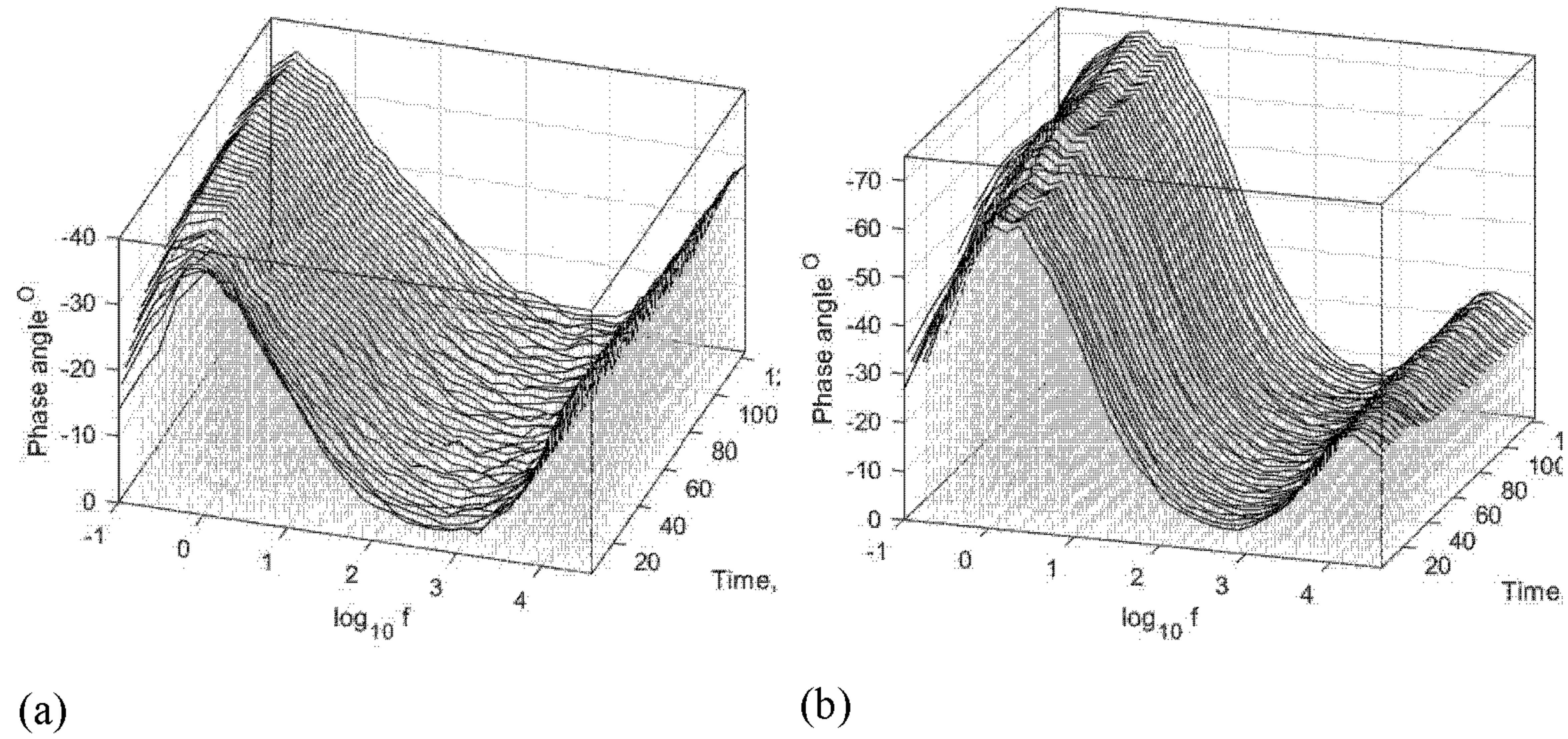


Figure 4

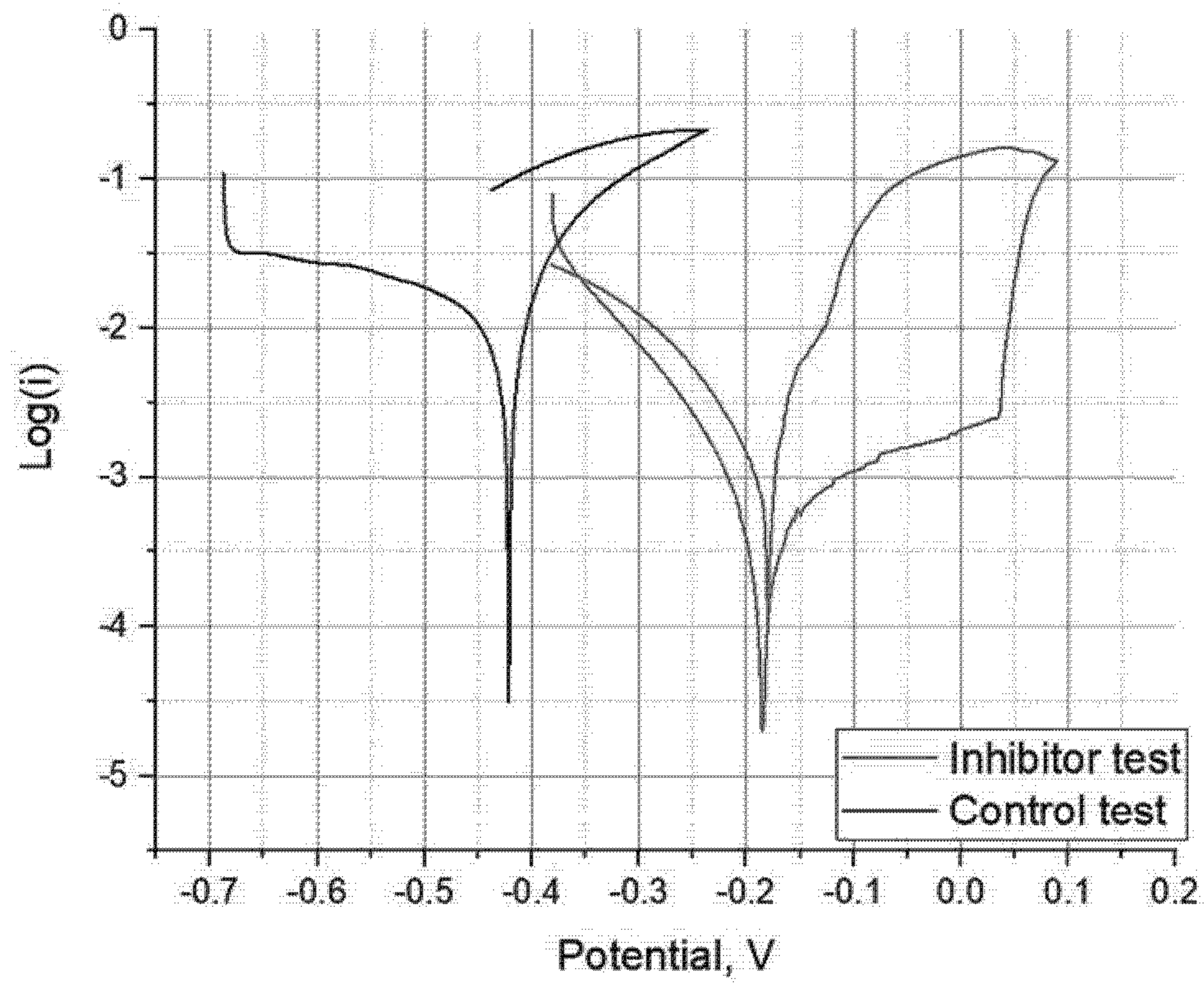


Figure 5

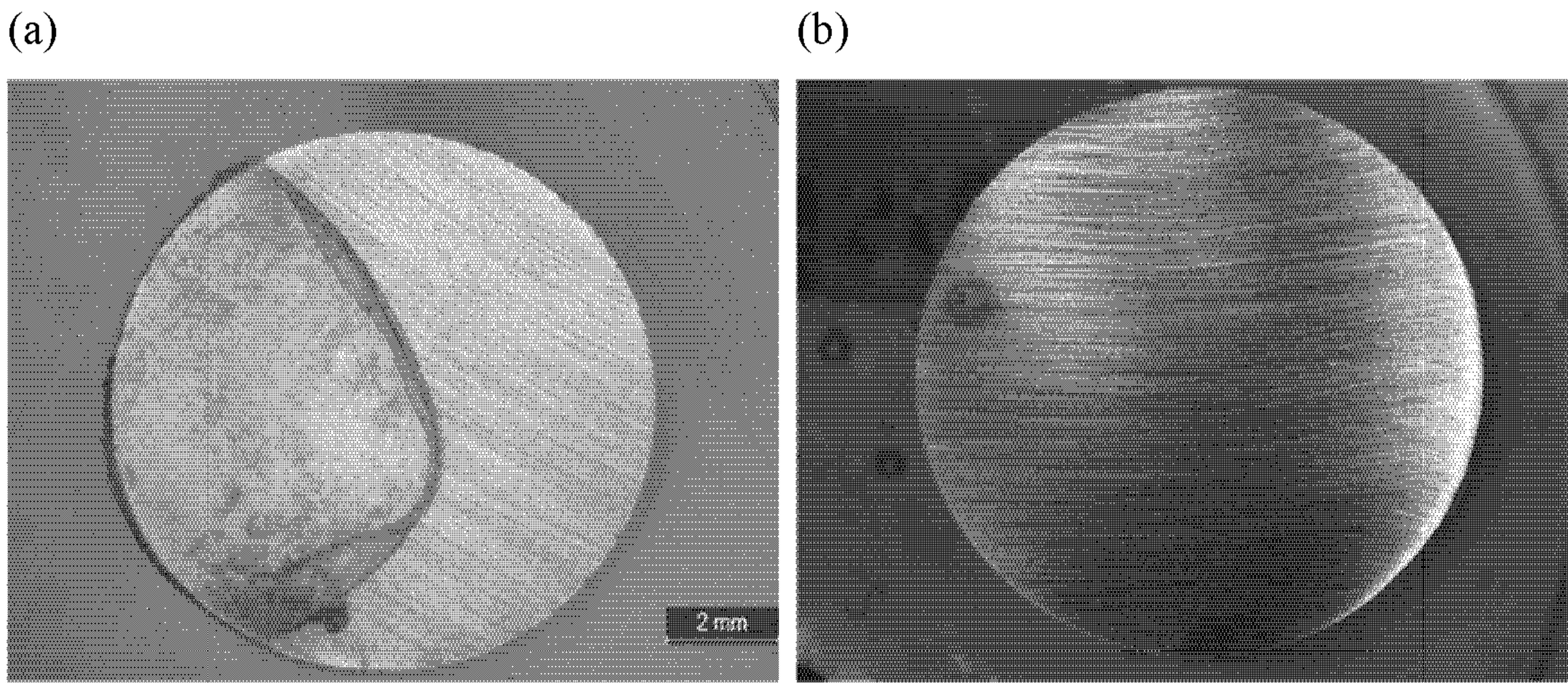


Figure 6

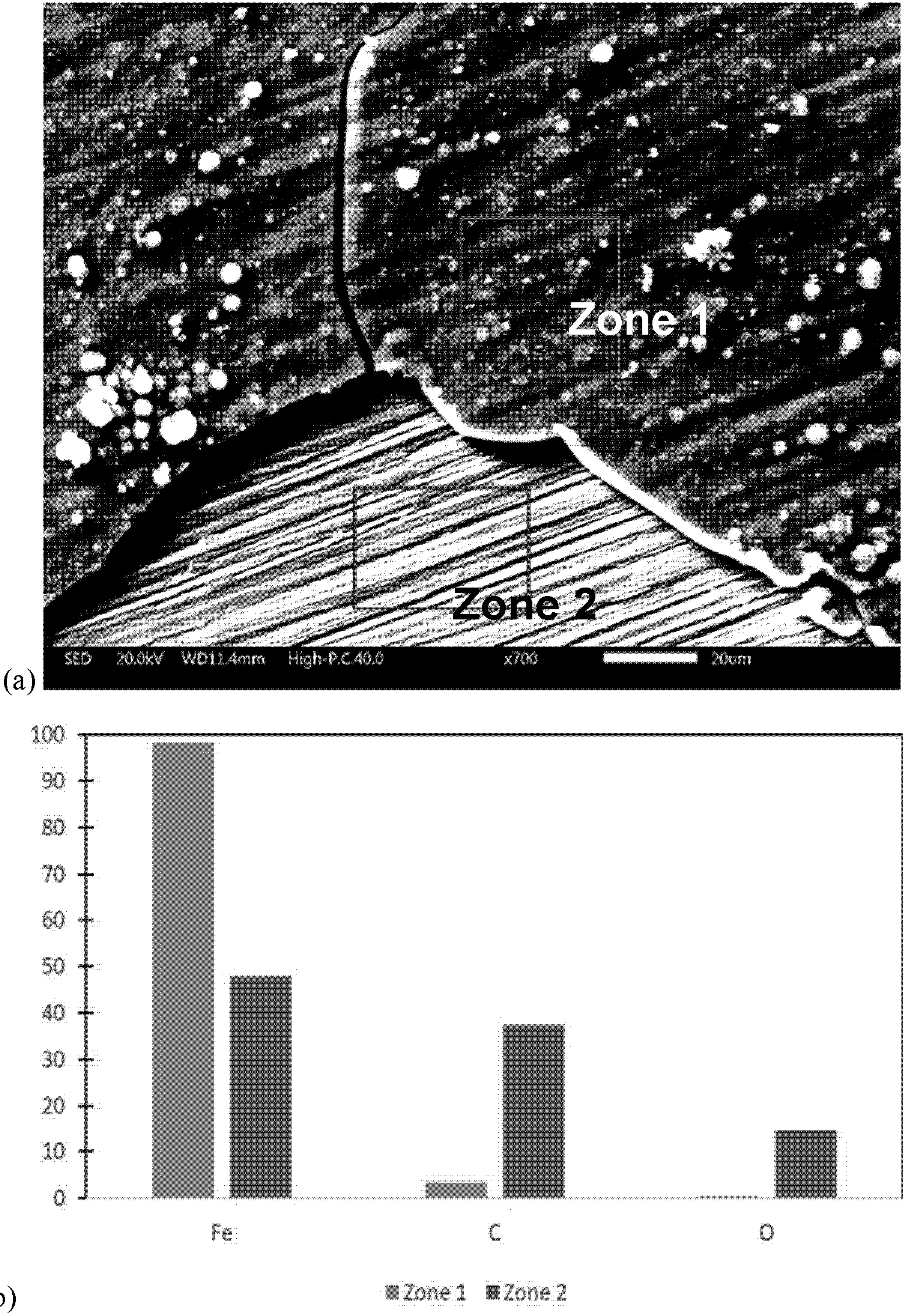


Figure 7

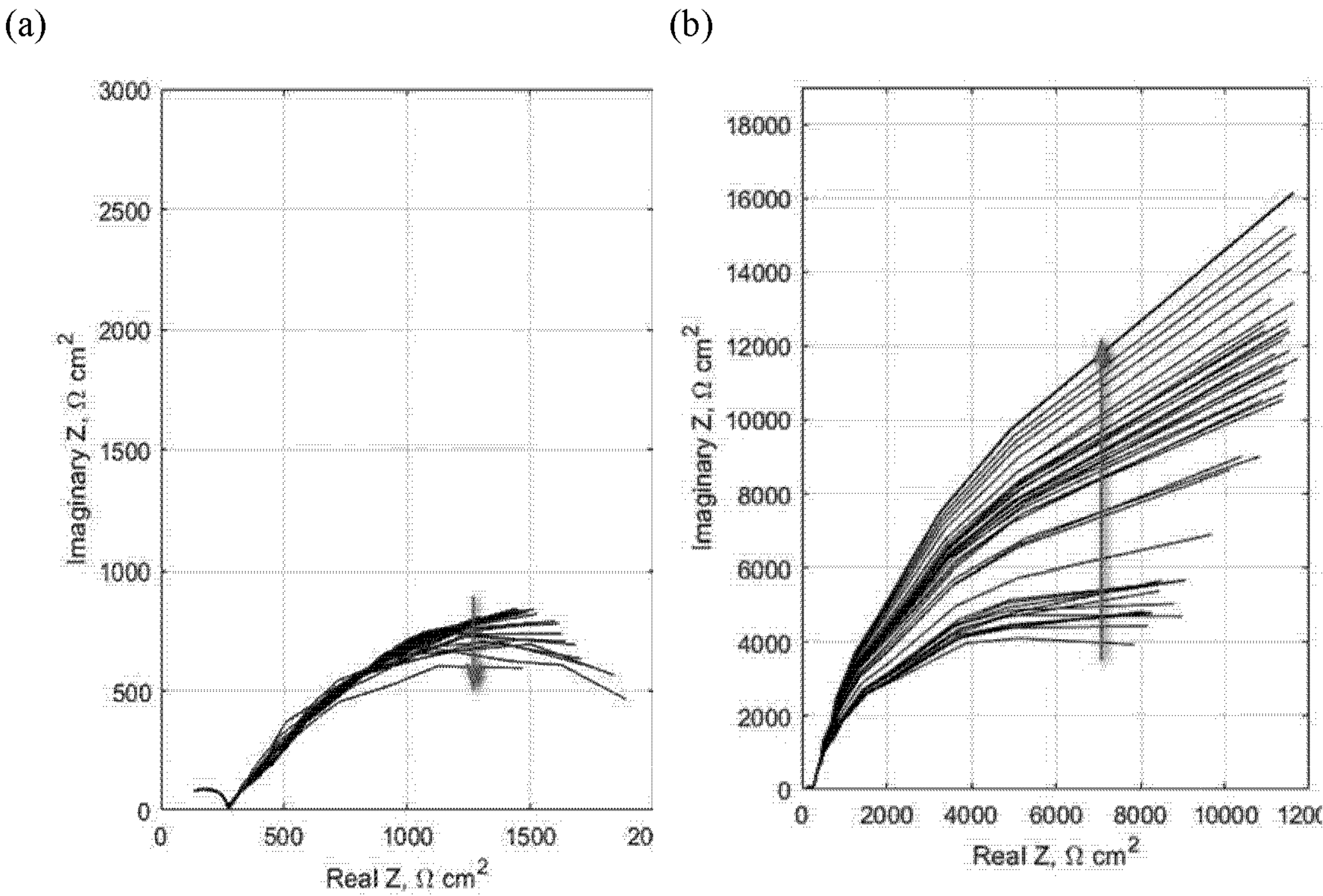


Figure 8

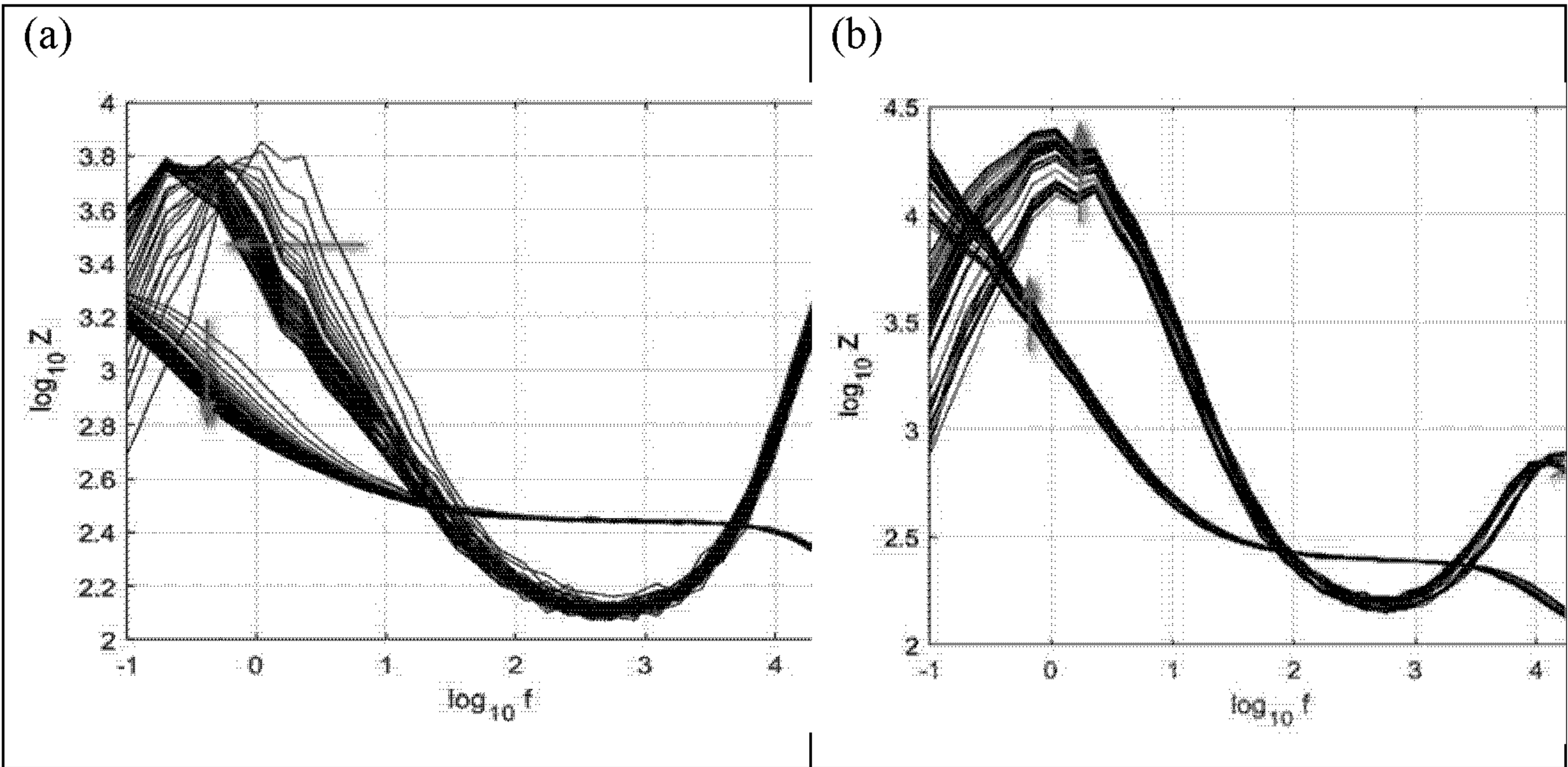


Figure 9

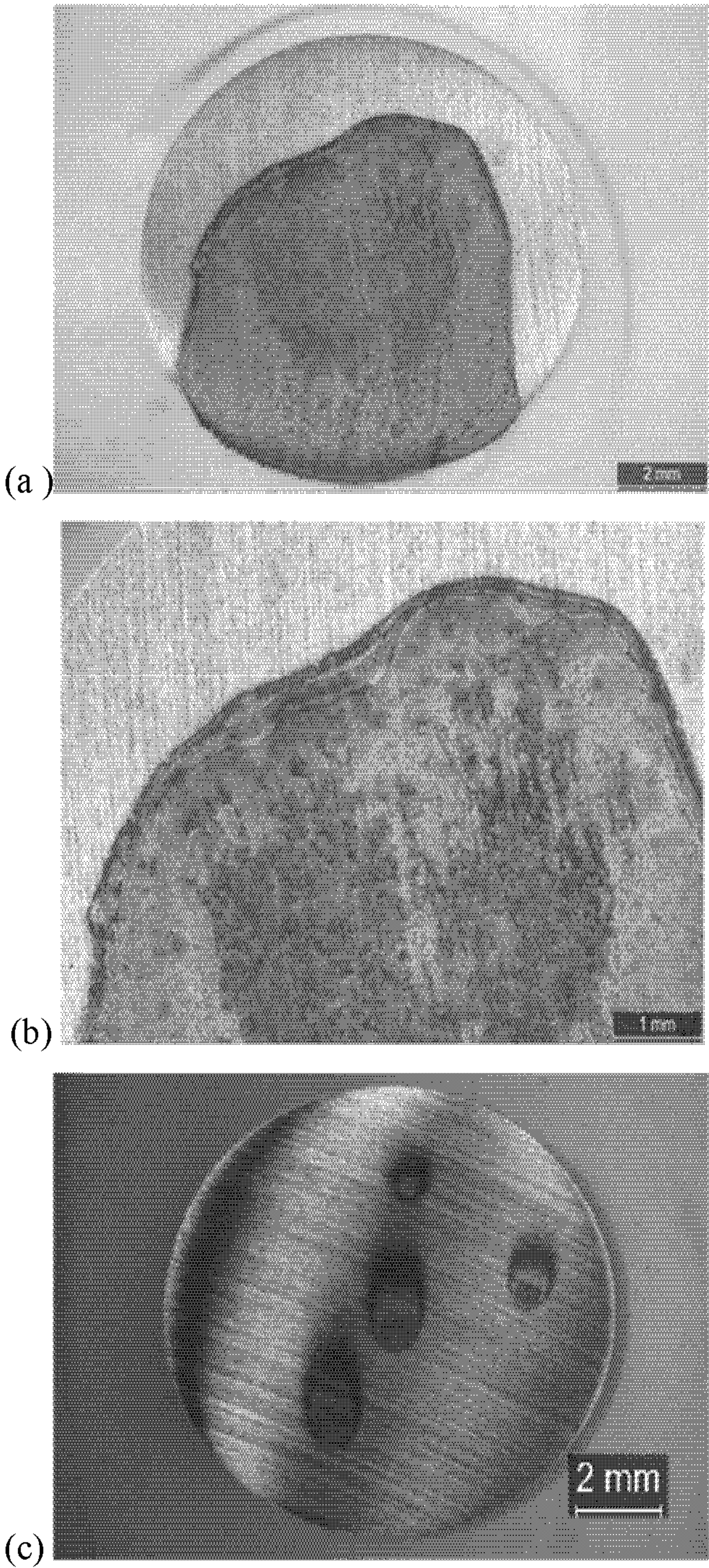


Figure 10

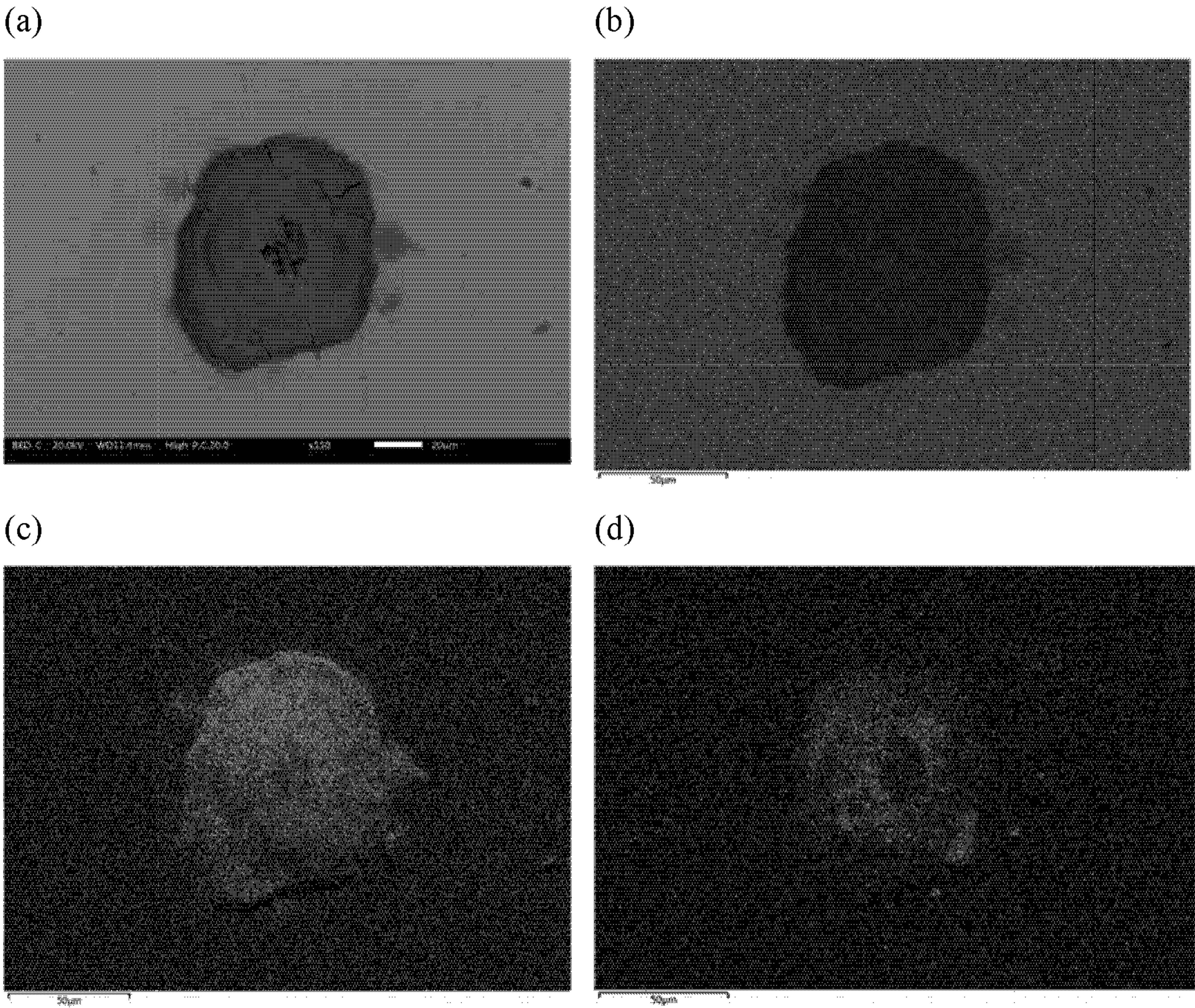


Figure 11

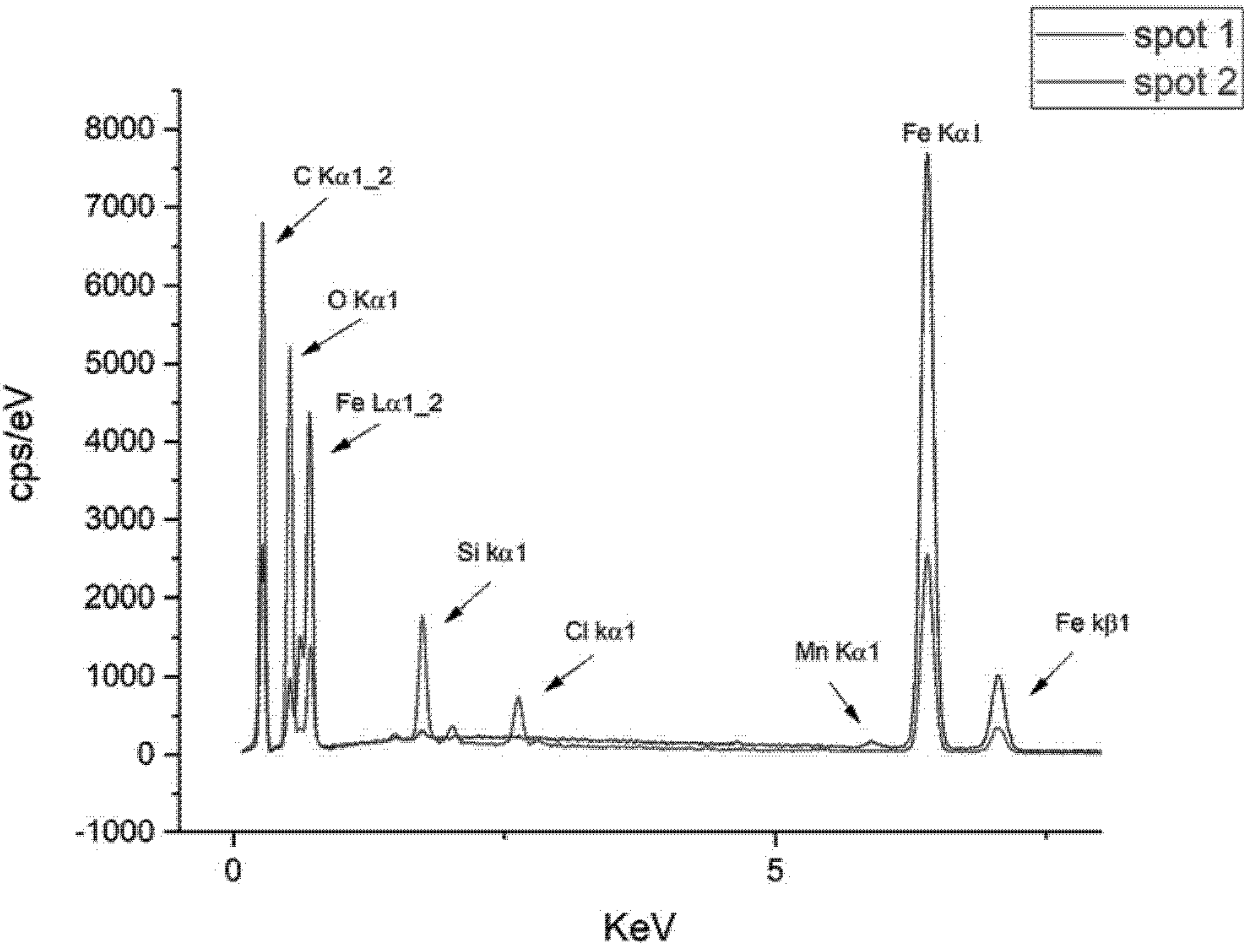


Figure 12

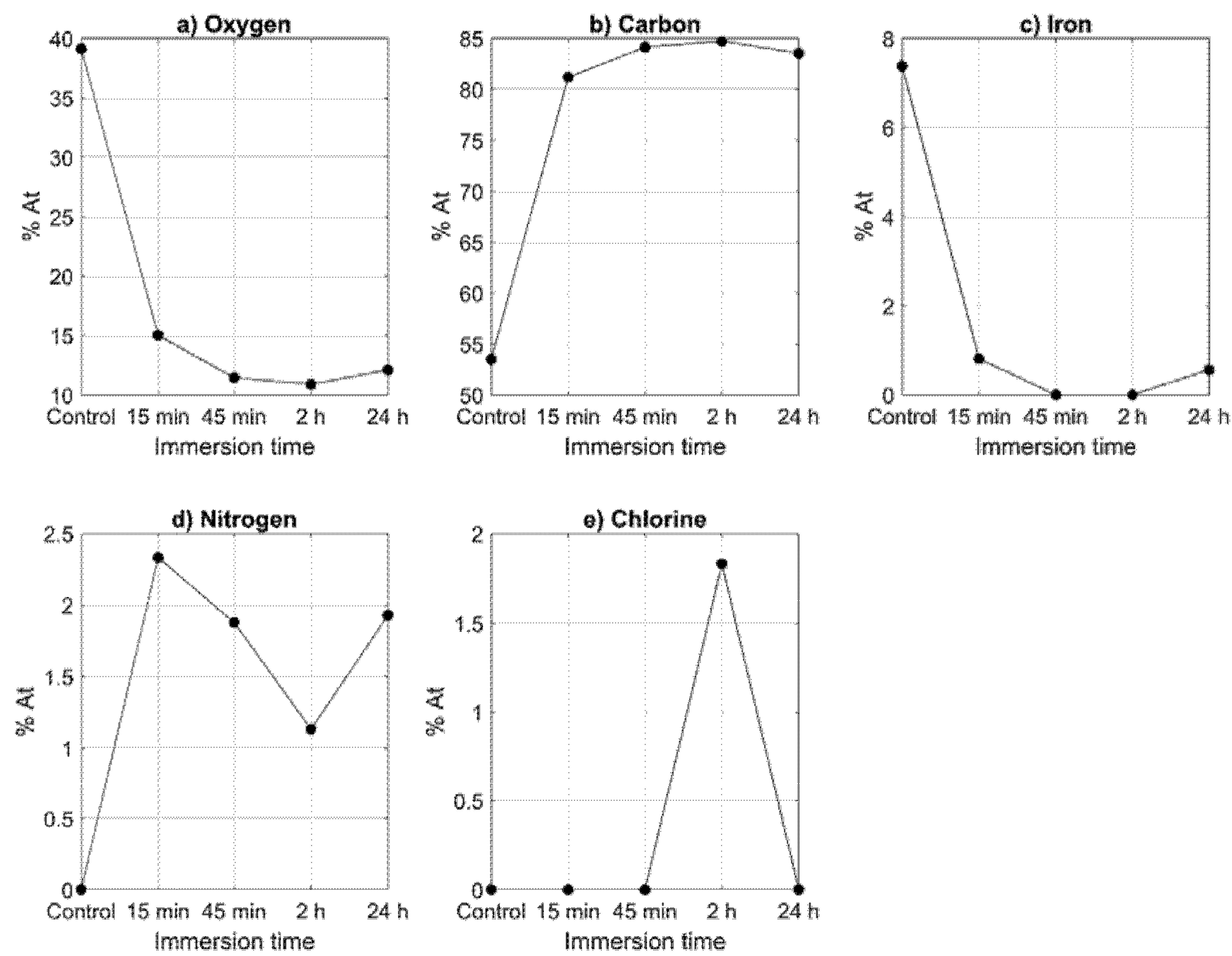


Figure 13

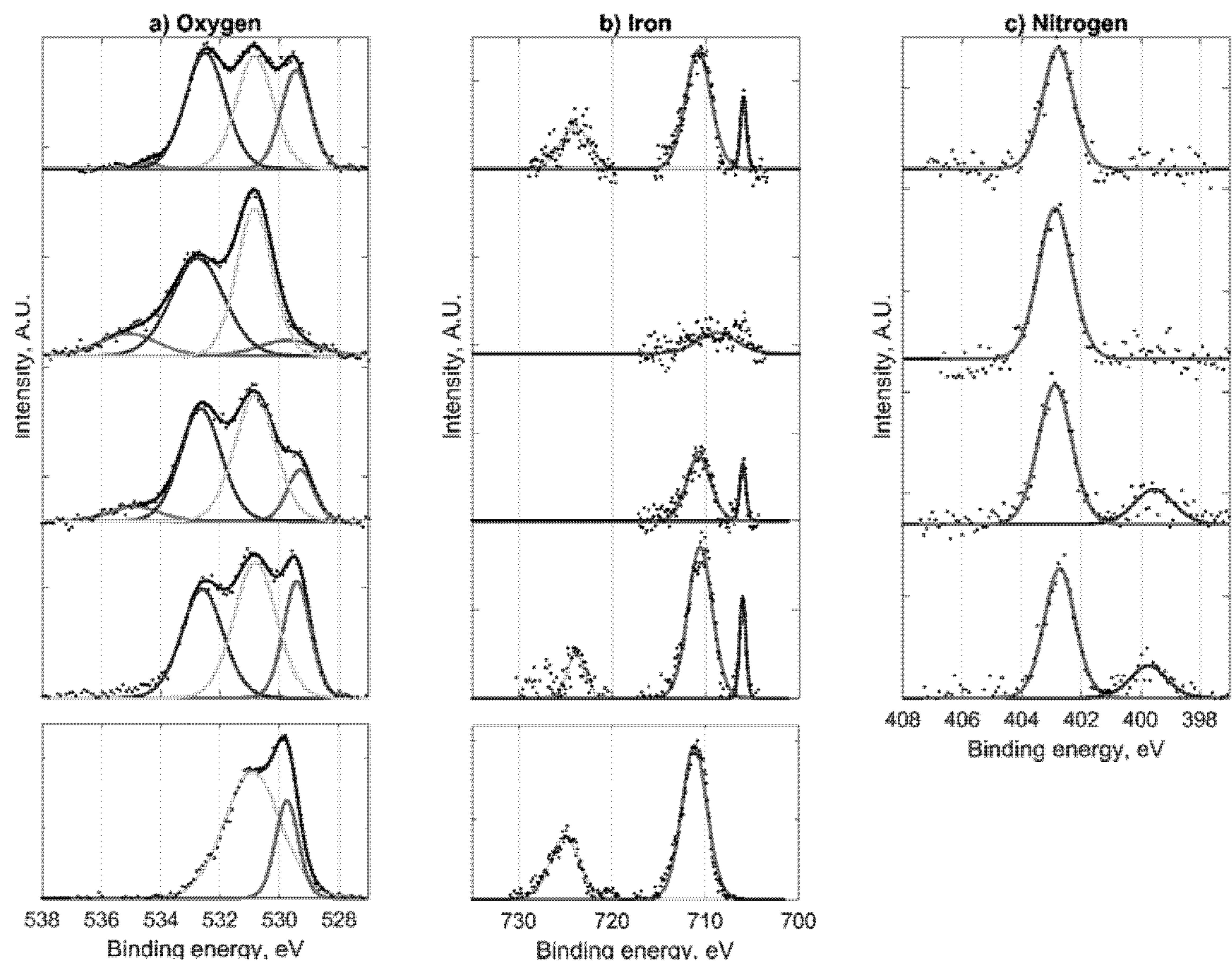


Figure 14

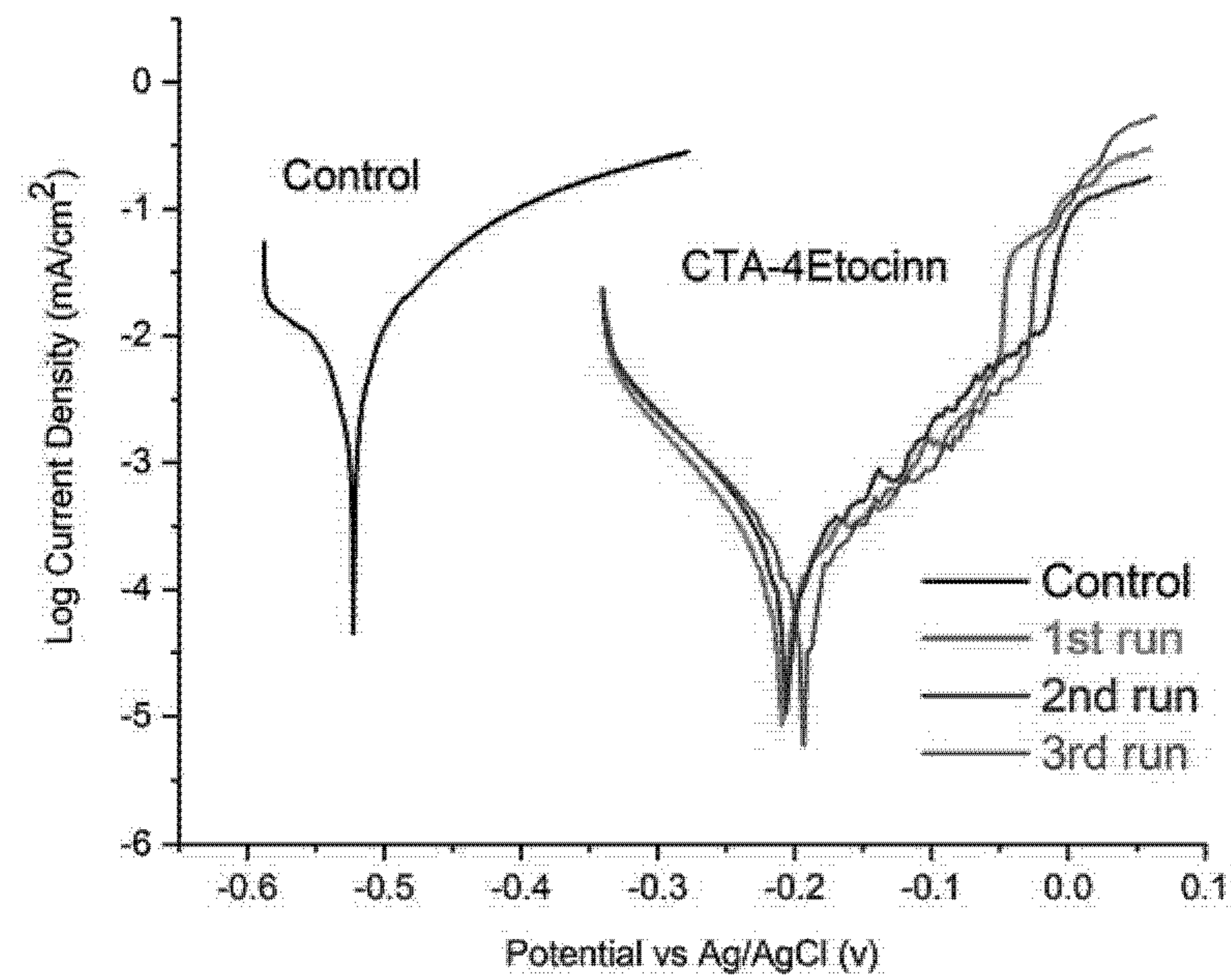


Figure 15

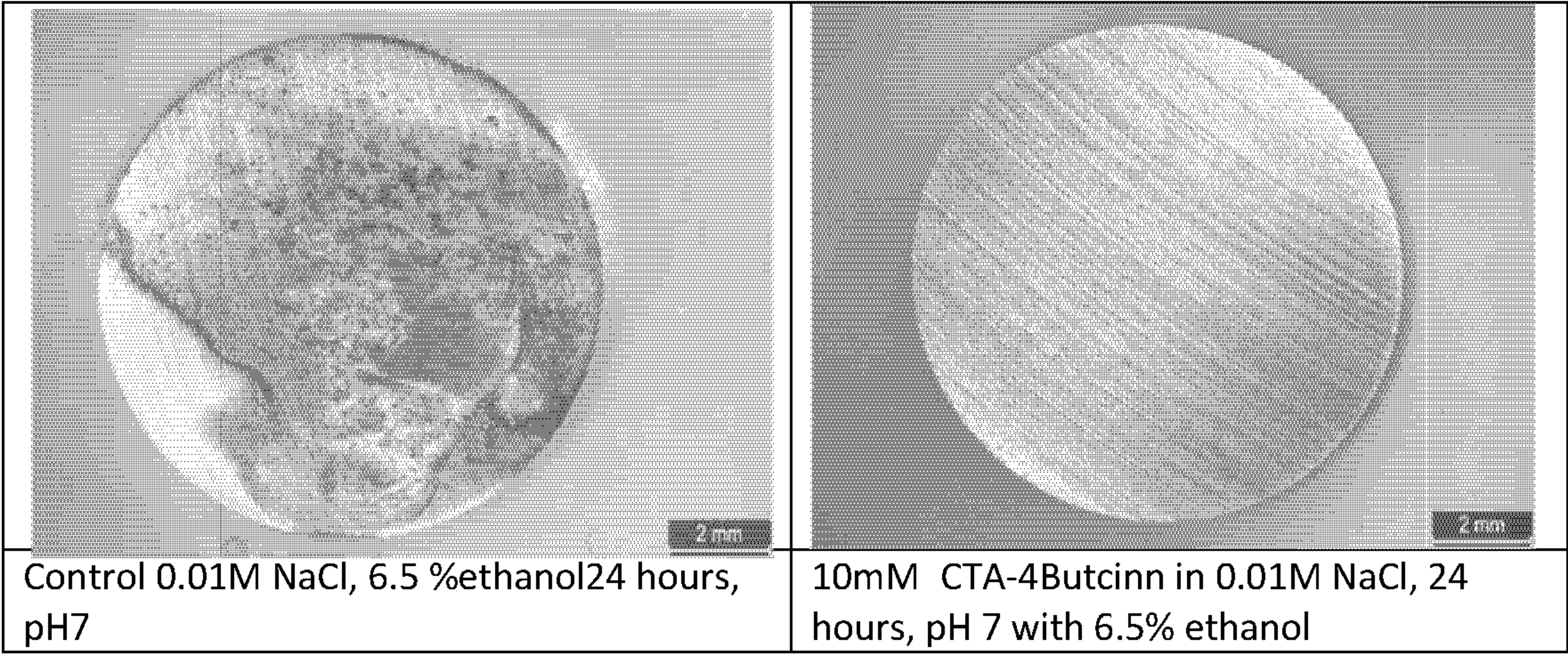


Figure 16

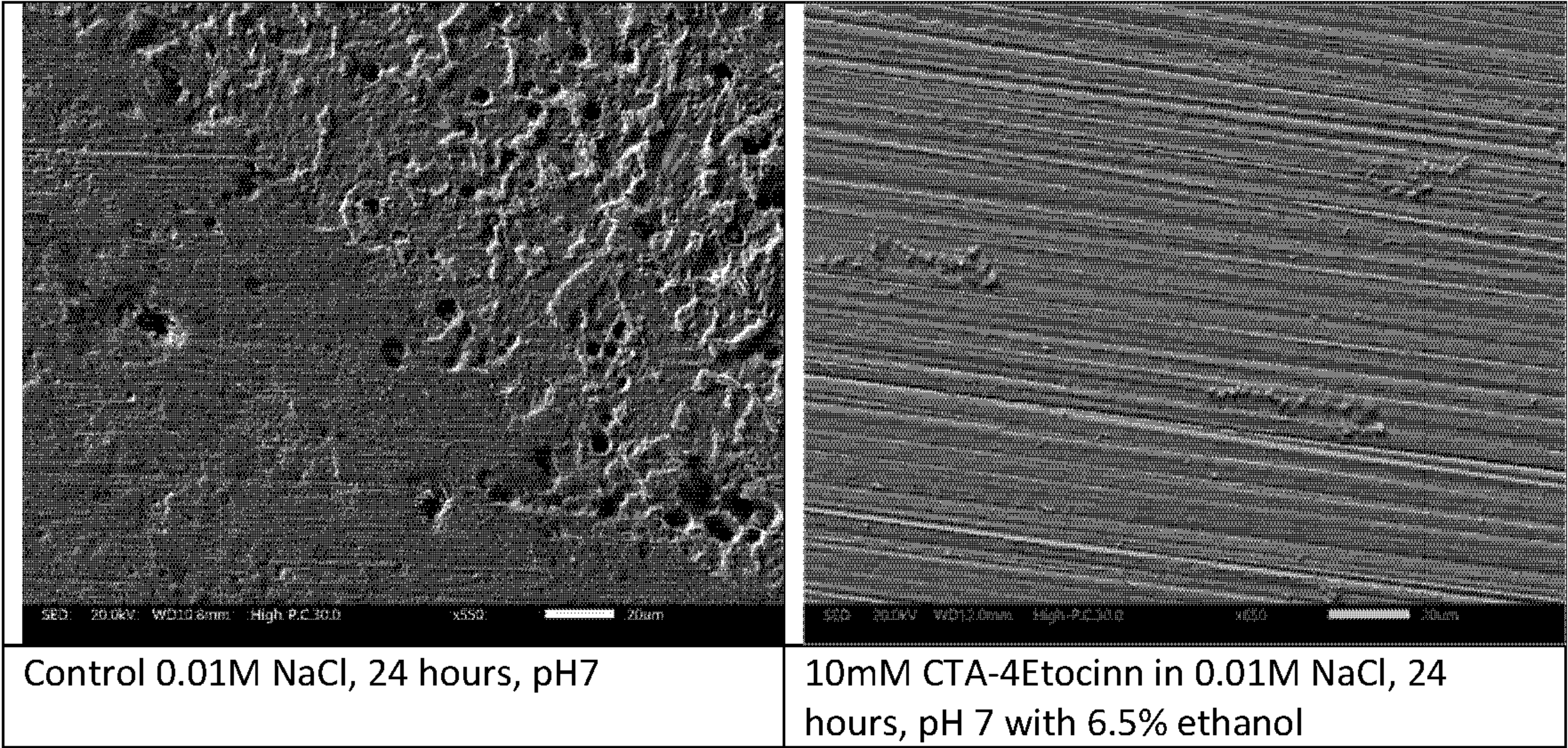


Figure 17

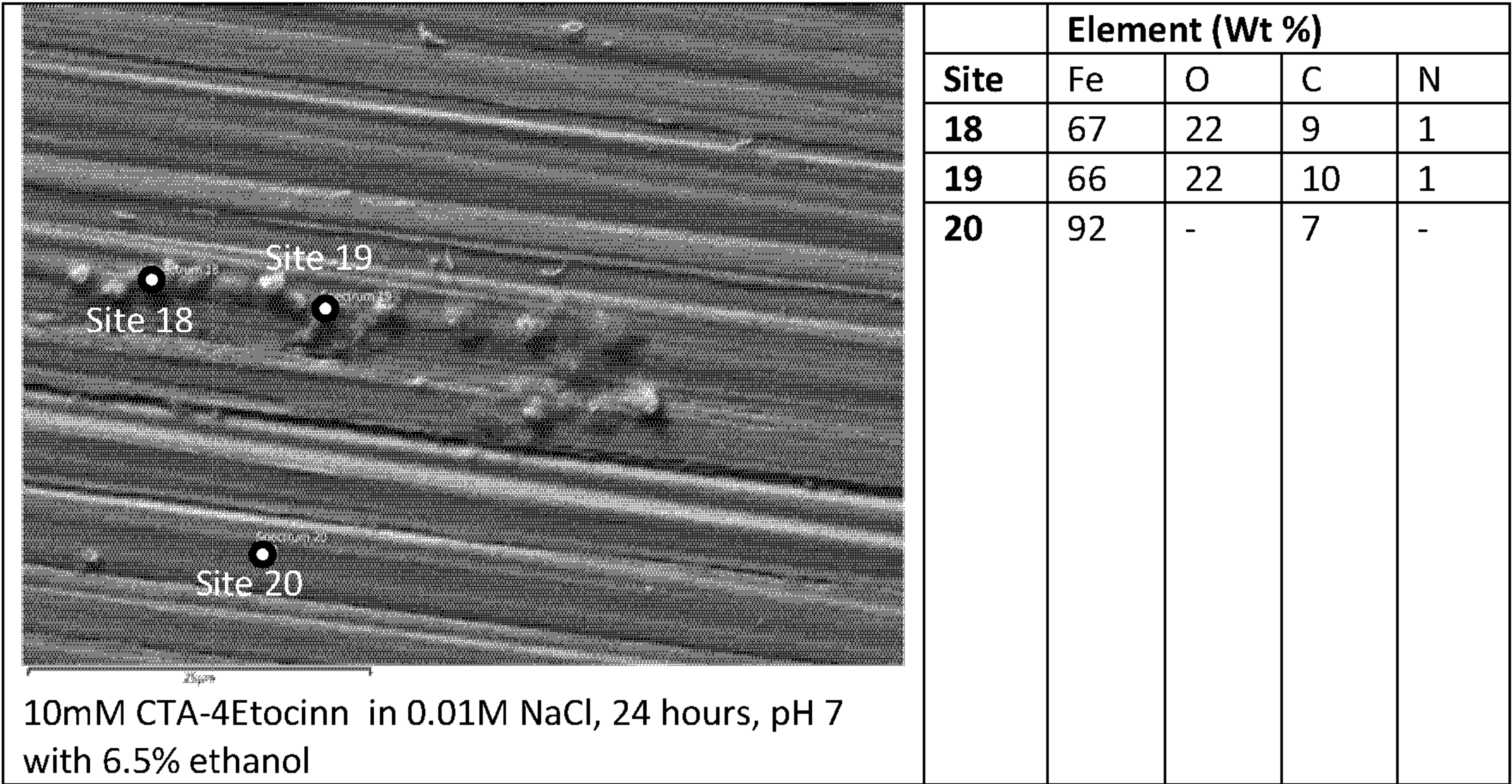


Figure 18

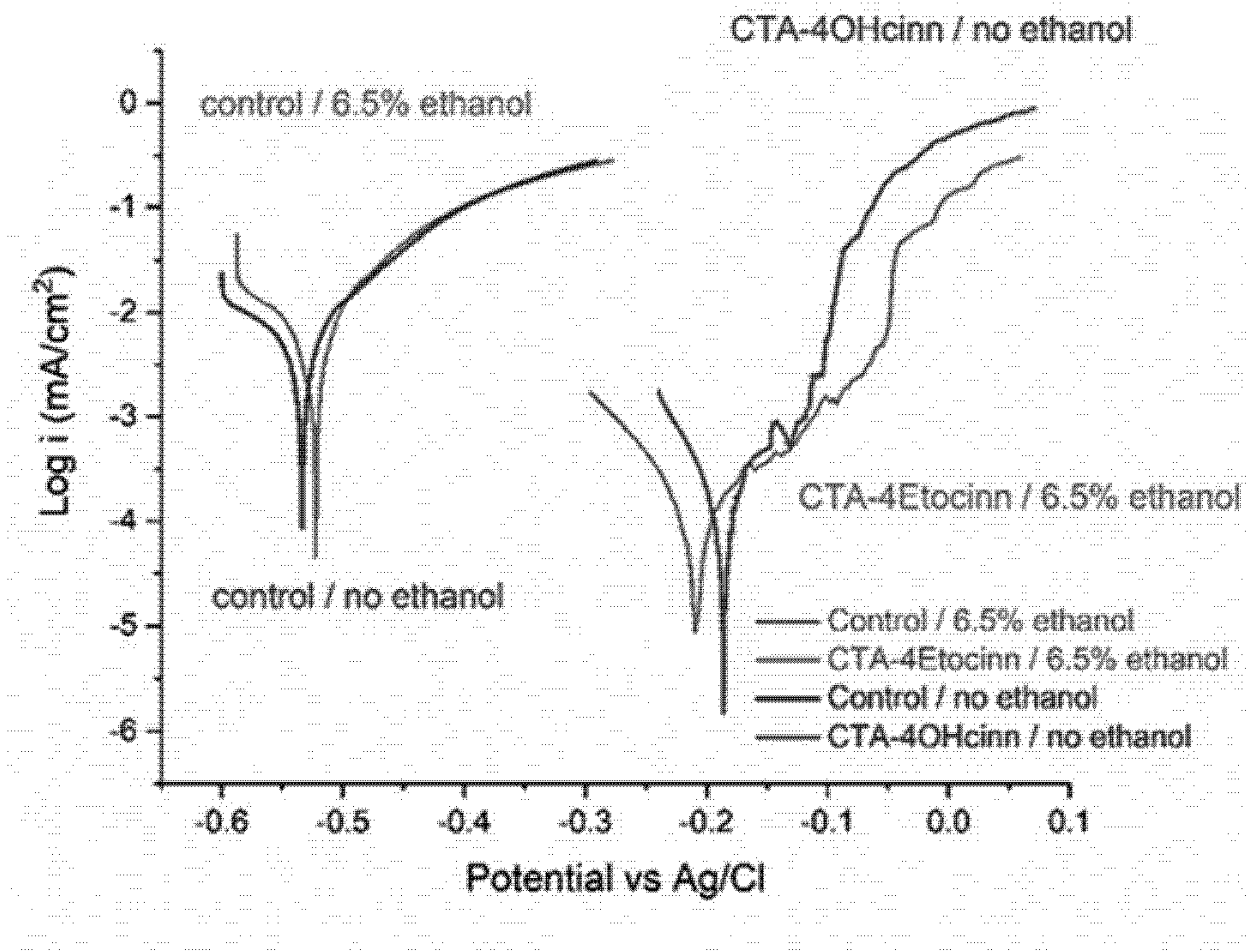


Figure 19a

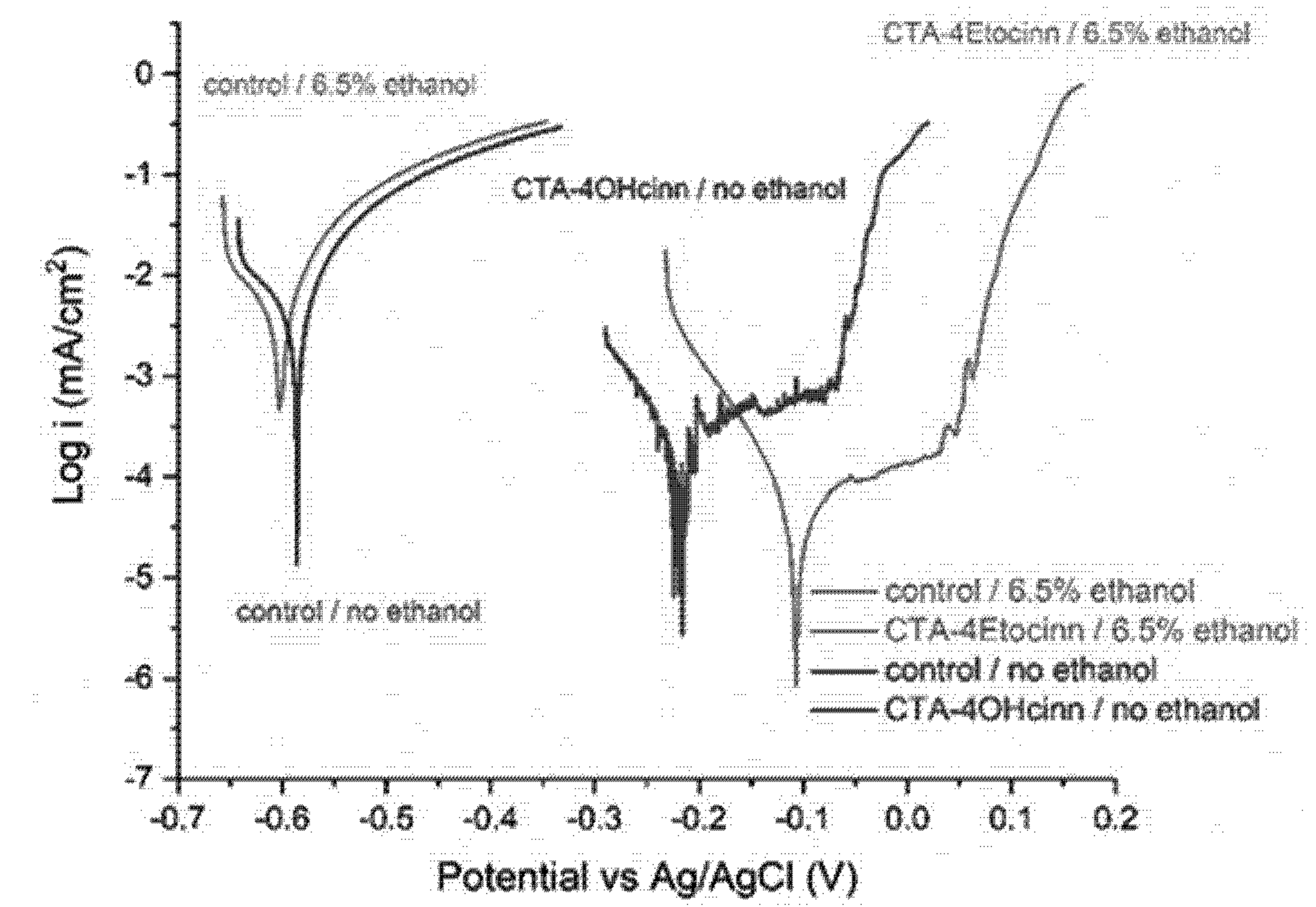


Figure 19b

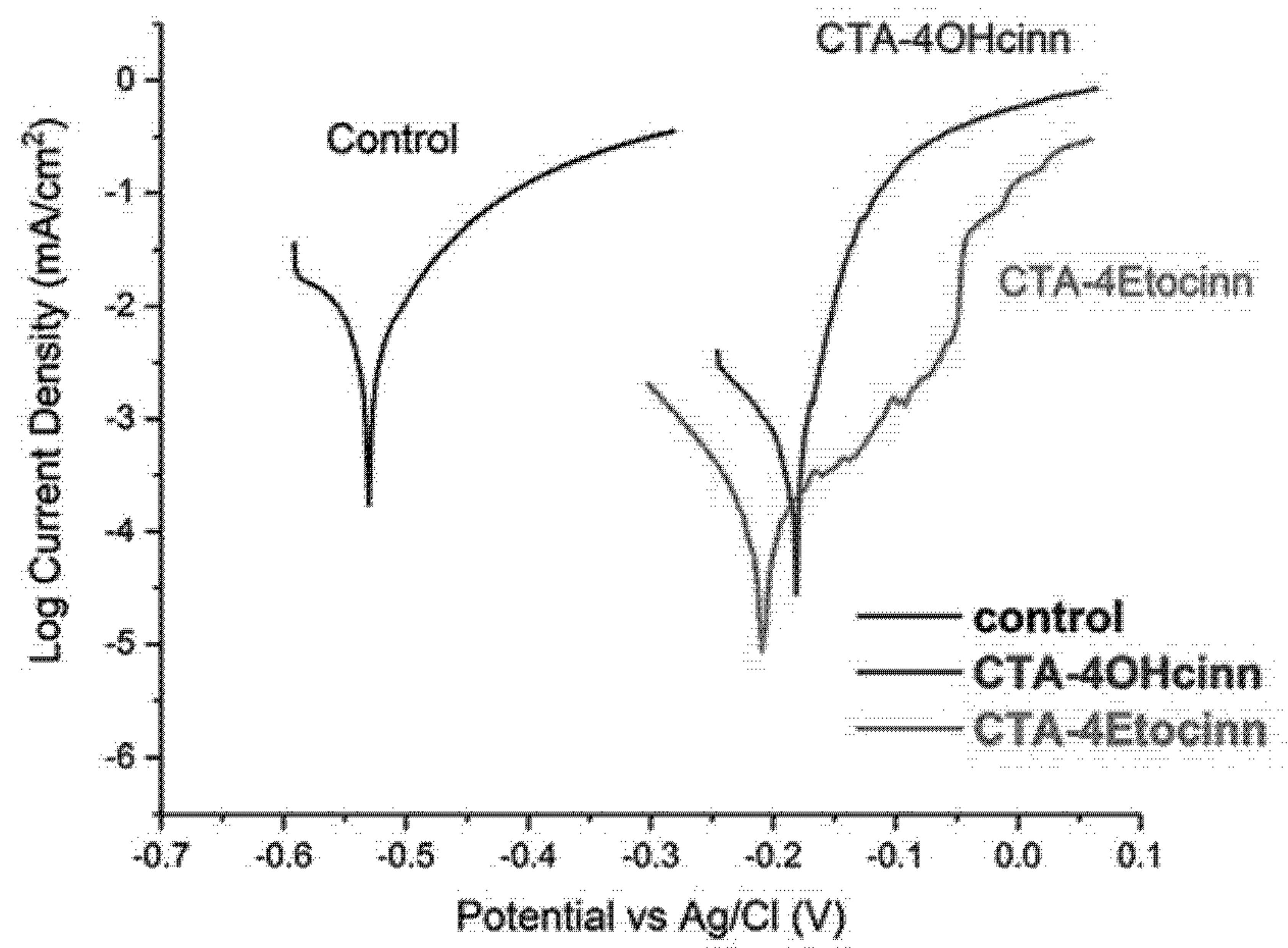


Figure 20a

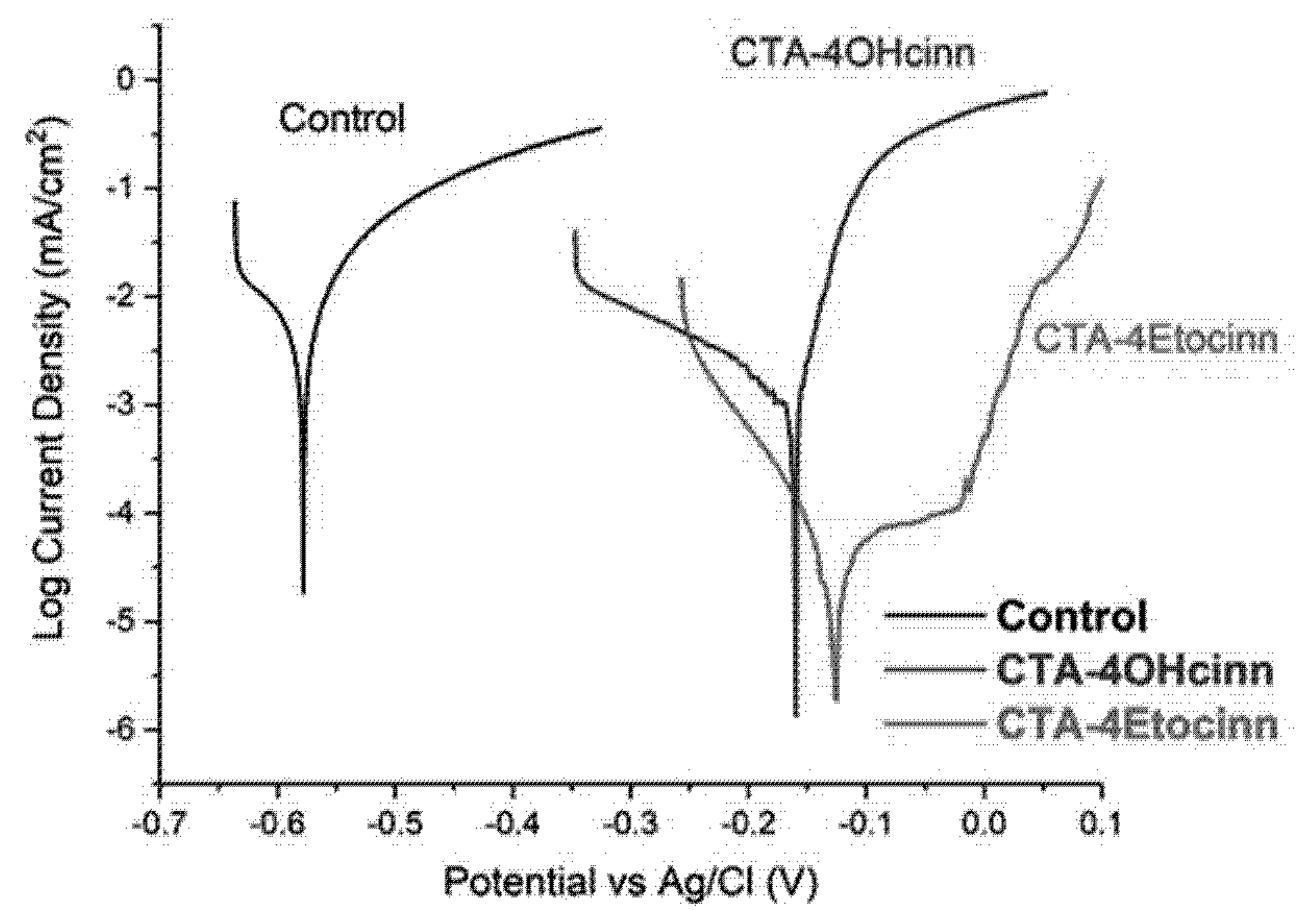


Figure 20b

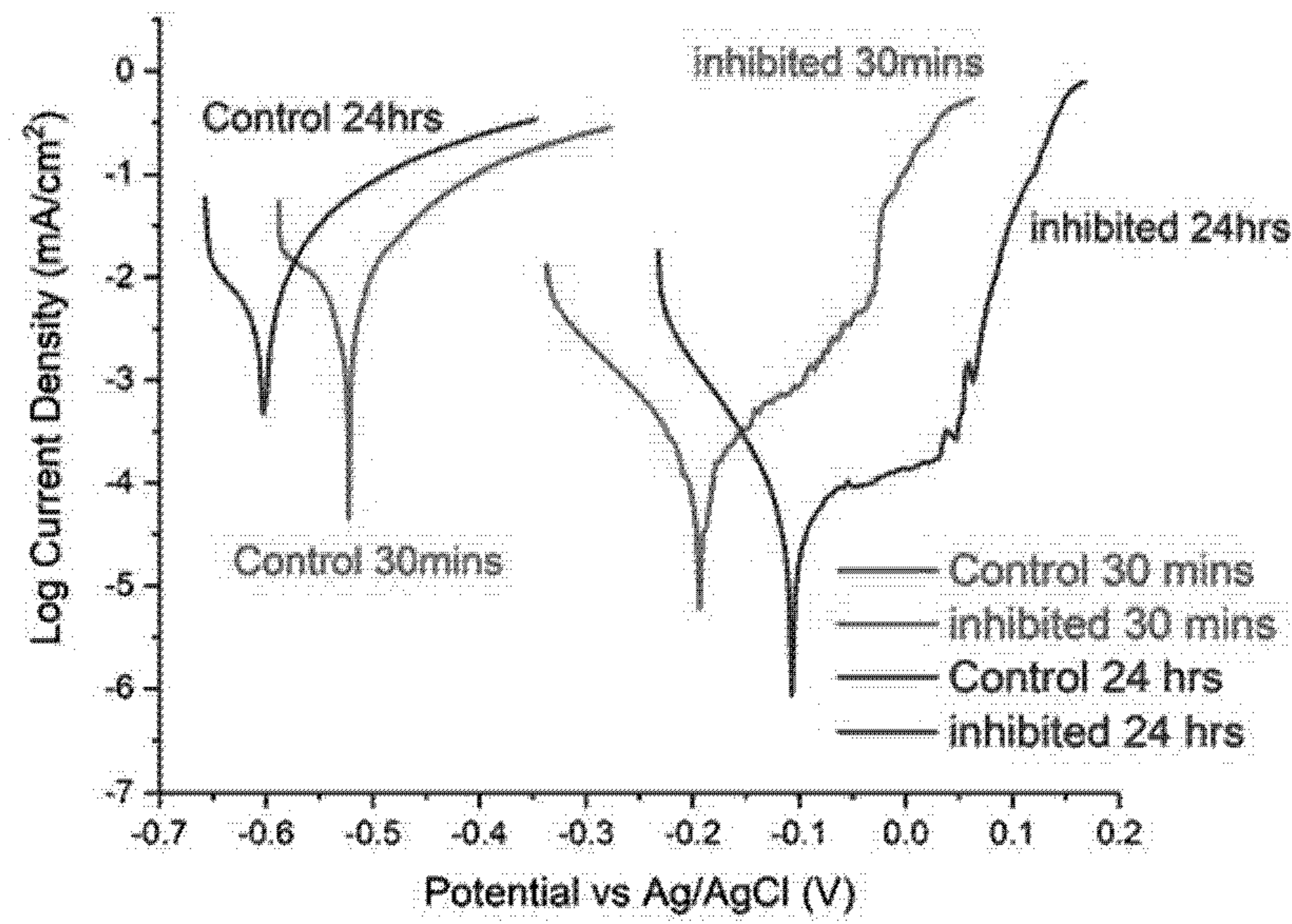


Figure 21

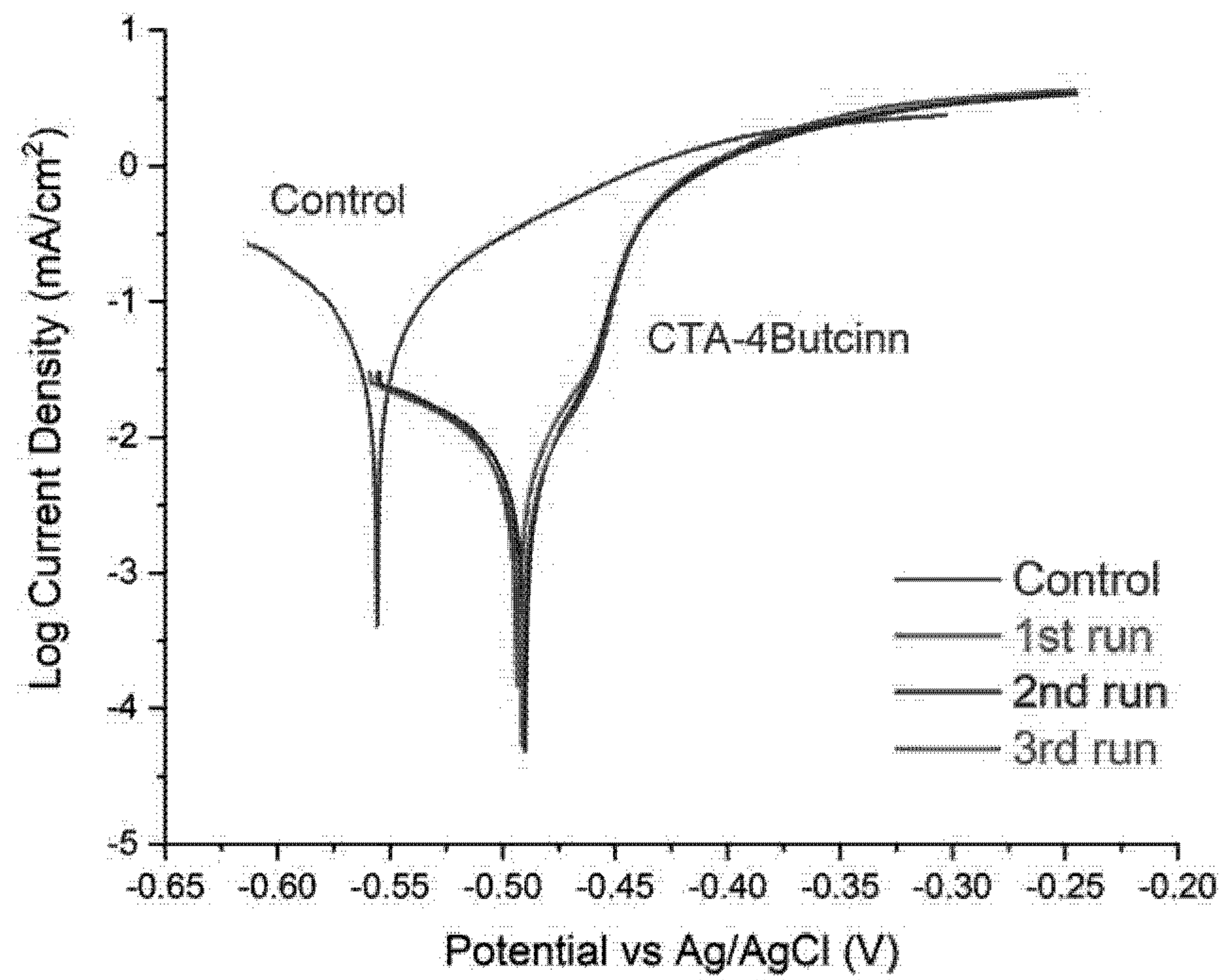


Figure 22a

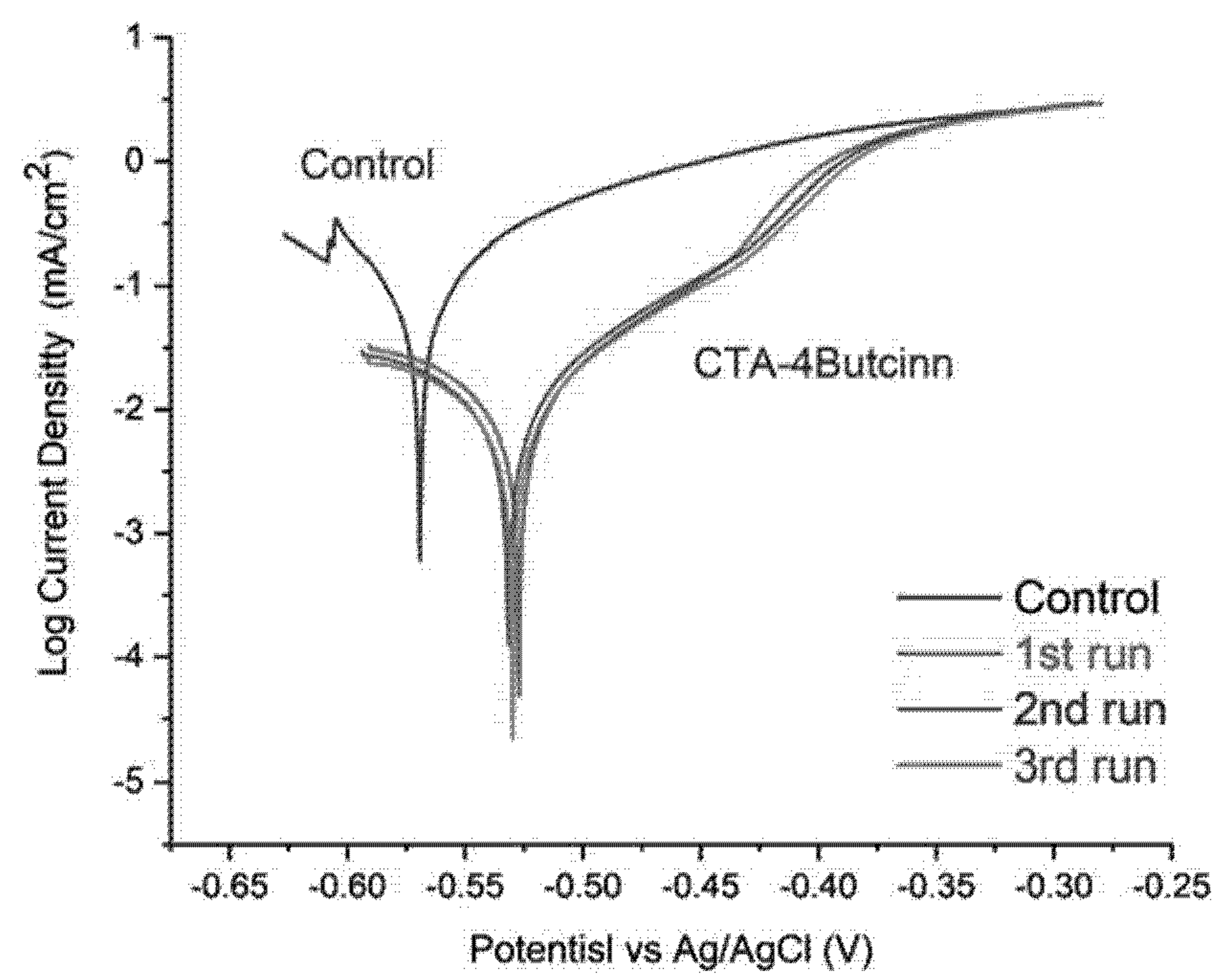


Figure 22b

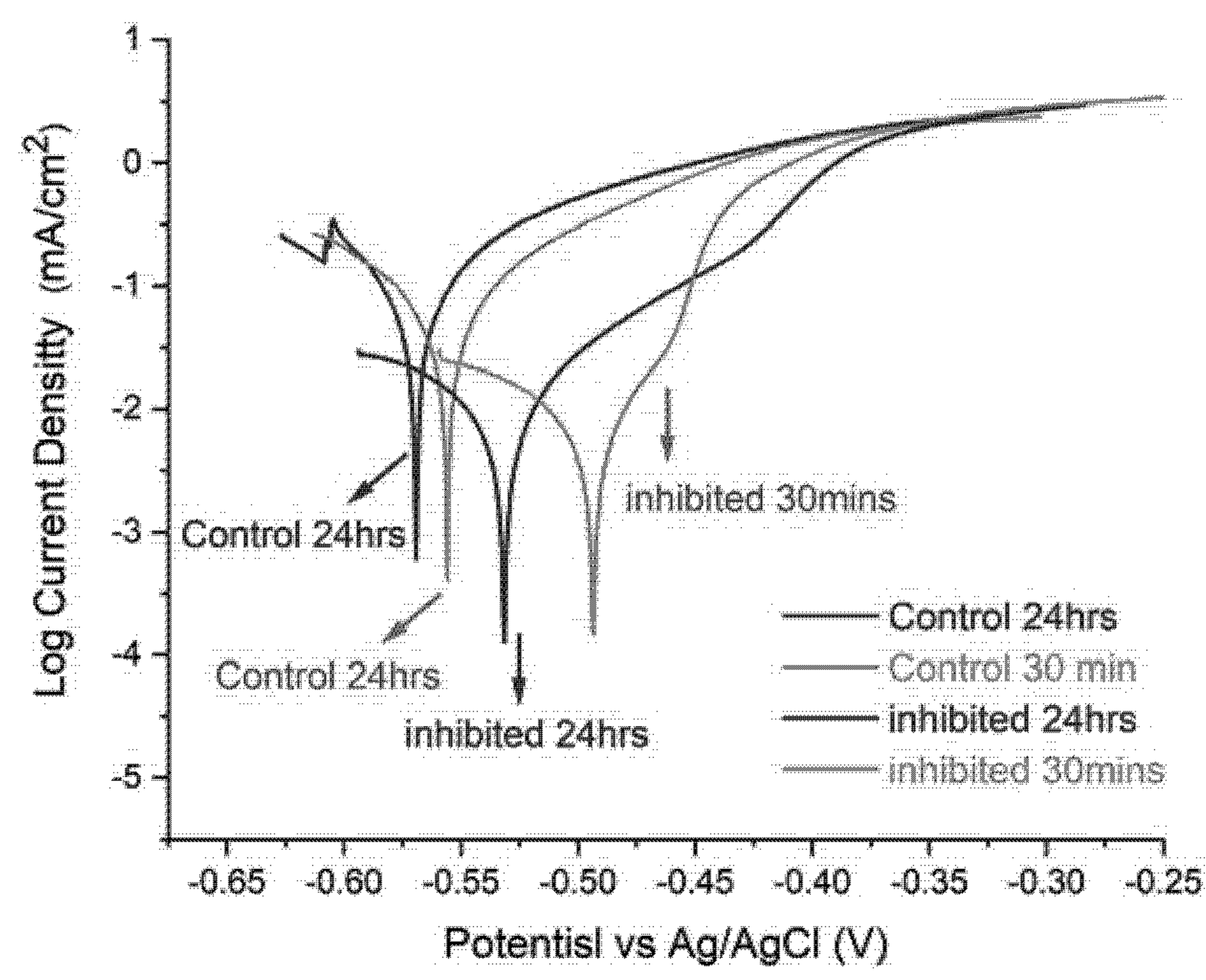


Figure 22c

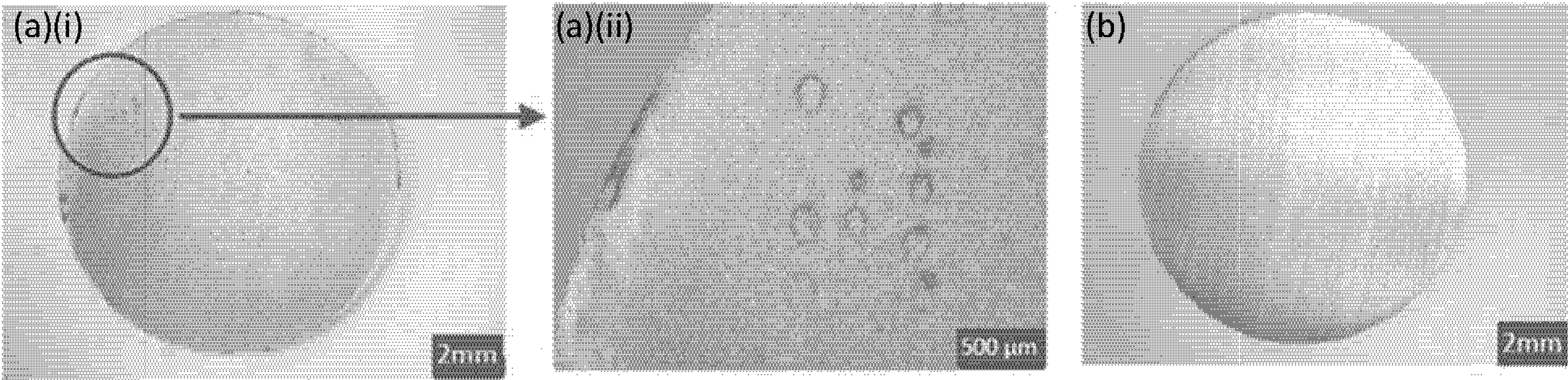


Figure 23

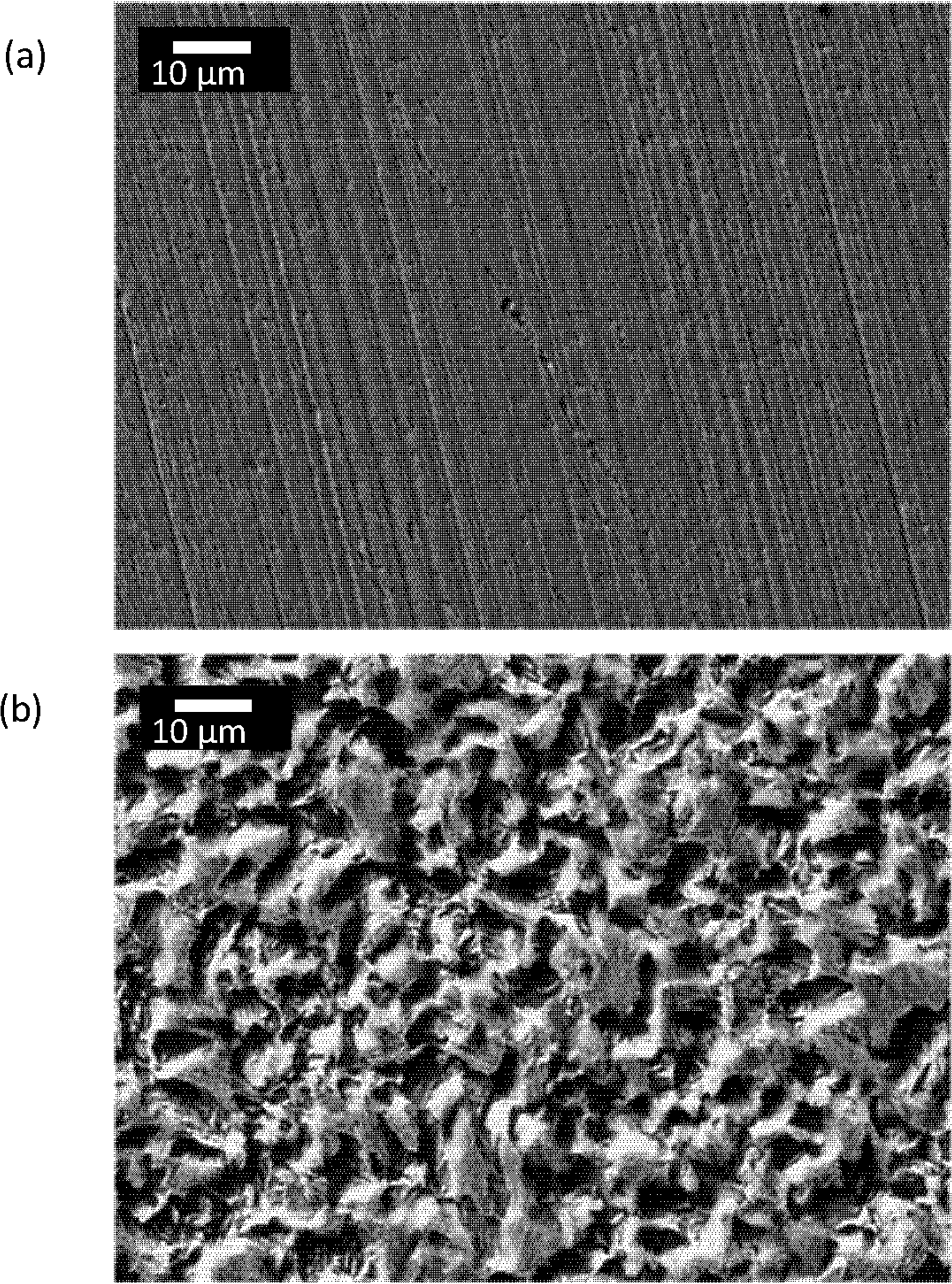


Figure 24

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2020/051259

## A. CLASSIFICATION OF SUBJECT MATTER

**C23F 11/12 (2006.01) C23F 11/14 (2006.01) C23F 11/173 (2006.01) C09D 5/08 (2006.01) C09D 125/18 (2006.01)**  
**C09D 139/04 (2006.01) C09K 8/54 (2006.01) C09K 15/04 (2006.01) C23G 1/06 (2006.01)**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**PATENW, GOOGLE/SCHOLAR, CAPLUS, REGISTRY, ESPACENET, IPC/CPC:** C23F11/10, C23C22, C09K15/04, C09D5[00,08], C09D13/04, C08, C09, B01J, H01, C08J2300/10, C08J3/[24/28], C08J7/04, C09D201/02, C08F2/[46,48],  
**Keywords:** cinnamic, acid, coumaric, salicylate, trimesic, benz[oate,oic,oyl], nalidixate, +phth+, +gallic+, +caffeic+, +caftaric+, corrosion inhibitor, anti\*, ionic liquid, polyionic, IL, ILs, PIL, PILs, polymeris\*, photo\*, UV, metal, carboxylate, aromatic, anion, phenylacrylic, phenylpropenoic, cation, \*[o,i][n,l]nium, coating, counter, Applicant/Inventor search

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
|           | Documents are listed in the continuation of Box C                                  |                       |

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

|                                                                                                                                                                         |                                                                                                                                                                                                                                                  |  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
| * Special categories of cited documents:                                                                                                                                |                                                                                                                                                                                                                                                  |  |
| "A" document defining the general state of the art which is not considered to be of particular relevance                                                                | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |  |
| "D" document cited by the applicant in the international application                                                                                                    | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |  |
| "E" earlier application or patent but published on or after the international filing date                                                                               | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |  |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "&" document member of the same patent family                                                                                                                                                                                                    |  |
| "O" document referring to an oral disclosure, use, exhibition or other means                                                                                            |                                                                                                                                                                                                                                                  |  |
| "P" document published prior to the international filing date but later than the priority date claimed                                                                  |                                                                                                                                                                                                                                                  |  |

Date of the actual completion of the international search  
8 December 2020

Date of mailing of the international search report  
08 December 2020

## Name and mailing address of the ISA/AU

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## Authorised officer

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(ISO 9001 Quality Certified Service)  
Telephone No. +61262833130

| INTERNATIONAL SEARCH REPORT                           |                                                                                                                                                                                                                                                                                                                                                                                                                                                     | International application No.              |
|-------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|
| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                                                                                                     | PCT/AU2020/051259                          |
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                  | Relevant to claim No.                      |
| X                                                     | ACA 2019 Program, Issued 11 November 2019; Corrosion Inhibition of Mild Steel 1030 With Cetrimonium 4-Hydroxycinnamate Jhonatan Soto Deakin University 111, pg 4 of 5. Available online URL> <a href="https://conference.corrosion.com.au/wp-content/uploads/2019/11/10448ACA_CP2019_Program_vCHAIRS-3.pdf">https://conference.corrosion.com.au/wp-content/uploads/2019/11/10448ACA_CP2019_Program_vCHAIRS-3.pdf</a> pg.4 of 5; conference abstract | 1-2, 8-16, 20-21, 23-24, 26, 30            |
| X                                                     | Chong, Alison L. et al:"Synergistic Corrosion Inhibition of Mild Steel in Aqueous Chloride Solutions by an Imidazolinium Carboxylate Salt", ACS Sustainable Chem. Eng. 2016, 4, 1746–1755<br>title; abstract; Figure 1; Experimental                                                                                                                                                                                                                | 1-2, 8-10, 12-14, 16, 20-21, 23-24, 26, 30 |
| X                                                     | Chong, Alison L. et al:"Novel imidazolinium ionic liquids and organic salts" Electrochimica Acta 159 (2015) 219–226<br>title; abstract; Figs. 1-2; whole document                                                                                                                                                                                                                                                                                   | 1-2, 8-10, 12-14, 16, 20-21, 23-26, 30     |
| X                                                     | Somers. AE et al:"Recent Developments in Environment-Friendly Corrosion Inhibitors for Mild Steel" Journal of the Indian Institute of Science VOL 96:4 Oct.–Dec. 2016 journal.iisc.ernet.in<br>abstract; Fig.1; Table.1; whole document                                                                                                                                                                                                             | 1-6, 8-10, 12-14, 16-20, 24-30             |
| X                                                     | CN 109096216 A (LANZHOU INST CHEMICAL PHYSICS CAS) 28 December 2018<br>abstract; claims; whole document                                                                                                                                                                                                                                                                                                                                             | 1-3, 8-10, 12-14, 16, 20-21, 23-25, 30     |
| X                                                     | US 6171521 B1 (MEYER) 09 January 2001<br>abstract; col.2, lns 1-50; col.3, lns 55-60; col.4, lns 9-20; col.5, lns 11-22; col.7, lns 1-37; col.8, lns 1-3; Tables I-II, Products 4, 9; claims                                                                                                                                                                                                                                                        | 1-3, 7-10, 12-16, 20-21, 25, 30            |
| X                                                     | JP 2016-060927 A (ASAHI KAGAKU KOGYO CO LTD) 24 April 2016<br>abstract; claims; whole document                                                                                                                                                                                                                                                                                                                                                      | 1, 8-10, 12-13                             |
| X                                                     | US 20160010035 A1 (LIU WEN DAR et al.) 14 January 2016<br>abstract; para 22-30, 55-57, 66-75, 99 onwards; Tables II and III; Examples 2-3                                                                                                                                                                                                                                                                                                           | 1, 8-10, 12-13                             |
| X                                                     | DE 2405861 A1 (BOEHM FRANZ CHEM PROD) 08 August 1974<br>abstract; pg.3, third paragraph; pg.4, first full paragraph                                                                                                                                                                                                                                                                                                                                 | 1-3, 8-10, 12-14, 16, 20-21, 23-26, 30     |
| X                                                     | Cheng G. et al:"Integrated Antimicrobial and Nonfouling Hydrogels to Inhibit the Growth of Planktonic Bacterial Cells and Keep the Surface Clean" Langmuir 2010, 26(13), 10425–10428<br>title; abstract; pg.10426, lhc first full paragraph; Experimental                                                                                                                                                                                           | 1-2, 7-14, 20-21, 23-25, 30                |
| X                                                     | Seter M, et al:"Cetrimonium Nalidixate as a Multifunctional Inhibitor to Combat Biofilm Formation and Microbiologically Influenced Corrosion" Aust. J. Chem. 2013, 66, 921–929<br>title; abstract; Results and Discussion                                                                                                                                                                                                                           | 1, 8-10, 12-13                             |
| X                                                     | WO 2018222924 A1 (ARIZONA BOARD OF REGENTS ON BEHALF OF NORTHERN ARIZONA UNIVERSITY et al.) 06 December 2008<br>title; abstract; pgs.1-6, 12-14, 16; claims                                                                                                                                                                                                                                                                                         | 1-5, 8-18, 20-21, 23-24, 26-28, 30         |
| Form PCT/ISA/210 (fifth sheet) (July 2019)            |                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                            |

| INTERNATIONAL SEARCH REPORT                           |                                                                                                                                                                    | International application No. |
|-------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                    | PCT/AU2020/051259             |
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages                                                                                 | Relevant to claim No.         |
| X                                                     | US 20110288227 A1 (LEWANDOWSKI ET AL.) 24 November 2011<br>title; abstract; para 4, 7, 10-11, 19, 24, 27, 40; Scheme II; Table 1; Examples 1-26, para 123; Table 2 | 1-30                          |
| X                                                     | US 20140377717 A1 (3M INNOVATIVE PROPERTIES COMPANY) 25 December 2014<br>abstract; para 9-25, 27-32, 45, 50, 148-153                                               | 1-30                          |
| X                                                     | US 20130059975 A1 (LEWANDOWSKI ET AL.) 07 March 2013<br>title; abstract; para 1-7, 18-20, 30 onwards; whole document                                               | 1-30                          |
| X                                                     | US 20140213726 A1 (LEWANDOWSKI ET AL.) 31 July 2014<br>title; abstract; para 2-21                                                                                  | 1-30                          |
| X                                                     | US 6372237 B1 (BOUSSOUIRA ET AL.) 16 April 2002<br>abstract; whole document                                                                                        | 25                            |
| X                                                     | US 20170143839 A1 (KEMPHARM, INC.) 25 May 2017<br>abstract; whole document                                                                                         | 25                            |
| X                                                     | US 7179841 B2 (ZIELINSKI ET AL.) 20 February 2007<br>abstract; whole document                                                                                      | 25                            |
| X                                                     | US 7294369 B2 (HARDING ET AL.) 13 November 2007<br>abstract; whole document                                                                                        | 25                            |
| A                                                     | Jiayin Yuan et al:"Poly(ionic liquid)s: Polymers expanding classical property profiles"<br>Polymer 52 (2011) 1469-1482<br>whole document                           |                               |
| P,X                                                   | CN 110724065 A (LANZHOU INST CHEMICAL PHYSICS CAS; QINGDAO CENTER OF RESOURCE CHEMISTRY AND NEW MAT) 24 January 2020<br>abstract; whole document                   | 1-4, 8-16, 20-21, 23-25,      |
| Form PCT/ISA/210 (fifth sheet) (July 2019)            |                                                                                                                                                                    |                               |

**Box No. II    Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:  
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box No. III    Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

**See Supplemental Box for Details**

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|
| INTERNATIONAL SEARCH REPORT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | International application No.<br>PCT/AU2020/051259 |
| Supplemental Box                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                    |
| <p><b>Continuation of: Box III</b></p> <p>This Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.</p> <p>This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:</p> <ol style="list-style-type: none"><li>1. Claims 1-24, 26-30 are directed to coating systems comprising a corrosion inhibitor comprising onium cation and aromatic carboxylic acid anion pair. The feature of the corrosion inhibitor and anion/cation pair is specific to this group of claims.</li><li>2. Claim 25 is directed to aromatic carboxylic acid compounds per se represented by Formula 1a (with limited exclusion proviso). The feature of compounds falling within the Markush scope of Formula 1a is specific to this group of claims.</li></ol> <p>PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.</p> <p>When there is no special technical feature common to all the claimed inventions there is no unity of invention.</p> <p>In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is a compound of formula 1a as per claim 25.</p> <p>However this feature does not make a contribution over the prior art because it is disclosed in:</p> <p>D3-D6, D9-D10, D12-D20</p> <p>Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied <b>a posteriori</b>.</p> |                                                    |
| Form PCT/ISA/210 (Supplemental Box) (July 2019)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                    |

| INTERNATIONAL SEARCH REPORT                                                                                                                                                                                                                                           |                  | International application No. |                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-------------------------------|------------------|
| Information on patent family members                                                                                                                                                                                                                                  |                  | PCT/AU2020/051259             |                  |
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                  |                               |                  |
| Patent Document/s Cited in Search Report                                                                                                                                                                                                                              |                  | Patent Family Member/s        |                  |
| Publication Number                                                                                                                                                                                                                                                    | Publication Date | Publication Number            | Publication Date |
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