Supplementary Material for:

Structure and Long-Term Stability of Alkylphosphonic Acid Monolayers on SS316L Stainless Steel

Medea Kosian,[†] Maarten M. J. Smulders,[†] Han Zuilhof*[,†,‡]

† Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands

‡ Department of Chemical and Materials Engineering, King Abdulaziz University, 21589 Jeddah, Saudi Arabia

E-mail: Han.Zuilhof@wur.nl

Table of Contents

1. Monovalent phosphonic acid monolayer characterization S-3

1.1 XPS data S-3

1.2 FTIR (IRRAS) data S-7

1.3 AFM Data S-11

2. Monovalent phosphonic acid monolayer – Long-term stability S-12

2.1 Contact angle data S-12

2.2 XPS data: P variation S-14

2. Dendritic phosphonic acids S-25

2.1 NMR data S-25

2.2 XPS data S-31

2.3 FTIR (IRRAS) data S-32

3. Dendritic phosphonic acids - Long-term stability S-34

3.1 Contact angle data S-34

3.2 XPS data S-35

3.3 FTIR (IRRAS) data S-40

4. Assigned XPS survey scan of SS316L S-43

1. Monovalent phosphonic acid monolayer characterization

1.1 XPS data

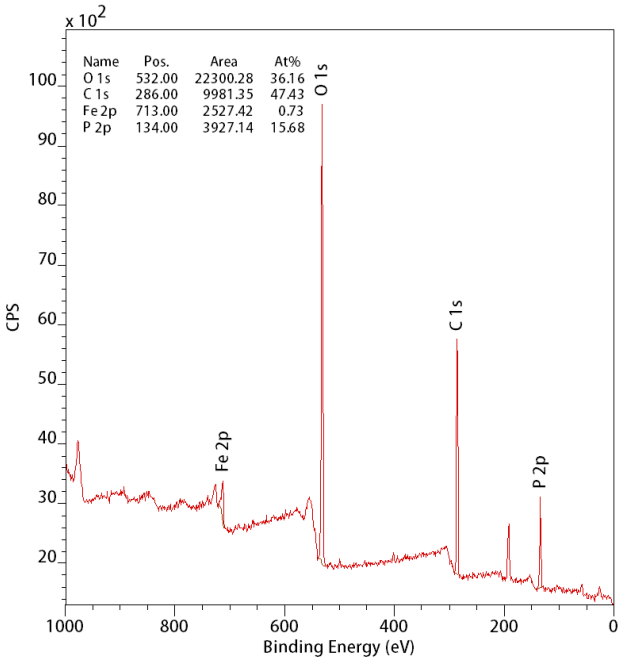

Figure S1. XPS survey scan of SS316L modified with propylphosphonic acid (C_3), revealing a C/P ratio of 3.02 and a P/Fe ratio of 21.48.

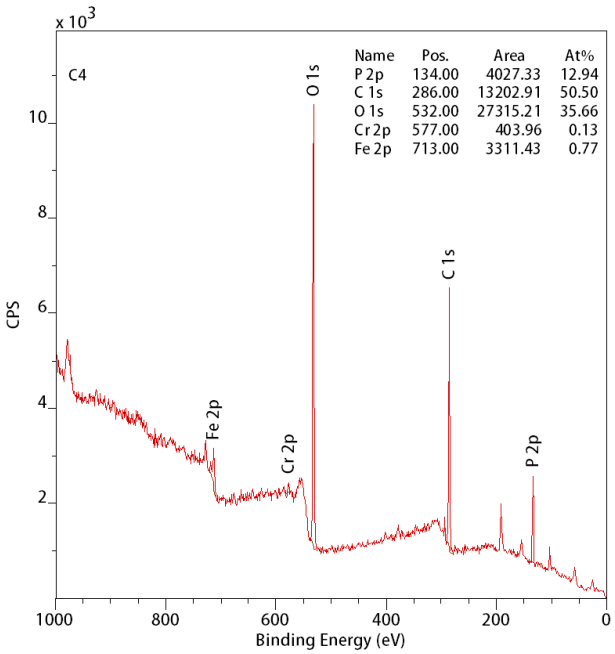

Figure S2. XPS survey scan of SS316L modified with butylphosphonic acid (C_4), revealing a C/P ratio of 3.91 and a P/Fe ratio of 16.80.

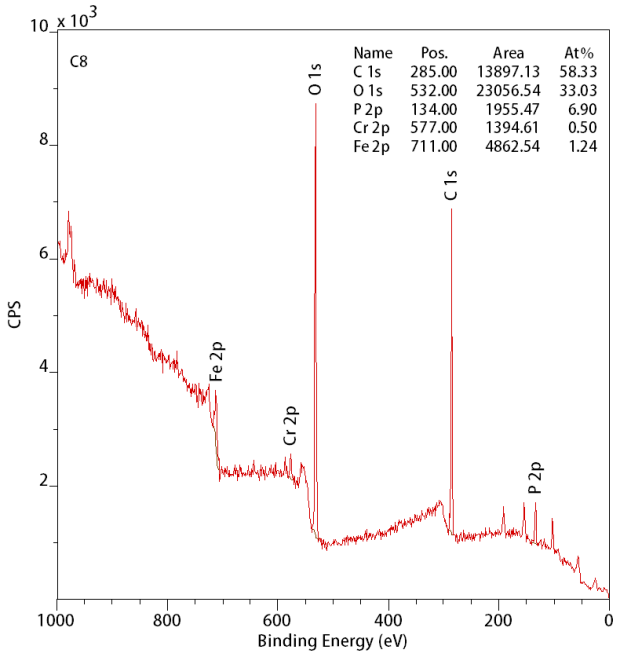

Figure S3. XPS survey scan of SS316L modified with octylphosphonic acid (C_8), revealing a C/P ratio of 8.45 and a P/Fe ratio of 5.56.

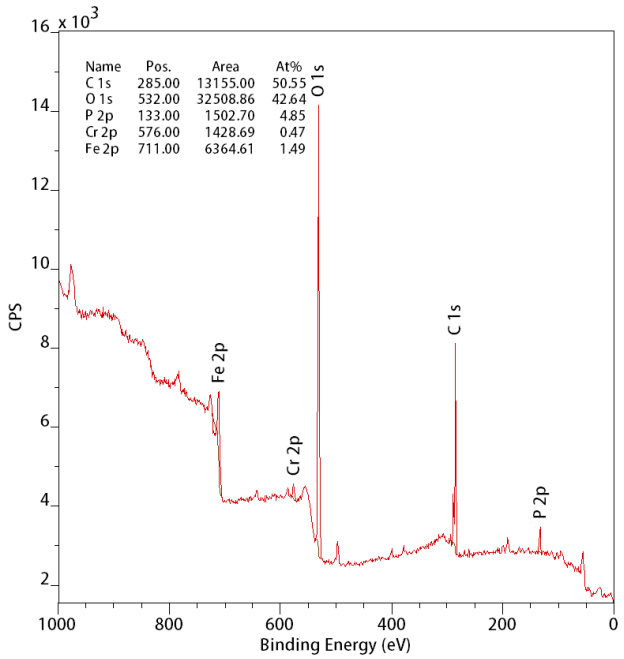

Figure S4. XPS survey scan of SS316L modified with decylphosphonic acid (C_{10}), revealing a C/P ratio of 10.42 and a P/Fe ratio of 3.25.

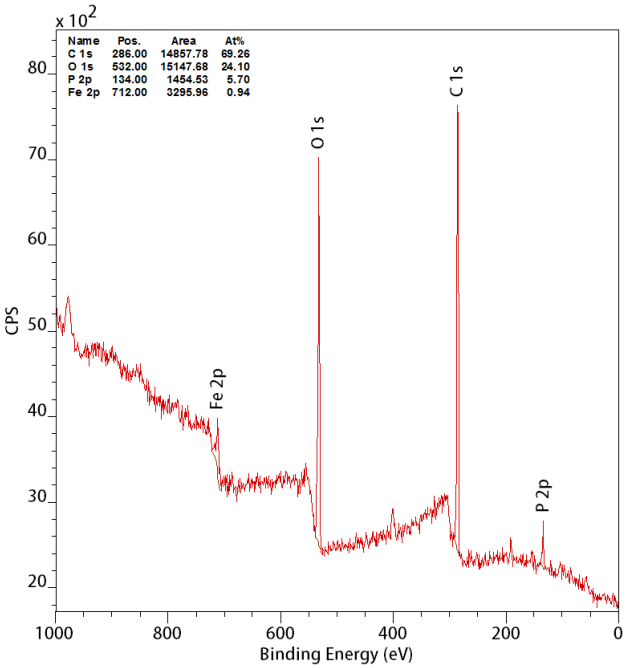

Figure S5. XPS survey scan of SS316L modified with dodecylphosphonic acid (C_{12}), revealing a C/P ratio of 12.15 and a P/Fe ratio of 6.06.

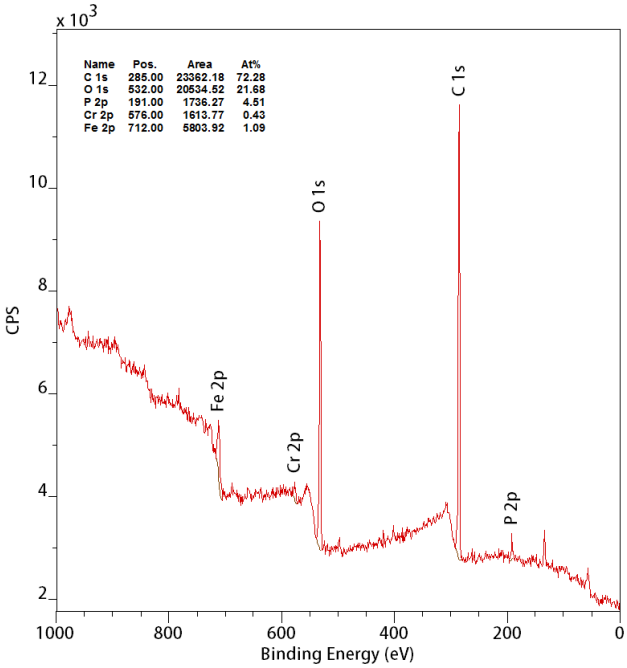

Figure S6. XPS survey scan of SS316L modified with hexadecylphosphonic acid (C_{16}), revealing a C/P ratio of 16.02 and a P/Fe ratio of 4.13.

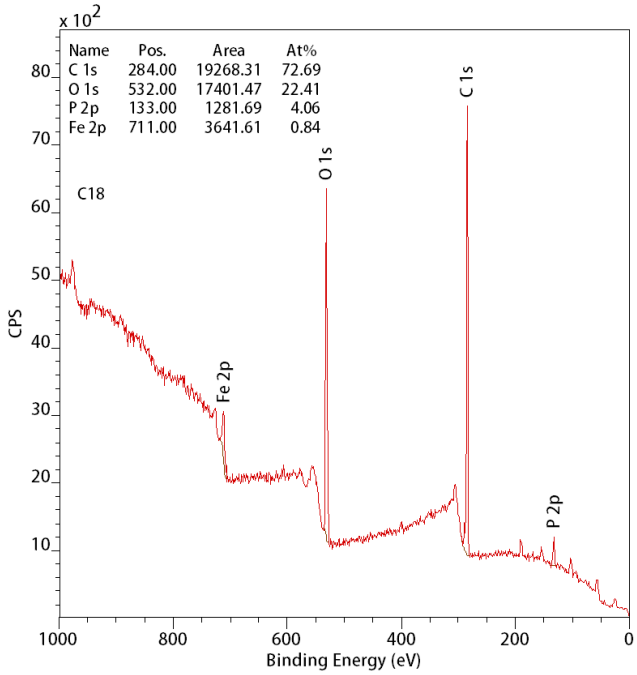

Figure S7. XPS survey scan of SS316L modified with octadecylphosphonic acid (C_{18}), revealing a C/P ratio of 17.90 and a P/Fe ratio of 4.83.

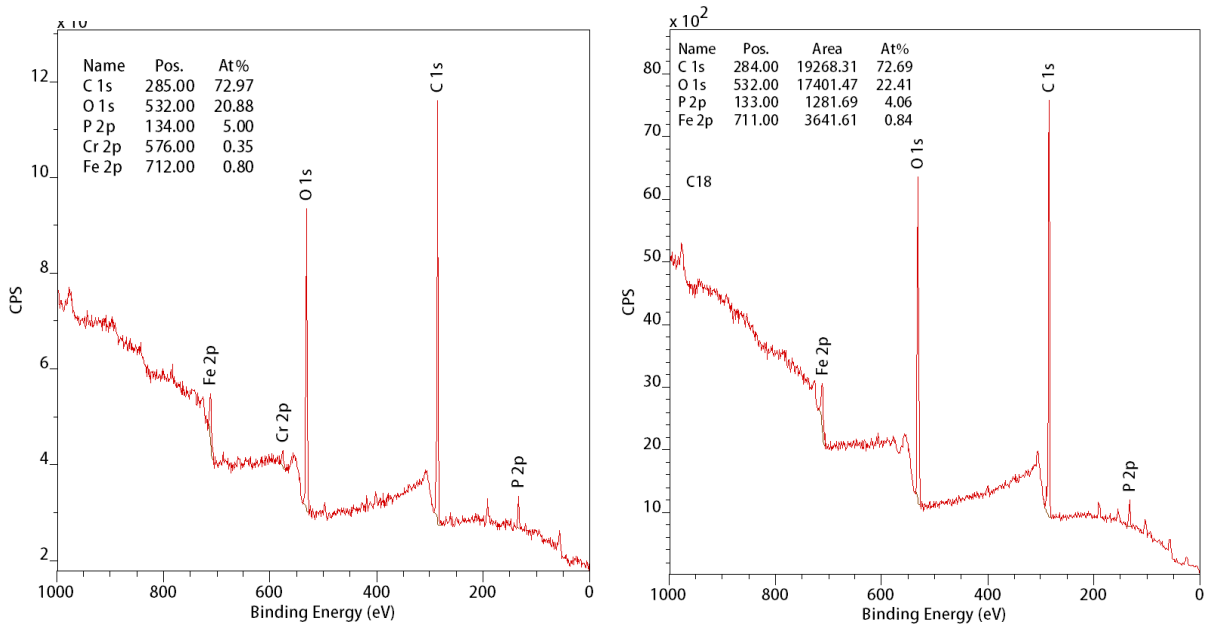

Figure S8. XPS survey scan of SS316L modified with octadecylphosphonic acid (C_{18}) before (left) and after (right) washing with MeOH.

1.2 FTIR (IRRAS) data

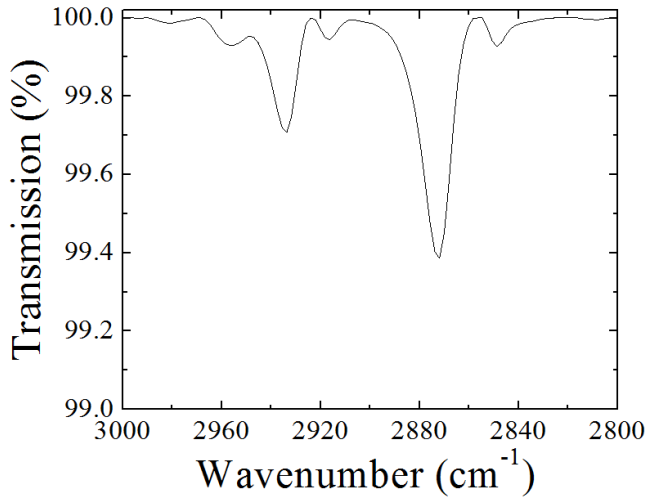

Figure S9. IR spectrum (C–H stretch region) of propylphosphonic acid (C_3) on stainless steel.

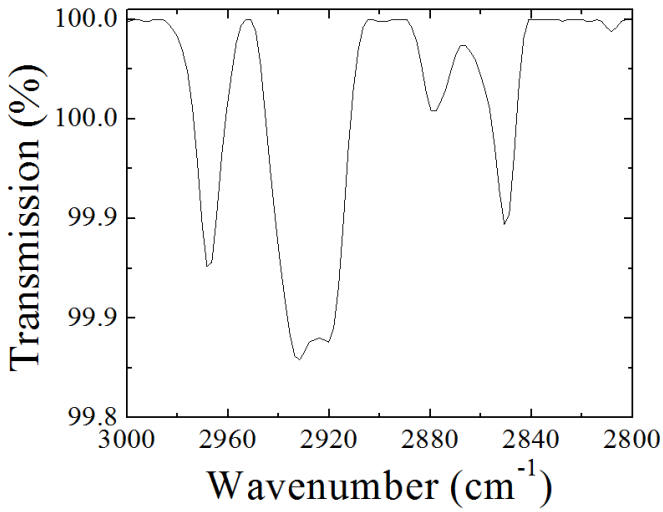

Figure S10. IR spectrum (C–H stretch region) of butylphosphonic acid (C_4) on stainless steel.

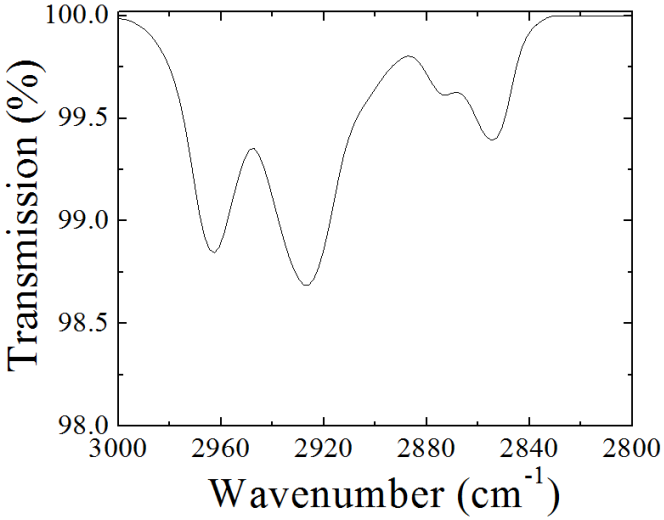

Figure S11. IR spectrum (C–H stretch region) of octylphosphonic acid (C_8) on stainless steel.

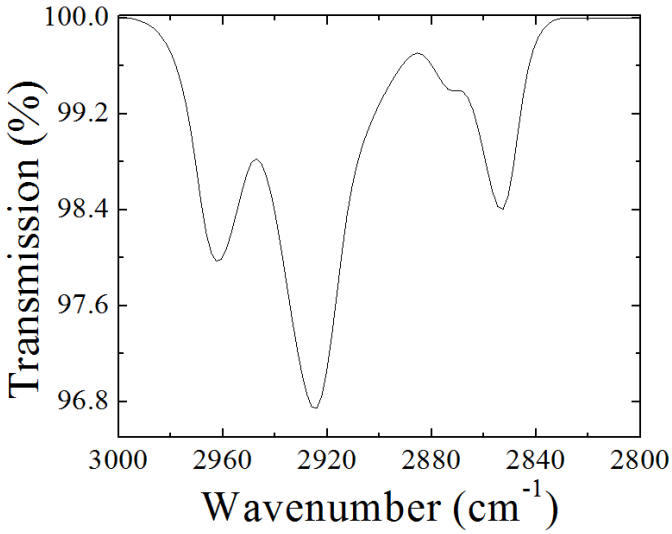

Figure S12. IR spectrum (C–H stretch region) of decylphosphonic acid (C_{10}) on stainless steel.

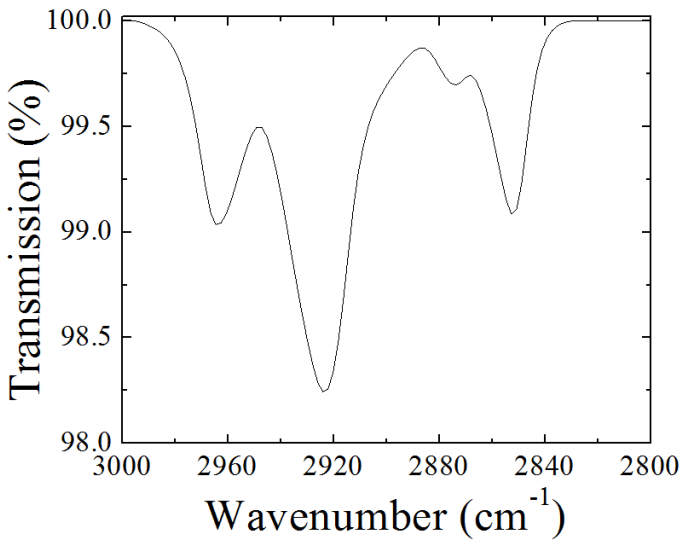

Figure S13. IR spectrum (C–H stretch region) of dodecylphosphonic acid (C_{12}) on stainless steel.

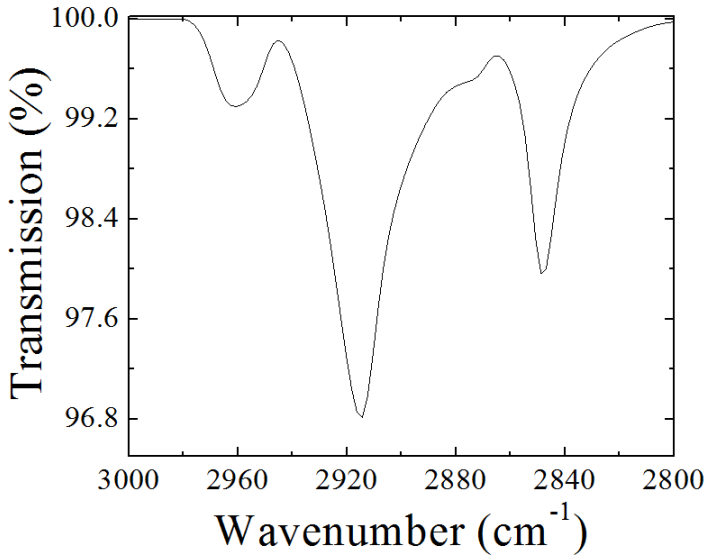

Figure S14. IR spectrum (C–H stretch region) of hexadecylphosphonic acid (C_{16}) on stainless steel.

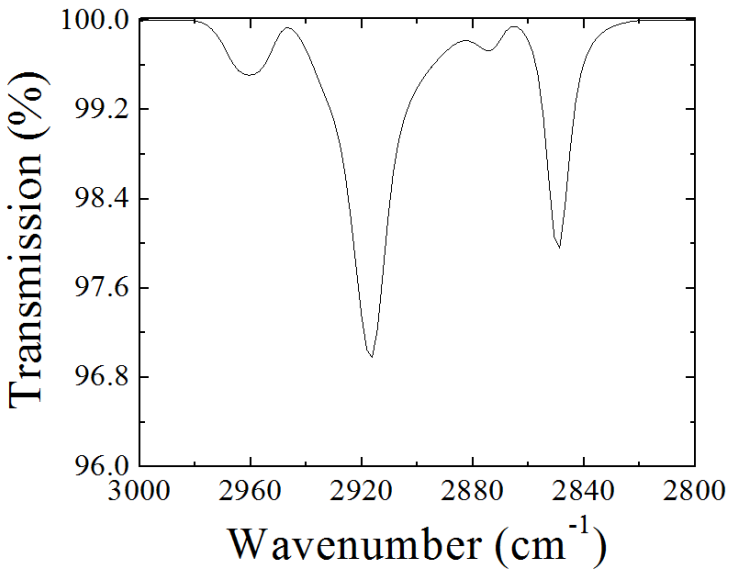

Figure S15. IR spectrum (C–H stretch region) of octadecylhosphonic acid (C_{18}) on stainless steel.

1.3 AFM Data

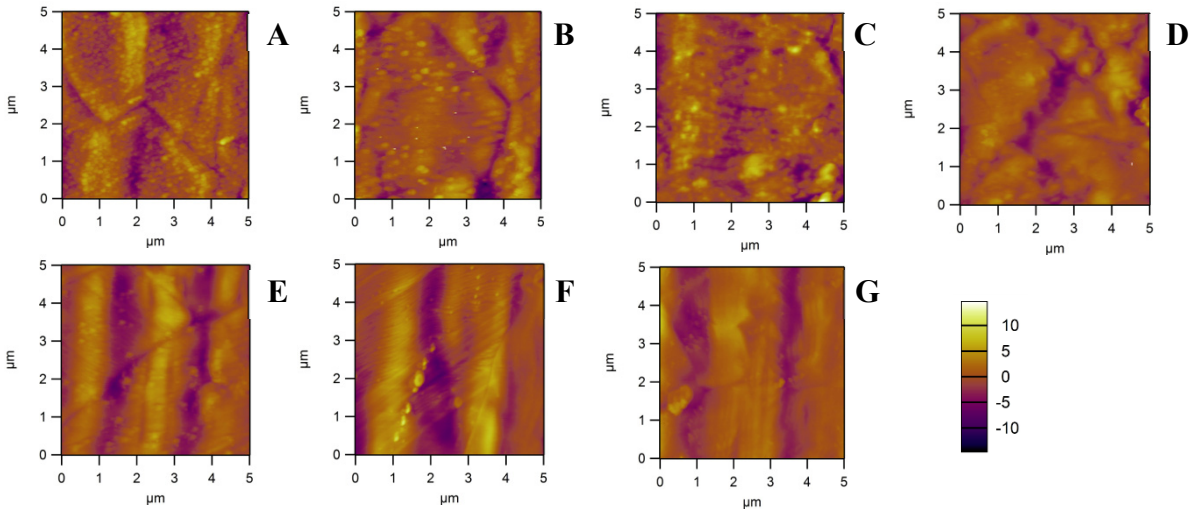

Figure S16. AFM scans of SS316L modified with (A) propylphosphonic acid, (B) butylphosphonic acid, (C) octylphosphonic acid, (D) decylphosphonic acid, (E) dodecylphosphonic acid, (F) hexadecylphosphonic acid, and (G) octadecylphosphonic acid.

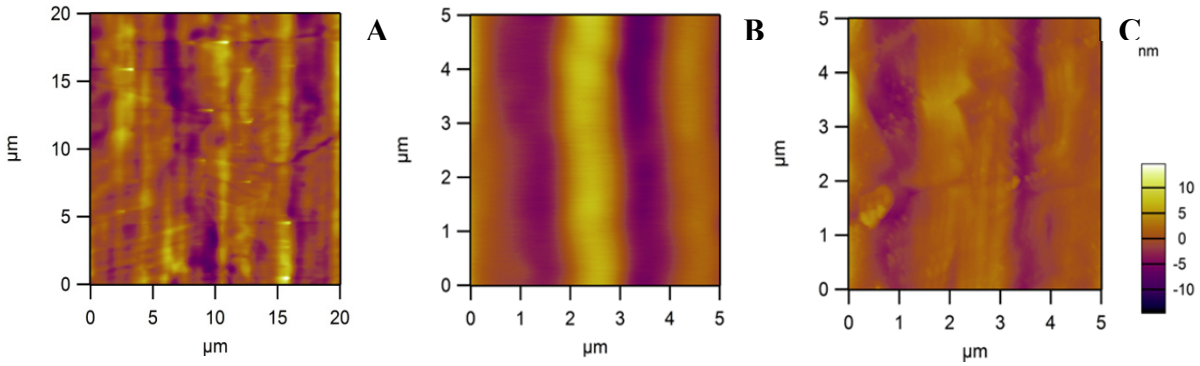

Figure S17. AFM scans of unmodified SS316L of 20 μm^2 (A) and 5 μm^2 (B) surface area showing lines attributed to the manufacturing process. (C) shows a scan of SS316L modified with octadecylphosphonic acid.

2. Monovalent phosphonic acid monolayer – Long-term stability

2.1 Contact angle data

pH 7 (MilliQ) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
3	93.4	92.8	78.55	74.9
4	92	91	69.7	66.2
8	99	97.1	93.75	92.1
10	100.8	99.4	98.6	97.9
12	104.2	103.3	102.3	97.1
16	105.4	104.4	103.5	102.4
18	107.8	104.7	103.1	102.6

Buffer (PBS) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
3	96.5	56.4	56.0	55.4
4	90.2	81.3	80.1	67.2
8	98	95.5	86.6	85.6
10	102	99.3	99.5	92.6
12	101.4	100.8	99.1	97.6
16	104.5	101.5	99.3	96.7
18	107.7	106	102.6	101

Acid (pH 3) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
3	74.7	73	71.8	64.4
4	91.2	84.5	82.5	71
8	98.8	98.4	96.6	92.6
10	99.2	97.2	94.6	93.2
12	102.2	101.3	100	99.6
16	105.7	104.8	103.9	102.1
18	107.1	106.6	105.6	105.5

Alkali (pH 11) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
3	95.8	39.2	36.8	24.2
4	91.8	38.3	32.8	29.2
8	100.6	53.3	47.8	42.6
10	100.9	56.3	52.1	42.6
12	102	81	69.9	64
16	106.8	96.4	92.6	70.6
18	108.5	103.2	89.3	87.3

Heat (120 °C)				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
3	89.8	85.5	68.6	68
4	93.6	85.1	65.8	63.3
8	96.4	96.2	79.2	74.4
10	102	99.4	77.9	67.6
12	102.9	100.6	87.3	77.6
16	103.4	102.6	86.1	76.7
18	106.8	106.2	92.6	81.7

2.2 XPS data: P variation

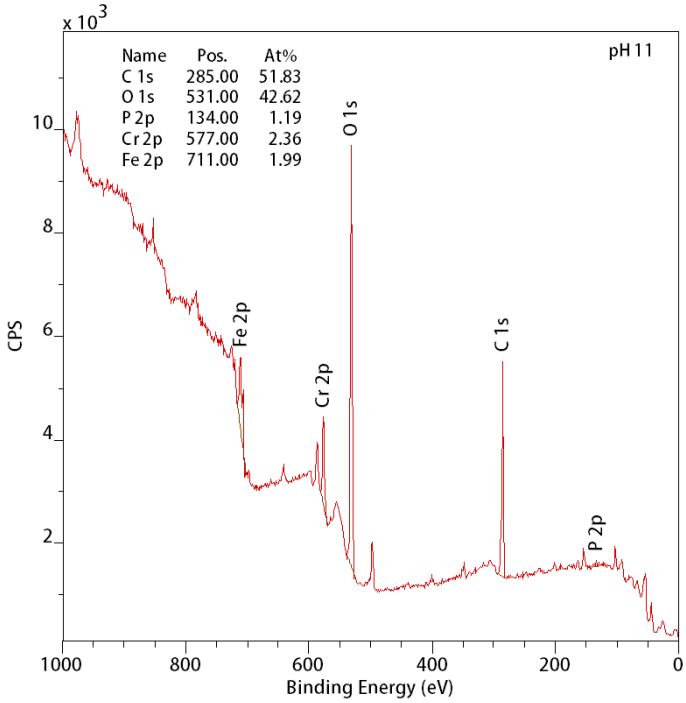

Figure S18. XPS survey scan of SS316L modified with decylphosphonic acid (C_{10}) after 30 days at pH 11, revealing a C/P ratio of 43.55.

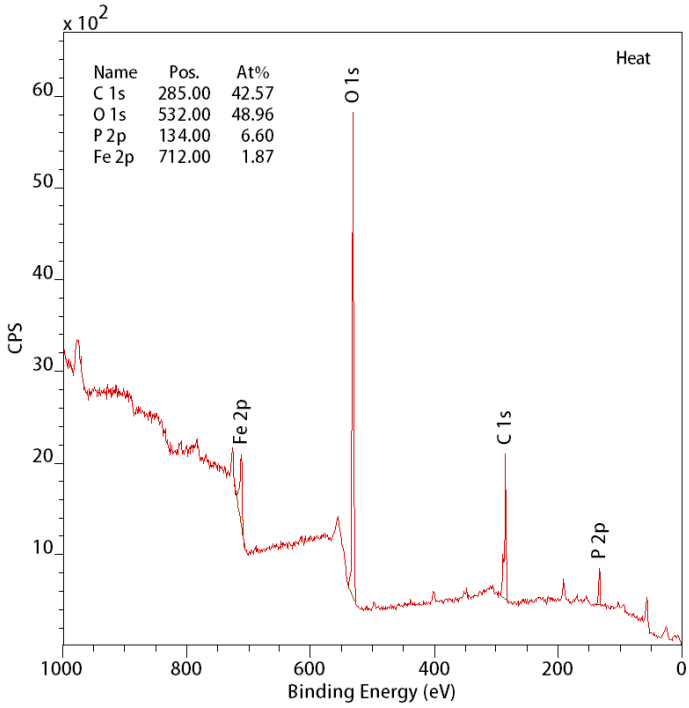

Figure S19. XPS survey scan of SS316L modified with decylphosphonic acid (C_{10}) after 30 days at 120 °C, revealing a C/P ratio of 6.45.

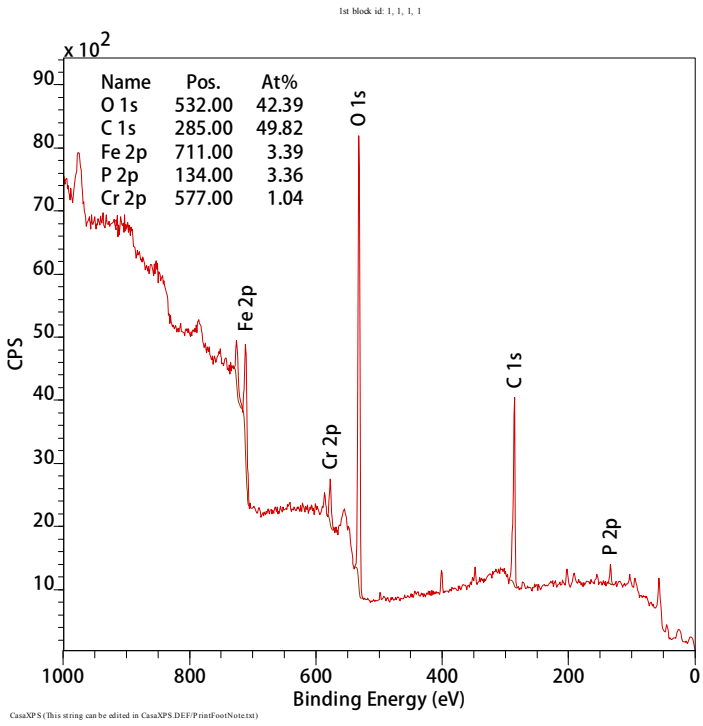

Figure S20. XPS survey scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in neutral MilliQ water, revealing a %P of 3.36 and a C/P ratio of 14.8.

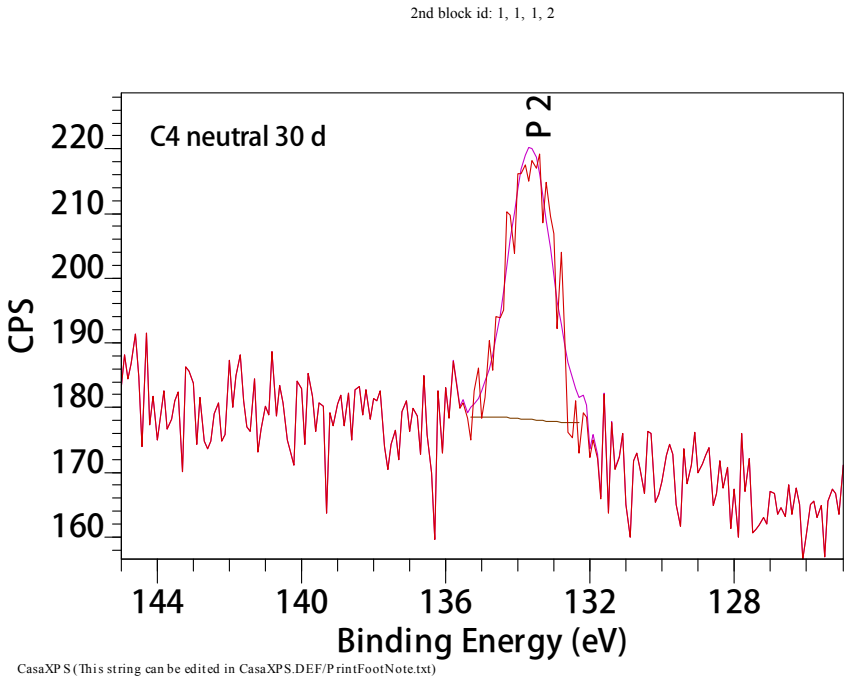

Figure S21. XPS P narrow scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in neutral MilliQ water.

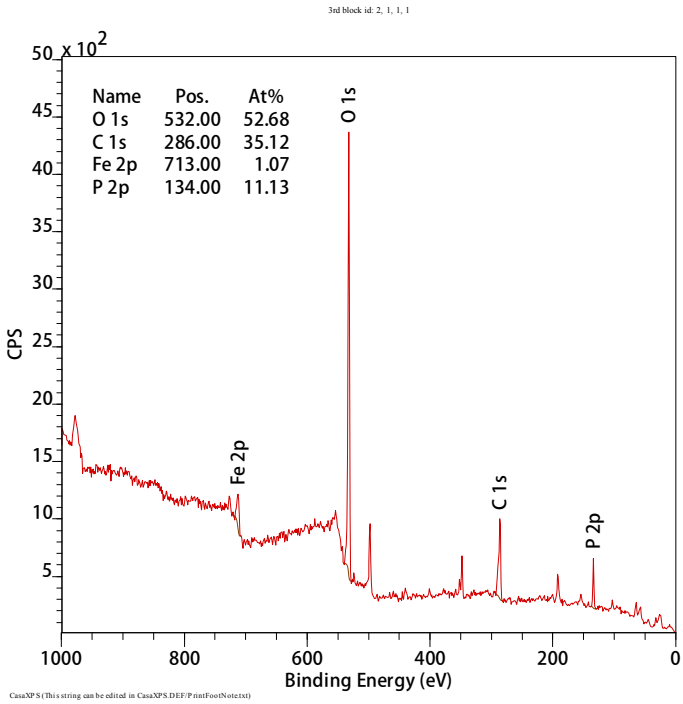

Figure S22. XPS survey scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in 10 mM PBS buffer at pH 7.4, showing a %P of 11.13 and a C/P ratio of 3.1.

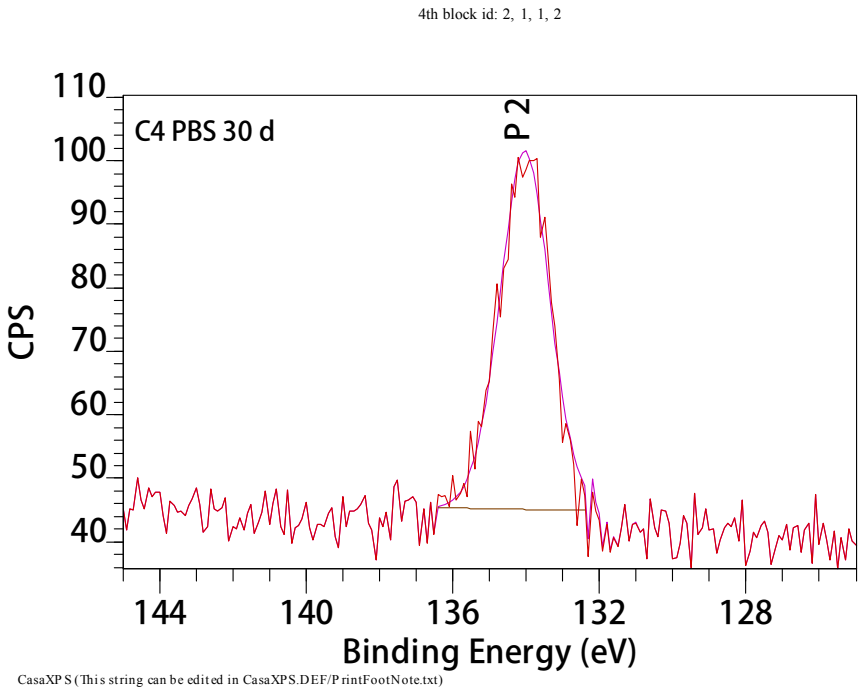

Figure S23. XPS P narrow scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in 10 mM PBS buffer at pH 7.4.

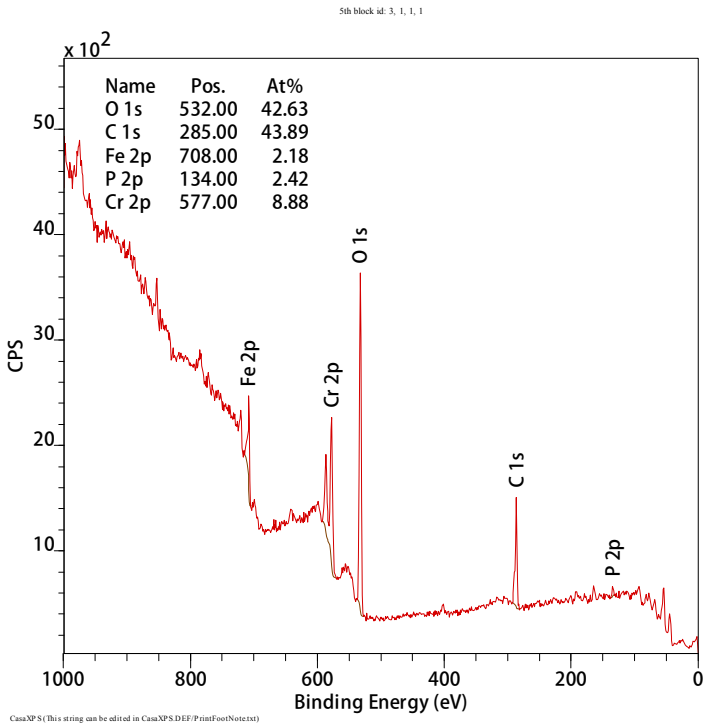

Figure S24. XPS survey scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in HCl solution at pH 3, showing a %P of 2.42 and a C/P ratio of 18.1.

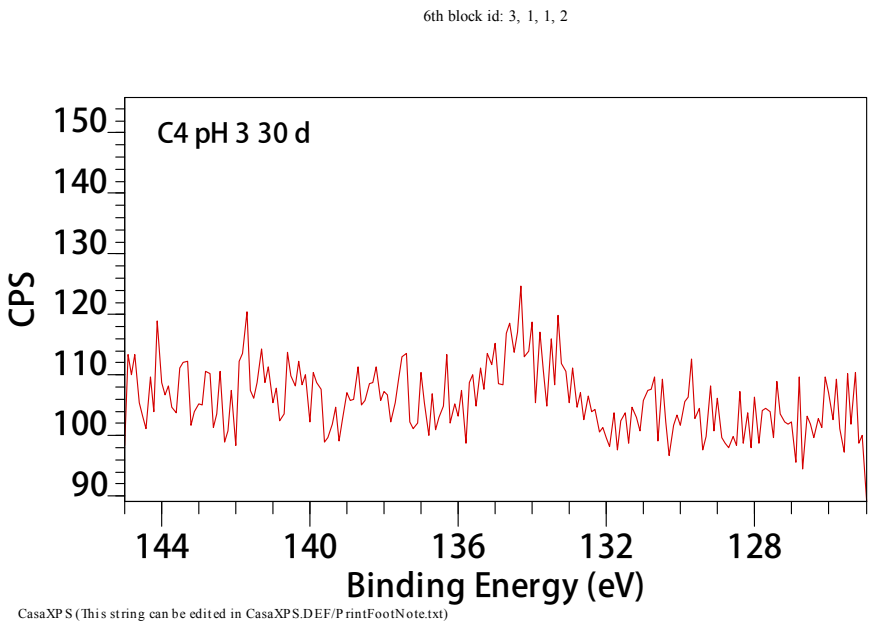

Figure S25. XPS P narrow scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in HCl solution at pH 3, showing near disappearance of the P signal.

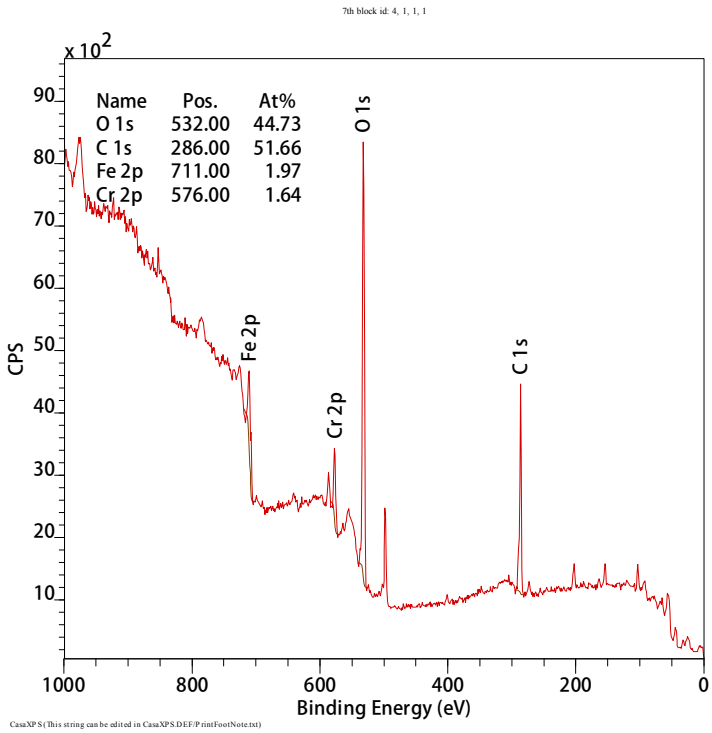

Figure S26. XPS survey scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in NaOH solution at pH 11, showing almost complete disappearance of the P signal.

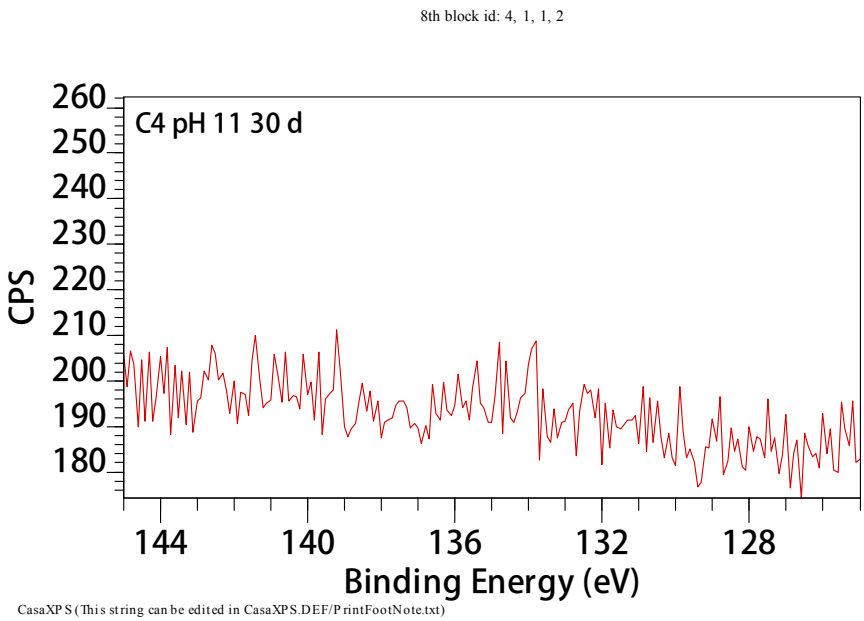

Figure S27. XPS P narrow scan of SS316L modified with butylphosphonic acid (C_4) after 30 d in NaOH solution at pH 11, showing near complete disappearance of the P signal.

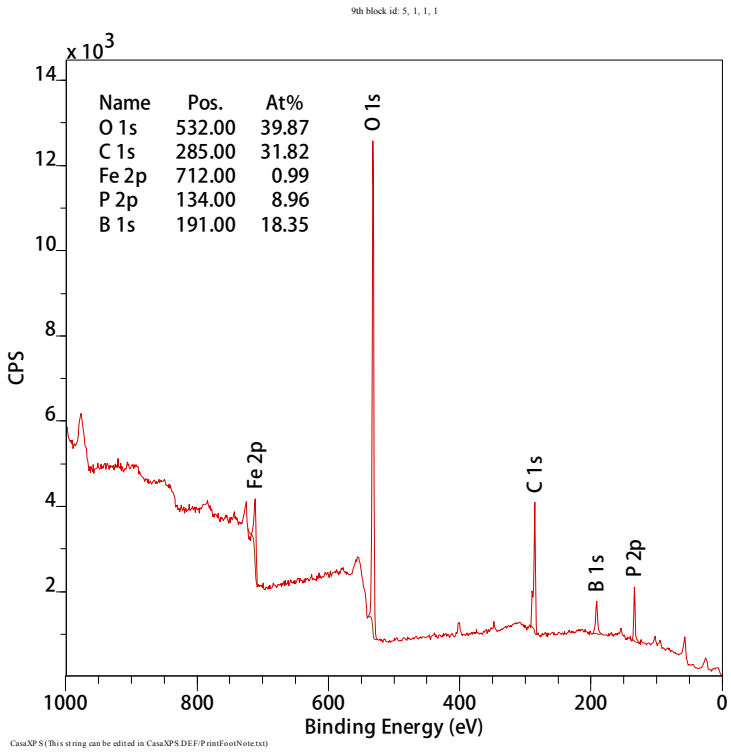

Figure S28. XPS survey scan of SS316L modified with butylphosphonic acid (C_4) after 30 d at 120 °C, showing a %P of 8.96 and a C/P ratio of 3.6.

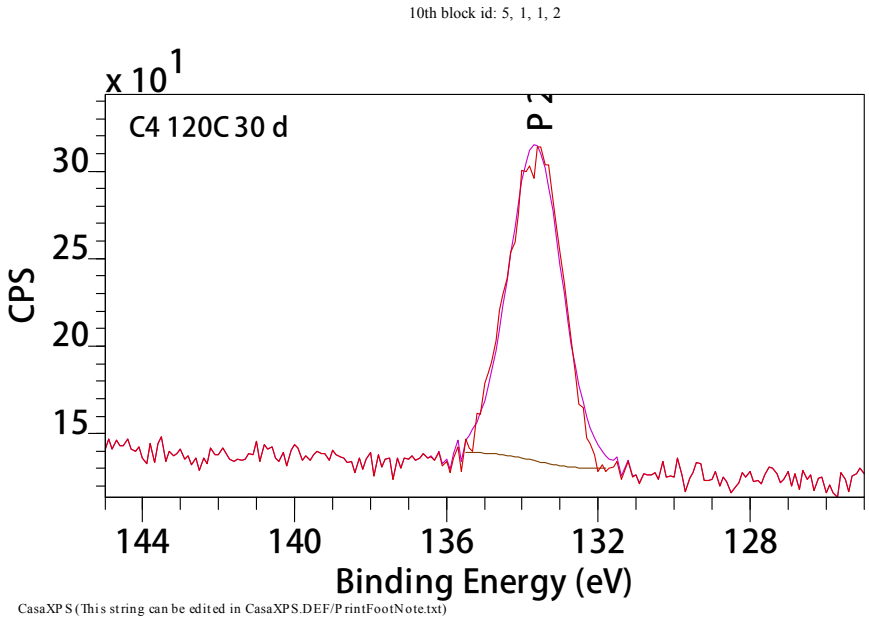

Figure S29. XPS P narrow scan of SS316L modified with butylphosphonic acid (C_4) after 30 d at 120 °C.

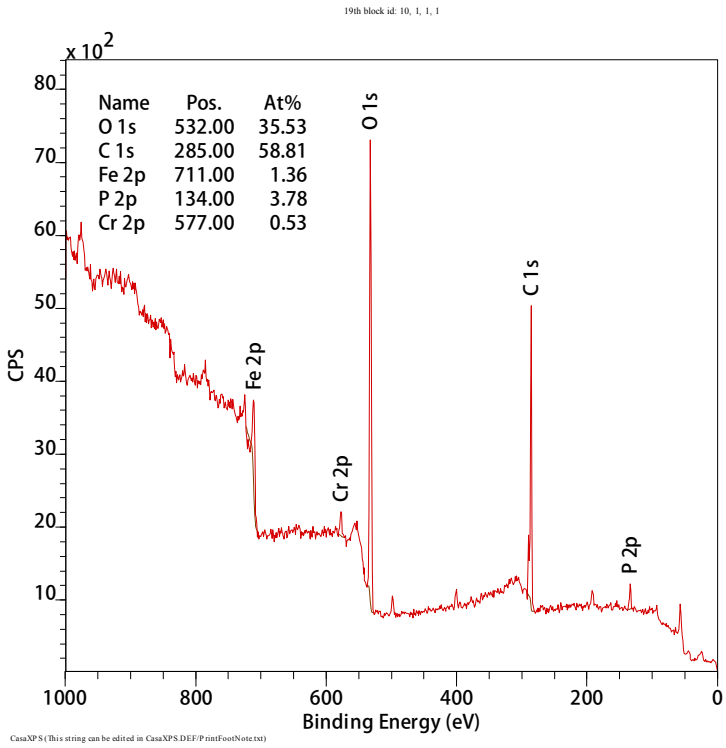

Figure S30. XPS survey scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in neutral MilliQ water, showing a %P of 3.78 and a C/P ratio of 15.6.

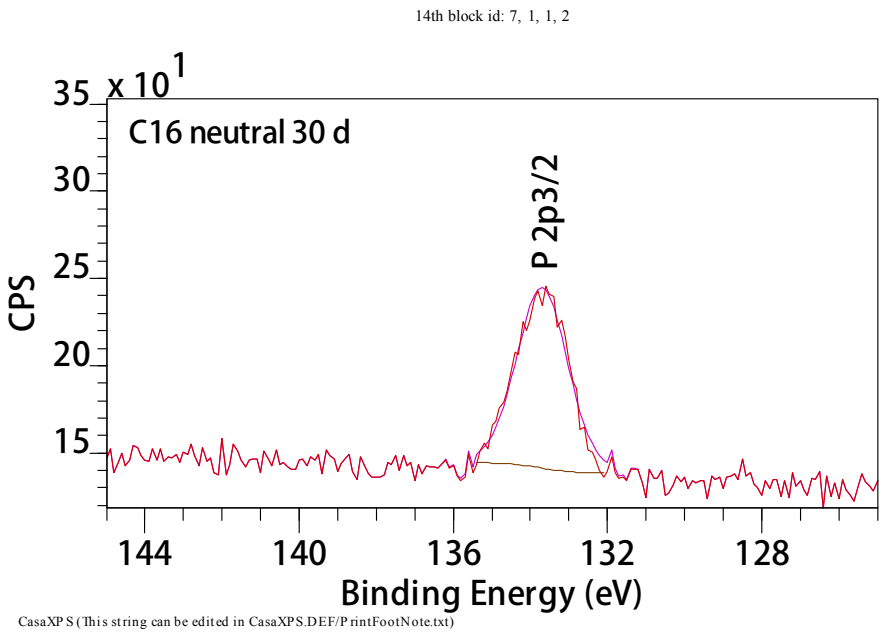

Figure S31. XPS P narrow scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in neutral MilliQ water.

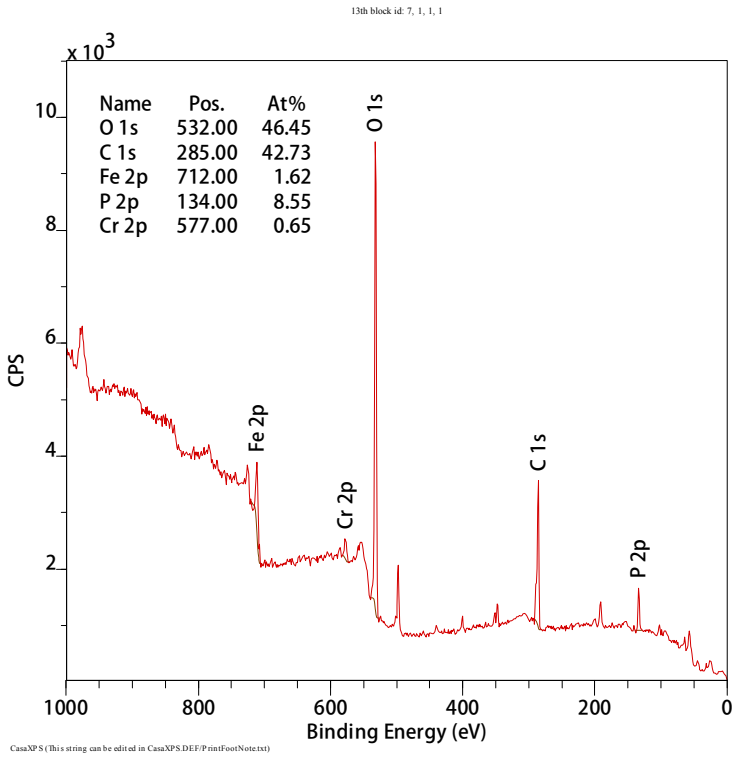

Figure S32. XPS survey scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in 10 mM PBS buffer at pH 7.4, showing a %P of 8.55 and a C/P ratio of 5.

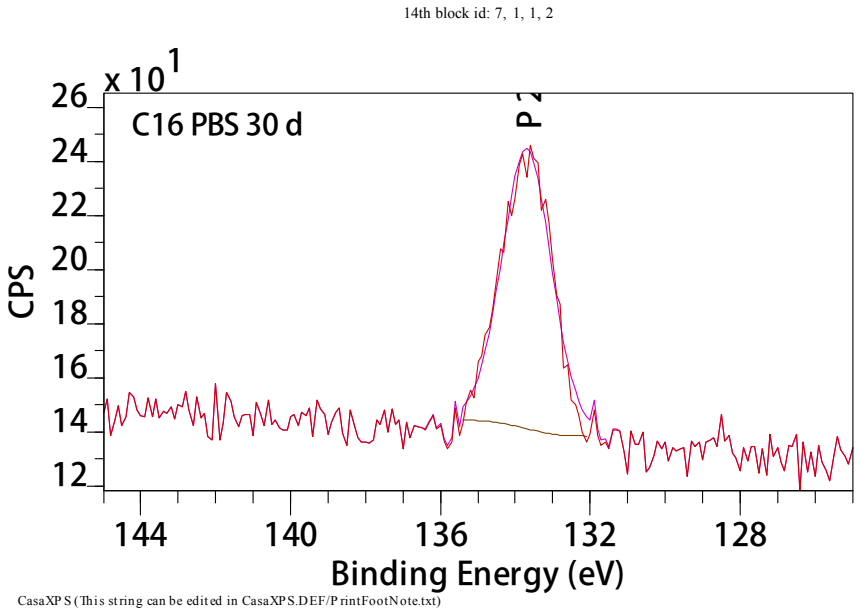

Figure S33. XPS P narrow scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in 10 mM PBS buffer at pH 7.4.

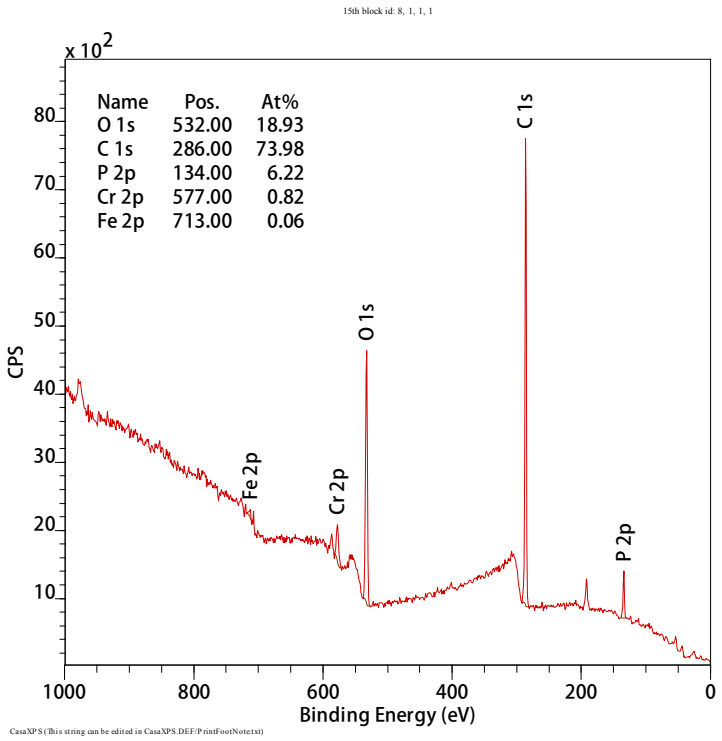

Figure S34. XPS survey scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in HCl solution at pH 3, showing a %P of 6.22 and a C/P ratio of 11.9.

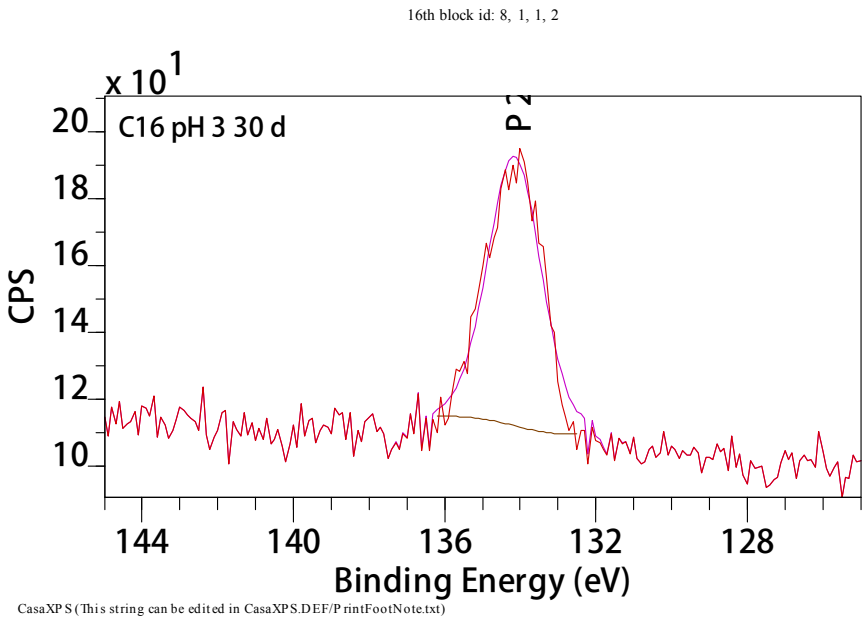

Figure S35. XPS P narrow scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in HCl solution at pH 3, showing retention of the P signal in contrast with butylphosphonic acid.

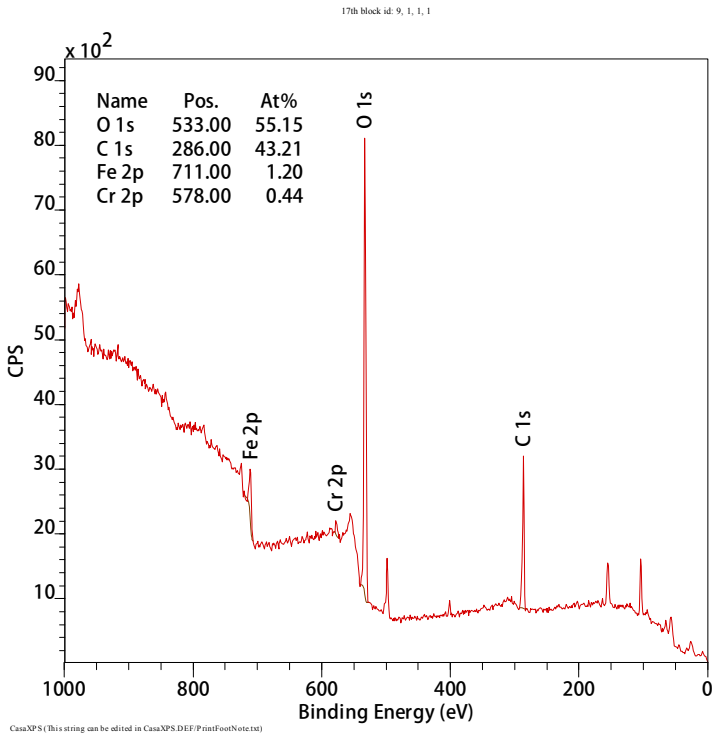

Figure S36. XPS survey scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in NaOH solution at pH 11, showing virtually complete disappearance of P content.

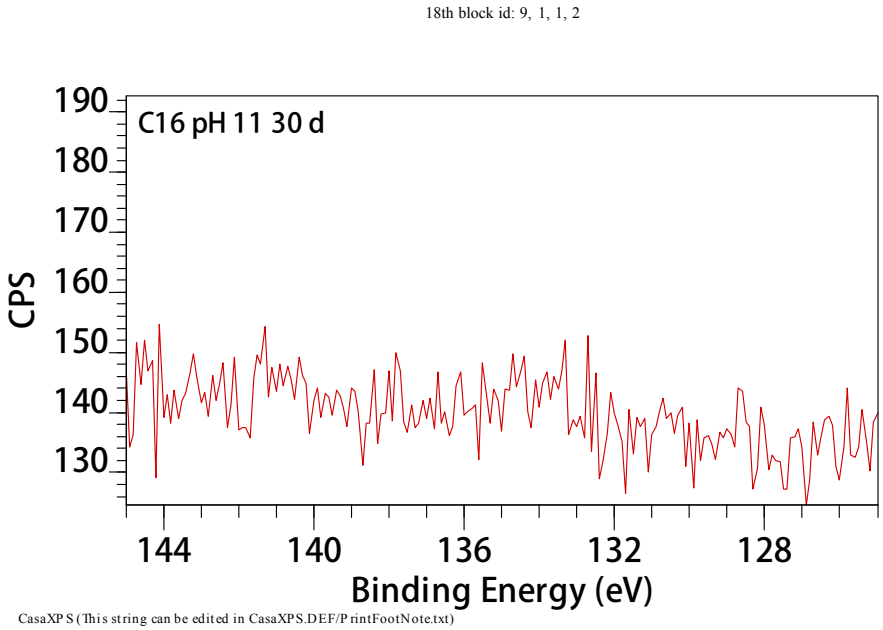

Figure S37. XPS P narrow scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d in NaOH solution at pH 11, showing disappearance of the P signal.

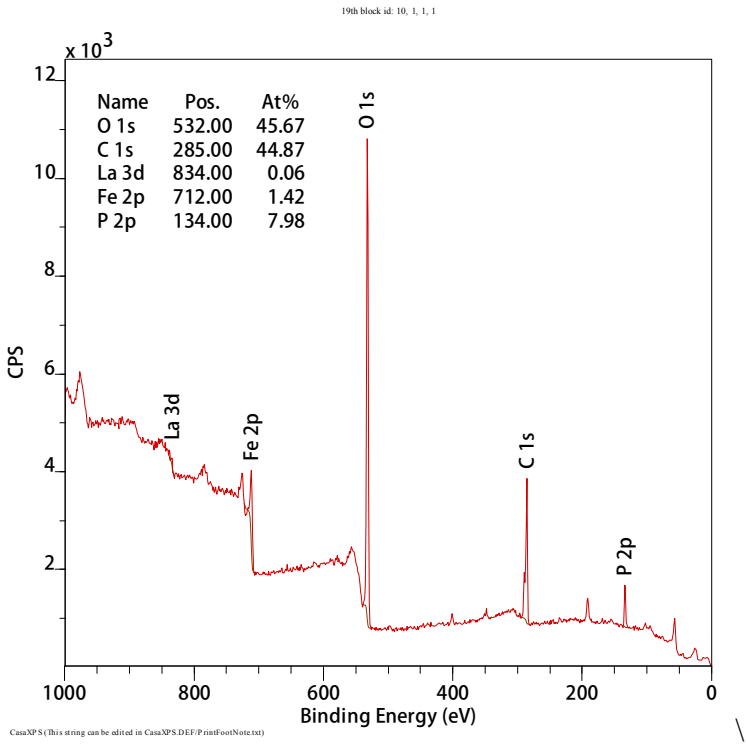

Figure S38. XPS survey scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d at 120 °C, showing a %P of 7.98 and a C/P ratio of 5.6.

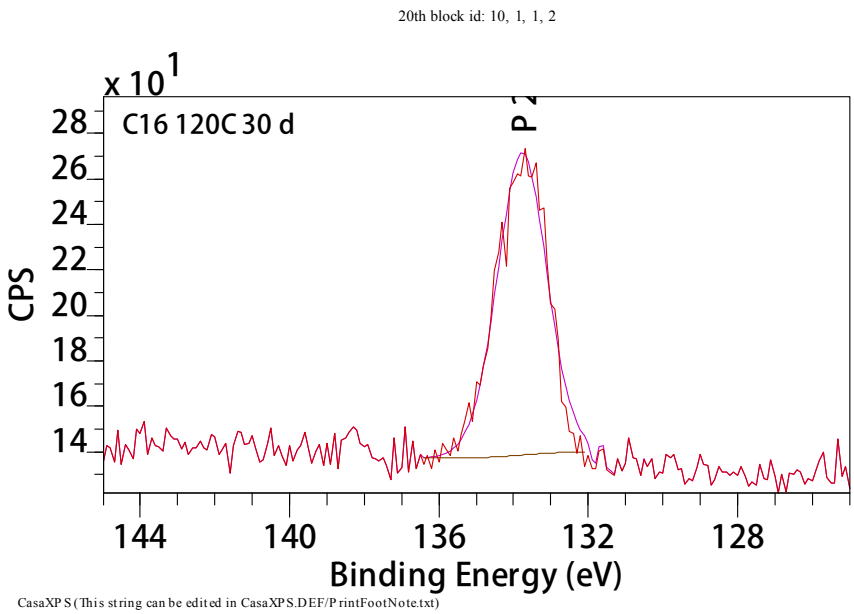

Figure S39. XPS P narrow scan of SS316L modified with hexadecylphosphonic acid (C_{16}) after 30 d at 120 °C.

2. Dendritic phosphonic acids

2.1 NMR data

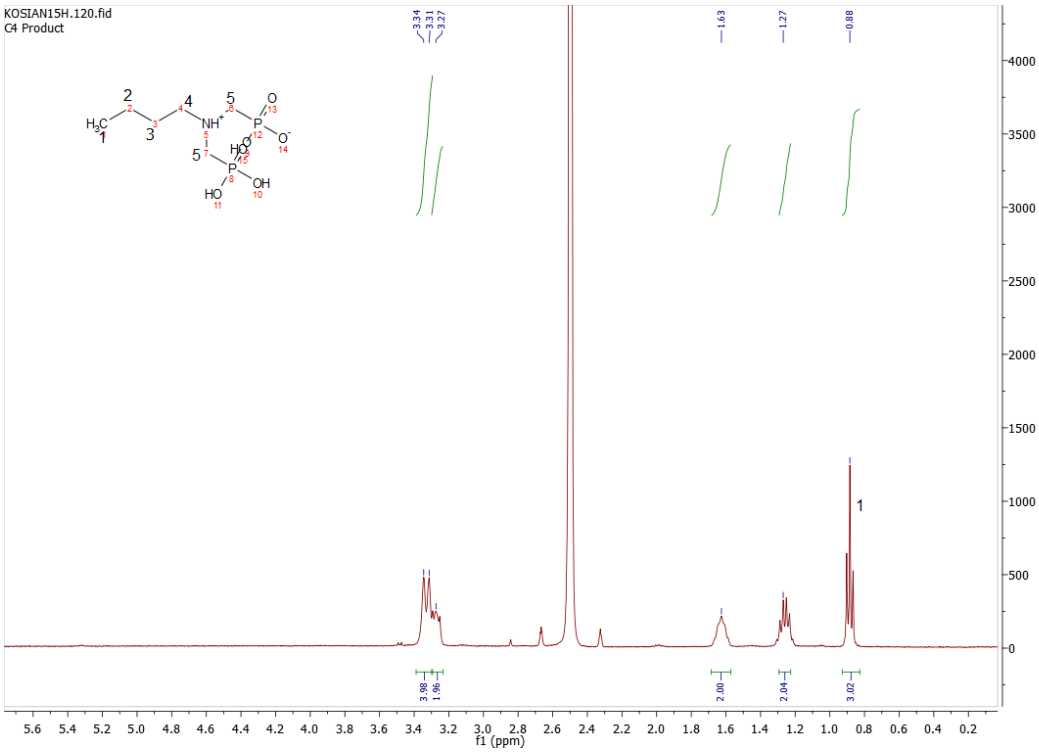

Figure S40. ^{1}H NMR spectrum of dendritic butylphosphonic acid **1**.

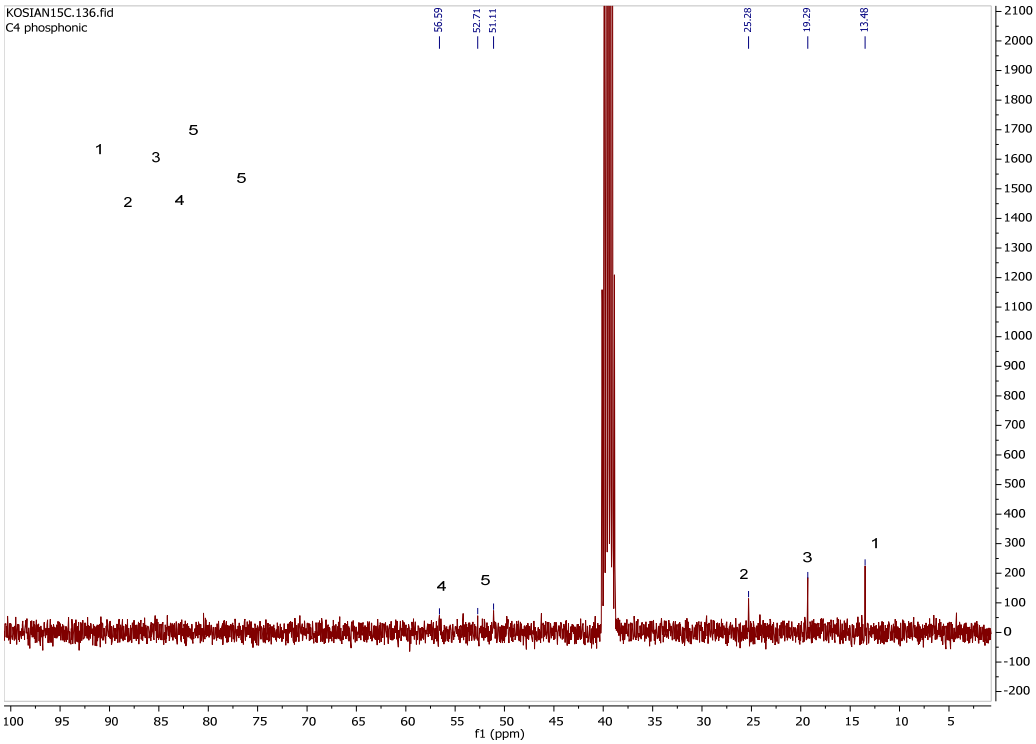

Figure S41. ^{13}C NMR spectrum of dendritic butylphosphonic acid **1**.

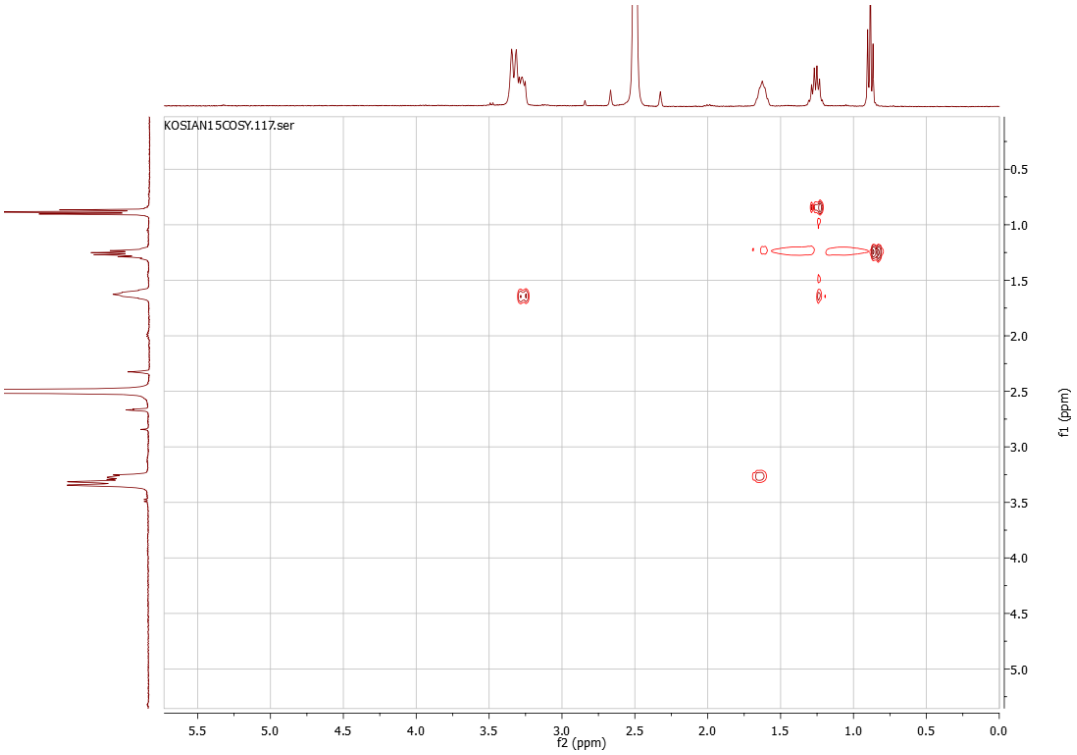

Figure S42. COSY 2D-NMR spectrum of dendritic butylphosphonic acid **1**.

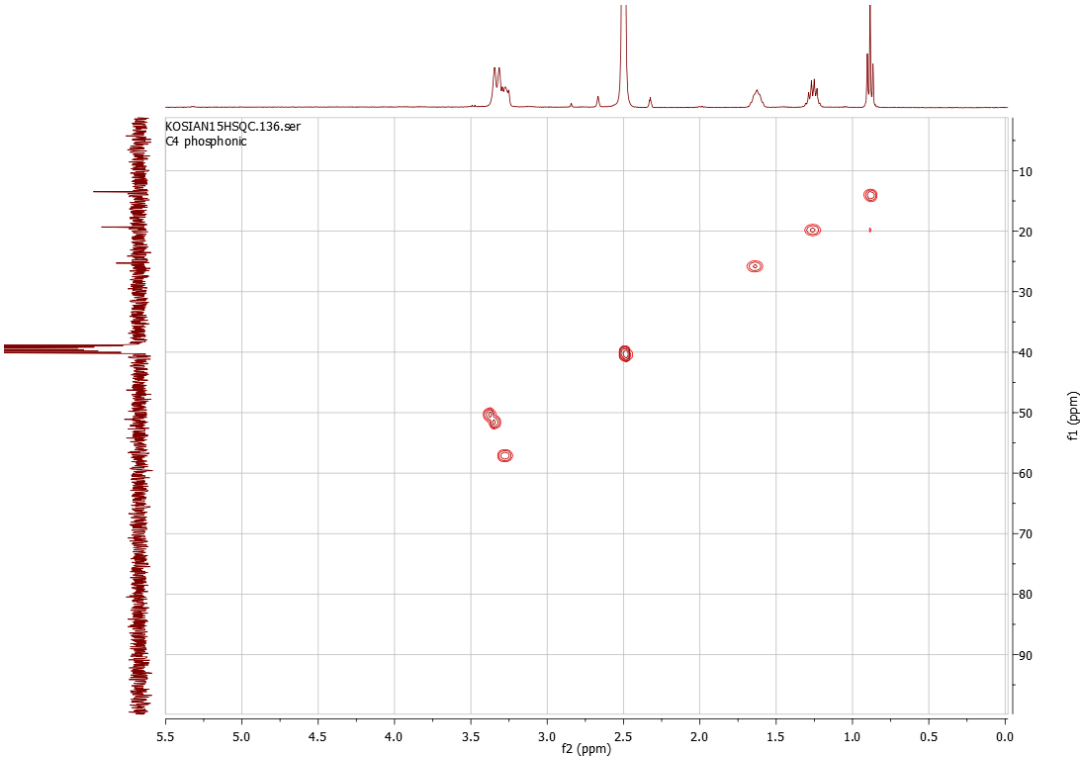

Figure S43. HSQC 2D-NMR spectrum of dendritic butylphosphonic acid **1**.

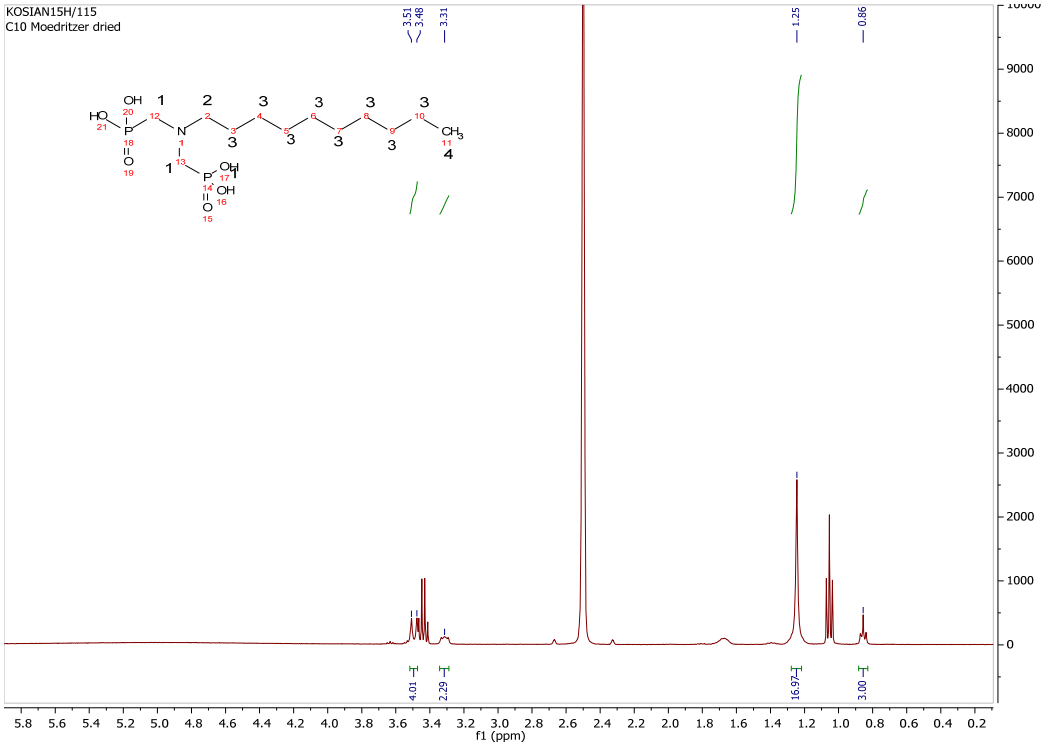

Figure S44. ^{1}H NMR spectrum of dendritic decylphosphonic acid **2**.

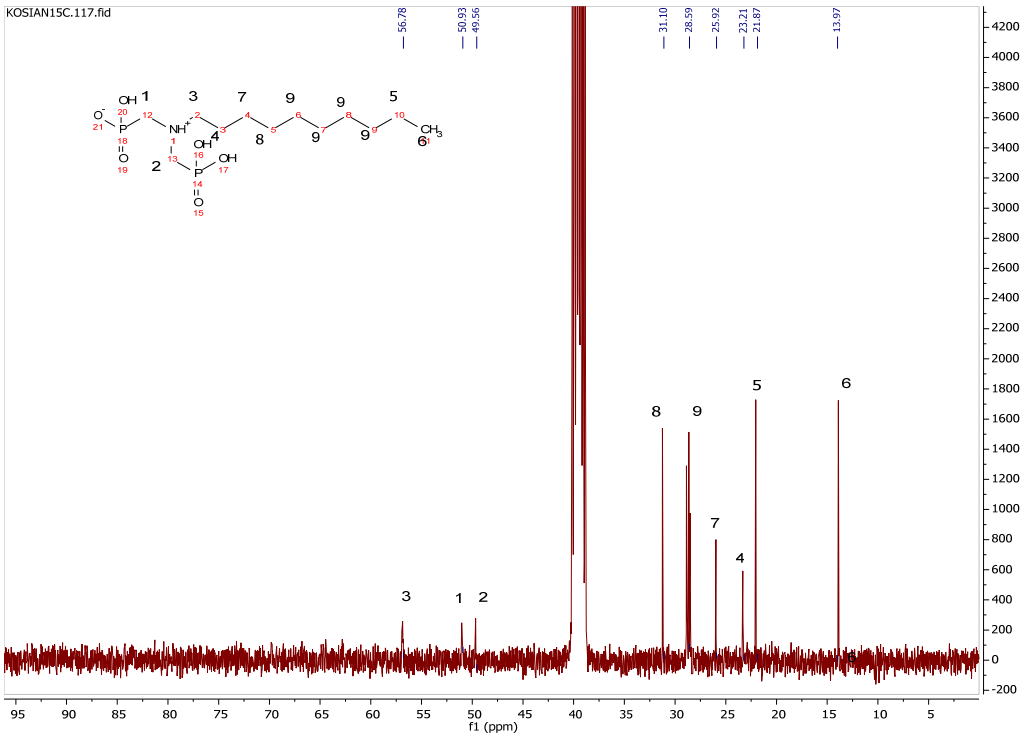

Figure S45. ^{13}C NMR spectrum of dendritic decylphosphonic acid **2**.

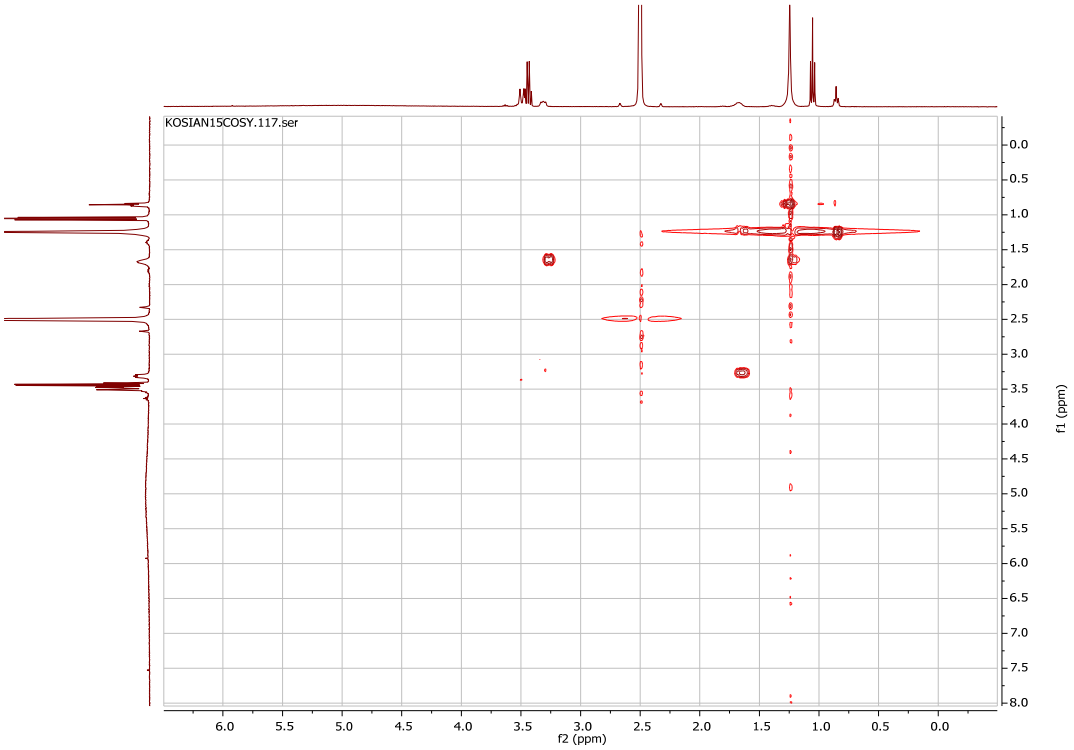

Figure S46. COSY 2D-NMR spectrum of dendritic decylphosphonic acid **2**.

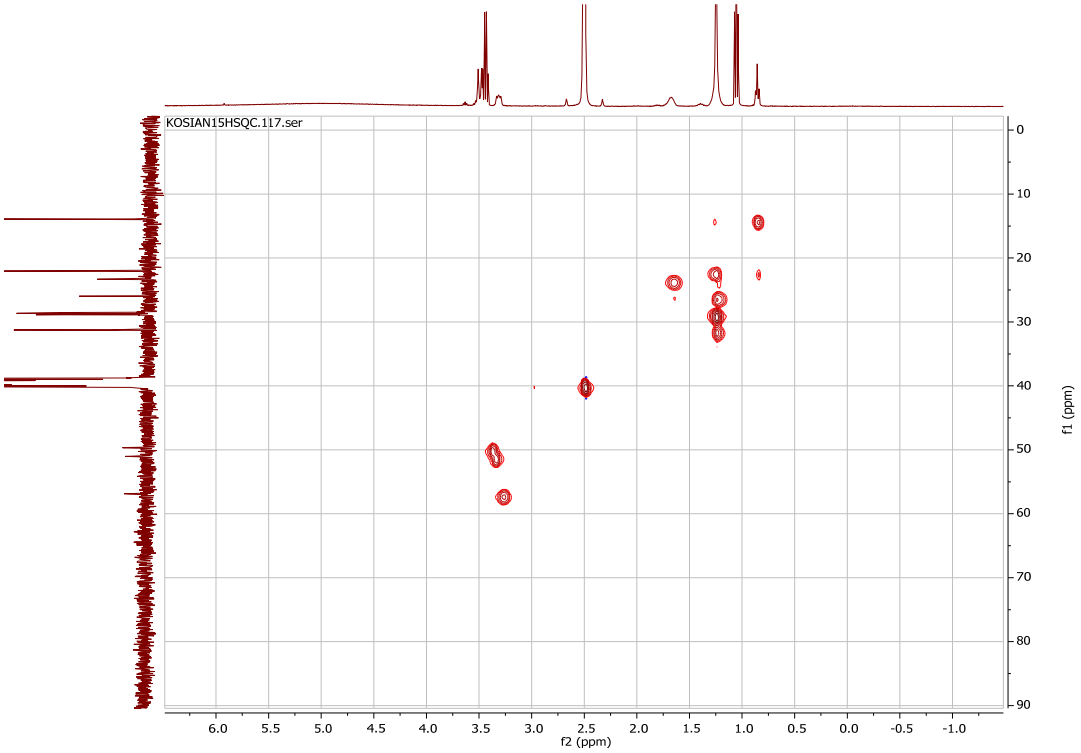

Figure S47. HSQC 2D-NMR spectrum of dendritic decylphosphonic acid **2**.

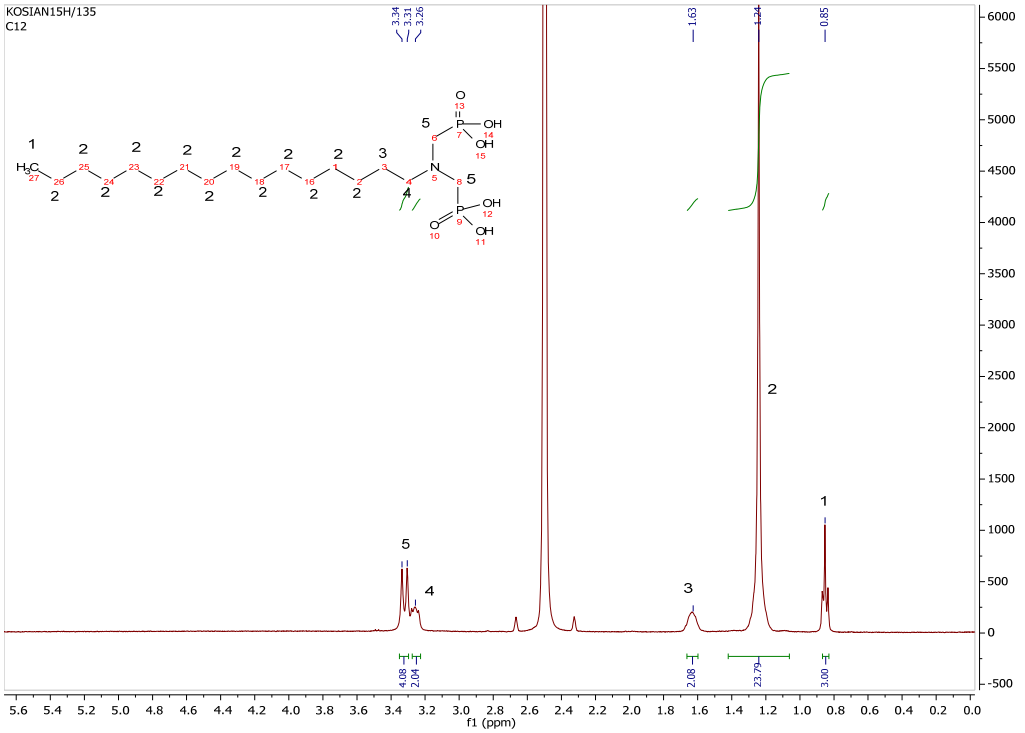

Figure S48. ^{1}H NMR spectrum of dendritic hexadecylphosphonic acid **3**.

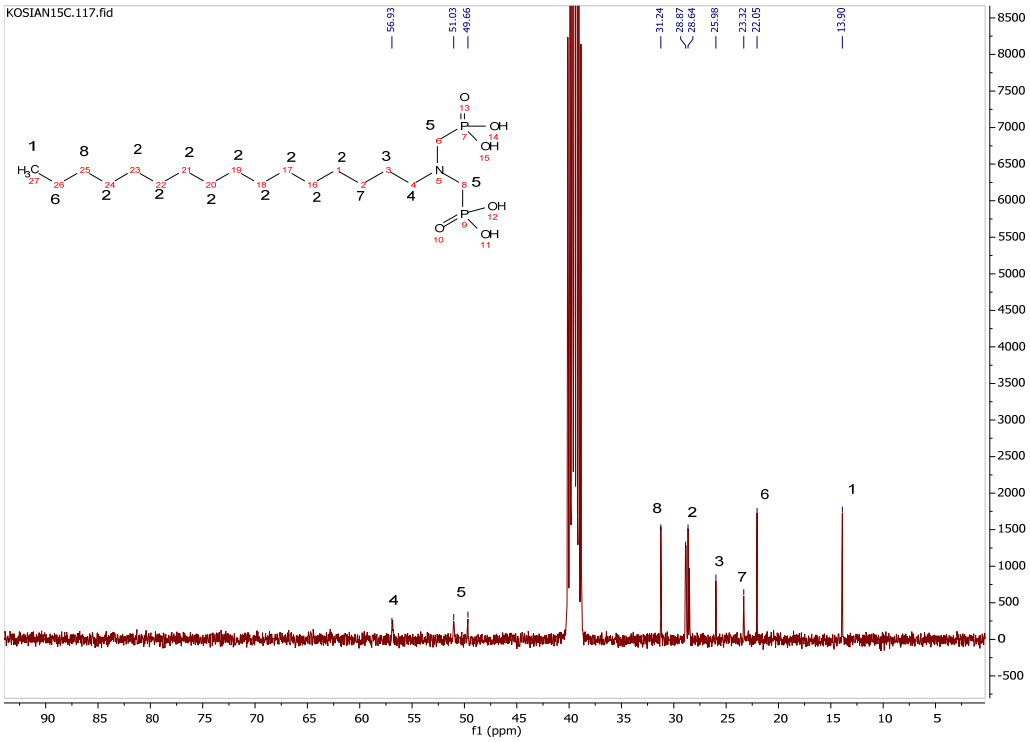

Figure S49. ^{13}C NMR spectrum of dendritic hexadecylphosphonic acid **3**.

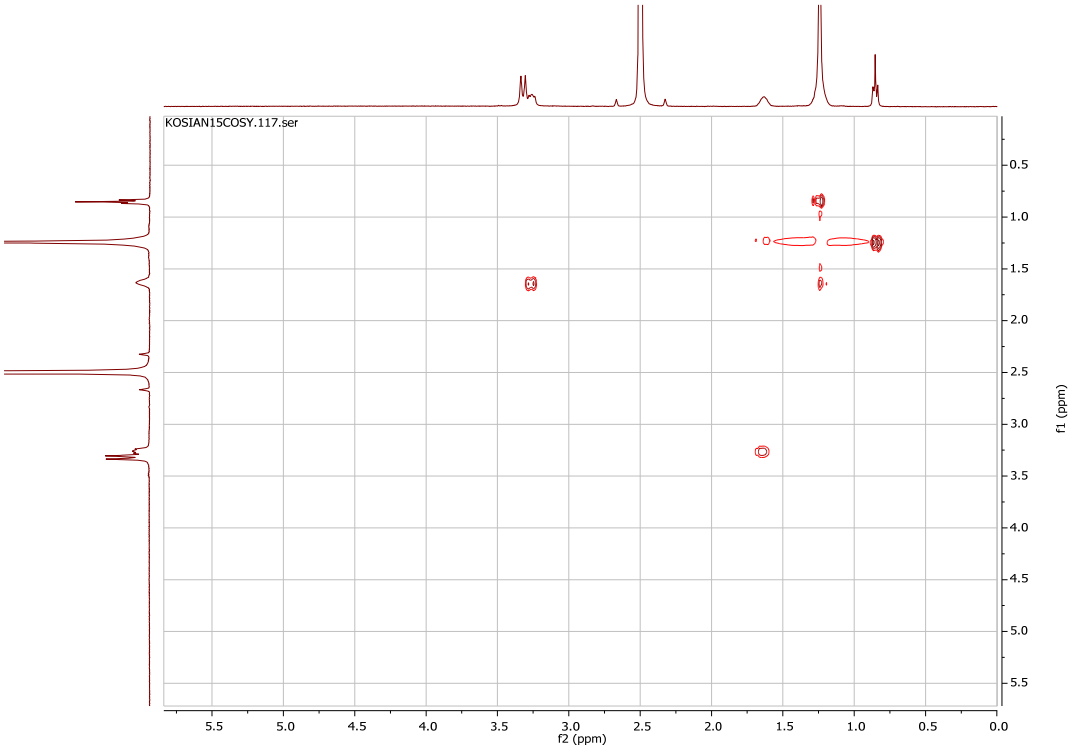

Figure S50. COSY 2D-NMR spectrum of dendritic hexadecylphosphonic acid **3**.

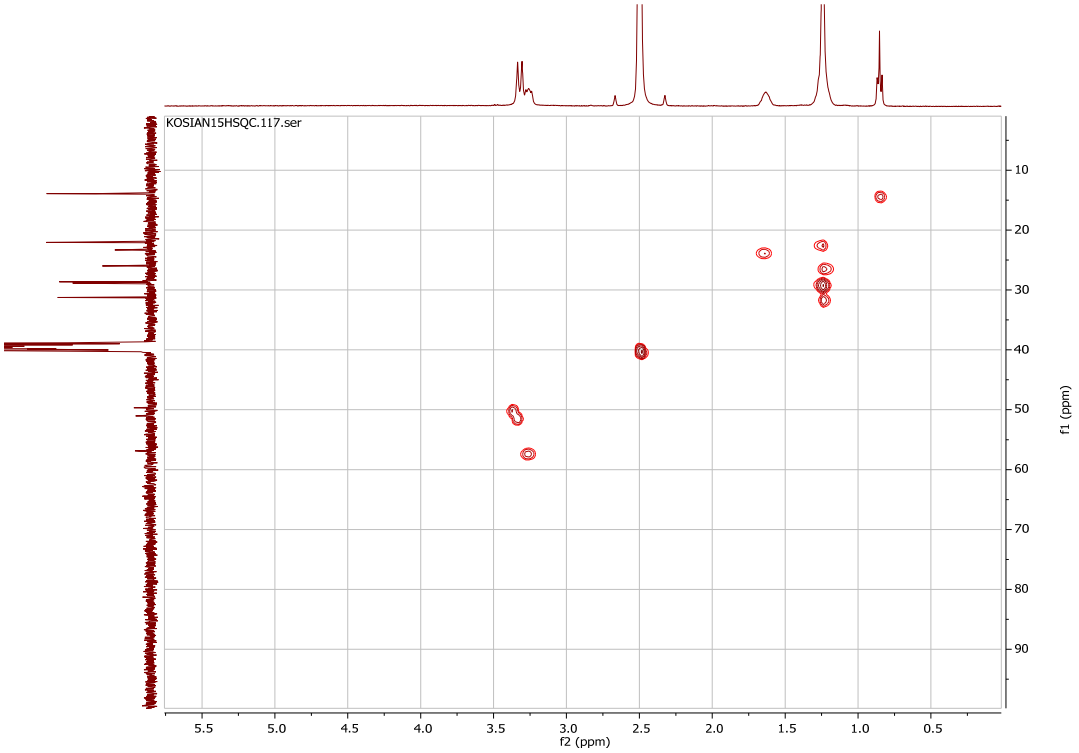

Figure S51. HSQC 2D-NMR spectrum of dendritic hexadecylphosphonic acid **3**.

2.2 XPS data

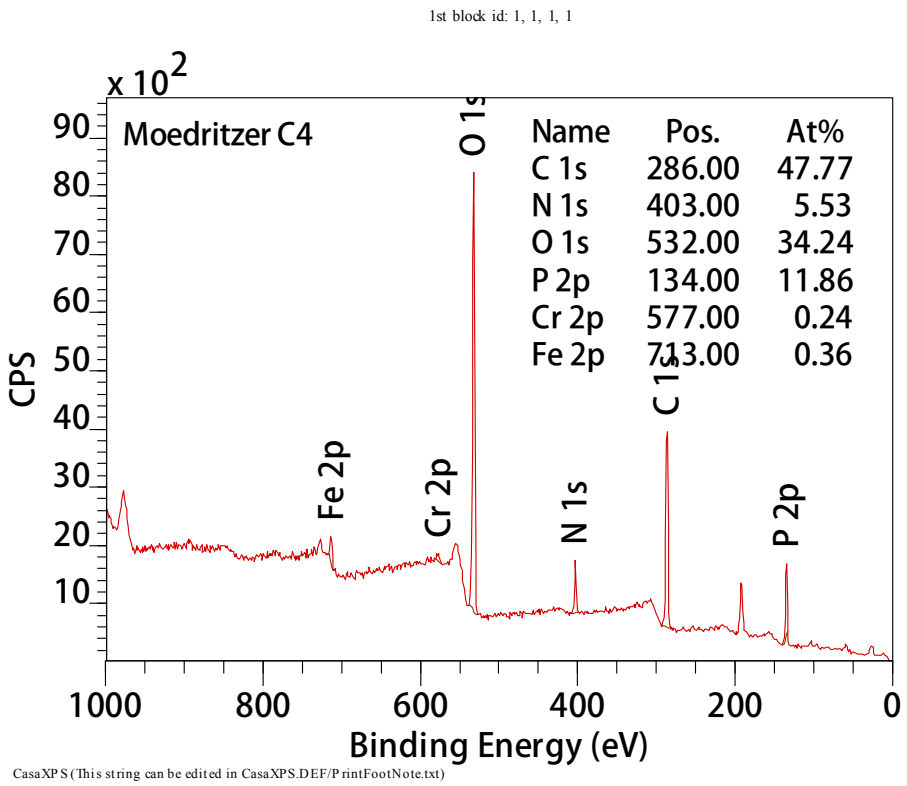

Figure S52. XPS survey scan of SS316L modified with dendritic butylphosphonic acid **1**.

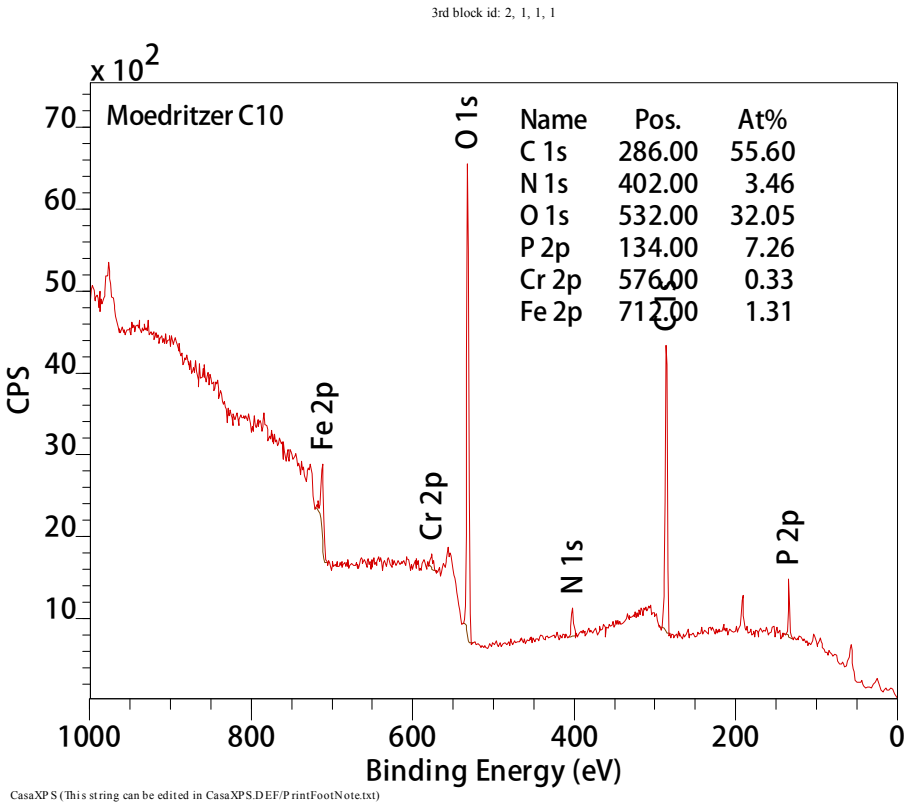

Figure S53. XPS survey scan of SS316L modified with dendritic decylphosphonic acid **2**.

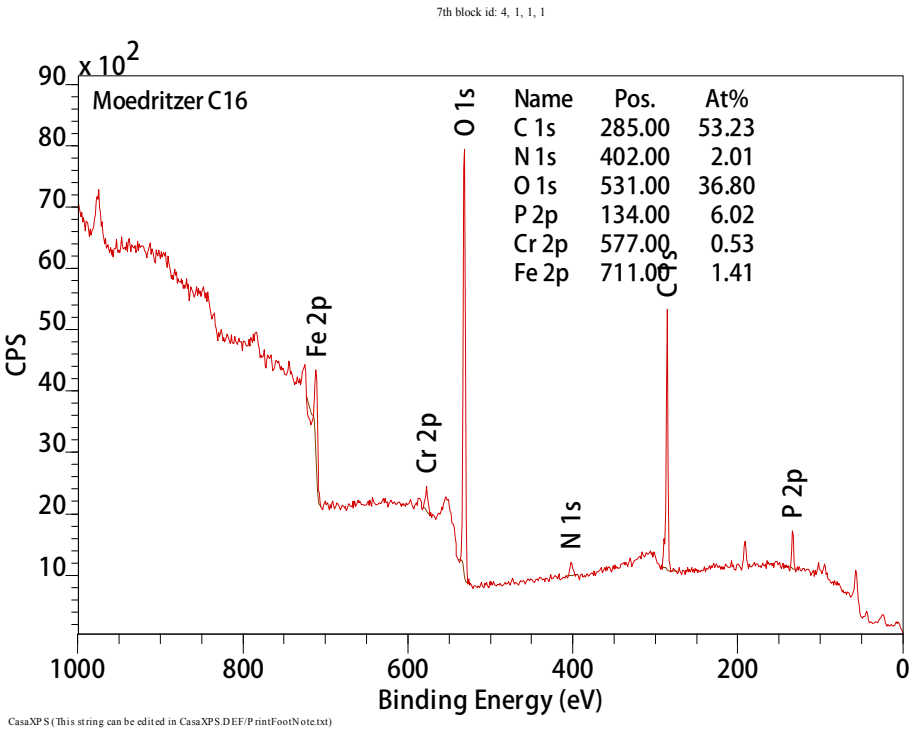

Figure S54. XPS survey scan of SS316L modified with dendritic hexadecylphosphonic acid **3**.

2.3 FTIR (IRRAS) data

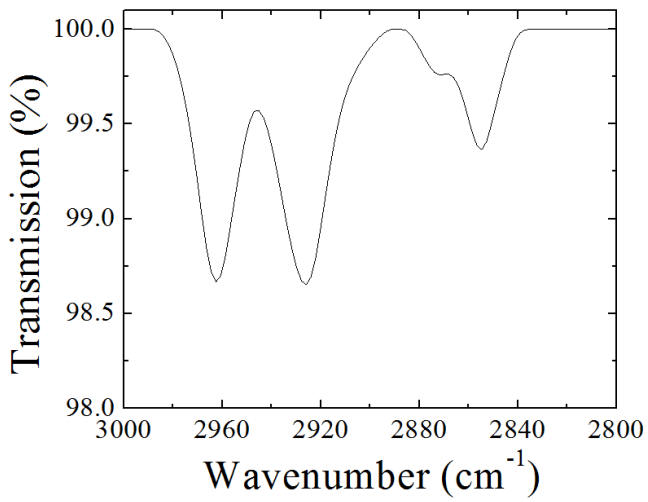

Figure S55. IR spectrum (C–H stretch region) of dendritic phosphonic acid **1** (C_4) on stainless steel.

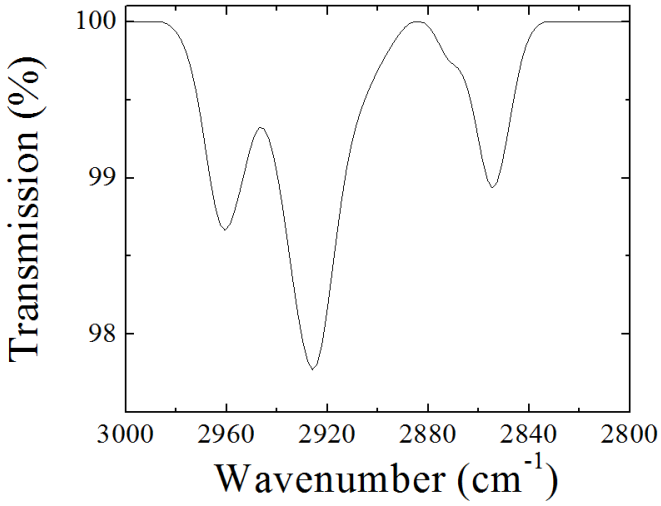

Figure S56. IR spectrum (C–H stretch region) of dendritic phosphonic acid **2** (C_{10}) on stainless steel.

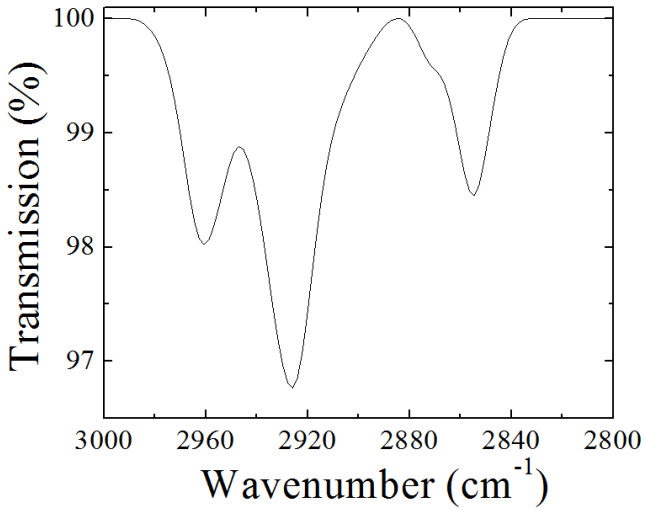

Figure S57. IR spectrum (C–H stretch region) of dendritic phosphonic acid **3** (C_{16}) on stainless steel.

3. Dendritic phosphonic acids - Long-term stability

3.1 Contact angle data

pH 7 (MilliQ) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
4	79.0	41.2	38.1	
10	95.6	95.1	89.0	
16	100.0	98.0	97.1	

Buffer (PBS) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
4	80.0	48.8	45.7	
10	95.0	94.2	88.3	
16	100.6	96.5	94.2	

Acid (pH 3) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
4	79.0	53.3	37.9	
10	95.5	93.0	87.5	
16	100.8	97.7	94.6	

Alkali (pH 11) solution				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
4	79.8	25.2	10.0	
10	95.5	83.2	77.4	
16	100.1	89.9	81.6	

Heat (120 °C)				
Chain length	**Initial**	**1 day**	**7 days**	**30 days**
4	79.0	57.2	39.2	
10	95.6	89.8	83.2	
16	100.1	93.4	85.7	

3.2 XPS data

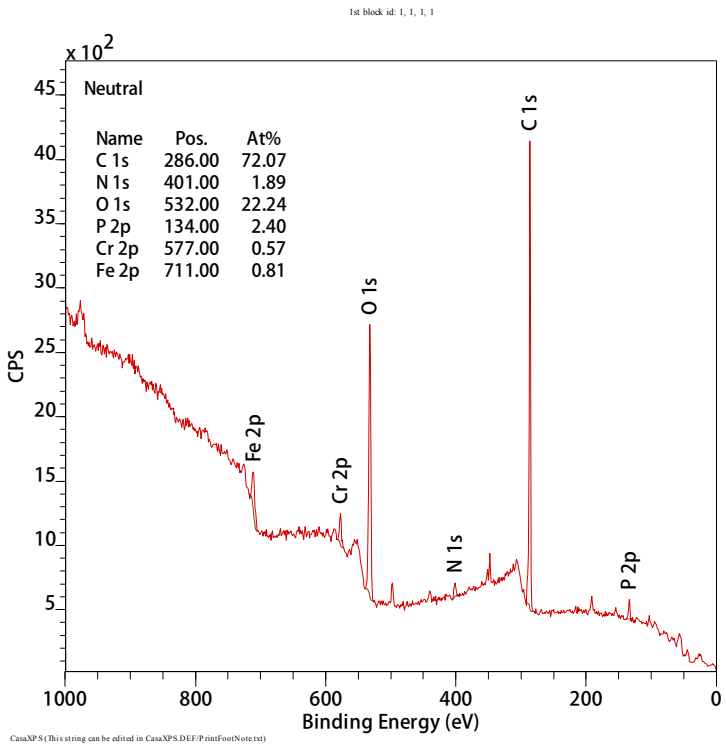

Figure S58. XPS survey scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in neutral solution.

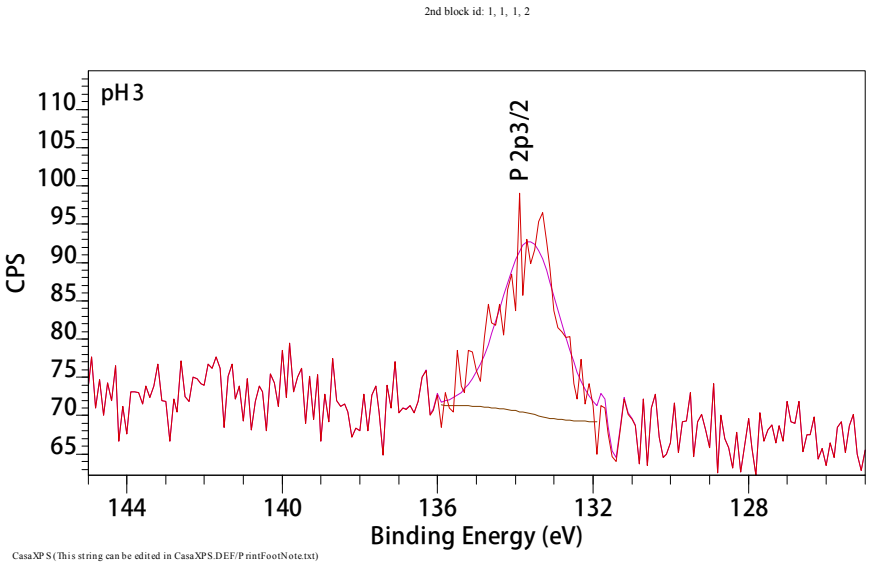

Figure S59. XPS P narrow scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in neutral solution.

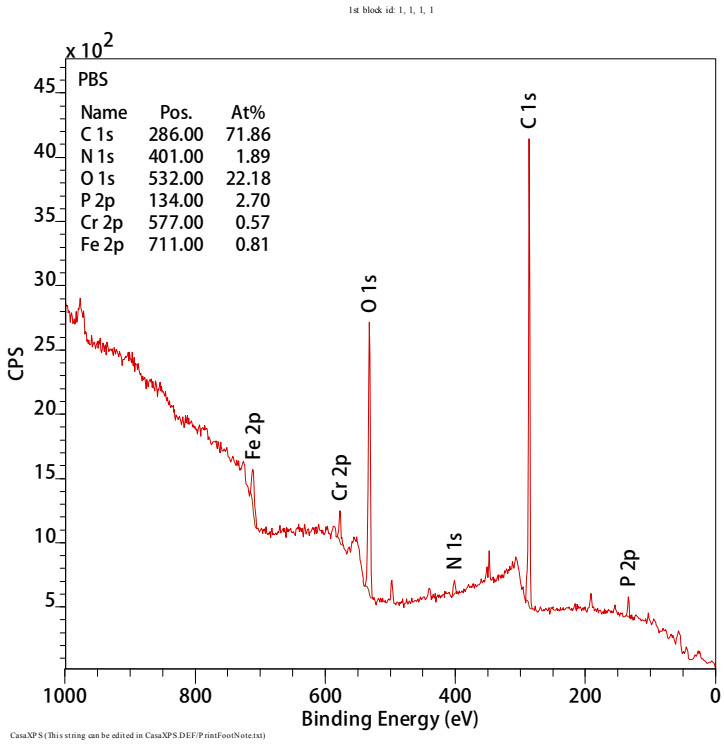

Figure S60. XPS survey scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in 10 mM PBS buffer solution.

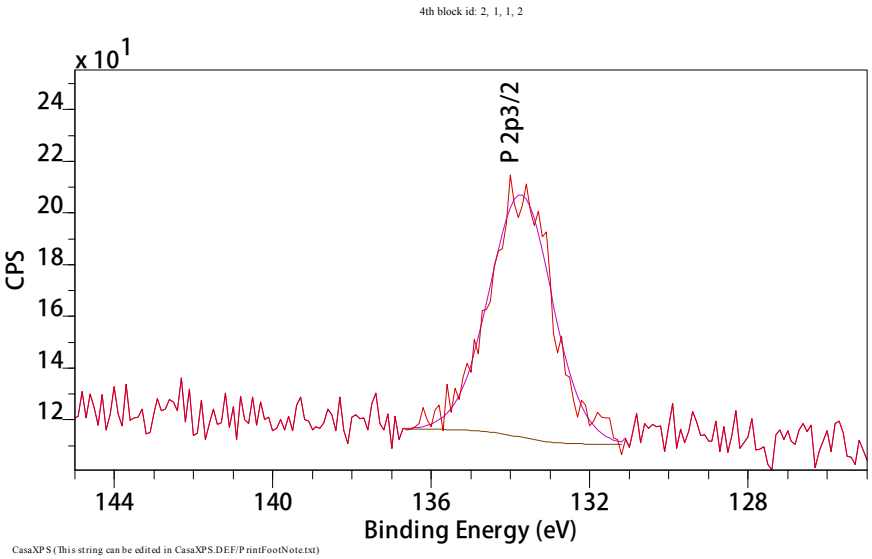

Figure S61. XPS P narrow scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in 10 mM PBS buffer solution.

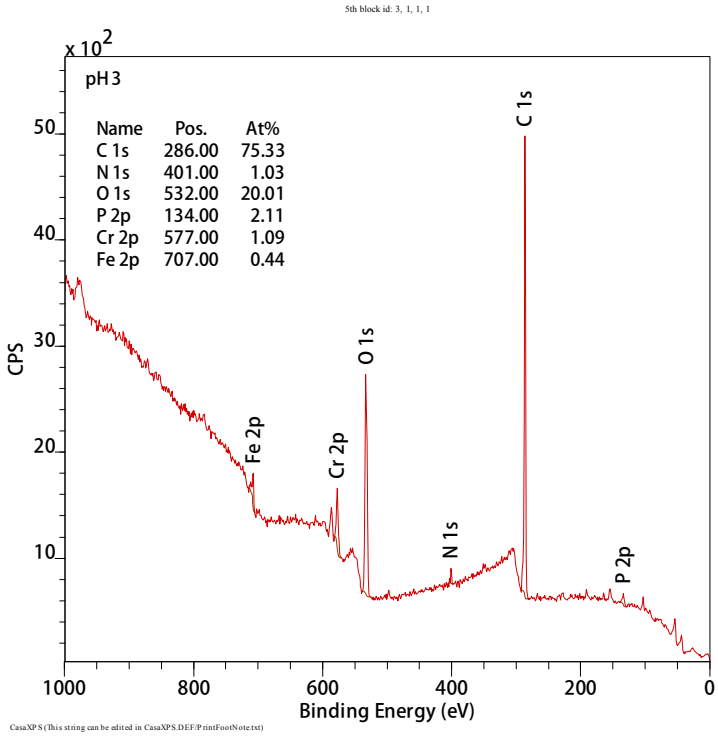

Figure S62. XPS survey scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in HCl solution at pH 3.

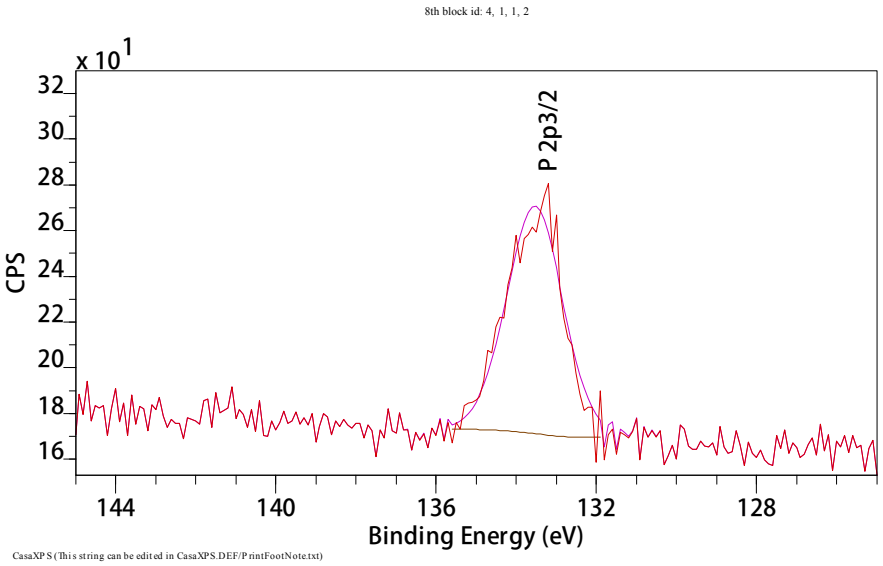

Figure S63. XPS P narrow scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in HCl solution at pH 3.

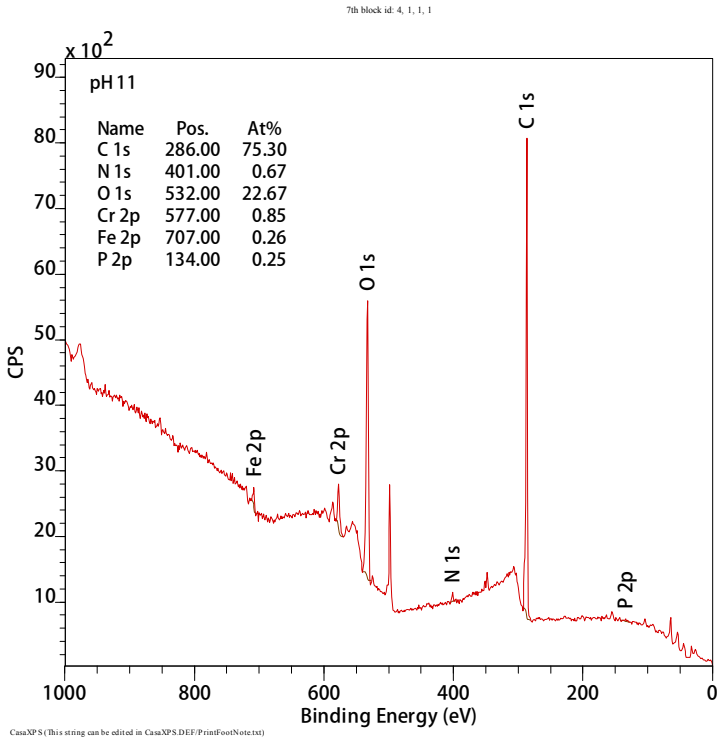

Figure S64. XPS survey scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in NaOH solution at pH 11.

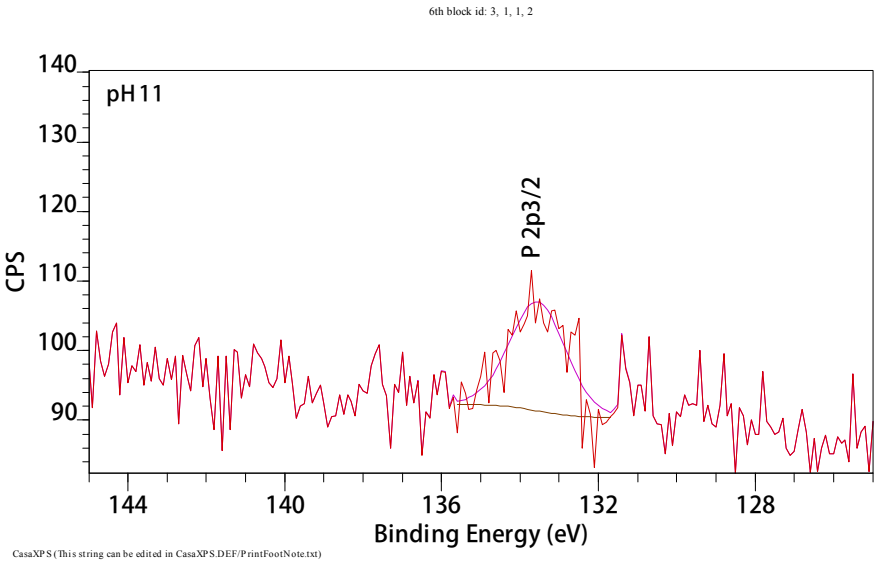

Figure S65. XPS P narrow scan of SS316L modified with dendritic phosphonic acid **3** after 30 d in NaOH solution at pH 11.

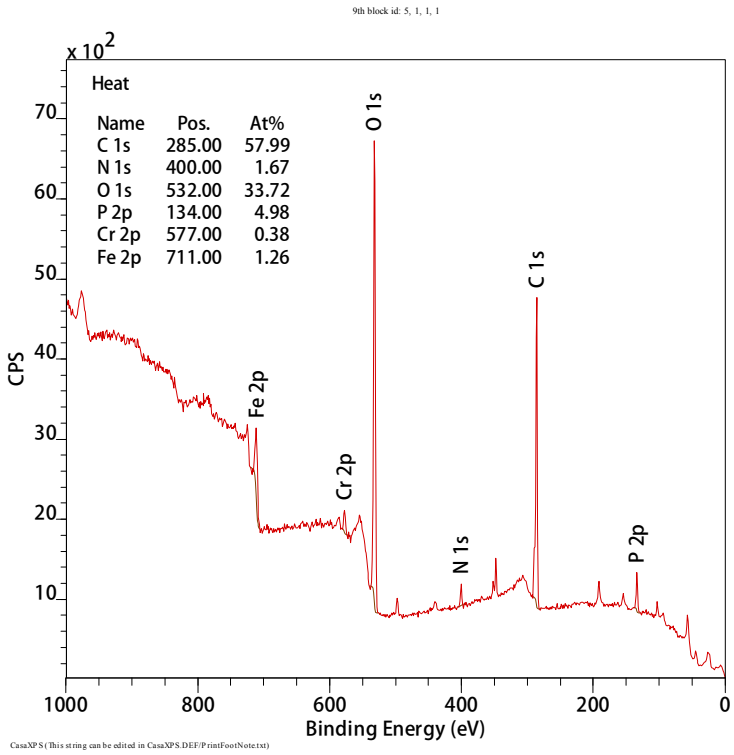

Figure S66. XPS survey scan of SS316L modified with dendritic phosphonic acid **3** after 30 d at 120 °C.

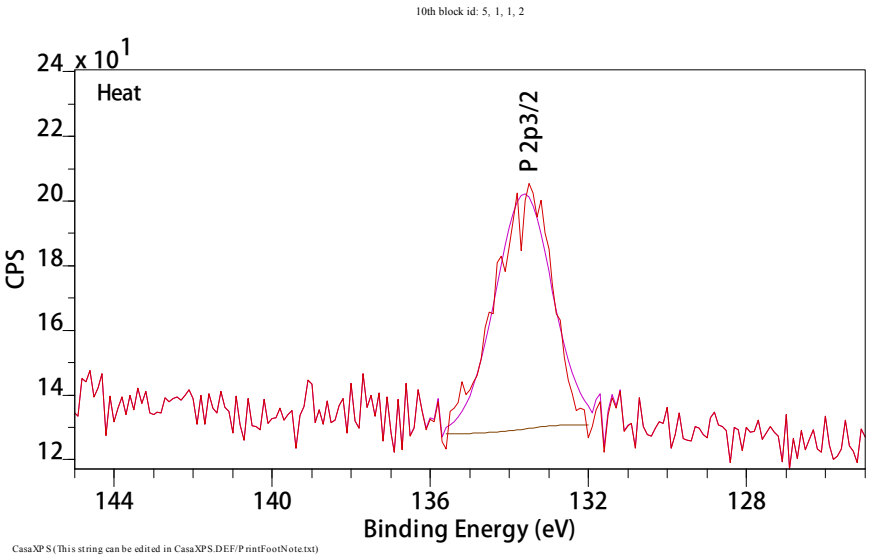

Figure S67. XPS P narrow scan of SS316L modified with dendritic phosphonic acid **3** after 30 d at 120 °C.

3.3 FTIR (IRRAS) data

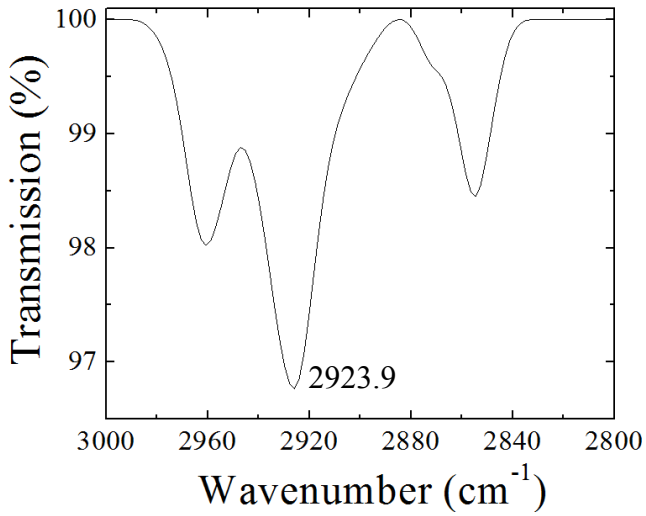

Figure S68. IR spectrum (C–H stretch region) of dendritic phosphonic acid **3** (C_{16}) on stainless steel after 30 d of exposure to neutral solution.

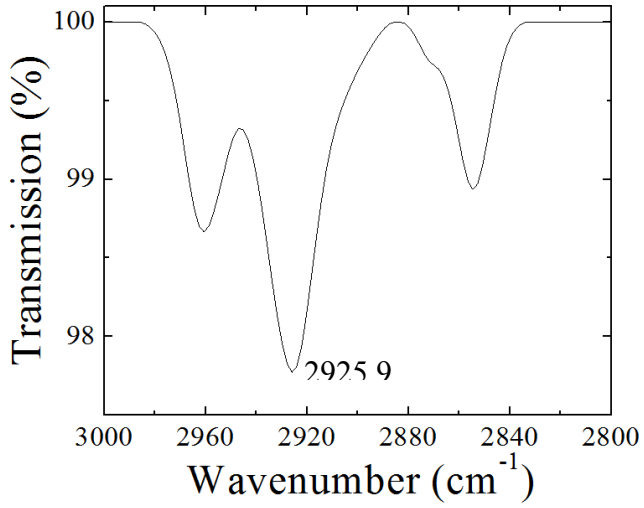

Figure S69. IR spectrum (C–H stretch region) of dendritic phosphonic acid **3** (C_{16}) on stainless steel after 30 d of exposure to 10 mM PBS buffer solution.

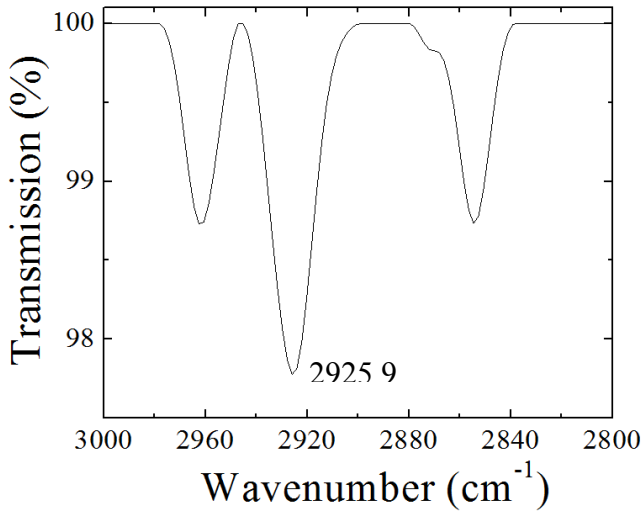

Figure S70. IR spectrum (C–H stretch region) of dendritic phosphonic acid **3** (C_{16}) on stainless steel after 30 d of exposure to HCl solution at pH 3.

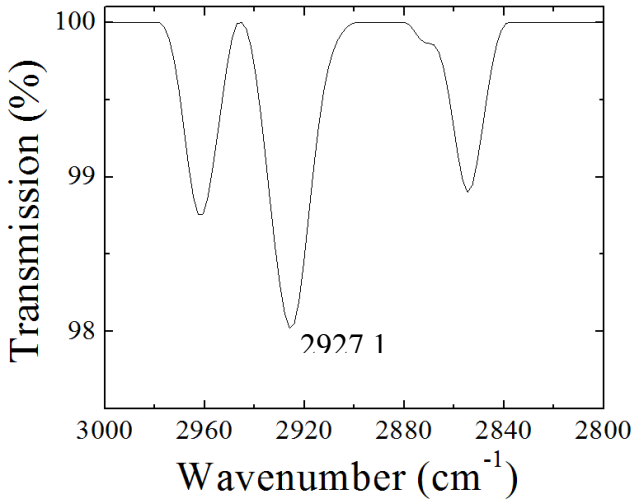

Figure S71. IR spectrum (C–H stretch region) of dendritic phosphonic acid **3** (C_{16}) on stainless steel after 30 d of exposure to NaOH solution at pH 11.

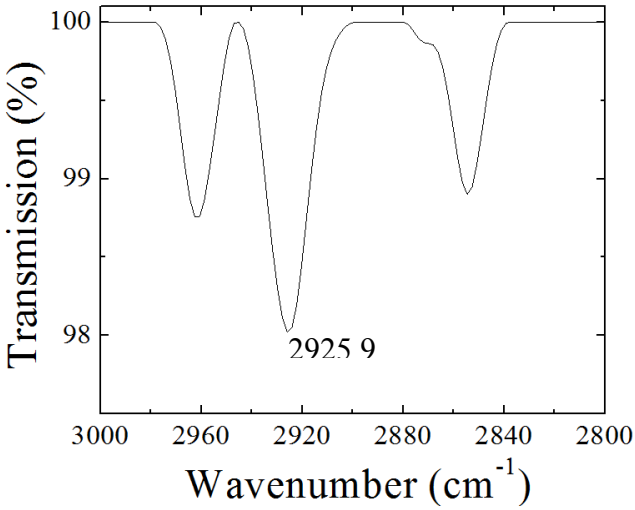

Figure S72. IR spectrum (C–H stretch region) of dendritic phosphonic acid **3** (C_{16}) on stainless steel after 30 d of exposure to 120 °C.

4. Assigned XPS survey scan of SS316L

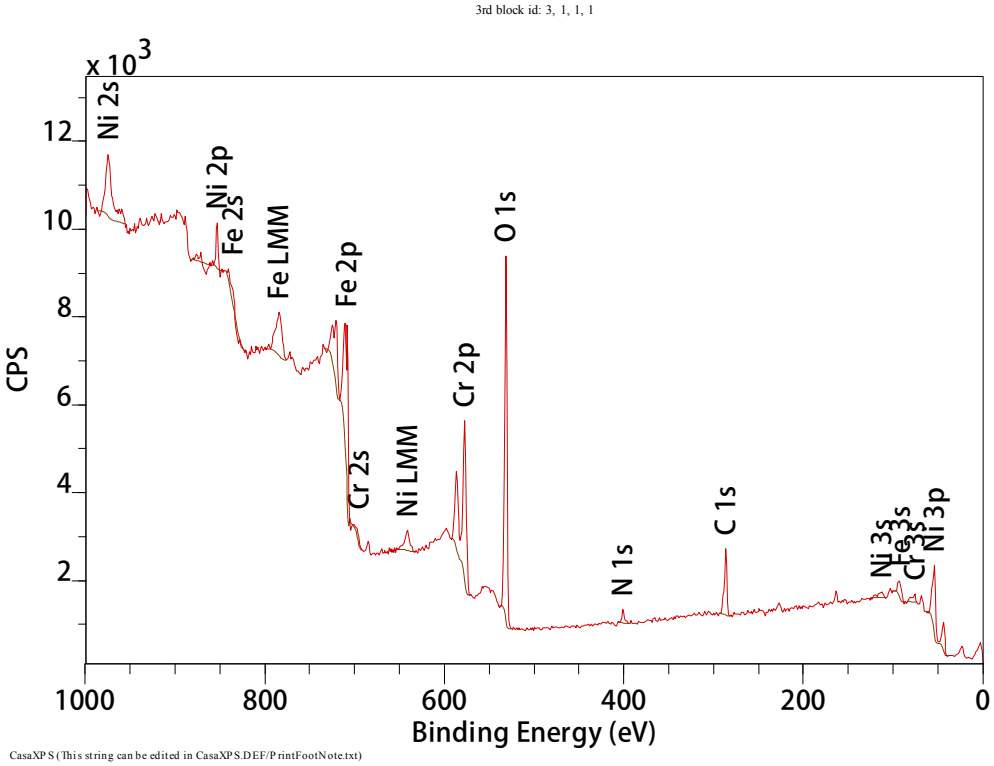

Figure S73. Fully assigned XPS survey scan of SS316L.