

Electrochemical Iodination through the In Situ Generation of Iodinating Agents: A Promising Green Approach

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Supplementary Materials:

S1: Data for the identification of 2A and 3A reactions.

List of the possible reaction to which anodic peaks 2A and 3A could be assigned.

2A	$I_2 + 2 H_2O \rightarrow 2HIO + 2H^+ + 2e^-$	$E_{vs SHE} (V) = 1.354 - 0.0591 \text{ pH}$	(S1)
	$I^- + H_2O \rightarrow HIO + H^+ + 2e^-$	$E_{vs SHE} (V) = 0.987 - 0.0295 \text{ pH}$	(S2)
	$I_3^- + 3 H_2O \rightarrow 3HIO + 3H^+ + 4 e^-$	$E_{vs SHE} (V) = 1.213 - 0.0443 \text{ pH}$	(S3)
3A	$HIO + 2 H_2O \rightarrow IO_3^- + 5 H^+ + 4 e^-$	$E_{vs SHE} (V) = 1.134 - 0.0739 \text{ pH}$	(S4)
	$IO^- + 2 H_2O \rightarrow IO_3^- + 4 H^+ + 4 e^-$	$E_{vs SHE} (V) = 0.972 - 0.0591 \text{ pH}$	(S5)
	$I_3^- + 9 H_2O \rightarrow 3 HIO_3 + 15 H^+ + 16 e^-$	$E_{vs SHE} (V) = 1.145 - 0.0554 \text{ pH}$	(S6)
	$I_3^- + 9 H_2O \rightarrow 3 IO_3^- + 18 H^+ + 16 e^-$	$E_{vs SHE} (V) = 1.154 - 0.0665 \text{ pH}$	(S7)
	$I_2 + 6 H_2O \rightarrow 2 HIO_3 + 10 H^+ + 10 e^-$	$E_{vs SHE} (V) = 1.169 - 0.0591 \text{ pH}$	(S8)
	$I_2 + 6 H_2O \rightarrow 2 IO_3^- + 12 H^+ + 10 e^-$	$E_{vs SHE} (V) = 1.178 - 0.0709 \text{ pH}$	(S9)
	$I^- + 3 H_2O \rightarrow HIO_3 + 5 H^+ + 6 e^-$	$E_{vs SHE} (V) = 1.077 - 0.0493 \text{ pH}$	(S10)
	$I^- + 3 H_2O \rightarrow IO_3^- + 6 H^+ + 6 e^-$	$E_{vs SHE} (V) = 1.085 - 0.0591 \text{ pH}$	(S11)

Figure S1 and **Table S1** reporting the experimental linear dependencies on pH of first, second and third oxidation peak reported in **Figure 2a)** of KI 2 mM on a GC electrode.

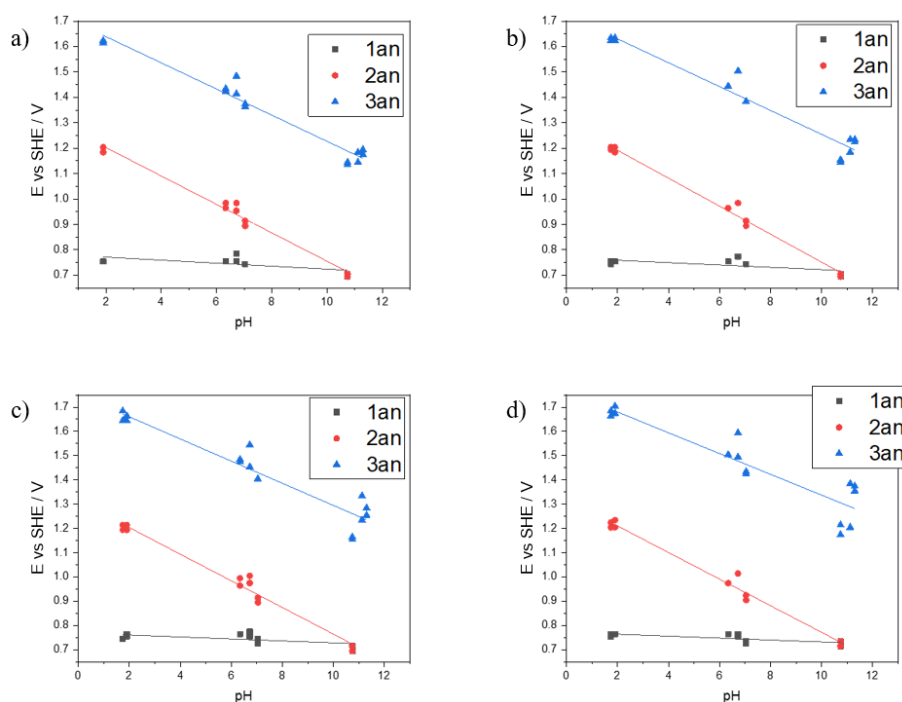


Figure S1: Plots potential (E) vs pH of anodic peak at a) 10, b) 20, c) 50 and d) 100 mV s^{-1} . WE = GC, RE = SCE, CE = Pt, electrolyte = phosphate buffer solution 0.5 M at various pH, analyte = KI 2 mM.

Table S1: Values of intercepts and slopes obtained from plot E vs pH for each oxidation peak at each scan rate.

10 mV/s			20 mV/s		
Peak	Intercept (vs SHE)	Slope	Peak	Intercept (vs SHE)	Slope
1A	0.78 ± 0.02	-0.006 ± 0.002	1A	0.76 ± 0.01	-0.005 ± 0.002
2A	1.31 ± 0.02	-0.056 ± 0.003	2A	1.30 ± 0.01	-0.055 ± 0.002
3A	1.74 ± 0.03	-0.051 ± 0.003	3A	1.72 ± 0.03	-0.047 ± 0.003
50 mV/s			100 mV/s		
Peak	Intercept (vs SHE)	Slope	Peak	Intercept (vs SHE)	Slope
1A	0.77 ± 0.01	-0.004 ± 0.002	1A	0.77 ± 0.01	-0.004 ± 0.001
2A	1.31 ± 0.02	-0.055 ± 0.003	2A	1.32 ± 0.02	-0.055 ± 0.003
3A	1.75 ± 0.03	-0.046 ± 0.004	3A	1.77 ± 0.04	-0.043 ± 0.005

S2: Screening of suitable phenolic molecules susceptible of electrophilic attack.

The potential screening of suitable phenolic molecules susceptible of electrophilic attack is reported in **Table S2**.

Table S2: Electrophilic attack susceptible phenolic substances screening in phosphate buffer 0.5 M pH 6.5.

Reactant	Oxidation peak potential vs SCE (V)	Observation (pH 6.5)
Phenol	-	Direct oxidation, polymerization products
4-nitrophenol	~ 0.89	Probable polymerization
Resorcinol	~ 0.7	Potential not high enough
5-sulfosalicylic acid	~ 0.9	Can be used
Benzoic acid	~ 0.93	Very little, overlapped with iodate peak
5-aminoisophthalic acid	~ 0.82	Can be used
5-hydroxyisophthalic acid	~ 0.83	Can be used
3-hydroxybenzyl alcohol	~ 0.65	Potential not high enough

S3: Electrosynthesis current drop in the case of 5-hydroxyisophthalic acid.

Average current drop of 5-hydroxyisophthalic acid in the case of HIO (**Table S3**) and I₂ (**Table S4**) production are below reported.

Table S3: Report of peak current values and current drop of 5-hydroxyisophthalic acid peak for different iodination (iodinating agent: HIO) at the start and at the theoretical end of the reaction.

HIO Sample	t ₀ peak current (j / mA cm ⁻²)	TE peak current (j / mA cm ⁻²)	Current drop (%)
1	0.3287	0.1786	45.7
2	0.2988	0.1632	45.5
3	0.3905	0.2247	42.5
4	0.3963	0.2314	41.6
5	0.3840	0.2183	43.2

Table S4: Report of peak current values and current drop of 5-hydroxyisophthalic acid peak for different iodination (iodinating agent: I₂) at the start and at the theoretical end of the reaction.

I ₂ Sample	t ₀ peak current (j / mA cm ⁻²)	TE peak current (j / mA cm ⁻²)	Current drop (%)
1	0.5727	0.3822	33.3
2	0.5203	0.3276	37.0
3	0.3640	0.2390	34.3

S4: 5-hydroxyisophthalic acid iodination mixture MS analyses

MS analyses of peaks at 1.50 (di-iodinated product), 4.69 (mono-iodinated product) and 5.41 (di-iodinated product) minutes are reported in **Figure S2**, **Figure S3** and **Figure S4**.

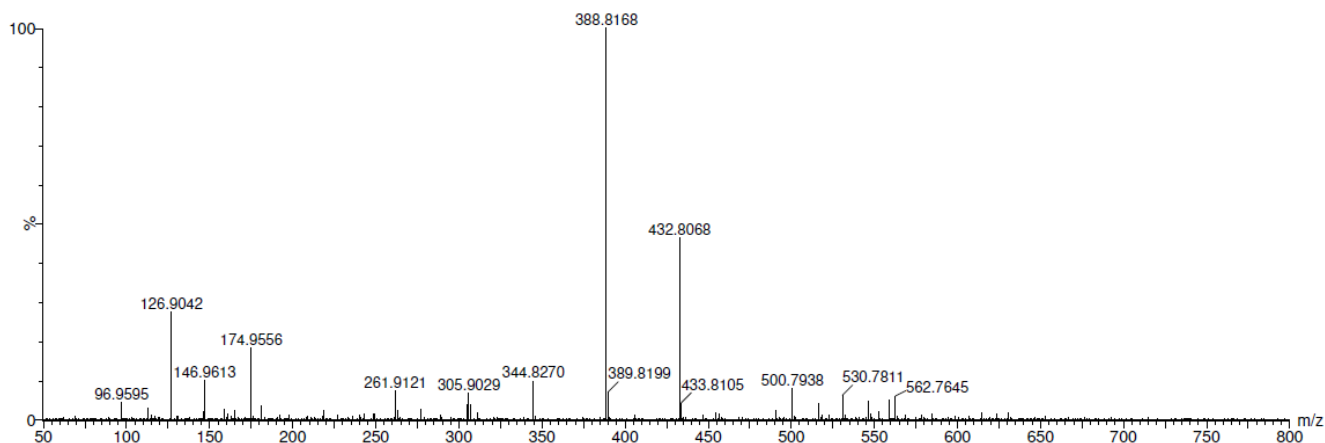


Figure S2: MS analysis of the 1.50 minutes peak, corresponding to the di-iodinated product (m/z 432.81). m/z 388.82 is the resulting product of the loss of a -COO^- group.

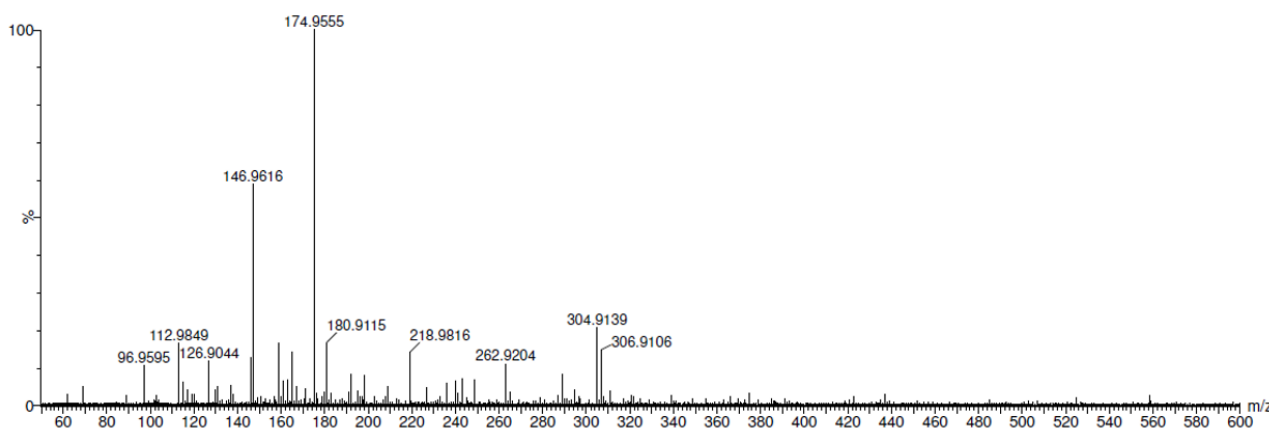


Figure S3: MS analysis of the 4.69 minutes peak, corresponding to the mono-iodinated product (m/z 306.91). The ion with m/z 174.96 is referred to the analytical background (it is also present in the blank).

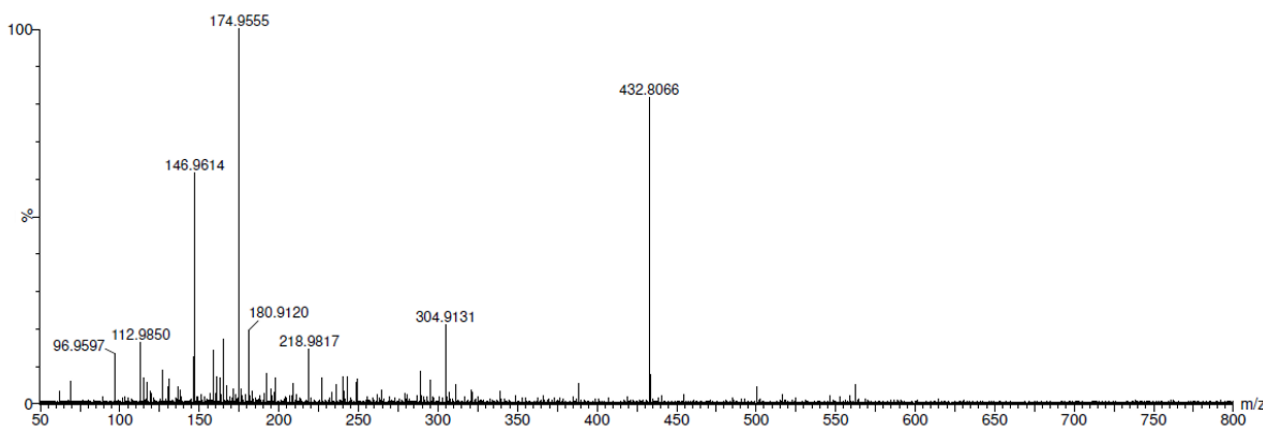


Figure S4: MS analysis of the 5.41 minutes peak, corresponding to the di-iodinated product (m/z 432.81). The ion with m/z 174.96 is referred to the analytical background (it is also present in the blank).

S5: 5-sulfosalicylic acid iodination mixture MS analyses

MS analyses of peaks at 1.06 (5-sulfosalicylic acid), 3.02 (mono-iodinated product) and 5.97 (decarboxylated di-iodinated product) minutes are reported in **Figure S5**, **Figure S6** and **Figure S7**.

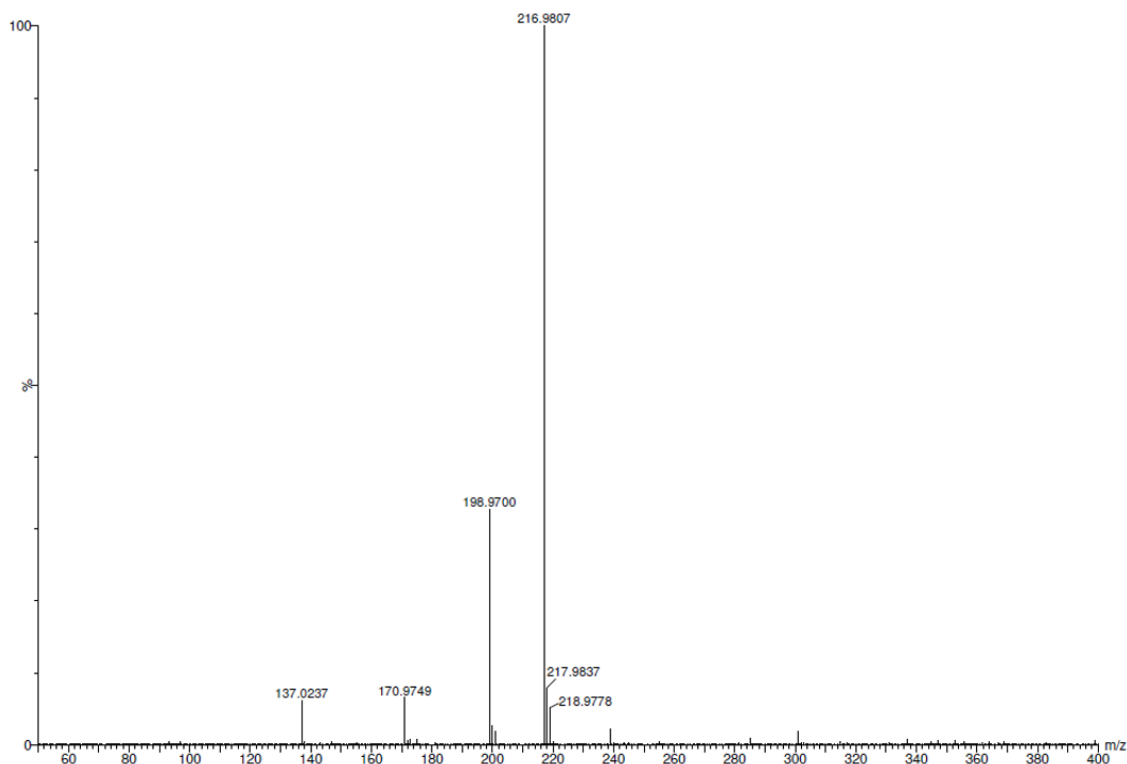


Figure S5: MS analysis of the 1.06 minutes peak, corresponding to the 5-sulfosalicylic acid (m/z 216.98).

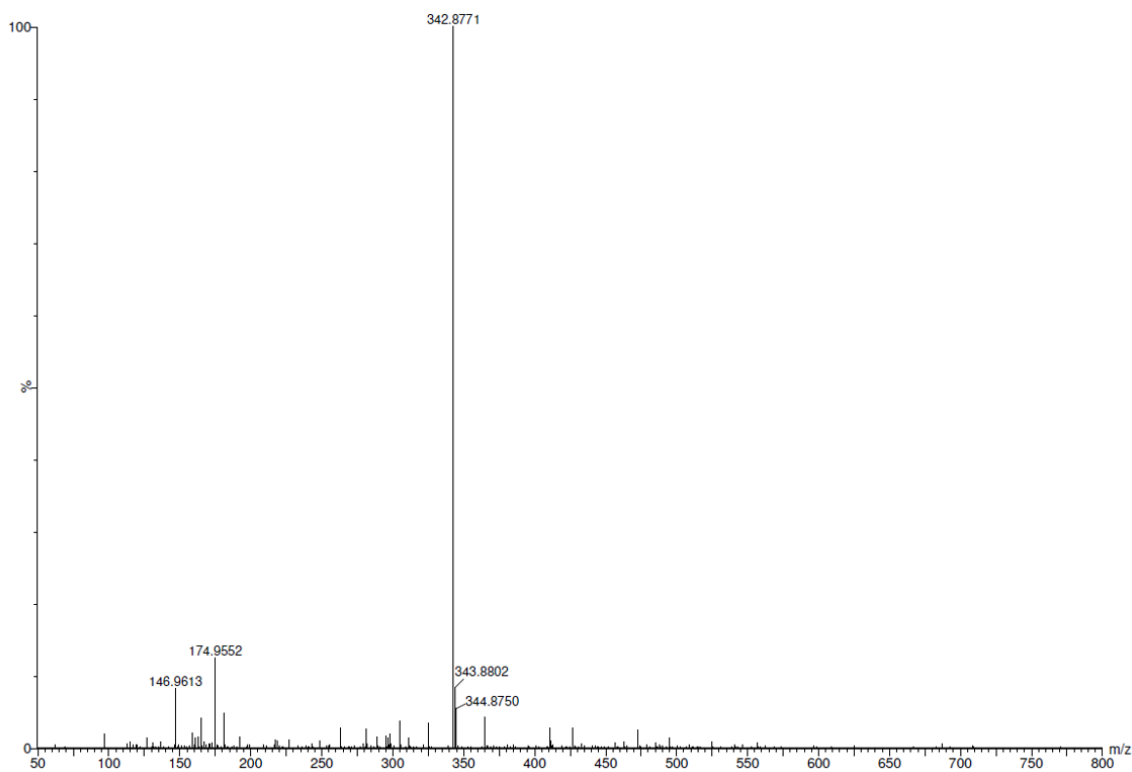


Figure S6: MS analysis of the 3.02 minutes peak, corresponding to the mono-iodinated product (m/z 342.88).

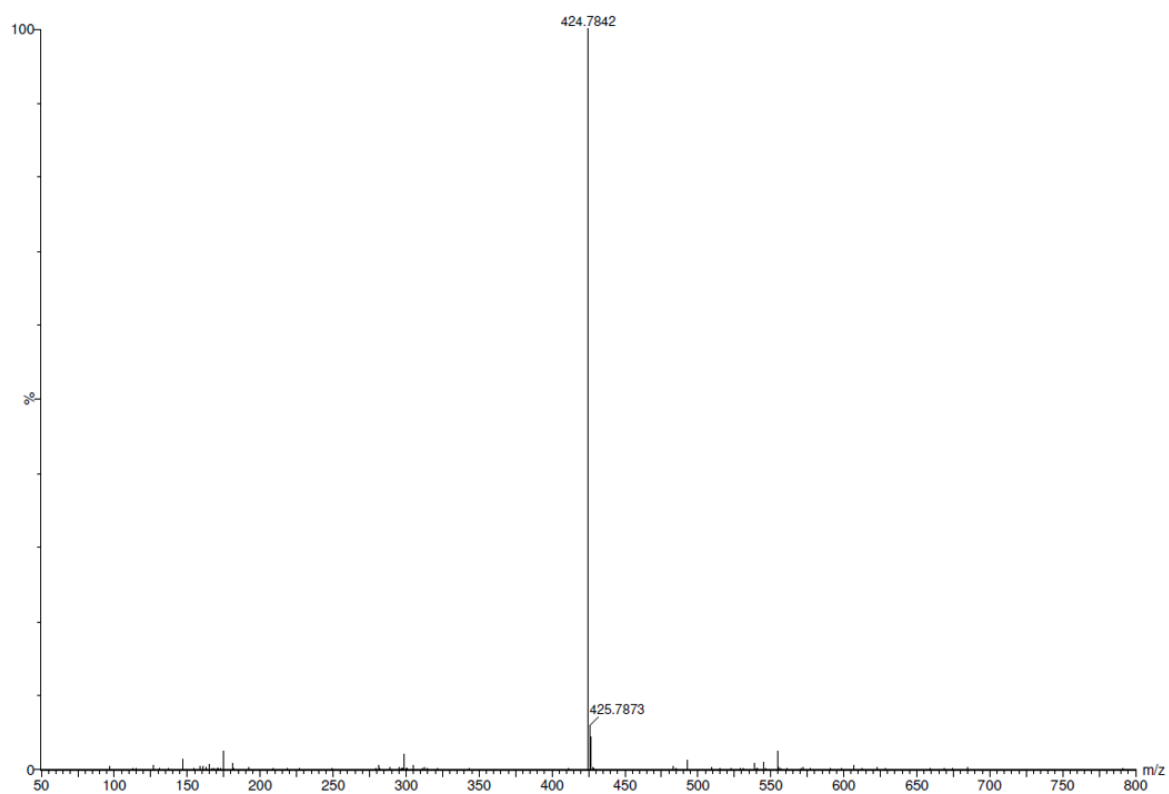


Figure S7: MS analysis of the 5.97 minutes peak, corresponding to the decarboxylated di-iodinated product (m/z 424.78).

S6: NMR spectra of 3,5-diiodo-4-hydroxybenzenesulfonic acid

5-sulfosalicylic acid iodination product 3,5-diiodo-4-hydroxybenzenesulfonic acid ^1H , APT, HSQC and HMBC NMR spectra are reported in **Figure S8**, **Figure S9**, **Figure S10** and **Figure S11** respectively.

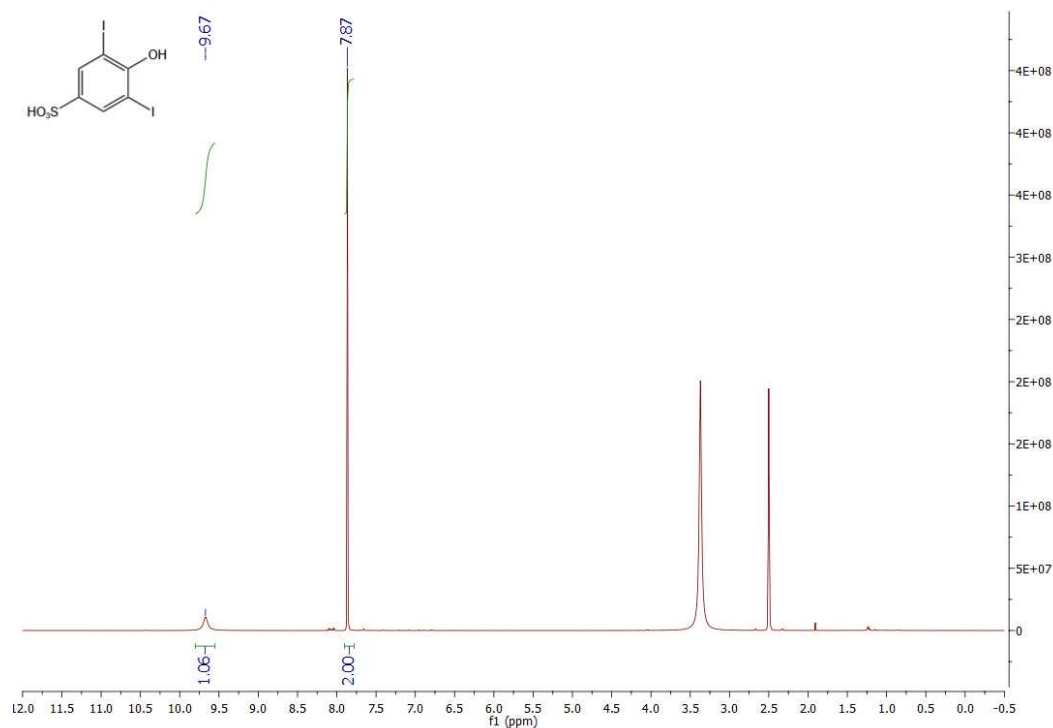


Figure S8: ^1H -NMR spectrum of 3,5-diiodo-4-hydroxybenzenesulfonic acid (decarboxylated di-iodinated product, peak at 5.97 min in UPLC-PDA-HR-MS analysis). ^1H -NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.67 (s, 1H, OH), 7.87 (s, 2H, H-2 and H-6).

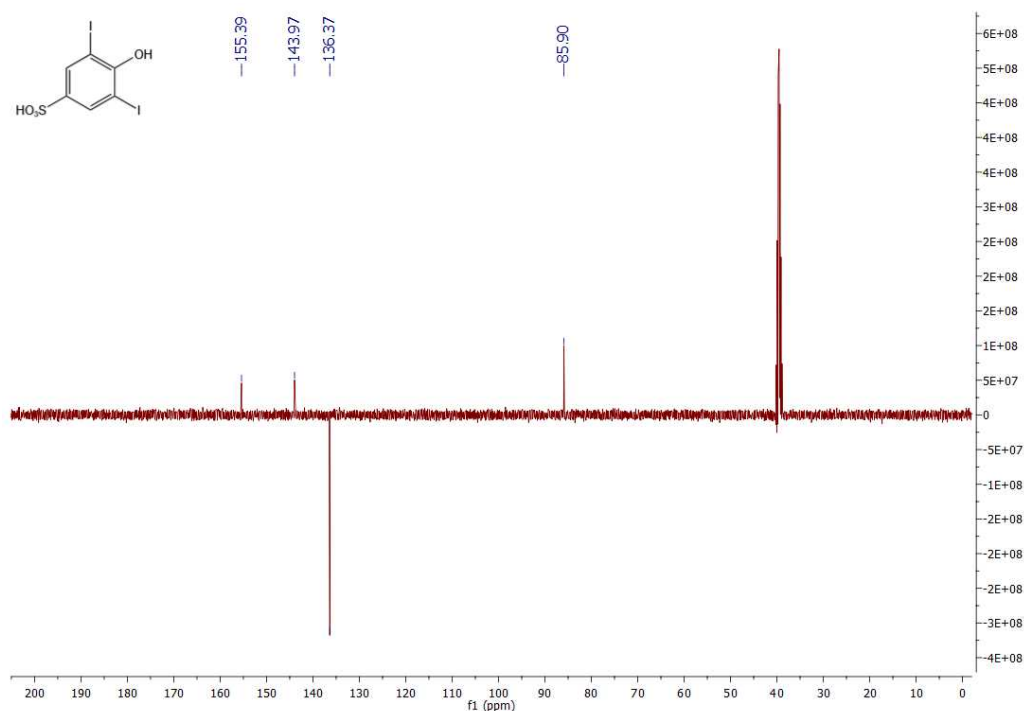


Figure S9: APT (Attached Proton Test) NMR spectrum of 3,5-diiodo-4-hydroxybenzenesulfonic acid (decarboxylated di-iodinated product, peak at 5.97 min in UPLC-PDA-HR-MS analysis). Positive peaks are secondary and quaternary carbons, negative peaks are primary and tertiary carbons. ^{13}C -NMR (101 MHz, $\text{DMSO}-d_6$) δ 155.39 (C-4), 143.97 (C-1), 136.37 (C-2, C-6) and 85.90 (C-3, C-5).

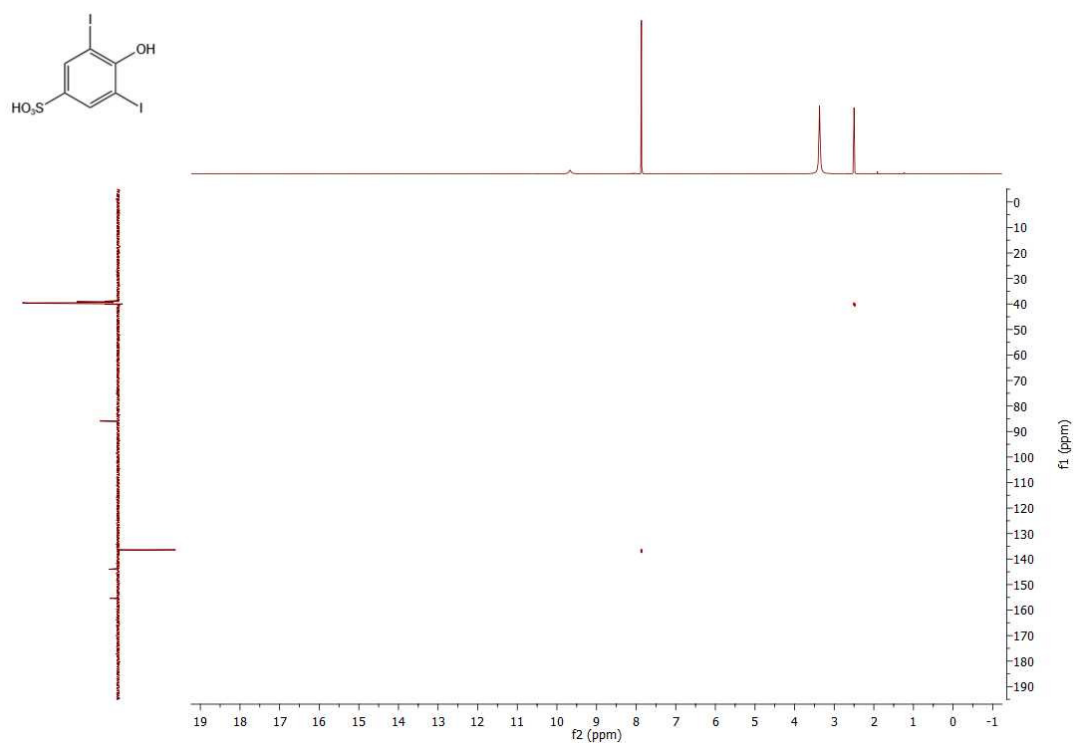


Figure S10: HSQC NMR (Heteronuclear Single Quantum Correlation) spectrum of 3,5-diiodo-4-hydroxybenzenesulfonic acid (decarboxylated di-iodinated product, peak at 5.97 min in UPLC-PDA-HR-MS analysis).

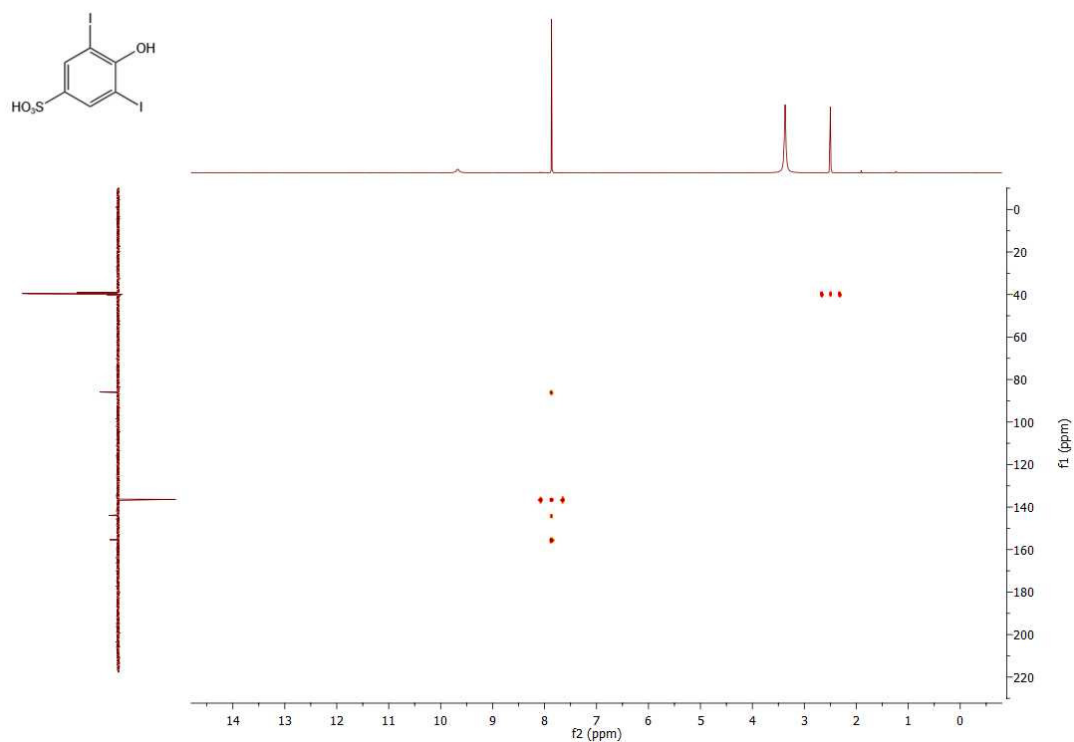


Figure S11: HMBC NMR (Heteronuclear Multiple Bond Correlation) spectrum of 3,5-diiodo-4-hydroxybenzenesulfonic acid (decarboxylated di-iodinated product, peak at 5.97 min in UPLC-PDA-HR-MS analysis).

S7: Experimental set-up for electroiodination

Experimental set-up for electroiodination of 5-hydroxyisophthalic acid and 5-sulfosalicylic acid 15 mM.

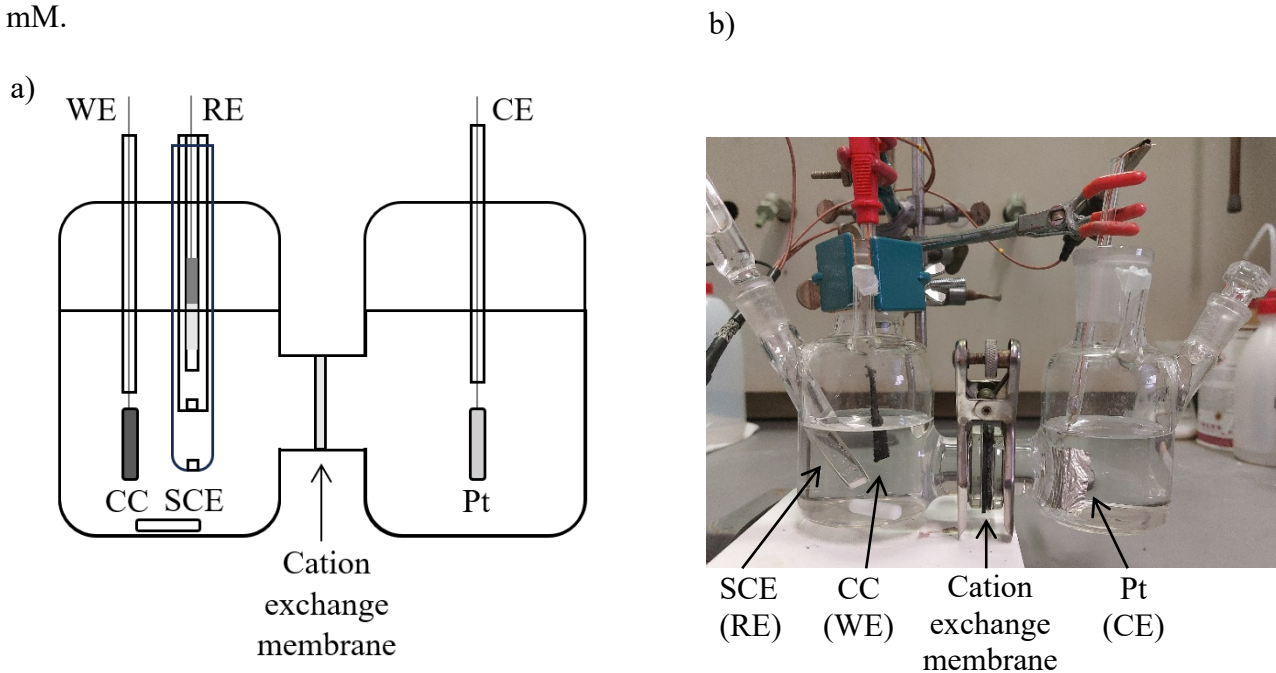


Figure S12: a) scheme and b) picture of the divided cell for electrosynthesis of 5-hydroxyisophthalic acid and 5-sulfosalicylic acid 15 mM. WE= working electrode, RE= reference electrode (equipped with a KNO_3 1 M double salt bridge), CE= counter electrode, CC= carbon cloth, SCE= saturated calomel electrode.