SUPPORTING INFORMATION

Perfluorinated Zinc Porphyrin Sensitized Photoelectrosynthetic Cells for Enhanced TEMPO-Mediated Benzyl Alcohol Oxidation

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^{1}H- and ^{19}F-NMR spectra of dyes and precursors

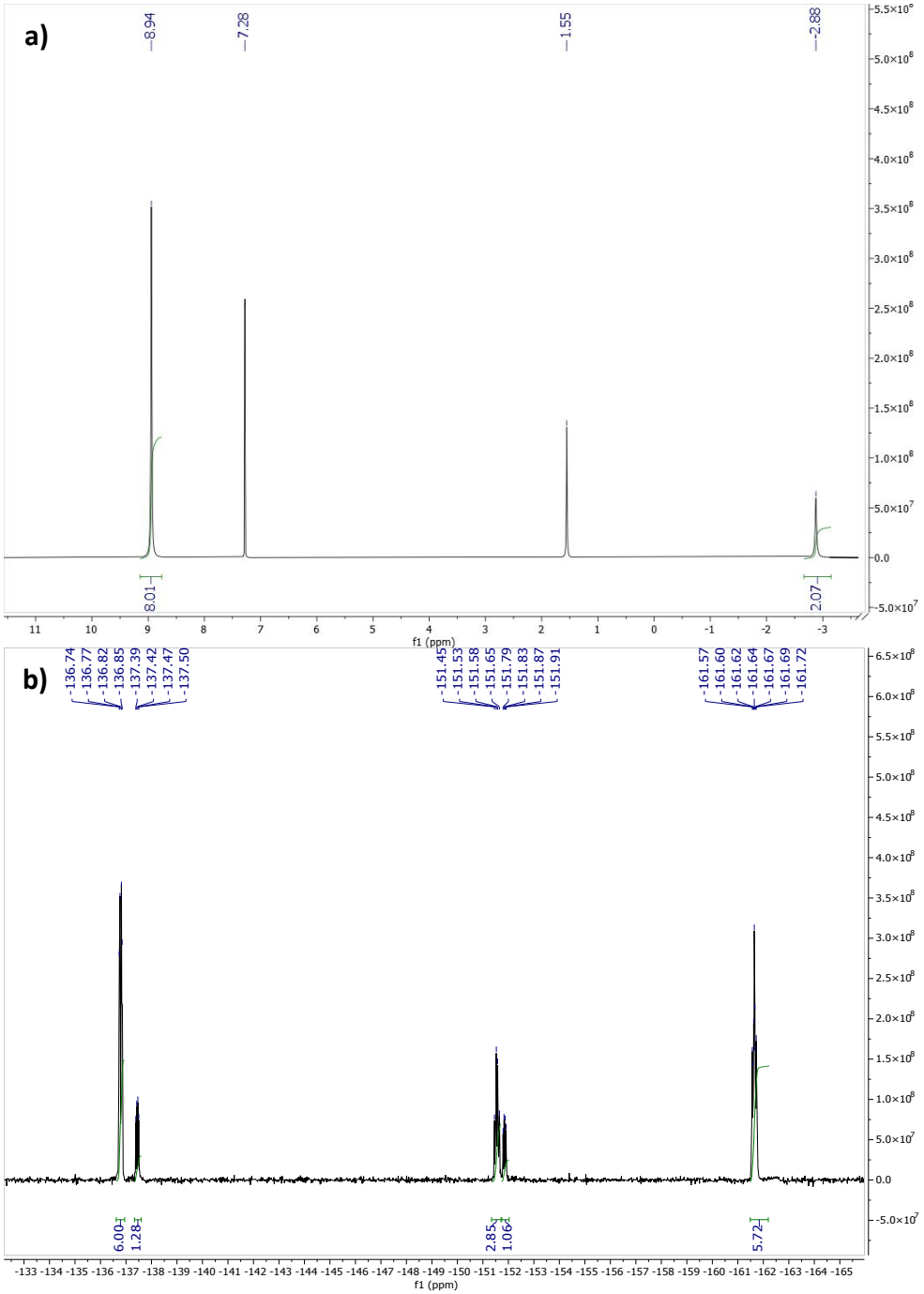


Figure S1: *^{1}H*-NMR (a) and *^{19}F*-NMR (b) spectra of TFP-N_3

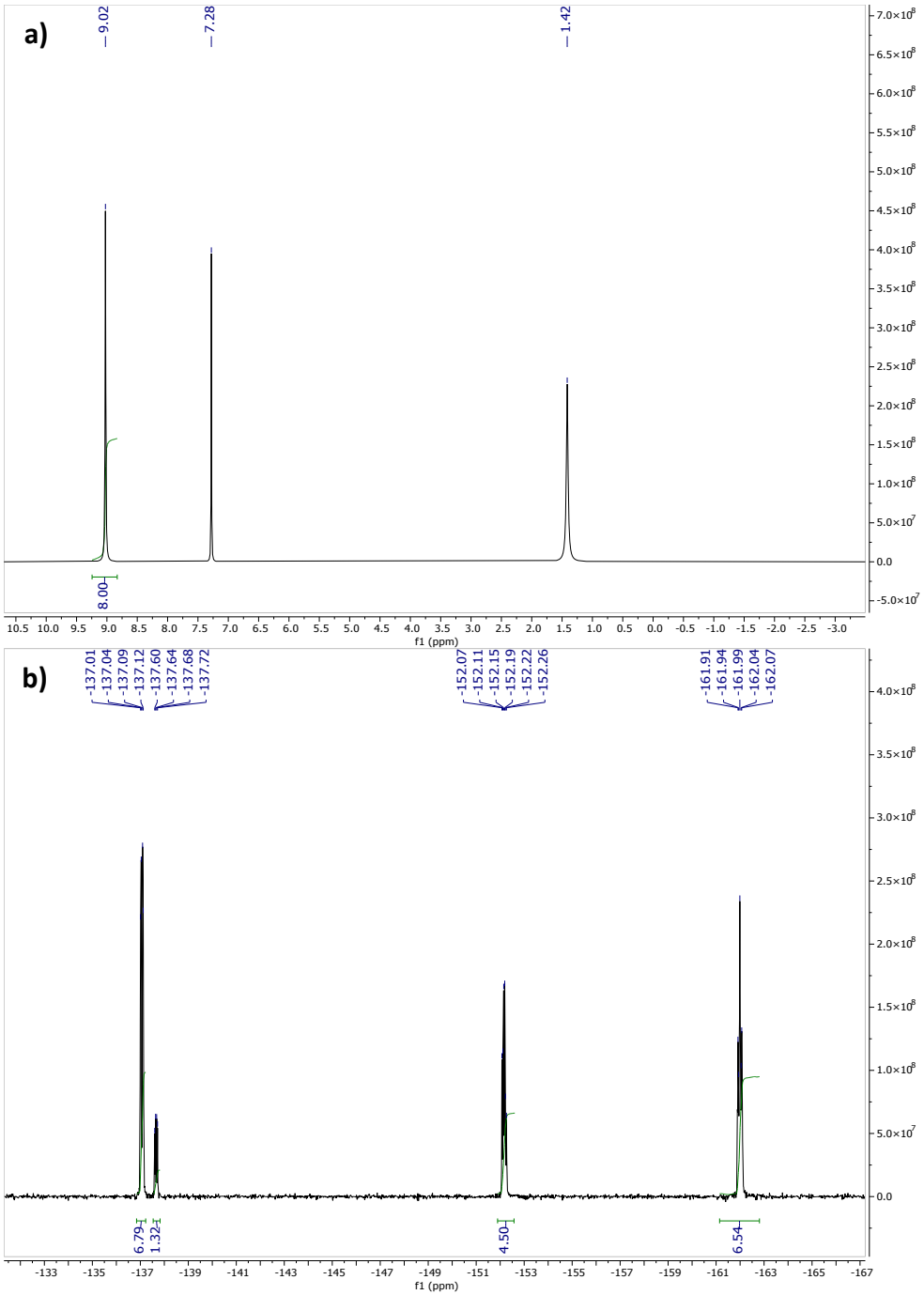


Figure S2: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of ZnTFP-N_3

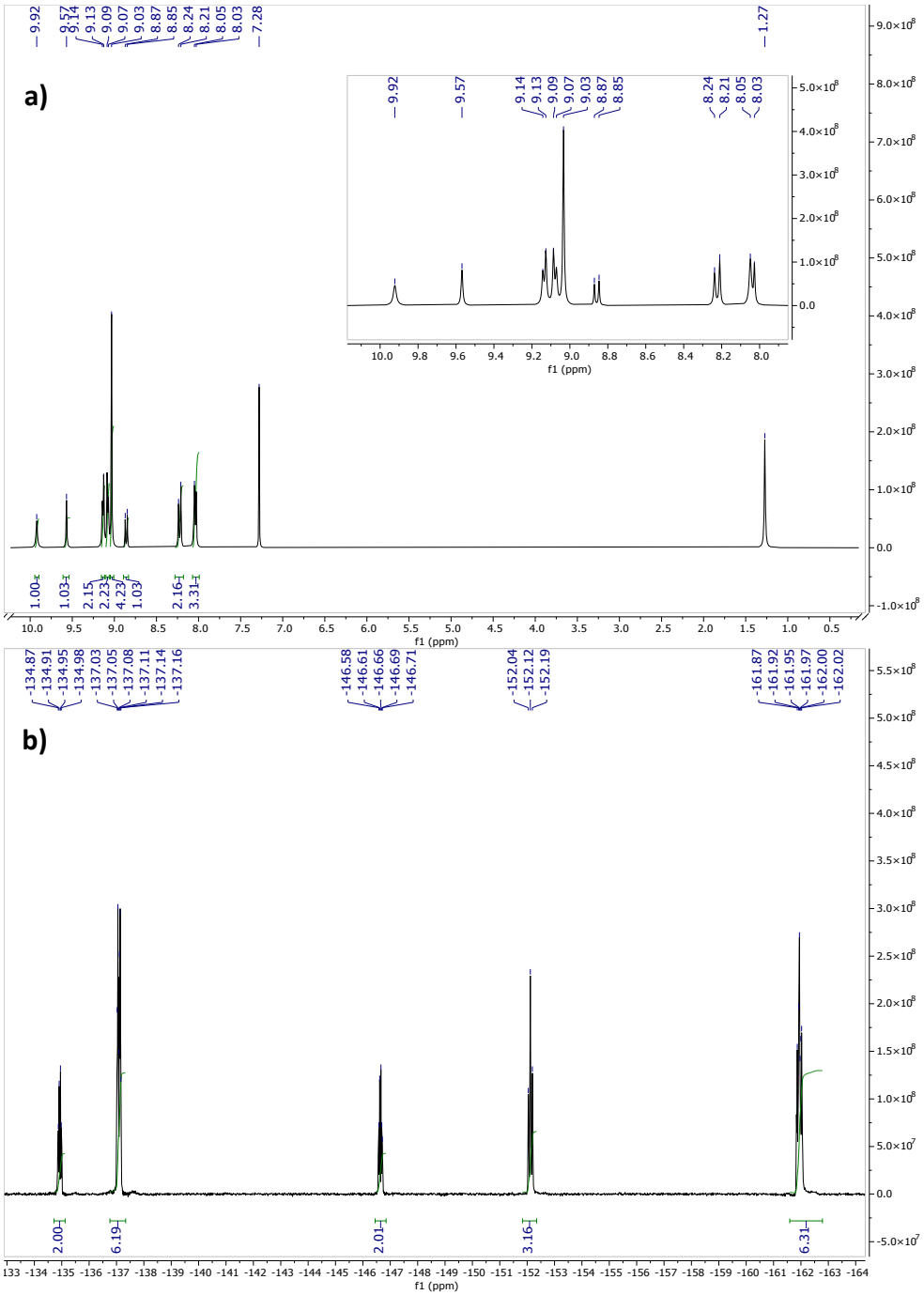


Figure S3: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of ZnTFP-*CHO*

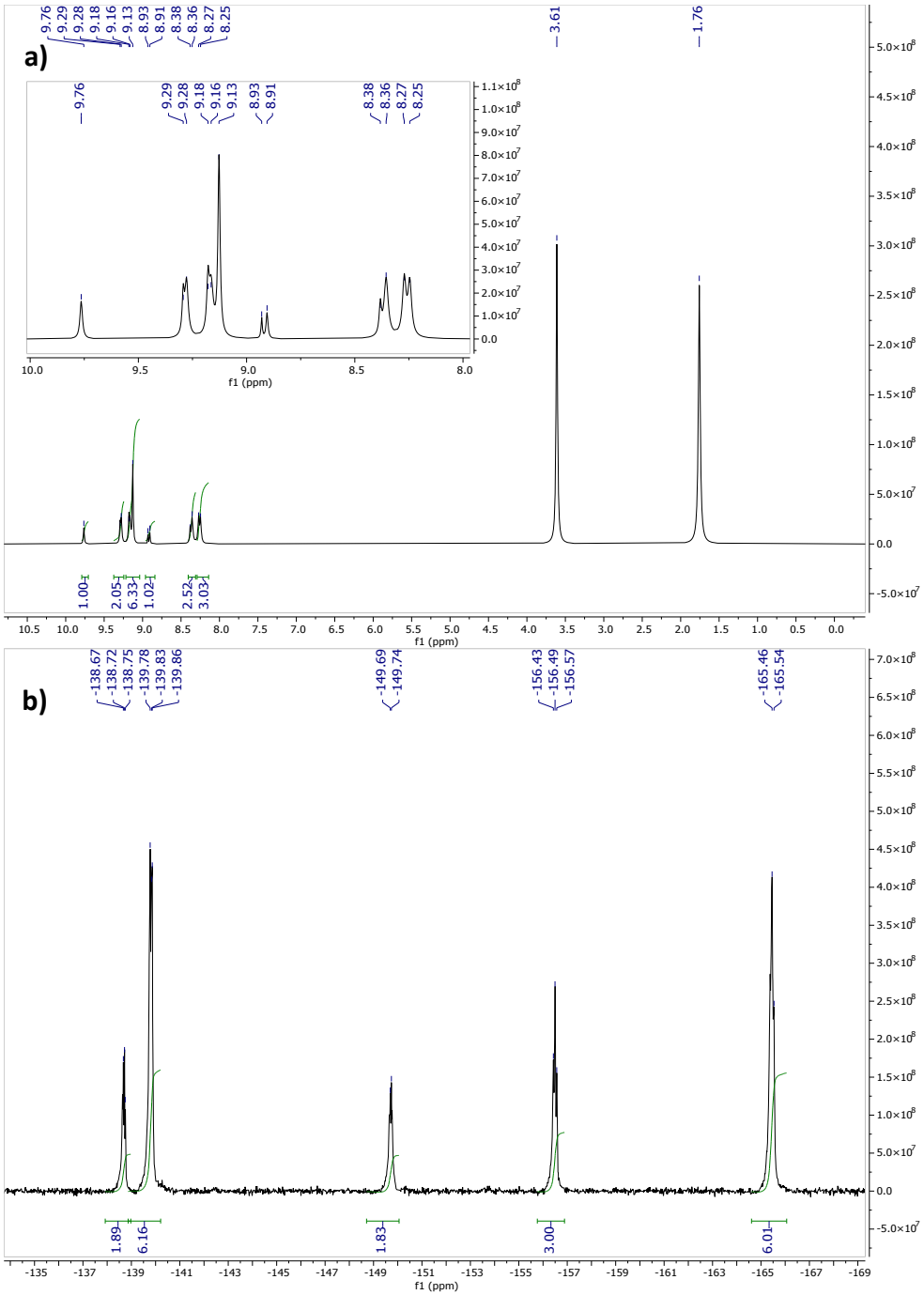


Figure S4: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of **CLICK-3**

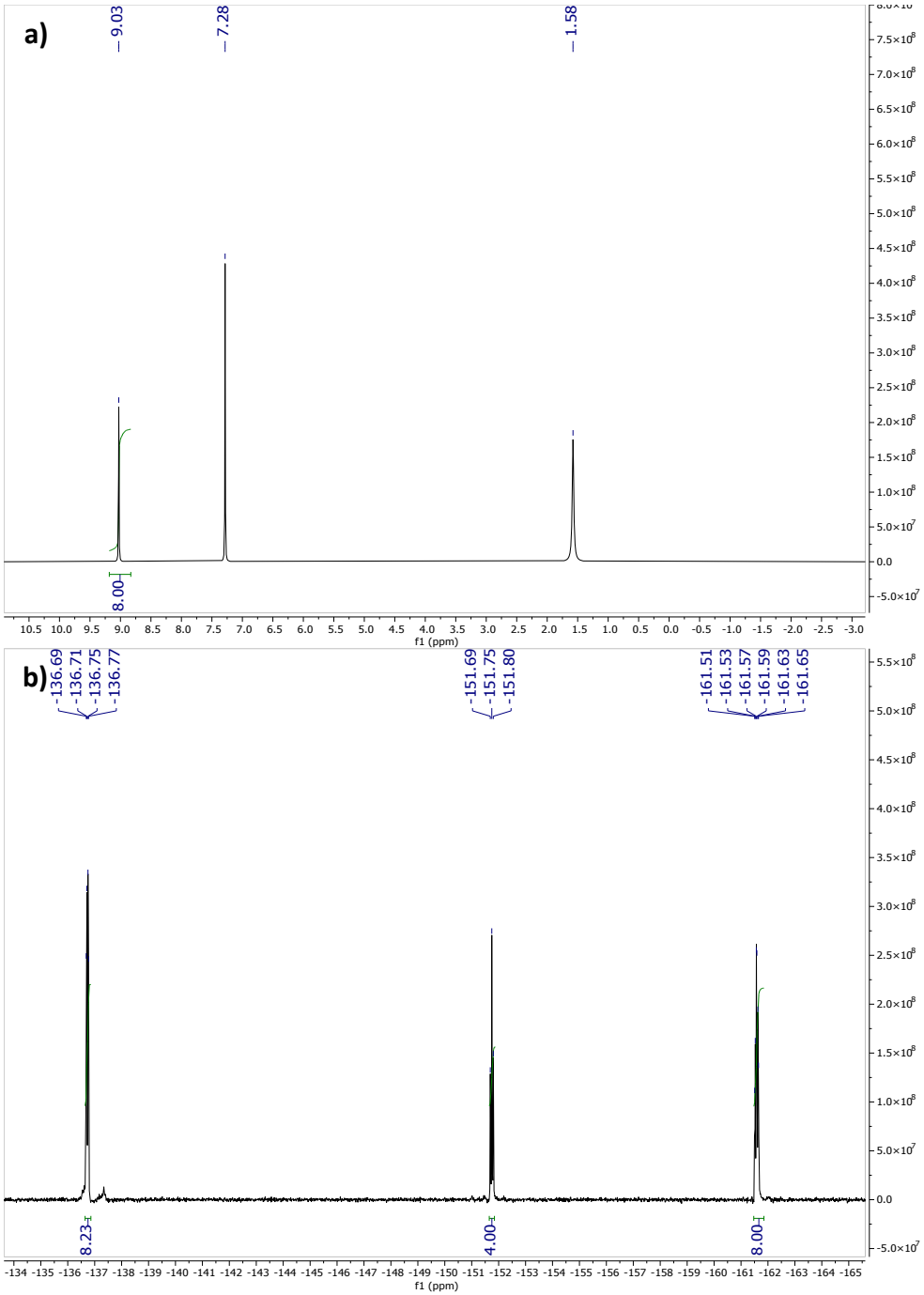


Figure S5: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of ZnTFP

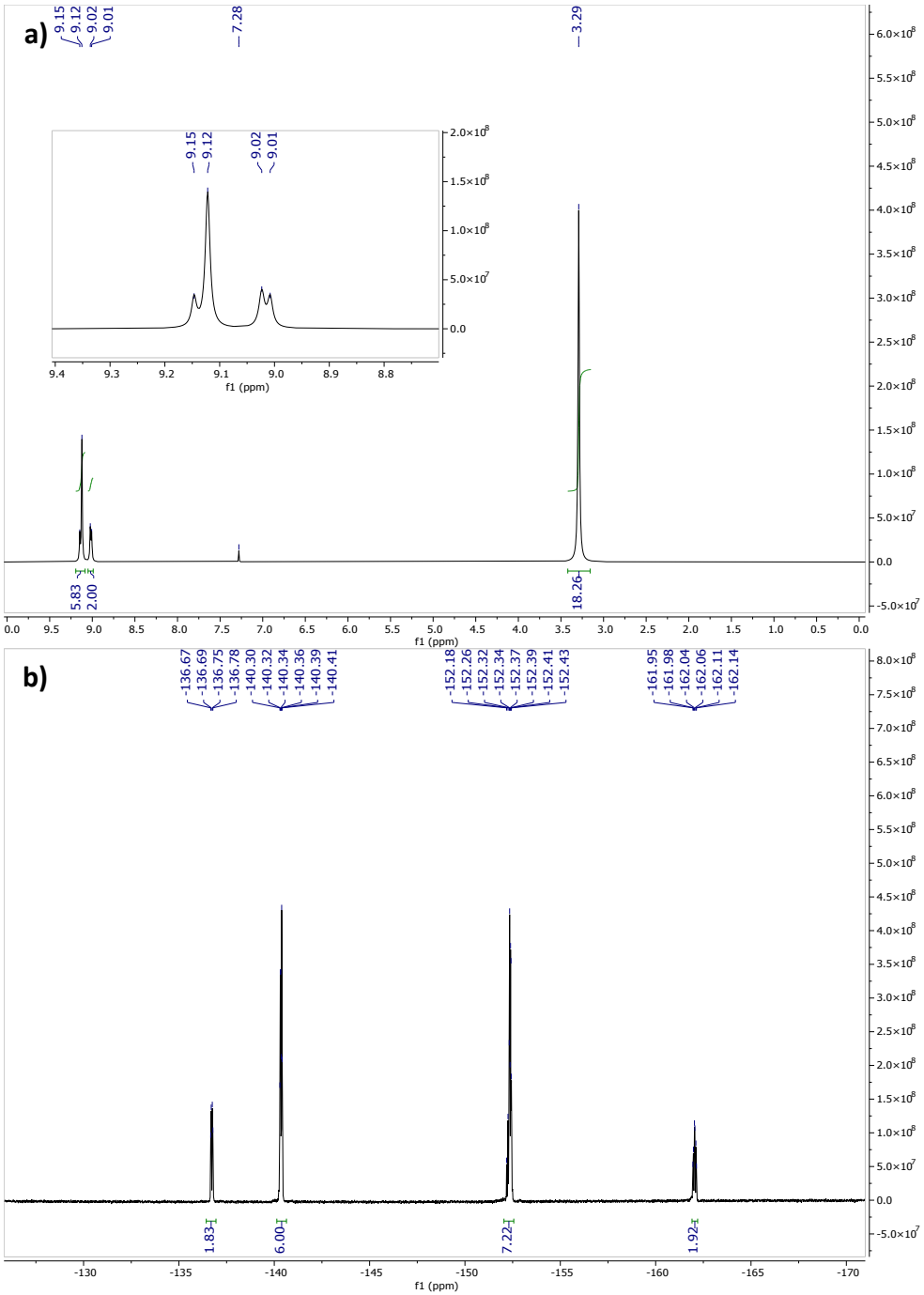


Figure S6: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn3DP

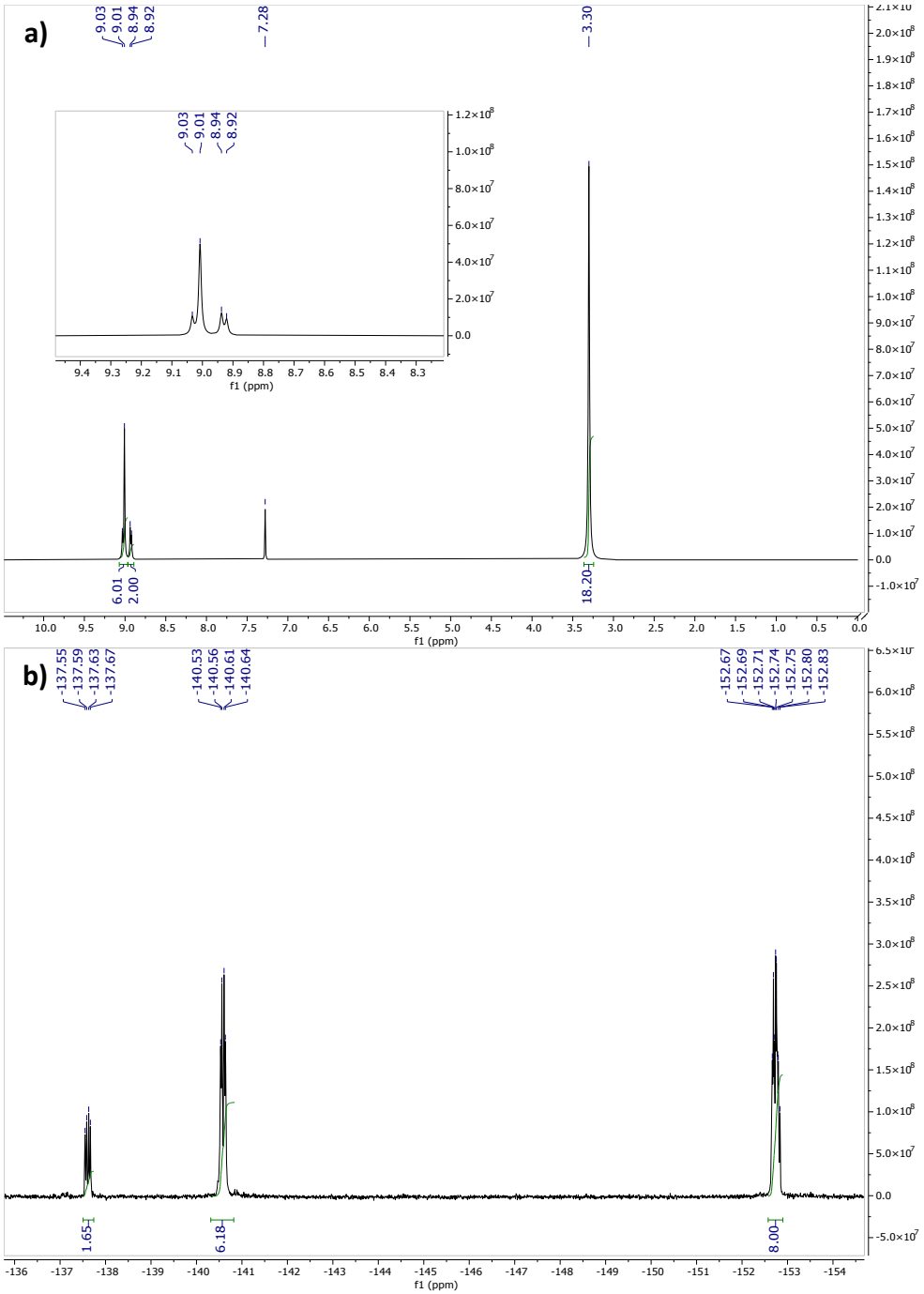


Figure S7: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn3DP-N_3

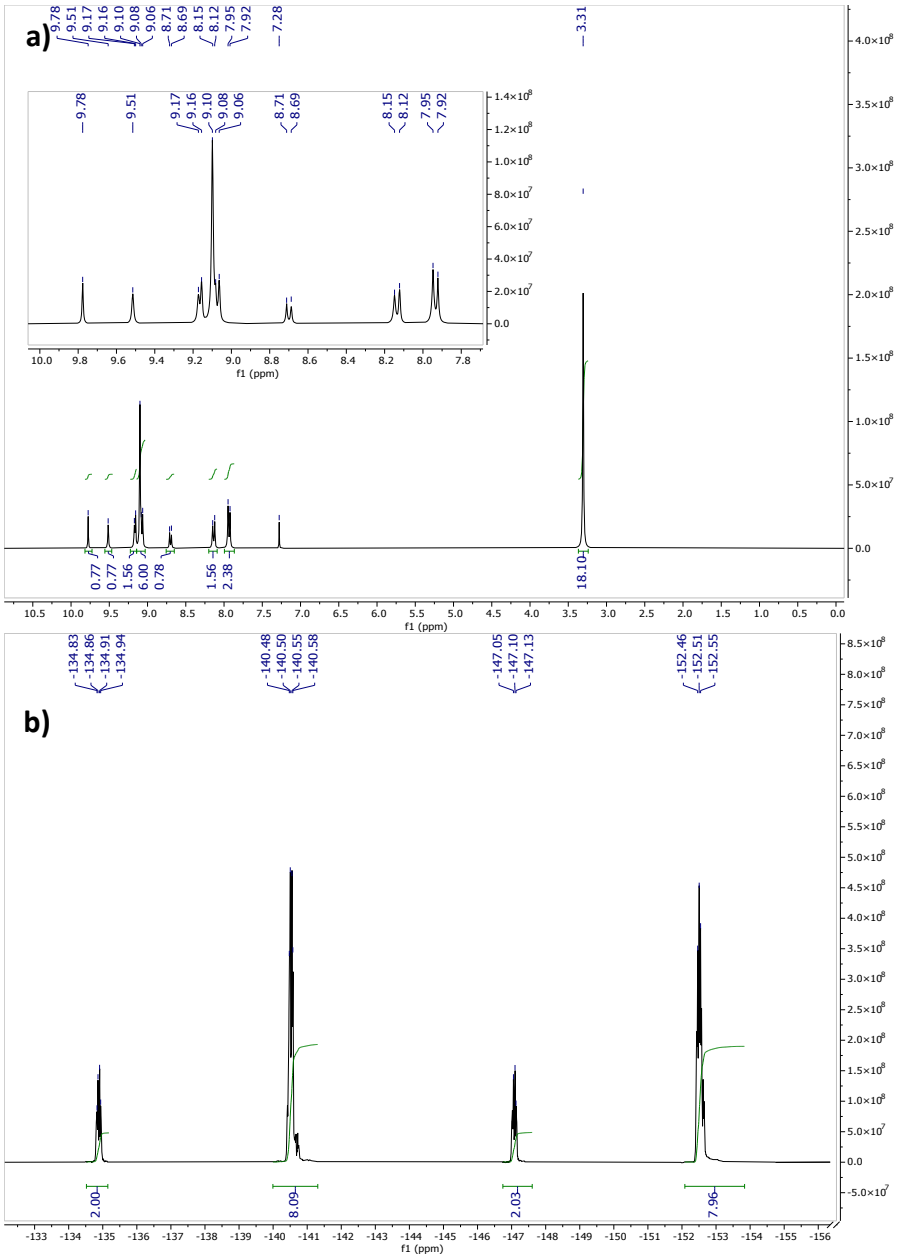


Figure S8: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn3DP-*CHO*

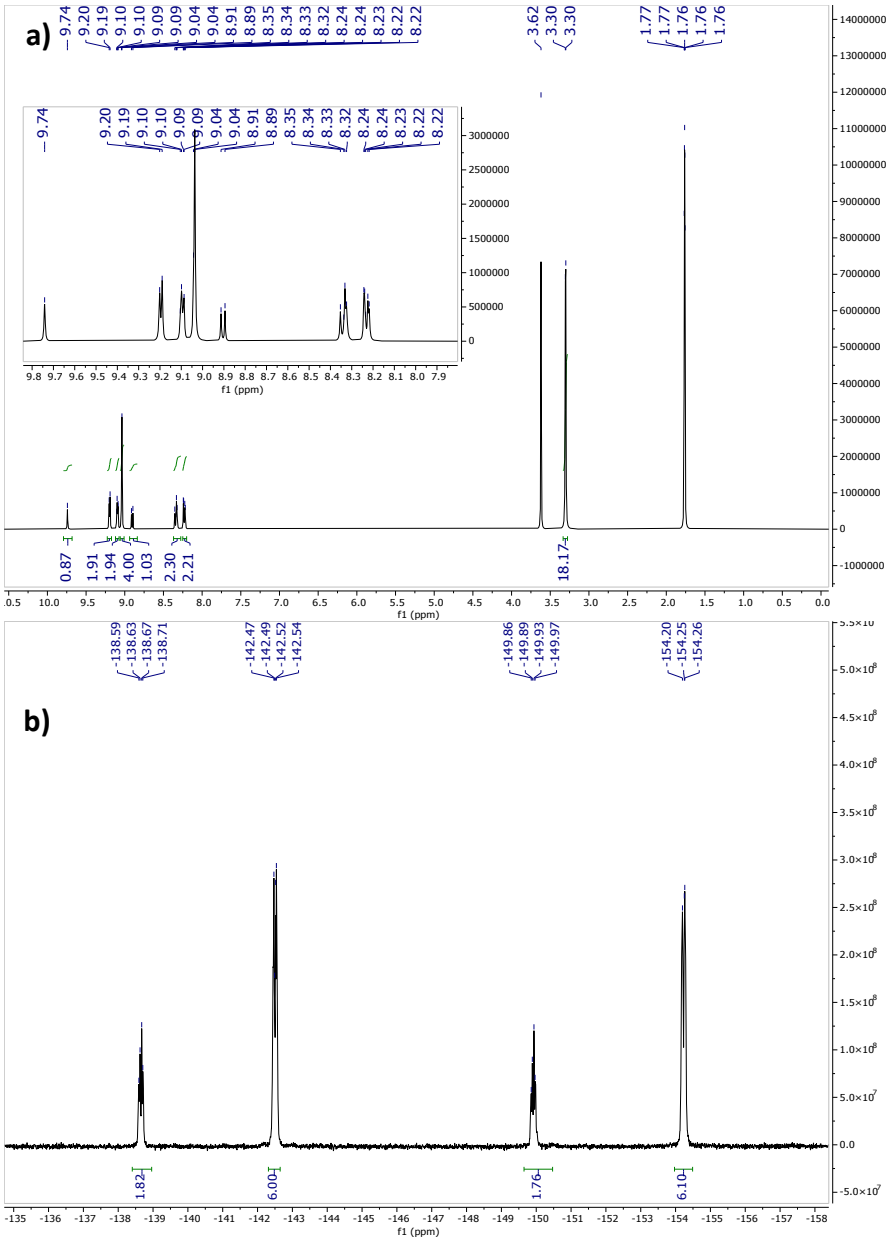


Figure S9: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of **CLICK-4**

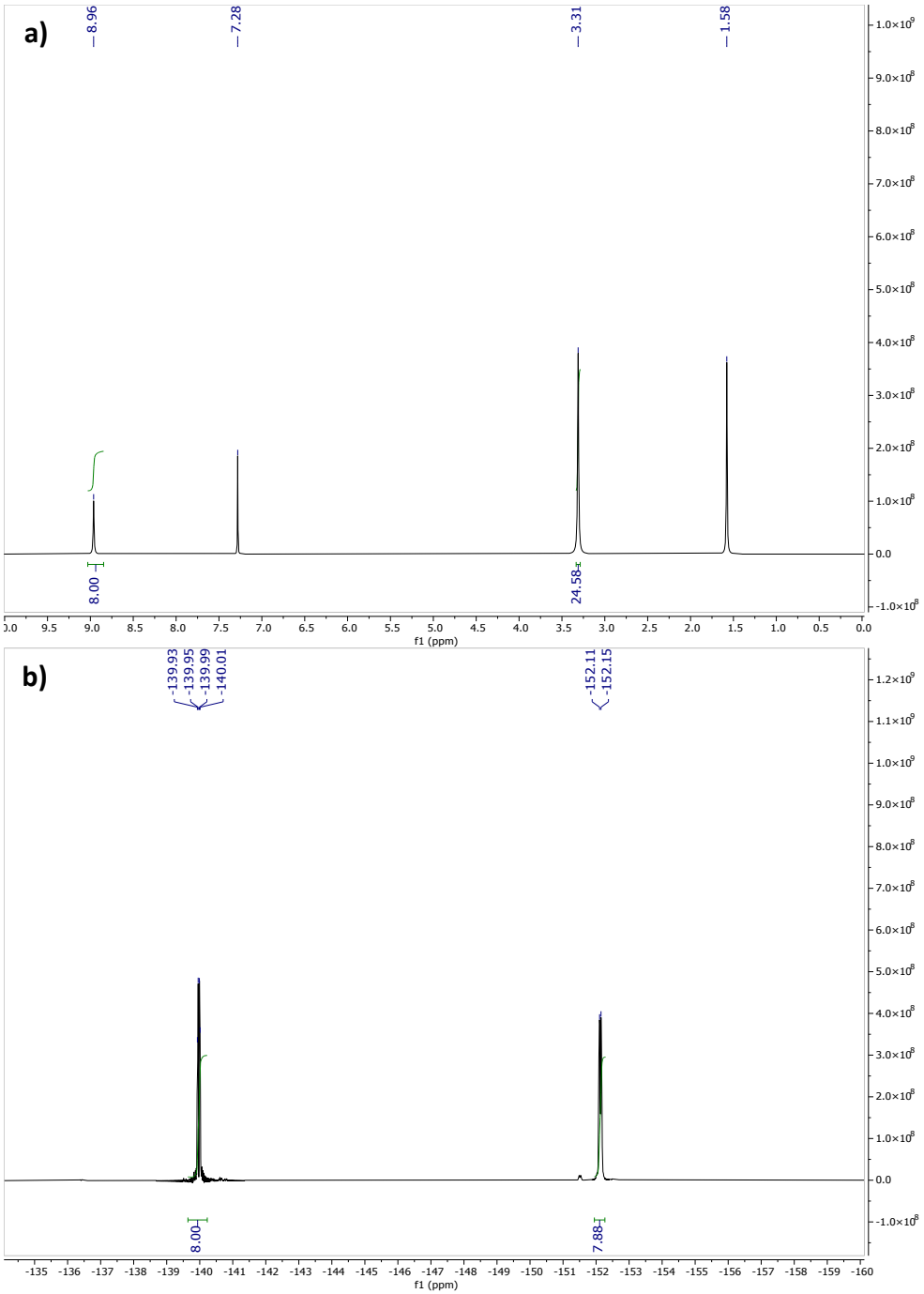


Figure S10: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of ZnA4P

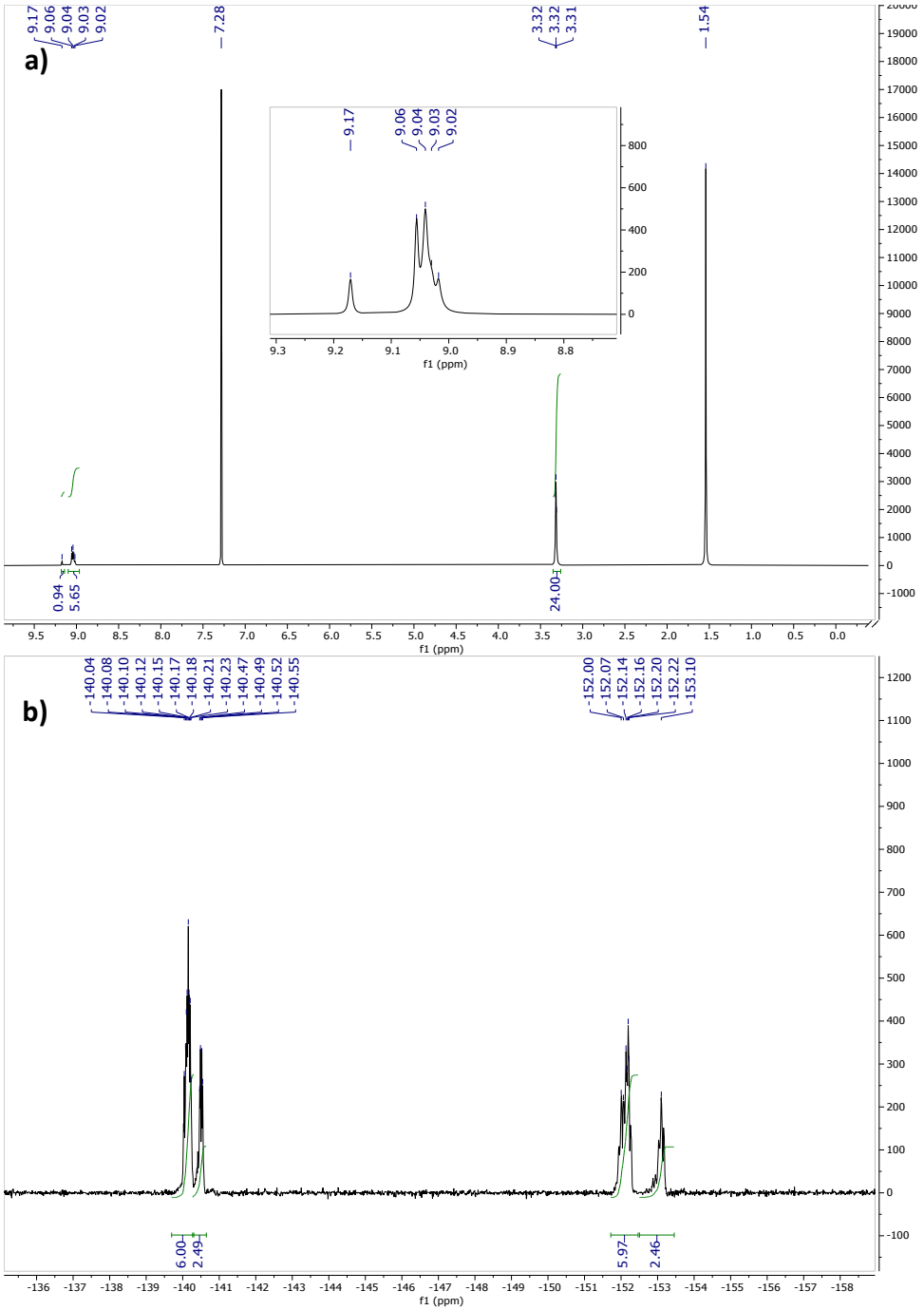


Figure S11: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn4DP-*Br*

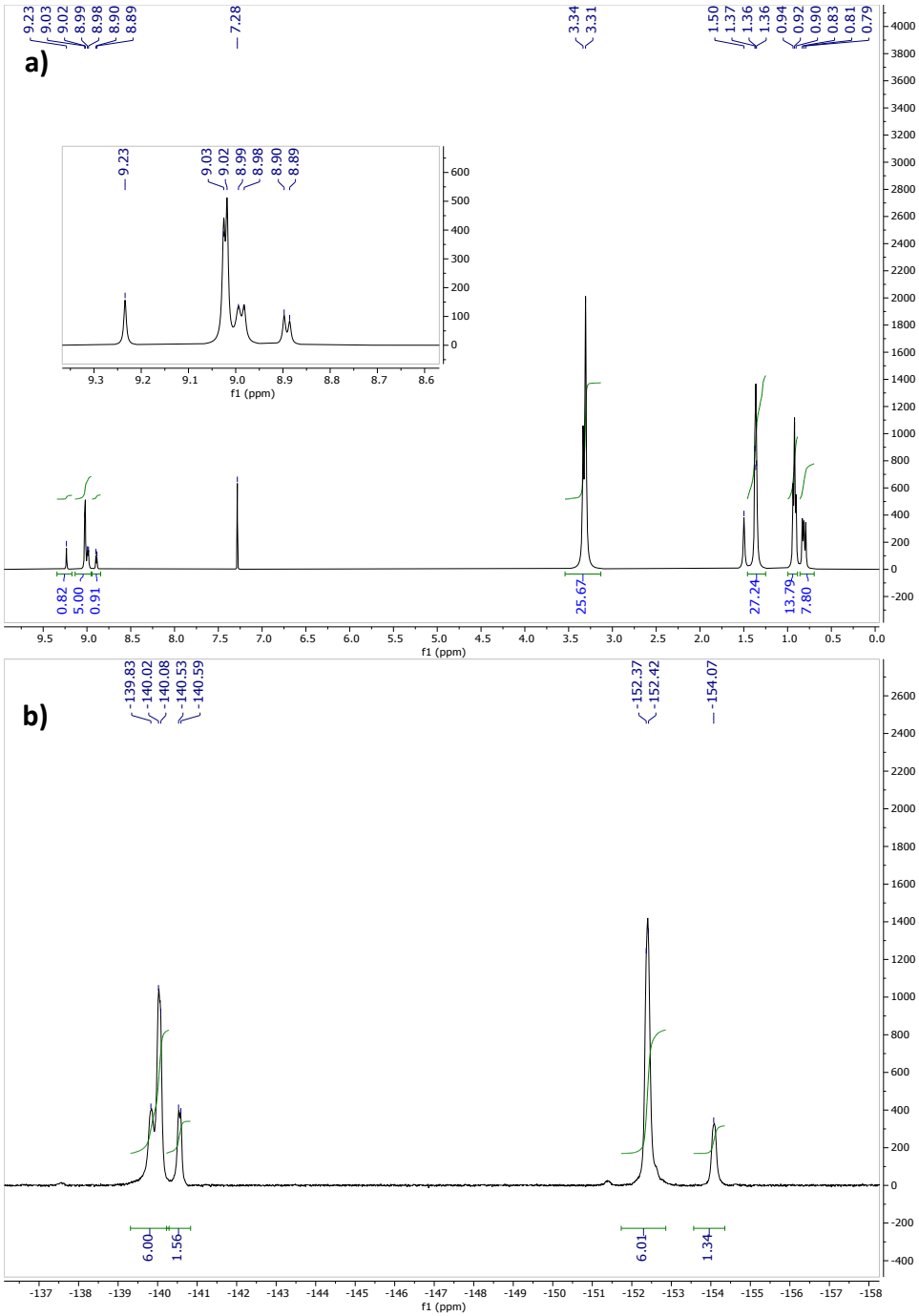


Figure S12: : *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn4DP-*Si*

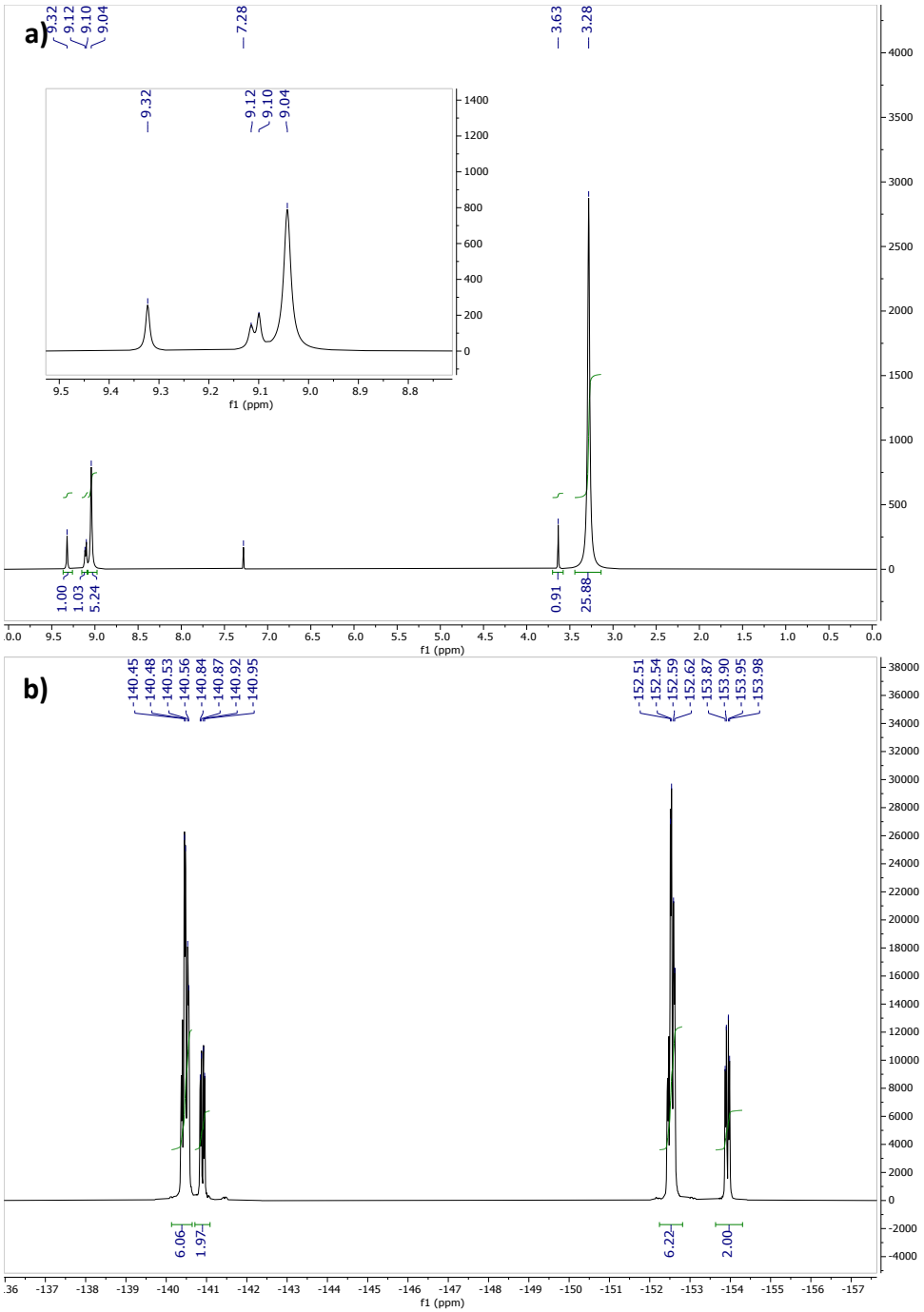


Figure S13: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn4DP-*CH*

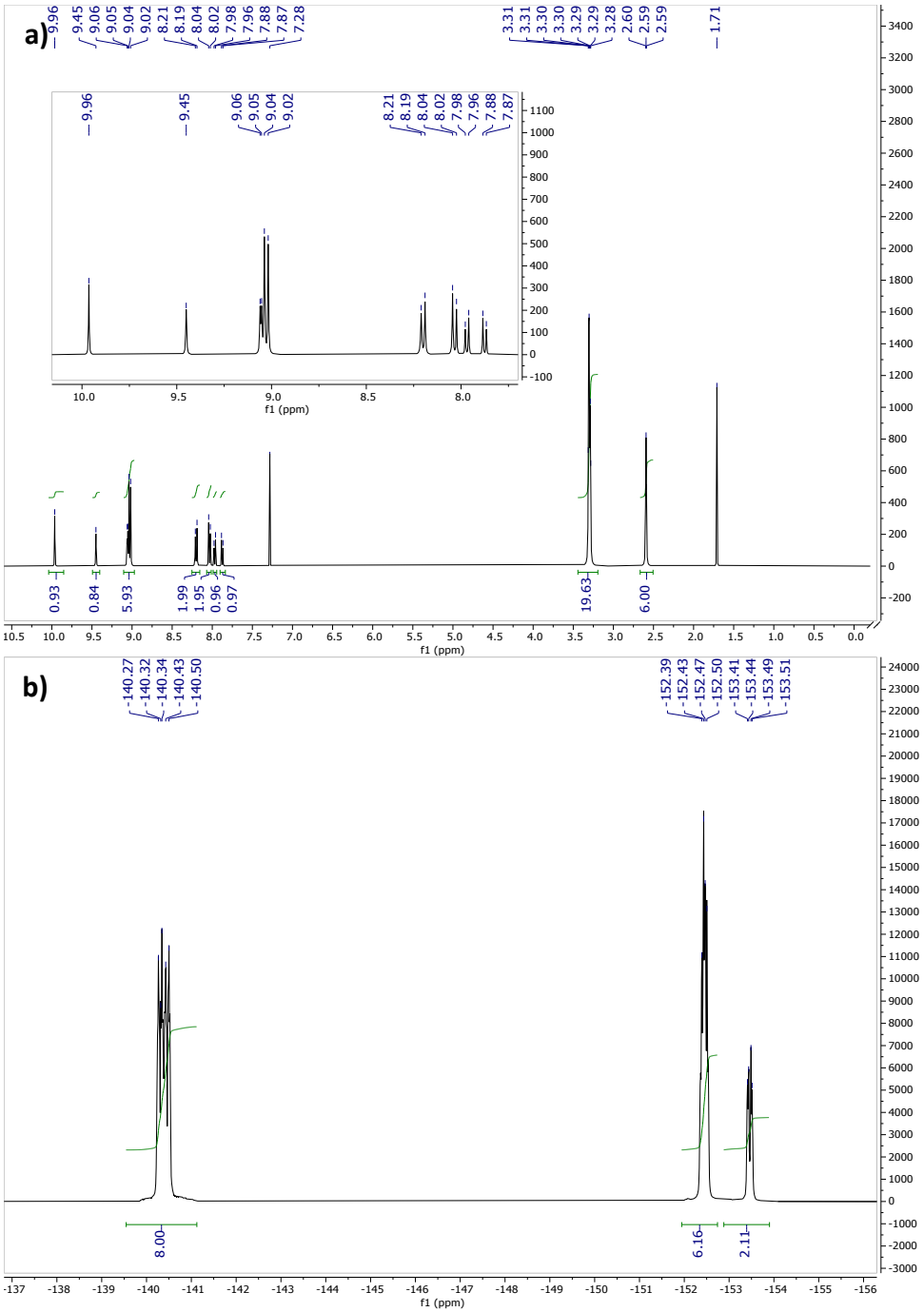


Figure S14: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of Zn4DP-*CHO*

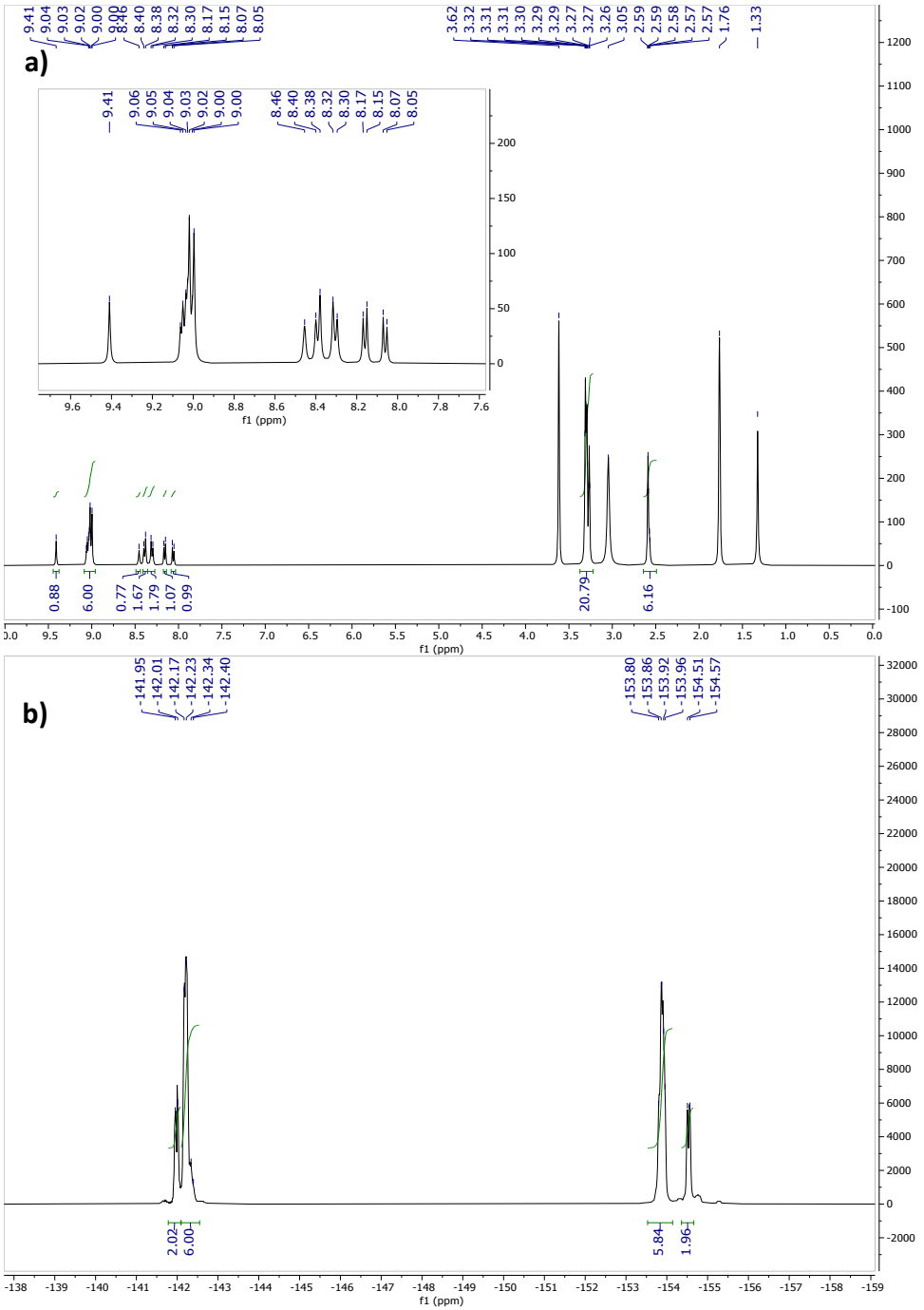
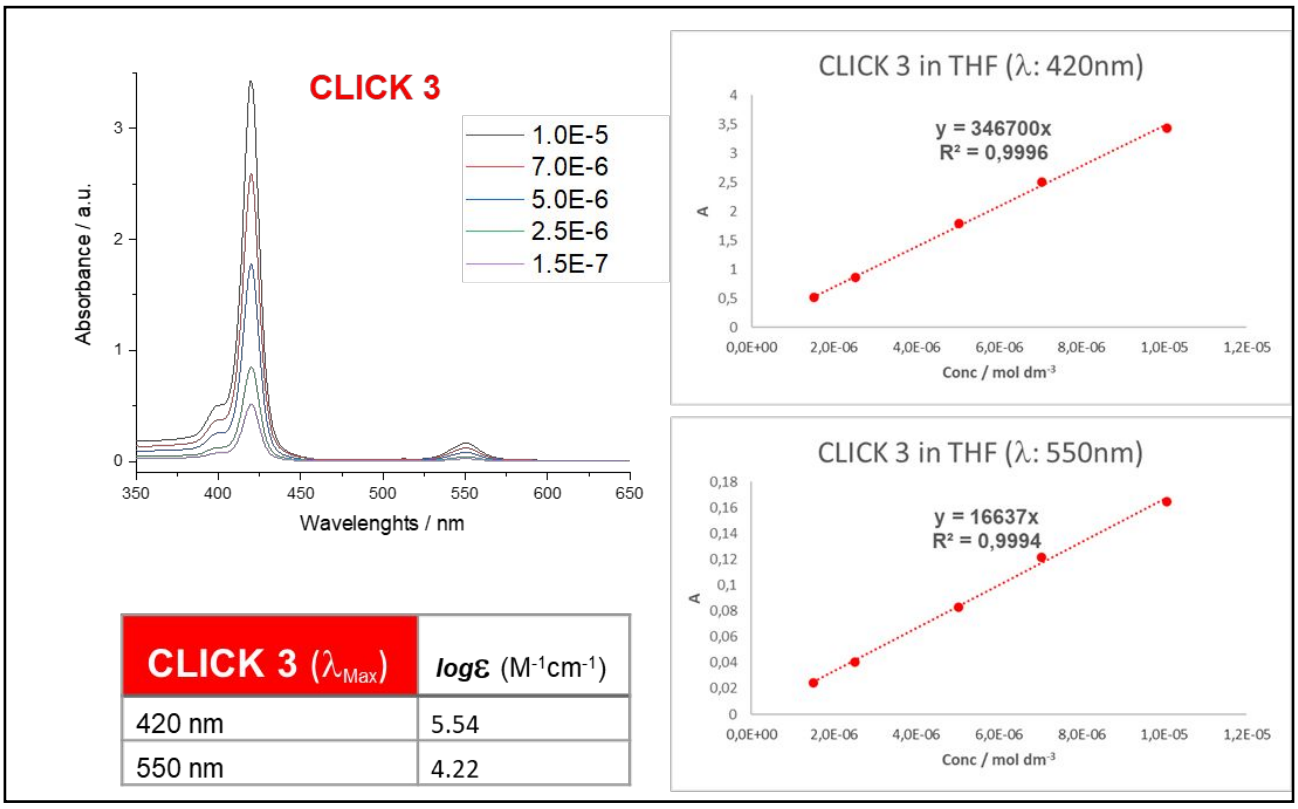


Figure S15: *[1]H*-NMR (a) and *[19]F*-NMR (b) spectra of **BETA-4**

Absorption and emission properties of the dyes in solution



CLICK 3 (λ_{Max})	*logε* ($M^{-1}cm^{-1}$)
420 nm	5.54
550 nm	4.22

Figure S16: Uv-Vis spectra of CLICK-3 diluted solutions and ε-coefficients of the main absorption bands.

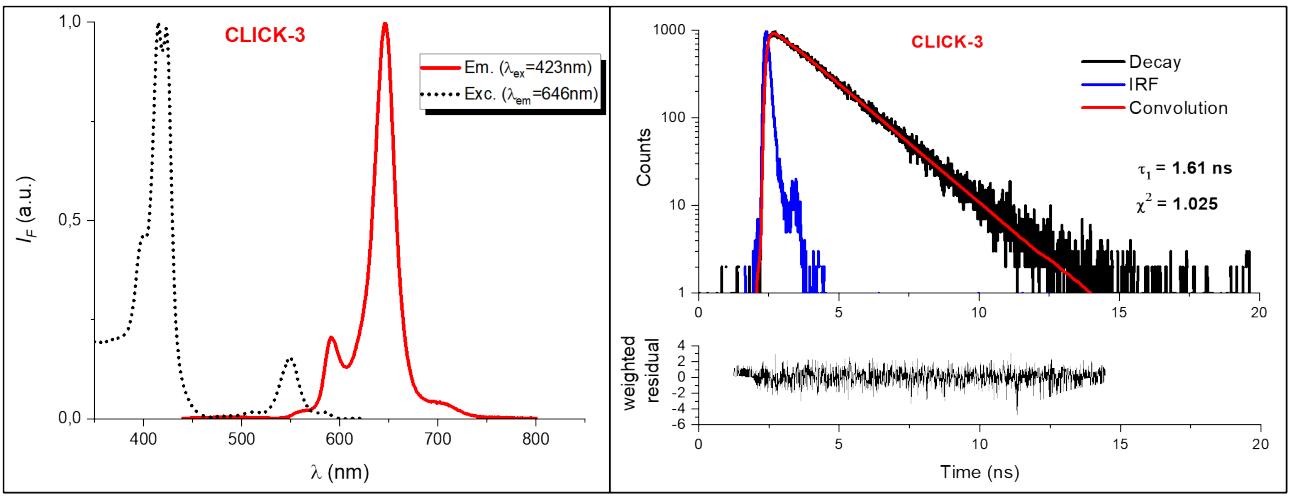
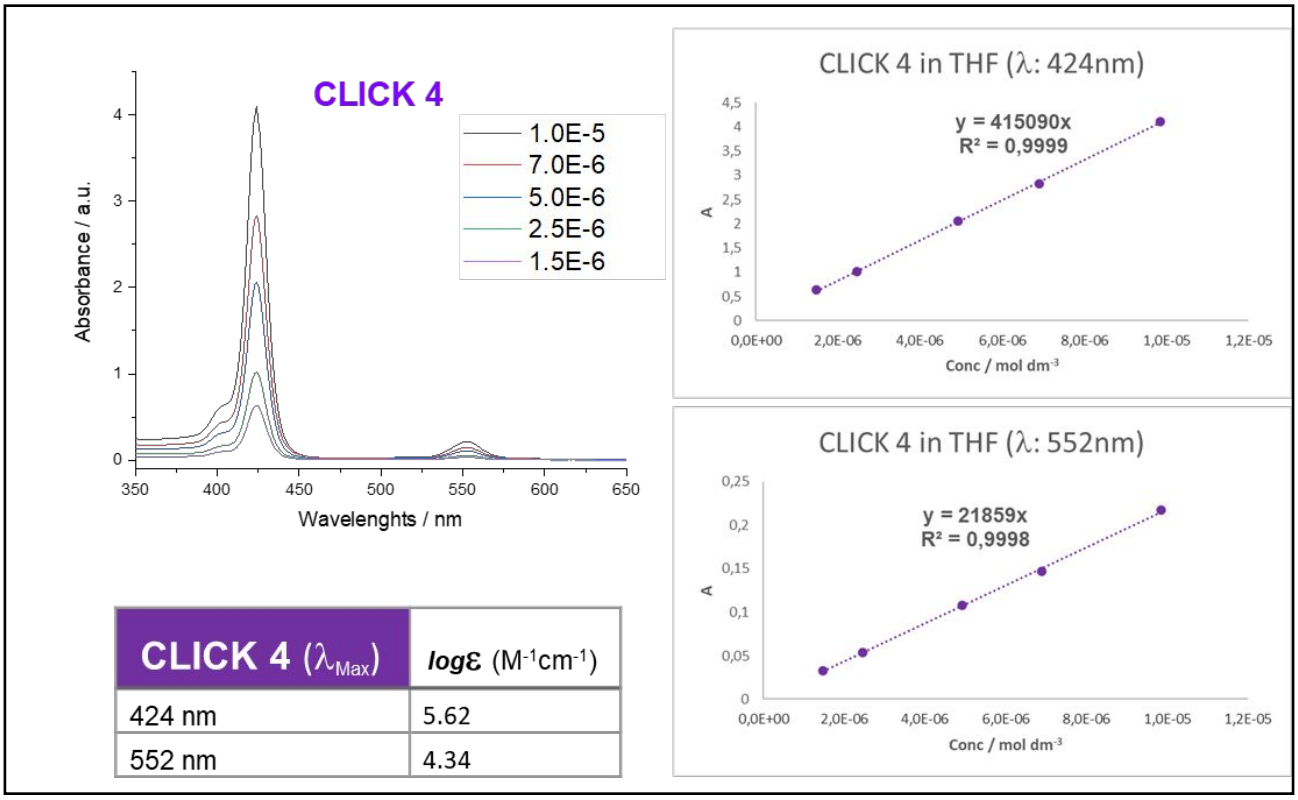


Figure S17: Excitation and emission spectra of CLICK-3 diluted solutions and the Fluorescence decay of the main emission band.



CLICK 4 (λ_{Max})	*logε* ($M^{-1}cm^{-1}$)
424 nm	5.62
552 nm	4.34

Figure S18: Uv-Vis spectra of CLICK-4 diluted solutions and ε-coefficients of the main absorption bands.

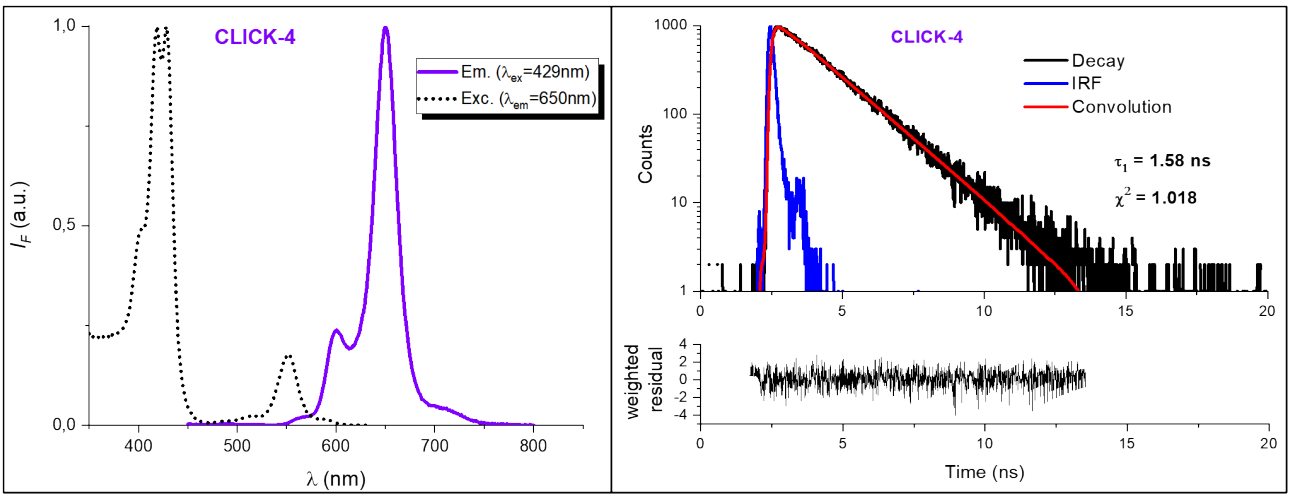
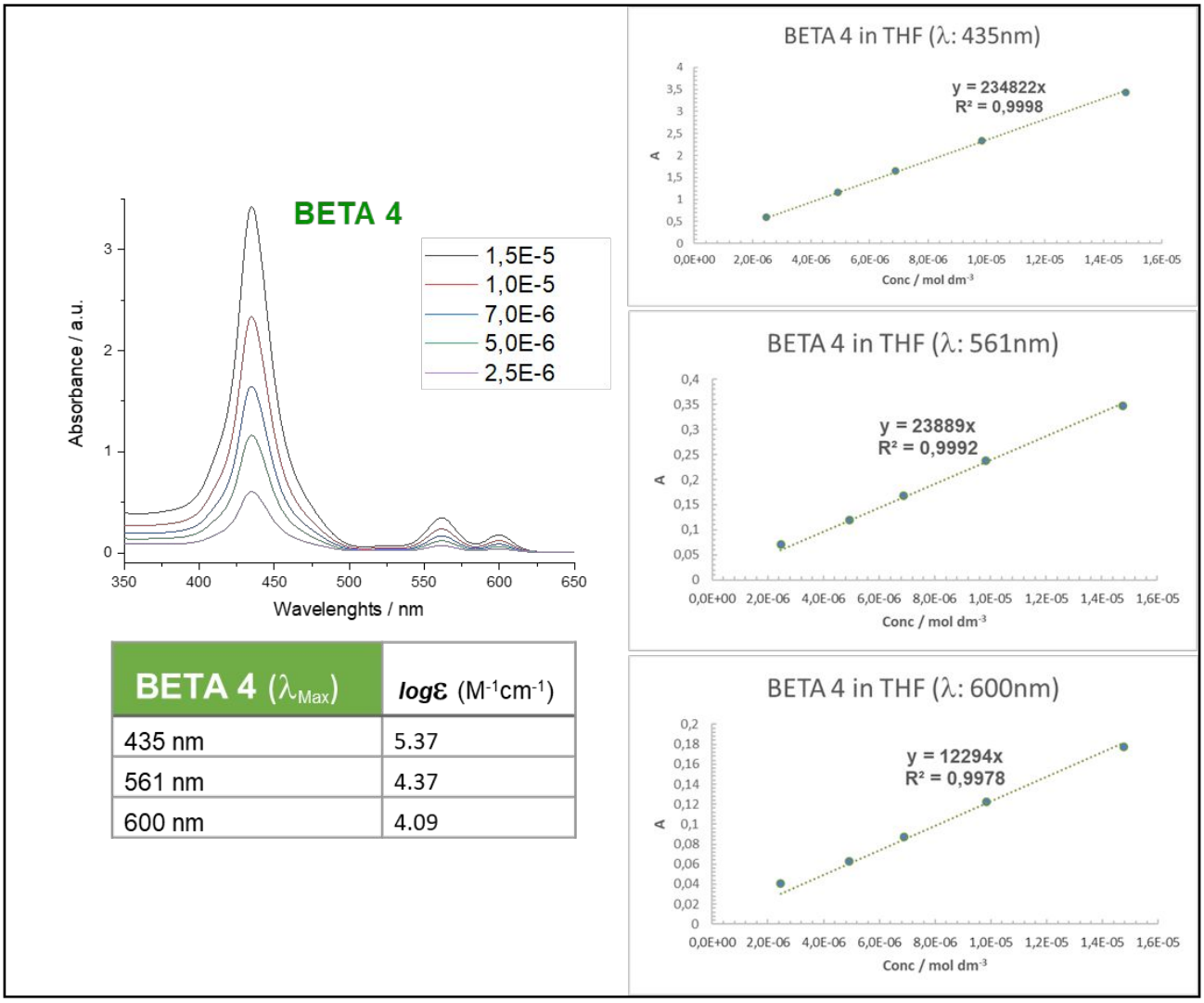


Figure S19: Excitation and emission spectra of CLICK-4 diluted solutions and the Fluorescence decay of the main emission band.



BETA 4 (λ_{Max})	*logε* ($M^{-1}cm^{-1}$)
435 nm	5.37
561 nm	4.37
600 nm	4.09

Figure S20: Uv-Vis spectra of BETA-4 diluted solutions and ε-coefficients of the main absorption bands.

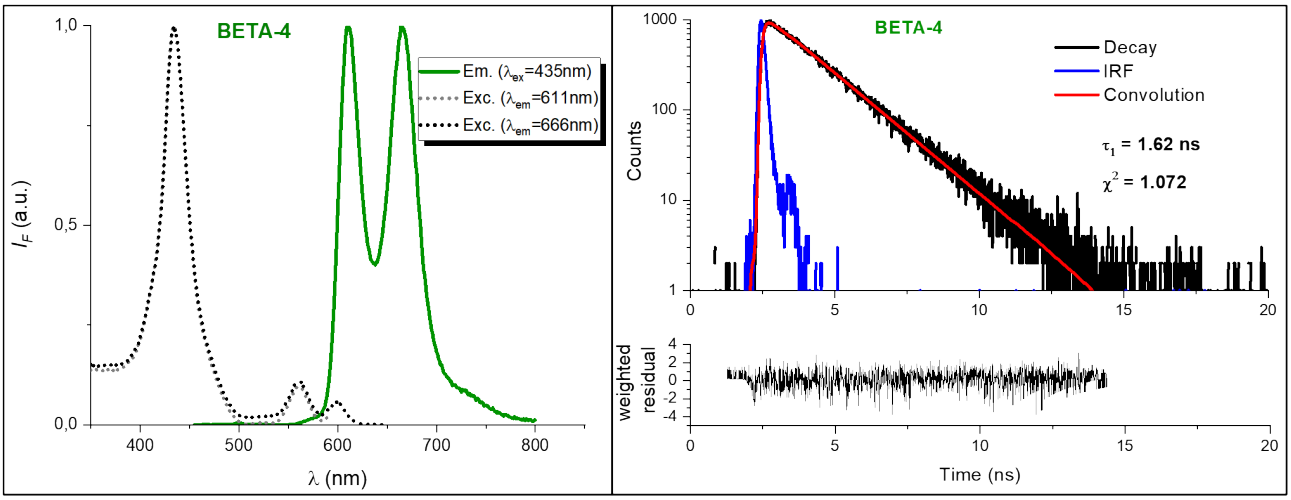


Figure S21: Excitation and emission spectra of BETA-4 diluted solutions and the Fluorescence decay of the main emission band.

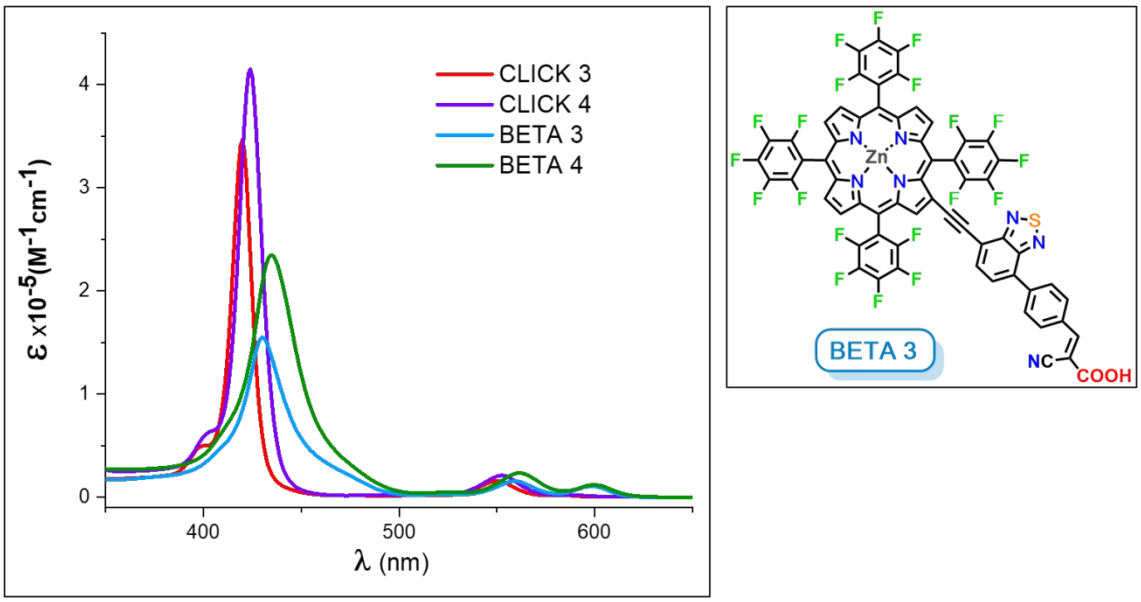


Figure S22: ε-normalized absorption spectra in THF solution of the synthesized dyes compared with the reference dye BETA 3.[1]

Electrochemical Features of the Dyes in solution

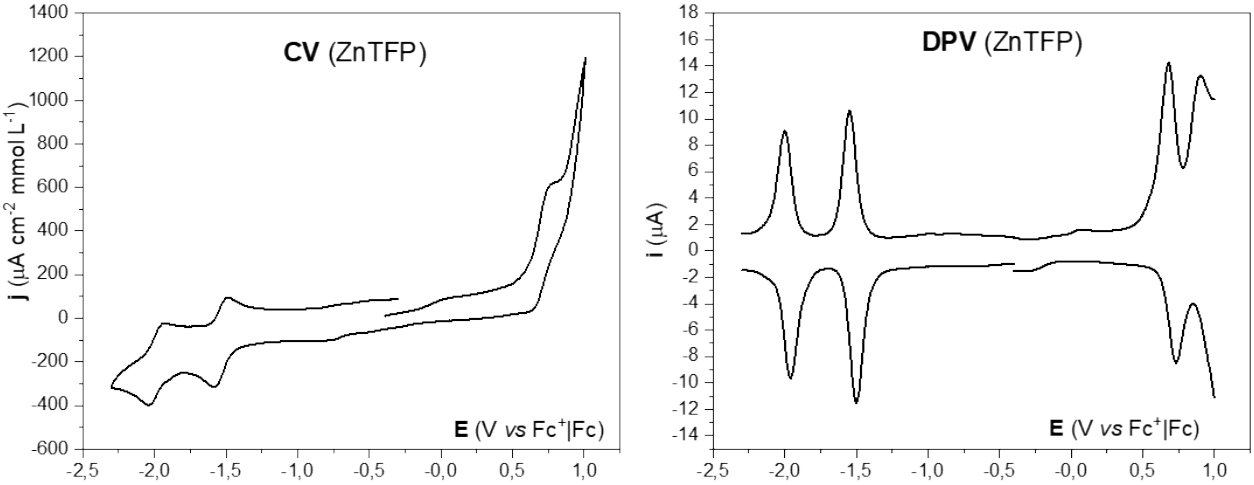
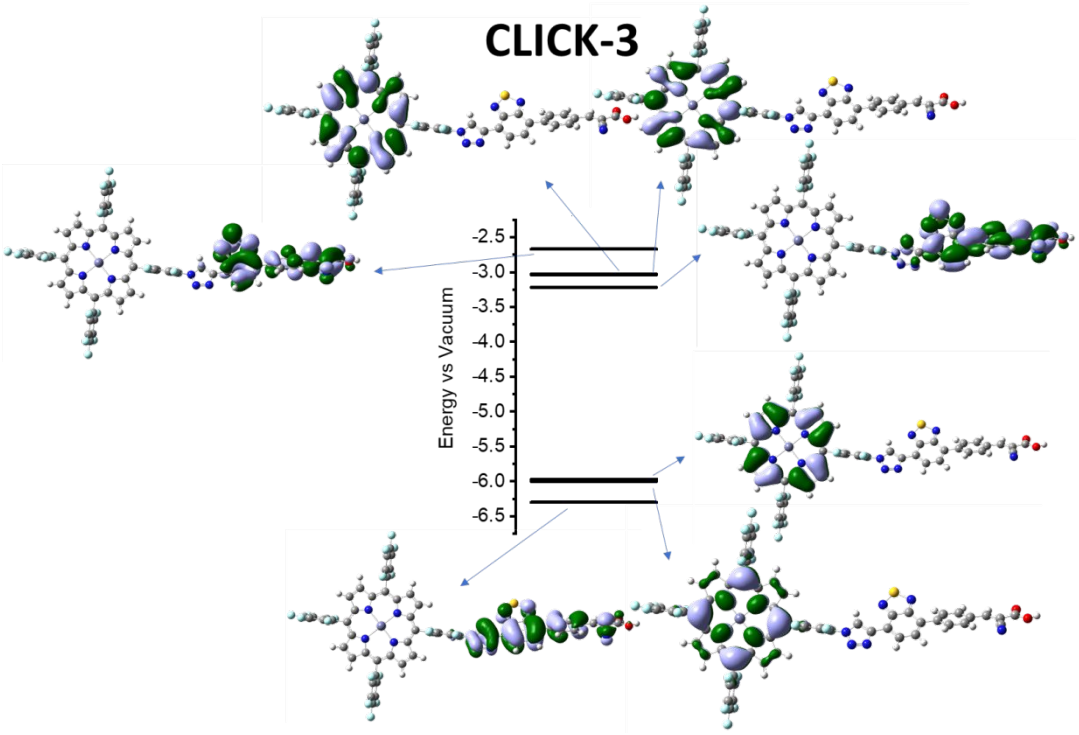


Figure S23: CV and DPV features of the unsubstituted porphyrins ZnTFP

Computational Details



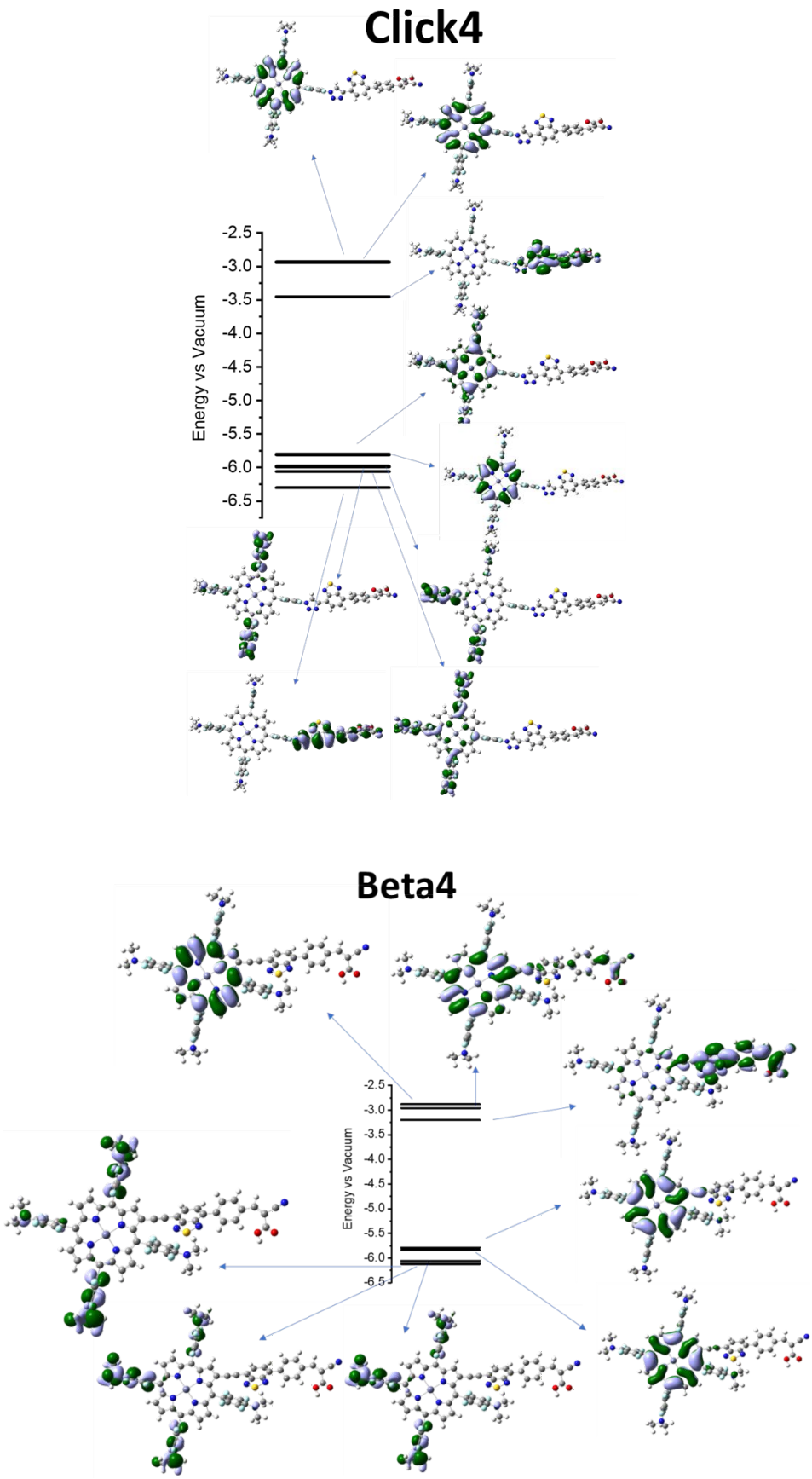


Figure S24: Energy levels of the KS orbitals for our family of porphyrins, along with heir corresponding isodensity surfaces.

(a) (b)

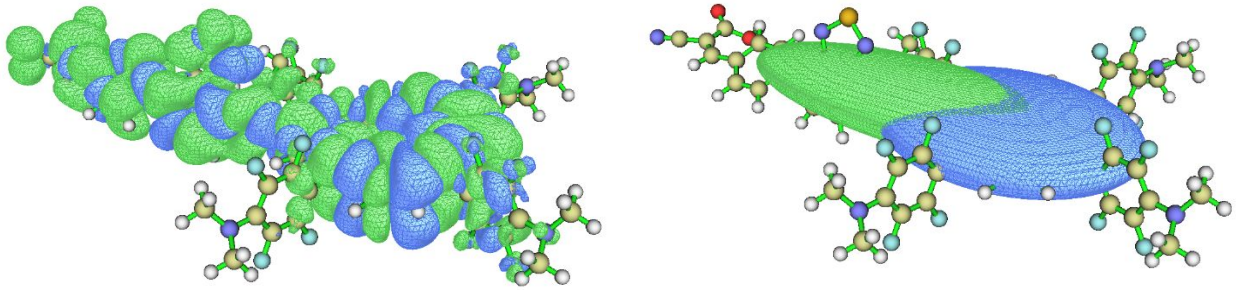


Figure S25: Graphical representation of (a) the dipole moment density along the X-axis and (b) the centroids of charge (C_+ and C_-) for the lowest transition for **BETA-4**.

(a) (b)

(c) (d)

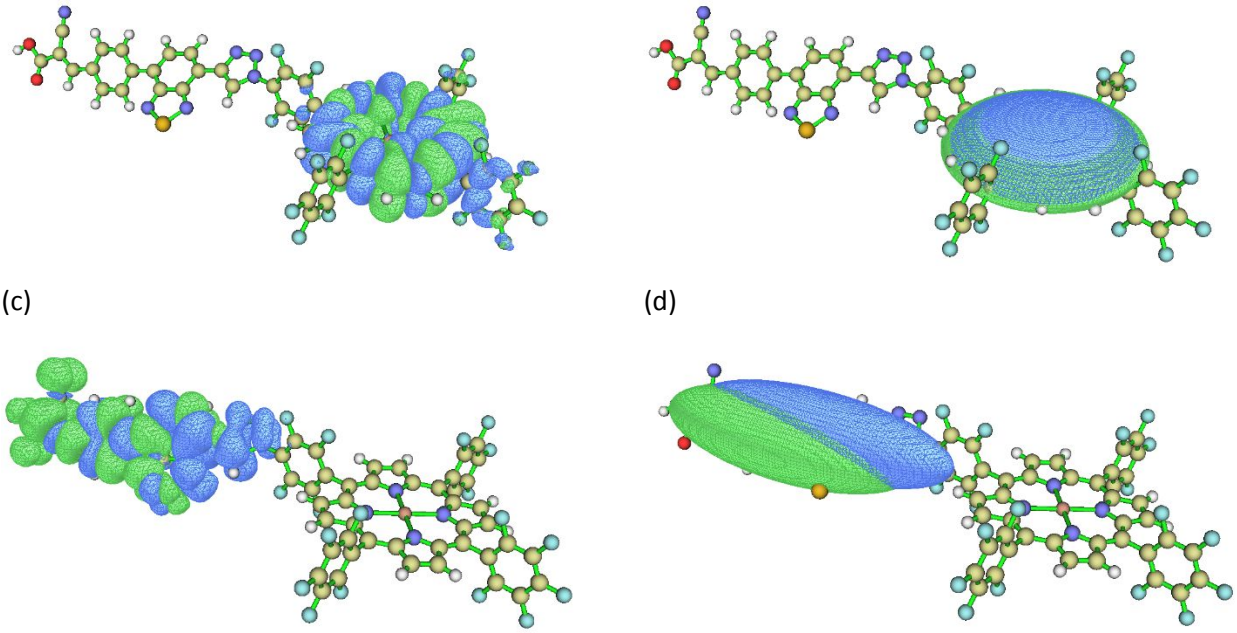
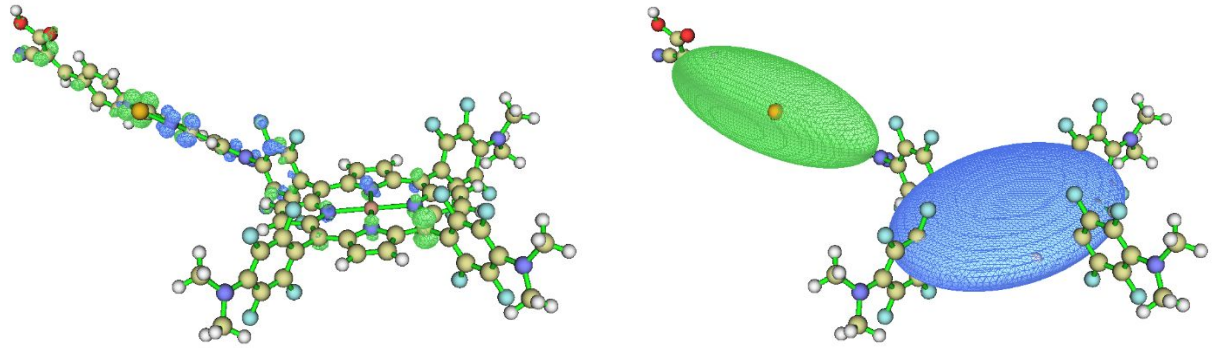


Figure S26: Graphical representation of the dipole moment density along the X-axis and the centroids of charge (C_+ and C_-) for the (a-b) lowest and (c-d) the fifth lowest transitions for **CLICK-3**.

(a) (b)



(c) (d)

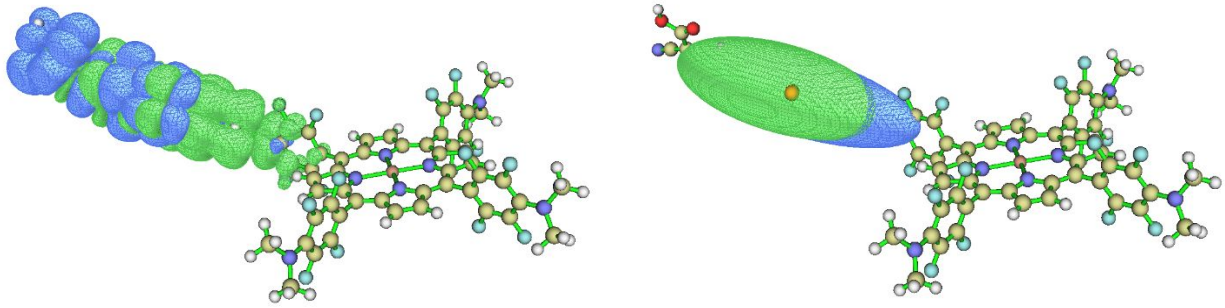


Figure S27: Graphical representation of the dipole moment density along the X-axis and the centroids of charge (C_+ and C_-) for the (a-b) lowest and (c-d) the seventh lowest transitions for **CLICK-4**.

Spectroscopic and Electrochemical Characterization on Thin Film

(a) (b)

(c) (d)

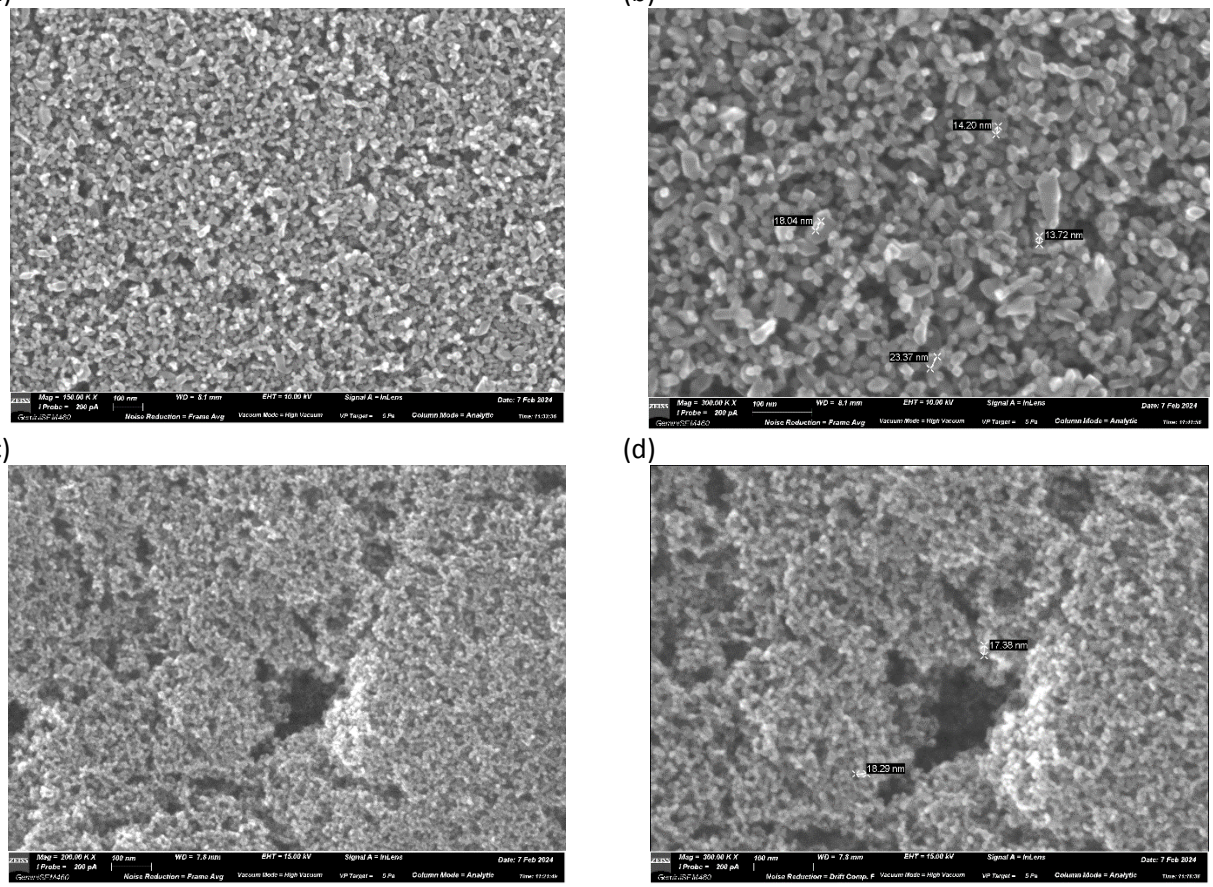


Figure S28: SEM images for (a-b) TiO_2 and (c-d) SnO_2/TiO_2. The images were collected at 200K and 300K magnification.

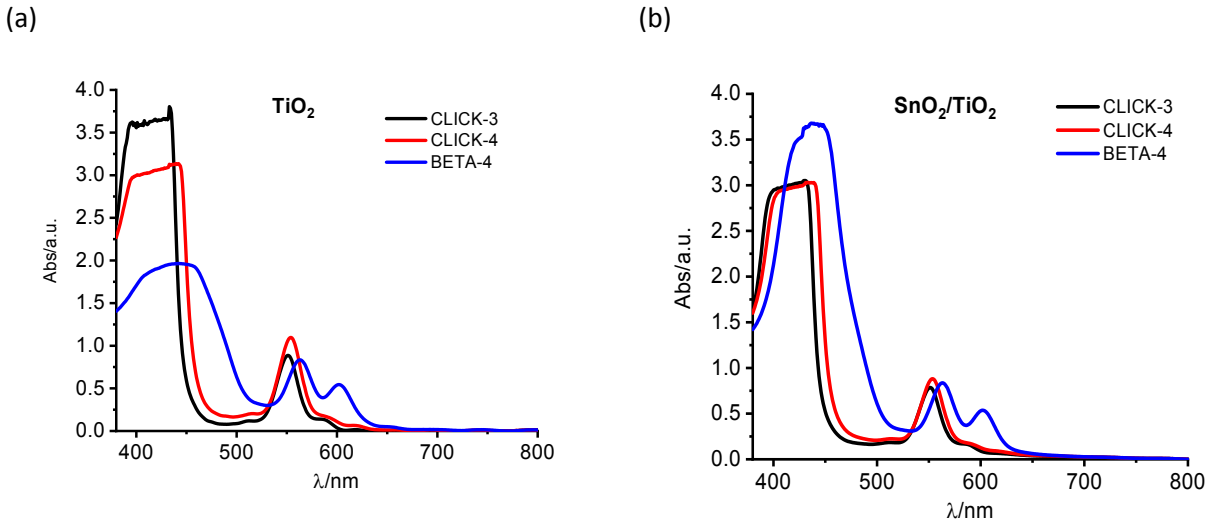


Figure S29: Absorption spectra for **CLICK-3**, **CLICK-4**, and **BETA-4** supported onto (a) TiO_2 and (b) SnO_2/TiO_2. The spectra were collected against an undyed electrode.

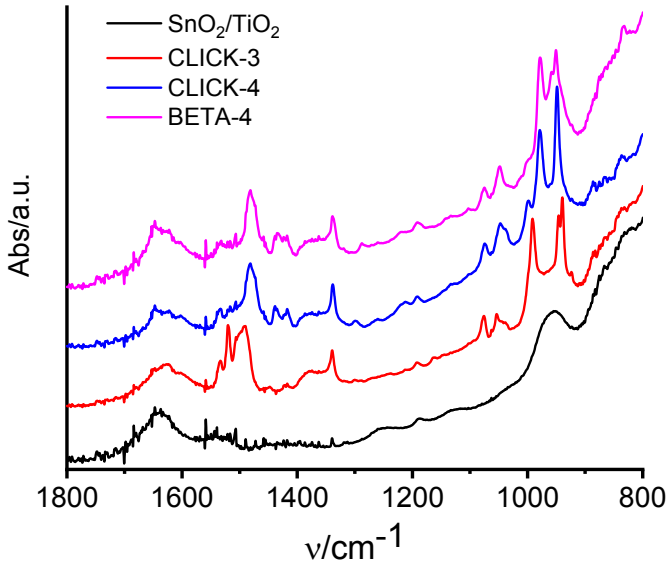


Figure S30: ATR-FTIR spectra for **CLICK-3**, **CLICK-4**, and **BETA-4** supported onto SnO_2/TiO_2. The spectrum of undyed SnO_2/TiO_2 is reported for comparison.

Transient absorption spectroscopy

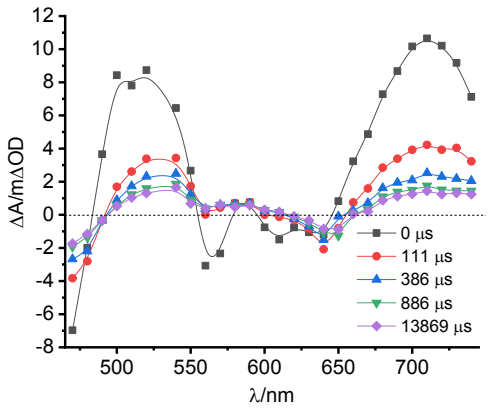
Table S1: Lifetimes for the Zinc porphyrins in toluene:ethanol 1:1 solution. The lifetime was calculated by averaging three different wavelengths.

Entry	$\tau_{T1\text{-}S0}/\mu s$
CLICK-3	66
CLICK-4	11
BETA-4	65

Table S2: Transient absorption ratio for our series anchored onto ZrO_2 and SnO_2/TiO_2.

Entry	ZrO_2	SnO_2/TiO_2
CLICK-3	$\frac{A_{460}}{A_{700}} = 15$	$\frac{A_{460}}{A_{700}} = 4.27$
CLICK-4	$\frac{A_{460}}{A_{700}} = 7$	$\frac{A_{460}}{A_{700}} = 2.97$
BETA-4	$\frac{A_{510}}{A_{730}} = 2.02$	$\frac{A_{510}}{A_{730}} = 1.05$

(a)



(b)

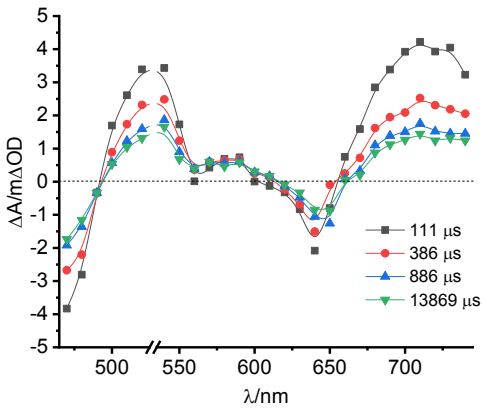


Figure S31: (a) Transient absorption spectra for **BETA-4** onto SnO_2/TiO_2 in contact with 0.1M $LiClO_4$/ACN on a longer time scale. (b) Magnification of the 111 µs - 13869 µs delay. P=29 mJ/cm^2/pulse. 10 KΩ input impedance.

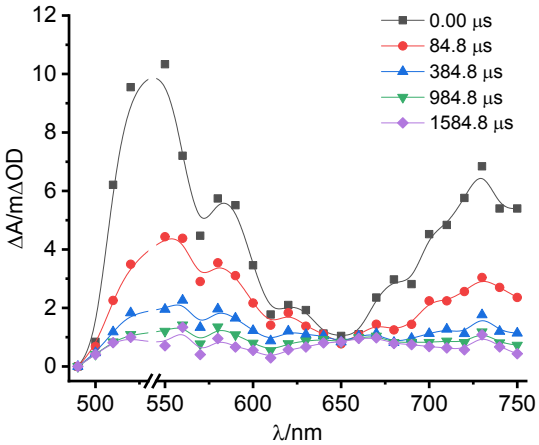


Figure S32: Transient absorption spectra for **BETA-4** onto ZrO_2 in contact with 0.1 M ascorbate pH 5. P=29 mJ/cm^2/pulse. 10 KΩ input impedance.

Photoelectrochemical Characterization

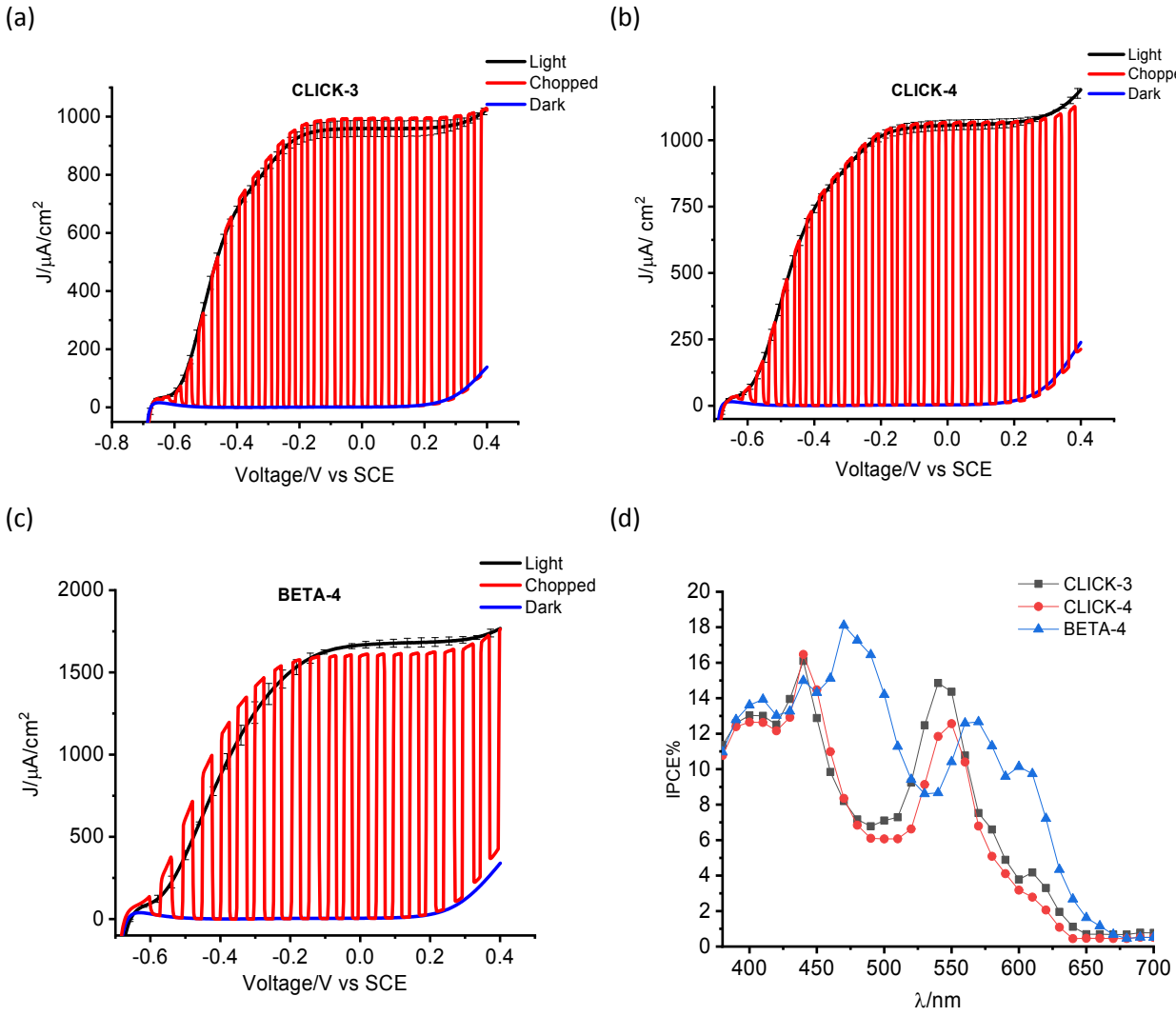


Figure S33: (a)-(c) Photocurrent density – Voltage curves for **CLICK-3**, **CLICK-4** and **BETA-4** onto TiO_2 in contact with 0.1 M Sodium Ascorbate pH 5. Black, red and blue lines represent the Photocurrent density under AM1.5G conditions, under chopped illumination and in dark. JVs were collected in the presence of a 420 nm cut-off (d) IPCE of the same dyed electrode under 0.10V Vs SCE polarization.

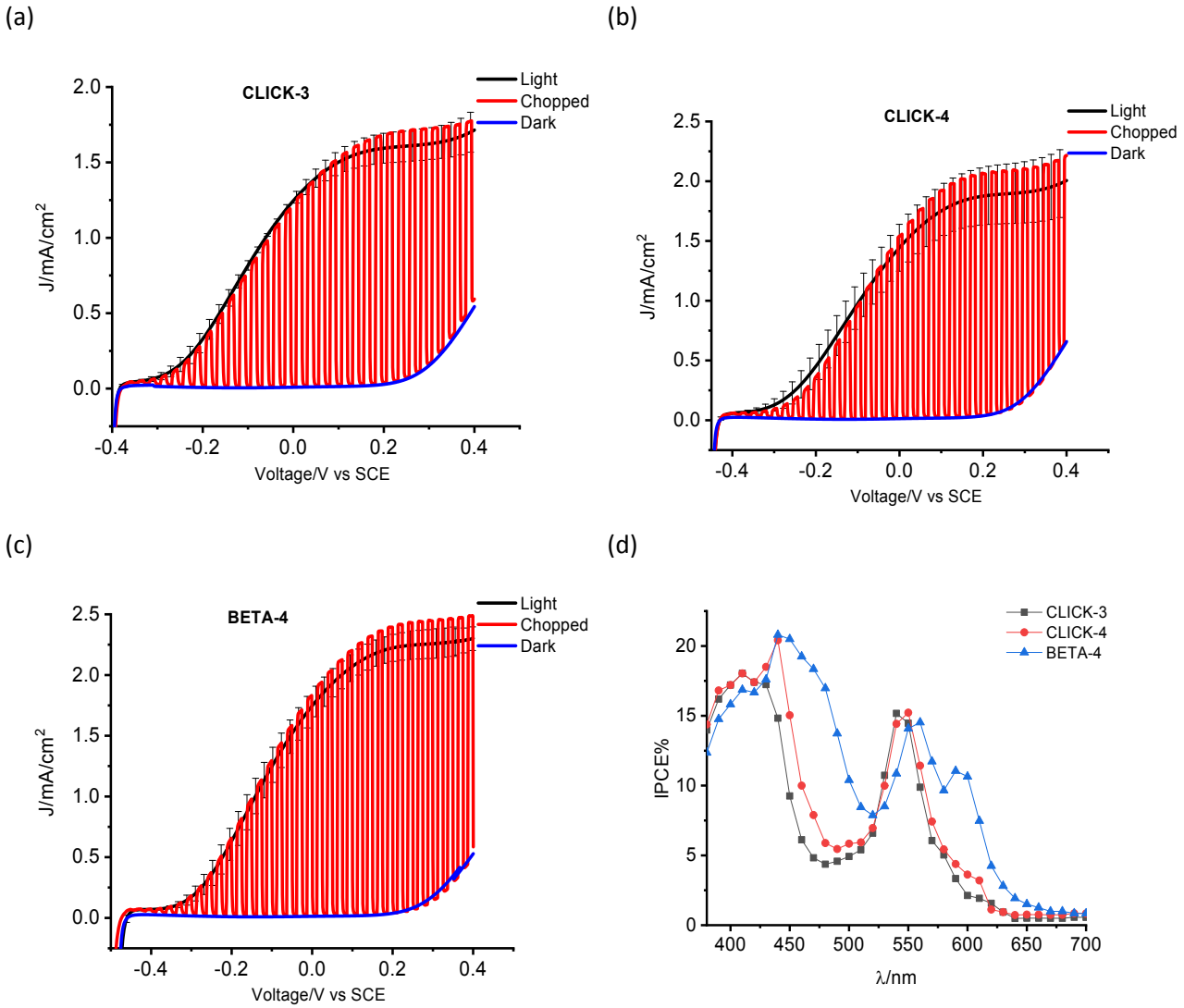


Figure S34: (a)-(c) Photocurrent density – Voltage curves for **CLICK-3**, **CLICK-4** and **BETA-4** onto SnO_2/TiO_2 in contact with 0.1 M Sodium Ascorbate pH 5. Black, red and blue lines represent the Photocurrent density under AM1.5G conditions, under chopped illumination and in dark. JVs were collected in the presence of a 400 nm cut-off (d) IPCE of the same dyed electrode under 0.15V Vs SCE polarization.

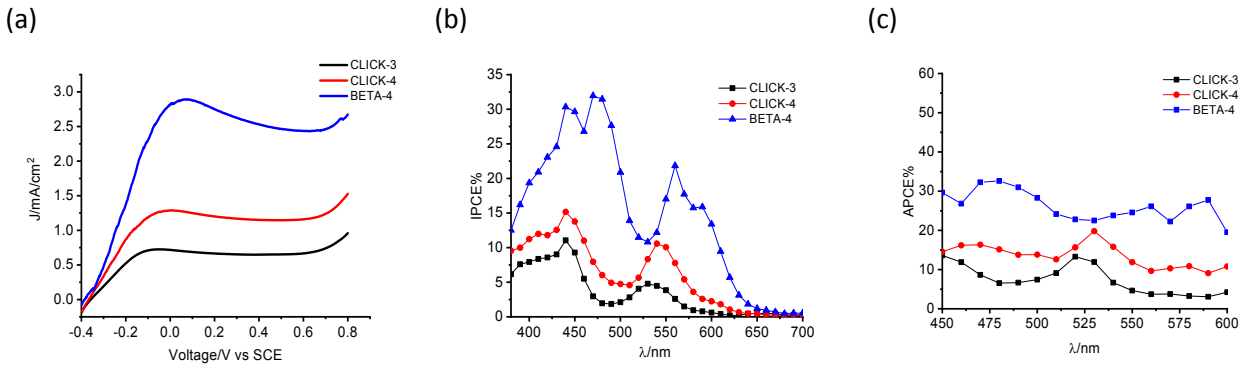


Figure S35: (a) Photocurrent density – Voltage curves for **CLICK-3**, **CLICK-4**, and **BETA-4** onto SnO_2/TiO_2 in contact with 0.1 M LiI/ACN. JVs were collected in the presence of a 400 nm cut-off (b) IPCE% and (c) APCE% spectra of the electrodes reported in (a).

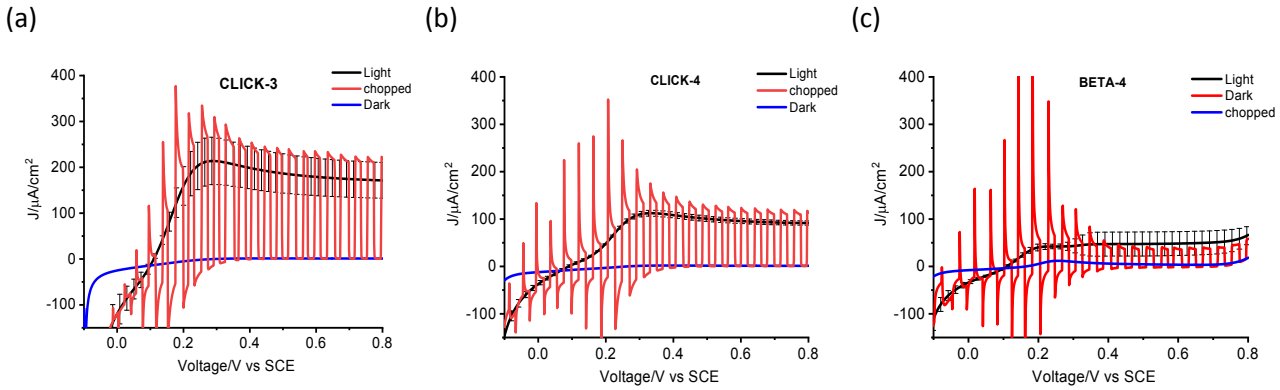


Figure S36: Photocurrent density – Voltage curves for (a) **CLICK-3**, (b) **CLICK-4**, and (c) **BETA-4** onto SnO_2/TiO_2 in contact with 0.1 M HBr/0.3 M NaBr water solution. JVs were collected in the presence of a 400 nm cut-off.

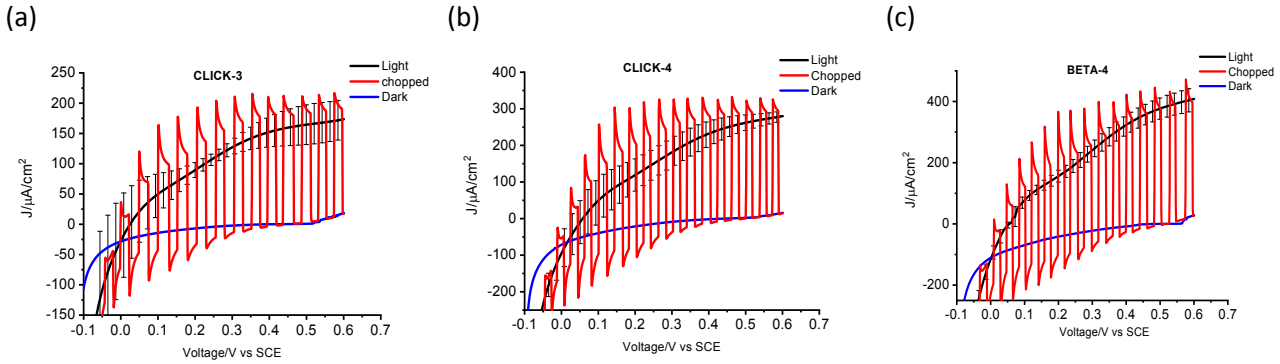


Figure S37: Photocurrent density – Voltage curves for (a) **CLICK-3**, (b) **CLICK-4**, and (c) **BETA-4** onto SnO_2/TiO_2 in contact with 10 mM TEMPO/ACN. The electrodes were illuminated from the front side. JVs were collected in the presence of a 400 nm cut-off.

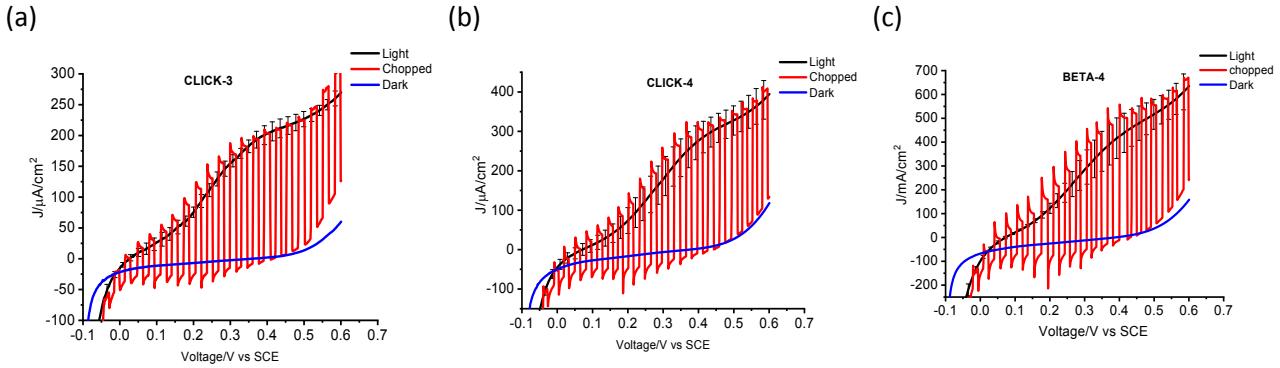


Figure S38: Photocurrent density – Voltage curves for (a) **CLICK-3**, (b) **CLICK-4**, and (c) **BETA-4** onto SnO_2/TiO_2 in contact with 50 mM TEMPO/ACN. The electrodes were illuminated from the back side. JVs were collected in the presence of a 400 nm cut-off.

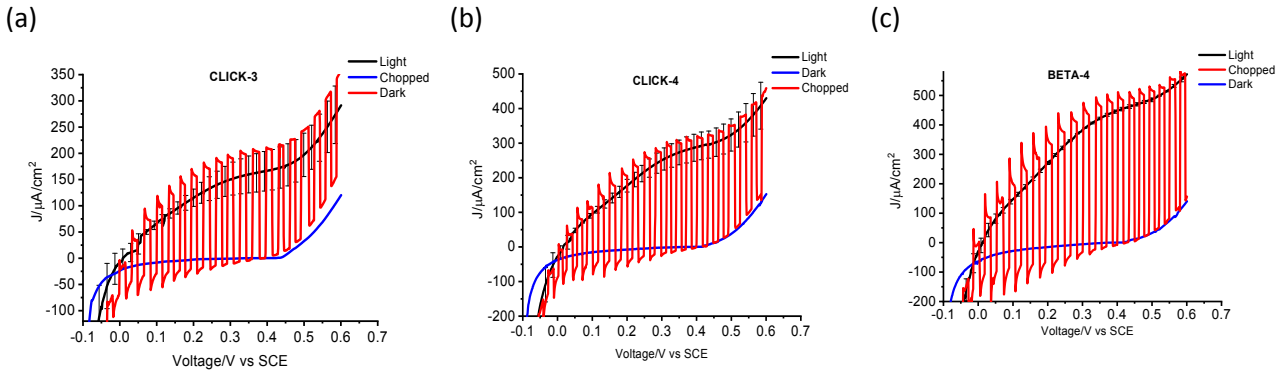


Figure S39: Photocurrent density – Voltage curves for (a) **CLICK-3**, (b) **CLICK-4**, and (c) **BETA-4** onto SnO_2/TiO_2 in contact with 100 mM TEMPO/ACN. The electrodes were illuminated from the back side. JVs were collected in the presence of a 400 nm cut-off.

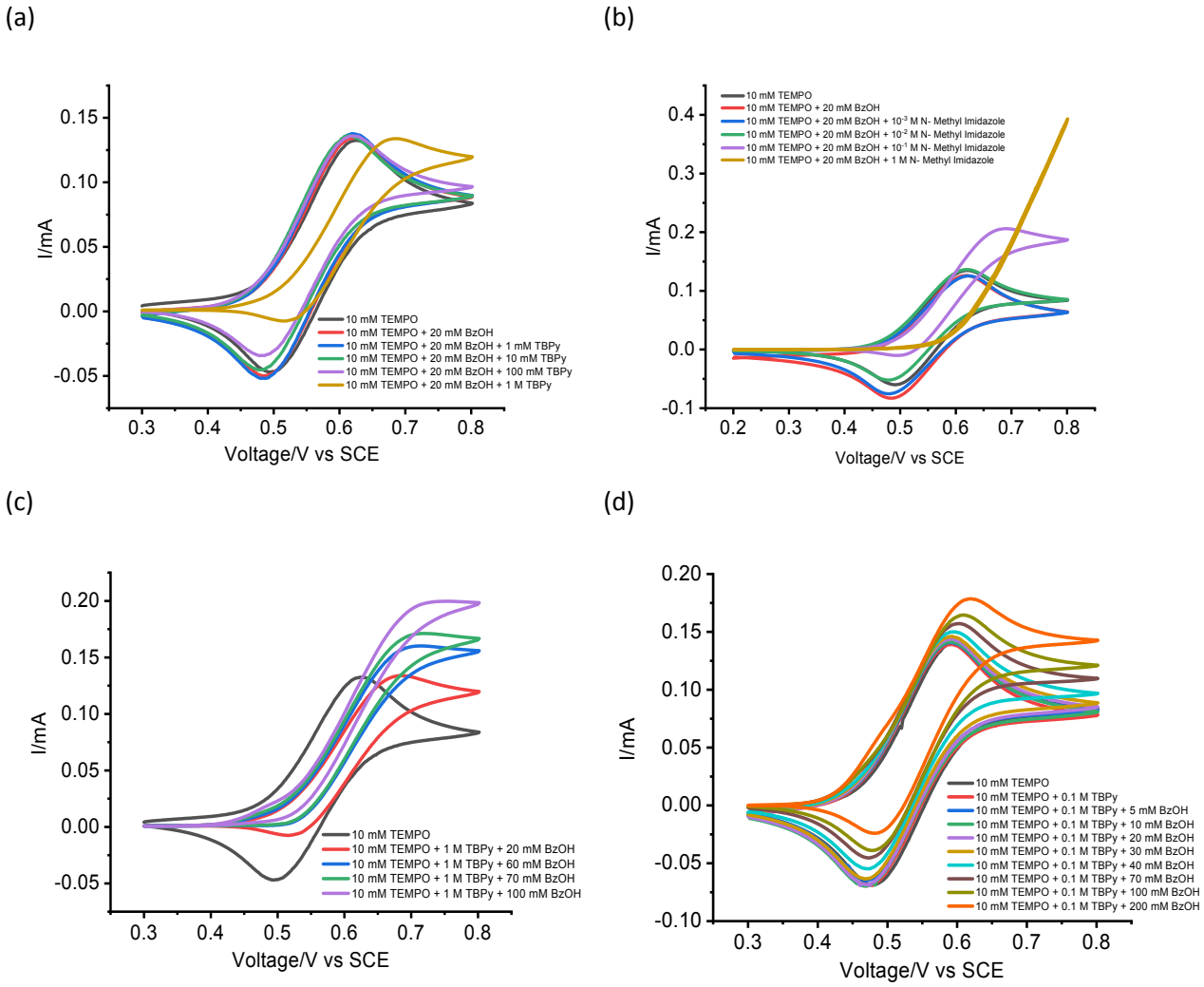


Figure S40: Electrocatalysis experiments performed with a glassy carbon in a 10 mM TEMPO/ACN solution by increasing (a) concentration of TBPy, (b) concentration of N-Methyl Imidazole, (c) concentration of BzOH with 1 M TBPy, and (d) concentration of BzOH with 0.1 M TBPy.

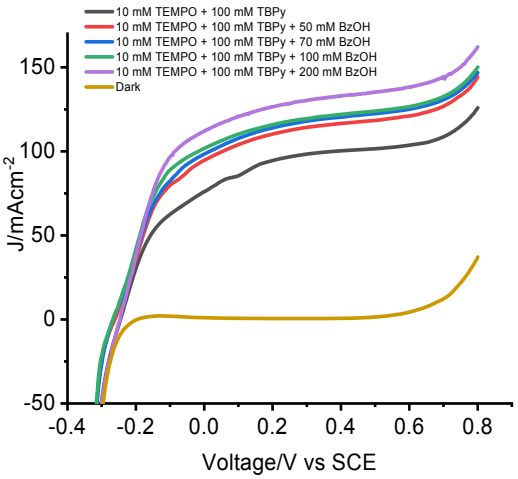


Figure S41: JV curves for **BETA-4** on SnO_2/TiO_2 by increasing the BzOH concentration in the presence of a 400 nm cut-off.

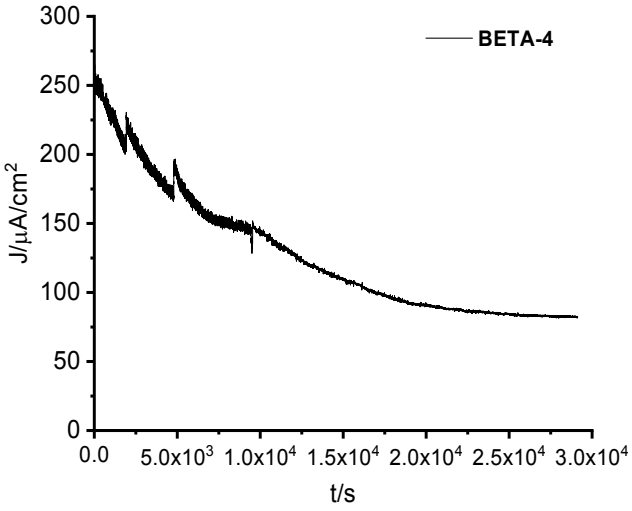


Figure S42: Representative bulk electrolysis for **BETA-4** onto SnO_2/TiO_2 electrodes in a two-compartment cell at 0.4 V. vs SCE. Anolyte: 10 mM TEMPO/70 mM BzOH/0.1 M $LiClO_4$/0.1 M TBPy/ACN. Catholyte: 10 mM TEMPO/0.1 M $LiClO_4$/ACN. The electrolysis was collected in the presence of a 400 nm cut-off. To speed up the reaction the electrolysis was recorded under 2 SUN.

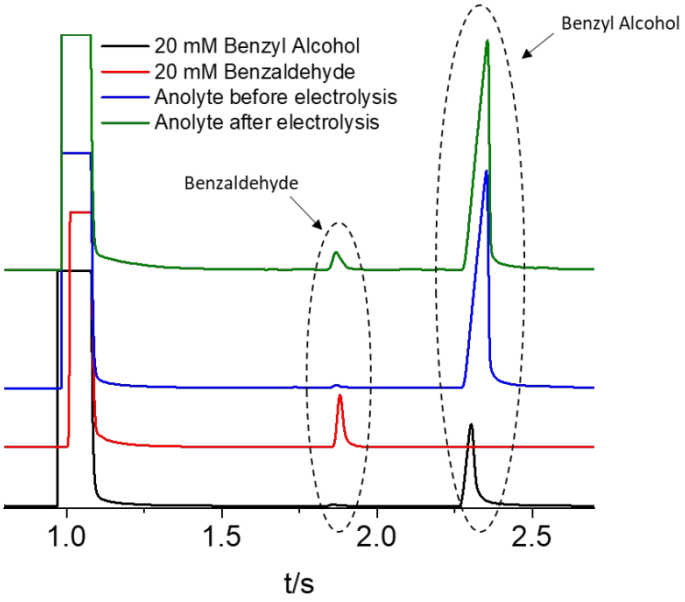


Figure S43: Chromatogram of 20 mM Benzyl Alcohol (BzOH) acetonitrile solution (black line), 20 mM Benzaldehyde acetonitrile solution (red line), Anolyte before electrolysis (10 mM TEMPO/70 mM BzOH/0.1 M $LiClO_4$/0.1 M TBPy/ACN) (blue line) and a representative Anolyte after the electrolysis (green line).

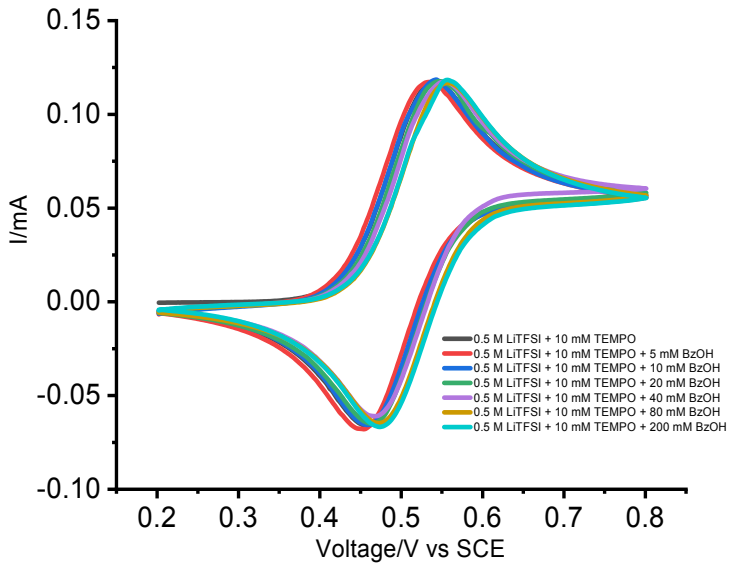


Figure S44: Electrocatalysis experiments performed with a glassy carbon in a 10 mM TEMPO/0.5M LiTFSI/ACN solution by increasing the BzOH concentration.

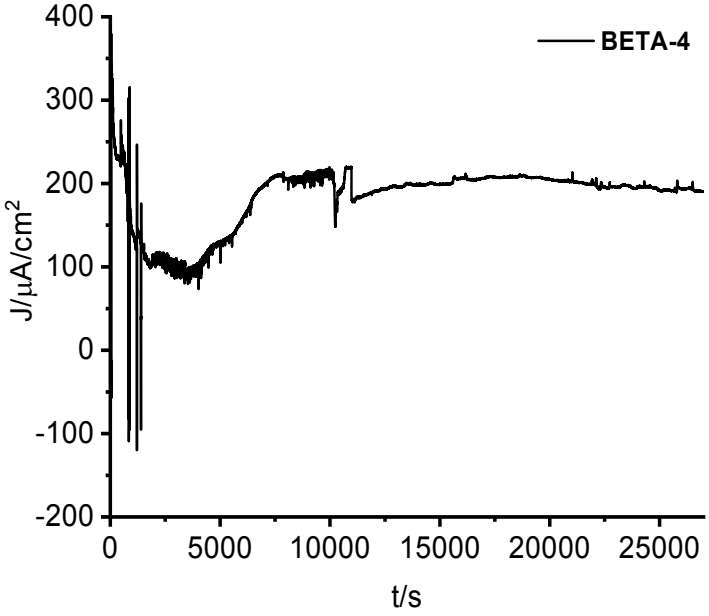


Figure S45: Representative bulk electrolysis for **BETA-4** onto SnO_2/TiO_2 electrodes in a two-compartment cell at 0.4 V. vs SCE. Anolyte: 10 mM TEMPO/70 mM BzOH/0.5 M/ACN. Catholyte: 10 mM TEMPO/0.5 M LTFSI/ACN. The electrolysis was collected at 1 SUN in the presence of a 400 nm cut-off.

References

(1) Berardi, S.; Caramori, S.; Benazzi, E.; Zabini, N.; Niorettini, A.; Biroli, A. O.; Pizzotti, M.; Tessore, F.; Di Carlo, G. Electronic Properties of Electron-Deficient Zn(II) Porphyrins for HBr Splitting. *App Sci* **2019**, *9*, 2739. https://doi.org/10.3390/app9132739.