

Supplementary Information

General Methods

Structure-properties relationship of atomically-precise silver acetylide clusters in the electroreduction of CO₂

*Leonard Curet,^a Dominique Foix,^a Stephane Ducos,^a Laurent Billon,^a Emilio Palomares,^{b,c} Aurelien Viterisi^{*a}*

*Corresponding authors

aurelien.viterisi@univ-pau.fr

^a *Universite de Pau et Pays de l'Adour, E2S UPPA, CNRS, IPREM UMR 5254
Technopole Hélioparc
2 avenue du Président Pierre Angot
64053 PAU CEDEX 09*

^b *Institute of chemical research of Catalonia (ICIQ)*

Avda. Països Catalans, 16

43007 Tarragona

^c *ICREA. Passeig Lluís Companys, 28,*

E-08010. Barcelona. Spain.

Experimental Section

Materials

25% ammonia solution (for analysis EMSURE® ISO, Reag. Ph Eur), silver nitrate (ReagentPlus®, ≥99.0% for titration), absolute ethanol, Nafion® perfluorinated resin (5 wt% solution in a mixture of lower aliphatic alcohols containing 5% water), 4-ethynyltoluene (97%), 1-Octyne (97%), 4-Ethynylanisole (97%), 4-Ethynyl- α,α,α -trifluorotoluene (97%), 4-tert-Butylphenylacetylene (96%), 3-ethynylthiophene (96%), 1-Ethynylpyrene and potassium bicarbonate (ACS reagent, 99.7%, powder, crystals, or granules) were purchased from Sigma-Aldrich. 4-Ethynyl-N,N-diphenylaniline(97%) was purchased from BLDpharm. $K_4(Fe(CN)_6 \cdot 3H_2O)$ (>99%) was purchased from ChemLab. Vulcan XC-72 carbon black, FAB PK AEM membrane (Fumasep) and Sigracet GDL (39BB) were purchased from Fuel Cell Store. Methanol (>99.5%, Pharmapur®, Ph Eur, BP, NF) was obtained from Scharlab. CDC13 (99.8%) and D₂O were purchased from Innovachem. All electrolytes were prepared using Milli-Q water.

Materials characterization

NMR

The ¹H-NMR analyses were conducted using a Bruker Ultrashield spectrometer with a ¹H frequency of 400 MHz.

MP-AES

MP-AES measurements were performed on an Agilent 4210 model using a 1000 ppm Ag standard (prepared from AgNO₃) and diluted accordingly in a 3% HNO₃ solution to obtain a calibration curve ranging from 1 to 20 ppm (6 points). Quantification was done by preparing precisely a 1000 ppm solution of AgPh in a mixture of trifluoroacetic acid and Milli-Q water. The prepared solution was then diluted in HNO₃ (3%) to obtain a 10 ppm concentration of the compound.

XPS

X-ray Photoelectron Spectroscopy (XPS) measurements were conducted using a Thermo K-alpha spectrometer equipped with a 120 mm mean radius Hemispherical Analyzer (HAS) and a microfocused monochromated radiation source (Al K α , 1486.6 eV), with a continuously variable microspot size ranging from 30 to 400 μ m in diameter. These measurements were performed under ultra-high vacuum (UHV) conditions, with a residual pressure of 1×10^{-9} mbar. The X-ray power operated at 72 W (12 kV, 6 mA) for a typical 400 μ m beam diameter. The spectra were recorded in the constant Pass Energy (PE) mode, specifically CAE, which was used for both wide high-sensitivity survey spectra (PE = 200 eV) and high-energy resolution analyses (PE = 20 eV) to achieve quantitatively resolved chemical analyses. To compensate for charge effects, a charge neutralization system employing low-energy electrons was employed.

For data analysis, the spectra were mathematically fitted using Casa XPS software, employing a least-squares algorithm and a non-linear baseline. The fitting of peaks in the experimental curves was achieved through a combination of Gaussian (70%) and Lorentzian (30%) distributions. Only core-level spectra for elements with the highest photoionization cross-section were recorded to ensure the extraction of more reliable information.

Powder XRD

Powder X-ray Diffraction (PXRD) characterization was performed using a Bruker D2 Phaser powder diffractometer equipped with a Cu K α radiation source with a wavelength of 1.5406 Å. XRD patterns were recorded in the 2 θ range of 10° to 80° with a step size of 0.021° and a counting time of 0.05 seconds per step. The crystallite sizes were determined using DIFFRAC.EVA software.

ATR-IR

ATR-IR characterization was performed on a Nicolet iS50 (Thermo Scientific) with 64 scans.

Gas quantification

Permanent gases were identified and quantified using gas chromatography (GCMS-QP2010-plus, Shimadzu, Japan) equipped with a packed column (ShinCarbon ST, 2m; 0.53 mm, mesh80/100, Restek, USA) for permanent gas separation. Helium (6.0, Alphagaz 2, AirLiquide) was used as carrier gas. A Dielectric-Barrier Discharge Ionisation Detector (BID, Shimadzu, DL < 0.1ppm) was used to quantify all permanent gases (H₂, CO, Methane, Ethane, ethylene) with a range of calibration curves made from 0.1, 1 and 10% standard mixtures in CO₂ with at least 4 points for each calibration curve ($R^2 > 0.98$). A relative linearity is observed between calibration curves indicating a trustworthy method for results comparison between each calibration curve. Sampling from the electrolysis cell's headspace was carried out via a proprietary automated sampling system operating solenoid valve at timed intervals, transferring a sample of the cell's head space to a GC-sample loop (500 μ L) followed by the subsequent injection to the GC column.

3-Electrodes Cell Electrochemical Characterization

Electrochemical tests were conducted using a custom-made three-electrode, leak-tight cell. The anode, consisting of a platinum wire, was enclosed in a bridge tube. The cell was filled with 40 mL of a 1 M KHCO₃ solution as the electrolyte. The reference electrode employed was an Ag/AgCl electrode immersed in a 3M KCl solution ($E_0 = 0.210$ vs NHE). The working electrode was a Gas Diffusion Electrode (GDE) with a surface area of 2 cm², integrated into a support structure, exposing 1 cm² of its surface directly to the electrolyte.

The pH value of the CO₂-saturated electrolyte was measured to be 6.8 before electrolysis. The potentials were measured against Ag/AgCl (3M). iR compensation losses between the working and reference electrodes were measured using electrochemical impedance spectroscopy (EIS) measurements from 100kHz to 0.1Hz. Electrode potential after iR correction converted to the RHE (Reversible Hydrogen Electrode) scale using **Error! Reference source not found.** pH value is measured to be 7.8 for the CO₂-saturated electrolyte and 8.4 when saturated with N₂. The overpotential (η) was calculated according to **Equation S4-2**¹. Faradaic efficiency was calculated from (**Equation S4-3**). The intrinsic activity of the catalyst was calculated from **Equation S4-4** and **Equation S4-5**. For Turnover Number and Turnover Frequency respectively.

Before chronoamperometry experiments, the electrolyte underwent a 15 min purge with either N₂ or CO₂ (at a flow rate of 35 mL/min). This purge was done using a Mass Flow Controller (MFC) (Bronkhorst EL-FLOW prestige FG-201CV) and constant stirring to eliminate air from both the solution

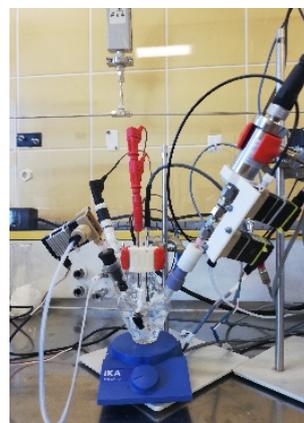


Figure S1. 3-electrodes Electrochemical Cell

and the cell headspace. Electrochemical tests were carried out using a potentiostat PGSTAT 204 (Metrohm).

$$E \text{ (RHE)} = E \text{ (Ag/AgCl)} + 0.059 * \text{pH} + E_0 \text{ (Ag/AgCl)} \quad \text{Equation S4-1}$$

With $E \text{ (Ag/AgCl)}$ the measured corrected potential, $E^0 \text{ (Ag/AgCl)}=0.210 \text{ V}$ the standard potential at 3M KCl, $\text{pH}=7.8$ in CO_2 saturated 1M KHCO_3 solution

$$\eta = E - E_{\text{RHE}}^0 \quad \text{Equation S4-2}$$

With $E_{\text{RHE}}^0 = -0.075 \text{ V}$ for the CO_2 to CO reduction at $\text{pH} = 7.8$

Faradaic efficiency was obtained by direct quantification of the gas products:

$$\text{Faradaic efficiency (\%)} = \frac{Q_{\text{exp}}}{Q_{\text{theo}}} \times 100 = \frac{z \times n \times F}{Q} \times 100 \quad \text{Equation S4-3}$$

Where z is the number of electrons involved in the reaction, n is the number of moles of generated product, F is the Faraday constant, and Q is the charge passed during the catalytic experiment.

Calculation of TON and TOF

Turnover Number (TON) and Turnover frequency (TOF) for CO production were calculated from the following equations:

$$\text{TON} = \frac{n_{\text{max CO}}}{n_{\text{active sites}}} \quad \text{Equation S4-4}$$

$$\text{TOF} = \frac{\text{TON}}{t_{\text{experiment}}} \quad \text{Equation S4-5}$$

With $n_{\text{max CO}}$ corresponding to the CO production at a given potential or current and $n_{\text{active sites}}$ corresponding to the number of active catalytic species on the electrode and $t_{\text{experiment}}$ the experiment time in seconds.

Following a common methodology²⁻⁵, the Electrochemically active surface area (ECSA) of the electrode was estimated by probing the redox reaction of the ferricyanide/ferrocyanide couple. Cyclic voltammetry (CV) were recorded at various scan rates (5, 10, 15 and 20 mV/s) with a 25 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in a 0.1 M KCl supporting electrolyte solution. The solution was initially degassed with N_2 . Then the potential of the working electrode was swept between 700 mV and -200 mV vs. Ag/AgCl (3 M KCl) at variable scan rates (mV s^{-1}). Between each CV, the solution was bubbled with N_2 and stirred to quickly reach back to the initial conditions.

Electrochemically active surface areas (ECSA) were estimated from the Randles-Sevcik equation, as follows:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C \quad \text{Equation S4-6}$$

with I_p : reduction peak current, n : number of moles of electrons per mole of electroactive species, A : area of electrode (cm^2), D : diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), ν : scan rate (V s^{-1}), C : concentration (mol cm^{-3}). The diffusion coefficient of ferricyanide is $3.85 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and its concentration $25 \times 10^{-6} \text{ mol cm}^{-3}$. The ECSA (A) is estimated from the slope of the plot of I_p versus $\nu^{1/2}$.

The surface loading ($\Gamma[\text{Ag}]$ as mol cm^{-2}) of the catalyst was calculated through the integration of the reduction wave at -0.218V vs RHE attributed to $\text{Ag}^+ \rightarrow \text{Ag}$ on the CV scans (**Figure S**) using the equation:

$$\Gamma[\text{Ag}] = q/nFA \quad \text{Equation S4-7}$$

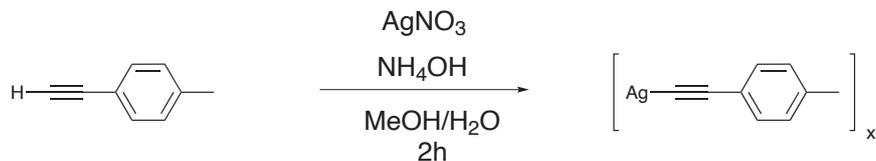
where q is the charge (C) obtained from integration of the reduction peak divided by the scan rate, n the number of electrons involved the redox process per Ag center ($n = 1$), F is the Faraday constant (96485 C mol^{-1}), and A is the electrode surface area (0.724 cm^2).

The obtained value was then correlated with the amount of Ag deposited on the electrode ($1.85 \mu\text{mol}$) which corresponds to 6.96% of active silver catalyst on the electrode.

CV and LSV electrodes preparation

The Electrodes were prepared following a modified procedure from M. Robert et al ⁶. Vulcan XC-72 Carbon Black (3 mg) was sonicated in Absolute ethanol (2mL) for 30min. To the slurry was added Nafion© perfluorinated resin (10 μL of a 5 wt% solution in a mixture of lower aliphatic alcohols containing 5% water) and the mixture was sonicated for 30min. To this mixture was added a suspension of the acetylide (0.8 mg) in absolute ethanol (1mL) and the mixture was sonicated for 30min. The suspension was then deposited by dropcasting on a gas diffusion layer (Sigracet 39BB; 2 cm^2) at 80°C . The electrodes were then dried under reduced pressure at 40°C overnight.

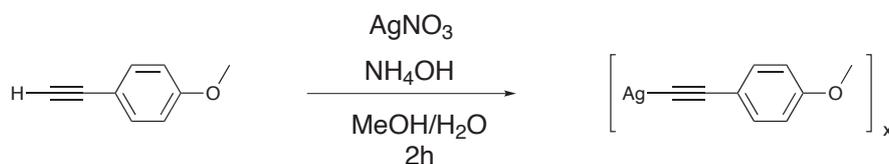
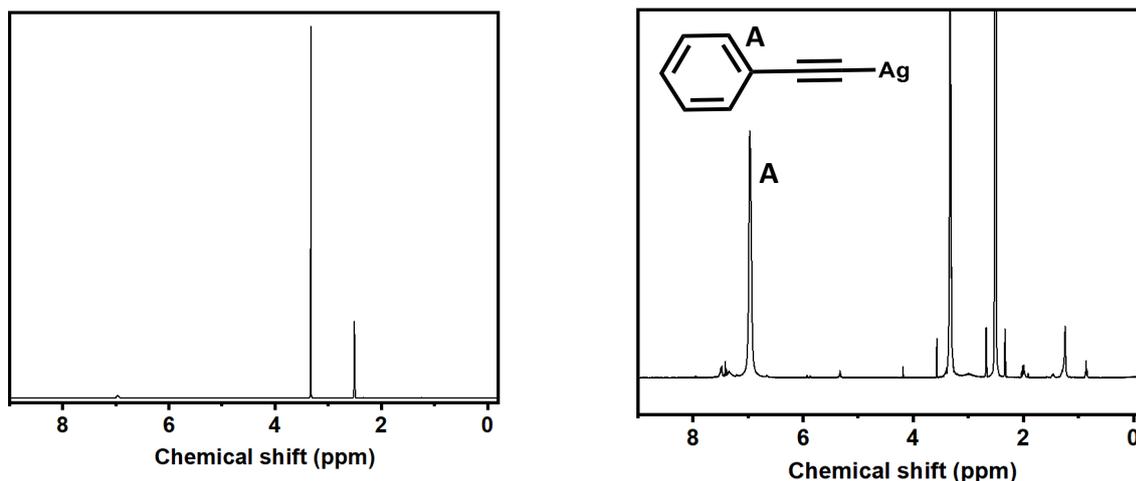
Material Synthesis



AgNO_3 (293 mg; 1.72 mmol) was solubilized in a mixture of MeOH (12 mL) and water (4 mL). To this solution was added NH_4OH until the brown colour completely disappeared. A solution of 4-ethynyltoluene (100 mg; 86 μmol) in MeOH (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered, and the resulting white solid was washed with water, then MeOH and dried under a reduced atmosphere at 45°C for 48H. The product was obtained as an insoluble hydrophobic white powder (189mg; 99% yield for a 1:1 complex) sensitive to light but stable under atmospheric conditions (>6 months).

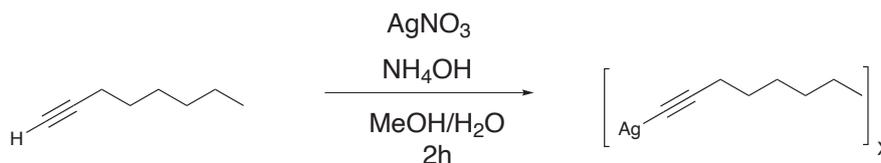
MP-AES: Ag (%mass) 46.3

^1H NMR (400 MHz) DMSO-d_6 : 6.97 (6H,s)



AgNO_3 (257 mg; 1.51 mmol) was solubilized in a mixture of MeOH (12 mL) and water (4 mL). To this solution was added NH_4OH until the brown colour completely disappeared. A solution of 4-ethynylanisole (100 mg; 757 μmol) in MeOH (10mL) was added slowly to the mixture. A precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered, and the resulting white solid was washed with water, then MeOH and dried under a reduced atmosphere at 45°C for 48H. The product was obtained as an orange insoluble hydrophobic powder (180mg;99%), which is stable under atmospheric conditions (> 6 months).

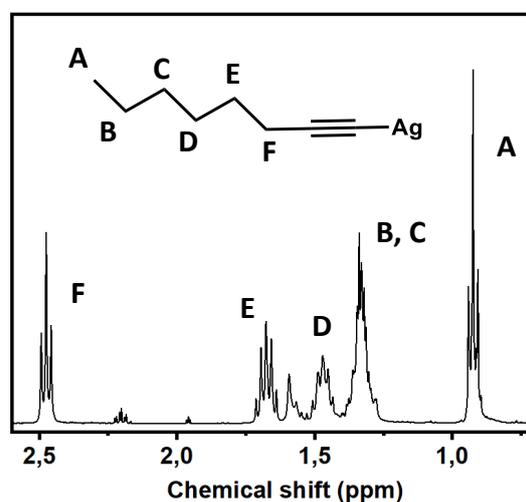
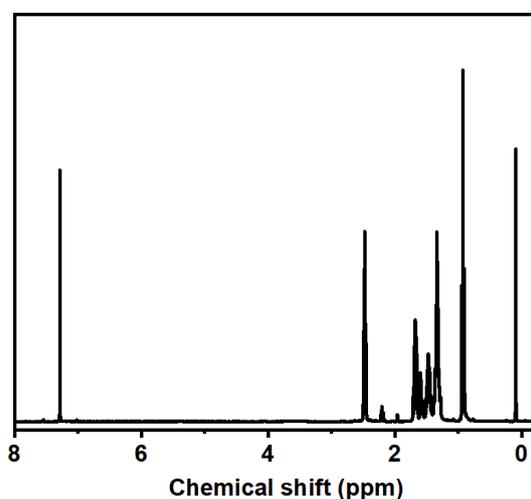
MP-AES : Ag (%mass) 52.6



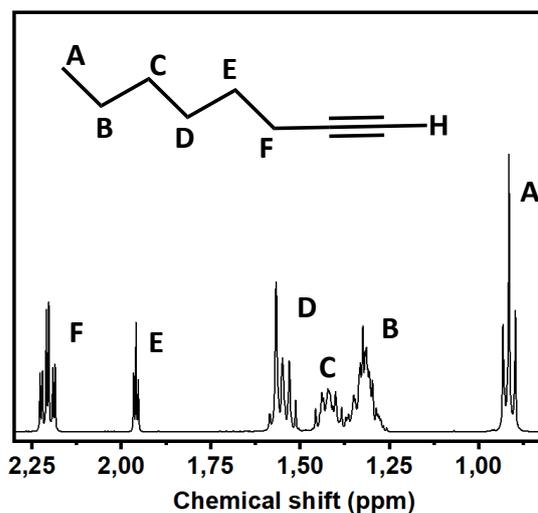
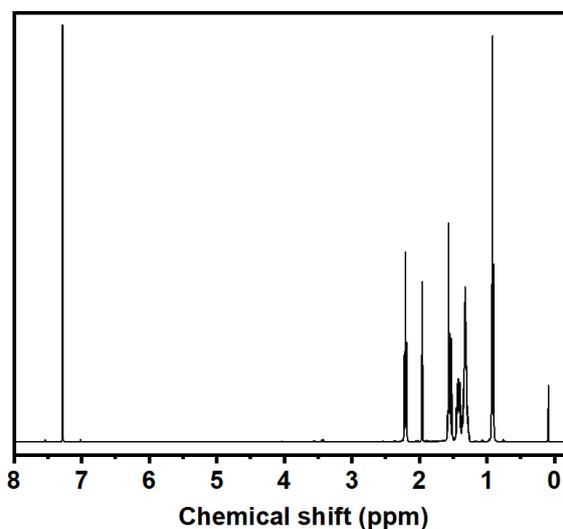
AgNO₃ (154 mg 907 μmol) was solubilized in a mixture of MeOH (12mL) and water (4mL). To this solution was added NH₄OH until the brown color completely disappeared. A solution of 1-octyne (50mg; 454 μmol) in MeOH (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered and the resulting white solid was washed with water then MeOH and dried under reduced atmosphere at 45°C for 48h. the product was sensitive to light and formed a dark powder soluble in chloroform (96 mg ; 97%).

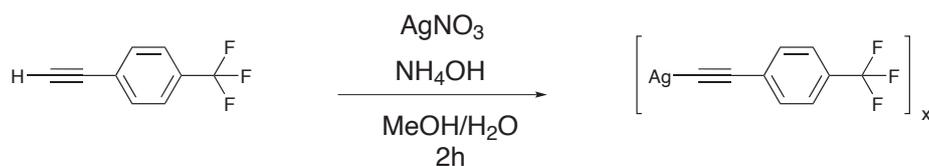
MP-AES : Ag(%mass) 66.4

¹H NMR (400 MHz) CDCl₃: 0.92 (t, 3H, J=6.7Hz) ; 1.31(m, 4H) ; 1.45(m, 2H) ; 1.66 (q, 2H, J=7.4Hz) ; 2.48 (t, 2H, J=7.4Hz)



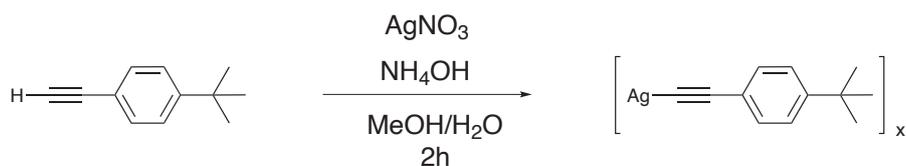
Octyne: ¹H NMR (400 MHz) CDCl₃: 0.91 (t, 3H, J=6.8Hz) ; 1.32 (m, 2H) ; 1.42 (m, 2H) ; 1.54 (q, 2H, J=7.4Hz) ; 1.96 (t, 2H, J=2.7Hz) ; 2.48 (td, 2H, J=2.7, 7.4 Hz)





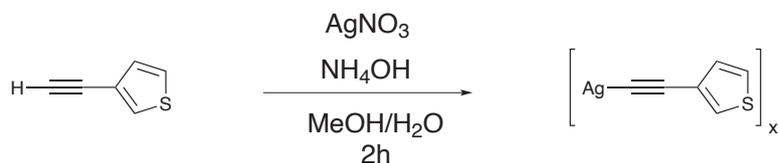
AgNO₃ (400 mg; 2.35 mmol) was solubilized in a mixture of MeOH (12mL) and water (4mL). To this solution was added NH₄OH until the brown color completely disappeared. A solution of 4-Ethynyl- α,α,α -trifluorotoluene (200 mg; 1.17 mmol) in MeOH (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered and the resulting white solid was washed with water then MeOH and dried under reduced atmosphere at 45°C for 48h. The product was obtained as a insoluble hydrophobic white powder (321mg; 99%) sensitive to light but stable under atmospheric conditions (>6 months).

MP-AES : Ag(%mass) 47.3



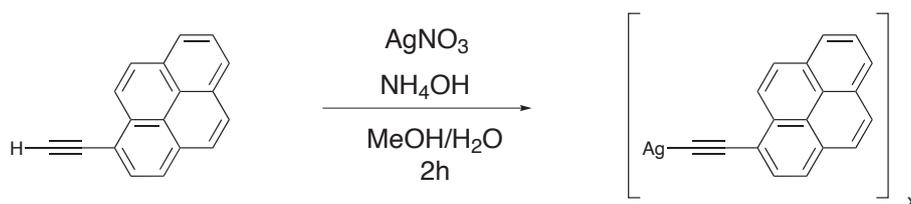
AgNO₃ (215 mg ; 1.26 mmol) was solubilized in a mixture of MeOH (12mL) and water (4mL). To this solution was added NH₄OH until the brown color completely disappeared. A solution of 4-tert-Butylphenylacetylene (100 mg ; 632μmol) in MeOH (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered and the resulting insoluble hydrophobic white solid was washed with water then MeOH and dried under reduced atmosphere at 45°C for 48H. (124mg; 74%)

MP-AES : Ag(%mass) 49.5



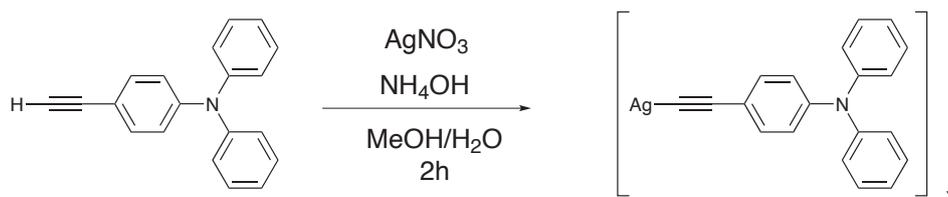
AgNO₃ (470 mg; 2.77 mmol) was solubilized in a mixture of MeOH (12mL) and water (4mL). To this solution was added NH₄OH until the brown color completely disappeared. A solution of 3-ethynylthiophene (150 mg; 1.39 mmol) in MeOH (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered and the resulting pale yellow insoluble solid was washed with water then MeOH and dried under reduced atmosphere at 45°C for 48H (292 mg; 98%)

MP-AES : Ag(%mass) 54



AgNO₃ (75 mg ; 442 μmol) was solubilized in a mixture of MeOH (12mL) and water (4mL). To this solution was added NH₄OH until the brown color completely disappeared. A solution of 1-ethynylpyrene (50mg; 221 μmol) in MeOH:DCM (1:1) (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered and the resulting red insoluble hydrophobic solid was washed with water then MeOH and dried under reduced atmosphere at 45°C for 48H. (55mg; 75 %)

MP-AES : Ag(%mass) 42.9



AgNO₃ (126 mg;742 μmol) was solubilized in a mixture of MeOH (12mL) and water (4mL). To this solution was added NH₄OH until the brown color completely disappeared. A solution of 4-Ethynyl-N,N-diphenylaniline (100mg; 371 μmol) in MeOH:DCM (1:1) (10mL) was added slowly to the mixture. A white precipitate formed directly and the solution was stirred at RT for 2h. The solution was filtered and the resulting yellow insoluble hydrophobic solid was washed with water then MeOH and dried under reduced atmosphere at 45°C for 48H. (98mg; 70%)

MP-AES : Ag(%mass) 33.9

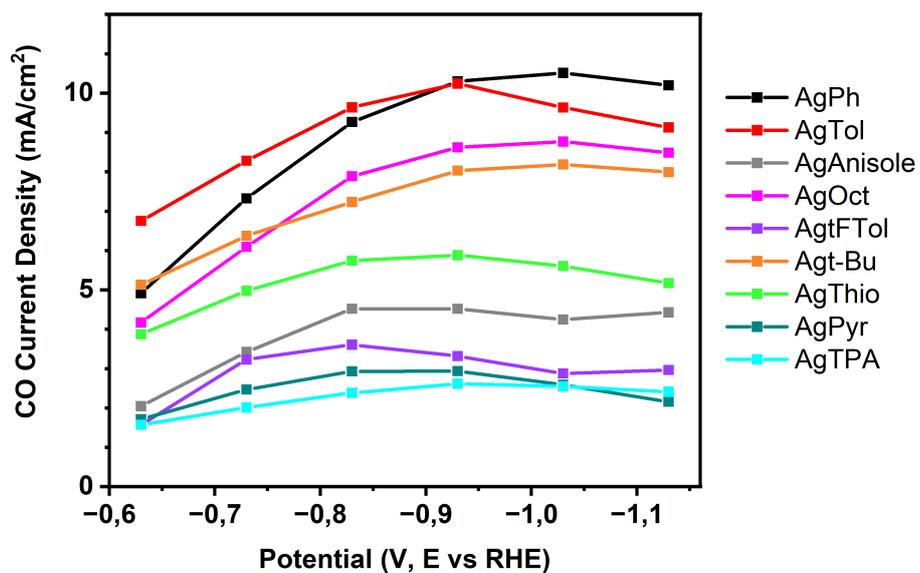


Figure S1: CO current density evolution with potential of the deposited Ag species on GDE substrates in CO₂ saturated 1 M KHCO₃ solution. **Fully carbonated groups are increasing CO current density compared to heteronuclear ligands. Bulky and π -extended structures seem to disfavor reactivity**

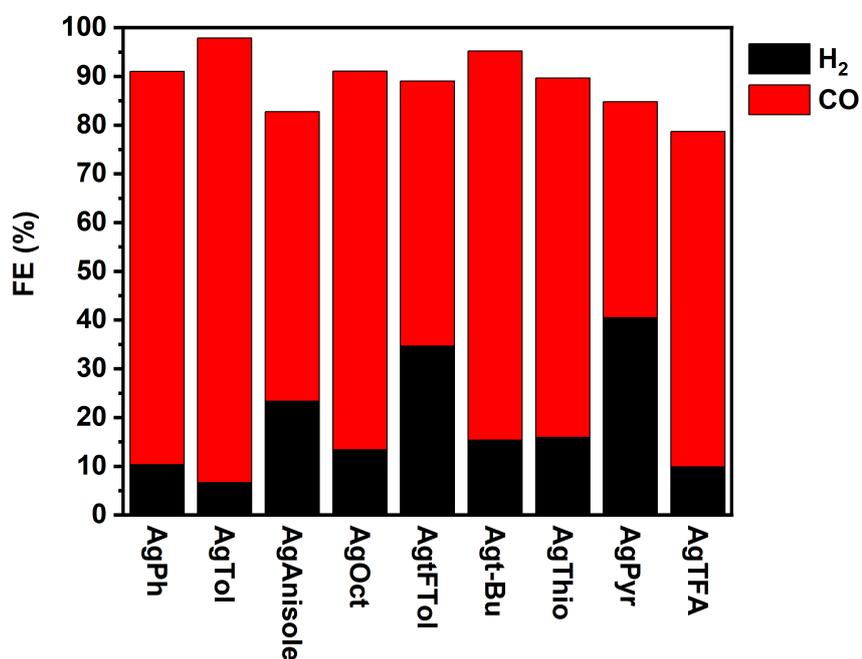


Figure S2. Faradaic efficiency comparison at -0.63V vs RHE from Chronoamperometry (CA)(15min) of the deposited Acetylides on GDE substrates in a CO₂ saturated 1 M KHCO₃.

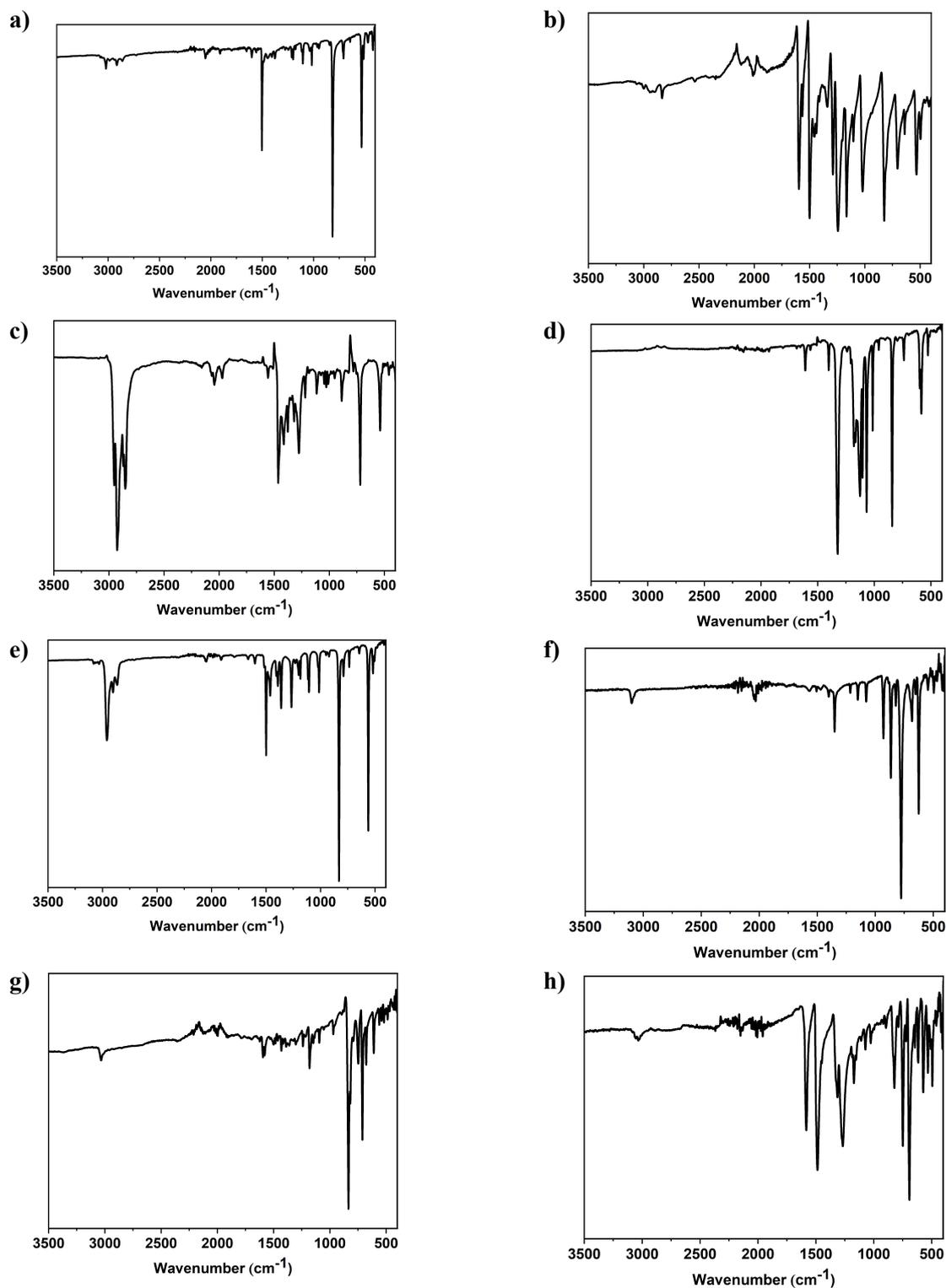


Figure S4: IR-ATR of **a)** AgTol **b)** AgAnisole **c)** AgOct **d)** AgtFTol **e)** Agt-Bu **f)** AgThio **g)** AgPyr **h)** AgTPA. The disappearance of the strong C=C-H band is assumed to be due to the formation of the C≡C-Ag bond.

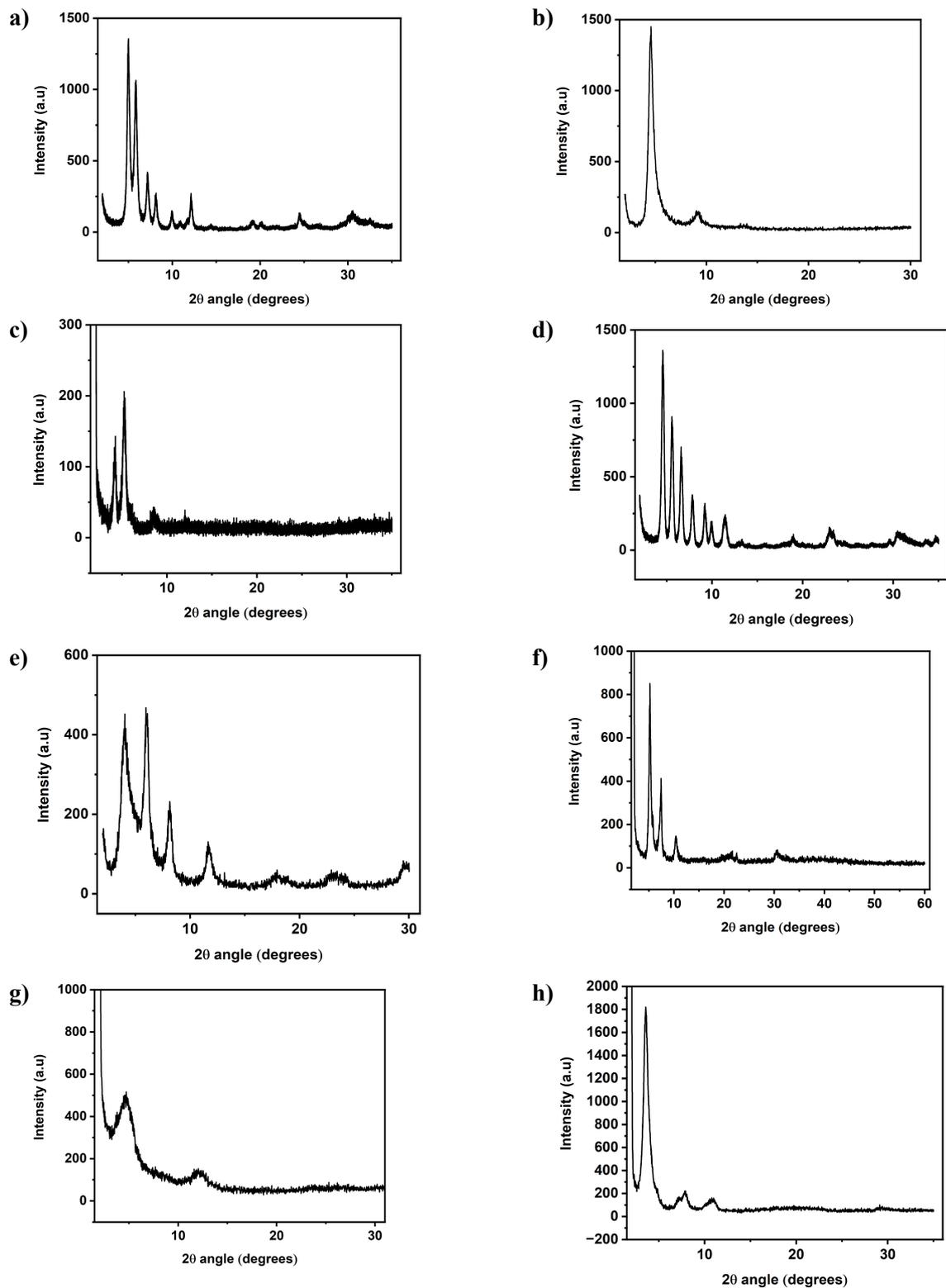
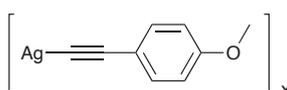
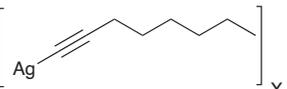
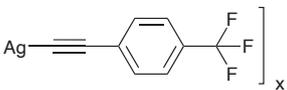
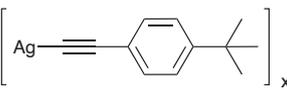
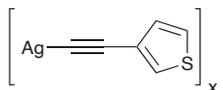


Figure S5: Powder X-Ray diffraction (PXRD) of a) AgTol b) AgAnisole c) AgOct d) AgtFTol e) Agt-Bu f) AgThio g) AgPyr h) AgTPA.

Table S1: Sample crystallinity and crystallite size calculated by Scherrer equation.

Compound	Crystallinity (%)	crystallite size (Å)
AgTol	85	305
AgAnisole	83	173
AgOct	76	427
AgTFol	88	270
Ag-Bu	83	250
AgThio	88	260
AgPyr	72	64
AgTPA	81	154

Table S2: XPS Elemental quantification. AgAnisole C/O ratio is 5.9 and O/Ag ratio is 1.3. The C1s XPS spectra indicates the presence of carbonate species explaining the relatively inaccurate elemental ratio ; AgTFol C/F is 2.33 and AgThio C/S is 4.37.

Compound	C	O	Ag	S	F	Si	C/Ag
	72.4	12.2	9.4	0.9	4.5	1.6	7.7
	81.4	2.4	15.6	0.9			5.2
	62.9	0.6	9.6		26.9		6.6
	87.9	1.9	10.3				8.5
	65.6	1.7	16.9	15	0.9	0.9	3.9

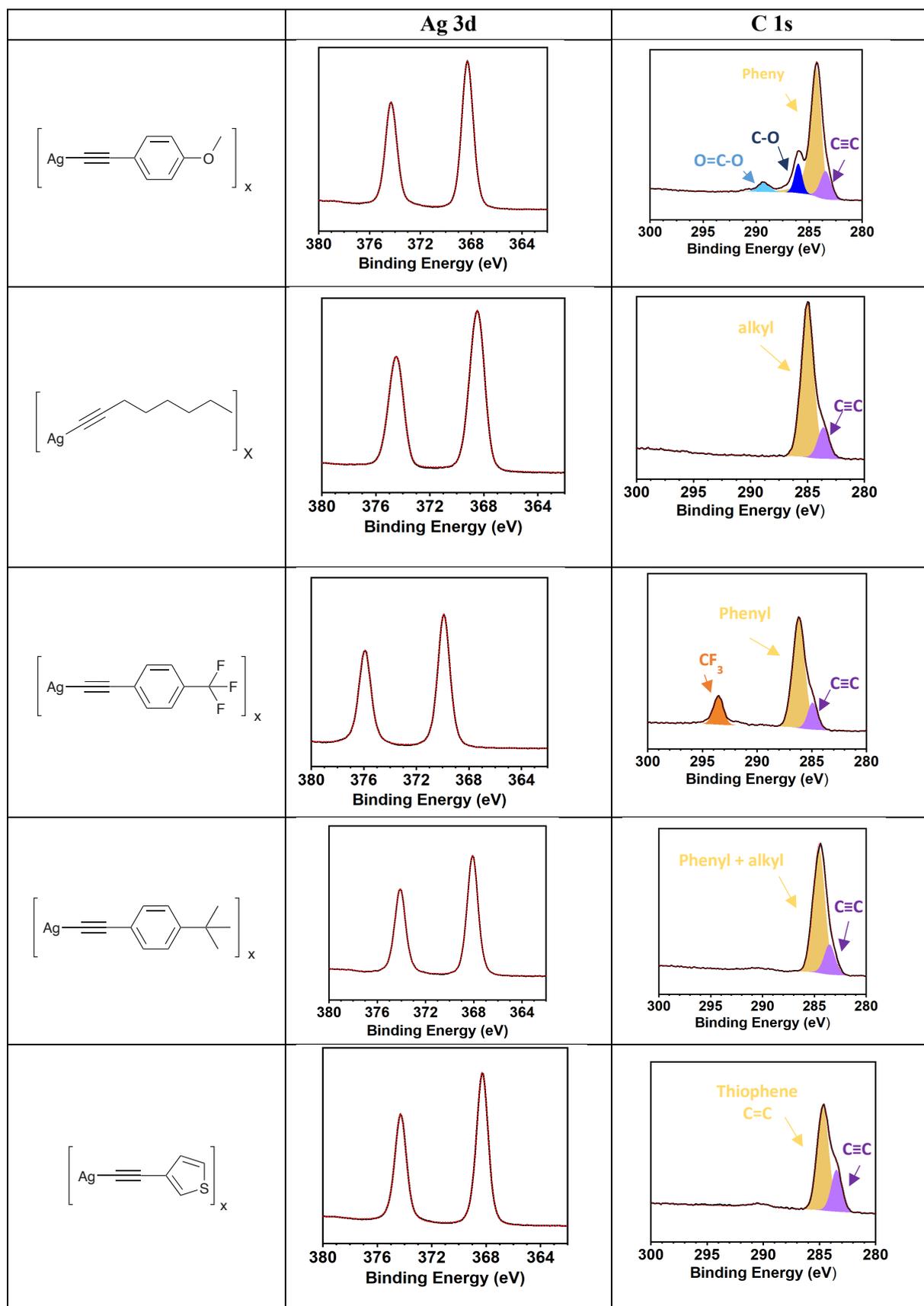


Figure S6 XPS spectra (Ag 3d and C1s regions) of *AgAnisole*, *AgOct*, *AgtFTol*, *Agt-Bu* and *AgThio*.

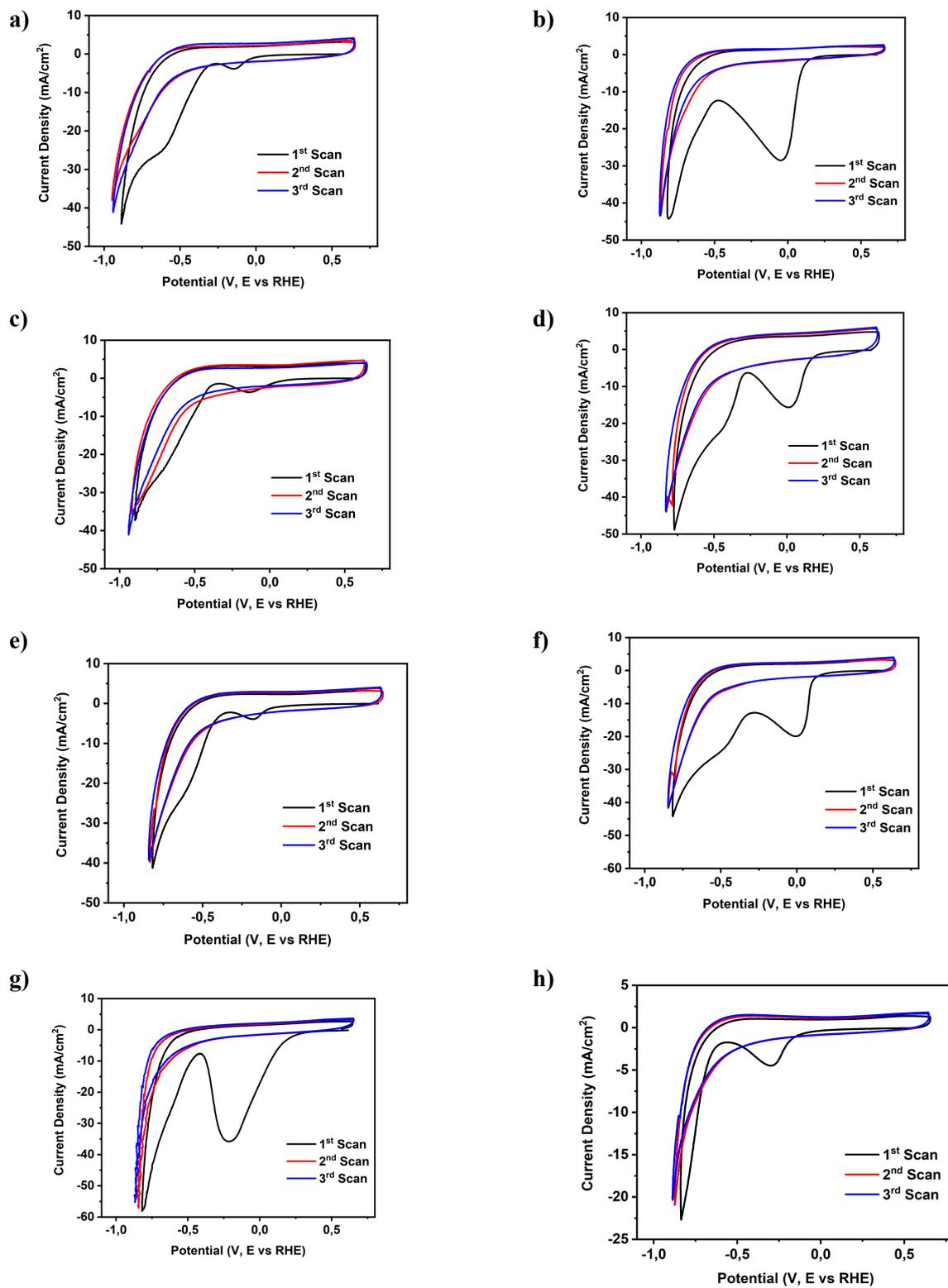


Figure S7: CV measurement at 100 mV/s (3 scans) on the GDE substrate in a N₂ saturated 1 M KHCO₃ solution. a) AgTol b) AgAnisole c) AgOct d) AgtFTol e) *Ag*t-Bu f) *Ag*Thio g) *Ag*Pyr h) *Ag*TPA

Table S3. MP-AES quantification (10 ppm solution in 3% HNO₃ prepared from a 1000 ppm solution in TFA: H₂O (1:3)) The results are obtained from a calibration curve of 6 points between 1 and 20 ppm made from a 1000 ppm AgNO₃ solution in 3% HNO₃ (R²=0.998). The measured value is in accordance with 1:1 complex being the major product

Compound	Ag content (mass%)
AgPh*	50.7
AgTol	46.3
AgAnisole	52.6
AgOct	66.4
AgtFTol	47.3
Agt-Bu	49.5
AgThio	54.0
AgPyr	42.9
AgTPA	33.9

Table S4. reduction peak potential integration, electroactive species and active silver loading calculations.

Compound	Potential (V vs RHE)	Q (mC)	Γ [Ag] (nmol)	active Ag (load%)
AgPh	-0.208	9.02	129	7
AgTol	-0.184	2.55	36.4	1.6
AgAnisole	-0.046	7.11	90	3.6
AgOct	-0.179	5.83	342	1.8
AgtFTol	0.024	5.83	34.2	1.4
Agt-Bu	-0.233	3.08	37.2	2
AgThio	-0.014	31.7	342	17
AgPyr	-0.215	98	1270	80
AgTPA	-0.270	6.93	226	18

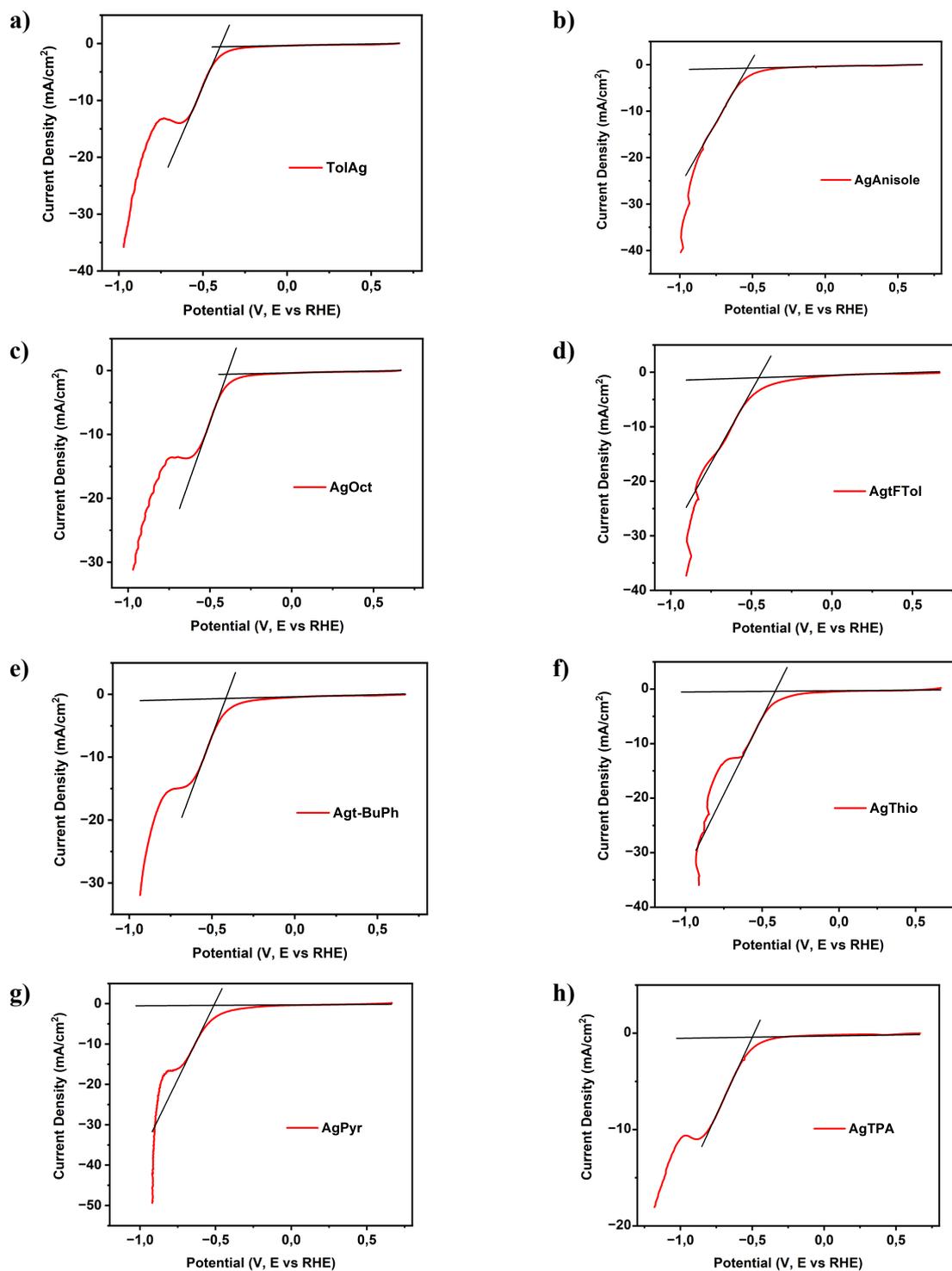
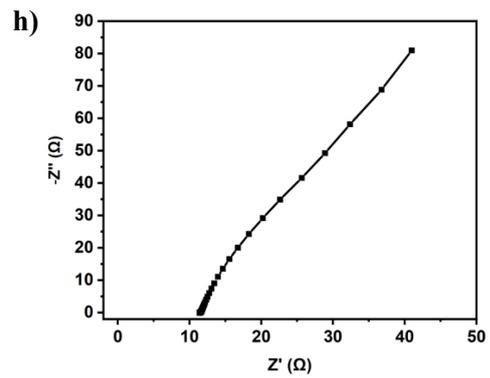
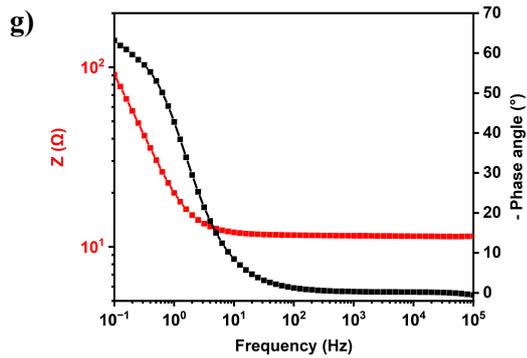
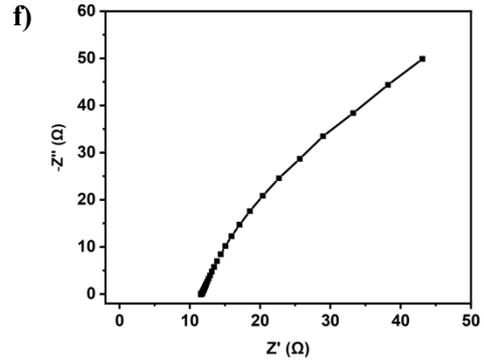
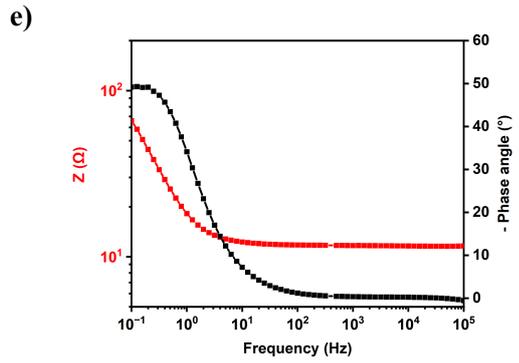
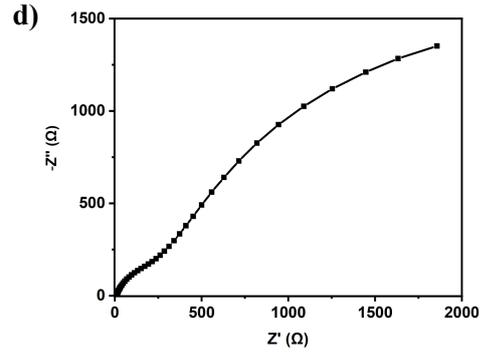
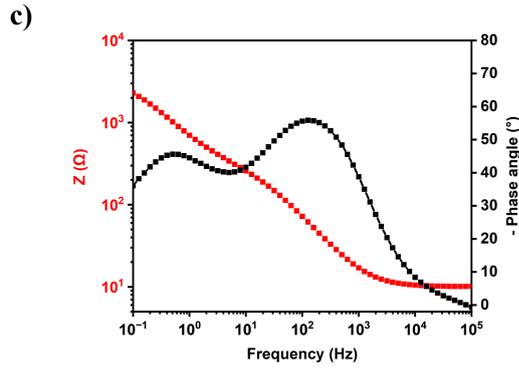
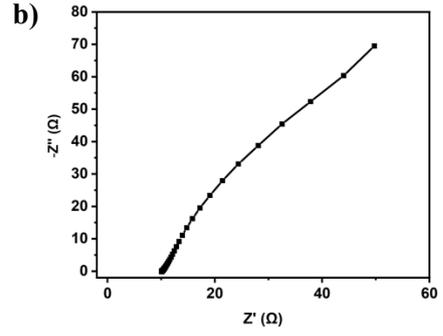
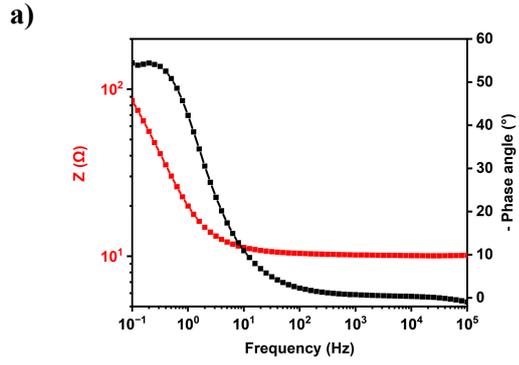


Figure S8. LSV measurement at 10 mV/s (2nd scan) of the deposited materials on GDE substrates in CO₂ saturated 1 M KHCO₃ solution **a)** AgTol **b)** AgAnisole **c)** AgOct **d)** AgtFTol **e)** *Agt-Bu* **f)** *AgThio* **g)** *AgPyr* **h)** *AgTPA*

Table S5. Onset potential and CO₂RR overpotentials. CO₂RR overpotentials were calculated from the thermodynamic -0.53 V vs SHE for CO₂ to CO conversion (converted as -0.069 V vs RHE).

Compound	Onset potential (V vsRHE)	CO ₂ RR Overpotential (V vsRHE)
AgPh*	-0,45	-0,38
AgTol	-0,41	-0,35
AgAnisole	-0,54	-0,47
AgOct	-0,40	-0,33
AgtFTol	-0,47	-0,40
Agt-Bu	-0,42	-0,35
AgThio	-0,42	-0,35
AgPyr	-0,52	-0,44
AgTPA	-0,50	-0,43



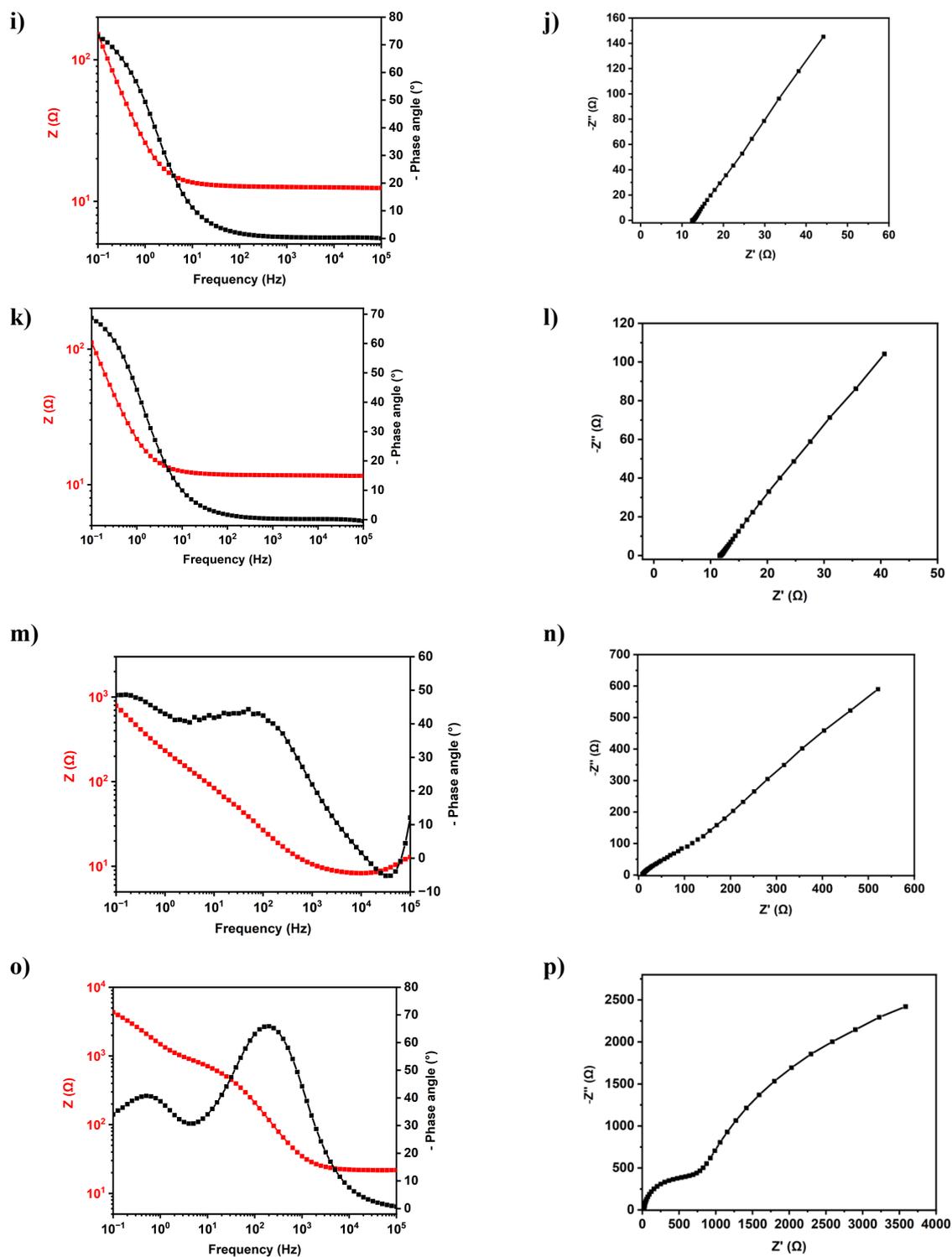
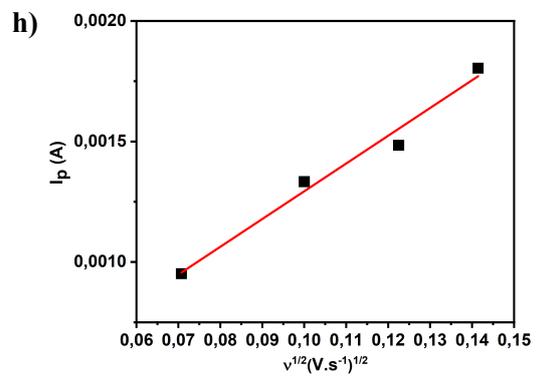
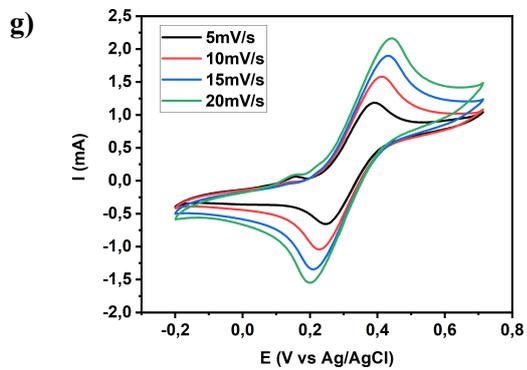
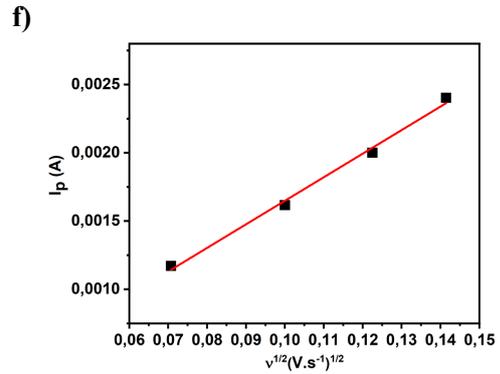
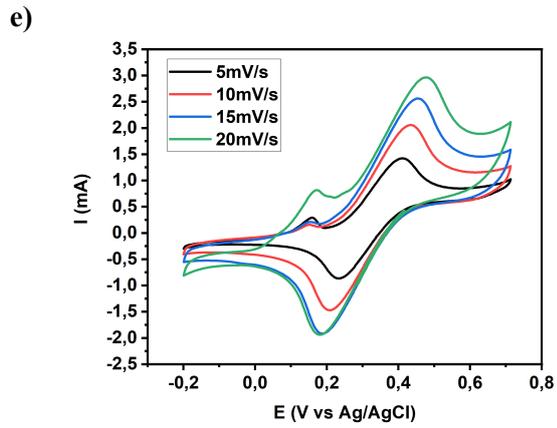
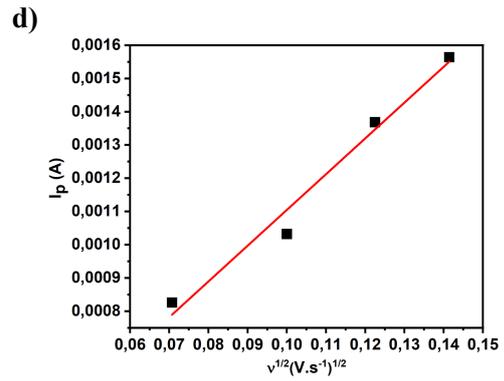
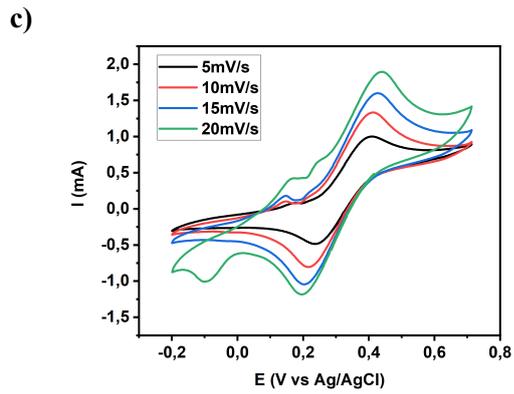
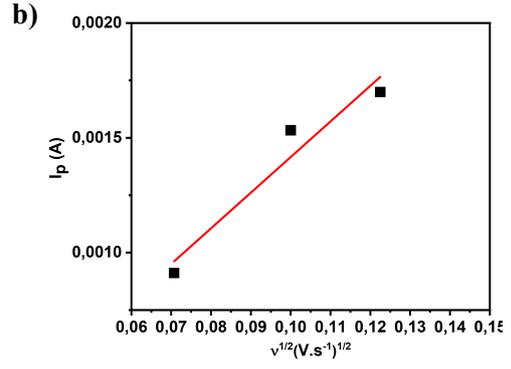
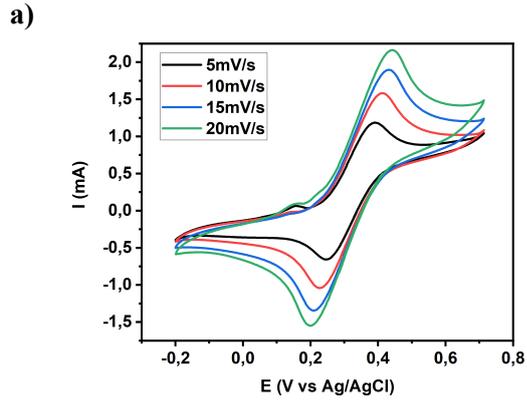


Figure S9. Electrochemical Impedance Spectroscopy (EIS) AgTol **a**) Bode plot **b**) Nyquist plot; AgAnisole **c**) Bode plot **d**) Nyquist plot; AgOct **e**) Bode plot **f**) Nyquist plot; AgtFTol **g**) Bode plot **h**) Nyquist plot; *Agt-Bu* **i**) Bode plot **j**) Nyquist plot; *AgThio* **k**) Bode plot **l**) Nyquist plot *AgPyr*; **m**) Bode plot **n**) Nyquist plot; *AgTPA* **o**) Bode plot **p**) Nyquist plot.



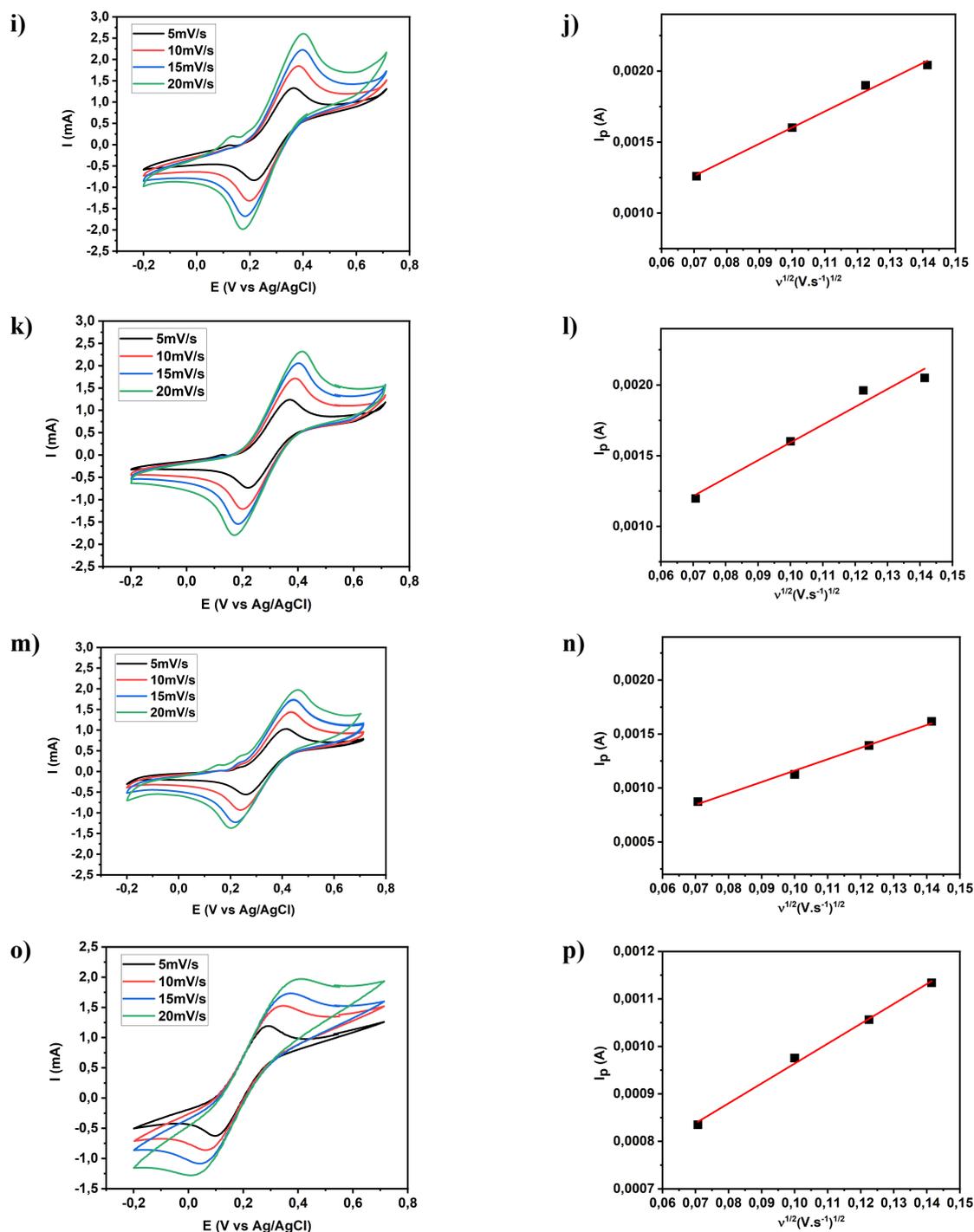


Figure S10. Cyclic voltammograms (CV) of a 25 mM potassium ferrocyanide in a 0.1M KCl solution using an AgAnisole electrode at various scan rates (5, 10, 15 and 20mV/s) and peak current as a function of the square root of the scan rate variation. AgTol **a)** CV scans **b)** fitted curve; AgAnisole **c)** CV scans **d)** fitted curve; AgOct **e)** CV scans **f)** fitted curve AgtFTol **g)** CV scans **h)** fitted curve *AgT-Bu* **i)** CV scans **j)** fitted curve *AgThio* **k)** CV scans **l)** fitted curve *AgPyr* **m)** CV scans **n)** fitted curve *AgTPA* **o)** CV scans **p)** fitted curve.

Table S6. The ECSA is calculated from the slope of the plot using the Randles-Sevcik equation.

Compound	ECSA (cm ²)
AgPh*	0.72
AgTol	1.17
AgAnisole	0.81
AgOct	1.31
AgtFTol	0.87
Agt-Bu	0.86
AgThio	0.96
AgPyr	0.80
AgTPA	0.30

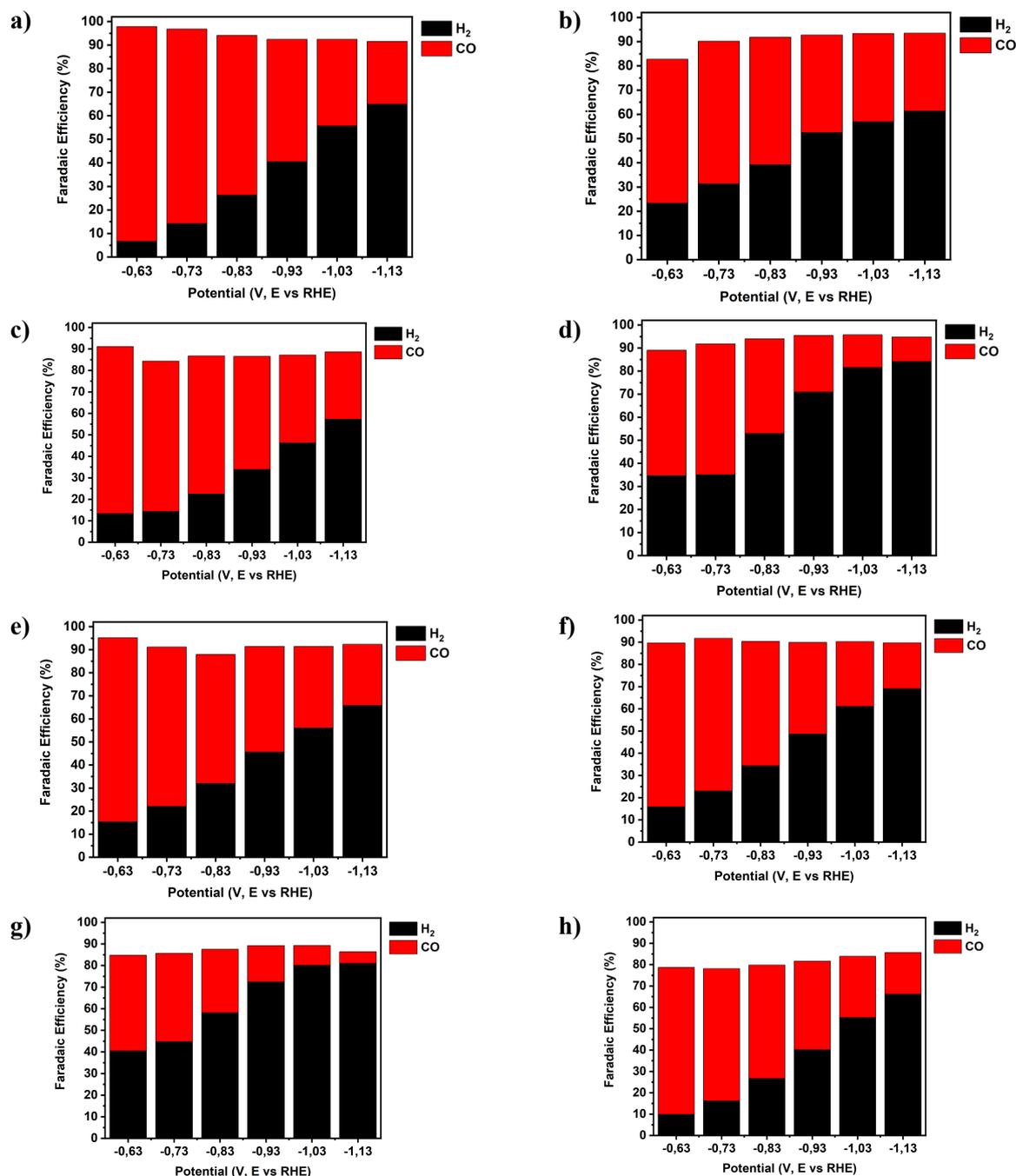


Figure S11. Faradic efficiencies (FE) from direct GC quantification of 15 min long Chronoamperometry (CA) of the deposited materials on the GDE substrate in a CO₂ saturated 1 M KHCO₃ between -0.63 and -1.13 applied potentials (V, E vs RHE) with a step of 0.1 V. **a)** AgTol **b)** AgAnisole **c)** AgOct **d)** AgtFTol **e)** Agt-Bu **f)** AgThio **g)** AgPyr **h)** AgTPA

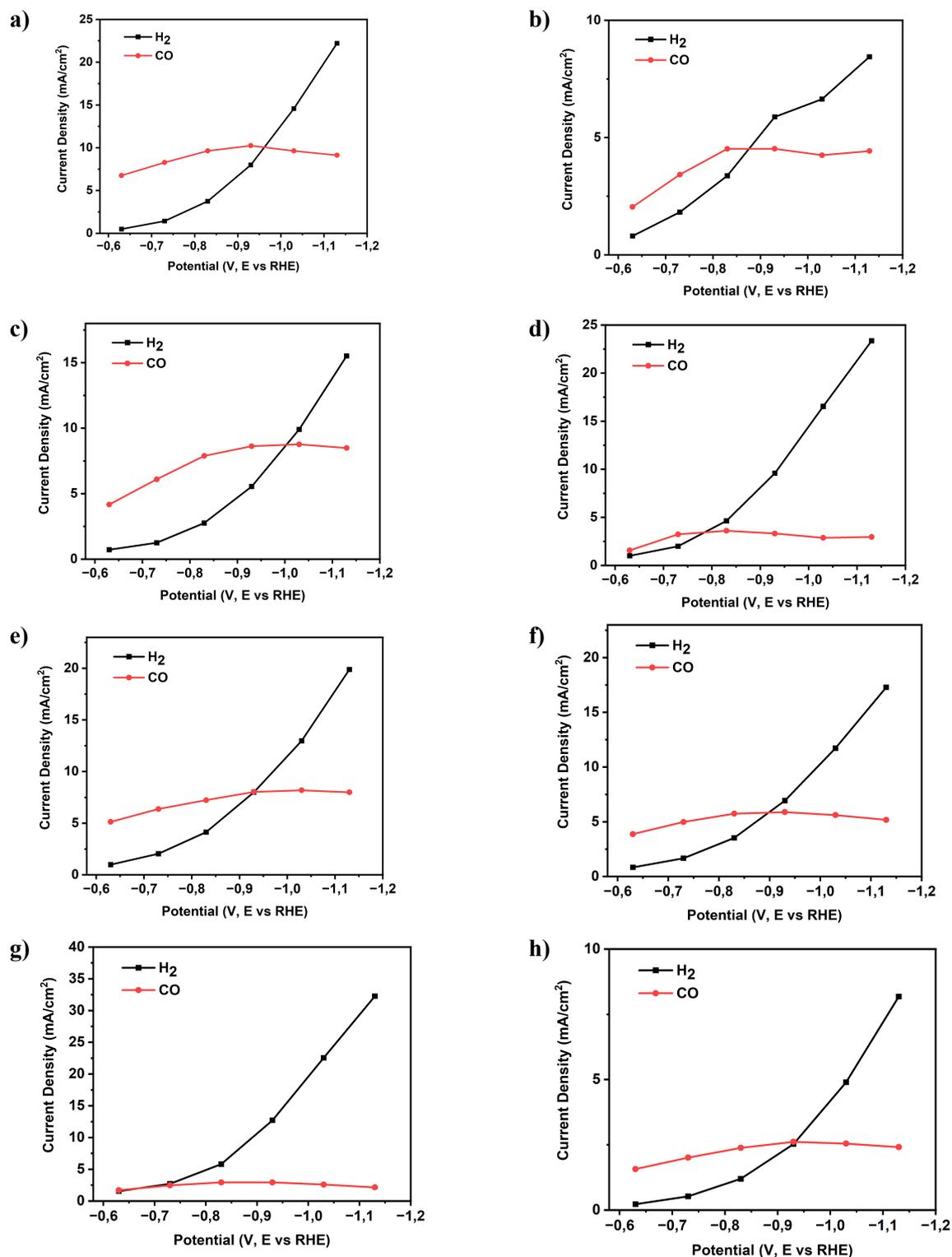


Figure S12. CO and H₂ partial Current densities between -0.63 and -1.13 applied potentials (V, E vs RHE) with a step of 0.1 V (15min chronoamperometry) in the 1M KHCO₃ aqueous solution **a)** AgTol **b)** AgAnisole **c)** AgOct **d)** AgtFTol **e)** Agt-Bu **f)** AgThio **g)** AgPyr **h)** AgTPA

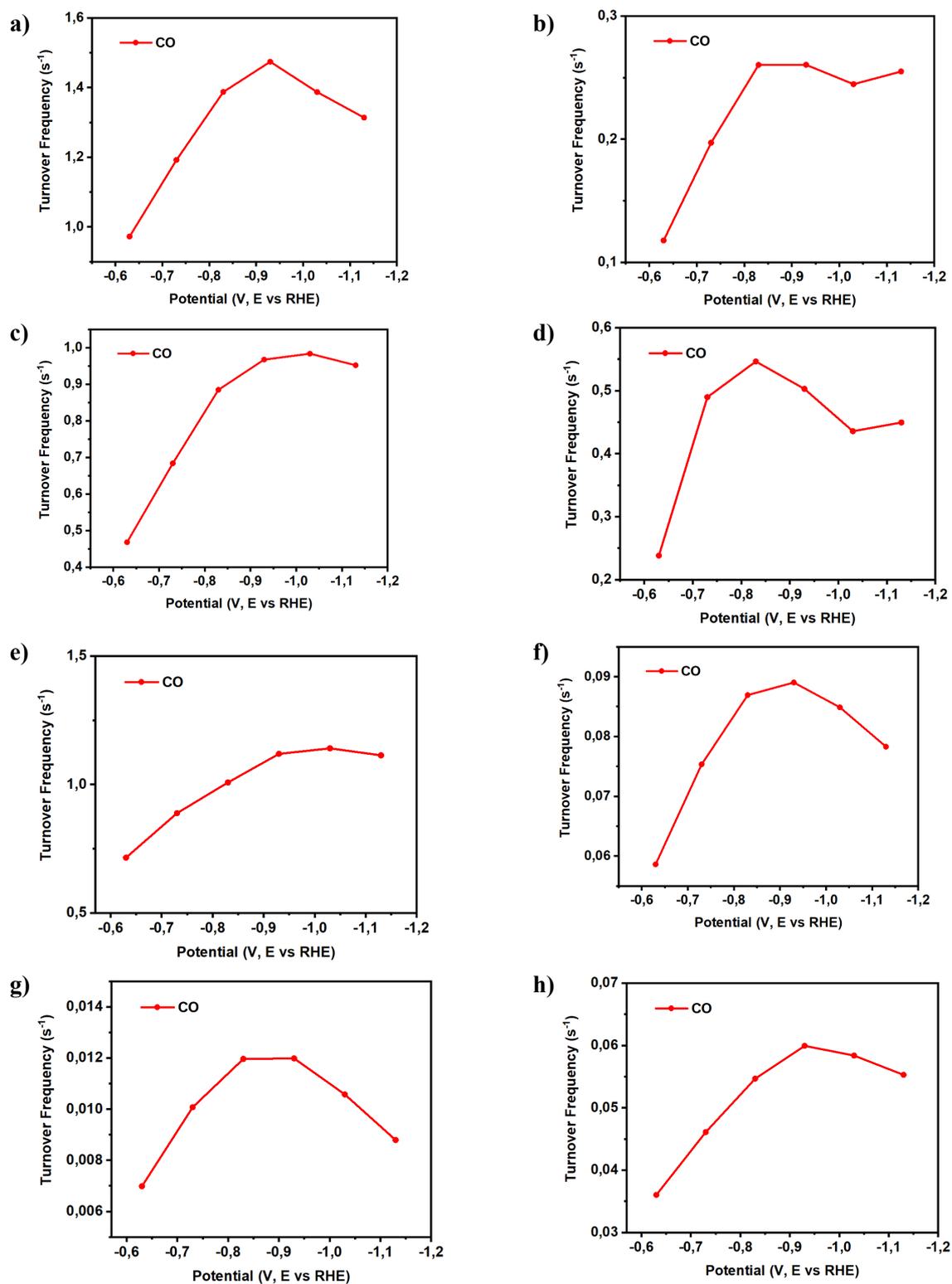


Figure S13. Calculated TOF variation for CO_2RR a) AgTol b) AgAnisole c) AgOct d) AgtFTol e) Agt-Bu f) AgThio g) AgPyr h) AgTPA

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