Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information.

Hydrosilylation and electroreduction of CO_2 using a Zirconocene Hydride Catalyst

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Content

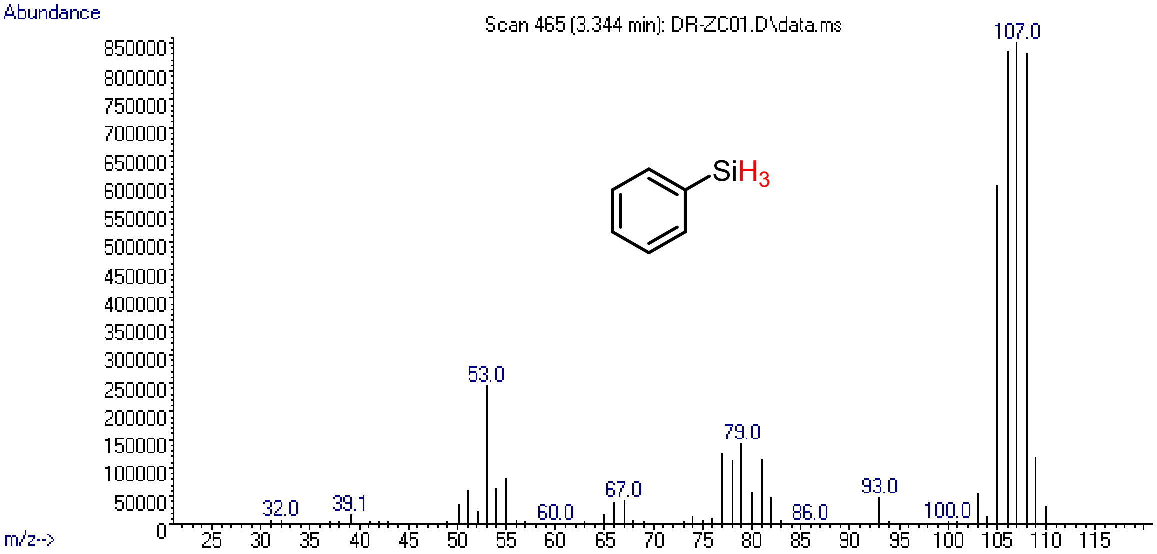


Figure 1S. MS for Phenylsilane

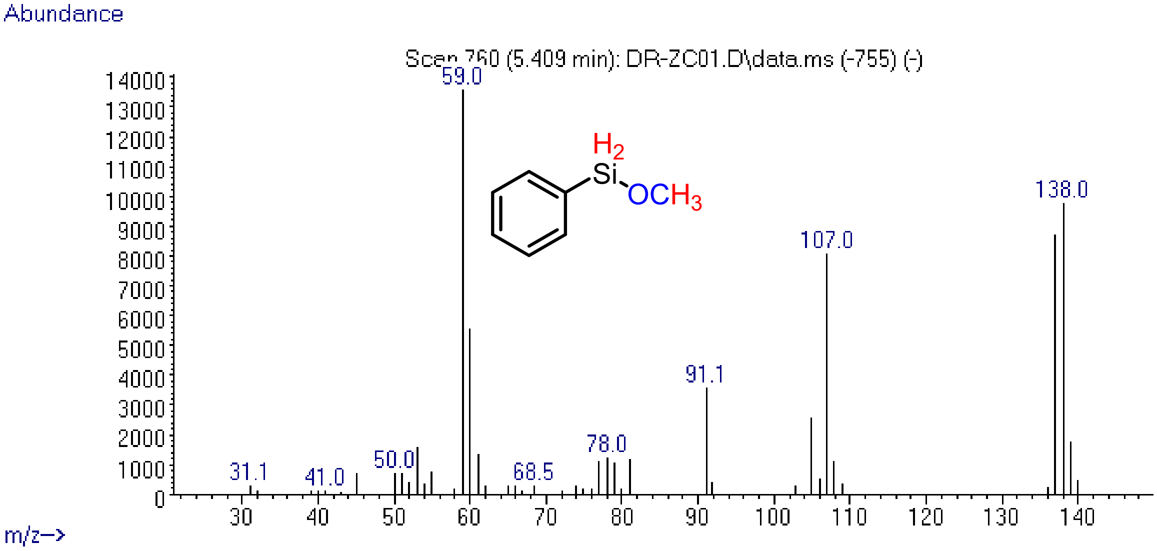


Figure 2S. MS for Methoxy(phenyl)silane

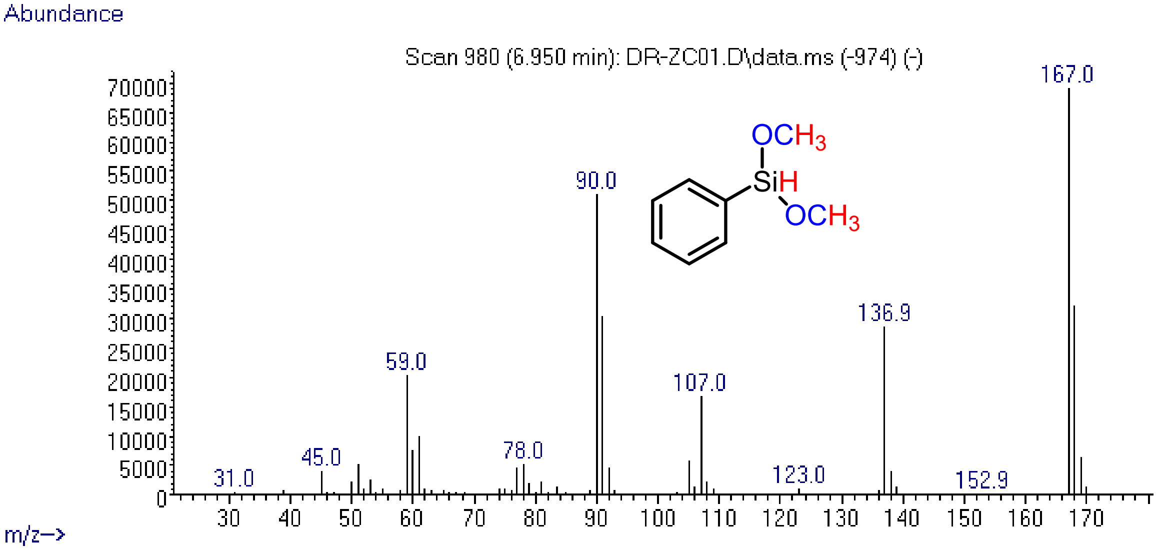


Figure 3S. MS for dimethoxy(phenyl)silane

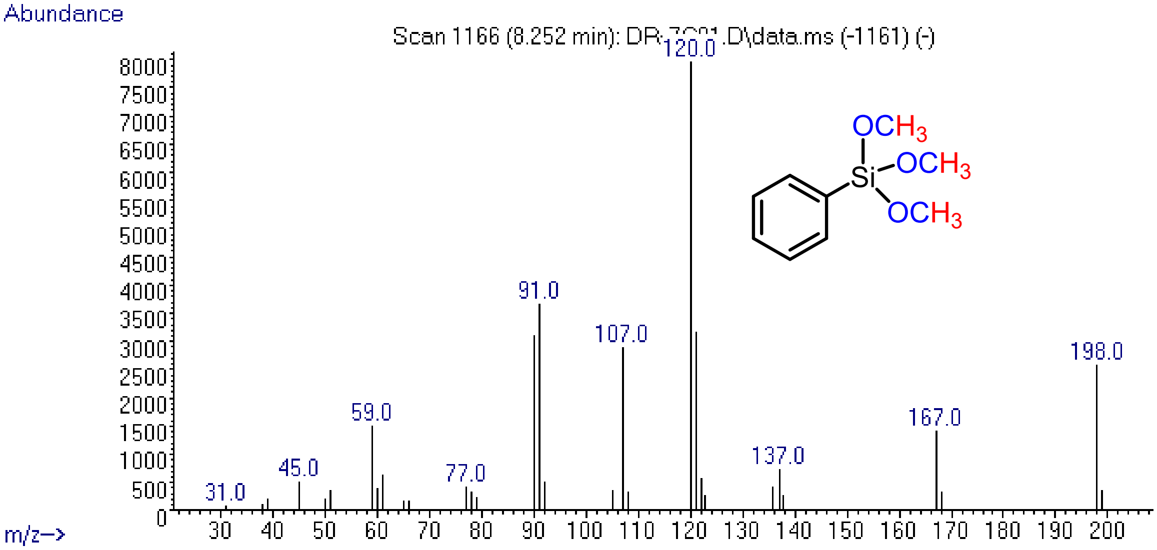


Figure 4S. MS for trimethoxy(phenyl)silane

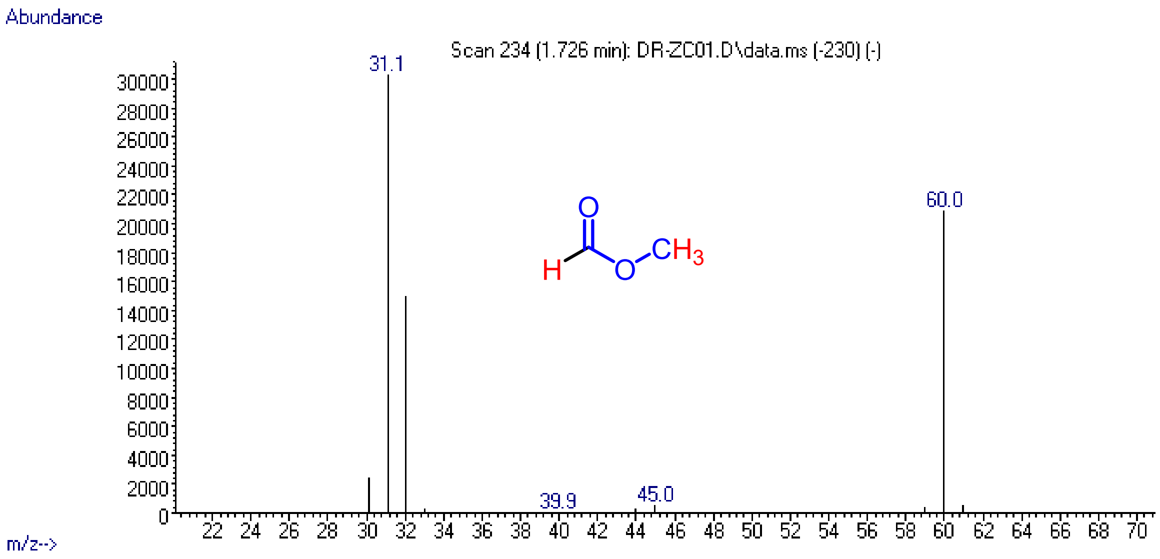


Figure 5S. MS for Metyl-formate

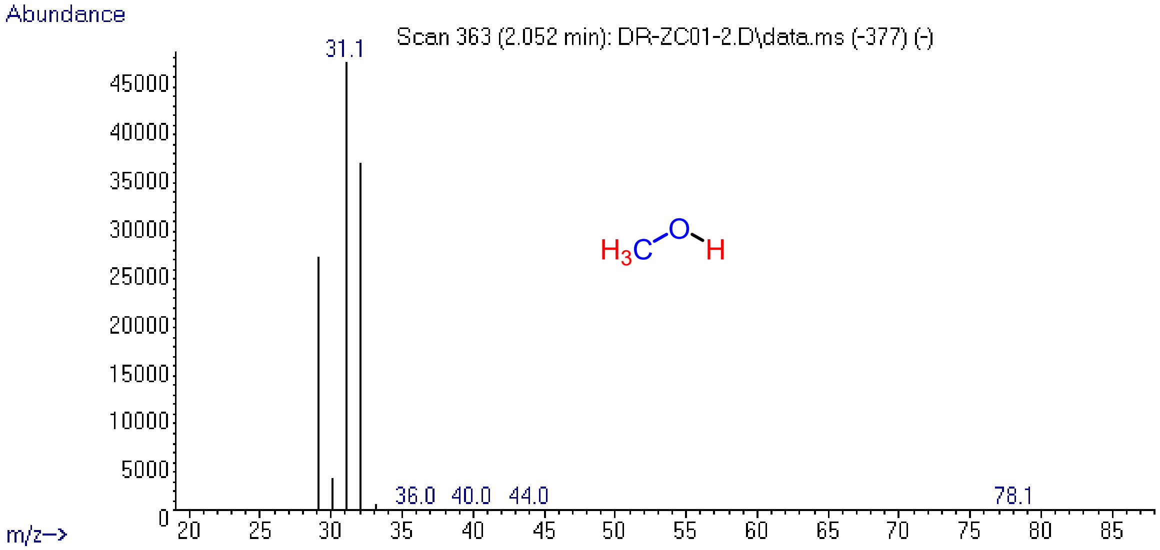


Figure 6S. MS for Methanol

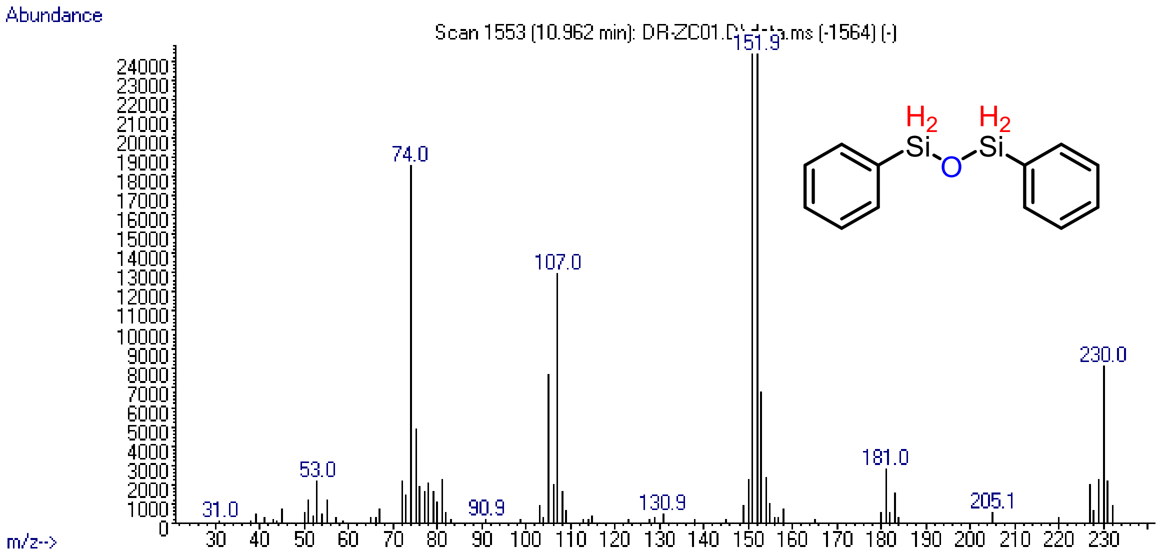


Figure 6S. MS for 1,3-diphenyldisiloxane

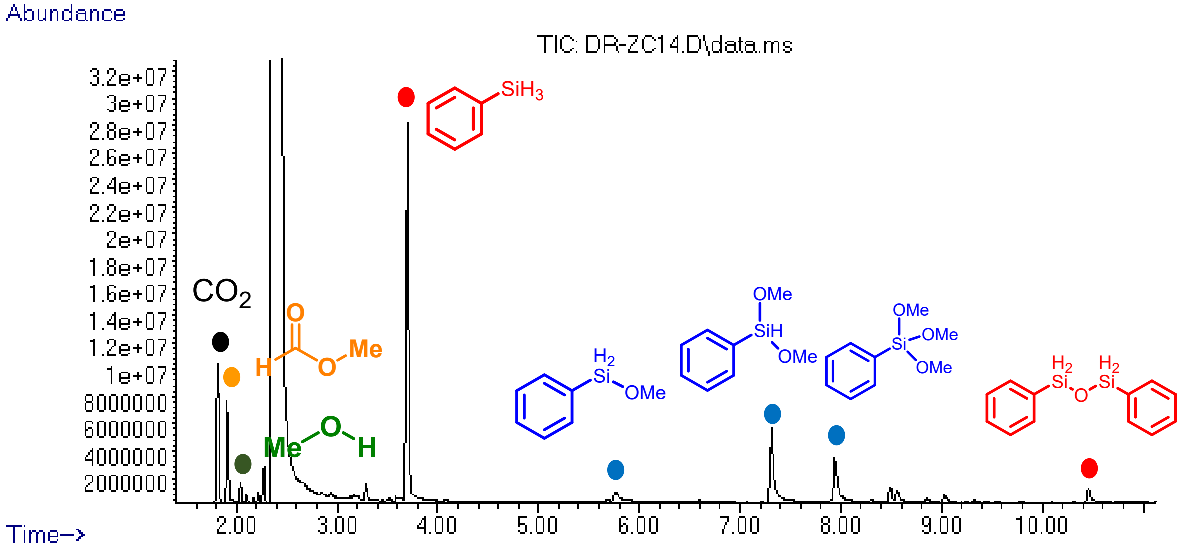


Figure 7S. Typical GC for crude mixture for CO2 hydrosilylation reaction. 100 °C, 24 h in THF.

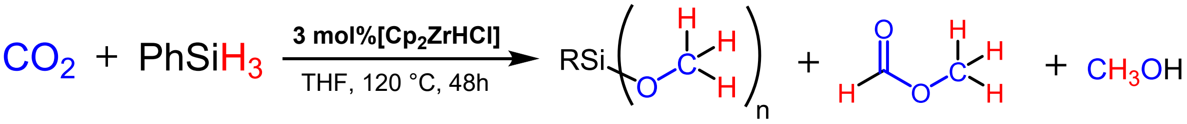


Table 1S. Promotors used for CO_2 hydrosilylation reaction[a]

Entry	**Promotor**	**%SiOMe**	**% FM**	**% MeOH**	**% Conv**
1	KF	31	5	4	40
2	TBAF	nd	nd	nd	>99
3	$B(Et)_3$	68	8	2	80
4	H_2O	nd	traces	traces	<1

[a] Reactions were performed using 0.012 mmol $[Cp_2ZrHCl]$ with 0.401 mmol $PhSiH_3$ at 120 °C under 100 psi CO_2. Yields and conversion were determined by GC-MS

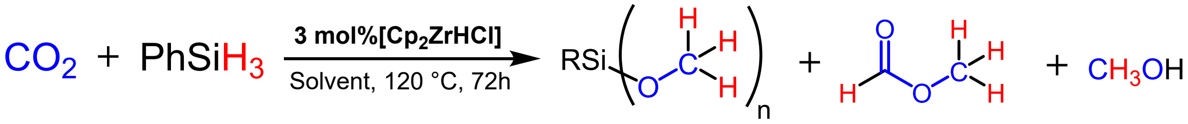


Table 2S. Solvents used for CO_2 hydrosilylation reaction[a]

Entry	Solvent	%SiOMe	% FM	% MeOH	% Conv
1	THF	92	5	3	>99
2	Dioxane	4	1	0	5
3	Toluene	nd	nd	nd	0
4	ACN	nd	nd	nd	>99

[a] Reactions were performed using 0.012 mmol [Cp_2ZrHCl] with 0.401 mmol $PhSiH_3$ at 120 °C under 100 psi CO_2. Yields and conversion were determined by GC-MS

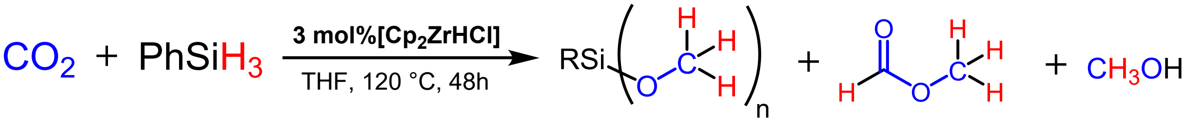


Table 3S. Different pressures of CO_2 at the hydrosilylation reaction[a]

Entry	CO_2 (psi)	%SiOMe	% FM	% MeOH	% Conv
1	100	87	8	2	97
2	80	72	25	1	98
3	50	27	65	4	96

[a] Reactions were performed using 0.012 mmol [Cp_2ZrHCl] with 0.401 mmol $PhSiH_3$ at 120 °C for 48 h. Yields and conversion were determined by GC-MS

Quantification of methanol at the optimized reaction

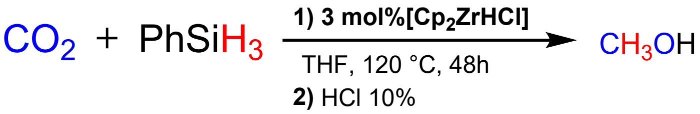
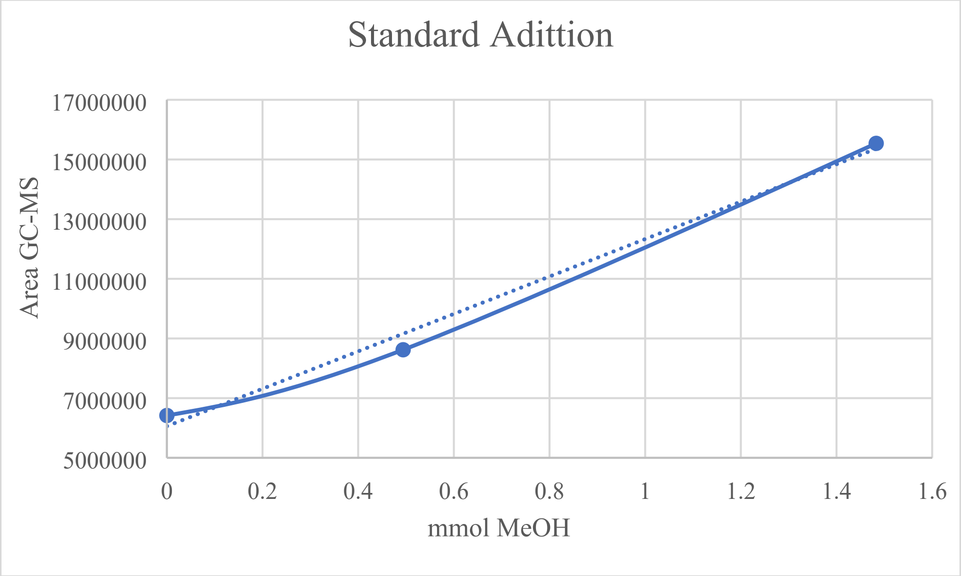


Table 5S. Addition of MeOH to the crude reaction

Addition	mmol MeOH	Area
0	0	6417951
20 uL	0.494	8621609
60 uL	1.483	15539820

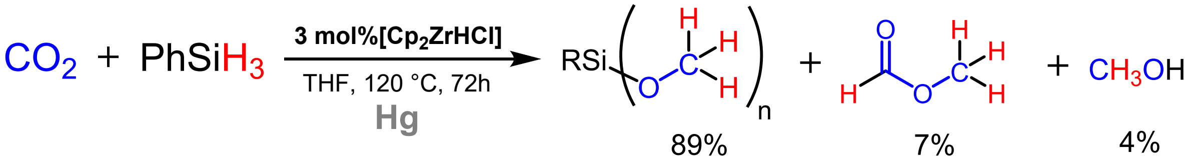


The negative intercept on the x-axis corresponds to the amount of the analyte in the test sample. This value is given by b/a, the ratio of the intercept and the slope of the regression line.

Moles of MeOH in the crude reaction: 0.031mmol

$$\%Yield_{MeOH} = \frac{0.9662\ mmol}{1.203\ mmol\ H^-} \times 100 = 80.31\% \approx 80\%$$

Hg drop test of the optimized reaction



Reaction of CO_2 with $[Cp_2ZrHCl]$

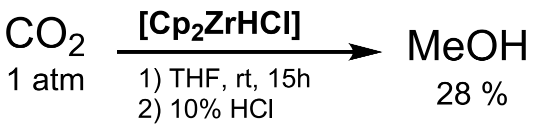
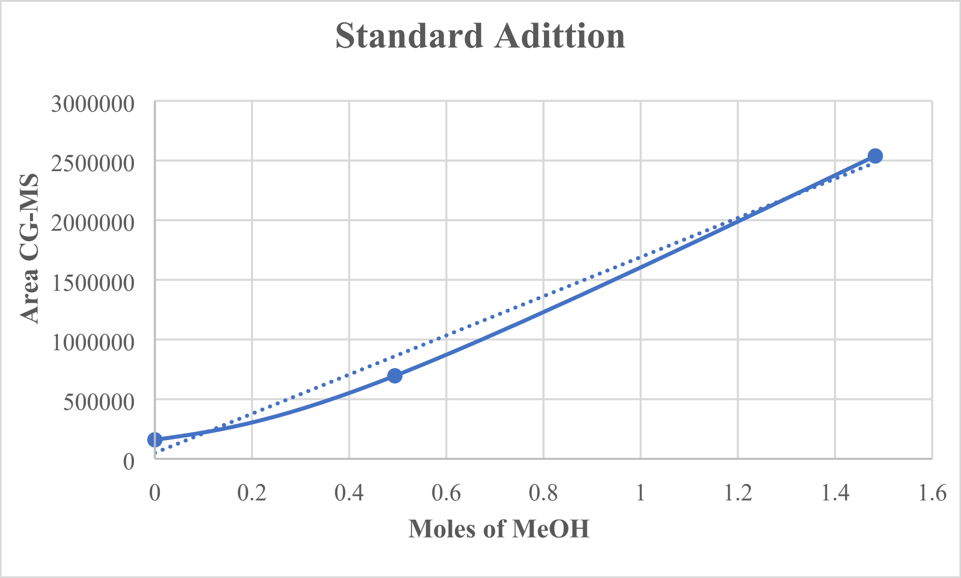


Table 5S. Addition of MeOH to the crude reaction

Addition	mmol MeOH	Area
0	0	159584
20 uL	0.494	695799
60 uL	1.483	2538090



Graphic 1S. Addition Standard (MeOH) to the crude reaction

The negative intercept on the x-axis corresponds to the amount of the analyte in the test sample. This value is given by b/a, the ratio of the intercept and the slope of the regression line.

Moles of MeOH in the crude reaction: 0.031mmol

$$\%Yield_{MeOH} = \frac{0.030mmol}{0.1146mmol} \times 100 = 26.18\% \approx 26\%$$

Figure 9S. ^{1}H-NMR of the reaction of CO_2 with $[Cp_2ZrHCl]$

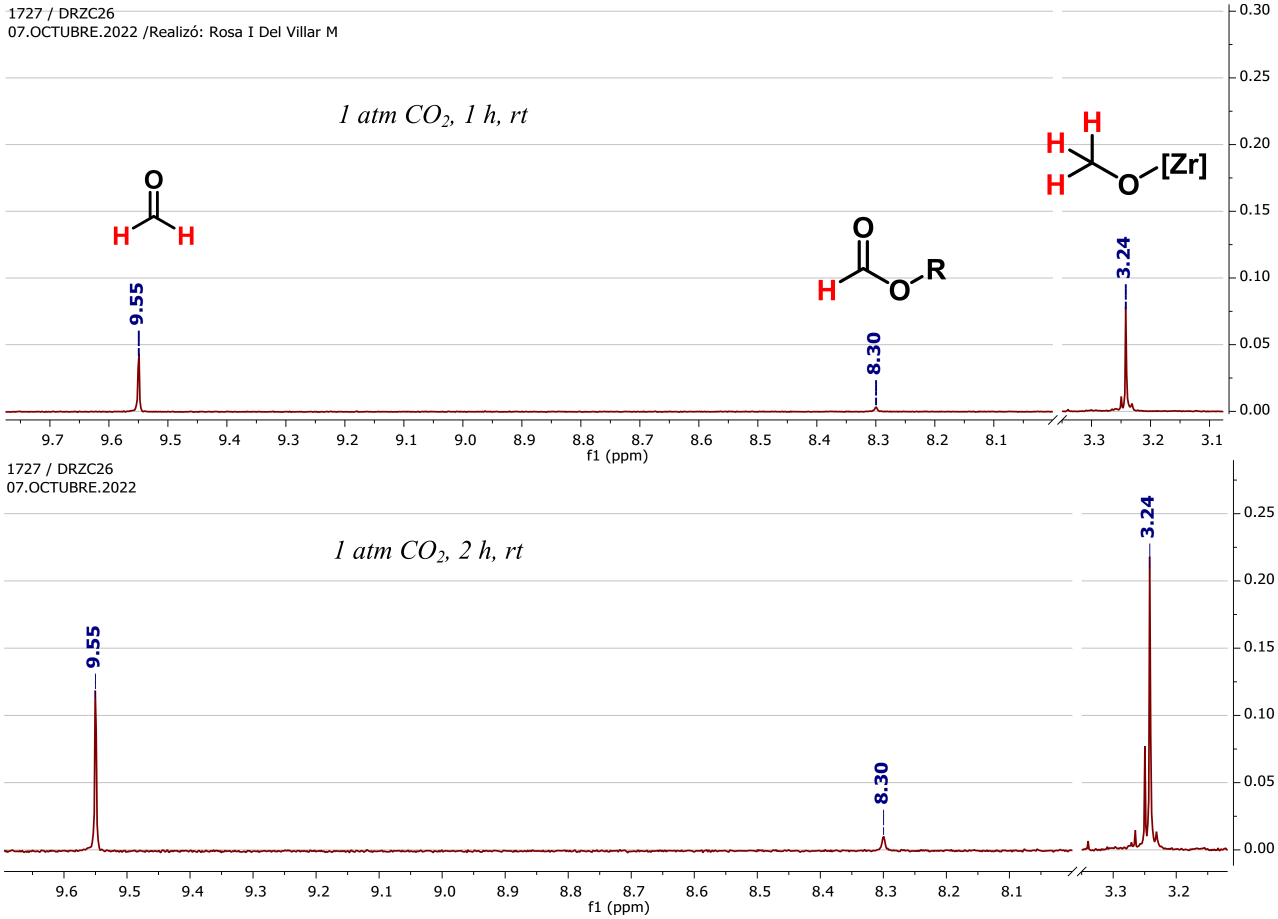


Figure 10S. ^{13}C-NMR of the reaction of CO_2 with $[Cp_2ZrHCl]$

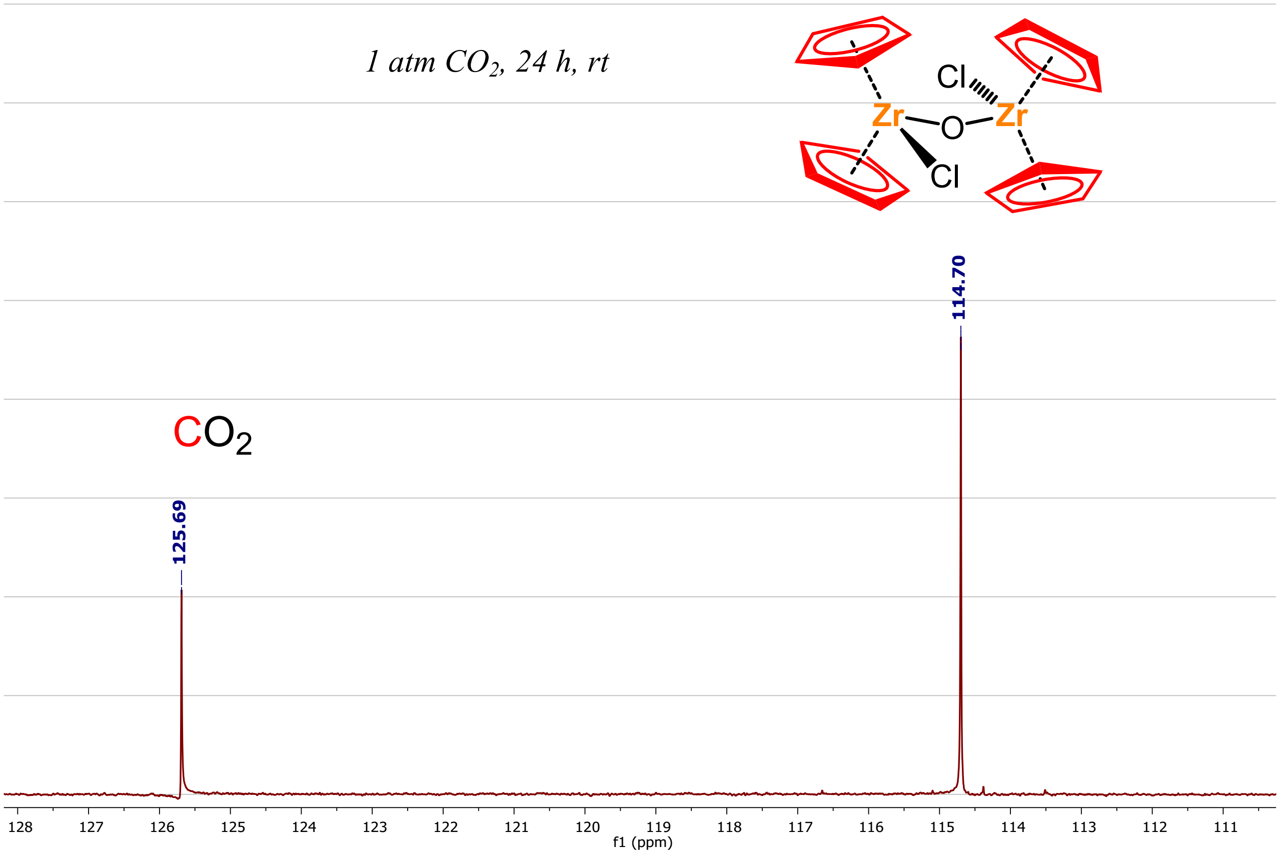


Figure 11S. Cyclic voltammetry of [Cp_2ZrHCl] in argon

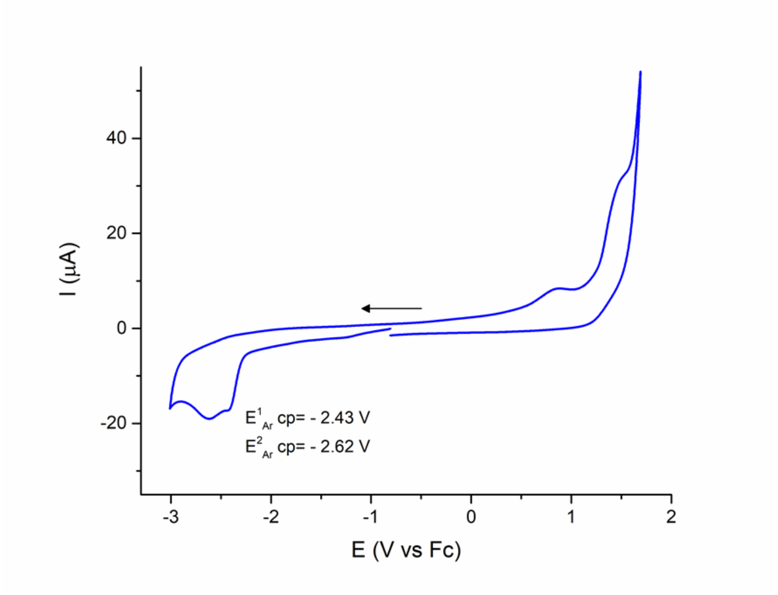


Figure 12S. Cyclic voltammetry of [Cp_2ZrHCl] with $PhB(OH)_2$

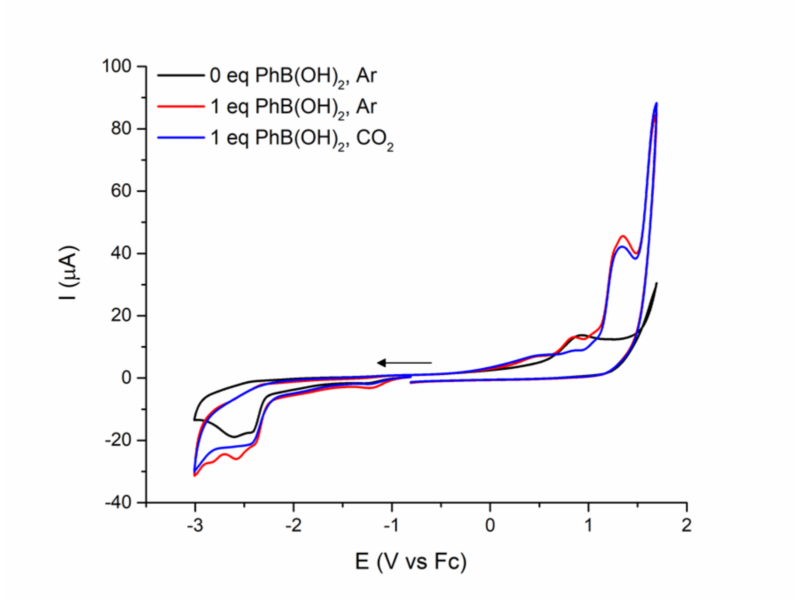


Figure 13S Cyclic voltammetry of [Cp_2ZrHCl] with H_2O

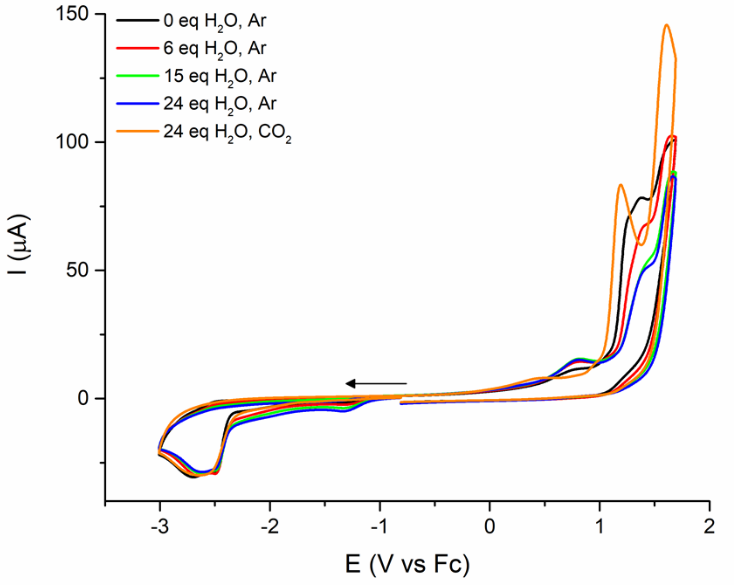


Figure 14S Cyclic voltammetry of [Cp_2ZrHCl] with AcOH

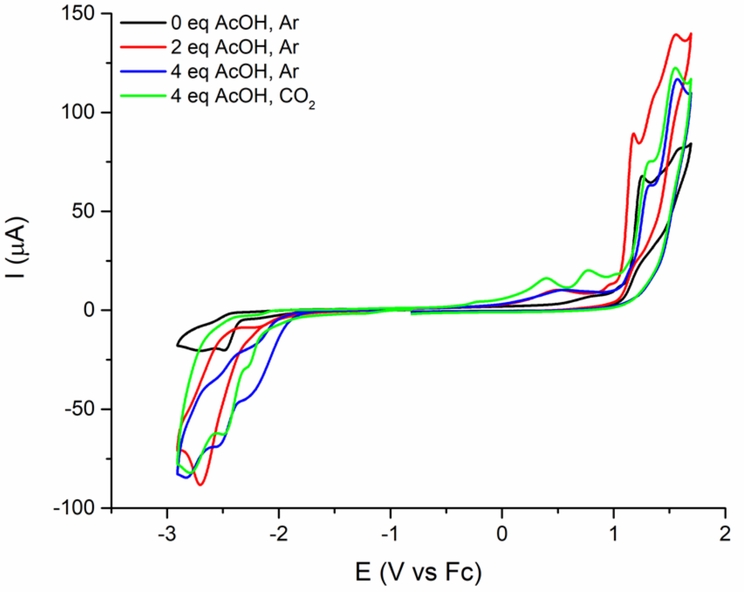
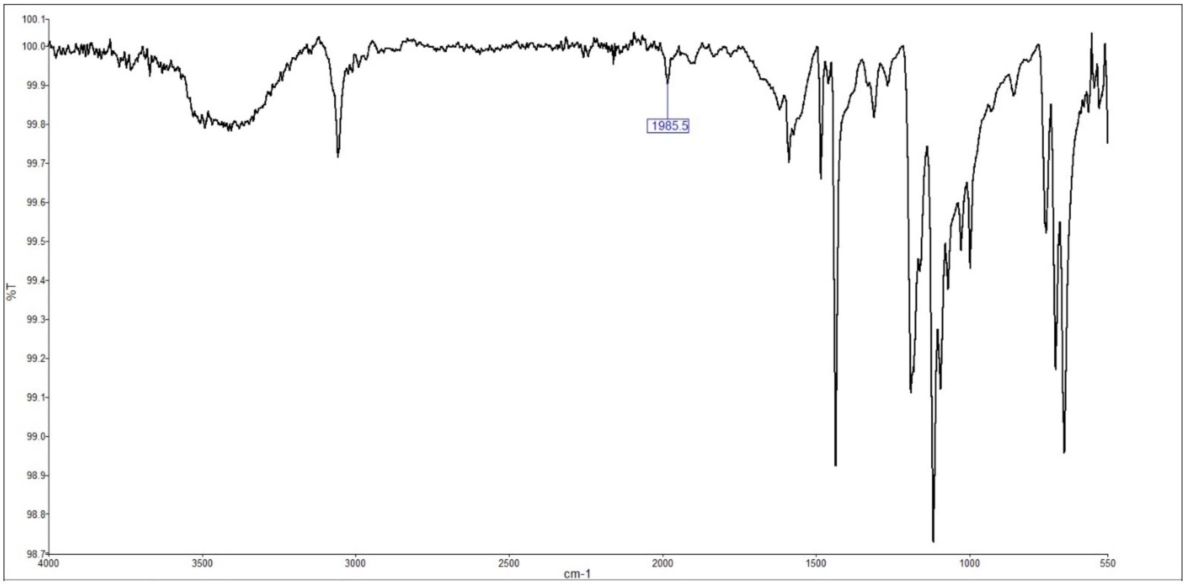
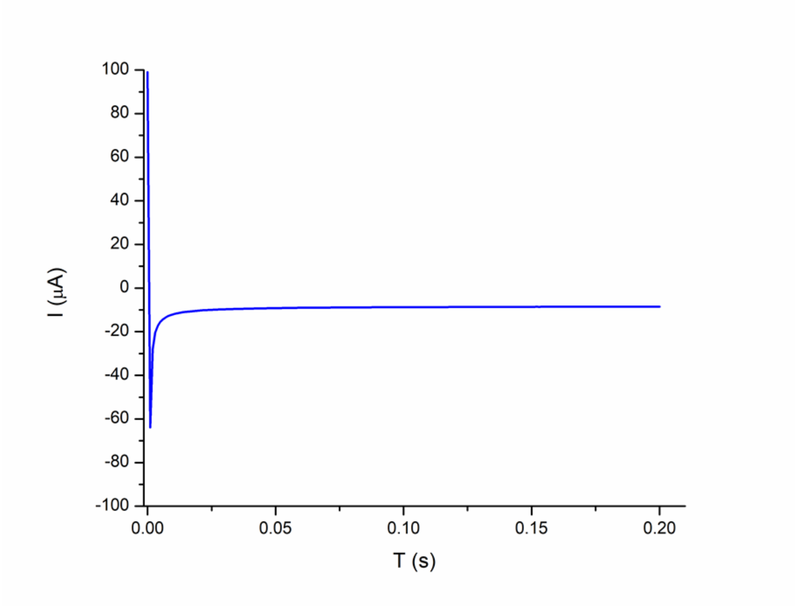


Figure 15S. FTIR resulting from the reaction of Wilkinson's reagent with the outlet gas of the chronoamperometry.



Calculation of Faradic Efficiency



An approximate calculation of the faradaic efficiency (FE) was made with the data obtained from chronoamperometry (equation 1).[1] The estimated proportion of Wilkinson's catalyst containing CO was 6.7%.

$$FE\,(\%) = {(n_{pro} \times n_e^{CO} \times F)}/{Q} \qquad \text{Ec. 1}$$

Where n_{pro} are the moles of product, $n_e{}^{CO}$ is the number of electrons for CO, F is a constant (96485 C mol-1) and Q is the total charge that passes during electrolysis.

$$J(mA * cm^{-2}) = \frac{I}{A} \qquad \text{Ec. 2}$$

$$J = -2.13\ mA * cm^{-2}$$

Where I = -0.064 mA, this was a value at the start of chronoamperometry, A = 0.03 cm^2 at -2.8 V.

Being FE_{CO} = 8.3%, with current density J = -2.13 mA cm_2 at -2.8 V. It is estimated that the calculated FE is below the real value of the process, due to the limitations of the CO quantification method. Likewise, the amount of H_2 generated is currently unknown, so selectivity data is not included.

References

(1) N. Eliaz, E. Gileadi, Physical Electrochemistry – Fundamentals, Techniques, and Applications, 2nd Edition, Wiley-VCH, 2019

Figure 16S. GC for the reaction mixture of chronoamperometry with $PhCO_2H$

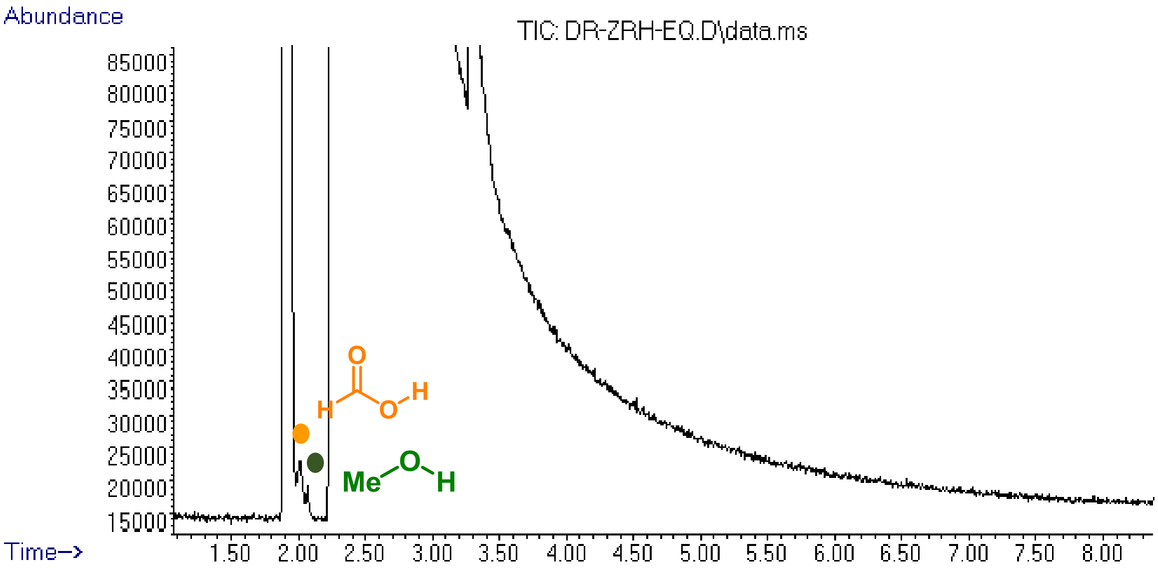


Figure 17S. MS for Formic Acid

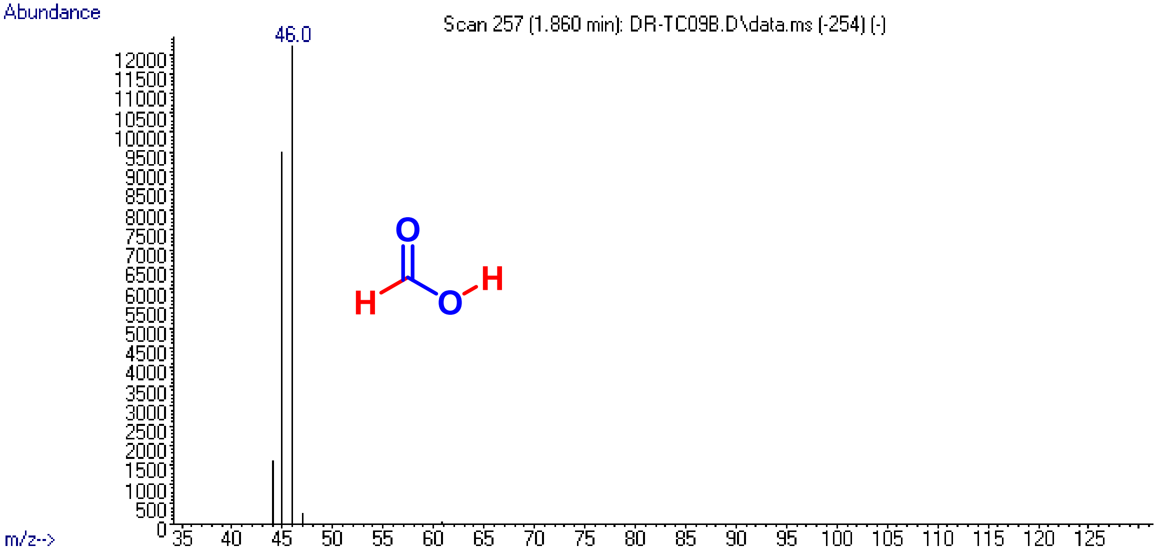


Figure 18S. Full spectrum of ^{1}H-NMR of the reaction of CO_2 with $[Cp_2ZrHCl]$

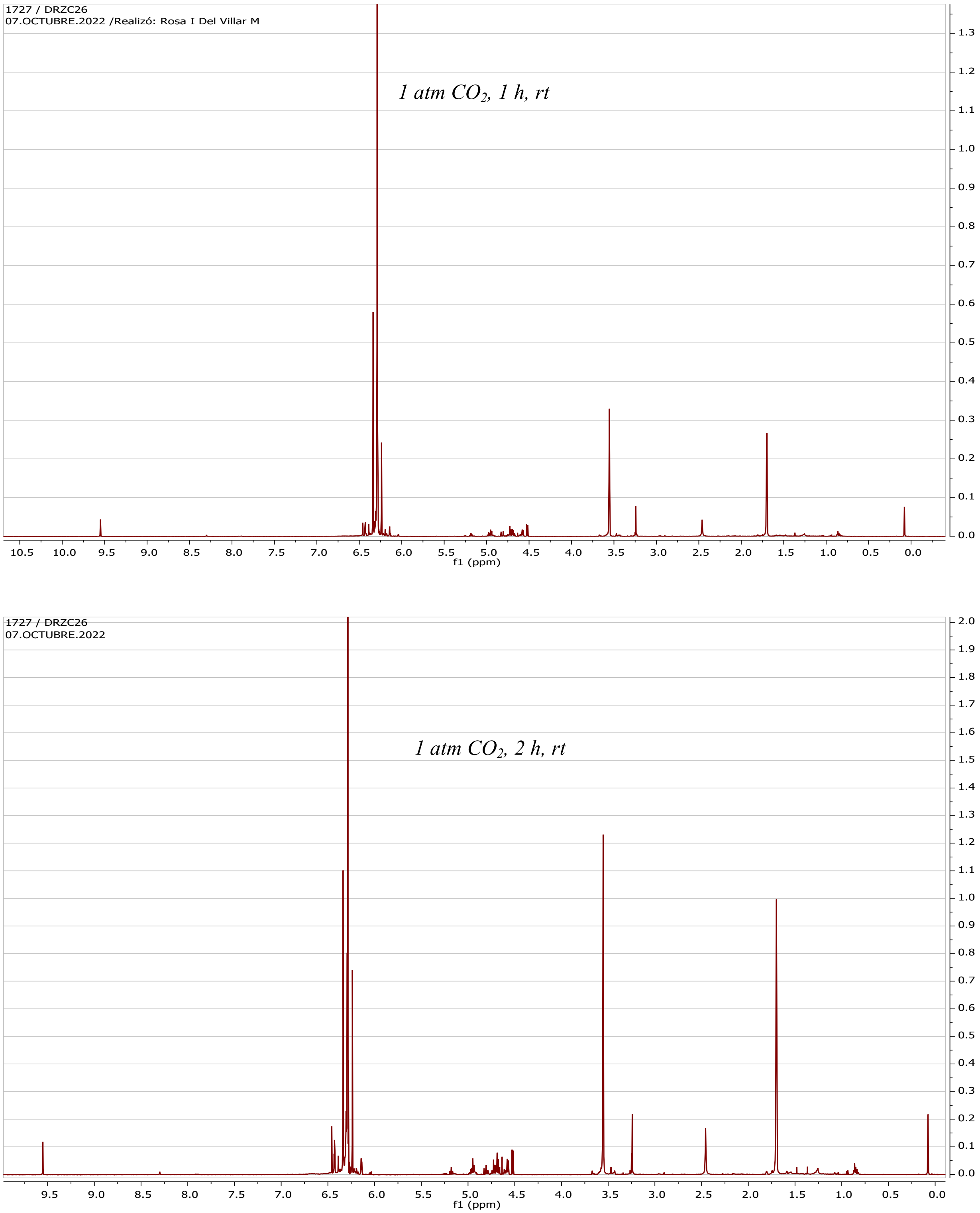


Figure 19S. Electrochemical control experiments in absence of [Cp_2ZrHCl]