Supporting information for

Multi-step oxidative carboxylation of olefins with carbon dioxide combining electrochemical and 3D printed flow reactors

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Table of Contents

1. Experimental details

1.1. Materials

All reagents and solvents used were commercially available: Glycidyl methacrylate (97%, Aldrich), Pentaerythritol-tetraacrylate (PETA) (>99%, Aldrich), phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide (97%, Aldrich), ink (ELEGOO translucent LCD UV-Curing), styrene oxide (97%, Aldrich), styrene, 4-(trifluromethyl)styrene (98%, Aldrich),, 4-(methoxy)styrene (97%, Aldrich), tetrabutylammonium chloride (TBA.Cl) (97%, Aldrich) and tetrabutylammonium bromide (TBA.Br) (99%, Aldrich). All the solvents were used as received from Scharlab.

1.2. General characterization protocols

Fourier Transform Infrared (FT-IR) spectra were acquired with a Pike single-reflection ATR diamond/ZnSe accessory in a JASCO FT/IR-4700 instrument.

Thermal gravimetric analysis was performed on TGA-DSC3 analyser from Mettler Toledo. Samples for TGA analysis were heated in an inert atmosphere up to 800 ^{o}C with a heating rate of 10 ^{o}C/min.

3D printers: A DLP printer (Asiga PICO2) and a MSLA printer (Elegoo mars 2 Pro), were the 3D printers employed. The DLP printing system was equipped with a LED light source operating at 405 nm. The Elegoo Mars 2 Pro printer was equipped with a 2560 × 1620 mono liquid crystal display (LCD), illuminating at 405 nm. The CAD files were designed and converted to STL-type files using SolidWorks CAD software. The digital light processing fabrication in both printers began by slicing the 3D CAD model into individual 2D images for projecting onto the photocurable liquid. For Asiga PICO2 printer, the additive manufacturing software used to create slices was Asiga Composer. For the Elegoo Mars 2 Pro 3D printer the slicer software employed was ChituBox.

The conversion of CO_2 cycloaddition reactions was calculated by ^{1}H NMR spectra, carried out using a Bruker Avance III HD 300 or 400 spectrometer (300 or 400 MHz for ^{1}H).

1.3. 3P printing methodology

3DP-SIL composition: The printer tank was filled with 50.0 mL a monomeric solution containing 60% by weight of GMA, 40% by weight of PETA, and 2w% of the photoinitiator (Phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide) regarding the monomers, 0,1 phr Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyhydrocinnamate) and 0,1 phr Methyl Red (only for the R2 reactor). The 3D structure was obtained according to the digital design downloaded in the printer (column R1 and R2). Once the 3D structure was printed, the object was extracted from the platform, washed with IPA (3 x 25 mL) and cured at 60 ºC for 15 min under UV lamp.

Printing Parameters of 3DP objects: All the objects were printed in Elegoo mars 2 Pro, in vertical position. **R1:** column length: 11.5 cm, column diameter: 0.95 cm, 18 s exposure time, 22 s bottom exposure time, total printing time: 17 h. **R2:** column length: 11.5 cm, column diameter: 0.95 cm, 18 s exposure time, 22 s bottom exposure time, total printing time: 17 h.

2. Results

2.1 Oxidation reaction

Table S1. Evaluation of solvent and electrolyte for epoxidation reaction. [a]

Ent.	Solvent (vol%)	Electrolyte	I (mA)	Aldehyde	Epoxide	Halohydrin
1	$DMSO_{80}/ H_2O_{20}$	$TEA.BF_4$	20	-	-	-
2	$Acetone_{80}/ H_2O_{20}$	$TEA.BF_4$	20	✓	-	-
3	$Acetone_{80}/ H_2O_{20}$	$TEA.BF_4$	27	✓	-	-
4	THF_{50}/ H_2O_{50}	$TEA.BF_4$	20	✓	-	-
5	THF_{50}/ H_2O_{50}	$TEA.BF_4$	27	✓	-	-
6	THF_{80}/ H_2O_{20}	$TEA.BF_4$	20	✓	-	-
7	THF_{80}/ H_2O_{20}	$TEA.BF_4$	27 [b]	✓	-	-
8	$MeCN_{80}/ H_2O_{20}$	$TEA.BF_4$	20	✓	-	-
9	$MeCN_{80}/ H_2O_{20}$	$TEA.BF_4$	27	✓	-	-
10	**$MeCN_{80}/ H_2O_{20}$**	**TBA.Br**	**20**	**-**	✓	**-**
11 [c]	$MeCN_{80}/ H_2O_{20}$	TBA.Br	20	-	✓	✓

[a]*Reaction conditions:* 0.5 mmol of styrene,1 mmol of electrolyte, 10 mL of solvent, 0.05 mL/min flow rate, maximum power set to 12 V. Carbon sheet as working electrode and a stainless steel as the counter electrode. [b] Degradation. [c] Membrane reactor.

Table S2. Evaluation of electrode for epoxidation reaction. [a]

Entry	Working electrode	Electrolyte	Conv. (%)	Conv. Epoxide (%)	Conv. Halohydrin (%)
1	Flexible graphite	TBA.Br	100	72	16
2	Glassy carbon	TBA.Br	100	80	10
3	Glassy carbon	TBA.Cl	100	50	-

[a]*Reaction conditions:* 0.5 mmol of styrene,1 mmol of electrolyte, 10 mL of solvent (MeCN 80%/ H_2O 20%), 0.05 mL/min flow rate, 20 mA. Stainless steel as the counter electrode.

2.2 3D printed structures and characterization

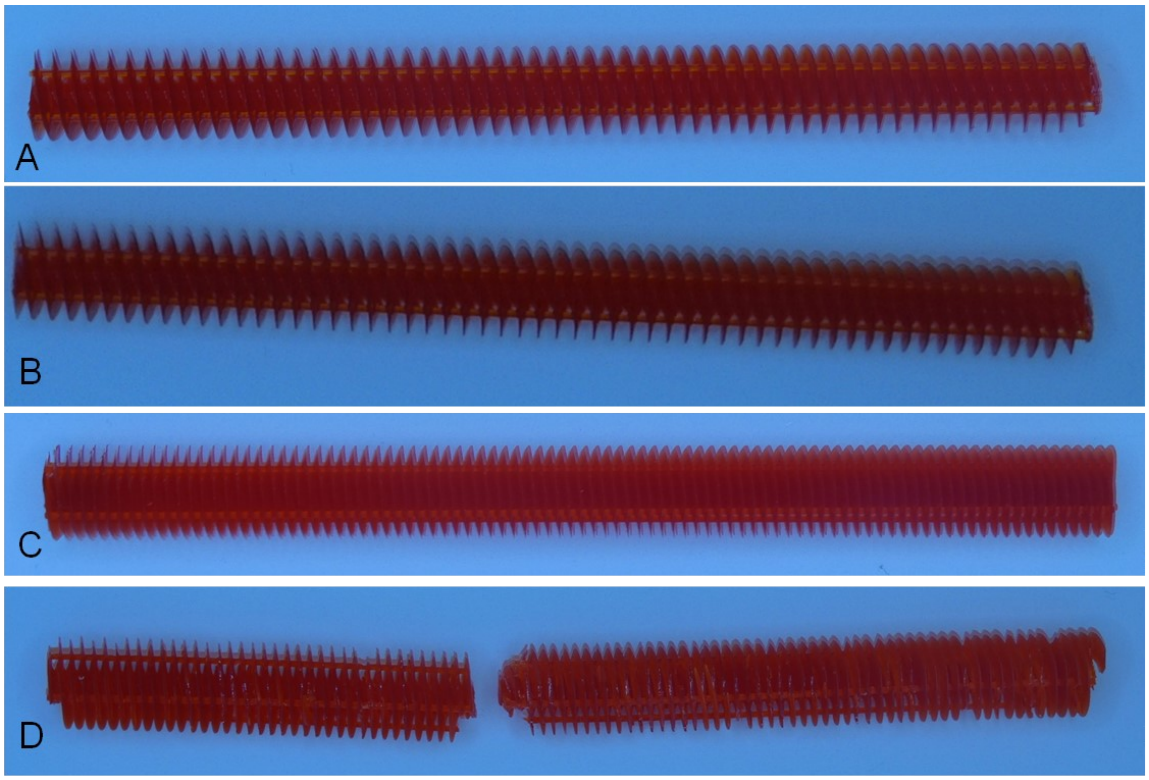

Figure S1. Photos of the reactors before and after reaction: A) Design R1 before reaction; B) Design R1 after reaction C) Design R2 before reaction; D) Design R2 after reaction.

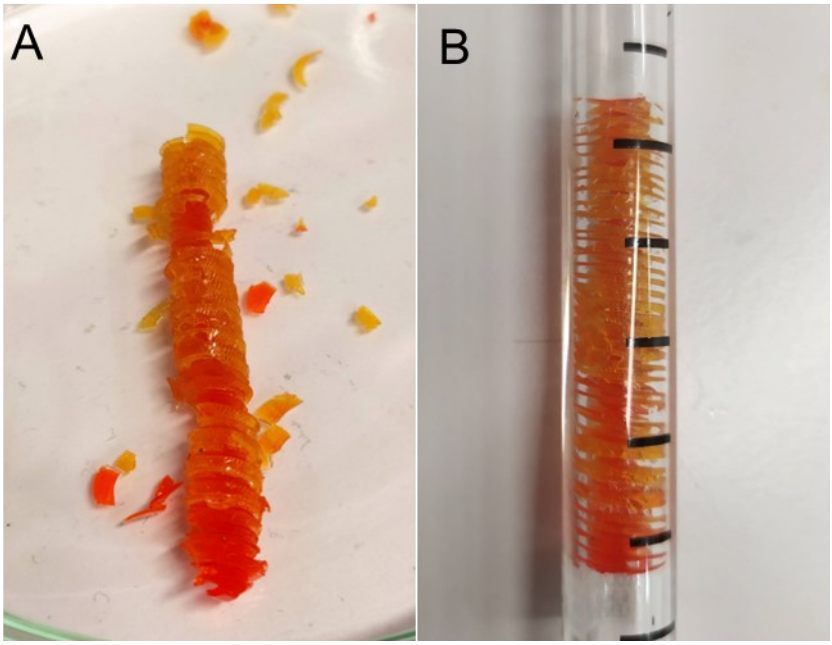

Figure S2. Photos reactors after reaction. A) first design without columns. B) first design with 4 columns.

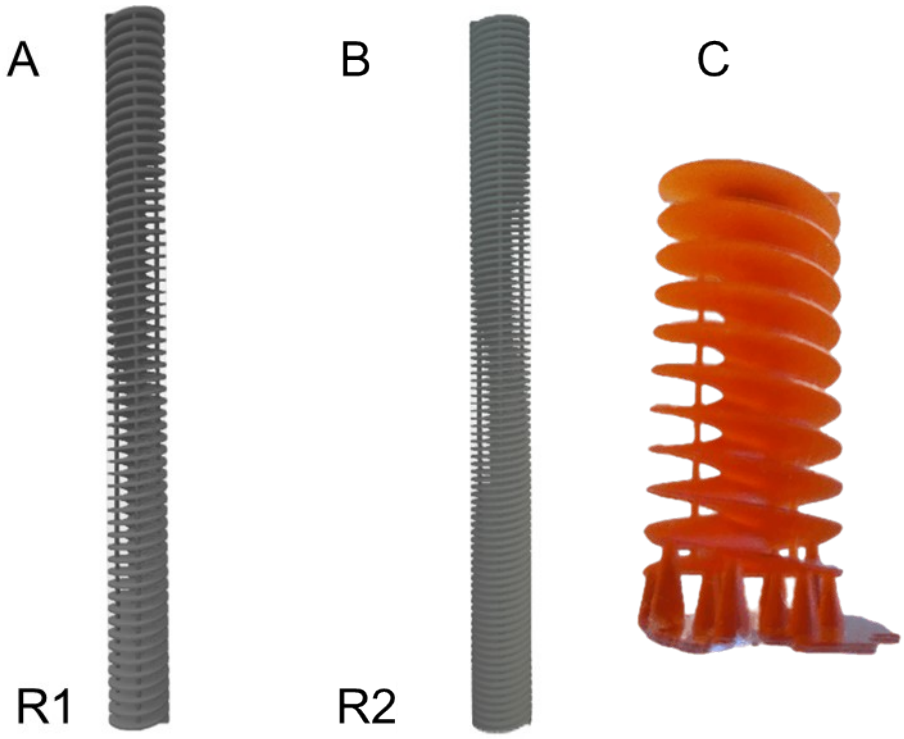

Figure S3. Computer-aided design (SolidWorks or CAD) of structured reactors A) Design R1; B) Design R2; C) Shorter version of printed column before remove the supports.

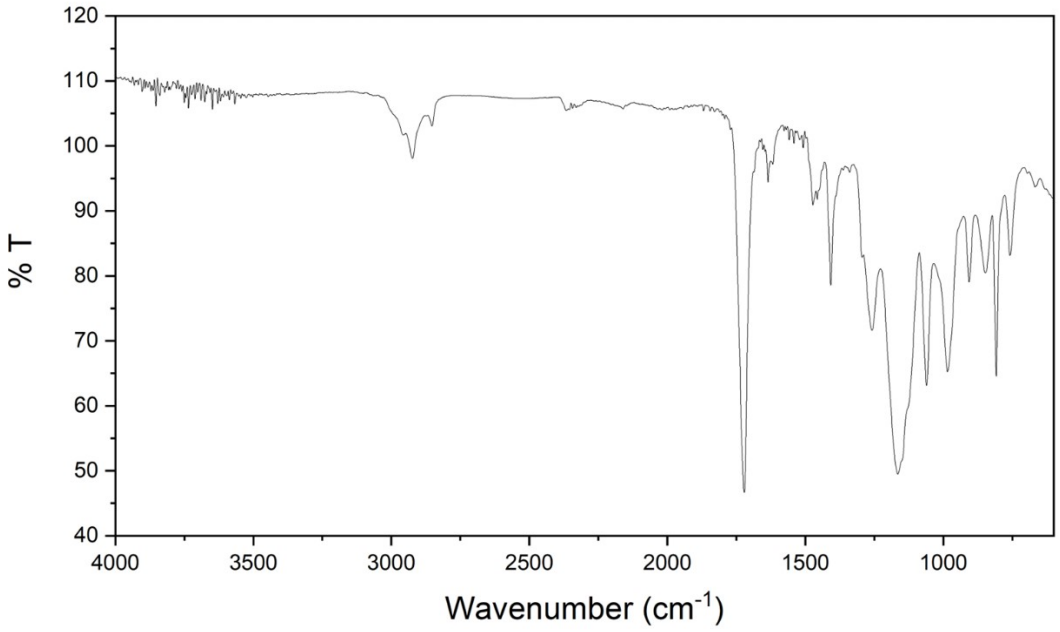

Figure S4. FTIR spectra of optimized formulation used to print the reactor.

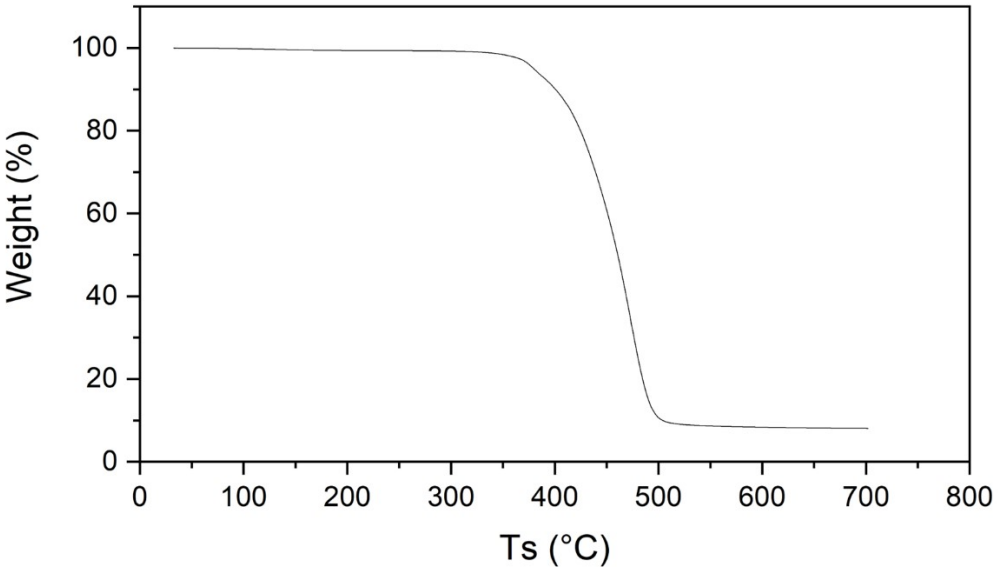

Figure S5. TGA analysis of optimized formulation used to print the reactor.

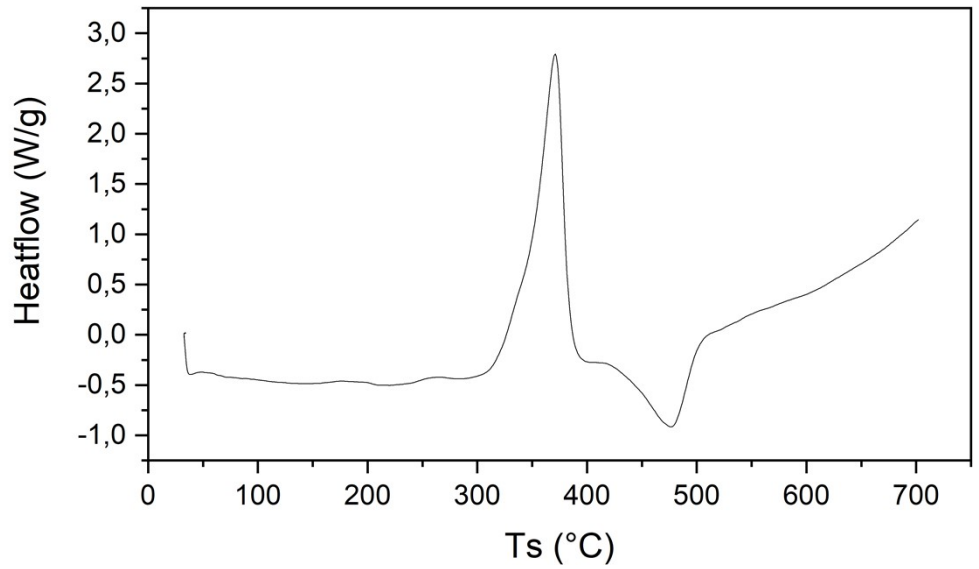

Figure S6. DSC analysis of optimized formulation used to print the reactor.

2.3. NMR analysis of oxidative carboxylation reaction

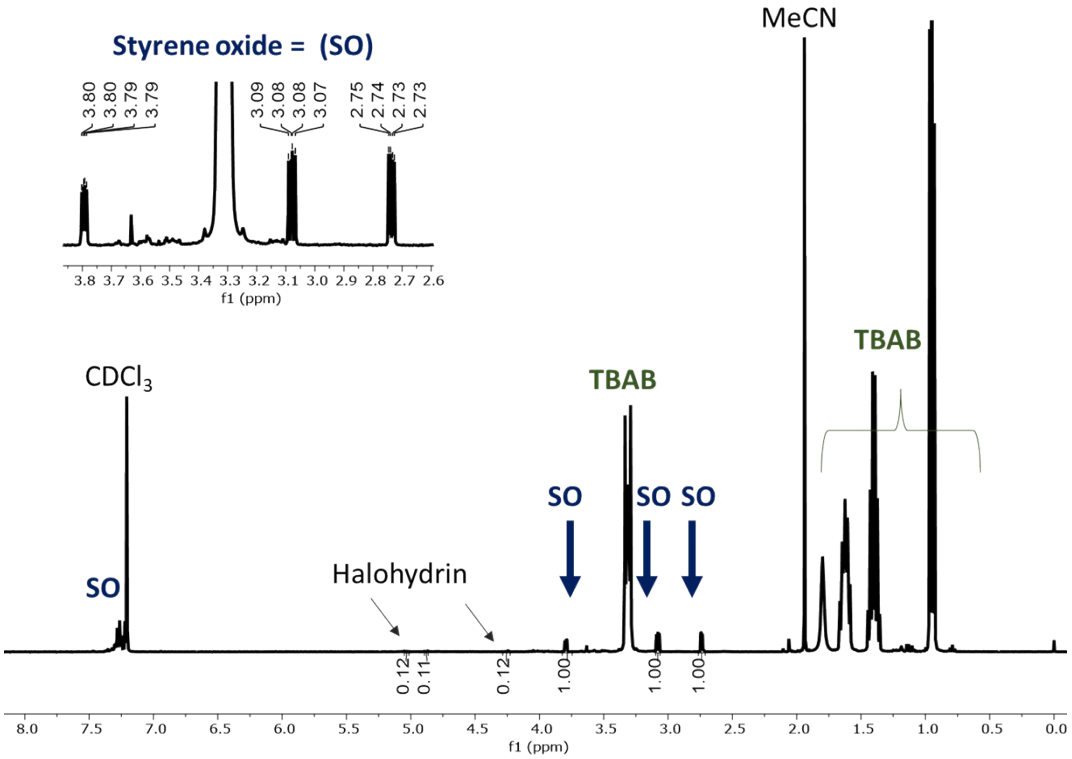

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of reaction 1 (electrochemical oxidation) using styrene as substrate (optimized condition).

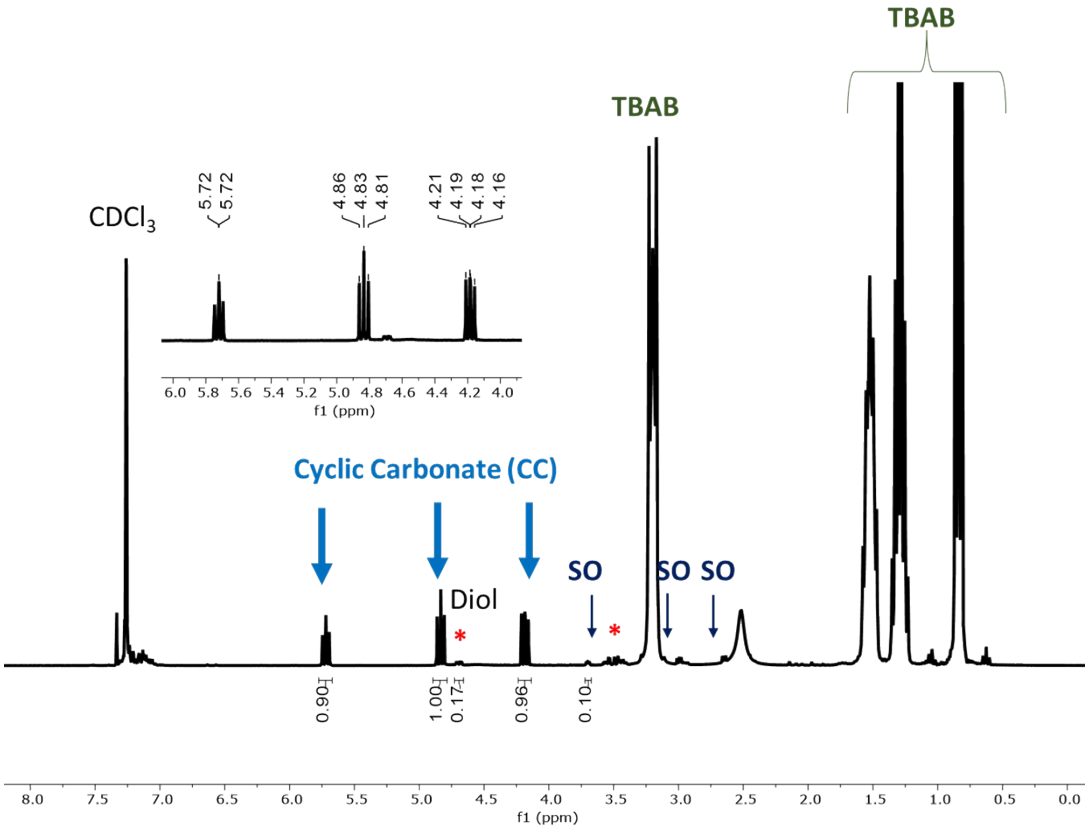

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of reaction 2 (CO_2 cycloaddition) using styrene oxide as substrate (optimized condition).

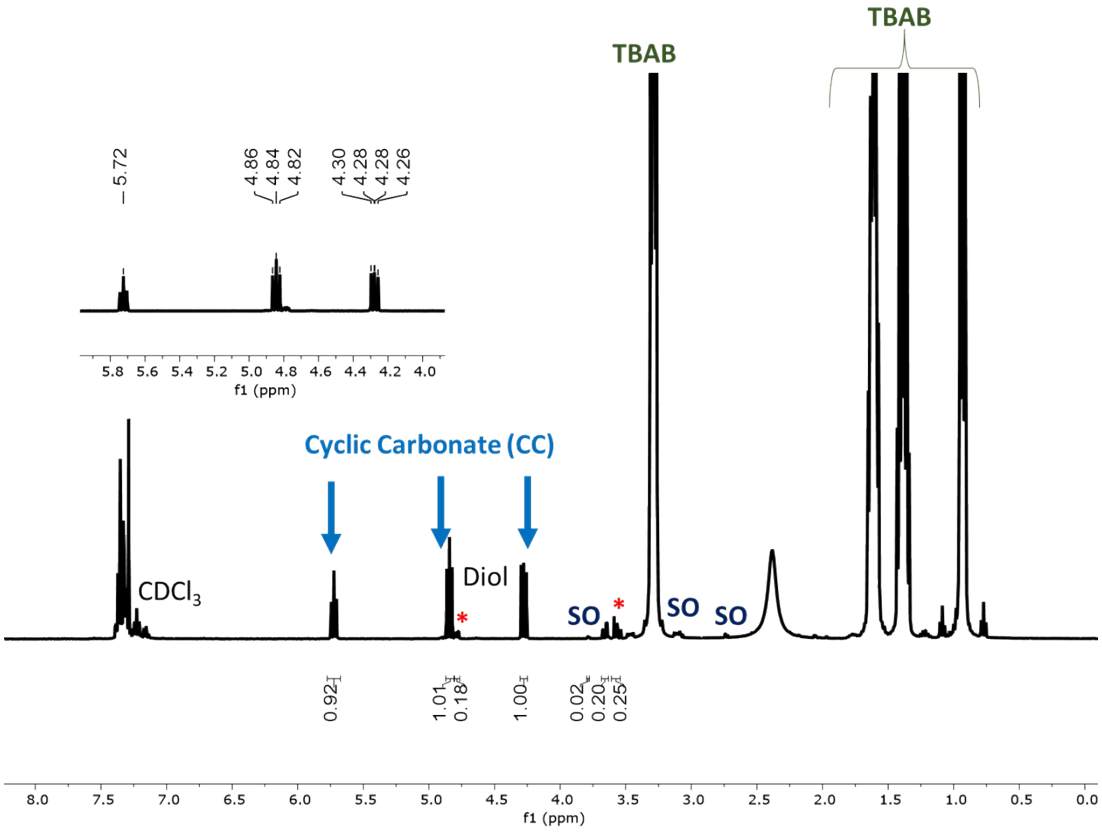

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of combined reaction using styrene as substrate.

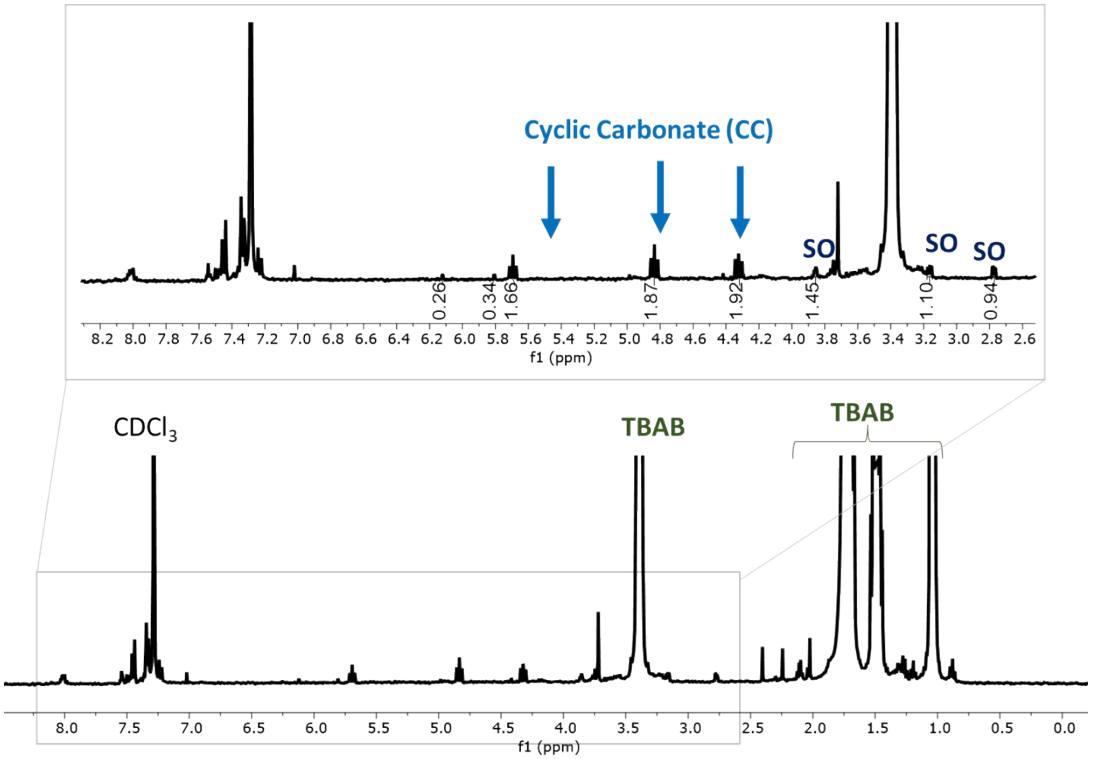

Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of combined reaction using 4-(chloro)styrene as substrate.

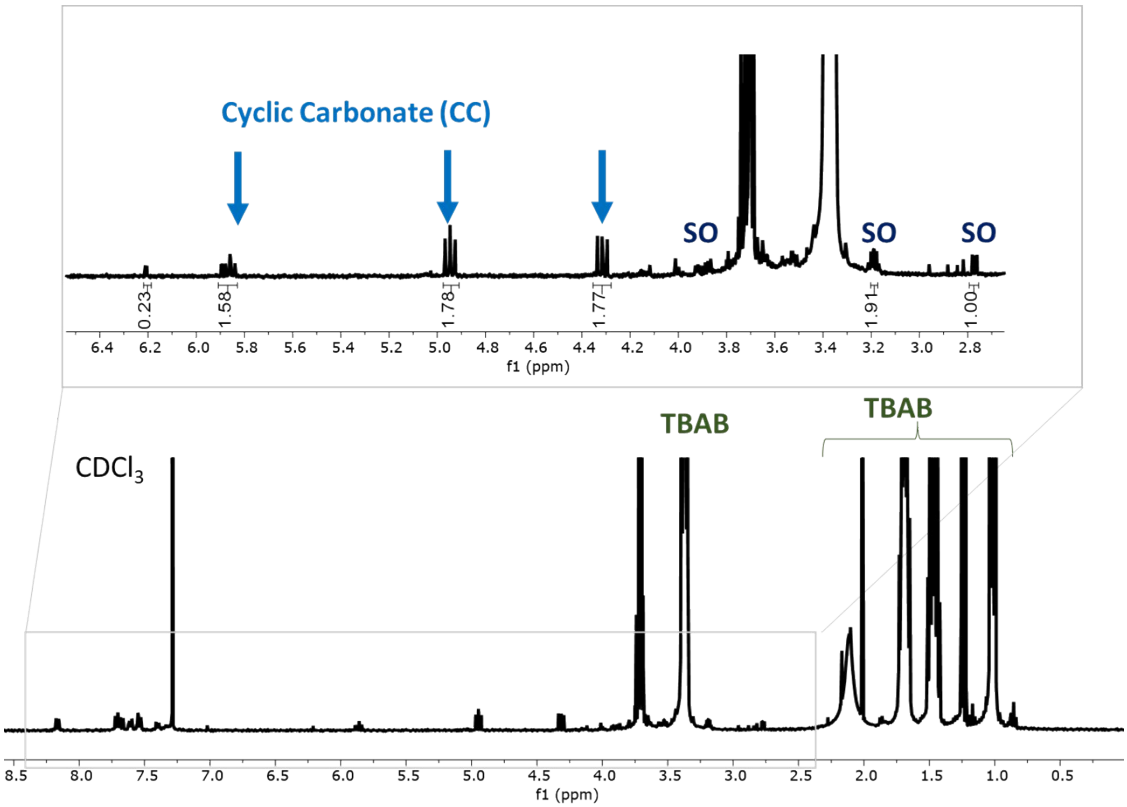

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of combined reaction using 4-(trifluoromethyl)styrene as substrate.

3. Continuous flow apparatus

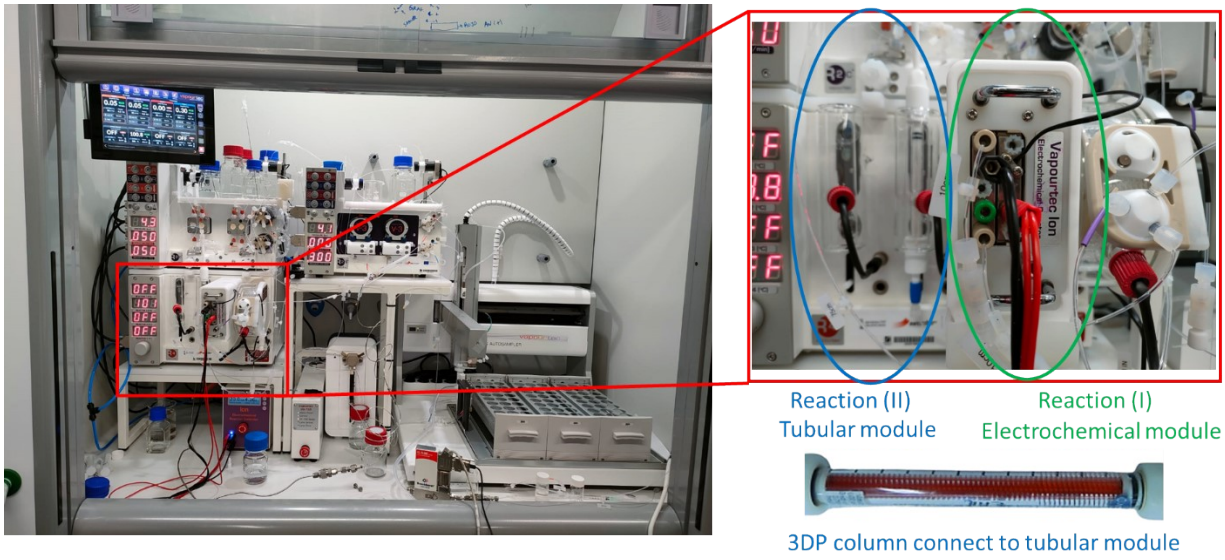

Figure S12. Vapourtec continuous flow system combining electrochemical and tubular modules.