Rapid CO_2 Coupling to Propargylic Alcohols: Unlocking the Production of α-Alkylidene Cyclic Carbonates via Continuous Flow

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Materials.

Solvents	Purity (%)	CAS number	Supplier
Acetonitrile	99.9	75-05-8	Fisher chemical
Dimethylsulfoxide	99.9	67-68-5	Thermo Fisher Scientific
N,N-dimethylformamide		68-12-2	
Tetrahydrofuran	99.8	109-99-9	Fisher chemical
Dichloromethane	99.8	75-09-2	Fisher chemical
Toluene	99.8	108-88-3	Fisher chemical
Ethanol	99	64-17-5	TechniSolv
n-Hexane	99	110-54-3	Fisher chemical
Methanol	99.9	67-56-1	Fisher chemical
Deuterated chloroform	99.8	865-49-6	Eurisotop
Deuterated dimethylsulfoxide	99.8	2206-27-1	Eurisotop
Chemicals	**Purity (%)**	**CAS number**	**Supplier**
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	98	6674-22-2	Merck
Silver oxide	98	20667-12-3	ABCR
Silver nitrate	99.8	7761-88-8	Merck
Silver triflate	99	2923-28-6	Merck
Silver tungstate	99	13465-93-5	ABCR
Silver trifluoroacetate	97	2966-50-9	ABCR
Silver iodide	99.9	7783-96-2	Merck
Silver carbonate	99	534-16-7	Merck
Sodium benzoate	99	532-32-1	Merck
Sodium acetate anhydrous	99	127-09-3	Vel SA
Potassium acetate	99	127-08-2	Merck
1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride	97	250285-32-6	ABCR
1,3-Diisopropyl-1H-imidazol-3-ium chloride	97	139143-09-2	Fluorochem
1,3-Dicyclohexylimidazolium chloride	95	181422-72-0	Fluorochem
1-Methylimidazole	99	616-47-7	Merck
Imidazole	99	288-32-4	Across
Calcium carbonate	99	471-34-1	Merck
Magnesium sulfate	99.9	7487-88-9	VWR
Benzyl bromide	99	100-39-0	Janssen
Celite 545	NA	68855-54-9	Merck
2-Dicyclohexylphosphino-2'-(N,N-dimethylamino)biphenyl (DavePhos)	97	213697-53-1	ABCR
Triphenylphosphine	99	603-35-0	Merck
3-Methyl-1-penten-4-yn-3-ol	98	3230-69-1	Merck
1-Ethynylcyclohexanol	99	78-27-3	Thermo Fisher Scientific
3,5-Dimethyl-1-hexyn-3-ol	98	107-54-0	Merck
2-Propyn-1-ol	99	107-19-7	Merck
2-Hexyn-1-ol	97	764-60-3	Thermo Scient.Chemical
3-Methyl-1-butyn-3-ol	98	115-19-5	Merck
Heptylamine	99	111-68-2	Merck
Merrifield resin (3.5-4.5 mmol/g Cl)	NA	55844-94-5	Merck
QuadraPure® TU macroporous, 400-600 µm	NA	NA	Merck

Silver acetate and silver benzoate were freshly synthesized before use by mixing an aqueous solution of silver nitrate with aqueous solutions of sodium acetate or sodium benzoate respectively. The precipitates were filtered and washed with ethanol then methanol then dried in oven under vacuum till complete dryness. The salts were kept in bottle wrapped with Al foil to limit light exposure.

1. Continuous flow materials:

The continuous-flow setup was composed of perfluoroalkoxyalkane (PFA) tubing 1/16 (1.58 mm outer diameter, 762 µm internal diameter) connected using super flangeless PEEK connectors and ferrule fitting for 1/16" OD tubing. Chemyx Stainless-Steel Syringes (20 mL) were used for the feed solutions, which were connected to each other using a PEEK T-mixer. The injection was performed with Chemyx Fusion 6000. Thermoregulation was ensured with a heating plate serie MR Hei Model Hei-Tec with a PT 1000 temperature sensor, or Branson 1510 ultrasonic bath (frequency of 40 kHz) at the desired temperature or column thermostat Jetstream 2 Plus. Heterogeneous catalysts were packed in Waters stainless-steel column (1x 4.6 x 30 mm and 1x 4.6 x 250 mm) with integrated filters at the inlet and outlet.

Item	***Details***	***Vendor***	***Reference***
Connectors	Super Flangeless Nuts, natural PEEK 1/4-28 thread for 1/16" OD tubing	INACOM	P-255X
	Super Flangeless Ferrule Tefzel (ETFE) and SS ring 1/4-28 thread for 1/16" OD tubing	INACOM	P-259X
	One Piece PEEK Fingertight Fitng, for 1/16", 10-32, PEEK Black	INACOM	6000-282
Mixers	T-mixer, natural PEEK 1/4-28 thread for 1/16" o.d. tubing, 0.02" through hole	INACOM	P-712
	High Pressure Static Mixing Tee with UHMWPE Frit	INACOM	U-466
Tubings	PFA Tubing High Purity 1/16" OD x .030" ID x 50ft	INACOM	1632L
Syringes	20cc stainless steel syringe with 1/16th and 1/8th Swagelok fitting	KR Analytical Ltd	SS020
Syringe pump	High force Chemyx Fusion 6000-X	KR Analytical Ltd	NA

BPR	Back Pressure Regulator P-785, 75 psi (5.2 bar), volume of 131 µl, PEEK	INACOM	P-762
	Dome–type Back Pressure Regulator (BPR-10)	Zaiput Flow Technologies	BPR-10
Check valve	Check Valve Inline Assembly with Fittings	INACOM	CV-3000
MFC	ThalesNano gas module	ThalesNano	NA
	Brankhorst mass flow controller Prestige	Gefran	NA

2. Characterization methods.

NMR: 1H NMR, HSQC, HMBC and COSY spectra were recorded at 298 K with a Bruker Avance III HD spectrometer (B0 = 9.04 T) (400 MHz) and treated with MestReNova software.

SEM: A field-emission gun microscope TESCAN CLARA under a 15-kV accelerating voltage and high vacuum was used for the morphological characterization of pristine and modified supported catalysts by scanning electron microscopy (SEM). All samples were coated with gold before characterization.

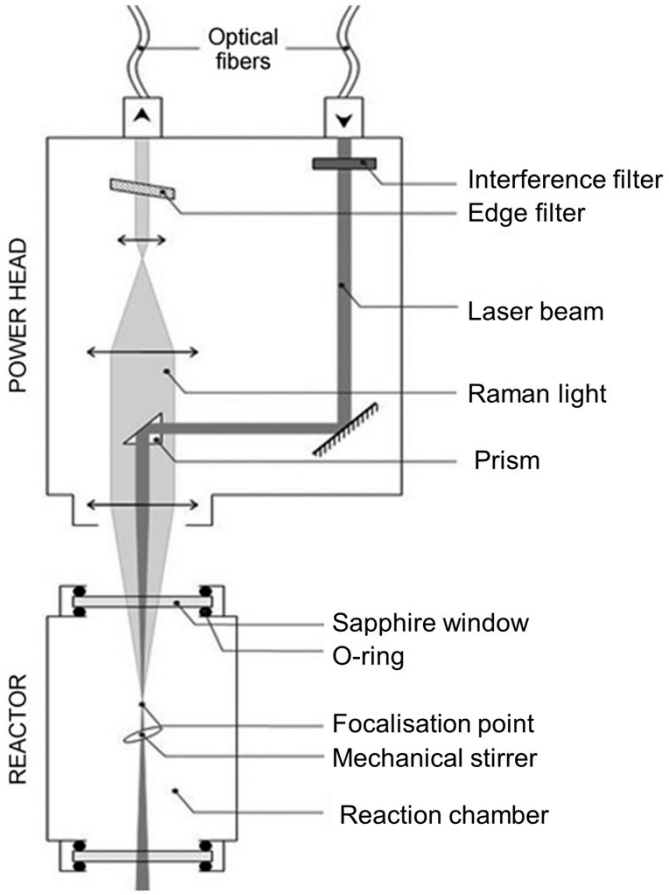
Nitrogen adsorption: To measure the specific surface area (SSA), a Micromeritics® GeminiTM VII Series (model 2390a) was utilized. All samples were degassed with N_2 at 100 °C before analysis and the measurements were performed with N_2 at 77.36 K using 5 points with relative pressure P/P_0 from 0.05 to 0.15 and 10 seconds time interval between each pressure measurements and a tolerance of ΔP of 0.01%. Free space was evaluated with He gas, which is not adsorbed by the samples. The BET (Brunauer, Emmett, and Teller) surface area method was used to obtain the specific surface area in m^2/g. Sample weights were always above 100 mg (around 150 mg) for better accuracy on the measurements.

Elemental Analyses: All the analyses for C, H, N, Cl and Ag were performed by a certified lab MikroLab in Germany.

ICP-OES: Residual silver content in the samples were measured by inductively coupled plasma (ICP) with Varian 720-E5 apparatus equipped with an optical emission spectrometer for the detection.

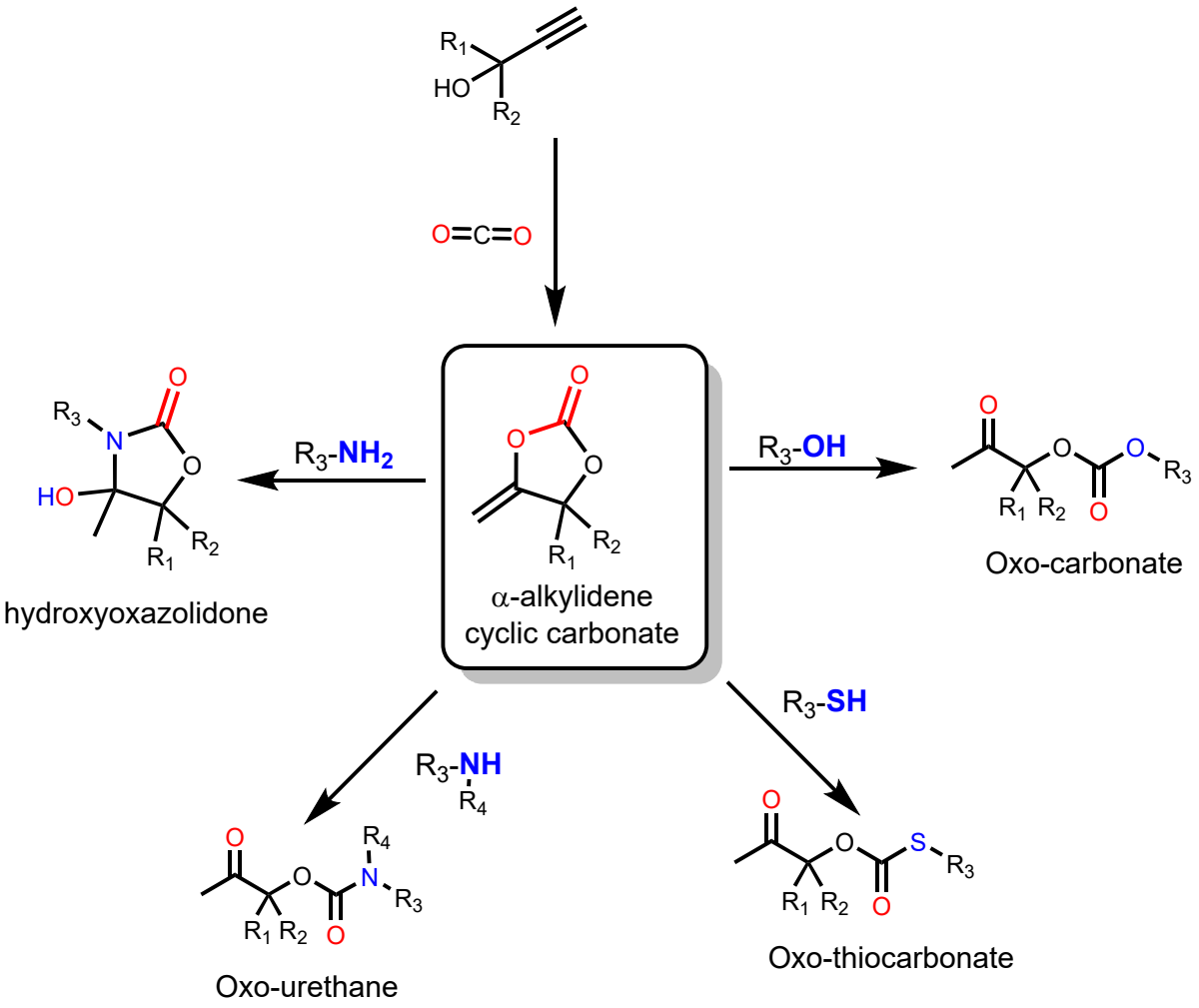
Raman Spectroscopy: Raman spectra were obtained using a remote optical probe (Powerhead – commercialised by Jobin Yvon) allowing to record spectra directly in the reaction chamber that consisted in a stainless-steel reactor suitable for high-pressure measurements (up to 400

bar) and high temperature (up to 100 °C) equipped with a mechanical stirrer (330 rpm). The optical probe is interfaced to a laser beam with a wavelength of 532 nm for excitation (MLL-U-532, Optoelectronics Tech. Co) and to a LabRam 300 Horiba Jobin Yvon spectrometer for signal detection. Grating with a groove density of 600/mm was used to obtain spectra in the wavenumber range 160 - 4170 cm-1. The laser power focused in the reaction chamber was ≈ 200 mW.



Experimental setup to measure *in-situ* the Raman signal of the ongoing reaction.

3. Supplementary figures and tables



Scheme S1. Synthesis of α-alkylidene cyclic carbonate and the resulting products upon the addition of several nucleophiles.

Table S1. Silver salts and co-catalysts screening for the carbonatation of 2-Methyl-3-butyn-2-ol in acetonitrile.

Entry	Silver Salt	Co-cata.	Conv. (%)	Selectivity (%)	Solubility
1	AgI	TBAPh	17	> 99	No
2	AgOAc	DBU	2	ND	No
3	AgOAc	$(C_7H_9)_4NI$	3	ND	No
4	AgOAc	PPh_3	3	ND	No
5	AgOAc	DavePhos	59	> 99	Partial[a]
6	Ag_2CO_3	DavePhos	>99	87	No
7	Ag_2CO_3	PPh_3	99	UI	No
8	Ag_2CO_3[b]	PPh_3	97	UI	No
9	Ag(OTf)	/	0	ND	Yes
10	Ag(OTf)	PPh_3	0	ND	Yes
11	$AgCF_3CO_2^-$	/	0	ND	No
12	$AgCF_3CO_2^-$	PPh_3	traces	ND	Yes
13	$Ag_2(WO_4)$	/	0	ND	No
14	$Ag(WO_4)$	PPh_3	2	ND	No
15	AgI	PPh_3	0	ND	No
16	Agbenzoate	PPh_3	traces	ND	Yes
17	$AgNO_3$	PPh_3	0	ND	Yes
18	IPrAgOAc	/	>99	> 99	Yes

Reaction conditions: 8 mmol of 2-Methyl-3-butyn-2-ol in 4 mL of acetonitrile, 40 °C, 30 minutes, 5 bar, 2 mol% of catalyst and 2 mol% of co-catalyst if applicable in a stainless-steel autoclave. [a] Become soluble during reaction. [b] 1 mol% of Ag_2CO_3 and 2 mol% of PPh_3. ND and UI stand for not determined and unidentified impurities, respectively. The conversion and selectivity were determined by NMR of the crude reaction mixture in $CDCl_3$.

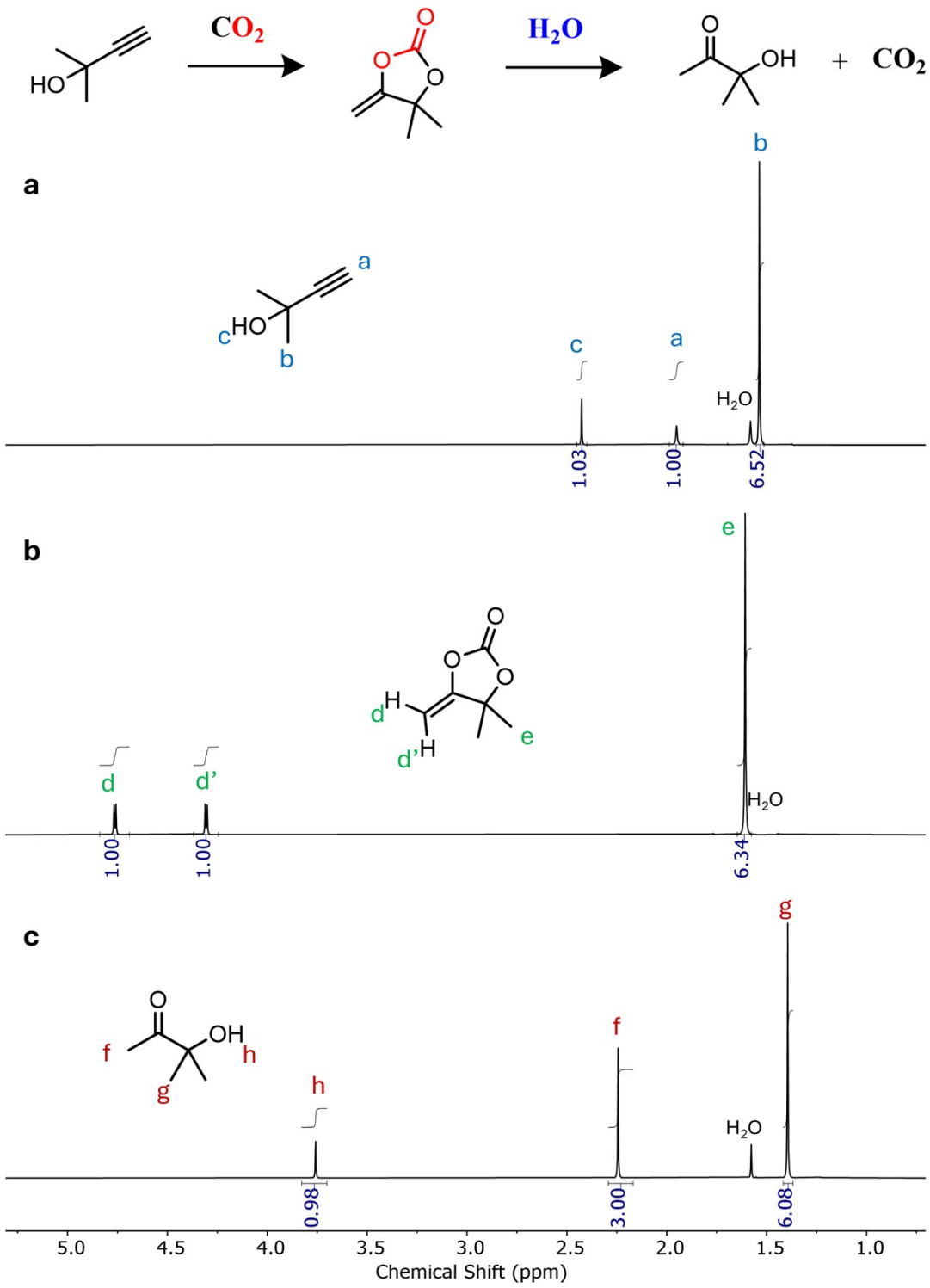


Figure S1. [1]H NMR spectra of a) 2-Methyl-3-butyn-2-ol, b) 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (DMACC) and c) 3-Hydroxy-3-methyl-2-butanone in deuterated chloroform.

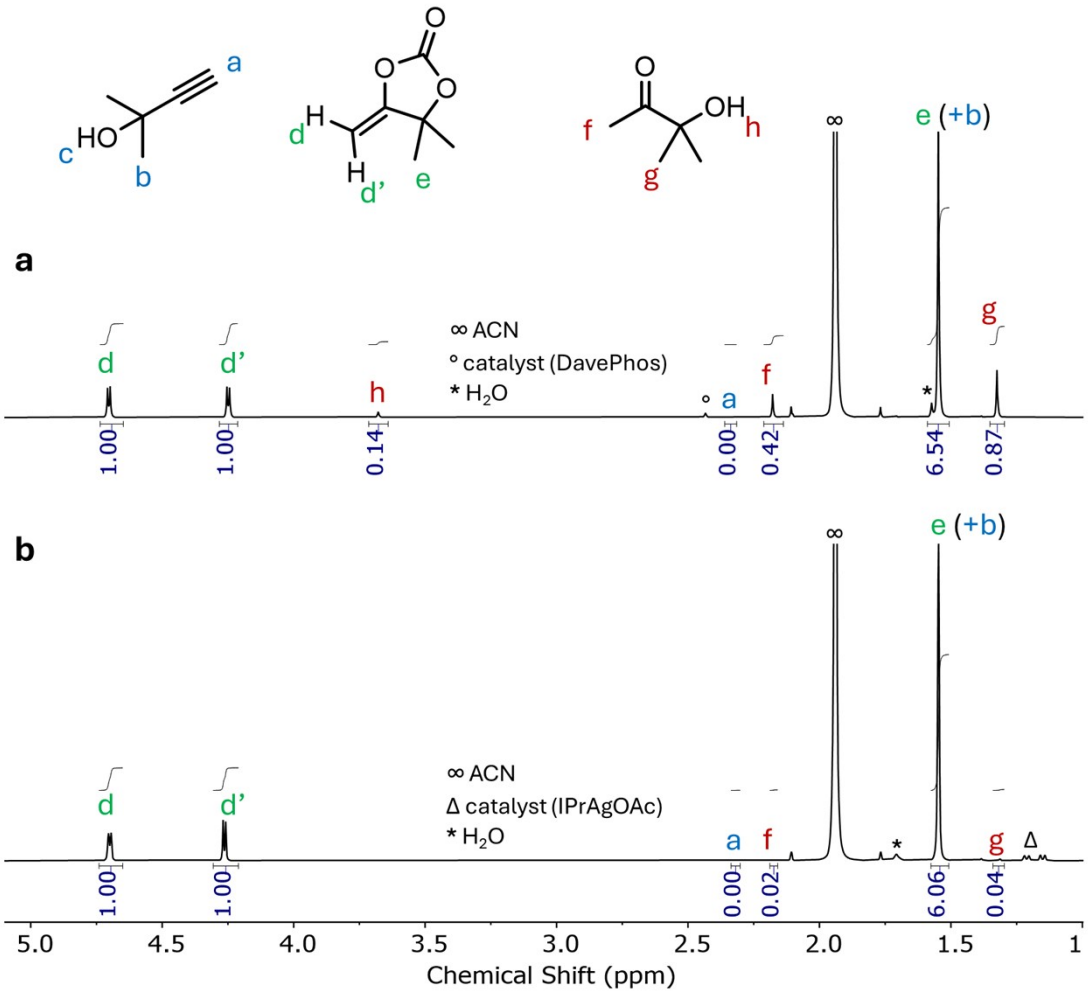


Figure S2. ^{1}H NMR spectra of the crude reaction mixtures using a) silver carbonate / DavePhosphine and b) IPrAgOAc as catalysts (Table S1, entries 6 and 18).

Calculation of 2-Methyl-3-butyn-2-ol conversion:

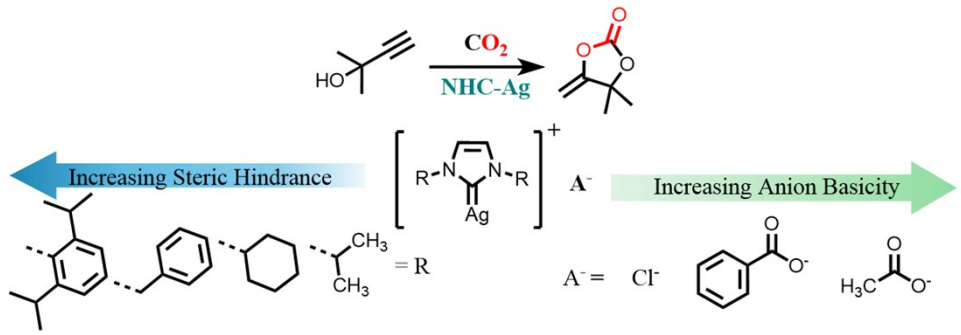
The conversion and the selectivity were determined using NMR of crude reaction mixture (Figure S2) according to the following equation:

$$Conversion\ (\%) = \frac{\int d + \int g/6}{\int d + \int g/6 + \int a}\ x\ 100$$

$$Selectivity\ (\%) = \frac{\int d}{\int d + \int g/6}\ x\ 100$$

the different protons are attributed in Figure S1 and S2. Note that the authors define the selectivity as the proportion of the product of interest amongst all the products formed.

Table S2. Silver carbene catalyst optimization for the carboxylative cyclization of 2-Methyl-3-butyn-2-ol in batch.



Entry	R	Anion	Solvent	Conv. (%)[a]	Select. (%)[a]	Solubility
1	Diisopropylphenyl	Chloride	CH_3CN	2	>99	Sol.
2	Diisopropylphenyl	Benzoate	CH_3CN	67	>99	Sol.
3	Diisopropylphenyl	Acetate	CH_3CN	**100**	>99	Sol.
4	Benzyl	Acetate	CH_3CN	9	>99	Insol.[b]
5	Cyclohexyl	Acetate	CH_3CN	2	>99	Insol.[b]
6	Isopropyl	Acetate	CH_3CN	2	>99	Insol.[b]
7	Isopropyl	Acetate	DMSO	31-34	>99	Sol.
8	Isopropyl	Acetate	DMF	24-27	>99	Sol.
9	Isopropyl	Acetate	THF	5	>99	Sol.

Reaction conditions: 8 mmol of 2-Methyl-3-butyn-2-ol in 4 mL solvent, 2 mol% catalyst, 40 °C for 30 minutes at a CO_2 pressure of 5 bar. [a] Determined by NMR of the crude in $CDCl_3$ except for entry 8 for which DMF-d_7 was used.[b] Precipitation upon addition of propargylic alcohol.

A slight precipitation was also observed with IPrAgOAc in acetonitrile after a few hours, the solutions of IPrAgOAc and 2-Methyl-3-butyn-2-ol in acetonitrile were freshly prepared prior the reaction.

Table S3. Optimization of the carboxylative cyclization of 2-Methyl-3-butyn-2-ol using IPrAgOAc as the catalyst.

Entry	Solvent	Time (min)	Temp. (°C)	Press. (bar)	Cata. loading (mol%)	Conversion (%)
1	CH_3CN	30	40	5	2	> 99
2	CH_3CN	15	40	5	2	72
3	DMSO	15	40	5	2	35
4	CH_3CN	15	40	10	2	93
5	CH_3CN	15	50	5	2	100
6	CH_3CN	5	50	5	2	41
7	CH_3CN	5	50	10	2	81
8	**CH_3CN**	**5**	**50**	**10**	**2 + 2mol% DBU**	**99**

Reaction conditions: 8 mmol of 2-Methyl-3-butyn-2-ol in 4 mL of solvent with the catalyst in a stainless-steel autoclave. The conversion and selectivity were determined by NMR of the crude reaction mixture in $CDCl_3$.

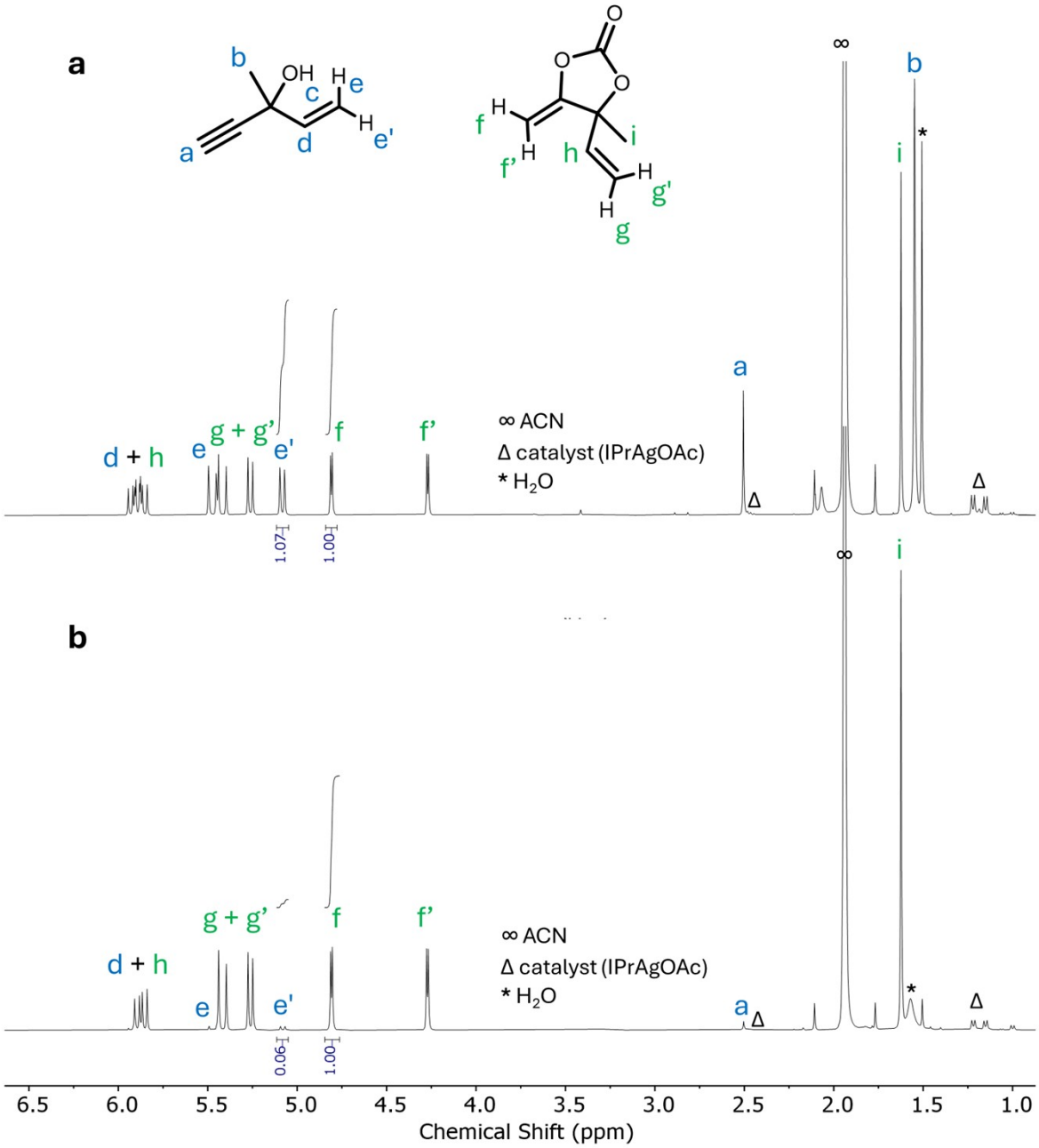


Figure S3. [1]H NMR spectra of the crude reaction mixtures in deuterated chloroform of the carboxylative cyclization of **1b** using a) condition A: 5 bar, 40 °C, 30 min of reaction and b) condition B: 15 bar, 50 °C and 10 min of reaction.

Conversion calculation:

The conversion was determined using NMR of crude reaction mixture according to the following equation, no side product was detected, and we considered a selectivity of 100%.

$$Conversion\ (\%) = \frac{\int f}{\int e + \int e'} x\ 100$$

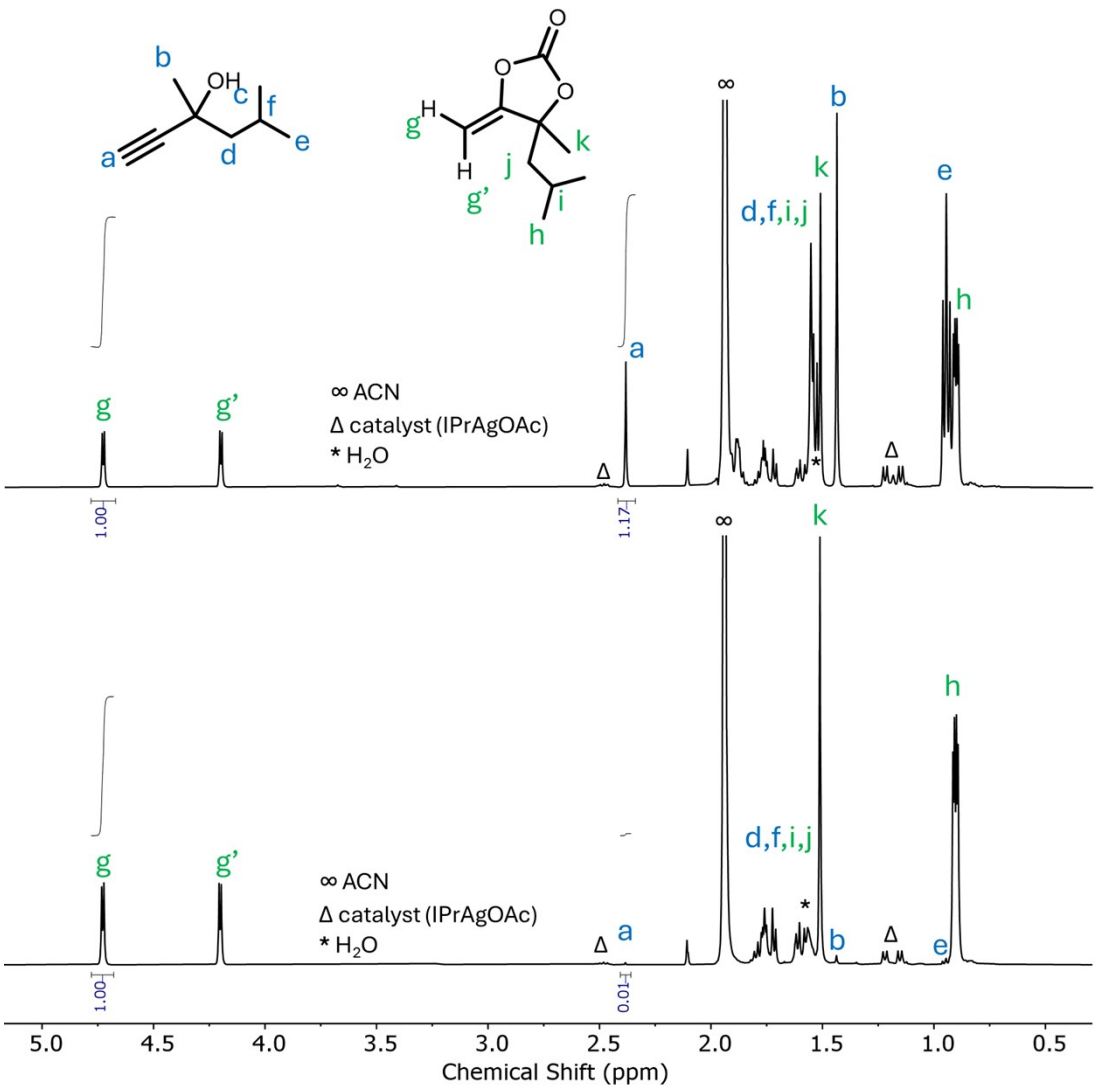


Figure S4. NMR spectra of the crude reaction mixtures in deuterated chloroform of the carboxylative cyclization of **1c** using a) condition A: 5 bar, 40 °C, 30 min of reaction and b) condition B: 15 bar, 50 °C and 10 min of reaction.

Conversion calculation:

The conversion was determined using NMR of crude reaction mixture according to the following equation, no side product was detected, and we considered a selectivity of 100% for the calculation of the conversion.

$$Conversion\ (\%) = \frac{\int g}{\int g + \int a}\ x\ 100$$

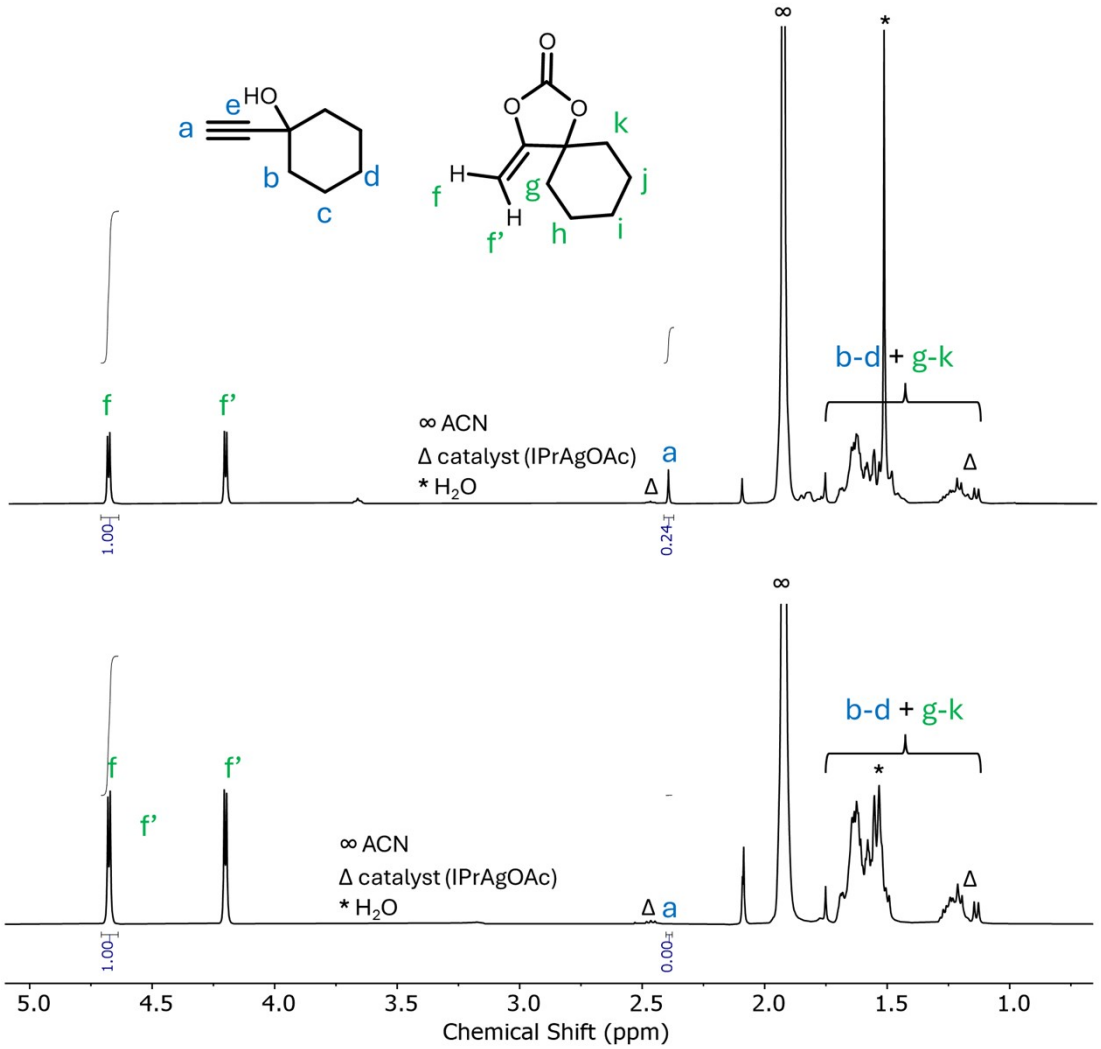


Figure S5. ^{1}H NMR spectra of the crude reaction mixtures in deuterated chloroform of the carboxylative cyclization of **1d** using a) condition A: 5 bar, 40 °C, 30 min of reaction and b) condition B: 15 bar, 50 °C and 10 min of reaction.

Conversion calculation:

The conversion was determined using NMR of crude reaction mixture according to the following equation, no side product was detected or identified. Thus, we considered a selectivity of 100 % for the calculation of the conversion.

$$Conversion\ (\%) = \frac{\int f}{\int f + \int a}\ x\ 100$$

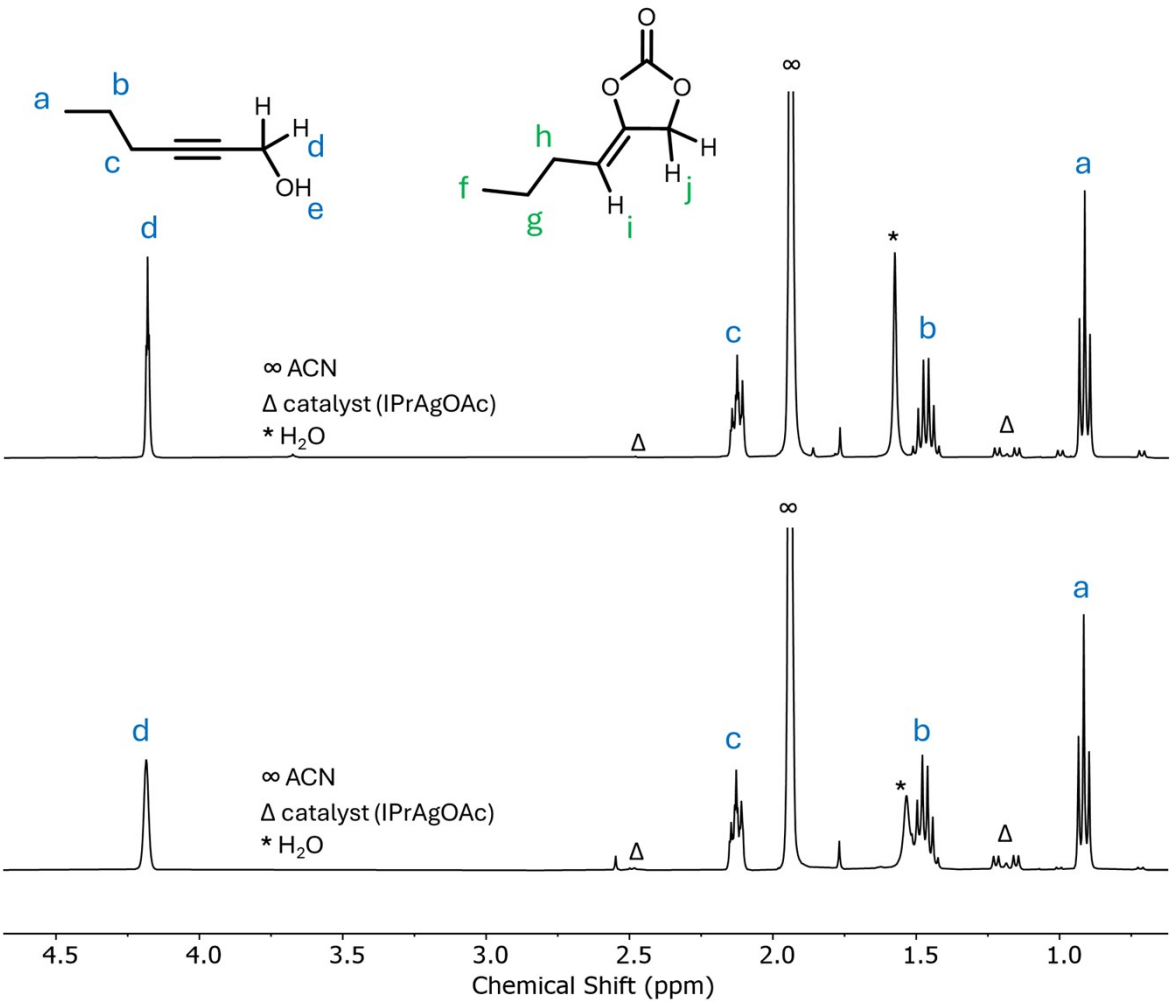


Figure S6. ^{1}H NMR spectra of the crude reaction mixtures in deuterated chloroform of the carboxylative cyclization of **1e** using a) condition A: 5 bar, 40 °C, 30 min of reaction and b) condition B: 15 bar, 50 °C and 10 min of reaction.

Conversion calculation:

The conversion was determined using NMR of crude reaction mixture. No product was detected for both conditions. **Conversion of 0%**

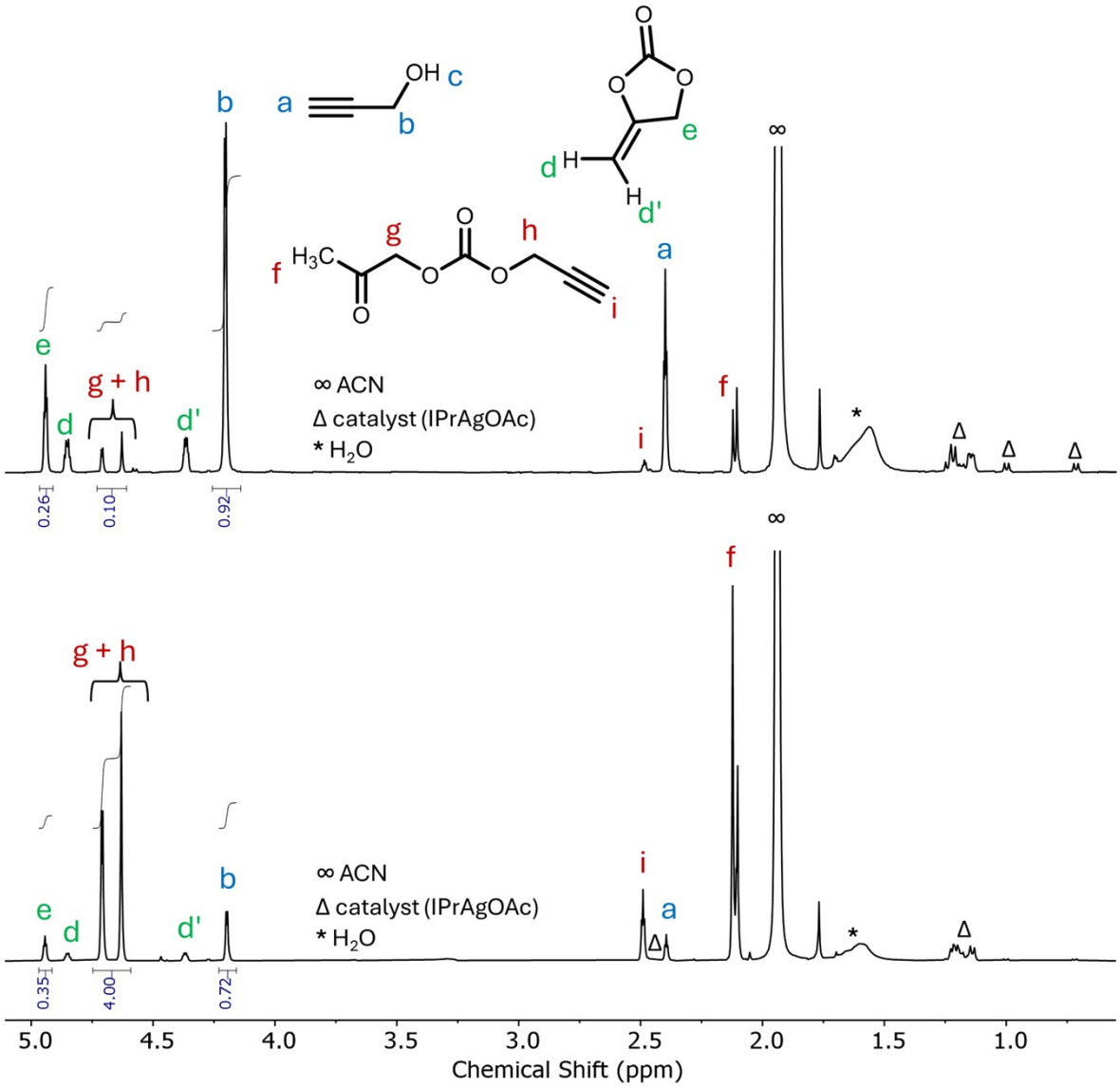


Figure S7. [1]H NMR spectra of the crude reaction mixtures in deuterated chloroform of the carboxylative cyclization of **1f** using a) condition A: 5 bar, 40 °C, 30 min of reaction and b) condition B: 15 bar, 50 °C and 10 min of reaction.

Conversion calculation:

The conversion and selectivity were determined using NMR of crude reaction according to the following equation. A side product consisting in the opening of the cyclic carbonate with the starting propargyl alcohol was detected.

$$Conversion\ (\%) = \frac{\int e + 2 * \int (g+h)/2}{\int e + \int b + 2 * \int (g+h)/2}\ x\ 100$$

$$Selectivity\ (\%) = \frac{\int d}{\int d + \int (g+h)/2}\ x\ 100$$

the different protons are attributed in Figure S7. Note that the authors define the selectivity as the proportion of the product of interest amongst all the products formed.

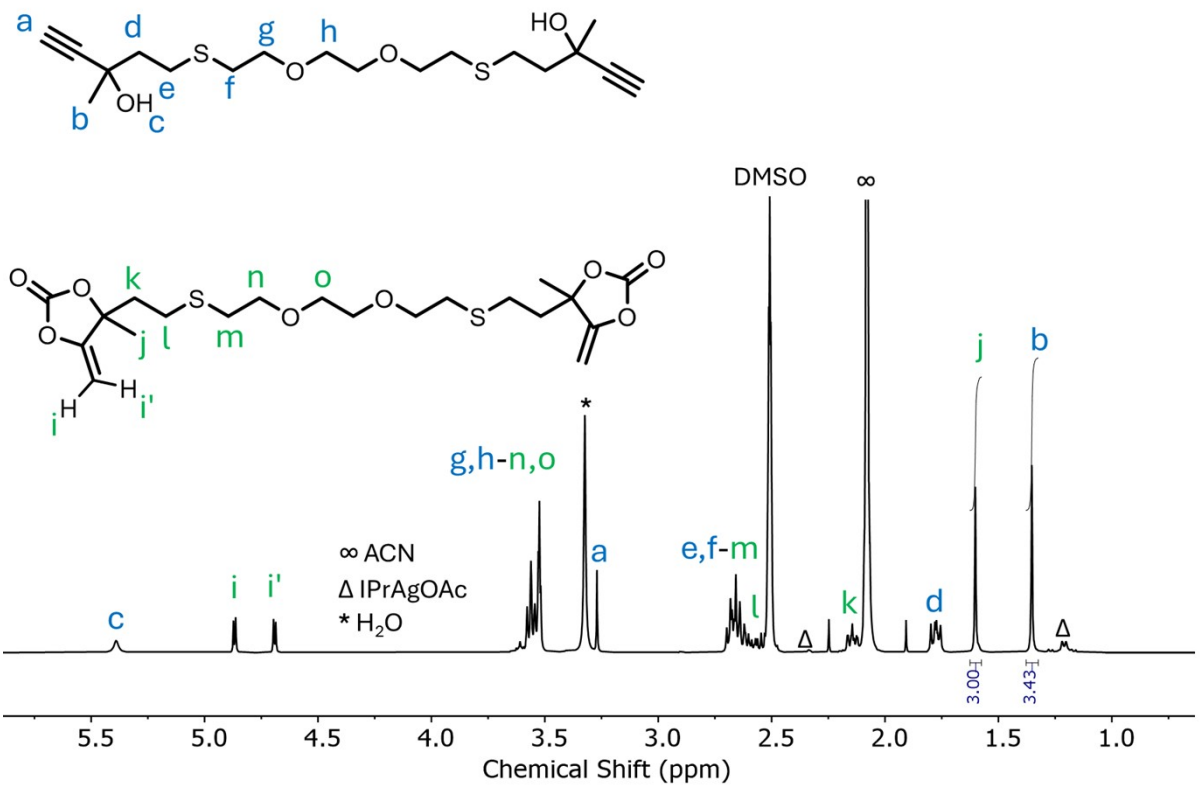


Figure S8. ^{1}H NMR spectra of the crude reaction mixtures in deuterated DMSO of the carboxylative cyclization of **1g** using condition B: 4 mmol of **1g** in 4 mL acetonitrile, 2 mol% of IPrAgOAc and DBU, 15 bar, 50 °C and 10 min of reaction.

Conversion calculation:

The conversion was determined using NMR of crude reaction mixture according to the following equation, no side product was detected or identified. Thus, we considered a selectivity of 100 % for the calculation of the conversion.

$$Conversion\ (\%) = \frac{\int j}{\int j + \int b}\ x\ 100$$

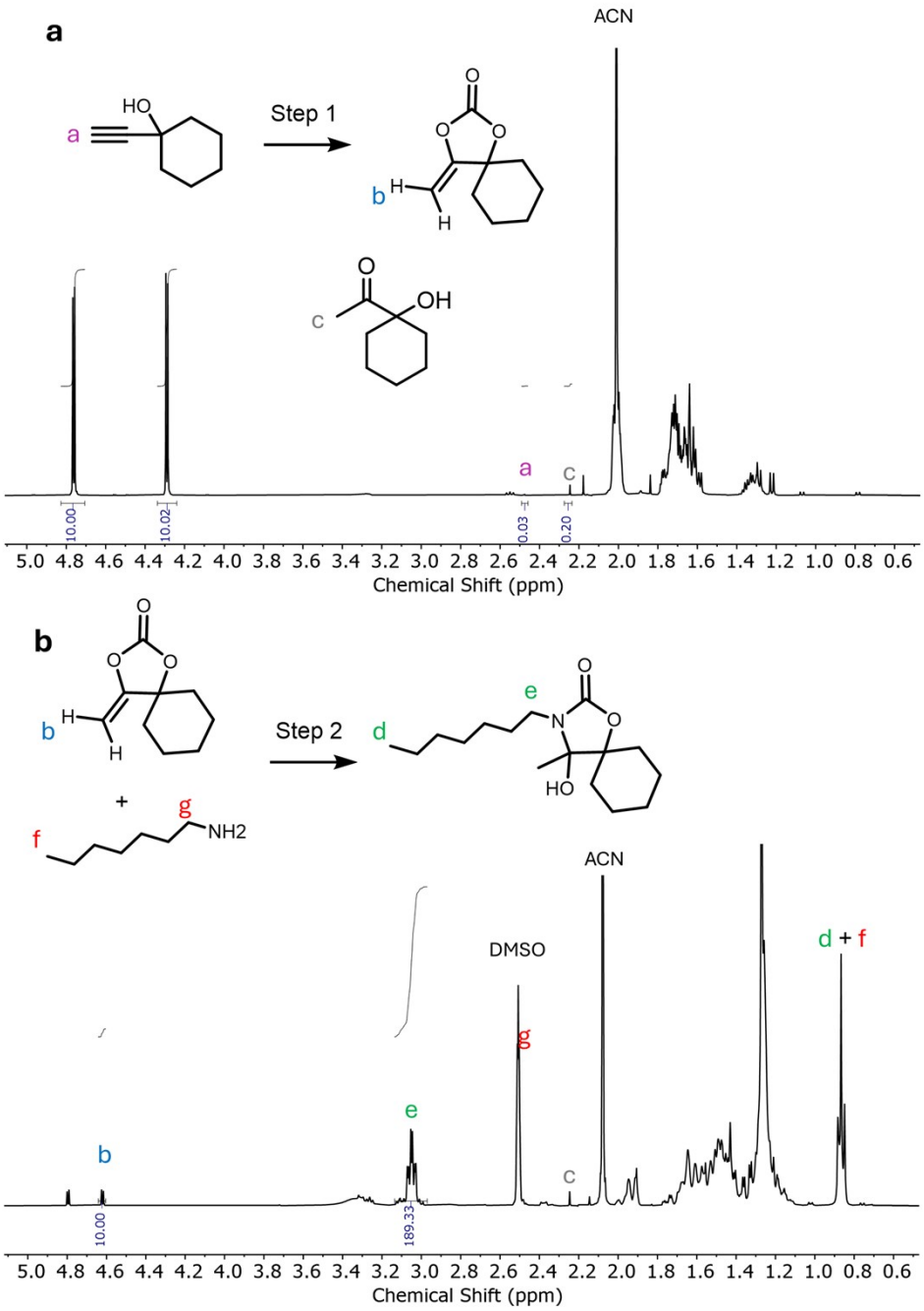


Figure S9. ^{1}H NMR spectra of the crude mixtures in flow setup after a) CO_2 addition to the propargylic alcohol **1d** (3.5 M) in the first reactor (**2d**, first step) in deuterated chloroform and b) the aminolysis of the resulting αCC (**3d**, second step) in deuterated DMSO

Conversion calculation:

First step:

Detection of traces of hydroxy-ketone coming from the hydrolysis of the product.

$$Conversion\ (\%) = \frac{\int a + \int c/3}{\int a + \int c/3 + \int b}\ x\ 100\ and\ \ Selectivity\ (\%) = \frac{\int a}{\int a + \int c/3}$$

Second step:

no side reaction detected, so we assume a selectivity of 100 % for this step.

$$Conversion\ (\%) = \frac{\int e/2}{\int b + \int e/2}\ x\ 100$$

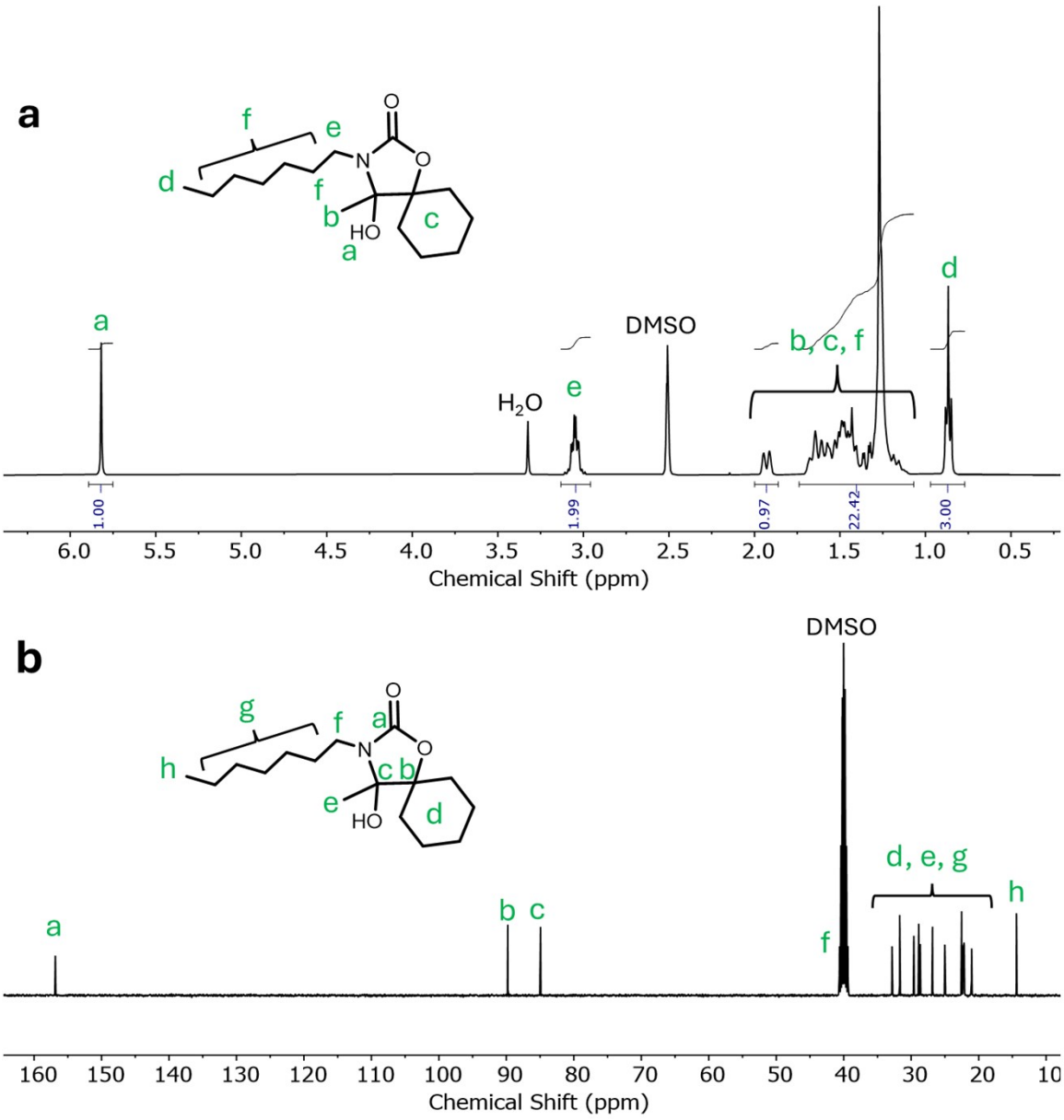


Figure S10. ^{1}H and ^{13}C NMR spectra of recrystalized **3d** in deuterated DMSO

Table S4. Elemental analyses and N_2 adsorption isotherms performed on pristine Merrifield resin and after each step of its modification.

Sample	C (wt%)	N (wt%)	Cl (wt%)	Ag (wt%)	SSA[f] ($m^2 g^{-1}$)	Functionalization (mmol g^{-1})	
Pristine MR	78. 6	< 0.01	12.8	*ND*	0.6	3.6	Cl[a]
MR1	70.9	7.1	9.1	*ND*	1.4	2.5	Imidazolium Cl[b]
MR2	71.1	6.7	3.3	*ND*	0.9	1.8	Imidazolium acetate[a]
MR3[e]	63.0	6.1	3.9	15.5	3.8	1.4	Silver [c,d]

Measured by elemental analyses using [a] the chloride content, [b] the nitrogen content, [c] the silver content. The silver is expected to be under the form of silver carbene acetate but contamination by Ag_2O and silver carbene chloride are not excluded. [e] Silver content measured after treatment with ammonia. [f] The specific surface area is determined via BET analysis of N_2 adsorption isotherm measured at 77.36 K.

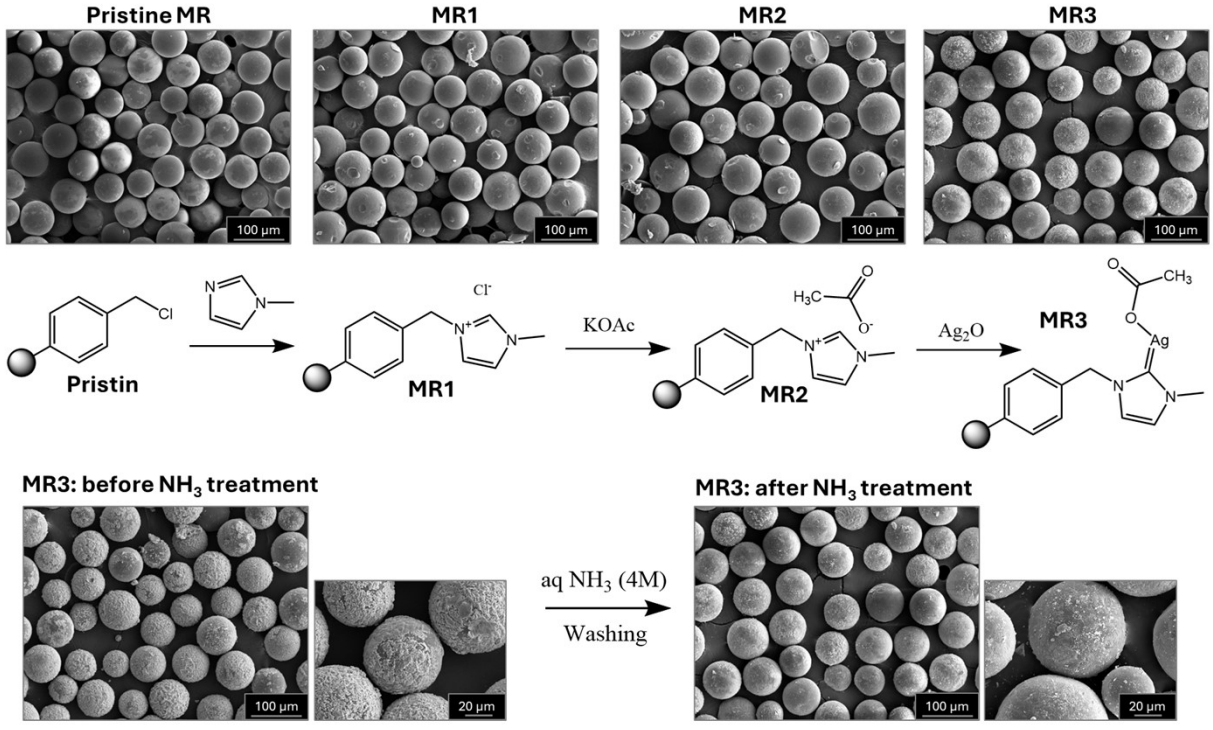


Figure S11. SEM images of the Merrifield's resin (MR) beads pristine and after modification steps. In the lower part, SEM images before and after treatment of **MR3** with aqueous ammonia (4M)

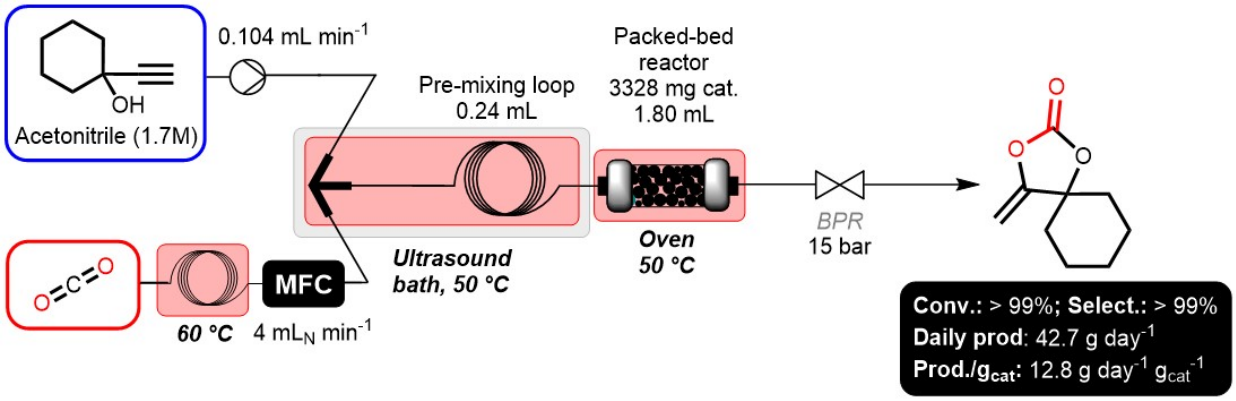
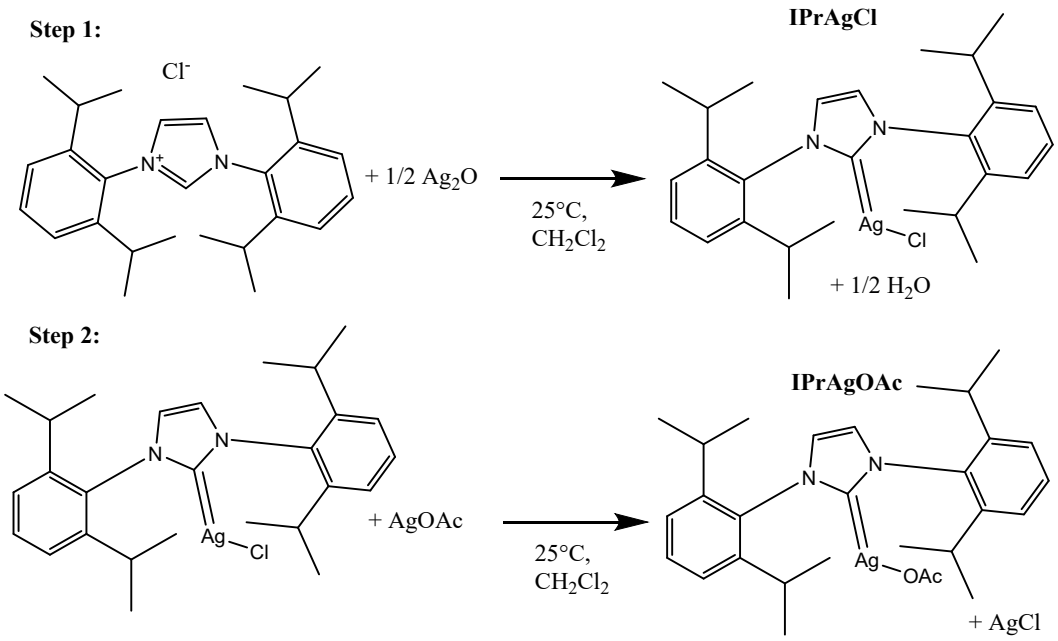


Figure S12. Continuous flow setup with a packed-bed reactor consisting of an immobilized *N*-heterocyclic carbene silver acetate complex on Merrifield resin beads to catalyse the carbonatation of **1d** without DBU.

4. Synthesis of *N*-heterocyclic carbene silver complexes.

Synthesis of [1,3-Bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] Silver chloride (IPrAgCl) and acetate (IPrAgOAc).



Scheme S2. Two steps procedure to synthesize IPrAgOAc catalyst.

Step1: In a typical experiment, both 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (9.1386 g, 21.5 mmol) and silver oxide (2.9894 g, 12.9 mmol) were suspended in 140 mL dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of Celite packed in a column. The orange solution was then concentrated using rotary evaporator and precipitated in n-hexane. The off-white precipitate was filtered on Buchner and washed with hexane followed by drying at 55 °C under vacuum overnight to afford the product (IPrAgCl) with 78 % yield. The product was analyzed by NMR in $CDCl_3$.

Step2: In a typical experiment, IPrAgCl (8.5267 g, 16 mmol) was suspended with silver acetate (2.8308 g, 17 mmol) in 130 mL of dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of Celite packed in a column. The yellowish solution was then concentrated using rotary evaporator and precipitated in n-hexane. The white precipitate was filtered on Buchner and washed with hexane followed by drying at 55 °C under vacuum overnight to afford the product (IPrAgOAc) with 90 % yield (8.012 g). The product was analyzed by NMR in $CDCl_3$ (or DMSO-d_6). Note that the product was slightly contaminated with $(IPr)_2AgOAc$ that forms when the complex stayed in solution for a few hours. The amount that is formed depends on the solvent (see Figure S16).

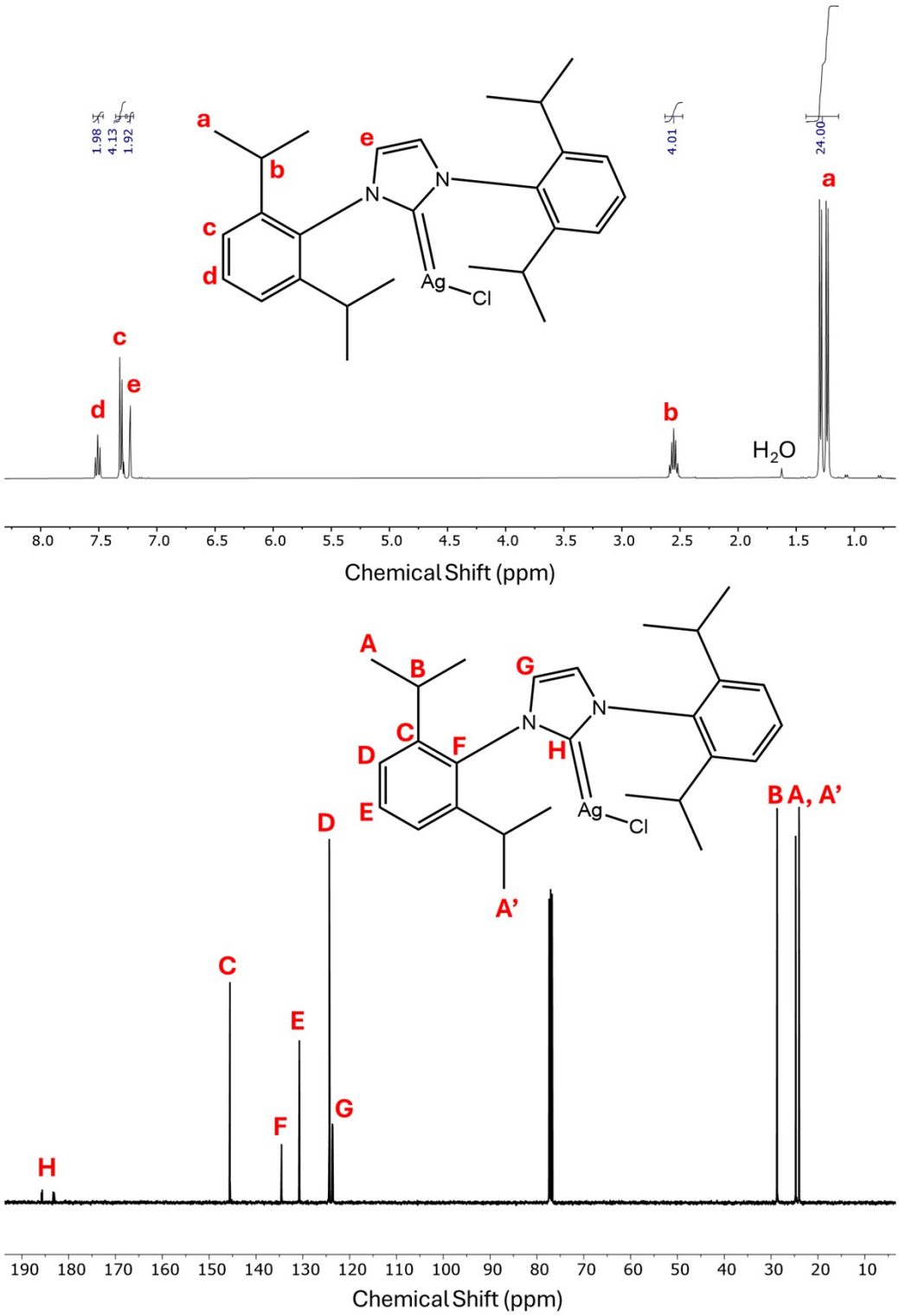


Figure S13. ^{1}H- and ^{13}C-NMR spectra of IPrAgCl in deuterated chloroform

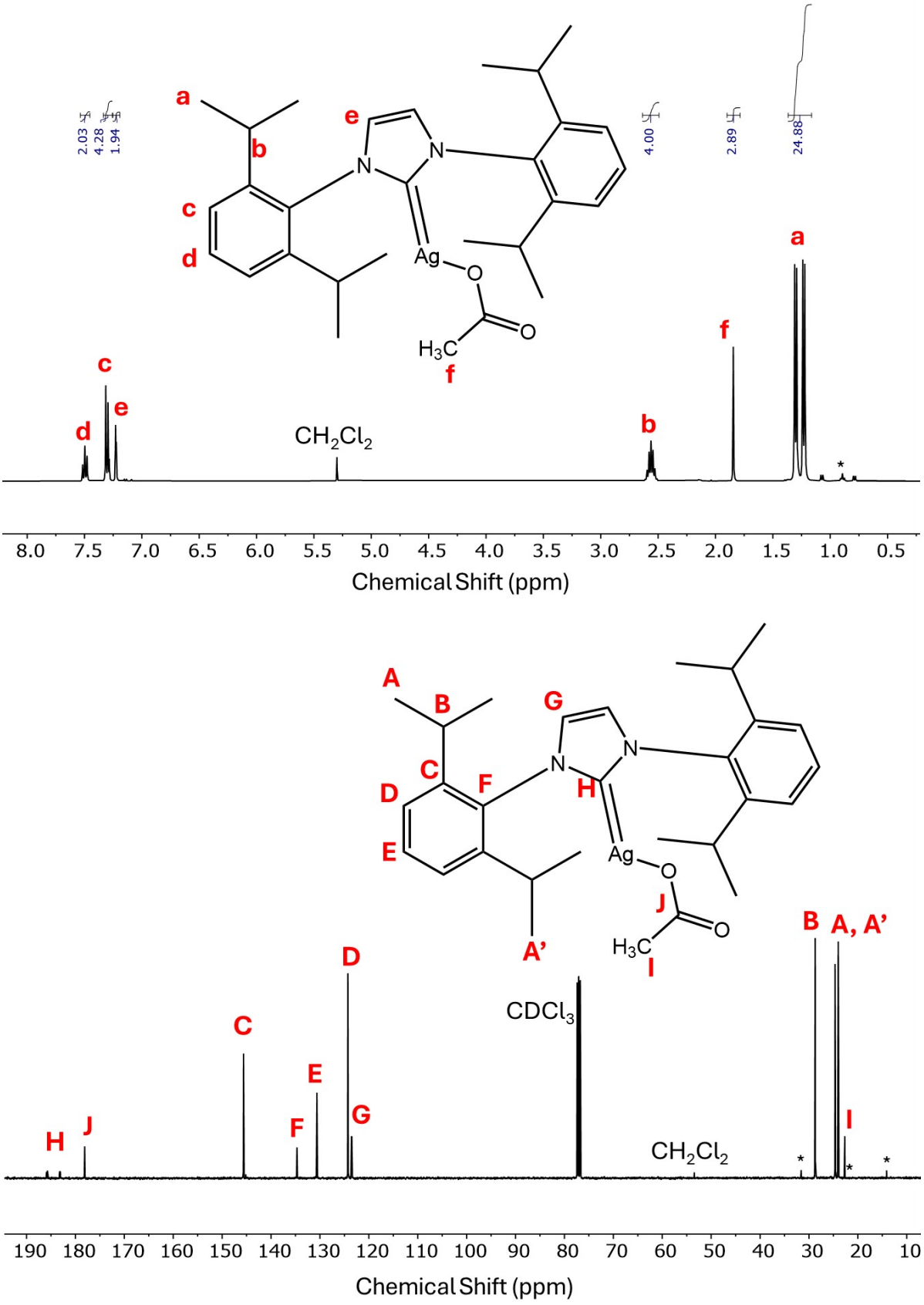


Figure S14. ^{1}H- and ^{13}C-NMR spectra of IPrAgOAc in deuterated $CDCl_3$.

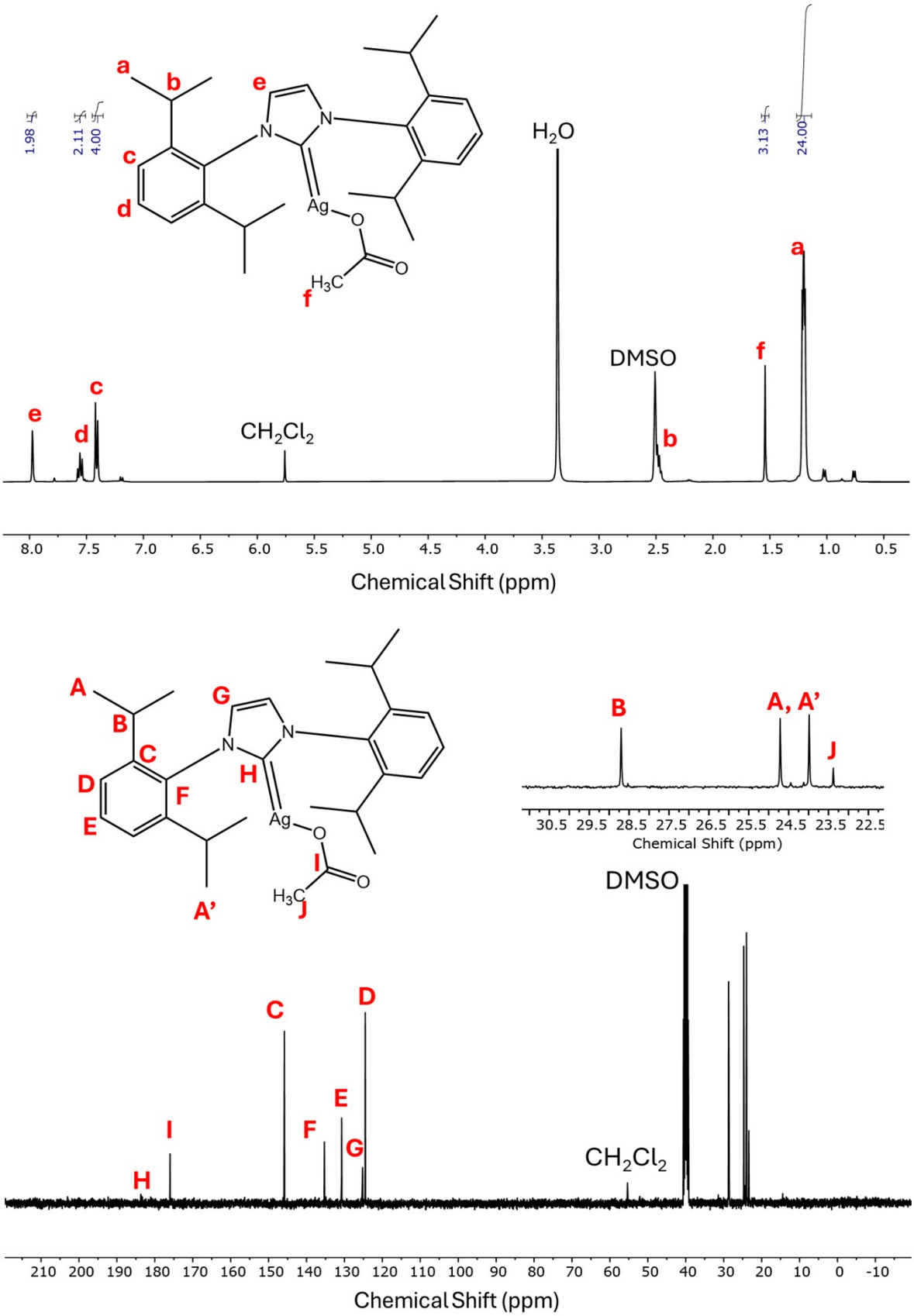


Figure S15. ^{1}H- and ^{13}C-NMR spectra of IPrAgOAc in deuterated DMSO.

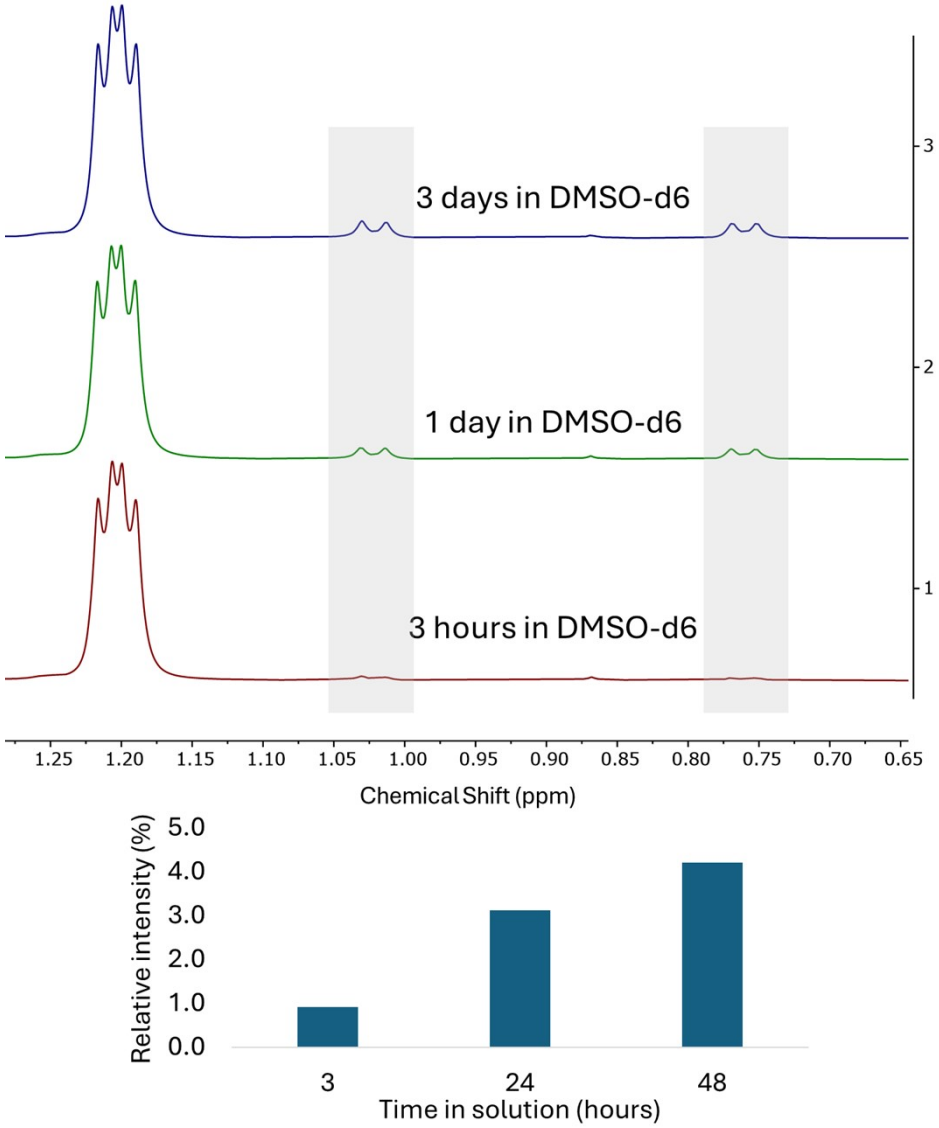
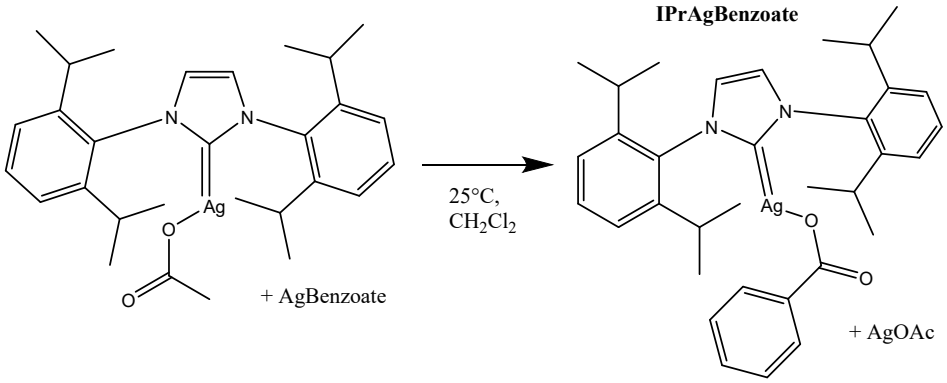


Figure S16. ^{1}H NMR spectra of IPrAgOAc in DMSO-d_6 after 3, 24 and 48 hours in NMR tube at room temperature. Chart of the impurity evolution over time monitored by following the relative intensity of the signal at 0.77 ppm compared to the main peak at 1.20 ppm.

Synthesis of [1,3-Bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] Silver benzoate (IPrAgBenzoate).



Scheme S3. Synthesis of IPrAgBenzoate catalyst.

IPrAgOAc synthesized previously (1.0658 g, 2.0 mmol) and silver benzoate freshly synthesized (0.4854g, 2.12 mmol) were suspended in 15 mL dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred for 2 days, and the resulting mixture was filtered through a few cm of Celite packed in a column. The solution was then concentrated using rotary evaporator and precipitated in n-hexane. The precipitate was filtered on Buchner and washed with hexane followed by drying at 60 °C under vacuum overnight to afford the product (IPrAgBenzoate) with 84 % yield. The product was analyzed by NMR in $CDCl_3$.

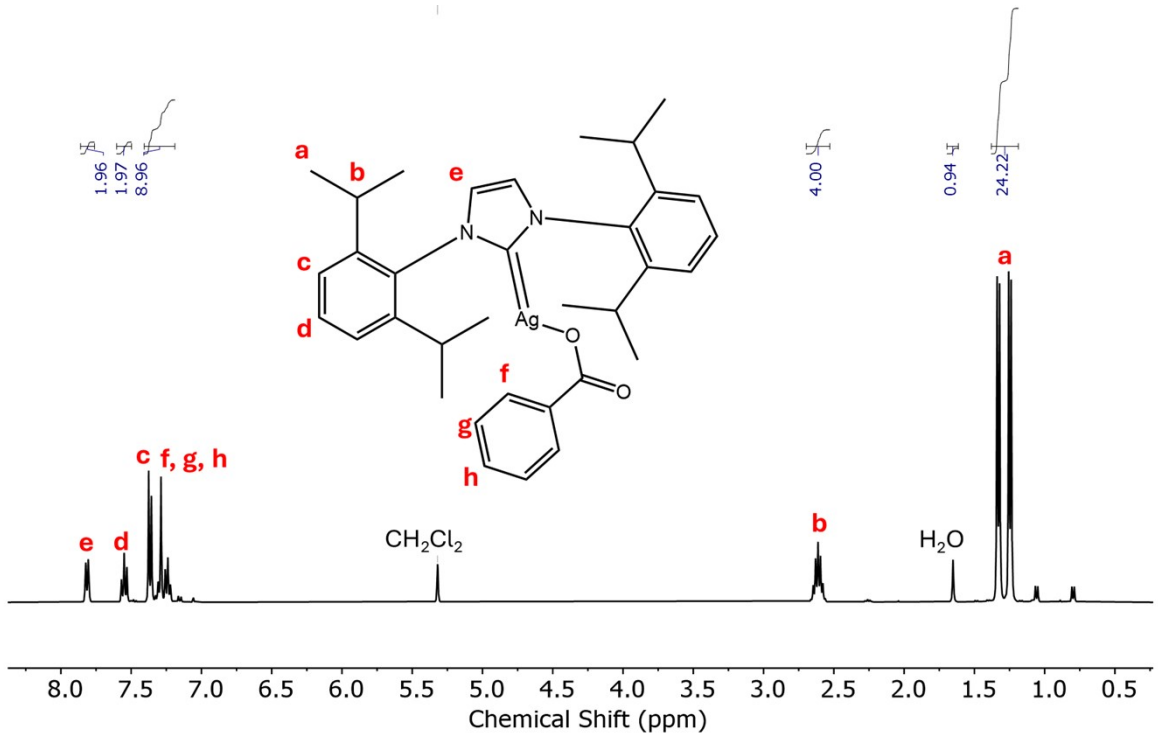
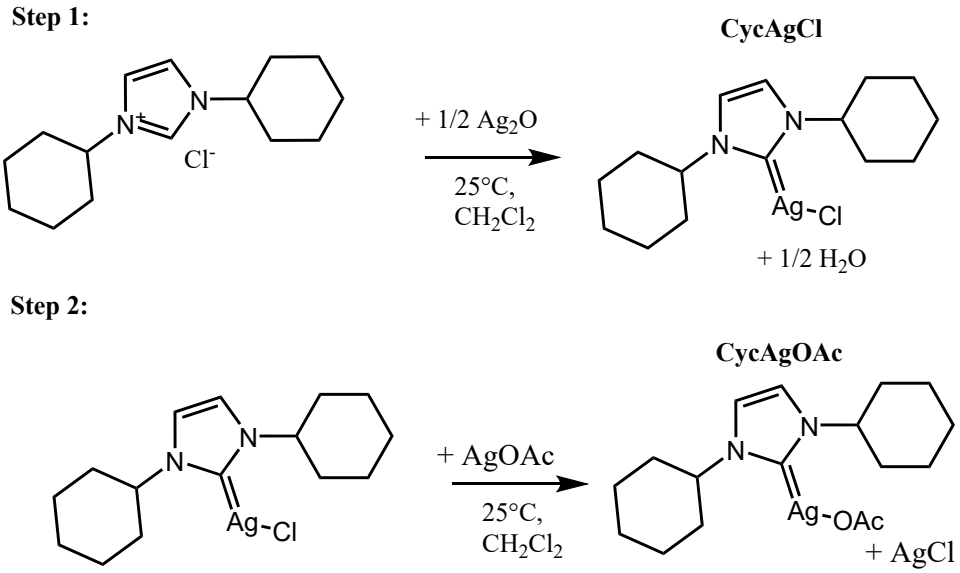


Figure S17. ^{1}H NMR spectrum of IPrAgBenzoate in deuterated chloroform.

Synthesis of [1,3-Dicyclohexyl-1H-imidazol-2(3H)-ylidene] Silver chloride (CycAgCl) and acetate (CycAgOAc):

Step1: 1,3-dicyclohexylimidazolium chloride (5.38 g, 20 mmol) and silver oxide (2.78 g, 12 mmol) were suspended in 100 mL dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of Celite packed in a column. The orange solution was then dried in rotary evaporator followed by drying at 45 °C under vacuum overnight to afford 6.67 g of a brownish powder (CycAgCl) (89 % yield). The product was analyzed by NMR in $CDCl_3$ and used without further purification in the next step.

Step2: CycAgCl (5.63 g, 15 mmol) was suspended with silver acetate (2.65 g, 17 mmol) in 75 mL of dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of Celite packed in a column. The orange solution was then dried in rotary evaporator followed by drying at 45 °C under vacuum for 4 hours to afford 5.62 g of an orange powder (CycAgOAc). 5.22 g of the product were recrystallized using CH_2Cl_2/hexane mixture at -20 °C for 8 hours. The crystals were filtered on Buchner and washed with hexane before being dried at 45 °C for 1 day. The orangish crystals (4.96 g, 90% overall yield) were analyzed by NMR in $CDCl_3$.



Scheme S4. Two steps procedure to synthesize CycAgOAc catalyst.

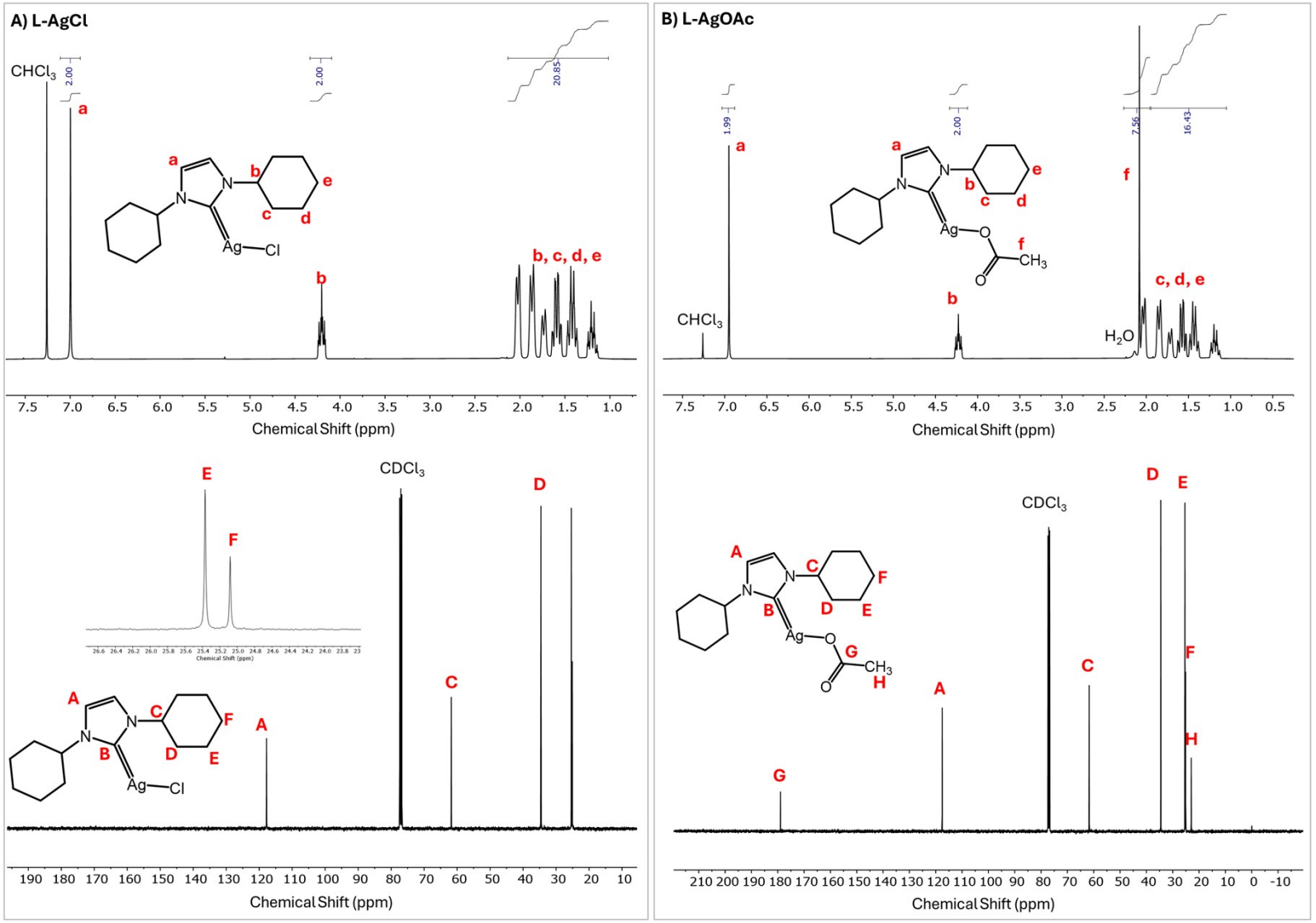
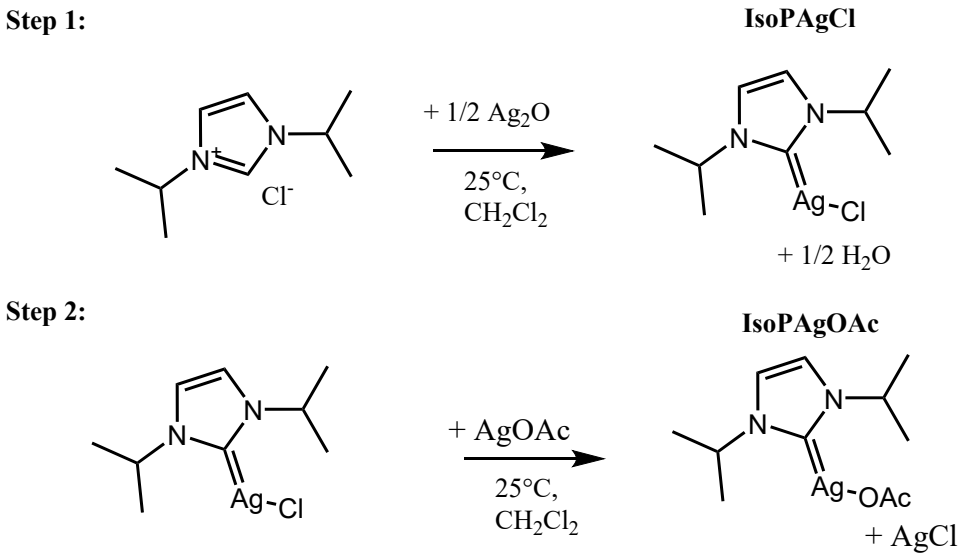


Figure S18. ^{1}H and ^{13}C NMR spectra of CycAgCl and CycAgOAc in deuterated chloroform.

Synthesis of [1,3-Diisopropyl-1H-imidazol-2(3H)-ylidene] Silver chloride (IsoPAgCl) and acetate (IsoPAgOAc):

Step1: 1,3-diisopropylimidazolium chloride (5.6610 g, 30 mmol) and silver oxide (4.1713 g, 18 mmol) were suspended in 150 mL dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of Celite packed in a column. The dark brown solution was then dried in rotary evaporator followed by drying at 45 °C under vacuum overnight to afford 5.8315 g of a brownish powder (IsoPAgCl) (66 % yield). The product was analyzed by NMR in DMSO-d_6 and used without further purification in the next step. Note that the compound once in solution was very sensitive to light with apparition of brown-black precipitate.

Step2: IsoPAgCl (5.0245 g, 17 mmol) was suspended with silver acetate (3.0077 g, 18 mmol) in 85 mL of dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of Celite packed in a column. The brown solution was then dried in rotary evaporator followed by drying at 45 °C under vacuum 4 hours to afford 4.9828 g of a brown powder (IsoPAgOAc). 4.5002 g of the product were precipitated using cold CH_2Cl_2/hexane mixture. The precipitates were filtered on Buchner and washed with hexane before being dried at 45 °C for 1 day. The brown powder (3.6943 g, 75% overall yield) was analyzed by NMR in $CDCl_3$.



Scheme S5. Two steps procedure to synthesize IsoPAgOAc catalyst.

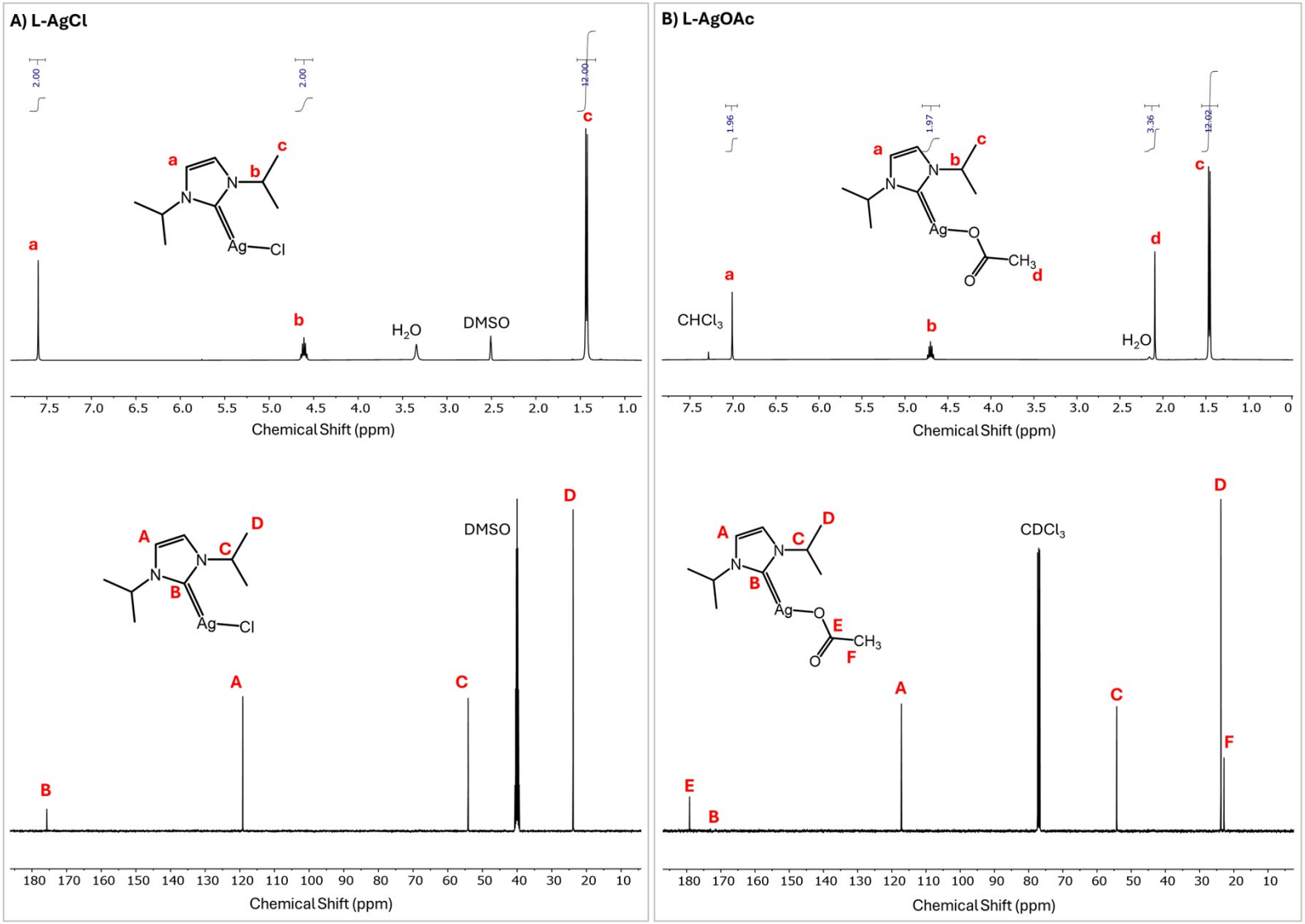
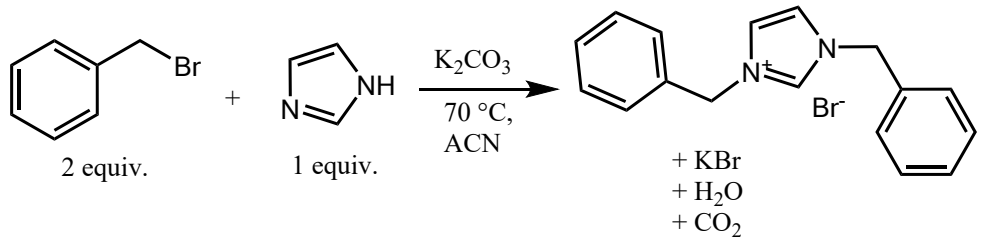


Figure S19. ^{1}H- and ^{13}C-NMR spectra of IsoPAgCl in DMSO-d_6 and IsoPAgOAc in $CDCl_3$.

Synthesis of [1,3-Dibenzyl-1H-imidazol-2(3H)-ylidene] Silver bromide (BnzAgCl) and acetate (BnzAgOAc):

Synthesis of 1,3-dibenzylimidazolium bromide: Benzyl bromide (10.2618 g, 60 mmol), 1H-imidazole (2.0424 g, 30 mmol) and potassium carbonate (6.2192 g, 45 mmol) were placed in a 250 mL round-bottom flask with 180 mL of acetonitrile. The suspension was heated at 70 °C overnight. The solvent was removed, 400 mL of MiliQ water were added and the product was extracted with 4 x 100 ml of dichloromethane. The organic phases were combined and dried using $MgSO_4$. The dichloromethane was evaporated to afford a viscous off-white liquid. The latter was cooled down with liquid nitrogen to obtain a solid and this solid was washed quickly with cold diethyl ether then dried under vacuum at 65 °C overnight yielding an orangish waxy solid (4.2208 g, 42.7 % yield) and analyzed by NMR in $CDCl_3$ (Figure SX). The product (1,3-dibenzylimidazolium bromide) was used without further purification for the synthesis of **[**1,3-Dibenzyl-1H-imidazol-2(3H)-ylidene**]** Silver bromide.



Scheme S6. Synthesis of 1,3-dibenzylimidazolium bromide.

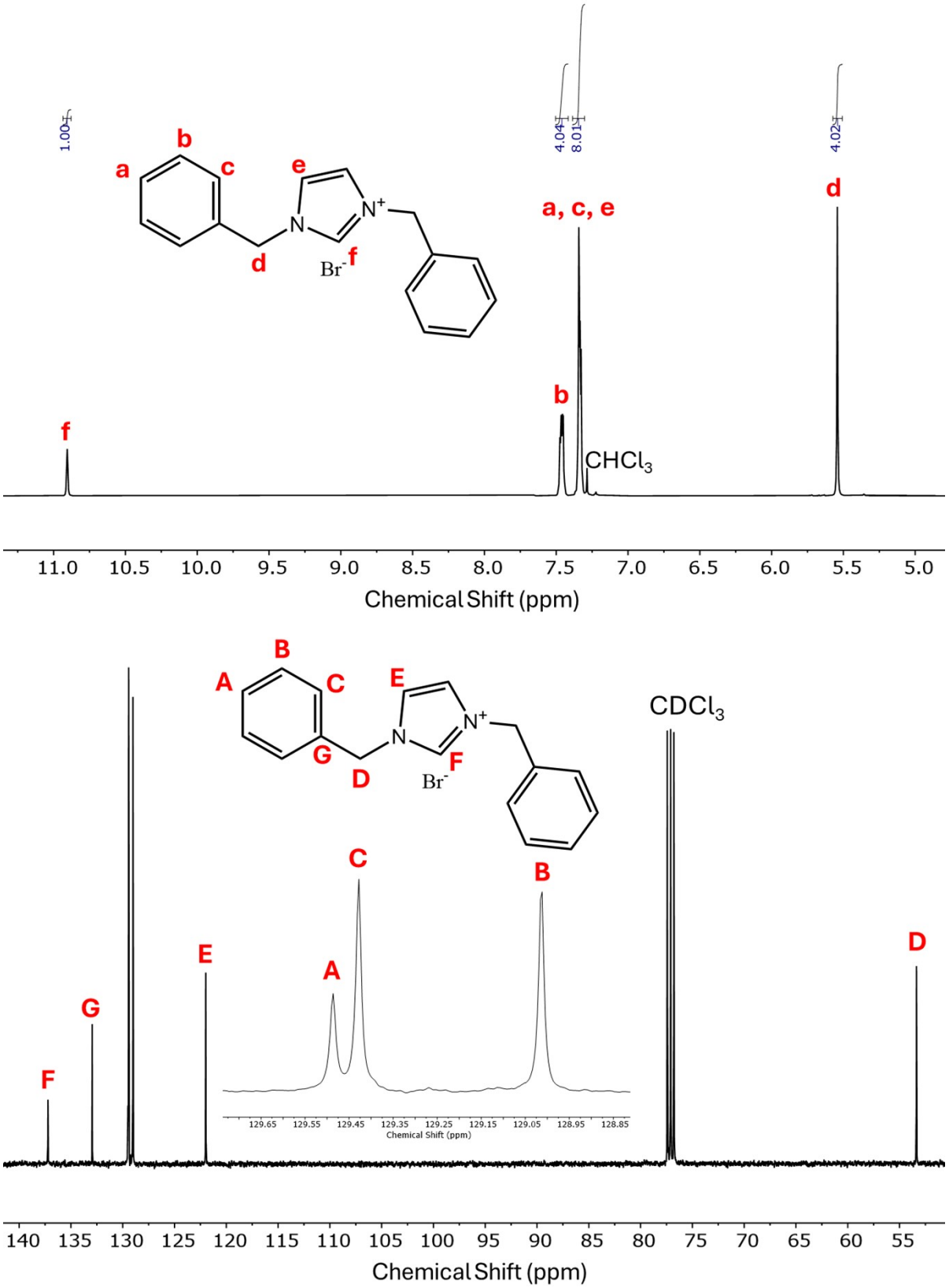
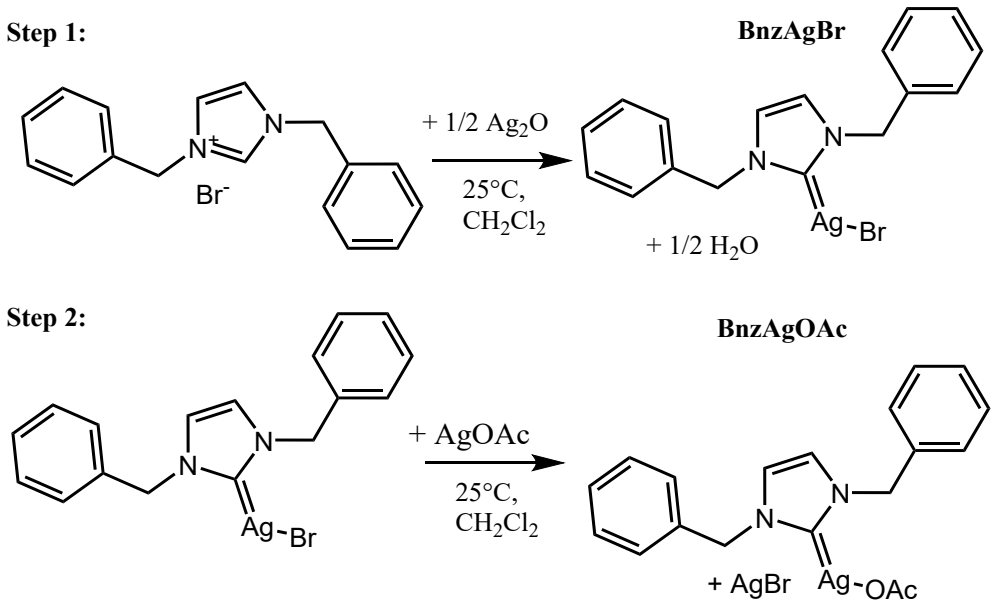


Figure S20. ^{1}H and ^{13}C NMR spectra of IPrAgOAc in deuterated DMSO.

Step1: 1,3-diisopropylimidazolium bromide (2.8479 g, 8.7 mmol) and silver oxide (1.3904 g, 6 mmol) were suspended in 50 mL dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was place under Argon and stirred overnight, and the resulting mixture was filtered through a few cm of celite packed in a column. The yellow solution was then dried in rotary evaporator followed by drying at 45 °C to afford 1.3932 g of a yellowish product (BnzAgBr) (35 % yield). The product was analyzed by NMR in DMSO-d6 and used without further purification in the next step. Note that the compound once in solution was very light-sensitive.

Step2: 1.1775 g of BnzAgBr (2.7 mmol) were suspended with 0.5308 g of silver acetate (3.2 mmol) in 15 mL of dry dichloromethane in a round-bottom flask equipped with a magnetic stirrer and wrapped in Al foil to avoid light exposure. The suspension was placed under Argon and stirred for 2 days, and the resulting mixture was filtered through a few cm of celite packed in a column. The brown solution was then dried in rotary evaporator followed by drying at 45 °C under vacuum overnight to afford 1.12 g of product (BnzAgOAc). The product was analyzed by NMR in $CDCl_3$.



Scheme S7. Two steps procedure to synthesize BnzAgOAc catalyst.

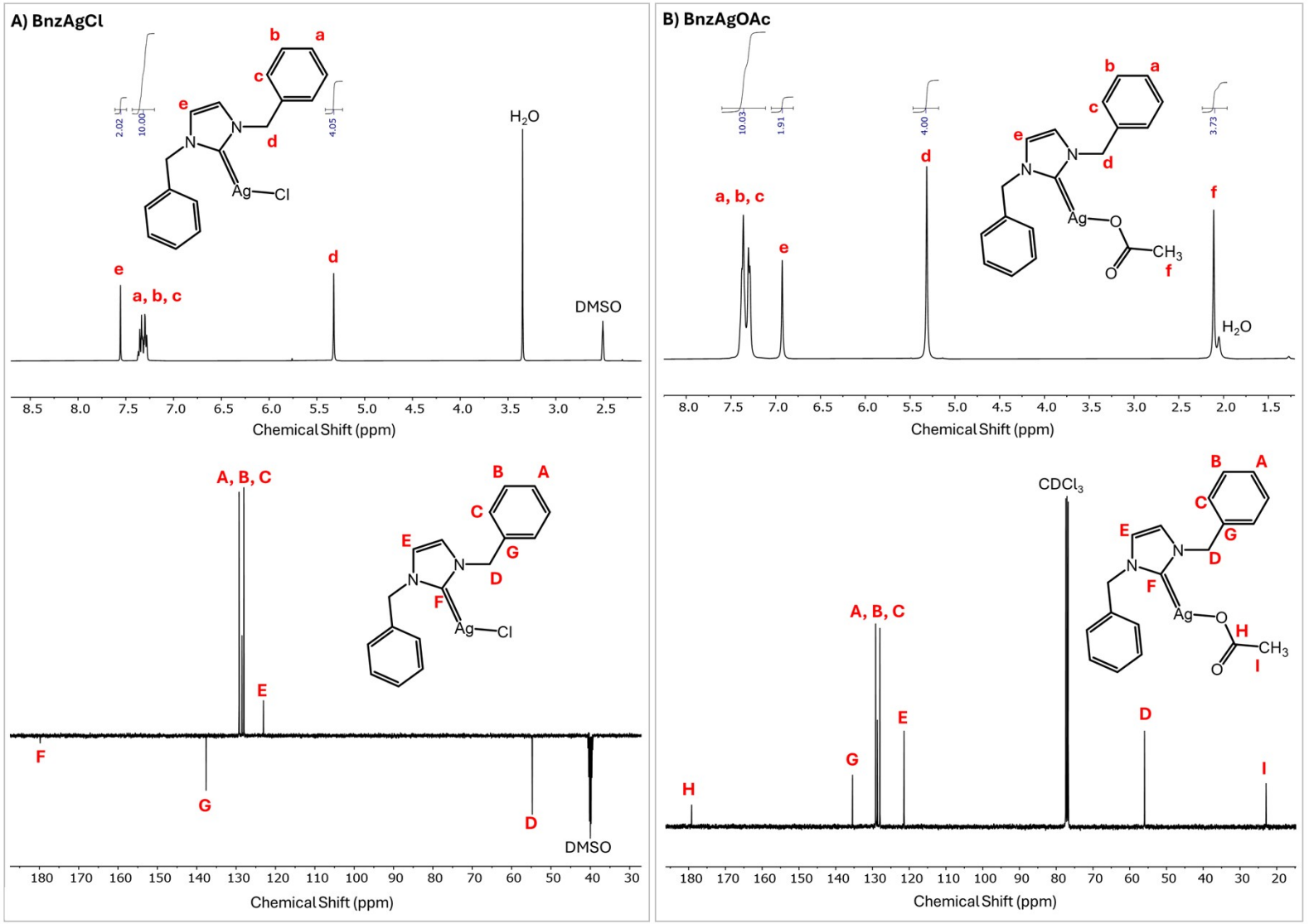


Figure S21. ^{1}H and ^{13}C NMR spectra of BnzAgCl in deuterated DMSO and BnzAgOAc in deuterated chloroform

5. Synthesis of supported catalyst

Merrifield Resin (MR) modification. Adapted from literature,[1] the MR was modified in three steps. Elemental analyses and SEM analyses were performed between each step.

Step 1: Quaternization. In a 100 mL round bottom flask, 10 g of MR (4 mmol Cl/g) were suspended in 40 mL of a solvent mixture (1:1 v:v acetonitrile:toluene) and added with 40 mL of methylimidazole (500 mmol). The suspension was heated up to 80°C for 24 hours without stirring to avoid damaging the beads. The resulting suspension was filtered on a Büchner funnel and washed successively with 400 mL of toluene, acetonitrile, and ethanol. A sample was withdrawn (200 mg) and dried at 40°C for 48 hours under vacuum for SEM and elemental analysis. The rest of the beads (**MR1**) were used without further purification in the subsequent stage.

Step 2: Anion exchange. The beads (**MR1**) were suspended in 150 mL of ethanol and added with 22.7 g of potassium acetate in a beaker. The suspension was shaken for 3 days, filtered on a Büchner funnel, and washed with methanol. The beads were resuspended in 200 mL of methanol and shaken for 1 day to remove the residual KOAc and the formed KCl, the latter being poorly soluble in ethanol but soluble in methanol. The beads were filtered, washed with more methanol, and dried at 55°C for 24 hours to afford 12.97 g of product (**MR2**). The beads were analyzed using SEM and elemental analysis.

Step3: Silver carbene synthesis. In a round bottom flask wrapped in Al foil, 11.76 g of **MR2** were suspended in 115 mL of dry dichloromethane with 4.40 g of silver oxide and stirred gently with a magnetic stirrer for 24 hours. The resulting suspension was filtered on Buchner and washed with 1) dichloromethane, 2) ethanol, 3) aqueous ammonia (4M) and 4) ethanol. The brown beads were then dried at 55 °C under vacuum overnight. SEM analysis revealed that the beads were covered with solid deposit. Thus, 9 g of these beads were suspended in 160 mL of aqueous solution of ammonia (4M) and stirred gently for 6 hours. The resulting suspension was filtered and washed with 500 mL of water and 500 mL of ethanol before being dried at 55°C under vacuum to afford 7.83 g of lighter brown beads (about 13 wt% loss). The beads (**MR3**) were analyzed by SEM revealing a much cleaner surface and by elemental analysis.

6. Catalysts screening: batch procedure

Carboxylative cyclisation of 2-Methyl-3-butyn-2-ol: In a representative experiment, a stainless-steel autoclave with a nominal volume of 12 ml, equipped with a magnetic stirrer, and a gas inlet/outlet was charged with 4 mL of acetonitrile, 8 mmol of 2-Methyl-3-butyn-2-ol and 2 mol% of catalyst (and 2 mol% of co-catalyst). The autoclave was equilibrated at the desired temperature and run during a given time (5-30 minutes) at a given pressure of CO_2 (5-15 bar). The crude reaction mixture was analysed by ^1H NMR in $CDCl_3$ (or DMF-d6) to determine the conversion.

Figure S22. stainless-steel autoclave with a nominal volume of 12 ml.

Purification.

A purification protocol was designed to remove most of the silver catalyst (IPrAgOAc). The synthesis of DMACC was done on a scale of 10 mL of a solution of 35 mmol of 2-Methyl-3-butyn-2-ol (2.9442 g) with 2 mol% of IPrAgOAc (0.2054 g, 0.7 mmol) and 2 mol% of DBU (0.1066 g, 0.7 mmol) in acetonitrile (5.11 g). The reaction was carried out at 50 °C, 15 bar for 30 minutes. The conversion was checked by NMR in $CDCl_3$ reaching > 99 % with a selectivity > 99% (traces of hydroxy-ketone, the hydrolysed carbonates). After the reaction, the mixture was placed in a vial with 500 mg of Quadrapur TU (thiourea-based resin) beads and stirred overnight. The next day, the yellowish solution was eluted through a silica gel column (4 cm high, column diameter of 2 cm, 3.5 mL acetonitrile) by the assistance of a slight nitrogen pressure. The solvent was then removed under vacuum at 40 °C using rotary evaporator and finally dried at room temperature with a vacuum pump to afford a yield of 85%. NMR of the product showed silver were left under the form of the complex $(IPr)_2AgOAc$. No trace of IPrAgOAc nor DBU was detected. The remaining amount of silver (196.2 ppm) was measured via inductively coupled plasma optical emission spectrometry (ICP-OES) after acid digestion (2 mL of concentrated HNO_3) of 253.8 mg of sample which were diluted with MiliQ water afterward to end up with a 25 mL solution. The purification protocol thus allowed the removal

of 96 % of the silver. Note that all the synthesized cyclic carbonates can be distilled under vacuum as done elsewhere[2] to get completely rid of the silver.

7. Kinetics of CO_2 addition to propargylic alcohols monitored by Raman spectroscopy:

2-Methyl-3-butyn-2-ol (1a): a solution of 1.94 mL of 2-Methyl-3-butyn-2-ol in 10 mL of acetonitrile with 2 mol% of IPrAgOAc (222 mg) and 2 mol% DBU (59.8 µL) was prepared and placed at 50 °C, preheated for 15 minutes before setting the CO_2 pressure of 10 bar. The final conversion was determined by NMR in $CDCl_3$ (> 99%). During the kinetic, spectra were acquired every 30 s with two acquisitions of 2 s. Note that, precipitations could occur during the measurement reducing the signal quality over time.

1-Ethynyl-1-cyclohexanol (1d): Preparation of 1) 100 mL of a 1.7 M solution of **1d** with 2 mol% of IPrAgOAc and 2 mol% of DBU in acetonitrile, 2) 25 mL of a 1.7 M solution of **1d** with 2mol% IPrAgOAc and no DBU in acetonitrile and 3) 25 mL of a 3.5 M solution of **1d** with 2 mol% of IPrAgOAc and 2 mol% of DBU in acetonitrile. For each experiment, 15 mL of the solutions were used. During the kinetics, spectra were acquired every 30 s with two acquisitions of 3 s for the 1.7 M solutions while for the test with the 3.5 M solution, spectra were acquired every 15 s with two acquisitions of 1.5 s. Note that, though no precipitation was observed with **1d**, a reddish colour of the solutions was always observed after the reactions probably due to the formation of some silver nanoparticles. Details about the experimental setup used for Raman measurements have already been described by Grignard et al.[3,4]

The obtained spectra were zoomed between 1600 and 2350 cm^{-1}, baseline-corrected with a 5^{th} degree polynomial fit using the Savitsky-Golay algorithm and normalised to the band of acetonitrile at 2220 cm^{-1} (C≡N stretching). To obtain the kinetic profiles, each experimental spectrum was decomposed with two reference spectra (pure reactant (t_0) and product obtained in acetonitrile (t_{final})) and the relative contribution of each component was obtained with a classical least square algorithm. Finally, relative contributions of both components were converted to molar percent using a calibration model built with the same spectral decomposition method applied to mixture containing known concentration of reactant and product. Experimental profiles reported as molar percent were then fitted with an exponential decay function and the time necessary to obtain 50% of conversion ($t_{50\%}$) were calculated accordingly.

8. Flow chemistry setup.

Homogeneous catalysed carboxylative cyclisation of propargylic alcohols at microscale

Continuous flow reactors consisted in modular coil assemblies constructed with high purity PFA capillaries (1.58 mm of outer diameter and 762 µm of internal diameter) equipped with Super Flangeless nuts and ferrules (IDEX/Upchurch Scientific), as well as a High-Pressure Static Mixing Tee (arrowhead). The liquid feed was handled with High force Chemyx Fusion 6000-X and the gaseous feed was regulated with a ThalesNano gas module (0-100 mL_N) mass flow controller, both equipped with check valves (IDEX/Upchurch Scientific). The downstream pressure was regulated with a dome-type backpressure regulator (BPR-10 Zaiput Flow Technologies). Thermoregulation of the reactor was performed by immerging the coil in thermoregulated bath (50 °C). To ensure good mixing between the gas and the liquid feeds the High-Pressure Static Mixing Tee was immerged in a Branson 1510 ultrasonic bath (frequency of 40 kHz) at 45 °C. The feed A consisted of propargyl alcohol solution in acetonitrile of given concentrations containing IPrAgOAc catalyst and DBU (2 mol% each). The solutions were prepared fresh before the experiments and were used directly for maximum 10 hours except if stated otherwise. The crude product was collected at the outlet and directly analysed by NMR in $CDCl_3$.

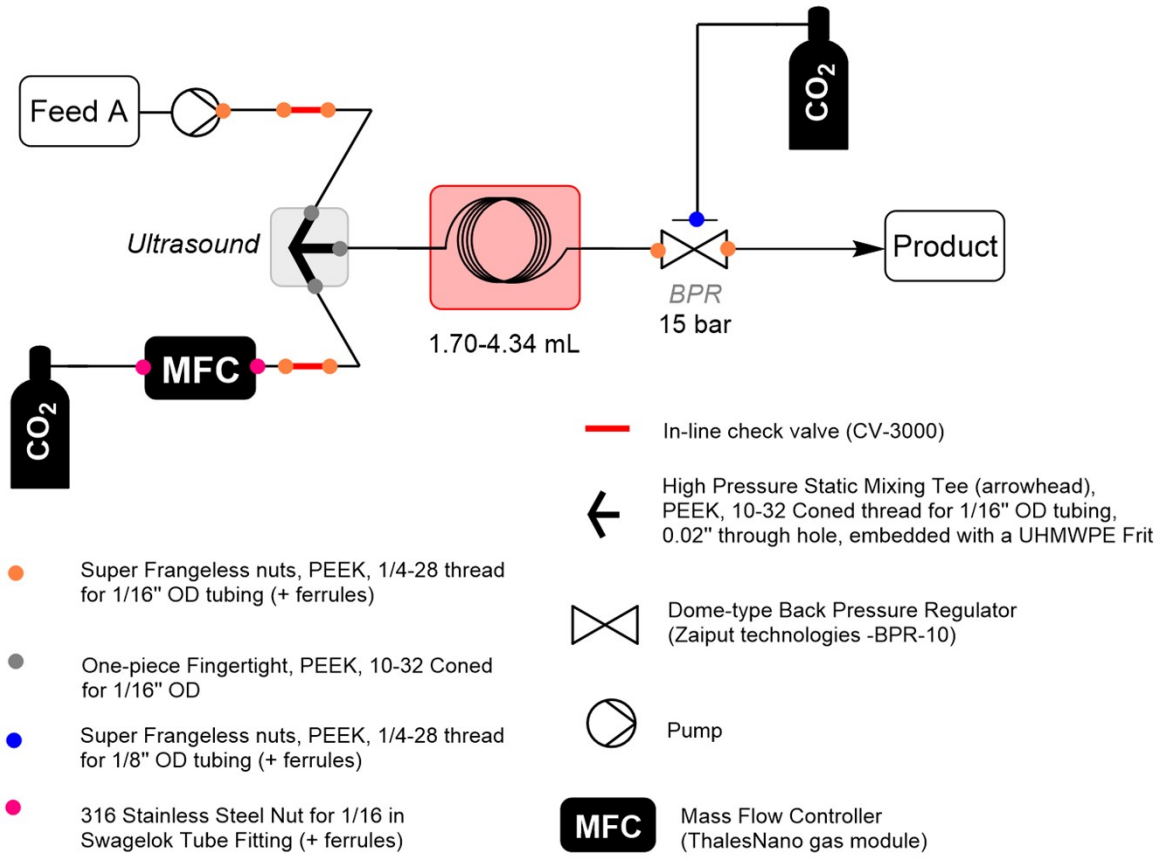


Figure S23. Setup for the carbonatation of propargylic alcohols at microscale.

The 1.7 M solutions were prepared by adding propargylic alcohols (42.5 mmol, **1a**: 3.5721 g; **1c**: 5.3635 g; **1d**: 5.2777 g; **1g** (0.85 M): 7.9592 g), DBU (0.85 mmol, 129.4 mg, 127.1 µL), IPrAgOAc (0.85 mmol, 0.4722 g) in a 25 mL volumetric flask and the latter was completed with acetonitrile. The 3.5 M solution of **1d** was prepared by adding **1d** (87.5 mmol, 10.8658 g), DBU (1.75 mmol, 0.2664 g, 261.7 µL) and IPrAgOAc (1.75 mmol, 0.9721 g) in a 25 mL volumetric flask completed with acetonitrile. Those solutions consisted in feed A and were injected at flow rate of 0.110, 0.100, 0.270, 0.104 mL min^{-1} depending on the conditions used (Figure 5). The CO_2 was injected with a flow rate of 8, 4, and 19 mL_N min^{-1} depending on the conditions used (Figure 5). After complete stabilisation of the system (at least 25 minutes), the reaction mixture was collected and sampled by NMR in $CDCl_3$ to monitor the conversion.

Homogeneous catalysed carboxylative cyclisation of propargylic alcohols concatenated with the addition of amine to produce oxazolidone at microscale.

Continuous flow reactors consisted in modular coil assemblies constructed with high purity PFA capillaries (1.58 mm of outer diameter and 762 µm of internal diameter) equipped with Super Flangeless nuts and ferrules (IDEX/Upchurch Scientific), as well as a High-Pressure Static Mixing Tee (arrowhead). The liquid feeds were handled with High force Chemyx Fusion 4000-X independent motors dual syringe pumps and the gaseous feed was regulated with Bronkhorst EL FLOW Prestige mass flow controller both equipped with check valves (IDEX/Upchurch Scientific). The downstream pressure was regulated with a dome-type backpressure regulator (BPR-10 Zaiput Flow Technologies). Thermoregulation of High-Pressure Static Mixing Tee and reactor I was ensured by immerging both parts in a a Branson 1510 ultrasonic bath (frequency of 40 kHz) at 50 °C. The reactor II and the T mixer were immerged in another bath heated at 55 °C. The feed A consisted of 1-ethynyl-1-cyclohexanol solution (3.5 M) in acetonitrile and DBU (2 mol%) and the feed B was composed of heptylamine (6 M) in acetonitrile with DBU (3 mol%). The solutions were freshly prepared before the experiments and used directly (maximum 10 hours). The crude product was collected at the outlet directly analysed by NMR in $CDCl_3$ for the α-alkylidene cyclic carbonate product (reactor I) and in deuterated DMSO for the oxazolidone product (reactor II) to determine the conversions and selectivity (Figure S10). The product was purified by recrystallization in acetonitrile yielding a whitish crystal characterized by ^{1}H and ^{13}C NMR in deuterated DMSO. No silver was detected by ICP (below the threshold of 1 ppm).

The 3.5 M solution of **1d** was prepared by adding **1d** (87.5 mmol, 10.8658 g), DBU (1.75 mmol, 0.2664 g, 261.7 µL) and IPrAgOAc (1.75 mmol, 0.9721 g) in a 25 mL volumetric flask completed with acetonitrile. The solution consisted in feed A and was injected at flow rate of 0.104 mL min^{-1} (Figure 6). The CO_2 was injected with a flow rate of 8 mL_N min^{-1} (Figure 6).

After complete stabilisation of the system (30 minutes), the reaction mixture was collected and sampled by NMR in $CDCl_3$ to monitor the conversion to ensure that complete conversion was achieved. The first module was then plugged on the second module. The second solution (feed B) was prepared by adding heptylamine (150 mmol, 17.2830 g) and DBU (4.5 mmol, 0.6851 g) in a 25 mL volumetric flask and completed it with acetonitrile. The solution was injected in the system with a flow rate of 0.06 mL min^{-1}. The system was stabilized for 35 minutes before sampling the outlet by NMR in deuterated DMSO to monitor the conversion. Note that the product quickly solidifies when coming back at r.t. It can be purified by cold recrystallisation in acetonitrile.

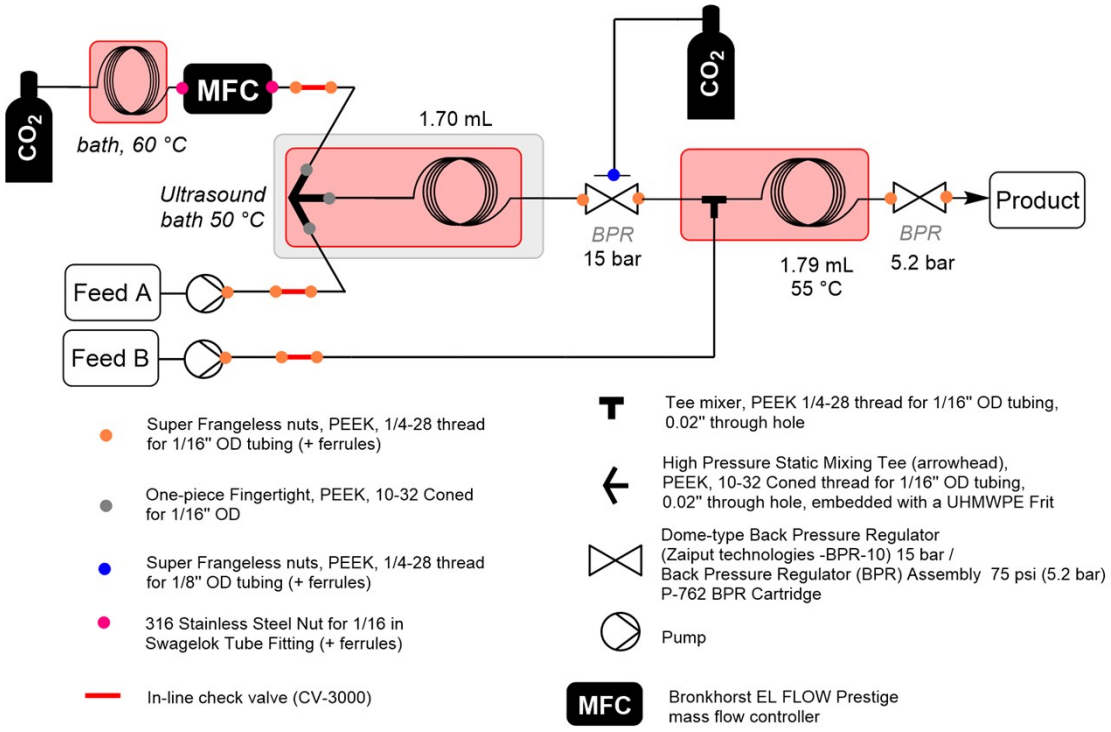


Figure S24. Setup for the carbonatation of propargylic alcohols concatenated with the addition of amine to produce oxazolidone at microscale.

Heterogeneous catalysed carboxylative cyclisation of propargylic alcohols at microscale with DBU cocatalyst.

Continuous flow reactors consisted in modular coil assemblies constructed with high purity PFA capillaries (1.58 mm of outer diameter and 762 µm of internal diameter) equipped with Super Flangeless nuts and ferrules (IDEX/Upchurch Scientific), as well as a High-Pressure Static Mixing Tee (arrowhead). The packed-bed reactor consists in a Waters guard column (4.6 x 30 mm) filled with 350 mg of modified resin catalyst. Acetonitrile was then passed through the column to fill the empty space. The internal volume (0.22 mL) was measured by differential gravimetry, comparing the mass of the column before and after being filled with acetonitrile. The liquid feed was handled with High force Chemyx Fusion 6000-X and the gaseous feed was regulated with a Bronkhorst EL FLOW Prestige mass flow controller, both equipped with check valves (IDEX/Upchurch Scientific). The downstream pressure was regulated with a dome-type

backpressure regulator (BPR-10 Zaiput Flow Technologies). Thermoregulation was performed by immerging the High-Pressure Static Mixing Tee, the PFA coil and the packed-bed reactor in thermoregulated ultrasound bath Branson 1510 ultrasonic bath (frequency of 40 kHz) at 50 °C. A 25 mL solution of 2-Methyl-3-butyn-2-ol (1.7 M, 3.5721 g) containing 129.5 mg of DBU in acetonitrile (15.8324 g) was prepared and injected with a flow rate of 0.040 mL min^{-1} (feed A). The CO_2 was injected with a flow rate of 2 mL_N min^{-1}. After complete stabilisation of the system (75 minutes), the reaction mixture was collected for 255 minutes (10.2 mL) and sampled by NMR in $CDCl_3$ to monitor the conversion.

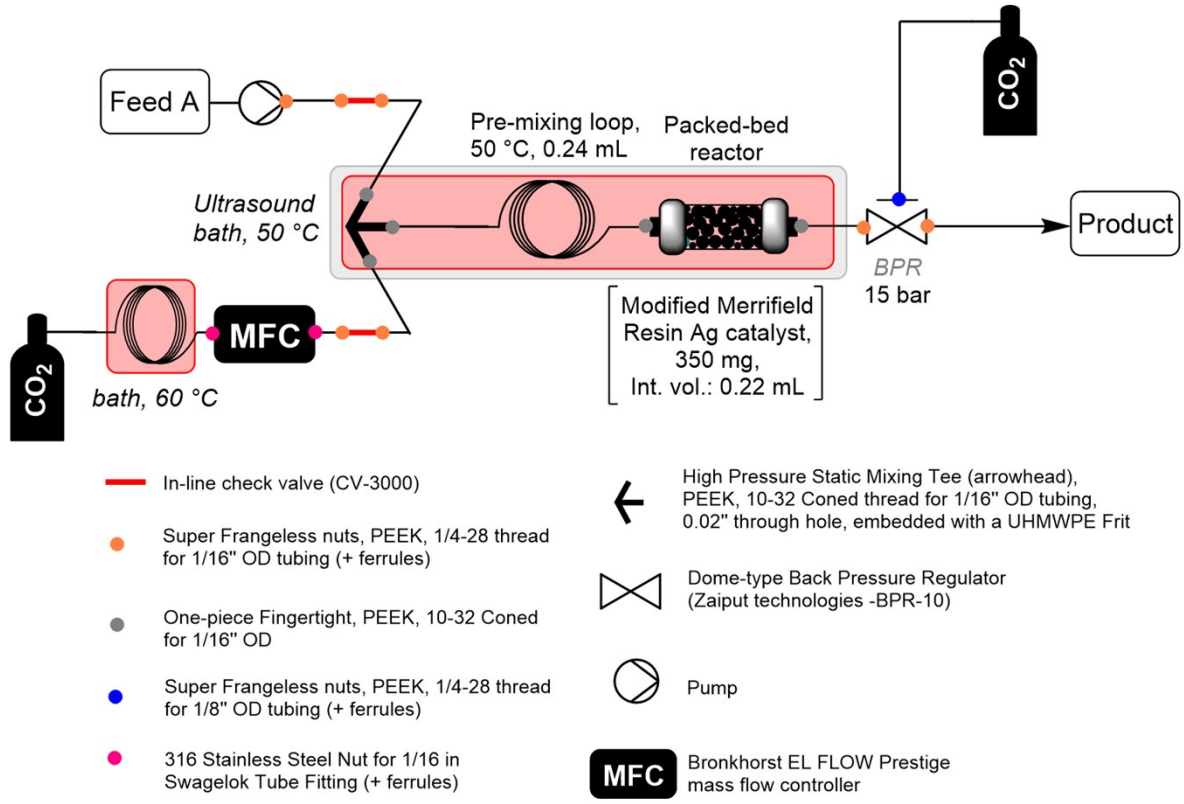


Figure S25. Setup for the carbonatation of propargylic alcohols at microscale.

Purification for heterogeneous catalyst.

A purification protocol was designed to purify the final product from remaining propargylic alcohol and co-catalyst (DBU). The silver catalyst is supported and does not require to be removed after synthesis. As mentioned above, 10.2 mL of solution were collected and then purified. The purification consisted in extraction using diethyl ether (3x 20 mL) and water (60 mL). The organic phases were collected and dried on $MgSO_4$, and the solvent was removed via rotary evaporation and the final liquid was dried in vacuum oven at 25 °C to afford an isolated yield of 70.6% yield. As expected, no silver that was detected by ICP (1 ppm detection threshold).

Heterogeneous catalysed carboxylative cyclisation of propargylic alcohols at microscale without DBU.

Continuous flow reactors consisted in modular coil assemblies constructed with high purity PFA capillaries (1.58 mm of outer diameter and 762 µm of internal diameter) equipped with Super Flangeless nuts and ferrules (IDEX/Upchurch Scientific), as well as a High-Pressure Static Mixing Tee (arrowhead). The packed-bed reactor consisted in a Waters column (4.6 x 250 mm) filled with 3328 mg of modified resin catalyst. Acetonitrile was then passed through the column to fill the empty space. The internal volume (1.80 mL) was measured by differential gravimetry, comparing the mass of the column before and after being filled with acetonitrile. The liquid feed was handled with High force Chemyx Fusion 6000-X and the gaseous feed was regulated with a Bronkhorst EL FLOW Prestig mass flow controller, both equipped with check valves (IDEX/Upchurch Scientific). The downstream pressure was regulated with a dome-type backpressure regulator (BPR-10 Zaiput Flow Technologies). The thermoregulation of the PFA premixing loop and the High-Pressure Static Mixing Tee was ensured by immerging the parts in a thermoregulated ultrasound bath Branson 1510 ultrasonic bath (frequency of 40 kHz) at 50 °C while the column was heated in a column thermostat Jetstream 2 Plus set at 50.0 °C. The feed A consisted of 1-Ethynyl-1-cyclohexanol solution in acetonitrile (1.7 M). The solution was freshly prepared before the experiment. The crude product was collected at the outlet and directly analysed by NMR in $CDCl_3$. However, at a higher concentration of 3.5 M, the column clogged almost immediately. This observation is consistent with the trend observed for the homogeneous catalyst (Table S2): the less bulky the NHC, the lower its stability towards propargylic alcohols, potentially leading to NHC exchange and silver-propargylic alcohol precipitation. In this case, the nitrogen atoms bear benzyl groups from the resin attachment point and methyl groups from the methyl imidazole used. However, replacing the latter with the more stable diisopropylphenyl substituent was challenging due to the low reactivity caused by its bulkiness. The 1.7 M solution of **1d** was prepared by adding propargylic alcohol (42.5 mmol, 5.2777 g) in a 25 mL volumetric flask and the latter was completed with acetonitrile. The solution was injected with a flow rate of 0.104 mL min^{-1} (feed A). The CO_2 was injected with a flow rate of 4 mL_N min^{-1}. After complete stabilisation of the system (40 minutes), the reaction mixture was sampled by NMR in $CDCl_3$ to monitor the conversion. We let the system run for 90 minutes to check its stability, no clogging was observed. However, when a 3.5 M solution of **1d** was tested, the column clogged almost immediately.

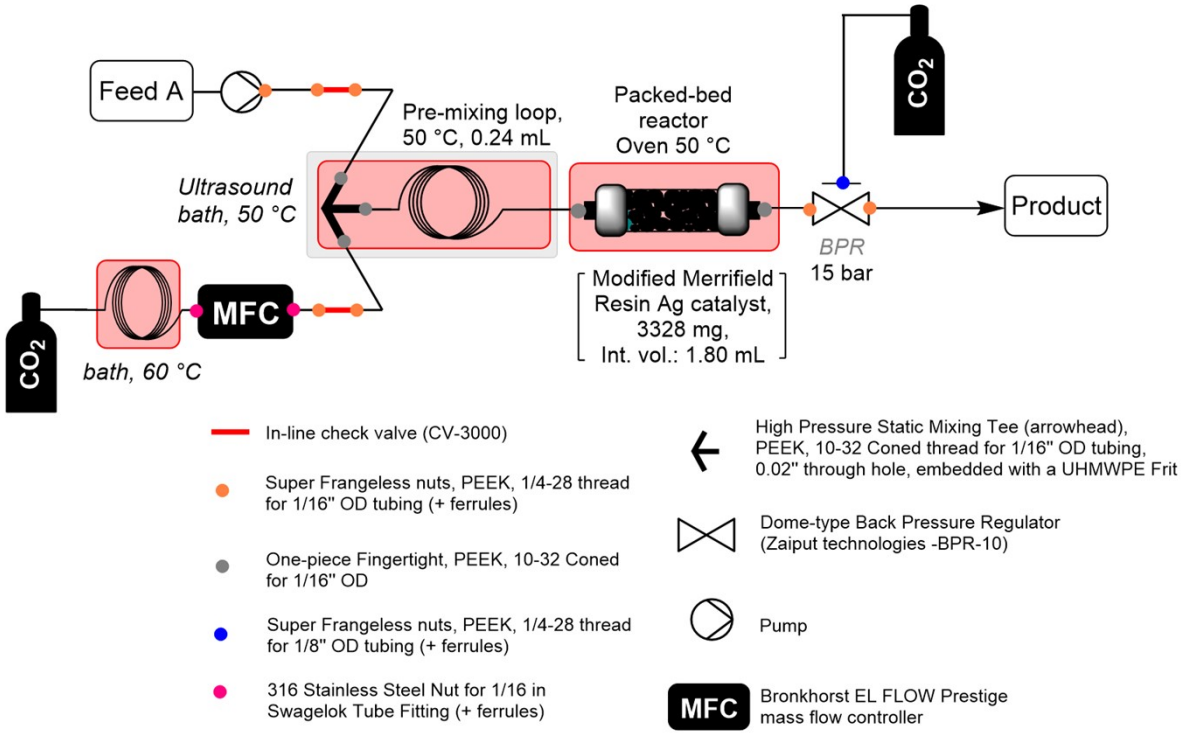


Figure S26. Setup for the carbonatation of propargylic alcohols at microscale.

9. Metrics calculated in this paper

1) Daily production (g day^{-1})

Batch process.

$$Daily\ prod. = Amount * \frac{MM}{1000} * \frac{1}{time} * \frac{Conv.}{100} * \frac{Select.}{100}$$

where amount corresponds to amount of propargylic alcohol (mmol) per batch, MM is the molar mass of the resulting α-alkylidene cyclic carbonate (g mole^{-1}), time corresponds to the time required to complete one run includes the reaction time plus an additional 5 minutes to account for the handling time by an experienced operator. The conversion and selectivity are defined above and determined for each experiment.

Continuous flow process.

$$Daily\ prod. = Flow\ rate * Conc. * MM * 1.44 * \frac{Conv.}{100} * \frac{Selectivity}{100}$$

where the flow rate corresponds to the feeding flow rate of propargylic alcohol (mL min^{-1}), Conc. is the concentration of the corresponding solution (mole L^{-1}) and MM is the molar mass of the resulting α-alkylidene cyclic carbonate (g mole^{-1}). The conversion and selectivity are defined above and determined for each experiment. 1.44 is a factor to obtain the value in the final metric (g day^{-1}).

2) Production per catalyst amount (g day^{-1} g_{cat}^{-1}) for heterogeneous catalysis.

$$Production\ per\ catalyst\ amount = \frac{daily\ production}{catalyst\ amount}$$

where the **daily production** is the above defined quantity, and the **catalyst amount** is the quantity of heterogenous catalyst packed in the column expressed in g day^{-1} and g respectively.

3) Space-time yield (STY) (kg h^{-1} L^{-1})

$$STY = \frac{daily\ production}{24 * V_R}$$

where the **daily production** is the above defined quantity and $\mathbf{V_R}$ is the total volume of the batch / continuous flow reactor expressed in g day^{-1} and mL respectively.

4) E-factor

The Environmental factor (E-factor)[5] is calculated for the scaled-up batch process with the inclusion of the catalyst (IPrAgOAc), the solvent (acetonitrile) and the hydrolysis side product (hydroxy-ketone) in order to obtain the most accurate estimation of waste generation. The E factor depends only on the amount of the materials involved in the synthesis and in the purification but not on the synthesis method if the quantities, concentrations, etc remain identical. For a reaction that reaches complete conversion and uses the same purification process, the E factors for batch and flow methods are indistinguishable, except for the quantity of CO_2 used. Unfortunately, determining the amount of CO_2 consumed in batch mode very difficult. We worked at constant pressure (open cylinder), making it infeasible to account for CO_2 in the reactor's dead volume and the amount dissolved in the solvent up to saturation. Therefore, we have chosen to make a scale-up in batch to work on the purification process (DBU and silver removal) but since the reaction outcomes are the same as in flow (>99% conversion, >99 % selectivity), the purification protocol would be identical. We thus used the CO_2 amount of flow (1 equivalent) to calculate the E-factor. It gives access to the honest E-factor that would have been obtained if the reaction was carried out in flow directly. The E-factor is determined here by using the batch data and purification on the scale of 35 mmol of propargyl alcohol when involving an equimolar amount of CO_2 as permitted by flow. While the production of fine chemicals is usually associated with E-factor values ranging between 5 and 50, our upstream carbonation process gives an E-factor of **2.32**, therefore highlighting its reduced environmental footprint. When the downstream purification is included in the calculation, the E-factor increases to **3.50**, considering Quadrapur Resin and silica as waste compounds.

$$E-factor = \frac{\sum_j m_{input,j} - m_{product}}{m_{product}}$$

Considering a 35 mmol scale feed containing:

Prop Alcohol	2.94 g
catalyst	0.21 g
DBU	0.11 g
acetonitrile	7.86 g
CO_2	1.54 g
Quadrapur resin	0.5 g
silica	4 g

DMACC	3.81 g

Table S5. Comparison of batch metrics determined for this work and the main studies in the literature for the synthesis of 2-Methyl-3-butyn-2-ol (**2a**)

Study	Molar mass	Amount per batch	time per batch[a]	Reactor volume	Yield	Selectivity[b]	Isolated Yield	Daily Production	Space-time yield
	g mol^{-1}	mmol	min	mL	%	%	%	g day^{-1}	kg h^{-1} L^{-1}
Org. Lett. 2019, 21, 5, 1422–1425	128.13	5	1085	40	n.a.	n.a.	87	0.7	7.7E-04
Adv. Synth. Catal. 2016, 358, 1251-1258	128.13	2.5	725	10	96	n.a.	95	0.6	2.5E-03
ChemSusChem 2015, 8, 821-827	128.13	2.5	65	10	92	n.a.	n.a.	6.5	2.7E-02
Angew. Chem. Int. Ed. 2017, 56, 10394-10398	128.13	260	485	80	n.a.	n.a.	70	69.2	3.6E-02
This work	128.13	8	35	12	99	99	n.a.	41.3	1.4E-01
This work (scale-up)	128.13	35	35	12	99	99	85	155.3	5.4E-01

[a] 5 minutes were added to all reaction time per batch to account for the time needed for reactor handling. [b] When the selectivity was not available, we accounted a selectivity of 100 %. [c] For the daily production and STY, the isolated yield was used instead of the yield when available.

Table S6. Batch metrics calculated for the homogeneous catalytic systems done in the paper.

Batch homogeneous catalysis								
Product	**Molar mass**	**Amount per batch**	**time per batch**	**Reactor volume**	**Yield**	**Selectivity**	**Daily Production**	**Space-time yield**
	g mol^{-1}	mmol	min	mL	%	%	g day^{-1}	kg h^{-1} L^{-1}
2a	128.13	8	35.00	12.00	99	99	41.3	0.14
2b	140.14	8	35.00	12.00	48	99	21.9	0.08
	140.14	8	15.00	12.00	94	99	100.2	0.35
2c	170.21	8	35.00	12.00	46	99	25.5	0.09
	170.21	8	15.00	12.00	99	99	128.1	0.44
2d	168.19	8	35.00	12.00	81	99	44.4	0.15
	168.19	8	15.00	12.00	99	99	126.6	0.44
2e	142.15	8	35.00	12.00	0	0	0.0	0.00
	142.15	8	15.00	12.00	0	0	0.0	0.00
2f	88.06	8	35.00	12.00	28	84	6.8	0.02
	88.06	8	15.00	12.00	86.0	15	8.7	0.03
2g	462.57	4	15.00	12.00	47.0	99	82.6	0.29

Table S7. Continuous flow metrics calculated for the homogeneous catalytic systems done in the paper.

Continuous Flow Homogeneous catalysis								
Product	**Molar mass**	**Flow rate**	**Concentration**	**Reactor volume**	**Conv.**	**Selectivity**	**Daily Production**	**Space-time yield**
	g mol^{-1}	mL min^{-1}	mol L^{-1}	mL	%	%	g day^{-1}	kg h^{-1} L^{-1}
2a	128.13	0.110	1.70	1.70	99.9	99.5	34.3	0.84
	128.13	0.100	1.70	1.70	99.9	99.4	31.1	0.76
2c	170.21	0.110	1.70	1.70	98.4	100	45.1	1.11
	170.21	0.100	1.70	1.70	99.3	100	41.4	1.01
2d	168.19	0.110	1.70	1.70	99.9	99.8	45.2	1.11
	168.19	0.100	1.70	1.70	99.9	99.8	41.0	1.01
	168.19	0.270	1.70	4.34	99.9	99.7	110.7	1.06
3d	168.19	0.104	3.50	1.70	99.8	99.3	87.4	2.14
	283.41	0.104	3.50	3.49	90.8	100	134.8	1.61
2g	462.57	0.110	1.70	1.70	2.0	100	2.5	0.06
	462.57	0.100	1.70	1.70	9.5	100	10.8	0.26

Table S8. Continuous flow metrics calculated for the heterogeneous catalytic systems done in the paper.

Continuous Flow Heterogeneous catalysis												
Product	**Molar mass**	**Flow rate**	**Conc.**	**Reactor volume**	**Catalyst amount**		**Conv.**	**Select.**	**Daily Prod.**	**Space-time yield**	**Prod. per catalyst amount**	
	g mol^{-1}	mL min^{-1}	mol L^{-1}	mL	mg	mmol*	%	%	g day^{-1}	kg h^{-1} L^{-1}	g day^{-1} g_{cat}^{-1}	mmol h^{-1} $mmol_{cat}^{-1}$
2a	128.13	0.040	1.7	0.46	349.5	0.49	92.7	99.0	11.5	1.04	32.9	8.3
2d	168.19	0.104	1.7	2.04	3328.0	4.66	100	99.8	42.7	0.87	12.8	2.3

*The catalyst amount is calculated using the functionalization density of silver (1.4 mmol g^{-1}) determined by elemental analysis. This amount represents the maximum possible catalytic sites per gram of materials. The real amount is probably lower as the heterogeneous catalyst might be contaminated with silver oxide used for its synthesis

10.References.

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