UNIVERSITAT ROVIRA i VIRGILI

Facultat de Química Tarragona

Application of clays in CO_2 valorisation reactions

MASTERS'S THESIS

SUPPORTING INFORMATION

eurecat
Centre Tecnològic de Catalunya

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1) C.E.C calculation

C.E.C calculations were made based on the method reported by Bergara and Vayer[1]

Table S1. Calibration curve concentration of Cu^{2+} vs Absorbance

Concentration (M)	Abs
0,0005	0,0343
0,001	0,0659
0,002	0,1274
0,004	0,2534
0,006	0,3778
0,008	0,4994
0,01	0,6247

y = 62,106x + 0,0038

Table S2. Results of C.E.C for each sample

Sample	Conditions	Abs	Concentration (M)	Dry mass (g)
S1	2h-100ºC-200	0,0959	0,001483	0,1583
S2	2h-160ºC-200	0,0827	0,00127	0,1598
S3	4h-100ºC-200	0,0951	0,00147	0,1521
S4	4h-160ºC-200	0,0841	0,001293	0,1597
S5	4h-160ºC-380	0,1013	0,00157	0,1429

$$5\text{mL sol A} \cdot \frac{0.05 \text{ mol complex}}{1000\text{mL sol A}} = 0{,}00025 \text{ initial mol}$$

$$100\text{ml sol B} \cdot \frac{[\text{Y}] \text{ mol complex (calibration curve)}}{100\text{ml sol}} = \text{Y final mol}$$

$$\text{Absorbed mols} = 0{,}00025 - \text{Y}$$

$$\text{Meq/100g} = absorbed\ mols \cdot \frac{2\ eq\ complex}{1 mol\ complex} \cdot \frac{1000 meq}{1\ eq} \cdot \frac{100 g\ total}{X\ mass\ dry} =$$

2) ESEM-EDX analysis of hectorite

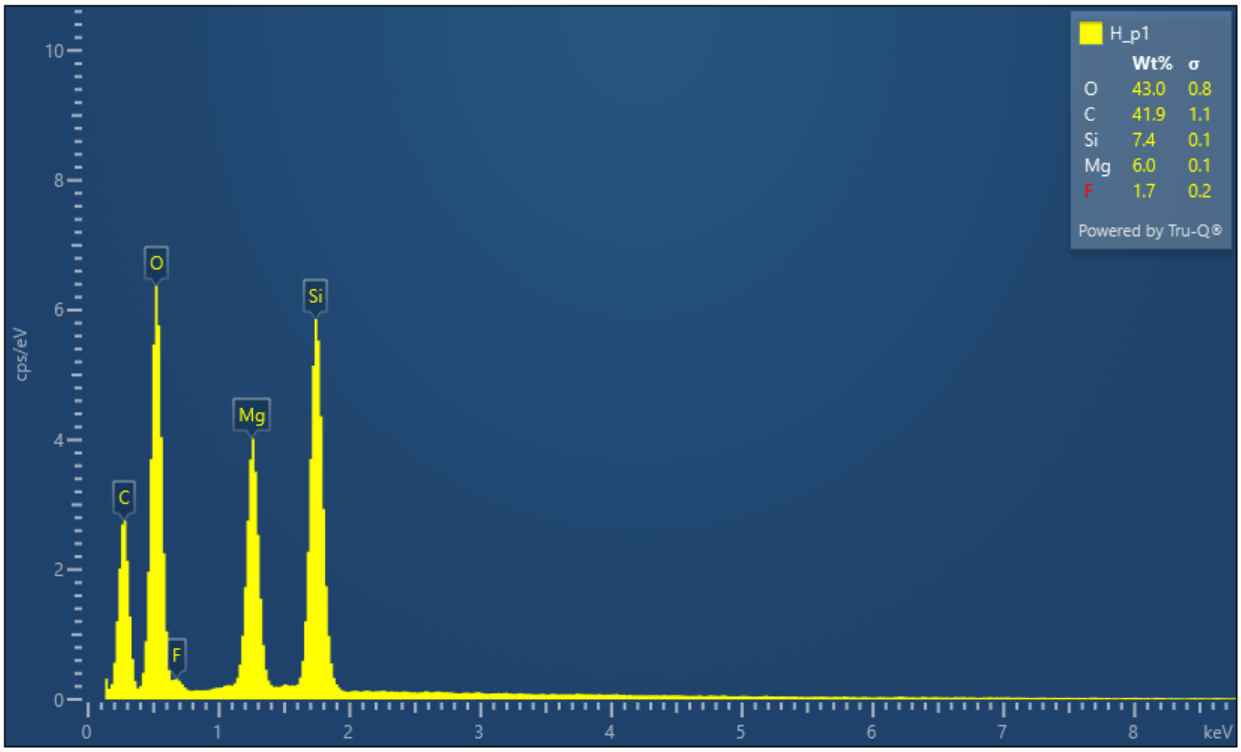


Figure S1. EDX analysis of hectorite sample S3

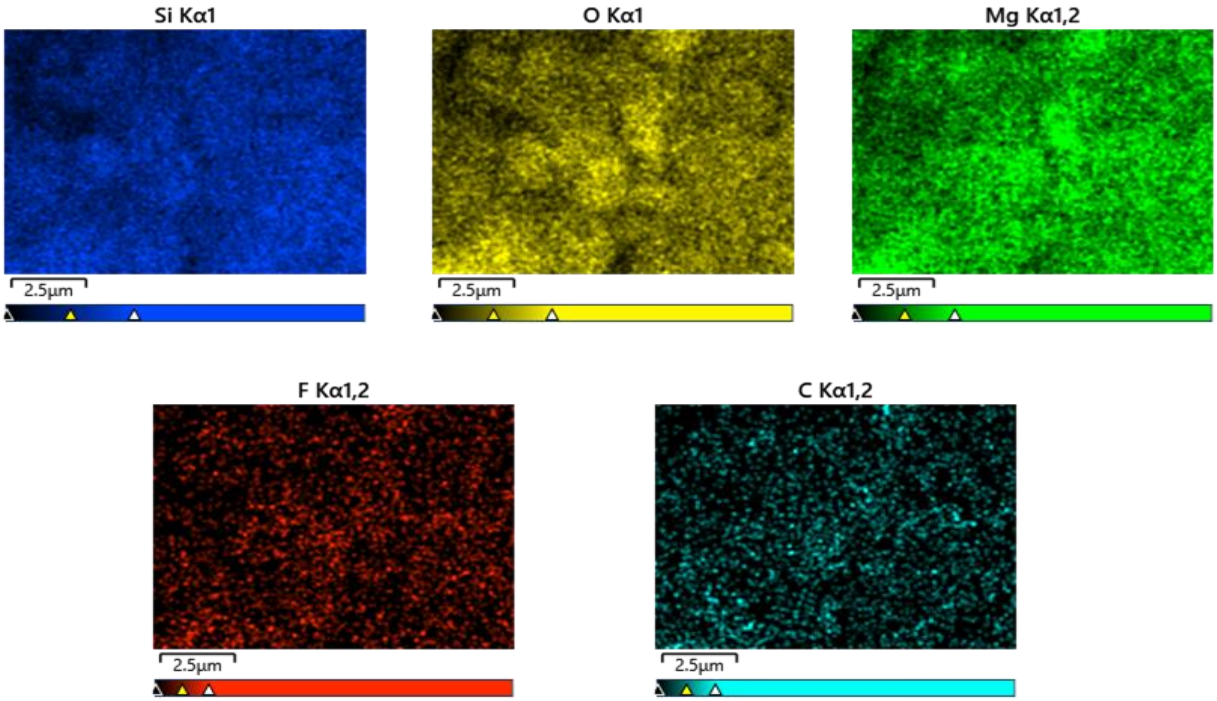


Figure S2. Mapping pictures of Hectorite S3 synthetised at 100ºC for 4h

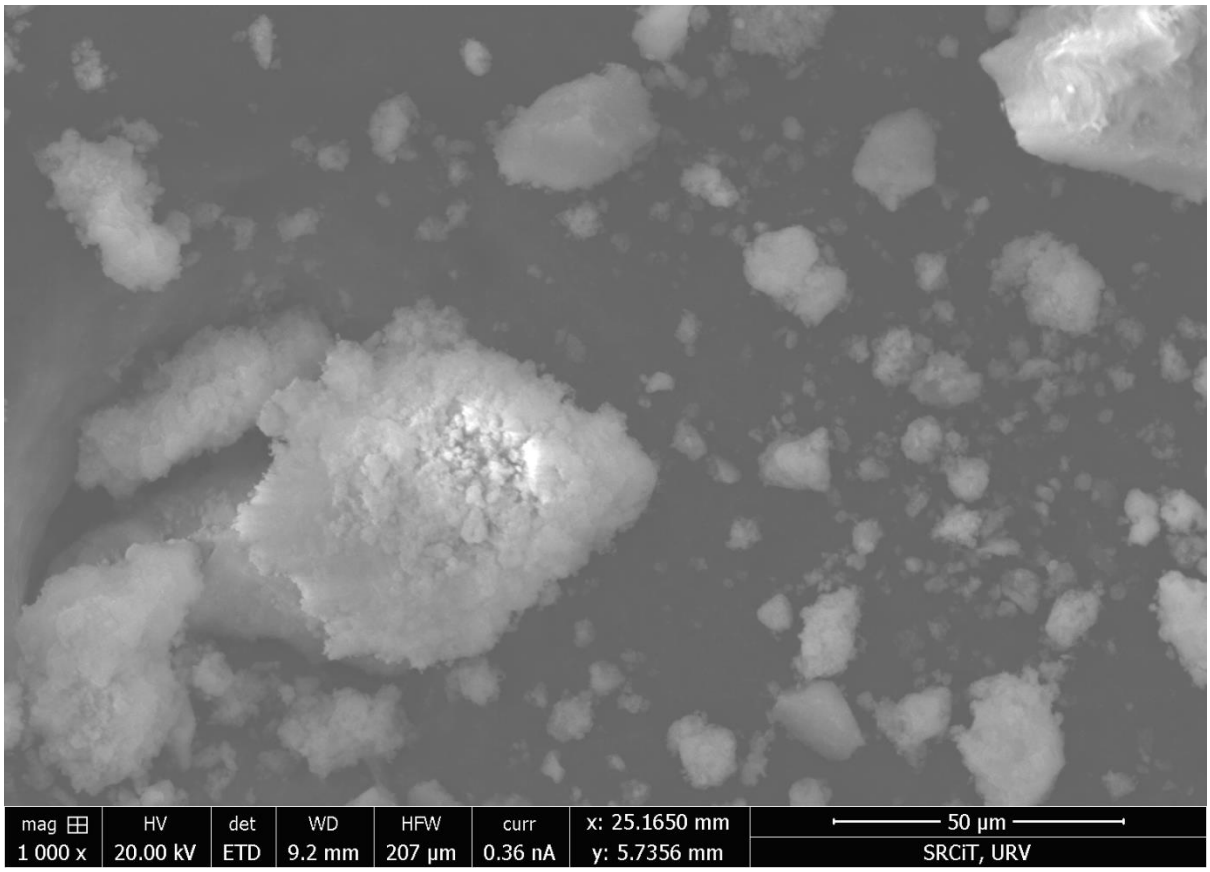


Figure S3. ESEM image of Hectorite S3 at 1000x

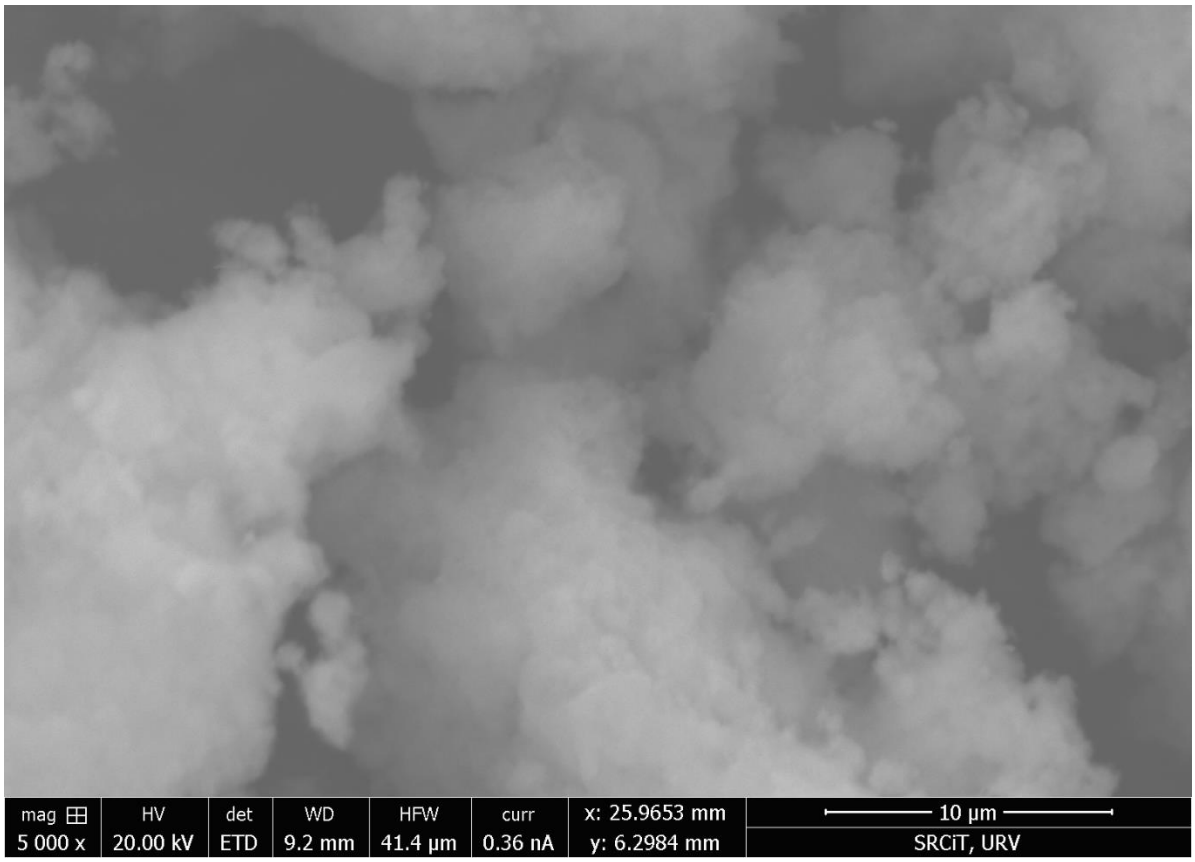


Figure S4. ESEM image of Hectorite S3 at 5000x

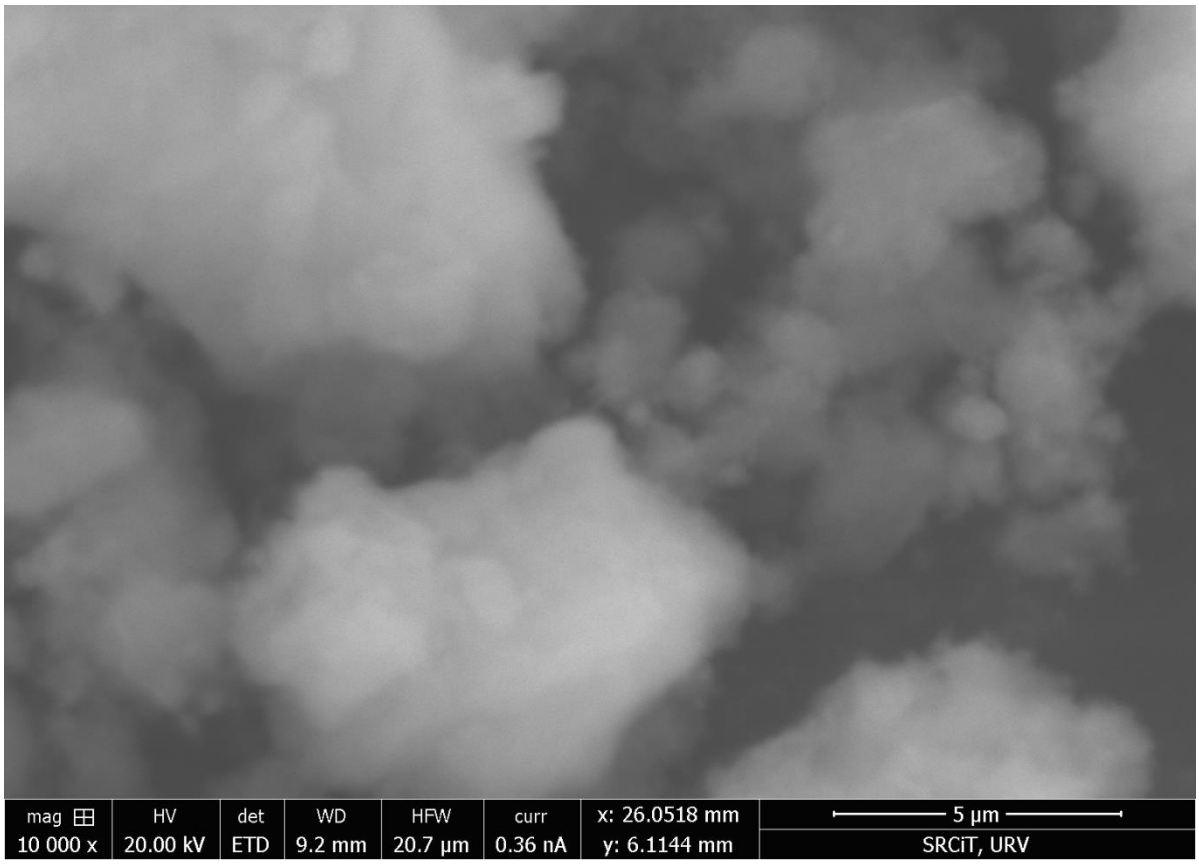
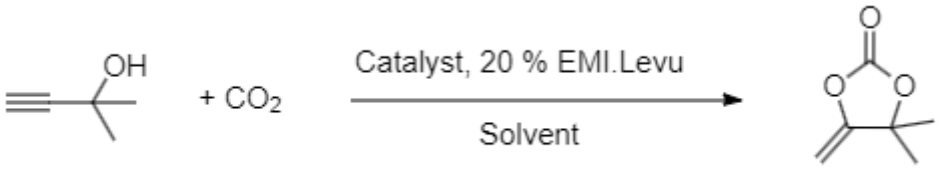


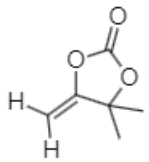
Figure S5. ESEM image of Hectorite S3 at 10000x

3) NMR yield calculation for the reaction system of CO_2 with 2-methylbut-3-yn-2-ol

The ^1H NMR spectra of the crude reaction mixture generated by 2-methylbut-3-yn-2-ol is used as an example for que quantitative determination of products using 1,3,5-trimethoxybenzene as internal standard. The deuterated solvent is $CDCl_3$.



Two protons belonging to the double bonds of α-alkylidene cyclic carbonates (red and green), show two clear individual peaks, characteristic for quantitative determination. The peak appearing at δ= 6.09 ppm (blue) represents three protons of 1,3,5-trimethoxybenzene. The NMR yield of the product can be calculated by the ratio of double bond proton and internal standard proton based on the exact amounts of 1,3,5-trimethoxybenzene and substrate.



4, 4-Dimethyl-5-methylene-[1,3]dioxolan-2-one

^1H NMR (500 MHz, $CDCl_3$) δ = 4.77 (d, J = 4.0 Hz, 1H), 4.33 (d, J = 4.0 Hz, 1H), 1.62 (s, 6H). (2)

Example: is = internal standard, p = product, s = substrate

m(is): 50mg, M (is) = 168.19g → n(is) = 0.3mmol

ratio (is/p) = (0.25 /3) : 1 = 0.083 → n(p) = n(is) / ratio (is/p) = 0.3 / 0.083 = 3.6 mmol

m(s)= 420,2mg, M(s) = 84,12 → n(s) = 5mmol

NMR yield = n(p) / n(s) = 3,6 / 5) 100 = 72%

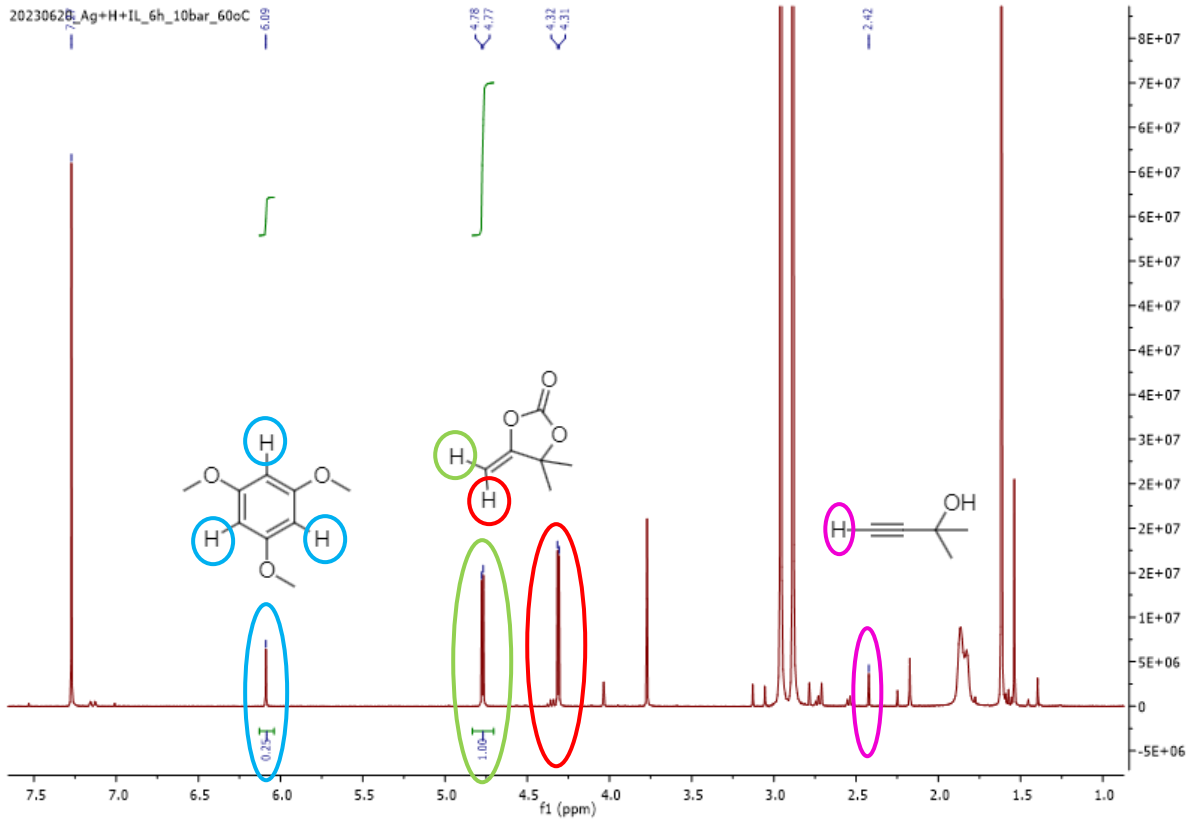


Figure S6. [1]H NMR crude reaction product generated by 2-methylbut-3-yn-2-ol and CO_2. Yield calculation

The conversion can be calculated by the ratio of triple bond proton of the substrate and internal standard proton based on the exact amounts of 1,3,5-trimethoxybenzene and substrate

The calculation of the conversion is the following:

m(is): 50mg, M (is) = 168.19g → n(is) = 0.3mmol

ratio (is/s) = (1,48 /3): 1 = 0.49 → n(s) = n(is) / ratio (is/s) = 0.3 / 0.49 = 0.6 mmol

n(s) initial = 5mmol

Conversion = 100-((n(s)unreacted / n(s)initial) x 100) = 100 – ((0.6 / 5) * 100) = 88 %

Selectivity = Yield / Conv = 0,72 / 0,88 = 82 %

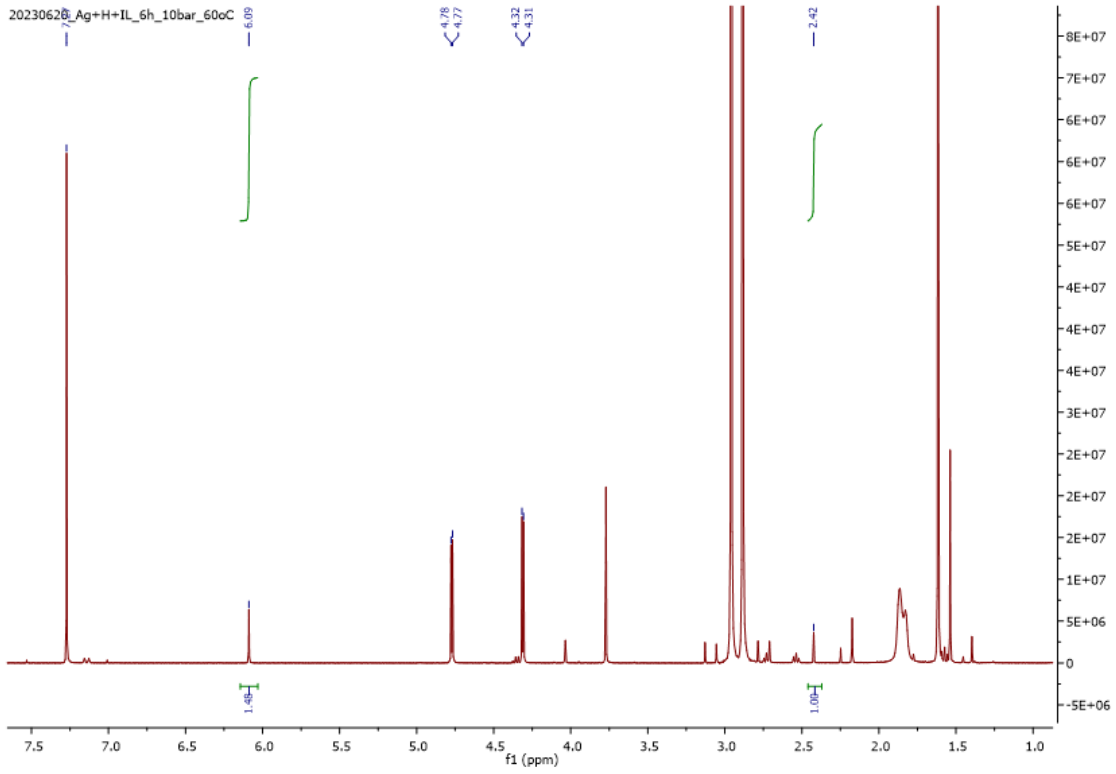
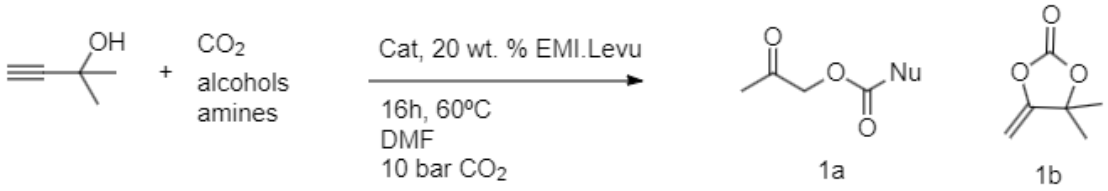


Figure S7. ^{1}H NMR crude reaction product generated by 2-methylbut-3-yn-2-ol and CO_2. Conversion calculation

4) ^{1}H NMR Spectra of carbonates and carbamates



The NMR yield is determined by the same procedure as with 4, 4-Dimethyl-5-methylene-[1,3]dioxolan-2-one. 1,3,5-trimethoxybenzene was used as internal standard. The NMR yield of the product can be calculated by the ratio of a signal characteristic from each carbonate/carbamate (1a) and internal standard proton based on the exact amounts of 1,3,5-trimethoxybenzene and substrate.

As product 1b was major in the cases of alcohols, some signals were overlapped with signals of 1a and it was more difficult to calculate the yield with a clear signal of 1a.

a) 2-Methyl-3-oxobutan-2-yl morpholine-4-carboxylate

^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.65 (t, J = 4.8 Hz, 4H), 3.46 (d, J = 33.6 Hz, 4H), 2.13 (s, 3H), 1.45 (s, 6H). [3]

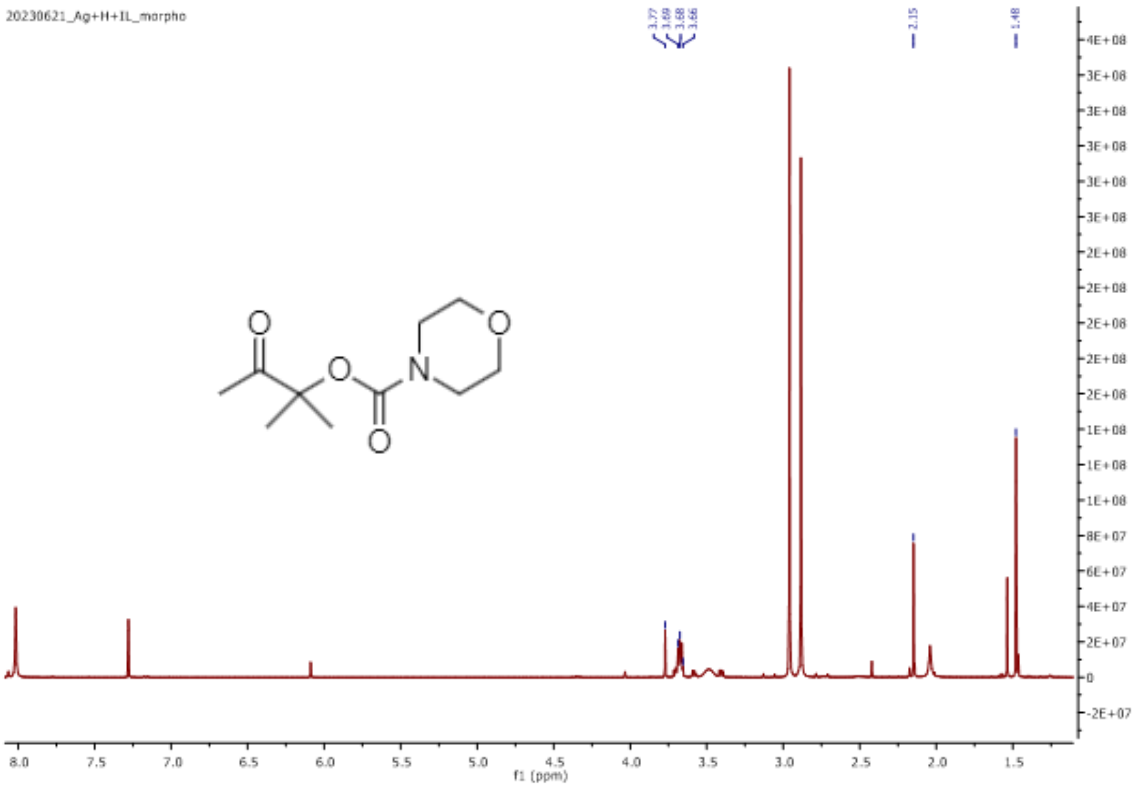


Figure S8. ^{1}H NMR crude reaction product of morpholine, 2-methylbut-3-yn-2-ol and CO_2

b) 2-Methyl-3-oxobutan-2-yl piperidine-1-carboxylate

^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.43 (d, J = 32.4 Hz, 4H), 2.14 (s, 3H), 1.60-1.64 (m, 2H), 1.52-1.56 (m, 4H), 1.46 (s, 6H). [3]

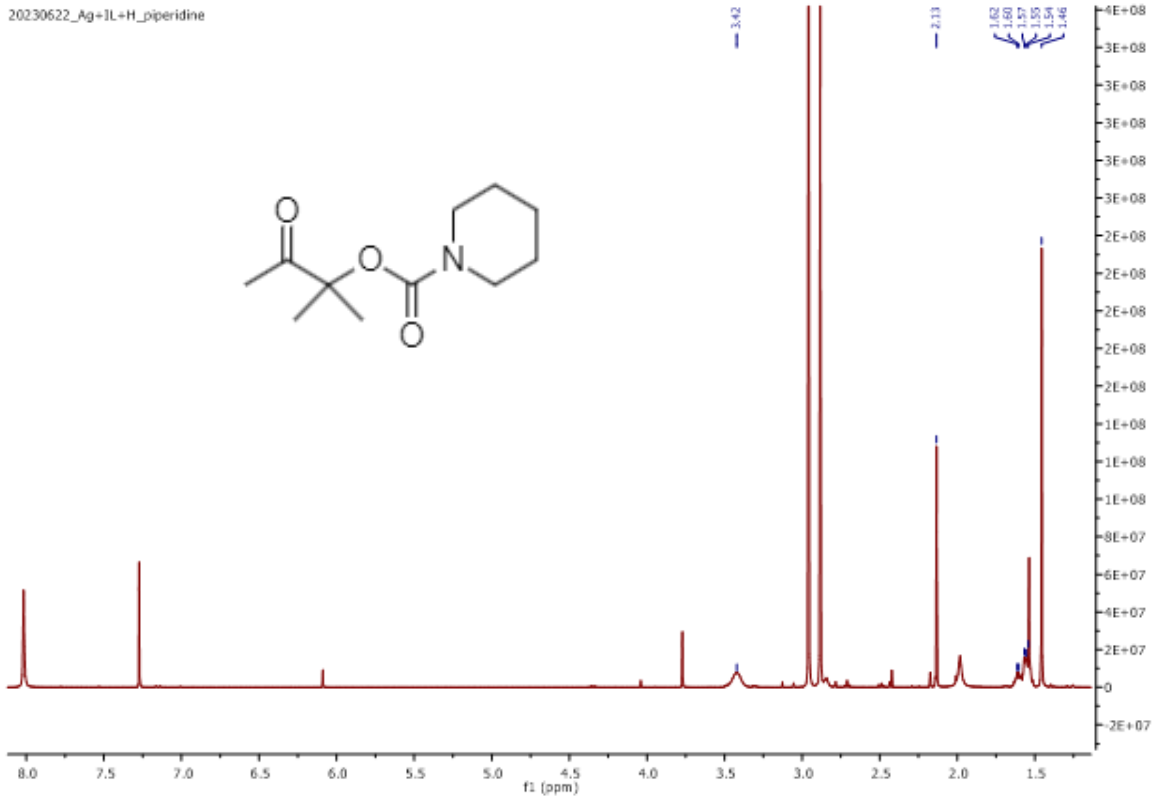


Figure S9. ^{1}H NMR crude reaction product of piperidine, 2-methylbut-3-yn-2-ol and CO_2

c) 4-Methoxybenzyl (2-methyl-3-oxobutan-2-yl) carbonate

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.32 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.09 (s, 2H), 3.80 (s, 3H), 2.12 (s, 3H), 1.50 (s, 6H). [3]

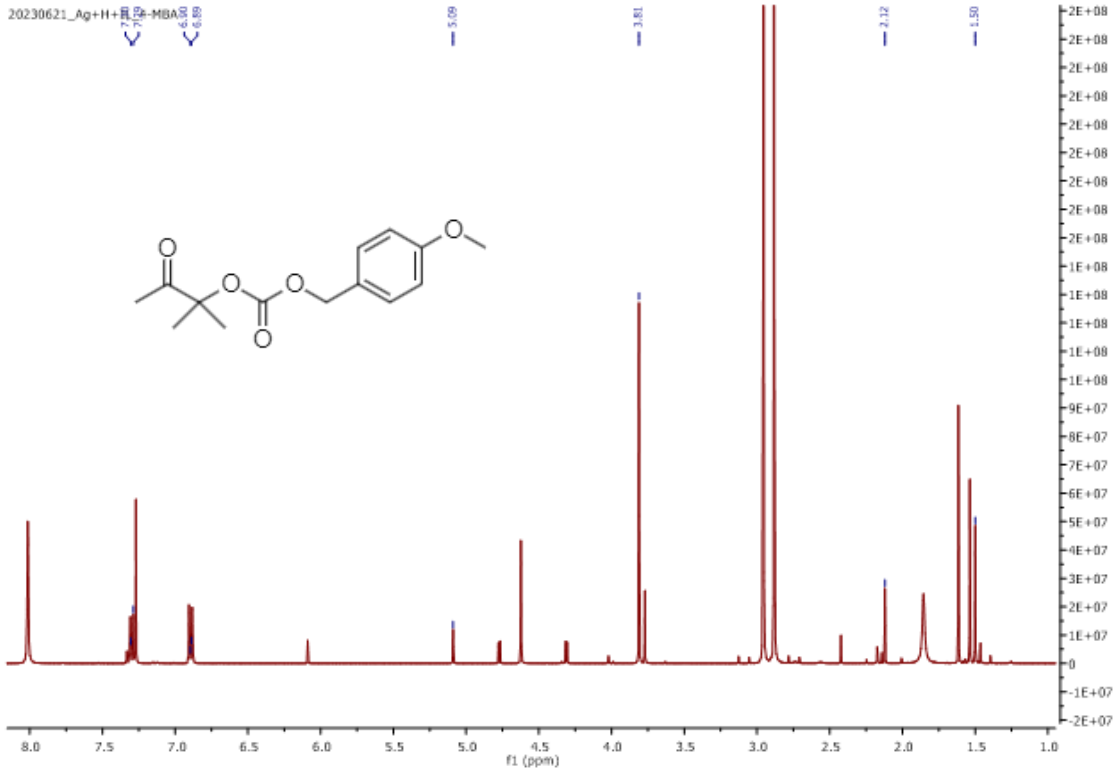


Figure S10. ^{1}H NMR crude reaction product of 4-Methoxybenzyl alcohol, 2-methylbut-3-yn-2-ol and CO_2

d) Cinnamyl (2-methyl-3-oxobutan-2-yl) carbonate

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.39 (d, J = 6.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.26-7.28 (m, 1H), 6.70 (d, J = 15.6 Hz, 1H), 6.28 (dt, J = 15.6, 6.5 Hz, 1H), 4.78 (dd, J = 6.9, 1.5 Hz, 2H), 2.18 (s, 3H), 1.53 (s, 6H). [3]

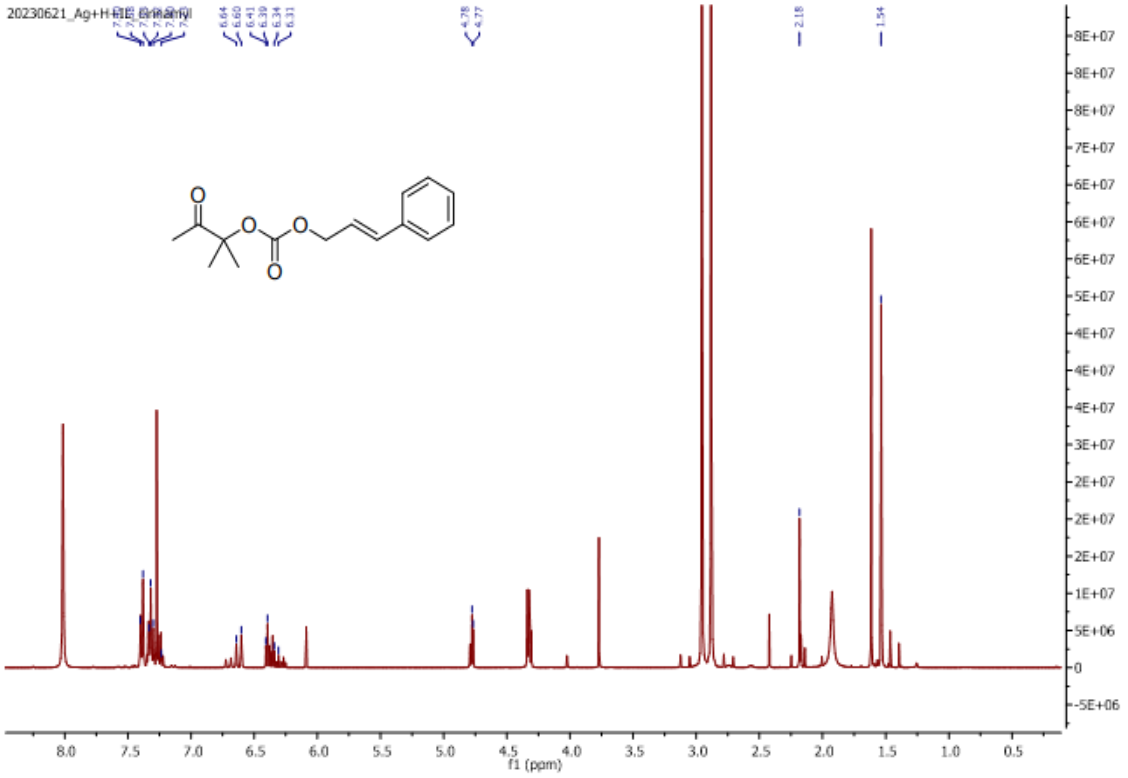


Figure S11. ^{1}H NMR crude reaction product of cinnamyl alcohol, 2-methylbut-3-yn-2-ol and CO_2

e) 2-Methyl-3-oxobutan-2-yl (1-phenylethyl) carbonate

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.29-7.38 (m, 5H), 5.69 (q, J = 6.8 Hz, 1H), 2.04 (s, 3H), 1.60 (d, J = 6.6 Hz, 3H), 1.50 (s, 3H), 1.45 (s, 3H). [(3)]

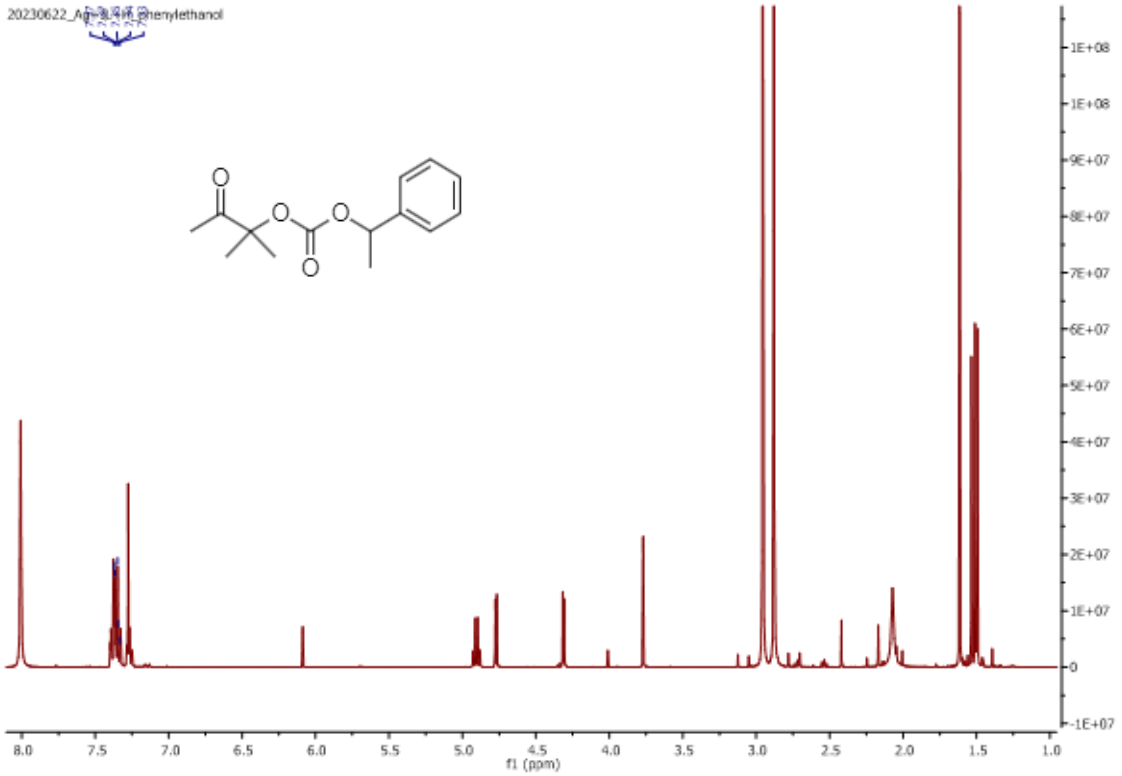


Figure S12. ^{1}H NMR crude reaction product of 1-phenyl-1-ethanol, 2-methylbut-3-yn-2-ol and CO_2

e) 4-Phenyl-1,3-dioxolan-2-one

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.42-7.46 (m, 3H), 7.36-7.37 (m, 2H), 5.68 (t, J = 8.4 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 4.34 (t, J = 8.4 Hz, 1H).(3)

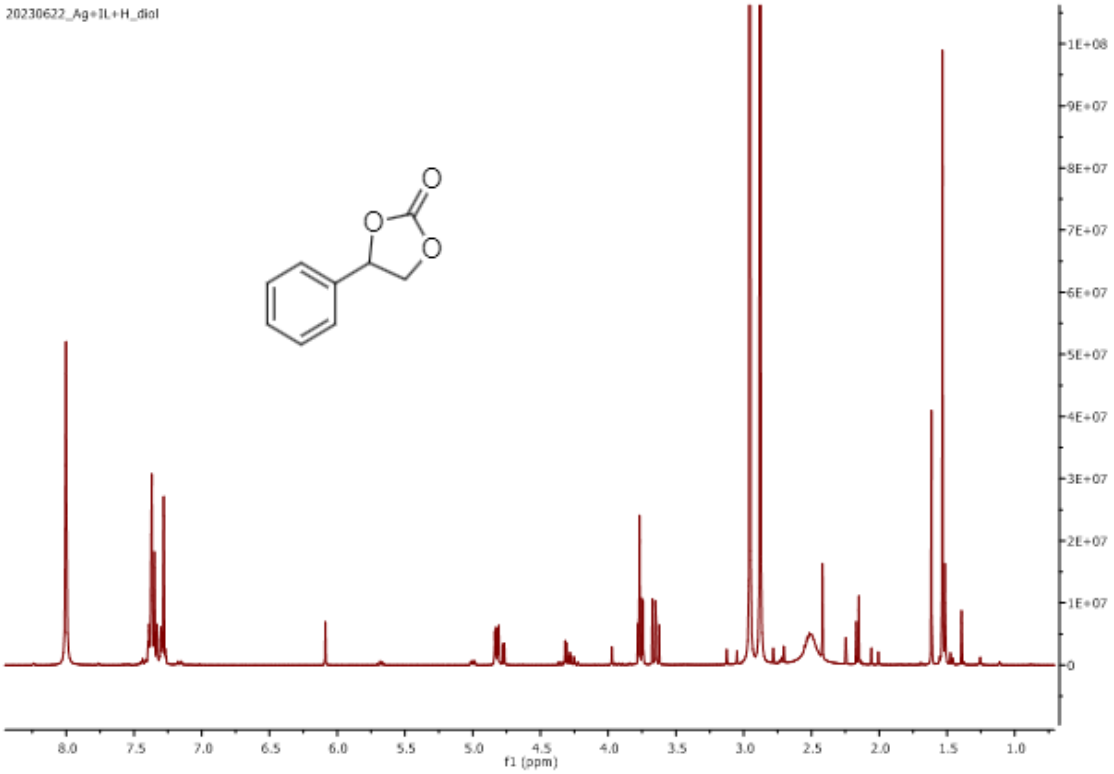


Figure S13. ^{1}H NMR crude reaction product of 1-Phenyl-1,2-ethanediol, 2-methylbut-3-yn-2-ol and CO_2

5) Bibliography

(1) Bergaya, F.; Vayer, M. CEC of Clays: Measurement by Adsorption of a Copper Ethylenediamine Complex. *Appl Clay Sci.* **1997**, *12* (3), 275–280.

(2) Yuan, Y.; Xie, Y.; Zeng, C.; Song, D.; Chaemchuen, S.; Chen, C.; Verpoort, F. A Recyclable AgI/OAc^- Catalytic System for the Efficient Synthesis of α-Alkylidene Cyclic Carbonates: Carbon Dioxide Conversion at Atmospheric Pressure. *Green Chem.* **2017**, *19* (13), 2936–2940.

(3) Seo, C.; Kim, S. E.; Kim, H.; Jang, H.-Y. CO_2 Fixation by Dual-Function Cu(triNHC) Catalysts as a Route to Carbonates and Carbamates via α-Alkylidene Carbonates. *ACS Sustainable Chem. Eng*. **2022**, 10 (17), 5643–5650.