

Supporting information for the article

Calcium carbide residue – promising hidden source of hydrogen

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S1. Materials and methods

Materials. Calcium carbide (granulated, particle size 0.1-1 mm, 75 % of acetylene (gas-volumetric as indicated by the supplier)), calcium metal (lump, 99%), magnesium (powder, 99%), aluminium (powder, 91%), calcium hydroxide (95%) were purchased from Sigma-Aldrich and used without further purification. Zinc metal (powder PRS (96%)), palladium (5% on activated carbon powder), ethyl cinnamate (98%) were purchased from Panreac, Alfa Aesar and abcr GmbH&Co, respectively, and used as received. Calcium was grinded in an argon flow before using.

Instrumentation. ^1H spectra were recorded using a Bruker Avance 400 NMR spectrometer. The ^1H chemical shifts were reported in ppm and were determined by referencing the peaks to the residual solvent peaks. The data were processed using MestReNova (version 6.0.2) desktop NMR data processing software.

XRD data were recorded by using a Bruker "D2 Phaser" powder diffractometer operating with X-ray tube radiation - $\text{CuK}\alpha_{1+2}$, wavelengths $\lambda_{\text{CuK}\alpha 1} = 1.54059 \text{ \AA}$ and $\lambda_{\text{CuK}\alpha 2} = 1.54443 \text{ \AA}$, tube operation mode 30 kV / 10 mA, position-sensitive detector, reflection geometry, Bragg-Brentano focusing scheme, sample rotation speed 20 rpm, diffraction angle interval $2\theta = 5(6.8)\text{-}90^\circ$, scanning step 0.02° , exposure at a point 0.7 seconds, $T=25^\circ\text{C}$, atmosphere – air.

The morphologies of the samples were observed on a Zeiss Merlin SEM. EDX measurement were performed at 20 kV of accelerating voltage with the Oxford Instruments INCA X-Act spectrometer mounted on Zeiss Merlin SEM.

S2. General procedures

Safety statement. *Hydrogen is a flammable gas and no more or less dangerous than other flammable organic solvents (like ether, pentane, etc.). Hydrogen gas must be handled according to the stated conditions.¹ In this work, no elevated pressure was observed, and hydrogen was used under atmospheric pressure (bubbling method). Although hydrogen was obtained under high temperature, no explosion was possible due to rapid cooling of released hydrogen, when transfer through joints and units. Note, the hydrogen was immediately removed from the heat zone and cooled. Open flame sources are strictly prohibited near the reaction set.*

General procedure for obtaining hydrogen from Ca(OH)₂ or CCRs and metals (Zn, Mg, Fe, Al, Ca). Calcium hydroxide or CCR (148 mg (or 152 mg for CCRs-d₂), 2 mmol) and metal powder (2.5 mmol) (preliminarily mixed) were placed in a 2 ml quartz tube. In the case of iron and calcium, the tube was additionally purged with argon. Then, the tube was connected to a silicone tube, the other end of which was lowered into a cylinder filled with water (Fig. S1). The quartz tube was placed in a tube furnace heated to an appropriate temperature (for zinc, magnesium, aluminium and iron - 700 °C, for calcium - 500 °C) and kept at this temperature until the gas evolution completed (in most cases, 45 minutes). The volume of the released gas corresponded to displaced water volume. To determine the composition of the residues remaining after the gas evolution, the test tube was connected to argon and cooled to room temperature.

Blank experiment. A quartz tube with calcium hydroxide (148 mg, 2 mmol) was placed using the system from the previous experiment (Fig. S1) into a tube furnace heated to 700 °C. As a result, 3 ml of gas was released for 45 minutes at an appropriate temperature. This volume was subtracted from the volume of the evolved gas in the hydrogen production experiments (Tables 1-3).

The procedure for obtaining CCR1. Calcium carbide (1.28 g, 20 mmol) was placed in a flask cooled in an ice bath. Water (2 ml, 111 mmol) was then added dropwise to the flask. After completion of the reaction, the mixture was additionally stirred for 30 minutes, filtered, and the residue was dried at 100 °C. The content of calcium hydroxide in the sample was determined using powder XRD.

The procedure for obtaining CCR2. The inorganic residue after fenchol vinylation was taken as the residue after carbide hydrolysis.² KF (2.03 g, 35 mmol), KOH (1.79 g, 32 mmol), fenchol (4.54 g, 30 mmol), DMSO (30 ml), calcium carbide (5 g, 78 mmol) and water (2.5 ml, 139 mmol) were loaded into a pressure vessel. The reactor was closed and the reaction mixture was stirred at 130 °C for 4 hours, cooled to room temperature, and filtered. The residue was additionally washed with water (2 × 10 ml) and acetone (10 ml), then dried at 100 °C. The content of calcium hydroxide in the sample was determined using powder XRD.

The procedure for obtaining CCR1-d₂ (air). Calcium carbide (1.28 g, 20 mmol) was placed in a flask and cooled in an ice bath. D₂O (2 ml, 100 mmol) was added dropwise to the flask. After completion, the mixture was additionally stirred for 30 minutes, filtered, and the residue was dried at 100 °C. The content of calcium hydroxide in the sample was determined using powder XRD.

The procedure for obtaining CCR1-*d*₂ (dioxane). The reaction was carried out in argon. Calcium carbide (1.28 g, 20 mmol) and 1,4-dioxane (5 mL) were placed in a flask cooled and in an ice bath. D₂O (1.5 ml, 75 mmol) was added dropwise to the flask. After completion, the mixture was additionally stirred for 10 minutes, filtered, and the residue was dried in vacuum. The content of calcium hydroxide in the sample was determined using powder XRD.

The procedure for obtaining CCR2-*d*₂. The inorganic residue after obtaining DPPEO₂-*d*₄ (reaction without base)³ was used as the residue after carbide hydrolysis. Diphenylphosphine oxide (500 mg, 2.5 mmol), DMSO-*d*₆ (5 ml), calcium carbide (640 mg, 10 mmol) and D₂O (0.8 ml, 40 mmol) were loaded into a pressure tube. Then the tube was closed and the reaction mixture was stirred at 130 °C for 5 hours, cooled to room temperature, and the reaction mixture was filtered. The inorganic residue on the filter was washed with methylene chloride (10 ml) from the reaction product and acetone (10 ml), then dried in vacuum. The content of calcium hydroxide in the sample was determined using powder XRD.

The procedure for obtaining CCR3-*d*₂. The inorganic residue after DPPEO₂-*d*₄ isolation (reaction with KF)³ was used as a residue after carbide hydrolysis. Diphenylphosphine oxide (500 mg, 2.5 mmol), 1,4-dioxane (4.5 ml), DMSO-*d*₆ (0.5 ml), KF (170 mg, 2.9 mmol), calcium carbide (640 mg, 10 mmol) and D₂O (0.8 ml, 40 mmol) were loaded into a pressure tube. Then the tube was closed and the reaction mixture was stirred at 80 °C for 3 hours, cooled to room temperature and filtered. The inorganic residue on the filter was washed with methylene chloride (10 ml) to remove the organic products, acetone (10 ml), and water (10 ml) to remove the base and again with acetone (10 ml), then dried in vacuum. The content of calcium hydroxide in the sample was determined using powder XRD.

General procedure for the hydrogenation of ethyl cinnamate using CCRs-derived hydrogen. The reaction was carried out according to the modified method.⁴ Ethyl cinnamate (26 µl, 0.16 mmol), 5% Pd/C (17 mg) and benzene (2.5 ml) were loaded into a flask with valve and stirred for 5 minutes at room temperature. Then, the reaction mixture was heated to 50 °C. Calcium hydroxide (142 mg, 1.92 mmol) and metal powder (2.4 mmol) (previously mixed) were loaded into a 2 ml quartz tube, the tube was connected to the flask with a silicon tube with a needle placed into the reaction mixture (Fig. S2). Then the quartz tube was placed in an oven heated to 700 °C (zinc) or 500 °C (calcium). Hydrogen evolution was observed. The reaction mixture in the flask was stirred at 50 °C. Hydrogen evolution completed after 45 minutes. Additional stirring for 45 minutes (as in the original method (1.5 hours))⁴ did not increase the alkene conversion (Table S1), so the reaction was carried out only during hydrogen evolution (45 minutes). In some cases, a new part of mixed calcium hydroxide and metal was added and the reaction mixture was stirred for additional 45 minutes. After that, the cooled reaction mixture was filtered through Celite pad and the solvent was evaporated.

The other substrates (Table S3) were hydrogenated using the same procedure.

Preparation of a dry catalyst for deuteration. The flask was charged with 5% Pd/C (100 mg) and benzene (5 ml), stirred for 5 minutes, then the solvent was evaporated, while the formation of palladium black was observed. The operations were repeated twice, after which the residue was dried in a vacuum. To carry out hydrogenation using

D₂, the required amount of catalyst was taken, and the reaction was carried out in 1 ml of benzene-*d*₆. In this case, the loading of other reagents was reduced by 2 times.

S3. Detailed hydrogen generation experiments



Figure S1. Hydrogen generation experiment system



Figure S2. Hydrogenation using hydrogen from CCRs

Table S1. Total table on optimizing of hydrogen evolution from calcium hydroxide with various metals.

Entry	Metal	T, °C	Ratio (Ca(OH) ₂ : Me), mol	Time, min	V _g , ^a mL	Yield, ^b %
1	Zn	500	1:1	45	12	21
2	Zn	650	1:1	45	30	62
3	Zn	700	1:1	45	37	78
4	Zn	750	1:1	45	37	78
5	Zn	700	1:1.25	45	45	97
6	Zn	700	1:1.5	150	37	78
7	Zn	650	1:1.25	45	35	74
8	Zn	750	1:1.25	60	43	92
9	Mg	700	1:1	60	32	67
10	Mg	700	1:1.25	60	33	69
11	Mg	700	1:1.5	90	33	69
12	Al	800	1:0.67	120	3	0
13	Fe (air)	700	1:0.67	120	12	21
14	Fe (Ar)	700	1:0.67	120	20	39
15	Fe (Ar)	700	1:1.25	45	16	30
16	Ca	500	1:1.25	45	41	87

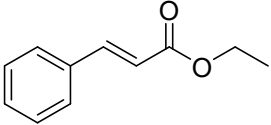
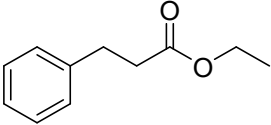
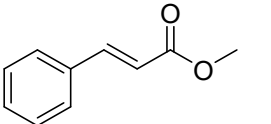
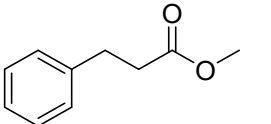
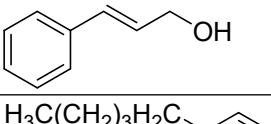
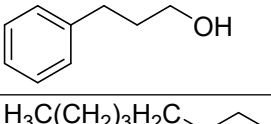
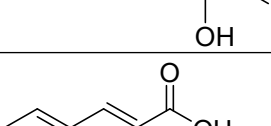
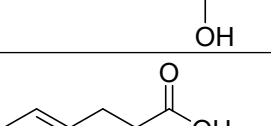
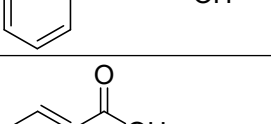
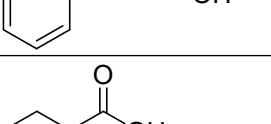
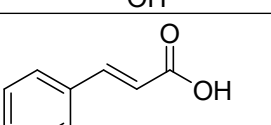
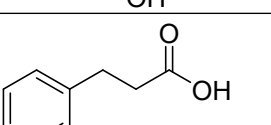
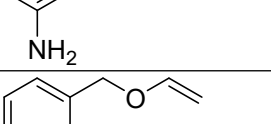
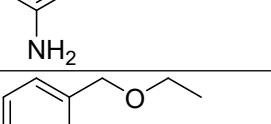
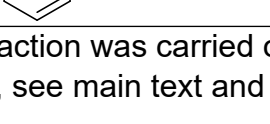
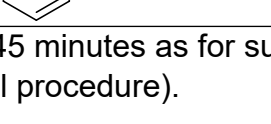
^a The volume of gas released into the cylinder. ^b Hydrogen yield calculated considering the purity of calcium hydroxide (97%) and a blank run (3 mL).

Table S2. Total table on hydrogenation of substrate **1** by hydrogen obtained from CCRs

Entry	Metal	H ₂ /D ₂ source	Yield, ^a %	DI, ^a %	Yield, ^b %	DI, ^b %
1	Zn	Ca(OH) ₂	32 (32) ^c	-	34 (34) ^c	-
2	Zn	CCR1	4	-	-	-
3	Zn	CCR2	5	-	-	-
4	Zn	CCR1-d ₂ ^d	3	67	-	-
5 ^e	Zn	CCR1-d ₂ ^d	8	75	9	76
6	Zn	CCR1-d ₂	2	f	2	f
7 ^e	Zn	CCR1-d ₂	9	61	10	58
8	Zn	CCR2-d ₂	5	52	13	62
9	Zn	CCR3-d ₂	-	-	13	74
10	Ca	Ca(OH) ₂	99	-	-	-
11	Ca	CCR1	95	-	-	-
12	Ca	CCR2	99	-	-	-
13	Ca	CCR1-d ₂ ^d	17	34	33	45
14 ^e	Ca	CCR1-d ₂ ^d	32	58	70	60
15	Ca	CCR1-d ₂	81	66	97	65
16 ^e	Ca	CCR1-d ₂	94	67	99	66
17	Ca	CCR2-d ₂	99	64	99	65
18	Ca	CCR3-d ₂	99	54	99	56

^a After addition the 1st part of the mixture to obtain hydrogen; the yield and deuterium incorporation (DI) were determined using ¹H NMR. ^b After addition the 2nd part of the mixture to obtain hydrogen; the yield and deuterium incorporation (DI) were determined using ¹H NMR. ^c After additional stirring of the mixture for 45 minutes after hydrogen evolution completed. ^d Air dried at 100 °C. ^e In benzene-*d*₆ and with the dry catalyst. ^f Was not determined due to low concentration in the mixture.

Table S3. Hydrogenation scope using hydrogen generated from CCR2 and Ca ^a

Entry	Substrate	Product	NMR yield, mol%
1			99
2			73
3			91
4			99
5			99
6			69
7			88
8			89

^a The reaction was carried out for 45 minutes as for substrate **1** (Table 4, entry 3, with calcium, see main text and general procedure).

S4. Determination of calcium hydroxide content in CCRs by powder XRD

Table S4. Quantitative phase analysis of samples (wt. %) according to full-profile analysis by the Rietveld method.

	Ca(OH) ₂	CCR1	CCR2	CCR1-d ₂ (air)	CCR1-d ₂ (dioxane)	CCR2-d ₂	CCR3-d ₂
Portlandite – Ca(OH) ₂	97.2	96.7	61.6	99.5	91.6	96.6	77.2
Calcite – CaCO ₃	2.8	1.1	2.4	<1	-	-	-
Graphite – C	-	1.5	2.0	<1	4.7	2.2	9.3
Calcium carbide – CaC ₂	-	<1	-	traces	1.2	<1	-
Aragonite – CaCO ₃	-	-	1.5	-	1.6	-	-
Vaterite – CaCO ₃	-	-	12.8	-	-	-	-
Fluorite – CaF ₂	-	-	19.7	-	-	-	10.8
CaO	-	-	-	-	<1	<1	2.7
Rp (%)*	8.4	9.0	10.1	9.8	8.7	9.9	9.7

(*) $R_p = \frac{\sum |y_i^{obs} - y_i^{calc}|}{\sum y_i^{obs}}$ - is the factor of convergence of the calculated and experimental X-ray profiles, y_i is the intensity at each experimental point of the X-ray diffraction pattern.

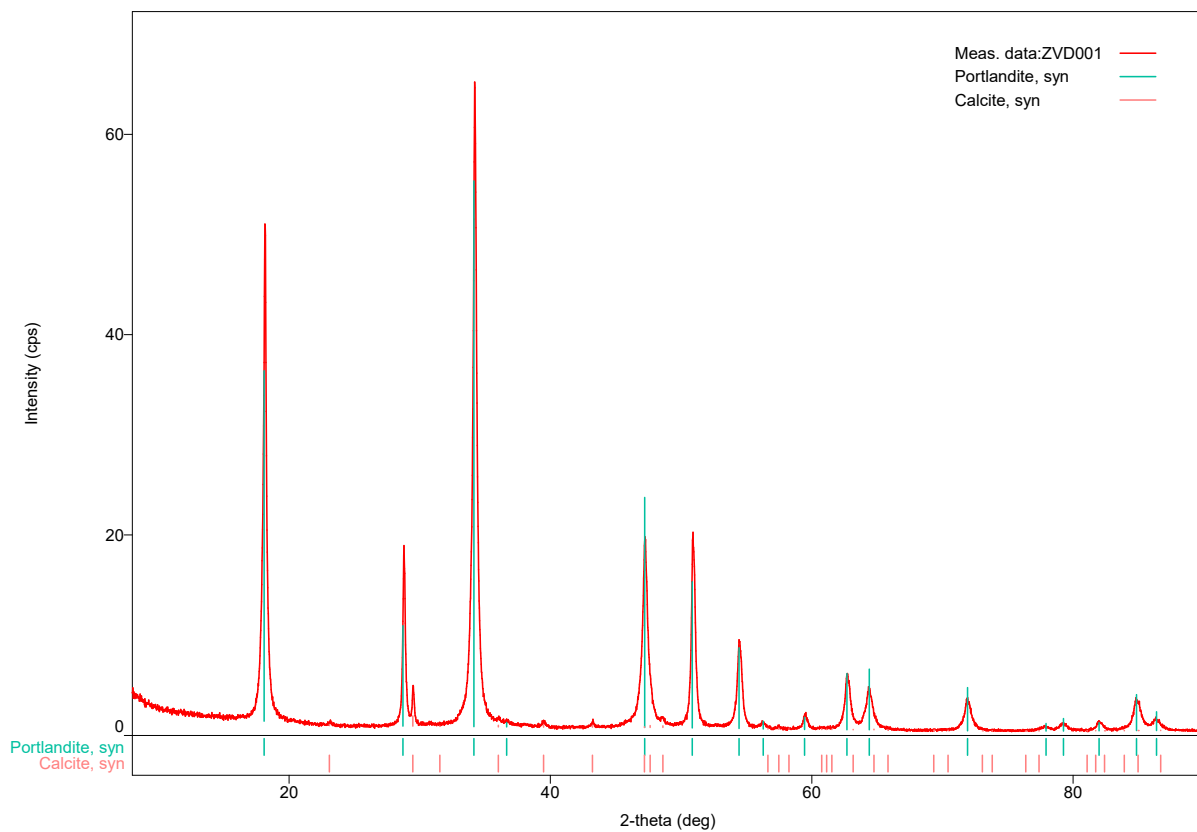


Figure S3. X-ray pattern of $\text{Ca}(\text{OH})_2$

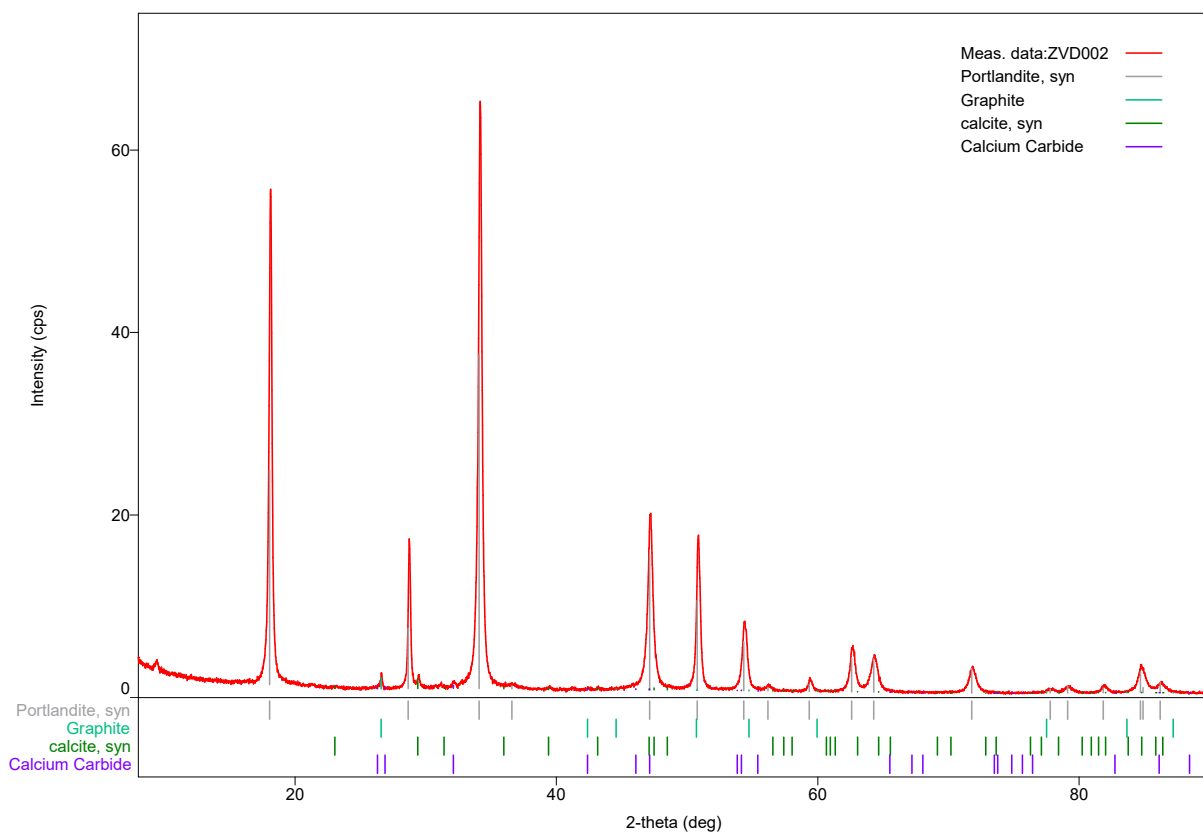


Figure S4. X-ray pattern of CCR1

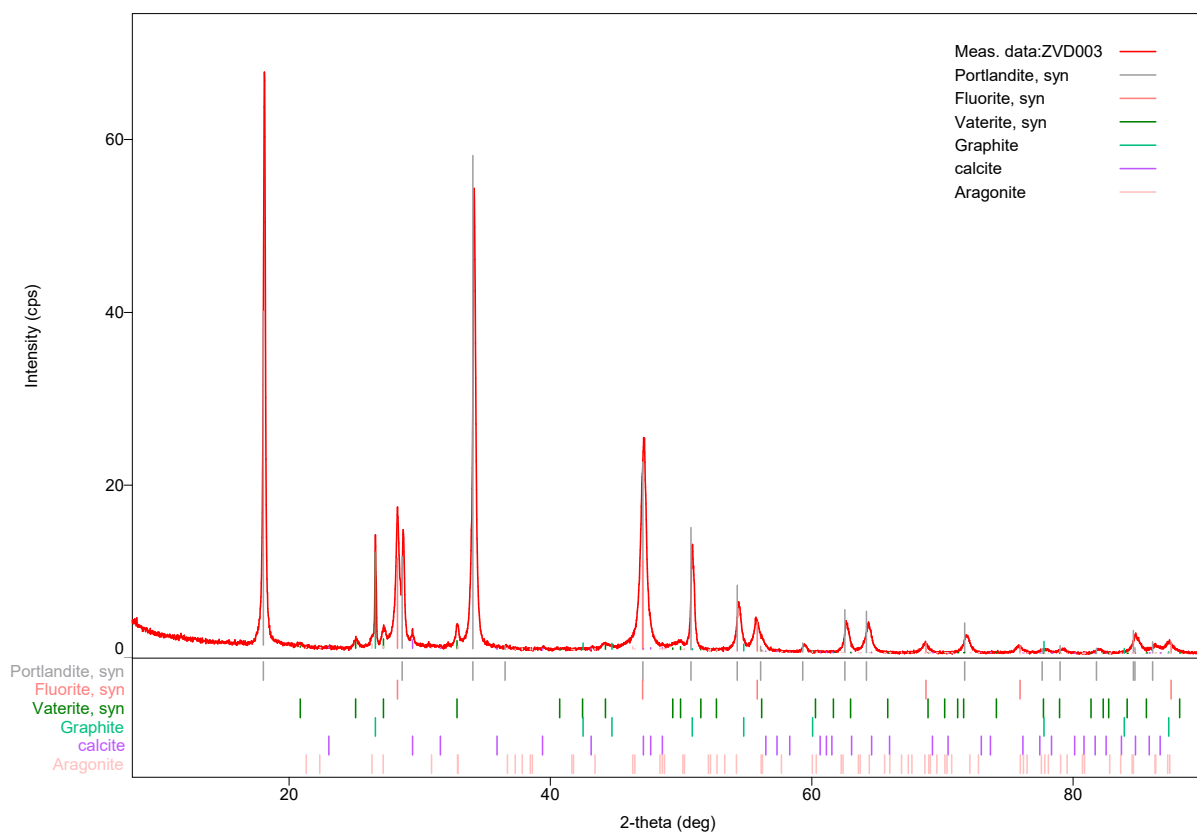


Figure S5. X-ray pattern of CCR2

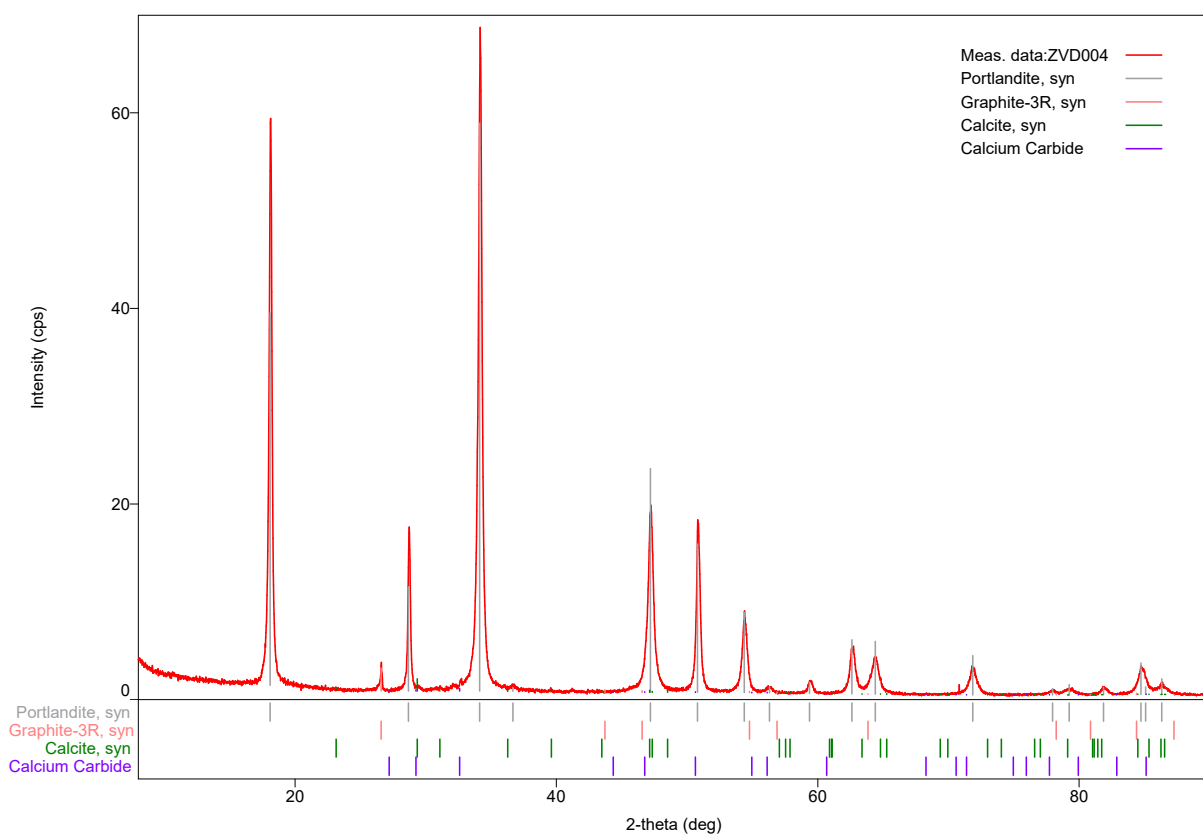


Figure S6. X-ray pattern of CCR1-d₂ (dried in air)

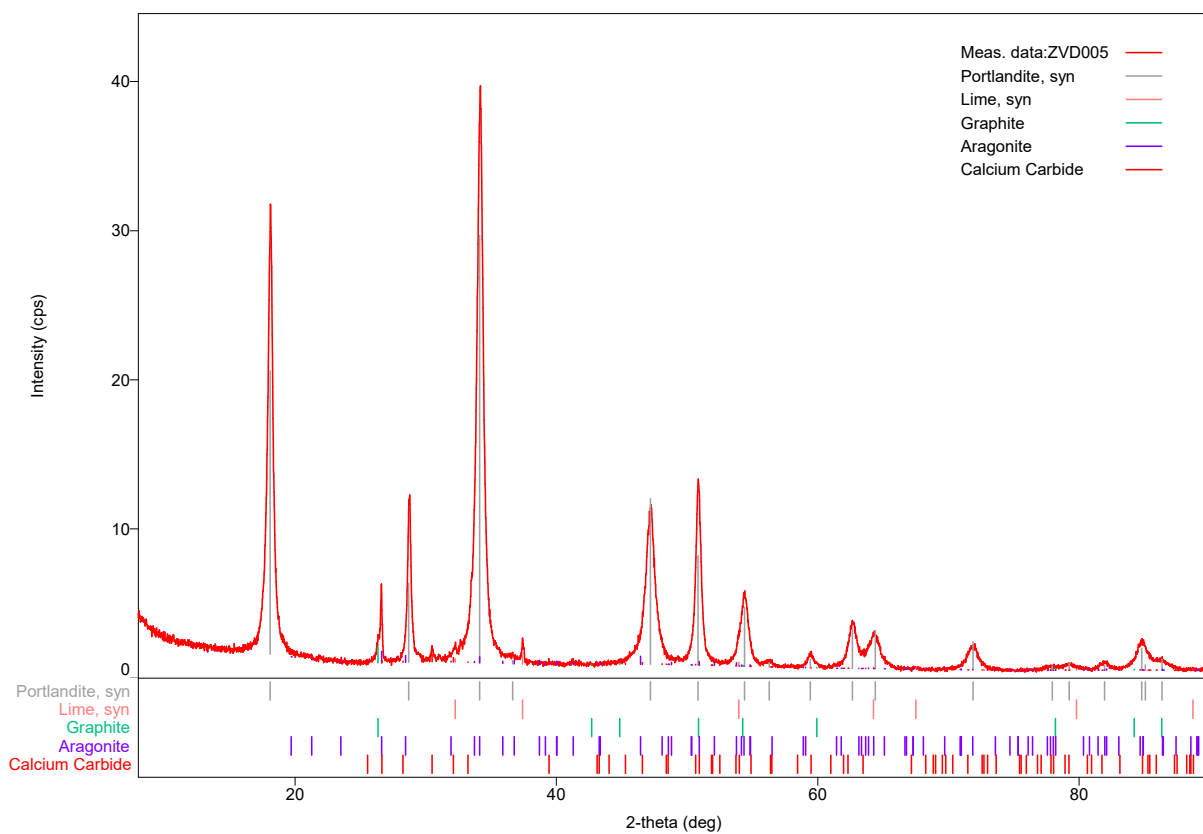


Figure S7. X-ray pattern of CCR2-d₂ (dried in vacuum)

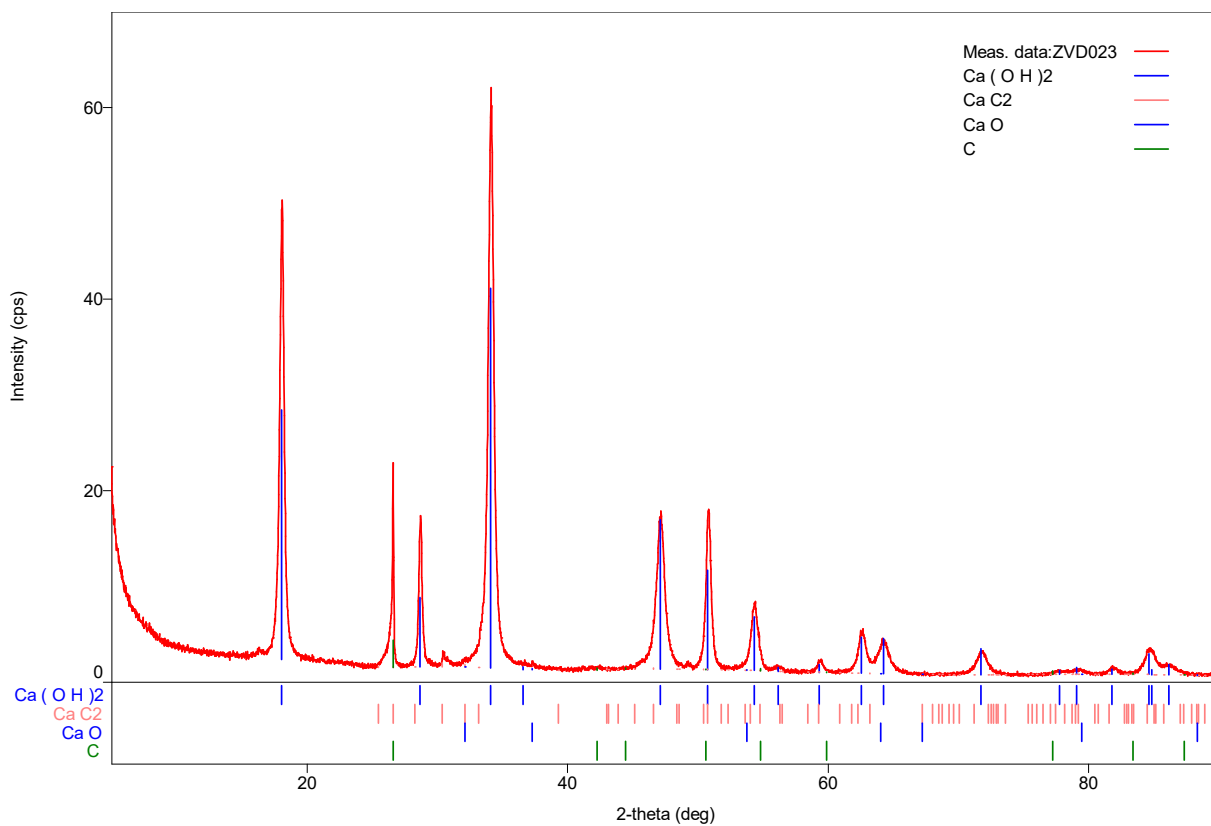


Figure S8. X-ray pattern of CCR2-d₂

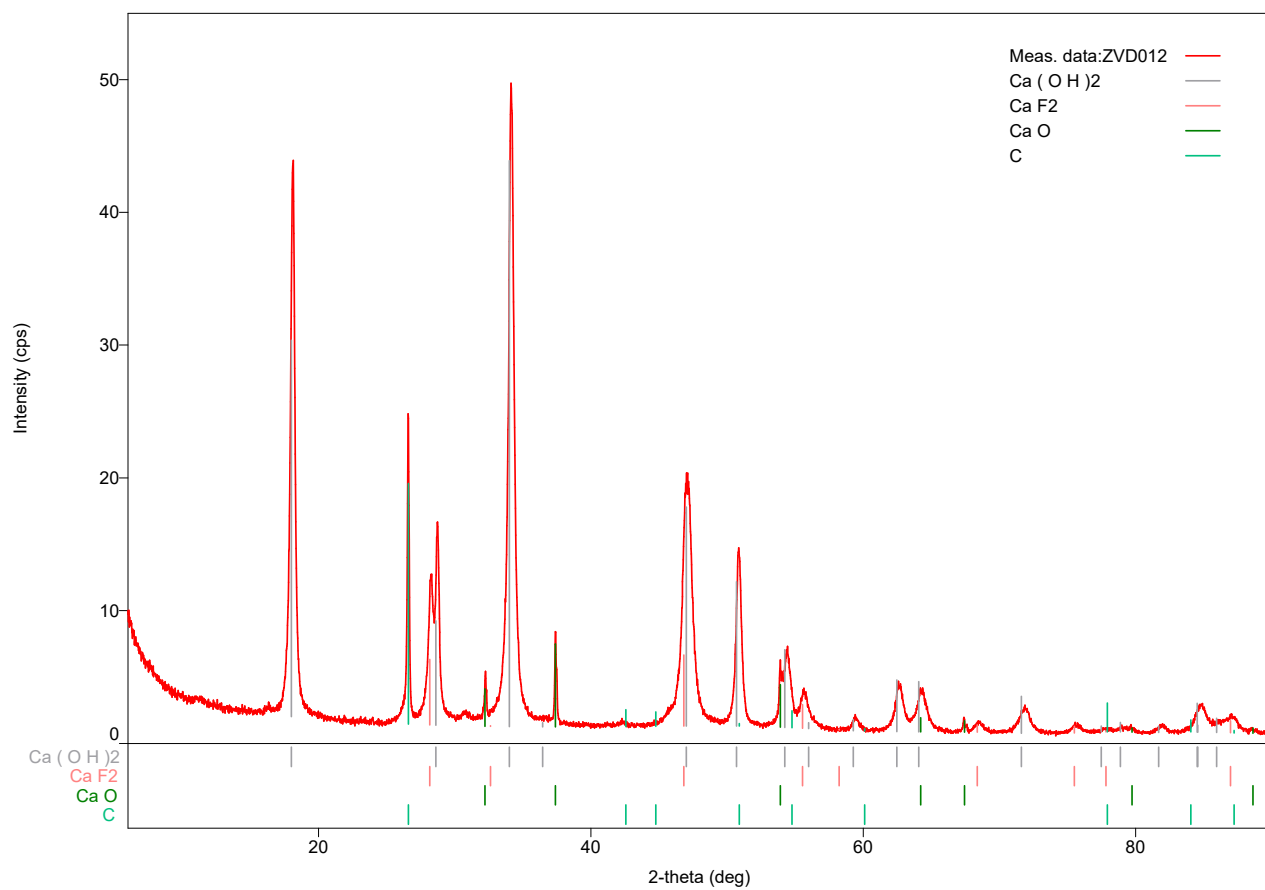


Figure S9. X-ray pattern of CCR3-d₂

S5. NMR spectra

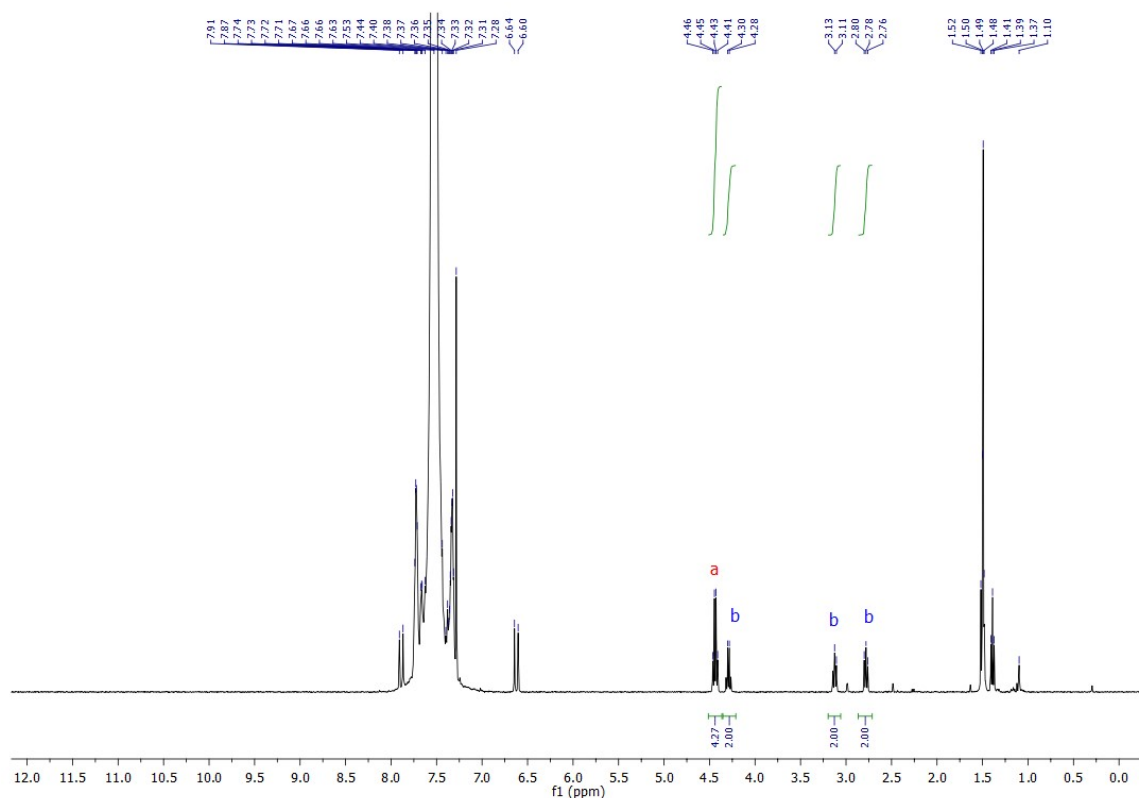


Figure S10. ¹H NMR (400 MHz, CDCl₃) spectrum of the reaction mixture after hydrogenation of **1** using Ca(OH)₂ and Zn to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

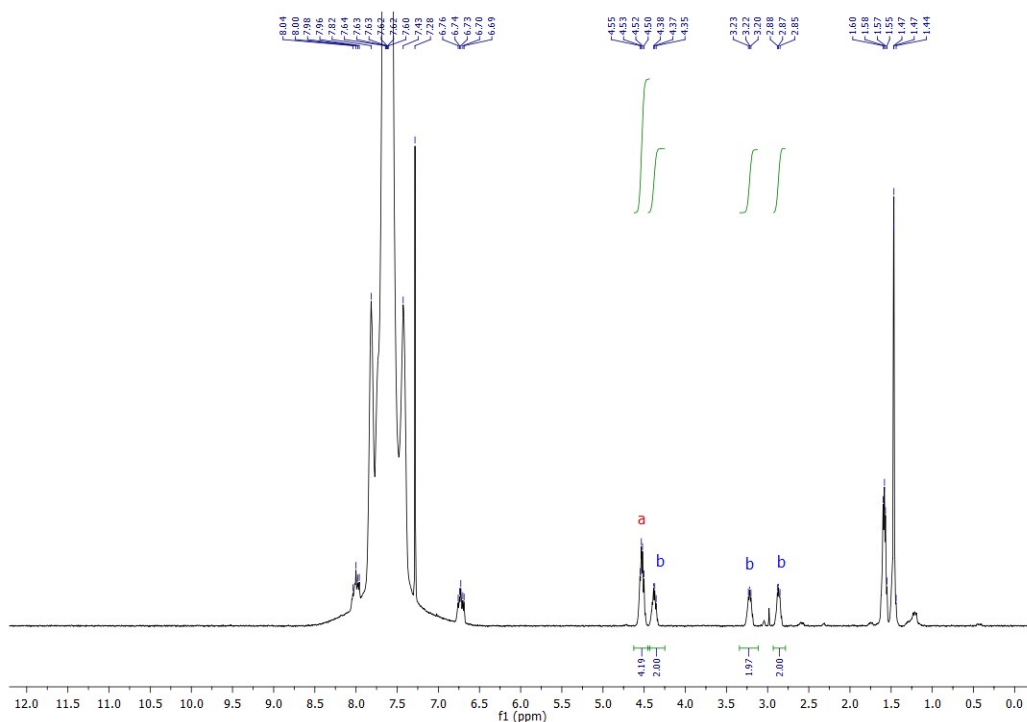


Figure S11. ¹H NMR (400 MHz, CDCl₃) spectrum of the reaction mixture after hydrogenation of **1** using Ca(OH)₂ and Zn to generate hydrogen (1st part, after 90 minutes): a - the signal of the initial substance, b - the signals of the product

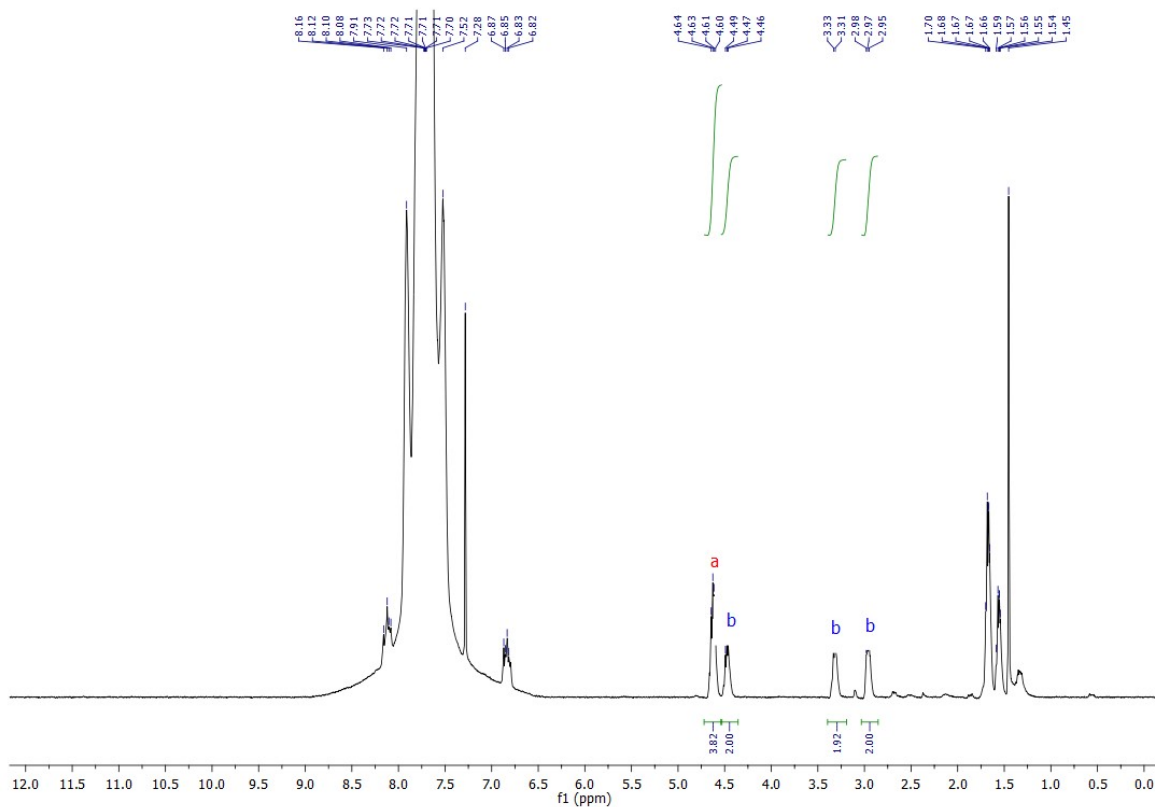


Figure S12. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using $\text{Ca}(\text{OH})_2$ and Zn to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

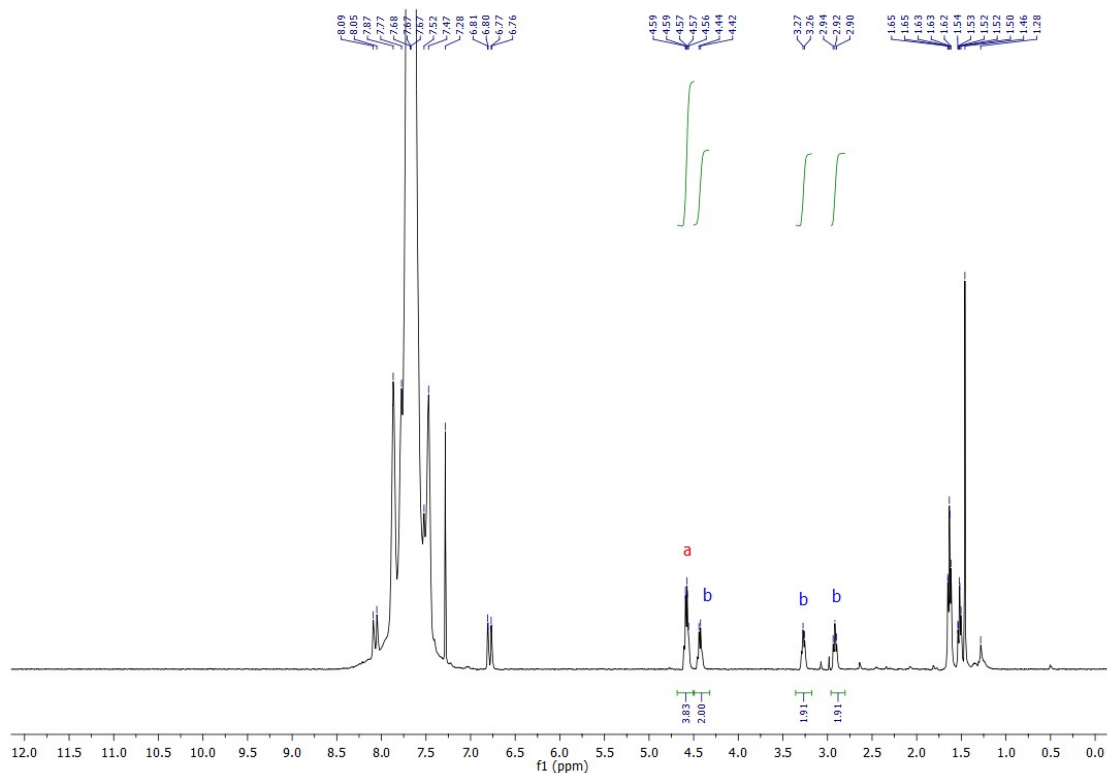


Figure S13. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using $\text{Ca}(\text{OH})_2$ and Zn to generate hydrogen (2nd part, after 90 minutes): a - the signal of the initial substance, b - the signals of the product

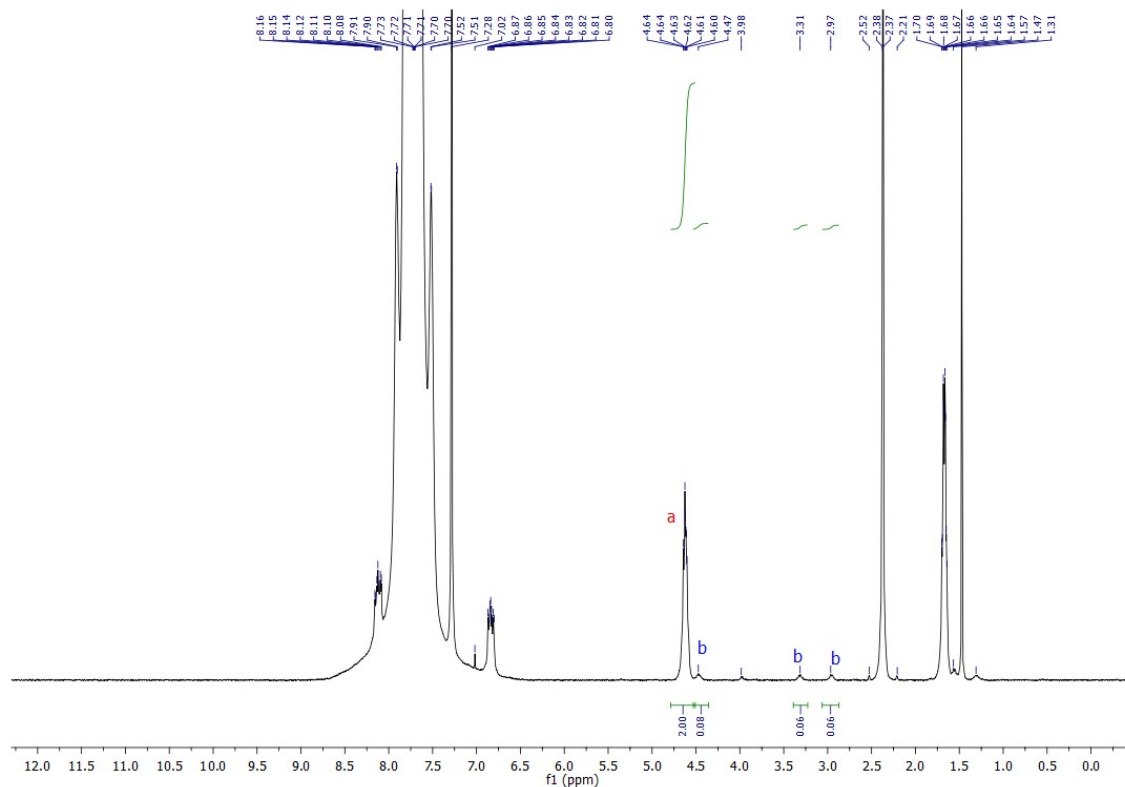


Figure S14. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1 and Zn to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

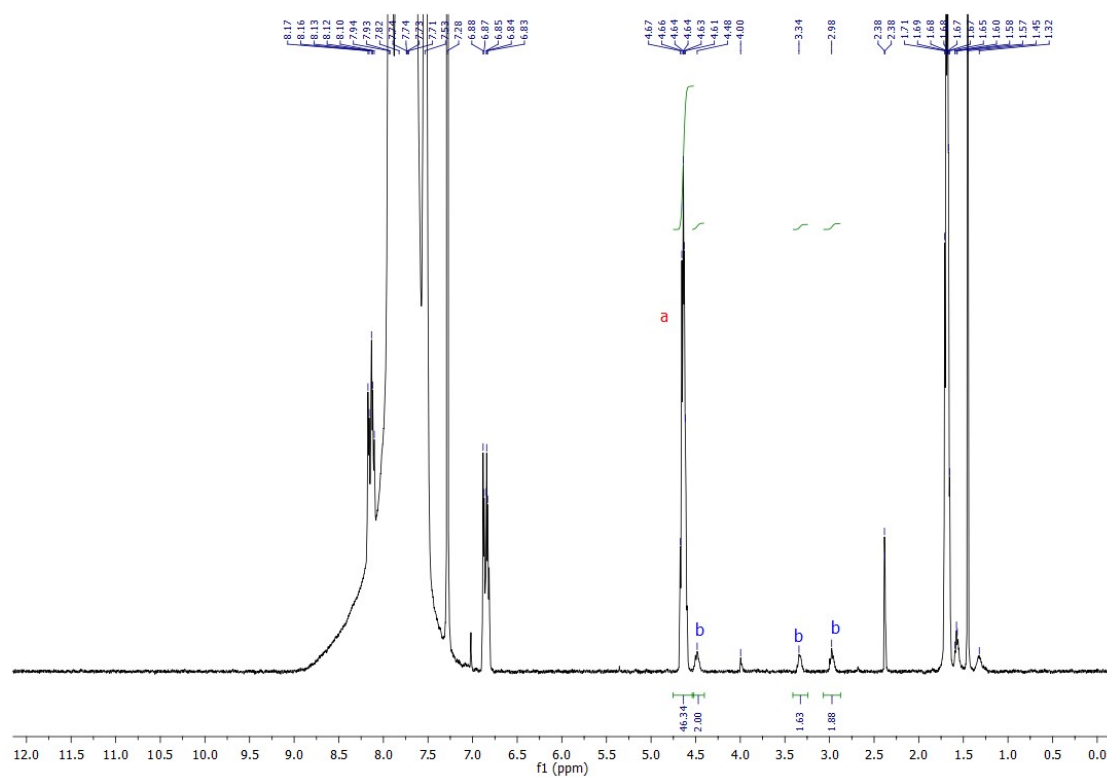


Figure S15. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR2 and Zn to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

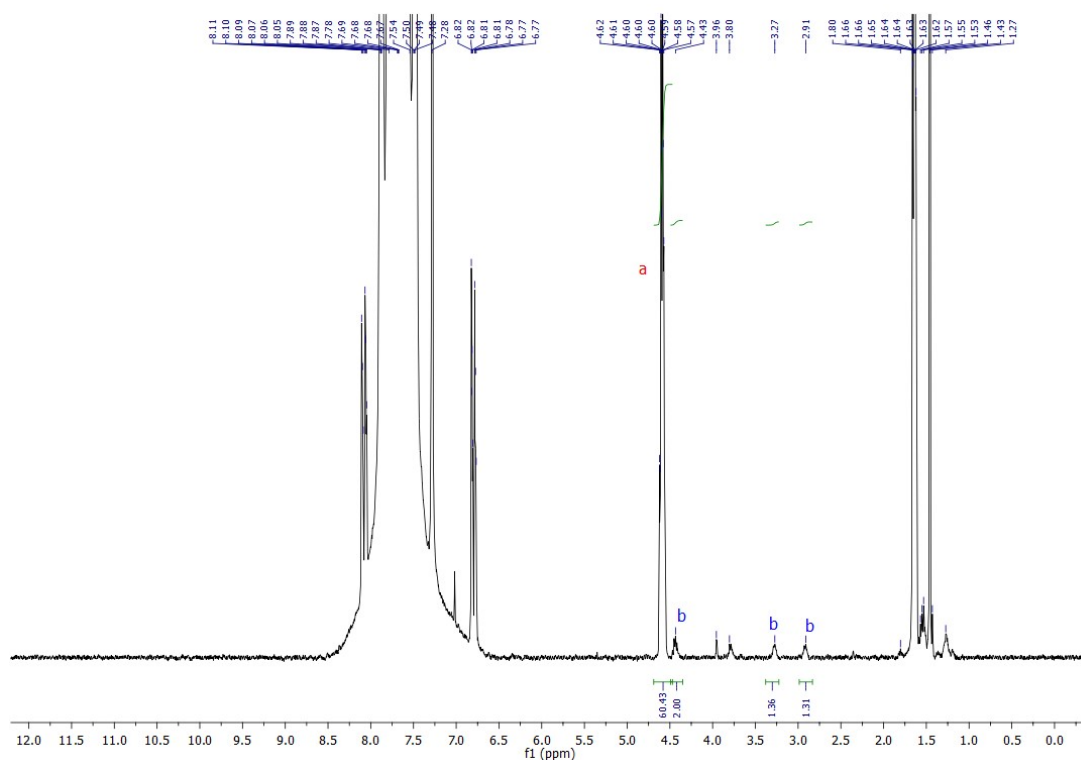


Figure S16. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (air) and Zn to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

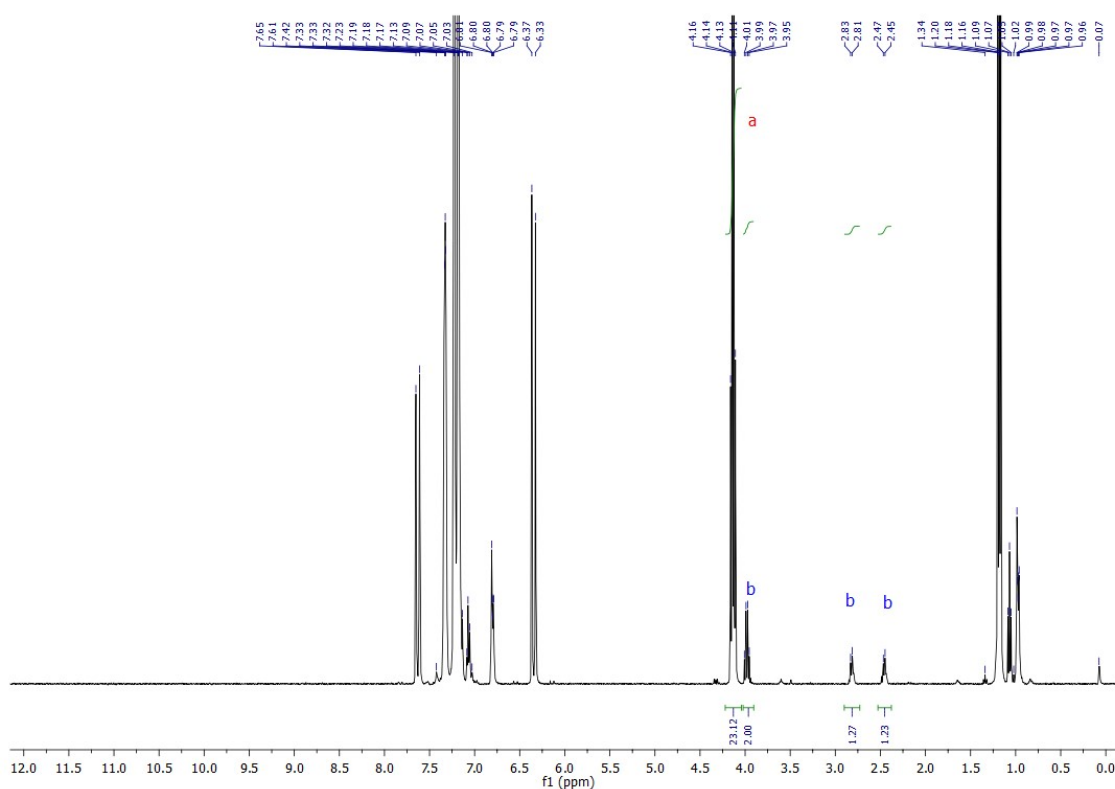


Figure S17. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (air) and Zn to generate hydrogen (1st part, after 45 minutes, using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

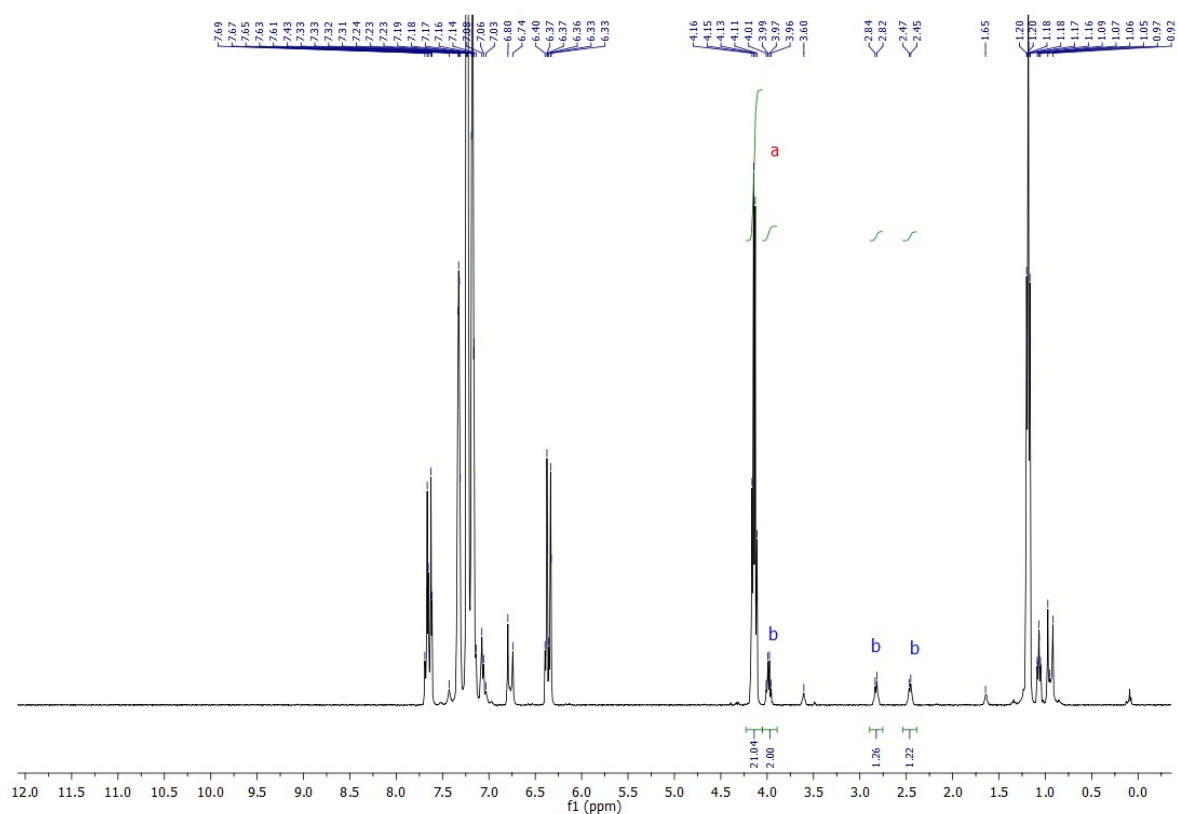


Figure S18. ¹H NMR (400 MHz, CDCl₃) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-*d*₂ (air) and Zn to generate hydrogen (2nd part, after 45 minutes, using benzene-*d*₆ and dry catalyst): a - the signal of the initial substance, b - the signals of the product

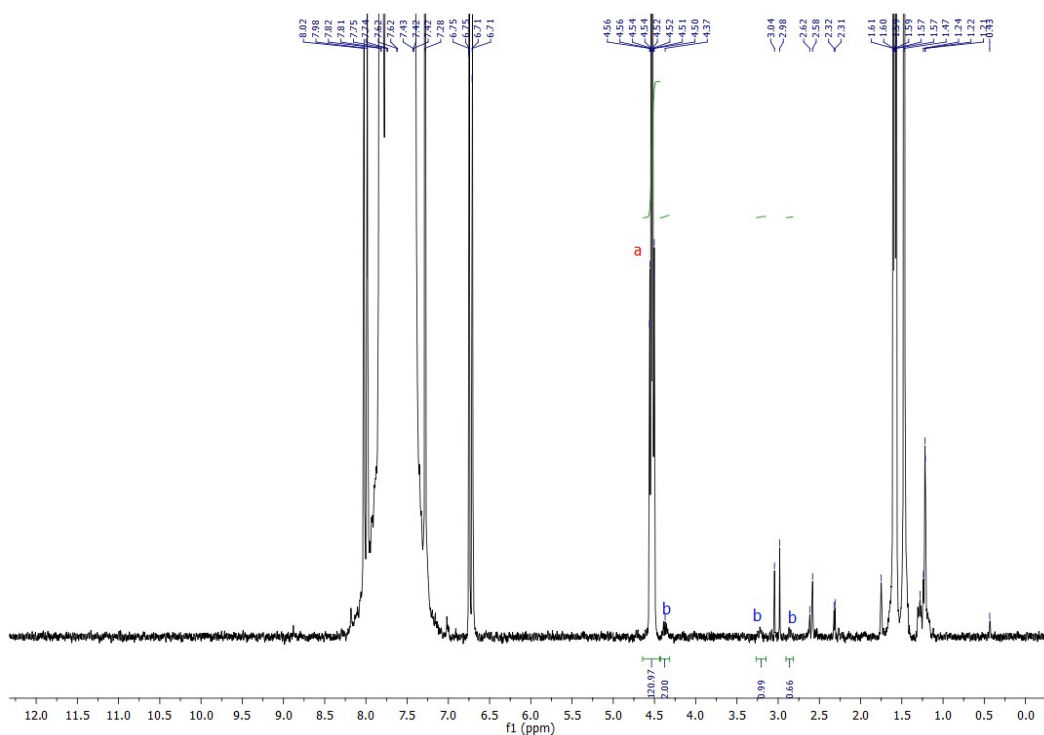


Figure S19. ¹H NMR (400 MHz, CDCl₃) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-*d*₂ (dioxane) and Zn to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

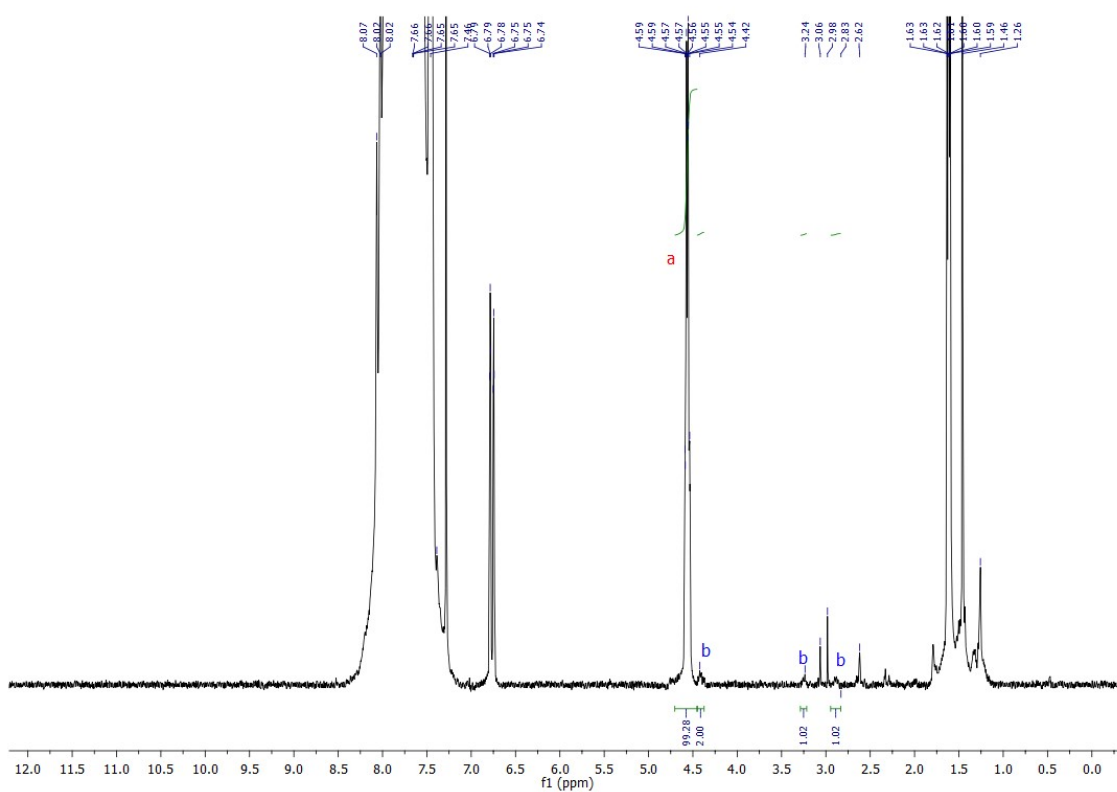


Figure S20. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (dioxane) and Zn to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

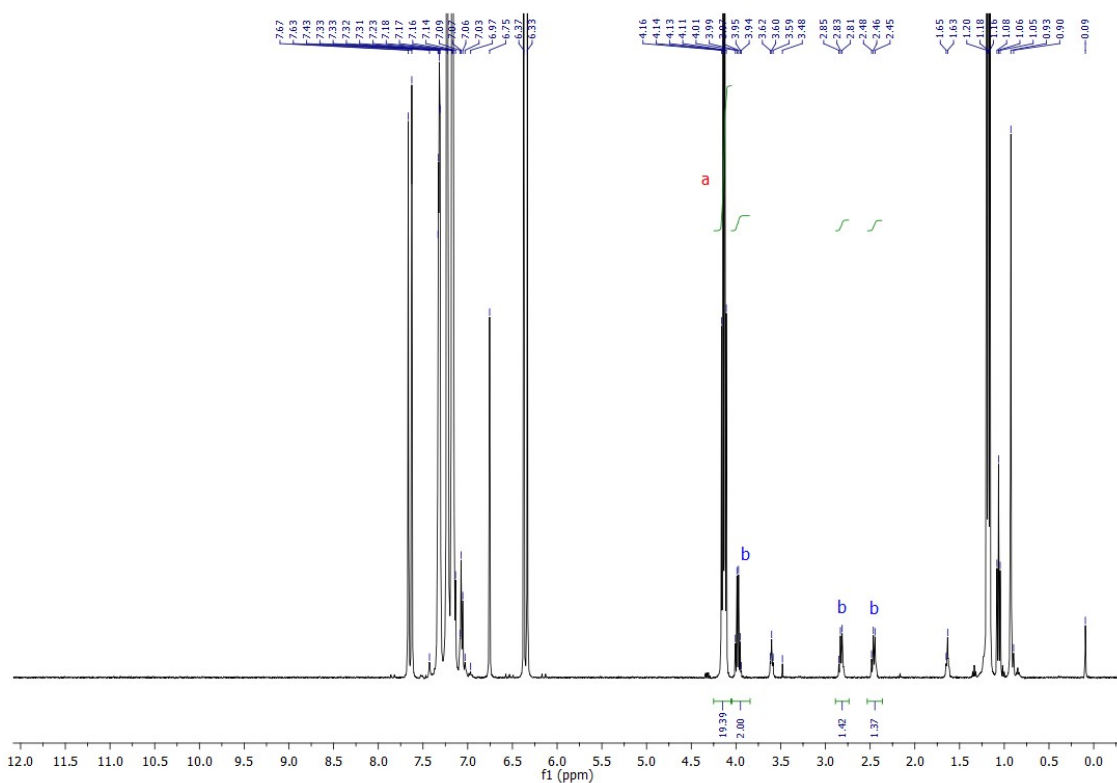


Figure S21. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (dioxane) and Zn to generate hydrogen (1st part, after 45 minutes using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

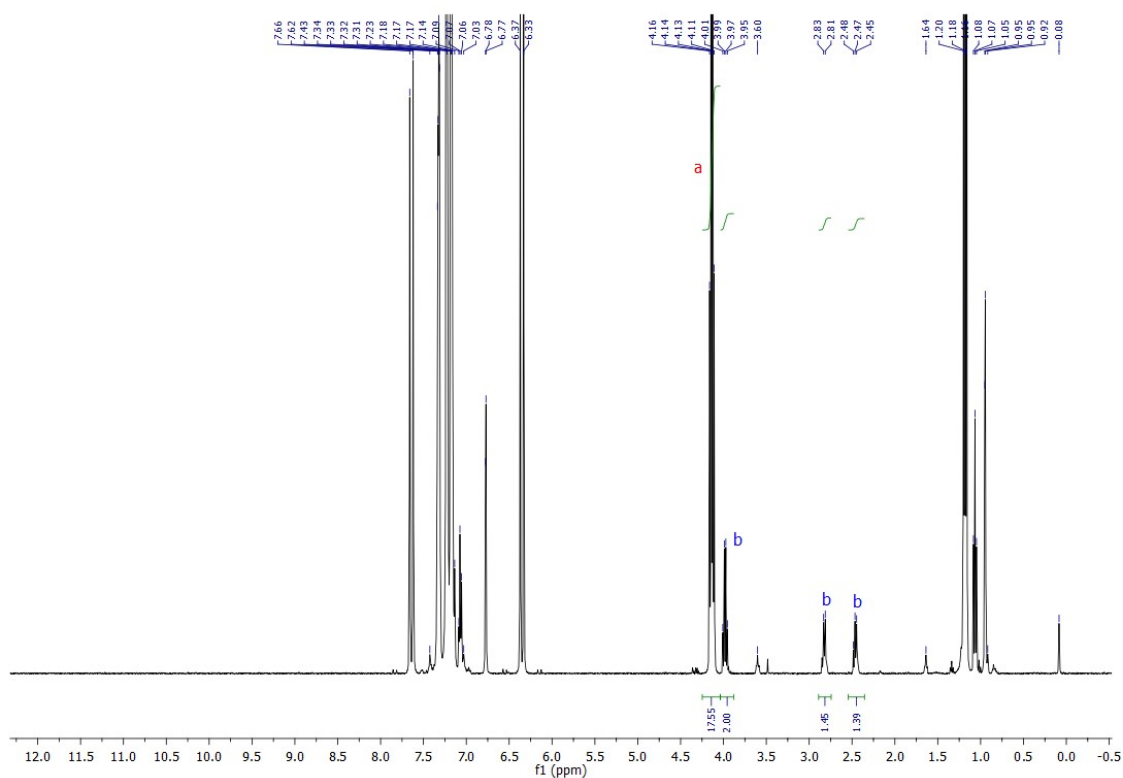


Figure S22. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1- d_2 (dioxane) and Zn to generate hydrogen (2nd part, after 45 minutes using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

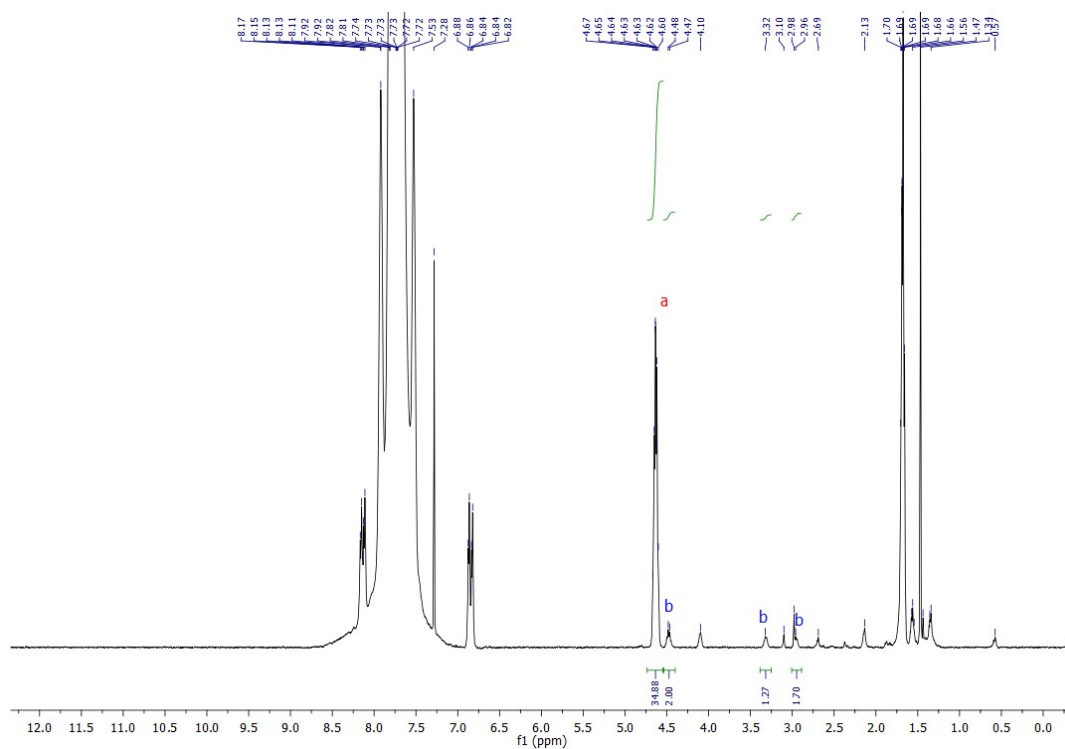


Figure S23. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR2- d_2 and Zn to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

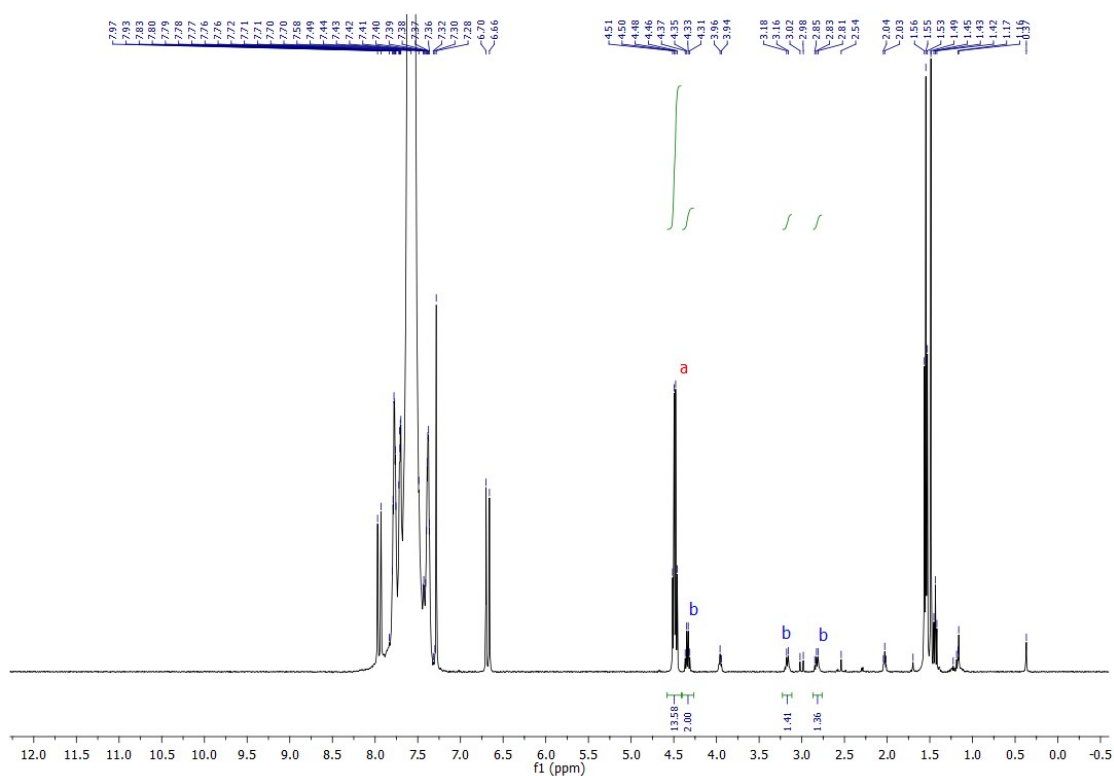


Figure S24. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using $\text{CCR2-}d_2$ and Zn to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

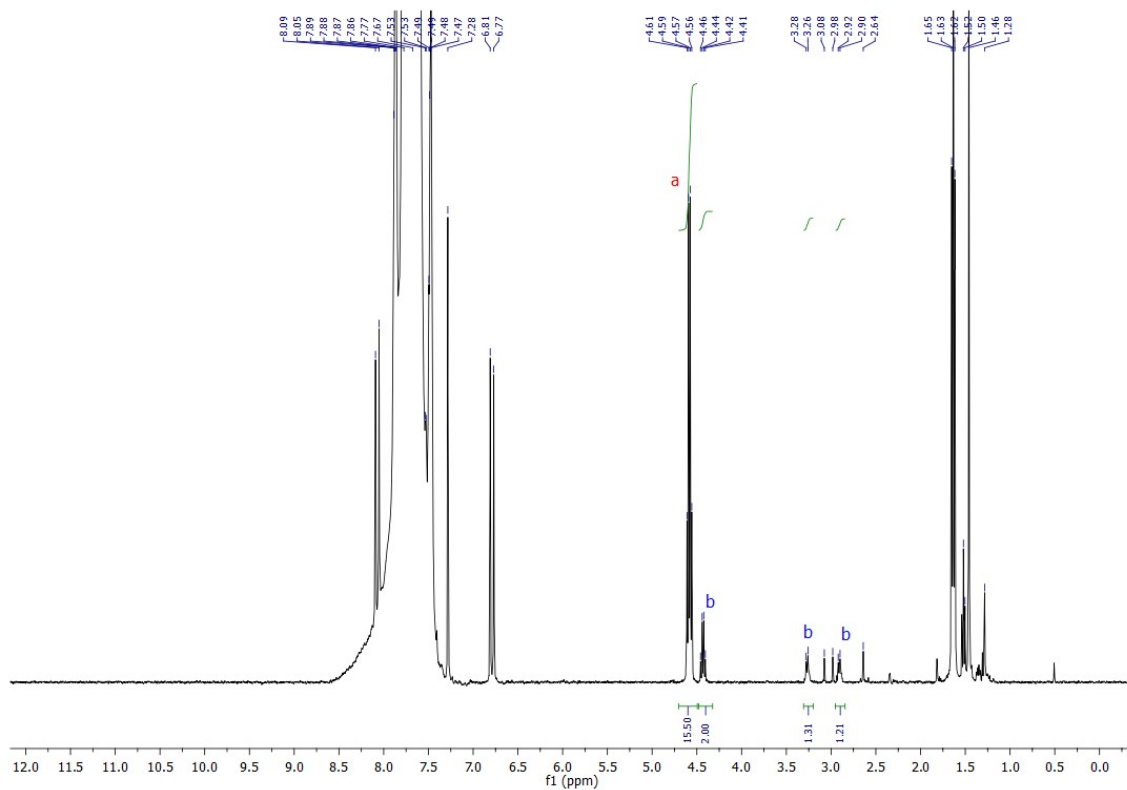


Figure S25. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using $\text{CCR3-}d_2$ and Zn to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

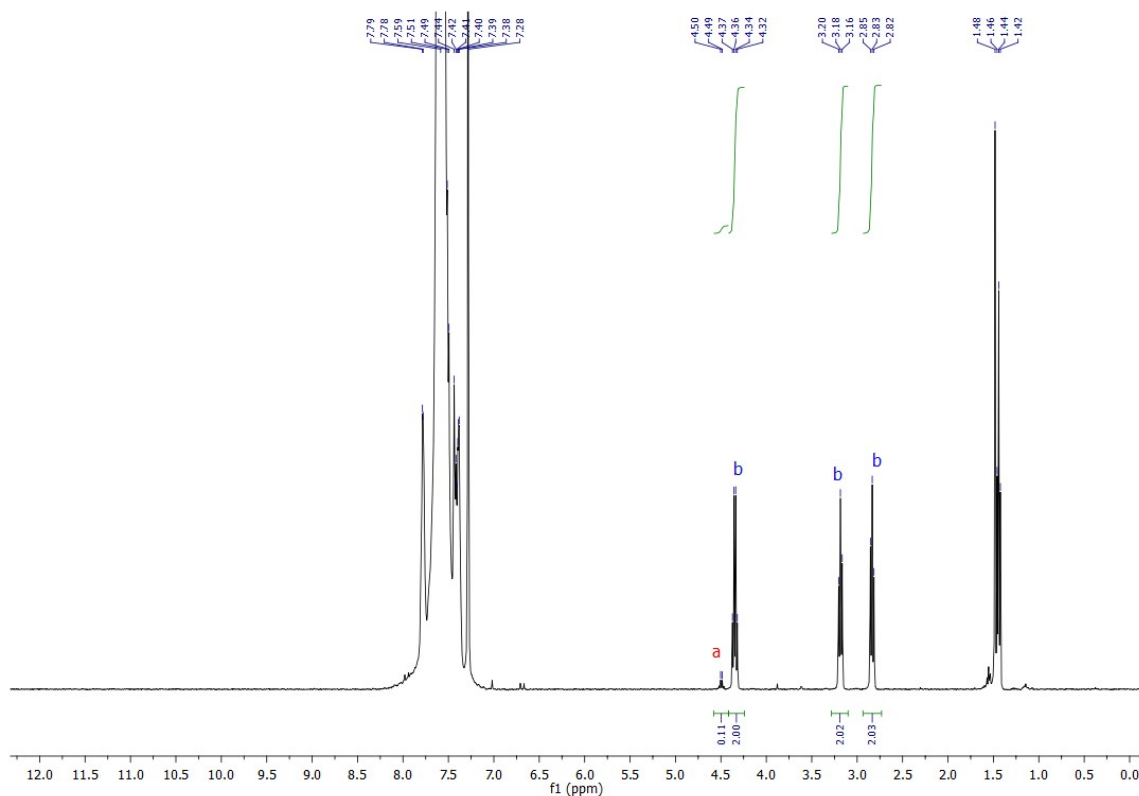


Figure S26. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using $\text{Ca}(\text{OH})_2$ and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

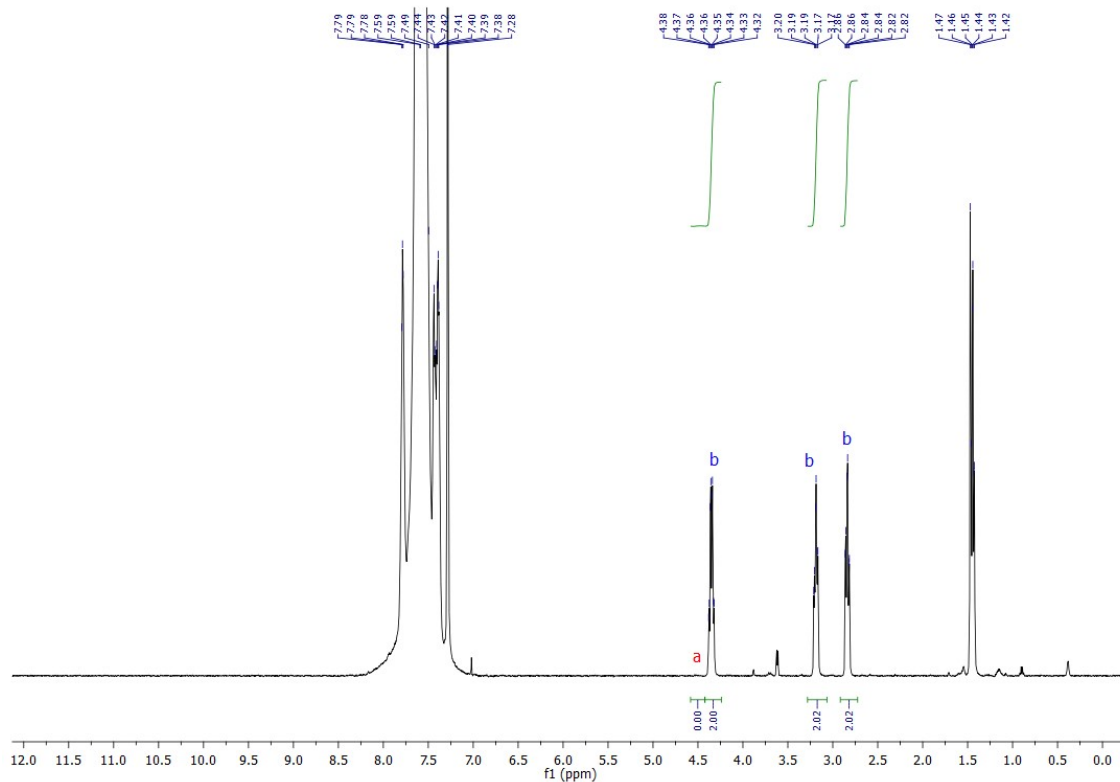


Figure S27. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1 and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

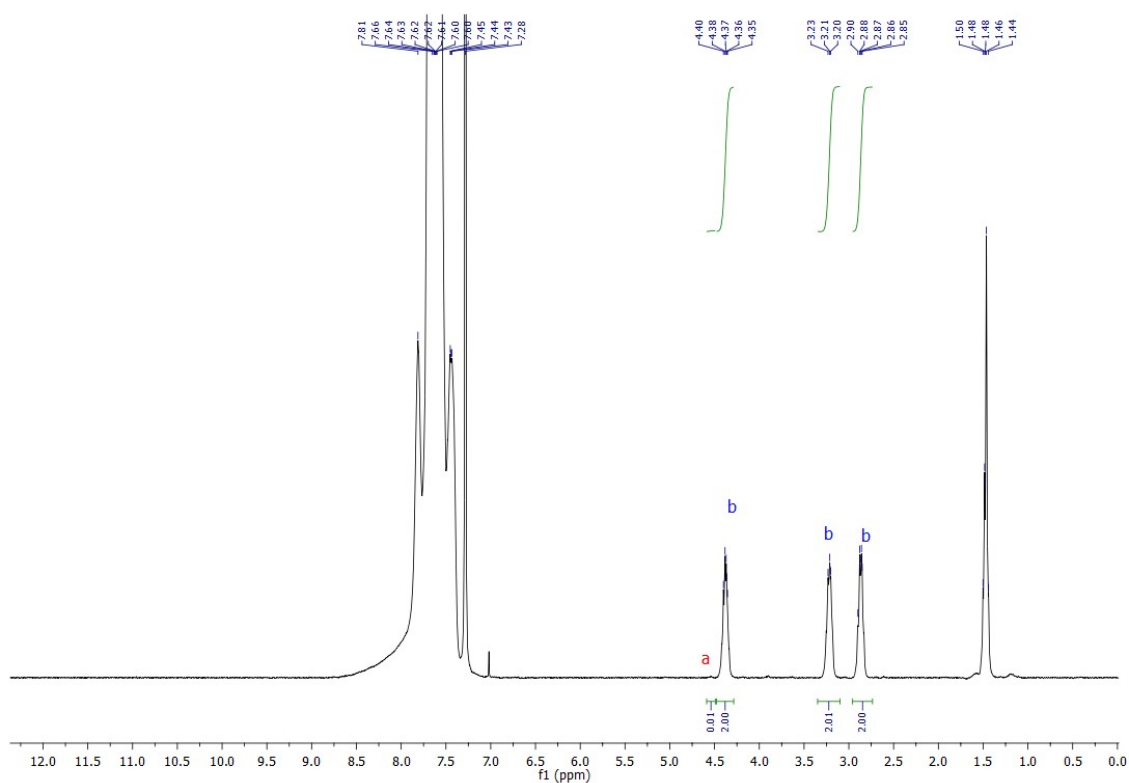


Figure S28. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR2 and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

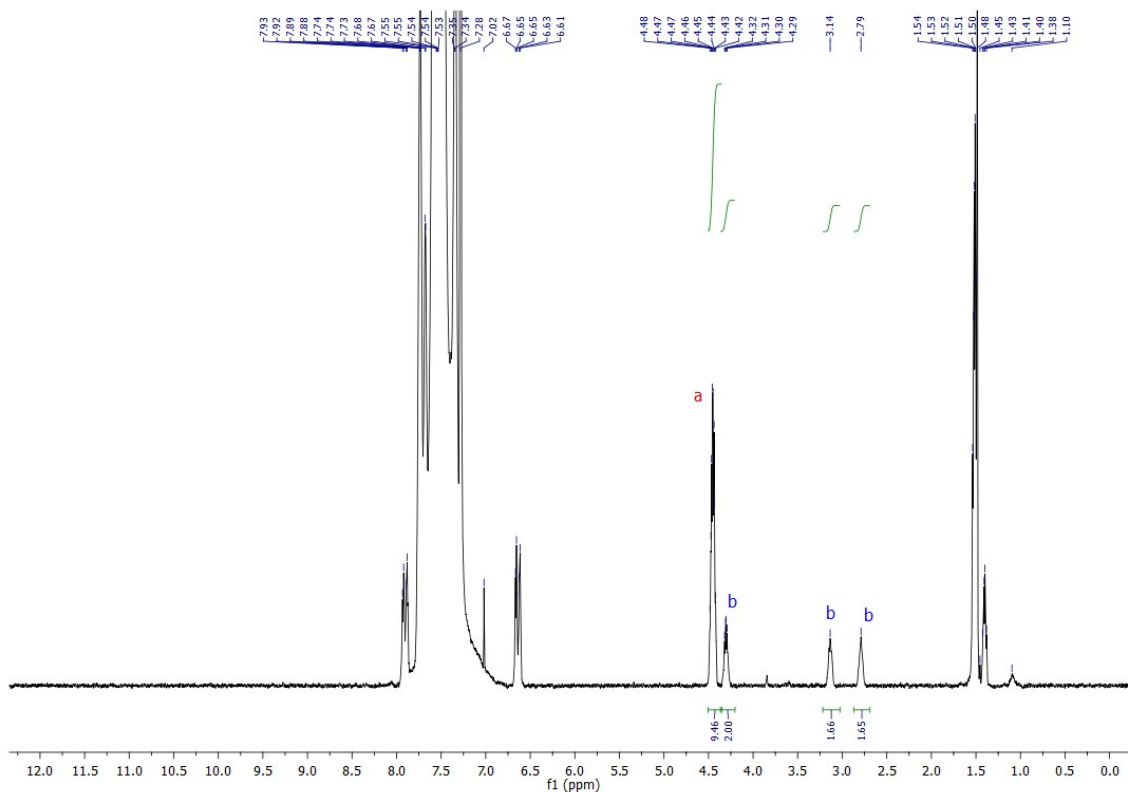


Figure S29. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1- d_2 (air) and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

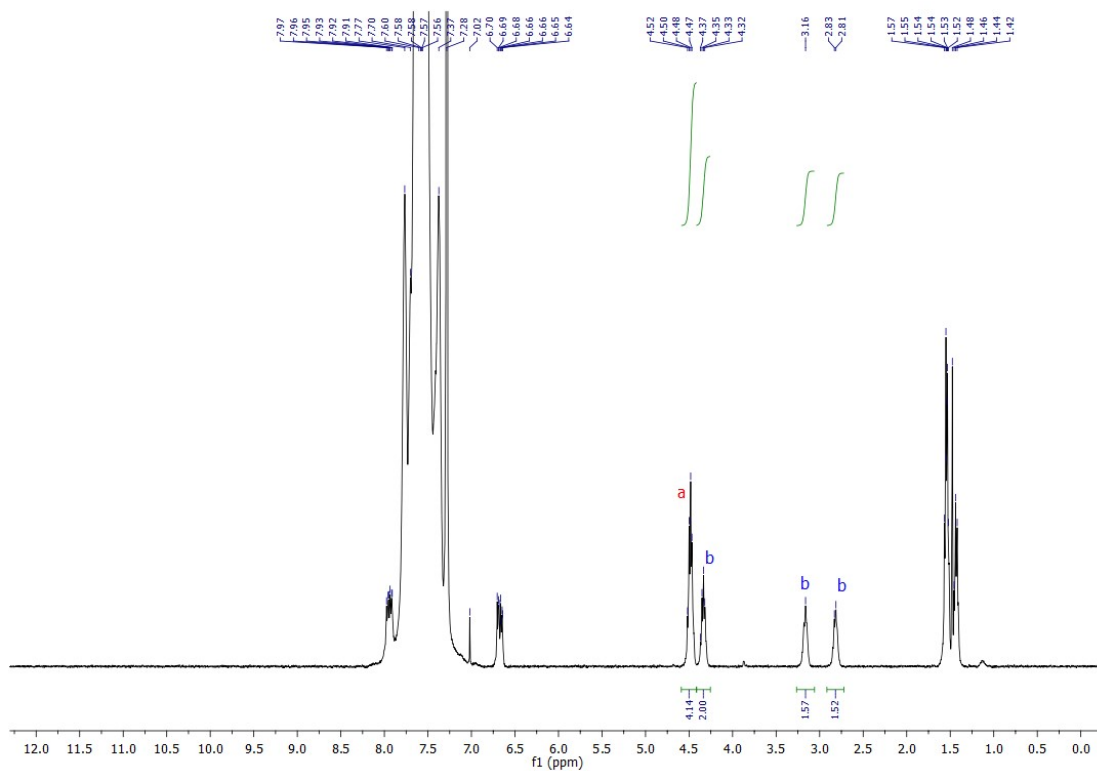


Figure S30. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1- d_2 (air) and Ca to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

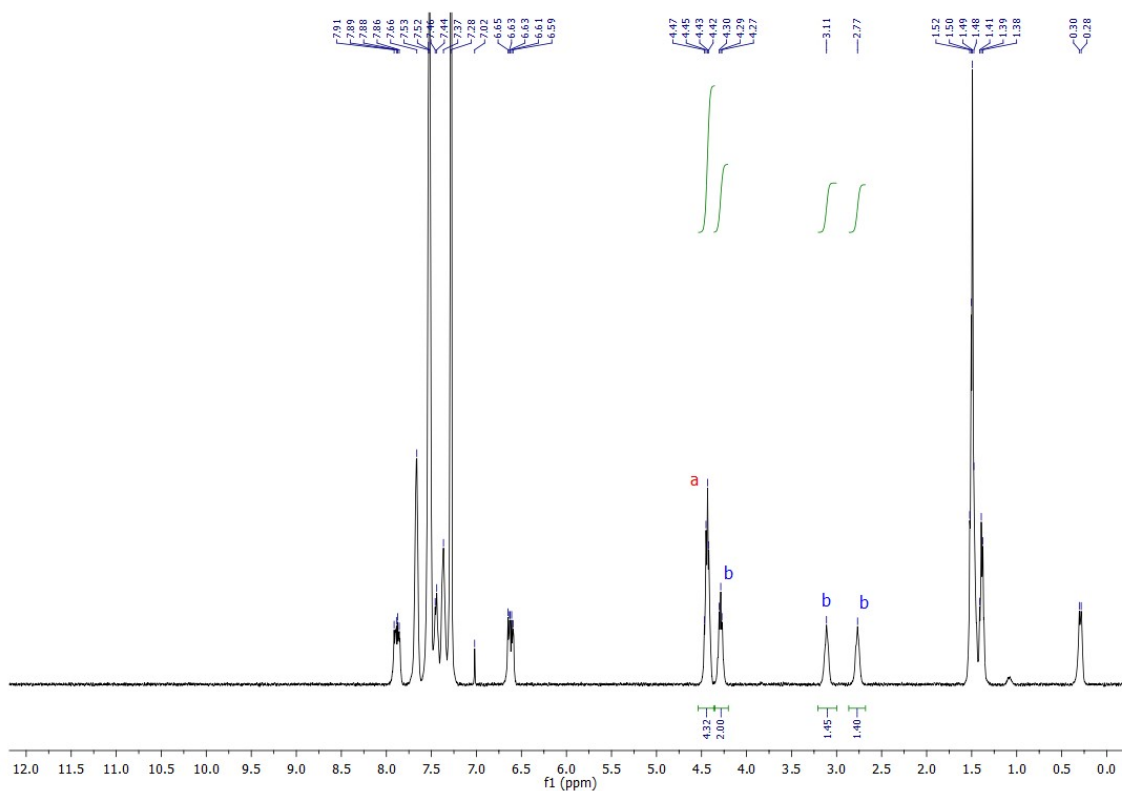


Figure S31. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1- d_2 (air) and Ca to generate hydrogen (1st part, after 45 minutes, using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

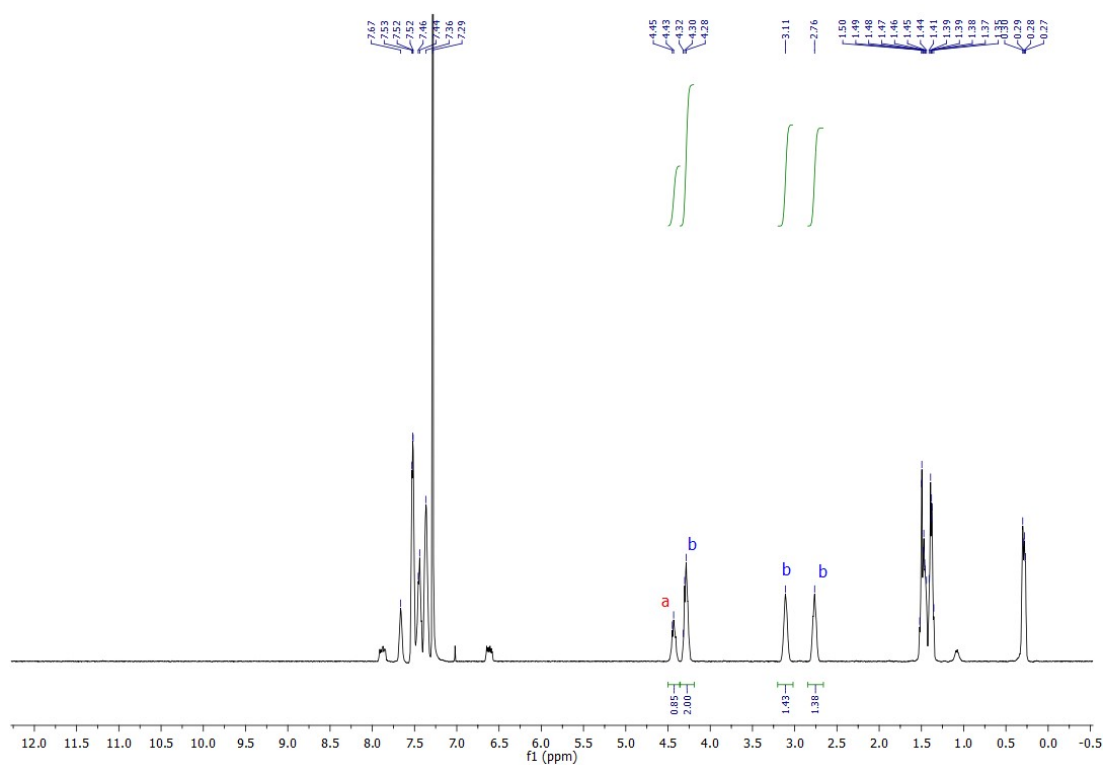


Figure S32. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (air) and Ca to generate hydrogen (2nd part, after 45 minutes, using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

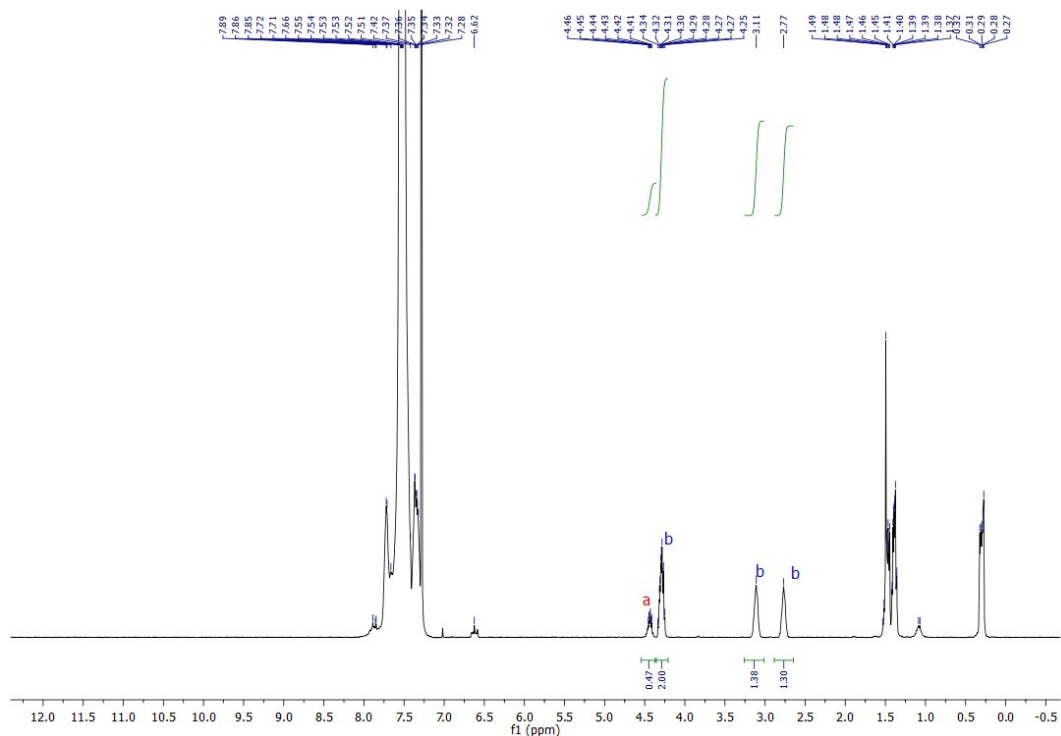


Figure S33. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (dioxane) and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

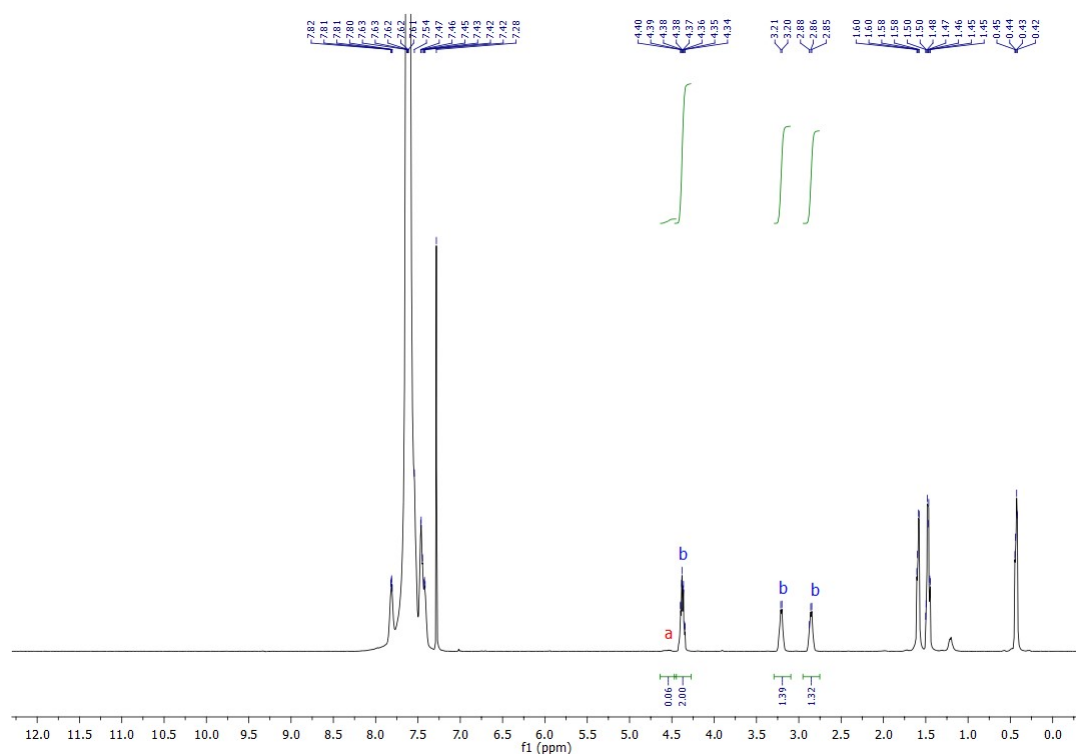


Figure S34. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (dioxane) and Ca to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

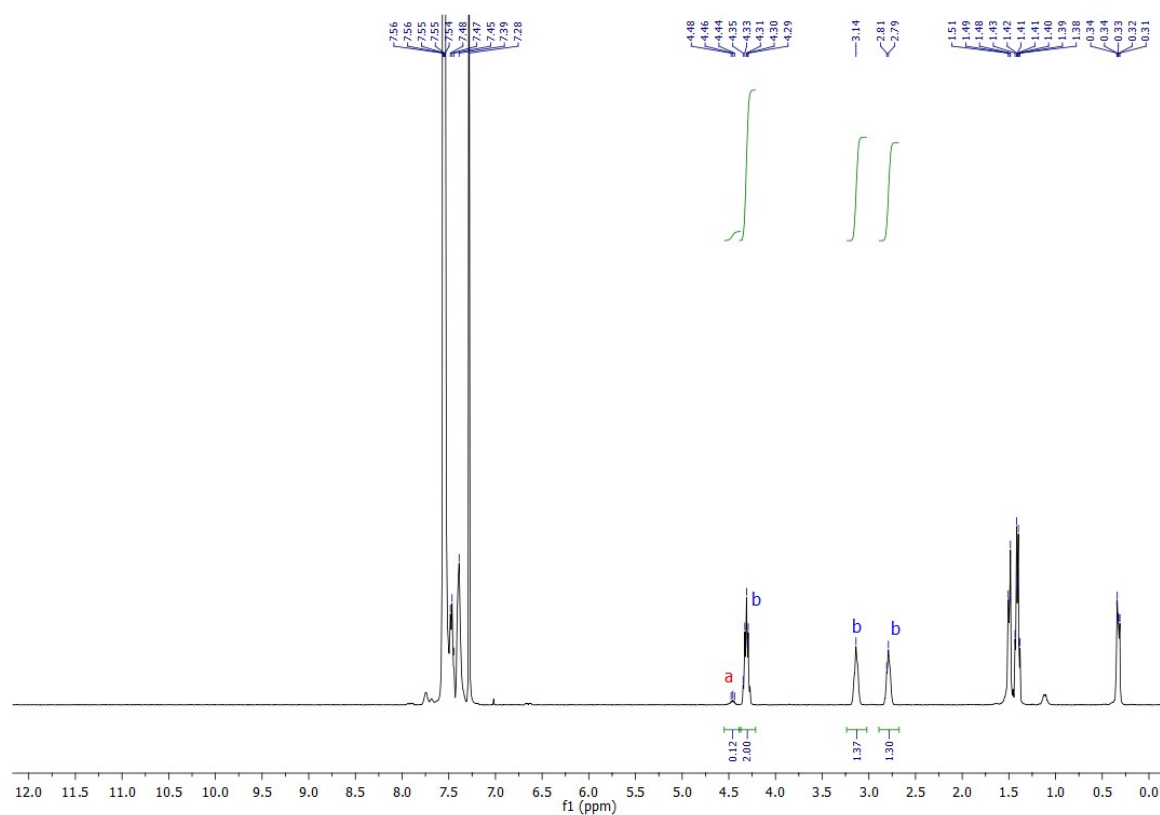


Figure S35. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1-d_2 (dioxane) and Ca to generate hydrogen (1st part, after 45 minutes using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

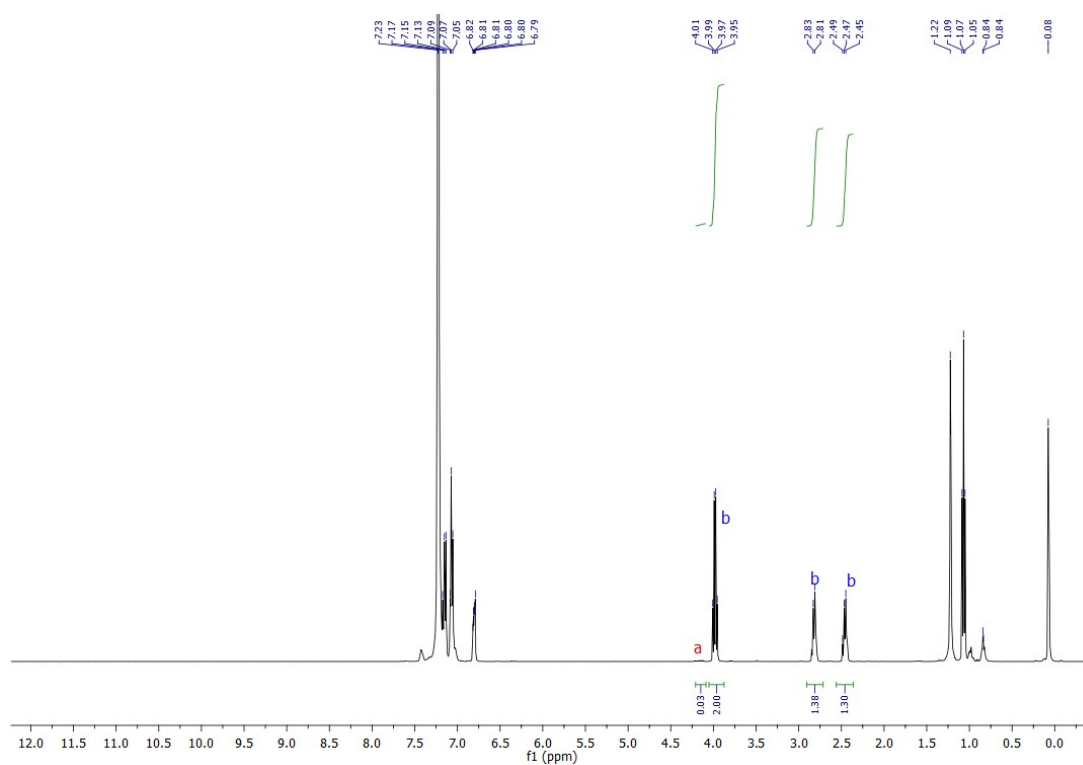


Figure S36. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR1- d_2 (dioxane) and Ca to generate hydrogen (2nd part, after 45 minutes using benzene- d_6 and dry catalyst): a - the signal of the initial substance, b - the signals of the product

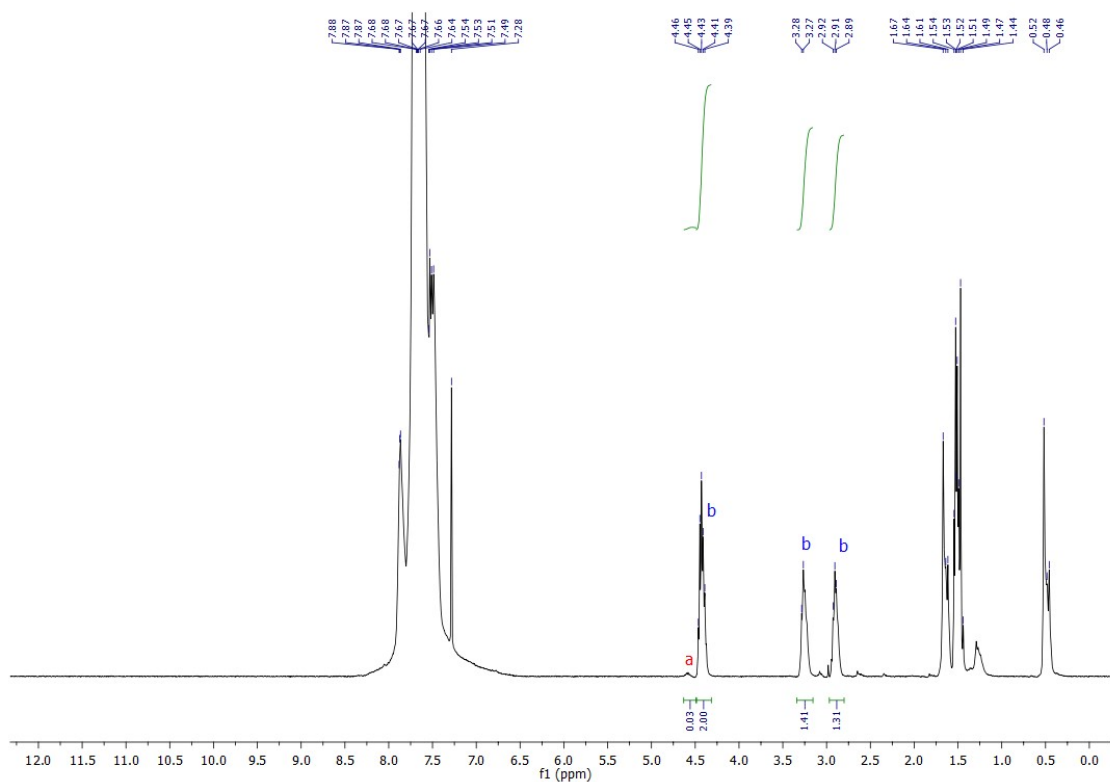


Figure S37. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR2- d_2 and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

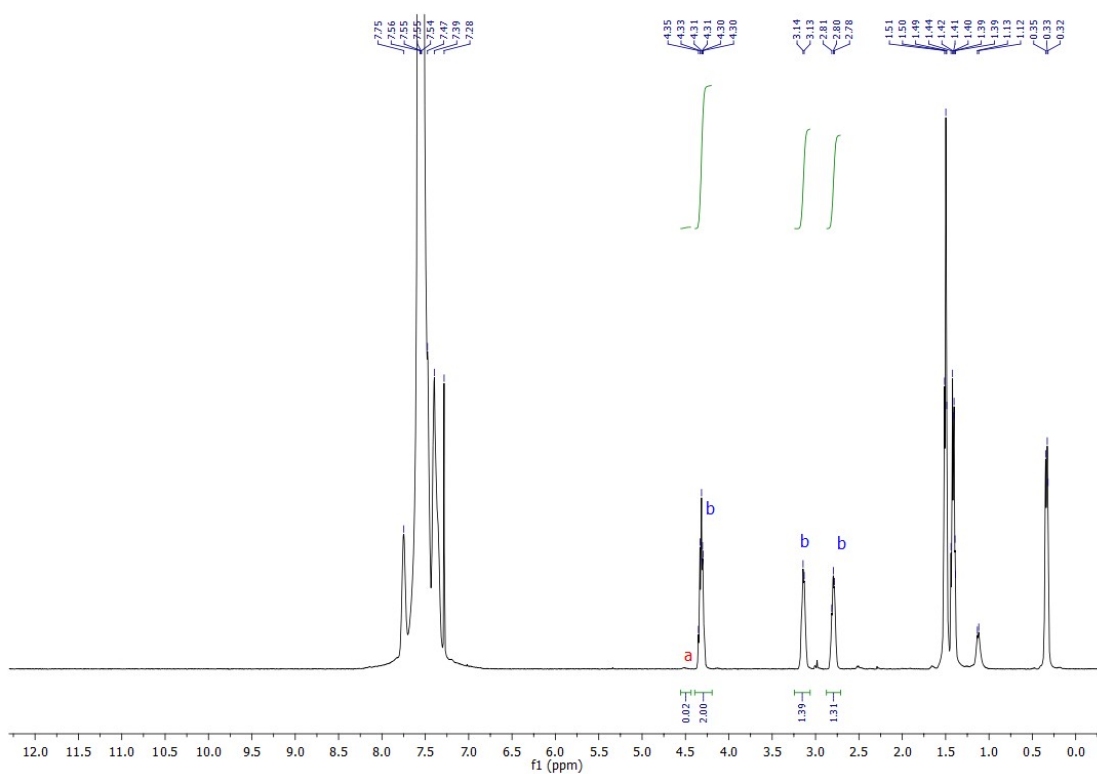


Figure S38. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR2-d_2 and Ca to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

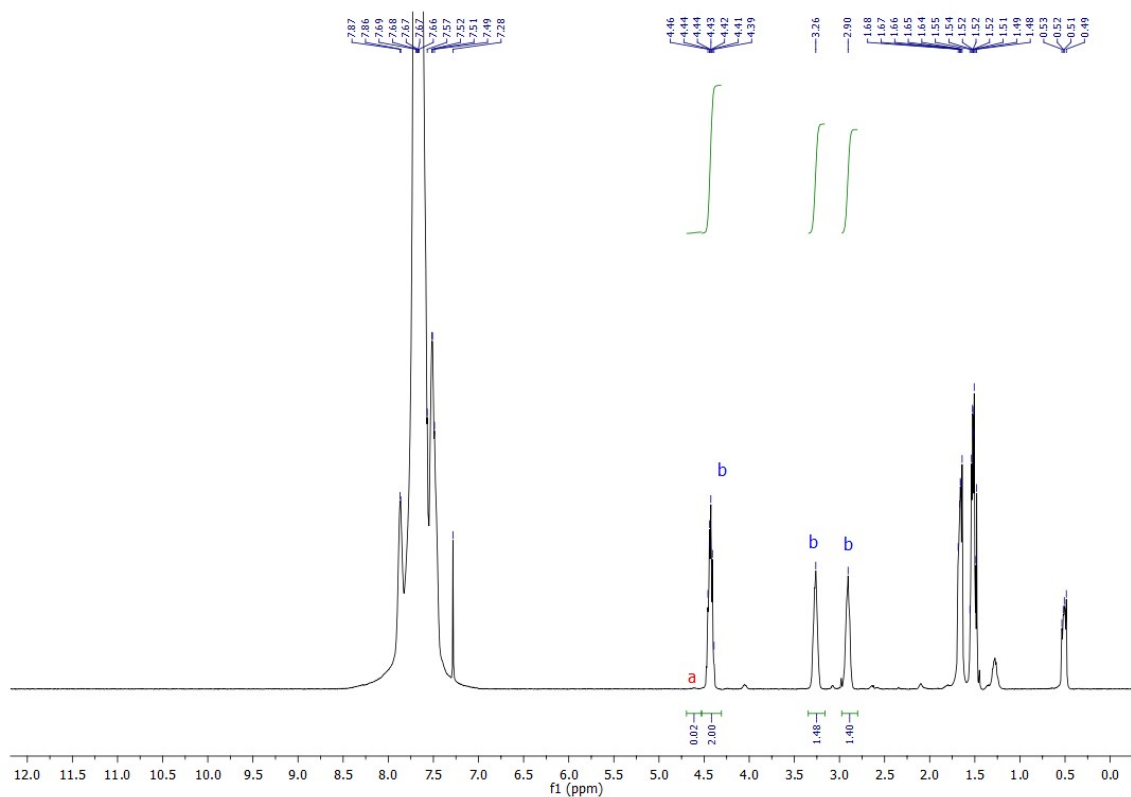


Figure S39. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR3-d_2 and Ca to generate hydrogen (1st part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product



Figure S40. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of **1** using CCR3-d_2 and Ca to generate hydrogen (2nd part, after 45 minutes): a - the signal of the initial substance, b - the signals of the product

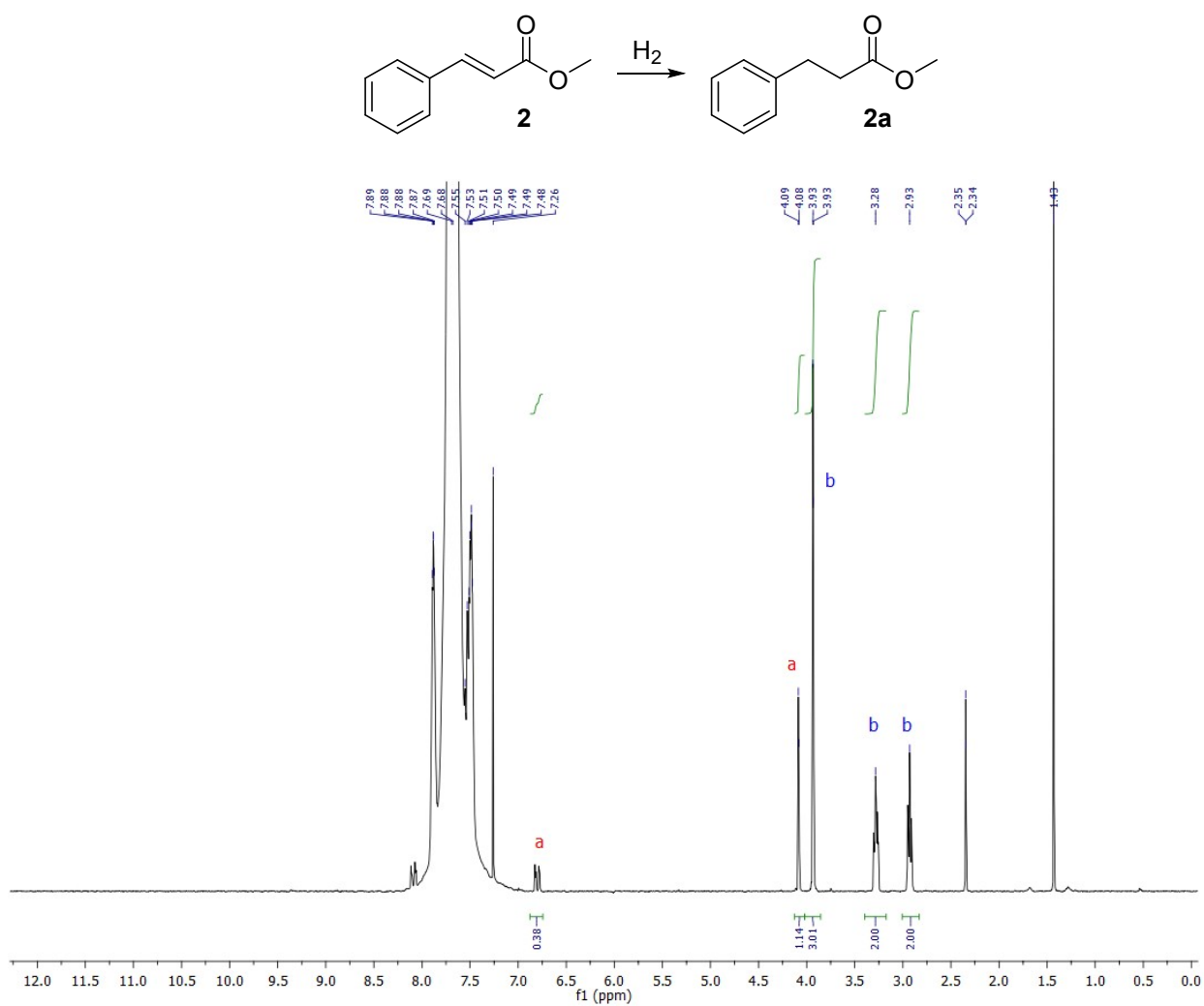


Figure S41. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of substrate **2** using CCR2 and Ca: a - the signals of the initial substance, b - the signals of the product

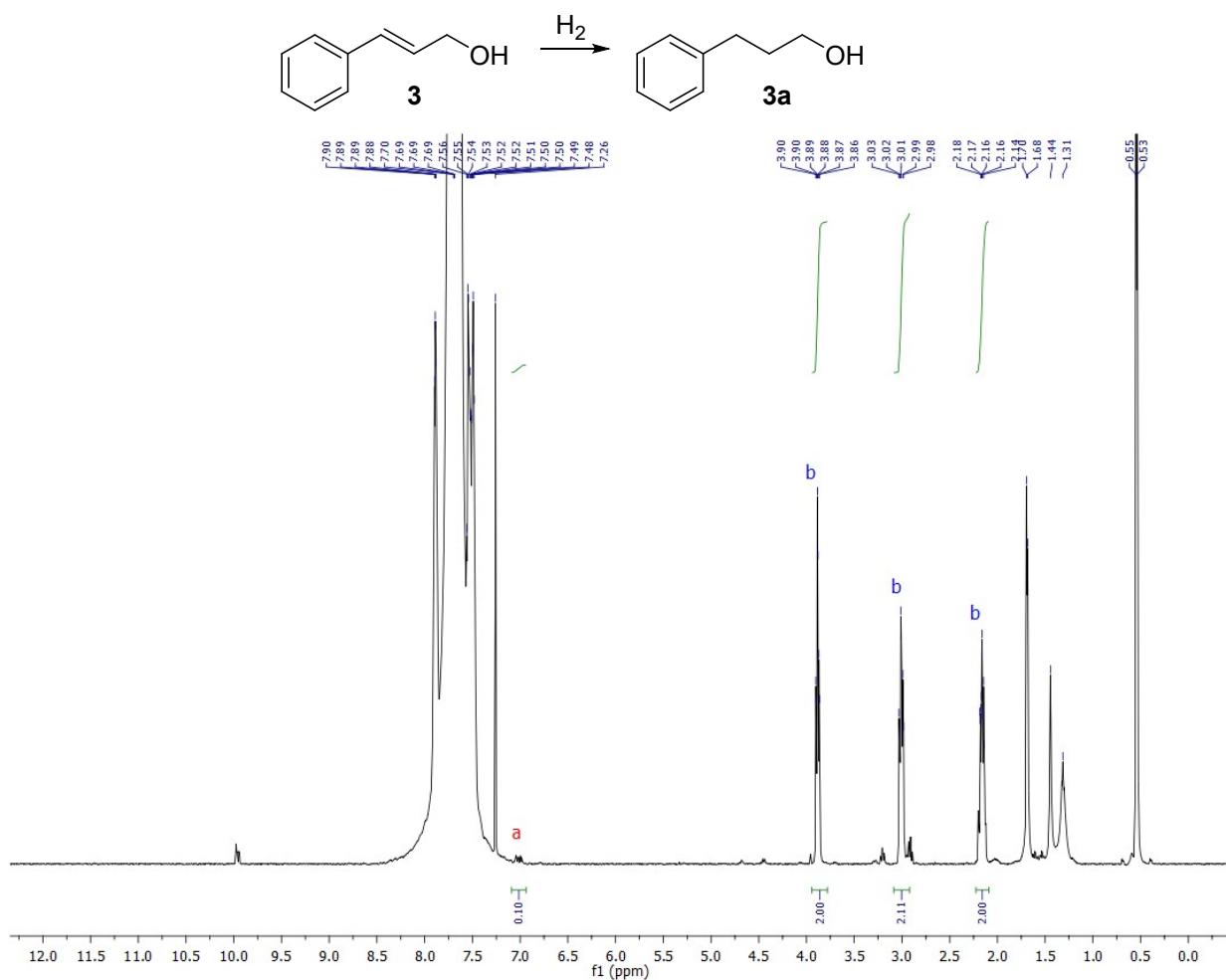


Figure S42. ¹H NMR (400 MHz, CDCl₃) spectrum of the reaction mixture after hydrogenation of substrate **3** using CCR2 and Ca: a - the signals of the initial substance, b - the signals of the product

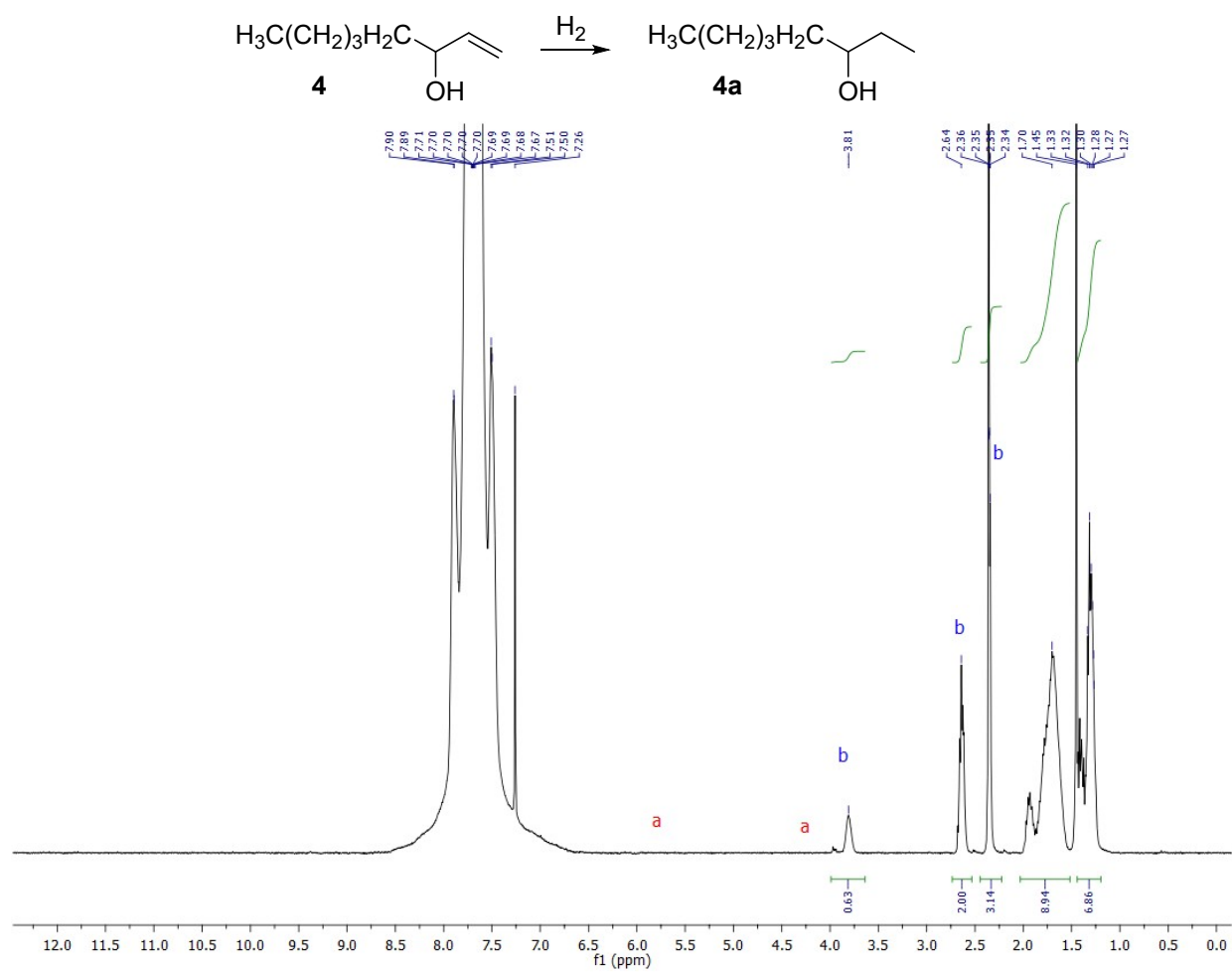


Figure S43. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of substrate **4** using CCR2 and Ca: a - the signals of the initial substance (absent), b - the signals of the product

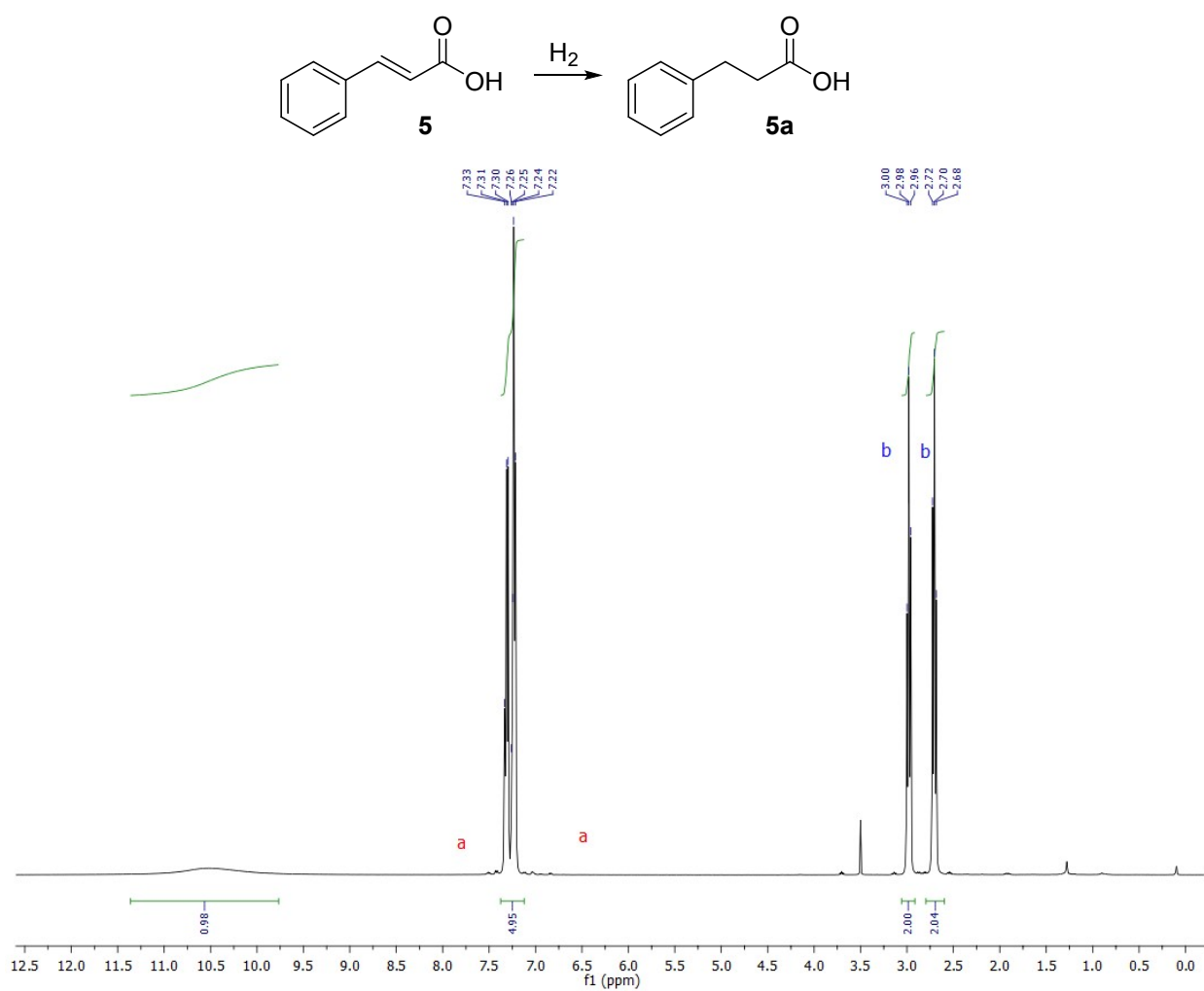


Figure S44. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture (after filtration and solvent evaporation) after hydrogenation of substrate **5** using CCR2 and Ca: a - the signals of the initial substance (absent), b - the signals of the product

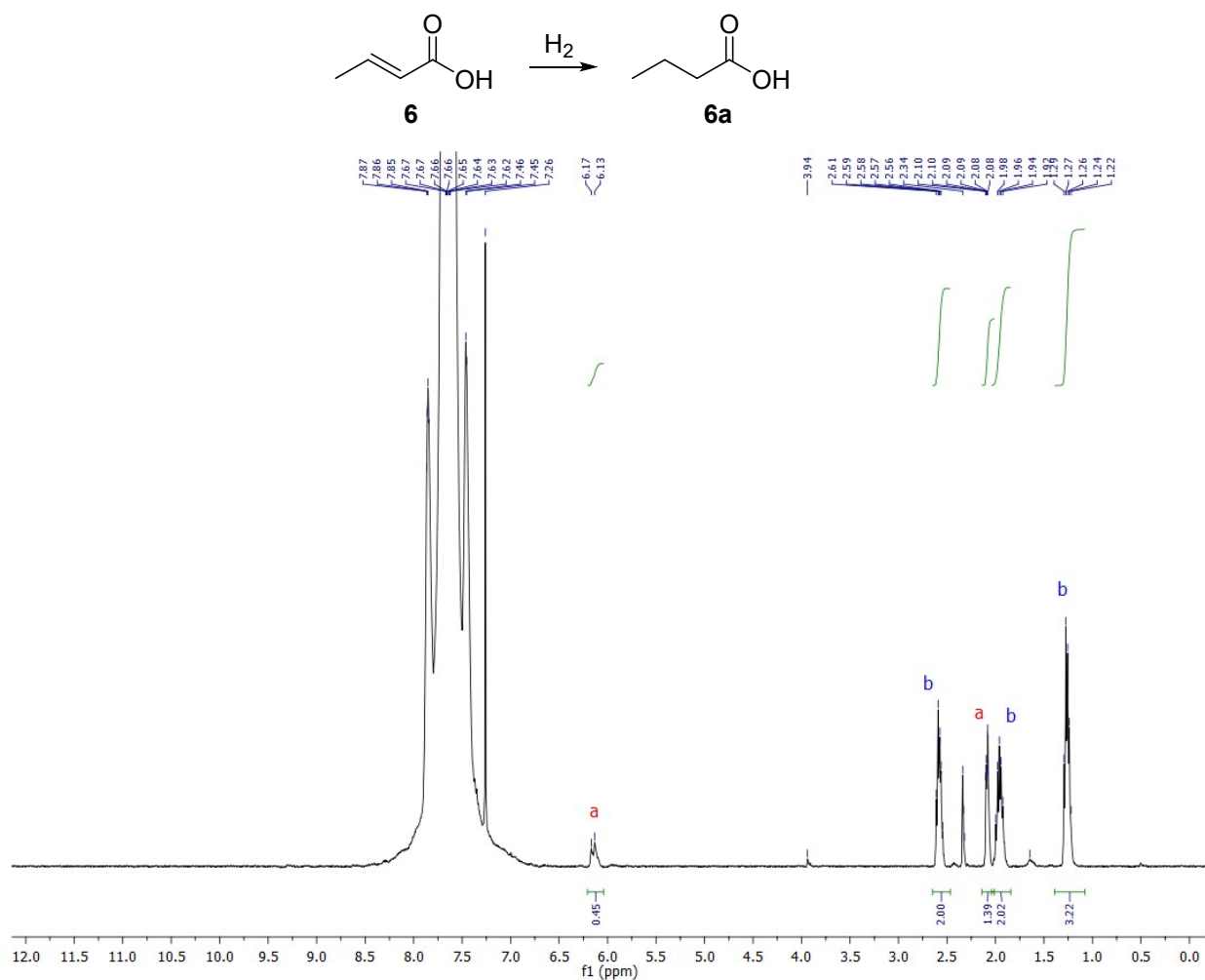


Figure S45. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of substrate **6** using CCR2 and Ca: a - the signals of the initial substance, b - the signals of the product

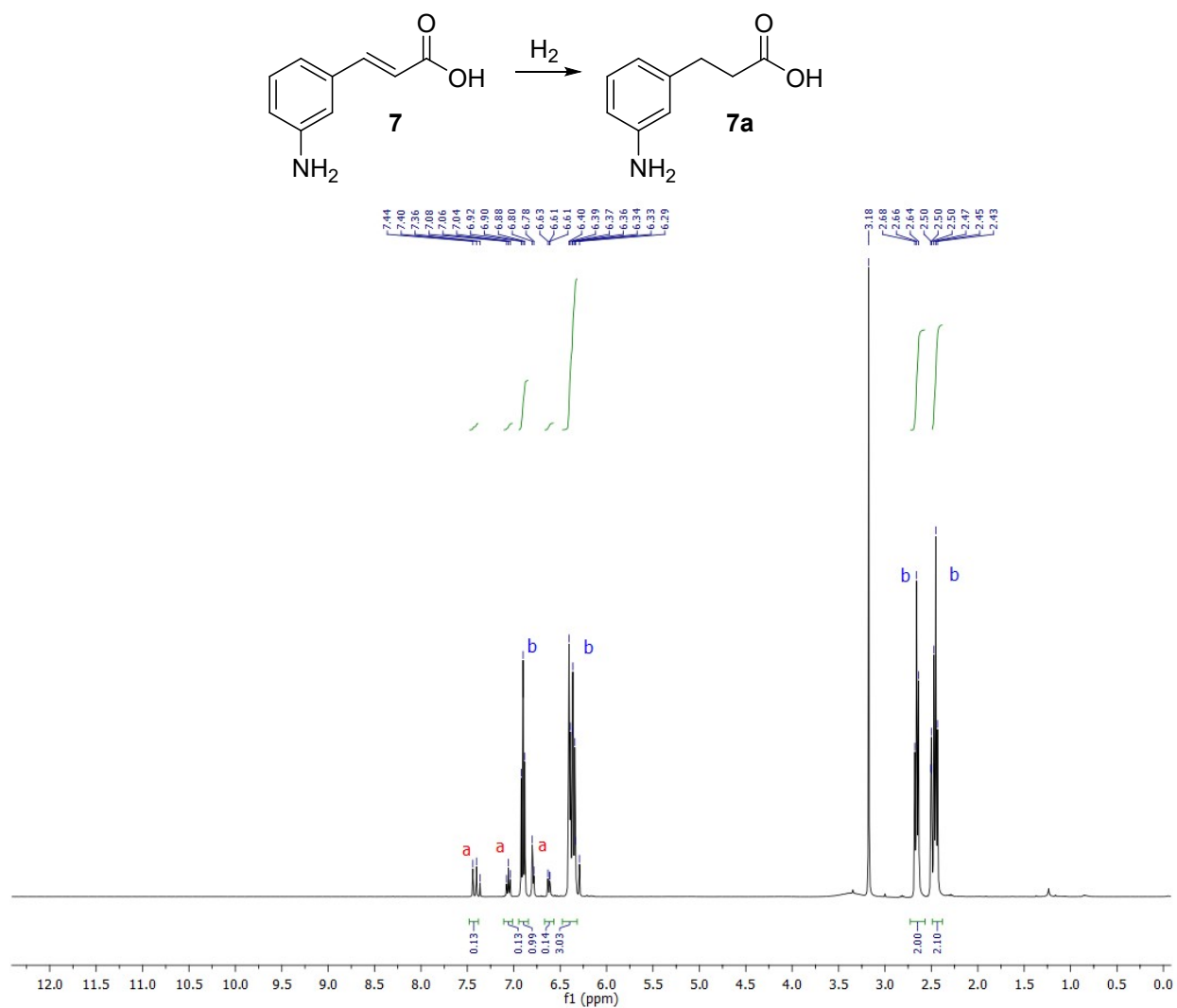


Figure S46. ¹H NMR (400 MHz, DMSO-*d*₆) spectrum of the reaction mixture (after filtration and solvent evaporation) after hydrogenation of substrate **7** using CCR2 and Ca: a - the signals of the initial substance, b - the signals of the product

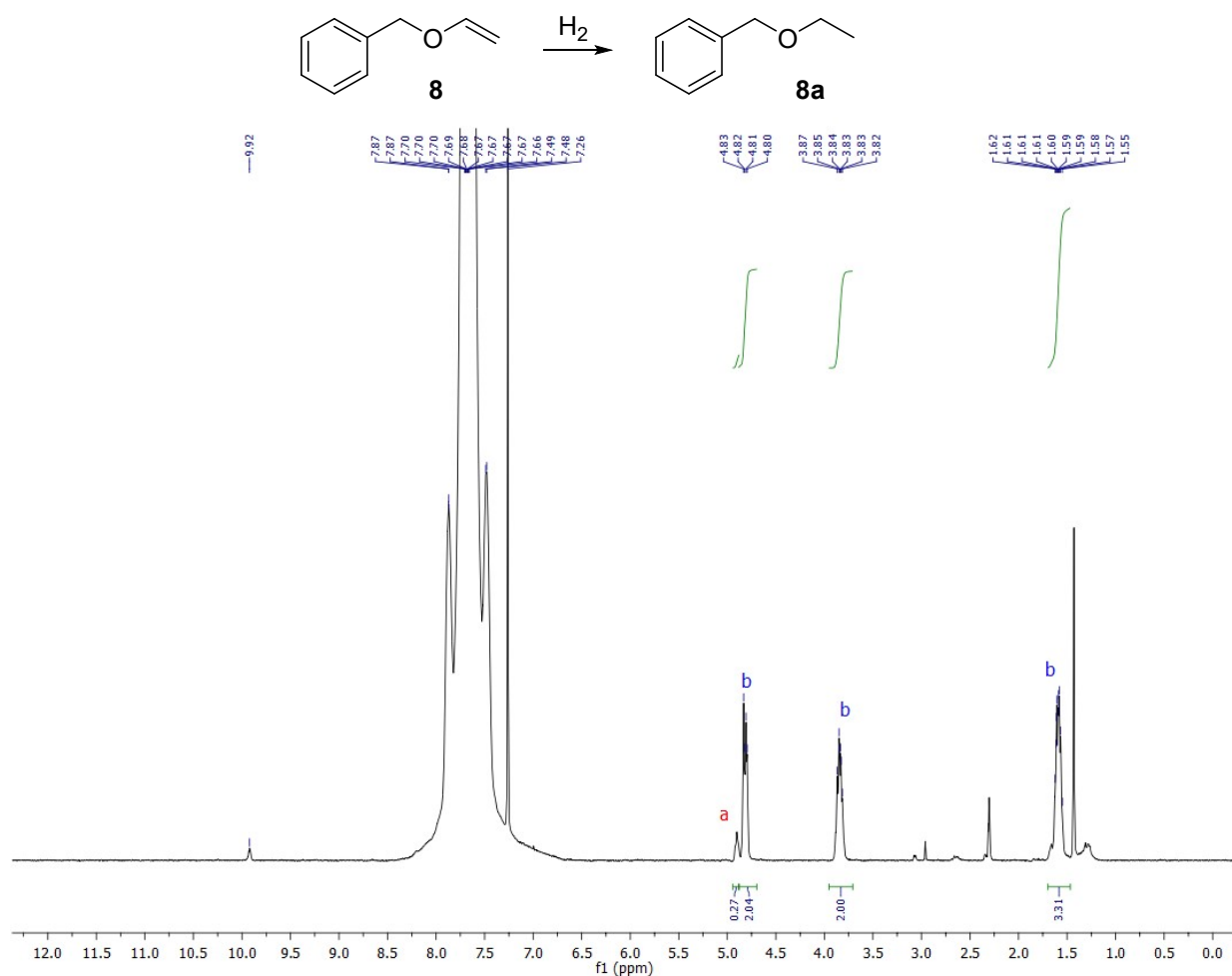


Figure S47. ^1H NMR (400 MHz, CDCl_3) spectrum of the reaction mixture after hydrogenation of substrate **8** using CCR2 and Ca: a - the signals of the initial substance, b - the signals of the product

S6. SEM and EDX data

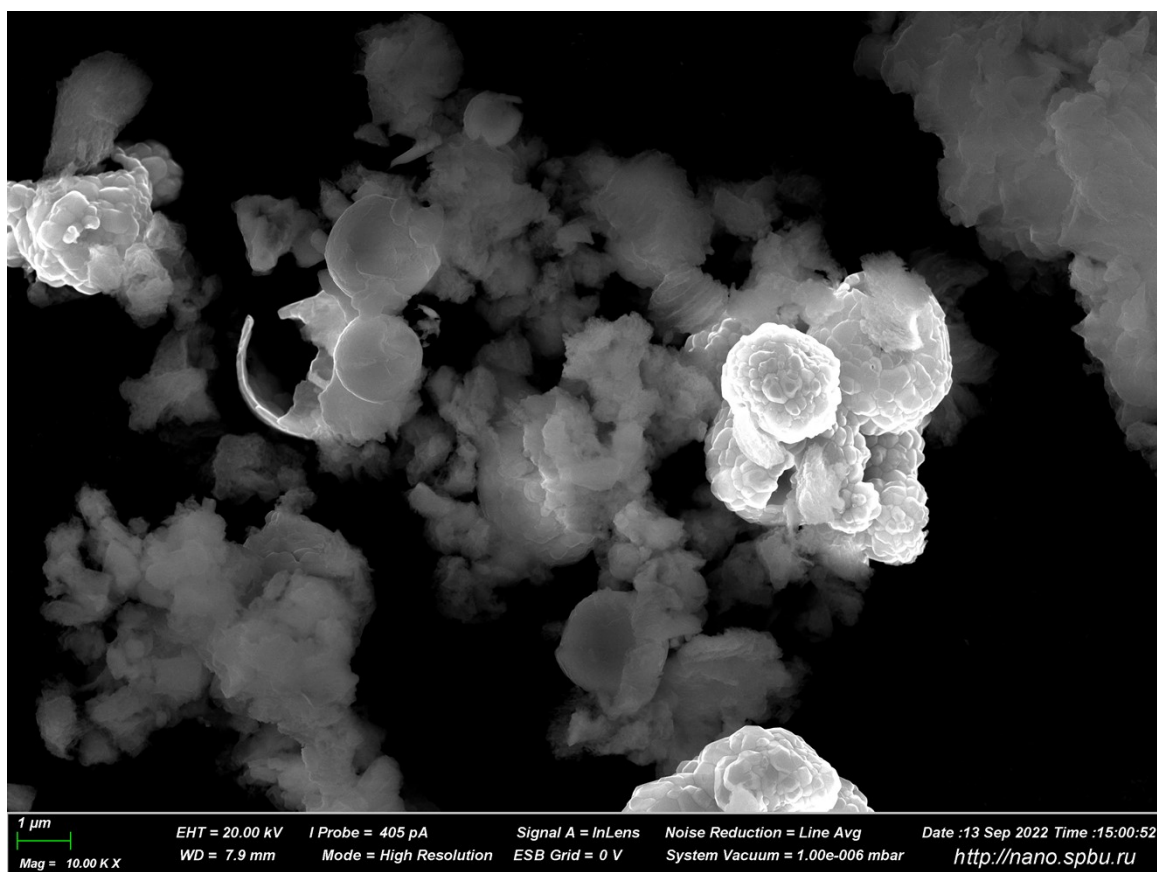


Figure S48. SEM image of the residue after the Zn + Ca(OH)₂ reaction. Scale bar 1 μm

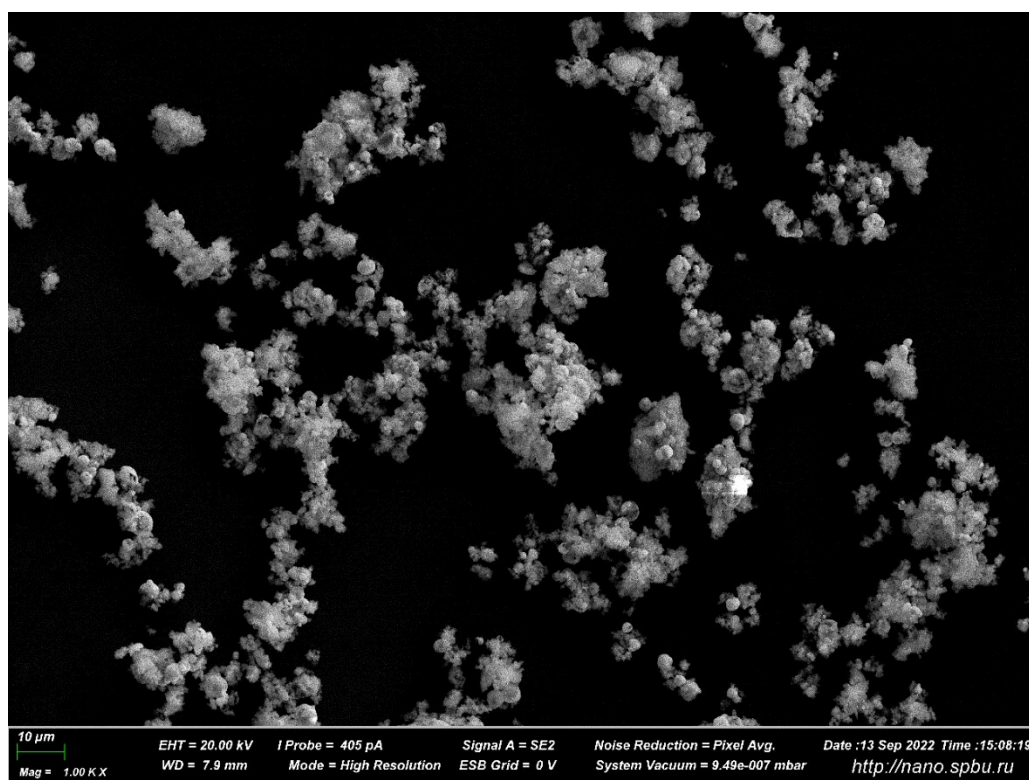


Figure S49. SEM image of the residue after the Zn + Ca(OH)₂ reaction. Scale bar 10 μm

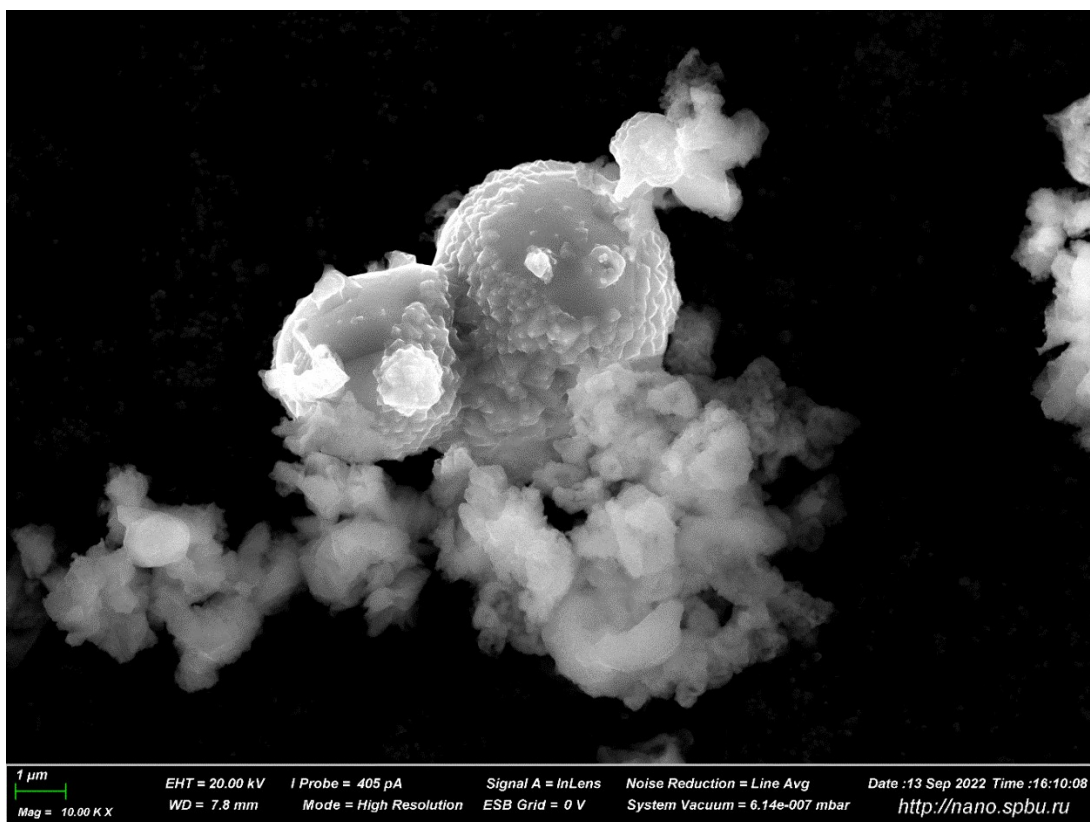


Figure S50. SEM image of the residue after the Fe + Ca(OH)₂ reaction. Scale bar 1 μm

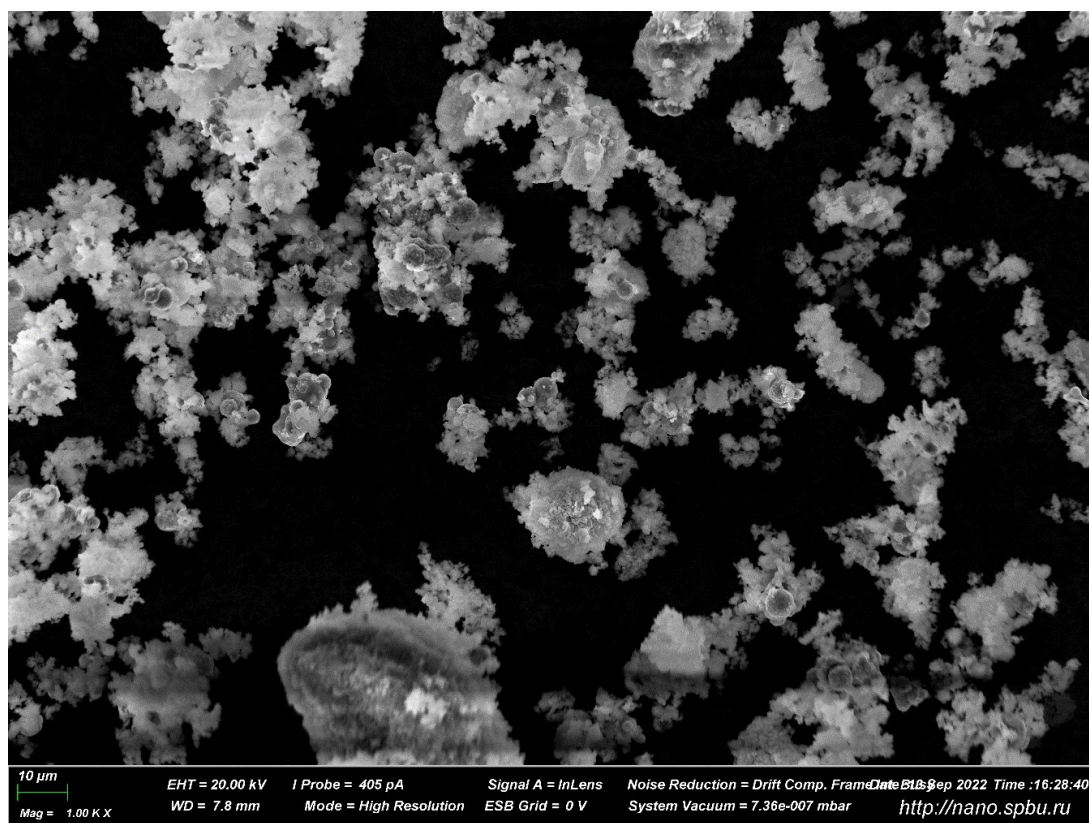


Figure S51. SEM image of the residue after the Fe + Ca(OH)₂ reaction. Scale bar 10 μm

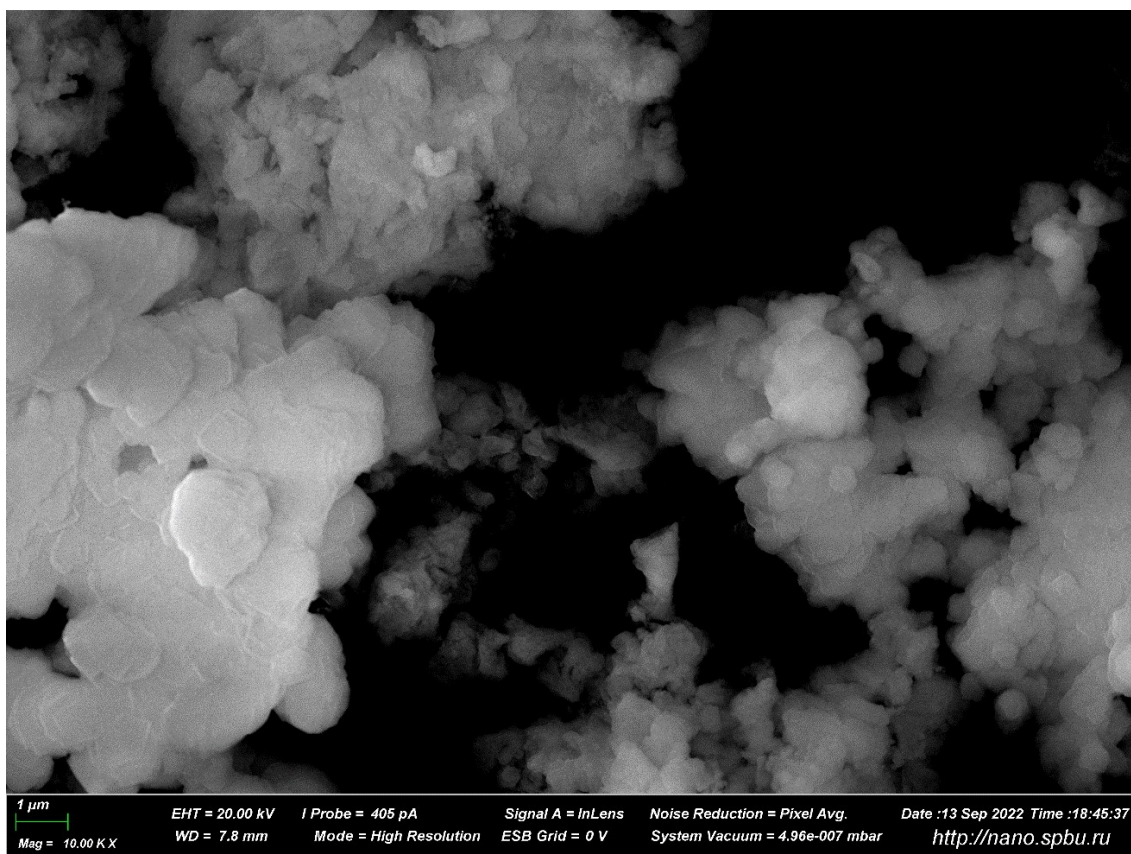


Figure S52. SEM image of the residue after the Mg + Ca(OH)₂ reaction. Scale bar 1 μm

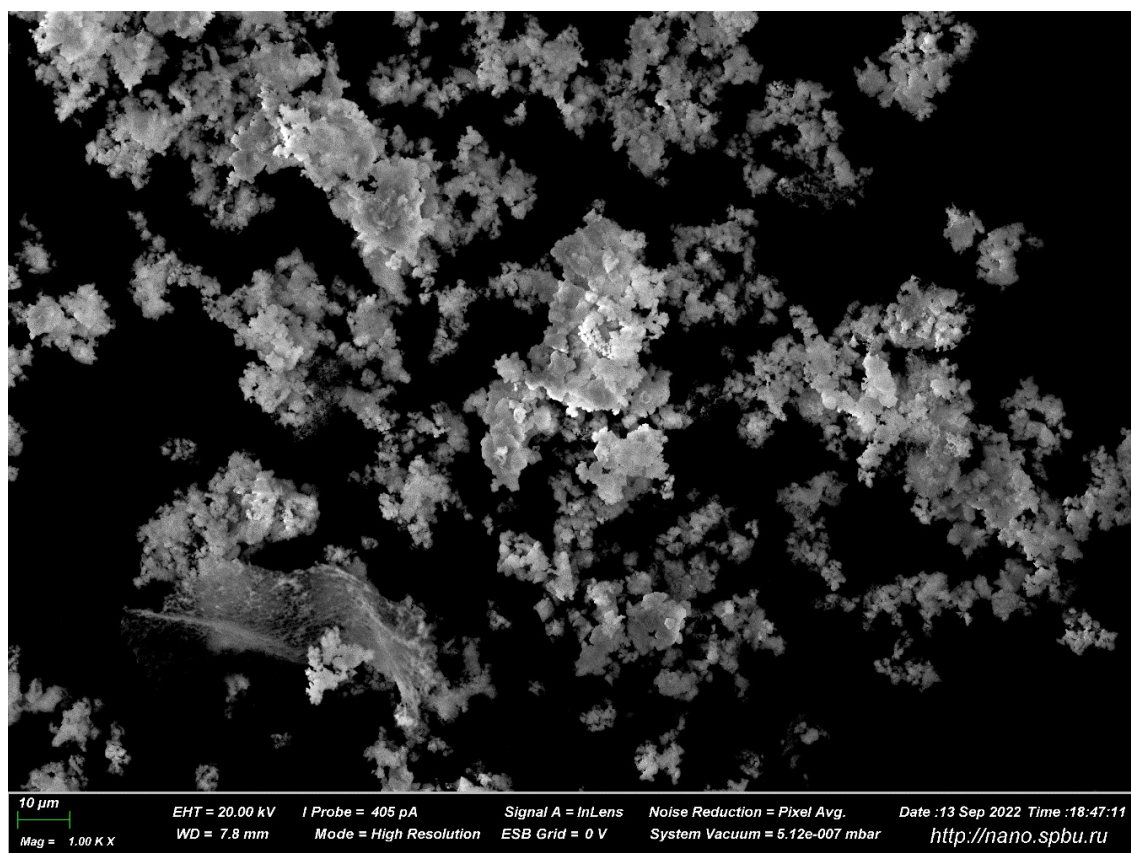


Figure S53. SEM image of the residue after the Mg + Ca(OH)₂ reaction. Scale bar 10 μm

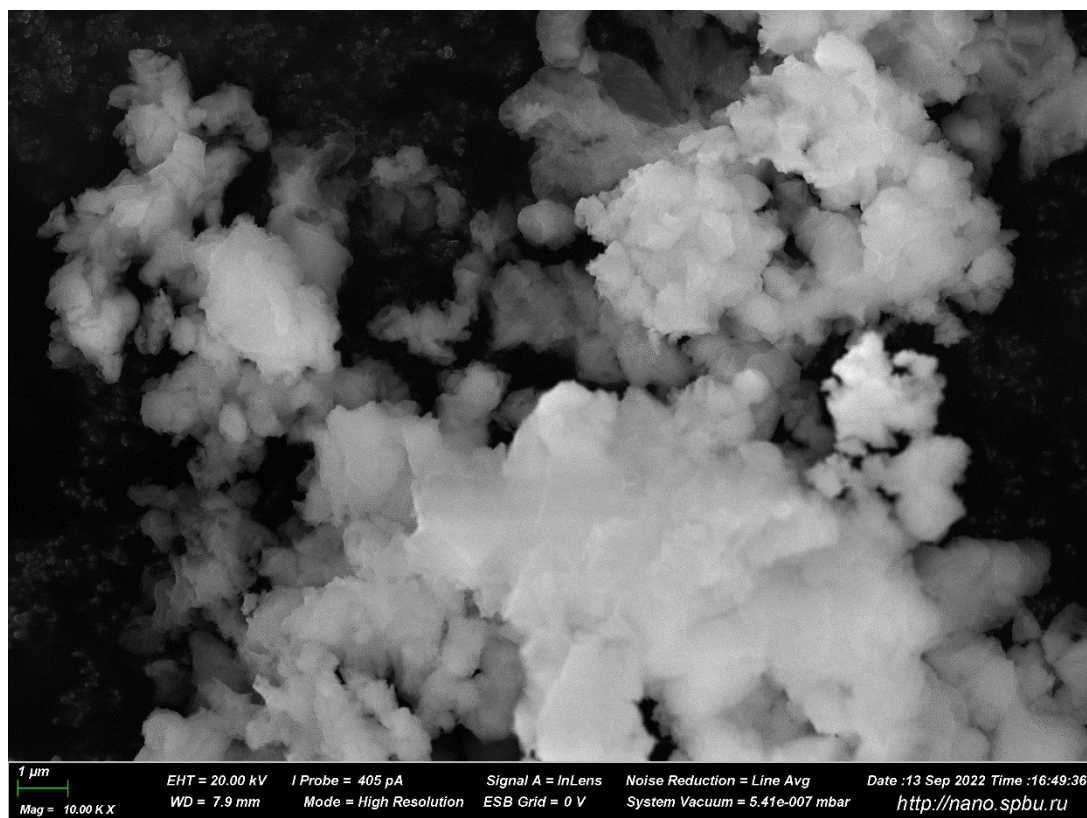


Figure S54. SEM image of the residue after the $\text{Ca} + \text{Ca}(\text{OH})_2$ reaction. Scale bar 1 μm

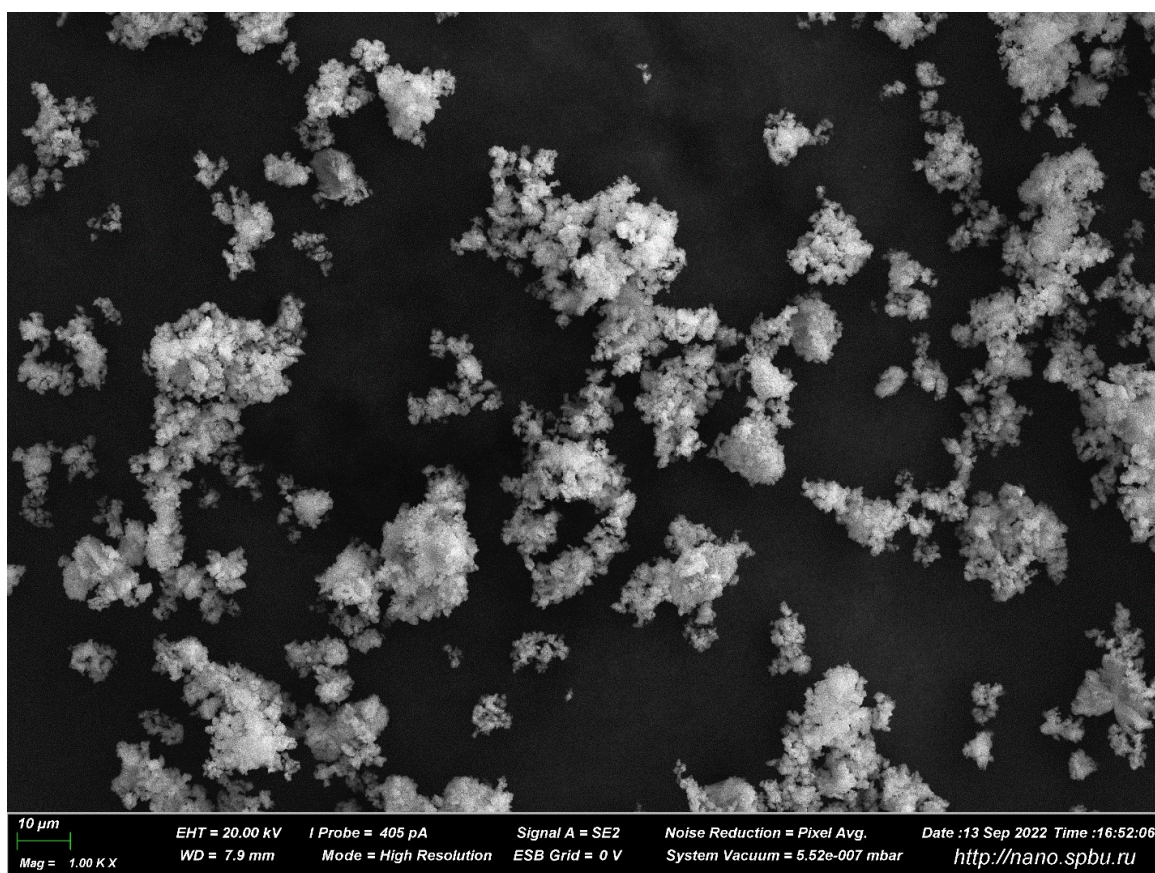


Figure S55. SEM image of the residue after the $\text{Ca} + \text{Ca}(\text{OH})_2$ reaction. Scale bar 10 μm

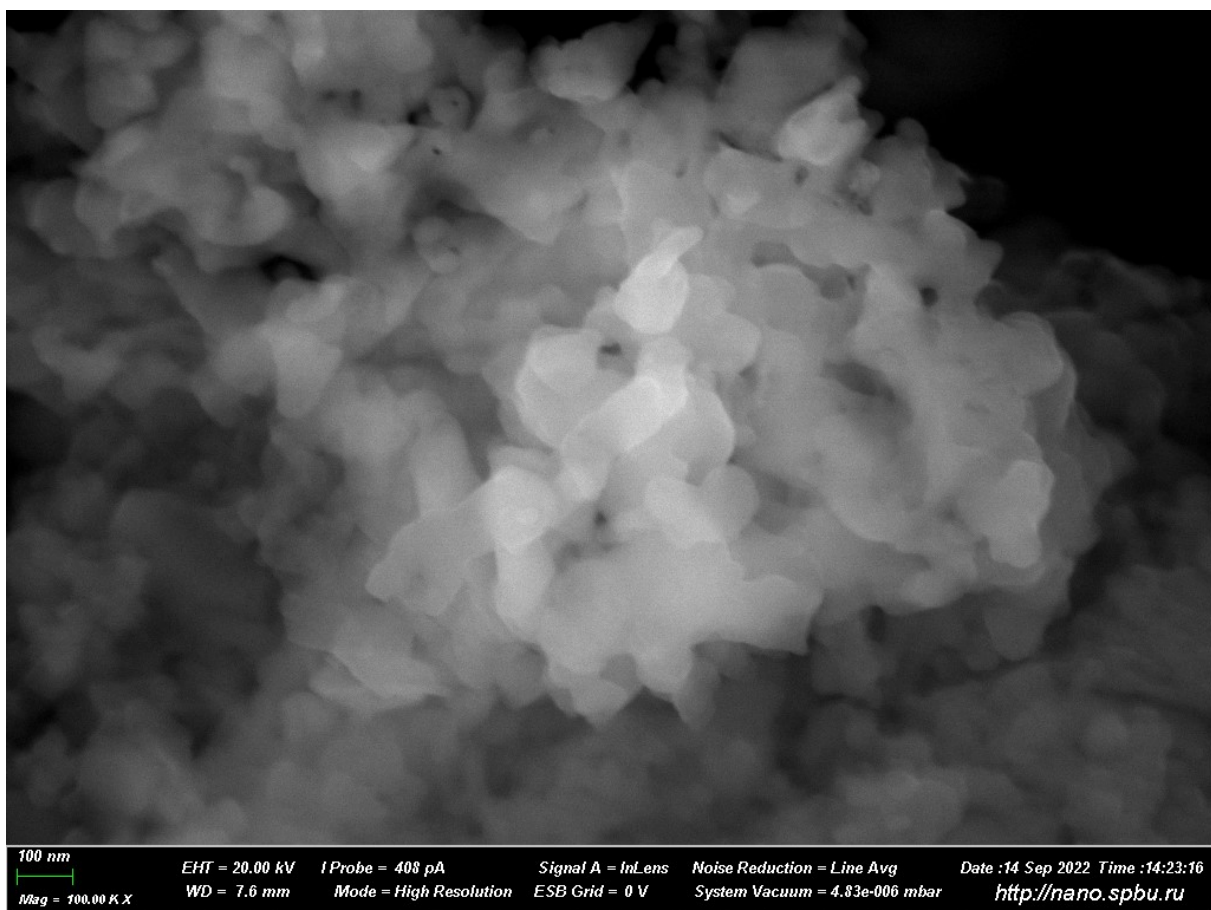


Figure S56. SEM image of the residue after the Ca + CCR1 reaction. Scale bar 100 nm

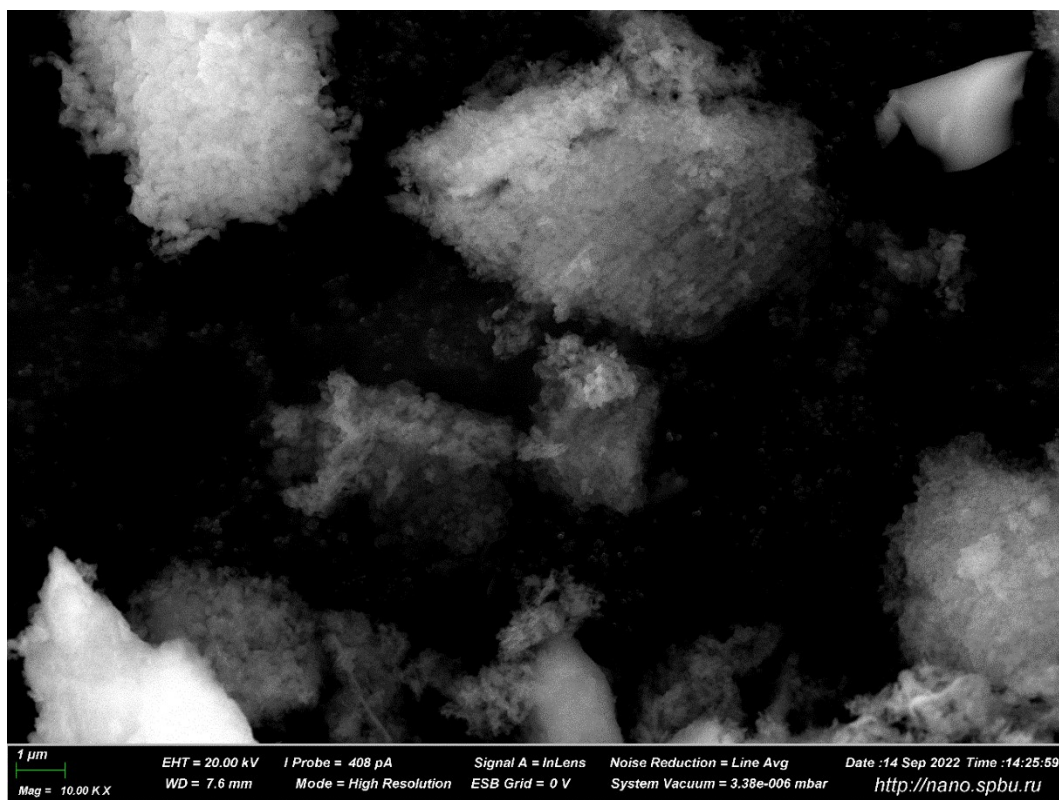


Figure S57. SEM image of the residue after the Ca + CCR1 reaction. Scale bar 1 μm

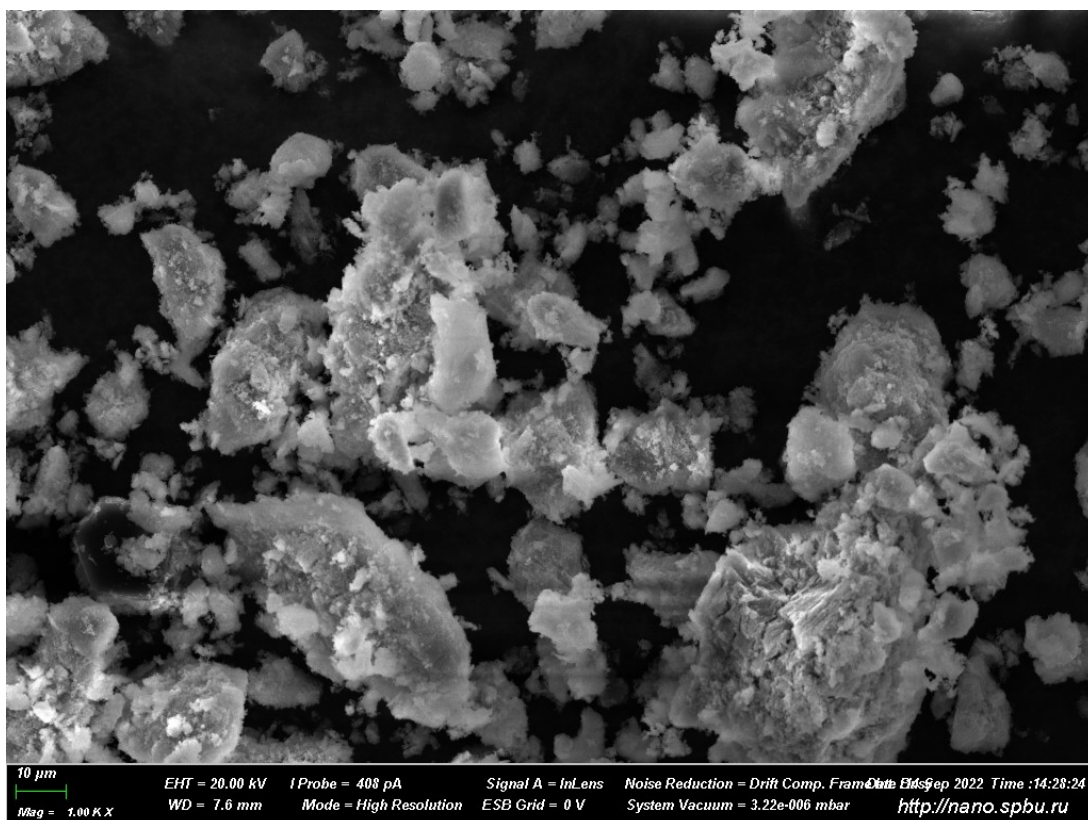


Figure S58. SEM image of the residue after the Ca + CCR1 reaction. Scale bar 10 μm

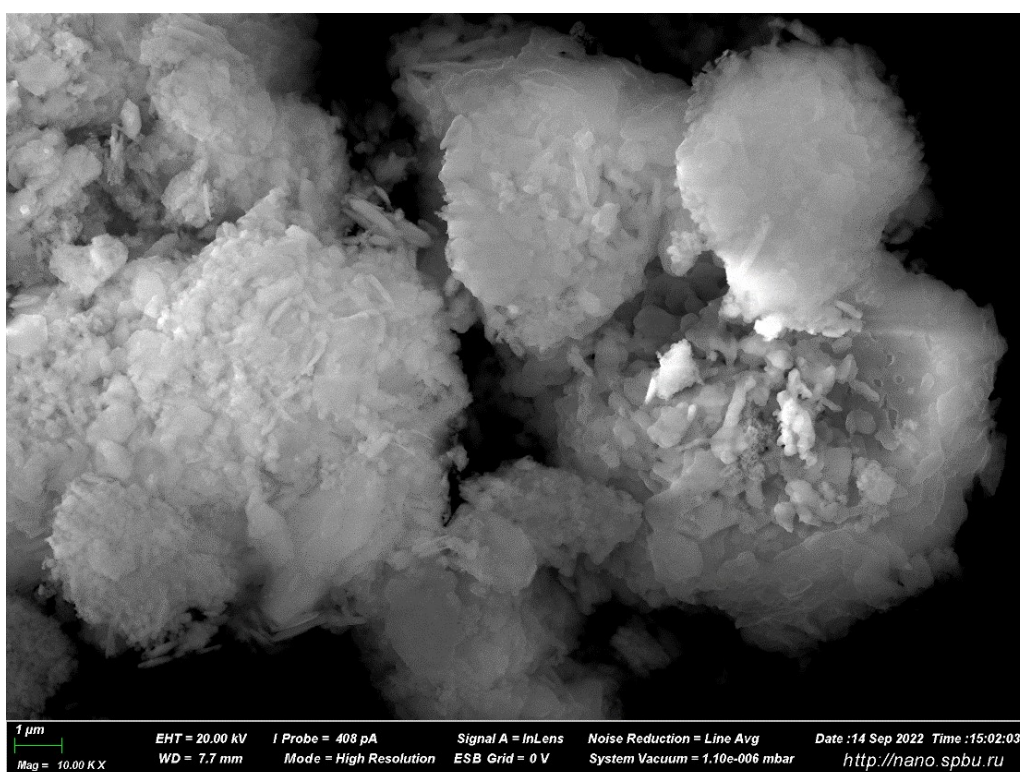


Figure S59. SEM image of the residue after the Ca + CCR2 reaction. Scale bar 1 μm

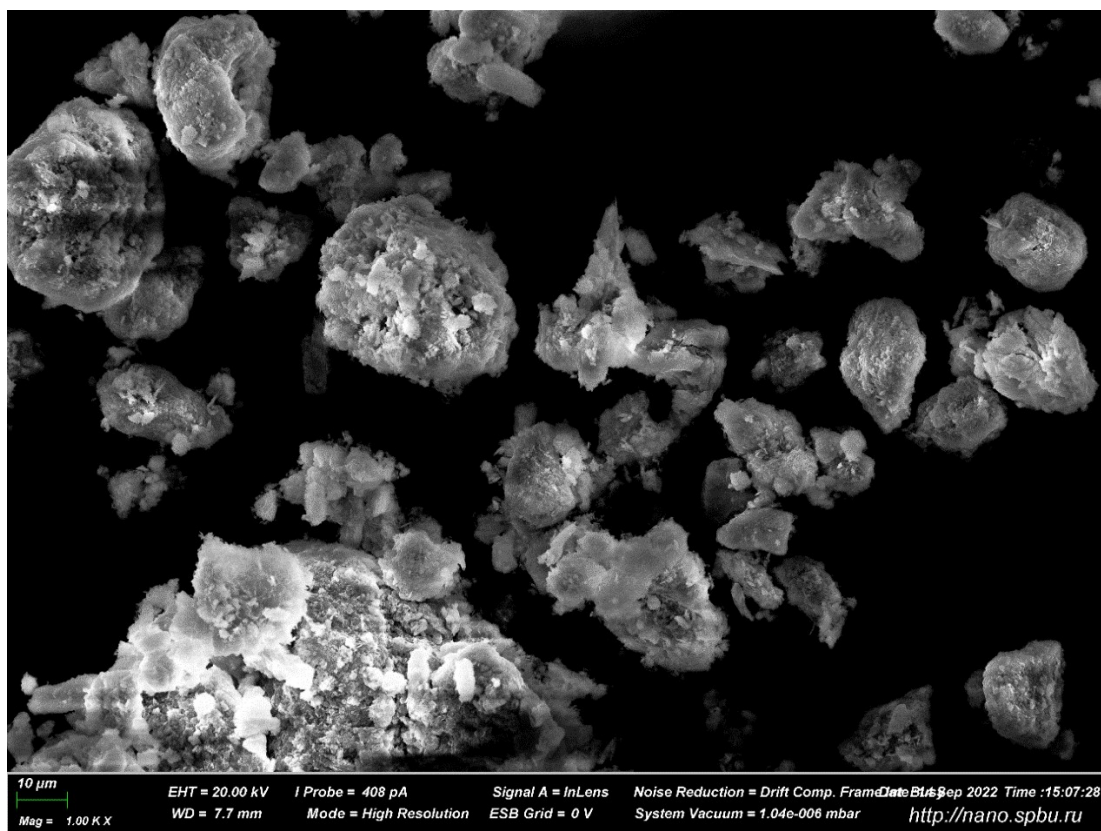


Figure S60. SEM image of the residue after the Ca + CCR₂ reaction. Scale bar 10 μm

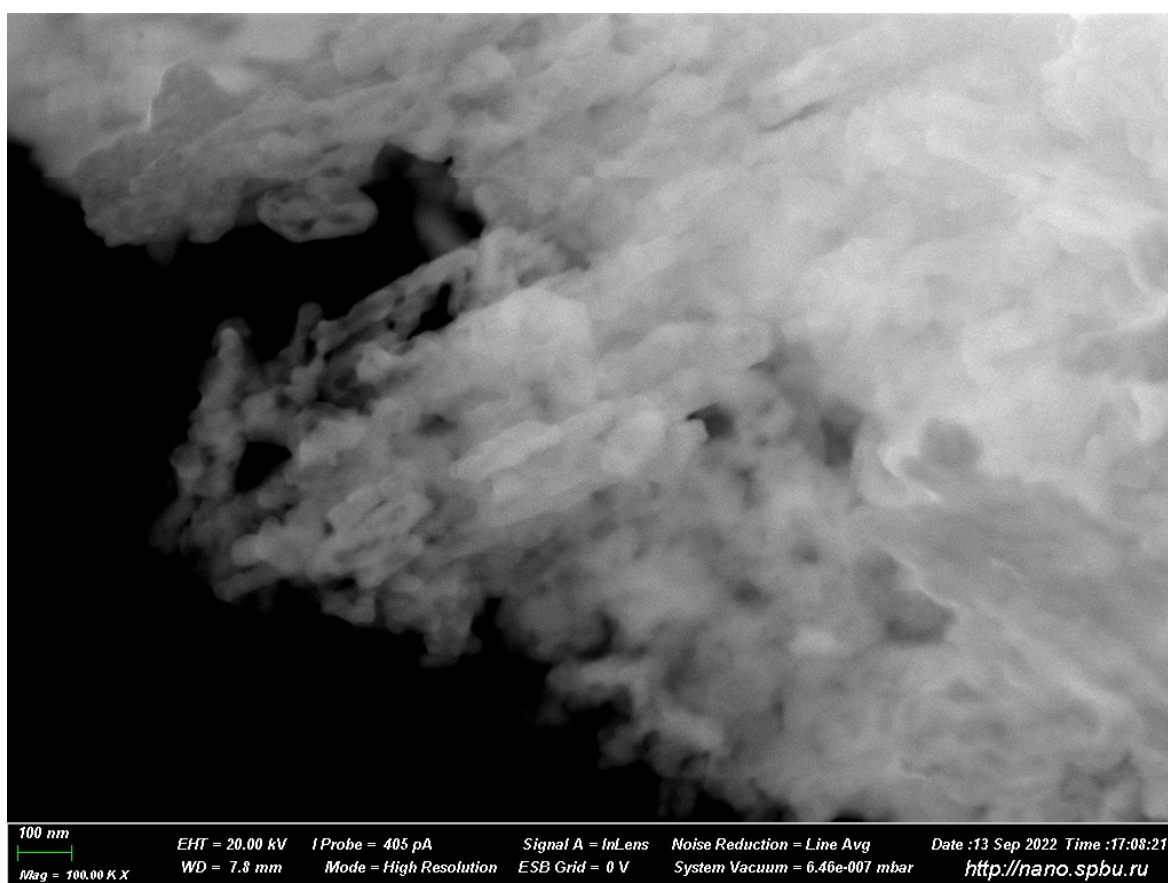


Figure S61. SEM image of the residue after the Ca + Ca(OD)₂ reaction. Scale bar 100 nm

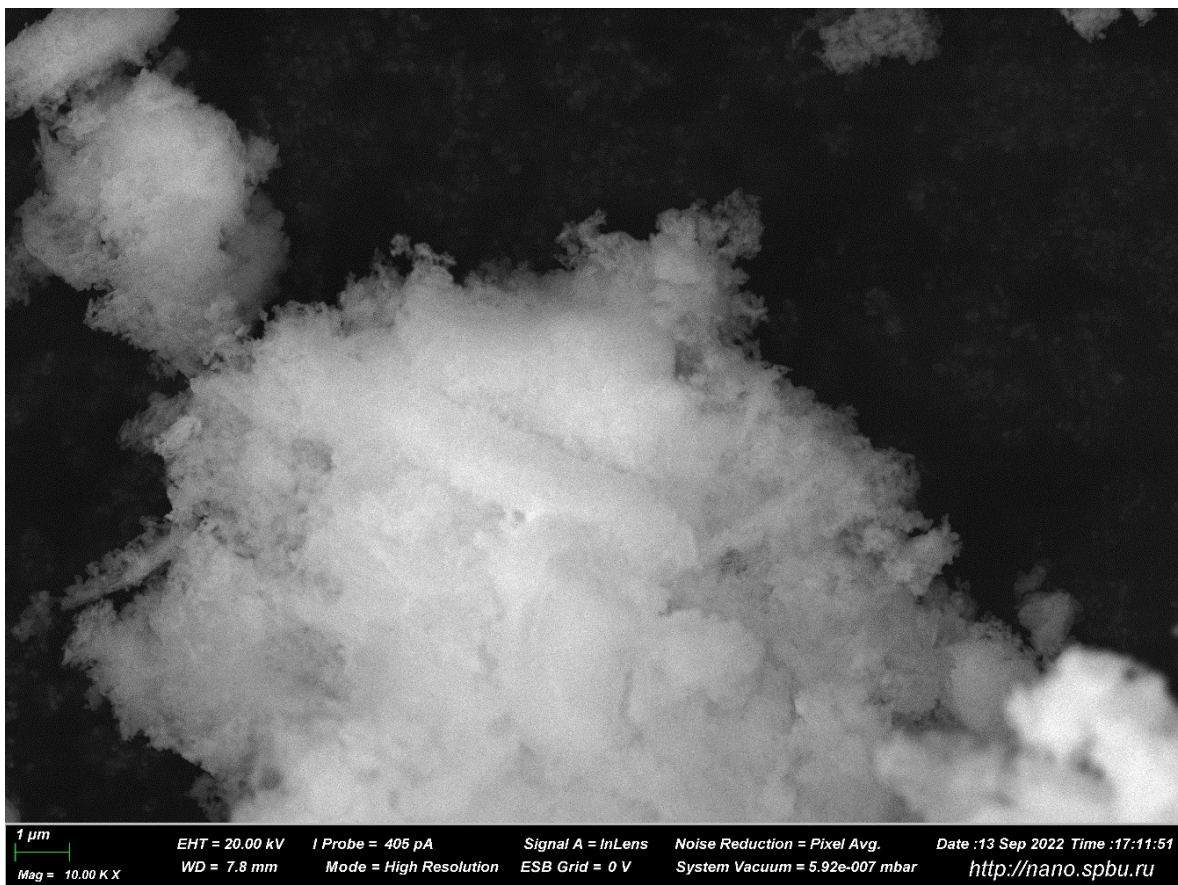


Figure S62. SEM image of the residue after the Ca + Ca(OD)₂ reaction. Scale bar 1 μm

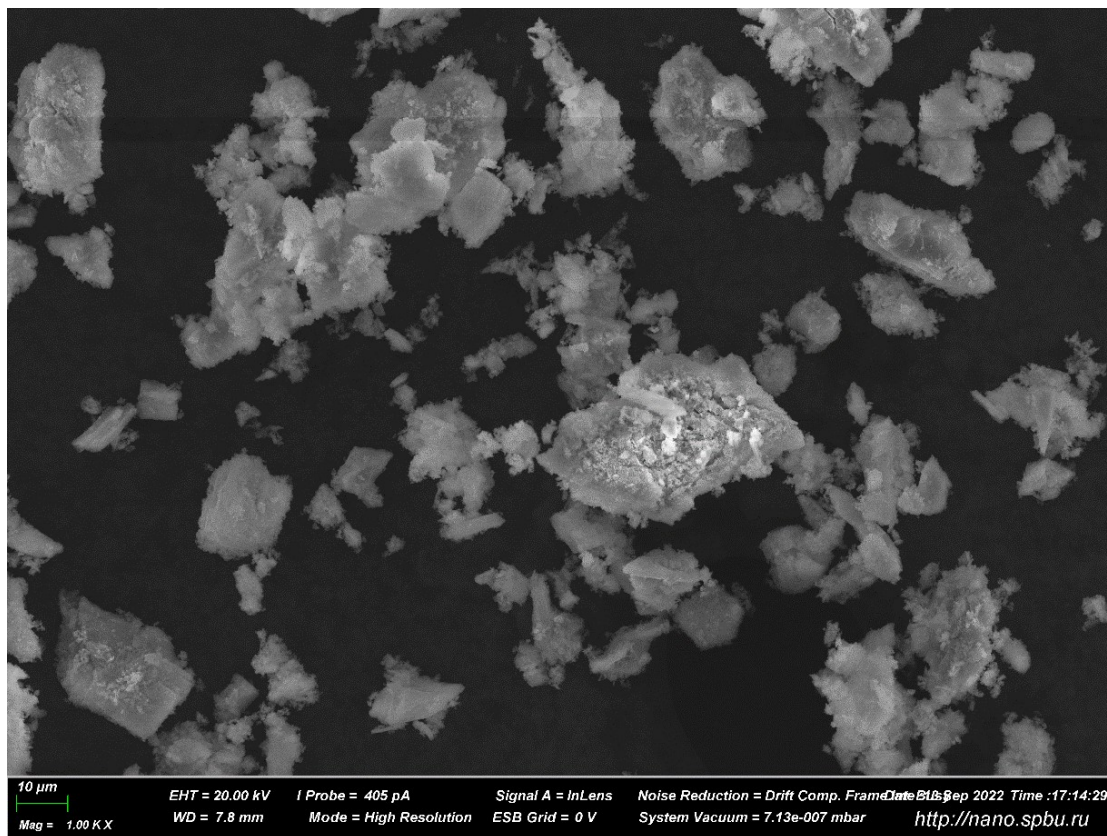
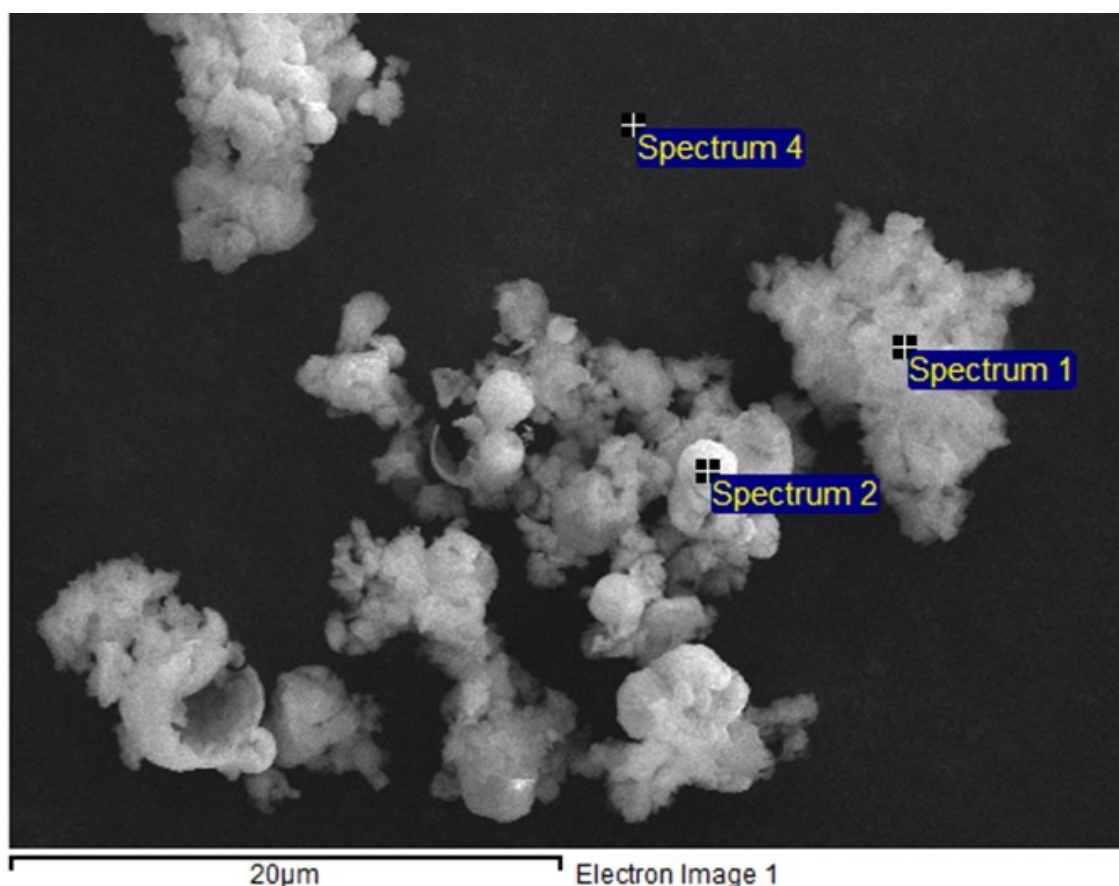


Figure S63. SEM image of the residue after the Ca + Ca(OD)₂ reaction. Scale bar 10 μm



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Ca	Zn
Spectrum 1	Yes	47.40	40.66	11.67	0.28
Spectrum 2	Yes	47.39	36.83	1.06	14.72
Sum Spectrum	Yes	84.15	13.06	1.60	1.20
Spectrum 4	Yes	91.68	8.26	0.06	
Max.		91.68	40.66	11.67	14.72
Min.		47.39	8.26	0.06	0.28

All results in atomic%

Figure S64. SEM image of the residue after the Zn + Ca(OH)₂ reaction (scale bar 20 μm) with the determination of the elemental composition in selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account

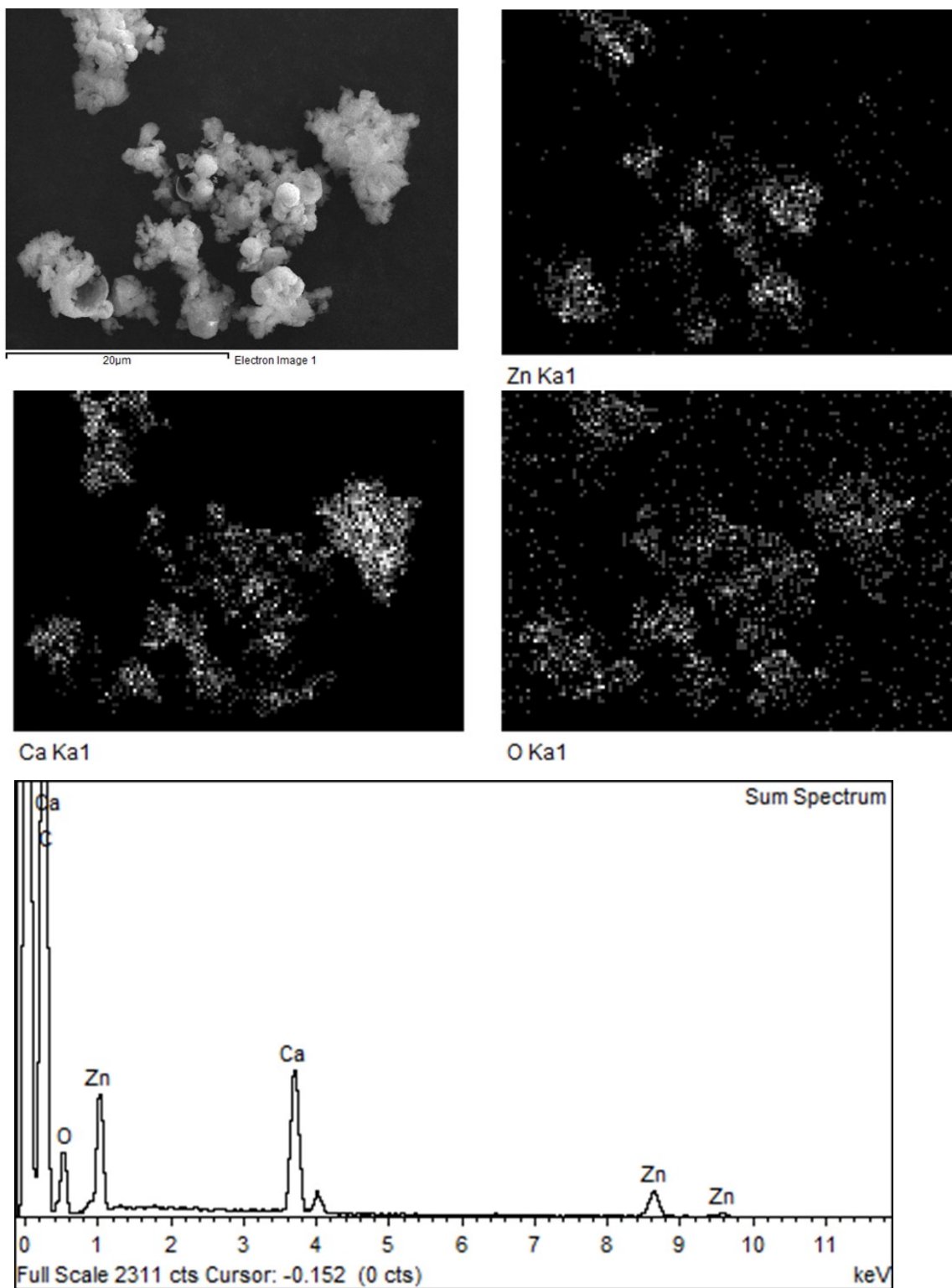
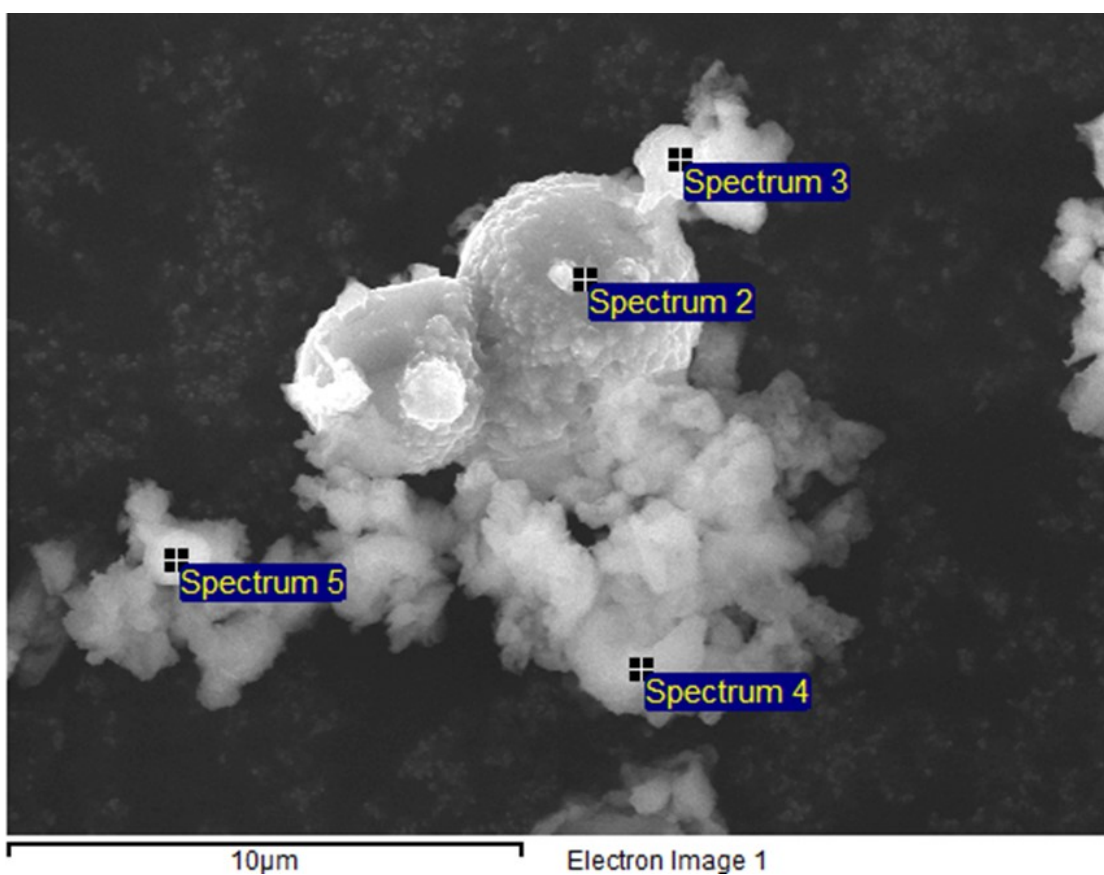


Figure S65. EDX mapping (with spectrum below) of the residue after the Zn + Ca(OH)₂ reaction. Scale bar 20 μm



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	Ca	Fe	Zn
Sum Spectrum	Yes	69.98	12.10	17.45	0.46
Spectrum 2	Yes	17.21	3.02	79.77	
Spectrum 3	Yes	39.88	8.02	52.10	
Spectrum 4	Yes	73.40	24.96	1.64	
Spectrum 5	Yes	82.18	16.16	1.67	
Max.		82.18	24.96	79.77	0.46
Min.		17.21	3.02	1.64	0.46

All results in atomic %

Figure S66. SEM image of the residue after the Fe + Ca(OH)₂ reaction (scale bar 10 μm) with the determination of the elemental composition in selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account

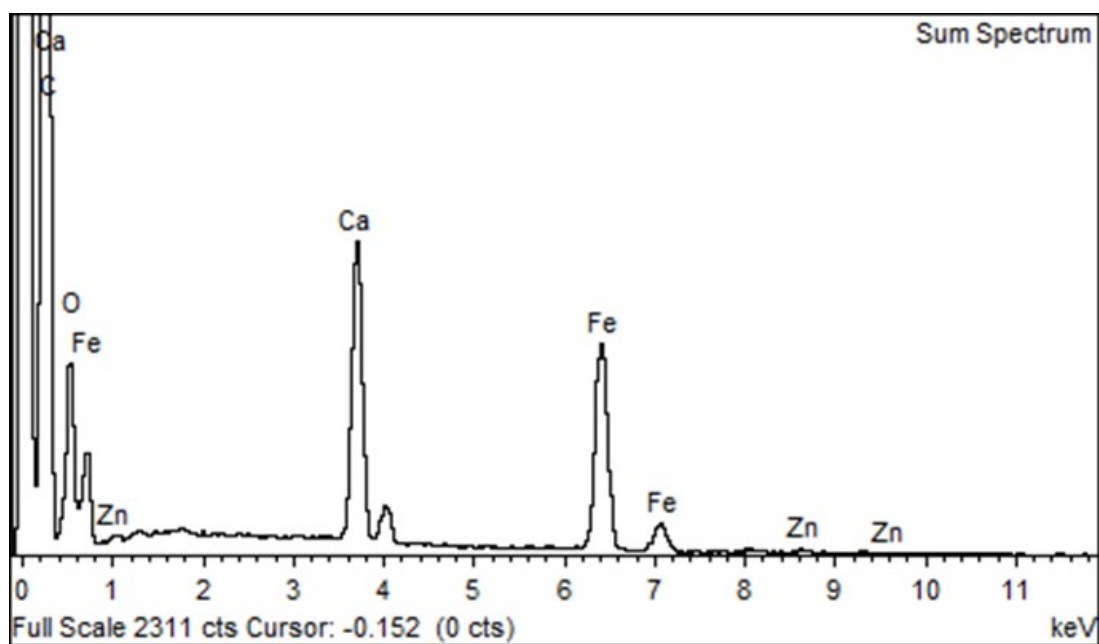
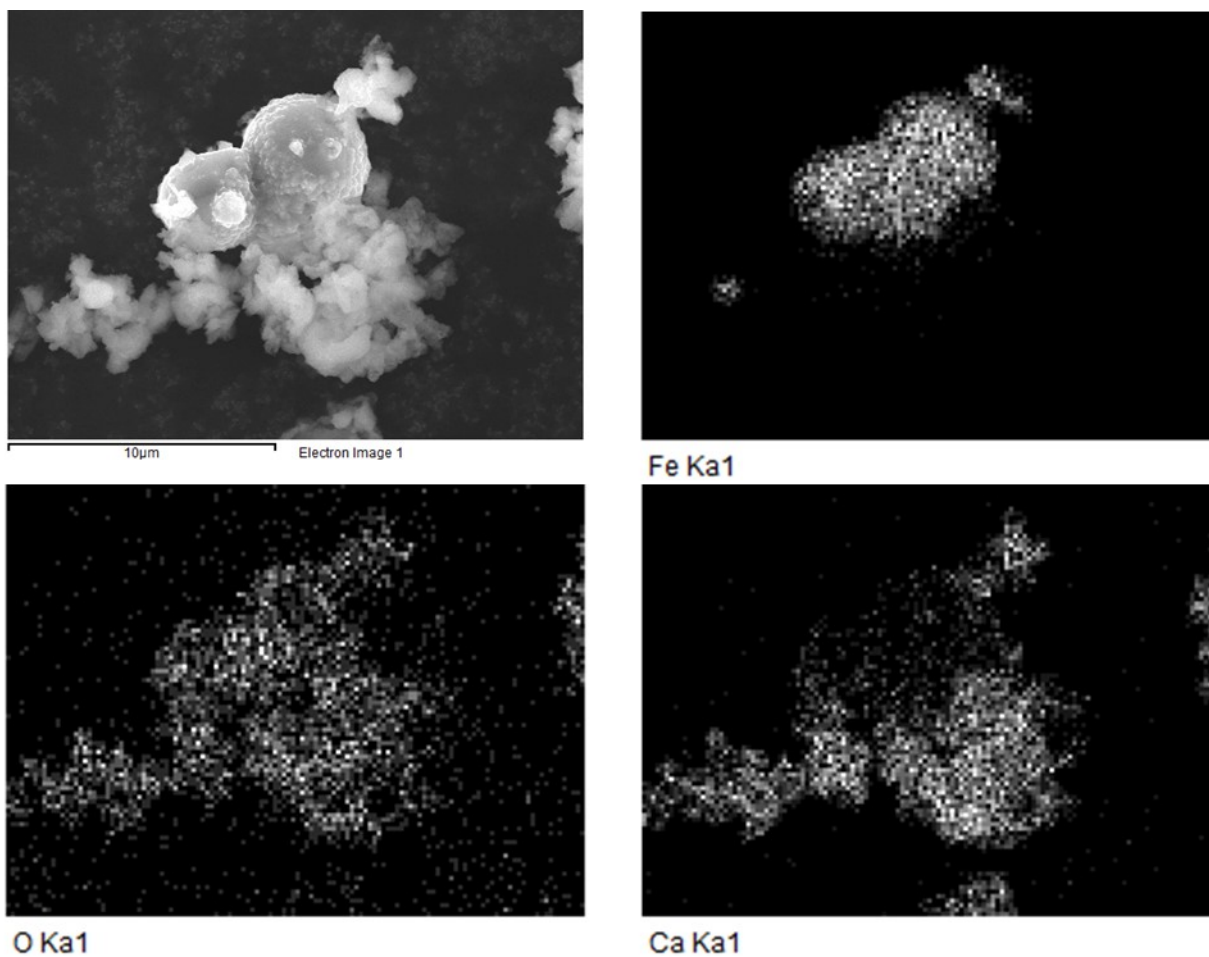
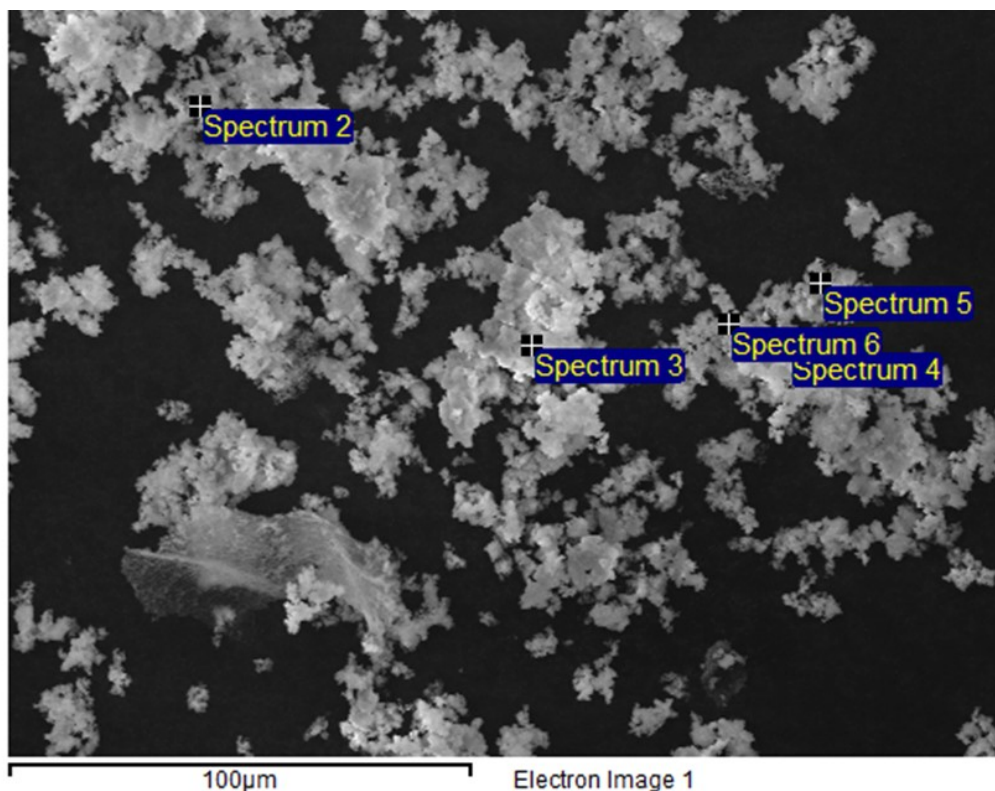


Figure S67. EDX mapping (with spectrum below) of the residue after the Fe + $\text{Ca}(\text{OH})_2$ reaction. Scale bar 10 μm

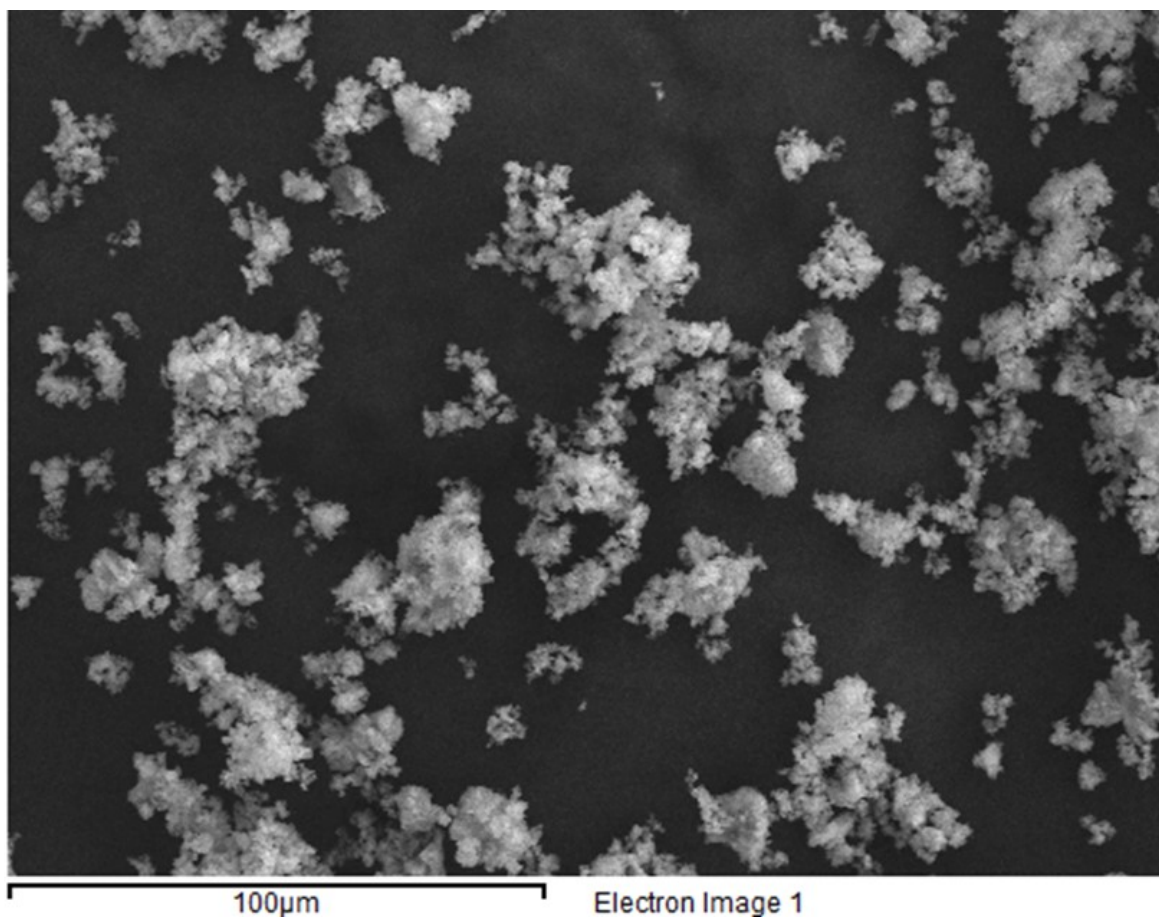


Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	Mg	Ca
Sum Spectrum	Yes	72.10	16.79	11.12
Spectrum 2	Yes	64.89	14.16	20.95
Spectrum 3	Yes	66.00	24.76	9.23
Spectrum 4	Yes	69.67	17.84	12.49
Spectrum 5	Yes	66.95	22.25	10.81
Spectrum 6	Yes	72.57	12.89	14.54
Mean		68.70	18.11	13.19
Std. deviation		3.23	4.60	4.20
Max.		72.57	24.76	20.95
Min.		64.89	12.89	9.23

All results in atomic%

Figure S68. SEM image of the residue after the Mg + Ca(OH)₂ reaction (scale bar 100 μm) with the determination of the elemental composition in selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Mg	Ca
Sum Spectrum	Yes	66.93	28.71	0.06	4.30
Mean		66.93	28.71	0.06	4.30
Std. deviation		0.00	0.00	0.00	0.00
Max.		66.93	28.71	0.06	4.30
Min.		66.93	28.71	0.06	4.30

All results in atomic%

Figure S69. SEM image of the residue after the $\text{Ca} + \text{Ca(OH)}_2$ reaction (scale bar 100 μm) with the determination of the elemental composition in selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account

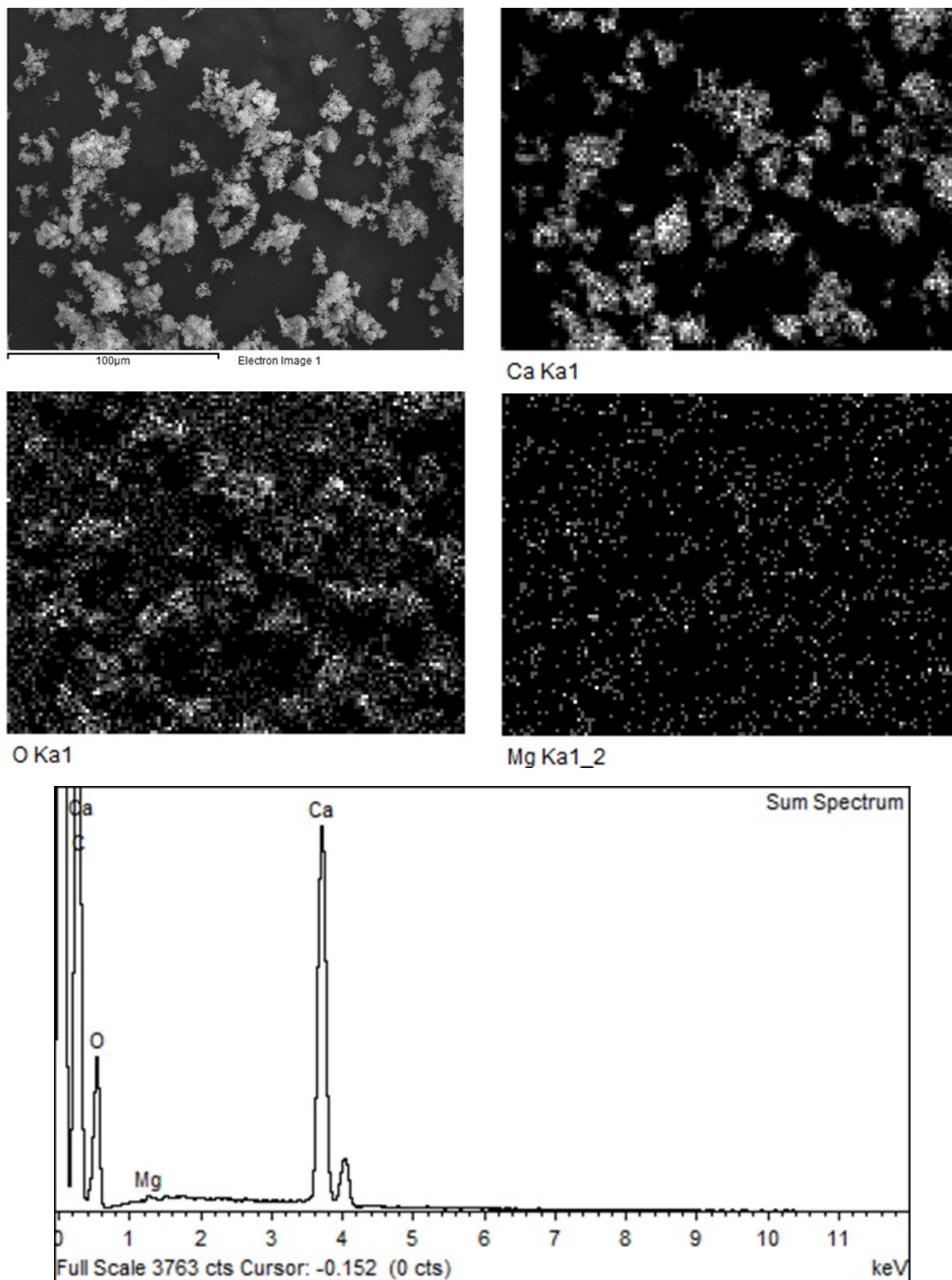
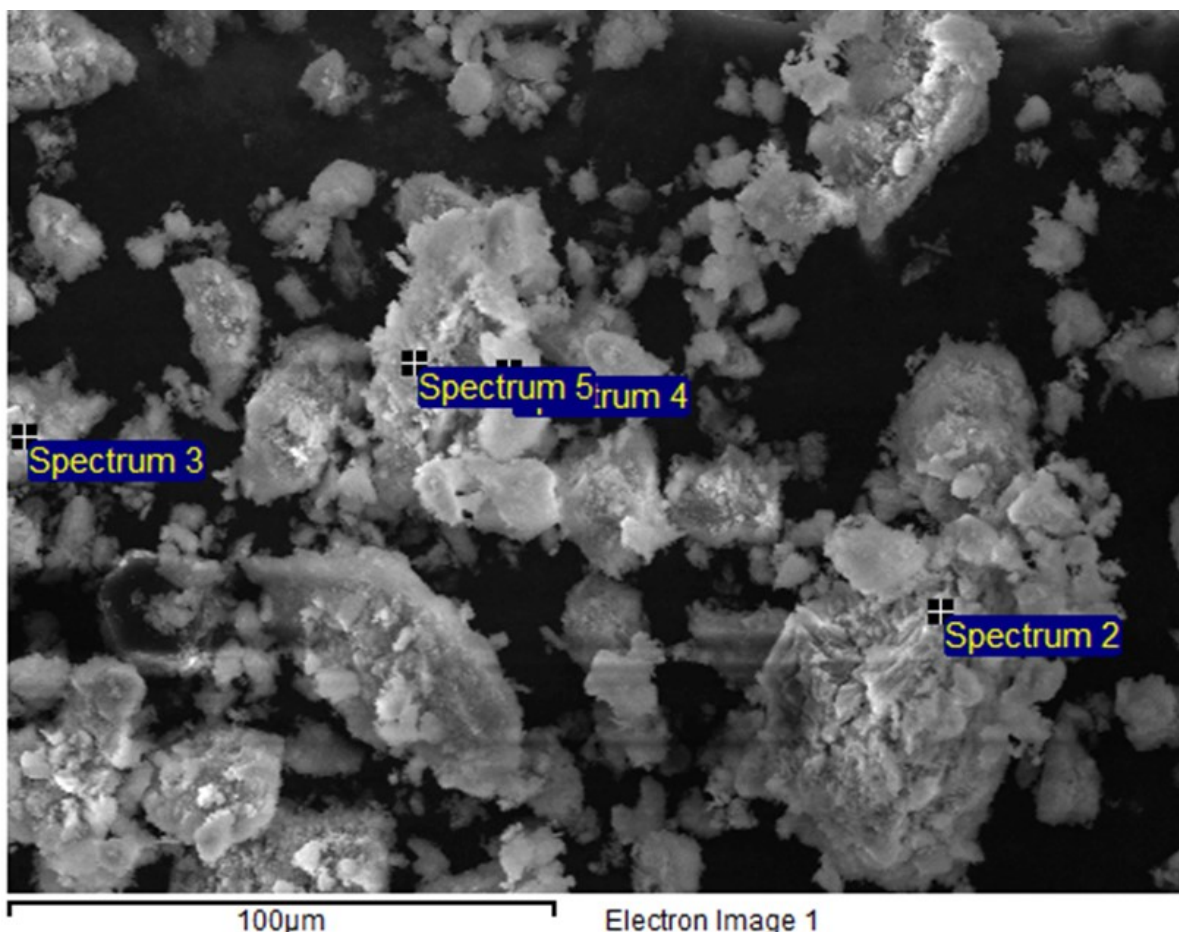


Figure S70. EDX mapping (with spectrum below) of the residue after the Ca + Ca(OH)₂ reaction. Scale bar 100 μm

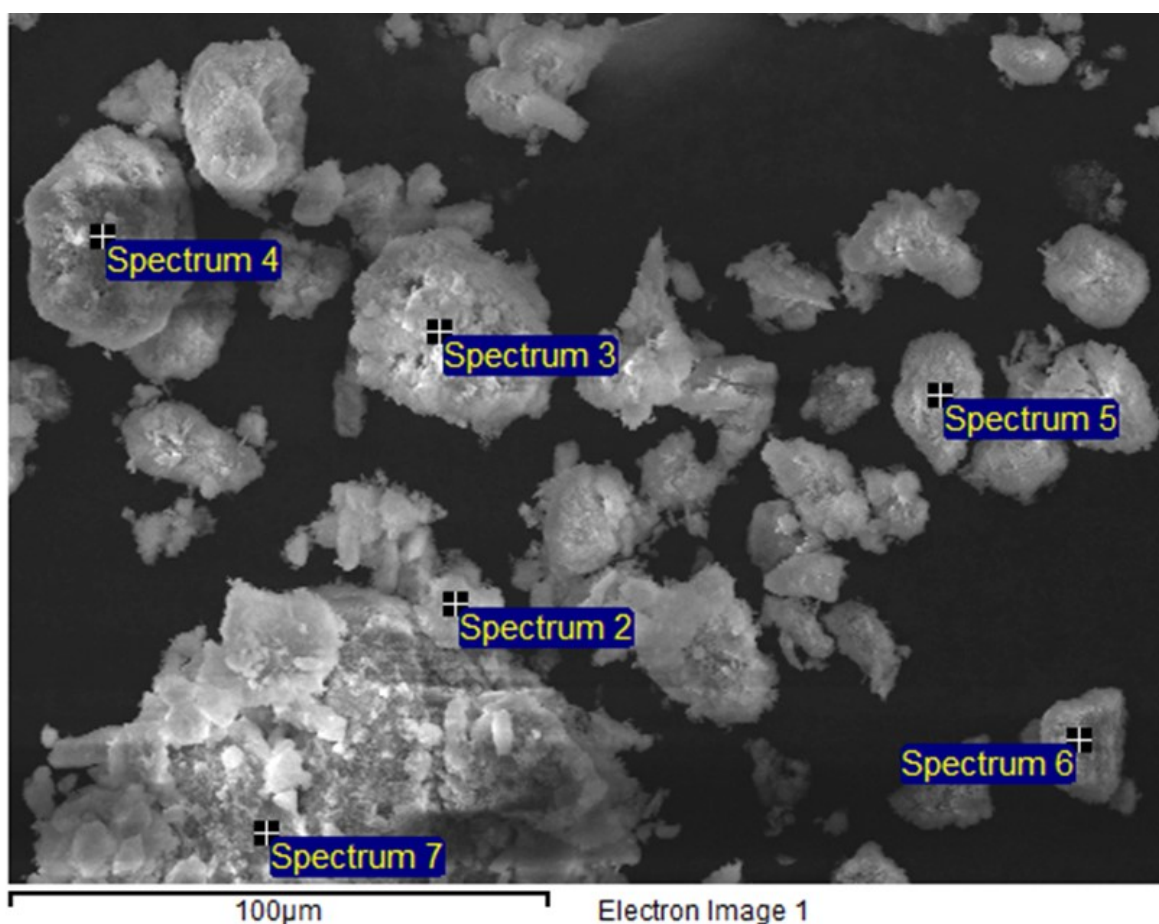


Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	Al	Si	S	Ca
Sum Spectrum	Yes	81.12	0.21	0.15	0.31	18.22
Spectrum 2	Yes	75.46			1.49	23.05
Spectrum 3	Yes	76.27	3.41	1.06	0.69	18.57
Spectrum 4	Yes	75.19				24.81
Spectrum 5	Yes	57.34				42.66
Max.		81.12	3.41	1.06	1.49	42.66
Min.		57.34	0.21	0.15	0.31	18.22

All results in atomic%

Figure S71. SEM image of the residue after the Ca + CCR1 reaction (scale bar 100 μm) with the determination of the elemental composition in the selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	F	Si	K	Ca
Sum Spectrum	Yes	61.08	16.29	0.27	0.51	21.85
Spectrum 2	Yes	28.10	49.90	1.18	1.21	19.61
Spectrum 3	Yes	49.87	29.83	0.40	0.82	19.08
Spectrum 4	Yes	65.52	15.36	0.46	0.42	18.24
Spectrum 5	Yes					100.00
Spectrum 6	Yes	75.17				24.83
Spectrum 7	Yes	63.52	11.39		0.68	24.41
Max.		75.17	49.90	1.18	1.21	100.00
Min.		28.10	11.39	0.27	0.42	18.24

All results in atomic%

Figure S72. SEM image of the residue after the Ca + CCR2 reaction (scale bar 100 µm) with the determination of the elemental composition in selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account

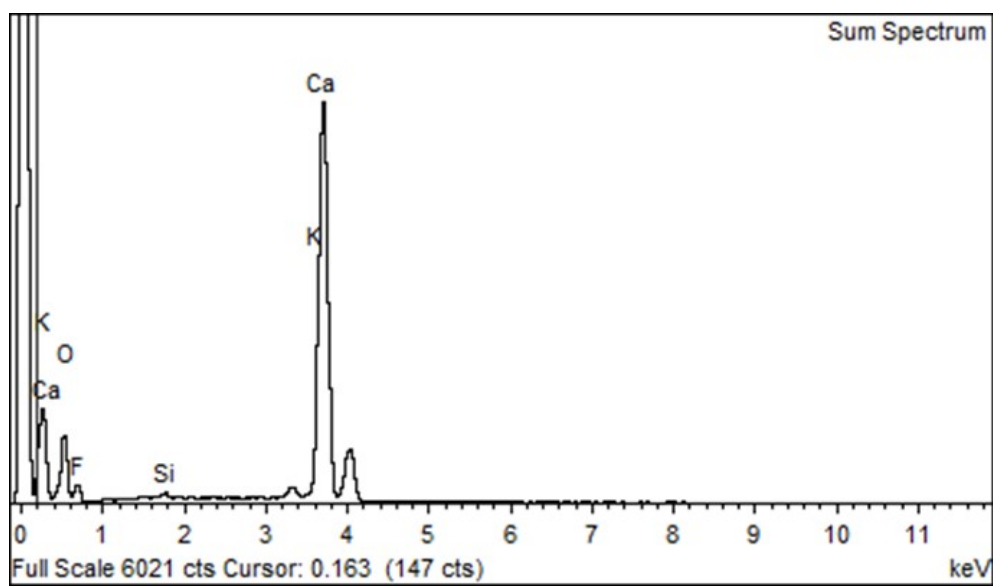
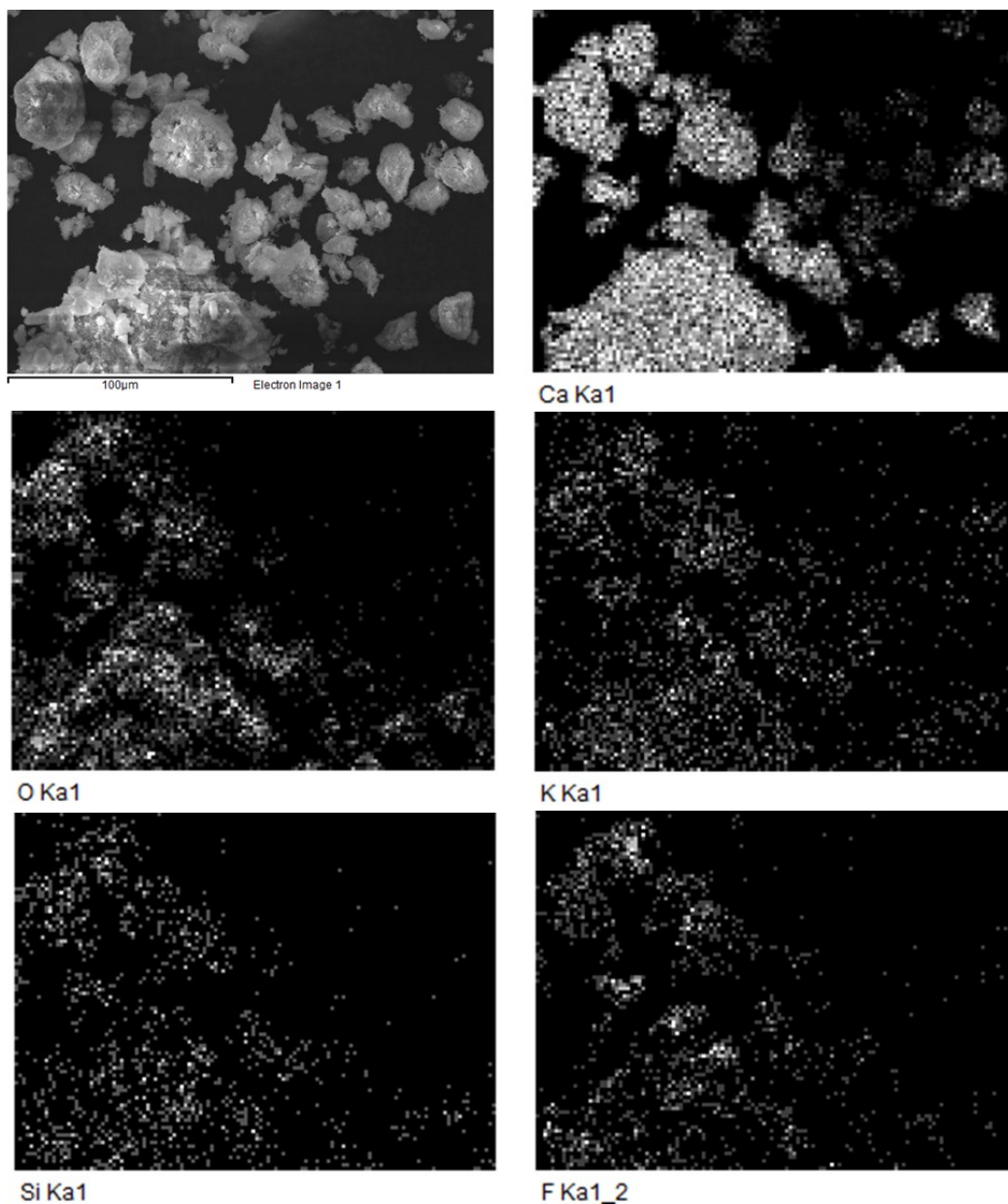
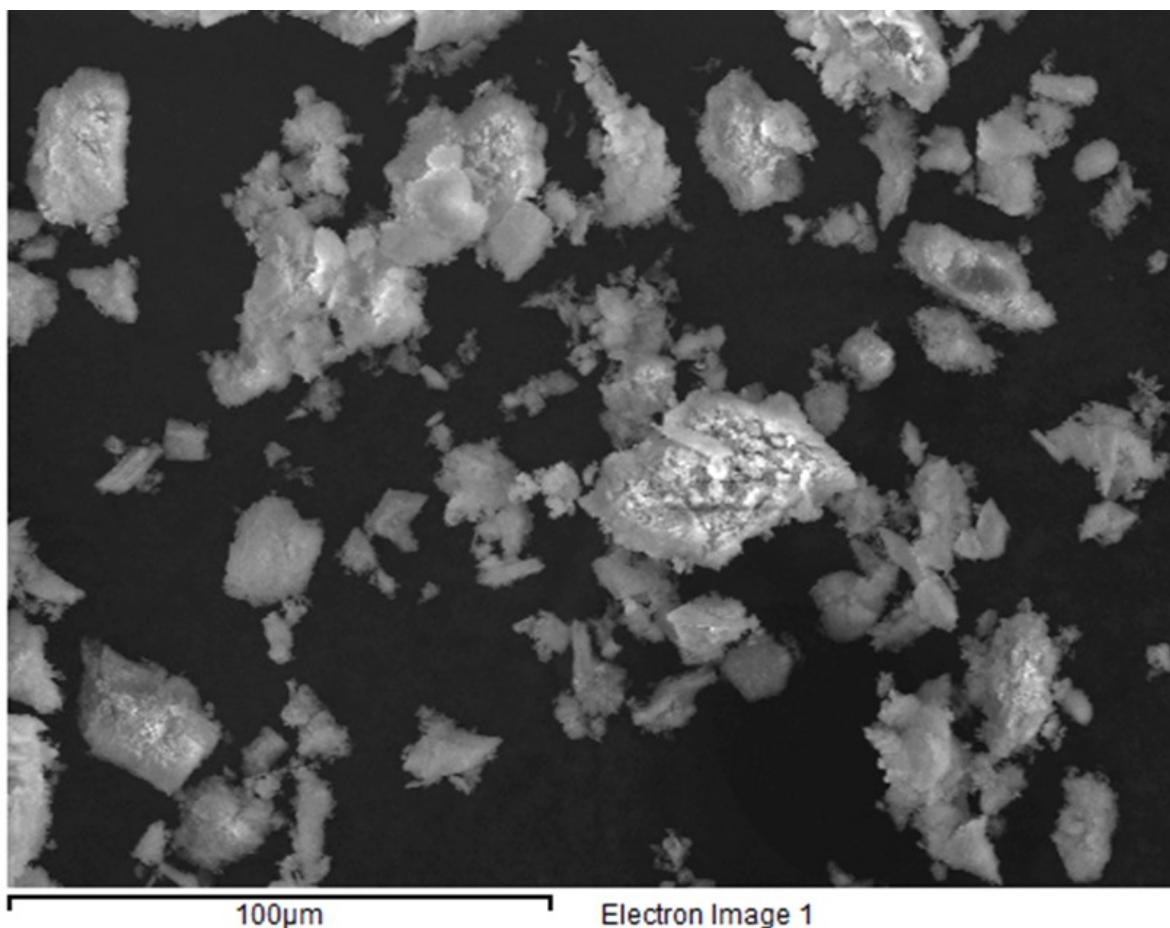


Figure S73. EDX mapping (with spectrum below) of the residue after the Ca + CCR2 reaction. Scale bar 100 µm



Processing option : All elements analysed (Normalised)

Spectrum	In stats	O	Al	Si	S	Ca
Sum Spectrum	Yes	80.19	0.10	0.15	0.29	19.27
Mean		80.19	0.10	0.15	0.29	19.27
Std. deviation		0.00	0.00	0.00	0.00	0.00
Max.		80.19	0.10	0.15	0.29	19.27
Min.		80.19	0.10	0.15	0.29	19.27

All results in atomic%

Figure S74. SEM image of the residue after the $\text{Ca} + \text{Ca}(\text{OD})_2$ reaction (scale bar 100 μm) with the determination of the elemental composition in selected areas. The surface on which was carried out contained C and O, so their value in the table was not taken into account

S7. Powder XRD of residues after hydrogen evolution

Table S5. Quantitative phase analysis of samples (wt. %) according to full-profile analysis by the Rietveld method.

Residue after reaction	Zn + Ca(OH) ₂	Fe + Ca(OH) ₂	Mg + Ca(OH) ₂	Ca + Ca(OH) ₂	Ca + CCR1	Ca + CCR2	Ca + CCR1-d ₂
Portlandite – Ca(OH) ₂	50.0	71.0	59.3	91.7	88.8	77.2	74.0
Calcite – CaCO ₃	-	10.1	-	3.7	3.9	5.8	3.1
Graphite – C	-	-	-	-	7.3	2.9	4.5
Calcium carbide – CaC ₂	-	-	-	-	-	2.7	3.4
Aragonite – CaCO ₃	-	-	-	-	-	<1	2.4
Fluorite – CaF ₂	-	-	-	-	-	10.5	-
CaO	-	-	3.2	4.6	-	-	12.6
ZnO	36.7	-	-	-	-	-	-
Zn	13.3	-	-	-	-	-	-
FeO	-	4.4	-	-	-	-	-
αFe	-	14.5	-	-	-	-	-
MgO	-	-	37.5	-	-	-	-
Rp (%)*	7.0	2.5	8.1	9.3	8.2	7.8	8.7

(*) $R_p = \frac{\sum |y_i^{obs} - y_i^{calc}|}{\sum y_i^{obs}}$ - is the factor of convergence of the calculated and experimental X-ray profiles, y_i is the intensity at each experimental point of the X-ray diffraction pattern.

Considering the decomposition of calcium hydroxide to CaO at the reaction temperature, it certainly cannot be in the final mixture. This means that the calcium hydroxide that is shown in powder XRD is formed either as a result of cooling the mixture in an argon flow (wet argon) or during sample preparation. Therefore, the entire amount of calcium hydroxide indicated in the original table was converted to mole percent and was taken into account as calcium oxide. Then the following table of the mixture composition after hydrogen evolution is obtained:

Table S6. The composition of residues after hydrogen evolution (mol. %).

	Zn + Ca(OH) ₂	Fe + Ca(OH) ₂	Mg + Ca(OH) ₂	Ca + Ca(OH) ₂	Ca + CCR1	Ca + CCR2	Ca + CCR1-d ₂
CaO	49.0	71.1	75.1	95.0	93.2	78.0	88.3
MeO	39.6	4.3	24.9	-	-	-	-
Me	11.4	11.0	-	-	-	-	-
CaF ₂	-	-	-	-	-	11.2	-
CaCO ₃	-	13.7	-	5.0	5.5	7.9	7.9
C	-	-	-	-	1.2	0.5	0.8
CaC ₂	-	-	-	-	-	2.4	3.1

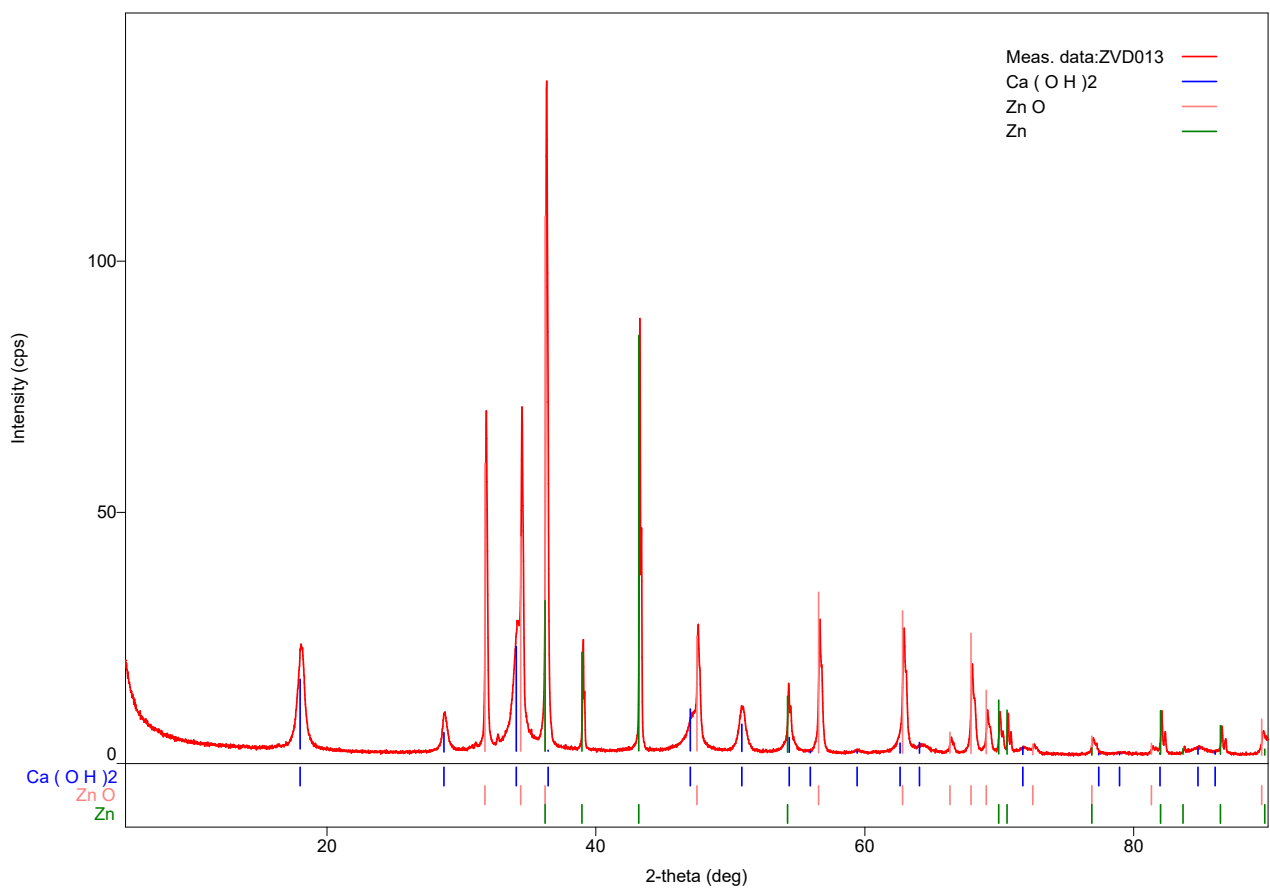


Figure S75. X-ray pattern of the residue after the Zn + Ca(OH)₂ reaction

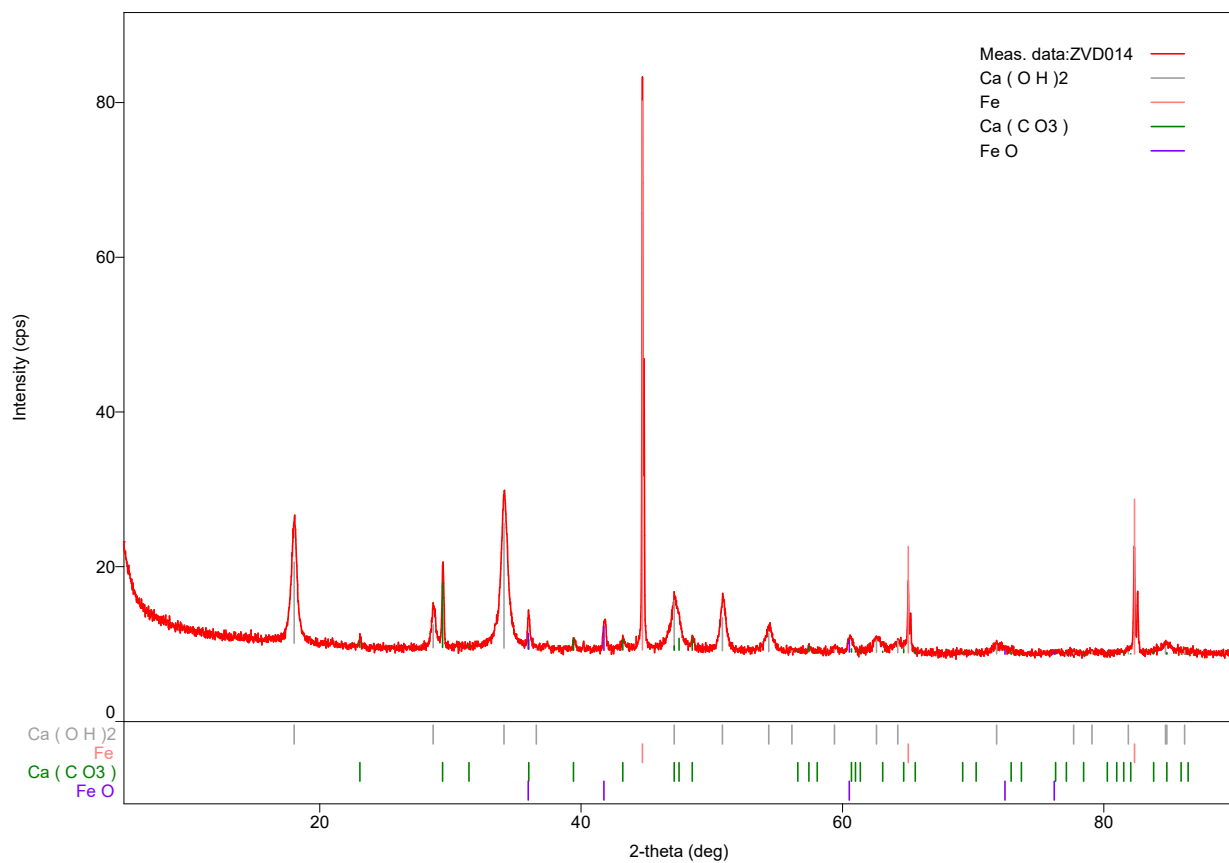


Figure S76. X-ray pattern of the residue after the Fe + Ca(OH)₂ reaction

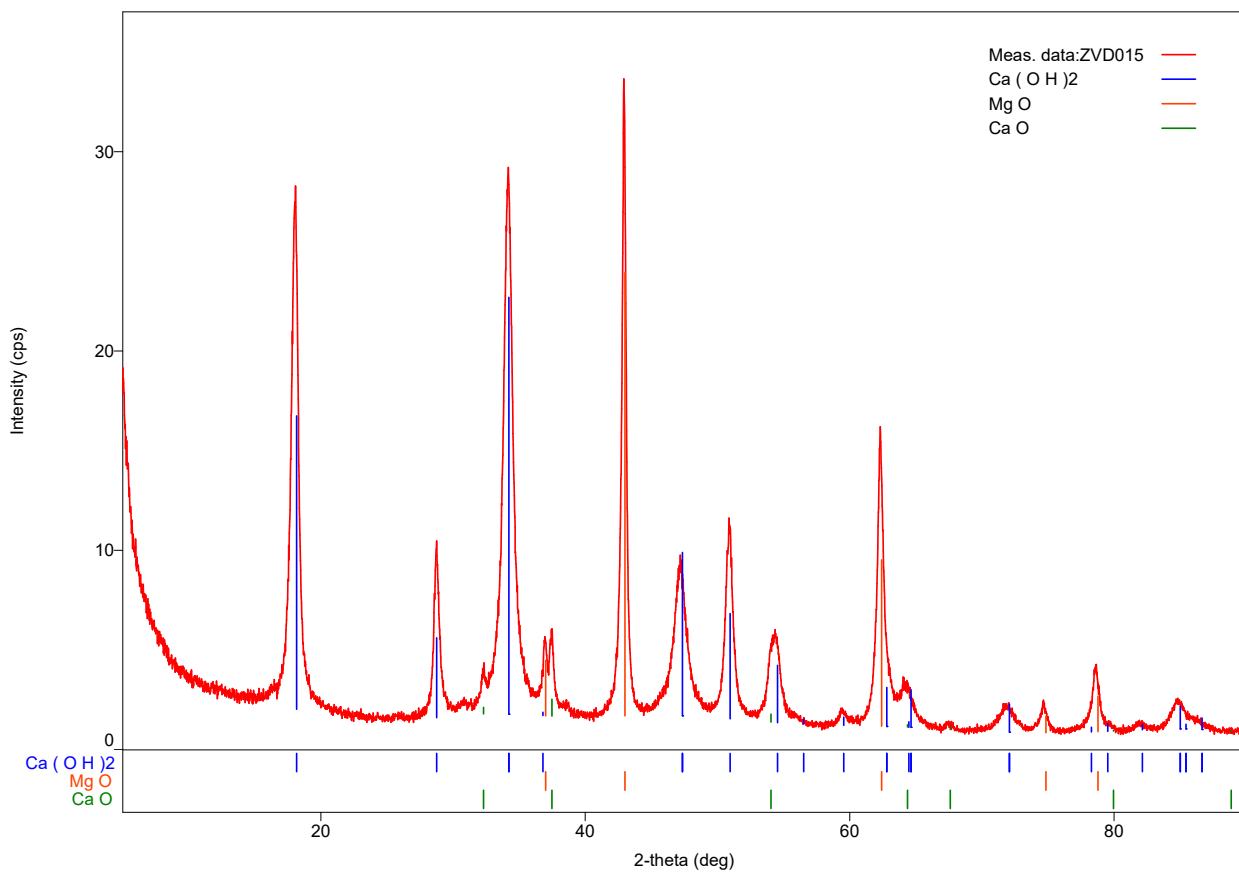


Figure S77. X-ray pattern of the residue after the Mg + Ca(OH)₂ reaction

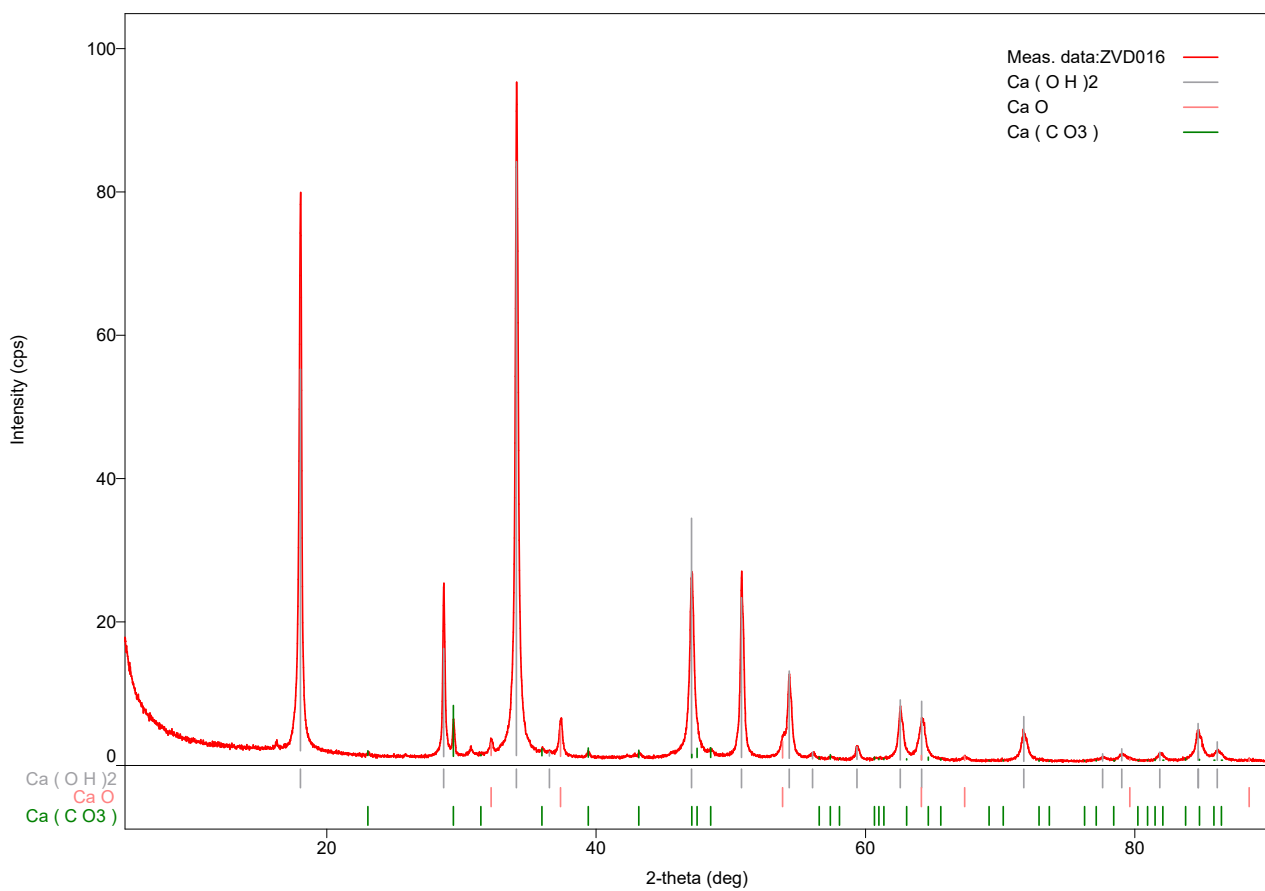


Figure S78. X-ray pattern of the residue after the Ca + Ca(OH)₂ reaction

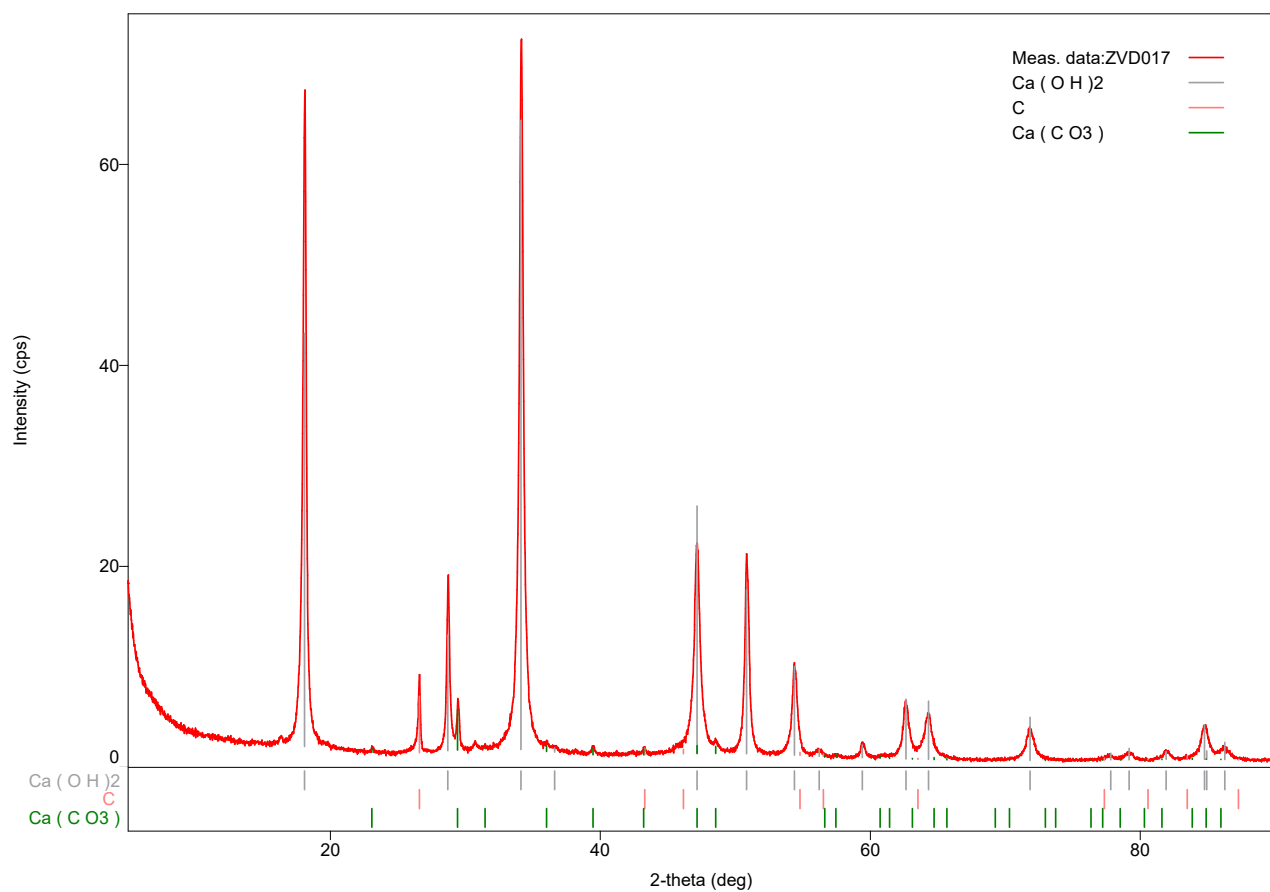


Figure S79. X-ray pattern of the residue after the Ca + CCR1 reaction

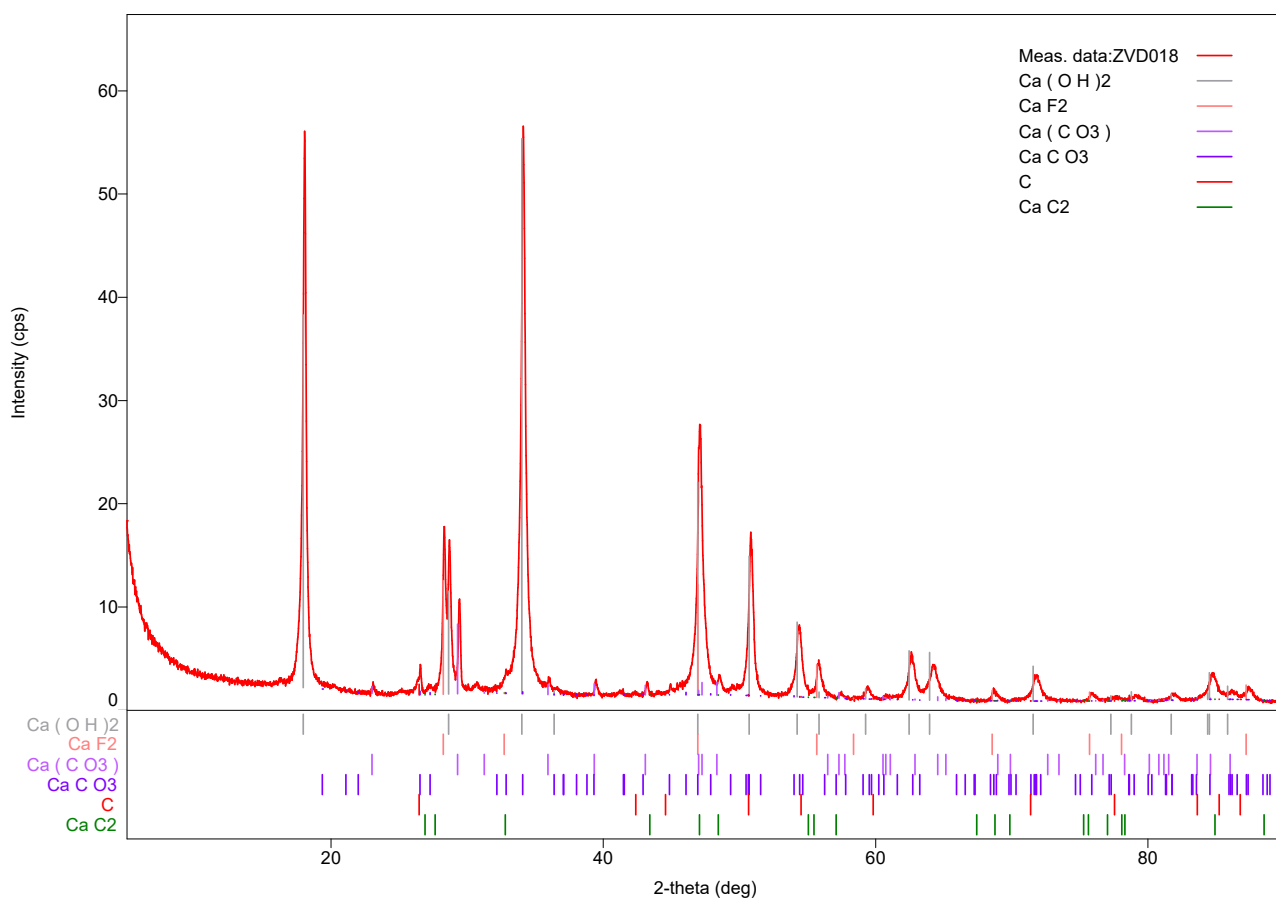


Figure S80. X-ray pattern of the residue after the Ca + CCR2 reaction

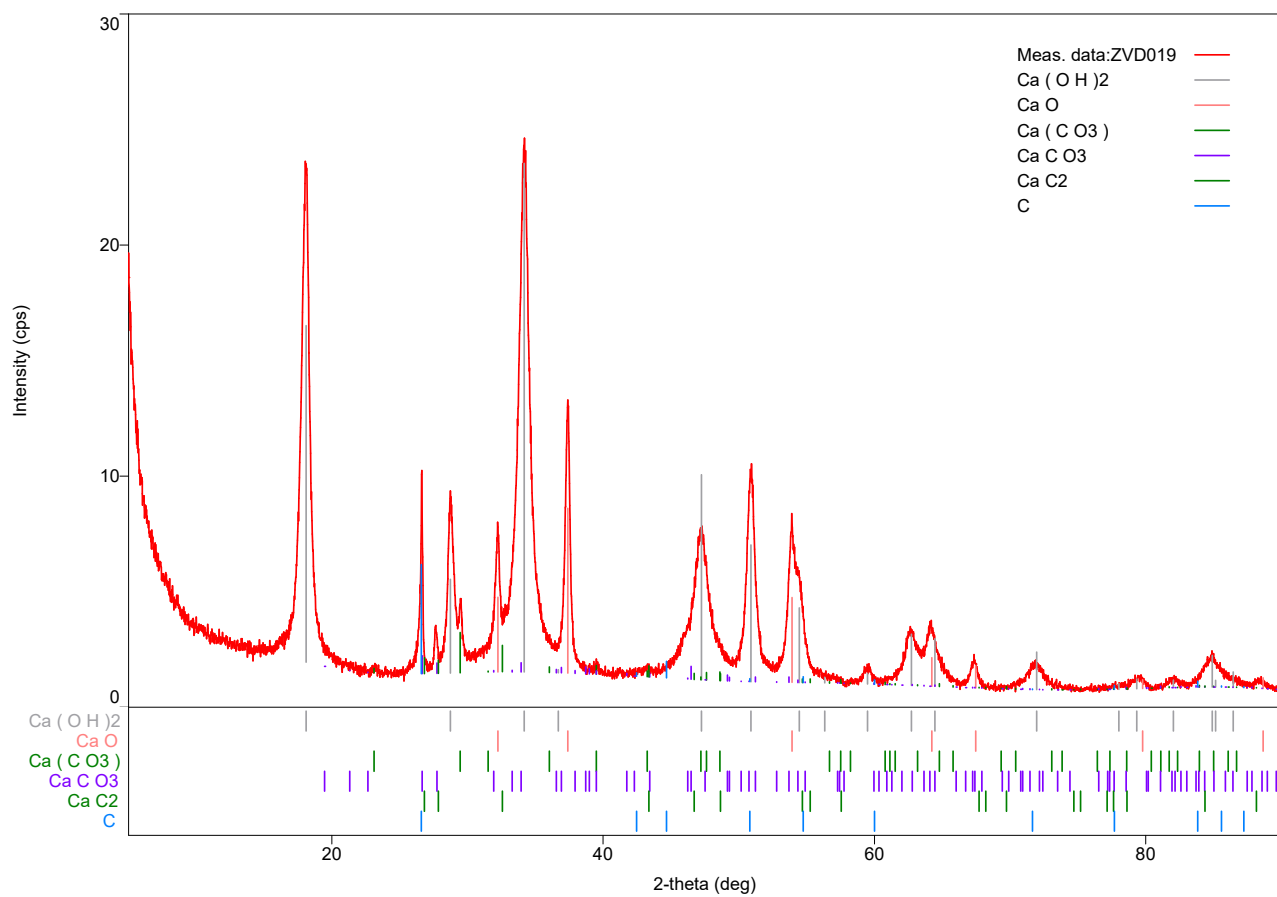


Figure S81. X-ray pattern of the residue after the Ca + CCR1-*d*₂ reaction

S8. References

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