*Supplementary information for:*

# Studying the significance of the parameters involved in the synthesis of Y-UiO-66 to improve product yield

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*Rare-earth, MOFs, RE-MOFs, Yttrium, Design of experiments*

## Materials

All solvents and reagents were purchased from commercial sources. N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), acetone, and nitric acid (70%) were purchased from Fisher Scientific (Fisher Chemical). $Y(NO_3)_3{\cdot}xH_2O$ and $Tb(NO_3)_3{\cdot}xH_2O$ were purchased from Thermo Scientific, $Ho(NO_3)_3{\cdot}xH_2O$ and $Yb(NO_3)_3{\cdot}xH_2O$, were purchased from Chemicals 101. 2,6-difluorobenzoic acid (2,6-DFBA) was purchased from Ambeed. Terephthalic acid (BDC) was purchased from Acros Organics.

Note: 2,6-dFBA was purified by dissolving in acetone (10 g in 20 mL), filtering the impurities and letting the acetone evaporate at room temperature. Not purifying this reagent or doing it with a different procedure might impact the reproducibility of the synthesis of the MOFs herein reported.

## Instrumentation

Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku MiniFlex diffractometer (measurements made over a range of $3° < 2\theta < 40°$ with a 0.100 °/s scanning speed). Neat samples were smeared onto a zero-background sample holder. Data were collected using a continuous coupled θ/2θ scan with Ni-filtered Cu*K*α (λ = 1.54178 Å).

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC 3+ equipped with an SDTA sensor, small furnace, and XP1 balance from room temperature to 800 °C at a rate of 10 °C/min under air.

Samples for nitrogen adsorption/desorption were activated using a Micromeritics Smart VacPrep instrument equipped with a hybrid turbo vacuum pump. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics TriStar II Plus instrument. Activation of all RE-UiO-66 samples was performed at 80 °C for 20 h.

$^1$H-NMR spectra were recorded on a 300 MHz Bruker spectrometer and the chemical shifts were referenced to the residual solvent peaks. Samples were digested using $D_2SO_4$ (12 drops) and then dissolved in DMSO-$d_6$ (0.65 mL).

Scanning electron microscopy (SEM) micrographs were collected on a Phenom ProX desktop SEM. Samples were dispersed on a carbon taped aluminium stub, coated with 5 nm of Au and placed

on a charge reducing sample holder. SEM images were collected at accelerating voltage of 10 kV and magnification of 1350x and 3800x.

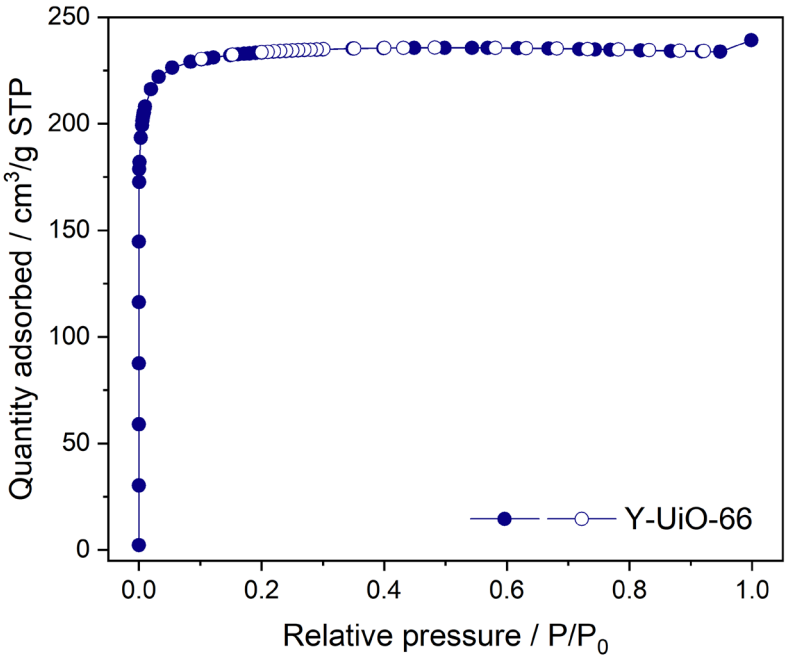
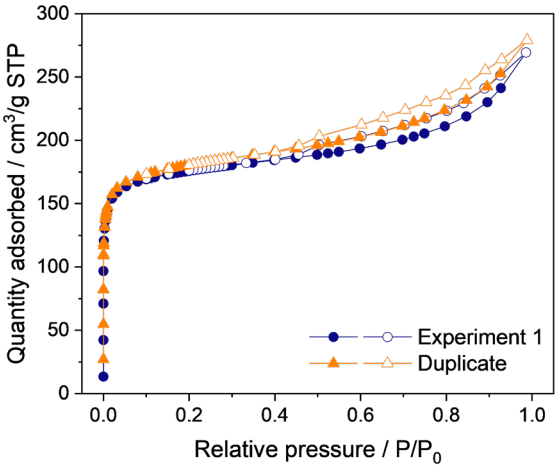
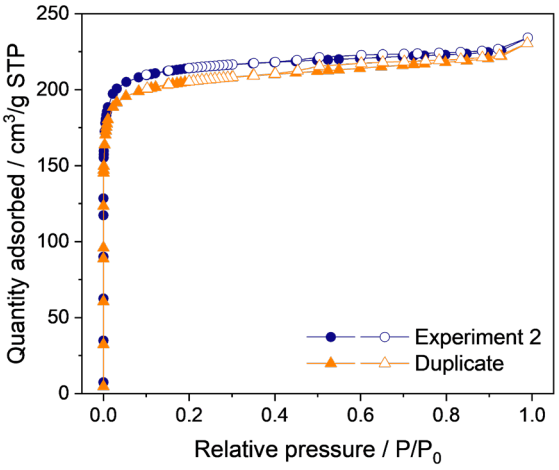


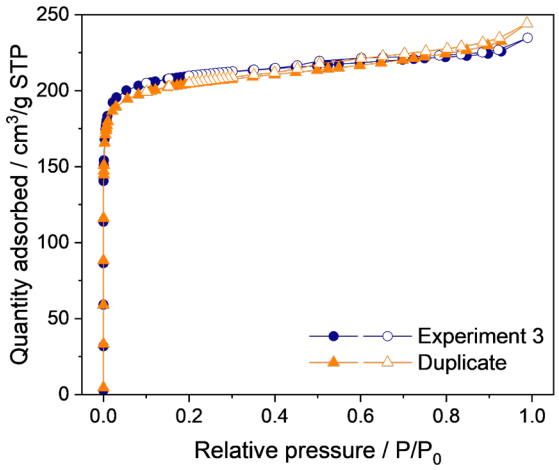

Figure S1 $N_2$ adsorption-desorption isotherm of Y-UiO-66 obtained using the reported procedure, presenting a surface area of 940 $m^2/g$. Closed circles correspond to adsorption and open correspond to desorption.

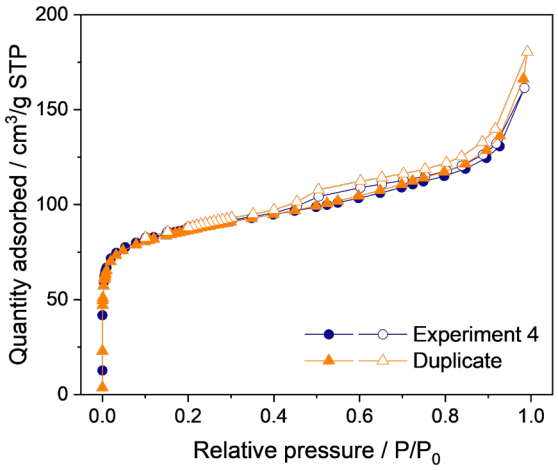
Table S1 Yields and surface areas obtained for the 16 experiments and their duplicates.

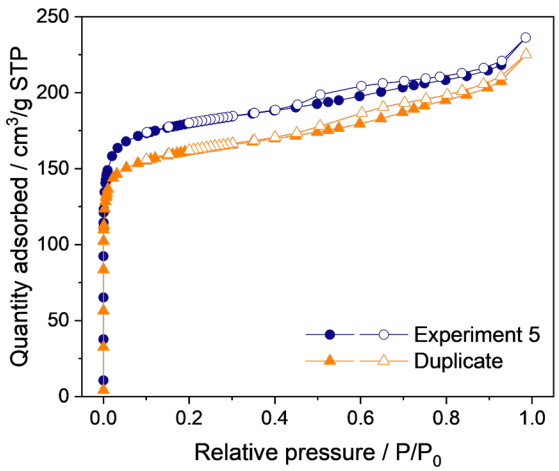
| Experiment | Temperature | Modulator | Linker | Time | Co-modulator | Water | Solvent | Original | | | Duplicate | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Yield (mg) | Yield (%) | Surface area ($m^2/g$) | Yield (mg) | Yield (%) | Surface area ($m^2/g$) |
| **1** | 1 | 1 | -1 | -1 | -1 | -1 | 1 | **33.4** | **67** | **675** | **35.1** | **70** | **686** |
| **2** | -1 | -1 | 1 | 1 | 1 | 1 | -1 | **33.6** | **67** | **850** | **39.8** | **80** | **814** |
| **3** | 1 | 1 | 1 | -1 | 1 | -1 | -1 | **32.2** | **64** | **832** | **38.9** | **78** | **809** |
| **4** | 1 | 1 | -1 | 1 | -1 | 1 | -1 | **28.5** | **57** | **326** | **25.0** | **50** | **311** |
| **5** | 1 | -1 | -1 | 1 | 1 | -1 | -1 | **31.5** | **63** | **699** | **34.1** | **68** | **622** |
| **6** | -1 | 1 | 1 | 1 | -1 | -1 | -1 | **36.3** | **73** | **968** | **31.4** | **63** | **837** |
| **7** | -1 | -1 | -1 | 1 | -1 | 1 | 1 | **35.3** | **71** | **907** | **31.1** | **62** | **850** |
| **8** | 1 | 1 | 1 | 1 | 1 | 1 | 1 | **33.8** | **68** | **605** | **36.2** | **72** | **566** |
| **9** | -1 | 1 | -1 | 1 | 1 | -1 | 1 | **38.0** | **76** | **889** | **37.0** | **74** | **834** |
| **10** | -1 | -1 | 1 | -1 | 1 | -1 | 1 | **19.0** | **38** | **920** | **21.7** | **43** | **789** |
| **11** | 1 | -1 | 1 | -1 | -1 | 1 | -1 | **34.7** | **69** | **792** | **34.9** | **70** | **770** |
| **12** | 1 | -1 | -1 | -1 | 1 | 1 | 1 | **36.0** | **72** | **770** | **35.8** | **72** | **716** |
| **13** | -1 | 1 | -1 | -1 | 1 | 1 | -1 | **23.9** | **48** | **1033** | **19.8** | **40** | **1177** |
| **14** | -1 | -1 | -1 | -1 | -1 | -1 | -1 | **20.8** | **42** | **1033** | **23.4** | **47** | **1069** |
| **15** | 1 | -1 | 1 | 1 | -1 | -1 | 1 | **29.6** | **59** | **668** | **32.5** | **65** | **533** |
| **16** | -1 | 1 | 1 | -1 | -1 | 1 | 1 | **35.9** | **72** | **946** | **34.1** | **68** | **880** |

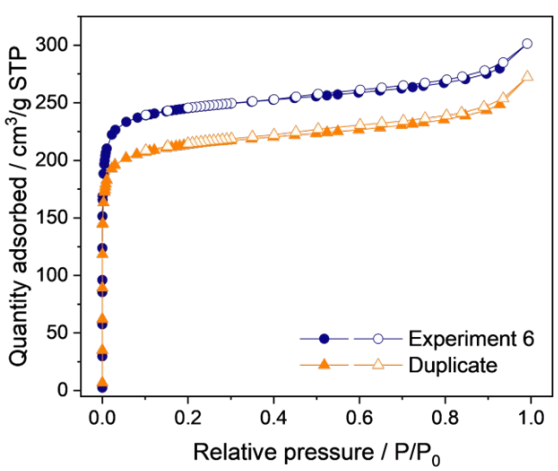

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 1
Duplicate

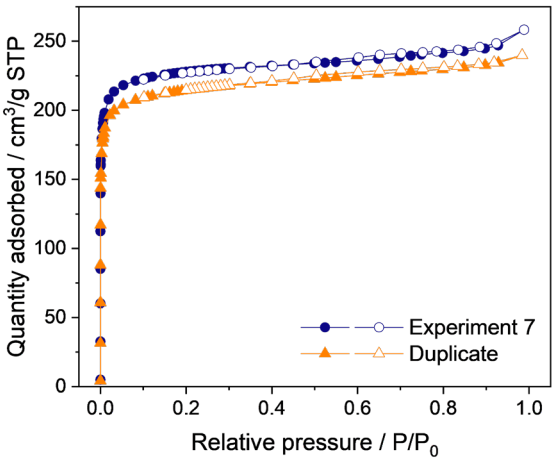

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 2
Duplicate

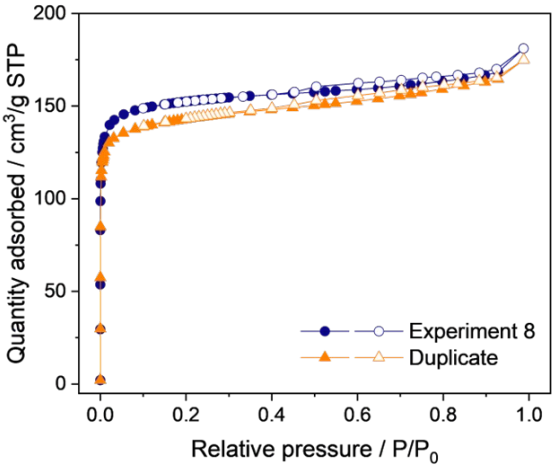

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 3
Duplicate

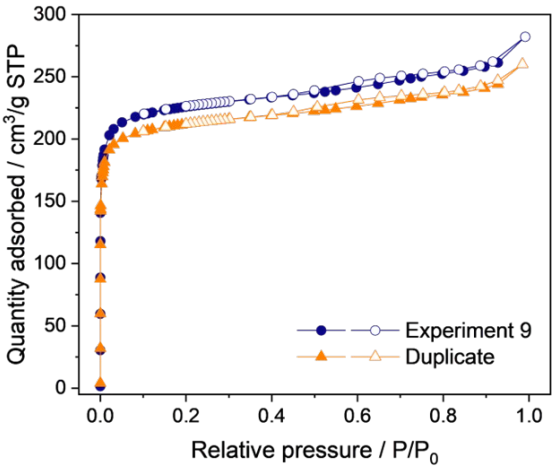

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 4
Duplicate

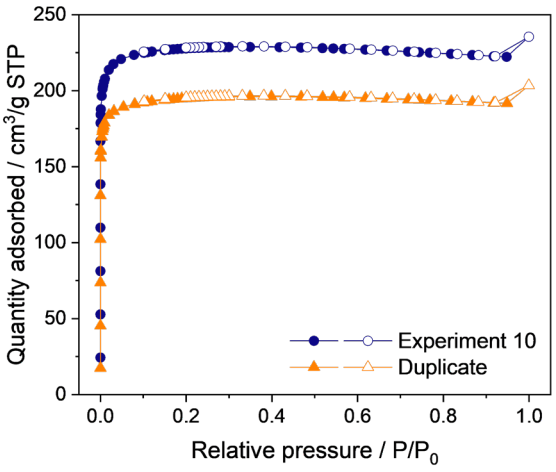

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 5
Duplicate

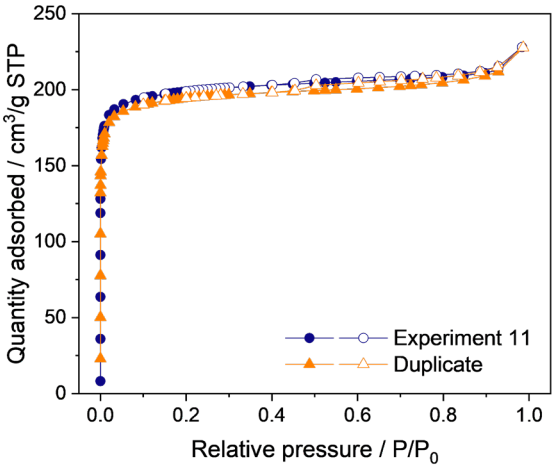

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 6
Duplicate

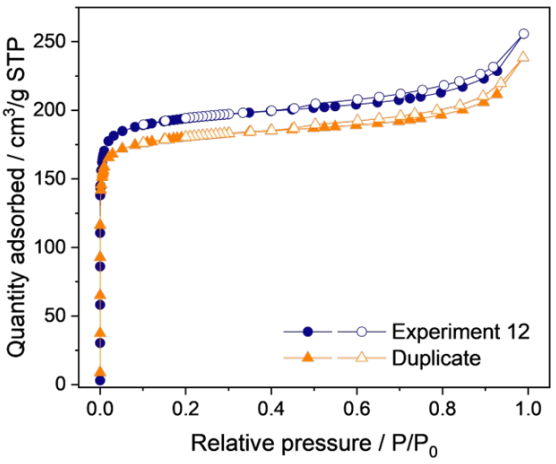

Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 7
Duplicate


Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 8
Duplicate


Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 9
Duplicate


Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 10
Duplicate


Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 11
Duplicate


Quantity adsorbed / cm³/g STP
Relative pressure / P/P0
Experiment 12
Duplicate

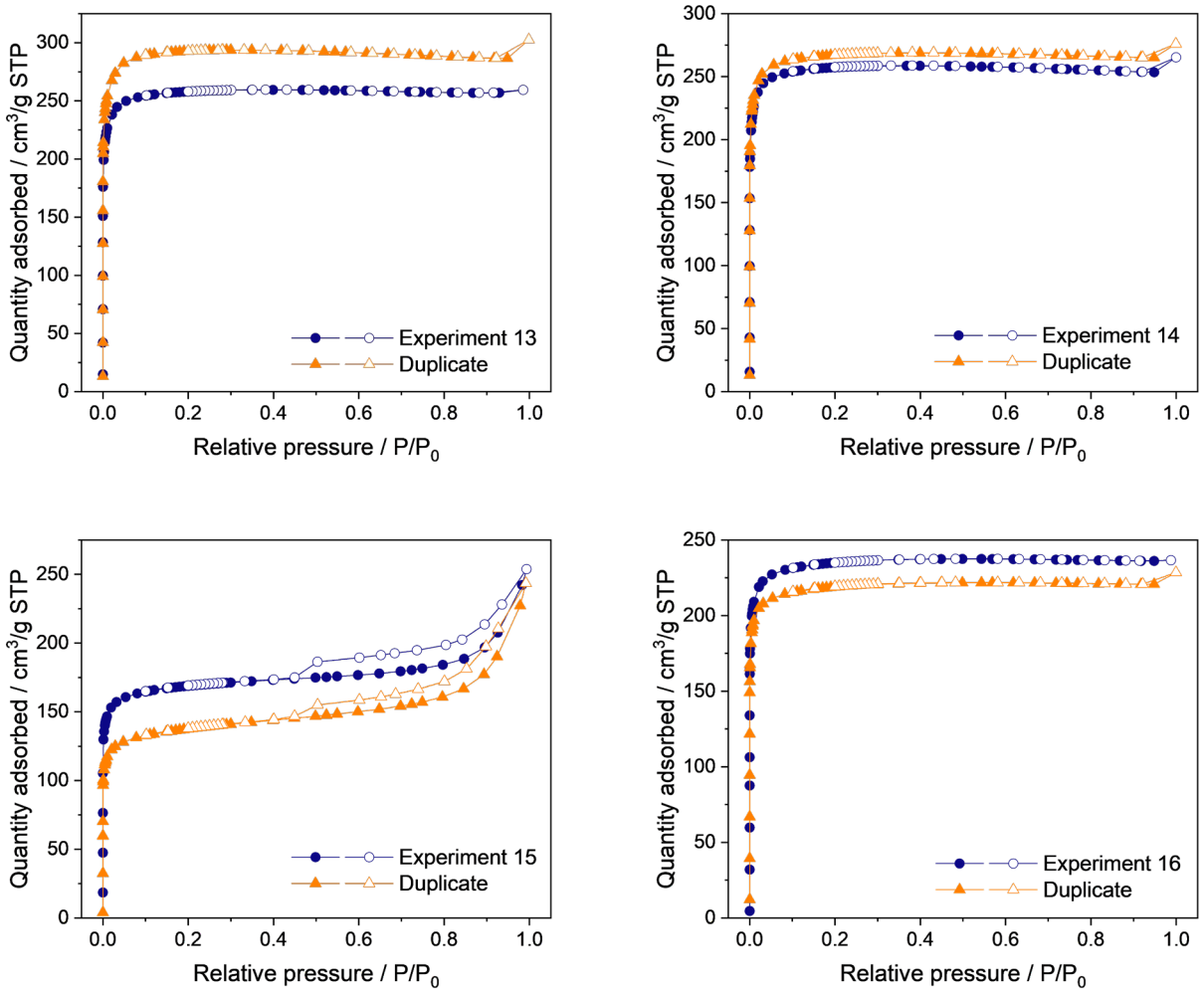



Figure S2 $N_2$ adsorption-desorption isotherms of Y-UiO-66 samples obtained from the 16 experiments of the DoE. Closed circles and triangles correspond to adsorption and open correspond to desorption.

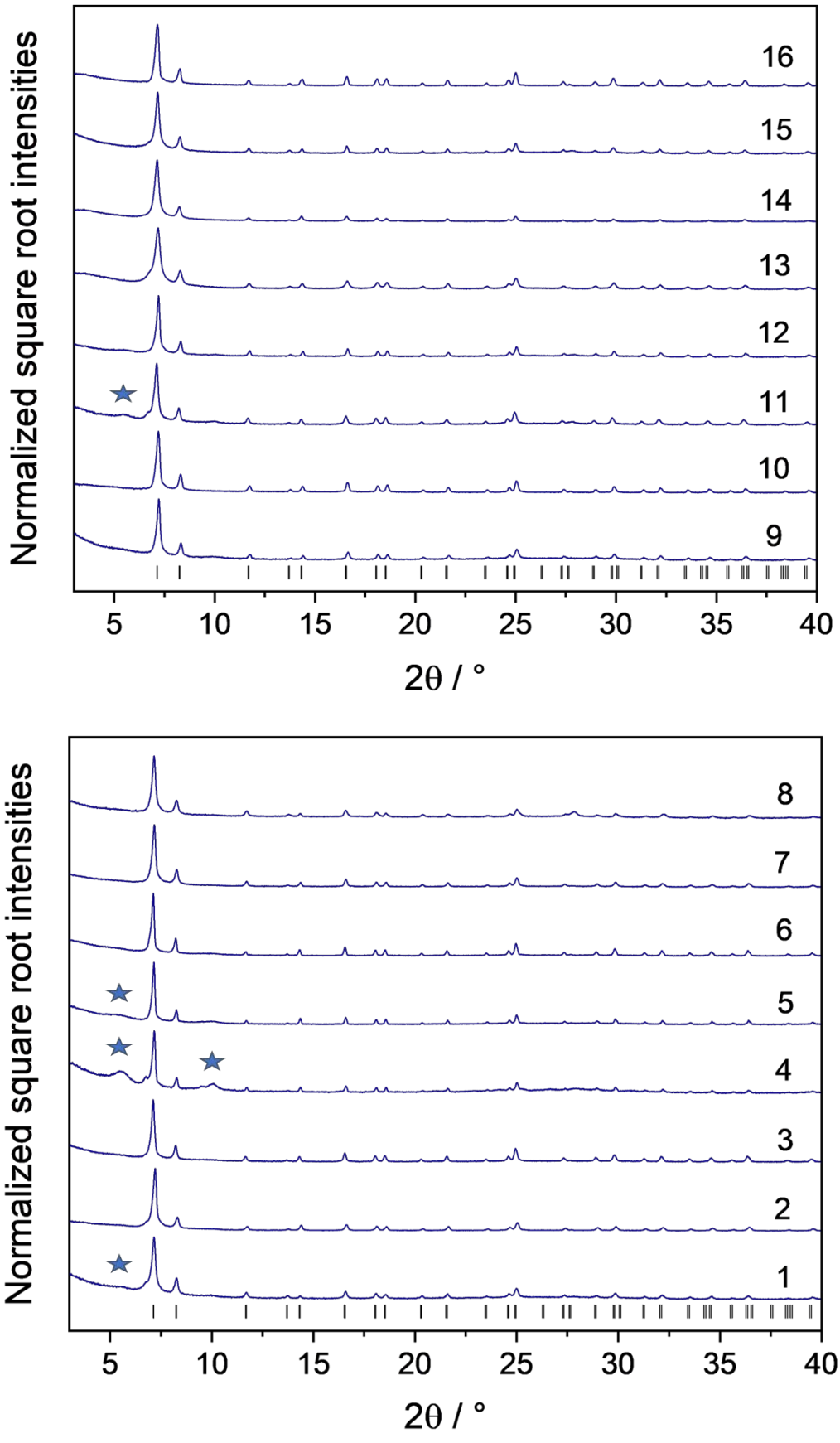



Figure S3 PXRD patterns of Y-UiO-66 samples obtained from the 16 experiments of the DoE. Stars indicate the peaks that do not correspond to allowed reflections (vertical bars).

In an attempt to identify the impurities leading to additional reflections in the PXRD patterns in Figure S3, the product of reaction #4 was digested in $D_2SO_4$ and DMSO-$d_6$ for $^1$H NMR spectroscopy. The $^1$H NMR spectrum (Figure S4) shows a small organic impurity at 2.3ppm, which is discussed in the main text on page 3 and can be removed by washing with MeOH. On one hand, it has been shown by Balkus et al.[1] that the reaction of RE metals with fluorinated modulators can give the corresponding $REF_3$ (peaks between 24 and 30 °2θ), sometimes layered with hydroxide (in this case, the peak around 5 °2θ is observed). All the reactions that presented additional peaks in the PXRD patterns (Figure S3) were performed at 130 °C, indicating that the high temperature might play a role in favouring the formation of this $REF_3$, layered with hydroxide, phase. We repeated reaction #4 without adding the linker and obtained $YF_3$ (Figure S5) confirming the identity of the impurity peaks.

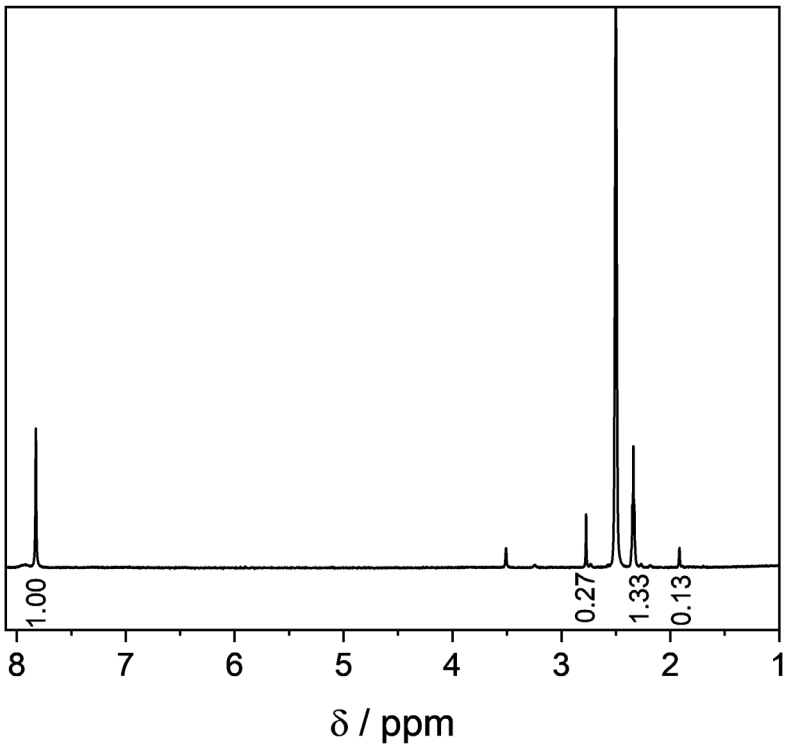



Figure S4 $^1$H NMR spectrum of Y-UiO-66 obtained with reaction #4.

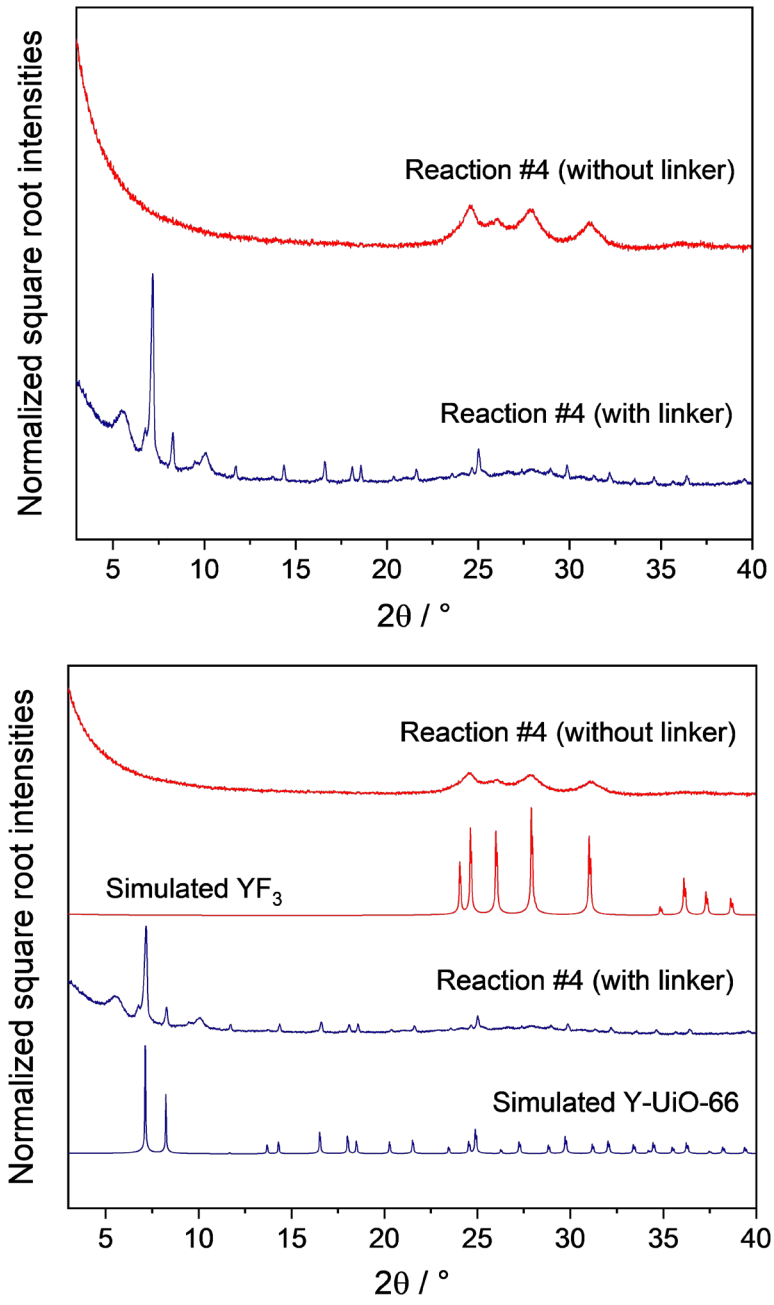



Figure S5 PXRD patterns of reaction #4 with and without linker, and the simulated pattern for Y-UiO-66 and $YF_3$ (ICSD 26595).

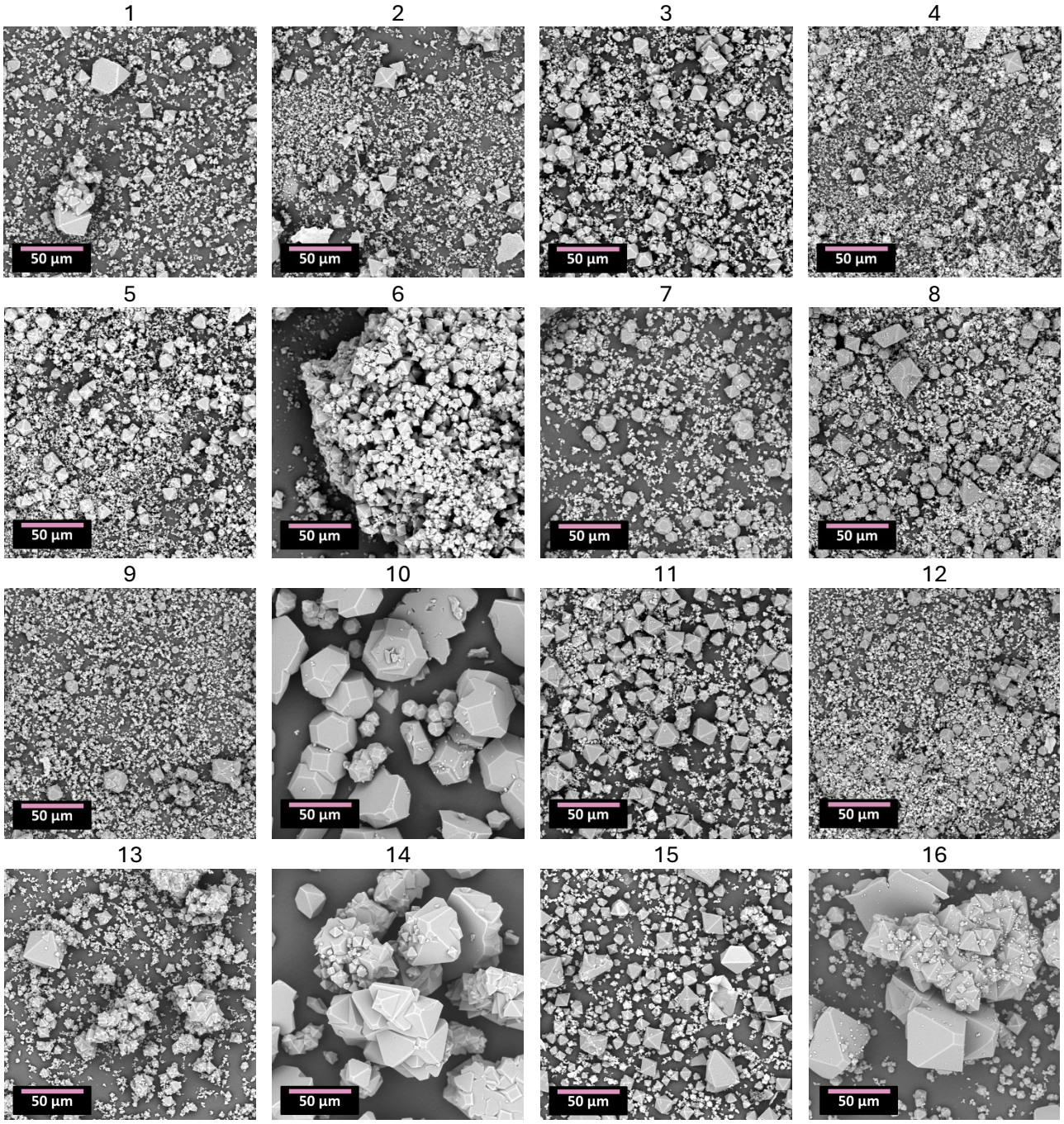



Figure S6 SEM images of Y-UiO-66 samples obtained from the 16 experiments of the DoE.

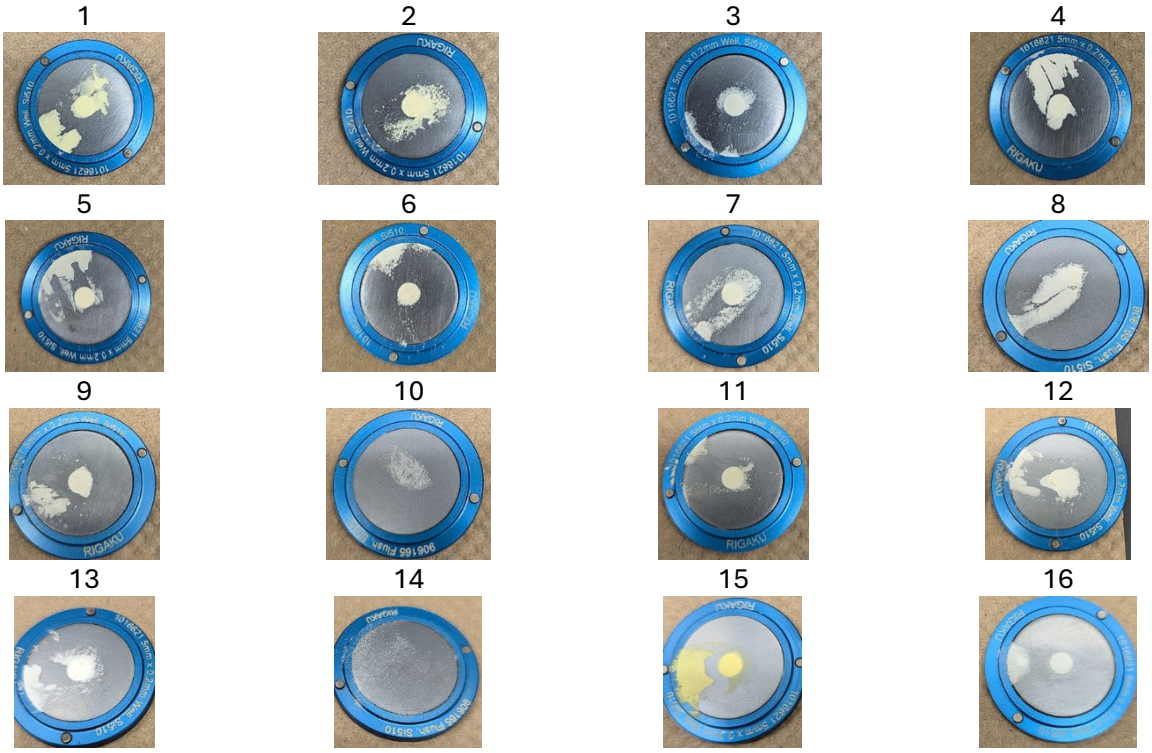



Figure S7 Pictures of Y-UiO-66 samples obtained from the 16 experiments of the DoE.

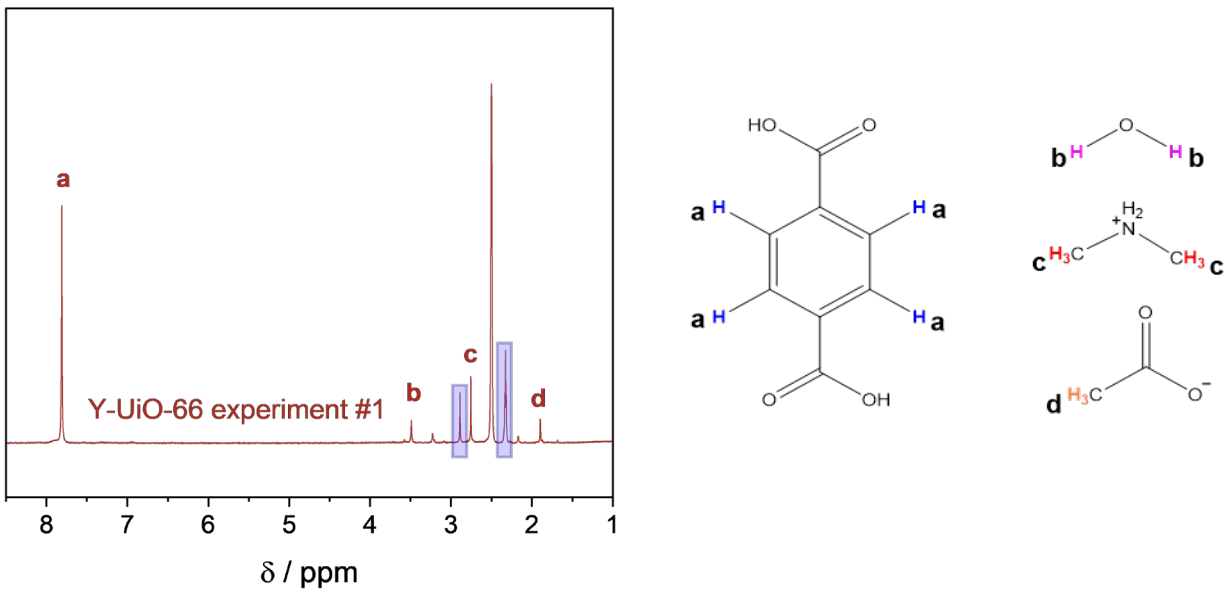



Figure S8 $^{1}$H NMR spectrum of Y-UiO-66 obtained in experiment 1. Blue boxes indicate the peaks that do not correspond to the MOF. Solvent: DMSO-$d_6$ (2.5 ppm), with $D_2SO_4$ for digestion.

Table S2 Chemical shifts and integrations for the $^{1}H$ NMR spectrum in Figure S6.

| H | δ (ppm) | Integration |
|---|---|---|
| BDC (Ha) | 7.8 | 1.00 |
| DMA (Hc) | 2.8 | 0.19 |
| Acetate (Hd) | 1.9 | 0.10 |
| Impurity 1 | 2.9 | 0.17 |
| Impurity 2 | 2.3 | 0.52 |

Table S3 p-values obtained for each main factor by running the ANOVA of the design.

| Factors | Lower Level (-1) | Higher Level (+) | Yield p-value | Surface area p-value |
|---|---|---|---|---|
| Temperature | 120 °C | 130 °C | $2.96 \times 10^{-3}$ | $1.95 \times 10^{-10}$ |
| Equivalents of modulator | 16 | 20 | 0.0875 | 0.191 |
| Equivalents of linker | 1 | 1.4 | 0.0261 | 0.955 |
| Time | 24 | 48 | $1.64 \times 10^{-3}$ | $3.15 \times 10^{-7}$ |
| Equivalents of co-modulator | 9 | 13.5 | 0.538 | 0.0471 |
| Volume of water | 0.1 mL | 0.2 mL | 0.112 | 0.0984 |
| Volume of solvent | 4 mL | 8 mL | 0.0260 | 0.0382 |

Table S4 p-values obtained for eight interactions by running the ANOVA of the design.

| Interaction | Yield p-value | Surface area p-value |
|---|---|---|
| Temperature*Modulator | 0.0171 | $3.06 \times 10^{-3}$ |
| Temperature*Linker | 0.538 | $1.39 \times 10^{-4}$ |
| Modulator*Linker | 0.0111 | $4.29 \times 10^{-3}$ |
| Temperature*Time | $5.71 \times 10^{-7}$ | 0.0184 |
| Modulator*Time | 0.0676 | 0.0233 |
| Linker*Time | 0.538 | 0.0184 |
| Time*Acid | $7.84 \times 10^{-4}$ | 0.378 |
| Modulator*Linker*Time | 0.0593 | 0.0670 |

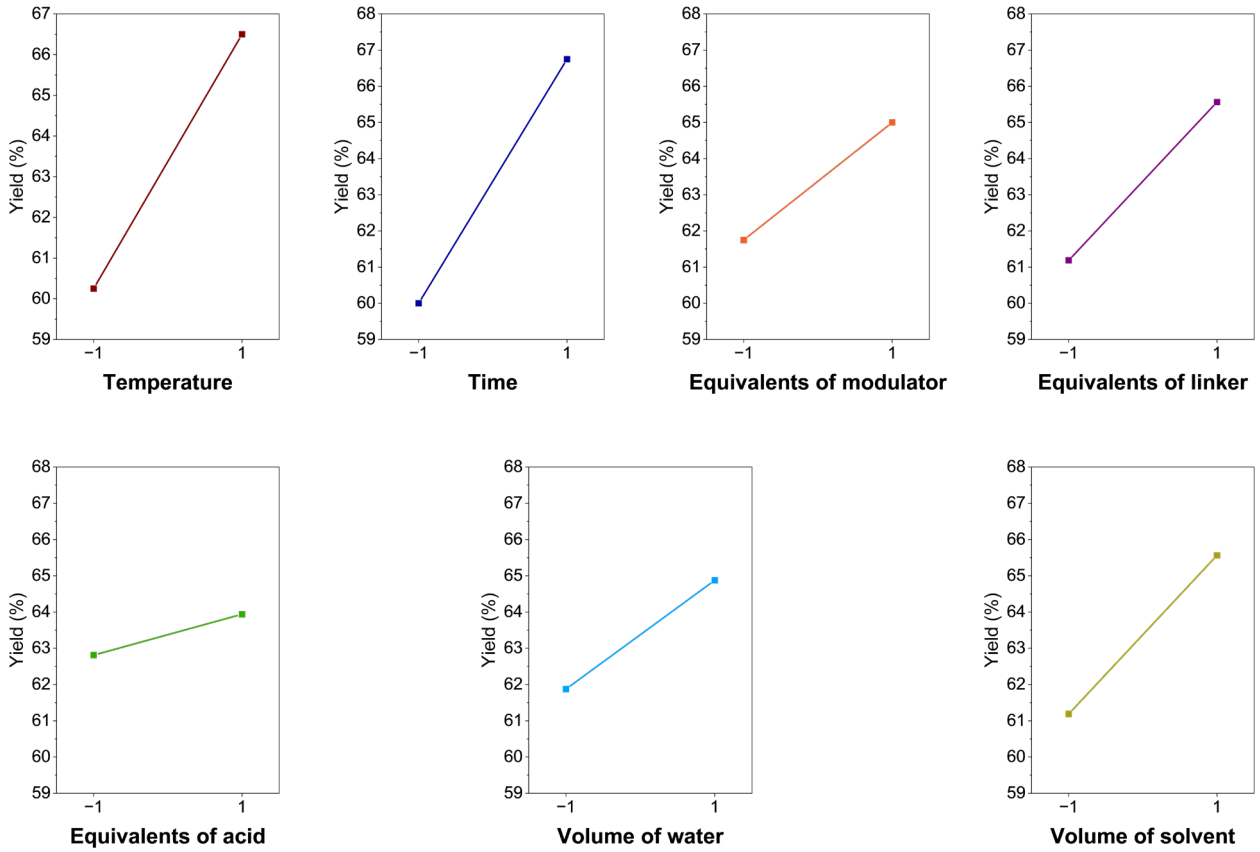



Figure S9 Main effects plots for yield

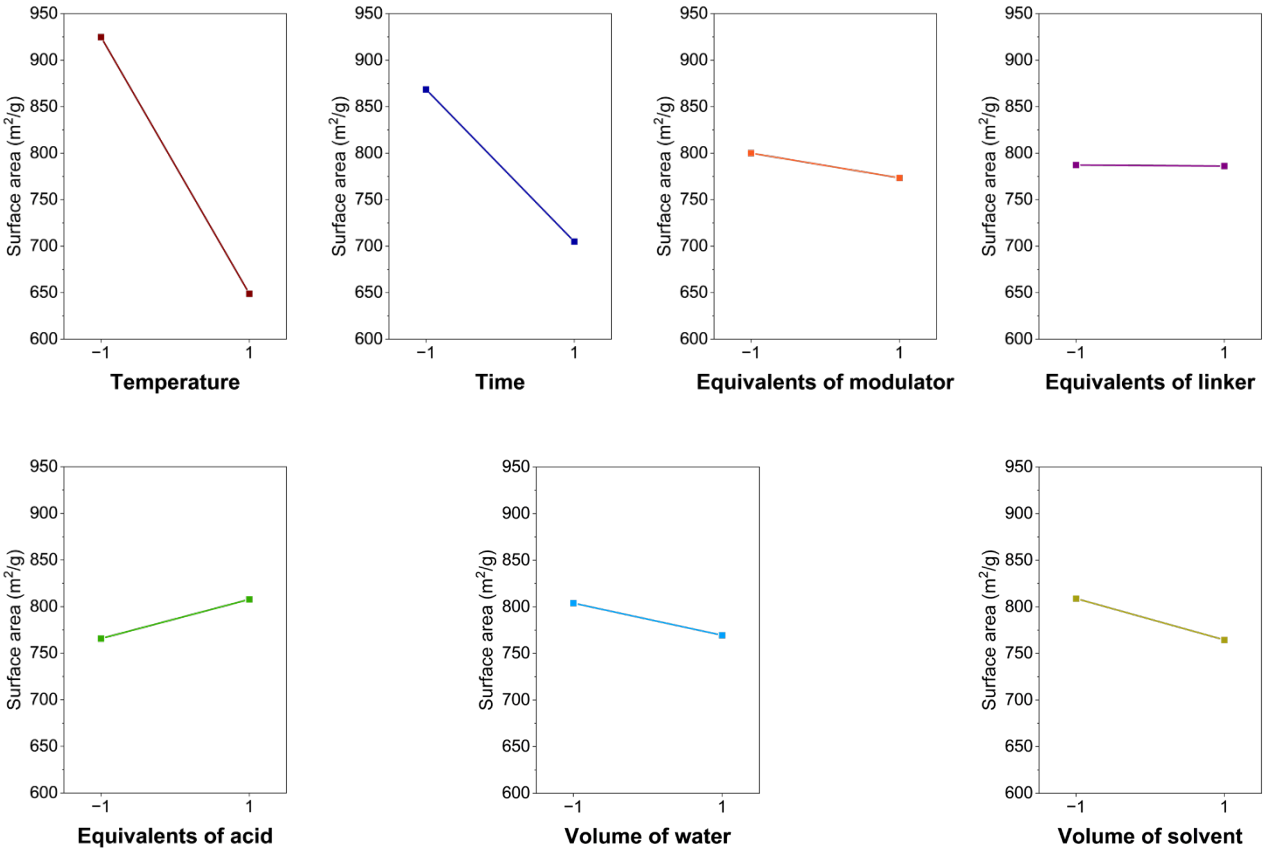



Figure S10 Main effects plots for surface area

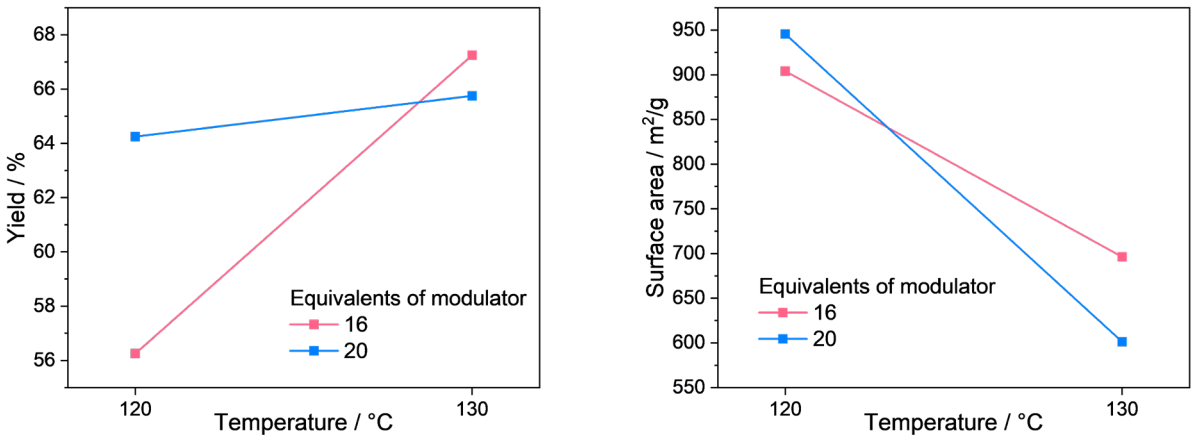



Figure S11 Interaction plots for Temperature*Equivalents of modulator

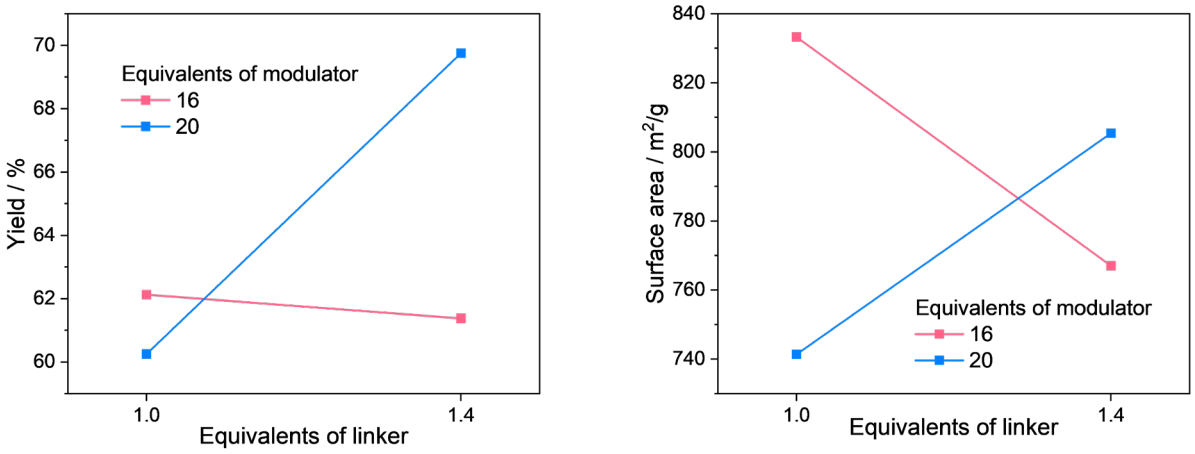



Figure S12 Interaction plots for Equivalents of linker*Equivalents of modulator

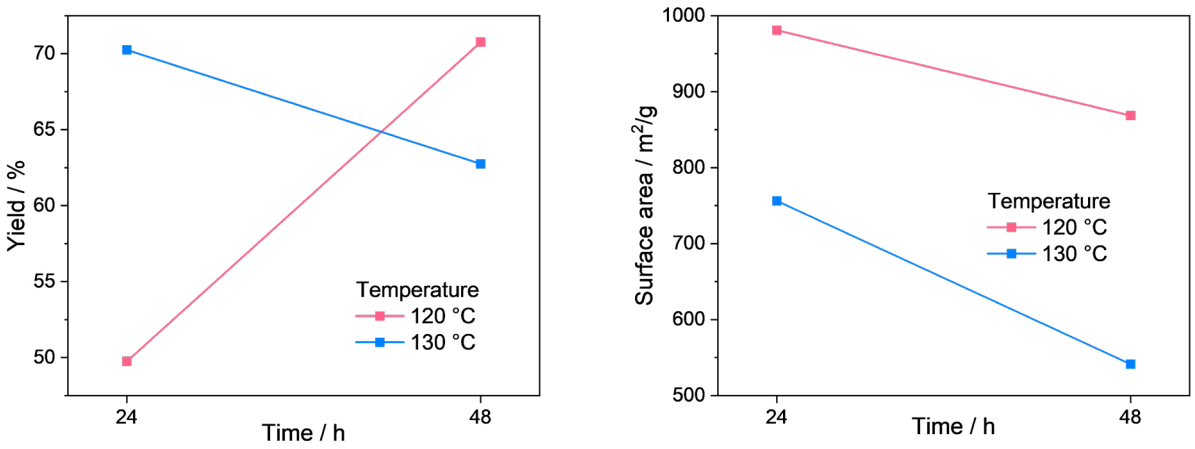



Figure S13 Interaction plots for Time*Temperature

Figure S14 Pictures of Y-UiO-66 samples prepared using six optimized synthetic parameters and 4 (left) and 8 mL (right) of DMAc.

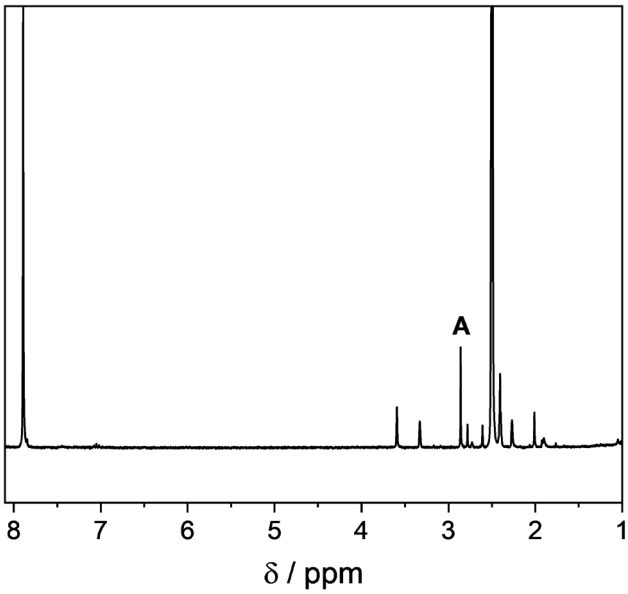



Figure S15 $^{1}$H NMR spectrum of the 4 mL reaction after 3 washes with methanol, where peak A is the one observed in all the yellow samples.

Table S5 Yield and surface area of Y-UiO-66 sampled prepared using six optimized synthetic parameters and varying volume of DMAc solvent.

| Solvent | Temperature | Modulator | Linker | Co-modulator | Water | Original | | | Duplicate | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Yield (mg) | Yield (%) | Surface area ($m^2/g$) | Yield (mg) | Yield (%) | Surface area ($m^2/g$) |
| 8 mL | 120 °C | 20 eq | 1.4 eq | 13.5 eq | 0.2 mL | **43.7** | **87** | **1030** | **40.5** | **81** | **1070** |
| 4 mL | 120 °C | 20 eq | 1.4 eq | 13.5 eq | 0.2 mL | **39.9** | **80** | **990** | **38.1** | **76** | **1080** |

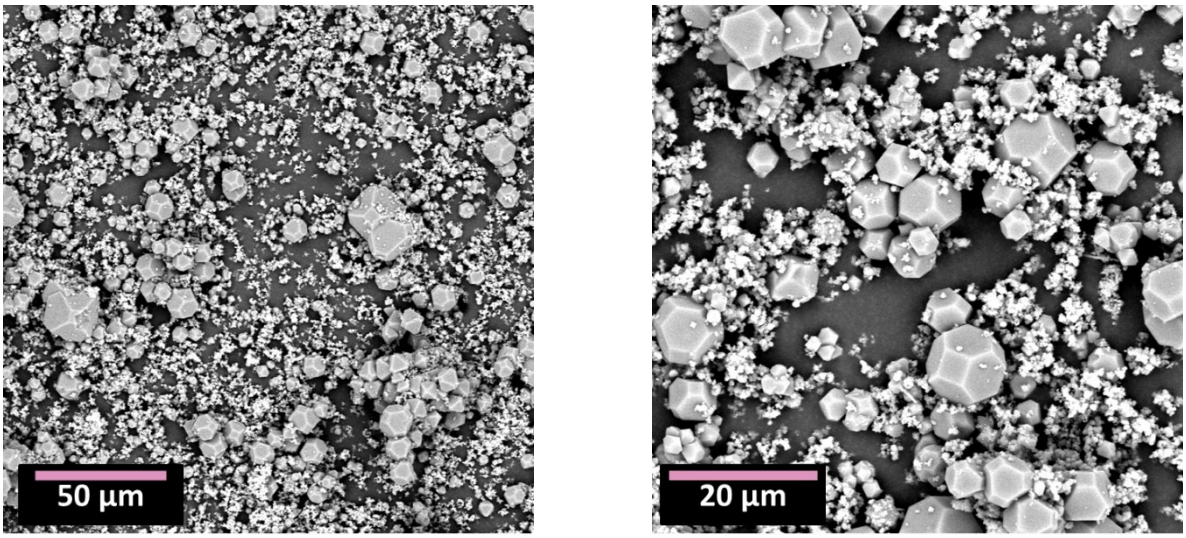



Figure S16 SEM images of Y-UiO-66 obtained using the optimized procedure

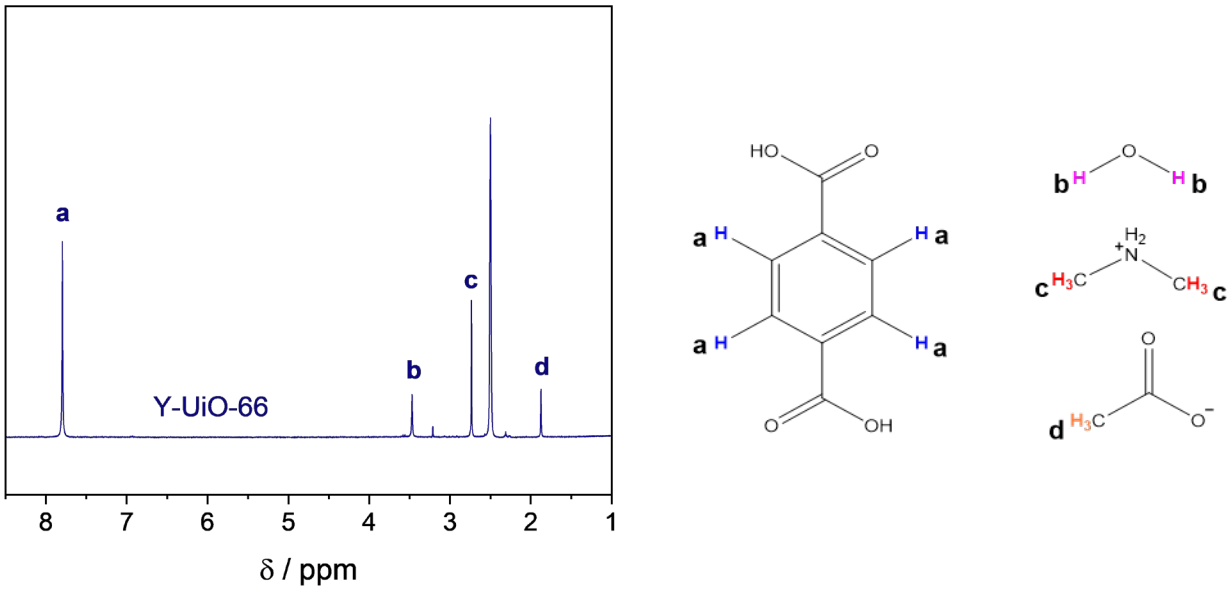



Figure S17 $^{1}$H NMR spectrum of Y-UiO-66 obtained using the optimized procedure. Solvent: DMSO-$d_6$ (2.5 ppm), and $D_2SO_4$ for digestion.

Table S6 Chemical shifts and integrations for the $^{1}$H NMR spectrum in Figure S14

| H | δ (ppm) | Integration |
|---|---|---|
| BDC (Ha) | 7.8 | 1.00 |
| DMA (Hc) | 2.8 | 0.39 |
| Acetate (Hd) | 1.9 | 0.19 |

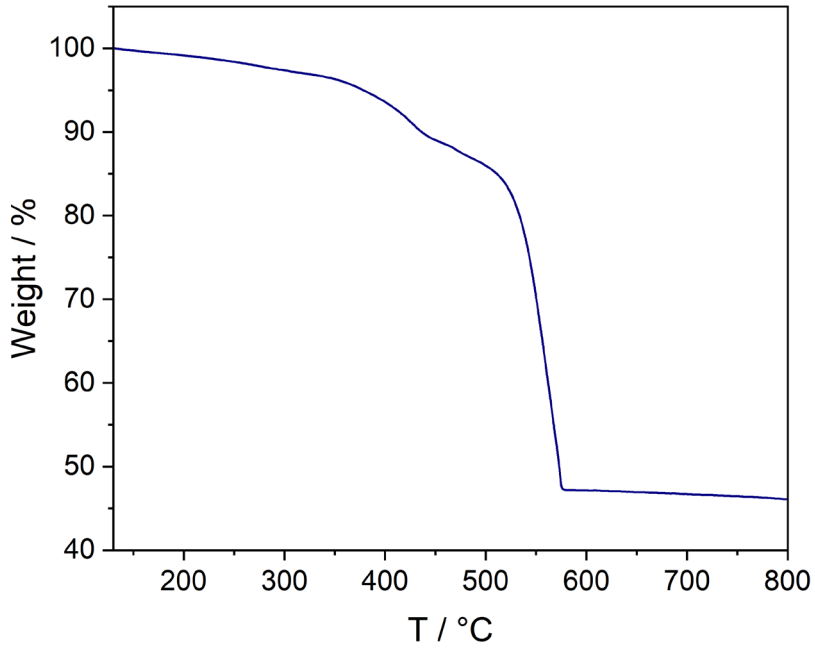



Figure S18 TGA of Y-UiO-66 obtained using the optimized procedure.

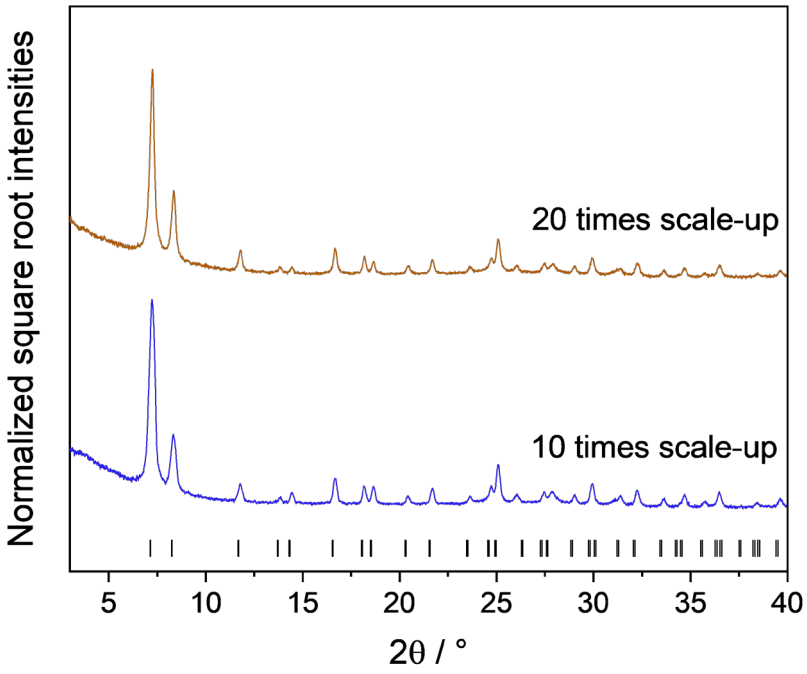



Figure S19 PXRD patterns of Y-UiO-66 samples obtained using the scaled-up procedures.

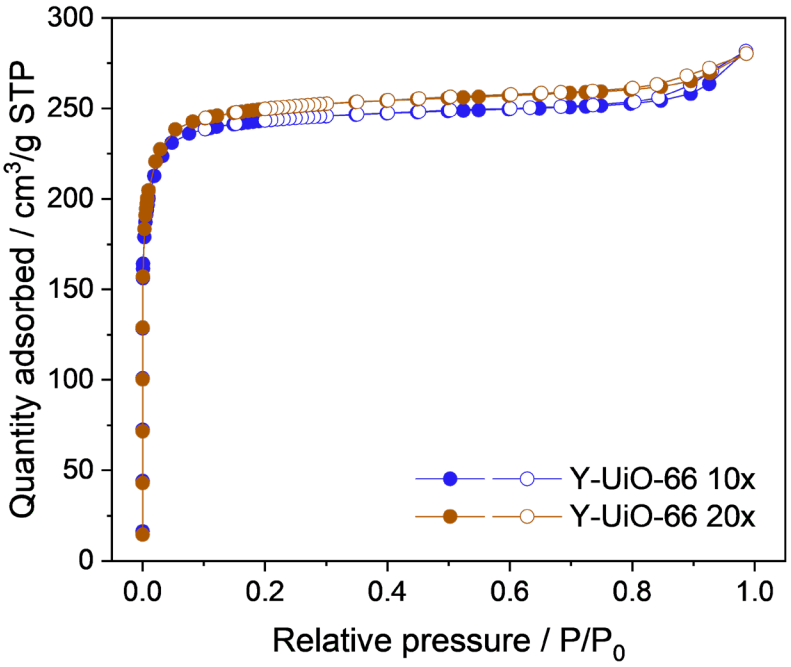



Figure S20 $N_2$ adsorption-desorption isotherms of Y-UiO-66 samples obtained using the scaled-up procedures. Closed circles correspond to adsorption and open correspond to desorption.

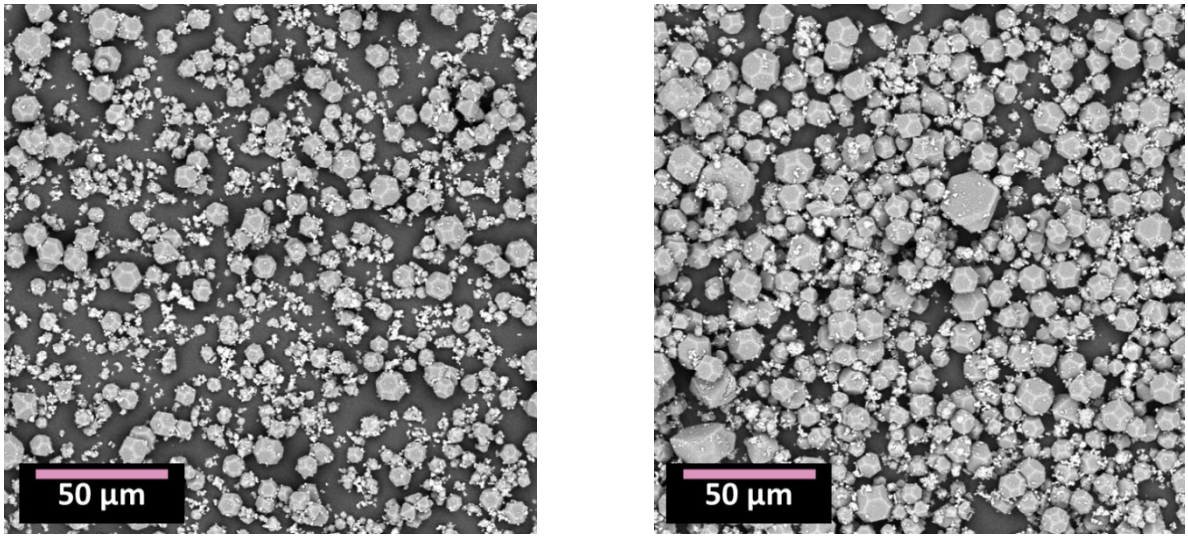



Figure S21 SEM images of Y-UiO-66 samples obtained using the scaled-up procedure 10x (left) and 20x (right).

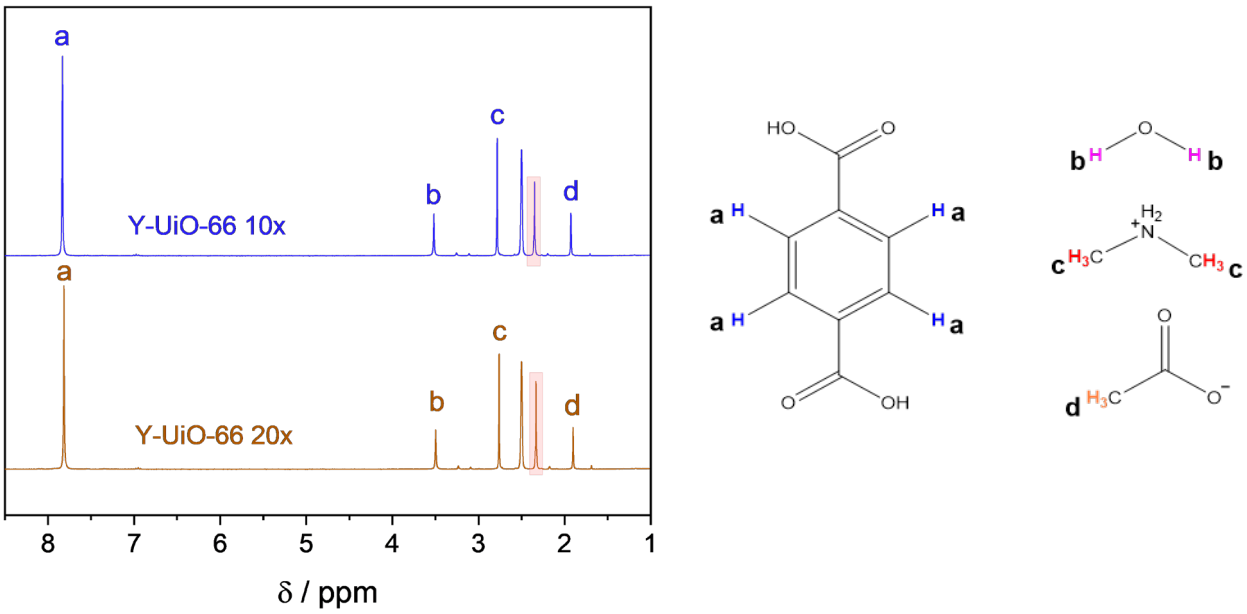



Figure S22 $^{1}$H NMR spectra of Y-UiO-66 samples obtained using the scaled-up procedure before methanol washes. Red boxes indicate the peaks that do not correspond to the MOF. Solvent: DMSO-$d_6$ (2.5 ppm), with $D_2SO_4$ for digestion.

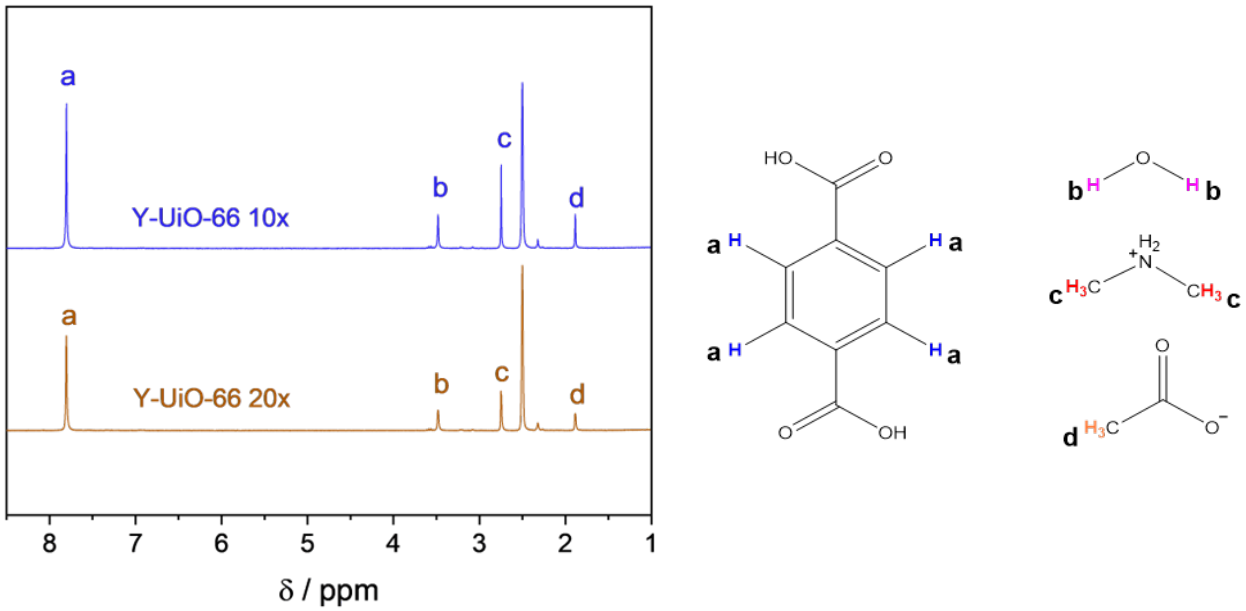



Figure S23 $^{1}$H NMR spectra of Y-UiO-66 samples obtained using the scaled-up procedure after methanol washes. Solvent: DMSO-$d_6$ (2.5 ppm), with $D_2SO_4$ for digestion.

Table S7 Chemical shifts and integrations for the $^{1}$H NMR spectra in Figures S19 and S20.

| H | δ (ppm) | Integrations | | | |
|---|---|---|---|---|---|
| | | 10x before MeOH | 10x after MeOH | 20x before MeOH | 20x after MeOH |
| BDC (Ha) | 7.8 | 1.00 | 1.00 | 1.00 | 1.00 |
| DMA (Hc) | 2.8 | 0.40 | 0.40 | 0.40 | 0.40 |
| Acetate (Hd) | 1.9 | 0.20 | 0.20 | 0.20 | 0.20 |
| Impurity | 2.3 | 0.34 | 0.06 | 0.40 | 0.09 |

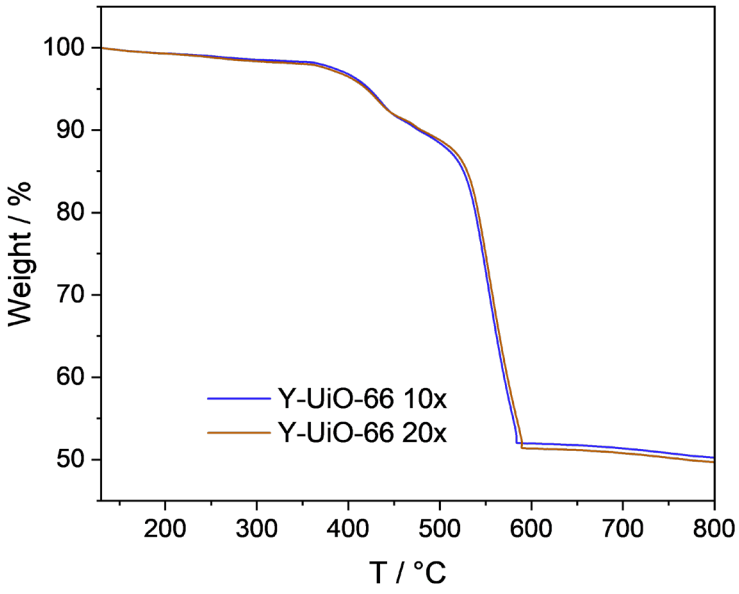



Figure S24 TGA for Y-UiO-66 samples obtained using the scaled-up procedure after methanol washes.

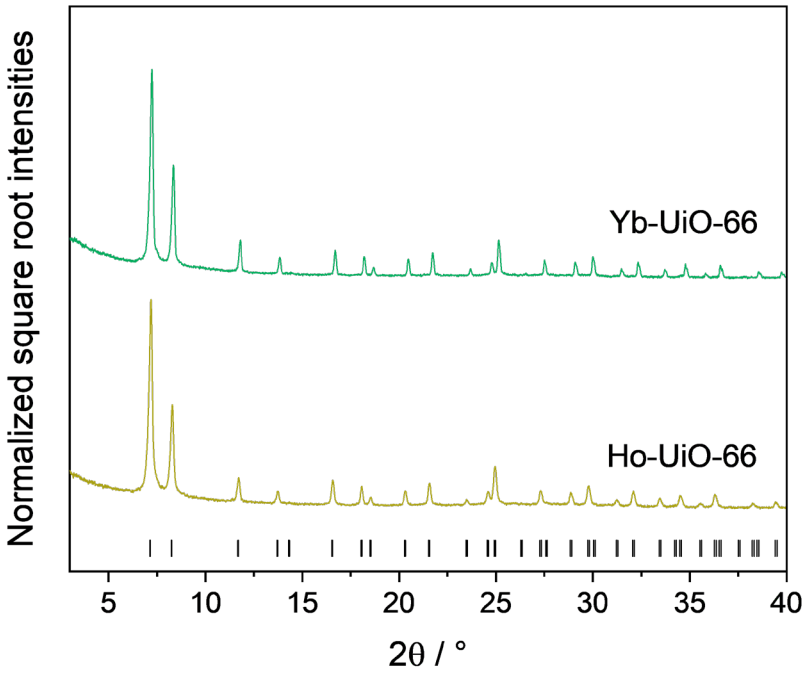



Figure S25 PXRD patterns of Ho-UiO-66 and Yb-UiO-66 samples synthesized using the newly optimized procedure based on the DoE results for Y-UiO-66.

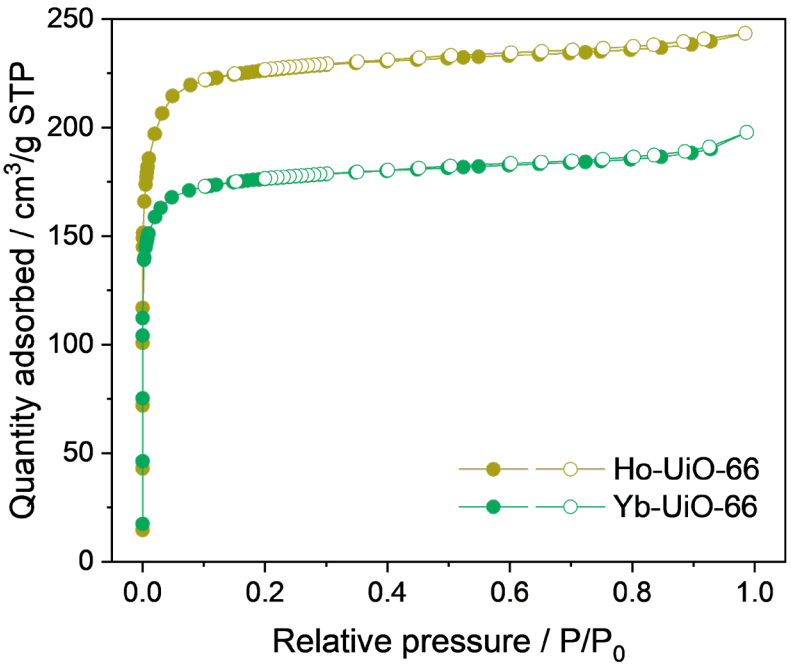



Figure S26 $N_2$ adsorption-desorption isotherms of Ho-UiO-66 and Yb-UiO-66 samples synthesized using the newly optimized procedure based on the DoE results for Y-UiO-66. Closed circles correspond to adsorption and open correspond to desorption.

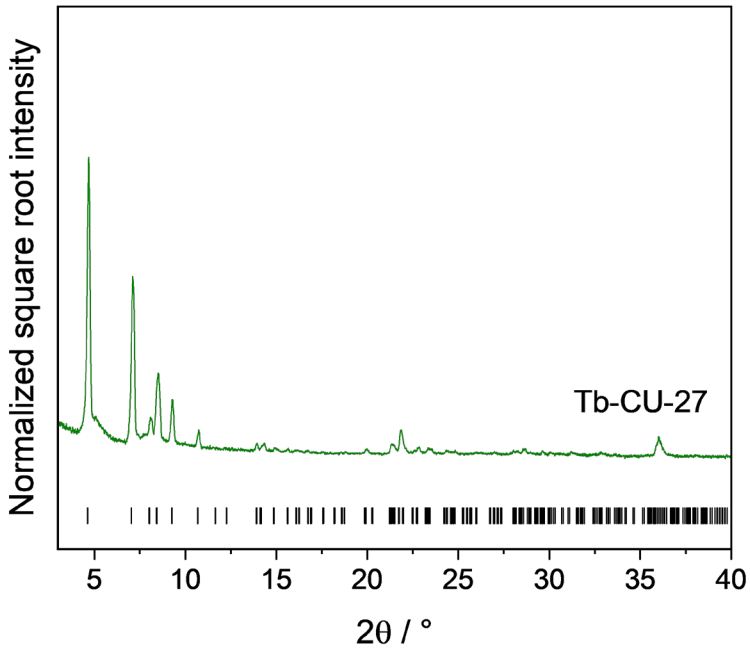



Figure S27 PXRD pattern of Tb-CU-27 synthesized using an optimized procedure adapted from the results obtained for the DoE for Y-UiO-66.

Table S8 Summary of the synthetic procedures to obtain RE-UiO-66

| MOF | Yield (%) | Surface area ($m^2/g$) | Reference |
|---|---|---|---|
| Y-UiO-66 | Not reported | 1360 | 2 |
| Y-UiO-66 | 39 | 1060 | 3 |
| Y-UiO-66 | 84 | 1050 | This work |
| Ho-UiO-66 | Not reported | 1000 | 2 |
| Ho-UiO-66 | 31 | 820 | 3 |
| Ho-UiO-66 | Not reported | 790 | 4 |
| Ho-UiO-66 | 88 | 890 | This work |
| Yb-UiO-66 | Not reported | 1080 | 2 |
| Yb-UiO-66 | 23 | 650 | 3 |
| Yb-UiO-66 | Not reported | 700 | 4 |
| Yb-UiO-66 | 82 | 700 | This work |

Reference 2 is the original procedure for the synthesis of RE-UiO-66. This report explores the synthesis in DMF, and how using a mixture of DMF:DMAc, or even DMAc alone, helps with reproducibility of the synthetic procedure. Furthermore, the addition of nitric acid is discussed with the same purpose. Reference 3 and 4 use the "best" procedure from the previous report (Reference 2) which is: 1 equivalent of linker, 16 equivalents of 2,6-dFBA, 8 mL of DMAc, 0.1 mL of water, 0.1 mL of nitric acid, 120 °C for 24 hours. This procedure leads to lower surface areas than the others reported in Reference 2, and the presence of dimethylammonium cations and acetate capping ligands is observed, suggesting a difference in the number of defects in the samples using this "best" procedure. Reference 3 also reports the use of RE acetates in place of RE nitrates for this "best" procedure, obtaining comparable results.

This work herein starts with the procedure from References 3 and 4, keeping the same reagents but improving the yield by varying their ratios and the reaction time.

**References**


1. Balkus, K. J.; Mortensen, M. L.; Simin, S.; Vizuet, J. P., Defluorination of organo-fluorine molecules by rare-earth ions resulting in fluoro-bridged metal-organic frameworks. U.S. Patent Application No. 18/303,914.
2. P. R. Donnarumma, S. Frojmovic, P. Marino, H. A. Bicalho, H. M. Titi and A. J. Howarth, *Chem. Commun*., 2021, 57, 6121-6124.
3. M. Richezzi, P. R. Donnarumma, C. Copeman and A. J. Howarth, *Chem. Commun.*, 2024, 60, 5173-5176.
4. P. R. Donnarumma, C. Copeman, M. Richezzi, J. Sardilli, H. M. Titi and A. J. Howarth, *Cryst. Growth Des.*, 2024, 24, 1619-1625.