Basics of MOFs and Related Organic Synthetic Applications

Anna (Qinyan) Cai

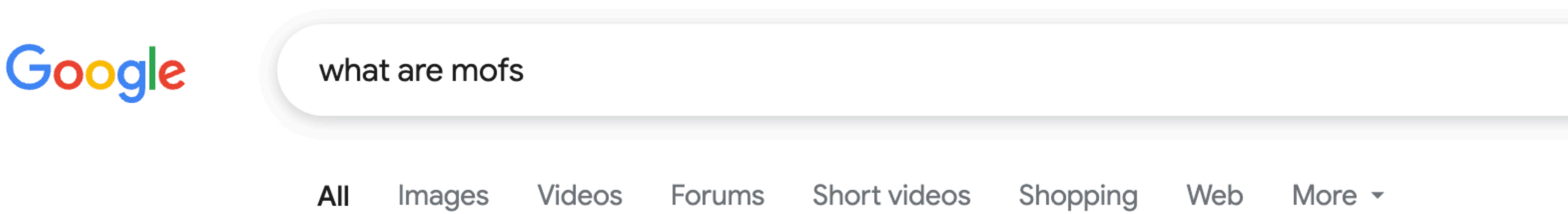
MacMillan Research Group

Literature Talk

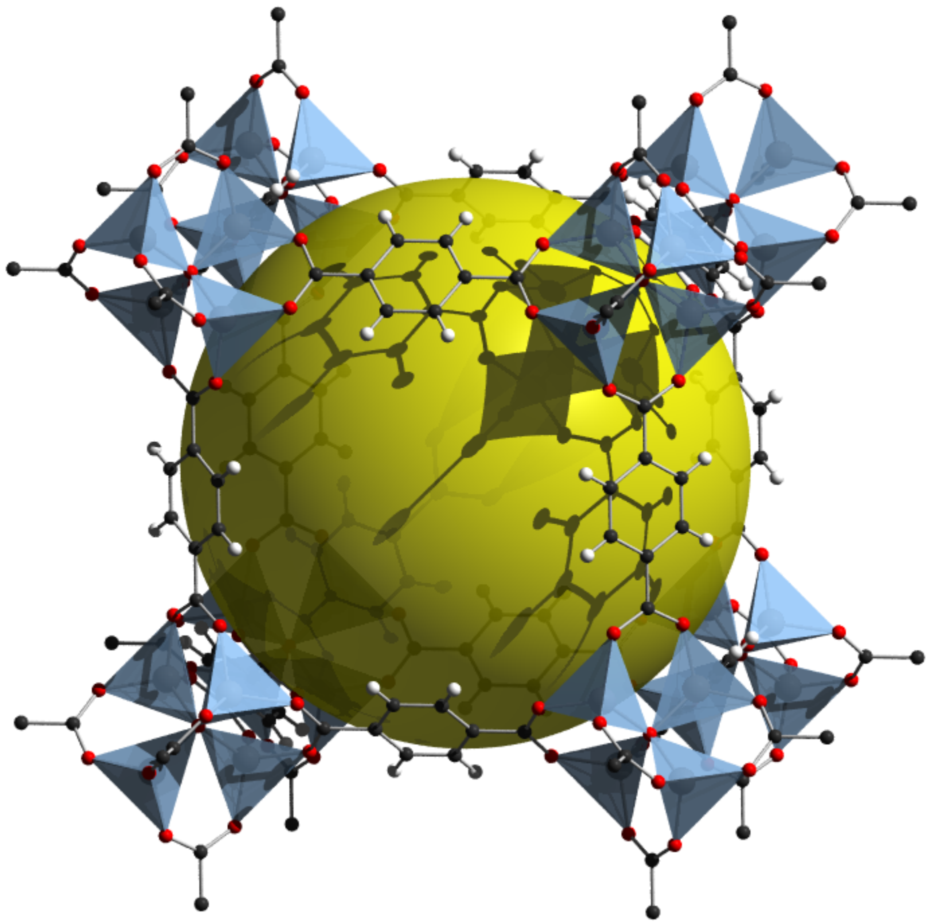
April 11th, 2025

MOFs

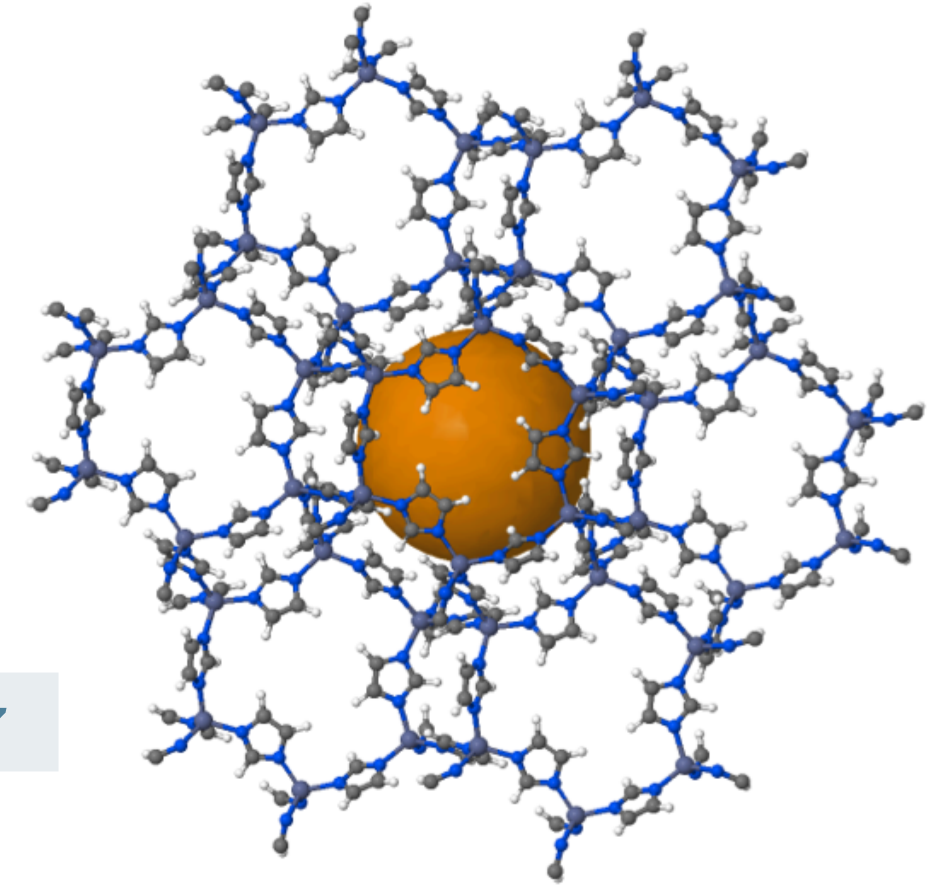
MOFs


Google
what are mofs
All
Images
Videos
Forums
Short videos
Shopping
Web
More

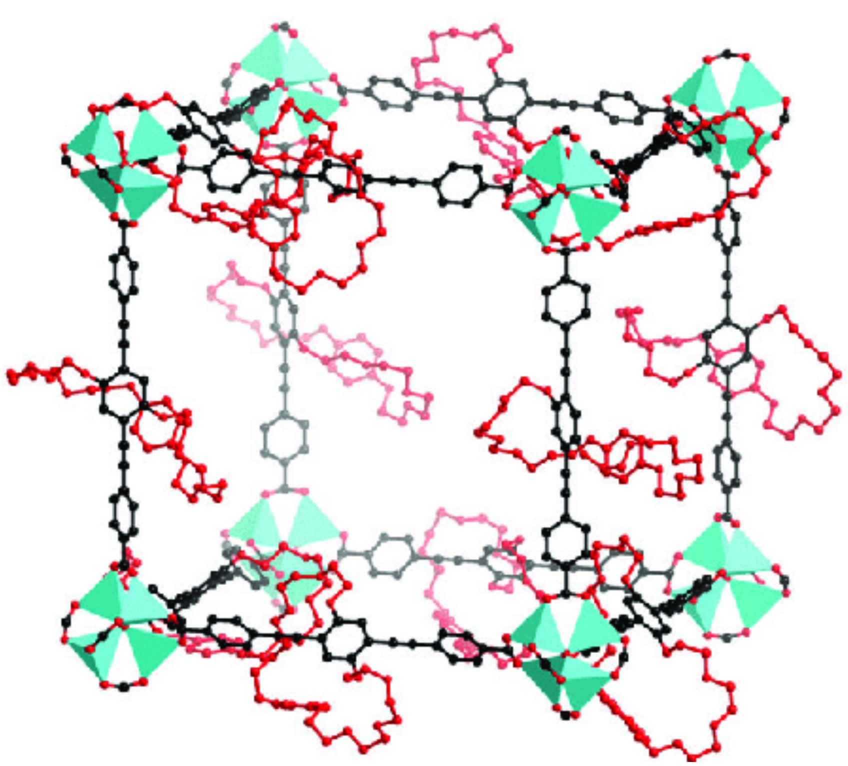
MOFs



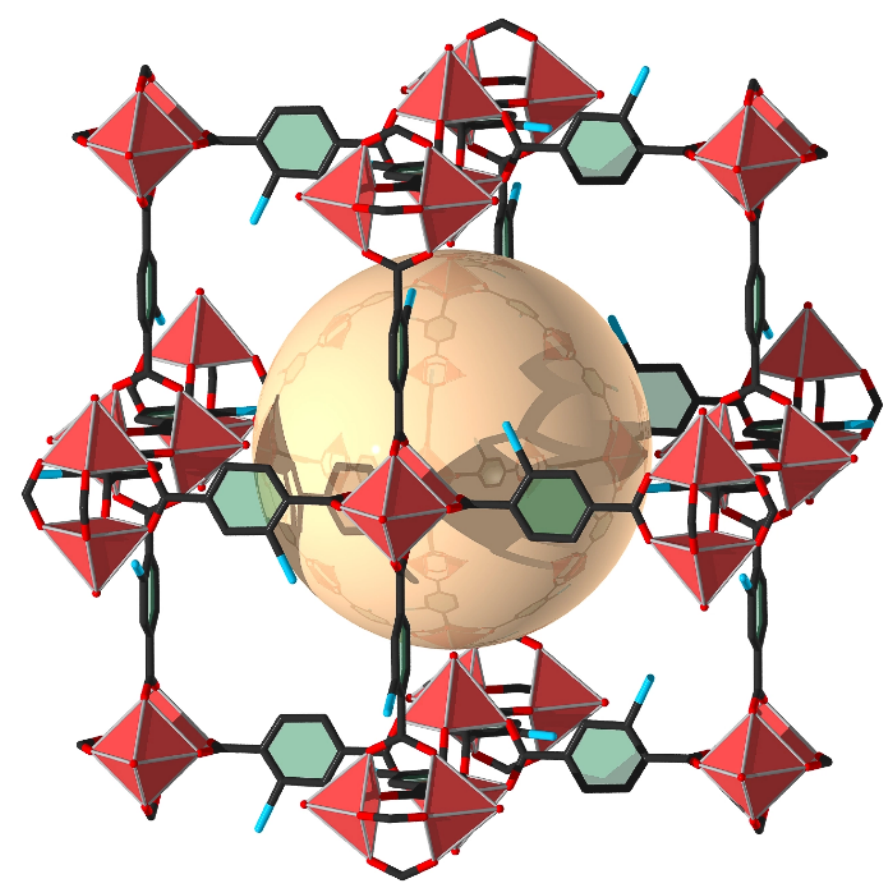
MOF - 5



MOF - 1777



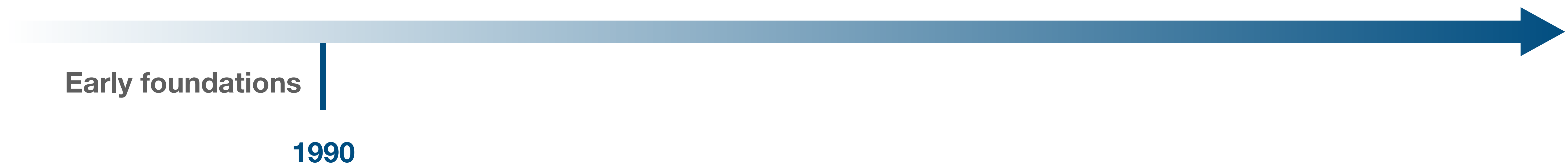
MOF - 1001



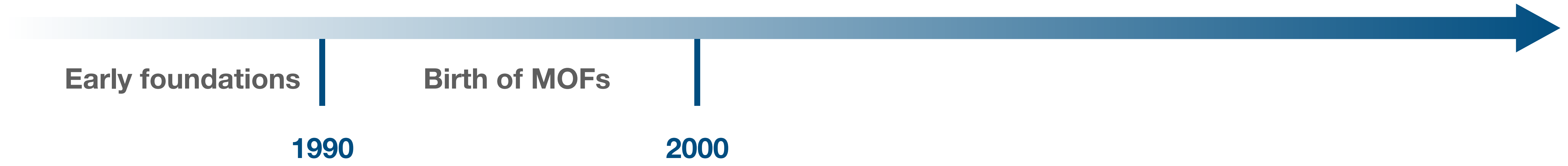
MOF - 101-2

Timeline

Timeline



Timeline



1st MOF synthesized by Yaghi, who coined the term “MOF”

Timeline

JACS **1995**, *117*, 10401–10402.

Early foundations

Birth of MOFs

1990

2000

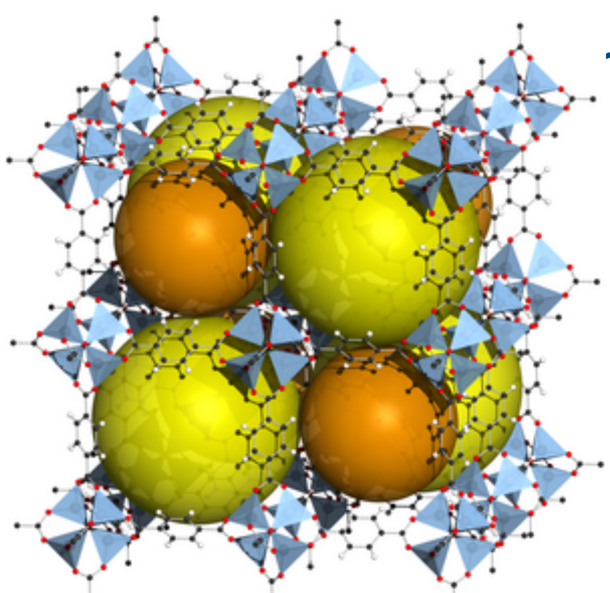
Timeline

1st MOF synthesized by Yaghi, who coined the term “MOF”

JACS **1995**, *117,* 10401–10402.

Early foundations | Birth of MOFs

1990 **2000**



Nature **1999**, *402,* 276–279.

Yaghi’s MOF-5:
high surface area
and porosity

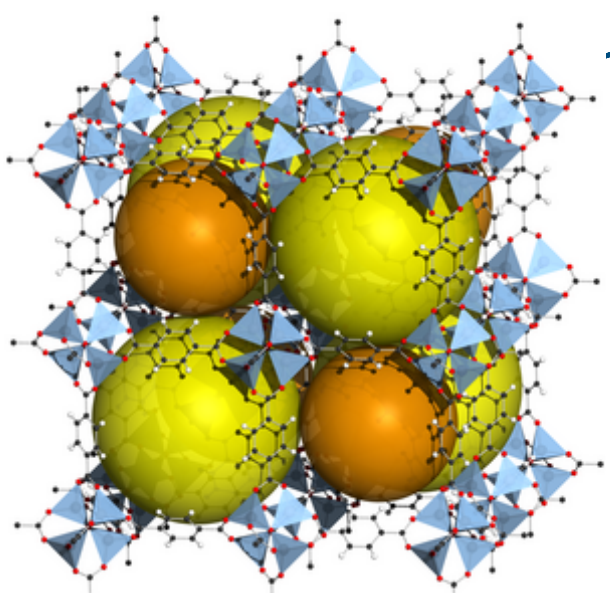
Timeline

1st MOF synthesized by Yaghi, who coined the term "MOF"

JACS **1995**, *117*, 10401–10402.

Early foundations | Birth of MOFs | Expansion and practical applications

1990 | 2000 | 2010



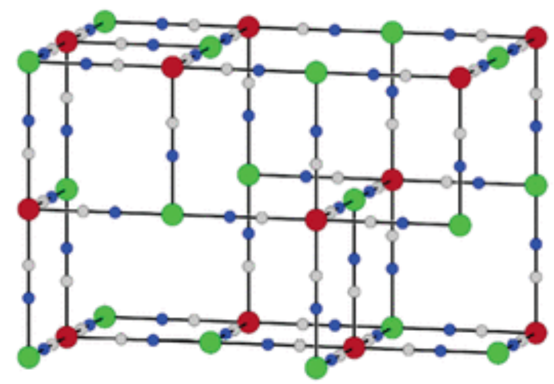
Nature **1999**, *402*, 276–279.

Yaghi's MOF-5:
high surface area
and porosity

Timeline

1st MOF synthesized by Yaghi, who coined the term "MOF"

JACS **1995**, *117,* 10401–10402.

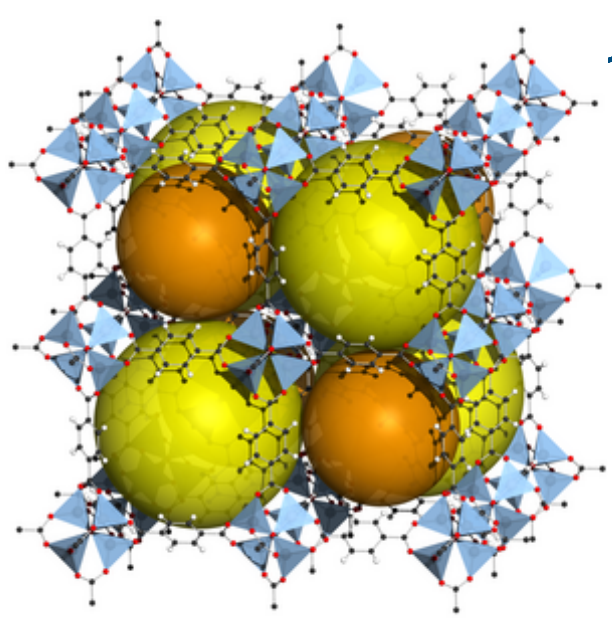


JACS **2005**, *127,* 6506–6507.

First MOF publication on **H_2 storage** from the Long group

Early foundations | **Birth of MOFs** | **Expansion and practical applications**

1990 | **2000** | **2010**



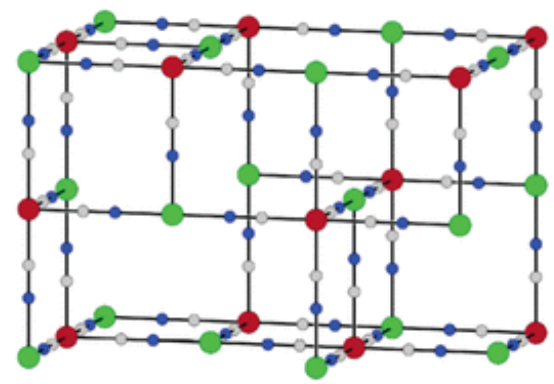
Nature **1999**, *402,* 276–279.

Yaghi's MOF-5:
high surface area and porosity

Timeline

1st MOF synthesized by Yaghi, who coined the term “MOF”

JACS **1995**, *117,* 10401–10402.

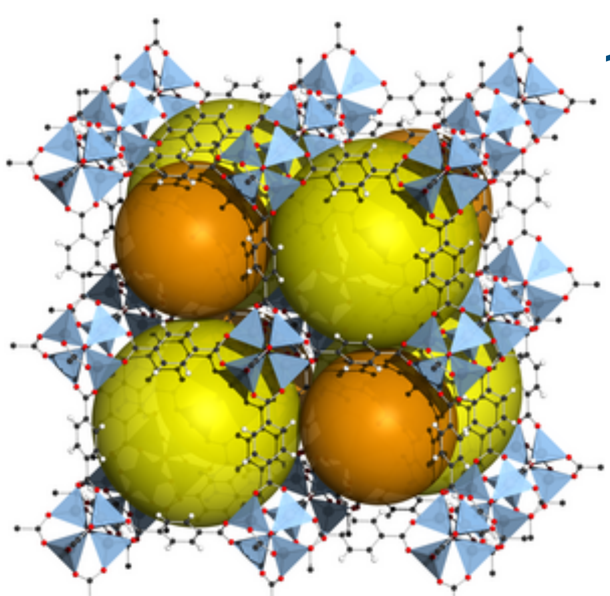


JACS **2005**, *127,* 6506–6507.

First MOF publication on **H_2 storage** from the Long group

Early foundations | Birth of MOFs | Expansion and practical applications | Commercial interests

1990 **2000** **2010** **Now**



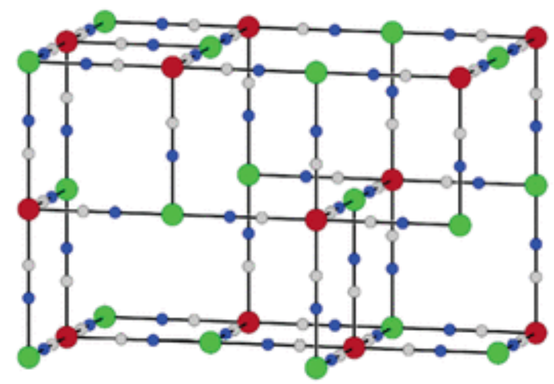
Nature **1999**, *402,* 276–279.

Yaghi’s MOF-5:
high surface area and porosity

Timeline

1st MOF synthesized by Yaghi, who coined the term "MOF"

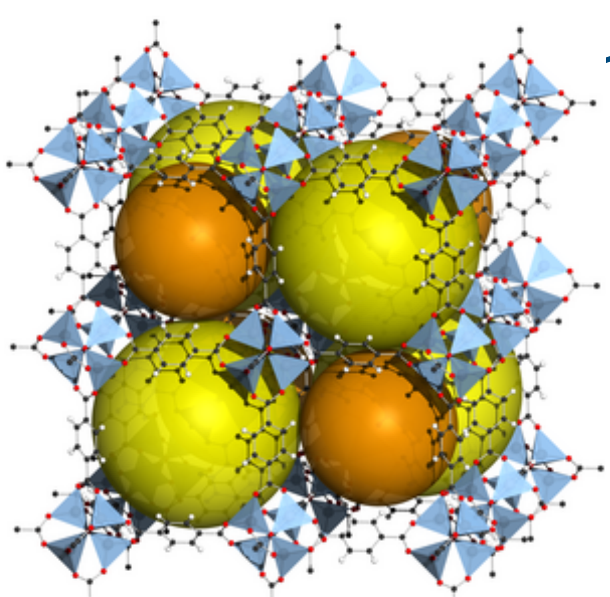
JACS **1995**, *117*, 10401–10402.



JACS **2005**, *127*, 6506–6507.

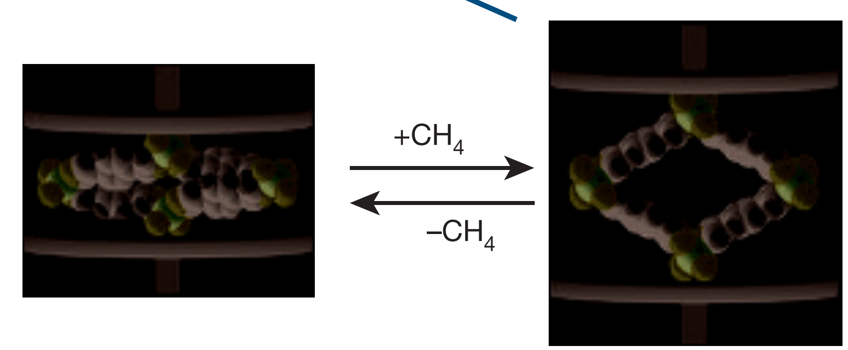
First MOF publication on **H_2 storage** from the Long group

Early foundations | **1990** | Birth of MOFs | **2000** | Expansion and practical applications | **2010** | Commercial interests | **Now**

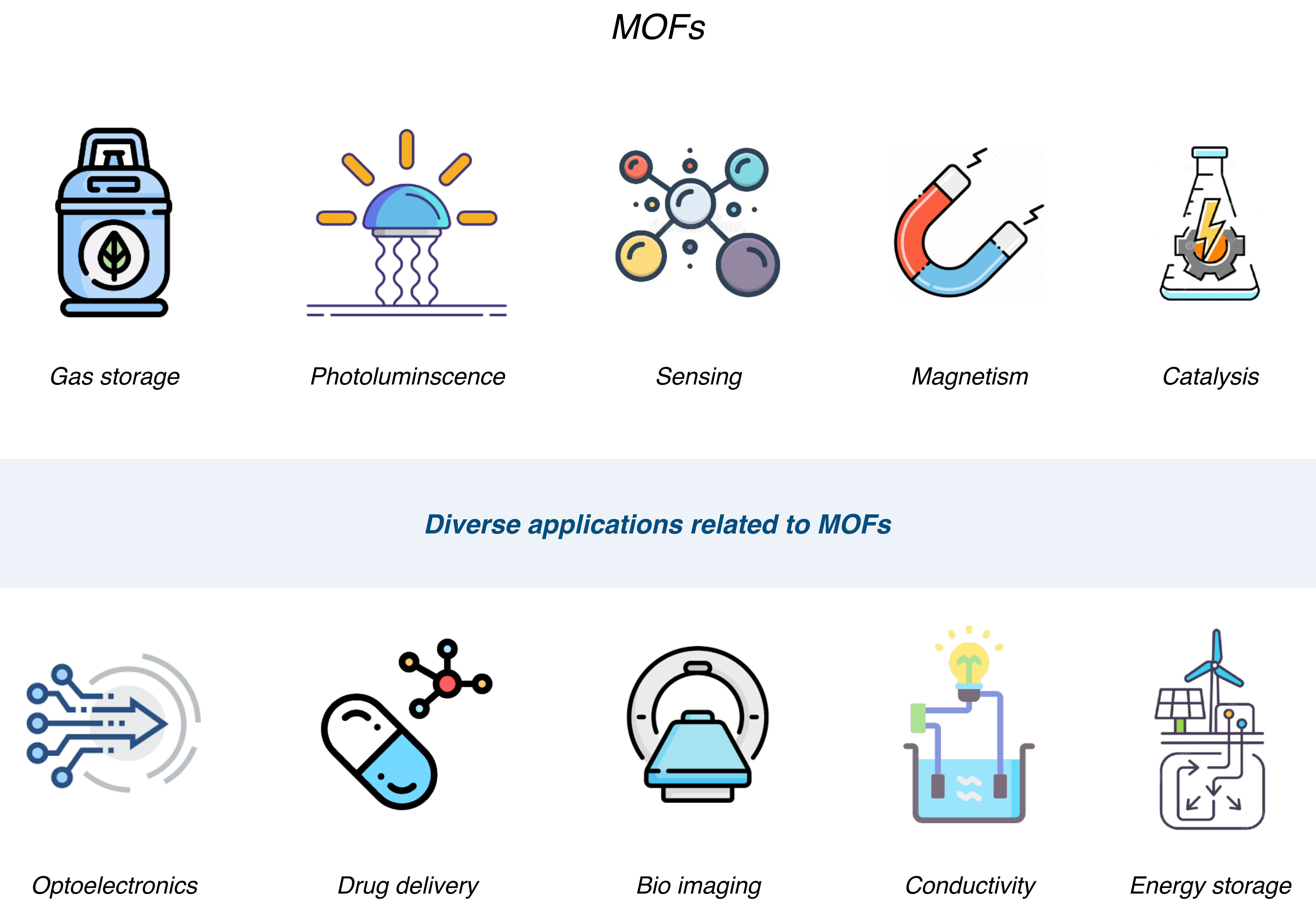


Nature **1999**, *402*, 276–279.

Yaghi's MOF-5:
high surface area and porosity



Nature **2015**, 527, 357 – 361.


MOFs
Gas storage
Photoluminscence
Sensing
Magnetism
Catalysis
Diverse applications related to MOFs
Optoelectronics
Drug delivery
Bio imaging
Conductivity
Energy storage

MOFs

Catalysis

Diverse applications related to MOFs

Outline

What are MOFs?

How to synthesize MOFs?

Organic synthetic applications MOFs

Outline

What are MOFs?

How to synthesize MOFs?

Organic synthetic applications MOFs

What are MOFs?

MOF: Metal-organic framework

What are MOFs?

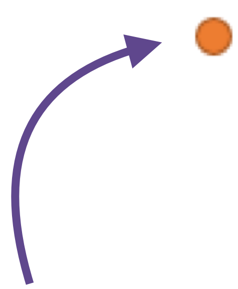
MOF: Metal-organic framework

class of crystalline materials with ultrahigh porosity

What are MOFs?

MOF: Metal-organic framework

class of crystalline materials with ultrahigh porosity

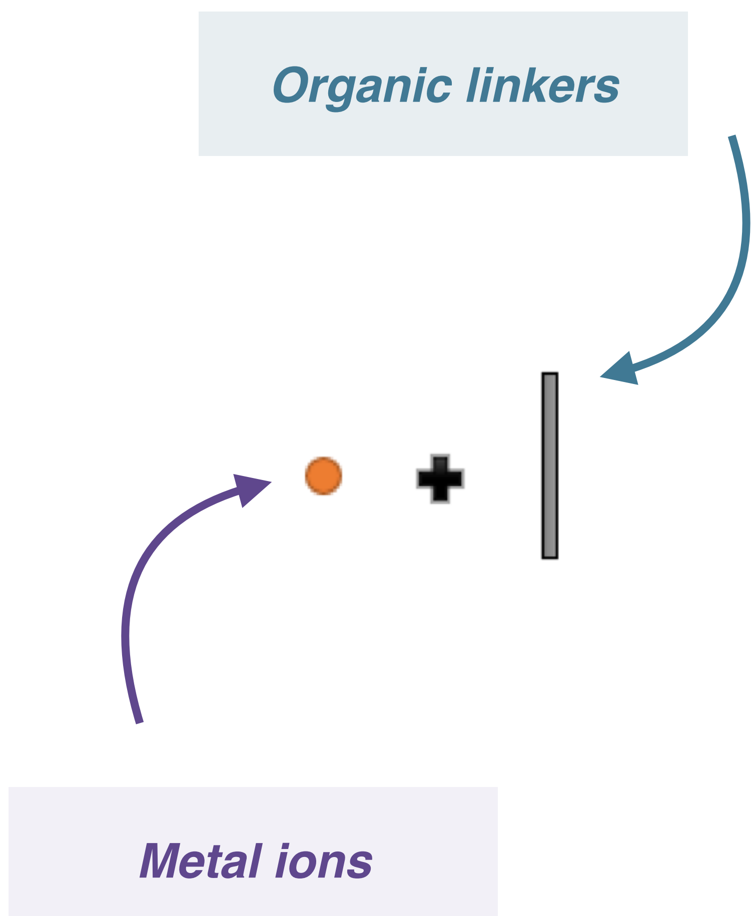


Metal ions

What are MOFs?

MOF: Metal-organic framework

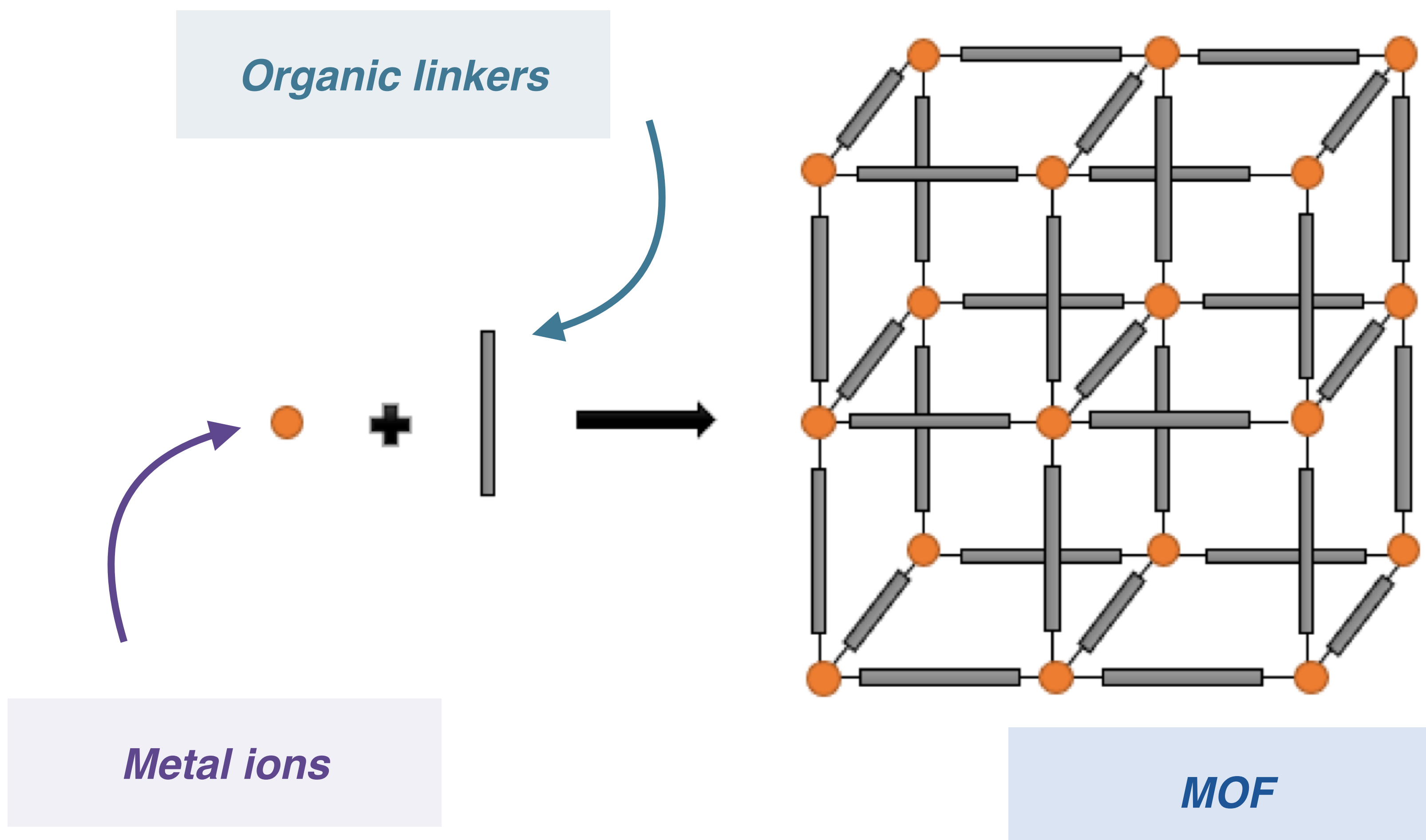
class of crystalline materials with ultrahigh porosity



What are MOFs?

MOF: Metal-organic framework

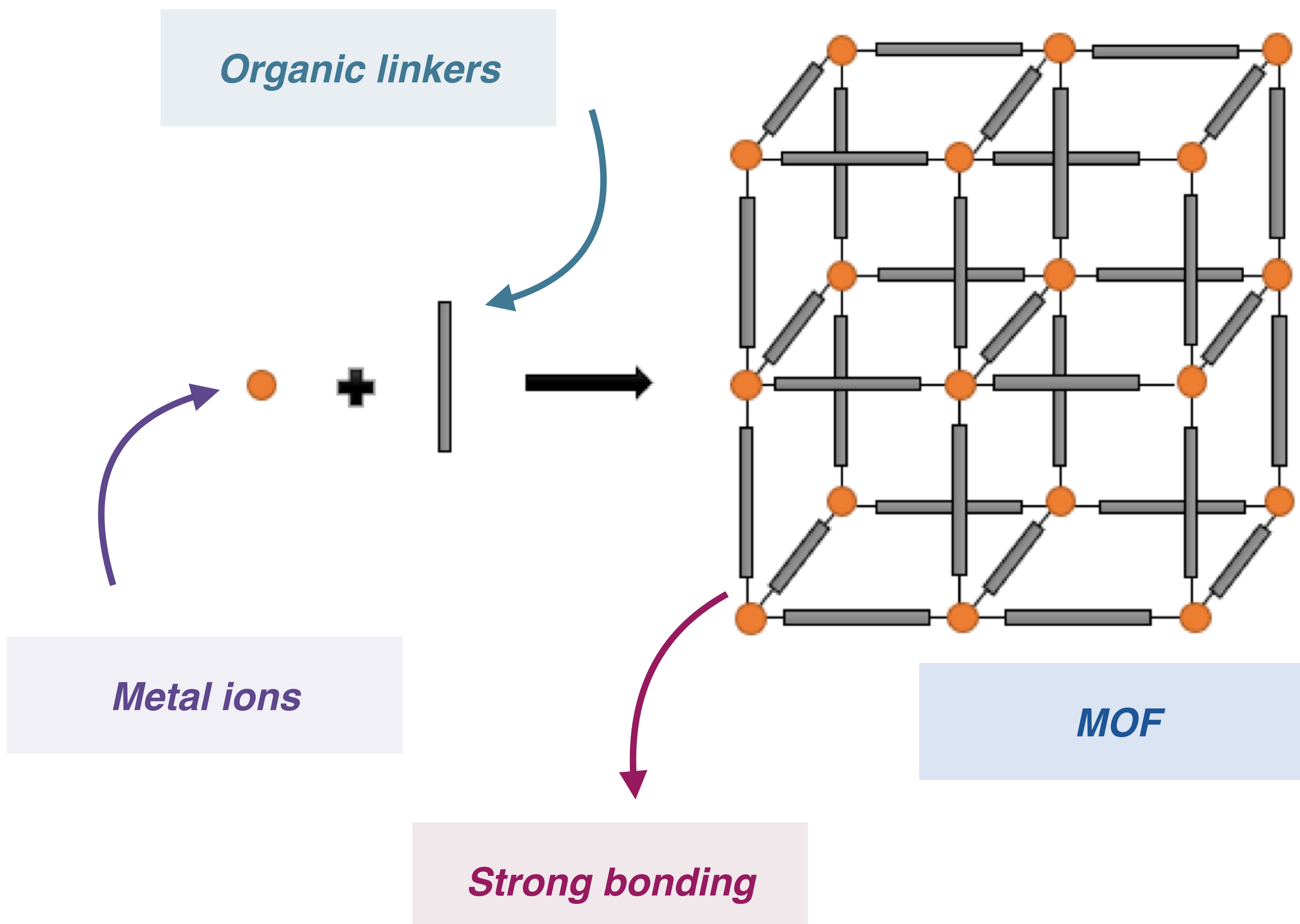
class of crystalline materials with ultrahigh porosity



What are MOFs?

MOF: Metal-organic framework

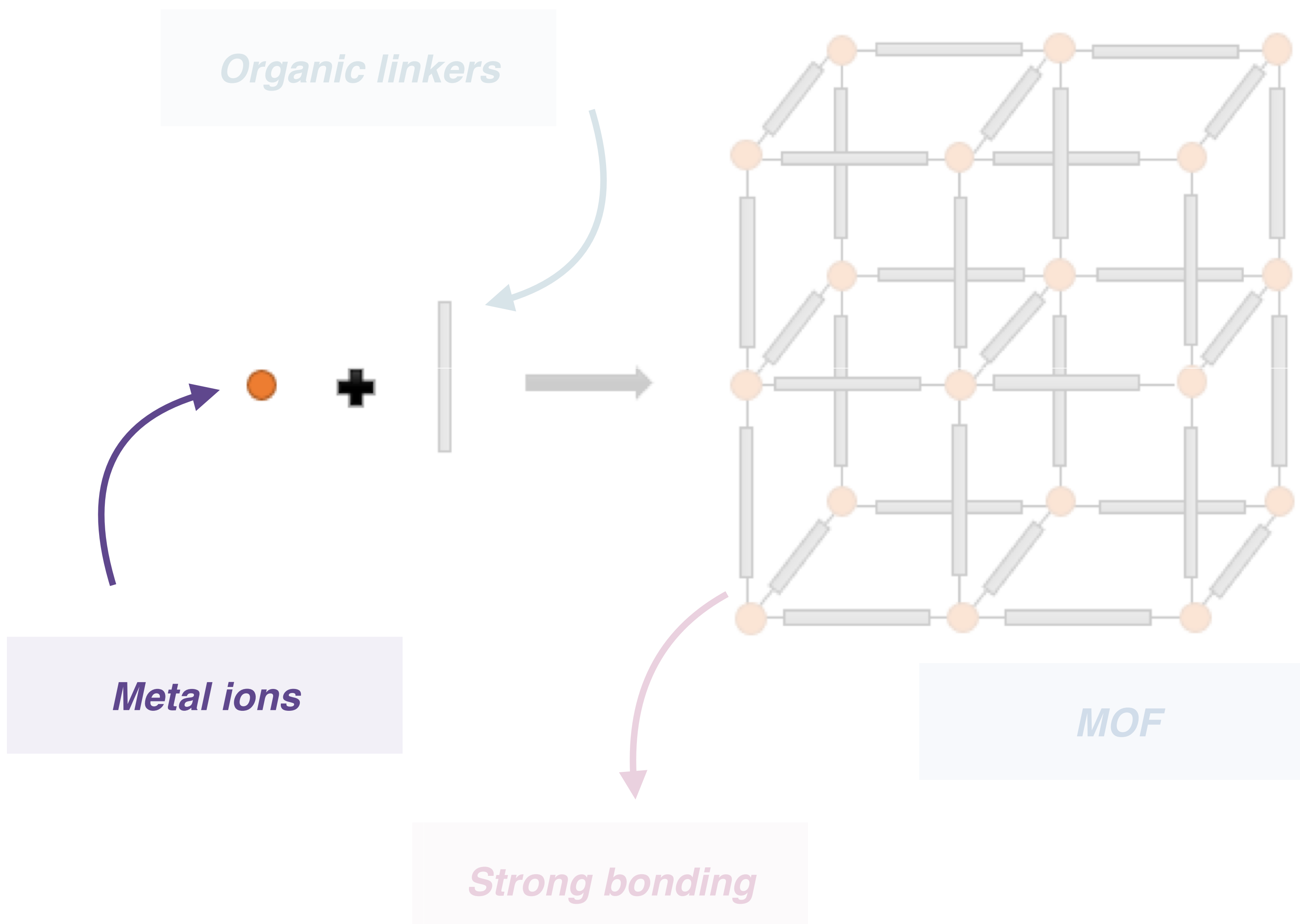
class of crystalline materials with ultrahigh porosity



What are MOFs?

MOF: Metal-organic framework

class of crystalline materials with ultrahigh porosity



Metal ions

Metal ions

Metal ions

Metal ions

Mg^{2+}

Mn^{2+}

Cu^{+}

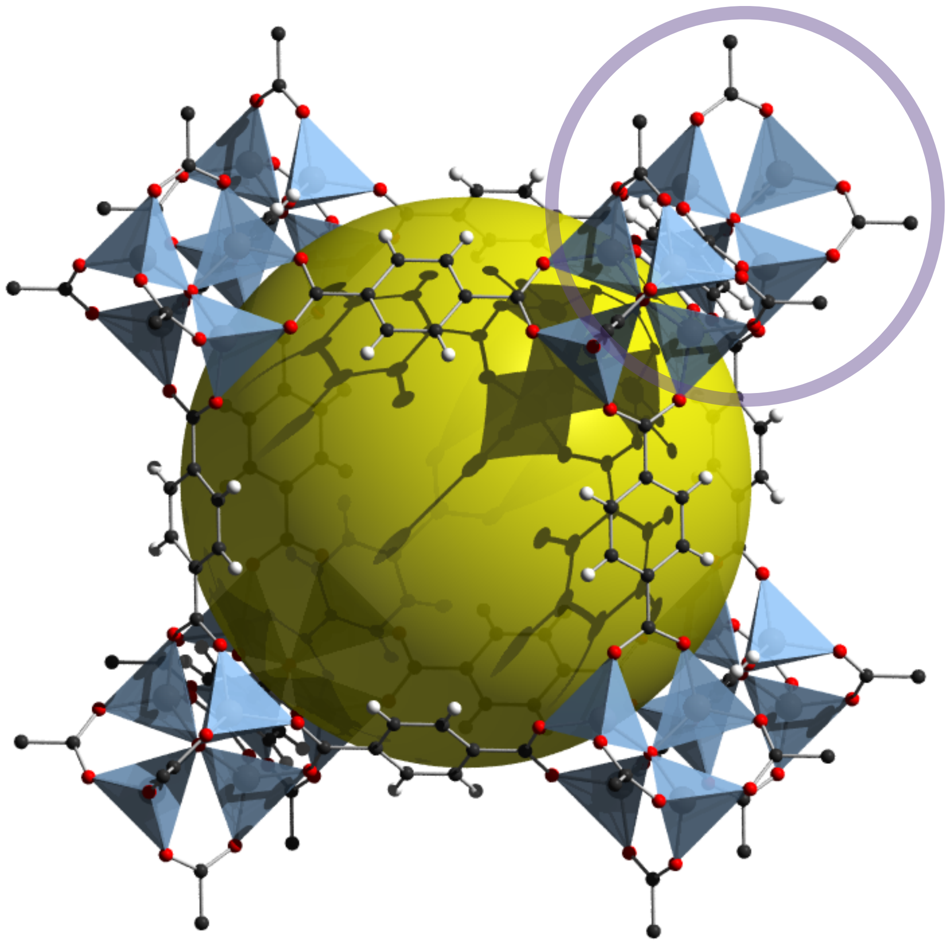
Al^{3+}

Metal ions

Metal ions: metal clusters

Metal ions

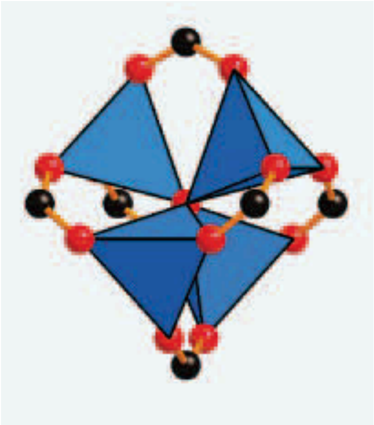
Metal ions: metal clusters



MOF - 5

Metal ions

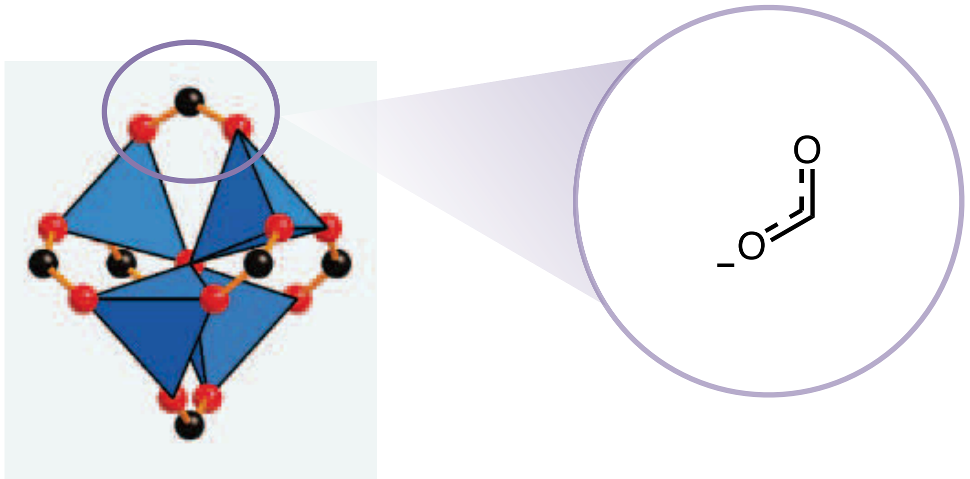
Metal ions: metal clusters



$Zn_4O(CO_2)_6$

Metal ions

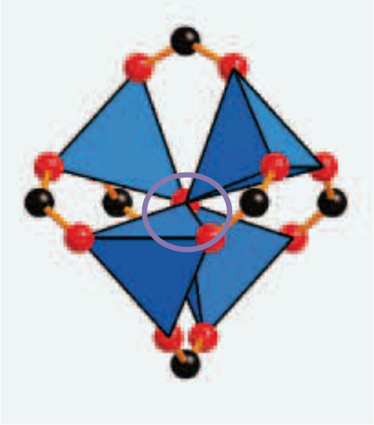
Metal ions: metal clusters



$Zn_4O(\mathbf{CO_2})_6$

Metal ions

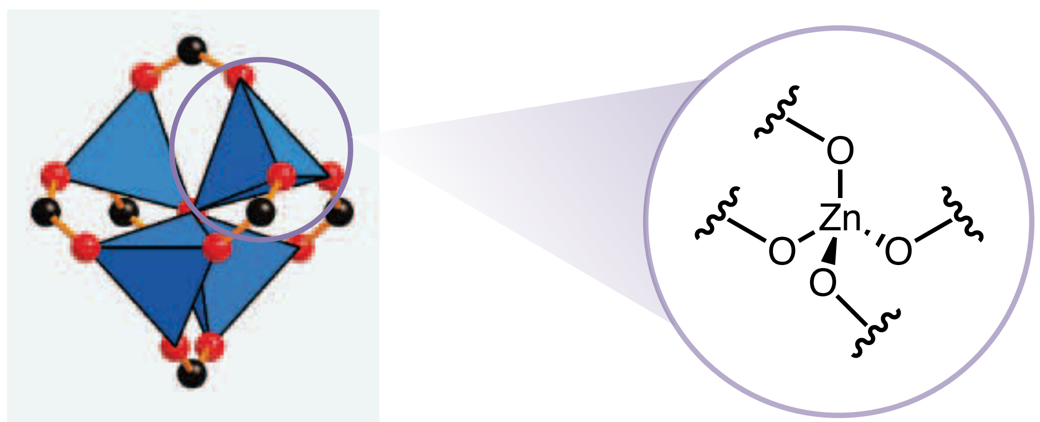
Metal ions: metal clusters



$Zn_4\mathbf{O}(CO_2)_6$

Metal ions

Metal ions: metal clusters

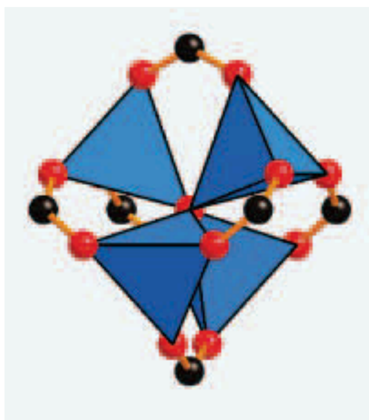


Zn$_4$O(CO$_2$)$_6$

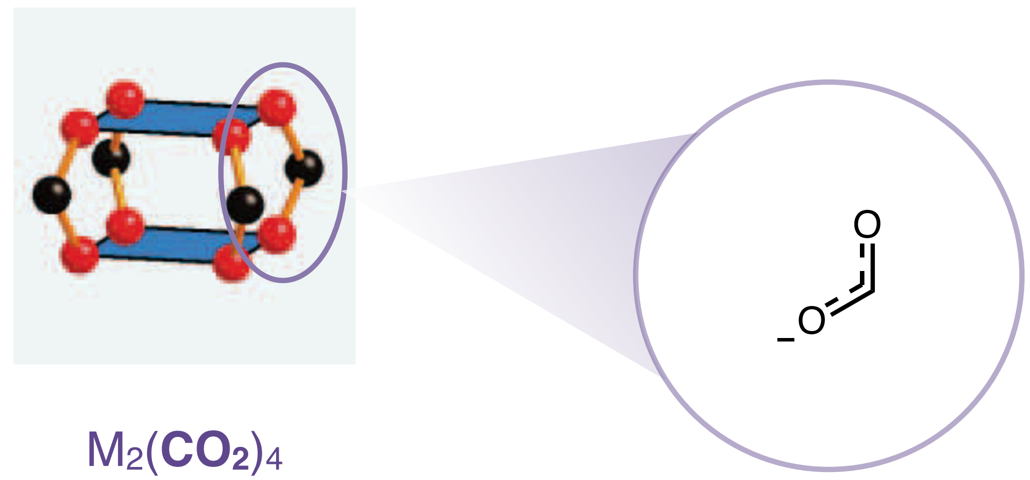
Tetrahedral

Metal ions

Metal ions: metal clusters



$Zn_4O(CO_2)_6$

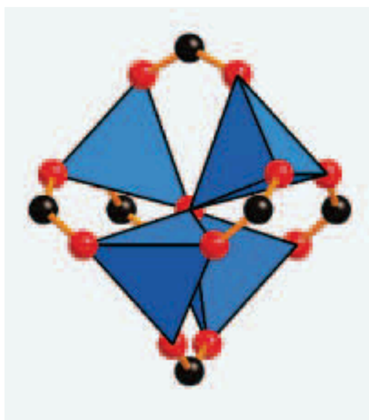


$M_2(\mathbf{CO_2})_4$

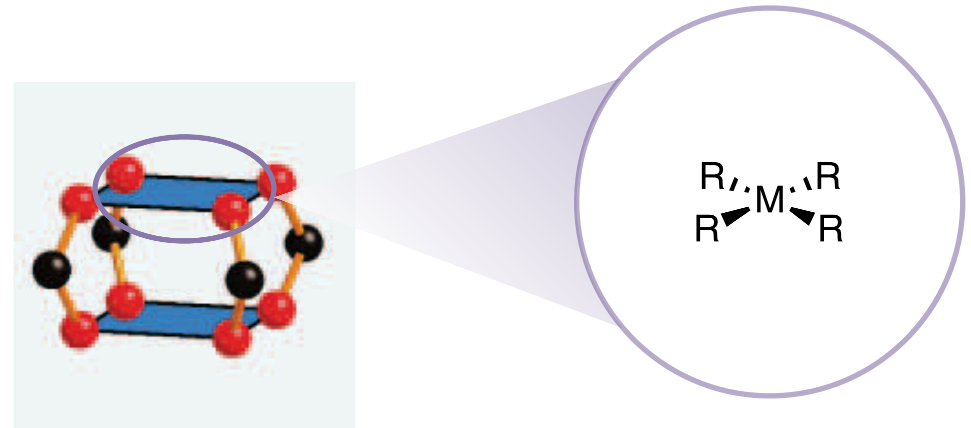
M = Cu, Zn, Fe, Mo, Cr, Co, Ru

Metal ions

Metal ions: metal clusters



$Zn_4O(CO_2)_6$



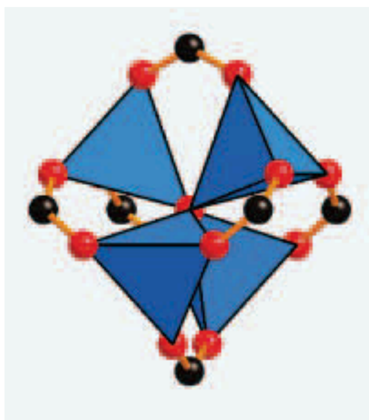
M_2 $(CO_2)_4$

M = Cu, Zn, Fe, Mo, Cr, Co, Ru

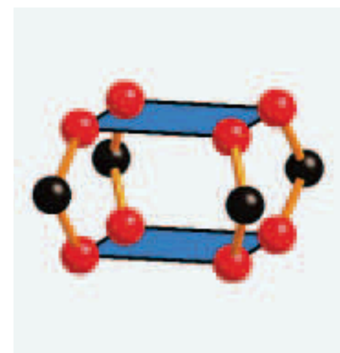
Square planar

Metal ions

Metal ions: metal clusters

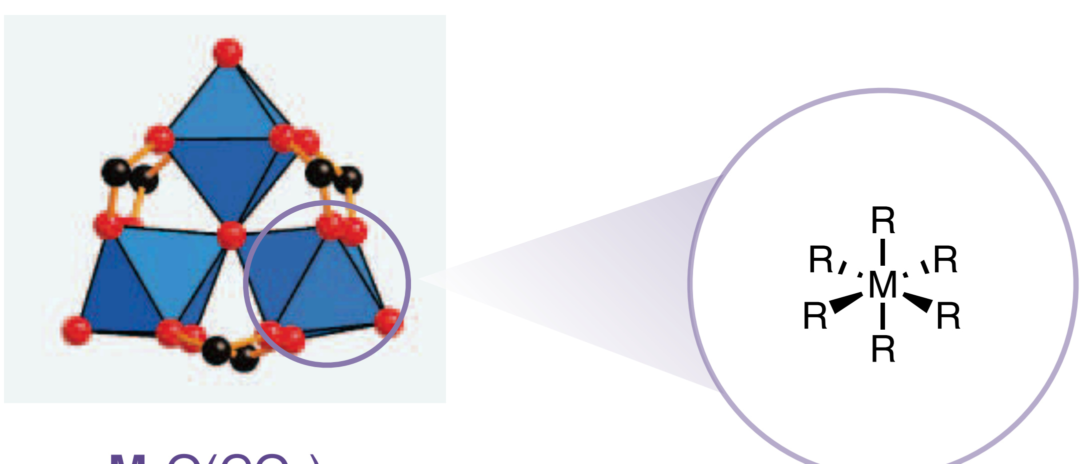


$Zn_4O(CO_2)_6$



$M_2(CO_2)_4$

M = Cu, Zn, Fe, Mo, Cr, Co, Ru



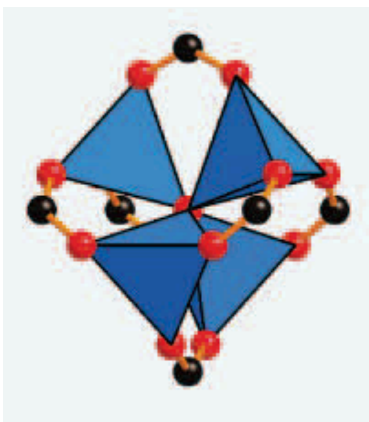
$\mathbf{M_3}O(CO_2)_6$

M = Zn, Cr, In, Ga

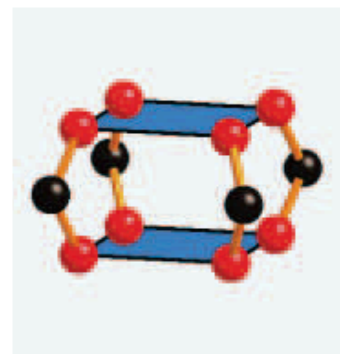
Octahedral

Metal ions

Metal ions: metal clusters

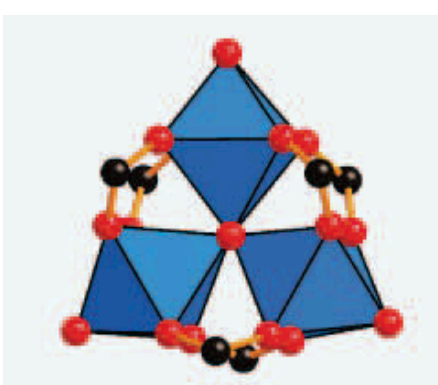


$Zn_4O(CO_2)_6$



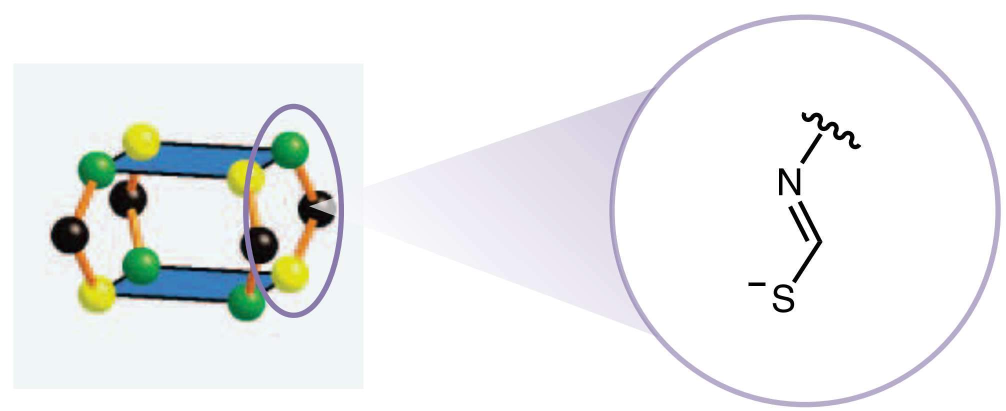
$M_2(CO_2)_4$

M = Cu, Zn, Fe, Mo, Cr, Co, Ru



$M_3O(CO_2)_6$

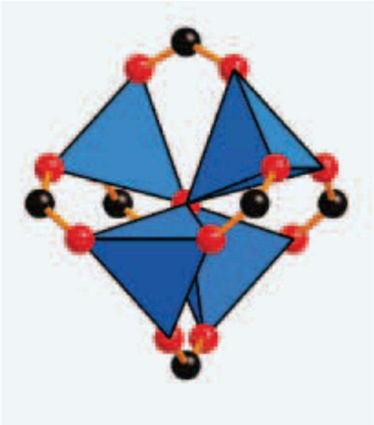
M = Zn, Cr, In, Ga



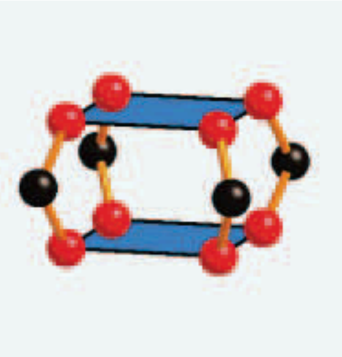
Cu_2(**CNS**)$_4$

Metal ions

Metal ions: metal clusters

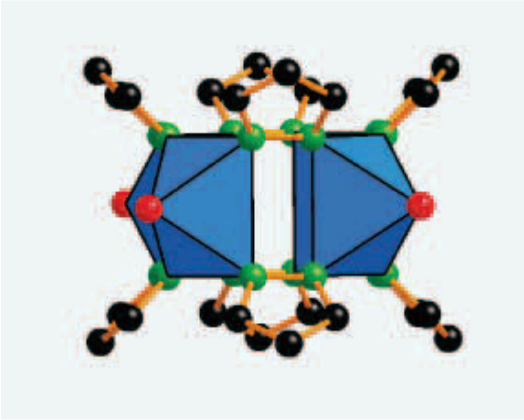


$Zn_4O(CO_2)_6$

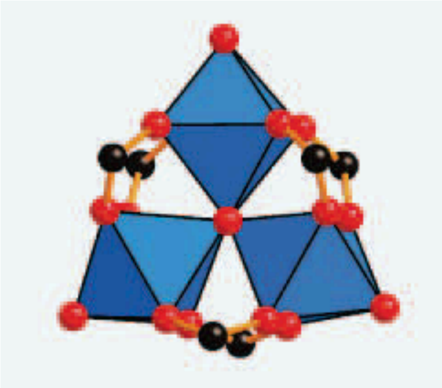


$M_2(CO_2)_4$

M = Cu, Zn, Fe, Mo, Cr, Co, Ru

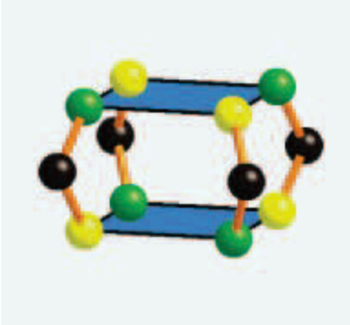


$Ni_4(C_3H_3N_2)_8$

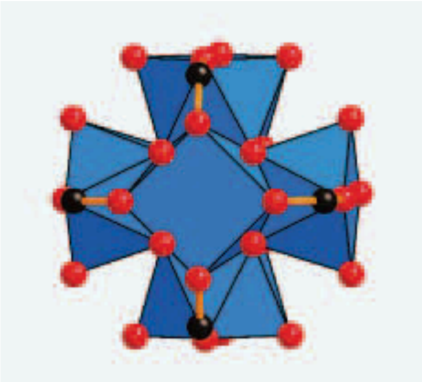


$M_3O(CO_2)_6$

M = Zn, Cr, In, Ga



$Cu_2(CNS)_4$

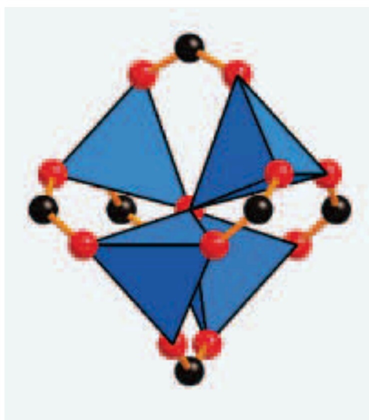


$Zr_2O_8(CO_2)_8$

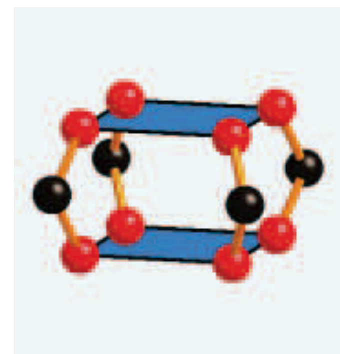
Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

Metal ions

Metal ions: metal clusters (secondary building units)

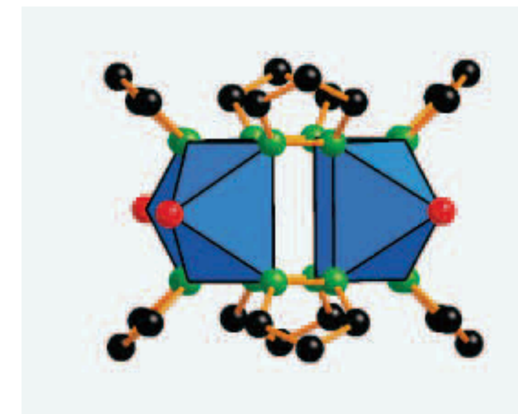


$Zn_4O(CO_2)_6$

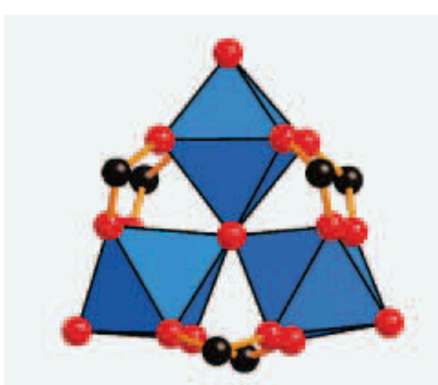


$M_2(CO_2)_4$

M = Cu, Zn, Fe, Mo, Cr, Co, Ru

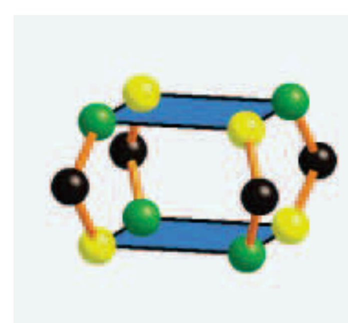


$Ni_4(C_3H_3N_2)_8$

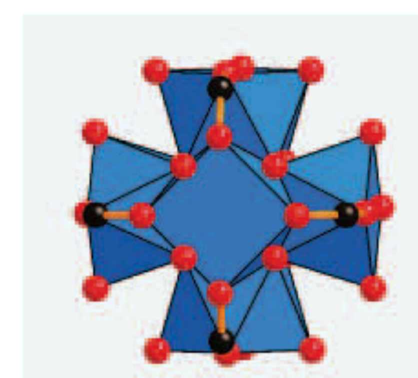


$M_3O(CO_2)_6$

M = Zn, Cr, In, Ga



$Cu_2(CNS)_4$



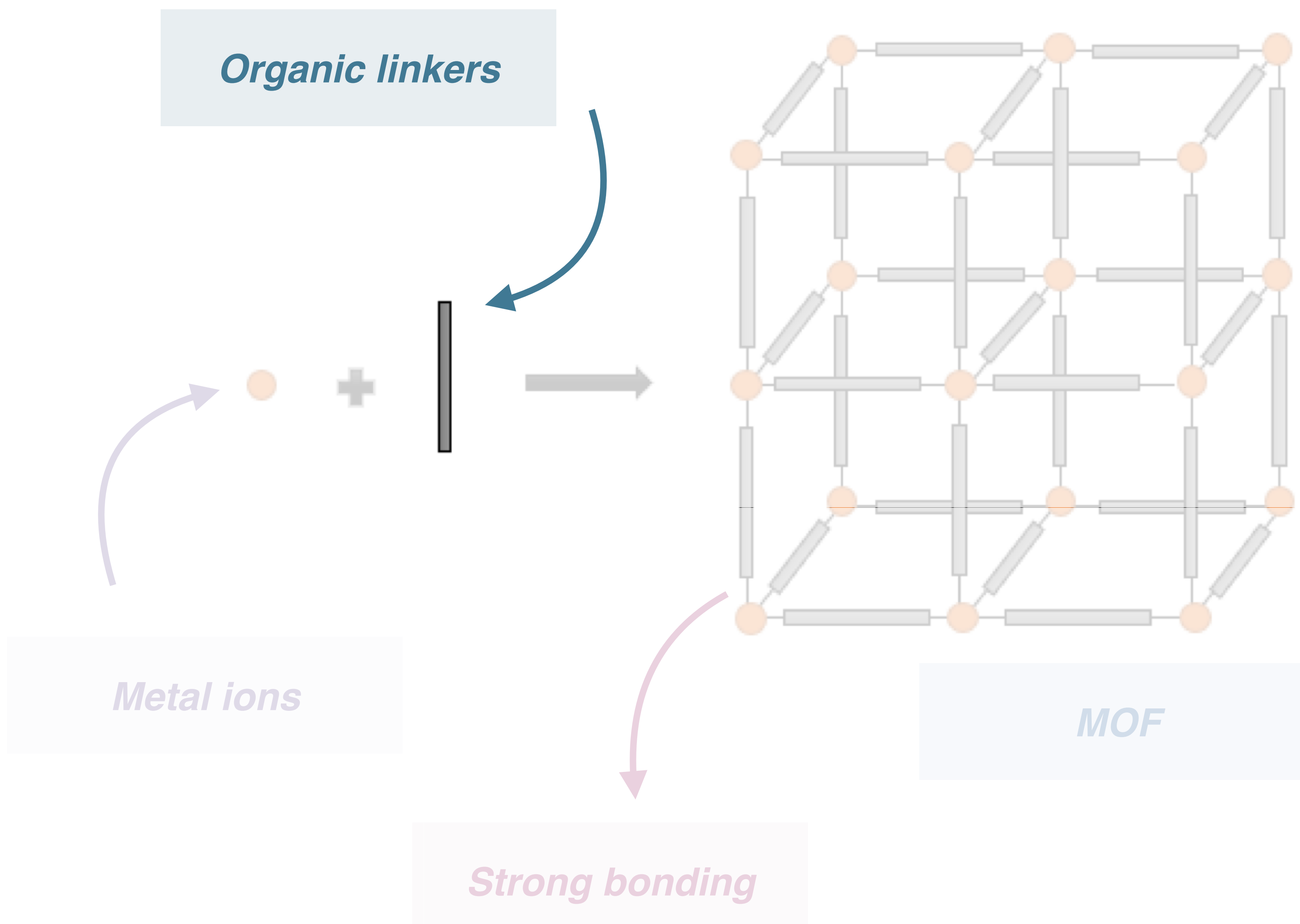
$Zr_2O_8(CO_2)_8$

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

What are MOFs?

MOF: Metal-organic framework

class of crystalline materials with ultrahigh porosity



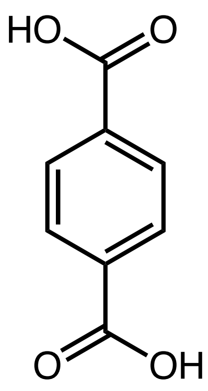
Organic linkers

Organic linkers: contain heteroatom

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

Organic linkers

Organic linkers: contain heteroatom

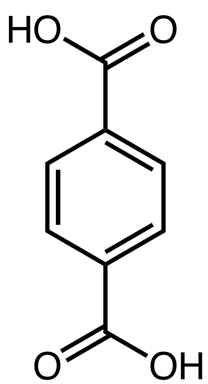


BDC

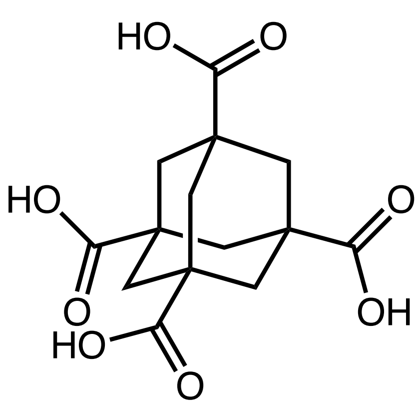
Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

Organic linkers

Organic linkers: contain heteroatom



BDC

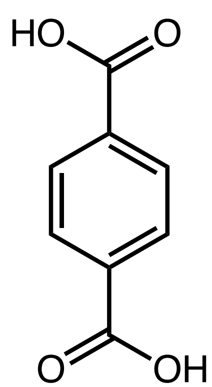


ATC

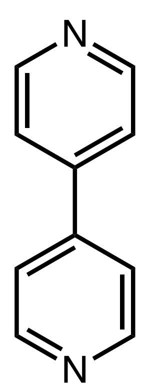
Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

Organic linkers

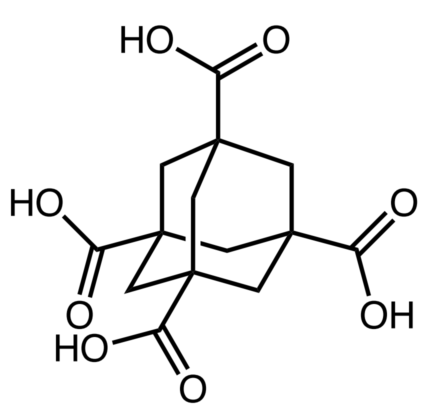
Organic linkers: contain heteroatom



BDC



4,4’-BPY

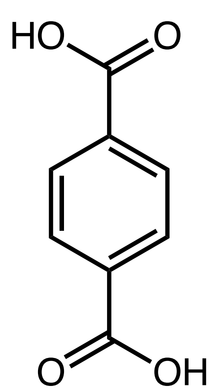


ATC

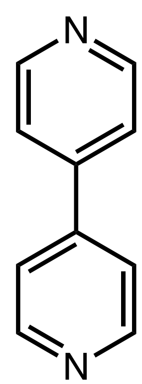
Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

Organic linkers

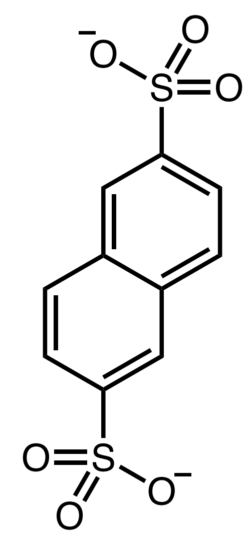
Organic linkers: contain heteroatom



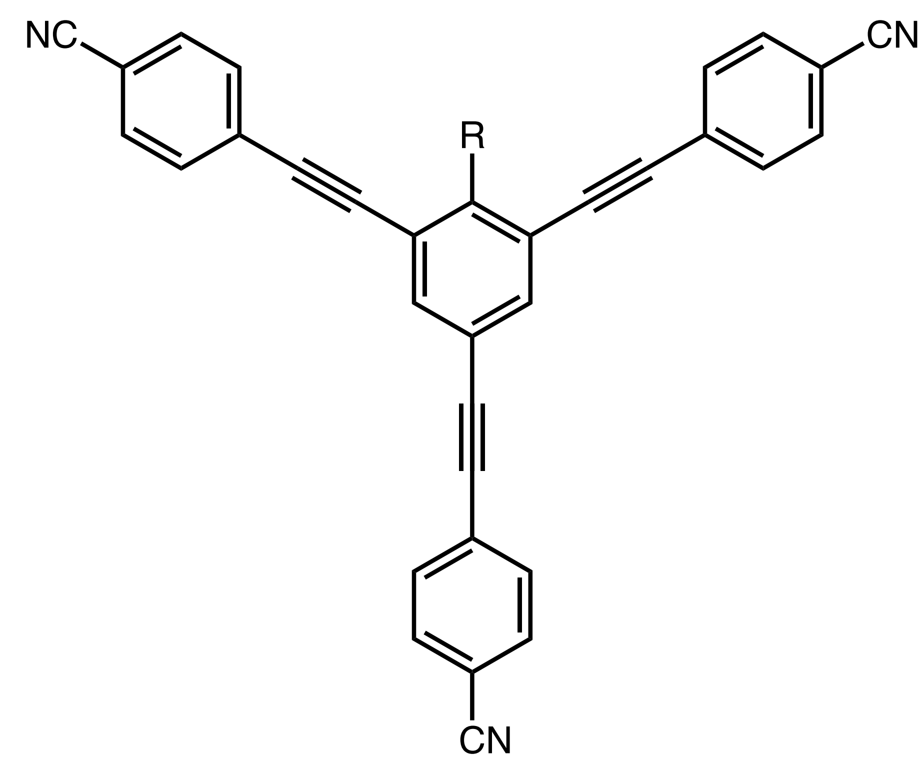
BDC



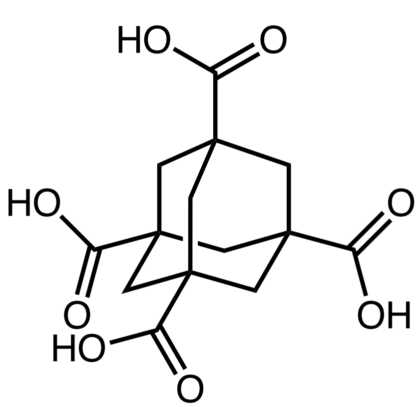
4,4’-BPY



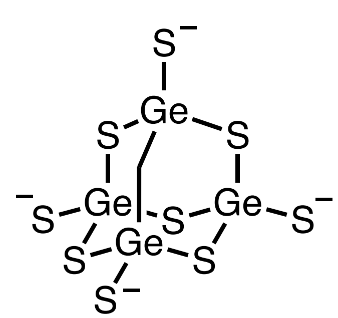
NDS2



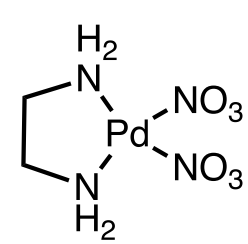
ECN



ATC



$Ge_4S_{10}^{4-}$



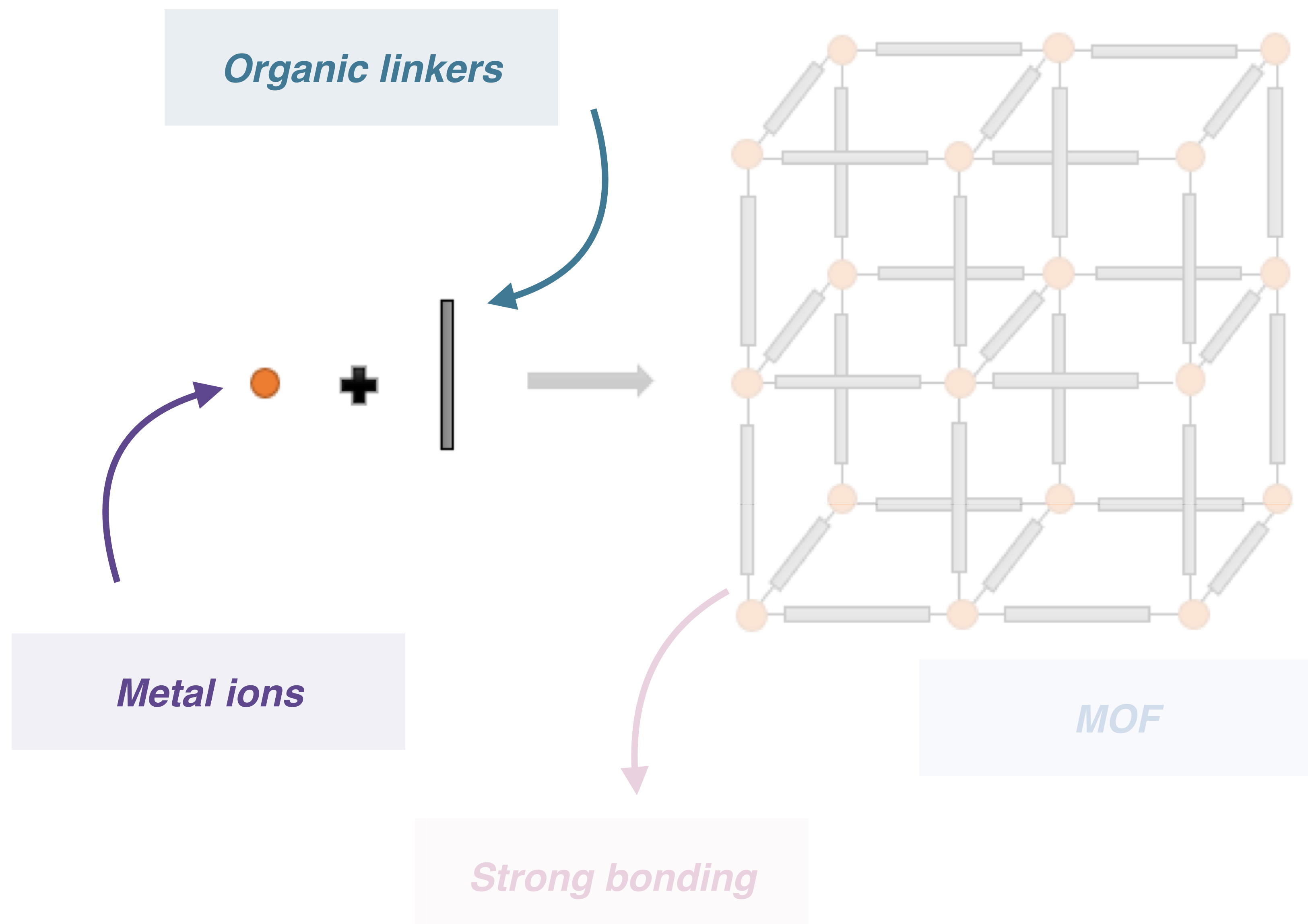
cis-PDA

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

What are MOFs?

MOF: Metal-organic framework

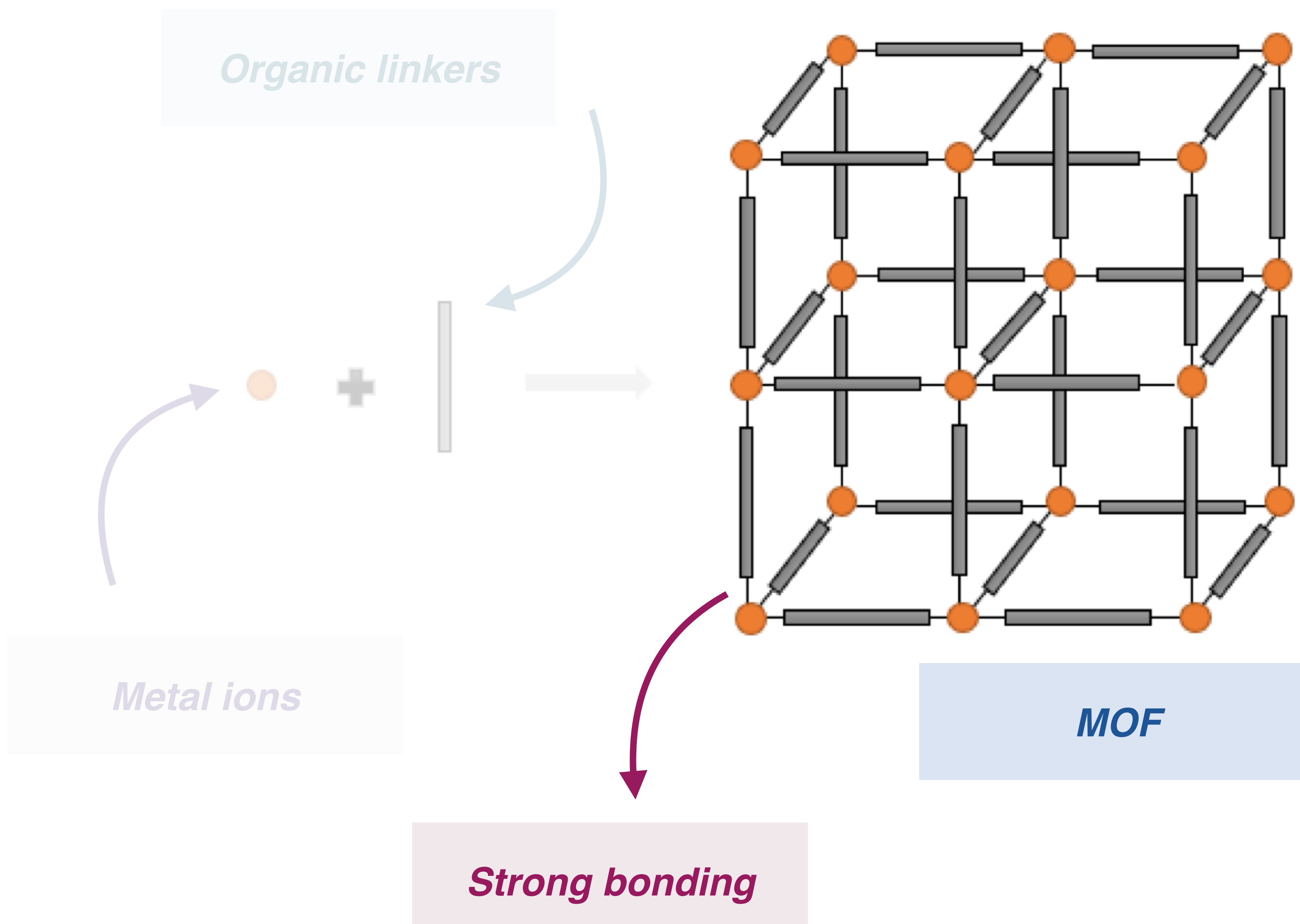
class of crystalline materials with ultrahigh porosity



What are MOFs?

MOF: Metal-organic framework

class of crystalline materials with ultrahigh porosity



Outline

What are MOFs?

How to synthesize MOFs?

Organic synthetic applications MOFs

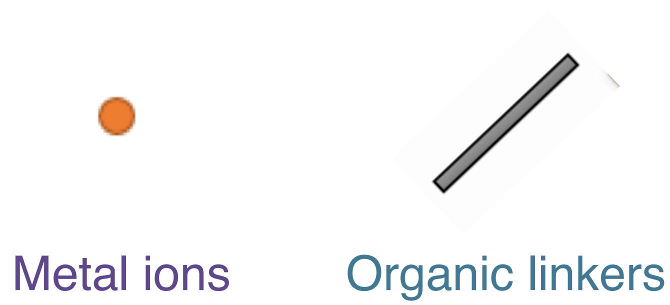
How to synthesize MOFs?

Reticular synthesis

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

How to synthesize MOFs?

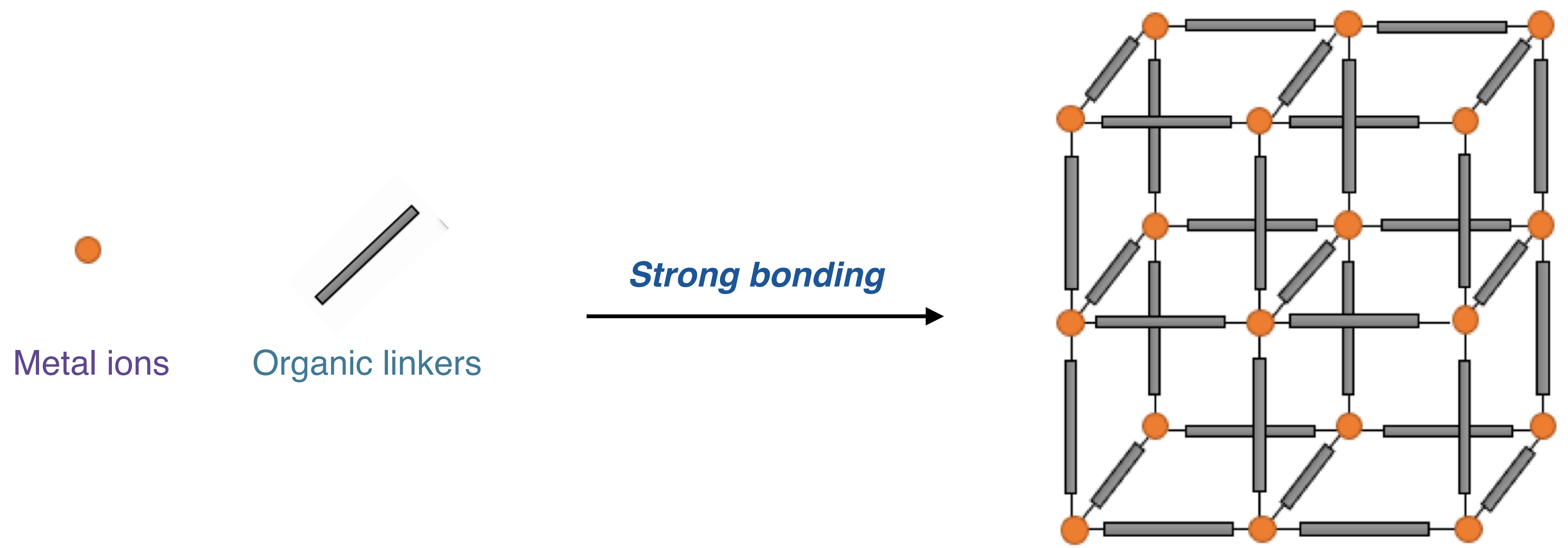
Reticular synthesis



Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013***, 341* (6149), 1230444.

How to synthesize MOFs?

Reticular synthesis



Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

How to synthesize MOFs?

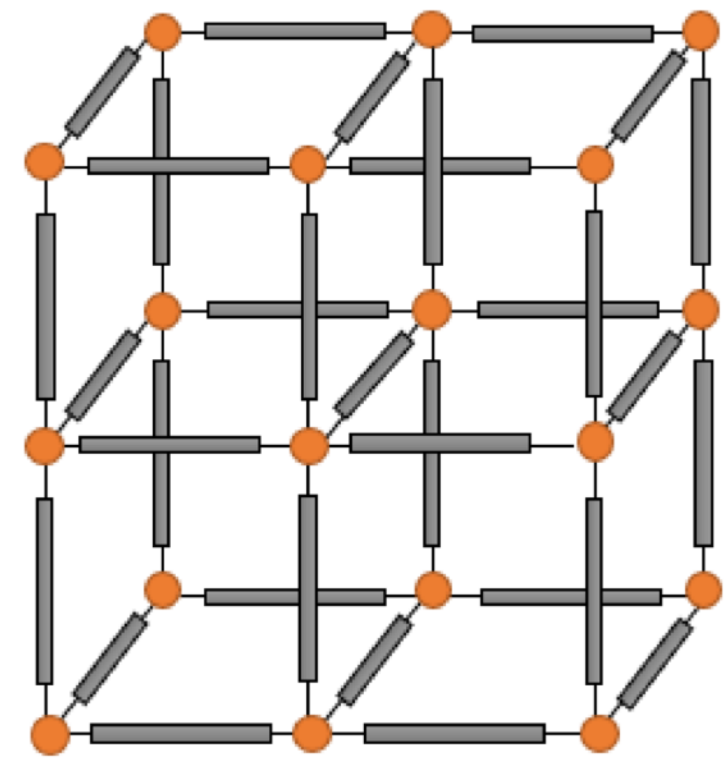
Reticular synthesis

Building blocks

Metal ions

Organic linkers

Strong bonding →



Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

How to synthesize MOFs?

Reticular synthesis

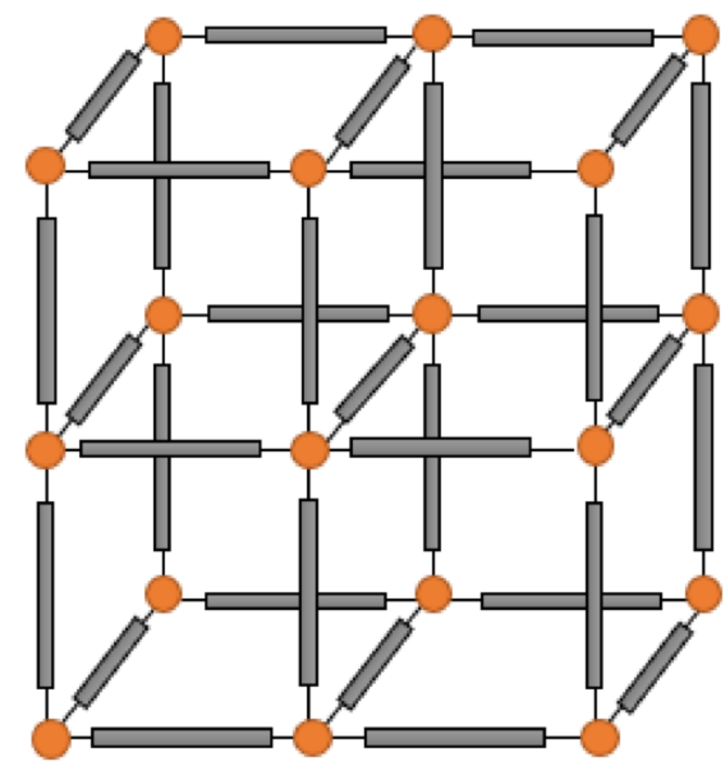
Building blocks

Metal ions

Organic linkers

Structural rigidity and integrity remained unchanged

Strong bonding



Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

How to synthesize MOFs?

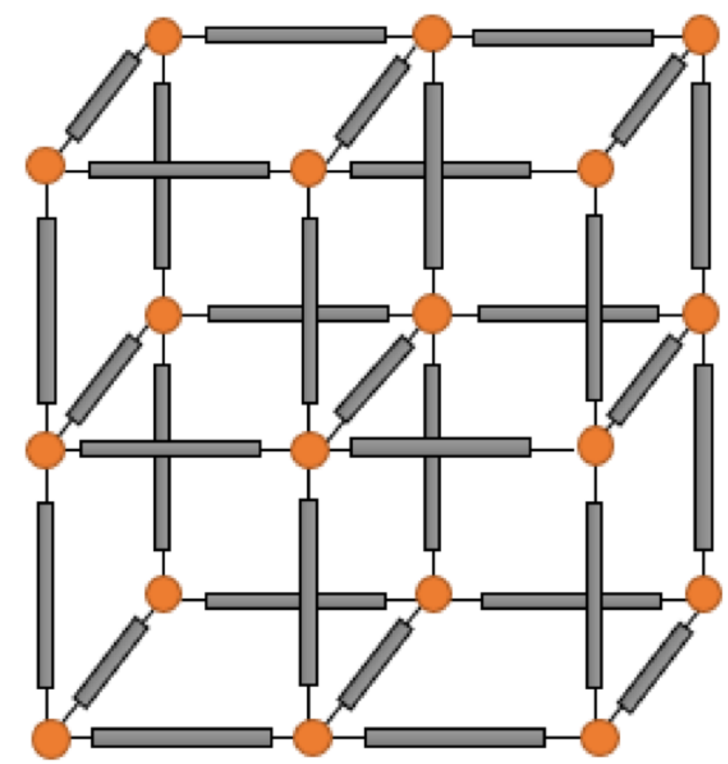
Reticular synthesis

Building blocks

Metal ions   Organic linkers

Structural rigidity and integrity remained unchanged

Strong bonding



Retrosynthesis: within the building blocks, bonds break and form

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

How to synthesize MOFs?

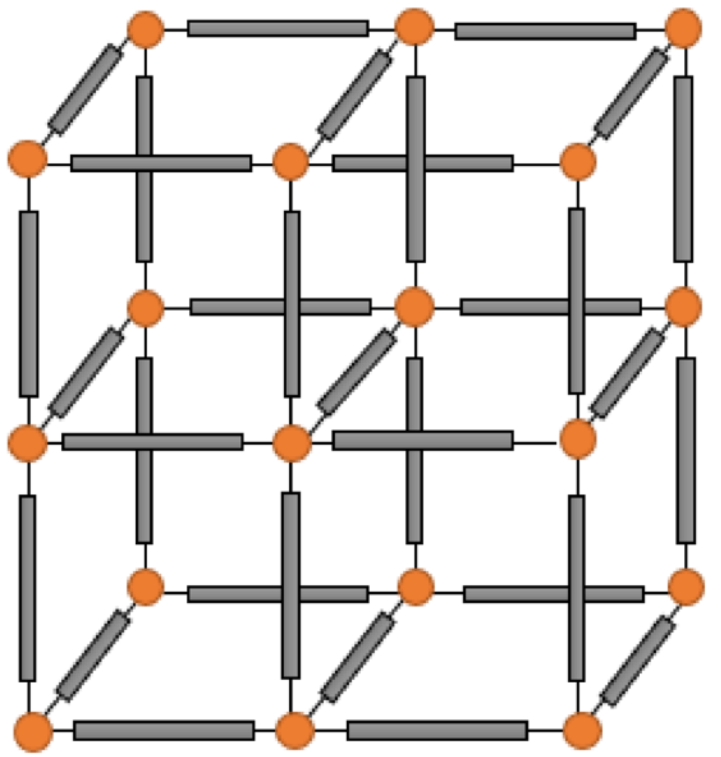
Reticular synthesis

Building blocks

Metal ions   Organic linkers

Structural rigidity and integrity remained unchanged

Strong bonding



Retrosynthesis: within the building blocks, bonds break and form

Supramolecular assembly: building blocks are linked by non-covalent interactions

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341* (6149), 1230444.

How to synthesize MOFs with experimental procedures?

Solvothermal synthesis

Electrochemical strategies

Mechanochemical strategies

Sonochemical strategies

Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chemistry of Materials* **2016**, *29* (1), 26-39.

How to synthesize MOFs with experimental procedures?

Solvothermal synthesis

Electrochemical strategies

Mechanochemical strategies

Sonochemical strategies

Microwave assisted synthesis

Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chemistry of Materials* **2016**, *29* (1), 26-39.

How to synthesize MOFs with experimental procedures?

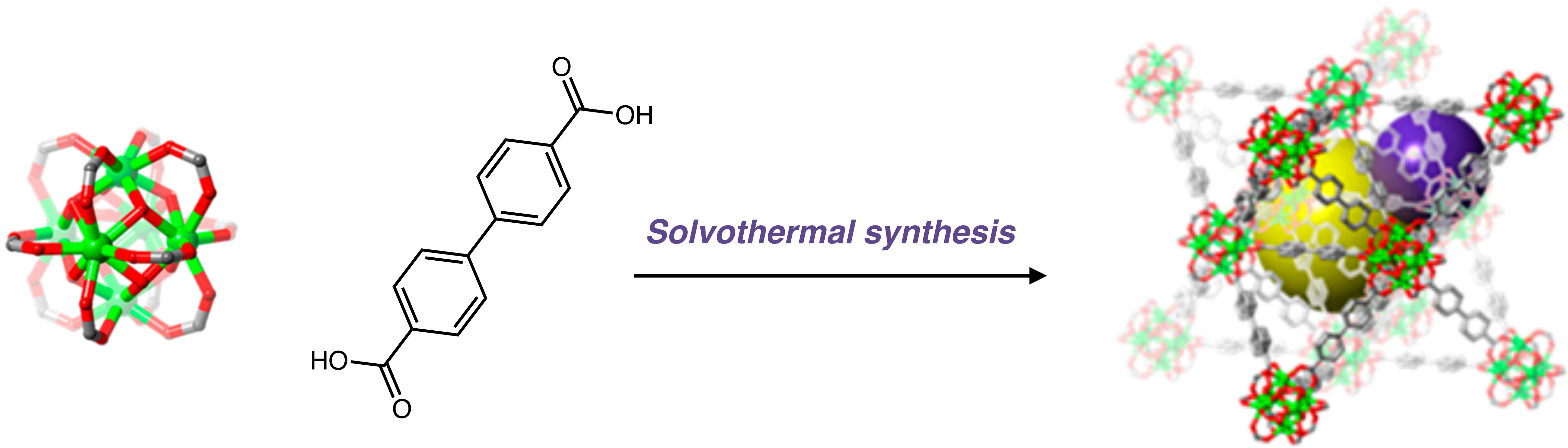
Solvothermal synthesis

Electrochemical strategies

Mechanochemical strategies

Sonochemical strategies

Microwave assisted synthesis



$Zr_6O_4(OH)_4$ BPDC UiO-67

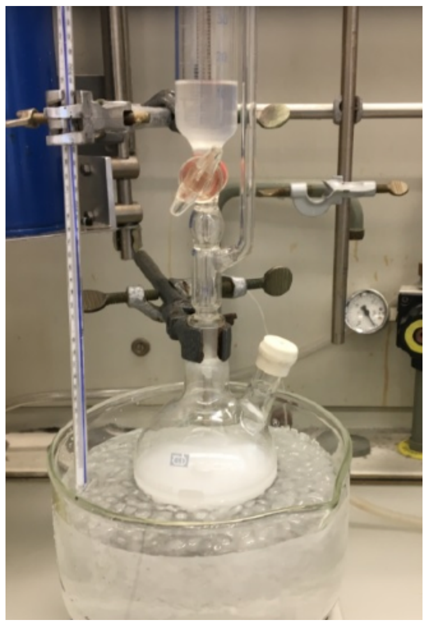
Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chemistry of Materials* **2016**, *29* (1), 26-39.

Solvothermal synthesis process

Streamline of organic synthesis

Solvothermal synthesis process

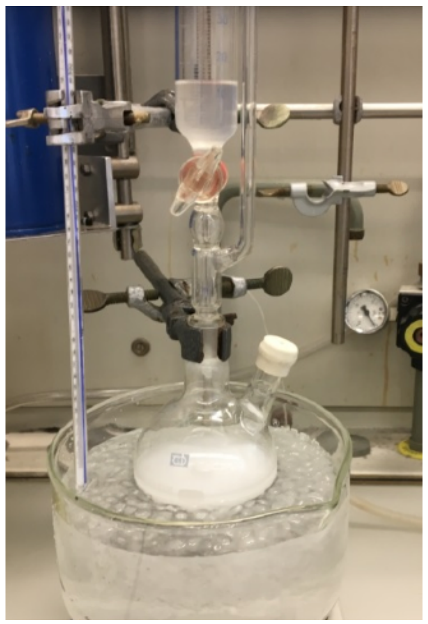
Streamline of organic synthesis



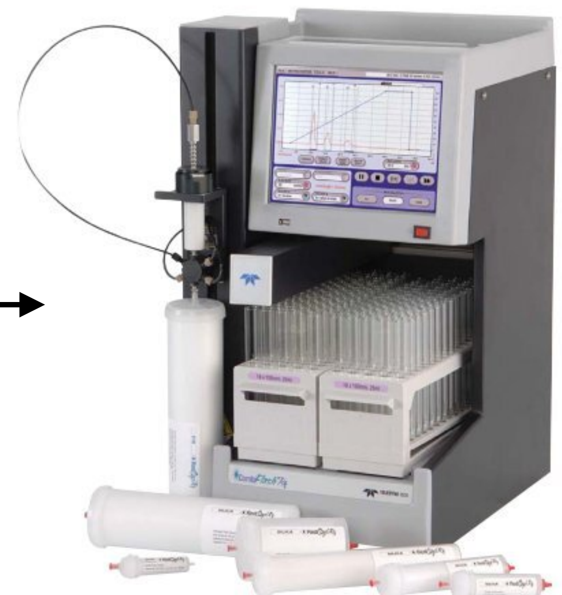
Reaction setup

Solvothermal synthesis process

Streamline of organic synthesis



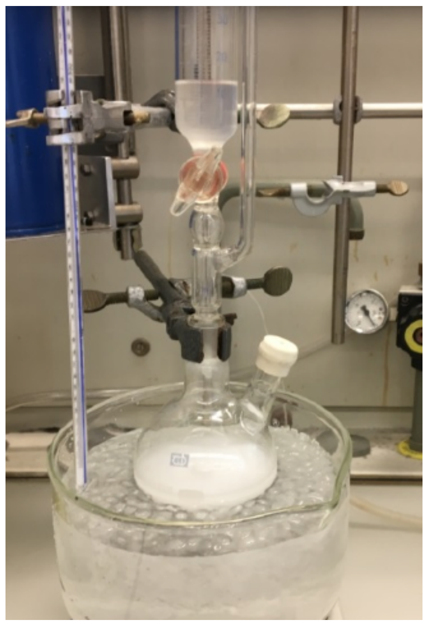
Reaction setup

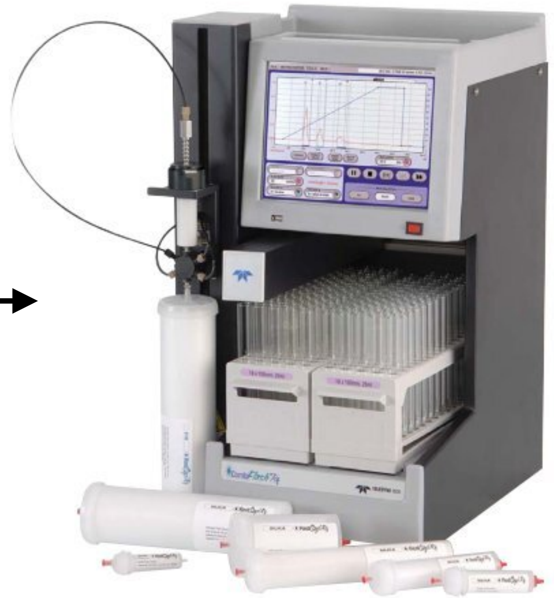


Purification

Solvothermal synthesis process

Streamline of organic synthesis





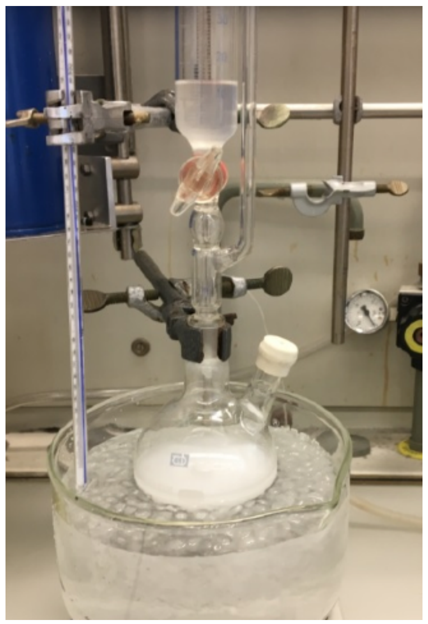
Reaction setup

Purification

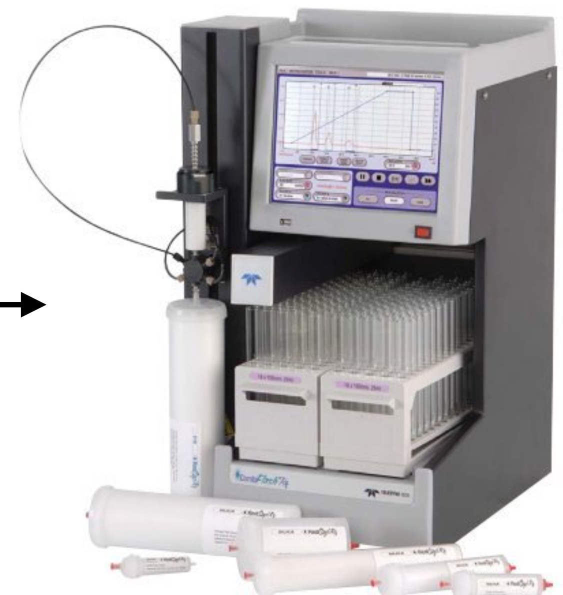
Structure analysis

Solvothermal synthesis process

Streamline of organic synthesis



Reaction setup



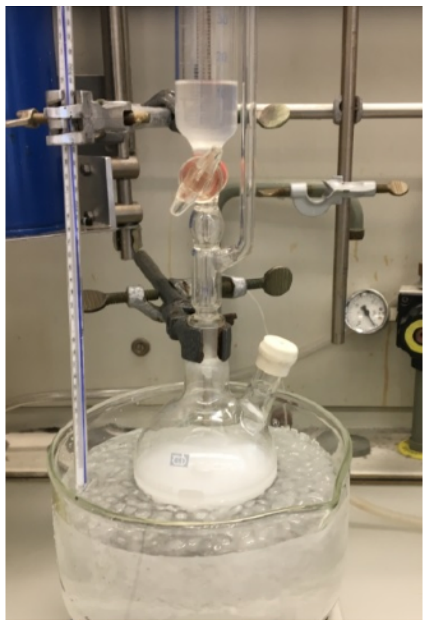
Purification

Structure analysis

Solvothermal synthesis

Solvothermal synthesis process

Streamline of organic synthesis



Reaction setup

Purification

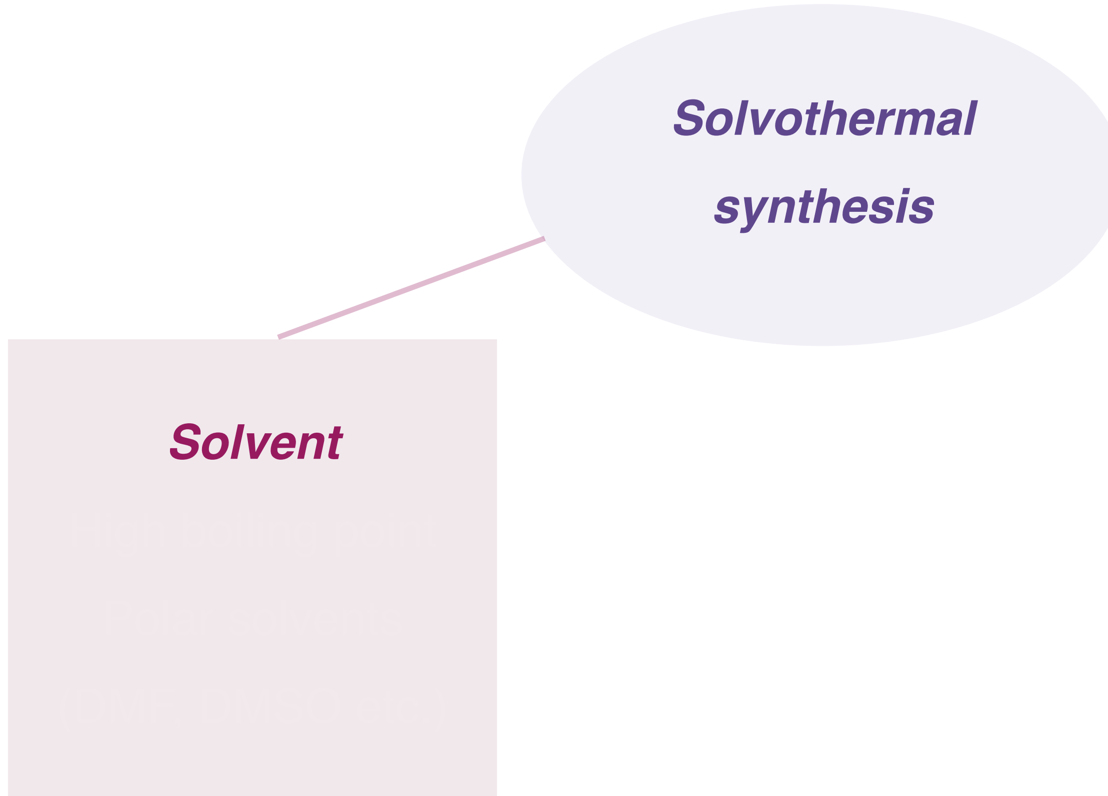
Structure analysis

Solvothermal synthesis

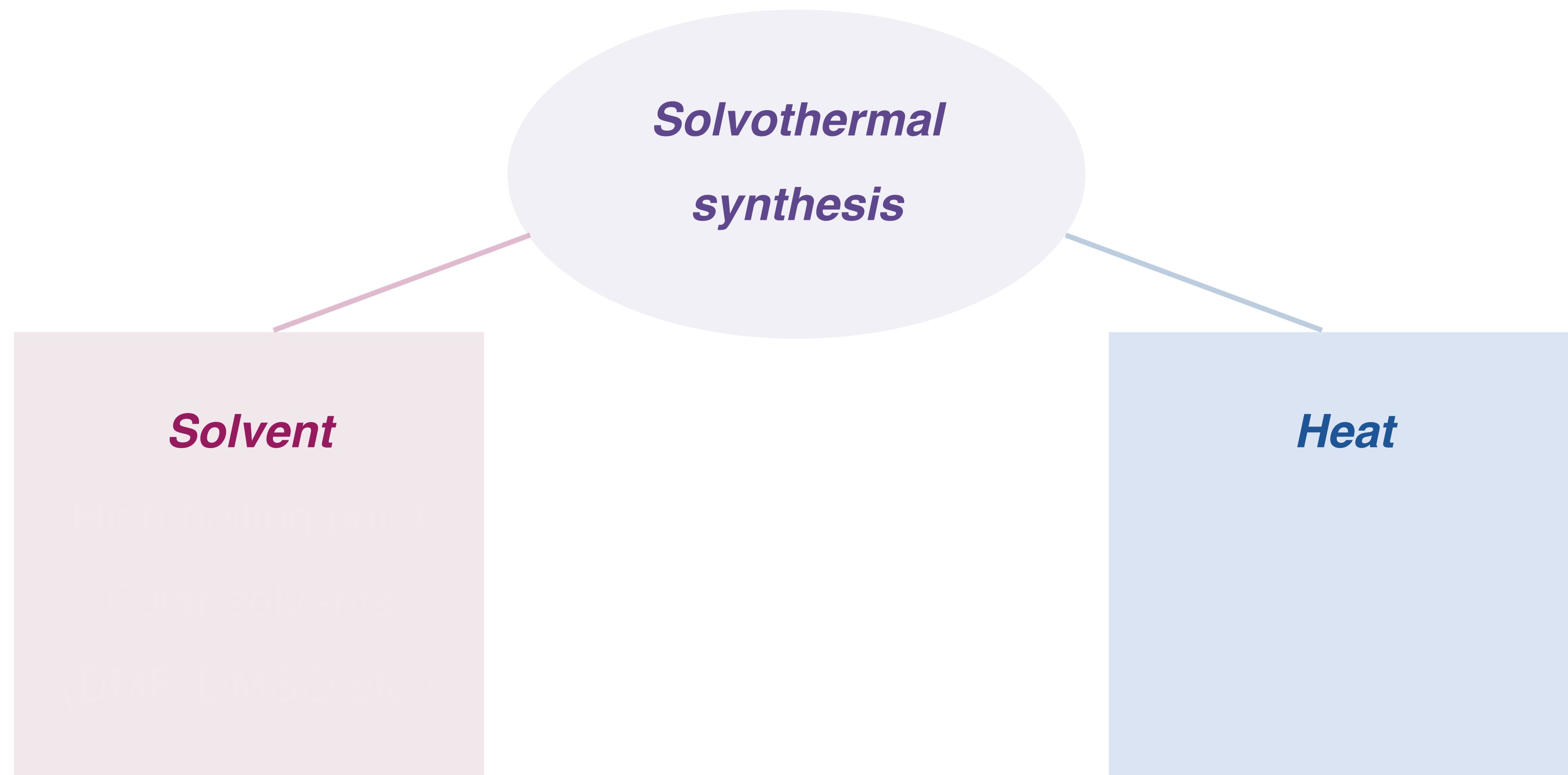
Solvothermal synthesis process — reaction setup for UiO-67

Solvothermal synthesis

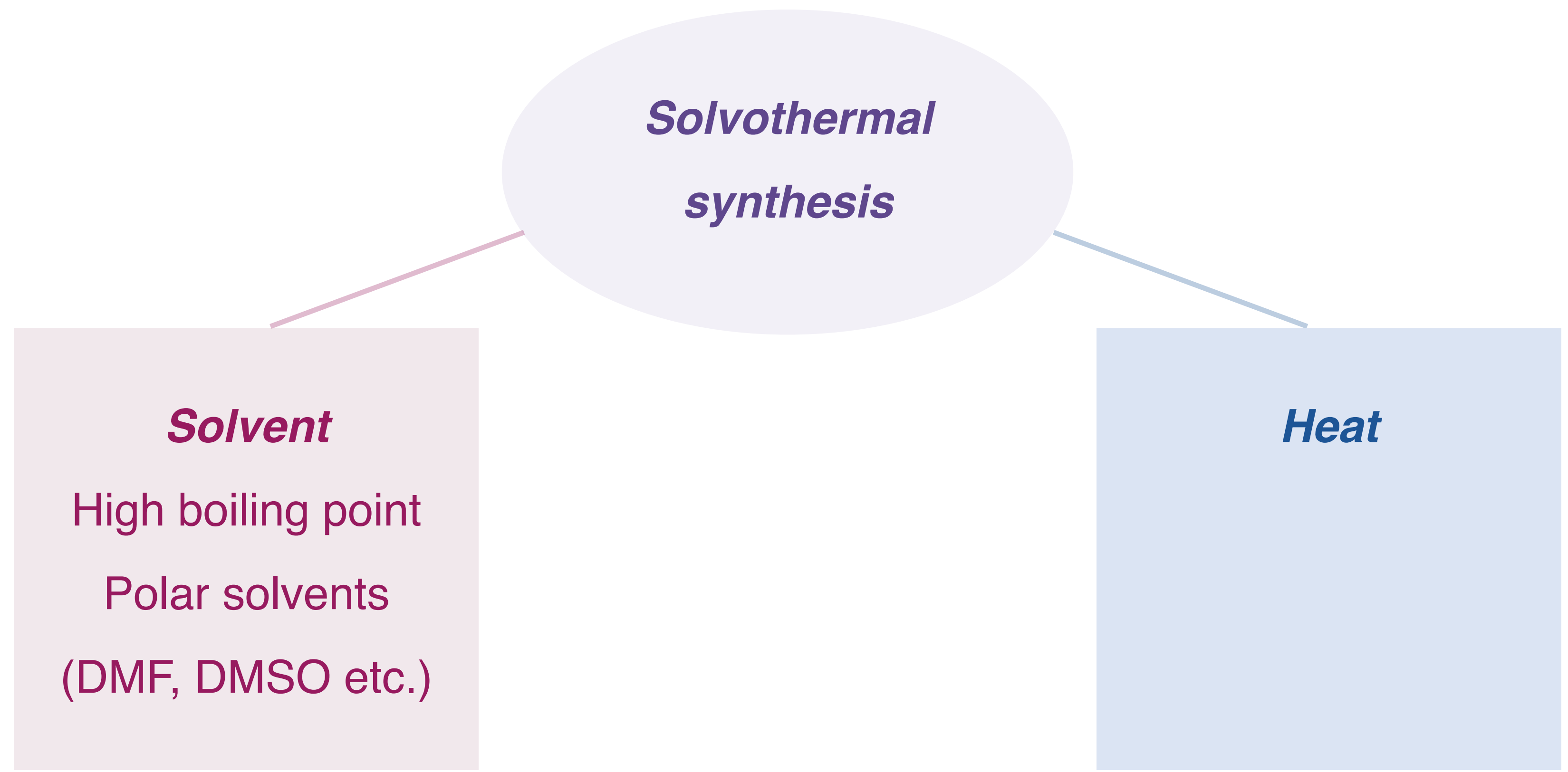
Solvothermal synthesis process — reaction setup for UiO-67



Solvothermal synthesis process — reaction setup for UiO-67



Solvothermal synthesis process — reaction setup for UiO-67



Solvothermal synthesis process — reaction setup for UiO-67

Solvothermal synthesis

Solvent

High boiling point

Polar solvents

(DMF, DMSO etc.)

Heat

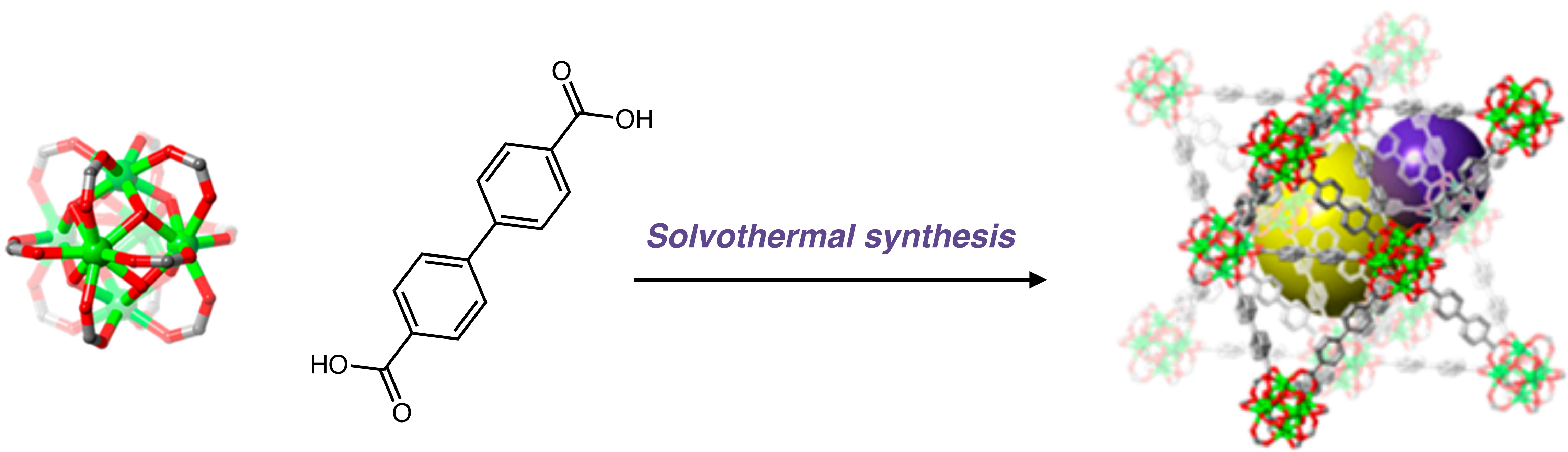
Oven or hot plates

(80 to 120 °C for 12 to 48 hours)

Solvothermal synthesis process — reaction setup for UiO-67

Solvothermal synthesis

Solvent	***Heat***
High boiling point Polar solvents (DMF, DMSO etc.)	Oven or hot plates (80 to 120 °C for 12 to 48 hours)



$Zr_6O_4(OH)_4$ BPDC UiO-67

Solvothermal synthesis process — reaction setup for UiO-67

Solvothermal synthesis

Solvent

High boiling point

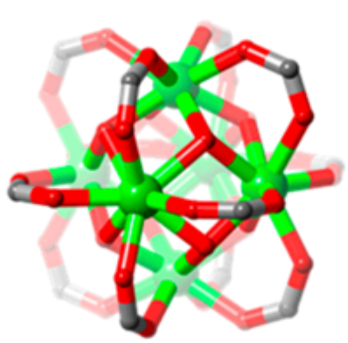
Polar solvents

(DMF, DMSO etc.)

Heat

Oven or hot plates

(80 to 120 °C for 12 to 48 hours)



$Zr_6O_4(OH)_4$

Solvothermal synthesis process — reaction setup for UiO-67

Solvothermal synthesis

Solvent

High boiling point

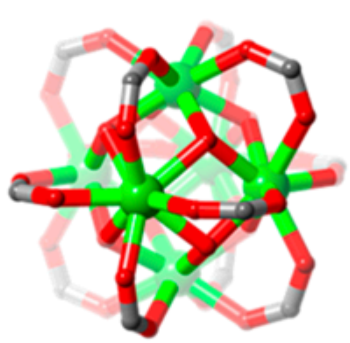
Polar solvents

(DMF, DMSO etc.)

Heat

Oven or hot plates

(80 to 120 °C for 12 to 48 hours)



$Zr_6O_4(OH)_4$

$ZrCl_4$

Solvothermal synthesis process — reaction setup for UiO-67

Solvothermal synthesis

Solvent

High boiling point

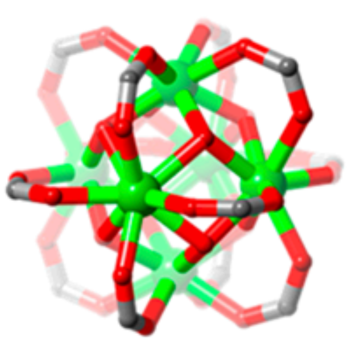
Polar solvents

(DMF, DMSO etc.)

Heat

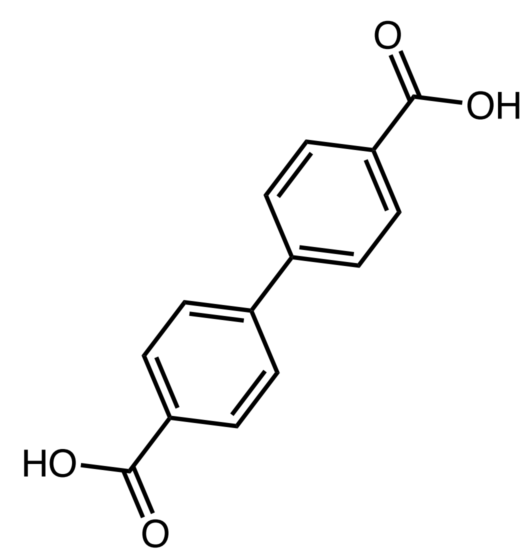
Oven or hot plates

(80 to 120 °C for 12 to 48 hours)



$Zr_6O_4(OH)_4$

$ZrCl_4$

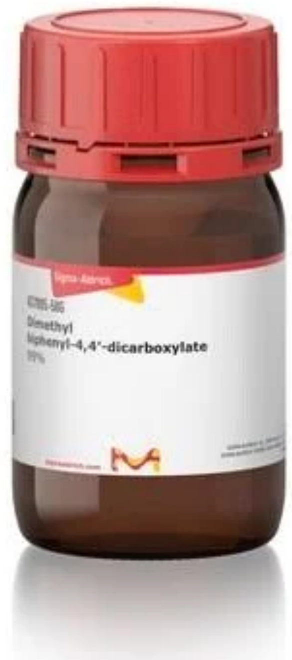


BPDC

4 4′-biphenyldicarboxylic acid

Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$



4 4′-biphenyldicarboxylic acid

Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$

4 4′-biphenyldicarboxylic acid

$\xrightarrow[\text{Heat}]{\text{DMF}}$

Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$

4 4′-biphenyldicarboxylic acid

$\xrightarrow[\text{Heat}]{\text{DMF}}$

Too fast crystalline growth with relatively amorphous structures

Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$

4 4′-biphenyldicarboxylic acid

$\xrightarrow[\text{Heat}]{\text{DMF}}$

Too fast crystalline growth with relatively amorphous structures

Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$

4 4′-biphenyldicarboxylic acid

$\xrightarrow[\text{Heat}]{\text{DMF}}$

Too fast crystalline growth with relatively amorphous structures

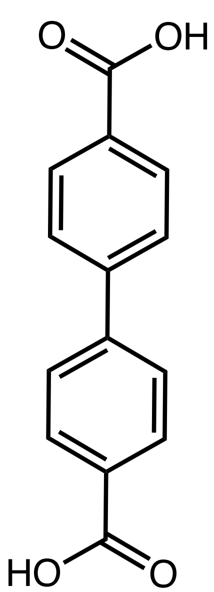
Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$

4 4′-biphenyldicarboxylic acid

$\xrightarrow[\text{Heat}]{\text{DMF}}$

Too fast crystalline growth with relatively amorphous structures



Organic linker

Two sides for crystal growth

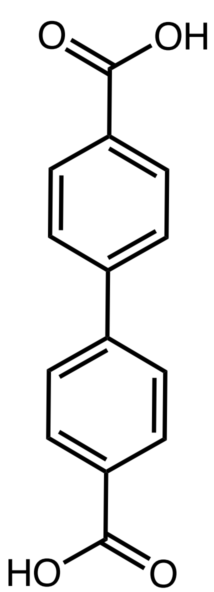
Solvothermal synthesis process — reaction setup for UiO-67

$ZrCl_4$

4 4′-biphenyldicarboxylic acid

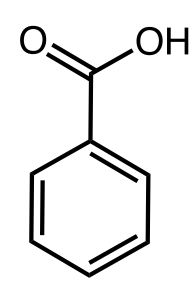
$\xrightarrow[\text{Heat}]{\text{DMF}}$

Too fast crystalline growth with relatively amorphous structures



Organic linker

Two sides for crystal growth



Modulator

Nonstructural, monotopic linker

Solvothermal synthesis process — reaction setup for UiO-67

Illustrative Synthesis:

UiO-67

Using benzoic acid as modulator

Solvothermal synthesis process — purification

Streamline of organic synthesis

Reaction setup

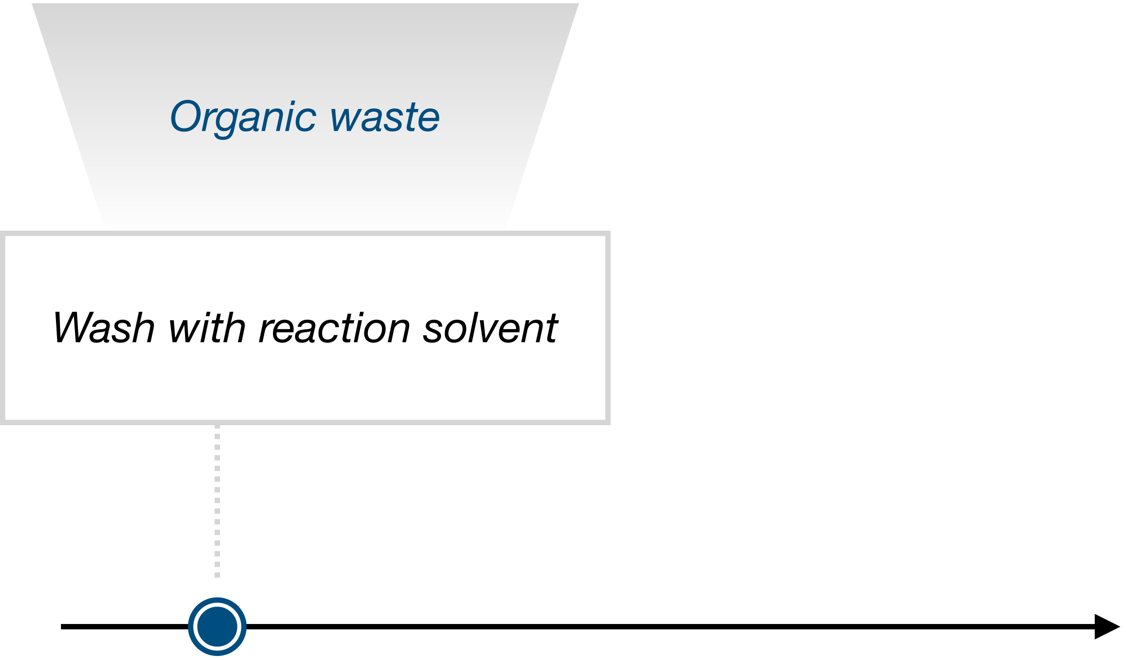
Purification

Structure analysis

Solvothermal synthesis

Solvothermal synthesis process — purification

Solvothermal synthesis process — purification



Solvothermal synthesis process — purification

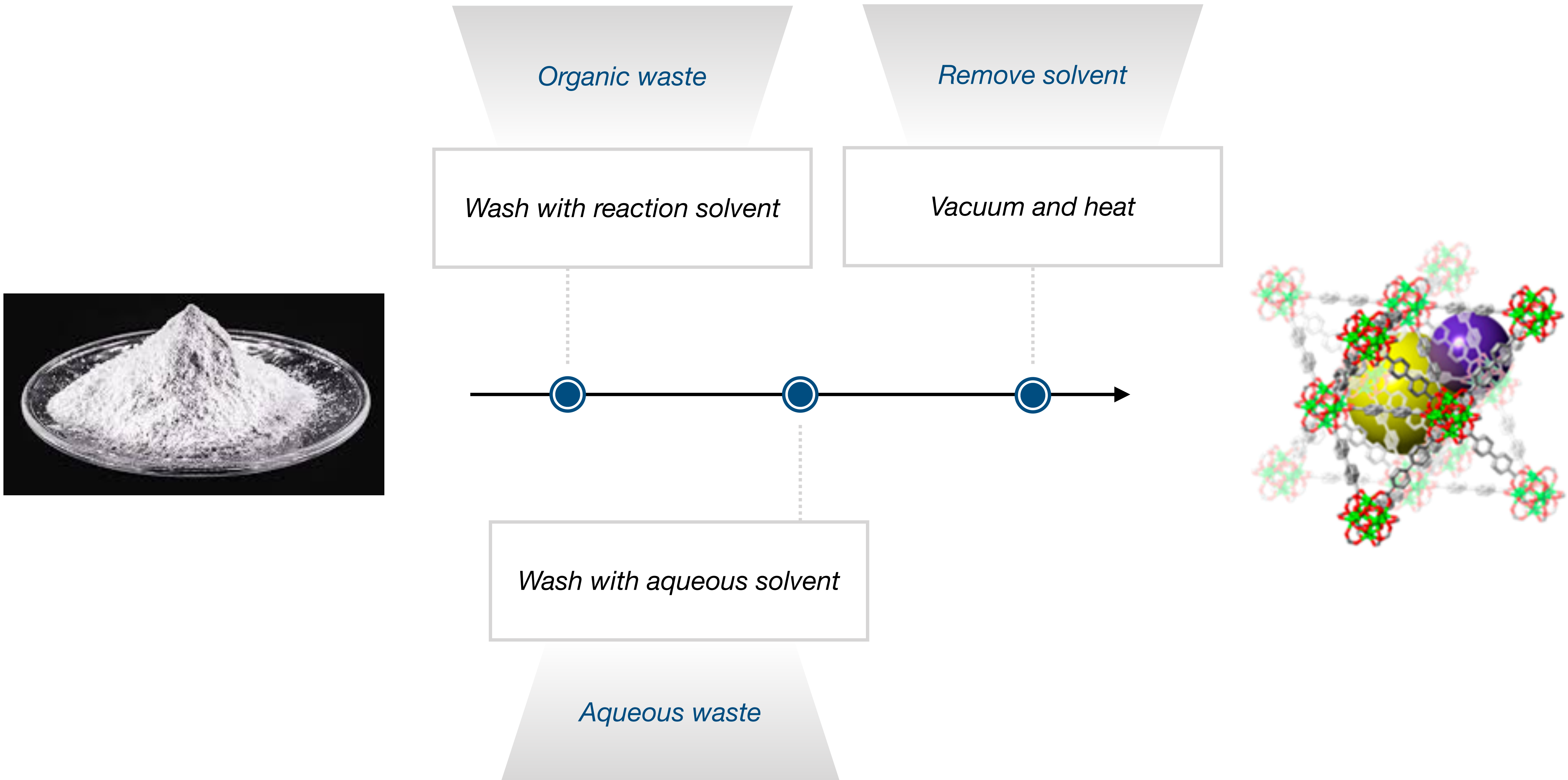
Organic waste

Wash with reaction solvent

Wash with aqueous solvent

Aqueous waste

Solvothermal synthesis process — purification



Solvothermal synthesis process — characterization

Streamline of organic synthesis

Reaction setup

Purification

Structure analysis

Solvothermal synthesis

Solvothermal synthesis process — characterization

Crystalline identification

Crystalline properties

Purity check

Solvothermal synthesis process — characterization

Crystalline identification

Crystalline properties

Purity check

Solvothermal synthesis process — characterization

Powder X-ray diffraction (PXRD)

Solvothermal synthesis process — characterization

Powder X-ray diffraction (PXRD)

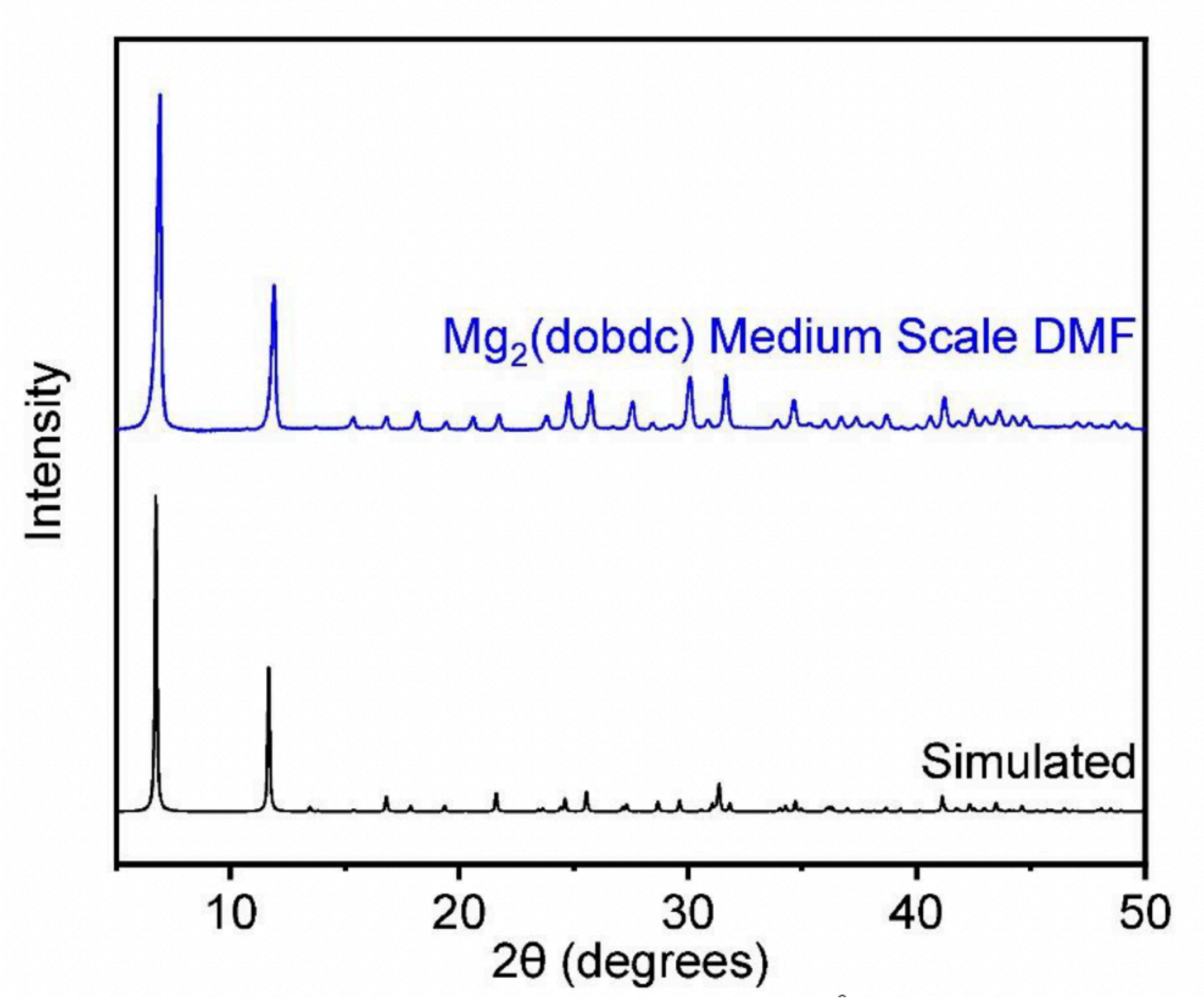
determine bulk crystallinity of MOF samples by comparing with simulated structures

Solvothermal synthesis process — characterization

Powder X-ray diffraction (PXRD)

determine bulk crystallinity of MOF samples by

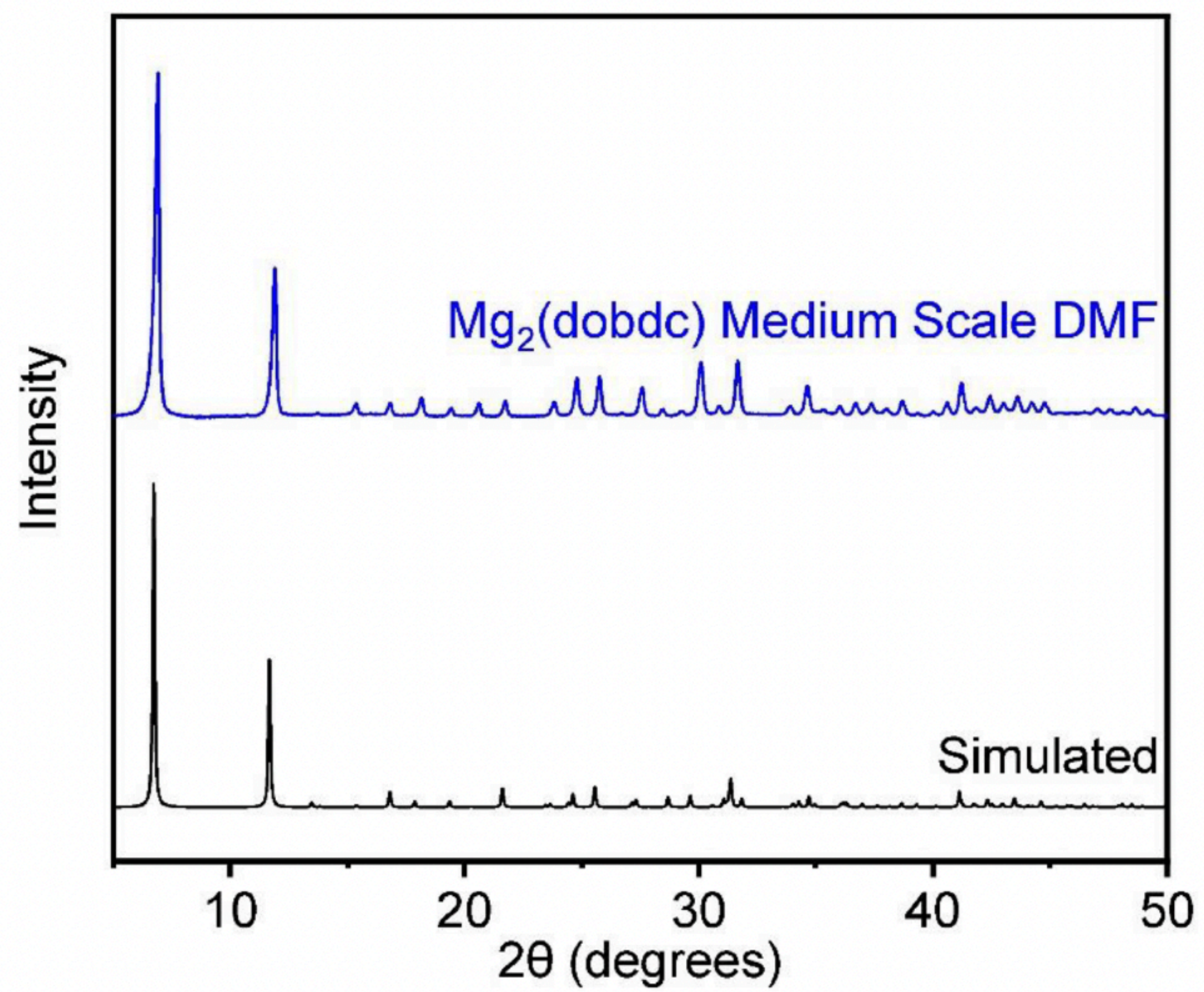
comparing with simulated structures



Solvothermal synthesis process — characterization

Powder X-ray diffraction (PXRD)

determine bulk crystallinity of MOF samples by comparing with simulated structures

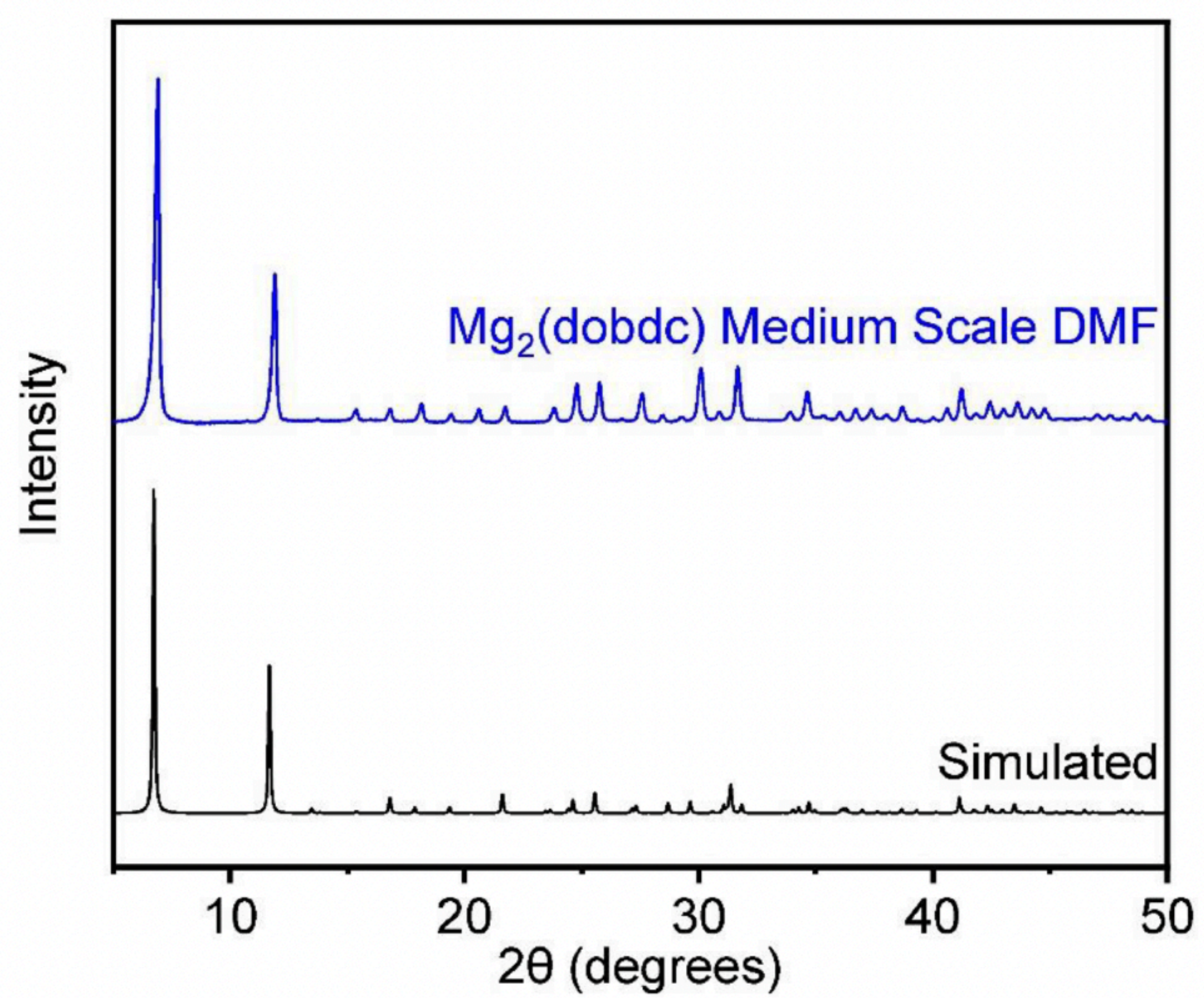


Single crystal X-ray diffraction

Solvothermal synthesis process — characterization

Powder X-ray diffraction (PXRD)

determine bulk crystallinity of MOF samples by comparing with simulated structures



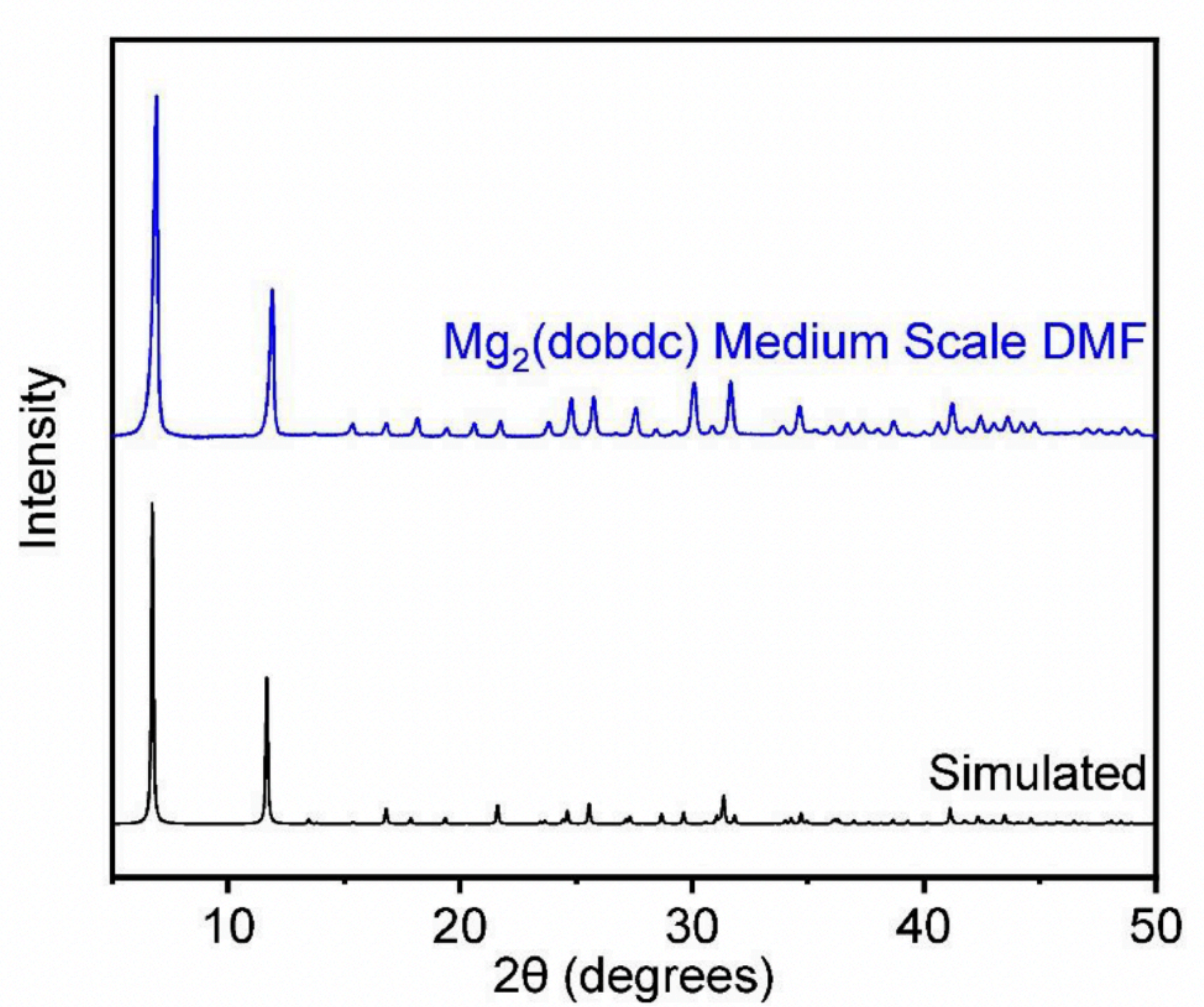
Single crystal X-ray diffraction

obtain direct crystal structure of MOFs

Solvothermal synthesis process — characterization

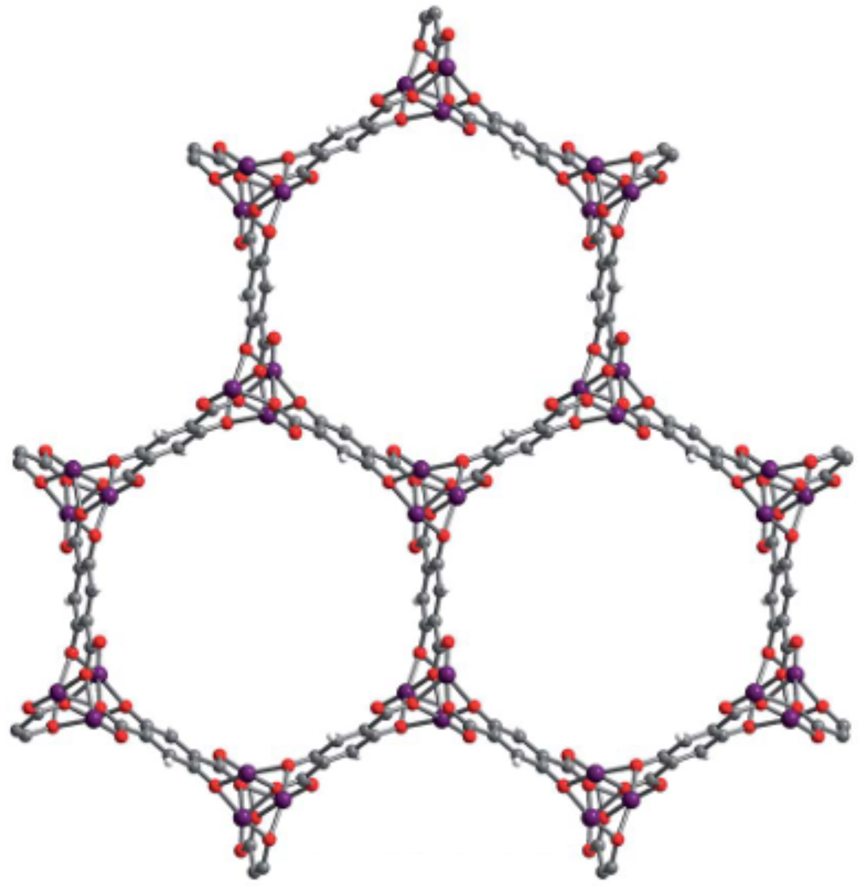
Powder X-ray diffraction (PXRD)

determine bulk crystallinity of MOF samples by comparing with simulated structures



Single crystal X-ray diffraction

obtain direct crystal structure of MOFs



Co_2(dobdc)

Dobdc = 2,5-dioxido1,4-benzenedicarboxylate

Solvothermal synthesis process — characterization

Crystalline identification

Crystalline properties

Purity check

Solvothermal synthesis process — characterization

Thermogravimetric analysis

Solvothermal synthesis process — characterization

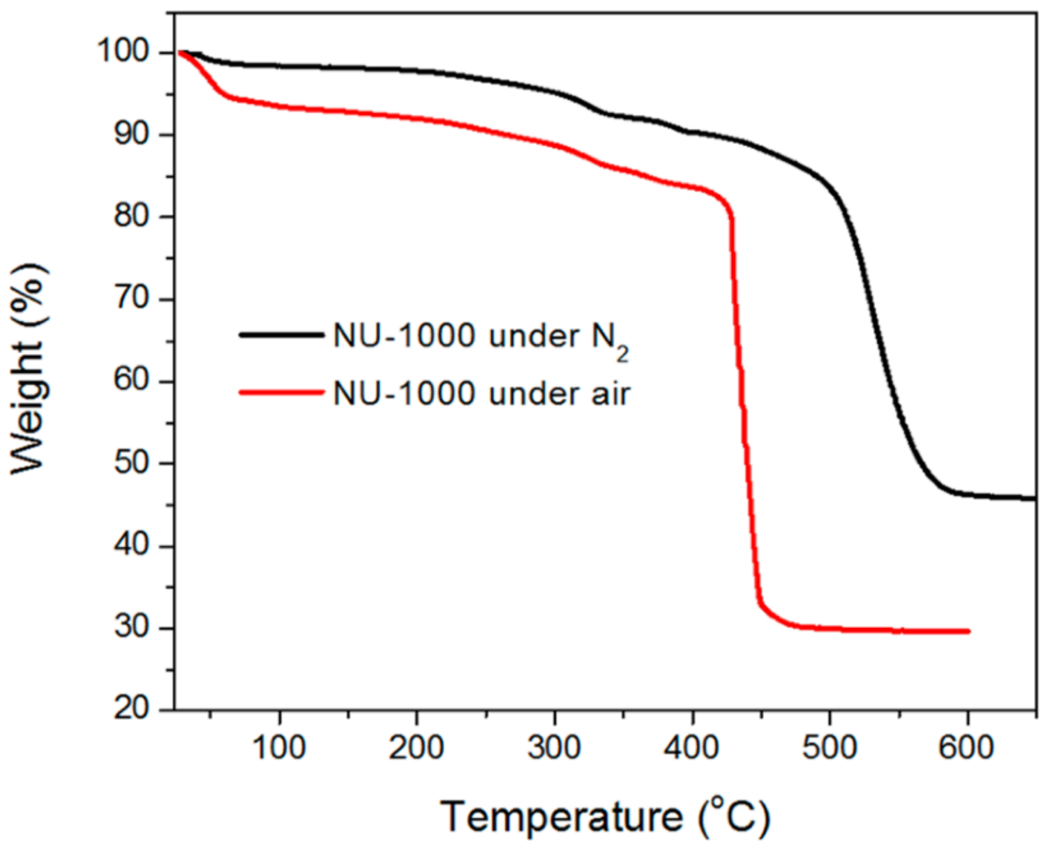
Thermogravimetric analysis

determine thermal stability of the MOFs

Solvothermal synthesis process — characterization

Thermogravimetric analysis

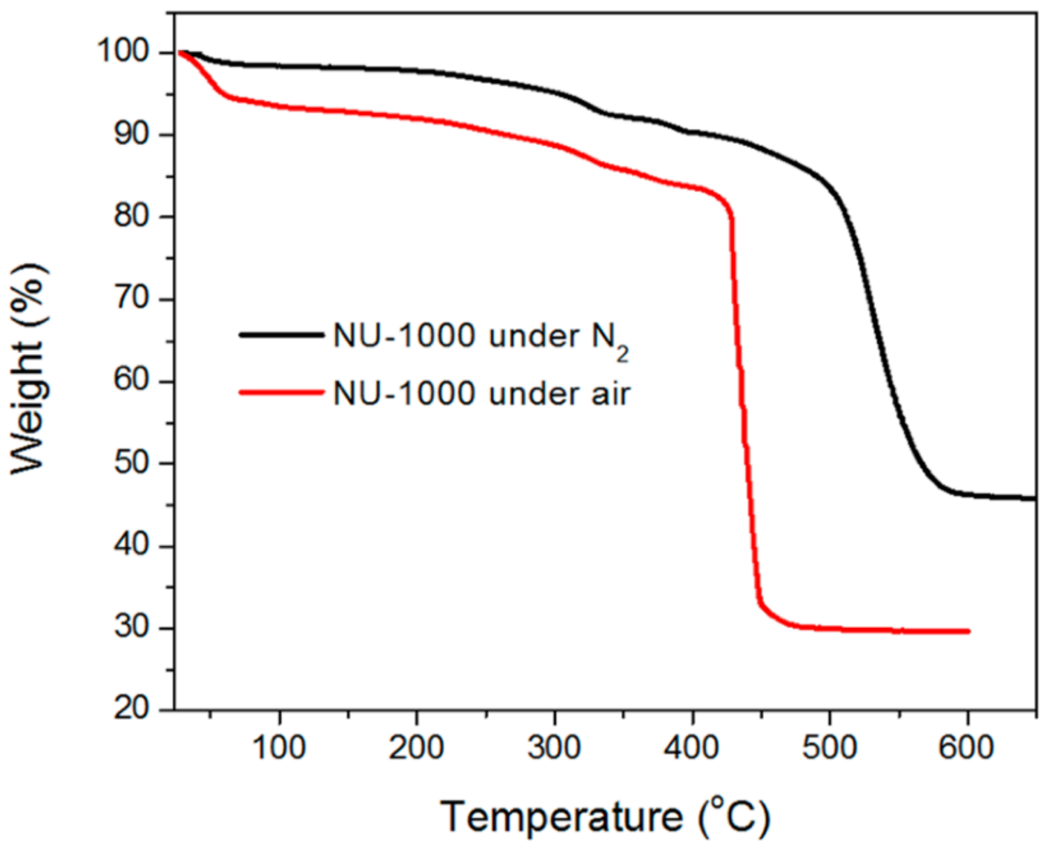
determine thermal stability of the MOFs



Solvothermal synthesis process — characterization

Thermogravimetric analysis

determine thermal stability of the MOFs

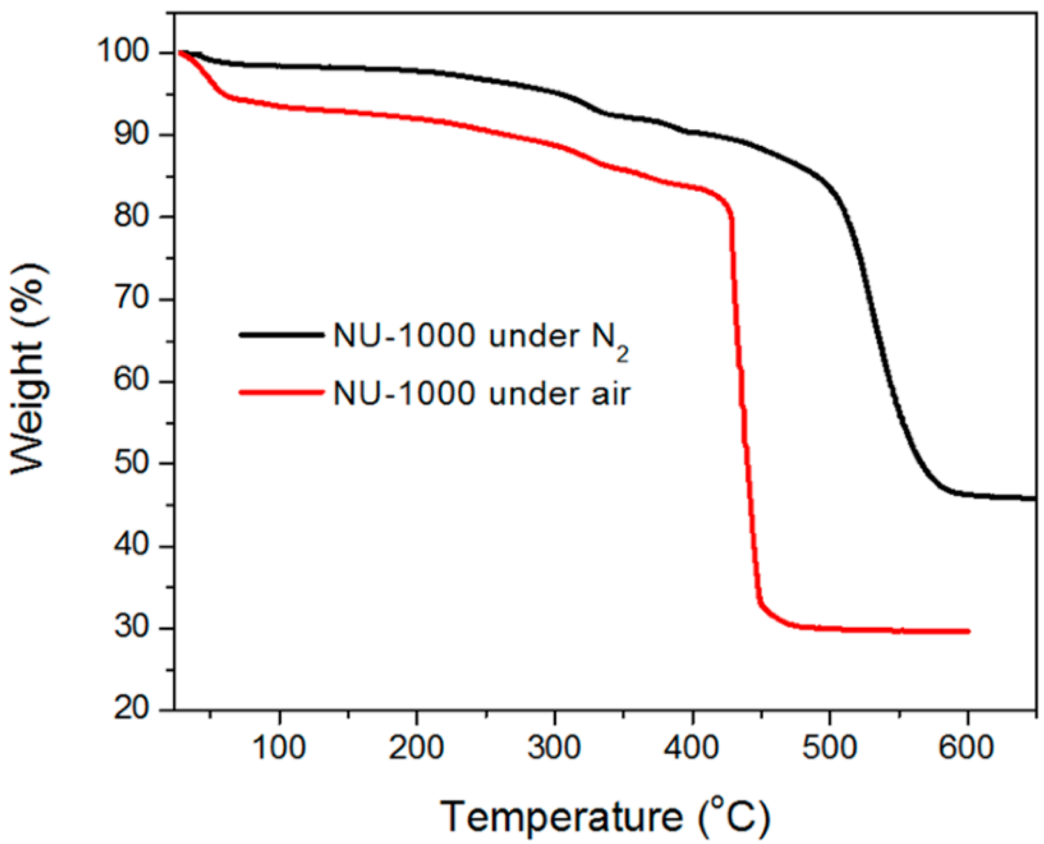


Aqueous stability testing

Solvothermal synthesis process — characterization

Thermogravimetric analysis

determine thermal stability of the MOFs



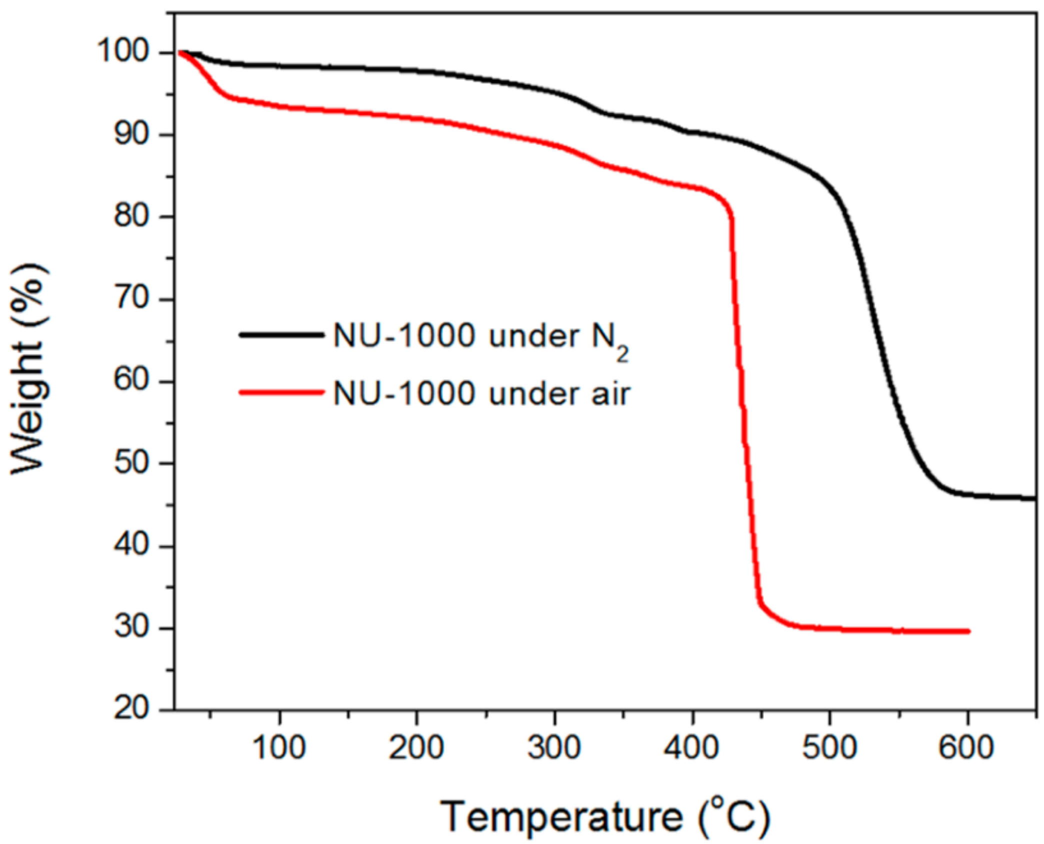
Aqueous stability testing

determine aqueous (pH) stability of the MOFs

Solvothermal synthesis process — characterization

Thermogravimetric analysis

determine thermal stability of the MOFs



Aqueous stability testing

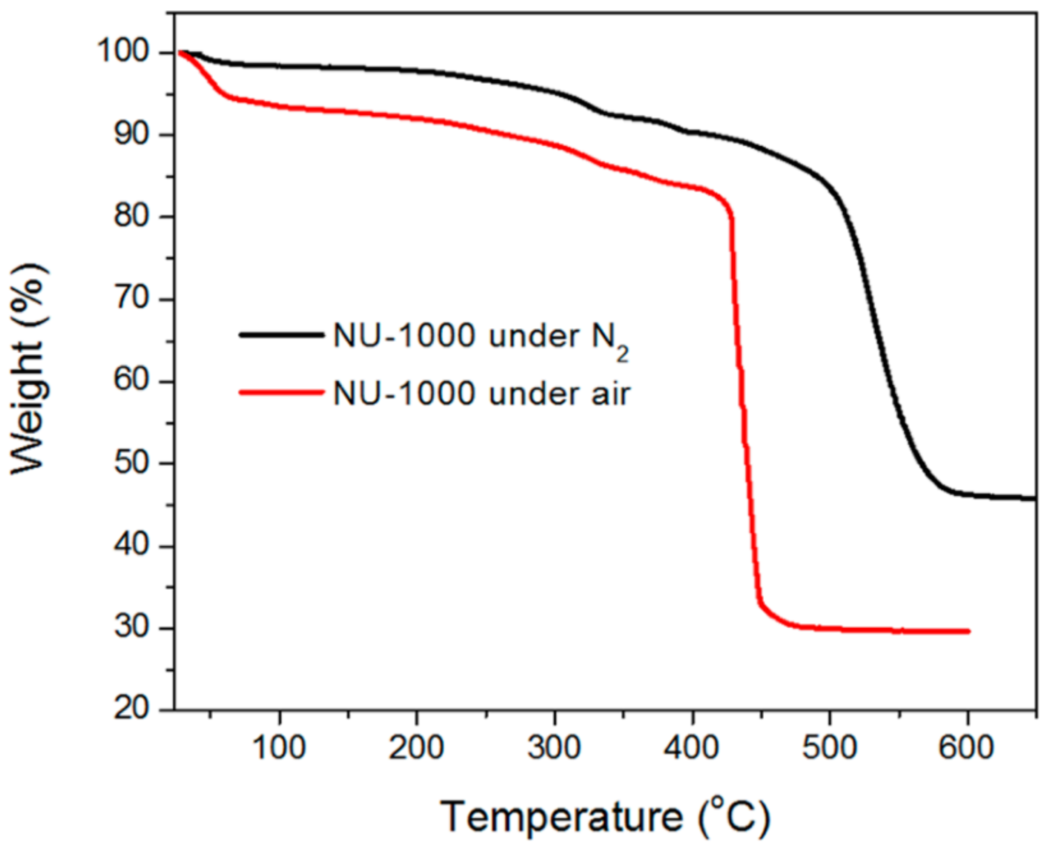
determine aqueous (pH) stability of the MOFs

$$\frac{\text{mass}_{\text{recovered}}}{\text{mass}_{\text{initial}}} \times 100 = \text{yield } \%$$

Solvothermal synthesis process — characterization

Thermogravimetric analysis

determine thermal stability of the MOFs



Aqueous stability testing

determine aqueous (pH) stability of the MOFs

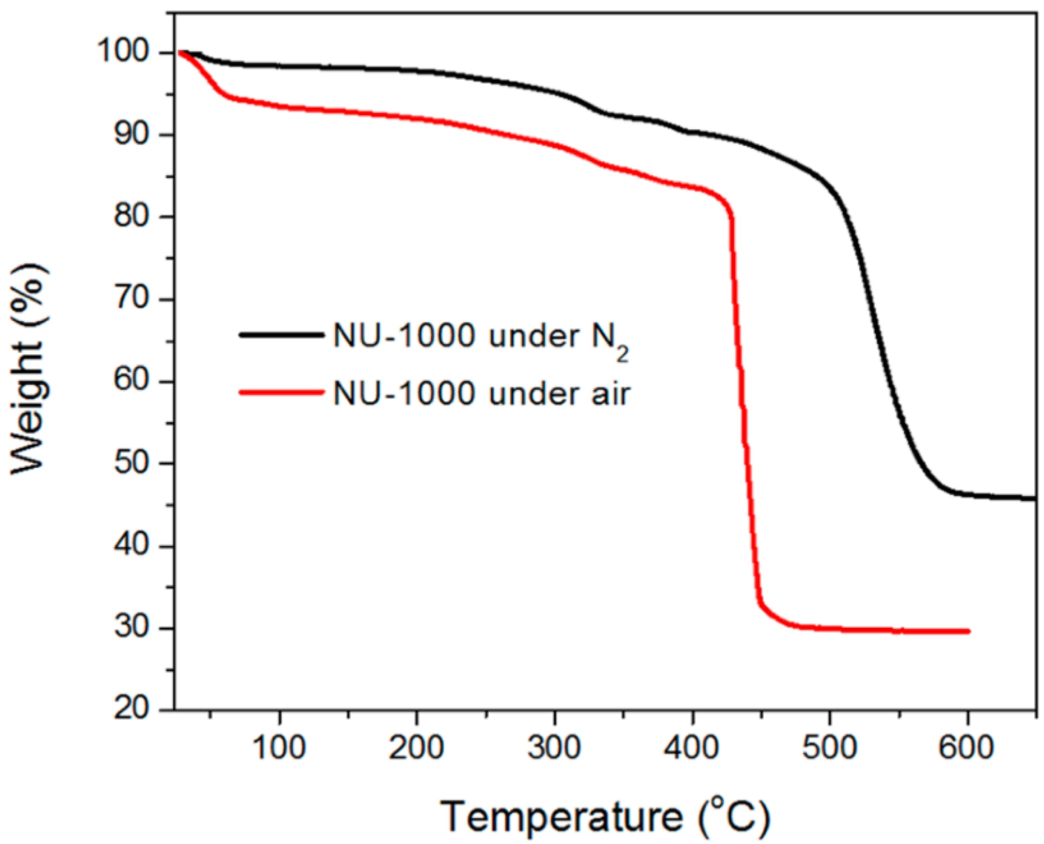
$$\frac{\text{mass}_{\text{recovered}}}{\text{mass}_{\text{initial}}} \times 100 = \text{yield } \%$$

Nitrogen adsorption and desorption isotherms

Solvothermal synthesis process — characterization

Thermogravimetric analysis

determine thermal stability of the MOFs



Aqueous stability testing

determine aqueous (pH) stability of the MOFs

$$\frac{\text{mass}_{\text{recovered}}}{\text{mass}_{\text{initial}}} \times 100 = \text{yield } \%$$

Nitrogen adsorption and desorption isotherms

determine surface areas and pore volumes

Solvothermal synthesis process — characterization

Solvothermal synthesis process — characterization

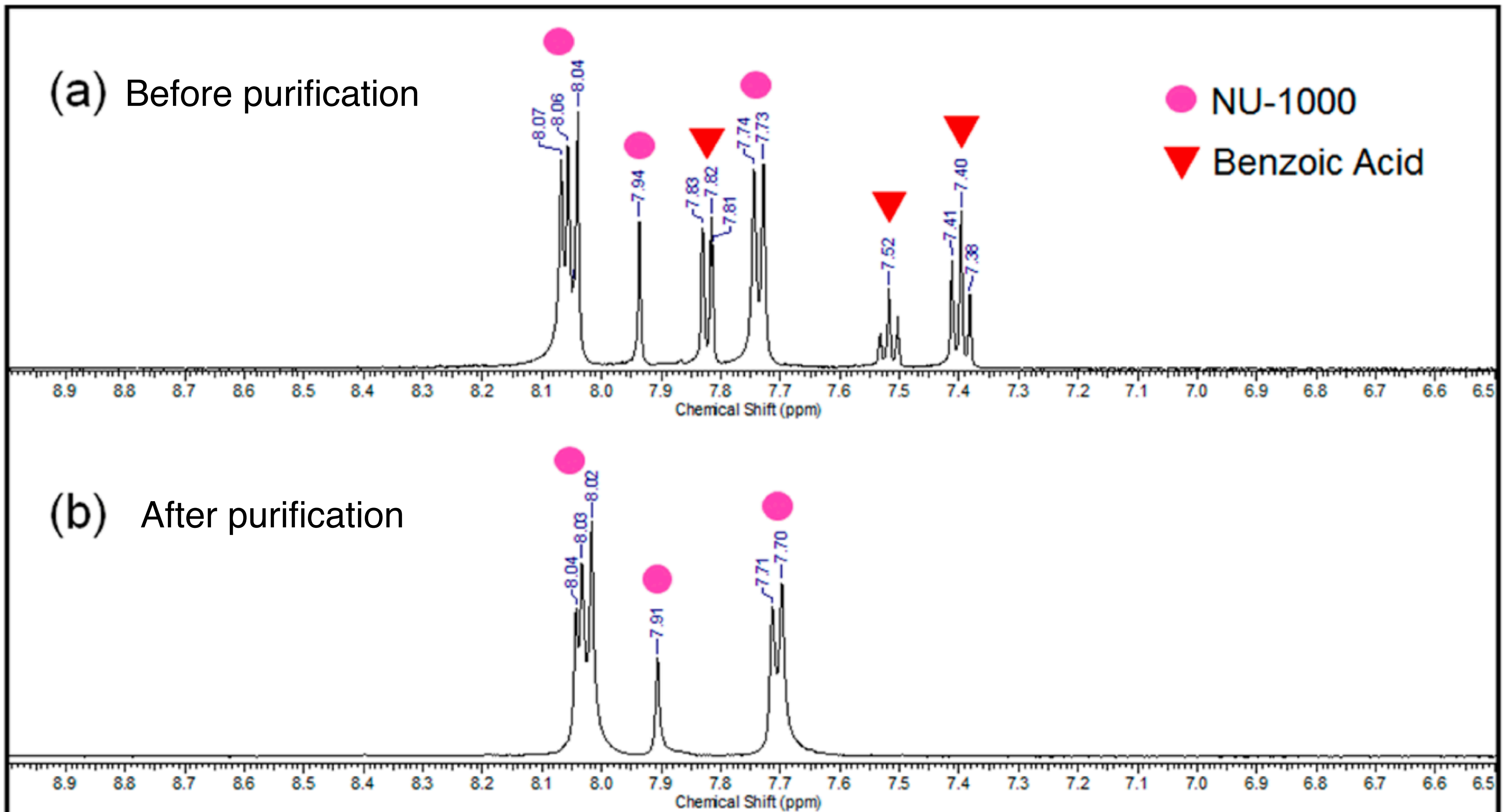
NMR spectroscopy

Confirm the absence of organic linkers, modulators and solvent molecules

Solvothermal synthesis process — characterization

NMR spectroscopy

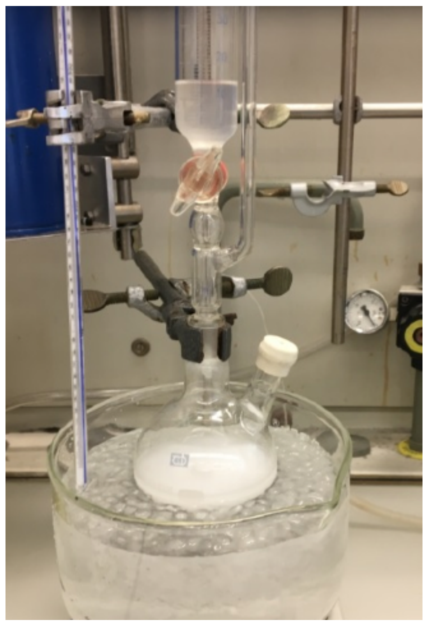
Confirm the absence of organic linkers, modulators and solvent molecules



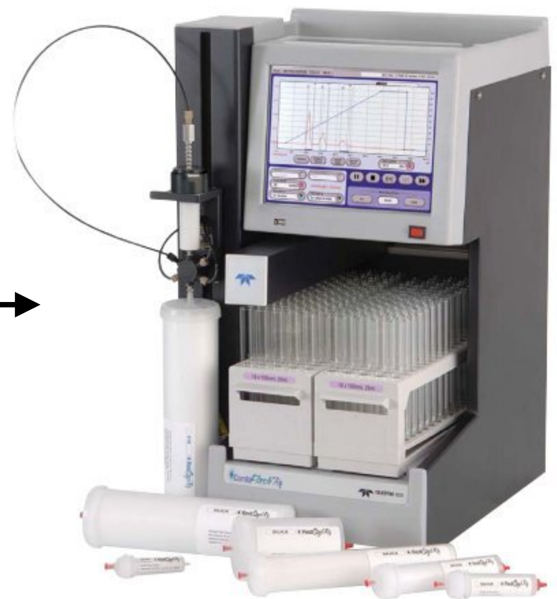
NU-1000

Solvothermal synthesis process

Streamline of organic synthesis



Reaction setup

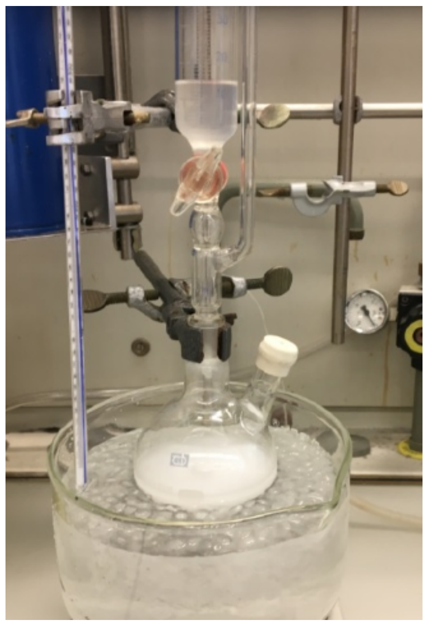


Purification

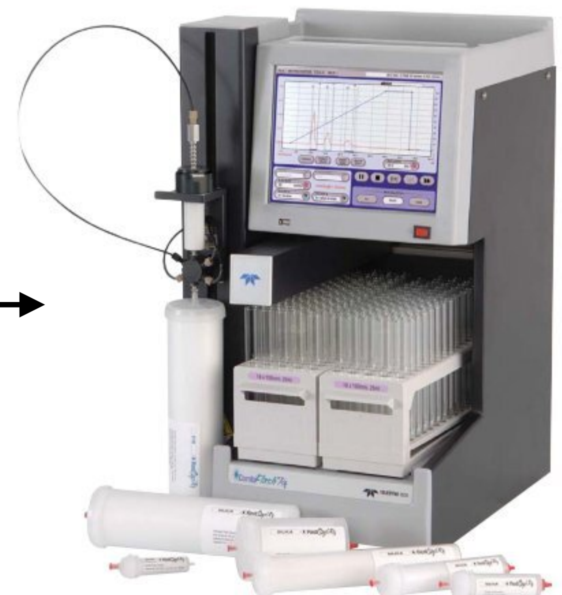
Structure analysis

Solvothermal synthesis process

Streamline of organic synthesis



Reaction setup



Purification

Structure analysis

Reaction setup	Purification	Structure analysis
Metal ion precursors	Solvent wash	Crystal structures
Organic linkers	Aqueous wash	Properties
Solvents and heat	Dry	Purity check

Outline

What are MOFs?

How to synthesize MOFs?

Organic synthetic applications MOFs

Organic synthetic applications of MOFs

What are possible organic synthetic applications of MOFs?

Case study 1: Enhanced reactivity

Case study 2: Novel reagents based on MOFs

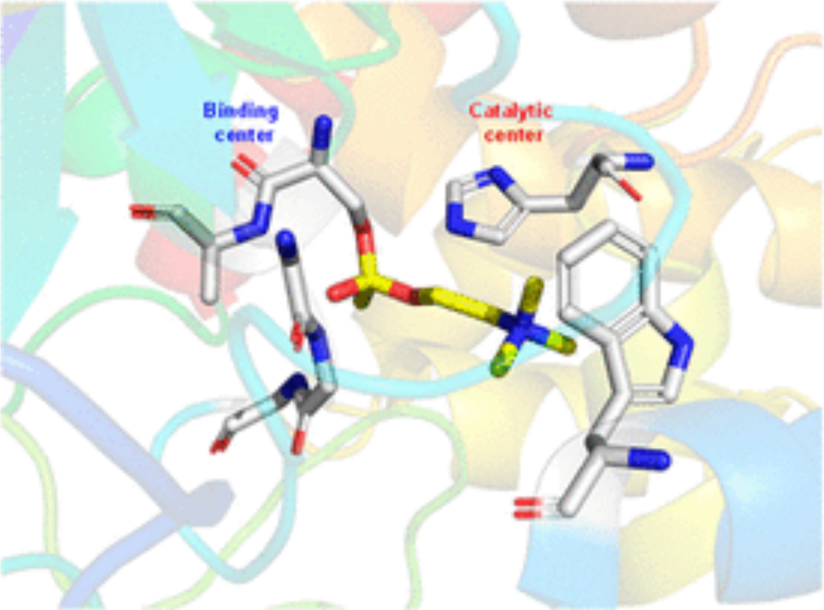
What are possible organic synthetic applications of MOFs?

Case study 1: Enhanced reactivity

Case study 2: Novel reagents based on MOFs

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Enzyme: multiple active sites

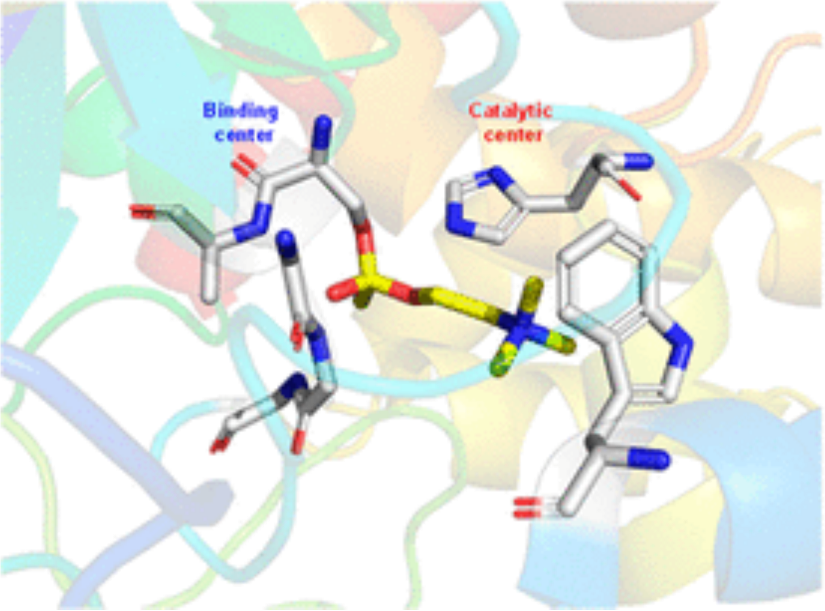


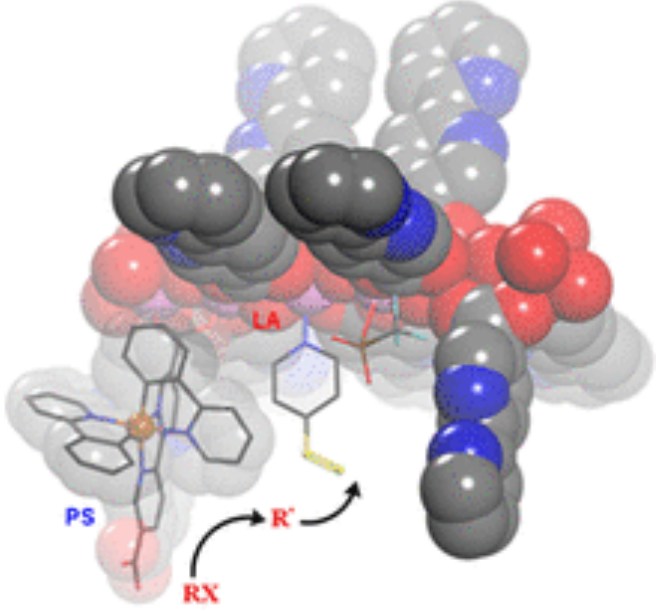
Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Enzyme: multiple active sites

MOF: multiple catalytic centers

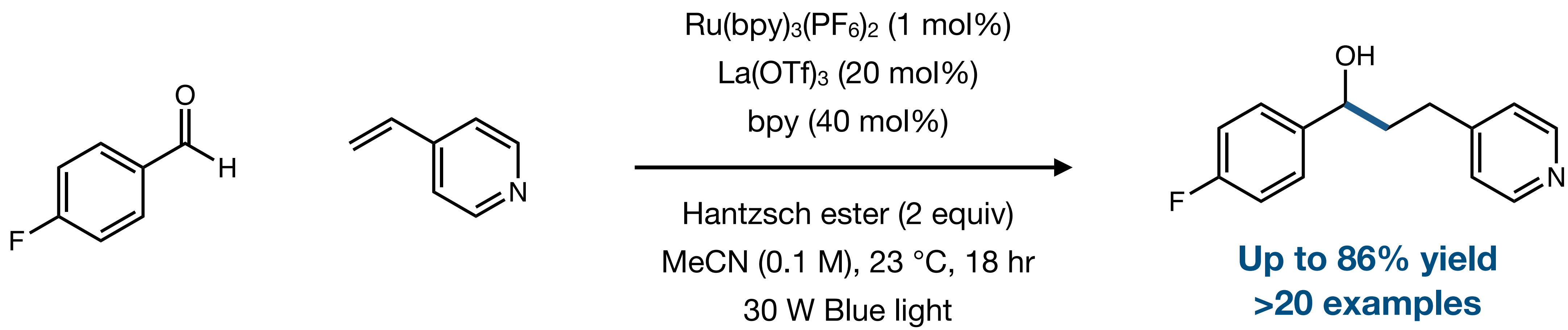




Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

■ Ngai, *JACS*, 2017

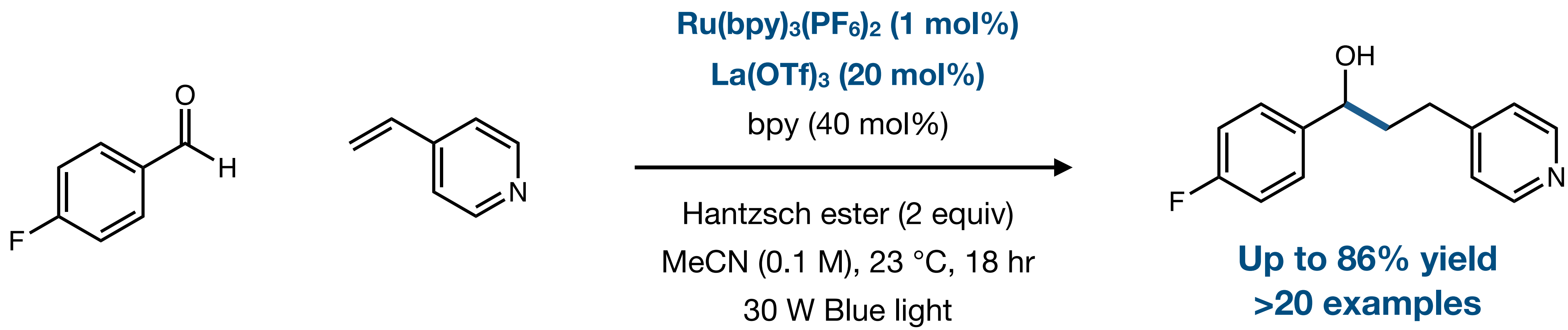


Up to 86% yield
>20 examples

Lee, K. N.; Lei, Z.; Ngai, M. Y. *J Am Chem Soc* **2017**, *139* (14), 5003-5006.
Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. *J Am Chem Soc* **2019**, *141* (13), 5437-5443.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

■ Ngai, *JACS*, 2017

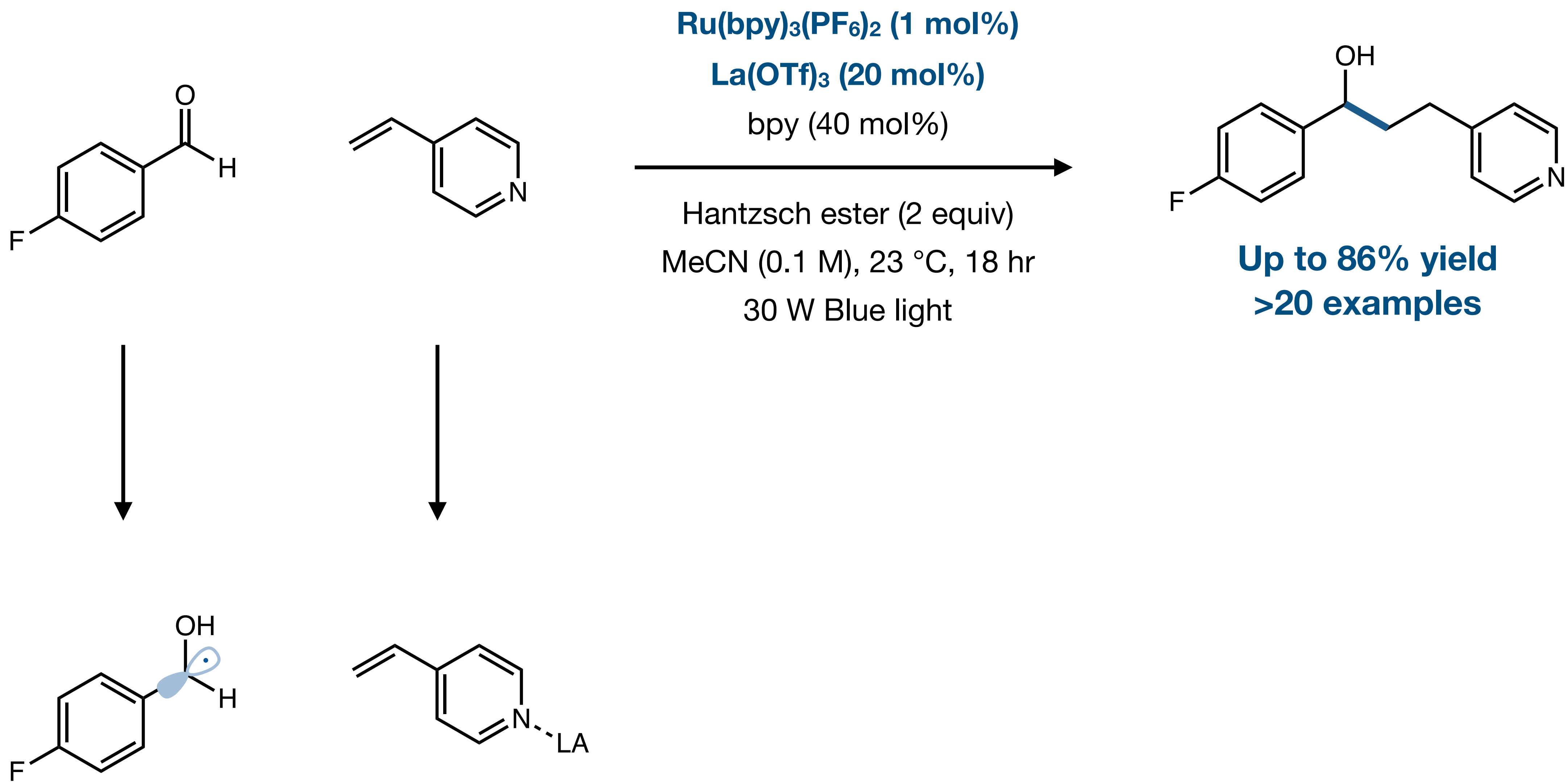


Up to 86% yield
>20 examples

Lee, K. N.; Lei, Z.; Ngai, M. Y. *J Am Chem Soc* **2017**, *139* (14), 5003-5006.
Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. *J Am Chem Soc* **2019**, *141* (13), 5437-5443.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

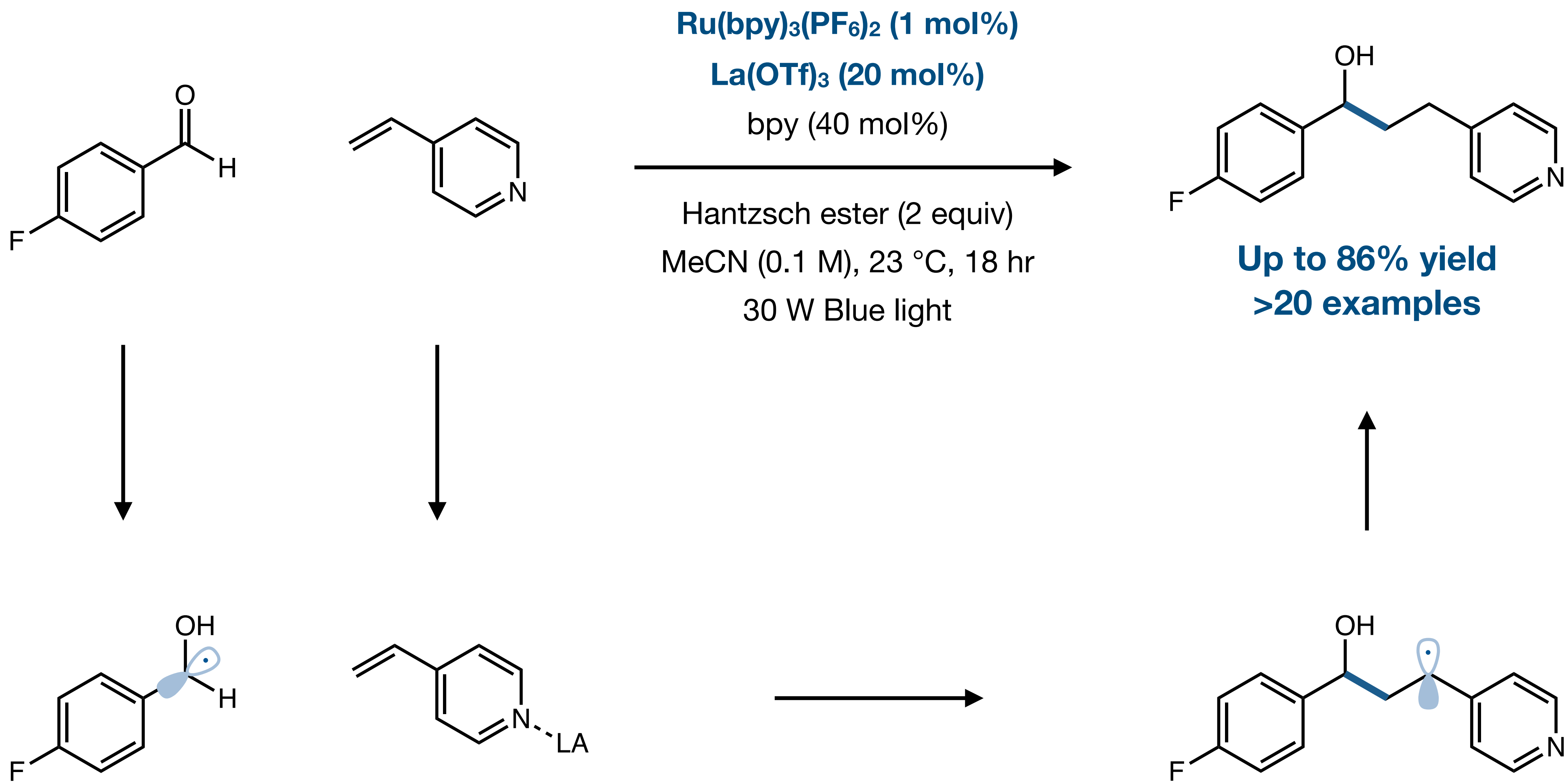
■ Ngai, *JACS*, 2017



Lee, K. N.; Lei, Z.; Ngai, M. Y. *J Am Chem Soc* **2017***, 139* (14), 5003-5006.
Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. *J Am Chem Soc* **2019***, 141* (13), 5437-5443.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

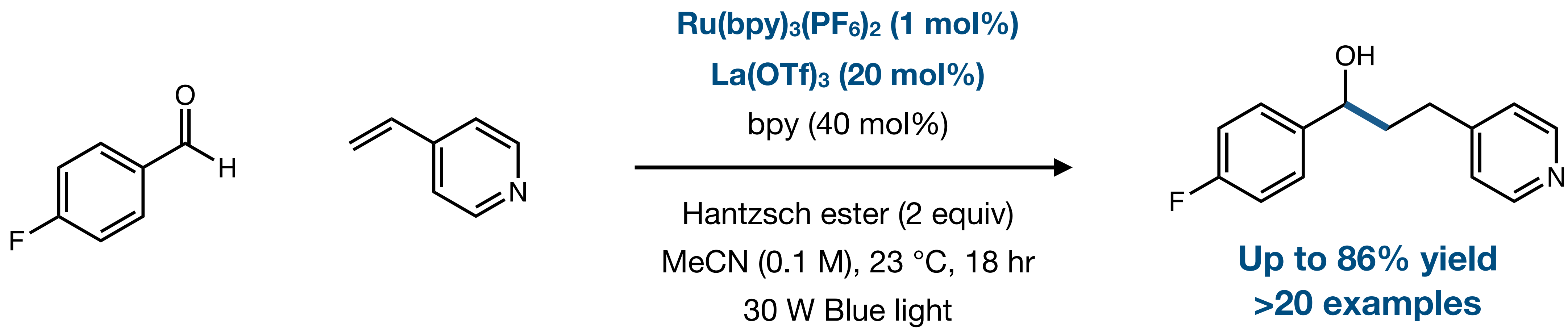
■ Ngai, *JACS*, 2017



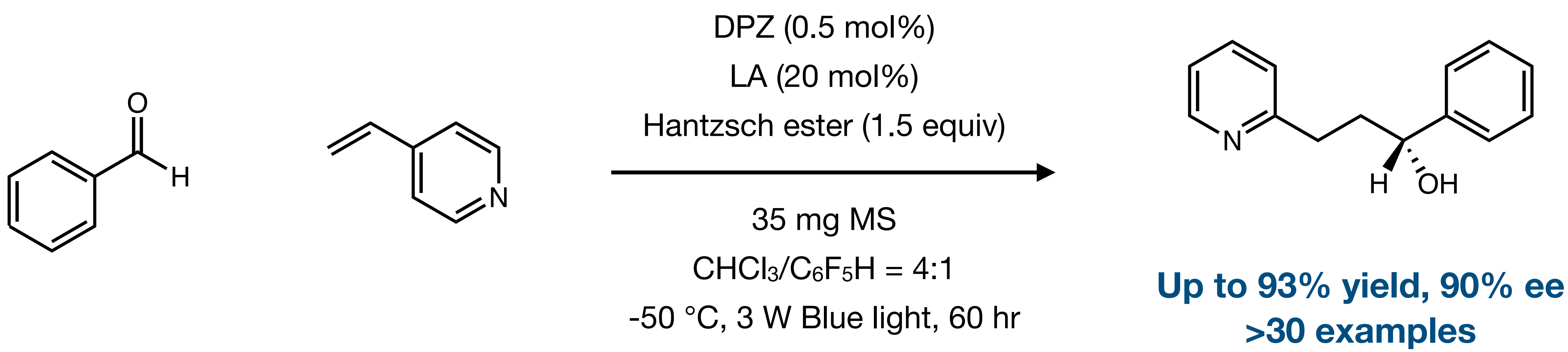
Lee, K. N.; Lei, Z.; Ngai, M. Y. *J Am Chem Soc* **2017**, *139* (14), 5003-5006.
Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. *J Am Chem Soc* **2019**, *141* (13), 5437-5443.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

■ Ngai, *JACS*, 2017



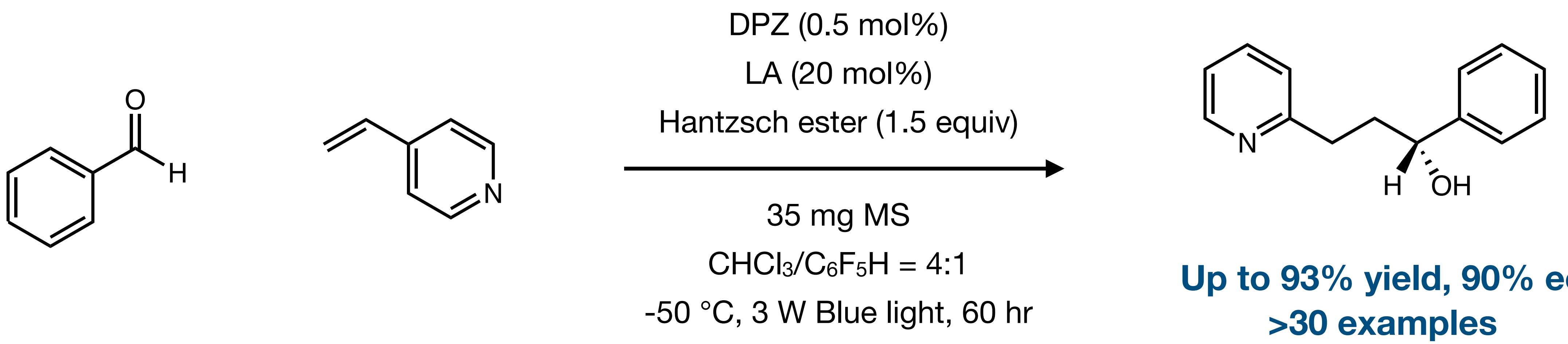
■ Jiang, *JACS*, 2019



Lee, K. N.; Lei, Z.; Ngai, M. Y. *J Am Chem Soc* **2017**, *139* (14), 5003-5006.
Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. *J Am Chem Soc* **2019**, *141* (13), 5437-5443.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

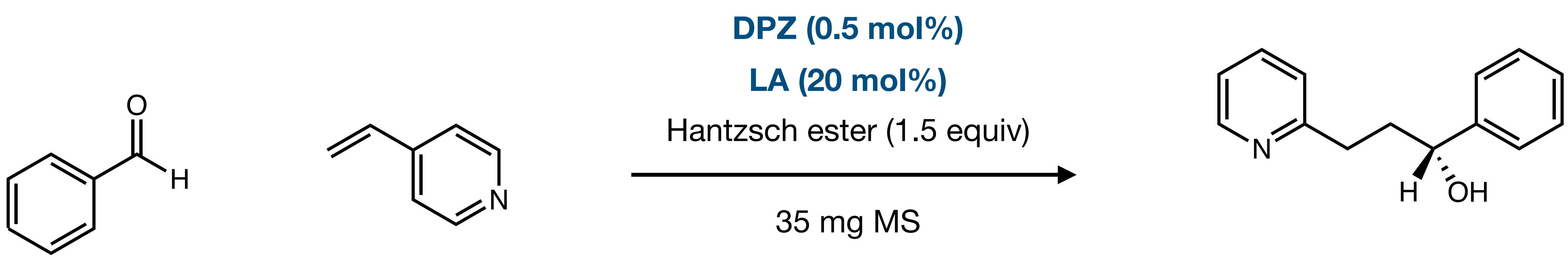
■ Jiang, *JACS*, 2019



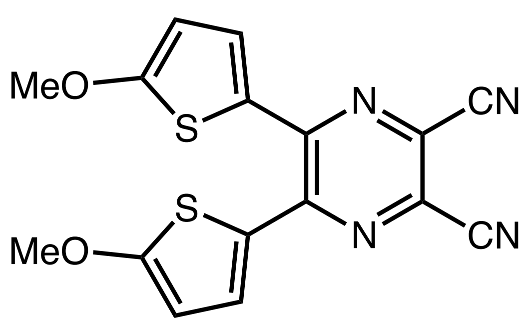
Up to 93% yield, 90% ee
>30 examples

Enhanced reactivity — MOF with dual active sites enabled cross coupling

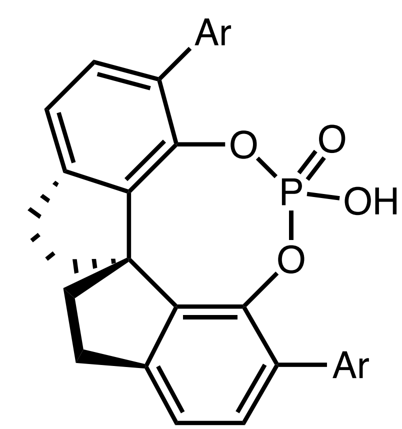
■ Jiang, *JACS*, 2019



Up to 93% yield, 90% ee
>30 examples



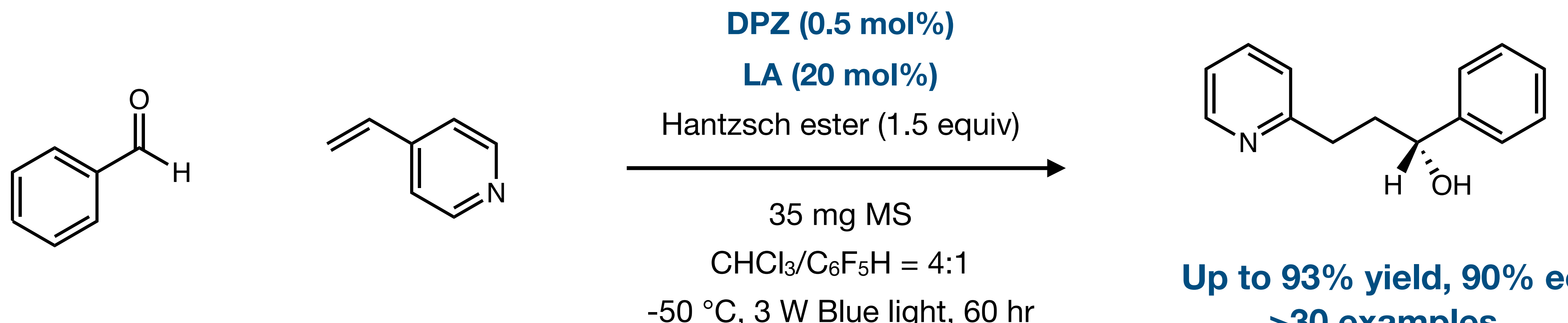
Photocatalyst: DPZ



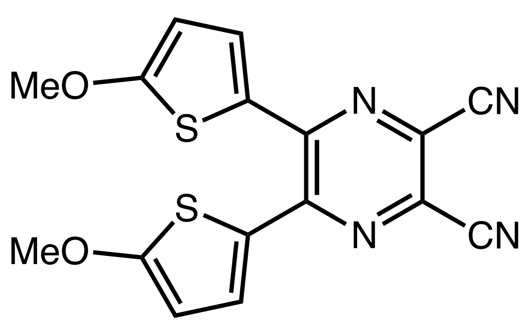
Ar = 2,4,6-$i$$Pr_3C_6H_2$

Enhanced reactivity — MOF with dual active sites enabled cross coupling

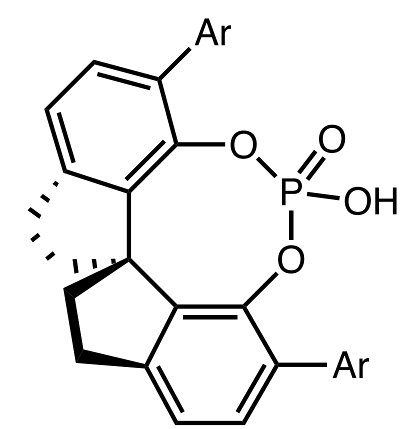
■ Jiang, *JACS*, 2019



Up to 93% yield, 90% ee
>30 examples



Photocatalyst: DPZ



Ar = 2,4,6-*i*$Pr_3C_6H_2$

Two key components: PC + Lewis acid

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Construction of MOF: Lewis acid (Al) + Ir

Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Construction of MOF: Lewis acid (Al) + Ir

$Al(NO_3)_3 \bullet H_2O$

0.14 mmol

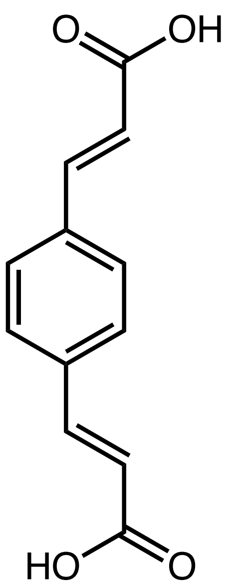
Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

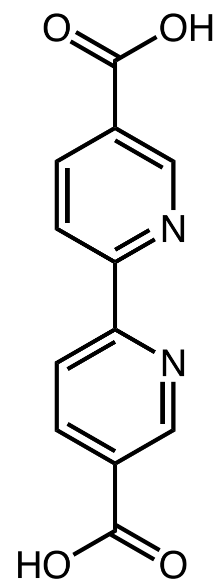
Construction of MOF: Lewis acid (Al) + Ir

$Al(NO_3)_3 \bullet H_2O$

0.14 mmol



2 equiv

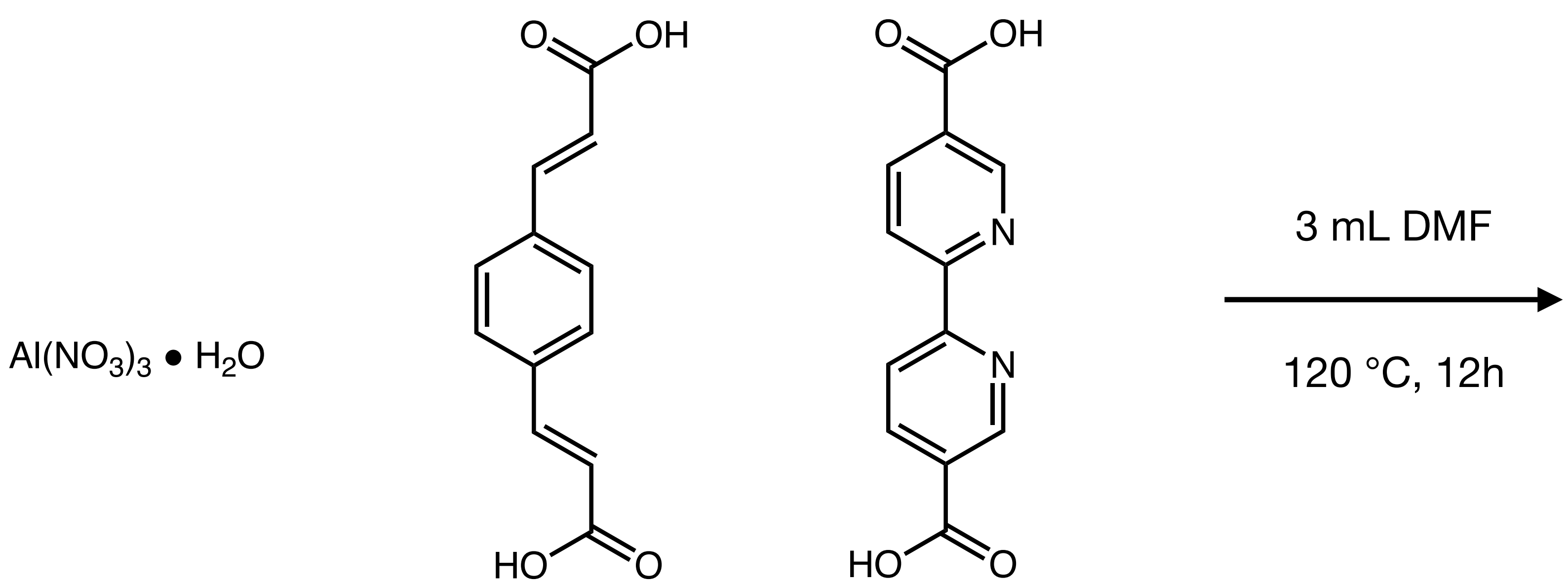


5.3 equiv

Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Construction of MOF: Lewis acid (Al) + Ir

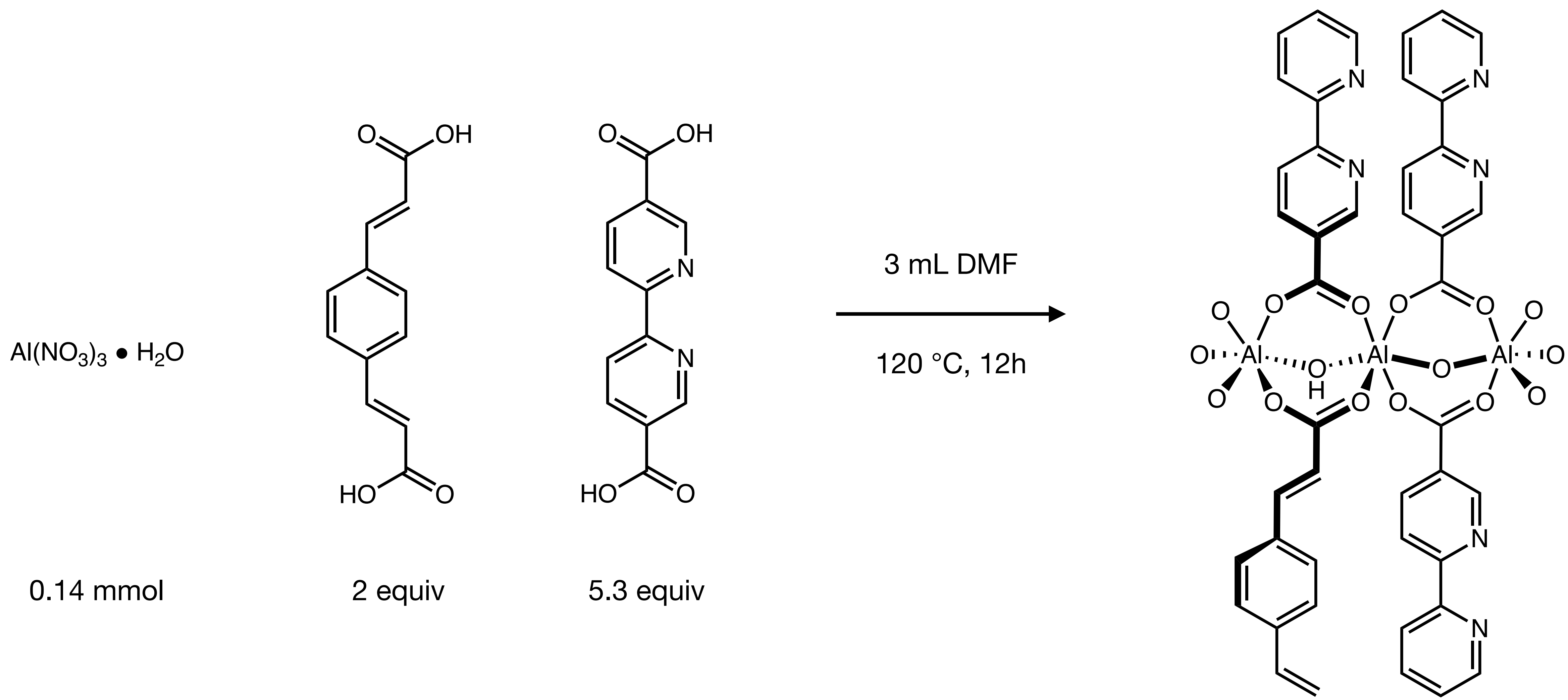


0.14 mmol | 2 equiv | 5.3 equiv

Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

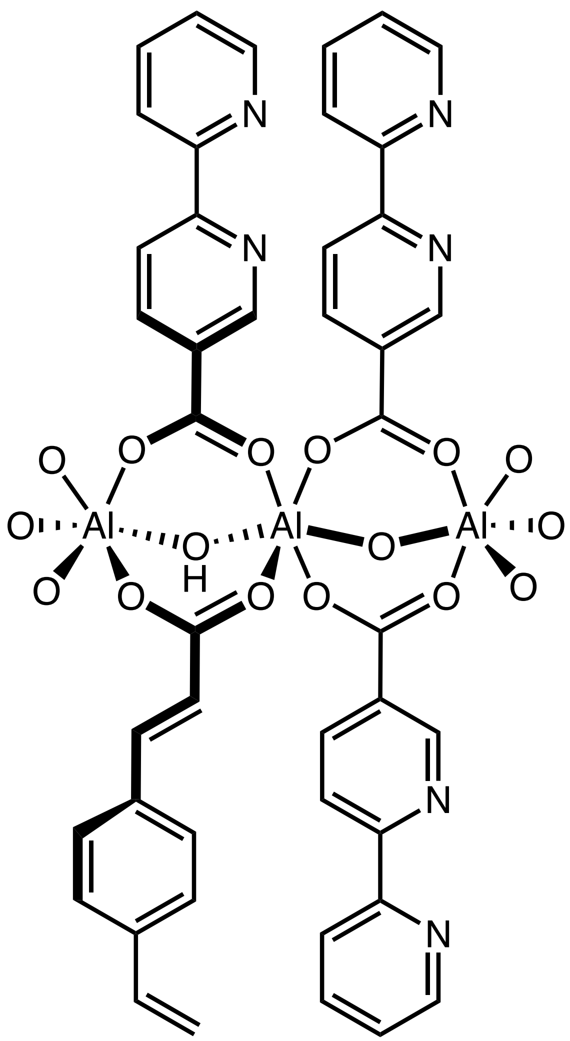
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

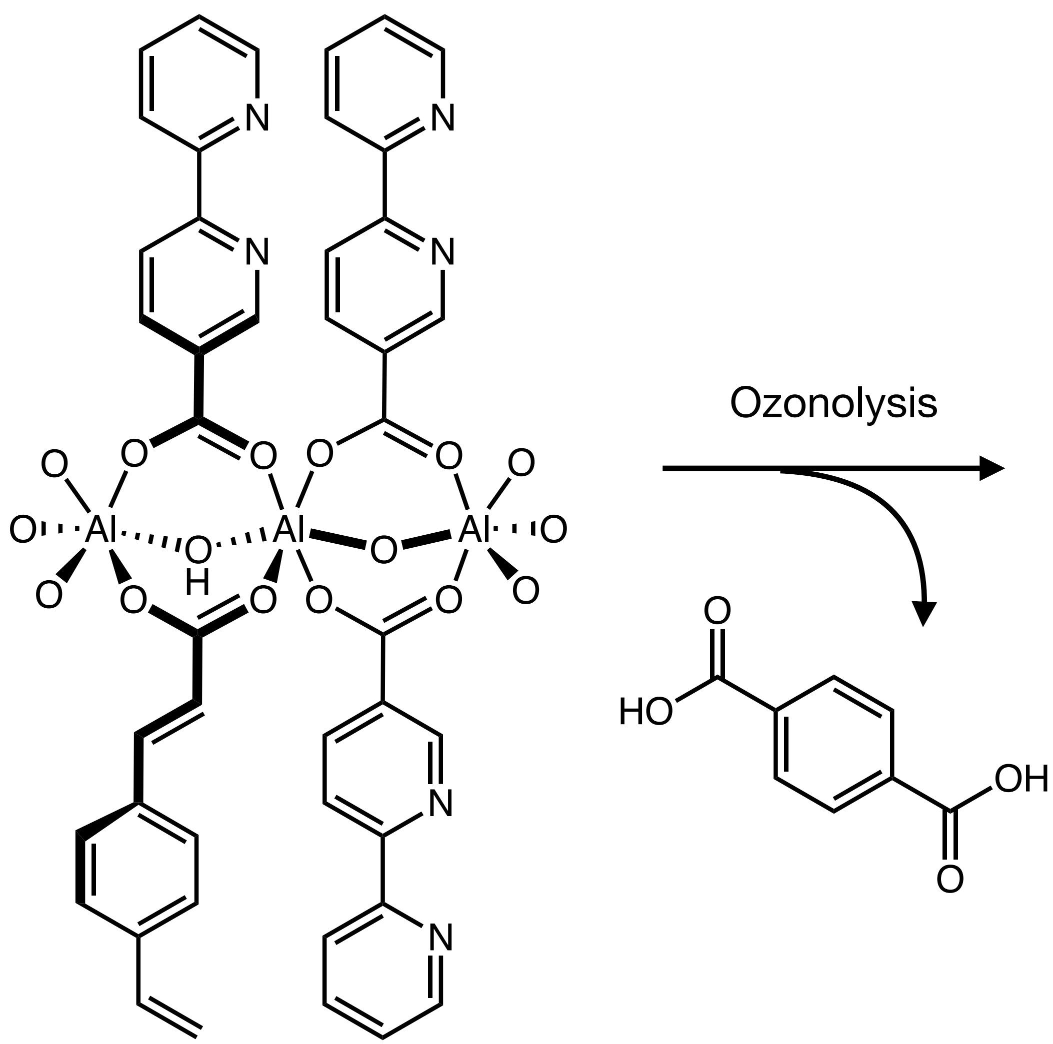
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

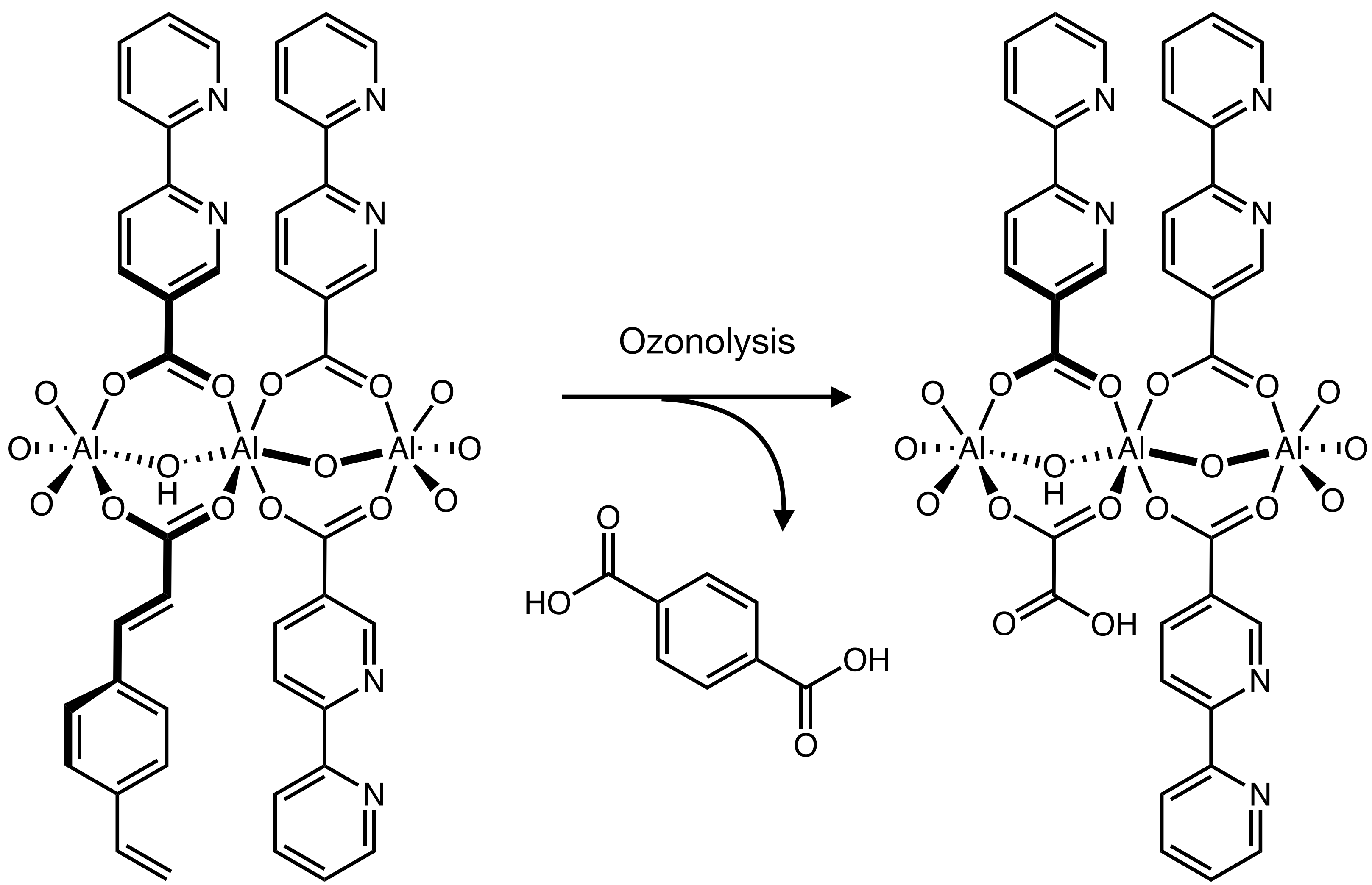
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

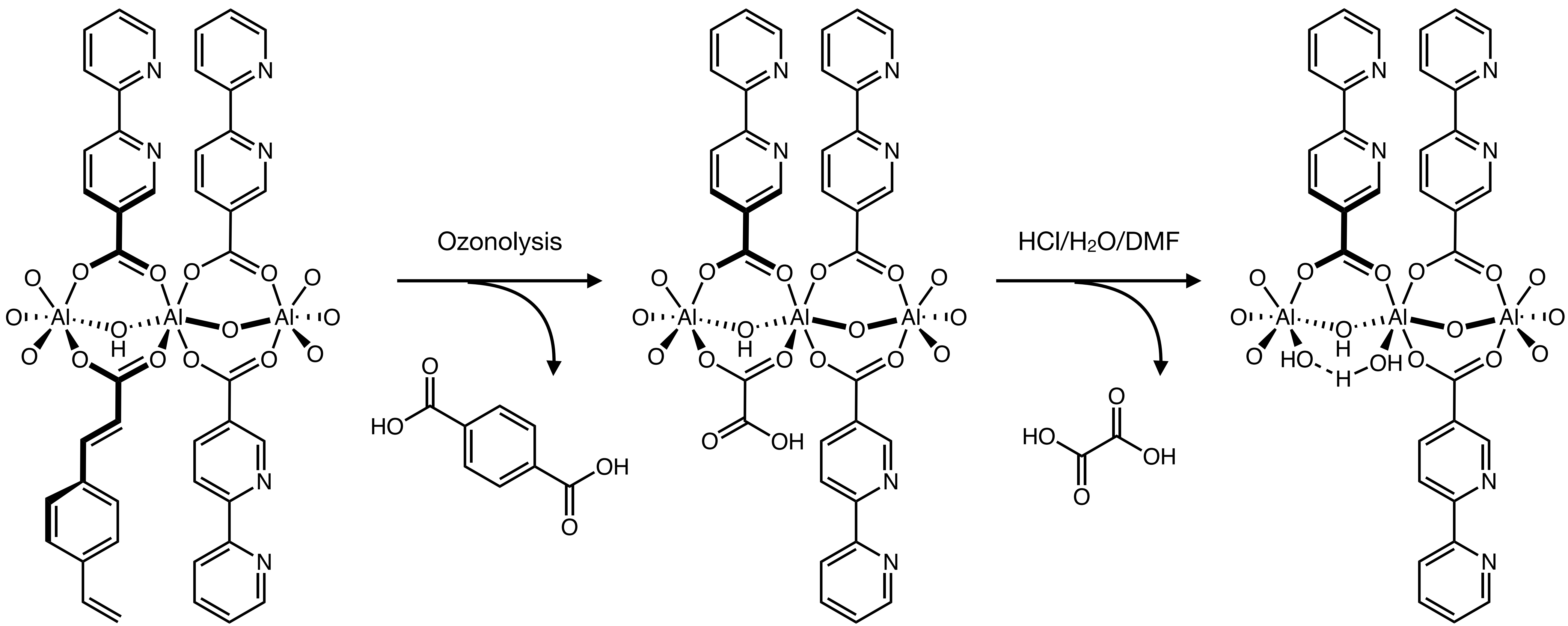
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

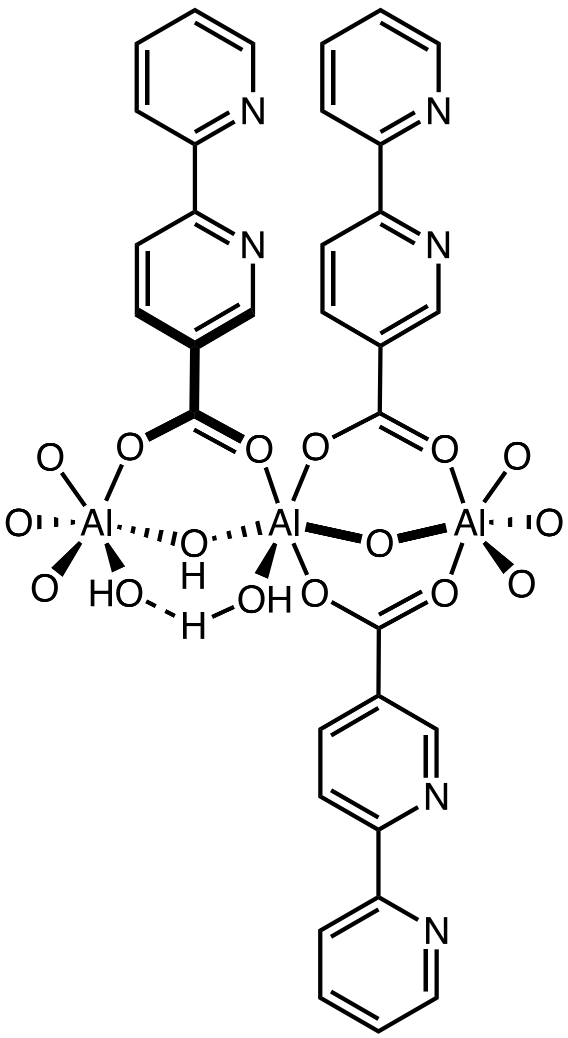
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

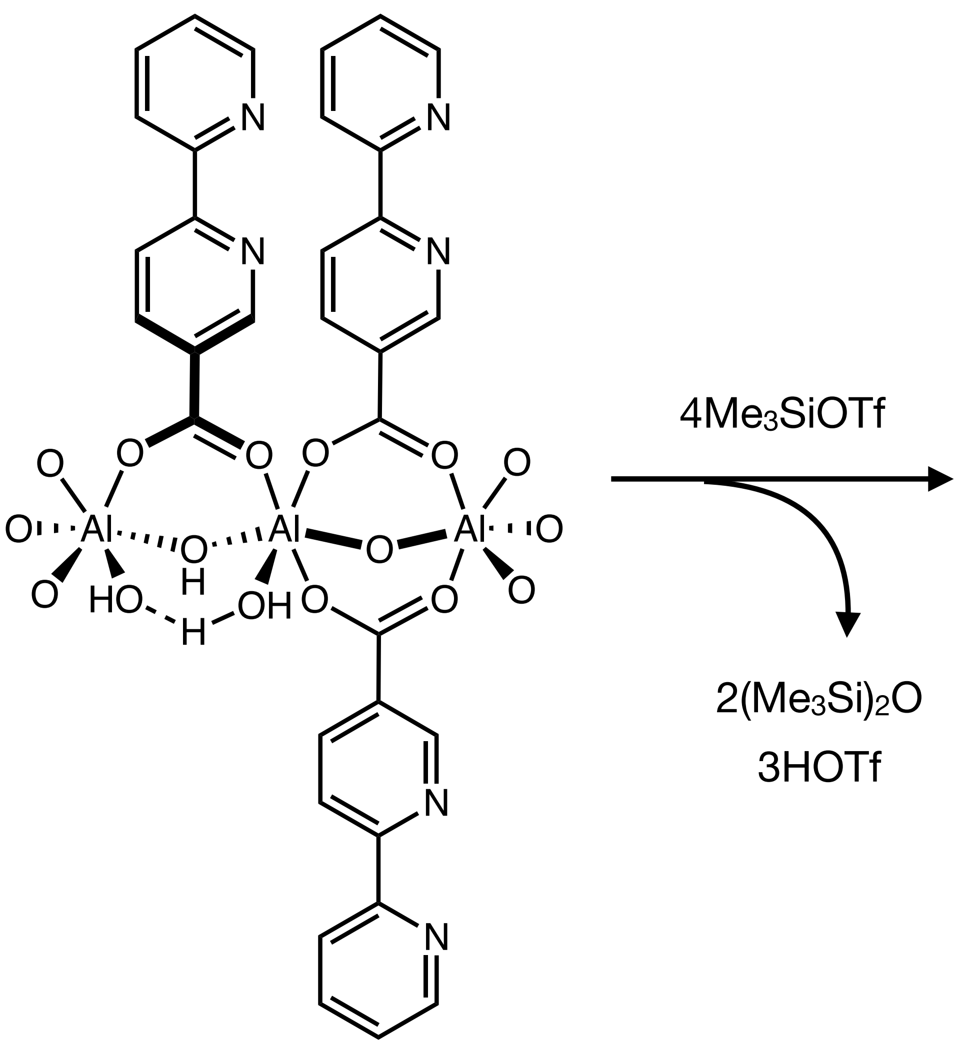
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

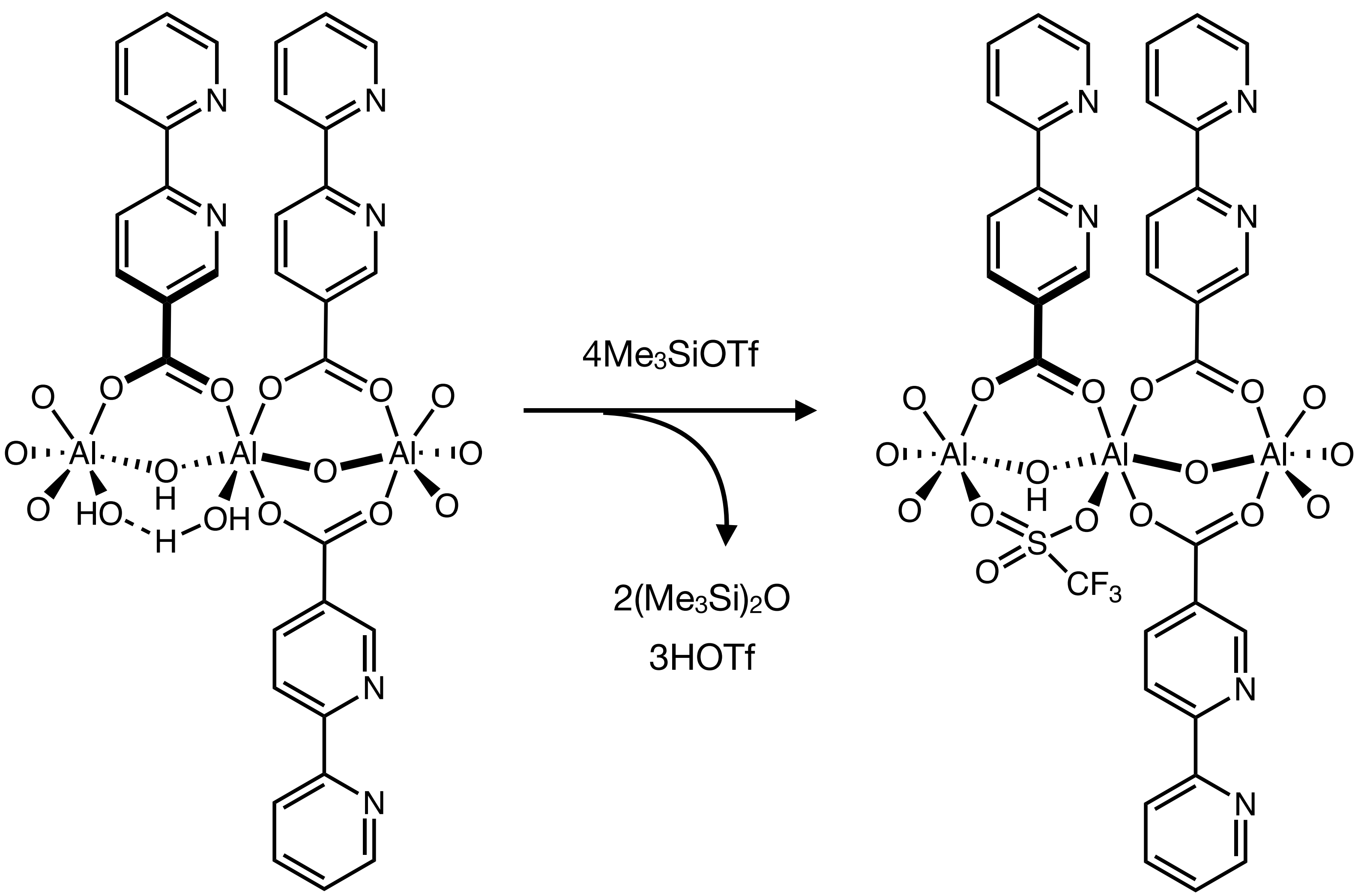
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

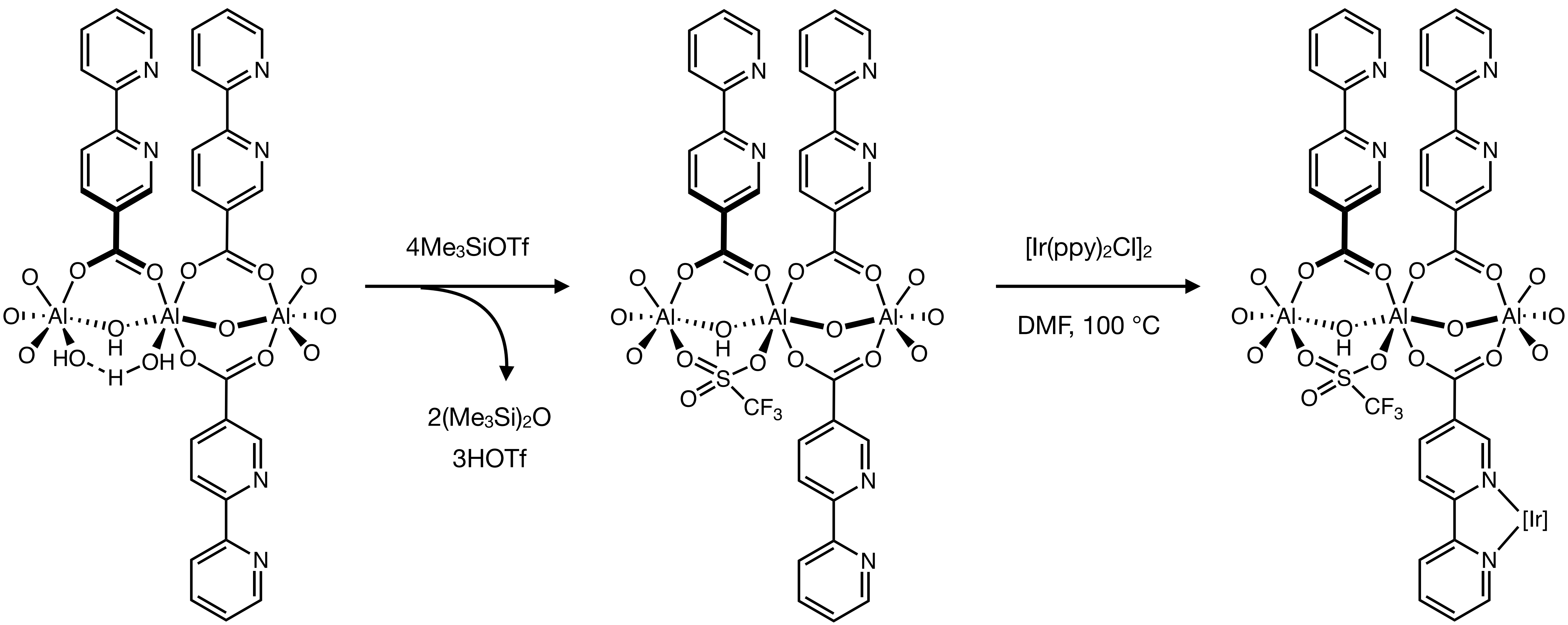
Construction of MOF: Lewis acid (Al) + Ir



Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Construction of MOF: Lewis acid (Al) + Ir

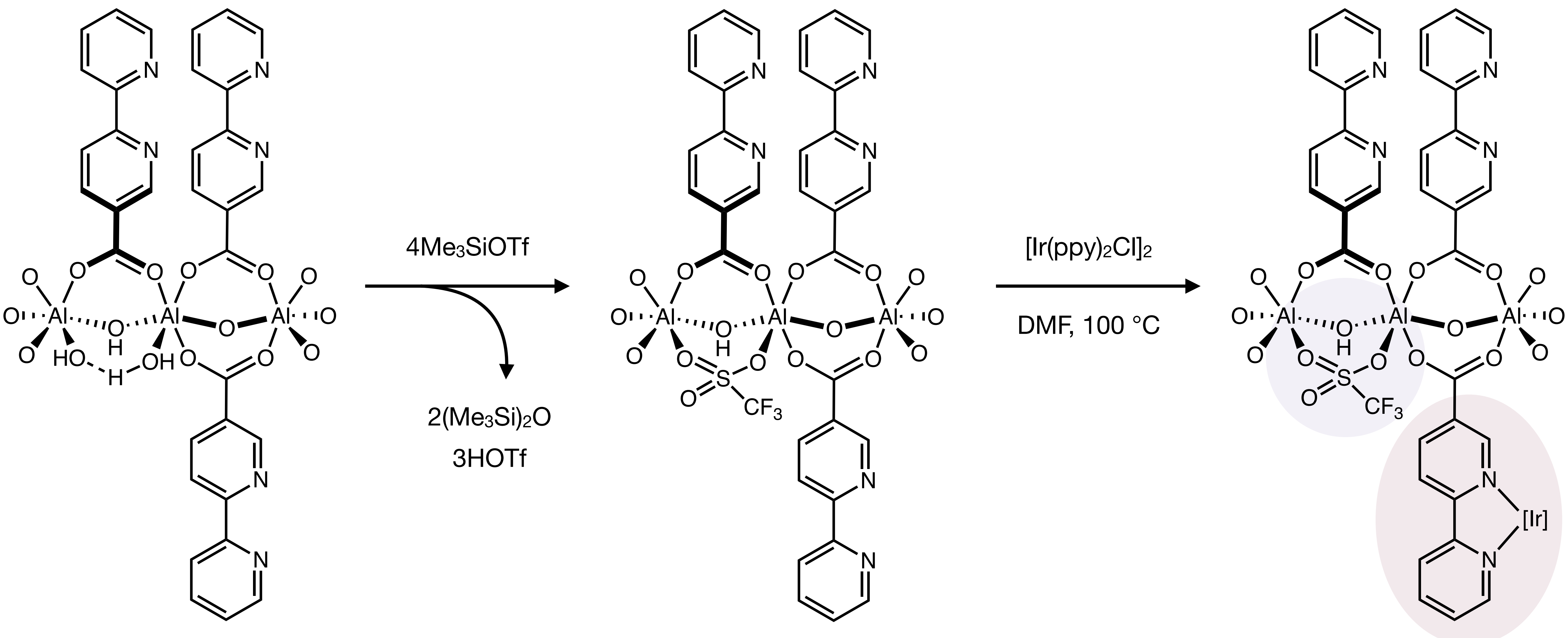


MOF 1-OTf-Ir: $Al(OH)(dcbpy)_{0.7}$ $[Ir(dcbpy)(ppy)_2Cl]_{0.1}(OTf)_4$

Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Construction of MOF: Lewis acid (Al) + Ir



MOF 1-OTf-Ir: $Al(OH)(dcbpy)_{0.7}$
$[Ir(dcbpy)(ppy)_2Cl]_{0.1}(OTf)_4$

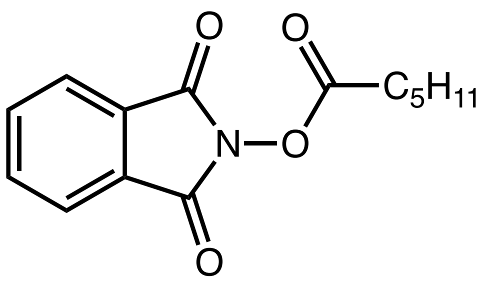
Quan, Y.; Song, Y.; Shi, W.; Xu, Z.; Chen, J. S.; Jiang, X.; Wang, C.; Lin, W. *J Am Chem Soc* **2020**, *142* (19), 8602-8607.

Enhanced reactivity — MOF with dual active sites enabled cross coupling

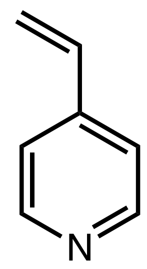
Catalytic reactivity

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity



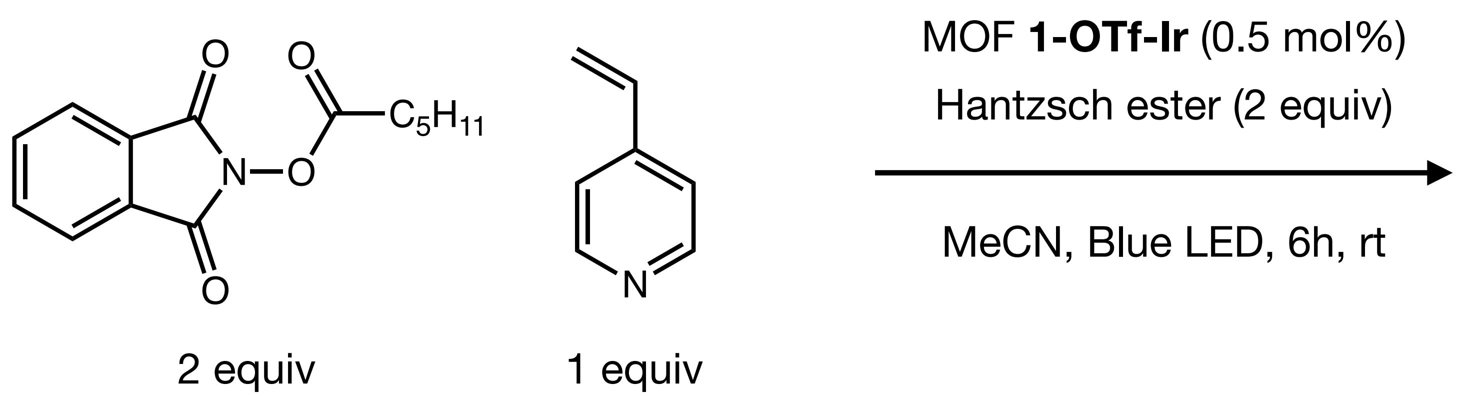
2 equiv



1 equiv

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity



Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

2 equiv

1 equiv

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

2 equiv

1 equiv

90% yield

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

variations from standard conditions	**1c** (%)
without light	none

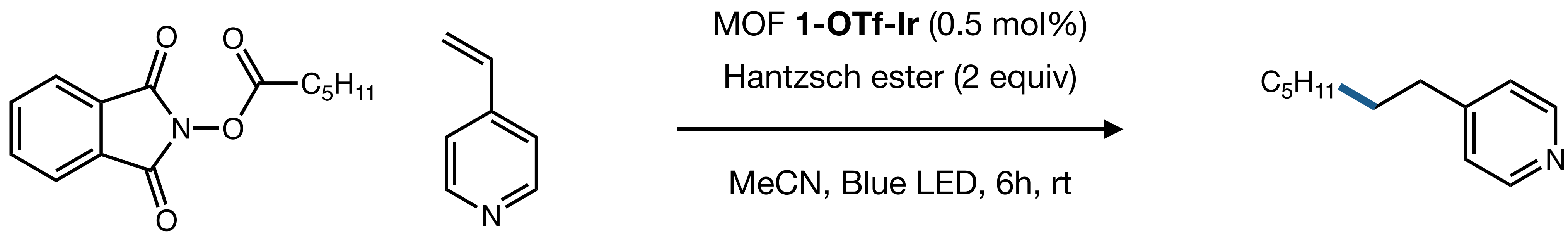
Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

variations from standard conditions	**1c** (%)
without light	none
without MOF **1**-OTf-Ir	trace

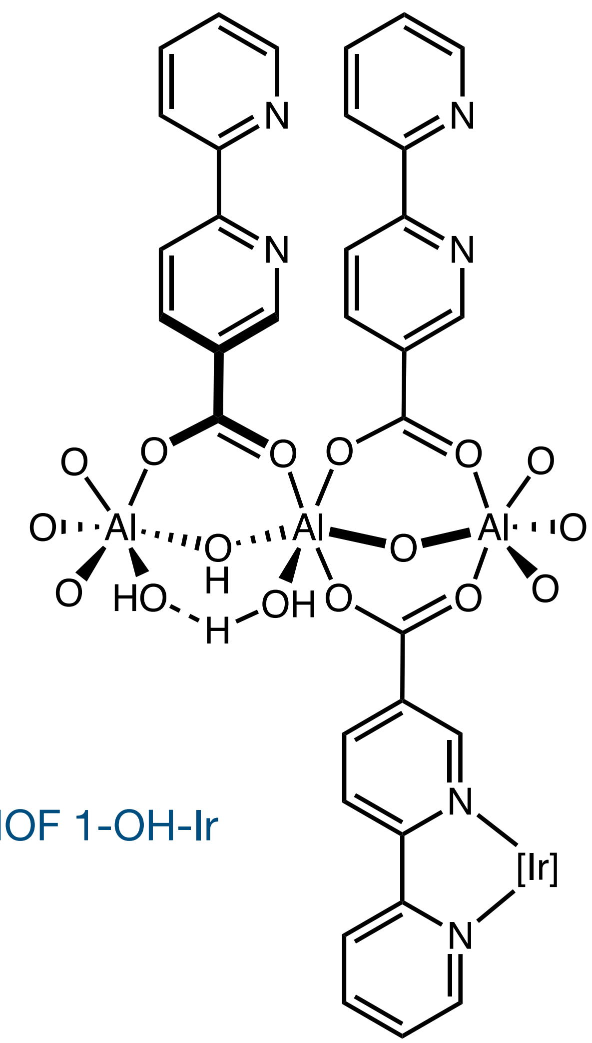
Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity



2 equiv 1 equiv **90% yield**

variations from standard conditions	**1c** (%)
without light	none
without MOF **1**-OTf-Ir	trace
MOF **1**-OH-Ir instead of MOF **1**-OTf-Ir	



MOF 1-OH-Ir

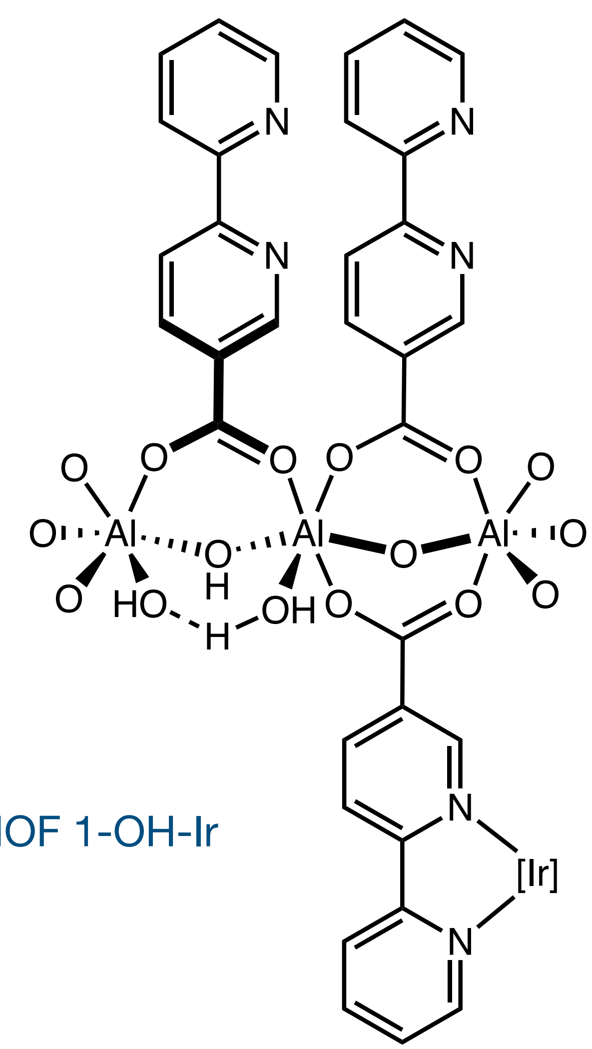
Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

2 equiv 1 equiv **90% yield**

variations from standard conditions	**1c** (%)
without light	none
without MOF 1-OTf-Ir	trace
MOF 1-OH-Ir instead of MOF 1-OTf-Ir	10

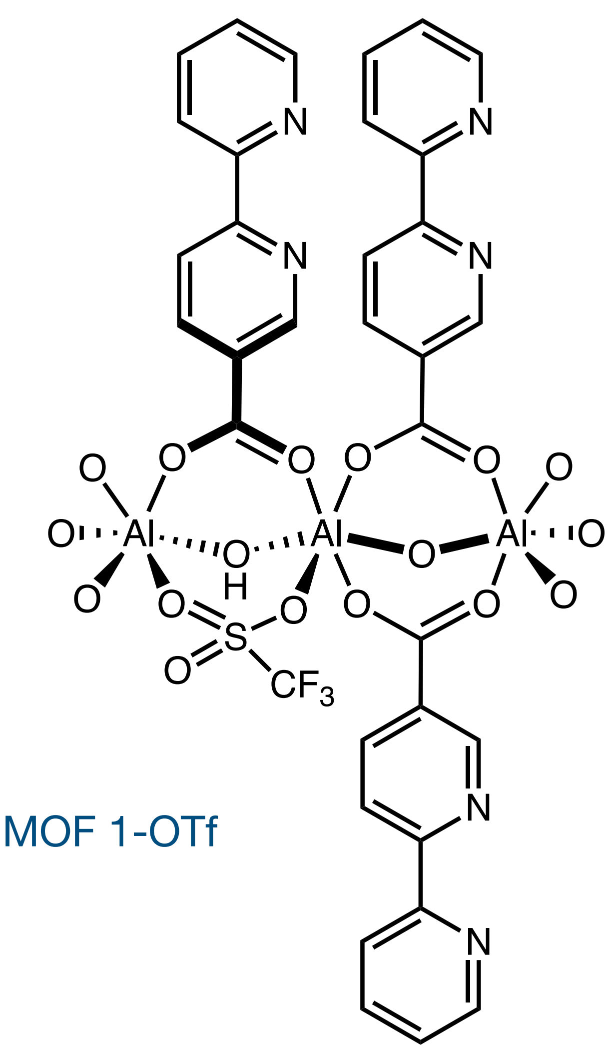
MOF 1-OH-Ir



Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

variations from standard conditions	**1c** (%)
without light	none
without MOF **1**-OTf-Ir	trace
MOF **1**-OH-Ir instead of MOF **1**-OTf-Ir	10
MOF **1**-OTf instead of MOF **1**-OTf-Ir	

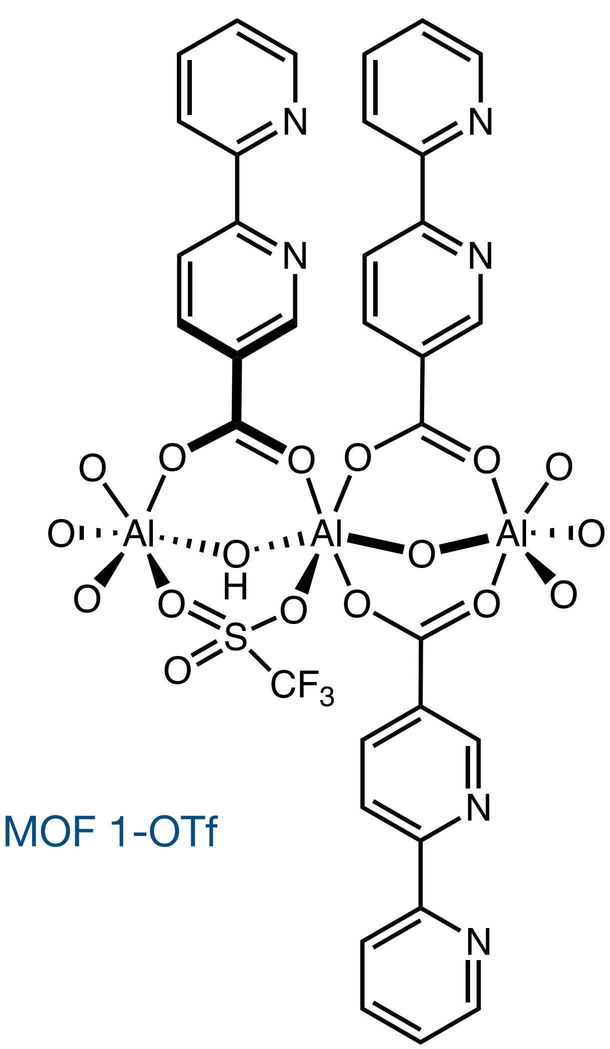


MOF 1-OTf

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

variations from standard conditions	1c (%)
without light	none
without MOF 1-OTf-Ir	trace
MOF 1-OH-Ir instead of MOF 1-OTf-Ir	10
MOF 1-OTf instead of MOF 1-OTf-Ir	8



MOF 1-OTf

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

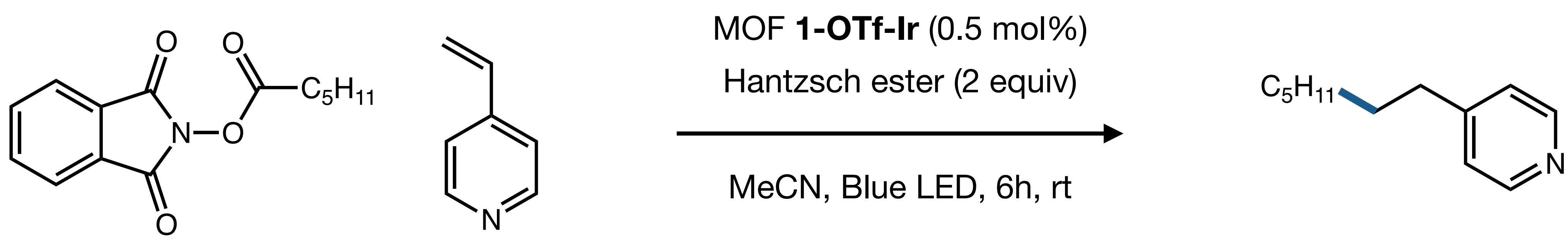
2 equiv

1 equiv

90% yield

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity



2 equiv

1 equiv

90% yield

Recycle of the 1-OTf-Ir

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

Recycle of the 1-OTf-Ir

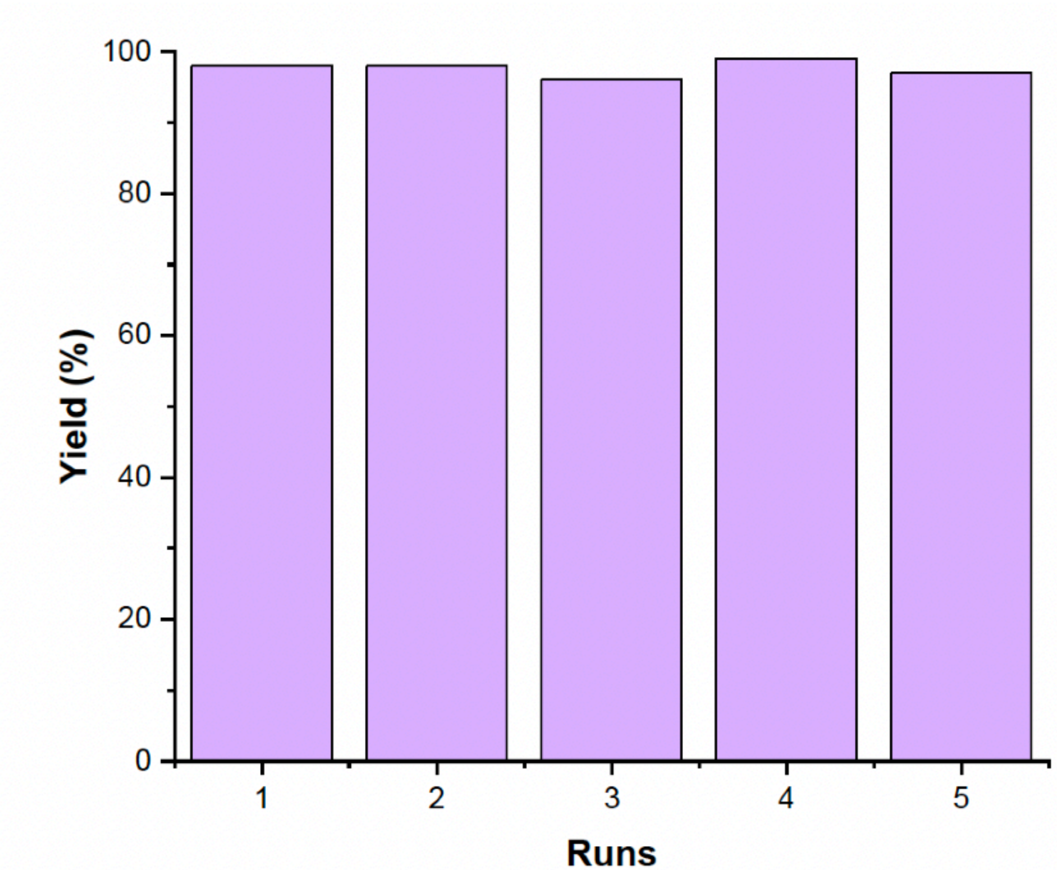
Centrifugation and MeCN wash

Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

Recycle of the 1-OTf-Ir

Centrifugation and MeCN wash



Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

2 equiv

1 equiv

90% yield

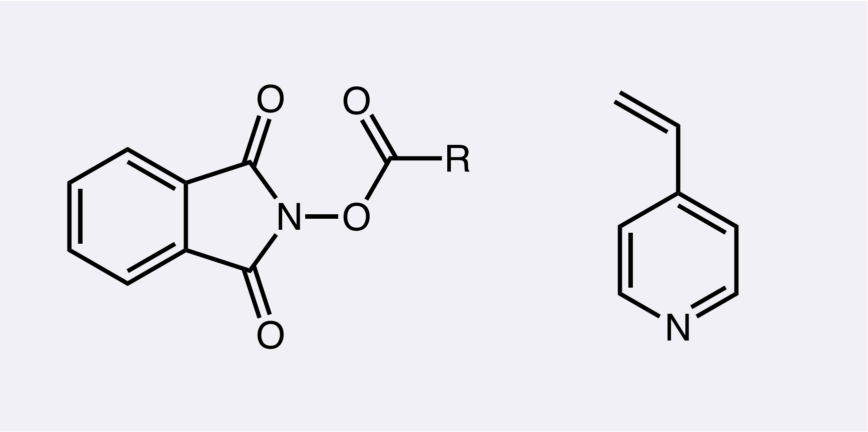
Enhanced reactivity — MOF with dual active sites enabled cross coupling

Catalytic reactivity

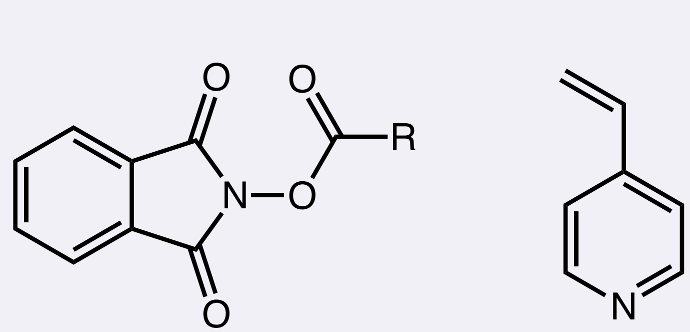
Enhanced reactivity — MOF with dual active sites enabled cross coupling

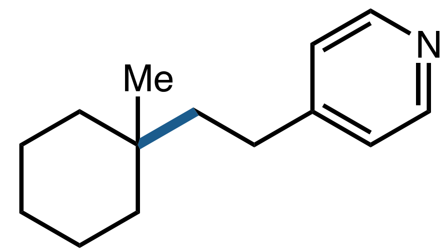
Catalytic reactivity

Enhanced reactivity — MOF with dual active sites enabled cross coupling

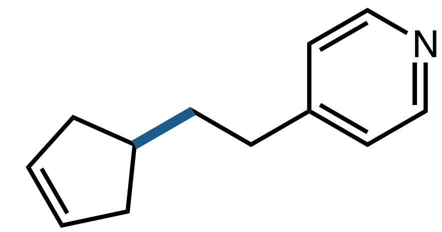


Enhanced reactivity — MOF with dual active sites enabled cross coupling

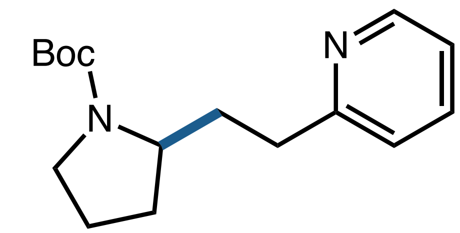




90% yield

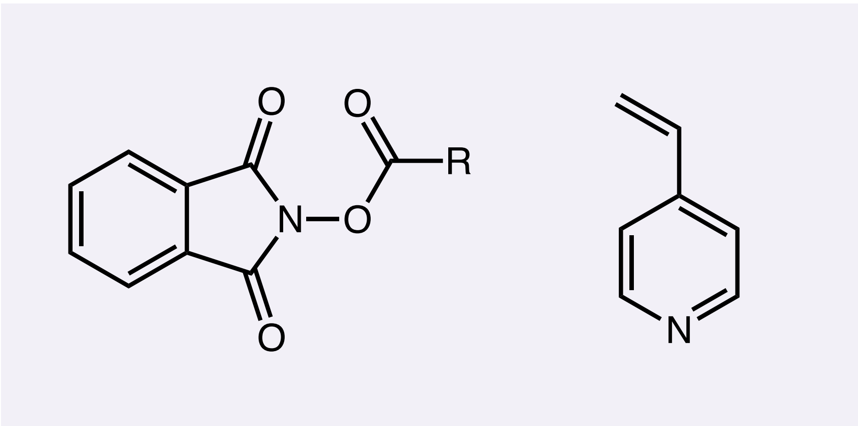


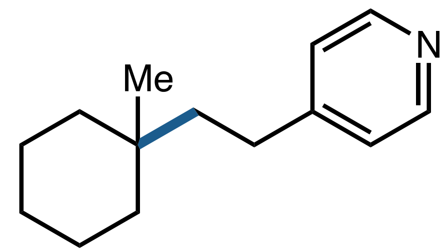
70% yield



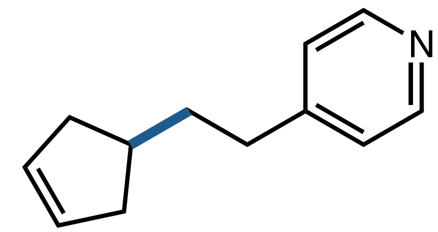
51% yield

Enhanced reactivity — MOF with dual active sites enabled cross coupling

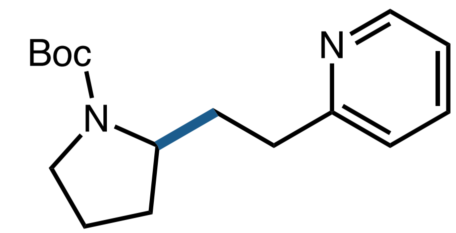




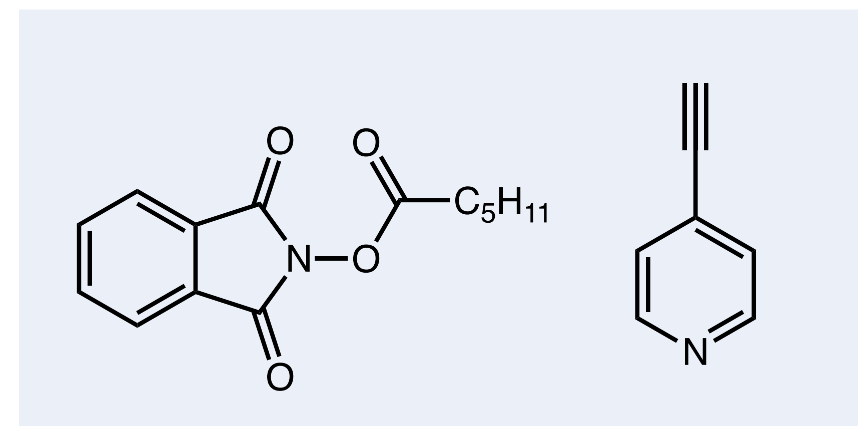
90% yield



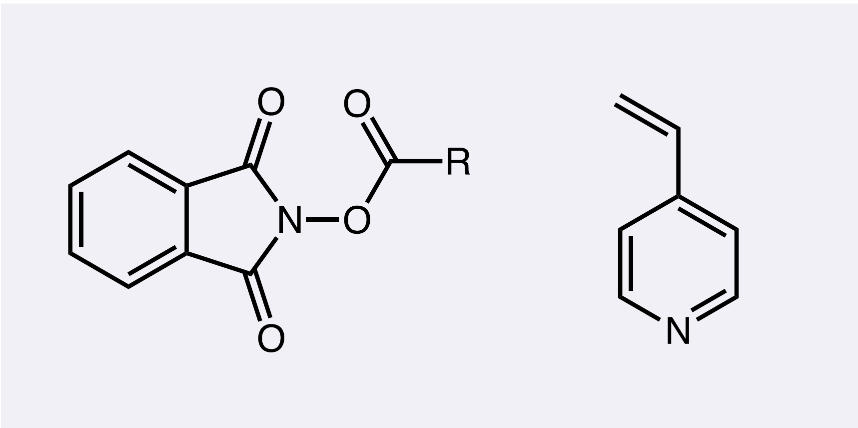
70% yield

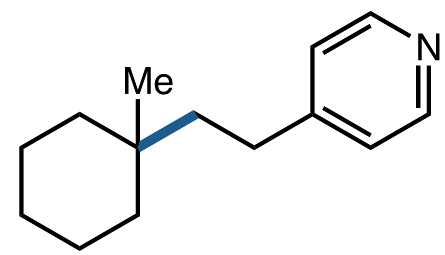


51% yield

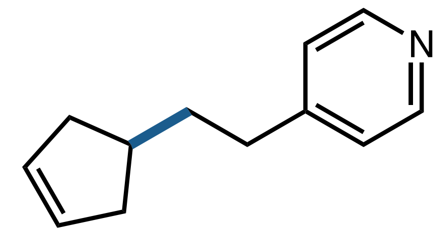


Enhanced reactivity — MOF with dual active sites enabled cross coupling

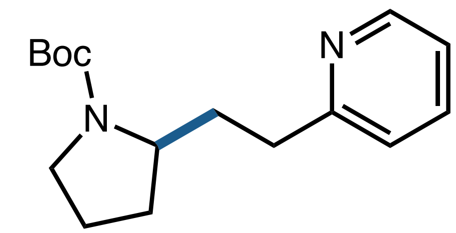




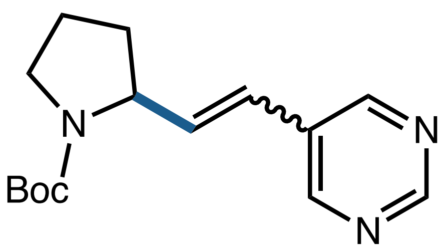
90% yield



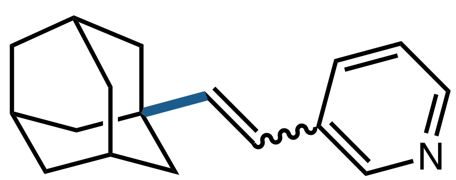
70% yield



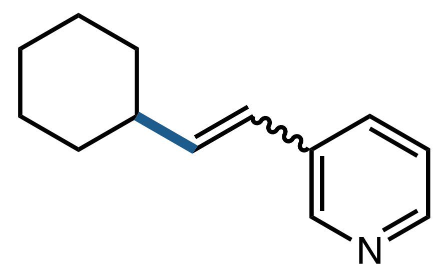
51% yield



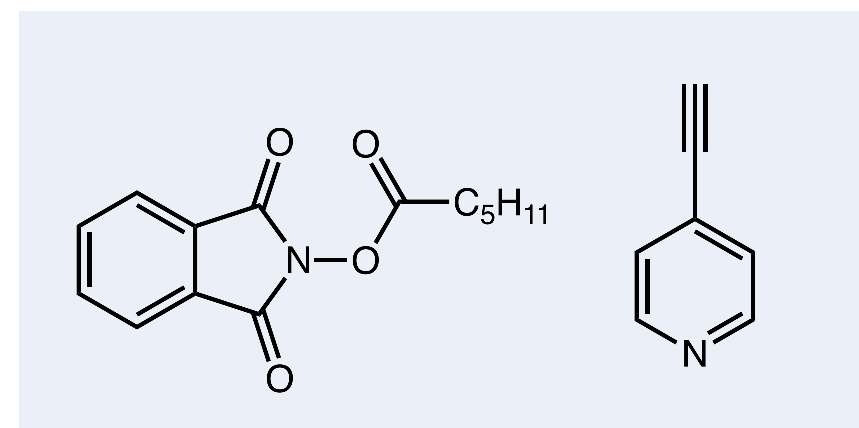
95% yield (Z/E = 3.3/1)



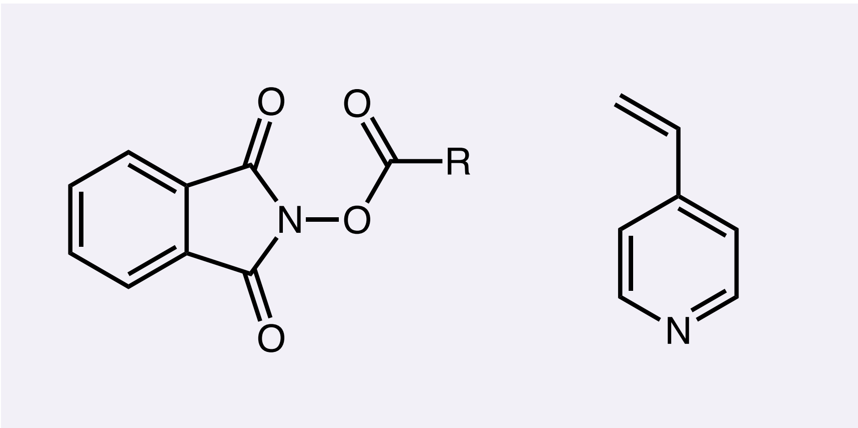
50% yield (Z/E = 10/1)

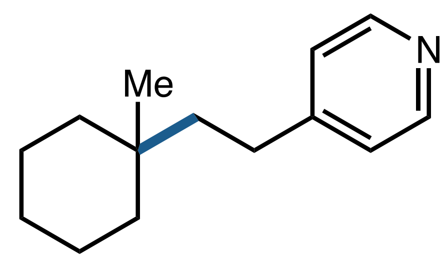


73% yield (Z/E = 1.9/1)

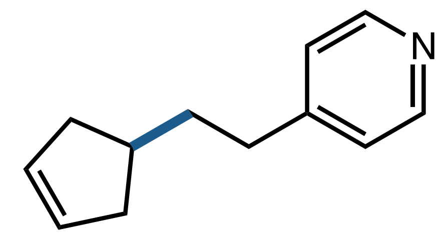


Enhanced reactivity — MOF with dual active sites enabled cross coupling

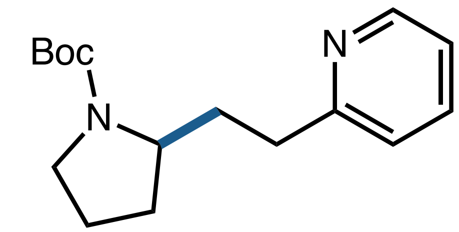




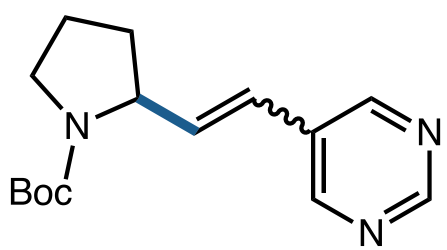
90% yield



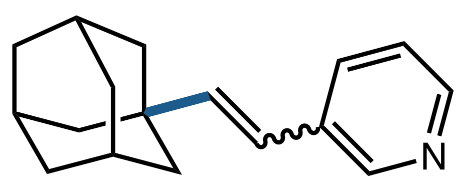
70% yield



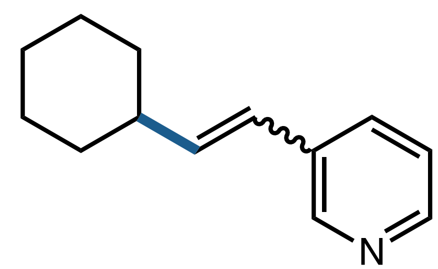
51% yield



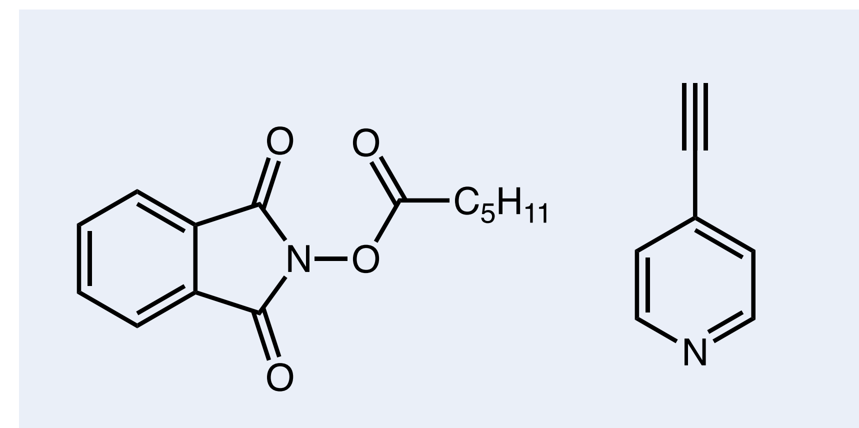
95% yield (Z/E = 3.3/1)

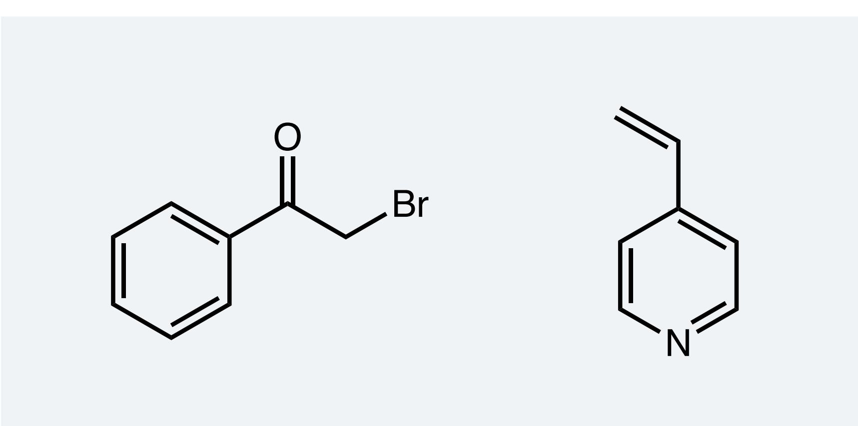


50% yield (Z/E = 10/1)

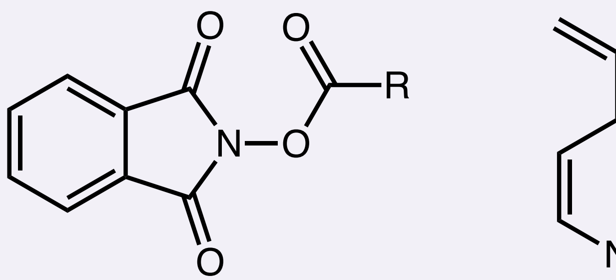


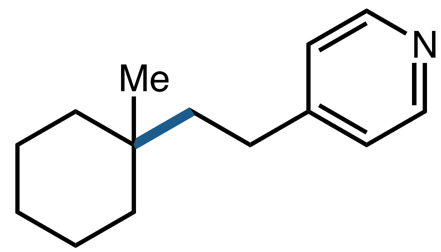
73% yield (Z/E = 1.9/1)



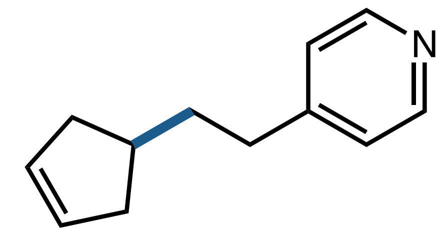


Enhanced reactivity — MOF with dual active sites enabled cross coupling

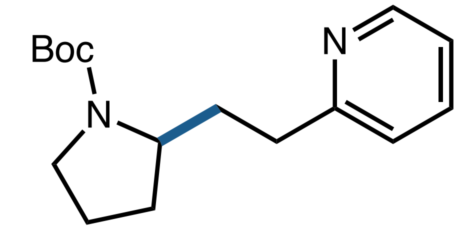




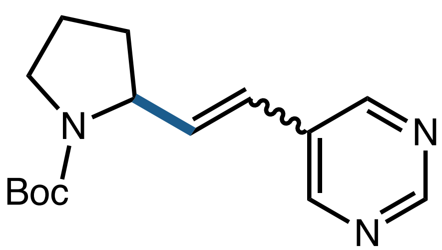
90% yield



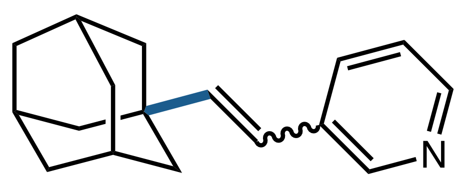
70% yield



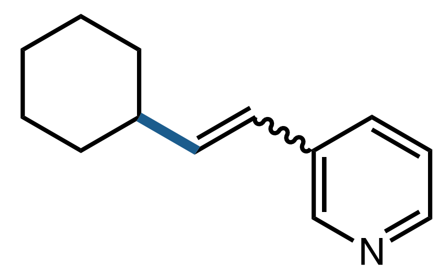
51% yield



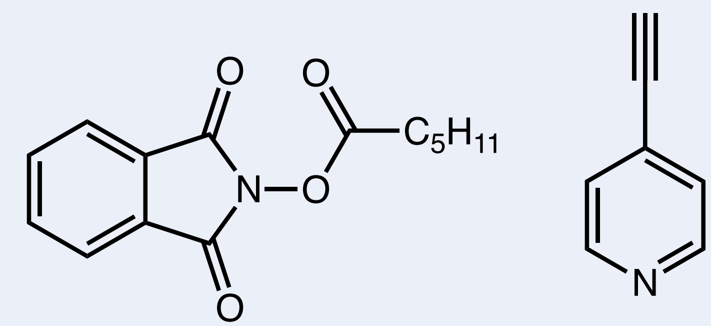
95% yield (Z/E = 3.3/1)

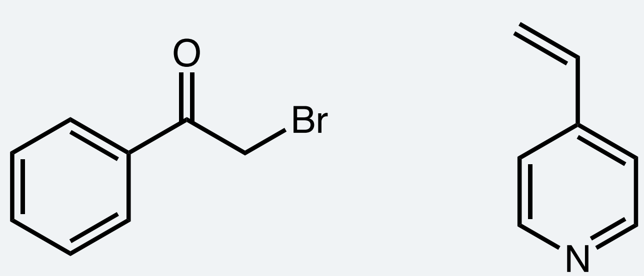


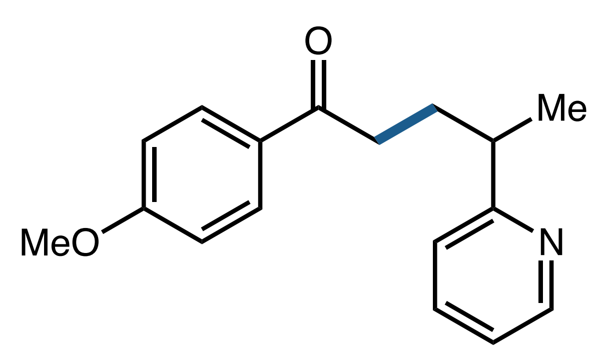
50% yield (Z/E = 10/1)



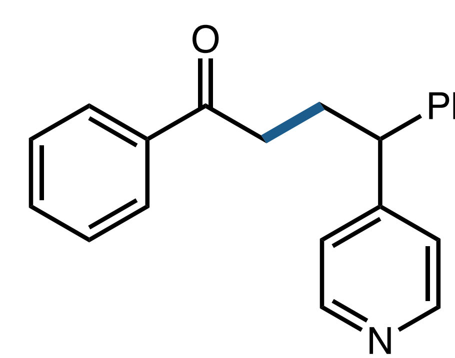
73% yield (Z/E = 1.9/1)







78% yield



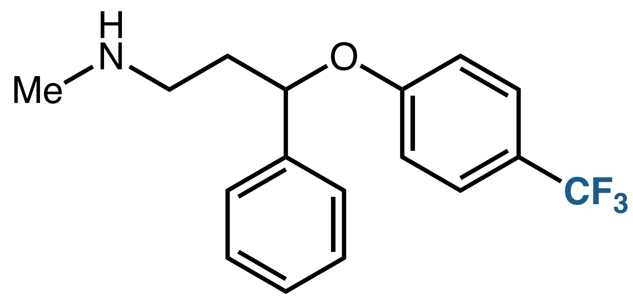
53% yield

What are possible organic synthetic applications of MOFs?

Case study 1: Enhanced reactivity

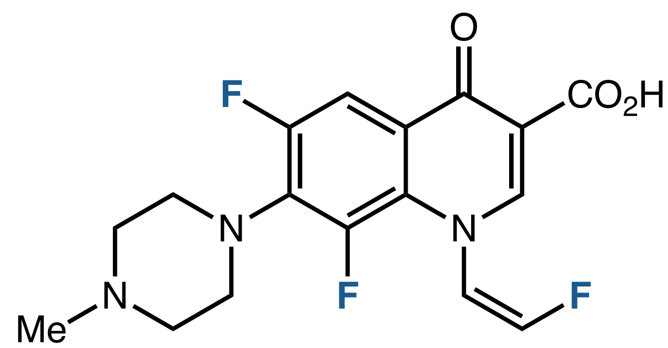
Case study 2: Novel reagents based on MOFs

Novel reagents based on MOFs



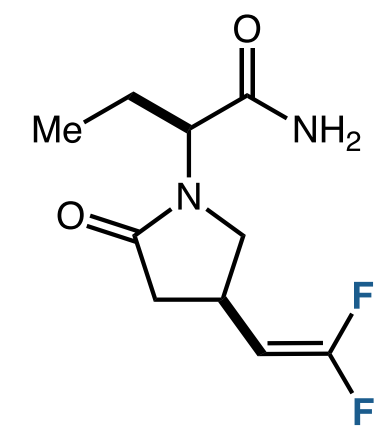
Fluoxetine

antidepressant



Fleroxacin analog

antibacterial

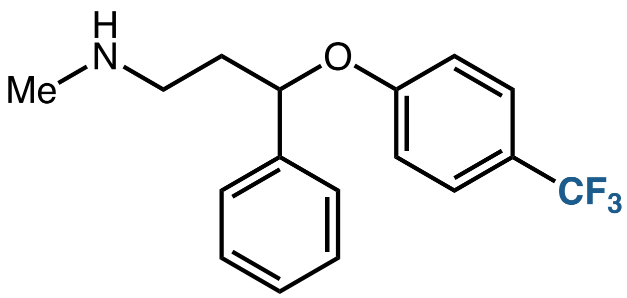


Seletracetam

anticonvulsant

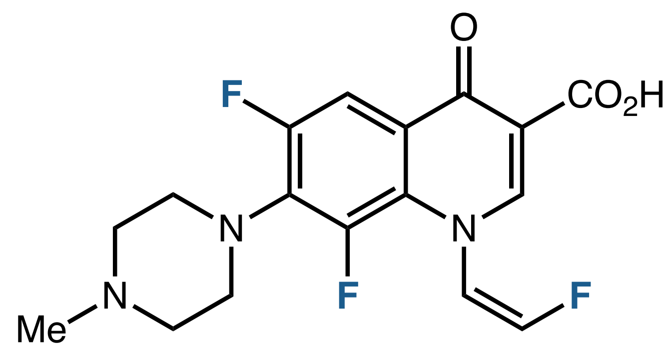
Keasler, K. T.; Zick, M. E.; Stacy, E. E.; Kim, J.; Lee, J. H.; Aeindartehran, L.; Runcevski, T.; Milner, P. J. *Science* **2023**, *381* (6665), 1455-1461.

Novel reagents based on MOFs



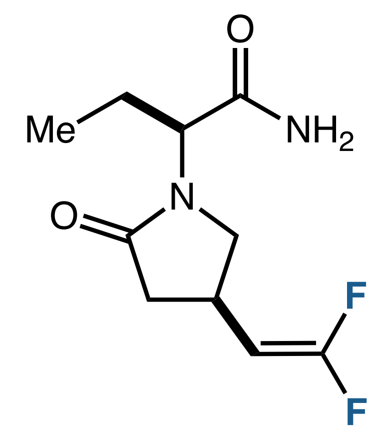
Fluoxetine

antidepressant



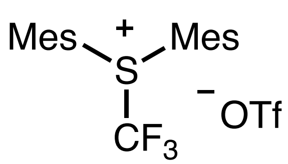
Fleroxacin analog

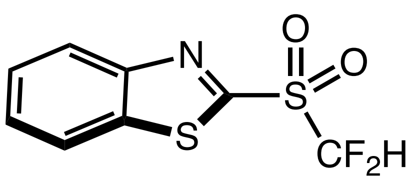
antibacterial

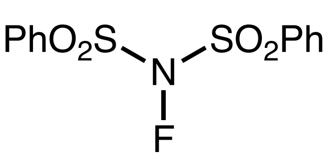


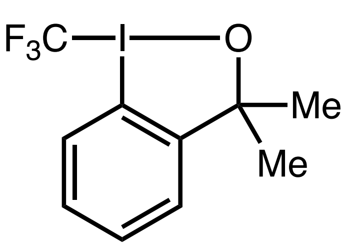
Seletracetam

anticonvulsant





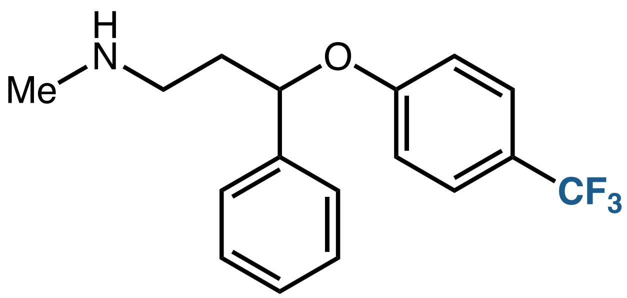




Well-established fluorination reagents

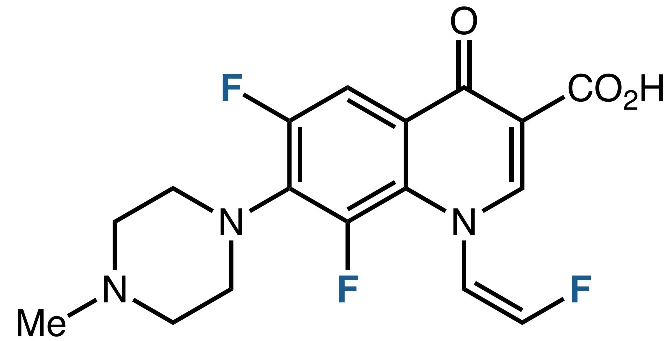
Keasler, K. T.; Zick, M. E.; Stacy, E. E.; Kim, J.; Lee, J. H.; Aeindartehran, L.; Runcevski, T.; Milner, P. J. *Science* **2023**, *381* (6665), 1455-1461.

Novel reagents based on MOFs



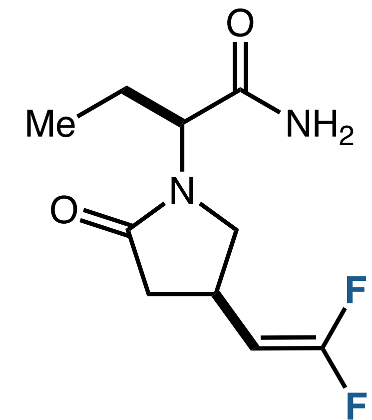
Fluoxetine

antidepressant



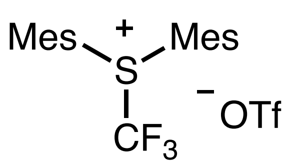
Fleroxacin analog

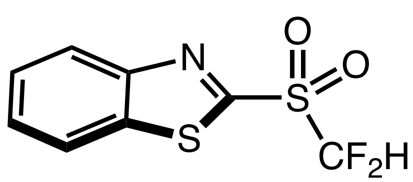
antibacterial

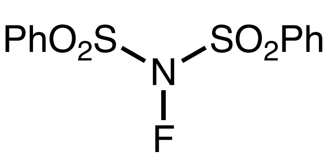


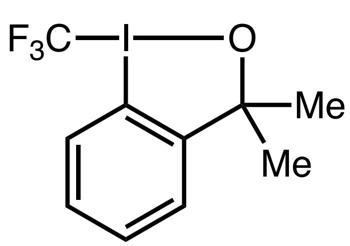
Seletracetam

anticonvulsant

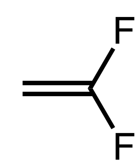




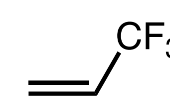




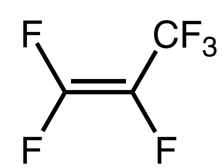
Well-established fluorination reagents



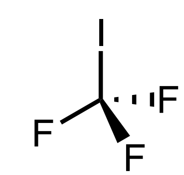
vinylidene fluoride
(VDF)



trifluoropropene
(TFP)



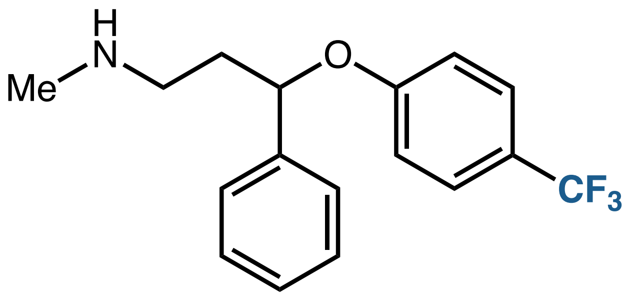
hexafluoropropene
(HFP)



trifluoromethyl iodide
(TEMI)

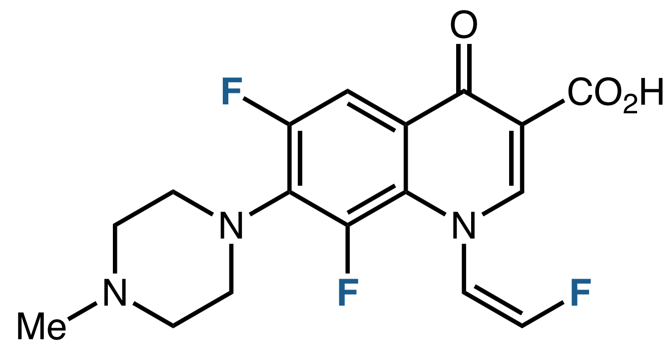
Keasler, K. T.; Zick, M. E.; Stacy, E. E.; Kim, J.; Lee, J. H.; Aeindartehran, L.; Runcevski, T.; Milner, P. J. *Science* **2023**, *381* (6665), 1455-1461.

Novel reagents based on MOFs



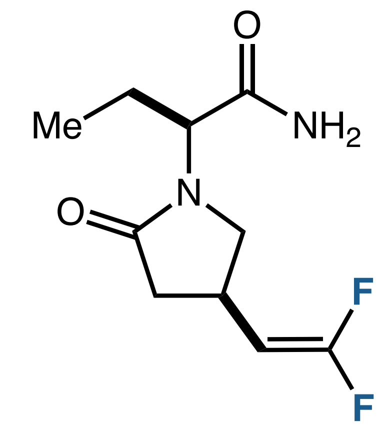
Fluoxetine

antidepressant



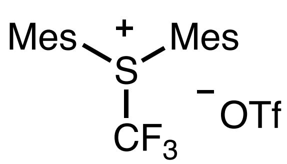
Fleroxacin analog

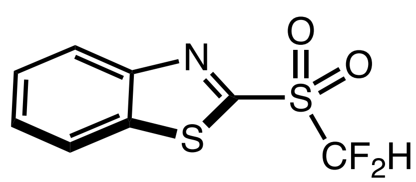
antibacterial

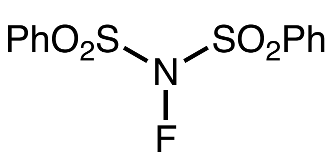


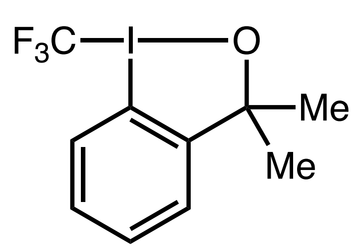
Seletracetam

anticonvulsant

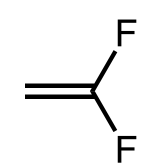




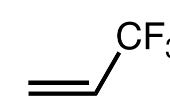




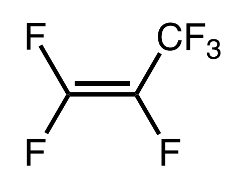
Well-established fluorination reagents



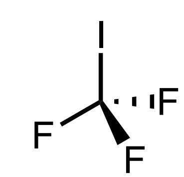
vinylidene fluoride
(VDF)



trifluoropropene
(TFP)



hexafluoropropene
(HFP)

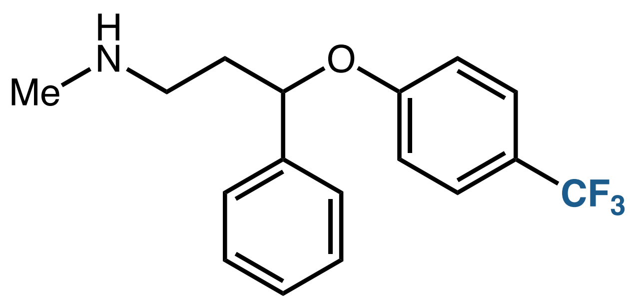


trifluoromethyl iodide
(TEMI)

Underexplored gaseous fluorination reagents

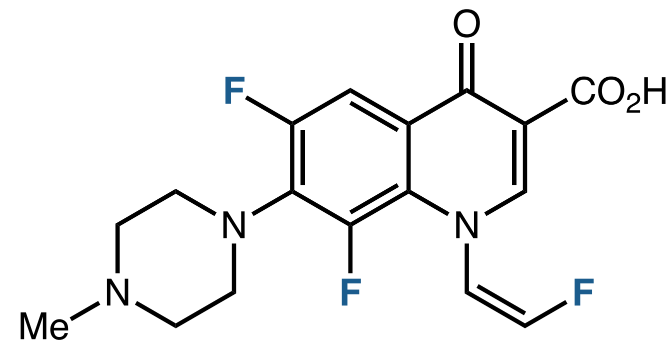
Keasler, K. T.; Zick, M. E.; Stacy, E. E.; Kim, J.; Lee, J. H.; Aeindartehran, L.; Runcevski, T.; Milner, P. J. *Science* **2023**, *381* (6665), 1455-1461.

Novel reagents based on MOFs



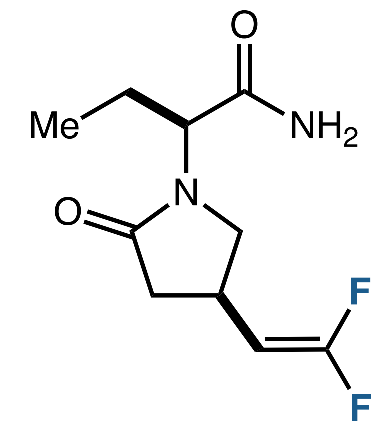
Fluoxetine

antidepressant



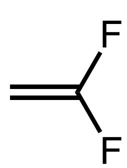
Fleroxacin analog

antibacterial



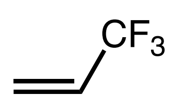
Seletracetam

anticonvulsant



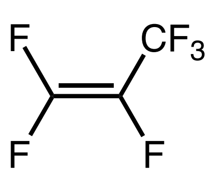
vinylidene fluoride

(VDF)



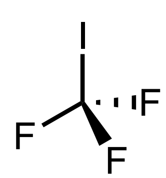
trifluoropropene

(TFP)



hexafluoropropene

(HFP)

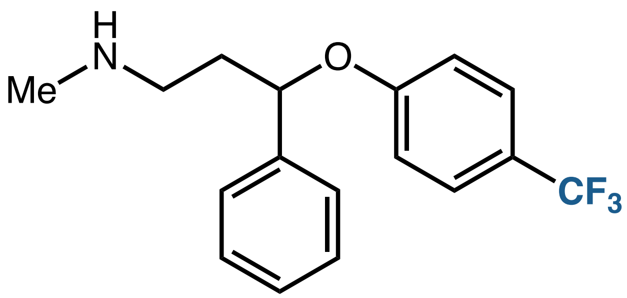


trifluoromethyl iodide

(TFMI)

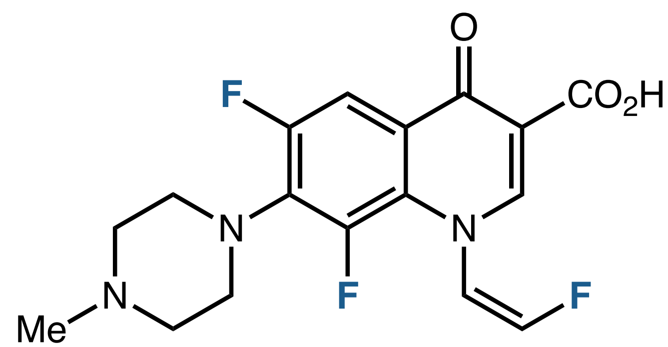
Underexplored gaseous fluorination reagents

Novel reagents based on MOFs



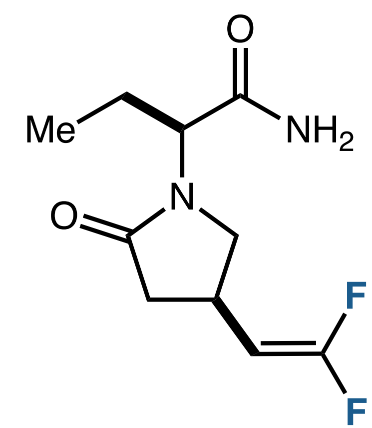
Fluoxetine

antidepressant



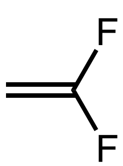
Fleroxacin analog

antibacterial

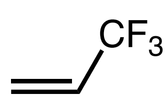


Seletracetam

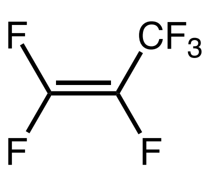
anticonvulsant



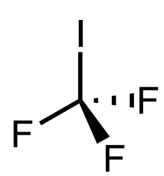
vinylidene fluoride
(VDF)



trifluoropropene
(TFP)



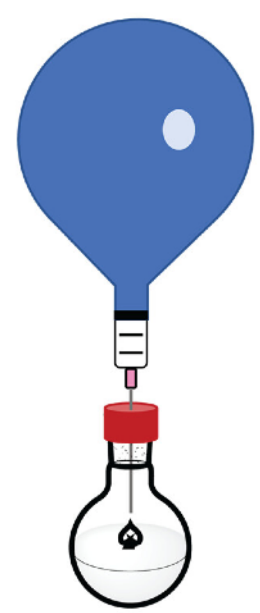
hexafluoropropene
(HFP)



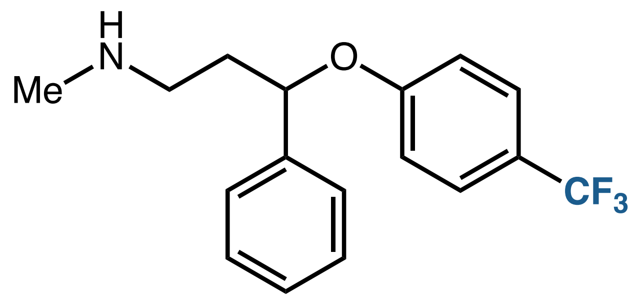
trifluoromethyl iodide
(TEMI)

Underexplored gaseous fluorination reagents

Balloon

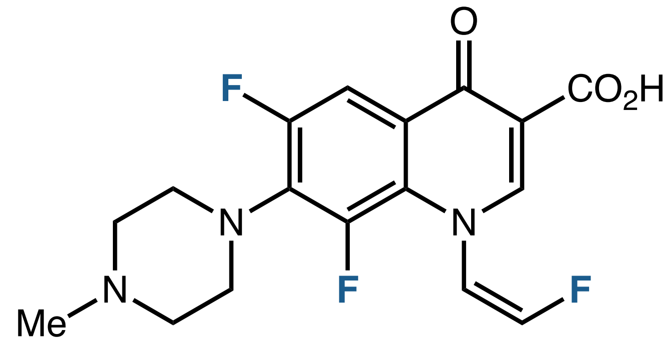


Novel reagents based on MOFs



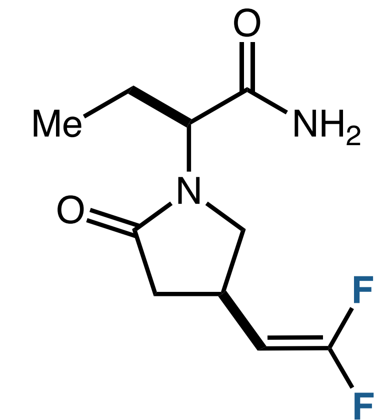
Fluoxetine

antidepressant



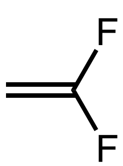
Fleroxacin analog

antibacterial

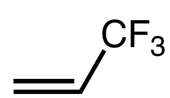


Seletracetam

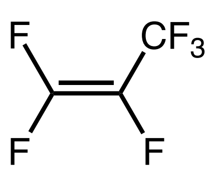
anticonvulsant



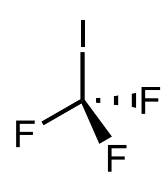
vinylidene fluoride
(VDF)



trifluoropropene
(TFP)



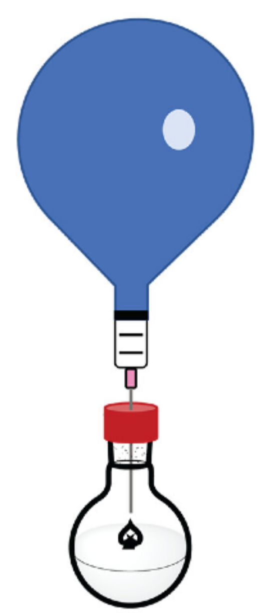
hexafluoropropene
(HFP)



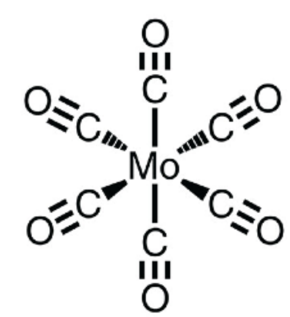
trifluoromethyl iodide
(TEMI)

Underexplored gaseous fluorination reagents

Balloon

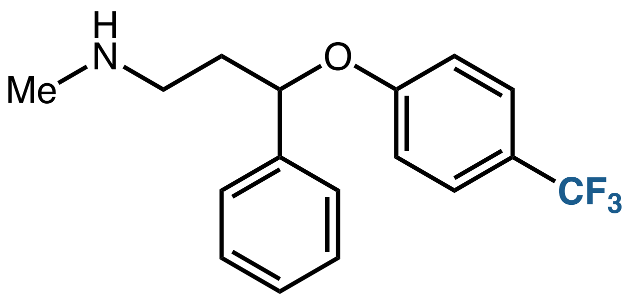


Molecular precursor



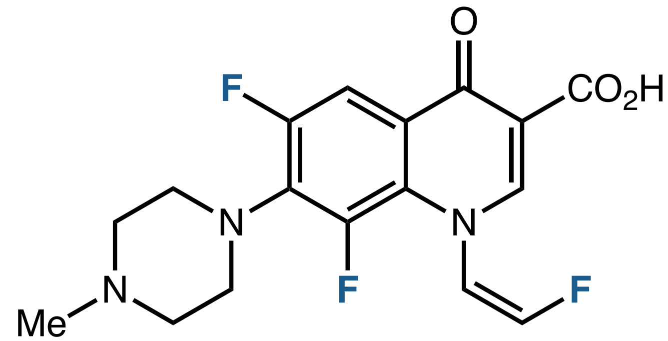
CO

Novel reagents based on MOFs



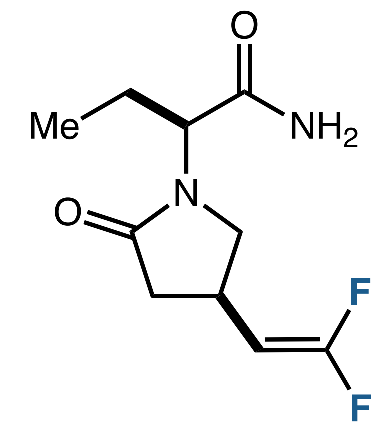
Fluoxetine

antidepressant



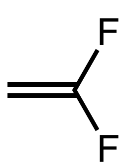
Fleroxacin analog

antibacterial



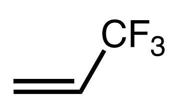
Seletracetam

anticonvulsant



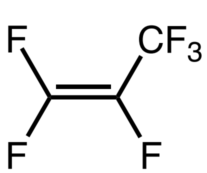
vinylidene fluoride

(VDF)



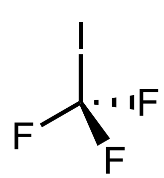
trifluoropropene

(TFP)



hexafluoropropene

(HFP)

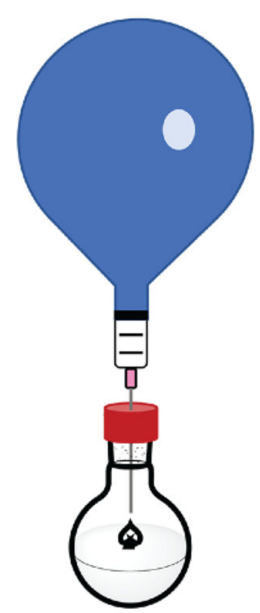


trifluoromethyl iodide

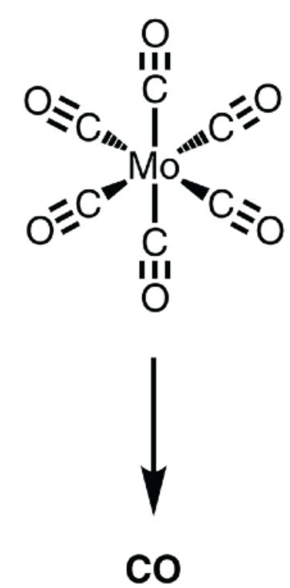
(TEMI)

Underexplored gaseous fluorination reagents

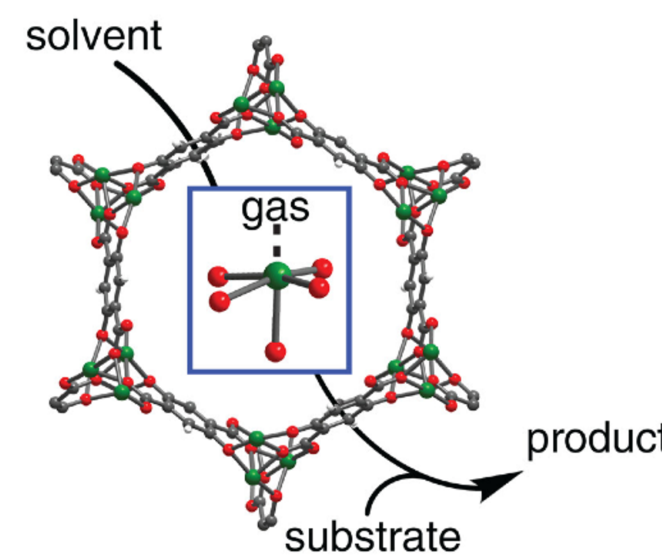
Balloon



Molecular precursor

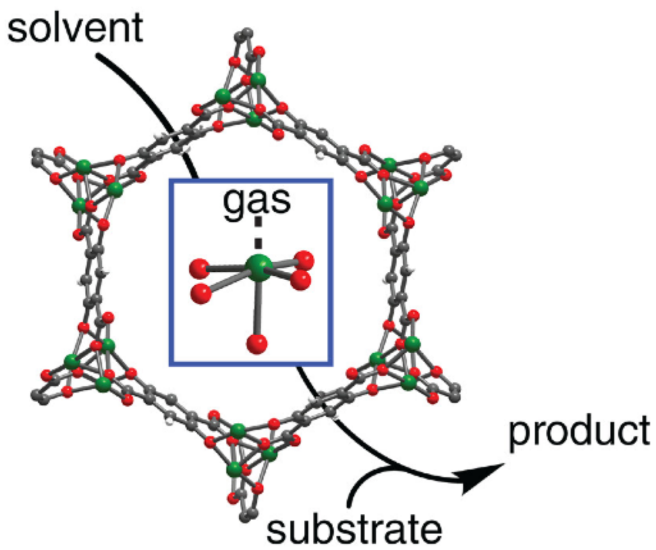


Porous reagent holders

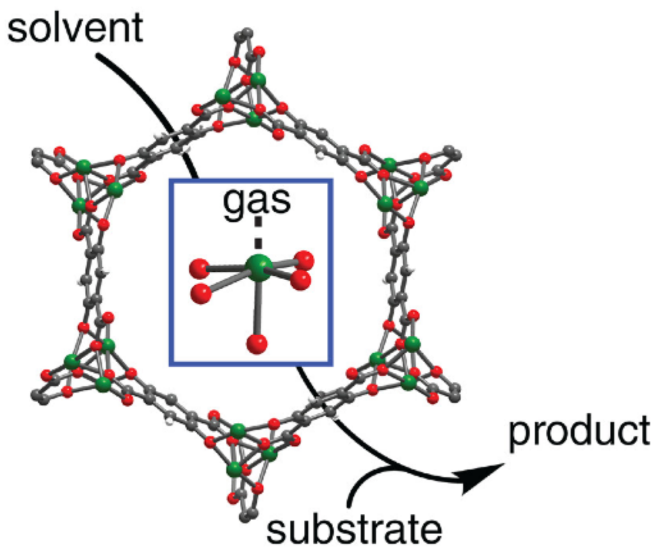


Keasler, K. T.; Zick, M. E.; Stacy, E. E.; Kim, J.; Lee, J. H.; Aeindartehran, L.; Runcevski, T.; Milner, P. J. *Science* **2023**, *381* (6665), 1455-1461.

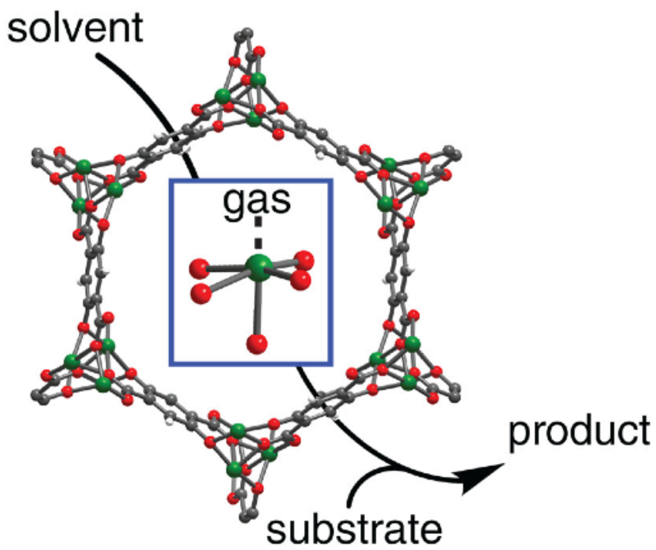
Novel reagents based on MOFs



Novel reagents based on MOFs

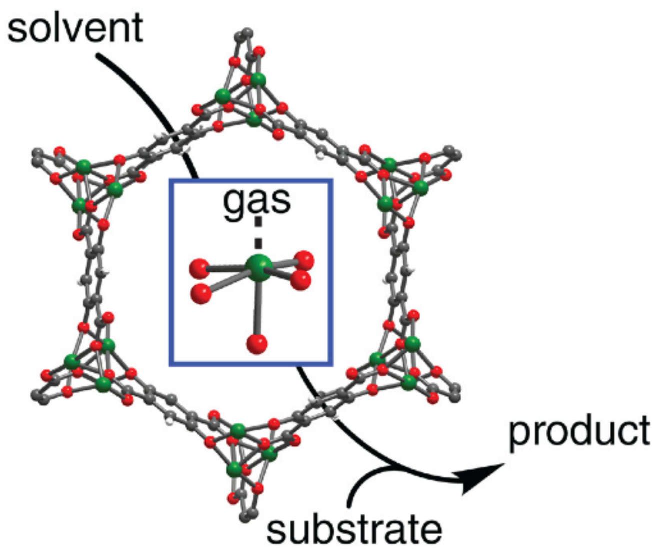


Novel reagents based on MOFs



Thermal and chemical stability

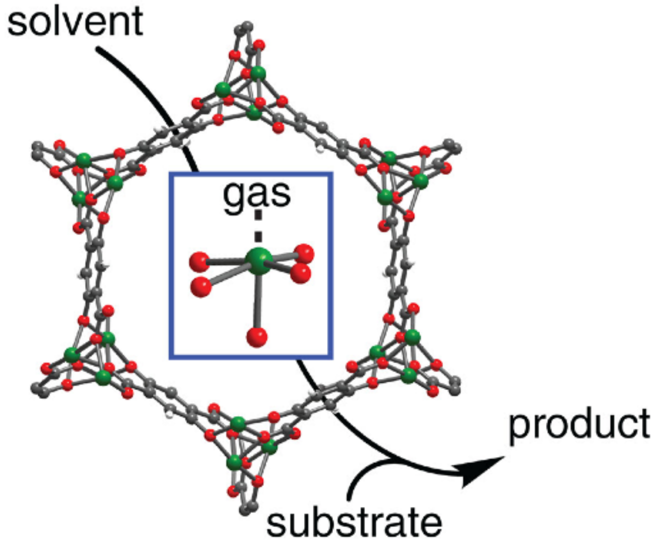
Novel reagents based on MOFs



Thermal and chemical stability

Maximum pore volume

Novel reagents based on MOFs

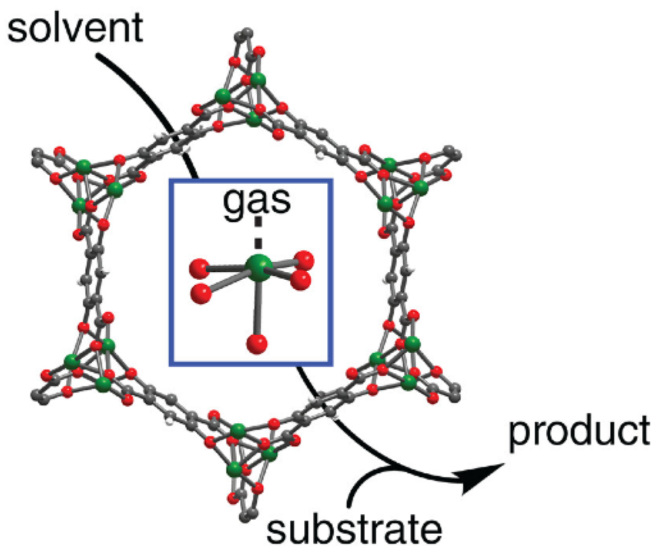


Thermal and chemical stability

Maximum pore volume

Favorable and reversible adsorption of fluorinated gases

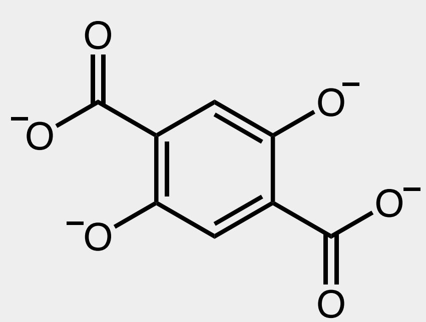
Novel reagents based on MOFs



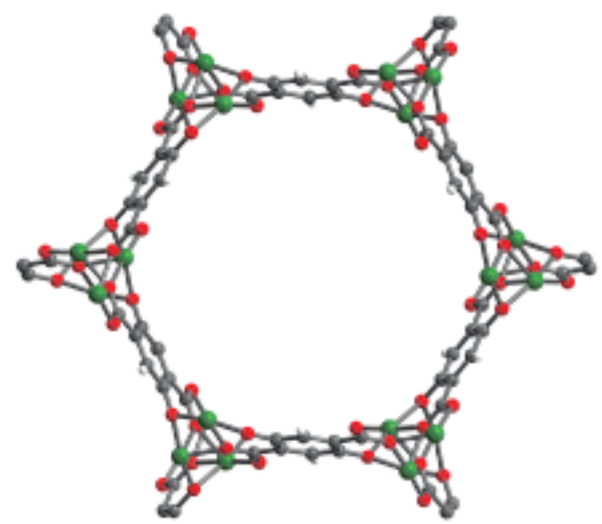
Thermal and chemical stability

Maximum pore volume

Favorable and reversible adsorption of fluorinated gases



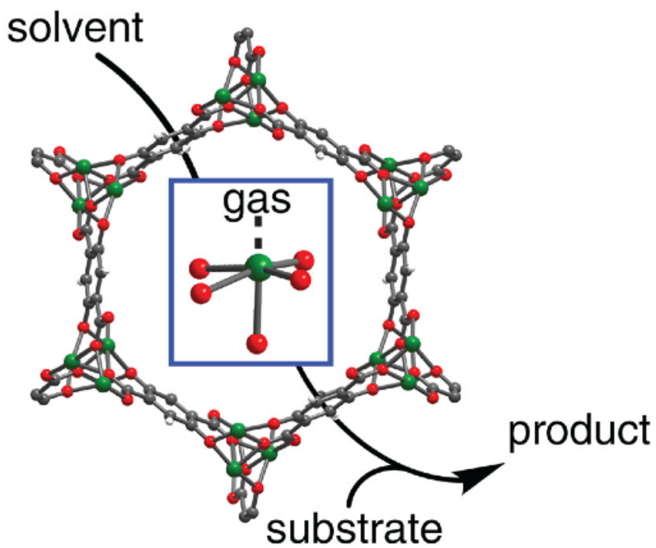
$dobdc^{4-}$



M_2(dobdc)

M = Mg, Mn, Fe, Co, Ni, Cu, Zn

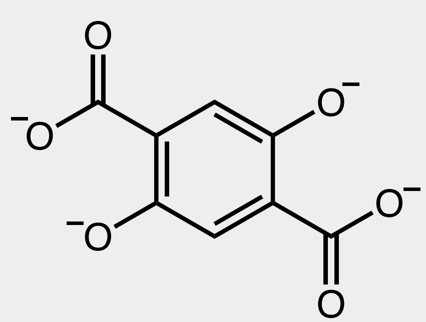
Novel reagents based on MOFs



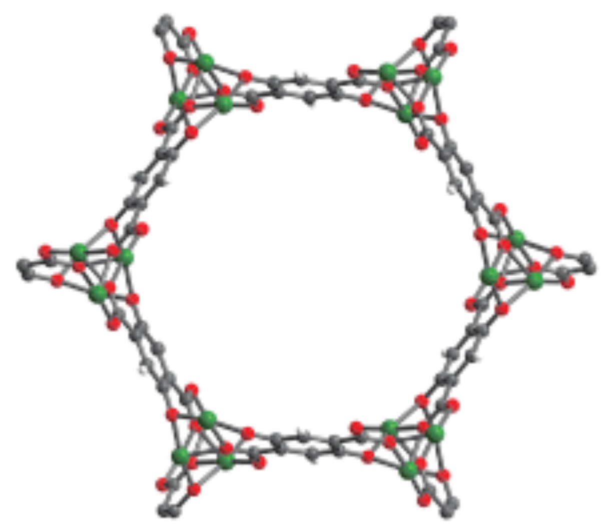
Thermal and chemical stability

Maximum pore volume

Favorable and reversible adsorption of fluorinated gases



dobdc^{4-}

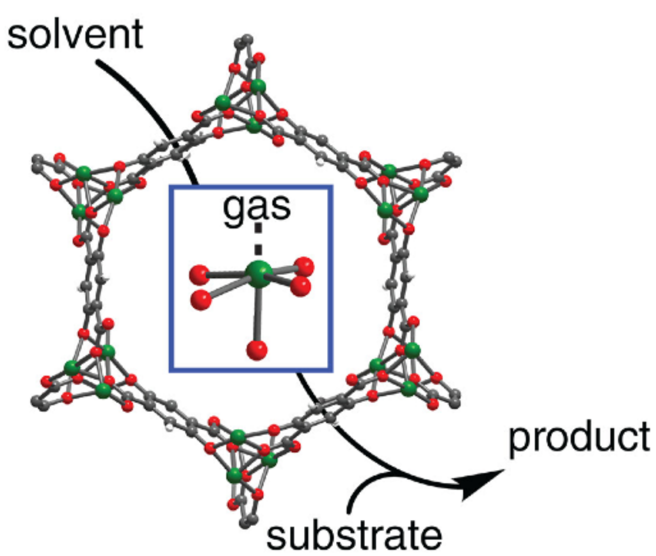


M_2(dobdc)

M = Mg, Mn, Fe, Co, Ni, Cu, Zn

✓ *high pore volume*

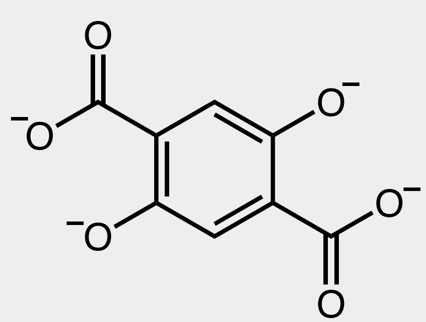
Novel reagents based on MOFs



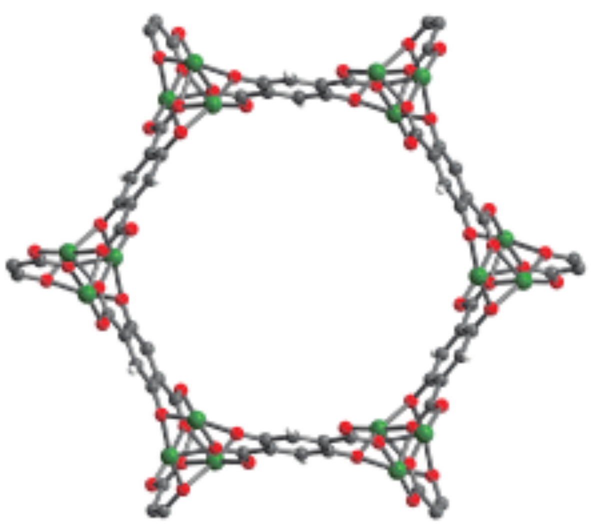
Thermal and chemical stability

Maximum pore volume

Favorable and reversible adsorption of fluorinated gases



dobdc^{4-}



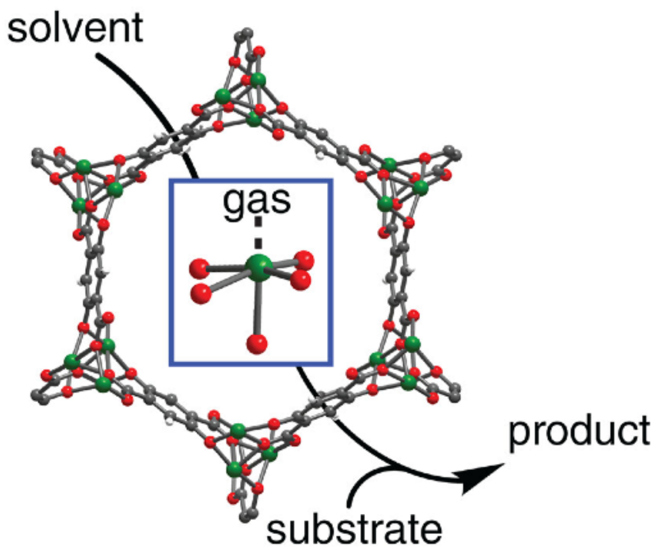
M_2(dobdc)

M = Mg, Mn, Fe, Co, Ni, Cu, Zn

✓ *high pore volume*

✓ *reversible adsorption*

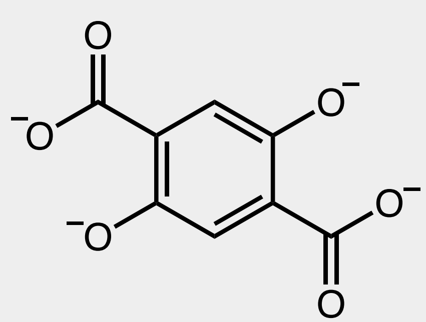
Novel reagents based on MOFs



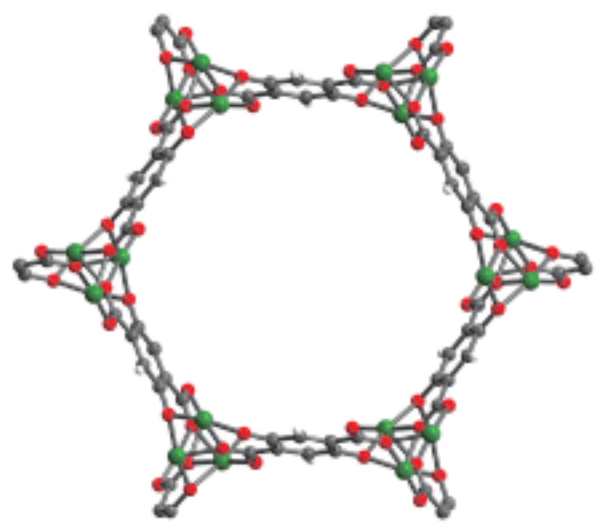
Thermal and chemical stability

Maximum pore volume

Favorable and reversible adsorption of fluorinated gases



$dobdc^{4-}$



M_2(dobdc)

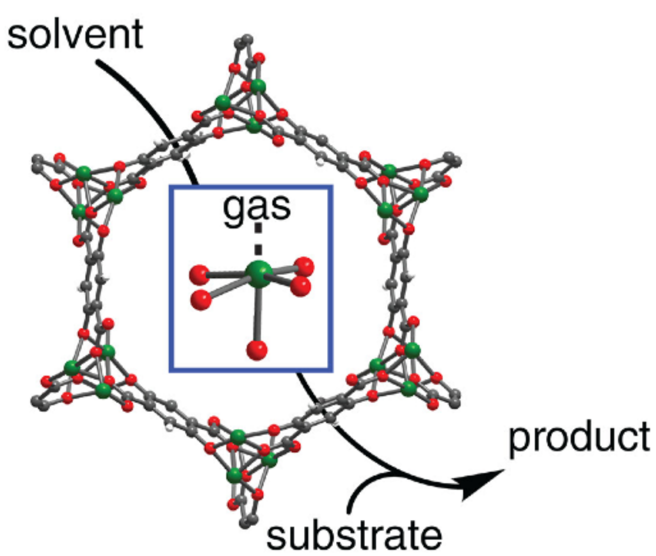
M = Mg, Mn, Fe, Co, Ni, Cu, Zn

✓ *high pore volume*

✓ *reversible adsorption*

✓ *high thermal stability*

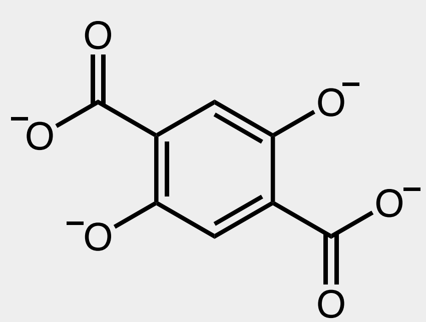
Novel reagents based on MOFs



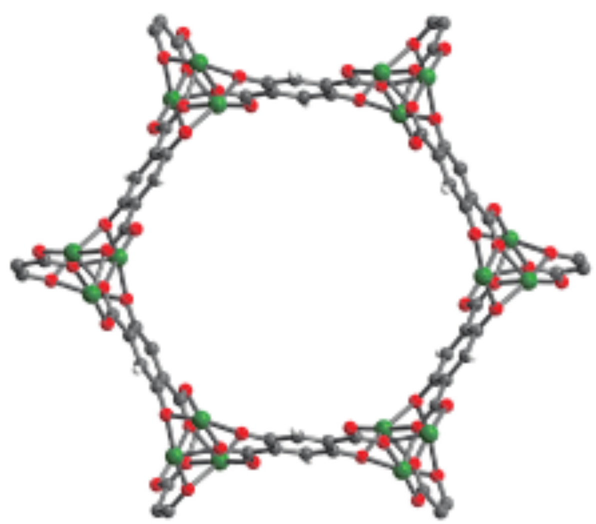
Thermal and chemical stability

Maximum pore volume

Favorable and reversible adsorption of fluorinated gases



dobdc^{4-}



M_2(dobdc)

M = Mg, Mn, Fe, Co, Ni, Cu, Zn

- ✓ *high pore volume*
- ✓ *reversible adsorption*
- ✓ *high thermal stability*

Which metal ion should be employed?

Quantitative evaluation

Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption ($-\Delta H$): large value indicates favorable adsorption

Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption ($-\Delta H$): large value indicates favorable adsorption

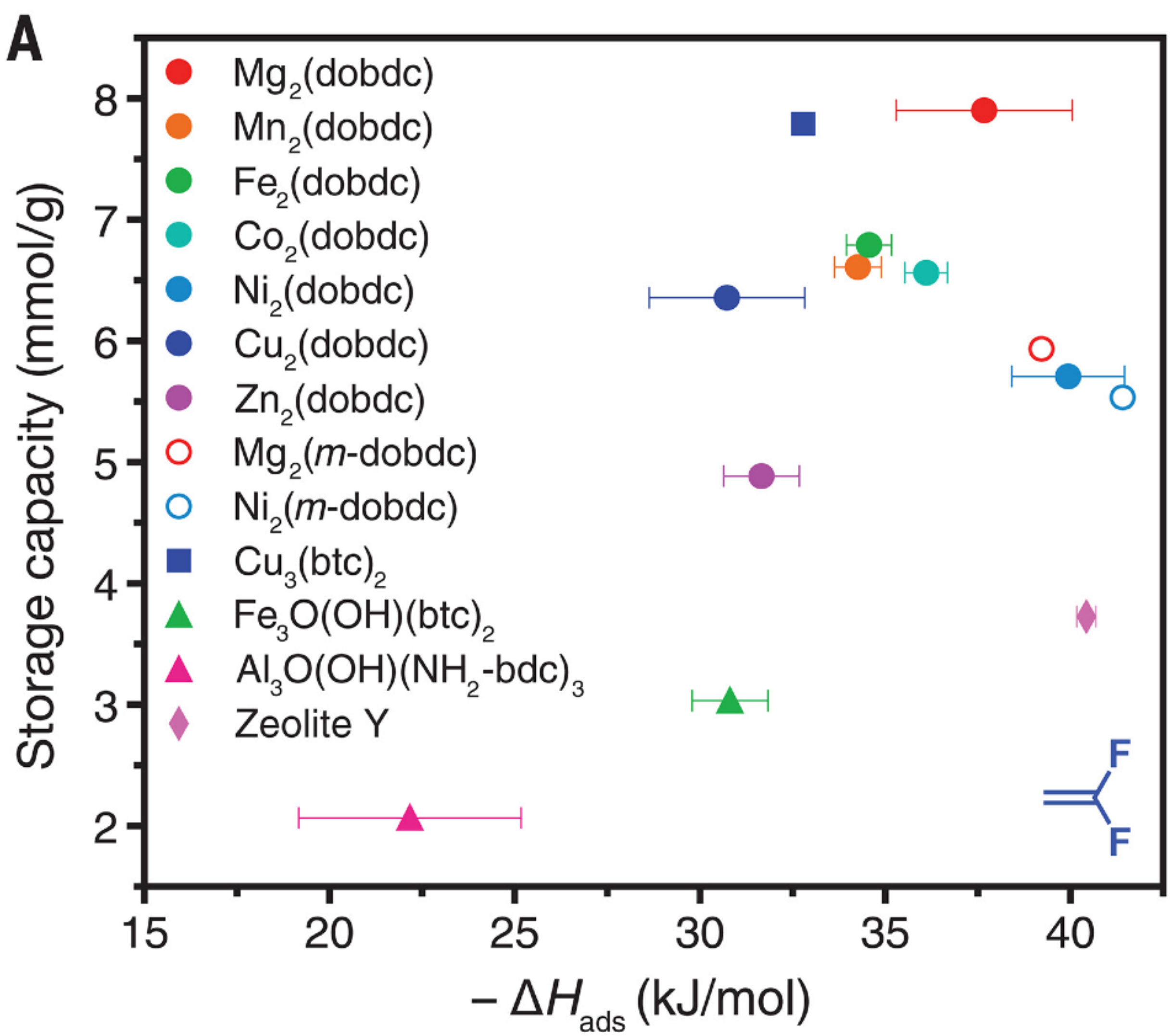
storage capacity: volume of fluorinated gases

Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases

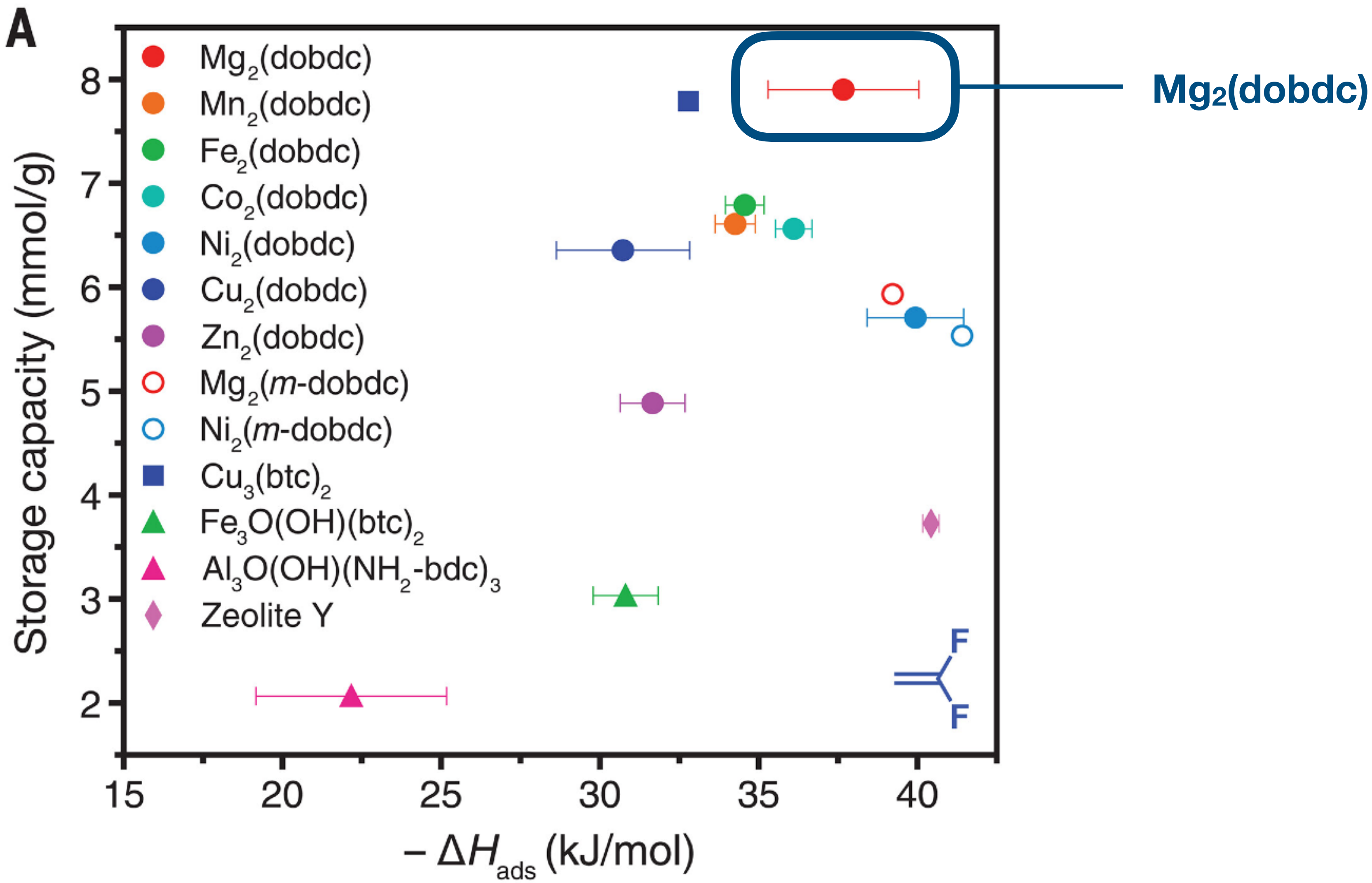


Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases

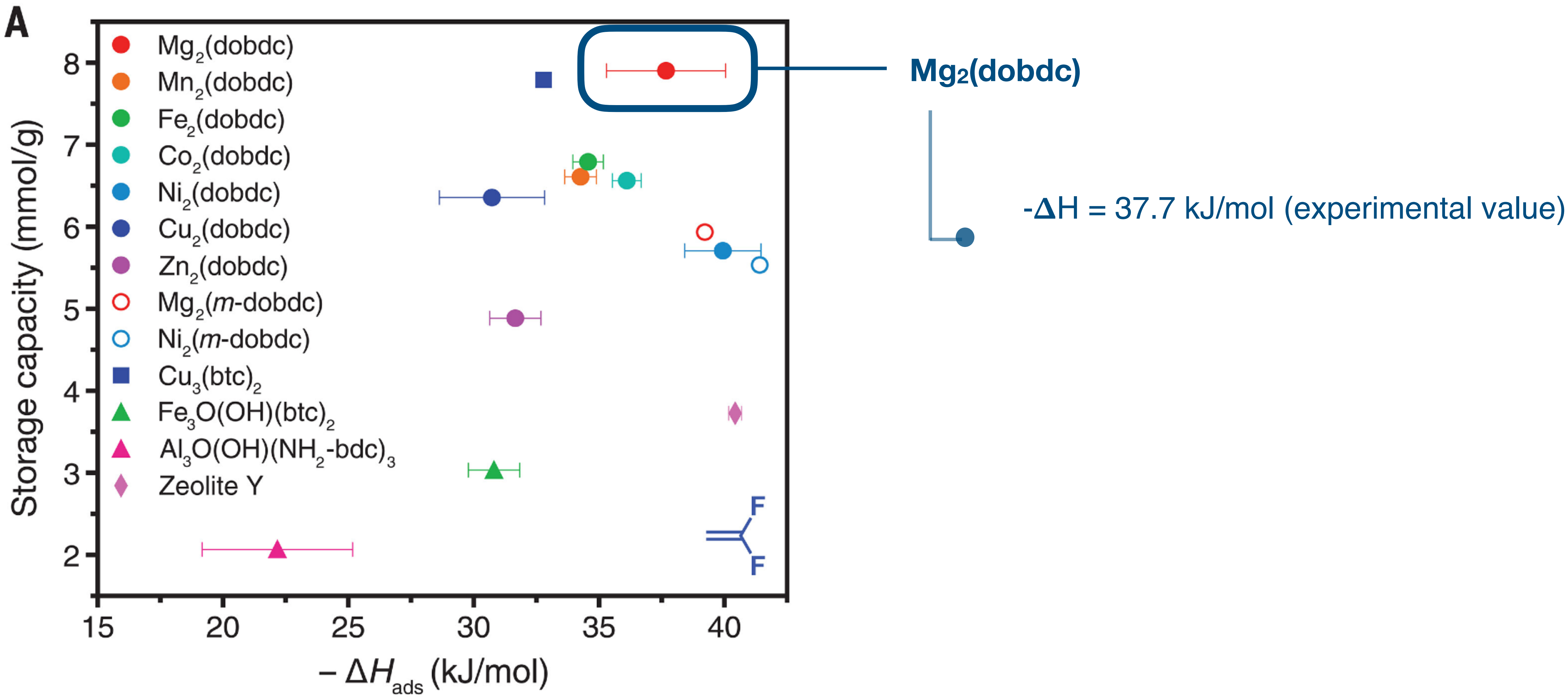


Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases

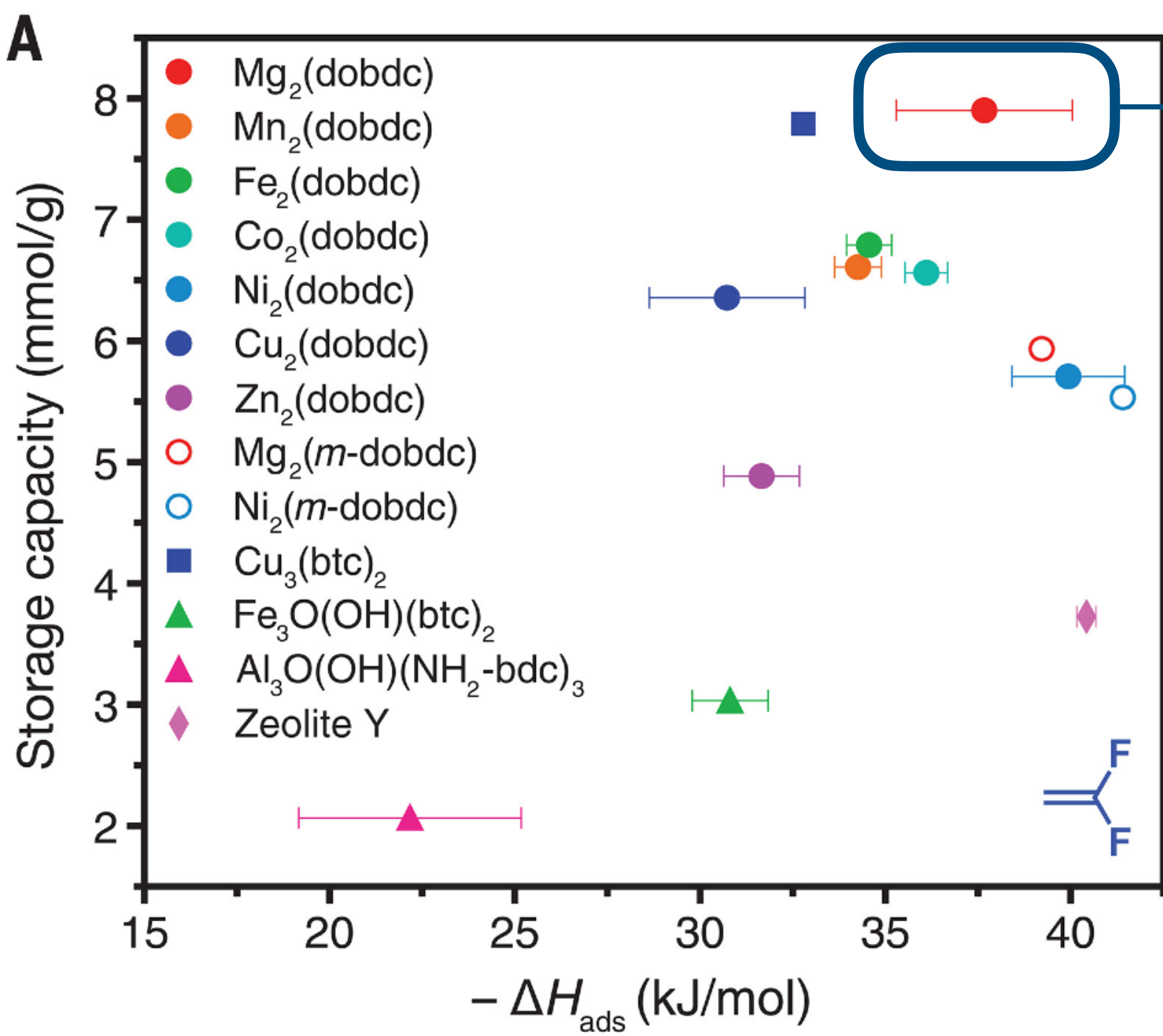


Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



Mg_2(dobdc)

-ΔH = 37.7 kJ/mol (experimental value)

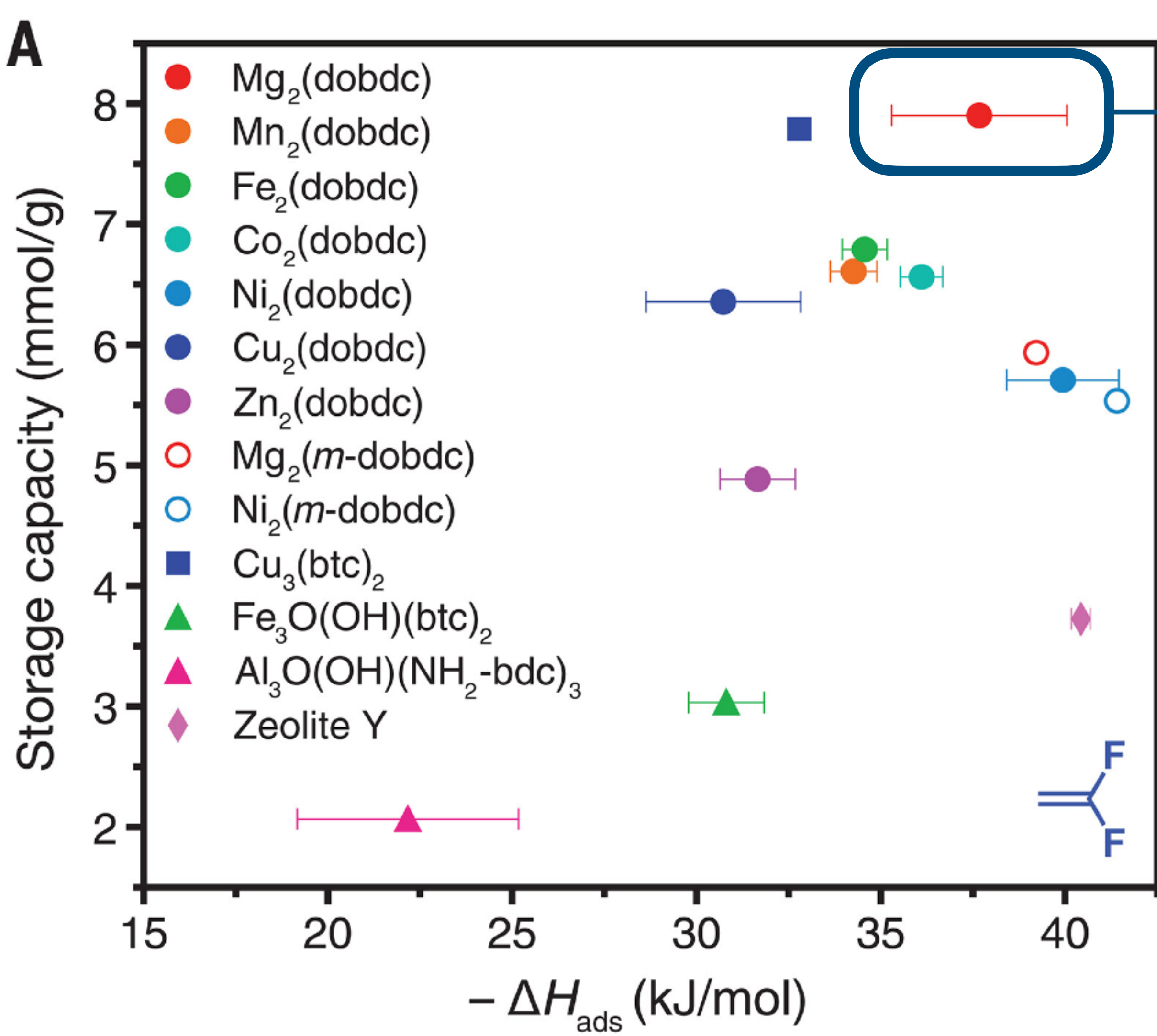
hard-soft acid-base match (Mg^{2+} and F)

Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



Mg_2(dobdc)

-ΔH = 37.7 kJ/mol (experimental value)

hard-soft acid-base match (Mg^{2+} and F)

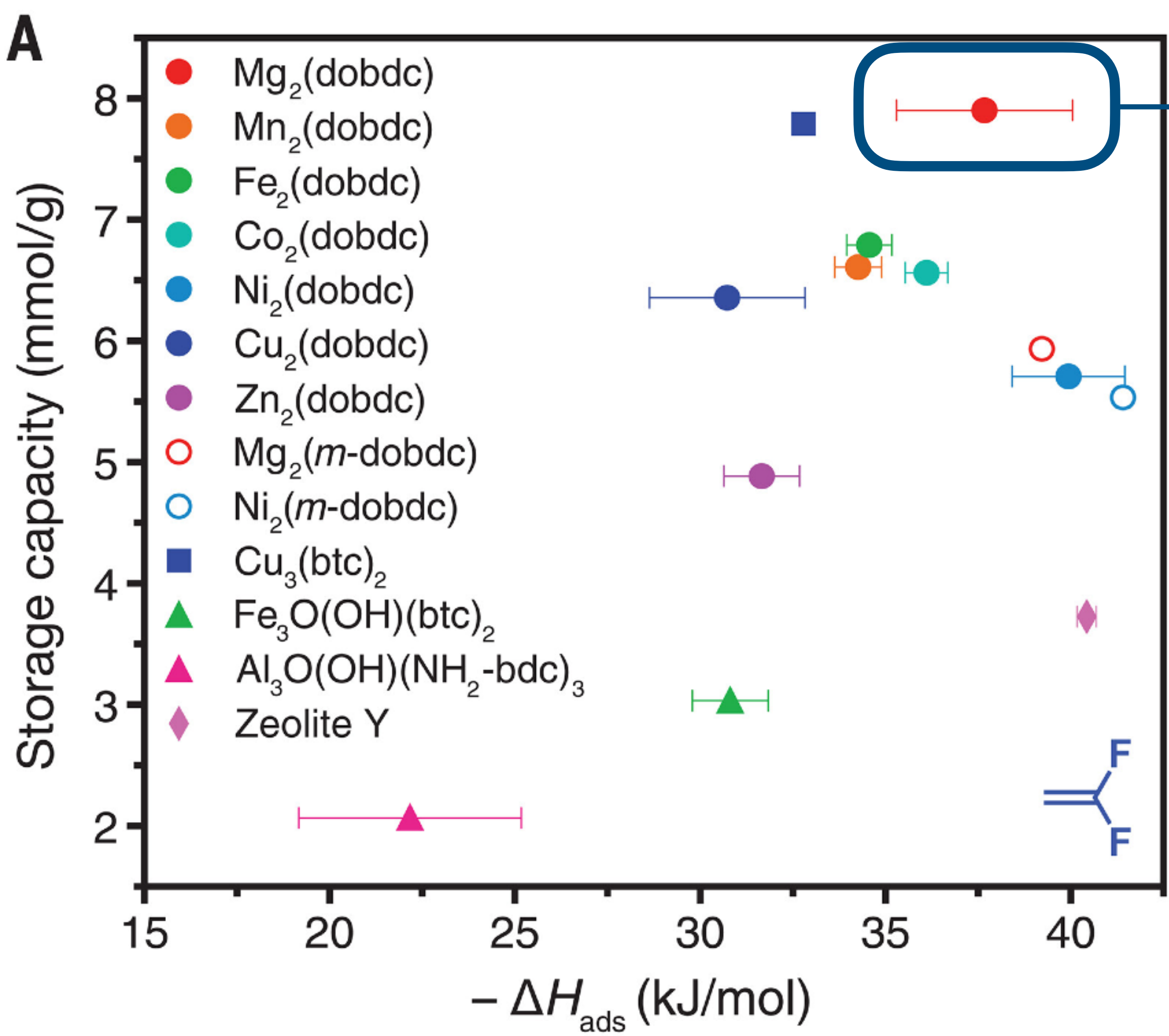
storage cap = 7.95 mmol/g, 34 wt%

Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



Mg_2(dobdc)

-ΔH = 37.7 kJ/mol (experimental value)

hard-soft acid-base match (Mg^{2+} and F)

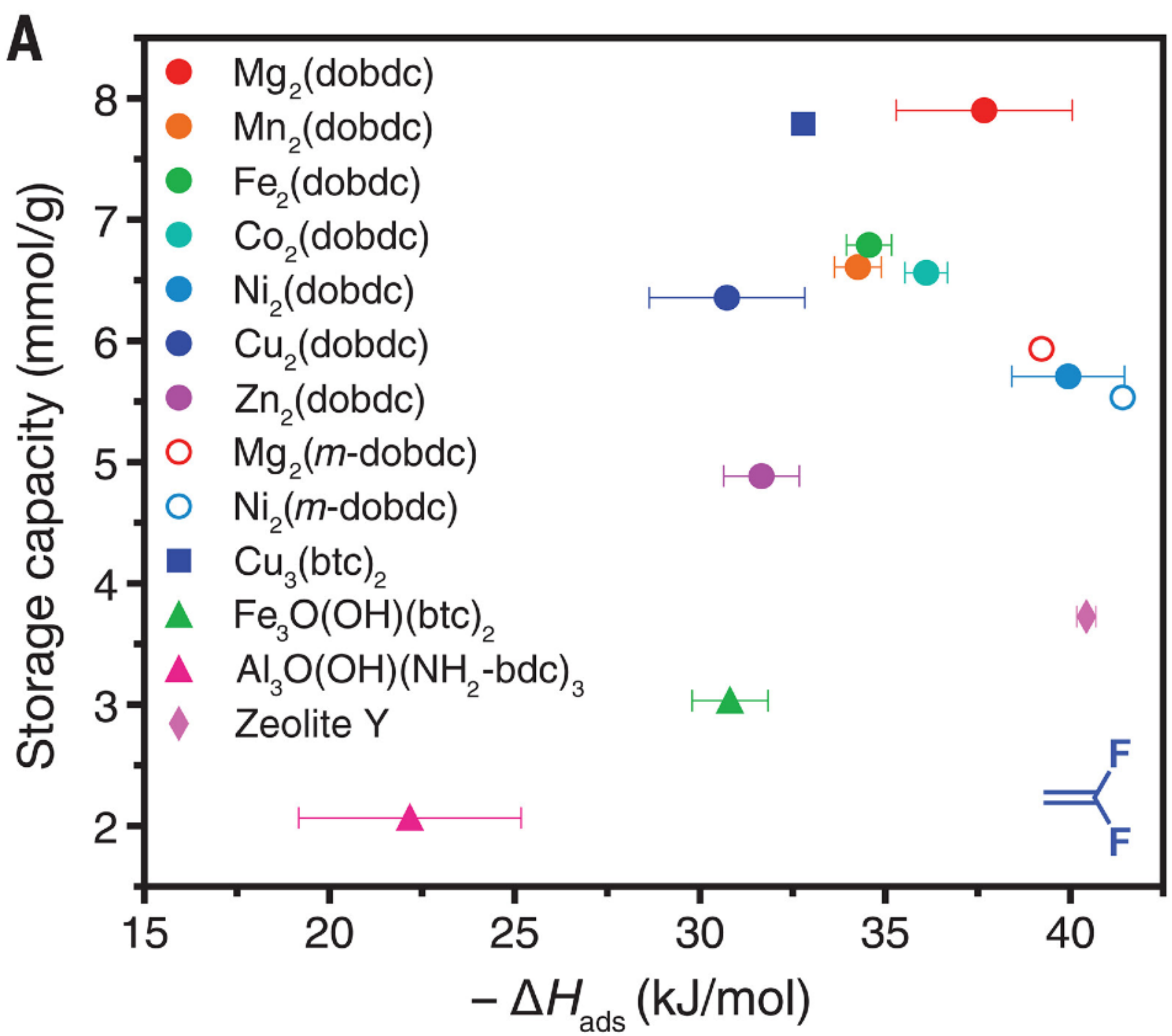
storage cap = 7.95 mmol/g, 34 wt%

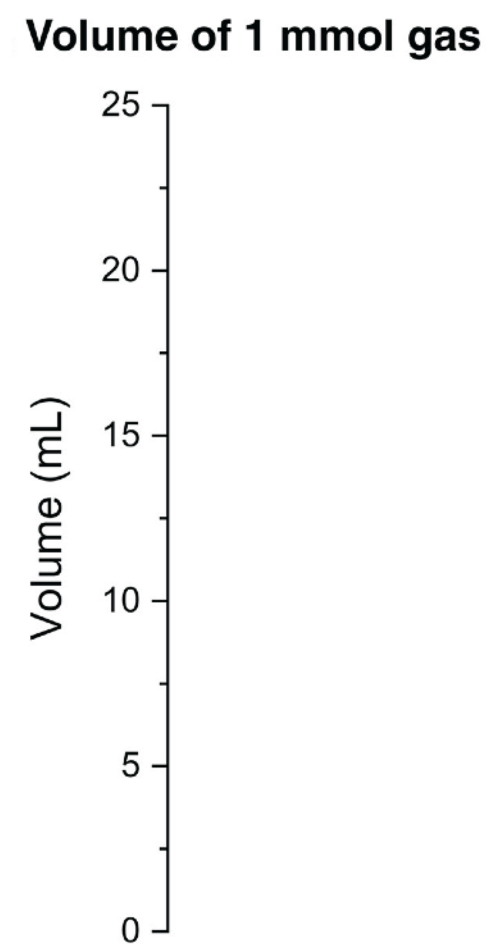
Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



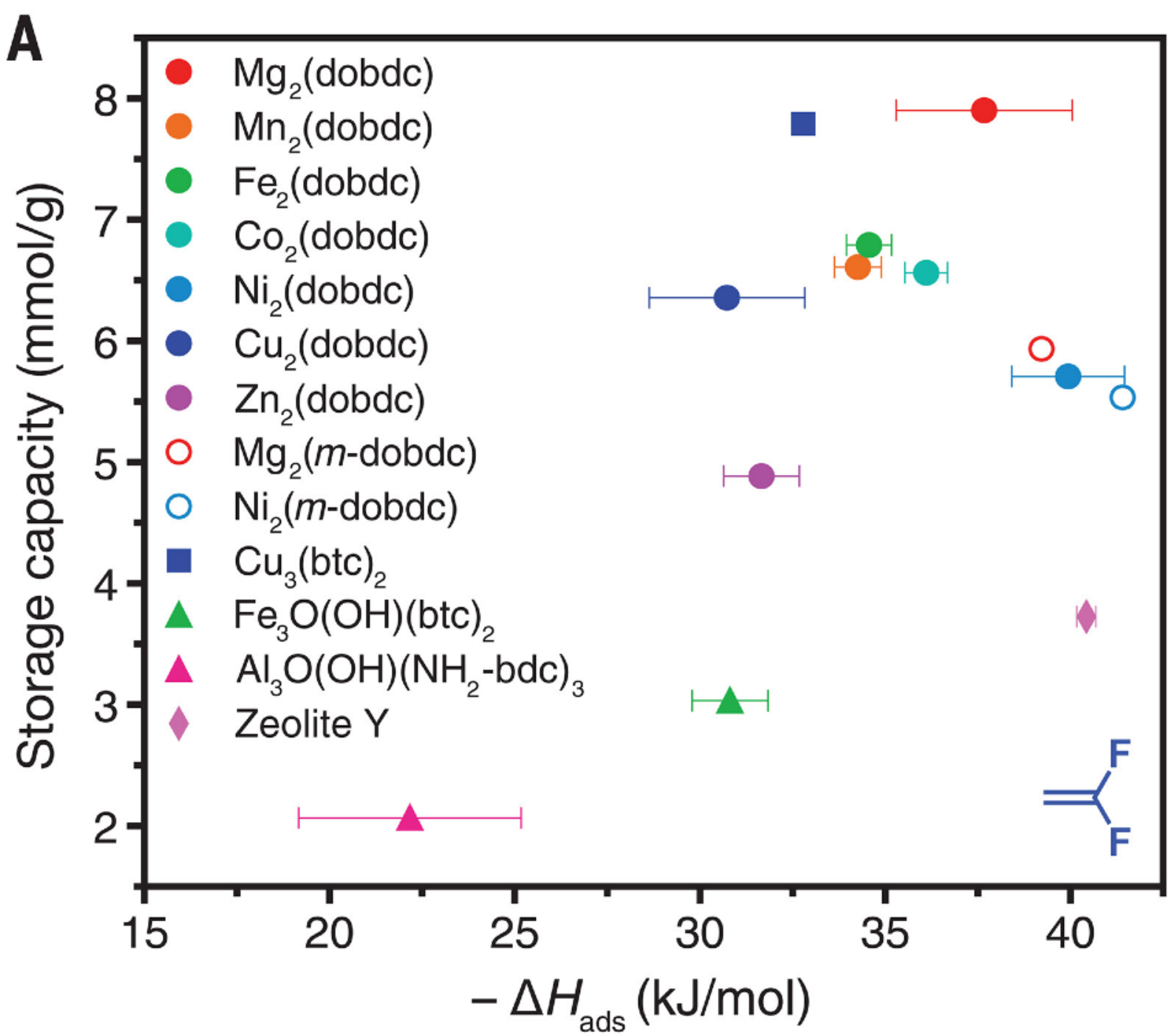


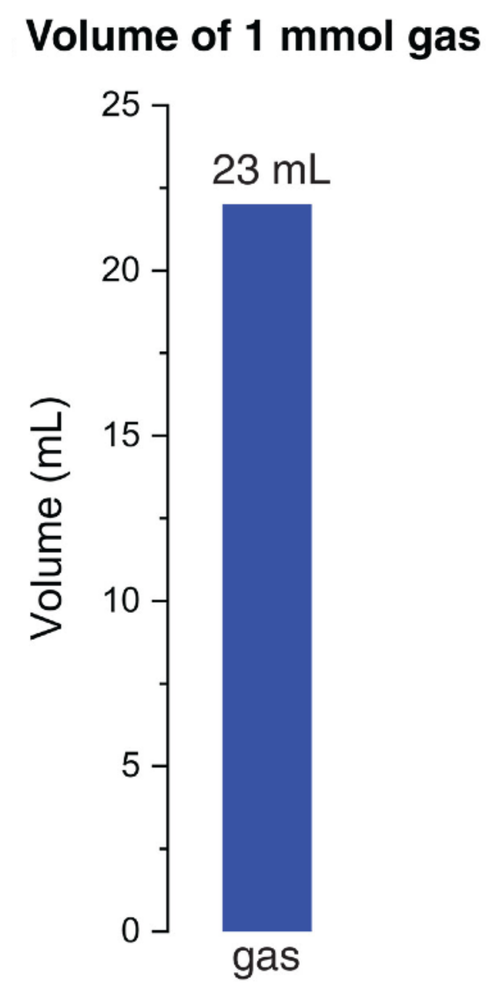
Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



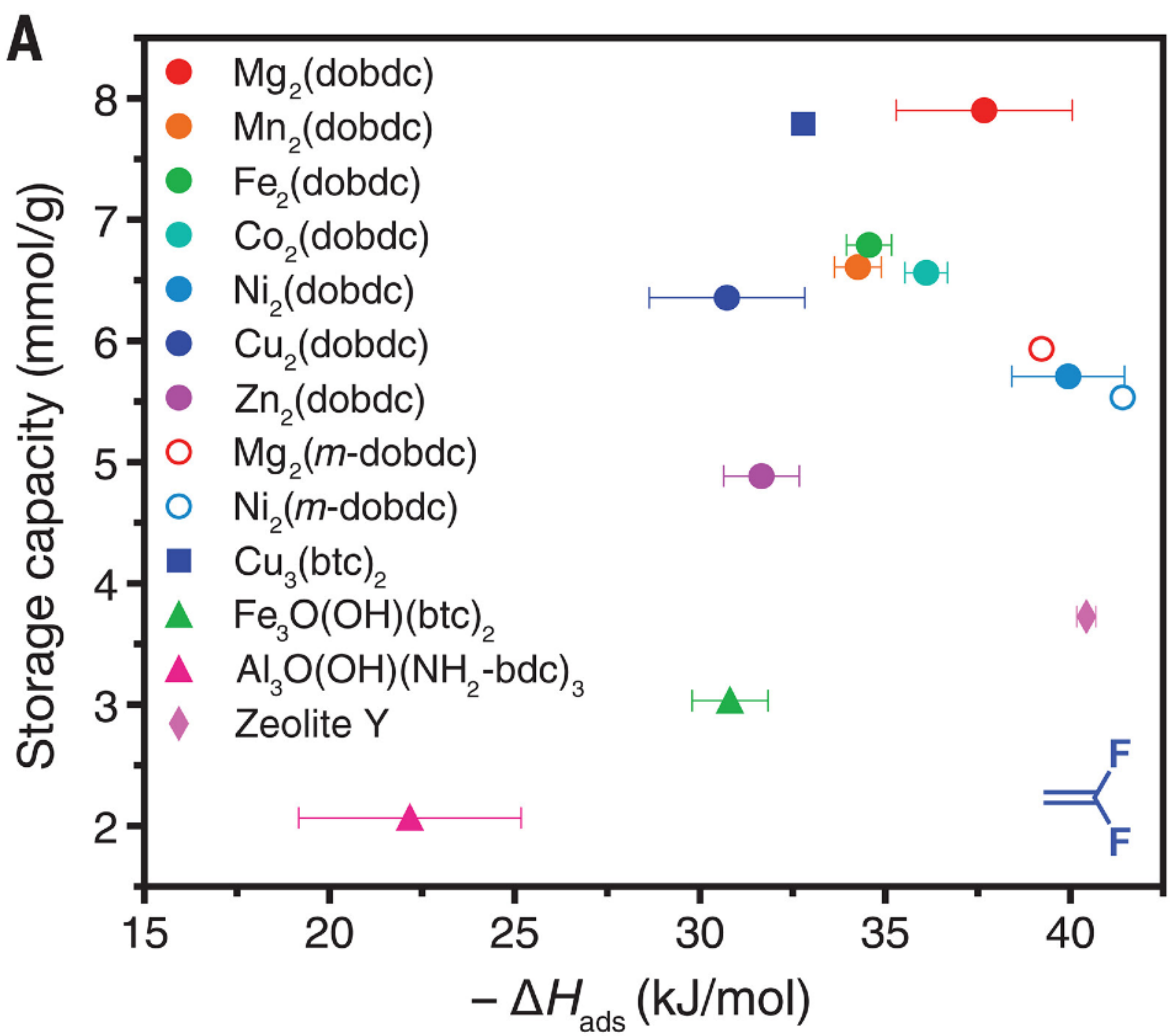


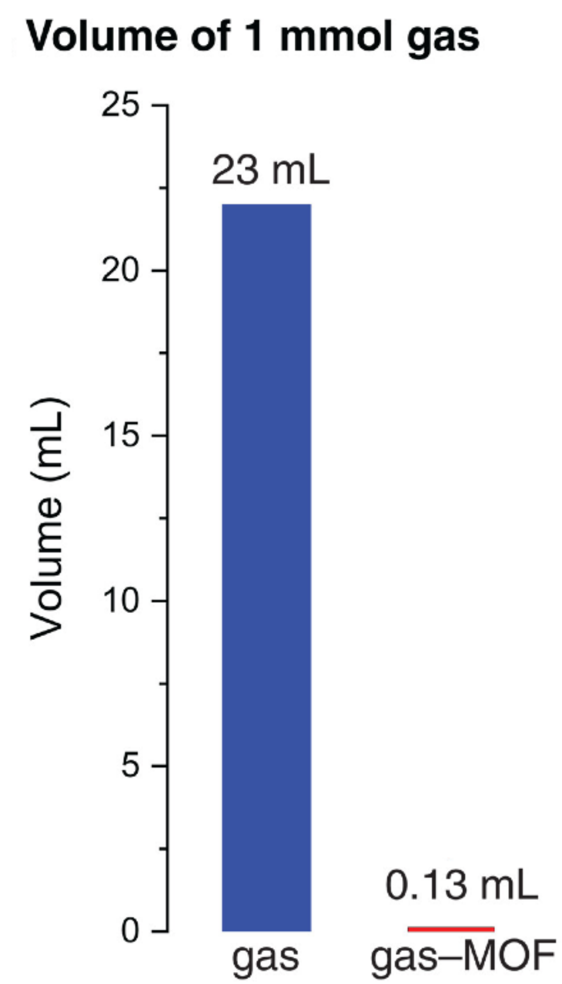
Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



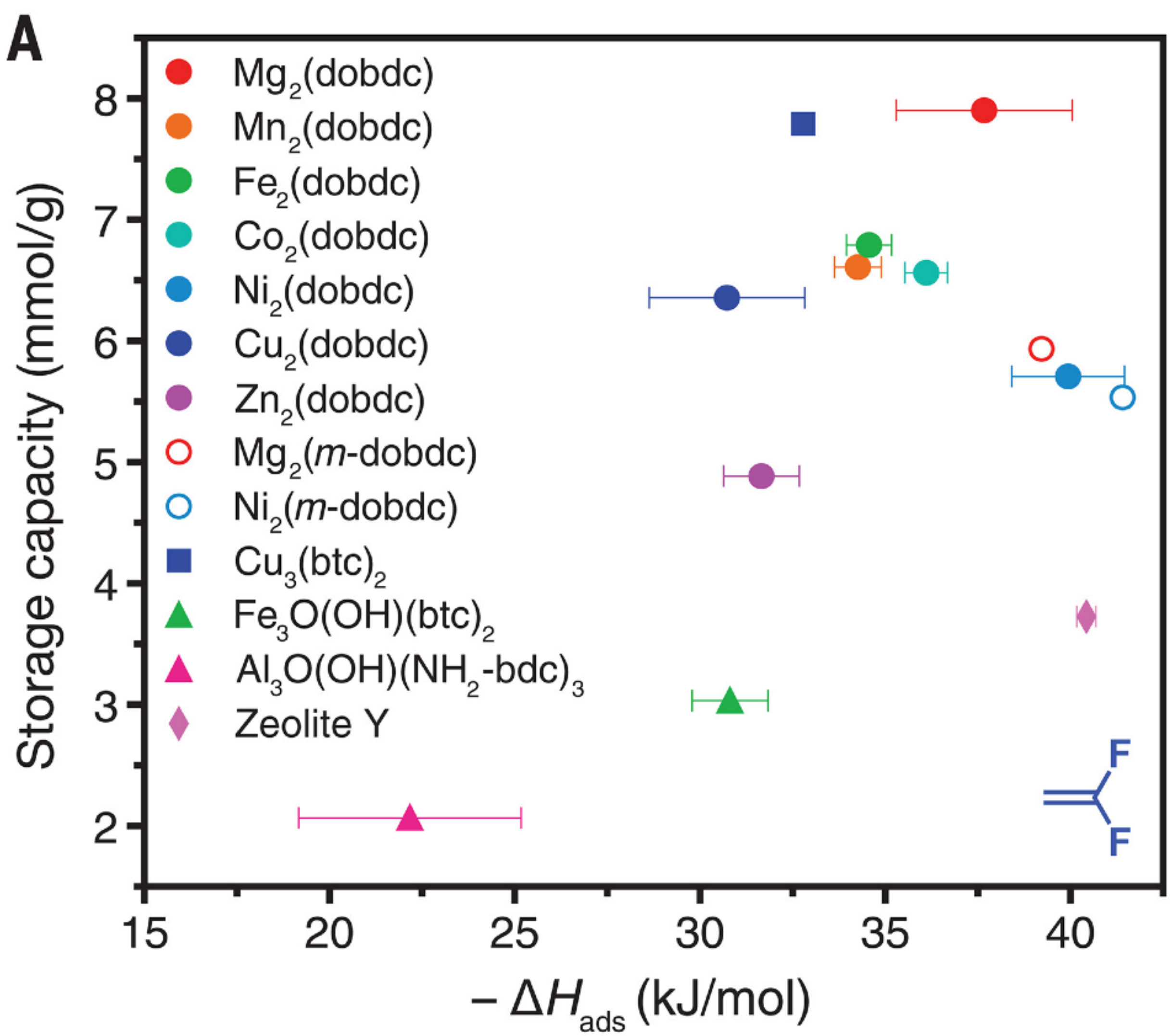


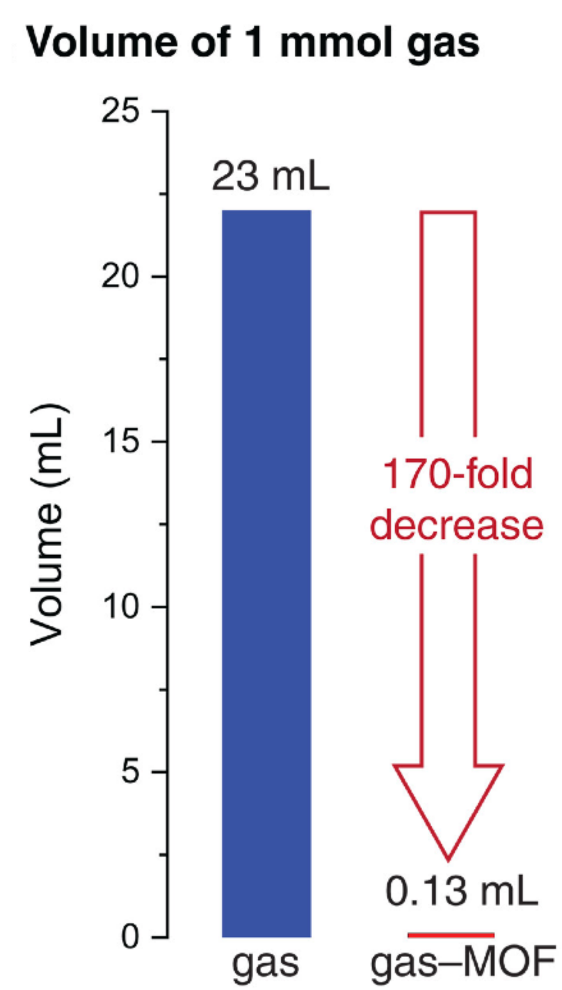
Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



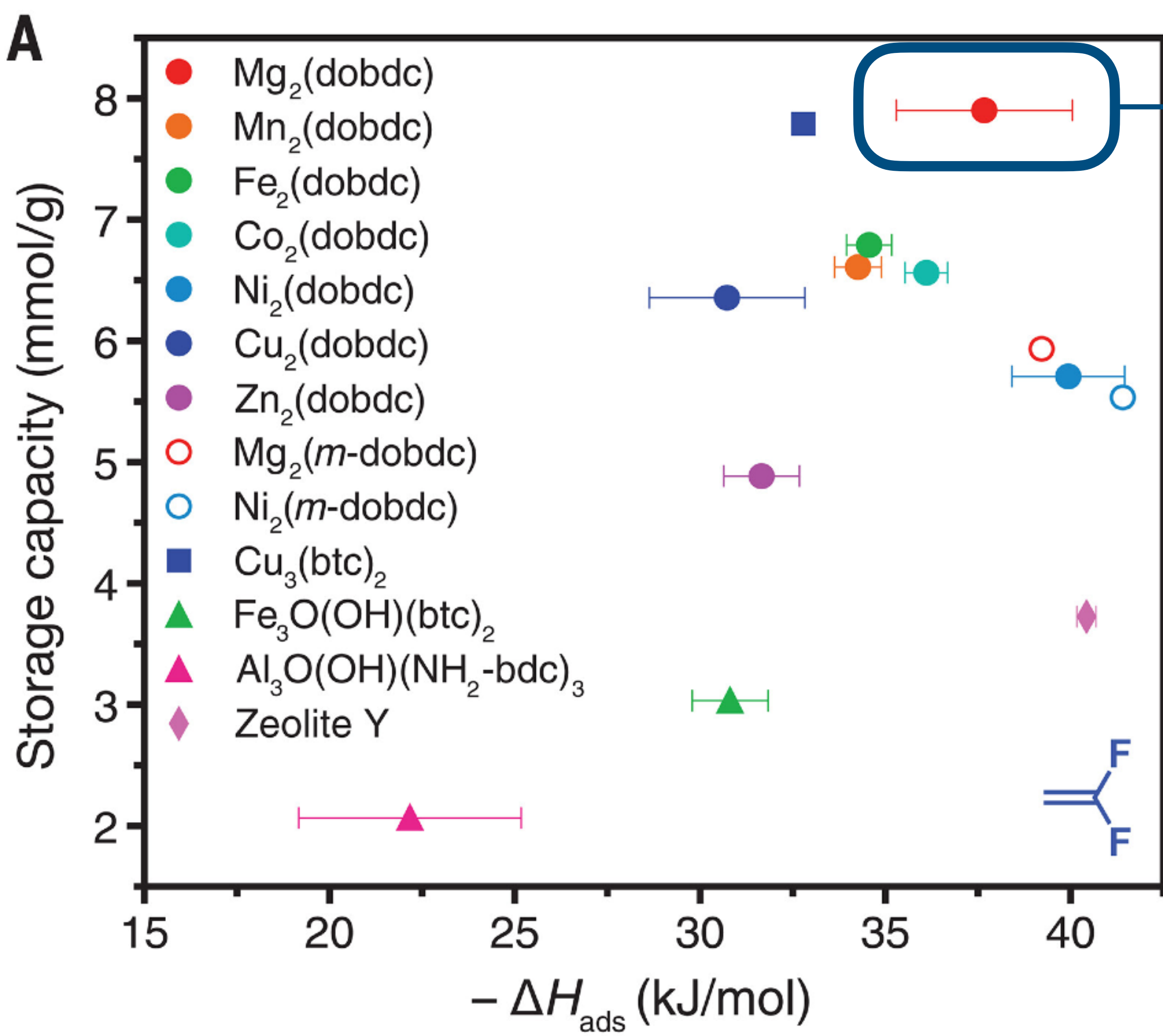


Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



Mg_2(dobdc)

- $-\Delta H$ = 37.7 kJ/mol (experimental value)

  hard-soft acid-base match (Mg^{2+} and F)

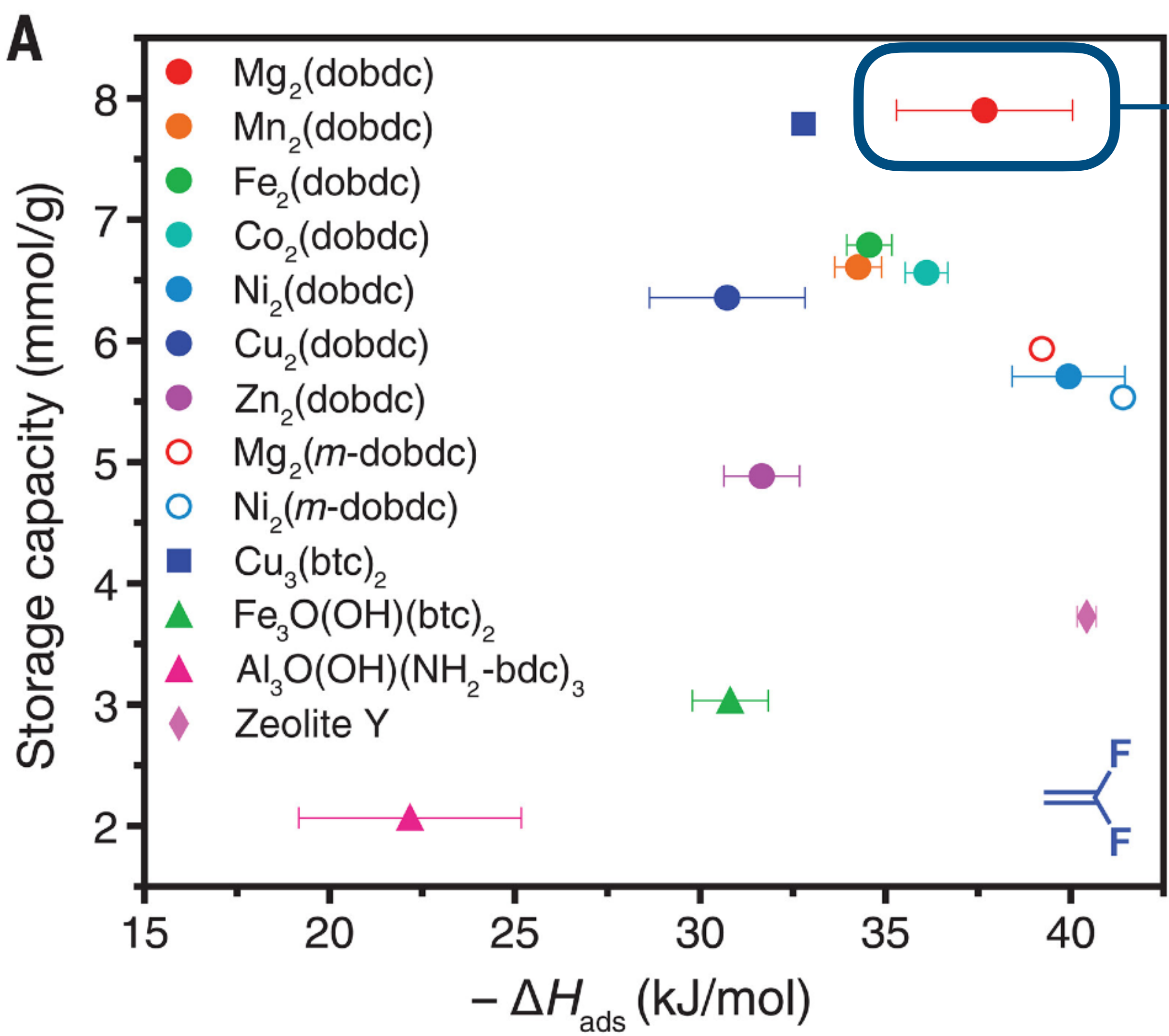
- **storage cap = 7.95 mmol/g, 34 wt%**

Novel reagents based on MOFs

Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



Mg_2(dobdc)

-ΔH = 37.7 kJ/mol (experimental value)

hard-soft acid-base match (Mg^{2+} and F)

storage cap = 7.95 mmol/g, 34 wt%

Under air: stable for one week at rt

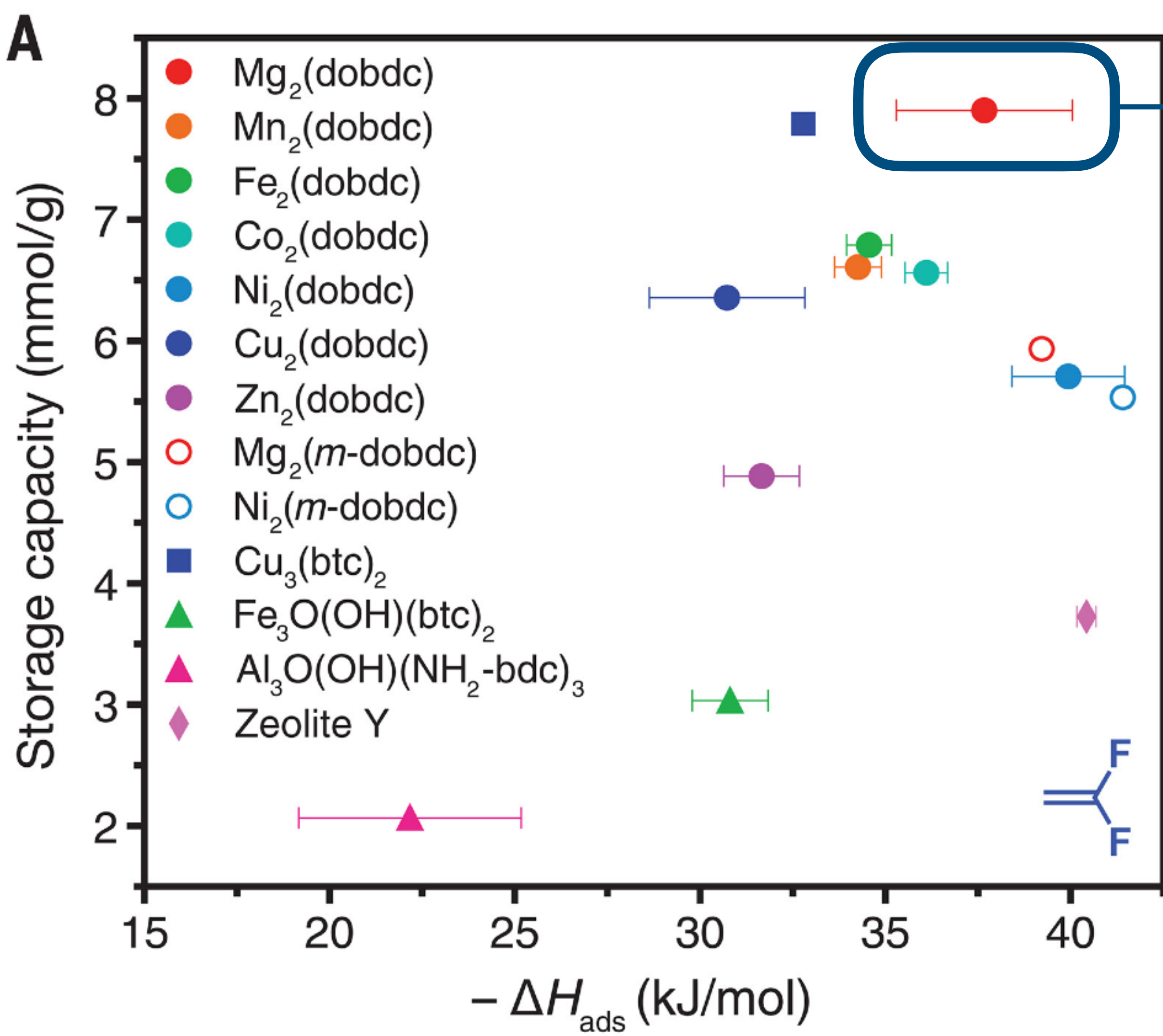
stable at 120 °C for 24 hr

Novel reagents based on MOFs

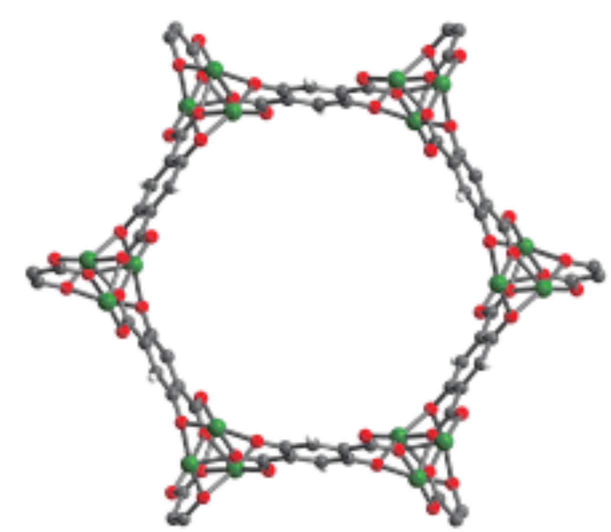
Quantitative evaluation

enthalpy of adsorption (-ΔH): large value indicates favorable adsorption

storage capacity: volume of fluorinated gases



Mg_2(dobdc)



Novel reagents based on MOFs

Activation of

Mg_2(dobdc) at 300 °C

Novel reagents based on MOFs

Activation of Mg_2(dobdc) at 300 °C

→

1 bar VDF gas at 0 °C for 40 min

Novel reagents based on MOFs

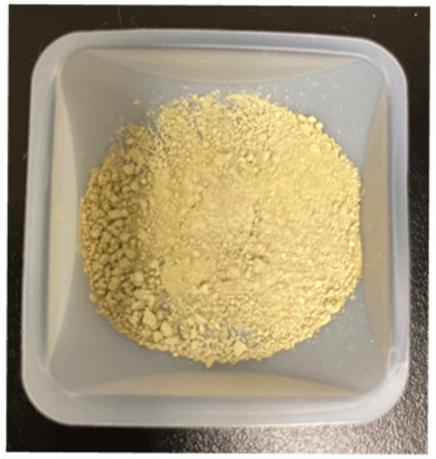
Activation of $Mg_2(dobdc)$ at 300 °C → ***1 bar VDF gas at 0 °C for 40 min*** → ***Bring into glovebox, freeze at -30 °C for 10 min***

Novel reagents based on MOFs

Activation of Mg_2(dobdc) at 300 °C → ***1 bar VDF gas at 0 °C for 40 min*** → ***Bring into glovebox, freeze at -30 °C for 10 min***

↓

VDF—Mg_2(dobdc)

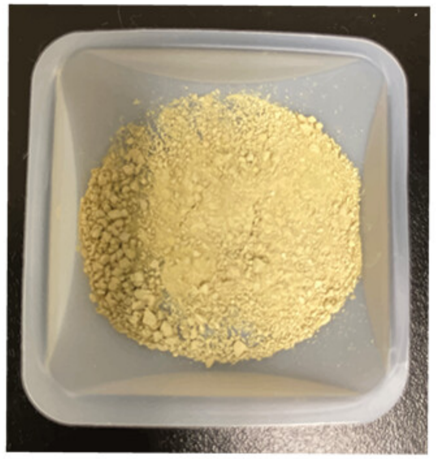


powder

Novel reagents based on MOFs

Activation of Mg_2(dobdc) at 300 °C → ***1 bar VDF gas at 0 °C for 40 min*** → ***Bring into glovebox, freeze at -30 °C for 10 min*** ↓

VDF—Mg_2(dobdc)



powder

wax capsule

Novel reagents based on MOFs

Activation of Mg_2(dobdc) at 300 °C

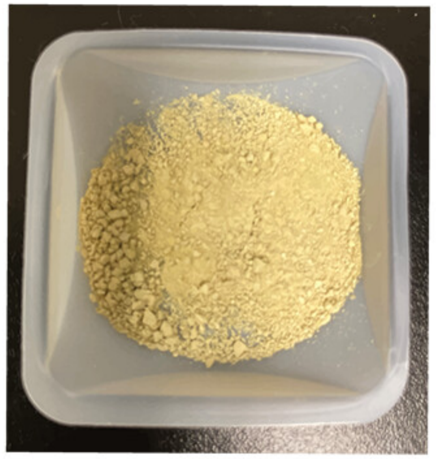
1 bar VDF gas at 0 °C for 40 min

Bring into glovebox, freeze at -30 °C for 10 min

VDF—Mg_2(dobdc)

solid-addition

funnel



powder

wax capsule

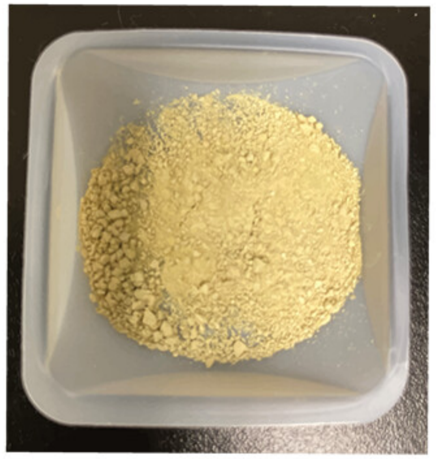
Novel reagents based on MOFs

Activation of Mg$_2$(dobdc) at 300 °C → ***1 bar VDF gas at 0 °C for 40 min*** → ***Bring into glovebox, freeze at -30 °C for 10 min***

↓

VDF—Mg$_2$(dobdc)

solid-addition funnel

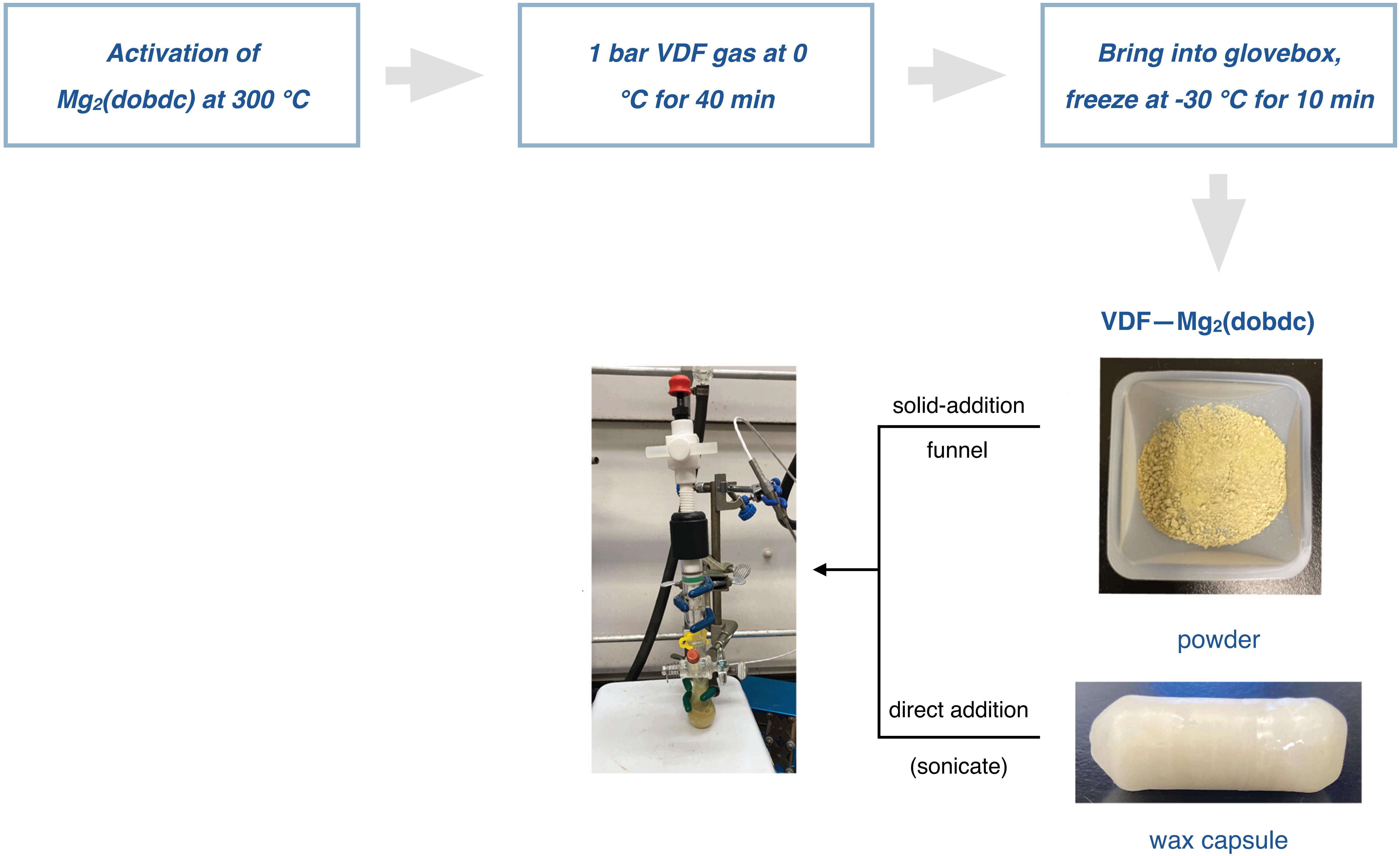


powder

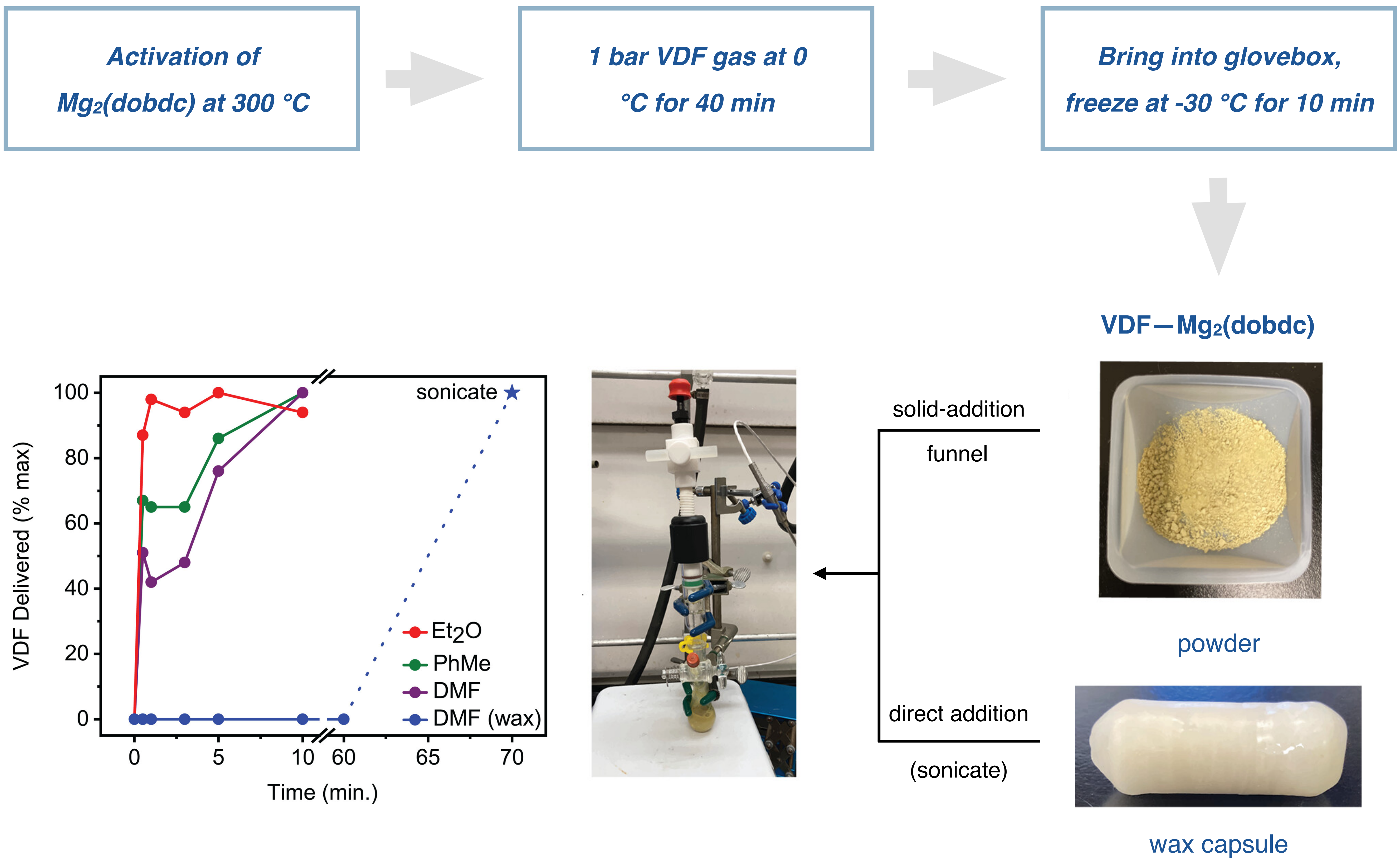
direct addition (sonicate)

wax capsule

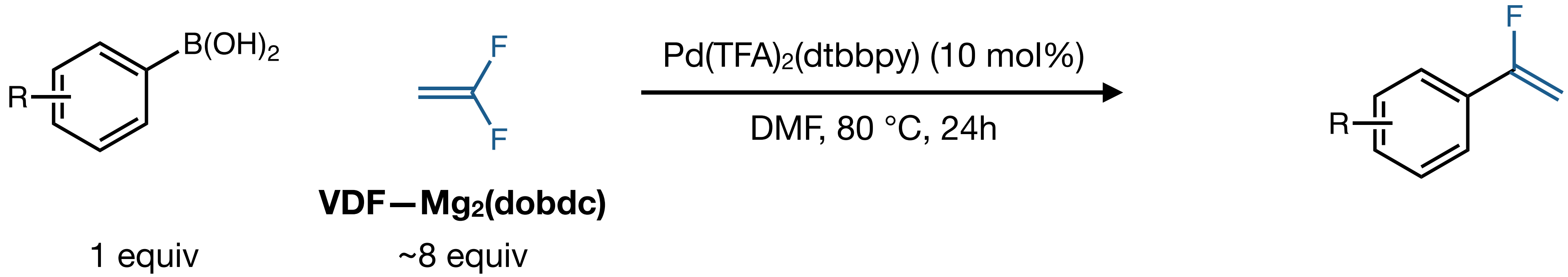
Novel reagents based on MOFs



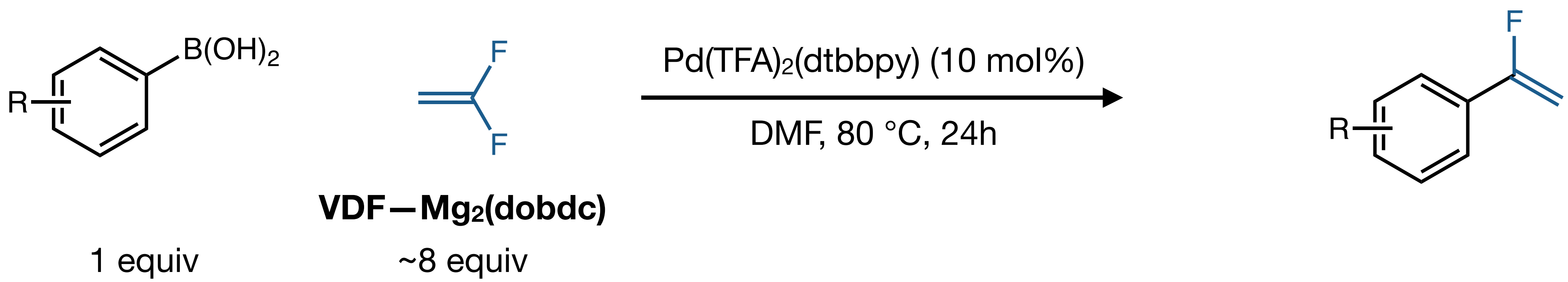
Novel reagents based on MOFs

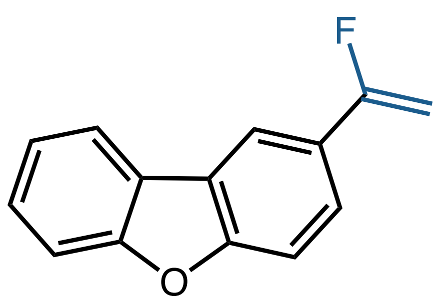


Novel reagents based on MOFs

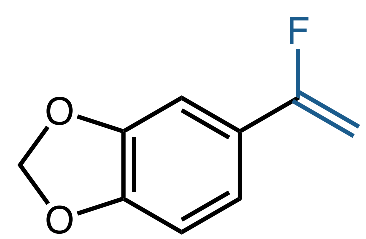


Novel reagents based on MOFs

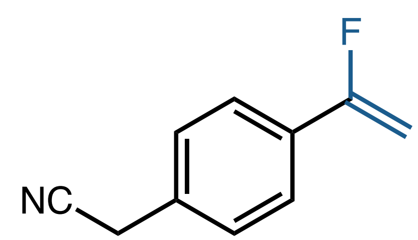




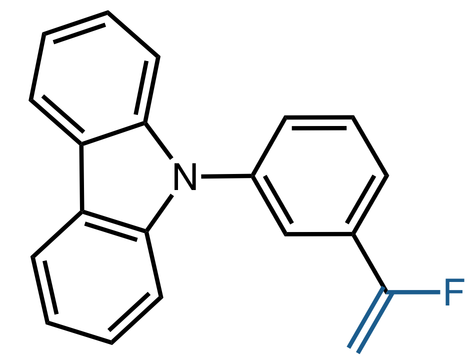
74% yield (wax: 80%)



66% yield (wax: 78%)

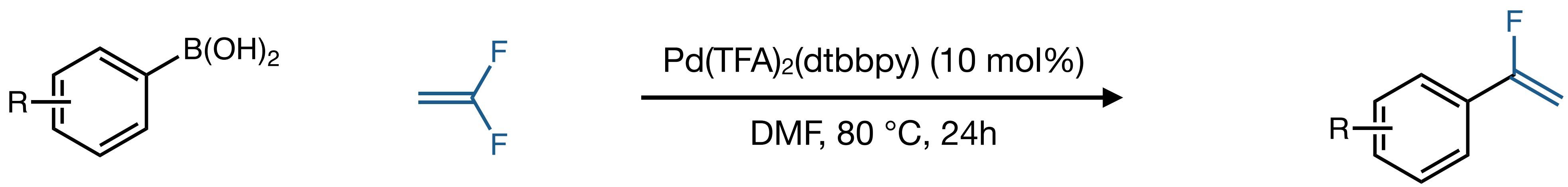


41% yield (wax: 65%)



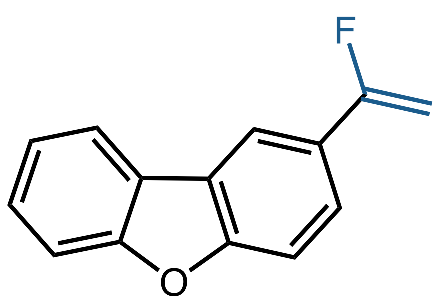
44% yield (wax: 63%)

Novel reagents based on MOFs

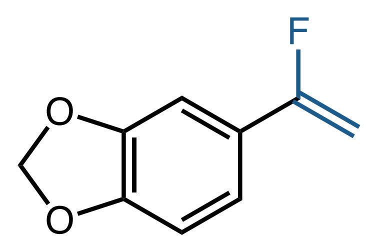


VDF—Mg$_2$(dobdc)

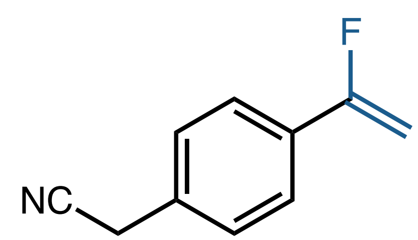
1 equiv ~8 equiv



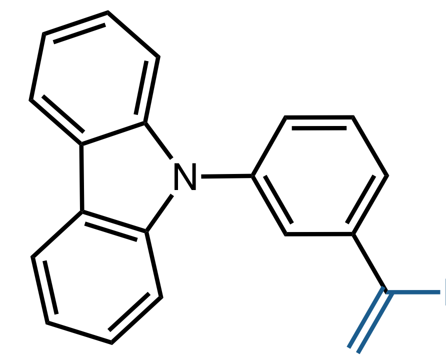
74% yield (wax: 80%)



66% yield (wax: 78%)



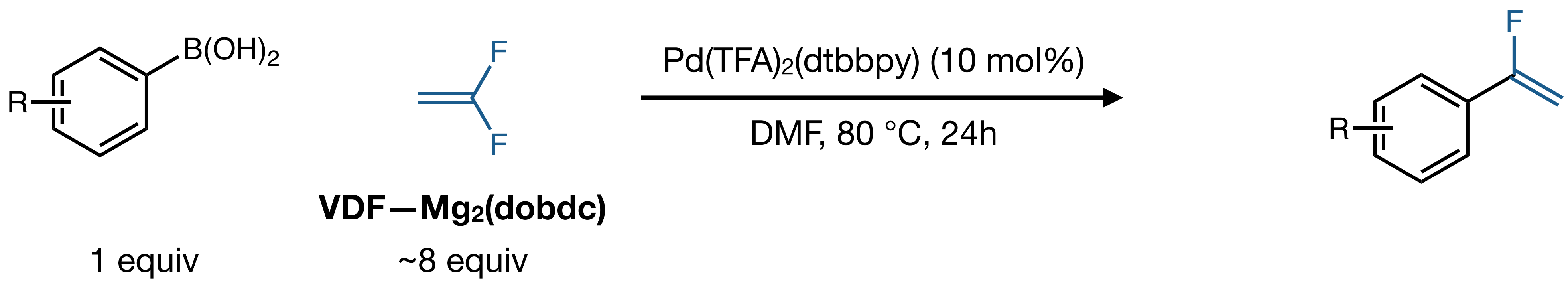
41% yield (wax: 65%)

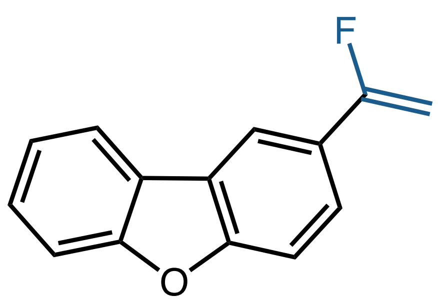


44% yield (wax: 63%)

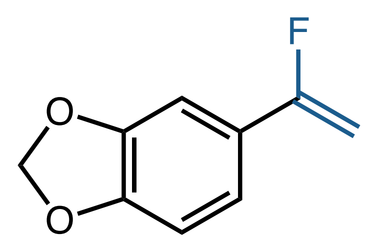
VDF—Mg$_2$(dobdc) stability study

Novel reagents based on MOFs

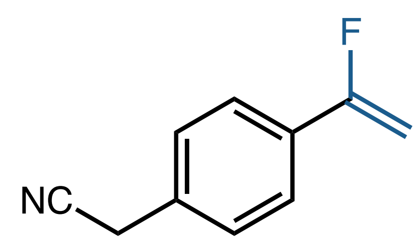




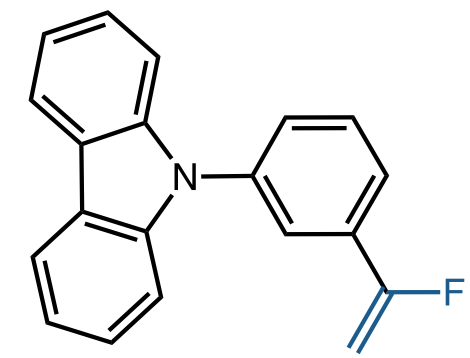
74% yield (wax: 80%)



66% yield (wax: 78%)

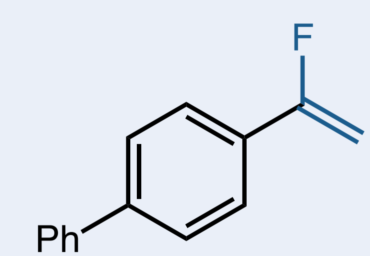


41% yield (wax: 65%)

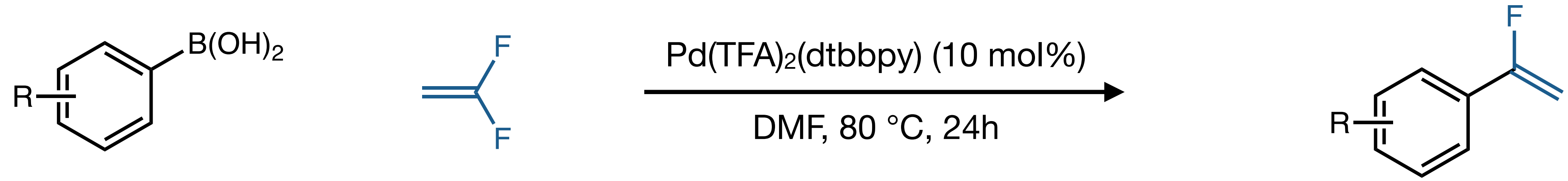


44% yield (wax: 63%)

VDF—Mg$_2$(dobdc) stability study



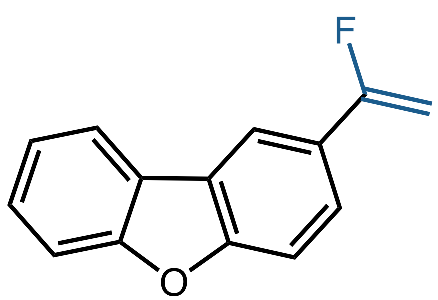
Novel reagents based on MOFs



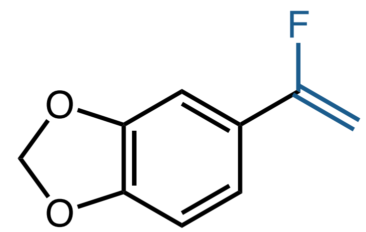
VDF—Mg_2(dobdc)

1 equiv

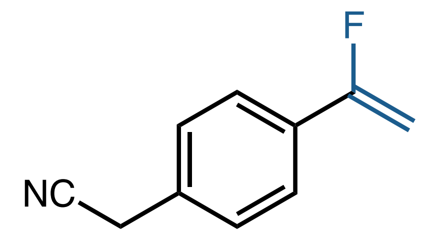
~8 equiv



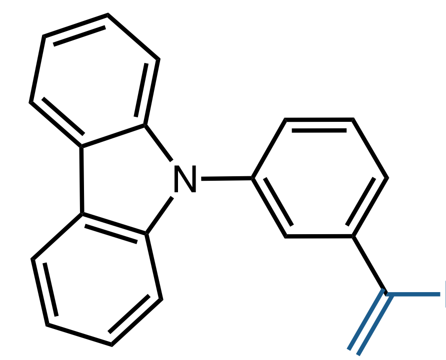
74% yield (wax: 80%)



66% yield (wax: 78%)



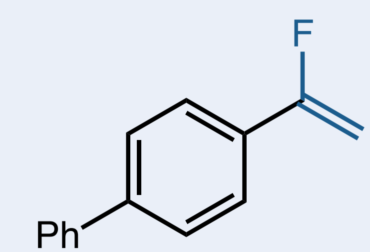
41% yield (wax: 65%)



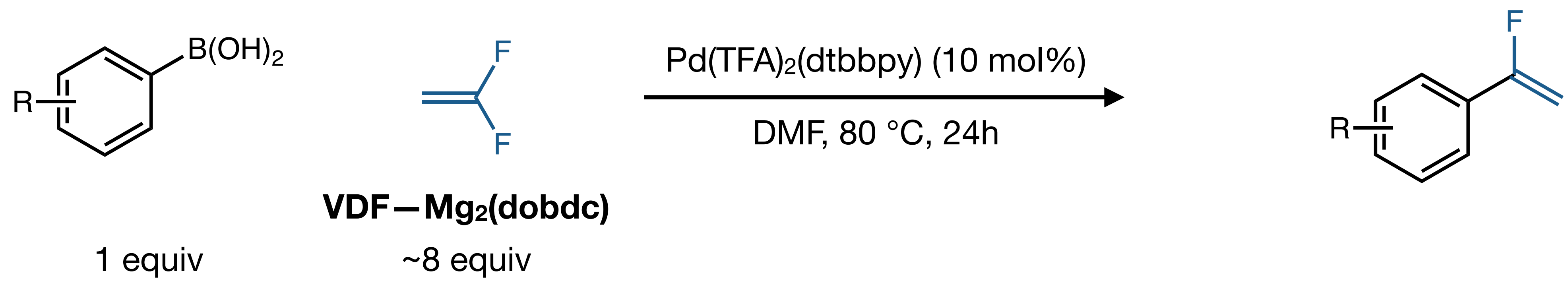
44% yield (wax: 63%)

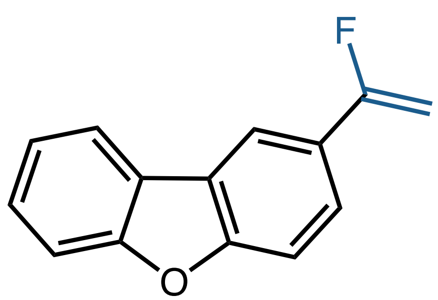
VDF—Mg_2(dobdc) stability study

Storage Duration	Glovebox Freezer	Lab Freezer	Desiccator	Wax Capsule
1 d				
3 d				
7 d				
14 d				
2 mos				

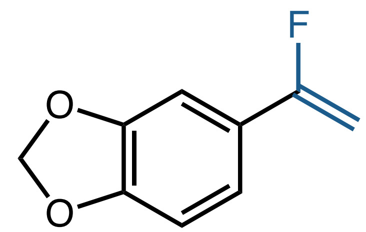


Novel reagents based on MOFs

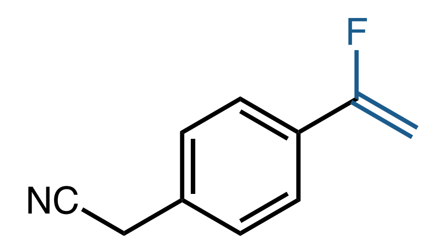




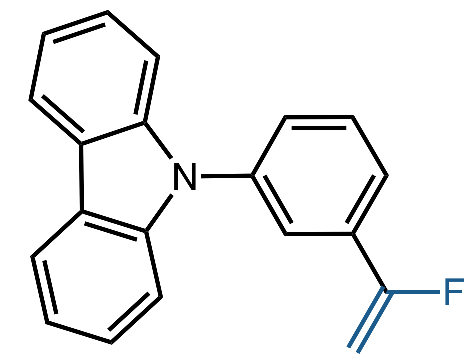
74% yield (wax: 80%)



66% yield (wax: 78%)



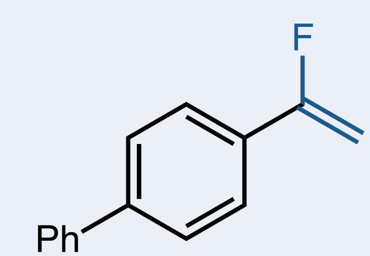
41% yield (wax: 65%)



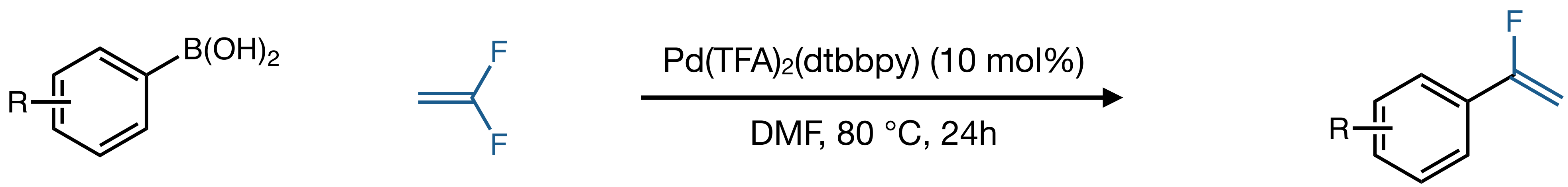
44% yield (wax: 63%)

VDF—Mg_2(dobdc) stability study

Storage Duration	Glovebox Freezer	Lab Freezer	Desiccator	Wax Capsule
1 d	83%			
3 d	88%			
7 d	82%			
14 d	60%			
2 mos	—			

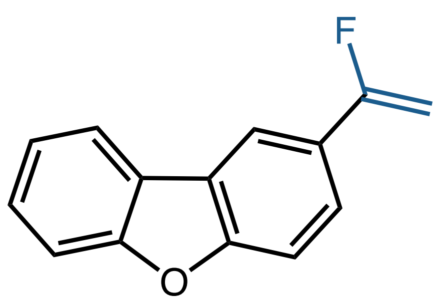


Novel reagents based on MOFs

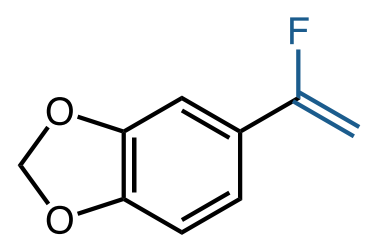


1 equiv

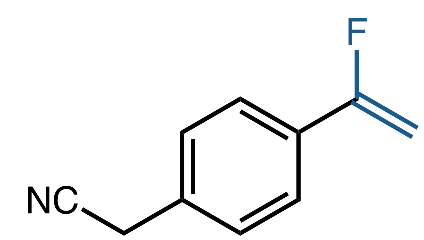
VDF—Mg_2(dobdc)
~8 equiv



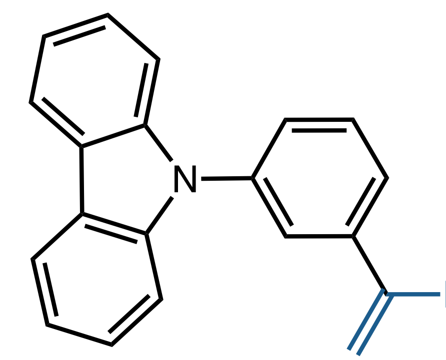
74% yield (wax: 80%)



66% yield (wax: 78%)



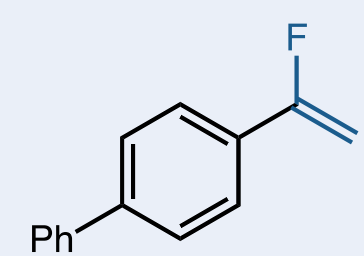
41% yield (wax: 65%)



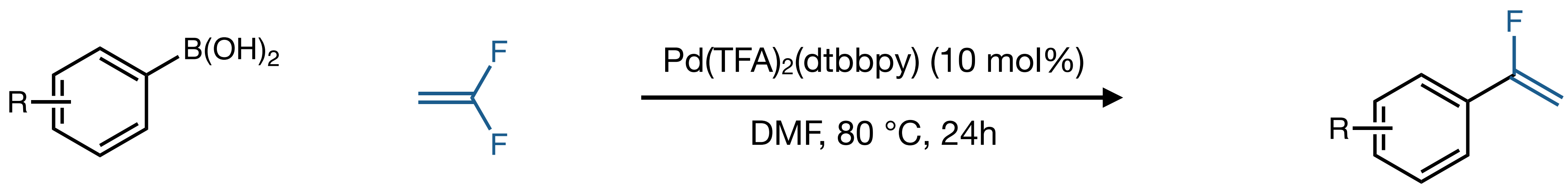
44% yield (wax: 63%)

VDF—Mg_2(dobdc) stability study

Storage Duration	Glovebox Freezer	Lab Freezer	Desiccator	Wax Capsule
1 d	83%	89%		
3 d	88%	83%		
7 d	82%	80%		
14 d	60%	64%		
2 mos	—	—		



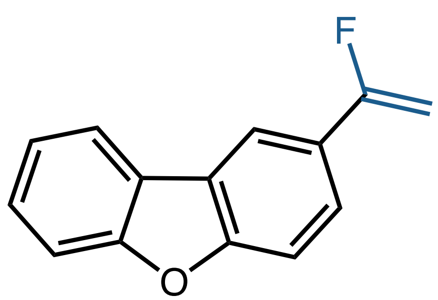
Novel reagents based on MOFs



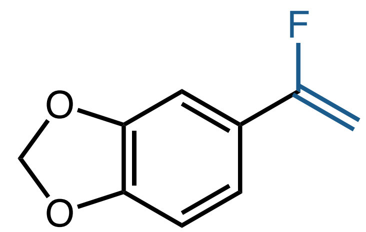
VDF—Mg$_2$(dobdc)

1 equiv

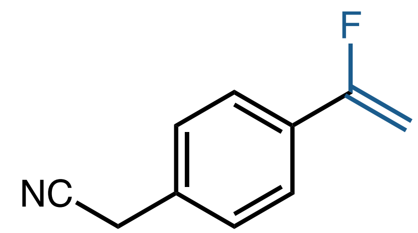
~8 equiv



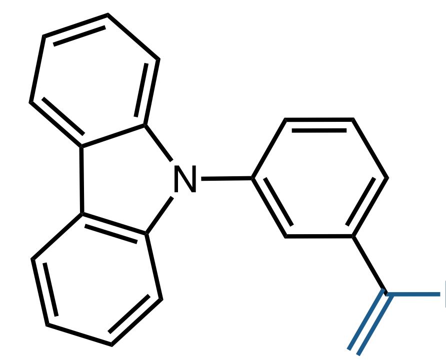
74% yield (wax: 80%)



66% yield (wax: 78%)



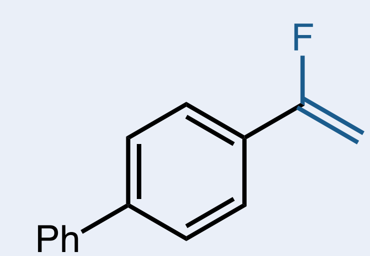
41% yield (wax: 65%)



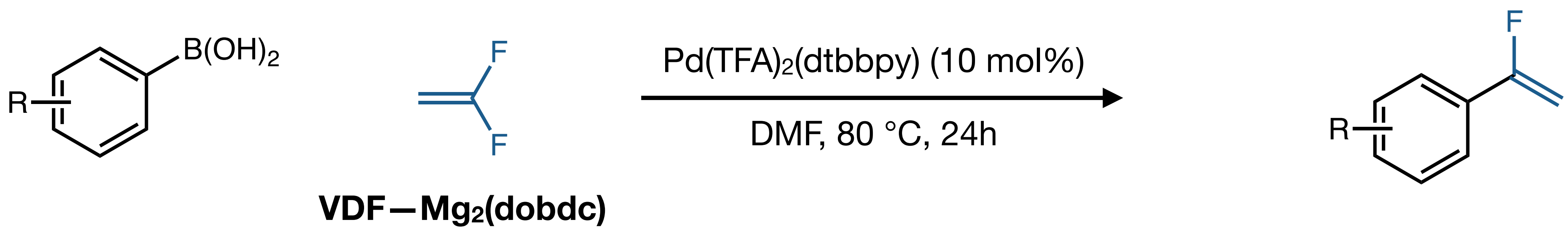
44% yield (wax: 63%)

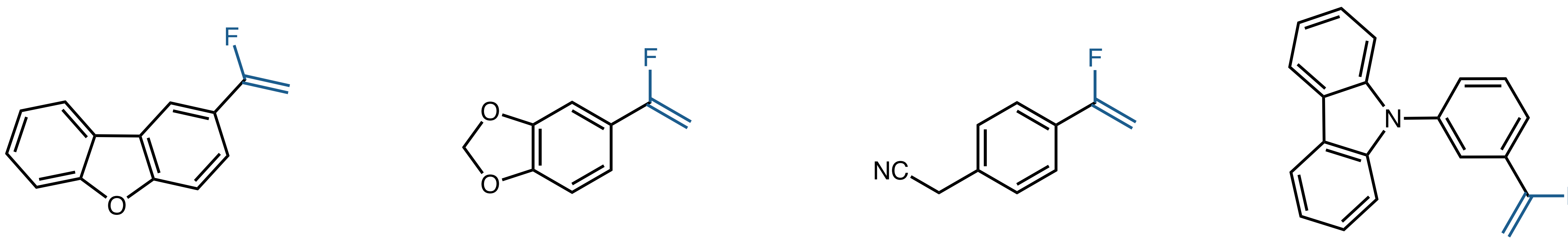
VDF—Mg$_2$(dobdc) stability study

Storage Duration	Glovebox Freezer	Lab Freezer	Desiccator	Wax Capsule
1 d	83%	89%	82%	
3 d	88%	83%	72%	
7 d	82%	80%	47%	
14 d	60%	64%	0%	
2 mos	—	—	—	



Novel reagents based on MOFs





74% yield (wax: 80%)

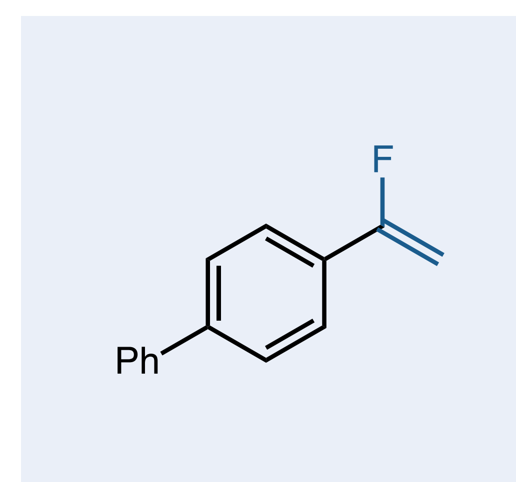
66% yield (wax: 78%)

41% yield (wax: 65%)

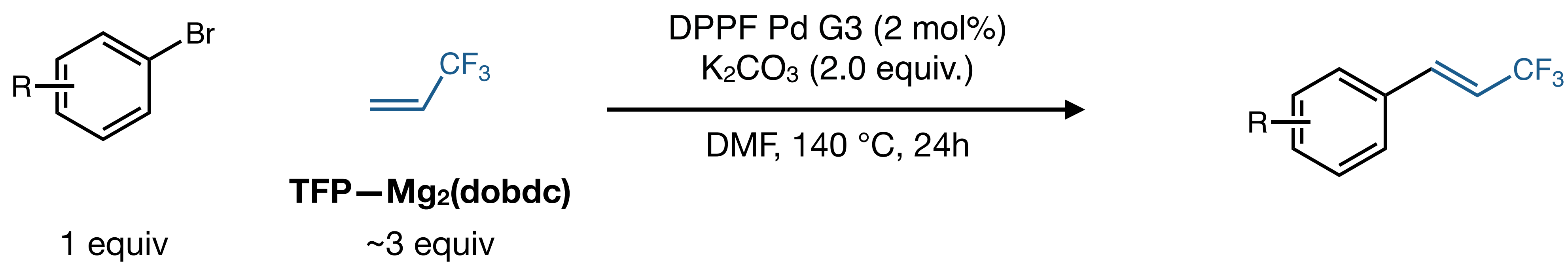
44% yield (wax: 63%)

VDF—Mg_2(dobdc) stability study

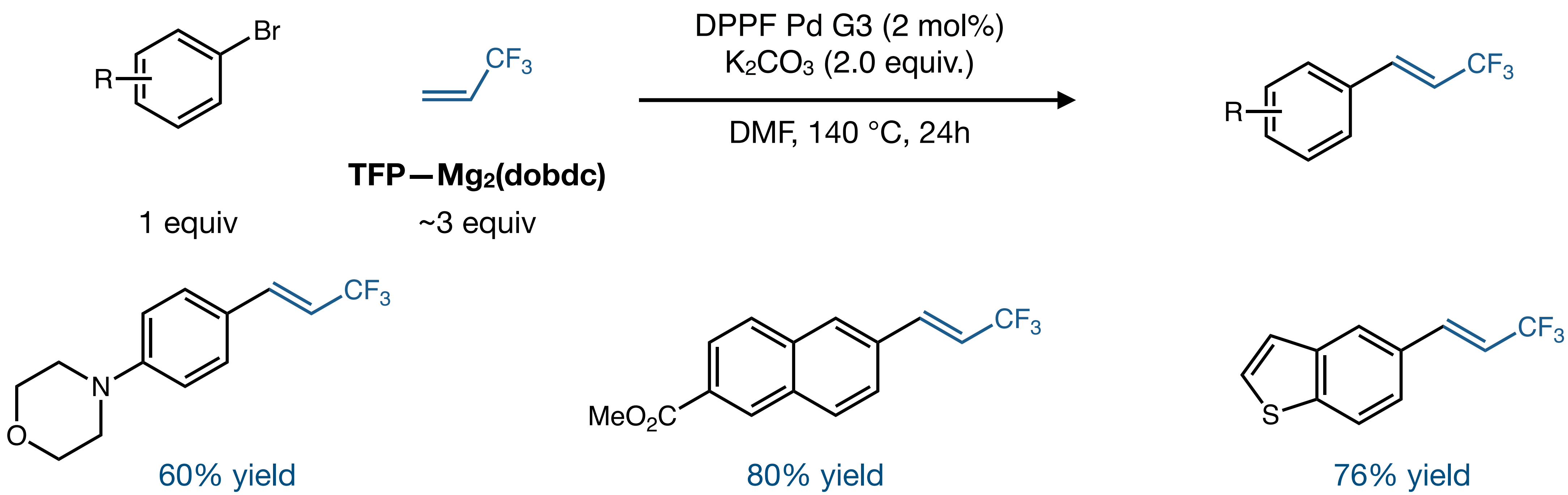
Storage Duration	Glovebox Freezer	Lab Freezer	Desiccator	Wax Capsule
1 d	83%	89%	82%	80%, 82%*
3 d	88%	83%	72%	77%
7 d	82%	80%	47%	81%
14 d	60%	64%	0%	82%
2 mos	—	—	—	77%, 81%*



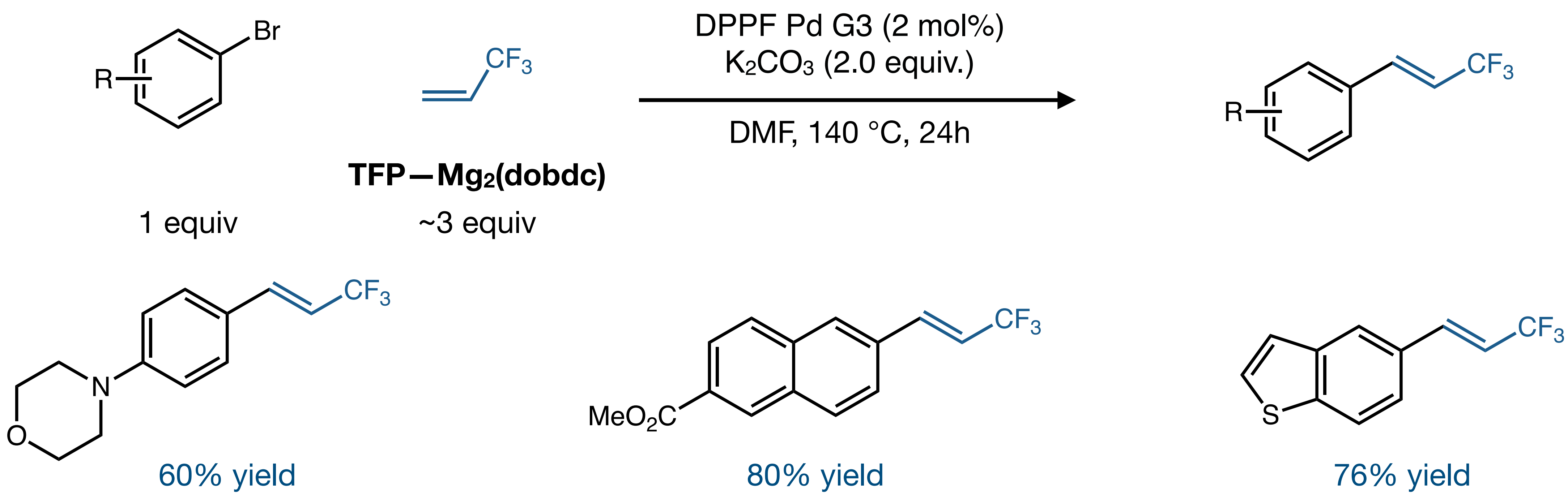
Novel reagents based on MOFs

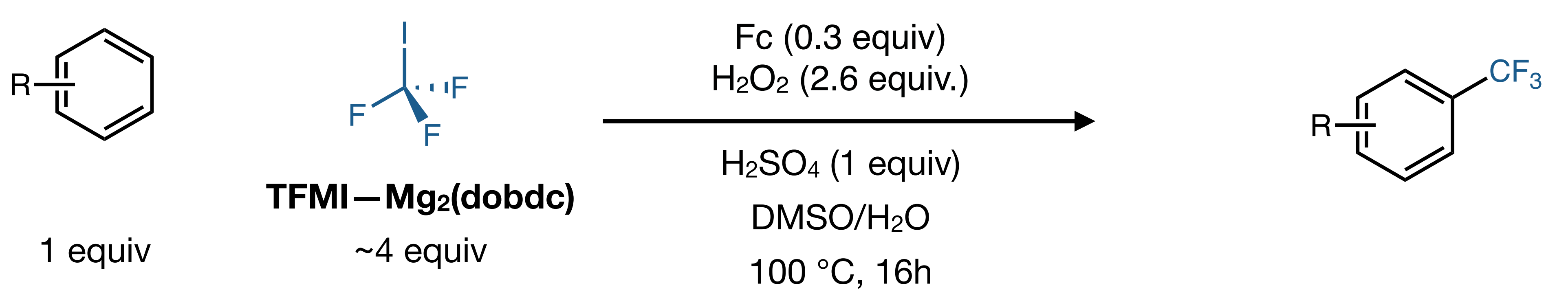


Novel reagents based on MOFs

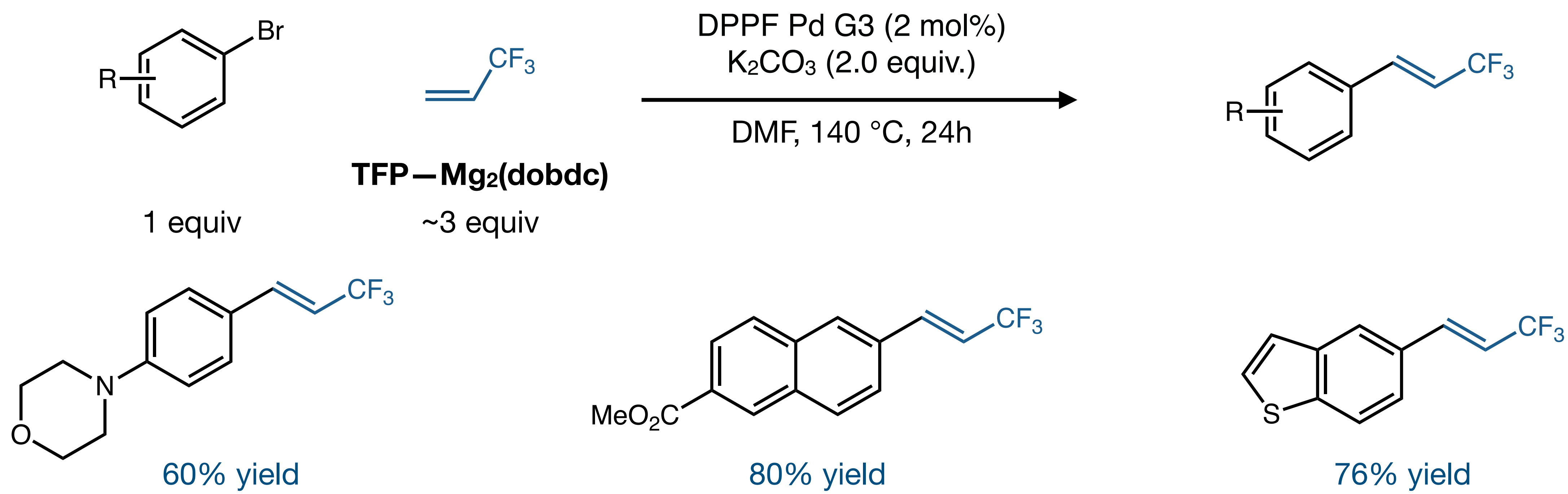


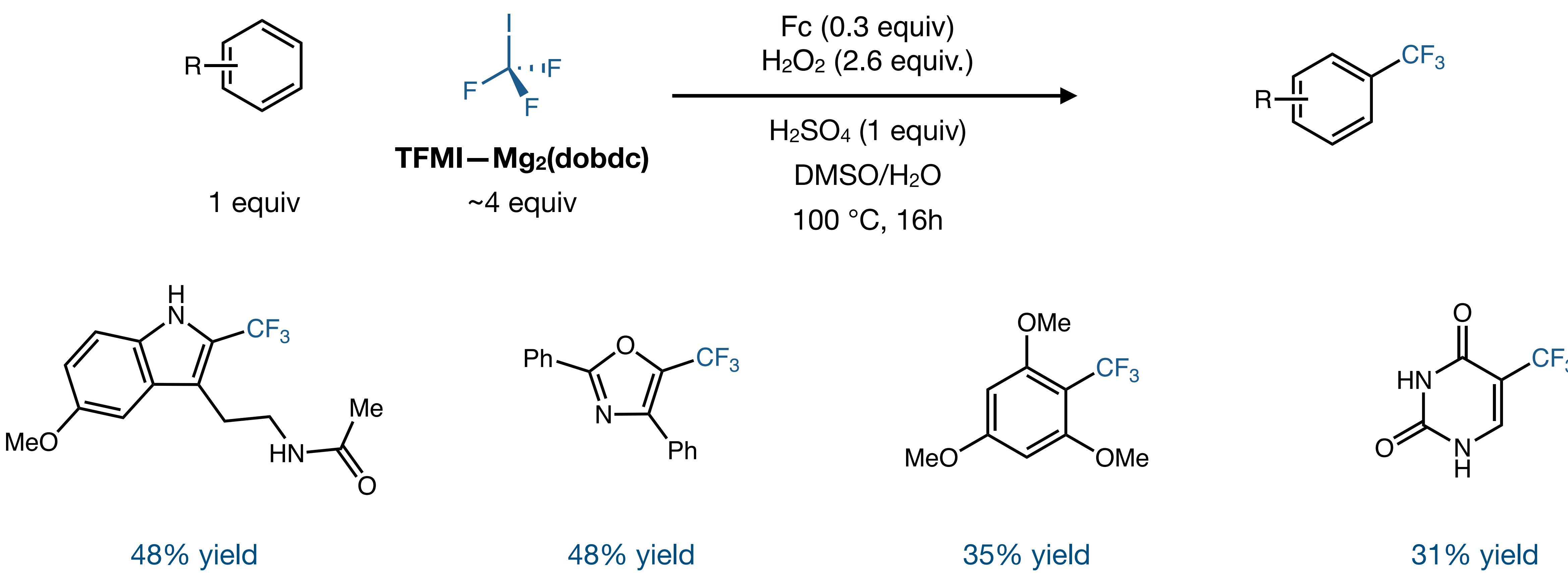
Novel reagents based on MOFs





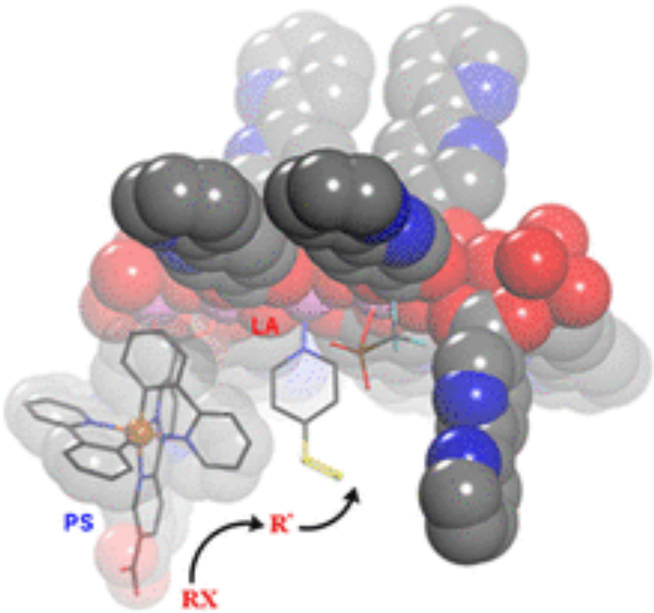
Novel reagents based on MOFs



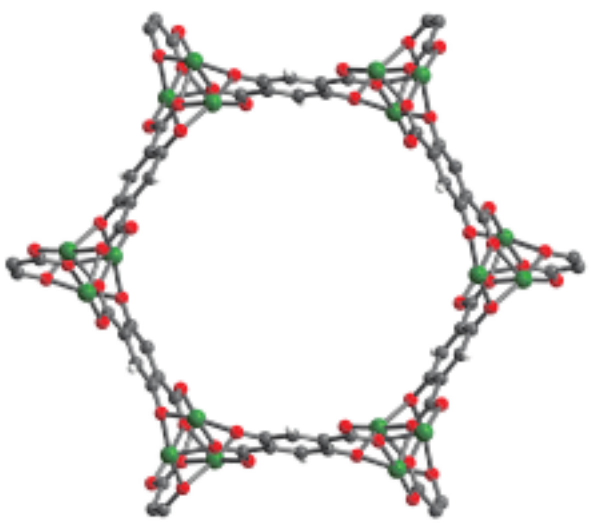


Organic synthetic applications of MOFs

What are possible organic synthetic applications of MOFs?



Case study 1: Enhanced reactivity



Case study 2: Novel reagents based on MOFs

Conclusions

What are MOFs?

How to synthesize MOFs?

Organic synthetic applications MOFs

Conclusions

What are MOFs?

How to synthesize MOFs?

Organic synthetic applications MOFs

"addressing currently unmet needs in catalysis instead of trying to outcompete homogeneous catalysts in areas where they excel"

Acknowledgements

Prof. David MacMillan

The MacMillan Group

Alkene-Alcohol Project

Iona McWhinnie

Dr. Nate Dow

Amy Chan

Cyclization of N-heterocycles

Noah Bissonnette

Prof. Saegun Kim

Advisory/General Committee

Prof. David MacMillan

Prof. John Groves

Prof. Erik Sorensen

Prof. Robert Knowles

Administration

Caroline Phillips

Meredith LaSalle-Tarantin

Patti Wallack

Instrumentation

Ken Conover

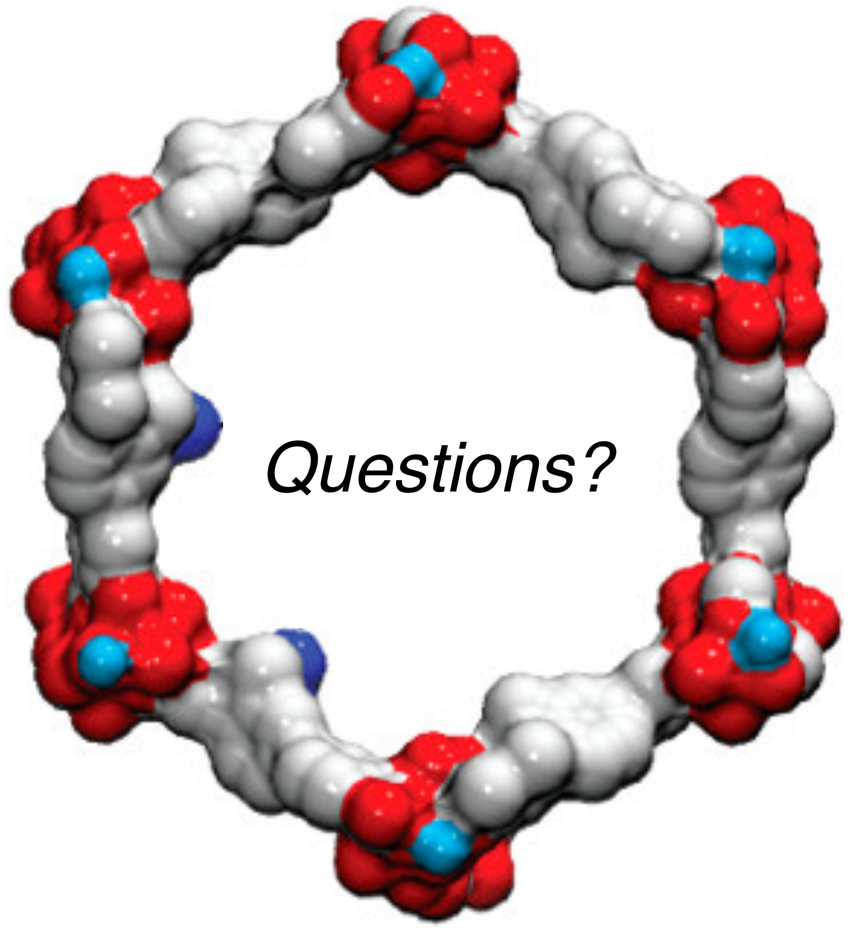
Dr. István Pelczer

Dr. John Eng

Dr. Phil Jeffrey

PRINCETON UNIVERSITY

Edward C. Taylor Fellowships


Questions?