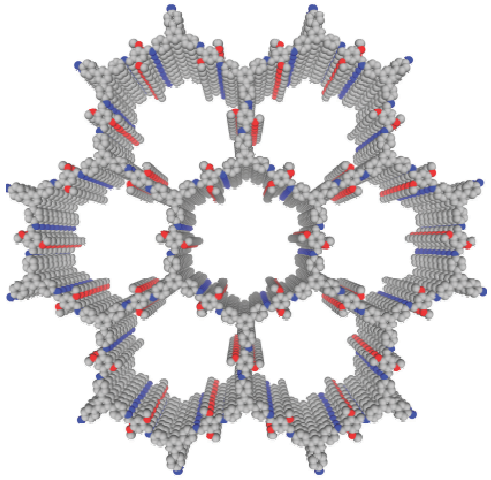
中国科学院大连化学物理研究所
DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES

文献报告

Covalent Organic Frameworks for *Heterogeneous* Catalysis

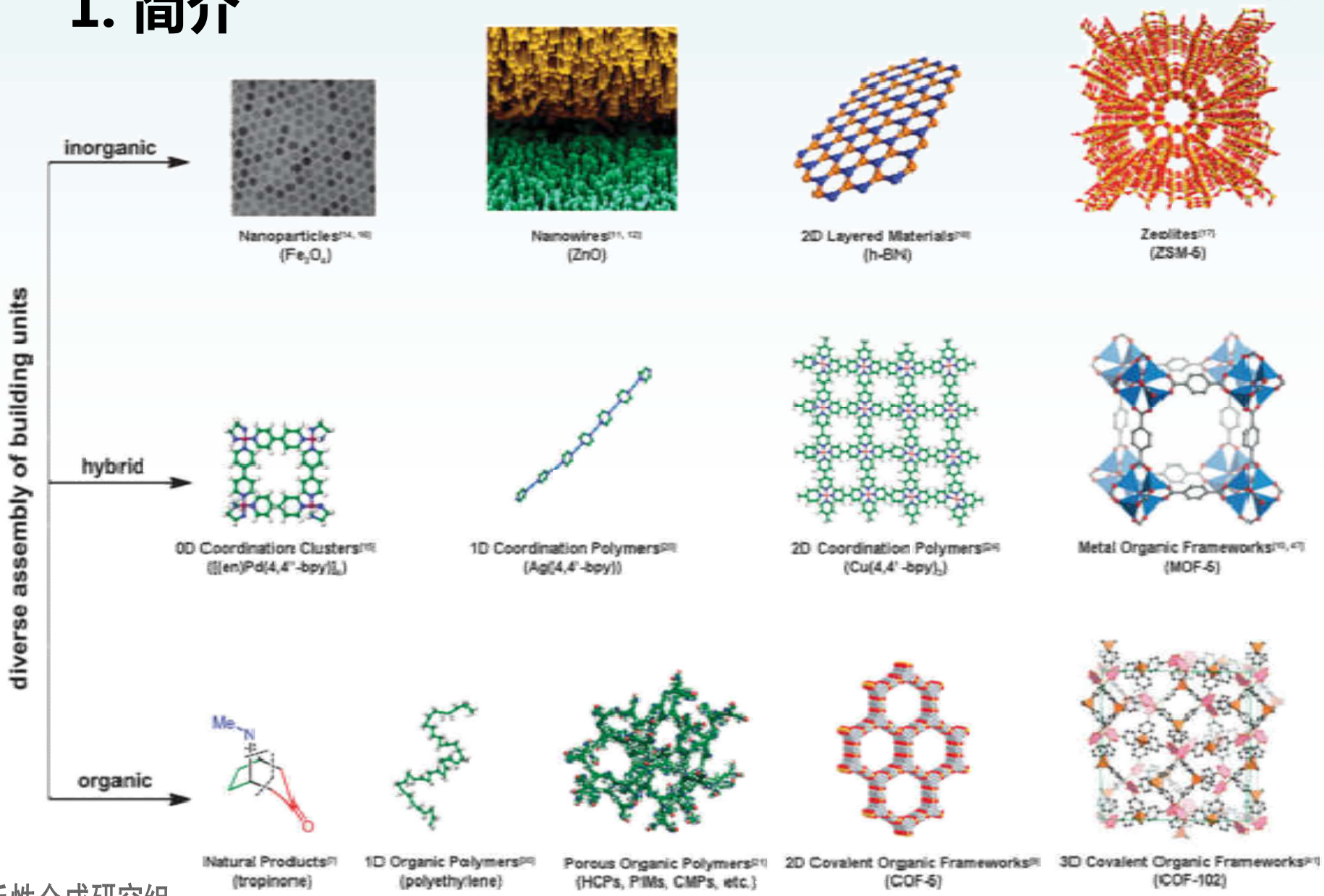


报告： 时磊　　检查：冯广收

手性合成研究组

目　录

1. 简介


diverse assembly of building units
inorganic
hybrid
organic
Nanoparticles
(Fe3O4)
Nanowires
(ZnO)
2D Layered Materials
(h-BN)
Zeolites
(ZSM-5)
0D Coordination Clusters
([(en)Pd(4,4'-bpy)]n)
1D Coordination Polymers
(Ag[4,4'-bpy])
2D Coordination Polymers
(Cu(4,4'-bpy)2)
Metal Organic Frameworks
(MOF-5)
Natural Products
(tropinone)
1D Organic Polymers
(polyethylene)
Porous Organic Polymers
(HCPs, PIMs, CMPs, etc.)
2D Covalent Organic Frameworks
(COF-5)
3D Covalent Organic Frameworks
(COF-102)

手性合成研究组

(nano)porous organic polymer

Amorphous

HCPs
Hypercrosslinked Polymers”

PIMs
Polymers of Intrinsic Microporosity

CMPs
Conjugated Microporous Polymers

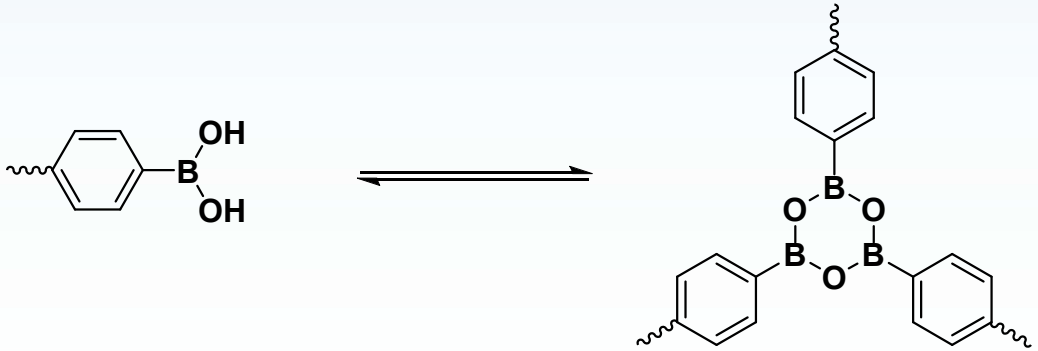
Crystalline

COFs
“Covalent Organic Frameworks”

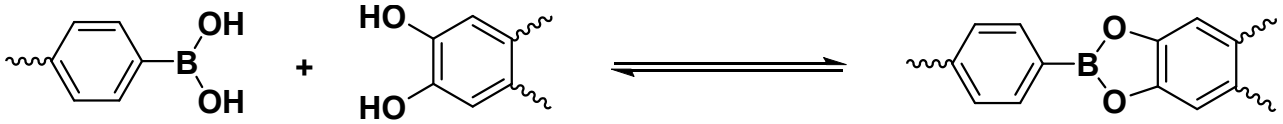
Covalent Bond

✓ *reversibility* ✓ *rigid planar*

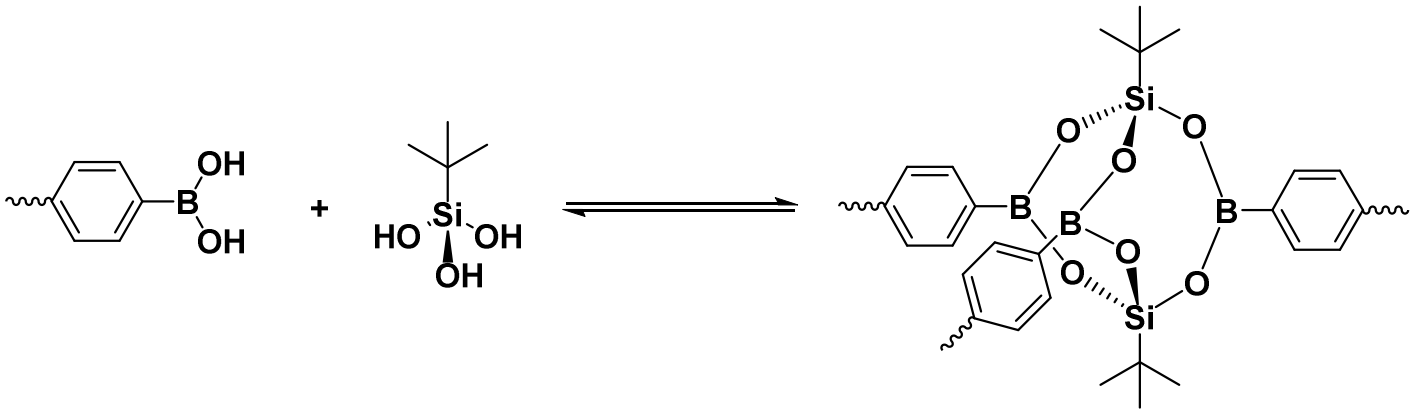
Boronate anhydride



Boronate Ester



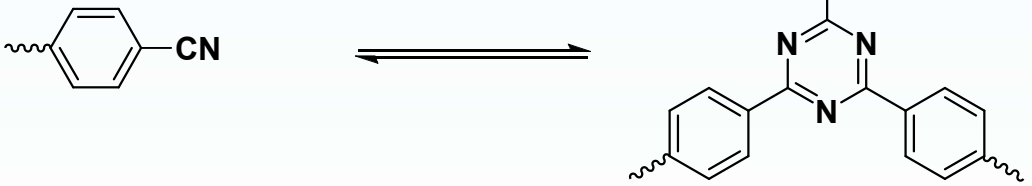
Borosilicate



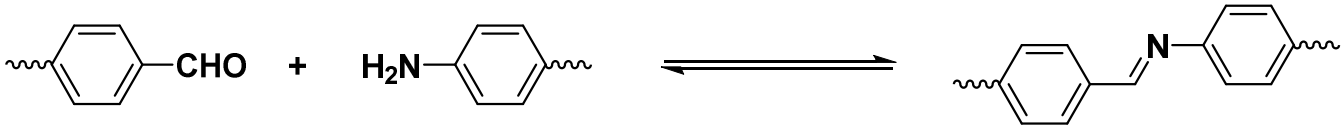
Covalent Bond

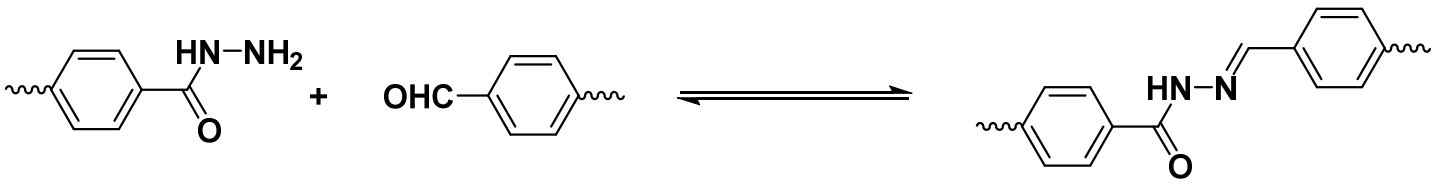
✓ ***reversibility*** ✓ ***rigid planar***

Nitrile Cyclotrimerization



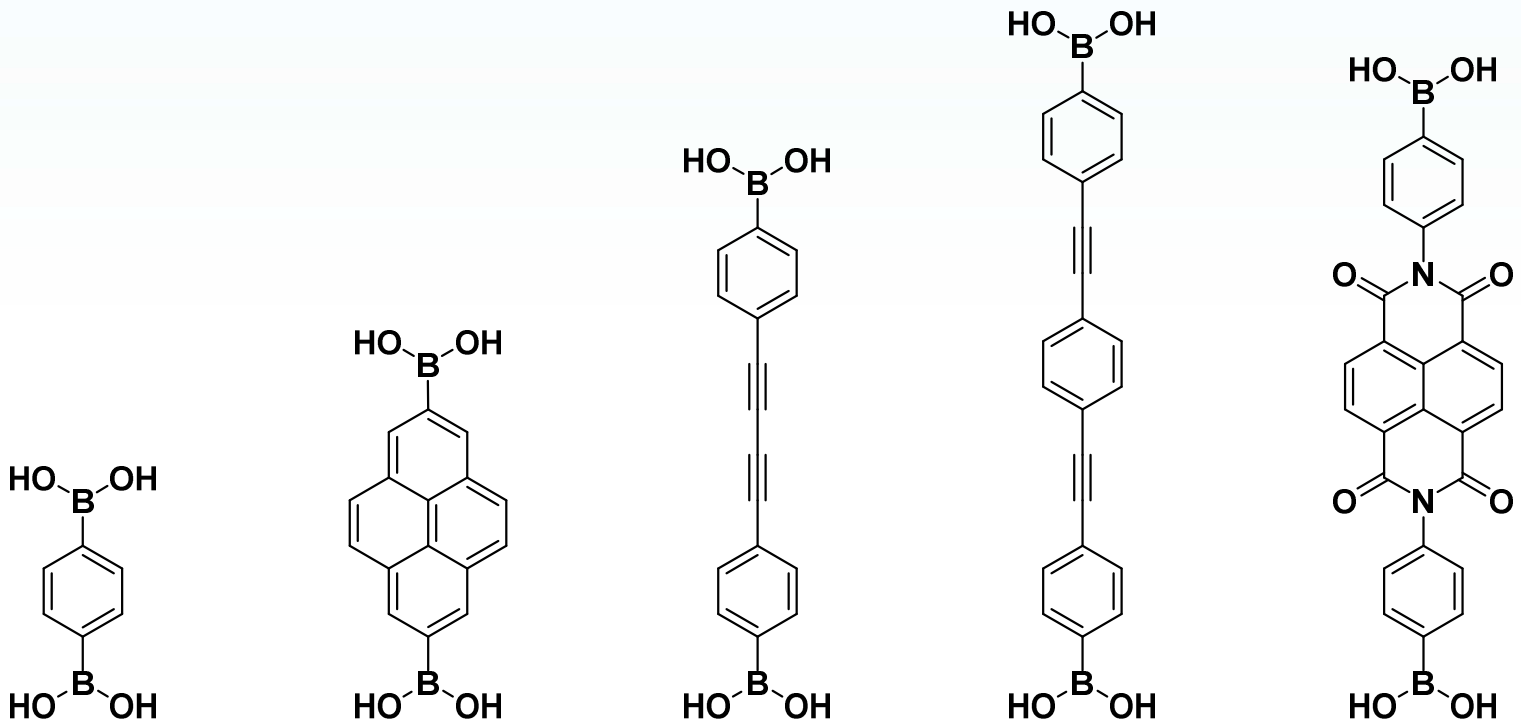
Imine Formation





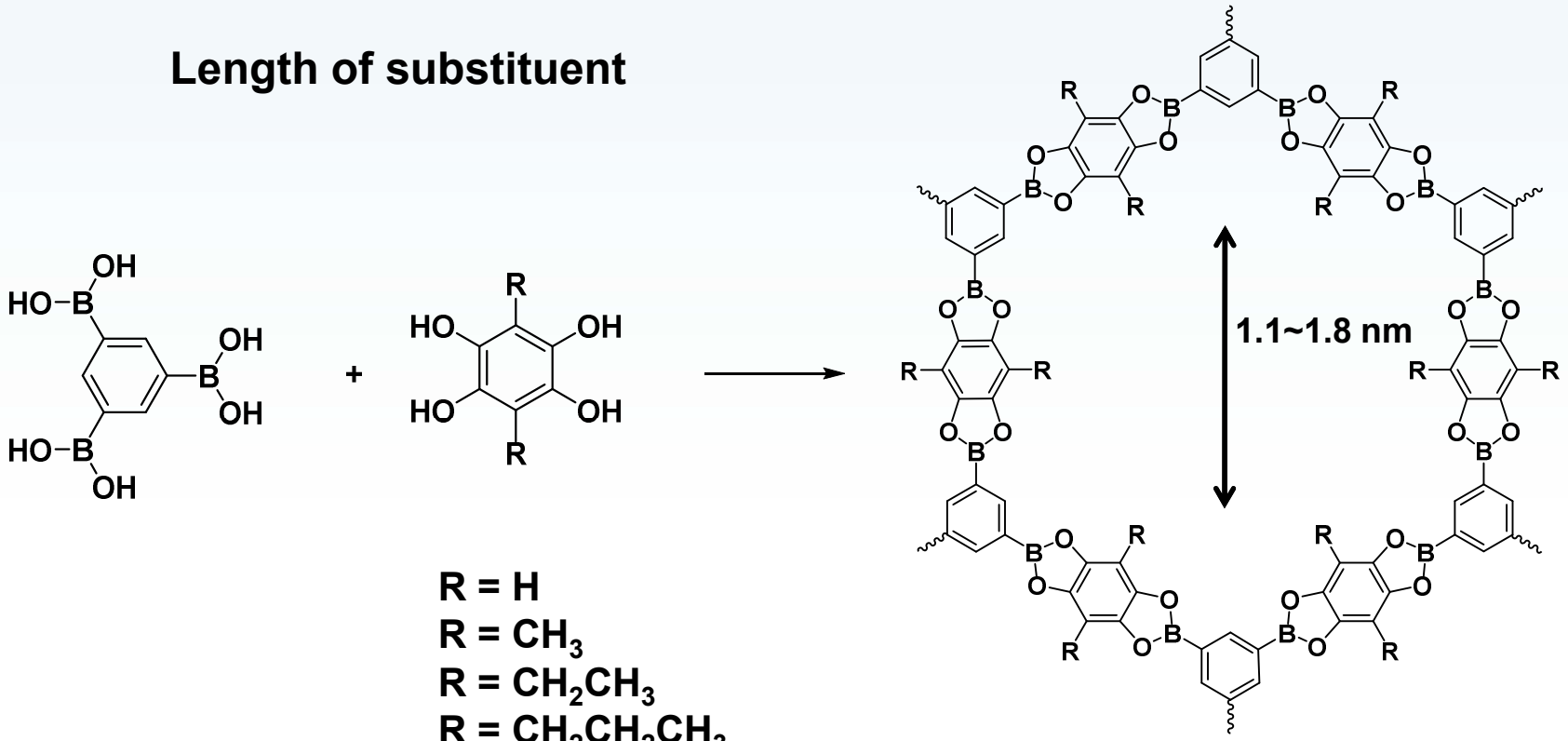
Porous structure

Length of units



The pore size

Length of substituent

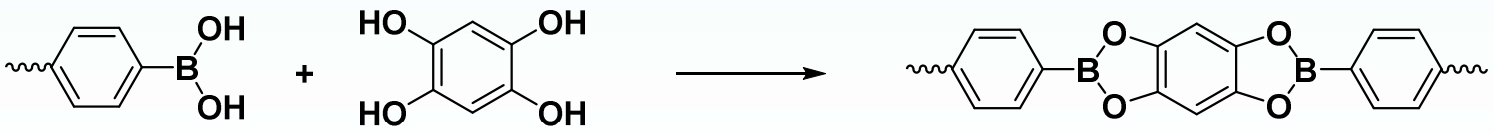


R = H
R = CH_3
R = CH_2CH_3
R = $CH_2CH_2CH_3$

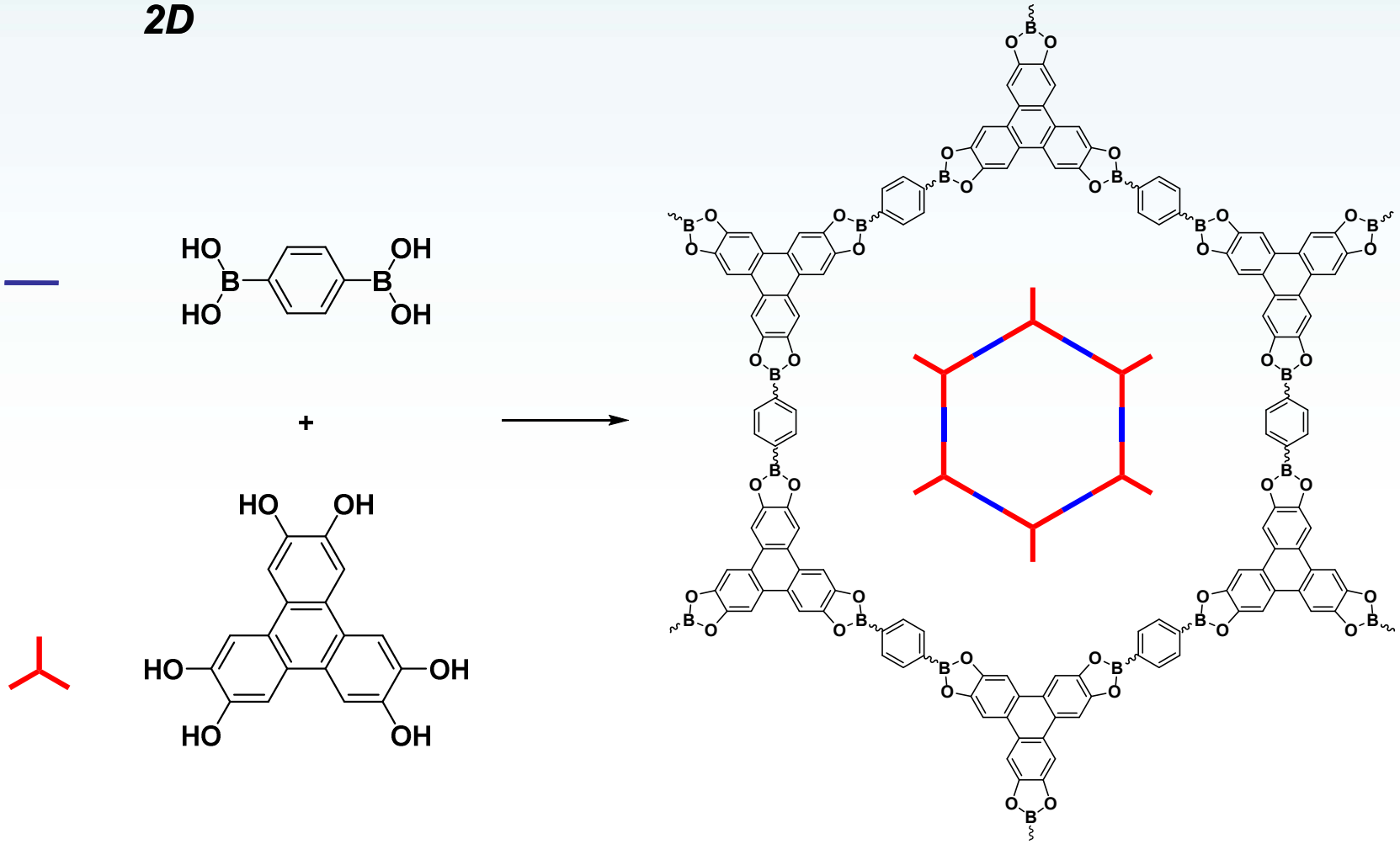
Topology

Shape of units

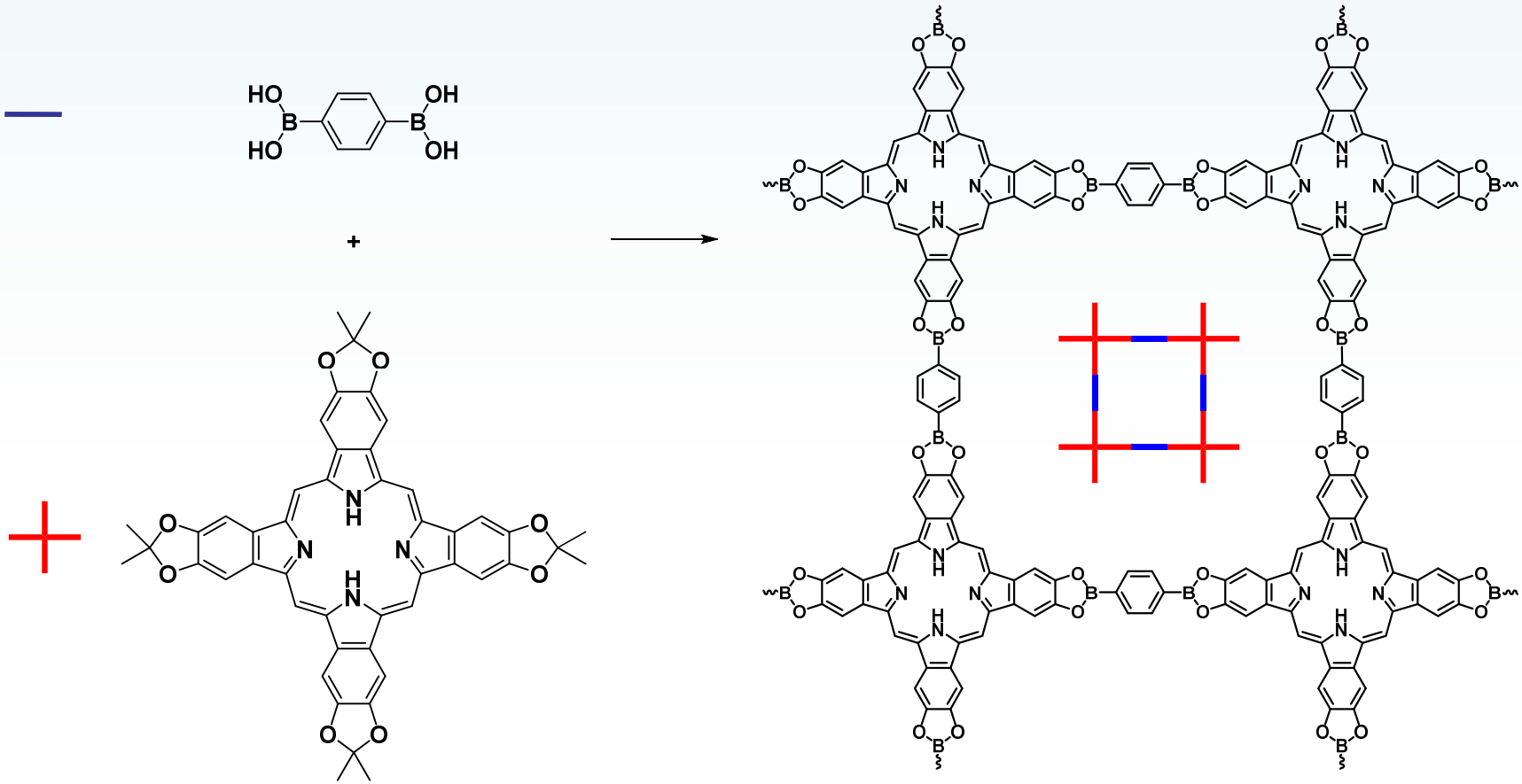
linear



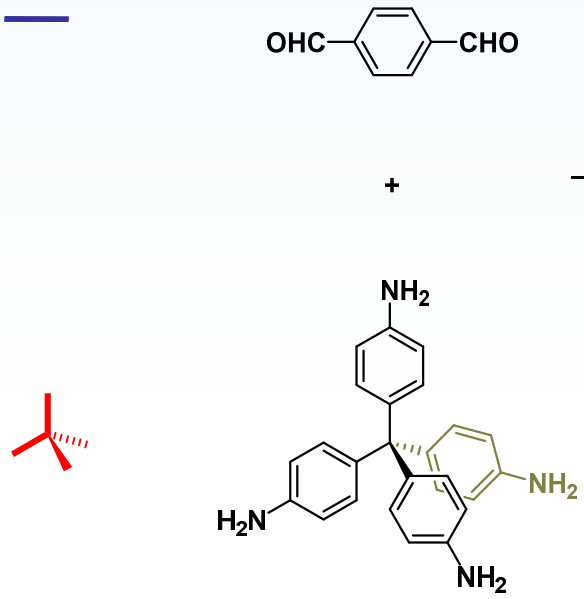
2D

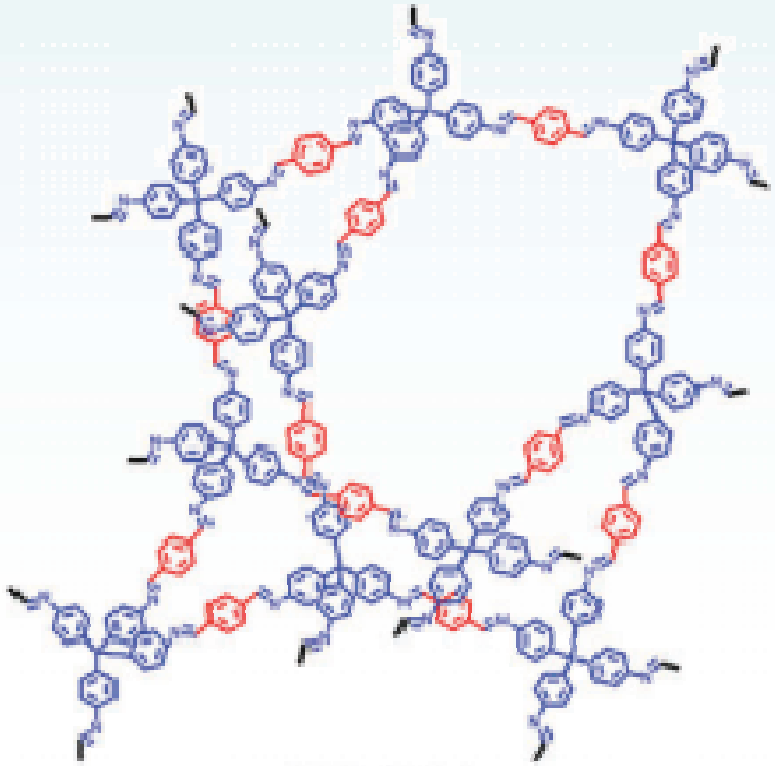


2D

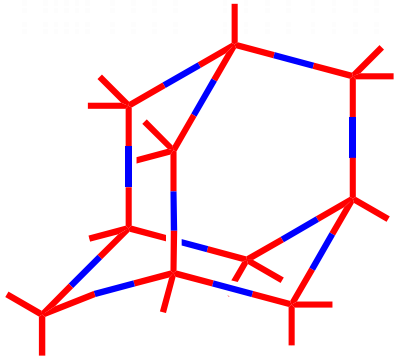


3D





COF-300



Synthesis of COFs

- **Solvothermal synthesis**

  2~9 days 80~120 °C

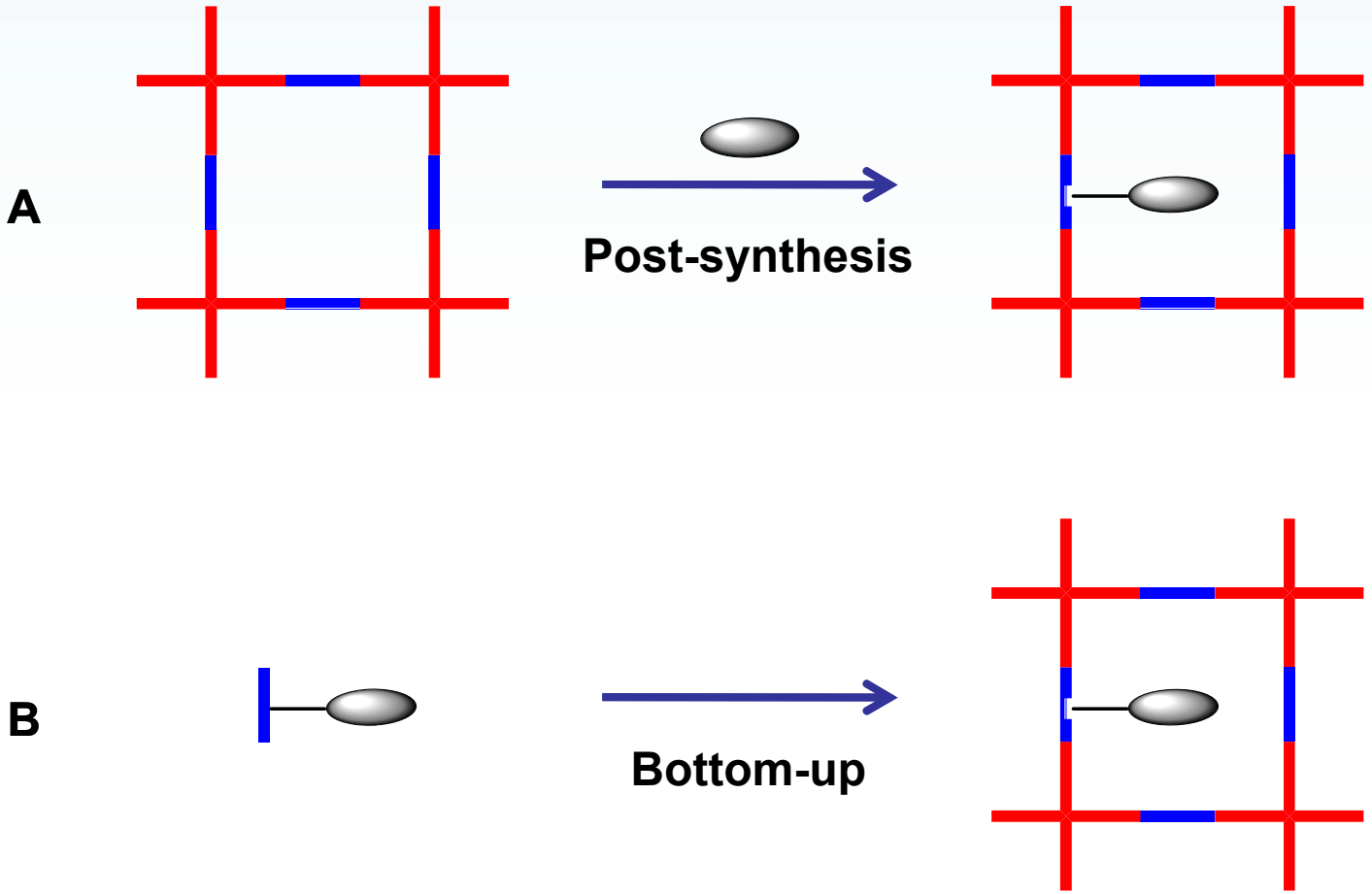
- **Ionothermal synthesis**

  Molten $ZnCl_2$ 400°C

- **Microwave synthesis**

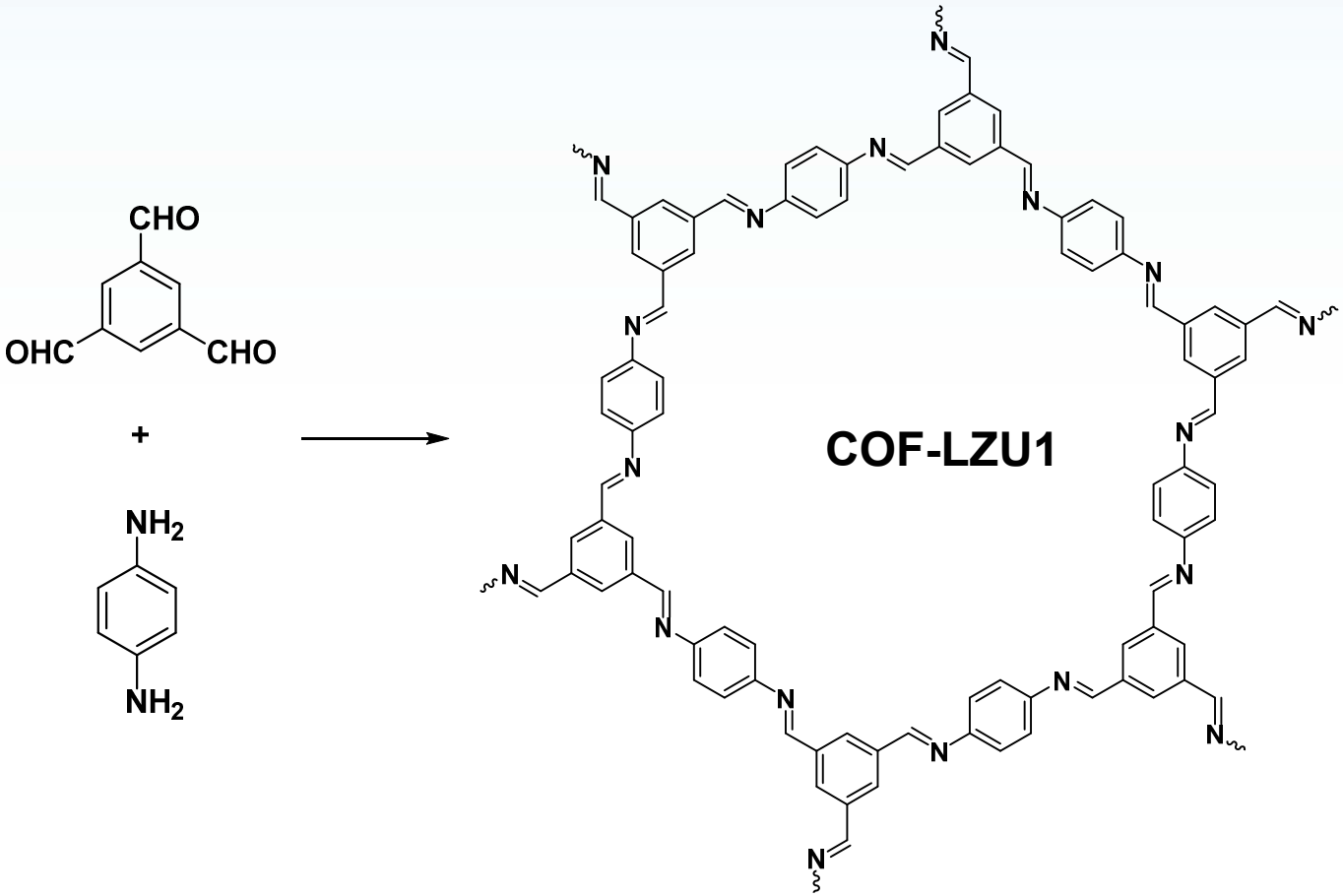
  200 times faster than solvothermal synthesis

Functionality

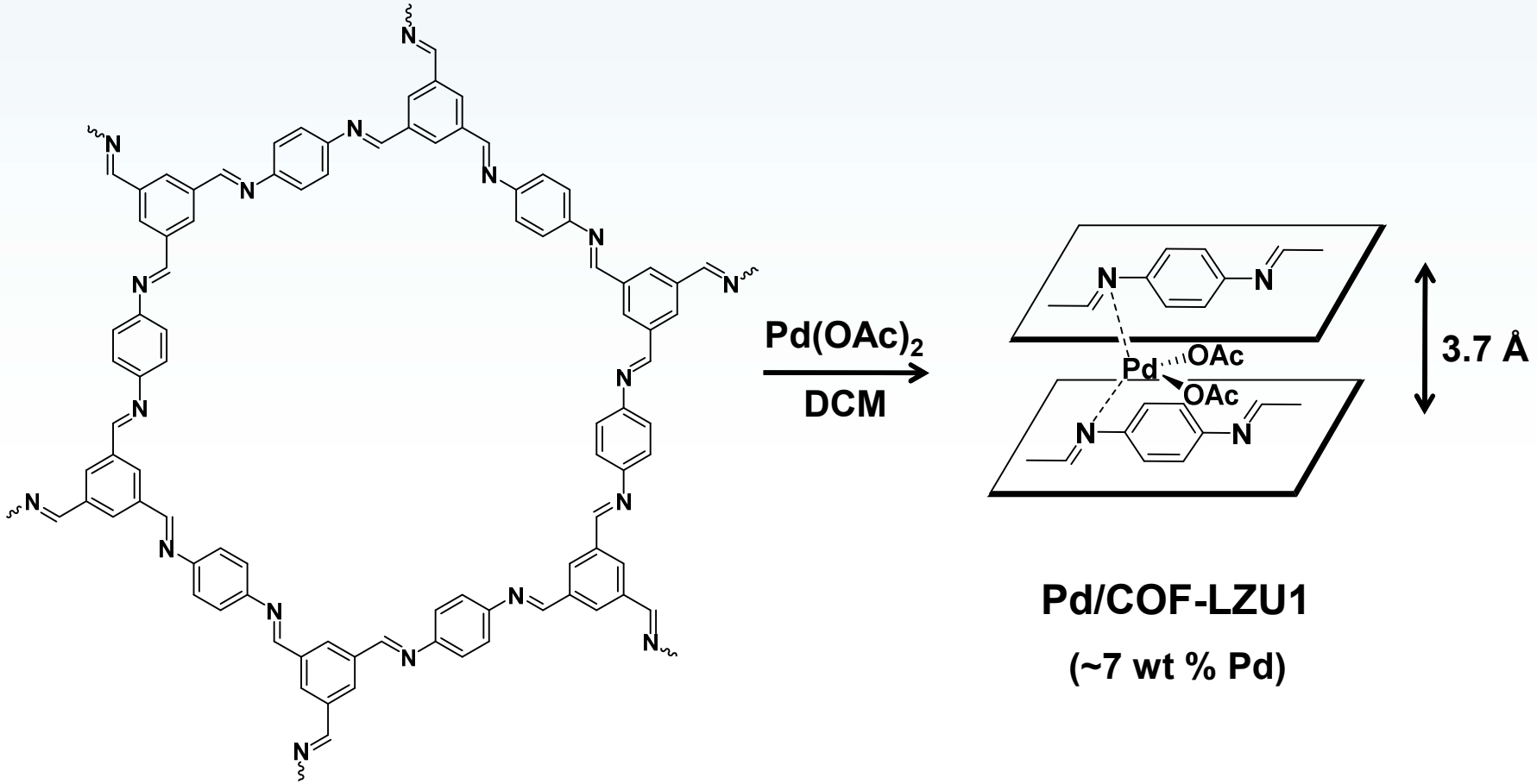


2. COF材料的催化应用

Suzuki coupling reaction



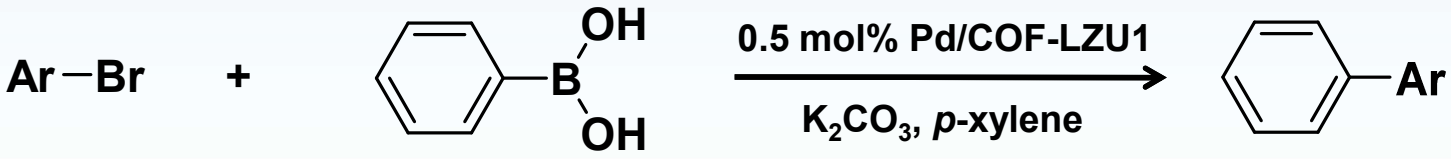
Wang, W. et al. *J. Am. Chem. Soc*. **2011**, *133*, 19816.

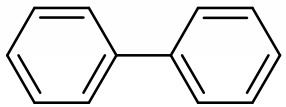


Pd/COF-LZU1

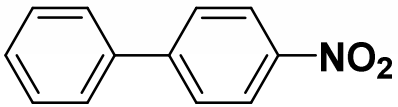
(~7 wt % Pd)

Wang, W. et al. *J. Am. Chem. Soc*. **2011**, *133*, 19816.

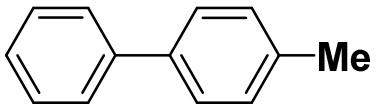




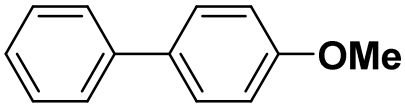
97%



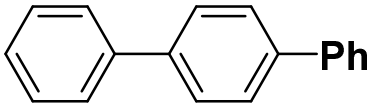
97%



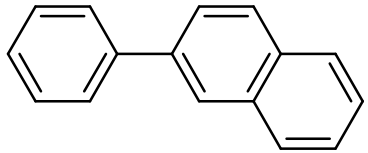
97%



96%



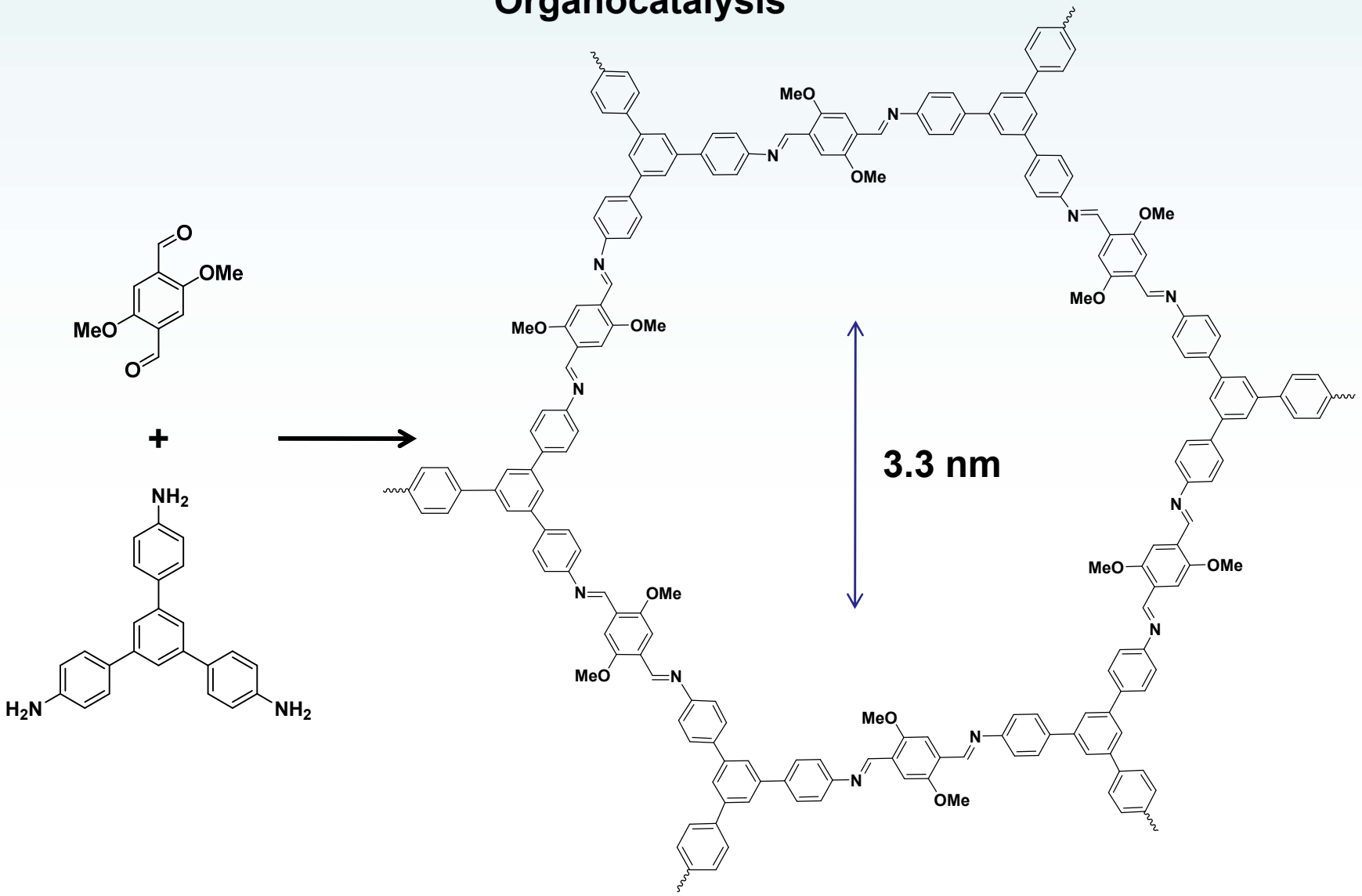
98%



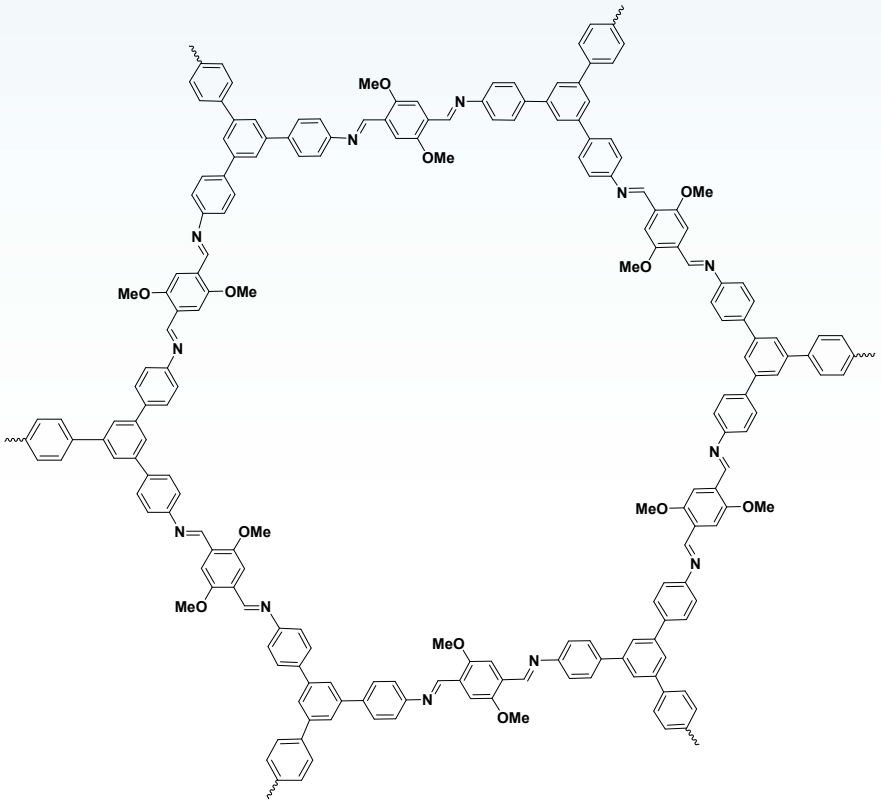
97%

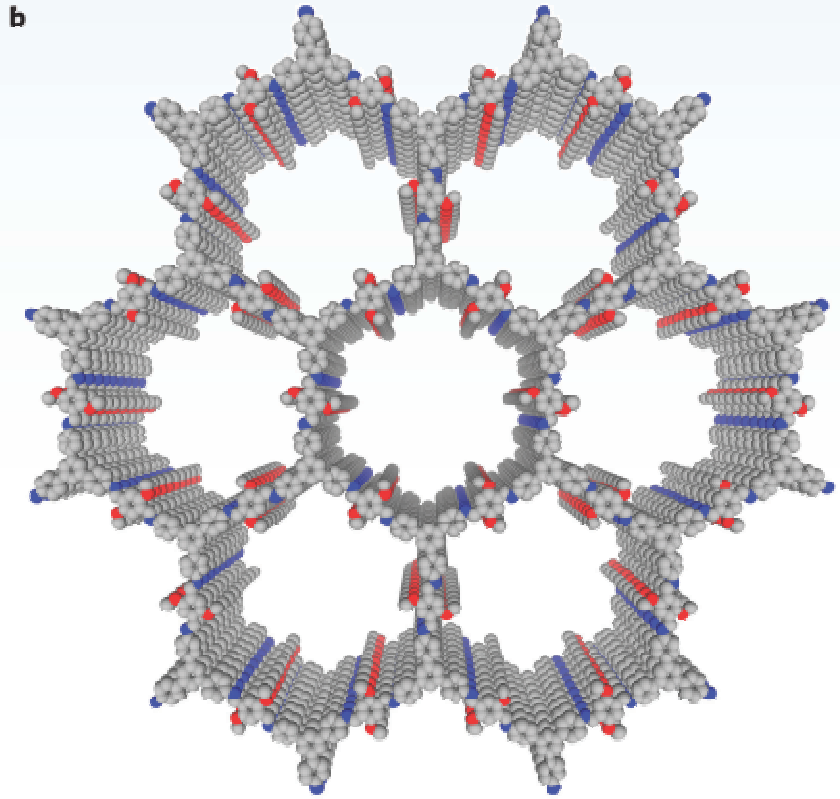
Wang, W. et al. *J. Am. Chem. Soc*. **2011**, *133*, 19816.

Organocatalysis

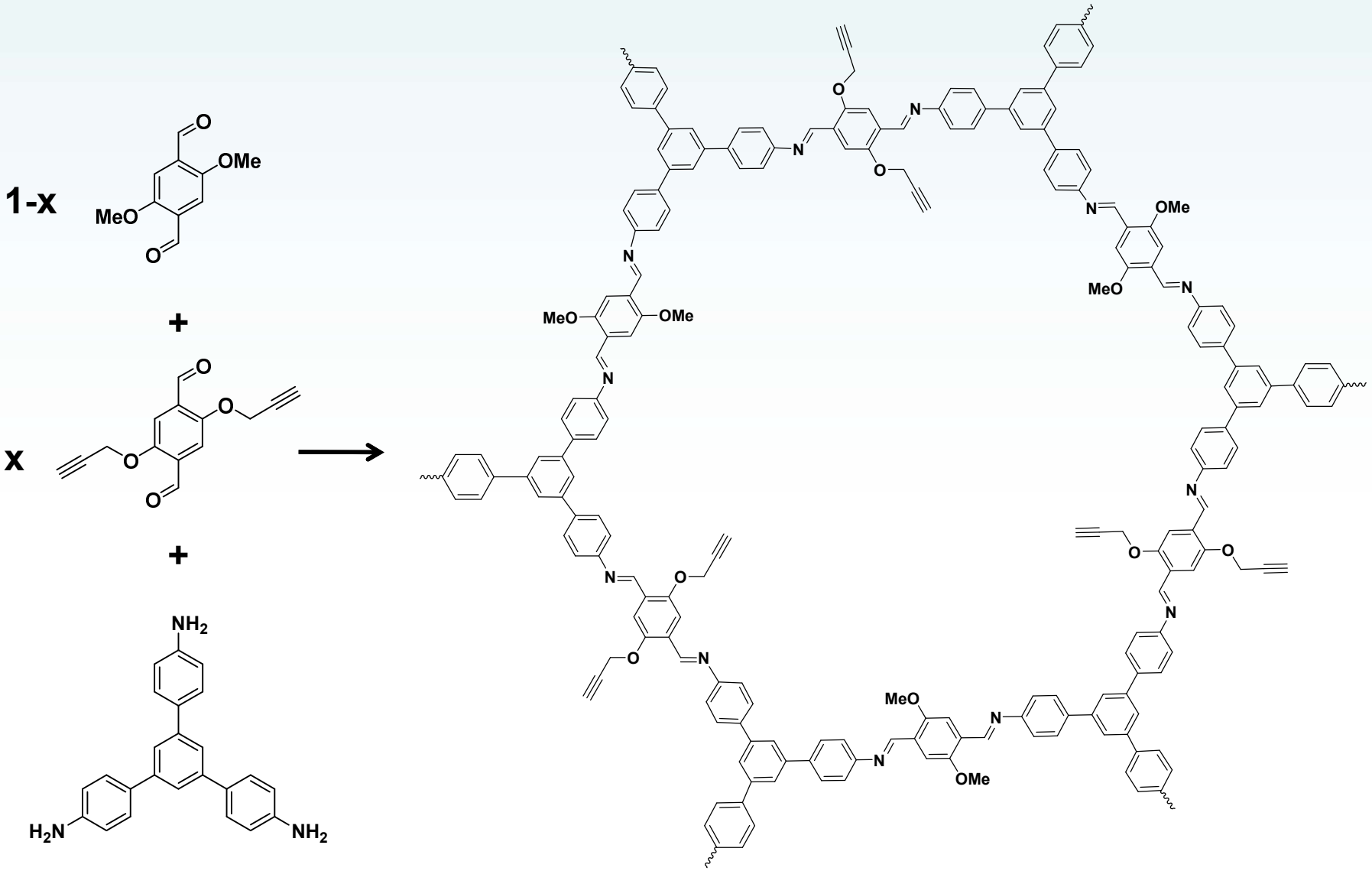


Jiang, D. et al. *Nature Chem.*, **2015**, *7*, 905.

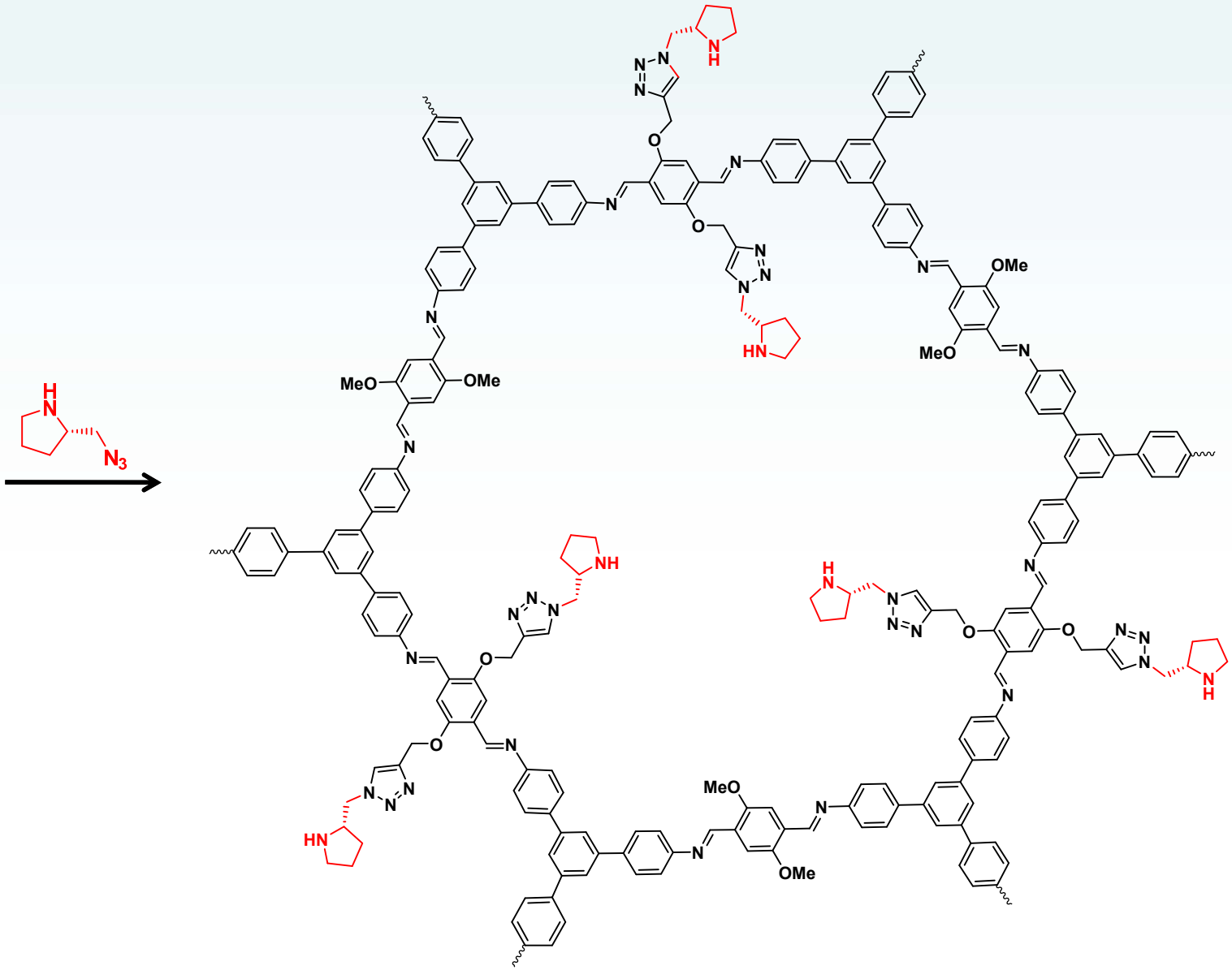




Jiang, D. et al. *Nature Chem.*, **2015**, *7*, 905.

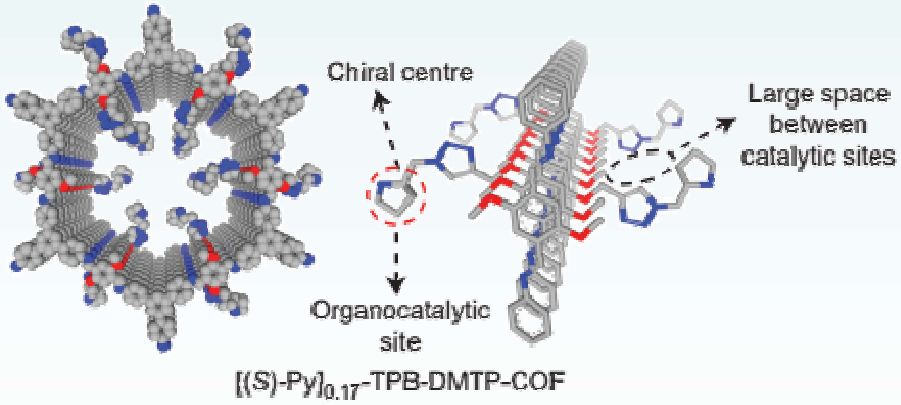


X= 0.17, 0.34, 0.50

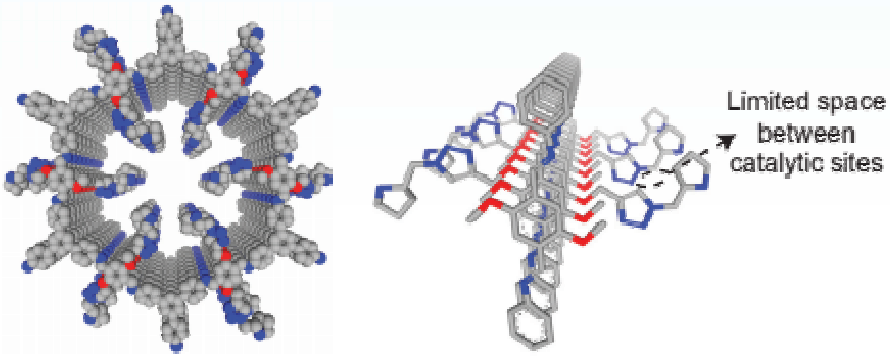


[(*S*)-Py]$_x$-TPB-DMTP-COFs X= 0.17,0.34,0.50

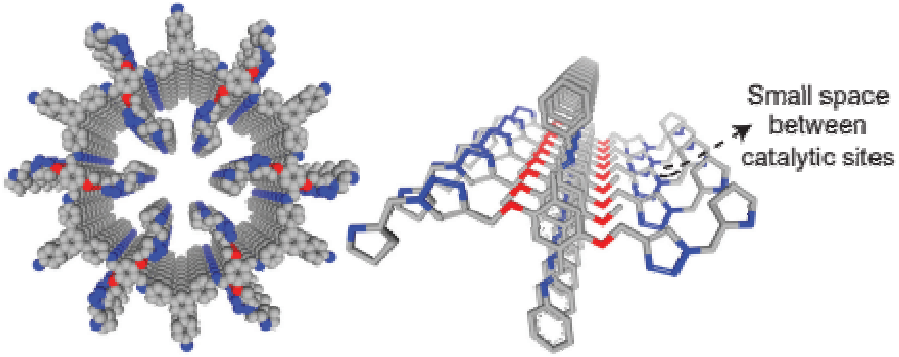
手性合成研究组



[(*S*)-Py]$_{0.17}$-TPB-DMTP-COF

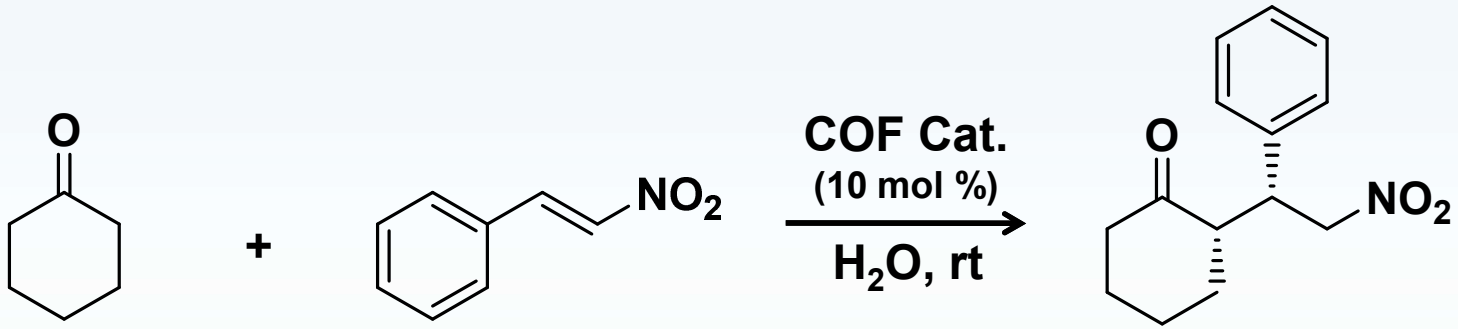


[(*S*)-Py]$_{0.34}$-TPB-DMTP-COF

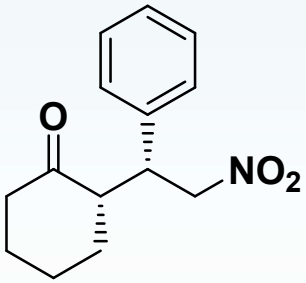


[(*S*)-Py]$_{0.50}$-TPB-DMTP-COF

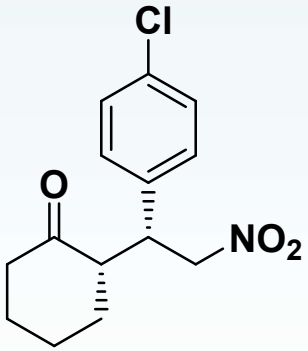
手性合成研究组



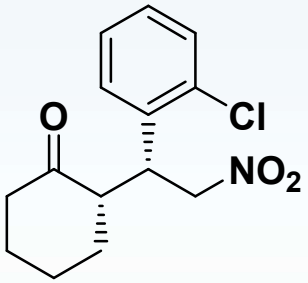
Entry	Catalyst	Time (h)	Conv. (%)	Yield (%)	Ee (%)	dr
1	[(*S*)-Py]$_{0.17}$-TPB-DMTP-COFs	12	100	95	92	90:10
2	[(*S*)-Py]$_{0.34}$-TPB-DMTP-COFs	17	100	93	91	90:10
3	[(*S*)-Py]$_{0.50}$-TPB-DMTP-COFs	34	100	95	89	88:12
4	((*S*)-1-(pyrrolidin-2-yl)methyl)-4-phenoxymethyl-triazole	22	100	96	92	91:9
5	[(*S*)-Py]$_{0.25}$-H_2P-COF	36	-	-	-	-



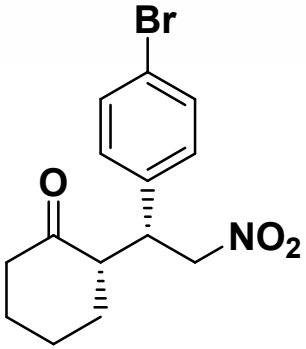
12 h, dr = 90/10
ee = 92%



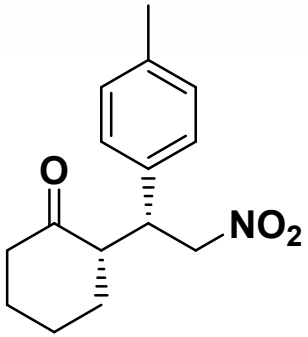
10 h, dr = 90/10
ee = 90%



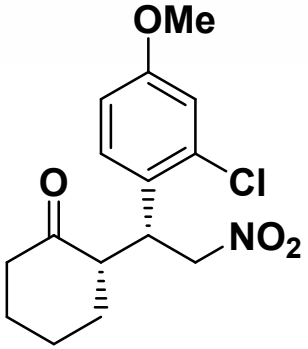
6 h, dr = 97/3
ee = 94%



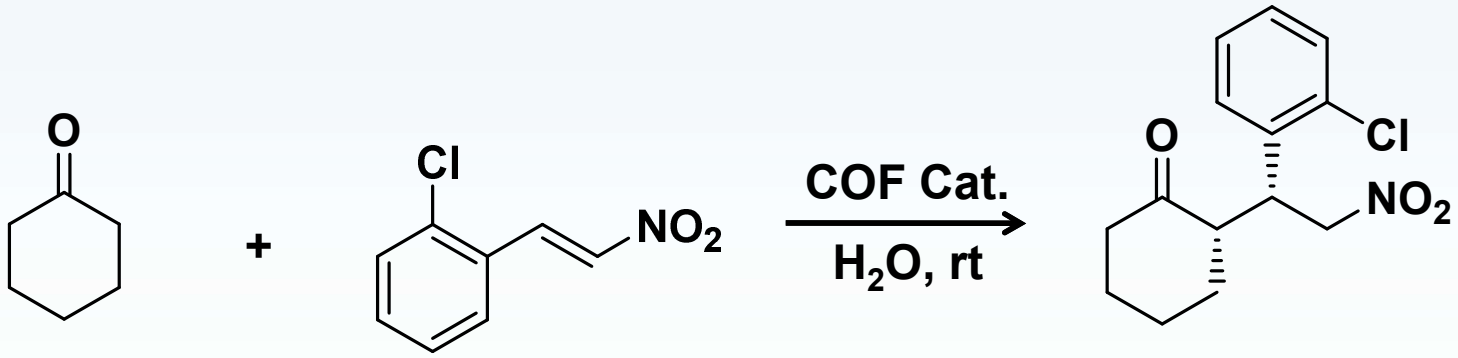
12 h, dr = 93/7
ee = 95%



16 h, dr = 92/8
ee = 93%



26 h, dr = 94/6
ee = 96%

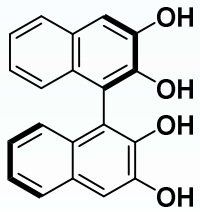


Cycle	Time (h)	Conv. (%)	Yield (%)	Ee (%)	dr	Ry(wt %)
1	6	100	95	94	97:3	>99
2	7	100	93	94	97:3	>99
3	8	100	94	94	97:3	>99
4	11	100	92	94	97:3	>99
5	13	100	92	93	97:3	>99

COF Cat. = [(*S*)-Py]$_{0.17}$-TPB-DMTP-COFs

展 望

- **手性COF材料 ⟶ 手性催化 手性分离**



- **模板法合成COF材料**

MOF ⟶ COF　　破坏配位键

COF ⟶ COF　　B-O键水解

2D ⟶ 3D　　环加成