

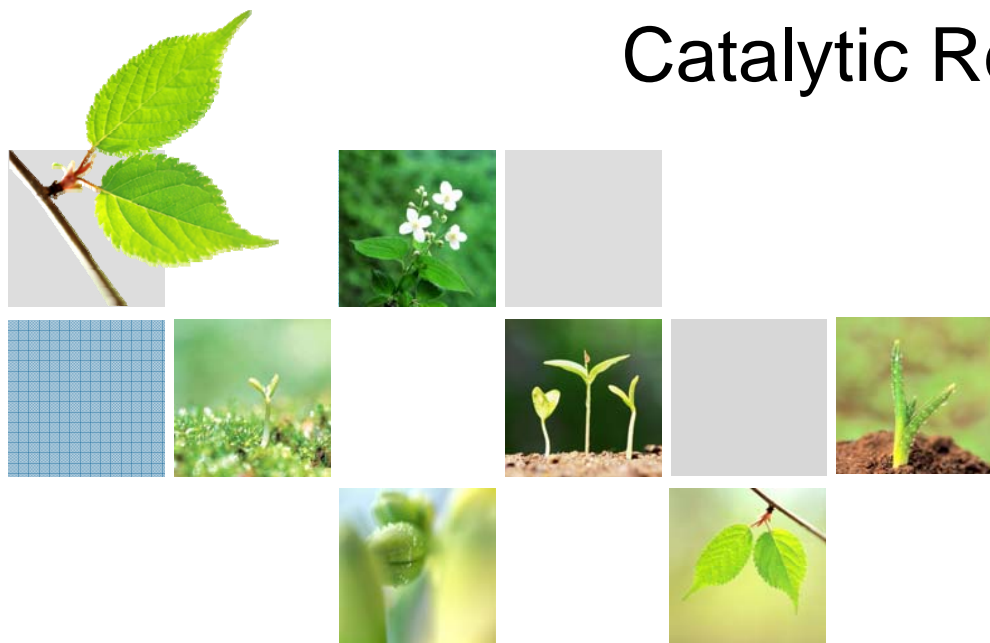
Literature Report 2009-12-08

Mesoporous Organosilicas with Acidic Frameworks and Basic Sites in the Pores: An Approach to Cooperative Catalytic Reactions

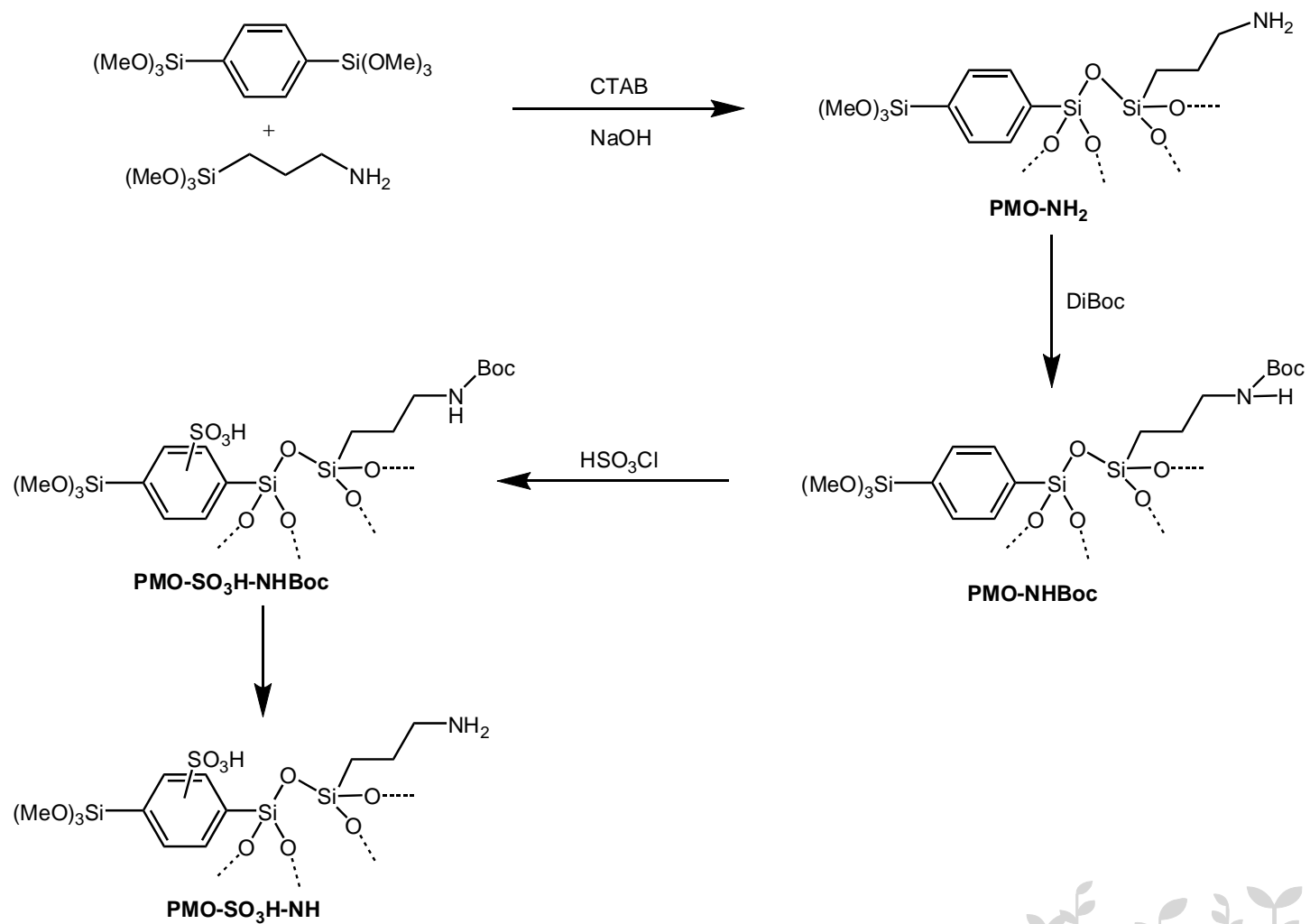
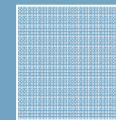
Yan Yang

Shylesh, S.;* Thiel, W. R.* *et al.*
Angew. Chem. Int. Ed.

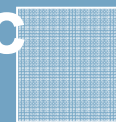
DOI: 10.1002/anie.200903985



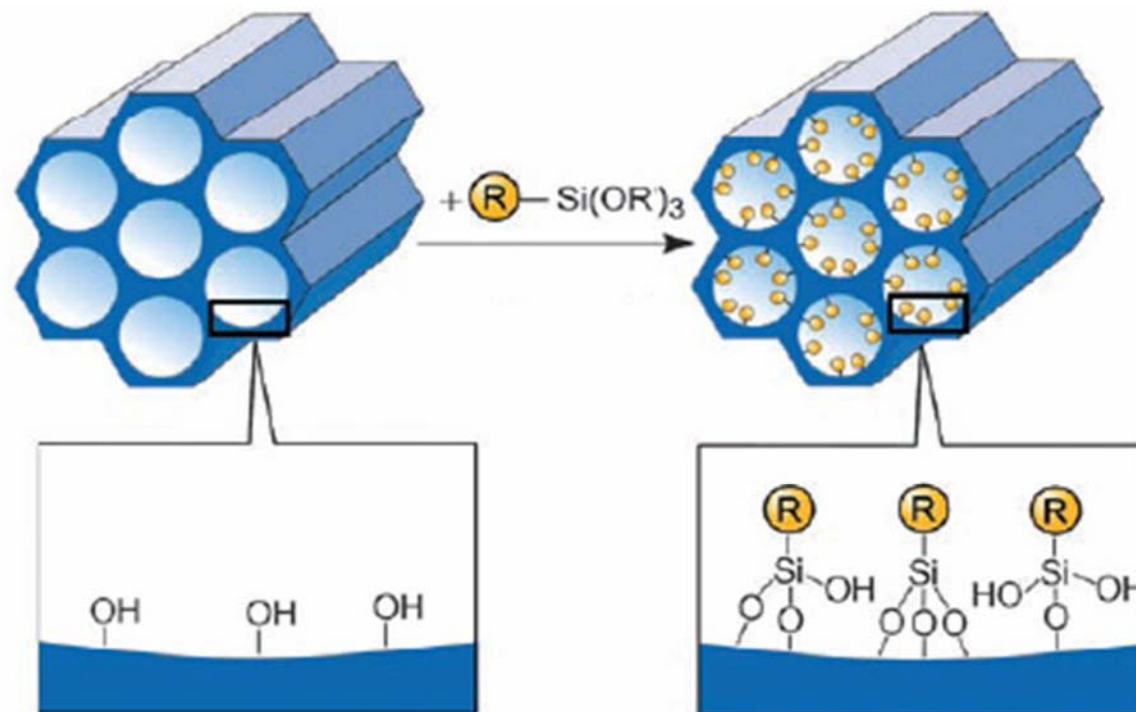
Synthetic Procedure



Modified Mesoporous Organic–Inorganic Hybrid Materials



---post-modification

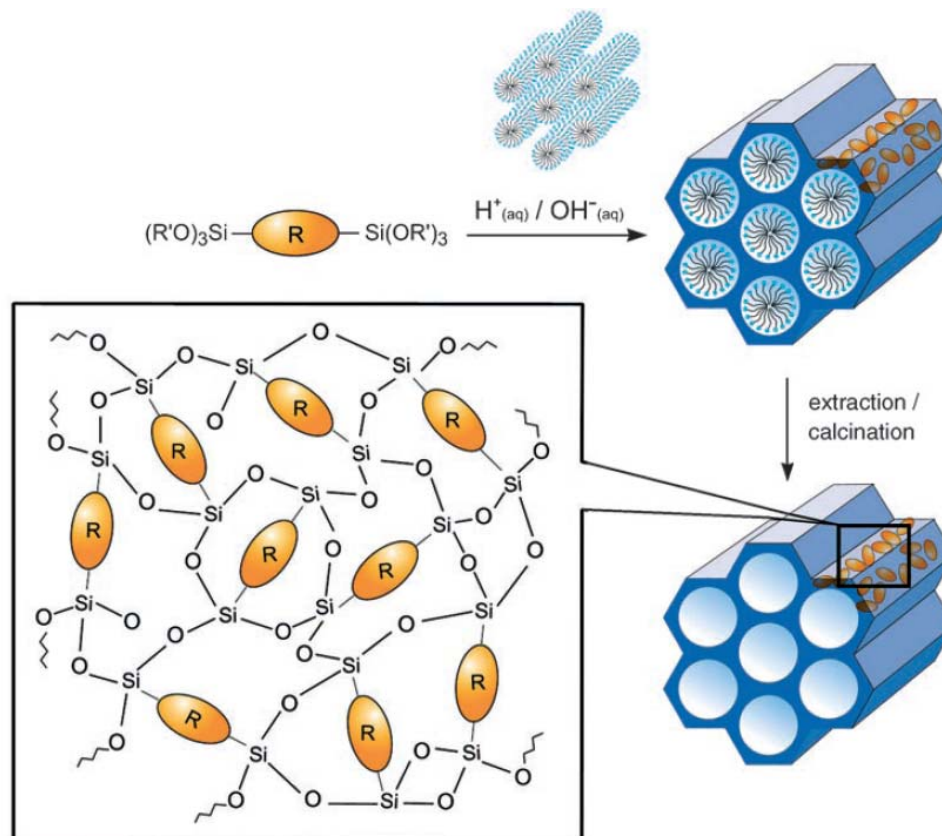


1) Post-Modification of mesoporous silica by grafting

Kemner, K. M. et al. *Science* **1997**, 276, 923.
Mou, C. Y. et al. *Langmuir* **2004**, 20, 3231.



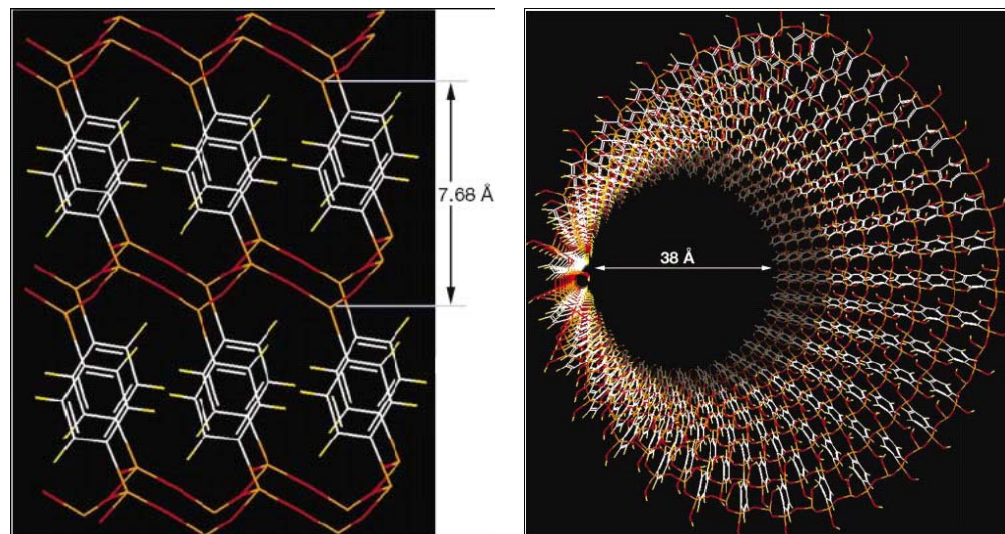
Periodic Mesoporous Organosilicas (PMOs)



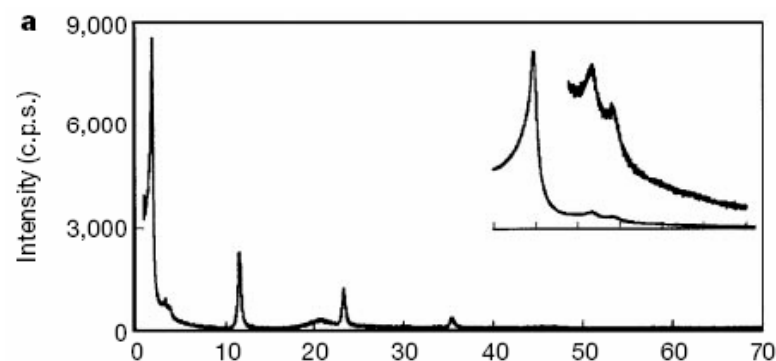
Schematic synthesis procedure of PMOs.



Periodic Mesoporous Organosilicas (PMOs)



Modeling images of phenylene-bridged PMOs with a crystal-like pore wall structure



Ozin, G. A. et al. *Nature* **1999**, 402, 867.
Stein, A. et al. *Chem. Mater.* **1999**, 11, 3302.
Inagaki, S. et al. *J. Am. Chem. Soc.* **1999**, 121, 9611.
Inagaki, S. et al. *Nature* **2002**, 416, 304

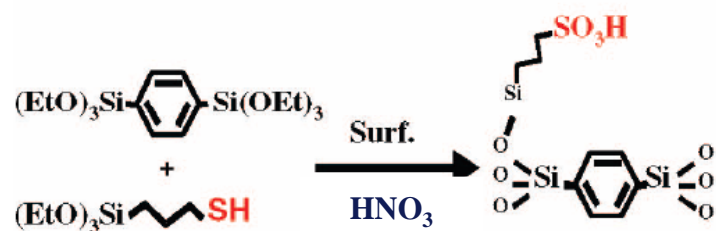


PMOs in Heterogeneous Catalysis

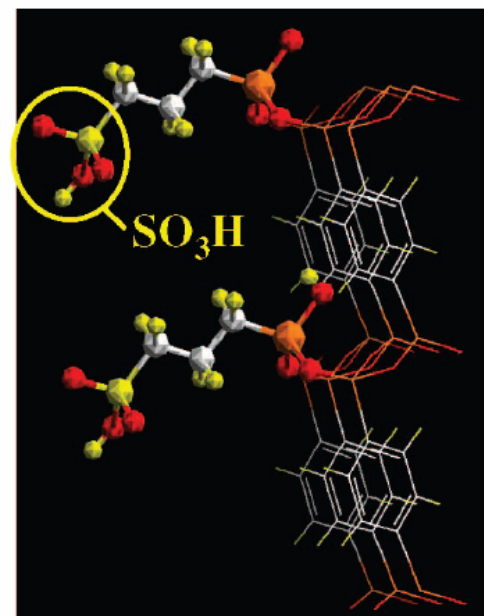


1. Graft or co-condensation

(a)



(b)



Yang, Q. H. et al. *J. Phys. Chem. B.* **2004**, 108, 7934.

Yang, Q. H.; Inagaki, S. et al. *J. Am. Chem. Soc.* **2002**, 124, 9694.

Yang, Q. H.; Inagaki, S. *J. Mol. Catal. A: Chem.* **2005**, 230, 85.

Characteration

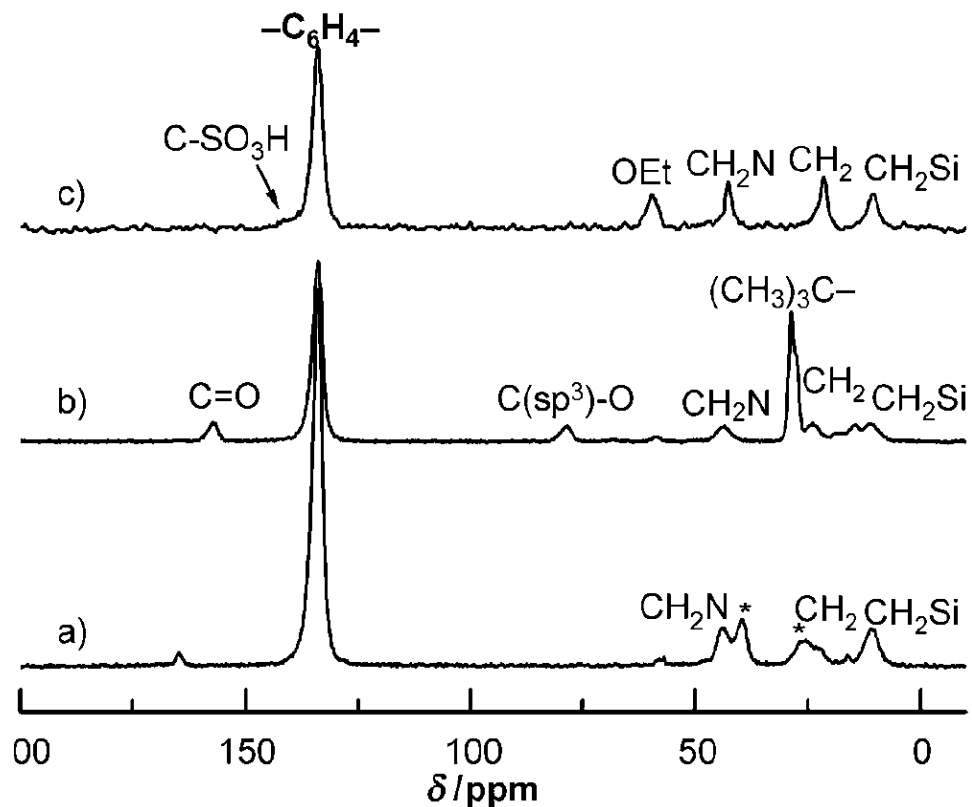


Figure 1. ^{13}C CP-MAS NMR spectra of a) PMO-NH₂, b) PMO-NHBoc, and c) PMO-SO₃H-NH₂. * in (a) denotes residual peaks of CTAB, which disappear after the sulfonation reaction (c).



Characteration

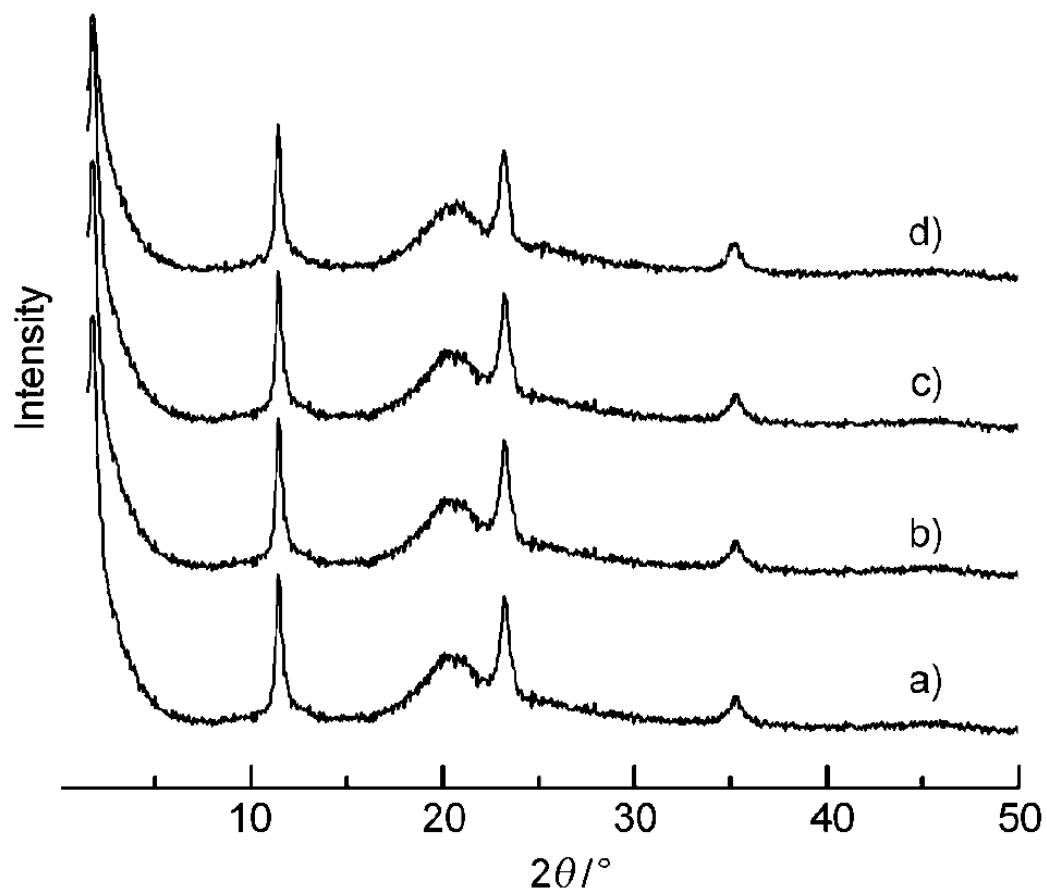
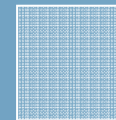


Figure 2. Powder X-ray diffraction patterns of a) PMO, b) PMO-NH₂, c) PMO-NHBoc, and d) PMO-SO₃H-NH₂.



Characteration

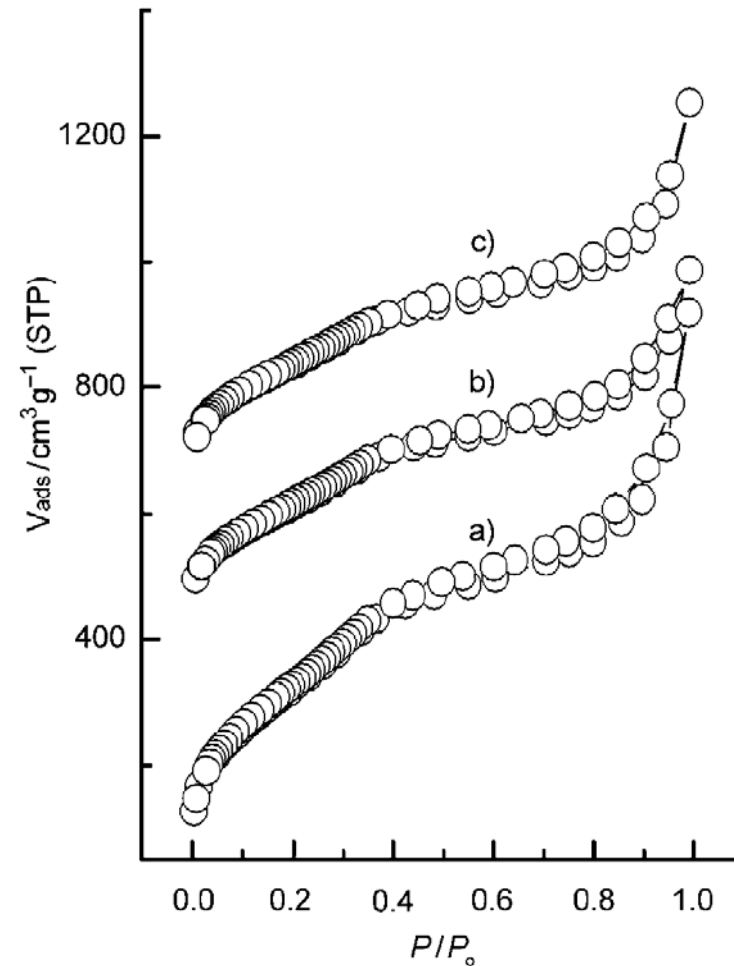
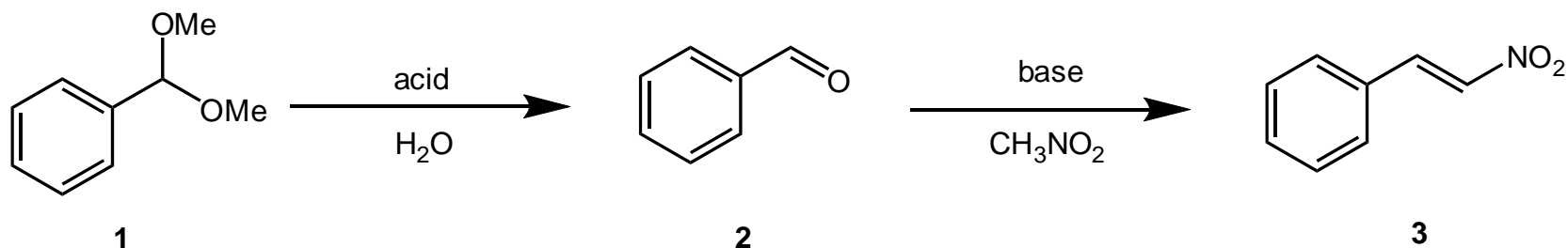


Figure 3. Nitrogen adsorption–desorption isotherms of a) PMO-NH₂, b) PMO-NHBoc, and c) PMO-SO₃H-NH₂



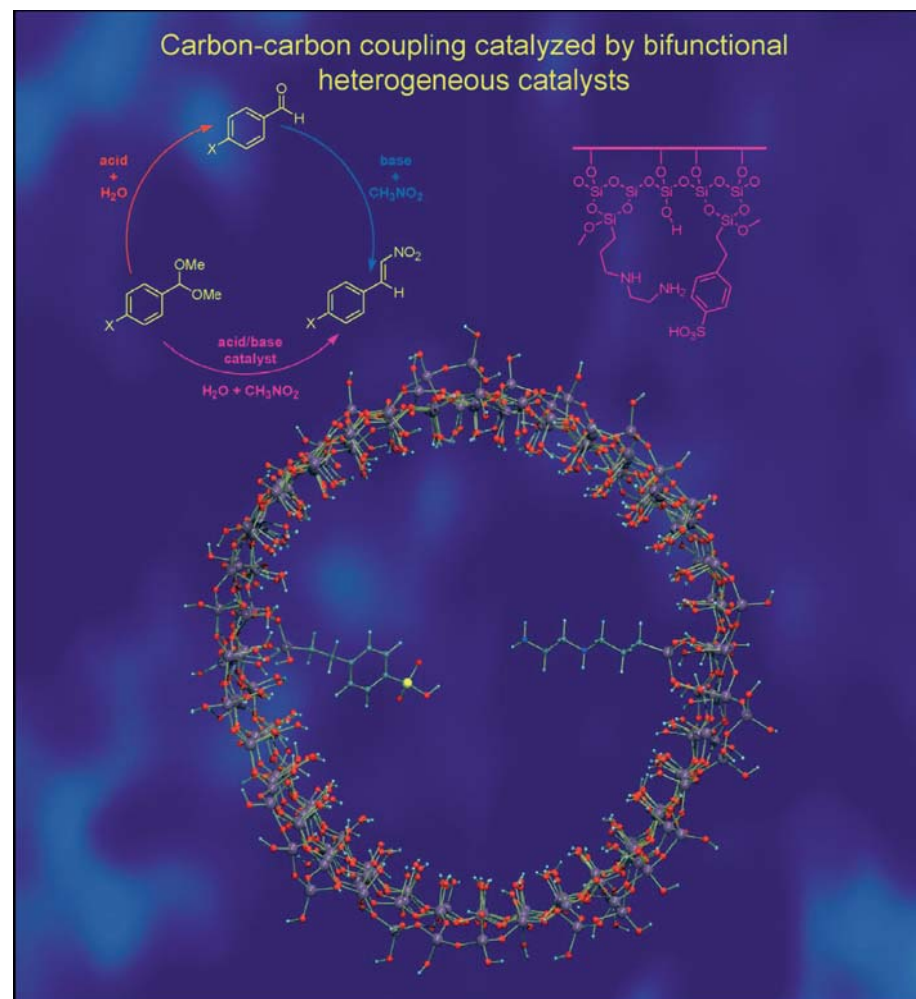
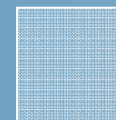
One pot reaction



Entry	Catalyst	Conv. of 1 [%]	Yield of 2 [%]	Yield of 3 [%]
1	PMO-SO ₃ H-NH ₂	100	2.5	97.5
2	PMO-SO ₃ H-NHBoc	100	100	0
3	PMO-NH ₂	trace	trace	trace
4	PMO-SO ₃ H-NH ₂ + <i>tert</i> -butyl amine	trace	trace	trace
5	PMO-SO ₃ H-NH ₂ + <i>p</i> -toluenesulfonic acid	100	100	trace

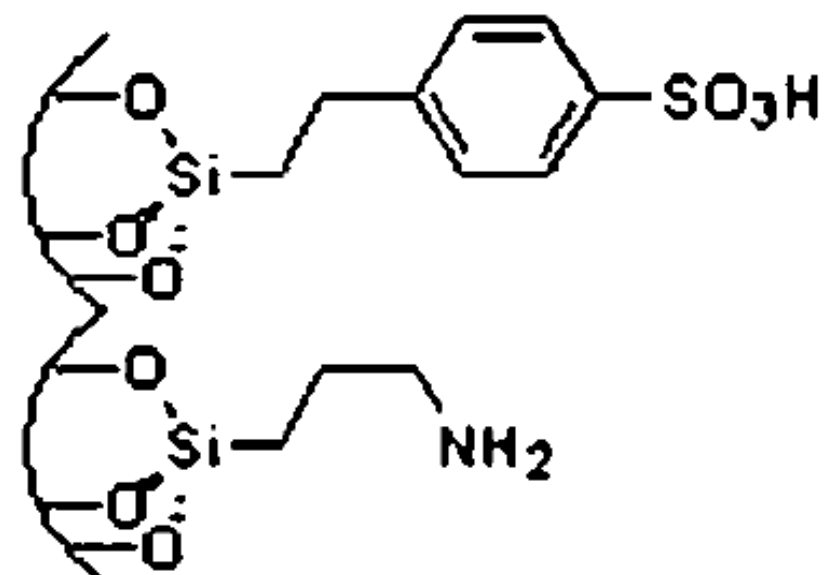
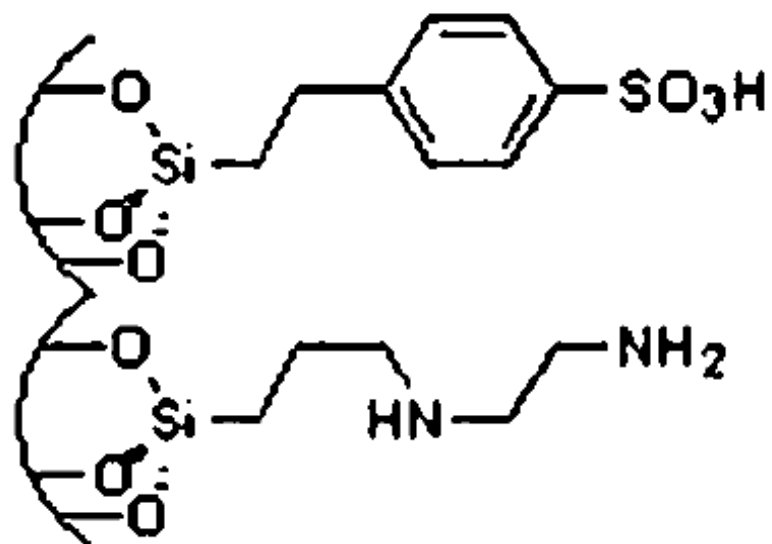
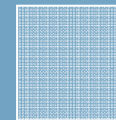


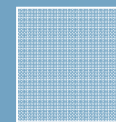
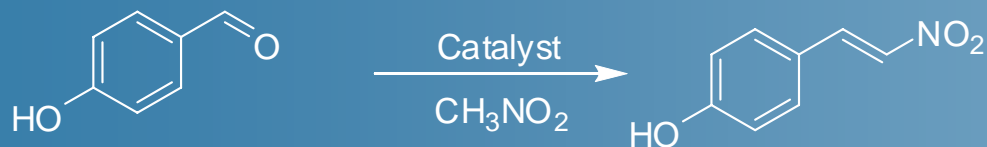
Previous Work



Chem. Eur. J. **2009**, 15, 7052.

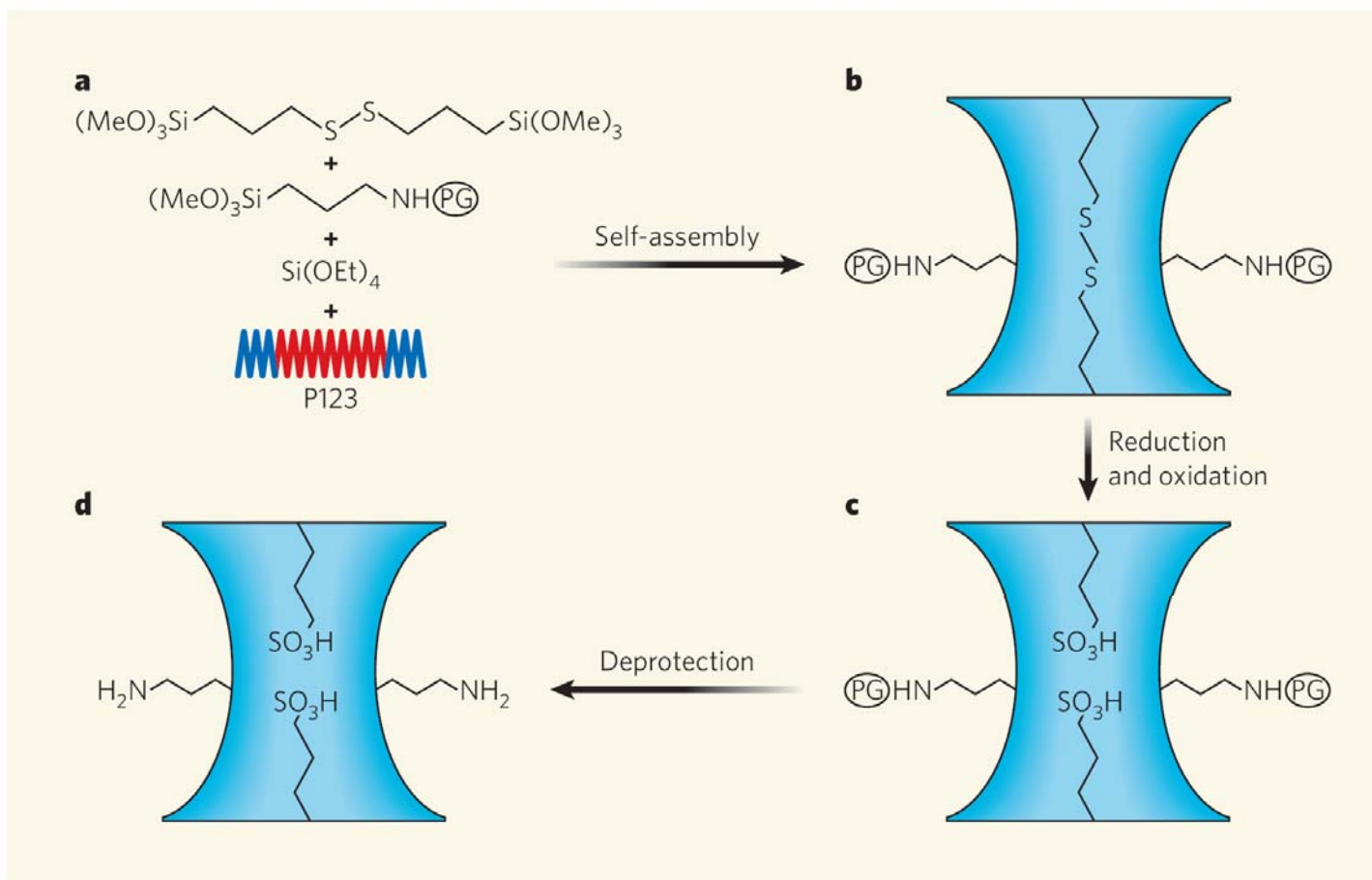






Entry	Catalyst	Time [h]	Yield [%]
1	MSN-NH ₂	6	33
2	MSN-NNH ₂	6	44
3	MSN-NEt ₂	12	trace
4	MSN-SO ₃ H	12	0
5	MSN-NH ₂ -SO ₃ H	6	60
6	MSN-NNH ₂ -SO ₃ H	6	96
7	MSN-NNH ₂ + MSN-SO ₃ H	6	54
8	MSN-NNH ₂ -SO ₃ H	4	100
9	Sil-MSN-NNH ₂ -SO ₃ H	6	0
10	MSN-NNH ₂ -Cl	6	71
11	MSN	12	0
12	MSN-NNH ₂ -SO ₃ H + <i>p</i> -toluene sulfonic acid	6	trace
13	MSN-NNH ₂ -SO ₃ H + <i>n</i> -hexylamine	6	55
14	<i>p</i> -toluene sulfonic acid + <i>n</i> -hexylamine	6	0

Bifunctionalized PMOs

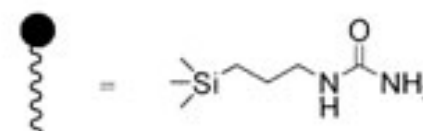
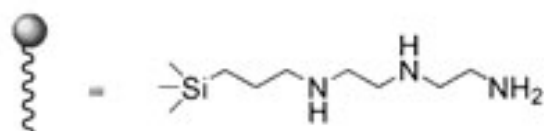
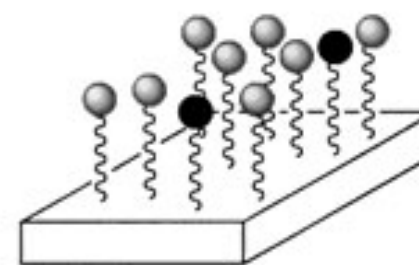
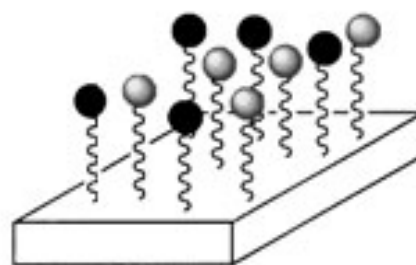
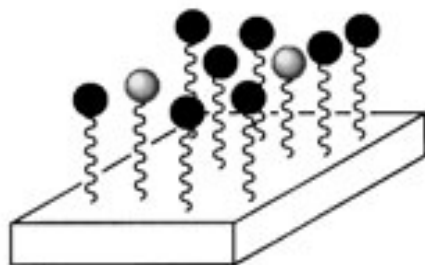
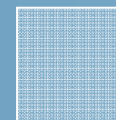


Alauzun, J.; Corriu, R. J. P. et al. *J. Am. Chem. Soc.* **2006**, *128*, 8718.

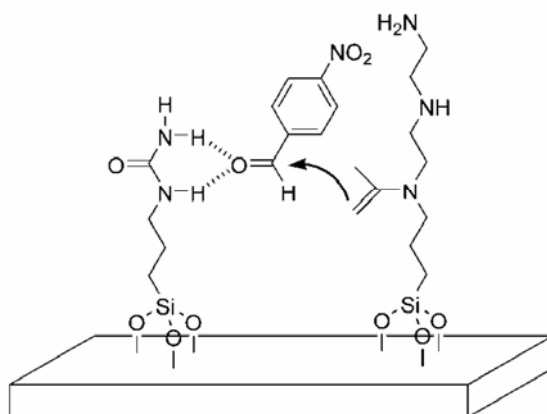
Jaroniec, M. et al. *Nature* **2006**, *442*, 638.



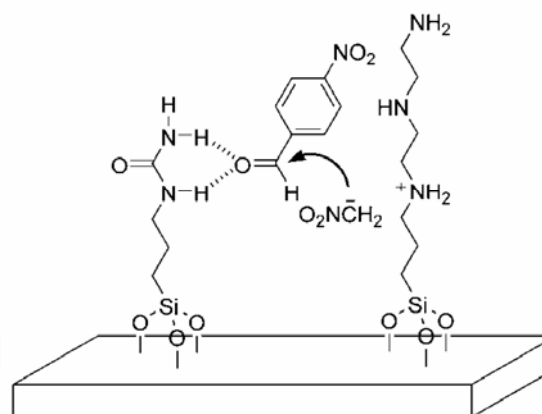
Functional Groups and Reactions Used



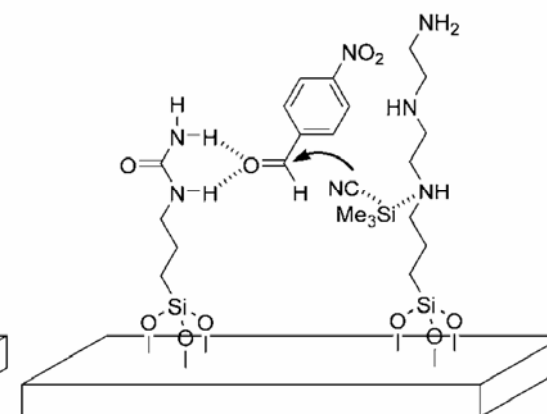
aldol reaction



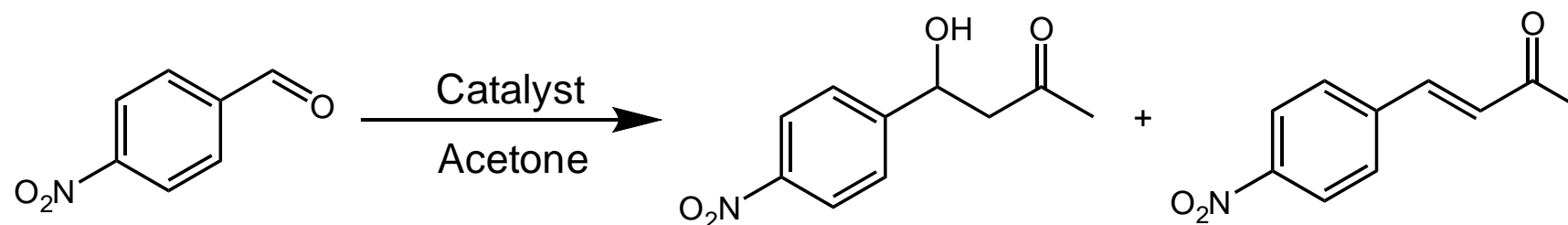
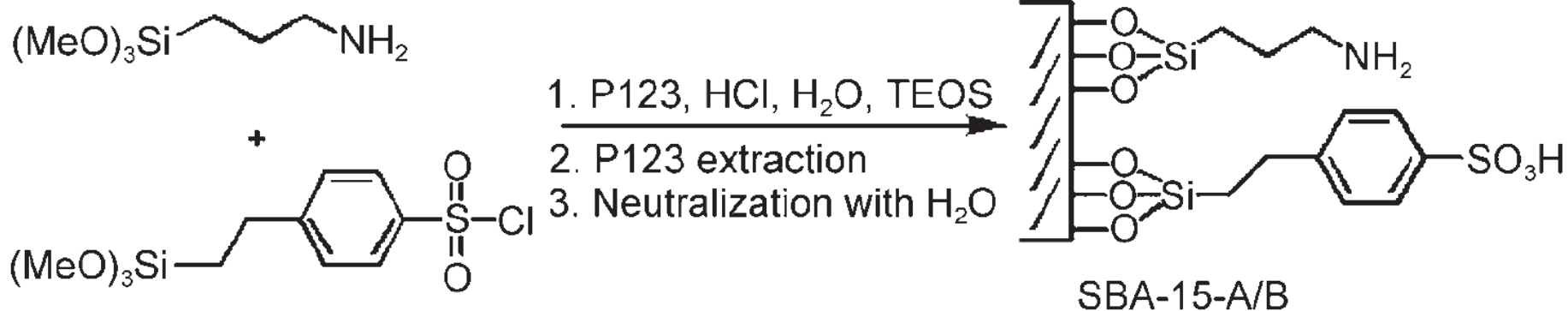
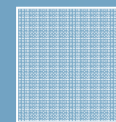
Henry reaction



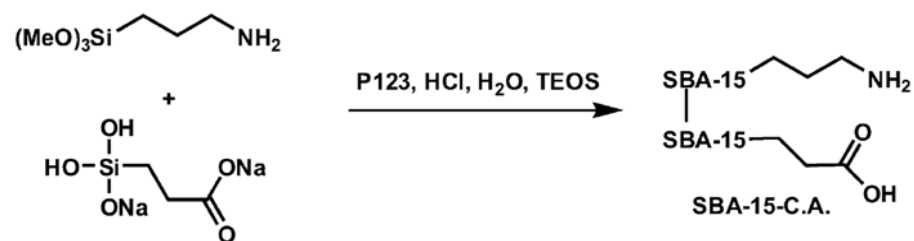
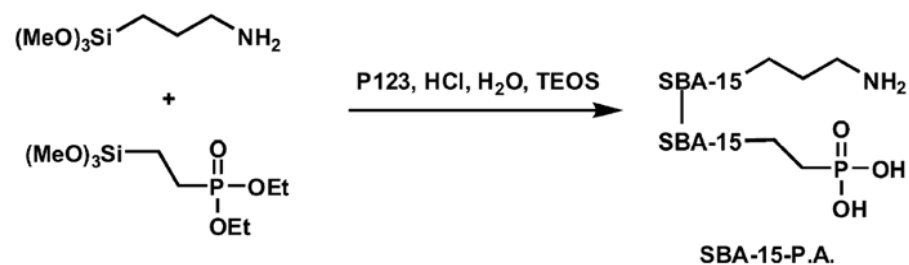
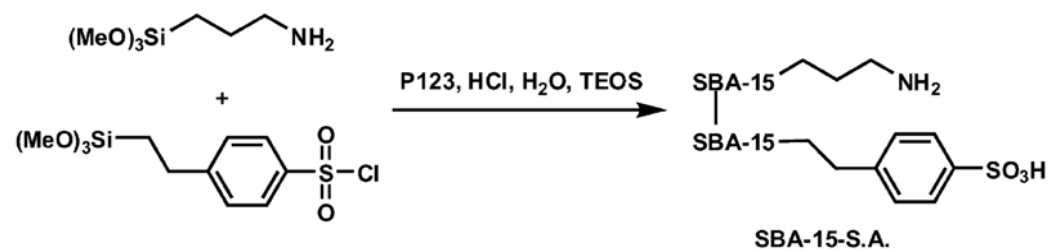
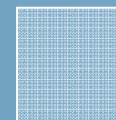
cyanosilylation



Functional Groups and Reactions Used



Functional Groups and Reactions Used



Functional Groups and Reactions Used

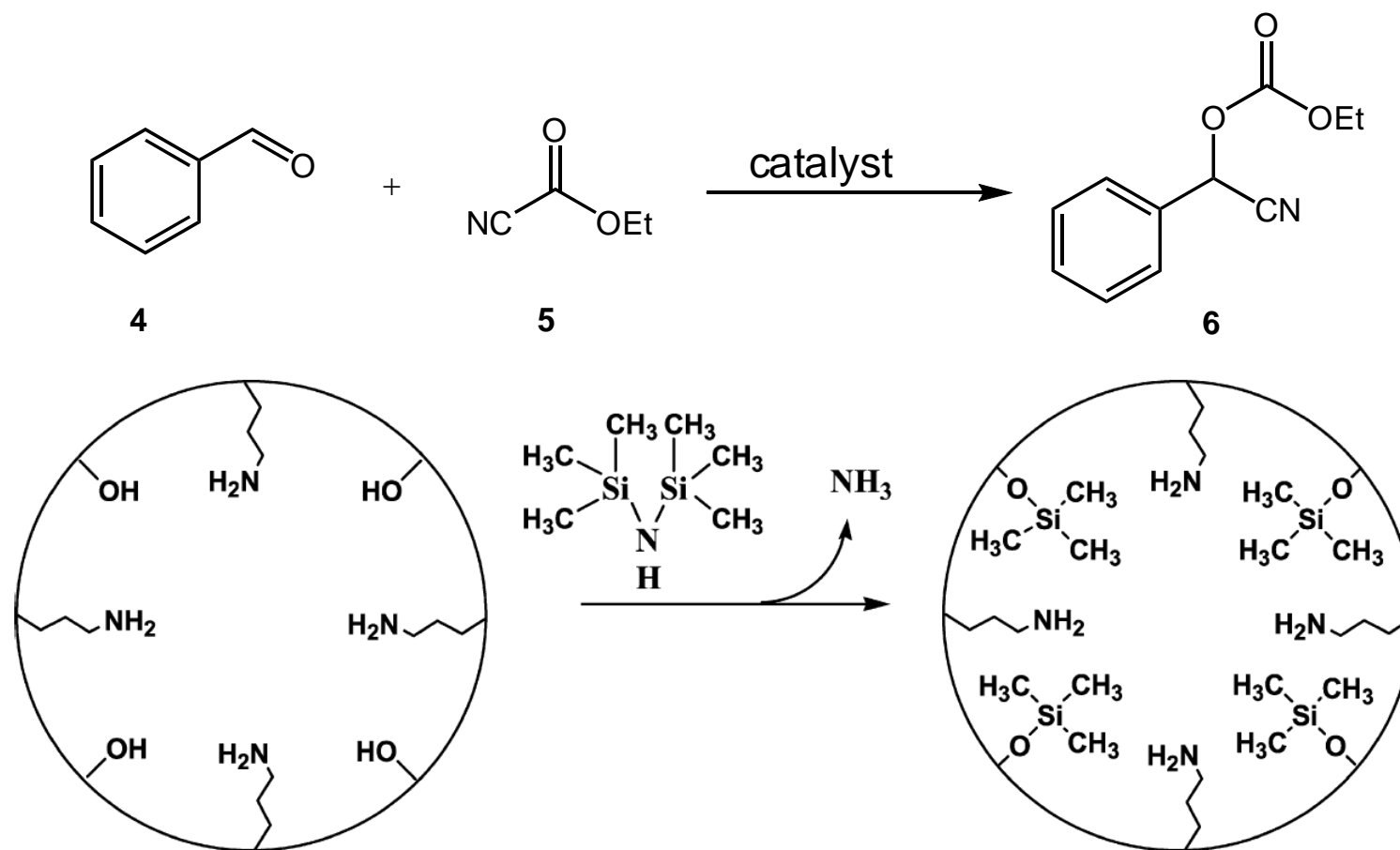
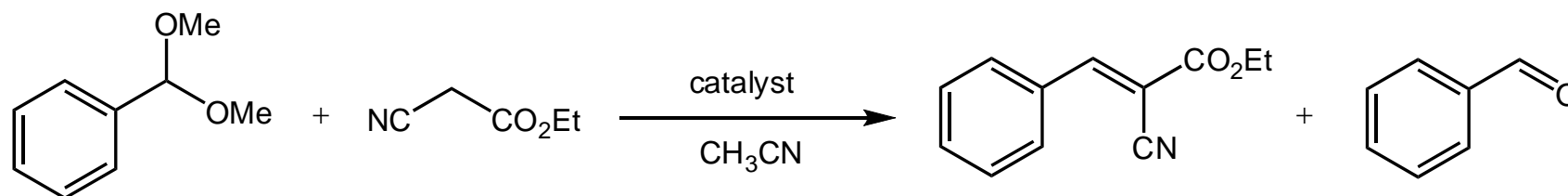


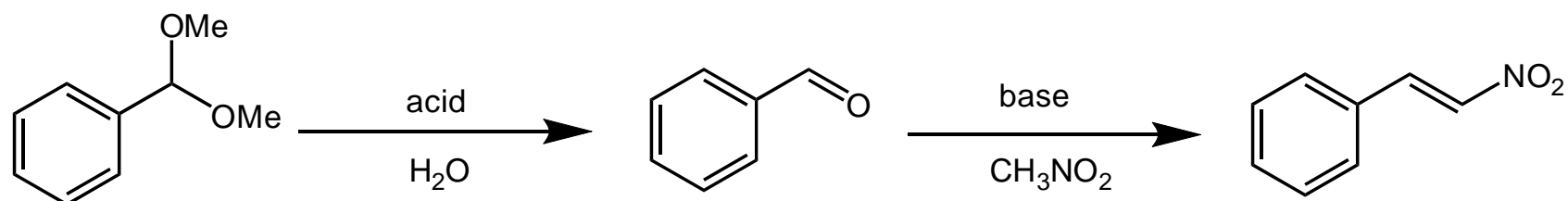
Fig. 1. Silylation reaction of aminopropyl-functionalized SBA-15 by HMDS.



One-pot Reaction



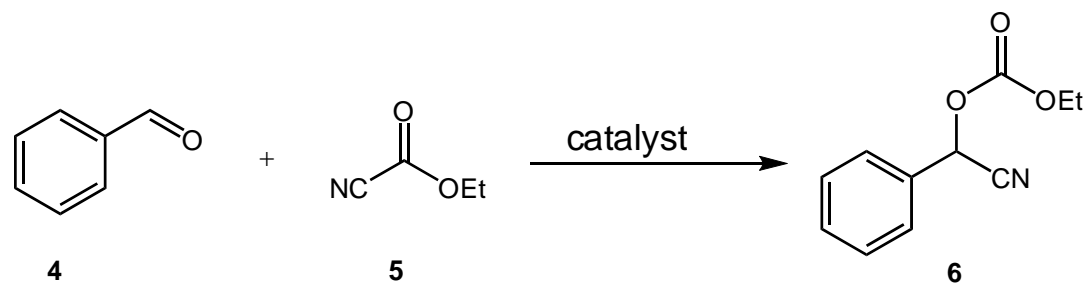
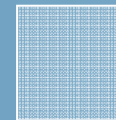
J. Am. Chem. Soc. **2009**, 131, 7944.



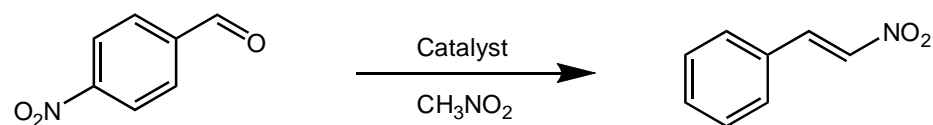
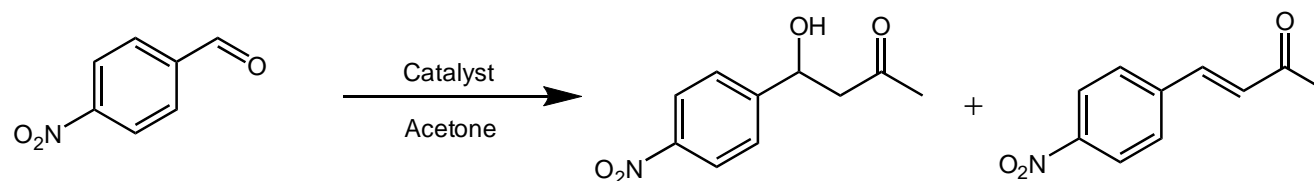
Angew. Chem. Int. Ed. DOI: 10.1002/anie.200903985



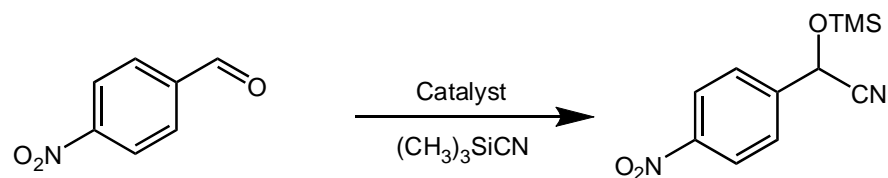
Other Reactions



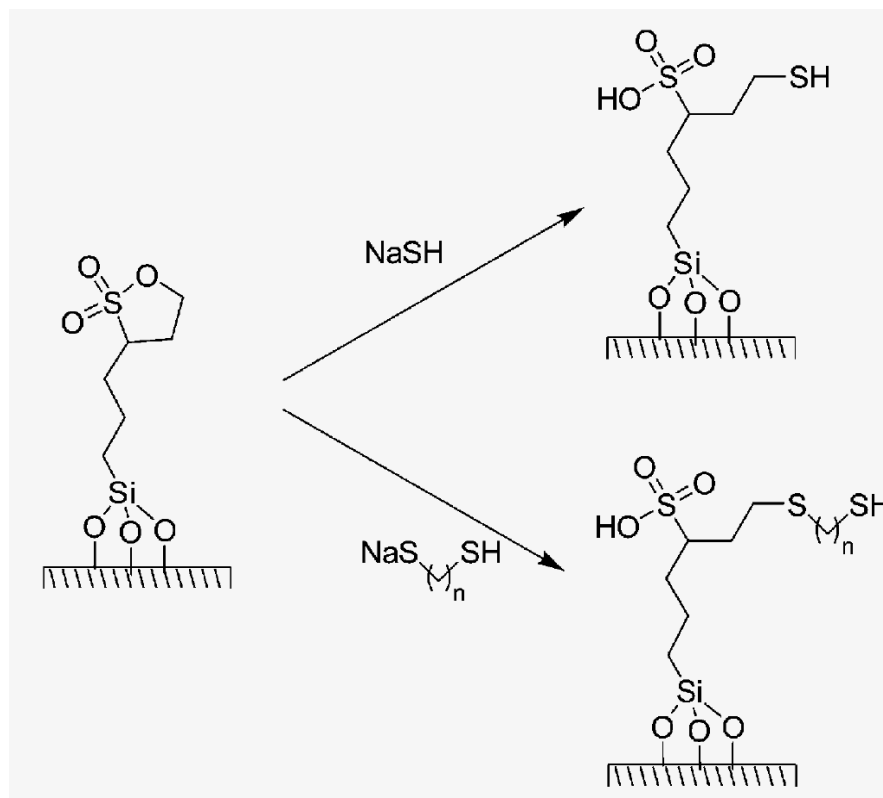
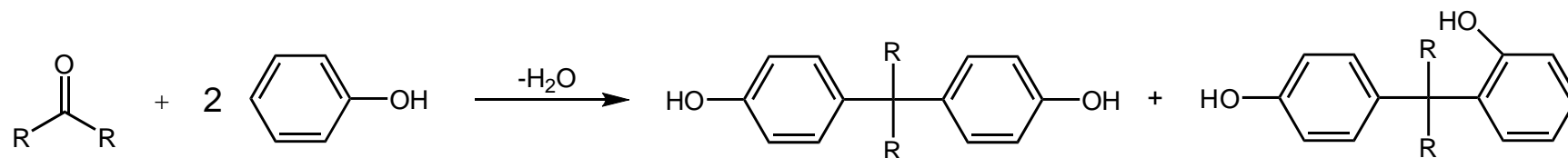
J. Am. Chem. Soc. **2007**, 129, 9540.
J. Catal. **2009**, 263, 181.



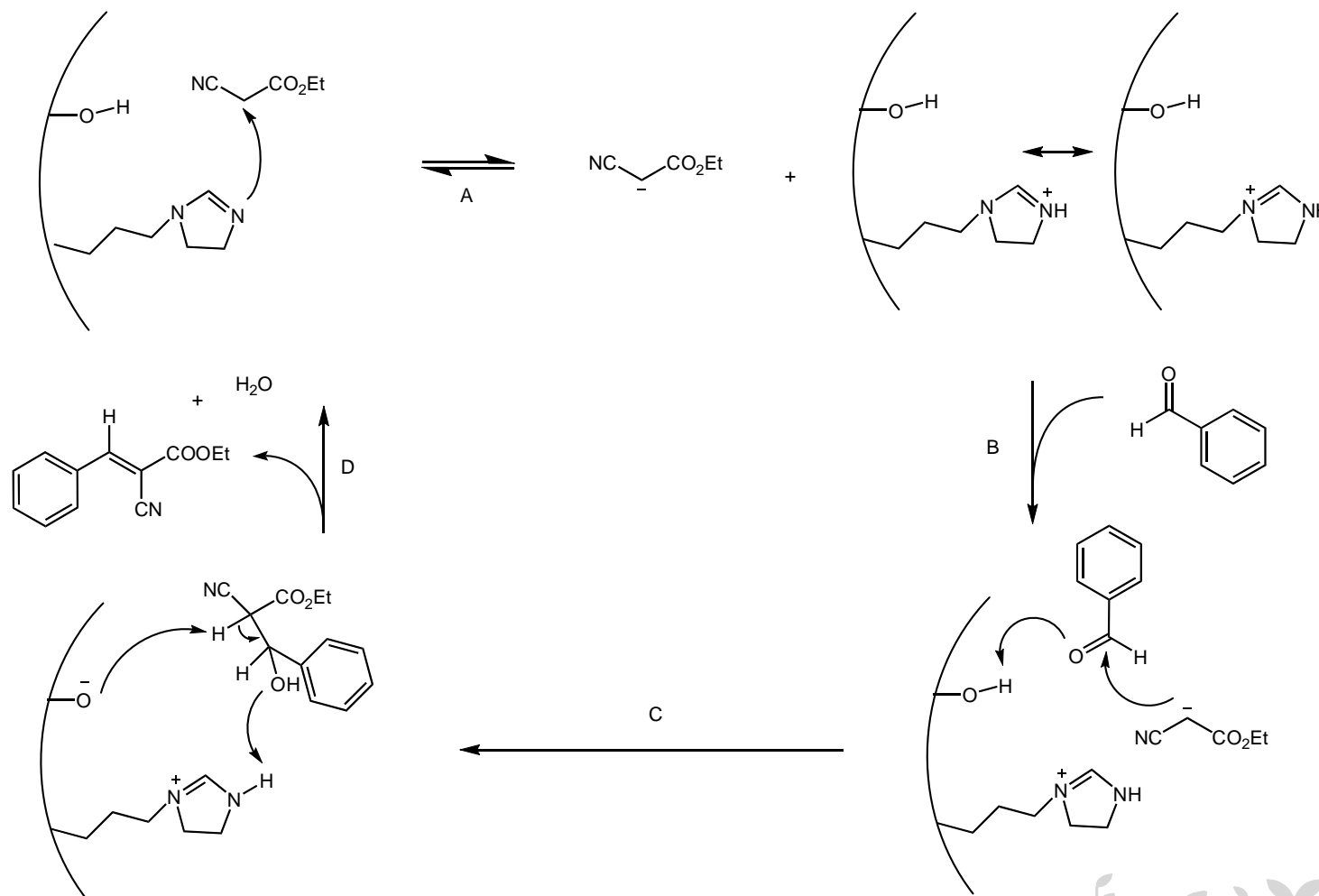
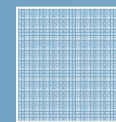
Angew. Chem. Int. Ed. **2005**, 44, 1826.



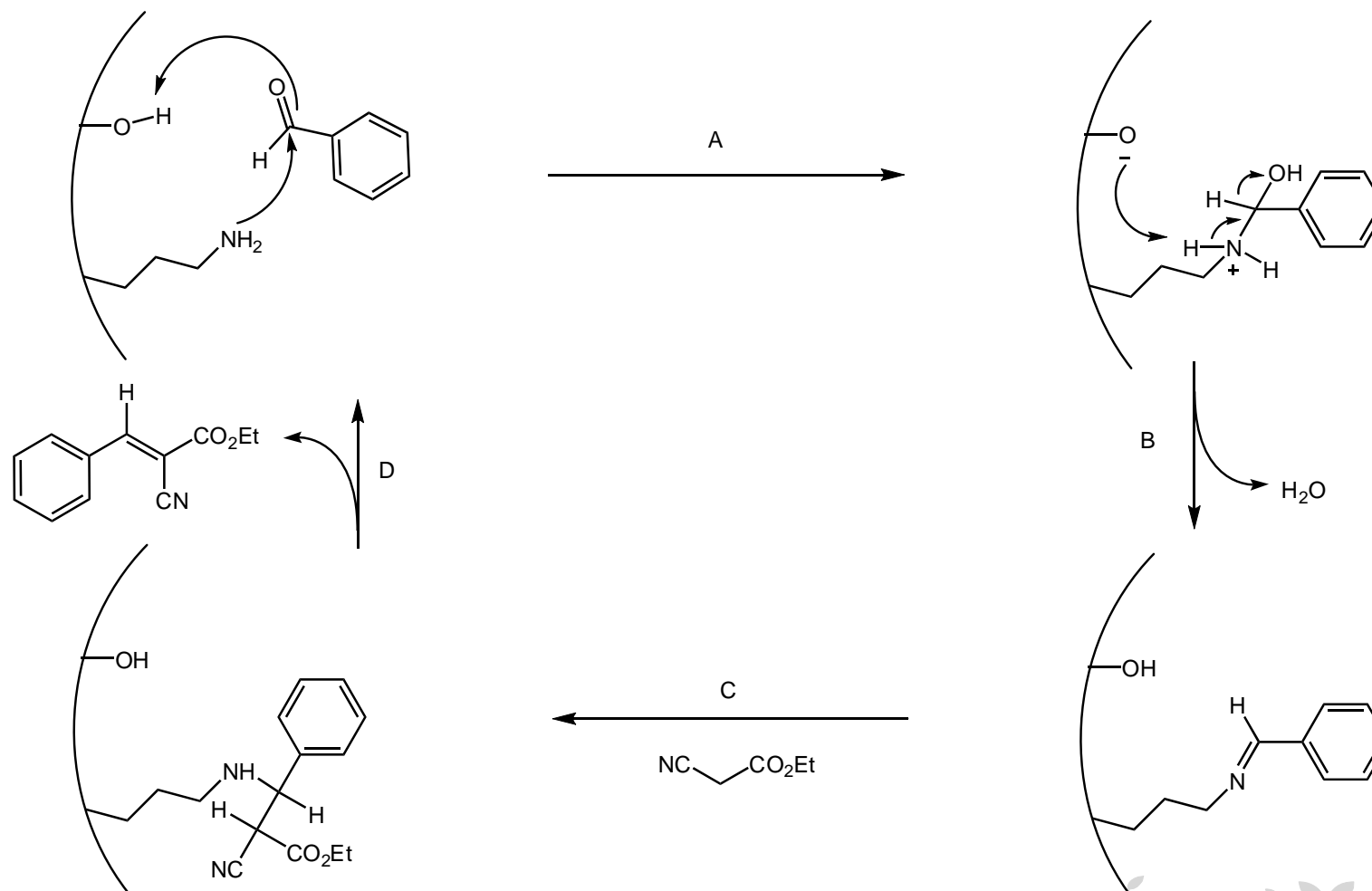
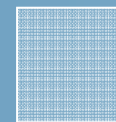
Locations of the Functional Groups



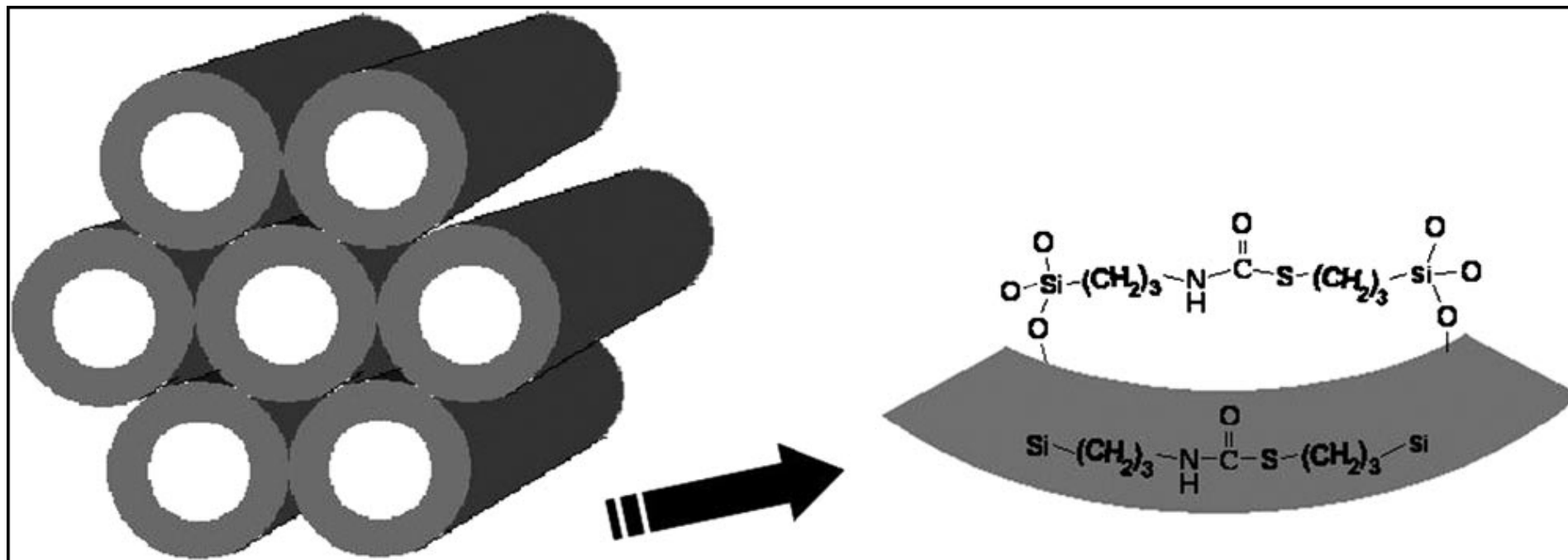
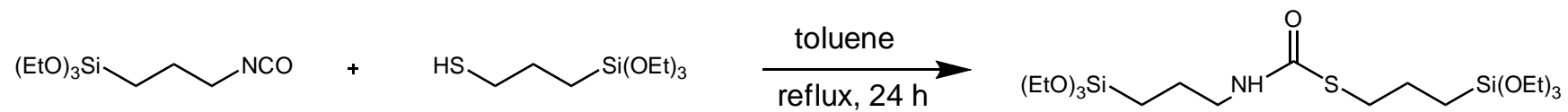
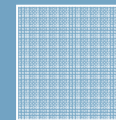
The Cooperative Ion-pair Mechanism

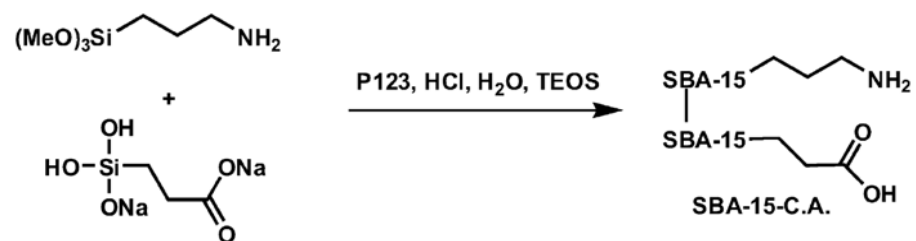
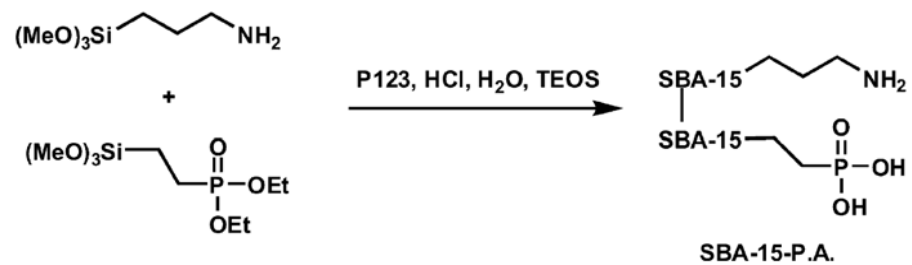
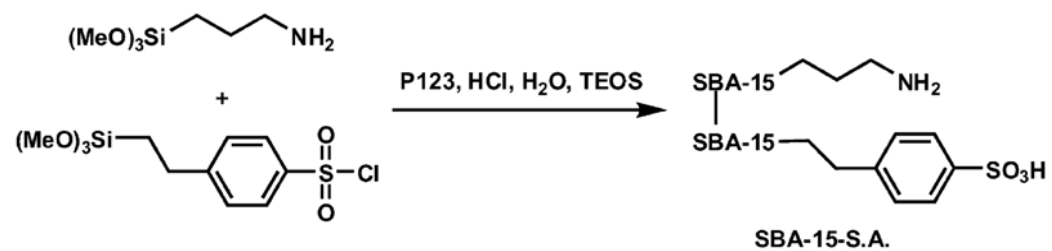
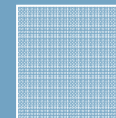


Cooperative Primary Amine Mechanism



New Silica Precursor







Recently there has been significant progress in mimicking nature's multistep reaction cascades for the synthesis of structurally complex organic molecules. Well-controlled multifunctionalization of solid supports can be an efficient strategy for the design of cooperative catalytic systems. This approach requires that the relative concentrations and the proper spatial arrangement of all functional groups are controlled. Biocatalysts such as enzymes immobilize mutually incompatible functional groups without destruction and allow these functional groups to act independently or in a cooperative manner. To mimic such multistep reaction sequences in one-pot reactions will be effective in terms of waste and cost reduction.





In summary, bifunctional mesoporous organosilicas possessing organic amines and sulfonic acid groups were successfully generated and used in a cooperative catalytic transformation. Compared to earlier reports, the current methodology benefits from a precise location and concentration of the active functional groups in a mesoporous phenylene silica with crystalline pore walls, in which the acidic groups reside mainly on hydrophobic benzene layers and the basic amino groups on hydrophilic silica layers for cooperative effects. Further investigation is currently underway regarding enhancement of the acid–base properties of the materials, additional catalytic enhancements, and advanced applications.





Thank You!

