Cooperative Catalysis by General Acid and Base Bifunctionalized Mesoporous Silica Nanospheres

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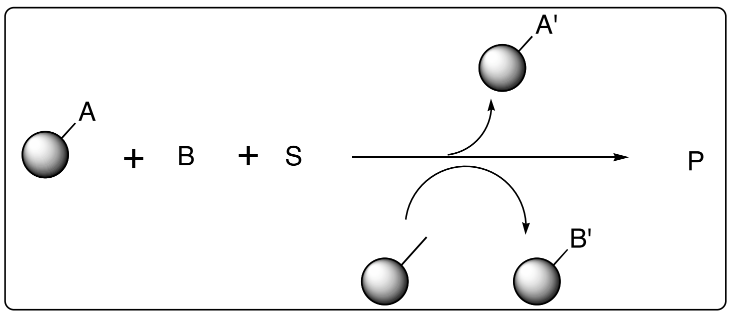
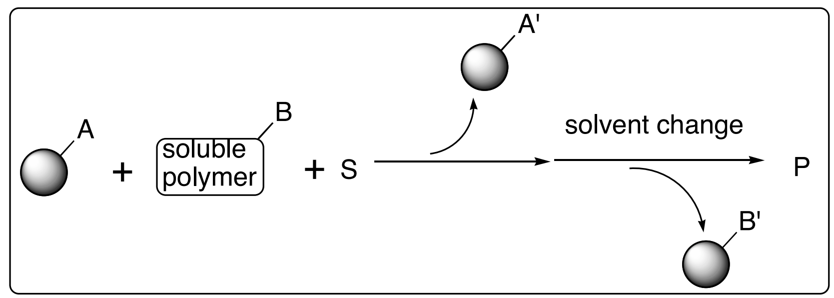
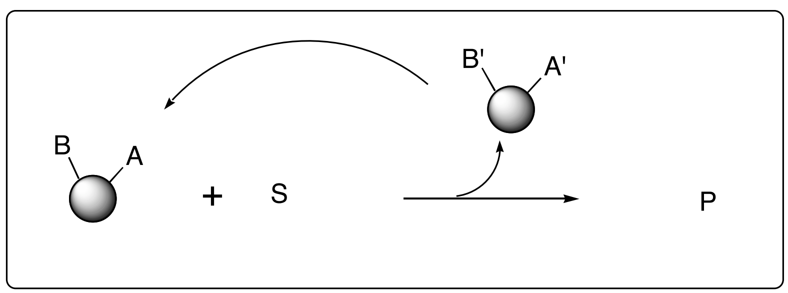
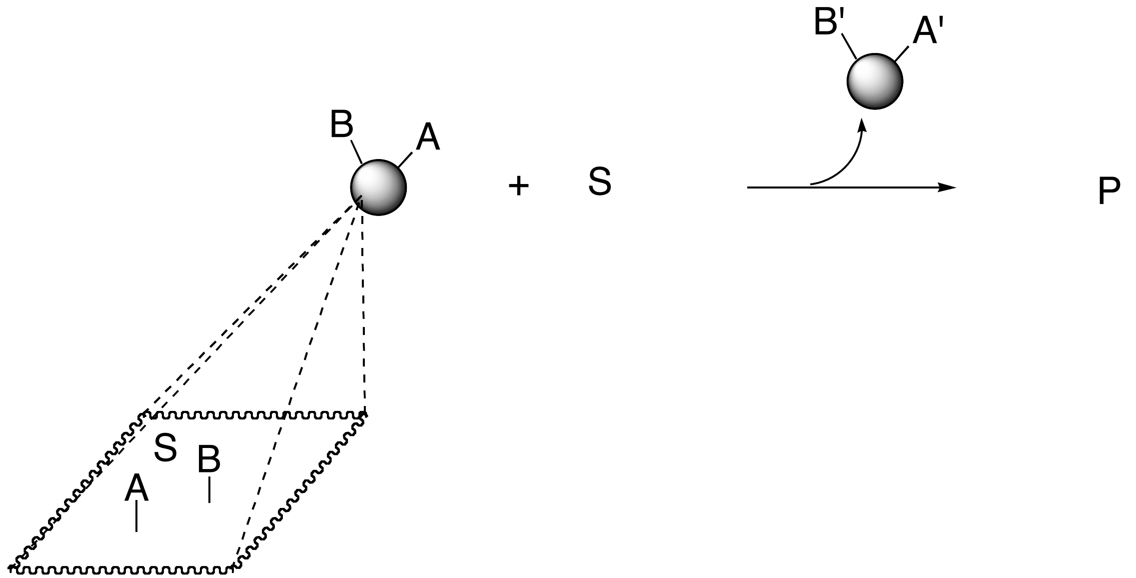


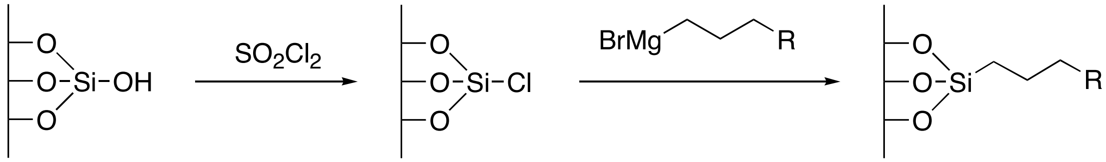


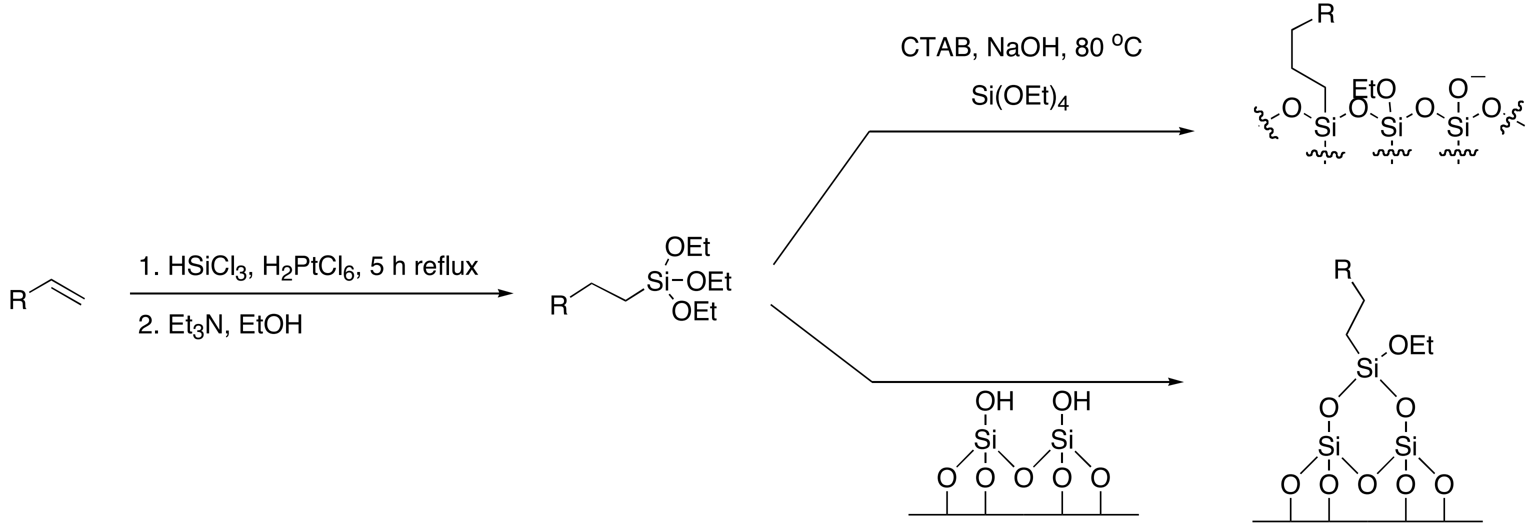




- with control of the relative concentration and proper spatial arrangements between these functional groups.
- Mesoporous material are porous materials with regularly arranged, uniform mesophores (2 nm to 50 nm in diameter).
- Large specific surface areas because of their numerous pores.
- Mesoporous silica nanosphere materials.

Grafting organosilanes onto a silanol-containing surface





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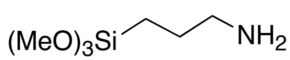
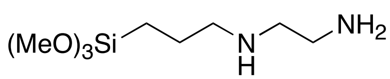


AAPTMS



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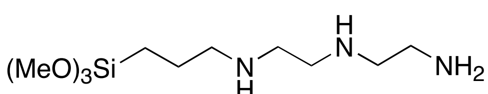
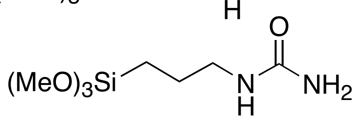


UDPTMS



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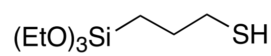

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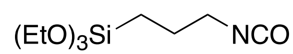
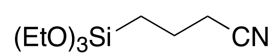
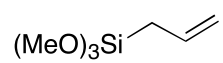


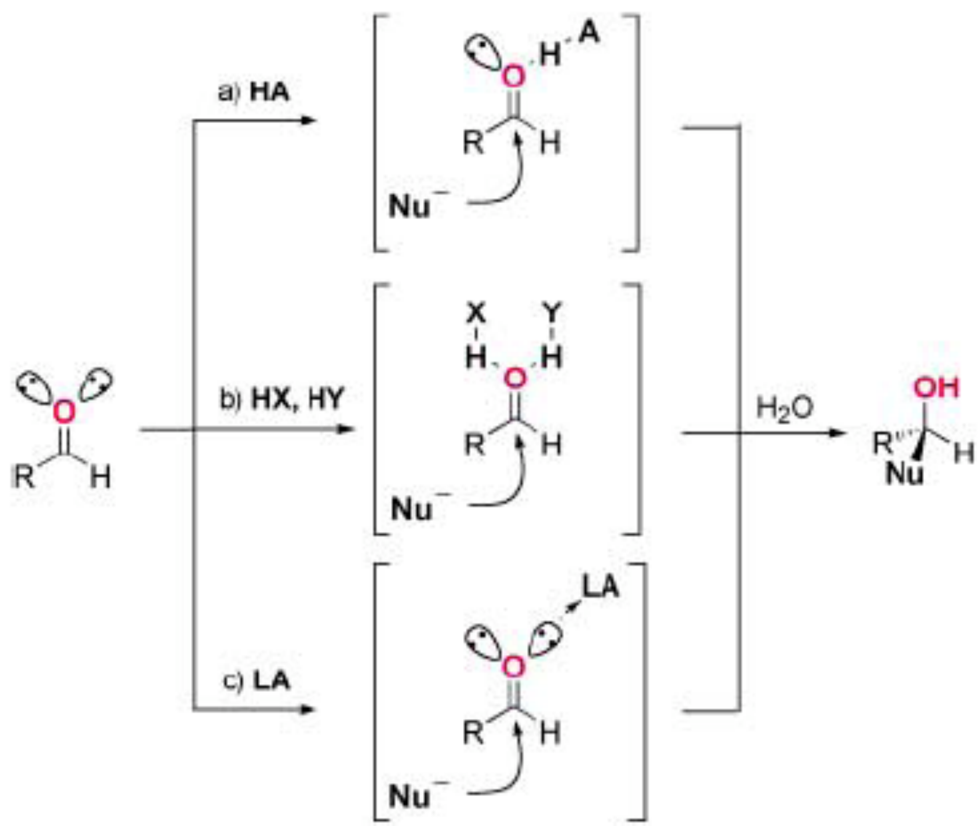
CPTES



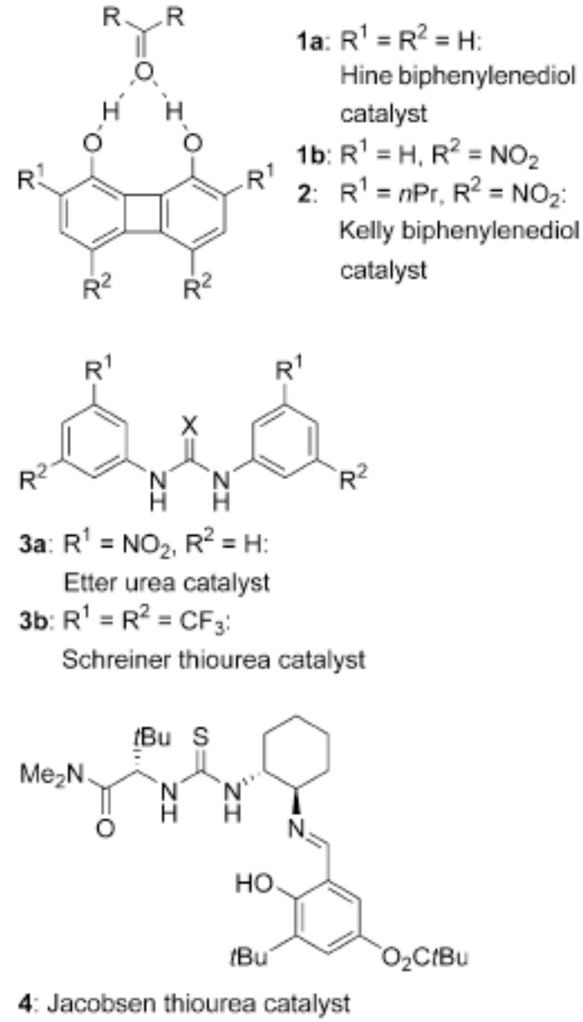
ALTMS



Chem. Rev. **2002**, *102*, 3589.
Chem. Mater. **2003**, *15*, 4247



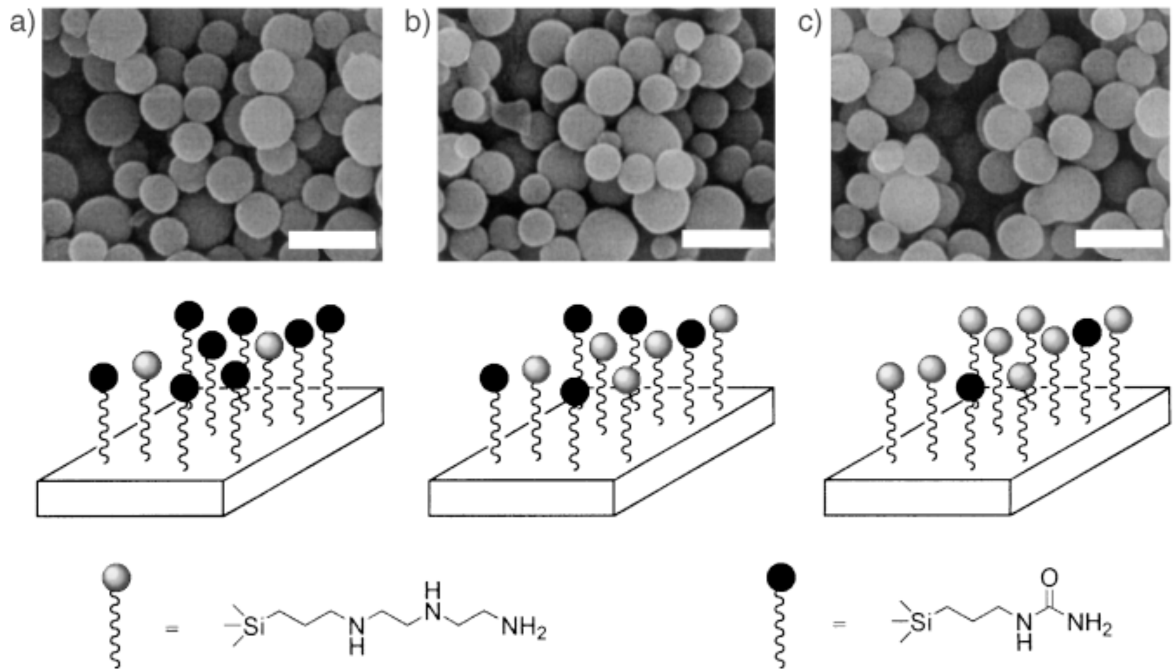
Scheme 2. Three modes of carbonyl activation by coordination: a) single hydrogen bond (e.g. preassociation or hydrogen bonding by a general acid HA), b) double hydrogen bonding, c) Lewis acid (LA) activation.



Scheme 1. Carbonyl activation by organic catalysts capable of double-hydrogen-bonding activation.

ACIEE, **2004**, *43*, 2062.

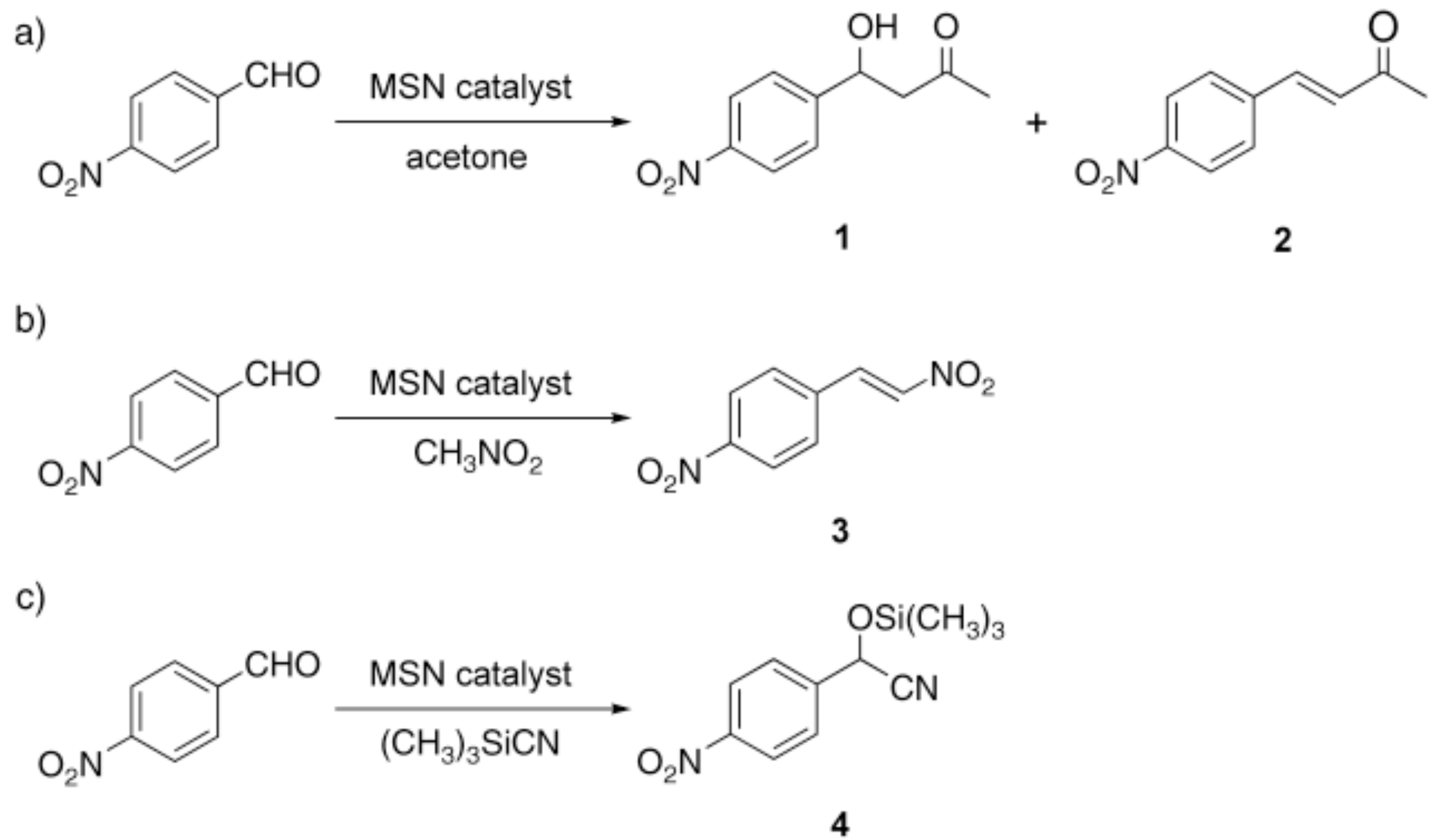
Schematic drawings of bifunctional MSNs



a) 2/8 AEP/UDP–MSN, b) 5/5 AEP/UDP– MSN, and c) 8/2 AEP/UDP–MSN.
Scale bar: 2.0 mm.

Solid state 13C CP MAS and 29Si MAS NMR.
By field-emission scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, and nitrogen adsorption and adsorption studies.
Total surface concentration of organic groups: a) 1.3, b) 1.0, c) 1.5 mmołg.
Concentration ratio of AEP/UDP: a) 2.5/7.5, b) 5.4/4.6, c) 6.7/3.3.

Model reactions: a) aldol, b) Henry, c) cyanosilylation



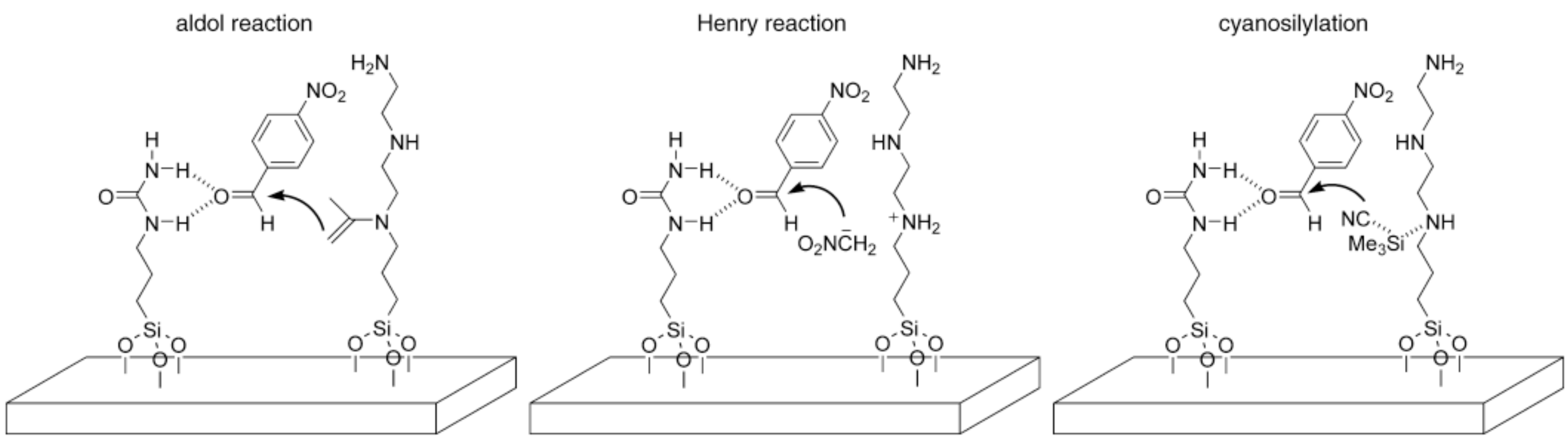
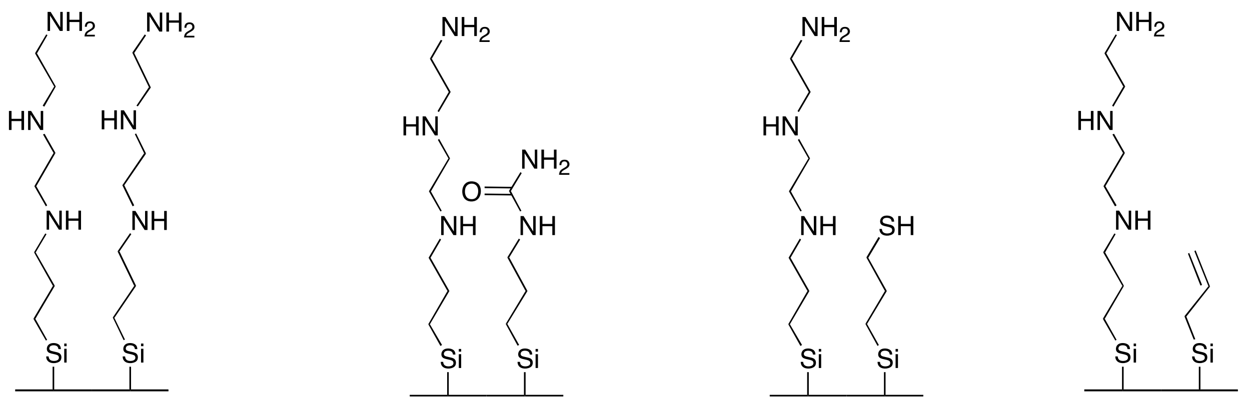
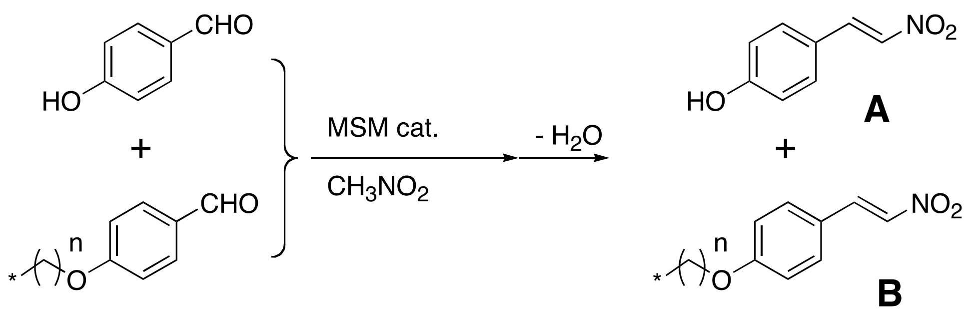

aldol reaction
Henry reaction
cyanosilylation

Table 1: TONs for the MSN-catalyzed reactions.[a]

Reaction	MSN catalyst	*T* [°C]	Product	TON
aldol	2/8 AEP/UDP	50	**1**, **2**	22.6
	5/5 AEP/UDP	50	**1**, **2**	11.9
	8/2 AEP/UDP	50	**1**, **2**	8.6
	AEP	50	**1**, **2**	5.4
	physical mixture[b]	50	**1**, **2**	6.4
	UDP	50	**1**, **2**	0.0[d]
	pure MSN[c]	50	**1**, **2**	0.0[d]
	2/8 AEP/CP	50	**1**, **2**	12.4
	5/5 AEP/CP	50	**1**, **2**	9.3
Henry	2/8 AEP/UDP	90	**3**	125.0
	5/5 AEP/UDP	90	**3**	91.1
	8/2 AEP/UDP	90	**3**	65.8
	AEP	90	**3**	55.9
	physical mixture[b]	90	**3**	79.2
	UDP	90	**3**	5.8
	pure MSN[c]	90	**3**	0.0[d]
	2/8 AEP/CP	90	**3**	78.0
	5/5 AEP/CP	90	**3**	71.0
cyanosilylation	2/8 AEP/UDP	50	**4**	276.1
	5/5 AEP/UDP	50	**4**	170.5
	8/2 AEP/UDP	50	**4**	109.4
	AEP	50	**4**	111.4
	physical mixture[b]	50	**4**	126.9
	UDP	50	**4**	45.9
	pure MSN[c]	50	**4**	43.0[d]



n = 7 (B/A)	0.92	1.10	2.21	2.58
Turnover for **A**	26.0	37.0	10.4	14.2
B	24.0	40.7	23.0	5.5



n = 0, 3, 7

n = 0, 3, 7

JACS, **2004**, *126,* 1010

- Bifunctionalized mesoporous silica nanosphere was demostrated as cooperative catalytic system.
- Various reactions were tested.
- These catalysts can be recycled.

- By fine-tuning the relative concentration and proper spatial arrangement of different functional groups, the multifunctionalized MSMs can serve as new solid-supported reagents.