Trans-1, 2-diaminocyclohexane mesoporous silica for asymmetric catalysis: enhancement of chirality through confinement space by plug effect

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Supporting Information

1. Experimental

a. Synthesis of N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane

To a solution of (1S, 2S)-(+)-1,2-diaminocyclohexane (46 mmol) was added (3-chloropropyl)triethoxysilane (92 mmol). The resulting solution was stirred at 80 °C for 18 h. The resulting mixture was rinsed with freshly distilled pentane. The solvent was pumped off from the filtrate. The yellowish solution was distilled and yielded product. The precursor was characterized by FT-IR spectrum and ^{1}H, ^{13}C NMR ($CDCl_3$) spectrum. Characterization is given in Scheme S1.

b. General procedure for synthesizing N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane functionalized mesoporous silica by hydrothermal method

In a typical synthesis, 83 g of mixed triblock copolymer P123 solution (P123: deionized water =1:15.6 weight ratio) and sodium metasilicate nonahydrate (SMS) solution 63.65 g (SMS of 48mmol) were stirred. And N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane (TPDC) was quickly added followed by concentrated hydrochloric acid (37.6%). The N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane (TPDC) to SiO_2 molar ratios in the initial synthesis mixture were 5 %, 7.5 % and 10% .The mixture was stirred at 40 °C for 1 h and aged at 100 °C for 24 h. The solid product was filtered and washed with copious amount of water and ethanol separately. The surfactant was removed by Soxhlet extraction method using ethanol for 24 h. The resulted products were denoted as DMS-n-HT (n is denoting as molar percentage of TPDC).

c. General procedure for synthesizing N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane functionalized mesoporous silica by microwave method

In a typical synthesis, 83 g of mixed triblock copolymer P123 solution (P123: deionized water =1 :15.6 weight ratio) and sodium metasilicate nonahydrate (SMS) solution 63.65 g (SMS of 48mmol) were stirred. And N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane (TPDC) was quickly added followed by concentrated hydrochloric acid (37.6%). The N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane (TPDC) to SiO_2 molar ratios in the initial synthesis mixture were 5 %, 7.5 % and 10% .The mixture was stirred at 40 °C for 1 h and aged at 100 °C for 2 h under microwave irradiation (300 W, 100%, Milestone). The solid product was filtered and washed with copious amount of water and ethanol separately. The surfactant was removed by Soxhlet extraction method using ethanol for 24 h. The resulted products were denoted as DMS-n-MW (n is denoting as molar percentage of TPDC).

d. Characterization

The powder X-ray powder diffraction (XRD) patterns were obtained on a Rigaku diffractometer using CuKα radiation (λ = 0.1547 nm). The N_2 adsorption–desorption isotherms and pore characterization were obtained by using a Micromeritics ASAP 2020 apparatus at liquid N_2 temperature. The pore size distribution (PSD) was calculated using the Barrett-Joyner-Halenda (BJH) formula. Thermogravimetric analyses (Bruker 2010 SA) were carried out to detect the decomposition temperature of the organic moieties grafted on the mesoporous silica. Transmission electron microscopic (TEM) images were taken using a JEM-3011 instrument (JEOL) equipped with a slow-scan CCD camera operating at 300 keV. The HPLC analysis was performed on Agilent Technologies (model 1200 series). Solid-state NMR spectra were collected through a DSX Bruker NMR 600 MHz The N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane (precursor) was analyzed by FT-IR (Nicolet), ^1H,^{13}C NMR ($CDCl_3$) spectrum (VARIAN UNITYINOVA400)

e. Typical procedure for addition reaction of trans-chlacone and nitroalkane

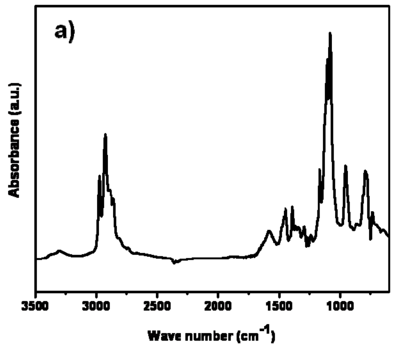
Toluene (3.0 mL), trans-chlacone (0.5 mmol), p-TsOH, nitroalkanes (3 eq, 1.5 mmol) were loaded in capped vial. Then catalyst (50 mg) (preactivated at 438 K prior to use) was added to the mixture and stirring was maintained for 24 h at room temperature. The residue was purified by column chromatography on silica gel (n-hexane (85 ml), ethyl acetate (15 ml)) affording Michael adducts as a white solid. The data of products are given in Scheme S2.

f. Procedure for synthesizing N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane functionalized mesoporous silica by post synthesis method

1g of SBA-15 and N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane (0.5 g) were added to a toluene (20 mL). The mixture was refluxed under stirring for 24 h. After filtration, the product was washed with toluene and dried. The product was designated as DMS-Post.

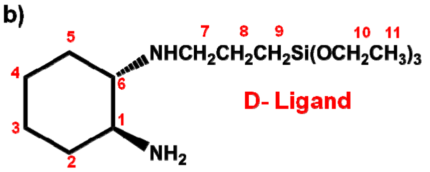
2. Results and discussions

❖ FT-IR Spectrum for chiral precursor



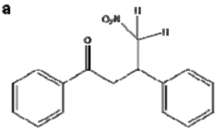
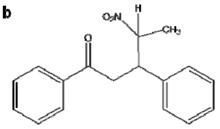
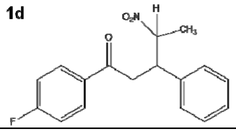
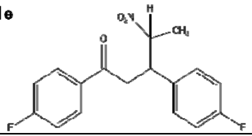
Assignment	Range
NH_2 & N-H wagging	660-900
C-N	1000-1250
CH_2 & CH_3 deformation	1438,1375,1341
NH_2 scissoring	1582
CH_3, CH_2 & CH	2850 3000
N-H	3299, 3371

❖ ^1H , ^{13}C NMR Assignment for chiral precursor



Atom Number	^1H NMR	^{13}C NMR
1	2.3	55.3
2	1.2, 1.9	35.4
3	1.7	24.9
4	1.2	25.1
5	C.8 ,1.9	31.0
6	1.9	61.5
7	2.4, 2.7	51.0
8	1.6	26.3
9	0.6	13.6
10	3.8	57.5
11	1.2	18.1

Scheme S1. FT-IR spectrum a) ^1H ($CDCl_3$), ^{13}C ($CDCl_3$) NMR assignment b) of N-[(triethoxysilyl)propyl]-(+)-(1S,2S)-1,2-diaminocyclohexane precursor

1a		The product was separated by silica gel column chromatography (85/15 N-hexane/Ethyl acetate): ^1H-NMR (400 MHz, $CDCl_3$) δ 7.914 (2H), δ 7.58-7.56 (1H), δ 7.48-7.44 (2H) , δ 7.36-7.32 (5H) , δ 4.86-4.81 (1H) , δ 4.72-4.67 (1H) , δ 4.23 (1H), δ 3.48-3.44 (2H)
1b		The product was separated by silica gel column chromatography (85/15 N-hexane/Ethyl acetate) : ^1H-NMR (400 MHz, $CDCl_3$, major diastereomer) δ 7.85-7.83 (2H), δ 7.54-7.52 (1H), δ 7.44-7.40 (2H) , δ 7.31-7.22 (5H), 4.91-4.87 (1H), 3.96-3.92 (1H) , 3.58-3.51 (1H), 3.29-3.24 (1H) , 1.42 (3H)
1d		The product was separated by silica gel column chromatography (85/15 N-hexane/Ethyl acetate) : ^1H-NMR (400 MHz, $CDCl_3$, major diastereomer) δ 7.95-6.97 (9H) , 4.99-4.97 (1H), 4.31-4.19 (1H), 3.96-3.92 (1H) , 3.68-3.57 (1H) , 1.42 (3H)
1e		The product was separated by silica gel column chromatography (85/15 N-hexane/Ethyl acetate) : ^1H-NMR (400 MHz, $CDCl_3$, major diastereomer) δ 7.88-6.97 (8H) , 5.07(1H) , 4.23-4.09 (1H), 3.73- 3.40 (2H) , 1.43-1.42 (3H)

Scheme S2. ^1H ($CDCl_3$) NMR assignment of product of addition reaction over 1a, 1b, 1d, 1e.

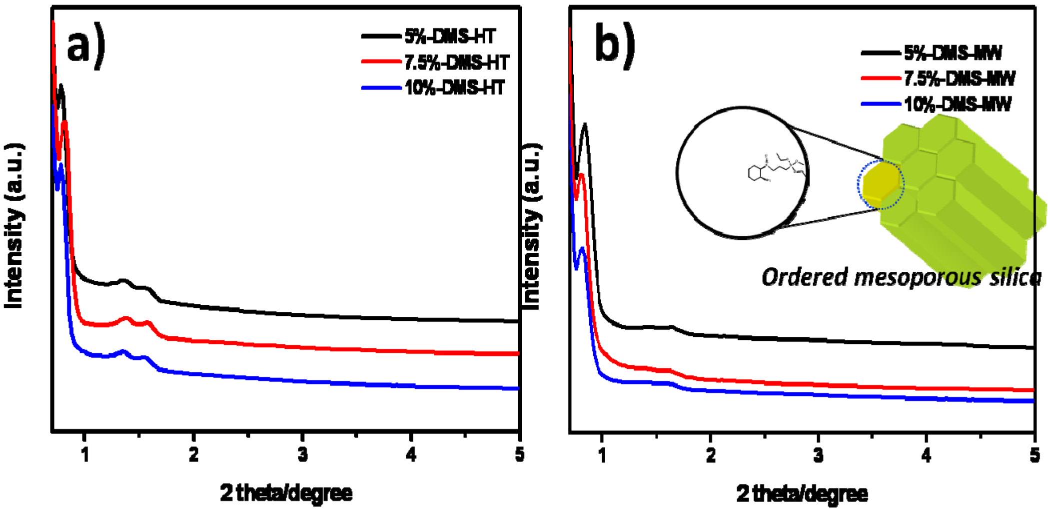
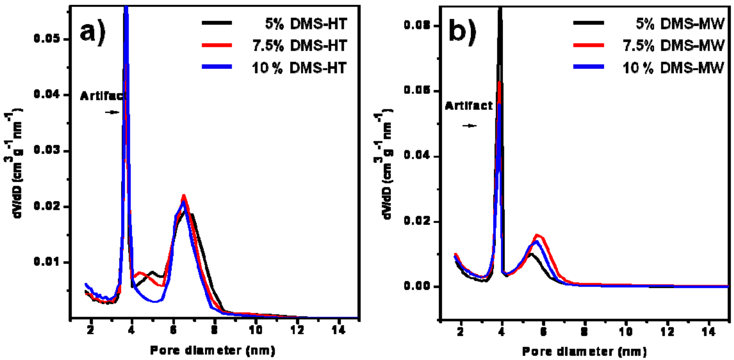
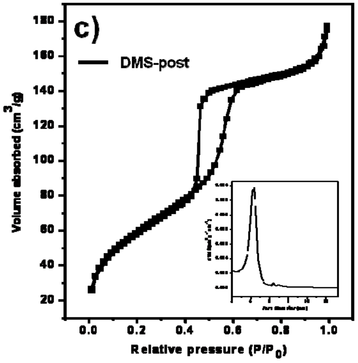


Figure S1. Powder XRD patterns of DMS-n *[n* = precursor to SiO_2 molar ratios in the initial synthesis mixture] synthesized by thermal method a) and DMS-n *[n* = precursor to SiO_2 molar ratios in the initial synthesis mixture] synthesized by microwave method b)





d)

Catalyst	BET surface area	V_t	Pore size (nm)
DMS-Post	230	0.3	4.4

Figure S2. Pore size distributions of DMS-n synthesized by hydrothermal method a) , DMS-n *s*ynthesized by microwave method b), nitrogen adsorption-desorption isotherms of DMS synthesized post synthesis method and (inset) pore size distributions by BJH calculation c), and physicochemical parameters for the DMS synthesized post synthesis method d)

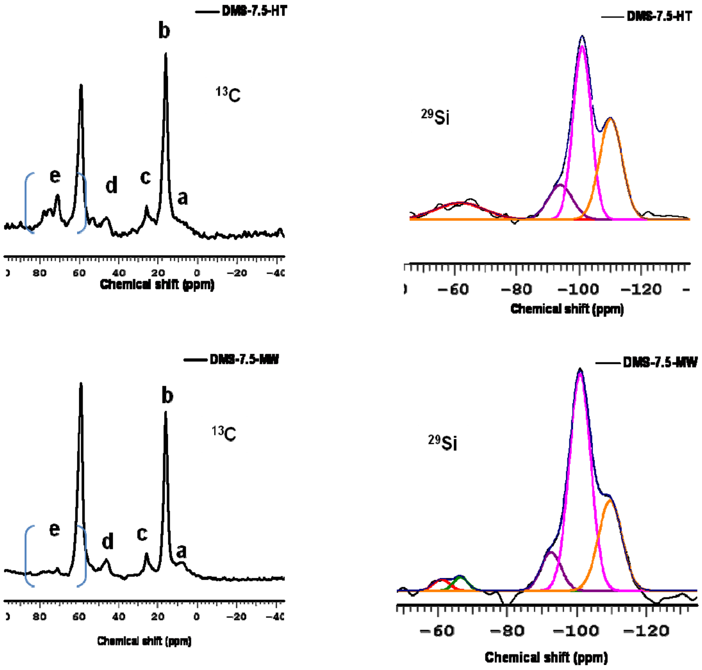


Figure S3. Solid-state ^{13}C CP-MAS NMR and ^{29}Si CP-MAS NMR spectra of mesoporous silica containing *trans*-(1*S*,2S)-diaminocyclohexane synthesized by hydrothermal method (DMS-7.5-HT) and mesoporous silica containing *trans*-(1*S*,2S)-diaminocyclohexane synthesized by microwave method (DMS-7.5-MW)

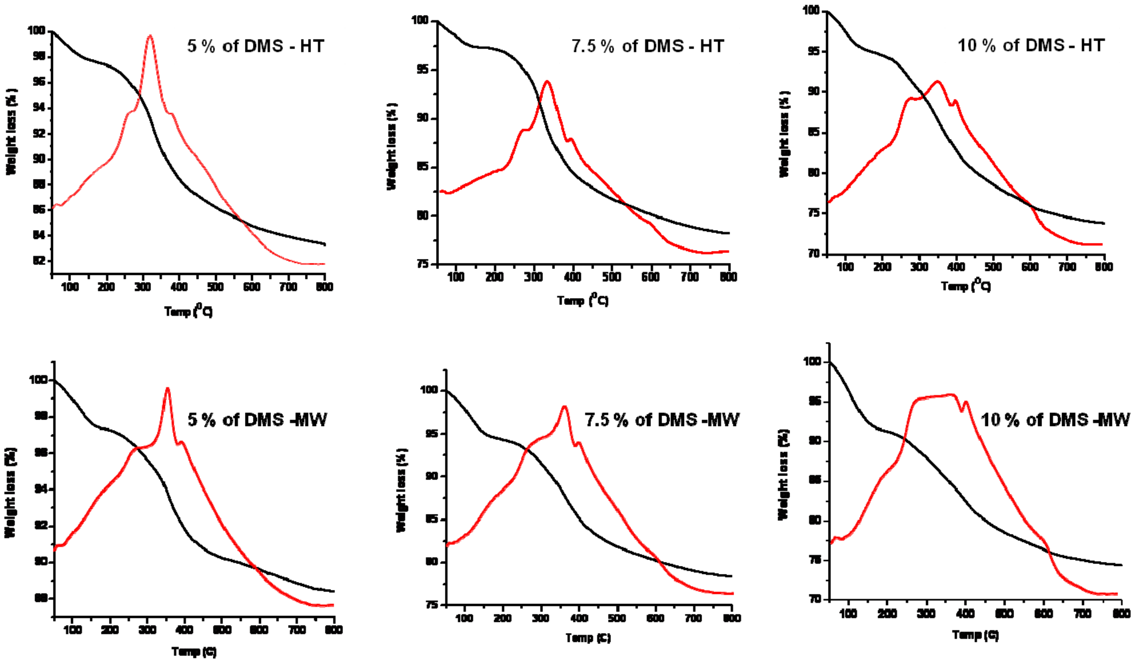


Figure S4. TG (black) – DTA (red) curve of mesoporous silica containing *trans*-(1*S*,2S)-diaminocyclohexane synthesized by hydrothermal method (DMS-n-HT) and mesoporous silica containing *trans*-(1*S*,2S)-diaminocyclohexane synthesized by microwave method (DMS-n-MW)

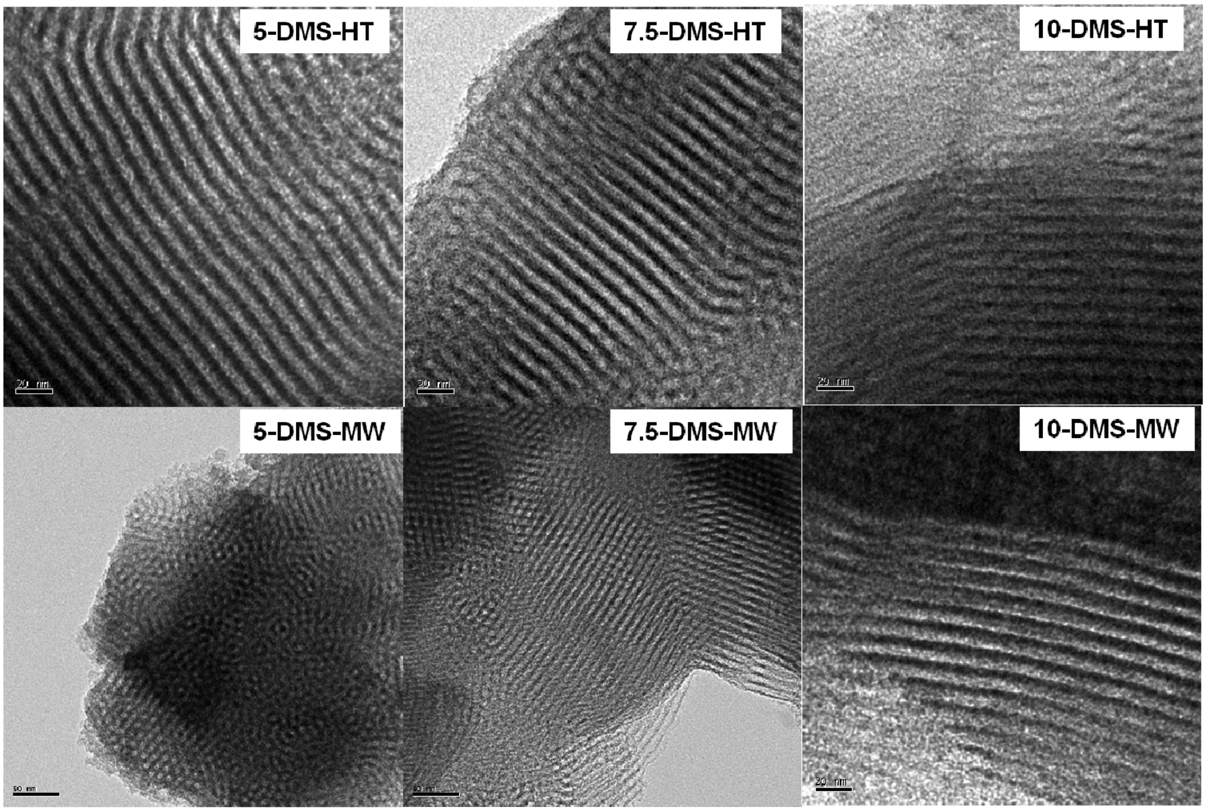
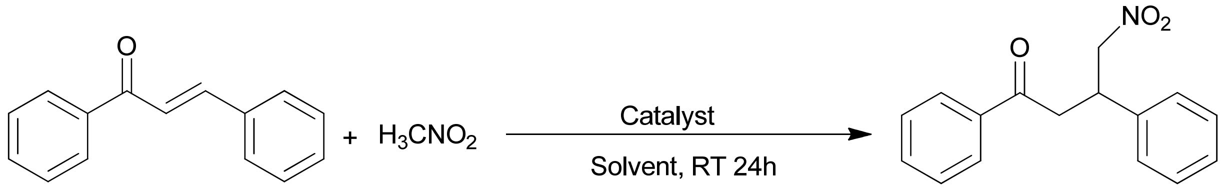


Figure S5. TEM images of mesoporous silica containing *trans*-(1*S*,2S)-diaminocyclohexane synthesized by hydrothermal method (DMS-n-HT) and mesoporous silica containing *trans*-(1*S*,2S)-diaminocyclohexane synthesized by microwave method (DMS-n-MW)

Table S1 Catalytic results of asymmetric 1,4-addition reaction of trans-chlacone and nitromethane



Entry	cat	yield (%)[a]	ee (%)[b]
1a -1	DMS-Post[e]	31/22[c]	31/24[d]
1a -2	DMS-5 – HT	48/45[c]	40/36[d]
1a -3	DMS-7.5 – HT	62/58[c]	68/66[d]
1a -4	DMS-10 – HT	73/69[c]	71/68[d]
1a -5	DMS-5 – MW	30/28[c]	43/39[d]
1a -6	DMS-7.5 – MW	53/51[c]	79/73[d]
1a -7	DMS-10 – MW	63/59[c]	76/70[d]

[a] Isolated yields by the column chromatography [b] enantioselectivity estimated by HPLC on a OD-H column. [c,d] results of recyclability test running 3 times [e] DMS-Post sample was synthesized by post synthesis mehod

Table S2 Catalytic results of asymmetric 1,4-addition reaction of trans-chlacone and nitroethane

Entry	cat	Yield (%)[a]	ee (%)[b]
1b -1	DMS-5 – HT	31	23
1b -2	DMS-7.5 – HT	75	57
1b -3	DMS-10 – HT	74	51
1b -4	DMS-5 – MW	20	35
1b -5	DMS-7.5 – MW	42	69
1b -6	DMS-10 – MW	45	65

[a] Isolated yields by the column chromatography [b] enantioselectivity estimated by HPLC on a OD-H column.

Table S4 Catalytic results of asymmetric 1,4-addition reaction of fluorochlacones and nitroethane

Entry	Catalyst	Conversion (%)[a]	ee (%)[b]
1d -1	DMS-Post	58	43
1d -2	DMS-7.5 – HT	70	91
1d -3	DMS-7.5 – MW	54	97
1e -1	DMS-Post	50	65
1e -2	DMS-7.5 – HT	63	87
1e -3	DMS-7.5 – MW	42	91

[a] Isolated yields by the column chromatography [b] enantioselectivity estimated by HPLC on a OD-H column.