Supporting Information

Enantioselective carbonyl-ene reaction on BINOLate/titanium catalyst encapsulated in magnetic nanoreactors

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Chemicals and Reagents

Ethyl glyoxylate (50% toluene solution), α-methylstyrene, Pluronic copolymer F127 ($EO_{106}PO_{70}EO_{106}$) were purchased from Sigma Aldrich Company. Ti(O*i*Pr)$_4$ was purchased from Alfa-Aesar (USA) and was distilled before use. Propyltrimethoxysilane (C3) and (*R*)-(+)-1,1’-bi-2-naphthol (*R*-(+)-BINOL) were purchased from Meryer Chemical Technology Company and Lianyungang Chiral Chemicals Company (China), respectively. Other reagents were purchased from Shanghai Chemical Reagent Incorporation of Chinese Medicine Group. All solvents are of analytical quality and dried by standard methods.

(*R*)-6,6′-dibromo-1,1’-bi-2-naphthol ((*R*)-6,6′-Br_2-BINOL) was synthesized according to literature method.[1] (*R*)-6,6′-Br_2-BINOL-Ti complexes were prepared through mixing (*R*)-6,6′-Br_2-BINOL and Ti(O*i*Pr)$_4$ with different molar ratio in CH_2Cl_2 at room temperature (1:1, 2:1, 3:1), which were denoted B_nTi (n=1, 2, 3). All the reactions were carried out under an argon atmosphere using standard Schlenk techniques.

Synthesis of magnetic FDU-12 with cage-like nanostructures

Mesoporous molecular sieve FDU-12 with a cage-like structure and monodisperse magnetite (Fe_3O_4) nanoparticles capped with oleic acid were synthesized according to the reported methods.[2, 3] Magnetic FDU-12 with cage-like nanostructures was synthesized as follows: as-synthesized FDU-12 (with F127 surfactant, 1 g) was suspended in cyclohexane (50 ml) containing 0.02 g of Fe_3O_4 nanoparticles. After ultrasonic treatment for 2 h, the mixture was mechanically stirred for 12 h at room temperature. After removing cyclohexane by rotatory evaporator at room temperature, the solid product was dried at 60 °C overnight. The sample was calcined at 500 °C for 4 h under N_2 atmosphere for carbonization of the surfactant, and the sample was denoted as FDU-CM (C and M refer to the FDU-12 respectively with carbonization and magnetic Fe_3O_4).

Encapsulation of (*R*)-6,6′-Br$_2$-BINOL-Ti complexes in the nanocages of FDU-CM and FDU-12

After evacuating at 120 °C for 6 h, FDU-CM (0.5 g) was dispersed in 2 mL of dry CH_2Cl_2 with desired amount (varied in the range of 12.5 to 100 mmol) of (*R*)-6,6′-Br$_2$-BINOL-Ti complexes. After stirring the mixture at reflux temperature for 24 h under Ar atmosphere, the CH_2Cl_2 was removed by slow volatilization. Propyltrimethoxysilane (0.75 mL) dissolved in dry hexane (3 mL) was added to the above solid. After refluxing for 24 h, the solid products were isolated by magnetic field and washed thoroughly with dry CH_2Cl_2. The filtrate was collected and used to caculated the Ti content through UV-vis spectra. The obtained catalysts were dried under vacuum. The sample was denoted as B$_n$Ti@FDU-CM (n=1, 2, 3).

For comparison, B$_2$Ti@FDU-12 was also synthesized using FDU-12 (obtained by calcining as-synthesized FDU-12 in air at 550 °C for 6 h) as the nanoreactor under otherwise the similar conditions to B$_n$Ti@FDU-CM.

The volume of per cage of FDU-CM is calculated as follows: $V_1 = 4\pi R_1^3/3 = 4\pi\times5^3/3 = 523\ \mathrm{nm}^3$, R_1 is the radius of per nanocage. B$_2$Ti molecular number in each cage: $n = N_{\mathrm{Ti(1g)}} \times 6.02 \times 10^{23}/(V_{\mathrm{meso}}/V_1)$, $N_{\mathrm{Ti(1g)}}$ is the mole amount of B$_2$Ti of per gram solid catalyst, V_{meso} is the total pore volume of FDU-CM.

Characterization

The nitrogen sorption experiments were performed at -196 °C on an ASAP 2020 instrument. The samples were outgassed at 120 °C for 5 h before the measurement. The Brunauer-Emmett-Teller (BET) surface area was evaluated from data in the relative pressure range of 0.05 to 0.25. The total pore volume was estimated from the amount adsorbed at the P/P_0 of 0.99. The pore diameter was determined from the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. UV-vis spectra were recorded on a 2550 spectrophotometer using dichloromethane as the reference. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV. ^{13}C (100.5 MHz) and ^{29}Si (79.4 MHz) cross-polarization magic angle spinning (CP-MAS) solid-state NMR experiments were recorded on a Varian infinity-plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. The experimental parameters for ^{13}C CP-MAS NMR experiments were 10-kHz spin rate, 2-s pulse delay, 6-min contact time and 1000-2000 scans. ^{29}Si signals were referenced to tetramethylsilane and the experimental parameters were 4-kHz spin rate, 180-s pulse delay, 10-min contact time, and 116 scans for ^{29}Si CP-MAS NMR experiments. Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 5 ^{o}C/min by using a NETZSCH STA-449F3 thermogravimetric analyzer. Raman spectroscopy was performed on a Jobin Yvon LabRam HR 800 instrument with a 325 nm excitation laser.

Typical procedure for enantioselective carbonyl-ene reactions and catalyst recycling

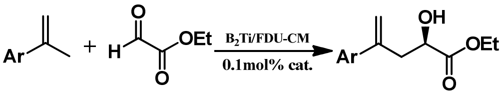
α-Methylstyrene (130 μL), and ethyl glyoxylate (50% toluene solution, 320 μL) were added to a Schlenk tube with the solid catalyst under Ar atmosphere. After the mixture was stirred at room temperature for a given period, the supernatant was removed via syringe for analysis. The catalyst isolated at the bottom of the tube through magnet field was extracted repeatedly with anhydrous CH_2Cl_2 under Ar atmosphere and dried for the next run. The combined supernatant and CH_2Cl_2 extract was concentrated and purified through chromatography on silica (ethyl acetate/hexane = 1:5) to obtain the carbonyl-ene product. The enantiomeric excess of carbonyl-ene product was analyzed by performing HPLC using a Chiralcel OJ column: eluent, hexane/2-propanol (97:3); flow rate, 1.0 mL/min; UV detection at λ=254 nm.

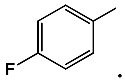
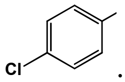
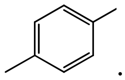
Table S1. Physicochemical properties of FDU-12 and FDU-CM before and after silylation, and the solid catalysts.

Sample	Ti content wt%	BET surface area (m^2g^{-1})	Pore volume[a] (cm^3g^{-1})	Cage size[b] (nm)
FDU-12	-	710	0.71	10.2
FDU-CM	-	841	0.92	10.7
B_2Ti@FDU-CM-1	0.064	685	0.71	10.5
B_2Ti@FDU-CM-2	0.093	591	0.55	10.2
B_2Ti@FDU-CM-3	0.142	490	0.50	9.9
B_2Ti@FDU-CM-4	0.186	321	0.44	9.9
B_2Ti@FDU-CM-5	0.211	271	0.37	9.8
B_2Ti@FDU-12	0.137	451	0.51	9.2

[a] Total pore volume obtained from the volume of N_2 adsorbed at $P/P_0 = 0.99$. [b] BJH method from adsorption branch.

Table S2. Results of enantioselective carbonyl-ene reactions between ethyl glyoxylate and representative olefins catalyzed by $B_2Ti@FDU\text{-}CM^a$



Entry	Olefin	Yield (%)[b]	ee (%)[c]
1		83.1	95.5
2		75.6	94.9
3		63.7	74.2

[a] Ti content of solid catalysts $B_2Ti@FDU\text{-}CM$ is 0.142 wt%; ethyl glyoxylate is 2.0 molar equivalent to olefin; room temperatue; 48 h; S/C is 1000, no solvent was added.

[b] Isolated products. [c] HPLC analysis using a Chiralcel OJ column.

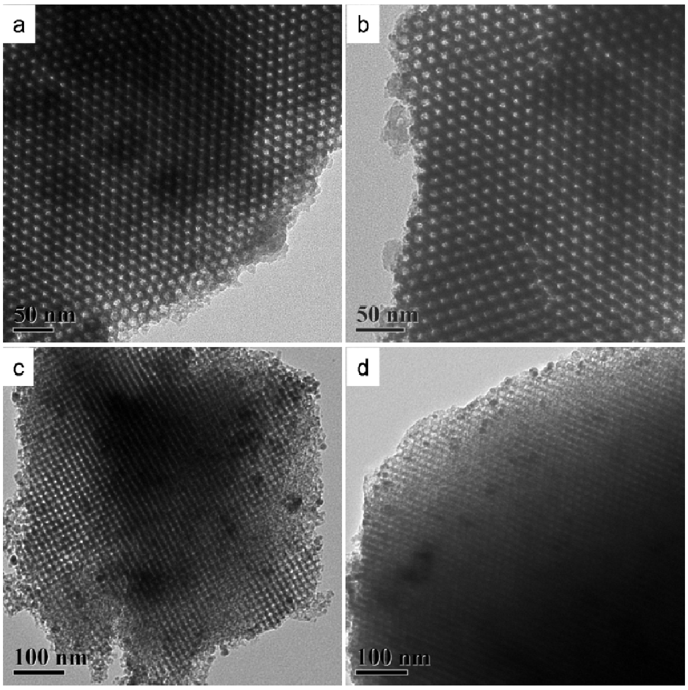


Figure S1. TEM images of (a) FDU-12, (b) B_2Ti@FDU-12, (c) FDU-CM and (d) B_2Ti@ FDU-CM (Ti content 0.142 wt%).

The TEM image of FDU-CM shows the highly ordered lattice array over large domains similar to that of FDU-12, suggesting that this sample has a uniform and well defined cubic mesostructure (*Fm3m*). Fe_3O_4 nanoparticles with mean particle size of about 11 nm are well-distributed on the FDU-CM. The surface loading of Fe_3O_4 nanoparticles has the advantages of not occupying the nanocage and imparting the magnetic properties to the sample.

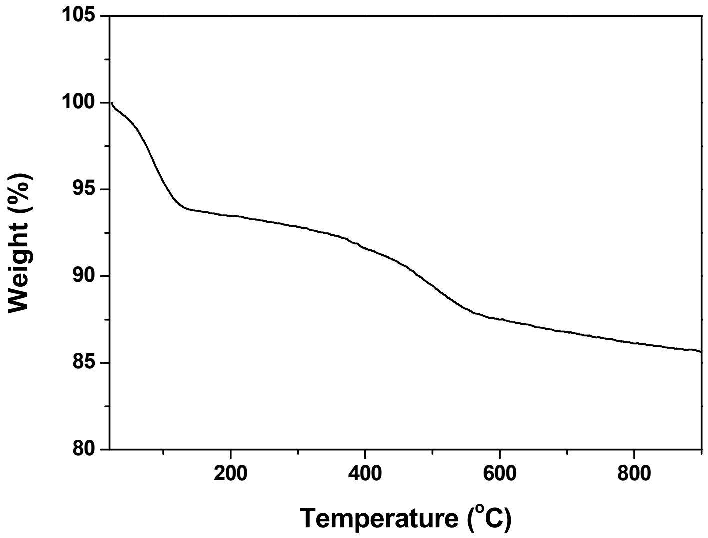


Figure S2. Weight losses measured by TGA for FDU-CM.

Based on the thermogravimetric analysis, the carbon content in FDU-CM is ~8%.

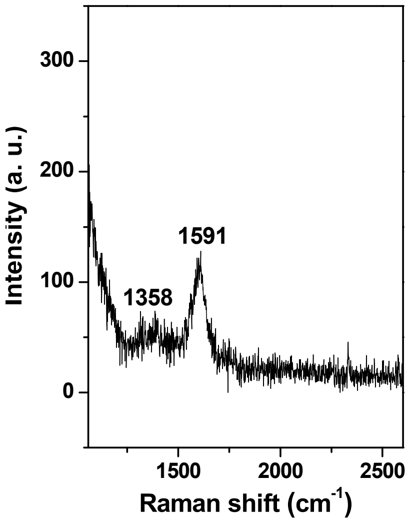


Figure S3. Raman spectrum of FDU-CM.

The Raman spectrum of FDU-CM shows D and G bands at 1358 cm^{-1} and 1591 cm^{-1}, respectively, which demonstrates the carbon species in the inner surface of the nanocages are amorphous.

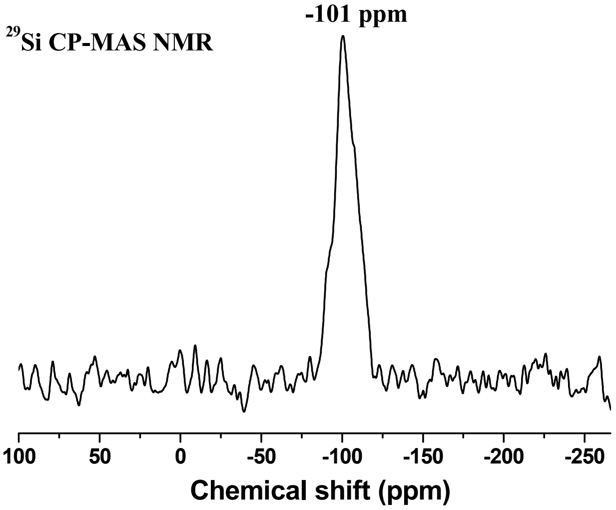


Figure S4. Solid state ^{29}Si CP-MAS NMR spectrum of FDU-CM.

The ^{29}Si CP-MAS NMR spectrum shows the signal at -101 ppm correspond to Q^3 [$Si(OH)(OSi)_3$]. The result means the existence of -Si-OH in FDU-CM, which is very important for silylation to decrease the pore entrance size.

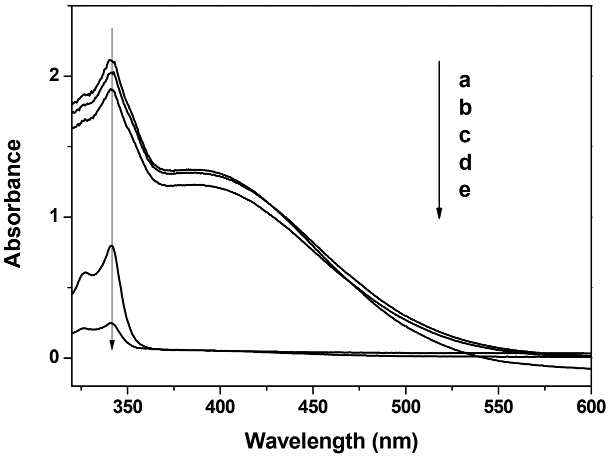


Figure S5. UV-vis spectra of (*R*)-6,6′-Br_2-BINOL-Ti complex (B_2Ti) in CH_2Cl_2 (a) and after adsorption with FDU-CM silylated with C3 (b), FDU-12 silylated with C3 (c), FDU-12 (d) and FDU-CM (e).

The efficiency of C3 in preventing (*R*)-6,6′-Br_2-BINOL-Ti complex from escaping the nanoreactor was characterized by adsorption experiment using (*R*)-6,6′-Br_2-BINOL-Ti as a probe molecule. UV-vis spectra before and after the adsorption are shown in Fig. S5. The intensities of the UV-vis bands decreased sharply compared with those of the original solution with FDU-CM and FDU-12 as adsorbents, which means the pore sizes of FDU-CM and FDU-12 are large enough for (*R*)-6,6′-Br_2-BINOL-Ti to enter the nanoreactors. After adsorption of (*R*)-6,6′-Br_2-BINOL-Ti with FDU-CM or FDU-12 silylated with C3 but without catalyst encapsulation, the intensities of the UV-vis bands remained almost the same as that of the original (*R*)-6,6′-Br_2-BINOL-Ti solution, indicating that silylation using C3 can effectively encapsulate (*R*)-6,6′-Br_2-BINOL-Ti in the nanocages of FDU-12 or FDU-CM.

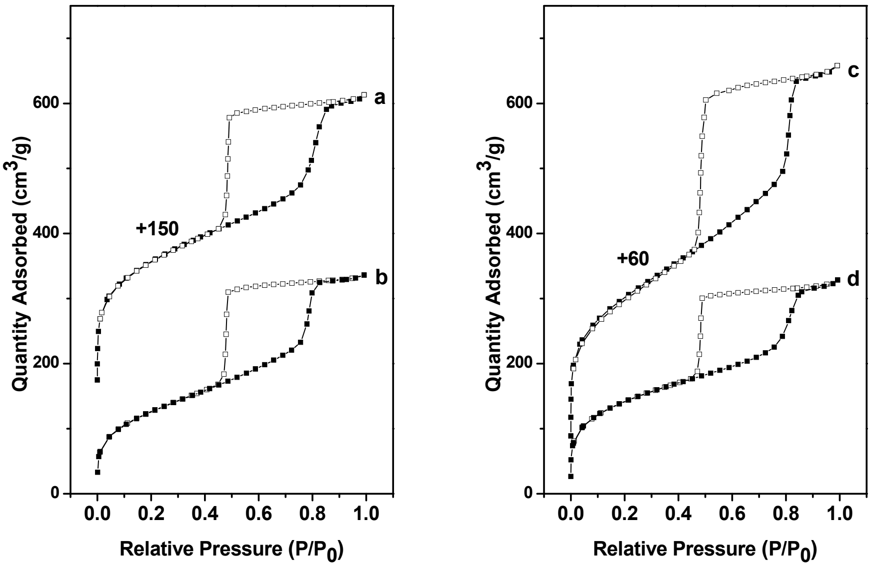


Figure S6. N_2 sorption isotherms of different samples: (a) FDU-12, (b) B_2Ti@FDU-12, (c) FDU-CM, (d) B_2Ti@FDU-CM (Ti content 0.142 wt%).

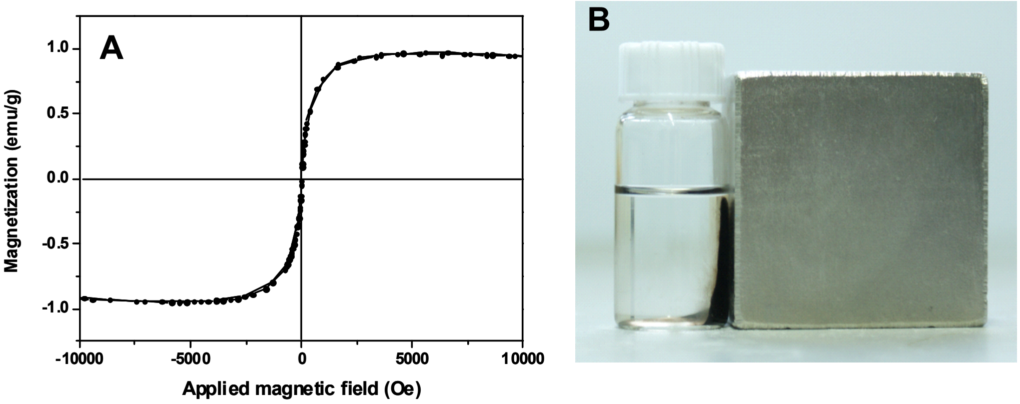


Figure S7. Magnetization curves of B_2Ti@FDU-12-C (A), and the photos of B_2Ti@FDU-CM separated from CH_2Cl_2 with a magnet (B).

The saturation magnetization curves measured at 300 K show no hysteresis loop, which means that B_2Ti@FDU-CM possess superparamagnetism. With an external magnetic field, B_2Ti@FDU-CM could be easily separated from CH_2Cl_2.

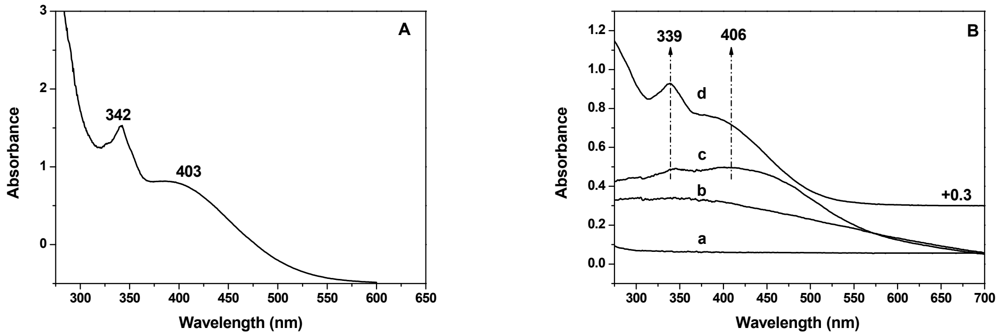


Figure S8. UV-vis spectra of (A) B_2Ti in dichloromethane, (B) solids (diffuse reflectance): (a) FDU-12-C3, (b) FDU-CM-C3, (c) B_2Ti@FDU-CM and (d) B_2Ti@FDU-12.

UV-vis diffuse reflectance spectroscopy was applied to characterize the catalysts encapsulated in the nanoreactor. The UV-vis spectrum of (*R*)-6,6′-Br_2-BINOL-Ti complex in dichloromethane shows two bands at 342 and 403 nm assigned to π-π* transition of phenyl ring on BINOL ligand and charge transfer transition of ligand to metal, respectively. Similar to the UV-vis spectrum of (*R*)-6,6′-Br_2-BINOL-Ti complex in solution, the diffuse reflectance UV-vis spectrum of B_2Ti@FDU-12 and B_2Ti@FDU-CM displayed two bands at 339 and 406 nm, which are not observed in the UV-vis spectrum of FDU-12-C3 and FDU-CM-C3 (The support was silylated with C3 but without catalyst encapsulation). The UV-vis diffuse reflectance spectra confirms that the homogeneous catalyst is successfully encapsulated in the nanoreactors.

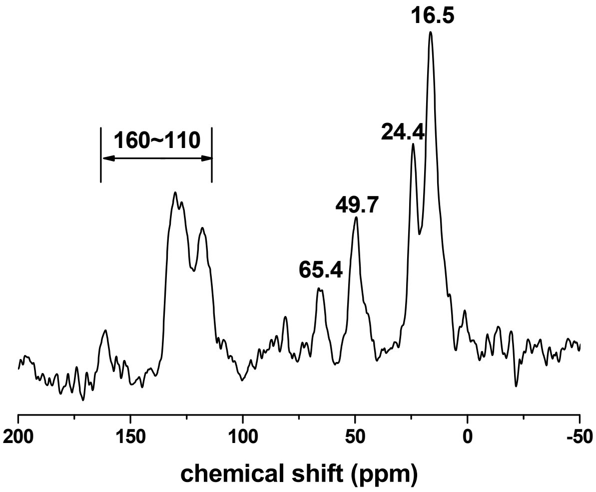


Figure S9. Solid state ^{13}C CP-MAS NMR spectrum of B_2Ti@FDU-CM (Ti content 0.211 wt%).

To further confirm the encapsulation of (*R*)-6,6′-Br_2-BINOL-Ti complex in the nanoreactor, the materials were characterized by ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectroscopy (Fig. S9). In the ^{13}C CP-MAS NMR spectrum of B_2Ti@FDU-CM, the signals in the range of 160 ~ 110 ppm were ascribed to aryl carbon atoms of (*R*)-6,6′-Br_2-BINOL, which confirmed the successful encapsulation of (*R*)-6,6′-Br_2-BINOL-Ti complex in the nanoreactor. The signals at 49.7, 24.4 and 16.5 ppm could be assigned to C^3, C^2, and C^1 carbon species of Si-$C^1H_2C^2H_2C^3H_2$, respectively, which was used to reduce the pore size. The signals centered at 65.4 ppm and 16.5 ppm (overlapped with the signal of C^1) were ascribed to C^4 and C^5 carbon species of Ti-O-$C^4H(C^5H_3)_2$ in the (*R*)-6,6′-Br_2-BINOL-Ti complex.

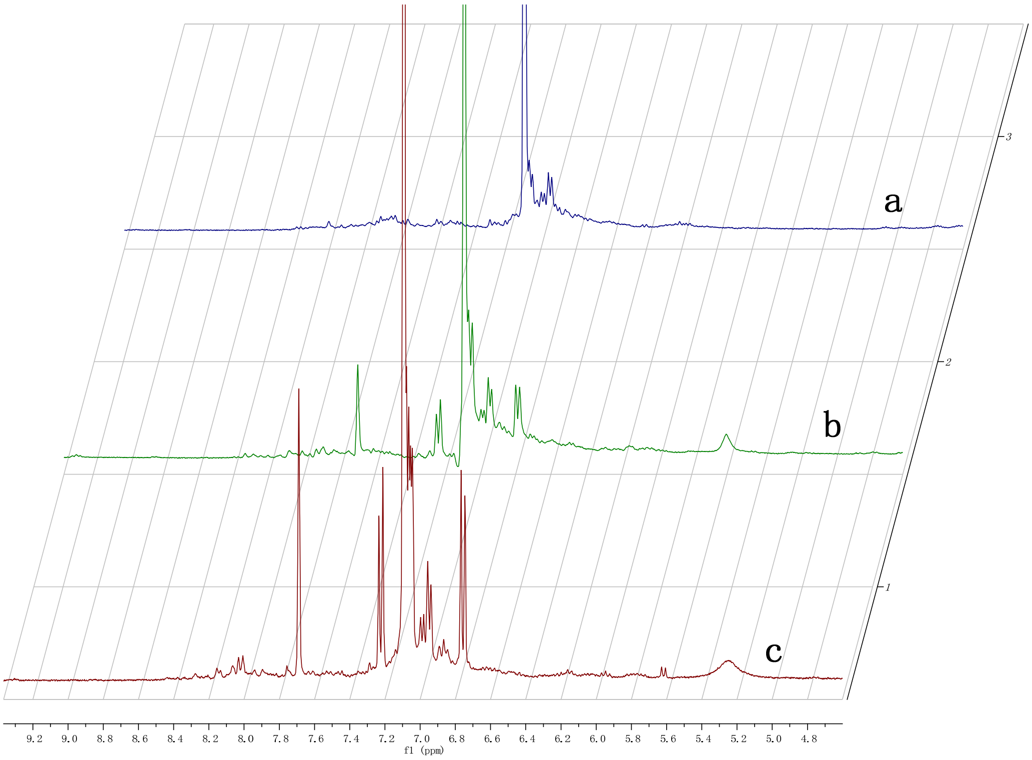


Figure S10. H NMR spectra taken in C_6D_6. (a) 6,6′-Br_2-BINOL/Ti(*i*OPr)$_4$ (1:1), (b) 6,6′-Br_2-BINOL/Ti(*i*OPr)$_4$ (2:1), and 6,6′-Br_2-BINOL/Ti(*i*OPr)$_4$ (3:1).

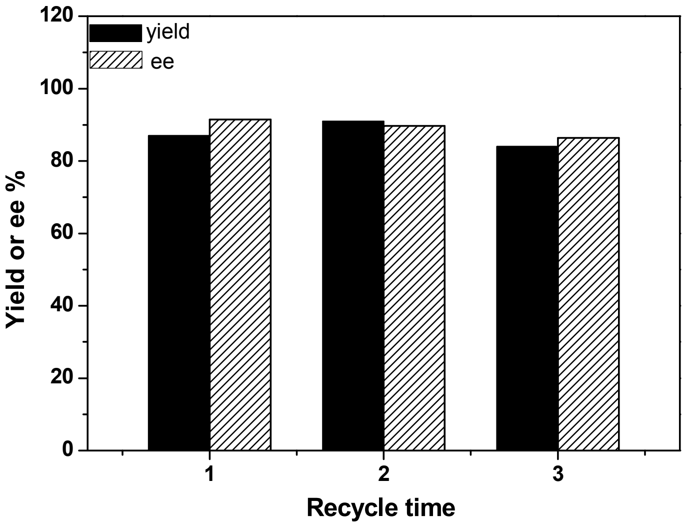


Figure S11. The recyclability tests of B_2Ti@FDU-CM for the enantioselective carbonyl-ene reaction. Reaction conditions: catalyst (B_2Ti@FDU-CM with 0.142 wt% of Ti content) is 1 mol % equivalent to α-methylstyrene; ethyl glyoxylate is 2.0 molar equivalent to α-methylstyrene, 0.5 mL toluene was added; room temperatue; the reaction time is 48, 56, 72 h for the first, second, third recycle, respectively.

References

1. H. Ishitani, M. Ueno and S. Kobayashi, *J. Am. Chem. Soc.*, 2000, **122**, 8180.
2. J. Fan, C. Z. Yu, T. Gao, J. Lei, B. Z. Tian, L. M. Wang, Q. Luo, B. Tu, W. Z. Zhou and D. Y. Zhao, *Angew. Chem. Int. Ed.*, 2003, **42**, 3146.
3. Z. G. Teng, J. Li, F. Yan, R. Zhao and W. S. Yang, *J. Mater. Chem.*, 2009, **19**, 1811.