

Towards Heterogeneous Organocatalysis: Chiral Iminium Cations Supported on Porous Materials for Enantioselective Alkene Epoxidation

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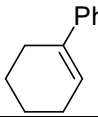
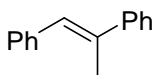
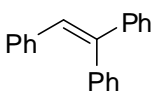
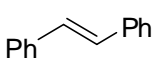
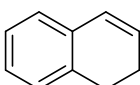
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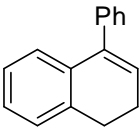
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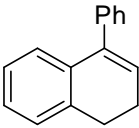
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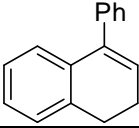
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Table S1. Catalytic asymmetric epoxidation of unfunctionalized alkenes mediated by dihydroisoquinolinium salts 6-12^a

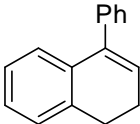
Catalyst 6	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min
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	100; 35	100; 40
	100; 90	100; 115
	100; 45	100; 45
	100; 5	100; 5

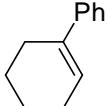
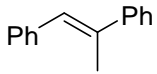
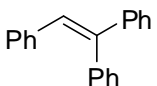
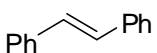
Catalyst 7	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min
	100; 22	100; 30

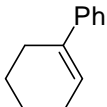
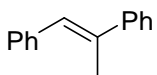
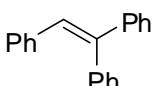
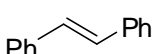
Catalyst 8	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min
	100; 100	100; 105

Catalyst 9	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min
	100; 10	100; 6

Catalyst 10	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min

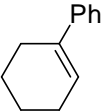
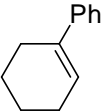
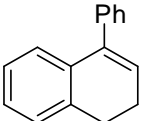
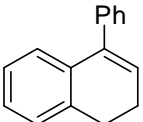
	100; 12	100; 10
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Catalyst 11	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min
	100; 12	100; 12
	100; 10	100; 6
	100; 12	100; 10
	100; 6	100; 12

Catalyst 12	BPh_4^-	Zeolite Y
	Conversion/%; time/min	Conversion/%; time/min
	100; 5	100; 6
	100; 10	100; 6
	100; 6	100; 3
	100; 5	100; 5

^aEpoxidation conditions: Iminium salt (10 mol%), Oxone (2 eq.), Na_2CO_3 (4 eq.), MeCN:H₂O (1:1), 0 °C. ^bConversion evaluated from the ¹H-NMR spectra by integration of alkene versus epoxide peaks.

Table S2. Catalytic asymmetric epoxidation of unfunctionalized alkenes mediated by dihydroisoquinolinium salt 1^a

	ee/% ^b	Conversion/% ^c	Time/min	Configuration ^d
 ⁻ BPh ₄ catalyst	40	100	5	(-)-1 <i>S</i> ,2 <i>S</i>
 Zeolite Y catalyst	40	61	360	(-)-1 <i>S</i> ,2 <i>S</i>
 ⁻ BPh ₄ catalyst	49	100	5	(-)-1 <i>S</i> ,2 <i>R</i>
 Zeolite Y catalyst	—	0 ^e	—	—

^a Epoxidation conditions: Iminium salt **1** (10 mol%), Oxone (2 eq.), Na₂CO₃ (4 eq.), MeCN:H₂O (1:1), 0 °C. ^b Enantiomeric excess determined by ¹H-NMR spectroscopy with Eu(hfc)₃ (0.1 eq.) as chiral shift reagent or by chiral HPLC on a chiracel OD Column. ^c Conversion evaluated from the ¹H-NMR spectra by integration of alkene versus epoxide peaks. ^d The absolute configuration of the major enantiomer was determined by comparison to those reported in the literature. ^e No conversion seen after 6 h.

Figure S1 provides a schematic illustration of iminium ion **13** in a 29 Å diameter MCM-41 channel. The channel structure is obtained from a supercell of the dense silica cristobalite phase into which 29 Å diameter channels have been cut with a wall thickness of 7 Å. The resulting dangling bonds have been capped with hydrogen atoms to represent the surface termination by hydroxylation that will occur during the synthesis procedure. Si atoms have then been randomly replaced by Al to give the experimental Si/Al ratio of 12. The porous structure has also been optimized using a molecular mechanics approach which reduced the crystallinity of the channel walls. This illustration gives an impression of the relative size of the organocatalyst and channel structure.

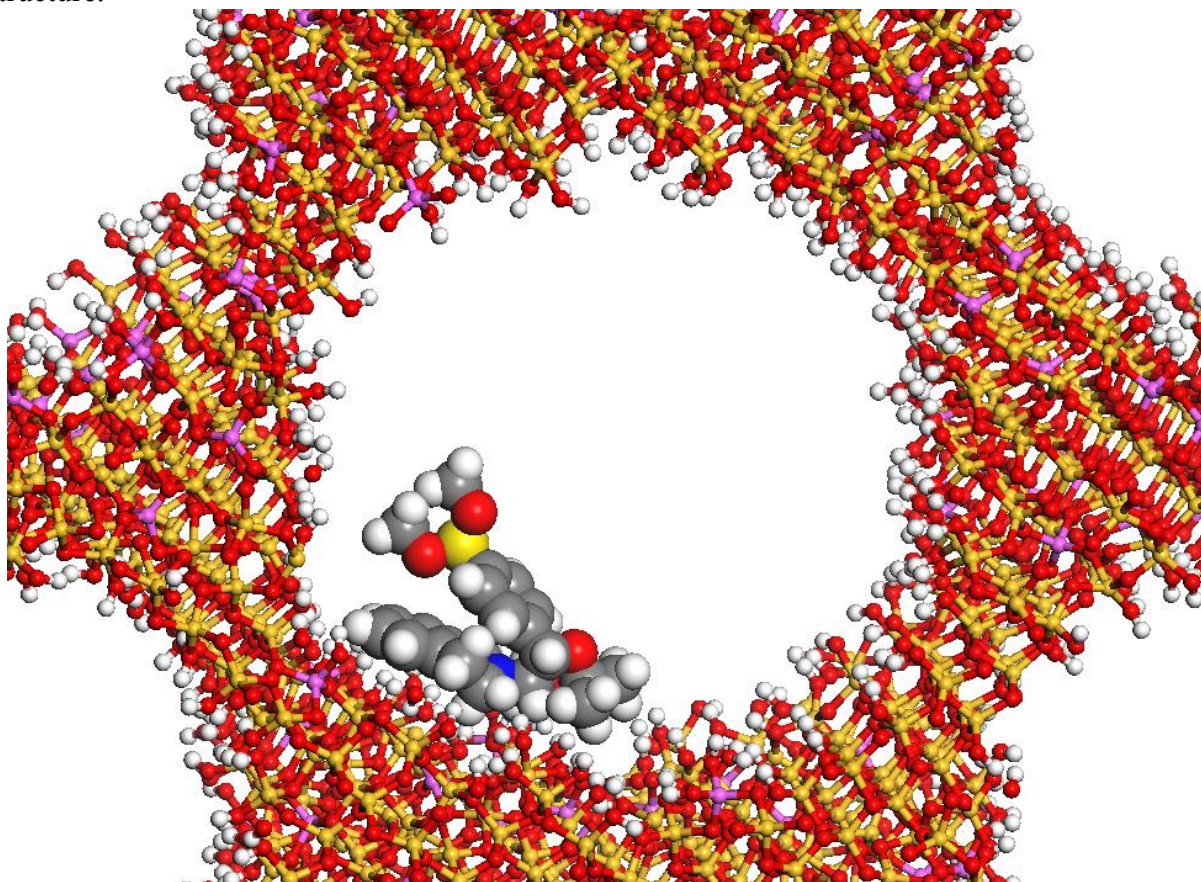
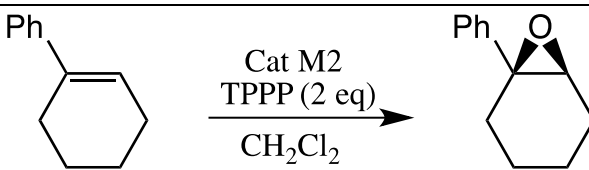
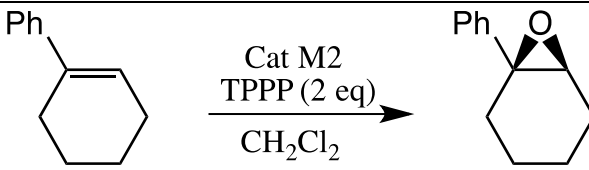
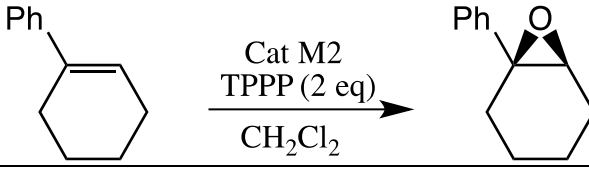
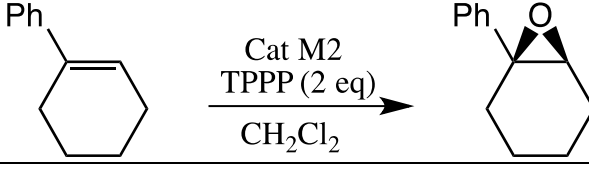
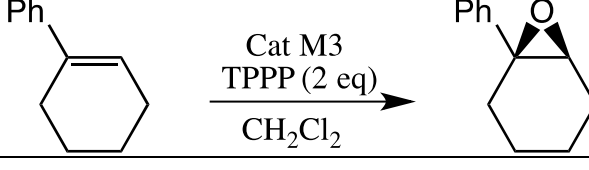
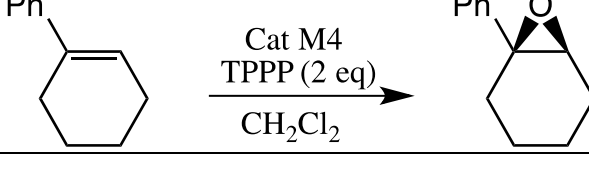


Figure S1. The iminium ion is shown in space fill with C atoms grey, N atoms blue, H atoms white and S atoms yellow. The MCM-41 framework is shown using ball and stick with Si atoms yellow, Al atoms pink, O atoms red and H atoms white.

Table S3. Reusability of Al-MCM-41-supported catalysts

	Use	Conv/%	Temp/C	Time/h	ee/% ^a
	1	56	−40	6	32 (29)
	2	43	−40	6	32
	3	20	−40	6	32
	Use	Conv/%	Temp/C	Time/h	ee/% ^a
	1	100	−40	24	32 (29)
	2	50	−40	24	32
	3	0	−40	24	—
	Use	Conv/% ^b	Temp/C	Time/h	ee/% ^a
	1	100	−40	24	32
	2	63	−40	24	32
	3	0	−40	24	—
	Use	Conv/% ^c	Temp/C	Time/h	ee/% ^a
	1	100	−40	24	31
	2	100	−40	24	32
	3	53	−40	24	32
	Use	Conv/%	Temp/C	Time/h	ee/% ^a
	1	60	−40	24	74 (75)
	2	29	−40	24	73
	Use	Conv/%	Temp/C	Time/h	ee/% ^a
	1	100	−40	24	37 (38)
	2	46	−40	24	37

^a Values in parentheses indicate the ees obtained in the corresponding homogeneous reactions

^b Catalyst dried at 60 °C prior to re-use

^c Catalyst stirred in dichloromethane for 24 hours prior to drying and re-use

Figure S2. Magic angle spinning NMR spectroscopy performed on catalyst **M13**, and ^{13}C solution spectrum of **13** with a tetrafluoroborate counter-ion. Clearly identifiable bands in the MAS spectrum can be attributed to the various functional groups including the iminium species, phenyl ring system and the sulfone methyl group.

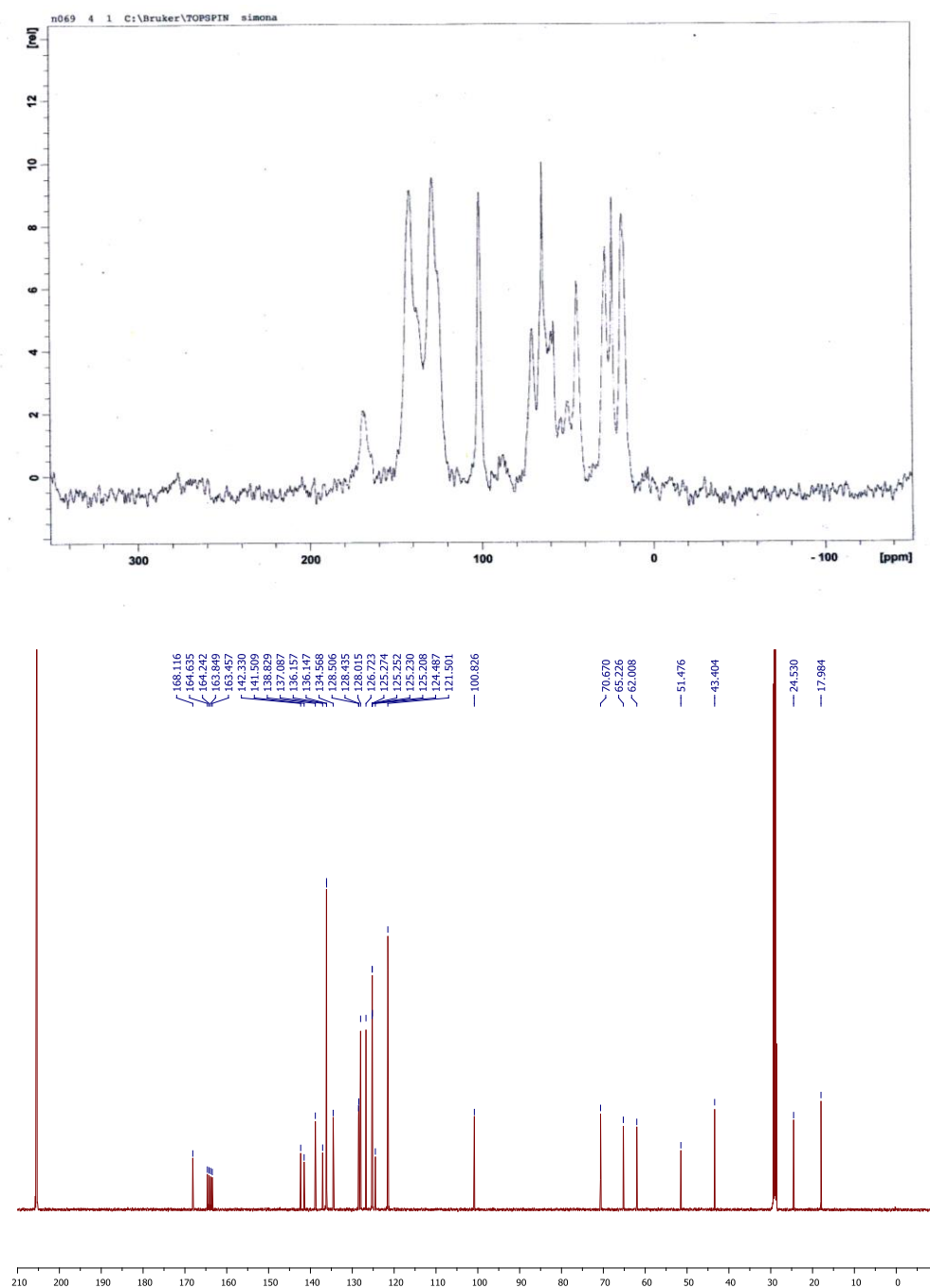


Figure S2

Zeolite Y, which belongs to the class of faujasites (naturally occurring mineral zeolite), consists of regular 12 Å cubo-octahedron or sodalite supercages consisting of 24 tetrahedra of either SiO_4^{4-} or AlO_4^{5-} connected through their 8 Å hexagonal faces (Figure).



Figure S3. Zeolite Y

MCM-41 is an amorphous mesoporous silica consisting of one-dimensional hexagonal channels formed by rod-shaped surfactant templates (Figure). MCM channels are much larger than those of zeolites, with diameters between 15 and 100 Å, depending on the surfactant used in their preparation.

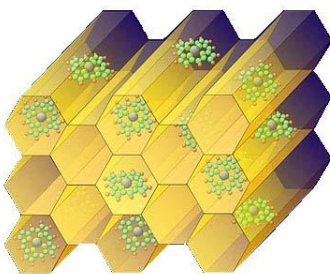


Figure S4. MCM

General experimental detail

All infra red spectra were acquired using thin film spectra on sodium chloride plates using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer.

All ^1H and ^{13}C NMR spectra were measured at 300 MHz with a Varian Gemini 2000 spectrometer, and at 400 MHz with a Varian Unity+ spectrometer. CDCl_3 with TMS (tetramethylsilane) as the internal reference was used as the solvent (unless stated otherwise).

Mass spectra were recorded using a Jeol-SX102 instrument with electron impact (E.I.) and fast atom bombardment (F.A.B.). The EPSRC national mass spectrometry service at the University of Wales, Swansea, utilizing electrospray (E.S.) ionization was also used.

Optical rotation measurements were obtained using a B&S ADP-440 spectrometer, operating at a wavelength (λ) of 589 nm and corresponding sodium line (D) at the temperatures indicated. All solvents used were spectrophotometric grade and the samples were prepared using volumetric flasks.

A Büchi B-545 melting point instrument was used to record melting points.

Microanalyses were performed on a Perkin-Elmer Elemental Analyser 2400 CHN at Loughborough University.

Flash chromatographic procedures were performed using Merck Kieselgel silica gel 60 (70-230 mesh). Reactions were monitored using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel gel 60 F254 silica gel. Visualization of plates was performed by UV radiation at a wavelength (λ) of 254 nm, or staining by an ethanolic solution of phosphomolybdic acid (acidified using concentrated sulphuric acid) dip, followed by charring where appropriate.

Reactions performed under anhydrous conditions used glassware dried at 150 °C overnight and under a nitrogen atmosphere. Reaction solvents were obtained commercially dry, except dichloromethane which was distilled from calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical.

Enantiomeric excesses were determined by either proton nuclear magnetic resonance spectroscopy (^1H -NMR), or by chiral reverse phase high performance liquid chromatography (Chiral RP-HPLC). Nuclear magnetic resonance spectra were recorded on a Varian Unity+ 400 MHz spectrometer in the presence of europium (III) tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as the chiral shift reagent and tetramethylsilane as the internal standard.