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Catalytic Asymmetric Epoxidation of Unfunctionalised Olefins using Silica, LDH and Resin-Supported Sulfonato-Mn(salen) Complex

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Abstract: Sulfonated chiral Mn(salen) catalyst immobilised onto various supports such as silica, LDH and resin afforded remarkably higher rates and ees of up to 96% for the asymmetric epoxidation of unfunctionalised olefins. The LDH and resin supported (*R,R*)-**1** catalysts were recovered quantitatively by simple filtration and reused for several times with consistent ees and insignificant loss of activity.

Keywords: chiral epoxides; enantiomeric excess; LDH; resin; silica; sulfonated chiral Mn(salen) catalyst

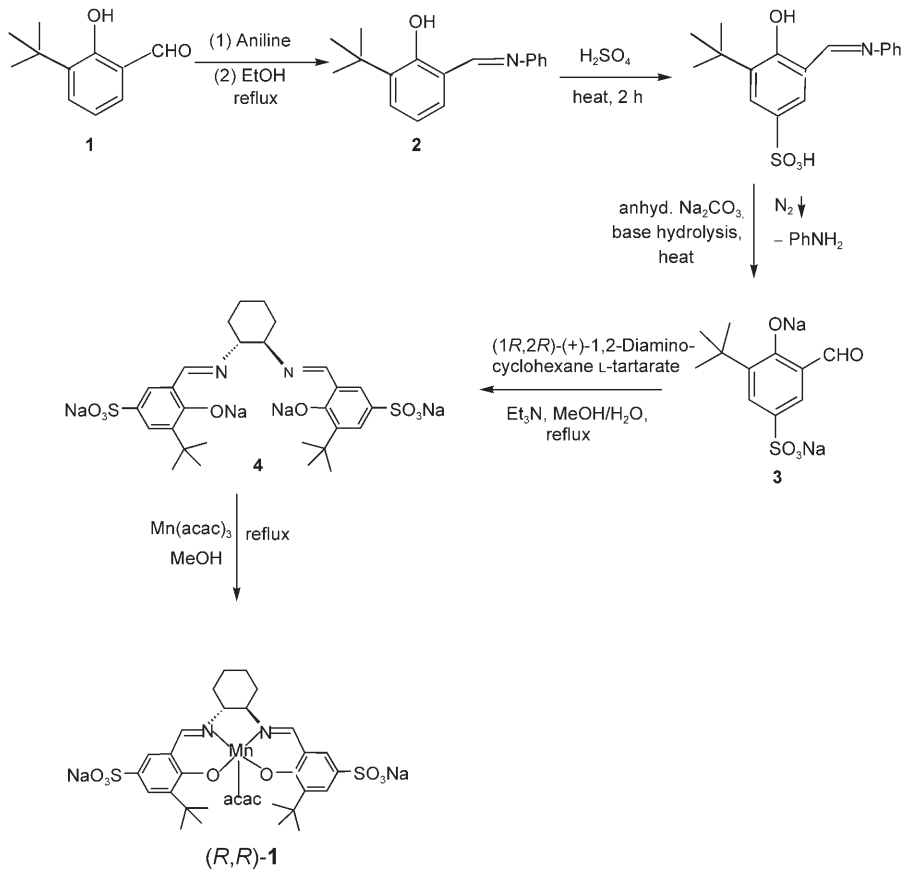
Introduction

The increasing demand of the chemical and pharmaceutical industries for enantiomerically pure compounds has prompted the development of several chirotechnologies which aim to exert the ultimate control over a chemical reaction by directing its enantioselectivity (ee). Due to the importance of chiral epoxides, asymmetric epoxidation (AE) has become a useful preparative method in organic synthesis.[1] Chiral Mn(salen) complexes developed by Jacobsen, Katsuki, and coworkers are effective catalysts for AE of olefins with high levels of enantioselectivity.[2,3] However, such homogeneous catalysts are not easily recovered for reuse. In contrast, the immobilisation of transition metal complexes on solid supports can provide catalysts that are easier to handle and sometimes exhibit improved activities and selectivities induced by the support.[4]

A number of groups have tried to immobilise chiral salen complexes on various supports.[5] Salvadori's group reported a chiral Mn(salen) complex immobilised on silica gel for the AE of olefins with moderate ees for the first time.[6a] Chiral Mn(salen) containing sulfonic anions and devoid of *t*-butyl moieties intercalated into Zn^{II}-Al^{III} LDH were used for the epoxidation of *R*-(+)-limonene to give 80% selectivity and 34% de.[6b] Polymer-supported, Katsuki-type catalysts afforded consistently excellent ees, but with decreased yields in the AE of 1,2-dihydronaphthalene.[6c] Chiral Mn(salen) catalysts immobilised in porous materials *via* phenylsulfonic spacer groups were effective catalysts in the AE of α-methylstyrene and *cis*-β-methylstyrene.[6d] We report herein the immobilisation of the chiral sulfonated Mn(salen) complex onto various supports without any spacer groups and their evaluation in the AE of unfunctionalised olefins. For this purpose, we have incorporated ionic sodium salts of sulfonyl groups at the 5 and 5′ positions of the chiral salen ligand, which enables facile heterogenisation onto a variety of supports such as silica gel, LDH, and resin. This sulfonated Mn(salen) complex (*R,R*)-**1** is grafted on silica gel through weak hydrogen bonding. Although the silica-supported Mn(salen) complex gives excellent ees, there is leaching of Mn from the support. To overcome this leaching problem, we have prepared LDH- and resin-supported (*R,R*)-**1**, which indeed show consistent activity and enantioselectivity in the AE of unfunctionalised olefins.

Results and Discussion

The preparation of the catalyst (*R,R*)-**1** is shown in Scheme 1. The approach to ligand **4** requires sulfonation of the known compound **2** and then coupling with the (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartarate. Sulfonation of protected aldehyde **2** selectively gave *para*-sulfonated compound **3**, as confirmed by ^{1}H NMR. Ligand **4** was successfully converted into its Mn complex



Scheme 1. Synthesis of (*R*,*R*)-**1**.

(*R*,*R*)-**1** by treatment with $Mn(acac)_3$ in methanol. This sulfonated Mn(salen) complex was readily anchored on the silica support by refluxing in acetonitrile overnight to give a brown heterogeneous complex silica-(*R*,*R*)-**1**. Mg-Al-Cl-LDH was prepared according to the reported procedure.[7] Sulfonated (*R*,*R*)-**1** anion was ion exchanged onto LDH and quaternary ammonium groups covalently bound to modified resin to obtain LDH-(*R*,*R*)-**1** and resin-(*R*,*R*)-**1** catalysts, respectively.

All of these catalysts were characterised by FT-IR, PXRD, MS, AAS and CHNS analysis. The homogeneous (*R*,*R*)-**1** exhibits IR bands at 1040 cm^{-1} and 1118 cm^{-1} associated with the symmetric and anti-symmetric stretching modes of the SO_3^- moiety, together with other IR bands at 1624 cm^{-1} (CH=N), 1540 cm^{-1} (C–O), 570 cm^{-1} (Mn–O) and 410 cm^{-1} (Mn–N), which were retained in the anchored complexes with slight displacements, confirming the successful immobilisation of (*R*,*R*)-**1** on to the supports.[8] In activated silica, the absorption band at 3490 cm^{-1} indicates hydroxy groups of isolated silanols. The absorption band at 3464 cm^{-1} in silica-(*R*,*R*)-**1** gave evidence for the $-SO_3$...HOSi interaction between (*R*,*R*)-**1** and silica. These results demonstrate that the catalyst (*R*,*R*)-**1** was anchored on to silica through hydrogen bonding. Zwitterionic Rh(I) catalysts containing sulfonated group have been grafted on to a high surface-area silica using an immobilisation procedure based on the capability of the sulfonated tail of the sulfonyl unit to link to the silanol groups of the support *via* hydrogen bonding.[9] Our strategy for such supported, hydrogen-bonded catalysts is slightly different because the sodium salts of the sulfonated complexes are not zwitterionic in nature.

X-ray diffraction of the powdered sample of LDH-(*R*,*R*)-**1** shows the same pattern characteristic of LDH.[10] No new significant peaks were observed in the XRD pattern corresponding to an insoluble Mg or Al salt that would indicate the formation of new phases. X-ray powder diffraction patterns of the initial LDH and LDH-(*R*,*R*)-**1** hardly differ in the range of $2\theta = 3^\circ - 65^\circ$. The d_{003} reflection corresponds to the interlamellar distance plus the thickness of mineral sheet (4.8 Å). Since no new phase is detected clearly in the XRD pattern, the intercalation must proceed homogeneously by local structural distortion of the layers, resulting in an irregular stacking of the individual layers within the crystal structure.[11] The possible structures for the catalysts are depicted in Figure 1. The Mn contents in silica-(*R*,*R*)-**1**, LDH-(*R*,*R*)-**1**, and resin-(*R*,*R*)-**1** were found to be 0.036 $mmol \cdot g^{-1}$, 0.076 $mmol \cdot g^{-1}$ and 0.1 $mmol \cdot g^{-1}$, respectively by atomic absorption spectroscopy (AAS).

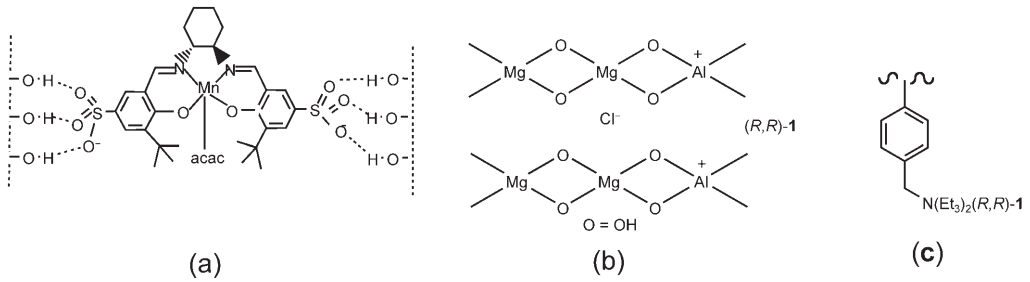
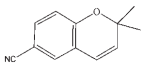
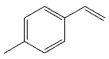


Figure 1. The structures of (**a**) silica-(*R,R*)-**1**, (**b**) LDH-(*R,R*)-**1**, and (**c**) resin-(*R,R*)-**1**.

Table 1. Asymmetric epoxidation of unfunctionalised olefins.

Entry	Olefin	Method[a]	Time [min]	Yield [%]	ee [%]
1		A	<5	100 (100, 90, 75)[b]	89 (85, 79, 56)[b]
		B	<5	100 (100, 94, 79, 75)[b]	95 (91, 71, 50, 45)[b]
		C	<5	100 (100, 95, 92, 85)[b]	94 (94, 94, 93, 92)[b]
		D	<5	100 (100, 96, 90, 88)[b]	96 (96, 96, 96, 96)[b]
2		A	<5	100	92
		B	<5	100	94
		C	<5	100	93
		D	<5	100	97
3		A	<10	100	25
		B	10	100	40
		C	<5	100	44
		D	<5	100	48
4		A	<10	100	26
		B	10	100	30
		C	<5	100	31
		D	<5	100	33
5		A	60	100	18
		B	120	100	42
		C	<5	100	29
		D	<5	100	35

[a] Method A – *reaction conditions:* (*R,R*)-**1** (1 mol %), olefin (1 mmol), NMO (5 mmol), *m*-CPBA (3 mmol), CH_3CN (3 mL) at −20 °C; Method B – *reaction conditions:* silica-(*R,R*)-**1** (1 mol %), olefin (1 mmol), NMO (5 mmol), *m*-CPBA (3 mmol), CH_3CN (3 mL) at −20 °C; Method C – *reaction conditions:* LDH-(*R,R*)-**1** (1 mol %), olefin (1 mmol), NMO (5 mmol), *m*-CPBA (3 mmol), CH_3CN (3 mL) at −20 °C; Method D – *reaction conditions:* resin-(*R,R*)-**1** (1 mol %), olefin (1 mmol), NMO (5 mmol), *m*-CPBA (3 mmol), CH_3CN (3 mL) at −20 °C.

[b] Values in parenthesis correspond to the recycling experiments.

The AE reactions of 6-cyanochromene, indene, *trans*-stilbene, styrene and 4-methylstyrene catalyzed by Mn(III) salen complexes (*R,R*)-**1** and silica (*R,R*)-**1**, LDH-(*R,R*)-**1**, and resin-(*R,R*)-**1** catalysts conducted in acetonitrile gave epoxides in quantitative yields and up to 96% ees using *m*-CPBA as oxidant and NMO as axial base (Table 1). With indene as the substrate the ee achieved is 94% as against 38% for a chiral Mn(salen) catalyst attached to silica *via* a covalent linker.[6a] The products were analyzed by ^{1}H NMR and ee values were determined by HPLC using a Chiracel OD-H column. The reaction rates are higher even with 1 mol % of catalyst.

In heterogeneous recycling experiments, silica-(*R,R*)-**1** shows a decrease in yield and ee for each cycle, in contrast, the LDH-(*R,R*)-**1** and resin-(*R,R*)-**1** catalysts recovered quantitatively by simple filtration exhibit slight decrease in activity and consistent ee. The leaching of

the metal after the first cycle was determined by AAS and it was found to be 33% in silica-(*R,R*)-**1** and was negligible in LDH-(*R,R*)-**1** and resin-(*R,R*)-**1**. The insignificant leaching of the Mn into solution is attributed to the strong ionic bond between the complex and support.

The homogeneous catalyst (*R,R*)-**1** produces chiral epoxides in quantitative yields and the ees are 89% for 6-cyanochromene, 18% for *trans*-stilbene and 25% for styrene. Immobilisation of the catalyst (*R,R*)-**1** on silica, LDH and resin results in similar yields but the ee values are higher than for the homogeneous counterparts. This increase in ee values is due to the spatial constraints imposed by the immobilisation.[12]

Conclusion

In summary, an inorganic $-SO_3Na$ group has been used to immobilise a chiral Mn(salen) complex on silica, LDH, and resin for AE of unfunctionalised olefins. We have successfully prepared LDH-(*R,R*)-**1** and resin-(*R,R*)-**1** catalysts to overcome the leaching problem associated with silica-(*R,R*)-**1**. We found that resin-(*R,R*)-**1** is an efficient catalyst and can be reused for 5 cycles with consistent ees.

Experimental Section

All chemicals were purchased from Aldrich and were used as received. 2-*tert*-Butylsalicylaldehyde was prepared by following a reported literature procedure starting from 2-*tert*-butylphenol.[13] All solvents used were analytical grade and used as received from Merck India Pvt. Ltd. Commercial column chromatography grade silica gel (60–120 mesh) was first calcined at 200 °C for 6 h prior to use. No high purity nitrogen was used and all reactions were conducted at −20 °C in acetonitrile. The ^{1}H NMR spectra of samples were recorded on Varian-Unity 400 MHz, and Bruker-Avance-300 MHz spectrometers using TMS as an internal standard in $CDCl_3$. IR spectra were recorded on a Perkin Elmer instrument. The positive and negative ion electrospray mass spectra (ES-MS) were recorded on a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK). X-ray powder diffraction (PXRD) data were collected on a Siemens/D-5000 diffractometer using Cu-Kα radiation ($\lambda = 1.5405$ Å). High performance liquid chromatography (HPLC) was performed using an Agilent-1100 series liquid chromatograph equipped with a single pump and UV detector (fixed at 216 nm) using a CHIRACEL-OD-H capillary column with 2-propanol/hexane as eluting agent. For these studies, only crude reaction products were used, as the reactions were quantitative in all substrates. Optical rotations were obtained on an automated JASCO P-1020 Polarimeter, and the values were reported in absolute rotations: $[\alpha]_D^{temperature}$ [concentration *c* in g/100 mL of solvent]. Elemental analysis was carried out on an ELEMENTAR VARIO-EL CHNS analyzer.

General Procedure for the Synthesis of (*R,R*)-1

***(a) Synthesis of disodium 3-tert-butyl-salicylaldehyde 5-sulfonate* (3):**[14] 2-*tert*-Butylsalicylaldehyde (**1**; 33.7 mmol) was charged in a 100-mL round-bottomed flask containing aniline (33.7 mmol) in dry ethanol (40 mL) and the mixture stirred at reflux temperature for 20 h. Thereafter, the reaction mixture was allowed to cool to 0 °C for 1 h. Then, the solvent was removed under reduced pressure to obtain protected aldehyde **2** as a brownish yellow oil; yield: 8.5 g (>99%).

This compound was charged in a 100-mL round-bottomed flask containing five times its weight of concentrated sulfuric acid, which gave upon stirring a clear orange solution. This solution was heated for 2 h at 105–110 °C. Then the reaction mixture was allowed to cool at 0 °C for 30 min, then ice-pieces were added to induce crystallisation of *N*-phenyl-3-*tert*-butylsalicylaldimine-5-sulfonic acid, which was then filtered, washed with small quantities of ice-water to remove excess sulfuric acid and then dried under vacuum to afford the sulfonated aldehyde product as yellow powder; yield: 8.0 g (73%).

The deprotection was executed by a simple base hydrolysis by dissolving the compound in boiling distilled water (200 mL), and then anhydrous sodium carbonate was added in small portions until the evolution of carbon dioxide ceased. This mixture was then heated to boiling and nitrogen gas was passed continuously to remove aniline. This process was repeated several times until the water vapour showed no alkaline response to pH paper while maintaining the volume of the water constant by adding more water if and when needed. Then, the aqueous solution was evaporated to dryness under reduced pressure, and the residue washed with chloroform (300 mL) to remove organic impurities. Then the crude compound was redissolved in a small amount of boiling water and precipitated with THF as yellow powder. This bright yellow coloured disodium 3-*tert*-butyl-salicylaldehyde-5-sulfonate (**3**) (7.5 g; yield: 97%) was dried under vacuum and used without further purification. ^{1}H NMR (400 MHz, D_2O): $\delta = 9.95$ (s, 1H), 7.66 (d, 1H, $J = 2.3$ Hz), 7.55 (d, 1H, $J = 2.3$ Hz), 1.22 (s, 9H); ES-MS: (negative): $m/z = 257$ $[(M-2\ Na)+H]^-$; anal. calcd. for $C_{11}H_{12}SO_5Na_2$: C 43.7, H 3.9, S 10; found: C 43.5, H 3.85, S 9.1.

***(b) Synthesis of chiral ligand* 4:** The compound **3** (2.6 mmol) was charged in a round-bottomed flask containing methanol (50 mL). To the reaction mixture (1*R*,2*R*)-(+)-diaminocyclohexane L-tartarate (1.6 mmol) and triethylamine (5 mL) were added and the mixture stirred at room temperature for 17 h. Then, the reaction mixture was filtered to remove the triethylamine salt of tartaric acid. Then the filtrate was concentrated under reduced pressure and washed with chloroform to obtain the bright yellow-coloured product **4**; yield: 550 mg (81%).^{1}H NMR (300 MHz, D_2O): $\delta = 8.49$ (s, 1H), 8.58 (s, 1H), 7.86 (d, 1H, $J = 2.1$ Hz), 7.64 (d, 1H, $J = 2.1$ Hz), 7.78 (d, 1H, $J = 3.4$ Hz), 7.75 (d, 1H, $J = 3.4$ Hz), 2.9–3.1 (m,1H), 2.75–2.91 (m,1H), 1.1–2.1 (m, 8H), 1.45 (s, 9H), 1.41 (s, 9H); ^{13}C NMR (300 MHz, D_2O, dioxane as internal standard): $\delta = 169.23$, 165.44, 167.11, 167.01, 140.74, 140.47, 134.04, 133.75, 130.09, 129.09, 118.89, 118.48, 70.75, 70.26, 68.21, 36.20, 33.34, 33.34, 30.45, 25.42; IR (KBr): $\nu = 1626$, 1540,1118, 1039 cm^{-1}; ES-MS (negative): $m/z = 651$, 593, 353, 296; $[\alpha]_D^{25}$: −165.2 (c 0.01, H_2O); anal. calcd. for $C_{28}H_{34}N_2O_8Na_4S_2 \cdot 2\,H_2O$: C 46.79, H 5.29, N 3.89; found: C 46.62, H 5.13, N 3.80.

(c) Synthesis of (R,R)-1: The compound **4** (0.450 g) was charged in a 100-mL round-bottomed flask containing methanol (15 mL) and $Mn(acac)_3$ (0.230 g) and the mixture stirred at

reflux temperature for 12 h. Then the reaction mixture was filtered and the precipitate was washed with dichloromethane (50 mL) to remove unreacted $Mn(acac)_3$. Thereafter the solid was collected and dried under vacuum to afford the brown-coloured compound (*R,R*)-**1**; yield: 71%. The ^1H NMR spectrum of (*R,R*)-**1** is featureless due to its paramagnetism. ES-MS (positive): $m/z = 691$ $[M-acac]^+$; ES-MS (negative): $m/z = 645$ $[M-(acac+2\ Na)]^-$; IR (KBr): $\nu = 1634$, 1528, 1110, 1041 cm^{-1}; $[\alpha]_D^{25}$: -497 (*c* 0.01, H_2O); anal. calcd. for $C_{33}H_{41}N_2O_{10}Na_2S_2Mn$: C 50.12, H 5.18, N 3.54; found: C 49.5, H 5.24, N 3.25.

Preparation of Silica-(*R,R*)-1

150 mg of (*R,R*)-**1** were suspended in 100 mL of acetonitrile and sonicated for one hour at room temperature. To this suspension, activated silica gel (3.0 g; preheated at 200 °C for 2 h) was added and the mixture refluxed for 24 h. The resultant silica gel was centrifuged and washed several times with acetonitrile until the colour of the supernatant solution disappeared. The solid catalyst was dried at room temperature. The Mn content in the heterogeneous catalyst was found to be 0.036 mmol·g^{-1} by AAS. IR (KBr): $\nu = 3464$, 1624, 1540, 570, 410 cm^{-1}.

Preparation of LDH-(*R,R*)-1

100 mg of (*R,R*)-**1** were dissolved in 10 mL of deionised-decarbonated water and sonicated for one hour at room temperature under nitrogen. To this solution, Mg-Al-Cl hydrotalcite (1.0 g) was added, and the mixture stirred at 25 °C for 12 h under a nitrogen atmosphere. The resultant exchanged LDH was centrifuged and washed several times with 100 mL of deionised-decarbonated water, 50 mL of acetonitrile and 10 mL of acetone. The solid catalyst was then dried at room temperature. The Mn content in the heterogeneous catalyst was found to be 0.076 mmol·g^{-1} by AAS. IR (KBr): $\nu = 1625$, 1542, 554, 418 cm^{-1}.

Preparation of Resin-(R,R)-1

The resin was obtained by quaternisation of triethylamine (1.05 mL) with 0.5 g of chloromethylated styrene-divinylbenzene copolymer (Merrifield resin, 2% cross-linked, 200–400 mesh, *ca.* 2 mmol·g^{-1} Cl, Aldrich) in chloroform (10 mL) under reflux for 24 h. 0.5 g of quaternary ammonium resin were suspended in 10 mL of water containing 100 mg of (*R,R*)-**1**. This mixture was stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 100 mL of water, 50 mL of acetonitrile, and 10 mL of methanol and finally vacuum-dried to obtain resin-(*R,R*)-**1**. The Mn content was found to be 0.1 mmol·g^{-1} by AAS. IR (KBr): $\nu = 1644$, 1556, 578, 421 cm^{-1}.

Epoxidation of Olefins under Homogeneous Conditions

A mixture of 6-cyanochromene (1 mmol, 0.1852 g), NMO (5 mmol, 0.537 g), (*R,R*)-**1** (0.008 g, 1 mol %) and *m*-CPBA (3 mmol, 0.518 g) in acetonitrile (3 mL) was stirred at −20 °C for the appropriate time (entry 1, Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was concentrated and 10 mL of dichloromethane were added, the catalyst was extracted into the aqueous layer which was concentrated and reused for another cycle. The organic layer was washed with saturated sodium hydroxide and brine to remove *m*-CPBA and dried over anhydrous sodium sulfate. The crude product was analysed by HPLC without any further purification. The advantage of this system is no flash column chromatography is needed after the reaction in homogeneous conditions and the homogeneous catalyst was reused for four cycles by concentrating the aqueous layer.

Epoxidation of Olefins under Heterogeneous Conditions

A mixture of 6-cyanochromene (1 mmol, 0.1852 g), NMO (5 mmol, 0.537 g), silica-(*R,R*)-**1** (0.300 g, 1 mol %) and *m*-CPBA (3 mmol, 0.518 g) in acetonitrile (3 mL) was stirred at −20 °C for the appropriate time (entry1, Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was centrifuged to separate the catalyst which was reused for another cycle. Acetonitrile was removed from the resultant solution under reduced pressure, 10 mL of dichloromethane were added, the mixture was washed with saturated sodium hydroxide and brine to remove *m*-CPBA and dried over anhydrous sodium sulfate. The crude product was analysed by HPLC without any further purification. The same procedure was followed for the reactions with LDH-(*R,R*)-**1** (0.100 g) and with resin-(*R,R*)-**1** (0.050 g).

Acknowledgements

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