Electronic Supplementary Information (ESI) for

Heterogeneous enantioselective synthesis of chromans via the oxa-Michael-Michael cascade reaction synergically catalyzed by grafted chiral bases and inherent hydroxyls on mesoporous silica surface

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Figures and illustrations

**Fig. S1** XRD pattern of SBA-15-SH.

**Fig. S2** N\(_2\) adsorption-desorption isotherms of SBA-15-SH (left) and the corresponding pore size distribution (right).

**Fig. S3** HRTEM images of SBA-15-SH.
Fig. S4 $^{13}$C CP/MAS NMR spectra of

a) SBA-Py, b) SBA-MPy, c) SBA-Py-Py, d) SBA-Py-Diph.
Fig. S5 Vacuum FT-IR images of a) SBA-15-SH, b) Py-Diph, c) SBA-Py-Diph and d) SBA-Py-Diph-CH$_3$

Compared with SBA-SH (Fig. S5a), the appearance of the bands at 1630 and 710 cm$^{-1}$ for SBA-Py-Diph (Fig. S5c), which are attributed to characteristic bands of benzene ring in Py-Diph (Fig. S5b), confirming the immobilization of chiral amine. Moreover, the decrease of Si-OH at 3394 cm$^{-1}$ [1,2] for SBA-Py-Diph-CH$_3$ (Fig. S5d) indicates that most of the hydroxyls were capped.
**Fig. S6** XRD patterns of

a) SBA-Py, b) SBA-MPy, c) SBA-Py-Py, d) SBA-Py-Diph.

**Fig. S7** N\textsubscript{2} adsorption-desorption isotherms of a) SBA-Py, b) SBA-MPy, c) SBA-Py-Py, d) SBA-Py-Diph and the corresponding pore size distribution.
Fig. S8 HRTEM images of
a) SBA-Py, b) SBA-MPy, c) SBA-Py-Py, d) SBA-Py-Diph
For SBA-15-SH (Fig. S9a), the first step from room temperature to 100 °C corresponds to the removal of the surface adsorbed water (7%). The second step in the temperature range from 150 to 600 °C involves the dehydroxylation of silica and the decomposition of the -SH \(^3\) (11%). While after grafting (Fig. S9b), the second step (18%) also contains the decomposition of grafted Py-Diph. Based on the differential on this weigh loss, the content of organic species was thus calculated to be 0.511 mmol/g, showing a good accordance with the element analysis result of 0.504 mmol/g.
The resonances attributed to the silicon in Q₄ [Si(SiO)₄] and Q₃ [Si(SiO)₃OH] linkages are observed at -110 and -100 ppm. The resonances attributed to the silicon connected the organic functional groups linkages (Tₙ) are observed at -68 and -50 ppm. The silanol density could be quantified by the curve fitting and deconvolution of $^{29}$Si MAS NMR signals according to the following calculated formula:[5]

$$\text{Silanol density (}\mu\text{mol} \cdot \text{g}^{-1}) = \sum W_{Qn} \cdot M_{Qn} + \sum W_{Tm} \cdot M_{Tm} + \sum W_{Si(CH3)_3} \cdot M_{Si(CH3)_3}.$$  

Wherein W represents the peak area percentage and M represents the molar mass of Qₙ, Tₙ, and Si(CH₃)₃ (n=3, 4 and m=2, 3). The molar fractions of Q₄, Q₃, T₂, and T₃ sites are 34.20%, 29.47%, 6.42% and 29.91% respectively from Fig. S8. So the density of OH is calculated to be 9.43 $\mu$mol/m².

**Fig. S10** $^{29}$Si MAS NMR spectrum of SBA-15-SH
In order to explore the role of surface silanols, we cap the hydroxyls of all the heterogeneous catalyst by post-modification with -Si(CH$_3$)$_3$ groups. Taking SBA-Py-Diph-CH$_3$ for example, as shown in the $^{29}$Si CP/MAS NMR spectra, the resonance assigned to the -Si(CH$_3$)$_3$ groups appears at 13 ppm. Moreover, the intensity of Q$_3$ decreases and Q$_4$ increases, further confirming the successful silylation of surface silanols.

Fig. S11 $^{29}$Si MAS NMR spectra of a) SBA-Py-Diph, and b) SBA-Py-Diph-CH$_3$

Fig. S12 XRD patterns of the reused catalyst SBA-Py-Diph.
Fig. S13 N$_2$ adsorption-desorption isotherm of the reused SBA-Py-Diph and the corresponding pore size distribution.

Fig. S14 HRTEM images of the reused SBA-Py-Diph.
### Tables and illustrations

**Table S1** Textural parameters of the thiol-functionalized mesoporous silica and the chiral amine grafted catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{100}) (nm)</th>
<th>Pore size(^{[a]}) (nm)</th>
<th>(S_{BET}) (m(^2)g(^{-1}))</th>
<th>Pore volume (cm(^3)g(^{-1}))</th>
<th>Wall Thickness(^{[b]}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-SH</td>
<td>9.58</td>
<td>6.28</td>
<td>517</td>
<td>0.636</td>
<td>1.65</td>
</tr>
<tr>
<td>SBA-Py</td>
<td>9.70</td>
<td>6.28</td>
<td>487</td>
<td>0.544</td>
<td>1.71</td>
</tr>
<tr>
<td>SBA-MPy</td>
<td>9.68</td>
<td>6.28</td>
<td>479</td>
<td>0.527</td>
<td>1.70</td>
</tr>
<tr>
<td>SBA-Py-Py</td>
<td>10.02</td>
<td>6.28</td>
<td>443</td>
<td>0.455</td>
<td>1.87</td>
</tr>
<tr>
<td>SBA-Py-Diph</td>
<td>10.20</td>
<td>6.28</td>
<td>402</td>
<td>0.408</td>
<td>1.96</td>
</tr>
<tr>
<td>SBA-Py-Diph(^{[c]})</td>
<td>10.17</td>
<td>6.27</td>
<td>411</td>
<td>0.50</td>
<td>1.95</td>
</tr>
</tbody>
</table>

\(^{[a]}\) pore size at the maximum distribution; \(^{[b]}\) estimated as the difference between the parameter \(a\) from XRD patterns and the pore size from \(N_2\) sorption; \(^{[c]}\) used for 5 runs.

**Table S2** The density of chiral basic sites and the ratio of silanol to basic sites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N content/mass (mmol/g)</th>
<th>N content/area (μmol/m(^2))</th>
<th>Basic sites (μmol/m(^2))</th>
<th>Acid/base sites (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-Py</td>
<td>0.771</td>
<td>1.610</td>
<td>1.610</td>
<td>5:1</td>
</tr>
<tr>
<td>SBA-MPy</td>
<td>0.684</td>
<td>1.340</td>
<td>1.340</td>
<td>7:1</td>
</tr>
<tr>
<td>SBA-Py-Py</td>
<td>0.521</td>
<td>1.052</td>
<td>1.052</td>
<td>9:1</td>
</tr>
<tr>
<td>SBA-Py-Diph</td>
<td>0.504</td>
<td>0.943</td>
<td>0.943</td>
<td>10:1</td>
</tr>
<tr>
<td>SBA-Py-Diph(^{[a]})</td>
<td>0.499</td>
<td>0.876</td>
<td>0.876</td>
<td>11:1</td>
</tr>
</tbody>
</table>

\(^{[a]}\) used for 5 runs.
Experimental

Materials

All commercial chemicals were used as received without further purification if not specially indicated. The anhydrous solvents such as toluene and THF were obtained by a standard method.

Characterization

Powder X-ray diffraction (XRD) patterns were carried out on a Bruker D8 focus X-ray diffractometer with Cu Kα radiation (30 mA, 45 kV). Nitrogen adsorption desorption experiments were obtained at on a Quantachrome Autosorb-1 system. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The mesopore size distribution was calculated using the Barret-Joyner-Halenda (BJH) method from the desorption branches of nitrogen isotherms. High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL 2100 transmission electron microscopy operated at 300 kV. The solid state NMR experiments were carried out on a Bruker Avance 300 MHz solid-state spectrometer with a commercial 4 mm MAS NMR probe at frequencies of 75.5 and 59.6 MHz for 13C CP/MAS and 29Si MAS. 1H and 13C NMR spectra were acquired on Bruker Avance 400 MHz NMR spectrometer. HPLC analysis was performed on a Varian Prostar 210 HPLC with Prostar 325 UV-Vis detector. Elemental analysis of N was performed using a VarioEL (Elmentar Analysen systeme Gmbh) elemental analyzer. Vacuum FT-IR spectra were recorded using a Nicolet 380 (Thermo) spectrophotometer in the range of 4000-300 cm⁻¹ with 1 cm⁻¹ resolution with with the pristine sample pellets treated in vacuum for 6h. Thermogravimetric analysis and differential thermal analysis (TG-DTA) were carried out on a Pyris Diamond TG/DTA thermal analysis system by PerkinElmer Instrument.
Catalyst Preparations

**SBA-15-SH:** The synthesis was performed according to the reported procedure\(^6\) with a molar ratio of TEOS: Surfactant: HCl: H\(_2\)O equal to 1: 0.017: 6: 140. Organosilane 3-mercaptopropyltrimethoxysilane, as the source of thiol groups, was introduced into the mixture with a molar ratio percentage of MPTMS/(MPTMS+TEOS) equal to 20%. A certain amount of P123, as template, was dissolved slowly in a mixture of water and 2 M hydrochloric acid (36-38%) aqueous solution at room temperature. Then TEOS was added dropwise into the mixture at 40°C, followed by the addition of MPTMS 45 min later. After strong stirring for another 20 h, the mixture was removed into Teflon-lined autoclaves and aged for 48 h at 140°C. The resulting solid was filtered and washing with water and ethanol. The template (P123) was removed by the extraction method with anhydrous ethanol at 70°C for 24 h for three times. The final white solid was obtained after drying overnight at 40°C in atmosphere, denoted as SBA-15-SH.

**(S)-2-Allyloxymethyl-1-methyl-pyrrolidine (abbreviated as MPy)**:\(^7\) A solution of N-methyl-L-prolinol (0.576 g, 5 mmol) in anhydrous THF (20 mL) was added dropwise to a suspension of NaH (60% mineral oil, 434.05 mg, 10.84 mmol) in anhydrous THF (10 mL) at 0°C under nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h. Then 18-crown-6 (131.74 mg, 0.5 mmol) and allyl bromide (1.10 ml, 12.46 mmol) were then added simultaneously. The mixture was stirred for 1 h at ambient temperature, and then at 50°C overnight. After cooling to ambient temperature, water (100 mL) was added. The aqueous phase was extracted with hexane in order to remove the unreacted allyl bromide. The organic phase was dried using MgSO\(_4\) and concentrated under reduced pressure to give the desired product. The crude product was directly purified by silica gel chromatography.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=5.96-6.06\) (m, 1H, -CH=CH\(_2\)), 5.14-5.19 (m, 2H, -CH=CH\(_2\)), 3.94-3.97 (m, 2H, -OCH\(_2\)CH=), 3.64-3.68(m, 1H, -OCH\(_2\)CH-), 3.35-3.45 (m, 1H, \(\alpha\)-CH Pro), 3.02-3.05 (m, 2H, \(\alpha\)-CH Pro), 1.66-1.95 (m, 4H, \(\beta\)-CH\(_2\) Pro).

The synthesis of (S)-2-Allyloxyethyl-pyrrolidine (abbreviated as Py) and (S)-2-(Allyloxy-diphenyl-methyl)-pyrrolidine (abbreviated as Py-Diph) adopted the same
method as described above.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=5.86-5.96\) (m, 1H, -CH=CH\(_2\)), 5.11-5.22 (m, 2H, -CH=CH\(_2\)), 3.92-4.02 (m, 2H, -OCH\(_2\)CH=), 3.20-3.28 (m, 1H, -OCH\(_2\)CH=), 3.35-3.45 (m, 1H, \(\alpha\)-CH Pro), 2.85-3.05 (m, 2H, \(\alpha\)-CH Pro), 1.60-1.90 (m, 4H, \(\beta\)-CH\(_2\) Pro).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=7.30-7.70\) (m, 10H, C\(_6\)H\(_5\)-), 5.86-5.96 (m, 1H, -CH=CH\(_2\)), 5.05-5.22 (m, 2H, -CH=CH\(_2\)), 3.90-3.97 (m, 2H, -OCH\(_2\)CH=), 3.02-3.07 (m, 1H, -OCH\(_2\)CH=), 3.45-3.55 (m, 1H, \(\alpha\)-CH Pro), 2.65-2.75 (m, 2H, \(\alpha\)-CH Pro), 1.80-2.00 (m, 4H, \(\beta\)-CH\(_2\) Pro).

(S)-(5-Allyloxy-pyrrolidin-2-yl)-pyrrolidin-1-yl-methanone (abbreviated as Py-Py): Py-Py was obtained through the esterification reaction between N-tert-Butoxycarbonyl-(S)-5-Allyloxy-pyrrolidine-2-carboxylic acid and pyrrolidine. N-tert-Butoxycarbonyl-(S)-5-allyloxy-pyrrolidine-2-carboxylic acid was first synthesized using the similar synthesis method for Mpy with the additional acidified procedure. After the removing of the unreacted allyl bromide, the aqueous phase was acidified to pH 2-3 by adding a solution of NaHSO\(_4\) (2 M), and was then extracted with ethyl acetate. The organic phase was dried using MgSO\(_4\) and concentrated under reduced pressure to give the desired product. The crude product was directly purified by silica gel chromatography.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=5.86-5.96\) (m, 1H, -CH=CH\(_2\)), 5.17-5.33 (m, 2H, -CH=CH\(_2\)), 3.94-4.14 (m, 2H, -OCH\(_2\)CH=), 3.60-3.70 (m, 1H, \(\alpha\)-CH Pro), 2.05-2.15 (m, 1H, \(\alpha\)-CH Pro), 1.50-1.80 (m, 4H, \(\beta\)-CH\(_2\) Pro), 1.43 (s, 9H, C(CH\(_3\))\(_3\)).

Dicyclohexylcarbodiimide (DCC, 1.07g, 5.15mmol) was then added into a solution of N-tert-Butoxycarbonyl-(S)-5-Allyloxy-pyrrolidine-2-carboxylic acid (1.391g, 5mmol) in CH\(_2\)Cl\(_2\) (10 mL) under 0\(^\circ\)C and stirred for 30 min. A solution of pyrrolidine (0.366g, 5.15mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added slowly into the mixture and stirred at room temperature for 16 h under nitrogen atmosphere. Diethyl ether (25 mL) was then added into the resulting mixture to transfer the excessive DCC to the white precipitate (N,N-dicyclohexylurea, DCU), then removed by filtration. The solvent was evaporated, and then dried in vacuum. The boc group was removed in 10 mL of CH\(_2\)Cl\(_2\)/TFA (v/v=3) for 3 h. The crude product was directly purified by silica
gel chromatography.

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta=5.86-5.96 \text{ (m, 1H, -CH=CH}_2\text{), 5.17-5.33 \text{ (m, 2H, -CH=CH}_2\text{), 3.94-4.14 (m, 2H, -OCH}_2\text{CH=), 3.60-3.70(m, 1H, } \alpha-\text{CH Pro), 3.54-3.73 (m, 5H, } \alpha-\text{CH Pro), 1.50-1.80 (m, 8H, } \beta-\text{CH}_2\text{ Pro).} \]

**Chiral amines grafting:** The covalent linkage to graft the chiral amine was performed through the addition reaction between -C=C and -SH.[9] SBA-15-SH (1 g) was added into a degassed solution of each chiral amine (1.5 mmol, Py, Py-Py, Py-Diph) and AIBN (0.024 g, 0.145 mmol) in 40 ml of anhydrous toluene. The mixture was stirred at 110 °C for 72 h under nitrogen atmosphere. After cooling to the ambient temperature, the solid was filtered and washed thoroughly with toluene and CH\(_2\)Cl\(_2\). The light yellow powder was dried at 40°C in vacuum for 24 h. The resulting catalyst were denoted as SBA-R (R stands for the different chiral amine sites).

**Post-silylation of silanols:** The catalyst (500mg) was added into a degassed solution of trimethylmethoxysilane (1 ml) in 50 ml of anhydrous toluene. The mixture was stirred at 110 °C for 24 h under nitrogen atmosphere. After cooling to the ambient temperature, the solid was filtered and washed with toluene and CH\(_2\)Cl\(_2\). The light yellow powder was dried at 40°C in vacuum for 24 h. The silylated solids were denoted with a suffix “-CH\(_3\)“.

**Catalytic testing**

**Asymmetric oxa-Michael-Michael cascade reaction between 2-nitrovinyl phenol and 3-methyl-2-butenal:**[10] The heterogeneous catalysts were dried under vacuum at 100°C for 12 h prior to use. Typically, 0.1 mmol of 2-nitrovinyl phenol, 0.3 mmol of 3-methyl-2-butenal, 1.0 mL of solvent, and catalyst (20 mol\% of amine) were oscillated in a micro reaction flask at 25°C for 72 h. After removal of the catalyst by filtration, the conversion and yield were determined by \[^{1}\text{H NMR analysis with dimethyl maleate as the internal standard. The enantioselectivity was determined with HPLC. Homogeneous catalysts were also dried before to use.} \]

**Asymmetric cascade reaction between 2-(2-nitrovinyl)-phenols and 3-phenyl-2-propynal:**[11] Typically, 0.1 mmol of 2-nitrovinyl phenol, 0.12 mmol of 3-
phenyl-2-propynal, 1.0 mL of solvent, and catalyst (20 mol% of amine) were oscillated in a micro reaction flask at 25°C for 72 h. After removal of the catalyst by filtration, the conversion and yield were determined by 1H NMR analysis with dimethyl maleate as the internal standard. The enantioselectivity were determined with HPLC.

Asymmetric cascade reaction between 2-aminobenzaldehyde and β-nitrostyrolene:[12] Typically, 0.1 mmol of 2-aminobenzaldehyde, 0.12 mmol of β-nitrostyrene, 1.0 mL of solvent, and catalyst (20 mol% of amine) were oscillated in a micro reaction flask at 40°C for 72 h. After removal of the catalyst by filtration, the conversion and yield were determined by 1H NMR analysis with dimethyl maleate as the internal standard. The enantioselectivity were determined with HPLC.

Asymmetric cascade reaction between trans-2-hydroxy-β-nitrostyrene and butyraldehyde:[13] Typically, 0.1 mmol of trans-2-hydroxy-β-nitrostyrene, 0.3 mmol of butyraldehyde, 1.0 mL of solvent, and catalyst (20 mol% of amine) were oscillated in a micro reaction flask at 35°C for 48 h. After removal of the catalyst by filtration, a solution of the hemiacetal in CH2Cl2 (1 mL) and PCC (65 mg, 0.3 mmol) was stirred at ambient temperature for 20h until the completion of reaction. Then the conversion and yield were determined by 1H NMR analysis with dimethyl maleate as the internal standard. The enantioselectivity were determined with HPLC.

Catalyst was recycled easily from the reaction system by filtration. The resulting solid was thoroughly rinsed with methylene chloride and ethanol for 5 times separately and dried in vacuum at 40 °C for the recycling catalytic experiments.

Reference

6. S. Wu, Y. Han, Y. C. Zou, J. W. Song, L. Zhao, Y. Di, S. Z. Liu, F. S. Xiao,


Data of products
(3R, 4R)-2,2-Dimethyl-4-nitromethyl-chroman-3-carbaldehyde

IR: 2981, 1721, 1553, 1455, 1490, 1455, 1375, 1250, 758 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ=9.94 (s, 1H), 7.12-7.22 (m, 2H), 6.89-6.90 (m, 1H), 6.83–6.88 (m, 1H), 4.69-4.80 (m, 2H), 4.02-4.07 (m, 1H), 3.26-3.28 (d, 1H), 1.72 (s, 3H), 1.19 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ= 200.14, 152.72, 129.00, 126.90, 121.52, 118.82, 118.38, 77.71, 74.41, 57.39, 31.31, 28.46, 21.36; MS (m/z): 249(M⁺).

HPLC analysis of 2-Dimethyl-4-nitromethyl-chroman-3-carbaldehyde:

Column: CHIRALPAK-OD-H
Flow Phase: isopropanol/n-hexane (v/v=10/90)
Flow Rate: 0.8 mL/min
Detection Wavelength: 254 nm

Racemic product: t=28.81 min, 50.2%; t=34.14 min, 49.8%.

Product catalyzed by SBA-Py:
(3R,4R): t=28.19 min, 85.5%; (3R,4S): t=35.17 min, 14.5%, ee: 71%.
Product catalyzed by SBA-MPy:

(3R,4R): \( t=29.75 \text{ min}, 76.5\% \); (3R,4S): \( t=35.79 \text{ min}, 23.5\%, \text{ ee: } 53\% \).

Product catalyzed by SBA-Py-Py:

(3R,4R): \( t=29.43 \text{ min}, 90.5\% \); (3R,4S): \( t=36.18 \text{ min}, 9.5\%, \text{ ee: } 81\% \).
Product catalyzed by SBA-Py-Diph:

(3R,4R): t=28.79 min, 98%; (3R,4S): t=35.53 min, 1%, ee: 97%.

(R)-4-Nitromethyl-2-phenyl-4H-chromene-3-carbaldehyde:
IR: 2981, 2918, 2862, 1724, 1633, 1583, 1585, 1489, 1365, 1290, 1258, 1218, 1114, 800, 760, 701; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=9.59\) (s, 1H), 7.61 (d, 2H), 7.56-7.58 (m, 1H), 7.51 (t, 2H), 7.29-7.34 (m, 2H), 7.17-7.24 (m, 2H), 4.69-4.73 (m, 2H), 4.62-4.66 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta=190.22, 169.38, 150.69, 131.67, 130.60, 130.43, 129.33, 128.6, 128.5, 125.9, 119.7, 117.1, 111.5, 79.6, 32.2\); MS (m/z): 296 ([M+H]\(^+\)).

HPLC analysis of 2-Dimethyl-4-nitromethyl-chroman-3-carbaldehyde:

Column: CHIRALPAK-AS-H

Flow Phase: isopropanol/n-hexane (v/v=30/70)

Flow Rate: 0.6 mL/min

Detection Wavelength: 254 nm

Racemic product: t=24.26 min, 50.1%; t=35.33 min, 49.9%.
Product catalyzed by SBA-Py-Diph:
R: t=24.93 min, 98%; S: t=36.29 min, 2%, ee: 96%.

(R)-3-Nitro-2-phenyl-1,2-dihydro-quinoline:

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta=7.98 \text{ (s, 1H), 7.40–7.35 (m, 2H), 7.32–7.28 (m, 3H),} \\
& 7.20–7.16 \text{ (m, 2H), 6.71 (t, 1H), 6.46 (d, 1H), 5.99 (s, 1H), 4.70 (s, 1H); } \\
\text{13C NMR (101 MHz, CDCl}_3\text{): } & \delta= 144.38, 142.16, 134.13, 131.29, 131.26, 130.92, 129.01, \\
& 128.85, 128.77, 126.28, 118.65, 114.93, 113.41, 55.51. \text{ HRMS (ESI): calcd for} \\
& \text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2 \text{ [M]+ m/z 251.27; found 251.21.} \\
\text{HPLC analysis of (R)-3-Nitro-2-phenyl-1,2-dihydro-quinoline:} \\
\text{Column: CHIRALPAK-AS-H} \\
\text{Flow Phase: isopropanol/n-hexane (v/v=85/15)} \\
\text{Flow Rate: 1.0 mL/min} \\
\text{Detection Wavelength: 254 nm}
\end{align*}
\]
Racemic product: $t=13.11$ min, 49.93%; $t=16.61$ min, 50.07%.

Product catalyzed by SBA-Py-Diph:
S: $t=13.11$ min, 2%; R: $t=16.61$ min, 97%, ee: 95%.
(3R, 4S)-3-Ethyl-4-nitromethyl-chroman-2-one:

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta=7.40–7.10 \text{ (m, 4H)}, 4.55 \text{ (dd, 1H)}, 4.22 \text{ (t, 1H)}, 3.87 \text{ (t, 1H)}, 2.80 \text{ (dd, 1H)}, 2.10-2.05 \text{ (m, 1H)}, 1.60 \text{ (m, 1H)}, 1.10 \text{ (t, 3H)}; \\
\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{): } & \delta= 168.8, 150.8, 130.1, 128.1, 124.9, 122.6, 117.3, 75.4, 43.3, 37.3, 19.9, 11.9; \text{ MS (m/z): 235 (M}^+\text{, 23)}
\end{align*}
\]

HPLC analysis of (R)-3-Nitro-2-phenyl-1,2-dihydro-quinoline:

Column: CHIRALPAK-AD-H
Flow Phase: isopropanol/n-hexane (v/v=10/90)
Flow Rate: 0.8 mL/min
Detection Wavelength: 254 nm

Racemic product: t=10.79 min, 49.93%; t=14.61 min, 49.7%.
Product catalyzed by SBA-Py-Diph:

t = 10.56 min, 3%; R: t = 14.33 min, 97%, ee: 94%.
Appendix

$^1$H/$^{13}$C NMR spectra