# A Facile Assembly of Bifunctional, Magnetically Retrievable Mesoporous Silica for Enantioselective Cascade Reactions 

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## Experimental

1. General: All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. Tetraethoxysilane (TEOS), 1,4-bis(triethyoxysilyl)ethane, cetyltrimethylammonium bromide (CTAB), fluorocarbon surfactant ( $\mathrm{FC}-4: \quad\left[\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{O}\left(\mathrm{CF}\left(\mathrm{CF}_{3}\right) \mathrm{CF}_{2} \mathrm{O}\right)_{2} \mathrm{CF}\left(\mathrm{CF}_{3}\right) \mathrm{CONH}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{~N}^{+}\right.$ $\left.\left.\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{CH}_{3}\right] \mathrm{I}^{-}\right)$, 4-(2-(trimethoxysilyl)ethyl)benzene-1-sulfonyl chloride, 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine [(S,S)-TsDPEN], $\mathrm{PdCl}_{2}$, $(\text { MesityleneRuCl })_{2}$ were purchased from Sigma-Aldrich Company Ltd and used as received. Compound of (S,S)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylenediamine [J. Mater. Chem. 2010, 20, 1970-1975.] were synthesized according to the reported literature.
2. Characterization: Ru and Pd loading amounts in the catalyst were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV . Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV . Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas ( $S_{\text {BET }}$ ) of samples were determined from the linear parts of BET plots ( $p / p_{0}=0.05-1.00$ ). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with ${ }^{1} \mathrm{H}$ frequency of $400.1 \mathrm{MHz},{ }^{13} \mathrm{C}$ frequency of 100.5 MHz and ${ }^{29} \mathrm{Si}$ frequency of 79.4 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz , TPPM decoupling is applied in the during acquisition period. ${ }^{1} \mathrm{H}$ cross polarization in all solid state NMR experiments was employed using a contact time of 2 ms and the pulse lengths of $4 \mu \mathrm{~s}$.
3. General procedure for the preparation of catalyst 5. In a typical synthesis, (First step for the preparation of $\mathbf{3}$ ) the obtained solids $\mathbf{1}(0.20 \mathrm{~g})$ were suspended in an alkaline solution $(0.35 \mathrm{~mL}$ of NaOH $(2.0 \mathrm{M})$ in mixed 125.0 mL of water and 50.0 mL of ethanol with ultrasonication for 20 minutes. After that, an aqueous solution $(0.04 \mathrm{~g}$, 0.044 mmol$)$ of $\mathrm{FC}-4$ (FC-4: $\left.\left[\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{O}\left(\mathrm{CF}\left(\mathrm{CF}_{3}\right) \mathrm{CF}_{2} \mathrm{O}\right)_{2} \mathrm{CF}\left(\mathrm{CF}_{3}\right) \mathrm{CONH}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{~N}^{+}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{CH}_{3}\right] \mathrm{I}^{-}\right)$, 0.08 g (0.22 mmol) of cetyltrimethylammonium bromide (CTAB) and $0.20 \mathrm{~mL}(25 \mathrm{wt} \%)$ of $\mathrm{NH}_{3} \cdot \mathrm{H}_{2} \mathrm{O}$ in 3.0 mL of water) was added, and the mixture was stirred at $38^{\circ} \mathrm{C}$ for another 30 minutes. Next, $0.89 \mathrm{~g}(2.50 \mathrm{mmol})$ of $1,2-$ bis(triethoxysilyl)ethane and $0.15 \mathrm{~g}(0.30 \mathrm{mmol})$ of ( $S, S$ )-ArDpen-siloxane (2) in 2.0 mL of ethanol (2 minutes later) were added at room temperature, and the mixture was stirred under vigorous stirring for further 1.5 h . Finally, the temperature was raised to $80^{\circ} \mathrm{C}$ and the mixture was stirred at $80^{\circ} \mathrm{C}$ for another 3 h . After cooling the above mixture down to room temperature, the solid was collected by filtration to afford the $\mathrm{ArDpen} @ \mathrm{SiO}_{2} @ \mathrm{Pd} / \mathrm{C} @ \mathrm{Fe}_{3} \mathrm{O}_{4}(\mathbf{3})$ as a black powder. (Second step for the selective etching) To remove the surfactant, the collected $\mathbf{3}$ were dispersed in 120 mL of solution ( $80 \mathrm{mg}(1.0 \mathrm{mmol})$ of ammonium nitrate in 120 mL ( $95 \%$ ) of ethanol), and the mixture was stirred at $60^{\circ} \mathrm{C}$ for 10 h . After cooling the above mixture down to room temperature, the solids were filtered and washed with excess water and ethanol, and dried at $60{ }^{\circ} \mathrm{C}$ under vacuum overnight to afford the ArDpen@ $\mathrm{Pd} / \mathrm{C}^{\mathrm{C}} \mathrm{Fe}_{3} \mathrm{O}_{4}$ (4) as a dark-gray powder. (Third step for the coordination) 50.0 mg of $\left(\mathrm{MesRuCl}_{2}\right)_{2}(0.086 \mathrm{mmol})$ was added to a suspension of $4(0.50 \mathrm{~g})$ in 20.0 mL of dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at room temperature, and the resulting mixture was stirred at $25^{\circ} \mathrm{C}$ for 12 h . The solids were filtered and rinsed with excess dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. After Soxhlet extraction for 4.0 h in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, the solids were collected and dried at $60^{\circ} \mathrm{C}$ under vacuum overnight to
afford the magnetic catalyst 5 as a light-gray powder. An inductively coupled plasma optical emission spectrometer (ICP-OES) analysis showed that the Pd and Ru loadings were $41.63 \mathrm{mg}(0.39 \mathrm{mmol}$ of Pd) and 9.27 mg ( 0.091 mmol of Ru ) per gram of catalyst, respectively. ${ }^{13} \mathrm{C}$ CP/MAS NMR ( 161.9 MHz ): 161.5-121.1 ( $\underline{C}$ of Ph and Ar groups), 109.7, 106.2 ( $\underline{C}$ of mesitylene), 78.2-72.9 ( $\underline{C} \mathrm{H}$ of -NCHPh ), 67.8-64.2 ( $\underline{C}$ of $-\mathrm{N}_{\underline{C}} \mathrm{H}_{2}$ and $-\mathrm{N}_{\mathrm{C}} \mathrm{H}_{3}$ in CTAB molecule), 38.4-28.7 $\left(\underline{\mathrm{C}} \mathrm{H}_{2}\right.$ of $-\underline{\mathrm{C}} \mathrm{H}_{2} \mathrm{Ar}$ and $\underline{\mathrm{C}}$ of $\underline{\mathrm{C}} \mathrm{H}_{3} \underline{\mathrm{C}} \mathrm{H}_{2}-$ in CTAB molecule), $24.4\left(\underline{C} \mathrm{H}_{3}\right.$ of mesitylene), 15.0-0.9 $\left(\underline{C} \mathrm{H}_{2}\right.$ of $\left.-\underline{\mathrm{C}} \mathrm{H}_{2} \mathrm{Si}\right) \mathrm{ppm} .{ }^{29} \mathrm{Si}$ MAS/NMR (79.4 $\mathrm{MHz}): \mathrm{T}^{2}(\delta=-57.7 \mathrm{ppm}), \mathrm{T}^{3}(\delta=-65.9 \mathrm{ppm}), \mathrm{Q}^{3}(\delta=-102.6 \mathrm{ppm}), \mathrm{Q}^{4}(\delta=-112.7 \mathrm{ppm})$.
4. General procedure for the enantioselective cascade reactions. A typical procedure was as follows. (For successive reduction/ATH enantioselective cascade reductions of styryl-substituted aromatic ketones) Catalyst $5\left(21.98 \mathrm{mg}, 2.0 \mu \mathrm{~mol}\right.$ of $\mathrm{Ru}, 8.57 \mu \mathrm{~mol}$ of Pd , based on ICP analysis), $\mathrm{HCO}_{2} \mathrm{Na}(1.0$ mmol ), ketones ( 0.10 mmol ), and 4.0 mL of the mixed solvents ( ${ }^{( } \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O} \mathrm{v} / \mathrm{v}=3 / 1$ ) were added sequentially to a 10.0 mL round-bottom flask. The mixture was then stirred at $50^{\circ} \mathrm{C}$ for $6-12 \mathrm{~h}$. (For successive reduction/ATH enantioselective cascade reductions of styryl-substituted aromatic ketones: catalyst 5 ( $21.98 \mathrm{mg}, 2.0 \mu \mathrm{~mol}$ of $\mathrm{Ru}, 8.57 \mu \mathrm{~mol}$ of Pd , based on ICP analysis), $\mathrm{HCO}_{2} \mathrm{Na}$ ( 1.0 mmol ), iodoacetophenones ( 0.10 mmol ) and boronic acids $(0.12 \mathrm{mmol})$, and 4.0 mL of the mixed solvents $\left({ }^{i} \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O} \mathrm{v} / \mathrm{v}=3 / 1\right)$ were added sequentially to a 10.0 mL round-bottom flask. The mixture was then stirred at $60^{\circ} \mathrm{C}$ for $12-16 \mathrm{~h}$ ). During this period, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated by centrifugation ( $10,000 \mathrm{rpm}$ ) for the recycling experiment. The aqueous solution was extracted with ethyl ether $(3 \times 3.0 \mathrm{~mL})$. The combined ethyl ether extracts were washed with aqueous $\mathrm{Na}_{2} \mathrm{CO}_{3}$ and brine, and then dehydrated with $\mathrm{Na}_{2} \mathrm{SO}_{4}$. After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired product. The $e e$ values were determined using an HPLC analysis with a UV-Vis detector and a Daicel chiralcel column ( $\Phi 0.46 \times 25 \mathrm{~cm}$ ).

Figure S1. FT-IR spectra of 4 and catalyst 5.


Figure S2. TG/DTA curves of 4 and catalyst 5.


Explanation: The TG/DTA curves of ArDpen@Pd/C@Fe $\mathrm{CO}_{4}(\mathbf{4})$ and catalyst 5 was treated in the air as shown above. For the ArDpen @ $\mathrm{Pd} / \mathrm{C} @ \mathrm{Fe}_{3} \mathrm{O}_{4}(4)$, an endothermic peak around 351 K with weight loss of (100-93.1) $6.9 \%$ could be attributed to the release of physical adsorption water. In addition, the weight loss of (93.1-66.2) $28.9 \%$ between 440 K and 1200 K could be assigned to the oxidation of the organic moieties (including alkyl-linked ArDPEN moiety, alkyl fragments and part of the residual surfactants). Because the totally weight loss of organic moieties was $28.9 \%$ per $93.1 \%$ the extracted catalyst when eliminated the part of water, meaning the whole weight loss $31.1 \%$ of the oxidation of the organic molecules per $100 \%$ materials.

For catalyst 5, it was found easily that a similar endothermic peak around 349 K with weight loss of (100-91.9) $8.1 \%$ were strongly similar to that of parent $\mathbf{4}$ due to the release of physical adsorption water. It was worth mentioning that the all exothermic peaks were combined into one complicated exothermic peak between 400 K and 1200 K with weight loss of (91.9-62.0) $29.9 \%$ could be assigned to the oxidation of organic molecules (including alkyl-linked MesityleneRuArDPEN complexes, alkyl fragments and part of the residual surfactants). Because the totally weight loss of organic moieties was $29.9 \%$ per $91.9 \%$ the extracted catalyst when eliminated the part of water, meaning the whole weight loss $32.5 \%$ of the oxidation of the organic molecules per $100 \%$ materials.

As compared the weight loss of $\mathbf{5}$ with $\mathbf{4}$, the weight loss of the MesityleneCl moieties was $1.4 \%$ (32.531.1) per $100 \%$ materials. This finding means that the mole amounts of [MesityleneCl] in $\mathbf{5}$ is 0.009003 $\mathrm{mol} \%(\mathrm{Mr}=155.5)$, demonstrating the $9.1741 \mathrm{mg}(0.09003 \mathrm{mmol}$ of Ru$)$ of the Ru loading per gram of 5.

Figure S3. Solid-state ${ }^{13} \mathrm{C}$ CP/MAS NMR spectra of $\mathbf{4}^{\prime}$ and catalyst $\mathbf{5}^{\prime}$.


Figure S4. Solid-state ${ }^{29}$ Si MAS NMR spectra of $\mathbf{4}^{\prime}$ and catalyst $\mathbf{5}^{\prime}$.


Figure S5. (a) SEM and TEM (b) images of catalyst 5.


Figure S6. Nitrogen adsorption-desorption isotherms of $\mathbf{4}$ and catalyst 5.


Figure S7. Time course for the cascade reaction of $(E)$-1-(4-styrylphenyl)ethanone catalyzed by 5 (the reaction was performed with $2.0 \mathrm{mmol} \% \mathrm{Ru}$ and $8.57 \mathrm{mmol} \% \mathrm{Pd}$ of catalyst 5 , 1 equivalent of $(E)-1-(4-$ styrylphenyl)ethan-1-one, and 10.0 equivalent of HCOONa at $50^{\circ} \mathrm{C}$ )


Table S1. Optimizing reaction conditions for the Suzuki cross-coupling/ATH cascade reaction of 4iodoacetophenone and phenylboronic acid.


| Entry | Solvent | base (H-resource) | ${ }^{\circ} \mathbf{C}$ | Time (h) | Yield (\%) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 1 | ${ }^{i} \mathrm{PrOH}$ | $\mathrm{K}_{2} \mathrm{CO}_{3}(1.0$ equiv.) | 70 | 6 | 99 |
| 2 | ${ }^{i} \mathrm{PrOH}$ | $\mathrm{K}_{2} \mathrm{CO}_{3}(1.0$ equiv.) | 60 | 3 | 99 |
| 3 | ${ }^{i} \mathrm{PrOH}$ | $\mathrm{HCOONa}(10.0$ equiv.) | 60 | 3 | 98 |
| 4 | $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{HCOONa}(10.0$ equiv.) | 60 | 3 | 68 |
| 5 | ${ }^{i} \mathrm{PrOH}$ | $\mathrm{HCOONa}(10.0$ equiv.) | 50 | 3 | 90 |
| 6 | ${ }^{i} \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O}(2 / 1)$ | $\mathrm{HCOONa}(10.0$ equiv.) | 60 | 3 | 93 |
| 7 | ${ }^{i} \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O}(3 / 1)$ | $\mathrm{HCOONa}(10.0$ equiv.) | 60 | 3 | 99 |
| 8 | ${ }^{i} \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O}(4 / 1)$ | HCOONa (10.0 equiv.) | 60 | 3 | 99 |

Reaction conditions: Catalyst $5(38.50 \mathrm{mg}, 3.50 \mu \mathrm{~mol}$ of $\mathrm{Ru}, 15.0 \mu \mathrm{~mol}$ of Pd, based on ICP analysis), iodoacetophenones ( 1.0 mmol ), boronic acids ( 1.20 mmol ), and 10.0 mL of co-solvents were added sequentially to a 10.0 mL round-bottom flask. Yields were determined by ${ }^{1} \mathrm{H}-\mathrm{NMR}$ analysis.

Figure S8．HPLC analyses for chiral products．
（S）－1－（［1，1＇－biphenyl］－4－yl）ethan－1－ol（8a）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n － hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=19.1 \mathrm{~min}($ major $\left.), \mathrm{t}_{2}=21.8 \mathrm{~min}\right)$ ．



| Table view of compound |  | RetTime ［min］ | Peak | Area | Height $\uparrow$ | Area\% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| －－化合物表视图 |  |  |  |  |  |  |
| IDF | 名称 | 保留时间 | 崔 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（4＇－fluoro－［1，1＇－biphenyl］－4－yl）ethanol（8b）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n －hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=20.0 \mathrm{~min}($ major $\left.), \mathrm{t}_{2}=23.1 \mathrm{~min}\right)$ ．


| － 化合物表视图 $^{\text {a }}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名解 | 保留时间 | 峰き | 面积 | 高度 | 面积x |
| 1 | RT19．984 | 19．984 | 1 | 37610519 | 1091614 | 49.9786 |
| 2 | RT23． 153 | 23.153 | 2 | 37642766 | 952890 | 50.0214 |
|  |  |  |  |  |  |  |



Table view of

| comp | pound <br> Name | RetTime ［min］ | Peak $\uparrow$ | Area $\uparrow$ | Height $\uparrow$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 可化合物表视图 |  |  |  |  |  |  |  |
| ID | 名称 | 保鼻时间 | 峰 | 面积 | 高度 | 面积x |  |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 |  | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 |  | 1． 9471 |

（S）－1－（4＇－chloro－［1，1＇－biphenyl］－4－yl）ethanol（8c）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=20.0 \mathrm{~min}$（major）， $\mathrm{t}_{2}=26.2 \mathrm{~min}$ ．



Table view of

| compound |  | RetTime ［min］ | Peak | Area $\uparrow$ | Height $\uparrow$ | $\text { Area } \%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name $\uparrow$ |  |  |  |  |  |
| － 化合物表视图 |  |  |  |  |  |  |
| ID＊ | 名称 | 保留时间 | 嵮 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（3＇－chloro－［1，1＇－biphenyl］－4－yl）ethanol（8d）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=17.6 \mathrm{~min}($ major $), \mathrm{t}_{2}=19.9 \mathrm{~min}$ ．）



| Table view of compound |  | RetTime ［min］ | Peak | Area $\uparrow$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| 可化合物表视图 |  |  |  |  |  |  |
| ID＊ | 名称 | 保留时间 | 峌 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（4＇－（trifluoromethyl）－［1，1＇－biphenyl］－4－yl）ethanol（8e）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n －hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=14.3 \mathrm{~min}($ major $), \mathrm{t}_{2}=$ 19.8 min ）．


| 므化合 | 表视图 |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 垸 | 面积 | 高度 | 面积x |
| 1 | RT14．327 | 14.327 | 1 | 10142838 | 309187 | 50.7120 |
| 2 | RT19．815 | 19.815 | 2 | 9858015 | 235404 | 49.2880 |
| 4 1 ｜参数 $\lambda$ 结果 $A$ 组参数 $\wedge$ 组结果／ |  |  |  |  | 1 |  |



| －－化合物表视图 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名妳 | 保留时间 | 峰 | 面积 | 高度 | 面积× |
| \％ | RT15． 955 | 15． 955 | 1 | 1054952 | 33847 | 97． 1651 |
| 2 | RT20． 137 | 20.137 | 2 | 30779 | 802 | 2． 8349 |
| 4 ${ }^{\text {V }}$ \参数 $\lambda$ 结果 $/$ 组参数 $\lambda$ 组结果／ |  |  |  |  |  |  |

Table view of

| compound |  | RetTime ［min］ $\uparrow$ | Peak | $\begin{gathered} \text { Area } \\ \uparrow \end{gathered}$ | Height $\uparrow$ | Area\％ $\uparrow$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |
| －化合物表视图 |  |  |  |  |  |  |  |
| ID： | 名称 | 保畕时间 | 峔 | 面积 | 高度 | 面积x |  |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 |  | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 |  | 1.9471 |

（S）－1－（3＇－（trifluoromethyl）－［1，1＇－biphenyl］－3－yl）ethan－1－ol（8f）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent：n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=13.9 \mathrm{~min}$（major）， $\mathrm{t}_{2}=$ 15.1 min ．）



| Table view of compound |  | RetTime ［min］ $\uparrow$ | Peak | Area $\uparrow$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| 可化合物表视图 |  |  |  |  |  |  |
| ID： | 名称 | 保畕时间 |  | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（4＇－methyl－［1，1＇－biphenyl］－4－yl）ethanol（8g）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=15.5 \mathrm{~min}($ major $), \mathrm{t}_{2}=20.8 \mathrm{~min}$ ．$)$



| Table view of compound |  | RetTime ［min］ | Peak $\uparrow$ | Area $\uparrow$ | Height $\uparrow$ | $\begin{gathered} \text { Area } \% \\ 4 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| 可化合物表视图 |  |  |  |  |  |  |
| ID＊ | 名称 | 保留时问 | 㟨 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（3＇－methyl－［1，1＇－biphenyl］－4－yl）ethanol（8h）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=34.6 \mathrm{~min}($ major $), \mathrm{t}_{2}=38.3 \mathrm{~min}$ ．$)$


| － 化合物表视图 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 峰 | 面积 | 高度 | 面积x |
| 1 | RT34．678 | 34.678 | 1 | 5100761 | 90544 | 50.3999 |
| 2 | RT38． 308 | 38.308 | 2 | 5019808 | 81629 | 49.6001 |
|  |  |  |  |  |  |  |



Table view of

| compound |  | RetTime ［min］ $\uparrow$ | Peak | Area | Height | Area\％ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  | $\uparrow$ | $\uparrow$ |  |  |
| 口化合物表视图 |  |  |  |  |  |  |
| ID | 名称 | 保留时间 | 峰 | 面积 | 高度 | 面积x |
| 1 | RT16．273 | 16.273 | 1 | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 | 2 | 577094 | 24437 | 1.9471 |

(S)-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanol (8i): (HPLC: Chiracel AD-H, detected at 254 nm , eluent: n-hexane $/ 2$-propanol $=97 / 3$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=31.2 \mathrm{~min}($ major $), \mathrm{t}_{2}=36.0 \mathrm{~min}$. )

（S）－1－（4－（thiophen－3－yl）phenyl）ethan－1－ol（8j）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n － hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=28.4 \mathrm{~min}, \mathrm{t}_{2}=33.5 \mathrm{~min}$（major））．


| Table view of compound |  | RetTime ［min］ $\uparrow$ | Peak $\uparrow$ | Area |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  |  |  |  |  |
| － 化合物表视图 |  |  |  |  |  |  |
| ID＊ | 名称 | 保畄时间 | 峔 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（［1，1＇－biphenyl］－3－yl）ethanol（8k）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n － hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=18.1 \mathrm{~min}, \mathrm{t}_{2}=19.8 \mathrm{~min}$（major））．



| compound |  | RetTime ［min］ $\uparrow$ | Peak | Area | Height | Area\％ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  |  |  |  |  |
| －化合物表视图 |  |  |  |  |  |  |
| ID | 名称 | 保留时间 | 峰 | 面积 | 高度 | 面积x |
| 1 | RT16．273 | 16.273 | 1 | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 | 2 | 577094 | 24437 | 1.9471 |

（S）－1－（4＇－fluoro－［1，1＇－biphenyl］－3－yl）ethanol（81）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=21.1 \mathrm{~min}, \mathrm{t}_{2}=23.4 \mathrm{~min}$（major） ）．


| － 化合物表视图 $^{\text {a }}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 峰 | 面积 | 高度 | 面积x |
| 1 | RT21． 133 | 21.133 | 1 | 2611782 | 70430 | 50.0428 |
| 2 | RT23． 402 | 23.402 | 2 | 2607317 | 64381 | 49．9572 |
| 1 1 \参数入结果 $/$ 组参数 人组结果／ |  |  |  |  |  |  |



| － 化合物表视图 $^{\text {a }}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 峰き | 面积 | 高度 | 面积× |
| 1 | RT20． 332 | 20.332 | 1 | 375076 | 9454 | 2． 4642 |
| 2 | 1RT22．711 | 22.711 | 2 | 14845774 | 314556 | 97.5358 |
| 1－\参数 $\lambda$ 结果 $/$ 组参数入组结果／ |  |  |  |  |  |  |

Table view of

| comp | ound <br> Name | RetTime ［min］ | Peak | Area | Height $\uparrow$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 可化合物表视图 |  |  |  |  |  |  |  |
| ID | 名称 | 保留时间 | 巄 | 面积 | 高度 | 面积x |  |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 |  | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 |  | 1.9471 |

（S）－1－（4＇－chloro－［1，1＇－biphenyl］－3－yl）ethanol（8m）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=22.2 \mathrm{~min}, \mathrm{t}_{2}=25.4 \mathrm{~min}$（major） ）


| －${ }^{\text {－化合物表视图 }}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID | 名称 | 保留时间 | 㨍 | 面积 | 高度 | 面积： |
| 1 | RT22．276 | 22.276 | 1 | 1214208 | 30711 | 50.0071 |
| 2 | RT25． 437 | 25.437 | 2 | 1213865 | 27531 | 49.9929 |
| 4 $\mathrm{V}^{\text {P }}$ 参数 $\lambda$ 结果 组参数 组结果／ |  |  |  |  | 1 |  |



| Table view of compound |  | RetTime ［min］ | Peak 4 | Area | Height $\uparrow$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  |  |  |  |  |
| － 化合物表视園 |  |  |  |  |  |  |
| ID＊ | 名称 | 保留时间 | 詮考 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18． 111 | 18.111 |  | 577094 | 24437 | 1.9471 |

(S)-1-(3'-chloro-[1,1'-biphenyl]-3-yl)ethanol (8n): (HPLC: Chiracel AD-H, detected at 254 nm , eluent: n-hexane $/ 2$-propanol $=97 / 3$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=16.4 \mathrm{~min}, \mathrm{t}_{2}=19.6 \mathrm{~min}($ major $)$ ).



（S）－1－（4＇－（trifluoromethyl）－［1，1＇－biphenyl］－3－yl）ethanol（80）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： n －hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=17.8 \mathrm{~min}$（major）， $\mathrm{t}_{2}=20.1 \mathrm{~min}$ ）．


| － 化合物表视图 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 㟉 | 面积 | 高度 | 面积＊ |
| 1 | RT17． 896 | 17.896 | 1 | 51754939 | 1579956 | 49.9229 |
| 2 | RT20． 167 | 20.167 | 2 | 51914871 | 1225897 | 50.0771 |
|  |  |  |  |  |  |  |



Table view of

| comp | pound <br> Name | RetTime ［min］ | Peak $\uparrow$ | Area $\uparrow$ | Height <br> $\uparrow$ | $i^{\text {Area } \%}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| －化合物表视图 |  |  |  |  |  |  |
| ID | 名称 | 保留时间 | 㙖 | 面积 | 高度 | 面积x |
| 1 | R716． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1． 9471 |

（S）－1－（（4＇－methyl－［1，1＇－biphenyl］－3－yl）ethanol（8p）：（HPLC：Chiracel AD－H，detected at 254 nm ， eluent：nhexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=18.4 \mathrm{~min}, \mathrm{t}_{2}=22.0 \mathrm{~min}($ major $)$ ）．


| 可化合物表视图 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 峰き | 面积 | 高度 | 面积： |
| 1 | RT18． 448 | 18.448 | 1 | 732203 | 21988 | 50.2275 |
| 2 | RT22．070 | 22.070 | 2 | 725571 | 19222 | 49.7725 |
| 1－${ }^{\text {d }}$ 参数 $\lambda$ 结果 组参数 $\lambda$ 组结果／$^{\text {／}}$ |  |  |  |  |  |  |



（S）－1－（（3＇－methyl－［1，1＇－biphenyl］－3－yl）ethanol（8q）：（HPLC：Chiracel AD－H，detected at 254 nm ，eluent： nhexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=14.6 \mathrm{~min}, \mathrm{t}_{2}=17.2 \mathrm{~min}$（major））



| Table view of compound |  | RetTime ［min］ | Peak | Area $\uparrow$ | Height | $i^{\text {Area } \%}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| － 化合物表视图 $^{\text {a }}$ |  |  |  |  |  |  |
| IDF | 名称 | 保留时间 | 竬 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

(S)-1-((4'-methoxy-[1,1'-biphenyl]-3-yl)ethanol (8r): (HPLC: Chiracel AD-H, detected at 254 nm , eluent: n-hexane $/ 2$-propanol $=97 / 3$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=36.0 \mathrm{~min}, \mathrm{t}_{2}=41.8 \mathrm{~min}($ major $)$ ).

(S)-1-(3-(thiophen-3-yl)phenyl)ethan-1-ol (8s): (HPLC: Chiracel AD-H, detected at 254 nm , eluent: nhexane $/ 2$-propanol $=97 / 3$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}, \mathrm{t}_{1}=28.4 \mathrm{~min}, \mathrm{t}_{2}=30.8 \mathrm{~min}($ major $)$ ) .



Table view of

（S，S）－1，1＇－（［1，1＇－biphenyl］－4，4＇－diyl）diethanol（8t）：（HPLC：Chiracel AD－H，detected at 254 nm ， eluent： n －hexane $/ 2$－propanol $=92.5 / 7.5$ ，flow rate $\left.=1.0 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}\right)$ ．


| －－化合物表视图 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID 7 | 名称 | 保留时间 | 崯 | 面积 | 高度 | 面积 ${ }^{\text {x }}$ |
| 1 | RT30． 089 | 30.089 | 1 | 2394397 | 33256 | 25． 1914 |
| 2 | RT37． 741 | 37.741 | 2 | 4708024 | 53748 | 49.5331 |
| 3 | RT41．984 | 41.984 | 3 | 2402385 | 24645 | 25.2755 |





(S)-1-(4-phenethylphenyl)ethan-1-ol: (10a) (HPLC: Chiracel OB-H, detected at 254 nm , eluent: n hexane $/ 2$-propanol $=99 / 1$, flow rate $=0.8 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ).



Table view of

（S）－1－（4－（4－fluorophenethyl）phenyl）ethan－1－ol：（10b）（HPLC：Chiracel OB－H，detected at 254 nm ， eluent： n－hexane $/ 2$－propanol $=99 / 1$ ，flow rate $=0.8 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ）．


| － 化合物表视图 $^{\text {a }}$ |  |  |  |  |  |  | 6d视图 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ID＊ | 名称 | 保留时间 | 崯 | 面积 | 高度 | 面积x |  |
| 1 | RT37． 103 | 37.103 | 1 | 7777028 | 58647 |  | 50.8190 |
| 2 | RT43． 171 | 43.171 | 2 | 7526352 | 40681 |  | 49.1810 |



Table view of

(S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol: (10c) (HPLC: Chiracel OB-H, detected at 254 nm , eluent: n-hexane $/ 2$-propanol $=99 / 1$, flow rate $=0.8 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ).



Table view of

（S）－1－（4－（4－chlorophenethyl）phenyl）ethan－1－ol：（10d）（HPLC：Chiracel OB－H，detected at 254 nm ， eluent： n －hexane $/ 2$－propanol $=98 / 2$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ）．



| Table view of compound |  | RetTime ［min］ $\uparrow$ | Peak | Area | Height | Area\％ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  |  |  |  |  |
| 므化合物表视图 |  |  |  |  |  |  |
| ID | 名称 | 保留时间 | 鹳 | 面积 | 高度 | 面积x |
| 1 | RT16．273 | 16.273 | 1 | 29062298 | 1157381 | 98.0529 |
| 2 | ｜RT18．111 | 18.111 | 2 | 577094 | 24437 | 1.9471 |

(S)-1-(4-(4-methylphenethyl)phenyl)ethan-1-ol: (10e) (HPLC: Chiracel OB-H, detected at 254 nm , eluent: $n$-hexane $/ 2$-propanol $=98 / 2$, flow rate $=0.8 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ).



Table view of

（S）－1－（4－（3－methylphenethyl）phenyl）ethan－1－ol：（10f）（HPLC：Chiracel OB－H，detected at 254 nm ， eluent：n－hexane $/ 2$－propanol $=98 / 2$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ）．


Table view of

| compound |  | RetTime ［min］ $\uparrow$ | Peak | Area | Height $\uparrow$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name $\uparrow$ |  |  |  |  |  |  |
| －化合物表视图 |  |  |  |  |  |  |  |
| ID： | 名称 | 保鼻时间 | 峰 | 面积 | 高度 | 面积x |  |
| 1 | R716． 273 | 16.273 |  | 29062298 | 1157381 |  | 98.0529 |
| 2 | KT18．111 | 18.111 |  | 577094 | 24437 |  | 1.9471 |

（S）－1－（4－（4－methoxyphenethyl）phenyl）ethan－1－ol：（10g）（HPLC：Chiracel OB－H，detected at 254 nm ， eluent： n－hexane $/ 2$－propanol $=98 / 2$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ）．



Table view of

| compound |  | RetTime ［min］ | Peak $\uparrow$ | Area $\uparrow$ | Height $\uparrow$ | $i_{i}^{\text {Area } \%}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  |  |  |  |  |
| － 代合物表视图 |  |  |  |  |  |  |
| ID： | 名称 | 保留时间 |  | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（3－phenethylphenyl）ethan－1－ol：（10h）（HPLC：Chiracel OJ－H，detected at 254 nm ，eluent：n－ hexane $/ 2$－propanol $=98 / 2$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ）．



Table view of

| comp | ound <br> Name | RetTime ［min］ | Peak | Area | Height $\uparrow$ | Area\% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| － 代合物表视图 |  |  |  |  |  |  |
| ID | 名称 | 保㽞时间 | 㟽 | 面积 | 高度 | 面积x |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

（S）－1－（3－（4－fluorophenethyl）phenyl）ethan－1－ol：（10i）（HPLC：Chiracel OJ－H，detected at 254 nm ， eluent：n－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ）．



Table view of

| compound |  | RetTime ［min］ $\uparrow$ | Peak | Area $\uparrow$ | Height $\uparrow$ | Area\% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name |  |  |  |  |  |
| － 化合物表视图 $^{\text {a }}$ |  |  |  |  |  |  |
| ID | 名称 | 保留时间 | 竬 | 面积 | 高度 | 面积 ${ }^{\text {x }}$ |
| 1 | RT16． 273 | 16.273 |  | 29062298 | 1157381 | 98.0529 |
| 2 | KT18．111 | 18.111 |  | 577094 | 24437 | 1.9471 |

(S)-1-(3-(3-fluorophenethyl)phenyl)ethan-1-ol: (10j) (HPLC: Chiracel OJ-H, detected at 254 nm , eluent: $n$-hexane $/ 2$-propanol $=97 / 3$, flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ).



（S）－1－（3－（4－chlorophenethyl）phenyl）ethan－1－ol：（10k）（HPLC：Chiracel OJ－H，detected at 254 nm ， eluent：$n$－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ）．



Table view of

| comp | ound <br> Name | RetTime ［min］ $\uparrow$ | Peak | Area $\uparrow$ | Height $\uparrow$ | $\text { Area } \%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| －化合物表视图 |  |  |  |  |  |  |
| ID＊ | 名称 | 保留时间 | 峰 | 面积 | 高度 | 面积x |
| 1 | RT16．273 | 16.273 | 1 | 29062298 | 1157381 | 98.0529 |
| 2 | RT18．111 | 18.111 | 2 | 577094 | 24437 | 1.9471 |

(S)-1-(3-(4-methylphenethyl)phenyl)ethan-1-ol: (101) (HPLC: Chiracel OJ-H, detected at 254 nm , eluent: $n$-hexane $/ 2$-propanol $=97 / 3$, flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ).



（S）－1－（3－（3－methylphenethyl）phenyl）ethan－1－ol：（10m）（HPLC：Chiracel OJ－H，detected at 254 nm ， eluent：$n$－hexane $/ 2$－propanol $=97 / 3$ ，flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25{ }^{\circ} \mathrm{C}$ ）．



| Table view of compound |  | RetTime ［min］ $\uparrow$ | Peak | Area | Height | $\text { Area } \%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Name f |  |  |  |  |  |
| ［口化合物表视图 |  |  |  |  |  |  |
| ID＊ | 名称 | 保留时间 | 㭠き | 面积 | 高度 | 面积x |
| 1 | RT16．273 | 16.273 | 1 | 29062298 | 1157381 | 98.0529 |
| 2 | ｜RT18．111 | 18.111 | 2 | 577094 | 24437 | 1.9471 |

(S)-1-(3-(4-methoxyphenethyl)phenyl)ethan-1-ol: (10n) (HPLC: Chiracel AS-H, detected at 254 nm , eluent: n -hexane $/ 2$-propanol $=96 / 4$, flow rate $=1 \mathrm{~mL} / \mathrm{min}, 25^{\circ} \mathrm{C}$ ).



Table view of


Table S2. Reusability of catalyst 5 in the Suzuki cross-coupling/ATH cascade reaction of 4iodoacetophenone and phenylboronic acid. ${ }^{[a]}$

| Entry | $\mathbf{1}$ | $\mathbf{2}$ | $\mathbf{3}$ | $\mathbf{4}$ | $\mathbf{5}$ | $\mathbf{6}$ | $\mathbf{7}$ | $\mathbf{8}$ | $\mathbf{9}$ | $\mathbf{1 0}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Yield [\%] | 96 | 96 | 96 | 95 | 94 | 94 | 94 | 93 | 91 | 82 |
| ee [\%] | 96 | 96 | 95 | 95 | 95 | 95 | 93 | 93 | 93 | 90 |

${ }^{\text {a }}$ Reaction conditions: catalyst $5\left(219.80 \mathrm{mg}, 20.0 \mu \mathrm{~mol}\right.$ of $\mathrm{Ru}, 85.70 \mu \mathrm{~mol}$ of Pd , based on ICP analysis), $\mathrm{HCO}_{2} \mathrm{Na}(10.0$ mmol ), iodoacetophenones ( 1.0 mmol ) and boronic acids ( 1.2 mmol ), and 40.0 mL of ( ${ }^{i} \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O} \mathrm{v} / \mathrm{v}=3 / 1$ ) were added sequentially to a 100.0 mL round-bottom flask. The mixture was then stirred at $60^{\circ} \mathrm{C}$ for 12 h . Yields were determined by ${ }^{1} \mathrm{H}-\mathrm{NMR}$ analysis and $e e$ values were determined by chiral HPLC analysis.

Figure S9. HPLC analyses for the 5-catalyzed Suzuki cross-coupling/ATH cascade reaction of 4iodoacetophenone and phenylboronic acid.

## Recycling experiment part:

## Recycle 1.



Recycle 2.


Recycle 3.


## Recycle 4.



Recycle 5.


Recycle 6.


Recycle 7.


Recycle 8.


Recycle 9.


Recycle 10


Table view of


Table S3. Reusability of catalyst 5 in the successive reduction/ATH of ( $E$ )-1-(4-styrylphenyl)than-1one. ${ }^{[a]}$

| Entry | $\mathbf{1}$ | $\mathbf{2}$ | $\mathbf{3}$ | $\mathbf{4}$ | $\mathbf{5}$ | $\mathbf{6}$ | $\mathbf{7}$ | $\mathbf{8}$ | $\mathbf{9}$ | $\mathbf{1 0}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Yield [\%] | 97 | 97 | 95 | 96 | 94 | 94 | 93 | 92 | 91 | 83 |
| ee [\%] | 98 | 98 | 97 | 97 | 96 | 95 | 95 | 95 | 95 | 95 |

${ }^{\text {a }}$ Reaction conditions: Catalyst $5\left(219.80 \mathrm{mg}, 20.0 \mu \mathrm{~mol}\right.$ of $\mathrm{Ru}, 85.70 \mu \mathrm{~mol}$ of Pd , based on ICP analysis), $\mathrm{HCO}_{2} \mathrm{Na}(10.0$ $\mathrm{mmol}),(E)-1$-(4-styrylphenyl)than-1-one ( 1.0 mmol ), and 40.0 mL of co-solvents ( ${ }^{i} \mathrm{PrOH} / \mathrm{H}_{2} \mathrm{O} \mathrm{v} / \mathrm{v}=3 / 1$ ) were added sequentially to a 100.0 mL round-bottom flask. The mixture was then stirred at $50^{\circ} \mathrm{C}$ for 6 h . Yields were determined by ${ }^{1} \mathrm{H}-\mathrm{NMR}$ analysis and $e e$ values were determined by chiral HPLC analysis.

Figure S10. HPLC analyses for the 5-catalyzed reduction/ATH of (E)-1-(4-styrylphenyl)than-1-one.

## Recycling experiment part:

Recycle 1.


## Recycle 2.



Recycle 3.


Recycle 4.


Recycle 5.


Recycle 6.


Recycle 7.


Recycle 8.


Recycle 9.


Table view of


Figure S11. The characterizations of chiral products (The ${ }^{1} \mathrm{H}$ NMR and GC - MS spectra of all chiral products).

## (S)-1-([1,1'-biphenyl]-4-yl)ethan-1-ol (8a).







(S)-1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-ol (8b).


(S)-1-(4'-chloro-[1,1'-biphenyl]-4-yl)ethan-1-ol (8c).


(S)-1-(3'-chloro-[1,1'-biphenyl]-4-yl)ethan-1-ol (8d)


(S)-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-ol (8e)

$$
\begin{aligned}
& \underbrace{\sim}
\end{aligned}
$$





(S)-1-(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-ol (8f)


$\xrightarrow[1]{\infty}$




(S)-1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-ol (8g)


$\underset{i}{i}$

$\int$
$\mid$


(S)-1-(3'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-ol (8h).


$\underset{\sim}{\infty} \stackrel{\circ}{\sigma} \underset{\sim}{\sigma} \underset{\sim}{\gamma}$
运




(S)-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-ol (8i).

(S)-1-(4-(thiophen-3-yl)phenyl)ethan-1-ol (8j).




(S)-1-([1,1'-biphenyl]-3-yl)ethan-1-ol (8k).






(S)-1-(4'-fluoro-[1,1'-biphenyl]-3-yl)ethan-1-ol (81).


$\underbrace{8 . \infty} \underset{\substack{\infty \\ j \\ j}}{ }$


1



(S)-1-(4'-chloro-[1,1'-biphenyl]-3-yl)ethan-1-ol (8m).

4

$\stackrel{\infty}{\infty}$



(S)-1-(3'-chloro-[1,1'-biphenyl]-3-yl)ethan-1-ol (8n).


|  |  |  |  |  |  | $\begin{aligned} & \text { 'O } \\ & \hline- \\ & \hline \end{aligned}$ |  |  |  |  |  |  | $\stackrel{\text { T }}{\substack{\text { rim }}}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8.0 | 7.5 | 7.0 | 6.5 | 6.0 | 5.5 | 5.0 | 4.5 | $\begin{gathered} 4.0 \\ \mathrm{f} 1(\mathrm{ppm}) \end{gathered}$ | 3.5 | 3.0 | 2.5 | 2.0 | 1.5 | 1.0 | 0.5 | 0.0 |


(S)-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)ethan-1-ol (80).

$\underbrace{\text { ºg }}$
$\stackrel{\infty}{\infty} \stackrel{n}{\sim}$





(S)-1-(4'-methyl-[1,1'-biphenyl]-3-yl)ethan-1-ol (8p).


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 ( (
(S)-1-(3'-methyl-[1,1'-biphenyl]-3-yl)ethan-1-ol (8q).

(S)-1-(4'-methoxy-[1,1'-biphenyl]-3-yl)ethan-1-ol (8r).


$\stackrel{\bullet}{i}$
$\stackrel{\sim}{1} \stackrel{n}{n} \stackrel{4}{4}$





(S)-1-(3-(thiophen-3-yl)phenyl)ethan-1-ol (8s).


$(S, S)-1,1^{\prime}-\left(\left[1,1^{\prime}-\right.\right.$ biphenyl $]-4,4^{\prime}$-diyl)diethanol (8t).






(S)-1-(4-phenethylphenyl)ethan-1-ol (10a).


(S)-1-(4-(4-fluorophenethyl)phenyl)ethan-1-ol (10b).








(S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol (10c).


(S)-1-(4-(4-chlorophenethyl)phenyl)ethan-1-ol (10d).

(S)-1-(4-(4-methylphenethyl)phenyl)ethan-1-ol (10e).

(S)-1-(4-(3-methylphenethyl)phenyl)ethan-1-ol (10f).

(S)-1-(4-(4-methoxyphenethyl)phenyl)ethan-1-ol (10g).

(S)-1-(3-phenethylphenyl)ethan-1-ol (10h).


(S)-1-(3-(4-fluorophenethyl)phenyl)ethan-1-ol (10i).


(S)-1-(3-(3-fluorophenethyl)phenyl)ethan-1-ol (10j).


(S)-1-(3-(4-chlorophenethyl)phenyl)ethan-1-ol (10k).

(S)-1-(3-(4-methylphenethyl)phenyl)ethan-1-ol (101).

(S)-1-(3-(3-methylphenethyl)phenyl)ethan-1-ol (10m).

(S)-1-(3-(4-methoxyphenethyl)phenyl)ethan-1-ol (10n).



