**Supporting Information for**

**One-pot synthesis of optically pure \( \beta \)-hydroxy sulfones via a heterogeneous ruthenium/diamine–promoted nucleophilic substitution–asymmetric transfer hydrogenation tandem process**

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Figure S1. TG/DTA curves of the parallel pure material, the ArDPEN@MSNs (2) and catalyst 3.
Explanation: The TG/DTA curve of the parallel pure material, the ArDPEN@MSNs (2) and catalyst 3 were treated in the air as shown above.

For the pure material, an endothermic peak around 355K with weight loss of (100-95.971) 4.029% could be attributed to the release of physical adsorption water while the comprehensive endothermic peaks between 430K and 1100K with weight loss of (95.971-84.730) 11.241% could be assigned to the release of the residual CTAC surfactant (cetyl-trimethylammonium chloride) within the parallel pure material. Apparently, the totally weight loss of the residual CTAC surfactant was 11.241% per 95.971% the parallel pure material when eliminated the part of water, meaning the 11.712% weight loss of the residual CTAC surfactant per 100% materials. This finding is strongly same as that reported in the literature (V. Cauda, A. Schlossbauer, J. Kecht, A. Zürner, T. Bein, Am. Chem. Soc., 2009, 131, 11361).

For ArDPEN@MSNs (2), it was found easily that an endothermic peak around 340 K with weight loss of (100-84.566) 15.434% could be attributed to the release of physical adsorption water. All exothermic peaks between 430K and 1100K with weight loss of (84.566-54.169) 30.397% could be assigned to the oxidation of organic molecules (including ArDPEN moiety, alkyl fragments and part of the residual CTAC surfactant). Because the totally weight loss of organic moieties was 30.397% per 84.566% of 2 when eliminated the part of water, meaning the whole weight loss 35.944% of the oxidation of the organic molecules (including Ru/diaime complexes, ArDPEN moiety, alkyl fragments and part of the residual CTAC surfactant (V. Cauda, A. Schlossbauer, J. Kecht, A. Zürner, T. Bein, Am. Chem. Soc., 2009, 131, 11361) per 100% materials.

For catalyst 3, an endothermic peak around 348 K with weight loss of (100-94.00) 6.00% could be attributed to the release of physical adsorption water. In addition, the weight loss of (94.00-53.828) 40.172% between 430 and 1100 K could be assigned to the oxidation of the organic moieties (including Ru/diaime complexes, ArDPEN moiety, alkyl fragments and part of the residual CTAC surfactant). Because the totally weight loss of organic moieties was 40.172% per 94.00% of catalyst 3 when eliminated the part of water, meaning the whole weight loss 42.736% of the oxidation of the organic molecules (including Ru/diaime complexes, ArDPEN moiety, alkyl fragments and part of the residual CTAC surfactant) per 100% materials.

In contrast to TG/DTA curve of ArDPEN@MSNs (2) and catalyst 3, the true weight loss of ArCl moieties is 6.792% (42.736-35.945), meaning the mole amounts of ArCl is 0.0404 mol% (6.792/168: Mr = 168 for ArCl). The mole amount of Ru (Mr = 101) in the material is 0.404 mmol (40.83 mg) per gram material.
Figure S2. FT-IR spectra of the ArDPEN@MSNs (2) and catalyst 3.
Figure S3. Enantioselective tandem nucleophilic substitution-asymmetric transfer hydrogenation of α-bromoketones and sodium sulfonates for one-pot synthesis of chiral β-hydroxy sulfones

Translation of Chinese to English is as follows:

(S)-1-phenyl-2-(phenylsulfonyl)ethanol (6a): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-(4-fluorophenyl)-2-(phenylsulfonyl)ethanol (6b): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 ºC).

![HPLC chromatogram of (S)-1-(4-fluorophenyl)-2-(phenylsulfonyl)ethanol (6b)](image)

- RetTime [min]: 7.280, Area: 29377113, Area% Heigh: 100.00, Eluent: n-hexane/2-propanol = 90/10, Flow rate: 1.0 mL/min, Temp: 25 ºC.

- Peaks:
  - Peak 1: RetTime: 6.235, Area: 2300475, Height: 50.40, Eluent: n-hexane/2-propanol = 90/10, Flow rate: 1.0 mL/min, Temp: 25 ºC.
  - Peak 2: RetTime: 6.740, Area: 2280656, Height: 49.54, Eluent: n-hexane/2-propanol = 90/10, Flow rate: 1.0 mL/min, Temp: 25 ºC.
(S)-1-(2-fluorophenyl)-2-(phenylsulfonyl)ethanol (6c): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-(3-fluorophenyl)-2-(phenylsulfonyl)ethanol (6d): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 ºC).
(S)-1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanol (6e): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 ºC).
(S)-1-(3-chlorophenyl)-2-(phenylsulfonyl)ethanol (6f): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-(3-bromophenyl)-2-(phenylsulfonyl)ethanol (6g): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol =90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-(4-trifluromethylphenyl)-2-(phenylsulfonyl)ethanol (6h): (HPLC: Chiracel OJ-H, detected at 215 nm, eluent: n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, 25 ºC).
(S)-2-(phenylsulfonyl)-1-tolyethanol (6i): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethanol (6j): (HPLC: Chiracel OJ-H, detected at 215 nm, eluent: n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, 25 ºC).
(S)-1-(phenylsulfonyl)butan-2-ol (6k): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-phenyl-2-tosylethanol (6l): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol =90/10, flow rate = 1.0 mL/min, 25 °C).
(S)-1-(4-flourophenyl)-2-tosylethanol (6m): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol =90/10, flow rate = 1.0 mL/min, 25 ºC).
(S)-1-(4-chlorphenyl)-2-tosylethanol (6n): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 ºC).
(S)-1-(4-triflourophenyl)-2-tosylethanol (60): (HPLC: Chiracel AD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25 ºC).
(S)-1-(4-methylphenyl)-2-tosylethanol (6p): (HPLC: Chiracel OJ-H, detected at 215 nm, eluent: n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, 25 ºC).
Table S1. Reusability of catalyst 3 for the nucleophilic substitution–ATH tandem reaction of 2–bromophenylethanone and sodium benzenesulfinate.\(^a\)

<table>
<thead>
<tr>
<th>Run time</th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tr>
<td>Yield [%]</td>
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<td>95</td>
<td>94</td>
<td>94</td>
<td>94</td>
<td>92</td>
<td>82</td>
</tr>
<tr>
<td>ee [%](^b)</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
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\(^a\) Reaction conditions: catalyst 3 (123.50 mg, 0.050 mmol of Ru based on ICP analysis), 2–bromophenylethanone (1.0 mmol), sodium benzenesulfonate (1.2 mmol), and HCOONa (5.0 mmol), 20.0 mL H\(_2\)O/iPrOH (1:3, v/v), and reaction time (2 h). \(^b\) Determined by chiral HPLC analysis (see Fig. S4 of ESI)

Figure S4. Plot of yield of (S)–1–phenyl–2–(phenylsulfonyl)ethanol versus reaction time for seven successive cycles in the nucleophilic substitution–ATH tandem reaction of 2–bromophenylethanone and sodium benzenesulfonate catalysed by 5.0 mmol % of catalyst 3 at 40\(^\circ\)C.
Figure S5. Reusability of catalyst 3 for the tandem nucleophilic substitution-asymmetric transfer hydrogenation of 2-bromophenylethanone and sodium benzenesulfinate.
Recycle 3.

Recycle 4.

Recycle 5.
Recycle 6.

Recycle 7.