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A substitution/dynamic kinetic resolution – Asymmetric transfer hydrogenation tandem process for preparation of stereocenters β-hydroxy sulfones

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ABSTRACT

A noval method for the synthesis of optically active β-hydroxy sulfones was developed. Through a substitution/dynamic kinetic resolution–asymmetric transfer hydrogenation, the presented method was based on one-pot enantioselective organic transformations of α–bromoindenones and sodium arylsulfinate. The protocol employed $RuCl_2$[(S,S)–TsDPEN](mesitylene) as a catalyst, and sodium formate as a hydrogen source, affording various optically pure vicinal stereocenters β-hydroxy sulfones in high yields with excellent enantioselectivities (up to 99%) and diastereomeric ratios (up to 99:1) under mild reaction conditions.

1. Introduction

One–pot multi–step organic transformations, such as tandem reaction and sequential reaction, were particularly attractive due to atom economy and minimum workload. Another notable advantage of this reaction was the reduction of environmental pollution and cost [1–10]. Therefore, the synthesis of optically pure molecules via multi–step organic transformations was becoming popular in preparation of biologically active compounds [11–14]. It was well-known that optically pure cyclic *β*-hydroxy sulfones with two contiguous chiral centers can be converted into plenty types of biologically active molecules in medicinal chemistry [15–20]. The construction of these β-hydroxy sulfones has been used in many reactions, which in general consists of two steps, i.e. substitution and reduction (reported in Scheme 1). In particular, the enantioselective synthesis of these vicinal cyclic β-hydroxy sulfones and derivatives with two contiguous chiral centers were used in a dynamic kinetic resolution via asymmetric transfer hydrogenation (DKR–ATH) strategy [21,22]. Zhang's group [21] used RuCl[TsDPEN](*p*-cymene) as a catalyst and HCOOH–Et_3N as a hydrogen source to in a DKR–ATH organic transformations of four cyclic β-keto sulfones. In Wang's group, asymmetric hydrogenation method was applied to realize DKR–ATH organic transformations of a cyclic β-keto sulfone [22]. Despite of significant efforts made in the preparation of optically active cyclic β-hydroxy sulfones, the direct construction of 1,2–position stereocenters cyclic β-hydroxy sulfones through a multi–step enantioselective organic transformations with a tandem process has not been fully explored yet.

To explore various asymmetric transfer hydrogenation [23–28], a DKR–ATH method was use in our procedure to obtain an efficient organic transformations of β–substituted ketones into 1,3–position stereocenters phthalides [23]. By screening a series of *N*–(4–methyl)benzenesulfonylated 1,2–diphenylethylenediamine (TsDPEN)–based η^6–areneRu complexes and η^5–Cp*M complexes (Cp* = pentamethylcyclopentadiene) [29–31], η^6–mesityleneRuTsDPEN complex could behave efficiently as an optimal catalyst in substitution/DKR–ATH tandem process, furnishing optically pure 1,2–position stereocenters β-hydroxy sulfones with high yields, enantioselectivities (92–99% *ee*) and diastereomeric ratios (up to 99:1) under mild reaction conditions (shown in Scheme 1).

2. Experimental

2.1. Chemicals and instruments

At the outset of our research, the α–bromoindenones and 2-bromo-3,4-dihydronaphthalen-1(2*H*)-one were prepared according to the published procedures [32]. All other chemicals and solvents were of analytic grade and used as received except as specified. NMR spectra were measured on a Bruker DRX-400 spectrometer. HRMS data were recorded on a GC–TOF instrument by the ESI technique. Then, analytical HPLC was carried out with a Waters® Chromatography setup consisting of: Waters® 717plus Autosampler, Waters® 1525 Binary HPLC Pump, and Waters® 2478 Dual λ Absorbance Detector. The enantiomeric excesses (ee) were determined by using a Daicel Chiralpak®

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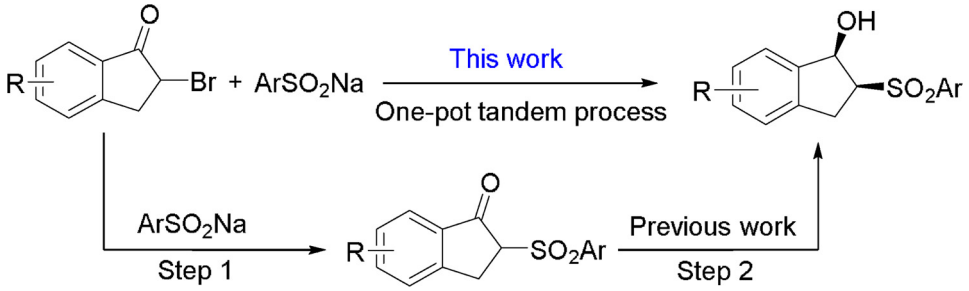


Scheme 1. One–pot Two–step Enantioselective Organic Transformations of α–bromoindenones to Chiral β-Hydroxy Sulfones.

column AD-H or Daicel Chiralcel® column OJ-H with the above HPLC setup.

2.2. Typical procedure for tandem enantioselective transformations of indenoes into chiral β-hydroxy sulfones

During the process, the catalyst (2.0 μmol, 5 mol%), α–bromoindanones (0.10 mmol), sodium arylsulfinate (0.40 mmol), HCOONa (1.0 mmol, 10 equiv) were added sequentially in H_2O/*i*-PrOH (4.0 mL, v/v = 1/3). The mixture was then stirred at 60 °C for 5 h. During this period, the reaction was monitored constantly by TLC. After completion of the reaction, the aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with $NaHCO_3$ and brine, and then dehydrated with Na_2SO_4.

After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired product. The *ee* values were determined by a HPLC analysis using a UV–vis detector (254 nm) and a Daicel chiralcel column (Φ 0.46 × 25 cm), and the dr values were determined by NMR.

(1*R*,2*S*)-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3a). white solid; 26 mg, 95% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.08–7.98 (m, 2H), 7.74–7.65 (m, 1H), 7.64–7.56 (m, 2H), 7.43–7.37 (m, 1H), 7.34–7.22 (m, 3H), 5.36–5.28 (m, 1H), 4.02–3.92 (m, 1H), 3.71 (dd, *J* = 16.1, 8.9 Hz, 1H), 3.27–3.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.9, 140.8, 140.5, 134.1, 129.6, 129.2, 129.1, 127.7, 125.3, 125.2, 74.1, 67.3, 31.9; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{14}NaO_3S$ 297.0556, found 297.0552; $[\alpha]_D^{25}$ = +14.163 (c = 0.220, $CHCl_3$). HPLC (AD-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 54.6 min (major), t_2 = 68.4 min.

(1*R*,2*S*)-2-tosyl-2,3-dihydro-1*H*-inden-1-ol (3b). white solid; 27 mg, 94% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.92 (d, *J* = 8.3 Hz, 2H), 7.45–7.35 (m, 3H), 7.35–7.18 (m, 3H), 5.30 (d, *J* = 5.8 Hz, 1H), 4.00–3.89 (m, 1H), 3.70 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.19 (dd, *J* = 16.1, 8.1 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.5, 144.0, 140.6, 138.0, 130.0, 129.3, 129.1, 127.7, 125.3, 125.2, 74.1, 67.3, 31.9, 21.7; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{16}NaO_3S$ 311.0712, found 311.0725; $[\alpha]_D^{25}$ = +13.784 (c = 0.284, $CHCl_3$). HPLC (AD-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 23.8 min (major), t_2 = 29.1 min.

(1*R*,2*S*)-2-((4-(*tert*-butyl)phenyl)sulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3c). white solid; 31 mg, 94% yield; 92% *ee*, 95:5 *dr*; ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 7.88 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.30–7.15 (m, 4H), 5.60 (d, *J* = 7.1 Hz, 1H), 5.14 (dd, *J* = 7.1, 5.9 Hz, 1H), 4.25–4.14 (m, 1H), 3.41 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.04 (dd, *J* = 15.8, 8.0 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 157.0, 144.0, 140.5, 138.0, 129.2, 129.1, 127.7, 126.4, 125.3, 125.2, 74.1, 67.4, 35.6, 31.9, 31.5; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{22}NaO_3S$ 353.1182, found 353.1185; $[\alpha]_D^{25}$ = +13.381 (c = 0.406, $CHCl_3$). HPLC (AD-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 13.5 min, t_2 = 15.9 min (major).

(1*R*,2*S*)-2-(mesitylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3d): white solid; 29 mg, 93% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48–7.39 (m, 1H), 7.38–7.24 (m, 3H), 7.03 (s, 2H), 5.42 (d, *J* = 5.4 Hz, 1H), 4.07–3.96 (m, 1H), 3.76 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.40 (s, 1H), 3.07 (dd, *J* = 15.7, 7.8 Hz, 1H), 2.74 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 144.2, 143.1, 140.8, 140.3, 135.3, 132.7, 129.0, 127.6, 125.2, 125.1, 74.7, 67.2, 31.1, 23.2, 21.1; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{20}NaO_3S$ 339.1025, found 339.1029; $[\alpha]_D^{25}$ = +11.289 (c = 0.552, $CHCl_3$). HPLC (AD-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 17.0 min, t_2 = 19.6 min (major).

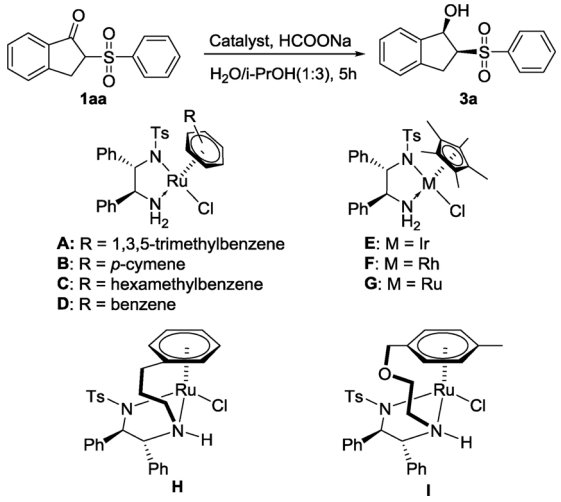
(1*R*,2*S*)-2-((4-fluorophenyl)sulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3e): white solid; 28 mg, 96% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.12–8.01 (m, 2H), 7.44–7.36 (m, 1H), 7.36–7.19 (m, 5H), 5.31 (d, *J* = 5.9 Hz, 1H), 4.02–3.92 (m, 1H), 3.69 (dd, *J* = 16.2, 8.7 Hz, 1H), 3.23 (dd, *J* = 16.2, 8.1 Hz, 1H), 3.13 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 166.3 (d, *J* = 252 Hz), 143.6, 140.2, 136.8, 132.5 (d, *J* = 9.8 Hz), 128.9, 127.5, 125.0 (d, *J* = 4 Hz), 116.4 (d, *J* = 23 Hz), 73.8, 67.3, 31.6; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* −103.04. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{13}FNaO_3S$ 315.0462, found 345.0464; $[\alpha]_D^{25}$ = +8.897 (c = 0.220, $CHCl_3$). HPLC (AD-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 20.6 min, (major) t_2 = 32.2 min.

(1*R*,2*S*)-2-((4-chlorophenyl)sulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3f): white solid; 29 mg, 95% yield; 98% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.00 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 6.7 Hz, 1H), 7.36–7.19 (m, 3H), 5.32 (d, *J* = 5.9 Hz, 1H), 4.04–3.90 (m, 1H), 3.71 (dd, *J* = 16.2, 8.8 Hz, 1H), 3.25 (dd, *J* = 16.3, 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.8, 140.4, 139.5, 139.2, 131.20 (d, *J* = 32.3 Hz), 129.6, 129.1, 127.7, 125.23 (d, *J* = 4.5 Hz), 74.0, 67.5, 31.7; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{13}ClNaO_3S$ 331.0166, found 331.0169; $[\alpha]_D^{25}$ = +5.742 (c = 0.320, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 20.6 min, t_2 = 27.1 min (major).

(1*R*,2*S*)-2-((4-bromophenyl)sulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3 g). white solid; 34 mg, 96% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.36–7.18 (m, 3H), 5.35–5.27 (m, 1H), 4.03–3.91 (m, 1H), 3.69 (dd, *J* = 16.2, 8.8 Hz, 1H), 3.23 (dd, *J* = 16.2, 8.1 Hz, 1H), 3.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.8, 140.4, 140.0, 132.6, 131.4, 130.0, 129.2, 129.1, 128.3, 127.7, 74.1, 67.4, 31.8; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{13}BrNaO_3S$ 374.9661, found 374.9665; $[\alpha]_D^{25}$ = +1.664 (c = 0.120, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 22.7 min (major), t_2 = 30.1 min.

(1*R*,2*S*)-2-((4-(trifluoromethyl)phenyl)sulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3 h). white solid; 31 mg, 92% yield; 94% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 8.17 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.29–7.15 (m, 4H), 5.69 (d, *J* = 7.1 Hz, 1H), 5.16 (dd, *J* = 7.1, 6.0 Hz, 1H), 4.44–4.32 (m, 1H), 3.45 (dd, *J* = 15.9, 8.1 Hz, 1H), 3.13 (dd, *J* = 15.9, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 144.4, 143.5, 140.1, 133.4 (q, *J* = 32 Hz), 130.2, 129.0, 127.5, 126.4 (q, *J* = 3.7 Hz), 125.0, 124.0 (q, *J* = 275 Hz), 73.8, 67.2, 31.4; ^{19}F NMR

Table 1
Screening the chiral catalyst for the DKR–ATH of 2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-one.[a]



entry	catalyst	yield (%)[b]	ee (%)[c]	dr[c]
1	**A**	99	99	99:1
2	**B**	95	99	98:2
3	**C**	95	99	98:2
4	**D**	95	99	99:1
5	**E**	90	99	99:1
6	**F**	97	99	99:1
7	**G**	trace	–	–
8	**H**	95	−57	1:99
9	**I**	95	−84	1:99

[a] Reaction conditions: 2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-one (0.10 mmol), HCOONa (1.0 mmol), solvent (4 mL).
[b] Isolated yield.
[c] Determined by chiral HPLC.

(376 MHz, $CDCl_3$) δ −63.22. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{13}F_3NaO_3S$ 365.0430, found 365.0433; $[\alpha]_D^{25} = -4.872$ (c = 0.328, $CHCl_3$)·HPLC (AD-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 14.0 min, t_2 = 18.4 min (major).

(1*R*,2*S*)-2-((2-fluorophenyl)sulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3i). white solid; 27 mg, 91% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.98 (m, 1H), 7.76–7.65 (m, 1H), 7.46–7.22 (m, 6H), 5.41 (d, *J* = 6.0 Hz, 1H), 4.39–4.24 (m, 1H), 3.81 (dd, *J* = 16.3, 8.4 Hz, 1H), 3.27 (dd, *J* = 16.3, 8.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.5 (d, *J* = 256 Hz), 143.8, 140.1, 137.0 (d, *J* = 8 Hz), 131.6, 128.7 (d, *J* = 15 Hz), 127.7, 125.6, 125.1 (d, *J* = 10 Hz), 117.8 (d, *J* = 22 Hz), 74.4, 67.5, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.43. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{13}FNaO_3S$ 315.0462, found 315.0463; $[\alpha]_D^{25} = -8.459$ (c = 0.340, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 28.3 min (major), t_2 = 31.2 min.

(1*R*,2*S*)-2-(naphthalen-2-ylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3j). white solid; 29 mg, 89% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.11–7.92 (m, 4H), 7.78–7.62 (m, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.36–7.18 (m, 3H), 5.35 (d, *J* = 5.7 Hz, 1H), 4.13–4.00 (m, 1H), 3.78 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.23 (dd, *J* = 16.1, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.9, 140.5, 138.0, 135.4, 132.3, 130.7, 130.1, 129.8, 129.5, 129.1, 128.5, 128.2, 127.7, 125.3, 125.2, 124.3, 74.2, 67.4, 31.9; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}NaO_3S$ 347.0712, found 347.0715; $[\alpha]_D^{25} = +7.452$ (c = 0.520, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 85/15, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 18.1 min (major), t_2 = 21.8 min.

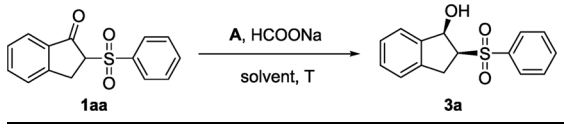
(1*R*,2*S*)-5-bromo-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3k). white solid; 34 mg, 95% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.99 (m, 2H), 7.75–7.67 (m, 1H), 7.66–7.57 (m, 2H), 7.45–7.37 (m, 2H), 7.31–7.24 (m, 1H), 5.34–5.26 (m, 1H), 4.02–3.94 (m, 1H), 3.70 (dd, *J* = 16.4, 8.6 Hz, 1H), 3.31 (d, *J* = 6.8 Hz, 1H), 3.19 (dd, *J* = 16.4, 8.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.4, 143.3, 140.6, 134.2, 130.6, 129.6, 129.2, 128.2, 127.2, 122.1, 73.6, 67.2, 31.7; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{13}BrNaO_3S$ 374.9661, found 374.9661; $[\alpha]_D^{25} = +19.582$ (c = 0.408, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 103.4 min (major), t_2 = 126.2 min.

(1*R*,2*S*)-5-chloro-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3l). white solid; 29 mg, 94% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.00 (m, 2H), 7.75–7.67 (m, 1H), 7.64–7.57 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27–7.20 (m, 2H), 5.31 (d, *J* = 5.9 Hz, 1H), 4.04–3.90 (m, 1H), 3.68 (dd, *J* = 16.3, 8.7 Hz, 1H), 3.17 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.82 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.0, 142.9, 140.6, 134.2, 133.5, 129.6, 129.2, 127.8, 126.8, 125.2, 73.5, 67.3, 31.7; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{13}ClNaO_3S$ 331.0166, found 331.0169; $[\alpha]_D^{25} = +21.381$ (c = 0.454, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 93/7, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 81.2 min (major).

(1*R*,2*S*)-6-methoxy-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3m). white solid; 30 mg, 97% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.88 (m, 2H), 7.64–7.56 (m, 1H), 7.56–7.45 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.24–5.09 (m, 1H), 3.94–3.85 (m, 1H), 3.70 (s, 3H), 3.53 (dd, *J* = 15.8, 8.6 Hz, 1H), 3.21 (d, *J* = 7.2 Hz, 1H), 3.03 (dd, *J* = 15.8, 8.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.4, 145.3, 140.9, 134.0, 132.2, 129.5, 129.2, 125.9, 115.5, 110.1, 74.2, 67.8, 55.7, 31.1; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{16}NaO_4S$ 327.0622, found 327.0665; $[\alpha]_D^{25} = +21.148$ (c = 0.204, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 47.5 min (major).

(1*R*,2*S*)-2-(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-ol

Table 2
Optimization of reaction conditions for the DKR–ATH of 2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-one.[a]



1aa 3a

entry	solvent	temp. (°C)	time (h)	yield (%)[b]	ee (%)[c]	dr[c]
1	H_2O/*i*-PrOH (1:3)	60	5	98	99	99:1
2	H_2O/*i*-PrOH (1:1)	60	5	93	99	86:14
3	H_2O/EtOH (1:3)	60	6	95	99	71:29
4	H_2O/MeOH (1:3)	60	6	85	98	93:7
5	H_2O/DMF (1:3)	60	12	95	99	98:2
6	H_2O/DMSO (1:3)	60	12	< 10	ND	ND
7	H_2O	60	6	83	97	97:3
8	H_2O/CH_2Cl_2 (1:3)	40	12	97	94	99:1
9	H_2O/DCE (1:3)	60	12	95	98	99:1
10	H_2O/*i*-PrOH (1:3)	r.t.	12	98	99	99:1
11	H_2O/*i*-PrOH (1:3)	40	7	98	99	99:1
12	H_2O/*i*-PrOH (1:3)	70	4	98	99	96:4

[a] Reaction conditions: catalyst A (2.0 μmol), 2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-one (0.10 mmol), HCOONa (1.0 mmol), 4.0 mL of solvent.
[b] Isolated yield.
[c] Determined by HPLC.

(3n). white solid; 27 mg, 94% yield; 99% *ee*, 99:1 *dr*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.97 (m, 2H), 7.77–7.68 (m, 1H), 7.68–7.58 (m, 2H), 7.31–7.10 (m, 4H), 5.11–5.04 (m, 1H), 3.40–3.21 (m, 2H), 3.15–3.05 (m, 1H), 2.92–2.76 (m, 1H), 2.56–2.39 (m, 1H), 2.33–2.20 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.8, 138.5, 135.7, 134.2, 130.6, 129.7, 129.5, 129.1, 128.5, 65.8, 65.3, 28.6, 18.0; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{16}NaO_3S$ 311.0712, found 311.0715; $[\alpha]_D^{25} = -8.171$ (c = 0.132, $CHCl_3$). HPLC (OJ-H, elute: Hexane/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 18.1 min (major), t_2 = 25.3 min.

3. Results and discussion

In this one-pot organic transformation, enantioselectivity was the most considerable objective. Therefore, the reaction conditions for the ATH process were optimized firstly. Based on our previous work [33], the chiral catalysts were screened in the co-solvent of H_2O/*i*-PrOH (1/3, v/v). As shown in Table 1, most of tested catalysts except **G** provided corresponding product with high yields. Low ee (57% and 84%) values were obtained with **H** and **I** as the catalyst (entry 8 and 9, Table 1). Excellent diastereomeric selectivities were observed with each catalyst (**A**-**I**). In this work, **A** was chosen as the catalyst for the present one-pot transformation approach. With the best ruthenium catalyst in hand, further study focuses on the optimization of the asymmetric transfer hydrogenation of 2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-one in the presence of catalyst **A**, and the results were displayed in Table 2. After getting good result in the solvent of H_2O/*i*-PrOH (1/3, v/v), this transformation in H_2O/*i*-PrOH (1:1) was also testified. Corresponding product was obtained with high yield, excellent enantioselectivities (99% ee) and medium diastereoselectivity (dr 86:14, entry 2, Table 2). Two other alcohols (methanol and ethanol) with water were also used as the reaction solvent. A little lower diastereoselectivity (dr value

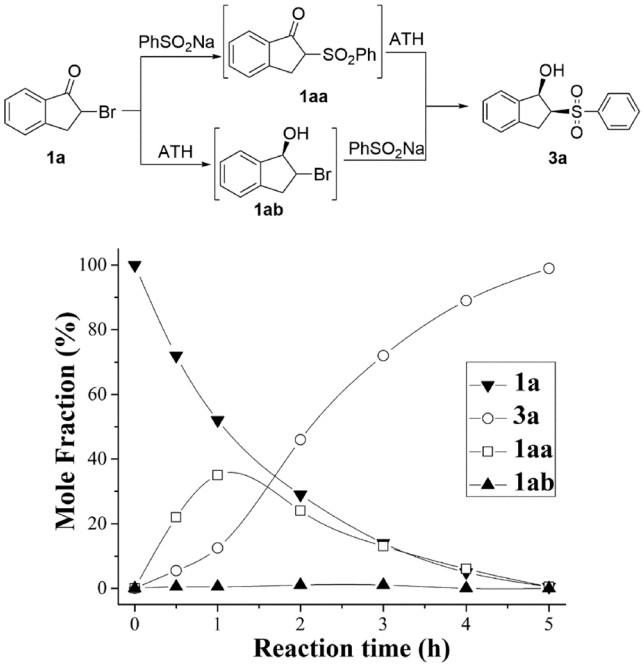
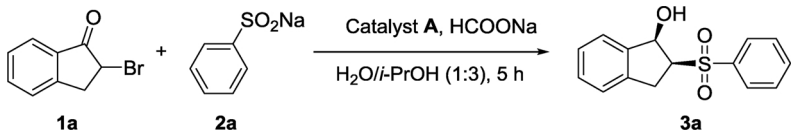


Fig. 1. Time course of the transformation of α–bromoindanone and sodium benzenesulfinate to (1*R*,2*S*)–2–(phenylsulfonyl)–2,3–dihydro–1*H*–indenol (Reactions were performed with 5.0 mol% of catalyst **A**, 0.1 mmol of α–bromoindanone and 4 equivalent of sodium benzenesulfinate, 10 equivalent of HCOONa in H_2O/*i*-PrOH (4.0 mL, v/v, 3:1) at 60 °C.

Table 3
Screening the chiral catalyst for the asymmetric transfer hydrogenation of 2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-one.[a]

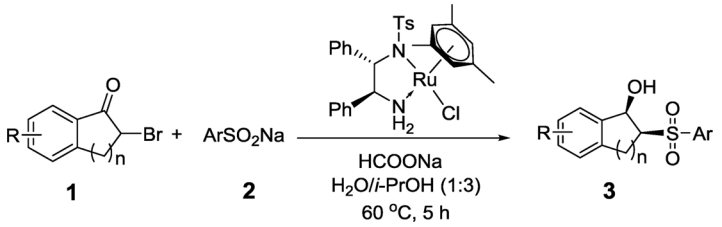


1a 2a 3a

entry	2a	yield (%)[b]	ee (%)[c]	dr[c]
1	2 eq	67	99	99:1
2	3 eq	83	99	99:1
3	4 eq	93	99	99:1
4	5 eq	95	99	93:7

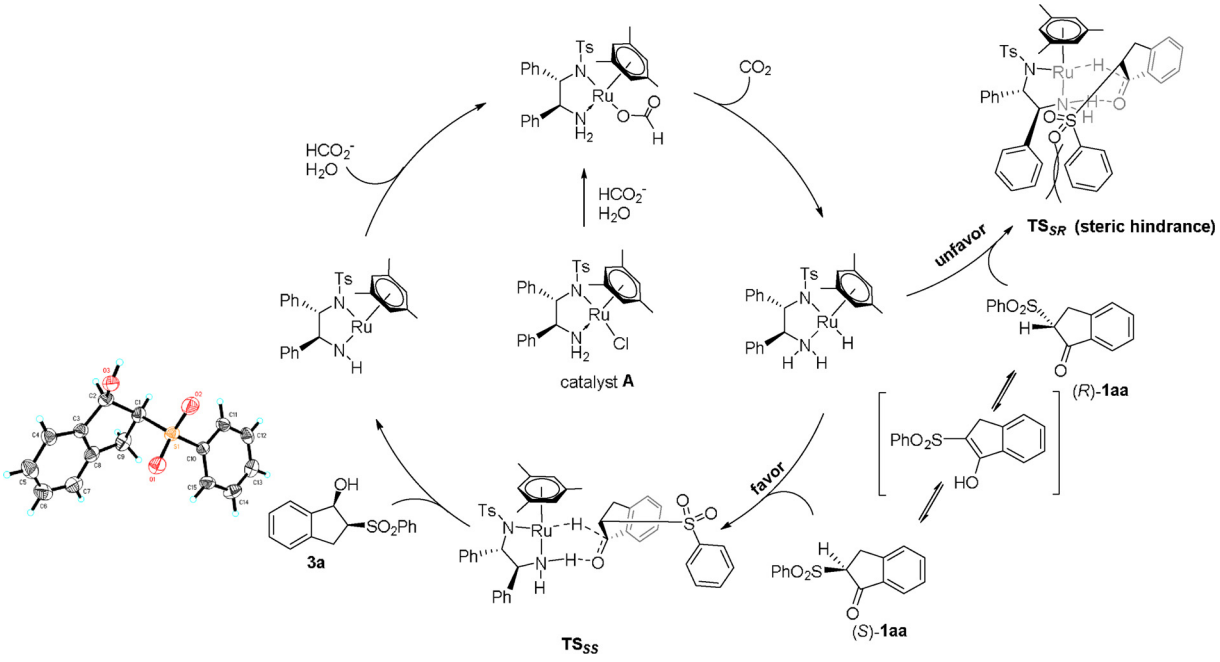
[a] Reaction conditions: catalyst **A** (2.0 μmol), α–bromoindanone (0.10 mmol), sodium benzenesulfinate, HCOONa (1.0 mmol), H_2O/*i*-PrOH (4.0 mL, v/v, 3:1).
[b] Isolated yield.
[c] Determined by chiral HPLC.

Table 4
The Substitution/DKR–ATH One-pot Enantioselective Tandem Reaction of α–Bromoindanones and Sodium Arylsulfinate.[a]



entry	3	n	R	Ar	yield (%)[b]	*ee* (%)[c]	*dr*[c]
1	**3a**	1	H	Ph	93	99	99:1
2	**3b**	1	H	4–MePh	94	99	99:1
3	**3c**	1	H	4–^{t}BuPh	94	92	95:5
4	**3d**	1	H	2,4,6–Me_3Ph	93	99	99:1
5	**3e**	1	H	4–FPh	96	99	99:1
6	**3f**	1	H	4–ClPh	95	98	99:1
7	**3g**	1	H	4–BrPh	96	99	99:1
8	**3h**	1	H	4–CF_3Ph	92	94	91:9
9	**3i**	1	H	2–FPh	91	99	99:1
10	**3j**	1	H	2–naphthyl	89	99	99:1
11	**3k**	1	5–Br	Ph	95	99	99:1
12	**3l**	1	5–Cl	Ph	94	99	99:1
13	**3m**	1	6–MeO	Ph	97	99	99:1
14	**3n**	2	H	Ph	94	99	99:1

[a] Reaction conditions: catalyst **A** (2.0 μmol), α–bromoindanone (0.10 mmol), sodium benzenesulfinate (0.40 mmol), HCOONa (1.0 mmol), H_2O/*i*-PrOH (4.0 mL, v/v, 3:1), reaction temperature: 60 °C.
[b] Isolated yield.
[c] Determined by HPLC (See ESI).



Scheme 2. Proposed catalytic mechanism and (b) the X–Ray Structure of **3a**.

71:29) and yield (85%) were obtained in H_2O/EtOH (1:3) and H_2O/MeOH (1:3), respectively (entries 3 and 4, Table 2). More reaction time was needed to complete the transformation in the co-solvent of polar aprotic solvents (DMF and DMSO) and water (entries 5 and 6, Table 2). Only 83% yield was observed when the reaction was carried out in water (entry 7, Table 2). Longer reaction time was needed in two-phase system (entries 8 and 9, Table 2). Moreover, through the further optimization of the reaction temperature, It was found that lower reaction temperature reduced reaction rate (entries 10 and 11, Table 2), while the enhanced temperature reduced the diastereoselectivity (entry 12, Table 2). In combination with the results from the above studies, the asymmetric transfer hydrogenation was optimized and carried out in the presence of catalyst **A** in H_2O/*i*-PrOH (1/3, v/v) at 60 °C with HCOONa as hydrogen source.

Having established the efficient DKR-ATH of 2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-one, the substitution/DKR–ATH one-pot enantioselective tandem reaction was further investigated. It was found that the increased amount of sodium benzenesulfinate enhanced the

total yields (Table 3). However, diastereoselectivity started decreasing when 5 equivalent sodium benzenesulfinate was added (entry 4, Table 3). Therefore, 4 equivalent sodium benzenesulfinate was chosen for the one-pot reaction.

It was worth mentioning that such a clean substitution/DKR–ATH reaction of α–bromoindanone and sodium benzenesulfinate catalyzed by **A** could reach its catalytic completion within 5 h, which was the same with single step of ATH. This finding suggested the tandem behaviour in this substitution/DKR–ATH one-pot enantioselective reaction was better than that in two step reaction. In order to explore the nature of this tandem reaction, the time course of one–pot transformation of 2–(phenylsulfonyl)–2,3–dihydro–1*H*–indenone and sodium benzenesulfinate to (1*R*,2*S*)–2–(phenylsulfonyl)–2,3–dihydro–1*H*–indenol was investigated. As shown in Fig. 1, it was found that the substitution processes at first with the 2–bromoindenone (**1a**) decreases sharply, which was faster as seen by the formation of 2–(phenylsulfonyl)–2,3–dihydro–1*H*–indenone (**1aa**) in a maximum yield of 35%. Subsequently, the DKR–ATH of 2–(phenylsulfonyl)–2,3–dihydro–1*H*–indenone occurs quickly at the point where the maximum amount of **1aa** has been produced, providing the target product of (1*R*,2*S*)–2–(phenylsulfonyl)–2,3–dihydro–1*H*–indenol (**3a**). It was found that almost no **1ab** was detected during the reaction, which means the reaction was a tandem reaction.

After obtaining an efficient substitution/DKR–ATH one-pot enantioselective tandem reaction of α–bromoindanone and sodium benzenesulfinate, a series of α–bromoindenones and sodium arylsulfinate were further investigated to verify its general applicability in this tandem process. As shown in Table 4, various 2–bromoindenones and arylsulfinate could be transferred smoothly into optically pure 1,2–position stereocenters β-hydroxy sulfones in high yields with excellent enantioselectivities and diastereomeric ratios under the optimal reaction conditions. Also, it was found that the structures and electronic properties of substituents in the Ar group did not affect significantly their enantioselectivities, where both electron–withdrawing and electron–donating substituents connecting with Ar group were equally efficient on the basis of the catlaytic results (entries 2–10). Similarly, the structures and electronic properties of substituents in the aromatic ring at R_1 group did also not affect significantly their enantioselectivities as observed (entries 11–13). Besides the one–pot organic transformations of the α–bromoindanones described in Table 4, this substitution/DKR–ATH was also applied to the other kinds of tandem reaction. Taking 2-bromo-3,4-dihydronaphthalen-1(2*H*)-one as an example, the substitution/DKR–ATH one-pot enantioselective tandem reaction of 2-bromo-3,4-dihydronaphthalen-1(2*H*)-one and sodium benzenesulfinate also gave the chiral product of (1*R*,2*S*)-2-(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalenol in 94% yield with 99% *ee* and 99:1 *dr* under the same reaction conditions (entry 14).

The ATH proceeds in aqueous solution have been reported [34,35] and the proposed catalytic cycle was shown in Scheme 2. The catalyst precursor **A** was actived by HCOONa, which was proved by Noyori, Ikariya and co-workers [29]. Then the active catalyst combines with the substrate **1aa** and transfers hydrogen to it. As shown in Scheme 2, (*S,S*)-TsDPENRu-H-mesitylene, active catalyst, prefer combining with (*S*)-**1aa** rather than (*R*)-**1aa**. A diastereomeric transition state models was proposed, $\mathbf{TS}_{SS}$ (favorable transition state) and $\mathbf{TS}_{SR}$ (unfavorable transition state), for KR–ATH of **1a** with the active catalyst **A** in Scheme 2. Notably, the unfavorable transition state ($\mathbf{TS}_{SR}$) was attributed to the steric hindrance between the Ph group in TsDPEN molecule and the Ph groups in $-SO_2Ph$ moiety, whereas the favorable transition state ($\mathbf{TS}_{SS}$) has not the steric hindrance to afford the major enantiomer product **3a** that are similar to that reported by Bhanage's group [36]. In addition, (*R*)-**1aa** could be converted into (*S*)-**1aa** via enolization process, which provides the possibility of DKR. To determine chiral product's absolute stereochemistry, compound **3a** was investigated by a X–ray crystallographic analysis. As shown in Scheme 2, it was found that the absolute stereochemistry of **3a** could be determined as (1*R*,2*S*)–isomer configuration, confirming the product's absolute stereochemistry that are accorded with to the reported configuration [37].

4. Conclusion

In conclusions, through the use of RuCl[(*S,S*)–TsDPEN)](mesitylene) as a catalyst, an efficient substitution/DKR–ATH one-pot enantioselective tandem reaction of α–bromoindanones and arylsulfinate was presented. This reaction was carried out in a co-solvent of H_2O/*i*-PrOH (1/3, v/v) at 60 °C using HCOONa as a hydrogen source, affording various optically active 1,2–position stereocenters β-hydroxy sulfones in high yields with excellent enantioselectivities and diastereomeric ratios from a variety of α–bromoindanones.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.04.019.

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