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1) Experimental procedure for transfer hydrogenation of 1-phenyl-1,2-propanedione (2a) to (*S*)-1-phenyl-2-hydroxy-1-propanone, (*S*)-3a, catalyzed by RuCl[(1*S*,2*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethanediamine](η^6-*p*-cymene), (*S*,*S*)-1c

A mixture of triethylamine 620 μL (4.4 mmol) and formic acid 285 μL (7.5 mmol) was added to 1-phenyl-1,2-propanedione (**2a**) (1013 mg, 6.8 mmol) and RuCl[(1*S*,2*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethanediamine](η^6-*p*-cymene), (*S*,*S*)-**1c**, (14.5 mg, 2.2 x 10^{-2} mmol) and then the mixture was degassed by freeze-thaw cycles. The mixture was stirred at 10 °C for 24 h, then saturated brine was added. The crude reaction products were extracted with diethyl ether and the organic layer was separated, washed with water, dried over Na_2SO_4, passed through a silica gel pad, and concentrated under reduced pressure to give a 9:1 mixture of (*S*)-1-phenyl-2-hydroxy-1-propanone, (*S*)-**3a**, with 99% ee and (*S*)-1-phenyl-1-hydroxy-2-propanone, (*S*)-**4a**, with 12% ee with

an overall yield of 100%. (Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.)

3a, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.46 (d, J = 7.0 Hz, 3H, C*H*$_3$), 3.8 (brs, 1H, O*H*), 5.16 (q, J = 7.3 Hz, 1H, C*H*), 7.3-7.6 (m, 3H, aromatic ring protons, *m* and *p*), 7.92 (m, 2H, aromatic ring protones, *o*). (lit. ref 1)

4a, ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.08 (s, 3H, C*H*$_3$), 4.1 (brs, 1H, O*H*), 5.10 (s, 1H, C*H*), 7.3 (m, 5H, aromatic ring protons). (ref 1)

HPLC retention time: **3a**, (*R*) 50.5 min, (*S*) 30.0 min, **4a**, (*R*) 47.2 min, (*S*) 59.5 min. (Conditions: Chiralcel OB Hexane:2-propanol = 99:1, 0.5 ml/min, 35 °C, UV 254 nm)

Authentic samples of optically active **3a** and **4a** were obtained by the Sharpless dihydroxylation of enol ethers. (ref 2)

(1) Guthrie, J. P.; Cossar, *J. Can. J. Chem.* **1990**, *68*, 2067–2069.

(2) Hashiyama, T.; Morikawa, K.; Sharpless, K. B. *J. Org.* Chem. **1992**, *57*, 5067–5068.

2) Experimental procedure for transfer hydrogenation of 2a to *anti*-(1*R*,2*S*)-1-phenyl-1,2-propanediol, *anti*-(1*R*,2*S*)-5a, catalyzed by (*S*,*S*)-1c

A mixture of triethylamine 544 μL (3.9 mmol) and formic acid 250 μL (6.6 mmol) was added to 1-phenyl-1,2-propanedione (**2a**) (222 mg, 1.5 mmol) and (*S*,*S*)-**1c** (3.0 mg, 5.0 x 10^{-3} mmol) and the mixture was degassed by freeze-thaw cycles. The mixture was stirred at 40 °C for 24 h. In a similar work up procedure to described in 1), a 8:2 mixture of *anti*-(1*R*,2*S*)-1-phenyl-1,2-propanonediol, (1*R*,2*S*)-**5a**, with 97% ee and *syn*-(1*R*,2*R*)-1-phenyl-1,2-propanonediol, (1*R*,2*R*)-**5a**, with 6% ee with an overall yield of 95% was obtained. (Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.)

anti-**5a**, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.10 (d, J = 6.6 Hz, 3H, C*H*$_3$), 2.5 (brs, 2H, O*H*), 4.03 (m, 1H, C*H*CH$_3$), 4.69 (d, J = 4.4 Hz, 1H, C_6H_5C*H*), 7.2–7.7 (m, 5H, aromatic protones). (ref 1)

syn-(**5a**), ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.07 (d, J = 6.8 Hz, 3H, CH_3), 2.5 (brs, 2H, O*H*), 3.88 (m, 1H, $CHCH_3$), 4.38 (d, J = 7.3 Hz, 1H, C_6H_5CH), 7.2–7.7 (m, 5H, aromatic ring protons). (ref 1)

GLC retention time of acetonide of **5a**: *syn*-(1*R*,2*R*), 22.2 min, *syn*-(1*S*,2*S*), 24.2 min, *anti*-(1*R*,2*S*), 34.7 min, *anti*-(1*S*,2*R*), 38.2 min. (Conditions: Chirasil-DEX CB, column 0.25 mm x 25m, column temp 100 °C, injection temp 200 °C, detection temp 200 °C)

Authentic sample of optically active *syn*-**5a** was obtained by the Sharpless dihydroxylation of *trans*-β-methylstyrene[2)] and optically active *anti*-**5a** was obtained by the diastereoselective reduction of optically active **3a**. Ratio of stereoisomers of **5a** were determined by GLC analysis after conversion to acetonide derivatives.

(1) Bowlus, S. B.; Katzenellenbogen, J. A. *J. Org. Chem.* **1974**, *39*, 3309–3314.

(2) (a) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483–2547. (b) Kolb, H. C.; Sharpless, K. B.; *Tetrahedron Lett.* **1992**, *50*, 10515–10530. (c) Wang, L.; Sharpless, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 7568–7570.

3) Experimental procedure for transfer hydrogenation of (*S*)-3a to *anti*-(1*R*,2*S*)-5a catalyzed by (*S*,*S*)-1c

A mixture of triethylamine 544 μL (3.9 mmol) and formic acid 175 μL (4.7 mmol) was added to (*S*)-**3a** (225 mg, 1.5 mmol, 89% ee) and (*S*,*S*)-**1c** (3.0 mg, 5.0 x 10^{-3} mmol) and the mixture was degassed by freeze-thaw cycles. The mixture was stirred at 40 °C for 24 h, then work up as the similar way to 1) to give a 82:18 mixture of *anti*-(1*R*,2*S*)-1-phenyl-1,2-propanonediol, (1*R*,2*S*)-**5a**, with >99% ee and *syn*-(1*R*,2*R*)-1-phenyl-1,2-propanonediol, (1*R*,2*R*)-**5a**, with 45% ee in a quantitative yield. (Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.)

4) Experimental procedure for transfer hydrogenation of (*R*)-3a to *syn*-(1*R*,2*R*)-5a catalyzed by (*S*,*S*)-1c

A mixture of triethylamine 544 μL (3.9 mmol) and formic acid 175 μL (4.7 mmol) was added to (*R*)-**3a** (225 mg, 1.5 mmol, 89% ee, containing 2% of **4a**) and (*S*,*S*)-**1c** (3.0 mg, 5.0 x 10^{-3} mmol) and the mixture was degassed by freeze-thaw cycles. The mixture was stirred at 40 °C for 24 h, then work up as the similar way to 1) to give a 14:86 mixture of *anti*-(1*R*,2*S*)-1-phenyl-1,2-propanonediol, (1*R*,2*S*)-**5a**, with 64% ee and *syn*-(1*R*,2*R*)-1-phenyl-1,2-propanonediol, (1*R*,2*R*)-**5a**, with 96% ee in a quantitative yield. (Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.)

5) Experimental procedure for transfer hydrogenation of racemic 4a to *syn*-(1*R*,2*R*)-5a catalyzed by (*S*,*S*)-1c

A mixture of triethylamine 907 μL (6.5 mmol) and formic acid 292 μL (7.8 mmol) was added to racemic **4a** (375 mg, 2.5 mmol) and (*S*,*S*)-**1c** (3.0 mg, 5.0 x 10^{-3} mmol) and the mixture was degassed by freeze-thaw cycles. The mixture was stirred at 40 °C for 24 h. A similar work-up procedure to that described in 1) gave a 19:81 mixture of *anti*-(1*R*,2*S*)-1-phenyl-1,2-propanonediol, (1*R*,2*S*)-**5a**, with 74% ee and *syn*-(1*R*,2*R*)-1-phenyl-1,2-propanonediol, (1*R*,2*R*)-**5a**, with 83% ee with an overall yield of 91%. (Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.)

6) Spectral data for the transfer hydrogenation products and analytical conditions

Products obtained from the reaction of 2b

3b, ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.3 Hz, 3H, C*H*$_3$), 1.62 (m, 1H, C*H*HCH$_3$), 1.95 (m, 1H, CH*H*CH$_3$), 3.8 (br, 1H, O*H*), 5.07 (dd, *J* = 4.1, 6.3 Hz, 1H, C*H*), 7.2 (m, 3H, aromatic ring protons, *m* and *p*), 7.91 (m, 2H, aromatic ring protones, *o*).

4b, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.01 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 2.35 (m, 2H, C*H*$_2$CH$_3$), 4.3 (br, 1H, O*H*), 7.2 (m, 5H, aromatic ring protons).

GLC retention time of stereoisomers of **3b**, 39.2 min, 42.5 min, stereoisomers of **4b**, 40.8 min, 44.0 min. (Conditions: Chirasil-DEX CB, 0.25 mm x 25 m, column temp

50 °C (hold 10 min) up to 120 °C (10 °C/min), then hold, injection temp 200 °C, detection temp 200 °C)

anti-**5b**, ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.95 (t, J = 6.1 Hz, 3H, CH_3), 1.2–1.5 (m, 2H, CH_2), 2.5 (br, 2H, O*H*), 3.75 (m, 1H, CHC_2H_5), 4.69 (d, J = 4.6 Hz, 1H, C_6H_5CH), 7.3 (m, 5H, aromatic ring protones). (lit ref 1)

syn-**5b**, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.07 (d, J = 6.8 Hz, 3H, CH_3), 1.2–1.5 (m, 2H, CH_2), 2.5 (br, 2H, O*H*), 3.61 (m, 1H, CHC_2H_5), 4.45 (d, J = 6.8 Hz, 1H, C_6H_5CH), 7.3 (m, 5H, aromatic ring protons).

GLC retention time of acetonides of *anti*-**5b**, 24.2min, 26.8 min, *syn*-**5b**, 18.7 min, 19.4 min. (Conditions: Chirasil-DEX CB, 0.25 mm x 25 m, column temp 110 °C, injection temp 200 °C, detection temp 200 °C) (Ratio of stereoisomers of **5b** were determined by GLC analysis after conversion to acetonides.)

(1) Takeshita, M.; Miura, N.; Unuma, Y. *J. Chem. Soc., Perkin Trans 1* **1993**, 2901–2905.

Products obtained from the reaction of 2c

3c, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.45 (d, J = 7.1 Hz, 3H, CH_3), 3.84 (d, J = 6.6 Hz, 1H, O*H*) 3.89 (s, 3H, OCH_3), 5.11(m, 1H, C*H*), 6.98 (d, J = 8.8 Hz, 2H, aromatic ring protones, *m*), 7.92 (d, J = 8.8 Hz, 2H, aromatic ring protones, *o*). (lit ref 1)

GLC retention time of **3c**, (*R*) 40.75 min, (*S*) 45.60 min. (Conditions: Chirasil-DEX CB, 0.25 mm x 25 m, column temp 100 °C to 140 °C (2 °C/min), injection temp 200 °C, detection temp 200 °C)

$[\alpha]_D^{28}$–41.1 (*c* 1.12, CH_3OH) (lit. $[\alpha]_D^{25}$ –33.4 (*c* 1.05, CH_3OH), (*S*), ref 1)

anti-**5c**, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.08 (d, J = 6.3 Hz, 3H, CH_3), 2.5 (br, 2H, O*H*), 3.80(s, 3H, OCH_3), 3.98 (m, 1H, $CHCH_3$), 4.59 (d, J = 4.4 Hz, 1H, C_6H_5CH), 6.89 (m, 2H, aromatic ring protones, *o*), 7.28 (m, 2H, aromatic ring protones, *m*). (lit ref 2)

syn-**5c**, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.03 (d, J = 6.3 Hz, 3H, CH_3), 2.5 (br, 2H, O*H*), 3.80(s, 3H, OCH_3), 3.80 (m, 1H, $CHCH_3$), 4.30 (d, J = 7.6 Hz, 1H, C_6H_5CH),

6.89 (m, 2H, aromatic ring protones, *o*), 7.28 (m, 2H, aromatic ring protones, *m*). (lit ref 2)

GLC retention time of acetnides of stereo isomers of **5c**, *syn*-(1*R*,2*R*), 23.9 min, *syn*-(1*S*,2*S*), 24.7 min, *anti*-(1*R*,2*S*), 29.0 min, *anti*-(1*S*,2*R*), 31.8 min. (Conditions: Chirasil-DEX CB, 0.25 mm x 25 m, column temp 130 °C, injection temp 200 °C, detection temp 200 °C)

Authentic sample of *anti*-(1*R*,2*S*)-**5c** was obtained by the reaction of (*S*)-**3c**. (*S*)-**3c** with 92% ee reacted with $LiAlH_4$ in diethyl ether at –78 °C for 1 h giving 86:24 mixture of *anti*-(1*R*,2*S*)-**5c** with 98% ee and *syn*-(1*S*,2*S*)-**5c** with 49% ee in a quantitative yield. $[\alpha]_D^{27}$ –26.2 (*c* 1.30, $CHCl_3$)

(1). Honda, Y.; Ogi, A.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1027–1036.

(2) Sy, L.-K.; Brown, G. D. *J. Nat. Prod.* **1998**, *61*, 987–992.

Products obtained from the reaction of 2d

3d, ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.40 (dd, *J* = 1.5 Hz, 6.8 Hz, 3H, C*H*$_3$), 4.0 (br, 1H, O*H*), 5.00 (m, 1H, C*H*), 6.8–7.0 (m, 2H, aromatic ring protones, *m*), 8.00 (m, 1H, aromatic ring protones, *o*). $[\alpha]_D^{27}$+ 65 (*c* 1.2, $CHCl_3$) (lit. $[\alpha]_D^{27}$ +73 (*c* 1, $CHCl_3$), (*R*), ref 1)

4d, ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.14 (s, 3H, C*H*$_3$), 4.28 (br, 1H, O*H*), 5.37 (s, 1H, C*H*), 6.8–7.3 (m, 3H, aromatic ring protones).

GLC retention time of (*R*)-**3d**, 18.2 min, (*S*)-**3d**, 18.6 min, stereoisomers of **4d**, 22.0 min, 23.0 min. (Conditions: Chirasil-DEX CB, 0.25 mm x 25 m, column temp 110 °C (20 min hold) then up to 180 °C (10 °C/min), injection temp 200 °C, detection temp 200 °C)

(1) Gala, D.; DiBenedetto, D. J. ; Clark, J. E.; Murphy, B. L.; Schumacher, D. P.; Steinman, M. *Tetrahedron Lett.* **1996**, *37*, 611–614.