SUPPORTING INFORMATION

for

Asymmetric Hydrogenation of α-Chloro Aromatic Ketones Catalyzed by η^6-Arene/TsDPEN–Ruthenium(II) Complexes

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CONTNETS

(1) Procedure for the preparation of Ru(OTf)[(*S*,*S*)-Tsdpen](mesitylene) [(*S*,*S*)-3c]

A mixture of RuCl[(*S*,*S*)-Tsdpen](mesitylene)[1] (1.18 g, 1.9 mmol) and KOH (0.107 g, 1.9 mmol) in CH_2Cl_2 (30 mL) and water (3 mL) was stirred at room temperature for 10 min under an Ar[2] atmosphere. The CH_2Cl_2 layer was separated and dried over anhydrous Na_2SO_4, then over CaH_2. The purple organic layer containing Ru[(*S*,*S*)-Tsdpen](mesitylene)[1] was filtered through a filter paper and the filtrate was used for the preparation of Ru(OTf)[(*S*,*S*)-Tsdpen](mesitylene) [(*S*,*S*)-**3c**].

A solution of TfOH (140 μL, 1.60 mmol) in CH_2Cl_2[2] (10 mL) was added dropwise to CH_2Cl_2 solution (the total volume was adjusted to 90 mL) of Ru[(*S*,*S*)-Tsdpen](mesitylene) prepared as described above under an Ar atmosphere at room temperature over a period of 30 min. Then the solution was evapolated to a volume of 20 mL. Cooling the solution to –40 ˚C gave an orange precipitate. The precipitate was filtered and dried under reduced pressure to give (*S*,*S*)-**3c** (0.479 g, 41% yield).

^{1}H NMR (400 MHz, 21 mM in CD_2Cl_2) δ 2.16 (s, 3H, CH_3 of Ts), 2.33 (s, 9H, CH_3 of mesitylene), 3.69–3.77 (m, 1H, C*H*NH_2), 3.86–3.93 (m, 1H, N*H*H), 3.89 (d, *J* = 10.6 Hz, 1H, C*H*Ts), 4.94 (d, *J* = 10.5 Hz, 1H, NH*H*), 5.34 (s, 3H, aromatic protons of mesitylene), 6.51 (d, *J* = 7.3 Hz, 2H, aromatic protons), 6.73–6.77 (m, 4H, aromatic protons), 6.83–6.87 (m, 3H, aromatic protons), 7.13–7.21 (m, 5H, aromatic protons).

^{13}C NMR (100.4 MHz, 21 mM in CD_2Cl_2) δ 18.9, 21.3, 69.1, 75.0, 76.6, 103.8, 126.9, 127.3, 127.8, 128.5, 128.5, 128.9, 129.0, 129.2, 138.3, 138.9, 140.1, 142.2.

Anal. Calcd. for: C 50.60, H 4.52, N 3.81; found: C 50.55, H 4.60, N 3.69.

^{1}H and ^{13}C NMR charts of (*S*,*S*)-**3c** are attached in Part (7).

(2) Procedure for the asymmetric hydrogenation of α-chloroacetophenone (1a) with (*S*,*S*)-3a

Ru(OTf)[(*S*,*S*)-Tsdpen](*p*-cymene) [(*S*,*S*)-**3a**] was prepared according to our previous report.[3] The silanization of the glassware was necessary to secure the reproducibility of the hydrogenation. The detailed procedure was also indicated in the previous manuscript.[3]

α-Chloroacetophenone (**1a**) (256 mg, 1.5 mmol) and (*S,S*)-**3a**[3] (1.1 mg, 1.5 μmol) were placed in a 100-mL glass autoclave. The atmosphere was replaced with Ar gas, and methanol[4] (5.8 mL) was added to this mixture. Hydrogen[4] was initially introduced into the autoclave at a pressure of 10 atm, before being reduced to 1 atm. This procedure was repeated three times. Then the autoclave was pressurized with H_2 gas (10 atm), and the solution was stirred vigorously at 30 ˚C for 15 h. The ^{1}H-NMR and HPLC analysis indicated that (*R*)-2-chloro-1-phenylethanol [(*R*)-**2a**] with 96% ee was obtained in >99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (d, *J* = 3.2 Hz, 1H, OH), 3.64 (dd, *J* = 8.8 Hz and 11.3 Hz, 1H, C*H*HCl), 3.72 (dd, *J* = 3.6 Hz and 11.3 Hz, 1H, CH*H*Cl), 4.87–4.89 (m, 1H, C*H*OH), 7.31–7.38 (m, 5H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 130 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2a**, 19.6 min; (*R*)-**2a**, 21.6 min.

$[\alpha]_D^{25}$ –47.5 (*c* 1.7, cyclohexane), (lit. $[\alpha]_D^{25}$ –48.1, *c* 1.73, cyclohexane, 100% ee (*R*), Imuta, M.; Kawai, K.; Ziffer, H. *J. Org. Chem.* **1980**, *45*, 3352–3355).

^{1}H NMR and GLC charts of (*R*)-**2a** are attached in Part (7).

(3) Analytical data of hydrogenation products

(*R*)-2-Chloro-1-(3-methylphenyl)ethanol [(*R*)-2b]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H, CH_3), 2.73 (d, *J* = 2.8 Hz, 1H, OH), 3.64 (dd, *J* = 8.9 Hz and 11.2 Hz, 1H, C*H*HCl), 3.72 (dd, *J* = 3.4 Hz and 11.2 Hz, 1H, CH*H*Cl), 4.83–4.86 (m, 1H, C*H*OH), 7.14–7.26 (m, 4H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 140 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2b**, 19.0 min; (*R*)-**2b**, 19.4 min.

$[\alpha]_D^{25}$ –52.0 (*c* 1.0, $CHCl_3$).

The procedure used to determine the absolute configuration is described in Part (6).

(*R*)-2-Chloro-1-(4-methylphenyl)ethanol [(*R*)-2c]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 2.63 (s, 1H, OH), 3.64 (dd, *J* = 8.8 Hz and 11.2 Hz, 1H, C*H*HCl), 3.72 (dd, *J* = 3.4 Hz and 11.2 Hz, 1H, CH*H*Cl), 4.86 (dd, *J* = 3.4 Hz and 8.8 Hz, 1H, C*H*OH), 7.17–7.28 (m, 4H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 130 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2c**, 29.1 min; (*R*)-**2c**, 31.9 min.

$[\alpha]_D^{25}$ –54.2 (*c* 1.1, $CHCl_3$), (lit. $[\alpha]_D^{25}$ +47.2, *c* 1.10, $CHCl_3$, 92% ee (*S*), Basavaiah, D.; Reddy, J. G.; Chandrashekar, V. *Tetrahedron*: *Asymmetry* **2001**, *12*, 685–689).

(*R*)-2-Chloro-1-(4-methoxylphenyl)ethanol [(*R*)-2d]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.6 (br s, 1H, OH), 3.63 (dd, *J* = 8.7 Hz and 11.2 Hz, 1H, C*H*HCl), 3.70 (dd, *J* = 3.7 Hz and 11.2 Hz, 1H, CH*H*Cl), 3.80 (s, 3H, CH_3O), 4.85 (dd, *J* = 3.7 Hz and 8.7 Hz, 1H, C*H*OH), 6.89–6.91 (m, 2H, aromatic protons), 7.29–7.32 (m, 2H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 140 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2d**, 41.4 min; (*R*)-**2d**, 43.2 min.

$[\alpha]_D^{22}$ –49.9 (*c* 2.2, $CHCl_3$), (lit. $[\alpha]_D^{22}$ +40.2, *c* 2.2, $CHCl_3$, 91% ee (*S*), Wei, Z.-L.; Lin, G.-Q. *Tetrahedron* **1998**, *54*, 13059–13072).

(*R*)-2-Chloro-1-(3-hydroxyphenyl)ethanol [(*R*)-2e]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (dd, *J* = 8.3 Hz and 11.2 Hz, 1H, C*H*HCl), 3.70 (dd, *J* = 3.9 Hz and 11.2 Hz, 1H, CH*H*Cl), 3.93 (br s, 1H, OH), 4.82 (dd, *J* = 3.9 Hz and 8.3

Hz, 1H, C*H*OH), 6.78–6.77 (m, 1H, aromatic proton), 6.83–6.85 (m, 2H, aromatic protons), 7.16–7.21 (m, 1H, aromatic proton).

The HPLC analytical conditions were as follows: column, CHIRALCEL OB–H (4.6 mm i. d. x 250 mm); eluent, hexane/2-propanol = 95/5; flow rate, 0.8 mL/min; column temp, 25 ˚C; detection, UV 220 nm. The retention times were as follows: (*R*)-**2e**, 55.3 min; (*S*)-**2e**, 66.3 min.

$[\alpha]_D^{25}$ –40.3 (*c* 0.6, $CHCl_3$).

The absolute configuration was determined after conversion to the corresponding methyl ether by the conventional method.[6] The procedure used to determine the absolute configuration is described in Part (6).

(*R*)-2-Chloro-1-(2-chlorophenyl)ethanol [(*R*)-2f]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (br s, 1H, OH), 3.55 (dd, *J* = 8.5 Hz and 11.2 Hz, 1H, C*H*HCl), 3.90 (dd, *J* = 2.8 Hz and 11.2 Hz, 1H, CH*H*Cl), 5.29–5.31 (m, 1H, C*H*OH), 7.26–7.37 (m, 3H, aromatic protons), 7.62–7.65 (m, 1H, aromatic proton).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 130 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were: (*S*)-**2f**, 53.8 min; (*R*)-**2f**, 59.9 min.

$[\alpha]_D^{18}$ –61.2 (*c* 1.0, $CHCl_3$), (lit. $[\alpha]_D^{25}$ –2.6, *c* 1.0, $CHCl_3$, 7% ee (*R*), Wei, Z.-L.; Lin, G.-Q. *Tetrahedron* **1998**, *54*, 13059–13072).

(*R*)-2-Chloro-1-(3-chlorophenyl)ethanol [(*R*)-2g]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (br s, 1H, OH), 3.62 (dd, *J* = 8.7 Hz and 11.2 Hz, 1H, C*H*HCl), 3.74 (dd, *J* = 3.4 Hz and 11.2 Hz, 1H, CH*H*Cl), 4.88–4.91 (m, 1H, C*H*OH), 7.25–7.34 (m, 4H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium

(100 MPa); column temp, 150 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2g**, 23.9 min; (*R*)-**2g**, 24.6 min.

$[\alpha]_D^{21}$ –45.5 (*c* 0.5, $CHCl_3$), (lit. $[\alpha]_D^{21}$ +46.8, *c* 0.5, $CHCl_3$, >99% ee (*S*), Inoue, K.; Makino, Y.; Itoh, N. *Tetrahedron*: *Asymmetry* **2005**, *16*, 2539–2549).

(*R*)-2-Chloro-1-(4-chlorophenyl)ethanol [(*R*)-2h]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (d, *J* = 3.2 Hz, 1H, OH), 3.60 (dd, *J* = 8.7 Hz and 11.2 Hz, 1H, C*H*HCl), 3.72 (dd, *J* = 3.4 Hz and 11.2 Hz, 1H, CH*H*Cl), 4.86–4.90 (m, 1H, C*H*OH), 7.31–7.37 (m, 4H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 140 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2h**, 42.4 min; (*R*)-**2h**, 46.9 min.

$[\alpha]_D^{22}$ –45.3 (*c* 2.1, $CHCl_3$), (lit. $[\alpha]_D^{22}$ +44.2, *c* 2.1, $CHCl_3$, 97% ee (*S*), Wei, Z.-L.; Lin, G.-Q. *Tetrahedron* **1998**, *54*, 13059–13072).

(*R*)-2-Chloro-1-(3-trifluoromethylphenyl)ethanol [(*R*)-2i]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (d, *J* = 3.2 Hz, 1H, OH), 3.64 (dd, *J* = 8.6 Hz and 11.4 Hz, 1H, C*H*HCl), 3.77 (dd, *J* = 3.4 Hz and 11.4 Hz, 1H, CH*H*Cl), 4.96–4.99 (m, 1H, C*H*OH), 7.50–7.68 (m, 4H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 150 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were as follows: (*S*)-**2i**, 9.5 min; (*R*)-**2i**, 10.2 min.

$[\alpha]_D^{20}$ –36.5 (*c* 1.0, $CHCl_3$), (lit. $[\alpha]_D^{20}$ +42.8, *c* 1.0, $CHCl_3$, 97% ee (*S*), Hamada, T.; Torii, T.; Izawa, K.; Ikariya, T. *Tetrahedron* **2004**, *60*, 7411–7417).

(*R*)-2-Chloro-1-(4-methoxycarbonylphenyl)ethanol [(*R*)-2j]

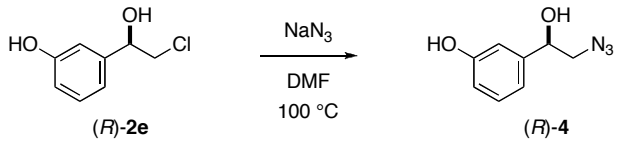
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (d, *J* = 3.2 Hz, 1H, OH), 3.64 (dd, *J* = 8.5 Hz and 11.2 Hz, 1H, C*H*HCl), 3.76 (dd, *J* = 3.4 Hz and 11.2 Hz, 1H, CH*H*Cl), 3.92 (s, 3H, CH_3O), 4.95–4.98 (m, 1H, C*H*OH), 7.45–7.48 (m, 2H, aromatic protons), 8.02–8.05 (m, 2H, aromatic protons).

The GLC analytical conditions were as follows: column, Chiralsil-DEX CB WCOT fused silica; df = 0.25 μm, 0.25 mm i.d. x 25 m (GL Sciences Inc.); carrier gas, helium (100 MPa); column temp, 170 ˚C; injection temp, 250 ˚C; detection temp, 275 ˚C. The retention times were: (*S*)-**2j**, 27.2 min; (*R*)-**2j**, 28.4 min.

$[\alpha]_D^{25}$ –41.8 (*c* 1.0, $CHCl_3$).

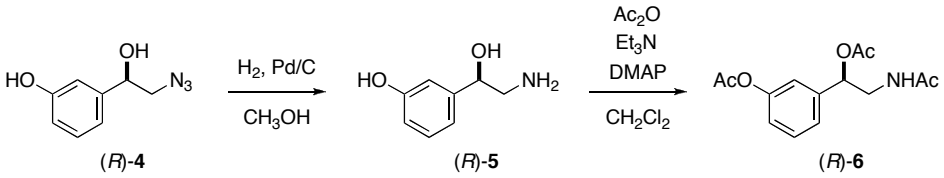
The procedure used to determine the absolute configuration is described in Part (6).

(4) Procedure for the preparation of (*R*)-norphenylephrine [(*R*)-5] from (*R*)-2e



(*R*)-**2e** (*R*)-**4**

A solution of the chlorohydrin (*R*)-**2e** (101.2 mg, 0.586 mmol) and sodium azide (193.3 mg, 2.97 mmol) in DMF (2 mL) was stirred at 100 °C for 8 h under an Ar atmosphere. The reaction mixture was allowed to cool to room temperature, and diluted with water. The mixture was extracted with ethyl acetate (15 mL x 3), and washed successively by water, then brine. The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure. The crude product was purified by thin layer chromatography (benzene:ethyl acetate = 3:1) to afford the azide (*R*)-**4** (97.9 mg, 0.546 mmol, 93% yield). $[\alpha]_D^{22}$ –67.8° (*c* 0.96, $CHCl_3$). IR (KBr neat) 3350, 2926, 2106, 1593, 1458, 1271, 1155, 1067, 875, 789, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (br s, 1H, OH), 3.41–3.50 (m, 2H, CH_2N_3), 4.84 (br t, 1H, C*H*OH), 5.08 (br s, 1H, OH), 6.78–6.80 (m, 1H, aromatic proton), 6.88–6.92 (m, 2H, aromatic protons), 7.22–7.26 (m, 1H, aromatic proton). ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.4, 73.1, 112.9, 115.6, 118.3, 130.0, 141.8, 155.7. HRMS (EI^+) *m*/*z* 179.0698 (M^+), calcd for $C_8H_9N_3O_2$: 179.0695.



(*R*)-**4** (*R*)-**5** (*R*)-**6**

A suspension of the azide (*R*)-**4** (95.8 mg, 0.535 mmol) and 10% Pd/C (38.4 mg) in methanol (4 mL) was vigorously stirred at 25 °C for 15 h under an ambient pressure of hydrogen. The catalyst was removed by filtration through a Celite® pad, followed by evaporation of the solvent, affording crude oil of the amine (*R*)-**5**. To a solution of this residue in CH_2Cl_2 (2 mL) was added triethylamine (0.60 mL, 4.3 mmol), acetic anhydride (0.30 mL, 3.2 mmol), and DMAP (10.8 mg, 0.088 mmol). After stirring at 25 °C for 5 h, water was added, and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (15 mL x 2), and the combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure. The crude product was purified by column chromatography (hexane:ethyl acetate:methanol = 10:20:1) to afford the triacetylated product (*R*)-**6** (0.13 g, 0.47 mmol, 87% yield). $[\alpha]^{24}_{D}$ –44.4° (*c* 1.29, $CHCl_3$). IR (KBr neat) 3287, 3076, 1737, 1656, 1543, 1371, 1202, 1043, 940, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 3H, CH_3CO), 1.96 (s, 3H, CH_3CO), 2.31 (s, 3H, CH_3CO), 3.54–3.61 (m, 1H, C*H*HNHAc), 3.66–3.72 (m, 1H, CH*H*NHAc), 5.69 (br s, 1H, N*H*Ac), 5.85 (dd, *J* = 7.7 Hz and 4.4 Hz, 3H, C*H*OH), 7.04–7.09 (m, 2H, aromatic protons), 7.21 (distorted d, 1H, aromatic proton), 7.39 (distorted d, 1H, aromatic proton). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.89, 20.92, 22.8, 44.0, 73.6, 119.5, 121.48 123.7, 129.5, 139.3, 150.6, 169.2, 170.0, 170.3. HRMS (EI^+) *m*/*z* 279.1105 (M^+), calcd for $C_{14}H_{17}NO_5$: 279.1106.

(5) Procedure for large-scale asymmetric hydrogenation of α-chloroacetophenone (1a)

α-Chloroacetophenone (**1a**) (206 g, 1.33 mol) and (*S,S*)-**3a** (1.02 g, 1.33 mmol) were added to methanol[4] (5.3 L) placed in a 20-L SUS autoclave. Hydrogen was initially introduced into the autoclave at a pressure of 5 atm, before being reduced to 1 atm. This procedure was repeated three times. Then the autoclave was pressurized

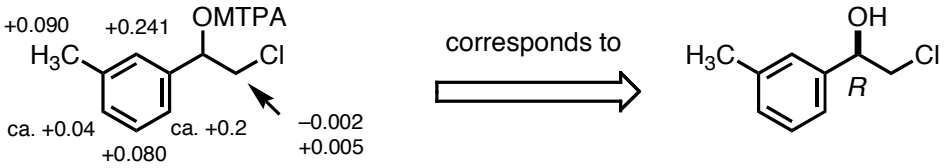
with H_2 gas (10 atm), and the solution was stirred vigorously at 30 ˚C for 10 h. The ^{1}H-NMR and GLC analysis indicated that (*R*)-2-chloro-1-phenylethanol [(*R*)-**2a**] with 96% ee was produced in a quantitative yield.

(6) Determination of the absolute configuration of (*R*)-2b, (*R*)-2e, and (*R*)-2j

The absolute configurations of (*R*)-**2b,** (*R*)-**2e,** and (*R*)-**2j** were estimated by ^{1}H-NMR analysis after conversion to the (*R*)- and (*S*)-2-methoxy-2-phenyl-2-(trifluoromethyl)acetic acid (MTPA) esters as described in the literature.[5] The data are shown in the scheme below.

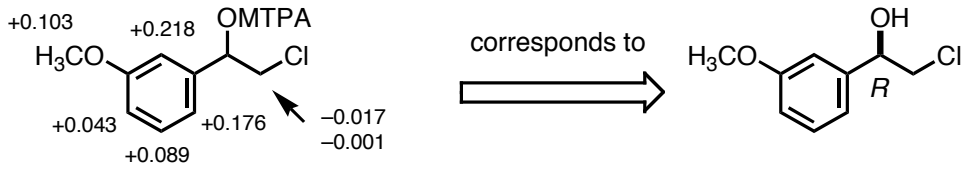
Determination of the absolute configuration of **2b**

$\Delta\delta = \delta_S - \delta_R$



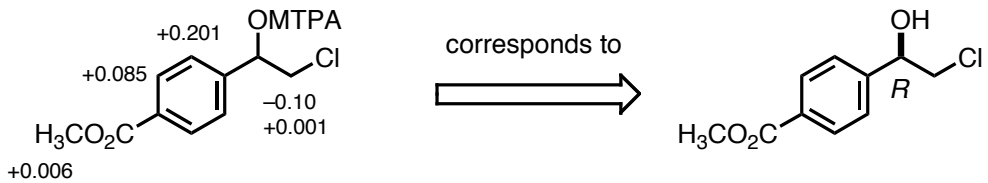
Determination of the absolute configuration of **2e** (in the form of methyl ether)

$\Delta\delta = \delta_S - \delta_R$



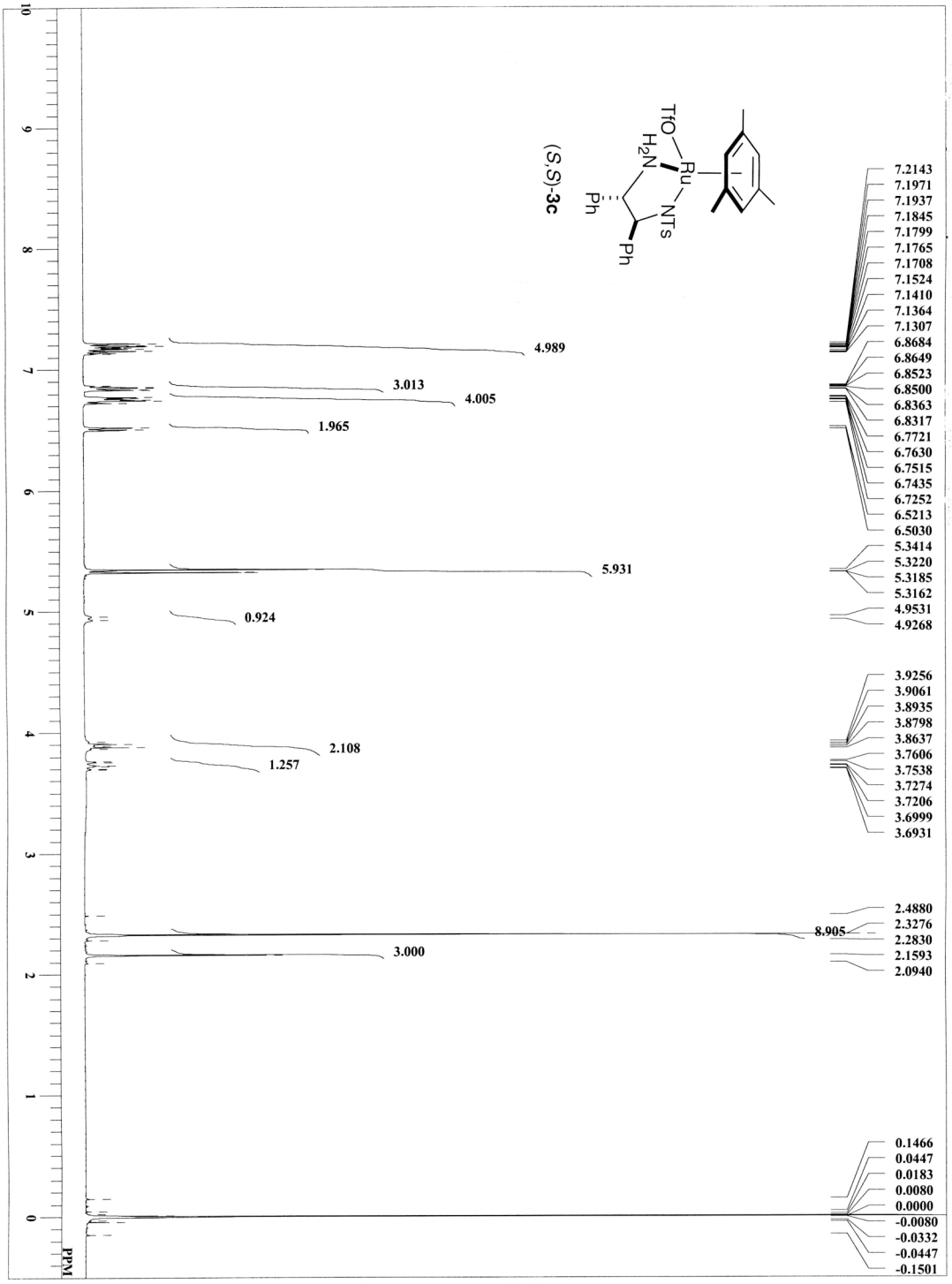
Determination of the absolute configuration of **2j**

$\Delta\delta = \delta_S - \delta_R$

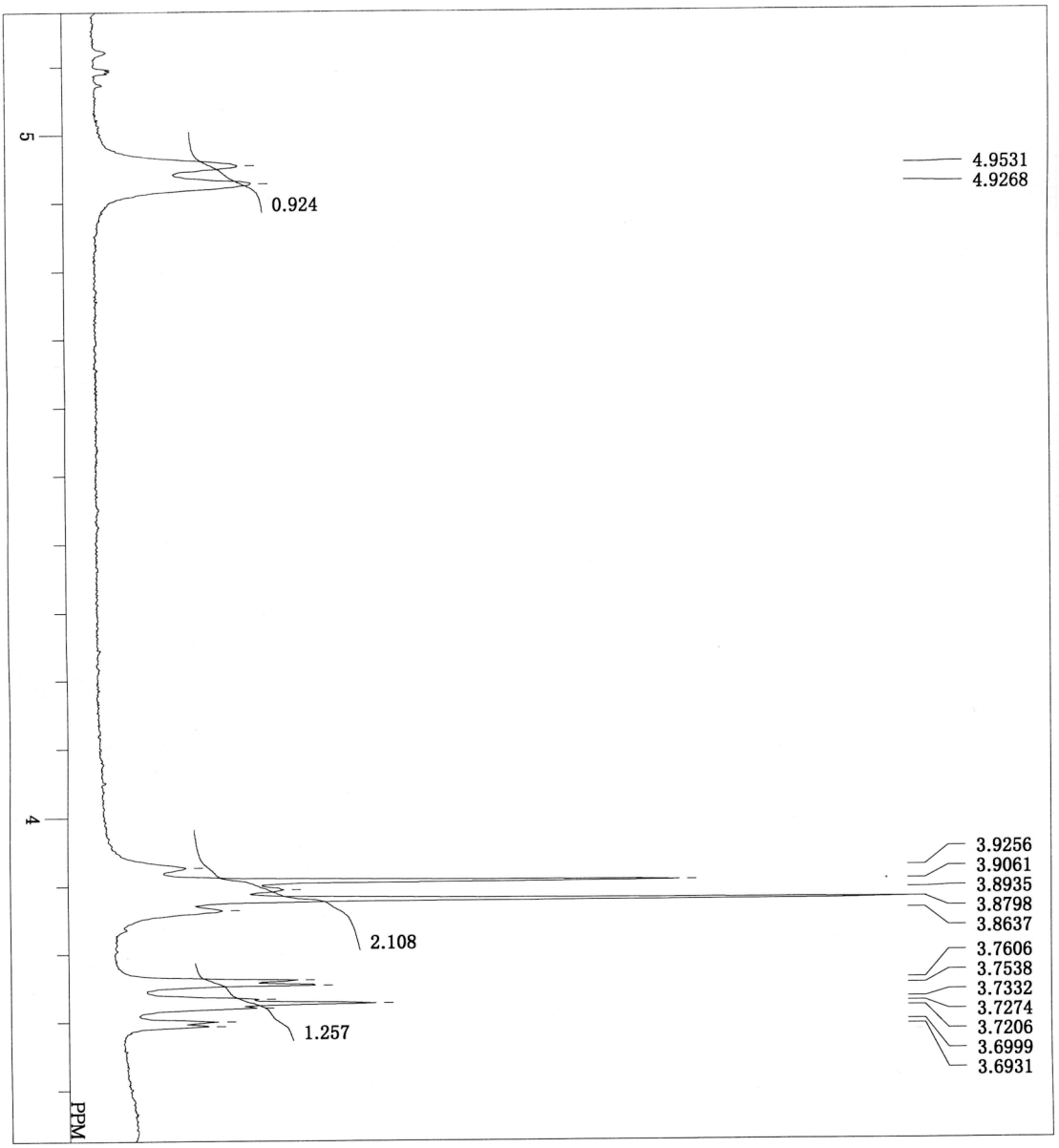


(7) NMR and GLC charts of 3c and 2a

^{1}H NMR chart of (*S*,*S*)-3c



^{1}H NMR chart of (*S*,*S*)-3c (continued): expansion at δ 3.5–5.2



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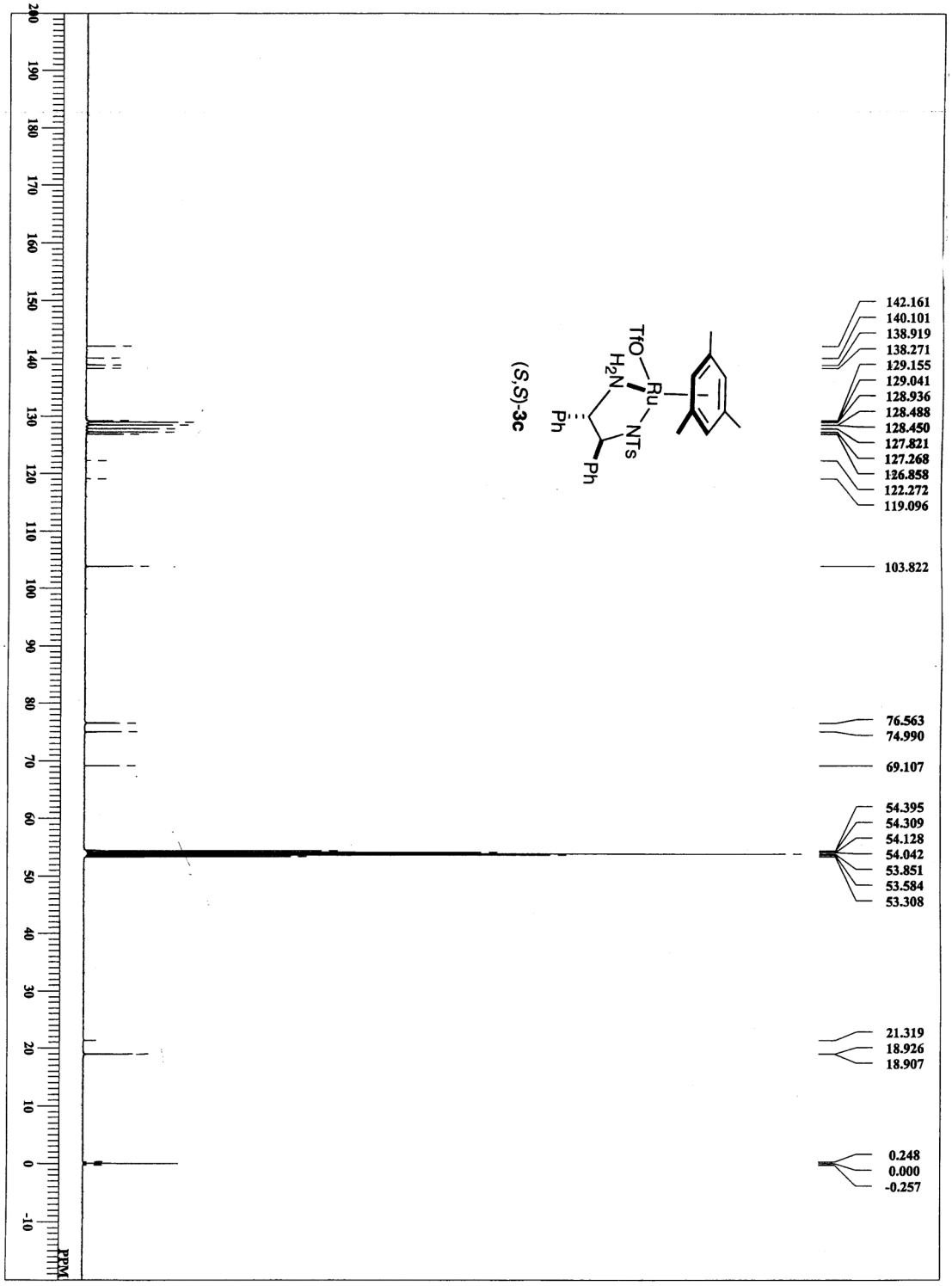
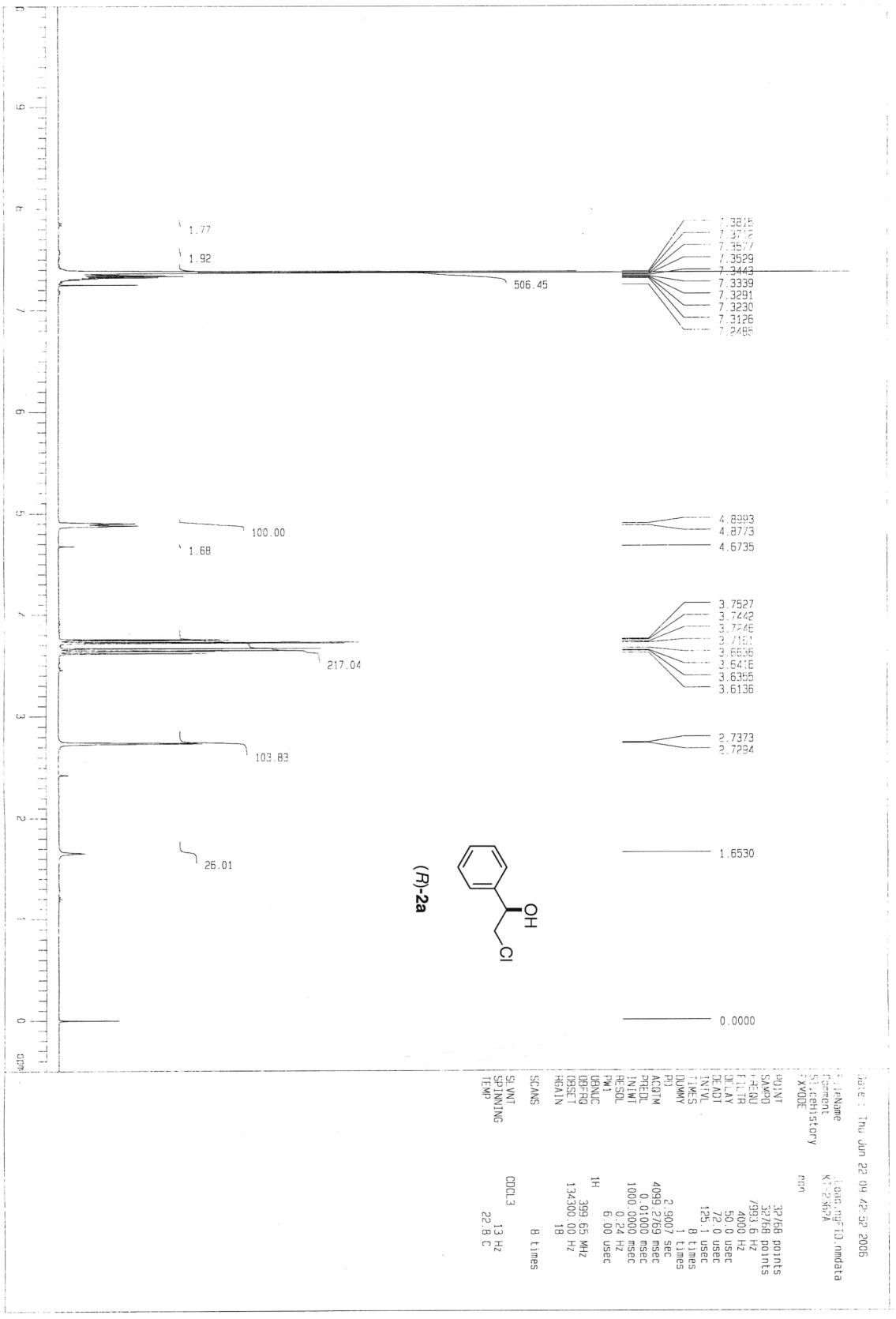
RGAIN 36

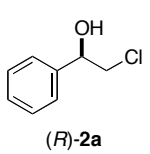
^{13}C NMR chart of (*S*,*S*)-3c



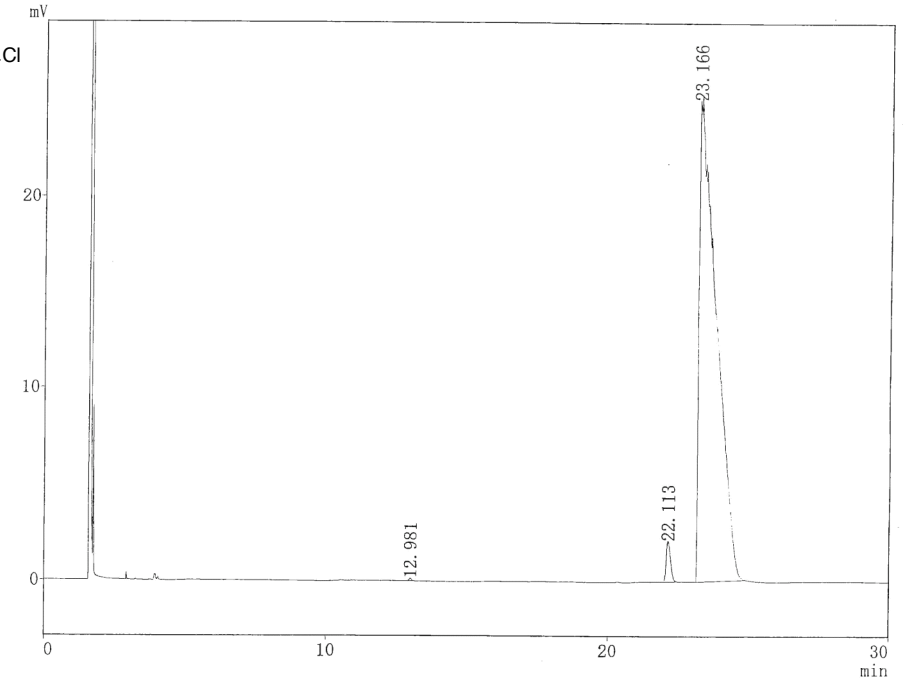
^{1}H NMR chart of (*R*)-2a



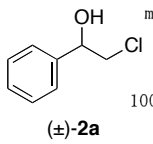
GLC charts of (*R*)-2a and (±)-2a



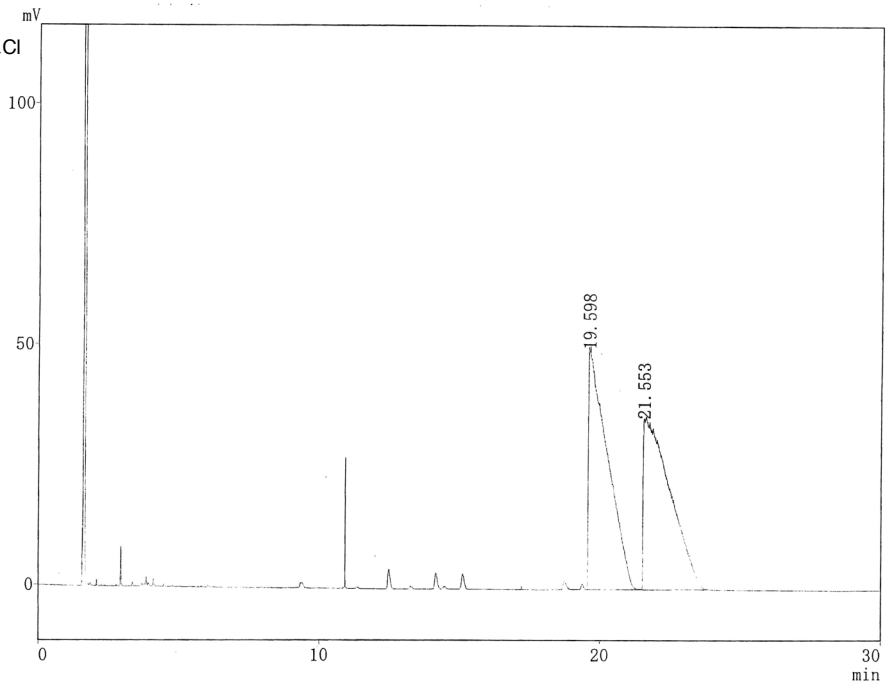
(*R*)-**2a**



PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	12.981	764	127			0.0710	
2	22.113	21987	2127			2.0426	
3	23.166	1053680	24906			97.8864	
		1076431	27160			100.0000	



(±)-**2a**



PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	19.598	2361633	50255			49.7485	
2	21.553	2385509	35522	V		50.2515	
		4747143	85776			100.0000	

Refrences and Notes

(1) (a) Haach, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288. (b) Fujii, A.; Hashiguchi, Uemura, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522. The chloride complexes, RuCl(Tsdpen)(*p*-cymene) and RuCl(Tsdpen)(mesitylene), are commercially available from Kanto Chemical Co., Inc.

(2) Argon gas (purity: >99.999 %) was purchased from Suzuki Shoukan. CH_2Cl_2 was used after distillation of commercial dehydrated CH_2Cl_2 (Kanto Chemical Co., Inc.) over P_2O_5.

(3) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724–8725.

(4) Methanol was used after distillation of commercial dehydrated methanol (Kanto Chemical Co., Inc.) over magnesium methoxide (from magnesium turnings). Hydrogen gas (purity: >99.99999 %) was purchased from Suzuki Shoukan.

(5) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096.

(6) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis, 3rd Edition*: John Wiley & Sons: New York, 1999; pp 249–250.