Electronic Supplementary Information

General

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a JEOL JNM-AL–400 instrument. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ–value in $CDCl_3$). Optical rotations were measured with a JASCO P–1020 polarimeter. Column chromatography was conducted on silica gel 60N (spherical, neutral), 63-210 mm, available from Kanto Chemical Co., Inc. Solvents were dried and distilled shortly before use. Reactions were carried out under nitrogen or argon, if necessary.

Synthesis of (CO)Ru-salen complexes 3 and 5

The requisite salicylaldehyde derivative **12** for the construction of complex **5** was synthesized as described in **Scheme S1**.

(*R*)-2'-Iodo-2-methoxymethoxy-1,1'-binaphtyl 7

Compound **6** (4.0 g, 12.1 mmol) that was prepared according to the reported procedure[1] was dissolved in THF (60 mL) under N_2 at –78 ˚C. *n*-BuLi (1.58 M, 8.4 mL, 13.2 mmol) was added to the solution and stirred for 1 h. Diethyl chlorophosphate (2.1 mL, 13.2 mmol) was added to the solution at the temperature, then warmed to room temperature, stirred for 1 h and re-cooled to –78 ˚C. The mixture was added to a solution of lithium/naphthalene (39.6 mmol, 3.3 eq) in THF (60 mL) and stirred for 1.5 h at the temperature. The mixture was treated with iodine (16.7 g, 65.8 mmol, 5.5 eq), stirred for another 2 h, warmed to room temperature, and concentrated in vacuo.[2] The residue was passed through a short silica gel column (hexane-toluene= 1/0-0/1) to obtain a *ca*. 1:1 mixture of **7** and **8**. Crystallization of the mixture from CH_2Cl_2/hexane gave pure **7** in 45% yield.

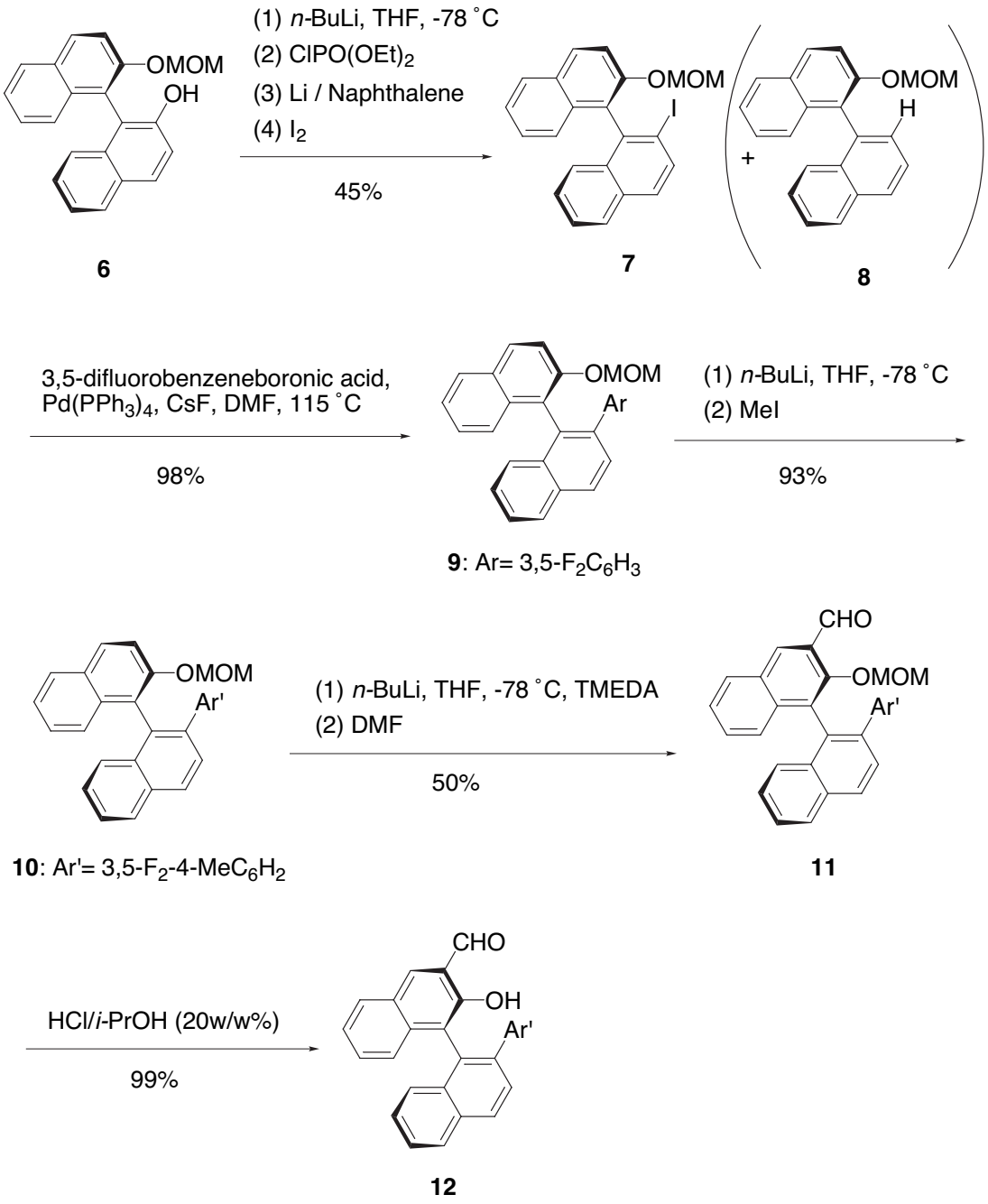
7: $[\alpha]_D^{25}$ +32 (*c* 0.32, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.05 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.90 (m, 2H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.47 (m, 1H), 7.37 (m, 1H), 7.25 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 1H), 5.11 (ABq, *J* = 7.1 Hz, 2H), 3.23 (s, 3H). Anal. Calcd. for $C_{22}H_{17}IO_2$: C, 60.02; H, 3.89. Found: C, 60.23; H, 3.89.

(*S*)-2-Methoxymethoxy -1,1'-binaphtyl 8

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.96-7.93 (m, 3H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.61 (dd, *J* = 7.3 and 7.8 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.48-7.44 (m, 2H), 7.37- 7.34 (m, 2H), 7.29-7.21 (m, 2H), 7.17 (d, *J* = 8.4 Hz 1H), 5.02 (ABq, *J* = 6.8 Hz, 2H), 3.13 (s, 3H).

(*R*)-2'-(3,5-Difluorophenyl)-2-methoxymethoxy-1,1'-binaphtyl 9

Compound **7** (1.0 g, 2.27 mmol), $Pd(PPh_3)_4$ (131 mg, 0.11 mmol, 5 mol%), cesium fluoride (1.03 g, 6.81 mmol, 3 eq) and 3,5-difluorophenylboronic acid (860 mg, 5.5 mmol, 2.4 eq) were added to *N,N*-dimethylformamide (DMF) (8 mL). The suspension was heated to 115 °C, stirred for 24 h at



Scheme S1

the temperature, and then cooled to room temperature.[3] The mixture was partitioned between diethyl ether and aqueous ammonium chloride, and the organic layer was dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane-ethyl acetate= 19:1) to give **9** in 98% yield.

9: $[\alpha]_D^{25}$ +39 (*c* 0.82, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.64 (m, 1H), 7.47 (m, 2H), 7.26 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.67 (m, 2H), 6.48 (m, 1H), 4.98 (ABq, *J* = 6.8 Hz, 2H), 3.14 (s, 3H). HRFABMS m/z Calcd. for $C_{28}H_{20}F_2O_2$ (M^+): 426.1445; found: 426.1431.

(a*R*)- 2'-(3,5-Difluoro-4-methylphenyl)-2-methoxymethoxy-1,1'-binaphtyl 10

Compound **9** (938 mg, 2.2 mmol) was dissolved in THF (5.6 mL) at –78 ˚C under N_2. To the solution was added *n*-BuLi (1.58 M, 1.4 mL, 2.2 mmol, 1.0 eq) and stirred for 1 h. At the temperature, iodomethane (415 μl, 6.7 mmol, 3 eq) was added to the solution, stirred for 1 h, and warmed to room temperature. The mixture was quenched with aqueous ammonium chloride and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel (hexane-ethyl acetate= 8:2) to give compound **10** in 93% yield.

10: $[\alpha]_D^{25}$ +51 (*c* 0.67, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 9.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.23 (m, 5H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 4.98 (ABq, 7.0 Hz, 2H), 3.15 (s, 3H), 2.01 (s, 3H). Anal. Calcd. for $C_{29}H_{22}F_2O_2$: C, 79.08; H, 5.03. Found: C, 79.11; H, 5.17.

(a*R*)- 2'-(3,5-Difluoro-4-methylphenyl)-3-formyl-2-methoxymethoxy-1,1'-binaphtyl 11

Compound **10** (865 mg, 2.0 mmol) was dissolved in THF (5 mL) at –78 ˚C under N_2. To the solution were added *n*-BuLi (1.58 M, 1.4 mL, 2.2 mmol, 1.1 eq) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) (325 μL, 2.2 mmol, 1.1 eq) and stirred for 1 h. At the temperature, DMF (750 μL, 9.7 mmol, 4.8 eq) was added to the solution, stirred for 1 h, and warmed to room temperature. The mixture was quenched with water and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel (hexane-ethyl acetate= 8:2) to give **11** in 50% yield.

11: $[\alpha]_D^{25}$ -11 (*c* 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.40 (s, 1H), 8.47 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.97 (m, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.49 (m, 2H), 7.35 (m, 2H), 7.20 (m, 2H), 6.61 (d, *J* = 8.1 Hz, 2H), 4.55 (ABq, *J* = 5.7 Hz, 2H), 2.91 (s, 3H), 2.01 (s, 3H).

(a*R*)- 2'-(3,5-Difluoro-4-methylphenyl)-3-formyl-2-hydroxy-1,1'-binaphtyl 12

Compound **11** (468 mg, 1.0 mmol) was dissolved in hydrochloric acid/isopropanol (20 w/w%, 10 mL) and the mixture was stirred overnight at room temperature. The mixture was neutralized with aqueous $NaHCO_3$ and extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel (hexane-ethyl acetate= 8:2) to give *o*-hydroxy aldehyde **12** in 99 % yield.

12: $[\alpha]_D^{25}$ -38 (*c* 0.08, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.49 (s, 1H), 10.14 (s, 1H), 8.23 (s, 1H), 8.04 (d, *J* = 8.6, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.90 (m, 1H), 7.58 (d, *J* = 8.6, 1H), 7.50 (m, 1H), 7.33 (m, 3H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.06 (m, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 2.00 (s, 3H). Anal. Calcd. for $C_{28}H_{18}F_2O_2$: C, 79.23; H, 4.27. Found: C, 79.10; H, 4.53.

(a*R*)-2'-[(4-*tert*-Butyldimethylsilyl)phenyl]-3-formyl-2-hydroxy-1,1'-binaphtyl 13

The title compound was prepared according to the reported procedure for the synthesis of (a*R*)-2'-(4-*tert*-butydiphenylsilylphenyl)-3-formyl-2-hydroxy-1,1'-binaphtyl.[4]

13: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.37 (s, 1H), 10.08 (s, 1H), 8.13 (s, 1H), 8.05 (d, *J* = 8.6, 1H), 7.97 (d, *J* = 8.3, 1H), 7.82 (m, 1H), 7.69 (d, *J* = 8.6, 1H), 7.48 (m, 1H), 7.32-7.25 (m, 4H), 7.13-7.09 (m, 5H), 0.65 (s, 9H), 0.13 (s, 6H).

Complexes **3** and **5** were prepared from **12** and **13**, respectively, according to the reported procedure for the synthesis of **1**.[5]

Complex 3

Anal. Calcd. For $C_{73}H_{72}N_2O_3RuSi_2 \cdot 1.0\ H_2O \cdot 1.5\ CH_2Cl_2$: C, 67.38; H, 5.84; N, 2.11. Found: C, 67.40; H, 5.84; N, 2.20

Complex 5

Anal. Calcd. For $C_{63}H_{44}F_4N_2O_3Ru \cdot 1.5H_2O \cdot 1.5CH_2Cl_2$: C, 64.10; H, 4.17; N, 2.32. Found: C, 64.09; H, 4.27; N, 2.32.

Typical Experimental Procedures

Aziridination of styrene using *p*-toluenesulfonyl azide

Complex **5** (1.0 mg, 0.9 μmol) was dried twice by azeotropical concentration of its toluene solution (0.25 mL) in vacuo under nitrogen atmosphere. MS 4A (20 mg), styrene (104 mg, 1.0 mmol) and 2-bromonaphthalene (40 mg, as the internal standard) were added to the dried **5**. To the mixture was added dichloromethane (0.5 mL) and the resulting suspension was stirred for 0.5 h at room temperature. *p*-Toluenesulfonyl azide (155 μL, 1.0 mmol) was added to the suspension and stirred for another 12 h. The yield of the corresponding aziridine was determined by ^{1}H NMR (400 MHz) analysis.

Aziridination of styrene using *p*-nitrobenzenesulfonyl azide

Azeotropically dried complex **5** (4.3 mg, 4 μmol) was placed in a Schlenk tube and purged with nitrogen. Subsequently, MS 4A (20 mg), styrene (10.4 mg, 0.1 mmol), and 2-bromonaphthalene (4.0 mg, as the internal standard) were placed in the tube. To the mixture was added dichloromethane (0.5 mL) and the resulting suspension was stirred for 0.5 h at room temperature. *p*-Nitrobenzenesulfonyl azide (22.8 mg, 0.1 mmol) was added to the suspension and stirred for 24 h. The yield of the corresponding aziridine was determined by ^{1}H NMR (400 MHz) analysis.

Determination of enantiomeric excesses of aziridines

2-Phenyl-1-(*p*-toluenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALCEL OJ-H (hexane:*i*-PrOH = 1:1, 0.5 mL/min, t_R = 23.8 min and t_S = 28.3 min). Absolute configurationwas determined to be *S* by comparison of the specific rotation.[6]

1-(*p*-Nitrobenzenesulfonyl)-2-phenylaziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALCEL OD-H (hexane:*i*-PrOH = 8:2, 0.5 mL/min, t_{major} = 100.5 min and t_{minor} = 107.7 min).

2-(*p*-Bromophenyl)-1-(*p*-toluenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALCEL OD-H (hexane:*i*-PrOH = 8:2, 0.5 mL/min, t_{major} = 56.5 min and t_{minor} = 53.0 min).

2-(*p*-Bromophenyl)-1-(*p*-nitrobenzenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALCEL OD-H (hexane:*i*-PrOH = 1:1, 0.45 mL/min, t_{major} = 47.7 min and t_{minor} = 37.4 min).

2-(*p*-Nitrophenyl)-1-(*p*-toluenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALPAK AD-H (hexane:*i*-PrOH= 2:1, 0.5 mL/min, t_{major} = 34.9 min and t_{minor} = 31.4 min).

2-(2-Naphthyl)-1-(*p*-toluenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALCEL OF (hexane:*i*-PrOH=2:1, 0.5 mL/min, t_{major} = 47.1 min and t_{minor} = 68.0 min).

2-Phenylethynyl-1-(*p*-toluenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALPAK AS-H (hexane:*i*-PrOH=7:3, 0.5 mL/min, t_{major} = 35.9 min and t_{minor} = 42.0 min).

1-(*p*-Nitrobenzenesulfonyl)-2-phenylethynylaziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALCEL OD-H (hexane:*i*-PrOH = 2:1, 0.5 mL/min, t_{major} = 35.7 min and t_{minor} = 43.0 min).

2-(*n*-Hexyl)-1-(*p*-toluenesulfonyl)aziridine

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALPAK AS-H (hexane:*i*-PrOH= 9:1, 0.4 mL/min, t_{major} = 66.2 min and t_{minor} = 70.5 min).

***N*-*p*-Toluenesulfonylindeno[1,2-b]azirine**

The enantiomeric excess was determined by HPLC analysis using DAICEL CHIRALPAK AD (hexane:*i*-PrOH= 15:1, 0.5 mL/min, $t_{1R,2S}$ = 38.3 min and $t_{1S,2R}$ = 42.6 min). Absolute configurationwas determined to be 1*S*,2*R* by comparison of the specific rotation.[6]

References

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