Supplementary Information

(2*S*,4*S*)-4-*tert*-Butyl-2,5,5-triphenyl-oxazolidine (5a)

A solution of aminoalcohol **4a** (1.21 g, 4.50 mmol) and benzaldehyde (0.55 mL, 5.4 mmol) in CH_2Cl_2 (70 mL) was stirred at room temperature for 24h in Ar. Solvent was removed under a reduced pressure. The residue was purified by flash chromatography to afford the oxazolidine **5a** (1.58 g, 98%).

5a : colorless crystal (AcOEt). mp 149-152 °C. $[\alpha]_D^{24} = -59.55$ (c 2.25, $CHCl_3$). IR (KBr) cm^{-1} : 3461. ^{1}H-NMR ($CDCl_3$) δ: 8.14 (s, (1/3)1H), 7.73-7.11 (m, 15H), 5.33 (s, (2/3)1H), 4.08 (s, (1/3)1H), 4.05 (s, (2/3)1H), 0.82 (s, (2/3)9H), 0.79 (s, (1/3)9H). ^{13}C-NMR ($CDCl_3$) δ: 162.22, 149.24, 147.00, 144.94, 135.73, 130.68, 129.35, 128.45, 128.04, 127.91, 127.72, 127.19, 127.05, 126.47, 126.32, 126.27, 125.85, 125.80, 88.21, 83.06, 80.12, 75.54, 36.28, 33.71, 29.55, 28.47. *Anal.* Calcd for $C_{25}H_{27}NO$: C, 83.99; H, 7.61; N, 3.92. Found: C, 84.02; H, 7.84; N, 3.85. EI-MS *m/z* : 357 (M^+) ; HRMS (EI) : calcd for $C_{25}H_{27}NO$ (M^+) 357.2093, found 357.2110.

(2*S*,4*S*)-4-*tert*-Butyl-2,5,5-triphenyl-oxazolidine trifluoroacetate (6a)

A solution of oxazolidine **5a** (578 mg, 1.62 mmol) and trifluoroacetic acid (0.12 mL, 1.62mmol) in CH_2Cl_2 (25 mL) was stirred at 0 °C for 1 min in Ar. Solvent was removed under a reduced pressure to give the oxazolidine salt **6a** in quantitative yield.

6a : colorless crystal (*n*-hexane). mp 70-72 °C. $[\alpha]_D^{20} = -102.88$ (c 2.08, $CHCl_3$). IR (KBr) cm^{-1} : 3368, 1666. ^{1}H-NMR ($CDCl_3$) δ: 7.71 (brs, 2H), 7.58 (d, J = 7.3Hz, 2H), 7.47-7.29 (m, 11H), 5.56 (s, 1H), 4.68 (s, 1H), 0.85 (s, 9H). ^{13}C-NMR ($CDCl_3$) δ: 143.25, 139.50, 130.67, 129.02, 128.99, 128.94, 128.92, 128.63, 128.28, 127.59, 127.57, 126.95, 126.92, 126.89, 89.82, 85.77, 71.72, 34.12, 27.65. *Anal.* Calcd for $C_{27}H_{28}F_3NO_3$: C, 68.78; H, 5.99; N, 2.97. Found: C, 68.79; H, 6.11; N, 2.86. FAB-MS *m/z* : 470 $(M-H)^-$.

General procedure for the DA reaction of 1, 2-dihydropyridine 9 with acrolein 10 using catalyst 6a.

To a CH_3CN (1.0 mL) solution of catalyst **6a** (0.02 mmol), cold water (0.052 mL) and distillated acrolein **10** (0.013 mL, 0.20 mmol) was added at 0 °C and the solution was stirred. After 1 min, 1,2-dihydropyridine **9** (80mg, 0.040 mmol) was added and the solution was stirred at 0 °C for 24h. The reaction was quenched by water. The reaction mixture was diluted with water and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and removed under reduced pressure to give crude DA adduct **11a**, which was used to the next reaction without purification.

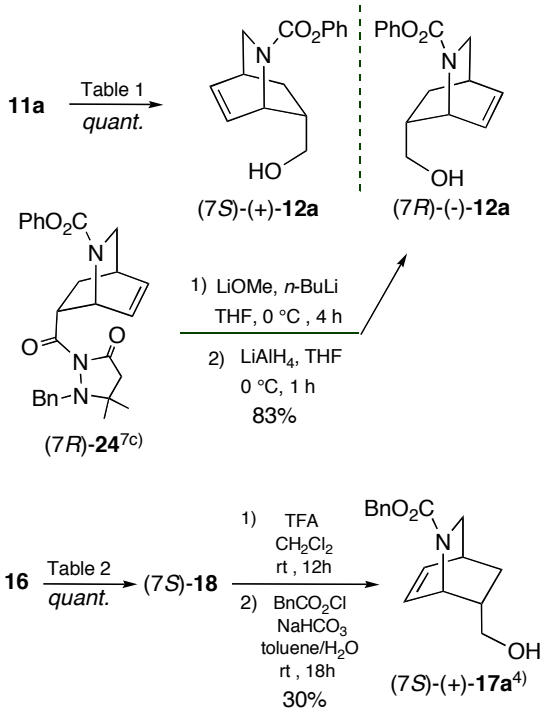
To a stirred solution of product **11a** in ethanol (2.0 mL), $NaBH_4$ (4.0 mg, 0.10 mmol) was added and the mixture was stirred at room temperature for 1 h. Solvent was evaporated under a reduced pressure. The reaction mixture was diluted with water and extracted with AcOEt. The combined organic extracts were washed with brine, dried over $MgSO_4$, removed under reduced pressure to give a crude DA adduct **12a**. The residue was purified by flash chromatography (SiO_2, *n*-hexane : AcOEt = 1 : 1) to afford the DA adduct **12a** in quantitative yield. The enantiomeric excess (ee) was determined by HPLC [DAICEL Chiralcel AD-H, 0.5 mL/min, *n*-hexane : 2-propanol = 85 : 15, t_r (major) = 21.64 min, t_r (minor) = 23.09 min for **12a** (>99% ee), DAICEL Chiralcel AD-H, 0.5mL/min, *n*-hexane : 2-propanol = 85 : 15, t_r (minor) = 16.97 min, t_r (major) = 20.50 min for **12b**]. For the ee's of other catalysts: catalyst **6b** (**12a**： 97% ee), **8a** (**12a**: 27% ee, **12b**: 29% ee), **8b** (**12a**: 85% ee, **12b**: 39% ee), **6e** (**12a**: 39% ee, **12b**: 18% ee), **6f** (**12a**: 33% ee), **6g** (**12a**: 42% ee).

(1*S*,4*S*,7*S*)-7-Hydroxymethyl-2-azabicyclo[2.2.2]oct-5-ene-2-carboxylic acid phenyl ester (12a) : colorless crystal (*n*-hexane/AcOEt). mp 110-112 °C. $[\alpha]_D^{21} = 95.00$ (c 1.00, $CHCl_3$). IR (KBr) cm^{-1} : 3507, 1694, 1408. ^{1}H-NMR ($CDCl_3$) δ: 7.36-7.32 (m, 2H), 7.18 (t, *J* = 7.2Hz, 1H), 7.13-7.10 (m, 1H), 6.41 (t, *J* = 7.0Hz, 1H), 5.01 (brs, (4/9)1H), 4.93 (brs, (5/9)1H), 3.50-3.06 (m, 4H), 2.82 (brs, 1H), 2.47 (brs, 1H), 1.86 (ddt, *J* = 11.6, 8.7, 2.9Hz, 1H), 0.96-0.85 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 151.34, 135.15, 134.80, 130.41, 129.89, 129.14, 125.07, 121.74, 65.49, 47.83, 47.42, 47.08, 41.53, 30.68, 26.05. *Anal.* Calcd for

$C_{24}H_{25}NO$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.65; H, 6.69; N, 5.41. EI-MS *m/z* : 259 (M^+) ; HRMS (EI) : calcd for $C_{15}H_{17}NO_3$ (M^+) 259.1208, found 259.1202.

The absolute stereochemistry assignment of the new DA adducts 11a, 16, 20, 21

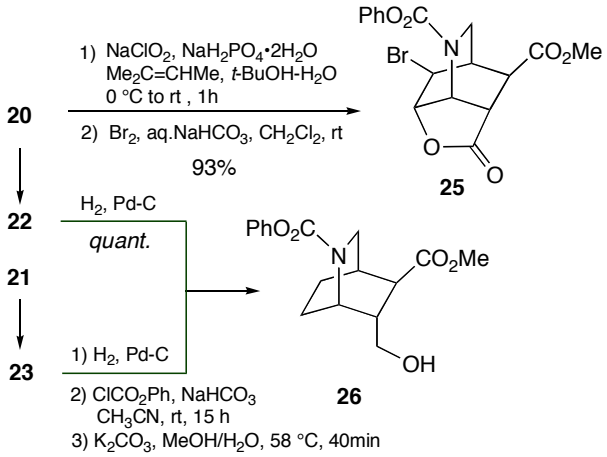
The absolute stereochemistry assignment of the new DA adducts **11a, 16, 20, 21** was carried out as follows (Scheme 1, 2). Both **11a** and the known (*7R*)-**24**[7c] were converted to the alcohol **12a** by the synthetic methodology as shown in Scheme 1. The compound **24** gave (7*R*)-(-)-**12a** and **11a** afforded the enantiomer (7*S*)-(+)-**12a** of (7*R*)-(-)-**12a**. On the other hands, the absolute stereochemistry of DA adduct **16** was determined by the conversation from 1-*tert*-butoxycarbonyl-**18a** to the known 1-benzyloxycarbonyl-**17a**.



Scheme 1 Determinations of the absolute stereochemistry of **11a,16**

To assign the structure of 1-phenoxycarbonyl-**20** by X-ray study, the compound was converted to bromolactone **25** (Scheme 2). Thus, the Kraus oxidation of **20** and the bromolactonization of the obtained carboxylic acid afforded the desired bromolactone **25**. On On the other hands, the absolute stereochemistry of 1-benzyloxycarbonyl-**21** was decided by

converting to **26**. Thus, compound **22** for which the absolute stereochemistry was determined, was converted to alcohol **26**, by reduction of the olefin moiety in **22**. The similar reduction of alcohol **23** that was derived from **20**, followed by the exchange from the Cbz group to the phenoxycarbonyl group on nitrogen at 2-position, and then the reaction with K_2CO_3/H_2O afforded the alcohol **26**.



Scheme 2 Determinations of the absolute stereochemistry of **20,21**