Supplementary Information

(2S,4S)-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$_2$Cl$_2$ (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. [α]$_D$ = -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.

(2S,4S)-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$_2$Cl$_2$ (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. [α]$_D$ = -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$_{25}$H$_{27}$F$_3$NO$_3$: 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 CH₃CN (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 MgSO₄, 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), NaBH₄ (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 MgSO₄, removed under reduced pressure to give a crude DA adduct 12a. The residue was purified by flash chromatography (SiO₂, 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, tᵣ (major) = 21.64 min, tᵣ (minor) = 23.09 min for 12a (>99% ee), DAICEL Chiralcel AD-H, 0.5mL/min, n-hexane : 2-propanol = 85 : 15, tᵣ (minor) = 16.97 min, tᵣ (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).

(1S,4S,7S)-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. [α]D⁰ = 95.00 (c 1.00, CHCl₃). IR (KBr) cm⁻¹: 3507, 1694, 1408. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 were converted to the alcohol 12a by the synthetic methodology as shown in Scheme 1. The compound 24 gave (7R)-(−)-12a and 11a afforded the enantiomer (7S)-(+) of (7R)-(−)-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-benzyloxy carbonyl-17a.

![Scheme 1 Determinations of the absolute stereochemistry of 11a, 16](image)

To assign the structure of 1-phenoxy carbonyl-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 the other hands, the absolute stereochemistry of 1-benzyloxy carbonyl-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 phenoxy carbonyl group on nitrogen at 2-position, and then the reaction with K₂CO₃/H₂O afforded the alcohol 26.

Scheme 2 Determinations of the absolute stereochemistry of 20, 21