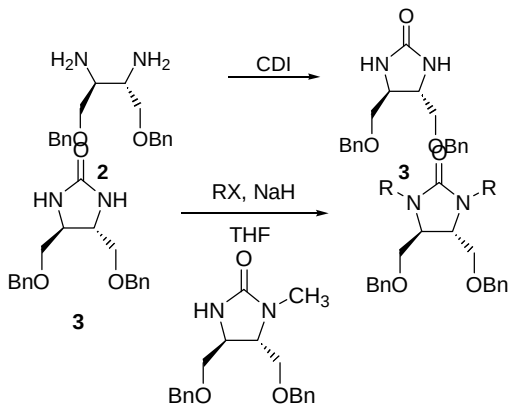
Supporting Information for *Angew. Chem. Int. Ed.* Z 18078

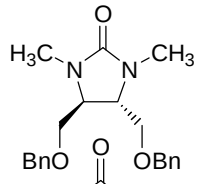
Novel 1,4-Diphosphanes Bearing Imidazolidin-2-one Backbone as Chiral Ligands: Highly Enantioselective Rh-Catalyzed Hydrogenation of Enamides**

Sang-gi Lee,* Yong Jian Zhang, Choong Eui Song,
Jae Kyun Lee, Jung Hoon Choi

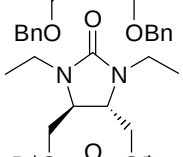
List of Schemes and Compounds in Supporting Information



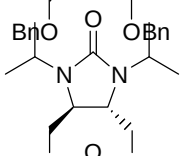
4. (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-dimethylimidazolidin-2-one



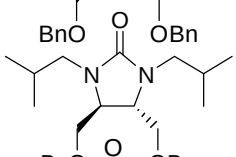
5. (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diethylimidazolidin-2-one



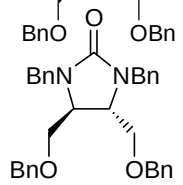
6. (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diiospropylimidazolidin-2-one



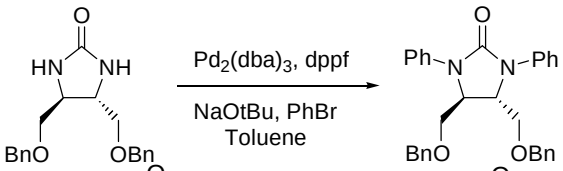
7. (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diiosbutylimidazolidin -2-one



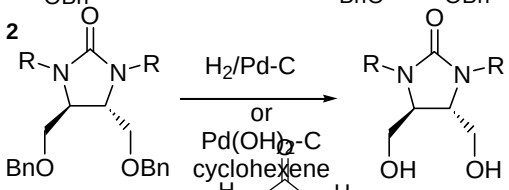
8. (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-dibenzylimidazolidin-2-one



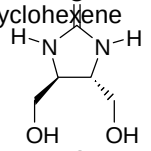
9. Synthesis of (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diphenylimidazolidin-2-one



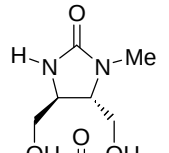
10. General Procedure for the debenzylation



11. (4*S*,5*S*)-4,5-Bis(hydroxymethylene)imidazolidin-2-one

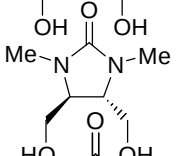


12. (4*S*,5*S*)-4,5-Bis(hydroxymethyl)-1-methylimidazolidin--2-one

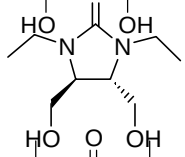


13. (4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-dimethylimidazolidin-2-one

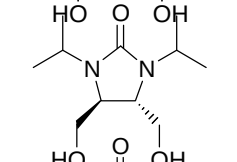
14. (4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-diethylimidazolidin--2-one



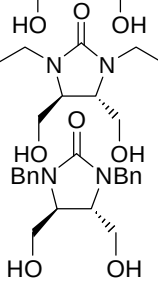
15 (4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-diisopropylimidazolidin-2-one



16. (4*S*,5*S*)-4,5-Bis(hydroxymethyl)-1,3-diisobutylimidazolidin--2-one

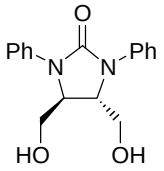


17. (4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-

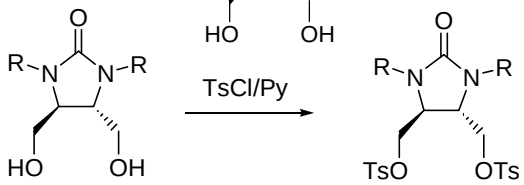


dibenzylimidazolidin-2-one

18. (4*S*,5*S*)-4,5-Bis(hydroxymethylENE)-1,3-diphenylimidazolidin-2-one



19. General procedure for *O,O'*-ditosylation of dihydroxy imidazolidin-2-one



20. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene) imidazolidin-2-one

21. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethyene)-1-methylimidazolidin-2-one

22. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-dimethylimidazolidin-2-one

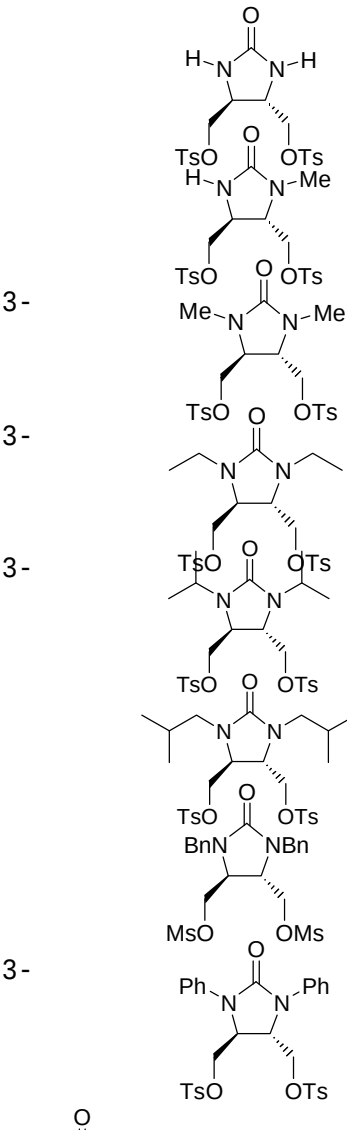
23. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diethylimidazolidin-2-one

24. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diisopropylimidazolidin-2-one

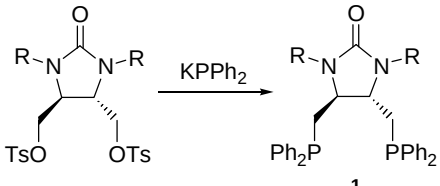
25. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diisobutylimidazolidin-2-one

26. (4*S*,5*S*)-4,5-Bis(methanesulfonyloxymethylene)-1,3-dibenzylimidazolidin-2-one

27. (4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diphenylimidazolidin-2-one



28. General procedure for the synthesis of (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene) -1,3-disubstitutedimidazolidin-2-ones (BDPMI, **1a**-**1h**)



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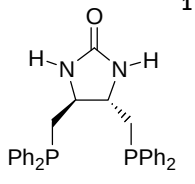
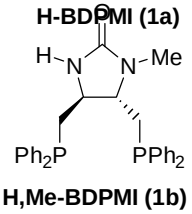
29. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene) imidazolidin-2-one (H-BDPMI, **1a**)



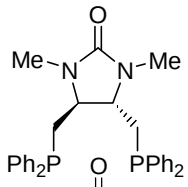
H-BDPMI (1a)

30. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1-methylimidazolidin-2-one (H,Me-BDPMI, **1b**)



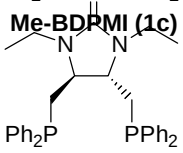
H,Me-BDPMI (1b)

31. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-dimethylimidazolidin-2-one (Me-BDPMI, **1c**)



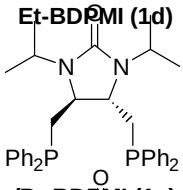
Me-BDPMI (1c)

32. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-diethylimidazolidin-2-one (Et-BDPMI, **1d**)



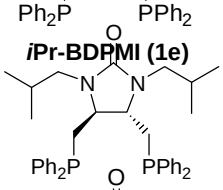
Et-BDPMI (1d)

33. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-diisopropylimidazolidin-2-one (*i*Pr-BDPMI, **1e**)



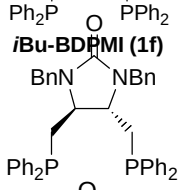
***i*Pr-BDPMI (1e)**

34. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethyl)-1,3-diisobutylimidazolidin-2-one (*i*Bu-BDPMI, **1f**)



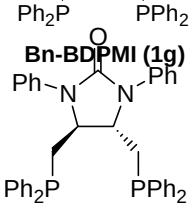
***i*Bu-BDPMI (1f)**

35. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-dibenzylimidazolidin-2-one (Bn-BDPMI, **1g**)



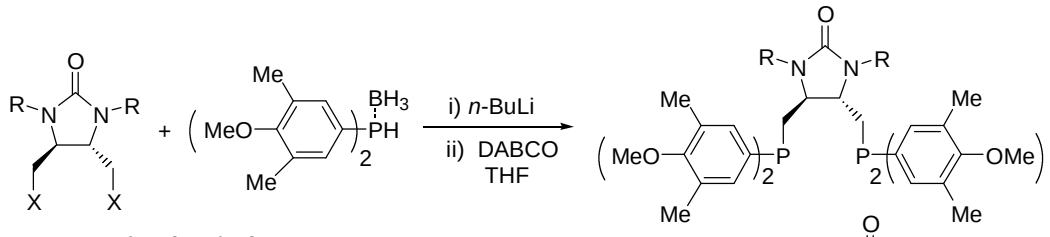
Bn-BDPMI (1g)

36. (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethyl)-1,3-diisobutylimidazolidin-2-one (Ph-BDPMI, **1h**)



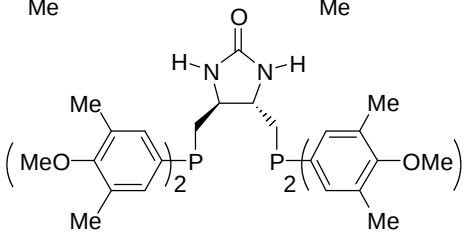
Ph-BDPMI (1h)

37. General procedure for the synthesis of (4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene)-1,3-disubstituted imidazolidin-2-ones (BDPMI, **1i-1k**)

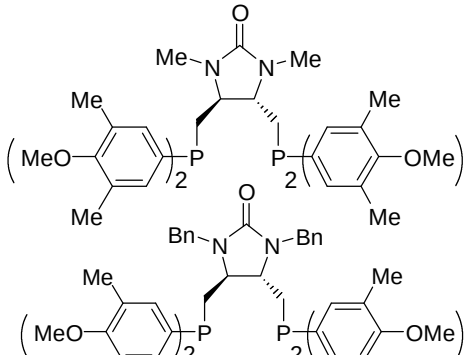


X = TsO for **1i** and **1 j**
X = MsO for **1k**

38. (4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene) imidazolidin-2-ones (**1i**)



39. (4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene)-1,3-dimethylimidazolidin-2-ones (**1j**)



40. (4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene)-1,3-dibenzylimidazolidin-2-ones (**1k**)

General

All reactions and manipulations were performed in a nitrogen atmosphere using standard Schelenk techniques. The reaction solvents were distilled prior to used (THF: distilled from sodium benzophenone ketyl, CH_2Cl_2: from CaH_2). All purchased reagents were used without further purification. Anhydrous solvents were transferred by oven-dried syringe. Flasks were flames dried under a stream of nitrogen. The NMR spectra were recorded at 300 MHz (^1H), 75.5 MHz (^{13}C) and 121 MHz (^{31}P). The chemical shifts were relative to TMS (as an internal reference) for ^1H NMR and $P(O)(OPh)_3$ (as an external reference) for ^{31}P NMR. Chemical analyses were carried out by the Advanced Analysis Center at Korea Institute of Science and Technology.

1. (4*S*,5*S*)-4,5-Bis(benzyloxymethyl)imidazolidin-2-one (3). A solution of (2*S*,3*S*)-2,3-diamino-1,4-dibenzyloxybutane (**2**) (0.1 g, 0.33 mmol) and carbonyldiimidazole (59 mg, 0.37 mmol) in CH_2Cl_2 was heated to reflux for 4 h. The reaction mixture was washed with 3% hydrochloric acid, water and aqueous NaCl solution, and dry over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica column chromatography to give 0.103 g of product. R_f = 0.33 (ethyl acetate:*n*-hexane = 3:1); Yield: (94%); m.p. 65-66 °C; $[á]^{25}_D$ = +77.4 (*c* = 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$) ä = 3.44 (d, *J* = 5.3 Hz, 4H; O-CH_2), 3.60 (m, 2H; N-CH), 4.50 (s, 4H; PhCH_2), 5.56 (s, 2H; NH), 7.24-7.36 (m, 10H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 54.74, 72.46, 73.32, 127.59, 127.73, 128.37,

137.61, 162.66; Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.90; H, 6.79; N, 8.53.

2. General procedure for the *N*-alkylation of 3. A solution of 4,5-bis(benzyloxymethyl)imidazolidin-2-one (**3**) (0.1 g, 0.3 mmol) in THF was added to a suspension of sodium hydride(16 mg, 0.67 mmol) in THF at 0 ^{o}C, and stirred at room temperature for 20 min. To this reaction mixture was added alkyl halide (0.67 mmol)(0.3 mmol of MeI used for monomethylation) at 0. The reaction temperature was warmed to room temperature, and stirred for 4 h. The reaction was quenched by addition of water, and extracted with CH_2Cl_2. The organic layer was washed with water, aqueous NaCl solution, and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica.

3.(4*S*,5*S*)-4,5-Bis(benzyloxymethyl)-1-methylimidazolidin-2-one. RX = MeI, R_f = 0.35(ethyl acetate:*n*-hexane = 3:1) Yield: 35%; oil; [á]$^{25}_{D}$ = +43.6 (*c* = 0.42, $CHCl_3$); ^{1}H NMR ($CDCl_3$) d = 2.79 (s, 3H, N-CH_3), 3.37-3.66 (m, 6H, N-CH and O-CH_2), 4.51 (s, 2H, Ph-CH_2-O), 4.53 (s, 2H, Ph-CH_2-O),5.02 (bs, 1H, NH), 7.25-7.36 (m, 10H, Ar-H); ^{13}C NMR ($CDCl_3$) ä = 29.17, 52.62, 60.21, 70.62, 72.78, 73.36, 73.38. 127.54, 127.59, 127.77, 128.41, 137.62, 137.64, 161.22; Anal. Calcd for $C_{20}H_{24}N_2O_3$: C, 70.56; H, 7.11; N, 8.23. Found: C, 70.0; H, 7.15; N, 8.01.

4.(4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-dimethylimidazolidin-2-one. RX = MeI; R_f = 0.19 (ethyl acetate:*n*-hexane = 2:1); Yield: 89%; Oil; [á]$^{25}_{D}$= +9.22 (*c* = 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 2.83 (s, 6H; N-CH_3), 3.36 (m, 2H; N-CH), 3.56 (m, 4H; O-CH_2), 4.55 (s, 4H; O-CH_2-Ph), 7.28-7.40 (m, 10H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 29.97, 58.49, 70.75, 73.39, 127.55, 127.77, 128.43, 137.75, 160.84; Anal. Calcd for $C_{21}H_{26}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C, 71.2; H, 7.39; N, 7.93.

5.(4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diethylimidazolidin-2-one. RX = EtI; R_f = 0.47 (ethyl acetate:*n*-hexane = 2:1); Yied: 91%; Oil; [á]$^{25}_{D}$ = +11.3 (*c* = 0.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 1.06 (t, *J* = 7.1 Hz, 6H; C-CH_3), 3.10 (dq, *J* = 7.0 Hz, 14.0 Hz, 2H; N-CH_{2a}), 3.45-3.56 (m, 8H; N-CH, N-CH_{2b} and O-CH_2), 4.52 (s, 4H, O-CH_2-Ph), 7.26-7.37 (m, 10H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 12.71, 36.60, 55.22, 70.75, 73.07, 127.26, 127.48, 128.16, 137.57, 159.46; Anal. Calcd for $C_{23}H_{30}N_2O_3$: C, 72.22; H, 7.91; N, 7.32.

Found: C, 71.6; H, 7.87; N, 7.40.

6.(4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diiospropylimidazolidin-2-one. RX = *i*-Pr-Br; R_f = 0.43 (ethyl acetate:*n*-hexane = 1:1); Yied: 16%; Oil; $[á]^{25}_D$ = -18.21 (*c* = 0.32, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 1.11 (d, *J* = 6.8 Hz, 6H; CH_3), 1.13 (d, *J* = 6.8 Hz, 6H; CH_3), 3.34 (dd, *J*=6.8, 9.5 Hz, 2H; O-CH_2) 3.47 (dd, *J*= 3.8, 9.5 Hz, 2H; O-CH_2), 3.60 (m, 2H; N-CH), 3.97 (septet, *J* = 6.8 Hz, 2H; CH), 4.52 (dd, *J* = 11.9, 26.0 Hz, 4H; O-CH_2-Ph), 7.26-7.34 (m, 10H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 19.88, 22.10, 44.59, 54.38, 71.90, 73.17, 127.62, 127.66, 128.33, 137.80, 159.35; Anal. Calcd for $C_{25}H_{34}N_2O_3$: C, 73.14; H, 8.35; N, 6.82. Found: C, 72.4; H, 8.25; N, 6.96.

7.(4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diiosbutylimidazolidin-2-one. RX = *i*-BuBr; R_f = 0.63 (ethyl acetate:*n*-hexane = 1:1); Yield: 43%; Oil; $[á]^{25}_D$ = -1.45 (*c* = 0.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 0.81 (d, *J* = 6.7 Hz, 6H; CH_3), 0.87 (d, *J* = 6.7 Hz, 6H; CH_3), 1.85 (m, 2H; CH), 2.85 (dd, *J* = 5.9, 13.9 Hz, 2H; N-CH_2), 3.21 (dd, *J* = 9.2, 13.9 Hz, 2H; N-CH_2), 3.45-3.57 (m, 6H; N-CH, O-CH_2), 4.53 (dd, *J* = 12.0, 16.7 Hz, 4H; O-CH_2-Ph), 7.28-7.40 (m, 10H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 20.06, 20.68, 27.20, 49.68, 56.46, 70.86, 73.77, 128.03, 128.16, 128.80, 138.20, 160.34; Anal. Calcd for $C_{27}H_{38}N_2O_3$: C, 73.94; H, 8.73; N, 6.39. Found: C, 73.4; H, 8.71; N, 6.88.

8.(4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-dibenzylimidazolidin-2-one. RX = BnBr; R_f = 0.68 (ethyl acetate:*n*-hexane = 1:2); Yield: 90%; Oil; $[á]^{25}_D$ = +6.22 (*c* = 0.43, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 3.39-3.45 (m, 6H; O-CH_2 and N-CH), 4.20 (d, *J* = 15.4 Hz, 2H; N-CH_2-Ph), 4.37 (s, 4H; O-CH_2-Ph), 4.90 (d, *J* = 15.4 Hz, 2H; N-CH_2-Ph), 7.20-7.35 (m, 20H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 46.11, 55.17, 70.15, 73.17, 127.12, 127.55, 127.66, 128.04, 128.33, 128.37, 137.51, 137.70, 160.23; Anal. Calcd for $C_{33}H_{34}N_2O_3$: C, 78.23; H, 6.76; N, 5.53. Found: C, 77.6; H, 6.91; N, 5.39.

9.Synthesis of (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)-1,3-diphenyl imidazolidin-2-one. A solution of $Pd_2(dba)_3$(15.3 ìmol, 14 mg, 5 mol%) and dppf (30.6 ìmol, 17 mg, 10 mol%) in toluene (5 mL) was degassed, and stirred at room temperature for 1 hour. To this solution were added bromobenzene (0.55 mmol, 86.6 mg) and sodium *tert*-butoxide (0.86 mmol, 82 mg) at room temperature, and stirred at room temperature for 30min. After addition of (4*S*,5*S*)-4,5-Bis(benzyloxymethylene)imidazolidin-2-one (**2**) (0.3 mmol, 0.1 g), then, the reaction mixture was refluxed for 12 h. Reaction

mixture was allowed to cool to room temperature and quenched by addition of water, filtered through celite. The filtrate was extracted with dichloromethane, dried over $MgSO_4$, filtered and evaporated the solvent. The residue was purified by column chromatography on silica. R_f = 0.33(ethyl acetate:*n*-hexane = 1:4); Yield: 96%; Oil; $[á]^{25}_D$ = -4.3 (*c* = 1.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 3.60-3.69 (m, 4H; O-CH_2), 4.46 (m, 2H; N-CH), 4.52 (s, 4H; O-CH_2-Ph), 7.14-7.54 (m, 20H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 56.79, 69.20, 73.72, 121.86, 124.45, 127.99, 128.17, 128.83, 129.34, 138.08, 138.88, 155.50; Anal. Calcd for $C_{31}H_{30}N_2O_3$: C, 77.80; H, 6.32; N, 5.85. Found: C, 77.6; H, 6.33; N, 5.74.

10. General Procedure for the debenzylation. A mixture of *O,O*-dibenzylated imidazolidin-2-one (1.8 mmol) and 10% palladium on charcoal (0.15g) in methanol was hydrogenated under 5 bar pressure of H_2 for 8 h (or 20% palladium hydroxide on charcoal(0.2 g) and cyclohexene(5 mL) in methanol(20 mL) and ethyl acetate(20 mL) was heated to reflux for 4 h). The catalyst was filtered off through celite, and the filtrate was concentrated. The residue was purified by column chromatography on silica to give Product.

11.(4*S*,5*S*)-4,5-Bis(hydroxymethylene)imidazolidin-2-one. Condition: H_2/Pd-C; R_f = 0.50 (methylenechloride:methanol = 3:1); yield: 82%; m.p. 107-108 ℃ ;$[á]^{25}_D$ = +79.9 (*c* = 1.0, MeOH); ^{1}H NMR (D_2O) ä = 3.49-3.57 (m, 6H, N-CH, and O-CH_2); ^{13}C NMR (D_2O) ä = 56.23, 63.54, 165.11; Anal. Calcd for $C_5H_{10}N_2O_3$: C, 41.09; H, 6.90; N, 19.17. Found: C, 40.4; H, 6.66; N, 19.3.

12.(4*S*,5*S*)-4,5-Bis(hydroxymethyl)-1-methylimidazolidin--2-one. Condition: H_2/Pd-C; R_f = 0.44 (methylenechloride:methanol=4:1); Yield: 95%; m.p. 123-5°C; $[á]^{25}_D$ = +40.3 (*c* = 0.42, MeOH); ^{1}H NMR (D_2O) ä = 2.83 (s, 3H, N-CH_3), 3.55-3.72 (m, 5H, N-CH and O-CH_{2a}), 3.92 (dd, 1H, *J* = 3.4, 12.4, O-CH_{2b}); ^{13}C NMR (D_2O) ä = 28.22, 53.76, 60.36, 61.54, 63.42, 163.92; Anal. Calcd for $C_6H_{12}N_2O_3$: C, 44.99; H, 7.55; N, 17.49. Found: C, 44.9; H, 7.37; N, 17.6.

13.(4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-dimethylimidazolidin-2-one. Condition: H_2/Pd-C; R_f = 0.41 (methylene chloride:methanol = 6:1); Yield: 99%; m.p. 138-140 °C; $[á]^{25}_D$ = +6.92 (*c* = 0.75, MeOH); ^{1}H NMR (D_2O) ä = 2.70 (s, 6H; N-CH_3), 3.37 (m, 2H, N-CH), 3.52 (d, *J* = 12.5 Hz, 2H, O-CH_2), 3.78 (d, *J* = 12.5, 2H, O-CH_2); ^{13}C NMR (D_2O) ä = 28.92, 59.33, 59.91, 163.11;

Anal. Calcd for $C_7H_{14}N_2O_3$: C, 48.26; H, 8.10; N, 16.08. Found: C, 47.8; H, 8.15; N, 15.7.

14.(4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-diethylimidazolidin--2-one.

Condition: H_2/Pd-C; R_f = 0.39 (methylene chloride:methanol = 8:1); Yield: 93%; m.p. 73-74 °C; $[á]^{25}_D$ = +1.85 (*c* = 0.60, MeOH); ^{1}H NMR (D_2O) ä = 0.92 (t, *J* = 7.1 Hz, 6H; CH_3), 2.95 (dq, *J* = 7.1, 14.5 Hz, 2H; N-CH_{2a}), 3.26 (dq, *J* = 7.3, 14.6 Hz, 2H; N-CH_{2b}), 3.34 (d, *J*=10.9Hz, 2H, O-CH_2), 3.45 (m, 2H; N-CH), 3.68 (d, *J* = 10.9 Hz, 2H; O-CH_2); ^{13}C NMR (D_2O) ä = 12.08, 36.55, 56.22, 60.06, 162.11; Anal. Calcd for $C_9H_{18}N_2O_3$: C, 53.45; H, 8.97; N, 13.85. Found: C, 53.3; H, 8.94; N, 13.4.

15.(4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-diisopropylimidazolidin-2-one.

Condition: H_2/Pd-C; R_f = 0.67 (methylene chloride:methanol = 6:1); Yield: 99%; Oil; $[á]^{25}_D$ = -28.6 (*c* = 1.57, MeOH); ^{1}H NMR (d_6-acetone) ä = 1.18 (d, *J* = 6.8 Hz, 6H; CH_3), 1.19 (d, *J* = 6.8 Hz, 6H, CH_3), 3.46-3.63 (m, 6H; O-CH_2 and N-CH), 3.90 (septet, *J* = 6.8 Hz, 2H; CH), 4.13 (t, *J* = 4.9 Hz, 2H; OH); ^{13}C NMR (d_6-acetone) ä = 19.59, 21.64, 45.12, 56.78, 64.32, 160.02; Anal. Calcd for $C_{11}H_{22}N_2O_3$: C, 57.37; H, 9.63; N, 12.16. Found: C, 57.4; H, 9.81; N, 11.9.

16.(4*S*,5*S*)-4,5-Bis(hydroxymethyl)-1,3-diisobutylimidazolidin-2-one.

Condition: H_2/Pd-C; R_f = 0.16 (ethyl acetate:*n*-hexane = 4:1); Yield: 99%; m.p. 50-51 °C; $[á]^{25}_D$ = -29.8 (*c* = 0.70, MeOH); ^{1}H NMR (d_6-acetone) ä = 0.83 (d, *J* = 6.6 Hz, 6H; CH_3), 0.89 (d, *J* = 6.6 Hz, 6H; CH_3), 1.97 (m, 2H; CH), 2.94 (dd, *J* = 5.9, 13.8 Hz, 2H; N-CH_2), 3.15 (dd, *J* = 9.4, 13.8 Hz, 2H; N-CH_2), 3.51 (m, 2H; N-CH), 3.66 (m, 4H; O-CH_2), 4.30 (t, *J* = 5.6 Hz, 2H; OH); ^{13}C NMR (d_6-acetone) ä = 19.64, 20.25, 26.86, 49.25, 57.85, 62.08, 160.88; Anal. Calcd for $C_{13}H_{26}N_2O_3$: C, 60.44; H, 10.14; N, 10.84. Found: C, 60.5; H, 10.2; N, 10.5.

17.(4*S*,5*S*)-4,5-Bis(hydroxymethylene)-1,3-dibenzylimidazolidin-2-one.

Condition: $Pd(OH)_2$-C/cyclohexene; R_f = 0.17 (ethyl acetate:*n*-hexane = 2:1); Yield: 81%; m.p. 139-140 °C; $[á]^{25}_D$ = +26.08 (c = 0.46, MeOH); ^{1}H NMR (DMSO-d_6) ä = 3.35-3.41 (m, 6H; N-CH and O-CH_2), 4.15 (d, *J* = 15.6 Hz, 2H; N-CH_{2a}-Ph), 4.71 (d, *J* = 15.6 Hz, 2H; N-CH_{2b}-Ph), 4.84 (t, *J* = 5.3 Hz, 2H; OH), 7.26-7.37 (m, 10H; Ar-H); ^{13}C NMR (DMSO-d_6) ä = 45.34, 56.59, 61.25, 127.44, 128.05, 128.86, 138.42, 160.01; Anal. Calcd for $C_{19}H_{22}N_2O_3$: C,

69.92; H, 6.79; N, 8.58. Found: C, 69.7; H, 6.82; N, 8.53.

18.(4*S*,5*S*)-4,5-Bis(hydroxymethylENE)-1,3-diphenylimidazolidin-2-one. Condition: H_2/Pd-C; R_f = 0.39 (ethyl acetate:*n*-hexane = 4:1); Yield: 87%; m.p. 150-152 °C; $[á]^{25}_D$ = +29.8(*c* = 0.51, MeOH); ^{1}H NMR (d_6-acetone) ä = 3.74 (dd, *J* = 2.4, 11.5 Hz, 2H; O-CH_{2a}), 3.80 (dd, *J* = 4.7, 11.5 Hz, 2H; O-CH_2), 4.32 (t, *J* = 5.7 Hz, 2H; OH), 4.51 (m, 2H; N-CH), 7.09 (t, *J* = 7.4 Hz, 2H; Ar-H), 7.36 (dd, *J* = 7.6, 8.4 Hz, 4H; Ar-H), 7.70 (d, *J* = 8.4 Hz, 4H; Ar-H); ^{13}C NMR (d_6-acetone) ä = 57.50, 60.93, 121.07, 123.44, 128.93, 139.83, 155.40; Anal. Calcd for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.1; H, 6.06; N, 9.51.

19. General procedure for *O,O'*-ditosylation of dihydroxyimidazolidin-2-one. To a solution of (4*S*,5*S*)-4,5-bis(hydroxymethyl)-1,3-dialkylated imidazolidin-2-one (0.68 mmol) in dry pyridine (10 mL)was added *P*-toluenesulfonyl chloride (0.33 g, 1.71 mmol) at -15 ℃ The reaction mixture was warmed to room temperature and stirred for 4 h. The reaction was quenched by addition of water, and extracted with methylene chloride. The combined organic layer was washed successively with 3% aqueous HCl solution, water and saturated aqueous NaCl solution. After drying over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica.

20.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)imidazolidin-2-one. R_f = 0.17 (ethyl acetate:*n*-hexane = 4:1); Yield: 77%; m.p. 171-172 °C; $[á]^{25}_D$ = +56.92 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (DMSO-d_6) ä = 2.41 (s, 6H; Ar-CH_3), 3.46 (m, 2H), 3.83 (dd, *J* = 4.5, 9.8 Hz, 2H; O-CH_2), 3.90 (dd, *J* = 3.5, 9.9 Hz, 2H; O-CH_2), 6.60 (bs, 2H; N-H), 7.47 (d, *J* = 8.2 Hz, 4H; Ar-H), 7.76 (d, *J* = 8.2 Hz, 4H; Ar-H); ^{13}C NMR (DMSO-d_6) ä = 21.98, 52.93, 71.91, 128.52, 131.09, 132.81, 146.02, 161.89; Anal. Calcd for $C_{19}H_{22}N_2O_7S_2$: C, 50.21; H, 4.88; N, 6.16. Found: C, 50.0; H, 4.86; N, 6.09.

21.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethyene)-1-methylimidazolidin-2-one. R_f = 0.35 (ethyl acetate:n-hexane = 5:1) Yield: 71%; mp, 14°C; $[á]^{25}_D$ = +40.7 (*c* = 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 2.48 (s, 6H, Ar-CH_3), 2.67 (s, 3H, N-CH_3), 3.49 (dd, 1H, *J* = 4.5, 9.3Hz, N-CH), 3.67 (dd, 1H, *J* = 5.3, 10.5Hz, N-CH), 3.95 (m, 2H, O-CH_2), 4.07 (d, 2H, *J* = 4.5Hz, O-CH_2), 4.79 (bs, 1H, NH), 7.40 (d, 4H, *J* = 7.7Hz, Ar-H), 7.79 (d, 2H, *J* = 8.1Hz, Ar-

H), 7.80 (d, 2H, *J* = 8.1Hz, Ar-H); ^{13}C NMR ($CDCl_3$) ä = 21.70, 28.77, 50.94, 58.71, 67.63, 70.08, 127.95, 130.14, 130.16, 132.10, 145.57, 145.61, 159.81; Anal. Calcd for $C_{20}H_{24}N_2O_7S_2$: C, 51.27; H, 5.16; N, 5.98. Found: C, 51.2; H, 5.21; N, 5.97.

22.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-dimethylimidazolidin-2-one. R_f = 0 .36 (ethyl acetate:*n*-hexane = 2:1); Yield: 86%; m.p. 144-145 °C; [á]$^{25}_D$ = +28.3 (*c* = 0.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 2.38 (s, 6H; Ar-CH_3), 2.54 (s, 6H; N-CH_3), 3.29 (m, 2H; N-CH), 3.94 (d, *J* = 3.4 Hz, 4H; O-CH_2), 7.29 (d, *J* = 8.2 Hz, 4H; Ar-H), 7.68 (d, *J* = 8.2 Hz, 4H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 21.64, 29.38, 56.69, 67.57, 127.89, 130.09, 132.14, 145.51, 159.50; Anal. Calcd for $C_{21}H_{26}N_2O_7S_2$: C, 52.27; H, 5.43; N, 5.81. Found: C, 51.6; H, 5.50; N, 5.62.

23.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diethylimidazolidin-2-one. R_f = 0.39(ethyl acetate:*n*-hexane = 2 : 1); Yield: 71%; m.p. 75-76 °C; [á]$^{25}_D$ = +22.1 (*c* = 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 0.88 (t, *J* = 7.1 Hz, 6H; CH_3), 2.40 (s, 6H; Ar-CH_3), 2.76 (dq, *J* = 7.1, 14.3 Hz, 2H; N-CH_2), 3.33 (dq, *J* = 7.3, 14.5 Hz, 2H, N-CH_2), 3.50 (m, 2H; N-CH), 3.91 (dd, *J* = 4.4, 10.9 Hz, 2H; O-CH_2), 3.96 (dd, *J* = 3.3, 10.8 Hz, 2H; O-CH_2), 7.32 (d, *J* = 8.2 Hz, 4H; Ar-H), 7.71 (d, *J* = 8.2 Hz, 4H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 12.40, 21.42, 36.13, 53.44, 67.65, 127.66, 129.90, 131.86, 145.30, 158.24; Anal. Calcd for $C_{23}H_{30}N_2O_7S_2$: C, 54.10; H, 5.92; N, 5.43. Found: C, 54.0; H, 5.92; N, 5.49.

24.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diisopropyl imidazolidin-2-one. R_f = 0.49(ethyl acetate:*n*-hexane = 2 : 1); Yield: 72%; m.p.125-126 °C; [á]$^{25}_D$ = +1.1(*c* = 0.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 0.99 (d, *J* = 6.8 Hz, 6H; CH_3), 1.00 (d, *J* = 6.8 Hz, 6H; CH_3), 2.44 (s, 6H; Ar-CH_3), 3.53 (dd, *J* = 3.1, 5.8 Hz, 2H; N-CH), 3.74 (dd, *J* = 6.8, 10.2 Hz, 2H; O-CH_2), 3.88 (septet, *J* = 6.8 Hz, 2H; CH), 3.96 (dd, *J* = 3.1, 10.2 Hz, 2H; O-CH_2), 7.37 (d, *J* = 8.1 Hz, 4H; Ar-H), 7.77 (d, *J* = 8.1 Hz, 4H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 19.64, 21.54, 21.87, 44.64, 52.74, 68.89, 127.90, 129.98, 132.12, 145.37, 158.30; Anal. Calcd for $C_{25}H_{34}N_2O_7S_2$: C, 55.74; H, 6.36; N, 5.20. Found: C, 55.8; H, 6.38; N, 5.19.

25.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diisobutyl imidazolidin-2-one. R_f = 0.62(ethyl acetate:*n*-hexane = 2:1); Yield: 75%; m.p. 51-52 °C; [á]$^{25}_D$ = +7.9(*c* = 0.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 0.70 (d, *J*

= 6.6 Hz, 6H; CH_{3a}), 0.77 (d, *J* = 6.6 Hz, 6H; CH_3), 1.61 (m, 2H; CH), 2.45 (s, 6H; SO_2CH_3), 2.52 (dd, *J* = 5.9, 14.2 Hz, 2H; N-CH_2), 3.07 (dd, *J* = 9.3, 14.2 Hz, 2H; N-CH_2), 3.53 (m, 2H; N-CH), 3.93 (dd, *J* = 5.0, 10.5 Hz, 2H; O-CH_2), 4.01 (dd, *J* = 3.1, 10.5 Hz, 2H; O-CH_2), 7.37 (d, *J* = 8.1 Hz, 4H; Ar-H), 7.76 (d, *J* = 8.1 Hz, 4H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 19.42, 19.99, 21.55, 26.51, 48.61, 54.31, 67.01, 127.91, 130.00, 132.02, 145.43, 158.96; Anal. Calcd for $C_{27}H_{38}N_2O_7S_2$: C, 57.22; H, 6.76; N, 4.94. Found: C, 57.4; H, 6.80; N, 4.97.

26.(4*S*,5*S*)-4,5-Bis(methanesulfonyloxymethylene)-1,3-dibenzylimidazolidin-2-one. Methanesulfonyl chloride was used instead of *p*-toluenesulfonyl chloride. R_f = 0.28 (ethyl acetate:*n*-hexane = 1:1); Yield: 74%; m.p. 94-96 °C; $[á]^{25}_D$ = –1.10 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 2.82 (s, 6H; SO_2CH_3), 3.56 (m, 2H, N-CH), 4.04 (dd, *J* = 2.8, 11.0 Hz, 2H, O-CH_2), 4.12 (dd, *J* = 4.2, 11.0 Hz, 2H, O-CH_2), 4.20 (d, *J* = 15.4 Hz, 2H; N-CH_2-Ph), 4.89 (d, *J* = 15.4 Hz, 2H; N-CH_2-Ph), 7.28-7.41(m, 10H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 37.44, 46.22, 53.99, 66.33, 127.98, 128.27, 128.94, 136.33, 159.70; Anal. Calcd for $C_{21}H_{26}N_2O_7S_2$: C, 52.27; H, 5.43; N, 5.81. Found: C, 52.2; H, 5.43; N, 5.72.

27.(4*S*,5*S*)-4,5-Bis(*p*-toluenesulfonyloxymethylene)-1,3-diphenyl imidazolidin-2-one. R_f = 0.24(ethyl acetate:*n*-hexane = 1:2); Yield: 73%; m.p. 169-170 °C; $[á]^{25}_D$ = +28.1(*c* = 0.74, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ä = 2.43 (s, 6H; Ar-CH_3), 4.05 (dd, *J* = 5.8, 10.7 Hz, 2H; O-CH_2), 4.17 (dd, *J* = 2.5, 10.7 Hz, 2H; O-CH_2), 4.41 (dd, *J* = 2.5, 4.3 Hz, 2H; N-CH), 7.12-7.30 (m, 14H; Ar-H), 7.68 (d, *J* = 8.3 Hz, 4H; Ar-H); ^{13}C NMR ($CDCl_3$) ä = 21.63, 54.73, 66.61, 121.71, 124.93, 127.86, 129.13, 130.04, 131.91, 136.88, 145.41, 154.07; Anal. Calcd for $C_{31}H_{30}N_2O_7S_2$: C, 61.37; H, 4.98; N, 4.62. Found: C, 61.0; H, 4.88; N, 4.55.

28.General procedure for the synthesis of (4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-disubstituted imidazolidin-2-ones (BDPMI, 1a-1h)

A solution of potassium diphenylphosphide (1.32 mL, 0.5 M THF solution, 0.66mmol) was added to a solution of (4*R*,5*R*)-4,5-bis(*p*-toluenesulfonyloxymethylene)imidazolidin-2-one (4,5-bis(*p*-methanesulfonyloxymethylene)imidazolidin-2-one for **1j**) (0.22 mmol) in THF

at 0°C, and stirred at room temperature for 12 h. The reaction mixture was filtered through celite and washed with degassed toluene. A filtrate was evaporated and purified by column chromatography on silica gel using degassed solvents.

29.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)imidazolidin-2-one (H-BDPMI, 1a). R_f = 0.30 (ethyl acetate:*n*-hexane = 3:1); yield: 76%; m.p. 138-140 ; $[á]^{25}_D$ = +41.72 (*c* = 0.34, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 2.28 (dd, *J* = 7.7, 13.6 Hz, 2H; P-CH_2), 2.39 (dd, *J* = 4.5, 13.4 Hz, 2H; P-CH_2), 3.62 (m, 2H; N-CH), 4.72 (bs, 2H; NH), 7.28-7.46 (m, 20H; Ar-H); ^{13}C NMR ($CDCl_3$): ä = 35.23, 35.42, 57.44, 57.57, 57.68, 57.80, 128.62, 128.72, 129.04, 129.07, 132.60, 132.86, 137.00, 137.16, 137.34,161.41; ^{31}P NMR ($CDCl_3$): ä = –6.37; Anal. Calcd for $C_{29}H_{28}N_2OP_2$: C, 72.19; H, 5.85; N, 5.81. Found: C, 71.4; H, 6.06; N, 5.54.

30.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1-methylimidazolidin-2-one (H,Me-BDPMI, 1b). R_f =0.57 (ethyl acetate:*n*-hexane = 4:1); yield: 73%; m.p. 44-45°C; $[á]^{25}_D$ = +18.9 (*c* = 0.20, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 2.16 (dd, 1H, *J* = 8.6, 13.6 Hz, P-CH_{2a}), 2.20 (ddd, 1H, *J* = 1.8, 9.0, 13.1 Hz, P-CH_{2a}), 2.44 (dd, 1H, *J* = 4.2, 13.7 Hz, P-CH_{2b}), 2.53 (ddd, 1H, *J* = 1.5, 3.4, 13.8 Hz, P-CH_{2b}), 2.62 (s, 3H, Me), 3.38 (m, 1H, N-CH), 3.67 (m, 1H, N-CH), 4.53 (bs, 1H, NH), 7.30-7.43 (m, 20H, Ar-H); ^{13}C NMR ($CDCl_3$): ä = 28.44, 32.10, 32.32, 35.96, 36.16, 53.93, 54.05, 54.15, 54.26, 62.81, 62.93, 63.06, 63.18, 128.57, 128.61, 128.67, 128.70, 128.77, 128.83, 128.94, 129.02, 129.15, 132.48, 132.60, 132.74, 132.80, 132.86, 133.01, 133.06, 137.02, 137.17, 137.34, 137.53, 137.68, 137.94, 138.10, 160.37; ^{31}P NMR($CDCl_3$): ä = -9.47, -6.75; Anal. Calcd for $C_{30}H_{30}N_2OP_2$: C, 72.57; H, 6.09; N, 5.64; Found: C, 71.1; H, 6.16; N, 5.29.

31.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-dimethylimidazolidin-2-one (Me-BDPMI, 1c). R_f = 0.28 (ethyl acetate:*n*-hexane = 1:1); yield: 70%; m.p. 39-40 ^{o}C; $[á]^{25}_D$ = –8.38 (*c* = 0.76, $CHCl_3$); ^{1}H NMR($CDCl_3$): ä = 2.26 (dd, *J* = 7.6, 13.9 Hz, 2H; P-CH_2), 2.48 (dd, *J* = 1.9, 13.9 Hz, 2H; P-CH_2), 2.60 (s, 6H; N-CH_3), 3.52 (m, 2H; N-CH), 7.28-7.40 (m, 20H; Ar-H); ^{13}C NMR($CDCl_3$): ä = 28.98, 32.32, 32.51, 59.32, 59.49, 59.66, 128.46, 128.51, 128.55, 128.60, 128.73, 128.87, 132.65, 132.75, 132.91, 133.02, 137.40, 137.56, 138.09, 138.25, 159.76; ^{31}P NMR ($CDCl_3$): ä = –10.17; Anal. Calcd for $C_{31}H_{32}N_2OP_2$: C, 72.93; H, 6.32; N, 5.49. Found: C, 72.5; H, 6.33; N,

5.46.

32.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-diethylimidazolidin-2-one (Et-BDPMI, 1d). R_f = 0.66 (ethyl acetate:*n*-hexane = 2:1); yield: 67%; viscous oil; [á]$^{25}_{D}$ = –26.8 (*c* = 0.33, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 0.90 (t, *J* = 7.2 Hz, 6H; CH_3), 2.19 (dd, *J* = 8.6, 13.8 Hz, 2H; P-CH_2), 2.44 (dd, *J* = 1.8, 13.8 Hz, 2H; P-CH_2), 2.77 (dq, *J* = 7.1, 14.2 Hz, 2H; N-CH_2), 3.47 (dq, *J* = 7.1, 14.3 Hz, 2H; N-CH_2), 3.67 (m, 2H; N-CH), 7.31-7.46 (m, 20H; Ar-H); ^{13}C NMR ($CDCl_3$): ä = 12.76, 31.93, 32.13, 35.35, 55.87, 56.06, 56.24, 128.47, 128.51, 128.56, 128.58, 128.62, 128.72, 128.89, 132.60, 132.65, 132.72, 132.77, 132.91, 132.96, 133.03, 133.07, 137.68, 137.74, 137.79, 137.85, 138.18, 138.23, 138.27, 138.33, 158.52; ^{31}P NMR ($CDCl_3$): ä = –9.82; Anal. Calcd for $C_{33}H_{36}N_2OP_2$: C, 73.59; H, 6.74; N, 5.20. Found: C, 73.3; H, 6.92; N, 4.99.

33.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-diisopropyl imidazolidin-2-one (*i*Pr-BDPMI, 1e). R_f = 0.29 (ethyl acetate:*n*-hexane = 2:3); yield: 74%; viscous oil; [á]$^{25}_{D}$ = –21.5 (*c* = 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 0.97 (d, *J* = 6.8 Hz, 6H; CH_3), 1.08 (d, *J* = 6.8 Hz, 6H; CH_3), 2.14 (dd, *J* = 10.8, 13.2 Hz, 2H; P-CH_2), 2.42 (d, *J* = 13.8 Hz, 2H; P-CH_2), 3.61 (m, 2H; N-CH), 3.86 (septet, *J* = 6.8 Hz, 2H; CH) 7.25-7.53 (m, 20H; Ar-H); ^{13}C NMR ($CDCl_3$): ä = 20.70, 22.17, 35.36, 35.45, 35.49, 35.57, 44.55, 55.66, 55.87, 56.07, 128.49, 128.55, 128.60, 128.99, 132.25, 132.38, 132.51, 132.63, 132.77, 133.11, 133.22, 133.36, 133.50, 133.62, 137.70, 137.78, 137.80, 137.88, 138.56, 138.63, 138.65, 138.71, 158.00; ^{31}P NMR ($CDCl_3$): ä = –9.55; Anal. Calcd for $C_{35}H_{40}N_2OP_2$: C, 74.19; H, 7.12; N, 4.94. Found: C, 73.4; H, 7.31; N, 4.72.

34.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethyl)-1,3-diisobutylimidazolidin-2-one (*i*Bu-BDPMI, 1f). R_f = 0.20 (ethyl acetate:*n*-hexane = 1:1); yield: 77%; m.p. 83-84 ^{o}C; [á]$^{25}_{D}$ = –23.5 (*c* = 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 0.77 (d, *J* = 6.6 Hz, 6H; CH_3), 0.78 (d, *J* = 6.6 Hz, 6H; CH_3), 1.49 (m, 2H; CH), 2.10 (dd, *J* = 10.7, 12.9 Hz, 2H; P-CH_2), 2.46 (d, *J* = 13.6 Hz, 2H; P-CH_2), 2.58 (dd, *J* = 5.2, 14.0 Hz, 2H; N-CH_2), 3.21 (dd, *J* = 9.5, 14.0 Hz, 2H; N-CH_2), 3.61 (m, 2H; N-CH), 7.26-7.52 (m, 20H; Ar-H); ^{13}C NMR ($CDCl_3$): ä = 19.95, 20.29, 26.77, 31.25, 31.46, 47.89, 56.73, 56.92, 57.12, 128.47, 128.52, 128.58, 128.61, 128.99, 132.36, 132.46, 132.59, 132.71, 132.84, 132.92, 133.06, 133.19, 133.28, 137.56, 137.63, 137.66, 137.73, 138.31,

138.46, 159.00; ^{31}P NMR ($CDCl_3$): ä = –9.50; Anal. Calcd for $C_{37}H_{44}N_2OP_2$: C, 74.73; H, 7.46; N, 4.71. Found: C, 74.2; H, 7.53; N, 4.65.

35.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethylene)-1,3-dibenzylimidazolidin-2-one (Bn-BDPMI, 1g). R_f = 0.28 (ethyl acetate:*n*-hexane = 1:1); yield: 74%; m.p. 47-49°C; [á]$^{25}_D$ = –33.40 (*c* = 1.47, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 1.92 (dd, *J* = 8.7, 13.9 Hz, 2H; P-CH_2), 2.34 (d, *J* = 12.9 Hz, 2H; P-CH_2), 3.49 (m, 2H; N-CH), 3.78 (d, *J* = 15.2 Hz, 2H; N-CH_2), 4.78 (d, *J* = 15.2 Hz, 2H; N-CH_2), 7.13-7.28 (m, 30H; Ar-H); ^{13}C NMR($CDCl_3$): ä = 32.61, 32.81, 45.37, 56.13, 56.32, 56.51, 127.30, 128.30, 128.39, 128.42, 128.43, 128.47, 128.48, 128.52, 128.58, 128.64, 132.49, 132.54, 132.68, 132.81, 132.86, 137.24, 137.43, 138.06, 138.12, 138.16, 138.22, 159.01; ^{31}P NMR ($CDCl_3$): ä = –10.01; Anal. Calcd for $C_{43}H_{40}N_2OP_2$: C, 77.93; H, 6.08; N, 4.23. Found: C, 77.6; H, 6.06; N, 4.23.

36.(4*S*,5*S*)-4,5-Bis(diphenylphosphanomethyl)-1,3-diisobutylimidazolidin-2-one (Ph-BDPMI, 1h). R_f = 0.50 (ethyl acetate:*n*-hexane = 1:4); yield: 70%; m.p. 54-55 ^{o}C; [á]$^{25}_D$ = +12.6 (*c* = 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 2.36 (dd, *J* = 11.9 Hz, 2H; P-CH_2), 2.54 (d, *J* = 13.9 Hz, 2H; P-CH_2), 4.37 (m, 2H; N-CH), 7.03-7.58 (m, 30H; Ar-H); ^{13}C NMR ($CDCl_3$): ä = 31.93, 32.01, 32.07, 32.15, 56.57, 56.77, 56.96, 119.81, 123.26, 128.49, 128.53, 128.59, 128.66, 128.71, 128.76, 128.85, 129.41, 132.11, 132.20, 132.32, 132.44, 132.53, 133.62, 133.69, 133.83, 133.97, 134.04, 136.90, 136.97, 137.01, 137.08, 137.48, 137.53, 137.61, 138.21, 153.55; ^{31}P NMR ($CDCl_3$): ä= –11.16; Anal. Calcd for $C_{41}H_{36}N_2OP_2$: C, 77.59; H, 5.72; N, 4.41. Found: C, 76.9; H, 5.86; N, 4.10.

37.General procedure for the synthesis of (4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene)-1,3-disubstituted imidazolidin-2-ones (BDPMI, 1i-1k)

n-Butyllithium (0.73 mmol, 1.6 M THF solution) was added to a solution of bis(3,5-dimethyl-4-methoxyphenyl)phosphane-borane complex(0.21 g, 0.66 mmol) in THF at –78 °C. The reaction mixture was wormed to room temperature and stirred for 30 min. And then, a solution of (4*R*,5*R*)-4,5-bis(*p*-toluenesulfonyloxymethylene)-1,3-disubstituted imidazolidin-2-one (for **1i** and **1j**) (0.22 mmol) (for **1k**, (4*R*,5*R*)-4,5-bis(*p*-methanesulfonyloxymethylene)-1,3-disubstituted imidazolidin-2-one) in THF

was added at room temperature. The reaction mixture was stirred for 5 h, and then DABCO (74 mg, 0.66 mmol) wad added in one portion and stirred at 50 for 3 h. After evaporation of the solvent, the residue was purified by column chromatography on silica.

38.(4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene]-imidazolidin-2-ones (1i). R_f = 0.25 (ethyl acetate:*n*-hexane = 2:1); yield: 78%; m.p. 77-78°C; [á]$^{25}_{D}$ = +15.8 (*c* = 0.20, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 2.07-2.26 (m, 4H, P-CH_2), 2.17 (s, 12H, CH_3), 2.19 (s, 12H, CH_3), 3.47 (m, 2H, CH), 3.64 (s, 12H, OCH_3), 4.71 (bs, 2H, NH), 6.98 (dd, 8H, *J*=7.4Hz, ArH); ^{13}C NMR ($CDCl_3$): ä = 15.14, 34.49, 34.68, 56.71, 56.84, 56.94, 57.07, 58.62, 130.18, 130.22, 130.29, 130.33, 130.58, 130.72, 130.91, 131.05, 132.10, 132.13, 132.37, 132.40, 156.91, 156.98, 160.54; ^{31}P NMR ($CDCl_3$): ä = -9.02; Anal. Calcd for $C_{41}H_{52}N_2O_5P_2$: C, 68.89; H, 7.33; N, 3.92; Found: C, 68.3; H, 7.8; N, 3.3.

39.(4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene]-1,3-dimethylimidazolidin-2-ones (1j). R_f = 0.34 (ethyl acetate:*n*-hexane = 1:1); yield: 74%; m.p. 60-61 °C; [á]$^{25}_{D}$ = -11.2 (*c* = 0.62, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ä = 2.15 (dd, 2H, *J*=7.5, 13.7Hz P-CH_2), 2.23 (s, 12H, CH_3), 2.24 (s, 12H, CH_3), 2.37 (dd, 2H, *J*=3.2, 13.9Hz, P-CH_2), 2.61 (s, 6H, N-CH_3), 3.42 (m, 2H, N-CH), 3.69 (s, 6H, OCH_3), 3.71(s, 6H, OCH_3), 7.05 (dd, 8H, J=7.3, 12.0Hz, ArH); ^{13}C NMR ($CDCl_3$): ä = 16.08, 29.15, 32.68, 32.87, 59.57, 59.85, 60.03, 131.01, 132.37, 132.51, 132.74, 132.88, 133.14, 133.22, 133.43, 133.51, 157.68, 157.78, 159.81; ^{31}P NMR ($CDCl_3$): ä = -12.72; Anal. Calcd for $C_{43}H_{56}N_2O_5P_2$: C, 69.52; H, 7.60; N, 3.77; Found: C, 69.2; H, 7.8; N, 3.6.

40.(4*S*,5*S*)-4,5-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphanomethylene]-1,3-dibenzylimidazolidin-2-ones (1k). R_f = 0.45 (ethyl acetate:*n*-hexane = 1:2); yield: 64%; m.p. 48-49 °C; [á]$^{25}_{D}$ = -25.8 (*c* = 0.20, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): ä = 1.78 (dd, 2H, *J* = 8.4, 13.4 Hz, P-CH_2), 2.18 (s, 12H, CH_3), 2.21 (s, 12H, CH_3), 2.18-2.28 (m, 2H, P-CH_2), 3.40 (m, 2H, N-CH), 3.69 (s, 6H, OCH_3), 3.70 (s, 6H, OCH_3), 3.85 (d, 2H, *J* = 15.3 Hz, $BnCH_{2a}$), 4.74 (d, 2H, *J* = 15.3 Hz, $BnCH_{2b}$), 6.89 (dd, 8H, *J* = 7.1, 27.9 Hz, ArH), 7.10-7.26 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$): ä = 16.08, 33.32, 33.52, 45.47, 56.44, 56.61, 56.79, 59.60, 127.21, 128.21, 128.41, 130.94, 132.36, 132.80, 133.15, 133.44, 137.76, 157.62, 157.72, 159.11; ^{31}P NMR ($CDCl_3$): ä

= -12.77; Anal. Calcd for $C_{55}H_{64}N_2O_5P_2$: C, 73.80; H, 7.21; N, 3.13; Found: C, 73.5; H, 7.3; N, 3.0.