Supporting Information

Chiral 3,4-Diazaphospholanes and Their Application to Catalytic Asymmetric Allylic Alkylation

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General Considerations. All syntheses were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Workup and flash chromatography of the amides were performed open to air. Ether and THF were distilled over Na/benzophenone; CH_2Cl_2 was distilled over P_2O_5 . Allyl acetates were synthesized by established procedures.^{1,2} Phthaloyl dichloride was placed under vacuum (400 mTorr) for 30 minutes to remove volatile impurities. Phenylphosphine and allylpalladium chloride dimer were purchased from Strem. Silver hexafluorophosphate was purchased from Pennwalt. All other chemicals were purchased from Aldrich.

NMR experiments: ^1H NMR (300 and 500 MHz), ^{13}C NMR (75.462 and 125.7 MHz), and ^{31}P NMR (121.49 and 202.4 MHz) were carried out on a Bruker AC-300 or a Varian 500. Chemical shifts for ^1H and ^{13}C NMR are referenced to solvent peaks and are reported in ppm vs. TMS. Chemical shifts for ^{31}P NMR are reported in ppm with 85% H_3PO_4 as external standard. ^1H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and integration).

Synthesis of Azine 1: The azine was prepared based on the procedure of Hencoch et al.³ Hydrazine monohydrate (1.5 mL, 30.9 mmol) in ethanol (20 mL) was added slowly to an ethanol solution (150 mL) of 2-carboxybenzaldehyde (9.52 g, 63.4 mmol). The resulting yellow solution was heated to 50 °C for 1 hr. After cooling to 0 °C, the yellow solid was isolated by filtration, rinsed twice with ethanol, and dried under vacuum for 20 minutes. The product was used without further purification. Yield = 91% of a yellow powder.

Synthesis of R,R-2: A THF suspension (250 mL) of the azine (20.0 mmol) was treated with phenyl phosphine (20.0 mmol) and stirred for five minutes. Phthaloyl dichloride (36.1 mmol) was added to the resulting yellow slurry and the solution was stirred at room temperature overnight. The THF was removed *in vacuo* to obtain a yellow oil. The oil was dissolved in a mixture of 150 mL Et₂O and 150 mL of a 10% aq. K₂CO₃ solution. The aqueous layer was isolated and rinsed three times with Et₂O. The aqueous layer was acidified by the careful addition of a 2M HCl solution that had been sparged with N₂. A white solid precipitated and was filtered, rinsed once with water (50 mL) and once with Et₂O (50 mL). The solid was then dried under vacuum overnight to give the racemic product in 88% yield.

The racemic diazaphospholane (17.6 mmol) was dissolved in THF (250 mL) and filtered through a Schlenk frit to remove trace solids. (*S*)- α -methylbenzylamine (15.5 mmol) was added to the solution and was heated gently for 5 minutes with a heat gun. Half of the THF was removed by passing N₂ over the solution. After seeding, the solution was left undisturbed for 4 days. The solution was separated from the crystals and the solid was rinsed with THF (3 x 50 mL). The white solid was dried under vacuum for 15 minutes. The crystals were dissolved in 10% aq. K₂CO₃ (100 mL) and the solution was rinsed with Et₂O (2 x 50 mL). The solution was acidified with 2M HCl until gas generation stopped. The solid was isolated by cannula filtration, followed by rinses with degassed water and Et₂O. The solid was dried under vac overnight to yield the chiral acid (2.71 g, 5.1 mmol). Enantiomeric purity of the diazaphospholane was verified by converting a small sample to **R,R-3a**. X-ray quality crystals were grown from THF/diethyl ether using vapor diffusion. The acid was identified as *R,R* by X-ray crystallography. Yield = 20%. ¹H NMR (d-DMSO): δ 6.30 (d, 1H, J = 8.1 Hz), 6.84 (t, 1H, J = 7.3 Hz), 6.97-7.11 (m, 4H), 7.15 (d, 1H, J_{H-P} = 16.9 Hz, PCHN), 7.16 (t, 2H, J = 7.4 Hz), 7.25 (t, 1H, J = 7.0 Hz), 7.47 (t, 1H, J = 7.6 Hz), 7.52 (d, 1H, J = 4.2 Hz, PCHN), 7.58 (t, 1H, J = 7.3 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.99 (m, 2H), 8.10 (d, 1H, J = 7.9 Hz), 8.16 (m, 1H), 8.29 (m, 1H); ¹³C NMR (d-DMSO): 59.1 (d, J_{C-P} = 19.3 Hz, PCHN), 60.8 (d, J_{C-P} = 32.2 Hz, PCHN), peaks at 120-145 ppm have not been assigned due to the complexity, 155.4 (s, CONN), 155.9 (s, CONN), 168.0 (s, CO₂H), 168.2 (s, CO₂H); ³¹P NMR: δ 1.9. EMM calcd for C₃₀H₂₀N₂O₆P [M-H]⁺: 535.1059, found: 535.1033.

S,S-2: The THF solution from the isolation of the (*R,R*) diazaphospholane was used. The THF was removed *in vacuo* and the resulting oil was dissolved in 10% aq. K₂CO₃. The solution was rinsed three times with 100 mL Et₂O, and the aqueous layer was acidified with 2M HCl. The solid was filtered by cannula and was rinsed with degassed water (50 mL) and Et₂O (50 mL). After drying under vacuum, 47% of the

enantiomerically enriched free acid diazaphospholane was recovered (8.3 mmol). This solid was dissolved in THF and (*R*)- α -methylbenzylamine (8.2 mmol) was added. The isolation and workup procedure used for **R,R-2** was followed to obtain the free acid **S, S-2**. The enantiomeric purity was determined by converting a small sample to the (*R*)-methylbenzylamide and verifying the presence of only one diastereomer by ^{31}P NMR. Yield = 28%. EMM calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_6\text{P}$ $[\text{M}-\text{H}]^-$: 535.1059, found: 535.1040.

General Procedure for Amide-phosphine Synthesis (**R,R-3a-i, k, m**; **S,S-3a, c, d**)

The resolved carboxylic acid diazaphospholane (1 mmol) was combined with 2.3 equivalents of the PyBOP coupling reagent. Methylene chloride (75mL) was added to the solid and stirred. This was followed by the addition of 2.3 equivalents of amine (or the hydrochloride salt) and 2.5 equivalents of diisopropylethylamine (DIEA). A further equivalent of DIEA was added to neutralize any equivalents of HCl that were added as the amine adducts. After stirring overnight (15hrs), methylene chloride was removed *in vacuo* and the reactions were checked for completeness by NMR. The product was dissolved in ethyl acetate and the organic layer was washed with saturated NaHCO_3 , 3M HCl, saturated NaHCO_3 and H_2O . The organic layer was dried over magnesium sulfate and the solvent was removed. The residue was purified by flash chromatography with 2:1 CH_2Cl_2 / ethyl acetate as eluent.

R,R-3a: Yield = 42% of a white solid. ^1H NMR (CDCl_3): δ 1.56 (d, 3H, $J = 7.1$ Hz, CH_3), 1.59 (d, 3H, $J = 6.7$ Hz, CH_3), 5.27 (quintet, 1H, $J = 7.1$, CHCH_3), 5.34 (quintet, 1H, $J = 7.3$ Hz, CHCH_3), 6.15 (d, 1H, $J = 8.1$), 6.70 (t, 1H, $J = 7.9$ Hz), 6.78 (d, 1H, $J_{\text{H-P}} = 18.6$ Hz, PCHN), 6.95 (b, 1H), 7.00 (t, 1H, $J = 7.3$ Hz), 7.06 (d, 1H, $J = 7.4$ Hz), 7.10 (t, 2H, $J = 7.8$ Hz), 7.18 (t, 2H, $J = 7.1$ Hz), 7.20-7.44 (m, 12H), 7.47 (d, 1H, $J = 2.9$ Hz, PCHN), 7.56 (d, 2H, $J = 6.8$ Hz), 7.85 (m, 2H), 8.26 (d, 1H, $J = 7.8$ Hz), 8.42 (d, 1H, $J = 8.42$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 22.8 (s, CH_3), 23.1 (s, CH_3), 49.8 (s, 2C, CHCH_3), 59.6 (d, $J_{\text{C-P}} = 21$ Hz, PCHN), 62.8 (d, $J_{\text{C-P}} = 37$ Hz, PCHN), peaks at 125-145 ppm have not been assigned due to the complexity, 157.1 (s, CONN), 157.5 (s, CONN), 168.1 (s, CONH), 168.4 (s, CONH); ^{31}P NMR (CDCl_3): δ 1.3 (d, $J_{\text{P-H}} = 18.6$ Hz). EMM calcd for $\text{C}_{46}\text{H}_{39}\text{N}_4\text{O}_4\text{PNa}$ $[\text{M}+\text{Na}]^+$: 765.2607, found: 765.2608.

R,R-3b: Yield = 72% of a white solid. ^1H NMR (CDCl_3): δ 3.72 (s, 3H, OCH_3), 3.76 (s, 6H, OCH_3), 3.83 (s, 3H, OCH_3), 5.37 (d, 1H, $J = 7.3$ Hz, $\text{NCH}(\text{CO}_2\text{CH}_3)_2$), 5.48 (d, 1H, $J = 7.4$ Hz, $\text{NCH}(\text{CO}_2\text{CH}_3)_2$), 6.19 (d, 1H, $J = 7.9$ Hz), 6.72 (m, 1H), 6.99 (d, 1H, $J_{\text{H-P}} = 17.4$ Hz, PCHN), 7.05 (m, 1H), 7.08-7.50 (m, 10H), 7.67 (m, 1H), 7.82 (m, 3H), 8.18 (d, 1H, $J = 7.4$ Hz), 8.26 (m, 1H), 8.40 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 54.0 (s, CO_2CH_3), 54.1 (s, CO_2CH_3), 54.2 (s, 2C, CO_2CH_3), 57.1 (s, $\text{CH}(\text{CO}_2\text{CH}_3)_2$), 57.2 (s, $\text{CH}(\text{CO}_2\text{CH}_3)_2$), 59.6 (d, $J_{\text{C-P}} = 23$ Hz, PCHN), 62.2 (d, $J_{\text{C-P}} = 36$ Hz, PCHN), peaks at 125-145 ppm have not been assigned due to the complexity, 157.0 (s, CONN), 157.4 (s, CONN), 167.2 (s, 2C, CO_2CH_3), 167.3 (s, CO_2CH_3), 167.4 (s, CO_2CH_3), 168.8 (s, CONH), 169.2 (s, CONH); ^{31}P NMR (CDCl_3): δ 1.8 (d, $J_{\text{P-H}} = 17.4$ Hz). EMM calcd for $\text{C}_{40}\text{H}_{35}\text{N}_4\text{O}_{12}\text{PNa}$ $[\text{M}+\text{Na}]^+$: 817.1887, found: 817.1854.

R,R-3c: Yield = 64% of a white solid. ^1H NMR (CDCl_3): δ 0.91 (t, 3H, $J = 7.4$ Hz, CH_2CH_3), 0.97 (t, 3H, $J = 7.3$ Hz, CH_2CH_3), 1.19 (d, 3H, $J = 6.6$ Hz, CHCH_3), 1.20 (d,

3H, $J = 6.8$ Hz, CHCH₃), 1.40-1.65 (m, 4H, CHCH₂CH₃), 3.95-4.20 (m, 2H, NCH(CH₃)CH₂CH₃), 6.10 (d, 1H, $J = 7.9$ Hz), 6.48 (d, 1H, $J = 8.4$ Hz), 6.68 (d, 1H, $J_{H-P} = 18.4$ Hz, PCHN), 6.68 (m, 1H), 6.92 (d, 1H, $J = 8.4$ Hz), 6.96-7.35 (m, 10H), 7.45 (d, 1H, $J = 3.1$ Hz), 7.55 (m, 1H), 7.84 (m, 2H), 8.24 (m, 1H), 8.41 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 11.1 (s, CH₂CH₃), 11.2 (s, CH₂CH₃), 21.1 (s, CHCH₃), 21.2 (s, CHCH₃), 30.3 (s, CH₂CH₃), 30.5 (s, CH₂CH₃), 47.7 (s, CHCH₃), 47.8 (s, CHCH₃), 59.5 (d, $J_{C-P} = 22$ Hz, PCHN), 62.6 (d, $J_{C-P} = 37$ Hz, PCHN), 157.1 (s, CONN), peaks at 125-145 ppm have not been assigned due to the complexity, 157.4 (s, CONN), 168.5 (s, CONH), 168.9 (s, CONH); ³¹P NMR (CDCl₃): δ 0.5 (d, $J_{P-H} = 18.4$ Hz). EMM calcd for C₃₈H₃₉N₄O₄PNa [M+Na]⁺: 669.2607, found: 669.2632.

R,R-3d: Yield = 79% of a yellow solid. ¹H NMR (CDCl₃): δ 3.68 (s, 3H, CO₂CH₃), 3.74 (s, 3H, CO₂CH₃), 5.67 (d, 1H, $J = 7.3$ Hz, NHCH(Ph)CO₂CH₃), 5.77 (d, 1H, $J = 7.3$ Hz, NHCH(Ph)CO₂CH₃), 6.09 (d, 1H, $J = 7.9$ Hz), 6.68 (d, 1H, $J_{H-P} = 19.1$ Hz, PCHN), 6.69 (m, 1H), 6.88 (d, 1H, $J = 7.5$ Hz), 6.95-7.50 (m, 21H), 7.66 (d, 1H, $J = 6.3$ Hz), 7.81 (m, 2H), 7.99 (d, 1H, $J = 7.4$ Hz), 8.22 (m, 1H), 8.37 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 53.4 (s, CHCO₂CH₃), 53.5 (s, CHCO₂CH₃), 57.6 (s, 2C, OCH₃), 59.3 (d, $J_{C-P} = 21$ Hz, PCHN), 62.5 (d, $J_{C-P} = 36$ Hz, PCHN), peaks at 125-140 ppm have not been assigned due to the complexity, 156.7 (s, CON(N)CH), 157.2 (s, CONN), 168.4 (s, CONH), 168.7 (s, CONH), 171.8 (s, COCH₃), 171.9 (s, COCH₃); ³¹P NMR (CDCl₃): δ 1.2 (d, $J_{P-H} = 19.1$ Hz). EMM calcd for C₄₈H₃₉N₄O₈PNa [M+Na]⁺: 853.2403, found: 853.2401.

R,R-3e: Yield = 51% of a white solid. ¹H NMR (CDCl₃): δ 3.68 (s, 3H, CO₂CH₃), 3.74 (s, 3H, CO₂CH₃), 4.06 (dd, 1H, $J = 18.2, 5.2$ Hz, NHCH₂CO₂CH₃), 4.08 (dd, 1H, $J = 18.2, 5.2$, NHCH₂CO₂CH₃), 4.32 (dd, 1H, $J = 18.2, 6.0$ Hz, NHCH₂CO₂CH₃), 4.44 (dd, 1H, $J = 18.2, 6.4$ Hz, NHCH₂CO₂CH₃), 6.18 (d, 1H, $J = 8.0$ Hz), 6.70 (m, 1H), 7.04 (t, 1H, $J = 7.5$ Hz), 7.06 (d, 1H, $J_{H-P} = 19.9$ Hz, PCHN), 7.09-7.45 (m, 10H), 7.48 (d, 1H, $J = 3.5$ Hz), 7.63 (m, 1H), 7.77-7.88 (m, 3H), 8.23 (m, 1H), 8.37 (m, 1H); ¹³C{¹H} NMR (CDCl₃): 42.1 (s, NHCH₂), 42.4 (s, NHCH₂), 53.0 (s, CO₂CH₃), 53.1 (s, CO₂CH₃), 59.7 (d, $J_{C-P} = 23$ Hz, PCHN), 62.4 (d, $J_{C-P} = 37$ Hz, PCHN), peaks at 125-140 have not been assigned due to the complexity, 157.0 (s, CONN), 157.4 (s, CONN), 169.2 (s, CONH), 169.8 (s, CONH), 171.0 (s, CO₂CH₃), 171.1 (s, CO₂CH₃); ³¹P NMR (CDCl₃): δ 2.2 (d, $J_{P-H} = 19.9$ Hz). EMM calcd for C₃₆H₃₁N₄O₈PNa [M+Na]⁺: 701.1777, found: 701.1744.

R,R-3f: Yield = 63% of a white solid. ¹H NMR (CDCl₃): δ 1.48 (d, 3H, $J = 7.2$ Hz, CHCH₃), 1.49 (d, 3H, $J = 7.2$ Hz, CHCH₃), 3.69 (s, 3H, CO₂CH₃), 3.76 (s, 3H, CO₂CH₃), 4.66 (dq, 1H, $J = 7.2, 7.2$ Hz, NHCHCH₃), 4.78 (dq, 1H, $J = 7.2, 7.2$ Hz, NHCHCH₃), 6.16 (d, 1H, $J = 8.3$ Hz, NHCHCH₃), 6.71 (m, 1H), 6.77 (d, 1H, $J_{H-P} = 18.6$ Hz, PCHN), 6.93 (d, 1H, $J = 7.7$ Hz), 6.97-7.45 (m, 11H), 7.53 (d, 1H, $J = 7.5$ Hz), 7.64 (m, 1H), 7.83 (m, 2H), 8.25 (m, 1H), 8.39 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 19.0 (s, CHCH₃), 19.1 (s, CHCH₃), 49.1 (s, CHCH₃), 49.2 (s, CHCH₃), 53.1 (s, CO₂CH₃), 53.2 (s, CO₂CH₃), 59.5 (d, $J_{C-P} = 23$ Hz, PCHN), 62.7 (d, $J_{C-P} = 36$ Hz, PCHN), Peaks at 125-135 ppm have not been assigned due to the complexity, 156.9 (s, CONN), 157.4 (s, CONN), 168.4 (CONH), 168.8 (CONH), 173.9 (s, CO₂CH₃), 174.0 (s, CO₂CH₃); ³¹P NMR (CDCl₃): δ 1.5 (d, $J_{P-H} = 18.6$ Hz). EMM calcd for C₃₈H₃₅N₄O₈PNa [M+Na]⁺: 729.2090, found: 729.2091.

R,R-3g: Yield = 83% of a white solid. ^1H NMR (CDCl_3): δ 2.97 (dd, 2H, $J = 4.6$, 17.2 Hz, $\text{CH}_2\text{CO}_2\text{Me}$), 3.07 (dd, 1H, $J = 4.9$, 17.1 Hz, $\text{CH}_2\text{CO}_2\text{Me}$), 3.13 (dd, 1H, $J = 5.0$, 17.1 Hz, $\text{CH}_2\text{CO}_2\text{Me}$), 3.66 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 4.92 (td, 1H, $J = 4.0$, 8.1 Hz, CHCH_2), 5.05 (td, 1H, $J = 4.0$, 8.1 Hz), 6.16 (d, 1H, $J = 8.2$ Hz), 6.71 (t, 1H, $J = 8.3$ Hz), 6.82 (d, 1H, $J_{\text{H-P}} = 18.6$ Hz, PCHN), 7.02 (t, 1H, $J = 7.5$ Hz), 7.09 (m, 3H), 7.20 (t, 3H, $J = 7.0$ Hz), 7.37 (m, 5H), 7.66 (d, 1H, $J = 7.8$ Hz), 7.68 (d, 1H, $J = 8.2$ Hz), 7.83 (m, 2H), 8.31 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 36.7 (s, CHCH_2), 36.9 (s, CHCH_2), 49.7 (s, 2C, CO_2CH_3), 52.8 (s, CO_2CH_3), 52.9 (s, CO_2CH_3), 53.5 (s, CHCH_2), 53.6 (s, CHCH_2), 59.6 (d, $J_{\text{C-P}} = 22$ Hz, PCHN), 62.7 (d, $J_{\text{C-P}} = 37$ Hz, PCHN), Peaks at 125-140 ppm have not been assigned due to the complexity, 156.8 (s, CONN), 157.3 (s, CONN), 168.6 (s, CONH), 169.0 (s, CONH), 171.77 (s, CO_2CH_3), 171.81 (s, CO_2CH_3), 172.2 (s, CO_2CH_3), 172.4 (s, CO_2CH_3); ^{31}P NMR (CDCl_3): δ 2.3 (d, $J_{\text{P-H}} = 18.6$ Hz). EMM calcd for $\text{C}_{42}\text{H}_{39}\text{N}_4\text{O}_{12}\text{PNa}$ $[\text{M}+\text{Na}]^+$: 845.2200, found: 845.2231.

R,R-3h: Yield = 87% of a white solid. ^1H NMR (CDCl_3): δ 3.08-3.32 (m, 4H, CHCH_2Ph), 3.64 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 4.87 (dt, 1H, $J = 7.5$, 5.7 Hz, NHCHCH_2), 5.03 (dt, 1H, $J = 8.1$, 6.1 Hz), 6.15 (d, 1H, $J = 6.9$ Hz), 6.69 (m, 1H), 6.70 (d, 1H, $J_{\text{H-P}} = 18.8$ Hz, PCHN), 6.78 (d, 1H, $J = 8.0$), 6.90-7.45 (m, 23H), 7.85 (m, 2H), 8.29 (m, 1H), 8.42 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 38.5 (s, CHCH_2), 38.8 (s, CHCH_2), 52.48 (s, CHCH_2), 52.52 (s, CHCH_2), 53.0 (s, CO_2CH_3), 53.1 (s, CO_2CH_3), 59.6 (d, $J_{\text{C-P}} = 21$ Hz, PCHN), 62.6 (d, $J_{\text{C-P}} = 36$ Hz, PCHN), peaks at 125-140 have not been assigned due to the complexity, 156.8 (s, CONN), 157.2 (s, CONN), 168.5 (s, CONH), 168.8 (s, CONH), 172.4 (s, CO_2CH_3), 172.6 (s, CO_2CH_3); ^{31}P NMR (CDCl_3): δ 2.4 (d, $J_{\text{P-H}} = 18.8$ Hz). EMM calcd for $\text{C}_{50}\text{H}_{43}\text{N}_4\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$: 881.2716, found: 881.2717.

R,R-3i: Yield = 93% of a white solid. ^1H NMR (CDCl_3): δ 1.26 (t, 3H, $J = 7.1$ Hz), 1.30 (t, 3H, $J = 7.3$ Hz), 1.49 (t, 6H, $J = 7.1$ Hz), 4.18 (q, 2H, $J = 7.2$ Hz, OCH_2CH_3), 4.23 (q, 2H, $J = 7.1$ Hz), 4.66 (dq, 1H, $J = 7.3$, NHCHCH_3), 4.77 (dq, 1H, $J = 7.3$ Hz, NHCHCH_3), 6.16 (d, 1H, $J = 7.9$ Hz), 6.71 (m, 1H), 6.79 (d, 1H, $J_{\text{H-P}} = 19.6$ Hz, PCHN), 6.85 (d, 1H, $J = 7.8$ Hz), 6.95-7.43 (m, 11H), 7.46 (d, 1H, $J = 7.0$ Hz), 7.63 (m, 1H), 7.83 (m, 2H), 8.26 (m, 1H), 8.39 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 14.8 (s, CH_2CH_3), 14.9 (s, CH_2CH_3), 19.2 (s, CHCH_3), 19.3 (s, CHCH_3), 49.2 (s, 2C, CHCH_3), 59.6 (d, $J_{\text{C-P}} = 23$ Hz, PCHN), 62.1 (s, CO_2CH_2), 62.3 (s, CO_2CH_2), 62.8 (d, $J_{\text{C-P}} = 35$ Hz, PCHN), Peaks at 125-140 ppm have not been assigned due to the complexity, 156.9 (s, CONN), 157.4 (s, CONN), 168.4 (s, CONH), 168.7 (s, CONH), 173.5 (s, CO_2CH_2), 173.6 (s, CO_2CH_2); ^{31}P NMR (CDCl_3): δ 1.7 (d, $J_{\text{P-H}} = 19.6$ Hz). EMM calcd for $\text{C}_{40}\text{H}_{39}\text{N}_4\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$: 757.2403, found: 757.2412.

R,R-3k: Yield = 81% of a white solid. ^1H NMR (CDCl_3): δ 1.48 (d, 3H, $J = 7.2$ Hz, CHCH_3), 1.51 (d, 3H, $J = 7.2$ Hz, CHCH_3), 3.61 (s, 3H, CO_2CH_3), 3.68 (s, 3H, CO_2CH_3), 4.72 (dq, 1H, $J = 7.7$, 7.3 Hz, NHCHCH_3), 4.83 (dq, 1H, $J = 8.0$, 7.4 Hz, NHCHCH_3), 6.17 (d, 1H, $J = 8.0$ Hz), 6.68 (t, 1H, $J = 7.9$ Hz), 7.04 (t, 1H, $J = 7.5$ Hz), 7.12 (d, 1H, $J_{\text{H-P}} = 18.7$ Hz, PCHN), 7.10-7.18 (m, 2H), 7.20-7.29 (m, 4H), 7.29-7.44 (m, 3H), 7.57 (d, 1H, $J = 3.5$ Hz), 7.62 (m, 2H), 7.83 (m, 2H), 8.02 (m, 1H), 8.24 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR

(CDCl₃): δ 18.3 (s, CHCH₃), 18.4 (s, CHCH₃), 48.4 (s, CHCH₃), 48.7 (s, CHCH₃), 52.5 (s, CO₂CH₃), 52.6 (s, CO₂CH₃), 59.2 (d, J_{C-P} = 22.9 Hz, PCHN), 61.6 (d, J_{C-P} = 36.0 Hz, PCHN), Peaks at 125-140 ppm have not been assigned due to the complexity, 156.6 (s, CONN), 156.9 (s, CONN), 168.3 (s, CONH), 168.8 (s, CONH), 173.6 (s, 2C, COCH₃); ³¹P NMR (CDCl₃): δ 1.9 (d, J_{P-H} = 18.7). EMM calcd for C₃₈H₃₅N₄O₈PNa [M+Na]⁺: 729.2090, found: 729.2057.

R,R-3m: Yield = 20% of a white solid. ¹H NMR (CDCl₃): δ (main product) 1.6-2.5 (m, 8H, CH₂), 3.55 (s, 3H, CO₂CH₃), 3.25-3.80 (m, 4H, C(O)NCH₂), 4.68 (dd, 1H, J = 8.1, 4.8 Hz, CHCO₂CH₃), 4.79 (dd, 1H, J = 8.4, 6.0 Hz, CHCO₂CH₃), 6.05 (d, 1H, J = 8.2 Hz), 6.35 (d, 1H, J_{H-P} = 20.0 Hz, PCHN), 6.61 (t, 1H, J = 7.4 Hz), 6.8-7.5 (m, 15H), 7.79 (m, 2H), 8.22 (m, 1H), 8.32 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ (main product) 25.87 (s, NCH₂CH₂), 25.90 (s, NCH₂CH₂), 30.3 (s, NCHCH₂), 30.4 (s, NCHCH₂), 50.2 (s, NCH₂CH₂), 50.7 (s, NCH₂CH₂), 52.8 (s, CO₂CH₃), 53.0 (s, CO₂CH₃), 58.7 (d, J_{C-P} = 20 Hz, PCHN), 59.1 (s, NCHCO₂CH₃), 59.2 (s, NCHCO₂CH₃), 60.6 (d, J_{C-P} = 38 Hz, PCHN), peaks at 125-140 ppm have not been assigned due to the complexity, 156.9 (s, CONN), 157.1 (s, CONN), 169.5 (s, CONCH), 169.7 (s, CONCH), 173.1 (s, CO₂CH₃), 173.3 (s, CO₂CH₃); ³¹P NMR (CDCl₃): δ -1.2 (d, J_{P-H} = 20 Hz, main peak), and other peaks at 0.0 and -4.4 with area ratio 100:40:8. EMM calcd for C₄₂H₃₉N₄O₈PNa [M+Na]⁺: 781.2403, found: 781.2406.

S,S-3a: Yield = 88% of a white solid. ¹H NMR (CDCl₃): δ 1.49 (d, 3H, J = 6.9 Hz, CHCH₃), 1.56 (d, 3H, J = 6.9 Hz, CHCH₃), 5.19 (dq, 1H, J = 7.3, 6.9 Hz, NHCHCH₃), 5.29 (dq, 1H, J = 7.3, 6.9 Hz, NHCHCH₃), 6.06 (d, 1H, J = 8.1 Hz), 6.60 (d, 1H, J_{H-P} = 19.0 Hz, PCHN), 6.66 (m, 1H), 6.77 (d, 1H, J = 7.4 Hz), 6.97-7.08 (m, 6H), 7.15-7.43 (m, 16H), 7.55 (d, 1H, J = 7.7 Hz), 7.84 (m, 2H), 8.24 (m, 1H), 8.41 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 22.7 (s, CHCH₃), 23.2 (s, CHCH₃), 50.2 (s, CHCH₃), 50.3 (s, CHCH₃), 59.4 (d, J_{C-P} = 22 Hz, PCHN), 62.4 (d, J_{C-P} = 37 Hz, PCHN), Peaks at 125-145 not assigned due to the complexity, 156.9 (s, CONN), 157.2 (s, CONN), 168.3 (CONH), 168.7 (CONH); ³¹P NMR (CDCl₃): δ 1.6 (d, J_{P-H} = 19.0 Hz). EMM calcd for C₄₆H₃₉N₄O₄PNa [M+Na]⁺: 765.2607, found: 765.2634.

S,S-3p: Yield = 94% of a white solid. ¹H NMR (CDCl₃): δ 0.90 (t, 3H, J = 7.5 Hz, CH₂CH₃), 0.94 (t, 3H, J = 7.4 Hz, CH₂CH₃), 1.46-1.66 (m, 4H, CH₂CH₂CH₃), 3.22-3.43 (m, 4H, NHCH₂CH₂), 6.12 (d, 1H, J = 8.0 Hz), 6.70 (d, 1H, J_{H-P} = 18.7 Hz, PCHN), 6.63-6.75 (m, 2H), 6.93-7.35 (m, 11H), 7.45 (d, 1H, J = 3.5 Hz), 7.53 (m, 1H), 7.83 (m, 2H), 8.23 (m, 1H), 8.38 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 12.2 (s, 2C, CH₂CH₃), 23.5 (s, CH₂CH₂CH₃), 23.6 (s, CH₂CH₂CH₃), 42.37 (s, NHCH₂CH₂), 42.41 (s, NHCH₂CH₂), 59.6 (d, J_{C-P} = 21 Hz, PCHN), 62.7 (d, J_{C-P} = 36 Hz, PCHN), Peaks at 124-140 ppm have not been assigned due to the complexity, 157.0 (s, CONN), 157.4 (s, CONN), 169.1 (s, CONH), 169.6 (s, CONH); ³¹P NMR (CDCl₃): δ 1.0 (d, J_{P-H} = 18.7 Hz). EMM calcd for C₃₆H₃₅N₄O₄PNa [M+Na]⁺: 641.2294, found: 641.2263.

S,S-3m: Yield = 91% of a white solid. ¹H NMR (CDCl₃): δ (main product) 1.7-2.4 (m, 8H, CH₂), 3.35 (s, 3H, CO₂CH₃), 3.52 (s, 3H, CO₂CH₃), 3.24-4.03 (m, 4H, C(O)NCH₂),

4.48 (dd, 1H, $J = 8.3, 4.4$ Hz, $\text{CH}_2\text{CHCO}_2\text{CH}_3$), 4.67 (dd, 1H, $J = 9.1, 3.3$ Hz, $\text{CH}_2\text{CHCO}_2\text{CH}_3$), 6.04 (d, 1H, $J = 7.9$ Hz), 6.50 (d, 1H, $J_{H-P} = 18.4$ Hz, PCHN), 6.62 (t, 1H, $J = 7.8$ Hz), 6.9-7.5 (m, 12H), 7.83 (m, 2H), 8.27 (m, 1H), 8.47 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 25.3 (s, NCH_2CH_2), 25.6 (s, NCH_2CH_2), 30.20 (s, NCHCH_2), 30.24 (s, NCHCH_2), 49.4 (s, 2C, NCH_2CH_2), 52.7 (s, CO_2CH_3), 52.8 (s, CO_2CH_3), 58.9 (s, $\text{NCHCO}_2\text{CH}_3$), 59.0 (d, $J_{C-P} = 20$ Hz, PCHN), 59.3 (s, $\text{NCHCO}_2\text{CH}_3$), 62.7 (d, $J_{C-P} = 37$ Hz), peaks at 125-140 ppm have not been assigned due to the complexity, 156.9 (s, CONN), 157.1 (s, CONN), 169.7 (s, CONCH_2), 169.9 (s, CONCH_2), 172.9 (s, CO_2CH_3), 173.3 (s, CO_2CH_3); ^{31}P NMR (CDCl_3): δ -0.88 (d, $J_{P-H} = 18.4$ Hz), additional peak at -2.7 with 11% of integrated area. EMM calcd for $\text{C}_{42}\text{H}_{39}\text{N}_4\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$: 781.2403, found: 781.2401.

Synthesis of R,R-3j: Synthesis procedure was identical to the general procedure described above. The product moved too slowly through the column using CH_2Cl_2 /ethyl acetate and was eluted using methanol. After column purification, the product was washed again using the general procedure described above. Yield = 34% of a white solid. ^1H NMR (CDCl_3): δ 3.36-4.06 (m, 40H, crown ether), 6.05 (d, 1H, $J = 7.9$ Hz), 6.15 (d, 1H, $J_{H-P} = 20.1$ Hz), 6.60 (t, 1H, $J = 8.1$ Hz), 6.90-7.38 (m, 12H), 7.82 (m, 2H), 8.25 (m, 1H), 8.40 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 47.1 (s, NCH_2), 48.2 (s, NCH_2), 51.4 (s, NCH_2), 52.0 (s, NCH_2), 59.5 (d, $J_{C-P} = 30$ Hz, PCHN), 63.2 (d, $J_{C-P} = 38$ Hz, PCHN), 69.0-72.5 (crown ether), peaks at 125-140 ppm have not been assigned due to the complexity, 156.8 (s, CONN), 157.0 (s, CONN), 171.2 (s, $\text{CON}(\text{CH}_2)_2$), 171.4 (s, $\text{CON}(\text{CH}_2)_2$); ^{31}P NMR (CDCl_3): δ -1.0 (broad). EMM calcd for $\text{C}_{50}\text{H}_{59}\text{N}_4\text{O}_{12}\text{PNa}$ $[\text{M}+\text{Na}]^+$: 961.3765, found: 961.3714.

Synthesis of S,S-3o: The resolved carboxylic acid diazaphospholane (1 mmol) was combined with 2.3 equivalents of the PyBOP coupling reagent. Methylene chloride (75mL) was added to the solid and stirred. This was followed by the addition of 2.3 equivalents of the amine salt and 7 equivalents of diisopropylethylamine (DIEA). After stirring overnight (15hrs), methylene chloride was removed *in vacuo* and the reaction was checked for completeness by NMR. The product was dissolved in 2M HCl and the aqueous layer was rinsed with ethyl acetate. After neutralizing the HCl by adding a saturated solution of NaHCO_3 , the product was extracted with methylene chloride. Flash chromatography was performed with 6:1 CH_2Cl_2 /methanol as eluent. Yield = 34% of a white solid. ^1H NMR (CDCl_3): δ 3.18 (m, 4H, NHCHCH_2), 3.57 (s, 3H, CO_2CH_3), 3.77 (s, 3H, CO_2CH_3), 4.80-4.95 (m, 2H, NHCHCH_2), 6.06 (d, 1H, $J = 8.2$ Hz), 6.58 (d, 1H, $J_{H-P} = 16.5$ Hz, PCHN), 6.69 (t, 1H, $J = 7.1$ Hz), 6.82 (s, 1H), 6.83 (m, 1H), 7.00 (s, 1H), 7.03 (m, 1H), 7.11 (m, 4H), 7.19 (m, 1H), 7.33-7.44 (m, 5H), 7.49 (s, 1H), 7.60 (s, 1H), 7.61-7.69 (m, 2H), 7.90 (m, 3H), 8.27 (m, 1H), 8.51 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 29.0 (s, CHCH_2), 30.3 (s, CHCH_2), 53.0 (s, CO_2CH_3), 53.3 (s, CO_2CH_3), 53.8 (s, CHCH_2), 54.1 (s, CHCH_2), 59.2 (d, $J_{C-P} = 19$ Hz, PCHN), 62.5 (d, $J_{C-P} = 33$ Hz, PCHN), peaks at 120-145 have not been assigned due to the complexity, 156.8 (s, CONN), 157.4 (s, CONN), 169.1 (s, CONH), 169.6 (s, CONH), 172.1 (s, CO_2CH_3), 172.4 (s, CO_2CH_3); ^{31}P NMR (CDCl_3): δ 2.6 (d, $J_{P-H} = 16.5$ Hz). EMM calcd for $\text{C}_{44}\text{H}_{39}\text{N}_8\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$: 861.2656, found: 861.2687.

Synthesis of Phosphine-Oxazolines **R,R**- and **S,S**-**3n**:

The procedure reported is based on literature precedent.⁴ The resolved carboxylic acid diazaphospholane (1 mmol) was combined with 2.3 equivalents of the PyBOP coupling reagent and 2.5 equivalents of L-valinol. Methylene chloride (75 mL) was added to the solid and stirred. This was followed by the addition of 2.5 equivalents of diisopropylethylamine (DIEA). After stirring overnight (15 hrs), solvent was removed *in vacuo* and the reactions were checked for completeness by NMR. The product was dissolved in ethyl acetate and the organic layer was washed with saturated NaHCO₃, 3M HCl, saturated NaHCO₃ and H₂O. The organic layer was dried over magnesium sulfate and the solvent was removed to give the crude products **R,R**- and **S,S**-**3I** as an oil. This product was used without further purification.

The oil was combined with 2.1 equivalents of *p*-toluenesulfonyl chloride in a Schlenk and placed under N₂. CH₂Cl₂ (100 mL), triethyl amine (1.0 mL) and a grain of DMAP were added. The solution was stirred for over 24 hours. Water (3 mL) was added to the solution and stirred for 1 hour. A further 50 mL of CH₂Cl₂ was added to the solution and the organic layer was rinsed 3 times with degassed H₂O (50 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The product was purified by flash chromatography (11:1 CH₂Cl₂/ethyl acetate).

R,R-3n: Yield = 14% of a white solid. ¹H NMR (CDCl₃): δ 0.57 (d, 3H, *J* = 6.6 Hz, CHCH₃), 0.62 (d, 3H, *J* = 6.5 Hz, CHCH₃), 0.68 (d, 3H, *J* = 6.5 Hz, CHCH₃), 0.74 (d, 3H, *J* = 6.7 Hz, CHCH₃), 1.45 (m, 1H, CHCH(CH₃)₂), 1.57 (m, 1H, CHCH(CH₃)₂), 3.74-4.39 (m, 6H), 6.15 (d, 1H, *J* = 7.8 Hz), 6.72 (t, 1H, *J* = 7.2 Hz), 6.94-7.39 (m, 9H), 7.57 (d, 1H, *J* = 14.8 Hz, PCHN), 7.78 (m, 1H), 7.84 (m, 2H), 7.95 (d, 1H, *J* = 4.1 Hz), 8.02 (m, 1H), 8.29 (m, 1H), 8.43 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 19.1 (s, CHCH₃), 19.3 (s, CHCH₃), 19.6 (s, 2C, CHCH₃), 33.4 (s, CH(CH₃)₂), 34.0 (s, CH(CH₃)₂), 61.0 (d, *J*_{C-P} = 21 Hz, PCHN), 62.9 (d, *J*_{C-P} = 34 Hz, PCHN), 70.1 (s, OCH₂), 70.5 (s, OCH₂), 74.4 (s, NCH), 74.5 (s, NCH), peaks at 120-145 ppm have not been assigned due to the complexity, peaks above 145 ppm were not identified; ³¹P NMR (CDCl₃): δ -3.0 (broad). EMM calcd for C₄₀H₄₀N₄O₄P [M+H]⁺: 671.2787, found: 671.2759.

S,S-3n: Yield = 11% of a white solid. ¹H NMR (CDCl₃): δ 0.50 (d, 3H, *J* = 6.6 Hz, CHCH₃), 0.52 (d, 3H, *J* = 6.9 Hz, CHCH₃), 0.62 (d, 3H, *J* = 6.6 Hz, CHCH₃), 0.68 (d, 3H, *J* = 6.7 Hz, CHCH₃), 1.37 (m, 1H, CHCH(CH₃)₂), 1.56 (m, 1H, CHCH(CH₃)₂), 3.87-4.01 (m, 4H, OCH₂CHN), 4.19-4.33 (m, 2H, NCHCH₂O), 6.13 (d, 1H, *J* = 8.3 Hz), 6.71 (t, 1H, *J* = 7.1 Hz), 6.97-7.39 (m, 9H), 7.83 (m, 3H), 8.01 (m, 1H), 8.07 (d, 1H, *J* = 3.8 Hz), 8.10 (d, 1H, *J*_{H-P} = 15.9 Hz), 8.31 (m, 1H), 8.42 (m, 1H); ¹³C{¹H} NMR (CDCl₃): δ 18.5 (s, CHCH₃), 18.7 (s, CHCH₃), 19.0 (s, CHCH₃), 19.6 (s, CHCH₃), 32.7 (s, CH(CH₃)₂), 33.9 (s, CH(CH₃)₂), 60.4 (d, *J*_{C-P} = 21 Hz, PCHN), 62.9 (d, *J*_{C-P} = 36 Hz, PCHN), 69.4 (s, OCH₂), 70.1 (s, OCH₂), 74.1 (s, NCH), 74.2 (s, NCH), peaks at 120-145 have not been assigned due to the complexity, peaks above 145 were not identified; ³¹P NMR (CDCl₃): δ -5.5 (broad). EMM calcd for C₄₀H₃₉N₄O₄P [M+H]⁺: 671.2787, found: 671.2813.

General procedure for Allylic Alkylation:

Dry CH₂Cl₂ (2.0 mL) was added to a mixture of [(η³-C₃H₅)PdCl]₂ (1.8 mg, 5 μmol), phosphine (20 μmol), NaOAc (approx. 5mg), and (if used) AgPF₆ / NaPF₆ (approx. 5 mg) in a septum-sealed vial under N₂. After stirring the solution at room temperature for 15 minutes, *N*, *O*-bis(trimethylsilyl)acetamide (0.7 mL, 3mmol), dimethyl malonate (0.3 mL, 3 mmol), and the allyl acetate (1.0 mmol) were added. This solution was stirred for 17 hours at room temperature. The solutions were diluted with 6 mL of 5:1 hexane/ethyl acetate and filtered twice through plugs of silica. The enantiomeric excess and yield of substrate **4a** were determined by chiral GC (β-DEX 120 column from Supelco, 30m x 0.25mm ID, undecane as internal standard). The absolute configuration of product was determined by comparison of GC retention times with literature values.⁵ The enantiomeric excess of **4b** was determined by chiral HPLC (Daicel's ChiralCel OD column with 99:1 hexane/isopropanol as mobile phase). The absolute configuration was determined by comparison of HPLC retention times with literature values.⁶ Yields of **4b** were determined by mass after dissolving residue in hexane, filtering, and removing solvent. Samples that had less than 100% conversion had the ratio of starting material to product accurately measured by NMR (relaxation delay = 20 seconds). This ratio was used to determine the mass of the product obtained.

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GC trace of Allylic Alkylation product with substrate **4a**, ligand (R, R)-**3f** and AgPF₆.
Conditions: Column Temp: 70 °C, Flow Rate: 1.8 mL/min