Supporting Information 1

Chiral Magnesium BINOL Phosphate Catalyzed Phopshination of Imines: Access to Enantioenriched α-Amino Phosphine Oxides

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General Information: All reactions were carried out in flame-dried or oven-dried screw-cap test tubes and were allowed to proceed under a dry argon atmosphere with magnetic stirring. Anhydrous acetonitrile was purchased from Aldrich., other solvents (toluene, dichloromethane, and THF) were purified by passing through a column of activated alumina under a dry argon atmosphere. Molecular Sieves (4Å) were flame-dried under high vacuum before use. Benzhydryl imines (**2a-j)** were synthesized according to the literature procedure.[1] Aldehydes were purchased from commercial sources and used without further purification. Diphenyl, di *t*-butyl and diethyl phosphine oxide were purchased from commercial sources and used without further purification. BINOL H(**1a**),[2] H(**1b**)[3] and H(**1c**)[4] were synthesized according to the known literature procedures. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F_{254}). Flash column chromatography was performed with Merck silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varian Prostar HPLC with a 210 binary pump and a 335 diode array detector. Optical rotations were performed on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700-μL cell with a path length of 1-dm. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance DPX-250 (250 MHz) and Varian Inova-400 spectrometer with chemical shifts reported relative to tetramethylsilane (TMS). ^{31}P NMR was recorded on a Varian Inova-400 instrument with H_3PO_4 as an external standard. The HRMS data were measured on a Agilent 1100 LC/MS ESI/TOF mass spectrometer with electro-spray ionization. Compounds described in the literature were characterized by comparing their ^{1}H NMR, ^{13}C NMR, and melting point (mp) to the reported values. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA.

Preparation of catalysts:[5]

H(1a) purified on silica gel: 'H(**1a**) purified on silica gel' was prepared by purification of H(**1a**) on silica gel using CH_2Cl_2/MeOH (10:1). The catalyst was obtained as a white solid.

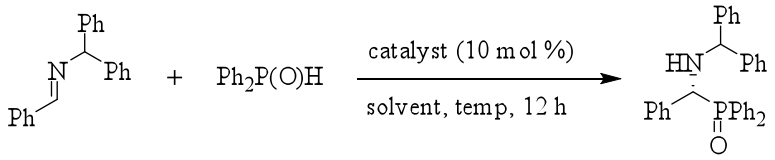
H(1a) washed with HCl: 'H(1a) washed with HCl' was prepared by purification of H(**1a**) on silica gel using CH_2Cl_2/MeOH (10:1).Upon purification, the catalyst was stirred in 6M HCl for 2 h and extracted with CH_2Cl_2. After removal of the solvent under reduced pressure, the catalyst was obtained as a white solid.

M(1a)$_n$: Catalyst was prepared in situ each time for phospha-Mannich reaction. To prepare M(**1a**)$_n$ (M = Na, Ca, Mg) (2.5 to 10 mol%), to a flame dry test tube was added 'H(**1a**) washed with HCl' (10 mol%) and NaOMe (10 mol%), or $Ca(OMe)_2$ (5 mol%) , or Mg(O*t*Bu)$_2$ (2.5 and 5 mol%). 1 mL each of CH_2Cl_2 and MeOH was added and reaction mixture was stirred for 1 h. After removal of solvent, 1 mL of CH_2Cl_2 was added and then removed under reduced pressure to obtain the catalyst as a white solid.

Mg(1a)$_2$ Characterization:

^{1}H NMR (400 MHz, DMSO): δ 7.24 (t, 4H, *J* = 7.6 Hz), 7.33 (t, 4H, *J* = 8.0 Hz), 7.43-7.58 (m, 24H), 7.85 (d, 4H, *J* = 8.8 Hz) 7.96 (s, 4H), 8.07 (d, 6H, *J* = 8.4 Hz), 8.11 (d, 6H, *J* = 8.4 Hz) 8.63 (s, 4H). ^{13}C NMR (100 MHz, DMSO) δ: 122.48, 122.50, 124.31, 124.51, 124.75, 124.97, 125.29. 126.01, 126.23, 126.29, 126.36, 127.43, 128.16, 128.26, 128.54, 129.51, 129.80, 130.44, 130.49, 131.25, 131.45, 131.47, 132.37, 132.42, 133.47, 149.48, 149.58. ^{31}P NMR (162 MHz, DMSO) δ 2.97. HRMS (MALDI) Calcd for $C_{96}H_{56}MgO_8P_2$ ($[M_{(n=2)}+2H]^{2+}$) m/z 1424.346 Found 1424.499. ($[M_{(n=2)}+NH_4]^+$) m/z 1440.364, Found 1440.178.

Table S1. Detailed optimization for the enantioselective addition of diphenylphine oxide to *N*-benzhydryl imine.



2a **3a** **4a**

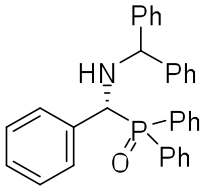
entry[a]	catalyst (mol %)	solvent	temp (°C)	yield, (%)[b]	ee, (%)[c]
1	H(**1a**) purified on silica gel (10)	toluene	40	82	75
2	H(**1a**) purified on silica gel (10)	toluene	0	56	83
3[d]	H(**1a**) purified on silica gel (10)	toluene	25	80	79
4	H(**1a**) purified on silica gel (10)	ether	25	82	83
5	H(**1a**) purified on silica gel (10)	$CHCl_3$	25	45	75
6	H(**1a**) purified on silica gel (10)	THF	25	82	87
7	H(**1a**) purified on silica gel (10)	acetone	25	52	90
8	H(**1a**) purified on silica gel (10)	$(CH_2)_2Cl_2$	25	82	89
9	H(**1a**) purified on silica gel (10)	CH_2Cl_2	25	84	89
10[e]	H(**1a**) purified on silica gel (10)	CH_2Cl_2	25	73	75

[a] General conditions: 1.2 equiv. of imine and 1.0 equiv. of diphenylphosphine oxide. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] 20 mol % catalyst loading. [e] 5 mol % catalyst loading.

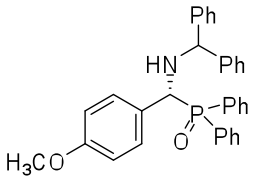
General procedure for preparation of racemates: The imine (**2a-j** and **5a-e**) (0.06 mmol), and diphylphosphine oxide (**3a**) (0.05 mmol) were weighed into a dry, re-sealable test tube with septa and stir bar. Dry dichloromethane (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature overnight. Dichloromethane was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the racemic product.

Imines which were generated *in situ,* corresponding aldehyde (0.06 mmol), diphenylmethane or amine/5H–Dibenzo[a,d]cyclohepten-5-amine[6] (0.05mmol), diphenylphosphine oxide (0.05 mmol), and 40 mg flame dried 4 Å molecular sieves were weighed into a dry, re-sealable test tube with septa and a stir bar. Dry dichloromethane (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature overnight. Dichloromethane was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the racemic product.

General procedure for chiral BINOL magnesium phosphate catalyzed asymmetric hydrophosphination of imines (2a-j): In a typical experiment the imine (0.06 mmol), diphenylphosphine oxide (0.05 mmol) and Mg(**1a**)$_2$ (5 mol%) were weighed into a dry, resealable test tube with septa and stir bar. Dry acetonitrile (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature for 12 h. Solvent was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the product.
Note: The absolute configuration of compound **4a** was determined by X-ray crystallographic analysis, and all the other products in Table 2, the absolute configuration is assumed by tentative analogy.



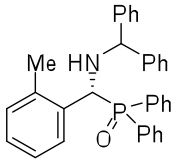
(-)-N-benzhydryl(diphenylphosphoryl)(phenyl)methanamine (4a) The reaction was performed in 0.05 mmol scale for 12 h using Mg (**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 23 mg, 96% yield, 93% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 7.87 min, $t_{\text{r-minor}}$ 11.88 min. $[\alpha]^{20}_{D}$ = -29.7° (c = 0.45, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.81 (d, 1H, J = 10.0 Hz), 4.15 (t, 1H, J = 10.0 Hz), 4.53 (s, 1H), 6.95-7.41 (m, 23H), 7.77 (t, 2H, J = 9.8 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 60.12 (d, ^1J = 80.0 Hz), 64.12 (d, ^3J = 13.1 Hz), 127.13, 127.20, 127.48, 127.94, 128.13, 128.28, 128.48, 128.54, 129.22, 129.31, 130.47, 130.72, 131.31, 131.45, 131.93, 132.07, 132.27, 135.53, 142.02, 143.72. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4. HRMS (ESI) Calcd for $C_{32}H_{29}NOP$ ($[M+H]^+$) m/z 473.1915, Found 473.1920.



(-)-N-benzhydryl(diphenylphosphoryl)(4-methoxyphenyl)methanamine (4b)

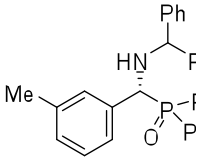
The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 24 mg, 95% yield, 90% ee. HPLC analysis: Chiralcel (S,S) WHELK-O1 (hexane/iPrOH = 75/25, 1.0 mL/min), $t_{\text{r-major}}$ 12.24 min, $t_{\text{r-minor}}$ 15.84 min. $[\alpha]^{20}_{D}$ = -20.1° (c = 2.8, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.71 (d, 1H, J = 10.0 Hz), 3.68 (s, 3H), 4.11 (t, 1H, J = 10.0 Hz), 4.54 (s, 1H), 6.68 (d, 2H, J = 8.8 Hz), 6.94-7.52 (m, 20H), 7.73-7.81 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 55.21, 59.29 (d, ^1J = 81.9 Hz), 63.87(d, ^3J = 13.7 Hz), 113.85, 113.87, 127.10, 127.27, 127.35, 127.52, 127.92, 128.10, 128.19, 128.24, 128.38, 128.41, 128.46, 128.58, 130.30, 130.38, 130. 63, 130.77, 131.31, 131.45, 131.73, 131.78, 131.90, 132.04, 132.18, 132.31, 142.04, 1

43.74, 159.23, 159.26. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6. HRMS (ESI) Calcd for $C_{33}H_{31}NO_2P$ ($[M+H]^+$) m/z 504.2016, Found 504.2032.



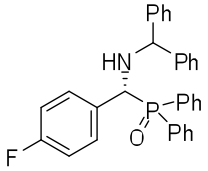
(-)- N-benzhydryl(diphenylphosphoryl)(o-tolyl)methanamine (4c)

The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 23 mg, 96% yield, 89% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 93/7, 1.0 mL/min), $t_{\text{r-major}}$ 7.27 min, $t_{\text{r-minor}}$ 10.88 min. $[\alpha]^{20}_D$ = -69.8° (c = 1.1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.38 (s , 3H), 2.88 (d, 1H, *J* = 10.0 Hz), 4.45-4.53 (m, 2H), 6.81-7.31 (m, 18H), 7.48-7.63 (m, 4H), 7.79-7.86 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.82, 54.78 (d, ^1J = 80.0 Hz), 64.17 (d, ^3J = 13.1 Hz), 126.53, 127.05, 127.12, 127.45, 127.67, 127.86, 128.06, 128.31, 128.40, 128.46, 128.83, 130.03, 130.80, 131.35, 131.50, 131.94, 131.98, 132.16, 132.30, 133.51, 137.59, 142.16, 143.64. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.9. HRMS (ESI) Calcd for $C_{33}H_{31}NOP$ ($[M+H]^+$) m/z 488.2126, Found 488.2140.



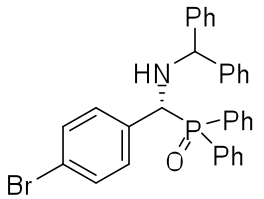
(-)- N-benzhydryl(diphenylphosphoryl)(m-tolyl)methanamine (4d) The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 23 mg, 95% yield, 92% ee, HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 93/7, 1.0 mL/min), $t_{\text{r-major}}$ 9.17 min, $t_{\text{r-minor}}$ 14.45 min. $[\alpha]^{20}_D$ = -23.6° (c = 1.35, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.16 (s , 3H), 2.81 (s, broad, 1H), 4.13 (d, 1H, *J* = 10.0 Hz), 4.56 (s, 1H), 6.86-7.34 (m, 19H), 7.42-7.54 (m, 3H), 7.74-7.82 (m, 2H). ^{13}C

NMR (62.5 MHz, $CDCl_3$): δ 21.37, 60.05 (d, ^1J = 80.0 Hz), 63.99 (d, ^3J = 13.1 Hz), 126.26, 126.35, 127.08, 127.32, 127.60, 127.81, 127.99, 128.18, 128.26, 128.37 , 128.41, 12 8.59, 129.00, 129.83, 129.92, 130.52, 130.68, 131.36, 131.42, 131.49, 13 1.74, 131.78, 131.94, 132.08, 132.22, 135.25, 137.95, 142.07, 143.75. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5. HRMS (ESI) Calcd for $C_{33}H_{31}NOP$ ($[M+H]^+$) m/z 488.2138, Found 488.2125.



(-)-N-benzhydryl(diphenylphosphoryl)(4-fluorophenyl)methanamine (4e)

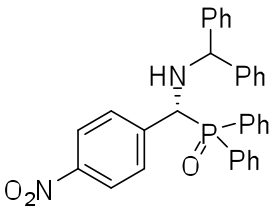
The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 23 mg, 95% yield, 90% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/2, 1.0 mL/min), $t_{\text{r-minor}}$ 12.77 min, $t_{\text{r-major}}$ 15.41 min. $[\alpha]^{20}_D$ = -25.2° (c = 1.35, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.85 (d, 1H, J = 10.0 Hz), 4.27 (t, 1H, J = 9.5 Hz), 4.62 (s, 1H), 6.92-7.45 (m, 19H), 7.54-7.66 (m, 3H), 7.87-7.94 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 59.30 (d, ^1J = 80.0 Hz), 64.03 (d, ^3J = 13.7 Hz), 115.20, 115.52, 126.53, 127.03, 127.22, 127.47, 127.59, 128.01, 128.15, 128.19, 128.29, 128.46, 128.53, 129.01, 130.25, 130.31, 130.64, 130.72, 130.76, 130.85, 131. 21, 131.35, 131.58, 131.62, 131.86, 131.92, 132.00, 141.82, 143.46. ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.4. HRMS (ESI) Calcd for $C_{32}H_{28}FNOP$ ($[M+H]^+$) m/z 492.1887, Found 492.1876.



(-)- N-benzhydryl(4-bromophenyl)(diphenylphosphoryl)methanamine (4f)

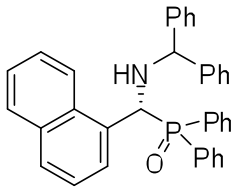
The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%)

The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 27 mg, 97% yield, 92% ee. HPLC analysis: Chiralcel (S,S) WHELK-O1 (hexane/iPrOH = 75/25, 1.0 mL/min), $t_{\text{r-major}}$ 9.61 min, $t_{\text{r-minor}}$ 12.71 min. $[\alpha]^{20}_{D}$ = -22.7° (c = 3.2, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.88 (d, 1H, *J* = 10.5 Hz), 4.26 (t, 1H, *J* = 10.5 Hz), 4.61 (s, 1H), 7.08-7.48 (m, 19H), 7.54-7.66 (m, 3H), 7.87-7.94 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 59.57 (d, ^1J = 79.4 Hz), 64.1 (d, ^3J = 13.1 Hz), 121.91, 121.96, 127.01, 127.26, 127.53, 128.10, 128.13, 128.28, 128.32, 128.49, 128.57, 130.06, 130.19, 130.78, 130.86, 131.22, 131.36, 131.53, 131.56, 131.62, 131.72, 131.75, 131.86, 132.00, 134.69, 141.72, 143.39. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1. HRMS (ESI) Calcd for $C_{32}H_{28}BrNOP$ ($[M+H]^+$) m/z 552.1086, Found 552.1065.



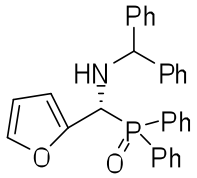
(-)-N-benzhydryl(diphenylphosphoryl)(4-nitrophenyl)methanamine (4g)

The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 25 mg, 97% yield, 95% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 75/25, 1.0 mL/min), $t_{\text{r-major}}$ 6.65 min, $t_{\text{r-minor}}$ 15.24 min. $[\alpha]^{20}_{D}$ = -24.5° (c = 1.15, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.85 (s, broad, 1H), 4.32 (s, broad, 1H,), 4.44 (s, 1H), 6.92-7.37 (m, 17H), 7.49-7.58 (m, 3H), 7.77-7.85 (m, 2H), 7.99 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 60.05 (d, ^1J = 76.8 Hz), 64.49 (d, ^3J = 13.1 Hz), 123.46, 126.92, 127.44, 127.74, 128.00, 128.29, 128.49, 128.57, 128.70, 129.52, 129.88, 129.96, 131.12, 131.26, 131.82, 131.96, 132.10, 132.37, 141.38, 142.96, 143.74, 147.53. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9. HRMS (ESI) Calcd for $C_{32}H_{28}N_2O_3P$ ($[M+H]^+$) m/z 519.1832, Found 519.1833.



(-)-N-benzhydryl(diphenylphosphoryl)(naphthalen-1-yl)methanamine (4h)

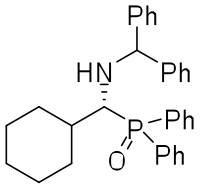
The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%) The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 25 mg, 95% yield, 96% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 10.55 min, $t_{\text{r-minor}}$ 15.77 min. $[\alpha]^{20}_{D}$ = -23.9° (c = 1.1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.02 (d, 1H, J = 8.5 Hz), 4.50 (s, 1H,), 5.14 (t, 1H, J =10.0 Hz), 6.82-7.28 (m, 18H), 7.41-7.69 (m, 6H), 7.82-7.98 (m, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 53.10 (d, ^1J = 81.2 Hz), 64.29 (d, ^3J = 13.7 Hz) 122.37, 125.24, 125.64, 126.47, 127.02, 127.12, 127.29, 127.39, 127.50, 12 7.68, 128.30, 128.35, 128.41, 128.50, 128.64, 130.92, 131.06, 131.24, 131.83, 131.87, 132.01, 132.15, 132.37, 133.33, 142.17, 143.64. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8. HRMS (ESI) Calcd for $C_{36}H_{31}NOP([M+H]^+)$ m/z 524.2072, Found 524.2061.



(+)-N-benzhydryl(diphenylphosphoryl)(furan-2-yl)methanamine (4i)

The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 22 mg, 93% yield, 91% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/2, 0.5 mL/min), $t_{\text{r-major}}$ 36.41 min, $t_{\text{r-minor}}$ 41.97 min. $[\alpha]^{20}_{D}$ = 9.4° (c = 1.15, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.69 (s, broad, 1H), 4.33 (d, 1H, J = 12 Hz), 4.64 (s, 1H), 6.17-6.22 (m, 2H), 6.97-7.54 (m, 19H), 7.72-7.79 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 54. 5 (d, ^1J = 84.3 Hz), 64.70 (d, ^3J = 12.5 Hz) , 110.16, 110.25, 110.62, 110.65, 127.08, 127.21, 127.38, 127.61, 128.02, 128.09, 128 .22, 128.41, 128.47, 128.81, 128.99, 130.23, 130.41, 131.22, 131.37, 131.69, 131.73,

131.84, 131.92, 131.98, 141.78, 142.60, 142.64, 143.53, 149.78. ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.5. HRMS (ESI) Calcd for $C_{30}H_{26}NNaO_2P$ ($[M+Na]^+$) m/z 486.1593, Found 486.1611.

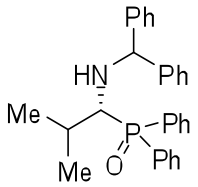


(-)-N-benzhydryl(cyclohexyl)(diphenylphosphoryl)methanamine (4j)

The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%) The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 23 mg, 96% yield, 91% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 98/2, 1.0 mL/min), $t_{\text{r-major}}$ 12.97 min, $t_{\text{r-minor}}$ 21.48 min. $[\alpha]^{20}_D$ = -3.5° (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.85-1.80 (m, 11H), 2.41 (bs, 1H), 3.23 (bs, 1H), 4.65 (s, 1H), 6.96-7.48 (m, 16H), 7.59-7.81 (m, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 25.01, 25.98, 26.09, 26.35, 26.96, 27.94, 32.89 (d, J = 12.5 Hz), 39.84 (d, J = 5.6 Hz), 58. 50 (d, ^1J = 70.0 Hz), 65.33 (d, ^3J = 6.2 Hz) , 127.02, 127.20, 127.48, 127.65, 127.83, 128.26, 128.35, 128.39, 128.51, 128.57, 128 .82, 128.95, 129.03, 130.65, 130.84, 130.98, 131.15, 131.29, 131.35, 131.62, 131.71, 132.62, 133.86, 133.95, 135.28, 142.79, 143.35. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8. HRMS (ESI) Calcd for $C_{32}H_{35}NOP$ ($[M+H]^+$) m/z 480.2451, Found 480.2461.

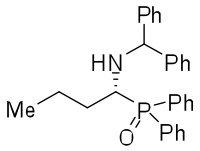
General procedure for three component chiral BINOL magnesium phosphate -catalyzed asymmetric hydrophosphination of imines (4k-n):

In a typical experiment the corresponding aldehyde (0.06 mmol), aminodiphenyl methane (0.06 mmol) diphenylphosphine oxide (0.05 mmol), Mg(**1a**)$_2$ (5 mol%) and 40 mg 4Å flame dried molecular sieves were weighed into a dry, resealable test tube with septa and stir bar. Dry acetonitrile (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature for 12 h. Solvent was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the product.



(-)-N-benzhydryl-1-(diphenylphosphoryl)-2-methylpropan-1-amine (4k)

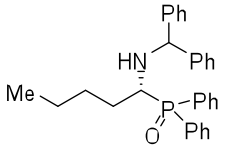
The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as an oil, 21 mg, 96% yield, 86% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 93/7, 1.0 mL/min), t $_{\text{r-major}}$ 5.80 min, t $_{\text{r-minor}}$ 7.68 min. $[\alpha]^{20}_{D}$ = -19.1° (c = 0.395, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.89-0.95 (m, 6H), 1.80-2.10 (m, 1H), 2.42 (s, broad, 1H), 3.29 (s, broad, 1H), 4.60 (s, 1H), 6.97-7.49 (m, 16H), 7.64-7.83 (m, 4H), ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 17.30 (d, ^3J = 0.9 Hz), 22.71 (d, ^2J = 13.7 Hz) , 29.9. (d, ^3J = 6.3 Hz), 58.3 (d, ^1J = 70.0 Hz), 65.24 (d, ^3J = 5.6 Hz) , 127.06, 127.25, 127.38, 127.59, 127.90, 128.20, 128.27, 128.38, 128.47, 128.65, 128 .85, 130.85, 130.99, 131.11, 131.25, 131.36, 131.40, 131.43, 131.47, 132.57, 133.90, 133.97, 135.32, 142.76, 143.41. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2. HRMS (ESI) Calcd for $C_{29}H_{30}NOP$ ($[M+H]^+$) m/z 440.2139, Found 440.2114.



(-)-N-benzhydryl-1-(diphenylphosphoryl)-*N*-propyl-1-methanamine (4l)

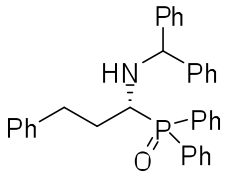
The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) as white semisolid, 19.2 mg, 88% yield, 62% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 90/10, 1.0 mL/min), t $_{\text{r-major}}$ 9.81 min, t $_{\text{r-minor}}$ 18.39 min. $[\alpha]^{20}_{D}$ = -7.1° (c = 0.435, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.730 (t, 3H, J = 7.2 Hz), 1.24 -1.28 (m, 1H), 1.51-1.57 (m, 2H), 1.66-1.75 (m, 1H), 2.05 (bs, 1H), 3.38 (bs, 1H), 4.70 (s, 1H), 7.05-7.55 (m, 16H), 7.72 (t, 2H, J = 8.0 Hz), 7.87 (t, 2H, J = 8.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.37, 19.66 (d, J = 8.0 Hz), 32.09, 53.8 (d, ^1J = 77.0 Hz), 64.84 (d, ^3J = 7.0 Hz) 127.31, 127.44, 127.73, 128.55, 128.64, 128.68,

128.78, 131.30, 131.38, 131.78, 143.2, 143.48. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8. HRMS (ESI) Calcd for $C_{29}H_{30}NOP$ ($[M+H]^+$) m/z 440.2138, Found 440.2158.



(-)-N-benzhydryl-1-(diphenylphosphoryl)-*N*-butyl-1-Methanamine (4m)

The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%) The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) an oil, 14.8 mg, 65% yield, 52% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 16.89 min, $t_{\text{r-minor}}$ 28.83 min. $[\alpha]^{20}_D$ = -3.4° (c = 0.765, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.68 (t, 3H, J = 7.2 Hz), 0.99 - 1.08 (m, 2H), 1.18 (bs, 1H), 1.35-1.53 (m, 2H), 1.62-1.74 (m, 1H), 3.31 (q, 1H, J =6.4 Hz), 4.63 (s, 1H), 6.98 - 7.00 (m, 2H), 7.07-7.18 (m, 6H), 7.32-7.49 (m, 8H), 7.63-7.82 (m, 4H), No *N-H* peak was observed. ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.95, 22.80, 28.34 (d, J = 7 Hz), 29.42 (d, J = 2.8 Hz), 53.83 (d, ^1J = 78.0 Hz), 64.81 (d, ^3J = 8.0 Hz), 127.26, 127.40, 127.67, 127.99 128.10, 128.50, 128.57 128.62, 128.72, 130.20, 130.39, 131.23, 131.31, 131.65, 131.74, 132.15 132.56, 133.05, 133.49, 143.15, 143.43. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.9 HRMS (ESI) Calcd for $C_{30}H_{32}NOP$ ($[M+H]^+$) m/z 454.2294, Found 454.2310.



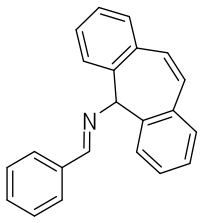
(-)-N-benzhydryl-1-(diphenylphosphoryl)-3-phenylpropane-1-amine (4n)

The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (hexane: ethyl acetate = 1:1) an oil, 17.5 mg, 73% yield, 48% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 44.08 mins, $t_{\text{r-minor}}$ 52.51 mins. $[\alpha]^{20}_D$ = -2.2° (c = 0.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79-1.90 (m, 1H), 1.98-2.09 (m, 1H), 2.34

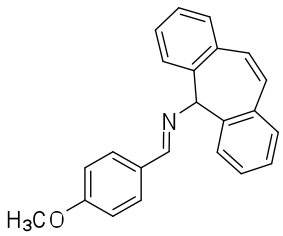
(bs, 1H), 2.51-2.59 (m, 1H), 2.79-2.86, (m, 1H) 3.44 (bs, 1H), 4.69 (s, 1H), 6.87 (d, 2H, *J* = 6.8 Hz), 7.04-7.06 (m, 2H), 7.13-7.25 (m, 11H), 7.35-7.39 (m, 2H), 7.46-7.50 (m, 3H), 7.54 - 7.58 (m, 1H), 7.65 (t, 2H, *J* = 7.6 Hz), 7.83 (t, 2H, *J* = 8.4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.94 (d, *J* = 4.0 Hz), 32.47, (d, *J* = 7.0 Hz), 53.4 (d, ^{1}J = 76.0 Hz), 64.87 (d, ^{3}J = 7.0 Hz), 126.04, 127.37, 127.54, 127.68, 127.85 128.56, 128.59, 128.65, 128.71, 128.85, 131.26, 131.35, 131.65, 131.74, 131.87, 141.99, 143.16, 143.47. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7. HRMS (ESI) Calcd for $C_{34}H_{32}NOP$ ($[M+H]^+$) m/z 502.2294, Found 502.2272, and calcd for ($[M+Na]^+$) m/z 524.2114, Found 524.2095.

General procedure for preparation of Imines (5a-e):

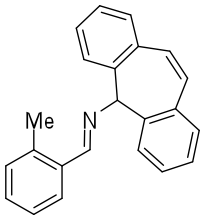
To a 100 ml round bottom flask was added corresponding aldehydes (1.1 equiv.), 5H–Dibenzo[a,d]cyclohepten-5-amine (1.0 equiv.), magnesium sulfate (5 equiv.), and methylene chloride (0.5 M) at room temperature. After few hours of stirring, resulting mixture was filtered off and evaporated to dryness to obtain the product as a white solid. The imines were purified by recrystallization using hexane/ethyl acetate.



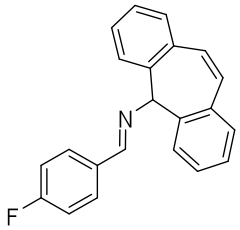
Preparation of **5a: 5a** was synthesized according to the know literature procedure.[6] Product was recrystallized using hexane: ethyl acetate (10:1) to give white solid product in 69% yield. M.P. 134-137 ˚C ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (bs, 1H), 7.12 (s, 2H), 7.24-7.26 (m, 2H), 7.36-7.38 (m, 4H), 7.49 (bs, 3H), 7.79 (bs, 2H), 7.97 (bs, 2H), 8.35 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.52, 124.87, 126.19, 128.06, 128.72, 128.83, 131.09, 131.44, 133.51, 136.59, 141.62, 161.68. HRMS (ESI) Calcd for $C_{22}H_{17}N$ ($[M+H]^+$) m/z 296.1434, Found 296.1450.



Preparation of **5b:** Product was recrystallized using hexane: CH_2Cl_2 (4:3) to give white solid product in 83% yield. M.P. 193-195 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 4.92 (bs, 1H), 6.97-6.99 (m, 2H) 7.13-7.23 (m, 4H), 7.35-7.33 (m, 4H) 7.76 (bs, 2H), 7.88 (bs, 2H), 8.25, (bs, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 55.60, 114.24, 125.04, 126.12, 128.02, 128.68, 129.67, 130.28, 131.45, 133.53, 141.84, 160.86, 162.05. HRMS (ESI) Calcd for $C_{23}H_{19}NO$ ($[M+H]^+$) m/z 326.1539, Found 326.1551.

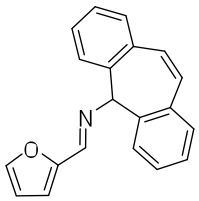


Preparation of **5c:** Product was recyrstallized using hexane: ethyl acetate (8:1) to give white solid product in 79% yield. M.P. 135-136 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67(s, 3H), 5.12 (bs, 1H), 7.29-7.38 (m, 5H), 7.48-7.53 (m, 6H), 7.95 (bs, 2H), 8.36 (bs, 1H), 8.76 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.89, 73.34, 124.87, 126.14 126.33, 128.01, 128.71, 130.59, 131.17, 131.44, 133.46, 134.38, 138.25 141.70, 160.73. HRMS (ESI) Calcd for $C_{23}H_{19}N$ ($[M+H]^+$) m/z 310.1590, Found 310.1577.



Preparation of **5d:** Product was recyrstallized using hexanes: ethyl acetate (5:1) to give white solid product in 83% yield. M.P. 150-152 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.99 (bs, 1H), 7.18 (bs, 4H), 7.25-7.29 (m, 2H), 7.39-7.42 (m, 4H) 7.79 (bs, 2H), 7.95 (bs, 2H), 8.30 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.38, 115.84, 116.06,

124.90, 126.28, 128.16, 128.75, 130.58, 130.66, 131.44, 132.91, 133.57, 141.50, 160.27, 163.46, 166.96. Anal calcd. for $C_{22}H_{16}FN$: C, 84.32; H, 5.15; N, 4.47. Found: C, 83.72; H, 5.08; N, 4.51.

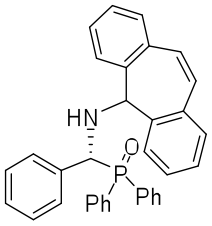


Preparation of **5e:** Product was recyrstallized using hexanes: ethyl acetate (10:1) to give yellowish white solid product in 77% yield. M.P. 124-126 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.96 (s, 1H), 6.48 (s, 1H), 6.81 (bs, 1H), 7.09 (bs, 2H), 7.23 - 7.25 (m, 1H), 7.33 -7.38 (m, 5H), 7.57 (bs, 1H), 7.70 (bs, 2H), 8.05 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.83, 111.97, 114.87, 126.48, 128.35, 128.84, 131.43, 133.64, 141.21, 145.22, 150.38, 152.09. HRMS (ESI) Calcd for $C_{20}H_{15}NO$ ($[M+H]^+$) m/z 286.1226, Found 286.1235.

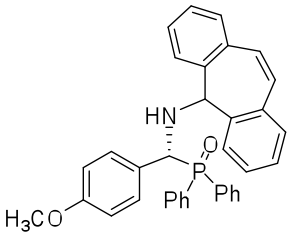
General procedure for chiral BINOL magnesium phosphate -catalyzed asymmetric hydrophosphination of imines (6a-e): In a typical experiment the imine (0.1 mmol), diphenylphosphine oxide (0.05 mmol) and Mg(**1a**)$_2$ (5 mol%) were weighed into a dry, resealable test tube with septa and stir bar. Dry CH_2Cl_2 (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature for 12h. Solvent was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the product. *Note1: The ^{1}H and ^{13}C NMR of products* ***6,*** *a minor isomer peaks were observed. The peaks for the minor isomer are not reported. The resulting minor peaks were due to the minor dibezocycloheptene system conformer. For more information please see ref. 19 in the main text.*

To determine absolute configuration, **6a** was deprotected using the procedure in scheme 1, yielding compound **7a.** The HPLC trace of compound **7a** generated from compound **6a** and compound **4a** gave 1st peak as a major peak. This establishes the compound **6a** and **4a** have same absolute configuration. For the other products in

Table 3, the absolute configuration is assumed by tentative analogy.

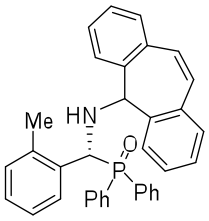


Preparation of **6a :** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 4:1) as white semisolid, 22.3 mg, 90% yield, 99% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/2, 1.0 mL/min), $t_{\text{r-major}}$ 32.96 min, $t_{\text{r-minor}}$ 45.60 min. $[\alpha]^{20}_D = 11.2°$ (c = 0.395, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (bs, 1H) 4.00 (s, 1H), 4.69 (s, 1H), 6.53-6.56 (m, 1H), 6.66-6.69 (m, 1H), 6.93 (d, 1H, J = 7.6 Hz), 7.12-7.39 (m, 18H), 7.50-7.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.86 (d, ^1J = 78.0 Hz), 66.60 (d, ^3J = 15.0 Hz), 121.99, 123.03, 125.68, 125.87, 127.48, 127.56, 127.67, 127.79, 127.91 128.08, 128.16, 128.28, 128.36, 128.55, 128.68, 128.83, 129.12, 129.17, 129.42, 129.52, 129.56, 130.02, 130.13, 130.34, 130.62, 130.70, 130.84, 131.66, 131.74, 131.92, 132.18, 132.41, 132.50, 134.26 134.47, 134.97, 137.95, 139.10. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4. HRMS (ESI) Calcd for $C_{34}H_{28}NOP$ ($[M+H]^+$) m/z 498.1981 Found 498.1967, and calcd for ($[M+Na]^+$) m/z 520.1801, Found 520.1780.

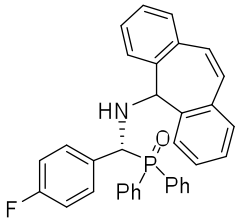


Preparation of **6b:** The reaction was performed in 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 4:1) as white semisolid, 23.7 mg, 92% yield, 93% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/2, 1.0 mL/min), $t_{\text{r-major}}$ 55.61 min, $t_{\text{r-minor}}$ 40.87 min. $[\alpha]^{20}_D = 11.5°$ (c = 0.94, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (bs, 1H),

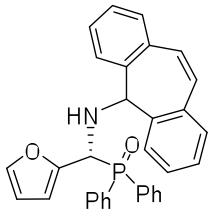
3.78 (s, 3H), 3.93 (d, 1H, J = 9.6 Hz). 4.67 (s, 1H), 6.50-6.66 (m, 2H), 6.76 (d, 2H, J = 8.4 Hz), 6.92-7.40 (m, 16H), 7.48-7.64 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.40, 60.10 (d, ^1J = 80.0 Hz) 66.33 (d, ^3J = 14.0 Hz), 113.85, 121.98, 123.04, 125.62, 125.78, 126.64, 127.41, 127.49, 128.02, 128.16, 128.26, 128.35, 128.80, 129.41, 129.99, 130.07, 130.29, 130.63, 131.62, 131.71, 131.85, 132.39, 132.48, 134.21, 134.38, 138.00, 139.15, 159.37. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2. HRMS (ESI) Calcd for $C_{35}H_{30}NO_2P$ ($[M+H]^+$) m/z 528.2087, Found 528.2100, and calcd for ($[M+Na]^+$) m/z 550.1906, Found 550.1921.



Preparation of **6c :** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 4:1) as white semisolid, 24.2 mg, 92% yield, 96% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 18.36 min, $t_{\text{r-minor}}$ 36.73 min. $[\alpha]^{20}_D$ = -19.7° (c = 0.255, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 3H), 2.46 (br, 1H), 4.25 (d, 1H, J = 6.4 Hz), 4.66 (s, 1H), 6.63 (q, 2H, J = 12 Hz), 6.82 (d, 1H, J = 7.2 Hz), 6.94 (d, 1H, J = 7.2 Hz), 7.11-7.67 (m, 20H).^{13}C NMR (100 MHz, $CDCl_3$): δ 19.23, 55.33 (d, ^1J = 80.0 Hz) , 66.54 (d, ^3J = 14.0 Hz), 121.86, 123.05, 125.65, 125.75, 126.26, 127.40, 127.49, 127.59, 127.91, 128.02, 128.21, 128.33, 128.55, 128.75, 129.32, 129.86, 130.10, 130.27, 130.46, 130.77, 131.69, 131.74, 131.83, 131.91, 132.67, 132.76, 134.27, 134.66, 138.02, 139.13. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7. HRMS (ESI) Calcd for $C_{35}H_{30}NOP$ ($[M+H]^+$) m/z 512.2138, ound 512.2134, and calcd for ($[M+Na]^+$) m/z 534.1957, Found 534.1954.



Preparation of **6d:** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 8:1) as white semisolid, 24.5 mg, 95% yield, 96% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 99/1, 1.0 mL/min), $t_{\text{r-major}}$ 86.61 mins, $t_{\text{r-minor}}$ 58.55 mins. $[\alpha]^{20}_D = 10.1$ (c = 0.705, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (bs, 1H), 3.97 (d, 1H, J = 9.6 Hz), 4.63 (s, 1H), 6.51-6.66 (m, 2H), 6.88–6.91 (m, 3H), 7.07-7.64 (m, 19 H),^{13}C NMR (100 MHz, $CDCl_3$): δ 60.16 (d, ^1J = 78.0 Hz), 66.50 (d, ^3J = 14.0 Hz), 115.18 115.39, 121.87, 122.88, 125.73, 125.87, 127.49, 127.60, 128.11, 128.27, 128.32, 128.38, 128.43, 128.87, 129.32, 129.94, 130.09, 130.33, 130.44, 130.63, 130.90, 130.98, 131.02, 131.54, 131.62, 131.79, 132.33, 132.42, 134.06 134.26, 137.73, 138.91, 161.33, 163.77. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2. HRMS (ESI) Calcd for $C_{34}H_{27}FNOP$ ($[M+H]^+$) m/z 516.1887, Found 516.1867, and Calcd for ($[M+Na]^+$) 538.1706, Found 538.1692.



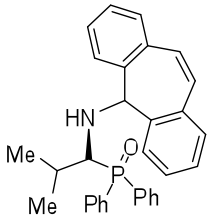
Preparation of **6e:** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 8:1) as white semisolid, 23.9 mg, 98% yield, 87% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/3, 1.0 mL/min), $t_{\text{r-major}}$ 37.24 mins, $t_{\text{r-minor}}$ 48.25 mins. $[\alpha]^{20}_D = 28.5$ (c = 0.37, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (bs, 1H), 4.15 - 4.12 (m, 1H), 4.75 (s, 1H), 6.08-6.28 (m, 2H), 6.54-6.72 (m, 2H), 6.98-7.70 (m, 19H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.01 (d, ^1J = 83.0 Hz), 67.63, (d, ^3J = 13.0 Hz), 110.15, 110.20, 110.85, 121.85, 122.76, 125.70, 125.87, 127.57, 128.18, 128.29, ,

128.32, 128.67, 129.55, 129.98, 130.11, 130.31, 130.66, 130.94, 131.15, 131.59, 131.68, 131.79, 131.90, 132.24, 132.33, 134.45, 134.59, 137.63, 138.74, 142.60, 149.69. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7. HRMS (ESI) Calcd for $C_{32}H_{26}NO_2P$ ($[M+H]^+$) m/z 488.1774, Found 488.1760, and calcd for ($[M+Na]^+$) 510.1593, Found 510.1573.

General procedure for three component chiral BINOL magnesium phosphate catalyzed asymmetric hydrophosphination of imines (6f-i):

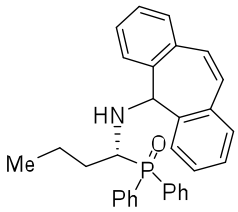
In a typical experiment the corresponding aldehyde (0.1 mmol), 5H–Dibenzo[a,d]cyclohepten-5-amine (0.1 mmol) diphenylphosphine oxide (0.05 mmol), Mg(**1a**)$_2$ (5 mol%) and 40 mg 4Å flame dried molecular sieves were weighed into a dry, resealable test tube with septa and stir bar. Dry CH_2Cl_2 (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature for 12h. Solvent was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the product.

Note: The ^{1}H and ^{13}C NMR of products ***6,*** *a minor isomer peaks were observed. The peaks for the minor isomer are not reported. The resulting minor peaks were due to the minor dibezocycloheptene system conformer. For more information please see ref. 19 in the main text.*

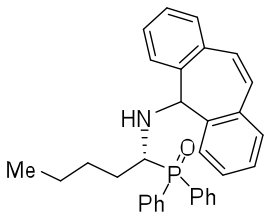


Preparation of **6f:** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 8:1) an oil, 16.6 mg, 72% yield, 85% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 93/7, 1.0 mL/min), $t_{\text{r-major}}$ 22.55 mins, $t_{\text{r-minor}}$ 44.71 mins. $[\alpha]^{20}_D = 50.1$ (c = 0.655, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.50 (d, 3H, J =6.8 Hz), 0.61 (d, 3H, J = 6.8), 1.08-1.23 (m, 1H), 1.98 (bs, 1H), 3.16 (s, 1H),), 4.25 (s,

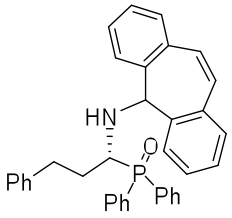
1H), 7.57-6.62 (m, 16H), 7.74 (t , 2H, J = 8.8 Hz) 7.92 (t, 2H, J = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.80, 22.02 (d, J = 13.0 Hz), 29.22 (d, J = 4.0 Hz), 60.36 (d, ^1J = 81.0 Hz), 68.70, (d, ^3J = 4.0 Hz), 121.99, 122.66, 125.55, 125.60, 127.27, 127.49, 128.16, 128.44, 128.54, 128.69, 128.80, 129.56, 129.92, 130.12, 130.40, 130.44, 131.04, 131.50, 131.59, 131.66, 132.46, 132.54, 133.99, 134.66, 138.86, 139.30. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7. HRMS (ESI) Calcd for $C_{31}H_{30}NO_2P$ ($[M+H]^+$) m/z 464.2138, Found 464.2141, and Calcd for ($[M+Na]^+$) 486.1957, Found 486.1962.



Preparation of **6g:** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 8:1) an oil, 16.9 mg, 73% yield, 80% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 22.53 mins, $t_{\text{r-minor}}$ 13.21 mins. $[\alpha]^{20}_D$ = -50.15 (c = 0.695, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.52 (t, 3H, J = 7.2 Hz) 0.74-1.57 (m, 4H), 1.88 (bs, 1H), 3.11-3.15 (m, 1H), 4.27 (s, 1H), 6.67-6.87 (m, 3H), 7.09-7.58 (m, 12H), 7.76 (t, 3H, J = 8.8 Hz) 7.91 (t, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.88, 19.39(d, J = 10.0 Hz), 32.34, 55.3 (d, ^1J = 87.0 Hz), 68.02 (d, ^3J = 5.0 Hz), 122.36, 125.63 125.79, 127.25, 127.53, 128.36, 128.41, 128.46, 128.69, 128.81, 129.65, 130.09, 130.39, 130.47, 130.87, 131.77, 131.94, 132.02, 132.52, 132.59, 133.67, 134.13, 138.89, 139.14. ^{31}P NMR δ 31.3 (162 MHz, $CDCl_3$). HRMS (ESI) Calcd for $C_{31}H_{30}NOP$ ($[M+H]^+$) m/z 464.2138, Found 464.2157.

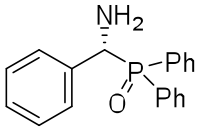


Preparation of **6h:** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 8:1) an oil, 19.1 mg, 80% yield, 73% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{\text{r-major}}$ 26.48 mins, $t_{\text{r-minor}}$ 20.87 mins. $[\alpha]^{20}_D$ = -63.2 (c = 0.745, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (t, 3H, *J* = 7.2 Hz) 0.66-1.88 (m, 5H), 1.52-1.62 (m, 1H), 1.85 (br, 1H) 3.04-3.08 (m, 1H), 4.21 (s, 1H), 6.61 (d, 1H, *J* = 6.4 Hz), 6.74 - 6.81 (m, 2H) 7.04-7.51 (m, 13H), 7.71 (t, 2H, *J* = 9.2 Hz), 7.84 (t, 2H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11 (d, *J* = 7.0 Hz), 22.43, 28.29 (d, *J* = 9.0 Hz), 29.86, 55.46 (d, ^1J = 87.0 Hz), 68.04 (d, ^3J = 5.0 Hz), 122.33, 125.60, 125.75, 127.22, 127.48, 127.68, 128.33, 128.37, 128.44, 128.66, 128.77, 129.62, 130.04, 130.37, 130.45, 130.87, 131.15, 131.23, 131.32, 131.74, 131.89, 131.98, 132.46, 132.54, 132.93 133.63 133.84, 134.11, 138.84, 139.11. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2. HRMS (ESI) Calcd for $C_{32}H_{32}NOP$ ($[M+H]^+$) m/z 478.2294 Found 478.2278, and Calcd ($[M+Na]^+$) 500.2114, Found 500.2093.



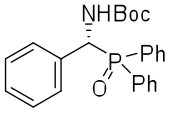
Preparation of **6i:** The reaction was performed on 0.05 mmol scale for 12 h using Mg(**1a**)$_2$ (5 mol%). The product was obtained by flash chromatography (CH_2Cl_2: ethyl acetate = 8:1) white semisolid, 22.6 mg, 86% yield, 93% ee. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 98/2, 1.0 mL/min), $t_{\text{r-major}}$ 43.08 mins, $t_{\text{r-minor}}$ 66.55 mins. $[\alpha]^{20}_D$ = -59.4 (c = 0.47, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41-1.51 (m, 1H), 1.79-1.91 (m, 1H), 2.04-2.11 (m, 1H), 2.31-2.38 (m, 1H), 3.11-3.16 (m, 1H), 4.33 (s, 1H), 6.62 (d, 1H, *J* = 6.8 Hz) 6.72-6.80 (m, 4H), 7.08-7.44 (m, 15H), 7.56-7.79 (m, 5H). No *N-H* Peak was observed. ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.48, 32.52, 54.80 (d, ^1J = 85.0 Hz), 67.91 (d, ^3J = 6.0 Hz), 122.30, 122.40, 126.00, 127.33, 127.63, 128.50, 128.55, 128.62, 128.68, 128.79, 129.68, 130.08, 130.15, 130.35, 130.46, 131.03, 131.83, 132.35, 132.43, 133.82, 134.29,

138.79, 139.24, 141.87. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5. HRMS (ESI) Calcd for $C_{36}H_{32}NOP$ ($[M+H]^+$) m/z 526.2294, Found 526.2285.



(-)-(diphenylphosphoryl)(phenyl)methanamine (7a).

To a 25 mL flame-dried round bottom flask filled with argon was added (-)-N-benzhydryl(diphenylphosphoryl)(phenyl)methanamine 90 mg (0.19 mmol, 93% ee) and 0.5 mL of anisole at room temperature. The flask was cooled to 0 °C and 400 uL of a solution of 8% (v/v)H_2SO_4 in TFA was added. The ice-bath was removed and the reaction mixture was stirred for 12 h. The reaction mixture was quenched by addition of saturated aq Na_2CO_3. 3 mL of ether was added and the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried over Na_2SO_4. The ether was removed by rotary evaporation and the residue was purified by flash chromatography (CH_2Cl_2: MeOH = 10:1) as a white solid, 47 mg, 80% yield, 93% ee. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 80/20, 1.0 mL/min), $t_{\text{r-major}}$ 11.95 min, $t_{\text{r-minor}}$ 15.49 min. $[\alpha]^{20}_D$ = -23.9° (c = 0.09, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.27 (s, 2H), 4.64 (d, 1H, *J* = 6.5 Hz), 7.10-7.48 (m, 13H), 7.79-7.86 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 56.83, (^1J = 84.1 Hz), 125.31, 127.74, 127.77, 128.09, 128.17, 128.24, 128.54, 128. 72, 129.04, 129.63, 129.80, 131.13, 131.32, 131.58, 131.72, 131.79, 131.91, 132.05, 1 32.12, 137.30. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.3. HRMS (ESI) Calcd for $C_{19}H_{19}NOP$ ($[M+H]^+$) m/z 308.1199, Found 308.1200.



Synthesis of 8a.

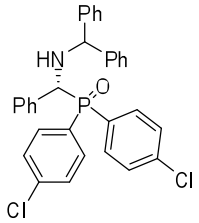
To a 25 mL flame-dried round bottom flask filled with argon was added (-)(diphenylphosphoryl)(phenyl)methanamine 17 mg (0.05 mmol, 93% ee), di-*tert*-butyl dicarbonate 24 mg (0.11 mmol) and 5 mL CH_3CN. The reaction mixture

was stirred at room temperature for 24h. The product was obtained by using column chromatography (CH_2Cl_2: MeOH, 20:1), 20 mg, Yield = 88%, ee = 88%. HPLC analysis: Chiralcel OD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 4.36 min, $t_{\text{r-minor}}$ 5.84 min. $[\alpha]^{20}_{D} = -77.3°$ (c = 0.37, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 9H), 5.55 (t, 1H, *J* = 7.6 Hz), 5.96 (d, 1H, *J* = 6.4 Hz), 7.21-7.10(m, 7H), 7.36-7.29 (m, 3H), 7.50 - 7.42 (m, 3H), 7.89 (t, 2H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.33, 53.98 (^1J = 75.0 Hz), 80.44, 128.03, 128.34, 128.45, 128.79, 128.89, 130.16, 130.22, 131.39, 131.48, 131.67, 131.75, 132.09, 132.35, 135.15, 155.13. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.0. HRMS (ESI) Calcd. for $C_{24}H_{26}NO_3P$ ($[M+H]^+$) m/z 408.1723, Found 408.1721, and calcd. for ($[M+Na]^+$) m/z 430.1542, Found 430.1533

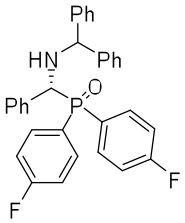
General procedure for preparation of racemates: The imine (0.06 mmol), phosphine oxide (**3b-e**) (0.05 mmol), and phenylphosphinic acid (10 mol%), were weighed into a dry, re-sealable test tube with septa and stir bar. Dry CH_3CN (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature overnight. Dichloromethane was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the racemic product.

General procedure for chiral Magnesium phosphate salt catalyzed asymmetric hydrophosphination of benzhydrylimines using substituted diphenyl phosphine oxides (9b-e):

In a typical experiment the benzhydrylimine (0.06 mmol), phosphine oxide (**3b-e**)[7] (0.05 mmol) and Mg(**1a**)$_2$ (5 mol%) were weighed into a dry, resealable test tube with septa and stir bar. Dry CH_3CN (0.5 mL) was added to the mixture via syringe and the resulting mixture was stirred at room temperature for 24 h. Solvent was removed by rotary evaporation to give a crude solid mixture that was purified by column chromatography to give the product

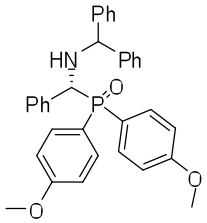


Preparation of 9b: The reaction was performed on 0.05 mmol scale of **3b.** The product was obtained by flash chromatography (Hexanes: ethyl acetate = 2:1) white semisolid, 25.2 mg, 93% yield, 84% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 22.88 mins, $t_{\text{r-minor}}$ 41.44 mins. $[\alpha]^{20}_{D}$ = -49.4 (c =1.06 , $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80 (d, 1H, *J* = 10.8 Hz), 4.09 (t, 1H, *J* = 11.2 Hz), 4.54 (s, 1H), 6.98 (t, 2H, *J* = 3.6 Hz), 7.09 – 7.18 (m, 17H) 7.45 (dd, 2H, ^1J = 8.8 Hz, ^2J = 2.4 Hz) 7.65-7.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.22 (^1J = 82.0 Hz), 64.25 (^3J = 14.0 Hz), 127.18, 127.48, 127.78, 128.43, 128.60, 128.71, 128.74, 128.82, 128.92, 129.04, 129.31, 129.36, 130.15, 130.36, 132.81, 132.90, 133.42, 133.52, 135.06, 138. 47, 138.50, 138.83, 138.87, 141.92, 143.55. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7. HRMS (ESI) Calcd. for $C_{32}H_{26}Cl_2NOP$ ($[M+H]^+$) m/z 542.12018, Found 542.11778, and calcd. for ($[M+Na]^+$) m/z 564.10213, Found 564.10155.

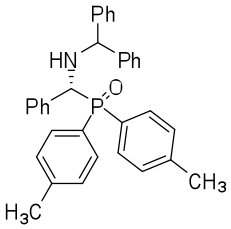


Preparation of **9c:** The reaction was performed on 0.05 mmol scale of **3c**. The product was obtained by flash chromatography (Hexanes: ethyl acetate = 2:1) white semi solid, 22.7 mg, 88% yield, 84% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 17.71 mins, $t_{\text{r-minor}}$ 25.47 mins. $[\alpha]^{20}_{D}$ = -30.0° (c = 0.86, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (d, 1H, *J* = 10.8 Hz), 4.17 (t, 1H, *J* = 10.8 Hz), 4.62(s, 1H), 6.88 (t, 2H, *J* = 8.4 Hz), 7.07 (bs, 2H), 7.16-7.35 (m, 17H), 8.80-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.19 (^1J = 82.0 Hz), 64.0 (^3J = 14.0 Hz), 115.21, 115.34, 115.42, 115.55, 115.66, 115. 75, 115.87, 126.94, 127.19,

127.47, 128.03, 128.05, 128.17, 128.42, 128.45, 128.47, 128.49, 129.04, 129.09, 133.64, 133.74, 133.83, 134.22, 134.32, 134.41, 135.00, 141.75, 143.36, 163.39, 163.43, 163.85, 163.88, 165.91, 165.95, 166.37, 166.40. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6. HRMS (ESI) Calcd. for $C_{32}H_{26}F_2NOP$ ($[M+H]^+$) m/z 510.17928, Found 510.17933, and calcd. for ($[M+Na]^+$) m/z 532.16123, Found 532.16073.



Preparation of **9d:** The reaction was performed on 0.05 mmol scale of **3d**. The product was obtained by flash chromatography (Hexanes: ethyl acetate = 1:1) white semisolid, 21.5 mg, 79% yield, 87% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 93/7, 0.8 mL/min), $t_{\text{r-major}}$ 30.75 mins, $t_{\text{r-minor}}$ 26.37 mins. $[\alpha]^{20}_{D}$ = -47.5° (c = 0.63, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (bs, 1H), 3.71 (s, 3H), 3.89 (s, 3H), 4.16 (d, 1H, J = 9.2 Hz), 4.59 (s, 1H), 6.69 (dd, 2H, ^1J = 9.2 Hz, ^2J = 6.8 Hz), 7.13-7.27 (m, 19H), 7.73 (d, 1H, J = 8.8 Hz), 7.75 (d, 1H, J = 8.8Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ 55.15, 55.36, 60.44 (^1J = 81.0 Hz), 63.93 (^3J = 13.0 Hz), 113.40, 113.53, 113.72, 113.85, 121.97, 122.03, 122.18, 122.22, 123.01,123.07,123.21, 123.26, 127.02, 127.07, 127.27, 127.65, 128.24, 128.32, 128.38, 129.16, 129.21, 133.19, 133.29, 133.76, 133.86, 135.67, 135.70, 142.05, 143.69, 161.92, 161.95, 162.34, 162.37. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8. HRMS (ESI) Calcd. for $C_{34}H_{32}NO_3P$ ($[M+H]^+$) m/z 534.21926, Found 534.21798, and calcd. for ($[M+Na]^+$) m/z 556.20120, Found 556.19939.



Preparation of **9e:** The reaction was performed on 0.05 mmol scale of **3e**. The product

was obtained by flash chromatography (Hexanes: ethyl acetate = 1:1) white semisolid, 15.7 mg, 63% yield, 89% ee. HPLC analysis: Chiralcel (S, S) WHELK-O1 (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-major}}$ 16.03 mins, $t_{\text{r-minor}}$ 22.31 mins. $[\alpha]^{20}_{D}$ = -41.7° (c = 0.715, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.47 (s, 3H), 2.85 (d, 1H, *J* = 10.8 Hz), 4.21 (t, 1H, *J* = 10.4 Hz), 4.62 (s, 1H), 6.99 (d, 2H, *J* = 6.8 Hz), 7.06 (bs, 2H), 7.19-7.38 (m, 17H), 7.74 (t, 2H, *J* = 8.4Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.44, 21.66, 60.15 (^1J = 80.0 Hz), 63.93 (^3J = 13.0 Hz), 126.87, 126.90, 127.02, 127.08, 127.26, 127.65, 127.67, 128.24, 128.32, 128.37, 128.43, 128.59, 128.70, 129.90, 129.02, 129.21, 129.26, 131.31, 131.40, 131.91, 132.0, 135.68, 141.66, 141.69, 142.05, 143.71. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1. HRMS (ESI) Calcd. for $C_{34}H_{32}NOP$ ($[M+H]^+$) m/z 502.22943, Found 502.22770, and calcd. for ($[M+Na]^+$) m/z 524.21137, Found 524.20894.

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ORTEP Drawing of X-ray Structure of Compound **8a**