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A Flexible, Highly Efficient Method for the Preparation of Homochiral Oxazaphospholidine-boranes†

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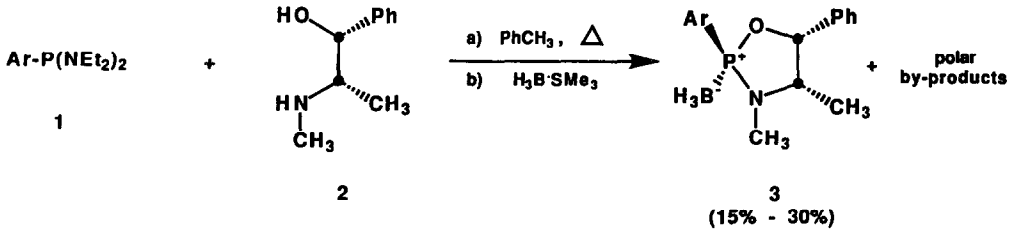
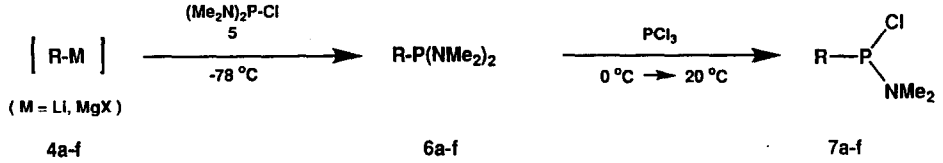
Abstract: An efficient and operationally simple procedure for the synthesis of 2-substituted 3,4-dimethyl-5-phenyloxazaphospholidine derivatives has been developed. This new method permits the large scale preparation of a range of electronically and sterically differentiated homochiral monophosphine precursors.

The immense potential that structurally varied homochiral mono- and bisphosphines hold for transition metal based asymmetric synthesis has recently stimulated renewed investigations into the synthesis of these compounds.[4-7] Our interests in asymmetric Rh(I) catalyzed [4+2] cycloisomerizations[8] as well as other enantioselective transformations that rely on catalysis encouraged us to examine several of the reported procedures for the preparation of monophosphines that are homochiral at phosphorus. Of the available methods, the procedures of Juge[4a] and Brown[5] appeared best suited for our needs. A crucial transformation that is common to *both* approaches involves the thermal condensation of bis(diethylamino)phenyl phosphine with (−)-ephedrine (2) to give the corresponding oxazaphospholidine.[4a,5] It was quickly determined, however, that the direct thermal condensation reaction involving alternative bis(diethylamino)aryl phosphines (e.g., 1) and (−)-ephedrine (2) was a highly capricious and non-general reaction. In a majority of the instances that were examined, *non-selective* condensations occurred between the bis(amino)phosphine precursors 1 and (−)-ephedrine (2) to give poor yields (ca., 15%-30%) of the desired complexes 3 after BMS treatment along with large amounts of polar by-products.

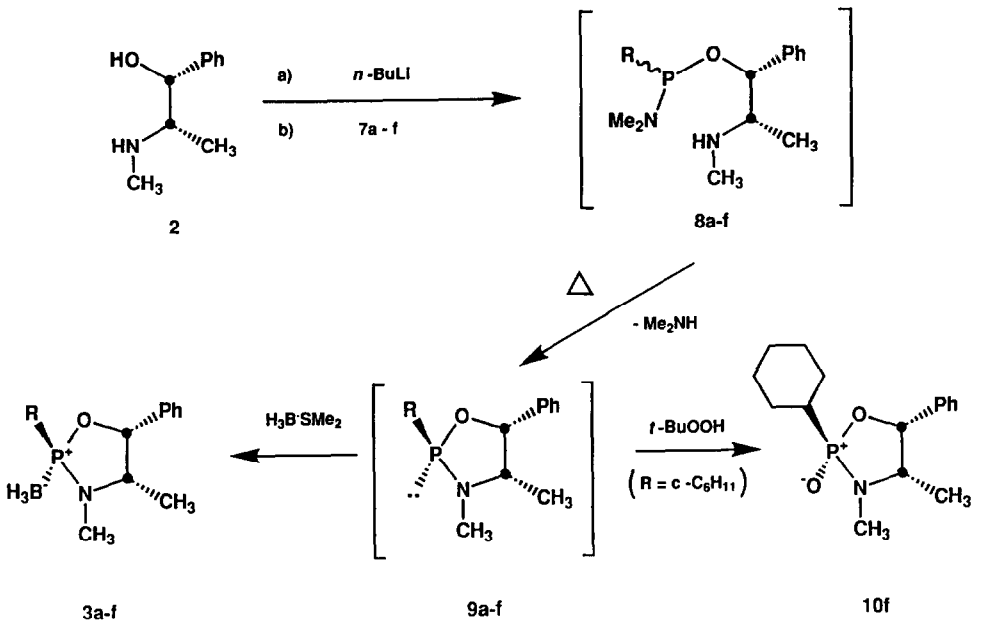


We reasoned that the generality of cyclocondensation might be restored if an efficient, "*ionic*", coupling reaction was employed to secure the *initial* phosphorus-oxygen bond *followed* by thermolytic ring closure. The successful implementation of this strategy and its application to the synthesis of a range of homochiral oxazaphospholidine derivatives is described below.

The chloro(dimethylamino) phosphines **7a-f** required for this study were conveniently prepared as follows. Treatment of $(Me_2N)_2P$-Cl **5**[9] with the requisite organolithium (or Grignard) reagents **4a-f** in ethereal solvents (−78 °C → 20 °C) gave the corresponding bis(dimethylamino) phosphines **6a-f** in 70%-92% yield. Exposure of **6a-f** to PCl_3 (1.0 equiv, 0 °C → 20 °C) followed by distillation at reduced pressure furnished **7a-f** in near quantitative yield along with Me_2NPCl_2 [which can be reconverted to $(Me_2N)_2P$-Cl via redistribution with $(Me_2N)_3P$[9]]. Monolithiation of (−)-ephedrine (**2**) with *n*-BuLi [*exactly* 1.00 equiv, 1,2-DME (*or THF*), −50 °C (*or* −78 °C)] followed by dropwise addition of **7a-f** [1.05 equiv, in 1,2-DME (*or THF*), −50 °C (*or* −78 °C)] with vigorous stirring and final warming to ambient temperature afforded reaction mixtures containing the non-cyclized phosphonamidites **8a-f**. Subsequent cyclization of **8a-f** to the corresponding oxazaphospholidines **9a-f** was achieved by heating at reflux for 12-18 h[10] with concomitant elimination of Me_2NH. Direct complexation of **9a-f** via the addition of 1.1 equiv of $H_3B \cdot SMe_2$ (0 °C) provided the desired complexes **3a-f** in excellent yield after recrystallization. Alternatively, oxidation of **9f** *in situ* (*t*-BuOOH) provided the corresponding 2-oxide **10f** in 72% yield. An indication of the preparative scope of the foregoing procedure is provided by the examples listed in **Table I**.



a: R = 2-$(CF_3)C_6H_4$
b: R = C_6F_5
c: R = 4-$(CH_3O)C_6H_4$
d: R = 2-(CH_3)-4-$(CH_3O)C_6H_3$
e: R = 2-(5-methylthienyl)
f : R = cyclohexyl



a: R = 2-$(CF_3)C_6H_4$
b: R = C_6F_5
c: R = 4-$(CH_3O)C_6H_4$
d: R = 2-(CH_3)-4-$(CH_3O)C_6H_3$
e: R = 2-(5-methylthienyl)
f : R = cyclohexyl

Table I. Isolated Yields and Melting Points of Oxazaphospholidine Derivatives

	Compound						
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**10f**
yield (%)	77	72	78	70	82	76	72
mp (°C)	106.6	104.9	82.0	100.2	76.3	99.0	143.2

The new procedure reported herein is prominently characterized by its ease of execution and overall chemical efficiency. Applications to the synthesis of sterically and electronically differentiated homochiral bisphosphines as well as the utilization of these ligands as mediators for asymmetric catalysis will be described in future reports from these laboratories.

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EXPERIMENTAL SECTION

General experimental details: Tetrahydrofuran (THF) and 1,2-dimethoxyethane (1,2-DME) were distilled from K. Diethyl ether (Et_2O) was distilled from Na–benzophenone. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), benzene, toluene and 2,2,2-trifluoroethanol (TFE) were distilled from CaH_2. The molarities indicated for organolithium reagents were established by titration with 2-butanol. ^1H NMR and ^{13}C NMR were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. ^{31}P NMR were measured at 202 MHz with a Bruker AM-500 spectrometer. ^1H NMR chemical shifts are reported as δ values in ppm relative to TMS. ^{31}P NMR chemical shifts are reported as δ values in ppm relative to the ^{31}P resonances H_3PO_4 (85%) (0.0) or triphenylphosphine (−6.0). ^1H NMR and ^{31}P NMR coupling constants are reported in Hz and refer to apparent multiplicities and not true coupling constants. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); sx (sextet); br (broad); m (multiplet); app d (apparent doublet); app t (apparent triplet); dd (doublet of doublets); etc. High resolution mass spectra were measured on a VG Analytical 7070E spectrometer by Dr. L. J. Sears. Infrared spectra were recorded with a Bruker IFS 25 IR. Melting points were determined with a Mel-Temp II melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter. Elemental Analyses were performed by Desert Analytics, Tucson, Arizona. TLC and column chromatography were done with E. Merck silica gel. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried vessels. Concentrations were performed under reduced pressure with a Büchi rotary evaporator.

Bis(dimethylamino)-4-methoxyphenyl phosphine (6c). 4-Bromoanisole (18.7 g, 0.100 mol) was added to a solution of *n*-BuLi (36.9 mL of a 2.98 M solution in heptane, 0.110 mol) in Et_2O (100 mL) at 0 °C. The reaction mixture was stirred for an additional 15 min at 0 °C. The resulting solution of 4-lithioanisole was then added dropwise to $(Me_2N)_2P$-Cl (14.7 g, 0.085 mol) in Et_2O (50 mL) at −78 °C. The mixture was then warmed slowly to 25 °C. After dilution with anhydrous Et_2O (50 mL), the solution was filtered under argon through celite. Concentration of the solution followed by purification of the yellow liquid by fractional distillation (100-110 °C, 1.1 torr) gave 20.7 g (92%) of **6c** as a viscous clear oil. ^1H NMR ($CDCl_3$) δ 7.29 (dd, J = 5.3, 8.6 Hz, 2H, Ar*H*), 6.89 (dd, J = 1.9, 8.6 Hz, 2H, Ar*H*), 3.80 (s, 3H, OCH_3), 2.72 (d, J = 9.2 Hz, 12H, NCH_3); ^{13}C NMR ($CDCl_3$) δ 141.2, 140.6, 132.6, 132.4, 113.9 (2C), 55.2, 41.6 (2C), 41.4 (2C).

6d: Fractional distillation (92 °C, 0.15 mm) gave 16.8 g (70%) of **6d**; ^1H NMR ($CDCl_3$) δ 7.31 (dd, J = 4.3, 8.6 Hz, 1H, Ar*H*), 6.72 (m, 2H, Ar*H*), 3.77 (s, 3H, OCH_3), 2.68 (d, J = 9.0 Hz, 12H,

NCH_3), 2.25 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 159.5, 142.0 (d, J = 22.7 Hz), 132.0 (d, J = 3.4 Hz), 130.0, 116.6, 110.4, 54.9, 41.1 (2C), 40.9 (2C), 20.4 (d, J = 13.1 Hz); ^{31}P NMR ($CDCl_3$) δ 97.3 (s).

6f: Fractional distillation (54 °C, 0.025 torr) gave 17.9 g (89%) of **6f**; ^1H NMR ($CDCl_3$) δ 2.61 (d, J = 8.6 Hz, 12H, NCH_3), 1.90-1.48 (m, 6H, Cy*H* envelope), 1.32-1.00 (m, 5H, Cy*H* envelope); ^{13}C NMR ($CDCl_3$) δ 41.0 (2C), 40.8 (2C), 34.1, 27.9, 27.6, 26.7, 26.6, 26.3; ^{31}P NMR ($CDCl_3$) δ 100.7 (s).

Chloro-(dimethylamino)-4-methoxyphenyl phosphine (7c). PCl_3 (12.6 g, 0.092 mol) was slowly added to **6c** (20.7 g, 0.092 mol) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, then warmed to 25 °C for 1 h. Purification of the resulting product by fractional distillation (135-145 °C, 0.60 torr) gave 18.7 g (99%) of **7c** as a viscous clear oil. ^1H NMR ($CDCl_3$) δ 7.60 (dd, J = 6.1, 8.7 Hz, 2H, Ar*H*), 6.96 (dd, J = 1.6, 8.7 Hz, 2H, Ar*H*), 3.83 (s, 3H, OCH_3), 2.65 (d, J = 13.0 Hz, 6H, NCH_3); ^{13}C NMR ($CDCl_3$) δ 141.3, 140.6, 132.5, 132.2, 113.9 (2C), 55.3, 40.0, 39.9.

7a: Fractional distillation (75 °C, 0.050 torr) gave 24.5 g (96%) of **7a**; ^1H NMR ($CDCl_3$) δ 8.34 (dd, J = 3.1, 8.0 Hz, 1H, Ar*H*), 7.72 (m, 1H, Ar*H*), 7.64 (t, J = 7.1 Hz, 1H, Ar*H*), 7.52 (t, J = 7.5 Hz, 1H, Ar*H*), 2.60 (d, J = 12.9 Hz, 6H, NCH_3); ^{13}C NMR ($CDCl_3$) δ 133.3, 133.2, 131.5, 130.1, 126.7 (m, CF_3), 126.1 (d, J = 2.3 Hz), 122.5 (d, J = 2.2 Hz), 40.0, 39.8; ^{31}P NMR ($CDCl_3$) δ 138.0 (d, J = 5.41 Hz).

7b: Fractional distillation (60 °C, 0.005 torr) gave 22.2 g (80%) of **7b**; ^1H NMR ($CDCl_3$) δ 2.80 (d, J = 13.8 Hz, 6H, NCH_3); ^{13}C NMR ($CDCl_3$) δ 149.3, 146.0, 142.1, 140.2, 136.8, 41.3, 41.1; ^{31}P NMR ($CDCl_3$) δ 110.5 (m).

7d: Fractional distillation (95 °C, 0.020 torr) gave 13.6 g (84%) of **7d**; ^1H NMR ($CDCl_3$) δ 7.93 (dd, J = 3.4, 8.6 Hz, 1H, Ar*H*), 6.82 (dd, J = 2.5, 8.6 Hz, 1H, Ar*H*), 6.72 (m, 1H, Ar*H*), 3.80 (s, 3H, OCH_3), 2.59 (d, J = 13.1 Hz, 6H, NCH_3), 2.40 (d, J = 1.5 Hz, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 162.0, 142.7 (d, J = 30.0 Hz), 133.8 (d, J = 5.0 Hz), 127.7 (d, J = 30.0 Hz), 116.8, 111.6, 55.2, 39.7, 39.5, 20.2 (d, J = 20.0 Hz); ^{31}P NMR ($CDCl_3$) δ 143.8 (s).

7e: Fractional distillation (63 °C, 1.00 torr) gave 20.6 g (99%) of **7e**; ^1H NMR ($CDCl_3$) δ 7.5-6.5 (m, 2H, thienyl Ar*H*), 2.32 (d, J = 13.6 Hz, 6H, NCH_3), 2.05 (s, 3H, thienyl CH_3); ^{31}P NMR ($CDCl_3$) δ 132.8 (s).

7f: Fractional distillation (75 °C, 1.00 torr) gave 15.8 g (92%) of **7f**; ^1H NMR ($CDCl_3$) δ 2.66 (d, J = 12.3 Hz, 6H, NCH_3), 2.06-1.58 (m, 6H, Cy*H* envelope), 1.38-1.00 (m, 5H, Cy*H* envelope); ^{13}C NMR ($CDCl_3$) δ 43.2, 42.9, 39.7, 27.2, 27.0, 26.9, 26.6, 26.2, 26.1, 26.1, 26.0, 25.9, 25.8; ^{31}P NMR ($CDCl_3$) δ 160.4 (s).

(2*R*, 4*S*, 5*R*)-2-(4-Methoxyphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-borane (3c). To a solution of (−)-ephedrine (0.086 mol, 14.1 g) in 1,2-DME (125 mL) containing 1,10-phenanthroline (~ 5 mg) at −50 °C was added *exactly* 1 eq. of *n*-BuLi (21.5 mL of a 4.00 M solution in heptane, 0.086 mol). To this solution was added **7c** (18.7 g, 0.0907 mol) in 1,2-DME (25 mL) at −50 °C. The resulting reaction mixture was then stirred vigorously and warmed slowly to 25 °C (~2 h), during which time a precipitate formed. A catalytic amount of chlorotrimethylsilane (500 μL, 5 mol %) was then added[10] and the reaction mixture was refluxed for 10 h. After cooling to 0 °C, $BH_3 \cdot S(CH_3)_2$ (8.5 mL of a 10.1 M solution, 0.086 mol) was added. The reaction mixture was then stirred for an additional 2 h at 25 °C. The resulting mixture was concentrated *in vacuo* to yield a beige viscous residue which was diluted with anhydrous benzene (100 mL) and filtered through florisil. Concentration of the solution followed by trituration with anhydrous methanol gave the title compound as a white solid. Recrystallization from anhydrous methanol afforded 22.2 g (82%) of the pure complex: mp 82 °C; ^{1}H NMR ($CDCl_3$) δ 7.78 (dd, J = 9.2, 9.4 Hz, 2H, Ar*H*), 7.4-7.2 (m, 5H, Ph*H*), 6.95 (dd, J = 1.7, 8.8 Hz, 2H, Ar*H*), 5.55 (dd, J = 2.5, 5.9 Hz, 1H, OC*H*), 3.82 (s, 3H, OCH_3), 3.65 (m, 1H, NC*H*), 2.61 (d, J = 10.9 Hz, 3H, NCH_3), 0.85 (d, J = 6.6 Hz, 3H, CH_3), 1.45-0.40 (broad envelope, BH_3); ^{13}C NMR ($CDCl_3$) δ 136.6, 136.0, 133.4, 133.2, 128.3, 128.2 (2C), 126.7, 126.6 (2C), 114.2, 114.1, 83.7, 59.4, 55.4, 29.4, 13.4; ^{31}P NMR ($CDCl_3$) δ 131.9 (d, J = 93.1 Hz); IR (film) 2974, 2934, 2902, 2839, 2380, 2340, 1596, 1501, 1259, 1114, 966 cm^{-1}. High resolution mass spectrum calcd. for $C_{17}H_{23}BNO_2P$: 315.1559. Found: 315.1530.

3a: Recrystallization from methylcyclohexane or methanol afforded 24.3 g (77%) of **3a**; mp 106.6-108.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.83 (dd, J = 7.5, 11.1 Hz, 1H, Ar*H*), 7.74 (m, 1H, Ar*H*), 7.60 (m, 2H, Ar*H*), 7.33 (m, 5H, Ph*H*), 5.21 (dd, J = 3.4, 6.0 Hz, 1H, OC*H*), 3.66 (m, 1H, NC*H*), 2.97 (d, J = 9.8 Hz, 3H, NCH_3), 0.81 (d, J = 6.6 Hz, 3H, CH_3), 1.75-0.40 (broad envelope, 3H, BH_3); ^{13}C NMR ($CDCl_3$) δ 136.0 (d, J = 5.5 Hz), 132.2, 132.1, 131.5 (d, J = 7.7 Hz), 131.2, 128.3 (2C), 128.2, 127.2, (m, CF_3), 126.2, 125.4, 121.8, 83.3 (d, J = 8.0 Hz), 58.3, 30.8 (d, J = 8.9 Hz), 13.1; ^{31}P NMR ($CDCl_3$) δ 131.3 (d, J = 89.5 Hz); IR (film) 2995, 2937, 2869, 2425, 2383, 1456, 1318, 1135, 973 cm^{-1}. High resolution mass spectrum calcd. for $C_{17}H_{20}BF_3NOP$: 353.1328. Found: 353.1315.

3b: Recrystallization from methylcyclohexane afforded 19.8 g (72%) of **3b**; mp 104.9-106.2 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H, Ph*H*), 5.43 (dd, J = 3.6, 6.4 Hz, 1H, OC*H*), 3.66 (m, 1H, NC*H*), 2.84 (d, J = 11.4 Hz, 3H, NCH_3), 0.80 (d, J = 6.4 Hz, 3H, CH_3), 1.75-0.30 (broad envelope, 3H, BH_3); ^{13}C NMR ($CDCl_3$) δ 148.8, 145.5, 141.8, 140.2, 136.8, 136.3, 136.2, 129.5, 129.3 (2C), 127.9, 127.3 (2C), 85.3 (d, J = 8.9 Hz), 58.6, 29.0 (d, J = 4.6 Hz), 14.1; ^{31}P NMR ($CDCl_3$) δ 121.5 (d, J = 61.8 Hz); IR (film) 2984, 2876, 2412, 2362, 1645, 1470, 1291, 979, 952 cm^{-1}. High resolution mass spectrum calcd. for $C_{16}H_{15}BF_5NOP$ $(M-H)^+$: 374.0904. Found: 374.0905.

3d: Recrystallization from methylcyclohexane or methanol afforded 19.3 g (70%) of **3d**; mp 100.2-101.6 °C; ^{1}H NMR ($CDCl_3$) δ 7.53 (m, 1H, Ar*H*), 7.32 (m, 5H, Ph*H*), 6.76 (m, 2H, Ar*H*), 5.30 (dd, J = 2.0, 5.7 Hz, 1H, OC*H*), 3.80 (s, 3H, OCH_3), 3.69 (m, 1H, NC*H*), 2.88 (d, J = 9.9 Hz, 3H, NCH_3), 2.64 (s, 3H, ArCH_3), 0.82 (d, J = 6.7 Hz, 3H, CH_3), 1.60-0.40 (broad envelope, 3H, BH_3); ^{13}C NMR ($CDCl_3$) δ 163.3, 144.2 (d, J = 14.6 Hz), 137.2 (d, J = 6.3 Hz), 132.8 (d, J = 10.9 Hz), 128.3 (2C), 128.1, 126.3 (2C), 125.6 (d, J = 52.1 Hz), 117.4 (d, J = 9.6 Hz), 110.5 (d, J = 9.7 Hz), 83.0 (d, J = 7.1 Hz), 59.3, 55.2, 30.6 (d, J = 8.7 Hz), 21.8, 13.2; ^{31}P NMR ($CDCl_3$) δ 132.8 (d, J = 90.1 Hz); IR (film) 2975, 2938, 2383, 1597, 1305, 1241, 1080, 962 cm^{-1}. High resolution mass spectrum calcd. for $C_{18}H_{25}BNO_2P$: 329.1716. Found: 329.1715.

3e: Recrystallization from ethanol, methanol or methylcyclohexane afforded 24.9 g (82%) of **3e**; mp 76.3 °C; ^{1}H NMR ($CDCl_3$) δ 8.0-7.3 (m, 7H, Ph*H* and thienyl Ar*H*), 5.58 (dd, J = 2.9, 6.0 Hz, 1H, OC*H*), 3.64 (m, 1H, NC*H*), 2.61 (d, J = 11.4 Hz, 3H, NCH_3), 2.53 (s, 3H, thienyl CH_3), 0.78 (d, J = 6.6 Hz, 3H, CH_3), 1.7-0.2 (broad envelope, 3H, BH_3); ^{13}C NMR ($CDCl_3$) δ 139.5, 139.4, 136.7, 129.0 (2C), 128.9, 128.1, 127.9, 127.3 (2C), 84.3, 59.9, 30.1, 16.1, 14.3; ^{31}P NMR ($CDCl_3$) δ 120.9 (d, J = 88.8 Hz); IR (film) 3066, 3031, 2975, 2959, 2844, 2399, 2373, 2340, 1436, 1213, 1179, 960, 845, 808, 749, 628 cm^{-1}. High resolution mass spectrum calcd. for $C_{15}H_{21}BNOPS$: 305.1175. Found: 305.1154.

3f: Recrystallization from methanol afforded 18.1 g (76%) of **3f**; mp 99.0-100.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5H, Ph*H*), 5.49 (dd, J = 1.0, 5.6 Hz, 1H, OC*H*), 3.67 (m, 1H, NC*H*), 2.70 (d, J = 9.8 Hz, 3H, NCH_3), 2.10-1.60 (m, 6H, Cy*H* envelope), 1.50-1.15 (m, 5H, Cy*H* envelope), 0.73 (d, J = 6.6 Hz, 3H, CH_3), 1.40-0.05 (broad envelope, 3H, BH_3); ^{13}C NMR ($CDCl_3$) δ 137.4, 129.1 (2C), 128.8, 127.0 (2C), 84.7 (d, J = 6.7 Hz), 60.3, 42.3 (d, J = 28.6 Hz), 30.6, 26.5, 26.4, 26.0 (2C), 25.8, 12.9; ^{31}P NMR ($CDCl_3$) δ 151.5 (d, J = 88.3 Hz); IR (film) 2984, 2973, 2926, 2853, 2368, 2341, 1455, 1191, 978, 767 cm^{-1}. High resolution mass spectrum calcd. for $C_{18}H_{24}BNOP$: 291.1924. Found: 291.1915.

(2*R*, 4*S*, 5*R*)-2-Cyclohexyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-oxide (10f). To a stirred solution of (−)-ephedrine (0.328 g, 2 mmol) in 1,2-DME (4 mL) containing 1,10-phenanthroline (~ 5 mg) at −50 °C was added *exactly* 1 eq. of *n*-BuLi (0.4 mL of a 5M solution in heptane, 2 mmol). To this solution was added **7b** (0.387 g, 2 mmol) at −78 °C. The reaction mixture was slowly warmed to 25 °C during which time a precipitate formed. To the warmed reaction mixture was added a catalytic amount of TMSCl (13 μL, 5 mol%)[10] and the reaction mixture was refluxed for 14 h. After cooling to −78 °C , 1.1 eq. of *t*-butyl hydroperoxide (0.33 mL of a 3M solution in toluene, 2.2 mmol) was added. Stirring was continued for 5 min. at −78 °C. The mixture was then allowed to warm to 25 °C and stirred for 16 h. The solvents were removed under reduced pressure

and the resulting crude residue was diluted with H_2O (50 mL) and extracted with $CHCl_3$ (3 x 30 mL). The $CHCl_3$ was then removed under reduced pressure to yield 0.522 g of a yellow crystalline material. Recrystallization from benzene/hexane yielded 0.421 g (72%) of **10f** as white needles: mp 143.2-144.6 °C; ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 5H, Ph*H*), 5.40 (dd, J = 3.8, 6.2 Hz, 1H, OC*H*), 3.62 (m, 1H, NC*H*), 2.70 (d, J = 9.4 Hz, 3H, NCH_3), 2.18-1.60 (m, 6H, Cy*H* envelope), 1.60-1.15 (m, 5H, Cy*H* envelope), 0.80 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 136.7, 128.3 (2C), 128.1, 126.2 (2C), 82.4, 59.2, 38.7, 37.0, 29.1, 27.0, 26.7, 26.6, 26.5, 26.3, 25.9, 14.0; IR (film) 2922, 2855, 1499, 1454, 1244, 1224, 1202, 976 cm^{-1}. High resolution mass spectrum calcd. for $C_{16}H_{24}NO_2P$: 293.1545. Found: 293.1550.

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† This article is dedicated to the memory of Professor Paul G. Gassman.

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2. Fellow of the Patricia Roberts Harris Foundation, 1990-93.
3. Recipient of the Harlan Byker Undergraduate Fellowship.
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