Stereoselective Synthesis of α -Silylamines by the Direct Addition of Silyl Anions to Activated Imines

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Supporting Information

General Information. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF and CH_2Cl_2 were purified by passage through a bed of activated alumina.¹ Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.² Purification of reaction products were carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and staining with ceric ammonium molybdate (CAM). Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^1H -NMR spectra were recorded on a Mercury 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl_3 at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, m = multiplet, b = broad; coupling constant(s) in Hz. Proton-decoupled ^{13}C -NMR spectra were recorded on a Mercury 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl_3 at 77.23 ppm). Proton-decoupled ^{31}P -NMR spectra were recorded on a Mercury 400 (162 MHz) spectrometer and are reported in ppm and were referenced to H_3PO_4 as an external standard. Proton-decoupled ^{19}F -NMR spectra were recorded on a Mercury 400 (376 MHz) spectrometer and are reported in ppm and were referenced to CFCl_3 in CDCl_3 as an external standard. Proton-decoupled ^{29}Si -NMR spectra were recorded on a Varian Inova 500 (99 Mhz) or Varian Inova 400 (80 Mhz) spectrometer and are reported in ppm and were referenced to tetramethylsilane in CDCl_3 as an external standard. Mass spectra data were obtained on a Varian 1200 quadrupole (MALDI), or Micromass Quattro II triple quadrupole HPLC/MS/MS (ESI).

Crystallographic Information. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART.³ The crystal-to-detector distance was 5.023 cm. Data was collected by a scan of 0.3° in ω in groups of 606 frames at settings of 0° , 120° , and 240° . Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Cell refinement and data reduction were carried out with the use of the program SAINT, and face-indexed absorption corrections were performed numerically with the use of the program XPREP. Then the program SADABS was employed to make incident beam and decay correction. The structure was solved by means of the direct methods program SHELXS of the SHELXTL-PC suite of programs.⁴ All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using the full-matrix

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518-1520.

(2) Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford, 1988.

(3) SMART Version 5.054 Data Collection and SAINT-Plus Version 6.45 Data Processing Software for the SMART System; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2003.

(4) Sheldrick, G. M. *SHELXTL PC Version 6.10 An Integrated System for Solving, refining, and Displaying Crystal Structure from Diffraction Data*; Siemens Analytical X-Ray instruments, Inc.: Madison, WI, 1994.

least-squares procedure. The crystallographic data can be obtained free of charge via the internet (www.ccdc.cam.ac.uk/conts/retrieving.html), by mail at Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK, by fax at (+44) 1223-336-033, or e-mail (deposit@ccdc.cam.ac.uk).

General procedure for the synthesis of *N*-diphenylphosphinoyl imines:

All imines were prepared using a modification to the procedure of Jennings and coworkers.⁵ As a sample procedure: To a 50 mL Schlenk flask was added *P,P*-diphenylphosphinic amide (0.90 g, 4.38 mmol), *m*-tolualdehyde (0.52 mL, 4.38 mmol), NEt₃ (2.14 mL, 15.3 mmol), and CH₂Cl₂ (30 mL). The mixture was then cooled to 0 °C. To this mixture was added a solution of TiCl₄ (2.19 mmol) in CH₂Cl₂ (2 mL) dropwise. After the addition was complete, typically 5 minutes, the mixture was stirred for 1 hour at 0 °C, then 1 hour at room temperature. The reaction mixture was then filtered through Celite to remove TiO₂ and washed with CH₂Cl₂. Rotary evaporation of the filtrate gave a solid mixture of imine and triethylamine hydrochloride. The residue was purified by flash column chromatography (70% EtOAc/hexane) to afford pure imine.

The *t*-butanesulfinimines used in this study were prepared using methods developed by Ellman and coworkers.⁶ *N*-(Diethoxyphosphoryl)aldimine was synthesized using the method reported by Barrow and coworkers.⁷

General procedure for protected α -silylamines:

To a 25 mL Schlenk flask was added 1 equivalent of imine (approx. 100 mg), and THF (3 mL), and the mixture was cooled to -78 °C. To this mixture was added 3 equivalents of silyl lithium (approx. 1M in THF). After stirring at -78 °C for 20 minutes, the reaction was quenched with 5% acetic acid in methanol (10 mL) at -78 °C. The mixture was taken up with ethyl acetate (20 mL), washed with water (1 x 10 mL), brine (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The unpurified reaction mixture was separated using flash chromatography (EtOAc/hexanes) to yield pure product.

(5) Jennings, W. B.; Lovely, C.J.; *Tetrahedron*. **1991**, *47*, 5561-5568.

(6) Ellman, J. A.; Cogan, D. A.; Liu, G. *J. Am. Chem. Soc.* **1997**, *119*, 9913-9914.

Selected Characterization Data:

***P,P*-diphenyl-*N*-(1-dimethylphenylsilylphenylmethylene)-phosphinic amide (7):**

Purified with 80% ethyl acetate/hexanes to yield 104.6 mg (88% yield) of colorless crystals. Mp: 128-131 °C; R_f = 0.50 (80/20 ethyl acetate/hexanes); IR (film) 3396, 3326, 3060, 1436, 1192, 1111, 723, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.55 (m, 4H), 7.48-7.28 (m, 9H), 7.26-7.06 (m, 5H), 6.79 (ap d, J = 7.3 Hz, 2H), 3.94 (dd, J = 11.0, 11.0 Hz, 1H), 3.20 (dd, J = 9.2, 9.2 Hz, 1H), 0.439 (s, 3H), 0.217 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 134.8, 132.7 (d, J = 10.1 Hz), 131.9 (d, J = 9.2 Hz), 131.8 (d, J = 2.8 Hz), 131.7 (d, J = 2.8 Hz), 130.0, 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 126.4, 125.6, 47.2 (d, J = 3.7 Hz), -4.5, -5.0; ^{31}P NMR (162 MHz, CDCl_3) δ 25.6; ^{29}Si NMR (99 MHz, CDCl_3) δ -0.64; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{27}\text{H}_{28}\text{NOPSi}$ [M+H] $^{+}$: 442.6. Found 442.5.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-1-naphthylmethylene)-phosphinic amide (9):**

Purified with 80% ethyl acetate/hexanes to yield 87 mg (64% yield) of colorless crystals. Mp: 117-120 °C; R_f = 0.50 (80/20 ethyl acetate/hexanes); IR (film) 3392, 1647, 1561, 1188, 1112 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.77-7.72 (m, 1H), 7.67-7.49 (m, 5H), 7.47-7.25 (m, 11H), 7.24-7.12 (m, 3H), 7.08-7.02 (m, 2H), 4.83 (dd, J = 10.4, 10.4 Hz, 1H), 3.36 (dd, J = 8.5, 9.2 Hz, 1H), 0.475 (s, 3H), 0.039 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.4 (d, J = 2.1 Hz), 139.4, 134.9, 134.7, 133.4 (d, J = 3.1 Hz), 132.5 (d, J = 10.1 Hz), 132.4, 131.9 (d, J = 9.2 Hz), 131.7 (d, J = 2.7 Hz), 131.5 (d, J = 2.7 Hz), 131.1 (d, J = 3.3 Hz), 130.3 (d, J = 2.0 Hz), 130.0, 128.6, 128.4 (d, J = 11.9 Hz), 128.1, 128.0, 126.1, 125.3, 125.3, 124.0, 122.9, 41.8, -3.9, -4.8 (m); ^{31}P NMR (162 MHz, CDCl_3) δ 25.4; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{31}\text{H}_{30}\text{NOPSi}$ [M+H] $^{+}$: 492.6. Found 493.0.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-3-methylphenylmethylene)-phosphinic amide (11):**

Purified with 80% ethyl acetate/hexanes to yield 105 mg (74% yield) of colorless crystals. Mp: 129-130 °C; R_f = 0.50 (80/20 ethyl acetate/hexanes); IR (film) 3451, 3223, 3048, 1429, 1187, 1113, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.52 (m, 4H), 7.48-7.14 (m, 11H), 7.04 (ap t, J = 7.3 Hz, 1H), 6.89 (ap d, J = 7.2 Hz, 1H), 6.63 (ap d, J = 7.2, 1H), 6.51 (s, 1H), 3.90 (dd, J = 11.0, 11 Hz, 1H), 3.19 (dd, J = 9.8, 9.5 Hz, 1H), 2.19 (s, 3H), 0.429 (s, 3H), 0.217 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.3 (d, J = 1.8 Hz), 137.2, 135.0, 134.8, 132.7 (d, J = 9.1 Hz), 131.9, 131.8, 131.7 (d, J = 2.8 Hz), 131.6 (d, J = 2.8 Hz), 129.9, 128.4 (d, J = 12.7 Hz), 128.2, 128.0, 128.0, 127.8, 127.3, 126.3, 123.5, 47.1 (d, J = 3.6 Hz), 21.6, -4.5, -5.0 (d, J = 22.7 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.6; ^{29}Si NMR (99 MHz, CDCl_3) δ -0.90 (d, J = 10.7 Hz); LRMS (MALDI-TOF): Mass calculated for $\text{C}_{28}\text{H}_{30}\text{NOPSi}$ [M+H] $^{+}$: 456.6. Found 457.1.

Crystal data for **11**: $\text{C}_{28}\text{H}_{30}\text{NOPSi}$, M_r = 455.59, crystal dimensions = 0.266 x 0.188 x 0.048 mm, triclinic, space group P1(bar), a = 9.7494(8), b = 12.3191(11), c = 12.4391(11) Å, α = 101.7890(10), β = 111.8390(10), γ = 107.5441(10)°, V = 1234.85(19) Å³, Z = 2, ρ_{calcd} = 1.225 g cm⁻³, $2\theta_{\mu\alpha\xi}$ = 57.264, number of measured reflections = 11425, number of unique reflections = 5762, number of parameters = 293, $R(F)$ = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. $R_w(F^2)$ = $\{\Sigma[(F_o^2 - F_c^2)^2]/\Sigma w F_o^4\}^{1/2}$ for all data, $w^{-1} = \sigma^2(F_o^2) + (0.077 F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$, $R_1(F)$ = 0.0492, $wR(F^2)$ = 0.1308, exposure time = 15s/frame. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. Reference number for the Cambridge data base: CCDC 257700.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-4-methoxyphenylmethylene)-phosphinic amide (14):** Purified with 80% ethyl acetate/hexanes to yield 111 mg (86% yield) of colorless crystals. Mp: 98-100 °C; R_f = 0.52 (80/20 ethyl acetate/hexanes); IR (film) 3215, 3043, 1507, 1435, 1245, 1173, 1104, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.67-7.57 (m, 4H), 7.45-7.19 (m, 11H), 6.71 (s, 4H), 3.87 (dd, J = 11.0, 10.4 Hz, 1H), 3.76 (s, 3H), 3.18 (dd, J = 9.8, 9.2 Hz, 1H), 0.425 (s, 3H), 0.217 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6, 135.0, 134.8, 134.6 (d, J = 1.8 Hz), 132.6 (d, J = 9.2 Hz), 131.9 (d, J = 9.2 Hz), 131.7 (d, J = 2.7 Hz), 131.6 (d, J = 2.7 Hz), 129.9, 128.4 (d, J = 11.9 Hz), 128.1 (d, J = 12.8 Hz), 128.0, 127.4, 113.4, 55.4, 46.4 (d, J = 4.6 Hz), -4.5, -5.1 (d, J = 1.8 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.4; LRMS (MALDI-TOF): Mass ($\text{M}+\text{Na}$) calculated for $\text{C}_{28}\text{H}_{30}\text{NO}_2\text{PSi}$ [$\text{M}+\text{Na}$] $^+$: 494.6. Found 495.3.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-4-fluorophenylmethylene)-phosphinic amide (15):** Purified with 80% ethyl acetate/hexanes to yield 114 mg (77% yield) of colorless crystals. Mp: 153-155 °C; R_f = 0.53 (80/20 ethyl acetate/hexanes); IR (film) 3362, 3208, 1185, 1119, 1110, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.66-7.54 (m, 4H), 7.49-7.18 (m, 11H), 6.88-6.70 (m, 4H), 3.92 (dd, J = 10.7, 10.7 Hz, 1H), 3.19 (dd, J = 9.2, 9.2 Hz, 1H), 0.431 (s, 3H), 0.222 (s, 3H); ^{13}C NMR (100MHz, CDCl_3) δ 162.3, 159.9, 138.3, 134.7, 134.5, 132.6 (d, J = 9.2 Hz), 131.9 (d, J = 9.2 Hz), 131.9, 131.8 (d, J = 1.8 Hz), 130.1, 128.5 (d, J = 11.9 Hz), 128.3, 128.2, 127.8 (d, J = 7.3 Hz), 114.9, 114.7, 46.5 (d, J = 4.6 Hz), -4.6, -5.1; ^{31}P NMR (162 MHz, CDCl_3) δ 25.6; ^{19}F NMR (376 MHz, CDCl_3) δ 15.0; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{27}\text{H}_{27}\text{FNOPSi}$ [$\text{M}+\text{H}$] $^+$: 460.2. Found 460.8.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-2-furylmethylene)-phosphinic amide (18):** Purified with 80% ethyl acetate/hexanes to yield 115 mg (91% yield) of colorless crystals. Mp: 105-106; R_f = 0.53 (80/20 ethyl acetate/hexanes); IR (film) 3366, 3198, 3053, 2957, 2648, 1437, 1250, 1190, 1122, 1111, 839, 726, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.24 (m, 16H), 6.17 (s, 1H), 5.75 (d, J = 2.4 Hz, 1H), 4.02 (dd, J

= 10.4, 10.4 Hz, 1H), 3.12 (dd, J = 9.8, 9.8 Hz, 1H), 0.413 (s, 3H), 0.350 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.5 (d, J = 2.7 Hz), 141.0, 135.2, 132.5, 132.4, 131.9, 131.8, 131.7 (d, J = 2.7 Hz), 129.9, 128.5 (d, J = 11.9 Hz), 128.2 (d, J = 11.9 Hz), 128.0, 110.5, 105.7, 40.4 (d, J = 5.4 Hz), -4.3, -4.9 (d, J = 1.9 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.6; ^{29}Si NMR (99 MHz, CDCl_3) δ -0.123, -0.231; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{25}\text{H}_{26}\text{NO}_2\text{PSi}$ $[\text{M}+\text{H}]^+$: 432.5. Found 432.8.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-4-chlorophenylmethylene)-phosphinic amide (17):** Purified with 80% ethyl acetate/hexanes to yield 102 mg (83% yield) of colorless crystals. Mp: 160-162; R_f = 0.50 (80/20 ethyl acetate/hexanes); IR (film) 3205, 3048, 1479, 1427, 1259, 1184, 1113 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.51 (m, 4H), 7.48-7.30 (m, 9H), 7.28-7.20 (m, 2H), 7.14-7.06 (m, 2H), 6.77-6.67 (m, 2H), 3.91 (dd, J = 10, 11 Hz, 1H), 3.19 (dd, J = 9.0, 9.0 Hz, 1H), 0.434 (s, 3H), 0.220 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2 (d, J = 1.6 Hz), 134.7, 134.4, 133.7, 133.1, 132.6 (d, J = 10.1 Hz), 131.9 (d, J = 9.2 Hz), 131.9 (d, J = 2.7 Hz), 131.9 (d, J = 2.7 Hz), 131.2, 130.2, 128.6, 128.5, 128.3, 128.2, 128.1, 127.7, 46.8 (d, J = 4.6 Hz), -4.6, -5.1; ^{31}P NMR (162 MHz, CDCl_3) δ 25.0; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{27}\text{H}_{27}\text{ClNO}_2\text{PSi}$ $[\text{M}]^+$: 476.0. Found 476.5.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-2-methoxyphenylmethylene)-phosphinic amide (13):** Purified with 80% ethyl acetate/hexanes to yield 144 mg (90% yield) of colorless crystals. Mp: 101-102 $^{\circ}\text{C}$; R_f = 0.47 (80/20 ethyl acetate/hexanes); IR (film) 3378, 3205, 1496, 1434, 1233, 1186, 1110 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.70-7.53 (m, 4H), 7.46-7.16 (m, 11H), 7.12-7.03 (m, 1H), 6.88-6.76 (m, 2H), 6.63 (ap d, J = 7.9 Hz, 1H), 4.27 (m, 1H), 3.43 (m, 4H), 0.405 (s, 3H), 0.214 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 136.2, 134.6, 133.8, 133.0, 132.6 (d, J = 9.2 Hz), 131.9 (d, J = 9.2 Hz), 131.7, 131.6 (d, J = 1.8 Hz), 131.4 (d, J = 2.7 Hz), 131.2, 129.5, 128.3 (d, J = 12.8 Hz), 128.0 (d, J = 12.8 Hz), 127.8, 126.6, 120.4, 109.9, 77.4, 54.7, -4.1, -4.9; ^{31}P NMR (162 MHz, CDCl_3) δ 25.9; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{28}\text{H}_{30}\text{NO}_2\text{PSi}$ $[\text{M}+\text{H}]^+$: 472.6. Found 472.9.

***P,P*-diphenyl-*N*-(1-dimethylphenylsilyl-2-chlorophenylmethylene)-phosphinic amide (16):** Purified with 80% ethyl acetate/hexanes to yield 76 mg (55% yield) of colorless crystals. Mp: 114-116; R_f = 0.57 (80/20 ethyl acetate/hexanes); IR (film) 3366, 3205, 3050, 1436 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.65-6.90 (m, 19H), 4.48 (dd, J = 10.4, 10.4 Hz, 1H), 3.21 (m, 1H), 0.490 (s, 3H), 0.211 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 134.8, 134.4, 132.7, 132.4 (d, J = 9.2 Hz), 131.9 (d, J = 9.2 Hz), 131.8, 131.8, 131.7, 131.5, 131.1, 130.1, 129.0, 128.4 (d, J = 11.9 Hz), 128.3, 128.0 (d, J = 3.0 Hz), 126.7, 126.6, 42.9 (d, J = 3.0 Hz), -4.1, -5.6 (d, J = 2.0 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.3; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{27}\text{H}_{27}\text{ClNO}_2\text{PSi}$ $[\text{M}+\text{H}]^+$: 477.0. Found 477.6.

***P,P*-diphenyl-*N*-(1-(dimethylphenylsilyl)-4-methylphenylmethylene)-phosphinic amide (12):** Purified with 80% ethyl acetate/hexanes to yield 112 mg (75% yield) of colorless crystals. Mp: 147-149 °C; R_f = 0.50 (80/20 ethyl acetate/hexanes); IR (film) 3203, 3049, 1432, 1255, 1182, 1108, 832, 747, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.58 (m, 4H), 7.46-7.27 (m, 9H), 7.26-7.18 (m, 2), 6.96 (ap d, J = 7.3 Hz, 2H), 6.70 (ap d, J = 7.3 Hz, 2H), 3.90 (dd, J = 11.0, 11.0 Hz, 1H), 3.21 (dd, J = 9.2, 9.8 Hz, 1H), 2.28 (s, 3H), 0.431 (s, 3H), 0.216 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4 (d, J = 1.8 Hz), 140.0 (d, J = 9.1 Hz), 139.8, 138.5, 137.9, 137.7 (d, J = 10.0 Hz), 137.3, 137.0 (d, J = 9.1 Hz), 136.7 (d, J = 2.8 Hz), 136.6 (d, J = 2.7 Hz), 134.9, 133.7, 133.4 (d, J = 12.8 Hz), 133.2 (d, J = 12.8 Hz), 133.0, 131.3, 46.9 (d, J = 4.5 Hz), 21.2, 0.582, -0.009 (d, J = 1.8 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.3; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{28}\text{H}_{30}\text{NOPSi}$ $[\text{M}+\text{H}]^+$: 456.6. Found 457.1.

***P,P*-diphenyl-*N*-(1-(dimethylphenylsilyl)-2-naphthylmethylene)-phosphinic amide (10):** Purified with 80% ethyl acetate/hexanes to yield 77 mg (61% yield) of colorless crystals. Mp: 158-161 °C; R_f = 0.50 (80/20 ethyl acetate/hexanes); IR (film) 3418, 3067, 1649, 1631, 1154, 1105 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.79-7.74 (m, 1H), 7.68-7.57 (m, 6H), 7.44-7.26 (m, 11H), 7.22-7.11 (m, 3H), 7.00-6.94 (m, 1H), 4.12 (dd, J = 11.0, 11.0 Hz, 1H), 3.33 (dd, J = 9.2, 9.2 Hz, 1H), 0.475 (s, 3H), 0.227 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.2 (d, J = 1.5 Hz), 134.8, 134.7, 133.4, 133.3, 132.6 (d, J = 9.2 Hz), 132.2, 132.0, 131.9 (d, J = 9.2 Hz), 131.8 (d, J = 1.8 Hz), 131.7 (d, J = 2.7 Hz), 131.4, 130.0, 128.5 (d, J = 11.9 Hz), 128.2, 128.1, 127.6, 127.5, 125.9, 125.4, 125.1, 124.5, 47.4 (d, J = 3.0 Hz), -4.42, -4.94 (d, J = 3.0 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.2; LRMS (MALDI-TOF): Mass ($\text{M}+1$) calculated for $\text{C}_{31}\text{H}_{30}\text{NOPSi}$ $[\text{M}+\text{H}]^+$: 492.6. Found 493.1.

***P,P*-diphenyl-*N*-(1-(dimethylphenylsilyl)-3-phenyl-2-propene)-phosphinic amide (19):** Purified with 80% ethyl acetate/hexanes to yield 93 mg (58% yield) of colorless crystals. Mp: 60-62 °C; R_f = 0.60 (80/20 ethyl acetate/hexanes); IR (film) 3365, 3198, 3055, 2957, 1437, 1250, 1189, 1121, 1111, 963, 908, 814, 727 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.80 (m, 2H), 7.73-7.68 (m, 2H), 7.57-7.55 (m, 2H), 7.48-7.17 (m, 14H), 6.24-6.10 (m, 2H), 3.65 (dt, J = 6.7, 9.8 Hz, 1H), 2.85 (dd, J = 8.9, 8.5 Hz, 1H), 0.48 (s, 3H), 0.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.6, 135.1, 134.5, 133.3 (d, J = 11.9 Hz), 132.5 (d, J = 9.2 Hz), 132.0 (d, J = 9.2 Hz), 131.8, 131.8, 131.8, 130.9 (d, J = 3.7 Hz), 130.0, 128.6, 128.5 (d, J = 3.7 Hz), 128.3, 128.2, 127.6, 126.9, 126.2, 27.7 (d, J = 4.5 Hz), -4.86 (d, J = 2.7 Hz), -4.97 (d, J = 2.7 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.6; ^{29}Si NMR (99 MHz, CDCl_3) δ -0.997 (d, J = 12.2 Hz); LRMS (MALDI-TOF): Mass calculated for $\text{C}_{29}\text{H}_{30}\text{NOPSi}$ $[\text{M}]^+$: 467.6. Found 467.6.

Phenylsulfonyl-*N*-(1-(dimethylphenylsilyl)-phenylmethylene)-phosphinic amide (6): Purified with 20% ethyl acetate/hexanes to yield 106 mg (63% yield) of colorless crystals. Mp: 157-159 °C; R_f = 0.50 (25/75 ethyl acetate/hexanes); IR (film) 3287, 3062, 2994, 1454, 1422, 1318, 1160 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.13 (m, 10H), 7.04-6.95 (m, 3H), 6.72-6.66 (m, 2H), 4.89 (d, J = 7.9 Hz, 1H), 4.16 (d, J = 8.5 Hz, 1H), 0.292 (s, 3H), 0.207 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 138.7, 134.5, 133.8, 132.2, 130.2, 128.6, 128.3, 128.0, 127.3, 126.4, 125.9, 50.0, -4.6, -5.4; ^{29}Si NMR (99 MHz,

CDCl_3) δ -0.961; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{21}\text{H}_{23}\text{NO}_2\text{SSi}$ $[\text{M}+\text{Na}]^+$: 404.6. Found 404.9.

***P,P*-diethoxy-*N*-(1-dimethylphenylsilyl-phenylmethylene)-phosphinic amide (8):**

Purified with 40% ethyl acetate/hexanes to yield 232 mg (53% yield) of colorless crystals. Mp: 72.5-73.5 °C; R_f = 0.70 (50/50 ethyl acetate/hexanes); IR (film) 3209, 2979, 1228, 1053, 1024, 964, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.28 (m, 5H), 7.22-7.02 (m, 3H), 6.97-6.90 (m, 2H), 3.92-3.77 (m, 2H), 3.75-3.66 (m, 2H), 3.42-3.22 (m, 2H), 1.18 (t, J = 7.5 Hz, 3H), 0.779 (t, J = 6.7 Hz, 3H), 0.301 (s, 3H), 0.217 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 134.51, 134.47, 129.8, 127.89, 127.85, 126.3, 125.6, 62.1, 62.02, 61.98, 47.6 (d, J = 5.5 Hz), 16.3 (d, J = 7.3), 15.6 (d, J = 8.2 Hz), -4.7, -5.4 (d, J = 3.7); ^{31}P NMR (162 MHz, CDCl_3) δ 9.29; ^{29}Si NMR (99 MHz, CDCl_3) δ -1.2 (d, J = 14.6 Hz); LRMS (MALDI-TOF): Mass ($\text{M}+\text{Na}+\text{H}$) calculated for $\text{C}_{19}\text{H}_{28}\text{NO}_3\text{PSi}$ $[\text{M}+\text{Na}+\text{H}]^+$: 401.5. Found 401.3.

***P,P*-diphenyl-*N*-(1-trimethylsilyl-4-methoxyphenylmethylene)-phosphinic amide (20):**

Purified with 50% ethyl acetate/hexanes to yield 144 mg (67% yield) of colorless crystals. Mp: 133-134 °C; R_f = 0.43 (50/50 ethyl acetate/hexanes); IR (film) 3209, 2957, 1515, 1431, 1241, 1171, 1039 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.61 (m, 4H), 7.47-7.16 (m, 6H), 6.85-6.68 (m, 4H), 3.75-3.66 (m, 4H), 3.25 (dd, J = 8.5, 8.5 Hz, 1H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.5, 135.2 (d, J = 2.5 Hz), 133.8, 132.8 (d, J = 10.1 Hz), 132.6, 132.0 (d, J = 9.2 Hz), 131.8 (d, J = 1.8 Hz), 131.6 (d, J = 1.8 Hz), 131.3, 128.5 (d, J = 11.9 Hz), 128.1 (d, J = 12.8 Hz), 127.2, 55.4, 46.7 (d, J = 3.6 Hz), -3.4 (d, J = 6.4 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 25.0; ^{29}Si NMR (99 MHz, CDCl_3) δ 5.02 (d, J = 9.2 Hz); LRMS (MALDI-TOF): Mass calculated for $\text{C}_{23}\text{H}_{28}\text{NO}_2\text{PSi}$ $[\text{M}+\text{H}]^+$: 410.5. Found 410.8.

***P,P*-diphenyl-*N*-(1-methyldiphenylsilyl-4-methoxyphenylmethylene)-phosphinic amide (21):**

Purified with 80% ethyl acetate/hexanes to yield 137 mg (80% yield) of colorless crystals. Mp: 165-166 °C; R_f = 0.32 (80/20 ethyl acetate/hexanes); IR (film) 3372, 3220, 3060, 1502, 1447, 1257, 1168, 1109 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.18 (m, 20H), 6.70-6.61 (m, 4H), 4.31 (dd, J = 10.4, 10.4 Hz, 1H), 3.73 (s, 3H), 3.29 (dd, J = 9.5, 9.5 Hz, 1H), 0.465 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.7, 135.7, 135.5, 134.2, 133.8, 133.3, 133.3, 132.9, 132.6 (d, J = 9.2 Hz), 132.1, 131.9 (d, J = 10.1 Hz), 131.7 (d, J = 2.7 Hz), 131.6 (d, J = 2.7 Hz), 130.0 (d, J = 13.7 Hz), 128.4 (d, J = 12.8 Hz), 128.1, 128.1, 128.0, 128.0, 113.4, 55.4, 45.0 (d, J = 4.6 Hz), -5.08; ^{31}P NMR (162 MHz, CDCl_3) δ 25.6; ^{29}Si NMR (99 MHz, CDCl_3) δ -7.23 (d, J = 13.0 Hz); LRMS (MALDI-TOF): Mass ($\text{M}+1$) calculated for $\text{C}_{33}\text{H}_{32}\text{NO}_2\text{PSi}$ $[\text{M}+\text{H}]^+$: 534.7. Found 535.2.

***P,P*-diphenyl-*N*-(1-dimethyl-(4-methyl)2-furylsilyl-4-methoxyphenylmethylene)-phosphinic amide (24):**

Purified with 80% ethyl acetate/hexanes to yield 48 mg (32% yield) of colorless crystals. Mp: 129.5-131 °C; R_f = 0.35 (80/20 ethyl acetate/hexanes); IR (film) 3376, 3198, 1504, 1432, 1275, 1243, 745 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.72-7.63 (m, 4H), 7.45-7.20 (m, 6H), 6.75-6.62 (m, 4H), 6.52 (ap d, J = 3.0 Hz, 1H), 5.99 (s, 1H), 3.87-3.66 (m, 5H), 2.27

(s, 3H), 0.381 (s, 3H), 0.062 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.7 (d, $J = 5.5$ Hz), 154.3, 134.6, 133.7, 133.2, 132.7 (d, $J = 10.1$ Hz), 132.0 (d, $J = 9.2$ Hz), 131.9, 131.8 (d, $J = 2.7$ Hz), 131.7 (d, $J = 1.8$ Hz), 128.5 (d, $J = 12.8$ Hz), 128.2 (d, $J = 11.9$ Hz), 127.6, 124.0, 113.5, 106.4, 55.4, 46.3 (d, $J = 3.7$ Hz), 14.0, -4.10, -5.40; ^{31}P NMR (162 MHz, CDCl_3) δ 25.2; ^{29}Si NMR (99 MHz, CDCl_3) δ -8.58 (d, $J = 11.6$ Hz); LRMS (MALDI-TOF): Mass calculated for $\text{C}_{27}\text{H}_{30}\text{NO}_3\text{PSi}$ [$\text{M}+\text{Na}$]: 498.6. Found 499.0.

***P,P*-diphenyl-*N*-(1-dimethyl--(2,4-dimethyl)-phenylsilyl-4-methoxyphenylmethylene)-phosphinic amide (23):**

Purified with 50% ethyl acetate/hexanes to yield 50 mg (53% yield) of colorless crystals. Mp: 137-139 °C; $R_f = 0.43$ (50/50 ethyl acetate/hexanes); IR (film) 3367, 3215, 3055, 2955, 1605, 1508, 1438, 1246, 1192, 1117, 1065, 1035, 838, 806, 727, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.49 (m, 4H), 7.46-7.16 (m, 7H), 7.04-6.97 (m, 2H), 6.84-6.68 (m, 4H), 9.98 (dd, $J = 10.8$, 10.8 Hz, 1H), 3.76 (s, 3H), 3.19 (dd, $J = 9.6$, 9.6 Hz, 1H), 2.34 (s, 3H), 2.17 (s, 3H), 0.347 (s, 3H), 0.312 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6, 144.5, 140.0, 135.9, 134.7 (d, $J = 1.8$ Hz), 133.2, 133.1, 132.5 (d, $J = 9.2$ Hz), 132.0 (d, $J = 10.1$ Hz), 131.9 (d, $J = 12.8$ Hz), 131.6 (d, $J = 2.7$ Hz), 131.4, 130.0, 128.4 (d, $J = 12.8$ Hz), 128.1 (d, $J = 12.8$ Hz), 127.2, 126.0, 113.5, 55.4, 46.4 (d, $J = 4.6$ Hz), 23.6, 21.5, -2.4, -3.3; ^{31}P NMR (162 MHz, CDCl_3) δ 24.92; ^{29}Si NMR (99 MHz, CDCl_3) δ -0.017 (d, $J = 12.2$ Hz); LRMS (MALDI-TOF): Mass calculated for $\text{C}_{30}\text{H}_{34}\text{NO}_2\text{PSi}$ [M]: 499.7. Found 499.8.

***tert*-Butyl dimethylphenylsilyl(phenylmethylene)carbamate (32):**

Purified with 10% ethyl acetate/hexanes to yield 56 mg (82% yield) of colorless crystals. Mp: 72-73 °C; $R_f = 0.82$ (25/75 ethyl acetate/hexanes); IR (film) 3745, 3276, 2972, 1696, 1489, 1489, 1365, 1250, 1169, 1113, 1003, 834, 735, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (major rotomer) 7.44-7.32 (m, 5H), 7.26-7.20 (m, 2H), 7.17-7.12 (m, 1H), 6.98-6.92 (m, 2H), 4.91 (m, 1H), 4.52 (d, $J = 7.3$ Hz, 1H), 1.40 (s, 9H), 0.343 (s, 3H), 0.271 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 141.7, 135.1, 134.5, 129.9, 128.2, 128.1, 126.0, 125.7, 79.7, 47.1, 28.6, -4.39, -4.70; ^{29}Si NMR (99 MHz, CDCl_3) δ -1.89; LRMS (MALDI-TOF): Mass calculated for $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{Si}$ [$\text{M}+\text{Na}$]: 364.5. Found 364.6.

***R,S*-*N*-(1-dimethylphenylsilylphenylmethylene)-*t*-butanesulfonamide (25):**

Purified with 40% ethyl acetate/hexanes to yield 124 mg (73% yield) of colorless crystals Mp: 91-92 °C; $[\alpha]_D = 53.2$ (c 0.47, CH_2Cl_2); $R_f = 0.57$ (50/50 ethyl acetate/hexanes); IR (film) 3430, 3245, 3063, 2956, 1250, 1114, 1062, 833, 814, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.00 (m, 10H), 4.08 (d, $J = 8.5$ Hz, 1H), 3.49 (d, $J = 8.5$ Hz, 1H), 1.01 (s, 9H), 0.375 (s, 3H), 0.248 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 134.7, 134.4, 129.9, 128.1, 127.9, 126.7, 126.1, 56.6, 52.9, 22.5, -4.25, -5.06; ^{29}Si NMR (99 MHz, CDCl_3) δ -1.66; LRMS (ESI) Mass calculated for $\text{C}_{19}\text{H}_{28}\text{NO}_2\text{SSi}$ [M]: 346.6. Found 346.2; Optical rotation of enantiomer (**ent-25**, (**S,S**)): $[\alpha]_D = -50.0$ (c 0.47, CH_2Cl_2); Crystal data for **ent-25** (**S,S**): $\text{C}_{19}\text{H}_{27}\text{NOSSi}$, $M_r = 345.57$, crystal dimensions = 0.470 x 0.068 x 0.024 mm, orthorhombic, space group $P 2_1 2_1 2_1$, $a = 6.4269(8)$, $b = 16.553(2)$, $c = 18.276(2)$ Å $a = 6.4269(8)$, $b = 16.553(2)$, $c = 18.276(2)$ Å, $\alpha = \beta = \gamma = 90.00^\circ$, $V = 1944(4)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.181$ g cm⁻³, $2\theta_{\mu\alpha\xi} = 57.294$, number of measured reflections = 18115, number of unique reflections = 4722, number of parameters = 217, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. $R_w(F^2) = \{\sum [(F_o^2 - F_c^2)^2] / \sum w F_o^4\}^{1/2}$ for all data, $w^{-1} = \sigma^2(F_o^2) + (0.0600 F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$, $R_1(F) = 0.0620$, $wR(F^2) = 0.1353$, exposure time = 20s/frame. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to

ride on the parent atoms, except the hydrogen on the nitrogen, which was located using difference electron density maps, the position was fixed and then was refined isotropically. Reference number for the Cambridge data base: CCDC 257698.

(*R,S*)-*N*-(1-dimethylphenylsilyl-4-methylphenylmethylene)-*t*-butanesulfinamide (26): Purified with 40% ethyl acetate/hexanes to yield 112 mg (72% yield) of colorless oil. $R_f = 0.60$ (50/50 ethyl acetate/hexanes); IR (film) 3315, 3224, 2955, 1511, 1250, 1114, 1064, 824 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.28 (m, 5H), 7.10–6.84 (m, 4H), 4.03 (d, $J = 8.5$ Hz, 1H), 3.43 (d, $J = 8.5$ Hz, 1H), 2.30 (s, 3H), 1.08 (s, 9H), 0.365 (s, 3H), 0.242 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 135.6, 135.0, 134.5, 129.9, 128.9, 128.0, 126.7, 56.6, 52.7, 22.5, 21.2, –4.10, –5.04; ^{29}Si NMR (99 MHz, CDCl_3) δ –2.02; LRMS (ESI) Mass calculated for $\text{C}_{20}\text{H}_{30}\text{NOSSi}$ $[M]^+$: 360.6. Found 360.2.

(*R,S*)-*N*-(1-dimethylphenylsilyl-4-methoxyphenylmethylene)-*t*-butanesulfinamide (27): Purified with 40% ethyl acetate/hexanes to yield 118 mg (75% yield) of colorless oil. $R_f = 0.57$ (50/50 ethyl acetate/hexanes); IR (film) 3429, 3252, 2955, 1610, 1510, 1248, 1062, 1040, 834, 811 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.28 (m, 5H), 6.98–6.92 (m, 2H), 6.82–6.74 (m, 2H), 4.00 (d, $J = 8.5$ Hz, 1H), 3.76 (s, 3H), 3.39 (d, $J = 8.5$ Hz, 1H), 1.08 (s, 9H), 0.355 (s, 3H), 0.233 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 134.9, 134.5, 133.3, 129.9, 128.0, 127.9, 113.7, 56.6, 55.3, 52.3, 22.5, –4.16, –5.00; ^{29}Si NMR (99 MHz, CDCl_3) δ –2.04; LRMS (ESI) Mass calculated for $\text{C}_{20}\text{H}_{30}\text{NO}_2\text{SSi}$ $[M]^+$: 376.6. Found 376.2.

(*R,S,R*)-*N*-(1-dimethylphenylsilyl-2-naphthylmethylene)-*t*-butanesulfinamide (29): Purified with 40% ethyl acetate/hexanes to yield 143 mg (90% yield) of colorless oil. $R_f = 0.67$ (50/50 ethyl acetate/hexanes); IR (film) 3327, 3227, 3051, 2957, 1250, 1114, 1067, 853, 820, 737 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.70 (m, 3H), 7.54–7.30 (m, 8H), 7.21–7.14 (m, 1H), 4.26 (d, $J = 8.5$ Hz, 1H), 3.60 (d, $J = 8.5$ Hz, 1H), 1.12 (s, 9H), 0.428 (s, 3H), 0.269 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.0, 134.7, 134.6, 133.4, 132.3, 130.1, 128.1, 127.8, 127.7, 126.0, 125.6, 125.3, 125.1, 56.8, 53.1, 22.6, –4.09, –4.94; ^{29}Si NMR (99 MHz, CDCl_3) δ –1.35; LRMS (ESI) Mass calculated for $\text{C}_{23}\text{H}_{30}\text{NOSSi}$ $[\text{M}]^+$: 396.6. Found 396.2.

(*R,S,R*)-*N*-(1-dimethylphenylsilyl-1-naphthylmethylene)-*t*-butanesulfinamide (28): Purified with 20% ethyl acetate/hexanes to yield 76 mg (60% yield) of colorless oil. $R_f = 0.37$ (50/50 ethyl acetate/hexanes); IR (film) 3323, 3245, 3048, 2956, 1252, 1114, 1067, 833, 817, 776 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (major diastereomer) 8.00–7.92 (m, 1H), 7.88–7.82 (m, 1H), 7.73–7.66 (m, 1H), 7.50–7.22 (m, 9H), 5.07 (d, $J = 7.3$ Hz, 1H), 3.70 (d, $J = 8.5$ Hz, 1H), 1.13 (s, 9H), 0.408 (s, 3H), 0.135 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.7, 134.5, 133.7, 130.7, 130.0, 129.0, 128.0, 126.6, 125.5, 125.5, 125.4, 125.4, 124.5, 123.0, 56.8, 53.2, 22.6, –3.57, –4.66; ^{29}Si NMR (99 MHz, CDCl_3) δ –0.445; LRMS (ESI) Mass calculated for $\text{C}_{23}\text{H}_{30}\text{NOSSi}$ $[\text{M}]^+$: 396.6. Found 396.2.

(*R,S,R*)-*N*-(1-dimethylphenylsilyl-2,2-dimethylpropyl)-*t*-butanesulfinamide (31): Purified with 40% ethyl acetate/hexanes to yield 120 mg (72% yield) of colorless crystals. Mp: 76–79 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = 13.4$ (c 0.50, CH_2Cl_2); $R_f = 0.67$ (50/50 ethyl acetate/hexanes); IR (film) 3429, 3376, 3121, 2955, 2867, 1248, 1015, 817 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.46 (m, 2H), 7.36–7.28 (m, 3H), 3.03 (d, $J = 9.2$ Hz, 1H), 2.90 (d, $J = 9.2$ Hz, 1H), 1.01 (s, 9H), 0.966 (s, 9H), 0.399 (s, 3H), 0.385 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 134.2, 129.3, 128.1, 59.2, 56.8, 35.8, 29.6, 23.0, –0.470, –1.28; ^{29}Si NMR (99 MHz, CDCl_3) δ –4.11; LRMS (ESI) Mass calculated for $\text{C}_{17}\text{H}_{32}\text{NOSSi}$ $[\text{M}]^+$: 326.6. Found 326.2. Crystal data for **31**: $\text{C}_{17}\text{H}_{31}\text{NOSSi} \cdot \text{H}_2\text{O}$; $M_r = 343.59$, crystal dimensions = 0.360 x 0.098 x 0.024 mm, orthorhombic, space group $P 2_1 2_1 2_1$, $a = 6.5692(13)$, $b = 15.207(3)$, $c = 20.303(4)$ Å, $\alpha = \beta = \gamma = 90.00^{\circ}$, $V = 2028.2(7)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.125$ g cm^{–3}, $2\theta_{\mu\alpha\text{xi}} = 43.952$, number of measured reflections = 18624, number of unique reflections = 4936, $\mu = 0.225$ mm^{–1}, min/max transmission = 0.93078/0.99184, number of parameters = 201, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. $R_w(F^2) = \{ \sum [(F_o^2 - F_c^2)^2] / \sum w F_o^4 \}^{1/2}$ for all data, $w^{-1} = \sigma^2(F_o^2) + (0.0505 F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$, $R_1(F) = 0.0592$, $wR(F^2) = 0.1279$, exposure time = 35s/frame. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms, except the hydrogen on the nitrogen, which was located using difference electron density maps, the position was fixed and then was refined isotropically. Reference number for the Cambridge data base: CCDC 257699.

(*R,R*)-*N*-(1-dimethylphenylsilyl-3-phenyl-2-propene)-*t*-butanesulfinamide (30):

Purified with 40% ethyl acetate/hexanes to yield 120 mg (72% yield) of colorless crystals. R_f = 0.47 (50/50 ethyl acetate/hexanes); IR (film) 3427, 3213, 3022, 2956, 1250, 1113, 1067, 833, 813, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.58-7.14 (m, 10H), 6.48-6.38 (m, 1H), 6.28-6.18 (m, 1H), 3.72 (t, J = 8.5 Hz, 1H), 3.05 (d, J = 9.2 Hz, 1H), 1.11 (s, 9H), 0.439 (s, 3H), 0.408 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.4, 135.0, 134.3, 130.4, 130.1, 128.7, 128.5, 128.2, 127.1, 126.4, 56.5, 51.9, 22.6, -4.55, -4.65; ^{29}Si NMR (99 MHz, CDCl_3) δ -2.09; LRMS (ESI) Mass calculated for $\text{C}_{21}\text{H}_{30}\text{NOSSi}$ $[\text{M}]^+$: 372.6. Found 372.2.

Experimental for *tert*-Butyl dimethylphenylsilyl(phenylmethylene)carbamate (32) from *P,P*-diphenyl-*N*-(1-dimethylphenylsilylphenylmethylene)-phosphinic amide: To a 25 mL Schlenk flask was added compound **7** (89 mg, 0.201 mmol) and 2 mL of THF. The solution was cooled to 0 °C, and conc. HCl (1.5 mL, 18.1 mmol) was added. After the disappearance of starting material (as measured by TLC), 5 mL of water was added, followed by K_2CO_3 (solid) to basify the solution (pH 9).⁸ The solution was then cooled to 0 °C and Boc_2O (53 mg, 0.24 mmol) was added. The reaction was then allowed to warm to room temperature over night. The mixture was taken up with ethyl acetate (20 mL), washed with water (1 x 10 mL), brine (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The unpurified reaction mixture was purified using flash chromatography (10% EtOAc/ hexanes) to yield pure product in 82% yield over 2 steps.

Experimental for *tert*-Butyl dimethylphenylsilyl(phenylmethylene)carbamate (32) from (*R,R*)-*N*-(1-dimethylphenylsilylphenylmethylene)-*t*-butanesulfinamide: To a 25 mL Schlenk flask was added compound **25** (233 mg, 0.67 mmol) and 3 mL of THF. The solution was cooled to 0 °C, and a 4N solution of HCl in dioxane⁹ (1.5 mL, 6.0 mmol) was added. After the disappearance of starting material (as measured by TLC), 2 mL of water was added, followed by K_2CO_3 (solid) to basify the solution (pH 9).⁶ The solution was then cooled to 0 °C and Boc_2O (175 mg, 0.80 mmol) was added. The reaction was then allowed to warm to room temperature over night. The mixture was taken up with ethyl acetate (20 mL), washed with water (1 x 10 mL), brine (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The unpurified reaction mixture was purified using flash chromatography (10% EtOAc/ hexanes) to yield pure product in 77% yield over 2 steps.

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