

# A Novel Resolution Procedure for the Preparation of P-Stereogenic Phosphine Oxides

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## Supporting Information

**TBS Azide 3:** Alcohol **4** (5.56g, 21.72 mmol) was dissolved in DMF (150 mL) and Et<sub>3</sub>N (15 mL) to which was then added TBSCl (10.84 g, 71.92 mmol). The resulting mixture was stirred for 3 h at r.t. and the solvents were removed *in vacuo* (55°C, 0.05 mmHg). The residue was taken up into ether and filtered through a pad of Celite<sup>®</sup> 545. The filtrate was then concentrated *in vacuo* to afford a thick orange oily residue which was then dissolved in benzene (150 mL). A catalytic quantity (5 drops) of DMF was added followed by SOCl<sub>2</sub> (9.5 mL, 128.8 mmol). The resulting solution was then heated to reflux for 12 h, quenched with saturated brine, and extracted with ether (3 x 200 mL). The combined organic extracts were then dried (MgSO<sub>4</sub>), filtered, and concentrated *in vacuo* to afford the desired product (7.76 g, 82% from **4**). The crude sulfonyl chloride was then dissolved in DMA (80 mL) and H<sub>2</sub>O (40 mL). To the solution was then added NaN<sub>3</sub> (4.54 g, 69.8 mmol) and the resulting mixture was heated to 60°C for 12 h. The cooled mixture was then extracted with Et<sub>2</sub>O (3 x 150 mL), washed with brine, dried (MgSO<sub>4</sub>), and concentrated to furnish a light yellow oil. The product was purified by column chromatography (15:1 hexanes/EtOAc) to afford the desired product. (6.13 g, 70%).  $\alpha_D^{20} = -36.2^\circ$  (c=5.5, CHCl<sub>3</sub>); (KBr) cm<sup>-1</sup> 2954, 2131; <sup>1</sup>H NMR (200 MHz)  $\delta$  4.06 (m, 1H), 3.97 (d, *J* = 14.0, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.10-1.88 (m, 1H), 1.86-1.49 (m, 4H), 1.47-1.06 (m, 3H), 1.05 (s, 3H), 0.90 (s, 9H), 0.89 (s, 3H), 0.11 (s, 3H), 0.08 (s, 3H); <sup>13</sup>C NMR (50 MHz)  $\delta$  75.8, 54.9, 50.4, 49.3, 44.5, 41.9, 28.6, 27.2, 25.8, 20.6, 20.1, 17.8, -4.1, -5.4; mass spectrum, *m/z* (relative intensity, %) 345 (M<sup>+</sup>-N<sub>2</sub>, 1), 288 (44), 115 (66), 73 (100). Exact mass calcd for C<sub>16</sub>H<sub>31</sub>N<sub>3</sub>O<sub>3</sub>SSi - C<sub>4</sub>H<sub>9</sub>: 316.1151. Found: 316.1120.

**Phosphinimine 6a:**  $\alpha_D^{20} = -39.7^\circ$  (c=0.86, CHCl<sub>3</sub>); Mp 175-177 °C; IR (KBr) cm<sup>-1</sup> 2930, 1452, 1110; <sup>1</sup>H NMR (200 MHz)  $\delta$  7.90-7.72 (m, 2H), 7.66-7.45 (m, 3H), 4.19 (m, 1H), 3.70 (dd, *J* = 13.8, 2.0 Hz, 1H), 2.81 (d, *J* = 13.8 Hz, 1H), 2.24-1.91 (m, 3H), 2.04 (d, *J* = 11.2 Hz, 3H), 1.90-1.07 (m, 16H), 1.00 (s, 3H), 0.91 (s, 9H), 0.82 (s, 3H), 0.16 (s, 3H), 0.06 (s, 3H); <sup>13</sup>C NMR (50 MHz)  $\delta$  134.2 (d, *J* = 3 Hz) 131.1 (d, *J* = 9 Hz), 128.7 (d, *J* = 12 Hz), 127.7 (d, *J* = 86 Hz), 76.3, 53.8 (d, *J* = 5 Hz), 50.4, 48.5, 44.6, 42.2, 38.7 (d, *J* = 71 Hz), 28.1, 27.4, 26.2, 26.0, 25.6, 25.1 (d, *J* = 3 Hz), 25.0 (d, *J* = 3 Hz), 20.9, 20.3, 17.9, 10.3 (d, *J* = 58 Hz), -4.4, -4.9; <sup>31</sup>P NMR (81 MHz)  $\delta$  23.3. mass spectrum, *m/z* (relative intensity, %) 551 (M<sup>+</sup>, 0.2), 536 (1), 494 (53), 268 (64), 73 (100). Exact mass calcd for C<sub>29</sub>H<sub>50</sub>NO<sub>3</sub>PSSi - C<sub>4</sub>H<sub>9</sub> : 494.2314. Found: 494.2339.

**Phosphinimine 7a:**  $\alpha_D^{20} = -10.0^\circ$  (c=1.06, CHCl<sub>3</sub>); Mp 147-149 °C; IR (KBr) cm<sup>-1</sup> 2930, 1452, 1110; <sup>1</sup>H NMR (200 MHz)  $\delta$  7.82-7.70 (m, 2H), 7.64-7.41 (m, 3H), 4.10 (m, 1H), 3.67 (dd, *J* = 13.8, 2.4 Hz, 1H), 2.81 (d, *J* = 13.8 Hz, 1H), 2.26-1.98 (m, 3H), 2.03 (d, *J* = 13 Hz, 3H), 1.98-1.02 (m, 16H), 0.99 (s, 3H), 0.87 (s, 9H), 0.85 (s, 3H), 0.14 (s, 3H), 0.06 (s, 3H); <sup>13</sup>C NMR (50 MHz)  $\delta$  132.3 (d, *J* = 3 Hz) 131.1 (d, *J* = 10 Hz), 128.7 (d, *J* = 12 Hz), 127.7 (d, *J* = 86 Hz), 76.4, 53.9 (d, *J* = 5 Hz), 50.4, 48.5, 44.6, 42.2, 38.7 (d, *J* = 72 Hz), 28.3, 27.4, 26.2, 26.0, 25.6, 25.2 (d, *J* = 3 Hz), 25.0 (d, *J* = 3 Hz), 20.9, 20.3, 17.9, 10.3 (d, *J* = 59 Hz), -4.4, -4.9; <sup>31</sup>P NMR (81 MHz)  $\delta$  23.2. mass spectrum, *m/z* (relative intensity, %) 551 (M<sup>+</sup>, 0.2), 536 (1), 494 (53), 268 (64), 73 (100). Exact mass calcd for C<sub>29</sub>H<sub>50</sub>NO<sub>3</sub>PSSi - C<sub>4</sub>H<sub>9</sub> : 494.2314. Found: 494.2365.

**Phosphinimine 6b:**  $\alpha_D^{20} = -13.5^\circ$  ( $c=2.46$ ,  $\text{CHCl}_3$ ); Mp 151-153 °C; IR (KBr)  $\text{cm}^{-1}$  2932, 1439, 1111;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.85-7.78 (m, 2H), 7.60-7.47 (m, 3H), 4.14-4.09 (m, 1H), 3.69 (d,  $J = 13.8$ , 1H), 2.85 (d,  $J = 13.8$  Hz, 1H), 2.52-2.44 (m, 1H), 2.21-2.06 (m, 1H), 2.04 (d,  $J = 12.7$  Hz, 3H), 2.01-1.45 (m, 15H), 1.00 (s, 3H), 0.88 (s, 9H), 0.85 (s, 3H), 0.14 (s, 3H), 0.06 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  132.7, 131.5 (d,  $J = 9$  Hz), 129.5 (d,  $J = 100$  Hz), 129.2 (d,  $J = 12$  Hz), 76.8, 54.3, 50.9, 49.0, 45.0, 42.6, 39.1 (d,  $J = 75$  Hz), 28.6, 27.8, 27.1 (d,  $J = 11$  Hz), 26.8 (d,  $J = 21$  Hz), 26.8, 26.4, 21.4, 20.7, 18.3, 12.5 (d,  $J = 60$  Hz), -4.0, -4.5;  $^{31}\text{P}$  NMR (81 MHz)  $\delta$  23.0. mass spectrum,  $m/z$  (relative intensity, %) 551 ( $\text{M}^+$ , 0.2), 536 (1), 494 (53), 268 (64), 73 (100). Exact mass calcd for  $\text{C}_{28}\text{H}_{48}\text{NO}_3\text{PSSi} - \text{CH}_3$  : 522.2627. Found: 522.2633.

**Phosphinimine 7b:**  $\alpha_D^{20} = -52.8^\circ$  ( $c=2.47$ ,  $\text{CHCl}_3$ ); Mp 152-154 °C; IR (KBr)  $\text{cm}^{-1}$  2956, 1462, 1111;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.83-7.77 (m, 2H), 7.62-7.44 (m, 3H), 4.13-4.07 (m, 1H), 3.69 (d,  $J = 13.8$ , 1H), 2.80 (d,  $J = 13.8$  Hz, 1H), 2.55-2.42 (m, 1H), 2.18-2.08 (m, 1H), 2.05 (d,  $J = 13.3$  Hz, 3H), 1.98-1.43 (m, 14H), 1.00 (s, 3H), 0.90 (s, 9H), 0.83 (s, 3H), 0.15 (s, 3H), 0.06 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  132.7 (d,  $J = 3$  Hz), 131.4 (d,  $J = 10$  Hz), 129.2 (d,  $J = 12$  Hz), 129.5 (d,  $J = 100$  Hz), 76.8, 54.3 (d,  $J = 6$  Hz), 50.8, 49.0, 45.0, 42.6, 39.2 (d,  $J = 74$  Hz), 28.6, 27.8, 27.1, 27.0, 26.8 (d,  $J = 10$  Hz), 26.7 (d,  $J = 10$  Hz), 26.4, 21.3, 20.7, 18.3, 12.4 (d,  $J = 60$  Hz), -4.0, -4.5;  $^{31}\text{P}$  NMR (81 MHz)  $\delta$  24.4. mass spectrum,  $m/z$  (relative intensity, %) 537 ( $\text{M}^+$ , 0.3), 522 (4), 480 (99), 328 (41), 254 (100). Exact mass calcd for  $\text{C}_{28}\text{H}_{48}\text{NO}_3\text{PSSi} - \text{CH}_3$  : 522.2627. Found: 522.2620.

**Phosphinimine 6c:**  $\alpha_D^{20} = -10.2^\circ$  ( $c=0.84$ ,  $\text{CHCl}_3$ ); Mp 149-150 °C; IR (KBr)  $\text{cm}^{-1}$  2928, 1439, 1113;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.85-7.64 (m, 2H), 7.61-7.41 (m, 3H), 4.08 (m, 1H), 3.66 (d,  $J = 18.0$ , 1H), 2.79 (d,  $J = 18.0$  Hz, 1H), 2.37 (m, 2H), 2.01 (d,  $J = 17.0$  Hz, 3H), 1.80-1.33 (m, 5H), 1.28-1.00 (m, 6H), 0.97 (s, 3H), 0.85 (s, 9H), 0.82 (s, 3H), 0.10 (s, 3H), 0.03 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  132.2 (d,  $J = 3$  Hz), 131.0 (d,  $J = 9$  Hz), 128.6 (d,  $J = 12$  Hz), 127.7 (d,  $J = 104$  Hz), 76.2, 53.7 (d,  $J = 5$  Hz), 50.3, 48.4, 44.5, 42.1, 29.5, 28.1, 27.2, 25.9, 20.8, 20.1, 17.8, 15.2 (m,  $2\times\text{CH}_3$ ), 10.9, 9.7, -4.9, -5.0;  $^{31}\text{P}$  NMR (81 MHz)  $\delta$  26.1. mass spectrum,  $m/z$  (relative intensity, %) 496 ( $\text{M}^+ - \text{CH}_3$ , 3), 454 (89), 302 (32), 228 (100). Exact mass calcd for  $\text{C}_{26}\text{H}_{46}\text{NO}_3\text{PSSi} - \text{CH}_3$  : 496.2471. Found: 496.2443.

**Phosphinimine 6d:**  $\alpha_D^{20} = +18.2^\circ$  ( $c=1.80$ ,  $\text{CHCl}_3$ ); IR (KBr)  $\text{cm}^{-1}$  2927, 1439, 1141;  $^1\text{H}$  NMR (200 MHz)  $\delta$  8.29-7.99 (m, 3H), 7.90 (d,  $J = 8.2$  Hz, 1H), 7.80 (d,  $J = 8.2$  Hz, 1H), 7.77 (d,  $J = 6.7$  Hz, 1H), 7.67-7.31 (m, 6H), 4.09 (m, 1H), 3.45 (d,  $J = 13.9$  Hz, 1H), 2.49 (d,  $J = 13.3$  Hz, 3H), 2.40 (d,  $J = 13.9$  Hz, 1H), 2.17-1.92 (m, 1H), 1.76-1.41 (m, 6H), 0.84 (s, 9H), 0.81 (s, 3H), 0.48 (s, 3H), 0.10 (s, 3H), 0.02 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  134.3 (d,  $J = 3$  Hz), 133.9 (d,  $J = 9$  Hz), 133.6 (d,  $J = 10$  Hz), 132.4 (d,  $J = 3$  Hz), 132.1 (d,  $J = 9$  Hz), 131.0 (d,  $J = 11$  Hz), 129.3, 129.0 (d,  $J = 13$  Hz), 128.2 (d,  $J = 72$  Hz), 127.4, 126.5, 126.0 (d,  $J = 7$  Hz), 124.7 (d,  $J = 15$  Hz), 124.2 (d,  $J = 103$  Hz), 76.1, 53.7 (d,  $J = 3$  Hz), 50.3, 48.4, 44.5, 42.1, 28.3, 27.3, 26.0, 20.6, 20.1, 17.9, 16.5 (d,  $J = 66$  Hz), -4.5, -4.9;  $^{31}\text{P}$  NMR (81 MHz)  $\delta$  12.6. mass spectrum,  $m/z$  (relative intensity, %) 595 ( $\text{M}^+$ , 0.2), 580 (1), 538 (33), 312 (100). Exact mass calcd for  $\text{C}_{33}\text{H}_{46}\text{SO}_3\text{SiPN} - \text{CH}_3$  : 580.2471. Found: 580.2462. Anal. Calcd for  $\text{C}_{33}\text{H}_{46}\text{SO}_3\text{SiPN}$ : C, 66.52; H, 7.78. Found C, 66.20; H, 7.70.

**Phosphinimine 7d:**  $\alpha_D^{20} = -101.4^\circ$  ( $c=1.36$ ,  $\text{CHCl}_3$ ); Mp 183-184 °C; IR (KBr)  $\text{cm}^{-1}$  2955, 1440, 1122;  $^1\text{H}$  NMR (200 MHz)  $\delta$  8.28-8.02 (m, 3H), 7.97-7.68 (m, 3H), 7.66-7.30 (m, 6H), 4.10-3.95 (m, 1H), 3.39 (d,  $J = 14.0$  Hz, 1H), 2.46 (d,  $J = 13.3$  Hz, 3H), 1.97 (d,  $J = 14.0$  Hz, 1H), 1.90-1.16 (m, 7H), 0.91 (s, 9H), 0.60 (s, 3H), 0.30 (s, 3H), 0.19 (s, 3H), 0.03 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  134.3 (d,  $J = 3$  Hz), 133.9 (d,  $J = 9$  Hz), 133.5 (d,  $J = 10$  Hz), 132.4 (d,  $J = 3$  Hz), 132.2 (d,  $J = 9$  Hz), 131.0 (d,  $J = 11$  Hz), 129.2, 129.0 (d,  $J = 13$  Hz), 127.6 (d,  $J = 102$  Hz), 127.5, 126.6, 126.2 (d,  $J = 7$  Hz), 124.8 (d,  $J = 15$  Hz), 124.1 (d,  $J = 97$  Hz), 76.0, 53.3, 50.2, 48.2, 44.3, 42.0, 28.0, 27.2, 26.1, 20.4, 19.8, 17.9, 16.6 (d,  $J$

= 66 Hz), -4.4, -5.0;  $^{31}\text{P}$  NMR (81 MHz)  $\delta$  12.9. mass spectrum,  $m/z$  (relative intensity, %) 595 ( $\text{M}^+$ , 0.3), 580 (2), 538 (39), 264 (100). Exact mass calcd for  $\text{C}_{33}\text{H}_{46}\text{S O}_3\text{SiPN} - \text{CH}_3$ : 580.2471. Found: 580.2485. Anal. Calcd for  $\text{C}_{33}\text{H}_{46}\text{SO}_3\text{SiPN}$ : C, 66.52; H, 7.78. Found C, 66.28; H, 7.52.

**Phosphinimine 6e:**  $\alpha_{\text{D}}^{20} = +6.6^\circ$  ( $c=5.45$ ,  $\text{CHCl}_3$ ); Mp 183-184  $^\circ\text{C}$ ; IR (KBr)  $\text{cm}^{-1}$  2953, 1439, 1114;  $^1\text{H}$  NMR (400 MHz)  $\delta$  8.72-8.68 (m, 2H), 8.58 (d,  $J = 17.0$  Hz, 1H), 8.08 (d,  $J = 7.5$  Hz, 1H), 8.01 (d,  $J = 7.0$  Hz, 1H), 7.89-7.28 (m, 9H), 4.12 (m, 1H), 3.48 (d,  $J = 13.8$  Hz, 1H), 2.58 (d,  $J = 13.3$  Hz, 3H), 2.45 (d,  $J = 13.8$  Hz, 1H), 2.08 (m, 1H), 1.82-1.30 (m, 5H), 0.98 (m, 1H), 0.84 (s, 9H), 0.82 (s, 3H), 0.52 (s, 3H), 0.13 (s, 3H), 0.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  137.7 (d,  $J = 9$  Hz), 133.0 (d,  $J = 3$  Hz), 132.8 (d,  $J = 2$  Hz), 132.4 (d,  $J = 9$  Hz), 132.0 (d,  $J = 94$  Hz), 131.8 (d,  $J = 59$  Hz), 131.5 (d,  $J = 11$  Hz), 130.7, 130.2, 129.0 (d,  $J = 25$  Hz), 129.6 (d,  $J = 13$  Hz), 127.9, 127.6, 127.4 (d,  $J = 10$  Hz), 129.1, 124.0, 123.1, 123.2 (d,  $J = 103$  Hz), 76.6, 54.3 (d,  $J = 3$  Hz), 50.8, 48.8, 45.0, 42.6, 28.8, 27.8, 26.4, 21.1, 20.5, 18.3, 16.9 (d,  $J = 65$  Hz), -4.0, -4.4;  $^{31}\text{P}$  NMR (162 MHz)  $\delta$  15.2. mass spectrum,  $m/z$  (relative intensity, %) 630 ( $\text{M}^+ - \text{CH}_3$ , 0.2), 588 (4), 362 (91), 314 (100). Exact mass calcd for  $\text{C}_{37}\text{H}_{48}\text{SO}_3\text{SiPN} - \text{C}_4\text{H}_9$ : 588.2158. Found: 588.2211.

**Phosphinimine 7e:**  $\alpha_{\text{D}}^{20} = -76.0^\circ$  ( $c=1.14$ ,  $\text{CHCl}_3$ ); Mp 224-225  $^\circ\text{C}$ ; IR (KBr)  $\text{cm}^{-1}$  2926, 1441, 1111;  $^1\text{H}$  NMR (200 MHz)  $\delta$  8.72 (t,  $J = 6.9$  Hz, 2H), 8.56 (d,  $J = 17.1$  Hz, 1H), 8.13 (d,  $J = 8.2$  Hz, 1H), 8.04 (d,  $J = 7.9$  Hz, 1H), 7.94-7.36 (m, 9H), 4.10 (m, 1H), 3.48 (d,  $J = 14.0$  Hz, 1H), 2.57 (d,  $J = 13.3$  Hz, 3H), 2.13 (d,  $J = 14.0$  Hz, 1H), 1.99-1.16 (m, 7H), 0.94 (s, 9H), 0.67 (s, 3H), 0.28 (s, 3H), 0.22 (s, 3H), 0.06 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  137.0 (d,  $J = 9$  Hz), 132.5 (d,  $J = 3$  Hz), 132.4, 131.0 (d,  $J = 11$  Hz), 130.9 (d,  $J = 11$  Hz), 130.4, 129.7, 129.6 (d,  $J = 22$  Hz), 129.0 (d,  $J = 13$  Hz), 129.1 (d,  $J = 50$  Hz), 127.5, 127.4, 127.3, 127.1, 123.4, 122.8 (d,  $J = 98$  Hz), 121.8, 76.1, 54.5, 50.2, 48.2, 44.4, 42.0, 28.0, 27.2, 26.1, 20.4, 19.9, 18.0, 16.7 (d,  $J = 67$  Hz), -4.4, -5.0;  $^{31}\text{P}$  NMR (81 MHz)  $\delta$  13.2. mass spectrum,  $m/z$  (relative intensity, %) 630 ( $\text{M}^+ - \text{CH}_3$ , 0.2), 588 (4), 362 (83), 314 (100). Exact mass calcd for  $\text{C}_{37}\text{H}_{48}\text{SO}_3\text{SiPN} - \text{C}_4\text{H}_9$ : 588.2158. Found: 588.2131.

**Phosphinimine 6f:**  $\alpha_{\text{D}}^{20} = -13.7^\circ$  ( $c=0.83$ ,  $\text{CHCl}_3$ ); IR (KBr)  $\text{cm}^{-1}$  2954, 1438, 1116;  $^1\text{H}$  NMR (400 MHz)  $\delta$  8.31 (d,  $J = 8.5$  Hz, 1H), 8.10 (d,  $J = 8.1$  Hz, 1H), 8.03-7.84 (m, 5H), 7.76-7.63 (m, 3H), 7.63-7.31 (m, 11H), 4.13 (m, 1H), 3.60 (d,  $J = 13.8$  Hz, 1H), 2.40 (d,  $J = 13.8$  Hz, 1H), 2.11-1.93 (m, 1H), 1.77-1.42 (m, 5H), 1.06-0.92 (m, 1H), 0.91 (s, 9H), 0.87 (s, 3H), 0.49 (s, 3H), 0.20 (s, 3H), 0.08 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  145.6 (d,  $J = 3$  Hz), 140.0, 136.7 (d,  $J = 12$  Hz), 134.8 (d,  $J = 3$  Hz), 134.5 (d,  $J = 9$  Hz), 134.1 (d,  $J = 11$  Hz), 133.5 (d,  $J = 9$  Hz), 133.3 (d,  $J = 11$  Hz), 132.9 (d,  $J = 3$  Hz), 129.7, 129.44 (d,  $J = 109$  Hz), 129.4, 129.3, 128.7, 127.94, 127.88 (d,  $J = 6$  Hz), 127.8 (d,  $J = 3$  Hz), 127.7, 127.6 (d,  $J = 106$  Hz), 127.0, 125.1 (d,  $J = 15$  Hz), 124.5 (d,  $J = 98$  Hz), 76.7, 54.0 (d,  $J = 4$  Hz), 50.8, 48.8, 45.0, 42.6, 28.6, 27.7, 26.5, 21.0, 20.5, 18.4, -4.0, -4.5;  $^{31}\text{P}$  NMR (162 MHz)  $\delta$  13.7. mass spectrum,  $m/z$  (relative intensity, %) 602 ( $\text{M}^+ - \text{OTBS}$ , 2), 525 (20), 450 (100). Exact mass calcd for  $\text{C}_{44}\text{H}_{52}\text{NO}_3\text{PSSi} - \text{C}_4\text{H}_9$ : 676.2471. Found: 676.2468.

**Phosphinimine 7f:**  $\alpha_{\text{D}}^{20} = -36.3^\circ$  ( $c=1.44$ ,  $\text{CHCl}_3$ ); IR (KBr)  $\text{cm}^{-1}$  2953, 1439, 1116;  $^1\text{H}$  NMR (400 MHz)  $\delta$  8.32 (d,  $J = 8.5$  Hz, 1H), 8.10 (d,  $J = 8.1$  Hz, 1H), 8.02-7.84 (m, 5H), 7.76-7.64 (m, 3H), 7.63-7.56 (m, 3H), 7.56-7.34 (m, 8H), 4.12 (m, 1H), 3.59 (d,  $J = 13.8$  Hz, 1H), 2.41 (d,  $J = 13.8$  Hz, 1H), 2.00-1.94 (m, 1H), 1.73-1.42 (m, 5H), 1.08-0.95 (m, 1H), 0.90 (s, 9H), 0.82 (s, 3H), 0.49 (s, 3H), 0.19 (s, 3H), 0.07 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  145.6 (d,  $J = 3$  Hz), 140.0, 136.7 (d,  $J = 12$  Hz), 134.7 (d,  $J = 3$  Hz), 134.5 (d,  $J = 9$  Hz), 133.8 (d,  $J = 11$  Hz), 133.6 (d,  $J = 11$  Hz), 133.5 (d,  $J = 9$  Hz), 132.9 (d,  $J = 3$  Hz), 129.8, 129.4, 129.3 (d,  $J = 121$  Hz), 129.2 (d,  $J = 13$  Hz), 128.7, 128.0, 127.9 (d,  $J = 7$  Hz), 127.82 (d,  $J = 109$  Hz), 127.77 (d,  $J = 8$  Hz), 127.7, 127.0, 125.1 (d,  $J = 15$  Hz), 124.5 (d,  $J = 98$  Hz), 76.7, 54.0 (d,  $J = 4$  Hz), 50.8, 48.8, 45.0, 42.6, 28.6, 27.7, 26.5, 21.0, 20.5, 18.3, -4.1, -4.5;  $^{31}\text{P}$  NMR

(162 MHz)  $\delta$  13.7. mass spectrum,  $m/z$  (relative intensity, %) 602 ( $M^+$ -OTBS, 1), 580 (1), 524 (27), 450 (75), 402 (81), 41 (100). Exact mass calcd for  $C_{44}H_{52}NO_3PSSi - C_4H_9$ : 676.2471. Found: 676.2495.

**Phosphine Oxide 8b:**  $\alpha_D^{20} = +33.3^\circ$  ( $c=1.62$ , MeOH); IR (KBr)  $cm^{-1}$  2960, 1438, 1167, 752;  $^1H$  NMR (400 MHz)  $\delta$  7.72-7.63 (m, 2H), 7.51-7.41 (m, 3H), 2.27-2.11 (m, 1H), 1.96-1.74 (m, 2H), 1.75-1.44 (m, 6H), 1.66 (d,  $J = 12.4$  Hz, 3H);  $^{13}C$  NMR (100 MHz)  $\delta$  134.2 (d,  $J = 94$  Hz), 131.8 (d,  $J = 3$  Hz), 130.7 (d,  $J = 9$  Hz), 128.9 (d,  $J = 11$  Hz), 40.0 (d,  $J = 74$  Hz), 27.1 (d,  $J = 9$  Hz), 26.8 (d,  $J = 9$  Hz), 26.73 (d,  $J = 1$  Hz), 26.70 (d,  $J = 1$  Hz), 15.2 (d,  $J = 69$  Hz);  $^{31}P$  NMR (162 MHz)  $\delta$  40.1. mass spectrum,  $m/z$  (relative intensity, %) 208 ( $M^+$ , 11), 167 (100), 140 (78), 125 (43). Exact mass calcd for  $C_{12}H_{17}OP$ : 208.1017. Found: 208.1029.