Supporting Information

Alkylation of Phosphine Boranes by Phase-Transfer Catalysis.

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General: Unless otherwise noted, all non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware. *t*-Butylphenylphosphine borane and diphenylphosphine borane were prepared from phenyldichlorophosphine and diphenylchlorophosphine respectively, according to the literature.[1] Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate or aqueous potassium permanganate. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer equiped with a Golden Gate Diamond ATR and are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. ^{1}H NMR spectra were recorded in deuteriochloroforme, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). Chemical shifts are reported in ppm on the d scale from an internal standard of residual chloroform (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in deuteriochloroforme, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of deuteriochloroform (77.0 ppm) on the d scale. ^{31}P NMR spectra were recorded in deuteriochloroforme, unless otherwise noted, on a Bruker ARX-400 spectrometer (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the peak of phosphoric acid (0 ppm) on the d scale. Mass spectra were obtained on a KRATOS MS-50 TC TA (FAB) or a Micromass Autospec-TOF (MAB) high resolution magnetic sector mass spectrometer by the Centre régional de spectrométrie de masse de l'Université de Montréal. The elementary analysis were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal. Analytical high performance liquid chromatography (HPLC) was carried out on a Hewlett Packard 1100 series system equipped with a quaternary pump and a diode-array detector. Data are reported as follows: column type, flow, solvent system and retention time (t_r).

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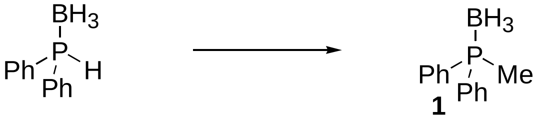
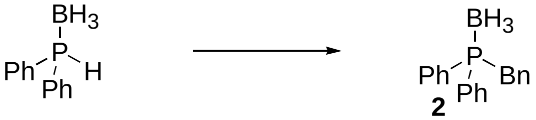
(1) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244-5252.

Standard Procedure A:



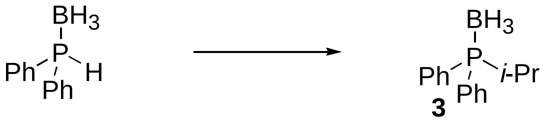
1

Diphenylmethylphosphine borane (1). To a mixture of diphenylphosphine borane (400 mg, 2.00 mmol) and tetrabutylammonium bromide (65 mg, 0.20 mmol) in 30% KOH_{aq} (10 mL) and toluene (10 mL) was added iodomethane (125 µL, 2.00 mmol) at room temperature. The mixture was stirred vigorously at room temperature for 3 h. The solution was diluted with ether, washed with water, brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (2% EtOAc/hexanes) providing the desired phosphine **1** as a colorless oil (375 mg, 88%): ^{1}H!NMR (300 MHz, $CDCl_3$) d 7.67-7.60 (m, 4H), 7.48-7.38 (m, 6H), 1.84 (d, *J* = 10 Hz, 3H), 0.95 (q (br), *J* = 120 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 132.2 (d, *J* = 10 Hz), 131.6 (d, *J* = 2 Hz), 130.9 (d, *J* = 56 Hz), 129.3 (d, *J* = 10 Hz), 12.3 (d, *J* = 40 Hz); ^{31}P NMR (101 MHz, $CDCl_3$) d 11.3 (q, *J* = 56 Hz); IR (neat) 2378, 1436, 1108, 1060, 1022, 889, 733, 689, 594 cm^{-1}; HMRS (MAB) calcd for $C_{13}H_{15}BP$ $[M-H^+]^+$: 213.1004. Found: 213.1001.



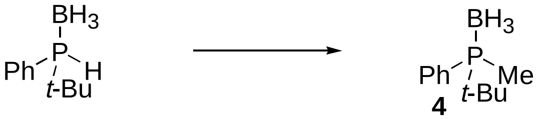
2

Diphenylbenzylphosphine borane (2). The title compound was prepared from diphenylphosphine borane (100 mg, 0.50 mmol) according to the standard procedure A described above. After 3 h, the desired phosphine **2** (123 mg, 85%) was obtained as a white solid after flash chromatography (2% EtOAc/hexanes): mp 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.65-7.60 (m, 4H), 7.52-7.41 (m, 6H), 7.20-7.13 (m, 3H), 6.96-6.94 (m, 2H), 3.61 (d, *J* = 12 Hz, 2H), 0.87 (q (br), *J* = 109 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 133.1 (d, *J* = 9 Hz), 132.2 (d, *J* = 5 Hz), 131.7 (d, *J* = 3 Hz), 130.7 (d, *J* = 5 Hz), 129.1 (d, *J* = 54 Hz), 129.1 (d, *J* = 10 Hz), 128.5 (d, *J* = 3 Hz), 127.4 (d, *J* = 3 Hz), 34.5 (d, *J* = 32 Hz); ^{31}P NMR (101 MHz, $CDCl_3$) d 19.3 (d, *J* = 65 Hz); IR (neat) 2373, 1434, 1105, 1056, 1028, 790, 733, 691, 592 cm^{-1}; Anal. Calcd for $C_{19}H_{20}BP$: C, 78.65; H, 6.95; Found: C, 78.40; H, 7.16.



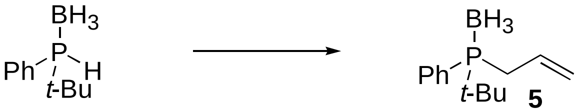
3

Diphenyl-*i*-propylphosphine borane (3). The title compound was prepared from diphenylphosphine borane (400 mg, 2.00 mmol) according to the standard procedure A described above. After 24 h, the desired phosphine **3** (395 mg, 82%) was obtained as a white solid after flash chromatography (2% EtOAc/hexanes): mp 77-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.78-7.73 (m, 4H), 7.51-7.42 (m, 6H), 2.72 (septet, *J* = 7 Hz, 1H) 1.17 (dd *J* = 9, 7 Hz, 6H), 0.95 (q (br), *J* = 120 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 133.0 (d, *J* = 8 Hz), 131.5 (s), 129.2 (d, *J* = 54 Hz), 129.1 (d, *J* = 10 Hz), 24.1 (d, *J* = 37 Hz), 17.3 (s); ^{31}P NMR (101 MHz, $CDCl_3$) d 25.9 (q, *J* = 70.0 Hz); IR (neat) 2969, 2377, 1437, 1142, 1106, 1073, 1040, 742, 685, 584 cm^{-1}; Anal. Calcd for $C_{15}H_{20}BP$: C, 74.41; H, 8.33; Found: C, 74.03; H, 8.37.



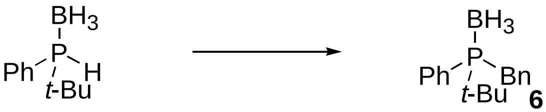
4

***t*-Butylmethylphenylphosphine borane (4).** The title compound was prepared from *t*-butylphenylphosphine borane (150 mg, 0.83 mmol) according to the standard procedure A described above. After 3 h, the desired phosphine **4** (148 mg, 91%) was obtained as a white solid after flash chromatography (2% EtOAc/hexanes): mp 81-82 °C; ^1H NMR (400 MHz, $CDCl_3$) d 7.70-7.64 (m, 2H,), 7.49-7.38 (m, 3H), 1.53 (d, *J* = 10 Hz, 3H), 1.06 (d, *J* = 14 Hz, 9H), 0.56 (t (br), *J* = 95 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 133.3 (d, *J* = 8 Hz), 131.5 (d, *J* = 2 Hz), 128.7 (d, *J* = 10 Hz), 128.0 (d, *J* = 51 Hz), 28.9 (d, *J* = 33 Hz), 25.6 (d, *J* = 3 Hz), 5.7 (d, *J* = 38 Hz); ^{31}P NMR (101 MHz, $CDCl_3$) d 26.3 (q. *J* = 55 Hz); IR (neat) 2973, 2383, 1474, 1436, 1107, 1064, 996, 952, 850, 736, 700, 690, 631, 608, 560 cm^{-1}; Anal. Calcd for $C_{11}H_{20}BP$: C, 68.08; H, 10.39; Found: C, 67.76; H, 10.93.



5

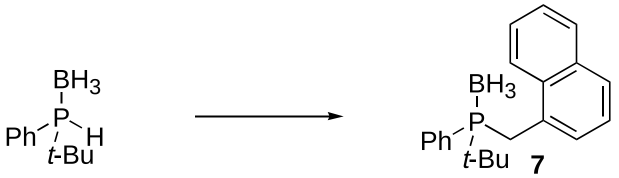
***t*-Butylallylphenylphosphine borane (5).** The title compound was prepared from *t*-butylphenylphosphine borane (150 mg, 0.83 mmol) according to the standard procedure A described above. After 1 h, the desired phosphine **5** (170 mg, 93%) was obtained as a white solid after flash chromatography (2% EtOAc/hexanes): mp 62-63 °C; ^1H NMR (400 MHz, $CDCl_3$) d 7.73-7.69 (m, 2H), 7.52-7.43 (m, 3H), 5.81-5.79 (m, 1H), 5.20-5.15 (m, 1H), 5.10-5.07 (m, 1H), 2.98-2.95 (m, 1H), 2.84-2.78 (m, 1H), 1.13 (d, *J* = 14 Hz, 9H), 0.56 (t (br), *J* = 119 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 134.1 (d, *J* = 8 Hz), 131.6 (s), 129.6 (d, *J* = 4 Hz), 128.6 (d, *J* = 9 Hz), 126.0 (d, *J* = 49 Hz), 120.1 (d, *J* = 11 Hz), 29.8 (d, *J* = 31 Hz), 25.9 (s), 25.6 (d, *J* = 33 Hz); ^{31}P NMR (101 MHz, $CDCl_3$) d 31.7 (q, *J* = 70 Hz); IR (neat) 2947, 2384, 1475, 1434, 1108, 1064, 996, 925, 850, 814, 783, 778, 701, 691, 631, 608, 560 cm^{-1}; Anal. Calcd for $C_{13}H_{22}BP$: C, 70.94; H, 10.07; Found: C, 70.98; H, 10.54.



6

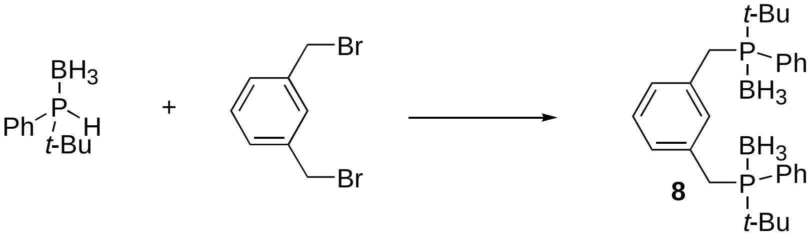
***t*-Butylbenzylphenylphosphine borane (6).** The title compound was prepared from *t*-butylphenylphosphine borane (150 mg, 0.83 mmol) according to the standard procedure A described above. After 1 h, the desired phosphine **6** (212 mg, 95%) was obtained as a white solid after flash chromatography (2% EtOAc/hexanes): mp 145-146 °C; ^1H NMR (300 MHz, $CDCl_3$) d 7.82-7.75 (m, 2H), 7.49-7.37 (m, 3H), 7.23-7.08 (m, 5H), 3.55 (t, *J* = 14 Hz, 1H), 3.32 (dd, *J* = 14, 9 Hz, 1H), 1.16 (d, *J* = 14 Hz, 9H), 0.56 (t (br), *J* = 119 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 134.4 (d, *J* = 8 Hz), 133.1 (d, *J* = 4 Hz), 131.7 (d, *J* = 2 Hz), 130.9 (d, *J* = 4 Hz), 128.6 (d, *J* = 2 Hz), 128.5 (d, *J* = 2 Hz), 127.2 (d, *J* = 3 Hz), 126.6 (d, *J* = 51 Hz), 30.4 (d, *J* = 31 Hz), 27.3 (d, *J* = 30 Hz), 26.2 (d, *J* = 2 Hz); ^{31}P NMR (101 MHz,

$CDCl_3$) d 34.2 (d, *J* = 70 Hz); IR (neat) 2960, 2394, 1473 1436, 1066, 842, 782, 740, 694, 629 cm^{-1}; Anal. Calcd for $C_{17}H_{24}BP$: C, 75.58; H, 8.95; Found: C, 75.35; H, 9.29.



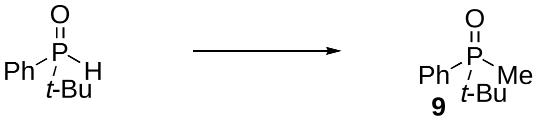
7

***t*-Butyl-2-methylnaphthylphenylphosphine borane (7).** The title compound was prepared from *t*-butylphenylphosphine borane (150 mg, 0.83 mmol) according to the standard procedure A described above. After 2 h, the desired phosphine **7** (221 mg, 83%) was obtained as a white solid after flash chromatography (2% EtOAc/hexanes): mp 148-150 °C; ^1H NMR (400 MHz, $CDCl_3$) d 8.03 (d, *J* = 8 Hz, 1H), 7.84-7.80 (m, 3H), 7.68 (d, *J* = 8 Hz, 1H), 7.51-7.38 (m, 5H), 7.30-7.22 (m, 2H), 3.97-3.88 (m, 2H), 1.28 (d, *J* = 14 Hz, 9H), 0.56 (t (br), *J* = 119 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 134.4 (d, *J* = 8 Hz), 134.2 (d, *J* = 1 Hz), 132.8 (d, *J* = 4 Hz), 131.7 (d, *J* = 2 Hz), 129.9 (d, *J* = 4 Hz), 129.1 (s), 128.6 (s), 128.53 (s), 128.49 (s), 128.0 (d, *J* = 3 Hz), 126.8 (s), 126.1 (d, *J* = 16 Hz), 125.4 (d, *J* = 3 Hz), 124.7 (s), 30.8 (d, *J* = 31 Hz), 26.3 (d, *J* = 2 Hz), 23.2 (d, *J* = 30 Hz); ^{31}P NMR (101 MHz, $CDCl_3$) d 34.7 (d, *J* = 70 Hz); IR (neat) 2941, 2357, 1434, 1392, 1062, 1014, 801, 780, 765, 732, 694, 627 cm^{-1}; HMRS (MAB) calcd for $C_{21}H_{25}BP$ $[M-H^+]^+$: 320.1865. Found: 320.1869.



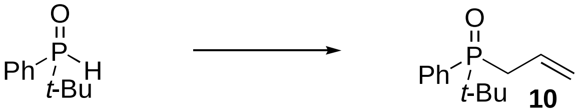
8

***P*,*P*-a,a'-Bis-*tert*-butylphenylphosphineborane-*m*-xylene (8).** To a mixture of *t*-butylphenylphosphine borane (102 mg, 0.57 mmol) and tetrabutylammonium bromide (6.1 mg, 0.019 mmol) in 50% KOH_{aq} (3.9 mL) and toluene (1.2 mL) was added a,a'-dibromo-*m*-xylene (50 mg, 0.19 mmol) at room temperature. The mixture was stirred vigorously at room temperature for 24 h. The solution was diluted with ether, washed with water, brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (2% EtOAc/hexanes) providing the desired phosphine **8** as a white solid (76 mg, 87%): mp 198-204 °C; ^1H NMR (300 MHz, $CDCl_3$) d 7.77-7.73 (m, 4H), 7.45-7.41 (m, 6H), 7.18-6.95 (m, 4H), 3.48-3.39 (m, 2H), 3.30-3.27 (m, 1H), 3.20-3.14 (m, 1H), 1.11 (d, *J* = 14 Hz, 18H), 0.56 (t (br), *J* = 119 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d 133.8 (d, *J* = 8 Hz), 133.7 (d, *J* = 8 Hz), 132.4 (d, *J* = 8 Hz), 131.0 (s), 128.7 (s), 128.1 (d, *J* = 87 Hz), 128.0 (d, *J* = 9 Hz), 125.5 (dd, *J* = 48, 22 Hz), 29.7 (dd, *J* = 30, 3 Hz), 26.7 (dd, *J* = 30, 13 Hz), 25.5 (s); ^{31}P NMR (101 MHz, $CDCl_3$) d 33.7 (m); IR (neat) 2959, 2376, 1474, 1464, 1436, 1365, 1107, 1064, 1018, 836, 810, 740, 695, 627 cm^{-1}; HMRS (MAB) calcd for $C_{28}H_{46}B_2NP_2$ $[M+NH_4^+]^+$: 480.3292. Found: 480.3309; Anal. Calcd for $C_{28}H_{42}B_2P_2$: C, 72.76; H, 9.16; Found: C, 72.32; H, 9.40.



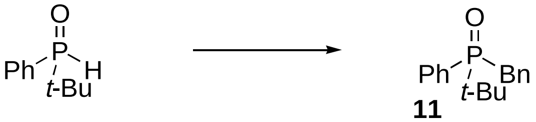
9

***t*-Butylmethylphenylphosphine oxide (9).** The title compound was prepared from *t*-butylphenylphosphine oxide (200 mg, 1.10 mmol) according to the standard procedure A described above. After 1 h, the desired phosphine **9** (181 mg, 84%) was obtained as a white solid after flash chromatography (5% MeOH/DCM): mp 79-81 °C; ^{1}H NMR (400 MHz, CDCl$_3$) d 7.72-7.67 (m, 2H,), 7.51-7.43 (m, 3H), 1.71 (d, J = 12 Hz, 3H), 1.11 (d, J = 15 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) d 131.36 (s), 131.28 (s), 131.2 (d, J = 90 Hz), 128.0 (d, J = 11 Hz), 32.9 (d, J = 71 Hz), 24.6 (d, J = 3 Hz), 10.6 (d, J = 66 Hz); ^{31}P NMR (101 MHz, CDCl$_3$) d 47.8 (s); IR (neat) 2947, 2868, 1476, 1437, 1168, 1113, 879, 745, 700, 631cm^{-1}; HMRS (MAB) calcd for $C_{11}H_{17}OP$ [M]$^+$: 196.1017. Found: 196.1018.



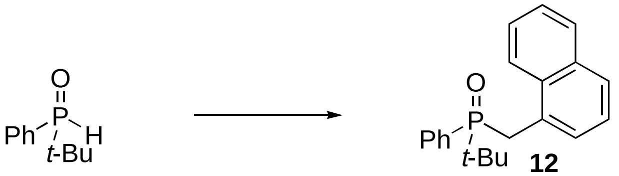
10

***t*-Butylallylphenylphosphine oxide (10).** The title compound was prepared from *t*-butylphenylphosphine oxide (200 mg, 1.10 mmol) according to the standard procedure A described above. After 3 h, the desired phosphine **10** (188 mg, 77%) was obtained as a white solid after flash chromatography (5% MeOH/DCM): mp 131-132 °C; ^{1}H NMR (300 MHz, CDCl$_3$) d 7.76-7.72 (m, 2H), 7.50-7.43 (m , 3H), 6.95-6.82 (m, 1H), 6.36-6.25 (m, 2H), 1.99 (d, J = 6 Hz, 2H), 1.11 (d, J = 15 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) d 149.0 (s), 132.0 (d, J = 8 Hz), 131.6 (d, J = 93 Hz), 131.5 (d, J = 2 Hz), 128.3 (d, J = 11 Hz), 119.5 (d, J = 93 Hz), 32.7 (d, J = 73 Hz), 24.4 (s), 20.9 (d, J = 17 Hz); ^{31}P NMR (101 MHz, CDCl$_3$) d 37.4 (s); IR (neat) 2966, 1629, 1474, 1437, 1167, 1110, 996, 817, 780, 751, 719, 627 cm^{-1}; HMRS (MAB) calcd for $C_{13}H_{19}BP$ [M]$^+$: 222.1174. Found: 222.1177.



11

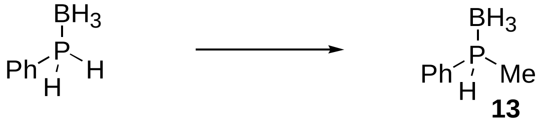
***t*-Butylbenzylphenylphosphine oxide (11).** The title compound was prepared from *t*-butylphenylphosphine oxide (200 mg, 1.10 mmol) according to the standard procedure A described above. After 3 h, the desired phosphine **11** (276 mg, 92%) was obtained as a white solid after flash chromatography (5% MeOH/DCM): mp 190-191 °C; ^{1}H NMR (300 MHz, CDCl$_3$) d 7.75-7.71 (m, 2H), 7.47-7.42 (m, 3H), 7.30-7.27 (m , 2H), 7.21-7.18 (m, 3H), 3.52 (t, J = 15 Hz, 1H), 3.42 (dd, J = 15, 9 Hz, 1H), 1.16 (d, J = 15 Hz, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) d 131.9 (d, J = 8 Hz), 131.2 (d, J = 3 Hz), 130.0 (s), 129.97 (s), 129.7 (d, J = 88 Hz), 128.2 (d, J = 2 Hz), 127.9 (d, J = 11 Hz), 126.4 (d, J = 2 Hz), 33.3 (d, J = 68 Hz), 31.2 (d, J = 59 Hz), 24.6 (s); ^{31}P NMR (101 MHz, CDCl$_3$) d 47.5 (s); IR (neat) 2970, 1437, 1170, 1134, 1112, 1066, 820, 765, 747, 718, 631 cm^{-1}; Anal. Calcd for $C_{17}H_{21}OP$: C, 74.98; H, 7.77; Found: C, 74.87; H, 7.98.



12

***t*-Butyl-2-naphthylphenylphosphine oxide (12).** The title compound was prepared from *t*-butylphenylphosphine oxide (200 mg, 1.10 mmol) according to the standard procedure A described above. After 6 h, the desired phosphine **12** (246 mg, 70%) was obtained as a white solid after flash chromatography (5% MeOH/DCM): mp 175-176 °C; ^{1}H NMR (400 MHz, CDCl$_3$) d 8.22 (d, *J* = 9 Hz, 1H), 7.79-7.75 (m, 3H), 7.67-7.65 (m, 1H), 7.55-7.52 (m, 1H), 7.47-7.38 (m, 5H), 7.26-7.24 (m, 1H), 4.07 (t, *J* = 15 Hz, 1H), 3.83 (dd, *J* = 15, 9 Hz, 1H), 1.24 (d, *J* = 15 Hz, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) d 133.8 (d, *J* = 2 Hz), 132.5 (d, *J* = 5 Hz), 132.0 (d, *J* = 8 Hz), 131.2 (d, *J* = 3 Hz), 128.7 (d, *J* = 58 Hz), 128.5 (d, *J* = 9 Hz), 128.4 (s), 128.3 (d, *J* = 6 Hz), 127.8 (d, *J* = 11 Hz), 127.3 (s), 125.9 (s), 125.5 (s), 125.0 (s), 124.4 (s), 33.7 (d, *J* = 68 Hz), 27.9 (d, *J* = 59 Hz), 24.6 (s); ^{31}P NMR (101 MHz, CDCl$_3$) d 47.0 (s); IR (neat) 2958, 2902, 2381, 1472, 1461, 1434, 1392, 1138, 1063, 1014, 801, 780, 765, 732, 694, 627 cm^{-1}; Anal. Calcd for $C_{21}H_{23}OP$: C, 78.24; H, 7.19; Found: C, 78.03; H, 7.25.

Standard Procedure B

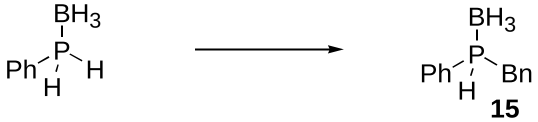


13

Phenylmethylphosphine borane (13). To a mixture of phenylphosphine borane (500 mg, 4.03 mmol) and tetrabutylammonium bromide (130 mg, 0.403 mmol) in water (20.2 mL) and toluene (20.2 mL) was added potassium hydroxide (226 mg, 4.03 mmol) followed by iodomethane (260 µL, 4.03 mmol) at room temperature. The mixture was stirred vigorously at room temperature for 12 h. The solution was diluted with ether, washed with water, brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (6% EtOAc/hexanes) providing the desired phosphine **13** as a colorless oil (500 mg, 90%): ^{1}H NMR (400 MHz, CDCl$_3$) d 7.73-7.67 (m, 2H), 7.55-7.44 (m, 3H), 5.32 (d of septet, *J* = 371, 6 Hz, 1H), 1.62 (dd, *J* = 11, 6 Hz, 3H), 0.83 (q (br), *J* = 100 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) d 132.7 (d, *J* = 9 Hz), 132.1 (d, *J* = 3 Hz), 129.5 (d, *J* = 10 Hz), 126.8 (d, *J* = 57 Hz), 8.6 (d, *J* = 39 Hz); ^{31}P NMR (101 MHz, CDCl$_3$) d -14.6 (q, *J* = 48 Hz); IR (neat) 3189, 2380, 1437, 1414, 1190, 1118, 1064, 995, 929, 736, 691 cm^{-1}; HMRS (MAB) calcd for $C_7H_{12}BP$ $[M]^+$: 138.07697. Found: 138.07671. The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK® AS, isocratic flow 1.0 mL/min, 10 % 2-propanol/hexanes, T_r 11.99, 14.46).

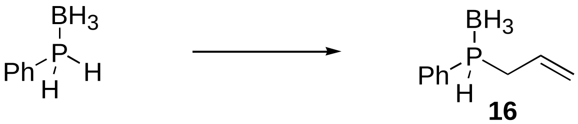
14

Phenylethylphosphine borane (14). The title compound was prepared from phenylphosphine borane (500 mg, 4.03 mmol) according to the standard procedure B described above. After 12 h, the desired phosphine **14** (520 mg, 85%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes): ^{1}H NMR (400 MHz, CDCl$_3$) d 7.70-7.64 (m, 2H), 7.56-7.34 (m, 3H), 5.38 (d of sextet, *J* = 368, 6 Hz, 1 H), 2.00-1.88 (m, 2H), 1.13 (dt, *J* = 18, 8 Hz, 3H), 0.80 (q (br), *J* = 95 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) d 133.3 (d, *J* = 9 Hz), 132.1 (d, *J* = 2 Hz), 129.4 (d, *J* = 10 Hz), 125.7 (d, *J* = 55 Hz), 17.3 (d, *J* = 37 Hz), 8.93 (d, *J* = 3 Hz); ^{31}P NMR (101 MHz, CDCl$_3$) d 2.2 (q, *J* = 44 Hz); IR (neat) 2972, 2377, 1437, 1117, 1069, 1048, 1025, 1010, 910, 886, 730, 691 cm^{-1}; HMRS (MAB) calcd for $C_8H_{14}BP$ [M]$^+$: 152.0926. Found: 152.0924



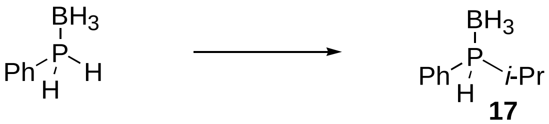
15

Phenylbenzylphosphine borane (15). The title compound was prepared from phenylphosphine borane (250 mg, 2.02 mmol) according to the standard procedure B described above. After 12 h, the desired phosphine **15** (350 mg, 81%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes): ^{1}H NMR (400 MHz, CDCl$_3$) d 7.53-7.46 (m, 3H), 7.41-7.36 (m, 2H), 7.28-7.21 (m, 3H), 7.02-6.98 (m, 2H), 5.50 (dddd, *J* = 373, 8, 7, 5 Hz, 1 H), 3.38 (ddd, *J* = 14, 10, 5 Hz, 1H), 3.21 (ddd, *J* = 14, 11, 7 Hz, 1H), 0.81 (q (br), *J* = 108 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) d 133.7 (s), 133.6 (d, *J* = 9 Hz), 132.3 (d, *J* = 2 Hz), 129.7 (d, *J* = 4 Hz), 129.3 (d, *J* = 10 Hz), 129.1 (d, *J* = 2 Hz), 127.6 (d, *J* = 3 Hz), 125.1 (d, *J* = 55 Hz), 32.6 (d, *J* = 31 Hz); ^{31}P NMR (101 MHz, CDCl$_3$) d 6.94 (q, *J* = 56.3 Hz); IR (neat) 2383, 1495, 1453, 1437, 1117, 1058, 936, 911, 742, 693 cm^{-1}; HMRS (MAB) calcd for $C_{13}H_{16}BP$ [M]$^+$: 214.1083. Found: 214.1079.



16

Phenylallylphosphine borane (16). The title compound was prepared from phenylphosphine borane (250 mg, 2.02 mmol) according to the standard procedure B described above. After 12 h, the desired phosphine **16** (260 mg, 79%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes): ^{1}H NMR (400 MHz, C_6D_6) d!7.33-7.28 (m, 2H), 7.03-6.90 (m, 3H), 5.41-5.30 (m, 1H), 4.82 (d of sextet, *J* = 369, 6 Hz, 1H), 4.75-4.72 (m, 1H), 4.64-4.58 (m, 1H), 2.23-2.08 (m, 2H), 1.60 (q (br), *J* = 99 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) d 133.6 (d, *J* = 8 Hz), 131.8 (s), 129.7 (d, *J* = 8 Hz), 129.2 (d, *J* = 10 Hz), 126.1 (d, *J* = 53 Hz), 119.8 (d, *J* = 10 Hz), 29.6 (d, *J* = 33 Hz); ^{31}P NMR (101 MHz, C_6D_6) d 0.26 (q, *J* = 53 Hz); IR (neat) 3058, 2917, 2380, 1733, 1437, 1372, 1240, 1045, 992, 913, 740, 692 cm^{-1}.



17

Phenyl-*i*-propylphosphine borane (17). The title compound was prepared from phenylphosphine borane (250 mg, 2.02 mmol) according to the standard procedure B described above. After 12 h, the desired phosphine **17** (250 mg, 75%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes): ^{1}H NMR (400 MHz, CDCl$_3$)

d 7.70-7.65 (m, 2H), 7.56-7.46 (m, 3H), 5.27 (dddd, *J* = 365, 13, 11, 7 Hz, 1H), 2.30-2.18 (m, 1H), 1.18 (ddd, *J* = 19, 17, 7 Hz, 6H), 0.63 (t (br), *J* = 102 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) d 133.8 (d, *J* = 8 Hz), 132.1 (d, *J* = 2 Hz), 129.3 (d, *J* = 10 Hz), 125.2 (d, *J* = 53 Hz), 24.2 (d, *J* = 35 Hz), 18.2 (d, *J* = 50 Hz); ^{31}P NMR (101 MHz, CDCl$_3$) d 16.0 (q, *J* = 44 Hz); HMRS (MAB) calcd for $C_9H_{16}BP$ [M]$^+$: 166.1083. Found: 166.1087.