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Supporting Information

Analytical HPLC: Waters 244 M 6 KA Cabinet System with M 590 SDS 230 pump, U 6 K injection system, M 440 EB UV-detector and R401 or 410 differential refraktometer, Spectra Physics SP 4100 integration unit, column with 600x4 mm internal diameter, Macherey-Nagel Nucleosil 50-10, flow 2 ml/min.
Preparative HPLC: programmable pump Waters 590 with Perfusor VI injector, peak-separator 2150, R 401 differential refraktometer, column 250x16 mm internal diameter, Macherey-Nagel Nucleosil 50-10, flow 10 ml/min.
Abbrevations: hexane (H), acetone (A).

The assignements s ($C_{quart.}$), d (CH), t (CH_2) and q (CH_3) for the ^{13}C NMR signals base on DEPT 135 and DEPT 90 spectra; for compounds containing phosphorus the second multiplicity (given with coupling constant) results from $^{n}J_{C\text{-}P}$, the assignment was proven by additional $^{1}H/^{31}P$ decoupled ^{13}C NMR spectra.

Reaction of **3a** with $Pd_2dba_3 \cdot CHCl_3$:
Column (H/A, 2:1), R_f(H:A=1:1)=0.35, analytical HPLC (H/MeCN, 10:2.5 + 40% ether), preparative HPLC (H/2-propanol/MeCN, 85:15:7), yield 95%.
4a: IR (neat, NaCl): $\tilde{\nu}$ = 2986 cm^{-1}, 2939, 2876, 1756, 1710, 1678, 1620, 1447, 1371, 1302, 1195, 1098, 1020. ^{1}H-NMR ([D$_6$]acetone, 250 MHz): δ = 1.23 (t, J = 7.1 Hz, 6 H), 1.24 (t, J = 7.1 Hz, 6 H), 1.27 (d, J = 6.9 Hz, 6 H), 1.37 (d, J = 6.9 Hz, 6 H), 1.37 (s, 6 H), 2.15 (s, 6 H), 4.07-4.15 (m, 8 H), 4.66 (q, J = 6.9 Hz, 2 H), 4.80 (q, J = 6.9 Hz, 2 H). ^{13}C-NMR ([D$_6$]acetone, 62.9 MHz): δ = 14.34 (q, 4 C), 17.33 (q, 2 C), 17.46 (q, 2 C), 20.26 (q, 2 C), 27.83 (q, 2 C), 37.28 (s, 2 C), 38.96 (s, 2 C), 47.60 (s, 2 C), 60.86 (t, 2 C), 61.03 (t, 2 C), 68.53 (d, 2 C), 69.36 (d, 2 C), 171.54 (s, 2 C), 172.00 (s, 2 C), 172.44 (s, 2 C), 172.78 (s, 2 C). ^{1}H-NMR ([D$_3$]acetonitrile, 250 MHz): δ = 1.21 (t, J = 6.9 Hz, 6 H), 1.23 (t, J = 6.9 Hz, 6 H), 1.27 (d, J = 7.0 Hz, 6 H), 1.32 (d, J = 7.0 Hz, 6 H), 1.30 (s, 6 H), 1.94 (s, 6 H), 4.07-4.13 (m, 8 H), 4.56 (q, J = 7.0 Hz, 2 H), 4.72 (q, J = 6.9 Hz, 2 H). MS (FAB); m/z (%): 818 (5) [(^{106}Pd) M$^+$], 673 (4), 529 (5). $[\alpha]_D^{20}$ = -161.8 (c = 2.05, CH_3CN).
5a: IR (neat, NaCl): $\tilde{\nu}$ = 2984 cm^{-1}, 2937, 2878, 1754, 1711, 1676, 1621, 1447, 1371, 1301, 1193, 1098, 1021, 911, 857. ^{1}H-NMR ([D$_3$]acetonitrile, 250 MHz): δ = 1.15 (t, J = 7.1 Hz, 6 H),

1.23 (t, J = 7.1 Hz, 6 H), 1.29 (s, 6 H), 1.34 (d, J = 6.9 Hz, 6 H), 1.44 (d, J = 6.9 Hz, 6 H), 1.77 (s, 6 H), 4.01-4.16 (m, 8 H), 4.64-4.77 (m, 4 H). MS (FAB); m/z (%): 841 (5) [(^{106}Pd) M^+ + Na], 818 (5) [(^{106}Pd) M^+], 673 (14), 527 (10). $[\alpha]_D^{20}$ = +54.3 (c = 1.50, CH_3CN).

Reaction of **3b** with $Pd_2dba_3\cdot CHCl_3$:

Column (H/A, 4:1), R_f(H:A=4:1)=0.25, analytical HPLC (H/MeCN, 10:2.5 + 40% ether), preparative HPLC (H/2-propanol/MeCN, 85:15:7), yield 82%.

4b: IR (neat, NaCl): ṽ = 2981 cm^{-1}, 2935, 1745, 1708, 1458, 1449, 1393, 1368, 1312, 1250, 1202, 1161, 1131, 1097, 1033, 934, 876, 847, 819, 740. ^{1}H-NMR ([D_3]acetonitrile, 400 MHz): δ = 1.25 (d, J = 7.0 Hz, 6 H), 1.27 (d, J = 6.9 Hz, 6 H), 1.31 (s, 6 H), 1.42 (s, 18 H), 1.43 (s, 18 H), 2.13 (s, 6 H), 4.45 (q, J = 7.0 Hz, 2 H), 4.56 (q, J = 6.9 Hz, 2 H). ^{13}C-NMR ([D_6]acetone, 62.9 MHz): δ = 17.32 (q, 2 C), 17.72 (q, 2 C), 20.46 (q, 2 C), 28.01 (q, 2 C), 28.09 (q, 12 C), 37.27 (s, 2 C), 38.40 (s, 2 C), 47.97 (s, 2 C), 69.09 (d, 2 C), 69.89 (d, 2 C), 81.14 (s, 2 C), 81.48 (s, 2 C), 170.77 (s, 4 C), 172.54 (s, 2 C), 173.09 (s, 2 C). MS (FAB); m/z (%): 930 (1) [(^{106}Pd) M^+]. $[\alpha]_D^{20}$ = -202.9 (c = 0.55, CH_3CN).

5b: from HPLC only impure material was obtained; the amount was too small for further purification. For the *dr*-value the integral over all other compounds than **4b** were added together; so the real ratio of **4b**:**5b** is better.

Reaction of **3c** with $Pd_2dba_3\cdot CHCl_3$:

Column (H/A, 5:4), R_f(H:A=1:1)=0.25, analytical HPLC (H/MeCN, 10:2.5 + 40% ether), preparative HPLC (H/2-propanol/MeCN, 12:3:2), yield 99%.

4c: IR (neat, NaCl): ṽ = 2989 cm^{-1}, 2951, 2874, 1757, 1738, 1711, 1447, 1369, 1309, 1286, 1204, 1175, 1133, 1097, 1062, 914, 848, 821. ^{1}H-NMR ([D_3]acetonitrile, 250 MHz): δ = 1.29 (s, 6 H), 1.35 (d, J = 6.9 Hz, 6 H), 1.44 (d, J = 7.0 Hz, 6 H), 1.77 (s, 6 H), 3.57 (s, 6 H), 3.66 (s, 6 H), 4.75 (m, 4 H). ^{13}C-NMR ([D_3]acetonitrile, 62.9 MHz): δ = 17.03 (q, 2 C), 17.48 (q, 2 C), 19.78 (q, 2 C), 27.0 (q, 2 C), 36.48 (s, 2 C), 42.17 (s, 2 C), 48.76 (s, 2 C), 52.09 (q, 2 C), 52.12 (q, 2 C), 68.85 (d, 2 C), 69.29 (d, 2 C), 172.18 (s, 4 C), 172.50 (s, 2 C), 172.73 (s, 2 C). MS (FAB); m/z (%): 762 (20) [(^{106}Pd) M^+]. $[\alpha]_D^{20}$ = -228.1 (c = 0.73, CH_3CN).

5c: R_f(H:A=1:1)=0.25. IR (neat, NaCl): ṽ = 2987 cm^{-1}, 2953, 2876, 1758, 1705, 1692, 1448, 1368, 1305, 1286, 1199, 1174, 1133, 1062, 986, 914, 848, 817. ^{1}H-NMR ([D_3]acetonitrile, 250 MHz): δ = 1.27 (d, J = 6.8 Hz, 6 H), 1.29 (s, 6 H), 1.32 (d, J = 6.9 Hz, 6 H), 2.13 (s, 6 H), 3.63

(s, 6 H), 3.65 (s, 6 H), 4.56 (q, J = 7.0 Hz, 2 H), 4.74 (q, J = 6.9 Hz, 2 H). ^{13}C-NMR ([D$_3$]acetonitrile, 62.9 MHz): δ = 17.22 (q, 2 C), 17.70 (q, 2 C), 20.11 (q, 2 C), 27.63 (q, 2 C), 37.42 (s, 2 C), 43.10 (s, 2 C), 48.99 (s, 2 C), 52.26 (q, 2 C), 52.29 (q, 2 C), 68.99 (d, 2 C), 69.54 (d, 2 C), 172.53 (s, 2 C), 173.08 (s, 2 C), 173.37 (s, 2 C), 174.14 (s, 2 C). MS (FAB); m/z (%): 762 (20) [(^{106}Pd) M$^+$]. $[\alpha]_D^{20}$ = +47.1 (c = 2.36, CH_3CN).

Reaction of **3d** with $Pd_2dba_3 \cdot CHCl_3$:

Column (H/A, 2:1), R_f(H:A=1:1)=0.35, analytical HPLC (H/MeCN, 10:2.5 + 40% ether), preparative HPLC (H/2-propanol/MeCN, 85:15:7), yield 95%.

4d: ^{1}H-NMR ([D$_3$]acetonitrile, 250 MHz): δ = 1.15 (t, J = 7.1 Hz, 6 H), 1.23 (t, J = 7.1 Hz, 6 H), 1.29 (s, 6 H), 1.34 (d, J = 6.9 Hz, 6 H), 1.44 (d, J = 6.9 Hz, 6 H), 1.77 (s, 6 H), 4.01-4.16 (m, 8 H), 4.64-4.77 (m, 4 H). MS (FAB); m/z (%): 841 (5) [(^{106}Pd) M$^+$ + Na], 818 (5) [(^{106}Pd) M$^+$], 673 (14), 527 (10).

5d: IR (neat, NaCl): $\tilde{\nu}$ = 2986 cm^{-1}, 2939, 2876, 1756, 1710, 1678, 1620, 1447, 1371, 1302, 1195, 1098, 1020, 913, 860. ^{1}H-NMR ([D$_6$]acetone, 250 MHz): δ = 1.23 (t, J = 7.1 Hz, 6 H), 1.24 (t, J = 7.1 Hz, 6 H), 1.27 (d, J = 6.9 Hz, 6 H), 1.37 (d, J = 6.9 Hz, 6 H), 1.37 (s, 6 H), 2.15 (s, 6 H), 4.07-4.15 (m, 8 H), 4.66 (q, J = 6.9 Hz, 2 H), 4.8 (q, J = 6.9 Hz, 2 H). ^{13}C-NMR ([D$_6$]acetone, 62.9 MHz): δ = 14.34 (q, 4 C), 17.33 (q, 2 C), 17.46 (q, 2 C), 20.26 (q, 2 C), 27.83 (q, 2 C), 37.28 (s, 2 C), 38.96 (s, 2 C), 47.60 (s, 2 C), 60.86 (t, 2 C), 61.03 (t, 2 C), 68.53 (d, 2 C), 69.36 (d, 2 C), 171.54 (s, 2 C), 172.0 (s, 2 C), 172.44 (s, 2 C), 172.78 (s, 2 C). ^{1}H-NMR ([D$_3$]acetonitrile, 250 MHz): δ = 1.21 (t, J = 6.9 Hz, 6 H), 1.23 (t, J = 6.9 Hz, 6 H), 1.27 (d, J = 7.0 Hz, 6 H), 1.32 (d, J = 7.0 Hz, 6 H), 1.30 (s, 6 H), 1.94 (s, 6 H), 4.07-4.13 (m, 8 H), 4.56 (q, J = 7.0 Hz, 2 H), 4.72 (q, J = 6.9 Hz, 2 H). MS (FAB); m/z (%): 818 (5) [^{106}Pd (M$^+$)], 673 (4), 529 (5). $[\alpha]_D^{20}$ = +161.8 (c = 2.05, $CHCl_3$).

Reaction of **3e** with $Pd_2dba_3 \cdot CHCl_3$:

Column (H/A, 3:1), R_f(H:A=2:1)=0.30, analytical HPLC (H/MeCN, 10:2.5 + 40% ether), preparative HPLC (H/2-propanol/MeCN, 85:15:7), yield 70%.

4e: IR (neat, NaCl): $\tilde{\nu}$ = 2984 cm^{-1}, 2939, 2876, 1747, 1738, 1722, 1713, 1682, 1462, 1454, 1375, 1305, 1286, 1205, 1180, 1135, 1095, 1062, 996, 937, 872, 821, 749. ^{1}H-NMR ([D$_3$]acetonitrile, 400 MHz): δ = 1.14 (d, J = 6.2 Hz, 6 H), 1.17 (d, J = 6.3 Hz, 6 H), 1.21 (d, J = 6.2 Hz, 6 H), 1.23 (d, J = 6.3 Hz, 6 H), 1.30 (s, 6 H), 1.33 (d, J = 6.9 Hz, 6 H), 1.45 (d, J =

7.0 Hz, 6 H), 1.77 (s, 6 H), 4.63 (q, J = 7.0 Hz, 2 H), 4.69 (q, J = 6.9 Hz, 2 H), 4.90 (m, 2 H), 4.96 (m, 2 H). MS (70 eV); m/z (%): 874 (17) [(^{106}Pd) M$^+$].

5e: IR (neat, NaCl): $\tilde{\nu}$ = 2983 cm^{-1}, 2938, 2877, 1753, 1732, 1709, 1682, 1462, 1454, 1374, 1300, 1196, 1174, 1134, 1096, 1035, 936, 910, 816, 747. ^{1}H-NMR ([D$_3$]acetonitrile, 800 MHz): δ = 1.20 (d, J = 6.3 Hz, 6 H), 1.21 (d, J = 6.3 Hz, 12 H), 1.23 (d, J = 6.3 Hz, 6 H), 1.27 (d, J = 7.0 Hz, 6 H), 1.30 (s, 6 H), 1.31 (d, J = 6.9 Hz, 6 H), 1.95 (s, J = 6 H), 4.53 (q, J = 7.0 Hz, 2 H), 4.67 (q, J = 6.9 Hz, 2 H), 4.94 (m, 2 H).^{13}C-NMR ([D$_6$]acetone, 62.9 MHz): δ = 17.21 (q, 2 C), 17.76 (q, 2 C), 20.27 (q, 2 C), 21.81 (q, 4 C), 21.90 (q, 2 C), 21.97 (q, 2 C), 27.86 (q, 2 C), 37.34 (s, 2 C), 43.12 (s, 2 C), 48.99 (s, 2 C), 68.75 (d, 2 C), 69.04 (d, 2 C), 69.10 (d, 2 C), 69.81 (d, 2 C), 171.53 (s, 2 C), 172.29 (s, 2 C), 173.03 (s, 2 C), 174.05 (s, 2 C). MS (FAB); m/z (%): 874 (17) [(^{106}Pd) M$^+$]. $[\alpha]_D^{20}$ = +119.7 (c = 2.36, CH$_3$CN).

Reaction of **4a** with **6**:

Column (H/A, 4:1), R$_f$(H:A=3:1)=0.30, yield 84%.

7: IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 2985, 2939, 2909, 2873, 1750, 1710, 1437, 1378, 1372, 1352, 1300, 1293, 1188, 1132, 1095, 1053, 1023, 886, 753. ^{1}H-NMR ([D$_6$]acetone, 250 MHz): δ = 0.90 (s, 6 H), 1.19 (t, J = 7.1 Hz, 6 H), 1.31 (t, J = 6.7 Hz, 6 H), 1.36 (d, J = 7.1 Hz, 6 H), 1.38 (s, 6 H), 1.38 (d, J = 7.1 Hz, 6 H), 1.42 (s, 6 H), 2.33-2.42 (m, 2 H), 2.96-3.06 (m, 2 H), 4.08 (q, J = 7.1 Hz, 4 H), 4.29-4.41 (m, 4 H), 4.44-4.51 (s, 2 H), 4.68 (q, J = 6.9 Hz, 2 H), 5.08 (q, J = 6.9 Hz, 2 H), 7.19-7.32 (m, 12 H), 7.60 (m, 4 H), 7.88 (m, 4 H). ^{13}C-NMR ([D$_6$]acetone, 62.9 MHz): δ = 14.38 (q, 2 C), 14.66 (q, 2 C),17.79 (d, 2 C), 17.93 (d, 2 C), 19.79 (q, 2 C), 27.29 (q, 2 C), 27.63 (q, 2 C), 31.30 (t, m, 2 C), 38.01 (s, 2 C), 51.72 (s, m, 2 C), 56.63 (s, m, 2 C), 61.07 (t, 2 C), 61.44 (t, 2 C), 69.36 (d, 2 C), 69.56 (d, 2 C), 79.44 (s, m, 2 C), 109.70 (s), 128.22 (d, m, 4 C), 129.20 (d, m, 4 C), 130.53 (d, 2 C), 130.71 (d, 2 C), 134.21 (d, m, 4 C), 134.66 (d, m, 4 C), 135.59 (s, m, 2 C), 137.65 (s, m, 2 C), 171.65 (s, 2 C), 172.78 (s, 2 C), 172.98 (s, 2 C), 173.60 (s, m, 2 C). MS (FAB); m/z (%): 1316 (3) [(^{106}Pd) M$^+$], 818 [(^{106}Pd) M$^+$-DIOP].

Reaction of **5a** with **6**:

Column (H/A, 4:1), R$_f$(H:A=3:1)=0.30, yield 86%.

8: IR (neat, NaCl): $\tilde{\nu}$ = 3059 cm^{-1}, 2986, 2937, 1749, 1706, 1671, 1441, 1373, 1302, 1205, 1098, 1051, 915, 883, 856, 809. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.82 (s, 6 H), 0.97 (s, 6 H), 1.13 (t, J = 7.1 Hz, 6 H), 1.22 (t, J = 7.1 Hz, 6 H), 1.40 (d, J = 7.1 Hz, 6 H), 1.51 (s, 6 H), 1.54 (d, J =

7.1 Hz, 6 H), 2.20-2.29 (m, 2 H), 2.94 (m, 2 H), 3.98-4.11 (m, 8 H), 4.46 (s, 2 H), 4.71 (q, J = 7.1 Hz, 2 H), 5.41 (q, J = 7.1 Hz, 2 H), 7.19-7.32 (m, 12 H), 7.60 (m, 4 H), 7.88 (m, 4 H). ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ = 14.07 (q, 2 C), 14.15 (q, 2 C),16.82 (d, 2 C), 17.93 (d, 2 C), 19.0 (q, 2 C), 25.75 (q, 2 C), 27.0 (q, 2 C), 30.34 (t, m, 2 C), 36.08 (s, 2 C), 52.52 (s, m, 2 C), 54.94 (s, m, 2 C), 60.36 (t, 2 C), 60.60 (t, 2 C), 68.69 (d, 2 C), 68.92 (d, 2 C), 78.53 (s, m, 2 C), 109.08 (s), 127.83 (d, m, 4 C), 128.50 (d, m, 4 C), 129.66 (d, 2 C), 129.90 (d, 2 C), 132.73 (d, m, 4 C), 133.21 (d, m, 4 C), 135.09 (s, m, 2 C), 135.83 (s, m, 2 C), 171.54 (s, 2 C), 171.59 (s, 2 C), 172.42 (s, 2 C), 175.32 (s, m, 2 C). ^{31}P-NMR ($CDCl_3$, 162 MHz): δ = -2.06. MS (FAB); m/z (%): 1316 (2) [(^{106}Pd) M^+].

Reaction of **4a** with **9**:

Yellow crystals from *n*-pentane/A, 5:1 at 5°C, yield 87%.

10: m.p. 169° C. IR (neat, NaCl): ṽ = 2986 cm^{-1}, 2940, 2876, 1747, 1713, 1689, 1447, 1371, 1312, 1194, 1132, 1098, 1060, 1022, 883, 861, 798, 763. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.25 (t, J = 7.0 Hz, 6 H), 1.28 (t, J = 7.0 Hz, 6 H), 1.34 (d, J = 5.4 Hz, 6 H), 1.36 (d, J = 5.0 Hz, 6 H), 1.40 (s, 6 H), 1.88 (s, 6 H), 1.95 (m, 2 H), 4.0 (m, 2 H), 4.11-4.22 (m, 8 H), 4.78-4.90 (m, 4 H), 6.17 (m, 2 H), 6.44 (m, 2 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 13.72 (q, 4 C), 16.59 (q, 2 C), 17.0 (q, 2 C), 20.05 (q, 2 C), 25.86 (q, 2 C), 38.38 (s, 2 C), 49.41 (s, 2 C), 51.15 (d, 2 C), 56.65 (s, 2 C), 60.40 (t, 2 C), 60.59 (t, 2 C), 67.85 (d, 2 C), 68.27 (d, 2 C), 72.69 (t), 106.09 (d, 2 C), 113.79 (d, 2 C), 170.65 (s, 2 C), 170.99 (s, 2 C), 171.23 (s, 2 C), 171.94 (s, 2 C). $C_{41}H_{56}O_{16}Pd$ (911.28): calcd. C 54.04, H 6.19; found C 54.28, H 6.43. MS (70 eV); m/z (%): 819 (11) [(^{106}Pd) M^+ - NBD], 91 (68) [NBD^+ - H].

Reaction of **5c** with **9**:

Yellow crystals from *n*-pentane/A, 5:1 at 5°C, yield 82%.

11: m.p. 167° C. IR (neat, NaCl): ṽ = 2985 cm^{-1}, 2929, 2863, 1746, 1689, 1445, 1371, 1334, 1303, 1199, 1131, 1199, 1045, 985, 794. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.34 (d, J = 7.1 Hz, 6 H), 1.38 (d, J = 6.9 Hz, 6 H), 1.39 (s, 6 H), 1.86 (s, 6 H), 1.94-1.98 (m, 2 H), 3.69 (s, 6 H), 3.73 (s, 6 H), 3.99-4.01 (m, 2 H), 4.83 (q, J = 7.1 Hz, 2 H), 4.88 (q, J = 6.9 Hz, 2 H), 6.16-6.19 (m, 2 H), 6.41-6.44 (m, 2 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 16.81 (q, 2 C), 17.22 (q, 2 C), 20.21 (q, 2 C), 25.97 (q, 2 C), 38.66 (s, 2 C), 49.65 (s, 2 C), 51.42 (d, 2 C), 51.65 (q, 2 C), 51.87 (q, 2 C), 56.83 (s, 2 C), 67.97 (d, 2 C), 68.34 (d, 2 C), 73.01 (t), 106.45 (d, 2 C), 114.01 (d, 2 C), 171.25 (s, 2 C), 171.37 (s, 2 C), 171.44 (s, 2 C), 172.61 (s, 2 C). MS (FAB); m/z (%): 855 (3) [(^{106}Pd) M^+], 91 (84) [NBD^+].