Electronic Supplementary Information for

Palladium complexes derived from *N*,*N*-bidentate NH-iminophosphorane ligands: synthesis and use as catalysts in the Sonogashira reaction

Mateo Alajarin,*[a] Carmen Lopez-Leonardo,*[a] Pilar Llamas-Lorente,[a] Rosalia Raja[a], Delia Bautista[b] and Raul-Angel Orenes

[a]*Departamento de Química Orgánica, Facultad de Química, Regional Campus of International Excellence ''Campus Mare Nostrum'', Universidad de Murcia, E-30100 Murcia, Spain; E-mail: alajarin@um.es, melill@um.es*
[b]*Servicio Universitario de Instrumentación Científica, Edificio SACE, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain; E-mail: dbc@um.es*

General procedure for the synthesis of compounds 4-6. A mixture of the corresponding iminophosphorane **1-3** (0.45 mmol), benzene (15 mL) and the corresponding amine (10 equiv, 4.5 mmol) was stirred for 2-24 h under reflux (N_2) until disappearance of the starting material (checked by TLC using silica gel plates deactivated with 5% Et_3N in *n*-hexane and AcOEt as eluent). The solvent and the excess of amine were removed in vacuo to give compounds **4-6** as yellow oils.

4a (R^1 = 4-$CH_3C_6H_4$, R^2 = R^3 = H, R^4 = ^{n}Pr). Yellow oil (0.16 g, 93%); ν_{max}(film)/cm^{-1}: 3278, 1501, 1483, 1438, 1321, 1107, 734, 692; ^{1}H NMR (300 MHz; $CDCl_3$): δ 0.83 (t, 3H, $^3J_{HH}$ 7.3, $CH_2CH_2CH_3$), 1.37 (sex, 2H, $^3J_{HH}$ 7.3, $CH_2CH_2CH_3$), 1.67 (br s, 1H, NH), 2.18 (s, 3H, CH_3), 2.44 (t, 2H, $^3J_{HH}$ 7.3, $CH_2CH_2CH_3$), 2.65 (dt, 2H, $^2J_{HP}$ 11.4, $^3J_{HH}$ 7.1, PCH_2), 2.86 (dt, 2H, $^3J_{HP}$ 12.0, $^3J_{HH}$ 7.1, CH_2N), 6.62 (d, 2H, $^3J_{HH}$ 8.0, H_{Ar}), 6.82 (d, 2H, $^3J_{HH}$ 8.0, H_{Ar}), 7.42-7.54 (m, 6H, Ph_2), 7.74-7.81 (m, 4H, Ph_2); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 11.57 ($CH_2CH_2CH_3$), 20.33 (CH_3), 22.93 ($CH_2CH_2CH_3$), 28.60 (d, $^1J_{CP}$ 72.7 Hz, PCH_2), 43.01 (d, $^2J_{CP}$ 2.2 Hz, CH_2N), 51.37 ($CH_2CH_2CH_3$), 122.52 (d, $^3J_{CP}$ 18.5 Hz, C_2), 125.94 (C_4), 128.61 (d, $^3J_{CP}$ 11.4 Hz, C_m), 129.16 (d, $^4J_{CP}$ 1.5 Hz, C_p), 130.78 (d, $^1J_{CP}$ 88.6 Hz, C_i), 131.43 (d, $^2J_{CP}$ 8.9 Hz, C_o), 131.45 (d, $^4J_{CP}$ 2.9 Hz, C_3), 148.37 (d, $^2J_{CP}$ 3.4 Hz, C_1); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 6.16.

4b (R^1 = 4-$CH_3C_6H_4$, R^2 = R^3 = H, R^4 = ^{i}Pr). Yellow oil (0.16 g, 95%); ν_{max}(film)/cm^{-1}: 3277, 1601, 1499, 1438, 1377, 1324, 1111, 813, 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 6H, $^3J_{HH}$ 6.2, $CH(CH_3)_2$], 1.46 (br s, 1H, NH), 2.18 (s, 3H, CH_3), 2.62 (dt, 2H,

$^{2}J_{HP}$ 11.2, $^{3}J_{HH}$ 7.2 Hz, PCH_2), 2.67 [sept, 1H, $^{3}J_{HH}$= 6.2 Hz, C*H*$(CH_3)_2$], 2.85 (dt, 2H, $^{3}J_{HP}$ 12.4, $^{3}J_{HH}$ 7.2, CH_2N), 6.62 (d, 2H, $^{3}J_{HH}$ 8.0, H_{Ar}), 6.81 (d, 2H, $^{3}J_{HH}$ 8.0, H_{Ar}), 7.43-7.53 (m, 6H, Ph_2), 7.75-7.80 (m, 4H, Ph_2); $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ 20.49 (CH_3), 22.74 [$CH(CH_3)_2$], 28.94 (d, $^{1}J_{CP}$ 73.1, PCH_2), 40.67 (d, $^{2}J_{CP}$ 1.8, CH_2N), 48.29 [*C*H$(CH_3)_2$], 122.65 (d, $^{3}J_{CP}$ 18.6, C_2), 126.13 (C_4), 128.78 (d, $^{3}J_{CP}$ 11.3, C_m), 129.33 (d, $^{4}J_{CP}$ 1.5, C_3), 130.91 (d, $^{1}J_{CP}$ 89.5, C_i), 131.60 (d, $^{2}J_{CP}$ 9.0, C_o), 131.63 (d, $^{4}J_{CP}$ 2.9, C_p), 148.50 (d, $^{2}J_{CP}$ 3.5, C_1); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 5.77; *m/z* (EI): 377 (M^+ + 1, 2%), 318 (35), 290 (100), 214 (60), 183 (80); HRMS (ESI): calcd for $C_{24}H_{30}N_2P$ [M + H]$^+$, 377.2141; found, 377.2144.

4c (R^1 = 4-$CH_3C_6H_4$, R^2 = R^3 = H, R^4 = ^{n}Bu). Yellow oil (0.17 g, 98%); ν_{max}(film)/cm^{-1}: 3278, 1601, 1501, 1480, 1433, 1322, 1108, 822, 740, 711, 693; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, 3H, $^{3}J_{HH}$ 7.1, $CH_2CH_2CH_2CH_3$), 1.25-1.33 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.46 (br s, 1H, NH), 2.18 (s, 3H, CH_3), 2.46 (t, 2H, $^{3}J_{HH}$ 6.8, $CH_2CH_2CH_2CH_3$), 2.65 (dt, 2H, $^{2}J_{HP}$ 11.1, $^{3}J_{HH}$ 7.1, PCH_2), 2.86 (dt, 2H, $^{3}J_{HP}$ 11.8, $^{3}J_{HH}$ 7.1, CH_2N), 6.62 (d, 2H, $^{3}J_{HH}$ 8.0, H_{Ar}), 6.82 (d, 2H, $^{3}J_{HH}$ 8.0, H_{Ar}), 7.43-7.53 (m, 6H, Ph_2), 7.75-7.81 (m, 4H, Ph_2); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 13.91 ($CH_2CH_2CH_2CH_3$), 20.33 (CH_3), 20.43 ($CH_2CH_2CH_2CH_3$), 28.59 (d, $^{1}J_{CP}$ 72.4, PCH_2), 32.02 ($CH_2CH_2CH_2CH_3$), 43.14 (d, $^{2}J_{CP}$ 1.5, CH_2N), 49.29 ($CH_2CH_2CH_2CH_3$), 122.62 (d, $^{3}J_{CP}$ 18.5, C_2), 126.13 (C_4), 128.73 (d, $^{3}J_{CP}$ 11.4, C_m), 129.28 (d, $^{4}J_{CP}$ 1.5, C_p), 130.89 (d_{right}, C_i), 131.54 (d, $^{2}J_{CP}$ 8.9, C_o), 131.58 (d, $^{4}J_{CP}$ 2.9, C_3), 148.42 (d, $^{2}J_{CP}$ 3.5, C_1); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 6.13; *m/z* (EI): 391 (M^+ + 1, 20%), 302 (92), 291 (73), 259 (85), 201 (100), 99 (99); HRMS (ESI): calcd for $C_{25}H_{32}N_2P$ [M + H]$^+$, 391.2298; found, 391.2303.

4d (R^1 = 4-$CH_3OC_6H_4$, R^2 = R^3 = H, R^4 = ^{n}Pr). See reference 8b.

4e (R^1 = 4-$CH_3OC_6H_4$, R^2 = R^3 = H, R^4 = ^{n}Bu). Yellow oil (0.18 g, 97%); ν_{max}(film)/cm^{-1}: 3297, 1500 , 1462, 1434, 1332, 1103, 825, 715, 693; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, 3H, $^{3}J_{HH}$ 7.1, $CH_2CH_2CH_2CH_3$), 1.18-1.38 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.61 (br s, 1H, NH), 2.47 (t, 2H, $^{3}J_{HH}$ 7.0, $CH_2CH_2CH_2CH_3$), 2.64 (dt, 2H, $^{2}J_{HP}$ 11.3, $^{3}J_{HH}$ 7.3, PCH_2), 2.86 (dt, 2H, $^{3}J_{HP}$ 11.9, $^{3}J_{HH}$ 7.3, CH_2N), 3.68 (s, 3H, OCH_3), 6.50 (d, 2H, $^{3}J_{HH}$ 9.5, H_{Ar}), 6.60 (d, 2H, $^{3}J_{HH}$ 9.5, H_{Ar}), 7.42-7.54 (m, 6H, Ph_2), 7.74-7.81 (m, 4H, Ph_2); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 13.83 ($CH_2CH_2CH_2CH_3$), 20.25 ($CH_2CH_2CH_2CH_3$), 28.48 (d, $^{1}J_{CP}$ 71.9, PCH_2), 31.95 ($CH_2CH_2CH_2CH_3$), 43.07 (CH_2N), 49.21 ($CH_2CH_2CH_2CH_3$), 55.39 (OCH_3), 114.18 (C_3), 123.18 (d, $^{3}J_{CP}$ 17.9, C_2), 128.64 (d,

$^{3}J_{CP}$ 11.2, C_m), 130.98 (d, $^{1}J_{CP}$ 90.3, C_i), 131.45 (d, $^{2}J_{CP}$ 8.2, C_o), 131.48 (d, $^{4}J_{CP}$ 2.7, C_p), 144.51 (d, $^{2}J_{CP}$ 2.9, C_1), 151.67 (C_4); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 5.61; *m/z* (EI): 407 (M^+ + 1, 9%), 307 (40), 302 (93), 259 (84), 201 (100), 183(43), 100 (99); HRMS (ESI): calcd for $C_{25}H_{32}N_2OP$ $[M + H]^+$, 407.2247; found, 407.2252.

4f (R^1 = 4-BrC_6H_4, R^2 = R^3 = H, R^4 = ^{i}Pr). Yellow oil (0.18 g, 92%); ν_{max}(film)/cm^{-1}: 3284, 1572, 1476 , 1432, 1321, 1107, 823, 746, 694; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 [d, 6H, $^{3}J_{HH}$ 6.2, $CH(CH_3)_2$], 1.51 (br s, 1H, NH), 2.54 (dt, 2H, $^{2}J_{HP}$ 11.3, $^{3}J_{HH}$ 7.2, PCH_2), 2.61 [sept, 1H, $^{3}J_{HH}$= 6.2 Hz, $CH(CH_3)_2$], 2.85 (dt, 2H, $^{3}J_{HP}$ 12.5, $^{3}J_{HH}$ 7.2, CH_2N), 6.56 (d, 2H, $^{3}J_{HH}$ 8.5, H_{Ar}), 7.06 (d, 2H, $^{3}J_{HH}$ 8.5, H_{Ar}), 7.44-7.57 (m, 6H, Ph_2), 7.69-7.79 (m, 4H, Ph_2); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 22.64 [$CH(CH_3)_2$], 28.84 (d, $^{1}J_{CP}$ 73.5, PCH_2), 40.46 (d, $^{2}J_{CP}$ 2.3, CH_2N), 48.18 [$CH(CH_3)_2$], 109.08 (C_4), 124.36 (d, $^{3}J_{CP}$ 18.8, C_2), 128.83 (d, $^{3}J_{CP}$ 11.4, C_m), 129.58 (d, $^{1}J_{CP}$ 90.0, C_i), 131.32 (d, $^{4}J_{CP}$ 1.5, C_3), 131.44 (d, $^{2}J_{CP}$ 9.1, C_o), 131.81 (d, $^{4}J_{CP}$ 2.8, C_p), 150.50 (d, $^{2}J_{CP}$ 3.4, C_1); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 7.77. *m/z* (EI): 441 (M^+ + 1, 2), 382 (18), 355 (76), 185 (100), 183 (84); HRMS (ESI): calcd for $C_{23}H_{27}BrN_2P$ $[M + H]^+$, 441.1090; found, 441.1092.

5a (R^1 = 4-$CH_3C_6H_4$, R^2 = C_6H_5, R^3 = H, R^4 = ^{n}Pr). Yellow oil (0.19 g, 95%); ν_{max}(film)/cm^{-1}: 3344, 1604, 1507, 1438, 1335, 1101, 754, 718; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.76 (t, 3H, $^{3}J_{HH}$ 7.3, $CH_2CH_2CH_3$), 1.33 (sex, 2H, $^{3}J_{HH}$ 7.3, $CH_2CH_2CH_3$), 2.17 (s, 3H, CH_3), 2.41-2.47 (m, 2H, $CH_2CH_2CH_3$), 3.23 (ddd, 1H, $^{2}J_{HH}$ 12.1, $^{3}J_{HH}$ 9.9, $^{3}J_{HP}$ 7.6, CH_AH_B), 3.42 (ddd, 1H, $^{2}J_{HH}$ 12.1, $^{3}J_{HP}$ 7.6, $^{3}J_{HH}$ 4.5 Hz, CH_AH_B), 3.84 (ddd, 1H, $^{2}J_{HP}$ 11.2, $^{3}J_{HH}$ 9.9, $^{3}J_{HH}$ 4.5, PCH), 6.58 (d, 2H, $^{3}J_{HH}$ 8.1, H_{Ar}), 6.79 (d, 2H, $^{3}J_{HH}$ 8.1, H_{Ar}), 7.15-7.27 (m, 9H, Ph + Ph_2), 7.28-7.38 (m, 1H, Ph_2), 7.45-7.60 (m, 3H, Ph_2), 7.80-7.90 (m, 2H, Ph_2) and not observable NH; $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ 11.66 ($CH_2CH_2CH_3$), 20.54 (CH_3), 22.94 ($CH_2CH_2CH_3$), 48.10 (d, $^{1}J_{CP}$ 76.2, PCH), 49.90 (CH_2N), 51.34 ($CH_2CH_2CH_3$), 123.10 (d, $^{3}J_{CP}$ 17.8, C_2), 125.91 (C_4), 127.38 (d, $^{5}J_{CP}$ 3.0, $C_{4'}$), 127.99 (d, $^{3}J_{CP}$ 11.3, C_m), 128.16 (d, $^{4}J_{CP}$ 2.4, $C_{3'}$), 128.62 (d, $^{1}J_{CP}$ 87.2, C_i), 128.82 (d, $^{3}J_{CP}$ 10.8, C_m), 129.16 (d, $^{4}J_{CP}$ 1.5, C_3), 130.11 (d, $^{1}J_{CP}$ 78.8, C_i), 130.28 (d, $^{3}J_{CP}$ 5.4, $C_{2'}$), 131.27 (d, $^{4}J_{CP}$ 2.8, C_p), 131.76 (d, $^{4}J_{CP}$ 2.8, C_p), 132.49 (d, $^{2}J_{CP}$ 8.4, C_o), 132.52 (d, $^{2}J_{CP}$ 8.5, C_o), 134.86 (d, $^{2}J_{CP}$ 5.6, $C_{1'}$) 148.59 (d, $^{2}J_{CP}$ 4.1, C_1); $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$): δ 8.44; *m/z* (EI): 453 (M^+ + 1, 9%), 452 (M^+, 19), 393 (96), 381 (95), 291 (100), 275 (53), 214 (69), 212 (56), 183 (63); HRMS (ESI): calcd for $C_{30}H_{34}N_2P$ $[M + H]^+$, 453.2454; found, 453.2459.

5b (R^1 = 4-BrC_6H_4, R^2 = C_6H_5, R^3 = H, R^4 = ^{n}Pr). Yellow oil (0.22 g, 96%); ν_{max}(film)/cm^{-1}: 3350, 1569, 1483, 1436, 1344, 1105 , 734, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.79 (t, 3H, $^3J_{HH}$= 7.4 Hz, $CH_2CH_2CH_3$), 1.37 (sex, 2H, $^3J_{HH}$ 7.3, $CH_2CH_2CH_3$), 2.42-2.55 (m, 2H, $CH_2CH_2CH_3$), 3.22 (ddd, 1H, $^2J_{HH}$ 12.1, $^3J_{HP}$ 7.8, $^3J_{HH}$ 4.7, CH_AH_B), 3.41 (ddd, 1H, $^2J_{HH}$ 12.1, $^3J_{HP}$ 9.5, $^3J_{HH}$ 9.5, CH_AH_B), 3.95 (br s, 1H, PCH), 6.50 (d, 2H, $^3J_{HH}$ 8.7, H_{Ar}), 7.02 (d, 2H, $^3J_{HH}$ 8.7, H_{Ar}), 7.07-7.22 (m, 9H, Ph + Ph_2), 7.36-7.39 (m, 1H, Ph_2), 7.49-7.59 (m, 3H, Ph_2), 7.80-7.85 (m, 2H, Ph_2) and not observable NH; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 11.62 ($CH_2CH_2CH_3$), 22.72 ($CH_2CH_2CH_3$), 47.39 (d, $^1J_{CP}$ 76.8, PCH), 49.60 (CH_2N), 51.13 ($CH_2CH_2CH_3$), 109.16 (C_4), 124.75 (d, $^3J_{CP}$ 18.0, C_2), 127.32 (d, $^1J_{CP}$ 86.7, C_i), 127.62 (d, $^5J_{CP}$ 2.8, $C_{4'}$), 128.18 (d, $^3J_{CP}$ 11.9, C_m), 128.25 (d, $^4J_{CP}$ 2.9, $C_{3'}$), 128.98 (d, $^3J_{CP}$ 11.1, C_m), 129.27 (d_{left}, C_i), 130.13 (d, $^3J_{CP}$ 5.4, $C_{2'}$), 131.26 (C_3), 131.70 (d, $^4J_{CP}$ 2.6, C_p), 132.14 (d, $^4J_{CP}$ 2.6, C_p), 132.44 (d, $^2J_{CP}$ 8.6, C_o), 132.60 (d, $^2J_{CP}$ 8.5, C_o), 134.22 (d, $^2J_{CP}$ 5.5, $C_{1'}$) 150.55 (d, $^2J_{CP}$ 1.6, C_1); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 9.80; *m/z* (EI): 518 (M^+ + 2, 81%), 517 (M^+ + 1, 75), 516 (M^+, 100), 183 (20), 132 (100); HRMS (ESI): calcd for $C_{29}H_{31}BrN_2P$ $[M + H]^+$, 517.1403; found, 517.1406.

5c (R^1 = 4-BrC_6H_4, R^2 = C_6H_5, R^3 = H, R^4 = ^{i}Pr). Yellow oil (0.23 g, 98%); ν_{max}(film)/cm^{-1}: 3350, 1573, 1450, 1438, 1340, 1103, 739, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 [d, 3H, $^3J_{HH}$ 6.6, $CH(CH_3)_2$], 0.90 [d, 3H, $^3J_{HH}$ 6.5, $CH(CH_3)_2$], 2.69 [m, 1H, $CH(CH_3)_2$], 3.23 (ddd, 1H, $^2J_{HH}$ 12.0, $^3J_{HP}$ 8.0, $^3J_{HH}$ 4.1, CH_AH_B), 3.36 (ddd, 1H, $^2J_{HH}$ 12.0, $^3J_{HH}$ 9.7, $^3J_{HP}$ 8.0, CH_AH_B), 3.80 (br s, 1H, PCH), 6.50 (d, 2H, $^3J_{HH}$ 8.6, H_{Ar}), 7.03 (d, 2H, $^3J_{HH}$ 8.6, H_{Ar}), 7.10-7.22 (m, 9H, Ph + Ph_2), 7.35-7.38 (m, 1H, Ph_2), 7.49-7.60 (m, 3H, Ph_2), 7.80-7.85 (m, 2H, Ph_2) and not observable NH; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.66 [$CH(CH_3)_2$], 22.84 [$CH(CH_3)_2$], 47.40 (CH_2N), 48.02 (d, $^1J_{CP}$ 77.9, PCH), 48.14 [$CH(CH_3)_2$], 109.03 (C_4), 124.90 (d, $^3J_{CP}$ 18.0, C_2), 127.42 (d_{right}, C_i), 127.61 (d, $^5J_{CP}$ 2.9, $C_{4'}$), 128.19 (d, $^3J_{CP}$ 11.3, C_m), 128.29 (d, $^4J_{CP}$ 2.4, $C_{3'}$), 128.99 (d, $^3J_{CP}$ 11.1, C_m), 129.74 (d_{left}, C_i), 130.24 (d, $^3J_{CP}$ 5.3, $C_{2'}$), 131.28 (d, $^4J_{CP}$ 1.0, C_3), 131.62 (d, $^4J_{CP}$ 2.6, C_p), 132.09 (d, $^4J_{CP}$ 2.7, C_p), 132.45 (d, $^2J_{CP}$ 8.8, C_o), 132.54 (d, $^2J_{CP}$ 9.4, C_o), 134.50 (d, $^2J_{CP}$ 5.6, $C_{1'}$) 150.70 (d, $^2J_{CP}$ 4.2, C_1); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 9.12; *m/z* (EI): 518 (M^+ + 2, 61%), 517 (M^+ + 1, 30), 516 (M^+, 100), 501 (96), 356 (51), 183 (66), 162 (100); HRMS (ESI): calcd for $C_{29}H_{31}BrN_2P$ $[M + H]^+$, 517.1403; found, 517.1404.

5d (R^1 = 4-BrC_6H_4, R^2 = C_6H_5, R^3 = H, R^4 = ^{n}Bu). Yellow oil (0.2 g, 97%); ν_{max}(film)/cm^{-1}: 3293, 1577, 1456, 1341, 1105, 1069, 1037, 1022, 999; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, 3H, $^3J_{HH}$ 7.3, $CH_2CH_2CH_2CH_3$), 1.42-1.50 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.47-2.59 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.71 (t, 2H, $^3J_{HH}$ 6.9, $CH_2CH_2CH_2CH_3$), 3.22 (ddd, 1H, $^2J_{HH}$ 12.1, $^3J_{HP}$ 7.9, $^3J_{HH}$ 6.2, CH_AH_B), 3.42 (ddd, 1H, $^2J_{HH}$ 12.1, $^3J_{HP}$ 9.8, $^3J_{HH}$ 8.2 , CH_AH_B), 3.99 (br s, 1H, CHP), 6.49 (d, 2H, $^3J_{HH}$ 8.7, H_{Ar}), 7.02 (d, 2H, $^3J_{HH}$ 8.7, H_{Ar}), 7.14-7.24 (m, 9H, Ph + Ph_2), 7.37-7.41 (m, 1H, Ph_2), 7.50-7.61 (m, 3H, Ph_2), 7.81-7.84 (m, 2H, Ph_2) and not observable NH; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.89 ($CH_2CH_2CH_2CH_3$), 20.32 ($CH_2CH_2CH_2CH_3$), 31.62 ($CH_2CH_2CH_2CH_3$), 47.17 (d, $^1J_{CP}$ 76.7, PCH), 48.97 (CH_2N), 49.65 ($CH_2CH_2CH_2CH_3$), 109.30 (C_4), 124.72 (d, $^3J_{CP}$ 17.9, C_2), 127.11 (d, $^1J_{CP}$ 85.5, C_i), 127.67 (d, $^5J_{CP}$ 2.9, $C_{4'}$), 128.22 (d, $^3J_{CP}$ 11.8, C_m), 128.29 (d, $^4J_{CP}$ 2.9, $C_{3'}$), 129.02 (d, $^3J_{CP}$ 11.1, C_m), 129.15 (d_{left}, C_i), 130.13 (d, $^3J_{CP}$ 5.3, $C_{2'}$), 131.30 (C_3), 131.79 (d, $^4J_{CP}$ 2.6, C_p), 132.21 (d, $^4J_{CP}$ 2.7, C_p), 132.49 (d, $^2J_{CP}$ 8.6, C_o), 132.69 (d, $^2J_{CP}$ 8.5, C_o), 134.13 (d, $^2J_{CP}$ 5.3, $C_{1'}$) 150.21 (d, $^2J_{CP}$ 4.2, C_1); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 10.73; *m/z* (EI): 532 (M^+ + 2, 73%), 531 (M^+ + 1, 60), 530 (M^+, 100), 458 (96), 201 (45), 183 (98); HRMS (ESI): calcd for $C_{30}H_{33}BrN_2P$ $[M + H]^+$, 531.1559; found, 531.1559.

6a (R^1 = 4-$CH_3C_6H_4$, R^2 = H, R^3 = CH_3, R^4 = ^{n}Pr). Yellow oil (017 g, 97%); ν_{max}(film)/cm^{-1}: 3257, 1607, 1504, 1437, 1326, 737, 696 ; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85 (t, 3H, $^3J_{HH}$ 7.3, $CH_2CH_2CH_3$), 1.07 (dd, 3H, $^3J_{HH}$ 6.2, $^4J_{HP}$ 1.4, CH_3CH), 1.30-1.42 (m, 2H, $CH_2CH_2CH_3$), 2.17 (s, 3H, CH_3), 2.22-2.35 (m, 2H, $CH_2CH_2CH_3$), 2.42-2.52 (m, 1H, PCH), 2.62-3.01 (m, 3H, PCH + CH_3CHN + NH), 6.60 (d, 2H, $^3J_{HH}$ 8.0, H_{Ar}), 6.81 (d, 2H, $^3J_{HH}$ 8.0, H_{Ar}), 7.42-7.50 (m, 6H, Ph_2), 7.74-7.83 (m, 4H, Ph_2); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 11.95 ($CH_2CH_2CH_3$), 20.52 (CH_3), 22.58 (d, $^3J_{CP}$ 12.7, CH_3CH), 23.19 ($CH_2CH_2CH_3$), 35.54 (d, $^1J_{CP}$ 75.2, PCH_2), 49.05 (d, $^2J_{CP}$ 3.5, CH_3CH), 49.17 ($CH_2CH_2CH_3$), 122.62 (d, $^3J_{CP}$ 18.7, C_2), 126.22 (C_4), 128.78 (d, $^3J_{CP}$ 11.4, C_m), 128.85 (d, $^3J_{CP}$ 11.1, C_m), 129.50 (d, $^4J_{CP}$ 1.6, C_3), 130.45 (d, $^1J_{CP}$ 78.7, C_i), 131.33 (d, $^2J_{CP}$ 9.3, C_o), 131.47 (d, $^1J_{CP}$ 85.2, C_i), 131.65 (d, $^4J_{CP}$ 3.2, 2 C_p), 131.94 (d, $^2J_{CP}$ 9.0, C_o), 148.24 (d, $^2J_{CP}$ 3.9, C_1); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 6.78; *m/z* (EI): 391 (M^+ + 1, 15%), 390 (M^+, 10), 291 (100), 183 (43), 105 (41).

6b (R^1 = 4-$CH_3C_6H_4$, R^2 = H, R^3 = CH_3, R^4 = ^{n}Bu). Yellow oil (0.17 g, 92%); ν_{max}(film)/cm^{-1}: 3417, 1614, 1504, 1438, 1315, 1108, 751, 715; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77 (t, 3H, $^3J_{HH}$ 7.1, $CH_2CH_2CH_2CH_3$), 0.96 (dd, 3H, $^3J_{HH}$ 6.3 Hz, $^4J_{HP}$ 1.3

Hz, C*H*$_3$CH), 1.13-1.26 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.75 (s, 3H, CH$_3$), 2.17-2.25 (m, 2H, CH$_3$CH$_2$CH$_2$C*H*$_2$), 2.36-2.42 (m, 1H, PCH), 2.56-2.65 (m, 1H, PCH), 2.79-2.89 (m, 1H, CH$_3$C*H*N), 6.51 (d, 2H, $^3J_{HH}$ 8.4, H$_{Ar}$), 6.71 (d, 2H, $^3J_{HH}$ 8.4, H$_{Ar}$), 7.35-7.42 (m, 6H, Ph$_2$), 7.65-7.72 (m, 4H, Ph$_2$) and not observable NH; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.77 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 20.20 (CH$_3$), 20.32 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 22.41 (d, $^3J_{CP}$ 12.5, *C*H$_3$CH), 31.92 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 35.24 (d, $^1J_{CP}$ 74.5, PCH$_2$), 48.09 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 48.65 (d, $^2J_{CP}$ 3.3, CH$_3$*C*H), 122.39 (d, $^3J_{CP}$ 19.0, C$_2$), 125.68 (C$_4$), 128.47 (d, $^3J_{CP}$ 11.3, C$_m$), 128.54 (d, $^3J_{CP}$ 11.1, C$_m$), 129.03 (d, $^4J_{CP}$ 1.1, C$_3$), 129.95 (d$_{right}$, C$_i$), 131.16 (d, $^2J_{CP}$ 9.1, C$_o$), 131.45 (d, $^4J_{CP}$ 2.5, 2 C$_p$), 131.60 (d, $^2J_{CP}$ 8.8, C$_o$), 131.86 (d$_{left}$, C$_i$), 148.24 (d, $^2J_{CP}$ 3.7, C$_1$) ; ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 5.13; HRMS (ESI): calcd for C$_{26}$H$_{34}$N$_2$P [M + H]$^+$, 405.2454; found, 405.2457.

6c (R^1 = 4-CH$_3$OC$_6$H$_4$, R^2 = H, R^3 = CH$_3$, R^4 = ^{n}Pr). Yellow oil (0.17 g, 93%); ν_{max}(film)/cm^{-1}: 3258, 1614, 1500, 1438, 1314, 1111, 826, 747, 716; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.77 (t, 3H, $^3J_{HH}$ 7.4, CH$_2$CH$_2$C*H*$_3$), 0.98 (dd, 3H, $^3J_{HH}$ 6.3, $^4J_{HP}$ 1.3, C*H*$_3$CH), 1.21-1.33 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 2.18-2.26 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 2.56-2.66 (m, 2H, PCH$_2$), 2.85-2.87 (m, 1H, CH$_3$C*H*N), 3.61 (s, 3H, OCH$_3$), 6.52-6.55 (m, 4H, H$_{Ar}$), 7.38-7.46 (m, 6H, Ph$_2$), 7.66-7.71 (m 4H, Ph$_2$) and not observable NH; ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 11.84 (CH$_2$CH$_2$C*H*$_3$), 22.53 (d, $^3J_{CP}$ 12.7, *C*H$_3$CH), 23.09 (CH$_2$*C*H$_2$CH$_3$), 35.30 (d, $^1J_{CP}$ 74.1, PCH$_2$), 48.74 (d, $^2J_{CP}$ 3.2, CH$_3$*C*H), 49.01 (*C*H$_2$CH$_2$CH$_3$), 55.42 (OCH$_3$), 114.17 (C$_3$), 123.08 (d, $^3J_{CP}$ 18.5, C$_2$), 128.61 (d, $^3J_{CP}$ 11.1, C$_m$), 128.69 (d, $^3J_{CP}$ 11.0, C$_m$), 129.82 (d$_{right}$, C$_i$), 131.43 (d, $^2J_{CP}$ 9.4, C$_o$), 131.55 (d, $^4J_{CP}$ 3.9, 2 C$_p$), 131.70 (d, $^1J_{CP}$ 85.0, C$_i$), 131.95 (d, $^2J_{CP}$ 9.1, C$_o$), 144.51 (d, $^2J_{CP}$ 3.7, C$_1$), 151.55 (C$_4$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 4.60; HRMS (ESI): calcd for C$_{25}$H$_{32}$N$_2$P [M + H]$^+$, 407.2247; found, 407.2251.

6d (R^1 = 4-CH$_3$OC$_6$H$_4$, R^2 = H, R^3 = CH$_3$, R^4 = ^{n}Bu). Yellow oil (0.14 g, 92%); ν_{max}(film)/cm^{-1}: 3418, 1614, 1500, 1438, 1316, 1028, 826, 750, 717, 698; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.78 (t, 3H, $^3J_{HH}$ 7.1, CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.97 (dd, 3H, $^3J_{HH}$ 6.3, $^4J_{HP}$ 1.3, C*H*$_3$CH), 1.13-1.27 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 2.19-2.26 (m, 3H, PCH + C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.57-2.67 (m, 1H, PCH), 2.81-2.89 (m, 1H, CH$_3$C*H*N), 3.60 (s, 3H, OCH$_3$), 6.50-6.56 (m, 4H, H$_{Ar}$), 7.35-7.44 (m, 6H, Ph$_2$), 7.66-7.73 (m 4H, Ph$_2$) and not observable NH; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.96 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 20.47 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 22.60 (d, $^3J_{CP}$ 12.5, *C*H$_3$CH), 32.13 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 35.32 (d, $^1J_{CP}$ 73.5, PCH$_2$), 48.33 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 48.85 (d, $^2J_{CP}$ 2.8, CH$_3$*C*H), 55.49 (OCH$_3$),

114.24 (d, $^4J_{HH}$ 1.2, C_3), 123.16 (d, $^3J_{CP}$ 18.5, C_2), 128.67 (d, $^3J_{CP}$ 11.3, C_m), 128.76 (d, $^3J_{CP}$ 11.1, C_m), 130.85 (d, $^1J_{CP}$ 92.3, C_i), 131.37 (d, $^2J_{CP}$ 9.0, C_o), 131.50 (d, $^4J_{CP}$ 2.7, 2 C_p), 131.79 (d, $^2J_{CP}$ 8.9, C_o), 131.80 (d, $^1J_{CP}$ 85.2, C_i), 144.56 (d, $^2J_{CP}$ 3.6, C_1), 151.63 (C_4); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 4.53; HRMS (ESI): calcd for $C_{26}H_{35}N_2OP$ [M + H]$^+$, 421.2403; found, 421.2407.

General procedure for the synthesis of compounds 10 and 11. A mixture of the *N*-4-tolyl-*P*,*P*-diphenyl-*P*-alkenyl iminophosphorane **2** or **3** (0.45 mmol) and (±)-α-methylbenzylamine (2 equiv, 0.9 mmol) was heated for 18 h. The reaction crude was chromatographed on silica gel deactivated with 5% Et_3N in *n*-hexane (elution with AcOEt) to give **10** or **11**.

10 (R^1 = 4-$CH_3C_6H_4$, R^2 = Ph, R^3 = H). Yield of diastereoisomers mixture: 0.2 g (85%), dr (*l*/*u*): 1/1. Colourless oil. ν_{max}(film)/cm^{-1}: 3232, 1605, 1505, 1438, 1332, 1113, 906, 840, 733; ^1H NMR (300 MHz; $CDCl_3$): δ 1.18 [d, 3H, $^3J_{HH}$ 6.6, C*H*$_3$CH (*l* or *u*)], 1.21 [d, 3H, $^3J_{HH}$ 6.6, C*H*$_3$CH (*l* or *u*)], 2.16 [s, 3H, CH_3 (*l* or *u*)], 2.17 [s, 3H, CH_3 (*l* or *u*)], 3.10-3.29 [m, 4H, CH_2N (*l* and *u*)], 3.64 [q, 1H, $^3J_{HH}$ 6.6, CH_3C*H* (*l* or *u*)], 3.69 [q, 1H, $^3J_{HH}$ 6.6, CH_3C*H* (*l* or *u*)], 3.72-3.90 (m, 2H, CHP (*l* and *u*)], 6.51 [d, 4H, $^3J_{HH}$ 8.1, H_{Ar} (*l* and *u*)], 6.74-6.78 [m, 4H, H_{Ar} (*l* and *u*)], 6.98-7.02 [m, 5H, Ph (*l* and *u*)], 7.07-7.24 [m, 21H, Ph + Ph_2P (*l* and *u*)], 7.24-7.52 [m, 10H, Ph_2P (*l* and *u*)], 7.65-7.74 (m, 4H, Ph_2P (*l* and *u*)]; $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ 20.55 [CH_3 (*l* and *u*)], 24.26 [*C*H$_3$CH (*l* or *u*)], 24.49 [*C*H$_3$CH (*l* or *u*)], 47.61 [CH_2N (*l* or *u*)], 47.76 [d, $^1J_{CP}$ 74.4, CHP (*l* or *u*)], 48.41 [d, $^1J_{CP}$ 75.0, CHP (*l* or *u*)], 48.63 [CH_2N (*l* or *u*)], 57.21 [CH_3*C*H (*l* or *u*)], 58.17 [CH_3*C*H (*l* or *u*)], 123.07 [d, $^3J_{CP}$ 16.8, C_2 (*l* and *u*)], 125.96 [C_4 (*l* and *u*)], 126.64-128.78 [aromatics (*l* and *u*)], 129.18 [C_3 (*l* and *u*)], 130.39 [br s, $C_{2'}$ (*l* and *u*)], 131.28 [C_p (*l* or *u*)], 131.62 [C_p (*l* or *u*)], 132.42-132.78 [C_o (*l* and *u*)], 134.86 [d, $^2J_{CP}$ 5.2, $C_{1'}$ (*l* or *u*)], 135.35 [d, $^2J_{CP}$ 5.6, $C_{1'}$ (*l* or *u*)], 145.10 [$C_{1''}$ (*l* or *u*)], 145.53 [$C_{1''}$ (*l* or *u*)], 148.52 [C_1 (*l* and *u*)]; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 7.55 (*l* or *u*), 8.14 (*l* or *u*); *m/z* (EI): 515 (M$^+$ + 1, 5), 514 (M$^+$, 10), 393 (92), 381 (93), 291 (100), 275 (44), 214 (60), 212 (48), 185 (44), 183 (48).

11 (R^1 = 4-$CH_3C_6H_4$, R^2 = H, R^3 = CH_3). Yield of diastereoisomers mixture: 0.19 g (94%), dr (*l*/*u*): 2/3.

l-***11***: Yield: 0.06 g (30%); ν_{max}(film)/cm^{-1}: 3270, 1606, 1506, 1436, 1327, 1107, 816, 733, 695; ^1H NMR (300 MHz; $CDCl_3$): δ 0.91 (dd, 3H, $^3J_{HH}$ 6.2, $^4J_{HP}$ 1.0, C*H*$_3$CHCH$_2$P), 1.20 (d, 3H, $^3J_{HH}$ 6.6, C*H*$_3$CHPh), 2.18 (s, 3H, CH_3), 2.35 (ddd, 1H, $^2J_{HH}$

14.8, $^{2}J_{HP}$ 9.8, $^{3}J_{HH}$ 5.0, C*H*$_A$H$_B$), 2.71 (ddd, 1H, $^{2}J_{HH}$ 14.8, $^{2}J_{HP}$ 12.0, $^{3}J_{HH}$ 7.0, CH$_A$*H*$_B$), 2.98 [m, 1H, NC*H*(CH$_3$)CH$_2$P], 3.65 [q, 1H, $^{3}J_{HH}$ 6.6, NC*H*(CH$_3$)Ph], 6.61 (d, 2H, $^{3}J_{HH}$ 8.0, H$_{Ar}$), 6.81 (d, 2H, $^{3}J_{HH}$ 8.0, H$_{Ar}$), 7.04-7.29 (m, 5H, Ph), 7.37-7.54 (m, 6H, PPh$_2$), 7.72-7.81 (m, 4H, PPh$_2$); ^{13}C{^{1}H} NMR (75 MHz; CDCl$_3$): δ 20.55 (CH$_3$), 23.64 (d, $^{3}J_{CP}$ 10.4, *C*H$_3$CHCH$_2$P), 24.05 (*C*H$_3$CHPh), 35.84 (d, $^{1}J_{CP}$ 73.1, CH$_2$P), 47.36 (d, $^{2}J_{CP}$ 2.3, *C*HCH$_2$P), 56.02 (*C*HPh), 122.80 (d, $^{3}J_{CP}$ 19.1, C$_2$), 126.08 (C$_4$), 126.58 (2 signals), 128.29, 128.81 (d, $^{3}J_{CP}$ 11.0, 2 C$_m$), 129.42 (C$_3$), 130.33 (d, $^{1}J_{CP}$ 79.5, C$_i$), 131.59 (br s, 2 C$_p$), 131.65 (d, $^{2}J_{CP}$ 9.3, C$_o$), 131.69 (d, $^{1}J_{CP}$ 88.6, C$_i$), 131.87 (d, $^{2}J_{CP}$ 9.3, C$_o$), 146.73 (C$_{1'}$), 148.61 (d, $^{2}J_{CP}$ 2.9, C$_1$); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 4.75; *m/z* (EI): 452 (M$^+$, 2), 331 (11), 305 (15), 304 (26), 291 (100), 290 (43), 185 (16), 183 (34).

u-***11***: Yield: 0.11 g (54%); ν_{max}(film)/cm^{-1}: 3249, 1606, 1506, 1437, 1331, 1108, 910, 822, 733, 693; ^{1}H NMR (300 MHz; CDCl$_3$): δ 0.99 (dd, 3H, $^{3}J_{HH}$ 6.0, $^{4}J_{HP}$ 1.7, C*H*$_3$CHCH$_2$P), 1.28 (d, 3H, $^{3}J_{HH}$ 6.6, C*H*$_3$CHPh), 2.18 (s, 3H, CH$_3$), 2.19-2.24 (m, 1H, C*H*$_A$H$_B$), 2.66-2.80 [m, 2H, CH$_A$*H*$_B$ + NC*H*(CH$_3$)CH$_2$P], 3.77 [q, 1H, $^{3}J_{HH}$ 6.6, NC*H*(CH$_3$)Ph], 6.62 (d, 2H, $^{3}J_{HH}$ 8.0, H$_{Ar}$), 6.83 (d, 2H, $^{3}J_{HH}$ 8.0, H$_{Ar}$), 7.12-7.28 (m, 5H, Ph), 7.31-7.50 (m, 6H, PPh$_2$), 7.57-7.73 (m, 4H, PPh$_2$); ^{13}C{^{1}H} NMR (75 MHz; CDCl$_3$): δ 20.56 (CH$_3$), 22.18 (d, $^{3}J_{CP}$ 15.1, *C*H$_3$CHCH$_2$P), 25.08 (*C*H$_3$CHPh), 36.71 (d, $^{1}J_{CP}$ 78.3, CH$_2$P), 45.46 (d, $^{2}J_{CP}$ 4.1, *C*HCH$_2$P), 55.01 (*C*HPh), 122.62 (d, $^{3}J_{CP}$ 19.1, C$_2$), 126.13 (C$_4$), 126.50, 126.93, 128.32, 128.59 (d, $^{3}J_{CP}$ 11.6, C$_m$), 128.87 (d, $^{3}J_{CP}$ 11.0, C$_m$), 129.45 (C$_3$), 130.25 (d, $^{1}J_{CP}$ 90.4, C$_i$), 131.46 (d, $^{2}J_{CP}$ 8.7, C$_o$), 131.47 (br s, C$_p$), 131.58 (br s, C$_p$), 131.83 (d, $^{1}J_{CP}$ 79.6, C$_i$), 132.13 (d, $^{2}J_{CP}$ 9.3, C$_o$), 145.35 (C$_{1'}$), 148.49 (d, $^{2}J_{CP}$ 4.1, C$_1$); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 6.20; *m/z* (EI): 452 (M$^+$, 1), 331 (9), 305 (15), 304 (28), 291 (100), 290 (39), 185 (19), 183 (31).