Supporting Information

**General procedure for the synthesis of ureaphosphines.** 5 mmol (1 equiv) of aminophosphine was dissolved in 40 mL CH$_2$Cl$_2$. To this vigorously stirred solution was added 5.5 mmol (1.1 equiv) of isocyanate. The reaction mixture was stirred for 2 h. Solvents were evaporated in vacuo to provide the crude product, which was washed with hexanes (3 x). Remaining solvents were evaporated in vacuo and the product was obtained in quantitative yield (>95% purity).

1-(2-(diphenylphosphino)ethyl)-3-phenylurea (L1). White powder. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 2.28 (t, 2H, CH$_2$CH$_2$NH, $J = 7.2$ Hz), 3.4 (m, 2H, CH$_2$NH), 5.4 (t, 1H, NHCH$_2$, $J = 5.5$ Hz), 6.93 (s, 1H, NHPh), 7.02 (t, 1H, ArH, $J = 6.9$ Hz), 7.1-7.4 (m, 14H, ArH). $^{31}$P($^1$H) NMR (CDCl$_3$, 121.5 MHz) $\delta$ -20.316. $^{13}$C($^1$H) NMR (CDCl$_3$, 125.7 MHz) $\delta$ 29.248 (d, $J_{C-P} = 12.8$ Hz, CH$_2$), 37.500 (d, $J_{C-P} = 21.5$ Hz, CH$_2$), 120.703, 123.421, 128.600, 128.654, 128.831, 129.201, 132.695, 132.844, 137.791, 137.885, 138.849, 156.335 (NHC-NH). HRMS (FAB$^+$): $m/z$ calculated for C$_{21}$H$_{22}$ON$_2$P ([MH]$^+$): 349.1470; observed: 349.1471. Solution IR (20 mM, CDCl$_3$), $\nu$ = 3432 cm$^{-1}$ (NH band), 1672 cm$^{-1}$ (CO urea band).

1-((1S,2S)-2-(diphenylphosphino)-1,2-diphenylethyl)-3-phenyl urea (L2). White powder. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 4.17 (t, 1H, CH, $J = 5.1$ Hz), 5.21 (d, 1H, CH-NH, $J = 8.4$ Hz), 5.48 (m, 1H, CH), 6.27 (s, 1H, NH-Ph), 6.8-8.0 (m, 25H, ArH). $^{31}$P($^1$H) NMR (CDCl$_3$, 121.5 MHz) $\delta$ -9.949. $^{13}$C($^1$H) NMR (CDCl$_3$, 75.7 MHz) $\delta$ 50.931, 51.158, 56.415, 56.690, 121.103, 123.836, 126.942, 127.686, 127.913, 128.100, 128.107, 128.479, 129.223, 129.369, 129.886, 131.019, 131.132, 133.510, 136.664, 136.858, 136.971, 138.573, 139.980, 140.029, 154.765 (NHC-NH). HRMS (FAB$^+$): $m/z$ calculated for C$_{33}$H$_{30}$N$_2$OP ([MH]$^+$): 501.2096; observed: 501.2091.

1-(2((11bS)-3H-dinaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl)ethyl)-3-phenylurea (L3). White powder. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.38 (m, 1H, CH$_2$), 1.62 (m, 1H, CH$_2$), 2.11 (m, 1H, CH$_2$), 2.44 (m, 1H, CH$_2$), 2.51 (m, 1H, CH$_2$), 2.69 (m, 1H, CH$_2$), 3.38 (m, 2H, CH$_2$), 5.71 (t, 1H, NHCH$_2$, $J = 5.4$ Hz), 6.97 (t, 1H, ArH, $J = 7.5$ Hz), 7.2-7.6 (m, 13H, 12 ArH + 1 NHPh), 7.8-8.0 (m, 4H, ArH). $^{31}$P($^1$H) NMR (CDCl$_3$, 202.3 MHz) $\delta$ -0.518. $^{13}$C($^1$H) NMR (CDCl$_3$, 125.7 MHz) $\delta$ 27.289 (d, $J_{C-P} = 18.1$ Hz), 28.876 (d, CH$_2$, $J_{C-P} = 19.6$ Hz), 31.856 (d, CH$_2$, $J_{C-P} = 14.6$ Hz), 37.324 (d, CH$_2$, $J_{C-P} = 19.2$ Hz), 120.609, 123.423, 125.048, 125.105, 126.027, 126.084, 126.669, 126.724, 127.057, 127.970, 128.046, 128.299, 128.407, 129.269, 132.176, 132.259, 132.373, 132.750, 132.944, 133.028, 133.421, 134.415, 136.664, 136.858, 136.971, 137.084, 138.573, 139.980, 140.029, 154.765 (NHC-NH). HRMS (FAB$^+$): $m/z$ calculated for C$_{31}$H$_{28}$ON$_2$P ([MH]$^+$): 475.1939; observed: 475.1938.
1-((1S,2S)-2-((11bS)-3H-dinaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl)-1,2-diphenylethyl)-3-phenylurea (L4). White powder. 1H NMR (CDCl$_3$, 500 MHz) δ 1.83 (s, 2H, CH$_2$), 2.46 (m, 1H, CH$_2$), 2.61 (m, 1H, CH$_2$), 3.11 (t, 1H, CH, $J = 5$ Hz), 5.63 (m, 1H, CH), 6.26 (d, 1H, N-HCH, $J = 8.5$ Hz), 6.69 (s, 1H, NHPh), 7.0-8.0 (m, 27H, ArH).

31P{1H} NMR (CDCl$_3$, 202.3 MHz) δ 8.016.

13C{1H} NMR (CDCl$_3$, 125.7 MHz) δ 29.405 (d, CH$_2$, $J_{CP} = 24$ Hz), 30.859 (d, CH$_2$, $J_{CP} = 15.6$ Hz), 49.440 (d, CH, $J_{CP} = 23.3$ Hz), 57.405 (d, CH, $J_{CP} = 20.2$ Hz), 121.504, 124.016, 125.047, 125.188, 124.245, 126.054, 126.138, 126.950, 126.987, 127.034, 127.347, 127.703, 128.159, 128.210, 128.522, 129.865, 126.183, 132.299, 132.585, 132.954, 133.307, 133.558, 134.908, 138.034, 138.823, 141.318, 155.622 (NHC=ONH). HRMS (FAB$^+$): $m/z$ calculated for C$_{43}$H$_{36}$ON$_2$P ([MH]$^+$): 627.2565; observed: 627.2577.

[Rh(L1-κ$^2$O,P)(ndbd)]BF$_4$. To a Schlenk flask filled with equimolar amounts of L1 and [Rh(ndbd)$_2$]BF$_4$ was added CH$_2$Cl$_2$. After five minutes of vigorous stirring, solvents were evaporated in vacuo. The complex was used without further purification. Yellow powder. 1H NMR (CDCl$_3$, 500 MHz) δ 1.44 (s, 2H, Rh-ndbd), 2.58 (t, 2H, CH$_2$CH$_2$NH, $J = 10$ Hz), 3.26 (s, 2H, Rh-ndbd), 3.84 (m, 2H, CH$_2$NH), 3.92 (s, 2H, Rh-ndbd), 5.35 (s, 2H, Rh-ndbd), 6.68 (t, 1H, CH$_3$NH, $J = 5.5$ Hz), 7.1-7.6 (m, 15H, ArH), 7.71 (s, 1H, NHPh). 31P{1H} NMR (CDCl$_3$, 202.3 MHz) δ 31.4 (d, $J_{P-Rh} = 170$ Hz). 13C{1H} NMR (CDCl$_3$, 125.7 MHz) δ 29.476, 29.668, 39.066, 51.9981, 64.116, 90.512, 120.729, 124.234, 128.648, 128.813, 129.010, 129.286, 129.369, 131.435, 132.657, 132.754, 137.365, 161.506 (NHC=ONH). HRMS (FAB$^+$): $m/z$ calculated for C$_{28}$H$_{29}$N$_2$OPRh ([MH]$^+$): 543.1073; observed: 543.1074. Solution IR (20 mM, CDCl$_3$), $\nu = 1572$ cm$^{-1}$ (CO$_2$urea band).

**General procedure hydrogenation experiments.** Substrates S1, S2, S3, S4 and S5 were prepared according to published procedures. The hydrogenation experiments were carried out in an Accelerator SLT workstation of Chemspeed Technologies under inert conditions. The reaction mixtures were beforehand prepared *in situ* by addition of CH$_2$Cl$_2$ to a Schlenk flask filled with the appropriate amounts of metal precursor, ligand and substrate. The reaction mixtures were subsequently injected manually into a reaction vial of the Accelerator SLT workstation. Next, the automated program of the Accelerator SLT workstation was started, putting the reaction mixtures under an atmosphere of dihydrogen and mixing the reaction mixtures by vortex shaking. Product samples were prepared directly after completion of the program. S1, S2 and S5 were analyzed using an Interscience Trace GC Ultra (FID detector, CP-Chiralsil-DexCB column). S3 and S4 were analyzed using a Shimadzu 10A
HPLC, equipped with a UV-detector (Column: Chiralpak AD, eluent: n-hexane:isopropyl alcohol = 90:10, flow rate: 0.6 ml.min\(^{-1}\)).

**DFT calculations.** The geometry optimizations were carried out with the Turbomole program\(^4\) coupled to the PQS Baker optimizer.\(^5\) Geometries were fully optimized at the BP86\(^6\) level using the SV(P) basis set\(^7\) on all atoms (small-core pseudopotential\(^8\) on rhodium).

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