Appendix

1 Materials and methods

1.1 Chemistry section

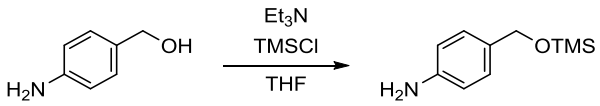
1.1.1 Equipments

1.1.1.1 Nuclear magnetic resonance

All ^{1}H and ^{13}C-NMR spectra were recorded on Bruker 300 or 500 spectrometer. ^{1}H-NMR and ^{13}C-NMR chemical shifts are reported on the scale in ppm relative to TMS (0 ppm), $CDCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C) or CD_2Cl_2 (5.32 ppm). Spectral features were designed as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad.

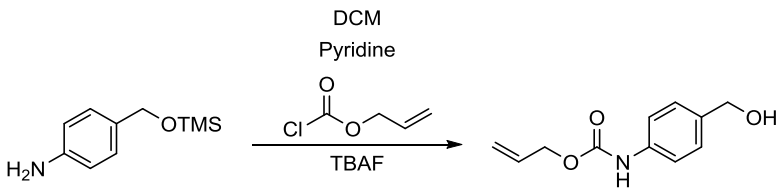
1.1.2 Synthesis of fluorogenic substrates

1.1.2.1 Umbelliferon prodrug



4-(((trimethylsilyl)oxy)methyl)aniline was synthesized following a routine procedure. A flame-dried round bottom flask is filled with 4-aminobenzyl alcohol (248 mg, 2 mmol) under Ar. Then, 4 mL distilled THF (0.5 M) is added by syringe. The flask is then submerged in an ice bath to cool the mixture to 0 °C. Then, NEt_3 (0.56 mL, 2 equiv. 4 mmol) is added by syringe, followed immediately by TMSCl (0.29 mL, 1.2 equiv., 2.3 mmol) dropwise. The ice bath is removed and the reaction is stirred overnight at room temperature. On the next day, the mixture is filtered on a celite pad to remove the ammonium salt and is concentrated under vacuum to yield the desired product as an orange oil. Yield = 350 mg, 74%. No purification, the crude is used in the next step immediately.

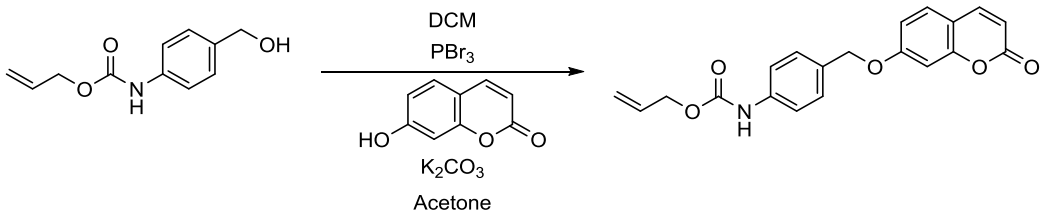
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.63 (s, 2H), 0.14 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.71, 131.12, 128.43, 115.14, 64.82, -0.15.



allyl (4-(hydroxymethyl)phenyl)carbamate was synthesized following a routine procedure. A round bottom flask containing the crude starting material (350 mg, 1.47 mmol) was purged with argon. Then, 5 mL of distilled DCM (0.3 M) is added by syringe. Brown solution. Then, the flask is

then submerged in an ice bath to cool the mixture to 0 °C. Then, pyridine (0.24 mL, 2 equiv. 2.94 mmol) is added by syringe, followed immediately by allyl chloroformate (178 µL, 1.62 mmol, 1.1 equiv.) under argon. The ice bath is removed and the reaction is stirred overnight at room temperature. On the next day, TBAF (1 M in THF, 1.7 mL, 1.2 equiv.) is added dropwise and the solution is stirred for 1 hour at RT. Then, EtOAc is added and the solution is washed twice with HCl 1 M and then twice with $NaHCO_3$ saturated. After drying with Na_2SO_4, the volume is reduced to a minimum. The crude brown oil is filtered on a silicagel pad to yield a pale orange solid which is pure enough for the next step.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.72 (s, 1H), 5.97 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.66 (dt, *J* = 5.7, 1.4 Hz, 2H), 4.64 (s, 2H).



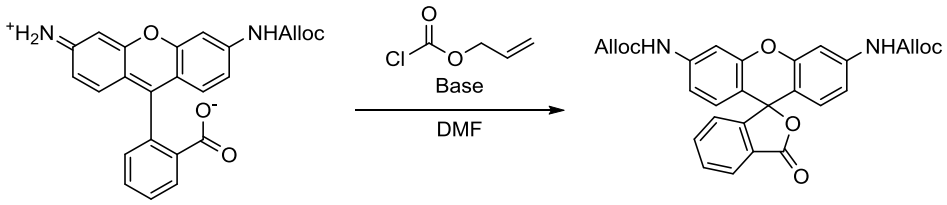
Allyl (4-(((2-oxo-2H-chromen-7-yl)oxy)methyl)phenyl)carbamate was synthesized following a routine procedure. A round bottom flask containing allyl (4-(hydroxymethyl)phenyl)carbamate (103 mg, 0.5 mmol) is purged by argon. Dichloromethane (5 mL, 0.1 M) is added. The flask is then submerged in an ice bath to reach 0 °C. Then, PBr3 (52 µL, 0.55 mmol, 1.1 equiv.) is added dropwise by syringe. The reaction mixture is stirred for 2-3 min at 0 °C during which it can take a slight orange coloration. The flask is then removed from the ice bath and allowed to reach room temperature. After 1h stirring, 5 mL water are added and the mixture is stirred for 5 more min at room temperature. The phases are separated in a separatory funnel and the organic phase is washed by brine once. After drying with Na_2SO_4, the solvent is removed to give the crude bromide as a white to slight reddish solid. It was not characterized but immediately used in the next step. The crude bromide is then dissolved in acetone (5 mL, 0.1 M). Then, umbelliferon (90 mg, 0.54 mmol, 1.1 equiv.) is added in one portion. Then, potassium carbonate (172 mg, 1.12 mmol, 2.5 equiv.) is added in one portion and the reaction medium turns yellow. It was allowed to stir overnight at room temperature. On the next day, the volume was reduced by half by rotavap. Ethyl acetate was added and the organic phase was washed 3 times with saturated $NaHCO_3$ solution until the water phase is perfectly colorless. After drying, the solvent is removed by rotary

evaporator. Flash column purification using 10-30% ethyl acetate in petroleum ether. The product is obtained as a white powder. Yield: 168 mg, 97%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 9.5, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 3H), 6.94 – 6.85 (m, 2H), 6.84 (bs, 1H), 6.25 (d, *J* = 9.5 Hz, 1H), 5.96 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.4, 1.3 Hz, 1H), 5.06 (s, 2H), 4.67 (dt, *J* = 5.7, 1.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.94, 161.36, 155.90, 153.27, 143.54, 138.17, 132.44, 130.76, 128.91, 128.73, 118.95, 118.46, 113.38, 113.31, 112.83, 102.01, 70.28, 66.06.

1.1.2.2 Rhodamine bis-alloc



The rhodamine 110 bis-alloc was synthesized according to an adapted literature procedure. Rhodamine 110 (508 mg, 0.137 mmol, 1 equiv.) was dissolved in dry DMF (0.5 mL) under argon and cooled to 0°C. Then, pyridine (39 µL, 0.48 mmol, 3.5 equiv.) was added by micro syringe, followed by allylchloroformate (52 µL, 0.48 mmol, 3.5 equiv.) dropwise. The resulting red reaction mixture was allowed to warm to room temperature while stirring overnight. Thereafter, EtOAc (10 mL) was added to the metallic red solution which was transferred to a separator funnel and washed twice with 5% HCl (8 mL). Small amounts of saturated $NaHCO_3$ were used to eliminate emulsion formation. The ethyl acetate layer was collected and combined with two further ethyl acetate washings (10 mL each), washed with saturated $NaHCO_3$ (10 mL), dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting oil was subjected to column chromatography on silica gel with PE/EtOAc (2:1). The resulting product was isolated as a white solid (20 mg, 19%).

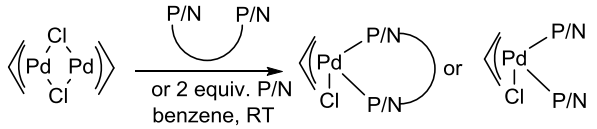
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.07 – 7.97 (m, 1H), 7.74 – 7.57 (m, 2H), 7.46 (d, *J* = 2.2 Hz, 2H), 7.15 – 7.06 (m, 3H), 7.00 (dd, *J* = 8.6, 2.2 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 5.96 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 2H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 2H), 5.27 (dq, *J* = 10.4, 1.3 Hz, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 4H).

1.1.3 Synthesis of catalysts

1.1.3.1 Commercial catalysts

Catalysts **Ru1** (Meggers catalyst), **Pd10**, **Pd11**, **Pd23**, **Pd24**, **Pd25**, **Pd26**, **Pd27**, **Pd28**, **Pd29**, **Pd30**, **Pd31**, **Pd32**, **Pd33**, **Pd34**, **Pd39** and **Pd41**.

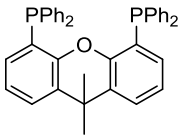
1.1.3.2 General procedure



All the allylpalladium chloride (N,N) or (P,P) were prepared following an adapted literature procedure[82]. A glass vial with a magnetic bar was filled with η^3-allylpalladium chloride dimer (20 mg, 0.055 mmol), followed by 3 mL benzene. After complete dissolution, the diphosphine (1 equiv.) or the monophosphine (2 equiv.) is added in one portion. The mixture is stirred at RT for typically 1 hour. In the case of diphosphines, a yellow to orange solid precipitates and is collected by filtration on paper, followed by washing with Et_2O. In the case of monophosphines, no precipitate is observed and the solution was reduced under reduced pressure and precipitation was made adding *n*-pentane. The solid was filtered on a filter paper and dried under vacuum.

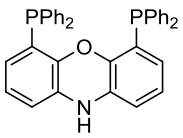
1.1.3.3 Characterizations

(allyl)PdCl(Xantphos) = **Pd1**



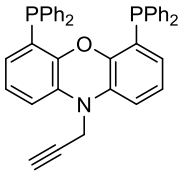
^{1}H NMR (300 MHz, Methylene Chloride-d2) δ 7.63 (dd, J = 7.8, 1.4 Hz, 2H), 7.37 – 7.20 (m, 20H), 7.15 (t, J = 7.8 Hz, 2H), 6.56 (t, J = 7.6 Hz, 2H), 5.66 (dd, J = 19.5, 9.5 Hz, 1H), 3.70 – 3.53 (m, 4H), 1.65 (s, 6H).

(allyl)PdCl(N-Xantphos) = **Pd12**



^{1}H NMR (300 MHz, DMSO-d_6) δ 9.26 (s, 1H), 7.53 – 7.39 (m, 413), 7.26 – 7.14 (m, 8H), 7.02 (d, *J* = 2.9 Hz, 4H), 6.09 (t, *J* = 10.1 Hz, 1H), 5.97 (ddd, *J* = 8.1, 6.2, 3.0 Hz, 2H), 3.59 (d, *J* = 10.0 Hz, 2H).

(allyl)PdCl(JoePhos) = **Pd14**

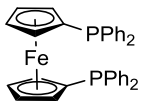


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 19H), 7.06 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.03 – 6.91 (m, 2H), 6.19 (td, *J* = 7.9, 7.3, 2.4 Hz, 2H), 5.78 (q, *J* = 10.1 Hz, 1H), 5.06 (tt, *J* = 12.3, 6.6 Hz, 1H), 4.46 (d, *J* = 2.5 Hz, 2H), 3.96 (s, 2H), 3.64 (d, *J* = 6.6 Hz, 3H), 2.55 (d, *J* = 11.9 Hz, 1H), 2.35 – 2.23 (m, 1H).

^{31}P NMR (121 MHz, $CDCl_3$) δ 3.40.

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.03, 135.55, 133.27, 133.18, 132.51, 132.21, 131.97, 130.32, 128.87, 128.80, 128.73, 128.45, 126.70, 124.83, 117.94, 115.43, 109.03, 79.18, 78.97, 78.79, 77.37, 77.16, 74.39, 60.46, 34.37.

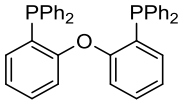
(ally)PdCl(Dppf) = **Pd18**



Msb118

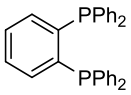
^{1}H NMR (300 MHz, Methylene Chloride-d2) δ 8.06 – 7.72 (m, 2H), 7.72 – 7.37 (m, 18H), 6.01 – 5.60 (m, 1H), 4.57 – 4.09 (m, 8H), 3.82 (s, 4H). ^{13}C NMR (75 MHz, Methylene Chloride-d2) δ 133.53, 131.59, 129.19, 128.40, 75.87, 73.58.

(allyl)PdCl(DPEPhos) = **Pd13**



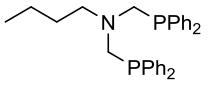
^{1}H NMR (300 MHz, Methylene Chloride-d^{2}) δ 7.52– 7.22 (m, 22H), 7.00 (t, J = 7.6 Hz, 2H), 6.96 – 6.85 (m, 2H), 6.77 (ddd, J = 9.6, 7.7, 1.7 Hz, 2H), 5.86 – 5.75 (m, 1H), 3.73 (s, 4H).

(allyl)PdCl(Dppbz) = **PdPd17**



^{1}H NMR (300 MHz, Chloroform-d) δ 7.65 (dd, J = 5.5, 3.3 Hz, 4H), 7.45 (pd, J = 7.2, 6.2, 3.6 Hz, 21H), 5.91 (t, J = 10.6 Hz, 1H), 4.23 (dt, J = 10.0, 4.6 Hz, 4H).

(allyl)PdCl(PPh_2-N) = **Pd9**

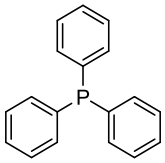


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.98 – 7.75 (m, 1H), 7.54 (d, *J* = 6.3 Hz, 8H), 7.40 – 7.18 (m, 12H), 5.70 – 5.48 (m, 1H), 4.00 (s, 3H), 3.84 (s, 3H), 2.63 (t, *J* = 7.4 Hz, 2H), 1.88 (s, 2H), 1.44 – 1.21 (m, 2H), 1.12 – 0.96 (m, 1H), 0.80 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.46, 133.38, 133.30, 130.36, 128.60, 128.53, 128.46, 119.48, 77.16, 71.10, 70.88, 70.66, 62.83, 62.69, 54.57, 54.31, 54.04, 27.81, 20.39, 14.09.

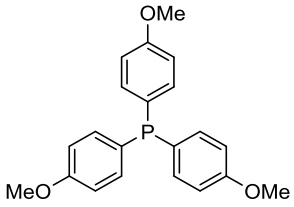
^{31}P NMR (121 MHz, $CDCl_3$) δ 3.73.

(allyl)PdCl(PPh_3)$_2$ = **Pd21**



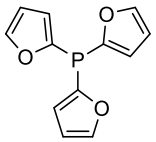
^{1}H NMR (300 MHz, Methylene Chloride-d2) δ 7.72 – 7.31 (m, 30H), 5.73 – 5.53 (m, 1H), 4.68 (t, J = 7.3 Hz, 2H), 3.71 (dd, J = 13.7, 9.9 Hz, 2H), 3.14 (s, 2H), 2.86 (d, J = 12.1 Hz, 2H).

(allyl)PdClTris(MeOPh)phosphine = **Pd45**



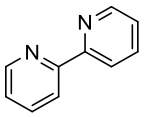
^{1}H NMR (300 MHz, Methylene Chloride-*d*2) δ 7.55 – 7.43 (m, 12H), 6.99 – 6.86 (m, 12H), 5.69 – 5.53 (m, 1H), 4.62 (td, *J* = 7.3, 2.1 Hz, 2H), 3.82 (d, *J* = 2.7 Hz, 18H), 3.23 – 2.68 (m, 2H).

(allyl)PdCl(1-furyl) = **Pd36**



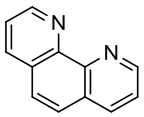
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 1.8, 0.7 Hz, 6H), 6.80 (dd, *J* = 3.5, 0.8 Hz, 6H), 6.45 (dd, *J* = 3.5, 1.7 Hz, 6H), 6.07 (tt, *J* = 13.6, 7.4 Hz, 1H), 4.86 (d, *J* = 7.4 Hz, 2H), 3.89 (d, *J* = 13.6 Hz, 2H).

(allyl)PdCl(bpy) = **Pd2**



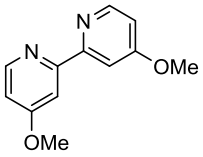
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 8.2 Hz, 2H), 8.76 (d, *J* = 5.3 Hz, 2H), 8.24 (t, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 6.6 Hz, 2H), 6.13 – 5.79 (m, 1H), 3.92 (bs, 2H), 2.85 (d, *J* = 11.5 Hz, 2H).

(allyl)PdCl(phen) = **Pd4**



^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.20 (d, *J* = 4.5 Hz, 2H), 8.27 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.82 (s, 2H), 7.65 (dd, *J* = 8.1, 4.3 Hz, 2H), 6.12 (d, *J* = 10.0 Hz, 1H), 3.12 (m, 4H).

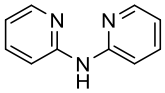
(allyl)PdCl(bpy-méthoxy) = **Pd3**



^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 2.6 Hz, 2H), 8.44 (d, *J* = 6.3 Hz, 2H), 7.01 (dd, *J* = 6.3, 2.6 Hz, 2H), 5.88 (t, *J* = 9.8 Hz, 1H), 4.39 (s, 6H), 4.07 (s, 2H), 3.38 (d, *J* = 12.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.25, 157.68, 153.68, 118.58, 115.06, 110.54, 77.44, 60.69, 59.02.

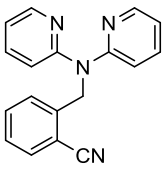
(allyl)PdCl(bpa) = **Pd5**



^{1}H NMR (300 MHz, Chloroform-*d*) δ 12.37 (s, 1H), 8.38 (d, *J* = 8.6 Hz, 2H), 8.18 (ddd, *J* = 5.9, 1.9, 0.7 Hz, 2H), 7.75 (ddd, *J* = 8.8, 7.1, 1.8 Hz, 2H), 6.86 (ddd, *J* = 7.2, 5.8, 1.3 Hz, 2H), 5.99 (s, 1H), 3.89 (d, *J* = 7.1 Hz, 2H), 3.37 (d, *J* = 12.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.47, 139.73, 118.20, 117.45, 77.23, 62.26.

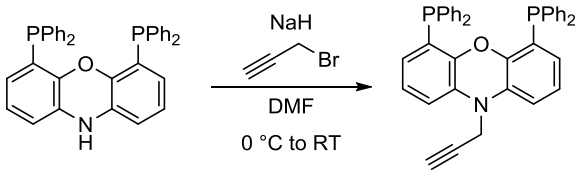
(allyl)PdCl(bpa-CN) = **Pd7**



^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 4.9 Hz, 2H), 7.74 – 7.56 (m, 4H), 7.47 (td, *J* = 7.7, 1.4 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.04 – 6.87 (m, 2H), 5.72 (s, 2H), 5.45 (ddd, *J* = 18.9, 12.4, 6.8 Hz, 2H), 4.08 (d, *J* = 6.7 Hz, 4H), 3.01 (d, *J* = 12.1 Hz, 4H).
(allyl)PdCl(MeCN)$_2$ = **Pd16** ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.59 (m, *J* = 8.0 Hz, 12H), 7.52 – 7.37 (br m, 12H), 6.05 (dt, *J* = 13.6, 6.5 Hz, 1H), 4.05 (dd, *J* = 19.2, 6.2 Hz, 4H).

1.1.3.4 Alternative ligands' syntheses

1.1.3.4.1 JOEPHOS



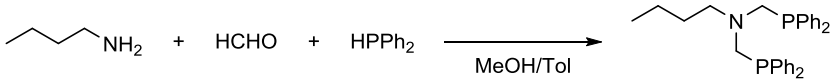
JoePhos was synthesized according to an adapted literature procedure[83]. N-Xantphos (103.1mg, 0.186 mmol) is dissolved in 2.5 mL anhydrous DMF in a flame-dried RB flask under Ar. The flask is cooled to 0 °C by ice bath. Then, NaH (80% in mineral oil, 8.5 mg, 0.279 mmol, 1.5 equiv.) is added at once and the solution becomes dark orange to dark yellow or sometimes dark green or blue. After 15 min stirring at 0 °C, propargyl bromide (80% in toluene, 35 µL, 0.372 mmol, 2 equiv.) is added by micro syringe and the mixture is stirred at 0 °C for 5 min, and the ice bath is removed. The reaction is stirred for 3 more hours at room temperature. For the workup, 1 mL water is carefully added. Then, ethyl acetate is added and the organic phase was washed several times with brine and eventually with LiCl to remove the DMF. After drying with Na_2SO_4, the solvent is removed by rotavap. Then, the dark brown pasty oil is purified by silica gel filtration with 20% ethyl acetate in petroleum ether (100 mL) and the collected colourless fraction is evaporated to leave a off-white solid, which is the pure JoePhos (60 mg, 72%).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 (tq, *J* = 4.8, 2.2 Hz, 20H), 6.81 (t, *J* = 7.8 Hz, 2H), 6.73 (dd, *J* = 7.9, 1.6 Hz, 2H), 6.17 (dq, *J* = 7.6, 1.7 Hz, 2H), 4.30 (d, *J* = 2.4 Hz, 2H), 2.41 – 2.20 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.20, 148.06, 147.92, 137.04, 136.96, 136.87, 134.18, 134.04, 133.91, 133.29, 128.45, 128.39, 128.35, 128.30, 126.20, 125.49, 125.36, 125.23, 124.09, 112.69, 77.98, 73.03, 34.78.

^{31}P NMR (121 MHz, $CDCl_3$) δ -18.44.

1.1.3.4.2 N,N-BIS((DIPHENYLPHOSPHANYL)METHYL)BUTAN-1-AMINE

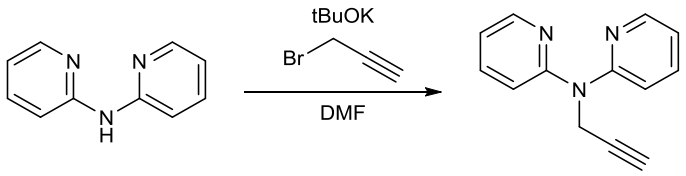


N,N-bis((diphenylphosphanyl)methyl)butan-1-amine was synthesized according to a literature procedure. To a three-necked 100 mL round bottomed flask, paraformaldehyde (0.23 g, 7.1 mmol) and 20 mL of degassed methanol were added under a flow of nitrogen gas. Then, 1.35 mL of diphenylphosphine were introduced to the reaction mixture via a syringe. After the mixture was stirred at room temperature for 2 h, butylamine (250 mg, 3.53 mmol) dissolved in methanol (10 mL) and toluene (20 mL) was added via a syringe. The mixture was heated to 60–70 °C and stirred overnight. Removal of all volatiles after cooling gave the product as a viscous liquid. Quantitative yield.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 – 7.36 (m, 8H), 7.36 – 7.23 (m, 12H), 2.84 (t, *J* = 7.3 Hz, 2H), 1.46 – 1.25 (m, 2H), 1.25 – 1.10 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

^{31}P NMR (121 MHz, $CDCl_3$) δ -27.90.

1.1.3.4.3 BPA PROPARGYL



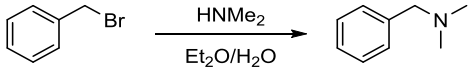
To a solution of di(pyridin-2-yl)amine (171 mg, 1 mmol) in dry DMF (5 mL, 0.2 M) potassium tert-butoxide (0.16 g, 1.44 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. Then 80% solution of propargyl bromide in toluene (0.3 mL, 2.7 mmol) was added dropwise and the stirring was continued for 24 h. The reaction mixture was poured into water (25 mL). The resulting solid was filtered off, washed with water and purified by column chromatography (silica gel, CH_2Cl_2) to give the following N-(prop-2-yn-1-yl)-N-(pyridin-2-yl)pyridin-2-amine as an off-white solid (88.3 mg, 42%). The solid is very unstable and darkens within 2 days if stored on the bench. It needs to be stored at -18 °C under Ar.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.40 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 2H), 7.57 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 2H), 7.23 (dt, *J* = 8.4, 0.9 Hz, 2H), 6.92 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 2H), 5.06 – 4.97 (m, 2H), 2.15 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.43, 148.55, 137.53, 117.75, 114.63, 77.16, 70.55, 37.75.

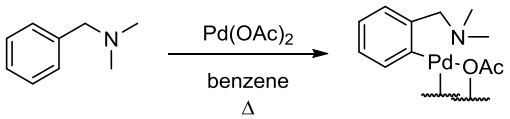
1.1.3.5 Other catalysts

1.1.3.5.1 PD CLAVER



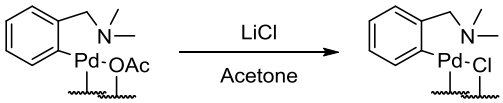
N,N-dimethyl-1-phenylmethanamine was synthesized following a routine procedure. A 50 mL round bottom flask is filled with benzyl chloride (1.8 mL, 15.8 mmol) and 15 mL of diethyl ether (PA). Then, dimethylamine (40% in water, 10 mL, 79 mmol, 5 equiv) are added from a measuring glass cylinder. The mixture is vigorously stirred for 4 h at room temperature. The phases are then separated and the organic phase is washed with 10 mL of 1M HCl, then by brine. After drying with Na_2SO_4, the solvent is evaporated and the product is put under vacuum to remove the rests of dimethylamine. The crude product is pure enough for the next step. It is obtained as a slightly yellow oil. Yield: 56%, 1.194g

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 (m, 5H), 3.42 (s, 2H), 2.24 (s, 6H).



A round-bottom flask is filled with N,N-dimethyl-1-phenylmethanamine (28.9 mg, 0.214 mmol, 1.2 equiv.) followed by benzene (3 mL, 0.06 M). Then, palladium (II) acetate (40 mg, 0.178 mmol, 1 equiv) is added. The bright orange mixture is heated in closed vessel at 50 °C overnight during which it turns brown in one hour and then very dark yellow on the next morning. The mixture is cooled down to room temperature and filtered on a celite pad with DCM for washing. The solution is concentrated to a minimum volume and a yellow solid is obtained after addition of hexanes. The bright yellow solid is obtained by filtration of paper. A second cycle can be performed. It is obtained as a bright yellow powder. Yield: 50%, 28 mg

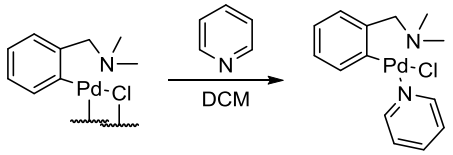
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.99 (ddd, *J* = 16.8, 7.3, 1.4 Hz, 2H), 6.93 – 6.82 (m, 2H), 3.57 (d, *J* = 13.7 Hz, 1H), 3.08 (d, *J* = 13.8 Hz, 1H), 2.80 (s, 2H), 2.05 (d, *J* = 4.8 Hz, 6H).



A round-bottom flask is filled with the palladacycle-acetate (28 mg, 0.047 mmol) followed by 3 mL of a saturated solution of LiCl in acetone (30 mg in 3 mL, 15 equiv.). The heterogeneous yellow mixture is stirred overnight protected from light in an aluminum foil. On the next day, the mixture

seems to be darker yellow. The solvent is removed by rotavap and DCM is added to fully re-dissolve the palladacycle. The inorganic salts are removed by celite filtration. The bright yellow solution is concentrated to a minimum volume and a yellow solid is obtained after addition of hexanes. The bright yellow solid is obtained by filtration of paper. A second cycle can be performed. It is obtained as a bright yellow powder. Yield: 90%, 23.3 mg.

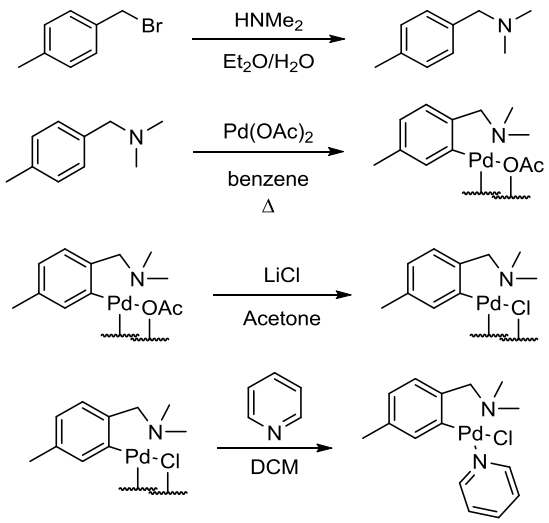
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.23 – 7.10 (m, 1H), 6.96 (dd, *J* = 6.9, 1.3 Hz, 1H), 6.87 (t, *J* = 6.4 Hz, 3H), 3.93 (s, 3H), 2.85 (d, *J* = 8.3 Hz, 10H).



The chloro palladacyle (25.8 mg, 0.047 mmol) is dissolved in 1 mL DCM (0.02 M) in a round bottom flask. Then, pyridine (30 µL, 8 equiv., 0.880 mmol) is added by syringe. The yellow solution decolorizes within 2 seconds and turns very pale yellow. After 15 min of stirring, the volume of solvent is reduced to 25% and diethyl ether is added, during which an abundant white precipitate appears. The precipitate is obtained by filtration of paper. A second cycle can be performed. It is obtained as a fluffy white powder. The complex is purified by flash chromatography with 5-20% ethyl acetate in DCM. Yield: 22.8 mg, 69%. A suitable crystal for X-Ray Diffraction was obtained by slow diffusion of diethyl ether in a DCM solution.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.89 (dt, *J* = 5.0, 1.6 Hz, 2H), 7.89 – 7.74 (m, 1H), 7.49 – 7.33 (m, 2H), 7.06 – 6.93 (m, 2H), 6.87 – 6.69 (m, 1H), 6.12 – 5.93 (m, 1H), 3.98 (s, 2H), 2.94 (s, 6H).

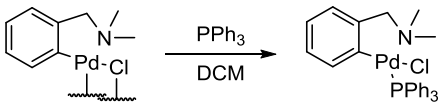
1.1.3.5.2 CLAVER PALLADACYCLE METHYL



For the 3 last steps, the exact same methods for the palladacycle were used.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.89 (dt, *J* = 5.0, 1.6 Hz, 2H), 7.91 – 7.76 (m, 1H), 7.52 – 7.34 (m, 2H), 6.91 – 6.77 (m, 2H), 5.80 (t, *J* = 1.1 Hz, 1H), 3.94 (s, 2H), 2.92 (s, 6H), 2.08 (s, 3H).

1.1.3.5.3 PD CLAVER(PPH3)

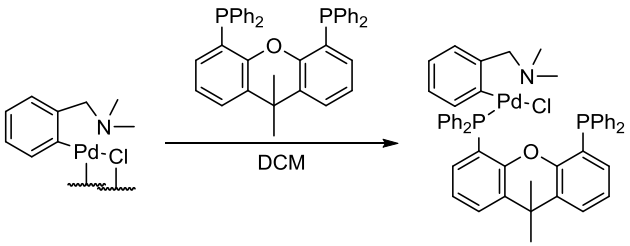


The chloro palladacyle (25.8 mg, 0.047 mmol) is dissolved in 1 mL DCM (0.02 M) in a round bottom flask. Then triphenylphosphine (2 equiv.) is added. The yellow solution is stirred for 2 hours. Then, the volume of solvent is reduced to 25% and diethyl ether is added, during which a pale-yellow precipitate appears. The precipitate is obtained by filtration of paper. A second cycle can be performed. It is obtained as a yellow powder. The complex is purified by flash chromatography with 5-20% ethyl acetate in DCM.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.84 – 7.62 (m, 6H), 7.36 (dtd, *J* = 10.6, 7.0, 1.9 Hz, 10H), 7.00 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.82 (td, *J* = 7.2, 1.5 Hz, 1H), 6.45 – 6.29 (m, 2H), 4.07 (s, 2H), 2.85 (s, 6H).

^{31}P NMR (121 MHz, $CDCl_3$) δ 42.97, 23.87.

1.1.3.5.4 SUPER CLAVER



The chloro palladacyle (25.8 mg, 0.047 mmol) is dissolved in 1 mL DCM (0.02 M) in a round bottom flask. Xantphos (2 equiv.) is added. The yellow solution is stirred for 2 hours. Then, the volume of solvent is reduced to 25% and diethyl ether is added, during which a pale-yellow precipitate appears. The precipitate is obtained by filtration of paper. A second cycle can be performed. It is obtained as a yellow powder. The complex is purified by flash chromatography with 5-20% ethyl acetate in DCM.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 – 7.30 (m, 4H), 7.22 (t, *J* = 7.3 Hz, 5H), 7.10 (t, *J* = 7.5 Hz, 9H), 6.96 (t, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.77 (s, 0H), 6.76 – 6.68 (m, 1H), 6.30 – 6.23 (m, 2H), 3.84 (s, 2H), 2.63 (t, *J* = 1.4 Hz, 6H), 1.52 (d, *J* = 28.2 Hz, 10H).

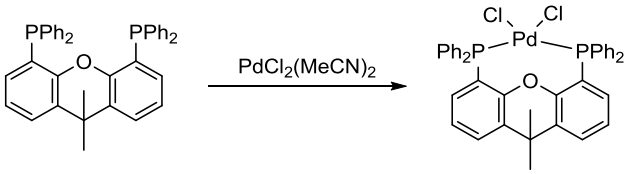
^{13}C NMR (75 MHz, $CDCl_3$) δ 134.64, 134.44, 133.78, 130.35, 129.08, 128.04, 127.87, 123.06, 72.48, 50.19, 34.43.

^{31}P NMR (121 MHz, $CDCl_3$) δ 22.08 (s), 3.56 (bs).

1.1.3.5.5 (P,P)PDCL$_2$

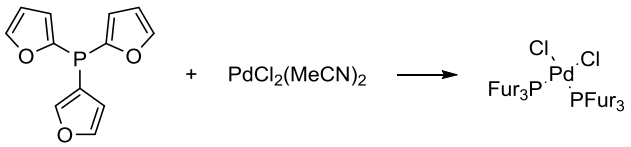
General procedure : $PdCl_2(MeCN)_2$ (20 mg) and the diphosphine (1 equiv.) or the monophosphine (2 equiv.) are suspended in dichloromethane (2 mL). After 30 min stirring, the mixture was poured in pentane and a yellow solid was collected by filtration as a yellow powder (yield: quantitative).

XantphosPdCl$_2$ = **Pd35**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.47 (ddd, *J* = 9.1, 7.7, 1.3 Hz, 2H), 7.37 (d, *J* = 10.0 Hz, 8H), 7.31 – 7.24 (m, 2H), 7.23 – 7.15 (m, 4H), 7.05 (td, *J* = 8.0, 7.6, 2.4 Hz, 8H), 1.86 (s, 6H).

Fur$_3$P = **Pd36**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.47 (d, *J* = 1.9 Hz, 2H), 7.24 (dd, *J* = 3.5, 0.9 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.48 – 6.43 (m, 1H), 6.34 (dt, *J* = 3.3, 1.5 Hz, 2H).
Mixture cis-trans 2 :1