Supplementary Information (SI) for Catalysis Science & Technology.

Supporting information for:

Continuous centrifugation and filtration for assessing the catalytic significance of metal nanoparticles forming in situ during the palladium-catalyzed arylation of *N*-methylindole

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General considerations

Unless otherwise specified chemicals were purchased from commercial sources and used as received. $IMesPd(OAc)_2$[1] and the free IMes carbene[2] were prepared using previously reported procedures. The preparations of IMes and $IMesPd(OAc)_2$ were conducted in a nitrogen filled glovebox. The THF used in the preparations of IMes and $IMesPd(OAc)_2$ was sparged with nitrogen and dried by passage through alumina solvent purification columns prior to use. All solvents used in in the preparations of IMes and $IMesPd(OAc)_2$ were stored over activated[3] 3Å molecular sieves for a minimum of 12 hours prior to use.

Equipment and instrumentation

Centrifuge

Centrifugation was performed on a Hettich ROTINA 380 R, Benchtop Centrifuge, heatable and coolable up to +90 °C with a 45° angle rotor.

NMR

NMR spectra were recorded on a Bruker Avance III FT-NMR (500 MHz) or Varian Mercury FT-NMR (300 MHz) spectrometer.

GC-FID

GC-FID chromatograms were collected using an Agilent 7890A GC-FID equipped with an HP-5 column (30 m x 0.32 mm x 0.25 µm).

DLS

DLS data were collected on a Malvern Panalytical Zetasizer Ultra with 632.8 nm, 10 mW HeNe laser.

HRMS

High resolution mass spectrometry was performed on an Agilent LC/Q-TOF 6545XT BioConfirm system with an AJS ESI (electrospray ionization with heated, nitrogen sheath gas).

SEM/STEM/EDS

Sample imaging was performed using a JEOL 7200 Schottky field-emission Scanning Electron Microscope. Elemental composition data was obtained using an Oxford X-maxN 150 mm^2 EDS detector.

Computed tomography

Scans were acquired on a NeoScan N80 X-Ray Micro-Computed Tomography Scanner. Scans were recorded with a resolution of 8 μm per pixel.

Independent synthesis, isolation, and NMR characterization of 2-(4-(*tert*-butyl)phenyl)-1-methyl-1H-indole

This synthesis is based on a method reported for a related compound.[4] In a glovebox *N*-methylindole (535 mg, 4.08 mmol, 1 eq), Pd(OAc)$_2$ (45.5 mg, 0.203 mmol, 0.050 eq) were combined. In air acetic acid (40 mL) and 4-*tert*-butylphenylboronic acid (1.12 g, 6.31 mmol, 1.5 eq) were added. The mixture was stirred at room temperature (approximately 20 °C) for four days. The volatiles were removed by rotary evaporation. The residue was dissolved in dichloromethane (125 mL), washed with saturated aqueous sodium bicarbonate (2x 125 mL), dried over MgSO$_4$, and the volatiles removed by rotary evaporation. The residue was purified by silica gel column chromatography monitored by TLC. The column was flushed with hexanes which eluted an impurity ($R_f = 0.2$ in hexanes) then hexanes: ethyl acetate (98:2). The fractions found to contain 2-(4-(*tert*-butyl)phenyl)-1-methyl-1H-indole by TLC ($R_f = 0.05$ in hexanes) were combined and the volatiles removed by rotary evaporation to yield 2-(4-(*tert*-butyl)phenyl)-1-methyl-1H-indole (611 mg, 2.31 mmol, 56.9 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70 (d, J = 7.9 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.42 (d, J = 9.2 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.62 (s, 1H), 3.80 (s, 3H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 151.03, 141.77, 138.43, 130.04, 129.19, 128.16, 125.66, 121.62, 120.51, 119.91, 109.68, 101.50, 34.82, 31.49, 31.31. mp 129-130 °C (lit.[5] 112-114 °C). HRMS (ESI-QTOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}N$ 264.1747; Found 264.1744.

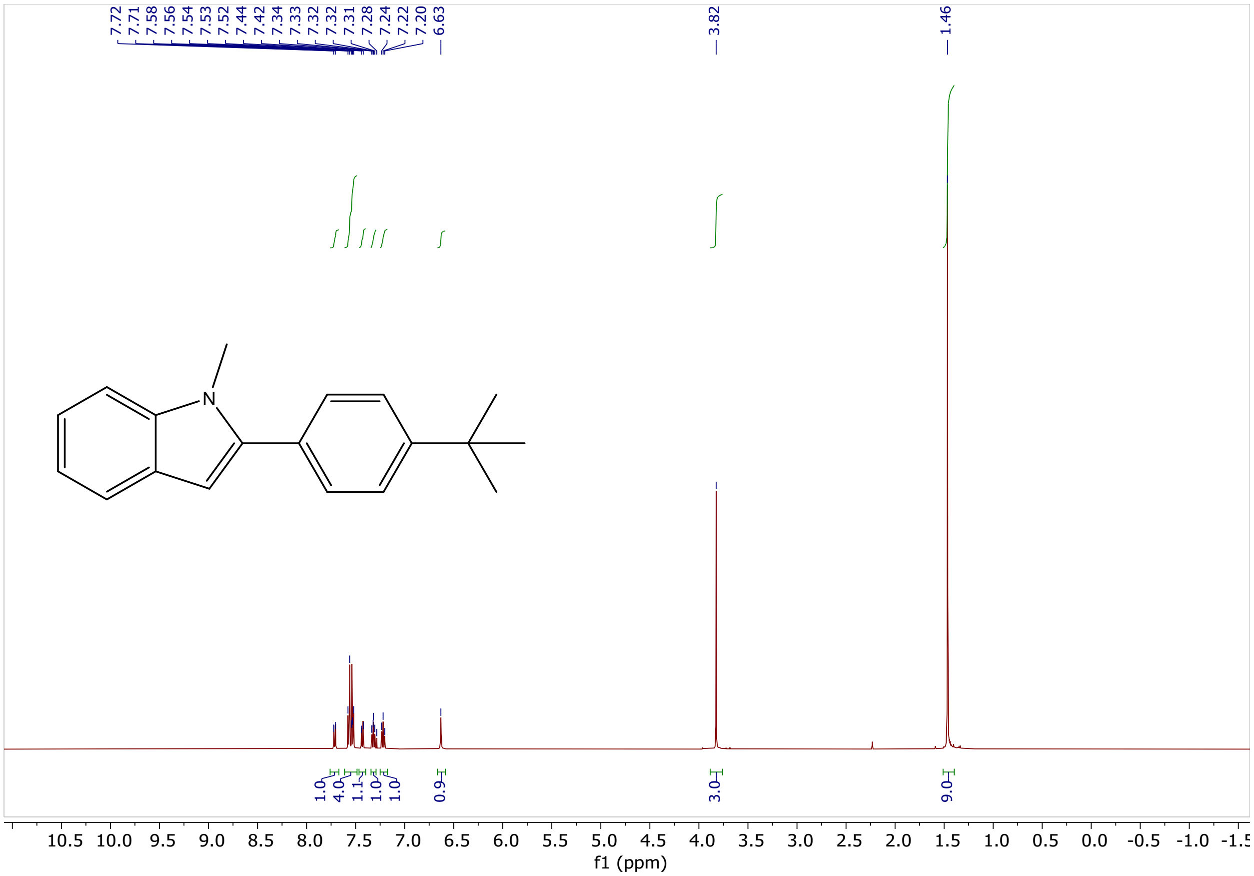

Figure S1. ^{1}H NMR of 2-(4-(*tert*-butyl)phenyl)-1-methyl-1H-indole in $CDCl_3$, 500 MHz, 298 K.

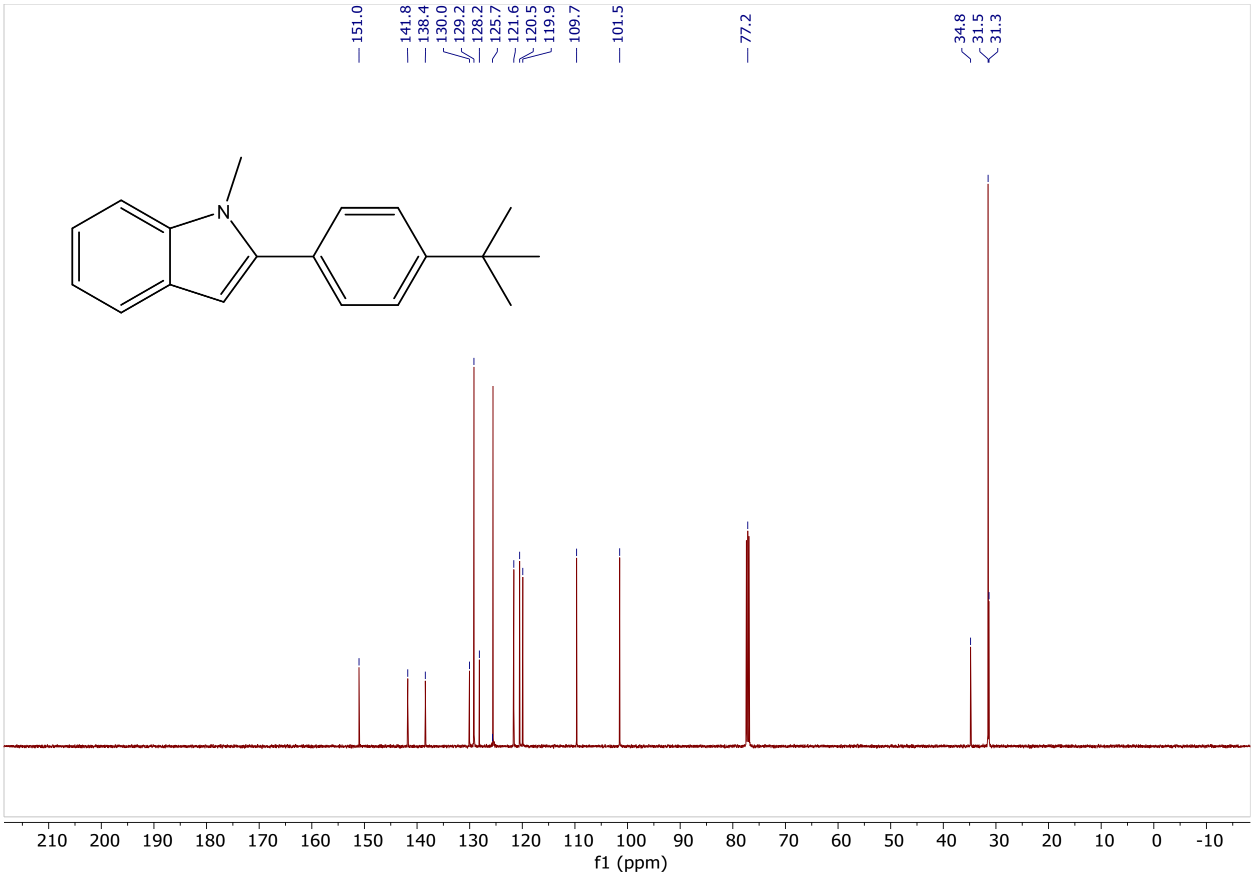

Figure S2. $^{13}C\{^{1}H\}$ NMR of 2-(4-(*tert*-butyl)phenyl)-1-methyl-1H-indole in $CDCl_3$, 126 MHz, 298 K.

Synthesis of Pd nanoparticles in polyvinylpyrrolidone matrix

This synthesis is based on a previous report.[6] A flask was charged with palladium (II) chloride (27.2 mg, 0.153 mmol). Aqueous HCl (0.2 M, 1.4 mL, 0.00028 mmol) and deionized water (70.6 mL) were added. The mixture was stirred at room temperature for 1 hour after which time water (67.2 mL), polyvinylpyyolidone (0.3244 g), and ethanol (100 mL) were added. The mixture was heated at reflux for 4.5 hours then allowed to cool. The solvent was removed under reduced pressure yielding a black solid. The resulting solid was resuspended in water (4 mL). This suspension was stored for up to two weeks and was sonicated immediately prior to each use.

STEM characterization and size distribution analysis of Pd nanoparticles synthesized in polyvinylpyrrolidone matrix

An aliquot of the Pd nanoparticles in polyvinylpyrrolidone matrix suspended in water (0.4 mL) was subjected to centrifugation at 31000 g for 1 hour (25 °C). The majority of the supernatant was removed with a pipette leaving the pellet at the bottom undisturbed. An aqueous solution of cetrimonium bromide (1 mM, 0.4 mL) was added and sample was sonicated. The suspension was subjected to centrifugation at 31000 g for 30 minutes (25 °C) then washed twice more with cetrimonium bromide solution as described above. After the final wash was removed by pipette, water (0.020 mL) was added. The sample was sonicated and a drop of the suspension (2.5 μL) was deposited on a carbon-coated copper grid. Scanning transmission electron microscopy (STEM) imaging was conducted using a JEOL-7200F field emission SEM operated at 30 kV with a working distance of 3.4 nm. Size distribution analysis was performed using ImageJ.[7]

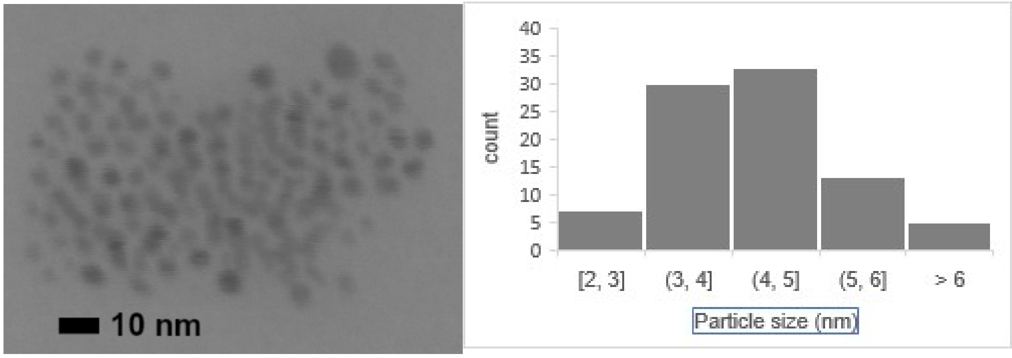

Figure S3. Left- STEM image of Pd nanoparticles in polyvinylpyrrolidone matrix. Right- size distribution histogram.

Preparation of ethanol suspension of Pd nanoparticles in polyvinylpyrrolidone matrix

An aliquot of the Pd nanoparticles in polyvinylpyrrolidone matrix suspended in water (0.6 mL) was subjected to centrifugation at 31000 g for 1 hour (25 °C). The majority of the supernatant was removed with a pipette leaving the pellet at the bottom undisturbed. Ethanol (0.6 mL) was added and the sample was sonicated. The suspension was subjected to centrifugation at 31000 g for 30 minutes (25 °C) then the supernatant was removed by pipette. Two additional washes with ethanol (0.6 mL) were preformed as described above. After the final wash the solid was suspended in ethanol (0.6 mL).

Procedure for charging centrifuge tubes with MOLYKOTE®[8] high vacuum grease

Using a 1 mL plastic syringe, a small drop of grease was deposited in the bottom of the centrifuge tube halfway up to the 0.1 mL line then moving up the side depositing a small line up the tube. A total volume of approximately 0.1 mL of grease was used per centrifuge tube. The grease along the sides of the tube were spread around to form a more uniform layer, while the drop of grease initially deposited at the bottom was left undisturbed.

Procedure for centrifugation time course studies of C–H arylation reaction with Pd nanoparticles in polyvinylpyrrolidone matrix

In a nitrogen-filled glovebox *N*-methylindole (50.4 mg, 0.384 mmol, 1 eq) and the iodonium salt bis(4-(*tert*-butyl)phenyl)iodonium trifluoromethyl sulfonate (266.0 mg, 0.471 mmol, 1.23 eq, CAS: 84563-54-2) were weighed into separate vials. The vials were brought out of the glovebox and benzophenone (92.9 mg, 0.510 mmol, 1.33 eq) was added to the vial with *N*-methylindole. The iodonium salt was dissolved in glacial acetic acid (6 mL) and transferred with a Pasteur pipette to the vial containing *N*-methylindole. Additional glacial acetic acid (5.67 mL) was used to ensure complete transfer of the *N*-methylindole. Ethanol (2.34 mL) was then added and the mixture was stirred for 5 minutes.

A Pasteur pipette was used to add 1 mL of the mixture to centrifuge tubes that were pre-charged with MOLYKOTE® high vacuum grease (above). The tubes were held vertically during the addition. This procedure charges each centrifuge tube with *N*-methylindole (0.027 mmol), iodonium salt (0.034 mmol), and benzophenone (0.036 mmol).

The centrifuge was preheated to the desired temperature and programed for the desired rotation and run time of the data point. The ethanol suspension of Pd nanoparticles in polyvinylpyrrolidone matrix (92 μL, 0.00137 mmol Pd) was then added to the desired number of replicate tubes. The tubes were capped, inverted once, rapidly loaded into the pre-heated centrifuge and accelerated to the desired rotation.

After the indicated time the tubes were removed from the centrifuge. As quickly as possible after a tube was removed from the centrifuge 10 drops of the reaction mixture were diluted in ethyl acetate (2 mL) and saturated aqueous sodium bicarbonate (2 mL) was added to neutralize the reaction. The organic layer was then transferred to a GC vial for analysis by GC-FID.

No Pd nanoparticle solution was added to the T=0 timepoints.

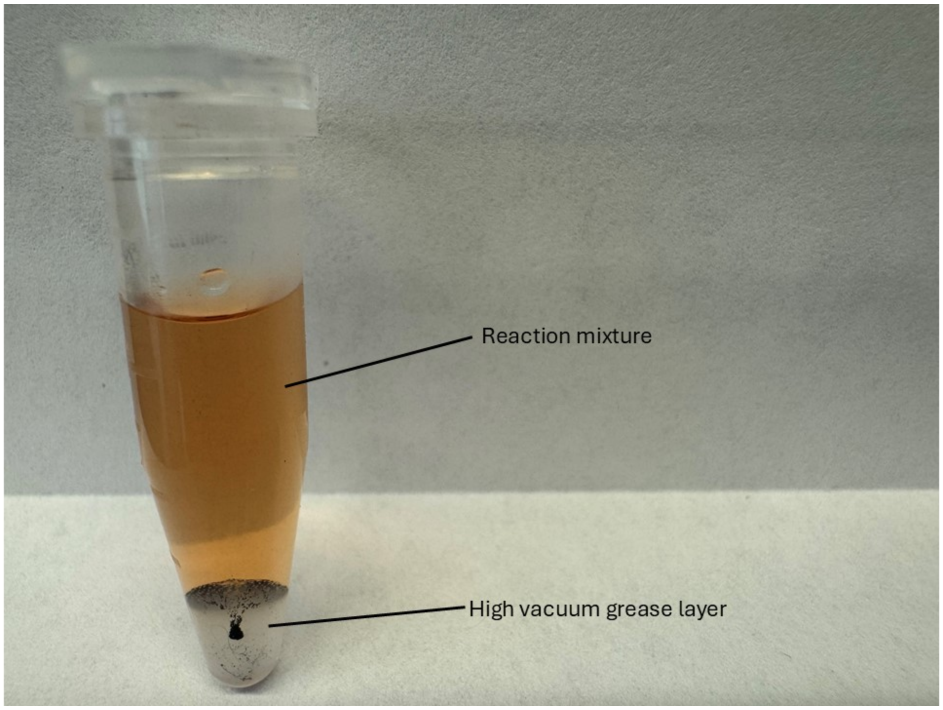

Figure S4. Photo of a typical reaction mixture for a reaction conducted under continuous centrifugation.

Reaction time course for C–H arylation of *N*-methylindole catalyzed by PVP nanoparticles at 70 °C

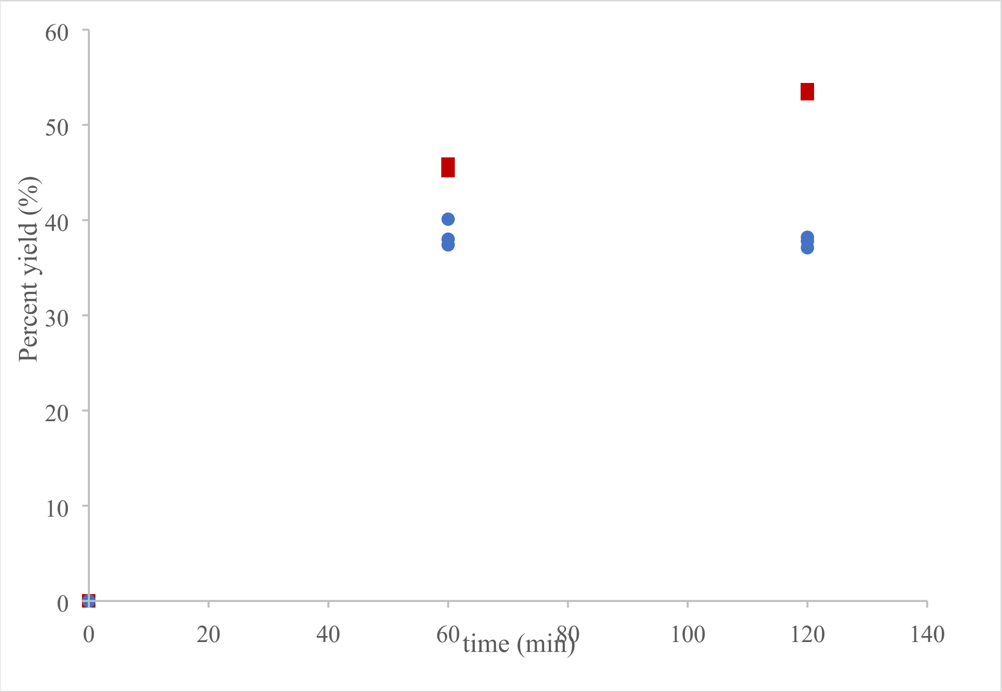

Figure S5. Time course for the formation of 2-(4-(*tert*-butyl)phenyl)-1-methyl-1H-indole in the reaction of *N*-methylindole (1 eq), bis(4-(*tert*-butyl)phenyl)iodonium triflate (CAS: 84563-54-2, 1 eq), at 70 °C in 5:1 AcOH/EtOH, in the presence of a Pd nanoparticles in polyvinylpyrrolidone matrix (0.5 mol % Pd) pre-catalyst, a benzophenone internal standard, and MOLYKOTE® high vacuum grease. Blue circles (•) indicate a reaction with the centrifuge on (RCF = 39677 g) and red squares (▪) represent a reaction at RCF = 1 g. Each point represents the analysis of an independent reaction. Percentages are relative to the theoretical yield (product).

Calculation to estimate mass transfer time for preformed nanoparticles

Inputs and assumptions:

r, particle radius, 2.5 nm = 2.5×10^{-9} m based on average particle size by SEM

$\boldsymbol{\rho_p}$, particle density, 12020 kg/m^3 assuming elemental palladium[9]

$\boldsymbol{\rho_f}$, fluid density, 1049 kg/m^3 assuming pure acetic acid.[9] The actual density will be lower because of the added ethanol but for an estimate with one significant figure the density is treated as 1000 kg/m^3.

g', acceleration of the centrifuge, 39000 g = 39000 x 9.81 m/s^2 = 382590 m/s^2

η, dynamic viscosity approximated as the dynamic viscosity of acetic acid at 25 °C,[10] 0.001115 Pa*s. Adding ethanol will change the second significant digit.[10] Increasing the temperature decreases the dynamic viscosity. The viscosity of acetic acid decreases by almost a factor of 2 as the temperature increases from 20 °C to 70 °C.[11] For this estimate the largest viscosity is used to give a lower bound on the velocity.

Equation used in previous calculations of nanoparticle velocity.[12]

$$v = \frac{(2\, r^2\, (\rho_p - \rho_f)\, g')}{9\, \eta}$$

$$v = \frac{\left(2\, (2.5\, x\, 10^{-9}\, m\,)^2 \left(12000\, \frac{kg}{m^3} - 1{,}00\, \frac{kg}{m^3}\right) 380000\, \frac{m}{s^2}\right)}{9\, (0.001\, Pa * s)}$$

$$v \approx 6\, x\, 10^{-6} \frac{m}{s}$$

A particle at the top of the reaction mixture would need to travel approximately 1 cm to reach the interface between the reaction mixture and the vacuum grease. Given the velocity estimate above this corresponds to a travel time of 2000 seconds, approximately 30 minutes. Particles located closer to the interface initially reach the interface faster.

Procedure for DLS time course studies of C–H arylation with molecular precatalysts

The acetic acid used in this procedure was filtered through a 0.22 µm PTFE syringe filter prior to use. A quartz cuvette with screw cap was rinsed with nanopure water (5x 2 mL) then acetic acid (2 mL) and allowed to air dry upside down.

In a nitrogen-filled glovebox *N*-methylindole (14.8 mg, 0.113 mmol, 1 eq) and the iodonium salt bis(4-(*tert*-butyl)phenyl)iodonium 4-methylbenzene sulfonate (73.0 mg, 0.129 mmol, 1.14 eq, CAS: 131717-99-2), were weighed into separate vials. The vials were brought out of the glovebox. The iodonium salt was dissolved in acetic acid (1.5 mL) and transferred with a Pasteur pipette to the vial containing *N*-methylindole. Additional acetic acid (1 mL) was used to ensure complete transfer of the *N*-methylindole. Ethanol (0.5 mL) was then added to the mixture and was left to stir for 10 minutes. The reaction mixture was filtered through a 0.22 µm PTFE syringe filter into the DLS cuvette.

A stock solution of the palladium precatalyst in THF was prepared. $Pd(OAc)_2$ (34.1 mg, 0.1519 mmol) was dissolved in THF (3 mL) or $IMesPd(OAc)_2$ (26.2 mg, 0.050 mmol) was dissolved in THF (3 mL). The stock solution was filtered through a 0.22 µm PTFE syringe filter prior to use.

The DLS instrument was preheated to the desired temperature and programmed with the desired scan frequency. The palladium precatalyst $IMesPd(OAc)_2$ (170 µL, 0.00561 mmol) or $Pd(OAc)_2$ (95 µL, 0.00481 mmol) was added to the cuvette. The cuvette was inverted, wiped with lens paper, and inserted into the instrument.

CT imaging studies

In a nitrogen filled glovebox, *N*-methylindole (29.7 mg, 0.226 mmol, 1 eq) and the iodonium salt, bis(4-(*tert*-butyl)phenyl)iodonium 4-methylbenzene sulfonate (118.6 mg, 0.210 mmol, 0.929 eq, CAS: 131717-99-2) were measured out in separate vials. The vials were removed from the glovebox. The iodonium salt was dissolved in glacial acetic acid (2.5 mL) and transferred with a pasteur pipet to the vial containing *N*-methylindole. Additional glacial acetic acid (2.5 mL) was used for rinsing. Ethanol (1 mL) was then added to the mixture and left to stir for 10 minutes. A Pasteur pipette was used to add 1 mL of the mixture to centrifuge tubes that were pre-charged with MOLYKOTE® high vacuum grease (above).

A stock solution of $Pd(OAc)_2$ (32.9 mg, 0.147 mmol, 0.650 eq) and THF (3 mL) was prepared or an ethanol suspension of Pd nanoparticles in polyvinylpyrrolidone matrix was prepared as described above.

Tubes were charged with Pd as described in Table S1, inverted twice, and exposed to the centrifugation conditions noted in the table. The tubes were then imaged using micro-CT.

Table S1. Micro-CT images of centrifuge tubes containing Pd-catalyzed C-H functionalization reaction mixtures and MOLYKOTE® high vacuum grease.

Pd precatalyst	**Pd stock solution quantity**	**Reaction time, temp**	**Rotation**	**Image**
Pd(OAc)$_2$	39 µL, 0.00191 mmol	30 min, 30 °C	50 rpm (1 rcf)	
Pd(OAc)$_2$	39 µL, 0.00191 mmol	30 min, 30 °C	13000 rpm (39677 RCF)	
Pd nanoparticles	147 µL, 0.00379 mmol	30 min, 50 °C	50 rpm (1 rcf)	
Pd nanoparticles	147 µL, 0.00379 mmol	30 min, 50 °C	13000 rpm (39677 rcf)	

Procedure for centrifugation time course studies of C–H arylation reaction with $Pd(OAc)_2$.

In a nitrogen-filled glovebox *N*-methylindole (52.9 mg, 0.403 mmol, 1 eq) and the iodonium salt bis(4-(*tert*-butyl)phenyl)iodonium 4-methylbenzene sulfonate (229.0 mg, 0.406 mmol, 1.01 eq, CAS: 131717-99-2) were weighed into separate vials. The vials were brought out of the glovebox and benzophenone (73.9 mg, 0.406 mmol, 1.01 eq), was added to the vial with *N*-methylindole. The iodonium salt was dissolved in acetic acid (5 mL) and transferred with a Pasteur pipette to the vial containing *N*-methylindole. Additional acetic acid (5 mL) was used to ensure complete transfer. Ethanol (2 mL) was then added to the mixture and was stirred for 10 minutes.

A Pasteur pipette was used to add 1 mL of the mixture to centrifuge tubes that were pre-charged with MOLYKOTE® high vacuum grease (above). The tubes were held vertically during the addition. This procedure charges each centrifuge tube with *N*-methylindole (0.033 mmol), iodonium salt (0.034 mmol), and benzophenone (0.033 mmol).

A stock solution $Pd(OAc)_2$ (34.8 mg, 0.155 mmol) in THF (3 mL) was prepared. The centrifuge was preheated to the desired temperature and programed for the desired rotation and run time of the data point. The precatalyst solution in THF (32 µL, 0.00165 mmol, 5 mol %) was then added to the desired number of replicate tubes. The tubes were capped, inverted three times, rapidly loaded into the pre-heated centrifuge and accelerated to the desired rotation.

After the indicated time the tubes were removed from the centrifuge. As quickly as possible after a tube was removed from the centrifuge 10 drops of the reaction mixture were diluted in ethyl acetate (2 mL) and saturated aqueous sodium bicarbonate (2 mL) was added to neutralize the reaction. The organic layer was then transferred to a GC vial for analysis by GC-FID.

No Pd solution was added to the T=0 timepoints.

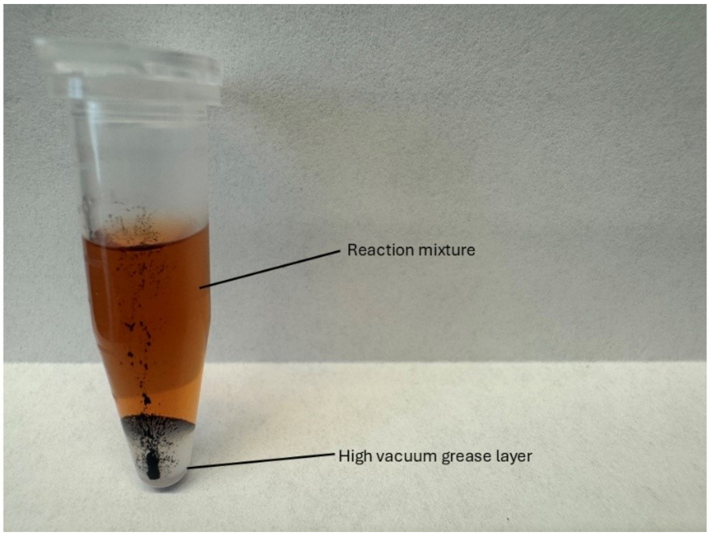

Figure S6. Photo of a typical reaction mixture for a reaction conducted under continuous centrifugation.

Isolation of nanoparticles generated from $Pd(OAc)_2$ for SEM and EDS analysis

The reaction was conducted above with the centrifuge off but in a centrifuge tube that had not been charged with MOLYKOTE® high vacuum grease. After the reaction was complete the mixture was centrifuged to give a dark pellet. The precipitate was washed with ethanol, suspended in ethanol by sonication, and deposited on a 400 mesh copper/carbon grid. Scanning electron microscopy imaging was conducted using a JEOL-7200F field emission SEM operated at 15 kV with a working distance of 1 nm.

EDS analysis of nanoparticles generated in situ from $Pd(OAc)_2$

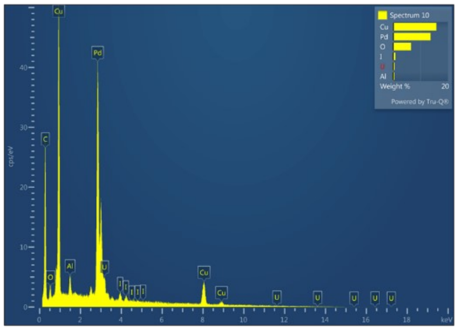

Figure 7. EDS analysis of nanoparticles formed during the reaction of *N*-methylindole and an aryl iodonium salt in the presence of a $Pd(OAc)_2$ pre-catalyst. The particles were deposited on a 400 mesh copper/carbon grid.

Procedure for centrifugation time course studies of C–H arylation reaction with $IMesPd(OAc)_2$.

In a nitrogen-filled glovebox *N*-methylindole (103.9 mg, 0.792 mmol, 1 eq) and the iodonium salt bis(4-(*tert*-butyl)phenyl)iodonium 4-methylbenzene sulfonate (466.0 mg, 0.825 mmol, 1.05 eq, CAS: 131717-99-2) were weighed into separate vials. The vials were brought out of the glovebox and benzophenone (147.1 mg, 0.813 mmol, 1.02 eq) was added to the vial with *N*-methylindole. The iodonium salt was dissolved in acetic acid (10 mL) and transferred with a Pasteur pipette to the vial containing *N*-methylindole. Additional acetic acid (5 mL) was used to ensure complete transfer. Ethanol (4.2 mL) was then added to the mixture and was stirred for 10 minutes.

A Pasteur pipet was used to add 1 mL of the mixture to centrifuge tubes that were pre-charged with MOLYKOTE® high vacuum grease (above). The tubes were held vertically during the addition. This procedure charges each centrifuge tube with *N*-methylindole (0.031 mmol), iodonium salt (0.033 mmol), and benzophenone (0.033 mmol).

A stock solution $IMesPd(OAc)_2$ (18.3 mg, 0.035 mmol) in THF (1.5 mL) was prepared. The centrifuge was preheated to the desired temperature and programed for the desired rotation and run time of the data point. The precatalyst solution in THF (69 µL, 0.0015 mmol, 5 mol %) was then added to the desired number of replicate tubes. The tubes were capped, inverted once, rapidly loaded into the pre-heated centrifuge and accelerated to the desired rotation.

After the indicated time the tubes were removed from the centrifuge. As quickly as possible after a tube was removed from the centrifuge 10 drops of the reaction mixture were diluted in ethyl acetate (2 mL) and saturated aqueous sodium bicarbonate (2 mL) was added to neutralize the reaction. The organic layer was then transferred to a GC vial for analysis by GC-FID.

No Pd solution was added to the T=0 timepoints.

Procedure for filtration experiments

In a nitrogen-filled glovebox *N*-methylindole (27.0 mg, 0.206 mmol, 1 eq), the iodonium salt bis(4-(*tert*-butyl)phenyl)iodonium 4-methylbenzene sulfonate (115.7 mg, 0.205 mmol, 0.995 eq, CAS: 131717-99-2) were weighed into separate vials. The vials were removed from the glovebox and benzophenone (34.6 mg, 0.190 mmol, 0.922 eq), was added to the vial with *N*-methylindole. The iodonium salt was dissolved in acetic acid (2.5 mL) and transferred with a Pasteur pipette to the vial containing *N*-methylindole. Additional acetic acid (2.5 mL) was used to ensure complete transfer. Ethanol (1 mL) was added, and the mixture was stirred for 10 minutes. The stock solution was then divided into 1 mL portions and placed into plastic tubes. Each tube contains *N*-methylindole (0.0342 mmol), benzophenone (0.0313 mmol), and iodonium salt (0.0340 mmol).

A stock solution of $Pd(OAc)_2$ (34.1 mg, 0.152 mmol) in THF (3 mL) was prepared. The precatalyst solution in THF (34 µL, 0.00172 mmol, 5 mol %) was then added to each centrifuge tube. The tubes were capped, inverted once, and heated to 30 °C. At each time point an aliquot was removed with a Pasteur pipette and ten drops of the aliquot were, diluted into ethyl acetate (2 mL) and saturated aqueous sodium bicarbonate (2 mL) was added to neutralize the reaction. The organic layer was then transferred to a GC vial for analysis by GC-FID.

For the filtration, Pasteur pipettes were prepared with glass fiber filter and 1 cm of celite. At the desired filtration time a reaction mixture was passed through the filter. The effluences were collected in clean tubes and exposed to continued heating at 30 °C.

No Pd solution was added to the T=0 timepoints.

Procedure for alkene oxidation in DSMO/ethanol/water mixture

In nitrogen atmosphere, a vial was charged with 4-methoxystyrene (100 mg, 0.7453 mmol, 1 eq). A separate vial was charged with benzoquinone (72.5 mg, 0.6708 mmol, 0.9 eq), DMSO (1.8 mL), and trifluoroacetic acid (57 µL, 0.08493 mmol, 1 eq). In air, ethanol (3 mL) and water (1.2 mL) were added to the benzoquinone solution. The benzoquinone solution was transferred to the vial containing the 4-methoxystyrene which prompted a color change from yellow to orange. Phenanthrene (33.2 mg, 0.1863 mmol, 0.25 eq) was added as an internal standard and the mixture was sonicated until the solid dissolved. Aliquots of this solution (700 µL) were then dispensed into centrifuge tubes that were pre-charged with MOLYKOTE® high vacuum grease (above).

A stock solution of $Pd(OAc)_2$ was prepared by dissolving ~20 mg of $Pd(OAc)_2$ in 5 mL of THF. The amount of stock solution added to the tube was calculated based on the amount of substrate and catalyst that had been weighed in order to achieve 1 mol % stock solution in each tube. The centrifuge was preheated to the desired temperature and programed for the desired rotation and run time of the data point. The precatalyst solution in THF was then added to the desired number of replicate tubes. The tubes were capped, inverted once, rapidly loaded into the pre-heated centrifuge and accelerated to the desired rotation.

After the indicated time the tubes were removed from the centrifuge. A sample of the reaction mixture (5 drops) was added to DCM (2 mL) and washed with saturated aqueous $NaHCO_3$ (1 mL). The bottom organic layer was separated for GC-FID quantification.

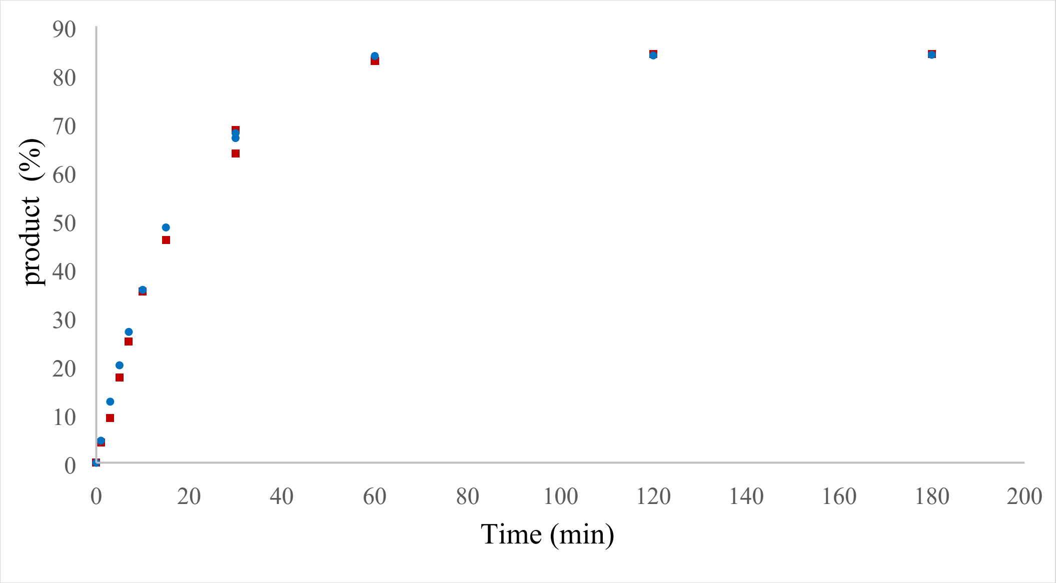

Figure S8. Time course for the formation of 4-methoxyacetophenone in the reaction of 4-methoxystyrene (1 eq), benzoquionone (0.9 eq), at 35 °C in 3:5:2 DMSO:EtOH:H_2O, in the presence of $Pd(OAc)_2$ (1 mol %) pre-catalyst, a phenanthrene internal standard, and MOLYKOTE® high vacuum grease. Circles (•) indicate a reaction with the centrifuge on (RCF = 39677 g) and squares (▪) represent a reaction at RCF = 1 g. Each point represents the analysis of an independent reaction. Percentages are relative to the theoretical yield (product).

The remaining reaction mixture was photographed (Figure S9).

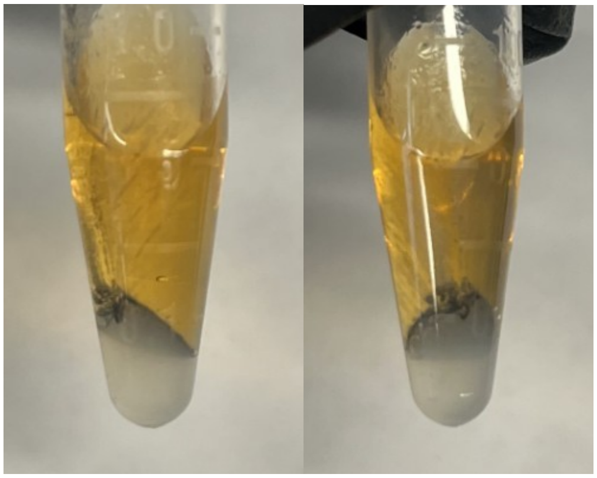

Figure S9. Photos of centrifuge tubes from a Pd-catalyzed alkene oxidation reaction after centrifugation (35 °C for 4 hours at 39677 g). A black solid is visible at the interface between the reaction mixture and the MOLYKOTE® high vacuum grease.

References

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