Supporting Information for

A dichotomy in cross-coupling site-selectivity in a dihalogenated heteroarene: Influence of mononuclear Pd, Pd clusters and Pd nanoparticles – the case for exploiting Pd catalyst speciation

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1.0. General Information

1.1. Compound Preparatory Techniques and Methods for In-laboratory Analysis

Reagents were purchased from Merck (Sigma-Aldrich), Alfa Aesar, Acros Organics or Fluorochem and used as received unless otherwise stated. Pd(OAc)$_2$ (indicated as >99% purity based on Pd; nitrite-free as judged by IR and NMR spectroscopic analysis) was obtained from Precious Metals Online (PMO) and used as received. Triphenylphosphine (PPh$_3$) was purified by recrystallization from hot ethanol and dried under high vacuum, before being stored over P$_2$O$_5$ for ca. 7 days. THF was dried by refluxing over finely-sliced sodium metal (2 × 8 hours) before being distilled, transferred to an ampoule via cannula and subsequently deoxygenated by bubbling with argon for ca. 30 min. THF-$d_8$ and CD$_2$Cl$_2$ were freeze-pump-thaw degassed before being distilled into an ampoule and stored under Ar. Petroleum ether (petrol/PET) refers to the fraction of petroleum that distils at 40-60 °C. Brine refers to a saturated, aqueous solution of NaCl.

2,4-Dibromopyridine 1 was purchased from Fluorochem and used as received (special note: significant bromide impurities in material purchased from other suppliers were found, likely to be bromide salts, thus the purity was checked by $^1$H NMR using trimethoxylbenzene as an external standard; typical purity was >99%). Aryl boronic acids were purchased from Tokyo Chemical Industries (TCI) or Fluorochem and used as received. N-tetrabutylammonium hydroxide ($n$-Bu$_4$NOH (aq.)) was purchased (Merck) as a 1.5 M aqueous solution, diluted to 1.0 M using deionised water before being transferred into an ampoule and deoxygenated by bubbling through with N$_2$ on a Schlenk line. KOH (1.0 M, aq.) was prepared in-house using deionised H$_2$O and deoxygenated by bubbling through with N$_2$ and stored in a J. Youngs tap-sealed ampoule. Phenylmagnesium bromide (5) solution (1.2 mL, 1.0 M in THF) was purchased from Merck. After receipt, the solution was transferred via cannula, driven by N$_2$ balloon pressure, into an oven-dried ampoule, sealed with a J. Youngs tap. Tetra-$n$-butylammonium bromide ($n$-Bu$_4$NBr) and tetra-$n$-octylammonium bromide ($n$-octyl$_4$NBr) were purchased from Merck and used as received, taking care to minimise exposure to air, due to their hygroscopicity.

$[\text{Pd}_3(\mu\text{-Cl})(\mu\text{PPh}_3)_2(\text{PPh}_3)_3]\text{Cl}$ (abbreviated to Pd$_3$Cl$_2$ in the paper) was prepared according to an adapted literature procedure.$^1$ [Pd($^6$(PPh$_3$)$_4$)] was prepared using an established literature procedure, published by D. R. Coulson and stored in an Argon-filled glovebox at -30 °C.$^2$

All reactions were carried out using an Ar-filled glovebox or by Schlenk techniques (high vacuum, liquid nitrogen trap on a standard in-house built dual line), to eliminate atmospheric air or adventitious moisture from the reaction systems. Room temperature upper and lower limits are stated as 13-25 °C, but typically 21 °C was recorded. Thin layer chromatography (TLC) was carried out using Merck 5554 aluminium–backed silica plates (silica gel 60 F254) and spots were visualized using UV light (at 254 nm). Retention factors (R$_f$) are reported in parentheses along with the solvent system used. Flash column chromatography was performed using Sigma-Aldrich 60 Å silica gel (SiO$_2$. particle size 40–63 μm) and a solvent system as reported in the text.
1.2 Instrument Details and Methods for Compound Characterisation

NMR spectra were obtained in the solvent indicated in the text below, using a Bruker AVIIIHD 500 instrument (500 MHz \[^1H\], 470 MHz \[^19F\], 203 MHz \[^31P\] 125 MHz \[^{13}C\]) or JEOL ECX400 or JEOL ECS400 spectrometer (400 MHz \[^1H\], 101 MHz \[^{13}C\] and 377 MHz \[^19F\]). Chemical shifts (δ) are reported in parts per million (ppm) and were referenced to the residual non-deuterated solvent of the deuterated solvent used; CHCl₃: δ \[^1H\] = 7.26 and \[^{13}C\] = 77.16 (CDCl₃), CD₂Cl₂: \(^1H = 5.31\) (CDHCl₂) and \[^{13}C\] = 54.0, THF-d₈ δ \[^1H\] = 3.59 (OCH₂CH₂), \[^{13}C\] = 67.57 OCH₂CH₂, \(^1H = 1.73\) (OCH₂CH₂) \[^{13}C\] = 25.37 (OCH₂CH₂). Spectral data was typically collected at 298 K (25 °C).

\(^{31}P\) NMR spectral data were collected with proton decoupling, unless otherwise stated. \(^{31}P\) NMR spectra were typically recorded using 128 scans and a spectral window of 300 ppm (δ 250 to -50 ppm). Chemical shifts for \(^{31}P\) resonances were calibrated by externally referencing to an 85% H₃PO₄ in H₂O (w/w). This was practically carried out by inserting a sealed, vacuum-dried capillary tube containing 85% H₃PO₄ in H₂O (w/w) into an NMR tube containing the sample of interest, collecting a \(^{31}P\) NMR spectrum and setting the H₃PO₄ resonance to 0 ppm. All \(^{31}P\) and \(^{13}C\) NMR spectra were obtained with \(^1H\) decoupling. All NMR spectra were processed using MestReNova (MNova) software (using versions 12–14).

HRMS ESI-MS spectra were measured using a Bruker Daltronics microTOF MS, Agilent series 1200LC with electrospray ionisation (ESI) or on a Thermo LCQ using electrospray ionisation, with <5 ppm error recorded for all HRMS samples. LIFDI mass spectrometry was carried out using an JEOL AccuTOF GCx-plus instrument (JMS-T200GC), fitted with a probe produced by Linden CMS. The probe was equipped with 13 µm emitters on an AccuTOF. Alternatively, LIFDI-MS was carried out using a Waters GCT Premier MS Agilent 7890A GC instrument. Mass to charge ratios (m/z) are reported in Daltons. High resolution mass spectra (HRMS) are reported with <5 ppm error (ESI and LIFDI). For clarity, LIFDI data are reported for \(^{106}Pd\), the most abundant natural isotope of Pd, which is part of ‘exact mass’ values.

Infrared spectra were obtained using a Bruker ALPHA-Platinum FTIR Spectrometer with a platinum-diamond ATR sampling module.

Melting points were recorded using a Stuart digital SMP3 melting point analysis machine.

Elemental analysis (Carbon, Hydrogen and Nitrogen (CHN) content) was carried out on an Exeter Analytical Inc. CE-440 analyser.

For single crystal X-ray crystallographic analysis details, see Section 4.
2. Experimental Details

2.1. General Procedure: Pd$_3$(OAc)$_6$/nPPh$_3$ Ratio Experiments (Figure 1 – Main Paper)

Scheme S1 Summarising the conditions and reagents used for the SMCC between 2,4-dibromopyridine 1 and 4-fluorobenzeneboronic acid 2a. Conversions and site-selectivities were determined by analysing the $^1$H NMR spectrum of a sample taken after 1 hour.

An oven-dried Schlenk tube (Flask 1) charged with Pd$_3$(OAc)$_6$ (6.7 mg, 0.03 mmol {3 mol%/Pd}) and triphenylphosphine (Table S1) was evacuated and backfilled with N$_2$. THF (2.5 mL; dry, degassed) was added via a syringe and the immediately formed greenish-yellow suspension was stirred in an oil bath which was pre-heated to 40 °C. Another oven-dried Schlenk tube (Flask 2) was charged with 2,4-dibromopyridine (236.9 mg, 1.00 mmol, 1 equiv.) and p-fluorophenylboronic acid 2a (167.9 mg, 1.20 mmol) and subsequently evacuated and backfilled with N$_2$. After 30 minutes of stirring, the contents of Flask 1 were transferred into Flask 2 via a cannula and the resulting mixture was stirred for 5 mins in order to thermally equilibrate at 40 °C. Aqueous Tetra-$N$-butylammonium hydroxide (2.5 mL, 1.0 M, degassed) was then added (t$_0$) to commence the reaction.

Samples (ca. 125 µL), taken at the specified times using a 1000 µL syringe were rapidly quenched by dissolution in CH$_2$Cl$_2$ solution before being filtered through a pipette fitted with a Celite® plug (ca. 1 cm depth) (to remove black particles). The filtrate was concentrated in vacuum to reveal a reddish-brown oil which was dissolved in CDCl$_3$ (0.5 mL) for NMR sampling. Samples were analysed according to the procedure highlighted in Section 2.7.
Table S1 Detailing the ratio of Pd₃(OAc)₆ to PPh₃, alongside the quantity (mmol and mg) of triphenylphosphine PPh₃ used in each reaction.

| Pd₃(OAc)₆:PPh₃ (mol%:mol%) | Pd:P ratio | Amount of PPh₃ (mmol) | Mass of PPh₃ (mg) |
|----------------------------|-------------|-----------------------|-------------------|
| 1:0                       | 1:0         | N/A                   | N/A               |
| 1:1.5                     | 1:0.5       | 0.015                 | 3.9               |
| 1:3                       | 1:1         | 0.03                  | 7.9               |
| 1:4.5                     | 1:1.5       | 0.045                 | 11.8              |
| 1:6                       | 1:2         | 0.06                  | 15.7              |
| 1:7.5                     | 1:2.5       | 0.075                 | 19.7              |
| 1:9                       | 1:3         | 0.09                  | 23.6              |
| 1:12                      | 1:4         | 0.12                  | 31.5              |

2.2. Base and Additive Effects – SMCC Reactions (Table 1 – Main Paper)

Scheme S2 Conditions and reagents for the investigation into base and additive effects on the model site-selective SMCC reaction at 1, catalysed by [Pd₃(μ-Cl)(μ-PPh₃)₂(PPh₃)₃]Cl or Pd(OAc)₂/1 or 2 PPh₃.

An oven-dried Schlenk tube (Flask 1) charged with 2,4-dibromopyridine 1 (236.9 mg, 1.0 mmol), para-anisyl boronic acid 2b (182.4 mg, 1.2 mmol) Pd Cat. (3 mol% Pd loading; see Table S2 for specifics) was evacuated and backfilled with N₂. Depending on the reaction, the salt additive was added at this point (See Table S3 for amounts used). The flask atmosphere was then evacuated and backfilled with N₂ before THF (2.5 mL; dry, degassed) was added via a syringe and stirred for 5 minutes at 40 °C (pre-heated oil bath). After this time, aqueous base (2.5 mL, 1.0 M, degassed) was added (t₀) to commence the reaction. The resulting reaction solution was hence stirred at 40 °C. Samples (ca. 125 µL), taken at the specified times using a 1000 µL syringe were rapidly quenched by...
dissolution in CH$_2$Cl$_2$ solution before being filtered through a pipette fitted with a Celite® plug (ca. 1 cm depth) (to remove black particles). The filtrate was concentrated in vacuum to reveal a reddish-brown oil which was dissolved in CDCl$_3$ (0.5 mL) for NMR sampling. See Section 2.7, for details of sample analysis.

**Table S2 Catalyst/PPh$_3$ amounts used**

| Catalyst/PPh$_3$ amount | m / mg  | n / mmol |
|-------------------------|---------|----------|
| Pd$_3$(OAc)$_6$ / {3PPh$_3$} | 6.7 / {7.9} | 0.01 / {0.03} |
| Pd$_3$(OAc)$_6$ / {6PPh$_3$} | 6.7 / {15.7} | 0.01 / {0.06} |
| [Pd$_3$($\mu$-Cl)(μ-PPh$_2$)$_2$(PPh$_3$)$_3$]Cl | 15.5 | 0.01 |

**Table S3 Additive amounts used**

| Additive     | m / mg | n / mmol |
|--------------|--------|----------|
| n-Bu$_4$NBr  | 805    | 2.5      |
| n-Oct$_4$NBr | 1367   | 2.5      |

### 2.3. Product Evolution Curves for Site-selective SMCC Reactions at 2,4-Dibromopyridine 30 (Figure 2 – Main Paper)

![Scheme S3 Conditions and reagents for the product evolution assays on the model site-selective SMCC reaction between 1 and 2b, catalysed by [Pd$_3$(μ-Cl)(μ-PPh$_2$)$_2$(PPh$_3$)$_3$]Cl or Pd(OAc)$_2$/2PPh$_3$.](image)

To an oven-dried Schlenk tube, 2,4-dibromopyridine 1 (473 mg, 2.0 mmol, 1.0 equiv.), para-anisylboronic acid 2b (365 mg, 2.4 mmol, 1.2 eq) and ‘Pd catalyst’ (3 mol%/Pd, see Table 4) were added. The flask was sealed (Suba-seal®), THF (2.5 mL; dry, degassed) was added using a syringe and the resulting mixture was magnetically stirred for 5 minutes, in a pre-heated oil bath. After this time, all solids were seen to have dissolved into a clear
solution and the temperature of the reaction was measured at 40 ± 0.5 °C using an internal thermocouple. The cross-coupling reaction was then initiated by addition of tetra-n-butylammonium hydroxide solution (aq. 2.5 mL, 1.0 M→0.5 M, 2.5 equiv.) which was added by a rapid injection using a syringe over the Suba-seal®. The reaction was stirred, and samples were taken at the 0, 2.5, 5, 7.5, 10, 15, 20, 25, 40, 50, 60, 80 and 100 minutes. Samples (ca. 100 µL), taken at the specified times via a 1000 µL syringe were rapidly quenched by dissolution in CH₂Cl₂ before being filtered through a pipette fitted with a Celite® plug (ca. 1 cm depth) (to get rid of any particulate Pd). Each filtrate was concentrated in vacuum to reveal a reddish-brown oil which was dissolved in CDCl₃ (0.5 mL) for NMR sampling. Each NMR spectrum was analysed according to the method reported below (Section 2.7) and the results were graphed using Origin 2018 software.

| Table 4 Catalysts, loadings and masses used in product evolution assays (Graphs A & B, Figure 2 – main paper) |
|-------------------------------------------------|--------|----------------|---------|
| Pd Catalyst                                    | mol / %| n / mmol        | m / mg  |
| [Pd₃(μ-Cl)(μ-PPh₂)₂(μ-PPh₃)]Cl (Pd₃Cl₂, Graph A) | 1      | 0.02           | 30.9    |
| Pd₃(OAc)₆/{2PPh₃} (Graph B)                    | 1/{6}  | 0.02/{0.012}   | 13.5/{31.5} |

2.4. Site-selectivity in Kumada-Corriu Cross-couplings at 1 (Table 2 – Main Paper)

Scheme S4 Conditions and reagents used for the Kumada cross-coupling of 2,4-dibromopyridine 1 with phenylmagnesium bromide 5
A Schlenk flask (Flask 1) was charged with Pd\(_3\)(OAc)_6 (6.7 mg, 0.01 mmol, 1 mol%, Table S5) and PPh\(_3\) (3, 6, or 12 mol%, Table S5), tetra-N-octylammonium bromide (805.92 mg, 1.5 equiv.) and sealed (rubber septum) before being evacuated and backfilled with N\(_2\) three times. THF (2.5 mL; dry, deoxygenated) was added and the resulting mixture was stirred at 23 °C for 0.5 or 24 hours.

A second Schlenk tube (Flask 2) was charged with 2,4-dibromopyridine before being evacuated and backfilled with N\(_2\) three times. THF (1.3 mL) was added and the resulting clear solution was stirred at room temperature. After the specified premixing time, the contents of Flask 1 were transferred via cannula to Flask 2. The resulting mixture was allowed to equilibrate for 1 minute with stirring after which time phenylmagnesium bromide solution (5, 1.2 mL, 1.0 M in THF => total volume of 5 mL) was added in a rapid injection. The subsequent solution was stirred for one hour.

A sample (125 µL) was taken via a syringe and quickly quenched by addition to a vial containing 100 µL of NH\(_4\)Cl solution (aq., sat.). EtOAc (2 mL) was added to the sample and the resulting mixture was vigorously shaken. The EtOAc was removed using a pipette and the aqueous layer was extracted with another aliquot of EtOAc (2 mL). The combined organics were filtered through a MgSO\(_4\) plug (ca. 1 cm depth) which was washed through with EtOAc (1 mL). The filtrate was concentrated in vacuo to afford a yellow oil which was dissolved in CDCl\(_3\) and subjected to \(^1\)H NMR analysis (see Section 2.7).

Table S5 Detailing ratio of Pd\(_3\)(OAc)_6 to PPh\(_3\), alongside the quantity (mmol and mg) of triphenylphosphine PPh\(_3\) used in this study.

| Pd\(_3\)(OAc)_6:PPh\(_3\) (mol%:mol%) | Pd:P ratio | Amount of PPh\(_3\) (mmol) | Mass of PPh\(_3\) (mg) |
|-------------------------------------|------------|--------------------------|-----------------------|
| 1:3                                 | 1:1        | 0.03                     | 7.9                   |
| 1:6                                 | 1:2        | 0.06                     | 15.7                  |
| 1:12                                | 1:4        | 0.12                     | 31.5                  |
2.5. *Para*-substituent Effects on Site-selectivity in SMCC Reactions at 1 (Figures 3 & 4 – Main Paper)

An oven-dried Schlenk tube, charged with a Pd catalyst (3 mol%/Pd, see Table S6), 2,4-dibromopyridine 1 (236.9 mg, 1.0 mmol), boronic acid 2a-f (1.2 mmol), (Scheme S5) was sealed (Suba-seal®) before being evacuated and backfilled with N₂. THF (2.5 mL; dry, degassed) was added via a syringe (over the Suba-seal®) and the resulting solution was stirred in an oil bath which was pre-heated to 40 °C for 5 mins in order to thermally equilibrate. *Tetra-n-butylammonium* hydroxide solution (2.5 mL, 1.0 M; degassed) was then added (t₀) to commence the reaction.

Samples (ca. 125 µL), taken at 1 hour using a 1000 µL (1 mL) gas-tight syringe were rapidly quenched by dissolution in CH₂Cl₂ solution before being filtered through a pipette fitted with a Celite® plug (ca. 1 cm depth) (to remove black particles). The filtrate was concentrated in vacuo to furnish a reddish-brown oil which was dissolved in CDCl₃ (0.5 mL) for NMR sampling (see Section 2.7).

### Table S6 Catalyst amounts used

| Pd Cat. | m / mg | n / mmol |
|---------|--------|----------|
| Pd₂(dba)₃.CHCl₃ [2PPh₃] | 16.5 {7.9} | 0.015 {0.03} |
| [Pd₃(μ-Cl)(μ-PPh₂)₂(PPh₃)₃]Cl | 15.5 | 0.01 |
| Pd₃(OAc)₆ {PPh₃} | 6.7 {7.9} | 0.01{0.03} |
2.6. General Workup Procedure for SMCC Reactions

The above cross-coupling reactions (from Sections 2.1-2.5) were worked-up using the following procedure. After the reaction time, the reaction solution was quenched using a of NH$_4$Cl (sat. aq). The organics were then extracted using EtOAc ($4 \times 10$ mL) and combined before drying over MgSO$_4$, filtered and subsequently concentrated in vacuo. The resulting residue, which generally appeared as a reddish-brown oil, could be purified by column chromatography (SiO$_2$) using a hexane or petroleum ether/EtOAc solvent system. See Section 3 for purification details for specific compounds.

2.7. $^1$H NMR Analysis of NMR Samples of Cross-coupling Reactions

The reaction conversion and site-selectivity of cross-coupling reactions at 2,4-dibromopyridine 1 were determined using a $^1$H NMR spectroscopy-based assay of crude reaction samples (unless otherwise stated). Crude reaction samples were prepared according to the relevant method. Products were identified from the crude reaction mixtures by reference to literature published data or, if the product was not reported, by comparison to characterisation data obtained for the isolated product. The pyridyl-$H_6$ protons of the starting materials and products were generally well-resolved, due to the significant deshielding (proximity to electronegative N), thus, integration of these protons was generally used to determine the relative amounts of starting material and products; C$_2$Ar, C$_4$Ar and diaryl (see Figure S1 for a typical example of how this integration was done for each reaction).
Figure S1 Method used for identifying and quantifying products of site-selective cross-coupling reactions at 2,4-dibromopyridine by $^1$H NMR spectroscopy. A) crude NMR spectrum, B) expansion of aromatic region, allowing for the characterisation of products, C) Expansion of the pyridine-$H_6$ region, integration of which allowed for determination of reaction conversion and site-selectivity of the reaction.

How conversion and site-selectivity data was obtained:

\[ \text{e.g. Overall Conversion} \ (\%) = \frac{\text{integration C2+C4+diaryl}}{\text{integration S.M.} + \text{C2+C4+diaryl}} \times 100 = 87.6\% \]

Conversion of given product e.g. C2 (\%) = \[ \frac{\text{integration C2}}{\text{integration S.M.} + \text{C2+C4+diaryl}} \times 100 = 15.7\% \]

Table 7 Example, processing of integration data

|                | S.M. (1) | C4Ar | C2Ar | diaryl |
|----------------|----------|------|------|--------|
| Integral       | 0.79     | 3.71 | 1.00 | 0.87   |
| Conversion (%) | 12.4     | 58.2 | 15.7 | 13.7   |

The above method was validated using an internal standard, 1,3,5-trimethoxybenzene. 1,3,5-Trimethoxybenzene (56.0 mg, 0.333 mmol) was added as a solid, alongside the other solids of the reaction mixture: Pd(OAc)$_2$/1PPh$_3$, 2,4-dibromopyridine 1 (1.0 mmol) and the para-substituted phenylboronic acid (2a-f, 1.20 mmol). The reaction was carried out and sampled as highlighted in Section 2.5. The sample was analysed by $^1$H NMR spectroscopic analysis (Figure S2) (see Section 3 below for specific details concerning product identification).
Figure S2 A $^1$H NMR spectrum (400 MHz, CDCl$_3$), showing how the pyridine-H$_6$ peaks representing 1 and the three SMCC products were quantified against the aryl-H resonance of the 1,3,5-trimethoxybenzene internal standard ('Int Std') in a crude reaction sample.

The products could then be quantified against the internal standard as follows (Table S8), providing confidence in the assay as a validated quantitative method.

Table S8 An example of how the method of analysis of the crude SMCC reaction mixture was validated by use of a 1,3,5-trimethoxybenzene internal standard. *Internal standard = Peak at $\delta_H$ 6.08 ppm, representing 3 × Aryl-H protons was used.

|                | S.M. (1) | C4Ar | C2Ar | diaryl | Int Std* |
|----------------|----------|------|------|--------|----------|
| Integral       | 0.67     | 9.88 | 1.00 | 1.09   | 12.67    |
| Conversion (%) | 5.3      | 78.2 | 7.9  | 8.6    | N/A      |
| Conversion (%) against Int Std* | 5.3 | 78.0 | 8.0  | 8.6    | N/A      |

2.8. Oxidative Addition Reaction of [Pd$^0$(PPh$_3$)$_4$] to 1 (Figure 6 – Main Paper)

Scheme S6 The direct reaction between [Pd$^0$(PPh$_3$)$_4$] and 2,4-dibromopyridine 1.
[Pd⁰(PPh₃)₄] (0.20 g, 0.173 mmol) was treated with 2,4-dibromopyridine 1 (41.0 mg, 0.173 mmol) at room temperature, in toluene (0.5 mL dry, degassed) with stirring for 16 hours, according to the experimental method previously reported by Cid and co-workers (Scheme S6).³ After removing the toluene solvent in vacuo and washing the residue with diethyl ether (3 × 0.5 mL; dry, degassed), ³¹P spectroscopic analysis of a CD₂Cl₂ solution of the crude reaction product (a. Figure S3) confirmed the site-selectivity of the oxidative addition, with resonances at δP 22.8, 24.3, 27.6, respectively, representing products in a ratio of OA_C₂Br:OA_C₄Br:OA_C₂Br-dinuc = 1.00:0.04:0.03 (verified against data reported by Cid and co-workers) under the conditions.³ According to ³¹P NMR spectroscopic analysis, the C2/C4-selectivity for the oxidative addition is ca. 25:1, consistent with the overall C2-selectivity observed for the SMCC reactions employing [Pd⁰(PPh₃)₄].

Figure S3 (LEFT.) ³¹P NMR spectrum (162 MHz, CD₂Cl₂), showing the distribution of products oxidative addition of [Pd⁰(PPh₃)₄] to 1. (RIGHT.) ¹H NMR spectrum of the same crude sample (400 MHz, CD₂Cl₂), showing OA_C₂Br as the major species, H₃ and H₅ protons on the 4-bromopyridiyl ligand have been assigned.

Crystals were grown by carefully layering the above CD₂Cl₂ solution with excess dry, degassed hexane (1:3 v/v). The crystalline product could therefore be isolated for further characterisation (vide infra) in a 26% yield of isolated OA_C₂Br product (unoptimized crystallisation). Upon subjecting one such crystal to XRD analysis, the solid-state structure was confirmed as being that of the OA_C₂Br oxidative addition product (Figure S4).
Figure S4 XRD structure of a single crystal of OA_{C2-Br}, obtained from the reaction of 2,4-dibromopyridine 1 with [Pd^0(PPh$_3$)$_4$].

$^1$H NMR spectroscopic analysis of a CD$_2$Cl$_2$ solution of the crude reaction product showed significantly shielded aromatic resonances, at δ 6.65 and 6.23 ppm (Right, Figure S3), which were assigned as –H$_3$ and –H$_5$ protons on the 4-bromopyridyl ligand based on their coupling constants and relative integrations. This upfield-shifting of these proton resonances is likely a result of the interaction of the aromatic ring currents associated with the proximal phenyl moieties. Such an interaction is evident in the crystal structure (Figure S4), which shows an interfacial π-stacking interaction – the 4-bromopyridyl ligand is sandwiched between two phenyl groups from the trans-configured triphenylphosphine ligands, providing further support that the crystal obtained (XRD) is the major species observed by $^1$H NMR spectroscopic analysis (in solution).

Characterisation Data for Bromo(4-bromo-C2-pyridinyl)bis(triphenylphosphine)Palladium$^\text{II}$ OA$_{C2-Br}$$^3$

(N.B. in solution OA$_{C2-Br}$ converts over time to the dimer product OA$_{C2-Br\text{-dinauc}}$ with release of uncoordinated PPh$_3$, therefore after isolation by crystallisation during solution characterisation of OA$_{C2-Br}$ (by e.g. NMR spectroscopy) a mixture of the three species rapidly arises)

$^{31}$P NMR (202 MHz, dichloromethane-$d_2$) δ 22.84 (s) ppm. $^1$H NMR (500 MHz, dichloromethane-$d_2$) δ 7.64 – 7.54 (m, 12H, PPh$_3$), 7.44 – 7.36 (m, 7H, PPh$_3$ (6H) + pyridyl-C$_6$-H(1H)), 7.35 – 7.28 (m, 12H), 6.66 (d, J = 1.9 Hz, 1H, pyridyl-C$_3$-H), 6.23 (dd, J = 5.3, 1.9 Hz, 1H, pyridyl-C$_5$-H) ppm.

ESI-MS Data (+ve mode) mode: Found 786.0328 [M–Br]$^+$ Calc. (for C$_{42}$H$_{39}$O$_6$P$_2$Pd$_2$) 786.0301.

IR (v/cm$^{-1}$, ATR): 3049 (w, C–H), 1589 (m), 1535 (m), 1525 (m), 1480 (m), 1433 (s), 1346 (m), 1186 (m), 1094 (m), 998 (m), 807 (m), 740 (br, m), 690 (br, s), 517 (br, s), 499 (s).
Elemental analysis (% CHN), calculated for C_{41}H_{33}Br_{2}NP_{2}Pd: C, 56.74; H, 3.83; N, 1.61; Found: C, 56.55; H, 3.79; N, 1.61.

See Section 4 for X-Ray Crystallographic Data (ijsf1805).

2.9. Reaction of Pd_{3}(OAc)_{6} with 3 Equivalents of PPh_{3} (Figure 7 – Main Paper)

Scheme S7 Conditions used for the reaction between Pd_{3}(OAc)_{6} and 3 PPh_{3} (Pd:P = 1:1) in THF-d_{8}

NMR reaction monitoring: Pd_{3}(OAc)_{6} (2.25 ± 0.05 mg, 3.3 µmol) and PPh_{3} (1 equiv., 2.60 ± 0.05 mg) were carefully weighed and transferred into a J. Youngs NMR tube (in an Ar-filled Glove box). THF-d_{8} (0.5 mL) was added and the sample was shaken, forming a reddish-brown solution, which was swiftly introduced to an NMR spectrometer where data was collected (within ca. 15 minutes). The NMR evidence for the formation of 4 is discussed in the main paper. The presence of 4 was evident by detection of [Pd^II(μ2-OAc)(κ-OAc)(PPh_{3})]_{2} as a [M–OAc]^+ cation, m/z = 913.01877, by LIFDI-MS after immediate analysis of the reaction solution upon mixing [Pd_{3}(OAc)_{6}] with 3 PPh_{3} (i.e. Pd:PPh_{3} = 1:1). Thusly, an NMR time course was recorded, tracking the degradation of 4 (δ_{P} 19.6 ppm) with time, along with the formation of unidentified degradation products. Integration data as a function of time was recorded using MNova software data analysis function and plotted in the form of a graph (Figure S5). Based on its chemical shift, the peak detected at δ_{P} 24.6 ppm was assigned to O=PPh_{3}, a minor product of this process. TEM imaging of similar post-reaction solutions has been reported by our group^1 (see later).

Figure S5 The process used to monitor the degradation of 4 and the concomitant formation of the new products over 12 hours. A: Stack of 31P NMR spectra, recorded each hour throughout the process. B: Profiles for the 31P resonances (integral data), as a function of time.
**H NMR analysis of the degraded solution of Pd₃(OAc)₆ and 3 PPh₃**

Acetic anhydride was detected by comparison of the H NMR spectrum of the post-reaction mixture with the H NMR spectrum containing an authentic sample, both in THF- (Figure S6). Acetic acid was also detected as a by-product of the process and they appear in the post-reaction solution in an apparent molecular ratio (Ac₂O:AcOH) of 1:3 (based on integration of the H resonances). This observation is in-keeping with one acetate ligand being acylated per degradation of 4, and the other three acetate ligands picking up a proton from the reaction mixture and converting to acetic acid. H NMR spectroscopic analysis of the post-reaction mixture indicated significant degradation to acetate and phenyl-containing products (which are concomitant with the new phosphorus-containing species detected by ³¹P NMR spectroscopic analysis).

![Figure S6 Expanded H NMR stack of: A. the post-reaction solution of Pd(OAc)₂/1PPh₃ (ca. 12 hours after mixing); B. An authentic sample of acetic anhydride in THF-d₈.](image)

**Characterisation Data for [Pd^II(μ₂-OAc)(κ-OAc)(PPh₃)]₂ 4**

4 was not isolated in preparative form from solution due to its instability (vide supra and discussion in the main paper). The following data is presented for its characterisation in solution after direct reaction between Pd₃(OAc)₆ and 3 equivalents of PPh₃, in THF-d₈ as highlighted above.

H NMR (500 MHz, THF-d₈) δ 7.90 (m, 12H), 7.54 – 7.46 (br m, 6H), 7.36 (m, 12H), 1.35 (s, 12H).

³¹P NMR (203 MHz, THF-d₈) δ 19.55 (s).

LIFDI-MS Data (+ve mode): Found 913.0309 [M–OAc]⁺ Calculated (for C₃₂H₃₇O₆P₂Pd₂) 913.0188.

S16
IR (ν/cm⁻¹, ATR): 1634 (s, κ-CO₂asym), 1557 (br, s, μ-CO₂asym), 1409 (s, μ-CO₂sym), 1309 (br, s, κ-CO₂sym).

Isolation of single crystal of 4

A Schlenk tube was charged with Pd₃(OAc)₆ (6.7 mg, 0.01 mmol) and 3 equivalents of PPh₃ ([7.9 mg, 0.03 mmol]: Pd:P = 1:1). The Schlenk tube atmosphere was evacuated and backfilled with N₂ before being put on ice. THF (2.5 mL; pre-cooled to 0 °C) was added and the resulting mixture was stirred at 0 °C for 5 minutes, appearing as a brownish-red solution. A sample (0.5 mL) was taken via a syringe and added to a J. Youngs-type NMR tube under Schlenk conditions, on ice. The reaction mixture was then layered with pre-cooled hexane and swiftly stored at -18 °C. This crystal data is presented in the main paper and in Section 4 of this document.
3. Characterisation of Organic Products

3.1. 2,4-Disubstituted Pyridines: Suzuki-Miyaura/Kumada Cross-coupling Reactions

3.1.1. SMCC of 1 with 4-Fluorophenylboronic acid (2a)

Products could be identified from crude reaction mixtures (Figure S7). Characterisation data matched that reported in the literature, and/or with data collated for (novel) isolated compounds reported *vide infra*.

![Figure S7](image-url)

Figure S7 $^1$H NMR spectrum (400 MHz, CDCl$_3$) showing 3a$_{C4-Ar}$, 3a$_{C2-Ar}$ and 3a$_{diaryl}$ product identification from a crude reaction mixture. (note: small differences in $^1$H chemical shift from authenticated products are seen here).
2-Bromo-4-(4-fluorophenyl)pyridine (3aC\textsubscript{4-Ar})

![Chemical structure]

Although the title compound is commercially available, no literature data was found for its characterization or any alternative syntheses. It was isolated from the reaction mixture using flash chromatography (SiO\textsubscript{2}) and a hexane/EtOAc (95:5) solvent system with a gradient, starting from neat hexane. Yield from the model SMCC, catalysed by Pd\textsubscript{3}Cl\textsubscript{2} (Section 2.5) = 161.9 mg (65%). Appeared as a colorless solid. Melting point – 157.0-158.9 °C.

\textsuperscript{1}H NMR (400 MHz, Chloroform-d) \(\delta\) 8.40 (dd, \(J = 5.1, 0.7\) Hz, 1H, pyridyl-C\textsubscript{6}-H), 7.66 (dd, \(J = 1.6, 0.7\) Hz, 1H, pyridyl-C\textsubscript{5}-H), 7.63 – 7.54 (m, 2H, aryl), 7.41 (dd, \(J = 5.2, 1.6\) Hz, 1H, pyridyl-C\textsubscript{3}-H), 7.24 – 7.13 (m, 2H) ppm.

\textsuperscript{13}C NMR (101 MHz, Chloroform-d) \(\delta\) 163.8 (d, \(J_{C-F}= 250.4\) Hz, C–F), 150.6 (C), 150.2 (C–H), 143.1 (C), 132.9 (d, \(J_{C-F}= 3.3\) Hz, aryl-C\textsubscript{q}), 129.0 (d, \(J = 8.3\) Hz, aryl-C–H), 125.8 (C–H), 120.8 (C–H), 116.4 (d, \(J_{C-F}= 21.7\) Hz, aryl-C–H) ppm.

\textsuperscript{19}F NMR (376 MHz, Chloroform-d) \(\delta\) -111.18 (ddd, \(J = 13.7, 8.3, 5.2\) Hz).

IR (v/cm\textsuperscript{-1}, ATR): 3051 (w), 1587 (m), 1528 (m), 1512 (m), 1455 (m), 1370 (m), 1300 (m), 1223 (m), 1159 (m), 1126 (m), 1102 (m), 1080 (m), 1040 (m), 986 (m), 963 (m), 883 (m), 822 (vs), 754 (m), 685 (m), 593 (m), 554 (s), 517 (m), 434 (m).

HRMS ESI-MS m/z = 251.9816 [M+H]\textsuperscript{+}: C\textsubscript{11}H\textsubscript{8}BrFN requires 251.9824

R\textsubscript{f} (hexane/EtOAc 95:5) = 0.11

4-Bromo-2-(4-fluorophenyl)pyridine (3aC\textsubscript{2-Ar})

![Chemical structure]

Compound characterisation data agrees with that previously reported in literature.\textsuperscript{3} It was isolated from the reaction mixture using flash chromatography (SiO\textsubscript{2}) with a hexane/EtOAc (95:5) solvent system, which was run
with a gradient, starting from neat hexane. Yield from the model SMCC (Section 2.5), catalysed by Pd$_3$Cl$_2$ = 21 mg (8%). Appeared as a colourless oily film.

$^1$H NMR (400 MHz, Chloroform-d) δ 8.49 (d, J = 5.3 Hz, 1H, pyridyl-C$_6$-H), 8.01 – 7.91 (m, 2H, aryl), 7.86 (d, J = 1.8 Hz, 1H, pyridyl-C$_6$-H), 7.40 (dd, J = 5.2, 1.8 Hz, 1H, pyridyl-C$_6$-H), 7.22 – 7.11 (m, 2H, aryl) ppm.

$^{13}$C NMR (101 MHz, Chloroform-d) δ 164.0 (d, $^1J_{CF} = 249.5$ Hz, Cq), 157.9 (C), 150.5 (C–H), 134.3 (C), 133.8 (C), 129.1 (d, $^3J_{CF} = 8.5$ Hz), 125.4 (C–H), 123.8 (C–H), 116.0 (d, $^2J_{CF} = 21.8$ Hz) ppm.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -111.70 (ddd, $^J = 13.8$, 8.5, 5.5 Hz), ppm.

HRMS ESI-MS m/z = 251.9814 [M+H]$^+$: C$_{11}$H$_8$BrFN requires 251.9824.

R$_f$ (TLC, hexane/EtOAc 95:5) = 0.29

2,4-Bis-(4-fluorophenyl)pyridine (3a$_{diaryl}$)$^6$

![Diagram of 2,4-Bis-(4-fluorophenyl)pyridine (3a$_{diaryl}$)]

Compound characterisation data agrees with that previously reported in literature.$^6$ It was isolated from the reaction mixture using flash chromatography (SiO$_2$) a hexane/EtOAc (95:5) solvent system, which was run with a gradient, starting from neat hexane. Yield from an SMCC reaction (Section 2.5), catalysed by Pd$_3$Cl$_2$ = 50.0 mg (19%). Appeared as a colorless powder.

$^1$H NMR (400 MHz, Chloroform-d) δ 8.71 (dd, J = 5.1, 0.7 Hz, 1H, pyridyl-C$_6$-H), 8.07 – 7.99 (m, 2H, aryl), 7.82 (dd, J = 1.7, 0.8 Hz, 1H, pyridyl-C$_6$-H), 7.69 – 7.62 (m, 2H, aryl), 7.39 (dd, J = 5.1, 1.7 Hz, 1H, pyridyl-C$_5$-H), 7.23 – 7.12 (m, 4H, aryl) ppm.

$^{13}$C NMR (101 MHz, Chloroform-d) δ 164.1 (d, $^1J_{CF} = 249.8$ Hz, Cq–F), 163.6 (d, $^1J_{CF} = 250.6$ Hz, Cq–F), 157.3 (CH, 150.3, 148.5, 135.7 (d, $^3J_{CF} = 3.1$ Hz, aryl–C–H), 134.7 (d, $^3J_{CF} = 3.3$ Hz aryl–C–H), 129.1 – 128.6 (m), 120.2 (C), 118.4 (C), 116.3 (d, $^2J_{CF} = 21.7$ Hz, aryl–C–H), 115.9 (d, J = 21.6 Hz, aryl–C–H) ppm.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -112.75 (ddd, J = 13.3, 8.3, 5.2 Hz), -112.72 (ddd, J = 14.0, 8.6, 5.2 Hz) ppm.

HRMS ESI-MS m/z =268.0932 [M+H]$^+$ : C$_{17}$H$_{12}$F$_2$N requires 268.0938

R$_f$ (TLC, hexane/EtOAc 95:5) = 0.05.
3.1.2. SMCC of 1 with 4-Anisylboronic acid (2b)

Products could be identified from crude reaction mixtures (Figure S8). Characterisation data matched that reported in the literature, and/or with data collated for isolated compounds reported *vide infra*.

![NMR spectrum](image)

Figure S8 $^1$H NMR spectrum (400 MHz, CDCl$_3$) showing 3b$_{C4-Ar}$, 3b$_{C2-Ar}$ and 3b$_{diaryl}$ product identification from a crude reaction mixture. (note: small differences in $^1$H chemical shift from authenticated products are seen here).

**2-Bromo-4-(4-anisyl)pyridine (3b$_{C4-Ar}$)**

Compound characterisation data agrees with that previously reported in literature. It was isolated from the reaction mixture using flash chromatography (SiO$_2$) and a hexane/EtOAc (95:5) solvent system, which was run with a gradient starting from neat hexane. Yield from the model SMCC (Section 2.1, 3.0 mmol scale in 2,4-dibromopyridine 1), catalysed by Pd$_3$(OAc)$_6$/3PPh$_3$ = 510.5 mg (64 %). Appearance as a colorless powder. Melting point – 55.5-56.9 °C (57 °C lit.).
**1**H NMR (400 MHz, Chloroform-**d**) δ 8.37 (dd, *J* = 5.3, 0.7 Hz, 1H, *pyridyl*-**C**₆-H), 7.68 (dd, *J* = 1.7, 0.7 Hz, 1H, *pyridyl*-**C**₅-H), 7.62 – 7.53 (m, 2H, *aryl*), 7.44 (dd, *J* = 5.3, 1.7 Hz, 1H, *pyridyl*-**C**₃-H), 7.05 – 6.97 (m, 2H, *aryl*), 3.87 (s, 3H, OCH₃) ppm.

**13**C NMR (101 MHz, Chloroform-**d**) δ 161.2 (C), 151.2 (C), 150.2 (C–H), 142.8 (C), 128.9 (C), 128.45(C–H), 125.3 (C–H), 120.4 (2C–H), 114.9 (C–H), 55.6 (C–OCH₃) ppm.

**IR (v, ATR):** 3045 (w, C–H), 2935 (w, C–H), 2832 (w, C–H), 1609 (m), 1586 (s), 1515(s), 1457(m), 1429 (m), 1418(m), 1375 (m), 1292 (m), 1247 (vs), 1126 (m), 1082 (m), 1045 (m), 1018 (m), 986 (vs), 755 (m), 665 (m), 568 (m), 435 (m).

**HRMS ESI-MS m/z = 264.0019 [M+H]+:** *C₁₂H₁₁BrNO* requires 264.0019.

Elemental analysis (% CHN), calculated for *C₁₂H₁₀BrNO:* C, 54.57; H, 3.82; N, 5.30; Found: C, 54.48; H, 3.88; N, 5.13. Rᵣ (TLC, Petroleum ether/EtOAc, 85:15) = 0.10.

**4-Bromo-2-(4-anisyl)pyridine (3bC₂-A)**

![4-Bromo-2-(4-anisyl)pyridine](image)

Compound characterisation data agrees with that previously reported in literature.³ It was isolated from the reaction mixture using flash chromatography (SiO₂) with a hexane/EtOAc (95:5) solvent system, which was run with a gradient starting from neat hexane. Yield from the model SMCC (section 2.1, 3.0 mmol scale in 2,4-dibromopyridine 1), catalysed by *Pd₃(OAc)₆/3PPh₃* = 72.9 mg (9%). Appeared as a colorless powder.

**1**H NMR (400 MHz, Chloroform-**d**) δ 8.46 (d, *J* = 5.3 Hz, 1H, *pyridyl*-**C**₆-H), 7.97 – 7.89 (m, 2H, *aryl*), 7.84 (d, *J* = 1.8 Hz, 1H, *pyridyl*-**C**₅-H), 7.34 (dd, *J* = 5.3, 1.8 Hz, 1H, *pyridyl*-**C**₃-H), 7.04 – 6.95 (m, 2H, *aryl*), 3.87 (s, 3H, OCH₃) ppm.

**13**C NMR (101 MHz, Chloroform-**d**) δ 161.0 (C), 158.6 (C), 150.3 (C–H), 133.6 (C), 130.6 (C), 128.5 (C–H), 124.6(C–H), 123.2 (C–H), 114.3 (C–H), 55.5 C–OCH₃).

HRMS ESI-MS m/z = 264.0019 [M+H]+: *C₁₂H₁₁BrNO* requires 264.0019.

Rᵣ (TLC, Petroleum ether/EtOAc, 85:15) = 0.27.
2,4-Bis(4-anisyl)pyridine (3b diaryl)

![Chemical structure image]

Compound characterisation data agrees with that previously reported in literature. It was isolated from the reaction mixture using flash chromatography (SiO$_2$) with a hexane/EtOAc (95:5) solvent system, which was run with a gradient starting from neat hexane. Yield, from the model SMCC (Section 2.5, 3.0 mmol scale in 2,4-dibromopyridine 1), catalysed by Pd$_3$(OAc)$_6$/3PPh$_3$ = 98.0 mg (11%). Appeared as a colorless powder.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.65 (dd, J = 5.2, 0.8 Hz, 1H, pyridyl-C$_6$-H), 8.04 – 7.94 (m, 2H, aryl), 7.83 (dd, J = 1.8, 0.8 Hz, 1H pyridyl-C$_3$-H), 7.68 – 7.58 (m, 2H, aryl), 7.36 (dd, J = 5.2, 1.8 Hz, 1H, pyridyl-C$_5$-H), 7.01 (dd, J = 8.8, 3.4 Hz, 4H, aryl), 3.86 (s, 6H, OCH$_3$, overlapping) ppm.

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 160.6 (2C), 157.6 (C), 149.7 (C), 149.0 (C–H), 132.0 (C), 130.9 (C), 128.4 (C–H), 128.4 (C–H), 119.2 (C–H), 117.6 (C–H), 114.6 (C–H), 114.2 (C–H), 55.5 (C–CH$_3$), 55.5 (C–OCH$_3$) ppm.

HRMS ESI-MS m/z = 292.1332 [M+H]$^+$: C$_{11}$H$_9$FN requires 292.1338.

$R_f$ (TLC, Petroleum ether/EtOAc, 85:15) = 0.07.
3.1.3. SMCC of 1 with Phenylboronic acid (2c)

Products could be identified from crude reaction mixtures (Figure S9). Characterisation data matched that reported in the literature,\(^3\) and/or with data collated for isolated compounds reported vide infra.

Figure S9 \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\)) showing 3\(_{C4-Ar}\), 3\(_{C2-Ar}\) and 3\(_{diaryl}\) from a crude post-reaction mixture. (note: small differences in \(^1\)H chemical shift from authenticated products are seen here).

2-Bromo-4-phenylpyridine (3\(_{C4-Ar}\))\(^3\)

![Chemical structure of 2-Bromo-4-phenylpyridine (3\(_{C4-Ar}\))](image)

Compound characterisation data agrees with that previously reported in literature.\(^3\) It was isolated from the reaction mixture, catalysed by Pd\(_3\)Cl\(_5\) (Section 2.5) using flash chromatography (SiO\(_2\)) with a hexane/EtOAc (95:5) solvent system, which was run with a gradient starting from neat hexane. Yield = 145.5 mg (61%) Appeared as a colorless powder. Melting point – 65.0-67.1 °C.\(^3\)

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.41 (dd, \(J = 5.2, 0.7\) Hz, 1H, pyridyl-C\(_6\)-H), 7.70 (dd, \(J = 1.7, 0.7\) Hz, 1H pyridyl-C\(_5\)-H), 7.65 – 7.56 (m, 2H, aryl), 7.54 – 7.42 (m, 4H, pyridyl-C\(_6\)-H{1H}, aryl{3H}) ppm.
$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 151.5 (C), 150.5 (C–H), 143.0 (C), 136.8 (C), 129.8 (aryl-C–H), 129.4 (aryl-C–H), 127.2 (aryl-C–H), 126.0 (C–H), 121.0 (C–H) ppm.

IR (v/cm$^{-1}$, ATR): 3057 (d, C–H), 1584 (m), 1526 (m), 1502 (m), 1454 (m), 1444 (m), 1369 (m), 1335 (w), 1317 (w), 1135 (m), 858 (m), 755 (m), 698 (m), 690 (s), 611 (m).

HRMS ESI-MS m/z = 232.1122 [M+H]$^+$: C$_{17}$H$_{14}$N requires 232.1121.

Elemental analysis (% CHN), calculated for C$_{11}$H$_8$BrN: C, 56.44; H, 3.44; N, 5.98 Found: C, 56.48; H, 3.51; N, 5.89.

4-Bromo-2-phenylpyridine (3c$_{2Ar}$)

![4-Bromo-2-phenylpyridine](image)

Reaction data for this compound, characterised as part of the crude post-reaction mixture, matched that previously reported in literature (see Figure S9 above).  

$^1$H NMR (400 MHz, Chloroform-$d$) δ 8.49 (d, J = 5.2 Hz, 1H, pyridyl-C$_6$-H), 7.95 (m, 2H, aryl), 7.88 (dd, J = 1.8, 0.6 Hz, 1H, pyridyl-C$_3$-H), 7.65 – 7.54 (m, 2H, aryl), 7.39 (dd, J = 5.3, 1.8 Hz, 1H, pyridyl-C$_5$-H) ppm.

HRMS ESI-MS m/z = 232.1122 [M+H]$^+$: C$_{13}$H$_{14}$BrN requires 232.1121.

2,4-Bis-phenylpyridine (3c$_{diaryl}$)

![2,4-Bis-phenylpyridine](image)

Reaction data for this compound, obtained as part of the crude post-reaction mixture, matched that previously reported in literature (see Figure S9 above). Appearance, colorless powder.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 8.75 (d, J = 5.1 Hz, 1H, pyridyl-C$_6$-H), 8.09 – 8.02 (m, 2H, aryl), 7.94 (dd, J = 1.8, 0.8 Hz, 1H, pyridyl-C$_3$-H), 7.74 – 7.67 (m, 2H, aryl), 7.56 – 7.40 (m, 7H, aryl [6H], pyridyl-C$_5$-H [1H]) ppm.

HRMS ESI-MS m/z = 233.9912 [M+H]$^+$: C$_{13}$H$_{14}$BrN requires 233.9913.
3.1.4. SMCC of 1 with 4-Tolylboration acid (2d)

Products could be identified from crude reaction mixtures (Figure S10). Characterisation data matched that reported in the literature,\textsuperscript{3, 7-8} and/or with data collated for isolated compounds reported \textit{vide infra}.

![Figure S10](image)

Figure S10 $^1$H NMR spectrum (400 MHz, CDCl$_3$) showing 3d$_{C4-Ar}$, 3d$_{C2-Ar}$ and 3d$_{diaryl}$ product identification from a crude reaction mixture. (note: small differences in $^1$H chemical shift from authenticated products are seen here).

2-Bromo-4-(4-toly)pyridine (3d$_{C4-Ar}$)\textsuperscript{8}

![Compound](image)

Compound characterisation data agrees with that previously reported in literature.\textsuperscript{8-9} It was isolated from the reaction mixture using flash chromatography (SiO$_2$) with a hexane/EtOAc (95:5 v/v) solvent system (Section 2.5, catalysed by Pd$_3$Cl$_2$), which was run with a gradient. Yield = 133.7 mg (54%). Appeared as a colorless powder. Melting point – 72.5-72.9 °C (68-70°C lit.).\textsuperscript{9}
\[^1\text{H}\] NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.38 (dd, \(J = 5.2, 0.7\) Hz, 1H, pyridyl-C\(_6\)-H), 7.69 (dd, \(J = 1.7, 0.7\) Hz, 1H, pyridyl-C\(_3\)-H), 7.53–7.48 (m, 2H, aryl), 7.44 (dd, \(J = 5.2, 1.7\) Hz, 1H, pyridyl-C\(_5\)-H), 7.33–7.27 (m, 2H, aryl), 2.42 (s, 3H, CH\(_3\)) ppm.

\[^{13}\text{C}\] NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 151.4 (C), 150.4 (C–H), 143.0 (C–H), 140.2 (C), 133.8 (C), 130.1 (C–H), 127.0 (C–H), 125.7 (C–H), 120.7 (C), 21.4 (C–CH\(_3\)) ppm.

IR (v/cm\(^{-1}\), ATR): 3011 (w, C–H), 2959 (br,w, C–H), 2852 (w, C–H), 1571 (m), 1543 (m), 1511 (m), 1450 (m), 1106 (m), 1042 (m), 984 (m), 866 (m), 802 (vs), 751 (m), 681 (m), 585 (m), 426 (m).

HRMS ESI-MS m/z = 248.0067 [M+H\(^+\)]: C\(_{12}\)H\(_{11}\)BrN requires 248.0069.

Elemental analysis (\% CHN), calculated for C\(_{12}\)H\(_{10}\)BrN: C, 58.09; H, 4.06; N, 5.65, Found: C, 57.89; H, 4.08; N, 5.54.

\(\text{R}_f\) (TLC, hexane/EtOAc 95:5 (v/v) = 0.17.

4-Bromo-2-(4-tolyl)pyridine (3d\(_{\text{c2-Ar}}\))

![Structure of 4-Bromo-2-(4-tolyl)pyridine](image)

Compound characterisation data agrees with that previously reported in literature.\(^3\) It was isolated from the reaction mixture using flash chromatography (SiO\(_2\)) with a hexane/EtOAc (95:5, v/v) solvent system (Section 2.5, catalysed by Pd\(_3\)Cl\(_2\)), which was run with a gradient, starting from neat hexane. Yield = 28.3 mg (11%). Appeared as a colourless oil.

\[^1\text{H}\] NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.48 (d, \(J = 5.3\) Hz, 1H, pyridyl-C\(_6\)-H), 7.88 (s, 1H, pyridyl-C\(_3\)-H), 7.87–7.84 (m, 1H, aryl), 7.37(dd, \(J = 5.3, 1.8\) Hz, 1H, pyridyl-C\(_5\)-H), 7.32–7.27 (m, 2H, aryl), 2.41 (s, 3H, CH\(_3\)) ppm.

\[^{13}\text{C}\] NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 159.0 (C), 150.4 (C–H), 139.9 (C), 135.3 (C), 133.5 (C), 129.7 (C–H), 127.0(C–H), 125.0 (C–H), 123.7 (C–H), 21.4 (C–CH\(_3\)) ppm.

IR (v/cm\(^{-1}\), ATR): 3009 (w, C–H) 2959 (br,w, C–H), 2852(w, C–H), 1569 (m), 1542 (m), 1510 (m), 1468 (m), 1448 (m), 1408 (m), 1374 (m), 1314 (m), 1260 (m), 1091 (m), 1044 (m), 1015 (m), 807 (vs), 749 (m), 731 (m), 660 (m), 585 (m), 426 (m).

HRMS ESI-MS m/z = 248.0067 [M+H\(^+\)] : C\(_{12}\)H\(_{11}\)BrN requires 248.0069.

\(\text{R}_f\) (TLC, hexane/EtOAc 95:5 (v/v) = 0.28.

S27
Compound characterisation data agrees with that previously reported in literature. It was isolated from the reaction (Section 2.1, catalyzed by \( \text{Pd}_3\text{Cl}_2 \)) mixture using flash chromatography with a hexane/EtOAc (95:5 v/v) solvent system, which was run with a gradient starting from neat hexane. Yield = 24.6 mg (9%). Appeared as a colorless powder.

\(^1^\text{H} \text{NMR} (400 \text{ MHz, Chloroform-}d) \ \delta \ 8.70 \ (\text{dd, } J = 5.2, 0.8 \text{ Hz, } 1\text{H, pyridyl-}C_6\text{-H}), 8.02 - 7.93 \ (\text{m, } 2\text{H, aryl}), 7.90 \ (\text{dd, } J = 1.7, 0.8 \text{ Hz, } 1\text{H pyridyl-C}_3\text{-H}), 7.70 - 7.55 \ (\text{m, } 2\text{H, aryl}), 7.41 \ (\text{dd, } J = 5.2, 1.7 \text{ Hz, } 1\text{H, pyridyl-C}_5\text{-H}), 7.26 - 7.35 \ (\text{m, } 4\text{H, aryl}), 2.43 \ (\text{s, } 6\text{H, } 2 \times \text{CH}_3 \text{ (overlapping))}.

HRMS ESI-MS m/z = 260.1437 \ [\text{M+H}]^+ : \text{C}_{19}\text{H}_{18}\text{N requires 260.1434}.

\( R_f \) (TLC, hexane/EtOAc 95:5 v/v) = 0.10.
3.1.5. SMCC of 1 with 4-Chlorophenylboronic acid (2e)

Products could be identified from crude reaction mixtures (Figure S11). Characterisation data matched that reported in the literature,\(^7,^{10-11}\) and/or with data collated for (novel) isolated compounds reported *vide infra.*

![Figure S11](image)

**Figure S11** \(^1\)H NMR spectrum (500 MHz, CDCl\(_3\)) showing 3e\(_{C4-Ar}\), 3e\(_{C2-Ar}\) and 3e\(_{diaryl}\) compound identification from a crude reaction mixture. (note: small differences in \(^1\)H chemical shift from authenticated products are seen here).

2-Bromo-4-(4-chlorophenyl)pyridine (3e\(_{C4-Ar}\))\(^10\)

![Compound Structure](image)

Compound characterisation data agrees with that previously reported in literature. It was isolated from the reaction mixture (Section 2.5, catalyzed by Pd\(_3\)Cl\(_2\)) using flash chromatography (SiO\(_2\)) with a hexane/EtOAc (98:2 v/v) solvent system, which was run with a gradient starting from neat hexane. Yield from reaction catalysed by Pd\(_3\)Cl\(_2\) = 110.7 mg (41%). Appeared as a colorless powder. Melting point – 138.2–139.5 °C (129-131°C lit.).\(^10\)
$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 8.41 (dd, $J$ = 5.2, 0.7 Hz, 1H, \textit{pyridyl-C$_6$H}), 7.66 (dd, $J$ = 1.7, 0.7 Hz, 1H, \textit{pyridyl-C$_5$H}), 7.57 – 7.50 (m, 2H, aryl), 7.50 – 7.44 (m, 2H, aryl), 7.42 (dd, $J$ = 5.2, 1.7 Hz, 1H, \textit{pyridyl-C$_3$H}) ppm.

$^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 150.7 (\textit{pyridyl-C}), 143.2 (C), 136.1 (C), 135.2 (C), 129.6 (aryl-C–H), 128.4 (aryl-C–H), 125.8 (\textit{pyridyl-C–H}), 120.7 (\textit{pyridyl-C–H}) ppm.

IR (v/cm$^{-1}$, ATR): 3053 (w, C–H), 3018(w, C–H), 1586 (s), 1496 (m), 1406 (m), 1370 (m), 1093(s), 1081 (m), 1043 (m), 1012 (m), 792 (s), 760 (s), 509 (m), 475 (m), 422 (m).

HRMS ESI-MS m/z = 267.9519 [M+H]$^+$: C$_{11}$H$_8$BrClN requires 267.9523

Elemental analysis (% CHN), calculated for C$_{11}$H$_8$BrClN: C, 49.20; H, 2.63; N, 5.22; Found: C, 49.05; H, 2.54; N, 5.03.

$R_f$ (TLC, PET/EtOAc, 98:2, {v/v}) = 0.33.

4-Bromo-2-(4-chlorophenyl)pyridine (3e$_{C2-Ar}$)

Compound characterisation data agrees with that previously reported in literature. It was isolated from the reaction mixture (Section 2.5) using flash chromatography (SiO$_2$) with a hexane/EtOAc (98:2 v/v) solvent system, which was run with a gradient. Yield from reaction catalysed by Pd$_3$Cl$_2$ = 34.7 mg (12.9%). Appeared as a colorless powder.

$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 8.49 (dd, $J$ = 5.3, 0.6 Hz, 1H, \textit{pyridyl-C$_6$H}), 7.98 – 7.88 (m, 2H, aryl), 7.87 (dd, $J$ = 1.8, 0.6 Hz, 1H, \textit{pyridyl-C$_5$H}), 7.54 – 7.37 (m, 5H, aryl(4H) \textit{pyridyl-C$_3$H} (1H)) ppm.

$^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 157.77, 150.58, 136.59, 135.99, 133.76, 129.23, 128.42, 125.68, 123.85 ppm.

IR (v/cm$^{-1}$, ATR): 2957(w), 2920 (w), 2852 (w), 1586 (m), 1570 (m), 1542 (m), 1455 (m), 1372 (m), 1076 (m), 1041 (m), 1015 (m), 985 (m), 802 (vs), 750 (m), 681 (m), 574 (m), 556 (m), 526 (m), 501 (m), 473 (m), 424 (m).

HRMS ESI-MS m/z = 267.9518 [M+H]$^+$: C$_{11}$H$_8$BrClN requires 267.9523

$R_f$ (TLC, PET/EtOAc (98:2)) = 0.22.
2,4-Bis(4-chlorophenyl)pyridine (3e_daryl) 7

![Chemical Structure](image)

Compound characterisation data agrees with that previously reported in literature. 7 It was isolated from the reaction mixture (Section 2.5) using flash chromatography with a hexane/EtOAc (98:2) solvent system, which was run with a gradient starting from neat hexane. Yield from reaction catalysed by Pd3Cl2 = 22.9 mg (8%). Appeared as a colorless powder.

1H NMR (400 MHz, Chloroform-d) δ 8.73 (dd, \( J = 5.1, 0.8 \) Hz, 1H, pyridyl-C_{6}-H), 8.04 – 7.93 (m, 2H, aryl), 7.85 (dd, \( J = 1.7, 0.8 \) Hz, 1H, pyridyl-C_{3}-H), 7.67 – 7.56 (m, 2H, aryl), 7.53 – 7.43 (m, 4H, aryl), 7.42 (dd, \( J = 5.1, 1.7 \) Hz, 1H, pyridyl-C_{5}-H) ppm.

13C NMR (101 MHz, Chloroform-d) δ 157.16 (C), 150.46 (pyridyl-C–H), 148.38 (C), 137.84 (C), 136.93 (C), 135.57 (C), 135.47 (aryl-C–H), 129.54 (aryl-C–H), 129.14 (aryl-C–H), 128.50 (aryl-C–H), 128.44 (aryl-C–H), 120.40 (pyridyl-C–H), 118.40 (pyridyl-C–H) ppm.

HRMS ESI-MS m/z = 300.0338 [M+H]^+ : C_{17}H_{12}Cl_{2}N requires 300.0347.

R_{f} (TLC, PET/EtOAc, 98:2 {v/v}) = 0.11.
3.1.6. SMCC of 1 with 4-Trifluoromethyl-phenylboronic acid (2f)

Products could be identified from crude reaction mixtures (Figure S12). Characterisation data matched that reported in the literature,\textsuperscript{7,12} and/or with data collated for isolated compounds reported \textit{vide infra}.

![Figure S12](image.png)

Figure S12 \textsuperscript{1}H NMR spectrum (500 MHz, CDCl\textsubscript{3}) showing \(3f_{C4-Ar}\), \(3f_{C2-Ar}\) and \(3f_{diaryl}\) compound identification from a crude reaction mixture. (note: small differences in \textsuperscript{1}H chemical shift from authenticated products are seen here).

\subsection*{2-Bromo-4-(4-trifluoromethylphenyl)pyridine (3f\textsubscript{C4-Ar})\textsuperscript{12}}

![Chemical structure](image.png)

Compound characterisation data agrees with that previously reported in literature.\textsuperscript{12} It was isolated from a reaction mixture (Section 2.5, \textit{Pd}\textsubscript{3}Cl\textsubscript{2}) using flash chromatography (SiO\textsubscript{2}) with a hexane/EtOAc (98:2 v/v) solvent system, which was run with a gradient starting from neat hexane. Yield from reaction catalysed by \textit{Pd}\textsubscript{3}Cl\textsubscript{2} = 141.3 mg (47%). Appeared as a colorless powder. Melting point – 115.0-117 °C (123.5-124.5 °C lit.).\textsuperscript{12}

\textsuperscript{1}H NMR (500 MHz, Chloroform-\textit{d}) \(\delta\) 8.46 (dd, \(J = 5.2, 0.6\) Hz, 1H, \textit{pyridyl-C\textsubscript{6}}–H), 7.74 – 7.79 (m, 2H, \textit{aryl}), 7.73 – 7.66 ((m, 2H, \textit{aryl}) + \{\textit{pyridyl-C\textsubscript{3}}–H\}), 7.47 (dd, \(J = 5.2, 1.6\) Hz, 1H, \textit{pyridyl-C\textsubscript{5}}–H) ppm.

S32
$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 150.4 (pyridyl-C–H), 149.5 (C), 142.9 (C), 140.0 (C), 131.4 (q, $^2J_{CF} = 33.0$ Hz aryl-C), 127.3 (aryl-C–H) 126.0 (q, $^3J_{CF} = 3.7$ Hz, aryl-C–H), 125.8 (C–H), 123.6 (q, $J = 272.4$ Hz; $^1J_{CF}$ CF$_3$) 120.7 (C–H) ppm.

$^{19}$F NMR (376 MHz, Chloroform-$d$) δ −62.65 ppm.

IR (v/cm$^{-1}$, ATR): 3019(w), 2981(w), 2831(w), 1608(m), 1585(m), 1515(s), 1457(m), 1429.42(m), 1374.92(m), 1292.08(m), 1184.00 (m), 1017.76(m), 814.70(s), 574.42(m), 567.88(m), 519.79(m).

HRMS ESI-MS m/z = 301.9773 [M+H]$^+$: C$_{12}$H$_8$BrF$_3$N requires 301.9787.

Elemental analysis (% CHN), calculated for C$_{12}$H$_7$BrF$_3$N: C 47.71; H, 2.34; N, 4.64 Found: C, 48.09; H, 2.63; N, 4.12.

R$_r$ (TLC, Hexane/EtOAc, 98:2 (v/v)) = 0.12.

**XRD analysis (ijsf1803; CCDC 2060853):**

Crystal was grown by vapour diffusion of pentane on a dichloromethane solution of 3f$_{C4-Ar}$.

Figure S13 Structure obtained from X-ray diffraction analysis of a single crystal of 2-bromo, 4-(4-trifluoromethylphenyl)pyridine (3f$_{C4-Ar}$).

The exact crystal run (by XRD) was subjected to $^1$H NMR spectroscopic analysis (700 MHz) which matched data of that of the isolated material (*vide supra*). This confirms conclusively the identity of the NMR characterised species as the C4-arylated product. Thus, X-ray crystallographic analysis shows distortion of the pyridine ring (Table S9 & Table S10).
Table S9 Analysis of selected bond angles from XRD analysis of a crystal of 3fC4-Ar

| Angle sweep               | Θ /° | deviation from 120 degrees |
|---------------------------|------|---------------------------|
| C(5)–N(1)–C(1)            | 115.21 | 4.79                     |
| N(1)–C(1)–C(2)            | 126.02 | -6.02                    |
| N(1)–C(5)–C(4)            | 124.25 | -4.25                    |
| C(1)–C(2)–C(2)            | 118.01 | 1.99                     |
| C(5)–C(4)–C(2)            | 119.17 | 0.83                     |
| C(2)–C(4)–C(4)            | 117.3 | 2.7                      |

Table S10 Analysis of selected bond lengths from XRD analysis of a crystal of 3fC4-Ar

| Bond                  | Bond length /Å |
|-----------------------|----------------|
| N(1)–C(1)             | 1.323(3)       |
| N(1)–C(5)             | 1.347(3)       |
| C(1)–C(2)             | 1.381(3)       |
| C(5)–C(4)             | 1.378(3)       |
| C(2)–C(4)             | 1.396(3)       |
| C(4)–C(2)             | 1.398(3)       |
| C(1)–Br(1)            | 1.906(2)       |

See Appendix 4 for further X-Ray Crystallographic Data (ijisf1803).

4-Bromo-2-(4-trifluoromethylphenylphenyl)pyridine (3fC2-Ar)

To our knowledge, data for this compound was not previously reported within literature. It was isolated from the crude reaction mixture, catalysed by Pd3Cl2 (Section 2.5) using PTLC (SiO2) with a hexane/EtOAc (98:2) solvent system. Yield from reaction catalysed by Pd3Cl2 = 3.7 mg (1 %). Multiple solvent runs were needed to allow separation from the starting material. Appeared as a colorless powder.

1H NMR (400 MHz, Chloroform-d) 8.54 (dd, J = 5.2, 0.6 Hz, 1H; pyridyl-C6-H), 8.07 – 8.13 (m, 2H, aryl), 7.94 (dd, J = 1.8, 0.6 Hz, 1H, pyridyl-C5-H), 7.71 – 7.76 (m, 2H, aryl), 7.47 (dd, J = 5.2, 1.8 Hz, 1H, pyridyl-C5-H).

S34
$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 157.4 (C), 150.7 (C–H), 141.4 (C), 133.9 (C), 131.6 (q, $^{3}J_{CF} = 32.6$ Hz, C$_{3}'$), 127.5 (C–H), 126.3 (C–H), 126.0 (q, $^{3}J_{CF} = 3.8$ Hz, C$_{3}’$–H), 124.4 (C–H), 124.2 (q, $^{1}J_{CF} = 272.2$ Hz, CF$_{3}$).

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -62.56 ppm.

HRMS ESI-MS m/z = 301.9773 [M+H]$^+$: C$_{12}$H$_{7}$F$_{3}$BrN requires 301.9787.

IR (v/cm$^{-1}$, ATR): 3071 (w), 3054 (w), 2934 (w), 1616 (w), 1566 (m), 1548 (m), 1466 (m), 1376 (m), 1323 (s), 1263 (m), 1169 (s), 1110 (s), 1091 (s), 1070 (s), 1042 (m), 1011 (m), 851 (s), 754 (m), 687 (m), 606 (s), 434 (s).

Elemental analysis (% CHN), calculated for C$_{12}$H$_{7}$F$_{3}$BrN: C 47.71; H, 2.34; N, 4.64 Found: C, 47.15; H, 2.37; N, 4.56.

$R_{f}$ (TLC, Hexane/EtOAc, 98:2 (v/v)) = 0.33.

**Bis-2,4-(4-trifluoromethylphenyl)pyridine (3f$_{diaryl}$)$^7$**

![Diagram of Bis-2,4-(4-trifluoromethylphenyl)pyridine (3f$_{diaryl}$)](image)

Identified in the crude reaction mixture by comparison to literature reported $^1$H NMR spectroscopic data (see above)$^7$.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.80 (dd, $J$ = 5.1, 0.8 Hz, 1H), 8.18 – 8.14 (m, 2H), 7.50 (dd, $J$ = 5.1, 1.7 Hz, 1H) ppm. (partial data, from crude $^1$H NMR)

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -62.47, -62.55 ppm. (partial data, from crude $^1$H, $^{19}$F NMR)

HRMS ESI-MS m/z = 368.0858 [M+H]$^+$: C$_{19}$H$_{12}$F$_{6}$N requires 368.0868.

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S35
3.2. Synthesis of Tris-imidazolium Tribromide (6)

3.2.1. Step 1 – Synthesis of 1,3,5-Tris(bromomethyl)-2,4,6-triethyl-benzene

\[
\text{HBr, AcOH, Zn, (CH}_2\text{O)}_n \quad \text{(all in excess)} \\
90^\circ \text{C, 48 hours}
\]

Adapted procedure\textsuperscript{13–14}: An oven dried round bottomed flask, fitted with a water condenser, was charged with Zn powder (2.5 g, 38 mmol) and AcOH (25 mL, 436.5 mmol). HBr in AcOH (33% wt, 25 mL) was added over a 30-minute period with magnetic stirring until completely dissolved, resulting in a deep orange solution. 1,3,5-Triethylbenzene (5 g, 31 mmol), paraformaldehyde (10 g, 333 mmol, 10.7 eq.) and HBr in AcOH (33% wt, 74 mL, 1238 mmol, 39.9 equiv.) were then added and the solution heated to 90 °C for 48 hours, resulting in a dark brown solution. After this time, the solution was left to cool slowly to room temperature with magnetic stirring, resulting in precipitation of a yellow powder over the course of 2 hours. The solid was filtered, washed with H\textsubscript{2}O (3 × 50 mL) and allowed to dry under vacuum (~7.5 × 10\textsuperscript{-3} mmHg) for 24 hours, yielding a pale-yellow solid (7.83 g (57%)). The data obtained matched with the literature.\textsuperscript{13–14} Melting point – 171.0-173.0 °C.\textsuperscript{14}

\textsuperscript{1}H NMR (400 MHz, 8 scans, Chloroform-\textit{d}) δ 4.57 (s, 6H, CH\textsubscript{2}CH\textsubscript{3}), 2.93 (q, J = 7.7 Hz, 6H), 1.33 (t, J = 7.7 Hz, 9H, CH\textsubscript{2}CH\textsubscript{3}) ppm.

\textsuperscript{13}C NMR (101 MHz, Chloroform-\textit{d}) δ 145.1 (Ar), 132.7 (Ar), 28.7 (CH\textsubscript{2}Br), 22.8 (CH\textsubscript{3}), 15.7 (CH\textsubscript{3}) ppm.

IR (\textit{v}, ATR, solid state, cm\textsuperscript{-1}): 2966 (s), 2931 (m), 2901 (m), 2871 (m), 1714 (w, broad), 1571 (m), 1452 (s), 1204 (s), 1041 (m), 957 (m), 898 (m), 764 (s), 705 (s), 587 (s), 502 (s).

EI-MS m/z = 437.91699 [M]+: C\textsubscript{15}H\textsubscript{21}Br\textsubscript{3} requires 437.91934.
Adapted Procedure\textsuperscript{15}: To a mixture of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (3 g, 6.83 mmol), 2-methylimidazole (9.05 g, 8.3 mL, 110.2 mmol, 16 equiv) and MeOH (75 mL) was added. The mixture was stirred at reflux (65 °C) for 48 hours. After this time, the solvent was removed in vacuum yielding a yellow, oily solid. Solids were dissolved in water (20 mL) and NaHCO\textsubscript{3} (aq. sat.) (20 mL) was added. The organic layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 30 mL) and the combined organic layer was concentrated in vacuo to yield a yellow oil. A precipitate subsequently began to appear over time at room temperature. For purification by crystallisation, the precipitate was taken up in the minimum hot water under reflux conditions and allowed to cool slowly to room temperature, before being stored in a fridge overnight to aid further crystallisation. The crude product was filtered off and washed with diethyl ether (3 × 10 mL) to give needle-like crystals 1.54 g, 51%.

\textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 6.83 (s, 3H, NCH\textsubscript{3}CHN), 6.19 (s, 3H, NCH\textsubscript{3}CHN), 5.02 (s, 6H, ArCH\textsubscript{2}N), 2.58 (q, $J = 7.6$ Hz, 6H, CH\textsubscript{3}CH\textsubscript{3}), 2.52 (s, 9H, NC(CH\textsubscript{3})N), 1.00 (t, $J = 7.6$ Hz, 9H, CH\textsubscript{3}CH\textsubscript{3}).

\textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) $\delta$ 145.2 (Ar), 144.5 (NC(CH\textsubscript{3})N), 131.4 (Ar), 127.0 (NCH\textsubscript{3}CHN), 117.7 (NCH\textsubscript{3}CHN), 43.7 (CH\textsubscript{2}N), 23.4 (CH\textsubscript{3}Ar), 15.4 (CH\textsubscript{3}), 13.5 (CH\textsubscript{3}) ppm.

\textsuperscript{13}C NMR DEPT 135 (101 MHz, DMSO-\textit{d}_6) $\delta$ 127.0, 117.7, 43.7 (ve, sp\textsuperscript{3} CH\textsubscript{2}), 23.4 (ve, sp\textsuperscript{3} CH\textsubscript{3}), 15.4, 13.5 ppm.

Disappearance of quaternary signals at $\delta$ 145.2, 144.5, 131.4 ppm.

HRMS ESI-MS m/z = 445.3072[M+H]\textsuperscript{+}, APCI-MS m/z : 445.309087 [M+H]\textsuperscript{+} : C\textsubscript{27}H\textsubscript{37}N\textsubscript{6} requires 445.3080.

IR (v, ATR, solid state, cm\textsuperscript{-1}): 3495 (m, broad), 3179 (m, very broad), 2966 (m), 2926 (m), 2871 (w), 1684 (m, broad), 1531 (m), 1496 (m), 1452 (s), 1417 (s), 1383 (s), 1259 (s), 1135 (s), 987 (s), 729 (s), 680 (s), 591 (s).
**XRD analysis for 6 (ijsf2006):**

Figure S14 Structure of 1,3,5-tris(methyl(2-methylimidazole))-2,4,6-triethylbenzene, obtained via X-ray diffraction of a single crystal. Thermal ellipsoids are set at 50% probability, H$_2$O molecules of crystallisation and H atoms are omitted for clarity) Selected bond lengths /Å: C4-C5 = 1.505(12); C14-N1 = 1.381(2); N3-C20 = 1.361(3); C16-N1 = 1.356(2); C8-N1 = 1.4777(19); N2-C11 = 1.377(3). Selected bond angles /° C5-C7-C8 = 110.828(6); C6-C14A-N3A = 112.058(); C4-C9-N1 = 110.40(15) (ijsf2006; CCDC 2060856).

3.2.3. Step 3 – Synthesis of 2-Methyl-3-(3-methylbutyl)-1-[[2,4,6-triethyl-3,5-bis([[2-methyl-3-(3-methylbutyl)-1H-imidazol-3-ium-1-yl]methyl])phenyl[methyl]-1H-imidazol-3-ium (6)
**Adapted procedure**¹⁶: A stirred solution of 1,3,5-tris(methyl(2-methylimidazole))-2,4,6-triethylbenzene (1.5 g, 3.375 mmol, 1 equiv.) and 2-methyl-4-bromobutane (2.55 mL, 20.25 mmol, 6 equiv.) in MeCN (60 mL) was heated to reflux overnight. The solvent was partially evaporated, and a colorless, powdery precipitate appeared after addition of diethyl ether. The resulting solid was filtered and washed with diethyl ether to yield the title compound which appeared as a colorless powder and was subsequently dried under high vacuum (~7.5 × 10⁻³ mmHg) and stored under nitrogen, 2.09 g yield (69%). Note: colorless powder product was very hygroscopic, reversibly forming a transparent gel when exposed to atmospheric H₂O. It was sealed under an N₂ atmosphere to prevent absorption of moisture. Melting point – 138.2-139.5 °C

¹H NMR (400 MHz, 64 scans, CDCl₃) δ 7.50 (d, J = 2.2 Hz, 3H, NCH₃), 7.26 (d, J = 2.2 Hz, 3H, NCH₃), 5.51 (s, 6H, ArCH₂N), 4.07 (t, J = 6.0 Hz, 6H, N’CH₂), 3.05 (s, 9H, NC(CH₃)N), 2.58 (q, J = 7.5 Hz, 6H, CH₂CH₃), 1.75 – 1.59 (m, 9H, with broad H₂O overlapping, Alkyl), 1.12 (t, J = 7.5 Hz, 9H, CH₂CH₃), 0.96 (d, J = 6.4 Hz, 18H, CH(CH₃)₂) ppm.

¹³C NMR (101 MHz, 1024 scans, CDCl₃) δ 148.7 (Ar), 143.3 (NC(CH₃)N), 128.3 (Ar), 122.4 (NCHCN), 121.9 (NCHCN), 47.4 (CH₃N), 47.2 (N’CH₂), 38.4 (Alk), 25.7 (Alk), 24.3 (CH₂Ar), 22.3 (Alk), 16.1 (Alk), 12.0 (Alk) ppm.

HRMS ESI-MS m/z = 219.1857 [M+H]⁺, C₄₂H₆9N₆ requires 219.1856.

IR (ν, ATR, solid state, cm⁻¹): 2956.96(br, s), 2970.81 (m), 1575.52(m), 2523.01 (m), 1505.04 (m), 1463.95 (s), 1434.50 (s), 1388.32 (m), 1367.62 (m), 1249.55 (m), 1193.72 (s), 1174.52 (m), 1074.19 (w), 1041.33 (w), 921.49 (w), 767.73 (br, s), 668.22 (m).

Elemental analysis (% CHN), calculated for C₄₂H₇₂Br₃N₆O₁.5 (as the hydrate, modelled containing 1.5 H₂O molecules), C 54.22; H, 7.72; N, 9.20 Found: C, 54.14; H, 7.75; N, 9.36.

### 3.2.4. Assessment of the effects of tris-imid.3Br 6 in a SMCC reaction between 1 and 2b

Tris-imidazolium tribromide 6 was applied to the benchmark SMCC conditions (see conditions and results below), catalyzed by our optimized catalyst precursor system, Pd(OAc)₂/1 PPh₃. We noted a marked rise in site-selectivity at 1, exhibiting a 3bₐr:3b₂Ar ratio of 17.6:1, with a relatively low formation of 3bₐr product.

![Diagram](image-url)

99% conversion {3bₐr:3b₂Ar} = 17.6:1

5% 88% 7%

3bₐr 3b₂Ar 3bₐr

p-MeO-C₆H₄ – B(OH)₂

p-MeO-C₆H₄ = Ar
3.3. Synthetic Utility Employing a C4-Site-Selective SMCC Reaction First, Followed by an Ullmann Coupling

4-[4-anisyl, 2-pyridinyl]oxy]-benzeneacetic acid methyl ester

\[ \text{Model reaction conditions Pd\(\text{OAc}_2\)/3PPH\_3 as the catalyst system (Section 2.1).} \]

**Step 1** Site-selective SMCC at 2,4-dibromopyridine: 2-bromo,4-(4-anisyl)pyridine (3b\(_{4,Ar}\)) was synthesised using the model reaction conditions Pd\(\text{OAc}_2\)/3PPH\_3 as the catalyst system (Section 2.1). An oven-dried Schlenk tube (Flask 1) charged with Pd\(\text{OAc}_2\) (23.6 mg, 0.03 mmol (3 mol%/Pd)) and triphenylphosphine (23.6 mg, 0.03 mmol) was evacuated and backfilled with N\(_2\). THF (2.5 mL; dry, degassed) was added via a syringe and the immediately formed greenish-yellow suspension was stirred in an oil bath which was pre-heated to 40 °C. Another oven-dried Schlenk tube (Flask 2) was charged with 2,4-dibromopyridine 1 (710 mg, 3.00 mmol, 1 equiv.) and p-anisylboronic acid 2b (479 mg, 3.15 mmol) and subsequently evacuated and backfilled with N\(_2\). After 30 minutes of stirring, the contents of Flask 1 were transferred into Flask 2 via a cannula and the resulting mixture was stirred for 5 mins in order to thermally equilibrate at 40 °C. Aqueous tetra-N-butylammonium hydroxide (2.5 mL, 1.0 M, degassed) was then added (t\(_0\)) to commence the reaction. The reaction was stirred overnight at 40 °C. After the reaction time the reaction solution was quenched using a of NH\(_4\)Cl (sat. aq.). The organics were extracted using EtOAc (4 × 10 mL) before being combined and dried over MgSO\(_4\), filtered and subsequently concentrated in vacuo. The resulting residue, which appeared as a reddish-brown oil was adsorbed to silica and purified by flash chromatography (SiO\(_2\)) using a Hexane or petroleum ether/EtOAc (85:15) solvent system to give the product which appeared as a colourless oil (550 mg, 69%).

**Step 2** Ullman Coupling at 3b\(_{4,Ar}\): Adapted from a procedure published by Zhao et al.\(^{17}\) A Schlenk tube, charged with Cul (18.6 mg, 0.1 mmol) and TMEDA (11.4 mg, 0.1 mmol) was evacuated and backfilled (three times), before being dissolved in dry, degassed toluene (5 mL) and subsequently stirred for 30 min at 23 °C. Cesium carbonate (638.6 mg, 2 mmol) and methyl (4-hydroxy-phenyl)-acetate (166.2 mg, 1.00 mmol) were added into the mixture (as solids) and stirred at room temperature for another 4 h. Finally, solution of 2-bromo,4-(4-anisyl)-pyridine 3b\(_{4,Ar}\) (200 mg, 0.758 mmol) in dry toluene (3 mL) was added (total volume = 8 mL => 0.125 M {respect to pyridine substrate}). The reaction mixture was placed in oil-bath which was preheated to 110 °C (refluxed, under a sealed system, with a cold
finger) under a nitrogen atmosphere for 24 h. Reaction progress was monitored by TLC (85:15 v/v Pet ether/ EtOAc). On completion, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum (Schlenk) before the residue was dissolved in CH$_2$Cl$_2$ (20 mL), filtered (sinter funnel) and concentrated in vacuum to afford the crude product which appeared as a colorless powder, 264 mg (53%) yield of isolated product (Step 2). Melting point – 103.2-104.0 °C.

$^1$H NMR (400 MHz, Chloroform-d) δ 8.19 (d, J = 5.3 Hz, 1H, pyridyl-C$_6$–H), 7.59 (d, J = 8.8 Hz, 2H, aryl), 7.33 (d, J = 8.5 Hz, 2H, aryl), 7.19 (dd, J = 5.3, 1.6 Hz, 1H, pyridyl-C$_5$–H), 7.13 (d, J = 8.5 Hz, 2H, aryl), 7.09 (d, J = 1.5 Hz, 1H, pyridyl-C$_5$–H), 6.98 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H, CH$_3$), 3.71 (s, 3H, CH$_3$), 3.64 (s, CH$_2$).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 172.6 (C), 165.0 (C), 161.2 (C), 154.0 (C), 152.3 (C), 148.5 (C–H), 130.7 (C–H), 130.2 (C–H), 128.8 (C–H), 121.8 (C–H), 117.1 (C–H), 115.1 (C–H), 109.1 (C–H), 55.5 (CH$_{aliph}$), 52.2 (CH$_{aliph}$), 40.7 (CH$_{aliph}$).

IR (v/ cm$^{-1}$, ATR): 3038 (w, C–H), 2953 (w, C–H), 2895 (w, C–H), 2842 (w,C–H), 1734 (m, C=O stretch), 1601 (m), 1393.9 (m), 1217 (m), 1164 (br. m), 1028 (m), 812 (s).

HRMS ESI-MS [M+H] m/z = 350.1387: C$_{21}$H$_{20}$NO$_4$ requires 350.1391.

R$_f$(TLC, PET/EtOAc, 85:15 (v/v)) = 0.15.
4. X-Ray Crystallography

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-Kα radiation (λ = 1.54184 Å using an EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with “Crysalis”. Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. OLEX2 was used for overall structure solution and refinement. Within OLEX2, the algorithm used for structure solution was “ShelXT dual-space”. Refinement was carried out by full-matrix least-squares used the SHELXL-97 algorithm within OLEX2. All non-hydrogen atoms were refined anisotropically. Crystalmaker® software was used to visualise the structures as well as generating the figures presented herein.

**ijsf1805: Bromo(4-bromo-C2-pyridinyl)bis(triphenylphosphine) (OA_{2-Br})**

**Refinement Special Details**

See Figure S4 for single crystal structure image. The asymmetric unit contained half of the complex plus 1.25 dichloromethanes (in 3 discrete positions). All were reflected about a central mirror plane parallel to the ac plane. In addition, the quarter dichloromethane was also at an inversion centre. The carbon of the quarter dichloromethane was disordered over two sites due to the centre of inversion. The complex was disordered with the bromopyridyl ring being modelled in two positions with refined occupancies of 0.858:0.142(2). The ring of the minor form was constrained to be a regular hexagon with bond-lengths of 1.39 Å. Several of the atoms of the bromopyridyl were restrained to be in the same plane. Closely proximal atoms in the bromopyridyl ring were constrained to have the same ADP, namely C1 & C1A, N1 & C2A, C5 & C3A, C3, C4A & C5A and C2 & N1A.
Table S11 X-Ray Diffraction Data for OA\textsubscript{C2-Br}

| Identification code | ijsf1805 (CCDC 2060854) |
|---------------------|--------------------------|
| Empirical formula   | C\textsubscript{43.5}H\textsubscript{38}Br\textsubscript{2}Cl\textsubscript{5}NP\textsubscript{2}Pd |
| Formula weight      | 1080.16                  |
| Temperature/K       | 110.00(10)               |
| Crystal system      | Monoclinic               |
| Space group         | \textit{I2/m}            |
| a/Å                 | 17.3326(4)               |
| b/Å                 | 14.8308(3)               |
| c/Å                 | 18.9185(4)               |
| α/°                 | 90                       |
| β/°                 | 116.862(3)               |
| γ/°                 | 90                       |
| Volume/Å\textsuperscript{3} | 4338.4(2)               |
| Z                   | 4                        |
| ρ\textsubscript{calc}/g/cm\textsuperscript{3} | 1.654                     |
| μ/mm\textsuperscript{1} | 9.392                     |
| F(000)              | 2148.0                   |
| Crystal size/mm\textsuperscript{3} | 0.205 × 0.125 × 0.025   |
| Radiation           | CuKα (λ = 1.54184)       |
| 2θ range for data collection/° | 7.936 to 134.16         |
| Index ranges        | -19 ≤ h ≤ 20, -17 ≤ k ≤ 13, -22 ≤ l ≤ 20 |
| Reflected reflections collected | 16229                   |
| Independent reflections | 4047 [R\textsubscript{int} = 0.0235, R\textsubscript{sigma} = 0.0185] |
| Data/restraints/parameters | 4047/6/285               |
| Goodness-of-fit on F\textsuperscript{2} | 1.164                   |
| Final R indexes [I≥2σ (I)] | R\textsubscript{1} = 0.0373, wR\textsubscript{2} = 0.0886 |
| Final R indexes [all data] | R\textsubscript{1} = 0.0386, wR\textsubscript{2} = 0.0893 |
| Largest diff. peak/hole / e Å\textsuperscript{3} | 0.85/-1.24              |
2-Bromo-4-(4-trifluoromethylphenyl)pyridine (3f\textsubscript{C4-Ar})

Refinement Special Details

See Figure S13 for single crystal structure image. The fluorine atoms within the CF\textsubscript{3} group were disordered and modelled in two positions with refined occupancies of 0.820:0.180(18), the ADPs of the fluorine atoms were restrained to be approximately isotropic.

Table S12 X-Ray Diffraction Data for 2-bromo-4-(4-trifluoromethylphenyl)pyridine (3f\textsubscript{C4-Ar})

| Identification code | ijsf1803 (CCDC 2060853) |
|---------------------|--------------------------|
| Empirical formula   | C\textsubscript{12}H\textsubscript{7}BrF\textsubscript{3}N         |
| Formula weight      | 302.10                   |
| Temperature/K       | 110.05(10)               |
| Crystal system      | orthorhombic             |
| Space group         | Pbca                     |
| a/Å                 | 11.6735(2)               |
| b/Å                 | 6.98840(10)              |
| c/Å                 | 27.1656(4)               |
| α/°                 | 90                       |
| β/°                 | 90                       |
| γ/°                 | 90                       |
| Volume/Å\textsuperscript{3} | 2216.14(6)            |
| Z                   | 8                        |
| ρ\textsubscript{calc}/cm\textsuperscript{3} | 1.811                   |
| μ/mm\textsuperscript{1} | 5.253                    |
| F(000)              | 1184.0                   |
| Crystal size/mm\textsuperscript{3} | 0.307 × 0.176 × 0.043 |
| Radiation           | CuKα (λ = 1.54184)      |
| 2Θ range for data collection/° | 9.992 to 142.21         |
| Index ranges        | -14 ≤ h ≤ 13, -8 ≤ k ≤ 8, -33 ≤ l ≤ 26 |
| Reflections collected | 10677                  |
| Independent reflections | 2118 [R\text{int} = 0.0343, R\text{sigma} = 0.0200] |
| Data/restraints/parameters | 2118/36/182         |
| Goodness-of-fit on F\textsuperscript{2} | 1.056                |
| Final R indexes [I>=2σ (I)] | R\textsubscript{1} = 0.0283, wR\textsubscript{2} = 0.0756 |
| Final R indexes [all data] | R\textsubscript{1} = 0.0311, wR\textsubscript{2} = 0.0782 |
| Largest diff. peak/hole / e Å\textsuperscript{3} | 0.35/-0.39  |
ijsf1908: bis[μ-(acetato)]bis(acetato)bis(triphenylphosphine)dipalladium ([Pd\textsuperscript{II}(μ\textsubscript{2}-OAc)(κ-OAc)(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{2}) (4)

See Section 2.9 for details on how the compound was synthesised and how the crystal was isolated.

Figure S15 Structure obtained by X-ray diffraction analysis of a single crystal of [Pd\textsuperscript{II}(μ\textsubscript{2}-OAc)(κ-OAc)(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{2} (4). Thermal ellipsoids were set at 50% probability. Selected interatomic distances /Å: Pd1–P2 = 2.2329(7), Pd1–O1 = 2.0209(18), Pd1–O3 = 2.1062(19), Pd1–O5 = 1.999(2), Pd1–Pd2 = 3.0115(4). Selected bond angles /°: P2–Pd1–O1 = 88.62(5), O1–Pd1–O3 = 89.61(8) P2–Pd1–O5 = 92.11(6), O3–Pd1–O5 = 89.83(8). Torsion angles /°: O5–Pd1–Pd2–O7 = 89.766, O5–Pd1–Pd2–P1 = -4.867, P2–Pd1–Pd1–P2 = -99.500 (ijsf1908; CCDC 2060855).

Refinement Special Details
The asymmetric unit contained half a molecule, the other half being generated by a mirror plane.
Table S13 X-Ray Diffraction Data for ([Pd(\(\mu_2\)-OAc)(\(\kappa\)-OAc)(PPh\(_3\))]\(_2\)) (4)

| Identification code | ijsf1908 |
|---------------------|----------|
| Empirical formula   | \(\text{C}_{44}\text{H}_{42}\text{O}_8\text{P}_2\text{Pd}_2\) |
| Formula weight      | 973.51   |
| Temperature/K       | 110.05(10) |
| Crystal system      | monoclinic |
| Space group         | C2/c     |
| \(a/\text{Å}\)      | 20.9152(4) |
| \(b/\text{Å}\)      | 9.6486(2)  |
| \(c/\text{Å}\)      | 22.0620(4) |
| \(\alpha/^\circ\)   | 90       |
| \(\beta/^\circ\)    | 113.600(2) |
| \(\gamma/^\circ\)   | 90       |
| Volume/\(\text{Å}^3\) | 4079.80(15) |
| \(Z\)               | 4        |
| \(\rho_{\text{calc}}/\text{g/cm}^3\) | 1.585 |
| \(\mu/\text{mm}^{-1}\) | 8.292 |
| \(F(000)\)          | 1968.0   |
| Crystal size/\(\text{mm}^3\) | 0.201 × 0.151 × 0.088 |
| Radiation           | CuK\(\alpha\) (\(\lambda = 1.54184\)) |
| 2\(\Theta\) range for data collection/\(^\circ\) | 8.748 to 134.142 |
| Index ranges        | -24 \(\leq h \leq 23\), -11 \(\leq k \leq 11\), -26 \(\leq l \leq 23\) |
| Reflections collected | 7133 |
| Independent reflections | 3635 [\(R_{int} = 0.0200\), \(R_{sigma} = 0.0234\)] |
| Data/restraints/parameters | 3635/0/255 |
| Goodness-of-fit on \(F^2\) | 1.058 |
| Final R indexes [\(I > 2\sigma (I)\)] | \(R_1 = 0.0255\), \(wR_2 = 0.0659\) |
| Final R indexes [all data] | \(R_1 = 0.0279\), \(wR_2 = 0.0680\) |
| Largest diff. peak/hole / e \(\text{Å}^3\) | 0.67/-0.59 |
Refinement Special Details
The compound was prepared and crystallised as detailed in Section 3.2. See Figure S14 for single crystal structure image. The structure was disordered about a mirror plane parallel to the ac plane at b=0.25. In the central ring, C3 and C4 occupied a common site for both conformations.

Table S14: X-Ray Diffraction Data for 3,5-tris(methyl(2-methylimidazole))-2,4,6-triethylbenzene.

| Identification code | ijsf2006 (CCDC 2060856) |
|---------------------|--------------------------|
| Empirical formula   | C\(_{27}\)H\(_{42}\)N\(_{6}\)O\(_{3}\) |
| Formula weight      | 498.66 |
| Temperature/K       | 109.8(6) |
| Crystal system      | monoclinic |
| Space group         | P2\(_1\)/m |
| a/Å                 | 7.7470(4) |
| b/Å                 | 16.6589(11) |
| c/Å                 | 10.9761(6) |
| α/°                 | 90 |
| β/°                 | 100.387(5) |
| γ/°                 | 90 |
| Volume/Å\(^3\)     | 1393.33(14) |
| Z                   | 2 |
| \(\rho_{\text{calc}}\)/g/cm\(^3\) | 1.189 |
| \(\mu\)/mm\(^{-1}\) | 0.632 |
| F(000)              | 540.0 |
| Crystal size/mm\(^3\) | 0.216 \(\times\) 0.195 \(\times\) 0.092 |
| Radiation           | Cu K\(\lambda\) (\(\lambda\) = 1.54184) |
| 2\(\Theta\) range for data collection/° | 8.19 to 134.16 |
| Index ranges        | -6 ≤ h ≤ 9, -19 ≤ k ≤ 17, -13 ≤ l ≤ 12 |
| Reflections collected | 4940 |
| Independent reflections | 2573 \([R_{\text{int}} = 0.0239, R_{\text{sigma}} = 0.0348]\) |
| **Data/restraints/parameters**     | 2573/0/253   |
|-----------------------------------|--------------|
| **Goodness-of-fit on F^2**        | 1.039        |
| **Final R indexes [I>=2σ (I)]**  | R₁ = 0.0423, wR₂ = 0.0990 |
| **Final R indexes [all data]**   | R₁ = 0.0559, wR₂ = 0.1082 |
| **Largest diff. peak/hole / e Å⁻³** | 0.18/-0.16  |
5. NMR Spectral Data for Isolated Organic Compounds

**Figure S16** $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3a$_{C4-Ar}$

**Figure S17** $^{13}$C NMR (CDCl$_3$, 101 MHz, 2048 scans) spectrum of 3a$_{C4-Ar}$
**Figure S18** $^{19}$F NMR (CDCl$_3$, 376 MHz, 128 scans) spectrum of 3a$_{C4-Ar}$

**Figure S19** $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3a$_{C2-Ar}$
Figure S20 $^{13}$C NMR (CDCl$_3$, 101 MHz, 2048 scans) spectrum of 3a$_{C2-Ar}$.

Figure S21 $^{19}$F NMR (CDCl$_3$, 376 MHz, 128 scans) spectrum of 3a$_{C2-Ar}$.
Figure 22 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3a$_{diaryl}$

Figure S23 $^{13}$C NMR (CDCl$_3$, 101 MHz, 2048 scans) spectrum of 3a$_{diaryl}$
Figure S24 $^{19}$F NMR (CDCl$_3$, 376 MHz, 128 scans) spectrum of 3a$_{\text{diaryl}}$.

Figure S25 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3b$_{\text{C4-Ar}}$. 
Figure S26 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of 3bC$_2$-Ar.

Figure S27 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3bC$_2$-Ar.
Figure S28 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of 3b$_{C2-Ar^+}$.

Figure S29 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3b$_{diaryl}$.
Figure S30 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of 3b$_{diaryl}$.

Figure S31 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3C$_{C_{di}-Ar}$.
Figure S32 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of $3\text{c}_{\text{C}_4\text{-Ar}}$.

Figure S33 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of $3\text{d}_{\text{C}_4\text{-Ar}}$. 
Figure S34 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3d$_2$-Ar.

Figure S35 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of 3d$_2$-Ar.
Figure S36 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3d$_{diaryl}$.

Figure S37 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3e$_{C_4-Ar}$.
Figure S38 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of 3e$_{C2-Ar}$.

Figure S39 $^1$H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum of 3e$_{C2-Ar}$. 
Figure S40 $^{13}$C NMR ($\text{CDCl}_3$, 101 MHz, 1024 scans) spectrum of $3e_{\text{Cz-Ar}}$.

Figure S41 $^1$H NMR ($\text{CDCl}_3$, 400 MHz, 32 scans) spectrum of $3e_{\text{diaryl}}$. 

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Figure S42 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum of $3e_{diaryl}$.

Figure S43 $^1$H NMR (CDCl$_3$, 500 MHz, 64 scans) spectrum of $3f_{C_4-Ar}$. 
Figure S44 $^{13}$C NMR (CDCl$_3$, 125 MHz, 1024 scans) spectrum of 3f$_{C4-Ar}$.

Figure S45 $^{19}$F NMR (CDCl$_3$, 376 MHz, 128 scans) spectrum of 3f$_{C4-Ar}$. 
Figure S46 ¹H NMR (CDCl₃, 400 MHz, 32 scans) spectrum of 3f²⁴Ar.

Figure S47 ¹³C NMR (CDCl₃, 101 MHz, 2048 scans) spectrum of 3f²⁴Ar.
Figure S48 $^{19}$F NMR (CDCl$_3$, 376 MHz, 128 scans) spectrum of 3f$_2$-Ar.

Figure S49 1H NMR (CDCl$_3$, 400 MHz, 32 scans) spectrum for 1,3,5-tris(bromomethyl)-2,4,6-triethyl-benzene.
Figure S50 $^{13}$C NMR (CDCl$_3$, 101 MHz, 1024 scans) spectrum for 1,3,5-tris(bromomethyl)-2,4,6-triethyl-benzene.

Figure S51 $^1$H NMR(CDCl$_3$,400 MHz, 8 scans) of 1,3,5-tris(methyl(2-methylimidazole))-2,4,6-triethylbenzene.
Figure SS2 $^{13}$C NMR (DMSO-$d_6$, 101 MHz, 1024 scans) of 1,3,5-tris(methyl(2-methylimidazole))-2,4,6-triethylbenzene.

Figure SS3 $^{13}$C DEPT 135 Spectrum (DMSO-$d_6$, 101 MHz) of 1,3,5-tris(methyl(2-methylimidazole))-2,4,6-triethylbenzene.
Figure S54 $^1$H NMR (CDCl$_3$, 400 MHz, 64 scans) of TrisImid.3Br (6).

Figure S55 $^{13}$C NMR (CDCl$_3$, 101 MHz, 2048 scans) of TrisImid.3Br (6).
Figure S56 $^1$H NMR (CDCl$_3$, 400 MHz, 128 scans) of 4-[4-anisyl, 2-pyridinyl]oxy]-benzene acetic acid methyl ester.

Figure S57 $^{13}$C NMR (CDCl$_3$, 101 MHz, 2048 scans) of 4-[4-anisyl, 2-pyridinyl]oxy]-benzene acetic acid methyl ester.
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