Ion-Pair-Directed Borylation of Aromatic Phosphonium Salts

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Supporting Information

ABSTRACT: Control of positional selectivity in C–H activation reactions remains a challenge for synthetic chemists. Noncovalent catalysis has the potential to be a powerful strategy to address this challenge. As a part of our ongoing investigations into the use of ion-pairing interactions in site-selective catalysis, we demonstrate that several classes of aromatic phosphonium salts undergo iridium-catalyzed C–H borylation with a high selectivity for the arene meta position. This is achieved using a bifunctional bipyridine ligand bearing a pendant sulfonate group, which had previously been successful for borylation of aromatic ammonium salts. In this case, the phosphonium salts give a higher meta selectivity than the corresponding ammonium salts. We propose that the high selectivity occurs due to an attractive electrostatic interaction between the substrate and the ligand in the transition state for borylation.

The direct functionalization of arene C–H bonds using transition metal catalysis constitutes a highly effective method for elaboration of aromatic compounds. Numerous advances have been made, particularly over the last two decades. It is notable however that the majority of these advances result in a selective reaction at the arene ortho position, as a consequence of proximity to a directing group. Strategies that are able to reach further to the more remote meta and para positions are less common, and as a consequence, these positions are typically more difficult to access.1

We and others have recently been exploring strategies that exploit a temporary noncovalent interaction between a substrate and ligand to guide the reactive transition metal to a particular position in the selectivity-determining transition state for C–H bond functionalization.2 This approach builds on previous advances for controlling regioselectivity in reactions including aliphatic C–H activation,3 hydroformylation,4 and others. We have been particularly interested in applying this idea to control regioselectivity in arene C–H functionalization via C–H borylation, which has been investigated by a number of groups.5–7 Specifically, we were curious to explore a scenario in which the catalyst engages in ion-pairing interactions with the substrate, as this is far rarer than using hydrogen bonding and relatively unexplored.8 In our previous work, we developed an anionic bipyridine ligand (1) for application in iridium-catalyzed C–H borylation.9 This ligand bears a pendant sulfonate group, which we hypothesized may engage in attractive electrostatic interactions with a quaternary ammonium moiety in the substrate, directing C–H borylation to occur at the arene meta position. Gratifyingly, a high meta selectivity was obtained with a variety of chain lengths between the quaternary ammonium group and the arene, despite initial concerns that substantial substrate flexibility may be incompatible with the relatively low directionality of ion-pairing interactions. However, in these studies, we only examined quaternary ammonium salts as cationic groups on the substrates. Phosphonium salts have a number of important chemical applications as phase transfer catalysts, ionic liquids, and lipophilic cations. They can be transformed into reactive intermediates upon deprotonation to form ylides, as widely used in the Wittig reaction and variants.10,11 Several recent studies have shown that certain phosphonium salts can also be used in cross-coupling reactions.12 Hence, we were keen to explore whether our ion-pair-directed method for controlling regioselectivity in C–H borylation would be compatible with arenes bearing a phosphonium group, in order to demonstrate greater generality of the approach.

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We began our studies with trifluoromethyl-substituted benzyl trimethyl phosphonium salt 3a, possessing a tosylate counterion (Table 1). An initial evaluation with the standard borylation ligand dtbpy gave no conversion in THF at 50 °C (entry 1), but we found that switching to a more reactive tmphen ligand gave high conversion to a mixture of meta and para isomers with a poor selectivity, as expected (entry 2). We were happy to see that using our sulfonate ligand 1 in place of tmphen gave a good conversion with a 7:1 meta/para selectivity, in line with our hypothesis (entry 3). Under the same conditions, the same phosphonium cation but bearing bromide as the counteranion (2a) gave no conversion, presumably due to the very poor solubility of the starting material (entry 4); hence, we continued optimization using 3a.

An evaluation of solvents revealed that in 1,4-dioxane the meta selectivity was greatly improved (>20:1) and with full conversion (entry 5). The selectivity was reasonably tolerant to solvent variations (entries 6–8), although nonpolar solvents were not suitable, likely due to solubility issues (entry 9). A control borylation of 3a in dioxane with tmphen revealed a slight bias toward para selectivity, in this case, 3.3:1 para/meta (see values in parentheses). A bromo-substituted variant also worked very well, giving 17:1 m/p selectivity (4c). In the case of the electron-donating methyl substituent, a higher catalyst loading of 6 mol % Ir was required for good conversion, and this substrate too gave a high selectivity (4d). The small size of fluorine resulted in substrate 4e giving a mixture of isomers under borylation with tmphen, but with ligand 1, only the meta-borylated isomer was observed (>20:1). Finally, an unsubstituted benzylphosphonium salt also performed well (4f). In this case, it was not

Table 1. Evaluation of Ligand 1 on Benzylphosphonium Salt 3a

| entry | X   | ligand | solvent | meta/para | % conv |
|-------|-----|--------|---------|-----------|--------|
| 1     | OTs | dtbpy  | THF     |           | 0      |
| 2     | OTs | tmphen | THF     | 1:1.3     | 91     |
| 3     | OTs | 1      | THF     | 7:1       | 93     |
| 4     | Br  | 1      | THF     |           | 0      |
| 5     | OTs | 1      | dioxane | >20:1     | 100    |
| 6     | OTs | 1      | CHCl2   | >20:1     | 77     |
| 7     | OTs | 1      | CH3CN   | 12:1      | 92     |
| 8     | OTs | 1      | MTBE    | 7:1       | 32     |
| 9     | OTs | 1      | cyclohexane | 0      |        |
| 10    | OTs | tmphen | dioxane | 1:1.6     | 100    |

*Meta/para ratios are taken from the analysis of crude 1H NMR spectra. * Determined by 1H NMR referenced to 1,2-dimethoxyethane as the internal standard.

Scheme 1. Synthesis of Benzyl Phosphonium Salts 2 and 3

Scheme 2. Scope of Substituents on Benzylphosphonium Salts 3

1H NMR yield referenced to an internal standard quoted due to decomposition during purification. * Double catalyst loadings used, reaction at 70 °C. Three equiv of B2Pin2 used.

With optimal conditions in hand, we proceeded to evaluate the scope of the transformation. The substrates could be synthesized very readily from substituted benzyl bromides by benzylation of trimethylphosphine, followed by anion exchange with silver tosylate, both steps proceeding with generally high yields (Scheme 1). While the use of silver is not ideal from a cost standpoint, it is also possible to access these tosylate salts from benyl tosylates (see Scheme 3).

We first examined the 2-chloro-substituted salt and found that this also gave a high meta selectivity using ligand 1 (Scheme 2, 4b). Similarly to the CF3-substituted substrate, the use of tmphen gave some bias toward the para selectivity, in this case, 3.3:1 para/meta (see values in parentheses). A bromo-substituted variant also worked very well, giving 17:1 m/p selectivity (4c). In the case of the electron-donating methyl substituent, a higher catalyst loading of 6 mol % Ir was required for good conversion, and this substrate too gave a high selectivity (4d). The small size of fluorine resulted in substrate 4e giving a mixture of isomers under borylation with tmphen, but with ligand 1, only the meta-borylated isomer was observed (>20:1). Finally, an unsubstituted benzylphosphonium salt also performed well (4f). In this case, it was not
possible to stop at monoborylation, and so, 3 equiv of \( \text{B,Pin}_2 \) was used to obtain the \( \text{dimeta}- \) borylated product in a good yield. The iodo-substituted phosphonium salts 3g and 3h unfortunately were found to give no conversion with either tmphen or ligand 1. Interestingly, the triarylbenzylphosphonium salt 3i was also found to give no reaction with either ligand. It should be mentioned that in many cases small amounts of starting material were still present at the end of the reaction, and these were impossible to separate from the borylated products as the salts were not purified on silica and had to be precipitated. The yields quoted have been adjusted to reflect this based on the molar mass of the starting material (see Experimental Section).

Borylation of a pyridine-derived phosphonium salt was next examined to evaluate whether selectivity between the 4- and 5-positions could be obtained. In this case, the counterion exchange according to the previous substrate synthesis using silver failed in the presence of the basic pyridine. So an alternative approach was taken via the intermediate tosylate, which allows substrates to be accessed from benzyl alcohols. This approach can be advantageous for some substrates as it installs tosylate directly as the counterion (Scheme 3a). For the pyridine substrate 5a, it was quite challenging to prevent over borylation to 6c, but by stopping the reaction after 1 h, useful amounts of 6a, the product of borylation at C4, could be obtained and the C4/C5 ratio was 10:1 (corresponding to the \( m/p \) ratio in nonheteroarenes). In contrast, with tmphen, the C4/C5 ratio was \( \sim 1:1 \) (Scheme 3b).

We next sought to vary the carbon chain of the phosphonium salt to evaluate whether selectivity would be maintained if it is either extended or reduced. We were pleased to find that trifluoromethyl-substituted phenethyl phosphonium salt 7a gave \( >20:1 \) \( m/p \) selectivity in a good yield (Scheme 4a). In contrast, control borylation of this substrate with tmphen as a ligand gave 1:2 (Scheme 4b). In these cases, the selectivities are in general very high, and we envisage that this study provides further evidence of the utility of ion-pairing interactions in the design of new catalyst scaffolds for site-selective functionalization.

### EXPERIMENTAL SECTION

#### Materials and Methods

All reagents, unless otherwise stated, were used as supplied from commercial sources without further purification. \( \text{CH}_2\text{Cl}_2, \text{THF}, \) and \( \text{Et}_3\text{O} \) were purified by distillation on site under an inert atmosphere via the following processes: THF and \( \text{Et}_3\text{O} \) were predried over a sodium wire and then distilled from calcium hydride. \( \text{CH}_2\text{Cl}_2 \) and \( \text{n-hexane} \) were distilled from calcium hydride.

1H NMR spectra were recorded on a 600 MHz Bruker Avance DRX-600 spectrometer, 500 MHz Bruker DCH Cryoprobe, or 400 MHz QNP Cryoprobe. Chemical shifts are reported in ppm, and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent (\( \text{CDCl}_3 \), 7.26 ppm, \( \text{CD}_2\text{OD} \), 3.31 ppm, \( \text{CD}_3\text{SO} \), 2.50 ppm). 13C NMR spectra were recorded on the same spectrometers with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (\( \text{CDCl}_3 \), 77.16 ppm, 13\text{CD}_2\text{OD} \), 49.00 ppm, see Table 1 for \( \text{DMSO-d}_6, 39.51 \) ppm). Data are reported as follows: chemical shift \( \delta/\text{ppm}, \) multiplicity \( \text{s} = \text{singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or combinations thereof} \); 13C signals are singlets unless otherwise stated, coupling
constants $J$ in Hz, integration (1H only). $^1H$ COSY, HSQC, HMBC, and NOESY were used where appropriate to facilitate structural determination. The carbon attached to boron was generally not observed by $^{13}C$ NMR due to quadrupolar relaxation. $^1H$ NMR signals are reported to 2 decimal places and $^{13}C$ signals to 1 decimal place (2 decimals places if the peaks are not distinguishable with only 1 decimal place). $^{31}P$ NMR spectra were recorded on a 400 MHz Bruker Avance III HD spectrometer, and $^{15}N$ signals are reported to 2 decimal places. $^{31}P$ NMR spectra were recorded on a 600 MHz Bruker Avance DRX-600 spectrometer or a 400 MHz Bruker Avance III HD spectrometer, and $^{31}P$ signals are reported to 2 decimal places.

High-resolution mass spectra (HRMS) were recorded on a Waters Micromass LCT Premier TOF spectrometer using a positive electrospray ionization (ESI+). Measured values are reported to 4 decimal places and are within ±5 ppm of the calculated value. The calculated values are based on the most abundant isotope. Infrared (IR) spectroscopy was performed using a PerkinElmer Spectrum One FT infrared spectrophotometer sampling accessory, scanning from 4000–660 cm$^{-1}$. IR absorption maxima ($
u_{	ext{max}}$) are reported in wavenumbers (cm$^{-1}$).

**General Procedure for the Synthesis of Phosphonium 4-Methylbenzenesulfonates (GP1).** The corresponding phosphonium bromide (or chloride) salt and silver p-toluenesulfonate (1.1 equiv) were dissolved in CHCl$_3$. The reaction mixture was stirred at room temperature for 30 min and then filtered through MgSO$_4$. The filtrate was collected, and the solvent was removed under reduced pressure to afford the product.

**Trimethyl(2-(trifluoromethyl)benzyl)phosphonium Bromide (2a).** To a solution of 2-(trifluoromethyl)benzyl bromide (1.25 g, 5.2 mmol) in acetonitrile (10 mL) was added a 1.0 M solution of trimethylphosphine in toluene (5.8 mL, 5.8 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 1 h under an argon atmosphere. The solvent was then removed under reduced pressure and the salt precipitated with CHCl$_3$ and Et$_2$O (approximately a 1:10 ratio of CHCl$_3$/Et$_2$O). The salt was collected by filtration, washed with Et$_2$O, and dried in vacuo to yield the title compound as a white powder (1.58 g, 5.0 mmol, 96%). $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 7.85 (dd, $J = 7.7, 2.2$ Hz), 7.72 (dd, $J = 7.9$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 1H), 4.37 (d, $J = 16.7$ Hz, 2H), 2.24 (d, $J = 14.2$ Hz, 4H), $^{13}C$ (1H) NMR (151 MHz, CDCl$_3$) $\delta$ 130.0 (d, $J_{C-P} = 4.7$ Hz), 128.9 (d, $J_{C-P} = 3.8$ Hz), 128.8 (qd, $J_{C-P} = 29.8$ Hz, $J_{C-C} = 5.7$ Hz), 127.3 (d, $J_{C-P} = 121.7$ (m), 126.9 (dq, $J_{C-P} = 1.6$ Hz, $J_{C-C} = 9.0$ Hz), 123.9 (qd, $J_{C-P} = 27.8$ Hz, $J_{C-C} = 5.7$ Hz), 123.7 (d, $J_{C-P} = 27.9$ Hz, $J_{C-C} = 51.1$ Hz), $^31$P NMR (376 MHz, CDCl$_3$) $\delta$ -68.81 ppm. $^{31}P$ NMR (243 MHz, CDCl$_3$) $\delta$ 28.29. HRMS m/z (ESI+) [M – Br]$^+$ calc for [C$_6$H$_3$PBr]$^+$ 235.0858, found 235.0849.

**Trimethyl(2-(trifluoromethyl)benzyl)phosphonium 4-Methylbenzenesulfonate (3a).** Following GP1, the compound was formed using chloroform (0.65 g, 2 mmol) and silver p-toluenesulfonate (0.61 g, 2.2 mmol, 1.1 equiv), and chloroform (5 mL). The title compound was obtained as a white solid (0.78 g, 1.9 mmol, 93%). $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 7.8$ Hz, 2H), 7.59–7.56 (m, 1H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.18 (tt, $J = 7.8$, 2.1 Hz, 1H), 7.14–7.13 (d, $J = 7.9$ Hz, 2H), 4.10 (d, $J = 16.3$ Hz, 2H), 2.33 (s, 3H), 2.12 (d, $J = 14$ Hz, 2H), 1.72 (t, $J = 7.9$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.12 (d, $J = 7.9$ Hz, 2H), 4.06 (d, $J = 16.8$ Hz, 2H), 2.31 (s, 3H), 2.08 (d, $J = 14.4$ Hz, 9H), $^{13}C$ (1H) NMR (151 MHz, CDCl$_3$) $\delta$ 143.6, 139.4, 133.2 (d, $J_{C-P} = 4.8$ Hz), 133.0 (d, $J_{C-P} = 2.3$ Hz), 128.9 (q, $J_{C-P} = 30.2$ Hz, $J_{C-C} = 5.7$ Hz), 128.7, 128.65 (d, $J_{C-P} = 3.5$ Hz), 127.3 (d, $J_{C-P} = 1.7$ Hz, $J_{C-C} = 8.7$ Hz), 127.1 (m), 125.8, 124.0 (qd, $J_{C-P} = 27.3$ Hz, $J_{C-C} = 1.6$ Hz), 27.7 (d, $J_{C-P} = 50.3$ Hz), 21.3, 8.4 (d, $J_{C-P} = 54.1$ Hz); $^31$P NMR (376 MHz, CDCl$_3$) $\delta$ -58.86 ppm. $^{31}P$ NMR (243 MHz, CDCl$_3$) $\delta$ 29.07; HRMS m/z (ESI+) [M – OTs]$^+$ calc for [C$_6$H$_3$PBrS]$^+$ 246.0889, found 246.0883.

**Trimethyl(2-bromobenzyl)phosphonium Bromide (2b).** To a solution of 2-bromobenzyl bromide (0.67 mL, 5 mmol) in acetonitrile (10 mL) was added a 1.0 M solution of trimethylphosphine in THF (5.5 mL, 5.5 mmol, 1.1 equiv) dropwise. The reaction mixture was stirred at room temperature for 1 h under an argon atmosphere.
Tritylmethylbenzyl)phosphonium 4-Methylenezensulfonate (3f). Following GP1, the compound was formed using tritylmethylbenzyl)phosphonium bromide (0.99 g, 4 mmol), silver p-toluenesulfonate (1.23 g, 4 mmol, 1.1 equiv), and chloroform (10 mL). The mixture was stirred at room temperature for 1.5 h rather than 30 min. The title compound was obtained as a white solid (1.32 g, 3.9 mmol, 98%).

& NMR (600 MHz, CDCl3) δ 7.77 (d, J = 8.1 Hz, 2H), 7.27–7.26 (m, 3H), 7.23–7.21 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.93 (d, J = 16.4 Hz, 2H), 2.32 (s, 3H), 1.95 (d, J = 14.3 Hz, 9H); 31P (151 MHz, CDCl3) δ 143.8, 139.4, 130.2 (d, J,4P = 5.3 Hz, 129.2 (d, J,4P = 3.5 Hz, 128.1, 127.5 (d, J,4P = 9.2 Hz, 128.1 (d, J,4P = 3.9 Hz, 125.8, 29.9 (d, J,4P = 49.0 Hz), 21.3, 7.4 (d, J,4P = 54.5 Hz); 31P NMR (243 MHz, CD3OD) δ 27.16; HRMS m/z (ESI+) [M − OTs]− calcd for [C10H8P]+ 167.0984, found 167.0978.

(2-Iodobenzyl)trimethylphosphonium Bromide (2g). To a solution of 2-iodobenzyl chloride (0.60 mL, 5 mmol) in acetonitrile (10 mL) was added a 1.0 M solution of trimethylphosphine in toluene (11 mL, 11 mmol, 2.2 equiv) dropwise. The reaction mixture was stirred at room temperature for 3 h under an argon atmosphere. The solvent was removed, and the salt precipitated with Et2O and then dried in vacuo to yield the title compound as a white powder (0.92 g, 92 mmol, 84%): 1H NMR (400 MHz, DMSO-d6) δ 7.50–7.44 (m, 1H), 7.24–7.17 (m, 3H), 7.03 (d, J = 17.2 Hz, 2H), 1.83 (d, J = 14.8 Hz, 9H); 13C{1H} NMR (101 MHz, DMSO-d6) δ 162.5 (d, J,4C = 244.9 Hz, J,4C = 3.8 Hz, 145.7, 137.8, 132.3 (dd, J,c = 8.7 Hz, J,c = 8.7 Hz, 131.2 (dd, J,c = 8.7 Hz, J,c = 3.8 Hz, 128.2, 126.2 (dd, J,c = 3.0 Hz, J,c = 3.0 Hz, 125.6, 116.8 (dd, J,c = 22.2 Hz, J,c = 5.4 Hz, 115.0 (dd, J,c = 21.1 Hz, J,c = 4.0 Hz, 29.1 (d, J,c = 48.9 Hz, 20.9, 7.0 (d, J,c = 54.0 Hz); 31P NMR (376 MHz, DMSO-d6) δ -113.08 (d, J,p = 2.7 Hz); 31P NMR (243 MHz, CD3OD) δ 28.11. HRMS m/z (ESI+) [M − Br−]− calcd for [C10H8P]+ 167.0980, found 168.0882.

(3-Iodobenzyl)trimethylphosphonium 4-Methylenezensulfonate (3e). Following GP1, the compound was formed using (3-iodobenzyl)trimethylphosphonium chloride (0.44 g, 2 mmol), silver p-toluenesulfonate (0.61 g, 2.2 mmol, 1.1 equiv), and chloroform (10 mL). The title compound was obtained as a white solid (0.90 g, 90 mmol, 95%): 1H NMR (600 MHz, CDCl3) δ 7.85 (d, J = 8.0 Hz, 1H), 7.75 (s, J = 8.1 Hz, 2H), 7.53 (d, J = 7.8, 2.3 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 7.00 (tt, J = 8.0, 1.8 Hz, 1H), 4.11 (d, J = 16.2 Hz, 2H), 2.32 (s, 3H), 2.13 (d, J = 14.4 Hz, 9H); 31P (151 MHz, CDCl3) δ 140.6 (d, J,p = 3.2 Hz, 132.4 (d, J,c = 9.2 Hz, 131.8 (d, J,c = 4.9 Hz, 130.4 (d, J,c = 3.6 Hz, 129.5 (d, J,c = 9.2 Hz, 7.1 (d, J,c = 50.4 Hz); 31P NMR (376 MHz, DMSO-d6) δ -113.08 (d, J,p = 2.7 Hz); 31P NMR (243 MHz, CD3OD) δ 28.11. HRMS m/z (ESI+) [M − OTs]− calcd for [C10H8P]+ 299.9951, found 299.9940.

(3-Iodobenzyl)trimethylphosphonium Bromide (2h). To a solution of 3-iodobenzyl bromide (0.30 g, 1 mmol) in acetonitrile (2 mL) was added a 1.0 M solution of trimethylphosphine in toluene (1.1 mL, 1.1 mmol, 1.1 equiv) dropwise. The reaction mixture was stirred at room temperature for 1.5 h under an argon atmosphere, with the product being observed to precipitate from solution. The reaction mixture was then filtered, and the solids were washed with Et2O and then dried in vacuo to yield the title compound as a white powder (0.36 g, 0.97 mmol, 97%): 1H NMR (600 MHz, CD3OD) δ 7.79–7.77 (m, 2H), 7.39–7.37 (m, 3H), 7.24–7.21 (m, 1H), 3.76 (d, J = 163.6 Hz, 2H), 1.87 (d, J = 143.3 Hz, 9H); 31P (151 MHz, CDCl3) δ 138.5 (d, J,c = 3.9 Hz, 137.4 (d, J,c = 3.9 Hz, 131.0 (d, J,c = 9.0 Hz), 130.8 (d, J,c = 3.5 Hz), 129.0 (d, J,c = 5.0 Hz), 94.3 (d, J,c = 4.1 Hz), 29.2 (d, J,c = 49.8 Hz), 6.3 (d, J,c = 55.2 Hz); 31P NMR (243 MHz, CD3OD) δ 27.25; HRMS m/z (ESI+) [M − Br−]− calcd for [C10H8P]+ 292.9981, found 292.9983.

Benzyltrimethylphosphonium Bromide (2f). To a solution of benzyl bromide (1.2 mL, 10 mmol) in acetonitrile (20 mL) was added a 1.0 M solution of trimethylphosphine in toluene (11 mL, 11 mmol, 1.1 equiv) dropwise. The reaction mixture was stirred at room temperature for 1 h under an argon atmosphere, with the product being observed to precipitate from the solution. The reaction mixture was cooled on ice and then filtered, and the solids were washed with Et2O and then dried in vacuo to yield the title compound as a white powder (2.36 g, 96 mmol, 96%): 1H NMR (600 MHz, CDCl3) δ 7.43–7.41 (m, 2H), 7.38–7.34 (m, 3H), 4.27 (d, J = 161.6 Hz, 2H), 2.16 (d, J = 14.1 Hz, 9H); 31P (151 MHz, CDCl3) δ 130.1 (d, J,c = 5.4 Hz), 129.5 (d, J,c = 3.5 Hz), 128.5 (d, J,c = 4.0 Hz), 128.2 (d, J,c = 9.2 Hz), 30.6 (d, J,c = 49.6 Hz), 8.5 (d, J,c = 54.8 Hz); 31P NMR (243 MHz, CD3Cl) δ 26.32. HRMS m/z (ESI+) [M − Br−]− calcd for [C10H8P]+ 167.0984, found 167.0978.
silver p-toluenesulphonate (0.22 g, 0.8 mmol, 1.2 equiv), and chloroform (15 mL). The title compound was obtained as a white solid (0.28 g, 0.60 mmol, 90%): 1H NMR (600 MHz, DMSO-d6) δ 7.73–7.69 (m, 2H), 7.47–7.44 (m, 2H), 7.35–7.29 (m, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.10–7.08 (m, 2H), 3.69 (d, J = 16.9 Hz, 2H), 2.26 (s, 3H). 13C{1H} NMR (151 MHz, CDCl3) δ 149.5, 138.2 (d, J = 13.6 Hz, 5H), 137.6, 136.7 (d, J = 3.8 Hz), 113.2 (d, J = 7.7 Hz, 1H), 131.2 (d, J = 3.8 Hz, 3H), 129.3 (d, J = 7.7 Hz, 1H), 128.1, 125.5, 95.6 (d, J = 4.0 Hz, 3H), 28.9 (d, J = 4.0 Hz, 2H), 20.7, 7.0 (d, J = 54.0 Hz), 31P NMR (243 MHz, DMSO-d6) δ 32.78; HRMS m/z [M + OTs]⁺ calcd for [C6H4P]3+ 292.9951, found 292.9938.

(2-Chlorobenzyl)tri-p-tolylphosphonium 4-Methylbenzenesulfonate (3f): A solution of 2-chlorobenzyl bromide (0.25 mL, 2 mmol) and tri(p-tolyl)phosphine (0.85 g, 2.8 mmol, 1.4 equiv) in acetonitrile (10 mL) was stirred at 50 °C for 30 h under argon atmosphere. The solvent was then removed, and the crude product was used directly in the next step. The crude product and silver p-toluenesulfonate (0.61 g, 2.2 mmol, 1.1 equiv) were dissolved in chloroform (10 mL) and then stirred at room temperature for 2 h. Filtration through MgSO4 and removal of the solvent under reduced pressure yielded the crude product as a yellow solid, which was dried to a gray solid overnight and then was purified by flash column chromatography on silica gel (5% MeOH in CH2Cl2). NMR analysis of the filtrate showed that not all of the product was present as the tosylate; thus, the ion exchange reaction was repeated. Filtration through MgSO4 and removal of the solvent under reduced pressure yielded the title compound as a yellow solid (0.52 g, 0.87 mmol, 44% over two steps): 1H NMR (600 MHz, CDCl3) δ 7.75 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 12.5, 8.0 Hz, 6H), 7.44 (d, J = 7.8, 2.3 Hz, 1H), 7.38 (dd, J = 8.1, 3.5 Hz, 6H), 7.20–7.14 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.9 Hz, 2H), 5.15 (d, J = 14.4 Hz, 2H), 2.46 (s, 3H), 2.28 (s, 3H); 13C{1H} NMR (151 MHz, CDCl3) δ 146.1 (d, J = 3.0 Hz), 144.6, 138.2, 135.7 (d, J = 6.3 Hz, 3H), 134.1 (d, J = 10.3 Hz), 133.4 (d, J = 4.8 Hz, 1H), 130.8 (d, J = 13.0 Hz, 3H), 129.7 (d, J = 3.9 Hz, 1H), 129.4 (d, J = 3.2 Hz, 3H), 128.1, 127.7 (d, J = 3.6 Hz, 2H), 126.5 (d, J = 9.1 Hz, 1H), 126.2, 114.4 (d, J = 88.5 Hz, 2H), 27.8 (d, J = 50.3 Hz, 2H), 21.8 (d, J = 1.4 Hz, 21.2; 31P NMR (243 MHz, CDCl3) δ 21.71; HRMS m/z [M + OTs]⁺ calcd for [C6H4P]3+ 292.9951, found 292.9938.

Trimethyl[pyridin-2-ylmethyl]phosphonium 4-Methylbenzenesulfonate (5a): Powdered potassium hydroxide (0.88 g, 15.68 mmol) was added to a vigorously stirred solution of 2-pyridinemethanol (1.0 mL, 10.36 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred and heated in a deep-welled backfilled with argon. 1,4-Dioxane was then added for a reaction temperature of 80 °C, then stirred at 80 °C for 2 h. The resulting reaction mixture was stirred at 80 °C for 24 h. The solvent was then removed under reduced pressure; then Et2O was added, and the title phosphonate salt was isolated by filtration as a white solid (2.90 g, 6.91 mmol, 87%): 1H NMR (600 MHz, CD2OD) δ 6.78–6.77 (m, 7H), 6.26 (s, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 3.04–3.10 (m, 2H), 2.49–2.54 (m, 2H), 2.35 (s, 3H), 1.94 (d, J = 14.6 Hz, 9H); 13C{1H} NMR (151 MHz, CD2OD) δ 142.3, 140.2, 137.9 (d, J = 17.4, 1.5 Hz), 132.6, 131.2, 128.4, 127.6 (q, J = 29.5 Hz), 127.2, 125.8 (q, J = 5.7 Hz), 125.5, 124.7 (q, J = 272.9 Hz), 24.8 (d, J = 50.6 Hz), 23.9 (d, J = 2.0 Hz), 19.9, 6.2 (d, J = 54.6 Hz); 31P NMR (243 MHz, CD2OD) δ 27.33; HRMS (ESI+) calcd for [C9H17P1O3]⁺ 249.1014, found 249.1020.

General Procedure for Iridium-Catalyzed Borylation (GP2). The reactions were carried out in 4 mL 15 mm × 45 mm crimp top vials. The substrate (0.25 mmol), ligand 1 (3 mol %), B2Pin1 (1.5 equiv), and [Ir(COD)OMe]2 (1.5 mol %) were weighed and added to the vials, which were then sealed, evacuated, and backfilled with argon. 1,4-Dioxane was then added for a final substrate concentration of 0.2 M. The reaction mixture was stirred and heated in deep-welled heating blocks (IKA DB 5.2) for a specified amount of time, at a specified temperature, followed by removal of the solvent and analysis of the crude reaction mixture by 1H NMR. Purification was generally performed by addition of EtO2 to a concentrated CH3Cl solution of the crude reaction mixture, followed by filtration of the resulting precipitate.

Calculation of the Yield in Borylation Reactions. In some cases, small amounts of the starting material remained in the reactions, which were inseparable from the borylated products. The following procedure was then used to determine the yield of the borylated products. The ratio of borylated products to starting material was determined by NMR analysis, using the NMR of the isolated product. This ratio was used to calculate an average molecular weight in order to determine the mol% of product obtained, such that an overall yield could be obtained. The yield of the borylated products was then obtained by multiplying the overall yield by the fraction of borylated products present.

Assignment of meta and para Products. When possible, the coupling patterns in the aromatic region were used to assign the respective isomers. Otherwise, assignments were done using information from 2D NMR experiments (COSY, HSQC, HMBC, NOESY). Data for the para product was usually obtained from the tmphen control experiments by subtracting the signals for the meta product and starting material from the spectra.

Trimethyl[5-(4,4',5,5'-tetramethyl-1,3-di-oxaborolan-2-yl)-2-(trifluoromethyl)benzy]phosphonium 4-Methylbenzenesulfonate (4a). With Sulfate Ligand 1 (0.1 mmol Scale). Following GP2, the compound was formed using trimethyl[2-(trifluoromethyl)-
benzyl)phosphonium 4-methylbenzenesulfonate (3a) (40.8 mg, 0.1 mmol), \(\text{B}_2\text{Pin}_3\) (38 mg, 0.15 mmol, 1.5 equiv), [Ir(COD)OMe] (1 mg, 0.0015 mmol, 0.015 equiv), 1 (1.5 mg, 0.003 mmol, 0.03 equiv), and 1,4-dioxane (0.5 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of the crude \(^{1}H\) NMR with 1,2-dimethoxyethane as the internal standard showed >20:1 meta/para borylation, in 89% NMR yield.

With Sulfonate Ligand 1 (0.25 mmol Scale). Following GP2, the compound was formed using trimethyl(2-trifluoromethyl)benzyl)-phosphonium 4-methylbenzenesulfonate (3a) (102 mg, 0.25 mmol), \(\text{B}_2\text{Pin}_3\) (95 mg, 0.375 mmol, 1.5 equiv), [Ir(COD)OMe] (2.5 mg, 0.00375 mmol, 0.015 equiv), 1 (1.8 mg, 0.0075 mmol, 0.03 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of the crude \(^{1}H\) NMR with 1,2-dimethoxyethane as the internal standard showed 6:5 meta/para borylation, in 93% NMR yield. The meta product decomposed upon attempted isolation by precipitation with Et\(_2\)O; therefore, the crude NMR data was used in order to characterize the meta product.

**Compound 4a:** \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.82\) (d, \(J = 7.6\) Hz, 1H), 7.72 (d, \(J = 8.0\) Hz, 2H), 7.72 (s, 1H), 7.65 (d, \(J = 7.8\) Hz, 1H), 7.06 (d, \(J = 7.9\) Hz, 2H), 3.90 (d, \(J = 16.4\) Hz, 2H), 2.25 (s, 3H), 2.04 (d, \(J = 14.4\) Hz, 9H), 1.31 (s, 12H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta 143.6, 139.5, 137.8, 137.8 (d, \(J_{C-P} = 4.8\) Hz), 134.8 (d, \(J_{C-P} = 3.3\) Hz), 130.9 (d, \(J_{C-P} = 29.8\) Hz), 128.6, 126.9 (d, \(J_{C-P} = 9.3\) Hz), 126.4 (m), 125.9, 123.8 (d, \(J_{C-P} = 273.8\) Hz), 84.7, 80.0 (d, \(J_{C-P} = 48.6\) Hz), 24.2, 21.8, 8.4 (d, \(J_{C-P} = 54.3\) Hz); \(^{31}P\) NMR (376 MHz, CDCl\(_3\)) \(\delta -58.43\); HRMS m/z (ESI) \([M + OTs]^{+}\) calcld for \([\text{C}_{31}\text{H}_{29}\text{BF}_{2}\text{O}_{3}\text{P}]^{+}\) 561.1710, found 561.1706.

**With tmphen (0.25 mmol Scale).** Following GP2, the compound was formed using trimethyl(2-trifluoromethyl)benzyl)phosphonium 4-methylbenzenesulfonate (3a) (102 mg, 0.25 mmol), \(\text{B}_2\text{Pin}_3\) (95 mg, 0.375 mmol, 1.5 equiv), [Ir(COD)OMe] (2.5 mg, 0.00375 mmol, 0.015 equiv), tmphen (1.8 mg, 0.0075 mmol, 0.03 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of the crude \(^{1}H\) NMR with 1,2-dimethoxyethane as the internal standard showed 1:6.5 meta/para borylation, in 90% NMR yield. It was observed that it was possible to isolate the para product by precipitation with Et\(_2\)O, while the meta product decomposed.

**para Product:** \(^{1}H\) NMR (600 MHz, CDCl\(_3\)) \(\delta 7.78\) (d, \(J = 8.0\) Hz, 2H), 7.62 (d, \(J = 7.5\) Hz, 1H), 7.48–7.47 (m, 1H), 7.12 (d, \(J = 8.0\) Hz, 2H), 4.06 (d, \(J = 16.7\) Hz, 2H), 2.32 (s, 3H), 2.07 (d, \(J = 14.5\) Hz, 9H), 1.34 (s, 12H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta 143.7, 139.4, 136.2 (d, \(J_{C-P} = 3.1\) Hz), 133.9 (d, \(J_{C-P} = 6.3\) Hz), 133.7 (d, \(J_{C-P} = 6.1\) Hz), 132.1 (d, \(J_{C-P} = 4.9\) Hz), 130.0 (d, \(J_{C-P} = 9.3\) Hz), 128.7, 125.8, 84.4, 28.2 (d, \(J_{C-P} = 49.4\) Hz), 24.9, 21.3, 8.3 (d, \(J_{C-P} = 53.8\) Hz); \(^{31}P\) NMR (243 MHz, CDCl\(_3\)) \(\delta 29.54\).

**(2-Bromo-5-(4,4,5,5-tetramethyl-1,3-2-dioxaborolan-2-yl)-benzyl)(trimethylphosphonium 4-Methylbenzenesulfonate (4b). With Sulfonate Ligand 1.** Following GP2, the compound was formed using (2-bromobenzyl)trimethylphosphonium 4-methylbenzenesulfonate (3c) (104 mg, 0.25 mmol), \(\text{B}_2\text{Pin}_3\) (95 mg, 0.375 mmol, 1.5 equiv), [Ir(COD)OMe] (2.5 mg, 0.00375 mmol, 0.015 equiv), 1 (3.8 mg, 0.0075 mmol, 0.03 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of the crude \(^{1}H\) NMR showed >20:1 meta/para borylation. The solvent was removed, and the salts precipitated with Et\(_2\)O. This was followed by filtration through a bed of MgSO\(_4\) and elution of the salts with CH\(_2\)Cl\(_2\). Removal of the solvent under reduced pressure and drying in vacuo afforded the title compounds (15:50:35 meta/para/SM) as a brown solid (108 mg, 0.15 mmol borylated products, 62%, 1:3 meta/para).

**para Product:** \(^{1}H\) NMR (600 MHz, CDCl\(_3\)) \(\delta 7.81\) (s, 1H), 7.75 (d, \(J = 8.0\) Hz, 2H), 7.62 (d, \(J = 7.5\) Hz, 1H), 7.48–7.47 (m, 1H), 7.12 (d, \(J = 8.0\) Hz, 2H), 4.06 (d, \(J = 16.7\) Hz, 2H), 2.32 (s, 3H), 2.07 (d, \(J = 14.5\) Hz, 9H), 1.34 (s, 12H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta 143.7, 139.4, 136.2 (d, \(J_{C-P} = 3.1\) Hz), 133.9 (d, \(J_{C-P} = 6.3\) Hz), 133.7 (d, \(J_{C-P} = 6.1\) Hz), 132.1 (d, \(J_{C-P} = 4.9\) Hz), 130.0 (d, \(J_{C-P} = 9.3\) Hz), 128.7, 125.8, 84.4, 28.2 (d, \(J_{C-P} = 49.4\) Hz), 24.9, 21.3, 8.3 (d, \(J_{C-P} = 53.8\) Hz); \(^{31}P\) NMR (243 MHz, CDCl\(_3\)) \(\delta 29.54\).

**Note:**

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2. J. Org. Chem., 1998, 63, 13130–13134
3. DOI: 10.1021/jo0008787
4. J. Org. Chem. 2019, 84, 13124–13134
Sulfonate Ligand 1 with 3 mol % [Ir(COD)OMe], at 70 °C. Following GP2, the compound was formed using trimethyl(2-methylbenzyl)phosphonium 4-methylbenzenesulfonate (3d) (88 mg, 0.25 mmol), B2Pin2 (127 mg, 0.5 mmol, 2 equiv), [Ir(COD)OMe]2 (5.0 mg, 0.0075 mmol, 0.03 equiv), I (7.6 mg, 0.015 mmol, 0.06 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of crude 1H NMR showed 18:1 meta/para borylation. The solvent was removed, and the salts precipitated with Et2O. This was followed by filtration through a pad of MgSO4 and elution of the salts with CH2Cl2. Removal of the solvent under reduced pressure and drying in vacuo afforded the title compounds (90:5:5 meta/para/SM) as an orange solid (111 mg, 0.22 mmol borylated products, 89%, 18:1 meta/para).

**Compound 4d**: 1H NMR (600 MHz, CDCl3) δ 7.77 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 3.81 (d, J = 16.0 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 2.06 (d, J = 14.3 Hz, 9H), 1.33 (s, 12H), 13C{1H} NMR (101 MHz, CDCl3) δ 143.9, 144.6 (d, JCHP = 5.5 Hz), 139.2, 136.8 (d, JCHP = 5.0 Hz), 134.8 (d, JCHP = 3.7 Hz), 131.1 (d, JCHP = 3.1 Hz), 128.7, 126.6 (d, JCHP = 8.9 Hz), 125.9, 84.0, 27.8 (d, JCHP = 49.1 Hz), 24.9, 21.3, 20.5, 8.1 (d, JCHP = 54.0 Hz); 31P NMR (243 MHz, CDCl3) δ 28.79; HRMS m/z (ESI+) [M – OTs]− calc'd for [C37H33BrF3PO3] 707.1993, found 707.1988.

With tmmphen with 3 mol % [Ir(COD)OMe], at 70 °C. Following GP2, the compound was formed using trimethyl(2-methylbenzyl)phosphonium 4-methylbenzenesulfonate (3d) (88 mg, 0.25 mmol), B2Pin2 (127 mg, 0.5 mmol, 2 equiv), [Ir(COD)OMe]2 (5.0 mg, 0.0075 mmol, 0.03 equiv), tmmphen (3.6 mg, 0.015 mmol, 0.06 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of crude 1H NMR showed 1:1 meta/para/SM. This was followed by filtration through a pad of MgSO4 and elution of the salts with CHCl3. Removal of the solvent under reduced pressure and drying in vacuo afforded the title compounds (20:26:54 meta/para/SM) as a brown solid (84 mg, 0.09 mmol borylated products, 37%, 1:1:1 meta/para).

**para Product**: 1H NMR (600 MHz, CDCl3) δ 7.77 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 6.4 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 7.0 Hz, 1H), 6.93 (d, J = 9.1 Hz, 1H), 4.02 (d, J = 16.9 Hz, 2H), 2.33 (s, 3H), 1.97 (d, J = 14.4 Hz, 9H), 1.35 (s, 12H), 13C{1H} NMR (101 MHz, CDCl3) δ 167.2 (dd, JCHP = 253.0 Hz, JCHP = 4.0 Hz), 143.7, 139.6, 137.7 (dd, JCHP = 8.6 Hz, JCHP = 3.7 Hz), 134.7 (dd, JCHP = 9.2 Hz, JCHP = 9.2 Hz), 128.9, 125.8, 125.6 (dd, JCHP = 4.4 Hz, JCHP = 4.4 Hz), 116.9 (dd, JCHP = 23.6 Hz, JCHP = 5.5 Hz), 84.1, 29.6 (d, JCHP = 49.2 Hz), 24.8, 21.3, 7.5 (d, JCHP = 54.4 Hz); 31P NMR (376 MHz, CDCl3) δ −101.74 (d, JCHP = 2.9 Hz); 31P NMR (243 MHz, CDCl3) δ −27.84.

**1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl[(3-fluoro-4-fluorobenzyl)trimethylphosphonium 4-Methylbenzenesulfonate (4f). With Sulfonate Ligand L1.** Following GP2, the compound was formed using benzyltrimethylphosphonium 4-methylbenzenesulfonate (3f) (85 mg, 0.25 mmol), B2Pin2 (190 mg, 0.75 mmol, 3.0 equiv), [Ir(COD)OMe]2 (2.5 mg, 0.00375 mmol, 0.015 equiv), I (3.8 mg, 0.0075 mmol, 0.03 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. Analysis of crude 1H NMR showed >20:1 dimeta/para borylation. The solvent was removed, and the salts precipitated with Et2O. This was followed by filtration through a pad of MgSO4 and elution of the salts with CHCl3. Removal of the solvent under reduced pressure and drying in vacuo afforded the title compound (contaminated with <10% mono meta product) as a light orange solid (111 mg, 0.17 mmol diborylated product, 69%, >20:1 dimeta + monometa/para).

**Compound 4f**: 1H NMR (600 MHz, CDCl3) δ 8.22 (s, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 1.9 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 3.73 (d, J = 15.7 Hz, 2H), 2.31 (s, 3H), 2.04 (d, J = 14.3 Hz, 9H), 1.33 (s, 12H), 13C{1H} NMR (151 MHz, CDCl3) δ 143.7, 141.2 (d, JCHP = 5.5 Hz), 139.2, 138.6 (d, JCHP = 5.2 Hz), 128.7, 127.2 (d, JCHP = 8.9 Hz), 125.9, 84.1, 30.8 (d, JCHP = 49.2 Hz), 24.9, 21.3, 7.8 (d, JCHP = 54.6 Hz); 31P NMR (243 MHz, CDCl3) δ 26.98; HRMS m/z (ESI+) [M – OTs]− calc'd for [C43H39BrF3PO3] 419.2688, found 419.2685.

With tmmphen. Following GP2, the compound was formed using benzyltrimethylphosphonium 4-methylbenzenesulfonate (3f) (85 mg, 0.25 mmol), B2Pin2 (190 mg, 0.75 mmol, 3.0 equiv), [Ir(COD)OMe]2 (2.5 mg, 0.00375 mmol, 0.015 equiv), tmmphen (1.8 mg, 0.0075 mmol, 0.03 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 16 h at 50 °C. The solvent was removed, and the salts precipitated with Et2O. This was followed by filtration through a pad of MgSO4 and elution of the salts with CHCl3. Removal of the solvent under reduced pressure and drying in vacuo afforded a dark brown solid. NMR analysis revealed that this was a complex mixture of products (presumably a mixture of the starting material and meta, dimeta, and para products).

**Trimethyl[(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)methyl]phosphonium 4-Methylbenzenesulfonate (6a). With Sulfonate Ligand L1.** Following GP2, the compound was formed using trimethyl(pyridin-2-yl)methylphosphonium 4-methylbenzenesulfonate (5a) (85 mg, 0.25 mmol), B2Pin2 (95 mg, 0.375 mmol, 1.5 equiv), [Ir(COD)OMe]2 (2.5 mg, 0.00375 mmol, 0.015 equiv), I (3.8 mg, 0.0075 mmol, 0.03 equiv), and 1,4-dioxane (1.25 mL). The reaction mixture was stirred for 1 h at 50 °C. Analysis of the crude 1H
NMR with 1,2-dimethoxyethane as the internal standard showed 20:1 C4/C5 borylation, in 53% NMR yield (NMR yield used in this case due to possible contamination by the dimeta product). For isolation of the product, the solvent was removed. The resultant brown oil was washed with Et2O (add Et2O, decant off Et2O, repeat 10–15 times to remove most of the residual BPin). Drying in vacuo afforded the title compound as an orange powder initially, which became a brown oil upon standing.

**Compound 6a:** 1H NMR (400 MHz, CDCl3) δ 8.49 (d, J = 4.8, 1.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.65 (s, 1H), 7.56–7.55 (m, 1H), 7.12 (d, J = 7.9 Hz, 2H), 4.01 (d, J = 15.4 Hz, 2H), 2.32 (s, 3H), 2.14 (d, J = 14.6 Hz, 9H), 1.34 (s, 12H). 13C{1H} NMR (101 MHz, CDCl3) δ 150.3 (d, J_{C-P} = 1.7 Hz), 153.5 (d, J_{C-P} = 9.2 Hz), 143.7, 139.2, 129.9 (d, J_{C-P} = 7.6 Hz), 128.7, 127.9 (d, J_{C-P} = 1.7 Hz), 125.9, 84.8, 32.4 (d, J_{C-P} = 54.2 Hz). 31P NMR (162 MHz, CDCl3) δ 27.36, HRMS m/z (ESI+) for [M − OTs]· calculated for [C23H22BF4O3P]· [294.1789, found 294.1779]. Note that the peaks partially overlap with the SM in the 1H NMR spectrum.

**With tmphen.** Following GP2, the compound was formed using trimethyl(pyridin-2-yl)methylphosphonium 4-methylbenzenesulfonate (Sa) (85 mg, 0.25 mmol), BPin (95 mg, 0.375 mmol, 1.5 equiv), [Ir(COD)OMe]2 (2.5 mg, 0.00375 mmol, 0.015 equiv), B2Pin2 (381 mg, 1.5 mmol), and Sulfonate Ligand (0.25 mmol Scale). With Sulfonate Ligand (105.1 mg, 0.25 mmol), the compound was formed using GP2, the compound was formed using 1,2-dimethoxyethane as the internal standard showed 1:1.3 Ca/C5 borylation, in 60% NMR yield. For isolation of the product, the solvent was removed. The resultant brown oil was washed with Et2O. Drying in vacuo afforded the title compounds as an orange powder initially. This powder became a brown oil upon standing.

**CS Product:** 1H NMR (400 MHz, CDCl3) δ 8.77 (s, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 7.7 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 4.06 (d, J = 16.0 Hz, 2H), 2.29 (s, 3H), 2.05 (d, J = 14.6 Hz, 9H), 1.33 (s, 12H). 13C{1H} NMR (101 MHz, CDCl3) δ 155.1 (d, J_{C-P} = 1.7 Hz), 153.5 (d, J_{C-P} = 9.2 Hz), 143.7, 143.6, 139.4, 128.7, 125.8, 124.7 (d, J_{C-P} = 7.1 Hz), 84.8, 32.4 (d, J_{C-P} = 52.8 Hz), 24.9, 21.3, 8.8 (d, J_{C-P} = 54.9 Hz). 31P NMR (162 MHz, CDCl3) δ 25.78.

**Trimethyl[5-(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl)-2-trifluoromethylphenyl]phosphonium 4-Methylbenzenesulfonylate (8a). With Sulfonyl Ligand 1 (0.25 mmol Scale).** Following GP2, the compound was formed using 7a (105.1 mg, 0.25 mmol), BPin (127.4 mg, 0.50 mmol), [Ir(COD)OMe]2 (2.5 mg, 0.00375 mmol), and 1 (3.8 mg, 0.0075 mmol) in dioxane (1.25 mL). The mixture was stirred in a vial at 70 °C for 20 h. Analysis of crude 1H NMR showed a 26:1:2 ratio of meta/para starting material (26:1 meta/para borylation). Purification by evaporation of solvent and addition of ether, followed by filtration and drying in vacuo, gave the title compound as a light brown solid (109.2 mg, 0.200 mmol, 80%), as a mixture of a 42:1:2.3 ratio of meta/para starting material.

**Compound 8a:** 1H NMR (600 MHz, CD2OD, CDOD) δ 7.91 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 2.36–2.51 (m, 2H), 2.34 (s, 3H), 1.95 (d, J_{3J} = 14.6 Hz, 9H), 1.36 (s, 12H). 13C{1H} NMR (151MHz, CD2OD) δ 142.4, 140.1, 137.10, 137.12 (d, J = 17.0 Hz), 133.2, 130.0 (q, J_{2J} = 29.9 Hz), 128.8, 125.5, 123.3 (q, J_{2J} = 5.6 Hz), 124.5 (q, J_{2J} = 273 Hz), 84.3, 24.8 (d, J_{C-P} = 50.8 Hz), 23.8, 23.7, 19.9, 6.2 (d, J_{C-P} = 54.7 Hz). 31P NMR (243 MHz, CD2OD) δ 27.31; HRMS (ESI+) calculated for [M − OTs]· [C23H22BF4O3P]· [C18H28BF3O2P]+ 375.1872, found 375.1879.

**With tmphen Ligand (0.25 mmol Scale).** Following GP2, the compound was formed using 7a (105.1 mg, 0.25 mmol), BPin (127.0 mg, 0.50 mmol), [Ir(COD)OMe]2 (2.5 mg, 0.00375 mmol), and tmphen (2.0 mg, 0.0075 mmol) in dioxane (1.25 mL). The mixture was stirred in a vial at 70 °C for 20 h. Analysis of crude 1H NMR showed a 1:2:1 ratio of meta/para starting material. A small sample was triturated with diethyl ether in order to characterize the para isomer. This contained a 4:1:3 ratio of para/meta starting material.
The authors declare no competing financial interest.

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