Supporting Information

A Zinc Catalyzed C(sp³)—C(sp²) Suzuki–Miyaura Cross-Coupling Reaction Mediated by Aryl-Zincates

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General Remarks

Unless otherwise stated all manipulations were carried out using standard Schlenk techniques under argon or in an MBraun UniLab glovebox, under an atmosphere of argon. THF, 2MeTHF, dioxane and cyclopentyl methyl ether (CPME) were dried over and distilled from potassium and stored over activated 3 Å molecular sieves. Hexane was dried and distilled from either calcium hydride or NaK alloy and stored over a potassium mirror. All other reagents were purchased from commercial chemical suppliers and used as received. NMR spectra were recorded on Bruker AvanceIII-400, Bruker AvanceII-500 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless values and are frequency referenced relative to residual protio-impurities in the NMR solvents for $^1$H and $^{13}$C{$_1^1$H} respectively, while $^{11}$B{$^1$H}, $^{19}$F{$^1$H}, $^7$Li and $^{31}$P shifts are referenced relative to external BF$_3$-etherate, hexafluorobenzene, LiCl, and H$_3$PO$_4$ respectively. Coupling constants J are given in Hertz (Hz) as positive values regardless of their real individual signs. The multiplicity of the signals are indicated as “s”, “d”, or “q” for singlet, doublet, or quartet respectively. GC-MS analysis was performed on either of two instruments. An Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with triple axis detector, fitted with a HP-5Ms column, with dimensions 30 m length; 0.250 mm internal diameter; and 0.25 μm film. Or an Agilent Technologies 6890N GC equipped with an Agilent Technologies 5973N EI MSD, fitted with a HP-5MS column, with dimensions 30 m length; 0.250 mm internal diameter; and 0.25 μm film.

The relative response factors for GCMS analysis of the heterocoupled and homocoupled products derived from the fluorinated electrophile, 2b, were calculated using values from $^{19}$F{$^1$H} NMR spectra (with a delay time of 35s to allow full spin-lattice relaxation) where their integrals could be measured accurately. When these resonances were overlapped in the $^{19}$F{$^1$H} NMR spectra (which occurred in a number of solvents), GCMS analysis was used to calculate their ratio, and yields calculated by using the overall integral of the overlapped peak with this ratio applied (accounting for the 2 equivalents of electrophile involved in the homocoupled product). The relative response factors used in this calculation for GCMS analysis were calculated from the results where $^{19}$F resonances could be accurately integrated. Yields are based on the electrophile as the limiting reagent and for homocoupling impurities the $^{19}$F integrals are scaled by 0.5 to give a molar ratio vs. heterocoupling (i.e. A 1:1 hetero:homocoupled product ratio at full conversion, would be reported as 33 % : 33 %, due to the additional molecule of starting material required in the production of the homocoupled product). In a number of cases the $^{13}$C resonance for the carbon atom directly bonded to boron was not observed due to the effect of quadrupolar relaxation.
Synthesis of borate nucleophiles

General Procedure

The borates were synthesised according to a modified literature procedure. In an oven dried Schlenk flask, the appropriate arylboronic acid pinacol ester (1-1.05 eq.) was dissolved in anhydrous hexane and cooled to -78 °C before dropwise addition of tert-butyllithium (1.7M in pentane, 1 eq.). The reaction was allowed to warm to room temperature and stirred overnight at room temperature, over which period a precipitate formed. The borate was isolated by filtration, washed with anhydrous hexane and residual solvent removed under reduced pressure.

\[ \text{[Li}[(\text{tBu})(\text{Ph})\text{B(Pin)}]\text{]} \] (1a)

Synthesised according to the above general procedure, from phenylboronic acid pinacol ester (3 g, 14.7 mmol), and tBuLi (1.7M/pentane, 8.5 ml, 14.5 mmol). Isolated as a free flowing white powder. Yield: 3.6 g, 13.4 mmol, 92%. NMR spectroscopic data match previously reported values.

\[ \text{[Li}[(\text{tBu})(\text{p-tol})\text{B(Pin)}]\text{]} \] (1b)

Synthesised according to the above general procedure, from p-tolylboronic acid pinacol ester (1.136 g, 5.21 mmol) and tBuLi (1.7M/pentane, 3 ml, 5.1 mmol). Isolated as a free flowing white powder. Yield: 1.35 g, 4.8 mmol, 94%.

$^1$H NMR (d$_8$-THF, 400 MHz): δ 7.25 (d, J=7.53 Hz, 2 H), 6.79 (d, J=7.78 Hz, 2 H), 2.19 (s, 3 H), 1.13 (s, 6 H), 0.84 (s, 6 H), 0.61 ppm (s, 9 H)

$^{11}$B{$^1$H} NMR (d$_8$-THF, 128 MHz): δ 8.15 ppm

$^7$Li{$^1$H} NMR (d$_8$-THF, 155 MHz): δ 0.15 ppm

$^{13}$C{$^1$H} NMR (d$_8$-THF, 101 MHz): δ 133.32, 131.53, 126.88, 78.49, 30.93, 28.62, 28.14, 21.60 ppm
[Li][^Bu](ρ-MeO-C₆H₄-)B(Pin)] (1c)

Synthesised according to the above general procedure, from *para*-methoxyphenylboronic acid pinacol ester (650 µl, 3.22 mmol) and ^BuLi (1.7M/pentane, 1.9 ml, 3.23 mmol). Isolated as a free flowing white powder. Yield: 877 mg, 2.94 mmol, 91%.

1H NMR (d₈-THF, 400 MHz) : δ 7.26 (d, J=8.03 Hz, 2 H), 6.57 (d, J=8.28 Hz, 2 H), 3.66 (s, 3 H), 1.13 (s, 6 H), 0.84 (s, 6 H), 0.62 ppm (s, 9 H)

11B{¹H} NMR (d₈-THF, 128 MHz) : δ 8.11 ppm

7Li{¹H} NMR (d₈-THF, 155 MHz): δ 0.16 ppm

13C{¹H} NMR (d₈-THF, 101 MHz): δ 157.48, 133.88, 111.80, 78.54, 54.94, 30.94, 28.69, 28.18 ppm

[Li][^Bu](ρ-F₃CO-C₆H₄-)B(Pin)] (1d)

Synthesised according to the above general procedure, from 4-(trifluoromethoxy)phenyl boronic acid pinacol ester (490 mg, 1.7 mmol) and ^BuLi (1.7M/pentane, 1 ml, 1.7 mmol). Isolated as a free flowing off-white powder. Yield: 359 mg, 1.02 mmol, 60%.

1H NMR (d₈-THF, 400 MHz) : δ 7.46 (d, J=8.3 Hz, 2 H), 6.81 (d, J=7.5 Hz, 2 H), 1.11 (s, 6 H), 0.78 (s, 6 H), 0.60 ppm (s, 9 H)

11B{¹H} NMR (d₈-THF, 128 MHz) : δ 7.6 ppm

7Li{¹H} NMR (d₈-THF, 155 MHz): δ 0.02 ppm

19F{¹H} NMR (d₈-THF, 376 MHz): δ -58.2 ppm (s)

13C{¹H} NMR (d₈-THF, 101 MHz): δ 146.8, 134.6, 122.1 (q, J=253 Hz), 117.7, 78.6, 30.7, 28.7, 28.3 ppm
1e was isolated with a by-product that is tentatively assigned as [Li][(Me-C₄H₂S)₂B(Pin)] that accounts for approximately 13% of the overall amount, assignment is based on comparison to literature reports.³

³¹H NMR (d₈-THF, 400MHz) : 6.53 (d, J=3Hz 1 H) 6.49 (m, 1 H) 2.36 (s, 4 H) 1.11 (s, 10 H) 0.98 (s, 6 H) 0.66 ppm (s, 9 H)

³¹B{³¹H} NMR (d₈-THF, 128 MHz) : δ 7.5 ppm

Figure S 1: ¹H NMR spectrum (¹H- THF) of the aryl region of 1e. Inset: ¹¹B NMR spectrum
Synthesis of $[\text{Li}]\left(\text{n}^6\text{Bu}(\text{Ph})\text{B(Pin)}\right)$ (5)

$\begin{align*}
\text{Li} & \quad \text{B} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \\
\end{align*}$

Synthesised according to the above general procedure, from phenyl boronic acid pinacol ester (650 mg, 3.2 mmol) and $\text{n}^6\text{BuLi}$ (1.6M/hexane, 2 ml, 3.2 mmol). Isolated as a free flowing off-white powder. Yield: 678 mg, 79%. NMR spectroscopic data is consistent with previously reported values.$^1$

Synthesis of $[\text{Li}]\left(\text{O}^6\text{Bu}(\text{Ph})\text{B(Pin)}\right)$ (6)

$\begin{align*}
\text{Li} & \quad \text{B} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \\
\end{align*}$

An oven dried Schlenk tube was charged with phenyl boronic acid pinacol ester (500 mg, 2.5 mmol) and anhydrous hexane (9 ml) and a solution of lithium tert-butoxide (200 mg, 2.5 mmol) in hexane (10 ml) was added slowly. The homogenous mixture was stirred and of 2.5 ml THF was added, before stirring for a further 4 hrs. During this time, a white precipitate had formed, which was isolated by filtration and washed with anhydrous hexane (2 x 4ml). Residual solvent was removed under reduced pressure, giving a free flowing white powder in 258 mg. The solvent components were combined and stirred overnight leading to more precipitation which was isolated above to give a second crop of 133mgs. Combined yield of both crops = 56%.

$^1\text{H}$ NMR (protio-THF, 400 MHz) : $\delta$ 7.48 (d, $J=7.03$ Hz, 2 H) 6.93 (t, $J=7.28$ Hz, 2 H) 6.83 (t, $J=7.03$Hz, 1 H) 1.10 (s, 6 H) 0.97 (s, 9 H) 0.88 ppm (s, 6 H)

$^{11}\text{B}\{^1\text{H}\}$ NMR ($d_8$-THF, 128 MHz) : $\delta$ 6.7 ppm
Alkoxide activated borate – transmetallation with ZnBr₂

In an oven dried J Young’s NMR tube, [Li][[(O^tBu)(Ph)B(Pin)]] (20 mg, 0.07 mmol), and ZnBr₂ (8 mg, 0.035 mmol) were dissolved in anhydrous THF, with a DMSO-d₆ capillary. After 2 hours the mixture was analysed by \(^{11}\text{B}\) NMR spectroscopy, revealing loss of the starting material resonance at (6.7 ppm) and formation of the neutral PhBPin (30.6 ppm), indicating preferential transfer of the \(^{t}\text{BuO}^−\) group to the zinc bromide.

Figure S 2: \(^{11}\text{B}\) NMR spectrum of 6 before (bottom) and after (top) addition of ZnBr₂
Furthermore, attempts to use alkoxide borate 6 (1.5 eq.) /ZnBr₂ (10 mol%) to couple with 2b led to no heterocoupling (18 h at 60°C in 2-MeTHF).

Figure S 3: $^{19}$F NMR spectrum of the attempted coupling between 6 and 2b using ZnBr₂ catalysis (fluorobenzene added as a NMR standard)
Borate-to-ZnBr₂ Transmetallation in CPME and Cross-Coupling in benzene

A J. Youngs ampoule equipped was loaded with [PhBPin(Bu)][Li] (268.1 mg, 1.0 mmol) and anhydrous ZnCl₂ (68.2 mg, 0.5 mmol) prior to the addition of anhydrous CPME (2.0 mL). The reaction mixture was stirred at ambient temperature for 30 minutes prior to the removal of all volatiles to afford an oily residue. The residue was taken up in anhydrous benzene (2.0 mL) prior to the addition of 3-methoxybenzyl bromide (70 μL, 0.5 mmol) and the reaction mixture stirred for 1 h at ambient temperature which led to the deposition of a colourless solid. Filtration of the reaction mixture and analysis by ¹H NMR spectroscopy demonstrated the conversion to the desired diarylmethane Csp²-Csp³ cross-coupled product (Figure S4).

Figure S4: Crude ¹H NMR spectrum (C₆H₆/C₆D₆, 400 MHz, 298K) of the reaction mixture after 1 h at ambient temperature post the addition of 3-methoxybenzylbromide showing complete consumption of benzyl bromide and formation of the heterocoupling product 3a.
Preliminary catalysis investigations

In an oven dried J Young’s ampoule [Li][(Bu)(Ph)B(Pin)] 1a (94 mg, 0.35 mmol) and ZnPh₂ (5 mg, 0.02 mmol) and 3-methoxybenzyl bromide (32 µl, 0.23 mmol) were combined and dissolved in the appropriate solvent (2 ml). The reaction was heated to the desired temperature for 17 hours prior to addition of mesitylene (32 µl, 0.23 mmol) as an internal standard and transfer to an NMR tube under ambient conditions. Subsequently the mixture was diluted with DCM, filtered through a silica plug and analysed by GCMS.

Table S 1: Results from GCMS analysis

| Solvent, Temperature | Catalyst | 2a | 3a | 4a | Biphenyl |
|----------------------|----------|----|----|----|----------|
| CPME, 100°C          | ZnPh₂    | 0  | 1  | 0.61| 0.53     |
| CPME, 60°C           | ZnPh₂    | 0.92| 1  | 0.65| 0.57     |
| CPME, 100°C          | ZnCl₂    | 0  | 1  | 0.57| 0.47     |
| Dioxane, 60°C        | ZnPh₂    | 0.12| 1  | 0.03| 0.02     |

(GCMS integration as ratios vs 3a. Not calibrated for response factors)
Solvent optimisation reactions

General Procedure

In an oven dried J Young’s ampoule [Li][({Bu}(Ph)B(Pin))] 1a (94 mg, 0.35 mmol) and ZnBr₂ (5 mg, 0.02 mmol) were dissolved in the appropriate solvent (2 ml). Then 4-fluorobenzyl bromide (29 µl, 0.23 mmol) was added. The reaction was heated to the appropriate temperature for 18 hours before quenching with ethanol followed by addition of fluorobenzene (22 µl, 0.23 mmol) and mesitylene (32 µl, 0.23 mmol) as internal standards. The mixture was directly analysed by ¹⁹F NMR spectroscopy before dilution with DCM, filtration through a silica plug and analysis by GCMS.

Figure S 5: Representative ¹⁹F{¹H} NMR spectrum (from reaction using a 10:1 benzene / THF mixture)

Figure S 6: Representative GCMS trace (from reaction using a 10:1 benzene / THF mixture)
Trace metal control reactions

General Procedure

In an oven dried J Young’s ampoule [Li][(tBu)(Ph)B(Pin)] 1a (94 mg, 0.35 mmol) and the appropriate metal salt were dissolved in 2-MeTHF (2ml). 4-fluorobenzyl bromide (29 µl, 0.23 mmol) was added and the mixture heated to 60°C for 18 hours before quenching with ethanol or dilute HCl followed by addition of fluorobenzene (22 µl, 0.23 mmol) and mesitylene (32 µl, 0.23 mmol) as standards for analysis. When possible the mixture was directly analysed by $^{19}\text{F}$$^1\text{H}$ NMR spectroscopy before dilution with DCM, filtration through a silica plug and analysis by GCMS.

Without added catalyst:

![GCMS chromatogram](image)

**Figure S 7: GCMS chromatogram of the reaction without added catalyst (table 1 entry 6)**

The fraction at 9.65 min retention times has a m/z of 202.1 thus is not heterocoupling or biphenyl. Currently it is an unidentified by-product from the reaction.
Competition reaction Benzyl vs. Aryl bromide with palladium or zinc

In an oven dried J Young’s ampoule [Li][(Bu)(Ph)B(Pin)] 1a (135 mg, 0.5 mmol 2.1 eq.) and either Pd(PPh₃)₄ (8 mg, 3 mol%) or ZnBr₂ (5 mg, 10 mol%) and 4-bromobenzyl bromide (60 mg, 0.024 mmol) were added and then dissolved in 2-MeTHF (2 ml). The mixture was then heated to 60 °C for 24 hours, before quenching with dilute HCl (for Pd) or ethanol (for Zn), extraction into or dilution with DCM, filtration through a plug of silica and analysis by GCMS.

Scheme S 1: Aryl-bromide vs benzyl bromide competition control reactions

Table S 2: Competition reactions - area in GC chromatogram relative to mono-arylated product

| Catalyst   | 2c | 3c | 7c  |
|------------|----|----|-----|
| ZnBr₂      | 0  | 1  | 0.003|
| Pd(PPh₃)₄ | 0  | 1  | 1.41 |
Kumada coupling with ZnBr$_2$ and with FeBr$_2$

ZnBr$_2$ (5mg, 10 mol%) was added to an ampoule and dissolved in 1.5 ml 2-MeTHF. 4-fluorobenzylbromide was then added (29µl, 0.233 mmol, 1 equiv). PhMgBr (480µl, 0.725 M solution in 2-MeTHF, 0.35 mmol 1.5 eq.) was added slowly and the reaction was heated at 60°C for 18 h. The mixture was quenched by addition of 0.2 ml EtOH followed by addition of fluorobenzene (22 µl, 0.23 mmol) and mesitylene (32 µl, 0.23 mmol) as internal standards. The mixture was directly analysed by $^{19}$F{$^1$H} NMR spectroscopy before dilution with DCM, filtration through a silica plug and analysis by GCMS.

An identical procedure was used replacing ZnBr$_2$ with FeBr$_2$.

![Chemical reaction diagram](image.png)

Table S 3: Kumada coupling results$^a$

| Catalyst     | 3b  | 4b  | Biphenyl | Ratio 3b:4b$^b$ |
|--------------|-----|-----|----------|-----------------|
| ZnBr$_2$ (10%) | 0.09 | 0.75 | 1.03     | 0.13            |
| FeBr$_2$ (10%) | 0.70 | 0.66 | 0.98     | 1.19            |

$^a$GCMS integration vs. an internal mesitylene standard. $^b$Ratio with adjustment for relative response factors calculated from previous results using $^{19}$F NMR spectroscopy.

Attempted synthesis of cycloheptyl benzene

In an oven dried ampoule 1a (141 mg 0.525 mmol, 1.5eq) was dissolved in 2.25ml 2MeTHF. To this was added 750 µl of a 0.047M stock solution of ZnBr$_2$ in 2MeTHF (0.035mmol, 0.1 eq.), immediately followed by cycloheptyl bromide (48 µl, 0.35 mmol, 1 eq.). The reaction was heated at 60 °C for 24 hours before quenching with EtOH (~2ml), followed by extraction into DCM (3 x ~10 ml) and removal of solvent under reduced pressure. An aliquot was then taken for analysis by GC-MS. The desired product was produced in only trace quantities, with the major product being cycloheptene. This is in contrast to work by Bedford et al using iron catalysts which efficiently couple cycloheptyl bromide with 1a$^4$.

![GCMS Chromatogram](image.png)

Figure S 8: GCMS Chromatogram of the attempted coupling of cycloheptyl bromide with 1a
An analogous reaction was run using octylbromide in place of cycloheptylbromide under otherwise identical conditions. Analysis by GC-Ms again showed minimal coupling with the major species being the starting electrophile along with triphenylboroxine.

Figure S 9: GCMS Chromatogram of the attempted coupling of octyl bromide with 1a
Nucleophile optimisation reactions

General Procedure

In an oven dried J Young’s ampoule [Li][({\textsuperscript{a} or \textsuperscript{t}Bu})(Ph)B(Pin)] (94 mg, 0.35 mmol) and zinc bromide (5 mg, 0.02 mmol) were dissolved in 2-MeTHF (2 ml). 4-fluorobenzyl bromide (29 \mu l, 0.23 mmol) was added and the mixture heated to 60°C for 18 hours before quenching with ethanol followed by addition of fluorobenzene (22 \mu l, 0.23 mmol) and mesitylene (32 \mu l, 0.23 mmol) as internal standards. The mixture was directly analysed by \textsuperscript{19}F{\textsuperscript{1}H} NMR spectroscopy before dilution with DCM, filtration through a silica plug and analysis by GCMS.

Procedure for reaction using NaBPh\textsubscript{4}

In an oven dried ampoule NaBPh\textsubscript{4} (180 mg, 0.525 mmol, 1.5 eq) was dissolved/suspended in 2.25 ml 2MeTHF. To this 750 \mu l of a 0.047M stock solution of ZnBr\textsubscript{2} in 2MeTHF (0.035 mmol, 0.1 eq) was added, immediately followed by 4-fluorobenzyl bromide (44 \mu l, 0.35 mmol). The reaction was heated at 60 °C for 24 hours before quenching with ethanol (~0.2 ml), followed by extraction into DCM (3 x ~10 ml) and removal of solvent under reduced pressure. The solid was dissolved in CDCl\textsubscript{3} followed by addition of fluorobenzene (22 \mu l, 0.23 mmol) and mesitylene (32 \mu l, 0.23 mmol) as internal standards. The mixture was directly analysed by \textsuperscript{19}F{\textsuperscript{1}H} NMR spectroscopy and analysis by GCMS.

| Nucleophile        | Equivalents vs. 2b | \textbf{3b} / % yield | \textbf{4b} / % yield |
|--------------------|--------------------|-----------------------|-----------------------|
| 1a                 | 1.5                | 90                    | 1                     |
| 1a\textsuperscript{a} | 1.5                | 71                    | 1                     |
| 1a                 | 1.1                | 59                    | 4                     |
| 5\textsuperscript{b} | 1.5                | 47                    | trace                 |
| NaBPh\textsubscript{4}\textsuperscript{b} | 1.5                | 59                    | 10                    |

\textsuperscript{a}Borate generated \textit{in situ} (at -78°C for 20 minutes then warmed to RT and held for 1 h). \textsuperscript{b}24 hours, 80 °C. \textsuperscript{c}This is an overestimate as the resonance in the NMR spectrum is overlapped with impurities.
Attempted coupling using ArylBPin and ZnEt₂

A J. Youngs NMR tube was loaded with 4-Br-C₆H₄-BPin (84.9 mg, 0.3 mmol) and dissolved in a 0.5 ml mixture of C₆D₆/C₆H₆ and then ZnEt₂ was added (0.3 mL of a 1 M hexanes solution) to furnish a colourless homogenous reaction mixture. After rotating for 30 minutes multinuclear NMR spectroscopy revealed that minimal transmetallation had occurred (30 minutes was chosen to be comparable with the transmetallation with borate 1a on page S9). At this stage one equivalent of the electrophile, 3-methoxybenzylbromide) was added (0.3 mmol, 42 µL) which resulted in no observable change (visibly or by ¹¹B NMR spectroscopy) even after 1 h at 20°C. Subsequent heating overnight led to minimal Csp²-Csp³ coupling (as indicated by the resonance at 30.3 ppm in the ¹¹B NMR spectrum dominating which is consistent with the starting arylBPin reagent). Benzene was chosen as reaction solvent in this case to maximise the transmetallation and subsequent coupling (coordinating solvents would hinder both steps by binding to the zinc Lewis acids).

Fig S10: ¹H NMR spectrum of attempted cross coupling using ArylBpin/ZnEt₂

Fig S11: ¹¹B{¹H} NMR spectrum of attempted cross coupling using ArylBpin/ZnEt₂.
**Substrate scope screening reactions and experimental data**

**General Procedure**

In an oven dried ampoule the appropriate borate salt (0.525 mmol, 1.5 eq) was dissolved in 2.25 ml 2MeTHF. To this was added 750 µl of a 0.047M stock solution of ZnBr\(_2\) in 2MeTHF (0.035 mmol, 0.1 eq), immediately followed by the alkyl halide (0.35 mmol, 1 eq.). The reaction was heated at 60 °C for 24 hours before quenching with 1M aqueous HCl (~2ml), followed by extraction into DCM (3 x ~10 ml) and removal of solvent under reduced pressure. Triphenylmethane (85.5 mg, 0.35 mmol, 1 eq.) or mesitylene was added as an internal standard for NMR yield calculations and the mixture was dissolved in CDCl\(_3\) and analysed by NMR spectroscopy. An aliquot was then taken for analysis by GC-MS.

**1-benzyl 3-methoxybenzene (3a)**

![Structure of 1-benzyl 3-methoxybenzene (3a)](image)

Synthesised according to the above general procedure from 3-methoxybenzyl bromide (49 µl) and [Li][(tBu)(Ph)B(Pin)] (141 mg). \(^1\)H NMR spectroscopic data is consistent with previously reported values\(^5\). Yield 87% using triphenylmethane as an internal standard.

![NMR spectrum of the crude from the reaction to produce 3a](image)

**Figure S 102: \(^1\)H NMR spectrum of the crude from the reaction to produce 3a**
Figure S 113: GCMS chromatogram of crude reaction mixture from production of 3a
1-benzyl 4-fluorobenzene (3b)

Synthesised according to the above general procedure from 4-fluorobenzyl bromide (44 µl) and [Li][(tBu)(Ph)B(Pin)] (141 mg). $^1$H NMR spectroscopic data is consistent with previously reported values. Yield 85% using triphenylmethane as an internal standard.

Figure S 124: $^1$H NMR spectrum of the crude from the reaction to produce 3b
1-benzyl 4-bromobenzene (3c)

![Chemical Structure](image)

Synthesised according to the above general procedure from 4-bromobenzyl bromide (87.5 mg) and [Li][(tBu)(Ph)B(Pin)] (141 mg). $^1$H NMR spectroscopic data is consistent with previously reported values. Yield 75% using triphenylmethane as an internal standard.

*Figure S 135: $^1$H NMR spectrum of the crude from the reaction to produce 3c*

*Figure S 146: GCMS chromatogram of the crude from the reaction to produce 3c*
Diphenylmethane (3d)

Synthesised according to the above general procedure from benzyl bromide (42 µl) and [Li][[(tBu)(Ph)B(Pin)]] (141 mg). 1H NMR spectroscopic data is consistent with previously reported values7. Yield 82% using triphenylmethane as an internal standard. Alternatively synthesised according to the above general procedure from benzyl chloride and [Li][[(tBu)(Ph)B(Pin)]]. Yield 30 %

Figure S 157: 1H NMR spectrum of the crude from the reaction to produce 3d

Figure S 168: GCMS chromatogram of the crude from the reaction to produce 3d
1-benzyl 4-(trifluoromethyl)benzene (3e)

Synthesised according to the above general procedure from 4-(trifluoromethyl)benzyl bromide (54 µl) and [Li][tBu](Ph)B(Pin)] (141 mg). $^1$H NMR spectroscopic data is consistent with previously reported values$^6$. Yield 69% using triphenylmethane as an internal standard.

Figure S 179: $^1$H NMR spectrum of the crude from the reaction to produce 3e

Figure S 2018: GCMS chromatogram of the crude from the reaction to produce 3e
1-benzyl 4-methylbenzene (3f)

Synthesised according to the above general procedure from 4-methylbenzyl bromide and [Li][((tBu)(Ph)B(Pin)]). $^1$H NMR spectroscopic data is consistent with previously reported values. Yield 85% using triphenylmethane as an internal standard.

Figure S 19: $^1$H NMR spectrum of the crude from the reaction to produce 3f

Figure S 20: GCMS chromatogram of the crude from the reaction to produce 3f
Methyl 4-benzylbenzoate (3g)

Synthesised according to the above general procedure from methyl 4-(bromomethyl)benzoate (80 mg) and [Li][((^3^)Bu)(Ph)B(Pin))] (141 mg), with heating to 60°C for 72 hours. After this time the solvent was removed in vacuo without HCl quench. $^1$H NMR spectroscopic data is consistent with previously reported values. Yield: 58% using triphenylmethane as an internal standard.

Figure S 213: $^1$H NMR spectrum of the crude from the reaction to produce 3g

Figure S 224: GCMS chromatogram of the crude from the reaction to produce 3g
1-benzyl-4-methylsulfanyl-benzene (3h)

Synthesised according to the above general procedure from 4-(bromomethyl)phenyl methyl sulphide (76 mg) and [Li][{(Bu)(Ph)B(Pin)}] (141 mg). $^1$H NMR spectroscopic data is consistent with previously reported values$^6$. Yield: 64% using triphenylmethane as an internal standard.

Figure S 23: $^1$H NMR spectrum of the crude from the reaction to produce 3h

Figure S 24: GCMS chromatogram of the crude from the reaction to produce 3h
5-(phenyl)-1,3-benzodioxole (3i)

Synthesised according to the above general procedure from 5-(bromomethyl)-1,3-benzodioxole (75 mg) and [Li][(tBu)(Ph)B(Pin)] (141 mg). $^{1}$H NMR spectroscopic data is consistent with previously reported values. Yield: 86% using triphenylmethane as an internal standard.

Figure S 25: $^{1}$H NMR spectrum of the crude from the reaction to produce 3i

Figure S 26: GCMS chromatogram of the crude from the reaction to produce 3i
1-fluoro 4-(4-methoxybenzyl)benzene (3j)

Synthesised according to the above general procedure from 4-fluorobenzyl bromide (44 µl) and [Li][('Bu)(MeO-C₆H₄)B(Pin)] (157 mg). ¹H NMR spectroscopic data is consistent with previously reported values⁸. Yield 87% using triphenylmethane as an internal standard.

Figure S 279: ¹H NMR spectrum of the crude from the reaction to produce 3j

Figure S 3028: GCMS chromatogram of the crude from the reaction to produce 3j
1-methyl-4-(4-(trifluoromethyl)benzyl)benzene (3k)

Synthesised according to the above general procedure from 4-(trifluoromethyl)benzyl bromide (54 µl) and [Li][(t-Bu)(p-tol)B(Pin)] (148 mg). $^1$H NMR spectroscopic data is consistent with previously reported values. Yield 75% using triphenylmethane as an internal standard.

Figure S31: $^1$H NMR spectrum of the crude from the reaction to produce 3k

Figure S 32: GCMS chromatogram of the crude from the reaction to produce 3k
2-(4-fluorobenzyl)-5-methylthiophene (3l)

Synthesised according to the above general procedure from 4-fluorobenzyl bromide and crude [Li][L(‘Bu)(Me-C₄H₂S)B(Pin)] (1e). Purification of the crude mixture by silica gel column chromatography was attempted (using PET ether as eluent), although NMR analysis showed the product was present (25 mg 75 % yield) in 87% purity (therefore yield of the desired C2 functionalised = 65%), due to the presence of 13 % of the 3-isomer from Friedel Crafts functionalisation of the beta thiophene position, related chemistry has been observed previously using anisole-zinc Lewis acid reagents¹⁰.

Figure S 33: Top left, ¹H NMR spectrum of the columned products from the reaction to produce 3l. Top right, ¹⁹F NMR spectrum. Bottom, GCMS chromatogram of the reaction products from 3l.
The major isomer is assigned as the 2-(4-fluorobenzyl)-5-methyl isomer, while the minor isomer is assigned as the 3-(4-fluorobenzyl)-5-methyl isomer, based on two observations. Firstly, $^1$H NMR data for the analogous 2-phenyl-5-methyl isomer has been previously published$^{11}$, and this shows strong similarity to the major isomer of 3l, particularly the CH$_2$ benzyl resonances (4.07 vs 4.05 ppm). Additionally, HMBC shows that for the minor isomer, where each thienyl resonance is distinct, there is coupling between the benzyl protons and both thienyl carbon (containing a C-H) resonance, which would be much more likely to occur in the 3-(4-fluorobenzyl)-5-methyl isomer, as both of these positions are only separated by 3 bonds, whereas for the 2-(4-fluorobenzyl) isomer, one is separated by 4 bonds. However, since the thienyl resonances of the major isomer are coincident, completely unambiguous assignment is not possible. Finally, in the work reported herein using anisole derivatives very little Freidel Crafts substitution products are observed in contrast to previous work,$^{10}$ indicating the organometallic coupling is the preferred process in this work.

**Figure S 29: $^{13}$C($^1$H) (C$_6$D$_6$) NMR spectrum of the products from 3l**
Figure S 30: Aryl region of the HMBC spectrum of the products 3l. Minor product benzyl $^1$H resonance at 3.5 ppm, major product benzyl $^1$H resonance at 3.7
1-fluoro-4-(4-methylbenzyl)benzene (3m)

Synthesised according to the above general procedure from 4-fluorobenzyl bromide (44 μl) and [Li][(tBu)(p-tol)B(Pin)] (148 mg). $^1$H NMR spectroscopic data is consistent with previously reported values$^5$. Yield 90% using triphenylmethane as an internal standard.

Figure S 31: $^1$H NMR spectrum of the crude from the reaction to produce 3m

Figure S 32: GCMS chromatogram of the crude from the reaction to produce 3m
1,1-diphenylethane (3n)

Synthesised according to the above general procedure from (1-bromoethyl)benzene (48 µl) and [Li]([t-Bu](Ph)B(Pn)) (141 mg), with heating to 60°C for 72 hours. ¹H NMR spectroscopic data is consistent with previously reported values¹². Yield 59% using triphenylmethane as an internal standard.

Figure S 33: ¹H NMR spectrum of the crude from the reaction to produce 3n

Figure S 349: GCMS chromatogram of the crude from reaction to produce 3n
((4-methoxyphenyl)methylene)dibenzene (3o)

Synthesised according to the general procedure from diphenylbromomethane (87 mg) and [Li][B(t-Bu)(p-MeO-C₆H₄)B(Pin)] (157 mg), using mesitylene as an internal standard. $^1$H NMR spectroscopic data is consistent with previously reported values$^{13}$. Yield: 60%. A minor isomer is observed by GCMS, but the $^1$H NMR spectrum of other OMe- isomers are significantly different,$^{14}$ thus assignment of the major isomer as the para- product from organometallic cross coupling is unambiguous and consistent with previous work.$^{10}$

Figure S 40: $^1$H NMR spectrum of the crude from the reaction to produce 3o

Figure S 41 : GCMS chromatogram of the crude from the reaction to produce 3o. * minor isomer

Ratio of major to minor isomer (from GC-MS)) = 30:1
2-Methyl-3-phenyl-1-propene (3p)

Synthesised according to the above general procedure from 3-bromo-2-methylpropene (35 µl) and [Li][(tBu)(Ph)B(Pin)] (141 mg). $^1$H NMR spectroscopic data is consistent with previously reported values[ENREF_14]. Yield: 60% using triphenylmethane as an internal standard.

Figure S 42: $^1$H NMR spectrum of the crude from the reaction to produce 3p

Figure 43: GCMS chromatogram of the crude from the reaction to produce 3p
1-fluoro-4-(4-(trifluoromethoxy)benzyl)benzene (3q)

Synthesised according to the above general procedure from 4-fluorobenzyl bromide (22 μl) and [Li][('Bu)(F₃CO-C₆H₄-)B(Pin)] (90 mg) and 325 μl of a 0.047 M solution of ZnBr₂ (10 mol%). The reaction was quenched with ethanol and the conversion was measured by \(^{19}\)F NMR spectroscopy. Conversion: 30% after 24 hours.

Figure S44: \(^{19}\)F NMR spectrum of 3q
Radical inhibition studies

9,10 Dihydroanthracene

In an oven dried ampoule 9,10 dihydroanthracene (42 mg, 0.23 mmol, 1 eq.) and [Li][((tBu)(Ph))B(Pin)] (94 mg, 0.35 mmol, 1.5 eq) were dissolved in 1.5ml 2MeTHF. To this was added 500 µl of a 0.047M stock solution of ZnBr₂ in 2MeTHF (0.023 mmol, 0.1 eq), immediately followed by 4-fluorobenzyl bromide (29 µl, 0.23 mmol, 1 eq.). The reaction was heated at 60 °C for 18 hours before quenching with ethanol followed by addition of fluorobenzene (22 µl, 0.23 mmol) and mesitylene (32 µl, 0.23 mmol) as standards for analysis. The mixture was directly analysed by ¹⁹F NMR spectroscopy before dilution with DCM, filtration through a silica plug and analysis by GCMS.

Styrene

In an oven dried ampoule [Li][((tBu)(Ph))B(Pin)] (94 mg, 0.35 mmol, 1.5 eq) was dissolved in 1.5ml 2MeTHF. To this was added 500 µl of a 0.047M stock solution of ZnBr₂ in 2MeTHF (0.023 mmol, 0.1 eq), immediately followed by styrene (27 µl, 0.23 mmol, 1 eq.), and 4-fluorobenzyl bromide (29 µl, 0.23 mmol, 1 eq.). The reaction was heated at 60 °C for 18 hours and 30 minutes before quenching with ethanol followed by addition of fluorobenzene (22 µl, 0.23 mmol) and mesitylene (32 µl, 0.23 mmol) as standards for analysis. The mixture was directly analysed by ¹⁹F NMR spectroscopy before dilution with DCM, filtration through a silica plug and analysis by GCMS.

Table S 5: Radical inhibition studies

| Radical Trap | 3a / % yield | 4a / % yield |
|--------------|--------------|--------------|
| None         | 90           | 1            |
| DHA          | 92           | <1           |
| styrene      | 91           | <1           |
Zincate reactivity studies

Reaction of ZnBr₂ with [Li][tBuPhBPin] (1a)

An oven dried J Young’s NMR tube equipped with a DMSO-$d_6$ capillary insert was loaded with [Li][tBuPhBPin] (19 mg, 0.07 mmol) 2-MeTHF (0.7ml). The sample was analysed by $^1$H NMR spectroscopy prior to addition of zinc bromide (8 mg, 0.035 mmol) and sonication for 30s. The sample was analysed by $^{11}$B NMR spectroscopy showing complete consumption of the borate starting material and formation of tBuBPin.

Figure S45: $^{11}$B NMR spectrum of the reaction between ZnBr₂ and 1a
**Reaction of ZnPh$_2$ with [Li][tBuPhBPin] (1a)**

An oven dried J Young’s NMR tube equipped with a DMSO-$d_6$ capillary insert was loaded with [Li][tBuPhBPin] (86 mg, 0.32 mmol, 2 eq.), mesitylene (22.25 µl, 0.16 mmol as internal standard) and protio-2MeTHF (0.7ml). The sample was analysed by $^1$H NMR spectroscopy and diphenyl zinc (35 mg, 0.16 mmol, 2 eq.) was added and the sample heated to 60 °C for 90 minutes. The sample was analysed by $^1$H and $^{11}$B NMR spectroscopy showing transfer of 1 phenyl equivalent. The sample was then heated at 60 °C for a further 16 hours. Analysis by NMR spectroscopy showed that 1 equivalent of the neutral tBuBPin had been formed by integration vs. the mesitylene standard, suggesting formation of LiZnPh$_3$ but not Li$_2$ZnPh$_4$.

**Figure S46: $^{11}$B NMR spectrum of the reaction of ZnPh$_2$ with 2 eq. 1a**
Figure S47: $^1$H NMR spectrum of the reaction mixture after 18 hours heating to 60°C. N.B. neutral $^1$ButylBPin resonance indicated is tert-butyl 9H resonance

Interaction of ZnPh$_2$ with LiBr

An oven dried J Young’s NMR tube equipped with a DMSO-$d_6$ capillary insert was loaded with ZnPh$_2$ (55mg, 0.25 mmol), and 2-MeTHF (700 µl). The $^1$H NMR spectrum was measured. PhLi (22mg, 0.25 mmol) was added and the mix was sonicated for 40s. The mixture was analysed by $^1$H and $^7$Li NMR spectroscopy. A further equivalent of LiBr (22mg, 0.25 mmol total 0.5 mmol) was added, a further small shift in the $^1$H NMR aryl resonances was observed. At this point a small amount of white solid could be observed.
Figure S48: Aryl region of the $^1$H NMR spectrum in 2MeTHF of ZnPh$_2$ and increasing equivalents of lithium bromide
Reaction of ZnPh₂ with 1a in the presence of LiBr

An oven dried J Young’s NMR tube equipped with a DMSO-d₆ capillary insert was loaded with ZnPh₂ (27 mgs, 1eq.), LiBr (1 or 2 eq. 11mgs or 22mgs) and 2MeTHF was added (0.7 ml). [Li][tBuPhBPin] (33 mgs, 1eq.) was added and the solution was heated to 60 °C for 30 minutes prior to analysis by ¹H and ¹¹B{¹H} NMR spectroscopy, after standing at room temperature for 30 minutes, the solution was heated to 60°C and analysed by ¹H and ¹¹B{¹H} NMR spectroscopy after a further 30 minutes and after 18 hours at 60°C.

Table S6: Conversion based on ¹H NMR spectroscopy

| Equivalents LiBr | Time at 60 °C | Conversion of 1a to tBuBPin |
|-----------------|---------------|-----------------------------|
| 1               | 1 hour        | 43%                         |
|                 | 18 hours      | 87%                         |
| 2               | 1 hour        | 37%                         |
|                 | 18 hours      | 87%                         |

Figure S49: ¹H NMR spectra of the reactions of 1a with ZnPh₂ in the presence of (left) 1 eq. LiBr and (right) 2 eq. LiBr. Bottom, after 1 hour at 60°C; top, after 18 hours at 60°C. Stars: tBuBPin; triangles, 1a
Figure S50: $^{11}$B NMR spectrum of the reaction of 1a with ZnPh$_2$ in the presence of 2 eq. LiBr after heating to 60°C for 18 hours. Star: $^t$BuBPin; Triangle: 1a.

**Synthesis of Phenyllithium**

Solvent free phenyllithium was synthesised according to a modified literature procedure$^{16}$. Bromobenzene (1.4ml, 13.2 mmol) was dissolved in hexane and cooled to -80 °C, followed by dropwise addition of $n$-butyllithium (1.6M/hexanes, 8.2ml, 13.1 mmol) and allowed to warm slowly to room temperature. After stirring for 48 hours, a white precipitate had formed and was isolated by filtration and washed with hexane. $^1$H NMR data matched reported literature values.$^{17}$
Synthesis and Reaction of Li₂ZnPh₄ with 4-fluorobenzyl bromide

An oven dried J Young’s NMR tube equipped with a DMSO-\(d_6\) capillary insert was loaded with PhLi (26 mg, 0.32 mmol), ZnPh₂ (36 mg, 0.16 mmol), and 2-MeTHF (700 µl). The mixture was analysed by \(^1\)H, \(^7\)Li and \(^{13}\)C\{\(^1\)H\}\} NMR spectroscopy which showed one set of resonances consistent with formation of Li₂ZnPh₄ (based on the ipso \(^{13}\)C resonance and comparison to the work of Hevia et al.)\(^{17}\). To this mixture 4-fluorobenzyl bromide was added (20 µl, 0.16 mmol). After 20 minutes at room temperature analysis by \(^{19}\)F NMR spectroscopy revealed complete consumption of the starting material. Analysis by GCMS revealed the presence of only 1,2-bis(4-fluorophenyl)ethane.

Figure S51: Aryl region of the \(^{13}\)C\{\(^1\)H\}\} NMR spectrum of the reaction of ZnPh₂ with 2 equivalents of LiPh in 2-MeTHF before addition of the electrophile.
Figure S52: Aryl region of the $^1$H NMR spectrum in 2MeTHF of ZnPh$_2$ following the addition of 0 (bottom), 1 (middle), and 2 (top) equivalents of LiPh.

Figure S53: GCMS chromatogram of the reaction of Li$_2$ZnPh$_4$ with 4-fluorobenzyl bromide.
Interaction of LiZnPh$_3$ with LiBr

An oven dried J Young’s NMR tube equipped with a DMSO-$d_6$ capillary insert was loaded with ZnPh$_2$ (55mg, 0.25 mmol), Phenyllithium (21mg, 0.25 mmol) and 2-MeTHF (700 µl). Analysis by $^1$H NMR showed formation of LiZnPh$_3$. Then LiBr (22mg, 0.25 mmol) was added, and the mixture sonicated for 40s. Analysis by $^1$H NMR spectroscopy showed a small change in the aryl resonances. A further equivalent of LiBr (22mg, 0.25 mmol, total 0.5 mmol) was added, and analysis by $^1$H NMR spectroscopy showed no further interaction. At this stage the solution was not completely homogeneous.

![NMR spectra](image)

Figure S54: Aryl region of the $^1$H NMR spectrum in 2MeTHF of ZnPh$_2$ (bottom), on addition of LiPh (2nd), LiPh + LiBr (3rd) and LiPh + 2 equivalents of LiBr (top)
Synthesis and Reaction of ‘LiZnPh₃’ with 4-fluorobenzyl bromide

An oven dried J Young’s NMR tube equipped with a DMSO-<i>d₆</i> capillary insert was loaded with diphenylzinc (26 mg, 0.12 mmol, 1 eq.), phenyllithium (10 mg, 0.12 mmol, 1 eq.), and 2-MeTHF (600 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, and the solution was analysed by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, which showed formation of LiZnPh₃. After standing overnight, 4-fluorobenzyl bromide (15 µl, 0.12 mmol, 1 eq.) was added and the mixture heated to 60°C for 90 minutes. The reaction was quenched with ethanol. The reaction was analysed by <sup>19</sup>F NMR spectroscopy before dilution with DCM, filtration through a small silica plug and analysis by GCMS which showed the formation of 1-benzyl 4-fluorobenzene (59%) and 1,2-bis(4-fluorophenyl)ethane (11%).

![Figure S55: Aryl region of the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 'LiZnPh₃' before addition of electrophile](image-url)
Figure S56: $^{19}$F NMR spectrum of the reaction between LiZnPh$_3$ and 4-fluorobenzyl bromide

Figure S57: GCMS chromatogram of the reaction between 'LiZnPh$_3$' and 4-fluorobenzyl bromide
Synthesis and Reaction of ‘LiZnPh₃’ with 4-fluorobenzyl bromide in the presence of LiBr

An oven dried J Young’s NMR tube equipped with a DMSO-d₆ capillary insert was loaded with diphenylzinc (26 mg, 0.12 mmol, 1 eq.), phenyllithium (10 mg, 0.12 mmol, 1 eq.), lithium bromide (21 mg, 0.24 mmol, 2 eq.) and 2-MeTHF (600 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, and the solution was analysed by ¹H and ¹³C{¹H} NMR spectroscopy, which showed formation of LiZnPh₃. After standing overnight, 4-fluorobenzyl bromide (15 µl, 0.12 mmol, 1 eq.) was added and the mixture heated to 60°C for 90 minutes. The reaction was quenched with ethanol and fluorobenzene (1 eq.) was added as an internal standard. The reaction was analysed by ¹⁹F NMR spectroscopy which showed the formation of 1-benzyl 4-fluorobenzene (63%) and 1,2-bis(4-fluorophenyl)ethane (11%).

![Aryl region of the ¹³C{¹H} spectrum of 'LiZnPh₃' in the presence of LiBr before addition of the electrophile](attachment:image.png)
Figure S59: $^{19}$F NMR spectrum of the reaction between ‘LiZnPh₃’ and 4-fluorobenzyl bromide in the presence of LiBr
Synthesis and Reaction of ‘LiZnPh₃’ with 4-fluorobenzyl bromide in the presence of ‘BuBPin’

An oven dried J Young’s NMR tube equipped with a benzene-₆ capillary insert was loaded with diphenylzinc (26 mg, 0.12 mmol, 1 eq.), 1a (32 mg, 0.12 mmol, 1 eq.), and 2-MeTHF (600 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, heated for 18 hours at 60°C and was analysed by ¹H, ¹³C{¹H}, and ¹¹B NMR spectroscopy, which showed formation of LiZnPh₃ (based on the conversion of the majority of 1a to ‘BuBPin). Then 4-fluorobenzyl bromide (15 µl, 0.12 mmol, 1 eq.) was added and the mixture heated to 60°C for 90 minutes. The reaction was quenched with ethanol and analysed by ¹⁹F NMR before dilution with DCM, filtration through a small silica plug and analysis by GCMS which showed the formation of 1-benzyl 4-fluorobenzene (69%) and 1,2-bis(4-fluorophenyl)ethane (9%).

Figure S60: ¹¹B NMR spectrum of the reaction between ZnPh₂ and 1a after 18 hours at 60°C
Figure S61: Aryl region of the $^{13}\text{C}^{1}\text{H}$ NMR spectrum of the 'LiZnPh$_3$' synthesised from 1a and ZnPh$_2$ prior to the addition of electrophile

![Aryl region of the $^{13}\text{C}^{1}\text{H}$ NMR spectrum of the 'LiZnPh$_3$' synthesised from 1a and ZnPh$_2$ prior to the addition of electrophile](image)

Figure S62: $^{19}\text{F}$ NMR spectrum of the reaction of 'LiZnPh$_3$' synthesised from 1a and ZnPh$_2$ with 4-fluorobenzyl bromide

![$^{19}\text{F}$ NMR spectrum of the reaction of 'LiZnPh$_3$' synthesised from 1a and ZnPh$_2$ with 4-fluorobenzyl bromide](image)
Synthesis and Reaction of ‘LiZnPh₃’ with 4-fluorobenzyl bromide in the presence of LiBr at a catalytically relevant concentration (of 4-fluorobenzyl bromide)

An oven dried J Young’s NMR tube equipped with a DMSO-d₆ capillary insert was loaded with diphenylzinc (13 mg, 0.06 mmol, 1 eq.), phenyllithium (5 mg, 0.06 mmol, 1 eq.), lithium bromide (10 mg, 0.12 mmol, 2 eq.), and 2-MeTHF (520 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, and the solution was analysed by ¹H NMR spectroscopy. After standing overnight, 4-fluorobenzyl bromide (7.5 µl, 0.06 mmol, 1 eq., equivalent to the concentration that would be present at the start of the standard catalysis run) was added and the mixture heated to 60°C for 90 minutes. The reaction was quenched with ethanol and analysed by ¹⁹F NMR before dilution with DCM, filtration through a small silica plug and analysis by GCMS which showed the formation of 1-benzyl 4-fluorobenzene (60%) and 1,2-bis(4-fluorophenyl)ethane (9%).

Figure S63: ¹⁹F NMR spectrum of the reaction of LiZnPh₃ with 4-fluorobenzyl bromide in the presence of LiBr at lower concentration

Figure S64: GCMS chromatogram of the reaction of LiZnPh₃ with 4-fluorobenzyl bromide in the presence of LiBr at lower concentration
Synthesis and Reaction of ‘Li₂ZnPh₂Br₂’ with 4-fluorobenzyl bromide

An oven dried J Young’s NMR tube equipped with a DMSO-d₆ capillary insert was loaded with diphenylzinc (26 mg, 0.12 mmol, 1 eq.), lithium bromide (21 mg, 0.24 mmol, 1 eq.), and 2-MeTHF (600 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, and the solution was analysed by ¹H and ¹³C{¹H} NMR spectroscopy, which showed formation of some interaction of LiBr with ZnPh₂. After standing overnight, 4-fluorobenzyl bromide (15 µl, 0.12 mmol, 1 eq.) was added and the mixture heated to 60°C for 90 minutes. The reaction was quenched with ethanol and fluorobenzene (1 eq.) was added as an internal standard. The mixture was analysed by ¹⁹F NMR spectroscopy which showed the formation of 1-benzyl 4-fluorobenzene (3%) and 1,2-bis(4-fluorophenyl)ethane (10%).

Figure S65: Aryl region of the ¹³C{¹H} NMR spectrum of the zincate formed from ZnPh₂ and 2 eq. LiBr prior to addition of the electrophile

Figure S66: ¹⁹F NMR spectrum of the reaction between ‘Li₂ZnPh₂Br₂’ and 4-fluorobenzyl bromide
Synthesis and Reaction of ‘Li₂ZnPhBr₃’ with 4-fluorobenzyl bromide

An oven dried J Young’s NMR tube equipped with a DMSO-\textit{d}₆ capillary insert was loaded with zinc bromide (27 mg, 0.12 mmol, 1 eq.), phenyllithium (10 mg, 0.12 mmol, 1 eq.), lithium bromide (10 mg, 0.12 mmol, 1 eq.) and 2-MeTHF (600 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, and the solution was analysed by $^1$H and $^{13}$C\{$^1$H\} NMR spectroscopy, which showed reaction of ZnBr₂ with PhLi. After standing overnight, 4-fluorobenzyl bromide (15 µl, 0.12 mmol, 1 eq.) was added and the mixture heated to 60°C for 90 minutes. The reaction was quenched with ethanol and analysed by $^{19}$F NMR which showed no conversion of starting material.

Figure S67: Aryl region of the $^{13}$C\{$^1$H\} NMR spectrum of the bromide rich zincate prior to addition of the electrophile

Figure S68: $^{19}$F NMR spectrum of the reaction of ‘Li₂ZnPhBr₃’ with 4-fluorobenzyl bromide (coupling products expected at -118.75 ppm are not present)
Reaction of NaBPh$_4$ with ZnPh$_2$

An oven dried J Young’s NMR tube equipped with a DMSO-$d_6$ capillary insert was loaded with diphenyl zinc (35 mg, 0.16 mmol, 1 eq.), and sodium tetraphenylborate (55 mg, 0.16 mmol, 1 eq.) and 2-MeTHF (600 µl). The mixture was sonicated for 1 minute to aid dissolution of the solids, after standing at room temperature for 90 minutes, the mixture was analysed by $^{11}$B NMR spectroscopy revealing no phenyl group transfer. The mixture was heated to 60°C and analysed by $^{11}$B NMR spectroscopy after 3 hours and 41 hours, which showed the presence of only unreacted NaBPh$_4$ (no (2-MeTHF)-BPh$_3$ was observed).

![11B NMR spectrum of the attempted reaction of NaBPh$_4$ with ZnPh$_2$ after 41 hours at 60°C, showing no phenyl group transfer.](image)

**Figure S69**: $^{11}$B NMR spectrum of the attempted reaction of NaBPh$_4$ with ZnPh$_2$ after 41 hours at 60°C, showing no phenyl group transfer.
Triethylphosphine oxide Lewis acidity test

Reference values for Et₃PO in 2-MeTHF with relevant Lewis acidic species

In an oven dried J Young’s NMR tube Et₃PO was dissolved in 2-MeTHF (600 µl), and analysed by ³¹P NMR spectroscopy, which showed a chemical shift of 44.3 ppm. To this sample was added phenyl boronic acid pinacol ester (22.5 µl mg, 0.11 mmol), and the mixture was once again analysed by ³¹P NMR spectroscopy, showing a chemical shift of 44.6 ppm (no change in chemical shift). To the same sample, lithium bromide was added (10 mg, 0.11 mmol), some precipitate was observed, and the sample was analysed by ³¹P NMR spectroscopy, which showed a chemical shift of 58.3 ppm.

Et₃PO in representative reaction mixture

In an oven dried J Young’s ampoule [Li][(¹Bu)(Ph)B(Pin)] 1a (94 mg, 0.35 mmol) and ZnBr₂ (1 of a 2-MeTHF solution equating to 0.047 mmol) were dissolved in 2-MeTHF (2 ml). 4-fluorobenzyl bromide (29 µl, 0.23 mmol) was added. The reaction was heated to 60 °C for three hours before it was allowed to cool and triethylphosphine oxide (6.3 mg, 0.047 mmol) was added. The mixture was transferred to a J Young’s NMR tube and analysed by ³¹P NMR spectroscopy, which showed a chemical shift of 56.8 ppm for Et₃PO. This is compared to the value of 44.3 ppm obtained for free Et₃PO in 2-MeTHF.

Figure S70: ³¹P{¹H} NMR spectrum of triethylphosphine oxide (bottom), with LiBr (middle), and added to the catalytic mixture (after 3 h, see above, thus is in the presence of 1a/ ZnBr₂/ electrophile, top)
NMR Spectra of new compounds 1b

Figure S71: Top: $^1$H NMR spectrum (d$_8$-THF) Bottom: $^{13}$C($^1$H) NMR spectrum (d$_8$THF)
Figure S72: $^{11}$B{$^1$H} NMR spectrum (d$_8$-THF, 128 MHz)
Figure S73: $^1$H NMR (d$_8$-THF, 400MHz.)

Figure S74: $^{13}$C{$^1$H} NMR (d$_8$-THF, 101MHz)
Figure S75: $^1$H-$^1$B NMR spectrum (d$_8$THF, 128 MHz)
Figure S76: $^1$H NMR (d$_8$-THF, 400MHz.)

Figure S77: $^{13}$C{$^1$H} NMR (d$_8$-THF, 101MHz)
Figure S78: $^{11}\text{B}\{^{1}\text{H}\}$ NMR spectrum (d$_{6}$THF, 128 MHz)
Figure S79: $^1$H NMR spectrum (protio-THF, 400MHz)

Figure S80: $^{11}$B NMR spectrum (protio-THF) of 7
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