Supplementary Information for

Copper-Catalyzed Aminoboration from Hydrazones to Generate Borylated Pyrazoles

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I - General Methods

All reagents were used as received from commercial sources unless otherwise stated. Tetrahydrofuran, triethylamine and hexane were dried by passing through an alumina column under argon pressure on a push still solvent system. Toluene-$d_8$ was dried over CaH$_2$, degassed using three freeze-pump-thaw cycles, and vacuum transferred before use. B-Chlorocatecholborane was purchased from TCI Chemicals and used inside a N$_2$-filled glovebox without further purification. Manipulations were performed in a glovebox under nitrogen atmosphere unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using Merck F$_{250}$ plates and visualized under UV irradiation at 254 nm or using a basic aqueous solution of potassium permanganate. Flash chromatography was conducted using a Teledyne Isco Combiflash® Rf 200 Automatic Flash Chromatography System, and Teledyne Isco Redisep® 35–70 μm silica gel. All proton and carbon nuclear magnetic resonance ($^1$H and $^{13}$C) spectra were recorded on a Bruker DRX-400 spectrometer, Bruker DRX-500 spectrometer outfitted with a cryoprobe, or a Bruker AVANCE-600 spectrometer. Boron nuclear magnetic resonance ($^{11}$B NMR) spectra were recorded on a Bruker AVANCE-600 spectrometer. Fluorine nuclear magnetic resonance ($^{19}$F NMR) spectra were recorded on a Bruker AVANCE-600 spectrometer. All coupling constants were measured in Hertz (Hz). Chemical shifts were reported in ppm and referenced to the residual protiated solvent peak ($\delta_H = 7.26$ ppm for CDCl$_3$ in $^1$H NMR spectroscopy experiments; $\delta_C = 77.16$ ppm for CDCl$_3$ in $^{13}$C NMR spectroscopy experiments). $^{11}$B NMR and $^{19}$F NMR spectroscopy experiments were referenced to the absolute frequency of 0 ppm in the $^1$H dimension according to the Xi scale. High-resolution mass spectrometry (HRMS (ESI-TOF)) data were obtained at the University of California, Irvine.
II - Synthetic Procedures

A. General procedure for synthesis of alkynyl ketones SI-2(a–k)

Ketones were prepared according to a literature procedure.\(^1\) Using standard Schlenk line, to a flame-dried round bottom flask equipped with stir bar under N\(_2\) atmosphere was added acid chloride SI-1 (5.0 mmol, 1.0 equiv), PdCl\(_2\)(PPh\(_3\))\(_2\) (70. mg, 0.20 mmol, 2.0 mol%), CuI (38 mg, 0.40 mmol, 4.0 mol%), Et\(_3\)N (0.70 mL, 5.0 mmol, 1.0 equiv), and alkyne (5.0 mmol, 1.0 equiv) in dry THF (25 mL) at 25 °C. The resulting reaction mixture was stirred at room temperature under dynamic N\(_2\) and monitored by TLC until starting materials were completely consumed (\(t = \sim 1\) h). The reaction was quenched with saturated ammonium chloride (20 mL). The aqueous layer was extracted with EtOAc (3 \(\times\) 20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO\(_4\), filtered, and concentrated in vacuo. The resulting crude solid was purified by silica gel flash column chromatography using an elution gradient from 100% hexanes to 20% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo to afford SI-2.

1-phenylhept-2-yn-1-one (SI-2a) was obtained as yellow oil on a 20 mmol scale of starting material (3.314 g, 89% isolated yield). TLC (20% EtOAc/hexanes): \(R_f = 0.50\), visualized by UV
absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.14–8.13 (m, 2H), 7.61–7.58 (m, 1H), 7.49–7.46 (m, 2H), 2.51 (t, $J = 7.2$ Hz, 2H), 1.67 (quintet, $J = 7.2$ Hz, 2H), 1.51 (sextet, $J = 7.2$ Hz, 2H), 0.97 (t, $J = 7.2$ Hz, 3H). This spectrum is in agreement with previously reported spectral data.$^2$

1-(4-Methylphenyl)hept-2-yn-1-one (SI-2b) was obtained as orange oil at 40 °C (0.872 g, 87% isolated yield). TLC (20% EtOAc/hexanes): $R_f = 0.47$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 2.50 (t, $J = 7.2$ Hz, 2H), 2.50 (s, 3H), 1.66 (t, $J = 7.2$ Hz, 2H), 1.50 (sextet, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). This spectrum is in agreement with previously reported spectral data.$^3$

3-cyclopropyl-1-phenylprop-2-yn-1-one (SI-2c) was obtained as yellow oil (0.744 g, 87% isolated yield). TLC (20% EtOAc/hexanes): $R_f = 0.42$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.10 (d, $J = 7.8$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 2H), 1.55–1.51 (m, 1H), 1.06–1.00 (m, 2H). This spectrum is in agreement with previously reported spectral data.$^4$
1-phenyl-3-trimethylsilyl-prop-2-yn-1-one (SI-2d) was obtained as yellow oil (0.638 g, 63% isolated yield). DI water was used to quench the reaction mixture rather than saturated ammonium chloride. TLC (10% EtOAc/hexanes): $R_f = 0.67$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta 8.3$ (d, $J = 7.5$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 2H), 0.32 (s, 3H). This spectrum is in agreement with previously reported spectral data.$^5$

![SI-2e](image)

1-phenyl-3-(thiophen-3-yl)prop-2-yn-1-one (SI-2e) was obtained as orange oil (0.793 g, 75% isolated yield). TLC (20% EtOAc/hexanes): $R_f = 0.38$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta 8.22$–$8.20$ (m, 2H), 7.86–7.85 (m, 1H), 7.65–7.62 (m, 1H), 7.54–7.51 (m, 2H), 7.39–7.37 (m, 1H), 7.34–7.33 (m, 1H). This spectrum is in agreement with previously reported spectral data.$^6$

![SI-2f](image)

1-(thiophen-2-yl)hept-2-yn-1-one (SI-2f) was obtained as orange oil (0.854 g, 89% isolated yield). TLC (20% EtOAc/hexanes): $R_f = 0.58$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta 7.89$–$7.88$ (m, 1H), 7.68–7.67 (m, 1H), 7.15–7.13 (m, 1H), 2.48 (t, $J = 7.2$ Hz, 2H), 1.65 (t, $J = 7.2$ Hz, 2H), 1.50 (sextet, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). This spectrum is in agreement with previously reported spectral data.$^6$
3-(cyclohex-1-en-1-yl)-1-phenylprop-2-yn-1-one (SI-2g) was obtained as yellow oil (0.828 g, 79% isolated yield). TLC (10% EtOAc/hexanes): R_f = 0.48, visualized by UV absorbance. \(^1\)H NMR (CDCl\(_3\), 600 MHz): δ 8.15–8.13 (m, 2H), 7.61–7.58 (m, 1H), 7.49–7.47 (m, 2H), 6.58 (septet, \(J = 1.8\) Hz, 1H), 2.30–2.27 (m, 2H), 2.23–2.19 (m, 2H), 1.73–1.69 (m, 2H), 1.67–1.63 (m, 2H). This spectrum is in agreement with previously reported spectral data.\(^7\)

1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (SI-2h) was obtained as pale yellow solid (0.972 g, 71% isolated yield). TLC (20% EtOAc/hexanes): R_f = 0.39, visualized by UV absorbance. \(^1\)H NMR (CDCl\(_3\), 600 MHz): δ 8.21 (d, \(J = 7.8\) Hz, 2H), 7.80 (d, \(J = 7.8\) Hz, 2H), 7.70 (d, \(J = 7.8\) Hz, 2H), 7.66 (m, 1H), 7.54 (t, \(J = 7.2\) Hz, 2H). This spectrum is in agreement with previously reported spectral data.\(^8\)
1-(4-bromophenyl)hept-2-yn-1-one (SI-2i) was obtained as a clear brown solid on a 10.0 mmol scale of starting material (2.295 g, 87% isolated yield). TLC (20% EtOAc/hexanes): R_f = 0.55, visualized by UV absorbance. \(^1\)H NMR (CDCl₃, 500 MHz): δ 7.98 (d, \(J = 8.5\) Hz, 2H), 7.62 (d, \(J = 8.0\) Hz, 2H), 2.50 (t, \(J = 7.0\) Hz, 2H), 1.66 (quintet, \(J = 7.5\) Hz, 2H), 1.50 (sextet, \(J = 7.5\) Hz, 2H), 0.96 (t, \(J = 7.5\) Hz, 3H). This spectrum is in agreement with previously reported spectral data.\(^9\)

\[
\text{SI-2j}
\]

4,4-dimethyl-1-phenylpent-1-yn-3-one (SI-2j) was obtained as orange oil (0.623 g, 67% isolated yield). TLC (20% EtOAc/hexanes): R_f = 0.50, visualized by UV absorbance. \(^1\)H NMR (CDCl₃, 500 MHz): δ 7.59–7.57 (m, 2H), 7.47–7.43 (m, 1H), 7.38 (t, \(J = 7.5\) Hz, 2H), 1.28 (s, 9H). This spectrum is in agreement with previously reported spectral data.\(^10\)

\[
\text{SI-2k}
\]

1-(4-methoxyphenyl)hept-2-yn-1-one (SI-2k) was obtained as yellow oil (0.948 g, 88% isolated yield). TLC (20% EtOAc/hexanes): R_f = 0.36, visualized by UV absorbance. \(^1\)H NMR (CDCl₃, 500 MHz): δ 8.12–8.09 (m, 2H), 6.96–6.95 (m, 2H), 3.88 (s, 3H), 2.49 (t, \(J = 7.5\) Hz, 2H), 1.65 (t, \(J = 7.5\) Hz, 2H), 1.50 (sextet, \(J = 7.5\) Hz, 2H), 0.96 (t, \(J = 7.5\) Hz, 3H). This spectrum is in agreement with previously reported spectral data.\(^11\)
B. Preparation of alkynyl hydrazone 1a–1k

\[ \text{SI-2} \xrightarrow{\text{H}_2\text{NNHTs, H}_2\text{SO}_4, \text{EtOH}, 16 \text{ h, } 25 \text{ °C}} \text{1} \]

**General Procedure A:** Alkynyl hydrazones were prepared according to a literature procedure.\(^{11}\) Open to air, a 25 mL round bottom flask was charged with **SI-2** (1 mmol, 1.0 equiv), hydrazine (1.1 mmol, 1.1 equiv), EtOH (5 mL) and a stir bar. The flask was capped with a septum and sulfuric acid (1.1 mmol, 1.1 equiv) was added dropwise to the solution over 1 min via syringe. The reaction was allowed to stir for 18 h. A precipitate was present, which was then filtered using a cellulose filter paper and the solid was collected from the filter paper, dissolved in 20 mL of DCM. The organic layer was washed with saturated NaHCO\(_3\) (20 mL), brine (20 mL), dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. The crude solid was triturated using cold EtOH or recrystallized in hot (60 °C) EtOH (solid was collected after ~30 min), or purified through silica gel flash chromatography to afford hydrazone 1.

\[ \text{SI-2} \xrightarrow{\text{H}_2\text{NNHTs, Dioxane, 80 °C, 5 h}} \text{1} \]

**General Procedure B:** Alkynyl hydrazones were prepared according to a literature procedure.\(^{12}\) Open to air, a 25 mL round bottom flask was charged with **SI-2** (1 mmol, 1.0 equiv), \(p\)-toluenesulfonyl hydrazide (1.1 mmol, 1.1 equiv) and dioxane (5 mL). The flask was capped with a septum and the mixture was heated at 80 °C. The reaction mixture was stirred for 5–18 h at 80 °C, after which the mixture was cooled and then concentrated in vacuo. Crude solids were
triturated using EtOH (~5 mL) to afford hydrazone 1. Crude oils were purified by flash chromatography using elution gradients from 100% hexanes to 40% EtOAc in hexanes to afford hydrazone 1.

4-methyl-N'-(1-phenylhept-2-yn-1-ylidene)benzenesulfonohydrazide (1a) was obtained as white solid (0.273 g, 77% isolated yield) using general procedure A after 17 h, and the crude was triturated using cold EtOH (~5 mL). TLC (20% EtOAc/hexanes): Rf = 0.27, visualized by UV absorbance. 1H NMR δ 8.50 (s, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.82–7.80 (m, 2H), 7.36–7.33 (m, 3H), 7.31 J = 8.5 Hz, 2H), 2.57 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.67 (quintet, J = 7.5 Hz, 2H), 1.50 (sextet, J = 7.5 Hz, 2H), 0.98 (t, J = 7.5 Hz, 3H). This spectrum is in agreement with previously reported spectral data.13

4-methyl-N'-(1-(p-tolyl)hept-2-yn-1-ylidene)benzenesulfonohydrazide (1b) was obtained as white solid (0.141 g, 38% isolated yield) using general procedure A after 17 h, and the crude was triturated using cold EtOH (~5 mL). TLC (20% EtOAc/hexanes): Rf = 0.33, visualized by UV absorbance. 1H NMR (CDCl3, 600 MHz): δ 8.43 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 2.56 (t, J = 7.2, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 1.66 (quintet, J = 7.2, 2H), 2.56 (sextet, J = 7.2, 2H), 1.50 (t, J = 7.2, 2H), 0.97 (t, J = 7.2, 3H). 13C NMR (CDCl3, 125 MHz): δ 144.3, 140.4,
N’-(3-cyclopropyl-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1c) was obtained as white solid (0.081 g, 12% isolated yield) using general procedure B on a 2 mmol scale of starting material. The crude product was purified by silica gel chromatography using an elution gradient from 100% hexanes to 20% EtOAc. Rf = 0.19, visualized by UV absorbance. ¹H NMR (CDCl₃, 500 MHz): δ 8.46 (s, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.78–7.76 (m, 2H), 7.35–7.30 (m, 5H), 2.40 (s, 3H), 1.62–1.54 (m, 1H), 1.08–1.04 (m, 2H), 0.96–0.93 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 144.3, 136.3, 135.7, 134.4, 130.1, 129.8, 128.4, 128.0, 126.7, 111.0, 65.2, 21.7, 10.0, 0.5. HRMS (ESI+) m/z calcd for C₁₉H₁₈N₂O₂SNa ([M+Na]⁺) 361.0987, found 361.0985.

4-Methyl-N’-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (1d) was obtained as white solid (0.231 g, 62% isolated yield) using general procedure B (25 °C, and 17 h). The crude was triturated using cold EtOH (~5 mL). TLC (20% EtOAc/hexanes): Rf = 0.38, visualized by UV absorbance. ¹H NMR (CDCl₃, 500 MHz): δ 8.53 (s, 1H), 7.90–7.88 (d, J = 8.3 Hz, 2H), 7.81–7.79 (m, 2H), 7.36–7.34 (m, 3H), 7.33–7.31 (d, J = 8.3 Hz, 2H), 2.41 (s, 3H), 0.32 (s, 3H). This spectrum is in agreement with previously reported spectral data.¹⁴
4-methyl-N’-(1-phenyl-3-(thiophen-3-yl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (1e) was obtained as white solid (0.145 g, 19% isolated yield) using general procedure B on a 2 mmol scale of starting material. The crude was trituted using cold EtOH (~5 mL). TLC (20% EtOAc/hexanes): Rf = 0.35, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.55 (s, 1H), 7.91 (d, $J = 8.0$ Hz, 2H), 7.88–7.86 (m, 2H), 7.74 (m, 1H), 7.41–7.38 (m, 4H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.27–7.26 (m, 1H), 2.41 (s, 3H). This spectrum is in agreement with previously reported spectral data.$^{13}$

(E)-4-methyl-N’-(1-(thiophen-2-yl)hept-2-yn-1-ylidene)benzenesulfonohydrazide (1f) was obtained as white solid (0.937 g, 67% isolated yield) using general procedure A on a 4 mmol scale of starting material. The crude product was recrystallized using hot EtOH (60 °C) for 30 min. TLC (20% EtOAc/hexanes): Rf = 0.31, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.28 (s, 1H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.35–7.34 (m, 1H), 7.31–7.30 (m, 3H), 6.98–6.97 (m, 1H), 2.54 (t, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 1.64 (quintet, $J = 7.2$ Hz, 2H), 1.48 (sextet, $J = 7.2$ Hz, 2H), 0.97 (t, $J = 7.2$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 144.4, 140.0, 135.5, 132.3, 129.8, 128.6, 128.2, 128.1, 127.3, 106.3, 69.5, 30.2, 22.2, 21.8, 19.4, 13.6. HRMS (ESI+) $m/\text{z}$ calcd for C$_{18}$H$_{20}$N$_2$O$_2$S$_2$Na ([M+Na]$^+$) 383.0864, found 383.0850.
N'-((3-(cyclohex-1-en-1-yl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1g) was obtained as white solid (0.081 g, 21% isolated yield) using general procedure B (25 °C and 17 h). The crude product was triturated using cold EtOH (~5 mL). TLC (20% EtOAc/hexanes): R_f = 0.38, visualized by UV absorbance. ^1H NMR (CDCl_3, 600 MHz): δ 8.43 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.82–7.81 (m, 2H), 7.36–7.34 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), 6.44 (septet, J = 1.8 Hz, 1H), 2.41 (s, 3H), 2.27–2.25 (m, 2H), 2.23–2.19 (m, 2H). 1.74–1.70 (m, 2H). 13C NMR (CDCl_3, 125 MHz): δ 144.4, 140.7, 136.4, 135.7, 134.3, 130.1, 129.8, 128.5, 128.1, 126.7, 119.2, 107.1, 75.2, 28.9, 26.1, 22.1, 21.8, 21.3. HRMS (ESI+) m / z calcd for C_{22}H_{22}N_2O_2SNa ([M+Na]^+) 401.1300, found 401.1299.

4-methyl-N'-((1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (1h) was obtained as white solid (0.378 g, 85% isolated yield) using general procedure A for 17 h, and the crude product was triturated using cold EtOH (~5 mL). TLC (20% EtOAc/hexanes): R_f = 0.33, visualized by UV absorbance. ^1H NMR (CDCl_3, 500 MHz): δ 8.58 (s, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.88–7.86 (m, 2H), 7.74–7.69 (m, 4H), 7.33 (d, J = 8.5 Hz, 2H), 2.42 (s, 3H). This spectrum is in agreement with previously reported spectral data.^13
N’-(1-(4-bromophenyl)hept-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1i) was obtained as yellow solid (0.813 g, 51% isolated yield) using general procedure A. The crude product was purified by silica gel chromatography using an elution gradient from 100% hexanes to 20% EtOAc. TLC (20% EtOAc/hexanes): R\textsubscript{f} = 0.28, visualized by UV absorbance. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz): δ 8.48 (s, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 9.0 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.57 (t, J = 7.0 Hz, 2H), 2.41 (s, 2H), 1.66 (quintet, J = 7.0 Hz, 2H), 1.49 (sextet, J = 7.5 Hz, 2H), 0.98 (t, J = 7.5 Hz, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz): δ 144.5, 135.6, 135.3, 133.3, 131.6, 129.87, 128.2, 128.0, 124.5, 108.3, 67.8, 30.3, 22.2, 21.8, 19.5, 13.6. HRMS (ESI+) m / z calcd for C\textsubscript{20}H\textsubscript{22}BrN\textsubscript{2}O\textsubscript{2}S ([M+H]+) 433.0585, found 433.0571.

N’-(4,4-dimethyl-1-phenylpent-1-yn-3-ylidene)-4-methylbenzenesulfonohydrazide (1j) was obtained as white solid (0.455 g, 64% isolated yield) using general procedure A and a 2 mmol scale of starting material. The crude product was purified by silica gel chromatography using an elution gradient from 100% hexanes to 20% EtOAc. TLC (20% EtOAc/hexanes): R\textsubscript{f} = 0.30 visualized by UV absorbance. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): δ 8.16 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.52–7.50 (m, 2H), 7.46–7.37 (m, 3H), 7.31 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 1.17 (s, 9H). This spectrum is in agreement with previously reported spectral data.\textsuperscript{13}
N'-(1-(4-methoxyphenyl)hept-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1k) was obtained as white solid (0.183 g, 48% isolated yield) using general procedure A. The crude product was purified by silica gel chromatography using an elution gradient from 100% hexanes to 20% EtOAc. TLC (20% EtOAc/hexanes): R_f = 0.22 visualized by UV absorbance. \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta 8.38\) (s, 1H), \(7.87\) (d, \(J = 8.5\) Hz, 2H), \(7.74\) (m, 2H), \(7.30\) (d, \(J = 8.0\) Hz, 2H), \(6.86\) (m, 2H), \(3.82\) (s, 3H), \(2.56\) (t, \(J = 7.2\) Hz, 2H), \(2.40\) (s, 3H), \(2.40\) (s, 3H), \(1.66\) (quintet, \(J = 7.2\) Hz, 2H), \(1.49\) (sextet, \(J = 7.2\) Hz, 2H), \(0.97\) (t, \(J = 7.5\) Hz, 3H). \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta 144.3, 140.4, 136.7, 135.4, 133.6, 135.8, 131.7, 129.8, 129.2, 128.0, 126.7, 107.5, 70.2, 30.4, 22.2, 21.7, 21.5, 19.5, 13.7\). HRMS (ESI+) \(m/z\) calcd for C\(_{21}\)H\(_{24}\)N\(_2\)O\(_3\)S ([M+Na\(^+\)]\(^\) 407.1405, found 407.1405.

C. Optimization of B–N σ bond formation in 2a.

Amino boric ester 2a. The reaction was performed inside N\(_2\)-filled glovebox. A 1-dram vial was charged with 1a (35.4 mg, 0.100 mmol, 1.00 equiv). To this vial was added a base (0.100 mmol, 1 equiv) in \(d_8\)-toluene (0.20 mL) at 25 °C, then a boron source (0.100 mmol, 1.00 equiv) in \(d_8\)-toluene (0.10 mL) at 25 °C. Formation of 2a was monitored by \(^1\)H and \(^11\)B NMR spectroscopy and the results were reported in Table S1.
Table S1: Optimization of B–N σ bond formation in 2a

| Entry | R \(^3\) | [B] Source | Base | T (°C) | Results |
|-------|----------|------------|------|--------|---------|
| 1     | Ph       | HBcat      | None | 50     | No B–N bond formed |
| 2     | Ph       | ClBcat     | NaH  | 50–100 | No B–N bond formed, protonated pyrazole as major product |
| 3     | Ph       | BCl\(_3\)  | None | 23     | No B–N bond formed |
| 4     | Ph       | HBcat      | None | 110    | No B–N bond formed |
| 5     | Ph       | ClBcat     | Et\(_3\)N | 23 | B–N bond formed, not clean |
| 6     | Ts       | HBcat      | None | 80     | No B–N bond formed, 10% protonated pyrazole formed |
| 7     | Ts       | ClBcat     | NaH  | 80–110 | No B–N bond formed |
| 8     | Ts       | ClBcat     | Et\(_3\)N | 23 | 80% conversion |
| 9     | Ts       | ClBcat     | Et\(_2\)NH | 23 | No B–N bond formed |
| 10    | Ts       | ClBcat     | NaHCO\(_3\) | 23 | No B–N bond formed |
| 11    | Ts       | ClBcat     | pyridine | 23 | No B–N bond formed |
| 12    | Ts       | ClBcat     | 2,6-lutidine | 23 | 15% conversion |
| 13    | Ts       | ClBcat     | 2,6-tert-lutidine | 23 | No B–N bond formed |
| 14    | Ts       | ClBcat     | DMAP  | 23     | No B–N bond formed |
| 15    | Ts       | ClBcat     | DBU   | 23     | No B–N bond formed |

\(^a\)Reactions were carried out on a 0.10 mmol scale.

D. Optimization of aminoboration reaction conditions

Amino boric ester 2a. The reaction was performed inside N\(_2\)-filled glovebox. A 1-dram vial was charged with 1a (35.4 mg, 0.100 mmol, 1.00 equiv). To this vial was added a solution of B-chlorocatecholborane (15.4 mg, 0.100 mmol, 1.00 equiv) in \(d_8\)-toluene (0.20 mL) via pipet at 25 °C. The reaction mixture was stirred for 20 min at 25 °C, then Et\(_3\)N (14 μL, 0.10 mmol, 1.0 equiv) was added via gas-tight syringe to the reaction mixture, during which precipitation of
triethylammonium chloride was observed with concurrent generation of 2a. The precipitate was removed using a 0.2-μm Target® PTFE syringe filter, and the filtrate was used directly in the screen of reaction conditions without further purification. The results were summarized in Table 1.

E. General procedure NMR conversions

In a N2-filled glovebox, to a 1-dram vial containing alkynyl hydrazone 1 (0.10 mmol, 1.0 equiv) was added a solution of B-chlorocatecholborane (0.10 mmol, 1.0 equiv) in 0.2 mL d8-toluene via pipet. The reaction mixture was allowed to stirred at 25 °C for 20 min, producing a suspension. The base Et3N (0.10 mmol, 1.0 equiv) was then added to the resulting suspension via gas-tight syringe. The resulting suspension was allowed to stir at room temperature for 15 min. The precipitate was removed using a 0.2-μm Target® PTFE syringe filter, and the filtrate was dispensed into a vial containing the catalyst Cu(OTf)2 (0.0050 mmol, 5.0 mol %) and a stir bar. The vial was rinsed twice with d8-toluene (2 × 0.15 mL) and the rinses were transferred via syringe to the solution above. The vial was capped and the mixture was heated at 40 °C inside the glovebox for 24 h. The 1H NMR yield of 3 was measured using single scan 1H NMR spectroscopy (600 MHz, d8-toluene) using the internal phenanthrene standard. The table below shows the NMR spectroscopy yield calculated using this method.
Table S2: \(^1\)H NMR spectroscopy yield of borylated pyrazole 3

| R\(^1\) | R\(^2\) | NMR yield (%) | Time (h) | Temperature (°C) |
|---|---|---|---|---|
| 3a | Ph | Bu | 77% | 24 h | 40 °C |
| 3b | 4-MePh | Bu | 66% | 24 h | 40 °C |
| 3c | Ph | Cpr | 54% | 24 h | 40 °C |
| 3e | Ph | 3-thiophene | 73% | 24 h | 40 °C |
| 3f | 2-thiophene | Bu | 80% | 24 h | 40 °C |
| 3g | Ph | cyclohexenyl | 56% | 24 h | 40 °C |
| 3h | Ph | 4-CF\(_3\)Ph | 75% | 24 h | 40 °C |
| 3i | 4-BrPh | Bu | 78% | 24 h | 40 °C |
| 3k | 4-MeOPh | Bu | 74% | 24 h | 40 °C |

F. Synthesis of pinacol boronates 4: General procedure.

In a N\(_2\)-filled glovebox, to a 1-dram vial containing alkynyl hydrazone 1 (0.10 mmol, 1.0 equiv) was added a solution of B-chlorocatecholborane (0.10 mmol, 1.0 equiv) in 0.2 mL \(d_8\)-toluene via pipet. The reaction mixture was stirred at 25 °C for 20 min, producing a suspension. The compound Et\(_3\)N (0.10 mmol, 1.0 equiv) was then added to the resulting suspension via gas-tight syringe. The resulting suspension was allowed to stir at room temperature for 15 min. The precipitate was removed using a 0.2-μm Target® PTFE syringe filter, and the filtrate was dispensed into a vial containing the catalyst Cu(OTf)\(_2\) (0.0050 mmol, 5.0 mol %) and a stir bar. The vial was rinsed twice with \(d_8\)-toluene (2 × 0.15 mL) and the rinses were transferred via syringe to the solution above. The vial was capped and the mixture was stirred at 40 °C inside the glovebox for 24 h.
Pinacol (23.6 mg, 0.200 mmol, 2.00 equiv) was dissolved in anhydrous Et₃N (0.70 mL, 0.50 mmol, 5.0 equiv). The resulting solution was added to the reaction mixture, and the resulting suspension was stirred at 25 °C for 1 h. The reaction mixture was then removed from the glovebox. Volatiles were removed in vacuo. The resulting dark brown oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to 100% CH₂Cl₂. Solvents were removed in vacuo to afford the desired pinacol boronate 4. All of the pinacol boronates 4a–4k are missing one carbon signal in the ¹³C NMR spectroscopy data. This carbon atom is assigned to the carbon in the newly formed C–B σ bond. This is expected due to the quadrupolar relaxation of B.¹⁵

Pinacol boronate (4a) was obtained as a clear oil (38.3 mg, 74% isolated yield). TLC (40% CH₂Cl₂/hexanes): Rf = 0.08, visualized by UV absorbance. ¹H NMR (CDCl₃, 600 MHz): δ 7.91 (d, J = 8.4 Hz, 2H), 7.71–7.69 (m, 2H), 7.34–7.28 (m, 5H), 3.17 (t, J = 8.4 Hz, 2H), 2.40 (s, 3H), 1.67 (quintet, J = 7.2 Hz, 2H), 1.45 (sextet, J = 7.2 Hz, 2H), 1.27 (s, 12H), 0.96 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 150 MHz): δ 159.6, 157.4, 145.4, 135.6, 133.1, 129.9, 129.1, 128.7, 128.2, 127.8, 83.8, 33.8, 26.8, 24.9, 23.0, 21.8, 13.9. ¹¹B NMR (CDCl₃, 192 MHz): δ 29.9 (s). HRMS (ESI+) m/z calcd for C₂₆H₃₃BN₂O₄Na ([M+Na⁺]⁺) 503.2157, found 503.2155.
Pinacol boronate (4b) was obtained as a clear oil (31.0 mg, 63% isolated yield). TLC (40% CH$_2$Cl$_2$/hexanes): R$_f$ = 0.09, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 500 MHz): δ 7.90 (d, $J$ = 8.5 Hz, 2H), 7.61 (d, $J$ = 8.0 Hz, 2H), 7.28 (d, $J$ = 8.0 Hz, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H), 3.16 (t, $J$ = 8.0 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 1.67 (quintet, $J$ = 7.5 Hz, 2H), 1.45 (sextet, $J$ = 7.5 Hz, 2H), 1.28 (s, 12H), 0.96 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ 159.6, 157.3, 145.3, 138.5, 135.6, 130.2, 129.9, 128.9, 128.6, 128.2, 83.7, 33.8, 26.8, 24.9, 23.0, 21.8, 21.5, 13.9. $^{11}$B NMR (CDCl$_3$, 192 MHz): δ 30.1 (s). HRMS (ESI+) $m/z$ calcd for C$_{27}$H$_{36}$BN$_2$O$_4$S ([M+H]$^+$) 495.2494, found 495.2486.

Pinacol boronate (5.4c) was obtained as a light yellow oil (21.0 mg, 44% isolated yield). TLC (40% CH$_2$Cl$_2$/hexanes): R$_f$ = 0.06, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): δ 7.93 (d, $J$ = 8.4 Hz, 2H), 7.65–7.63 (m, 2H), 7.34–7.33 (m, 3H), 7.30 (d, $J$ = 8.4 Hz, 2H), 2.41 (s, 3H), 2.33–2.28 (m, 1H), 1.28 (s, 12H), 1.06–1.02 (m, 2H), 0.81–0.78 (m, 2H). $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 158.5, 154.7, 145.4, 135.6, 133.3, 129.9, 128.8, 128.6, 128.3, 128.1, 84.4, 29.8, 25.1, 21.8, 8.6, 8.5. $^{11}$B NMR (CDCl$_3$, 192 MHz): δ 30.3 (s). HRMS (ESI+) $m/z$ calcd for C$_{25}$H$_{30}$BN$_2$O$_4$S ([M+H]$^+$) 465.2024, found 465.2076.
Pinacol boronate (4d) was obtained as a yellow oil (31.8 mg, 64% isolated yield). TLC (40% CH₂Cl₂/hexanes): Rf = 0.30, visualized by UV absorbance. ¹H NMR (CDCl₃, 500 MHz): δ 7.89 (d, J = 8.5 Hz, 2H), 7.59–7.57 (m, 2H), 7.34–7.33 (m, 3H), 7.28 (d, J = 8.5 Hz, 2H), 2.41 (s, 3H), 1.23 (s, 12H), 0.51 (s, 9H). ¹³C NMR (CDCl₃, 150 MHz): δ 160.0, 152.0, 145.3, 135.4, 133.5, 129.7, 129.0, 128.8, 128.5, 128.0, 84.7, 25.7, 21.8, 1.2. ¹¹B NMR (CDCl₃, 192 MHz): δ 30.5 (s). HRMS (ESI+) m/z calcld for C₂₅H₃₃BN₂O₄SSiNa ([M+Na]⁺) 519.1926, found 519.1768.

Pinacol boronate (4e) was obtained as a white solid (30.2 mg, 60% isolated yield). TLC (40% CH₂Cl₂/hexanes): Rf = 0.11, visualized by UV absorbance. ¹H NMR (CDCl₃, 600 MHz): δ 7.80–7.78 (m, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.38–7.33 (m, 5H), 7.22–7.20 (m, 3H), 2.39 (s, 3H), 1.11 (s, 12H). ¹³C NMR (CDCl₃, 125 MHz): δ 158.5, 148.1, 145.5, 135.1, 132.8, 130.4, 129.8, 129.5, 129.0, 128.4, 128.24, 128.21, 127.4, 124.3, 84.2, 24.6, 21.8. ¹¹B NMR (CDCl₃, 192 MHz): δ 30.0 (s). HRMS (ESI+) m/z calcld for C₂₆H₂₇BN₂O₄S₂Na ([M+H]⁺) 529.1408, found 529.1426.
Pinacol boronate (4f) was obtained as a clear oil on a 0.20 mmol scale of starting material (73.1 mg, 74% isolated yield). TLC (50% CH$_2$Cl$_2$/hexanes): R$_f$ = 0.18, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.91 (d, $J$ = 8.4 Hz, 2H), 7.84–7.83 (m, 1H), 7.30–7.26 (m, 3H), 7.01–7.00 (m, 1H), 3.18 (t, $J$ = 7.8 Hz, 2H), 2.40 (s, 3H), 1.69–1.62 (m, 2H), 1.45 (sextet, $J$ = 7.2 Hz, 2H), 1.32 (s, 12H), 0.96 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 158.2, 153.6, 145.5, 135.9, 135.4, 129.9, 128.3, 128.2, 127.2, 126.5, 83.8, 33.8, 26.5, 25.0, 22.9, 21.8, 13.9. $^{11}$B NMR (CDCl$_3$, 192 MHz): $\delta$ 29.8 (s). HRMS (ESI+) $m/z$ calcd for C$_{24}$H$_{32}$BN$_2$O$_4$S$_2$ ([M+H]$^+$) 487.1901, found 487.1926.

Pinacol boronate (4g) was obtained as a light yellow solid (21.1 mg, 42% isolated yield). TLC (40% CH$_2$Cl$_2$/hexanes): R$_f$ = 0.08, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.83 (d, $J$ = 8.4 Hz, 2H), 7.77–7.75 (m, 2H), 7.34–7.33 (m, 3H), 7.26–7.25 (m, 1H), 5.50 (m, 1H), 2.42–2.39 (m, 5H), 2.16–2.15 (m, 2H), 1.84–1.80 (m, 2H), 1.74–1.71 (m, 2H), 1.25 (s, 12H). $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 156.4, 145.3, 136.6, 135.5, 132.9, 130.34, 130.31, 129.7, 128.8, 128.5, 128.2, 128.1, 84.0, 30.6, 25.7, 24.8, 22.7, 21.82, 21.80. $^{11}$B NMR (CDCl$_3$, 192 MHz): $\delta$ 30.5 (s). HRMS (ESI+) $m/z$ calcd for C$_{28}$H$_{34}$BN$_2$O$_4$S ([M+H]$^+$) 505.2338, found 505.2362.
**Pinacol boronate (4h)** was obtained as a light brown solid (41.3 mg, 73% isolated yield). TLC (40% CH$_2$Cl$_2$/hexanes): $R_f = 0.10$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.80–7.79 (m, 2H), 7.68–7.65 (m, 4H), 7.50 (d, $J = 7.8$ Hz, 2H), 7.38–7.37 (m, 3H), 7.26–7.24 (m, 2H), 2.41 (s, 3H), 1.05 (s, 12H). $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 158.9, 151.8, 145.8, 134.9, 134.1, 132.4, 131.5, 131.3, 131.2, 129.9, 129.2, 128.6, 128.3, 124.3, 124.3, 84.2, 24.5, 21.8. $^{11}$B NMR (CDCl$_3$, 192 MHz): $\delta$ 29.9 (s). $^{19}$F NMR (CDCl$_3$, 564 MHz): $\delta$ -62.7 (s). HRMS (ESI$^+$) $m/z$ calcd for C$_{29}$H$_{28}$BF$_3$N$_2$O$_4$SNa ([M+Na]$^+$) 591.1718, found 591.1669.

![Image of 4i](image1)

**Pinacol boronate (4i)** was obtained as a clear oil on a 0.20 mmol scale of starting material (76.1 mg, 68% isolated yield). TLC (40% CH$_2$Cl$_2$/hexanes): $R_f = 0.09$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.90 (d, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 7.5$ Hz, 2H), 7.46 (d, $J = 7.5$ Hz, 2H), 7.30 (d, $J = 7.5$ Hz, 2H), 3.18 (t, $J = 7.5$ Hz, 2H), 2.41 (s, 3H), 1.66 (quintet, $J = 7.2$ Hz, 2H), 1.45 (sextet, $J = 7.2$ Hz, 2H), 1.27 (s, 12H), 0.96 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 158.5, 157.8, 145.6, 135.4, 132.0, 131.0, 130.7, 130.0, 128.2, 123.0, 83.8, 33.8, 26.7, 24.9, 23.0, 21.8, 13.9. $^{11}$B NMR (CDCl$_3$, 192 MHz): $\delta$ 29.7 (s). HRMS (ESI$^+$) $m/z$ calcd for C$_{26}$H$_{32}$BBrN$_2$O$_4$SNa ([M+Na]$^+$) 581.1262, found 581.1269.

![Image of 4j](image2)
**Pinacol boronate (4j)** was obtained as a clear oil on a 0.20 mmol scale of starting material (71.0 mg, 74% isolated yield). TLC (50% CH₂Cl₂/hexanes): Rᵣ = 0.12, visualized by UV absorbance. ¹H NMR (CDCl₃, 600 MHz): δ 7.58 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 2.39 (s, 3H), 1.33 (s, 9H), 1.04 (s, 12H). ¹³C NMR (CDCl₃, 150 MHz): δ 168.4, 153.2, 145.0, 135.4, 130.7, 130.6, 129.4, 129.1, 128.1, 127.3, 84.0, 33.9, 30.0, 24.6, 21.8. ¹¹B NMR (CDCl₃, 192 MHz): δ 30.3 (s). HRMS (ESI⁺) m/z calcd for C₂₆H₃₃BN₂O₄Na ([M+Na]⁺) 503.2157, found 503.2159.

**Pinacol boronate (4k)** was obtained as a clear oil on a 0.20 mmol scale of starting material (70.4 mg, 69% isolated yield). TLC (40% CH₂Cl₂/hexanes): Rᵣ = 0.09, visualized by UV absorbance. ¹H NMR (CDCl₃, 600 MHz): δ 7.90 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 9.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 3.16 (t, J = 7.8 Hz, 2H), 2.40 (s, 3H), 1.66 (quintet, J = 7.2 Hz, 2H), 1.45 (sextet, J = 7.2 Hz, 2H), 1.28 (s, 12H), 0.96 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 150 MHz): δ 160.1, 159.3, 157.4, 145.3, 135.6, 130.3, 129.9, 128.1, 125.7, 113.2, 83.7, 55.4, 33.8, 26.7, 24.9, 23.0, 21.8, 13.9. ¹¹B NMR (CDCl₃, 192 MHz): δ 30.0 (s). HRMS (ESI⁺) m/z calcd for C₂₇H₃₅BN₂O₅Na ([M+Na]⁺) 533.2263, found 533.2255.

**G. Gram-scale preparation of 4f**

The gram-scale aminoboration reaction was conducted in a N₂-filled glovebox. To a 20-dram vial was added hydrazone 1f (1.08 g, 3.00 mmol, 1.00 equiv). The compound B-chlorocatecholborane
(462 mg, 3.00 mmol, 1.00 equiv) was dissolved in anhydrous toluene (4.0 mL) and transferred to the 20-dram vial via pipet. The mixture was allowed to react at 25 °C for 30 min, after which time a suspension had formed. To the resulting suspension was added Et₃N (0.42 mL, 3.0 mmol, 1.0 equiv) via syringe, and this mixture was allowed to sit at 25 °C for 90 min. The resulting precipitate was removed using two 0.2-μm Target® PTFE syringe filters due to the large amount of precipitate formed, and the filtrate was then dispensed into a 20-dram vial containing the catalyst Cu(OTf)_2 (54.0 mg, 0.150 mmol, 5.00 mol %) and a stir bar. The vial was capped and the reaction mixture was stirred for 24 h at 40 °C inside the glovebox.

Pinacol (708 mg, 6.00 mmol, 2.00 equiv) was dissolved in anhydrous Et₃N (2.1 mL, 15 mmol, 5.0 equiv). The resulting solution was added to the reaction mixture, and the resulting suspension was stirred at 25 °C for 1 h. The reaction mixture was then removed from the glovebox. Volatiles were removed in vacuo. The resulting dark brown oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to 100% CH₂Cl₂. Solvents were removed in vacuo to afford the desired pinacol boronate 4f as a clear oil (816 mg, 56% isolated yield). Spectral data were identical to those previously obtained for this compound on a smaller scale.

**H. Suzuki cross-coupling reaction of 4f**

![H. Suzuki cross-coupling reaction of 4f](image-url)
The Suzuki cross-coupling reaction was conducted according to literature procedure.\textsuperscript{16} To a 25-mL-round bottom flask were added boronate 4f (97.2 mg, 0.200 mmol, 1.00 equiv), PdCl$_2$(dppf)$\cdot$DCM (16.3 mg, 0.0200 mmol, 0.100 equiv), K$_3$PO$_4$ (127.2 mg, 0.600 mmol, 3.00 equiv), and 10 (50.0 μL, 0.400 mmol, 2.00 equiv) via gas-tight syringe in a N$_2$-filled glovebox. The flask was then capped with septum and brought outside the glovebox. Dioxane (1.5 mL) was purged with dynamic N$_2$ for 30 min. It was added via syringe to the reaction flask, which was then sealed with parafilm under static N$_2$ and heated at 85 °C for 44 h. The reaction mixture was cooled to 25 °C and quenched with DI H$_2$O (5 mL). The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The resulting dark oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to 10% EtOAc. Solvents were removed in vacuo to afford the desired 11 as a white solid (61.6 mg, 63% isolated yield). TLC (20% EtOAc/hexanes): $R_f$ = 0.35, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): δ 7.96 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 7.20 (d, $J$ = 4.8 Hz, 1H), 6.90 (d, $J$ = 3.6 Hz, 1H), 6.87–6.84 (m, 2H), 6.67–6.65 (m, 2H), 6.02 (s, 2H), 2.79 (t, $J$ = 7.8 Hz, 1H), 2.43 (s, 3H), 1.61–1.56 (m, 2H), 1.28 (septet, $J$ = 7.8 Hz, 2H), 0.84 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 148.8, 148.0, 147.7, 145.5, 135.4, 134.3, 130.0, 128.4, 127.2, 127.0, 126.4, 125.1, 124.4, 121.8, 111.1, 108.8, 101.4, 32.8, 25.2, 22.7, 13.8. HRMS (ESI+) $m/z$ calcd for C$_{25}$H$_{24}$N$_2$O$_4$S$_2$Na ([M+Na]$^+$) 503.1075, found 503.1070.
I. Bromination of 4i

The bromination reaction was conducted according to a literature procedure.\textsuperscript{17} Open to air, a 50 mL round-bottom flask was charged with pinacol boronate 4i (48.2 mg, 0.0862 mmol, 1.0 equiv), MeOH (3.0 mL) and a stir bar. A solution of CuBr\textsubscript{2} was prepared by dissolving CuBr\textsubscript{2} (115.6 mg, 0.517 mmol, 6.0 equiv) in 1.5 mL of water. This solution was fully transferred to the round-bottom flask via pipet. The reaction mixture was stirred and heated at 65 °C for 18 h, and allowed to cool to room temperature. The mixture was then diluted with 5 mL of EtOAc and washed with brine (1 × 5 mL). The aqueous layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}. The mixture was filtered and the filtrate was concentrated in vacuo. The resulting oil was purified by silica gel flash column chromatography using an elution gradient from 100% hexanes to 5% EtOAc in hexanes. Solvents were removed in vacuo to afford brominated pyrazole 12 as a white solid (30.0 mg, 68% isolated yield). TLC (10% EtOAc/hexanes): R\textsubscript{f} = 0.34, visualized by UV absorbance. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta\) 7.92–7.89 (m, 2H), 7.75–7.72 (m, 2H), 7.56–7.53 (m, 2H), 7.34–7.32 (m, 2H), 3.04–3.01 (m, 2H), 2.43 (s, 3H), 1.70–1.64 (m, 2H), 1.47 (sextet, \(J = 7.5\) Hz, 2H), 0.98 (t, \(J = 7.5\) Hz, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 150 MHz): \(\delta\) 151.2, 147.3, 134.7, 131.7, 130.2, 129.9, 129.8, 128.3, 123.8, 97.8, 31.4, 26.1, 22.7, 21.9, 13.9. HRMS (ESI\textsuperscript{+}) \(m/z\) calcd for C\textsubscript{20}H\textsubscript{21}Br\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S ([M+H]\textsuperscript{+}) 510.9691, found 510.9680.
Detosylation was conducted according to a literature procedure.\textsuperscript{18} Open to air, a 100 mL round-bottom flask was charged with pyrazole 12 (30.0 mg, 0.0537 mmol, 1.0 equiv) and MeOH (2 mL). A suspension of sodium hydroxide (7.4 mg, 0.19 mmol, 3.5 equiv) in MeOH (1 mL) was transferred into the round bottom flask via pipet. The reaction mixture was stirred and heated at 65 °C for 19 h, and then cooled to room temperature. The reaction mixture was diluted with 5 mL of EtOAc and quenched with 5 mL of saturated sodium bicarbonate. The aqueous layer was treated with 1 M NaOH (1 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (1 × 10 mL) and concentrated in vacuo. The resulting solid was purified by silica gel flash column chromatography using an elution gradient from 100% hexanes to 15% EtOAc in hexanes. Solvents were removed in vacuo to afford the pyrazole 13 as a white solid (11.9 mg, 54% isolated yield). TLC (20% EtOAc/hexanes): $R_f = 0.25$, visualized by UV absorbance. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.69 (s, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 2.63 (t, $J = 7.8$ Hz, 2H), 1.61 (quintet, $J = 7.8$ Hz, 2H), 1.35 (sextet, $J = 7.8$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 146.6, 146.0, 131.0, 131.8, 130.1, 129.2, 122.9, 92.7, 30.5, 25.4, 22.5, 13.9. HRMS (ESI+) $m/z$ calcd for C$_{13}$H$_{15}$Br$_2$N$_2$ ([M+H]$^+$) 358.9582, found 358.9585.
**K. Iridium-catalyzed C–H activation/borylation reaction sequence of 3f′**

Protonated pyrazole 3f′ was obtained as a byproduct as a white solid from the scale-up experiment above. $^1$H NMR (CDCl₃, 500 MHz): $\delta$ 7.89 (d, $J = 8.5$ Hz, 2H), 7.37–7.36 (m, 1H), 7.31–7.20 (m, 3H), 7.04–7.02 (m, 1H), 6.30 (s, 1H), 2.96 (t, $J = 7.5$ Hz, 2H), 2.40 (s, 3H), 1.69 (quintet, $J = 7.5$ Hz, 2H), 1.44 (septet, $J = 7.5$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (CDCl₃, 150 MHz): $\delta$ 150.19, 150.14, 145.4, 135.3, 134.9, 130.0, 128.0, 127.6, 126.5, 125.9, 106.5, 31.0, 26.8, 22.5, 21.8, 13.9. HRMS (ESI+) $m/z$ calcd for C$_{18}$H$_{20}$BN$_2$O$_2$S$_2$H ([M+H]$^+$) 361.1045, found 361.1037.

The reaction sequence was conducted in a N₂-filled glovebox according to literature procedure.$^{19}$ To a 1-dram vial was added [Ir(COD)OMe]$_2$ (4.0 mg, 0.0060 mmol, 0.030 equiv) and HBpin (51 μL, 0.34 mmol, 1.7 equiv) via gas-tight syringe. To a separate 1-dram vial was added dtbpy (1.6 mg, 0.0060 mmol, 0.030 equiv) and hexane (0.10 mL). The resulting clear solution was added via pipet to the first vial, resulting a dark brown suspension. The vial was rinsed with hexane (2 × 0.1 mL) and the rinses were also added. The suspension was then added via pipet into a 1-dram vial containing 3f′. The vial was rinsed with hexane (2 × 0.1 mL) and the rinses were also added. The reaction mixture was stirred at 25 °C for 1 h, after which the vial was removed from the glovebox. Volatile was removed in vacuo. The resulting brown crude mixture was purified by silica gel chromatography using an elution gradient from 100% hexanes to 10% EtOAc. The crude reaction showed only one product and unreacted starting material. Solvents were removed in vacuo.
to afford the 12 as a white solid (28.7 mg, 30% isolated yield). Borylation on the thiophene was
determined by proton integration and chemical shift by $^1$H NMR spectroscopy. Specifically, the
unambiguous pyrazole proton remained as the distinct and only signal in the 6–7 ppm range,
showing that borylation did not occur on the pyrazole ring. Additionally, one of the three thiophene
protons had been consumed. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.89 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J =
3.6$ Hz, 1H), 7.44 (d, $J = 3.6$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 6.30 (s, 1H), 2.96 (t, $J = 7.8$ Hz,
2H), 2.40 (s, 3H), 1.69 (quintet, $J = 7.2$ Hz, 2H), 1.44 (septet, $J = 7.8$ Hz, 2H), 1.34 (s, 12H), 0.96
(t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 150.1, 149.9, 145.5, 141.5, 137.6, 135.2, 130.0,
128.2, 127.0, 106.6, 84.4, 31.0, 26.8, 24.9, 22.5, 21.8, 14.0. $^{11}$B NMR (CDCl$_3$, 192 MHz): $\delta$ 28.4.
HRMS (ESI+) $m/z$ calcd for C$_{24}$H$_{31}$BN$_2$O$_4$S$_2$Na ([M+Na]$^+$) 509.1721, found 509.1718.

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Thio Bu Hydrazone (C)
13C spectrum with 1H decoupling
Ph cyclohexene Hydrazone
1H spectrum
1H spectrum using composite pulse for background suppression

Chemical structure of compound 4b
11B spectrum using composite pulse for background suppression
$^{1}H$ spectrum using composite pulse for background suppression

4f
11B spectrum using composite pulse for background suppression

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\text{Formula Image}
\]
*protonated pyrazole (thiophene)* 13 1 C:\Users\Scott\Desktop

$^1$H H N H Bu

3f

I - restored spin-echo $^{13}$C spectrum with $^{1}$H decoupling
