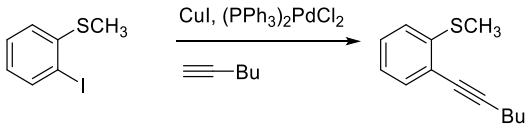
I. General Methods

All chemicals were used as received from commercial sources unless otherwise noted. Triethylamine, acetonitrile, toluene, tetrahydrofuran, *N*,*N*-dimethylformamide, and dichloromethane were purified by passage 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 prior to use. All manipulations were conducted using standard Schlenk techniques unless otherwise specified. Analytical thin layer chromatography (TLC) was performed using Merck F_{250} plates. Plates were visualized under UV irradiation (254 nm) and/or using a basic aqueous solution of potassium permanganate. Flash chromatography was conducted using a Teledyne Isco Combiflash® Rf 200 Automated Flash Chromatography System, and Teledyne Isco Redisep® 35–70 µm silica gel. All proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Bruker DRX-500 spectrometer outfitted with a cryoprobe, or a Bruker AVANCE-600 spectrometer outfitted with a cryoprobe. All boron nuclear magnetic resonance (^{11}B NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker AVANCE-600 spectrometer. All chemical shifts (δ) are reported in parts per million (ppm) downfield of tetramethylsilane, and referenced to the residual protiated solvent peak (δ = 7.26 ppm for $CDCl_3$, δ = 2.08 ppm for d_8-toluene; δ = 77.2 ppm for $CDCl_3$ or δ = 20.4 ppm for d_8-toluene in ^{13}C NMR spectroscopy experiments). ^{11}B and ^{19}F NMR spectroscopy experiments are referenced to the absolute frequency of 0 ppm in the ^{1}H dimension according to the Xi scale. High-resolution mass spectrometry data were obtained at the University of California, Irvine.

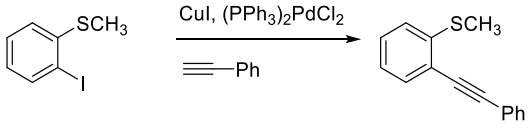
II. Synthetic Procedures

A. Preparation of Substrates 1a–1q



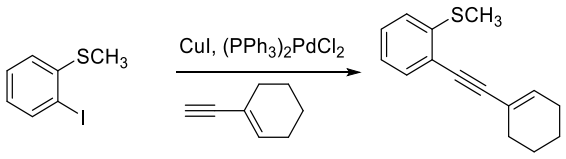
14 **1a**

(2-(Hex-1-yn-1-yl)phenyl)(methyl)sulfane (1a). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.28 mL, 2.0 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (42 mg, 0.10 mmol, 0.050 equiv), CuI (19 mg, 0.20 mmol, 0.10 equiv), Et_3N (6 mL), and a stir bar. 1-Hexyne (0.35 mL, 3.0 mmol, 1.5 equiv) was then added to the reaction mixture via syringe. The vial containing the resulting mixture was capped and removed from the glovebox, and the solution was stirred for 18 h. At this time, TLC indicated complete consumption of starting material. The reaction mixture was diluted with 100 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1a** as a yellow oil (360 mg, 89% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.47 (s, 3H), 1.64 (quin, *J*=7.9 Hz, 2H), 1.60–1.50 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[1]



6 **1b**

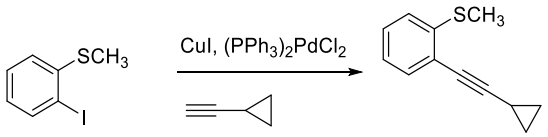
Methyl(2-(phenylethynyl)phenyl)sulfane (1b) was synthesized using a literature procedure[2] in 79% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.59–7.57 (m, 2H), 7.48 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37–7.32(m, 3H), 7.31–7.29 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 2.52 (s, 3H). This spectrum is in agreement with previously reported spectral data.[2]



6 **1c**

(2-(Cyclohex-1-en-1-ylethynyl)phenyl)(methyl)sulfane (1c) was synthesized using a literature procedure[2] in 89% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.37 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.05 (td, *J* = 7.6, 1.1 Hz,

1H), 6.27–6.25 (m, 1H), 2.48 (s, 3H), 2.28–2.26 (m, 2H), 2.16–2.15 (m, 2H), 1.70–1.68 (m, 2H), 1.63–1.61 (m, 2H). This spectrum is in agreement with previously reported spectral data.[2]



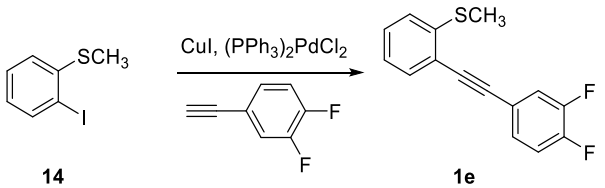
14 **1d**

(2-(Cyclopropylethynyl)phenyl)(methyl)sulfane (1d). A flask was charged with $(PPh_3)_2PdCl_2$ (421 mg, 0.600 mmol, 0.0500 equiv), CuI (57.3 mg, 0.300 mmol, 0.100 equiv), and a stir bar. The flask was then connected to a Schlenk line and evacuated and refilled with N_2 three times before *o*-iodothioanisole **14** (4.22 mL, 30.0 mmol, 1.00 equiv) and Et_3N (80 mL) were added via syringe. Cyclopropylacetylene (3.05 mL, 36.0 mmol, 1.20 equiv) was then syringed into the reaction mixture, which stirred for 18 h under dynamic N_2. At this time, analysis by TLC indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 30 mL), water (1 × 30 mL), and brine (1 × 30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1d** as a yellow liquid (5.5 g, 97% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.23 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.03 (td, *J* = 7.5, 1.1 Hz, 1H), 2.46 (s, 3H), 1.55–1.50 (m, 1H), 0.92–0.86 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 141.4, 132.3, 128.0, 124.1, 123.8, 121.9, 100.5, 73.2, 15.0, 9.0, 0.5.

HRMS (ESI+): Calculated for $C_{12}H_{12}SNa$ ($[M+Na]^+$), 211.0557; found 211.0560.



14 **1e**

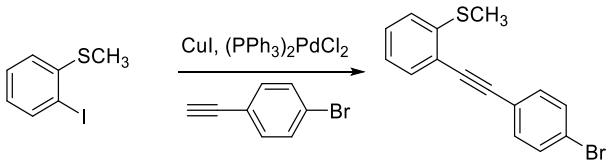
(2-((3,4-Difluorophenyl)ethynyl)phenyl)(methyl)sulfane (1e). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.22 mL, 1.6 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (56 mg, 0.080 mmol, 0.050 equiv), CuI (31 mg, 0.16 mmol, 0.10 equiv), Et_3N (3 mL), and a stir bar. 3,4-Difluorophenylacetylene (0.22 mL, 1.8 mmol, 1.1 equiv) was then added to the reaction mixture via syringe. The vial containing the resulting mixture was capped and removed from the glovebox, and the solution was stirred for 18 h. At this time, TLC indicated complete consumption of starting material. The reaction mixture was diluted with 100 mL EtOAc and washed with saturated NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4,

filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1e** as a yellow solid (330 mg, 79% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.39–7.36 (m, 1H), 7.32–7.31 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.16–7.11 (m, 2H), 2.52 (s, 3H).

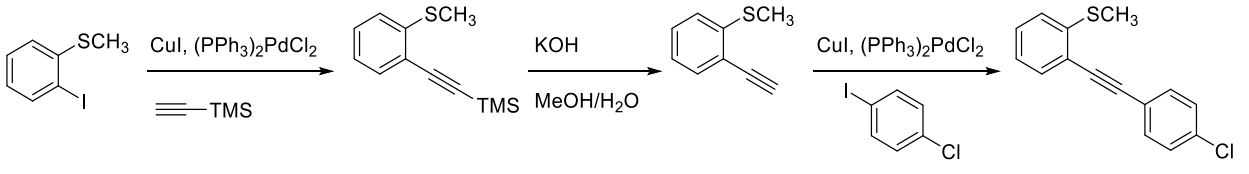
^{13}C NMR ($CDCl_3$, 126 MHz): δ 151.4 (dd, *J* = 77.7, 12.0 Hz), 149.4 (dd, *J* = 75.5, 12.6 Hz), 142.0, 132.4, 129.4–129.3 (m), 129.2–129.1 (m), 128.5–128.2 (m), 124.7–123.9 (m), 120.7, 120.6–120.1 (m), 118.0–117.8 (m), 117.3 (d, *J* = 19.9 Hz), 93.7, 87.5, 15.1.

HRMS (CI+): Calculated for $C_{15}H_{10}SF_2$ ([M]$^+$), 260.0471; found 260.0471.



14 **1f**

(2-((4-Bromophenyl)ethynyl)phenyl)(methyl)sulfane (1f). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.22 mL, 1.6 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (56 mg, 0.080 mmol, 0.050 equiv), CuI (31 mg, 0.16 mmol, 0.10 equiv), Et_3N (3 mL), and a stir bar. 4-Bromophenylacetylene (330 mg, 1.8 mmol, 1.1 equiv) was then added to the reaction mixture. The vial containing the resulting mixture was capped and removed from the glovebox, and the solution was stirred for 18 h. At this time, TLC indicated complete consumption of starting material. The reaction mixture was diluted with 100 mL EtOAc and washed with saturated NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1f** as a yellow solid (420 mg, 86% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50–7.46 (m, 3H), 7.44–7.43 (m, 2H), 7.32 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 2.51 (s, 3H). This spectrum is in agreeance with previously reported spectral data.[3]



14 **SI-1** **SI-2** **1g**

Trimethyl((2-(methylthio)phenyl)ethynyl)silane (SI-1) was synthesized using a literature procedure[2] in 98% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 (dd, *J* = 7.6, 0.2 Hz, 1H), 7.27 (td, *J* = 8.0, 1.5 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.06 (td, *J* = 7.6, 1.1 Hz,

1H), 2.48 (s, 3H), 0.30 (s, 9H). This spectrum is in agreement with previously reported spectral data.[2]

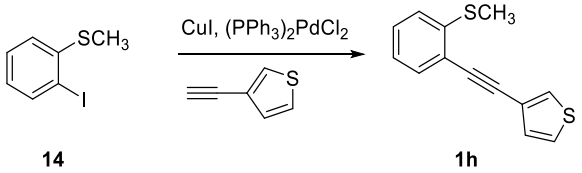
(2-Ethynylphenyl)(methyl)sulfane (SI-2) was synthesized using a literature procedure[4] in 99% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 3.48 (s, 1H), 2.49 (s, 3H). This spectrum is in agreement with previously reported spectral data.[4]

(2-((4-Chlorophenyl)ethynyl)phenyl)(methyl)sulfane (1g). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with 1-chloro-4-iodobenzene (270 mg, 1.1 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (39 mg, 0.056 mmol, 0.050 equiv), CuI (22 mg, 0.11 mmol, 0.10 equiv), and a stir bar. In a separate dram vial, **SI-2** (250 mg, 1.7 mmol, 1.5 equiv) was dissolved in Et_3N (2.3 mL). This solution was then added to the reaction vial via pipette, and the mixture-containing vial was capped and removed from the glovebox, and the solution was stirred for 18 h. At this time, TLC indicated complete consumption of starting material. The reaction mixture was diluted with 100 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1g** as a yellow oil (250 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50 (d, J = 10.2 Hz, 2H), 7.47 (d, J = 9.1 Hz, 1H), 7.33–7.30 (m, 3H), 7.18 (d, J = 9.6Hz, 1H), 7.12 (t, J = 9.1 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 141.8, 134.7, 132.8, 132.3, 129.0, 128.7, 124.3, 124.1, 121.7, 121.0, 94.7, 87.9, 15.1.

HRMS (CI+): Calculated for $C_{15}H_{10}SCl$ ($[M-H]^+$), 257.0192; found 257.0192.



14 **1h**

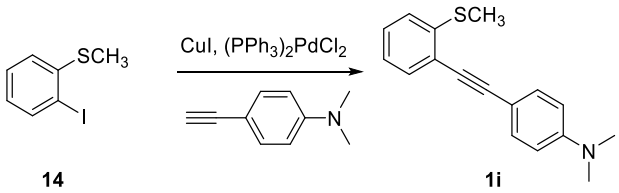
3-((2-(Methylthio)phenyl)ethynyl)thiophene (1h). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with **14** (0.35 mL, 2.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (88 mg, 0.13 mmol, 0.050 equiv), CuI (48 mg, 0.25 mmol, 0.10 equiv), Et_3N (5 mL), and a stir bar. 3-Ethynylthiophene (0.37 mL, 3.8 mmol, 1.5 equiv) was added to the reaction mixture via syringe. The vial containing the resulting mixture was then capped and removed from the glovebox, and the reaction mixture was stirred for 18 h. At this time, the reaction mixture was diluted with 100 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 10% EtOAc in hexanes.

Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1h** as a yellow oil (520 mg, 92% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.48 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 9.2 Hz, 1H), 7.21–7.18 (m, 2 H), 7.16–7.14 (m, 1H), 7.06 (d, *J* = 9.7 Hz, 1H), 7.01 (t, *J* = 9.0 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ 141.7, 132.3, 130.0, 129.0, 128.9, 125.6, 124.4, 124.2, 122.3, 121.3, 91.2, 86.6, 15.1.

HRMS (ESI+): Calculated for $C_{13}H_{10}S_2Na$ ([M+Na]$^+$), 253.0122; found 253.0117.



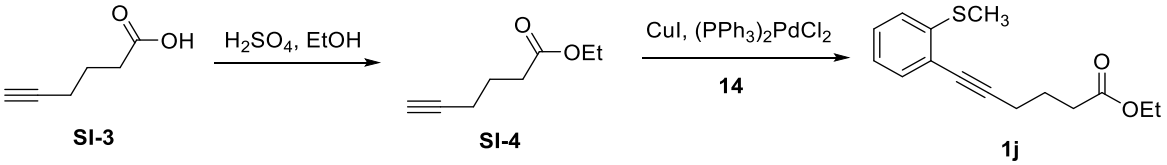
14 **1i**

***N,N*-Dimethyl-4-((2-(methylthio)phenyl)ethynyl)aniline (1i)**. In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.42 mL, 3.0 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (42 mg, 0.060 mmol, 0.020 equiv), CuI (6 mg, 0.03 mmol, 0.01 equiv), and a stir bar. In a separate dram vial, 4-ethynyl-*N,N*-dimethylaniline (500. mg, 3.45 mmol, 1.15 equiv) was dissolved in Et_3N (6 mL). This solution was then added to the vial containing the reaction mixture. The vial containing the resulting mixture was then capped, removed from the glovebox, and the solution was stirred for 18 h. At this time, TLC indicated complete consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 25 mL), water (1 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 20% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1i** as a yellow solid (780 mg, 97% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47 (d, *J* = 10.9 Hz, 3H), 7.26 (t, *J* = 9.5 Hz, 1H), 7.16 (d, *J* = 9.3 Hz, 1H), 7.10 (t, *J* = 9.0 Hz, 1H), 6.66 (d, *J* = 10.7 Hz, 2H), 2.99 (s, 6H), 6.51 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 150.3, 141.1, 132.8, 131.9, 128.0, 124.3, 124.1, 122.3, 111.9, 110.0, 97.4, 85.0, 40.3, 15.2.

HRMS (ESI+): Calculated for $C_{17}H_{17}NSNa$ ([M+Na]$^+$), 290.0979; found 290.0985.



SI-3 **SI-4** **1j**

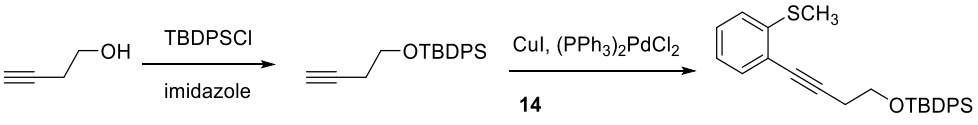
Ethyl hex-5-ynoate (SI-4) was prepared according to a literature procedure[5] in 87% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.14 (q, *J* = 7.1 Hz, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.27 (dt, *J* = 7.0, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.85 (quin, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[5]

Ethyl 6-(2-(methylthio)phenyl)hex-5-ynoate (1j). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.21 mL, 1.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (21 mg, 0.030 mmol, 0.020 equiv), CuI (2.9 mg, 0.015 mmol, 0.010 equiv), and a stir bar. In a separate dram vial, **SI-4** (250 mg, 1.8 mmol, 1.2 equiv) was dissolved in Et_3N (3 mL). This solution was then added to the reaction mixture. The vial containing the resulting mixture was capped, removed from the glovebox, and the solution was stirred for 18 h. The reaction mixture was then diluted with 150 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 25 mL), water (1 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 15% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1j** as a yellow oil (260 mg, 65% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.35 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 4.14 (q, *J* = 7.9 Hz, 2H), 2.57 (q, *J* = 7.0 Hz, 4H), 3.47 (s, 3H), 1.97 (quin, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 173.3, 141.3, 132.3, 128.3, 124.2, 123.8, 121.7, 95.9, 79.0, 60.4, 33.2, 24.0, 19.2, 15.0, 14.3.

HRMS (ESI+): Calculated for $C_{15}H_{18}O_2SNa$ ([M+Na]$^+$), 285.0925; found 285.0917.



SI-5 **SI-6** **1k**

(But-3-yn-1-yloxy)(tert-butyl)diphenylsilane (SI-6) was prepared according to a literature procedure[6] in 82% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.68 (d, *J* = 6.7 Hz, 4H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 4H), 3.79 (t, *J* = 7.0 Hz, 2H), 2.45 (dt, *J* = 7.1 2.6 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.06 (s, 9H). This spectrum is in agreement with previously reported spectral data.[6]

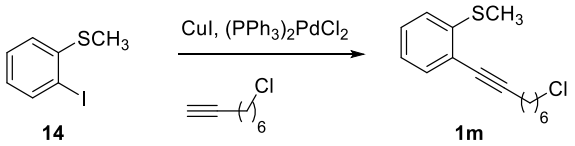
***tert*-Butyl((4-(2-(methylthio)phenyl)but-3-yn-1-yl)oxy)diphenylsilane** (**1k**). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.35 mL,

2.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (88 mg, 0.13 mmol, 0.050 equiv), CuI (48 mg, 0.25 mmol, 0.10 equiv), and a stir bar. In a separate dram vial, **SI-6** (1.2 g, 3.8 mmol, 1.5 equiv) was dissolved in Et_3N (5 mL). This solution was then added to the reaction mixture. The vial containing this resulting mixture was then capped and removed from the glovebox, and the solution was stirred for 18 h. The reaction mixture was then diluted with 200 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 25 mL), water (1 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1k** as a viscous yellow oil (610 mg, 57% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.74–7.72 (m, 4H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.40–7.37 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.26–7.24 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 3.94–3.91 (m, 2H), 2.79 (dt, *J* = 8.6, 1.6 Hz, 2H), 2.45 (s, 3H), 1.09 (s, 9H).

^{13}C NMR ($CDCl_3$. 151 MHz): δ 141.3, 135.7, 133.8, 132.5, 129.8, 128.3, 127.8, 124.2, 124.0, 121.9, 94.1, 79.2, 62.6, 26.9, 24.0, 19.4, 15.1.

HRMS (ESI+): Calculated for $C_{27}H_{30}OSSiNa$ ($[M+Na]^+$), 453.1684; found 453.1667.



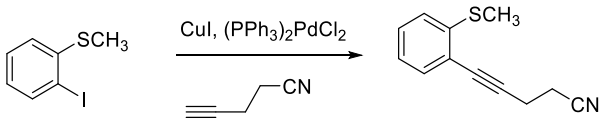
14 **1m**

(2-(8-Chlorooct-1-yn-1-yl)phenyl)(methyl)sulfane (1m). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.31 mL, 2.2 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (77 mg, 0.11 mmol, 0.050 equiv), CuI (42 mg, 0.22 mmol, 0.10 equiv), Et_3N (6.7 mL), and a stir bar. 8-Chloro-1-octyne (0.51 mL, 3.3 mmol, 1.5 equiv) was then added via syringe. The vial containing the resulting mixture was then capped and removed from the glovebox, and the solution was stirred for 18 h. The reaction mixture was then diluted with 200 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 25 mL), water (1 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1m** as a viscous yellow oil (520 mg, 89% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.24 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H) 7.05 (t, *J* = 7.5 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.50 (t, *J* = 6.9 Hz, 2H), 2.46 (s, 3H), 1.80 (quin, *J* = 6.8 Hz, 2H), 1.66 (quin, *J* = 6.9 Hz, 2H), 1.57–1.47 (m, 4H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ 141.3, 132.2, 128.2, 124.1, 123.7, 121.9, 97.1, 78.4, 45.1, 32.6, 28.5, 28.1, 26.5, 19.6, 15.0.

HRMS (CI+): Calculated for $C_{15}H_{19}ClSH$ ([M+H]$^+$), 267.0974; found 267.0972.



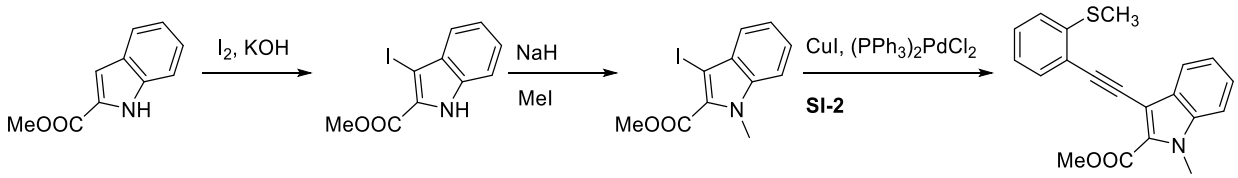
14 **1n**

5-(2-(Methylthio)phenyl)pent-4-ynenitrile (1n). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with *o*-iodothioanisole **14** (0.35 mL, 2.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (88 mg, 0.13 mmol, 0.050 equiv), CuI (48 mg, 0.25 mmol, 0.10 equiv), Et_3N (5 mL), and a stir bar. 4-Pentynenitrile (0.33 mL, 3.8 mmol, 1.5 equiv) was then added via syringe. The vial containing this resulting mixture was then capped and removed from the glovebox, and the solution was stirred for 18 h. The reaction mixture was then diluted with 200 mL EtOAc and washed with saturated aqueous NH_4Cl (1 × 25 mL), water (1 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 20% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1n** as a yellow oil (260 mg, 51% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.1 Hz, 1H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.1 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.6, 132.6, 129.0, 124.2, 123.9, 120.7, 118.5, 92.0, 80.6, 17.7, 17.1, 15.0.

HRMS (CI+): Calculated for $C_{12}H_{11}SNH$ ([M+H]$^+$), 202.0690; found 202.0681.



SI-7 **SI-8** **SI-9** **1o**

Methyl 3-iodo-1H-indole-2-carboxylate (SI-8) was prepared according to a literature procedure[7] in 71% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.32 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.39–7.37 (m, 2H), 7.25–7.22 (m, 1H), 4.00 (s, 3H). This spectrum is in agreement with previously reported spectral data.[7]

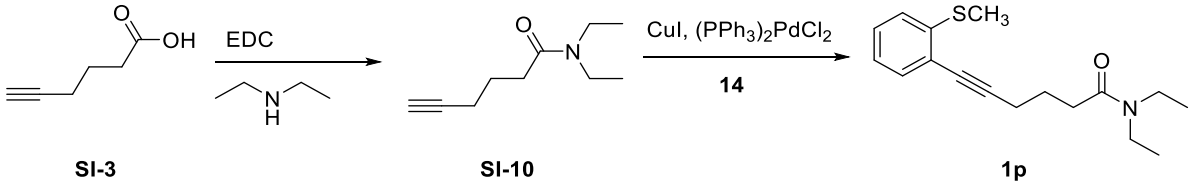
Methyl 3-iodo-1-methyl-1H-indole-2-carboxylate (SI-9) was prepared according to a literature procedure[7] in 63% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57 (d, *J* = 8.1 Hz, 1H), 7.40 (ddd, *J* = 15.2, 6.8, 1.1 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.23 (ddd, *J* = 14.9, 6.9, 0.9 Hz, 1H), 4.07 (s, 3H), 3.99 (s, 3H). This spectrum is in agreement with previously reported spectral data.[7]

Methyl 1-methyl-3-((2-(methylthio)phenyl)ethynyl)-1H-indole-2-carboxylate (1o). In an N_2-filled glovebox, a 20 mL scintillation vial was charged with **SI-9** (0.37 g, 1.2 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (17 mg, 0.024 mmol, 0.020 equiv), CuI (2.2 mg, 0.012 mmol, 0.010 equiv), Et_3N (1.5 mL), and a stir bar. In a separate dram vial, **SI-2** (0.21 g, 1.4 mmol, 1.2 equiv) and Et_3N (1 mL) were sequentially added. This solution was then added to the reaction mixture via pipette. The vial containing the resulting mixture was then capped and removed from the glovebox, and the solution was stirred for 18 h. The reaction mixture was then diluted with 200 mL of Et_2O and washed with saturated aqueous NH_4Cl (1 × 25 mL), water (1 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 15% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1o** as a light yellow solid (330 mg, 69% yield).

^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 7.88 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 7.6, 1.1 Hz, 1H), 7.28–7.25 (m, 2H), 7.18–7.11 (m, 2H), 7.07 (d, J = 7.9 Hz, 1H), 7.00 (dt, J = 7.5, 0.9 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 2.41 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 162.3, 141.2, 138.6, 132.5, 128.8, 128.6, 128.3, 126.1, 124.4, 124.2, 122.3, 122.2, 121.7, 110.5, 105.0, 93.1, 89.6, 52.1, 32.4, 15.3.

HRMS (ESI+): Calculated for $C_{20}H_{17}NO_2SNa$ ($[M+Na]^+$), 358.0878; found 358.0870.



***N*,*N*-Diethylhex-5-ynamide (SI-10)** was prepared according to a literature procedure[8] in 94% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.38–3.32 (m, 4H), 2.46–2.43 (m, 2H), 2.28–2.26 (m, 2H), 1.95–1.94 (m, 1H), 1.89–1.85 (m, 2H). 1.19 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[8]

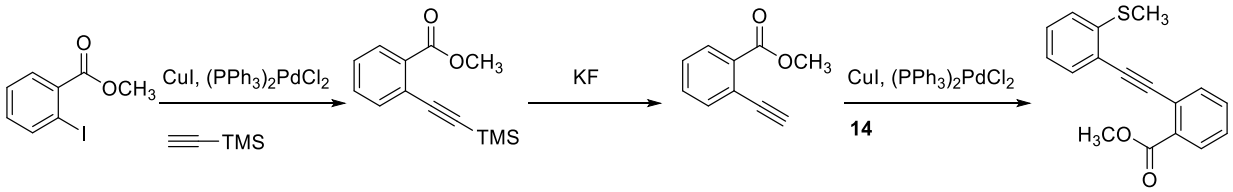
***N*,*N*-Diethyl-6-(2-(methylthio)phenyl)hex-5-ynamide (1p)**. A flask was charged with $(PPh_3)_2PdCl_2$ (42 mg, 0.060 mmol, 0.050 equiv), CuI (23 mg, 0.12 mmol, 0.10 equiv), and a stir bar. The flask was then connected to a Schlenk line and evacuated and refilled with N_2 three times before *o*-iodothioanisole **14** (0.17 mL, 1.2 mmol, 1.0 equiv) and Et_3N (3.6 mL) were added. Compound **SI-10** (0.30 g, 1.8 mmol, 1.5 equiv) was then added to the reaction mixture, and this solution was stirred for 18 h under dynamic N_2. At this time, analysis by TLC indicated full consumption of starting material. The reaction mixture was diluted with 200 mL DCM and washed with saturated NH_4Cl (1 × 30 mL), water (1 × 30 mL), and brine (1 × 30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column

chromatography using an elution gradient of 0% to 20% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1p** as a yellow oil (0.30 g, 87% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.29 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.19 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.99 (dt, *J* = 7.5, 1.0 Hz, 1H), 3.35–3.28 (m, 4H), 2.55–2.52 (m, 4H), 2.40 (s, 3H), 1,94 (quin, *J* = 6.8 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 171.7, 141.3, 132.4, 128.3, 124.3, 123.9, 122.0, 96.7, 78.9, 42.1, 40.3, 21.9, 24.4, 19.4, 15.1, 14.5, 13.3.

HRMS (ESI+): Calculated for $C_{17}H_{23}SNONa$ ([M+Na]$^+$), 312.1398; found 312.1392.



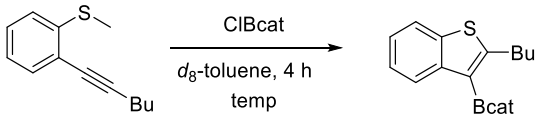
SI-11 **SI-12** **SI-13** **1q**

Methyl 2-((trimethylsilyl)ethynyl)benzoate (SI-12) was prepared according to a literature procedure[4] in 79% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.90 (app d, *J* = 7.6 Hz, 1H), 7.58 (app d, *J* = 7.5 Hz, 1H), 7.44 (td, *J* = 7.6, 0.8 Hz, 1H), 7.36 (app t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 0.27 (s, 9H). This spectrum is in agreement with previously reported spectral data.[4]

Methyl 2-ethynylbenzoate (SI-13) was prepared according to a literature procedure[4] in 84% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 3.40 (s, 1H). This spectrum is in agreement with previously reported spectral data.[4]

Methyl 2-((2-(methylthio)phenyl)ethynyl)benzoate (1q) was prepared according to a literature procedure[4] in 70% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.73 (dd. *J* = 7.6, 1.1 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.39 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.31 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.13 (dt, *J* = 7.5, 0.9 Hz, 1H), 3.93 (s, 3H), 3.39 (s, 3H). This spectrum is in agreement with previously reported spectral data.[4]

B. Reaction Condition Optimization



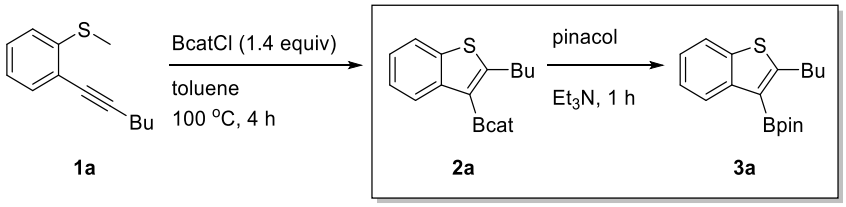
1a **2a**

In an N_2-filled glovebox, to a dram vial containing **1a** (80. mg, 0.39 mmol, 1.0 equiv) was added 1,3,5-triisopropylbenzene (20. μl, 0.083 mmol, 0.21 equiv) as an internal standard. To this mixture was added d_8-toluene (0.5–1.3 M with respect to **1a**). This mixture was then added to a dram vial containing *B*-chlorocatecholborane (1.0–1.4 equiv). After swirling to mix thoroughly, the reaction mixture was transferred to a J. Young NMR tube, which was capped, removed from the glovebox, and heated in a preheated oil bath for 4 h. The progress of the reaction was then examined at t = 4 h by single scan ^{1}H NMR spectroscopy, with the characteristic product (**2a**) peak at δ = 8.61 ppm in the ^{1}H NMR spectrum employed for integration relative to the internal standard. Entries 1–4 examined the effect of the equiv of ClBcat. Entries 5–8 examined the temperature dependence of the reaction, and entries 9–11 examined the effect of the concentration of **1a**. Entry 5 was found to be the best reaction conditions.

Table S1. Optimization of the Thioboration Reaction Conditions

Entry	ClBcat equiv	Concentration of 1a	Temp	^{1}H NMR Yield of 2a
1	1.0 equiv	1.3 M	100 °C	91
2	1.1 equiv	1.3 M	100 °C	91
3	1.2 equiv	1.3 M	100 °C	87
4	1.3 equiv	1.3 M	100 °C	91
5	1.4 equiv	1.3 M	100 °C	96
6	1.4 equiv	1.3 M	80 °C	78
7	1.4 equiv	1.3 M	60 °C	44
8	1.4 equiv	1.3 M	40 °C	27
9	1.4 equiv	0.5 M	100 °C	85
10	1.4 equiv	1.0 M	100 °C	86
11	1.4 equiv	1.5 M	100 °C	88

Table S2. Optimization of the Isolation Conditions of the Thioboration Reaction



In an N_2-filled glovebox, a dram vial was charged with **1a** (100. mg, 0.491 mmol, 1.00 equiv), which was then dissolved in toluene (0.38 mL) and added to a dram vial containing *B*-chlorocatecholborane (106 mg, 0.690 mmol, 1.40 equiv). The reaction mixture was sealed with a cap and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and diluted with 0.38 mL of toluene. In a separate vial, pinacol (1.5–3.0 equiv) was dissolved in Et_3N (1.0 mL, 7.4 mmol, 15 equiv). This solution was then added to the reaction mixture and a stir bar was added. The reaction mixture was sealed with a cap, brought out of the glovebox, and stirred for 1 h at room temperature. The

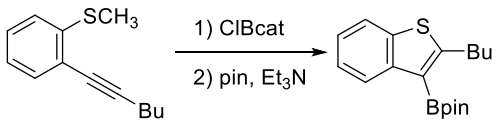
reaction mixture was then concentrated on a rotary evaporator (~10 Torr at 35 °C). An aliquot of this residue was removed and its mass was recorded as a fraction of the whole. To this aliquot was added 1,3,5-triisopropylbenzene, and this mixture was dissolved in $CDCl_3$. The ^1H NMR yield was calculated using the characteristic product (**3a**) peak at δ = 8.30 ppm in the ^1H NMR spectrum. Entry 3 was identified to be the best isolation conditions.

Entry	Pinacol equiv	^1H NMR yield of 3a
1	1.5	72
2	2.0	81
3	2.5	95
4	3.0	85

C. Synthesis and Isolation of Thioboration Products 3a–3q

General Remarks

For synthetic ease, all reactions were carried out in an N_2-filled glovebox unless otherwise specified. *B*-Chlorocatecholborane is water reactive and should be stored cool (0 °C or lower) when not in use. The ipso C–B bond is not detected by ^{13}C NMR spectroscopy.



1a **3a**

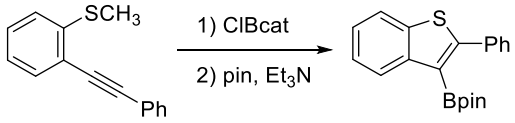
2-(2-Butylbenzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a). A dram vial was charged with **1a** (0.100 g, 0.490 mmol, 1.00 equiv) and 0.4 mL toluene. A separate vial was charged with *B*-chlorocatecholborane (0.106 g, 0.690 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial. This vial was then capped and then heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with 0.4 mL toluene. A separate vial was then charged with pinacol (0.174 g, 1.47 mmol, 2.50 equiv), Et_3N (1.0 mL, 7.4 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was then capped, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3a** as a yellow oil (0.13 g, 82% yield).

^1H NMR ($CDCl_3$, 600 MHz): δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.35 (td, *J* = 7.1, 1.1 Hz, 1H), 7.27–7.25 (m, 1H), 3.26 (t, *J* = 7.6 Hz, 2H), 1.75 (q, *J* = 7.4 Hz, 2H), 1.46 (sext., *J* = 7.4 Hz, 2H), 1.40 (s, 12H), 0.98 (t, *J* = 7.4, Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 161.5, 144.7, 139.5, 125.0, 124.2, 123.4, 121.6, 83.2, 35.0, 30.7, 25.1, 22.5, 14.0.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.3.

HRMS (ESI+): Calculated for $C_{18}H_{25}SBO_2Na$ ([M+Na]$^+$), 339.1570; found 339.1572.



1b **3b**

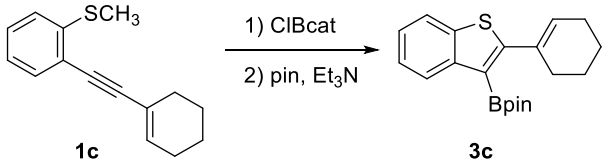
4,4,5,5-Tetramethyl-2-(2-phenylbenzo[*b*]thiophen-3-yl)-1,3,2-dioxaborolane (3b). A dram vial was charged with **1b** (67 mg, 0.30 mmol, 1.0 equiv) and toluene (0.2 mL). A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was capped and heated at 100 ^{o}C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.2 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.62 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was then capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3b** as a yellow oil (81 mg, 80% yield).

^{1}H NMR ($CDCl_3$, 600MHz): δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.64–7.62 (m, 2H), 7.42–7.38 (m, 4H), 7.32 (td, *J* = 8.1, 1.1 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.1, 144.9, 140.7, 135.6, 130.0, 128.5, 128.1, 125.3, 124.6, 124.1, 121.7, 83.8, 24.9.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.9.

HRMS (ESI+): Calculated for $C_{18}H_{25}SBO_2Na$ ([M+Na]$^+$), 339.1570; found 339.1572.



1c **3c**

2-(2-(Cyclohex-1-en-1-yl)benzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c). A dram vial was charged with **1c** (69 mg, 0.30 mmol, 1.0 equiv) and 0.2 mL toluene. A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was then capped and heated at 100 ^{o}C for 4 h. The reaction mixture was then cooled to room temperature and

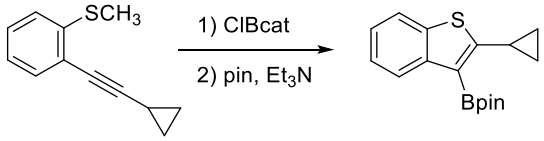
then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.63 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was then capped, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3c** as a yellow oil (88 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.18 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.36 (dd, J = 7.1, 1.1 Hz, 1H), 7.2 (dd, J = 7.2, 1.2 Hz, 1H), 6.10–6.08 (m, 1H), 2.54–2.51 (m, 2H), 2.26–2.23 (m, 2H), 1.85–1.81 (m, 2H), 1.75–1.71 (m, 2H), 1.42 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.4, 144.5, 139.5, 133.5, 129.4, 145.8, 124.2, 123.7, 121.6, 83.5, 30.7, 25.8, 25.0, 23.0, 22.0.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.1.

HRMS (CI+): Calculated for $C_{20}H_{25}SBO_2$ ($[M]^+$), 340.1672; found 340.1679.



1d **3d**

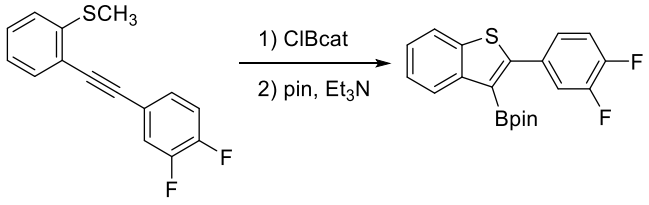
2-(2-Cyclopropylbenzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d). A dram vial was charged with **1d** (56 mg, 0.30 mmol, 1.0 equiv) and 0.2 mL toluene. A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was then capped and heated at 100 ^{o}C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.63 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3d** as a yellow solid (72 mg, 80% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.31 (d. J = 8.1 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 3.13–3.08 (m, 1H), 1.43 (s, 12H), 1.22–1.19 (m, 2H), 0.93–0.90 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 164.8, 144.9, 137.7, 124.6, 124.3, 123.3, 121.6, 83.2, 25.1, 13.3, 12.6.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.7.

HRMS (CI+): Calculated for $C_{17}H_{21}SBO_2$ ($[M]^+$), 300.1359; found 300.1361.



1e **3e**

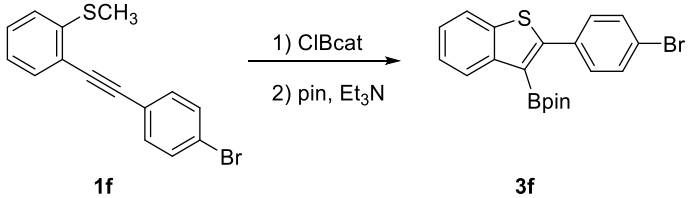
2-(2-(3,4-Difluorophenyl)benzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e). A dram vial was charged with **1e** (104 mg, 0.400 mmol, 1.00 equiv) and toluene (0.3 mL). A separate vial was charged with *B*-chlorocatecholborane (86 mg, 0.56 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the boron-containing vial, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.3 mL). A separate vial was then charged with pinacol (118 mg, 1.00 mmol, 2.50 equiv), Et_3N (0.83 mL, 6.0 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3e** as a light yellow solid (130 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.49–7.45 (m, 1H), 7.40 (t. *J* = 8.0 Hz, 1H), 7.35–7.32 (m, 2H), 7.18 (dt, *J* = 10.0, 8.4 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 152.6, 151.2 (dd, *J* = 126.2, 16.9 Hz), 149.2 (dd, *J* = 116.4, 17.0 Hz), 144.7, 140.5, 132.5 (dd, *J* = 6.7, 3.9 Hz), 126.1 (dd, *J* = 6.3, 3.5 Hz), 125.6, 124.8, 124.6, 121.7, 119.2 (d, *J* = 18.1 Hz), 116.9 (d, *J* = 17.4 Hz), 83.9, 24.9,

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.8.

HRMS (ESI+): Calculated for $C_{20}H_{19}SBF_2O_2Na$ ($[M+Na]^+$), 395.1068; found 395.1055.



1f **3f**

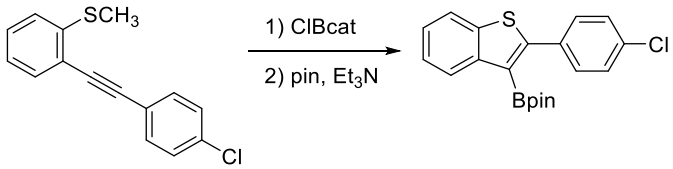
2-(2-(4-Bromophenyl)benzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f). A dram vial was charged with **1f** (91 mg, 0.30 mmol, 1.0 equiv) and toluene (0.2 mL). A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the boron-containing vial, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.2 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.63 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3f** as a yellow solid (110 mg, 89% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.51 (q, *J* = 8.5 Hz, 4H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.7, 144.9, 140.6, 134.5, 131.5, 131.2, 125.5, 124.7, 124.4, 122.8, 121.7, 83.8, 24.9.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.8.

HRMS (ESI+): Calculated for $C_{20}H_{20}SBBrO_2Na$ ([M+Na]$^+$), 473.0362; found 473.0355.



1h **3g**

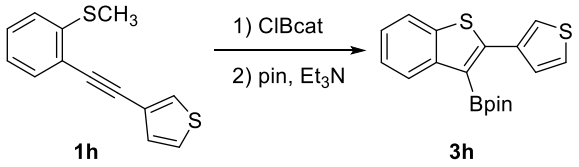
2-(2-(4-Chlorophenyl)benzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g). A dram vial was charged with **1g** (91 mg, 0.35 mmol, 1.0 equiv) and toluene (0.3 mL). A separate vial was charged with *B*-chlorocatecholborane (75 mg, 0.49 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.3 mL). A separate vial was then charged with pinacol (104 mg, 0.880 mmol, 2.50 equiv), Et_3N (0.73 mL, 5.3 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3g** as a white solid (92 mg, 71% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.42–7.36 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.7, 144.8, 140.6, 134.6, 134.1, 131.3, 128.2, 125.5, 124.7, 124.4, 121.7, 83.9, 24.9.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.6.

HRMS (ESI+): Calculated for $C_{20}H_{20}SBClO_2Na$ ([M+Na]$^+$), 393.0867; found 393.0864.



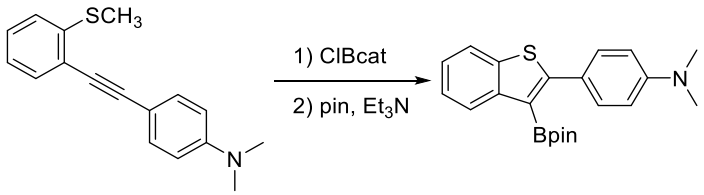
4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)benzo[*b*]thiophen-3-yl)-1,3,2-dioxaborolane (3h). A dram vial was charged with **1h** (92 mg, 0.40 mmol, 1.0 equiv) and toluene (0.3 mL). A separate vial was charged with *B*-chlorocatecholborane (86 mg, 0.56 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.3 mL). A separate vial was then charged with pinacol (120 mg, 1.0 mmol, 2.5 equiv), Et_3N (0.83 mL, 6.0 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3h** as a brown solid (0.10 g, 76% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.44 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.34 (td, *J* = 7.3, 1.1 Hz, 1H), 7.33 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.30 (app. t, *J* = 7.6 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 149.0, 145.0, 139.9, 136.0, 129.4, 125.3, 125.0, 124.8, 124.6, 124.2, 121.6, 83.8, 25.0.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.0.

HRMS (ESI+): Calculated for $C_{18}H_{19}S_2BO_2Na$ ([M+Na]$^+$), 365.0821; found 365.0814.



1i **3i**

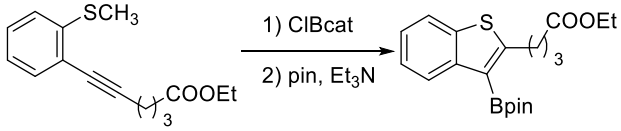
***N*,*N*-dimethyl-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)aniline (3i)**. A dram vial was charged with **1i** (80. mg, 0.30 mmol, 1.0 equiv) and toluene (0.2 mL). A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.2 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.62 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3i** as a yellow solid (68 mg, 60% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 6.3 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.02 (s, 6H), 1.37 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.2, 150.8, 145.4, 140.2, 130.7, 124.8, 124.3, 123.6, 123.5, 121.6, 111.8, 83.6, 40.6, 25.0.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.9.

HRMS (ESI+): Calculated for $C_{22}H_{26}SBNO_2Na$ ([M+Na]$^+$), 402.1679; found 402.1679.



1j **3j**

Ethyl-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)butanoate (3j). A dram vial was charged with **1j** (79 mg, 0.30 mmol, 1.0 equiv) and toluene (0.2 mL). A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the borane-containing vial, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.2 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.62 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction

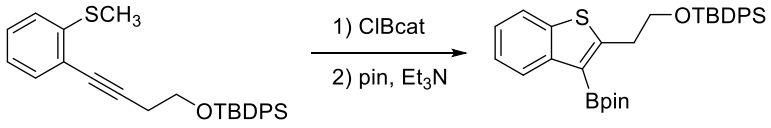
mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3j** as a viscous oil (87 mg, 77% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.27 (t, *J* = 7.1 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 7.4 Hz, 2H), 2.41 (t, *J* = 7.6 Hz, 2H), 2.09 (quin, *J* = 7.7 Hz, 2H), 1.40 (s, 12H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 173.4, 159.6, 144.5, 139.5, 125.1, 124.3, 123.6, 121.6, 83.2, 60.3, 33.7, 30.1, 27.7, 25.0, 14.3.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.3.

HRMS (ESI+): Calculated for $C_{20}H_{27}SBO_4Na$ ([M+Na]$^+$), 397.1625; found 397.1613.



1k **3k**

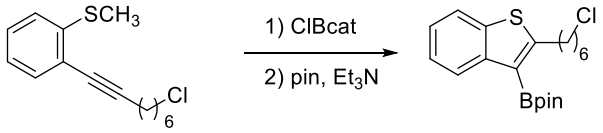
***tert*-Butyldiphenyl(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)ethoxy)silane (3k)**. A dram vial was charged with **1k** (110 mg, 0.25 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (54 mg, 0.35 mmol, 1.4 equiv) and toluene (0.2 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1k**, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.5 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.63 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3k** as a yellow oil (65 mg, 48% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.34 (d. *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 4H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.35–7.32 (m, 5H), 7.23–7.25 (m, 1H), 3.98 (t, *J* = 6.7 Hz, 2H), 3.53 (t, *J* = 6.4 Hz, 2H), 1.32 (s, 12H), 1.07 (s, 9H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 156.9, 144.4, 140.0, 135.7, 133.9, 129.6, 127.7, 125.1, 124.1, 123.5, 121.5, 83.2, 65.3, 34.4, 27.0, 25.0, 19.3.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 28.9.

HRMS (ESI+): Calculated for $C_{32}H_{39}SBO_3SiNa$ ([M+ Na]$^+$), 565.2386; found 565.2408.



1m **3m**

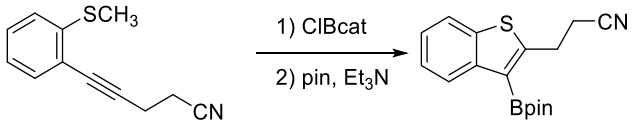
2-(2-(6-chlorohexyl)benzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m). A dram vial was charged with **1m** (80. mg, 0.30 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv) and toluene (0.2 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1m**, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.2 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.63 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3m** as a yellow oil (0.10 g, 89% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.31 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.34 (td, *J* = 7.3, 1.0 Hz, 1H), 7.26–7.23 (m, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.23 (t, *J* = 7.5 Hz, 2H), 1.81–1.73 (m, 4H), 1.51–1.42 (m, 4H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 161.0, 144.6, 139.4, 125.0, 124.2, 123.5, 121.6, 83.2, 45.3, 32.7, 32.6, 30.8, 28.5, 26.7, 25.1.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.2.

HRMS (ESI+): Calculated for $C_{20}H_{28}SBO_2ClNa$ ([M+ Na]$^+$), 401.1493; found 401.1486.



1n **3n**

3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)propanenitrile (3n). A dram vial was charged with **1n** (60. mg, 0.30 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (65 mg, 0.42 mmol, 1.4 equiv) and toluene (0.2 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1n**, and this vial was then sealed and heated at 100 °C for 4 h. The reaction mixture was then cooled to room

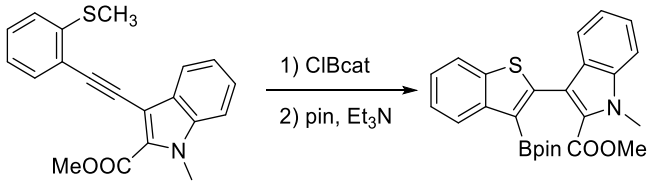
temperature and then diluted with toluene (0.2 mL). A separate vial was then charged with pinacol (89 mg, 0.75 mmol, 2.5 equiv), Et_3N (0.63 mL, 4.5 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3n** as a yellow solid (64 mg, 65% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36 (app. d, J = 8.0 Hz, 1H), 7.78 (dt, J = 7.1, 1.1 Hz, 1H), 7.37 (ddd, J = 15.2, 6.8, 1.2 Hz, 1H), 7.30 (ddd, J = 15.1, 6.9, 1.3 Hz, 1H), 3.55 (t, J = 7.5 Hz, 2H), 2.76 (t, J = 7.7 Hz, 2H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.7, 144.3, 139.5, 125.6, 124.7, 124.3, 121.8, 119.0, 83.7, 27.0, 25.1, 20.1.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.0

HRMS (ESI+): Calculated for $C_{17}H_{20}SBNO_2Na$ ([M+ Na]$^+$), 336.1209; found 336.1206.



1o **3o**

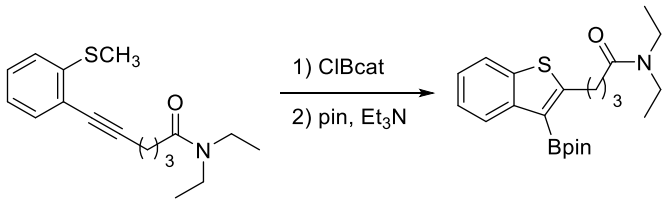
Methyl 1-methyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)-1*H*-indole-2-carboxylate (3o). A dram vial was charged with **1o** (116 mg, 0.350 mmol, 1.00 equiv). A separate vial was charged with *B*-chlorocatecholborane (75 mg, 0.49 mmol, 1.4 equiv) and toluene (0.3 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1o**, and this vial was then capped and heated at 100 ^{o}C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.3 mL). A separate vial was then charged with pinacol (103 mg, 0.880 mmol, 2.50 equiv), Et_3N (0.73 mL, 5.3 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3o** as a yellow solid (98 mg, 63% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.33 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.44–7.34 (m, 4H), 7.14 (td, J = 7.3, 0.8 Hz, 1H), 4.14 (s, 3H), 3.68 (s, 3H), 1.18 (s, 6H), 1.07 (s, 6H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 163.0, 147.5, 144.4, 141.2, 138.3, 128.0, 126.6, 125.4, 125.2, 124.2, 123.8, 122.1, 121.6, 120.9, 117.3, 110.0, 83.1, 51.6, 32.2, 25.0, 24.7.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.6.

HRMS (ESI+): Calculated for $C_{25}H_{26}SBNO_4Na$ ([M+ Na]$^+$), 470.1578; found 470.1559.



1p **3p**

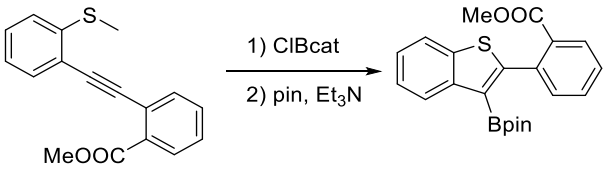
***N*,*N*-Diethyl-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)butanamide (3p)**. A dram vial was charged with **1p** (170 mg, 0.58 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (130 mg, 0.81 mmol, 1.4 equiv) and toluene (0.5 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1q**, and this vial was then capped and heated at 100 °C for 24 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.5 mL). A separate vial was then charged with pinacol (170 mg, 1.5 mmol, 2.5 equiv), Et_3N (1.1 mL, 7.9 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. At this time, the reaction mixture was diluted with 100 mL EtOAc and washed with water (3 × 10 mL) and brine (1 × 10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 40% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3p** as a yellow solid (163 mg, 70% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.24 (dd, *J* = 7.4, 1.1 Hz, 1H), 3.36 (q, *J* = 7.1 Hz, 2H), 3.31 (t, *J* = 7.2 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.10 (quint., *J* = 7.3 Hz, 2H), 1.38 (s, 12H), 1.11–1.08 (m, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 171.9, 160.2, 144.6, 139.5, 125.1, 124.2, 123.5, 121.6, 83.2, 42.0, 40.1, 32.4, 30.4, 28.1, 25.1, 14.4, 13.2.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.3.

HRMS (ESI+): Calculated for $C_{22}H_{32}SNBO_3Na$ ([M+ Na]$^+$), 424.2098; found 424.2085.



1q **3q**

Methyl 2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophen-2-yl)benzoate (3q). A dram vial was charged with **1q** (93 mg, 0.33 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (71 mg, 0.46 mmol, 1.4 equiv) and toluene (0.3 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1q**, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.3 mL). A separate vial was then charged with pinacol (97 mg, 0.83 mmol, 2.5 equiv), Et_3N (0.69 mL, 5.0 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3q** as a yellow solid (69 mg, 53% yield).

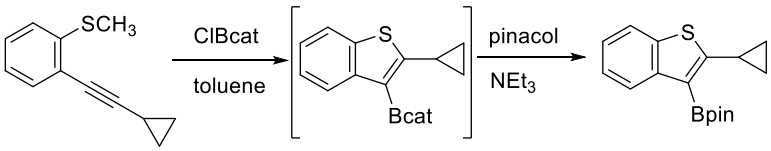
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32 (d. J = 8.0 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.52–7.45 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 3.64 (s, 3H), 1.18 (s, 12H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 167.6, 154.7, 143.9, 140.6, 136.8, 132.3, 131.8, 130.7, 129.8, 128.2, 125.6, 124.5, 124.0, 121.5, 83.2, 52.0, 24.8.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.2.

HRMS (ESI+): Calculated for $C_{22}H_{23}SBO_4Na$ ([M+ Na]$^+$), 417.1312; found 417.1305.

D. Multigram Scale Preparation of 3d

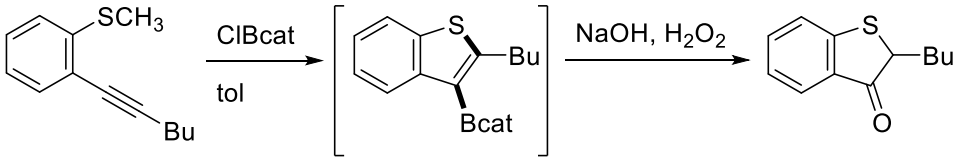


1d **2d** **3d**

In an N_2-filled glovebox, a Schlenk bomb was charged with a solution of **1d** (1.8 g, 9.7 mmol, 1.0 equiv) in toluene (3 mL) via pipette. A solution of *B*-chlorocatecholborane (2.1 g, 14 mmol, 1.4 equiv) in toluene (4.5 mL) was then added via pipette. The Schlenk bomb was then sealed, removed from the glovebox, and cooled to -78 °C using an isopropanol/dry ice bath. The headspace in the Schlenk bomb was then removed under reduced pressure (c.a. 10 mTorr for 10 sec) before resealing. The solution was then

stirred under static vacuum for 4 h at 100 °C in an oil bath. At this time, the reaction mixture was exposed to dynamic N_2 and cooled to room temperature before additional toluene (7 mL) was added. A solution of pinacol (2.9 g, 24 mmol, 3.0 equiv) in Et_3N (20. mL, 150 mmol, 15 equiv) was then added to the reaction mixture over 5 min and the resulting solution was stirred for 1 h at room temperature. The contents of the Schlenk bomb were then filtered over a bed of celite and rinsed with toluene (3 × 20 mL), and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3d** as a yellow solid (2.0 g, 69% yield). Spectral data were identical to those previously obtained for this compound.

E. In Situ Downstream Functionalization Reactions(Compounds 4–8)



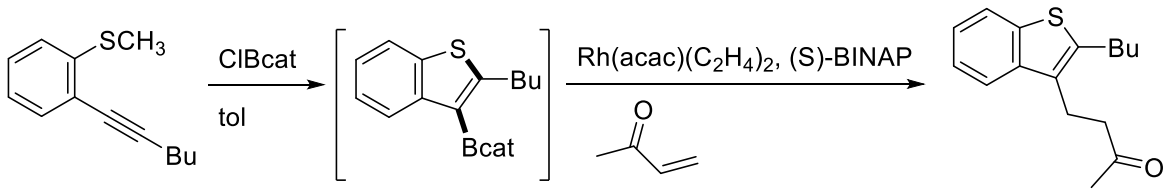
1a **2a** **4**

2-Butylbenzo[*b*]thiophen-3(2*H*)-one (4). In an N_2-filled glovebox, a dram vial was charged with **1a** (0.10 g, 0.49 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (106 mg, 0.690 mmol, 1.40 equiv) and toluene (0.4 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **1a**, and this vial was sealed, removed from the glovebox, and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and MeOH (1 mL) and a stir bar were added. NaOH (0.26 mL of a 3.0 M solution, 0.78 mmol, 1.6 equiv) and H_2O_2 (80. μL of a 30. wt% solution in H_2O, 0.78 mmol, 1.6 equiv) were then sequentially added. The reaction-containing vial was then capped and the solution was stirred for 1.5 h. The reaction mixture was then diluted with 100 mL EtOAc and washed with saturated NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **4** as a viscous yellow oil (73 mg, 72% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 3.20 (s, 1H), 2.07–2.03 (m, 1H), 1.95–1.90 (m, 1H), 1.64–1.58 (m, 1H), 1.36–1.33 (m, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 202.5, 150.6, 136.9, 128.4, 127.6, 125.3, 124.4, 93.5, 39.5, 26.7, 22.8, 14.0.

HRMS (CI+): Calculated for $C_{12}H_{15}SO$ ($[M+H]^+$), 207.0844; found 207.0844.



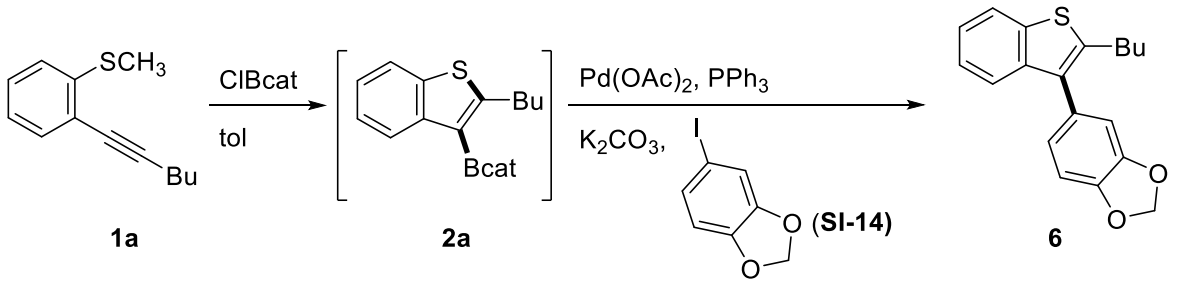
1a **2a** **5**

4-(2-Butylbenzo[*b*]thiophen-3-yl)butan-2-one (5). In an N_2-filled glovebox, a dram vial was charged with **1a** (0.200 g, 0.980 mmol, 2.00 equiv) and 0.8 mL toluene. A separate vial was charged with *B*-chlorocatecholborane (0.212 g, 1.37 mmol, 2.80 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 1 min to the boron-containing vial, and this mixture was heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature. A separate dram vial was charged with (S)-BINAP (15 mg, 0.25 mmol, 0.050 equiv) and a stir bar. A third dram vial was charged with $Rh(acac)(C_2H_4)_2$ (3.8 mg, 0.15 mmol, 0.030 equiv) and dioxane (0.5 mL). This solution was then added to the vial containing (S)-BINAP via pipette. To this vial was added the cooled reaction mixture, which was subsequently rinsed with dioxane (0.5 mL) to ensure quantitative transfer. The vial containing the resulting reaction mixture was then sealed with a septum vial cap, removed from the glovebox, and placed under dynamic N_2. Et_3N (0.34 mL, 2.5 mmol, 5.0 equiv), H_2O (0.1 mL), and methyl vinyl ketone (40. □L, 0.49 mmol, 1.0 equiv) were sequentially added via syringe. The vial was then removed from dynamic N_2, sealed with electrical tape, and heated to 100 °C. The reaction mixture then stirred for 3 h before being cooled to room temperature. The reaction mixture was diluted with 200 mL DCM and washed with saturated aqueous $NaHCO_3$ (1 × 20 mL), and water (3 × 15 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 20% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **5** as a yellow oil (91 mg, 71% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.28 (dd, *J* = 7.1, 1.1 Hz, 1H), 3.08 (t, *J* = 7.7 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.15 (s, 3H), 1.73–1.68 (m, 2H), 1.49–1.43 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 207.9, 141.3, 139.8, 138.5, 129.6, 123.9, 123.5, 122.4, 120.9, 43.4, 33.8, 30.1, 28.2, 22.5, 20.3, 14.0.

HRMS (ESI+): Calculated for $C_{16}H_{20}SONa$ ($[M+Na]^+$), 283.1133; found 283.1141.

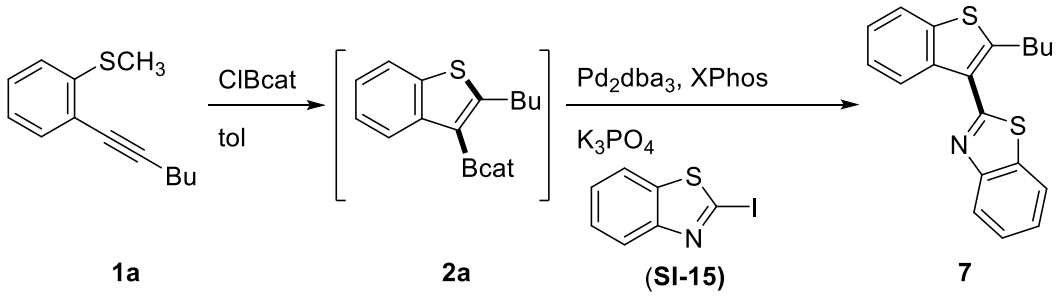


5-(2-Butylbenzo[*b*]thiophen-3-yl)benzo[*d*][1,3]dioxole (6). In an N_2-filled glovebox, a dram vial was charged with **1a** (82 mg, 0.40 mmol, 1.3 equiv). A separate vial was charged with *B*-chlorocatecholborane (86 mg, 0.56 mmol, 1.8 equiv) and toluene (0.3 mL). The resulting homogenous solution from the boron-containing vial was then added dropwise over c.a. 1 min to the vial containing **1a**, and this vial was sealed and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature. A separate dram vial was charged with $Pd(OAc)_2$ (9 mg, 0.04 mmol, 0.1 equiv), PPh_3 (21 mg, 0.080 mmol, 0.25 equiv), K_2CO_3 (0.20 mL of a 2.0 M solution, 0.40 mmol, 1.3 equiv), and EtOH (0.5 mL). This solution was then added to the vial containing the reaction mixture via pipette. A third dram vial was charged with **SI-14** (79 mg, 0.32 mmol, 1.0 equiv) and toluene (0.5 mL). This solution was then added to the vial containing the reaction mixture, and a stir bar was added. This vial was sealed and removed from the glovebox, and heated at 80 °C while stirring for 24 h. The reaction mixture was then diluted with 150 mL DCM and washed with saturated NH_4Cl (1 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **6** as a viscous yellow oil (65 mg, 66% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.83 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.52–7.51 (m, 1H), 7.33–7.30 (m, 2H), 7.0 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 1.3 Hz, 1H), 6.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.06 (s, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 1.71 (q, *J* = 7.7 Hz, 2H), 1.49–1.43 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 147.8, 146.9, 142.6, 140.6, 138.2, 133.1, 129.3, 124.2, 123.8, 123.6, 122.6, 122.2, 110.6, 108.6, 101.2, 34.0, 28.7, 22.4, 13.9.

HRMS (CI+): Calculated for $C_{19}H_{18}SO_2$ ($[M]^+$), 310.1028; found 310.1028.

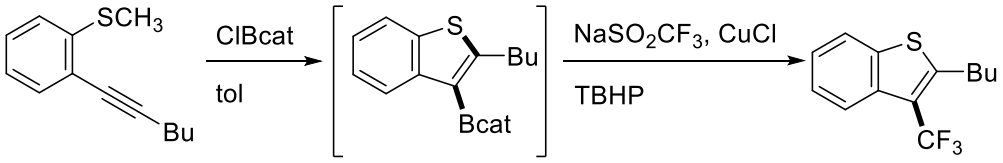


2-(2-Butylbenzo[*b*]thiophen-3-yl)benzo[*d*]thiazole (7). In an N_2-filled glovebox, a dram vial was charged with **1a** (123 mg, 0.600 mmol, 2.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (129 mg, 0.84 mmol, 2.8 equiv) and toluene (0.5 mL). The resulting homogenous solution from the boron-containing vial was then added dropwise over c.a. 1 min to the vial containing **1a**, and this vial was sealed and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature. A separate 20 mL scintillation vial was charged with Pd_2dba_3 (9 mg, 0.02 mmol, 0.05 equiv), XPhos (14 mg, 0.030 mmol, 0.10 equiv), **SI-15** (78 mg, 0.30 mmol, 1.0 equiv), K_3PO_4 (127 mg, 0.600 mmol, 1.00 equiv), and a stir bar. To this scintillation vial was added the contents from the dram vial, and 1-butanol (1.0 mL) was subsequently added. This vial was sealed and removed from the glovebox, and heated at 100 °C while stirring for 21 h. The reaction mixture was then diluted with 150 mL Et_2O, filtered over celite, washed with water (2 × 10 mL), and brine (1 × 10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 5% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **7** as a yellow solid (56 mg, 58% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.26 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 3.25 (t, *J* = 7.7 Hz, 2H) 1.80 (q, *J* = 7.7 Hz, 2H), 1.49–1.43 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 161.5, 153.5, 149.8, 139.0, 137.9, 135.4, 126.3, 125.5, 125.3, 125.0, 124.5, 123.5, 123.2, 122.1, 121.5, 33.8, 29.5, 22.6, 13.9.

HRMS (CI+): Calculated for $C_{19}H_{17}S_2N$ ($[M]^+$), 323.0802; found 323.0800.



1a **2a** **8**

2-Butyl-3-(trifluoromethyl)benzo[*b*]thiophene (8). In an N_2-filled glovebox, a dram vial was charged with **1a** (0.10 g, 0.49 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (76 mg, 0.49 mmol, 1.0 equiv) and toluene (0.4 mL). The resulting homogenous solution from the boron-containing vial was then added dropwise over c.a. 1 min to the vial containing **1a**, and this vial was sealed and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and the vial was removed from the glovebox. A round bottom flask was charged with $NaSO_2CF_3$ (230 mg, 1.5 mmol, 3.0 equiv), CuCl (49 mg, 0.49 mmol, 1.0 equiv), MeOH (1.0 mL), H_2O (0.8 mL), and a stir bar. To this flask was added the contents of the reaction-mixture containing vial, and this vial was rinsed with DCM (0.8 mL) and added to the flask. The flask was then sparged for 1 minute with N_2 before being cooled to 0 °C. *tert*-Butyl hydrogen peroxide (TBHP, 0.34 mL of a 70. wt% in H_2O solution, 2.5 mmol, 5.0 equiv) was added via syringe

over 2 min. The reaction mixture was stirred while warming to room temperature under dynamic N_2 for 18 h. The reaction mixture was then diluted with 150 mL Et_2O, filtered over celite, washed with saturated aqueous $NaHCO_3$ (1 × 15 mL), saturated aqueous $Na_2S_2O_3$ (1 × 15 mL), water (1 × 15 mL), and brine (1 × 15 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using 100% pentane as the eluent. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **8** as a white solid (47 mg, 37% yield).

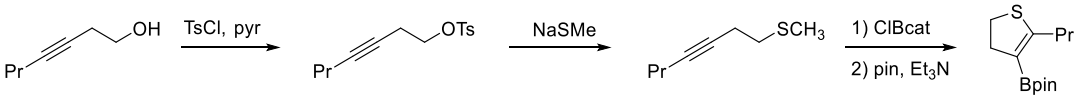
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.41 (td, *J* = 7.2, 1.1 Hz, 1H), 7.35 (td, *J* = 7.2, 1.1 Hz, 1H), 3.09–3.06 (m, 2H), 1.75 (q, *J* = 7.5 Hz, 2H), 1.46 (sext., *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 150.9 (q, *J* = 34 Hz), 137.7, 136.7, 125.1, 124.6, 123.6 (q, *J* = 272.3 Hz), 122.6 (q, *J* = 2.7 Hz), 122.0,120.1 (q, *J* = 32.8 Hz), 33.9, 29.1 (app. d, *J* = 2.0 Hz), 22.6, 13.9.

^{19}F NMR ($CDCl_3$, 565 MHz): δ 56.2 (s, 3F).

HRMS (CI+): Calculated for $C_{13}H_{13}SF_3$ ($[M]^+$), 258.0690; found 258.0697.

F. Borylated Dihydrothiophene Syntheses (Compounds 21a and 21b)



Hept-3-yn-1-yl 4-methylbenzenesulfonate (SI-17) was synthesized using a literature procedure[9] in 58% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 4.06 (q, *J* = 7.3 Hz, 2H), 2.51 (d, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.5 (d, *J* = 7.9 Hz, 2H), 1.44 (quin, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[9]

Hept-3-yn-1-yl(methyl)sulfane (18). A round bottom flask was charged with NaSMe (620 mg, 8.8 mmol, 2.0 equiv) and a stir bar. The flask was then sealed with a rubber septum and placed under dynamic N_2. To this flask was added DMF (5.5 mL). A separate flask was charged with **SI-17** (1.2 g, 4.4 mmol, 1.0 equiv), and DMF (5.5 mL). This solution was then transferred via syringe to the NaSMe-containing flask. The solution was then stirred for 18 h under dynamic N_2. At this time, the reaction mixture was diluted with 200 mL Et_2O, and the organic layer was washed with H_2O (8 × 15 mL) and brine (1 × 15 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to afford **18** as a yellow liquid that was used without further purification (260 mg, 41% yield).

^{1}H NMR (CDCl3, 600 MHz): δ 2.63 (t, *J* = 8.0 Hz, 2H), 2.47–2.44 (m, 2H), 2.14–2.11 (m, 5H), 1.50 (sext., *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 81.4, 78.6, 33.9, 22.5, 20.9, 20.0, 15.8, 13.6.

HRMS (CI+): Calculated for $C_8H_{14}SH$ ($[M+H]^+$), 143.0894; found 143.0896.

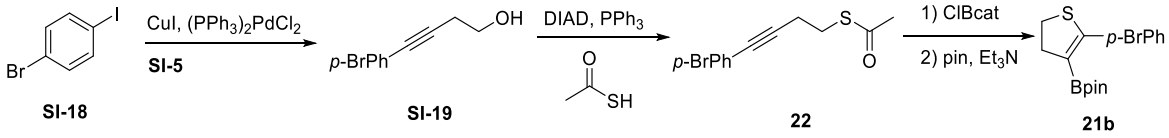
4,4,5,5-tetramethyl-2-(2-propyl-4,5-dihydrothiophen-3-yl)-1,3,2-dioxaborolane (21a). In an N_2-filled glovebox, a dram vial was charged with **18** (77 mg, 0.54 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (120 mg, 0.76 mmol, 1.4 equiv) and toluene (0.4 mL). The resulting homogenous solution from the boron-containing vial was then added dropwise over c.a. 1 min to the vial containing **18**, and this vial was then capped and heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.4 mL). A separate vial was then charged with pinacol (96 mg, 0.81 mmol, 1.5 equiv), Et_3N (0.37 mL, 2.7 mmol, 5 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **21a** as a yellow oil (83 mg, 60% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.13 (t, *J* = 8.6 Hz, 2H), 2.90 (t, *J* = 8.4 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.53 (q, *J* = 7.4 Hz, 2H), 1.24 (s, 12H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 161.8, 82.8, 39.9, 33.5, 32.8, 24.9, 23.2, 13.6.

^{11}B NMR (CDCl3, 193 MHz): δ 28.5.

HRMS (ESI+): Calculated for $C_{13}H_{24}SBO_2$ ($[M+H]^+$), 255.1593; found 255.1597.



4-(4-bromophenyl)but-3-yn-1-ol (SI-19) was synthesized using a literature procedure[10] in 82% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 3.82 (q, *J* = 5.6 Hz, 2H), 2.68 (t, *J* = 6.3 Hz, 2H), 1.76 (d, *J* = 6.3 Hz, 1H). This spectrum is in agreement with previously reported spectral data.[10]

S-(4-(4-bromophenyl)but-3-yn-1-yl) ethanethioate (22) was synthesized using an adapted procedure.[11] A round bottom flask was charged with PPh_3 (3.6 g, 14 mmol, 1.6 equiv) and a stir bar. This flask was sealed with a rubber septum and then THF (36 mL) was added. This solution was then cooled to 0 °C with an ice water bath. To this flask was added diisopropyl azodicarboxylate (DIAD, 2.7 mL, 14 mmol, 1.6 equiv) via syringe

over c.a. 10 min. This reaction mixture stirred at 0 °C for 30 min before a solution of **SI-19** (2.0 g, 8.9 mmol, 1.0 equiv) and thioacetic acid (1.0 mL, 14 mmol, 1.6 equiv) in THF (12 mL) was added over c.a. 5 min. The reaction mixture was then stirred under dynamic N_2 for 18 h while warming to room temperature. At this time, TLC indicated complete consumption of starting material. The reaction mixture was diluted with 150 mL Et_2O, and the organic layer was washed with saturated aqueous NH_4Cl (1 × 30 mL), water (1 × 30 mL), and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. To the resulting solid/oil mixture was added 50 mL of hexanes, and the resulting solution was filtered over a bed of celite to remove the precipitated PPh_3O. The filtrate was then concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient of 0% to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **22** as a yellow solid (2.1 g, 85% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.1 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 195.5, 133.2, 131.6, 122.5, 122.2, 89.0, 80.9, 30.8, 28.4, 20.7.

HRMS (CI+): Calculated for $C_{12}H_{12}BrOS$ ($[M+H]^+$), 282.9792; found 282.9804.

2-(2-(4-bromophenyl)-4,5-dihydrothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21b). In an N_2-filled glovebox, a dram vial was charged with **22** (110 mg, 0.39 mmol, 1.0 equiv). A separate vial was charged with *B*-chlorocatecholborane (83 mg, 0.54 mmol, 1.4 equiv) and toluene (0.3 mL). The resulting homogenous solution from the borane-containing vial was then added dropwise over c.a. 1 min to the vial containing **22**, and this vial was then capped and heated at 100 °C for 2 h. The reaction mixture was then cooled to room temperature and then diluted with toluene (0.3 mL). A separate vial was then charged with pinacol (170 mg, 1.4 mmol, 3.5 equiv), Et_3N (0.83 mL, 6.0 mmol, 15 equiv), and a stir bar. The reaction mixture was added dropwise over c.a. 1 min to this vial, which was capped, removed from the glovebox, and then stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 40% DCM/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **21b** as a yellow solid (76 mg, 52% yield).

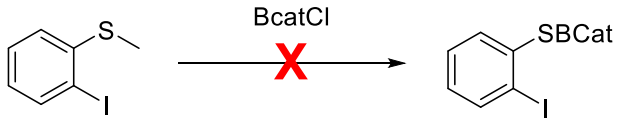
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.41 (app. d, J = 8.5 Hz, 2H), 7.36 (app. d, J = 8.5 Hz, 2H), 3.27 (t, J = 8.9 Hz, 2H), 3.12 (t, J = 8.3 Hz, 2H), 1.20 (s, 12H).

^{13}C NMR (CDCl3, 151 MHz): δ 155.4, 134.5, 130.9, 130.8, 122.7, 83.3, 42.1, 34.1, 24.7.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 28.8.

HRMS (ESI+): Calculated for $C_{16}H_{20}SBBrO_2Na$ ([M+Na]$^+$), 389.0361; found 389.0376.

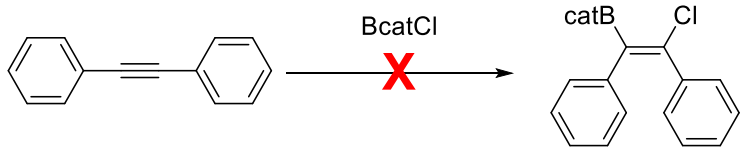
G. Procedure for ^{1}H NMR Spectroscopic characterization of the rate of demethylation of 2-iodothioanisole 14



14 **15**

This procedure was performed in an N_2-filled glovebox. A dram vial was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv) and 0.3 mL of d_8-toluene. To this vial was sequentially added **14** (75 μL, 0.50 mmol, 1.0 equiv) and mesitylene (40. μL, 0.17 mmol, 0.33 equiv) via syringe. The contents of this vial were then transferred to a J. Young NMR tube, which was sealed, and then removed from the glovebox and heated to 100 °C. Single-scan ^{1}H and ^{11}B NMR spectra were taken at time points *t* = 0 h, 2 h, and 4 h for which the tube was briefly removed from the heating bath. The resonances corresponding to **14** were compared to the internal standard to determine the percent of **14** remaining at *t* = 4 h (>95% **14** remaining at *t* = 4 h). Spectra are included in section IV.

H. Procedure for ^{1}H NMR spectroscopic characterization of the rate of chloroboration of diphenylacetylene 19



16 **17**

This procedure was performed in an N_2-filled glovebox. A dram vial was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv) and 0.3 mL of d_8-toluene. To this vial was sequentially added **16** (75 μL, 0.50 mmol, 1.0 equiv) and mesitylene (40. μL, 0.17 mmol, 0.33 equiv) via syringe. The contents of this vial were then transferred to a J. Young NMR tube, which was sealed, and then removed from the glovebox and heated to 100 °C. Single-scan ^{1}H and ^{11}B NMR spectra were taken at time points *t* = 0 h, 2 h, and 4 h for which the tube was briefly removed from the heating bath. The resonances corresponding to **16** were compared to the internal standard to determine the percent of **16** remaining at *t* = 4 h (>95% **16** remaining at *t* = 4 h). Spectra are included in section IV.

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IV. NMR Spectra