Supplementary Materials for

Catalyst-Free Synthesis of Borylated Lactones from Esters via Electrophilic Oxyboration

Darius J. Faizi, Adena Issaian, Ashlee J. Davis, and Suzanne A. Blum*
Department of Chemistry, University of California, Irvine, California 92697-2025
Email: blums@uci.edu

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I. General Methods

All chemicals were used as received from commercial sources unless otherwise noted. Triethylamine, acetonitrile, toluene, tetrahydrofuran, 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$_{254}$ 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-400 spectrometer, Bruker DRX-500 spectrometer outfitted with a cryoprobe, or a Bruker AVANCE-600 spectrometer. All boron nuclear magnetic resonance ($^{11}$B NMR) spectra were recorded on a Bruker AVANCE-600 spectrometer. All fluorine nuclear magnetic resonance ($^{19}$F NMR) spectra were recorded on a Bruker DRX-400. All chemical shifts ($\delta$) are reported in parts per million (ppm) downfield of tetramethylsilane, and referenced to the residual protiated solvent peak ($\delta$ = 7.26 ppm for CDCl$_3$, $\delta$ = 2.08 ppm for $d_8$-toluene, $\delta$ = 2.05 ppm for $d_6$-acetone, or $\delta$ = 1.94 ppm for CD$_3$CN in $^1$H NMR spectroscopy experiments; $\delta$ = 77.2 ppm for CDCl$_3$, $\delta$ = 29.8 ppm for $d_6$-acetone, $\delta$ = 20.4 ppm for $d_8$-toluene, or $\delta$ = 1.34 ppm for CD$_3$CN 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 Esters 1a-1p

**Methyl 2-(phenylethynyl)benzoate (1a).** A flask was charged with compound 10 (3.0 mL, 20 mmol, 1.0 equiv), (PPh₃)₂PdCl₂ (0.28 g, 0.40 mmol, 0.020 equiv), and CuI (0.15 g, 0.80 mmol, 0.040 equiv). The flask was then evacuated and refilled with N₂ three times before 40 mL of acetonitrile and Et₃N (22 mL, 160 mmol, 8.0 equiv) were added. Phenylacetylene (2.4 mL, 22 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N₂. At this time, analysis by TLC (5% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH₄Cl (1 × 45 mL), water (1 × 45 mL), brine (1 × 45 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 1a as a light yellow oil (4.2 g, 88% yield). ¹H NMR (CDCl₃, 600 MHz): δ 7.98 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.3 Hz, 1H), 7.59-7.57 (m, 2H), 7.40-7.35 (m, 4H), 3.97 (s, 3H). This spectrum is in agreement with previously reported spectral data.

**Methyl 2-(hex-1-yn-1-yl)benzoate (1b).** A flask was charged with compound 10 (0.73 mL, 5.0 mmol, 1.0 equiv), (PPh₃)₂PdCl₂ (0.070 g, 0.10 mmol, 0.020 equiv), and CuI (0.038 g, 0.20 mmol, 0.040 equiv). The flask was then evacuated and refilled with N₂ three times before 10 mL of acetonitrile and Et₃N (5.6 mL, 40 mmol, 8.0 equiv) were added. 1-Hexyne (0.63 mL, 5.5 mmol, 1.1 equiv) was then syringed into the reaction mixture, which then stirred for 18 h under dynamic N₂. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 100 mL EtOAc and washed with NH₄Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 1b as a light yellow oil (0.80 g, 74% yield). ¹H NMR (CDCl₃, 600 MHz): δ 7.88 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.3 Hz, 1H), 7.59-7.57 (m, 2H), 7.40-7.35 (m, 4H), 3.91 (s, 3H), 3.97 (s, 3H). This spectrum is in agreement with previously reported spectral data.
2.48 (t, \(J = 7.1\) Hz, 2H), 1.64-1.60 (m, 2H), 1.54-1.48 (m, 2H), 0.96 (t, \(J = 7.3\) Hz, 3H). This spectrum is in agreement with previously reported spectral data.\(^2\)

![Chemical structure of SI-1 and 1c](image)

**Methyl 4-acetoxy-2-(phenylethynyl)benzoate (1c).** A flask was charged with \((\text{PPh}_3)_2\text{PdCl}_2\) (0.022 g, 0.030 mmol, 0.020 equiv), and CuI (0.011 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with \(\text{N}_2\) three times before 4 mL of Et\(_3\)N were added. The reaction mixture was then sparged for 5 minutes before compound SI-1 (0.50 g, 1.6 mmol, 1.0 equiv) was added. Phenylacetylene (0.21 mL, 1.9 mmol, 1.2 equiv) was then added via syringe, and the reaction mixture was heated to 55 °C in an oil bath and stirred for 16 h under dynamic \(\text{N}_2\). At this time, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 100 mL DCM and washed with water (1 × 25 mL), brine (1 × 25 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The resulting oily 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 1c as a yellow solid (0.44 g, 95% yield).\(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 8.26 (s, 1H), 8.00-7.96 (m, 2H), 7.57-7.56 (m, 2H), 7.35-7.34 (m, 3H), 3.96 (s, 3H), 3.92 (s, 3H). This spectrum is in agreement with previously reported spectral data.\(^2\)

![Chemical structure of SI-2 and 1d](image)

**Methyl 2,5-bis(phenylethynyl)benzoate (1d)** A flask was charged with \((\text{PPh}_3)_2\text{PdCl}_2\) (0.017 g, 0.24 mmol, 0.040 equiv), and CuI (0.016 g, 0.12 mmol, 0.020 equiv). The flask was then evacuated and refilled with \(\text{N}_2\) three times before 4 mL of Et\(_3\)N were added. The reaction mixture was then sparged for 5 min before SI-2 (2.00 g, 5.87 mmol, 1.00 equiv) was added. Phenylacetylene (0.70 mL, 6.5 mmol, 1.1 equiv) was then added via syringe, and the reaction mixture was heated to 55 °C in an oil bath and stirred for 16 h under dynamic \(\text{N}_2\). At this time, analysis by TLC (5% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 100 mL DCM and washed with water (1 × 25 mL), brine (1 × 25 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The resulting oily 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 the minor product 1d as a white solid.
Ethyl hex-5-ynoate (SI-4) was prepared according to a literature procedure\(^4\) in 87% yield. \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 4.14 (q, \(J = 7.1\) Hz, 2H), 2.44 (t, \(J = 7.4\) Hz, 2H), 1.97 (t, \(J = 2.6\) Hz, 1H), 1.85 (quin, \(J = 7.2\) Hz, 1H), 1.26 (t, \(J = 7.2\) Hz, 3H). This spectrum is in agreement with previously reported spectral data.

Methyl 2-((trimethylsilyl)ethynyl)benzoate (SI-5). A flask was charged with compound 10 (5.2 mL, 38 mmol, 1.0 equiv), (PPh\(_3\))\(_2\)PdCl\(_2\) (0.53 g, 1.5 mmol, 0.020 equiv), and CuI (0.29 g, 1.5 mmol, 0.040 equiv). The flask was then evacuated and refilled with N\(_2\) three times before 76 mL of acetonitrile and Et\(_3\)N (40 mL, 300 mmol, 8 equiv) were added. Trimethylsilyl acetylene
(5.9 mL, 42 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N₂. At this time, analysis by TLC (5% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 300 mL Et₂O and washed with NH₄Cl (1 × 50 mL), water (1 × 50 mL), brine (1 × 50 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 SI-5 as a yellow oil (7.0 g, 79% yield). ¹H NMR (CDCl₃, 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.⁵

**Methyl 2-ethynylbenzoate (1f).** A flask was charged with compound SI-5 (2.9 g, 13 mmol, 1.0 equiv), 63 mL methanol, and potassium fluoride (2.6 g, 44 mmol, 3.5 equiv). The flask was then sealed with a ground glass stopper and heated to 40 °C while stirring for 3 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL Et₂O and washed with water (4 × 50 mL), brine (1 × 50 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo at ~10 Torr and 25 °C [warning: product is volatile], yielding 1f as a dark yellow/red liquid (1.7 g, 84% yield). ¹H NMR (CDCl₃, 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.⁶

![Reaction Scheme](image-url)

**Methyl 2-((4-chlorophenyl)ethynyl)benzoate (1g).** A flask was charged with compound SI-6 (0.36 g, 1.5 mmol, 1.0 equiv), (PPh₃)₂PdCl₂ (0.021 g, 0.030 mmol, 0.020 equiv), and CuI (0.012 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with N₂ three times before 3 mL of acetonitrile and Et₃N (1.7 mL, 12 mmol, 8.0 equiv) were added. Compound 1f (0.27 g, 1.7 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N₂. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et₂O and washed with NH₄Cl (1 × 40 mL), water (1 × 40 mL), brine (1 × 40 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 1g as a light yellow liquid that solidified upon standing at room temperature (0.34 g, 84% yield). ¹H NMR (CDCl₃, 500 MHz): δ 7.99 (dd, J = 7.9, 1.0 Hz, 1H),
7.64 (dd, \(J = 7.7, 0.9\) Hz, 1H), 7.52-7.49 (m, 3H), 7.40 (td, \(J = 7.7, 1.3\) Hz, 1H), 7.35-7.33 (m, 2H), 3.96 (s, 3H). This spectrum is in agreement with previously reported spectral data.\(^7\)

**Methyl 5-bromo-2-(4-cyanobut-1-yn-1-yl)benzoate (1h).** A flask was charged with compound ***SI-2*** (0.34 g, 1.0 mmol, 1.0 equiv), \((\text{PPh}_3)_2\text{PdCl}_2\) (0.014 g, 0.020 mmol, 0.020 equiv), and CuI (0.008 g, 0.04 mmol, 0.04 equiv). The flask was then evacuated and refilled with \(\text{N}_2\) three times before 2 mL of acetonitrile and \(\text{Et}_3\text{N}\) (1.1 mL, 8.0 mmol, 8.0 equiv) were added. Compound ***SI-7*** (0.10 mL, 1.1 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic \(\text{N}_2\). At this time, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and washed with \(\text{NH}_4\text{Cl}\) (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated in vacuo. The resulting oily 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 1h as a light yellow solid (0.25 g, 86% yield).

\(^1\text{H}\) NMR (CDCl\(_3\), 500 MHz): \(\delta 8.06\) (s, 1H), 7.57 (d, \(J = 8.3\) Hz, 1H), 7.40 (d, \(J = 8.3\) Hz, 1H), 3.92 (s, 3H), 2.84 (t, \(J = 7.2\) Hz, 2H), 2.69 (t, \(J = 7.2\) Hz, 2H).

\(^{13}\text{C}\) NMR (CDCl\(_3\), 125 MHz): \(\delta 165.2, 135.7, 134.9, 133.41, 133.38, 122.3, 122.0, 118.3, 91.7, 81.0, 52.6, 17.5, 17.2.\)

HRMS (Cl\(^+\)): Calculated for \(\text{C}_{13}\text{H}_{14}\text{BrN}_2\text{O}_2\) ([M+\(\text{NH}_4\)]\(^+\)), 309.0239; found 309.0230.

**Methyl 2-(thiophen-3-ylethynyl)benzoate (1i).** A flask was charged with compound ***10*** (0.22 mL, 1.5 mmol, 1.0 equiv), \((\text{PPh}_3)_2\text{PdCl}_2\) (0.021 g, 0.030 mmol, 0.020 equiv), and CuI (0.011 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with \(\text{N}_2\) three times before 3 mL of acetonitrile and \(\text{Et}_3\text{N}\) (1.7 mL, 12 mmol, 8.0 equiv) were added. Compound ***SI-8*** (0.17 mL, 1.7 mmol, 1.1 equiv) was then syringed into the reaction mixture, which was then stirred for 18 h under dynamic \(\text{N}_2\). At this time, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and...
washed with NH₄Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 1i as a light yellow solid (0.37 g, 78% yield).

1H NMR (CDCl₃, 600 MHz): δ 7.95 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.58-7.56 (m, 1H), 7.45 (td, J = 7.6, 1.3 Hz, 1H), 7.34 (td, J = 7.6, 1.3 Hz, 1H), 7.29 (dd, J = 4.9, 3.0 Hz, 1H), 7.23 (app. d, J = 5.0 Hz, 1H), 3.93 (s, 3H).

13C NMR (CDCl₃, 125 MHz): δ 166.7, 134.0, 131.8, 131.7, 130.5, 130.0, 129.2, 127.9, 125.5, 123.8, 122.5, 89.7, 87.9, 52.2.

HRMS (CI+): Calculated for C₁₄H₁₀SO₂ ([M]+), 242.0401; found 242.0390.

**methyl 2-(cyclohex-1-en-1-ylythynyl)benzoate (1j).** A flask was charged with compound 10 (0.22 mL, 1.5 mmol, 1.0 equiv), (PPh₃)₂PdCl₂ (0.021 g, 0.030 mmol, 0.020 equiv), and CuI (0.011 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with N₂ three times before 3 mL of acetonitrile and Et₃N (1.7 mL, 12 mmol, 8.0 equiv) were added. Compound SI-9 (0.20 mL, 1.7 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N₂. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et₂O and washed with NH₄Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 1j as a yellow oil (0.35 g, 96% yield). 1H NMR (CDCl₃, 600 MHz): δ 7.92 (dd, J = 7.9, 1.1 Hz, 1H), 7.52 (dd, J = 7.7, 1.0 Hz, 1H), 7.43 (td, J = 7.6, 1.3 Hz, 1H), 7.31 (td, J = 7.7, 1.2 Hz, 1H), 6.28 – 6.26 (m, 1H), 3.92 (s, 3H), 2.28 – 2.25 (m, 2H), 2.18 – 2.14 (m, 2H), 1.71-1.67 (m, 2H), 1.64-1.61 (m, 2H). This spectrum is in agreement with previously reported spectral data.⁸
Methyl (Z)-3-iodoacrylate (SI-11) was prepared according to a literature procedure\(^9\) in 75% yield. \(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 7.47 (d, \(J = 8.9\) Hz, 1H), 6.91 (d, \(J = 9.0\) Hz, 1H), 3.79 (s, 3H). This spectrum is in agreement with previously reported spectral data.

Methyl (Z)-11-chloroundec-2-en-4-ynoate (1k). This procedure was performed in a N\(_2\)-filled glove box. A 20 mL vial was charged with compound SI-11 (0.42 g, 2.0 mmol, 1.0 equiv), (PPh\(_3\))\(_2\)PdCl\(_2\) (0.105 mg, 0.150 mmol, 0.0750 equiv), CuI (0.014 g, 0.074 mmol, 0.037 equiv), and a stir bar. 5 mL of Et\(_3\)N were added. Compound SI-12 (0.37 mL, 2.4 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 \(^\circ\)C and stirred for 18 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and washed with NH\(_4\)Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The resulting oily 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 1k as a viscous yellow oil (0.19 g, 41% yield).

\(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 6.15 (dt, \(J = 11.3, 2.3, 2.3\) Hz, 1H), 6.05 (d, \(J = 11.4\) Hz, 1H), 3.75 (s, 3H), 3.55 (t, \(J = 6.7\), 2H), 2.47 (td, \(J = 7.0, 7.0, 2.1\) Hz, 2H), 1.80 (t, \(J = 6.8\) Hz, 2H), 1.61 (m, 2H), 1.47 (m, 4H).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 165.4, 127.2, 124.4, 104.2, 77.9, 51.5, 45.2, 32.6, 28.3, 28.2, 26.5, 20.1.

HRMS (Cl\(^+\)): Calculated for C\(_{12}\)H\(_{18}\)ClO\(_2\) ([M+H]\(^+\)), 229.0995; found 229.0990.

![Methyl (Z)-5-(thiophen-3-yl)pent-2-en-4-ynoate (1m)](image)

Methyl (Z)-5-(thiophen-3-yl)pent-2-en-4-ynoate (1m). A flask was charged with compound SI-11 (0.500 g, 2.35 mmol, 1.00 equiv), (PPh\(_3\))\(_2\)PdCl\(_2\) (0.124 mg, 0.176 mmol, 0.0750 equiv), CuI (0.017 g, 0.087 mmol, 0.037 equiv), and a stir bar. The flask was then evacuated and refilled with N\(_2\) three times before 5.3 mL of Et\(_3\)N was added. Compound SI-8 (0.28 mL, 2.8 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 \(^\circ\)C and stirred for 18 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et\(_2\)O and washed with NH\(_4\)Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The resulting oily 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 1m as a viscous light yellow oil (0.22 g, 48% yield).
**Ethyl (Z)-3-iodoacrylate (SI-14)** was prepared according to a literature procedure in 67% yield. \(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 7.43 (d, \(J = 8.9\) Hz, 1H), 6.89 (d, \(J = 8.9\) Hz, 1H), 4.25 (q, \(J = 7.1\) Hz, 2H), 1.32 (t, \(J = 7.1\) Hz, 3H). This spectrum is in agreement with previously reported spectral data.

**Ethyl (Z)-5-phenylpent-2-en-4-ynoate (1n)**. A flask was charged with compound SI-14 (0.50 g, 2.2 mmol, 1.0 equiv), (PPh\(_3\))\(_2\)PdCl\(_2\) (0.12 g, 0.17 mmol, 0.080 equiv), and CuI (0.015 g, 0.081 mmol, 0.040 equiv). The flask was then evacuated and refilled with N\(_2\) three times before 5 mL of Et\(_3\)N was added. Phenylacetylene (0.29 mL, 2.6 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 °C and stirred for 18 h under dynamic N\(_2\). At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et\(_2\)O and washed with NH\(_4\)Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The resulting oily 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 1n as a viscous light yellow oil (0.28 g, 63% yield). \(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 7.53 (dd, \(J = 7.4, 2.1\) Hz, 1H), 7.36-7.33 (m, 3H), 4.27 (q, \(J = 7.1\) Hz, 2H), 1.34 (t, \(J = 7.1\) Hz, 3H). This spectrum is in agreement with previously reported spectral data.

**Methyl (Z)-5-cyclopropylpent-2-en-4-ynoate (1p)**. This procedure was performed in a N\(_2\)-filled glove box. A 20 mL vial was charged with compound SI-11 (0.424 g, 2.00 mmol, 1.00 equiv), (PPh\(_3\))\(_2\)PdCl\(_2\) (0.112 g, 0.160 mmol, 0.0750 equiv), CuI (0.015 g, 0.080 mmol, 0.037 equiv), and a stir bar. 5 mL of Et\(_3\)N was added. Compound SI-15 (0.20 mL, 2.4 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 °C and stirred for 18 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting...
material. The reaction mixture was diluted with 150 mL Et₂O and washed with NH₄Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting oily 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 [NOTE: product may be volatile] to afford 115 mg of 1p as a yellow liquid in ~91% purity.

¹H NMR (CDCl₃, 600 MHz): δ 6.11 (dd, J = 11.4, 2.4 Hz, 1H), 6.01 (d, J = 11.3 Hz, 1H), 3.74 (s, 3H), 1.49 (ddt, J = 7.9, 5.3, 2.8, 2.8 Hz, 1H), 0.92 (m, 2H), 0.86 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz): δ 165.5, 126.7, 124.5, 108.3, 73.6, 51.5, 9.7, 1.1.
HRMS (Cl+): Calculated for C₉H₁₀O₂ ([M]+), 150.0681; found 150.0677.

B. Boron Electrophile Screen

Table S1 (Table 1 in Manuscript). Boron Reagent Variation

| Entry | Boron Electrophile [B] | Temp | Yield (%) |
|-------|------------------------|------|-----------|
| 1     | BBr₃                   | 45°C | 0         |
| 2     | BCl₃                   | 45°C | 0         |
| 3     | B-Chlorocatecholborane | 45°C | 25        |
| 4     | B-Chlorocatecholborane | 100°C| 75        |
| 5     | B-Bromocatecholborane  | 100°C| 48        |

General Procedure: Entries 1 and 2
This screen was carried out in a nitrogen-filled glove box. A 4 mL vial was charged with 1a (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. 0.6 mL (1.2 equiv) of a 1 M solution of either BBr₃ or BCl₃ was then added to the vial, and the vial was sealed and heated to 45 °C for 24 h. At this time, the reaction mixture was cooled down to room temperature. In a separate vial, pinacol (0.18 g, 1.5 mmol, 3.0 equiv) was dissolved in Et₃N (1.0 mL, 7.5 mmol, 15 equiv). This solution was then added to the reaction mixture. The resulting solution was then stirred for 1 h at room temperature. The solution was then concentrated in vacuo. Analysis of the resulting residue via ¹H NMR spectroscopy (CDCl₃, 600 MHz) and ¹¹B NMR Spectroscopy (CDCl₃, 126 MHz) confirmed that the desired product 3aa was not produced.

General Procedure: Entries 3-5
This screen was carried out in a nitrogen-filled glove box. A 4 mL vial was charged with 1a (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. In a separate vial, B-chlorocatecholborane (0.70 mmol, 1.4 equiv) or B-bromocatecholborane (0.70 mmol, 1.4 equiv) was added. The initial reaction vial was then transferred to the boron-containing vial via pipette,
and this vial was sealed and heated to the specified temperature for 24 h. At this time, the reaction mixture was cooled down to room temperature. In a separate vial, pinacol (0.18 g, 1.5 mmol, 3.0 equiv) was dissolved in Et₃N (1.0 mL, 7.5 mmol, 15 equiv). This solution was then added to the reaction mixture. The resulting solution was then stirred for 1 h at room temperature. The solution was then concentrated in vacuo. The resulting oily 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 3aa as a light yellow oil, which solidified upon standing. The ¹H NMR spectrum for each entry was then compared to the authentic sample (see section D, product 3aa) to establish identity.

C. Reaction Condition Optimization

Table S2. Optimization of the Oxyboration Reaction

| Entry | Equivalents of BcatCl | Temp (°C) | 2a:1a |
|-------|-----------------------|-----------|-------|
| 1     | 1.0 equiv             | 100       | 76:24 |
| 2     | 1.2 equiv             | 100       | 81:19 |
| 3     | 1.3 equiv             | 100       | 87:13 |
| 4     | 1.4 equiv             | 100       | 95:5  |
| 5     | 1.4 equiv             | 75        | 86:14 |
| 6     | 1.4 equiv             | 45        | 40:60 |

Reaction condition screening reactions were set up in a N₂-filled glovebox. 1a (118 mg, 0.500 mmol, 1.00 equiv) was dissolved in anhydrous d₈-toluene (0.50 mL) and added to a dram vial containing B-chlorocatecholborane in the below amounts (1.00–1.40 equiv). After mixing thoroughly, the reaction mixture was transferred to a J. Young NMR tube, removed from the glovebox, and heated in a preheated oil bath for 24 h. The progress of the reaction was then monitored by ¹H and ¹¹B NMR spectroscopy, with characteristic product (2a) peaks at δ = 8.26 ppm in the ¹H NMR spectrum, and δ ~ 32.1 ppm in the ¹¹B NMR spectrum in d₈-toluene. Note: the optimized concentration was 1.0 M was the best; when higher concentrations were tested, solubility issues were encountered.
D. Synthesis of O-Alkyl Esters and Screen

Ethyl 2-(phenylethynyl)benzoate (1q). A flask was charged with compound SI-16 (0.96 g, 3.5 mmol, 1.0 equiv), (PPh$_3$)$_2$PdCl$_2$ (0.049 g, 0.070 mmol, 0.020 equiv), and CuI (0.027 g, 0.14 mmol, 0.040 equiv). The flask was then evacuated and refilled with N$_2$ three times before 7 mL of acetonitrile and Et$_3$N (3.8 mL, 28 mmol, 8.0 equiv) were added. Phenylacetylene (0.42 mL, 3.8 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N$_2$. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH$_4$Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The resulting oily 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 1q as a light yellow oil (0.68 g, 78% yield). $^1$H NMR (CDCl$_3$, 600 MHz): δ 7.99 (dd, $J =$ 7.9, 0.8 Hz, 1H), 7.65 (dd, $J =$ 7.7, 0.6 Hz, 1H), 7.58-7.57 (m, 2H), 7.47 (app t, $J =$ 7.6 Hz, 1H), 7.38-7.34 (m, 4H), 4.44 (q, $J =$ 7.2 Hz, 2H), 1.41 (t, $J =$ 7.2 Hz, 3H). This spectrum is in agreement with previously reported spectral data.

Isopropyl 2-iodobenzoate (SI-18) was prepared according to a literature procedure in 56% yield. $^1$H NMR (CDCl$_3$, 500 MHz): δ 7.90 (dd, $J =$ 7.9, 1.0 Hz, 1H), 7.68 (dd, $J =$ 7.7, 1.7 Hz, 1H), 7.37 (td, $J =$ 7.7, 1.0 Hz, 1H), 7.10 (td, $J =$ 7.9, 1.7 Hz, 1H), 5.24 (hept, $J =$ 6.2 Hz, 1H), 1.39 (d, $J =$ 6.2 Hz, 6H). This spectrum is in agreement with previously reported spectral data.

Isopropyl 2-(phenylethynyl)benzoate (1r). A flask was charged with compound SI-18 (0.50 g, 1.7 mmol, 1.0 equiv), (PPh$_3$)$_2$PdCl$_2$ (0.024 g, 0.034 mmol, 0.020 equiv), and CuI (0.013 g, 0.070 mmol, 0.040 equiv). The flask was then evacuated and refilled with N$_2$ three times before 4 mL of acetonitrile and Et$_3$N (1.9 mL, 14 mmol, 8.0 equiv) were added. Phenylacetylene (0.21 mL, 1.9 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N$_2$. At this time, analysis by TLC (15% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH$_4$Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na$_2$SO$_4$, filtered, and...
concentrated in vacuo. The resulting oily 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 1r as a light yellow oil (0.39 g, 85% yield). $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.95 (dt, $J = 7.9, 1.0$ Hz, 1H), 7.65-7.63 (m, 1H), 7.58-7.56 (m, 2H), 7.50 (td, $J = 7.6, 1.4$ Hz, 1H), 7.39-7.34 (m, 4H), 5.30 (hept, $J = 6.2$ Hz, 1H), 1.38 (d, $J = 6.2$ Hz, 6H). This spectrum is in agreement with previously reported spectral data.$^{14}$

$\text{SI-19}$ \[\text{HO} \quad \text{CsF} \quad \text{Cul, (PPh$_3$)$_2$PdCl$_2$} \quad \text{Ph} \rightarrow \text{SI-20} \rightarrow \text{1s}$

$\text{1s}$

$\text{tert-Butyl 2-iodobenzoate (SI-20)}$ was prepared according to a literature procedure in 75% yield. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.94 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.68 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.37 (td, $J = 7.7, 1.0$ Hz, 1H), 7.10 (td, $J = 7.9, 1.7$ Hz, 1H), 1.6 (s, 29H). This spectrum is in agreement with previously reported spectral data.$^{13}$

$\text{tert-Butyl 2-(phenylethynyl)benzoate (1s)}$. A flask was charged with compound SI-20 (0.49 g, 1.6 mmol, 1.0 equiv), (PPh$_3$)$_2$PdCl$_2$ (0.022 g, 0.032 mmol, 0.020 equiv), and CuI (0.012 g, 0.064 mmol, 0.040 equiv). The flask was then evacuated and refilled with N$_2$ three times before 3 mL of acetonitrile and Et$_3$N (1.8 mL, 13 mmol, 8.0 equiv) were added. Phenylacetylene (0.20 mL, 1.8 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N$_2$. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH$_4$Cl (1 $\times$ 25 mL), water (1 $\times$ 25 mL), brine (1 $\times$ 25 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The resulting oily 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 1s as a light yellow oil (0.40 g, 90% yield). $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.86 (dd, $J = 7.9, 0.8$ Hz, 1H), 7.56 (dd, $J = 7.7, 0.8$ Hz, 1H), 7.51 (dd, $J = 8.1, 1.9$ Hz, 2H), 7.39 (td, $J = 7.7, 1.3$ Hz, 1H), 7.32-7.28 (m, 4H), 1.56 (s, 9H). This spectrum is in agreement with previously reported spectral data.$^{2}$
Table S3 (Table 3 in Manuscript). Mechanistic Insight from O-Alkyl Group Variance of the Oxyboration Reaction

| Entry | R  | $^1$H NMR Yield (%) 3aa |
|-------|----|------------------------|
| 1     | Me | 81                     |
| 2     | Et | 68                     |
| 3     | iPr | 60                    |
| 4     | tBu | 0                     |

General Procedure
This screen was carried out in a nitrogen-filled glove box. A 4 mL vial was charged with the desired O-alkyl ester (1a, 1q-1s) (0.50 mmol, 1.0 equiv) and 0.5 mL toluene. In a separate vial, B-chlorocatecholborane (0.70 mmol, 1.4 equiv) was added. The solution in the initial reaction vial was then transferred to the boron-containing vial via pipette, and this vial was sealed and heated to 100 °C for 24 h. At this time, the reaction mixture was cooled to room temperature. In a separate vial, pinacol (0.18 g, 1.5 mmol, 3.0 equiv) was dissolved in Et$_3$N (1.0 mL, 7.5 mmol, 15 equiv). This solution was then added to the reaction mixture via pipette. The resulting solution was then stirred for 1 h at room temperature and then concentrated in vacuo. An $^1$H NMR spectrum was then taken of each crude mixture in CDCl$_3$; mesitylene (50. μL, 0.36 mmol, 0.72 equiv) was added to the sample via gas tight syringe to determine the yield of the desired borylated isocoumarin 3aa. In entry 4 (R = tBu), the mesitylene was compared to characteristic peaks of the benzoic acid derivative of 1a from an authentic sample synthesized using a known procedure.$^{15}$

Procedure to Monitor the Formation of Isobutylene from Entry 4
A 4 mL vial was charged with compound 1s (0.10 g, 0.37 mmol, 1.0 equiv), 1,3,5-triisopropylbenzene (30 μL, 0.12 mmol, 0.24 equiv), and 0.4 mL $d_8$-toluene. In a separate vial, B-chlorocatecholborane (0.080 g, 0.52 mmol, 1.4 equiv) was added. The solution in the initial reaction vial was then transferred to the boron-containing vial via pipette, and then this mixture was transferred to a J-young tube via pipette. The tube was heated to 100 °C. $^1$H NMR spectra were taken at $t = 3$ h and 24 h to monitor isobutylene formation, as well as to confirm that catecholboronic ester 2s did not form.

E. Synthesis and Isolation of Carboxyboration Products 3aa-3p

General Remarks
For synthetic ease, these reactions were carried out in a nitrogen-filled glovebox unless specified otherwise. B-Chlorocatecholborane is water-reactive and should be stored cool (0 °C or lower) in a desiccator or glovebox when not in use. The ipso C–B bond is not detected by $^{13}$C NMR spectroscopy.
3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3aa). A vial was charged with 1a (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et₃N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3aa as a yellow oil (0.13 g, 75% yield).

1H NMR (toluene-d₈, 600 MHz): δ 8.32 (app dd, J = 7.9, 1.0 Hz, 1H), 7.92 (app dd, J = 7.9, 0.4 Hz, 1H), 7.52-7.50 (m, 2H), 7.27 (ddd, J = 15.3, 6.5, 1.5 Hz, 1H), 7.12-6.99 (m, 4H), 0.99 (s, 12H).

13C NMR (toluene-d₈, 125 MHz): δ 161.4, 160.9, 129.1, 128.7, 128.1, 128.1, 127.8, 125.3, 124.9, 84.0, 24.7, 20.7, 20.6, 20.3, 20.1.

11B NMR (toluene-d₈, 193 MHz): δ 31.5.

HRMS (ESI+): Calculated for C₂₁H₂₁BO₄Na ([M+Na]+), 371.1435; found 371.1434.

(1-oxo-3-phenyl-1H-isochromen-4-yl)Boronic acid (3ab). A vial was charged with 1a (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and transferred to a vial containing 1 mL of water, and the resulting mixture stirred vigorously for 18 h at room temperature. The solution was then filtered through a medium porosity fritted funnel. The solid was then rinsed with cold (~0 °C) water (3 × 3 mL).
The solid was dried in vacuo c.a. 10 mTorr for 18 h to afford 3ab as a light purple solid (0.088 g, 66% yield).

\(^1\)H NMR (CD\(_3\)CN, 600 MHz): \(\delta 8.27 (dd, J = 7.9, 0.9 \text{ Hz}, 1H), 7.81 (ddd, J = 15.2, 7.2, 1.4 \text{ Hz}, 1H), 7.76-7.75 (m, 2H), 7.65 (app d, J = 7.7 \text{ Hz}, 1H), (ddd, J = 15.2, 7.9, 0.5 \text{ Hz}, 1H), 7.53-7.49 (m, 3H), 6.51 (s, 2H).

\(^13\)C NMR (CD\(_3\)CN, 125 MHz): \(\delta 162.2, 155.2, 139.4, 135.0, 134.9, 129.9, 129.1, 128.7, 128.2, 127.5, 127.0, 121.0.

\(^{11}\)B NMR (CD\(_3\)CN, 193 MHz): \(\delta 30.0.

HRMS (ESI-): Calculated for C\(_{15}\)H\(_{11}\)BO\(_4\)Cl ([M+Cl] \(-\)), 301.0442; found 301.0441.

3-Phenyl-4-(trifluoro-\(\lambda^4\)-boranyl)-1H-isochromen-1-one, potassium salt (3ac). A vial was charged with 1a (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then concentrated in vacuo. The residue was then dissolved in 1 mL of acetone and then transferred via pipette to another flask containing a solution of KHF\(_2\) (0.137g, 1.80 mmol, 3.50 equiv) in 1.5 mL of H\(_2\)O. The resulting mixture was stirred for 1 h then concentrated in vacuo at c.a. 10 mTorr for 1 h. The product was then filtered through a medium porosity fritted funnel. The solid was then rinsed with cold (~0 °C) water (3 × 3 mL) and ether (3 x 3 mL). The solid was dried in vacuo c.a. 10 mTorr for 18 h to afford 3ac as a white solid (0.103 g, 63% yield).

\(^1\)H NMR ((CD\(_3\))\(_2\)CO, 600 MHz): \(\delta 8.37 (d, J = 8.1 \text{ Hz}, 1H), 8.16 (d, J = 7.7 \text{ Hz}, 1H), 7.68 (d, J = 6.4 \text{ Hz}, 2H), 7.64 (t, J = 7.7 \text{ Hz}, 1H), 7.40 (t, J = 7.4 \text{ Hz}, 1H), 7.31-7.30 (m, 3H).

\(^13\)C NMR ((CD\(_3\))\(_2\)CO, 600 MHz): \(\delta 168.5, 160.0, 148.8, 143.2, 138.2, 138.1, 135.4, 135.3, 135.2, 132.9, 131.9, 131.2, 126.3.

\(^{11}\)B NMR ((CD\(_3\))\(_2\)CO, 193 MHz): \(\delta 2.9.

\(^{19}\)F NMR ((CD\(_3\))\(_2\)CO, 376 MHz): \(\delta -131.6.

HRMS (ESI-): Calculated for C\(_{15}\)H\(_9\)BF\(_3\)O\(_2\) ([M-K] \(-\)), 289.0651; found 289.0640.
3-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3b). A vial was charged with 1b (0.108 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 (0.16 g, 97% yield).

1H NMR (CDCl3, 600 MHz): \( \delta \) 8.24 (d, \( J = 9.5 \) Hz, 1H), 8.04 (d, \( J = 9.9 \) Hz, 1H), 7.65 (td, \( J = 9.5, 1.5 \) Hz, 1H), 7.42-7.38 (m, 1H), 2.80 (t, \( J = 9.3 \) Hz, 2H), 1.72-1.66 (m, 2H), 1.39-1.38 (m, 14H), 0.92 (t, \( J = 8.9 \) Hz, 3H).

13C NMR (CDCl3, 125 MHz): \( \delta \) 166.6, 162.9, 139.8, 134.7, 129.2, 127.2, 126.6, 119.9, 84.0, 33.7, 30.9, 24.9, 22.5, 13.9.

11B NMR (CDCl3, 193 MHz): \( \delta \) 31.6.

HRMS (ESI+): Calculated for C19H25BO4K ([M+K]+), 367.1487; found 367.1481.

Methyl 1-oxo-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromene-6-carboxylate (3c). A vial was charged with 1c (0.147 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3c as a yellow solid (0.13 g, 65% yield).

1H NMR (CDCl3, 600 MHz): \( \delta \) 8.60 (d, \( J = 1.1 \) Hz, 1H), 8.40 (d, \( J = 8.2 \) Hz, 1H), 8.10 (dd, \( J = 8.2, 1.5 \) Hz, 1H), 7.71-7.70 (m, 2H), 7.49-7.43 (m, 3H), 3.99 (s, 3H), 1.35 (s, 12H).
$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 166.0, 161.8, 160.3, 139.7, 135.4, 134.2, 130.4, 129.9, 128.8, 128.4, 128.3, 128.1, 123.1, 84.8, 52.7, 24.8.

$^{11}$B NMR (CDCl$_3$, 193 MHz): $\delta$ 31.7.

HRMS (ESI+): Calculated for C$_{23}$H$_{23}$BO$_6$Na ([M+Na]$^+$), 429.1490; found 429.1499.

3-phenyl-7-(phenylethynyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3d). A vial was charged with 1d (0.168 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et$_3$N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3d as a yellow solid (0.15 g, 66% yield).

$^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.50 (s, 1H), 7.85-7.81 (m, 2H), 7.68 (app d, $J = 7.5$ Hz, 2H), 7.56-7.54 (m, 2H), 7.47-7.45 (m, 1H), 7.43-7.41 (m, 2H), 7.38-7.35 (m, 3H), 1.29 (s, 12H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 161.7, 160.5, 139.2, 137.3, 134.5, 132.7, 131.8.9, 130.3, 128.9, 128.8, 128.5, 128.2, 126.6, 123.1, 122.8, 120.3, 91.5, 88.3, 84.6, 24.9.

$^{11}$B NMR (CDCl$_3$, 193 MHz): $\delta$ 31.3.

HRMS (ESI+): Calculated for C$_{29}$H$_{25}$BO$_4$Na ([M+Na]$^+$), 471.1749; found 471.1759.

Ethyl 4-(1-oxo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-3-yl)butanoate (3e). A vial was charged with 1e (0.064 g, 0.23 mmol, 1.0 equiv) and 0.23 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane...
(0.050 g, 0.33 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.23 mL toluene. A separate vial was then charged with pinacol (0.083 g, 0.70 mmol, 3.0 equiv) and Et₃N (0.50 mL, 3.8 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3e as a yellow solid (0.050 g, 55% yield).

1H NMR (CDCl₃, 600 MHz): δ 8.25 (app d, J = 8.0 Hz, 1H), 8.08 (app d, J = 8.2 Hz, 1H), 7.66 (ddd, J = 11.8, 5.9, 1.1 Hz, 1H), 7.42 (app t, J = 7.6 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.87 (t, J = 7.4 Hz, 2H), 2.36 (t, J = 7.6 Hz, 2H), 2.05 (tt, J = 14.8, 7.5 Hz, 2H), 1.38 (s, 12H), 1.22 (t, J = 7.1 Hz, 3H).

13C NMR (CDCl₃, 125 MHz): δ 173.1, 165.2, 162.7, 139.3, 129.3, 127.5, 126.8, 120.0, 84.2, 60.4, 33.6, 33.1, 24.9, 23.7, 14.3.

11B NMR (CDCl₃, 193 MHz): δ 31.3.

HRMS (ESI-): Calculated for C₂₁H₂₇BO₆Na ([M+Na]+), 409.1802; found 409.1808.

(E)-((3-oxoisobenzofuran-1(3H)-ylidene)methyl)boronic acid (3f). A vial was charged with 1f (0.080 g, 0.50 mmol, 1.0 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 20 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then transferred to a vial containing 10 mL of water, and the resulting mixture stirred vigorously for 3 h at room temperature. The solution was then filtered through a medium porosity fritted funnel. The solid was then rinsed with cold (~0 °C) water (3 × 3 mL). The solid was then dried in vacuo c.a. 10 mTorr for 18 h to afford 3f as a white solid (0.058 g, 61% yield).

1H NMR (CD₃CN, 600 MHz): δ 8.60 (d, J = 9.6 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.79 (app t, J = 9.2 Hz, 1H), 7.65 (app t, J = 9.0 Hz, 1H), 6.34 (s, 2H), 5.48 (s, 1H).

13C NMR (CDCl₃, 125 MHz): δ 167.5, 157.2, 139.3, 135.6, 131.8, 127.5, 125.99, 125.4, 118.3.

11B NMR (CD₃CN, 193 MHz): δ 28.1.

HRMS (ESI-): Calculated for C₉H₇BO₄Cl ([M+Cl]⁺), 225.0128; found 225.0121.
HMQC was used to confirm the formation of the 5-exo-dig product. Because ipso B–C resonances are not detected in $^{13}$C NMR, the resonance at $\delta = 5.48$ ppm in the HMQC must be attached to an ipso B–C bond because no $^{13}$C NMR signal correlates.

3-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3g). A vial was charged with 1g (0.135 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et$_3$N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3g as a white solid (0.11 g, 60% yield).

$^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.34 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.73 (app t, $J = 7.7$ Hz, 1H), 7.64-7.62 (m, 2H), 7.52 (app t, $J = 7.7$ Hz, 1H), 7.41-7.39 (m, 2H), 1.31 (s, 12H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 162.3, 158.8, 139.5, 136.3, 135.0, 133.2, 130.4, 129.8, 128.5, 128.3, 126.6, 120.3, 84.7, 25.0.

$^{11}$B NMR (CDCl$_3$, 193 MHz): $\delta$ 31.4.

HRMS (ESI+): Calculated for C$_{21}$H$_{20}$BClO$_4$Na ($[M+Na]^+$), 405.1045; found 405.1048.

3-(7-bromo-1-oxo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-3-yl)propanenitrile (3h). A vial was charged with 1h (0.146 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was
then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et₃N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 25% 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 white solid (0.079 g, 39% yield).

1H NMR (CDCl₃, 600 MHz): δ 8.37 (d, J = 2.2 Hz, 1H), 8.18 (d, J = 8.7 Hz, 1H), 7.78 (dd, J = 8.7, 2.2 Hz, 1H), 3.26 (t, J = 7.4 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H), 1.40 (s, 12H).

13C NMR (CDCl₃, 125 MHz): δ 162.3, 160.7, 138.1, 137.7, 131.8, 129.4, 121.8, 121.8, 118.3, 84.6, 29.7, 25.0, 16.2.

11B NMR (CDCl₃, 193 MHz): δ 30.6.

HRMS (ESI+): Calculated for C₁₈H₁₉BBrNO₄Na ([M+Na⁺], 426.0492; found 426.0486.

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1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-3-yl)-1H-isochromen-1-one (3i).

A vial was charged with 1i (0.177 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et₃N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 white solid (0.13 g, 71% yield).

1H NMR (CDCl₃, 600 MHz): δ 8.31 (app d, J = 7.9 Hz, 1H), 7.78-7.76 (m, 1H), 7.74 (dd, J = 8.0, 0.3 Hz, 1H), 7.69 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 7.46 (ddd, J = 7.6, 7.6, 1.1 Hz, 1H), 7.43-7.42 (m, 1H), 7.35-7.33 (m, 1H), 1.34 (s, 12H).

13C NMR (CDCl₃, 125 MHz): δ 162.3, 154.5, 139.6, 135.9, 134.8, 129.7, 127.9, 127.7, 127.2, 126.4, 125.8, 120.2, 84.7, 25.1.

11B NMR (CDCl₃, 193 MHz): δ 31.8.
3-(cyclohex-1-en-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3j). A vial was charged with 1j (0.120 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3j as a yellow oil (0.14 g, 77% yield).

1H NMR (CDCl3, 600 MHz): δ 8.25 (app d, J = 7.8 Hz, 1H), 7.72 (app d, J = 8.0 Hz, 1H), 7.64 (app td, J = 7.6, 1.2 Hz, 1H), 7.41 (app td, J = 7.6, 1.0 Hz, 1H), 2.41-2.39 (m, 2H), 2.14-2.12 (m, 2H), 1.74-1.70 (m, 2H), 1.65-1.61 (m, 2H), 1.35 (s, 12H).

13C NMR (CDCl3, 125 MHz): δ 163.0, 162.7, 139.8, 134.6, 134.6, 132.0, 129.5, 127.5, 126.2, 120.2, 84.2, 26.3, 25.5, 25.0, 22.2, 21.7.

11B NMR (CDCl3, 193 MHz): δ 31.3.

HRMS (ESI+): Calculated for C21H25BO4Na ([M+Na]+), 375.1747; found 375.1744.

6-(6-chlorohexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-pyran-2-one (3k). A vial was charged with 1k (0.179 g, 0.780 mmol, 1.00 equiv) and 0.8 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.170 g, 1.10 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.8 mL toluene. A separate vial
was then charged with pinacol (0.272 g, 2.30 mmol, 3.00 equiv) and Et₃N (1.6 mL, 12 mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3k as a yellow oil that solidified upon standing (0.11 g, 41% yield).

1H NMR (CDCl₃, 600 MHz): δ 7.51 (d, J = 9.4 Hz, 1H), 6.07 (d, J = 9.4 Hz, 1H), 3.48 (t, J = 6.7 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H), 1.72 (M, 2H), 1.64 (quin, J = 7.6, 2H), 1.42 (t, J = 7.8 Hz, 2H), 1.32 (quin, J = 7.5 Hz, 2H), 1.26 (S, 12H).

13C NMR (CDCl₃, 125 MHz): δ 163.0, 162.7, 139.8, 134.6, 134.6, 132.0, 129.5, 127.5, 126.2, 120.2, 84.2, 26.3, 25.5, 25.0, 22.2, 21.7.

11B NMR (CDCl₃, 193 MHz): δ 30.2.

HRMS (ESI+): Calculated for C₁₇H₂₆ClBO₄ ([M]+), 340.1616; found 340.1609.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(thiophen-3-yl)-2H-pyran-2-one (3m). A vial was charged with 1m (0.096 g, 0.50 mmol, 1.0 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.500 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 21 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et₃N (1.0 mL, 7.5 mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3m as a yellow oil that solidified upon standing (0.090 g, 59% yield).

1H NMR (CDCl₃, 600 MHz): δ 8.07 (d, J = 2.1 Hz, 1H), 7.66 (d, J = 9.4 Hz, 1H), 7.56 (d, J = 5.0 Hz, 1H), 7.28 (dd, J = 5.1, 3.0 Hz, 1H), 6.20 (d, J = 9.4 Hz, 1H), 1.29 (s, 12H).

13C NMR (CDCl₃, 125 MHz): δ 164.1, 161.7, 149.6, 134.6, 129.6, 128.1, 125.1, 112.6, 84.6, 24.8.

11B NMR (CDCl₃, 193 MHz): δ 30.3.

HRMS (ESI+): Calculated for C₁₅H₁₇BO₄SNa ([M+Na]+), 327.0841; found 327.0834.
6-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-pyran-2-one (3n). A vial was charged with \( \mathbf{1n} \) (0.070 g, 0.35 mmol, 1.0 equiv) and 0.4 mL of toluene. A separate vial equipped with a stir bar was charged with \( B \)-chlorocatecholborane (0.075 g, 0.49 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.4 mL toluene. A separate vial was then charged with pinacol (0.124 g, 1.05 mmol, 3.00 equiv) and \( \text{Et}_3\text{N} \) (0.70 mL, 5.3 mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture 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 25% 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 \( \mathbf{3n} \) as a yellow crystalline solid (0.049 g, 47% yield).

\(^1\)H NMR (CDCl\(_3\), 600 MHz): \( \delta 7.65–7.63 \) (m, 3H), 7.47 (app t, \( J = 7.4 \) Hz, 1H), 7.39 (app t, \( J = 7.7 \) Hz, 2H), 6.27 (d, \( J = 9.3 \) Hz, 1H), 1.25 (s, 12H).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta 169.6, 162.1, 148.9, 133.3, 131.0, 129.5, 127.9, 113.0, 84.5, 24.7. \)

\(^{11}\)B NMR (CDCl\(_3\), 193 MHz): \( \delta 30.8. \)

HRMS (ESI+): Calculated for C\(_{17}\)H\(_{19}\)BO\(_4\)Na ([M+Na]\(^+\)), 321.1277; found 321.1283.

6-cyclopropyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-pyran-2-one (3p). A vial was charged with \( \mathbf{1p} \) (0.100 g, 0.670 mmol, 1.00 equiv) and 0.7 mL of toluene. A separate vial equipped with a stir bar was charged with \( B \)-chlorocatecholborane (0.144 g, 0.930 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.7 mL toluene. A separate vial was then charged with pinacol (0.237 g, 2.01 mmol, 3.00 equiv) and \( \text{Et}_3\text{N} \) (1.4 mL, 10. mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture 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 3p as a yellow solid (0.098 g, 56% yield).

$^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.52 (d, $J = 9.2$ Hz, 1H), 6.00 (d, $J = 9.4$ Hz, 1H), 2.73 (m, 1H), 1.28 (s, 12H), 1.21 (m, 2H), 0.99 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 176.3, 162.1, 149.3, 110.4, 84.1, 24.9, 13.9, 10.2.

$^{11}$B NMR (CDCl$_3$, 193 MHz): $\delta$ 30.9.

HRMS (Cl) Calculated for C$_{14}$H$_{19}$BO$_4$ ([M]$^+$), 262.1379; found 262.1368.

F. Multigram Scale Preparation of 3g

In a nitrogen-filled glove box, a Schlenk bomb was charged with a solution of 1g (2.50 g, 9.23 mmol, 1.00 equiv) in 4.6 mL toluene via pipette. A solution of B-chlorocatecholborane (1.99 g, 12.9 mmol, 1.40 equiv) in 4.6 mL toluene was then added via pipette. The Schlenk bomb was then sealed, brought outside of the glove box, 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 24 h at 100 °C in an oil bath. At this time, the reaction mixture was cooled to room temperature and returned to the glove box. A solution of pinacol (3.27 g, 27.7 mmol, 3.00 equiv) and Et$_3$N (19.2 mL, 139 mmol, 15.0 equiv) was then added to the reaction mixture over 5 min and the resulting solution was stirred for 1.5 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 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 3g as an off-white solid (2.5 g, 71% yield). Spectral data were identical to those previously obtained for this compound (see page S20).
G. Synthesis of 12

3-butylishoformane-1,4-dione (4). The initial oxyboration step was performed in a N₂-filled glove box. A vial was charged with 1b (0.108 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with B-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. The reaction mixture was then cooled to room temperature and taken out of the glovebox before 1 mL of methanol, NaOH (0.30 mL of a 3.0 M solution, 0.80 mmol, 1.6 equiv) and H₂O₂ (82 µL of a 30 wt% solution, 0.80 mmol, 1.6 equiv) were added. The reaction mixture was stirred for 2 h, then diluted with 100 mL EtOAc and washed with NH₄Cl (1 × 20 mL), water (1 × 20 mL), brine (1 × 20 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography using an elution gradient from 100% hexanes to 30% 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 12 as a yellow oil. (0.12 g, 56% yield).

¹H NMR (CDCl₃, 600 MHz): δ 8.27 (m, 1H), 8.06 (dd, J = 7.6, 1.0 Hz, 1H), 7.87-7.81 (m, 2H), 5.09 (dd, J = 7.5, 4.7 Hz, 1H), 2.06-1.99 (m, 2H), 1.49-1.44 (m, 2H), 1.39-1.30 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 192.7, 162.0, 135.7, 134.7, 131.6, 130.7, 128.3, 126.0, 84.6, 33.8, 26.7, 22.4, 13.9.

HRMS (ESI⁺): Calculated for C₁₃H₁₈NO₃ ([M+NH₄]⁺), 236.1287; found 236.1281.

H. Suzuki Cross-Coupling of 3g to Generate 13

3-(4-chlorophenyl)-4-(4-fluorophenyl)-1H-isochromen-1-one (13). This procedure was performed in a N₂-filled glove box. A 20 mL vial was charged with Pd(PPh₃)₄ (21 mg, 0.020 mmol, 0.030 equiv), THF (4.0 mL), 4-fluoriodobenzene (69 µL, 0.60 mmol, 1.0 equiv), 3g (0.229 g, 0.599 mmol, 2.00 equiv), sodium carbonate (1.2 mL of a 2.0 M aqueous solution, 2.3
mmol), and a stir bar. The vial was then quickly sealed and brought out of the glove box. The vial was then heated to 75 °C for 17 h. At this time, TLC (80:20 hex:EtOAc) indicated complete consumption of starting material. The reaction mixture was cooled to room temperature, then diluted with 100 mL EtOAc and washed with water (2 × 20 mL), brine (1 × 20 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The 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 13 as a yellow solid (0.12 g, 58% yield).

1H NMR (CDCl₃, 600 MHz): δ 8.43 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.29-7.16 (m, 9H).

13C NMR (CDCl₃, 125 MHz): δ 163.7, 162.0, 161.8, 150.2, 138.6, 135.3, 135.0, 133.0, 132.97, 130.6, 129.9, 128.6, 128.4, 125.3, 120.6, 116.7, 116.5.

HRMS (ESI+): Calculated for C₂₁H₁₂ClFO₂Na ([M+Na]⁺), 373.0407; found 373.0414.

I. Synthesis of Borylated Isoxazole Product 15

1-(4-bromophenyl)hept-2-yn-1-one (SI-22) was prepared according to a literature procedure in 86% yield. 1H NMR (CDCl₃, 600 MHz): δ 7.99 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 2.50 (t, J = 7.1 Hz, 2H), 1.66 (quin, J = 7.3 Hz, 2H), 1.50 (sxt, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H). This spectrum is in agreement with previously reported spectral data.

(Z)-1-(4-bromophenyl)hept-2-yn-1-one O-methyl oxime (14) was prepared according to a modified literature procedure. A round-bottom flask was charged with H₂NOMe·HCl (0.38 g, 4.5 mmol, 2.0 equiv), Na₂SO₄ (0.64 g, 4.5 mmol, 2.0 equiv), and a stir bar. The solids were suspended in 8 mL of MeOH. Pyridine (0.68 mL, 8.4 mmol, 3.7 equiv) and then ketone SI-23 (0.60 g, 2.3 mmol, 1.0 equiv) were consecutively added. The reaction was stirred at 25 °C for 23 h without special precautions for oxygen or moisture. The reaction was then quenched with 30 mL DI water and extracted with EtOAc (3 × 60 mL). The combined organic layers were washed with brine (30 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The 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 to afford 14 as light yellow oil (0.27 g, 41% isolated yield).

1H NMR (CDCl₃, 600 MHz): δ 7.70 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 4.07 (s, 3H), 2.54 (t, J = 7.2 Hz, 2H), 1.65 (quin, J = 7.3 Hz, 2H), 1.51-1.47 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

13C NMR (CDCl₃, 125 MHz): δ 139.4, 133.0, 131.6, 128.1, 123.9, 104.6, 71.2, 63.2, 30.5, 22.2, 19.6, 13.7.

HRMS (ESI+): Calculated for C₁₄H₁₇NBrO ([M+H]⁺), 294.0493; found 294.0493.
3-(4-bromophenyl)-5-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoxazole (15). A vial was charged with 14 (0.147 g, 0.500 mmol, 1.00 equiv) and 0.5 mL $d_8$-toluene [Note: the deuterated toluene was used to monitor this unoptimized reaction by $^1$H and $^{11}$B NMR spectroscopy]. A separate vial was charged with $B$-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which was then transferred to a J-Young tube via pipette. The tube was then heated to 100 °C for 48 h, and subsequently to 110 °C for 48 h. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et$_3$N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and 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 15 as an off-white solid (0.072 g, 35% yield).

$^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.72 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 3.01 (t, $J = 7.6$ Hz, 2H), 1.71 (quin, $J = 7.5$ Hz, 2H), 1.41-1.37 (m, 2H), 1.29 (s, 12H), 0.94 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 183.3, 165.2, 131.3, 130.7, 129.2, 123.8, 83.8, 30.6, 27.0, 24.8, 22.3, 13.8.

$^{11}$B NMR (CDCl$_3$, 193 MHz): $\delta$ 29.9.

HRMS (ESI+): Calculated for C$_{19}$H$_{25}$NBBrO$_3$ ([M]$^+$), 405.1115; found 405.1107.

J. Procedure for $^1$H NMR observation of the rate of demethylation of methyl 2-iodobenzoate 10

This procedure was performed in a N$_2$-filled glove box. A 4 mL vial was charged with $B$-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv) and 0.5 mL of $d_8$-toluene. To this vial was sequentially added 10 (75 $\mu$L, 0.50 mmol, 1.0 equiv) and 1,3,5-triisopropylbenzene (40 $\mu$L, 0.17 mmol, 0.33 equiv) via syringe. The contents of this vial were then transferred to a J-young tube, which was sealed, and then removed from the glove box. Single scan $^1$H and $^{11}$B NMR spectra were taken at time points $t = 0$ h, 18 h, and 24 h. The resonances corresponding to 10
were compared to the internal standard to determine the percent of 10 remaining at $t = 24 \text{ h}$ (>95% 10 remaining at 24 h).

III. References

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IV. NMR Spectra
$^{13}$C NMR

**1e**
$^1$H NMR
$^{13}$C NMR
$^1$H NMR
$^{13}$C NMR

3aa

Bpin

Ph
$^{11}$B NMR
$\text{Ph}$

$\text{B(OH)}_2$

$\text{3ab}$

$^1\text{H NMR}$
$\text{O}$

B(OH)$_2$

3ab

$^1$H NMR

(zoomed in)
\[ \text{MeOOC} \quad \text{Bpin} \quad \text{Ph} \]

$^1$H NMR
$^{13}$C NMR
$^{11}$B NMR

3c

MeOOC

Bpin

Ph
$^{13}$C NMR
$^1$B NMR
$\text{HO}_2\text{B}$

$3f$

$^1\text{H NMR}$
1D NOE Data
$^{13}$C NMR
$^{1}$H NMR
$13^C$ NMR

3h
$^{11}$B NMR
$^1$H NMR (zoomed in)
$^{13}$C NMR
3j

$^{13}$C NMR
$^{1}$H NMR
$^{11}$B NMR
$^{13}$C NMR

3m
$^{11}$B NMR

$3n$

[Chemical structure diagram]
$^1$H NMR
$^{11}$B NMR
$^{13}$C NMR
$^{13}$C NMR
$^{11}$B NMR
Crude $^1$H NMR after 24 h
Crude $^1$H NMR after 24 h
Crude $^1$H NMR after 24 h
$^1$H NMR after 2 h in $d_8$-toluene
$^1$H NMR after 24 h in $d_8$-toluene