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Note

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Chemoselective Rhodium-Catalyzed Borylation of Bromoiodoarenes Under Mild Conditions

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Supporting Information Placeholder

ABSTRACT:

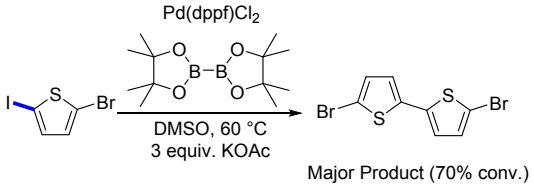
A chemoselective rhodium-catalyzed borylation has been developed for preparation of aryl boronates. The reaction proceeds under mild conditions with excellent selectivity for C-I bonds in bromoiodoarenes and exhibits broad functional group tolerance. This procedure can act as a complementary approach towards bifunctional arenes along with other metal-catalyzed borylations. Additionally, the reaction's utility in preparation of monomers for metal-catalyzed cross-coupling polymerization is demonstrated.

Organoboron compounds are highly versatile synthons used in the preparation of natural products, organic materials and conjugated polymers. The broad utility of these reagents in synthesis stems from their stability towards isolation and reactivity under the appropriate reaction conditions.[1-2] These features have led to the rapid development of borylation protocols, particularly for arenes (to be used in Suzuki-Miyaura reactions).[3-31] Transition-metal catalyzed approaches to install the boron moiety are especially useful since they are often tolerant of other functional groups that can then be used for orthogonal derivatization. Herein a mild, chemoselective rhodium-catalyzed borylation is reported that enables the preparation of arenes bearing both a boronate and a halogen.

Halogenated aryl boronates are particularly useful reagents for constructing conjugated polymers. They are generally prepared from dihalogenated substrates via metalation and quenching,[32-34] or by C-H borylation of halogenated arenes using an iridium catalyst.[35-38] To complement these approaches, we sought a transition-metal catalyzed borylation for C-I bonds in bromoiodoarenes. This protocol could then be employed to make monomers if the substrate is not compatible with metalation, or if the iridium-catalyzed C-H activation does not lead to the desired halogenated boronate. A catalyst suitable for thiophene derivatives was critical, as thiophenes are ubiquitous in conjugated materials.

The viability of $Pd(dppf)Cl_2$ for chemoselective borylation of 2-bromo-5-iodothiophene was evaluated using bis(pinacolato)diboron (B_2pin_2) as the borylating agent and KOAc as the base. This mirrored a protocol reported previously by Miyaura and coworkers in which 1-bromo-4-iodobenzene could be borylated selectively at the weaker C-I bond.[31] However, attempted borylation of the unsymmetrically halogenated 2-bromo-5-iodothiophene (Scheme 1) produced 5,5'-dibromo-2,2'-bithiophene as the major product (Figure S1). This likely results from initial borylation of the iodide, followed by cross-coupling of the remaining starting material and newly formed thiophene boronate. This led us to explore alternative strategies for direct isolation of the organoboron.

Scheme 1. Attempted borylation of 2-bromo-5-iodothiophene using bis(pinacolato)diboron with $Pd(dppf)Cl_2$.



Rhodium was considered as a substitute for palladium in this reaction since Murata and coworkers had reported that the 1,5-cyclooctadienerhodium(I) chloride dimer ($[Rh(COD)Cl]_2$) could convert aryl halides to aryl silanes.[39-42] The silylation was efficient and the authors noted higher reactivity for aryl iodide substrates in that work. Additionally, rhodium has also been used as a highly effective catalyst in a wide range of borylation chemistries.[43-49]

Borylation of 2-bromo-5-iodothiophene was attempted at ambient temperature with $[Rh(COD)Cl]_2$, B_2pin_2, and KOAc in dry 1,4-dioxane. The use of KOAc as a mild base was particularly important with these heterocyclic halogenated substrates, as the final product can be susceptible to protodeboronation. Under these conditions, excellent selectivity for the C-I bond was observed, with greater than 90% conversion to the desired aryl boronate (Figure 1). Interestingly, Miyaura had attempted to use Wilkinson's catalyst ($RhCl(PPh_3)_3$) in the original borylation of aryl halides without success.[31] We have noted that addition of phosphine to the reaction during borylation with $[Rh(COD)Cl]_2$ suppresses the reaction. Pinacolborane (HBpin) was also considered as a boron source, as this would improve the atom economy of the transformation, but the use of HBpin as opposed to B_2pin_2 predominantly afforded the reduced 2-bromothiophene. As

such, all further experiments were carried out with the diboron reagent.

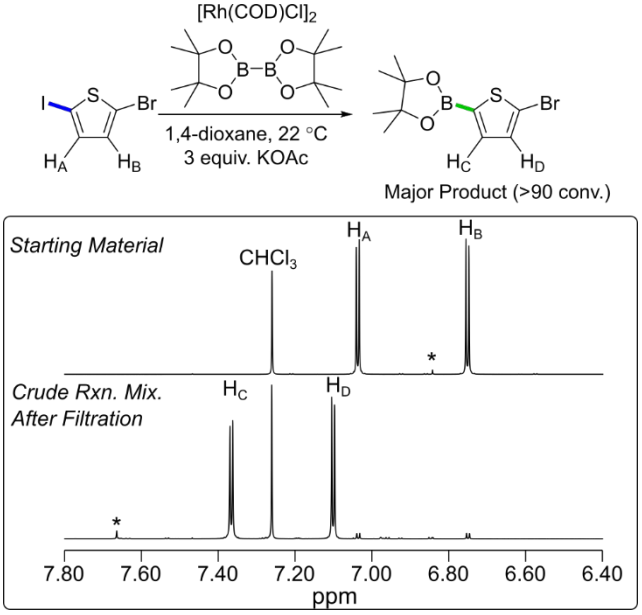


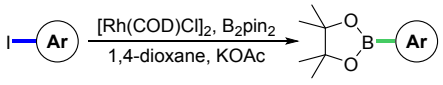
Figure 1. A stack plot of ^{1}H NMR spectra (500 MHz, 22 °C, $CDCl_3$) for 2-bromo-5-iodothiophene borylation with B_2pin_2 (aromatic region). The top spectrum corresponds to the starting material and the bottom spectrum corresponds to an aliquot from the reaction mixture. The * signals correspond to 2,5-diiodothiophene (top) and the diboronate (bottom).

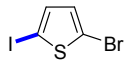
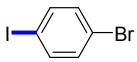
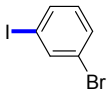
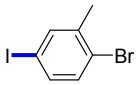
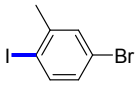
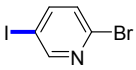
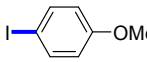
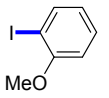
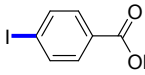
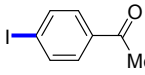
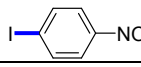
Reaction optimization was also explored with the thiophene derivative. Generally, low loadings of the rhodium catalyst were needed (0.5 mol % of the dimer) at either 22 °C or 50 °C for borylation. Going below 0.5 mol % of $[Rh(COD)Cl]_2$ resulted in lower conversion to the desired product (Figure S63). Excellent selectivity for the C-I bond was observed when B_2pin_2 was used as the limiting reagent (0.95 equiv relative to substrate) but increasing beyond 1 equiv. of B_2pin_2 did result in some C-Br activation and double borylation. Interestingly, 2-bromo-5-iodothiophene was >75% borylated after only 1 h (Figure S63), but all subsequent reactions were typically conducted for 24 h for consistency. Finally, three equiv. of KOAc were employed in these borylations, but two was shown to be enough with 2-bromo-5-iodothiophene (95% conv. after 24 h, Figure S64). Importantly, reactions carried out in the absence of the rhodium catalyst or KOAc did not proceed (Figure S62), highlighting the importance of both reagents in the reaction.

Building on the initial success with 2-bromo-5-iodothiophene (Table 1, Entry 1a), several other bromoiodobenzenes were investigated (Table 1, Entries 1b-1e). The *para* and *meta* dihalogenated benzene derivatives were easily borylated (Entries 1b and 1c). Methyl substitution *meta* to the iodine was tolerated (Entry 1d) but an *ortho* substituted methyl group resulted in much lower conversion at 22 °C (Entry 1e). Fortunately, carrying out the reaction at 50 °C resolved this issue, and conversion to the desired boronate was above 90% for all four benzene variants at this temperature. In addition to the thiophene and benzene, selective borylation of the C-I bond was observed for a bromoiodopyridine (Entry 1f).

The impact of functional groups was also probed by exploring a variety of benzene derivatives (Tables 1 and 2). These reactions all proceeded to near quantitative conversion (Entries 1g-1k and Entries 2a-2e), apart from 2d and 2e (*ortho* substituted iodoarenes), both of which had slightly lower conversion. Overall, the reaction was shown to be tolerant of ester, cyano, keto, nitro, chloro, fluoro, and alkoxy functional groups. Tolerance to the keto group was particularly valuable, as this enabled us to make a novel monomer (Entry 3b) for polymerization.

Table 1. Iodoarenes borylated using $[Rh(COD)Cl]_2$, B_2pin_2 and KOAc.



Entry	Substrate	Conversion (%) 22 °C	Conversion (%) 50 °C	Yield (%)
1a		91	89	58
1b		93	91	60
1c		99	99	68
1d		90	99	81
1e		56	91	64
1f		98	99	72
1g		99	97	73
1h		99	96	83
1i		99	99	81
1j		99	99	77
1k		98	99	82

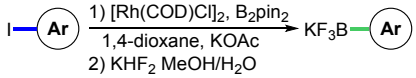
All reactions were conducted with the iodoarene (1 equiv.), B_2pin_2 (0.95-1.05 equiv.), KOAc (3 equiv.) and 0.5 mol % of $[Rh(COD)Cl]_2$. Conversion was determined by GC relative to an internal standard.

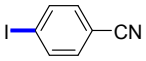
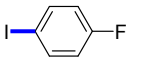
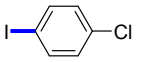
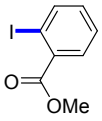
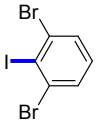
In some cases, difficulties with purification of the boronate products were noted, as yields were much lower than expected based on the conversion data. This is often the case with electron-poor arenes, which can be susceptible to protodeboronation.[2, 50-51] If isolation proved difficult, an alternative procedure was employed (Table 2). Upon completion of the borylation, the reaction mixture was treated directly with KHF_2 to convert the boronate into an isolable

potassium trifluoroborate salt (Table 2, Entries 2a-2e).[52-53] Unstable arylboronates have been isolated using this strategy previously.[54] These trifluoroborates can be purified via recrystallization and used directly in cross-coupling under the appropriate conditions.[52-53]

Generally, borylation and isolation of compounds with substituents located *ortho* to the iodine functionality were more challenging than *para*-substituted derivatives. While *p*-iodoanisole and *o*-iodoanisole were borylated with nearly identical conversion (Entries 1g and 1h), the *ortho* derivative partially hydrolyzed to the boronic acid during purification. This hydrolysis was consistent across repeated purification attempts, and the yield reported in Table 1 is as a mixture of boronate and boronic acid (Figure S7). Our current hypothesis is that the methoxy group destabilizes the boronate, facilitating degradation to the boronic acid contaminant.

Table 2. Iodoarenes borylated using $[Rh(COD)Cl]_2$, B_2pin_2 and KOAc and isolated as the trifluoroborate salt.



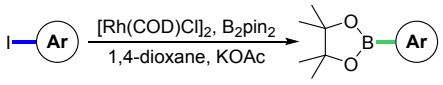
Entry	Substrate	Conversion (%) 22 °C	Conversion (%) 50 °C	Yield (%)
2a		49	99	69
2b		99	98	76
2c		99	99	73
2d		86	87	61
2e		83	79	-
2f		0	0	N/A

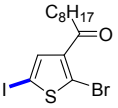
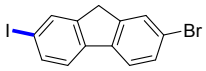
All reactions were completed with the iodoarene (1 equiv.), B_2pin_2 (0.95-1.05 equiv.), KOAc (3 equiv.) and 0.5 mol % of $[Rh(COD)Cl]_2$. Conversion was determined by GC relative to an internal standard.

Electron-withdrawing substituents such as bromide and methyl ester in the *para* position did not impact borylation, with >90% conversion to the desired products (Entries 1b and 1i). The related *ortho* derivatives (Entries 2d and 2e) produced <90% conversion, but only the 2-bromophenyl trifluoroborate salt could be isolated (Entry 2d). At this time, it is not clear why the related methyl ester derivative (Entry 2e) was difficult to isolate, as Molander and coworkers have prepared this derivative previously.[55] Finally, 1,3-dibromo-2-iodobenzene (Entry 2f) did not react under the borylation conditions; further work is necessary to determine whether this lack of reactivity is attributed to steric or electronic effects.

Ultimately, this method was developed to enable facile formation of organoboron precursors for eventual use as monomers in cross-coupling polymerization. For example, thiophene substrates bearing ester and ketone functionalities were borylated in 56% and 60% yield respectively (Table 3, Entries 3a and 3b). Another common type of monomer in cross-coupling polymerization, fluorene, could also be borylated using this rhodium-catalyzed strategy in 88% yield.

Table 3. Preparation of halogenated aryl boronate monomers for Suzuki-Miyaura polymerization.



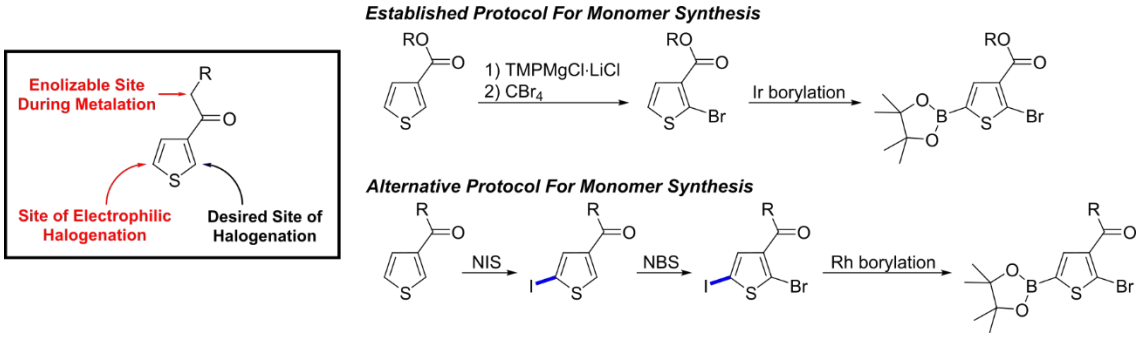
Entry	Substrate	Conversion (%) 22 °C	Conversion (%) 50 °C	Yield (%)
3a		82	82	56
3b		71	72	60
3c		99	99	88

All reactions were completed with the iodoarene (1 equiv.), B_2pin_2 (0.95 equiv), KOAc (3 equiv.) and 3 mol % of the $[Rh(COD)Cl]_2$. Conversion was determined by GC relative to an internal standard.

Successful application of the protocol to substrate 3b was particularly noteworthy, as the monomer is not easily accessible using established synthetic routes (Scheme 2). Efficient cross-coupling polymerization of five-membered heterocycles is typically achieved with a specific orientation of the reactive substituents on the ring.[56] Monomers that produce high yields and efficient polymerization bear a halogen in the 2-position, a solubilizing group in the 3, and a coupling partner in the 5. The solubilizing group *ortho* to the halogen provides steric stabilization to the M^{2+} species after oxidative addition during the polymerization process (particularly with nickel catalysts).[57]

2-halo-3-substituted thiophenes are challenging to prepare with carbonyl moieties at the 3-position, since electrophilic halogenation proceeds selectively with the undesired regiochemistry (Scheme 2). If the substituent in the 3-position is an ester, a metalation and quenching approach can be used to brominate the 2-position,[36, 58] and borylation can be carried out with iridium to form the desired monomer (Scheme 2, top right). However, replacement of the ester with a ketone limits the use of metalation due to the acidity of the α-protons. As an alternative, a successive halogenation approach can afford the bromoiodoarene, which can then be borylated using rhodium (Scheme 2, bottom right).

Scheme 2. Established and alternative synthetic protocols for the preparation of 2-halo-3-carbonyl-5-boronate thiophenes.



Future work will focus on exploring the reaction mechanism of this diboron reaction in more detail. A Rh-Bpin complex is likely the key to the entire process, but we do not have direct evidence of a Rh boryl complex yet. This species could conceivably form via oxidative addition of B_2pin_2, or by transmetalation of the diboron with an $^-$OAc ligated to Rh. The catalytic reaction does not proceed without KOAc, which supports transmetalation, though the order of the elementary steps for the overall reaction is still under investigation. A plausible mechanism would involve oxidative addition of the aryl iodide to the Rh-Bpin complex and reductive elimination of the Ar and Bpin fragments to yield the desired organoboron. This would suggest formation of Rh-Bpin prior to oxidative addition, though it could also conceivably form after addition of the aryl iodide. Detailed mechanistic studies are ongoing and should facilitate broader comparisons with other rhodium and iridium-catalyzed borylations in the future.

The borylation of aryl iodides described herein serves as a practical approach to building arenes with two different functionalities. The rhodium catalyst, B_2pin_2, and KOAc are all commercially available with no other necessary additives, and the reaction can be conducted at low catalyst loadings under mild conditions. It serves as a complementary approach to other methods used for borylation, with excellent regiocontrol governed by the location of the iodide. For example, since Ir-borylation is sterically driven, electrophilic halogenation followed by borylation can lead to specific organoborons that might be inaccessible otherwise, though more synthetic steps are needed. The mild reaction conditions and functional group tolerance of this catalytic reaction suggest it could be useful in borylating other challenging arenes in the future.

EXPERIMENTAL SECTION

Materials and Methods. All reactions and manipulations of air and water sensitive compounds were carried out under a dry N_2 atmosphere using an mBraun glovebox or standard Schlenk techniques with dried and degassed solvents. All reagents were purchased from commercial sources and used as received. Hexyl 2-bromothiophene-3-carboxylate was synthesized according to a literature procedure.[36] All solvents and chemicals used for extraction and column chromatography were used as received. Flash chromatography was completed using a Biotage Isolera One Flash Chromatography System using Aldrich technical grade silica gel (pore size 60 Å, 70-230 mesh, 63-200 μm). NMR data were in agreement with literature reports for 1a,[59] 1b,[31] 1c,[60] 1e,[61] 1f,[62] 1g,[31] 1h,[63] 1i,[31] 1j,[31] 1k,[31] 2a,[64] 2b,[64] 2c,[65] 3a[36].

NMR Analysis. All NMR experiments were collected at 300 K on a two-channel Bruker Avance III NMR instrument equipped with a Broad Band Inverse (BBI) probe, operating at 500 MHz for ^{1}H (126 MHz for $^{13}C\{^1H\}$, 160 MHz for $^{11}B\{^1H\}$, 470 MHz for ^{19}F). The ^{1}H NMR spectra are referenced to residual protio solvents (7.26 ppm for $CHCl_3$, 2.05 ppm for $(CD_3)_2CO$, 2.50 ppm for $(CD_3)_2SO$) and the $^{13}C\{^1H\}$ NMR spectra are referenced to either $CDCl_3$ (77.2 ppm), $(CD_3)_2CO$ (29.8 ppm), or $(CD_3)_2SO$ (39.5 ppm). ^{19}F and $^{11}B\{^1H\}$ spectra were referenced to the lock signal. In $^{13}C\{^1H\}$ NMR spectra collected for the borylated arenes, no signal is observed for the carbon atom directly attached to the boron due to quadrupolar relaxation.

Mass Spectrometry. DART-MS (positive mode, 150-300 °C) and ESI-MS measurements were performed on a Thermo Scientific Exactive Plus EMR Orbitrap Mass Spectrometer with He as the carrier gas. Samples were prepared as 0.2 mg/mL solutions (in diethyl ether or methanol). In some cases, $[2M + H]^+$ and $[M + NH_4]^+$ species were also observed.

GC-MS Analysis. GC-MS analysis was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. The GC column was a Restek fused silica capillary column (RTX-5). Helium was used as the carrier gas. The following conditions were used for all GC-MS analyses: injector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C/min; final temperature, 280 °C (the experiment with 1-fluoro-4-iodobenzene began at 50 °C with a temperature ramp of 10 °C/min and a final temperature of 170 °C). For conversion estimates, 0.02 mL aliquots were removed from borylation reactions at 0 h (all reagents added except the Rh cat.) and 24 h (unless otherwise noted) and diluted with 17.5 mL diethyl ether or ethyl acetate. This solution was then filtered through a 0.22 μm PTFE syringe filter into a 2 mL vial for analysis. Substrate signal area was determined relative to the internal standard.

Procedure 1. Rhodium-Catalyzed Borylation of Iodinated Arenes. In a N_2 filled glovebox, a 20 mL scintillation vial equipped with a Teflon screw cap was charged with an iodoarene (0.5 mmol), $[Rh(COD)Cl]_2$ (1.2 mg, 0.0024 mmol or 7.4 mg, 0.015 mmol), KOAc (147 mg, 1.5 mmol), B_2pin_2 (121 mg, 0.48 mmol or 134 mg, 0.53 mmol) and 2.5 mL dry 1,4-

dioxane. Trimethoxybenzene (29 mg, 0.17 mmol) was added as an internal standard for conversion experiments. The reaction vial was capped, removed from the glovebox, and stirred for 24 h (unless otherwise noted) at room temperature or 50 °C. The reaction mixture was filtered through a thin pad of celite, and the celite was washed with 100 mL diethyl ether. The mixture was concentrated using rotary evaporation and purified via column chromatography.

Procedure 2. Rhodium-Catalyzed Borylation of Iodinated Arenes Followed by Conversion to Potassium Trifluoroborates. In a N_2 filled glovebox, a 20 mL scintillation vial equipped with a Teflon screw cap was charged with an iodoarene (0.5 mmol), $[Rh(COD)Cl]_2$ (1.2 mg, 0.0024 mmol or 7.4 mg, 0.015 mmol), KOAc (147 mg, 1.5 mmol), B_2pin_2 (121 mg, 0.48 mmol or 134 mg, 0.53 mmol), and 2.5 mL dry 1,4-dioxane. Trimethoxybenzene (29 mg, 0.17 mmol) was added as an internal standard for conversion experiments. The reaction vial was capped, removed from the glovebox, and stirred for 24 h (unless otherwise noted) at room temperature or 50 °C. The reaction mixture was filtered through a 0.22 μm PTFE syringe filter into a 20 mL Nalgene bottle, equipped with a stir bar, containing MeOH (2 mL), H_2O (0.8 mL), and KHF_2 (450 mg, 5.8 mmol). This mixture was stirred at room temperature for 24 h and concentrated using rotary evaporation. The crude product was then extracted from the solid residue with 30 mL acetone, and further purified by reprecipitation into diethyl ether.

2-(5-bromothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a). Prepared following procedure 1 using 2-bromo-5-iodothiophene (144 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a colorless liquid (84 mg, 58%) using a gradient from 1:0 hexanes:CH_2Cl_2 to 0:1 hexanes:CH_2Cl_2 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 3.7 Hz, 1H), 7.10 (d, J = 3.7 Hz, 1H), 1.33 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.7, 131.5, 119.6, 84.5, 24.9. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 28.4. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{15}BBrO_2S$, 289.0069; found, 289.0065.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1b). Prepared following procedure 1 using 1-bromo-4-iodobenzene (141 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a colorless, crystalline solid (85 mg, 60%) using a gradient from 1:0 hexanes:CH_2Cl_2 to 0:1 hexanes:CH_2Cl_2 as the eluent. This reaction was also conducted at larger scale with 1-bromo-4-iodobenzene (1.00 g, 3.55 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$ (.0087 g, 0.018 mmol) with B_2pin_2 (0.86 g, 3.37 mmol), KOAc (1.05 g, 10.64 mmol) and 18 mL dioxane. Yield: 0.64 g (64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.52 – 7.48 (m, 2H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.5, 131.1, 126.4, 84.2, 25.0. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.0. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{17}BBrO_2$, 283.0505; found, 283.0502.

2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c). Prepared following procedure 1 using 1-bromo-3-iodobenzene (141 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a colorless, crystalline solid (96 mg, 68%) via sublimation at 30 °C and 200 mtorr. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 2.3, 1.1 Hz, 1H), 7.71 (dt, J = 7.5, 1.2 Hz, 1H), 7.58 (ddd, J = 7.9, 2.1, 1.1 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.7, 134.4, 133.3, 129.7, 122.6, 84.3, 25.0. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.5. HRMS (DART) (*m/z*): $[M+NH_4]^+$ calcd for $C_{12}H_{20}BBrNO_2$, 300.0770; found, 300.0769.

2-(4-bromo-3-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1d). Prepared following procedure 1 using 1-bromo-4-iodo-2-methylbenzene (148 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as an off-white solid (120 mg, 81%) using a gradient from 1:0 hexanes:EtOAc to 4:1 hexanes:EtOAc as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (br s, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.45 (dd, J = 7.9, 1.1 Hz, 1H), 2.40 (s, 3H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.3, 137.2, 133.7, 132.0, 128.9, 84.1, 25.0, 22.8. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.0. HRMS (ESI) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{19}BBrO_2$, 297.0661; found, 297.0647.

2-(4-bromo-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e). Prepared following procedure 1 using 4-bromo-1-iodo-2-methylbenzene (148 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a yellow oil (95 mg, 64%) using a gradient from 1:0 hexanes:CH_2Cl_2 to 1:4 hexanes:CH_2Cl_2 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 7.9 Hz, 1H), 7.33-7.32 (m, 1H), 7.29 (dd, J = 7.9, 2.0 Hz, 1H), 2.50 (s, 3H), 1.33 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.2, 137.5, 132.8, 128.1, 125.7, 83.8, 25.1, 22.1. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.2. HRMS (ESI) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{19}BBrO_2$, 297.0661; found, 297.0650.

2-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f). Prepared following procedure 1 using 2-bromo-5-iodopyridine (143 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a colorless crystalline solid (102 mg, 72%) via sublimation at 50 °C and 200 mtorr. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (dd, J = 2.1, 0.8 Hz, 1H), 7.88 (dd, J = 8.0, 2.1 Hz, 1H), 7.48 (dd, J = 8.0, 0.8 Hz, 1H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.2, 145.6, 144.6, 127.8, 84.7, 25.0. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.6. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{16}BBrNO_2$, 284.0457; found, 284.0449.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g). Prepared following procedure 1 using 1-iodo-4-methoxybenzene (117 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a white solid (85 mg, 73%) using a gradient from 1:0 hexanes:CH_2Cl_2 to 1:1 hexanes:CH_2Cl_2 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 6.93 – 6.87 (m, 2H), 3.83 (s, 3H), 1.33 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.3, 136.7, 113.5, 83.7, 55.3, 25.0. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.2. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}BO_3$, 235.1506; found, 235.1502.

2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1h). Prepared following procedure 1 using 1-iodo-2-methoxybenzene (117 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a white solid (97 mg, 83%) using a gradient from 1:0 hexanes:CH_2Cl_2 to 1:1 hexanes:CH_2Cl_2 as the eluent. The pinacol boronate was partially hydrolyzed to the boronic acid during purification; the yield includes both species. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.2, 1.9 Hz, 1H), 7.39 (ddd, J = 8.4, 7.3, 1.9 Hz, 1H), 6.94 (td, J = 7.3, 0.9 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.3, 136.9, 132.6, 120.4, 110.6, 83.6, 56.0, 25.0. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.9. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}BO_3$, 235.1506; found, 235.1502.

methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1i). Prepared following procedure 1 using methyl 4-iodobenzoate (131 mg, 0.5 mmol) and 0.5 mol %, $[Rh(COD)Cl]_2$. The title compound was obtained as a white solid (106 mg, 81%) using a gradient from 1:0 hexanes:EtOAc to 3:7 hexanes:EtOAc as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.89 – 7.85 (m, 2H), 3.92 (s, 3H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.3, 134.8, 132.5, 128.8, 84.4, 52.3, 25.1. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.9. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}BO_4$, 263.1455; found, 263.1443.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (1j). Prepared following procedure 1 using 1-(4-iodophenyl)ethan-1-one (123 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a white solid (95 mg, 77%) using a gradient from 1:0 hexanes: CH_2Cl_2 to 3:2 hexanes: CH_2Cl_2 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.91 – 7.87 (m, 2H), 2.62 (s, 3H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 198.6, 139.2, 135.1, 127.5, 84.4, 27.0, 25.1. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.6. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}BO_3$, 247.1506; found, 247.1495.

4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (1k). Prepared following procedure 1 using 1-iodo-4-nitrobenzene (125 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as an off-white solid (103 mg, 82%) using a gradient from 1:0 hexanes:EtOAc to 4:1 hexanes:EtOAc as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.17 (m, 2H), 7.99 – 7.94 (m, 2H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.0, 135.8, 122.6, 84.8, 25.1. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 30.4. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{17}BNO_4$, 250.1251; found, 250.1242.

Potassium 4-cyanophenyltrifluoroborate (2a). Prepared following procedure 2 using 4-iodobenzonitrile (114 mg, 0.5 mmol) and 0.5 mol% $[Rh(COD)Cl]_2$. The title compound was obtained as an off-white solid (72 mg, 69%) after reprecipitation from minimal acetone into diethyl ether (15 mL). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$) δ 133.2 (q, J = 1.7 Hz), 130.6, 120.7, 109.3. $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$) δ 2.9 (q, J = 51.0 Hz). ^{19}F NMR (470 MHz, $(CD_3)_2CO$) δ -144.2 (dd, J = 108.3, 51.3 Hz).

Potassium 4-fluorophenyltrifluoroborate (2b). Prepared following procedure 2 using 1-fluoro-4-iodobenzene (111 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a white solid (77 mg, 76%) after reprecipitation from minimal acetone into diethyl ether (15 mL). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.45 (app. t, J = 7.5 Hz, 2H), 6.82 (app. t, J = 9.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$) δ 162.5 (d, J = 238.6 Hz), 133.9 (dd, J = 6.7, 1.7 Hz), 113.3 (q, J = 18.6 Hz). $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$) δ 3.4 (q, J = 55.0 Hz). ^{19}F NMR (470 MHz, $(CD_3)_2CO$) δ -115.3 – -125.5 (m), -142.6 (dd, J = 115.5, 54.0 Hz).

Potassium 4-chlorophenyltrifluoroborate (2c). Prepared following procedure 2 using 1-chloro-4-iodobenzene (119 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a yellow solid (80 mg, 73%) after reprecipitation from minimal acetone into diethyl ether (15 mL). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.44 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$) δ 134.2 (q, J = 1.9 Hz), 131.2, 126.9. $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$) δ 3.3 (q, J = 53 Hz). ^{19}F NMR (470 MHz, $(CD_3)_2CO$) δ -143.1 (dd, J = 107.6, 53.1 Hz).

Potassium 2-bromophenyltrifluoroborate (2d). Prepared following procedure 2 using 1-bromo-2-iodobenzene (141 mg, 0.5 mmol), 0.5 mol % $[Rh(COD)Cl]_2$, B_2pin_2 (134 mg, 0.53 mmol), dry 1,4-dioxane (2.5 mL), the title compound was obtained as a brown solid (80 mg, 61%) after reprecipitation from minimal acetone into diethyl ether (15 mL). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.41 (dd, J = 7.3, 2.0 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 6.95 (td, J = 7.5, 2.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2SO$) δ 134.1 (q, J = 2.8 Hz), 131.4, 127.7, 127.3, 125.3. $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2SO$) δ 7.2 (q, J = 53 Hz). ^{19}F NMR (470 MHz, $(CD_3)_2SO$) δ -139.3 (dd, J = 95.6, 42.9 Hz).

hexyl 2-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carboxylate (3a). Prepared following procedure 1 using hexyl 2-bromo-5-iodothiophene-3-carboxylate (208 mg, 0.5 mmol) and 3 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a yellow liquid (117 mg, 56%) using a gradient from 1:0 hexanes:CH_2Cl_2 to 0:1 hexanes:CH_2Cl_2 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 4.27 (t, J = 6.7 Hz, 2H), 1.73 (ddt, J = 9.0, 7.8, 6.6 Hz, 2H), 1.48 – 1.39 (m, 2H), 1.38 – 1.28 (m, 16H), 0.93 – 0.87 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.2, 139.2, 132.6, 126.3, 84.8, 65.4, 31.6, 28.8, 25.9, 24.9, 22.7, 14.2. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 28.7. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{27}BBrO_4S$, 417.0906; found, 417.0890.

1-(2-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-3-yl)nonan-1-one (3b). Prepared following procedure 1 using 1-(2-bromo-5-iodothiophen-3-yl)nonan-1-one (214 mg, 0.5 mmol) and 3 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a yellow liquid (128 mg, 60%) using a gradient from 1:0 hexanes:EtOAc to 1:1 hexanes:EtOAc as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 2.90 (t, J = 7.4 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.38 – 1.20 (m, 22H), 0.92 – 0.85 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 195.4, 139.8, 138.3, 124.2, 84.9, 42.0, 32.0, 29.6, 29.4, 29.3, 24.9, 24.1, 22.9, 14.3. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 28.5. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{31}BBrO_3S$, 429.1270; found, 429.1253.

2-(7-bromo-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c). Prepared following procedure 1 using 2-bromo-7-iodo-9*H*-fluorene (185 mg, 0.5 mmol) and 0.5 mol % $[Rh(COD)Cl]_2$. The title compound was obtained as a white solid (163 mg, 88%) using 4:1 hexanes: CH_2Cl_2 as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.51 (dd, J = 8.1, 2.0 Hz, 1H), 3.89 (s, 2H), 1.37 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 146.0, 143.7, 142.3, 140.7, 133.8, 131.5, 130.1, 128.6, 121.8, 121.2, 119.5, 84.0, 36.8, 25.1. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.6. HRMS (ESI) (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{21}BBrO_2$, 371.0818; found 371.0807.

1-(thiophen-3-yl)nonan-1-one. To a 500 mL Schlenk flask were added thiophene-3-carbonyl chloride (5.86 g, 40.1 mmol), $Fe(acac)_3$ (g, mmol), and 200 mL THF. The reaction was cooled to 0 °C, and then octylmagnesium bromide solution (2.0 M in diethyl ether, 20.0 mL, 40 mmol) was added dropwise over 30 min. The reaction was stirred for an additional 1 h at 0 °C, and then 1 h at room temperature. 75 mL 1 M HCl was added to quench the reaction. The reaction mixture was concentrated using rotary evaporation and the resulting mixture was

transferred to a 500 mL separatory funnel, diluted with 250 mL deionized H_2O, and extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated using rotary evaporation. The crude product was purified using column chromatography on silica gel using a gradient from 1:0 hexanes:EtOAc to 3:1 hexanes:EtOAc as the eluent to afford an off-white solid (5.63 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 2.9, 1.2 Hz, 1H), 7.54 (dd, J = 5.0, 1.4 Hz, 1H), 7.30 (dd, J = 5.0, 2.9 Hz, 1H), 2.91 – 2.82 (m, 2H), 1.72 (p, J = 7.2 Hz, 2H), 1.43 – 1.20 (m, 10H), 0.92 – 0.84 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 195.2, 142.7, 131.8, 127.2, 126.4, 40.2, 32.0, 29.6, 29.6, 29.4, 24.6, 22.8, 14.3. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{21}OS$, 225.1313; found, 225.1309.

1-(5-iodothiophen-3-yl)nonan-1-one. In a 20 mL scintillation vial wrapped in aluminum foil, 1-(2-bromo-5-iodothiophen-3-yl)nonan-1-one (1.52 g, 6.78 mmol) was dissolved in 15 mL chloroform:acetic acid (7:3, v/v). N-iodosuccinimide (4.50 g, 20.0 mmol) was added in three portions to the stirring solution over 10 min. The reaction was stirred at room temperature for 24 h. The reaction solution was transferred to a separatory funnel, diluted with 500 mL of 1 M $Na_2S_2O_3$ solution and extracted with diethyl ether (3 × 150 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated using rotary evaporation. The crude product was purified using column chromatography on silica gel using a gradient from 1:0 hexanes:EtOAc to 4:1 hexanes:EtOAc as the eluent to afford a white solid (1.27 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 1.5 Hz, 1H), 7.67 (d, J = 1.5 Hz, 1H), 2.84 – 2.75 (m, 2H), 1.69 (p, J = 7.4 Hz, 2H), 1.40 – 1.21 (m, 10H), 0.92 – 0.83 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 193.6, 144.1, 137.2, 136.7, 74.8, 39.8, 32.0, 29.6, 29.5, 29.3, 24.5, 22.8, 14.3. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}IOS$, 351.0280; found, 351.0263.

1-(2-bromo-5-iodothiophen-3-yl)nonan-1-one. In a 100 mL round-bottomed flask wrapped in aluminum foil, 1-(5-iodothiophen-3-yl)nonan-1-one (1.43 g, 4.09 mmol) was dissolved in 41 mL DMF. N-bromosuccinimide (1.45 g, 8.15 mmol) was added in three portions to the stirring solution over ten min (at room temperature). The reaction was stirred at 47 °C for 18 h. The reaction solution was transferred to a separatory funnel, diluted with 500 mL of 1 M $Na_2S_2O_3$ solution and extracted with diethyl ether (3 × 150 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated using rotary evaporation. The crude product was purified using column chromatography on silica gel using a gradient from 1:0 hexanes:EtOAc to 9:1 hexanes:EtOAc as the eluent to afford a slightly yellow oil (1.49 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 2.88 (t, J = 7.3 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.40 – 1.21 (m, 10H), 0.93 – 0.84 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 193.9, 141.2, 138.5, 120.3, 73.0, 42.0, 32.0, 29.6, 29.4, 29.3, 24.1, 22.9, 14.3. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{19}BrIOS$, 428.9385; found, 428.9367.

Hexyl 2-bromo-5-iodothiophene-3-carboxylate. In a 20 mL scintillation vial wrapped in aluminum foil, hexyl 2-bromothiophene-3-carboxylate (0.79 g, 2.72 mmol) was dissolved in 6.8 mL chloroform:acetic acid (7:3, v/v). N-iodosuccinimide (0.73 g, 3.24 mmol) was added in three portions to the stirring solution over 10 min at 0 °C. The reaction was slowly warmed to room temperature, and stirred for 16.5 h. The reaction solution was transferred to a separatory funnel, diluted with 500 mL of 1 M $Na_2S_2O_3$ solution and extracted with diethyl ether (3 × 150 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated using rotary evaporation. The crude product was purified using column chromatography on silica gel using a gradient from 1:0 hexanes:EtOAc to 9:1 hexanes:EtOAc as the eluent to afford a colorless oil (0.96 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 4.27 (t, J = 6.6 Hz, 2H), 1.73 (ddt, J = 9.0, 7.8, 6.6 Hz, 2H), 1.47 – 1.38 (m, 2H), 1.37 – 1.28 (m, 4H), 0.95 – 0.86 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.7, 138.9, 133.4, 122.7, 72.3, 65.6, 31.6, 28.7, 25.9, 22.7, 14.2. HRMS (DART) (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}BrIO_2S$ 416.9021; found, 416.9002.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra, GC traces and MS data (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.
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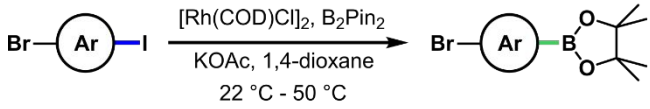

Mild conditions
Excellent chemoselectivity
Low catalyst loadings (1 mol%)
Broad functional group tolerance